Acid-Triggered Cascade Cyclization Pathways of Enynes: A Rapid Access to Fused Polycyclic Products

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Supporting Information

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Supporting Information

Experimental Section

General Methods:

IR spectra were recorded on a Bruker Tensor 37 (FTIR) spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 (400 MHz) as well as 600 (MHz) spectrometers at 295 K in $CDCl_3$; chemical shifts (δ ppm) and coupling constants (Hz) are reported in standard fashion concerning either internal standard tetramethylsilane (TMS) ($\delta H = 0.00$ ppm) or $CDCl_3$ ($\delta H = 7.26$ ppm). $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker Avance 400 (100 MHz) as well as 600 (150 MHz) spectrometer at RT in $CDCl_3$; chemical shifts (δ ppm) are reported relative to $CDCl_3$ [$\delta C = 77.00$ ppm (central line of the triplet)]. In the $^{13}C\{^{1}H\}$ NMR, the nature of carbons (C, CH, CH_2, and CH_3) was determined by recording the DEPT-135 spectra and is given in parentheses and noted as s = singlet (for C), d = doublet (for CH), t = triplet (for CH_2) and q = quartet (for CH_3). In the ^{1}H NMR, the following abbreviations were used throughout: s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, sept = septet, dd = doublet of the doublet, m = multiplet, and br. s = broad singlet. The assignment of signals was confirmed by ^{1}H, $^{13}C\{^{1}H\}$ CPD, and DEPT spectra. High-resolution mass spectra (HR-MS) were recorded on an Agilent 6538 UHD Q-TOF electron spray ionization (ESI) mode and atmospheric pressure chemical ionization (APCI) modes. All small-scale reactions were carried out by using a Schlenk tube. Reactions were monitored by TLC on silica gel using a combination of hexane and ethyl acetate as eluents. Solvents were distilled before use; a 60−80 °C boiling range of petroleum ether was used. $Pd(OAc)_2$, Et_3N, K_2CO_3, CuI, PPh_3, TfOH were purchased from Sigma-Aldrich and used as received. 2-Formyl-phenyl-boronic acids, 1-iodo-2-bromobenzenes, (2-(ethoxycarbonyl)phenyl)boronic acid, and phenyl acetylenes were purchased from BLD and were used as purchase. DMF, DCE, and Toluene were purchased from Avra and SRL and were used as they were received. Acme's silica gel (60−120 mesh) was used for column chromatography (approximately 20 g per 1 g of crude material).

The following 1-iodo-2-bromobenzenes derivatives **6a-6h** (Table-S1) are purchased and used as received.

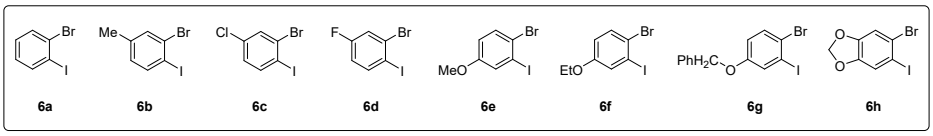


Table-S1: 1-Iodo-2-bromobenzenes **6a-6h**.

The following phenyl acetylenes **7a-7l** (Table-S2) are purchased and used as received.

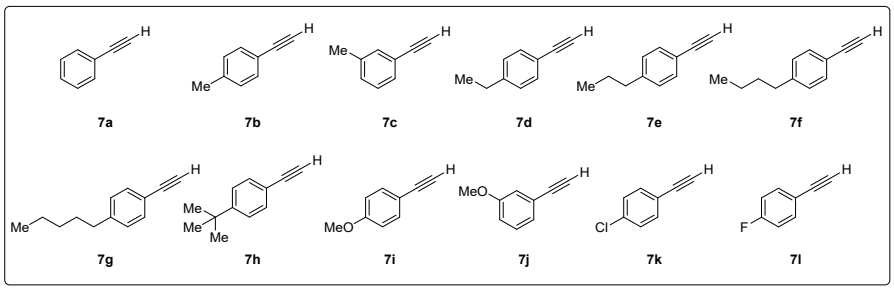


Table-S2: 1-Iodo-2-bromobenzenes **7a-7l**.

The following 1-bromo-2-(phenylethynyl)benzenes **8a-8aa** (Table-S3) are known in the literature except (**8m**, **8n**, **8q-8t**, & **8w-8z**) and were prepared according to the previous literature reports.[1]

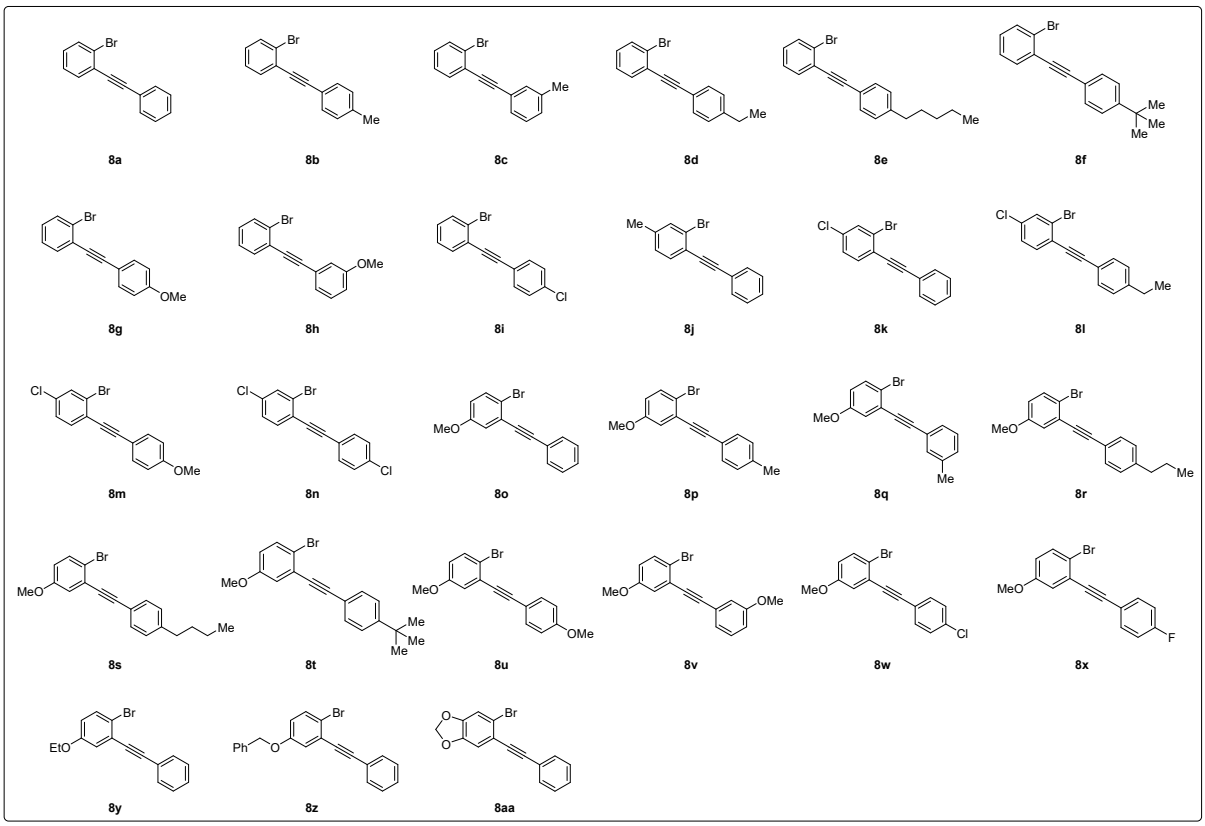


Table-S3: 1-Bromo-2-(phenylethynyl)benzenes **8a-8aa**.

The following boronic acids **9a-9d** (Table-S4) are purchased and used as received.

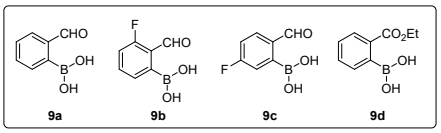
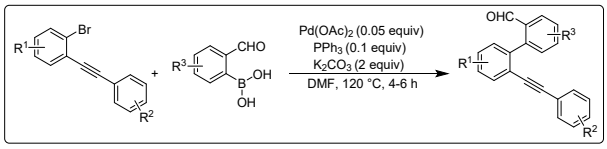


Table-S4: Boronic acids **9a-9d**.



Scheme S1: 2'-(Phenylethynyl)-[1,1'-biphenyl]-2-carbaldehydes **10**.

The following 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehydes **10a-10ac** (Table-S5) are known in the literature except (**10c-10f**, **10l-10n**, & **10p-10ac**) and were prepared according to the previous literature reports.[2,3]

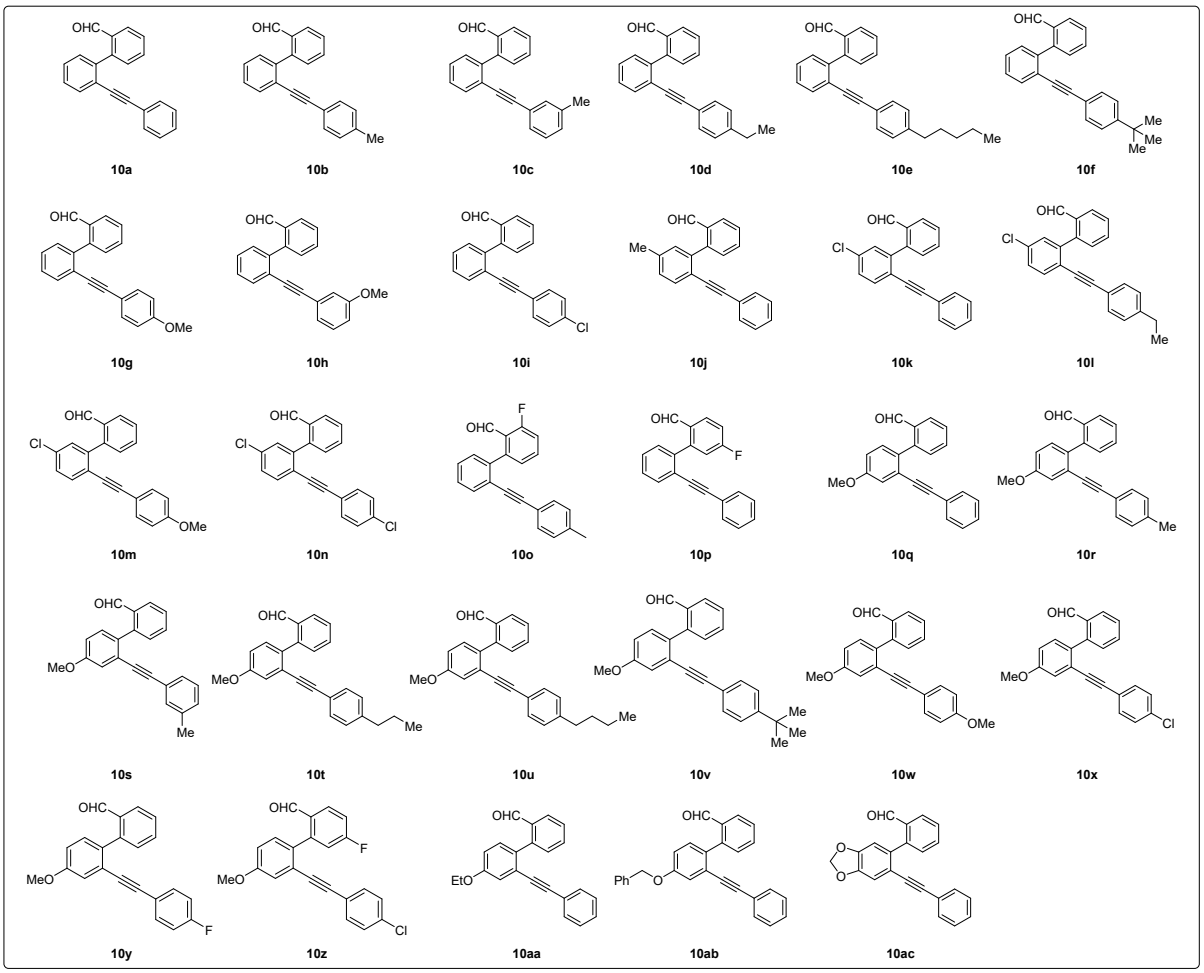
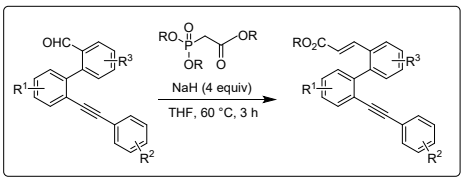


Table-S5: 2'-(Phenylethynyl)-[1,1'-biphenyl]-2-carbaldehydes **10a-10ac**.



Scheme S2: Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1**.

The following ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1a-1ah** (Table-S6) were prepared according to the previous literature reports.[4]

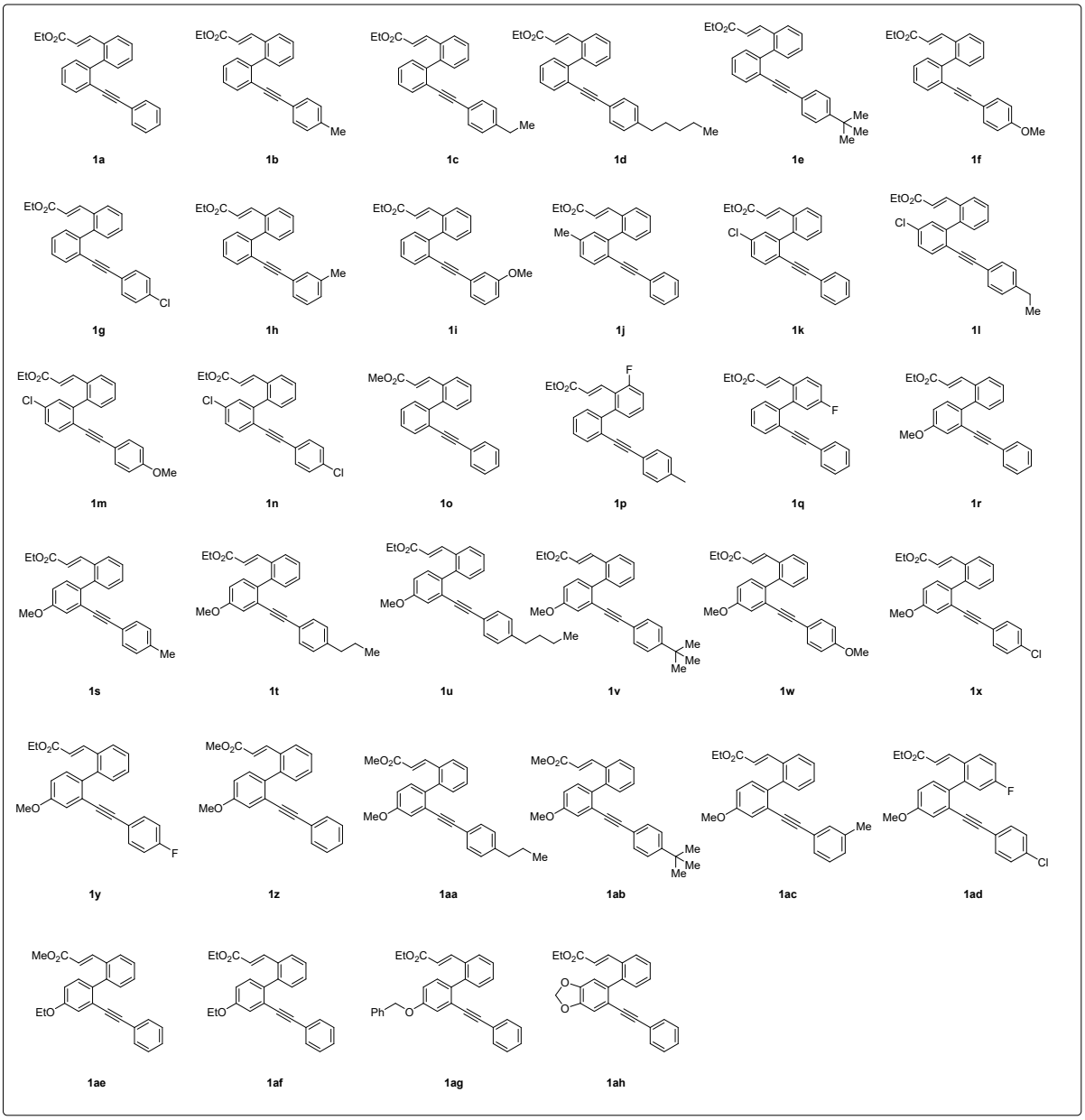
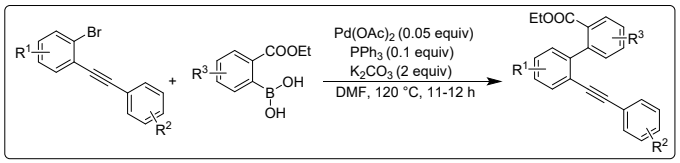


Table-S6: Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1a-1ah**.



Scheme S3: Ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylates **11**.

The following ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylates derivatives **11a-11e** (Table-S7) were prepared according to the previous literature reports.

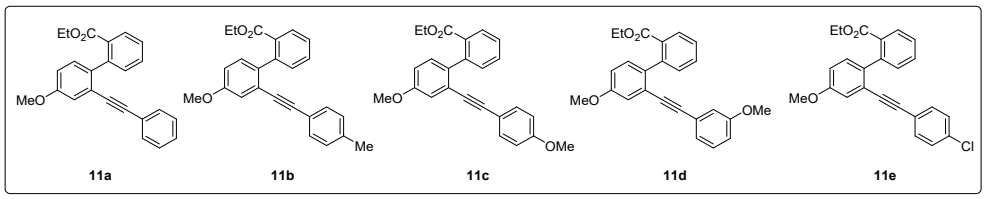
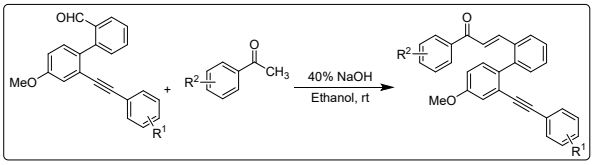


Table-S7: Ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylates **11a-11e**.



Scheme S4: 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethan-1-ones **12**.

The following 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethan-1-ones **12a-12e** (Table S8) were prepared according to the previous literature reports.

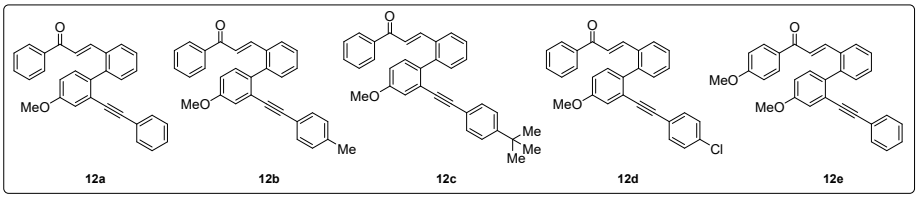


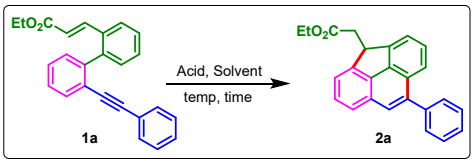
Table-S8: 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethan-1-one **12a-12e**.

Screening Conditions for the formation of 2a:

To begin with, ethyl(*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate **1a** was chosen as a model substrate, (for details, see the ESI, Schemes S1 & S2). Primarily, the synthesized precursor **1a** was subjected to acidic conditions with $ZnCl_2$ in DCE solvent at 80 °C; unfortunately, there was no sign of any product formation (Table S9, entry 1). However, as the temperature elevated to 100 °C and 120 °C, to our delight, product **2a** obtained with 15% and 40% yield, respectively (Table S9, entries 2 & 3); herein, the product **2a** formation is realized, *via* intramolecular 6-*endo-dig* and 5-*exo-trig* cyclization pathways on alkyne and enoate

moieties, respectively. Further, when ZnI_2 was employed as the Lewis acid, the yield of **2a** improved to 50% (Table S9, entry 4). Additionally, the reaction was also screened with strong Lewis acids, such as $AlCl_3$, and $FeCl_3$, but the results were not satisfactory (Table S9, entries 5 & 6). Furthermore, a variety of other acids [e.g., $Sc(OTf)_3$, $In(OTf)_3$, & $Yb(OTf)_3$] were examined as promoters; among them, $In(OTf)_3$ was found to be superior in furnishing the product **2a** in a moderate yield of 52% (Table S9, entries 7-9). While the reaction using $BF_3{\cdot}OEt_2$ at 100 °C for 4 h, produced the desired product **2a** with a declined yield of 40% (Table S9, entry 10). Delightfully, yields of **2a** were improved to 68% and 70% on subjecting the reactions by employing *p*-TSA·H_2O and CH_3SO_3H at 100 °C for 12 h (Table S9, entries 11 & 12). There was no further improvement in the yield of **2a** was observed when the reactions were explored with BCl_3 and TFA (Table S9, entries 13 & 14). Gratifyingly, the reaction of **1a** using TfOH (1 equiv) at 100 °C for 1 h afforded the desired product **2a** with a very good yield of 84% (Table S9, entry 15). In addition, the reactions in the presence of TfOH in different solvents, like THF, ACN, and 1,4-dioxane, were found to be less effective compared to DCE in producing product **2a** (Table S9, entries 16–18).

Table S9: Optimizing conditions for the synthesis of **2a**.[a,b]



S. No.	Acid (1 equiv)	Solvent (1 mL)	Temp (°C)	Time (h)	Yield **2a**[b] (%)
1	$ZnCl_2$	DCE	80	12	-
2	$ZnCl_2$	DCE	100	12	15
3	$ZnCl_2$	DCE	120	12	40
4	ZnI_2	DCE	120	12	50
5	$AlCl_3$	DCE	100	3	41
6	$FeCl_3$	DCE	100	3	50
7	$Sn(OTf)_3$	DCE	100	12	10
8	$In(OTf)_3$	DCE	100	12	52
9	$Yb(OTf)_3$	DCE	100	12	-
10	$BF_3{\cdot}OEt_2$	DCE	100	4	40
11	*p*-TSA·H_2O	DCE	100	12	68
12	CH_3SO_3H	DCE	100	12	70
13	BCl_3	DCE	100	12	40
14	TFA	DCE	100	12	65
15	**TfOH**	**DCE**	**100**	**1**	**84**
16	TfOH	THF	100	10	65
17	TfOH	ACN	100	5	70
18	TfOH	1,4-	100	12	60

		Dioxane			

Reaction conditions: [a]Reactions were carried out with 35 mg (0.1 mmol) of ethyl(*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate **1a** in DCE solvent (1 mL). [b]Isolated yields of the product **2a**.

Experimental:

General Procedure - 1 (GP-1) for the Preparation of 8m, 8n, 8q-8t, and 8w-8z:

To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-iodo-2-bromobenzene **6** (313–389 mg, 1 mmol), phenylacetylene **7** (112–174 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL) at room temperature. The resultant reaction mixture was subjected to an oil bath at 100 °C for 10-15 min; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), furnished the product **8m**, **8n**, **8q-8t**, and **8w-8z** (92–96%) as coloured solid/viscous oil.

General Procedure - 2 (GP - 2) for the Preparation of 10c-10f and 10l-10ac:

To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzene **8** (217–291 mg, 0.8 mmol), 2-formylphenylboronic acid **9** (135–151 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL) at room temperature under nitrogen atmosphere. The resultant reaction mixture was subjected to an oil bath at 120 °C for 4-6 h; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), furnished the product **10c-10f** and **10l-10ac** (55–85%) as coloured solid/viscous oil.

General Procedure - 3 (GP-3) for the Preparation of 11a-11e:

To an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8** (230–257 mg, 0.8 mmol), (2-(ethoxycarbonyl)phenyl)boronic acid

9d (174 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_3PO_4 (339.2 mg, 1.6 mmol) in DMF (1 mL) at room temperature under nitrogen atmosphere. The resultant reaction mixture was subjected to an oil bath at 120 °C for 11-12 h; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3 × 10 mL). The organic layers were washed with saturated NaCl solution, dried (Na_2SO_4) and filtered. Evaporation of the solvent(s) under reduced pressure and purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate), furnished the product **11a-11e** (45–50%) as yellow solid/semi solid.

General Procedure - 4 (GP-4) for the Preparation of 1a-1ah:

To an oven-dried round-bottomed flask equipped with a magnetic stir bar under nitrogen atmosphere, were added NaH (57.6 mg, 2.4 mmol) and anhydrous THF (1 mL) at 0 ℃ and stirred for 2 min. To the resultant solution at 0 ℃, was added the phosphonate reagent (538 and 504, 2.4 mmol) dropwise until the effervescence was stopped and golden-colored clear ylide solution was generated; the solution was continued to stir for 10 min at the same temperature. To the ylide reagent at 0 ℃, was added the solution of 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehydes **10** (169-233 mg, 0.6 mmol) in dry THF (0.5 mL) under nitrogen atmosphere. The resultant reaction mixture was subjected to an oil bath at 60 ℃ for 3 h; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **1a-1ah** (68-89%), coloured solid/viscous oil.

General Procedure - 5 (GP-5) for the Preparation of (2a-2i, and 3a-3o): To a solution of ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate **1** (101-131 mg, 0.3 mmol) in a Schlenk tube in dichloroethane solvent (1 mL), was added TfOH (45 mg, 0.3 mmol) under open air atmosphere. The resultant reaction mixture was subjected to an oil bath at 100 ℃ for 1-2 h; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude

material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **2a-2i**/**3a-3o** (70-93%) as coloured solid/viscous oil.

General Procedure - 6 (GP-6) for the Preparation of (4a-4e): To a solution of ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate **11** (107-117 mg, 0.3 mmol) in a Schlenk tube in dichloroethane solvent (1 mL), was added TfOH (67.5 mg, 0.45 mmol) under open-air atmosphere. The resultant reaction mixture was subjected to an oil bath at 100 ℃ for 6-8 h; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **4a-4e** (50-70%) as a maroon/purple solid.

General Procedure - 7 (GP-7) for the Preparation of (12a-12e): To a solution of 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10** (187-221 mg, 0.6 mmol) in a Schlenk tube in ethanol solvent (1 mL), was added acetophenone and 4-methoxy acetophenone (84 mg and 105 mg, 0.7 mmol) under open-air atmosphere and allowed the reaction mixture to stir at room temperature for 5 min. followed by the addition of 40 % NaOH solution in water dropwise; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **12a-12e** (65-70%), as coloured solid/viscous oil.

General Procedure - 8 (GP-8) for the Preparation of (5a-5e): To a solution of 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethan-1-one **12** (124-141 mg, 0.3 mmol) in a Schlenk tube in dichloroethane solvent (1 mL), was added TfOH (45 mg, 0.3 mmol) under open-air atmosphere. The resultant reaction mixture was subjected to an oil bath at 100 ℃ for 10 min-1 h; the progress of the reaction was monitored by TLC till the reaction was completed. The mixture was cooled to room temperature, quenched with aqueous ammonium chloride, and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the

crude material by silica gel column chromatography (petroleum ether/ethyl acetate) furnished the product **5a-5e** (56-67%), as coloured solid/viscous oil.

Absorption and fluorescence studies of 2f, 2n, 3f, 3m, 4c, & 4e:

Additionally, UV-visible absorption and fluorescence measurements were conducted for three classes of products (**2f**, **2n**, **3f**, **3m**, **4c**, & **4e**) in chloroform ($CHCl_3$). The absorption spectra of compounds **2f** and **2n** exhibit absorption maxima (λ_{max}) at 260 nm, within the range of 250–350 nm (Figure S1a). For compounds **3f** and **3m**, the absorption maxima are observed at 271 nm, with a broader absorption range of 250–400 nm (Figure S1b). In the case of compounds **4c** and **4e**, the absorption maxima are centered at 253 nm, within the 250–450 nm range (Figure S1c). These results demonstrate a red shift in the absorption range as the conjugation within the molecular structure increases. Notably, the installation of electron-withdrawing groups versus electron-donating groups does not significantly influence the absorption properties. Also, the fluorescence spectra for these compounds (Figure S1d, S1e, & S1f) reveal a similar trend, where the emission behavior aligns with the absorption characteristics. Overall, the UV-Vis. and fluorescence studies highlight that these phenanthrene derivatives are strong UV-Vis. absorbers, demonstrating promising properties for applications such as photocatalysis, optical devices, etc.

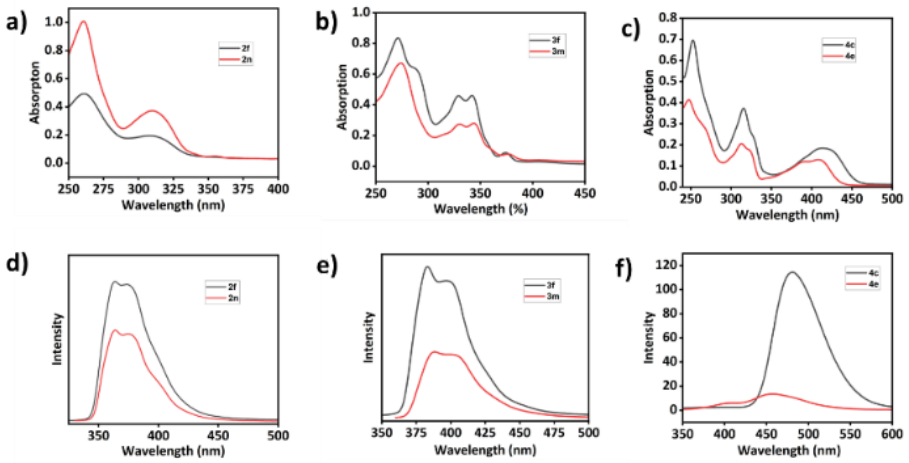
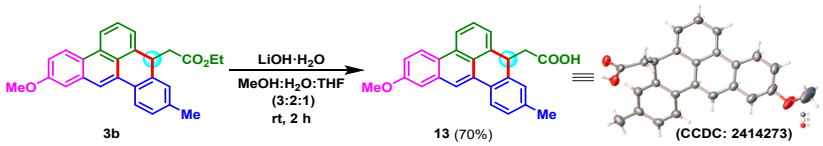


Figure S1: Electronic (a, b, & c) absorption, (d, e, & f) fluorescence spectra of **2f**, **2n**, **3f**, **3m**, **4c**, & **4e**.

Scheme S5: Hydrolysis of the ester **3b** to give **13**.[a,b]



Reaction conditions: [a]Compound **3b** (0.2 mmol), $LiOH·H_2O$ (0.3 mmol) in MeOH:H_2O:THF (3:2:1) (5 mL), rt, 2 h. [b]Isolated yield of **13**.

