Electronic Supplementary Material (ESI) for ChemComm.

Transition Metal-Free and Temperature Dependent One-Pot Access to Phenanthrene-Fused Heterocycles *via* 1,3-Dipolar Cycloaddition Pathway

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Supporting Information

Experimental:

General: IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) (δH = 0.00 ppm) or $CDCl_3$ (δH = 7.26 ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on Bruker Advance 400 (100 MHz) spectrometer at RT in $CDCl_3$. Chemical shifts (δ ppm) are reported relative to $CDCl_3$ [δC = 77.00 ppm (central line of the triplet)]. In ^{1}H 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 br. s = broad singlet. In $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. Melting points are recorded using Tempo and Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. A single crystal of **3ea**, **4ia**, and **10a** was selected and mounted on an Oxford SuperNova, Dual, Cu at zero, Eos diffractometer. The crystal was kept at 298 K during data collection. Using Olex2, the structure was solved with 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 by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; petroleum ether in the 60−80 °C boiling range was used. $Pd(OAc)_2$, K_3PO_4, acrylonitrile, and PPh_3 were purchased from Sigma-Aldrich and used as received. 2-bromobenzaldehydes, phenyl hydrazines, 2-formyl-phenyl-boronic acids, tosyl hydrazide, hydroxylamine, THF, DMF, and Cs_2CO_3 were purchased from Sigma-Aldrich/TCI/local sources and used as received. Acme's silica gel (60–120 mesh) was used for column chromatography (approximately 20 g per gram of crude material).

Table S1: The following 2-bromobenzaldehydes **16a**, **16e**, **16f**, and **16g** are purchased and used as received. While 2-iodobenzaldehydes **16b**, **16c**, and **16d** were prepared by literature reports.[1,2]

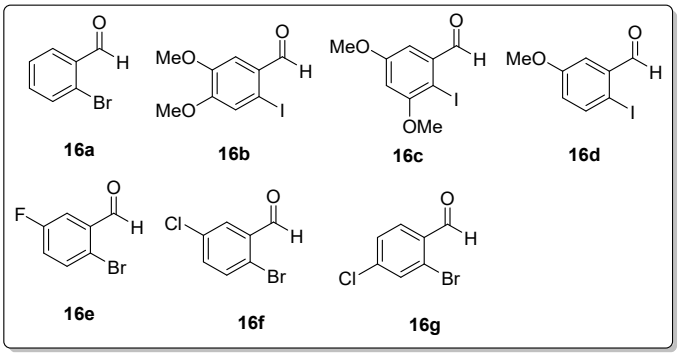


Table S2: The following 2-formylphenyl boronic acids are purchased and used as received.

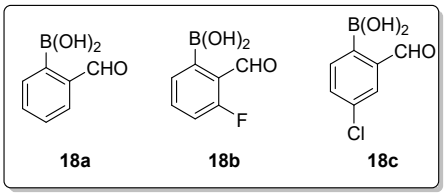
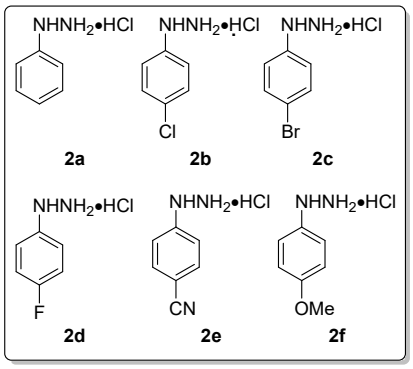


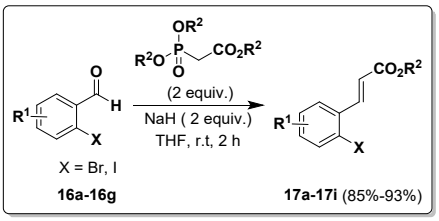
Table S3: The following phenylhydrazine hydrochlorides are purchased and used as received.



General Procedure 1 (GP-1) for the Preparation of 2-Halocinnamate Esters (17a-17i):

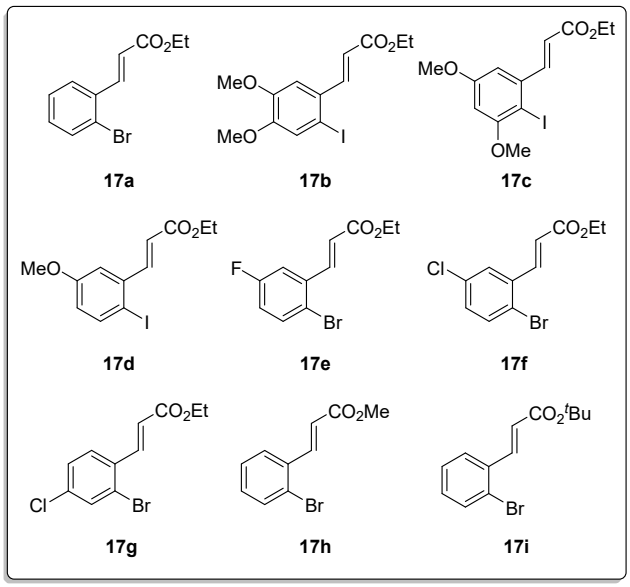
To an oven dried round bottom flask equipped with a magnetic stirring bar, were added 60% NaH (128 mg, 3.2 mmol), and THF (10 mL) under nitrogen atmosphere and cooled to ice temperature; then phosphonate reagent (0.9 ml, 4.5 mmol) was added dropwise through using a syringe until the solution becomes clear. To the resulted reagent, was added 2-haloarylaldehyde **16a-16g** (300-420 mg, 1.6 mmol). The reaction mixture was stirred at room temperature for 2 h, and the progress of the reaction was monitored by TLC until the reaction was completed. The reaction mixture was then quenched with aqueous NH_4Cl and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and

concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90%-97%) furnished the 2-halocinnamate ester **17a-17i** (85%-93%) as a pale yellow/colorless oil/white solids.



Scheme S1: Preparation of alkyl 2-Halocinnamate esters **17a-17i.**

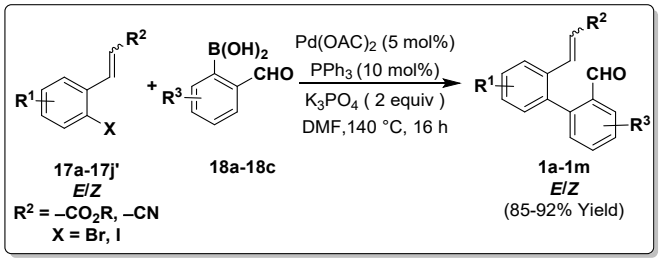
Table S4: The following 2-halocinnamate esters **17a-17i** except **17b** and **17c,** were known in the literature and prepared using the literature reports.[3–7]



General Procedure 2 (GP-2) for the Preparation of Alkyl (*E*)-3-(2'-formyl-[1,1'-iphenyl]-2-yl) acrylates/(*E/Z*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylonitriles (1a-1m):

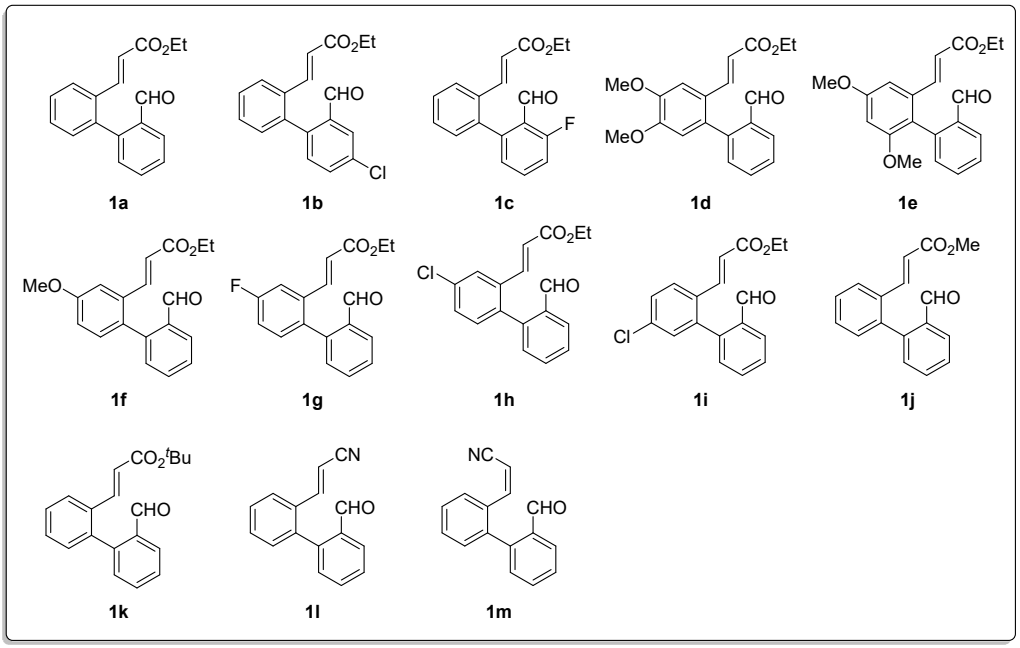
In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added (*E*) 2-bromocinnamate ester **17a-17i** /(*E*/*Z*)2-bromo-acrylonitrile **17a-17j'** (104-181 mg, 0.5 mmol), 2-formylphenylboronic acid **18a-18c** (84-103 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol %), PPh_3 (13 mg, 10 mol %), and K_3PO_4 (212 mg, 1 mmol) in DMF (2.0 mL) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 140 °C for 16-18 h in an oil bath. The reaction is monitored using TLC until the reaction is completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over

Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 85%-90%) furnished the product **1a-1m** (85%-92%) as pale yellow/yellow/colorless viscous liquids/white solids.



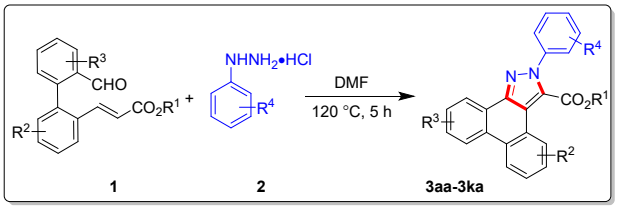
Scheme S2: Preparation of ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylates(**1a**-**1k**)/ (*E/Z*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylonitrile **1l** and **1m**.

Table S5: Following Alkyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a** is known in the literature[8] and (**1b**-1**k**)/ (*E*/*Z*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylonitriles (**1l** and **1m**) were prepared according to the GP-3.



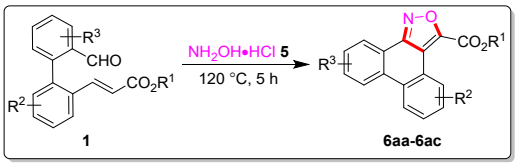
General Procedure 3 (GP-3) for the Synthesis of Phenanthrene-Fused Pyrazole Esters (3aa-3ka): To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added alkyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a-1k** (56-71 mg, 0.21 mmol), phenylhydrazine hydrochloride **2a-2f** (36-56 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 120 °C for 3-7 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. The reaction mixture was cooled to

room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90%-95%) furnished the product **3aa-3ka** (70%-78%) as a white/orange/maroon/pale yellow/yellow/brown solid.



Scheme S3: Synthesis of phenanthrene-fused pyrazole esters **3aa-3ka**.

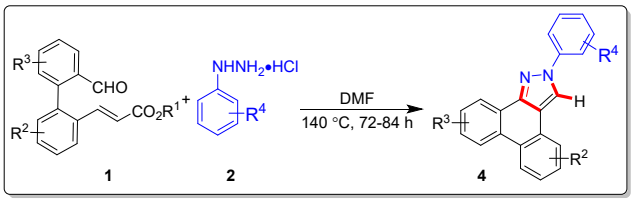
General Procedure 4 (GP-4) for the Synthesis of Phenanthrene-Fused Isoxazoles (6aa-6ac): To an oven dried Schlenk tube equipped with a magnetic stirring bar, were added alkyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a**, **1f** and **1j** (56-65 mg, 0.21 mmol), hydroxylamine hydrochloride **5** (17 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 120 °C for 5 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95%-98%) furnished the product **6aa-6ac** (57%-60%) as white solids.



Scheme S4: Synthesis of phenanthrene-fused isoxazoles **6aa-6ac**.

General Procedure 5 (GP-5) for the Synthesis of Phenanthrene-Fused Pyrazoles (4aa-4ga): To an oven dried Schlenk tube equipped with a magnetic stirring bar, were added alkyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a-1k** (56-71 mg, 0.21 mmol), phenylhydrazine hydrochloride **2a-2f** (36-56 mg 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 72-84 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20

mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90%-95%) furnished the product **4aa-4ag** (70%-76%), as white/brown/maroon solids.



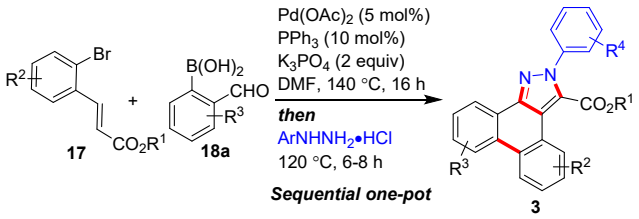
Scheme S5: Synthesis of phenanthrene-fused pyrazoles **4aa-4ia**.

General Procedure 6 (GP-6) for the Synthesis of 2*H*-Dibenzo Indazole Esters (9a+9a'-9c+9c'): To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added alkyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a-1k** (56-71mg, 0.21 mmol), *para*-toulenesulfonyl hydrazide **8** (47 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 60 °C for 6 h in an oil bath. TLC monitored the reaction until the reaction was completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **9a+9a'** to **9c+9c'** (74%-78%), as white/orange solids.

General Procedure 7 (GP-7) for the Sequential One-Pot Synthesis of Phenanthrene-Fused Pyrazole Esters (3aa, 3ab, 3af, 3ga and 3ia):

In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added (*E*) 2-bromo cinnamate **17a**, **17e**, and **17g** (60-66 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol), $Pd(OAc)_2$ (2.6 mg, 5 mol %), PPh_3 (5 mg, 10 mol %), and K_3PO_4 (99 mg, 0.47 mmol) in DMF (4.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 16-18 h in an oil bath. The reaction is monitored using TLC until the product **1a, 1g** and **1i** is formed. Then phenyl hydrazine hydrochloride **2a, 2b,** and **2f** (36-46 mg, 0.25 mmol) was added to the reaction mixture, continued further at 120 °C for 6-8 h. The reaction is monitored using TLC until the reaction is completed. Then reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography

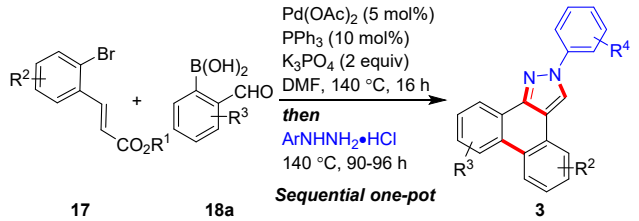
(petroleum ether/ethyl acetate 95%) furnished the product **3aa** (60%), **3ab** (58%), **3af** (59%), **3ag** (57%), **3ia** (57%) as pale yellow/yellow/colorless viscous liquids/white solids.



Scheme S6: Sequential one-pot synthesis of phenanthrene-fused pyrazole esters **3aa**, **3ab**, **3af**, **3ag**, and **3ia**.

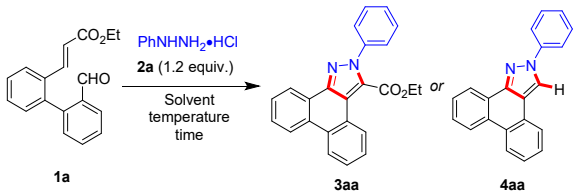
General Procedure 8 (GP-8) for the Sequential One-Pot Synthesis of Phenanthrene-Fused Pyrazoles (4aa and 4ga):

In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added (*E*) 2-bromo cinnamate **17a** and **17e** (60 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol), $Pd(OAc)_2$ (2.6 mg, 5 mol %), PPh_3 (5 mg, 10 mol %), and K_3PO_4 (99 mg, 0.47 mmol) in DMF (4.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 16-18 h in an oil bath. The reaction is monitored using TLC until the product **1a** and **1g** is formed. Then phenylhydrazine hydrochloride **2a** (37 mg, 0.25 mmol) was added to the reaction mixture, continued further at 140 °C for 90-96 h. The reaction is monitored using TLC until the reaction is completed. Then reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95%) furnished the product **4aa** (58%), and **4ga** (56%) as pale yellow/yellow/colorless viscous liquids/white solids.



Scheme S7: Sequential one-pot synthesis of phenanthrene-fused pyrazoles **4aa** and **4ga**.

Table S6. Optimization study to generate **3aa** and **4aa**.[a,b,c]



Entry	Solvent	Base (2 equiv.)	Temp (°C)	Time (h)	Yield (%)[b]	
					3aa	4aa
1	DMF	--	rt	24	trace	--
2	DMF	--	60	24	61	--
3	DMF	--	80	14	63	--
4	DMF	--	100	6	69	--
5	**DMF**	--	**120**	**3**	**76**	--
6[c]	DMF	--	120	3	72	--
7	DMF	--	140	1	73	trace
8	DMSO	--	120	3	74	--
9	DMA	--	120	3	72	--
10	DMF	NaOMe	120	3	74	--
11	DMF	K_2CO_3	120	3	73	--
12	Toluene	NaOMe	100	24	51	--
13	Toluene	NaOMe	120	18	64	--
14	MeOH	NaOMe	80	24	53	--
15	EtOH	NaOMe	80	18	61	--
16	^{t}BuOH	NaOMe	80	14	62	--
17	DMF	--	140	72	--	74

Reaction conditions: [a]Reactions were performed using 0.21 mmol of **1a** and 0.25 mmol of **2a** in 2 mL DMF solvent. [b]Yield of the isolated product after purification through silica gel column chromatography. [c]Phenylhydrazine **15** instead of phenylhydrazine hydrochloride **2a**.

To execute our synthetic strategy, to begin with, we have chosen ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a**, phenylhydrazine hydrochloride **2a** as model substrates. Thus, the reaction was conducted between **1a** (0.21 mmol) and **2a** (1.2 equiv; 0.25 mmol) in DMF solvent at room temperature for 24 hours, which resulted in the desired product **3aa,** albeit in trace amount (Table 1, entry 1). Subsequently, the reactions were tested at gradually raising temperatures of 60 to 100 °C, and we were pleased that the desired product **3aa** was obtained

in fair yields (Table 1, entries 2-4). We were delighted that the phenanthrene-fused pyrazole **3aa** obtained a 76% good yield at 120 °C for 3 h (Table 1, entry 5). While the reaction with phenylhydrazine **15** instead of phenylhydrazine hydrochloride **2a**, produced **3aa** in a lightly decreased yield of 72% (Table 1, entry 6). Further, at the elevated temperature of 140 °C, the yield of product **3aa** was slightly reduced, and started observing a trace of further reacted dealkoxycarbonylated product **4aa** from **3aa** (Table 1, entry 7). Besides, the reactions were screened with polar aprotic solvents such as DMSO and DMA and also with DMF in basic conditions, but no improvement in yields was observed (Table 1, entry 8-11). Also, the polar protic solvents, such as MeOH, EtOH, ^{t}BuOH an,d non-polar toluene solvents, turned out to be a bit inferior (Table 1, entries 12-16). Furthermore, to our delight, the reaction in DMF at 140 °C for 72 h, exlusively furnished **4aa** in 74% yield *via* dealkoxycarbonylation of *in-situ* generated **3aa** (Table 1, entry 17); this might be due to *in-situ* generated water, which could induce hydrolysis of the ester to give the acid and finally decarboxylation under thermal conditions. Based on this screening study, it was found that the conditions mentioned in entries 5 and 17 of Table 1 were best in affording the products **3aa** and **4aa**, respectively.

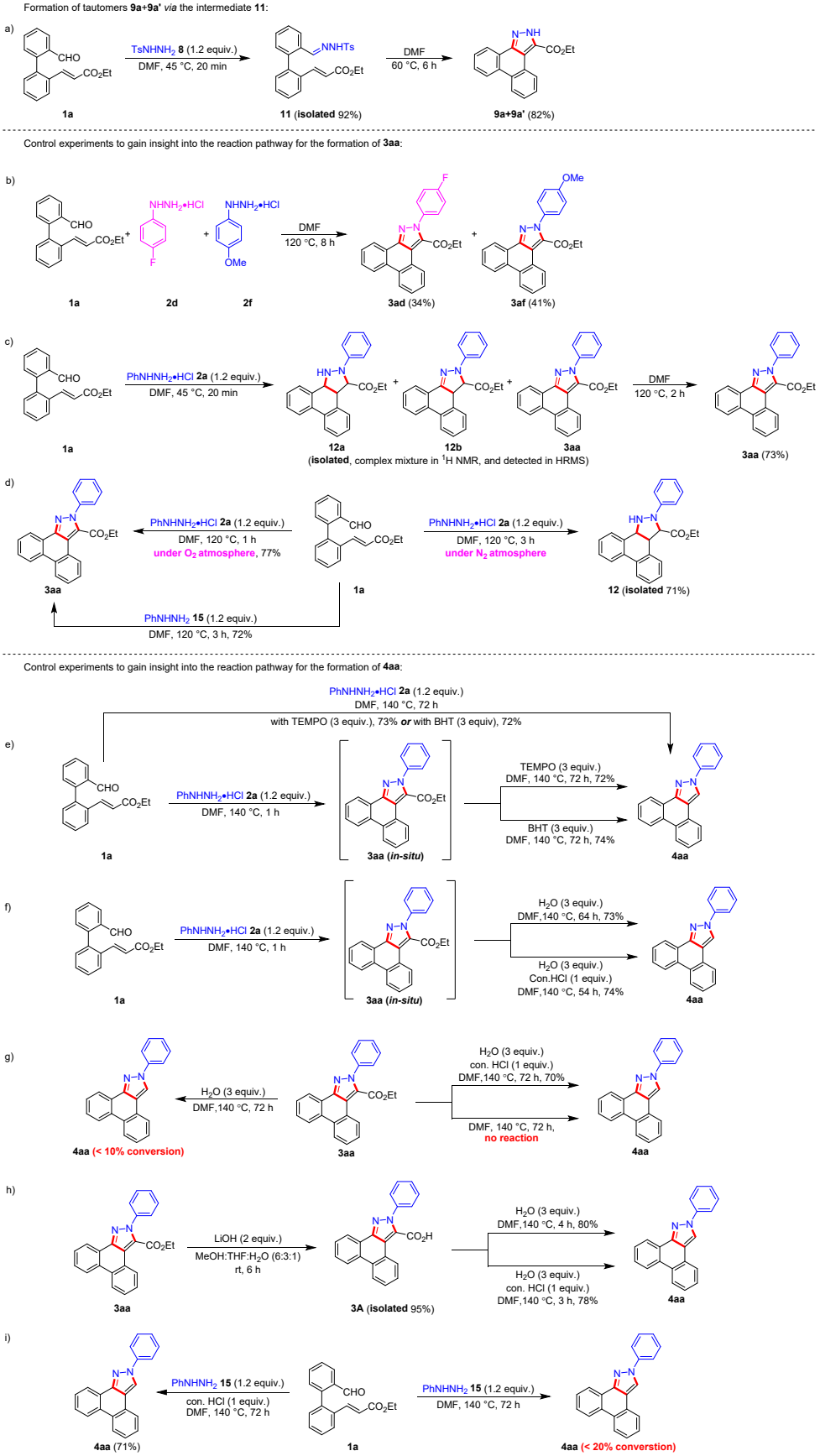
Scheme S8: Control experiments

In order to gain more insight into the reaction pathway, control experiments were investigated. Thus, initially, performed reaction **1a** with *para*-tosyl hydrazide **8** at low temperature 45 °C for 20 min, intermediate **11** was observed in 92% yield. Further, the reaction of the intermediate **11** under standard conditions afforded the mixture of **9a**+**9a'** in 4:1 (^{1}H NMR) ratio of 82% yield (Scheme S8 a). Next, carried out a competitive reaction of **2d** (1.1 equiv) and **2f** (1.1 equiv) with **1a** in DMF at 120 °C for 8 h; the corresponding products **3ad** and **3af** were observed in 34% and 41% of yields, respectively (Scheme S8 b). Slightly more yield of **3af** over **3ad** can be attributed to relatively more nucleophilic phenylhydrazine hydrochloride **2f**. Next, for the formation of **3aa**, performed a reaction by treating **1a** with phenylhydrazine hydrochloride **2a** at 45 °C for 20 min; this led to a complex mixture of intermediates **12a**, **12b** along with the product **3aa** (^{1}H NMR). To our delight, the mixture of intermediates **12a**, **12b**, and product **3aa** were detected in HRMS. Furthermore, continued the reaction with the same reaction mixture (**12a**, **12b**, and **3aa**) under standard conditions provided the product **3aa** in 73% yield (Scheme S8 c). Subsequently, the reaction of **1a** with simple phenylhydrazine **15** instead of phenylhydrazine hydrochloride **2a**, delivered **3aa** in 72% of yield. Next, for the formation of aromatized phenanthrene-fusedpyrazole ester **3**, conducted a reaction under an N_2 atmosphere as well as in an O_2 atmosphere; the reaction under N_2

atmosphere, under the standard conditions, furnished mostly the intermediate product **12a** in 71% yield (Scheme S8 d). Notably, the reaction is carried out in the O_2 atmosphere at 120 °C for 1 h, the product **3aa** was isolated in 77% yield; from which it can be ascertained that O_2 atmosphere favours the aromatization step (oxidation), while N_2 atmosphere impede the aromatization process (Scheme S8 d). Based on the above findings and literature report (*Org. Lett.*, 2008, **10**, 1307–1310), we came to know that the reaction is going through oxidative aromatization.

Besides, for the dealkoxycarbonylated phenanthrene-fused pyrazoles, we have performed some more control experimental studies. Firstly, to check whether the reaction is going through radical pathway or not, the reaction was conducted in the presence of radical scavengers TEMPO and BHT with **1a**, but no intermediate was trapped by scavengers and product **3aa** was formed exclusively in 73% and 72% of yields, resepctively. Additionally, also performed reaction with *in-situ* generated product **3aa** with TEMPO and BHT, there, **4aa** was formed in 72% and 74% yields resepctively, without arrpecialbe trapping intermediate (Scheme S8 d). Based on these observations, it can be confirmed that reaction is not proceeding through radical pathway. So, we investigated with some more studies for ionic pathway. Thus, the treatment of *in-situ* generated **3aa** with 3 equivalents of H_2O, at 140 °C for relatively less time (64 h), the product **4aa** was obtained in 73% of isolated yield. Also, the of *in-situ* generated **3aa** with 3 equivalants of H_2O and 1 equivalent of con. HCl, at 140°C for 54 h; interestingly, led to the formation of **4aa** in 74% yield in less time of 54 h (Scheme S8 e). Here, we understood that H_2O and acid would be playing a key role in the formation of **4aa** by facilitating the dealkoxycarbonylation. Next, to comprehend the acid role in the reaction, we carrid out some more control studies, when the reaction was performed with **3aa** alone in DMF under standard conditions, in which the intended product **4aa** has not been formed. While a reaction of **3aa** with 3 equivalnts of H_2O under standard conditions, resulted a poor 10% conversion to **4aa**. Next, the reaction of **3aa** was subjected with 3 equivalents of H_2O and 1 equivalent of con. HCl under standard conditions, which furnished **4aa** in 70% of isolatd yield (Scheme S8 f z). Moreover, we transformed phenanthropyrazole ester **3aa** to phenanthropyrazole acid **3A** under basic conditions, then treated it with H_2O at 140 °C for 4 h; this process gave **4aa** in 80% yield. While treating with 3 equivalents of H_2O and 1 equivalent of con. HCl with **3A** at 140 °C for 3 h, 78% yield of **4aa** was resulted (Scheme S8 g). So, further confirmation of acid role in the formation of product **4aa**, we performed reaction **1a** with simple phenylhydrazine **15** under standard conditions and noticed that only a 20% conversion happened to generate **4aa**.

While the reaction of **1a** with **15** and 1 equivalent of con. HCl under standard conditions, afforded **4aa** in 71% yield (Scheme S8 h). So, further confirmation of acid role in the formation of product **4aa**, performed a reaction of **1a** with simple phenylhydrazine **15** under standard conditions and noticed that a poor 20% conversion to **4aa**. While the reaction of **1a** with **15** and 1 equivalent of con. HCl under standard conditions, resulted **4aa** in 71% yield (Scheme S8 i). Based on these findings, it was understood that dealkoxycarbonylation product **4aa** was facilitated by acid hydrolysis of phenanthrene-fused pyrazole ester product **3aa** followed by decorboxylation of acid **3A** under thermal conditions.



Scheme S8: Control experiments

a) To an oven dried Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), *p*-toulene sulfonyl hydrazide **8** (0.25 mmol) in DMF (2.0 mL) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 45 °C for 20 min in an oil bath. The reaction was monitored by TLC until the reaction intermediate was formed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 40%) furnished the intermediate **11** (88 mg, 92%) as a brown viscous liquid. Further, we continued the reaction with intermediate **11** (60 mg, 0.13 mmol) at 60 °C for 6 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 65:35) furnished the product **9a+9a'** (31 mg, 82%) as pale-yellow solid. [TLC (petroleum ether/ethyl acetate 65:35, *Rf* (**1a**) = 0.9, *Rf* (**12**) = 0.5, *Rf* (**9a+9a'**) = 0.5, UV detection] (Scheme S8a).

b) To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a** (60 mg, 0.21 mmol), 4-flouro-phenylhydrazine hydrochloride **2d** (30 mg, 0.25 mmol, 4-methoxy-phenylhydrazine hydrochloride **2f** (44 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 120 °C for 8 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95%) furnished the product **3ad** (34%) and **3af** (41%) as a white and brown solid (Scheme S8b).

c) To an oven dried Schlenk tube equipped with a magnetic stir bar, were ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenylhydrazine hydrochloride **2a** (0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 45 °C for 30 min in an oil bath. The reaction was monitored by TLC complex intermediate **12** was formed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined,

dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the complex intermediate **12** in ^1H NMR. Then we further continued the same complex mixture **12** at 120 °C for 2 h furnished product **3aa** (57 mg, 73%) as brown solid. [TLC (petroleum ether/ethyl acetate 95:05, *Rf* (**1a**) = 0.4, *Rf* (**12**) = 0.6, UV detection]. **HRMS (ESI)** *m/z* (**12a**): $[(M + H)]^+$ calcd for $C_{24}H_{23}N_2O_2$ 371.1754; Found 371.1770. **HRMS (ESI)** *m/z* (**12b**): $[(M + H)]^+$ calcd for $C_{24}H_{21}N_2O_2$ 369.1598; Found 369.1620. **HRMS (ESI)** *m/z* (**3aa**): $[(M + H)]^+$ calcd for $C_{24}H_{19}N_2O_2$ 367.1441; Found 367.1473 (Scheme S8c).

d) To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 120 °C for 3 h in an oil bath, under N_2 atmosphere. The reaction was monitored by TLC until completion of the reaction. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:02) provided the intermediate **12a** (56 mg, 71%) as a white solid. mp = 135-138 °C [TLC (petroleum ether/ethyl acetate 95:05, *Rf* (**1a**) = 0.4, *Rf* (**12a**) = 0.6, UV detection].

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 120 °C for 3 h in an oil bath, under O_2 atmosphere. The reaction was monitored by TLC complex intermediate **12a** was formed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:02) provided **3aa** (60 mg, 77%) as brown solid. [TLC (petroleum ether/ethyl acetate 95:05, *Rf* (**1a**) = 0.4, *Rf* (**3aa**) = 0.6, UV detection]. (Scheme S8d).

e) To an oven dried Schlenk tube equipped with a magnetic stir bar, were ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenylhydrazine hydrochloride **2a** (0.25 mmol), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (98 mg, 0.63 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 72 h in an oil

bath. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (52 mg, 73%) as brown solid (Scheme S8e).

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenylhydrazine hydrochloride **2a** (0.25 mmol), butylated hydroxy toluene (BHT)(138 mg, 0.63 mmol), in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 72 h in an oil bath. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (52 mg, 72%) as brown solid (Scheme S8e).

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenylhydrazine hydrochloride **2a** (0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 1 h in an oil bath. The reaction was monitored by TLC complex intermediate **3aa** was formed. Then, added (2,2,6,6-tetramethyl-1-piperidinyloxy)TEMPO (98 mg, 0.63 mmol), and continued the reaction for 72 h. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (52 mg, 72%) as brown solid (Scheme S8e).

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Phenylhydrazine hydrochloride **2a** (0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 1 h in an oil bath. The reaction was monitored by TLC complex intermediate **3aa** was formed. Then added butylated hydroxy toluene (BHT)(138 mg, 0.63 mmol), under standard conditions and continued the reaction for 72 h. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by

adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (53 mg, 74%) as brown solid (Scheme S8e).

f) To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), Pheny hydrazine hydrochloride **2a** (0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 1 h in an oil bath. The reaction was monitored by TLC product **3aa** was formed. Then, added H_2O (0.01mL, 0.63 mmol) to the reaction mixture, and continued for 64 h in an oil bath. The reaction was monitored by TLC until the reaction completed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95%) furnished the product **4aa** (45 mg, 73%) as a brown solid. When the reaction carried out with H_2O (0.01mL, 0.63 mmol) and con.HCl (0.01 mL, 0.21 mmol), and the reaction mixture was stirred at 140 °C for 54 h in an oil bath, furnished the product **4aa** (45 mg, 73%) as brown solid (Scheme S8f).

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a** (60 mg, 0.21 mmol), Pheny hydrazine hydrochloride **2a** (0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 1 h in an oil bath. The reaction was monitored by TLC product **3aa** was formed. Then, added H_2O (0.01mL, 0.63 mmol) and con.HCl (0.01 mL, 0.21 mmol), to the reaction mixture, and continued for 54 h in an oil bath. The reaction was monitored by TLC until the reaction completed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95%) furnished the product **4aa** (45 mg, 74%) as a brown solid (Scheme S8f).

g) To an oven-dried Schlenk tube equipped with a magnetic stir bar was added ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3aa** (76 mg, 0.21 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 72 h in an oil bath, but, **4aa** was not observed. When reaction treated with H_2O (0.01 mL, 0.63 mmol), at 140°C for 72 h. The reaction was monitored by TLC but **4aa** was observed in 10% conversion (Scheme S8g).

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added (ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3aa** (76 mg, 0.21 mmol), H_2O (0.01mL, 0.63 mmol), and con.HCl (0.01 mL, 0.21 mmol) at 140 °C for 72 h in an oil bath. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (49 mg, 70%) as brown solid (Scheme S8g).

h) To the solution of **3aa** (200 mg, 0.54 mmol) in MeOH (3 mL), THF (1.5 mL), H_2O (0.5 mL) in 25 mL round bottom flask, was added $LiOH{\cdot}H_2O$ (45 mg, 1 mmol) at room temperature. The resulting reaction mixture was stirred at room temperature for 12 h. The organic solvents were removed under the reduced pressure, diluted with H_2O (15 mL), and to the aqueous phase, was added 2M HCl. The resulted solution was extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure and filtered through column chromatography, furnished the product **3A** (171 mg, 93%) as a white solid. mp = 135-138 °C (Scheme S8h).

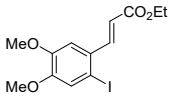
To an oven dried Schlenk tube equipped with a magnetic stir bar, were **3A** (70 mg, 0.21 mmol), H_2O (0.01mL, 0.63 mmol) in DMF (2 mL), stirred at 140 °C for 4 h in an oil bath. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (48 mg, 80%) as brown solid (Scheme S8h).

To an oven dried Schlenk tube equipped with a magnetic stir bar, were added **3A** (70 mg, 0.21 mmol), H_2O (0.01mL, 0.63 mmol), con.HCl (0.01mL, 0.21 mmol) in DMF (2 mL), stirred at 140 °C for 3 h in an oil bath. The reaction was monitored by TLC until the reaction completed. the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) provided the **4aa** (47 mg, 78%) as brown solid (Scheme S8h).

i) To an oven dried Schlenk tube equipped with a magnetic stir bar, were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a** (60 mg, 0.21 mmol), Phenyl hydrazine **15** (27 mg,

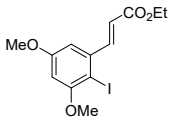
0.25 mmol) in DMF (2.0 mL) at room temperature, and the reaction mixture was stirred at 140 °C for 72 h in an oil bath, but 20% conversion of **4aa** was observed. While the reaction was carried out with con.HCl (0.01mL, 0.21 mmol), at 140 °C for 72 h. The reaction was monitored by TLC until the reaction was completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95:05) furnished the product **4aa** (44 mg, 71%) as a brown solid (Scheme S8i).

Characterization of Compounds:



17b

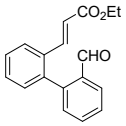
Ethyl (*E*)-3-(2-iodo-4,5-dimethoxyphenyl)acrylate (17b): GP 1 was carried out with 2-iodo-3,5-dimethoxybenzaldehyde **16b** (61 mg, 0.21 mmol), triethyl posphanoacetate (141 mg, 0.63 mmol) in 2 mL of DMF at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(2-iodo-4,5-dimethoxyphenyl)acrylate **17b** (68 mg, 91%), as a white solid. mp = 85-87 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**16b**) = 0.7, *Rf* (**17b**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3065, 2845, 1697, 1512, 1275, 1165, 981, 762. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, J = 15.8 Hz, 1H), 7.20 (s, 1H), 6.98 (s, 1H), 6.15 (d, J = 15.8 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 3.82 (s, 6H), 1.27 (t, J = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 166.3, 150.9, 149.3, 147.3, 129.7, 121.5, 118.7, 108.8, 91.3, 60.4, 56.1, 55.7, 141.2 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{13}H_{16}IO_4$ 363.0088; Found 363.0078.



17c

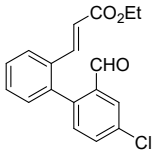
Ethyl (*E*)-3-(2-iodo-3,5-dimethoxyphenyl)acrylate (17c) : GP 1 was carried out with 2-iodo-4,5-dimethoxybenzaldehyde **16c** (61 mg, 0.21 mmol), triethyl phosphanoacetate (141 mg, 0.63 mmol) and NaH (17mg, 0.42 mmol) in 10 mL of THF at room temperature for 2 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(2-iodo-3,5-dimethoxyphenyl)acrylate **17c** (69 mg, 92%), as a white solid, mp = 88-90 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**16c**) = 0.7, *Rf*

(**17c**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2976, 2841, 1698, 1635, 1455, 11161, 1035, 829. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, J = 15.8 Hz, 1H), 6.71 (d, J = 2.6 Hz, 1H), 6.43 (d, J = 2.6 Hz, 1H), 6.27 (d, J = 15.8 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 166.3, 161.1, 159.3, 148.4, 139.7, 121.6, 103.9, 100.2, 83.1, 60.8, 56.7, 55.7, 14.4 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{13}H_{16}IO_4^+$ 363.0088; Found 363.0085.



1a

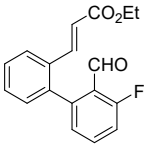
Ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1a): GP 2 was carried out with ethyl (*E*)-3-(2-bromophenyl)acrylate (130 mg, 0.5 mmol) **17a**, 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol) $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1a** (131 mg, 92%), as a pale yellow viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17a**) = 0.8, *Rf* (**1a**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2980, 2846, 1698, 1635, 1594, 1262, 1172, 760. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, J = 0.7 Hz, 1H), 8.05 (dd, J = 7.8, 1.3 Hz, 1H), 7.77 – 7.72 (m, 1H), 7.65 (ddd, J = 7.5, 7.5, and 1.5 Hz, 1H), 7.55 (dd, J = 7.6, 7.5, and 2.0, 1H), 7.48 – 7.44 (m, 2H), 7.41 (d, J = 15.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 6.35 (d, J = 15.9 Hz, 1H), 4.15 (q, J = 7.1 Hz, 2H), 1.24 (t, J = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.5, 166.4, 143.3, 141.9, 138.4, 134.3, 133.7, 133.6, 131.3 (2C), 129.6, 128.7, 128.5, 127.8, 126.5, 120.3, 60.5, 14.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{17}O_3$ 281.1172; Found 281.1167.



1b

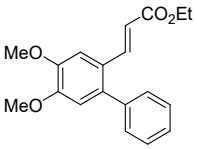
Ethyl (*E*)-3-(4'-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate (1b): GP 2 was carried out ethyl (*E*)-3-(2-bromophenyl)acrylate **17a** (130 mg,0.5 mmol), (4-chloro-2-formylphenyl) boronic acid **18b** (103 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished ethyl (*E*)-3-(4'-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1b** (144 mg, 90%), as a pale yellow

viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf* (**17a**) = 0.8, *Rf* (**1b**) = 0.4), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 3065, 2982, 1699, 1634, 1591, 1461, 1269, 1173, 761. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 7.93 (d, *J* = 2.3 Hz, 1H), 7.68 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.54 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.31 (d, *J* = 15.9 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 190.1, 166.2, 141.5, 141.4, 137.0, 135.3, 135.0, 133.7, 133.5, 132.7, 131.3, 129.7, 129.0, 127.5, 126.6, 120.7, 60.5, 14.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}ClO_3$ 315.0782; Found 315.0768.



1c

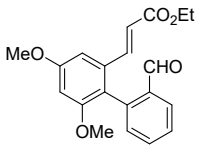
Ethyl (*E*)-3-(3'-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1c): GP 2 was carried out with ethyl (*E*)-3-(2-bromophenyl)acrylate **17a** (130 mg, 0.5 mmol), (3-fluoro-2-formylphenyl)boronic acid **18c** (93 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(3'-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1b** (132 mg, 87%) as a yellow viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17a**) = 0.8, *Rf* (**1c**) = 0.4), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2984, 1700, 1637, 1594, 1463, 1266, 1171, 977, 762. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.2 (dd, 7.0, 2.2 Hz, 1H), 7.66 – 7.56 (m, 1H), 7.49 – 7.41 (m, 2H), 7.39 (d, *J*= 15.9 Hz, 1H) 7.30 – 7.16 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 1H), 6.35 (d, *J*= 15.9 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 188.1 (d, $J_{C\text{-}F}$ = 3.8 Hz), 166.4, 163.16 (d, $J_{C\text{-}F}$ = 262.8 Hz),143.8 (d, $J_{C\text{-}F}$ = 1.2 Hz), 141.6, 138.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 134.7 (d, $J_{C\text{-}F}$ = 10.3 Hz), 133.1, 130.4, 129.6, 128.7, 127.3 (d, $J_{C\text{-}F}$ = 3.6 Hz), 126.3, 122.9 (d, $J_{C\text{-}F}$ = 6.8 Hz), 120.1, 116.4 (d, *J* = 21.3 Hz), 60.4, 14.1 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{18}H_{16}FO_3$ 299.1078; Found 299.1086.



1d

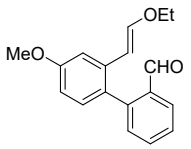
Ethyl (*E*)-3-(2'-formyl-4,5-dimethoxy-[1,1'-biphenyl]-2-yl) acrylate(1d): GP 2 was carried out ethyl (*E*)-3-(2-iodo-3,4-dimethoxyphenyl)acrylate **17b** (181 mg, 0.5 mmol), 2-

formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 18 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 85:15) furnished the ethyl (*E*)-3-(2'-formyl-4,5-dimethoxy-[1,1'-biphenyl]-2-yl) acrylate **1d** (149 mg, 88%), as white solid, mp = 110-112 °C. [TLC (petroleum ether/ethyl acetate 85:15), *Rf* (**17b**) = 0.9, *Rf* (**1d**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2940, 1702, 1637 1595, 1458, 1273, 1170, 755. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (d, *J* = 0.9 Hz, 1H), 7.94 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.56 (ddd, *J* = 7.5, 7.5 and 1.2 Hz, 1H), 7.45 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.26 (d, *J* = 16.0 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.13 (s, 1H), 6.67 (s, 1H), 6.19 (d, *J* = 15.8 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.80 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.4, 166.5, 150.2, 149.0, 142.9, 141.6, 134.4, 133.4, 132.1, 131.4, 128.3, 127.5, 126.1, 117.6, 113.5, 108.1, 60.2, 55.9, 55.8, 14.0 ppm. **HRMS (ESI)** *m/z*: $[M + K]^+$ calcd for $C_{20}H_{20}KO_5$ 379.0942; Found 379.0937.



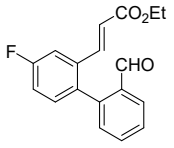
1e

Ethyl (*E*)-3-(2'-formyl-4,6-dimethoxy-[1,1'-biphenyl]-2-yl) acrylate (1e): GP 2 was carried out Ethyl (*E*)-3-(2-iodo-3,5-dimethoxyphenyl)acrylate **17c** (181 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 18 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 85:15) furnished the ethyl (*E*)-3-(2'-formyl-4,6-dimethoxy-[1,1'-biphenyl]-2-yl) acrylate **1e** (152 mg, 90%), as white solid, mp = 120-122 °C. [TLC (petroleum ether/ethyl acetate 85:15), *Rf* (**17c**) = 0.9, *Rf* (**1e**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2974, 2841, 1698,1636, 1591, 1338, 1163, 1033, 831.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.68 (d, *J* = 0.7 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.63 (ddd *J* = 7.5, 7.5 and 1.5 Hz, 1H), 7.51 (ddd, *J* = 7.5, 7.5, and 0.9 Hz, 1H), 7.32 (d, *J* = 15.9 Hz, 1H), 7.17 (dd, *J* = 7.6, 0.8 Hz, 1H), 6.85 (d, *J* = 2.3 Hz, 1H), 6.57 (d, *J* = 2.3 Hz, 1H), 6.32 (d, *J* = 15.9 Hz, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 3.68 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 192.1, 166.3, 160.7, 158.2, 142.4, 138.9, 135.5, 134.9, 133.6, 132.6, 128.2, 127.1, 120.4, 120.2, 101.9, 100.0, 60.4, 55.7, 55.4, 14.1 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{20}H_{21}O_5$ 341.1384; Found 341.1395.



1f

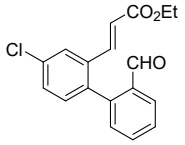
Ethyl (*E*)-3-(2'-formyl-4-methoxy-[1,1'-biphenyl]-2-yl) acrylate (1f): GP 2 was carried out with ethyl (*E*)-3-(2-iodo-5-methoxyphenyl) acrylate **17d** (166 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 88:12) furnished the ethyl (*E*)-3-(2'-formyl-4-methoxy-[1,1'-biphenyl]-2-yl) acrylate **1f** (137 mg, 89%) as a colourless viscous liquid. [TLC (petroleum ether/ethyl acetate 88:12, *Rf* (**17d**) = 0.7, *Rf* (**1f**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2976, 2843, 1700, 1636, 1599, 1278, 1175, 1039, 763. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.66 (d, *J* = 0.7 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.55 (ddd, *J* = 7.5, 7.5 and 1.5 Hz, 1H), 7.46 (ddd, 7.6, 7.6, and 0.9 Hz, 1H), 7.32 (d, *J* = 15.9 Hz, 1H), 7.20 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.16 (d, *J* = 2.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.27 (d, *J* = 15.9 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.7, 166.3, 159.7, 143.1, 142.0, 134.8, 134.6, 133.5, 132.5, 131.7, 130.9, 128.2, 127.7, 120.4, 115.8, 111.1, 60.5, 55.4, 14.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{19}H_{19}O_4$ 311.1278; Found 311.1279.



1g

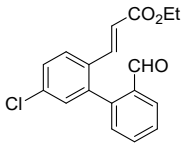
Ethyl (*E*)-3-(4-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1g): GP 2 was carried out Ethyl (*E*)-3-(2-bromo-5-fluorophenyl) acrylate **17e** (136 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(4-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1g** (126 mg, 85%) as a pale yellow viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf* (**17d**) = 0.8, *Rf* (**1g**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2979, 2841, 1699, 1636, 1599, 1461, 1173, 1038, 763. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.04 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66 (ddd, *J* = 7.5, 7.5 and 1.4 Hz, 1H), 7.57 (dd, 7.6, 7.6 Hz, 1H), 7.43 (dd, *J* =

9.7, 2.6 Hz, 1H), 7.34 (dd, *J* = 15.9, 1.5 Hz, 1H), 7.27 (m, 2H), 7.17 (ddd, *J* = 8.2, 8.2 and 2.6 Hz, 1H), 6.35 (d, *J* = 15.9 Hz, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.2, 166.1, 162.6 (d, $J_{C\text{-}F}$ = 248.5 Hz), 142.1, 140.8 (d, $J_{C\text{-}F}$ = 2.4 Hz), 135.7 (d, $J_{C\text{-}F}$ = 7.8 Hz), 134.5 (d, $J_{C\text{-}F}$ = 3.3 Hz), 134.4, 133.7, 132.9, 132.8, 131.5, 128.7, 128.2, 121.4, 116.7 (d, $J_{C\text{-}F}$ = 21.7 Hz), 112.9 (d, *J* = 22.5 Hz), 60.6, 14.1 ppm. **HRMS (ESI)** *m/z*: $[M + Na]^+$ calcd for $C_{18}H_{15}FNaO_3$ 321.0897; Found 321.0895.



1h

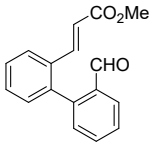
Ethyl (*E*)-3-(4-chloro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1h): GP 3 was carried out with ethyl (*E*)-3-(2-bromo-5-chlorophenyl)acrylate **17f** (144 mg, 0.5 mmol), 2-formyl phenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(4-chloro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1h** (140 mg, 90%) as a pale yellow viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10, *Rf* (**17g**) = 0.8, *Rf* (**1h**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2982, 1700, 1635, 1595, 1265, 1174, 1035, 760. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 7.96 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.65 (d, *J* = 2.1 Hz, 1H), 7.59 (ddd 7.5, 7.5, and 1.9 Hz, 1H), 7.50 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.25 (d, *J* = 15.9 Hz, 1H), 7.20 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 1H), 6.29 (d, *J* = 15.9 Hz, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.0, 166.0, 141.8, 140.5, 136.9, 135.3, 134.8, 134.2, 133.7, 132.4, 131.3, 129.5, 128.8, 128.4, 126.4, 121.5, 60.6, 14.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{16}ClO_3$ 315.0782; Found 315.0767.



1i

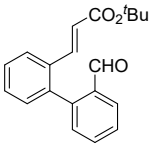
Ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1i): GP 2 was carried out with ethyl (*E*)-3-(2-bromo-4-chlorophenyl)acrylate **17g** (144 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg,

10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1i** (134 mg, 86%) as colurless viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17f**) = 0.8, *Rf* (**1i**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2984, 1704, 1635, 1602, 1456, 1271, 1176, 759. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.73 (d, *J* = 0.5 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.58 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.44 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.31 (d, *J* = 15.9 Hz, 1H), 7.29 (dd, *J* = 8.9, 1.5 Hz, 2H), 6.32 (d, *J* = 15.9 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 190.9, 166.1, 141.6, 140.6, 140.1, 135.6, 134.1, 133.8, 132.3, 131.1, 130.9, 129.0, 128.9, 128.3, 127.7, 120.7, 60.6, 14.1 ppm. **HRMS (ESI)** *m/z*: $[(M + NH_4)]^+$ calcd for $C_{18}H_{19}ClNO_3$ 332.1048; Found 332.1039.



1j

Methyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1j):GP 2 was carried out with methyl (*E*)-3-(2-bromophenyl) acrylate **17h** (120 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the methyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1j** (119 mg, 90%) as a pale yellow viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17h**) = 0.8, *Rf* (**1j**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 3061, 2924, 1722, 1603, 1554, 1513, 1401, 1221, 753. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.58 (d, *J* = 0.7 Hz, 1H), 7.90 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.62 – 7.57 (m, 1H), 7.51 (ddd, *J* = 7.5, 7.5, and 1.5 Hz, 1H), 7.42 (ddd, 7.6, 7.6, 0.9 Hz, 1H), 7.34 – 7.30 (m, 2H), 7.28 (d, *J* = 15.9 Hz, 1H), 7.19 – 7.10 (m, 2H), 6.21 (d, *J* = 15.9 Hz, 1H), 3.55 (s, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.4, 166.8, 143.2, 142.1, 138.4, 134.2, 133.6, 131.3, 131.3, 129.6, 128.7, 128.5, 127.8, 126.6, 119.8, 51.6 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{17}H_{15}O_3$ 267.1016; Found 267.1008.

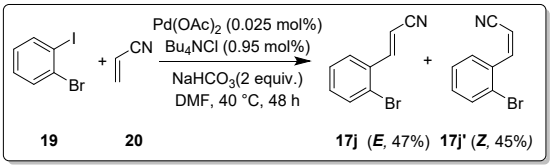


1k

Tert-butyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate (1k): GP 2 was carried out with tert-butyl (*E*)-3-(2-bromophenyl)acrylate **17i** (141 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the tert-butyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylate **1k** (130 mg, 85%) as a pale yellow viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17i**) = 0.8, *Rf* (**1k**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2976, 2845, 1698, 1634, 1595, 1199, 983, 760. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.62 (d, *J* = 0.7 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.66 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.55 (ddd, *J* = 7.5, 7.5, and 1.5 Hz, 1H), 7.45 (ddd, 7.6, 7.6, and 0.9 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.24 (d, *J* = 15.9 Hz, 2H), 7.2 (m, 2H), 6.22 (d, *J* = 15.9 Hz, 1H), 1.34 (s, 9H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.5, 165.7, 143.4, 140.7, 138.3, 134.3, 133.7, 133.6, 131.3, 131.2, 129.3, 128.6, 128.4, 127.7, 126.3, 121.9, 80.5, 28.0 (3C) ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{20}H_{21}O_3$ 309.1485; Found 309.1476.

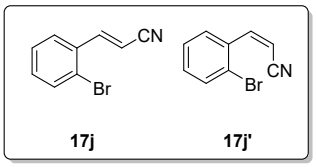
Preparation of 2-Bromo-acrylonitriles (17j and 17j'):

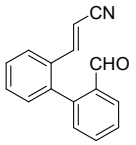
To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 2-bromo-2-iodobenzene **19** (300 mg, 1.06 mmol), acrylonitrile **20** (88 mg, 1.59 mmol), $Pd(OAc)_2$ (5.9 mg, 2.5 mol%), tetra-n-butyl ammonium chloride (371 mg, 1mmol), and $NaHCO_3$ (213 mg, 2.5 mmol) in DMF (5.0 mL) at room temperature under nitrogen atmosphere. The reaction resultant reaction mixture was stirred at 40 °C for 48 h in an oil bath. The reaction is monitored using TLC until the reaction is completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate, 98%) furnished the mixture of product **17j** (104 mg, 47%) and **17j'** (92 mg, 42%), as colorless liquids.



Scheme S10: Preparation of *E*/*Z*-3-(2-bromophenyl)acrylonitriles **17j** and **17j'**.

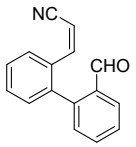
Table S7: Following *E*/*Z*-3-(2-bromophenyl)acrylonitriles were prepared using literature reports.[9,10]





1l

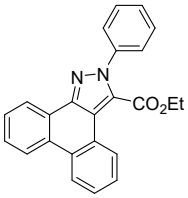
(*E*)-3-(2'-Formyl-[1,1'-biphenyl]-2-yl)acrylonitrile (1l): GP 2 was carried out (*E*)-3-(2-bromophenyl)acrylonitrile **17j** (104 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 (13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylonitrile **1l** (99 mg, 85%) as a colourless viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17j**) = 0.7, *Rf* (**1l**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3061, 2846, 2321, 1693, 1608, 1260, 1197, 967, 758. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.64 (d, *J* = 0.5 Hz, 1H), 7.99 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.64 – 7.58 (m, 2H), 7.53 (ddd, *J* = 7.5, 7.5 and 0.8 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.26 – 7.18 (m, 2H), 7.06 (d, *J* = 16.6 Hz, 1H), 5.74 (d, *J* = 16.6 Hz, 1H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) *δ* 191.0, 148.0, 142.3, 138.4, 134.2, 133.8, 132.6, 131.3, 131.2, 130.6, 128.9 (2C), 128.4, 125.6, 117.8, 98.0 ppm. **HRMS (ESI)** *m/z*: $[M + K]^+$ calcd for $C_{16}H_{11}KNO$ 272.0472; Found 272.0462.



1m

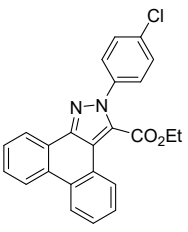
(*Z*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl) acrylonitrile (1m): GP 2 was carried out (*Z*)-3-(2-bromophenyl)acrylonitrile **17j'** (104 mg, 0.5 mmol), 2-formylphenylboronic acid **18a** (84 mg, 0.56 mmol), $Pd(OAc)_2$ (5.7 mg, 5 mol%), PPh_3 13 mg, 10 mol%), K_3PO_4 (212 mg, 1 mmol) in 2 mL of DMF at 140 °C for 16 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the (*Z*)-3-(2'-formyl-[1,1'-

biphenyl]-2-yl) acrylonitrile **1m** (94 mg, 81%) as a colourless viscous liquid. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**17j'**) = 0.7, *Rf* (**1m**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3061, 2848, 2215, 1691, 1596, 1196, 756. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.72 (d, *J* = 0.6 Hz, 1H), 8.21 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.03 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.65 (ddd, *J* = 7.5, 7.5, and 1.5 Hz, 1H), 7.59 – 7.48 (m, 3H), 7.35 (dd, 7.5, 1.5 Hz, 1H), 7.29 (dd, *J* = 7.6, 0.9 Hz, 1H), 6.86 (d, *J* = 12.1 Hz, 1H), 5.38 (d, *J* = 12.1 Hz, 1H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 191.2, 146.9, 142.9, 138.8, 134.2, 133.6, 132.8, 131.3, 131.0, 130.3, 128.8, 128.6, 127.8, 127.7, 116.8, 97.5 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{16}H_{12}NO$ 234.0913; Found 234.0904.



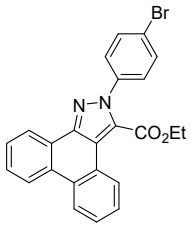
3aa

Ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3aa): GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3aa** (59 mg, 76%) as brown solid, mp = 130-133 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.3, *Rf* (**3aa**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3060, 2982, 1717, 1596, 1500, 1421, 1021, 759. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.78 (dd, *J* = 7.4, 1.9 Hz, 1H), 8.69 (dd, *J* = 7.6, 1.4 Hz, 1H), 8.60 (dd, *J* = 7.8, 1.7 Hz, 1H), 8.56 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.71 – 7.45 (m, 9H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.05 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.3, 146.1, 141.3, 130.7, 129.9, 129.1, 129.0 (2C), 128.7, 127.9, 127.5, 127.3, 126.9, 126.1, 125.8, 125.3 (3C), 125.1, 123.7, 123.3, 123.2, 117.9, 61.9, 13.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{19}N_2O_2$ 367.1441; Found 367.1455.



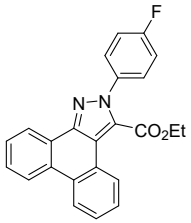
3ab

Ethyl 2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*] indazole-3-carboxylate (3ab): GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-chlorophenyl hydrazine hydrochloride **2b** (46 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*] indazole-3-carboxylate **3ab** (62 mg, 75%) as white solid, mp = 130-132 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.3, *Rf* (**3ab**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2976, 2924, 1716, 1493, 1372, 1203, 1088, 755. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 7.6, 1.8 Hz, 1H), 8.65 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.58 (dd, *J* = 7.1, 2.4 Hz, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 7.86 – 7.33 (m, 8H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.9, 146.3, 139.8, 134.5, 130.7, 129.9, 129.1 (2C), 128.9, 128.1, 127.5, 127.4, 127.0, 126.6 (2C), 125.9, 125.9, 124.9, 123.7, 123.3, 123.2, 118.1, 62.1, 13.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}ClN_2O_2$ 401.1051; Found 401.1067.



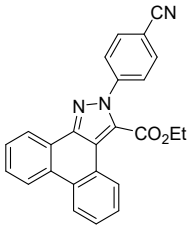
3ac

Ethyl 2-(4-bromophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ac): GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-Bromo phenyl hydrazine hydrochloride **2c** (56 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-bromophenyl)-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3ac** (68 mg, 72%) as maroon solid, mp = 132-134 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.3, *Rf* (**3ac**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3064, 2923, 2336, 1718, 1547, 1430, 1272, 757. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 7.7, 1.7 Hz, 1H), 8.65 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.59 (dd, *J* = 7.5, 2.0 Hz, 1H), 8.55 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.71 – 7.55 (m, 6H), 7.49 (d, *J* = 8.7 Hz, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 1.15 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.0, 146.4, 140.3, 132.2 (2C), 130.8, 130.0, 128.9, 128.2, 127.6, 127.5, 127.1, 126.9 (2C), 125.9, 125.9, 125.0, 123.8, 123.4, 123.3, 122.6, 118.3, 62.2, 13.7 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{24}H_{18}Br^{79}N_2O_2$ 445.0546; Found 445.0532; calcd for $C_{24}H_{18}Br^{81}N_2O_2$ 447.0526; Found 447.0512.



3ad

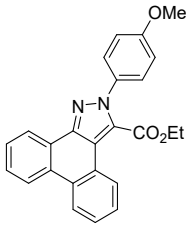
Ethyl 2-(4-fluorophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ad) : GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-flouro phenyl hydrazine hydrochloride **2d** (30 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 7 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-fluorophenyl)-2H-dibenzo[*e*,*g*]indazole-3-carboxylate **3ad** (60 mg, 74%) as white solid. mp = 135-137 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.3, *Rf* (**3ad**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3070, 2923, 1716, 1510, 1421, 1206, 1019, 757. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 7.3, 2.1 Hz, 1H), 8.55 (dd, J = 7.6, 1.6 Hz, 1H), 8.46 (dd, J = 7.4, 2.1 Hz, 1H), 8.44 – 8.39 (m, 1H), 7.58 – 7.40 (m, 6H), 7.18 – 7.08 (m, 2H), 4.21 (q, J = 7.1 Hz, 2H), 1.01 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, $J_{C\text{-}F}$ = 249.0 Hz, 161.9, 146.1, 137.4 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.7, 129.9, 129.2, 128.0, 127.5, 127.3 (3C), 127.2, 126.9, 125.9, 125.0, 123.7, 123.2 (d, $J_{C\text{-}F}$ = 13.7 Hz, 2C), 118.0, 115.9 (d, $J_{C\text{-}F}$ = 23.1 Hz, 2C), 62.0, 13.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}FN_2O_2$ 385.1347; Found 385.1338.



3ae

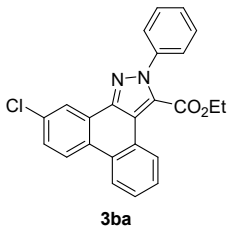
Ethyl 2-(4-cyanophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ae): GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-cyano phenyl hydrazine hydrochloride **2e** (42 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl 2-(4-cyanophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ae** (60 mg, 72%) as orange solid, mp = 163-165 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**1a**) = 0.5, *Rf* (**3ae**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2975, 2228, 1716, 1509, 1268, 1013, 793. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 7.8, 1.5 Hz, 1H), 8.63 (dd, J = 7.8, 1.4 Hz, 1H), 8.60 – 8.56 (m, 1H), 8.54 (d, J = 7.9 Hz, 1H), 7.84 (d,

J = 8.7 Hz, 2H), 7.75 (d, *J* = 8.7 Hz, 2H), 7.71 – 7.56 (m, 4H), 4.36 (q, *J* = 7.2 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H). ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.8, 147.1, 144.5, 133.0 (2C), 130.9, 130.2, 128.8, 128.5, 127.7, 127.6, 127.5, 126.1, 125.8 (2C), 125.6, 124.8, 123.8, 123.4, 123.3, 118.9, 118.1, 112.1, 62.4, 13.7 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{25}H_{18}N_3O_2$ 392.1394; Found 392.1394.



3ae

Ethyl 2-(4-methoxyphenyl)-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3af): GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-methoxy phenylhydrazine hydrochloride **2f** (44 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 93:07) furnished the ethyl 2-(4-methoxyphenyl)-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3af** (66 mg, 78%) as brown solid, mp = 160-162 °C. [TLC (petroleum ether/ethyl acetate 93:07), *Rf* (**1a**) = 0.9, *Rf* (**3af**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2928, 2847, 1716, 1513, 1247, 1205, 757. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 7.5, 1.9 Hz, 1H), 8.67 (dd, *J* = 7.7, 1.6 Hz, 1H), 8.60 (dd, *J* = 7.0, 2.6 Hz, 1H), 8.58 – 8.54 (m, 1H), 7.70 – 7.56 (m, 4H), 7.52 (d, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.9 Hz, 2H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.90 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.3, 159.8, 145.8, 134.4, 130.6, 129.8, 129.2, 127.8, 127.4, 127.3, 126.8, 126.7 (2C), 126.1, 125.8, 125.2, 123.7, 123.3, 123.2, 117.6, 114.1 (2C), 61.9, 55.6, 13.7 ppm. **HRMS** (ESI*) m/z*: $[(M + H)]^+$ calcd for $C_{25}H_{21}N_2O_3$ 397.1547; Found 397.1539.

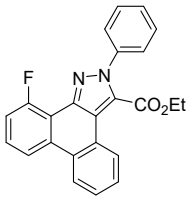


3ba

Ethyl 10-chloro-2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3ba) :

GP 3 was carried out with ethyl ethyl (*E*)-3-(4'-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1c** (65 mg, 0.21 mmol), and phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column

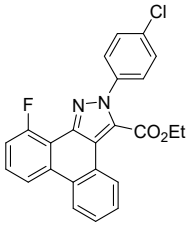
chromatography (petroleum ether/ethyl acetate: 95:05) furnished the Ethyl 10-chloro-2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3ba** (50 mg, 72%) as brown solid. mp =128-130 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1c**) = 0.3, *Rf* (**3ba**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2964, 2925, 1717, 1547, 1202, 1138, 1021, 756. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, J = 6.1, 3.4 Hz, 1H), 8.65 (d, J = 2.3 Hz, 1H), 8.50 (dd, J = 6.3, 3.2 Hz, 1H), 8.44 (d, J = 8.9 Hz, 1H), 7.66 – 7.45 (m, 8H), 4.30 (q, J = 7.2 Hz, 2H), 1.05 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.6, 146.0, 141.2, 133.1, 129.9, 129.1, 128.9 (2C, 128.8, 128.2, 128.0, 127.6, 127.2, 126.9, 125.5, 125.5(2C), 124.9, 124.9, 123.2, 123.1, 116.8, 62.1, 13.ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}ClN_2O_2$ 401.1051; Found 401.1042.



3ca

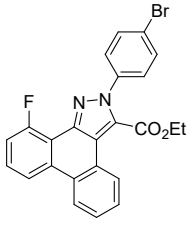
Ethyl 11-fluoro-2-phenyl-*2H*-dibenzo[*e,g*]indazole-3-carboxylate (3ca) :

GP 3 was carried out with ethyl (*E*)-3-(3'-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1b** (62 mg, 0.21 mmol), phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 11-fluoro-2-phenyl-*2H*-dibenzo[*e,g*]indazole-3-carboxylate **3ca** (57 mg, 72%) as yellow solid. mp =155-157 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1b**) = 0.3, *Rf* (**3ca**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 3055, 2978, 1716, 1594, 1496, 1315, 1204, 1104, 755. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.71 (dd, J = 5.9, 3.5 Hz, 1H), 8.57 (dd, J = 6.2, 3.4 Hz, 1H), 8.38 (d, J = 8.3 Hz, 1H), 7.68 – 7.57 (m, 5H), 7.56 – 7.45 (m, 3H), 7.38 (dd, J = 10.8, 8.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.05 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.5, 159.7 (d, $J_{C\text{-}F}$ = 255.5 Hz), 142.9 (d, $J_{C\text{-}F}$ = 5.4 Hz), 141.0, 133.4 (d, $J_{C\text{-}F}$ = 4.2 Hz), 129.0 (2C), 128.9 (d, $J_{C\text{-}F}$ = 2.5 Hz), 128.7, 128.6, 127.9, 127.9, 127.0, 126.2, 125.5, 125.4 (2C), 124.1, 119.0 (d, $J_{C\text{-}F}$ = 3.6 Hz), 118.3, 114.3, 114.0 (d, $J_{C\text{-}F}$ = 20.7 Hz), 62.1, 13.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}FN_2O_2$ 385.1347; Found 385.1360.



3cb

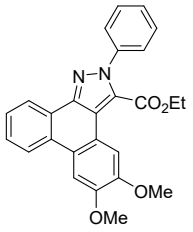
Ethyl 2-(4-chlorophenyl)-11-fluoro-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3cb): GP 3 was carried out with (*E*)-3-(3'-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1b** (62 mg, 0.21 mmol), 4-Chloro phenylhydrazine hydrochloride **2c** (44 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-chlorophenyl)-11-fluoro-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3cb** (62 mg, 72%) as pale yellow solid, mp =170-172 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1b**) = 0.3, *Rf* (**3cb**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2972, 2926, 2340, 1706, 1490, 1268, 1017, 750. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.70 (dd, J = 7.0, 2.4 Hz, 1H), 8.57 (dd, J = 7.3, 2.3 Hz, 1H), 8.38 (d, J = 8.2 Hz, 1H), 7.66 – 7.47 (m, 7H), 7.38 (ddd, J = 10.8, 8.1, 0.8 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 1.14 (t, J = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.2, 159.7 (d, $J_{C\text{-}F}$ = 255.7 Hz), 146.7, 143.2 (d, $J_{C\text{-}F}$ = 5.4 Hz), 139.6, 134.6, 133.4 (d, $J_{C\text{-}F}$ = 4.0 Hz), 129.2 (2C), 129.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.5, 128.1 (d, $J_{C\text{-}F}$ = 8.9 Hz), 128.0, 127.2, 126.6 (2C), 126.0, 125.6, 124.2, 119.1 (d, $J_{C\text{-}F}$ = 3.7 Hz), 118.6, 114.1 (d, $J_{C\text{-}F}$ = 20.6 Hz), 62.3, 13.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{17}ClFN_2O_2$ 419.0957; Found 419.0947.



3cc

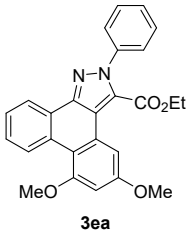
Ethyl 2-(4-bromophenyl)-11-fluoro-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3cc) :GP 3 was carried out with (*E*)-3-(3'-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1c** (62 mg, 0.21 mmol), 4-bromo phenylhydrazine hydrochloride **2c** (56 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the Ethyl 2-(4-bromophenyl)-11-fluoro-2*H*-dibenzo[e,g]indazole-3-carboxylate **3cc** (62 mg, 73%) as yellow solid, mp =165-170 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1c**) = 0.3, *Rf* (**3cc**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2924, 2344, 1703, 1481, 1266, 1013, 747. **^{1}H NMR** (400 MHz,

$CDCl_3$) δ 8.70 (dd, J = 7.1, 2.4 Hz, 1H), 8.57 (dd, J = 7.3, 2.3 Hz, 1H), 8.38 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 8.7 Hz, 2H), 7.64 – 7.58 (m, 3H), 7.51 (d, J = 8.8 Hz, 2H), 7.38 (ddd, J = 10.8, 8.1, 0.7 Hz, 1H), 4.35 (q, J = 7.1 Hz, 2H), 1.14 (t, J = 7.2 Hz, 3H).ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.2, 159.7 (d, $J_{C\text{-}F}$ = 255.5 Hz), 143.2 (d, $J_{C\text{-}F}$ = 5.5 Hz), 140.1, 133.5 (d, $J_{C\text{-}F}$ = 4.0 Hz), 132.2 (2C), 129.1 (d, $J_{C\text{-}F}$ = 2.4 Hz), 128.4, 128.2, 128.1, 128.0, 127.2, 126.9 (2C), 126.0, 125.6, 124.2, 122.6, 119.1 (d, $J_{C\text{-}F}$ = 3.6 Hz), 118.7, 114.1 (d, $J_{C\text{-}F}$ = 20.7 Hz), 62.3, 13.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{17}Br^{79}FN_2O_2$ 463.0452; Found 463.0458; calcd for $C_{24}H_{17}Br^{79}FN_2O_2$ 465.0431; Found 465.0443.



3da

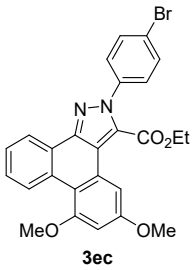
Ethyl 5,6-dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3da): GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)acrylate **1d** (71 mg, 0.21 mmol), and phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl 5,6-dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3da** (63 mg, 71%) as white solid, mp = °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**1d**) = 0.7, *Rf* (**3da**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2924, 1708, 1467, 1260, 1201, 1024, 760. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 7.9, 1.3 Hz, 1H), 8.62 (s, 1H), 8.41 (d, J = 8.2 Hz, 1H), 7.96 (s, 1H), 7.64 (ddd, J = 8.4, 7.1, and 1.5 Hz, 1H), 7.60 – 7.47 (m, 6H), 4.22 (q, J = 7.1 Hz, 2H), 4.12 (s, 3H), 4.08 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.9, 148.9, 148.5, 145.7, 141.8, 130.4, 128.9 (2C), 128.5, 127.7, 127.6, 126.4, 125.5 (2C), 124.3, 124.0, 123.2, 122.6, 120.1, 118.7, 108.0, 105.1, 61.6, 55.9, 55.8, 13.3 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{26}H_{23}N_2O_4$ 427.1652; Found 427.1666.



3ea

Ethyl 5,7-dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3ea):

GP 4 was carried out with ethyl (*E*)-3-(2'-formyl-4,6-dimethoxy-[1,1'-biphenyl]-2-yl)acrylate **1e** (71 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl 5,7-dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3ea** (62 mg, 70 %) as white solid, mp =128-130 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**1e**) = 0.7, *Rf* (**3ea**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3054, 2935, 2343, 1714, 1602, 1355, 1201, 1073, 756.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.45 (dd, J = 8.5, 0.8 Hz, 1H), 8.70 (dd, J = 7.8, 1.5 Hz, 1H), 8.04 (d, J = 2.5 Hz, 1H), 7.64 – 7.46 (m, 7H), 6.76 (d, J = 2.5 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 4.07 (s, 3H), 3.97 (s, 3H), 1.00 (t, J = 7.2 Hz, 3H). **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.6, 160.3, 158.9, 146.7, 141.3, 130.8, 129.2, 129.1, 129.0 (2C), 128.6, 128.4, 127.6, 125.7, 125.2 (2C), 124.3, 122.5, 118.2, 114.0, 100.5, 99.3, 62.0, 55.6, 55.3, 13.4 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{26}H_{23}N_2O_4$ 427.1652; Found 427.1667.

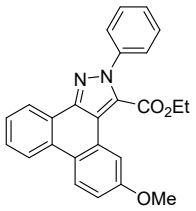


3ec

Ethyl 2-(4-bromophenyl)-5,7-dimethoxy-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3ec):

GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-4,6-dimethoxy-[1,1'-biphenyl]-2-yl)acrylate **1e** (71 mg, 0.21 mmol), and 4-Bromo phenyl hydrazine hydrochloride **2b** (56 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 90:10) furnished the ethyl 2-(4-bromophenyl)-5,7-dimethoxy-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3ec** (75 mg, 72%) as brown solid, mp = 170-172 °C. [TLC (petroleum ether/ethyl acetate 80:10), *Rf* (**1e**) = 0.7, *Rf* (**3ec**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2974, 2841, 1708, 1574, 1455, 1269, 1167, 751. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (dd, J = 8.4, 0.7 Hz, 1H), 8.66 (dd, J = 7.8, 1.5 Hz, 1H), 8.01 (d, J = 2.5 Hz, 1H), 7.66 (d, J = 8.7 Hz, 1H), 7.62 – 7.51 (m, 2H), 7.49 (d, J = 8.7 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 4.05 (s, 3H), 3.96 (s, 3H), 1.08 (t, J = 7.2 Hz, 3H). ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.3, 160.3, 158.9, 146.9, 140.3, 132.1 (2C), 130.8, 128.9, 128.9, 128.4, 127.7, 126.7 (2C), 125.8, 124.1, 122.5, 122.3, 118.4, 114.1, 100.7, 99.4, 62.2,

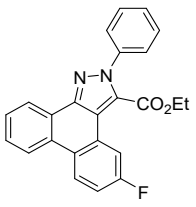
55.7, 55.3, 13.5 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{26}H_{22}Br^{79}N_2O_4$ 505.0757; Found 505.0774; calcd for $C_{26}H_{22}Br^{81}N_2O_4$ 507.0737; Found 507.0756.



3fa

Ethyl 5-methoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3fa):

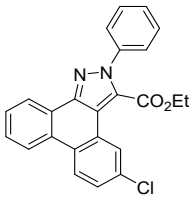
GP 3 was carried out with ethyl (*E*)-3-(2'-formyl-4-methoxy-[1,1'-biphenyl]-2-yl)acrylate **1f** (65 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 92:08) furnished the ethyl 5-methoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3fa** (60 mg, 73%) as white solid, mp =125-128 °C. [TLC (petroleum ether/ethyl acetate 92:08), *Rf* (**1f**) = 0.5, *Rf* (**3fa**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3058, 2984, 1714, 1610, 1460, 1207, 1041, 764. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (dd, J = 7.8, 1.3 Hz, 1H), 8.49 (d, J = 9.1 Hz, 1H), 8.45 (m, 2H), 7.66 – 7.47 (m, 7H), 7.21 (dd, J = 9.0, 2.7 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.1, 158.8, 146.4, 141.5, 130.8, 128.9 (2C), 128.9, 128.6, 127.9, 127.4, 126.4, 125.4 (2C), 125.0, 124.0, 123.5, 123.2, 122.7, 118.2, 115.4, 108.5, 61.9, 55.4, 13.4 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{25}H_{21}N_2O_3$ 397.1547; Found 397.1562.



3ga

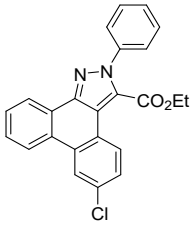
Ethyl 5-fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ga): GP 3 was carried out with ethyl (*E*)-3-(4-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1g** (62 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the Ethyl 5-fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ga** (58 mg, 73%) a pale yellow solid, mp = 133-135 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1g**) = 0.5, *Rf* (**3ga**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3059, 2978, 1715, 1610, 1455, 1305, 1025, 763. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.64 (dd, J =

7.7, 1.3 Hz, 1H), 8.55 (dd, J = 10.9, 2.7 Hz, 1H), 8.47 (m, 1H), 8.41 – 8.37 (m, 1H), 7.65 – 7.47 (m, 7H), 7.28 (ddd, J = 9.1, 7.8, and 2.7 Hz, 1H), 4.31 (q, J = 7.1 Hz, 2H), 1.07 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.76 (d, $J_{C\text{-}F}$ = 245.7 Hz), 161.7,146.1, 141.2, 130.2, 129.2, 129.0 (2C), 128.8, 128.0, 127.7 (d, $J_{C\text{-}F}$ = 9.7 Hz), 127.2, 126.3 (d, $J_{C\text{-}F}$ = 2.5 Hz), 125.6 (d, $J_{C\text{-}F}$ = 8.9 Hz), 125.4 (2C), 124.5, 123.2, 123.0, 117.4 (d, $J_{C\text{-}F}$ = 3.0 Hz), 114.7 (d, $J_{C\text{-}F}$ = 22.7 Hz), 111.7 (d, J = 23.8 Hz), 62.1, 13.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{18}FN_2O_2$ 385.1347; Found 385.1361.



3ha

Ethyl 5-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ha): GP 3 was carried out with ethyl (*E*)-3-(4-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1h** (65 mg, 0.21 mmol), phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 5-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ha** (62 mg, 75%) as yellow solid. mp = 158-160 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1h**) = 0.3, *Rf* (**3ha**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3061, 2981, 1715, 1498, 1418, 1203, 763. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.81 (d, J = 2.2 Hz, 1H), 8.62 (dd, 6.8, 2.2Hz, 1H), 8.41 – 8.33 (m, 2H), 7.63 – 7.46 (m, 8H), 4.33 (q, J = 7.2 Hz, 2H), 1.12 (t, J = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.5, 146.03, 141.1, 133.1, 129.8, 129.1, 128.9 (2C), 128.8, 128.2, 128.0, 127.6, 127.2, 126.9, 125.5, 125.4 (2C), 124.9, 124.9, 123.2, 123.1, 116.8, 62.1, 13.4 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{24}H_{18}ClN_2O_2$ 401.1051; Found 401.1066.

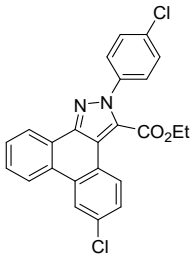


3ia

Ethyl 6-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ia):

GP 3 was carried out with ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1i** (65 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF

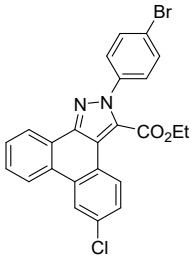
at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 6-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ia** (63 mg, 75%) as pale yellow solid, mp =135-137 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1i**) = 0.3, *Rf* (**3ia**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3060, 2981, 1716, 1464, 1424, 1206, 762. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 8.7, 1.2 Hz, 1H), 8.65 (m, 1H), 8.48 (m, 1H), 8.42 (dd, *J* = 6.4, 2.9 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.67 – 7.48 (m, 6H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.02 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.9, 145.8, 141.3, 132.8, 131.4, 129.5, 129.0 (2C), 128.9, 128.8, 128.0 (2C), 127.4(2C), 125.4 (2C), 125.3, 124.4, 123.5, 123.3, 123.2, 117.4, 62.0, 13.4 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{24}H_{18}ClN_2O_2$ 401.1051; Found 401.1060.



3ib

Ethyl 6-chloro-2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ib):

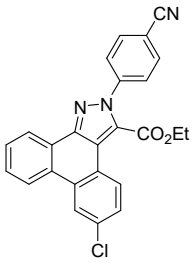
GP 3 was carried out with ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1i** (65 mg, 0.21 mmol), and 4-chloro phenyl hydrazine hydrochloride **2c** (44 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 7 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 6-chloro-2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ib** (64 mg, 71%) as orange solid, mp = 140-143 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1i**) = 0.3, *Rf* (**3ib**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2979, 2344, 1719, 1593, 1375, 1269, 747. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.7, 1.6 Hz, 1H), 8.64 – 8.56 (m, 1H), 8.45 (d, *J* = 2.4 Hz, 1H), 8.42 – 8.35 (m, 1H), 7.61-7.63 (m, 2H), 7.56 – 7.45 (m, 5H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.6, 146.0, 139.8, 134.7, 133.0, 131.5, 129.6, 129.1 (2C), 128.9, 128.2, 128.1, 127.5, 127.4, 126.7 (2C), 125.1, 124.2, 123.5, 123.3, 123.7, 117.7, 62.1, 13.5 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{17}Cl_2N_2O_2$ 435.0662; Found 435.0661.



3ic

Ethyl 2-(4-bromophenyl)-6-chloro-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ic):

GP 3 was carried out with ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1i** (65 mg, 0.21 mmol), and 4-Bromo phenylhydrazine hydrochloride **2b** (56 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 7 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-bromophenyl)-6-chloro-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3ic** (74 mg, 74%) as orange solid, mp = 165-168°C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1i**) = 0.3, *Rf* (**3ic**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3057, 2343, 1714, 1489, 1270, 1207, 758. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.7 Hz, 1H), 8.59 (dd, *J* = 7.0, 2.3 Hz, 1H), 8.43 (d, *J* = 2.1 Hz, 1H), 8.40 – 8.33 (m, 1H), 7.67 (d, *J* = 8.7 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.51 – 7.48 (m, 1H), 7.46 (d, *J* = 8.8 Hz, 2H), 4.31 (q, *J* = 7.2 Hz, 2H), 1.12 (t, *J* = 7.2 Hz, 4H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) *δ* 161.6, 146.1, 140.3, 133.01, 132.1 (2C), 131.5, 129.6, 128.8, 128.2, 128.1, 127.4, 127.4, 126.9 (2C), 125.1, 124.1, 123.4, 123.2, 123.1, 122.5, 117.7, 62.1, 13.5 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{17}ClBr^{79}N_2O_2$ 479.0156; Found 479.0152; calcd for $C_{24}H_{17}ClBr^{79}N_2O_2$ 481.0136; Found 481.0134.

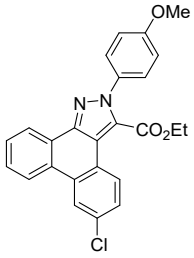


3ie

Ethyl 6-chloro-2-(4-cyanophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ie):

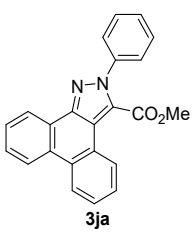
GP 3 was carried out with ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1i** (65 mg, 0.21 mmol), and 4-cyano phenylhydrazine hydrochloride **2e** (42 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 6-chloro-2-(4-cyanophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ie** (65 mg, 73%) as orange solid. mp = 183-185 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**1i**) = 0.6, *Rf* (**3ie**) = 0.5, UV

detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2978, 2915, 2343, 2224, 1706, 1600, 1273, 756. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.7 Hz, 1H), 8.59 (dd, *J* = 7.4, 1.9 Hz, 1H), 8.46 (d, *J* = 2.1 Hz, 1H), 8.39 (dd, *J* = 7.1, 2.2 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 2H), 7.73 (d, *J* = 8.6 Hz, 2H), 7.69 – 7.58 (m, 3H), 7.51 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.34 (q, *J*=7.2, 2H), 1.13 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.4, 146.7, 144.5, 133.4, 132.9 (2C), 131.6, 129.7, 128.6, 128.6, 128.2, 127.5 (2C), 125.8 (2C), 124.9, 123.9, 123.6, 123.4, 123.2, 118.4, 117.9, 112.2, 62.4, 13.6 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{25}H_{17}ClN_3O_2$ 426.1004; Found 426.0992.



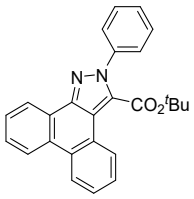
3if

Ethyl 6-chloro-2-(4-methoxyphenyl)-2*H*-dibenzo[*e,g*]indazole-3-carboxylate (3if): GP 3 was carried out with ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1i** (65 mg, 0.21 mmol), and 4-chloro phenyl hydrazine hydrochloride **2f** (44 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 6-chloro-2-(4-methoxyphenyl)-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3if** (65 mg, 73%) as brown solid. mp = 170-173 °C. [TLC (petroleum ether/ethyl acetate 93:07), *Rf* (**1i**) = 0.3, *Rf* (**3if**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 2979, 1715, 1514, 1250, 1205, 968, 766. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.7 Hz, 1H), 8.68 – 8.61 (m, 1H), 8.51 (d, *J* = 2.2 Hz, 1H), 8.44 (dd, 7.5,1.9 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.50-7.53 (m, 3H), 7.04 (d, *J* = 8.9 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.9, 159.9, 145.6, 134.4, 132.8, 131.4, 129.5, 129.1, 128.1, 128.0, 127.4, 127.4, 126.7 (2C), 125.4, 124.5, 123.5, 123.3, 123.3, 117.2, 114.1(2C), 62.0, 55.7, 13.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{25}H_{20}ClN_2O_3$ 431.1157; Found 431.1169.



3ja

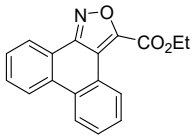
Methyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ja): GP 3 was carried out with methyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1j** (56 mg, 0.21 mmol), phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the methyl 2-phenyl-2*H*-dibenzo[*e,g*]indazole-3-carboxylate **3ja** (57 mg, 76%) as brown solid. mp = 135-138 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1j**) = 0.3, *Rf* (**3ja**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3051, 2947, 1716, 1547, 1427, 1204, 689.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72-8.68 (m, 2H), 8.54 (ddd, *J* = 9.3, 7.2, and 3.3 Hz, 2H), 7.69 – 7.45 (m, 9H), 3.83 (s, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 162.8, 146.0, 141.0, 130.6, 129.8, 129.0 (2C), 128.6, 127.9, 127.4, 127.3, 126.8, 125.9, 125.7, 125.6, 125.3, 125.0, 124.9 (2C), 123.6, 123.2, 123.1, 117.9, 52.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{23}H_{17}N_2O_2$ 353.1285; Found 353.1298.



3ka

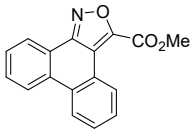
Tert-butyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ka)

GP 3 was carried out with tert-butyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1k** (64 mg, 0.21 mmol), phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 3 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the *tert*-butyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ka** (57 mg, 70%) as orange solid. mp = 145-148 °C. [TLC (petroleum ether/ethyl acetate 95:05, *Rf* (**1k**) = 0.3, *Rf* (**3ka**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2961, 2860, 1716, 1446, 1257, 1201, 1094, 761. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.84 – 8.79 (m, 1H), 8.67 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.56 (d, *J* = 7.7 Hz, 2H), 7.77 – 7.43 (m, 9H), 1.37 (s, 9H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.2, 145.9, 141.4, 130.7, 130.6, 129.7, 128.9(2C), 128.6, 127.8, 127.4, 127.3, 126.7, 126.3, 125.7(2C), 125.7, 125.2, 123.6, 123.2, 123.2, 117.4, 83.5, 27.6 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{23}H_{23}N_2O_2$ 395.1754; Found 353.1750.



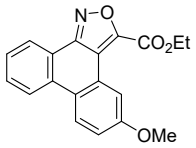
6aa

Ethyl phenanthro[9,10-*c*] isoxazole-3-carboxylate (6aa): GP 4 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), hydroxylamine hydrochloride **5** (17 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl phenanthro[9,10-*c*] isoxazole-3-carboxylate **5aa** (37 mg, 60%) as brown solid, mp = 132-135 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.3, *Rf* (**5aa**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2919, 2852, 2316, 1718, 1441, 1276, 1218, 752. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.41 (dd, *J* = 7.9, 1.6 Hz, 1H), 8.62 (dd, *J* = 7.9, 1.3 Hz, 1H), 8.49-8.45 (m, 2H), 7.77 – 7.71 (m, 1H), 7.71 – 7.60 (m, 3H), 4.61 (q, *J* = 7.1 Hz, 2H), 1.54 (d, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 158.3, 156.8, 153.8, 132.2, 130.9, 130.6, 129.2, 129.2, 128.2, 128.2, 124.6, 123.6, 123.5, 123.4, 121.6, 117.8, 62.5, 14.2 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{18}H_{14}NO_3$ 292.0968; Found 292.0967.



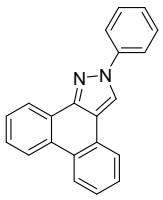
6ab

Methyl phenanthro[9,10-*c*] isoxazole-3-carboxylate (6ab): GP 4 was carried out with methyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1j** (56 mg, 0.21 mmol), hydroxylamine hydrochloride **5** (17 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the methyl phenanthro[9,10-*c*] isoxazole-3-carboxylate **5ab** (33 mg, 58%) as white solid. mp = 135-138°C. [TLC (petroleum ether/ethyl acetate 95:05, *Rf* (**1j**) = 0.3, *Rf* (**5ab**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2924, 1726, 1444, 1306, 1272, 1215, 756. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.37 (dd, *J* = 7.7, 1.4 Hz, 1H), 8.60 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.44 (dd, 7.2,7.2, 2H), 7.76 – 7.69 (m, 1H), 7.69 – 7.59 (m, 3H), 4.14 (s, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 158.7, 156.8, 153.4, 132.1, 130.9, 130.6, 129.3, 129.1, 128.3, 128.2, 124.6, 123.6, 123.5, 123.3, 121.6, 117.9, 53.1 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{17}H_{12}NO_3$ 278.0812; Found 278.0801.



6ac

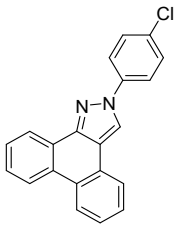
Ethyl 5-methoxyphenanthro[9,10-*c*] isoxazole-3-carboxylate (6ac): GP 4 was carried out with ethyl (*E*)-3-(2'-formyl-4-methoxy-[1,1'-biphenyl]-2-yl)acrylate **1f** (65 mg, 0.21 mmol), hydroxylamine hydrochloride **5** (17 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 5 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 5-methoxyphenanthro[9,10-*c*] isoxazole-3-carboxylate **6ac** (38 mg, 57%) as white solid. mp = 120-122 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1f**) = 0.3, *Rf* (**5ac**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3101, 2981, 1720, 1567, 1457, 1213, 758. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.8 Hz, 1H), 8.55 (dd, *J* = 7.9, 1.2 Hz, 1H), 8.30 (d, *J* = 9.2 Hz, 2H), 7.68 (ddd, *J* = 8.4, 7.3, 1.5 Hz, 1H), 7.54 (ddd, 8.1, 8.0, 1.1 Hz, 1H), 7.20 (dd, *J* = 9.0, 2.8 Hz, 1H), 4.59 (q, *J* = 7.1 Hz, 2H), 1.54 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 159.6, 158.5, 157.2, 153.8, 132.5, 130.7, 127.3, 125.1, 124.9, 124.7, 124.2, 123.0, 120.7, 118.3, 117.9, 111.7, 77.2, 62.6, 55.7, 14.4 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{19}H_{16}NO_4$ 322.1074; Found 322.1066.



4aa

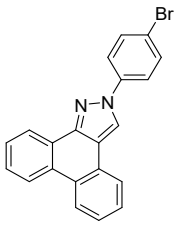
2-Phenyl-2*H*-dibenzo[*e*,*g*]indazole (4aa): GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 120 °C for 72 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the 2-phenyl-2*H*-dibenzo[*e,g]*indazole **4aa** (46 mg, 75%), as brown solid. mp = 160-163 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.6, *Rf* (**4aa**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3050, 2854, 1596, 1504, 1405, 1165, 753. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 – 8.70 (m, 1H), 8.67 (s, 1H), 8.54 (m, 2H), 8.11 – 8.05 (m, 1H), 7.97 (dd, *J* = 8.5, 0.9 Hz, 2H), 7.68 – 7.61 (m, 2H), 7.59 – 7.51 (m, 4H), 7.41 – 7.35 (m, 1H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 146.9, 140.4, 130.8, 129.5 (2C), 128.9, 127.6, 127.3, 127.2, 127.0, 126.8,

125.9, 125.8, 124.1, 123.8, 123.4, 123.2, 120.6, 120.0 (2C), 118.6 ppm. **HRMS (ESI)** *m/z*: [(M + H)]$^+$ calcd for $C_{21}H_{15}N_2$ 295.1230; Found 295.1239.



4ab

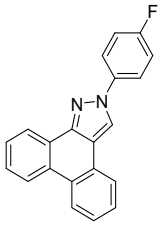
2-(4-Chlorophenyl)-2*H*-dibenzo[*e*,*g*]indazole (4ab): GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-chlorophenyl hydrazine hydrochloride **2c** (44 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 72 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the 2-(4-chlorophenyl)-2*H*-dibenzo[*e,g*]indazole **4ab** (50 mg, 73%) as white solid. mp = 155-158 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.6, *Rf* (**4ab**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2923, 2341, 1734, 1556, 1267, 1222, 754. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 6.3, 2.9 Hz, 1H), 8.54 (s, 1H), 8.51 (m, 2H), 8.01 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.62 (dd, *J* = 6.1, 2.1 Hz, 2H), 7.53 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.47 (d, *J* = 8.8 Hz, 2H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) *δ* 147.0, 138.9, 132.4, 130.8, 129.5(2C), 128.9, 127.7, 127.4, 127.3, 126.6, 126.1, 125.6, 124.1, 123.8, 123.4, 123.2, 120.9(2C), 120.3, 118.8 ppm. **HRMS (ESI)** *m/z*: [(M + H)]$^+$ calcd for $C_{21}H_{14}ClN_2$ 329.0840; Found 329.0845.



4ac

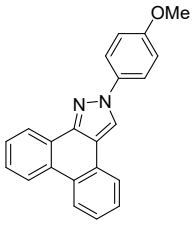
2-(4-Bromophenyl)-2H-dibenzo[*e*,*g*]indazole (**4ac**)**:** GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-flouro phenyl hydrazine hydrochloride **2b** (30 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 72 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the **2**-(4-bromophenyl)-2*H*-dibenzo[*e*,*g*]indazole **4ac** (56 mg, 71%) as maroon solid. mp = 165-167 °C. [TLC (petroleum ether/ethyl acetate 95:05, *Rf* (**1a**) = 0.6, *Rf* (**4ac**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3059, 2925, 1723, 1591, 1554, 1491, 956,

753. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 – 8.63 (m, 1H), 8.59 (s, 1H), 8.52 (dd, J = 6.2, 3.2 Hz, 2H), 8.07 – 8.01 (m, 1H), 7.85 – 7.80 (m, 2H), 7.63 (dt, J = 4.7, 1.3 Hz, 4H), 7.58 – 7.51 (m, 2H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 147.2, 139.5, 132.6 (2C), 130.9, 129.6, 129.0, 127.9, 127.5, 127.4, 126.7, 126.2, 124.2, 123.9, 123.5, 123.3, 121.3 (2C), 121.0, 120.4, 118.9 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{21}H_{14}Br^{79}N_2$ 373.0335; Found 373.0333; calcd for $C_{21}H_{14}Br^{81}N_2$ 375.0314; Found 375.0314.



4ad

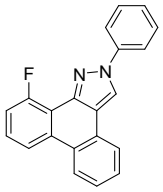
2-(4-Fluorophenyl)-2*H*-dibenzo[*e,g*]indazole (4ad): GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-flouro phenyl hydrazine hydrochloride **2d** (30 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 78 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the 2-(4-fluorophenyl)-2*H*-dibenzo[*e*,*g*]indazole (50 mg, 74%), as white solid. mp =158-160 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1a**) = 0.6, *Rf* (**4ad**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2924, 1602, 1509, 1463, 1249, 1190, 754. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 – 8.63 (m, 1H), 8.55 – 8.48 (m, 3H), 8.04 – 7.98 (m, 1H), 7.91 – 7.84 (m, 2H), 7.66 – 7.60 (m, 2H), 7.57 – 7.49 (m, 2H), 7.24 – 7.16 (m, 2H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.45 (d, $J_{C\text{-}F}$ = 246.7 Hz), 146.9, 136.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 130.8, 128.9, 127.6, 127.3, 127.3, 126.7, 126.0, 125.6, 124.0, 123.8, 123.4, 123.2, 1*m/z*: $[(M + H)]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; Found 313.1145.



4ae

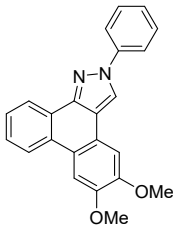
2-(4-Methoxyphenyl)-2*H*-dibenzo[*e,g*]indazole (4ae) : GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), 4-methoxy phenyl hydrazine hydrochloride **2f** (44 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 72 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl

acetate: 93:07) furnished the **2**-(4-methoxyphenyl)-2*H*-dibenzo[*e*,*g*]indazole **4ae** (52 mg, 76%) as white solid. mp = 156-158 °C. [TLC (petroleum ether/ethyl acetate 93:07), *Rf* (**1a**) = 0.6, *Rf* (**4ae**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2925, 2841, 1717, 1515, 1466, 1249, 754. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 – 8.66 (m, 1H), 8.54 (m, 3H), 8.05 (m, 1H), 7.84 (d, J = 8.3 Hz, 2H), 7.67 – 7.60 (m, 2H), 7.56 – 7.49 (m, 2H), 7.03 (d, J = 8.3 Hz, 2H), 3.87 (s, 3H). **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 158.7, 146.5, 134.1, 130.6, 128.8, 127.4, 127.3, 127.2, 126.9, 125.8, 124.0, 123.8, 123.4, 123.2, 121.6 (2C), 120.7, 118.4, 114.6 (2C), 55.5 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; Found 325.1346.



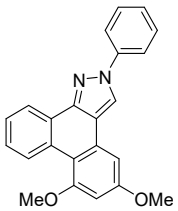
4ca

11-Fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole (4ca): GP 5 was carried out with ethyl (*E*)-3-(3'-fluoro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1b** (65 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 74 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 92:08) furnished the 11-fluoro-2-phenyl-2*H*-dibenzo[*e,g*]indazole **4ca** (58 mg, 72%) as black solid. mp = 167-170 °C. [TLC (petroleum ether/ethyl acetate 92:08), *Rf* (**1b**) = 0.5, *Rf* (**4ca**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2923, 2856, 2343, 1595, 1501, 1246, 1050, 753. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (d, J = 0.7 Hz, 1H), 8.52 (dd, J = 8.0, 1.2 Hz, 1H), 8.37 (d, J = 8.2 Hz, 1H), 8.10 (dd, J = 7.7, 1.4 Hz, 1H), 8.02 – 7.98 (m, 2H), 7.62 – 7.51 (m, 5H), 7.42 – 7.35 (m, 2H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 159.88 (d, $J_{C\text{-}F}$ = 254.9 Hz), 143.7 (d, $J_{C\text{-}F}$ = 5.2 Hz), 140.41, 133.5 (d, $J_{C\text{-}F}$ = 4.6 Hz), 130.9, 129.5(2C), 128.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.1, 127.6 (d, $J_{C\text{-}F}$ = 8.8 Hz), 127.2, 127.0, 126.2, 124.3, 124.0, 120.2(2C), 120.09, 119.40, 119.15 (d, $J_{C\text{-}F}$ = 3.6 Hz), 113.88 (d, $J_{C\text{-}F}$ = 20.5 Hz) ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; Found 313.1139.



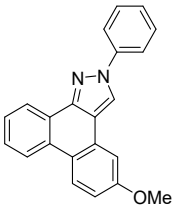
4da

5,6-Dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole (4da) : GP 5 was carried out with ethyl *E*-3-(2'-formyl-4,5-dimethoxy-[1,1'-biphenyl]-2-yl)acrylate **1d** (71 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 Ml of DMF at 140 °C for 84 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 88:12) furnished the **5,6-**dimethoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole **4da** (52 mg, 71%) as white solid. mp =160-162 °C. [TLC (petroleum ether/ethyl acetate 88:12), *Rf* (**1d**) = 0.9, *Rf* (**4da**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3054, 2942, 1703, 1601, 1561, 1265, 1214, 762. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.66 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.66 (dd, *J* = 7.6, 1.7 Hz, 1H), 8.51 (s, 1H), 8.38 – 8.28 (m, 1H), 7.95 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.95 (dd, *J* = 8.5, 1.0 Hz, 2H), 7.83 (s, 1H), 7.64 – 7.47 (m, 4H), 7.38 – 7.32 (m, 2H), 4.06 (s, 3H), 4.02 (s, 3H). **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 149.3, 148.1, 146.5, 140.5, 130.6, 129.5 (2C), 127.4, 126.9, 126.3, 124.9, 123.3, 122.8, 122.5, 120.8, 119.9 (2C), 119.6, 118.6, 105.5, 105.3, 55.9, 55.9 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{23}H_{19}N_2O_2$ 355.1441; Found 355.1436.



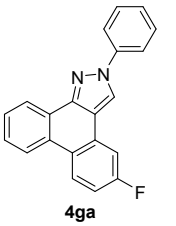
4ea

5,7-Dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole (4ea) : GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-4,6-dimethoxy-[1,1'-biphenyl]-2-yl)acrylate **1e** (71 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 84 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 88:12) furnished the 5,7-dimethoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole **4ea** (51 mg, 70%) as white solid. mp = 158-160 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**1e**) = 0.4, *Rf* (**4ea**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3061, 2935, 1603, 1459, 1398, 1214, 1058, 761. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.42 (dd, *J* = 8.3, 1.3 Hz, 1H), 8.71 (dd, *J* = 7.5, 1.8 Hz, 1H), 8.52 (s, 1H), 7.97 – 7.91 (m, 2H), 7.56-7.50 (m, 4H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 6.62 (d, *J* = 2.4 Hz, 1H), 4.03 (s, 3H), 3.92 (s, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ 160.6, 158.9, 147.3, 140.3, 131.1, 129.9, 129.4 (2C), 128.5, 127.3, 126.9, 125.6, 124.9, 122.5, 120.8, 119.9 (2C), 118.9, 112.9, 98.6, 98.1, 55.5, 55.3 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{23}H_{19}N_2O_2$ 355.1441; Found 355.1454.



4fa

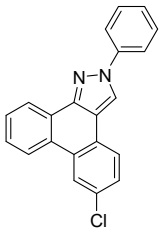
5-Methoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole (4fa) : GP 5 was carried out with ethyl (*E*)-3-(2'-formyl-4-methoxy-[1,1'-biphenyl]-2-yl)acrylate **1f** (65 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 72 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 92:08) furnished the 5-methoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole **4fa** (51 mg, 76%) as white solid. mp = 118-120 °C. [TLC (petroleum ether/ethyl acetate 92:08), *Rf* (**1f**) = 0.5, *Rf* (**4fa**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3052, 2927, 1713, 1606, 1557, 1466, 1261, 1214, 755. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.69 – 8.62 (m, 2H), 8.47 – 8.40 (m, 2H), 8.02 – 7.90 (m, 2H), 7.65 – 7.51 (m, 4H), 7.49 (d, *J* = 2.7 Hz, 1H), 7.40 – 7.35 (m, 1H), 7.13 (dd, *J* = 9.0, 2.7 Hz, 1H), 3.98 (s, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 158.7, 147.1, 140.4, 130.9, 129.4 (2C), 128.1, 127.6, 126.9, 126.3, 125.3, 124.7, 123.2, 122.8, 122.5, 120.5, 119.9(2C), 118.6, 114.1, 106.6, 55.3 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{22}H_{17}N_2O$ 325.1335; Found 325.1347.



4ga

5-Fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole (4ga) : GP 5 was carried out with Ethyl (*E*)-3-(2-bromo-5-fluorophenyl)acrylate **1g** (62 mg, 0.21 mmol), and phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 72 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the 5-fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole **4ga** (46 mg, 71%), as white solid. mp = 130-135 °C. [TLC (petroleum ether/ethyl acetate 95:08, *Rf* (**1g**) = 0.5, *Rf* (**4ga**) = 0.4, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3054, 2924, 1607, 1466, 1325, 1185, 757. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 – 8.61 (m, 1H), 8.53 (s, 1H), 8.46 – 8.34 (m, 2H), 7.97 – 7.88 (m, 2H), 7.66 – 7.57 (m, 3H), 7.57 – 7.49 (m, 2H), 7.42 – 7.34 (m, 1H), 7.24 – 7.15 (m, 1H). **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.9 (d, $J_{C\text{-}F}$ = 246.9 Hz), 146.9, 140.3, 130.3, 129.5 (2C), 128.5 (d, $J_{C\text{-}F}$ = 8.9 Hz), 127.7, 127.2, 127.1, 125.9, 125.85, 125.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 125.2, 123.3,

123.2, 120.9, 120.0 (2C), 118.1 (d, J_{C-F} = 3.1 Hz), 113.8 (d, J_{C-F} = 22.5 Hz), 109.4(d, J_{C-F} = 21.7 Hz) ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{21}H_{14}FN_2$ 313.1136; Found 313.1144.

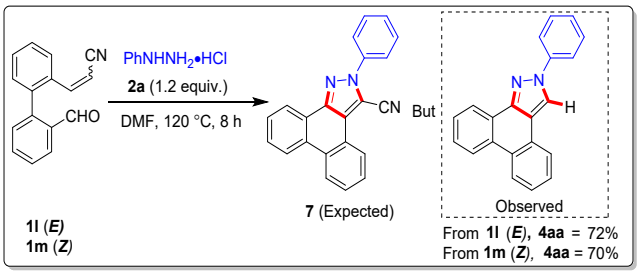


4ia

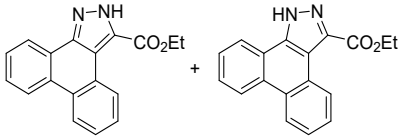
6-Chloro-2-phenyl-2*H*-dibenzo[*e,g*]indazole (4ia) : GP 5 was carried out with ethyl (*E*)-3-(5-chloro-2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1i** (65 mg, 0.21 mmol), and phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at 140 °C for 78 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the 6-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole 4ba (50 mg, 74%) as white solid. mp = 130-133 °C. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**1i**) = 0.6, *Rf* (**4ia**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2926, 1727, 1552, 1397, 1258, 1013, 789. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.68 – 8.60 (m, 1H), 8.53 (dd, *J* = 6.1, 2.5 Hz, 1H), 8.45 – 8.33 (m, 2H), 7.96 – 7.84 (m, 3H), 7.67 – 7.57 (m, 2H), 7.57 – 7.48 (m, 2H), 7.48 – 7.42 (m, 1H), 7.41 – 7.35 (m, 1H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 146.6, 140.3, 131.7, 130.2, 129.7, 129.5 (2C), 127.9, 127.7, 127.3, 127.2, 125.9, 125.3, 125.1, 123.7, 123.4, 123.3, 120.5, 120.0 (2C), 117.8 ppm. **HRMS (ESI)** *m/z*: $[M + H]^+$ calcd for $C_{24}H_{14}ClN_2$ 329.0840; Found 329.0845.

Synthesis of Phenanthrene-Fused Pyrazole (4aa) from *E*/*Z*-3-(2'-Formyl-[1,1'-biphenyl]-2-yl)acrylonitrile (1l and 1m):

To an oven dried Schlenk tube equipped with a magnetic stirring bar were added (*E/Z*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylonitrile **1l/1m** (49 mg, 0.21 mmol), and phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) in 2 mL of DMF at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 120 °C for 8 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. The reaction mixture was cooled to room temperature and quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 95%) furnished the product **4aa** in 72% (from **1l**) and 70% (from 1m) as brown solid.

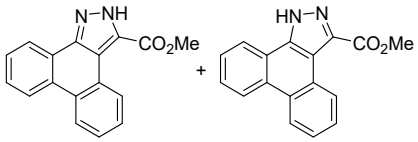


Scheme S4: Synthesis of **4aa** from **1l** and **1m**.



9a+9a'

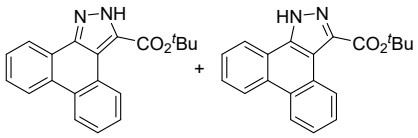
Ethyl 2*H*-dibenzo[*e,g*]indazole-3-carboxylate (9a+9a'): GP 6 was carried out with ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), and *P*-toluene sulfonyl hydrazide **8** (42 mg, 0.23 mmol) in 2 mL of DMF at 60 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 70:30) furnished a mixture of products **9a+9a'** (46 mg, 75%), as white solid. mp = 180-182 °C. [TLC (petroleum ether/ethyl acetate 70:30, *Rf* (**1a**) = 0.9, *Rf* (**9a+9a'**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3147, 2964, 1715, 1448, 1272, 1182, 754. **9a: ^{1}H NMR** (400 MHz, DMSO-*d6*; peaks due to the major isomer) δ 14.75 (s, 1H), 9.34 (d, J = 7.8 Hz, 1H), 8.79-8.83 (m, 2H), 8.61 – 8.46 (m, 1H), 7.83 – 7.59 (m, 4H), 4.48 (q, J = 7.1 Hz, 2H), 1.42 (t, J = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, DMSO-*d6*) δ 163.9, 138.2, 137.8, 129.7, 128.1, 127.9, 127.7, 127.5, 126.4, 126.1, 126.0, 124.0, 123.8, 122.3, 120.4, 115.5, 60.9, 14.3 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{18}H_{15}N_2O_2$ 291.1128; Found 291.1121.



9b+9b'

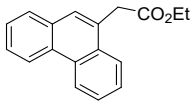
Methyl 2*H*-dibenzo[*e,g*]indazole-3-carboxylate (9b+9b'): GP 6 was carried out with Methyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1j** (55 mg, 0.21 mmol), and *P*-toluene sulfonyl hydrazide **8** (42 mg, 0.23 mmol) in 2 mL of DMF at 60 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 70:30) furnished the 2*H*-dibenzo indazole (46 mg, 78%), as white solid. mp = 182-184 °C. [TLC (petroleum ether/ethyl acetate 70:30, *Rf* (**1j**) = 0.9, *Rf* (**9b+9b'**) = 0.5), UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3178, 2343, 1718, 1435, 1267, 1187, 756. **^{1}H NMR** (400 MHz, DMSO-

d6, peaks due to the major isomer) δ 14.78 (s, 1H), 9.55-9.25 (m, 1H), 8.9-8.4 (m, 3H), 8.00-7.5 (m, 4H), 4.00 (s, 3H). **^{13}C{H} NMR** (101 MHz, DMSO-*d6*) δ 164.3, 137.9, 137.8, 129.7, 129.3, 128.1, 127.9, 127.7, 127.5, 126.4, 126.0, 124.1, 123.8, 122.3, 120.4, 115.6, 61.9, 52.1 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{17}H_{13}N_2O_2$ 277.0972; Found 277.0976.



9c+9c'

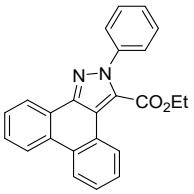
Tertiary butyl 2*H*-dibenzo[*e,g*]indazole-3-carboxylate (9c+9c'): GP 6 was carried out with tertiary butyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1k** (64 mg, 0.21 mmol), and *P*-toluene sulfonyl hydrazide **8** (42 mg, 0.23 mmol) in 2 mL of DMF at 60 °C for 6 h. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 70:30) furnished the product (48 mg, 74%) as white solid. mp = 178-180 °C. [TLC (petroleum ether/ethyl acetate 70:30, *Rf* (**1k**) = 0.5, *Rf* (**9c+9c'**) = 0.7, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 3098, 2968, 1717, 1606, 1409, 1280, 1133, 753. **^{1}H NMR** (400 MHz, $CDCl_3$, peaks due to the major isomer) δ 8.81 (s, 1H), 8.20 (d, J = 7.7 Hz, 1H), 7.98 (d, J = 8.6 Hz, 2H), 7.57 – 7.38 (m, 4H), 1.38 (s, 9H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 161.9, 138.6, 130.0, 128.1, 127.5, 126.9, 125.6, 125.4, 123.9, 123.2, 122.5, 121.6, 120.3, 116.1, 81.9, 28.1(3C) ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{20}H_{19}N_2O_2$ 319.1441; Found 319.1434.



9aa

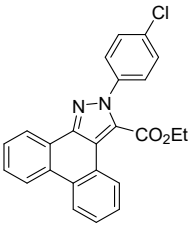
Ethyl 2-(phenanthren-9-yl)acetate (9aa): To an oven dried Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), *p*-toulene sulfonyl hydrazide **8** (42 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 120 °C for 1 h in an oil bath. The reaction was monitored by TLC until the reaction was completed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 98:02) furnished the minor product **9aa** as viscous liquid. [TLC (petroleum ether/ethyl acetate 70:30, *Rf* (**1a**) = 0.9, *Rf* (**11**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) v_{max} = 3025, 2950, 1735, 1439, 1259, 1150, 1010, 805. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.74 (dd, J = 7.4, 2.1 Hz, 1H), 8.67 (d, J = 8.2 Hz, 1H),

8.05 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.72 – 7.61 (m, 4H), 7.61 – 7.56 (m, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.13 – 4.09 (m, 2H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 171.6, 131.6, 131.1, 130.7, 130.2, 129.2, 128.8, 128.4, 126.8, 126.7, 126.6, 126.5, 124.5, 123.2, 122.5, 61.0, 39.8, 14.2 ppm. **HRMS (ESI)** *m/z*: $[M + NH_4]^+$ calcd for $C_{18}H_{20}NO_2$ 281.1489; Found 281.1476.



3aa

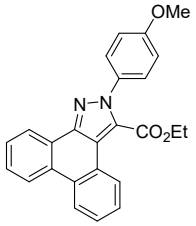
Sequential One Pot Synthesis of Ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3aa): GP 7 was carried out with ethyl (*E*)-3-(2-bromophenyl)acrylate **17a** (60 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 16 h. The reaction was monitored by TLC until the intermediate **1a** was formed. Then phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) was added to reaction mixture and continued at 120 °C for 6 h. The reaction was monitored by TLC until the product **3aa** was formed. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3aa** (51 mg, 60%), as brown solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17a**) = 0.8, *Rf* (**3aa**) = 0.5, UV detection].



3ab

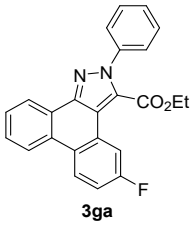
Sequential One Pot Synthesis of Ethyl 2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*] indazole-3-carboxylate (3ab): GP 7 was carried out with ethyl (*E*)-3-(2-bromophenyl)acrylate **17a** (60 mg, 0.23 mmol, 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 16 h. The reaction was monitored by TLC until the intermediate **1a** was formed. Then 4-chloro phenylhydrazine hydrochloride **2b** (46 mg, 0.25 mmol) was added to reaction mixture and continued at 120 °C for 8 h. The reaction was monitored by TLC until the product **3ab** was formed. Purification of the crude material by silica gel column chromatography (petroleum

ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ab** (54 mg, 58%), as white solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17a**) = 0.8, *Rf* (**3ab**) = 0.5, UV detection].



3ae

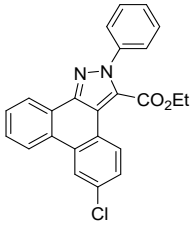
Sequential One Pot Synthesis of Ethyl 2-(4-methoxyphenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3af): GP 7 was carried out with ethyl (*E*)-3-(2-bromophenyl)acrylate **17a** (60 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 16 h. The reaction was monitored by TLC until the intermediate **1a** was formed. Then 4-methoxy phenyl hydrazine hydrochloride **2e** (46 mg, 0.25 mmol) was added to reaction mixture and continued at 120 °C for 6 h. The reaction was monitored by TLC until the product **3af** was formed. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-(4-chlorophenyl)-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3af** (55 mg, 59%), as brown solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17a**) = 0.8, *Rf* (**3af**) = 0.5, UV detection].



3ga

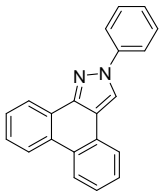
Sequential One Pot Synthesis of Ethyl 5-fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ga): GP 7 was carried out with ethyl (*E*)-3-(2-bromo-5-fluorophenyl)acrylate **17e** (62 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 17 h. The reaction was monitored by TLC until the intermediate **1g** was formed. Then phenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) was added to reaction mixture and continued at 120 °C for 6 h. The reaction was monitored by TLC until the product **3ga** was formed. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished Ethyl 5-fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-

carboxylate **3ga** (49 mg, 57%), as pale yellow solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17f**) = 0.8, *Rf* (**3ga**) = 0.5, UV detection].



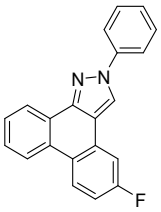
3ia

Sequential One Pot Synthesis of Ethyl 6-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (3ia): GP 7 was carried out with ethyl (*E*)-3-(2-bromo-5-fluorophenyl)acrylate (66 mg, 0.23 mmol) **17f**, 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 17 h. The reaction was monitored by TLC until the intermediate **1i** was formed. Thenphenylhydrazine hydrochloride **2a** (36 mg, 0.25 mmol) was added to reaction mixture and continued at 120 °C for 6 h. The reaction was monitored by TLC until the product **3ia** was formed. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished 6-chloro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate **3ia** (52 mg, 57%), as pale yellow solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17f**) = 0.8, *Rf* (**3ia**) = 0.5, UV detection].



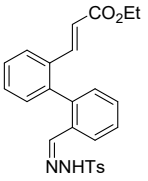
Sequential One Pot Synthesis of 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole (4aa):

GP 8 was carried out with ethyl (*E*)-3-(2-bromophenyl)acrylate **17a** (60 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 16 h. The reaction was monitored by TLC until the intermediate **1a** was formed. Then phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) was added to reaction mixture and continued at 140 °C for 90 h. The reaction was monitored by TLC until the product **4aa** was formed. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the ethyl 2-phenyl-2*H*-dibenzo[*e*,*g*]indazole **4aa** (40 mg, 58%), as brown solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17a**) = 0.8, *Rf* (**4aa**) = 0.5, UV detection].



Sequential one pot synthesis of 5-Fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole (4ga):

GP 8 was carried out with ethyl (*E*)-3-(2-bromo-5-fluorophenyl)acrylate **17e** (62 mg, 0.23 mmol), 2-formylphenylboronic acid **18a** (38 mg, 0.25 mmol) $Pd(OAc)_2$ (2.6 mg, 5 mol%), PPh_3 (5 mg, 10 mol%), K_3PO_4 (99 mg, 1 mmol) in 4 mL of DMF at 140 °C for 16 h. The reaction was monitored by TLC until the intermediate **1g** was formed. Then phenyl hydrazine hydrochloride **2a** (36 mg, 0.25 mmol) was added to reaction mixture and continued at 140 °C for 98 h. The reaction was monitored by TLC until the product **4ga** was formed. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate: 95:05) furnished the 5-Fluoro-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole **4ga** (39 mg, 56%), as white solid. [TLC (petroleum ether/ethyl acetate 95:05), *Rf* (**17a**) = 0.8, *Rf* (**4ga**) = 0.5, UV detection].