Synthesis of 2-(2-methoxy-10-methyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetic acid (13):

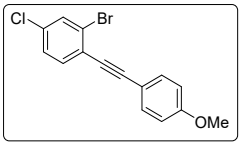
To an oven-dried round-bottomed flask equipped with a magnetic stir bar, were added ethyl 2-(2-methoxy-10-methyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetate **3b** (79 mg, 0.2 mmol) and $LiOH·H_2O$ (25 mg, 0.6 mmol) in MeOH:H_2O:THF (3:2:1) (5 mL) ratio under open air atmosphere and allowed the reaction mixture to stir at room temperature for 2 h. Completion of the reaction was monitored by TLC until the reaction is complete.; then MeOH was removed under reduced pressure. The reaction mixture was quenched with aqueous ammonium chloride and extracted with DCM (3×15 mL). The separated aqueous layer was acidified with 15% hydrochloric acid to pH = 2.0, The collected filtrate was extracted with DCM (2 × 15 mL); the organic layers were washed with saturated NaCl solution, dried (Na_2SO_4), and filtered. Removing the solvent from the combined fractions under reduced pressure, furnished the acid product 13 (51.5 mg, 70%), as brown solid; mp = 60–62 °C.

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3464, 2923, 2851, 1735, 1457, 1245, 1030, 829 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 9.1 Hz, 1H), 8.49 (d, J = 7.4 Hz, 1H), 8.24 (s, 1H), 8.04 (d, J = 8.1 Hz, 1H), 7.65 – 7.52 (m, 2H), 7.33 (d, J = 2.6 Hz, 1H), 7.30 (s, 1H), 7.26 – 7.21 (m, 2H), 4.86 (t, J = 7.1 Hz, 1H), 3.99 (s, 3H), 2.72 (dd, J = 15.0, 6.6 Hz, 1H), 2.59 (dd, J = 15.0, 7.6 Hz, 1H), 2.41 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 157.4, 136.9, 136.7, 135.6, 132.5, 129.6, 128.2, 127.9, 127.9, 127.3, 125.7, 124.4, 123.7, 123.5, 123.2, 123.1, 119.7, 118.2, 115.8, 107.7, 54.3, 40.8, 28.6, 20.1 ppm

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{25}H_{20}KO_3]^+$ 407.1044; found 407.1043.



2-Bromo-4-chloro-1-((4-methoxyphenyl)ethynyl)benzene (8m):

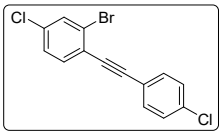
GP-1 was carried out with 1-iodo-2-bromobenzene **6c** (317 mg, 1 mmol), phenylacetylene **7i** (145 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8m** (295.9 mg, 92%), as brown solid; mp = 68–70 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6c**) = 0.7, R_f(**8m**) = 0.5, R_f(**7i**) = 0.6 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3052, 2837, 2216, 1603, 1507, 1246, 1027, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, J = 2.1 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.30 (d, J = 8.3 Hz, 1H), 7.11 (dd, J = 8.3, 2.1 Hz, 1H), 6.79 – 6.72 (m, 2H), 3.68 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 133.9, 133.3, 133.1 (2C), 132.0, 127.3, 125.7, 124.2, 114.5, 113.9 (2C), 95.0, 85.9, 55.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{15}H_{11}Br^{79}ClO]^+$ 320.9676; found 320.9692; calcd for $[C_{15}H_{11}Br^{81}ClO]^+$ 322.9656; found 322.9666.



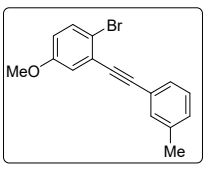
2-Bromo-4-chloro-1-((4-chlorophenyl)ethynyl)benzene (8n):

GP-1 was carried out with 1-iodo-2-bromobenzene **6c** (317 mg, 1 mmol), phenylacetylene **7k** (150 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **8n** (309.7 mg, 95%), as colourless solid; mp = 80–82 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**6c**) = 0.7, R_f(**8n**) = 0.6, R_f(**7k**) = 0.8 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3054, 2360, 1740, 1492, 1263, 1092, 827, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 2.1 Hz, 1H), 7.46 – 7.42 (m, 2H), 7.40 (d, J = 8.3 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.22 (dd, J = 8.4, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.9, 134.7, 133.6, 132.8 (2C), 132.3, 128.8 (2C), 127.5, 125.9, 123.7, 121.0, 93.6, 87.9 ppm.



1-Bromo-4-methoxy-2-(*m*-tolylethynyl)benzene (8q):

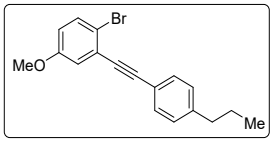
GP-1 was carried out with 1-iodo-2-bromo benzene **6e** (313 mg, 1 mmol), phenylacetylene **7c** (128 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8q** (289 mg, 96%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6e**) = 0.5, R_f(**8q**) = 0.4, R_f(**7c**) = 0.9 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3007, 2929, 1580, 1457, 1232, 1113, 1015, 786 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.9 Hz, 1H), 7.41 (d, J = 8.5 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 3.0 Hz, 1H), 6.76 (dd, J = 8.9, 3.1 Hz, 1H), 3.80 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 138.0, 133.0, 132.2, 129.6, 128.8, 128.2, 125.9, 122.5, 117.6, 116.4, 116.2, 93.9, 87.7, 55.5, 21.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{16}H_{14}Br^{79}O]^+$ 301.0223; found 301.0230; calcd for $[C_{16}H_{14}Br^{81}O]^+$ 303.0202; found 303.0214.



1-Bromo-4-methoxy-2-((4-propylphenyl)ethynyl)benzene (8r):

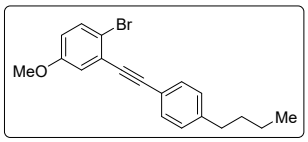
GP-1 was carried out with 1-iodo-2-bromobenzene **6e** (313 mg, 1 mmol), phenylacetylene **7e** (159 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8r** (309 mg, 94%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6e**) = 0.5, R_f(**8r**) = 0.4, R_f(**7e**) = 0.9 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2955, 2862, 1578, 1458, 1223, 1114, 1050, 806 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, J = 11.8, 8.5 Hz, 3H), 7.17 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 3.0 Hz, 1H), 6.75 (dd, J = 8.9, 3.0 Hz, 1H), 3.80 (s, 3H), 2.63 – 2.58 (m, 2H), 1.65 (dq, J = 14.8, 7.4 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 143.7, 132.9, 131.6 (2C), 128.5 (2C), 126.1, 119.9, 117.6, 116.3, 116.2, 93.9, 87.5, 55.5, 37.9, 24.3, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{18}H_{18}Br^{79}O]^+$ 329.0536; found 329.0536; calcd for $[C_{18}H_{18}Br^{81}O]^+$ 331.0515; found 331.0532.



1-Bromo-2-((4-butylphenyl)ethynyl)-4-methoxybenzene (8s):

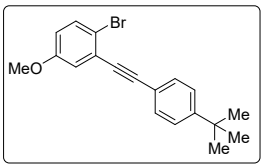
GP-1 was carried out with 1-iodo-2-bromobenzene **6e** (313 mg, 1 mmol), phenylacetylene **7f** (174 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8s** (316 mg, 92%), as yellow solid; mp = 58–60 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6e**) = 0.5, R_f(**8s**) = 0.4, R_f(**7f**) = 0.9 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 1579, 1460, 1224, 1115, 1016, 811, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 3H), 7.18 (d, J = 8.1 Hz, 2H), 7.08 (d, J = 3.0 Hz, 1H), 6.75 (dd, J = 8.9, 3.1 Hz, 1H), 3.80 (s, 3H), 2.67 – 2.57 (m, 2H), 1.66 – 1.54 (m, 2H), 1.36 (dq, J = 14.6, 7.3 Hz, 2H), 0.94 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 143.9, 132.9, 131.6 (2C), 128.5 (2C), 126.1, 119.9, 117.6, 116.3, 116.3, 93.9, 87.5, 55.5, 35.6, 33.4, 22.3, 13.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{20}Br^{79}O]^+$ 343.0692; found 343.0710; calcd for $[C_{19}H_{20}Br^{81}O]^+$ 345.0672; found 345.0696.



1-Bromo-2-((4-(*tert*-butyl)phenyl)ethynyl)-4-methoxybenzene (8t):

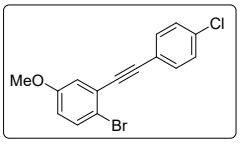
GP-1 was carried out with 1-iodo-2-bromobenzene **6e** (313 mg, 1 mmol), phenylacetylene **7h** (174 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8t** (329 mg, 96%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6e**) = 0.5, R_f(**8t**) = 0.4, R_f(**7h**) = 0.9 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2959, 1730, 1580, 1462, 1319, 1263, 1053, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 – 7.50 (m, 2H), 7.47 (d, J = 8.9 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.08 (d, J = 3.1 Hz, 1H), 6.75 (dd, J = 8.9, 3.1 Hz, 1H), 3.80 (s, 3H), 1.33 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 152.0, 133.0, 131.4 (2C), 126.1, 125.4 (2C), 119.7, 117.6, 116.3, 116.3, 93.9, 87.4, 55.5, 34.8, 31.1 (3C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{19}H_{20}Br^{79}O]^+$ 343.0692; found 343.0698; calcd for $[C_{19}H_{20}Br^{81}O]^+$ 345.0672; found 345.0680.



1-Bromo-2-((4-chlorophenyl)ethynyl)-4-methoxybenzene (8w):

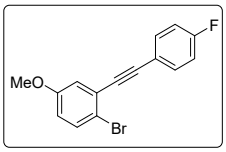
GP-1 was carried out with 1-iodo-2-bromobenzene **6e** (313 mg, 1 mmol), phenylacetylene **7k** (150 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8w** (302 mg, 94%), as off-white solid; mp = 52–54 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6e**) = 0.5, R_f(**8w**) = 0.4, R_f(**7k**) = 0.8 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2944, 2838, 1738, 1578, 1476, 1222, 1051, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 3H), 7.36 – 7.32 (m, 2H), 7.07 (d, J = 3.0 Hz, 1H), 6.77 (dd, J = 8.9, 3.1 Hz, 1H), 3.81 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 134.7, 133.0, 132.8 (2C), 128.7 (2C), 125.5, 121.2, 117.7, 116.6, 116.2, 92.4, 88.9, 55.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{15}H_{11}Br^{79}ClO]^+$ 320.9676; found 320.9650; calcd for $[C_{25}H_{19}Br^{79}ClO]^+$ 322.9656; found 322.9631.



1-Bromo-2-((4-fluorophenyl)ethynyl)-4-methoxybenzene (8x):

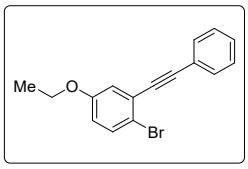
GP-1 was carried out with 1-iodo-2-bromobenzene **6e** (313 mg, 1 mmol), phenylacetylene **7l** (132 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8x** (281 mg, 92%), as orange solid; mp = 60–62 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6e**) = 0.5, R_f(**8x**) = 0.4, R_f(**7l**) = 0.8 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2943, 2839, 1581, 1460, 1319, 1219, 1030, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 2H), 7.46 (d, J = 8.9 Hz, 1H), 7.08 – 7.02 (m, 3H), 6.75 (dd, J = 8.9, 3.1 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7 (d, J = 250.3 Hz), 158.4, 133.6 (d, J = 8.4 Hz) (2C), 133.0, 125.7, 118.8 (d, J = 3.5 Hz), 117.7, 116.5, 116.2, 115.8 (d, J = 22.1 Hz) (2C), 92.5, 87.7, 55.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{15}H_{11}Br^{79}FO]^+$ 304.9972; found 304.9972; calcd for $[C_{15}H_{11}Br^{81}FO]^+$ 306.9951; found 306.9949.



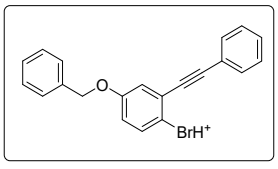
1-Bromo-4-ethoxy-2-(phenylethynyl)benzene (8y):

GP-1 was carried out with 1-iodo-2-bromobenzene **6f** (327 mg, 1 mmol), phenylacetylene **7a** (112 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8y** (286 mg, 95%), as brown solid; mp = 42–44 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6f**) = 0.5, R_f(**8y**) = 0.4, R_f(**7a**) = 0.9 UV 7detection]. **IR** (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3063, 2978, 1580, 1457, 1219, 1154, 1023, 749 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.47 (d, J = 8.9 Hz, 1H), 7.38 – 7.36 (m, 3H), 7.08 (d, J = 3.0 Hz, 1H), 6.76 (dd, J = 8.9, 3.0 Hz, 1H), 4.02 (q, J = 7.0 Hz, 2H), 1.42 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 133.0, 131.7 (2C), 128.6, 128.3 (2C), 125.8, 122.8, 118.3, 117.0, 116.1, 93.5, 88.1, 63.8, 14.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{16}H_{14}Br^{79}O]^+$ 301.0223; found 301.0209; calcd for $[C_{16}H_{14}Br^{81}O]^+$ 303.0202; found 303.0194.



4-(Benzyloxy)-1-bromo-2-(phenylethynyl)benzene (8z):

GP-1 was carried out with 1-iodo-2-bromobenzene **6g** (389 mg, 1 mmol), phenylacetylene **7a** (112 mg, 1.1 mmol), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), PPh_3 (10.5 mg, 0.04 mmol), CuI (3.8 mg, 0.02 mmol), Et_3N (404 mg, 4 mmol), and toluene (0.5 mL). Purification of the crude mixture

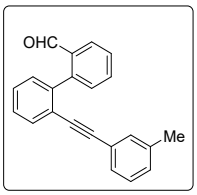
by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **8z** (345 mg, 95%), as yellow solid; mp = 50–52 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**6g**) = 0.5, R_f(**8z**) = 0.4, R_f(**7a**) = 0.9 UV 7detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3035, 2871, 1885, 1579, 1216, 1153, 1010, 739 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (ddd, J = 4.7, 2.3, 1.6 Hz, 2H), 7.36 (d, J = 8.9 Hz, 1H), 7.32 – 7.22 (m, 8H), 7.07 (d, J = 3.0 Hz, 1H), 6.71 (dd, J = 8.9, 3.0 Hz, 1H), 4.92 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 136.2, 133.0, 131.7 (2C), 128.7, 128.6 (2C), 128.3 (2C), 128.1, 127.4 (2C), 125.9, 122.7, 118.7, 117.2, 116.6, 93.7, 88.0, 70.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{21}H_{16}Br^{79}O]^+$ 363.0379; found 363.0384; calcd for $[C_{21}H_{16}Br^{81}O]^+$ 365.0359 ; found 365.0367.



2'-(*m*-tolylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10c):

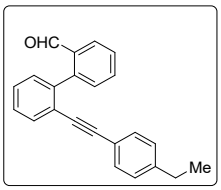
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8c** (217 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10c** (189.7 mg, 80%), as yellow viscous oil. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8c**) = 0.8, R_f(**10c**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2847, 2750, 1694, 1646, 1270, 1187, 756, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (d, J = 0.7 Hz, 1H), 8.10 (dd, J = 7.8, 1.2 Hz, 1H), 7.76 – 7.61 (m, 2H), 7.61 – 7.51 (m, 1H), 7.48 – 7.42 (m, 3H), 7.42 – 7.37 (m, 1H), 7.13 (dd, J = 7.5, 7.5 Hz, 1H), 7.07 (d, J = 7.6 Hz, 1H), 6.99 (dd, J = 9.7, 4.0 Hz, 2H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 144.3, 140.2, 137.8, 134.1, 133.4, 131.9, 131.8, 131.2, 130.2, 129.3, 128.3, 128.3, 128.1, 128.1, 128.1, 126.8, 123.7, 122.4, 93.9, 87.8, 21.1 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{17}O]^+$ 297.1274; found 297.1293.



2'-((4-Ethylphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10d):

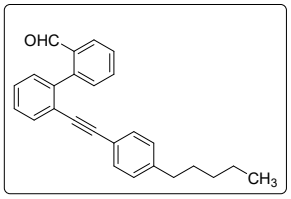
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8d** (228 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10d** (201 mg, 81%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8d**) = 0.8, R_f(**10d**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3058, 2855, 1693, 1596, 1262, 1193, 828, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (d, J = 0.9 Hz, 1H), 8.10 (dd, J = 7.8, 1.2 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.38 (m, 4H), 7.14 – 7.05 (m, 4H), 2.61 (q, J = 7.6 Hz, 2H), 1.20 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 144.8, 144.3, 140.1, 134.2, 133.4, 131.8, 131.2 (2C), 131.2, 130.2, 128.2 (2C), 128.1, 128.1, 127.8, 126.7, 123.9, 119.8, 94.0, 87.5, 28.8, 15.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{19}O]^+$ 311.1430; found 311.1436.



2'-((4-Pentylphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10e):

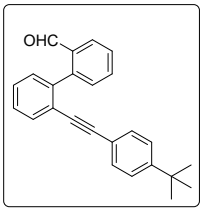
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8e** (262 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10e** (217 mg, 77%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8e**) = 0.8, R_f(**10e**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2854, 1692, 1595, 1269, 1193, 829, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (d, J = 0.7 Hz, 1H), 8.09 (dd, J = 7.8, 1.2 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.59 – 7.51 (m, 1H), 7.48 – 7.38 (m, 4H), 7.11 – 6.96 (m, 4H), 2.64 – 2.41 (m, 2H), 1.62 – 1.54 (m, 2H), 1.35 – 1.23 (m, 4H), 0.92 – 0.83 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 144.4, 143.6, 140.1, 134.2, 133.4, 131.9, 131.2, 131.1 (2C), 130.2, 128.3 (2C), 128.2, 128.1 (2C), 126.8, 123.9, 119.7, 94.1, 87.5, 35.8, 31.3, 30.8, 22.5, 13.9 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{24}NaO]^+$ 375.1719; found 375.1721.



2'-((4-(*tert*-Butyl)phenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10f):

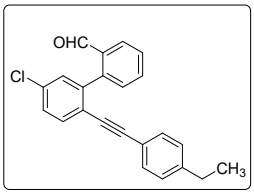
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8f** (250 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10f** (203 mg, 75%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8f**) = 0.8, R_f(**10f**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2959, 2862, 1693, 1655, 1265, 1159, 828, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (d, J = 0.7 Hz, 1H), 8.08 (dd, J = 7.8, 1.3 Hz, 1H), 7.69 – 7.59 (m, 2H), 7.56 – 7.49 (m, 1H), 7.44 – 7.36 (m, 4H), 7.26 – 7.21 (m, 2H), 7.09 (d, J = 8.6 Hz, 2H), 1.26 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 151.7, 144.4, 140.1, 134.2, 133.4, 131.8, 131.2 (2C), 130.9, 130.2, 128.2, 128.1 (2C), 126.8, 125.2 (2C), 123.9, 119.6, 93.9, 87.5, 34.7, 31.1 (3C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{23}O]^+$ 339.1743; found 339.1749.



5'-Chloro-2'-((4-ethylphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10l):

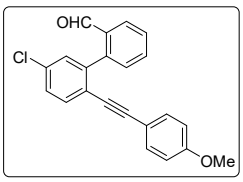
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8l** (256 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10l** (215 mg, 78%), as brown solid; mp = 62–64 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8l**) = 0.8, R_f(**10l**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2965, 2857, 1695, 1456, 1190, 1097, 827, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.10 (dd, J = 7.8, 1.1 Hz, 1H), 7.68 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.43 – 7.37 (m, 3H), 7.08 (s, 4H), 2.60 (q, J = 7.6 Hz, 2H), 1.19 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 145.1, 142.8, 141.8, 134.1 (2C), 133.6, 132.8, 131.2 (2C), 131.0, 130.1, 128.6, 128.4, 127.8 (2C), 127.1, 122.5, 119.4, 94.9, 86.5, 28.8, 15.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{23}H_{17}ClNaO]^+$ 367.0860; found 367.0864.



5'-Chloro-2'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10m):

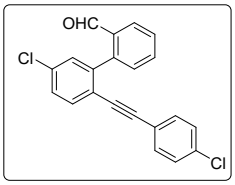
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8m** (257 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10m** (227 mg, 82%), as yellow solid; mp = 80–82 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8m**) = 0.6, R_f(**10m**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3057, 2844, 2215, 1694, 1510, 1251, 1027, 731 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.09 (dd, J = 7.8, 0.9 Hz, 1H), 7.68 (ddd, J = 7.5, 7.8, 1.2 Hz, 1H), 7.56 (dd, J = 7.9, 7.9 Hz, 2H), 7.43 – 7.38 (m, 3H), 7.11 – 7.07 (m, 2H), 6.77 (d, J = 8.8 Hz, 2H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 159.9, 142.8, 141.6, 134.1, 133.9, 133.6, 132.7 (2C), 132.7, 131.0, 130.0, 128.6, 128.4, 127.0, 122.7, 114.4, 113.9 (2C), 94.8, 86.0, 55.2 ppm.

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{22}H_{15}ClKO_2]^+$ 385.0392; found 385.0388.



4'-Chloro-2'-((4-chlorophenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10n):

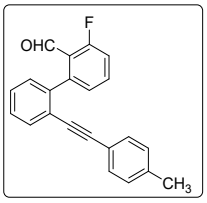
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8n** (261 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10n** (211 mg, 75%), as yellow solid; mp = 98–100 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8n**) = 0.8, R_f(**10n**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3060, 2845, 2063, 1692, 1495, 1252, 1091, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.09 (dd, J = 7.8, 1.2 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.61 – 7.54 (m, 2H), 7.41 (ddd, J = 6.5, 4.2, 1.3 Hz, 3H), 7.25 – 7.19 (m, 2H), 7.10 – 7.03 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 142.5, 141.9, 134.7, 134.6, 134.1, 133.6, 132.9, 132.4 (2C), 131.0, 130.1, 128.7, 128.6 (2C), 128.5, 127.1, 121.9, 120.7, 93.4, 88.0 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{21}H_{12}Cl_2NaO]^+$ 373.0157; found 373.0165.



3-Fluoro-2'-(*p*-tolylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10o):

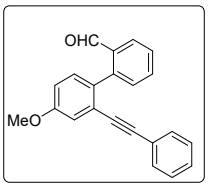
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8b** (217 mg, 0.8 mmol), 2-formylphenylboronic acid **9b** (151 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10o** (181 mg, 72%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8b**) = 0.8, R_f(**10o**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2857, 2760, 1697, 1601, 1451, 1239, 807, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 7.54 – 7.47 (m, 2H), 7.35 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 7.13 (ddd, J = 8.6, 8.6, 5.8 Hz, 2H), 7.05 – 7.01 (m, 2H), 6.98 (d, J = 8.0 Hz, 2H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.7 (d, J = 2.0 Hz), 162.2 (d, J = 262.1 Hz), 145.2 (d, J = 1.6 Hz), 139.9 (d, J = 2.4 Hz), 138.6, 134.3 (d, J = 10.2 Hz), 131.9, 131.1 (2C), 129.6, 129.0 (2C), 128.3, 128.2, 127.1 (d, J = 3.6 Hz), 123.2, 123.0 (d, J = 7.1 Hz), 119.5, 116.1 (d, J = 21.4 Hz), 94.1, 87.3, 21.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{16}FO]^+$ 315.1180; found 315.1185.



4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10q):

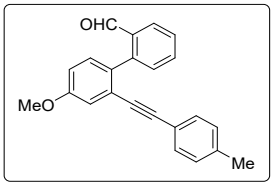
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8o** (230 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10q** (192 mg, 77%), as yellow solid; mp = 82–84 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8o**) = 0.6, R_f(**10q**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2840, 2750, 1688, 1594, 1222, 1038, 826, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (d, J = 0.6 Hz, 1H), 8.04 (dd, J = 7.8, 0.8 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.48 (dd, J = 7.6, 7.6 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.30 – 7.25 (m, 1H), 7.24 – 7.18 (m, 3H), 7.17 – 7.11 (m, 3H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 159.2, 144.0, 134.4, 133.4, 132.7, 131.5, 131.4, 131.3 (2C), 128.4, 128.2 (2C), 127.9, 126.8, 124.6, 122.5, 116.4, 115.2, 93.4, 88.2, 55.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{17}O_2]^+$ 313.1223; found 313.1229.



4'-Methoxy-2'-(*p*-tolylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10r):

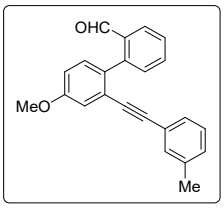
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8p** (241 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10r** (206 mg, 79%), as orange solid; mp = 96–98 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8p**) = 0.6, R_f(**10r**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2929, 2749, 1692, 1563, 1318, 1263, 1039, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.07 (dd, J = 7.8, 1.3 Hz, 1H), 7.64 (ddd, J = 7.5, 7.8, 1.4 Hz, 1H), 7.51 (dd, J = 7.6 Hz, 1H), 7.43 (dd, J = 7.6, 0.9 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.16 (d, J = 2.7 Hz, 1H), 7.10 – 7.03 (m, 4H), 7.00 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 159.2, 144.1, 138.6, 134.4, 133.3, 132.6, 131.5, 131.4, 131.1 (2C), 128.9 (2C), 127.8, 126.7, 124.8, 119.4, 116.2, 114.9, 93.7, 87.6, 55.5, 21.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{19}O_2]^+$ 327.1380; found 327.1382.



4'-Methoxy-2'-(*m*-tolylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10s):

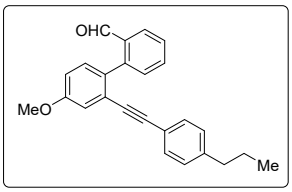
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8q** (241 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10s** (193 mg, 74%), as orange solid; mp = 64–66 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8q**) = 0.6, R_f(**10s**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3054, 2845, 1692, 1460, 1263, 1188, 1040, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.10 – 8.05 (m, 1H), 7.65 (ddd, J = 7.5, 7.4, 1.4 Hz, 1H), 7.52 (dd, J = 7.6, 7.6 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.16 (d, J = 2.6 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.07 (d, J = 7.7 Hz, 1H), 7.00 (ddd, J = 8.8, 2.7, 2.6 Hz, 3H), 3.89 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 159.2, 144.1, 137.8, 134.4, 133.3, 132.6, 131.8, 131.5, 131.4, 129.4, 128.4, 128.1, 127.8, 126.8, 124.7, 122.3, 116.3, 115.1, 93.6, 87.9, 55.48, 21.15 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{19}O_2]^+$ 327.1380; found 327.1373.



4'-Methoxy-2'-((4-propylphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10t):

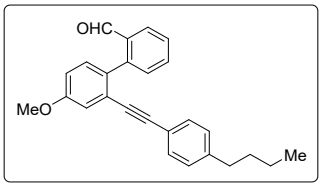
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8r** (263 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10t** (227 mg, 80%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8r**) = 0.6, R_f(**10t**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2852, 1691, 1597, 1465, 1223, 1039, 736 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.09 (dd, J = 7.8, 1.3 Hz, 1H), 7.65 (td, J = 7.5, 1.5 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.44 (dd, J = 7.6, 0.8 Hz, 1H), 7.31 (d, J = 8.5 Hz, 1H), 7.17 (d, J = 2.7 Hz, 1H), 7.12 (d, J = 8.2 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 7.00 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H), 2.55 (t, J = 7.2 Hz, 2H), 1.66 – 1.53 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 159.2, 144.1, 143.4, 134.4, 133.3, 132.6, 131.5, 131.4, 131.1 (2C), 128.4 (2C), 127.8, 126.7, 124.8, 119.7, 116.2, 114.9, 93.7, 87.6, 55.5, 37.9, 24.2, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{23}O_2]^+$ 355.1693 ; found 355.1685.



2'-((4-Butylphenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10u):

GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8s** (275 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21

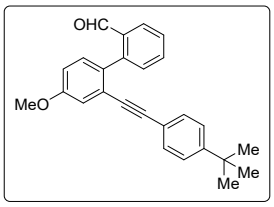
mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10u** (230 mg, 78%), as red viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8s**) = 0.6, R_f(**10u**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 2853, 1692, 1596, 1458, 1225, 1036, 821 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.07 (dd, J = 7.8, 1.3 Hz, 1H), 7.64 (ddd, J = 7.5, 7.8, 1.5 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.43 (dd, J = 7.7, 0.8 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.16 (d, J = 2.7 Hz, 1H), 7.08 (ddd, J = 8.5, 8.5, 3.1 Hz, 4H), 6.99 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H), 2.58 – 2.53 (m, 2H), 1.55 (ddd, J = 15.4, 11.0, 7.5 Hz, 2H), 1.31 (dd, J = 15.0, 7.4 Hz, 2H), 0.90 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 159.2, 144.1, 143.7, 134.4, 133.3, 132.6, 131.5, 131.4, 131.2 (2C), 128.4 (2C), 127.8, 126.8, 124.8, 119.6, 116.3, 115.0, 93.7, 87.6, 55.5, 35.5, 33.3, 22.2, 13.9 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{25}O_2]^+$ 369.1849; found 369.1848.



2'-((4-(*tert*-butyl)phenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10v):

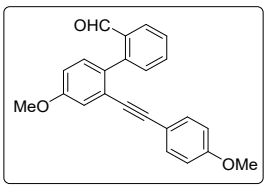
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8t** (275 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10v** (250 mg, 85%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8t**) = 0.6, R_f(**10v**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2959, 2863, 1729, 1655, 1507, 1227, 1039, 831 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.03 (dd, J = 7.8, 1.1 Hz, 1H), 7.58 (ddd, J = 7.5, 7.8, 1.4 Hz, 1H), 7.46 (dd, J = 7.6, 7.8 Hz, 1H), 7.39 – 7.35 (m, 3H), 7.23 (dd, J = 8.2, 1.3 Hz, 1H), 7.13 – 7.06 (m, 2H), 6.94 (dd, J = 8.5, 2.7 Hz, 1H), 3.82 (s, 3H), 1.23 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 159.2, 151.7, 144.1, 134.3, 133.3, 132.6, 131.5, 131.3, 130.9 (2C), 127.8, 126.7, 125.2 (2C), 124.8, 119.5, 116.2, 114.9, 93.6, 87.6, 55.4, 34.7, 31.0 (3C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{25}O_2]^+$ 369.1849; found 369.1846.



4'-Methoxy-2'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10w):

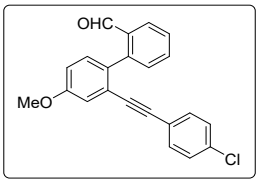
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8u** (254 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 93:7), furnished the product **10w** (214 mg, 78%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**8u**) = 0.6, R_f(**10w**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3007, 2841, 1698, 1599, 1454, 1232, 1031, 828 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.07 (d, J = 7.8 Hz, 1H), 7.64 (td, J = 7.5, 1.4 Hz, 1H), 7.50 (t, J = 7.5 Hz, 1H), 7.42 (dd, J = 7.6, 1.6 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.13 (dd, J = 8.3, 2.7 Hz, 3H), 6.98 (dd, J = 8.5, 2.7 Hz, 1H), 6.82 – 6.74 (m, 2H), 3.88 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 159.7, 159.2, 144.1, 134.4, 133.3, 132.7 (2C), 132.4, 131.5, 131.3, 127.8, 126.7, 124.9, 116.1, 114.8, 114.6, 113.9 (2C), 93.5, 87.1, 55.4, 55.2 ppm.