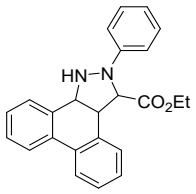


11

Ethyl (*E*)-3-(2'-((*Z*)-(2-tosylhydrazineylidene)methyl)-[1,1'-biphenyl]-2-yl)acrylate (11):

To an oven dried Schlenk tube equipped with a magnetic stir bar were added ethyl (*E*)-3-(2'-formyl-[1,1'-biphenyl]-2-yl)acrylate **1a** (60 mg, 0.21 mmol), *p*-toulene sulfonyl hydrazide **8** (42 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 45 °C for 20 min in an oil bath. The reaction was monitored by TLC until the reaction intermediate was formed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and Concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 70:30) furnished the intermediate **11** (88 mg, 92%) as a brown viscous liquid. [TLC (petroleum ether/ethyl acetate 70:30, *Rf* (**1a**) = 0.9, *Rf* (**11**) = 0.5, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3057, 2980, 1720, 1443, 1150, 1010, 736, 676. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 5.3, 4.0 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.69 – 7.64 (m, 1H), 7.42 – 7.32 (m, 5H), 7.31 – 7.27 (m, 2H), 7.14 – 7.07 (m, 2H), 6.27 (d, *J* = 16.0 Hz,

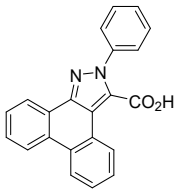
1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (101 MHz, $CDCl_3$) δ 166.5, 145.6, 144.1, 142.2, 139.7, 139.7, 135.3, 133.2, 131.4, 131.2, 130.7, 129.8, 129.6 (2C), 129.6, 128.3, 128.2, 127.8 (2C), 126.5, 126.1, 119.7, 60.4, 21.5, 14.1 ppm. **HRMS (ESI)** *m/z*: $[M + Na]^+$ calcd for $C_{25}H_{24}N_2NaO_4S$ 471.1349; Found 471.1358.



12a

Ethyl 2-phenyl-2,3,3a,11b-tetrahydro-1*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (12a):

IR: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2981, 1731, 1596, 1492, 1440, 1269, 1170, 1025, 745. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 7.1 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.45 (dd, *J* = 7.4, 7.4 Hz, 1H), 7.40 (ddd, *J* = 7.4, 7.4, and 0.9 Hz, 2H), 7.35 (ddd, *J* = 7.4, 7.4, and 1.1 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 2H), 6.89 – 6.84 (m, 1H), 4.60 (d, *J* = 13.6 Hz, 1H), 4.46 (d, *J* = 9.7 Hz, 1H), 4.38 – 4.30 (m, 2H), 3.86 (t, *J* = 13.3 Hz, 1H), 3.53 (dd, *J* = 12.9, 9.8 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ 173.6, 151.6, 135.0, 134.7, 134.5, 134.2, 128.9 (2C), 128.2, 128.2, 128.1, 127.9, 125.0, 124.8, 124.8, 123.1, 119.5, 113.4 (2C), 69.1, 63.2, 61.8, 56.6, 14.2 ppm.



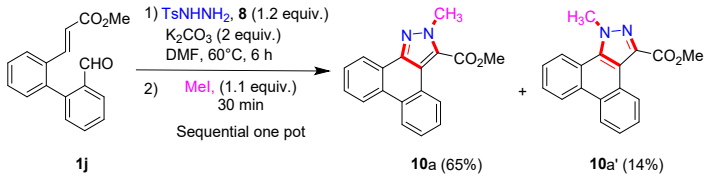
3A

2-phenyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylic acid (3A) :

IR: (MIR-ATR, 4000–600 cm-1) ν_{max} = 3388, 2925, 1712, 1492, 1443, 1201, 1028, 810. **^{1}H NMR** (600 MHz, DMSO-d6) δ 8.82 – 8.73 (m, 3H), 8.58 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.79 – 7.64 (m, 8H), 7.62 – 7.58 (m, 1H) ppm. **^{13}C{H} NMR** (151 MHz, DMSO-d6) δ 163.4, 144.9, 140.5, 130.6, 130.2, 129.3 (2C), 129.1, 128.8, 128.4, 127.9, 127.8, 127.1, 125.7, 125.0, 124.9 (2C), 124.5, 122.7, 115.8 ppm.

Transformation of products:

Sequential one pot Synthesis of methyl 2-methyl-2*H*/1*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (10a and 10a')



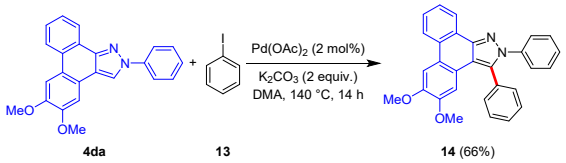
1j **10a** (65%) **10a'** (14%)

To an oven dried Schlenk tube equipped with a magnetic stir bar were added biaryl aldehyde ester **1a** (60 mg, 0.21 mmol), *p*-toluene sulfonyl hydrazide **8** (46 mg, 0.25 mmol) in DMF (2.0 mL) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 60 °C for 6 h in an oil bath. The reaction was monitored by TLC until the reaction completed then to the same reaction mixture added methyl iodide (35 mg, 0.025 mmol) and continued for 30 min. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and then extracted with ethyl acetate (3 × 30 mL). The organic layers were combined, dried over Na_2SO_4, and Concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate75:25) furnished the products **10a** (40 mg, 65%) and **10a'** (8 mg, 14%) as a brown and white solids, mp (**10a**) =105-108 °C, mp (**10a'**) =103-105 °C. [TLC (petroleum ether/ethyl acetate 75:25, *Rf* (**1j**) = 0.9, *Rf* (**9b**+**9b'**) = 0.4, *Rf* (**10a**) = 0.6, *Rf* (**10a'**) = 0.5, UV detection].

Methyl 2-methyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (10a): IR: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2949, 1710, 1434, 1325, 1270, 1040, 755. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.88 (dd, J = 6.9, 2.6 Hz, 1H), 8.61 – 8.56 (m, 2H), 8.54 (m, 1H), 7.66 – 7.53 (m, 4H), 4.38 (s, 3H), 4.11 (s, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ 161.7, 144.2, 130.1, 129.8, 127.8, 127.4, 127.3, 126.9, 126.4, 126.3, 126.1, 125.0, 123.4, 123.1, 122.6, 117.6, 52.3, 41.5 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{18}H_{14}N_2NaO_2$ 313.0947; Found 313.0934.

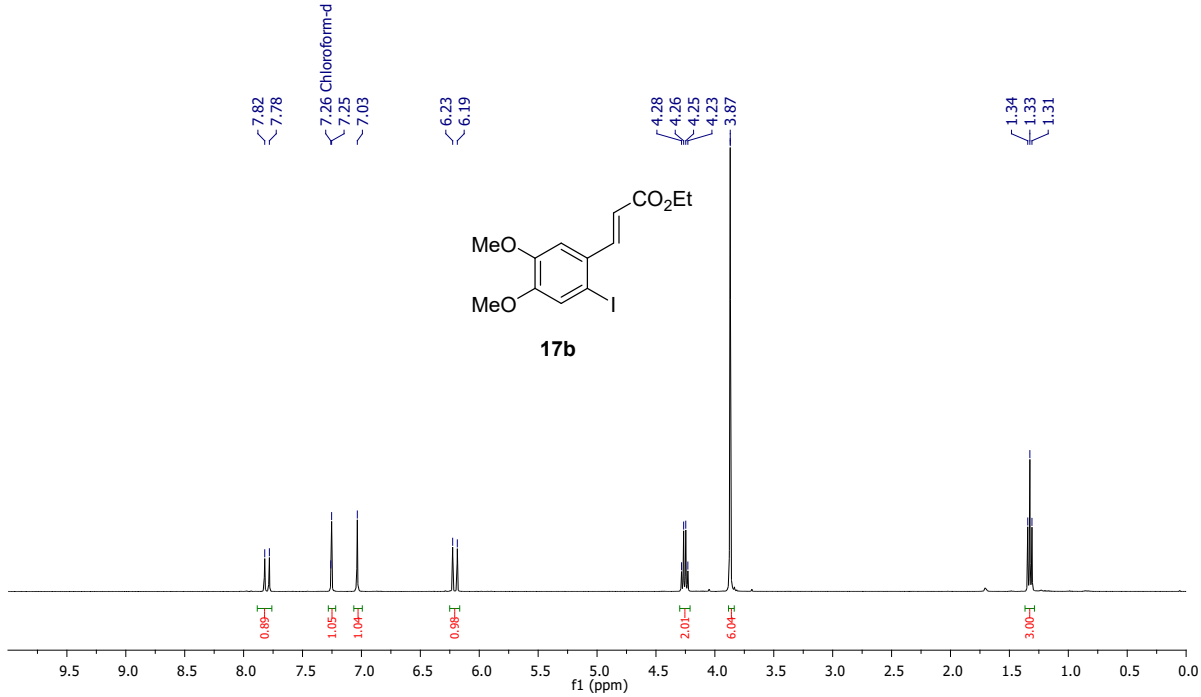
Methyl 2-methyl-2*H*-dibenzo[*e*,*g*]indazole-3-carboxylate (10a'): IR: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2943, 2344, 1717, 1444, 1277, 1157, 755. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.51 (dd, J = 8.2, 1.2 Hz, 1H), 8.74 (dd, 7.9, 1.7 Hz, 1H), 8.63 (dd, J = 8.5, 0.9 Hz, 1H), 8.43 (dd, J = 7.9, 1.5 Hz, 1H), 7.73 – 7.65 (m, 3H), 7.62 (ddd, J = 8.4, 7.0, 1.5 Hz, 1H), 4.60 (s, 3H), 4.11 (s, 3H) ppm. **HRMS (ESI)** *m/z*: $[(M + K)]^+$ calcd for $C_{18}H_{15}N_2O_2$ 291.1128; Found 291.1131.

C–H Arylation of 5,6-dimethoxy-2-phenyl-2*H*-dibenzo[*e*,*g*]indazole (14):

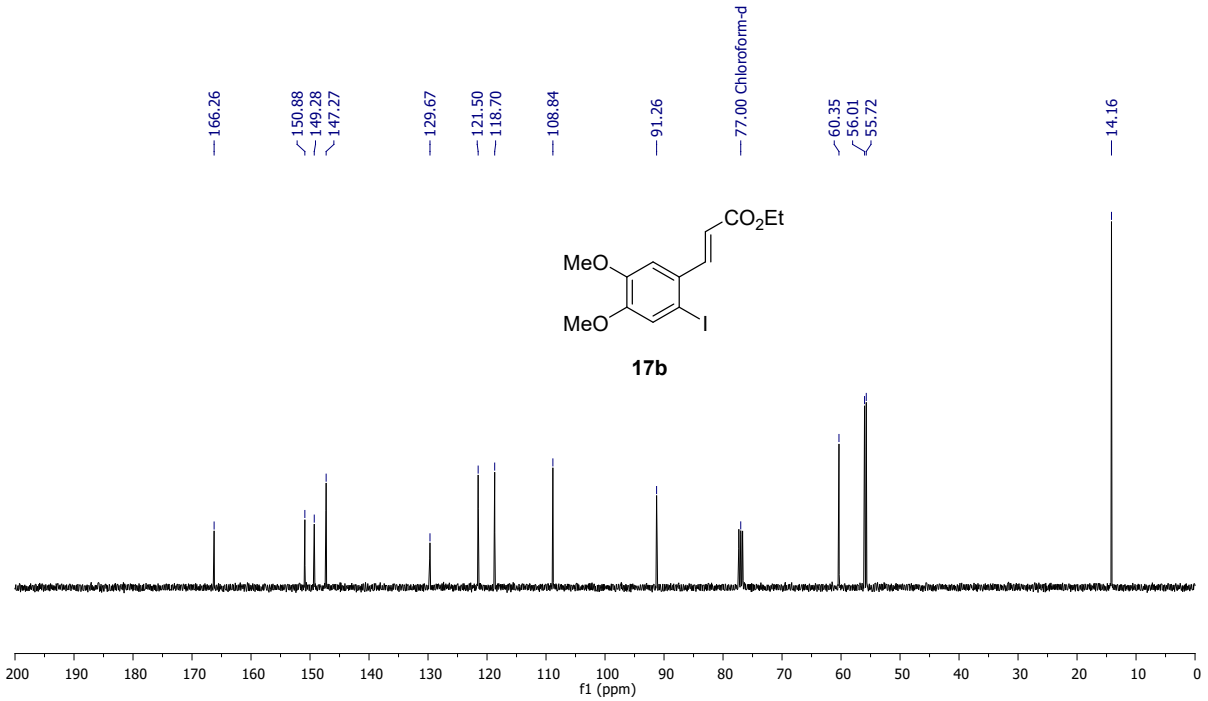


In an oven-dried Schlenk tube equipped with a magnetic stir bar were added 5,6-dimethoxy-2-phenyl-2*H*-dibenzo[*e,g*]indazole (20 mg, 0.05 mmol), iodo benzene (12.3 mg, 0.06 mmol), $Pd(OAc)_2$ (0.2 mg, 2 mol%), and K_2CO_3 (13.8 mg, 0.1 mmol) in DMF (2.0 mL) at room temperature under nitrogen atmosphere, and the reaction mixture was stirred at 140 °C for 14 h in an oil bath. The reaction is monitored using thin-layer chromatography until the reaction is completed. Then, the cooled reaction mixture was quenched by adding an aqueous NH_4Cl solution and extracted with ethyl acetate (3 × 20 mL). The organic layers were combined, dried over Na_2SO_4, and Concentrated under reduced pressure. purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 90:10) furnished the product **14** (16 mg, 66%) as a pale-yellow solid, mp = 160-163 °C. [TLC (petroleum ether/ethyl acetate 90:10), *Rf* (**4da**) = 0.5, *Rf* (**13**) = 0.9, *Rf* (**14**) = 0.6, UV detection]. **IR**: (MIR-ATR, 4000–600 cm-1) ν_{max} = 2933, 2840, 2340, 1512, 1364, 1262, 1028, 758. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 (dd, *J* = 7.7, 1.5 Hz, 2H), 8.40 (d, *J* = 7.9 Hz, 2H), 7.91 (s, 1H), 7.61 (m, 2H), 7.54 – 7.41 (m, 7H), 7.37 – 7.27 (m, 3H), 7.09 (s, 1H), 4.06 (s, 3H), 3.49 (s, 3H) ppm. **^{13}C{H} NMR** (151 MHz, $CDCl_3$) δ 148.7, 147.6, 145.6, 140.1, 136.7, 131.8, 131.2(2C), 130.6, 129.1, 128.9(2C), 128.8(2C), 127.5, 127.4, 126.4, 125.7(2C), 124.9, 123.3, 122.8, 122.8, 121.7, 115.5, 105.6, 105.0, 55.9, 55.2 ppm. **HRMS (ESI)** *m/z*: $[(M + H)]^+$ calcd for $C_{29}H_{23}N_2O_2$ 431.1754; Found 431.1746.

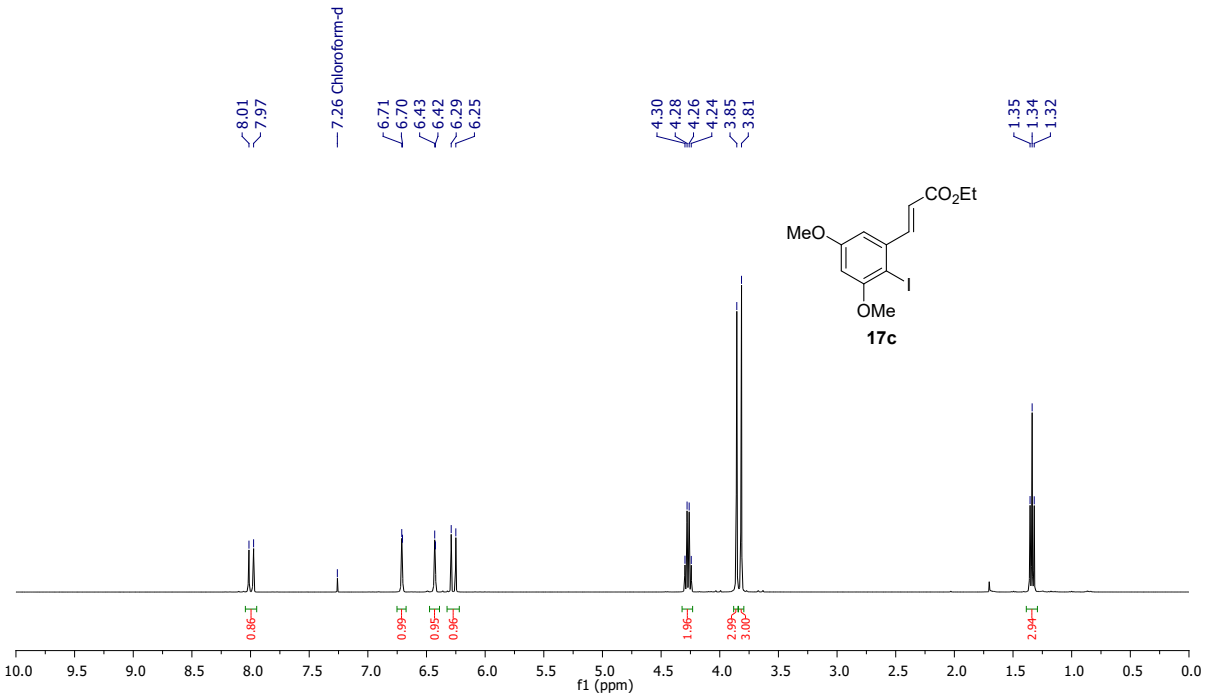
NMR Spectra:



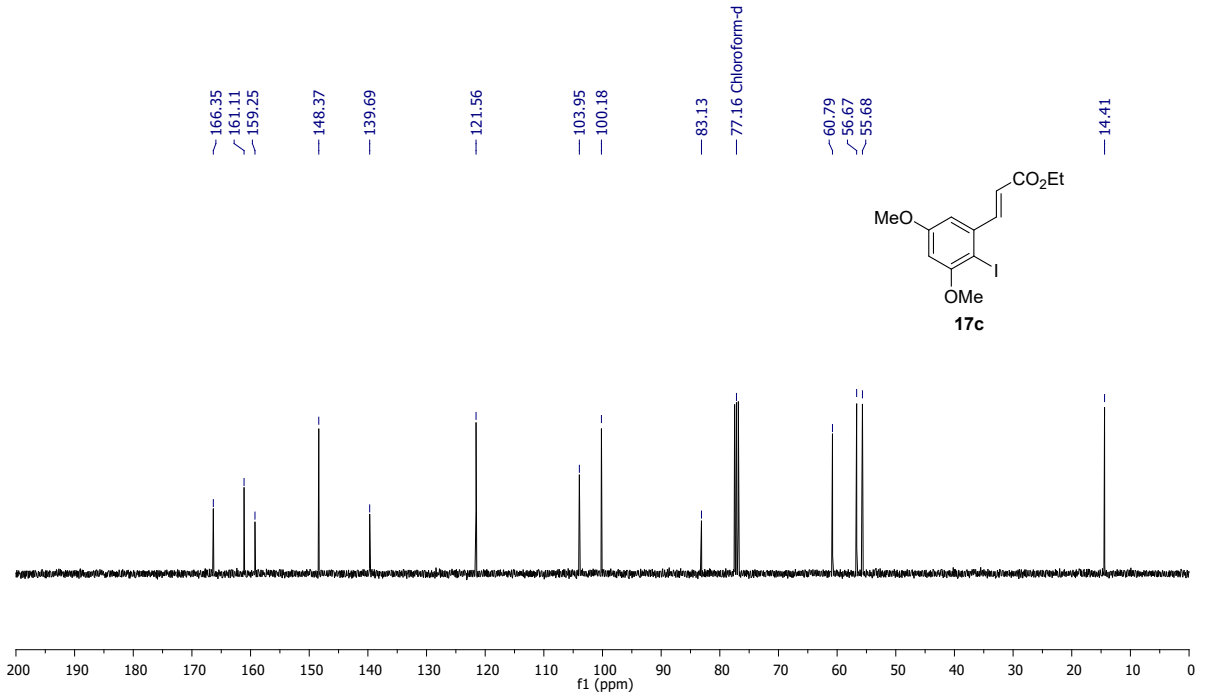
^{1}H NMR (400 MHz) spectrum of **17b** in $CDCl_3$.



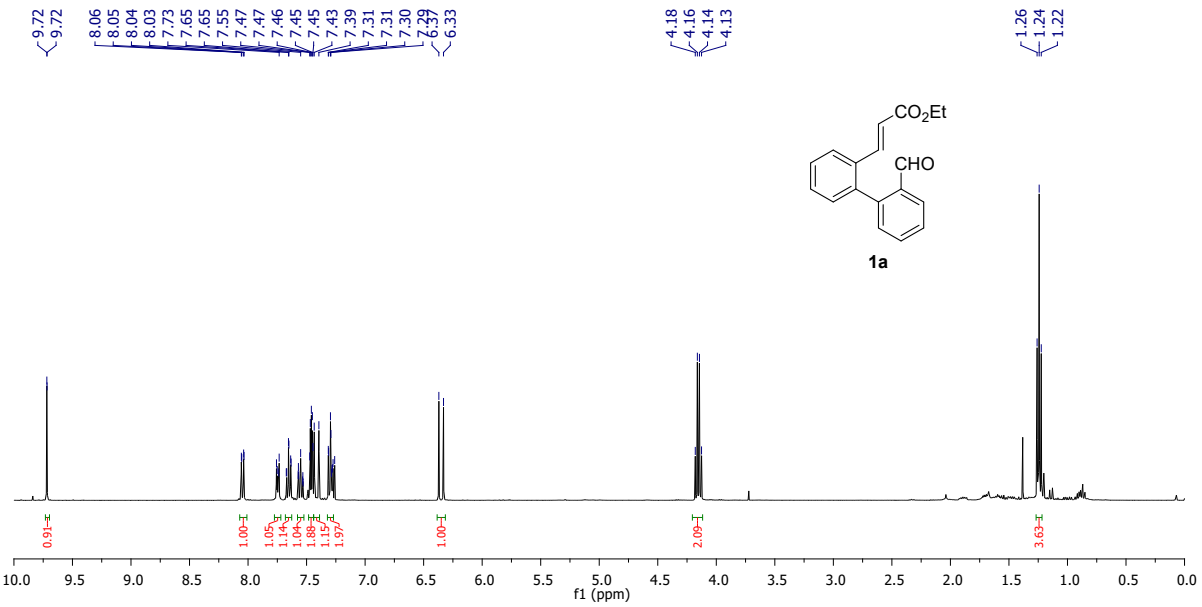
^{13}C{^{1}H} NMR (101 MHz) spectrum of **17b** in $CDCl_3$.



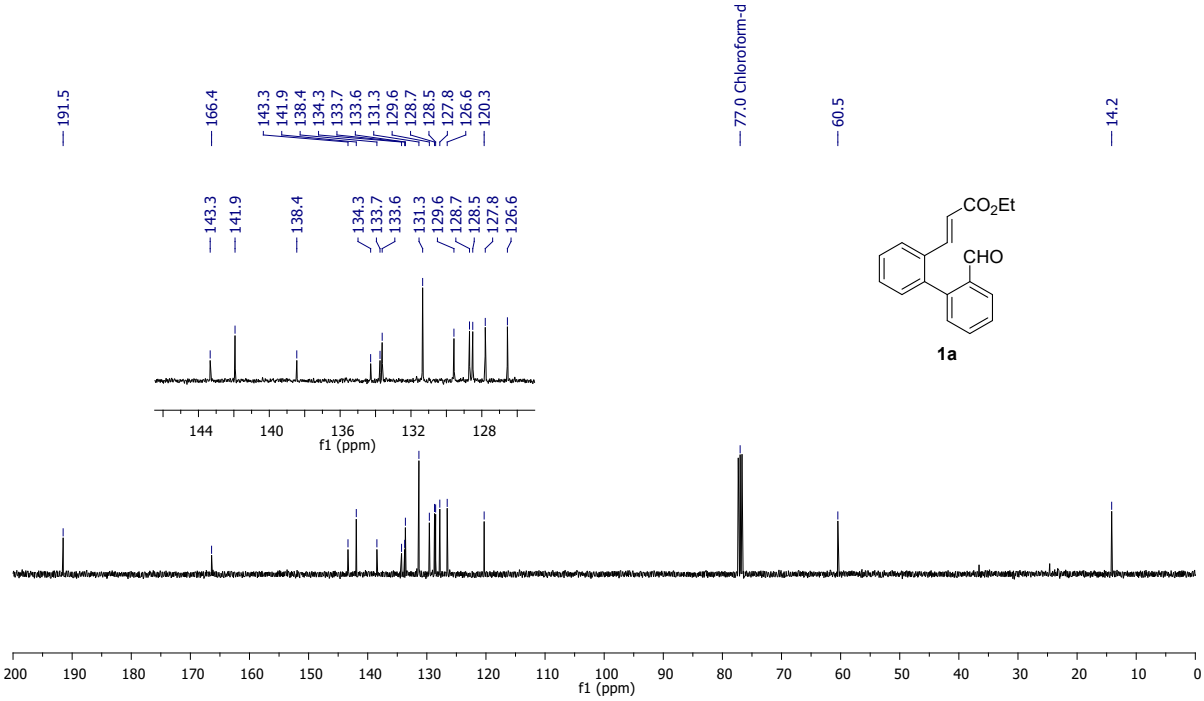
^{1}H NMR (400 MHz) spectrum of **17c** in $CDCl_3$.



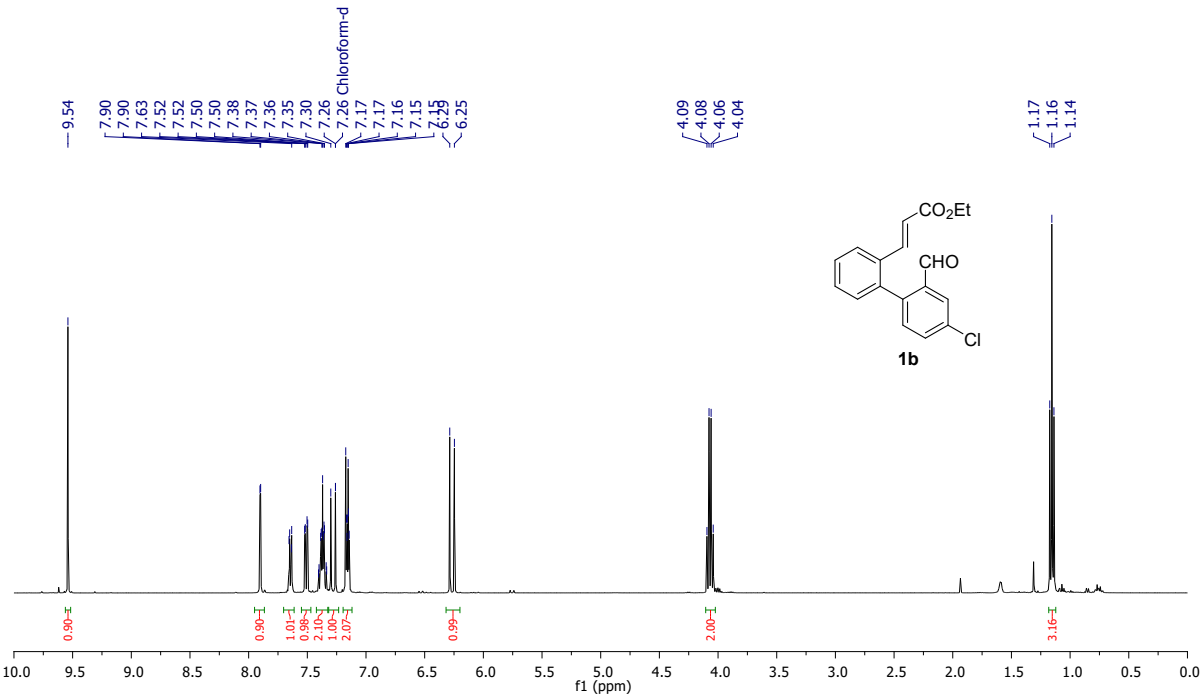
^{13}C{^{1}H} NMR (101 MHz) spectrum of **17c** in $CDCl_3$.



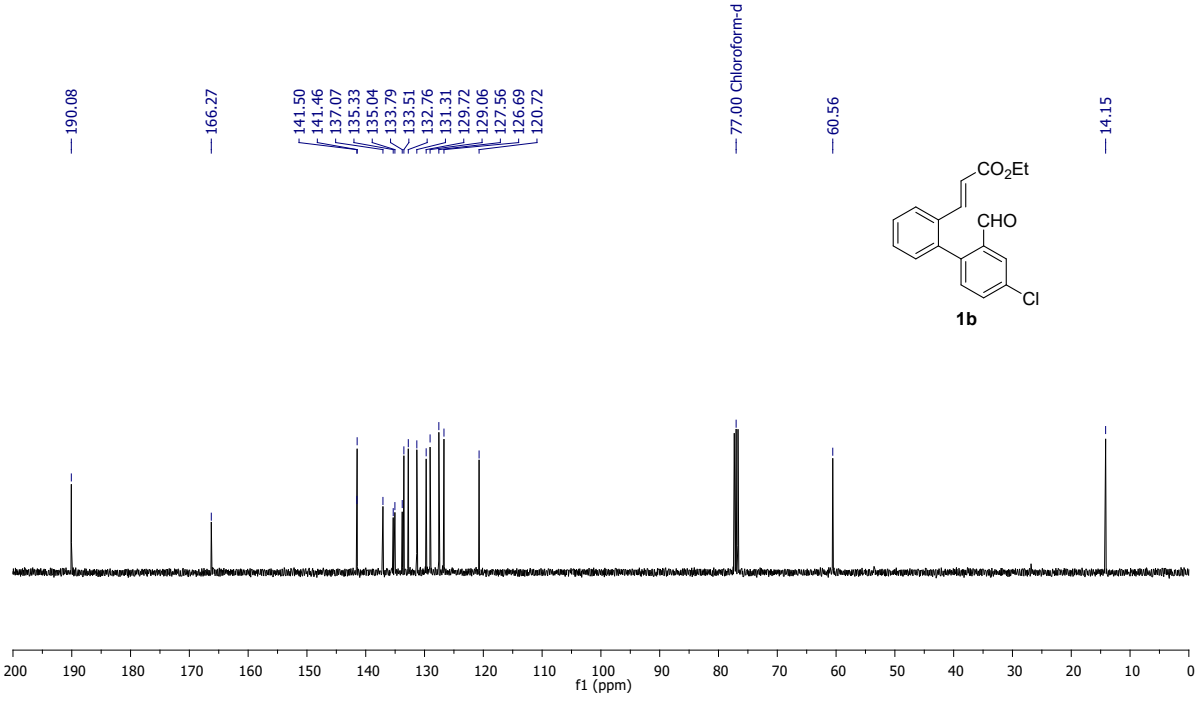
^{1}H NMR (400 MHz) spectrum of **1a** in $CDCl_3$.



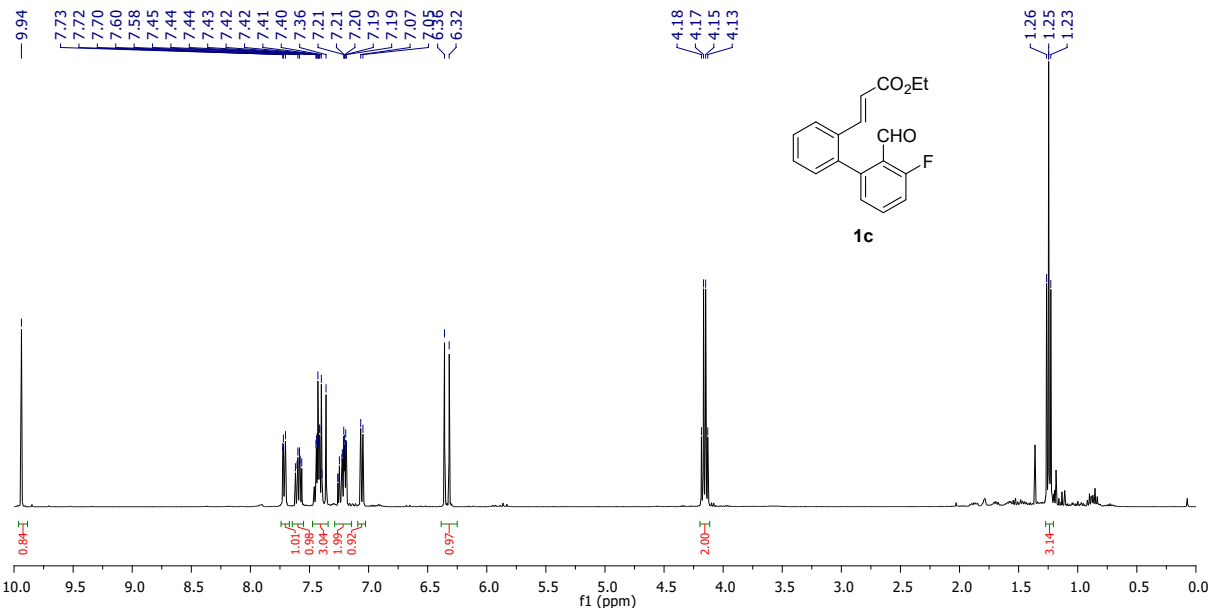
^{13}C{^{1}H} NMR (101 MHz) spectrum of **1a** in $CDCl_3$.



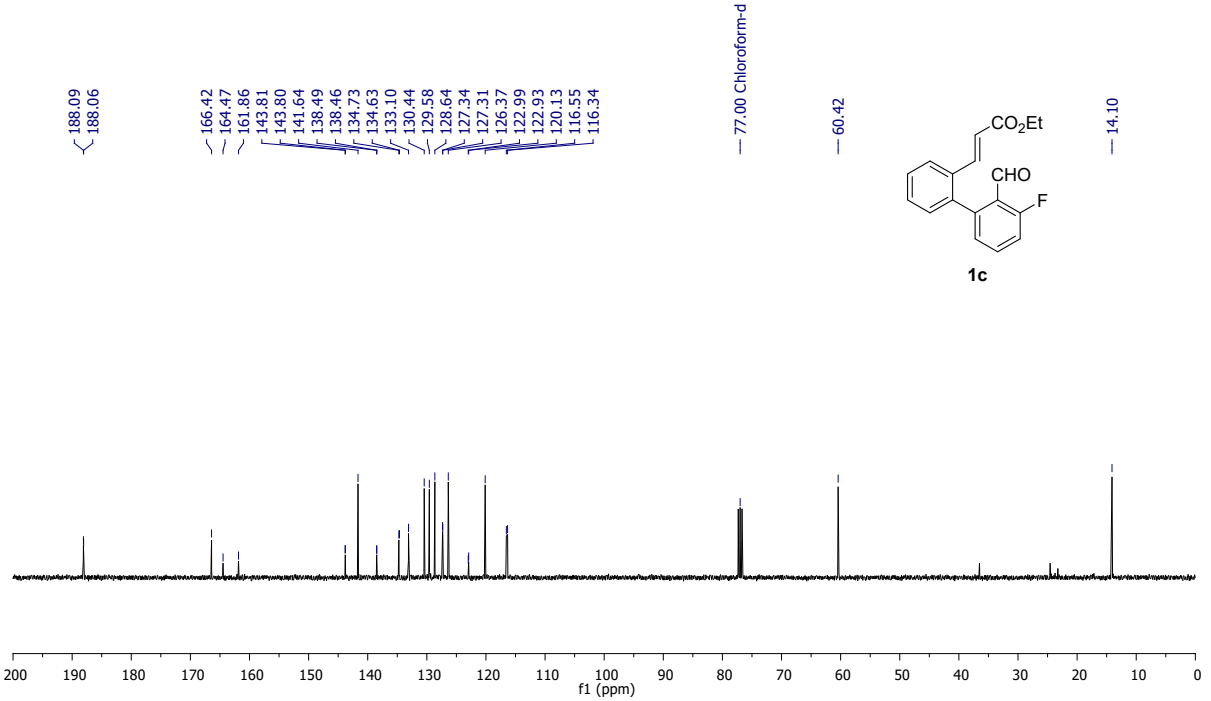
^{1}H NMR (400 MHz) Spectrum of compound **1b** in $CDCl_3$.



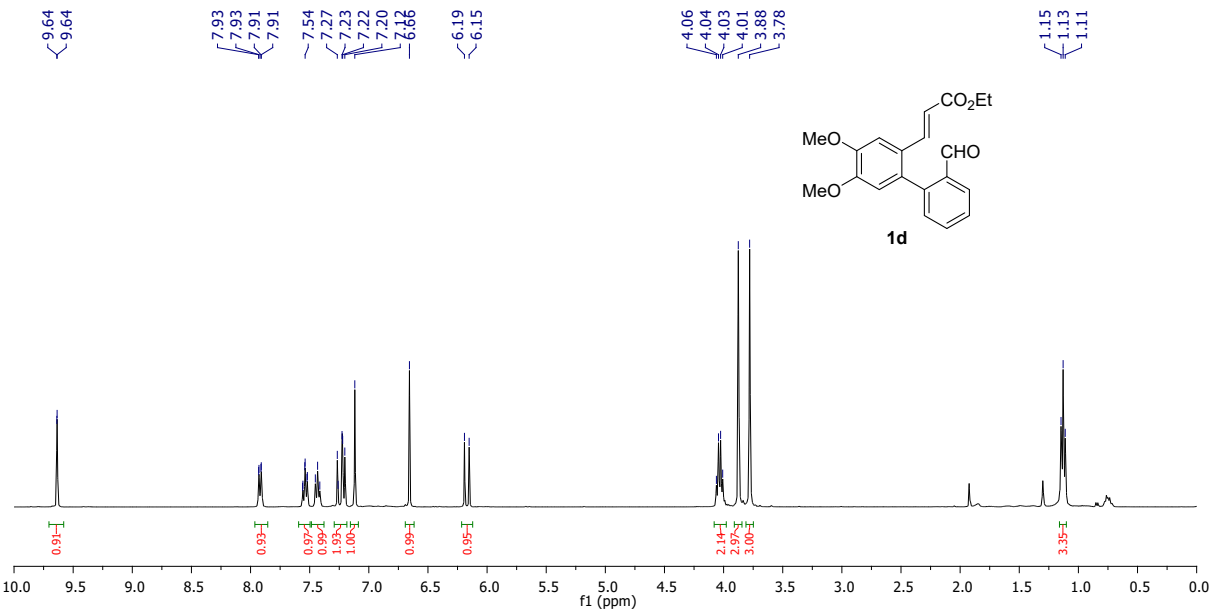
^{13}C{H} NMR (101 MHz) Spectrum of compound **1b** in $CDCl_3$.



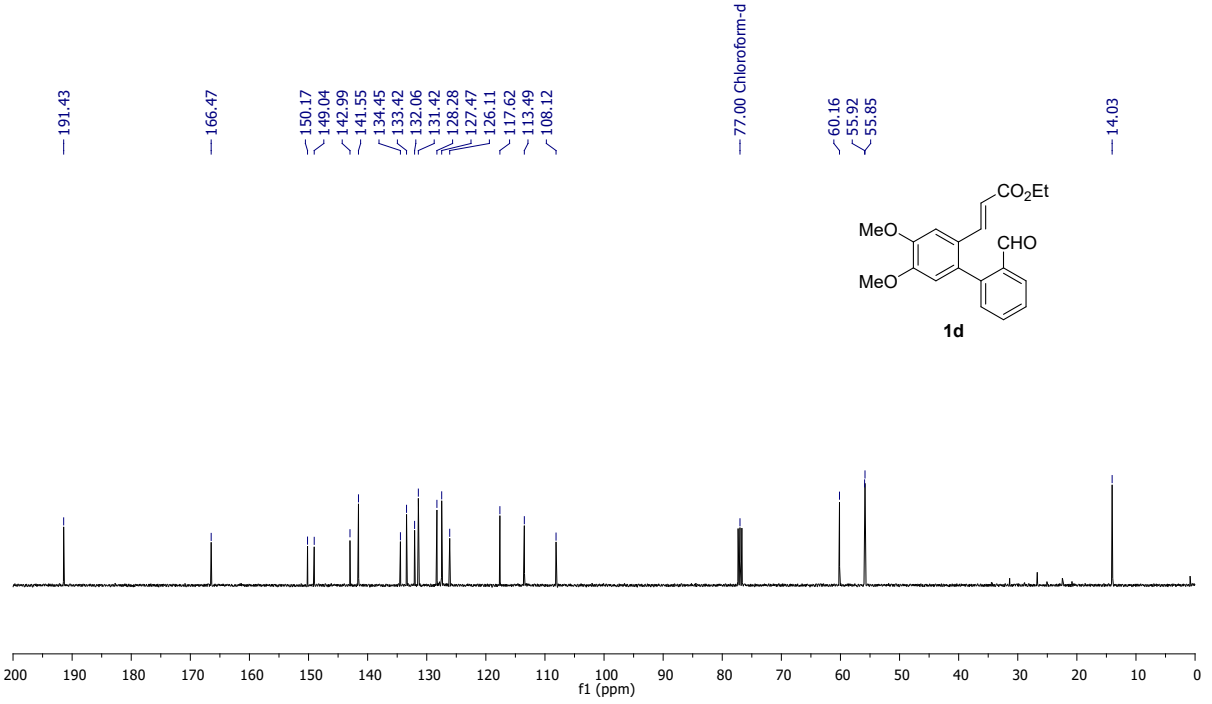
^{1}H NMR (400 MHz) Spectrum of compound **1c** in $CDCl_3$.



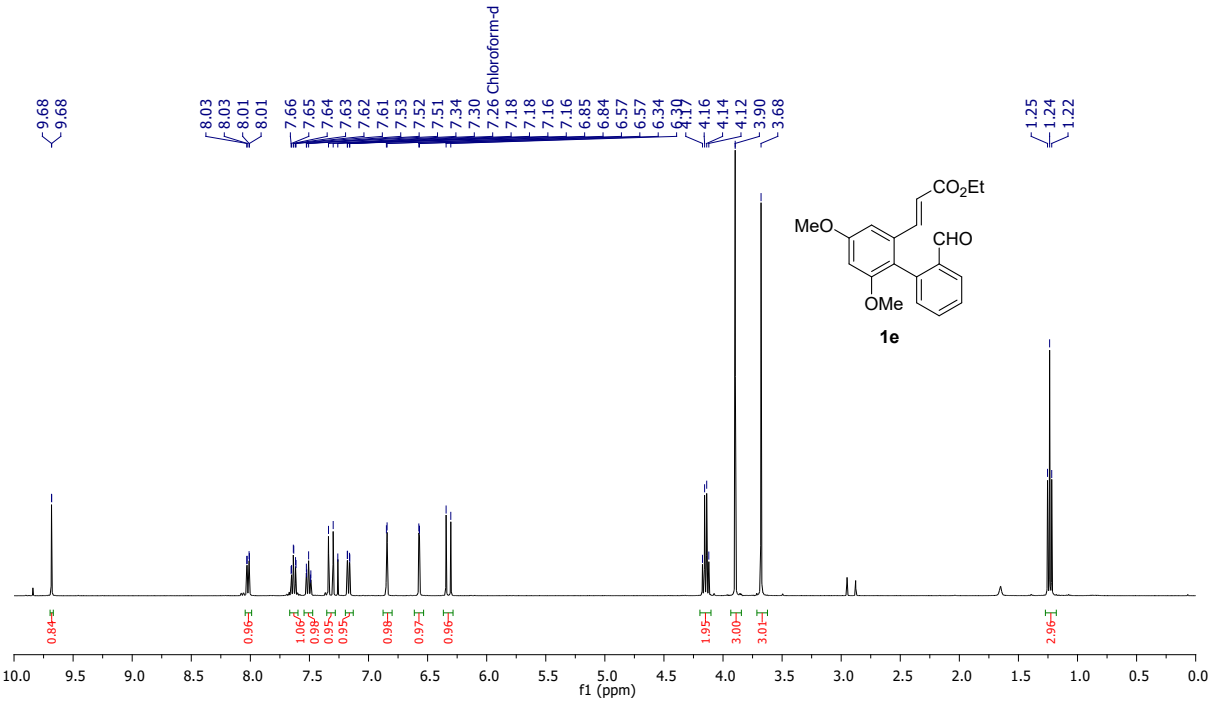
^{13}C{^{1}H} NMR (101 MHz) spectrum of **1c** in $CDCl_3$.



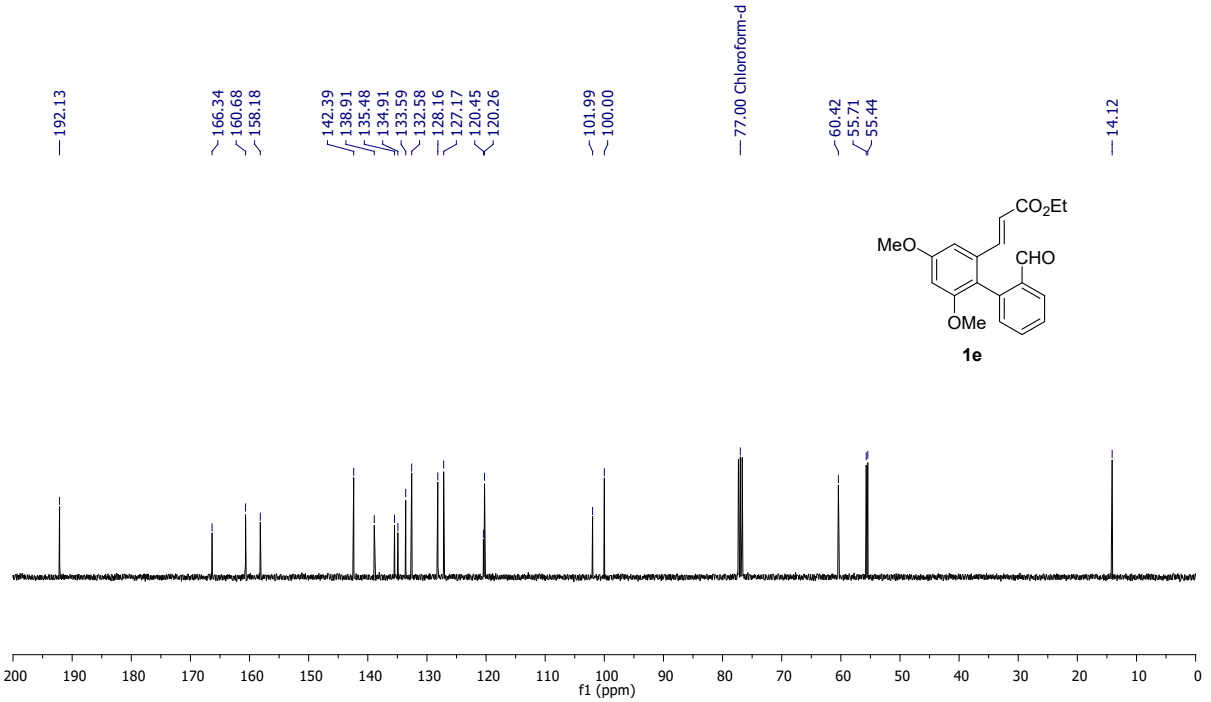
^{1}H NMR (400 MHz) Spectrum of compound **1d** in $CDCl_3$.



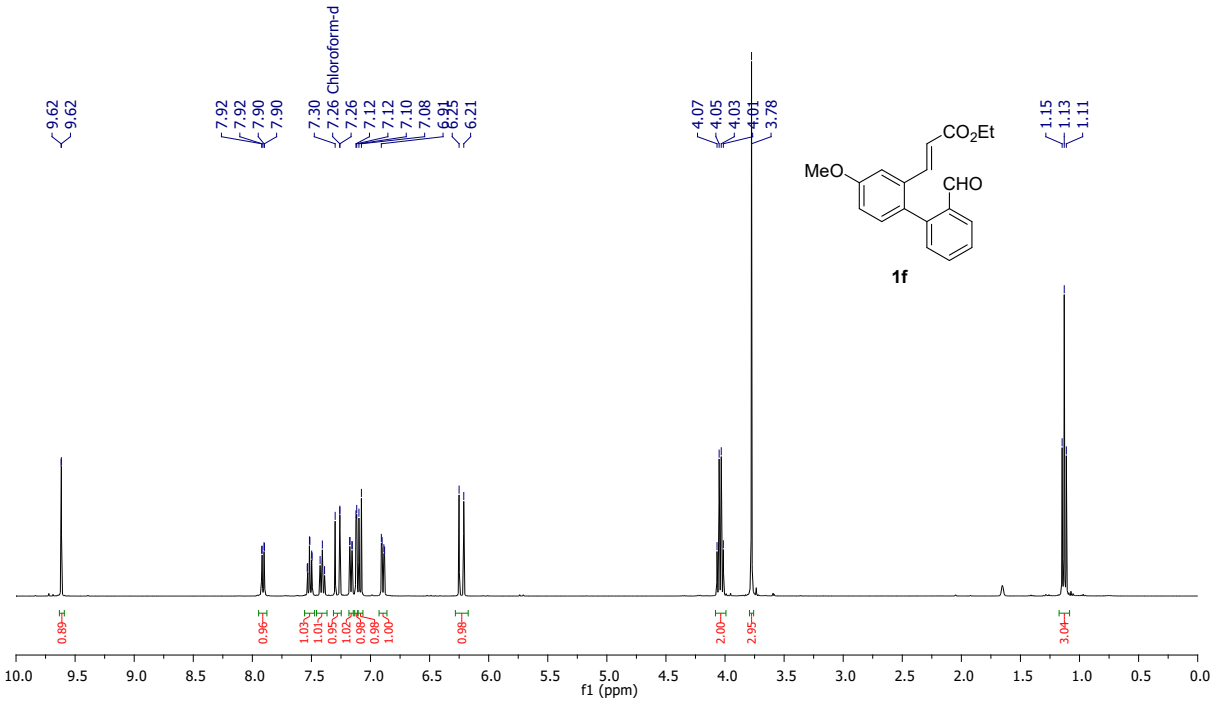
^{13}C{H} NMR (101 MHz) Spectrum of compound **1d** in $CDCl_3$.



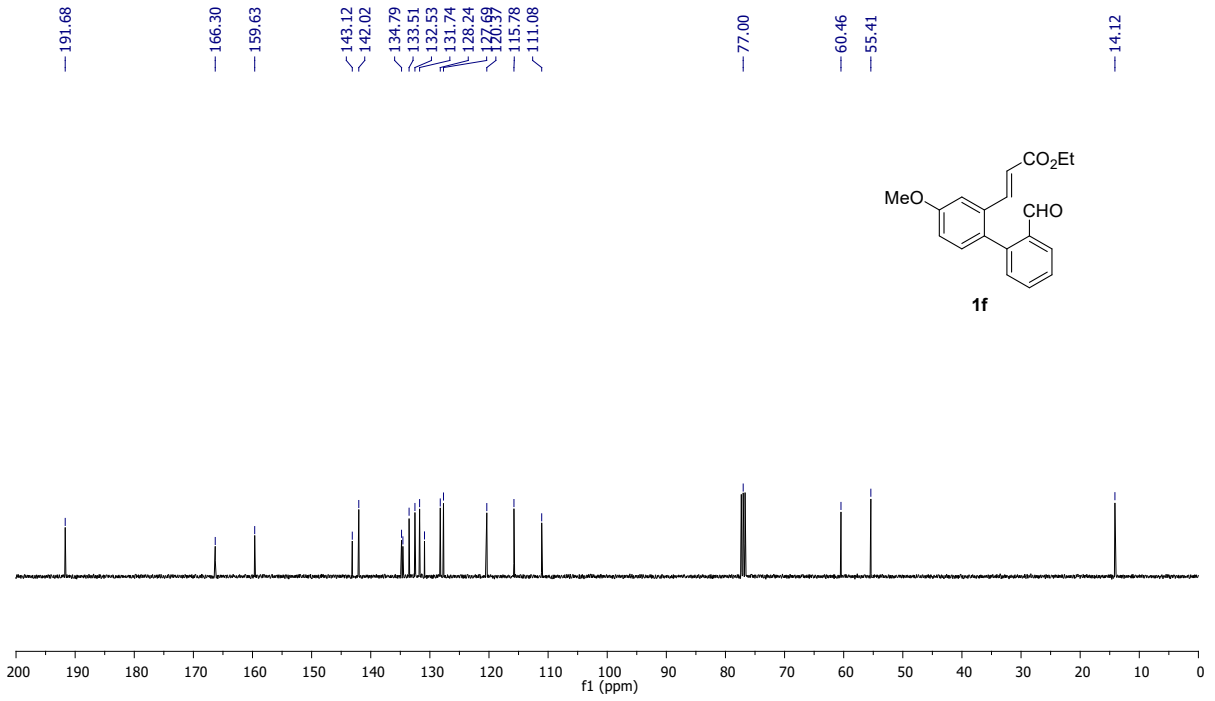
^{1}H NMR (400 MHz) Spectrum of compound **1e** in $CDCl_3$.



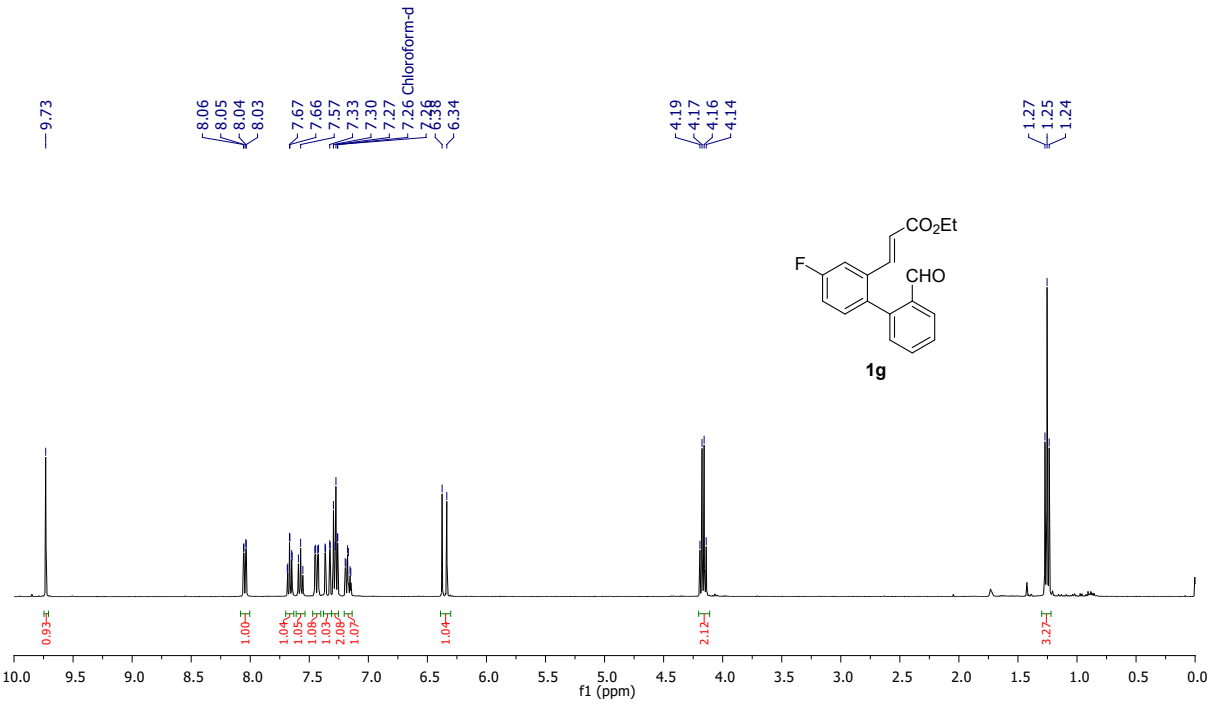
^{13}C{^{1}H} NMR (101 MHz) Spectrum of compound **1e** in $CDCl_3$.



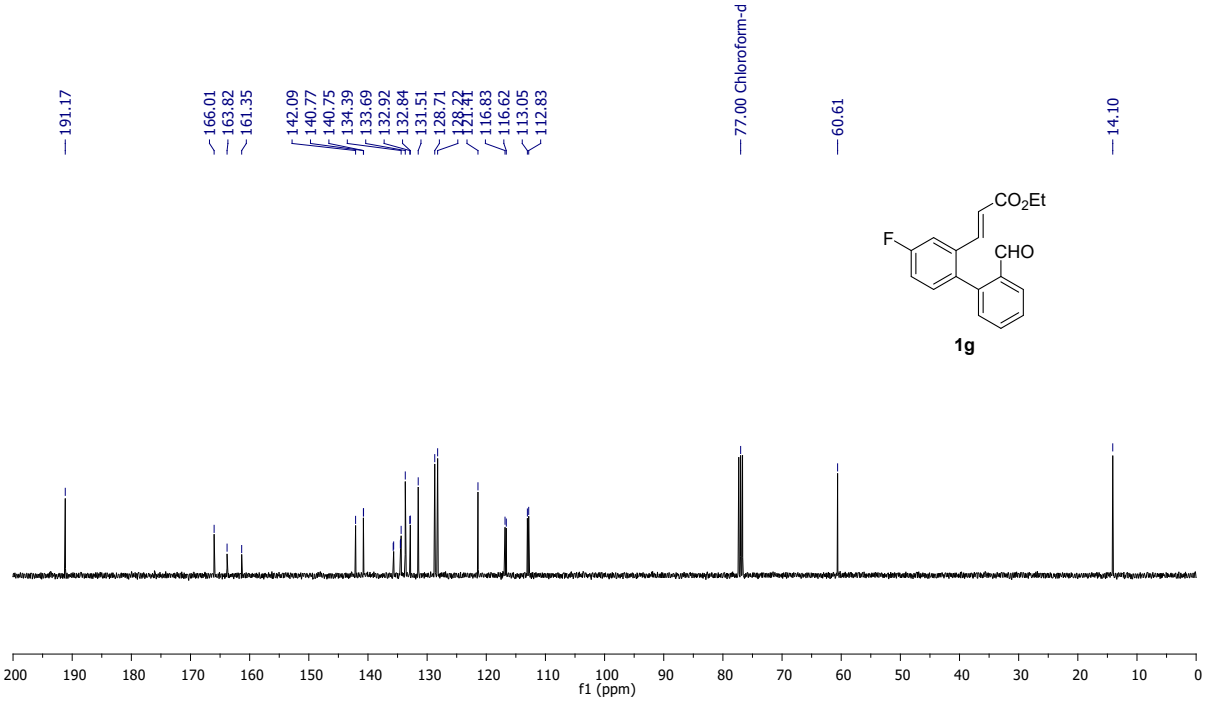
^{1}H NMR (400 MHz) Spectrum of compound **1f** in $CDCl_3$.



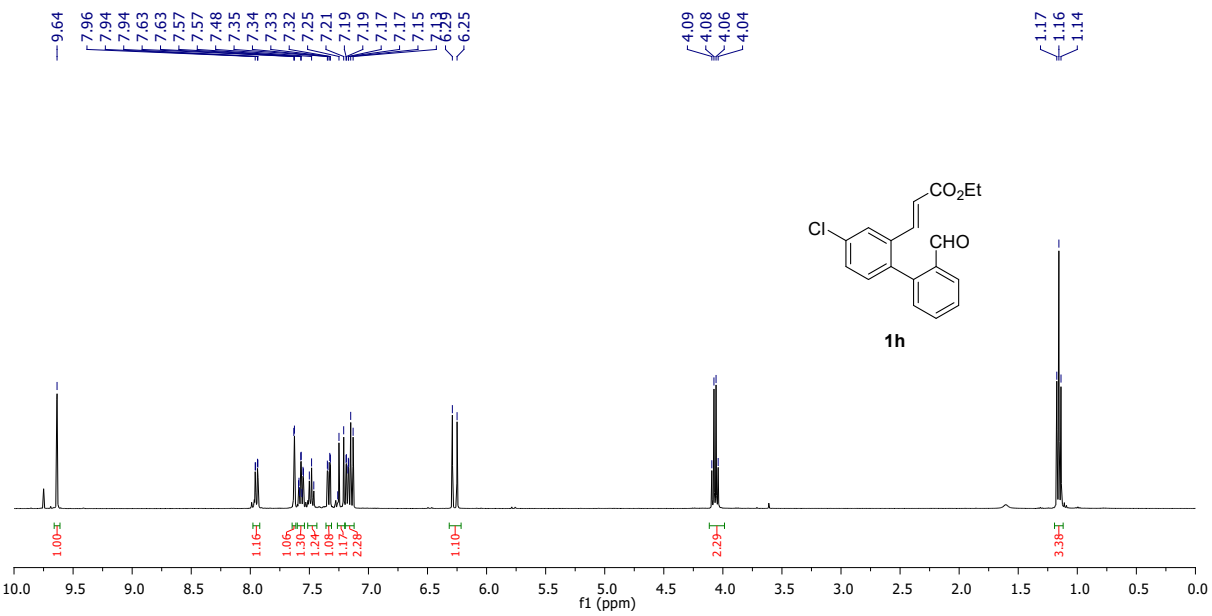
^{13}C{^{1}H} NMR (101 MHz) Spectrum of compound **1f** in $CDCl_3$.



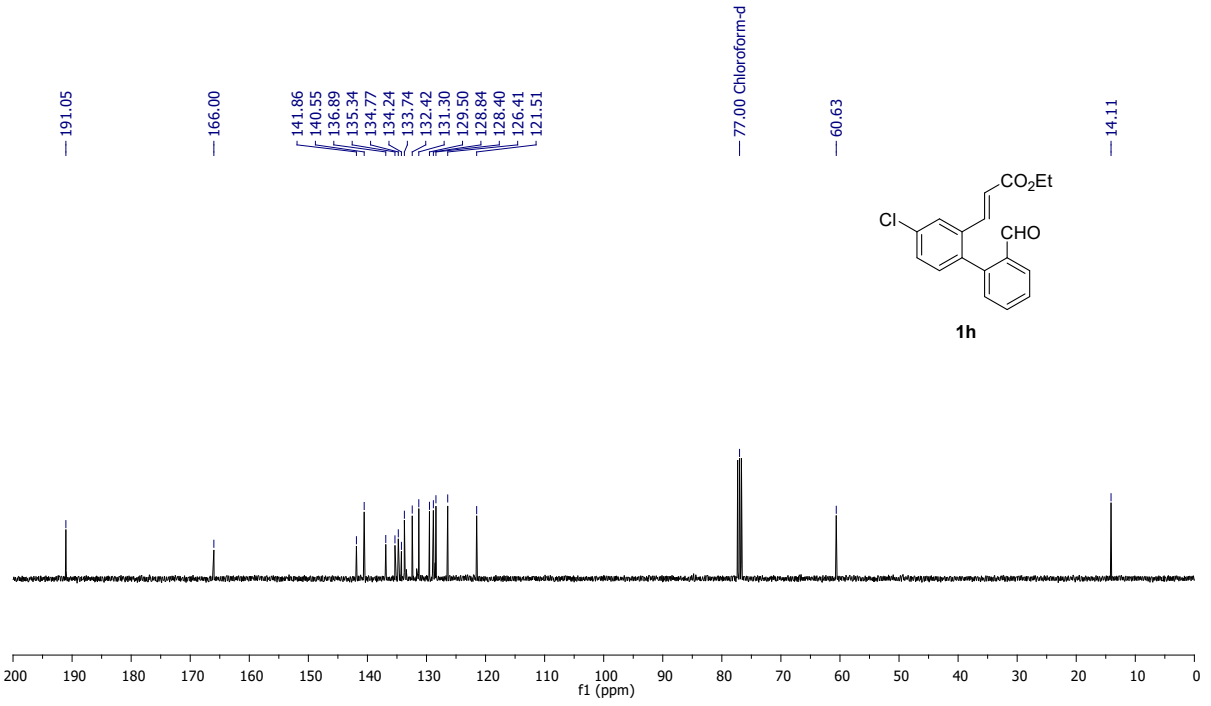
^{1}H NMR (400 MHz) Spectrum of compound **1g** in $CDCl_3$.



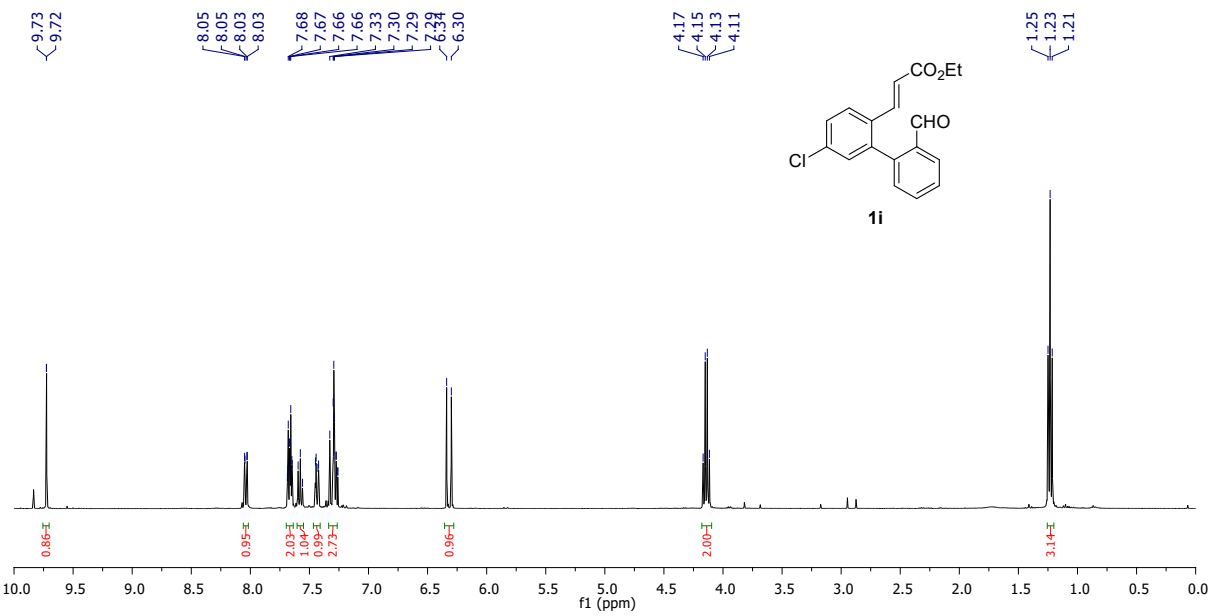
^{13}C{H} NMR (101 MHz) Spectrum of compound **1g** in $CDCl_3$.



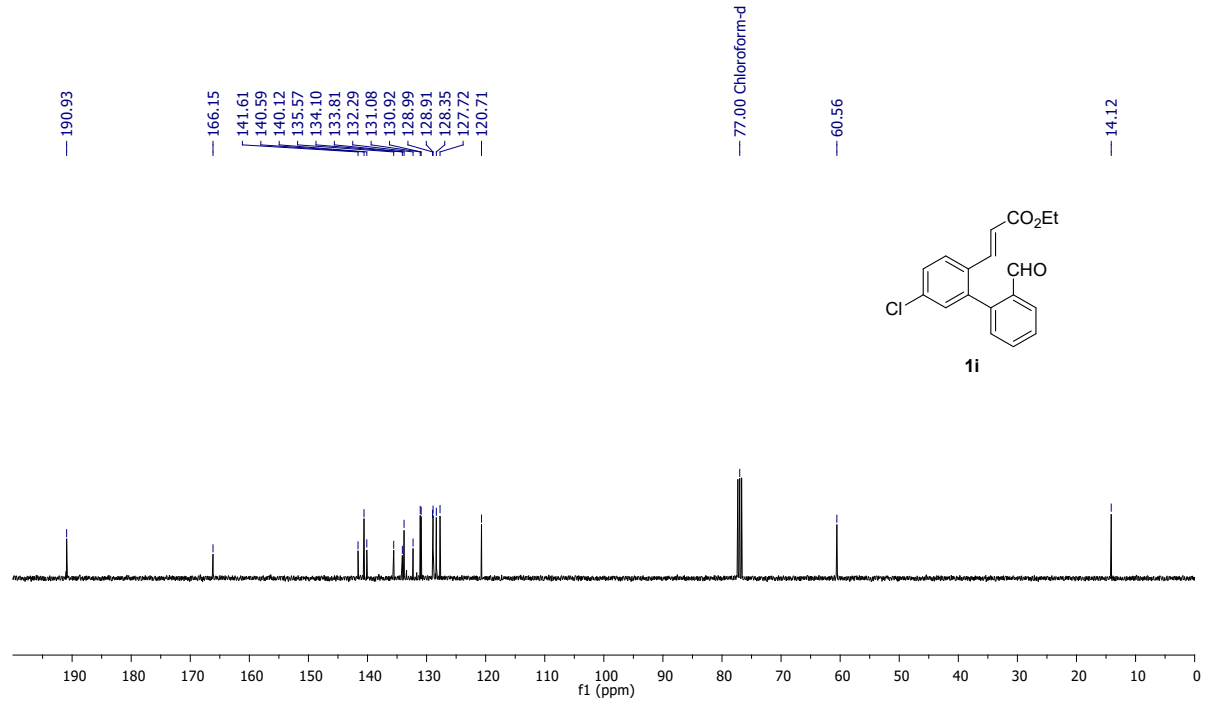
^{1}H NMR (400MHz) Spectrum of compound **1h** in $CDCl_3$.



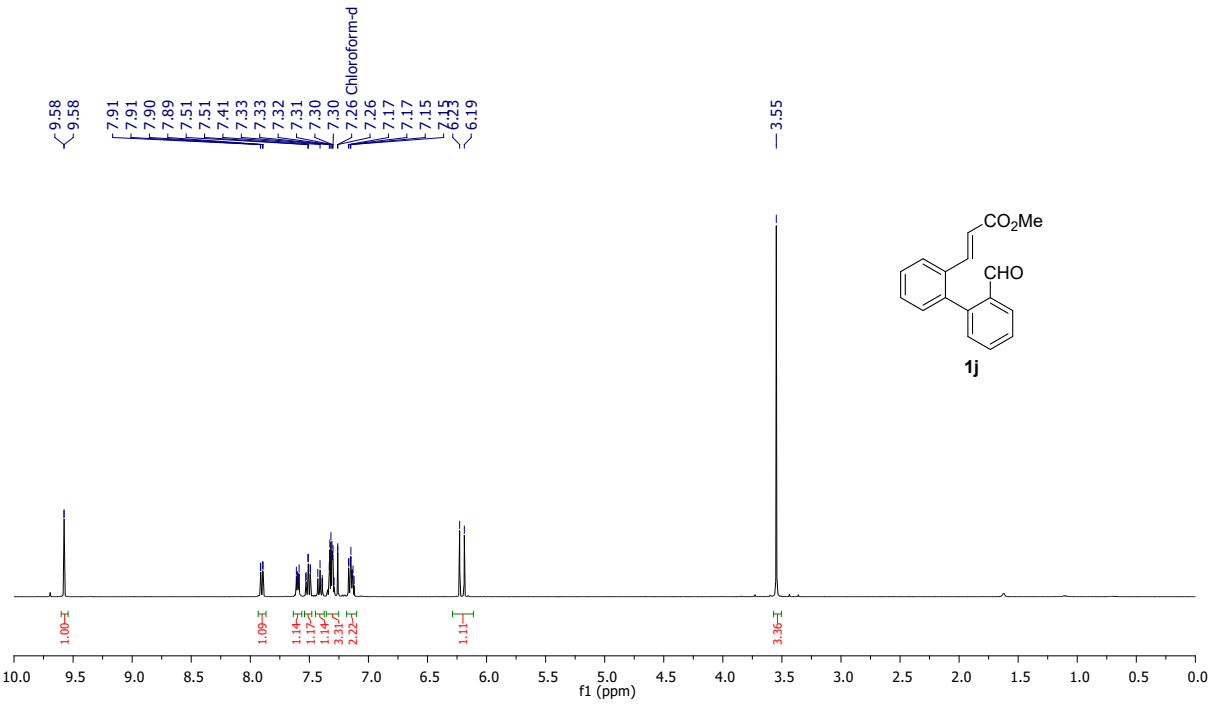
^{13}C{H} NMR (101 MHz) Spectrum of compound **1h** in $CDCl_3$.



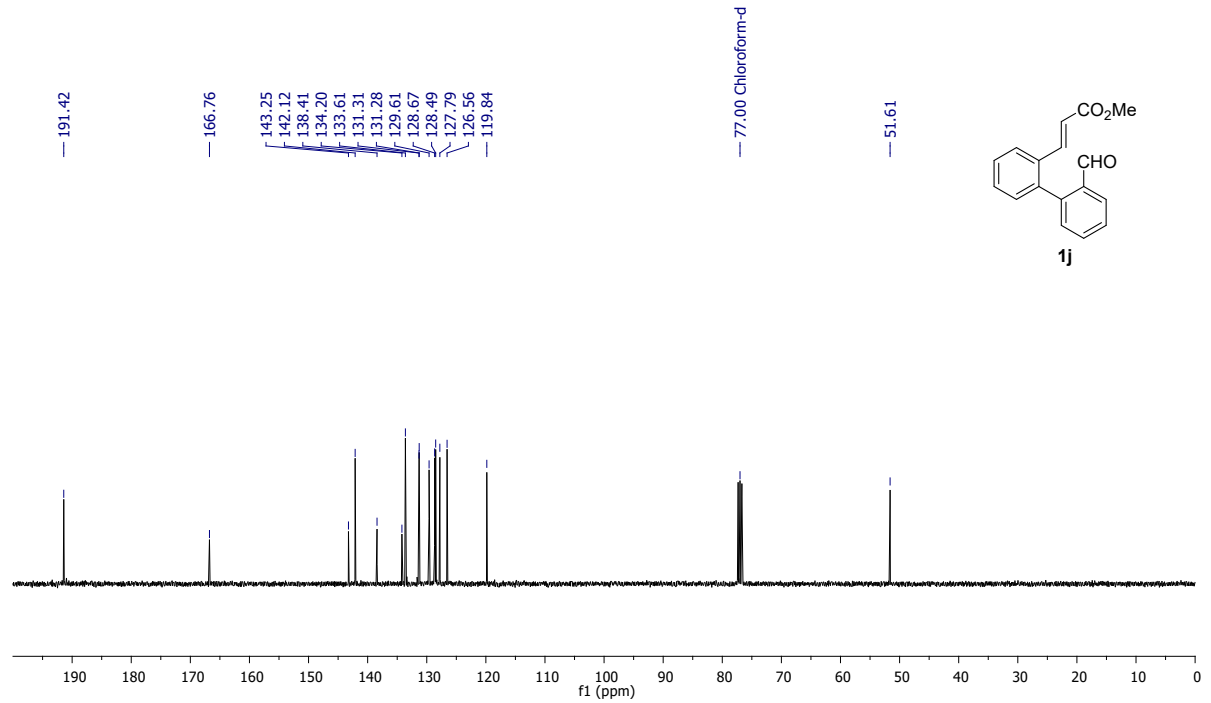
^{1}H NMR (400 MHz) Spectrum of compound **1i** in $CDCl_3$.



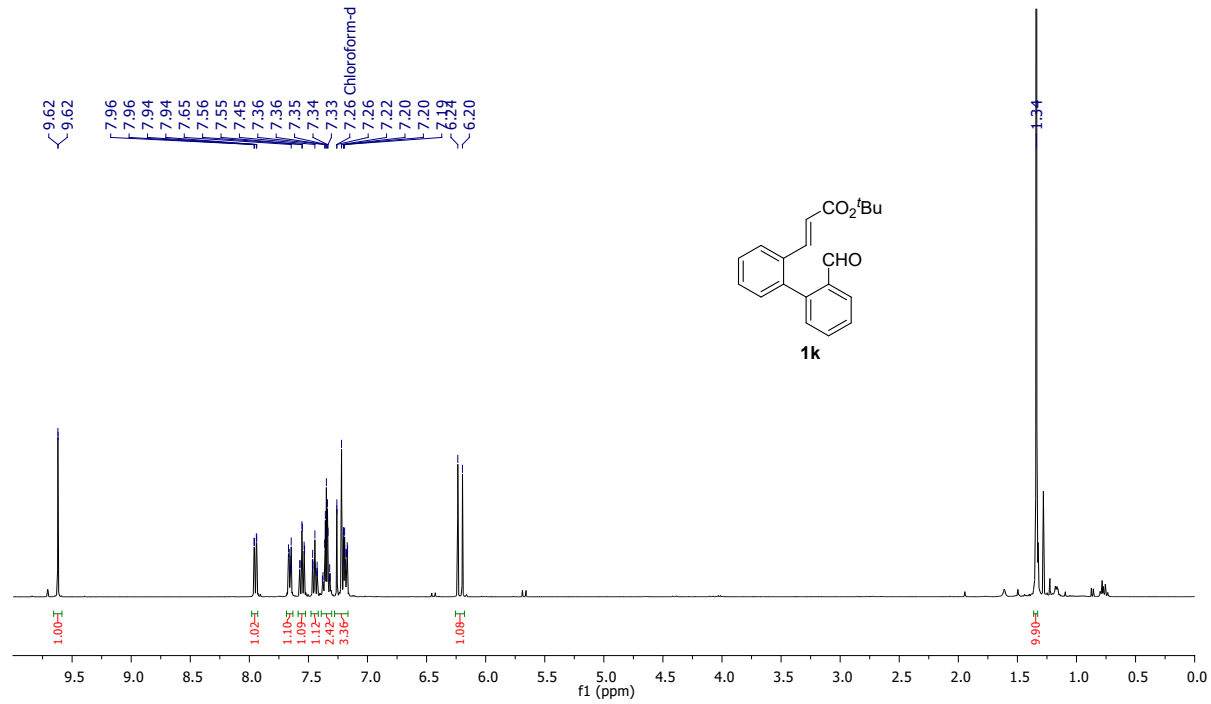
^{13}C{H} NMR (101 MHz) Spectrum of compound **1i** in $CDCl_3$.



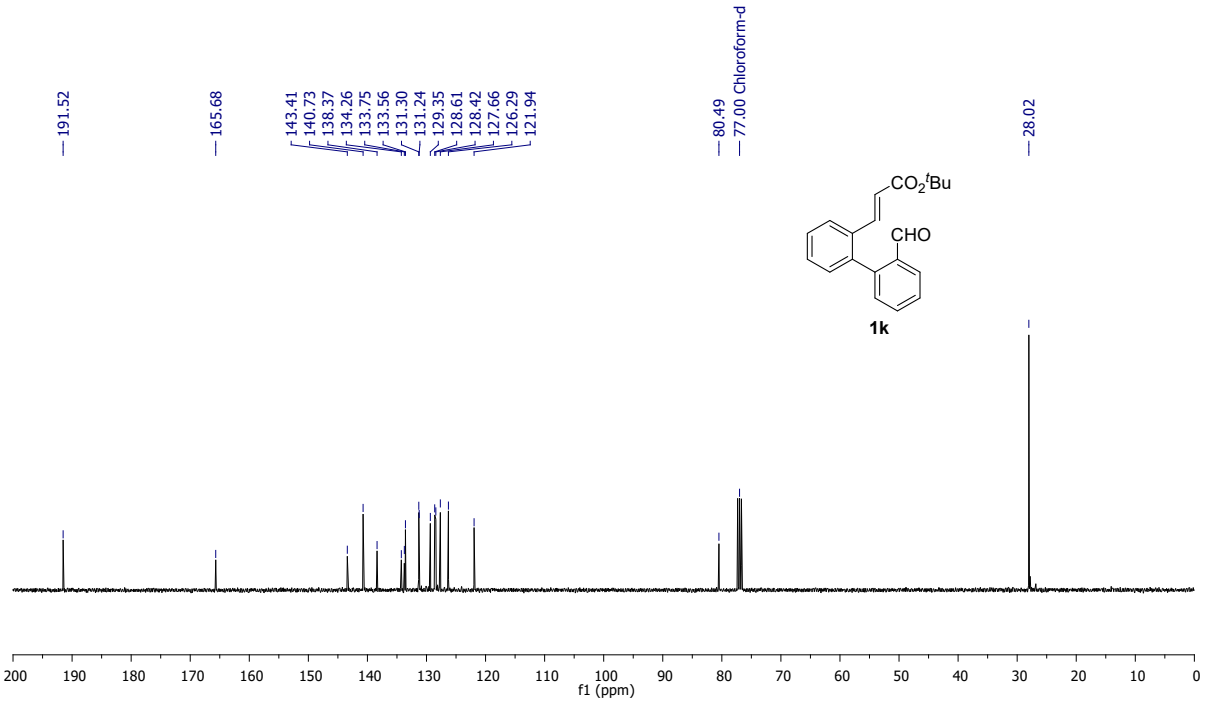
^{1}H NMR (400MHz) Spectrum of compound **1j** in $CDCl_3$.



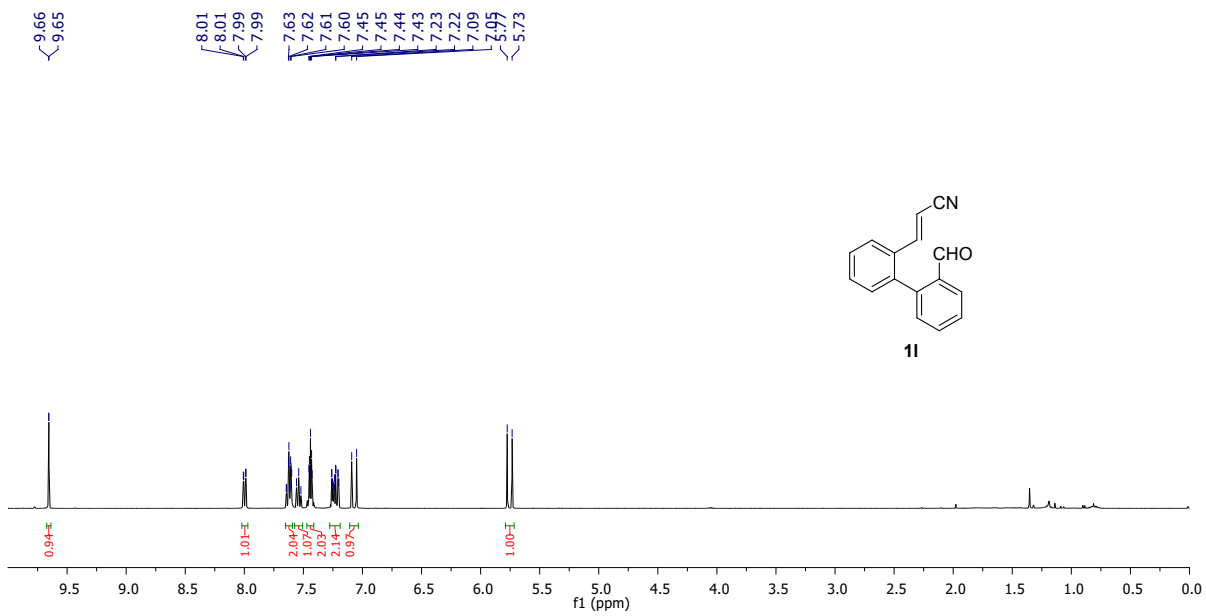
^{13}C{H} NMR (101 MHz) Spectrum of compound **1j** in $CDCl_3$.



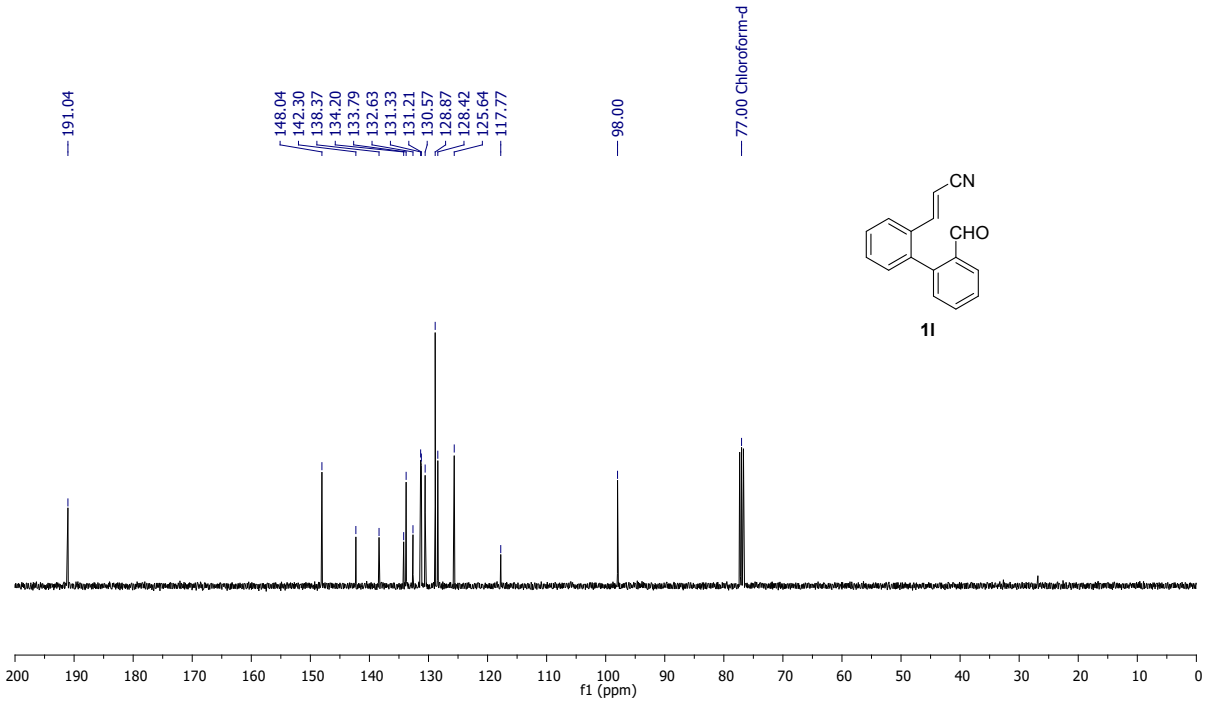
^{1}H NMR (400 MHz) Spectrum of compound **1k** in $CDCl_3$.



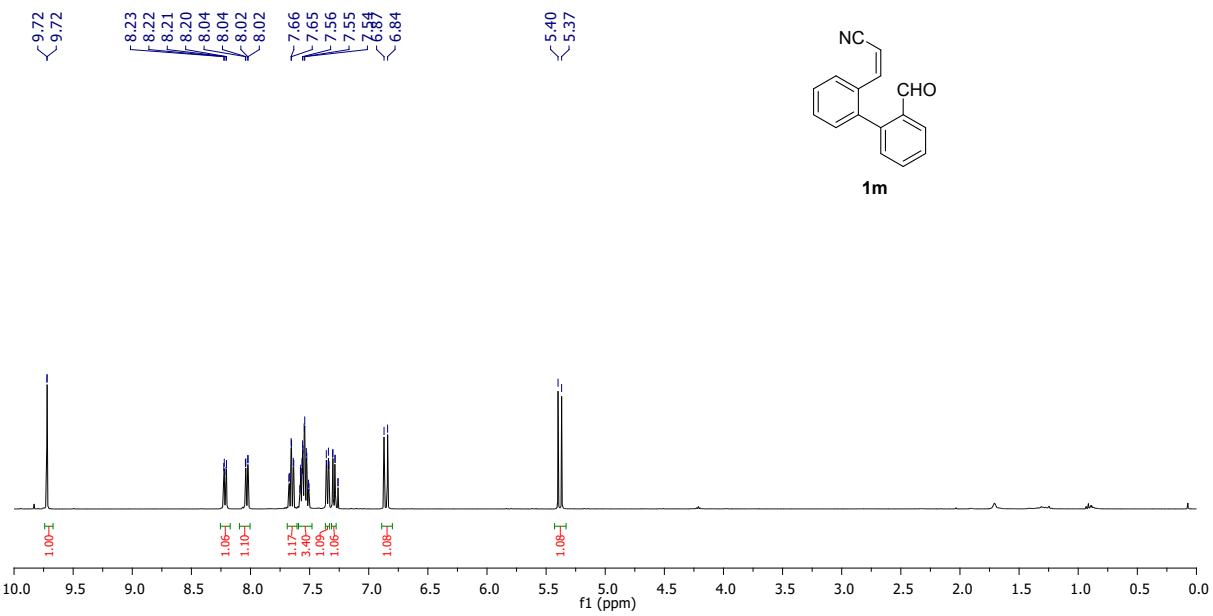
^{13}C{H} NMR (101 MHz) Spectrum of compound **1k** in $CDCl_3$.



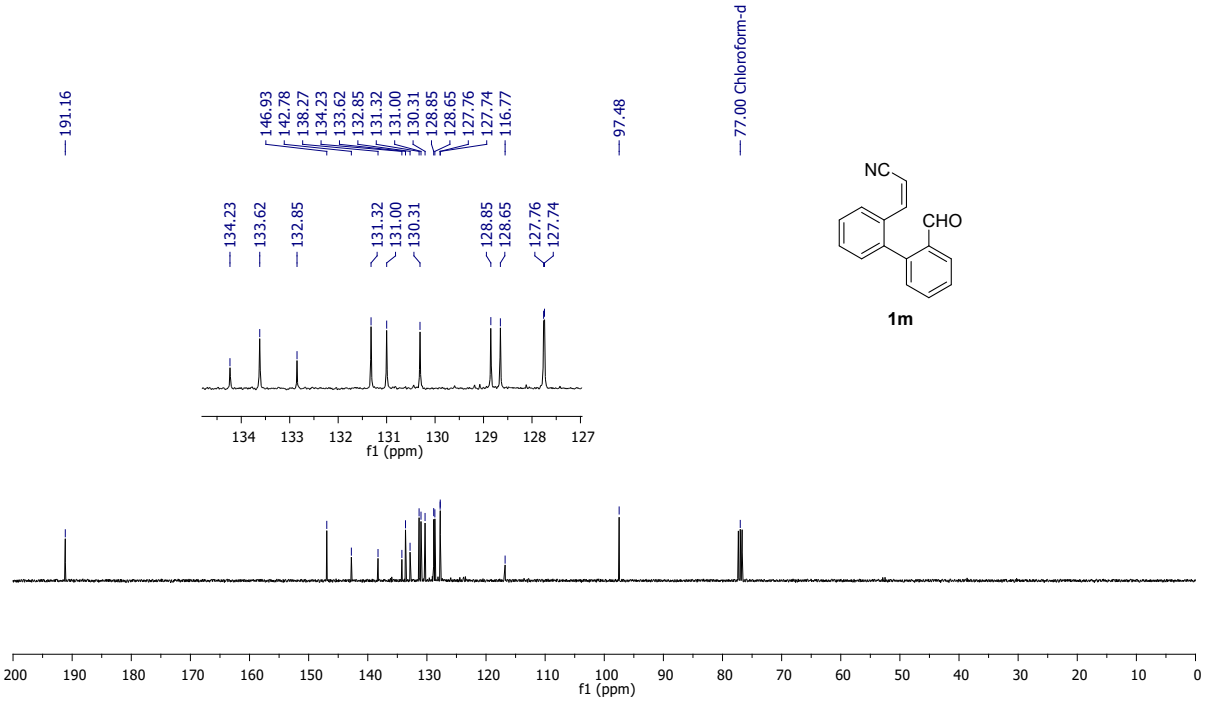
^{1}H NMR (400 MHz) Spectrum of compound **1l** in $CDCl_3$.



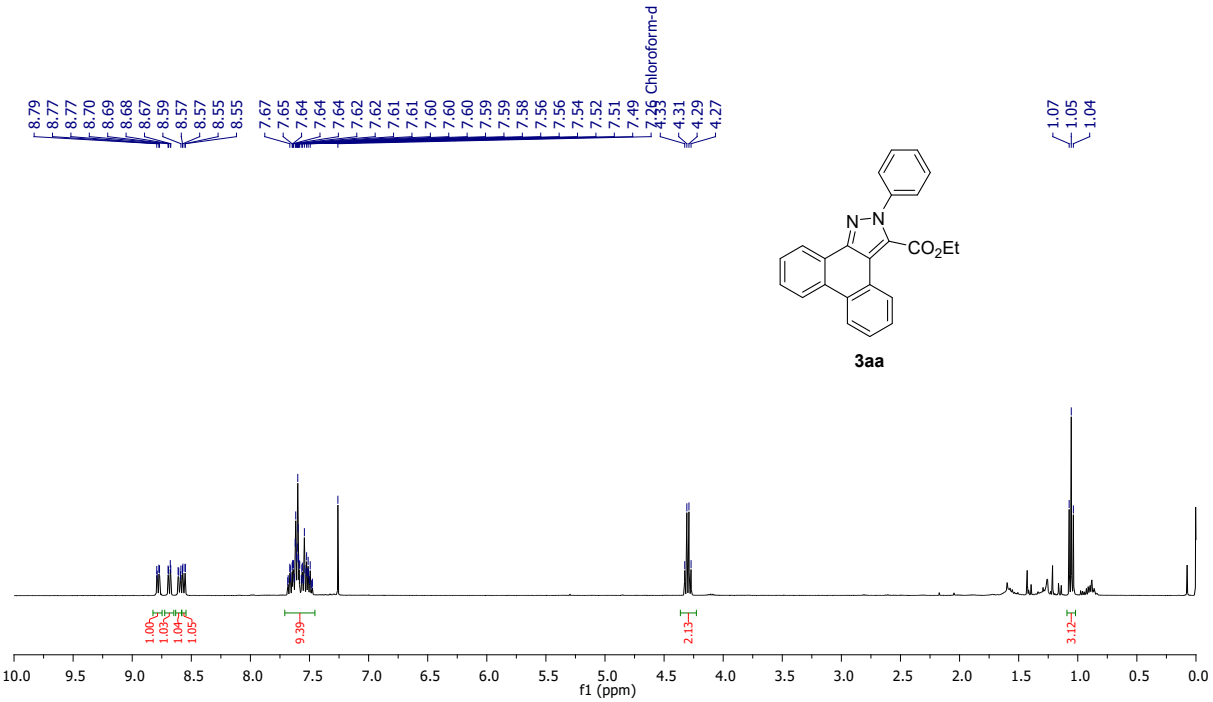
^{13}C{H} NMR (101 MHz) Spectrum of compound **1l** in $CDCl_3$.



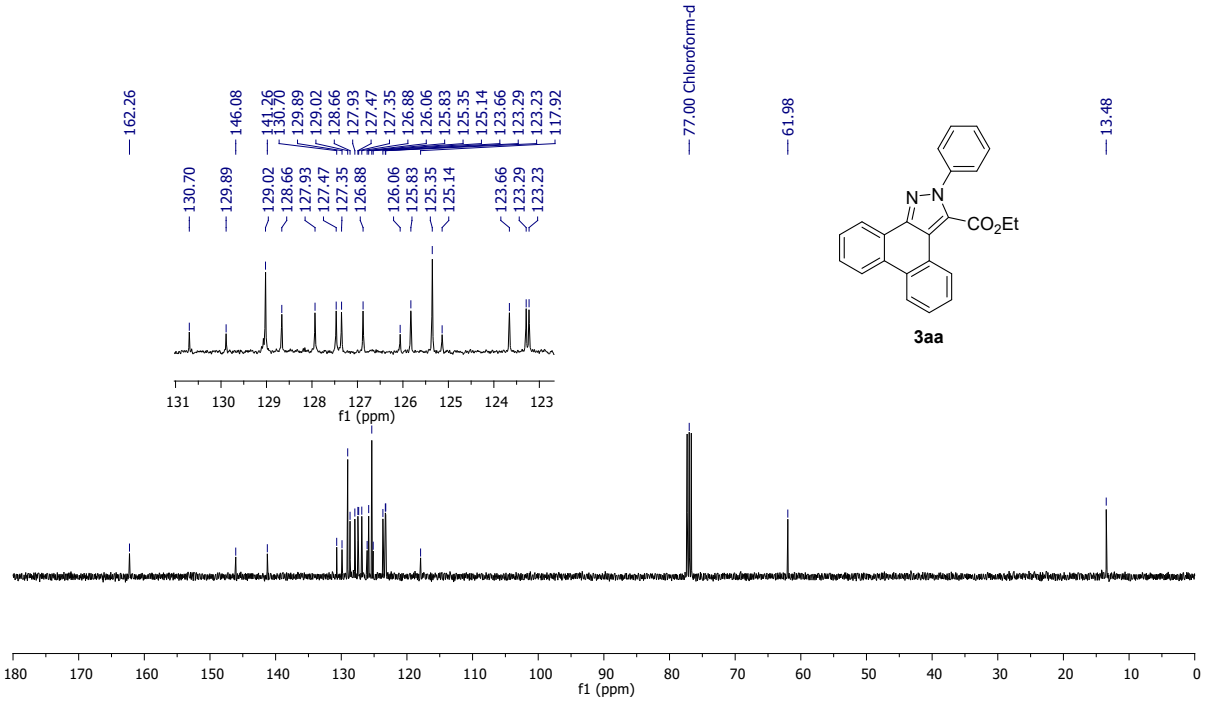
^{1}H NMR (400 MHz) Spectrum of compound **1m** in $CDCl_3$.



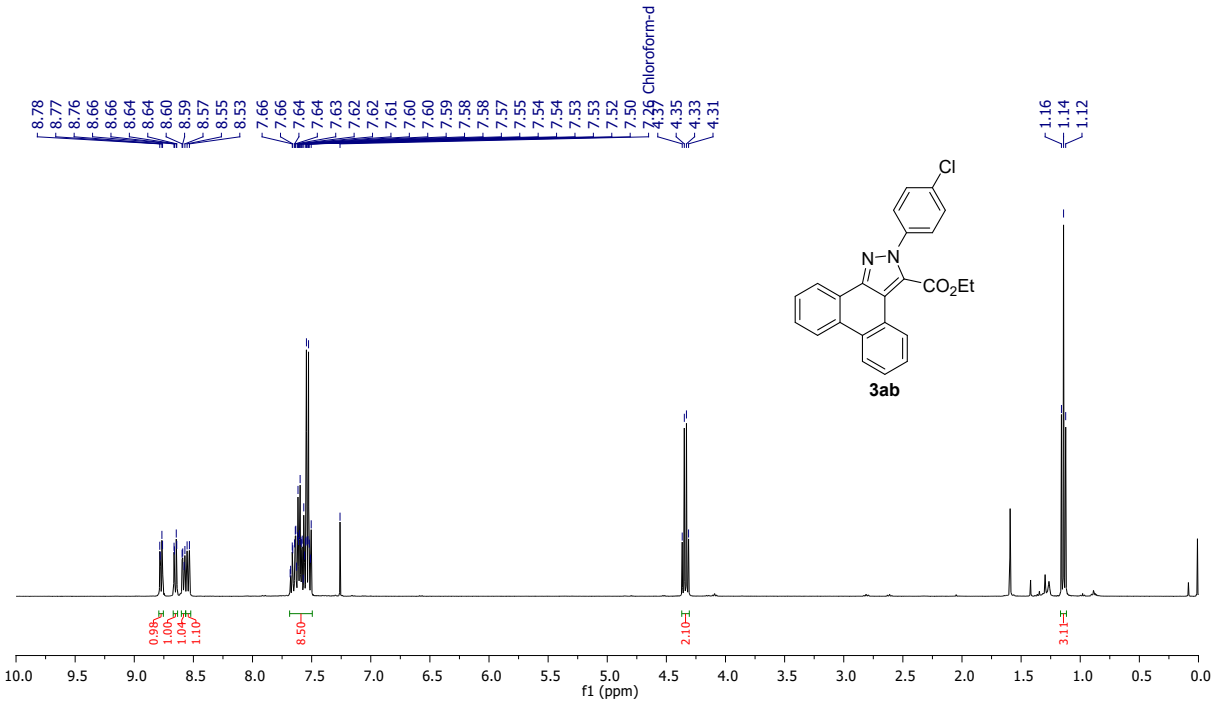
^{13}C{H} NMR (101 MHz) Spectrum of compound **1m** in $CDCl_3$.



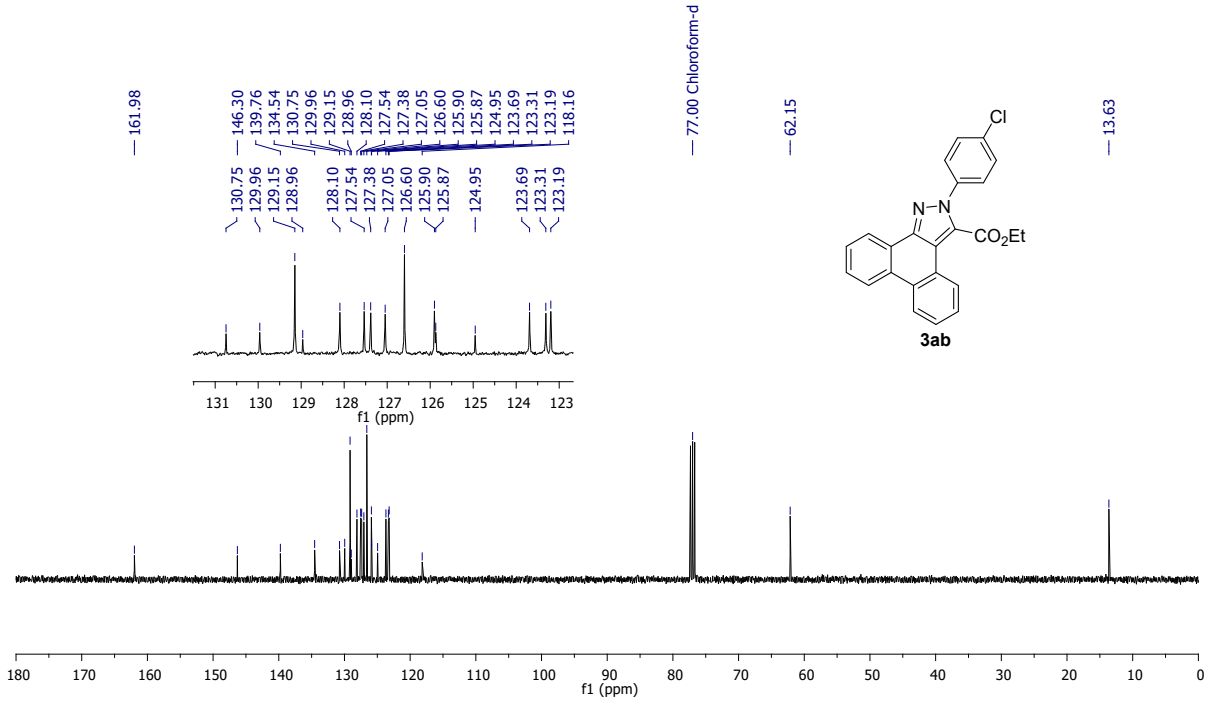
^{1}H NMR (400 MHz) spectrum of **3aa** in $CDCl_3$.



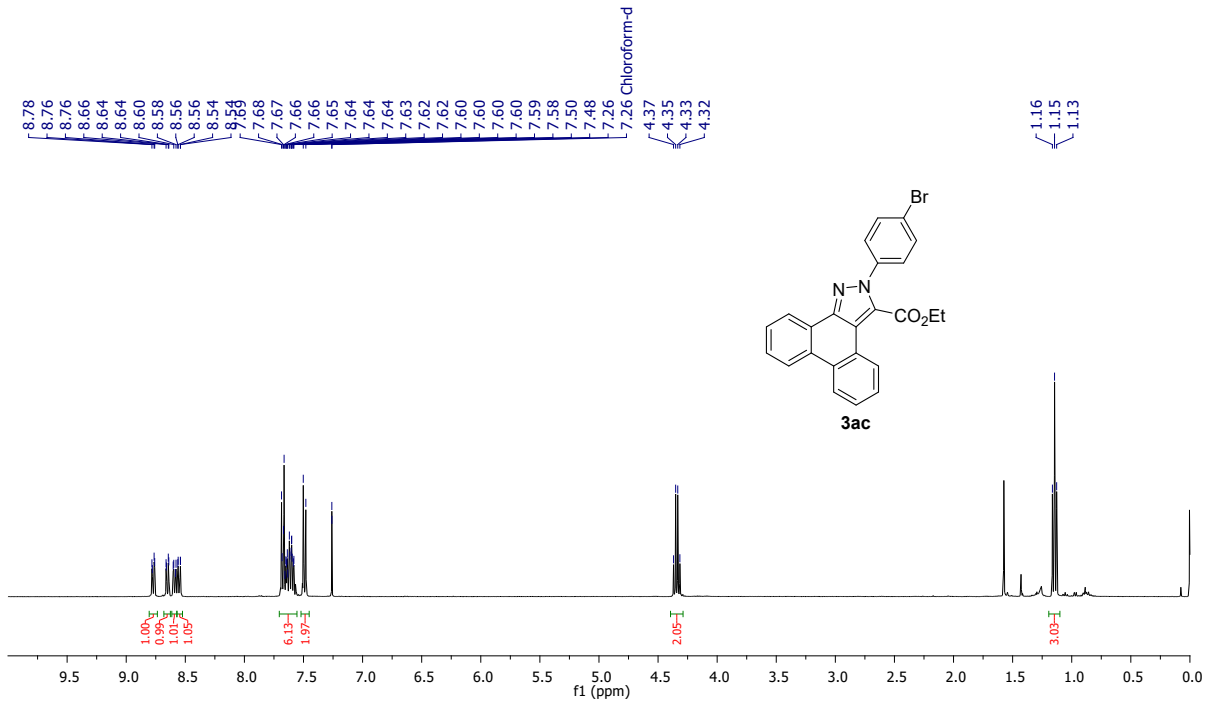
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3aa** in $CDCl_3$.



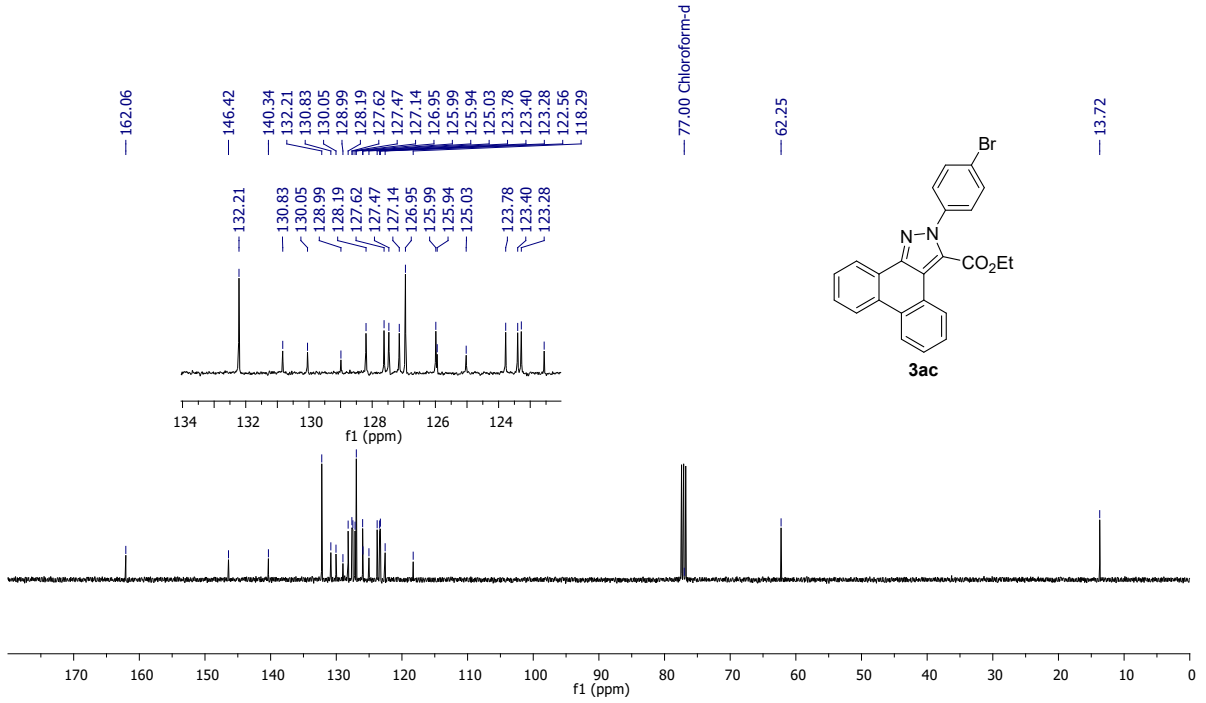
^{1}H NMR (400 MHz) spectrum of **3ab** in $CDCl_3$.



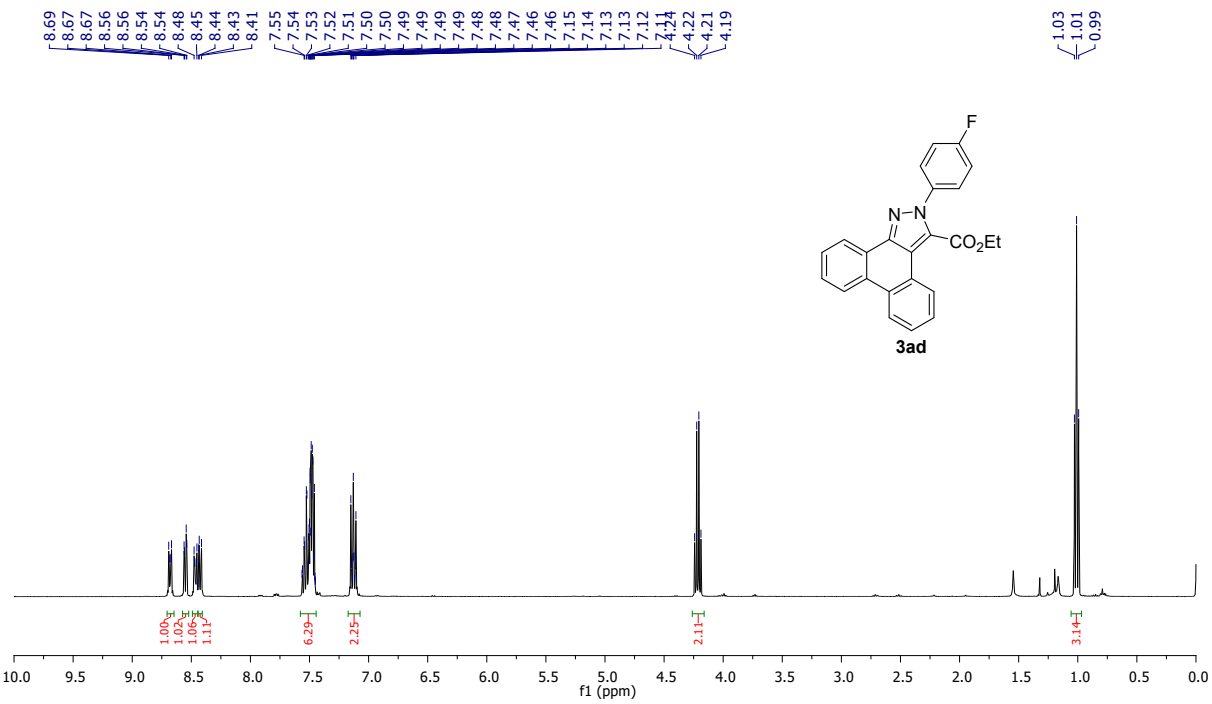
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ab** in $CDCl_3$.



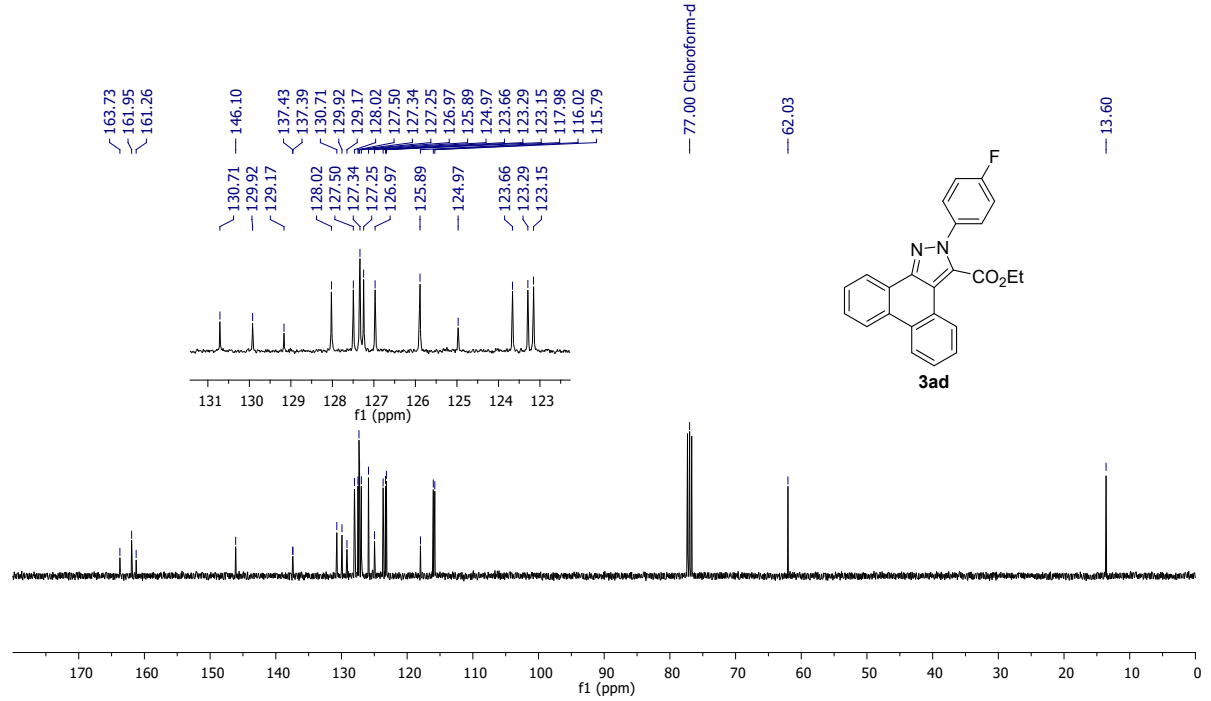
^{1}H NMR (400 MHz) spectrum of **3ac** in $CDCl_3$.



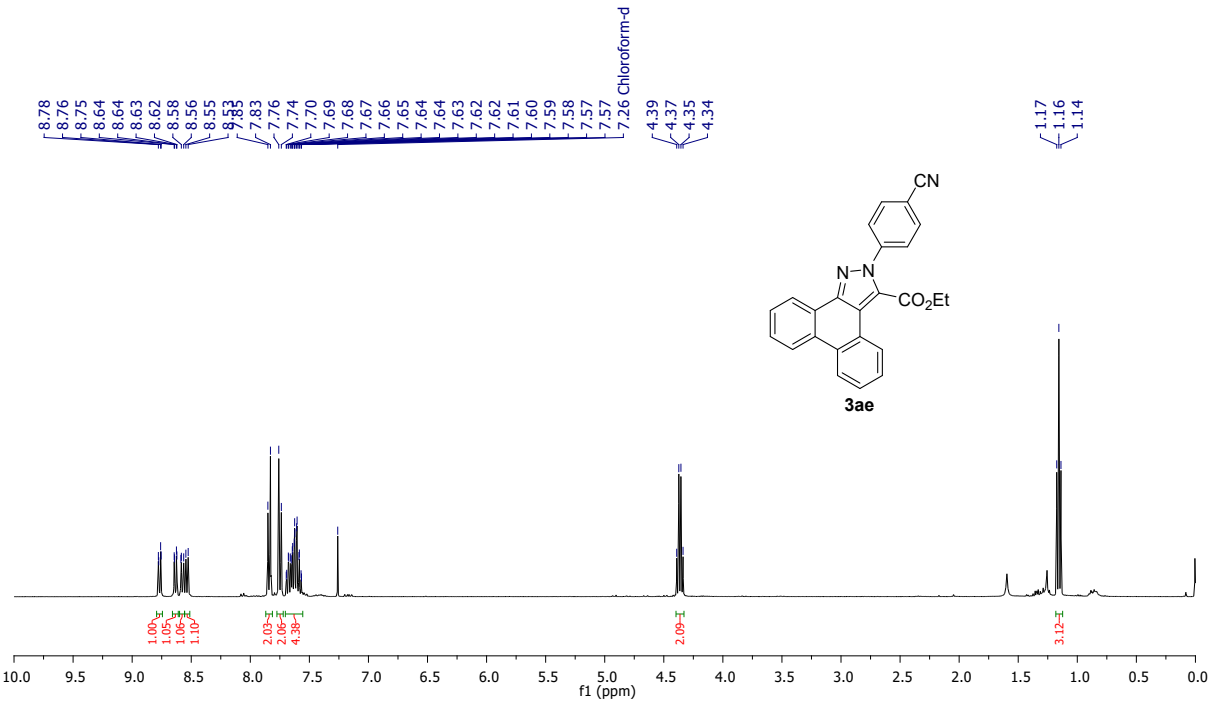
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ac** in $CDCl_3$.



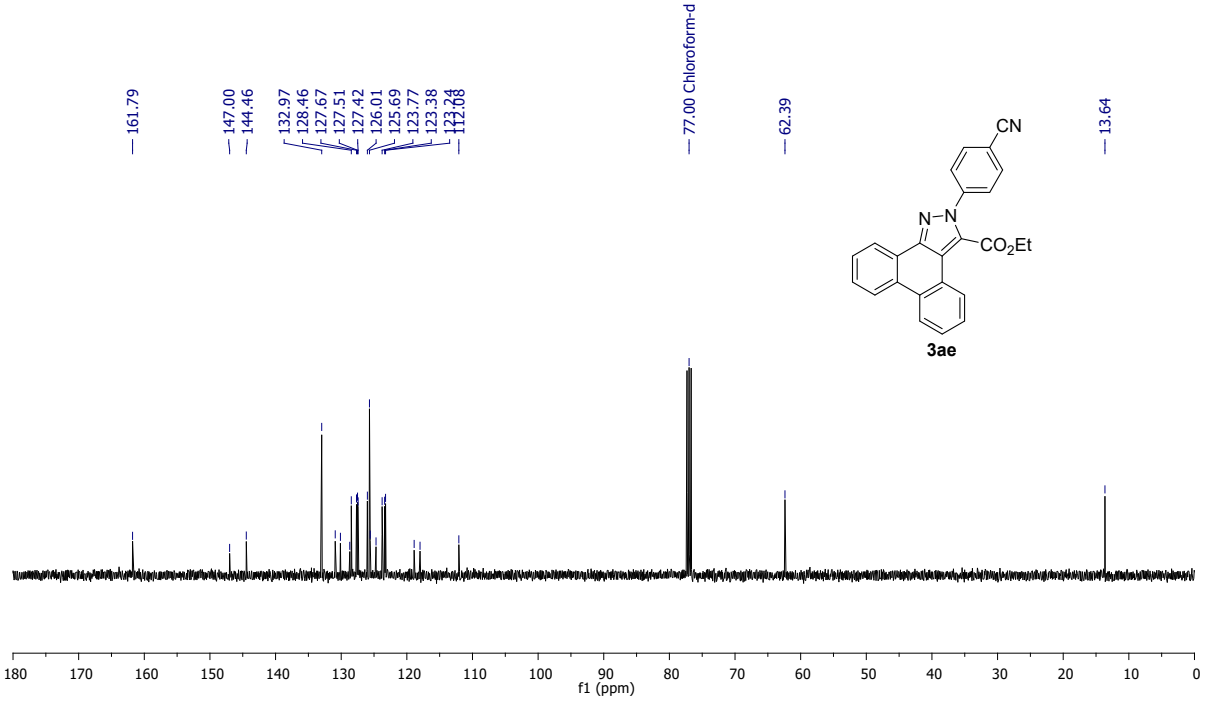
^{1}H NMR (400 MHz) spectrum of **3ad** in $CDCl_3$.



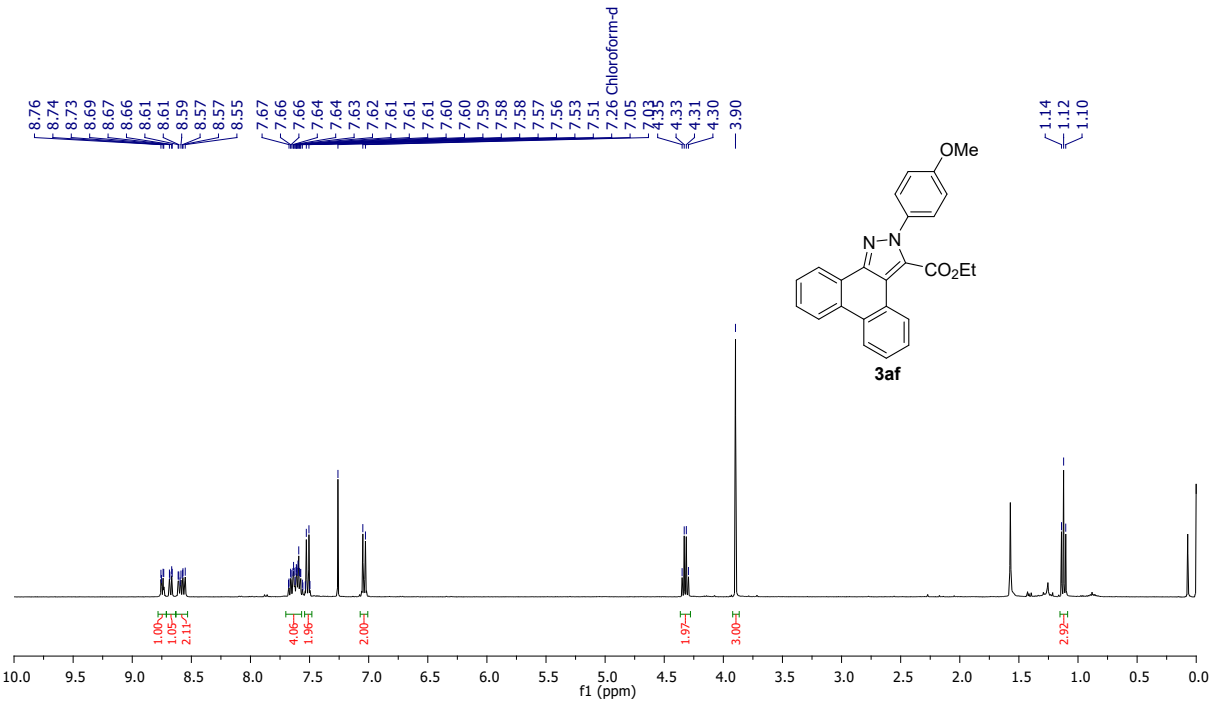
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ad** in $CDCl_3$.