HRMS (ESI) *m/z*: $[M+NH_4+(-H_2O)]^+$ calcd for $[C_{22}H_{17}NO]^+$ 311.1305; found 311.1318.



2'-((4-Chlorophenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10x):

GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8w** (257 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5),

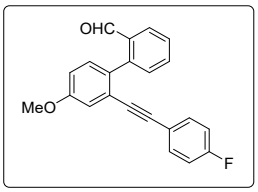
furnished the product **10x** (208 mg, 75%), as orange solid; mp = 110–112 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8w**) = 0.6, R_f(**10x**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2982, 1709, 1598, 1474, 1263, 1170, 1027, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.06 (dd, J = 7.8, 1.1 Hz, 1H), 7.65 (ddd, J = 7.5, 7.8, 1.4 Hz, 1H), 7.52 (dd, J = 7.6 Hz, 1H), 7.42 (dd, J = 7.6, 0.8 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.15 (d, J = 2.7 Hz, 1H), 7.12 – 7.08 (m, 2H), 7.02 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 159.3, 143.9, 134.5, 134.4, 133.4, 132.7, 132.4 (2C), 131.5, 131.4, 128.6 (2C), 127.9, 126.8, 124.3, 121.0, 116.3, 115.4, 92.2, 89.2, 55.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{16}ClO_2]^+$ 347.0833; found 347.0831.



2'-((4-Fluorophenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10y):

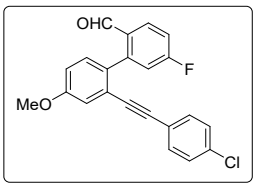
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8x** (244 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10y** (185 mg, 70%), as red solid; mp = 90–92 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8x**) = 0.6, R_f(**10y**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3062, 2842, 1690, 1504, 1220, 1039, 826, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 1H), 8.07 (dd, J = 7.8, 1.2 Hz, 1H), 7.65 (ddd, J = 7.5, 7.8, 1.4 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.42 (dd, J = 7.6, 0.8 Hz, 1H), 7.32 (d, J = 8.5 Hz, 1H), 7.19 – 7.12 (m, 3H), 7.01 (dd, J = 8.5, 2.7 Hz, 1H), 6.98 – 6.90 (m, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 162.5 (d, J = 250 Hz), 159.3, 144.0, 134.4, 133.4, 133.2 (d, J = 8.4 Hz) (2C), 132.6, 131.4 (d, J = 11.7 Hz) (2C), 127.9, 126.7, 124.4, 118.6 (d, J = 3.5 Hz), 116.3, 115.7, 115.4, 115.2, 92.3, 87.9, 55.5 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{16}FO_2]^+$ 331.1129; found 331.1130.



2'-((4-Chlorophenyl)ethynyl)-5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-carbaldehyde (10z):

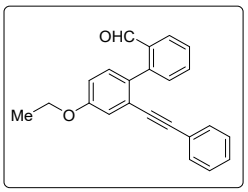
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8w** (257 mg, 0.8 mmol), 2-formylphenylboronic acid **9c** (151 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10z** (193 mg, 66%), as dark brown solid; mp = 96-98 ℃. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8w**) = 0.6, R_f(**10z**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3070, 2844, 1689, 1592, 1477, 1227, 1031, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.84 (s, 1H), 8.09 (dd, J = 8.7, 6.0 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 7.25 – 7.24 (m, 1H), 7.23 – 7.22 (m, 1H), 7.21 – 7.17 (m, 1H), 7.15 (d, J = 2.7 Hz, 1H), 7.14 (dd, J = 7.6, 2.0 Hz, 2H), 7.11 (dd, J =8.4, 2.1 Hz, 1H), 7.02 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 165.4 (d, J = 256.3 Hz), 159.6, 146.7 (d, J = 9.4 Hz), 134.7, 132.4 (2C), 131.3, 131.3, 131.0 (d, J = 2.7 Hz), 129.7 (d, J = 9.9 Hz), 128.7 (2C), 124.2, 120.8, 118.2 (d, J = 21.9 Hz), 116.6, 115.4, 115.4 (d, J = 21.8 Hz), 92.5, 88.7, 55.5 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{22}H_{14}ClFNaO_2]^+$ 387.0559; found 387.0586.



4'-Ethoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10aa):

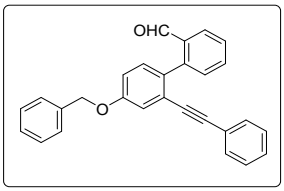
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8y** (241 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **10aa** (196 mg, 75%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8y**) = 0.6, R_f(**10aa**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2980, 2848, 1692, 1598, 1459, 1222, 1045, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H), 8.04 (dd, J = 7.8, 1.2 Hz, 1H), 7.60 (ddd, J = 7.5, 7.8, 1.4 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.39 (dd, J = 7.6, 0.8 Hz, 1H), 7.24 (s, 1H), 7.21 (d, J = 2.0 Hz, 1H), 7.20 – 7.19 (m, 1H), 7.16 – 7.10 (m, 3H), 6.95 (dd, J = 8.5, 2.7 Hz, 1H), 4.07 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 158.6, 144.1, 134.3, 133.3, 132.4, 131.5, 131.4, 131.2 (2C), 128.4, 128.2 (2C), 127.8, 126.7, 124.5, 122.5, 116.9, 115.6, 93.2, 88.3, 63.7, 14.7 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{19}O_2]^+$ 327.1380; found 327.1383.



4'-(Benzyloxy)-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (10ab):

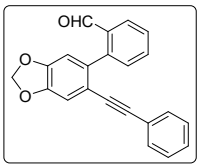
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8z** (291 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 93:7), furnished the product **10ab** (171 mg, 55%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**8z**) = 0.6, R_f(**10ab**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3057, 2899, 1692, 1496, 1264, 1150, 1036, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.03 (d, J = 7.8 Hz, 1H), 7.59 (ddd, J = 7.5, 7.6, 1.3 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.40 – 7.35 (m, 3H), 7.31 (dd, J = 8.5, 5.7 Hz, 1H), 7.24 (s, 1H), 7.23 – 7.17 (m, 4H), 7.13 (ddd, J = 7.4, 2.4, 1.5 Hz, 2H), 7.02 (dd, J = 8.5, 2.6 Hz, 1H), 5.09 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.9, 158.4, 143.9, 136.4, 134.3, 133.4, 132.9, 131.5, 131.4, 131.2 (2C), 128.7 (2C), 128.4, 128.2 (2C), 128.2, 127.9, 127.5 (2C), 126.8, 124.6, 122.5, 117.3, 115.8, 93.4, 88.2, 70.2 ppm.

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{28}H_{20}KO_2]^+$ 427.1095; found 427.1085.



2-(6-(Phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)benzaldehyde (10ac):

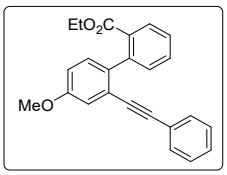
GP-2 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8aa** (241 mg, 0.8 mmol), 2-formylphenylboronic acid **9a** (135 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_2CO_3 (220.8 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 93:7), furnished the product **10ac** (183 mg, 70%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**8aa**) = 0.6, R_f(**10ac**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3062, 2907, 1694, 1474, 1223, 1037, 933, 761 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 8.07 (dd, J = 7.8, 1.2 Hz, 1H), 7.65 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.22 (dd, J = 5.1, 2.0 Hz, 3H), 7.12 (dd, J = 6.5, 3.2 Hz, 2H), 7.07 (s, 1H), 6.87 (s, 1H), 6.08 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.8, 148.1, 147.5, 144.0, 135.1, 134.4, 133.5, 131.3, 131.1 (3C), 128.2 (2C), 128.1, 126.8, 122.7, 117.1, 111.3, 110.4, 101.9, 92.1, 88.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{15}O_3]^+$ 327.1016 ; found 327.0987.



Ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate (11a):

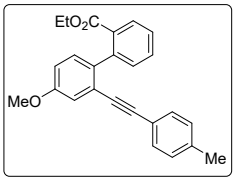
GP-3 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8o** (230 mg, 0.8 mmol), phenylboronic acid **9d** (174 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_3PO_4 (339.2 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **11a** (142 mg, 50%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8o**) = 0.7, R_f(**11a**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3062, 2975, 1714, 1560, 1406, 1279, 1088, 756 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, J = 7.8 Hz, 1H), 7.57 (td, J = 7.6, 1.2 Hz, 1H), 7.46 (dd, J = 11.0, 4.3 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.27 – 7.25 (m, 6H), 7.14 – 7.12 (m, 1H), 7.00 – 6.96 (m, 1H), 4.17 – 4.03 (m, 2H), 3.88 (s, 3H), 1.02 (td, J = 7.1, 1.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 158.4, 141.3, 137.1, 131.6, 131.5, 131.4 (2C), 131.3, 129.8, 129.8, 128.1 (2C), 128.1, 127.2, 123.1, 123.1, 116.1, 114.7, 92.1, 88.5, 60.8, 55.4, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{24}H_{21}O_3]^+$ 357.1485; found 357.1496.



Ethyl 4'-methoxy-2'-(*p*-tolylethynyl)-[1,1'-biphenyl]-2-carboxylate (11b):

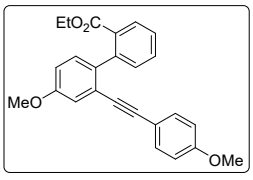
GP-3 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8p** (241 mg, 0.8 mmol), phenylboronic acid **9d** (174 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_3PO_4 (339.2 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **11b** (142 mg, 48%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8p**) = 0.7, R_f(**11b**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2930, 1714, 1599, 1457, 1227, 1040, 817, 764 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.7, 1.3 Hz, 1H), 7.55 (ddd, J = 7.5, 7.5, 1.5 Hz, 1H), 7.44 (ddd, J = 7.6, 7.6, 1.4 Hz, 1H), 7.39 – 7.33 (m, 1H), 7.23 (d, J = 8.5 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.10 (d, J = 2.7 Hz, 1H), 7.06 (d, J = 7.9 Hz, 2H), 6.95 (dd, J = 8.5, 2.7 Hz, 1H), 4.21 – 3.96 (m, 2H), 3.87 (s, 3H), 2.31 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 158.4, 141.4, 138.2, 137.1, 131.6, 131.5, 131.3 (2C), 131.3, 129.8, 129.7, 128.9 (2C), 127.2, 123.3, 120.0, 115.9, 114.6, 92.3, 87.9, 60.8, 55.38, 21.46, 13.71 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{23}O_3]^+$ 371.1642; found 371.1645.



Ethyl 4'-methoxy-2'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (11c):

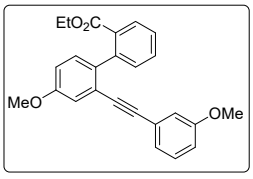
GP-3 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8u** (254 mg, 0.8 mmol), phenylboronic acid **9d** (174 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_3PO_4 (339.2 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 93:7), furnished the product **11c** (139 mg, 45%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**8u**) = 0.7, R_f(**11c**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2937, 1715, 1600, 1509, 1284, 1093, 825, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 7.8, 1.3 Hz, 1H), 7.59 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.48 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 7.39 (dd, J = 7.6, 1.1 Hz, 1H), 7.31 – 7.21 (m, 3H), 7.13 (d, J = 2.7 Hz, 1H), 6.98 (dd, J = 8.5, 2.7 Hz, 1H), 6.86 – 6.79 (m, 2H), 4.20 – 4.06 (m, 2H), 3.90 (s, 3H), 3.82 (s, 3H), 1.05 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 159.5, 158.4, 141.4, 136.9, 132.9 (2C), 131.6, 131.5, 131.3, 129.8, 129.7, 127.2, 123.5, 115.7, 115.2, 114.4, 113.8 (2C), 92.2, 87.3, 60.8, 55.4, 55.2, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{23}O_4]^+$ 387.1591; found 387.1604.



Ethyl 4'-methoxy-2'-((3-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (11d):

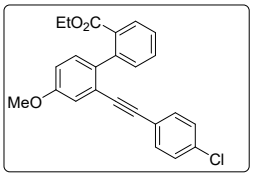
GP-3 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8v** (254 mg, 0.8 mmol), phenylboronic acid **9d** (174 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_3PO_4 (339.2 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 95:5 to 93:7), furnished the product **11c** (136 mg, 44%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 93:7), R_f(**8v**) = 0.7, R_f(**11c**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2928, 1717, 1596, 1464, 1275, 1042, 868, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (dd, J = 7.7, 0.9 Hz, 1H), 7.54 (dtd, J = 9.0, 7.5, 1.5 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.36 (dd, J = 7.6, 1.1 Hz, 1H), 7.26 – 7.10 (m, 3H), 6.96 (dd, J = 8.5, 2.7 Hz, 1H), 6.92 – 6.68 (m, 3H), 4.11 – 4.01 (m, 2H), 3.87 (s, 3H), 3.77 (s, 3H), 1.01 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 159.1, 158.4, 141.4, 137.3, 131.6, 131.3, 130.1, 129.8, 129.7, 129.1, 127.2, 127.0, 123.9, 123.1, 116.1, 115.9, 114.9, 114.8, 92.1, 88.4, 60.8, 55.4, 55.2, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{23}O_4]^+$ 387.1591; found 387.1596.



Ethyl 2'-((4-chlorophenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-carboxylate (11e):

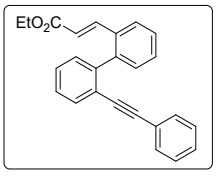
GP-3 was carried out with In an oven-dried Schlenk tube equipped with a magnetic stirring bar, were added 1-bromo-2-(phenylethynyl)benzenes **8w** (257 mg, 0.8 mmol), phenylboronic acid **9d** (174 mg, 0.9 mmol), $Pd(OAc)_2$ (8.9 mg, 0.04 mmol), PPh_3 (21 mg, 0.08 mmol), and K_3PO_4 (339.2 mg, 1.6 mmol) in DMF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 97:3 to 95:5), furnished the product **11e** (150.1 mg, 48%), as brown solid; mp = 60–62 °C. [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**8w**) = 0.7, R_f(**11e**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2969, 1715, 1477, 1271, 1175, 1037, 827, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, J = 7.8, 1.3 Hz, 1H), 7.55 (ddd, J = 7.5, 7.5, 1.4 Hz, 1H), 7.45 (ddd, J = 7.6, 7.6, 1.3 Hz, 1H), 7.34 (dd, J = 7.6, 1.1 Hz, 1H), 7.23 (ddd, J = 8.5, 6.3, 1.0 Hz, 3H), 7.20 – 7.15 (m, 2H), 7.09 (d, J = 2.7 Hz, 1H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 4.09 – 4.04 (m, 2H), 3.87 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.7, 158.4, 141.2, 137.2, 134.1, 132.6 (2C), 131.5, 131.5, 131.4, 129.8 (2C), 128.5 (2C), 127.3, 122.8, 121.6, 116.0, 114.9, 90.9, 89.5, 60.8, 55.4, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{24}H_{20}ClO_3]^+$ 391.1095; found 391.1103.



Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1a):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10a** (169 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography

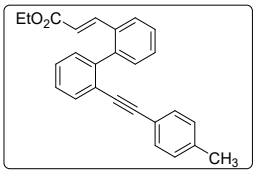
(petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1a** (180 mg, 85%), as off-white viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10a**) = 0.6, R_f(**1a**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2980, 1709, 1633, 1309, 1268, 1169, 1035, 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 1H), 7.65 (ddd, J = 22.3, 12.0, 8.9 Hz, 2H), 7.49 – 7.38 (m, 5H), 7.31 – 7.22 (m, 4H), 7.19 – 7.13 (m, 2H), 6.39 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 143.2, 142.3, 141.7, 133.2, 132.1, 131.2 (2C), 131.1, 130.2, 129.3, 128.1 (3C), 128.0, 127.9, 127.7, 126.0, 123.1, 123.1, 118.8, 92.9, 88.6, 60.2, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{25}H_{20}NaO_2]^+$ 375.1356; found 375.1356.



Ethyl (*E*)-3-(2'-(p-tolylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1b):

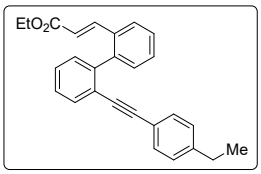
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10b** (178 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1b** (185 mg, 84%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10b**) = 0.6, R_f(**1b**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2968, 1709, 1633, 1309, 1168, 984, 806, 754 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.58 (m, 1H), 7.55 – 7.40 (m, 2H), 7.34 – 7.21 (m, 5H), 7.16 – 7.10 (m, 1H), 6.90 (s, 4H), 6.23 (d, J = 15.9 Hz, 1H), 4.02 (q, J = 7.1 Hz, 2H), 2.17 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.3, 142.2, 141.8, 138.2, 133.2, 131.9, 131.1 (2C), 131.1, 130.2, 129.3, 128.9 (2C), 127.9, 127.9, 127.7, 126.0, 123.3, 120.1, 118.8, 93.2, 87.9, 60.2, 21.4, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_2]^+$ 367.1693; found 367.1704.



Ethyl (*E*)-3-(2'-((4-ethylphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1c):

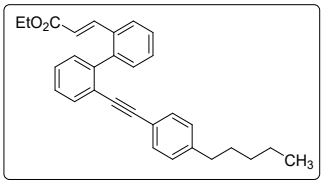
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10d** (186 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1c** (183 mg, 80%) as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10d**) = 0.6, R_f(**1c**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2969, 1709, 1632, 1309, 1268, 1167, 982, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.62 (m, 1H), 7.57 – 7.41 (m, 2H), 7.37 – 7.23 (m, 5H), 7.15 (ddd, J = 3.8, 3.8, 2.7 Hz, 1H), 6.95 (s, 4H), 6.25 (d, J = 15.9 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 2.49 (q, J = 7.6 Hz, 2H), 1.13 (t, J = 7.1 Hz, 3H), 1.08 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 144.5, 143.3, 142.2, 141.8, 133.2, 132.0, 131.2 (2C), 131.1, 130.2, 129.3, 127.9, 127.9, 127.7 (2C), 127.7, 126.0, 123.3, 120.3, 118.8, 93.2, 87.9, 60.2, 28.76, 15.30, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{27}H_{24}NaO_2]^+$ 403.1669; found 403.1671.



Ethyl (*E*)-3-(2'-((4-pentylphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1d):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10e** (211 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1d** (198 mg, 78%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10e**) = 0.6, R_f(**1d**) = 0.5 UV detection].

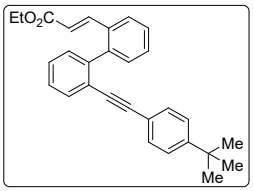
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 1711, 1633, 1309, 1267, 1167, 1036, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 1H), 7.56 – 7.42 (m, 2H), 7.36 – 7.24 (m, 5H), 7.15 (dd, J = 6.2, 2.7 Hz, 1H), 7.00 – 6.85 (m, 4H), 6.25 (d, J = 15.9 Hz, 1H), 4.05 (q, J = 7.1

Hz, 2H), 2.60 – 2.34 (m, 2H), 1.44 (dd, J = 15.9, 8.4 Hz, 2H), 1.27 – 1.15 (m, 4H), 1.13 (t, J = 7.1 Hz, 3H), 0.76 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.3, 143.2, 142.2, 141.8, 133.2, 132.0, 131.2 (2C), 131.1, 130.2, 129.3, 128.3 (2C), 127.9 (2C), 127.7, 126.0, 123.3, 120.3, 118.8, 93.3, 87.9, 60.2, 35.8, 31.4, 30.9, 22.5, 14.2, 13.9 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{30}H_{30}NaO_2]^+$ 445.2138; found 445.2139.



Ethyl (*E*)-3-(2'-((4-(tert-butyl)phenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1e):

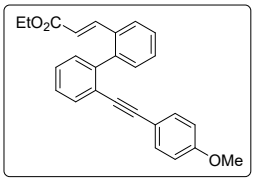
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10f** (203 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1e** (191 mg, 78%), as orange viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10f**) = 0.6, R_f(**1e**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2960, 1711, 1633, 1310, 1267, 1168, 834, 758 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.7, 1.7 Hz, 1H), 7.66 – 7.62 (m, 1H), 7.60 (d, J = 16.0 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.40 – 7.35 (m, 2H), 7.26 (ddd, J = 7.2, 5.6, 3.1 Hz, 3H), 7.08 (d, J = 8.5 Hz, 2H), 6.37 (d, J = 15.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 1.27 (s, 9H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 151.3, 143.3, 142.2, 141.8, 133.2, 131.9, 131.1, 130.9 (2C), 130.2, 129.3, 127.9 (2C), 127.6, 126.0, 125.1 (2C), 123.3, 120.1, 118.8, 93.2, 87.9, 60.2, 34.7, 31.1 (3C), 14.2 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{29}H_{32}NO_2]^+$ 426.2428; found 426.2409.



Ethyl (*E*)-3-(2'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1f):

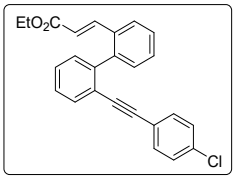
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10g** (187 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1f** (161 mg, 70%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10g**) = 0.4, R_f(**1f**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 1710, 1601, 1509, 1250, 1171, 1033, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 1H), 7.54 – 7.45 (m, 2H), 7.36 – 7.23 (m, 5H), 7.17 – 7.13 (m, 1H), 7.05 – 6.89 (m, 2H), 6.70 – 6.60 (m, 2H), 6.26 (d, J = 15.9 Hz, 1H), 4.05 (q, J = 7.1 Hz, 2H), 3.66 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 159.4, 143.3, 142.0, 141.9, 133.2, 132.7 (2C), 131.8, 131.1, 130.2, 129.3, 127.9, 127.7, 127.7, 125.9, 123.4, 118.7, 115.3, 113.8 (2C), 93.1, 87.4, 60.2, 55.2, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_3]^+$ 405.1461; found 405.1463.



Ethyl (*E*)-3-(2'-((4-chlorophenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1g):

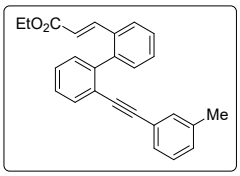
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10i** (190 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1g** (206 mg, 89%), as orange viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10i**) = 0.6, R_f(**1g**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2982, 1710, 1633, 1486, 1368, 1170, 1093, 759 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 1H), 7.66 – 7.58 (m, 1H), 7.55 (d, J = 16.0 Hz, 1H), 7.47 – 7.32 (m, 5H), 7.28 – 7.22 (m, 1H), 7.20 – 7.13 (m, 2H), 7.06 – 6.96 (m, 2H), 6.33 (d, J = 15.9 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 143.1, 142.4, 141.6, 134.0, 133.2, 132.4 (2C), 132.0, 131.1, 130.3, 129.3, 128.5 (2C), 128.4, 128.0, 127.8, 126.0, 122.8, 121.6, 118.9, 91.9, 89.6, 60.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{25}H_{19}ClNaO_2]^+$ 409.0966; found 409.0968.



Ethyl (*E*)-3-(2'-(m-tolylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1h):

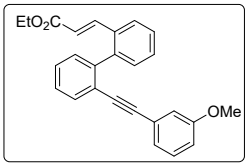
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10c** (178 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1h** (176 mg, 80%), as orange viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10c**) = 0.6, R_f(**1h**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2979, 1707, 1631, 1308, 1266, 1166, 1034, 752 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.67 – 7.53 (m, 2H), 7.47 – 7.34 (m, 5H), 7.25 (ddd, J = 7.2, 3.6, 2.5 Hz, 1H), 7.10 (dd, J = 7.6, 7.6 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 6.98 – 6.84 (m, 2H), 6.35 (d, J = 16.0 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 2.25 (s, 3H), 1.23 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 143.2, 142.2, 141.8, 137.7, 133.2, 132.1, 131.8, 131.1, 130.2, 129.3, 128.9, 128.3, 128.0 (2C), 127.9, 127.7, 126.0, 123.2, 122.9, 118.8, 93.2, 88.3, 60.2, 21.1, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_2]^+$ 367.1693; found 367.1709.



Ethyl (*E*)-3-(2'-((3-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1i):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10h** (187 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1i** (156 mg, 68%), as colourless viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10h**) = 0.4, R_f(**1i**) = 0.3 UV detection].

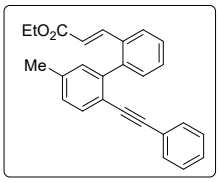
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 1709, 1588, 1476, 1370, 1171, 1039, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 1H), 7.65 – 7.59 (m, 1H), 7.57 (d, J = 16.0 Hz, 1H), 7.45 – 7.33 (m, 5H), 7.25 (ddd, J = 5.5, 3.0, 0.9 Hz, 1H), 7.15 – 7.05 (m, 1H), 6.78 (ddd,

J = 8.4, 2.6, 0.9 Hz, 1H), 6.74 – 6.68 (m, 1H), 6.62 (dd, J = 2.5, 1.4 Hz, 1H), 6.34 (d, J = 15.9 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.72 (s, 3H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 159.1, 143.2, 142.4, 141.8, 133.2, 132.0, 131.1, 130.2, 129.3, 129.2, 128.2, 127.9, 127.7, 126.0, 124.1, 123.7, 123.0, 118.8, 115.9, 114.8, 92.9, 88.5, 60.3, 55.2, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_3]^+$ 405.1461; found 405.1464.



Ethyl (*E*)-3-(5'-methyl-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1j):

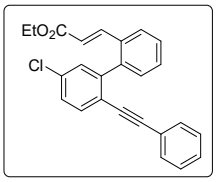
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10j** (178 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1j** (180 mg, 82%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10j**) = 0.6, R_f(**1j**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2980, 1707, 1631, 1309, 1266, 1166, 1033, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 1H), 7.65 (d, J = 16.0 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.51 – 7.40 (m, 3H), 7.28 – 7.20 (m, 4H), 7.19 – 7.14 (m, 2H), 7.13 (d, J = 4.3 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 4.20 (q, J = 7.1 Hz, 2H), 2.44 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 143.3, 142.2, 141.9, 138.3, 133.2, 131.9, 131.2 (2C), 131.0, 130.9, 129.3, 128.5, 128.1 (2C), 127.8 (2C), 125.9, 123.4, 120.2 118.6, 92.2, 88.8, 60.2, 21.45, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_2]^+$ 389.1512; found 389.1516.



Ethyl (*E*)-3-(5'-chloro-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1k):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10k** (190 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4

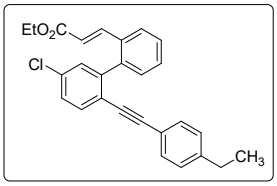
mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1k** (193 mg, 83%), as orange viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10k**) = 0.6, R_f(**1k**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2982, 1710, 1634, 1455, 1310, 1172, 1033, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 1H), 7.47 (d, J = 1.7 Hz, 1H), 7.44 (d, J = 5.9 Hz, 1H), 7.35 (ddd, J = 9.0, 5.5, 3.7 Hz, 2H), 7.30 – 7.25 (m, 2H), 7.19 (d, J = 2.1 Hz, 1H), 7.16 – 7.09 (m, 3H), 7.04 – 6.99 (m, 2H), 6.28 (d, J = 15.9 Hz, 1H), 4.07 (q, J = 7.1 Hz, 2H), 1.15 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 143.9, 142.6, 140.4, 133.9, 133.2, 133.1, 131.2 (2C), 130.8, 130.1, 129.5, 128.4, 128.3, 128.2 (2C), 128.0, 126.1, 122.8, 121.8, 119.3, 93.9, 87.5, 60.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{25}H_{19}ClNaO_2]^+$ 409.0966; found 409.0970.



Ethyl (*E*)-3-(5'-chloro-2'-((4-ethylphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1l):

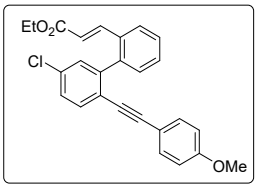
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10l** (207 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1l** (194 mg, 78%), brown solid; mp = 62–64 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10l**) = 0.6, R_f(**1l**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2972, 1714, 1635, 1458, 1311, 1269, 1173, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 1H), 7.57 (d, J = 5.8 Hz, 1H), 7.54 (d, J = 1.8 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.31 (m, 2H), 7.28 (d, J = 2.2 Hz, 1H), 7.08 – 7.00 (m, 4H), 6.37 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 2.60 (q, J = 7.6 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.6 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 144.8, 143.8, 142.7, 140.4, 133.7, 133.2, 132.9, 131.2 (2C), 130.8, 130.1, 129.5, 128.3, 127.9, 127.7 (2C), 126.0, 122.1, 119.9, 119.2, 94.2, 86.9, 60.3, 28.8, 15.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{27}H_{23}ClNaO_2]^+$ 437.1279; found 437.1275.



Ethyl (*E*)-3-(4'-chloro-2'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1m):

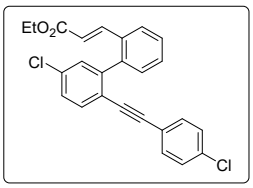
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10m** (208 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1m** (180 mg, 72%), as yellow solid; mp = 88–90 °C. [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10m**) = 0.6, R_f(**1m**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 1708, 1509, 1304, 1250, 1171, 1029, 732 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 1H), 7.56 (d, J = 15.9 Hz, 1H), 7.53 (d, J = 8.3 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.37 – 7.34 (m, 2H), 7.27 (d, J = 2.1 Hz, 1H), 7.07 – 7.02 (m, 2H), 6.78 – 6.73 (m, 2H), 6.37 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.76 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 159.6, 143.6, 142.7, 140.5, 133.5, 133.2, 132.8, 132.7 (2C), 130.8, 130.0, 129.4, 128.3, 127.1, 126.0, 122.2, 119.2, 115.1, 113.8 (2C), 94.0, 86.3, 60.3, 55.2, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{22}ClO_3]^+$ 417.1252; found 417.1269.



Ethyl (*E*)-3-(4'-chloro-2'-((4-chlorophenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1n):

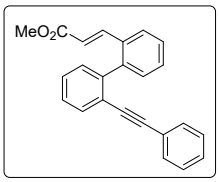
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10n** (211 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1n** (210 mg, 83%), as yellow solid; mp = 78–80 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10n**) = 0.6, R_f(**1n**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2982, 1708, 1309, 1265, 1169, 1090,1027, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 1H), 7.56 (d, J = 15.2 Hz, 1H), 7.53 (d, J = 2.4 Hz, 1H), 7.45 (dd, J = 5.6, 3.5 Hz, 2H), 7.36 (ddd, J = 6.1, 5.7, 2.5 Hz, 2H), 7.30 (d, J = 2.1 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.04 – 7.00 (m, 2H), 6.38 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 143.9, 142.5, 140.2, 134.3, 134.2, 133.2, 133.0, 132.4 (2C), 130.7, 130.2, 129.5, 128.5 (2C), 128.4, 128.0, 126.0, 121.5, 121.3, 119.3, 92.7, 88.5, 60.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{19}Cl_2O_2]^+$ 421.0757; found 421.0758.



Methyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1o):

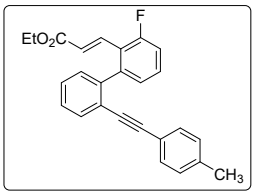
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10a** (169 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), methyl 2-(diethoxyphosphoryl)acetate (504 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1o** (172 mg, 85%), as orange viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10a**) = 0.6, R_f(**1o**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3057, 1710, 1632, 1436, 1270, 1165, 982, 753 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (dd, J = 7.4, 2.0 Hz, 1H), 7.56 – 7.51 (m, 1H), 7.48 (d, J = 15.9 Hz, 1H), 7.36 – 7.23 (m, 5H), 7.16 – 7.12 (m, 1H), 7.10 (qd, J = 3.7, 1.3 Hz, 3H), 7.02 (ddd, J = 7.8, 7.8, 2.2 Hz, 2H), 6.25 (d, J = 16.0 Hz, 1H), 3.56 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.2, 143.4, 142.3, 141.7, 133.1, 132.0, 131.2 (2C), 131.0, 130.1, 129.4, 128.1, 128.1 (2C), 128.0, 127.9, 127.7, 126.0, 123.1, 123.1, 118.4, 93.0, 88.6, 51.5 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{24}H_{18}NaO_2]^+$ 361.1199; found 361.1202.



Ethyl (*E*)-3-(3-fluoro-2'-(*p*-tolylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1p):

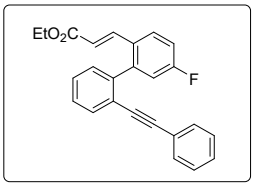
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10o** (189 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1p** (187 mg, 81%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10o**) = 0.6, R_f(**1p**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2976, 1711, 1635, 1452, 1260, 1170, 1034, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.49 (m, 1H), 7.37 – 7.24 (m, 4H), 7.19 – 7.15 (m, 1H), 7.11 (dd, J = 7.6, 1.1 Hz, 1H), 7.07 (dd, J = 10.1, 1.9 Hz, 1H), 7.01 – 6.93 (m, 4H), 6.41 (dd, J = 16.3, 0.6 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 2.23 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 161.8 (d, J = 253.7 Hz), 144.1 (d, J = 3.1 Hz), 141.4 (d, J = 2.4 Hz), 138.4, 137.1, 132.1, 131.2 (2C), 129.9, 129.8, 129.7, 128.9 (2C), 128.0, 126.8 (d, J = 3.2 Hz), 123.4, 123.3 (d, J = 4.2 Hz), 121.7 (d, J = 11.0 Hz), 119.9, 115.3 (d, J = 23.2 Hz), 93.5, 87.6, 60.3, 21.4, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{22}FO_2]^+$ 385.1598; found 385.1596.



Ethyl (*E*)-3-(5-fluoro-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1q):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10p** (180 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **1q** (155 mg, 70%), as brown solid; mp = 90–92 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**10p**) = 0.6, R_f(**1q**) = 0.5 UV detection].

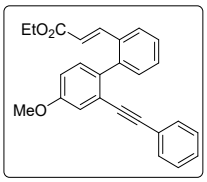
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3064, 2981, 1709, 1482, 1371, 1167, 1033, 756 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, J = 8.5, 5.7 Hz, 1H), 7.64 (dd, J = 5.8, 3.3 Hz, 1H), 7.50 (d, J = 16 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.28 – 7.21 (m, 4H), 7.21 – 7.09 (m, 4H), 6.28 (d, J = 15.9 Hz, 1H), 4.14 (q, J = 7.1 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 162.9 (d, J = 251 Hz), 143.9 (d, J = 8.3 Hz), 142.0, 140.9 (d, J = 1.3 Hz), 132.2 (2C), 131.3, 130.0, 129.6 (d, J = 3.2 Hz), 128.2 (2C), 128.2 (2C),

128.1, 128.1 (d, J = 8.8 Hz), 122.9 (2C), 118.6, 117.8 (d, J = 21.9 Hz), 115.2 (d, J = 21.7 Hz), 93.4, 88.1, 60.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{25}H_{23}FNO_2]^+$388.1707; found 388.1706.



Ethyl (*E*)-3-(4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1r):

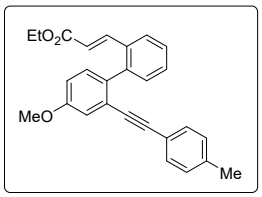
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10q** (187 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1r** (183 mg, 80%), as off-white viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10q**) = 0.6, R_f(**1r**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2973, 1708, 1599, 1459, 1312, 1168, 1037, 758 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 7.2 Hz, 1H), 7.61 (d, J = 16.0 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.25 – 7.19 (m, 3H), 7.18 – 7.11 (m, 4H), 6.96 (dd, J = 8.5, 2.7 Hz, 1H), 6.36 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.89 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.8, 143.5, 141.5, 134.9, 133.5, 131.4, 131.4, 131.3 (2C), 129.3, 128.1 (3C), 127.7, 126.0, 123.9, 123.1, 118.6, 116.5, 114.9, 92.7, 88.7, 60.2, 55.4, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_3]^+$ 405.1461; found 405.1464.



Ethyl (*E*)-3-(4'-methoxy-2'-(*p*-tolylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1s):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10r** (196 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1s** (195 mg, 82%), as

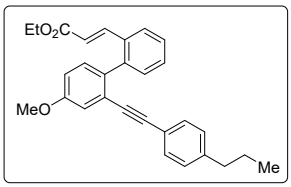
yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10r**) = 0.6, R_f(**1s**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2969, 1710, 1598, 1461, 1309, 1170, 987, 762 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 1H), 7.67 (d, J = 16.0 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.18 (dd, J = 5.6, 2.8 Hz, 2H), 7.10 – 7.03 (m, 4H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 6.40 (d, J = 15.9 Hz, 1H), 4.19 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.27 (t, J = 7.1 Hz, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 158.7, 143.5, 141.5, 138.2, 134.7, 133.4, 131.4, 131.3, 131.1 (2C), 129.2, 128.8 (2C), 127.6, 125.9, 124.1, 119.9, 118.5, 116.3, 114.6, 92.9, 88.0, 60.1, 55.3, 21.3, 14.1 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{27}H_{28}NO_3]^+$ 414.2064; found 414.2071.



Ethyl (*E*)-3-(4'-methoxy-2'-((4-propylphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1t):

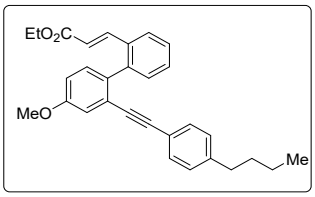
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10t** (213 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1t** (199 mg, 78%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10t**) = 0.6, R_f(**1t**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2961, 2360, 1708, 1560, 1312, 1224, 1037, 733 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 16.0 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.16 (dd, J = 7.5, 2.6 Hz, 2H), 7.06 (q, J = 8.1 Hz, 4H), 6.95 (dd, J = 8.5, 2.6 Hz, 1H), 6.37 (d, J = Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 2.60 – 2.44 (m, 2H), 1.61 – 1.57 (m, 2H), 1.25 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.8, 143.5, 143.0, 141.6, 134.7, 133.5, 131.4, 131.4, 131.2 (2C), 129.2, 128.3 (2C), 127.6, 126.0, 124.2, 120.2, 118.5, 116.4, 114.7, 92.9, 88.1, 60.2, 55.40, 37.9, 24.3, 14.2, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{29}H_{29}O_3]^+$ 425.2111; found 425.2108.



Ethyl (*E*)-3-(2'-((4-butylphenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (1u):

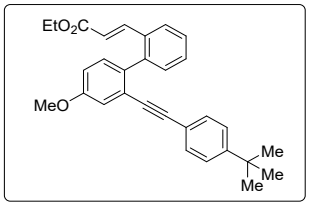
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10u** (220 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1u** (200 mg, 76%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10u**) = 0.6, R_f(**1u**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 1710, 1598, 1371, 1264, 1167, 1035, 760 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.64 (d, J = 16.0 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.17 (dd, J = 5.6, 2.8 Hz, 2H), 7.09 – 7.03 (m, 4H), 6.96 (dd, J = 8.5, 2.7 Hz, 1H), 6.38 (d, J = 15.9 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 2.60 (t, J = 7.2, 2H), 1.56 (dq, J = 12.8, 7.5 Hz, 2H), 1.33 (dd, J = 15.0, 7.4 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.8, 143.5, 143.3, 141.6, 134.7, 133.4, 131.4, 131.4, 131.2 (2C), 129.2, 128.3 (2C), 127.6, 126.0, 124.2, 120.2, 118.5, 116.3, 114.7, 93.0, 88.1, 60.2, 55.4, 35.5, 33.3, 22.2, 14.2, 13.9 ppm.

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{30}H_{30}KO_3]^+$ 477.1827; found 477.1838.



Ethyl (*E*)-3-(2'-((4-(*tert*-butyl)phenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (1v):

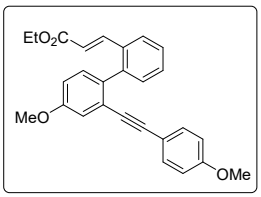
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10v** (221 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1v** (208 mg, 79%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10v**) = 0.6, R_f(**1v**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2961, 1709, 1599, 1404, 1263, 1169, 1031, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.65 (m, 1H), 7.55 (d, J = 16.0 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.21 – 7.16 (m, 2H), 7.09 (dd, J = 5.6, 2.8 Hz, 2H), 7.02 (d, J = 8.5 Hz, 2H), 6.88 (dd, J = 8.5, 2.6 Hz, 1H), 6.30 (dd, J = 16.0, 2.7 Hz, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.82 (s, 3H), 1.21 (s, 9H), 1.79 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 158.8, 151.4, 143.6, 141.6, 134.8, 133.5, 131.4, 131.4, 131.0 (2C), 129.3, 127.7, 126.0, 125.2 (2C), 124.2, 120.1, 118.6, 116.3, 114.8, 92.9, 88.1, 60.2, 55.4, 34.7, 31.1 (3C), 14.2 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{30}H_{34}NO_3]^+$ 456.2533; found 456.2518.



Ethyl (*E*)-3-(4'-methoxy-2'-((4-methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1w)

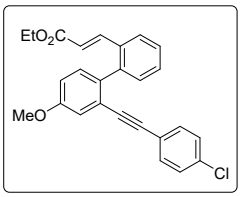
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10w** (205 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the product **1w** (176 mg, 71%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**10w**) = 0.6, R_f(**1w**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2966, 2210, 1707, 1598, 1247, 1169, 1030, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, J = 6.8 Hz, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.46 – 7.36 (m, 3H), 7.15 (dd, J = 8.5, 2.7 Hz, 2H), 7.08 (d, J = 8.7 Hz, 2H), 6.94 (dd, J = 8.5, 2.7 Hz, 1H), 6.76 (d, J = 8.8 Hz, 2H), 6.36 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 3.77 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 159.5, 158.8, 143.6, 141.6, 134.6, 133.5, 132.7 (2C), 131.4, 131.3, 129.2, 127.6, 125.9, 124.3, 118.5, 116.2, 115.2, 114.5, 113.8 (2C), 92.8, 87.5, 60.2, 55.4, 55.2, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_4]^+$ 413.1747; found 413.1739.



Ethyl (*E*)-3-(2'-((4-chlorophenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (1x)

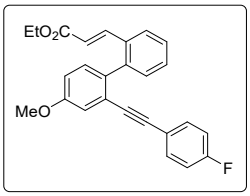
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10x** (208 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1x** (190 mg, 76 as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10x**) = 0.6, R_f(**1x**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2970, 1708, 1474, 1311, 1227, 1169, 1035, 761 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.4, 1.9 Hz, 1H), 7.61 (d, J = 16.0 Hz, 1H), 7.45 – 7.37 (m, 3H), 7.23 – 7.16 (m, 3H), 7.15 (d, J = 2.7 Hz, 1H), 7.07 – 7.03 (m, 2H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.8, 143.4, 141.4, 134.9, 134.1, 133.4, 132.4 (2C), 131.4, 131.4, 129.3, 128.5 (2C), 127.7, 125.9, 123.6, 121.5, 118.6, 116.4, 115.1, 91.5, 89.7, 60.2, 55.4, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{21}ClNaO_3]^+$ 439.1071 ; found 439.1056.



Ethyl (*E*)-3-(2'-((4-fluorophenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (1y):

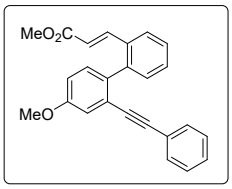
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10y** (198 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1y** (168 mg, 70%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10y**) = 0.6, R_f(**1y**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2978, 1708, 1597, 1466, 1312, 1168, 1036, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.44 – 7.38 (m, 3H), 7.19 – 7.09 (m, 4H), 6.98 – 6.89 (m, 3H), 6.37 (d, J = 16.0 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 162.3 (d, J = 249.6 Hz), 158.81, 143.4, 141.5, 134.8, 133.4, 133.1 (d, J = 8.4 Hz) (2C), 131.4 (2C), 129.3, 127.7, 126.0, 123.8, 119.1 (d, J = 3.5 Hz), 118.6, 116.4, 115.4 (d, J = 22.1 Hz) (2C), 114.9, 91.6, 88.4, 60.2, 55.4, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{26}H_{21}FKO_3]^+$ 439.1106; found 439.1119.



Methyl (*E*)-3-(4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1z):

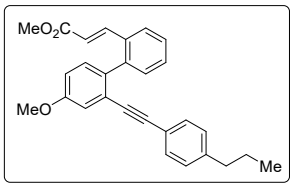
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10q** (187 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), methyl 2-(diethoxyphosphoryl)acetate (504 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1z** (166 mg, 75%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10q**) = 0.6, R_f(**1z**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3059, 2946, 1710, 1598, 1272, 1165, 1035, 753. cm^{-1}

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.72 (m, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.44 – 7.40 (m, 3H), 7.27 – 7.21 (m, 3H), 7.19 – 7.12 (m, 4H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 3.89 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 158.9, 143.8, 141.6, 134.9, 133.5, 131.5, 131.4, 131.3 (2C), 129.4, 128.1 (3C), 127.8, 126.1, 124.0, 123.1, 118.3, 116.5, 115.0, 92.8, 88.7, 55.5, 51.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{21}O_3]^+$ 369.1485; found 369.1512.



Methyl (*E*)-3-(4'-methoxy-2'-((4-propylphenyl)ethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1aa):

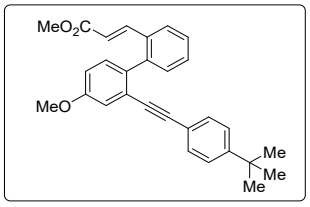
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10t** (213 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), methyl 2-(diethoxyphosphoryl)acetate (504 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1aa** (192 mg, 78%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10t**) = 0.6, R_f(**1aa**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2951, 1712, 1598, 1462, 1268, 1167, 1095, 698 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.16 (dd, J = 5.6, 2.9 Hz, 2H), 7.08 – 7.01 (m, 4H), 6.95 (dd, J = 8.5, 2.7 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 3.89 (s, 3H), 3.71 (s, 3H), 2.59 – 2.46 (m, 2H), 1.67 – 1.54 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 158.8, 143.8, 143.1, 141.6, 134.8, 133.4, 131.4, 131.3, 131.2 (2C), 129.3, 128.3 (2C), 127.7, 126.1, 124.2, 120.2, 118.2, 116.4, 114.7, 93.0, 88.1, 55.4, 51.5, 37.9, 24.3, 13.7 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{28}H_{26}NaO_3]^+$433.1774; found 433.1775.



Methyl (*E*)-3-(2'-((4-(*tert*-butyl)phenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (1ab):

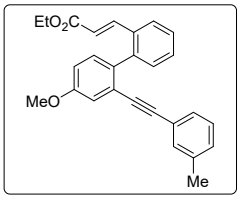
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10v** (221 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), methyl 2-(diethoxyphosphoryl)acetate (504 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1ab** (199 mg, 78%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10v**) = 0.6, R_f(**1ab**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2957, 1714, 1599, 1464, 1315, 1228, 1027, 804 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.59 (m, 1H), 7.49 (d, J = 16.0 Hz, 1H), 7.33 – 7.26 (m, 3H), 7.15 – 7.11 (m, 2H), 7.03 (dd, J = 5.6, 2.8 Hz, 2H), 6.95 (d, J = 8.4 Hz, 2H), 6.83 (dd, J = 8.5, 2.7 Hz, 1H), 6.24 (d, J = 16.0 Hz, 1H), 3.77 (s, 3H), 3.58 (s, 3H), 1.15 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.4, 158.8, 151.4, 143.8, 141.6, 134.8, 133.4, 131.4, 131.3, 131.0 (2C), 129.3, 127.7, 126.0, 125.2 (2C), 124.2, 120.0, 118.2, 116.3, 114.7, 92.9, 88.0, 55.4, 51.5, 34.7, 31.1 (3C) ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{29}H_{29}O_3]^+$ 425.2111; found 425.2112.



Ethyl (*E*)-3-(4'-methoxy-2'-(*m*-tolylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1ac):

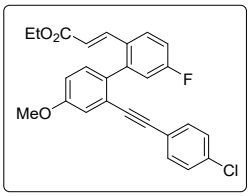
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10s** (196 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1ac** (193 mg, 81%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10s**) = 0.6, R_f(**1ac**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 1709, 1598, 1464, 1312, 1168, 1034, 691 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J = 6.8 Hz, 1H), 7.64 (d, J = 15.9 Hz, 1H), 7.46 – 7.40 (m, 3H), 7.20 – 7.10 (m, 3H), 7.06 (d, J = 7.7 Hz, 1H), 7.00 – 6.92 (m, 3H), 6.38 (d, J = 16.0 Hz, 1H), 4.18 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 2.28 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.8, 143.52, 141.5, 137.7, 134.8, 133.4, 131.7, 131.4, 131.4, 129.3, 129.0, 128.3, 128.0, 127.6, 126.0, 124.0, 122.9, 118.6, 116.4, 114.8, 92.9, 88.4, 60.2, 55.4, 21.1, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_3]^+$ 397.1798; found 397.1792.



Ethyl (*E*)-3-(2'-((4-chlorophenyl)ethynyl)-5-fluoro-4'-methoxy-[1,1'-biphenyl]-2-yl)acrylate (1ad):

GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10z** (219 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography

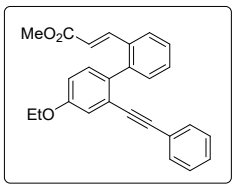
(petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1ad** (209 mg, 80%), as off brown powder; mp = 96–98 °C. [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10z**) = 0.6, R_f(**1ad**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2929, 1171, 1601, 1482, 1307, 1173, 1091, 824 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.2, 7.6 Hz, 1H), 7.52 (d, J = 16.0 Hz, 1H), 7.25 – 7.20 (m, 2H), 7.18 – 7.07 (m, 6H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 6.29 (d, J = 15.9 Hz, 1H), 4.16 (q, J = 7.1 Hz, 2H), 3.88 (s, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 162.9 (d, J = 251.3 Hz), 159.1, 143.6 (d, J = 8.5 Hz), 142.3, 134.3, 133.6, 132.5 (2C), 131.3, 129.8 (d, J = 3.1 Hz), 128.6 (2C), 128.0 (d, J = 8.5 Hz), 123.6, 121.4, 118.4, 118.1 (d, J = 21.5 Hz), 116.6, 115.2, 115.1 (d, J = 21.7 Hz), 91.9, 89.2, 60.3, 55.5, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{21}ClFO_3]^+$ 435.1158; found 435.1158.



Methyl (*E*)-3-(4'-ethoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1ae):

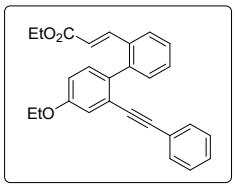
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10aa** (196 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), methyl 2-(diethoxyphosphoryl)acetate (504 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1ae** (183 mg, 80%), as off yellow solid; mp = 96–98 °C. [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10aa**) = 0.6, R_f(**1ae**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3060, 2942, 1712, 1598, 1315, 1169, 1041, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.71 (m, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.23 (dd, J = 5.1, 2.0 Hz, 3H), 7.18 – 7.12 (m, 4H), 6.95 (dd, J = 8.5, 2.6 Hz, 1H), 6.37 (d, J = 16.0 Hz, 1H), 4.12 (q, J = 7.0 Hz, 2H), 3.70 (s, 3H), 1.47 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 158.2, 143.7, 141.6, 134.7, 133.4, 131.4, 131.3, 131.3 (2C), 129.3, 128.1 (2C), 128.1, 127.7, 126.0, 123.9, 123.1, 118.2, 116.9, 115.4, 92.6, 88.7, 63.6, 51.5, 14.8 ppm.

HRMS (ESI) *m/z*: $[M+K]^+$ calcd for $[C_{26}H_{22}KO_3]^+$ 421.1201; found 421.1204.



Ethyl (*E*)-3-(4'-ethoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1af):

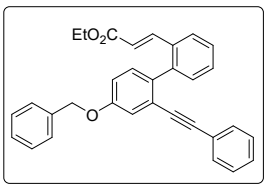
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10aa** (196 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the product **1af** (195 mg, 82%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10aa**) = 0.6, R_f(**1af**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3060, 2980, 1708, 1598, 1379, 1168, 1037, 740 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (d, J = 7.5 Hz, 1H), 7.63 (d, J = 16.0 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.25 – 7.21 (m, 3H), 7.15 (ddd, J = 4.5, 4.1, 2.6 Hz, 4H), 6.95 (dd, J = 8.5, 2.6 Hz, 1H), 6.37 (d, J = 15.9 Hz, 1H), 4.17 (q, J = 7.1 Hz, 2H), 4.11 (q, J = 7.0 Hz, 2H), 1.47 (t, J = 7.0 Hz, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 158.2, 143.5, 141.6, 134.7, 133.4, 131.4, 131.4, 131.3 (2C), 129.2, 128.1 (2C), 128.1, 127.7, 126.0, 123.9, 123.1, 118.5, 117.0, 115.4, 92.6, 88.8, 63.6, 60.2, 14.8, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_3]^+$ 397.1798; found 397.1833.



Ethyl (*E*)-3-(4'-(benzyloxy)-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylate (1ag):

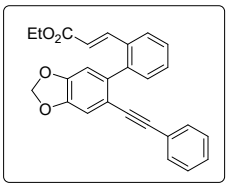
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10ab** (233 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the product **1ag** (232 mg, 87%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**10ab**) = 0.6, R_f(**1ag**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3061, 2930, 1709, 1598, 1312, 1171, 1032, 751 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75 (d, J = 7.3 Hz, 1H), 7.64 (d, J = 16.0 Hz, 1H), 7.50 (d, J = 7.5 Hz, 2H), 7.46 – 7.40 (m, 5H), 7.37 (dd, J = 8.4, 6.3 Hz, 1H), 7.27 (d, J = 2.7 Hz, 1H), 7.24 (dd, J = 9.0, 6.8 Hz, 3H), 7.18 (d, J = 8.5 Hz, 1H), 7.16 – 7.14 (m, 2H), 7.04 (dd, J = 8.5, 2.7 Hz, 1H), 6.38 (d, J = 15.9 Hz, 1H), 5.14 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 157.8, 143.5, 141.3, 136.3, 134.8, 133.1, 131.5, 131.4, 131.2 (2C), 129.3, 128.6 (2C), 128.1 (2C), 128.1 (2C), 127.7, 127.6 (2C), 125.9, 123.8, 122.8, 118.2, 116.9, 115.5, 92.6, 88.6, 69.9, 60.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{32}H_{26}NaO_3]^+$ 481.1774; found 481.1767.



Ethyl (*E*)-3-(2-(6-(phenylethynyl)benzo[*d*][1,3]dioxol-5-yl)phenyl)acrylate (1ah):

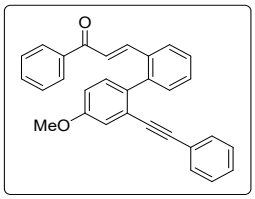
GP-4 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10ac** (196 mg, 0.6 mmol), NaH (57.6 mg, 2.4 mmol), ethyl 2-(diethoxyphosphoryl)acetate (538 mg, 2.4 mmol) and THF (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the product **1ah** (202 mg, 85%), as orange viscous oil [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**10ac**) = 0.6, R_f(**1ah**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3057, 2899, 1692, 1496, 1264, 1150, 1036, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 1H), 7.62 (d, J = 16.0 Hz, 1H), 7.44 – 7.40 (m, 2H), 7.38 (ddd, J = 3.6, 2.7, 1.9 Hz, 1H), 7.23 – 7.19 (m, 3H), 7.10 – 7.06 (m, 3H), 6.73 (s, 1H), 6.37 (d, J = 16.0 Hz, 1H), 6.06 (s, 2H), 4.18 (q, J = 7.1 Hz, 2H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 147.8, 147.1, 143.2, 141.5, 137.3, 133.5, 131.2, 131.0 (2C), 129.4, 128.1 (2C), 127.9, 127.8, 125.9, 123.3, 118.8, 116.4, 111.3, 110.5, 101.6, 91.5, 88.7, 60.3, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{26}H_{24}NO_4]^+$ 414.1700 ; found 414.1737.



(*E*)-3-(4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylprop-2-en-1-one (12a):

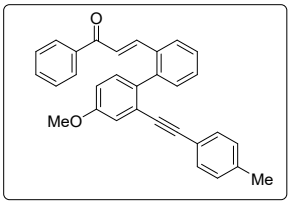
GP-7 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10q** (187 mg, 0.6 mmol), acetophenone (84 mg, 0.7 mmol), 40% NaOH in water dropwise, and Ethanol (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12a** (162 mg, 65%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10q**) = 0.5 and 0.6, R_f(**12a**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3056, 1727, 1596, 1457, 1318, 1216, 1027, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 3H), 7.68 (d, J = 15.8 Hz, 1H), 7.53 – 7.43 (m, 4H), 7.39 (t, J = 7.9, 7.7 Hz, 2H), 7.32 (d, J = 15.8 Hz, 1H), 7.24 – 7.19 (m, 4H), 7.16 – 7.11 (m, 3H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.0, 158.9, 144.0, 141.9, 138.1, 135.0, 134.2, 132.4, 131.4, 131.3 (3C), 129.6, 128.5 (2C), 128.3 (2C), 128.2 (2C), 128.1, 127.8, 126.4, 124.1, 123.3, 123.0, 116.4, 115.0, 92.8, 88.8, 55.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{23}O_2]^+$ 415.1693; found 415.1693.



(*E*)-3-(4'-Methoxy-2'-(*p*-tolylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylprop-2-en-1-one (12b):

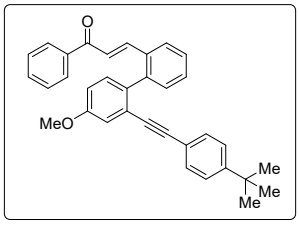
GP-7 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10r** (196 mg, 0.6 mmol), acetophenone (84 mg, 0.7 mmol), 40% NaOH in water dropwise, and Ethanol (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12b** (180 mg, 70%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10r**) = 0.5 and 0.6, R_f(**12b**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3056, 2926, 1597, 1458, 1319, 1218, 1030, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 3H), 7.69 (d, J = 15.8 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.36 (m, 2H), 7.32 (d, J = 15.8 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.15 (d, J = 2.7 Hz, 1H), 7.06 – 7.00 (m, 4H), 6.96 (dd, J = 8.5, 2.7 Hz, 1H), 3.88 (s, 3H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.1, 158.9, 144.1, 142.0, 138.3, 138.1, 134.9, 134.2, 132.4, 131.4, 131.2, 131.1 (2C), 129.5, 128.9 (2C), 128.5 (2C), 128.3 (2C), 127.7, 126.4, 124.3, 123.3, 119.9, 116.3, 114.8, 93.1, 88.2, 55.4, 21.4 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{31}H_{24}NaO_2]^+$ 451.1669; found 451.1663.



(*E*)-3-(2'-((4-(*tert*-butyl)phenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)-1-phenylprop-2-en-1-one (12c):

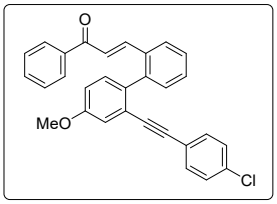
GP-7 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10v** (221 mg, 0.6 mmol), acetophenone (84 mg, 0.7 mmol), 40% NaOH in water dropwise, and Ethanol (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12c** (183 mg, 65%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10v**) = 0.5 and 0.6, R_f(**12c**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2958, 1733, 1656, 1459, 1319, 1215, 1026, 738 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.82 (m, 3H), 7.68 (d, J = 15.8 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.41 – 7.36 (m, 2H), 7.32 (d, J = 15.8 Hz, 1H), 7.26 – 7.19 (m, 3H), 7.15 (d, J = 2.7 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.96 (dd, J = 8.5, 2.7 Hz, 1H), 3.88 (s, 3H), 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.2, 158.9, 151.4, 144.2, 142.1, 138.1, 135.0, 134.2, 132.4, 131.4, 131.2, 131.0 (2C), 129.6, 128.5 (2C), 128.3 (2C), 127.7, 126.4, 125.2 (2C), 124.3, 123.4, 120.0, 116.3, 114.8, 93.0, 88.2, 55.4, 34.7, 31.1 (3C) ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{34}H_{30}NaO_2]^+$ 493.2138; found 493.2122.



(*E*)-3-(2'-((4-Chlorophenyl)ethynyl)-4'-methoxy-[1,1'-biphenyl]-2-yl)-1-phenylprop-2-en-1-one (12d):

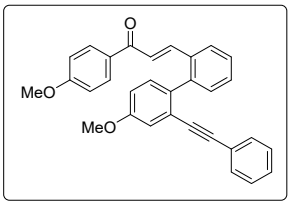
GP-7 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10x** (208 mg, 0.6 mmol), acetophenone (84 mg, 0.7 mmol), 40% NaOH in water dropwise, and Ethanol (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3), furnished the 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12d** (183 mg, 68%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**10x**) = 0.5 and 0.6, R_f(**12d**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2926, 1730, 1658, 1477, 1320, 1219, 1089, 822 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 3H), 7.67 (d, J = 15.8 Hz, 1H), 7.55 – 7.50 (m, 1H), 7.48 – 7.45 (m, 2H), 7.43 – 7.38 (m, 3H), 7.33 (d, J = 15.8 Hz, 1H), 7.22 (d, J = 8.5 Hz, 1H), 7.20 – 7.13 (m, 3H), 7.06 – 7.01 (m, 2H), 6.98 (dd, J = 8.5, 2.7 Hz, 1H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.8, 158.9, 143.9, 141.9, 138.0, 135.1, 134.2, 134.2, 132.5, 132.4 (2C), 131.4, 131.3, 129.6, 128.5 (2C), 128.4 (2C), 128.4 (2C), 127.8, 126.3, 123.7, 123.2, 121.5, 116.4, 115.2, 91.7, 89.8, 55.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{22}ClO_2]^+$ 449.1303; found 449.1289.



(*E*)-3-(4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-(4-methoxyphenyl)prop-2-en-1-one (12e):

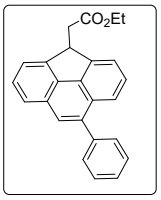
GP-7 was carried out with 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde **10q** (187 mg, 0.6 mmol), 4-methoxy acetophenone (105 mg, 0.7 mmol), 40% NaOH in water dropwise, and Ethanol (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 95:5), furnished the 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12e** (173 mg, 65%), as yellow solid; mp = 98-100 °C [TLC control (petroleum ether/ethyl acetate 95:5), R_f(**10q**) = 0.5 and 0.6, R_f(**12e**) = 0.3, UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3056, 2840, 1599, 1320, 1259, 1102, 1030, 730 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 – 7.82 (m, 3H), 7.67 (d, J = 15.7 Hz, 1H), 7.47 – 7.42 (m, 3H), 7.33 (d, J = 15.7 Hz, 1H), 7.25 – 7.22 (m, 2H), 7.20 (dd, J = 6.3, 2.4 Hz, 2H), 7.17 – 7.12 (m, 3H), 6.97 (dd, J = 8.5, 2.7 Hz, 1H), 6.89 – 6.86 (m, 2H), 3.88 (s, 3H), 3.85 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 163.1, 158.8, 143.1, 141.8, 135.2, 134.4, 131.4, 131.3 (3C), 131.0, 130.8 (2C), 129.3, 128.1 (2C), 128.1, 127.7, 126.4, 124.0, 123.2, 123.1, 116.4, 115.0, 113.6 (2C), 92.7, 88.9, 55.4, 55.4 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{31}H_{24}NaO_3]^+$ 467.1618; found 467.1602.



Ethyl 2-(8-phenyl-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2a):

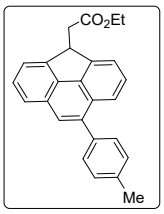
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1a** (106 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2a** (89 mg, 84%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1a**) = 0.4, R_f(**2a**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3050, 2977, 1729, 1248, 1204, 1157, 1026, 782 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.83 (s, 1H), 7.71 – 7.60 (m, 6H), 7.58 – 7.52 (m, 2H), 7.50 – 7.44 (m, 1H), 5.00 (t, J = 7.6 Hz, 1H), 4.33 (q, J = 7.2 Hz, 2H), 3.14 – 2.82 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 145.1, 144.5, 140.3, 139.1, 137.5, 136.8, 129.7 (2C), 128.5 (2C), 127.8, 127.8, 127.6, 127.4, 127.1, 125.5, 123.4, 122.5, 121.1, 120.8, 60.8, 45.7, 37.8, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{25}H_{20}NaO_2]^+$ 375.1356; found 375.1358.



Ethyl 2-(8-(*p*-tolyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2b):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1b** (110 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1),

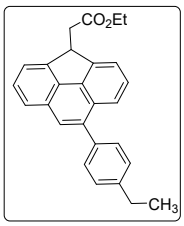
furnished the product **2b** (94 mg, 86%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1b**) = 0.4, R_f(**2b**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2974, 2922, 1727, 1509, 1162, 1102, 1028, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.81 (s, 1H), 7.71 – 7.56 (m, 6H), 7.36 (d, J = 7.8 Hz, 2H), 5.00 (t, J = 7.6 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.99 (d, J = 7.8 Hz, 2H), 2.49 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 145.1, 144.5, 139.0, 137.5, 137.4, 137.1, 136.7, 129.5 (2C), 129.2 (2C), 127.9, 127.7, 127.50, 127.3, 125.2, 123.3, 122.6, 120.9, 120.7, 60.8, 45.7, 37.9, 21.3, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_2]^+$ 367.1693; found 367.1693.



Ethyl 2-(8-(4-ethylphenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2c):

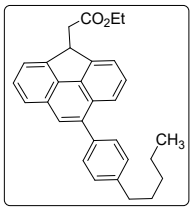
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1c** (114 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2c** (97 mg, 85%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1c**) = 0.4, R_f(**2c**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2967, 2925, 1729, 1453, 1203, 1158, 1026, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.0 Hz, 1H), 7.85 (dd, J = 6.2, 2.3 Hz, 1H), 7.82 (s, 1H), 7.71 – 7.60 (m, 6H), 7.39 (d, J = 8.0 Hz, 2H), 5.00 (t, J = 7.6 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.99 (d, J = 7.6 Hz, 2H), 2.79 (q, J = 7.6 Hz, 2H), 1.36 (t, J = 7.6 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 145.1, 144.5, 143.5, 139.1, 137.6, 137.5, 136.7, 129.6 (2C), 127.9 (2C), 127.9, 127.7, 127.5, 127.3, 125.3, 123.3, 122.7, 120.9, 120.7, 60.8, 45.7, 37.9, 28.6, 15.6, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_2]^+$ 381.1849; found 381.1848.



Ethyl 2-(8-(4-pentylphenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2d):

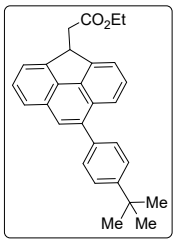
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1d** (127 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2d** (103 mg, 81%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1d**) = 0.4, R_f(**2d**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2858, 1730, 1504, 1203, 1157, 978, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.73 (s, 1H), 7.62 – 7.51 (m, 6H), 7.28 (d, J = 8.0 Hz, 2H), 4.91 (t, J = 7.6 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 2.90 (d, J = 7.6 Hz, 2H), 2.69 – 2.57 (m, 2H), 1.75 – 1.56 (m, 2H), 1.38 – 1.29 (m, 4H), 1.25 (t, J = 7.1 Hz, 3H), 0.87 (t, J = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.5, 145.1, 144.5, 142.2, 139.1, 137.6, 137.5, 136.7, 129.5 (2C), 128.5 (2C), 127.9, 127.7, 127.5, 127.3, 125.3, 123.3, 122.7, 120.9, 120.7, 60.8, 45.7, 37.9, 35.7, 31.6, 31.2, 22.6, 14.3, 14.1 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{31}O_2]^+$ 423.2319; found 423.2320.



Ethyl 2-(8-(4-(*tert*-butyl)phenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2e):

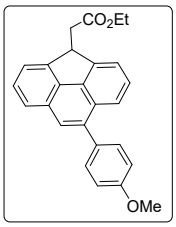
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1e** (122 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2e** (97 mg, 79%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1e**) = 0.4, R_f(**2e**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2959, 1729, 1456, 1368, 1203, 1157, 1025, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 1H), 7.86 (dd, J = 6.3, 2.2 Hz, 1H), 7.83 (s, 1H), 7.72 – 7.53 (m, 8H), 5.00 (t, J = 7.6 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 2.99 (d, J = 7.6 Hz, 2H), 1.45 (s, 9H), 1.34 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 150.3, 145.1, 144.5, 138.9, 137.5, 137.3, 136.7, 129.3 (2C), 127.9, 127.7, 127.5, 127.26, 125.4 (2C), 125.3, 123.3, 122.7, 120.9, 120.7, 60.8, 45.7, 37.9, 34.6, 31.4 (3C), 14.3 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{29}H_{32}NO_2]^+$ 426.2428; found 426.2409.



Ethyl 2-(8-(4-methoxyphenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2f):

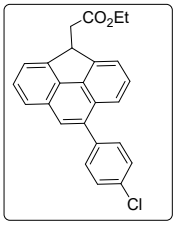
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1f** (115 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **2f** (103 mg, 90%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1f**) = 0.4, R_f(**2f**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2980, 1729, 1511, 1454, 1244, 1167, 1030, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.85 (ddd, J = 7.2, 7.2, 3.4 Hz, 1H), 7.80 (s, 1H), 7.73 – 7.57 (m, 6H), 7.14 – 7.04 (m, 2H), 5.00 (t, J = 7.6 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 2.99 (d, J = 7.7 Hz, 2H), 1.34 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.4, 159.1, 145.1, 144.4, 138.7, 137.5, 136.6, 132.7, 130.7, 127.9, 127.7 (2C), 127.5, 127.3, 125.1, 123.2, 122.6, 120.9, 120.6, 113.9 (2C), 60.8, 55.3, 45.7, 37.8, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_3]^+$ 383.1642; found 383.1634.



Ethyl 2-(8-(4-chlorophenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2g):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1g** (116 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude

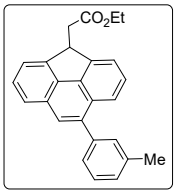
mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2g** (95 mg, 82%), as brown solid; mp = 58-60 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1g**) = 0.4, R_f(**2g**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2980, 1730, 1489, 1247, 1205, 1092, 1023, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.82 (m, 2H), 7.79 (s, 1H), 7.72 – 7.59 (m, 6H), 7.54 – 7.49 (m, 2H), 5.00 (t, J = 7.6 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 2.99 (d, J = 7.6 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 145.2, 144.5, 138.7, 137.7, 137.5, 136.8, 133.4, 130.9 (2C), 128.7 (2C), 127.9, 127.7, 127.6, 126.9, 125.6, 123.4, 122.2, 121.2, 121.0, 60.8, 45.7, 37.8, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{20}ClO_2]^+$ 387.1146; found 387.1137.



Ethyl 2-(8-(*m*-tolyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2h):

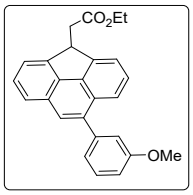
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1h** (110 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2h** (85 mg, 77%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1h**) = 0.4, R_f(**2h**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2974, 2922, 1729, 1596, 1198, 1162, 1030, 792 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.88 – 7.85 (m, 1H), 7.83 (s, 1H), 7.73 – 7.60 (m, 4H), 7.55 – 7.48 (m, 2H), 7.44 (dd, J = 7.5, 7.5 Hz, 1H), 7.29 (d, J = 7.4 Hz, 1H), 5.01 (t, J = 7.6 Hz, 1H), 4.34 (q, J = 7.1 Hz, 2H), 3.00 (dd, J = 7.6, 0.7 Hz, 2H), 2.50 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 145.1, 144.5, 140.2, 139.2, 138.1, 137.5, 136.7, 130.3, 128.3, 128.1, 127.8, 127.7, 127.5, 127.2, 126.8, 125.3, 123.3, 122.6, 121.0, 120.7, 60.8, 45.7, 37.9, 21.5, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{26}H_{26}NO_2]^+$ 384.1958; found 384.1961.



Ethyl 2-(8-(3-methoxyphenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2i):

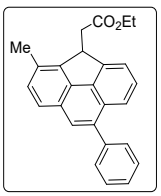
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1i** (115 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **2i** (95 mg, 83%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1i**) = 0.4, R_f(**2i**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 2852, 1730, 1591, 1460, 1158, 1035, 789 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.0 Hz, 1H), 7.88 – 7.84 (m, 1H), 7.84 (s, 1H), 7.72 – 7.58 (m, 4H), 7.49 – 7.42 (m, 1H), 7.30 – 7.22 (m, 2H), 7.02 (ddd, J = 8.3, 2.6, 0.9 Hz, 1H), 5.00 (t, J = 7.6 Hz, 1H), 4.33 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 2.99 (dd, J = 7.6, 0.6 Hz, 2H), 1.33 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 159.6, 145.1, 144.5, 141.7, 138.9, 137.5, 136.8, 129.5, 127.8, 127.8, 127.6, 127.1, 125.4, 123.4, 122.6, 122.2, 121.1, 120.9, 115.2, 113.0, 60.8, 55.3, 45.7, 37.8, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{26}H_{26}NO_3]^+$ 400.1907; found 400.1919.



Ethyl 2-(3-methyl-8-phenyl-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2j):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1j** (110 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2j** (85 mg, 77%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1j**) = 0.4, R_f(**2j**) = 0.5 UV detection].

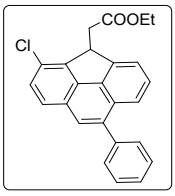
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2977, 1725, 1448, 1375, 1155, 1100, 1025, 735 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 6.8 Hz, 2H), 7.73 – 7.65 (m, 3H), 7.63 – 7.51 (m, 3H), 7.47 (dd, J = 9.6, 4.6 Hz, 2H), 5.03 (dd, J = 10.5, 3.8 Hz, 1H),

4.26 (q, *J* = 7.1 Hz, 2H), 3.48 (dd, *J* = 16.1, 3.9 Hz, 1H), 2.70 (s, 3H), 2.60 (dd, *J* = 16.1, 10.5 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 145.6, 141.3, 140.4, 138.0, 137.4, 136.9, 130.9, 130.3, 129.7 (2C), 128.4 (2C), 127.5, 127.3, 127.2, 126.1, 125.3, 123.7, 122.5, 121.2, 60.7, 45.3, 36.6, 18.9, 14.2 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_2]^+$ 367.1693; found 367.1698.



Ethyl 2-(3-chloro-8-phenyl-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2k):

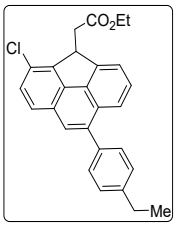
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1k** (116 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2k** (83 mg, 72%), as off-white solid; mp = 62–64 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1k**) = 0.4, R_f(**2k**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2971, 1730, 1589, 1479, 1338, 1161, 1027, 702 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.82 – 7.77 (m, 1H), 7.77 (s, 1H), 7.73 (d, *J* = 7.2 Hz, 1H), 7.70 – 7.61 (m, 3H), 7.57 – 7.51 (m, 3H), 7.50 – 7.43 (m, 1H), 5.11 (dd, *J* = 10.5, 3.6 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.80 (dd, *J* = 16.4, 3.8 Hz, 1H), 2.64 (dd, *J* = 16.4, 10.5 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1, 144.9, 140.2, 139.9, 139.3, 138.2, 137.0, 129.6 (2C), 128.7, 128.5 (2C), 128.2, 127.6, 127.5, 126.6, 126.2, 125.6, 124.9, 122.8, 121.8, 60.8, 46.2, 35.2, 14.1 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{20}ClO_2]^+$ 387.1146; found 387.1148.



Ethyl 2-(3-chloro-8-(4-ethylphenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2l):

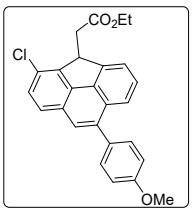
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1l** (124 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2l** (90 mg, 72%), as brown solid; mp = 78–80 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1l**) = 0.4, R_f(**2l**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2966, 1730, 1446, 1251, 1160, 1092, 1024, 798 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.1 Hz, 1H), 7.80 – 7.76 (m, 1H), 7.75 (s, 1H), 7.71 (d, J = 7.2 Hz, 1H), 7.65 – 7.53 (m, 4H), 7.38 (d, J = 8.2 Hz, 2H), 5.10 (dd, J = 10.5, 3.8 Hz, 1H), 4.24 (dt, J = 14.1, 7.0 Hz, 2H), 3.80 (dd, J = 16.4, 3.8 Hz, 1H), 2.78 (q, J = 7.6 Hz, 2H), 2.63 (dd, J = 16.4, 10.5 Hz, 1H), 1.35 (t, J = 7.6 Hz, 3H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 144.9, 143.6, 140.2, 139.3, 138.1, 137.2, 137.0, 129.5 (2C), 128.6, 128.1, 128.0 (2C), 127.6, 126.4, 126.3, 125.5, 124.6, 122.9, 121.7, 60.7, 46.2, 35.2, 28.6, 15.6, 14.1 ppm.

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{27}H_{27}ClNO_2]^+$ 432.1725; found 432.1742.



Ethyl 2-(3-chloro-8-(4-methoxyphenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2m):

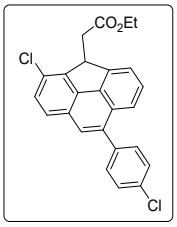
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1m** (125 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **2m** (99 mg, 79%), as brown solid; mp = 92–94 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1m**) = 0.4, R_f(**2m**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3052, 2978, 1730, 1510, 1450, 1245, 1027, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.1, 8.2 Hz, 1H), 7.77 (dd, J = 8.2, 2.8 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.64 (d, J = 8.0 Hz, 1H), 7.59 (ddd, J = 6.8, 2.1, 2.3 Hz, 2H), 7.54 (d, J = 8.3 Hz, 1H), 7.08 (d, J = 8.7 Hz, 2H), 5.10 (dd, J = 10.5, 3.6 Hz, 1H), 4.24 (q, J = 7.1 Hz, 2H), 3.92 (s, 3H), 3.79 (dd, J = 16.4, 3.7 Hz, 1H), 2.63 (dd, J = 16.4, 10.5 Hz, 1H), 1.24 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 159.2, 144.9, 140.2, 138.9, 138.0, 137.0, 132.4, 130.7 (2C), 128.6, 128.4, 128.2, 127.8, 126.3, 125.4, 124.5, 122.9, 121.7, 113.9 (2C), 60.8, 55.4, 46.2, 35.2, 14.2 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{26}H_{25}ClNO_3]^+$ 434.1517; found 434.1525.



Ethyl 2-(3-chloro-8-(4-chlorophenyl)-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2n)

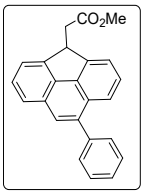
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1n** (126 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2n** (88 mg, 70%), as brown solid; mp = 110–112 °C. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1n**) = 0.4, R_f(**2n**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3054, 2924, 1726, 1447, 1217, 1161, 1018, 732 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 6.2 Hz, 2H), 7.65 – 7.61 (m, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 2H), 5.09 (dd, *J* = 10.5, 3.6 Hz, 1H), 4.24 (q, *J* = 6.8 Hz, 2H), 3.79 (dd, *J* = 16.5, 3.8 Hz, 1H), 2.64 (dd, *J* = 16.5, 10.5 Hz, 1H), 1.24 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.0, 145.0, 140.2, 138.4, 138.2, 137.10, 137.0, 133.6, 130.8 (2C), 128.8, 128.7 (2C), 128.4, 127.3, 126.8, 126.1, 125.6, 124.9, 122.4, 121.10, 60.8, 46.2, 35.2, 14.2 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{25}H_{22}Cl_2NO_2]^+$ 438.1022; found 438.1042.



Methyl 2-(8-phenyl-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2o):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1o** (101 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1),

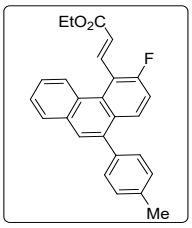
furnished the product **2o** (86 mg, 85%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1o**) = 0.4, R_f(**2o**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3050, 1733, 1434, 1352, 1207, 1161, 1011, 734 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.0 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.84 (s, 1H), 7.72 – 7.61 (m, 6H), 7.56 (dd, J = 10.2, 4.7 Hz, 2H), 7.51 – 7.45 (m, 1H), 5.01 (t, J = 7.7 Hz, 1H), 3.88 (s, 3H), 3.00 (dd, J = 7.7, 0.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 172.9, 145.0, 144.4, 140.3, 139.1, 137.5, 136.7, 129.6 (2C), 128.5 (2C), 127.8, 127.8, 127.6, 127.4, 127.2, 125.5, 123.4, 122.6, 121.0, 120.8, 51.9, 45.6, 37.6 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{24}H_{19}O_2]^+$ 339.1380; found 339.1379.



Ethyl (*E*)-3-(3-fluoro-10-(*p*-tolyl)phenanthren-4-yl)acrylate (2ip):

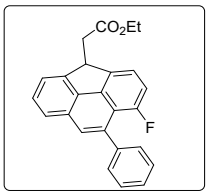
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1p** (115 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2ip** (81 mg, 70%), as brown viscous oil. [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1p**) = 0.4, R_f(**2ip**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2926, 1713, 1633, 1311, 1265, 1095, 1033, 755 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, J = 8.1 Hz, 1H), 8.19 (d, J = 16.3 Hz, 1H), 8.01 – 7.86 (m, 2H), 7.72 – 7.60 (m, 3H), 7.39 (d, J = 8.0 Hz, 2H), 7.37 – 7.30 (m, 3H), 6.70 (dd, J = 16.3, 3.1 Hz, 1H), 4.40 (q, J = 7.1 Hz, 2H), 2.49 (s, 3H), 1.43 (t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 159.1 (d, J = 251.1 Hz), 140.0, 138.3, 137.3, 137.3, 133.4, 131.5 (d, J = 2.9 Hz), 129.9 (2C), 129.7 (d, J = 10.3 Hz), 129.6 (d, J = 3.6 Hz), 129.1 (3C), 128.9, 128.5 (d, J = 8.6 Hz), 127.5, 127.4, 125.8, 123.5 (d, J = 9.9 Hz), 118.9 (d, J = 12.1 Hz), 115.1 (d, J = 26.2 Hz), 60.6, 21.2, 14.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{22}FO_2]^+$ 385.1598; found 385.1591.



Ethyl 2-(1-fluoro-9-phenyl-4*H*-cyclopenta[*def*]phenanthren-4-yl)acetate (2q):

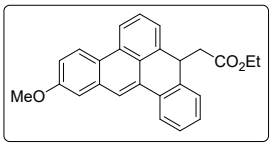
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1q** (111 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 99:1), furnished the product **2q** (79 mg, 71%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 99:1), R_f(**1q**) = 0.4, R_f(**2q**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2972, 1728, 1449, 1337, 1213, 1152, 1023, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.61 (ddd, J = 7.4, 7.1, 341 Hz, 4H), 7.51 (ddd, J = 11.4, 7.1, 5.2 Hz, 3H), 7.42 (ddd, J = 7.4, 3.7, 1.2 Hz, 1H), 7.27 – 7.19 (m, 1H), 4.88 (t, J = 7.6 Hz, 1H), 4.26 (q, J = 7.1 Hz, 2H), 2.95 (dd, J = 16.4, 7.3 Hz, 1H), 2.86 (dd, J = 16.4, 7.9 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 157.3 (d, J = 252.8 Hz), 145.9, 139.9, 139.8 (d, J = 3.6 Hz), 139.5 (d, J = 1.1 Hz), 138.7 (d, J = 7.7 Hz), 136.7 (d, J = 3.1 Hz), 129.6 (2C), 128.5 (2C), 128.1, 127.6, 127.4, 122.8, 121.6, 121.4 (d, J = 7.4 Hz), 119.1, 116.8 (d, J = 21.4 Hz), 112.3 (d, J = 21.3 Hz), 60.9, 45.2, 37.9, 14.3 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{25}H_{20}FO_2]^+$ 371.1442; found 371.1435.



Ethyl 2-(2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3a):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1r** (115 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3a** (103 mg, 90%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1r**) = 0.4, R_f(**3a**) = 0.5 UV detection].

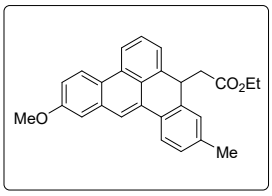
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2930, 1724, 1611, 1457, 1246, 1152, 1032, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, J = 9.1 Hz, 1H), 8.40 (d, J = 8.2 Hz, 1H), 8.20 (s, 1H), 8.07 (d, J = 7.9 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.45 (d, J = 7.1 Hz, 1H), 7.40 (dd, J = 7.5, 1.2 Hz, 1H), 7.33 (ddd, J = 7.6, 7.6, 1.5 Hz, 1H), 7.30 – 7.22 (m, 2H), 7.18 (dd, J = 8.9, 2.8 Hz,

1H), 4.83 (t, *J* = 7.2 Hz, 1H), 3.99 – 3.93 (m, 2H), 3.92 (s, 3H), 2.59 (dd, *J* = 14.5, 7.0 Hz, 1H), 2.49 (dd, *J* = 14.5, 7.4 Hz, 1H), 1.02 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 158.5, 137.9, 136.7, 133.5, 132.1, 130.7, 128.9, 128.5, 127.9, 127.3, 126.7, 125.6, 124.8, 124.8, 124.3, 124.2, 120.7, 119.8, 117.1, 108.8, 60.4, 55.4, 48.4, 42.2, 14.0 ppm.

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_3]^+$ 405.1461; found 405.1464.



Ethyl 2-(2-methoxy-10-methyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3b):

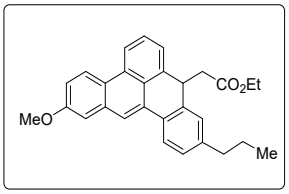
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1s** (119 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3b** (108 mg, 91%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1s**) = 0.4, R_f(**3b**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 1726, 1612, 1458, 1245, 1152, 1033, 801 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.1 Hz, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 8.16 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.45 (d, *J* = 7.1 Hz, 1H), 7.26 (d, *J* = 2.2 Hz, 1H), 7.21 (s, 1H), 7.20 – 7.13 (ddd, *J* = 8.1, 7.3, 2.1 Hz, 2H), 4.79 (t, *J* = 7.2 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 2.60 (dd, *J* = 14.4, 6.8 Hz, 1H), 2.49 (dd, *J* = 14.4, 7.6 Hz, 1H), 2.35 (s, 3H), 1.04 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 158.6, 137.1, 137.10, 136.1, 133.8, 130.9, 129.4, 129.2, 129.1, 128.4, 126.8, 125.7, 124.9, 124.8, 124.4, 124.3, 120.8, 119.3, 117.0, 108.9, 60.5, 55.5, 48.7, 42.3, 21.3, 14.2 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{27}H_{28}NO_3]^+$ 414.2064; found 414.2068.



Ethyl 2-(2-methoxy-10-propyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3c):

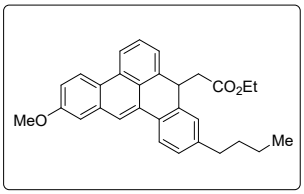
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1t** (127 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3c** (108 mg, 85%), as brown solid; mp = 82–84 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1t**) = 0.4, R_f(**3c**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2958, 1728, 1613, 1457, 1246, 1153, 1034, 800 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.0 Hz, 1H), 8.47 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.60 (dd, *J* = 8.1, 7.3 Hz, 1H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.27 (d, *J* = 1.3 Hz, 1H), 7.23 (ddd, *J* = 9.9, 8.5, 2.2 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 2.66 (dd, *J* = 13.5, 6.9 Hz, 1H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.54 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.70 (ddd, *J* = 14.7, 7.3, 1.8 Hz, 2H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 158.4, 142.7, 137.8, 136.9, 133.6, 130.7, 129.5, 129.1, 128.4, 127.6, 126.6, 125.6, 124.8, 124.6, 124.3, 124.2, 120.6, 119.3, 116.8, 108.7, 60.4, 55.4, 48.6, 42.2, 37.7, 24.4, 14.0, 13.8 ppm

HRMS (ESI) *m/z*: $[M+NH4]^+$ calcd for $[C_{29}H_{32}NO_3]^+$ 442.2377; found 442.2371.



Ethyl 2-(10-butyl-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3d):

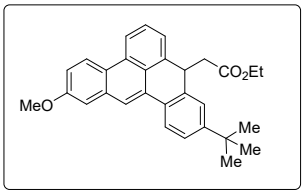
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1u** (131 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3d** (114 mg, 87%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1u**) = 0.4, R_f(**3d**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2934, 1733, 1613, 1454, 1368, 1262, 1033, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 9.1 Hz, 1H), 8.47 (d, *J* = 7.8 Hz, 1H), 8.23 (s, 1H), 8.04 (d, *J* = 8.1 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.33 (d, *J* = 2.6 Hz, 1H), 7.27 (s, 1H), 7.24 (ddd, *J* = 9.1, 4.4, 0.9 Hz, 2H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 2.68 (m, 2H), 2.62 (dd, *J* = 14.2, 7.3 Hz, 1H), 2.54 (dd, *J* = 14.4, 7.5 Hz, 1H), 1.66 (dt, *J* = 15.4, 7.5 Hz, 2H), 1.40 (dq, *J* = 14.7, 7.3 Hz, 2H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 158.5, 142.9, 137.9, 136.9, 133.7, 130.7, 129.5, 129.1, 128.4, 127.6, 126.7, 125.6, 124.8, 124.6, 124.3, 124.2, 120.7, 119.2, 116.9, 108.7, 60.4, 55.4, 48.6, 42.3, 35.4, 33.5, 22.4, 14.1, 13.1 ppm

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{30}H_{30}NaO_3]^+$ 461.2087 ; found 461.2071.



Ethyl 2-(10-(*tert*-butyl)-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3e):

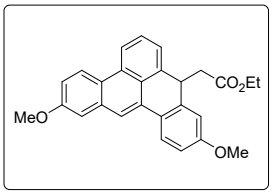
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1v** (131 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3e** (122 mg, 93%), as brown solid; mp = 130–132 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1v**) = 0.4, R_f(**3e**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2957, 1324, 1610, 1324, 1247, 1142, 1030, 733 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 9.1 Hz, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.24 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 7.0 Hz, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.44 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.34 (d, *J* = 2.6 Hz, 1H), 7.24 (dd, *J* = 9.2, 2.9 Hz, 1H), 4.91 (t, *J* = 7.3 Hz, 2H), 4.05 (s, 3H), 2.66 (dd, *J* = 14.4, 7.1 Hz, 1H), 2.55 (dd, *J* = 14.5, 7.5 Hz, 1H), 1.39 (s, 9H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 158.5, 151.1, 137.6, 137.0, 133.6, 130.7, 129.3, 129.0, 126.7, 125.6, 125.3, 124.8, 124.7, 124.5, 124.3, 124.0, 120.6, 119.3, 116.9, 108.7, 60.4, 55.4, 48.7, 42.6, 34.6, 31.3 (3C), 14.1 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{30}H_{34}NO_3]^+$ 456.2533; found 456.2532.



Ethyl 2-(2,10-dimethoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3f):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1w** (124 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 97:3),

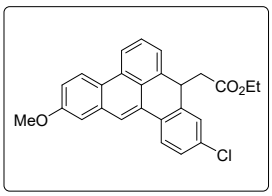
furnished the product **3f** (114 mg, 92%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 97:3), R_f(**1w**) = 0.4, R_f(**3f**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2931, 1723, 1607, 1457, 1238, 1162, 1031, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 9.1 Hz, 1H), 8.50 (d, J = 7.7 Hz, 1H), 8.15 (s, 1H), 8.05 (d, J = 8.7 Hz, 1H), 7.59 (dd, J = 8.1, 7.3 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.31 (d, J = 2.6 Hz, 1H), 7.22 (dd, J = 9.0, 2.7 Hz, 1H), 6.97 (ddd, J = 8.6, 8.6, 2.7 Hz, 2H), 4.86 (t, J = 7.1 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 3.88 (s, 3H), 2.67 (dd, J = 14.6, 6.9 Hz, 1H), 2.55 (dd, J = 14.6, 7.4 Hz, 1H), 1.10 (t, J = 7.2 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 159.5, 158.5, 139.6, 136.7, 133.7, 130.8, 129.0, 126.6, 125.8, 125.4, 124.1, 124.8, 124.4, 124.3, 120.7, 118.5, 116.7, 114.0, 112.7, 108.7, 60.5, 55.4, 55.3, 48.5, 42.5, 14.0 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_4]^+$ 413.1747; found 413.1738.