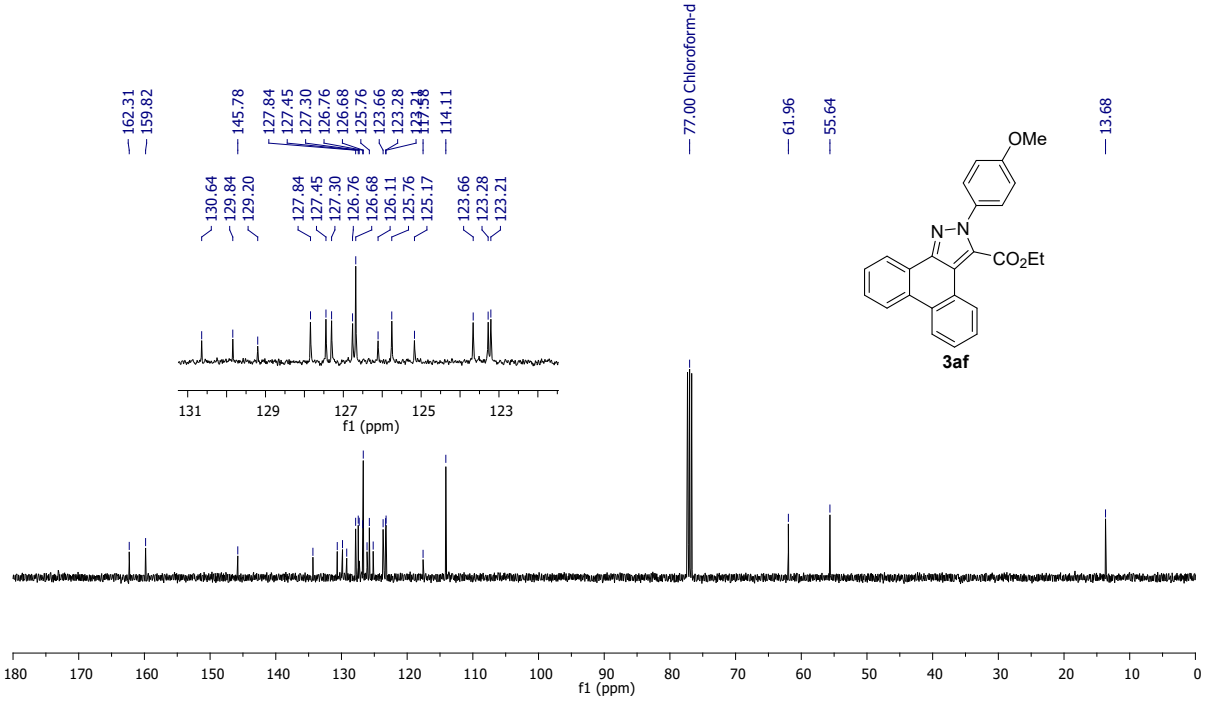
^{1}H NMR (400 MHz) spectrum of **3ae** in $CDCl_3$.



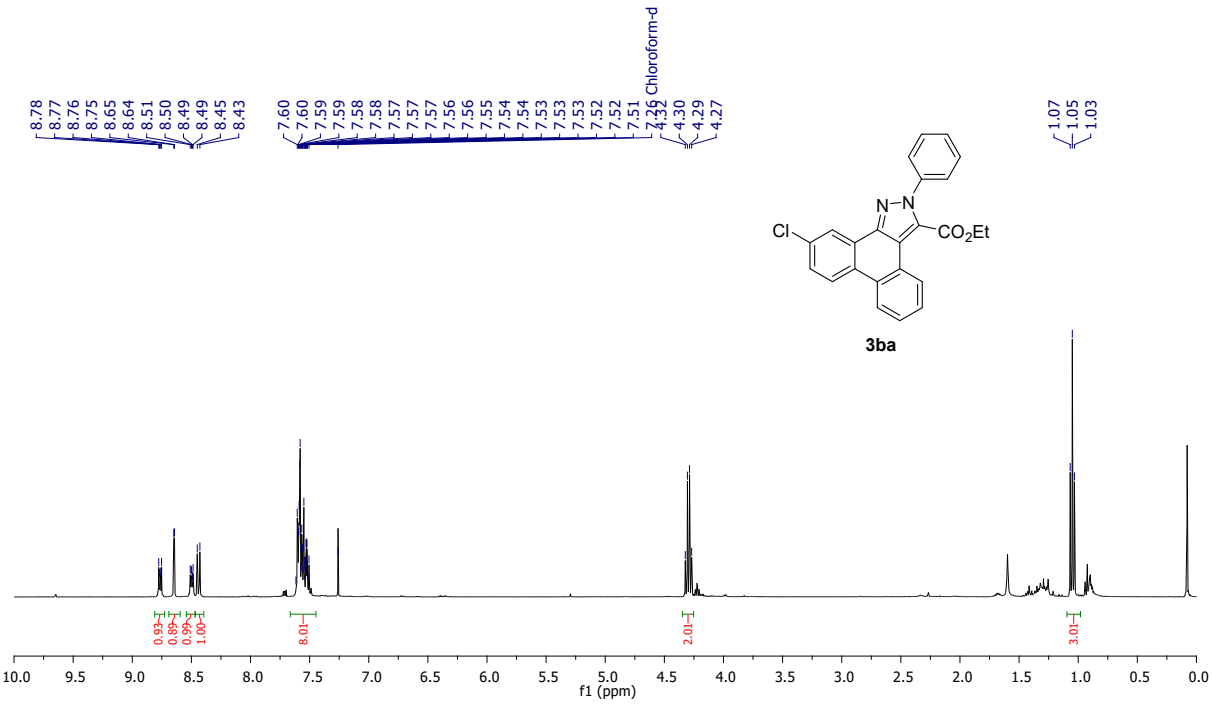
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ae** in $CDCl_3$.



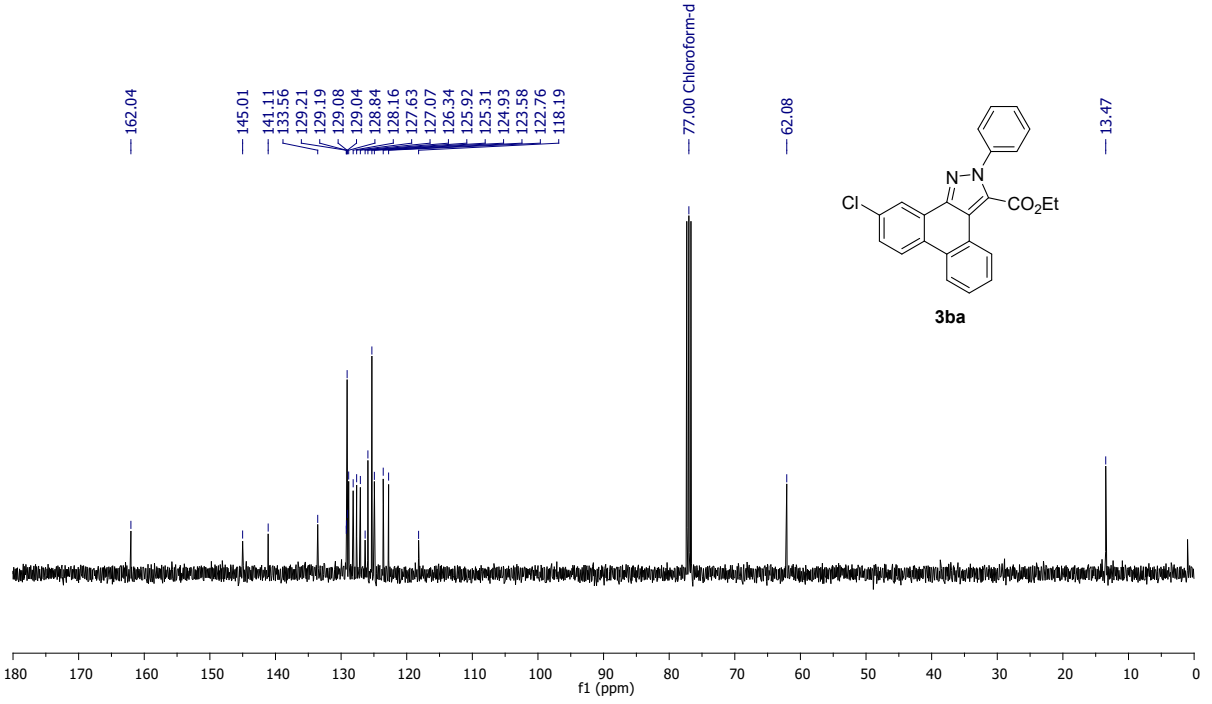
^{1}H NMR (400 MHz) spectrum of **3af** in $CDCl_3$.



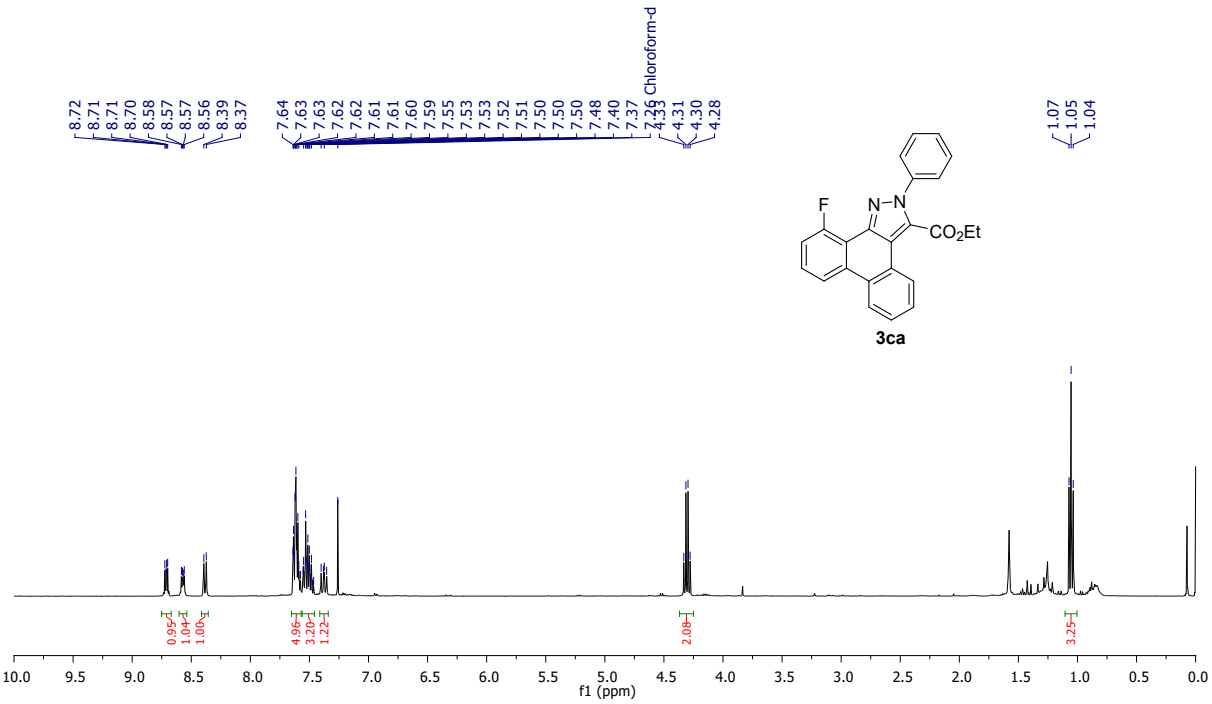
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3af** in $CDCl_3$.



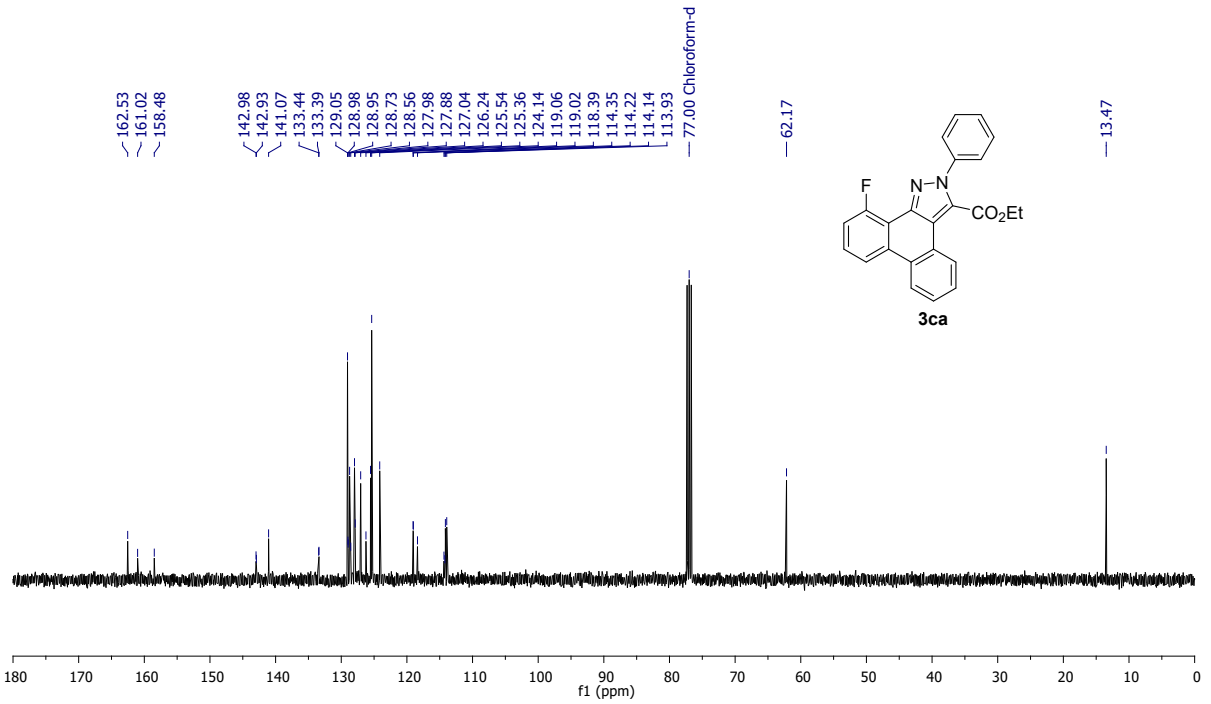
^{1}H NMR (400 MHz) spectrum of **3ba** in $CDCl_3$.



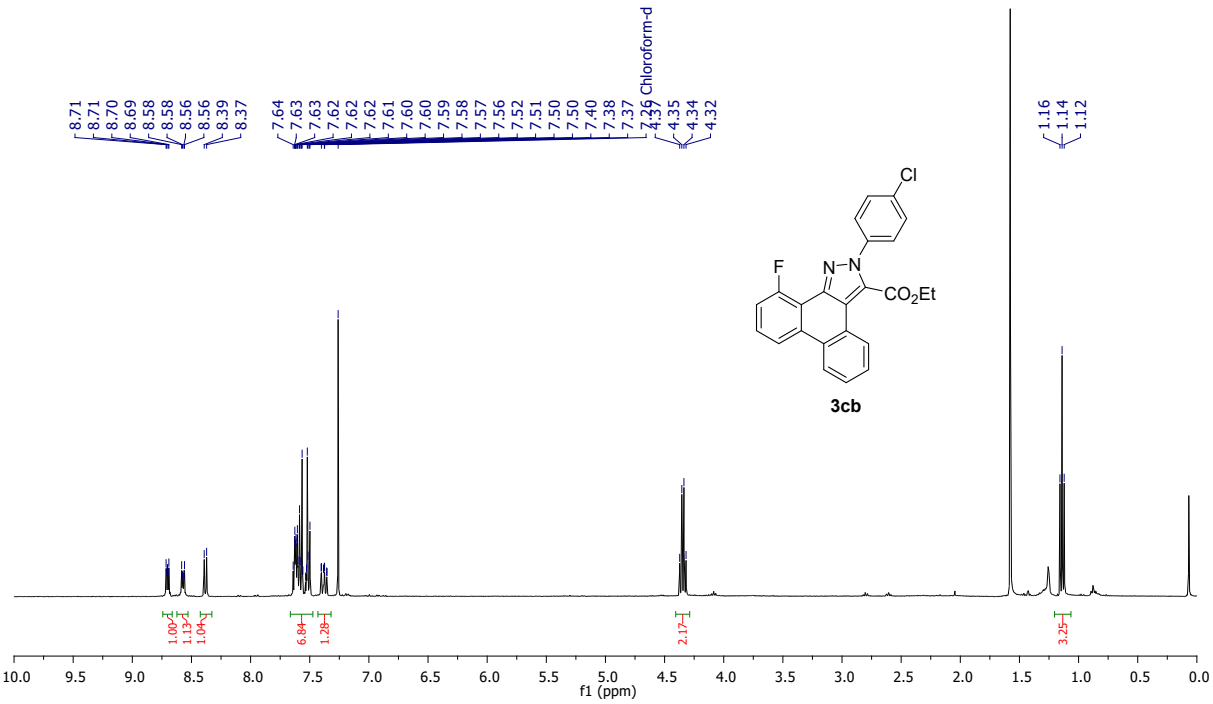
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ba** in $CDCl_3$.



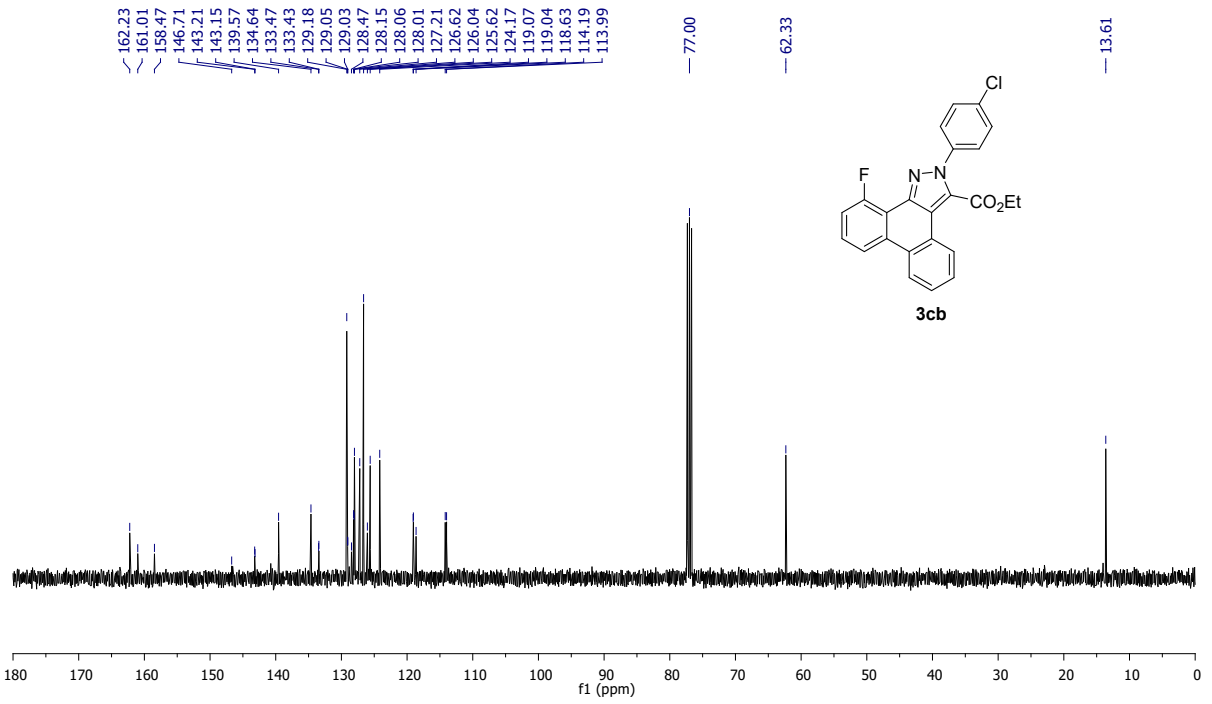
^{1}H NMR (400 MHz) spectrum of **3ca** in $CDCl_3$.



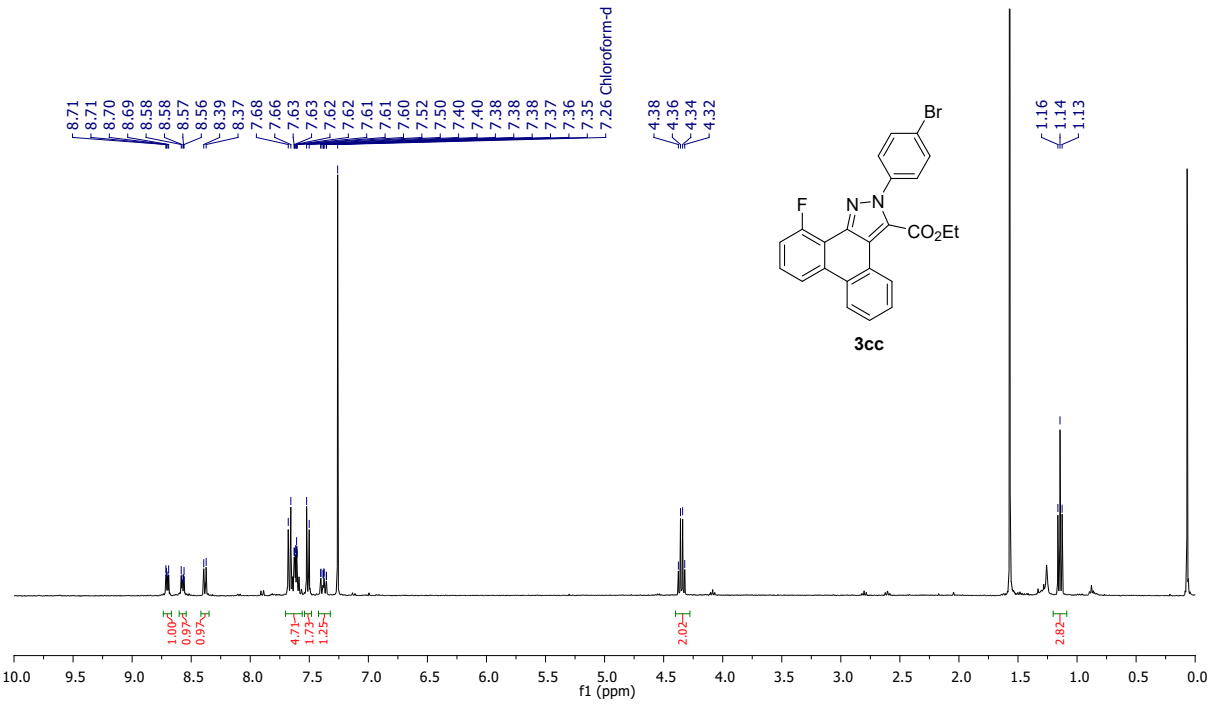
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ca** in $CDCl_3$.



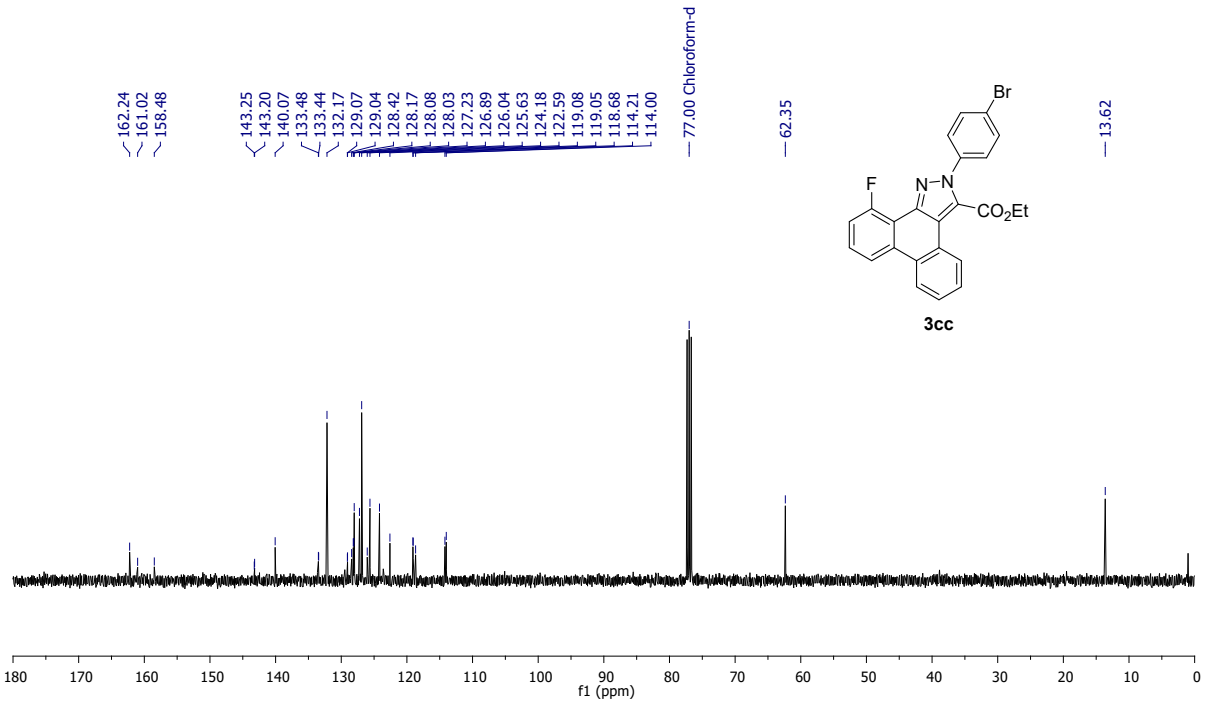
^{1}H NMR (400 MHz) spectrum of **3cb** in $CDCl_3$.



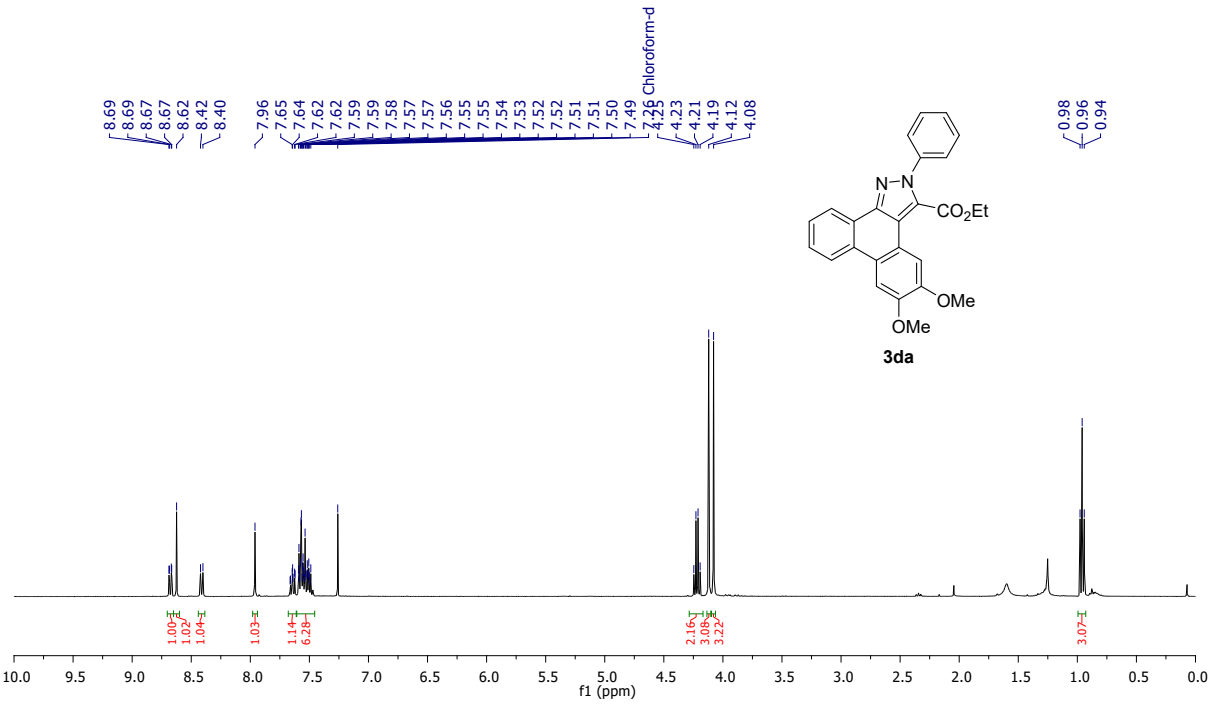
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3cb** in $CDCl_3$.



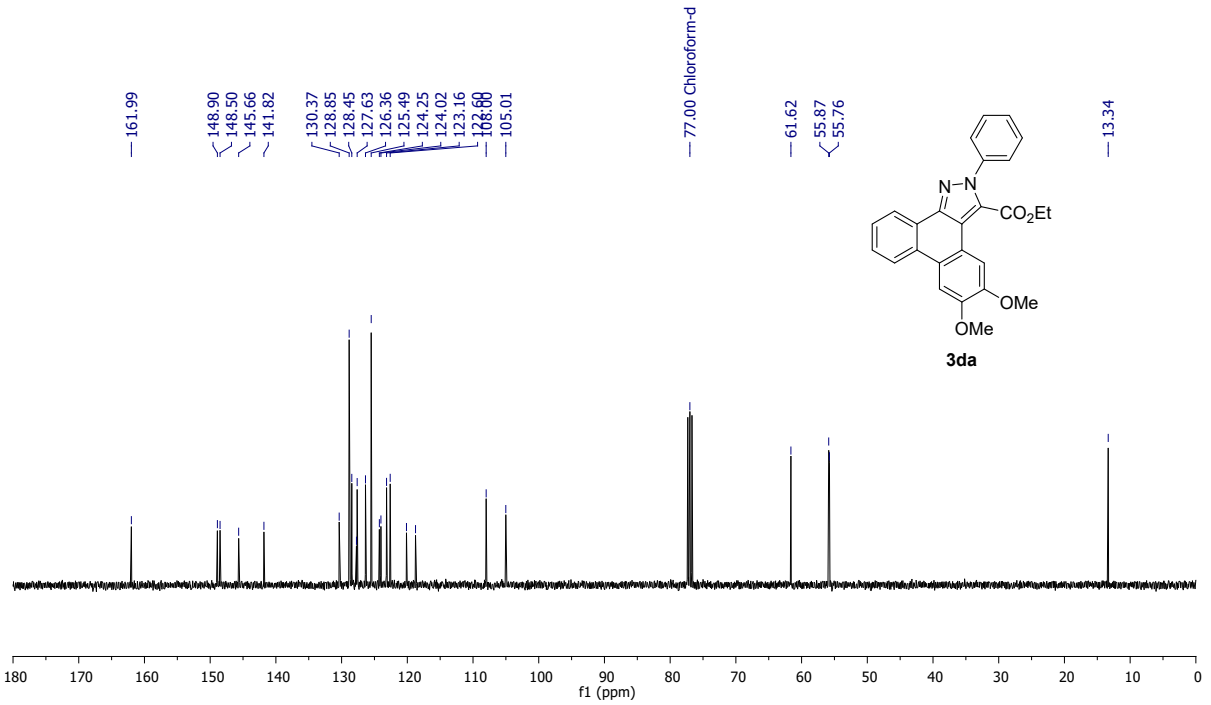
^{1}H NMR (400 MHz) spectrum of **3cc** in $CDCl_3$.



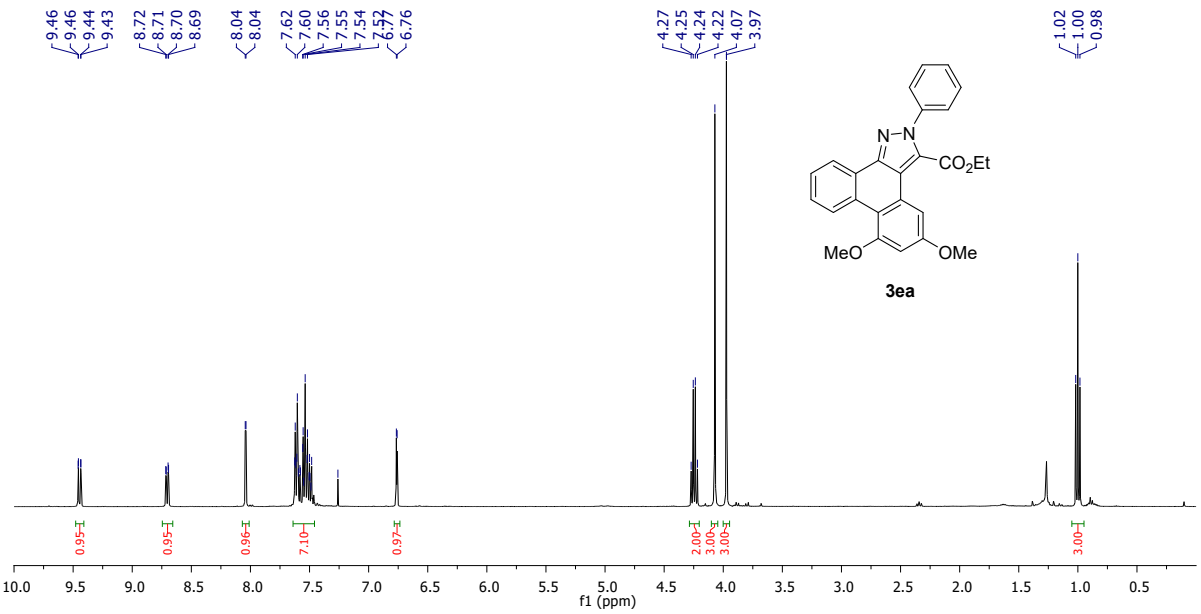
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3cc** in $CDCl_3$.



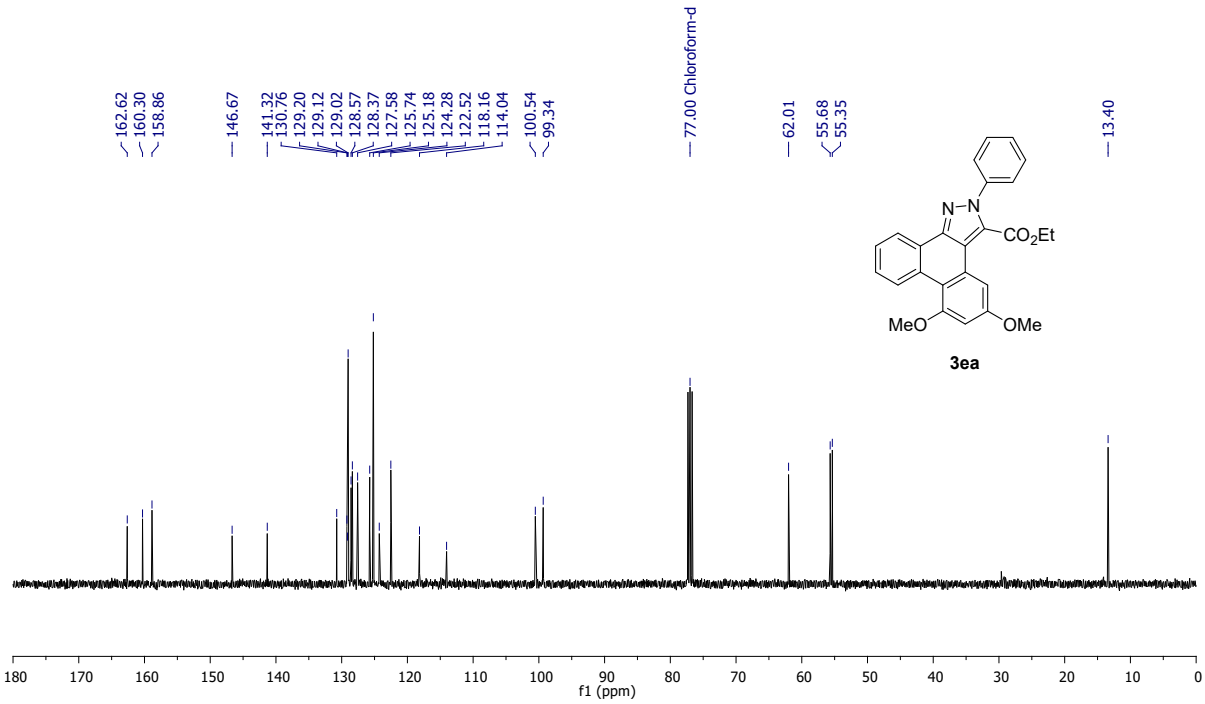
^{1}H NMR (400 MHz) spectrum of **3da** in $CDCl_3$.



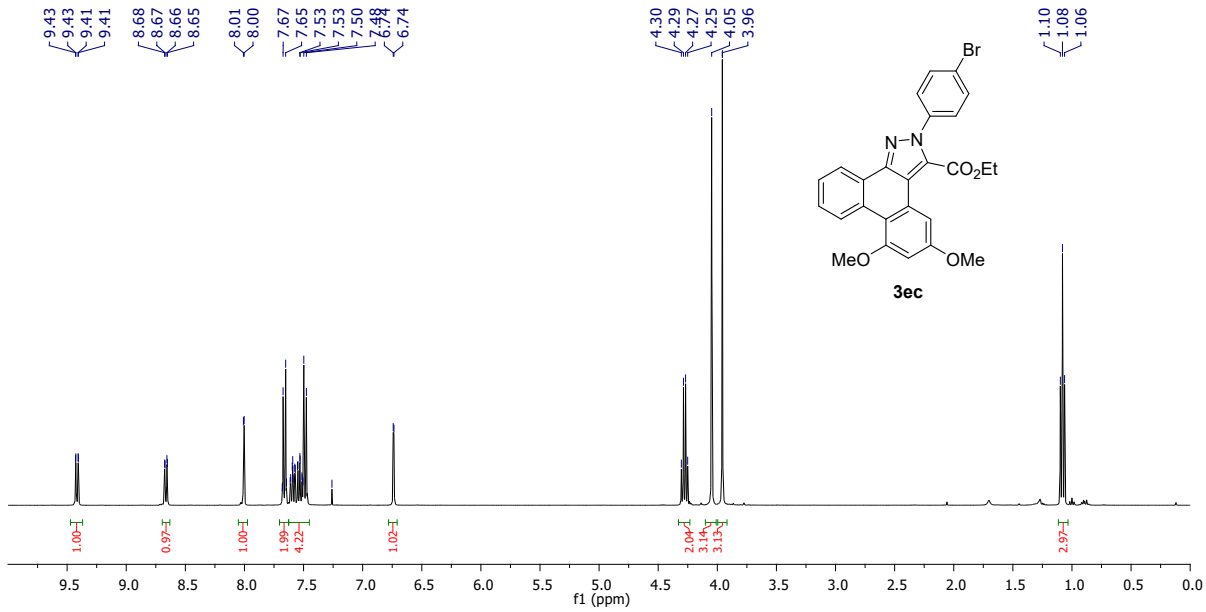
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3da** in $CDCl_3$.



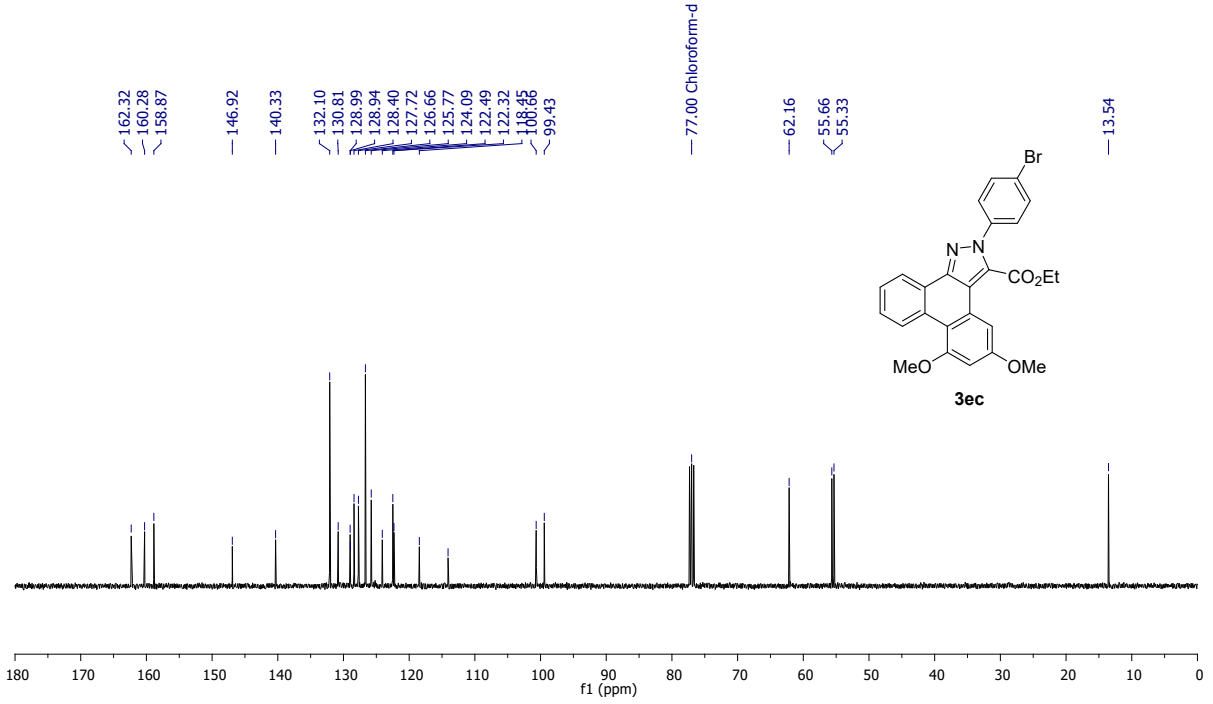
^{1}H NMR (400 MHz) spectrum of **3ea** in $CDCl_3$.



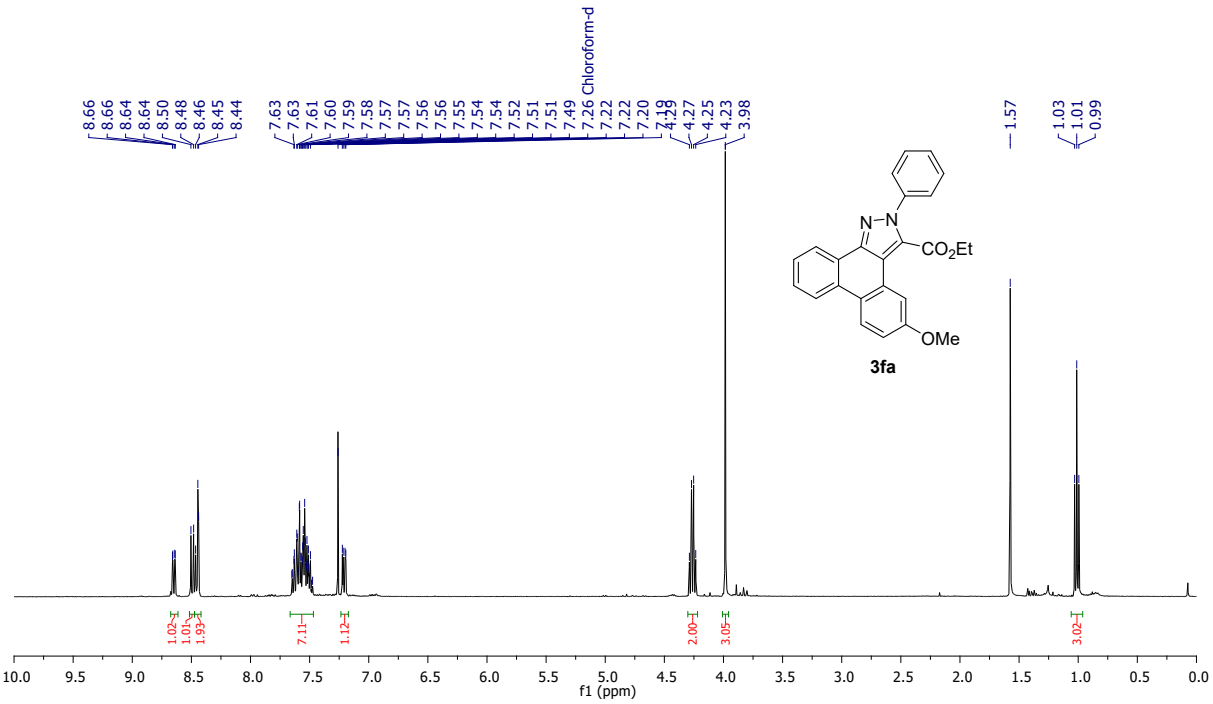
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ea** in $CDCl_3$.



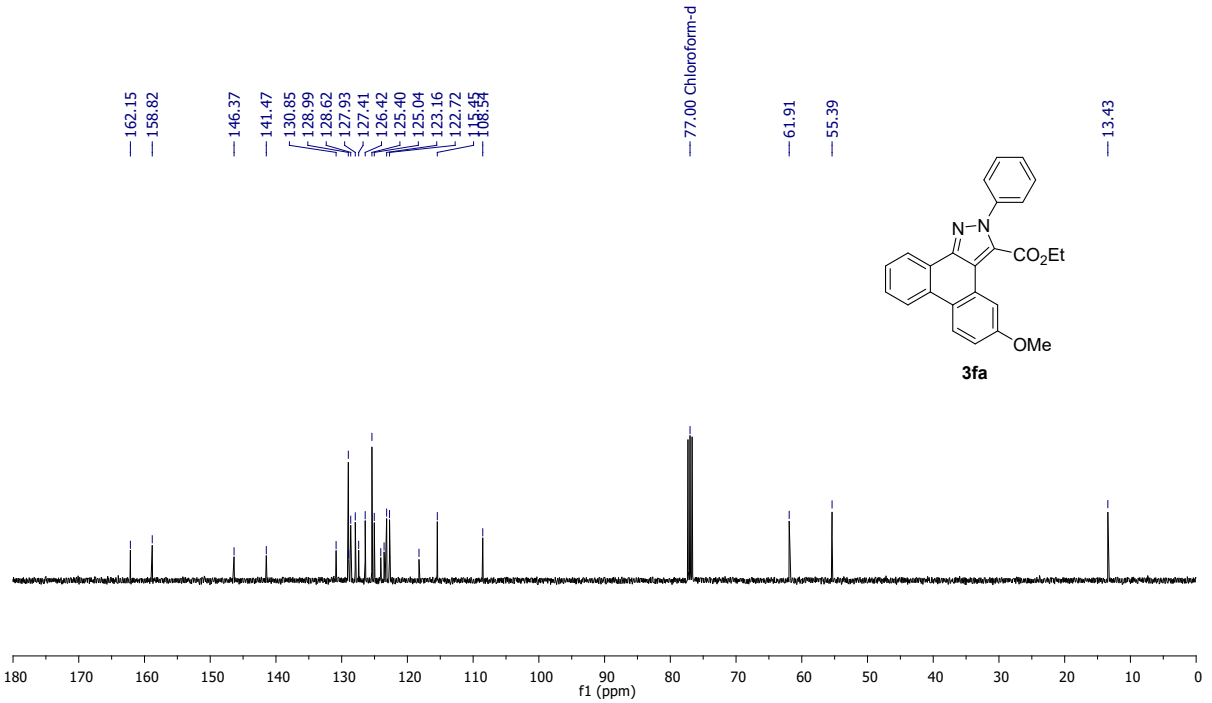
^{1}H NMR (400 MHz) spectrum of **3ec** in $CDCl_3$.



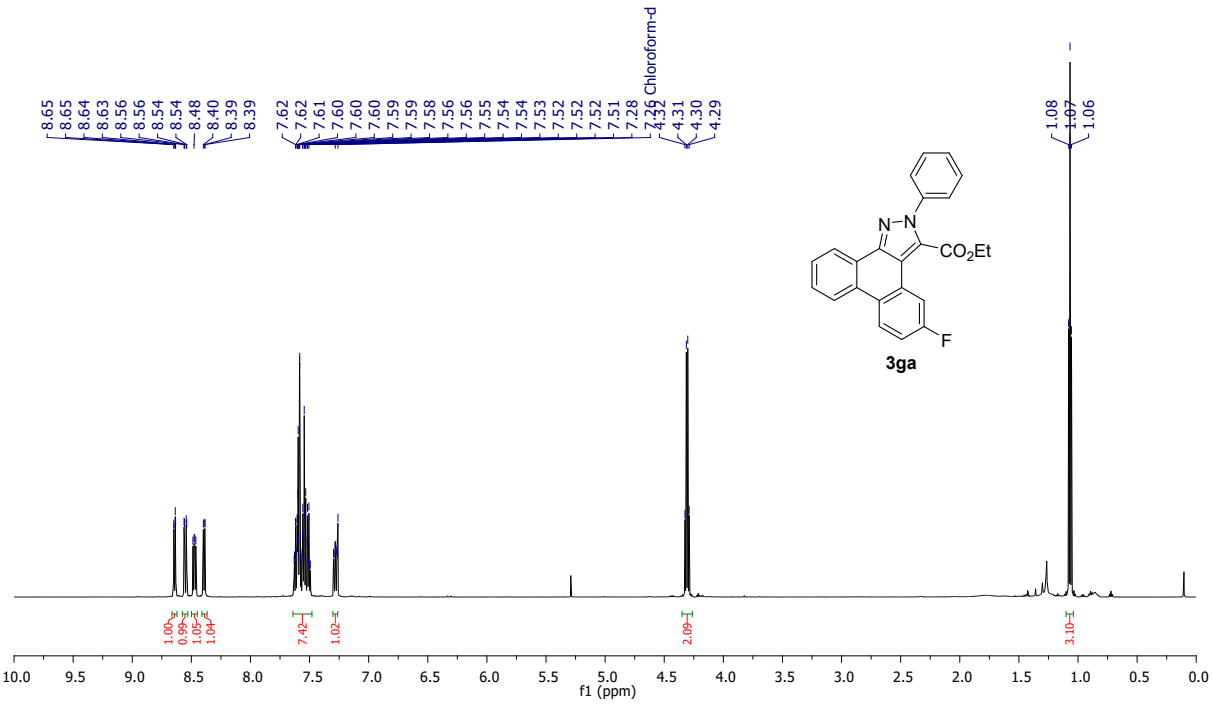
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ec** in $CDCl_3$.



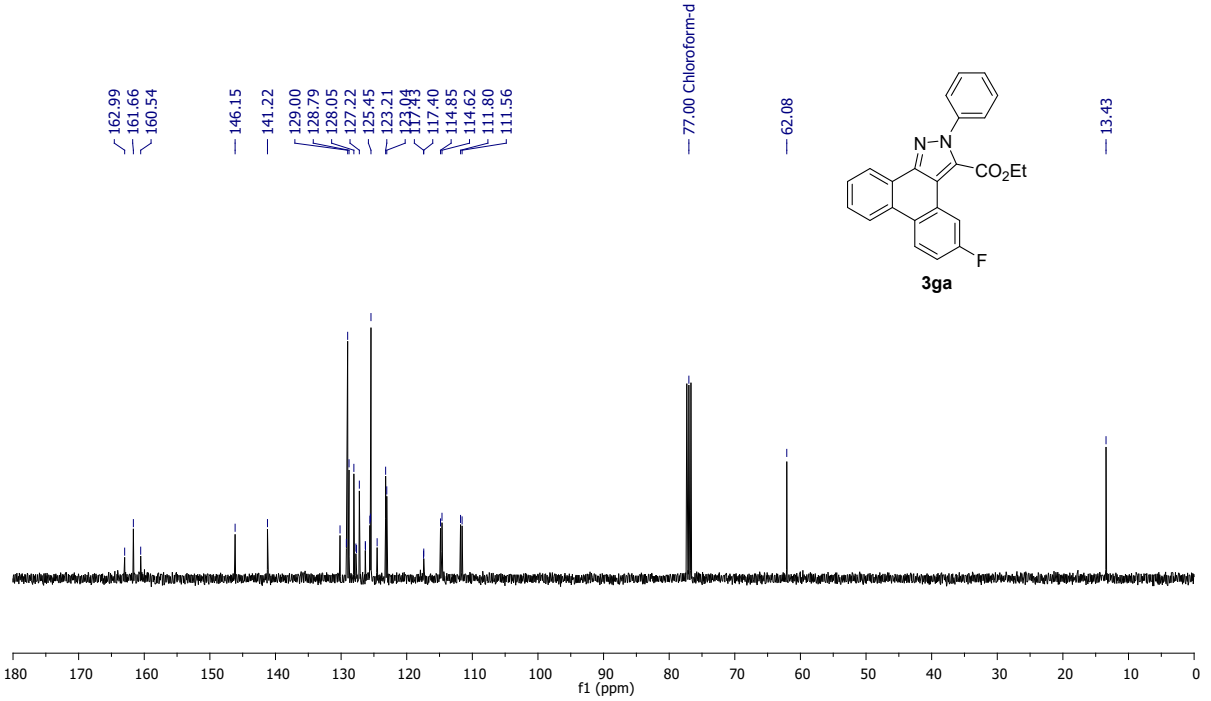
^{1}H NMR (400 MHz) spectrum of **3fa** in $CDCl_3$.



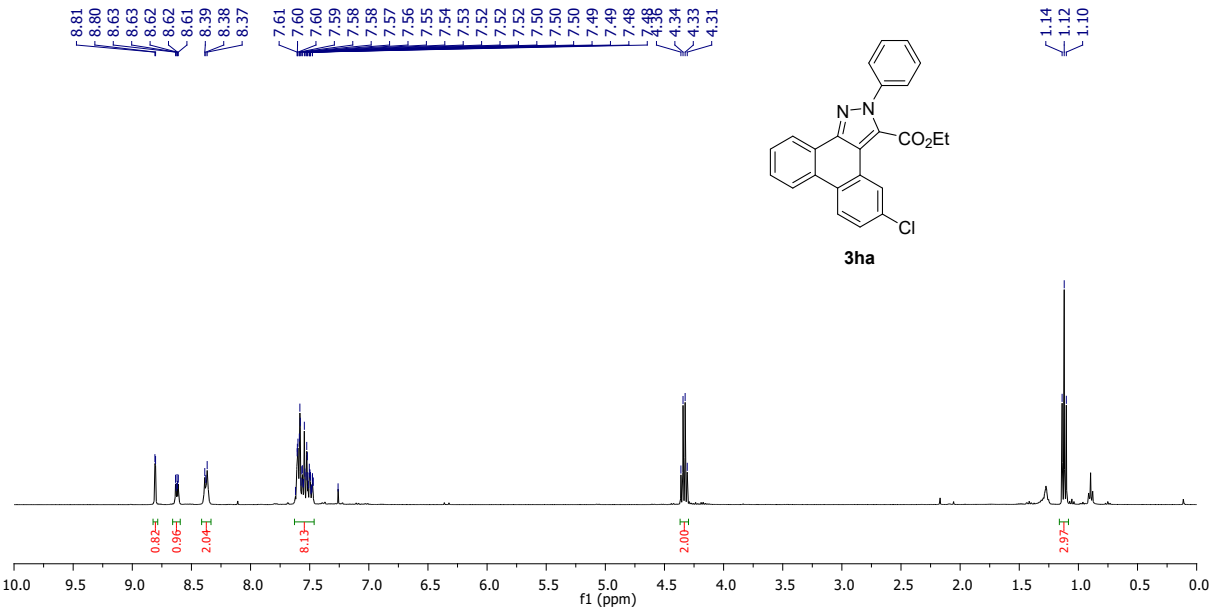
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3fa** in $CDCl_3$.



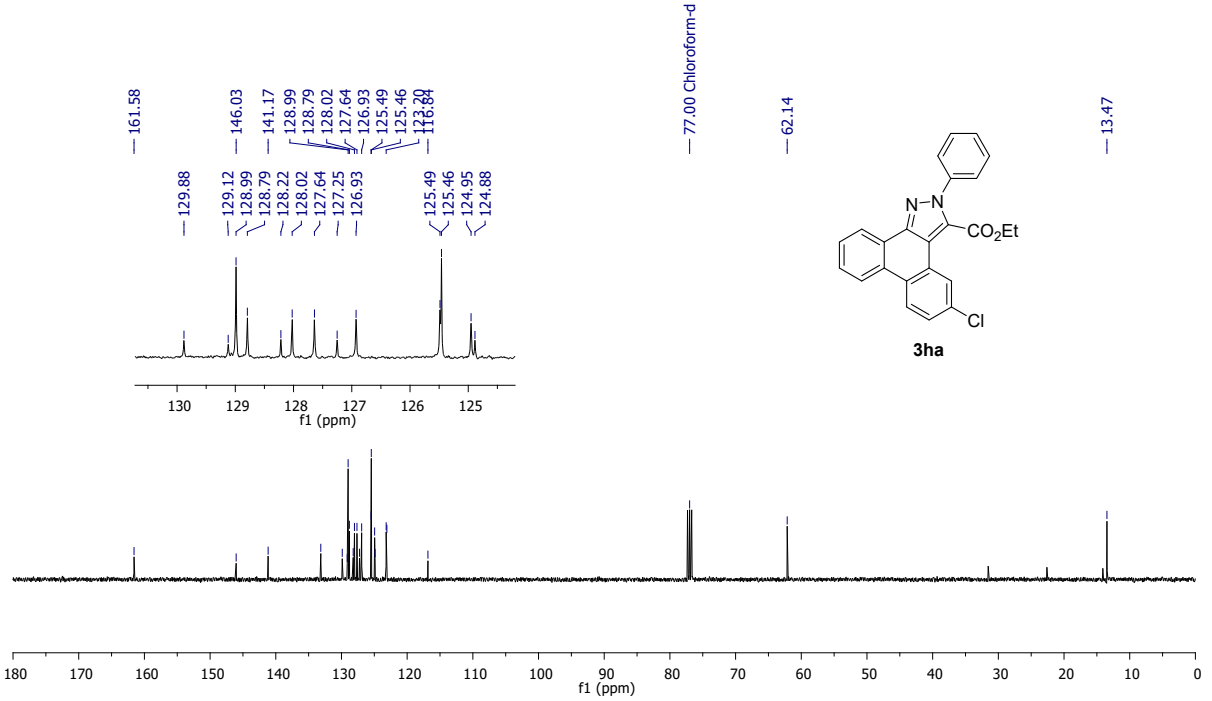
^{1}H NMR (600 MHz) spectrum of **3ga** in $CDCl_3$.



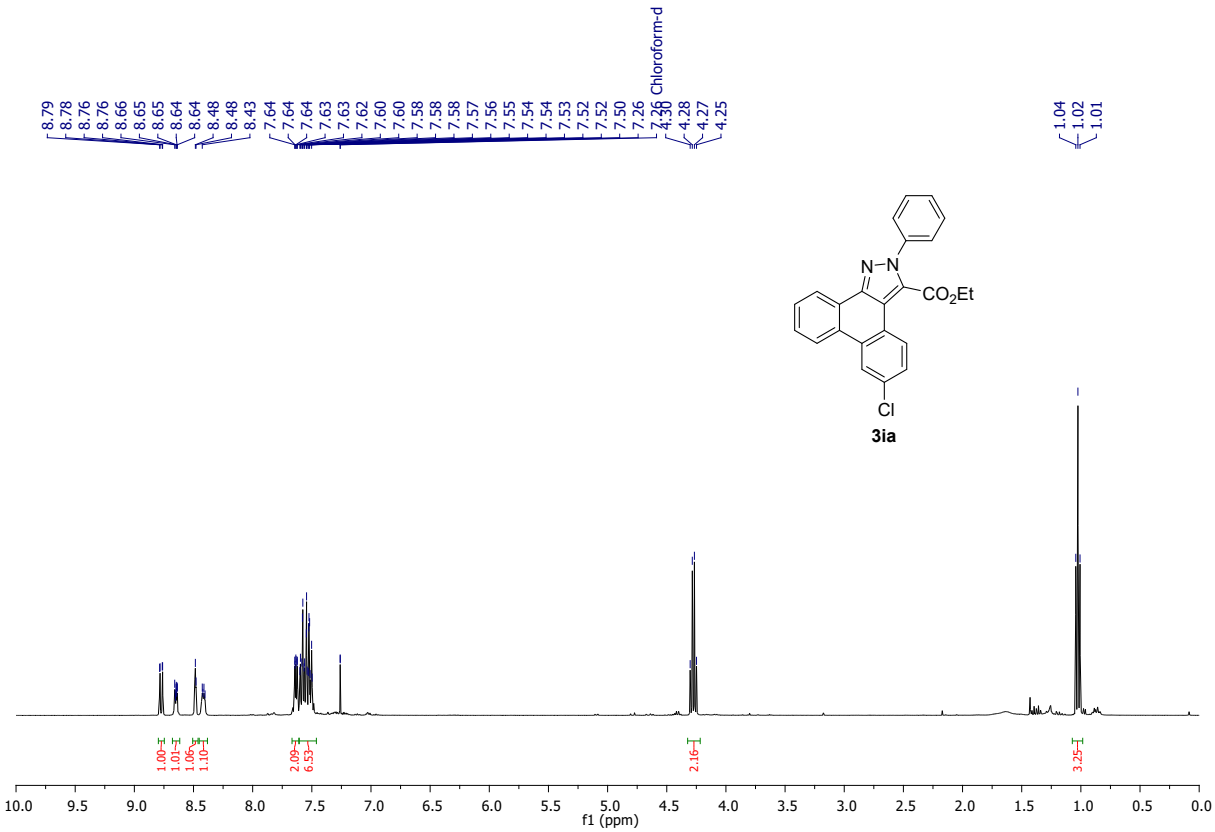
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ga** in $CDCl_3$.