Ethyl 2-(10-chloro-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3g):

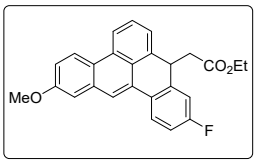
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1x** (125 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3g** (100 mg, 80%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1x**) = 0.4, R_f(**3g**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 1723, 1610, 1461, 1243, 1162, 1029, 733 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.47 (d, J = 9.0 Hz, 1H), 8.43 (d, J = 8.1 Hz, 1H), 8.13 (s, 1H), 7.96 (d, J = 8.6 Hz, 1H), 7.58 (dd, J = 8.1, 7.3 Hz, 1H), 7.47 (d, J = 7.1 Hz, 1H), 7.41 (d, J = 2.2 Hz, 1H), 7.31 (dd, J = 8.5, 2.2 Hz, 1H), 7.27 – 7.22 (ddd, J = 8.1, 7.3, 2.1 Hz, 2H), 4.79 (t, J = 7.2 Hz, 1H), 4.03 (q, J = 7.1 Hz, 2H), 3.97 (s, 3H), 2.61 (dd, J = 14.7, 7.3 Hz, 1H), 2.53 (dd, J = 14.7, 7.2 Hz, 1H), 1.11 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 158.5, 139.5, 136.0, 133.5, 133.3, 130.7 (2C), 128.3, 127.9, 127.5, 126.8, 125.6, 125.18, 124.8, 124.8, 124.3, 120.8, 119.1, 117.3, 108.8, 60.5, 55.4, 48.2, 41.8, 14.0 ppm

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{21}ClNaO_3]^+$ 439.1071; found 439.1055.



Ethyl 2-(10-fluoro-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3h)

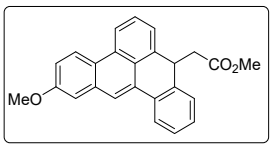
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1y** (120 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3h** (84 mg, 70%), as brown viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1y**) = 0.4, R_f(**3h**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3062, 2968, 1724, 1611, 1456, 1236, 1032, 802 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, J = 9.1 Hz, 1H), 8.42 (d, J = 7.9 Hz, 1H), 8.11 (s, 1H), 8.03 (dd, J = 8.8, 3.3 Hz, 1H), 7.56 (dd, J = 8.1, 7.3 Hz, 1H), 7.46 (d, J = 7.1 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.23 – 7.18 (m, 1H), 7.12 (d, J = 9.2 Hz, 1H), 7.05 (ddd, J = 8.5, 7.9, 2.7 Hz, 1H), 4.81 (t, J = 7.1 Hz, 1H), 4.00 (qd, J = 7.1, 0.8 Hz, 2H), 3.95 (s, 3H), 2.60 (dd, J = 14.7, 7.3 Hz, 1H), 2.52 (dd, J = 14.7, 7.0 Hz, 1H), 1.07 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 162.4 (d, J = 248.1 Hz), 158.5, 140.1 (d, J = 7.6 Hz), 136.1, 133.4, 130.7, 128.3 (d, J = 3.0 Hz), 128.1, 126.8, 126.2 (d, J = 8.3 Hz), 125.2, 124.8, 124.6, 124.3, 120.8, 119.6 (d, J = 1.4 Hz), 117.10, 114.8 (d, J = 21.3 Hz), 114.6 (d, J = 21.6 Hz), 108.8, 60.5, 55.4, 48.2, 42.1, 14.0 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{26}H_{25}FNO_3]^+$ 418.1813; found 418.1808.



Methyl 2-(2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3i):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1z** (110 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3i** (94 mg, 85%), as yellow powder; mp = 92–94 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1z**) = 0.4, R_f(**3i**) = 0.5 UV detection].

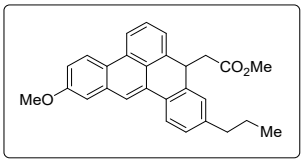
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2927, 1730, 1612, 1453, 1245, 1151, 1030, 767 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, J = 9.1 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 8.13 (d, J = 7.4 Hz, 1H), 7.63 – 7.57 (d, , J = 7.9 Hz, 1H), 7.50 (d, J = 7.1 Hz, 1H), 7.44

(d, J = 7.4 Hz, 1H), 7.40 (ddd, J = 7.6, 1.5 Hz, 1H), 7.34 (dd, , J = 7.9, 2.1 Hz, 2H), 7.24 (d, J = 7.4, Hz, 1H), 4.89 (t, J = 7.2 Hz, 1H), 3.98 (s, 3H), 3.54 (s, 3H), 2.66 (dd, J = 14.5, 7.0 Hz, 1H), 2.55 (dd, J = 14.5, 7.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 158.5, 137.8, 136.6, 133.5, 132.1, 130.7, 128.8, 128.4, 127.10, 127.3, 126.7, 125.5, 124.8, 124.7, 124.3, 124.7, 120.7, 119.9, 117.1, 108.8, 55.4, 51.5, 48.2, 42.2 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{25}H_{24}NO_3]^+$ 386.1751; found 386.1762.



Methyl 2-(2-methoxy-10-propyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3j):

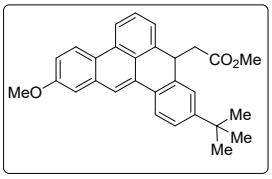
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1aa** (123 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3j** (102 mg, 83%), as brown solid; mp = 110–112 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1aa**) = 0.4, R_f(**3j**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2950, 1730, 1161, 1451, 1246, 1151, 1029, 799 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 9.0 Hz, 1H), 8.47 (d, J = 8.0 Hz, 1H), 8.24 (s, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.60 (dd, J = 8.1, 7.3 Hz, 1H), 7.51 (d, J = 7.1 Hz, 1H), 7.33 (d, J = 2.6 Hz, 1H), 7.27 (d, J = 1.3 Hz, 1H), 7.23 (ddd, J = 9.9, 8.5, 2.2 Hz, 2H), 4.88 (s, 3H), 4.00 (s, 3H), 2.66 (dd, J = 13.5, 6.9 Hz, 1H), 2.63 (t, J = 7.1 Hz, 2H), 2.54 (dd, J = 14.5, 7.5 Hz, 1H), 1.70 (ddd, J = 14.7, 7.3, 1.8 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.9, 158.4, 142.7, 137.7, 136.8, 133.6, 130.7, 129.5, 129.0, 128.3, 127.7, 126.6, 125.5, 124.7, 124.6, 124.3, 124.2, 120.7, 119.3, 116.8, 108.7, 55.3, 51.4, 48.3, 42.3, 37.7, 24.4, 13.8 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{28}H_{30}NO_3]^+$ 428.2220; found 428.2214.



Methyl 2-(10-(*tert*-butyl)-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3k)

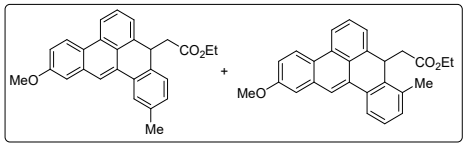
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1ab** (127 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3k** (117 mg, 92%), as brown solid; mp = 160–162 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1ab**) = 0.4, R_f(**3k**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2954, 1729, 1608, 1451, 1233, 1142, 1027, 805 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 9.1 Hz, 1H), 8.48 (d, J = 7.9 Hz, 1H), 8.25 (s, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.60 (dd, J = 7.3, 8.3 Hz,1H), 7.51 (d, J = 7.1 Hz, 1H), 7.47 (d, J = 2.0 Hz, 1H), 7.44 (dd, J = 8.3, 2.1 Hz, 1H), 7.34 (d, J = 2.6 Hz, 1H), 7.24 (dd, J = 9.2, 2.8 Hz, 1H), 4.91 (t, J = 7.4 Hz, 1H), 4.00 (s, 3H), 3.58 (s, 3H), 2.66 (dd, J = 14.4, 7.4 Hz, 1H), 2.56 (dd, J = 14.4, 7.3 Hz, 1H), 1.39 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 158.5, 151.2, 137.5, 137.0, 133.7, 130.8, 129.3, 129.0, 126.7, 125.6, 125.3, 124.8, 124.7, 124.6, 124.4, 124.1, 120.8, 119.4, 117.0, 108.8, 55.5, 51.6, 48.5, 42.7, 34.7, 31.3 (3C) ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{29}H_{29}O_3]^+$ 425.2111; found 425.2112.



Ethyl 2-(2-methoxy-11-methyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetate & Ethyl 2-(2-methoxy-9-methyl-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (1:0.6) (3l+3l'):

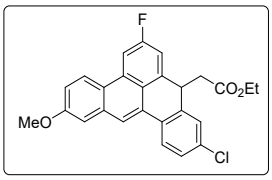
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1ac** (119 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3l+3l'** (83 mg, 70%), as brown solid; mp = 100–102 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1ac**) = 0.4, R_f(**3l+3l'**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2970, 1726, 1612, 1458, 1247, 1149, 1030, 732 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (2×d, J = 9.0 Hz, 1H), 8.43 (2×d, J = 7.9 Hz, 1H), 8.23 (2×s, 1H), 8.00 – 7.90 (m, 1H), 7.58 – 7.51 (m, 1H), 7.48 – 7.46 (m, 1H), 7.31 (2×dd, J = 9.6, 7.8 Hz, 2H), 7.23 – 7.11 (m, 2H), 4.93 (2×dd, J = 7.4, 3.1 Hz, 1H), 4.00 and 3.95 (2×q, J = 7.1 Hz, 2H), 3.95 (2×s, 3H), 2.63 – 2.28 (m, 2H), 2.55 and 2.43 (2×s, 3H), 1.06 and 1.05 (2×t, J = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5 (2C), 158.5 (2C), 136.9, 136.7, 136.6, 135.2, 135.1, 133.6, 133.6, 132.4, 131.8, 130.7, 130.7, 130.2, 129.6, 129.0, 128.9, 128.4, 126.9, 126.6, 126.5, 125.7, 124.8, 124.8, 124.8, 124.7, 124.7, 124.3, 124.2, 122.4, 120.7, 120.6, 120.0, 119.6, 117.0 (2C), 108.8, 108.8, 60.4 (2C), 55.4, 48.5, 45.3, 41.8 (2C), 38.9, 21.5, 19.1, 14.0 (2C) ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{27}H_{28}NO_3]^+$ 414.2064; found 414.2059.



Ethyl 2-(10-chloro-6-fluoro-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3m):

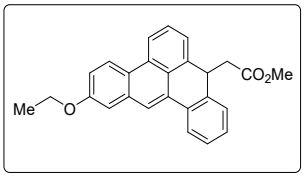
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1ad** (130 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3m** (98 mg, 75%), as orange solid; mp = 110–112 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1ad**) = 0.4, R_f(**3m**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2920, 1726, 1608, 1455, 1221, 1153, 1029, 821 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.98 (dd, *J* = 9.2, 3.0 Hz, 1H), 8.25 (s, 1H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.38 – 7.31 (m, 3H), 7.28 (ddd, *J* = 9.1, 2.7, 1.4 Hz, 1H), 4.83 (t, *J* = 7.2 Hz, 1H), 4.03 (qd, *J* = 3.6, 2.2 Hz, 2H), 4.00 (s, 3H), 2.60 (dd, *J* = 14.7, 7.0 Hz, 1H), 2.51 (dd, *J* = 14.7, 7.4 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 162.3 (d, *J* = 235.6 Hz), 158.6, 158.3 (d, *J* = 2.6 Hz), 139.3, 134.0, 133.8, 131.5 (d, *J* = 3.8 Hz), 130.7 (d, *J* = 3.0 Hz), 130.3, 129.1 (d, *J* = 26.0 Hz), 128.1, 127.8, 127.6, 125.8, 124.9 (d, *J* = 9.6 Hz), 122.7, 121.6, 117.3 (d, *J* = 2.5 Hz), 113.6 (d, *J* = 25.0 Hz), 109.1, 60.6, 55.3, 48.1, 41.8, 14.0 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{21}ClFO_3]^+$ 435.1158; found 435.1158.



Methyl 2-(2-ethoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3n):

GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1ae** (115 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude

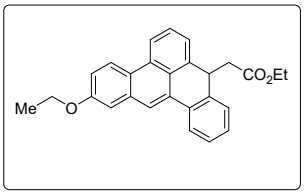
mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3n** (91 mg, 79%), as brown solid; mp = 96–98 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1ae**) = 0.4, R_f(**3n**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3051, 2927, 1730, 1609, 1451, 1236, 1035, 733 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 9.0 Hz, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.26 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.1 Hz, 1H), 7.52 (d, J = 7.1 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.40 (dd, J = 7.1, 8.1 Hz,1H), 7.33 (ddd, J = 8.1, 7.9, 2.1 Hz, 2H), 7.25 (d, J = 2.6 Hz, 1H), 4.90 (dd, J = 7.2, 7.6 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 4.01 (s, 3H), 2.65 (dd, J = 14.5, 7.0 Hz, 1H), 2.55 (dd, J = 14.6, 7.5 Hz, 1H), 1.53 (t, J = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 157.8, 137.8, 136.6, 133.5, 132.1, 130.7, 128.8, 128.4, 127.9, 127.3, 126.7, 125.5, 124.8, 124.7, 124.2, 124.2, 120.7, 119.9, 117.5, 109.6, 63.5, 51.5, 48.2, 42.2, 14.9 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{26}H_{23}O_3]^+$ 383.1642; found 383.1663.



Ethyl 2-(2-ethoxy-8*H*-benzo[*gh*]tetraphen-8-yl)acetate (3o):

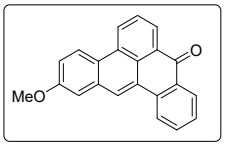
GP-5 was carried out with Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1af** (119 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2), furnished the product **3o** (95 mg, 80%), as off-white solid; mp = 110–112 °C. [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1af**) = 0.4, R_f(**3o**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2977, 1725,1611, 1457, 1239, 1148, 1036, 734 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.53 (d, J = 9.0 Hz, 1H), 8.48 (d, J = 8.1 Hz, 1H), 8.26 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.1 Hz, 1H), 7.52 (d, J = 7.1 Hz, 1H), 7.46 (d, J = 7.4 Hz, 1H), 7.40 (dd, J = 7.1, 8.1 Hz,1H), 7.33(ddd, J = 8.1, 7.9, 2.1 Hz, 2H), 7.25 (d, J = 2.6 Hz, 1H), 4.90 (dd, J = 7.2, 7.6 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 4.01 (q, J = 7.2 Hz, 2H), 2.65 (dd, J = 14.5, 7.0 Hz, 1H), 2.55 (dd, J = 14.6, 7.5 Hz, 1H), 1.53 (t, J = 7.0 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 157.8, 137.9, 136.7, 133.5, 132.1, 130.7, 128.8, 128.5, 127.9, 127.3, 126.7, 125.5, 124.8, 124.7, 124.3, 124.2, 120.7, 119.8, 117.4, 109.6, 63.5, 60.4, 48.4, 42.2, 14.9, 14.0 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{27}H_{25}O_3]^+$ 397.1798; found 397.1775.



2-Methoxy-8*H*-benzo[*gh*]tetraphen-8-one (4a):

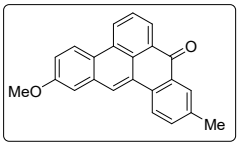
GP-6 was carried out with ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate **11a** (107 mg, 0.3 mmol), TfOH (67.5 mg, 0.45 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 90:10), furnished the product **4a** (65 mg, 70%), as yellow solid; mp = 200–202 °C. [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**11a**) = 0.5, R_f(**4a**) = 0.2 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 1735, 1646, 1594, 1456, 1310, 1031, 732 cm^{-1}.

^{1}H NMR(400 MHz, $CDCl_3$) δ 8.87 (dd, J = 8.2, 0.8 Hz, 1H), 8.72 (dd, J = 7.4, 1.1 Hz, 1H), 8.59 (s, 1H), 8.56 – 8.48 (m, 2H), 8.40 (d, J = 8.1 Hz, 1H), 7.89 – 7.83 (m, 1H), 7.78 – 7.73 (m, 1H), 7.61 – 7.55 (m, 1H), 7.33 (dd, J = 7.5, 2.5 Hz, 2H), 4.01 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.9, 158.7, 135.8, 133.0, 132.7, 130.7, 129.9, 128.7, 128.2, 128.1, 127.8, 127.5, 126.8, 126.5, 125.5, 125.0, 124.9, 124.1, 122.9, 118.9, 109.3, 55.4 ppm

HRMS (ESI) *m/z*: $[M+K+(-H_2O)]^+$ calcd for $[C_{22}H_{12}KO]^+$ 331.0520; found 331.0516.



2-Methoxy-10-methyl-8*H*-benzo[*gh*]tetraphen-8-one (4b):

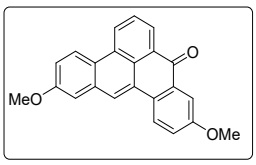
GP-6 was carried out with ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate **11b** (111 mg, 0.3 mmol), TfOH (67.5 mg, 0.45 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 90:10), furnished the product **4b** (53 mg, 55%), as yellow solid; mp = 188–190 °C. [TLC control (petroleum ether/ethyl acetate 90:10), R_f(**11b**) = 0.5, R_f(**4b**) = 0.2 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2926, 1719, 1647, 1599, 1254, 1174, 976, 758 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 8.2, 0.9 Hz, 1H), 8.74 (dd, J = 7.4, 1.2 Hz, 1H), 8.60 (s, 1H), 8.57 (d, J = 9.1 Hz, 1H), 8.32 (d, J = 8.2 Hz, 2H), 7.92 – 7.83 (m, 1H), 7.58 (dd, J = 8.3, 1.5 Hz, 1H), 7.34 (ddd, J = 8.9, 8.9, 2.6 Hz, 2H), 4.01 (s, 3H), 2.53 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 184.1, 158.7, 138.4, 134.3, 133.4, 132.8, 130.5, 130.0, 129.7, 128.9, 128.1, 127.8, 127.5, 126.8, 126.5, 125.0, 124.8, 124.2, 122.9, 118.7, 109.2, 55.4, 21.3 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{17}O_2]^+$ 325.1223; found 325.1236.



2,10-Dimethoxy-8*H*-benzo[*gh*]tetraphen-8-one (4c):

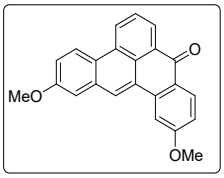
GP-6 was carried out with ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate **11c** (116 mg, 0.3 mmol), TfOH (67.5 mg, 0.45 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15), furnished the product **4c** (66 mg, 65%), as yellow solid; mp = 178–180 °C. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**11c**) = 0.5, R_f(**4c**) = 0.2 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2925, 2352, 1721, 1646, 1495, 1247, 1032, 757 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 – 8.91 (m, 1H), 8.77 (dd, J = 7.4, 1.2 Hz, 1H), 8.63 – 8.55 (m, 2H), 8.38 (d, J = 8.9 Hz, 1H), 8.00 – 7.94 (m, 1H), 7.94 – 7.87 (m, 1H), 7.40 – 7.32 (m, 3H), 4.02 (s, 3H), 4.00 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.7, 159.7, 158.7, 132.9, 131.9, 129.9, 129.2, 128.7, 128.1, 127.5, 126.7, 126.1, 125.1, 124.6, 124.6, 124.5, 124.1, 122.2, 118.4, 109.1, 108.6, 55.6, 55.4 ppm.

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{17}O_3]^+$ 341.1172; found 341.1164.



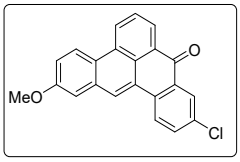
2,11-dimethoxy-8*H*-benzo[*gh*]tetraphen-8-one (4d):

GP-6 was carried out with ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate **11d** (116 mg, 0.3 mmol), TfOH (67.5 mg, 0.45 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15), furnished the product **4d** (51 mg, 50%), as yellow solid; mp = 158–160 °C. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**11d**) = 0.5, R_f(**4d**) = 0.2 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2854, 1724, 1597, 1455, 1366, 1264, 734 cm^{-1}.

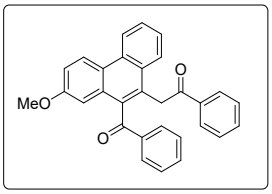
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.77 (m, 1H), 8.67 (dd, J = 7.4, 1.1 Hz, 1H), 8.50 (d, J = 8.9 Hz, 1H), 8.44 (d, J = 8.6 Hz, 2H), 7.87 – 7.75 (m, 1H), 7.72 (d, J = 2.4 Hz, 1H), 7.30 (dt, J = 4.7, 2.6 Hz, 2H), 7.09 (dd, J = 8.8, 2.4 Hz, 1H), 4.02 (s, 3H), 4.00 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 180.2, 162.1, 157.0, 136.4, 131.2, 128.2, 127.9, 126.8, 125.2, 124.7, 123.0, 122.9, 122.9, 122.8, 122.6, 117.4 (2C), 114.3 (2C), 108.3, 105.3, 54.1, 53.7 ppm.
HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{23}H_{17}O_3]^+$ 341.1172; found 341.1168.



10-Chloro-2-methoxy-8*H*-benzo[*gh*]tetraphen-8-one (4e):

GP-6 was carried out with ethyl 4'-methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carboxylate **11e** (117 mg, 0.3 mmol), TfOH (67.5 mg, 0.45 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 85:15), furnished the product **4e** (52 mg, 50%), as yellow solid; mp = 206–208 °C. [TLC control (petroleum ether/ethyl acetate 85:15), R_f(**11e**) = 0.5, R_f(**4e**) = 0.2 UV detection].
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 1719, 1597, 1461, 1261, 1089, 1025, 755 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 8.3, 1.0 Hz, 1H), 8.73 (dd, J = 7.5, 1.2 Hz, 1H), 8.59 (d, J = 9.6 Hz, 2H), 8.46 (d, J = 2.4 Hz, 1H), 8.36 (d, J = 8.7 Hz, 1H), 7.94 – 7.86 (m, 1H), 7.70 (dd, J = 8.6, 2.4 Hz, 1H), 7.38 (dd, J = 6.1, 2.6 Hz, 2H), 4.02 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 182.9, 158.9, 134.8, 134.3, 133.2, 132.7, 131.9, 130.2, 128.6, 128.6, 127.9, 127.6, 127.2, 126.4, 126.0, 125.1, 124.7, 124.4, 124.4, 119.3, 109.5, 55.5 ppm.
HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{22}H_{14}ClO_2]^+$ 345.0677; found 345.0688.



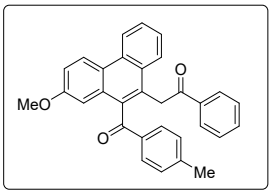
2-(10-Benzoyl-2-methoxyphenanthren-9-yl)-1-phenylethan-1-one (5a):

GP-8 was carried out with 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12a** (124 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6), furnished the product **5a** (80 mg, 62%), as red solid; mp = 132–134 °C. [TLC control (petroleum ether/ethyl acetate 94:6), R_f(**12a**) = 0.5, R_f(**5a**) = 0.3 UV detection].
IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2923, 1736, 1610, 1452, 1374, 1260, 1041, 732 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, J = 8.3 Hz, 1H), 8.67 (d, J = 9.2 Hz, 1H), 7.93 (dd, J = 8.3, 1.1 Hz, 2H), 7.90 (d, J = 7.3 Hz, 2H), 7.72 (d, J = 8.2 Hz, 1H), 7.68 (ddd, J = 8.2, 7.0, 1.1 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.53 – 7.47 (m, 2H), 7.44 (d, J = 7.8 Hz, 2H), 7.35 (t, J = 8.2, 7.9 Hz, 2H), 7.28 (dd, J = 9.2, 2.6 Hz, 1H), 6.86 (d, J = 2.6 Hz, 1H), 4.76 – 4.65 (m, 2H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.7, 195.9, 158.2, 137.2, 136.7, 136.4, 134.0, 133.3, 130.8, 130.2, 129.6, 128.7 (3C), 128.6 (2C), 128.1 (3C), 127.10, 127.3, 126.3, 125.1, 124.5, 124.4, 122.7, 117.1, 107.1, 55.2, 40.2 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{30}H_{23}O_3]^+$ 431.1642; found 431.1641.



2-(2-Methoxy-10-(4-methylbenzoyl)phenanthren-9-yl)-1-phenylethan-1-one (5b):

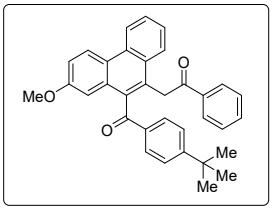
GP-8 was carried out with 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12b** (128 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6), furnished the product **5b** (80 mg, 60%), as red viscous oil [TLC control (petroleum ether/ethyl acetate 94:6), R_f(**12b**) = 0.5, R_f(**5b**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 3057, 2931, 1677, 1494, 1319, 1260, 1172, 731 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, J = 8.8, 8.8 Hz, 2H), 7.98 – 7.93 (m, 2H), 7.86 – 7.79 (m, 2H), 7.73 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 1.1 Hz, 1H), 7.56 – 7.51 (m, 2H), 7.49 – 7.40 (m, 2H), 7.29 – 7.26 (m, 1H), 7.15 (d, J = 8.2 Hz, 2H), 6.90 (d, J = 2.5 Hz, 1H), 4.76 – 4.65 (m, 2H), 3.70 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 195.9, 158.2, 145.1, 136.9, 136.5, 134.8, 133.2, 130.7, 130.2, 129.6, 129.4 (2C), 128.5 (4C), 128.2, 128.1 (2C), 127.8, 127.2, 126.2, 125.1, 124.4, 122.6, 117.0, 107.1, 55.2, 40.2, 21.7 ppm

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{31}H_{24}NaO_3]^+$ 467.1618; found 467.1601.



2-(10-(4-(*tert*-butyl)benzoyl)-2-methoxyphenanthren-9-yl)-1-phenylethan-1-one (5c):

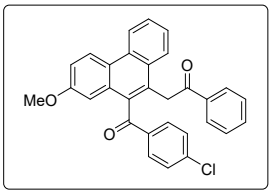
GP-8 was carried out with 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12c** (141 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6), furnished the product **5c** (92 mg, 63%), as maroon viscous oil [TLC control (petroleum ether/ethyl acetate 94:6), R_f(**12c**) = 0.5, R_f(**5c**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2924, 2858, 1733, 1605, 1454, 1264, 1114, 734 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (dd, J = 8.4, 8.8 Hz, 2H), 7.95 – 7.88 (m, 2H), 7.81 (d, J = 8.0 Hz, 2H), 7.74 (d, J = 8.2 Hz, 1H), 7.70 – 7.64 (m, 1H), 7.55 – 7.49 (m, 2H), 7.42 (dd, J = 7.6, 7.7 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 2.6 Hz, 1H), 6.90 (d, J = 2.6 Hz, 1H), 4.72 – 4.66 (m, 2H), 3.71 (s, 3H), 1.25 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 195.9, 158.2, 157.9, 136.9, 136.6, 134.8, 133.2, 130.8, 130.3, 130.0, 129.7, 128.5 (3C), 128.0 (3C), 127.8, 127.2, 126.2, 125.7 (2C), 124.5, 124.4, 122.7, 117.0, 107.3, 55.3, 40.3, 35.2, 30.94 (3C) ppm

HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{34}H_{30}NaO_3]^+$ 509.2087; found 509.2067.



2-(10-(4-Chlorobenzoyl)-2-methoxyphenanthren-9-yl)-1-phenylethan-1-one (5d):

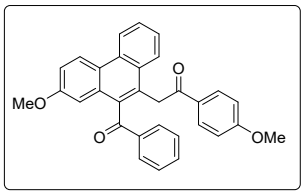
GP-8 was carried out with 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12d** (135 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 94:6), furnished the product **5d** (78 mg, 56%), as brown solid; mp = 150–152 °C. [TLC control (petroleum ether/ethyl acetate 94:6), R_f(**12d**) = 0.5, R_f(**5d**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2930, 1738, 1677, 1448, 1369, 1219, 1091, 737 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.68 (dd, J = 8.5, 6.6 Hz, 2H), 7.97 – 7.91 (m, 2H), 7.84 (d, J = 8.2 Hz, 2H), 7.74 – 7.66 (m, 2H), 7.58 (ddd, J = 4.9, 2.5, 1.3 Hz, 1H), 7.52 (ddd, J = 8.2, 7.1, 1.1 Hz, 1H), 7.46 (dd, J = 10.6, 4.8 Hz, 2H), 7.33 – 7.27 (m, 3H), 6.81 (d, J = 2.5 Hz, 1H), 4.80 – 4.60 (m, 2H), 3.72 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 199.4, 195.9, 158.3, 140.7, 136.4, 136.3, 135.5, 133.4, 131.5, 130.9, 129.9, 129.5, 129.1 (2C), 128.7 (3C), 128.1 (3C), 128.1, 127.4, 126.4, 125.1, 124.6, 122.7, 117.1, 107.1, 55.3, 40.1 ppm

HRMS (ESI) *m/z*: $[M+NH_4]^+$ calcd for $[C_{30}H_{25}ClNO_3]^+$ 482.1517; found 482.1502.



2-(10-Benzoyl-2-methoxyphenanthren-9-yl)-1-(4-methoxyphenyl)ethan-1-one (5e):

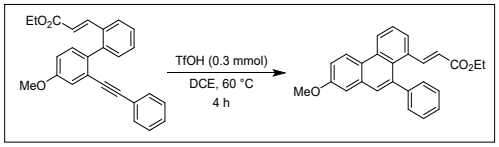
GP-8 was carried out with 4'-Methoxy-2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)-1-phenylethane-1-one **12e** (133 mg, 0.3 mmol), TfOH (45 mg, 0.3 mmol) and DCE (1 mL). Purification of the crude mixture by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 92:8), furnished the product **5e** (92 mg, 67%), as brown solid; mp = 98–100 °C. [TLC control (petroleum ether/ethyl acetate 92:8), R_f(**12e**) = 0.5, R_f(**5e**) = 0.3 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2922, 1734, 1656, 1498, 1256, 1170, 1037, 736 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.67 (dd, J = 7.9, 8.0 Hz, 2H), 7.95 – 7.88 (m, 4H), 7.74 (d, J = 8.3 Hz, 1H), 7.66 (ddd, J = 8.3, 7.1, 1.1 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.36 (dd, J = 8.1, 7.5 Hz, 2H), 7.28 (d, J = 2.6 Hz, 1H), 6.92 – 6.88 (m, 2H), 6.86 (d, J = 2.5 Hz, 1H), 4.70 – 4.59 (m, 2H), 3.86 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.7, 194.4, 163.6, 158.2, 137.3, 136.7, 134.0, 130.8, 130.4 (3C), 130.2, 129.7, 129.5, 128.7 (3C), 128.3, 127.2, 126.2, 125.2, 124.5, 124.4, 122.6, 117.0, 113.7 (2C), 107.1, 55.5, 55.2, 39.1 ppm

HRMS (ESI) *m/z*: $[M+H]^+$ calcd for $[C_{31}H_{25}O_4]^+$ 461.1747; found 461.1742.