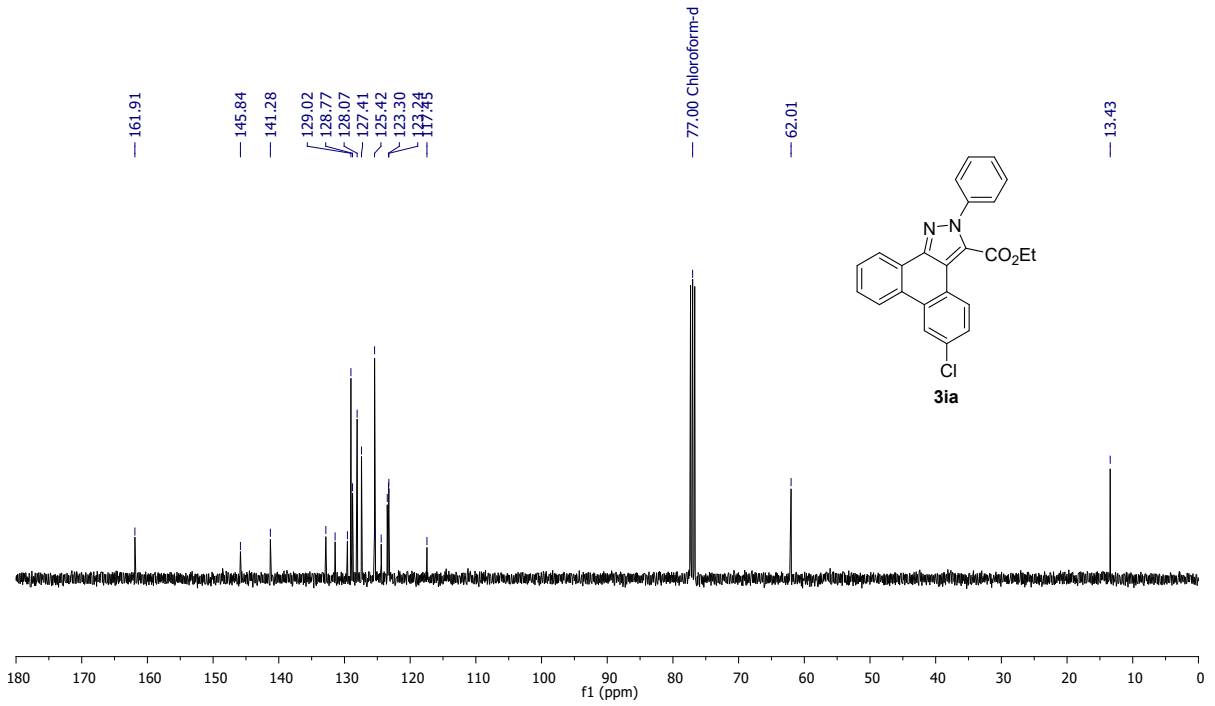
^{1}H NMR (600 MHz) spectrum of **3ha** in $CDCl_3$.



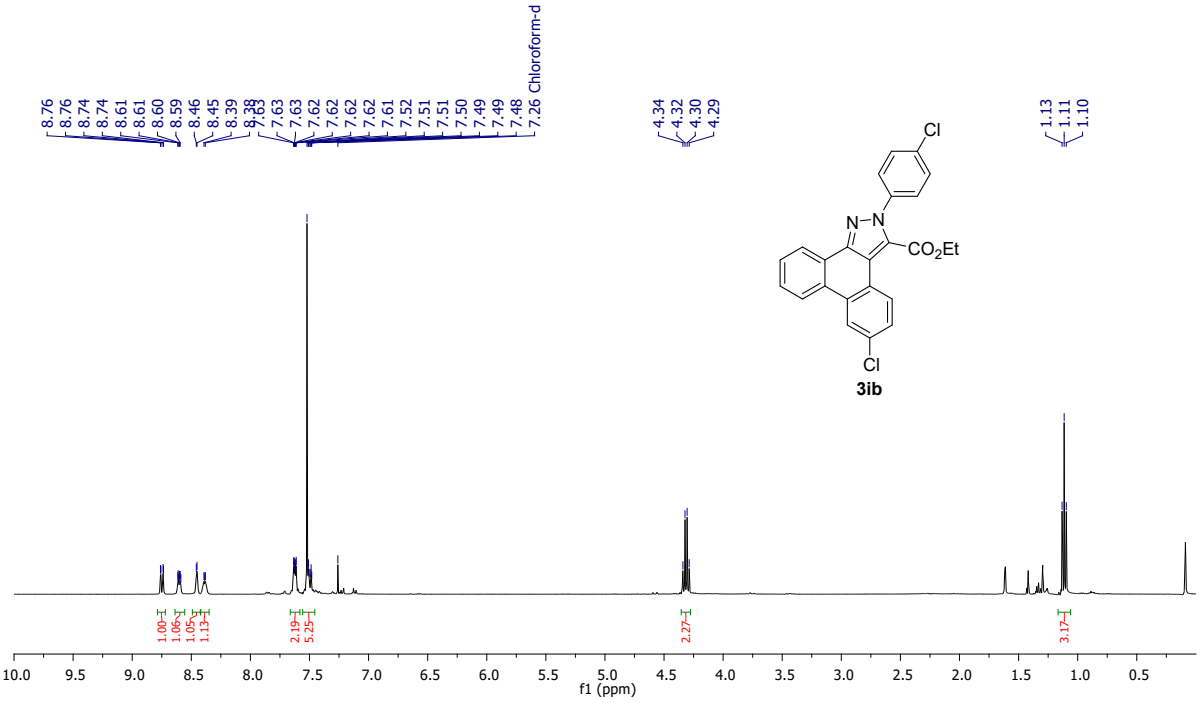
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ha** in $CDCl_3$.



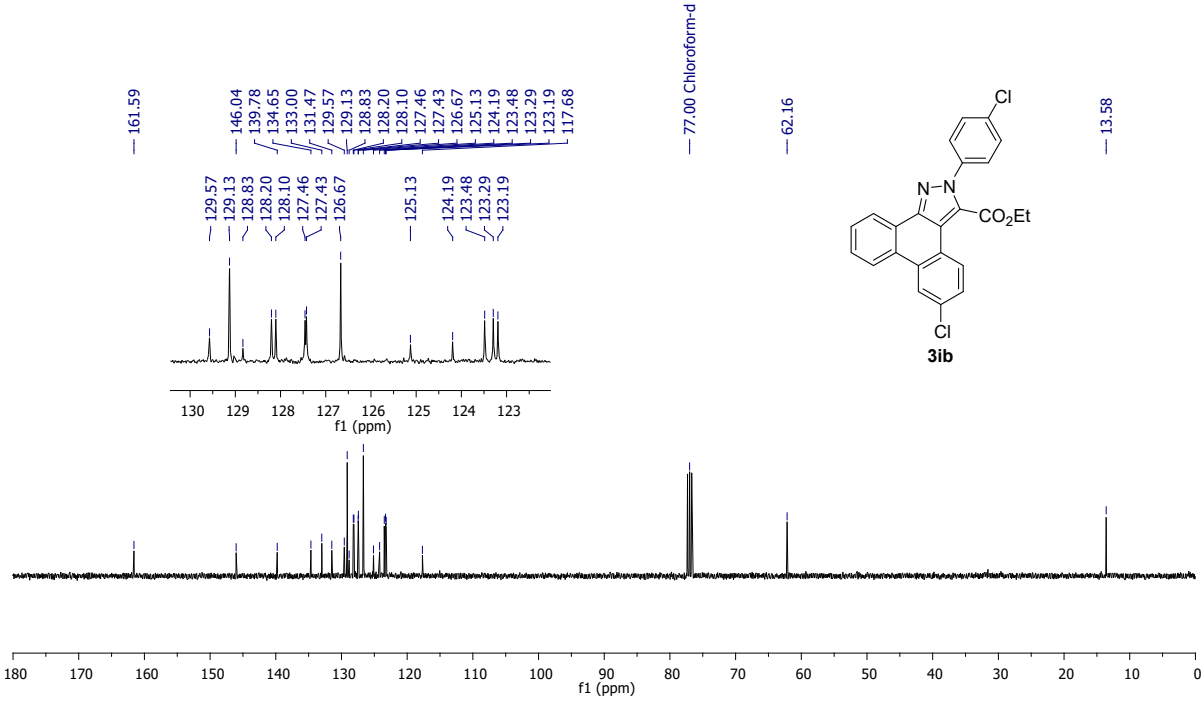
^{1}H NMR (400 MHz) spectrum of **3ia** in $CDCl_3$.



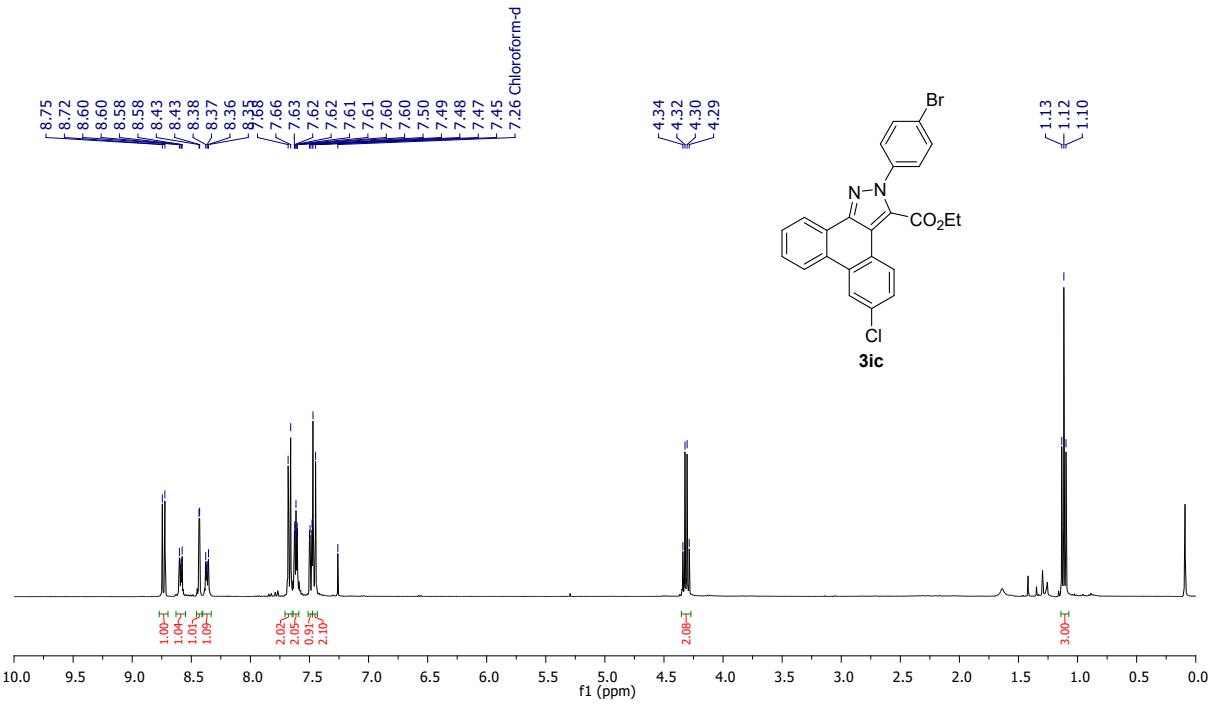
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ia** in $CDCl_3$.



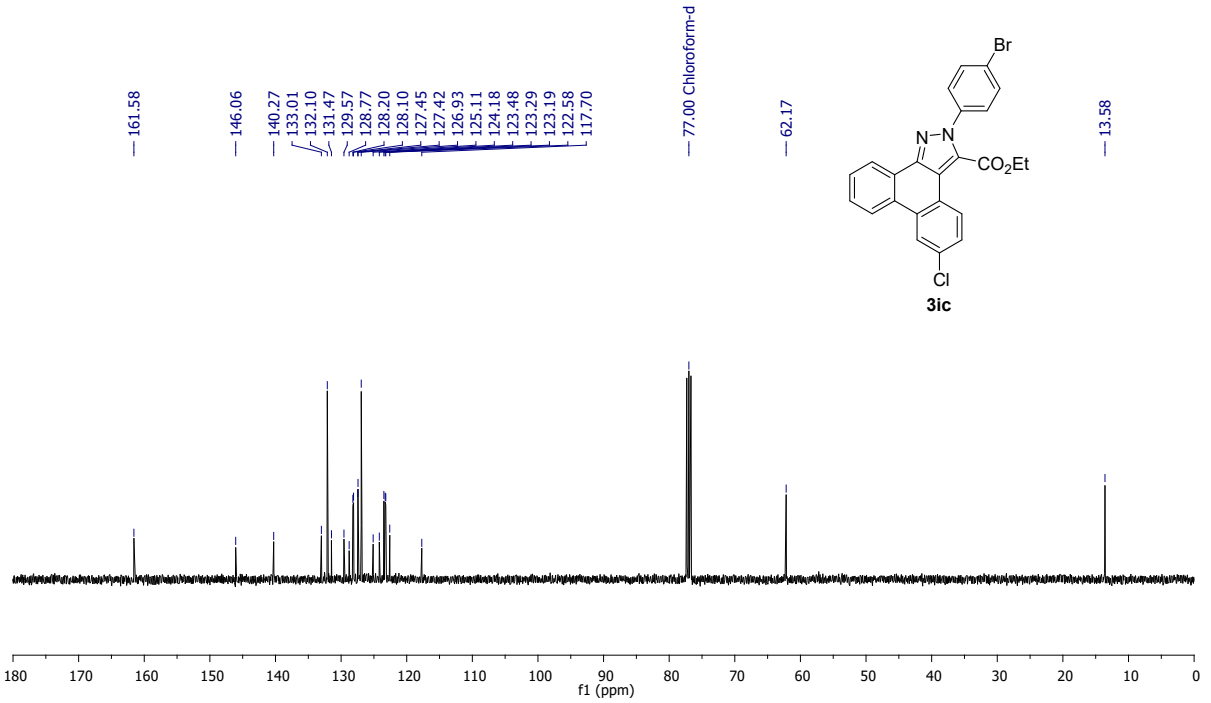
^{1}H NMR (400 MHz) spectrum of **3ib** in $CDCl_3$.



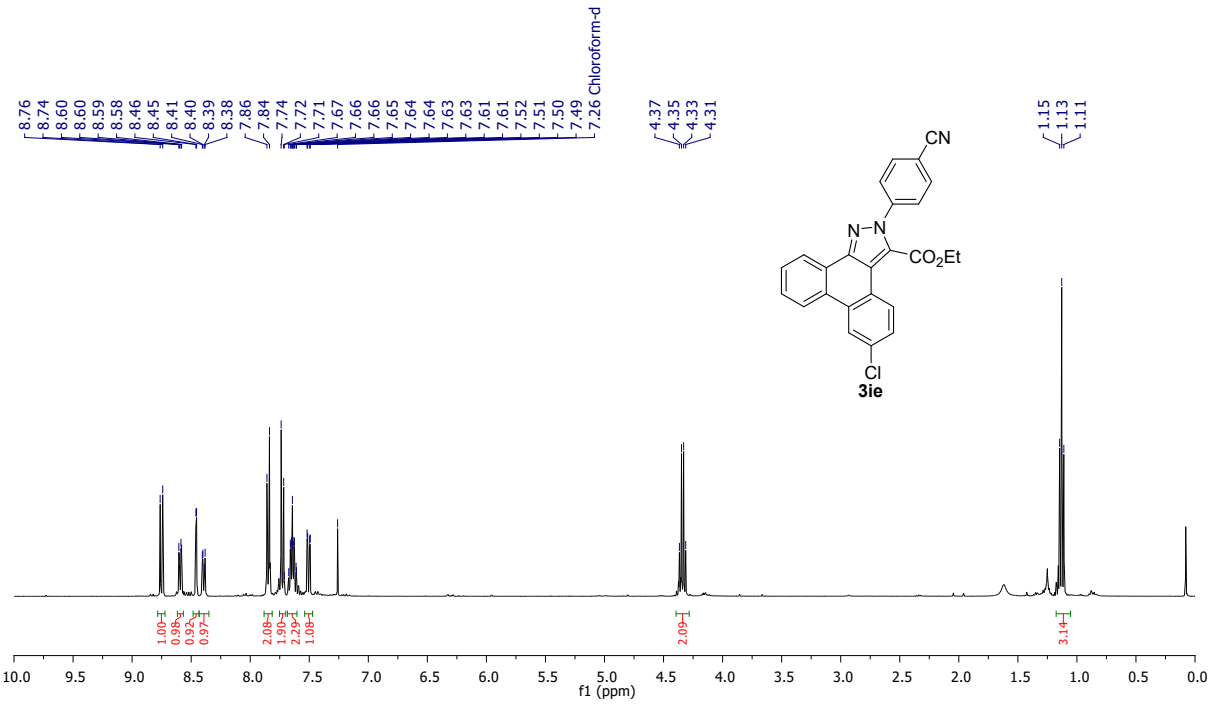
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ib** in $CDCl_3$.



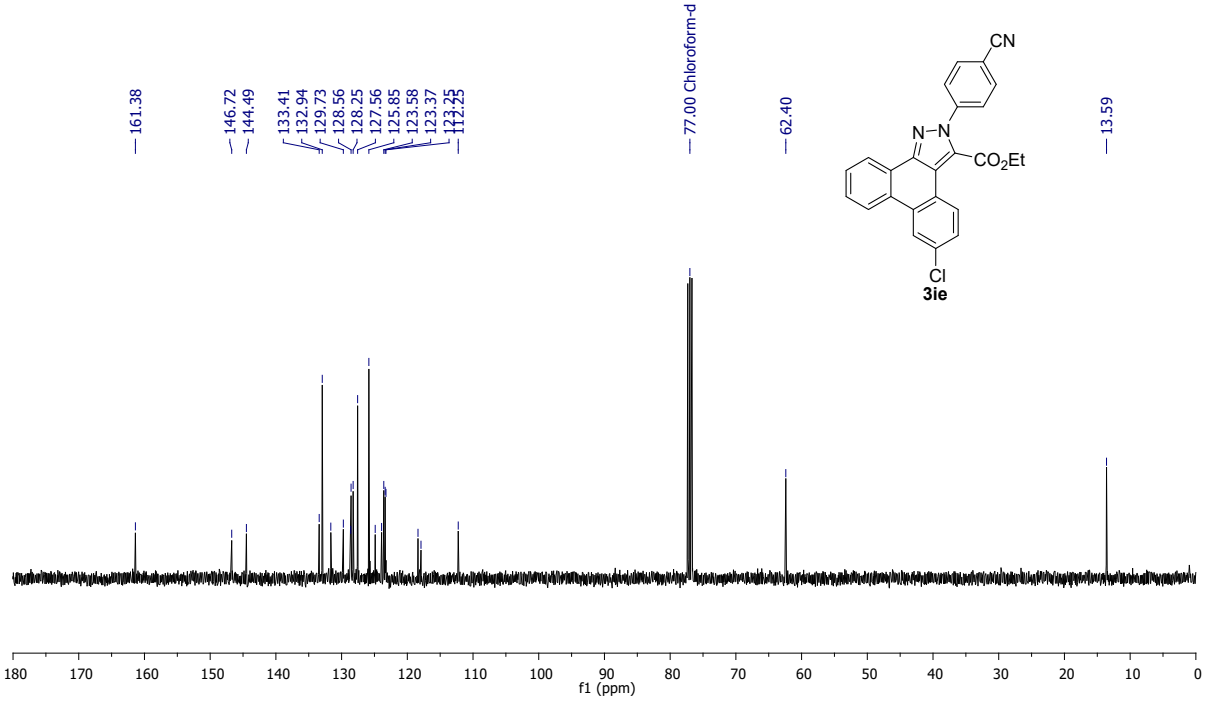
^{1}H NMR (400 MHz) spectrum of **3ic** in $CDCl_3$.



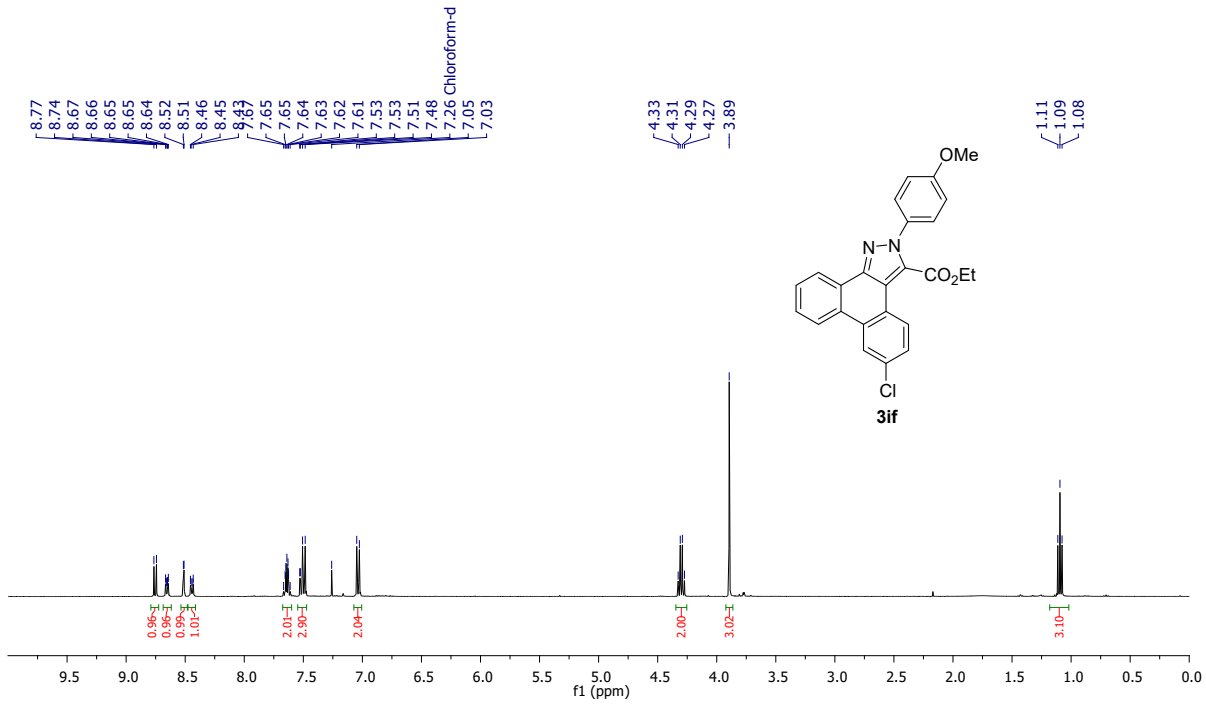
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ic** in $CDCl_3$.



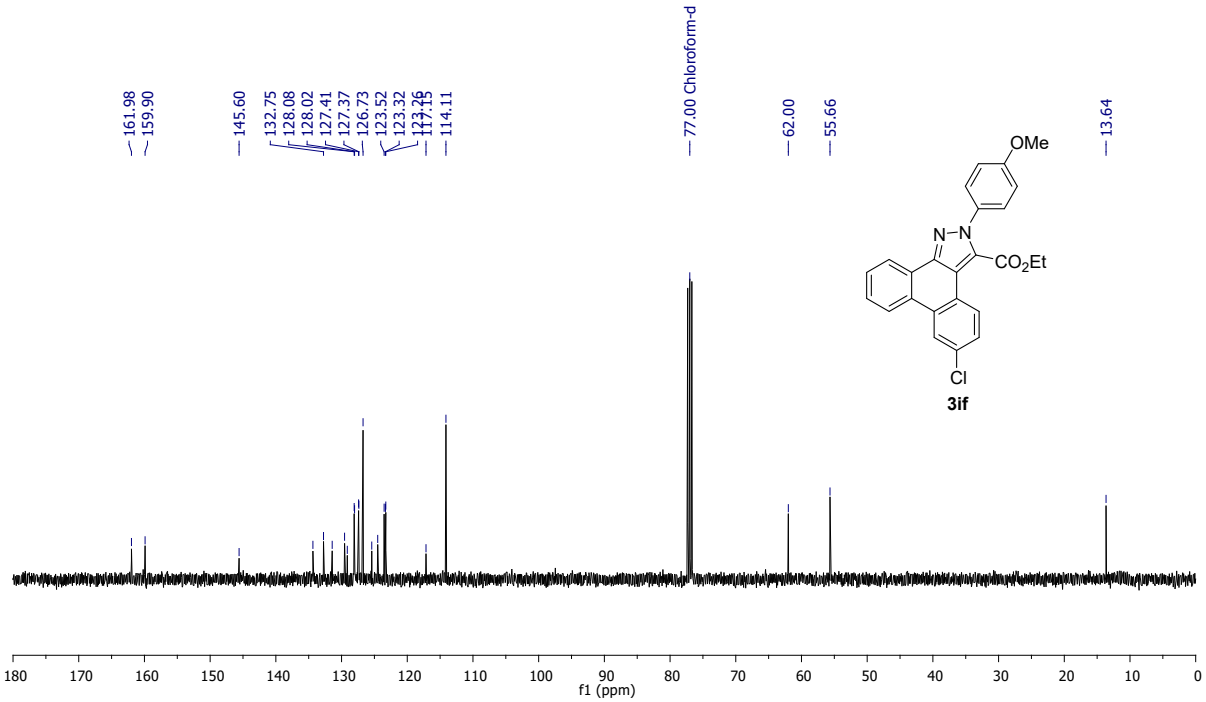
^{1}H NMR (400 MHz) spectrum of **3ie** in $CDCl_3$.



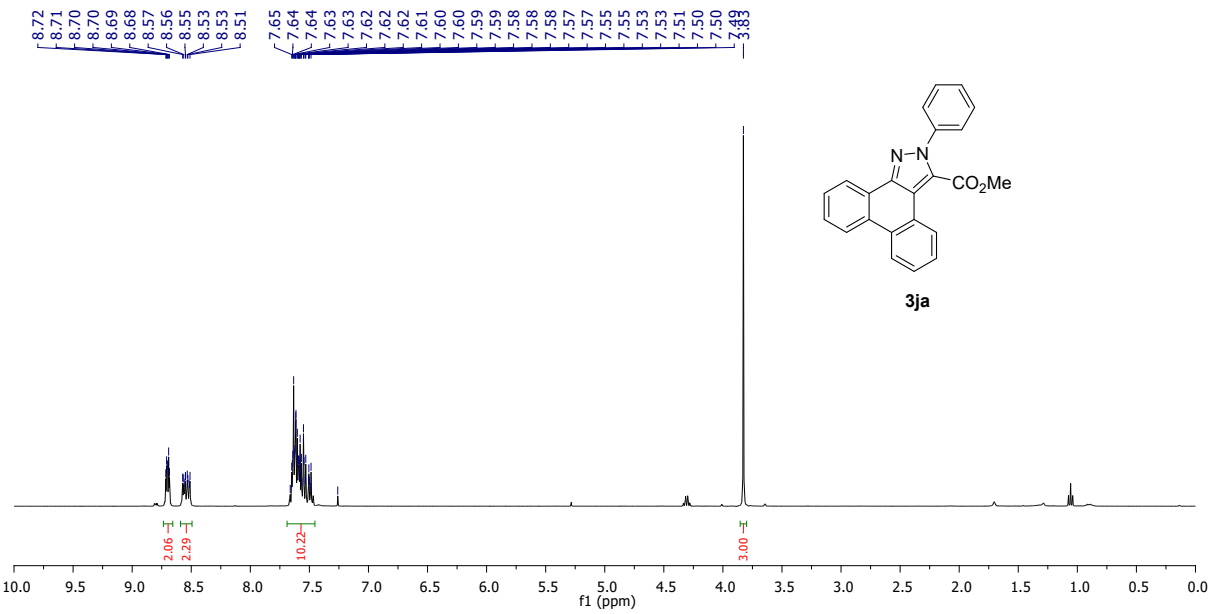
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ie** in $CDCl_3$.



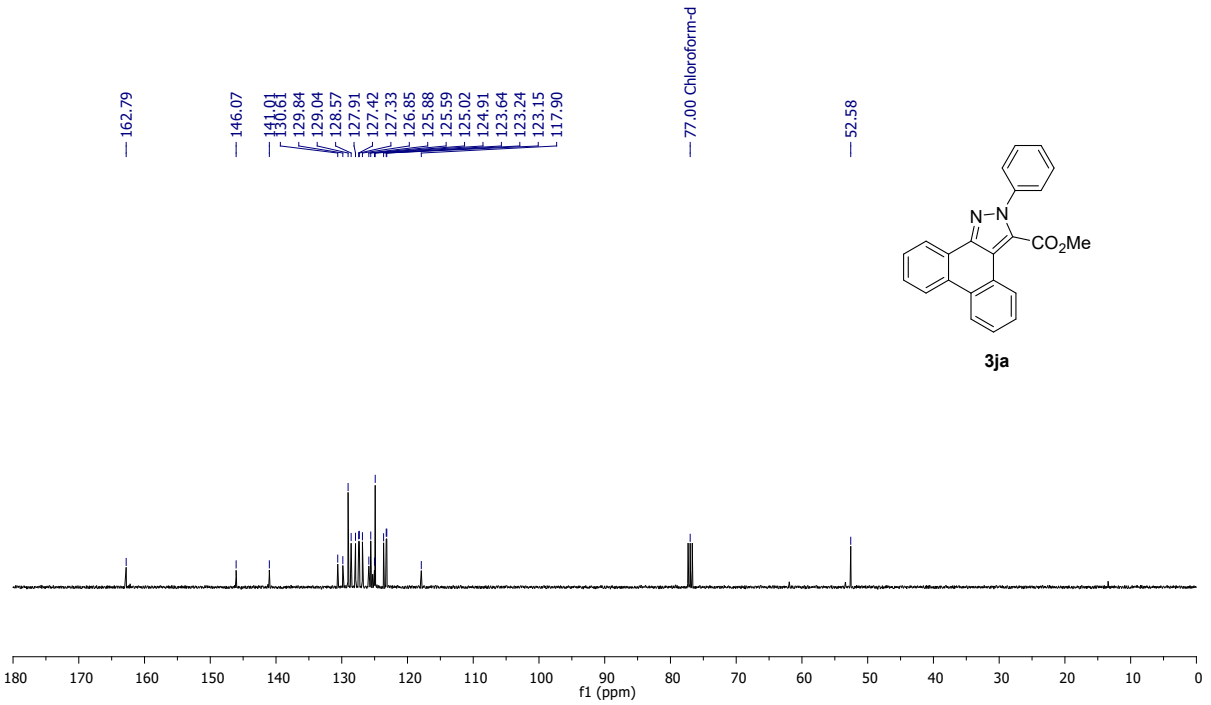
^{1}H NMR (400 MHz) spectrum of **3if** in $CDCl_3$.



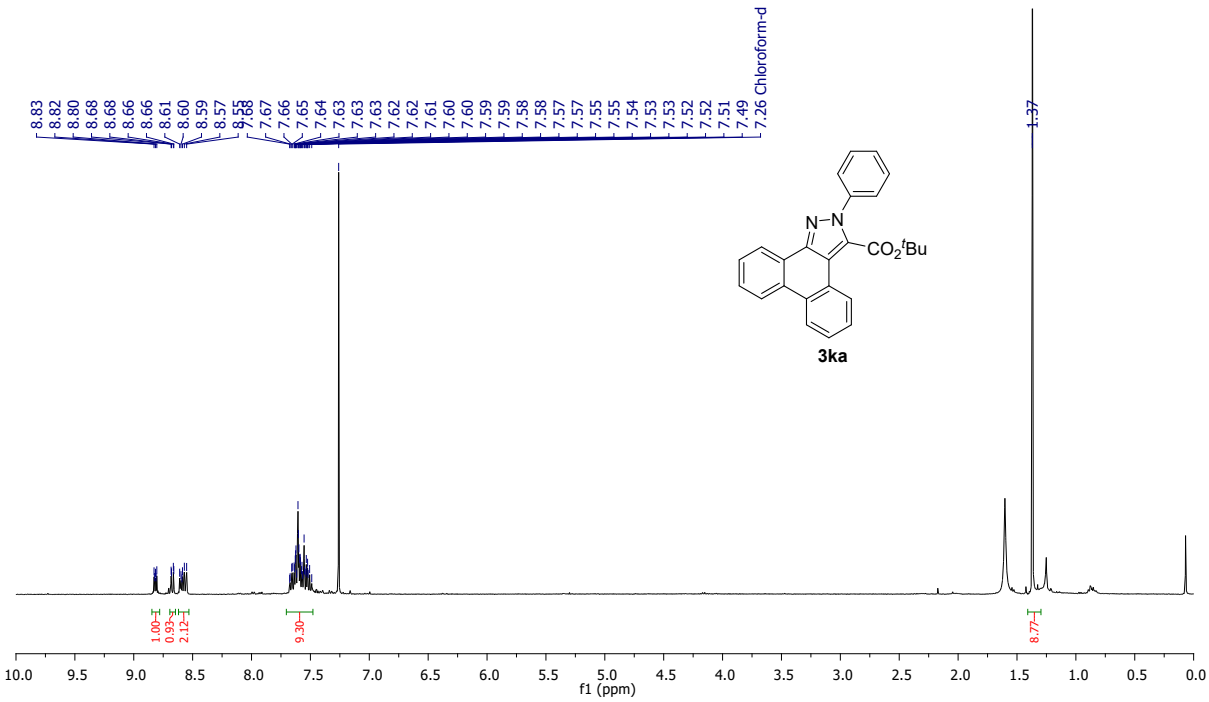
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3if** in $CDCl_3$.



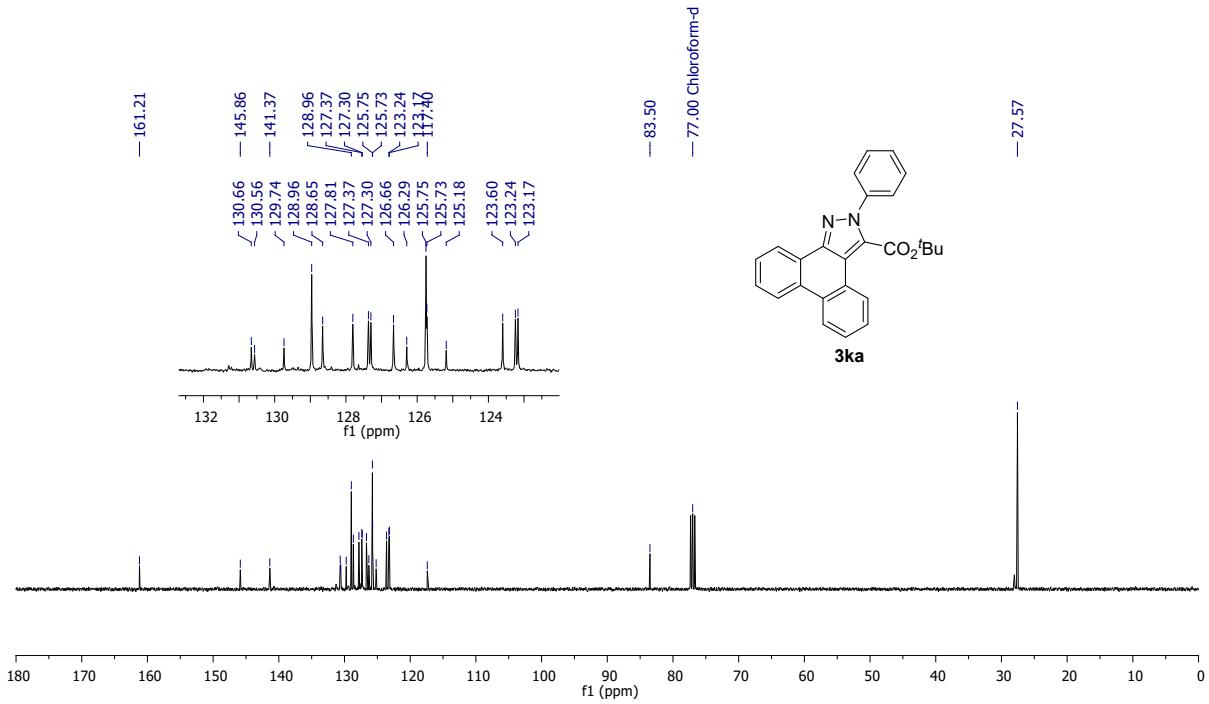
^{1}H NMR (400 MHz) spectrum of **3ja** in $CDCl_3$.



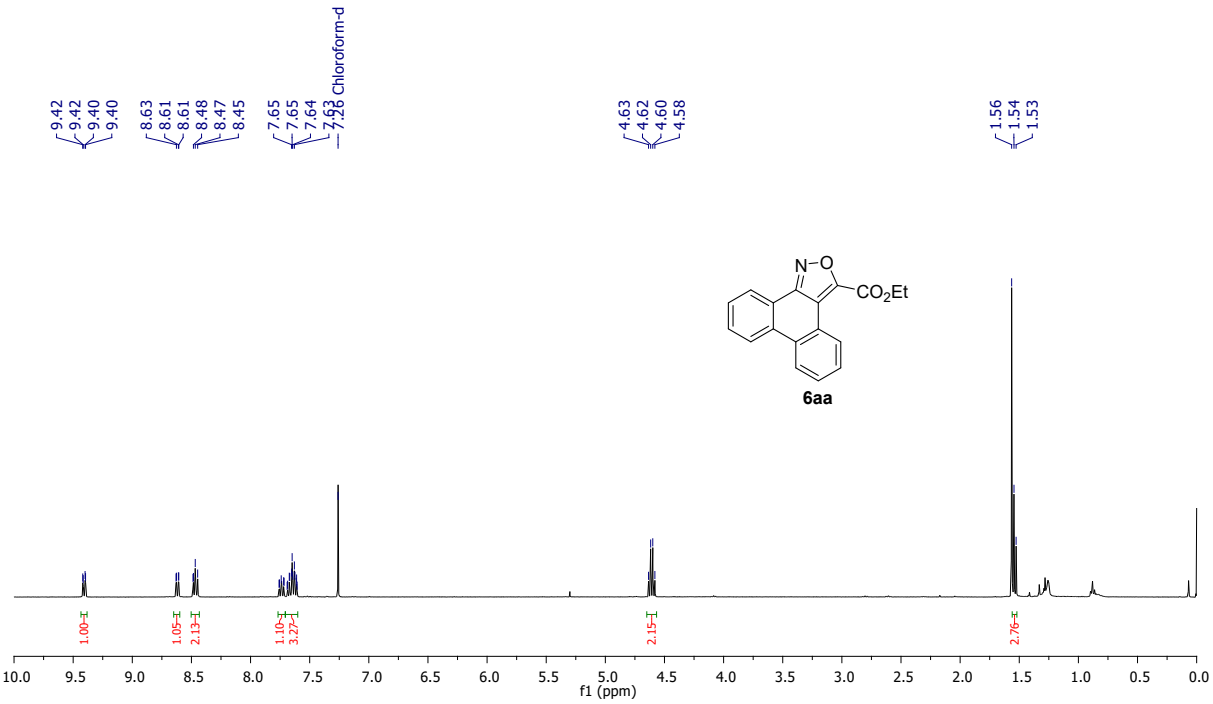
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ja** in $CDCl_3$.



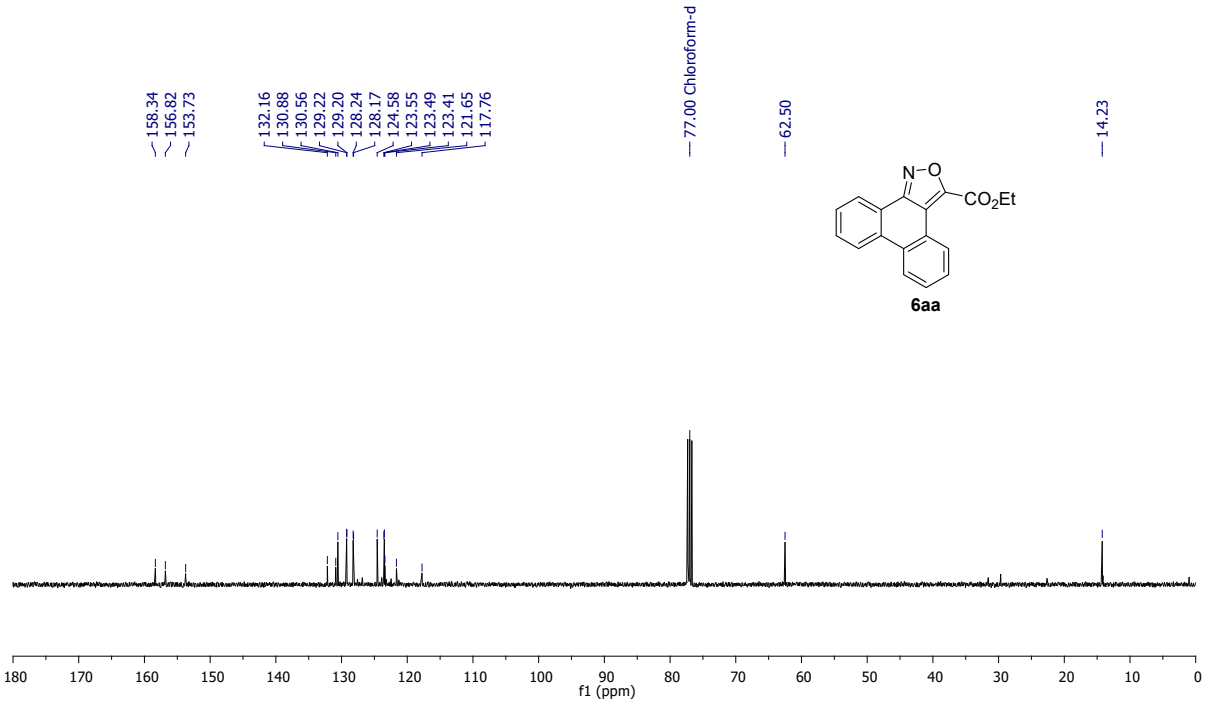
^{1}H NMR (400 MHz) spectrum of **3ka** in $CDCl_3$.



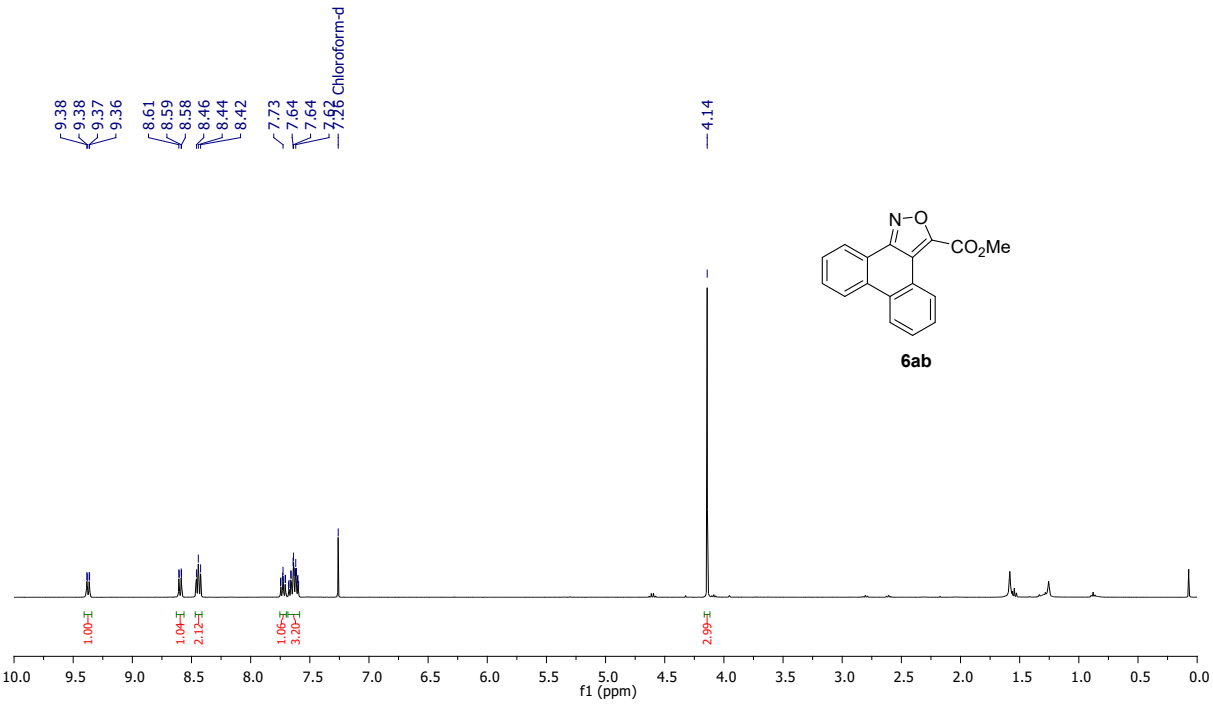
^{13}C{^{1}H} NMR (101 MHz) spectrum of **3ka** in $CDCl_3$.



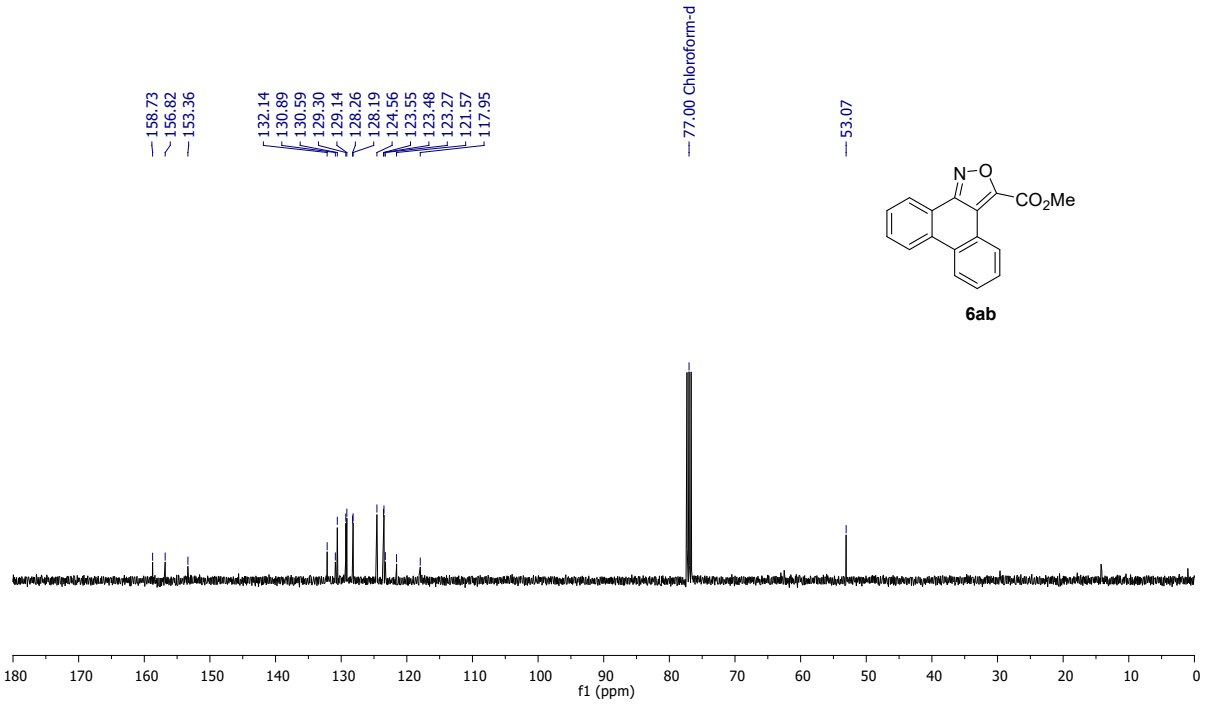
^{1}H NMR (400 MHz) spectrum of **6aa** in $CDCl_3$.



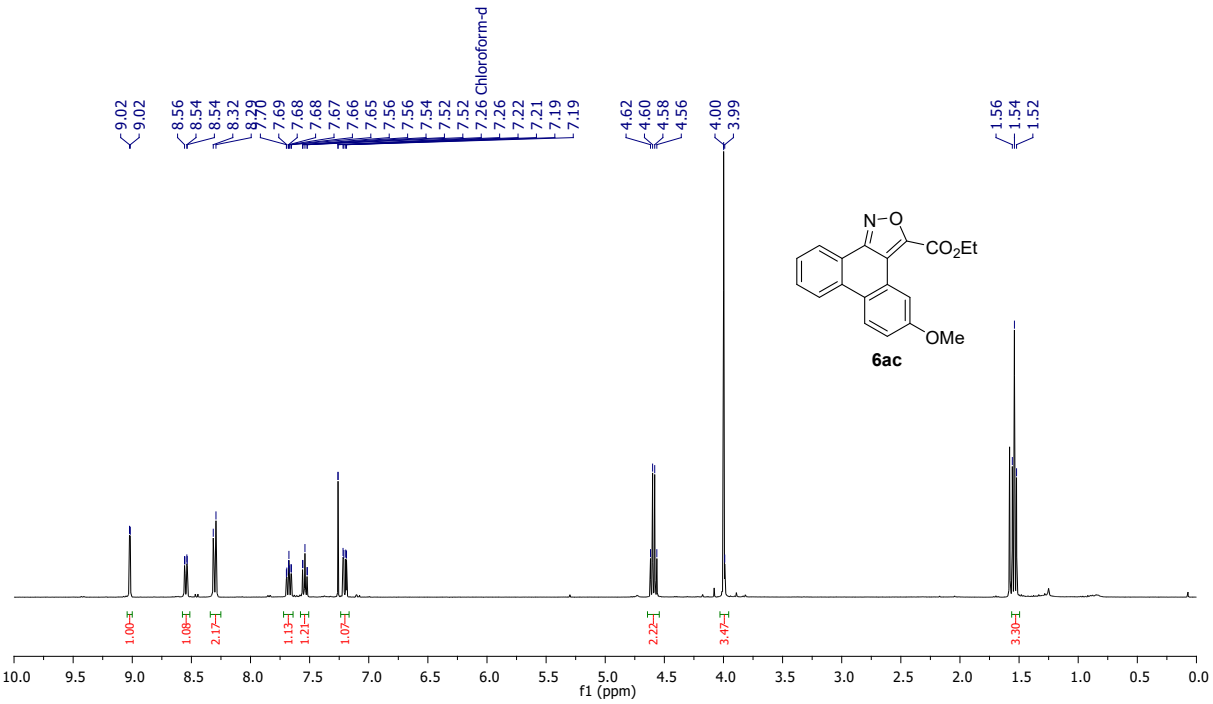
^{13}C{^{1}H} NMR (101 MHz) spectrum of **6aa** in $CDCl_3$.



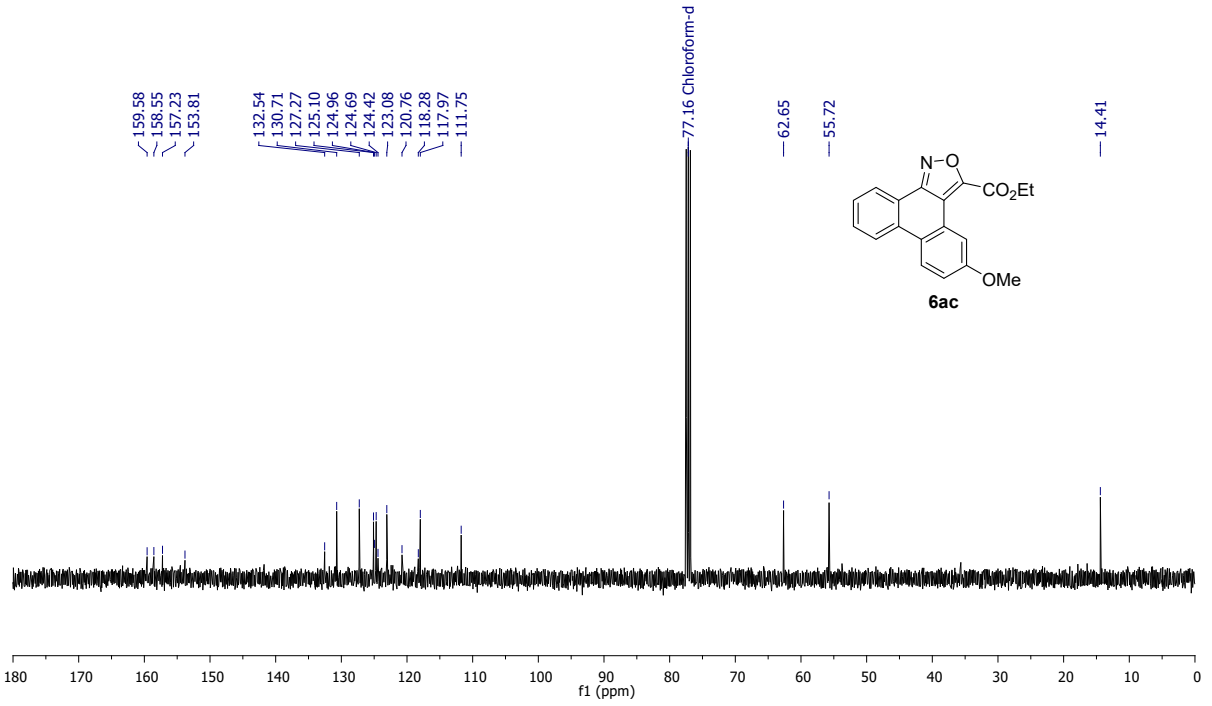
^{1}H NMR (400 MHz) spectrum of **6ab** in $CDCl_3$.



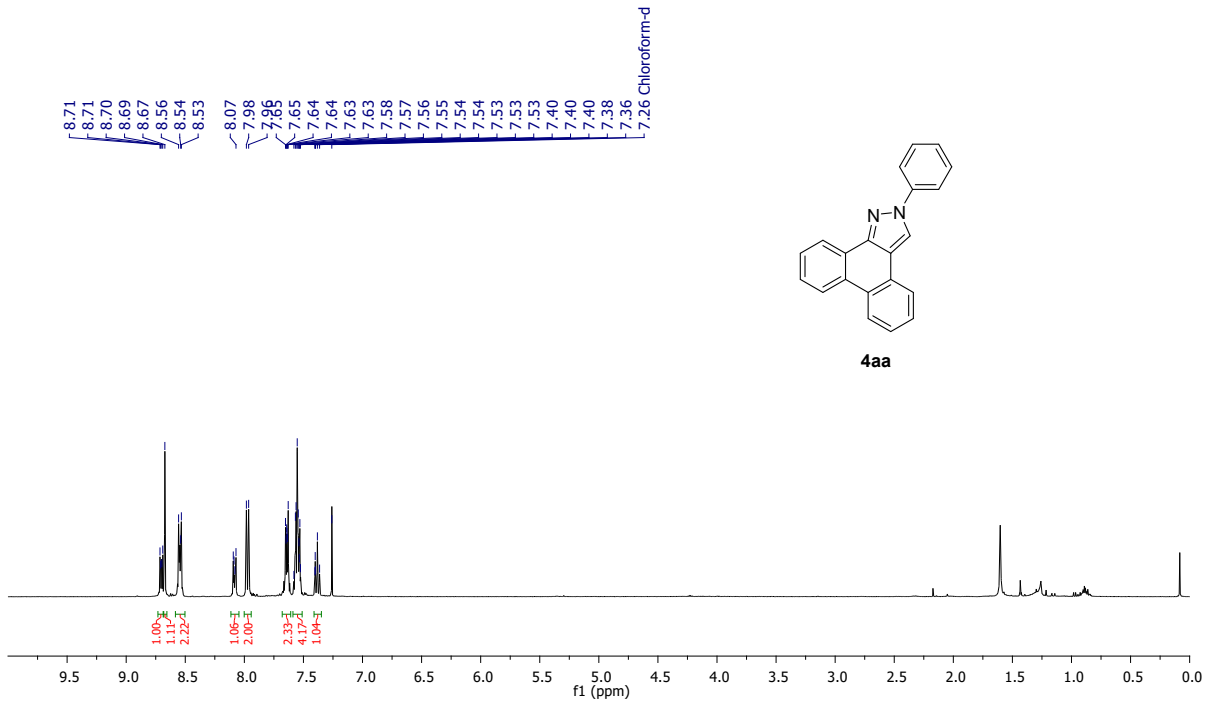
^{13}C{^{1}H} NMR (101 MHz) spectrum of **6ab** in $CDCl_3$.



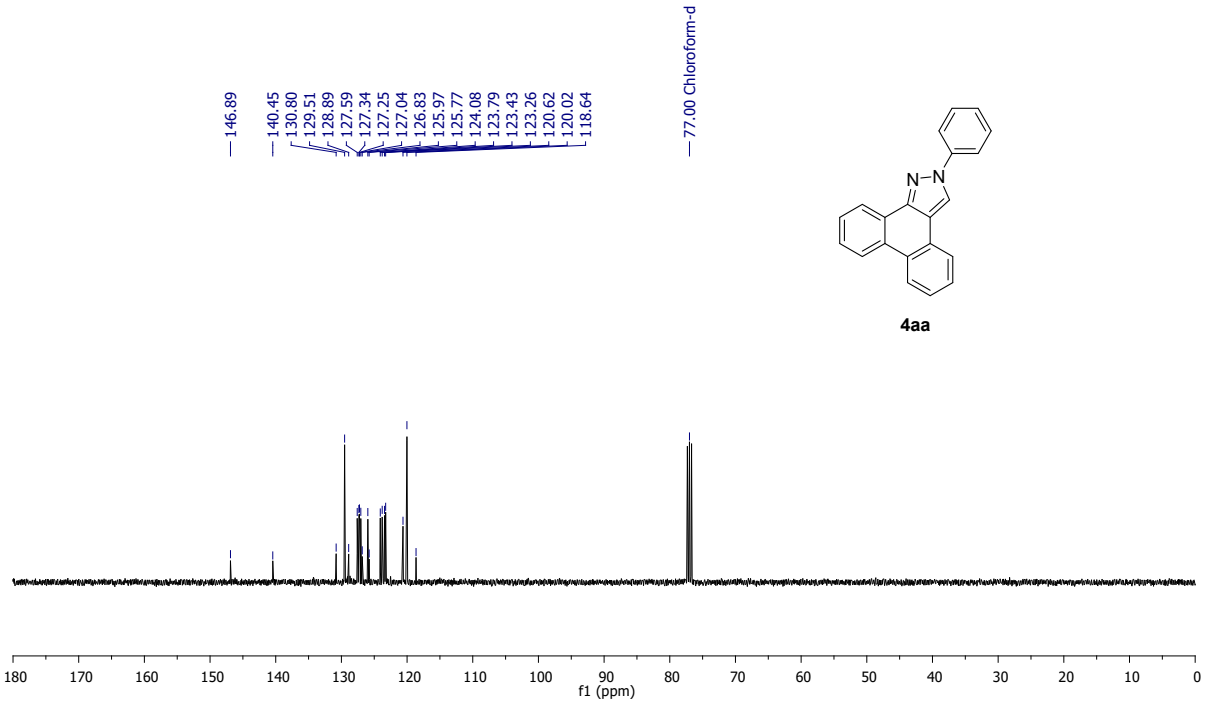
^{1}H NMR (400 MHz) spectrum of **6ac** in $CDCl_3$.