Scheme S6: Ethyl (*E*)-3-(7-methoxy-10-phenylphenanthren-1-yl)acrylate.

Synthesis of Ethyl (*E*)-3-(7-methoxy-10-phenylphenanthren-1-yl)acrylate (14):

To a solution of Ethyl (*E*)-3-(2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)acrylates **1r** (115 mg, 0.3 mmol) in a Schlenk tube in dichloroethane solvent (1 mL), was added TfOH (45 mg, 0.3 mmol)

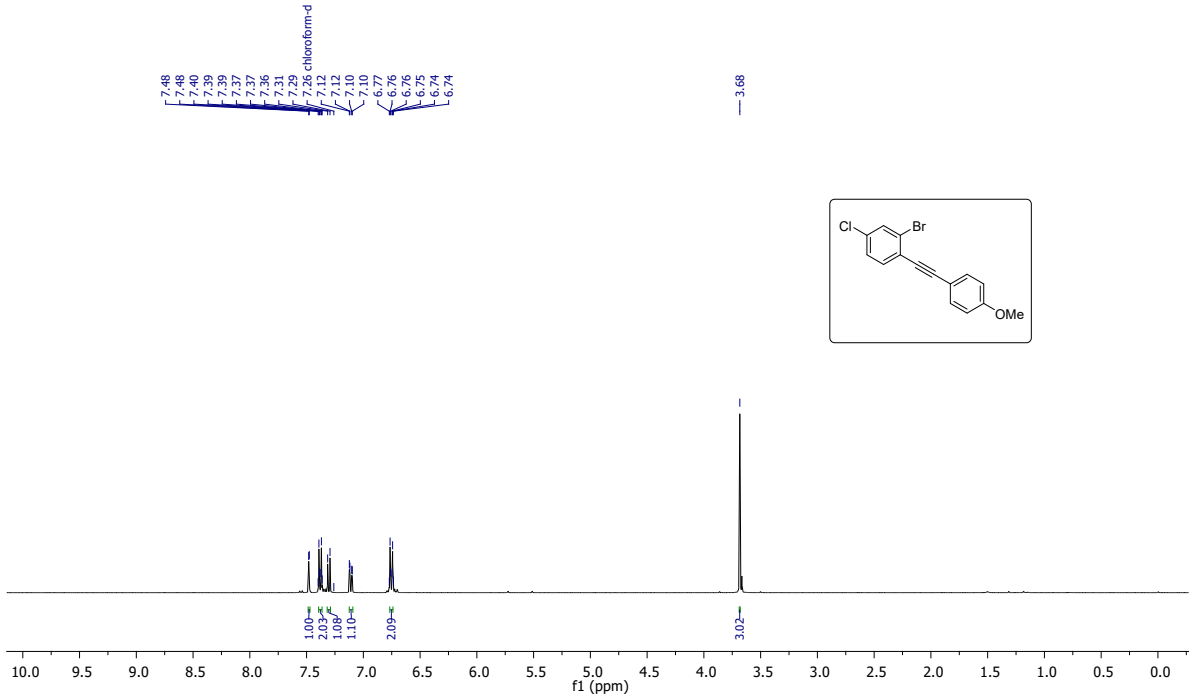
under open air atmosphere and allowed the reaction mixture to stir at 60 °C for 4 h. Completion of the reaction was monitored by TLC until the reaction is complete. The reaction mixture was quenched with aqueous ammonium chloride and extracted with ethyl acetate (3×15 mL). The combined organic layers were washed with brine solution, dried (Na_2SO_4), and evaporated under reduced pressure. Purification of the crude material by silica gel column chromatography (petroleum ether/ethyl acetate 100:0 to 98:2) furnished the product **14** (80.3 mg, 70%), as yellow viscous oil [TLC control (petroleum ether/ethyl acetate 98:2), R_f(**1r**) = 0.4, R_f(**14**) = 0.5 UV detection].

IR (MIR-ATR, 4000–600 cm^{-1}): ν_{max} = 2935, 2253, 1719, 1453, 1367, 1171, 903, 722 cm^{-1}.

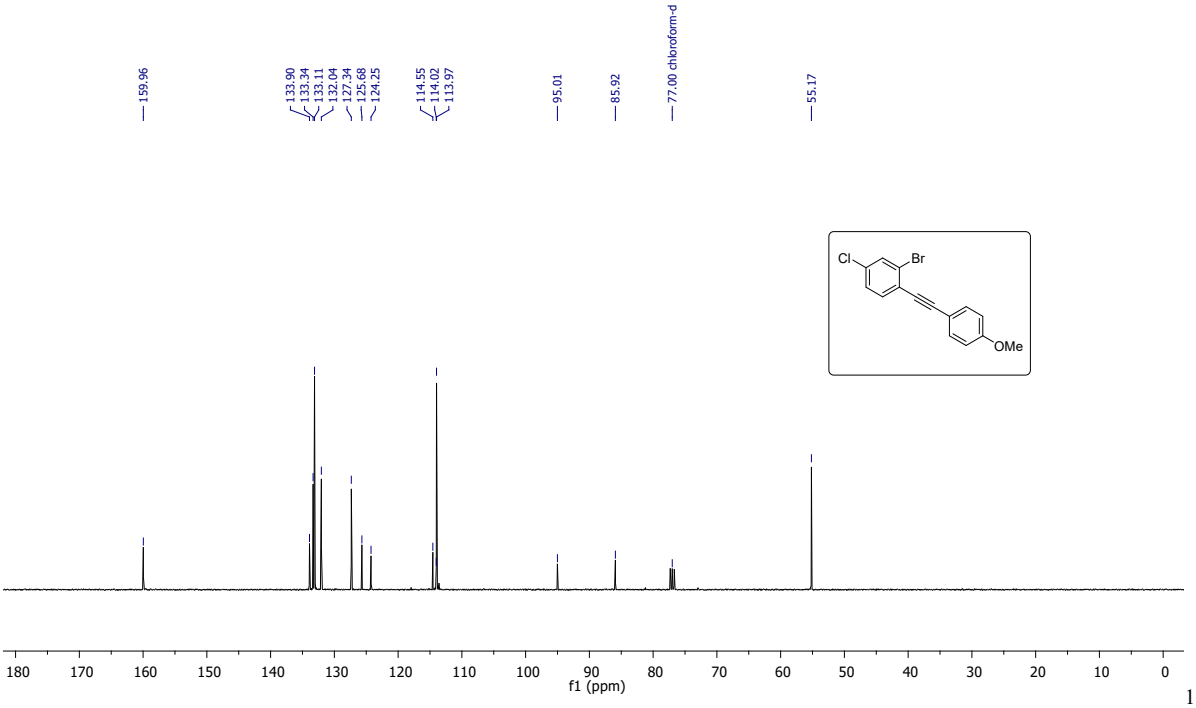
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, J = 15.7 Hz, 1H), 8.43 (d, J = 9.0 Hz, 1H), 7.90 (dd, J = 8.2, 1.0 Hz, 1H), 7.69 (d, J = 7.3 Hz, 1H), 7.65 (s, 1H), 7.52 (d, J = 4.3 Hz, 4H), 7.50 – 7.43 (m, 2H), 7.30 (dt, J = 9.0, 2.7 Hz, 2H), 6.57 (d, J = 15.7 Hz, 1H), 4.36 (q, J = 7.1 Hz, 2H), 3.98 (s, 3H), 1.40 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 158.4, 148.9, 140.7, 139.3, 134.4, 133.2, 131.3, 130.1, 130.0 (3C), 128.4, 128.3, 128.3 (2C), 127.9, 127.5, 124.9, 124.1, 118.8, 115.9, 109.0, 60.5, 55.4, 14.4 ppm.

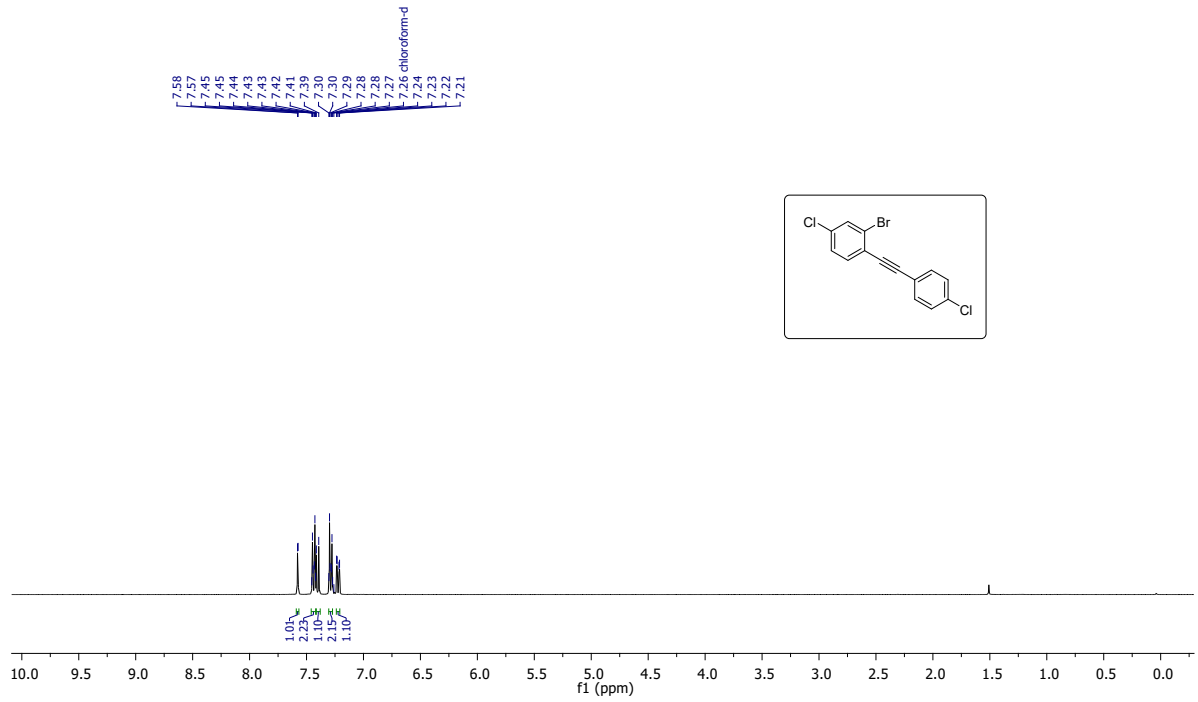
HRMS (ESI) *m/z*: $[M+Na]^+$ calcd for $[C_{26}H_{22}NaO_3]^+$ 405.1461; found 405.1441.



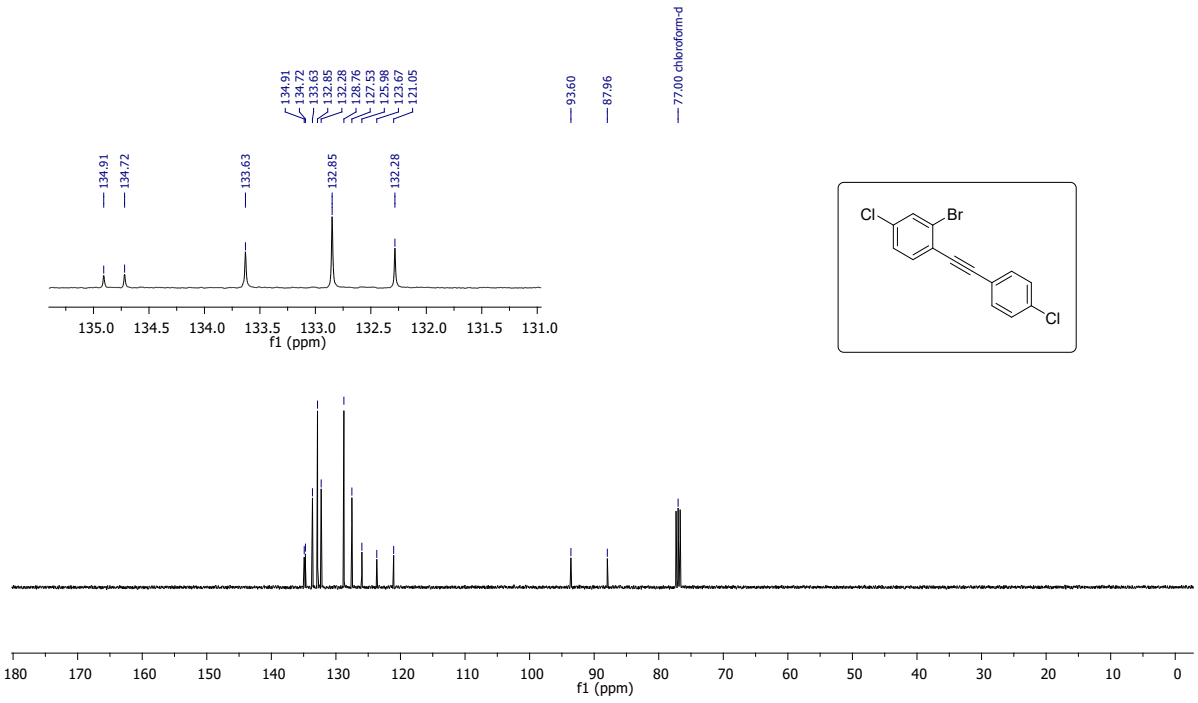
^{1}H NMR (400 MHz) spectrum of **8m** in $CDCl_3$



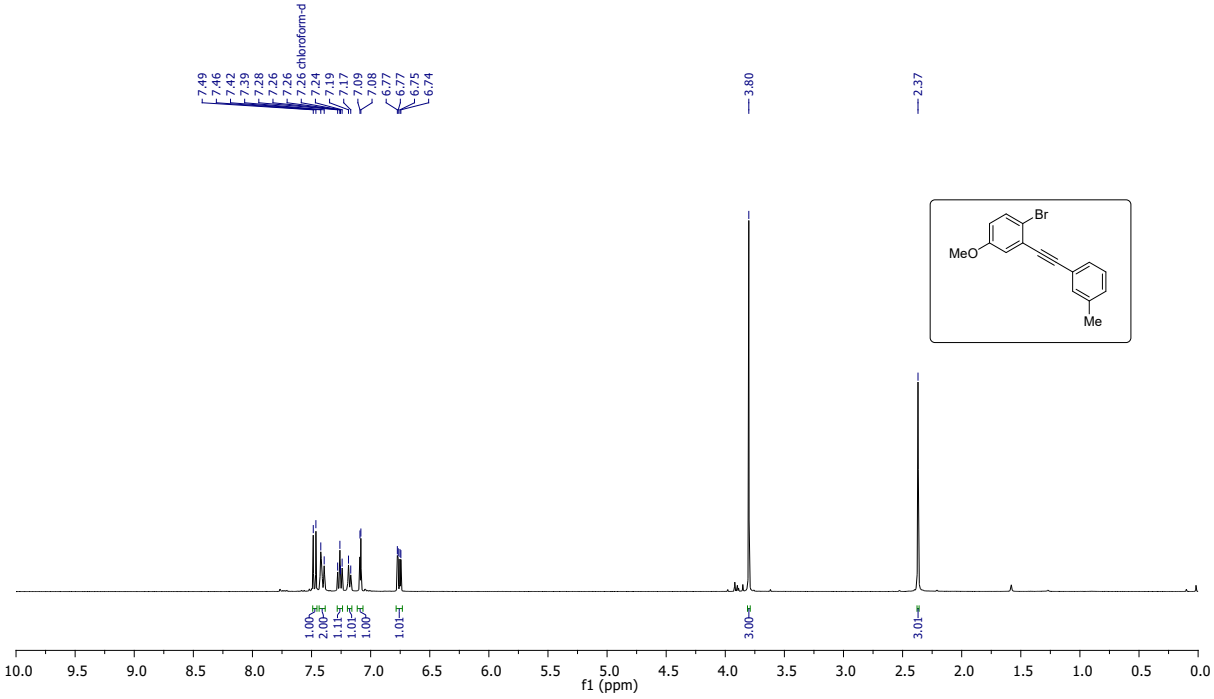
^{3}C{H} NMR (101 MHz) spectrum of **8m** in $CDCl_3$



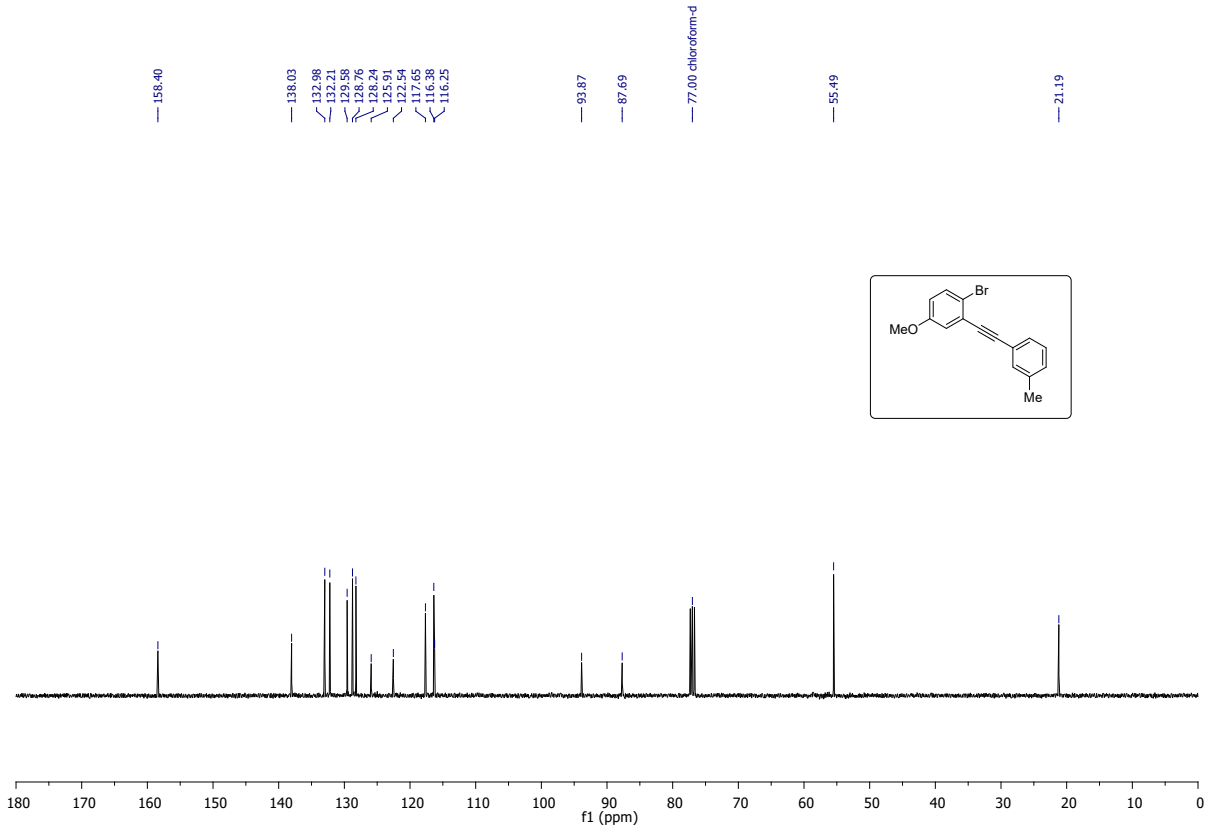
^{1}H NMR (400 MHz) spectrum of **8n** in $CDCl_3$



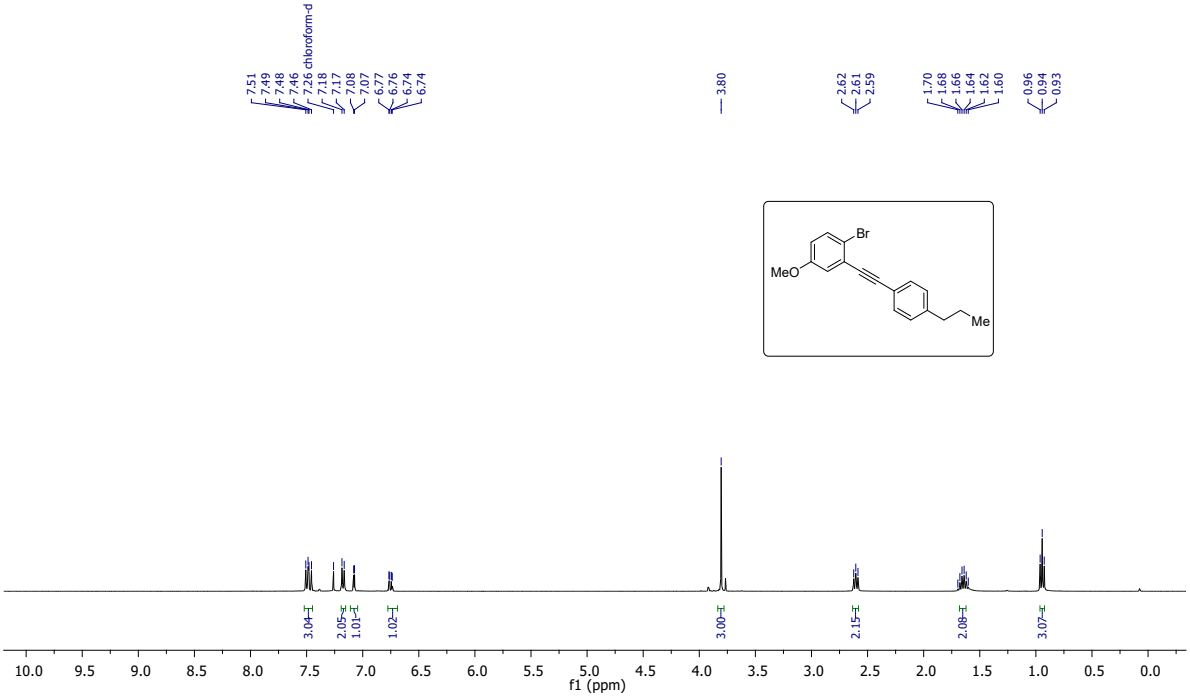
^{13}C{H} NMR (101 MHz) spectrum of **8n** in $CDCl_3$



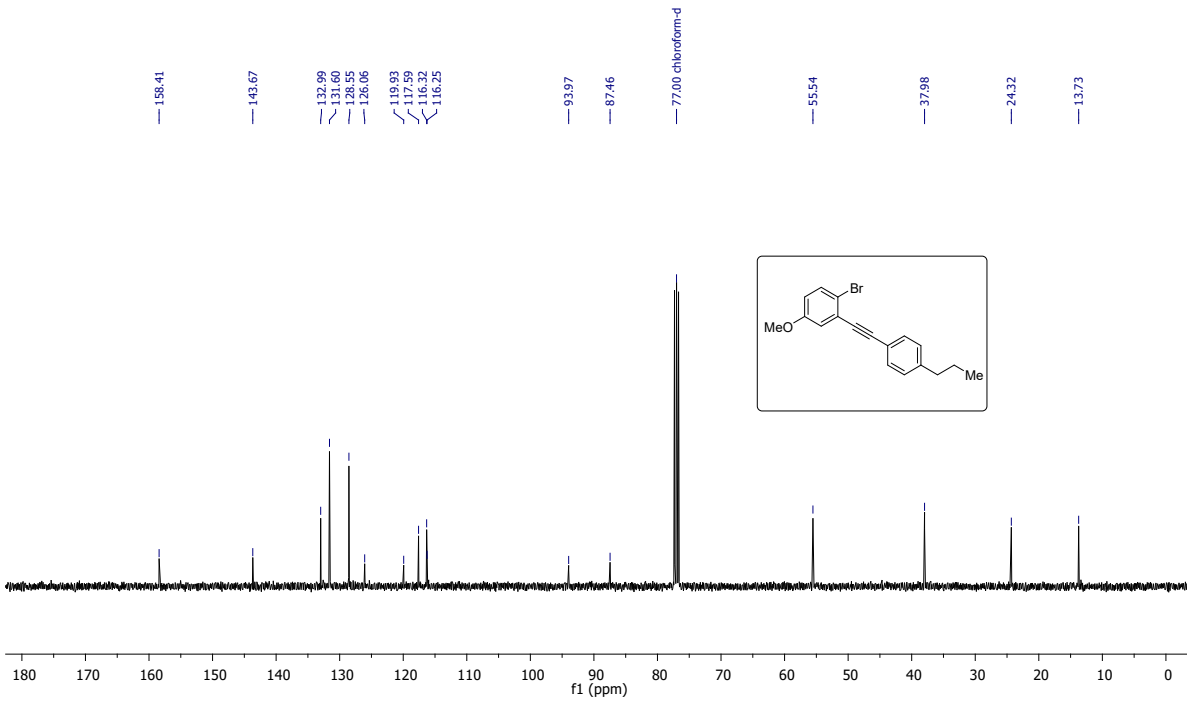
^{1}H NMR (400 MHz) spectrum of **8q** in $CDCl_3$



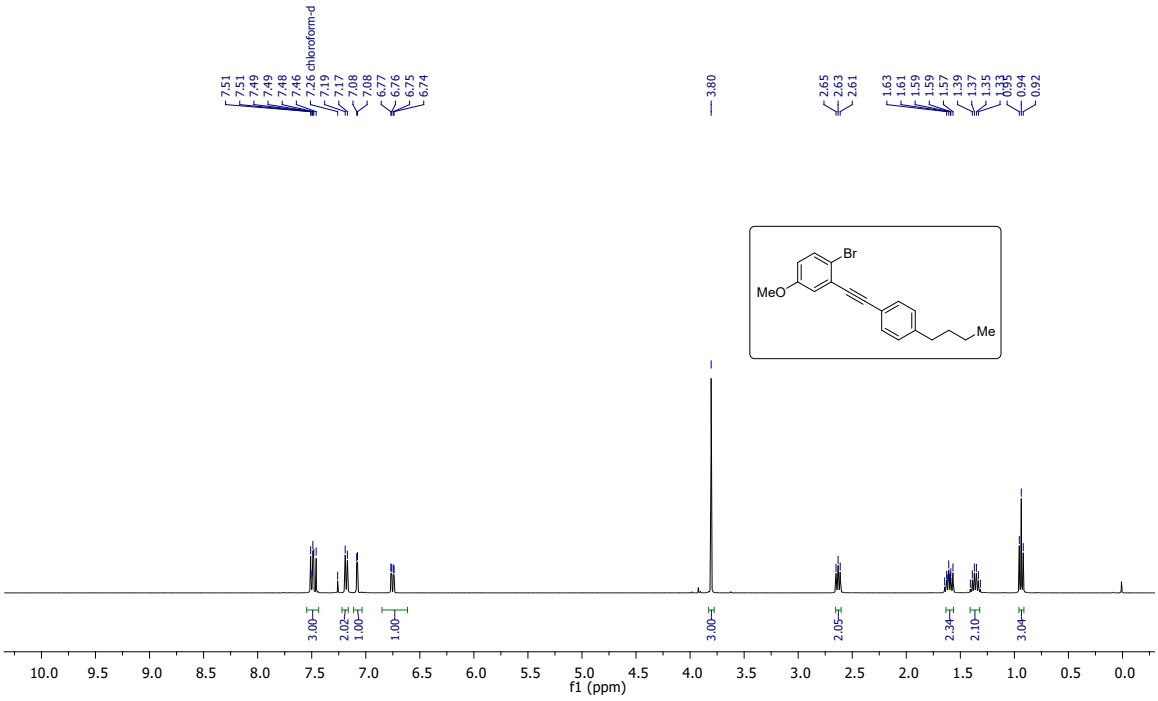
^{13}C{H} NMR (101 MHz) spectrum of **8q** in $CDCl_3$



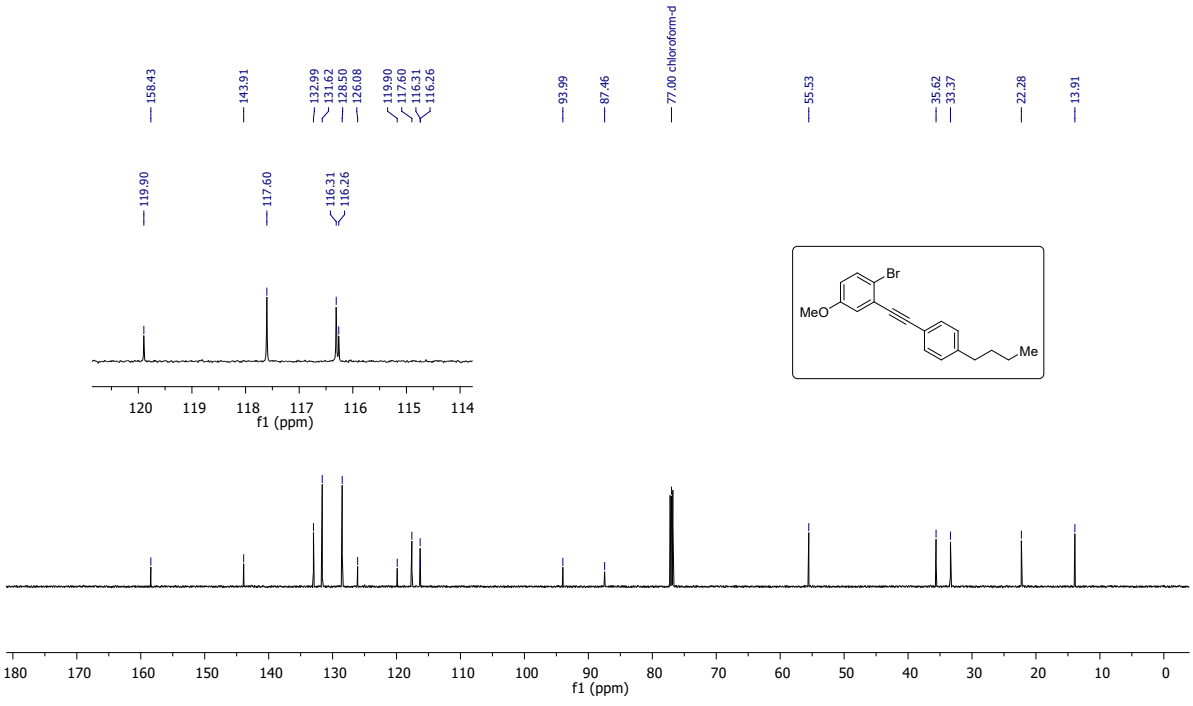
^{1}H NMR (400 MHz) spectrum of **8r** in $CDCl_3$