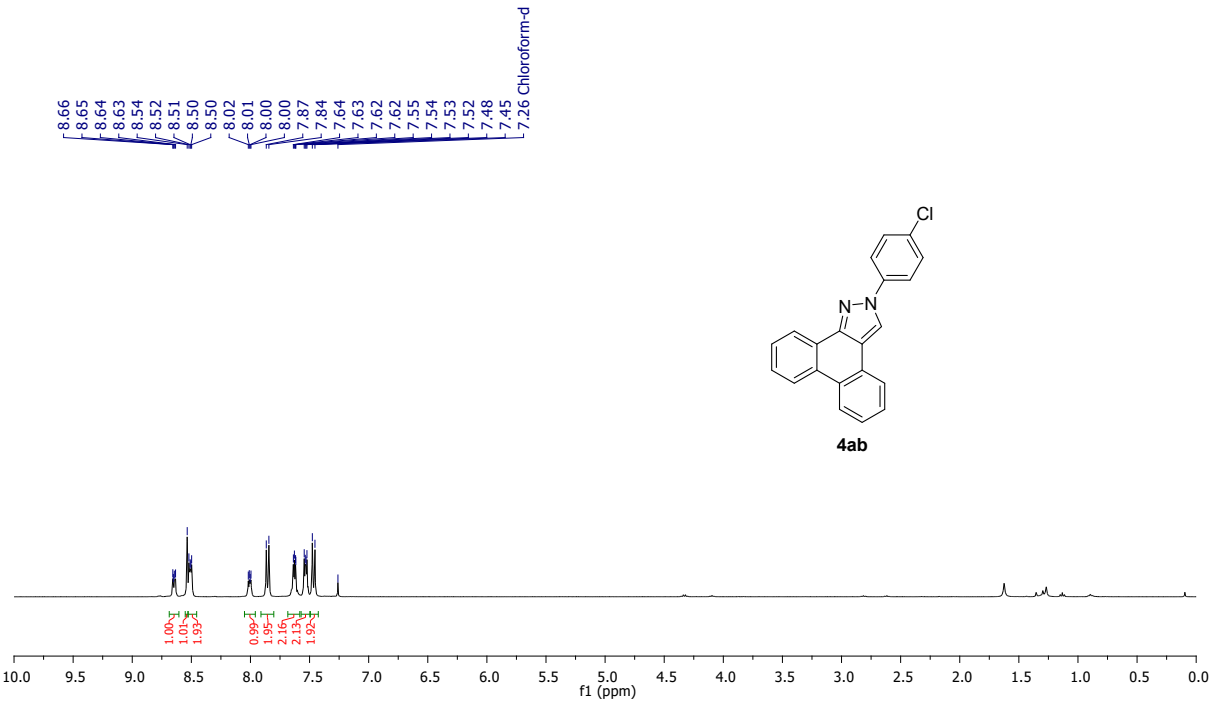
^{13}C{^{1}H} NMR (101 MHz) spectrum of **6ac** in $CDCl_3$.



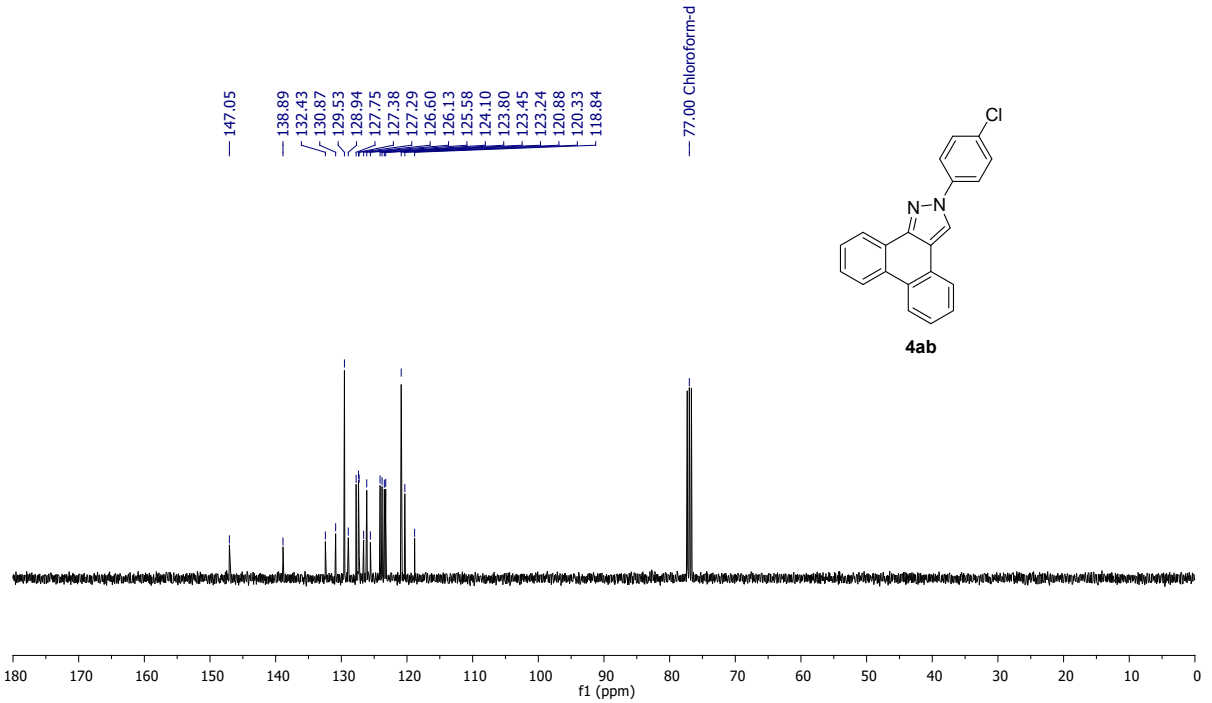
^{1}H NMR (400 MHz) spectrum of **4aa** in $CDCl_3$.



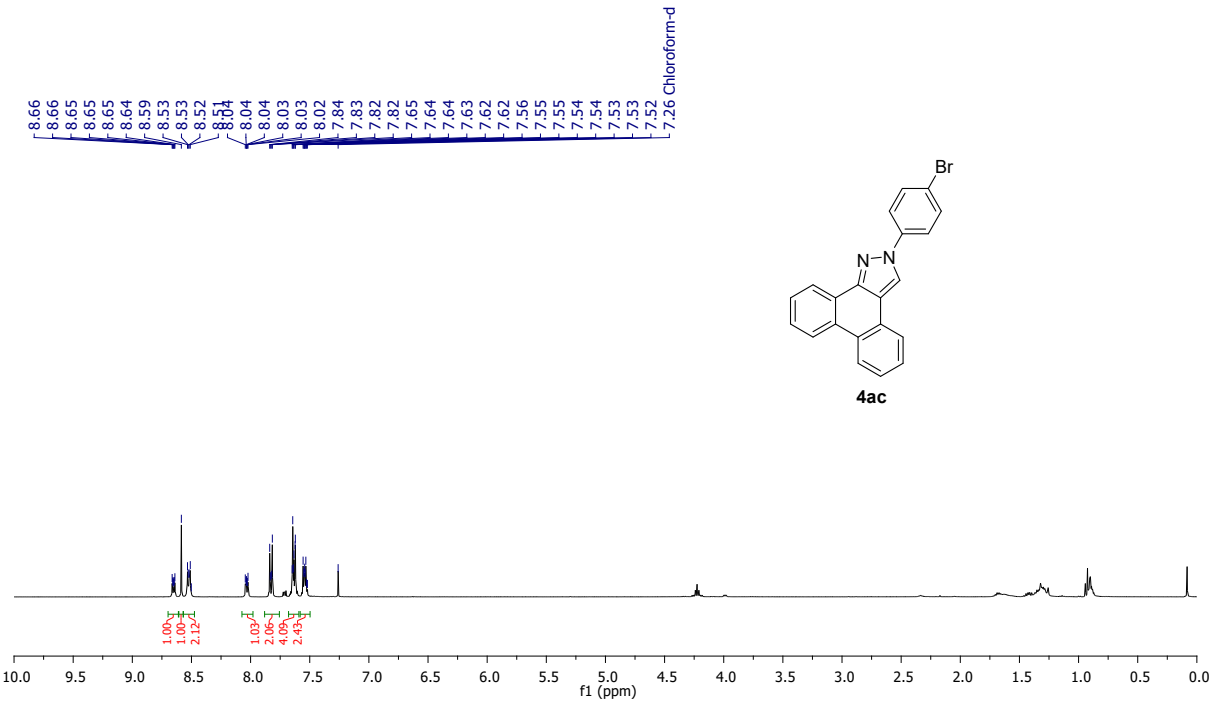
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4aa** in $CDCl_3$.



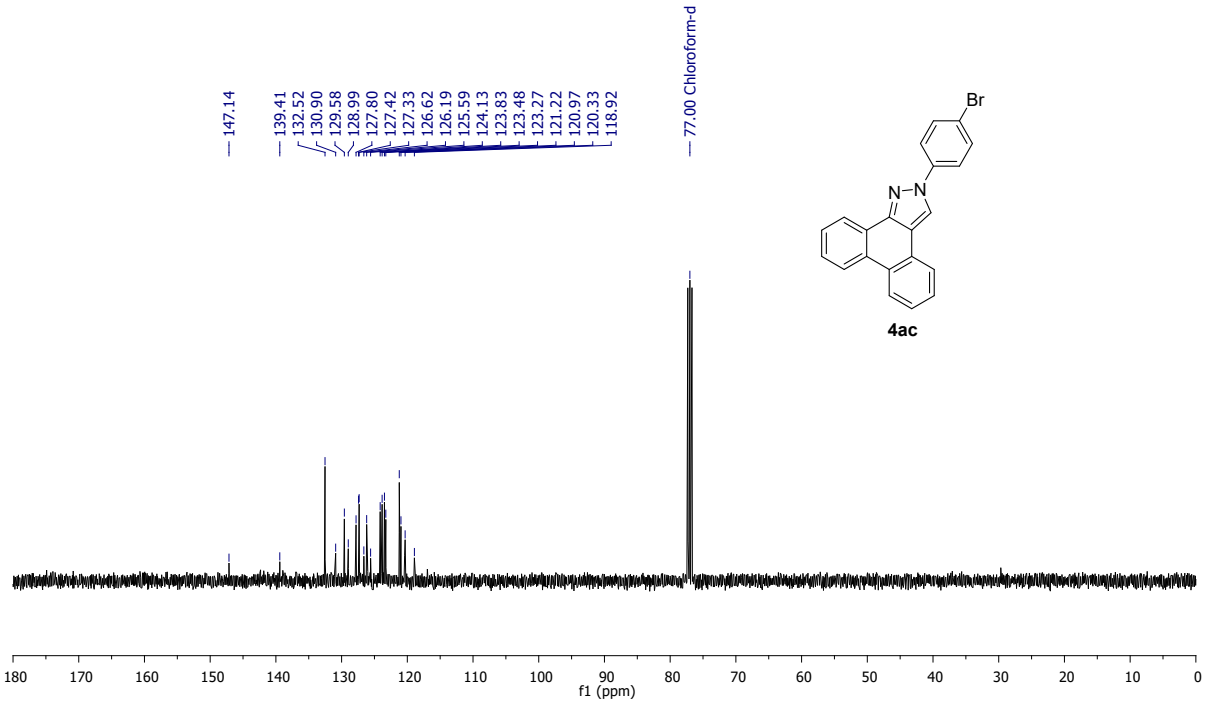
^{1}H NMR (400 MHz) spectrum of **4ab** in $CDCl_3$.



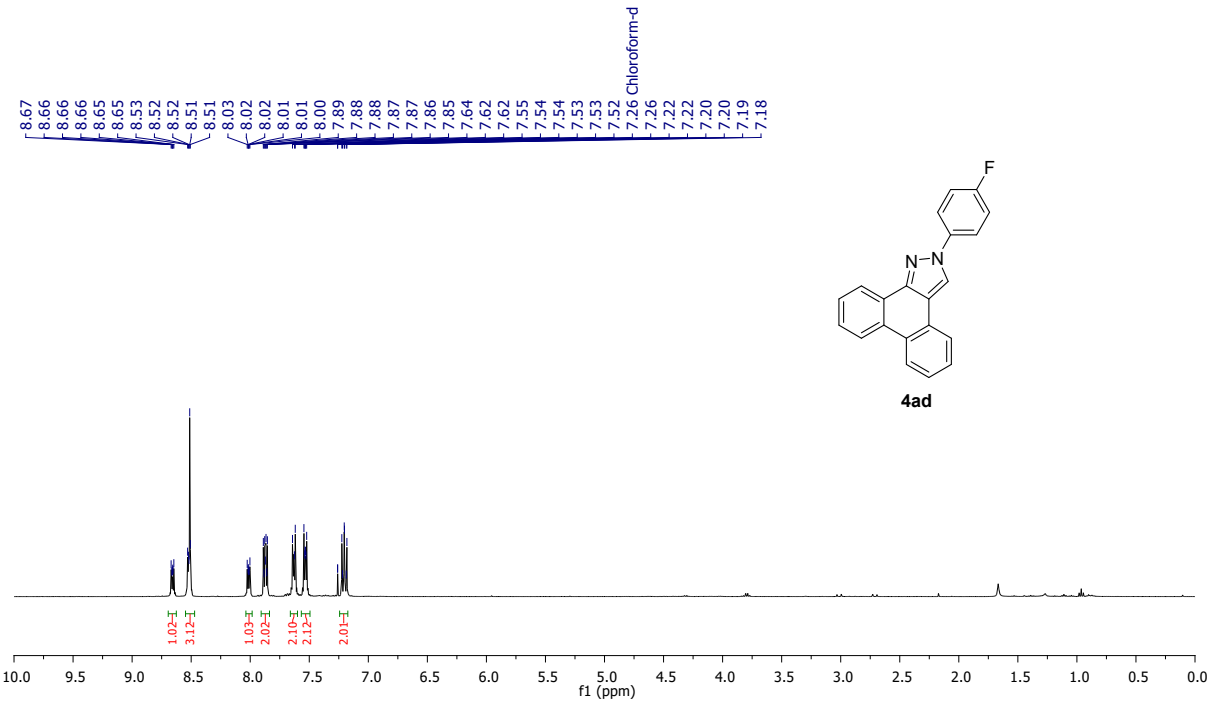
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ab** in $CDCl_3$.



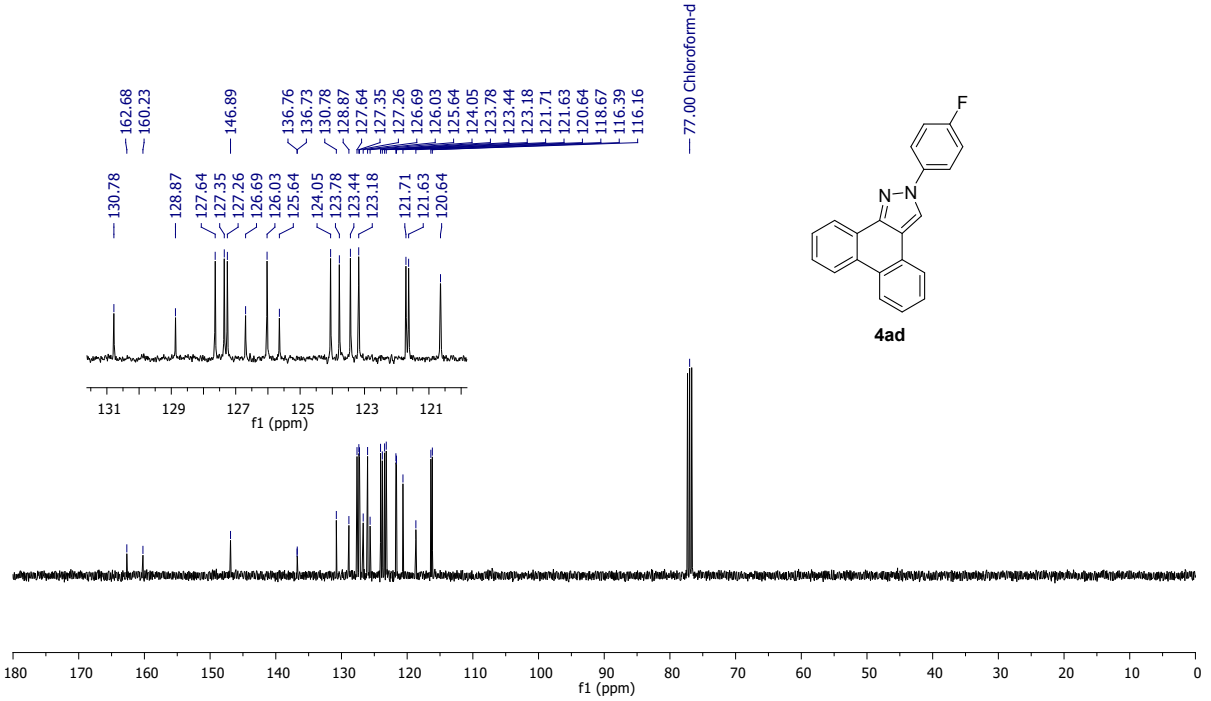
^{1}H NMR (400 MHz) spectrum of **4ac** in $CDCl_3$.



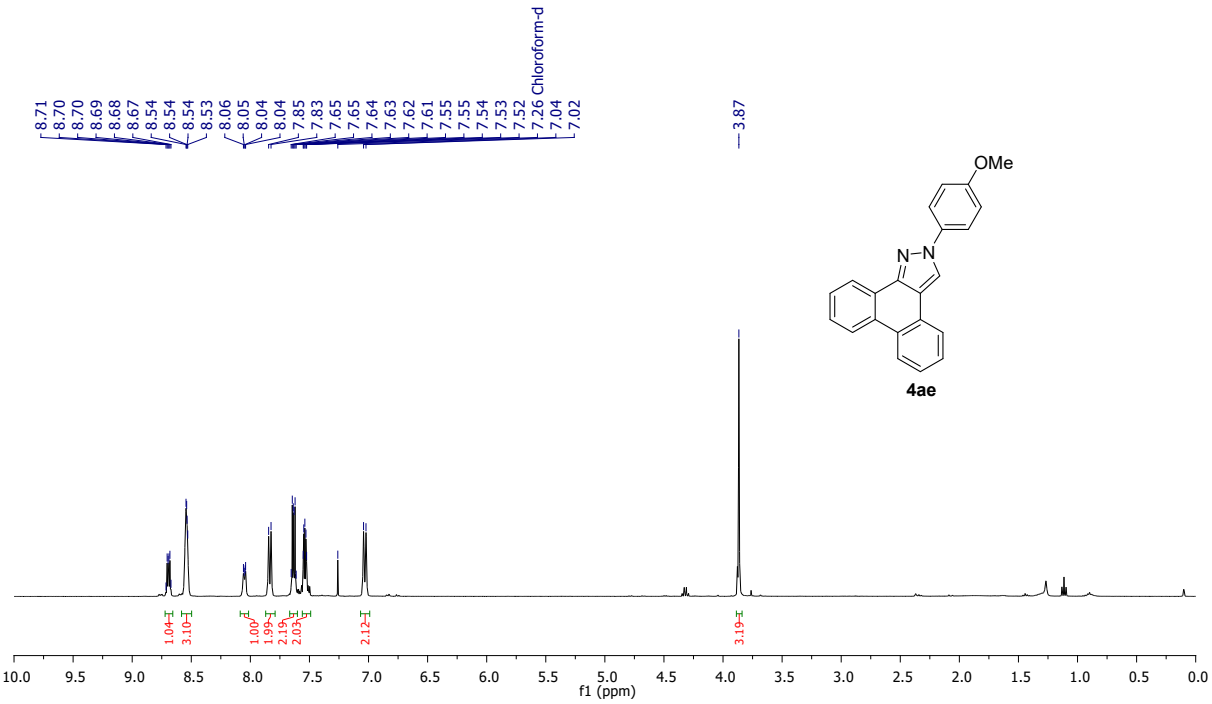
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ac** in $CDCl_3$.



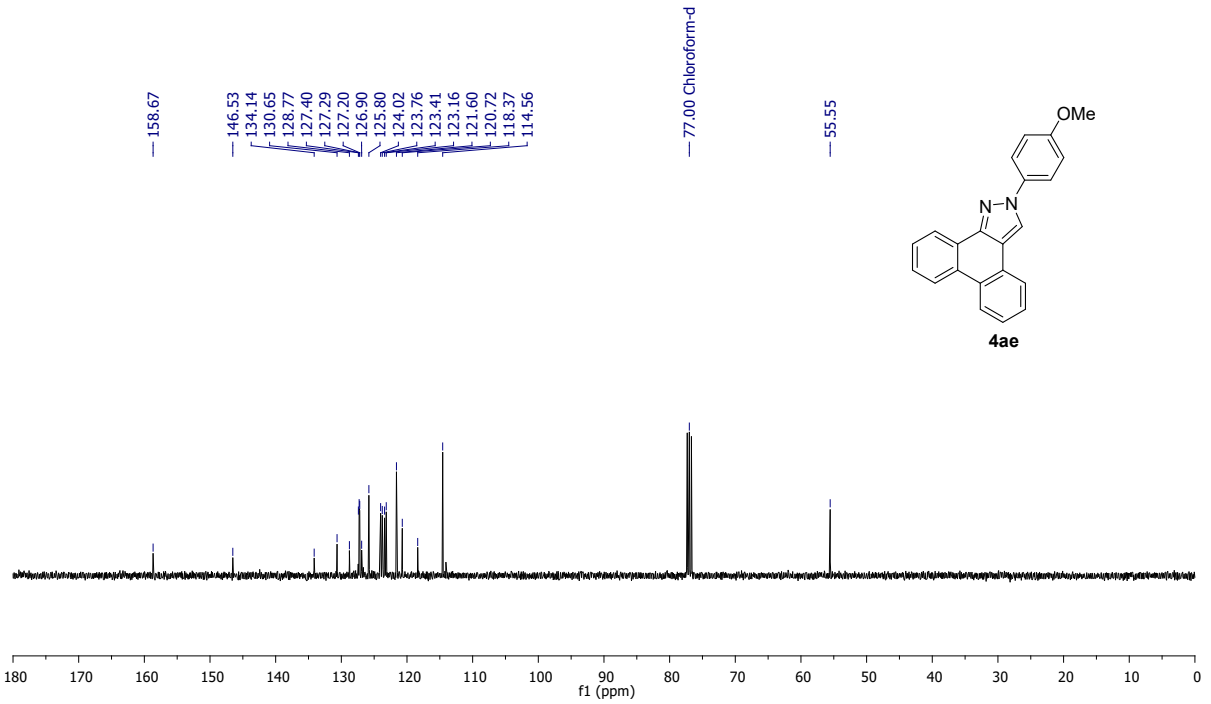
^{1}H NMR (400 MHz) spectrum of **4ad** in $CDCl_3$.



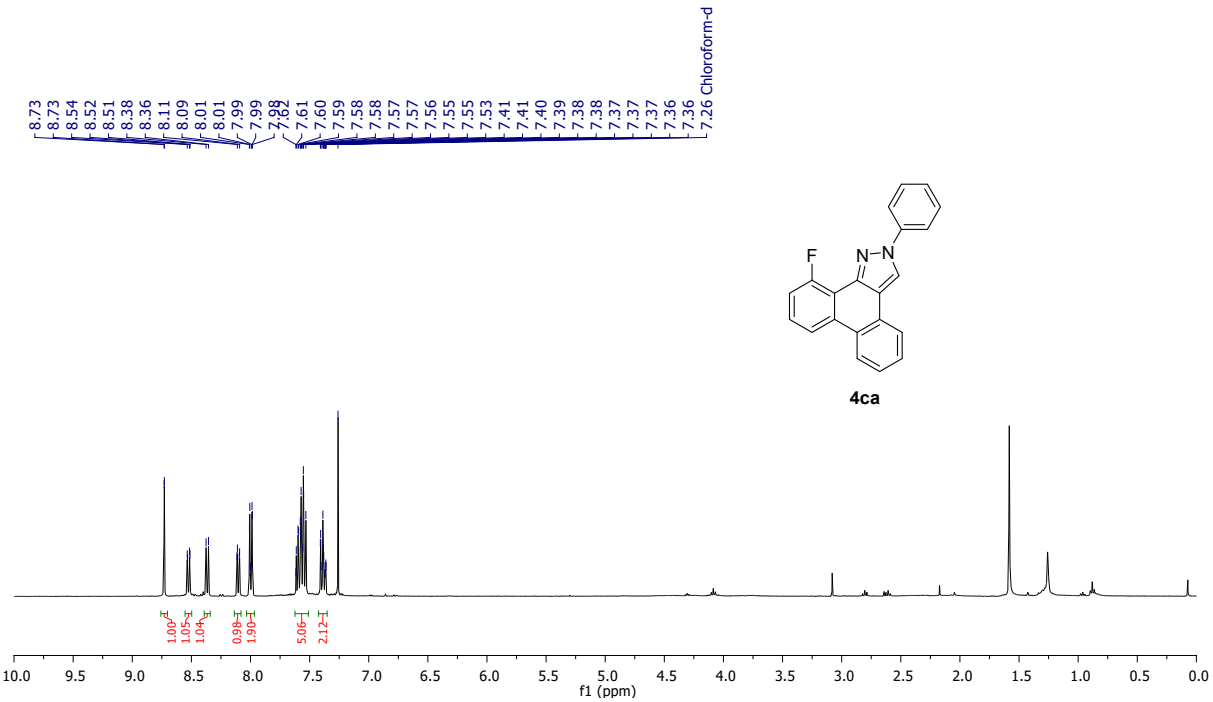
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ad** in $CDCl_3$.



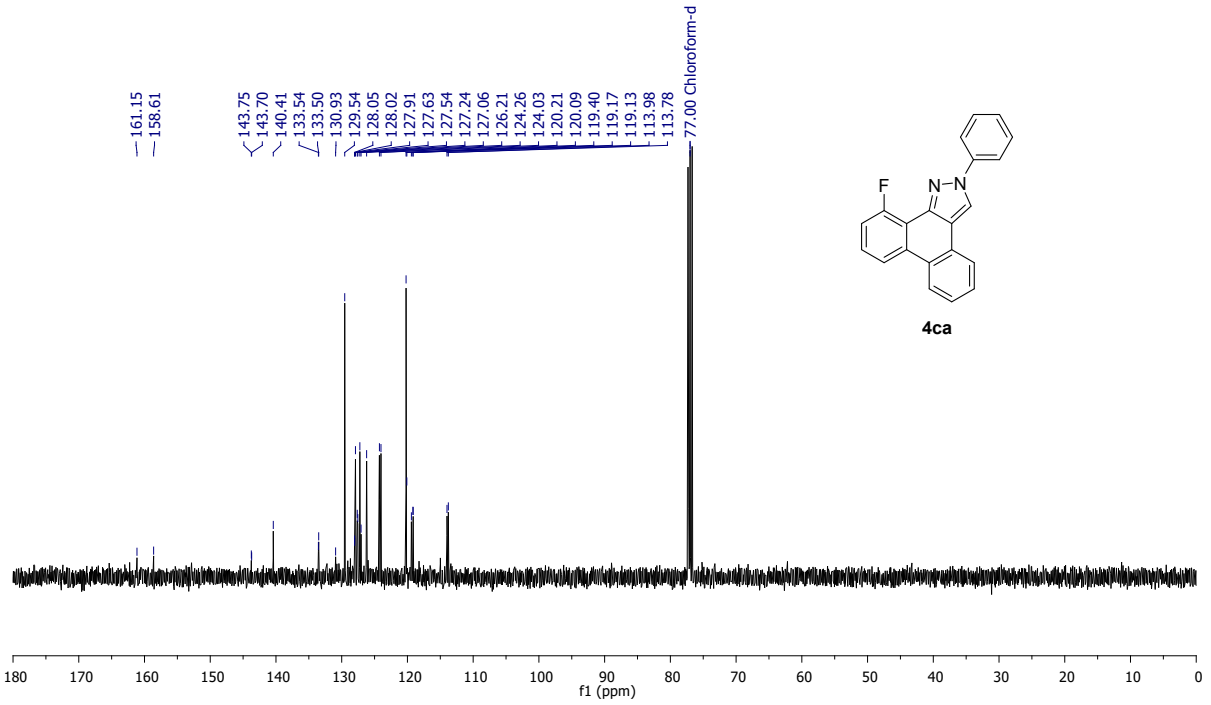
^{1}H NMR (400 MHz) spectrum of **4ae** in $CDCl_3$.



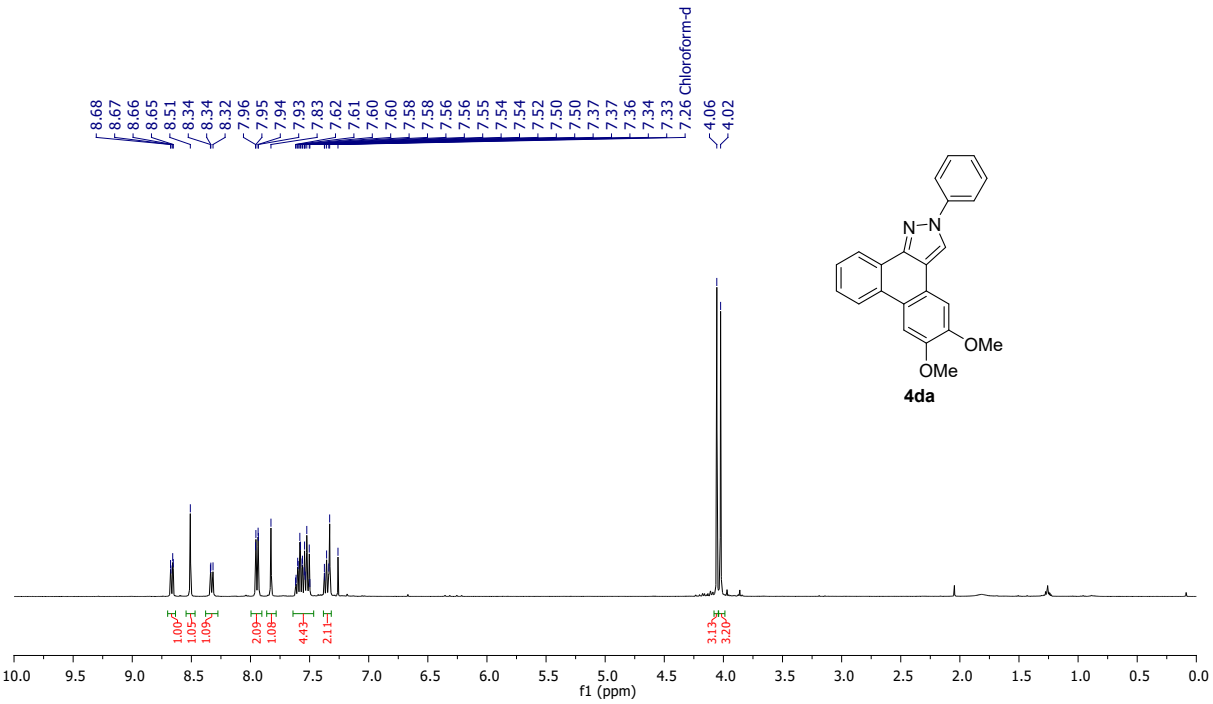
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ae** in $CDCl_3$.



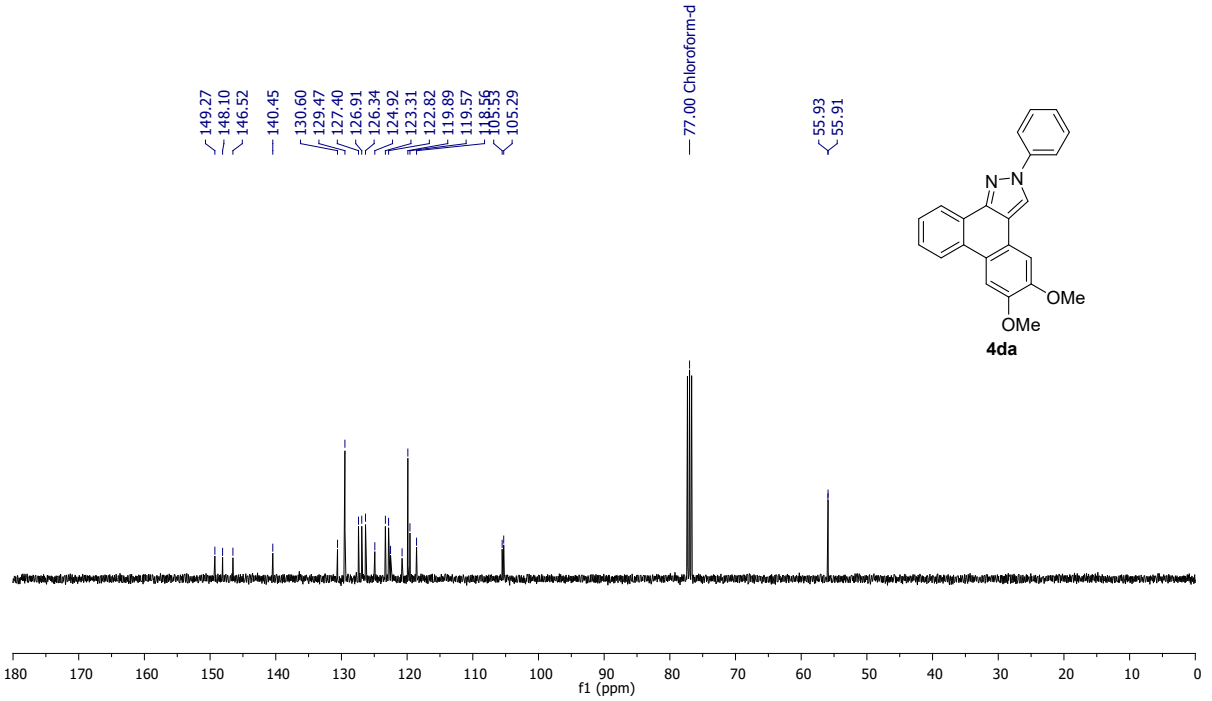
^{1}H NMR (400 MHz) spectrum of **4ca** in $CDCl_3$.



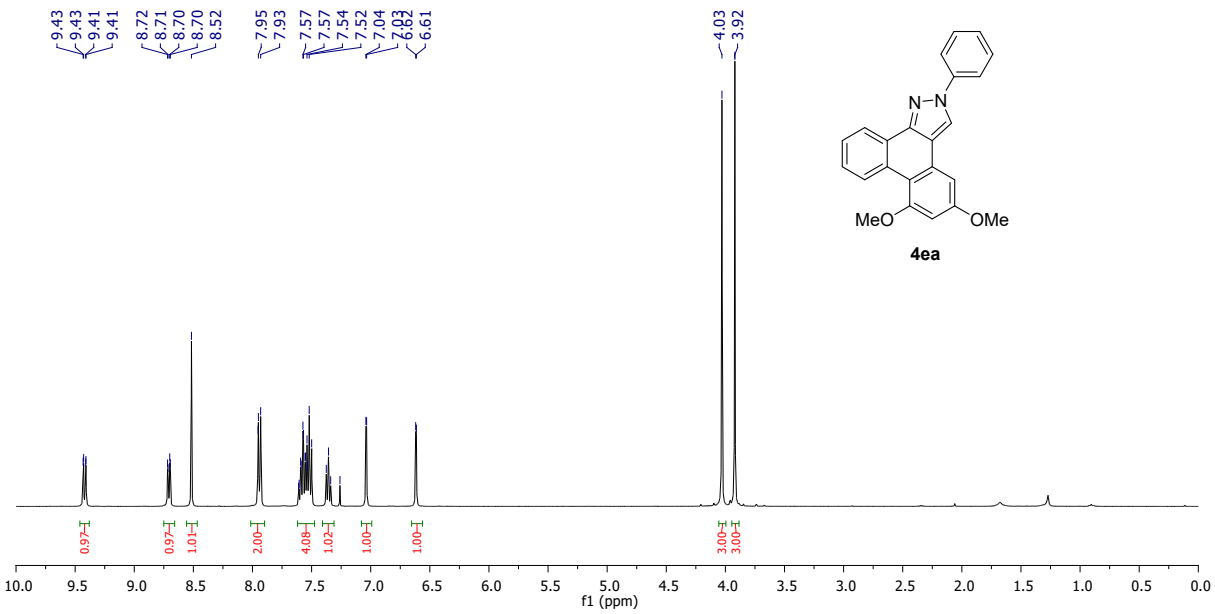
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ca** in $CDCl_3$.



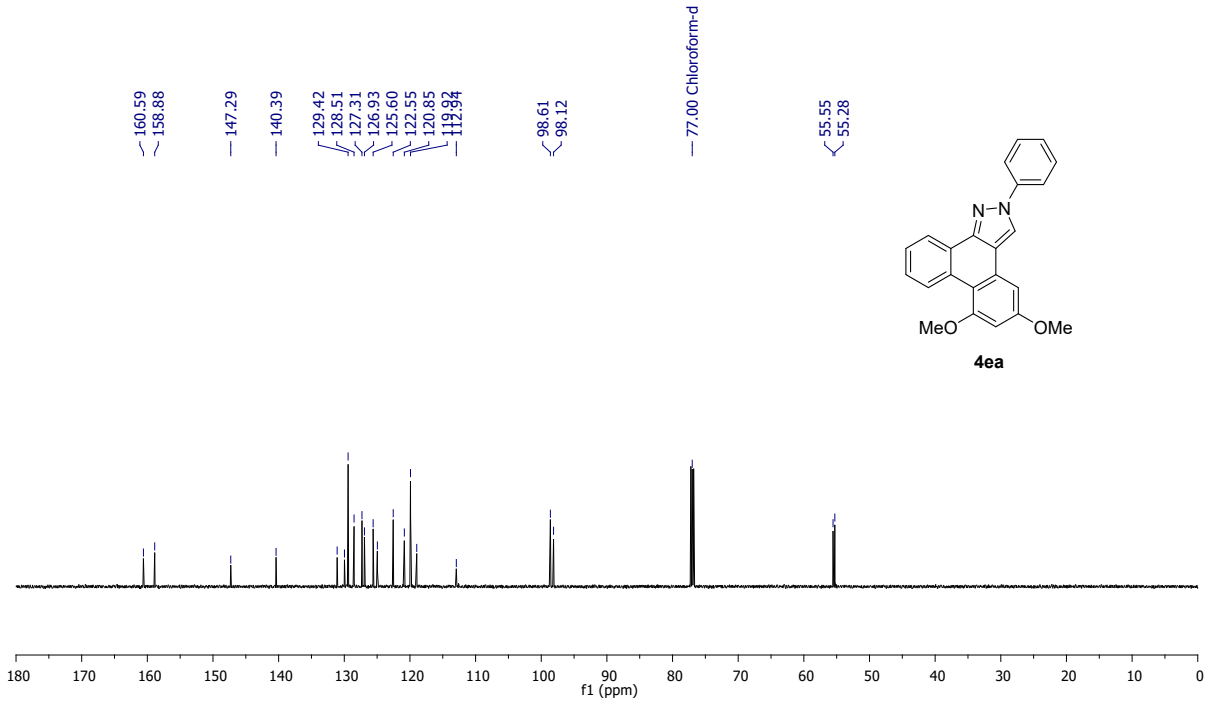
^{1}H NMR (400 MHz) spectrum of **4da** in $CDCl_3$.



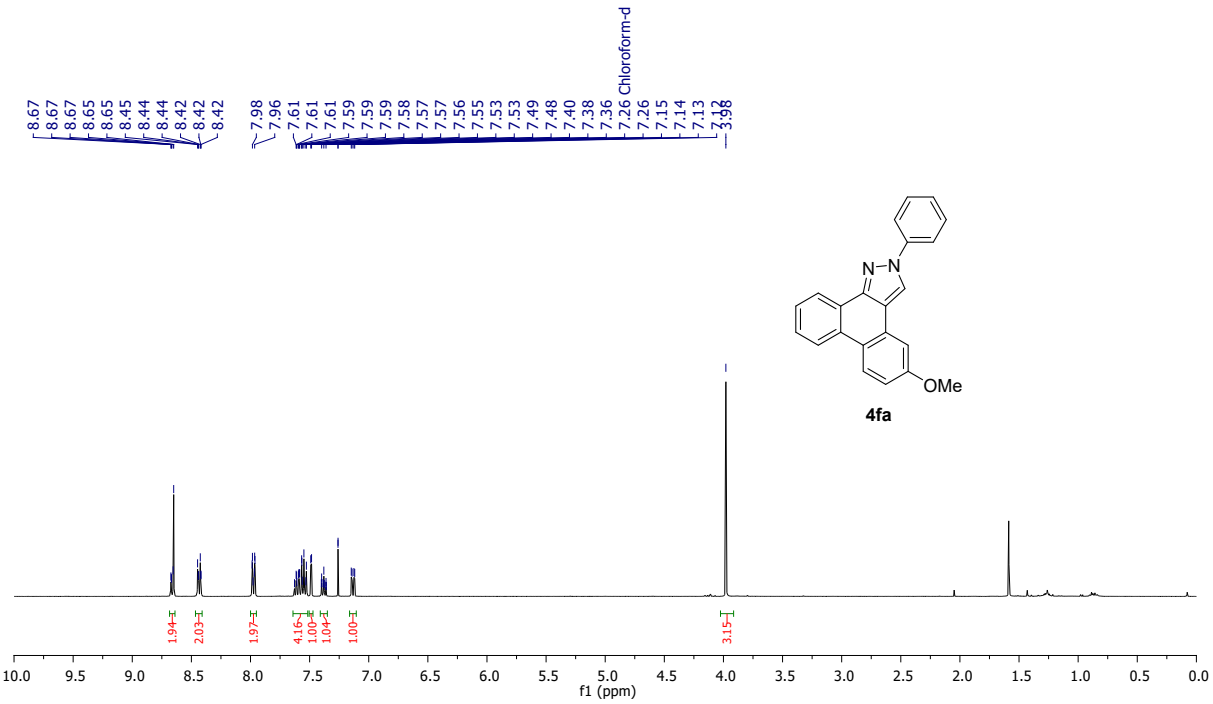
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4da** in $CDCl_3$.



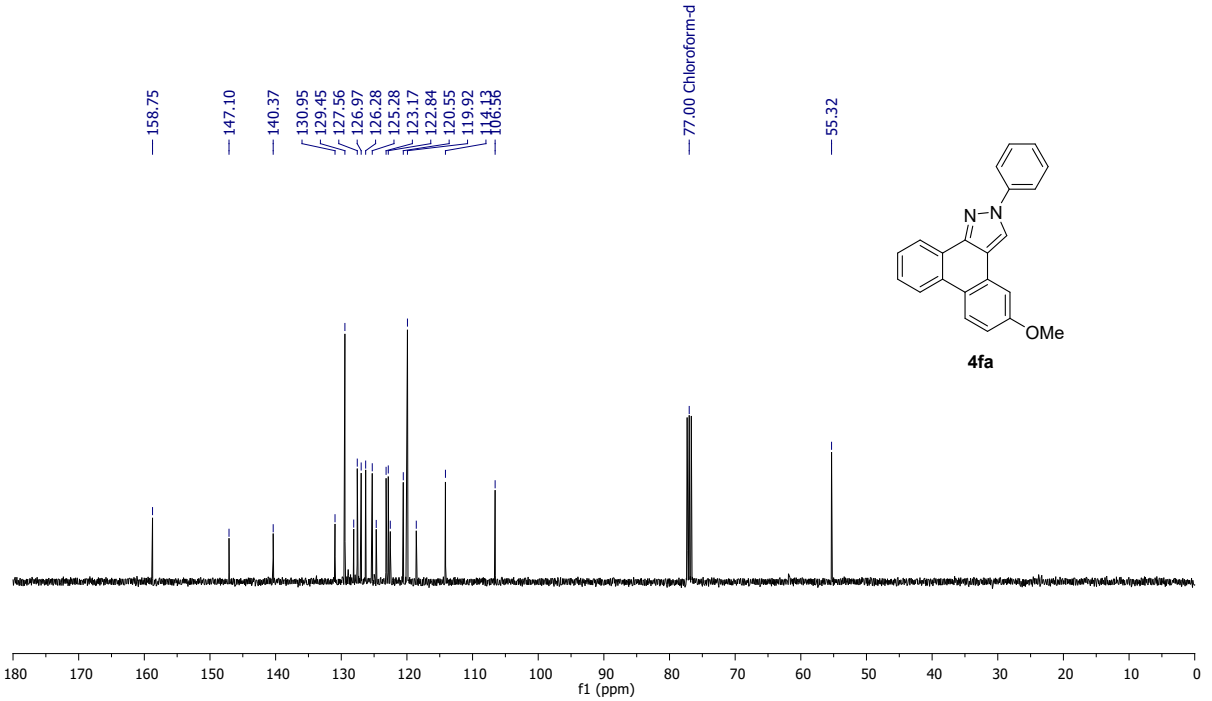
^{1}H NMR (400 MHz) spectrum of **4ea** in $CDCl_3$.



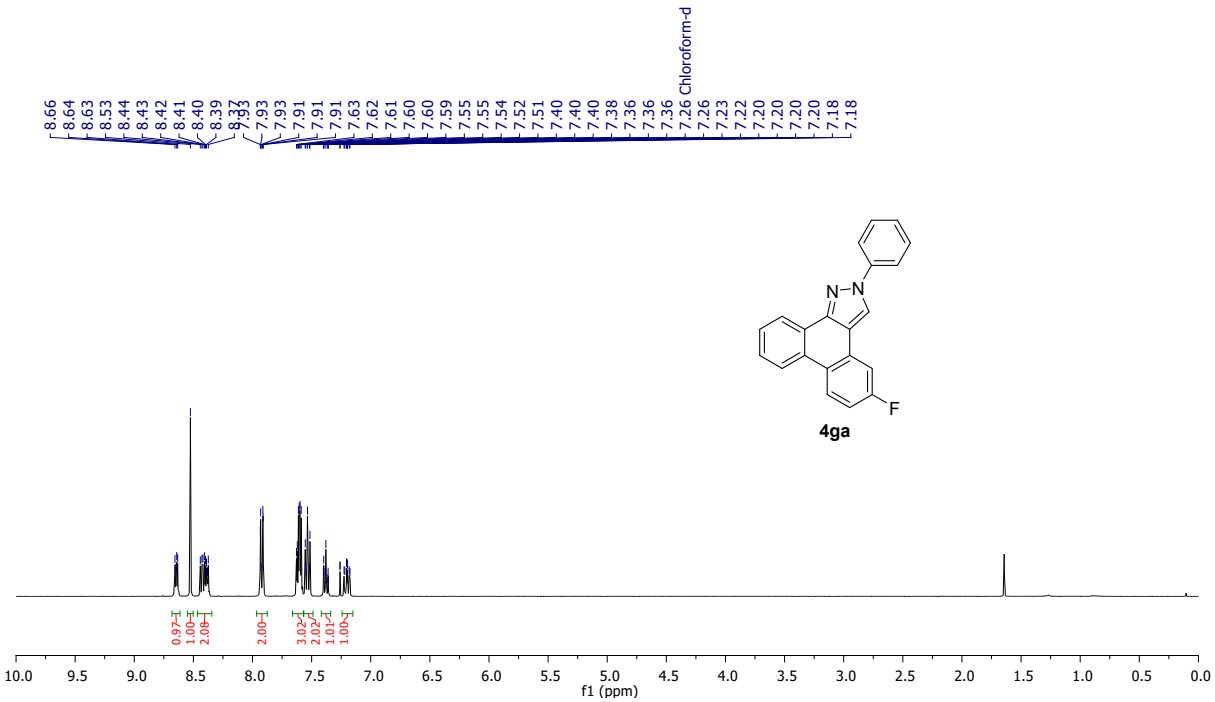
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ea** in $CDCl_3$.



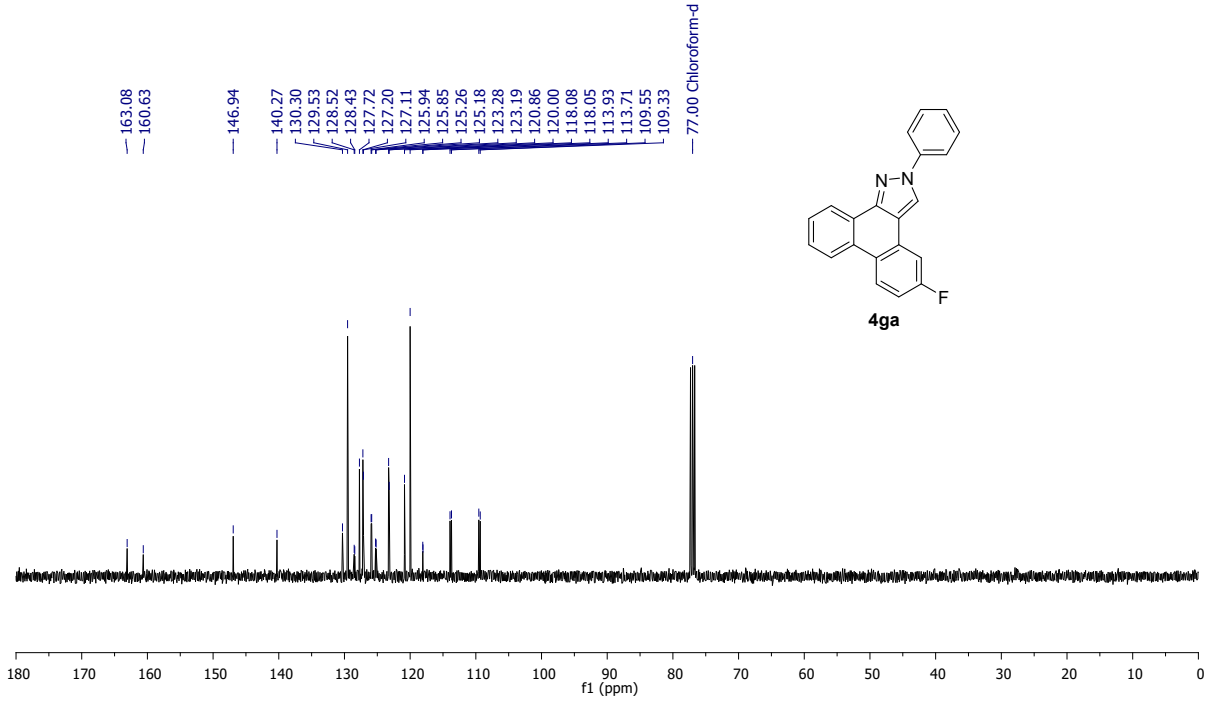
^{1}H NMR (400 MHz) spectrum of **4fa** in $CDCl_3$.



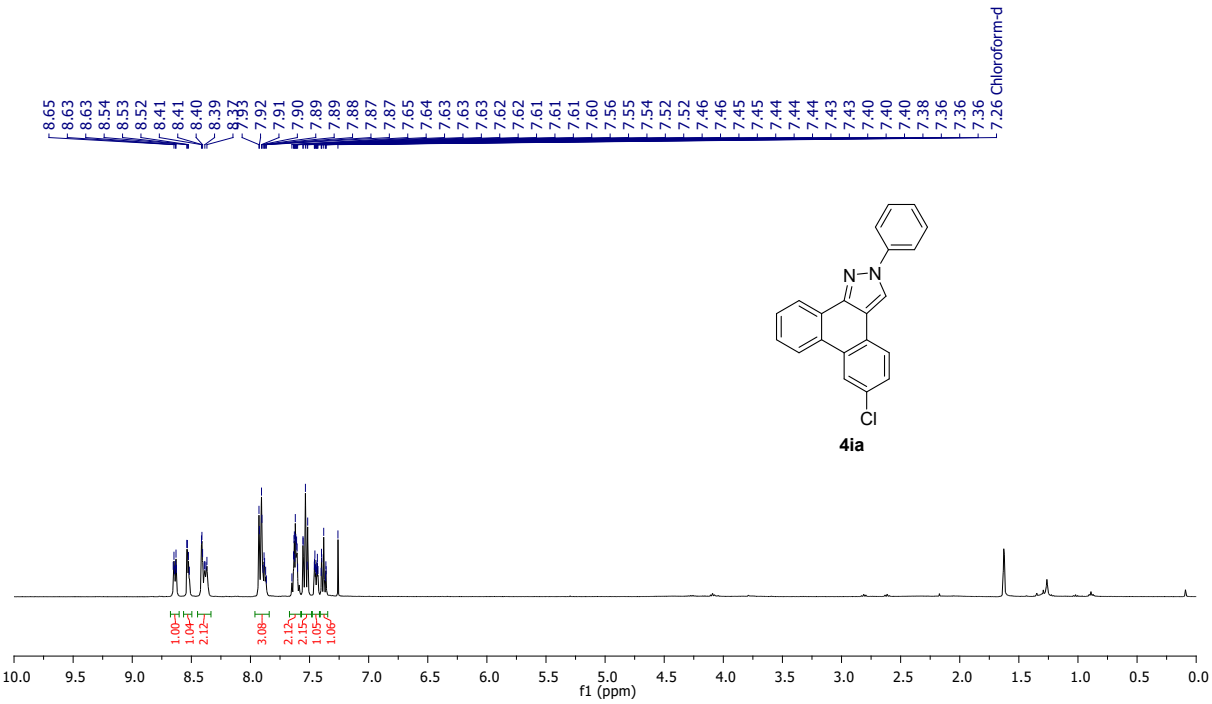
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4fa** in $CDCl_3$.



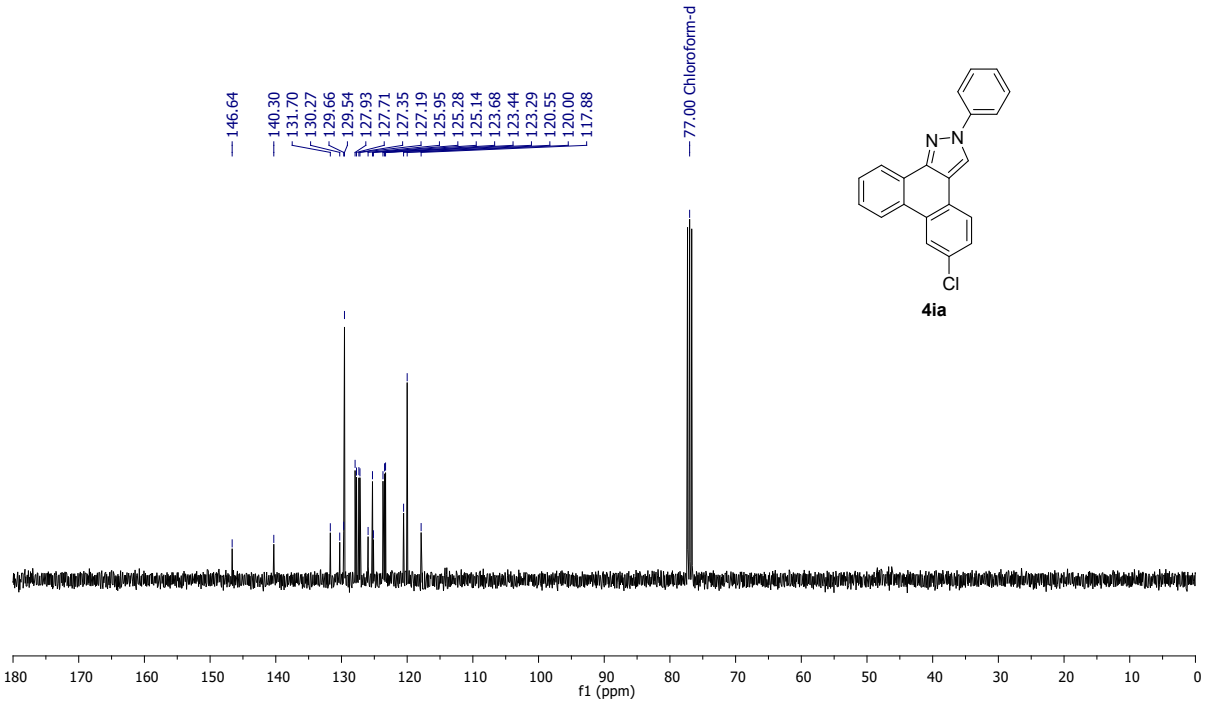
^{1}H NMR (400 MHz) spectrum of **4ga** in $CDCl_3$.



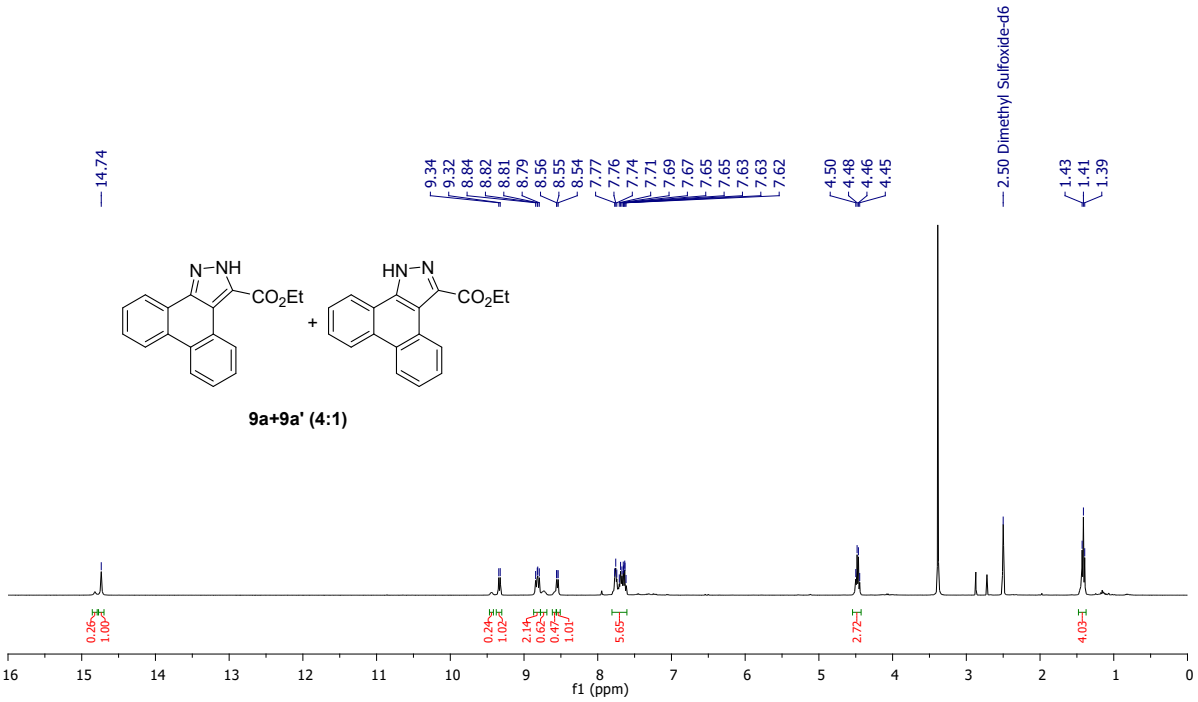
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ga** in $CDCl_3$.



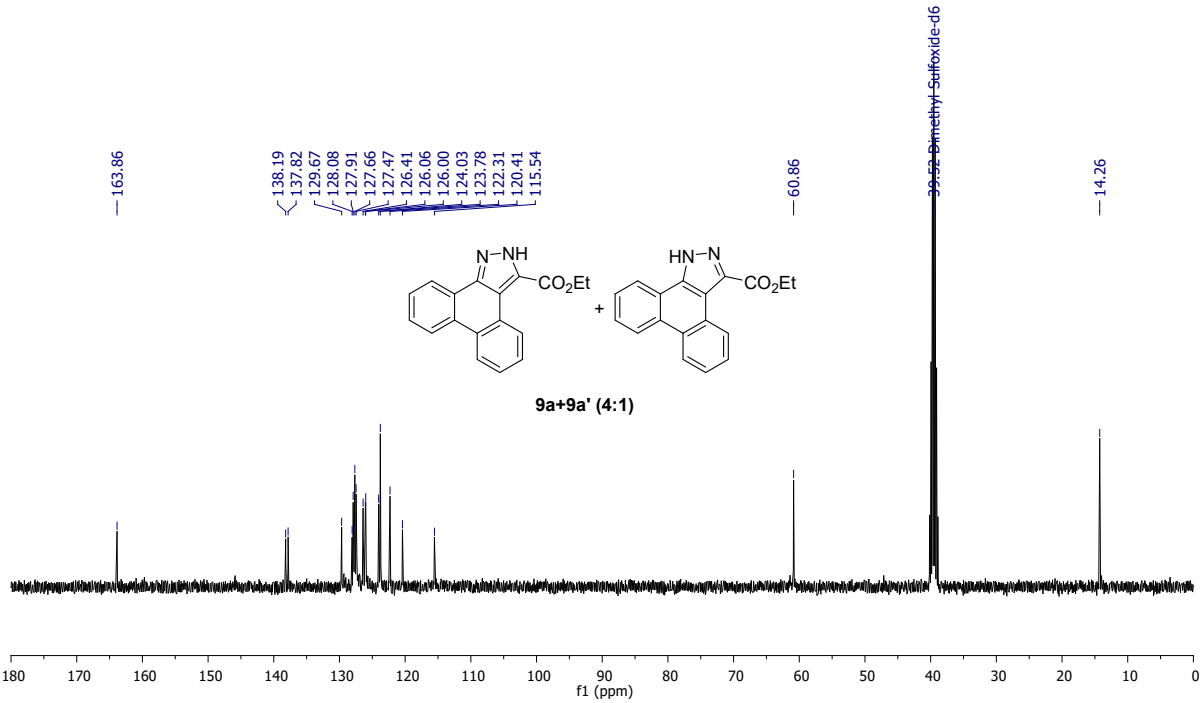
^{1}H NMR (400 MHz) spectrum of **4ia** in $CDCl_3$.



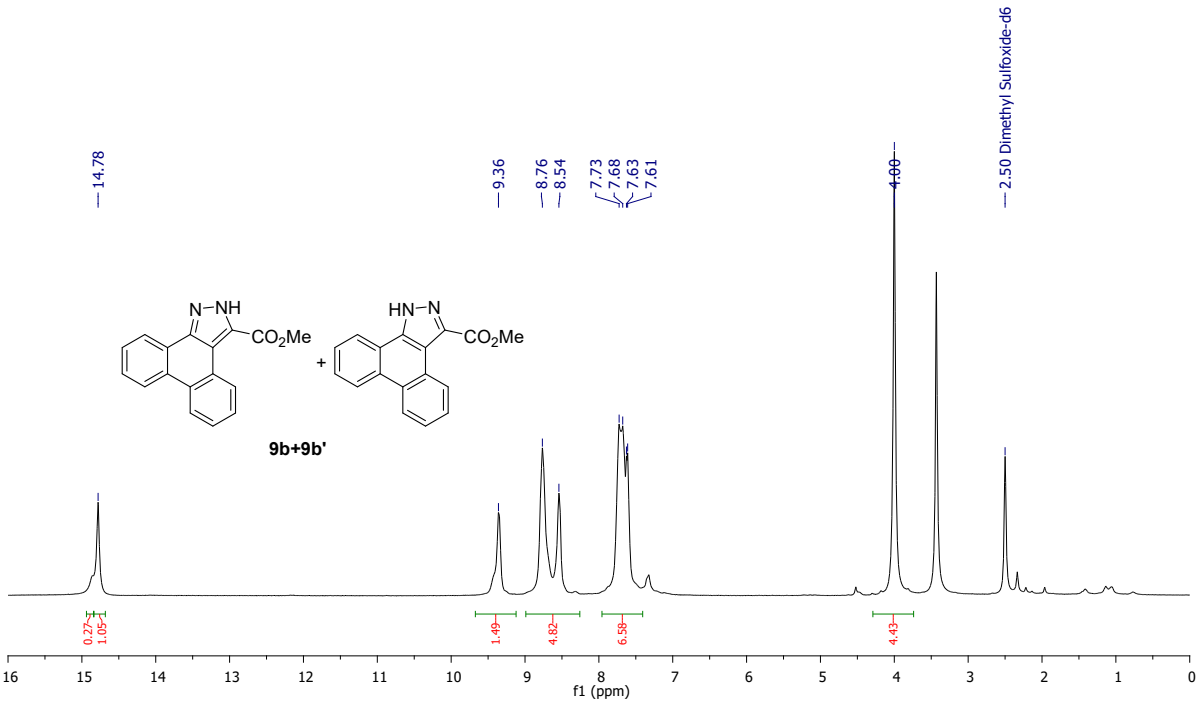
^{13}C{^{1}H} NMR (101 MHz) spectrum of **4ia** in $CDCl_3$.



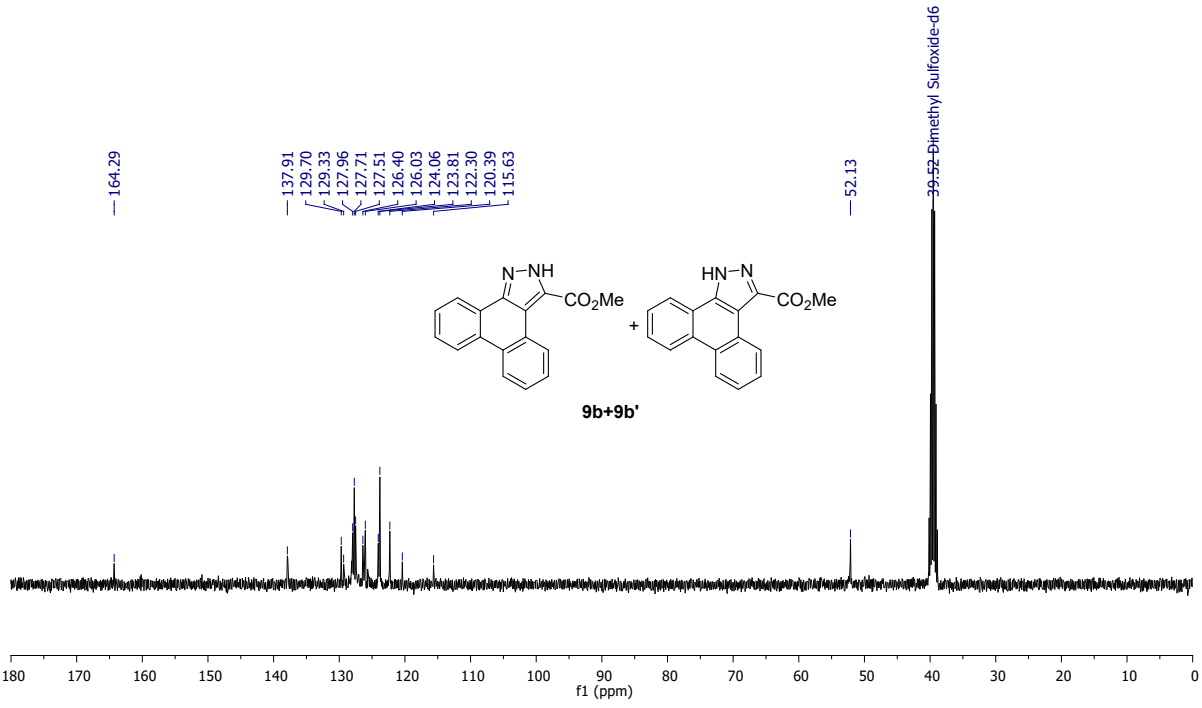
^{1}H NMR (400 MHz) spectrum of **9a**+**9a'** in DMSO-*d6*.



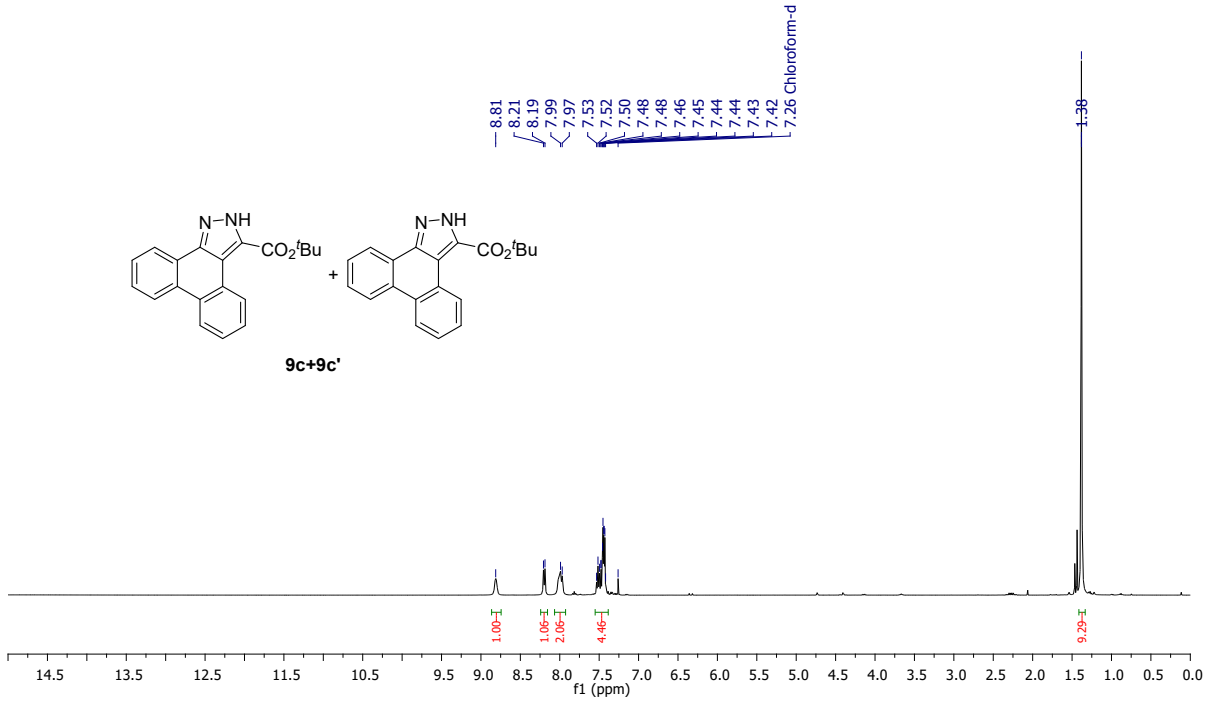
^{13}C{^{1}H} NMR (100 MHz) spectrum of **9a**+**9a'** in DMSO-*d6*.



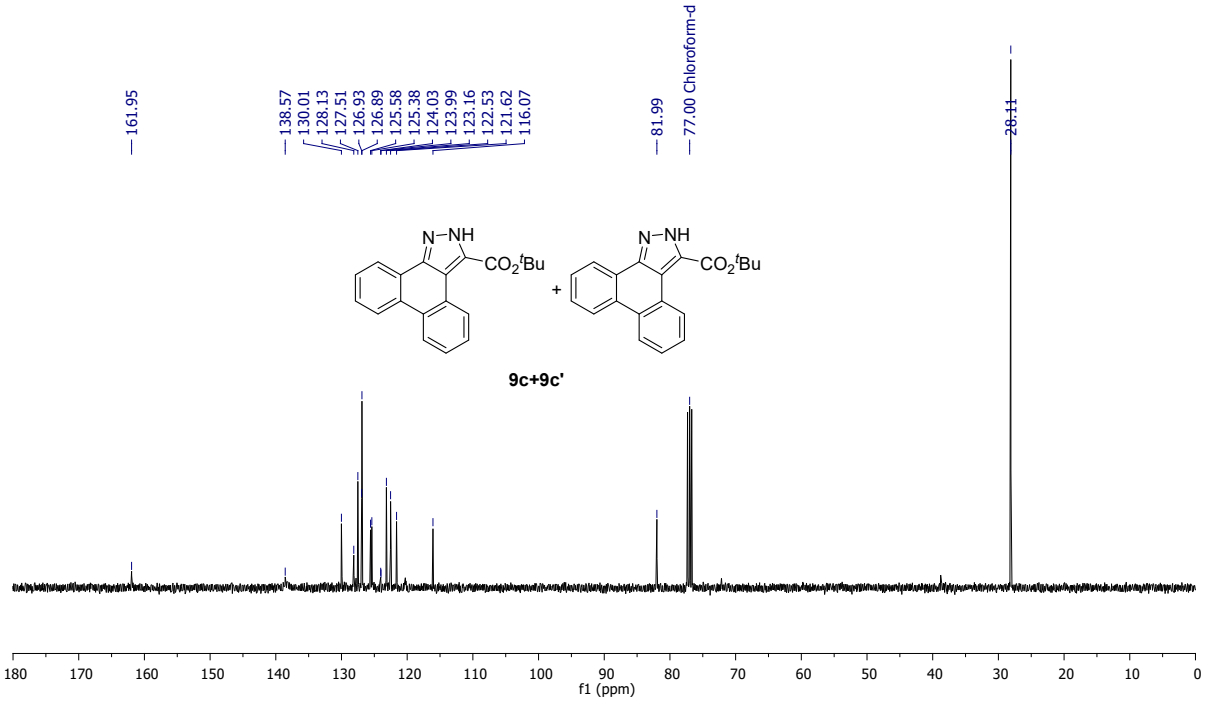
^{1}H NMR (400 MHz) spectrum of **9b**+**9b'** in DMSO-*d6*.



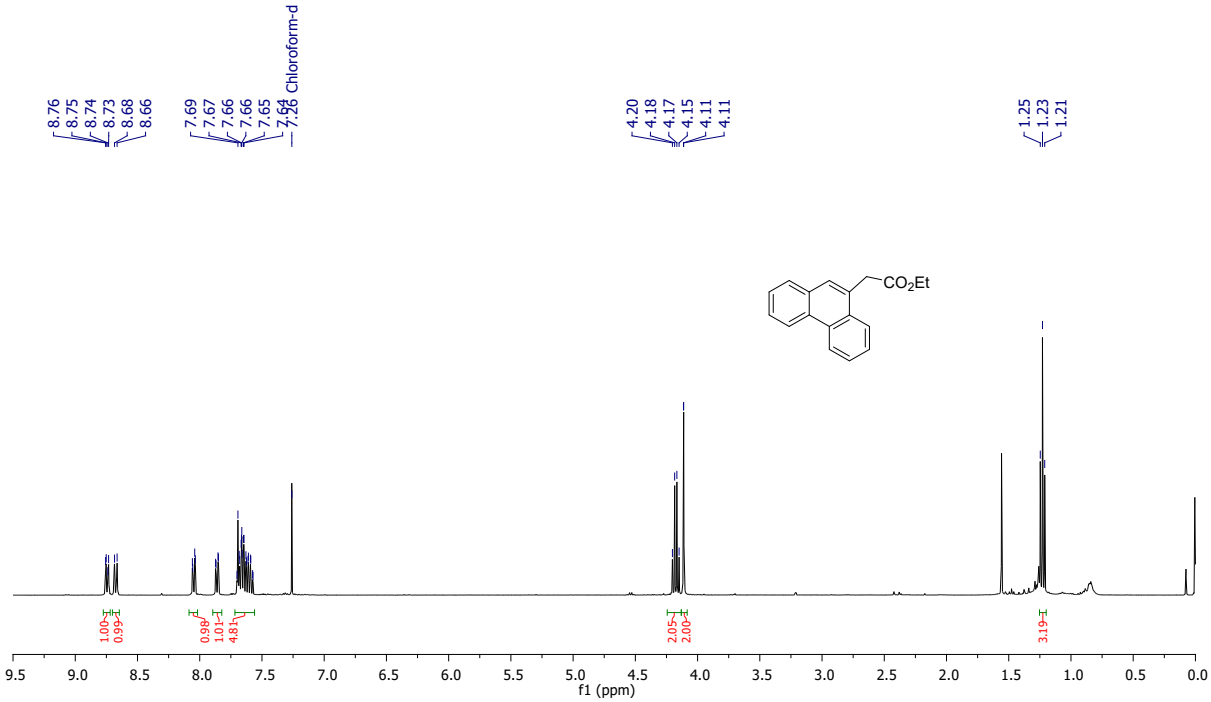
^{13}C{^{1}H} NMR (100 MHz) spectrum of **9b**+**9b'** in DMSO-*d6*.



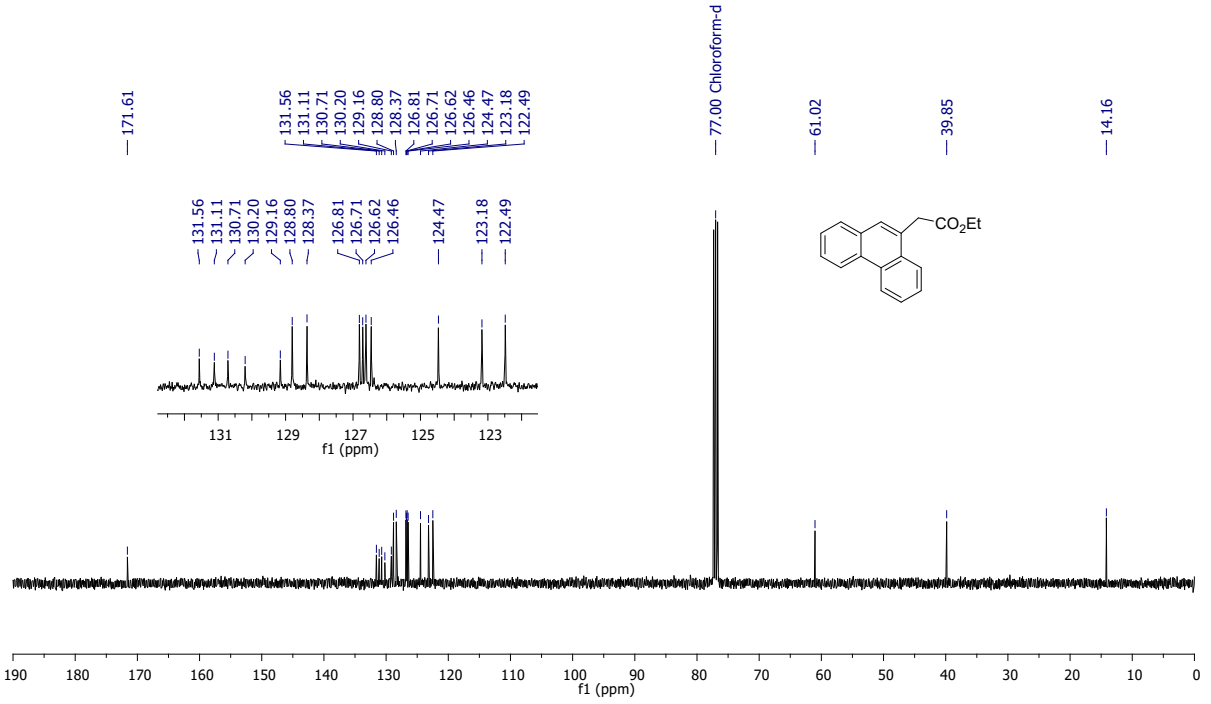
^{1}H NMR (400 MHz) spectrum of **9c+9c'** in $CDCl_3$.



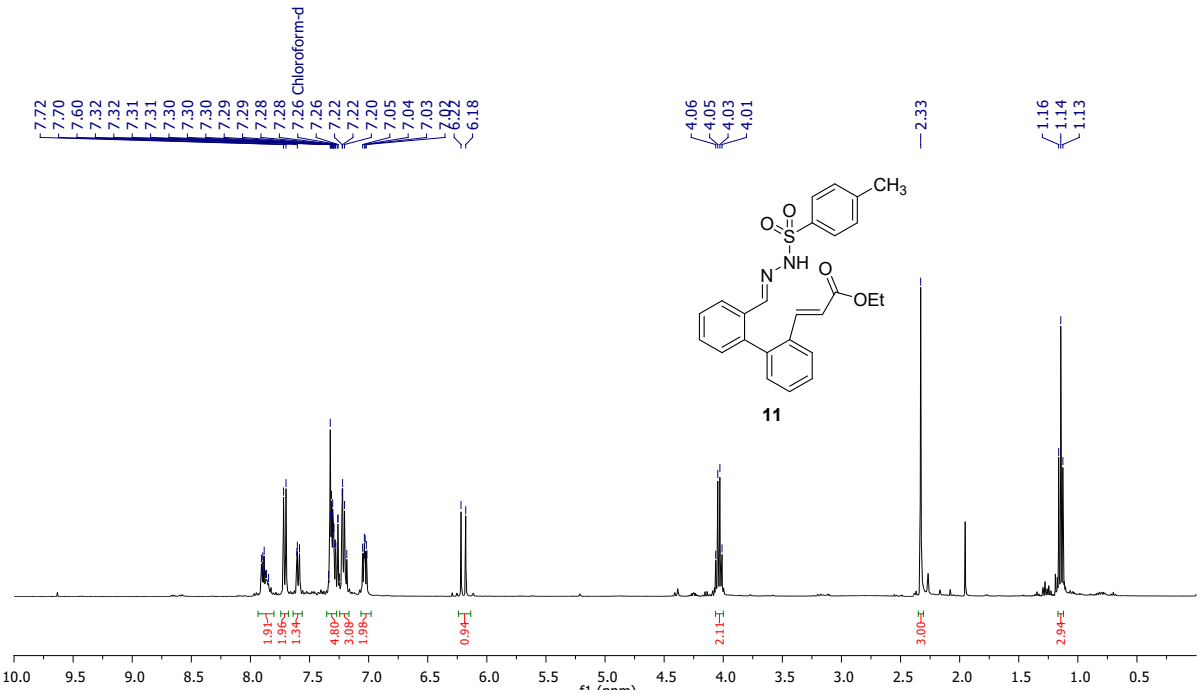
^{13}C{^{1}H} NMR (101 MHz) spectrum of **9c+9c'** in $CDCl_3$.



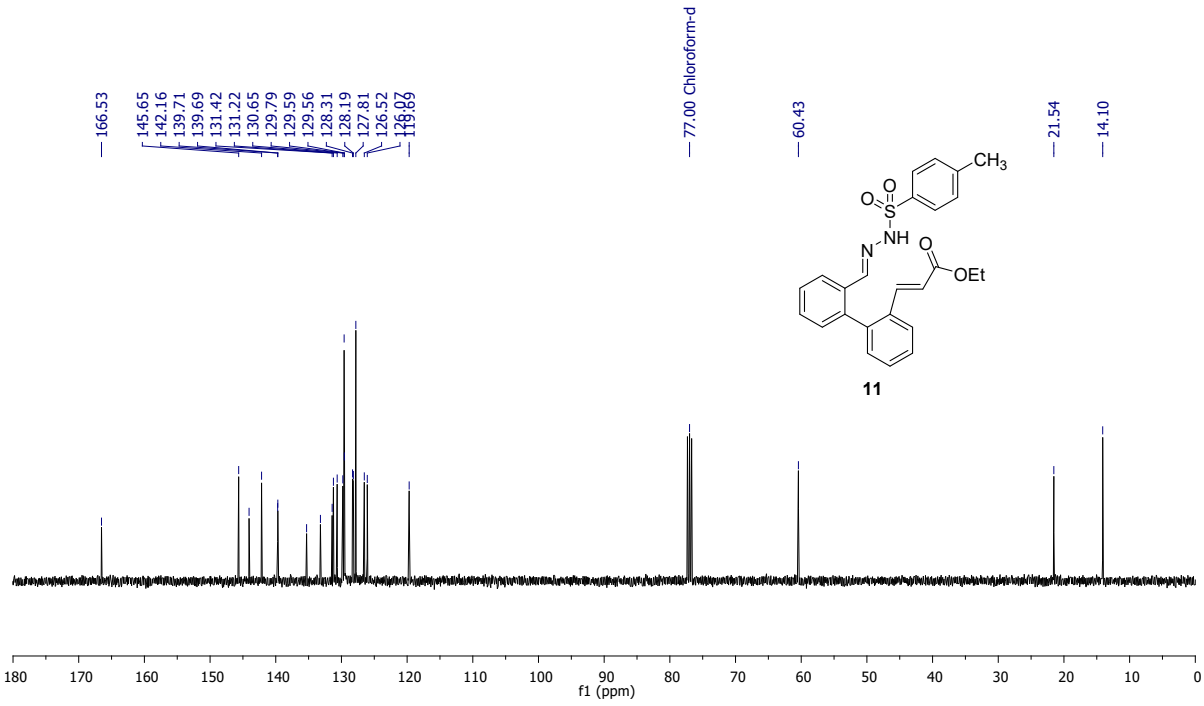
^{1}H NMR (400 MHz) spectrum of **9aa** in $CDCl_3$.



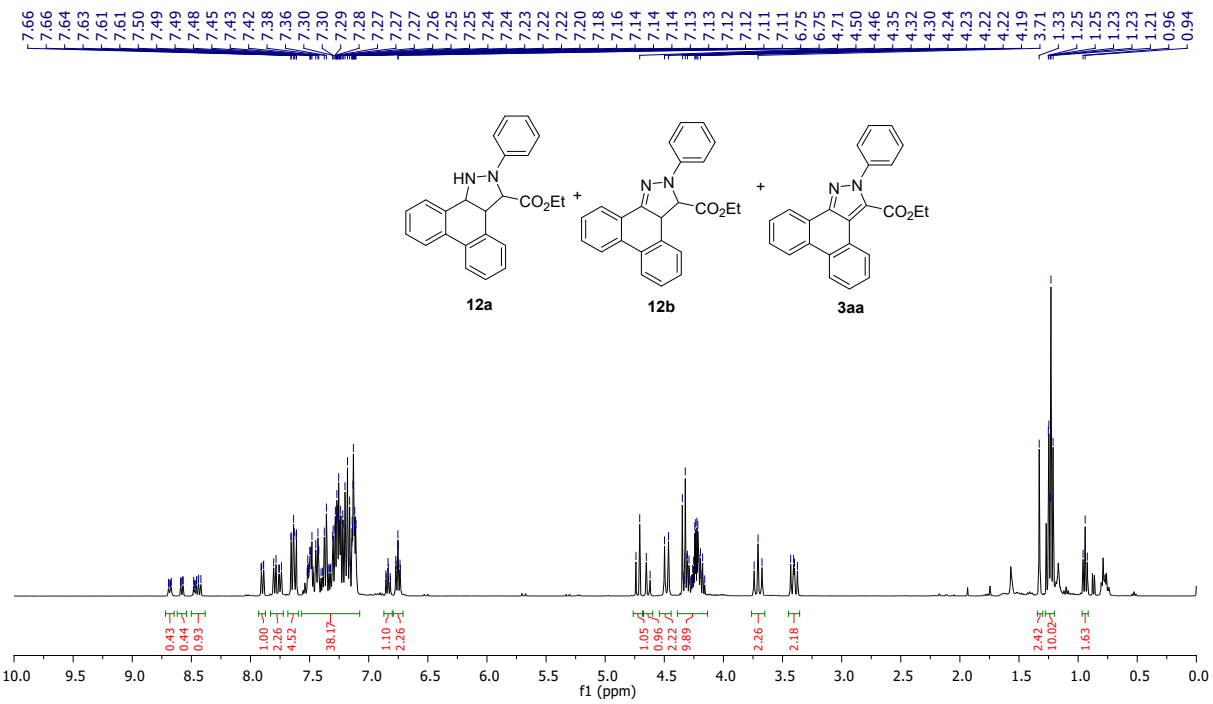
^{13}C{^{1}H} NMR (101 MHz) spectrum of **9aa** in $CDCl_3$.



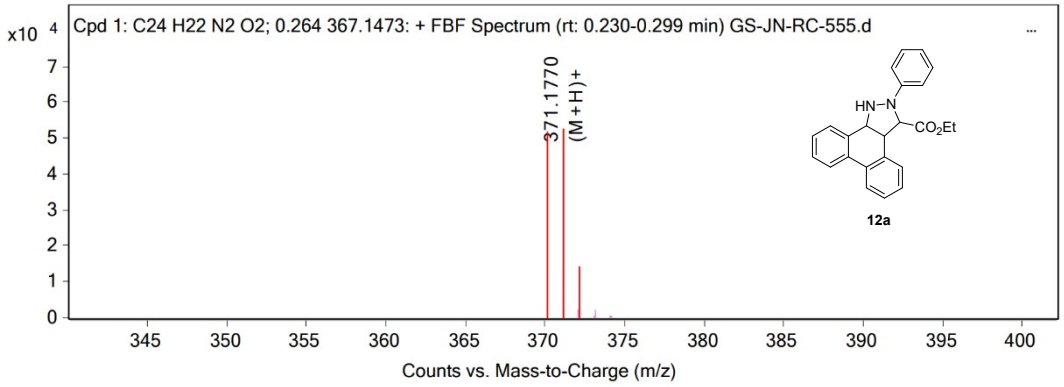
^{1}H NMR (400 MHz) spectrum of **11** in $CDCl_3$.

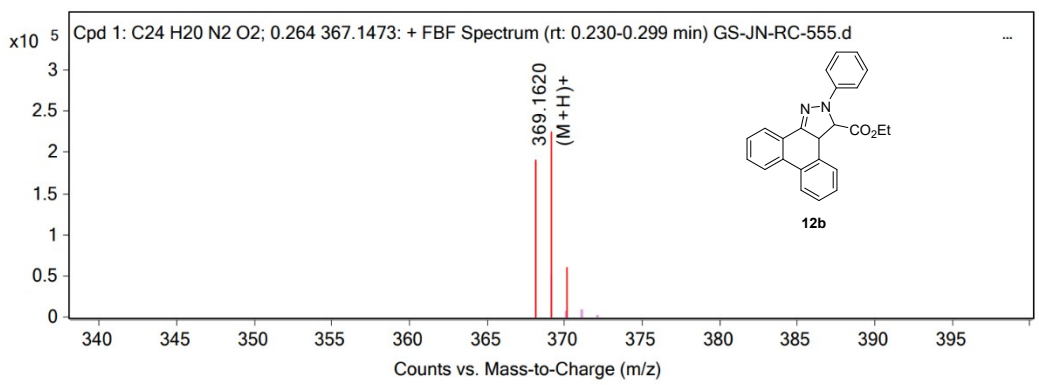


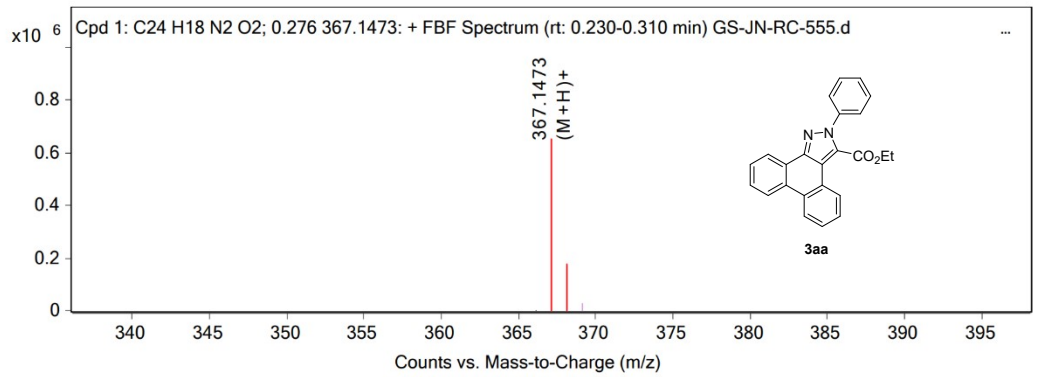
^{13}C{^{1}H} NMR (101 MHz) spectrum of **11** in $CDCl_3$.

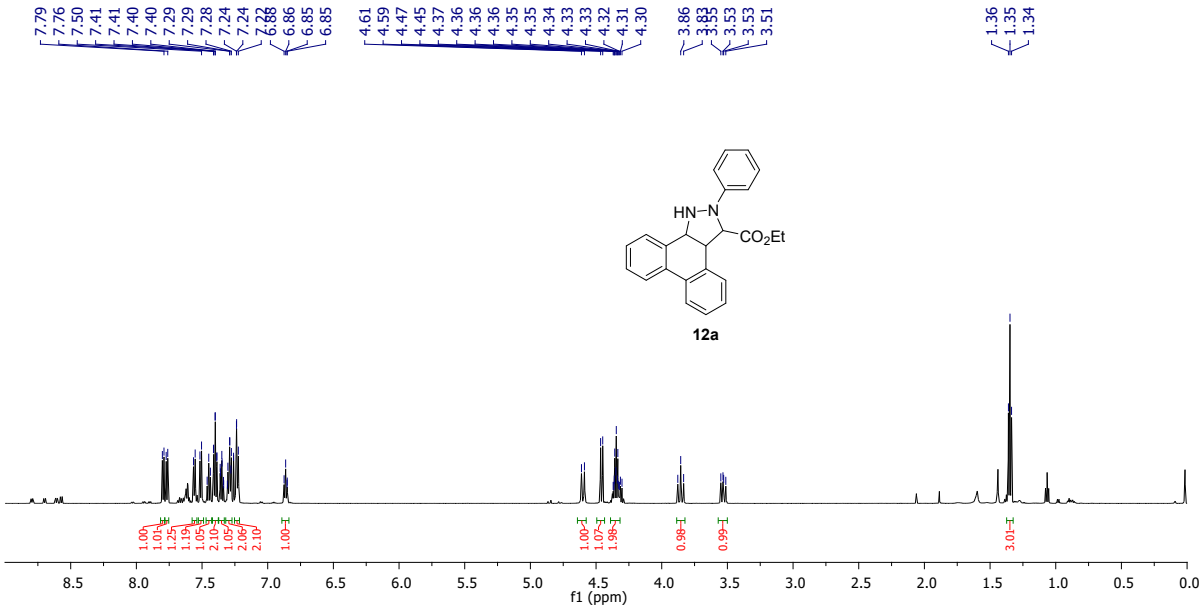


^{1}H NMR (400 MHz) spectrum of **12** in $CDCl_3$.

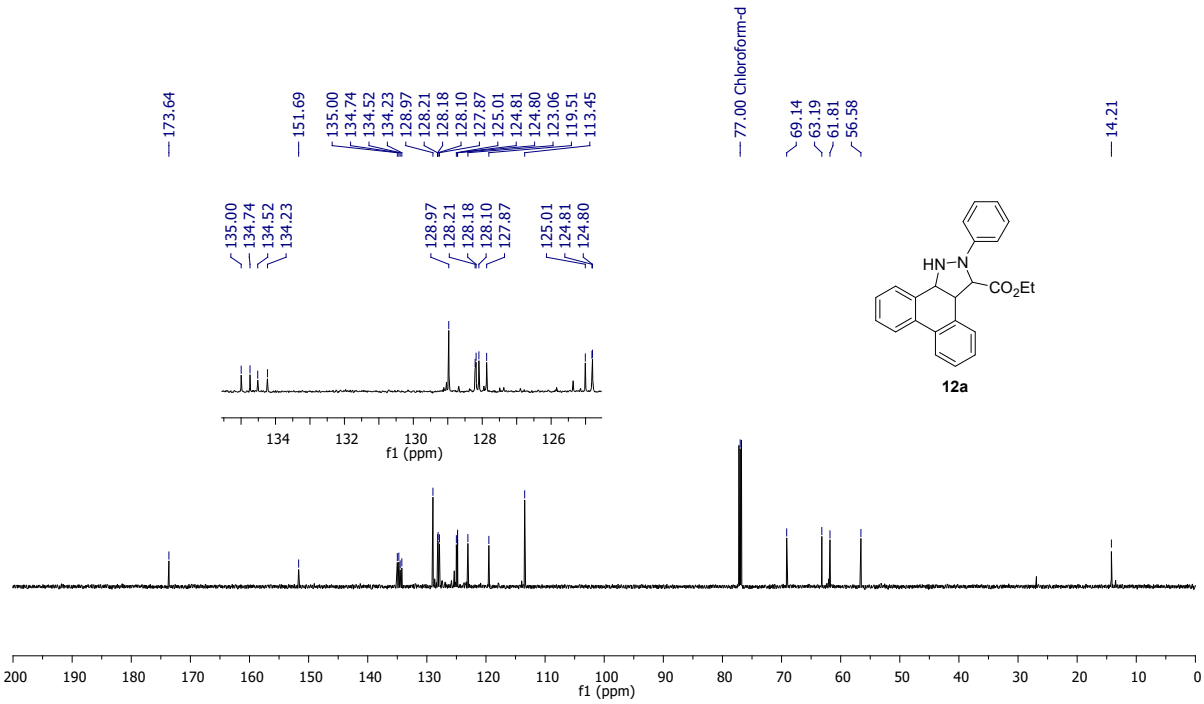




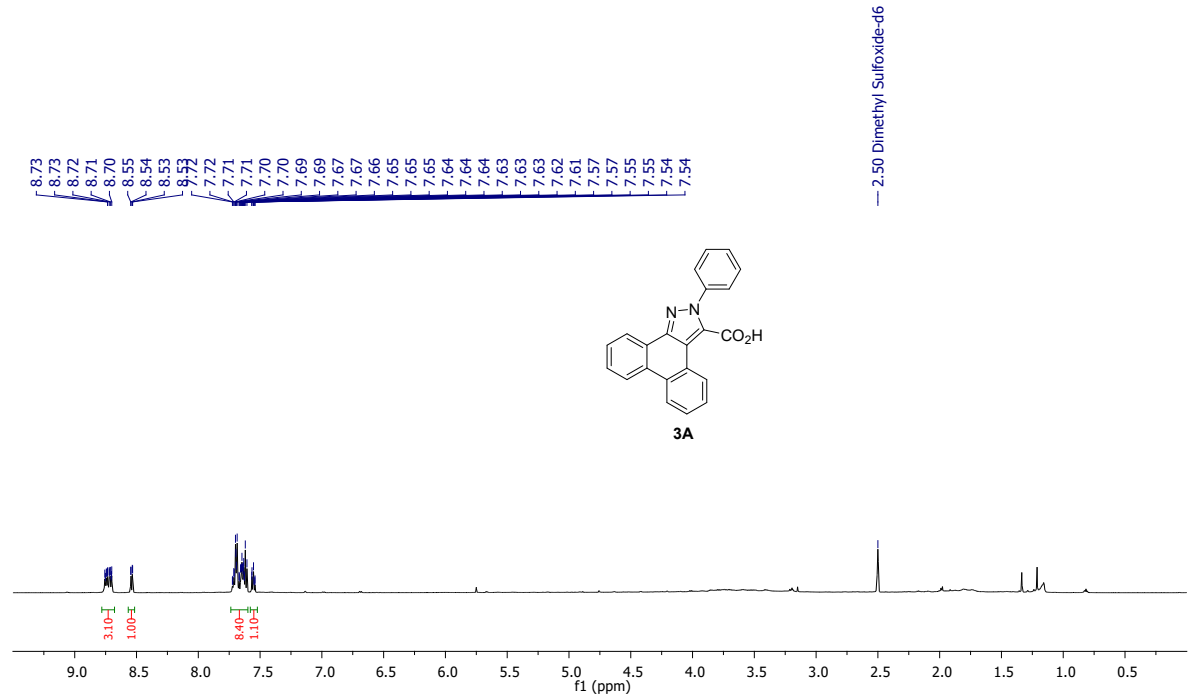




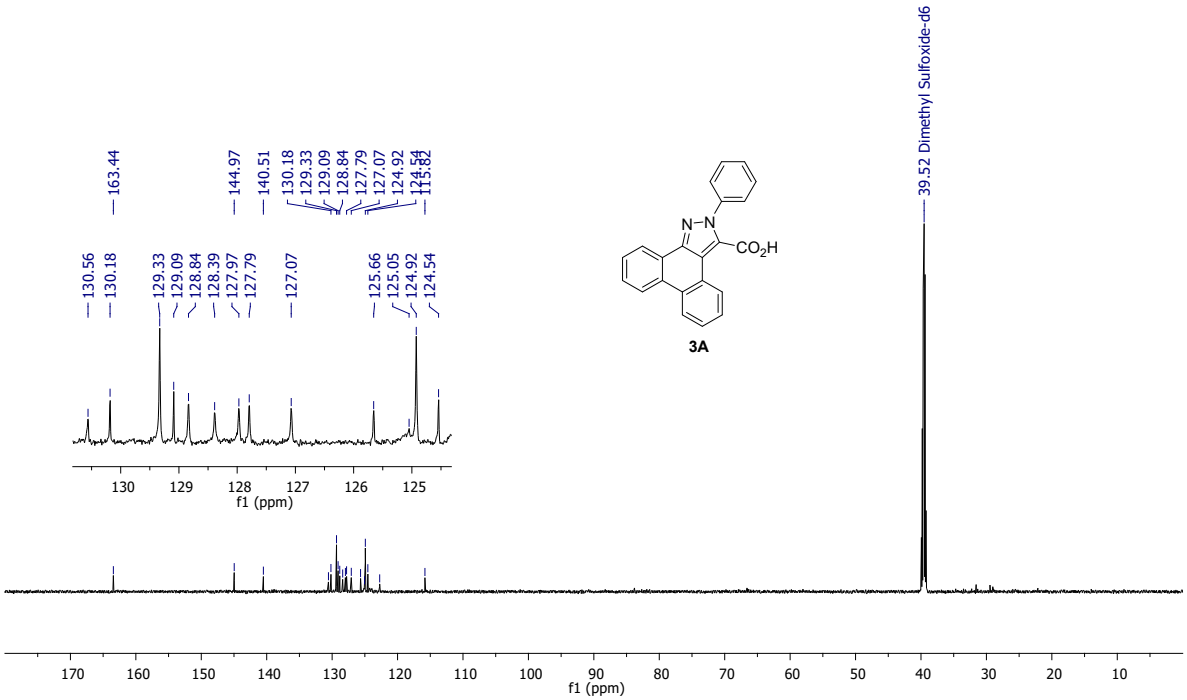
^{1}H NMR (600 MHz) spectrum of **12a** in $CDCl_3$.



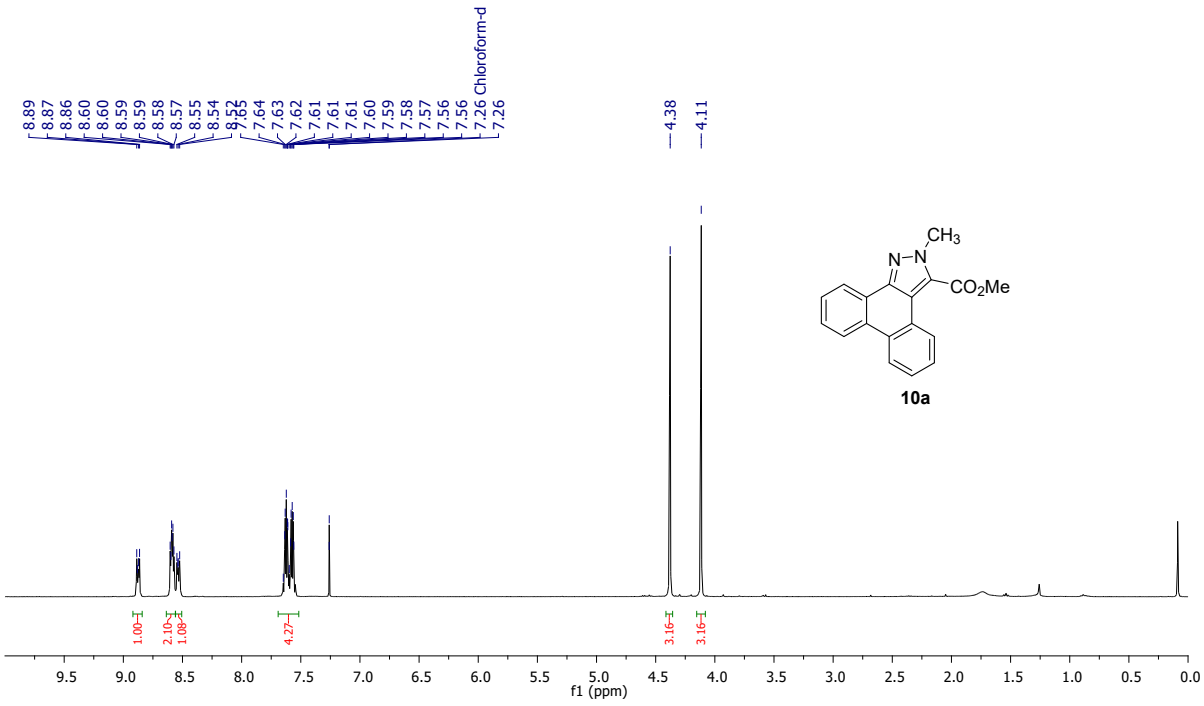
$^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of **12a** in $CDCl_3$.



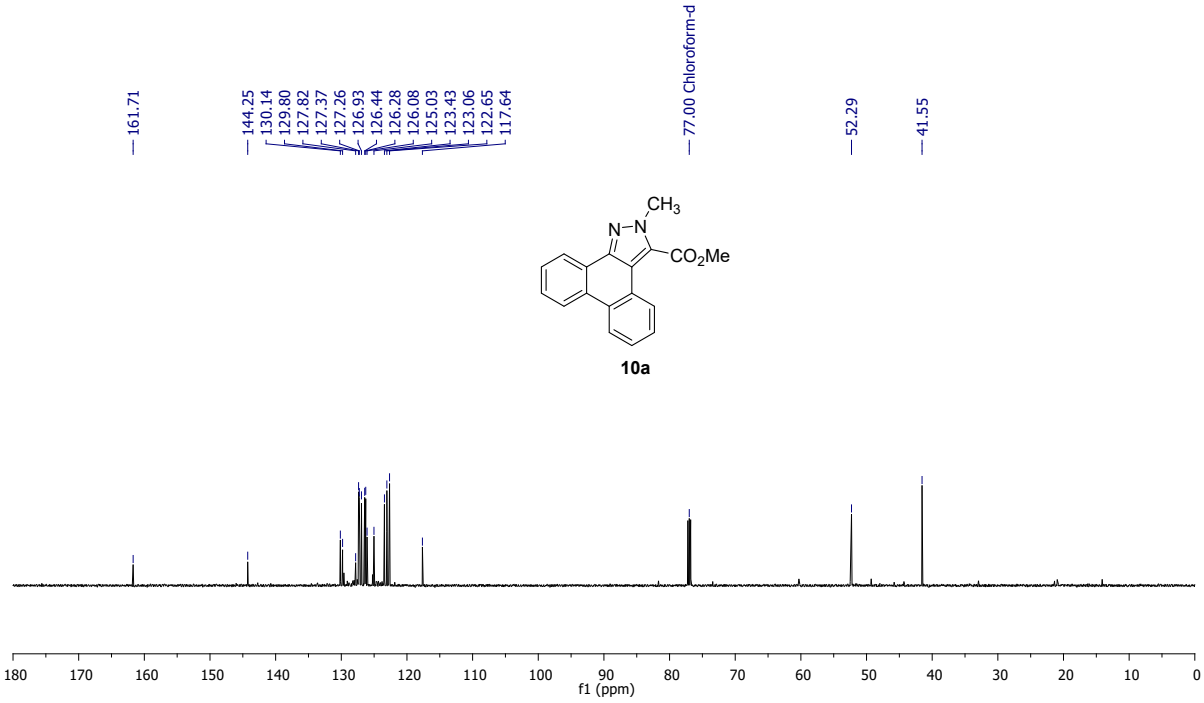
^{1}H NMR (600 MHz) spectrum of **3A** in DMSO-d6.



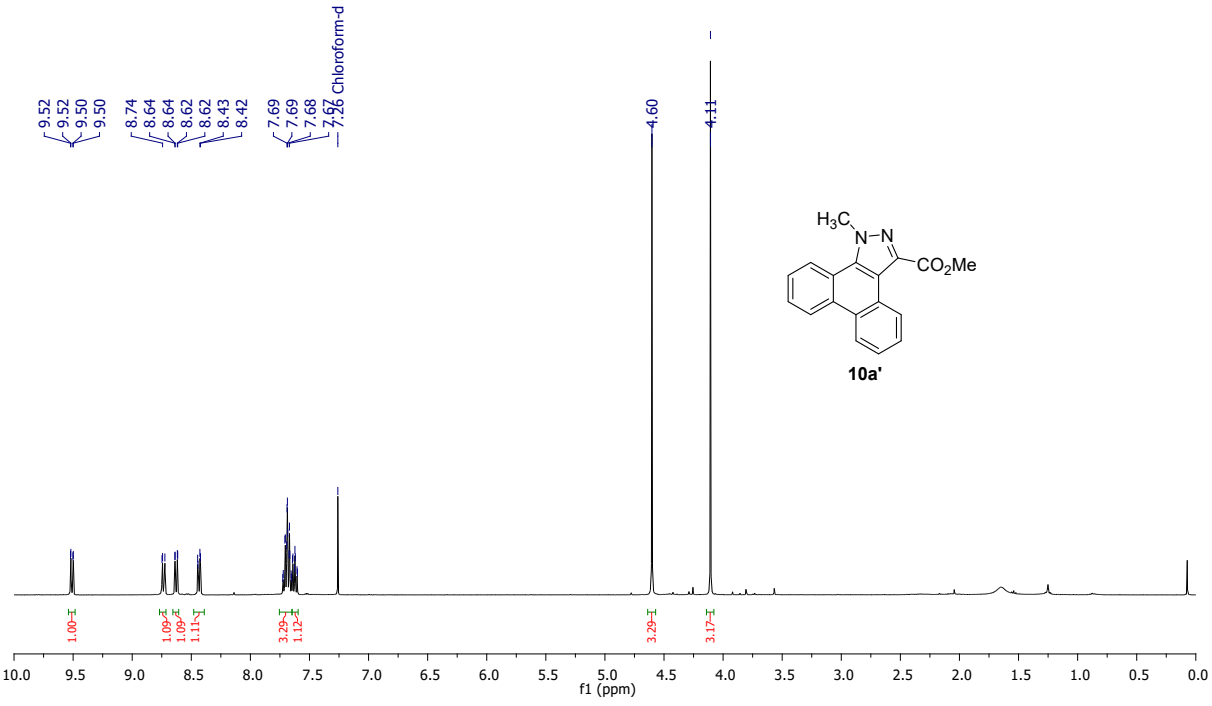
$^{13}C\{^{1}H\}$ NMR (151 MHz) spectrum of **3A** in $CDCl_3$.



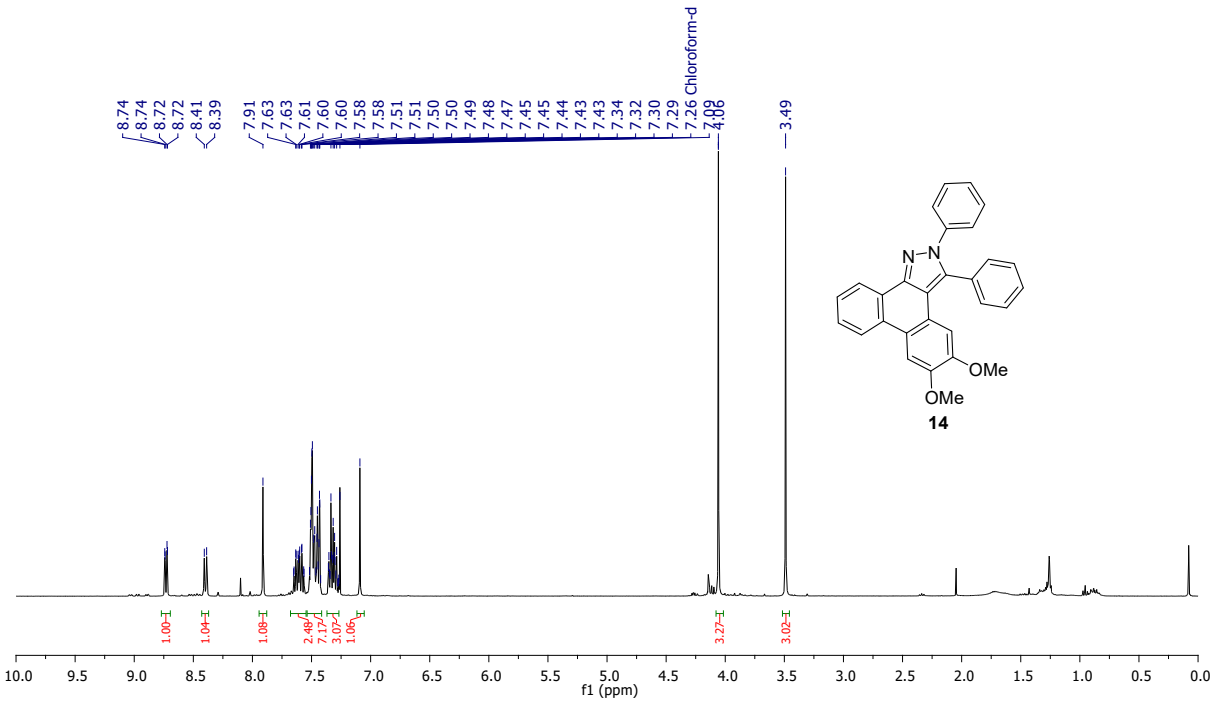
^{1}H NMR (400 MHz) spectrum of **10a** in $CDCl_3$.



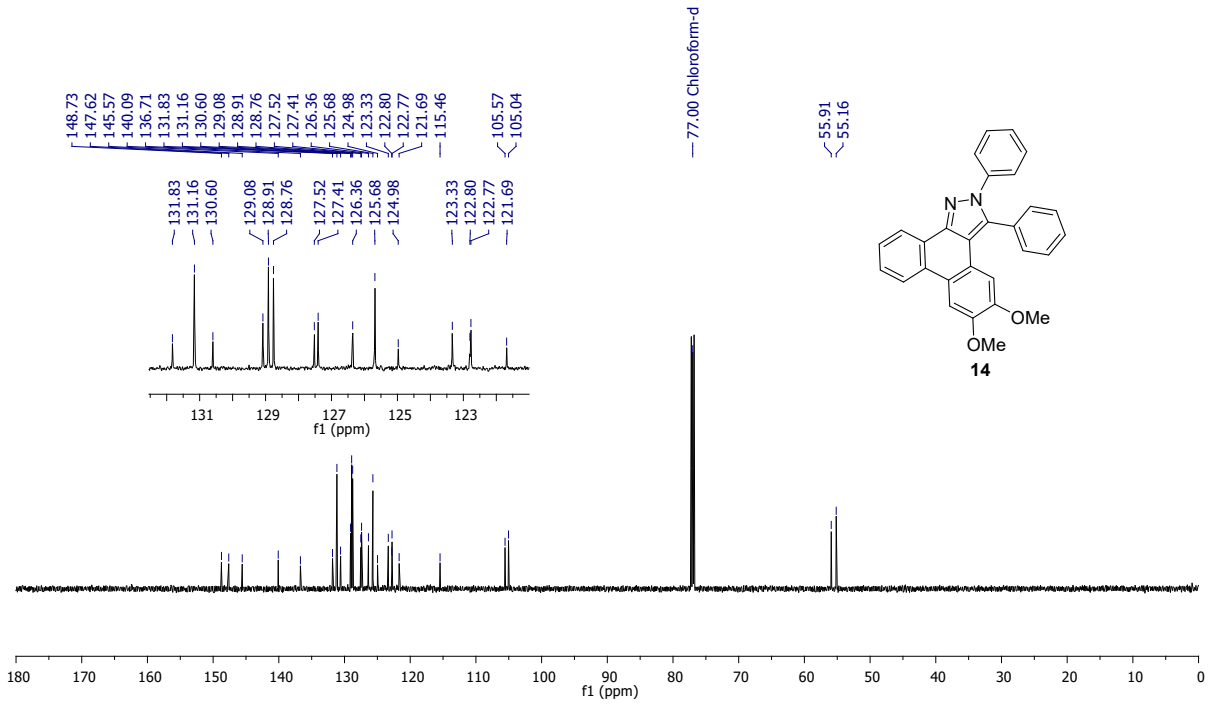
$^{13}C\{^{1}H\}$ NMR (100 MHz) spectrum of **10a** in $CDCl_3$.



^{1}H NMR (400 MHz) spectrum of **10a'** in $CDCl_3$.



^{1}H NMR (400 MHz) spectrum of **14** in $CDCl_3$.



^{13}C{^{1}H} NMR (151 MHz) spectrum of **14** in $CDCl_3$.

Crystal structure data:

X-Ray crystal structure of compound **3ea**:

Crystal of compound **3ea** were obtained by dissolving the product in CH_2Cl_2 and hexane (1:1) mixture and allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No:2293909 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk.

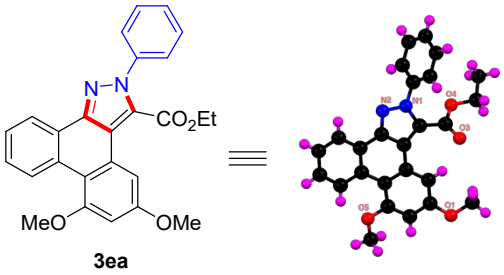


Figure S1: X-ray structure of the product **3ea** with the ellipsoids drawn at the 50% probability level.

Table 1 Crystal data and structure refinement for 3ea.

Identification code	3ea
Empirical formula	$C_{26}H_{22}N_2O_4$
Formula weight	426.45
Temperature/K	298
Crystal system	monoclinic
Space group	Cc
a/Å	13.0990(9)
b/Å	16.0302(11)
c/Å	10.1789(6)
α/°	90
β/°	90.324(2)
γ/°	90
Volume/Å^3	2137.3(2)
Z	4
ρ_{calc}g/cm^3	1.325
μ/mm^{-1}	0.090
F(000)	896.0
Crystal size/mm^3	0.7 × 0.6 × 0.5
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.082 to 54.584
Index ranges	-16 ≤ h ≤ 16, -20 ≤ k ≤ 20, -12 ≤ l ≤ 13
Reflections collected	21424
Independent reflections	4684 [R_{int} = 0.0449, R_{sigma} = 0.0343]
Data/restraints/parameters	4684/2/292

Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0364, wR_2 = 0.0842
Final R indexes [all data]	R_1 = 0.0469, wR_2 = 0.0912
Largest diff. peak/hole / e $Å^{-3}$	0.12/-0.15
Flack parameter	0.5

X-Ray crystal structure of compound 4ia:

Crystal of compound **4ia** were obtained by dissolving the product in CH_2Cl_2 and hexane (1:1) mixture and allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No:2293910 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk. Here, due to the bad quality of the crystal structure of **4ai,** B alert was observed.

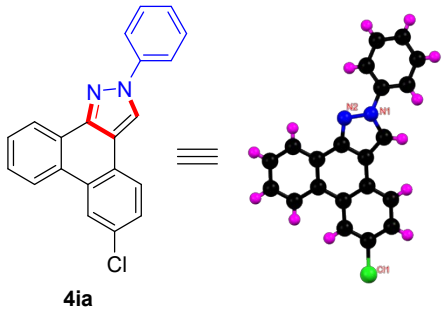


Figure 2: X-ray structure of the product **4ia** with the ellipsoids drawn at the 50% probability level.

Table 1 Crystal data and structure refinement for 4ia.

Identification code	4ia
Empirical formula	$C_{21}H_{13}ClN_2$
Formula weight	328.78
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.556(4)
b/Å	4.0074(12)
c/Å	30.397(7)
α/°	90
β/°	96.540(8)
γ/°	90
Volume/$Å^3$	1519.6(7)
Z	4
$\rho_{calc}g/cm^3$	1.437
μ/mm^{-1}	0.254
F(000)	680.0

Crystal size/mm^3	0.065 × 0.056 × 0.045
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.388 to 48.094
Index ranges	-14 ≤ h ≤ 14, -4 ≤ k ≤ 4, -34 ≤ l ≤ 34
Reflections collected	33432
Independent reflections	2407 [R_{int} = 0.2434, R_{sigma} = 0.1078]
Data/restraints/parameters	2407/0/218
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1159
Final R indexes [all data]	R_1 = 0.1257, wR_2 = 0.1448
Largest diff. peak/hole / e Å^{-3}	0.24/-0.24

X-Ray crystal structure of compound 10a:

Crystal of compound **10a** were obtained by dissolving the product in CH_2Cl_2 and hexane (1:1) mixture and allowing the solvent to slowly evaporate at room temperature. The crystal structure information for this compound has been deposited at the Cambridge Crystallographic Data Centre. CCDC No:2293913 contains the crystal structure information of this compound and can be obtained free of charge via http://www.ccdc.cam.ac.uk. Here, crystal **10a** has two molecules in one-unit cell.

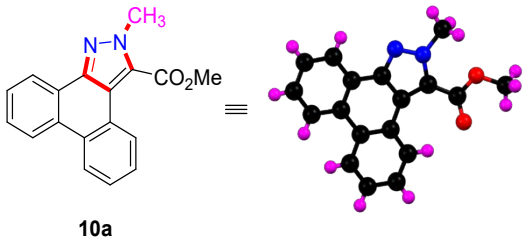


Figure 3: X-ray structure of the product **10a** with the ellipsoids drawn at the 50% probability level.

Table 1 Crystal data and structure refinement for 10a.

Identification code	10a
Empirical formula	$C_{36}H_{28}N_4O_4$
Formula weight	580.62
Temperature/K	297.00
Crystal system	triclinic
Space group	P-1

a/Å	8.8096(4)
b/Å	10.4907(5)
c/Å	16.2330(7)
α/°	94.848(2)
β/°	105.5620(10)
γ/°	90.870(2)
Volume/Å^3	1438.95(11)
Z	2
ρ_{calc}g/cm^3	1.340
μ/mm^{-1}	0.089
F(000)	608.0
Crystal size/mm^3	0.056 × 0.045 × 0.023
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.9 to 54.34
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	46378
Independent reflections	6389 [R_{int} = 0.0786, R_{sigma} = 0.0475]
Data/restraints/parameters	6389/0/402
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0675, wR_2 = 0.1766
Final R indexes [all data]	R_1 = 0.1215, wR_2 = 0.2103
Largest diff. peak/hole / e Å^{-3}	0.55/-0.40

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