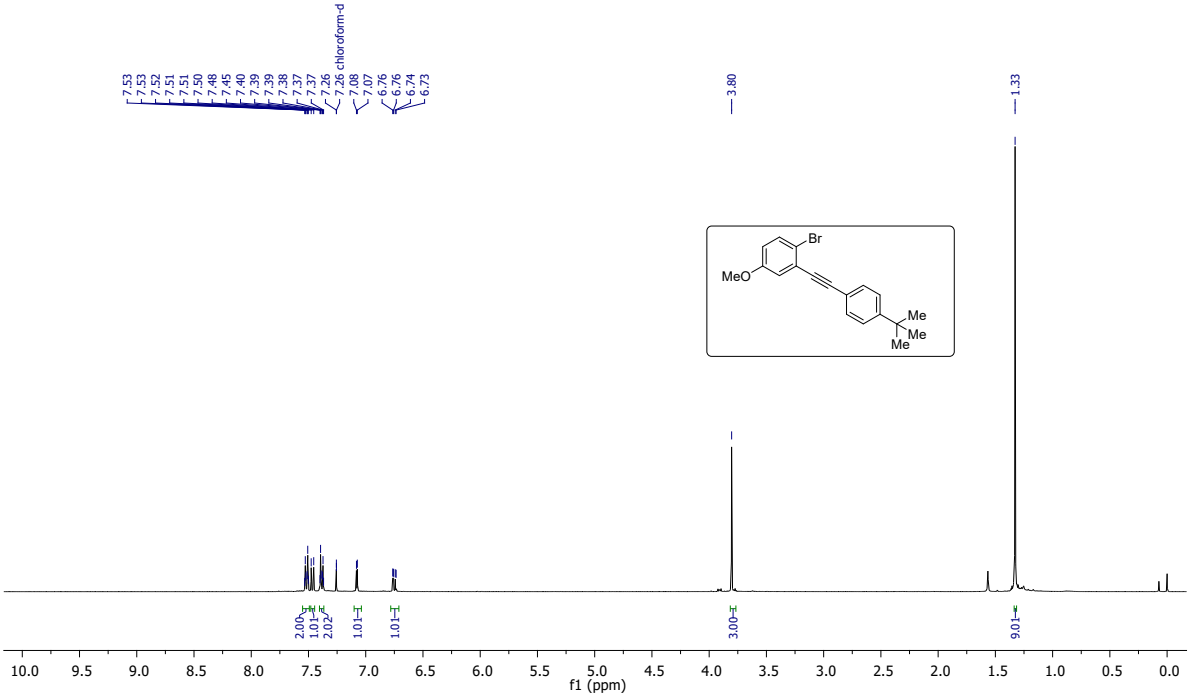
^{13}C{H} NMR (101 MHz) spectrum of **8r** in $CDCl_3$



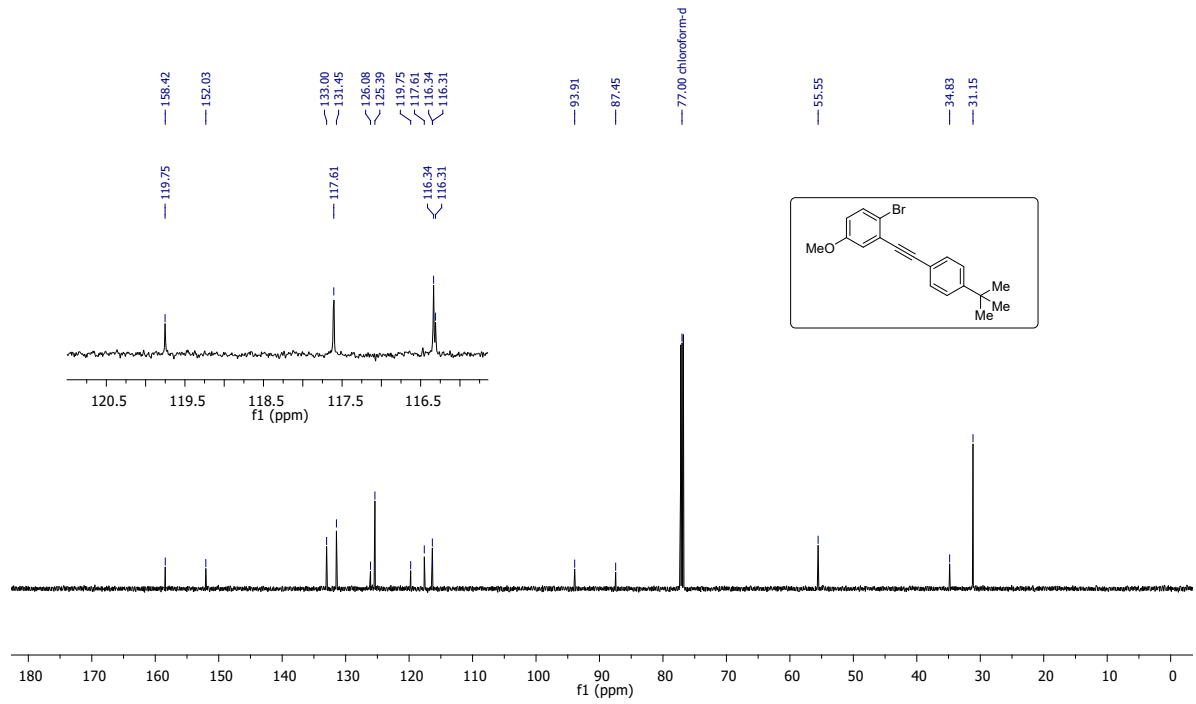
^{1}H NMR (400 MHz) spectrum of **8s** in $CDCl_3$



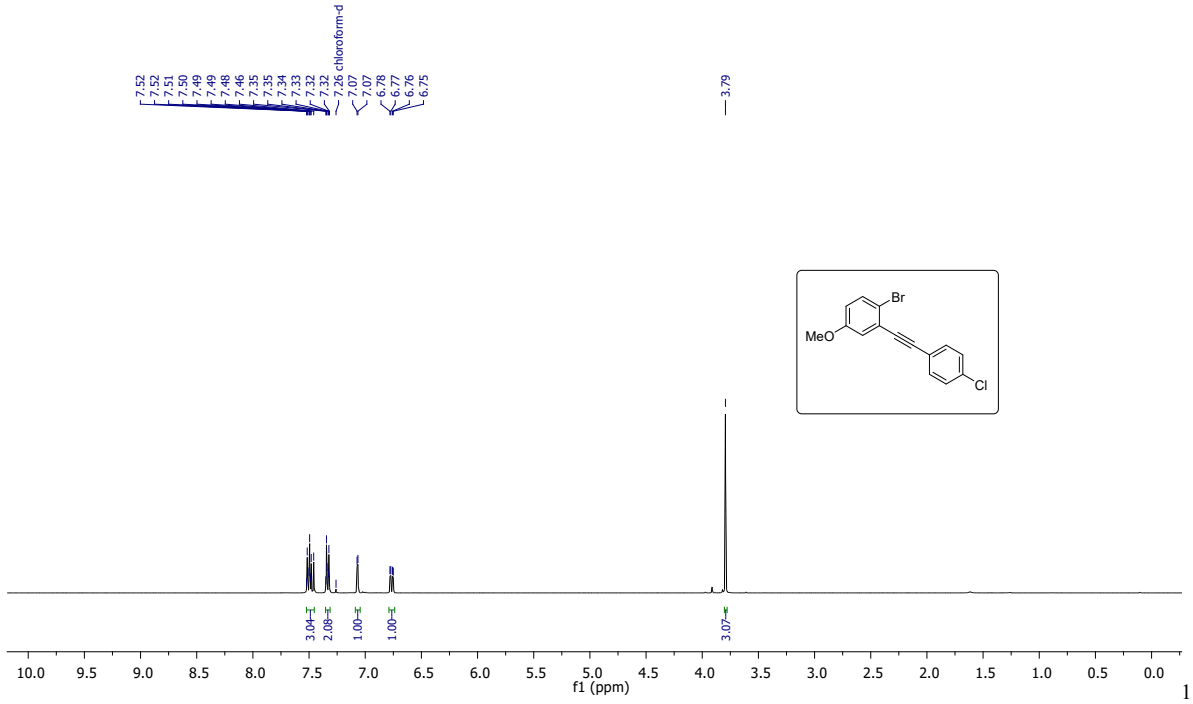
^{13}C{H} NMR (151 MHz) spectrum of **8s** in $CDCl_3$



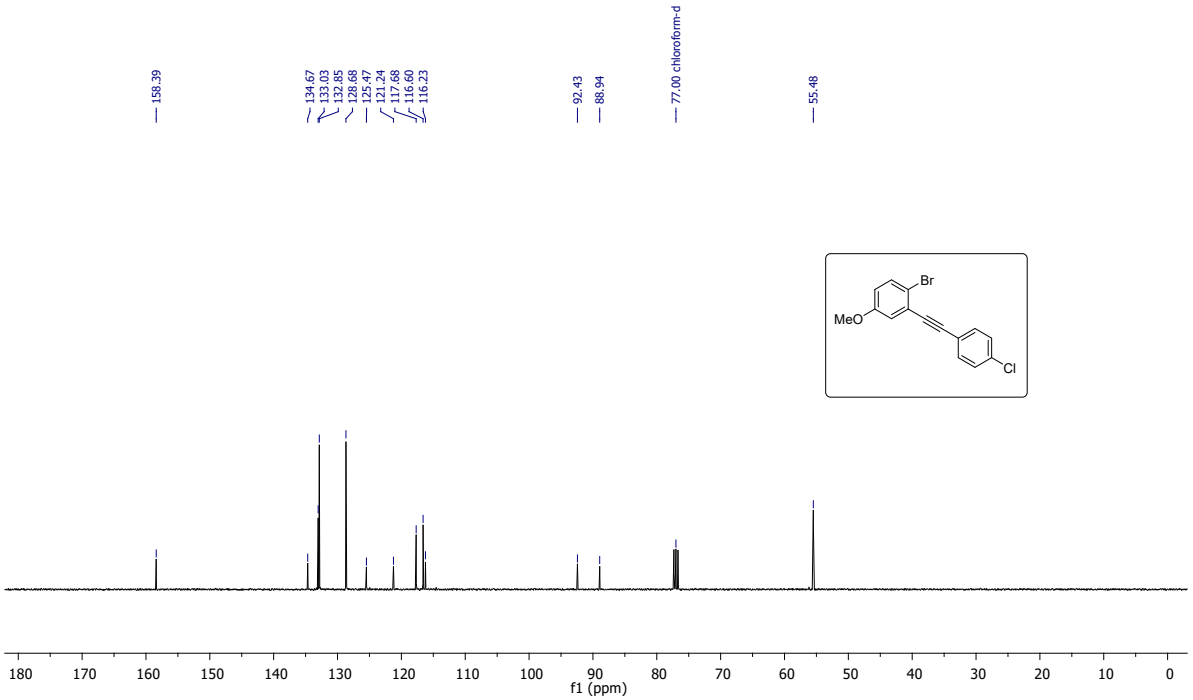
^{1}H NMR (400 MHz) spectrum of **8t** in $CDCl_3$



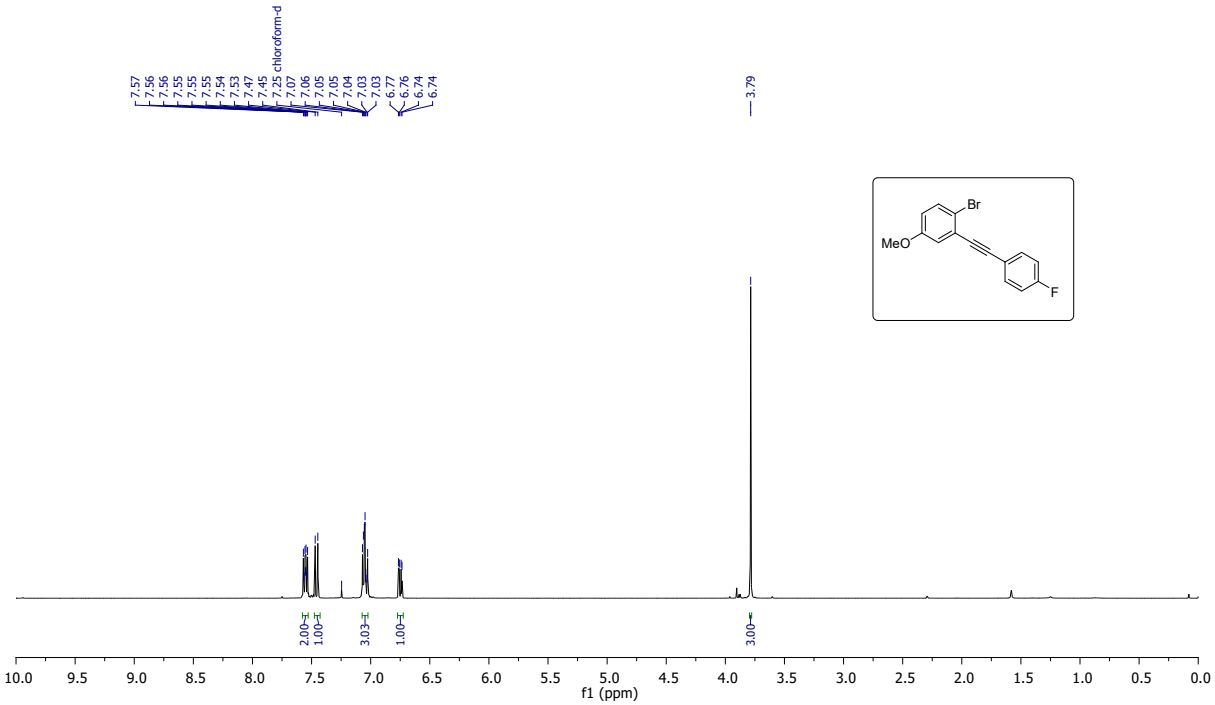
^{13}C{H} NMR (151 MHz) spectrum of **8t** in $CDCl_3$



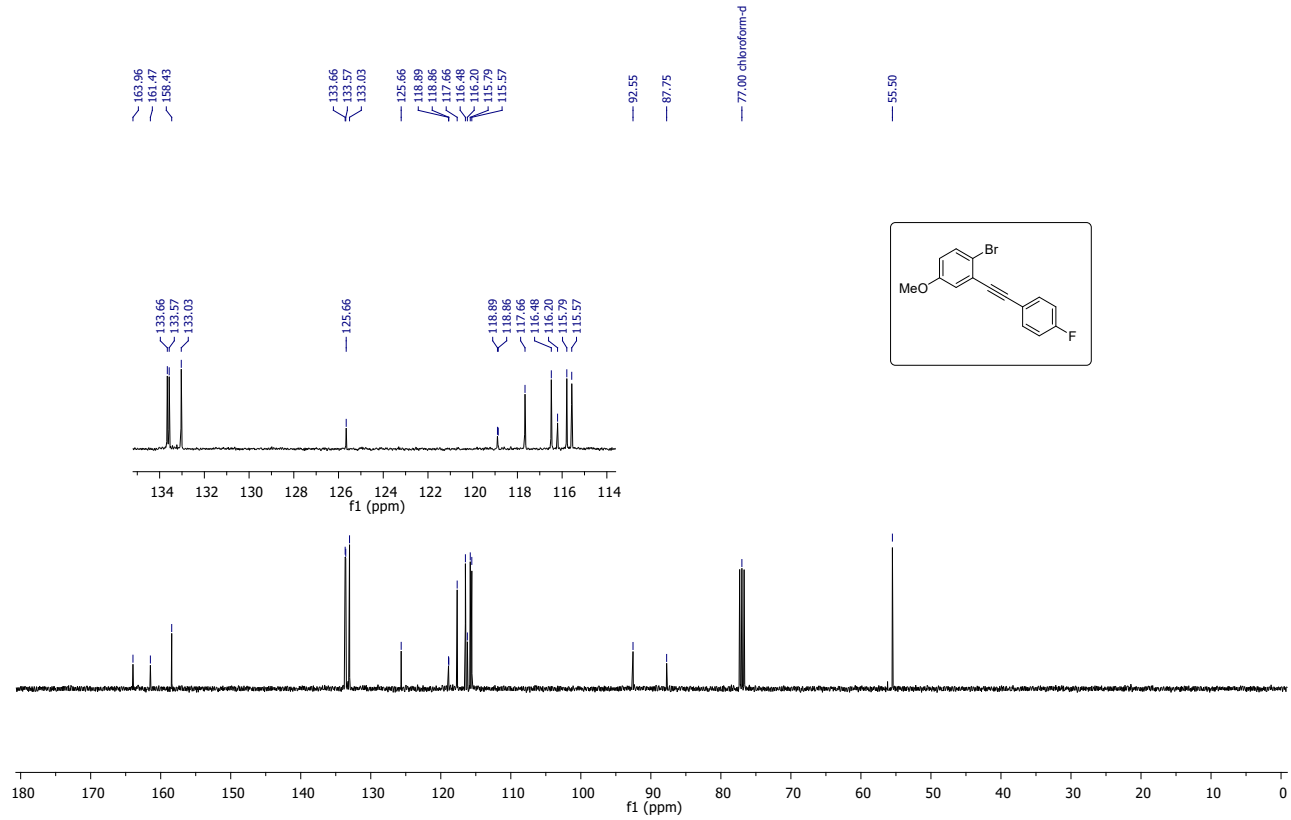
H NMR (400 MHz) spectrum of **8w** in $CDCl_3$



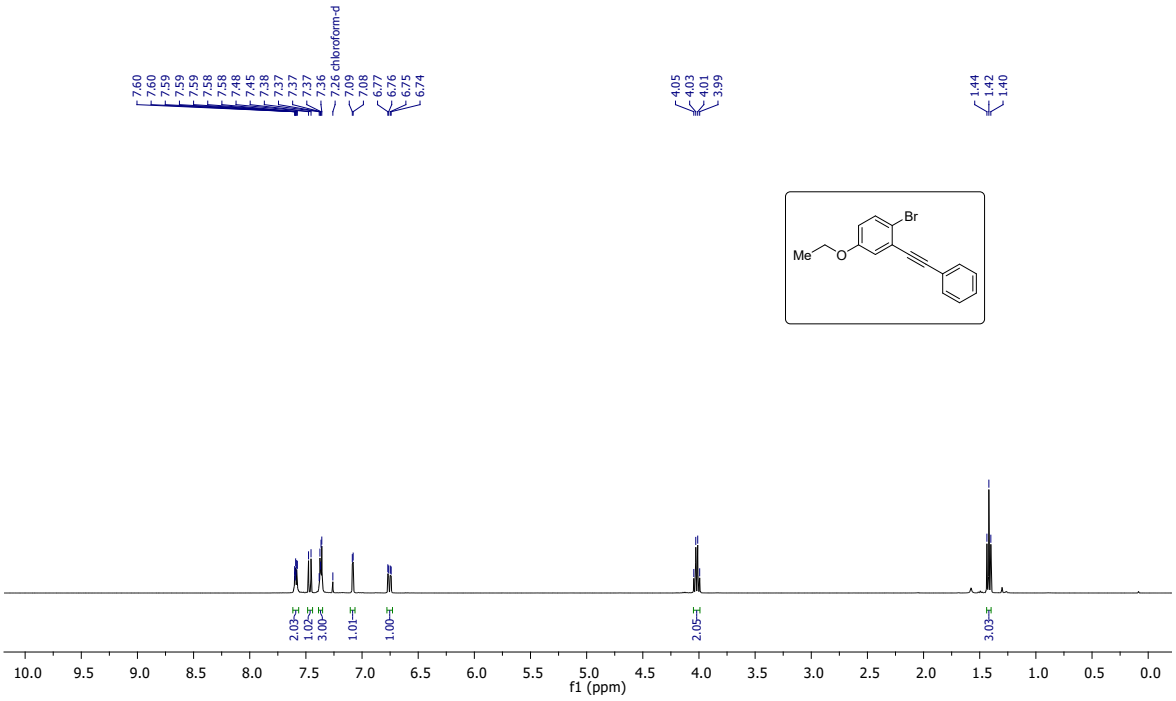
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **8w** in $CDCl_3$



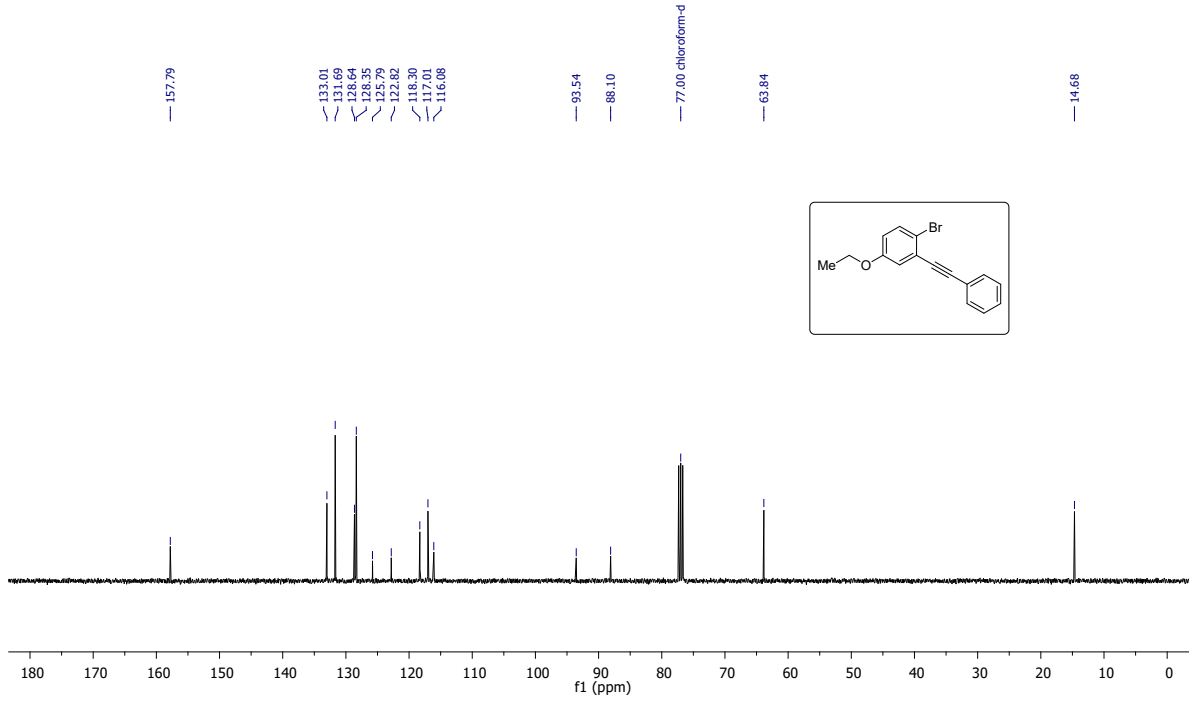
^{1}H NMR (400 MHz) spectrum of **8x** in $CDCl_3$



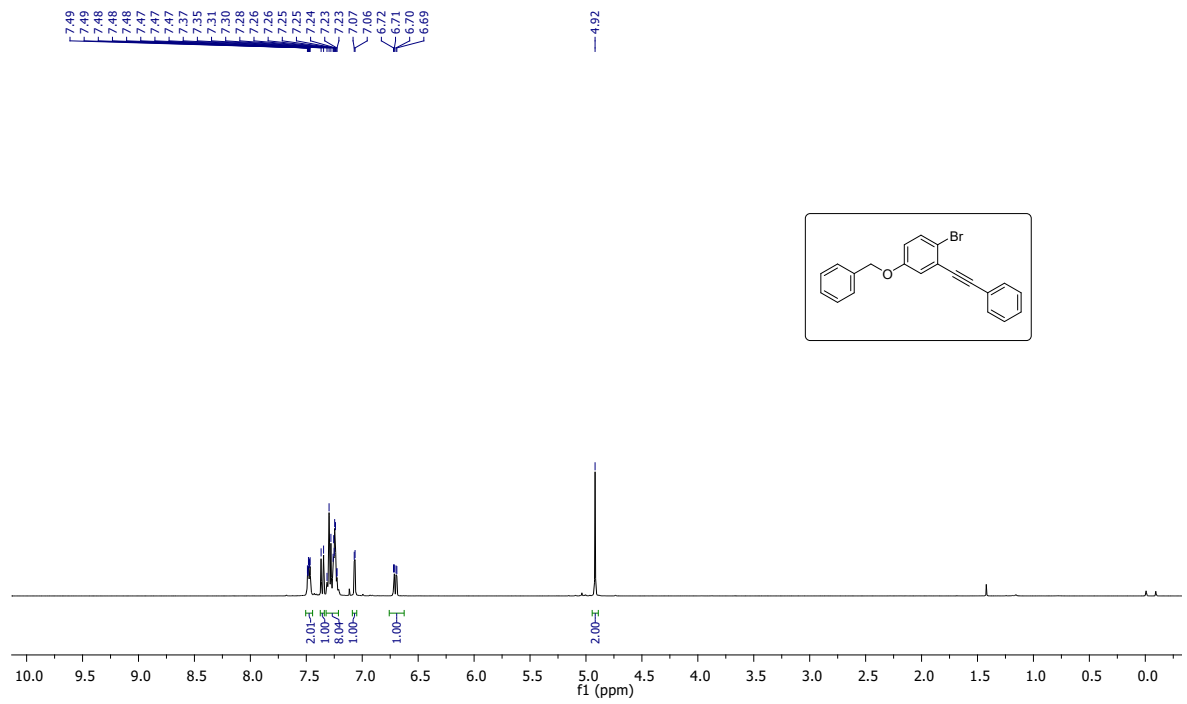
^{13}C{H} NMR (101 MHz) spectrum of **8x** in $CDCl_3$



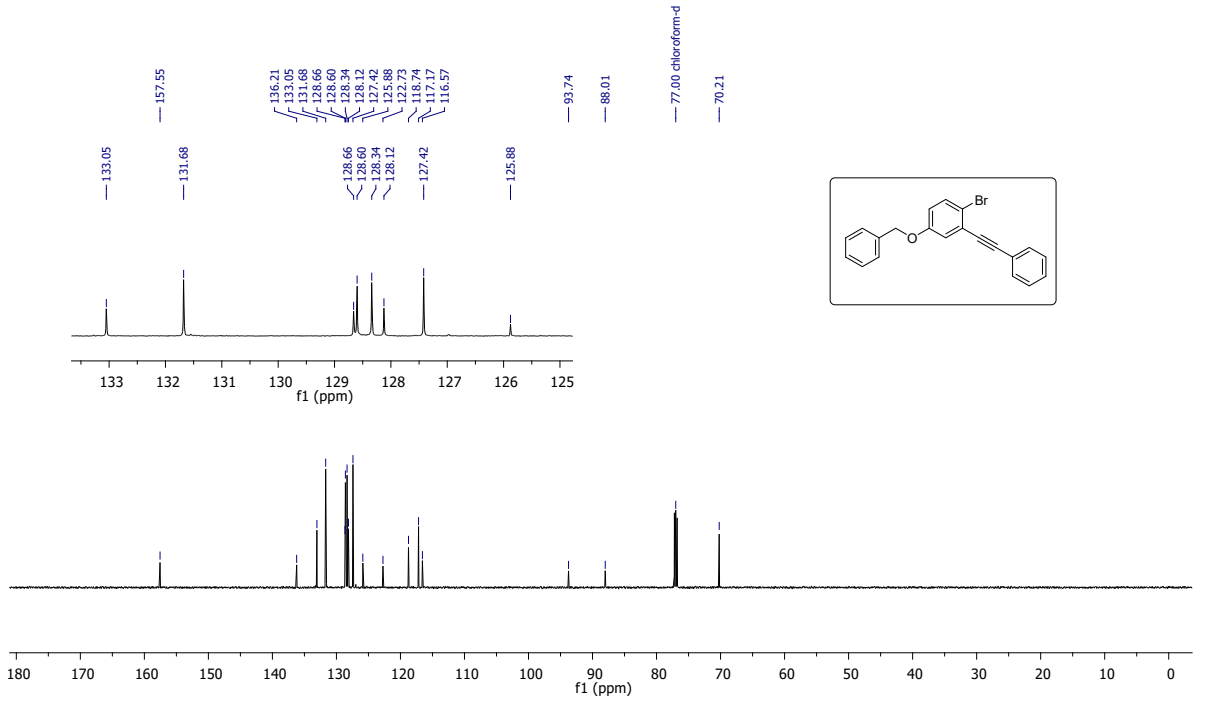
^{1}H NMR (400 MHz) spectrum of **8y** in $CDCl_3$



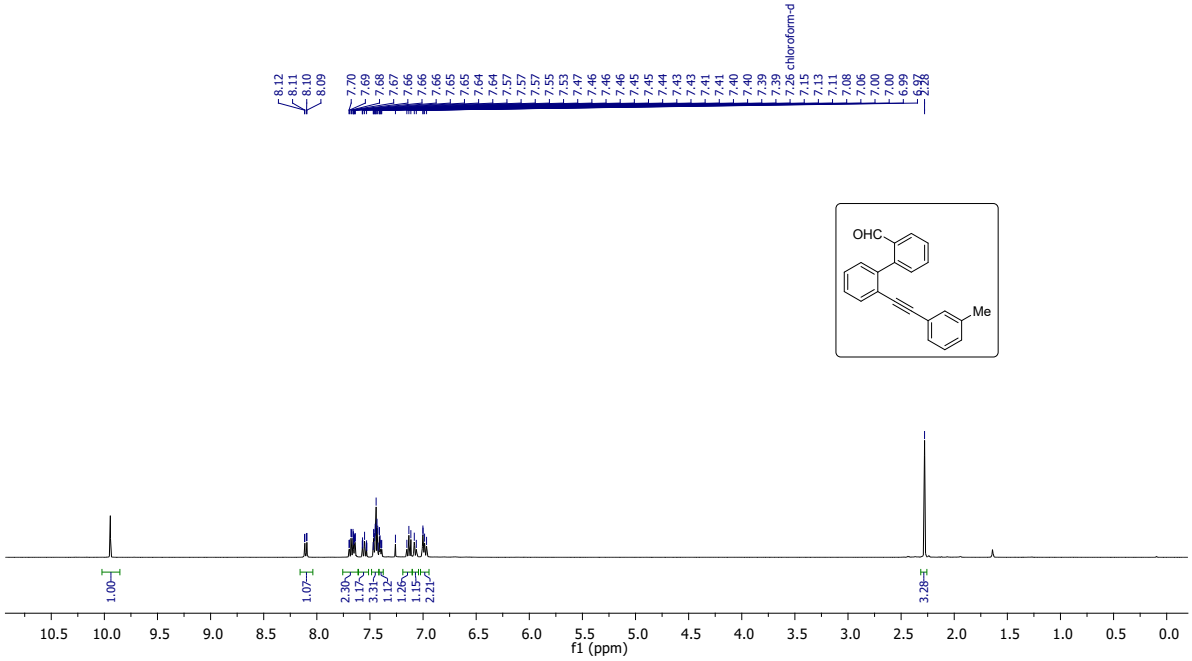
^{13}C{H} NMR (101 MHz) spectrum of **8y** in $CDCl_3$



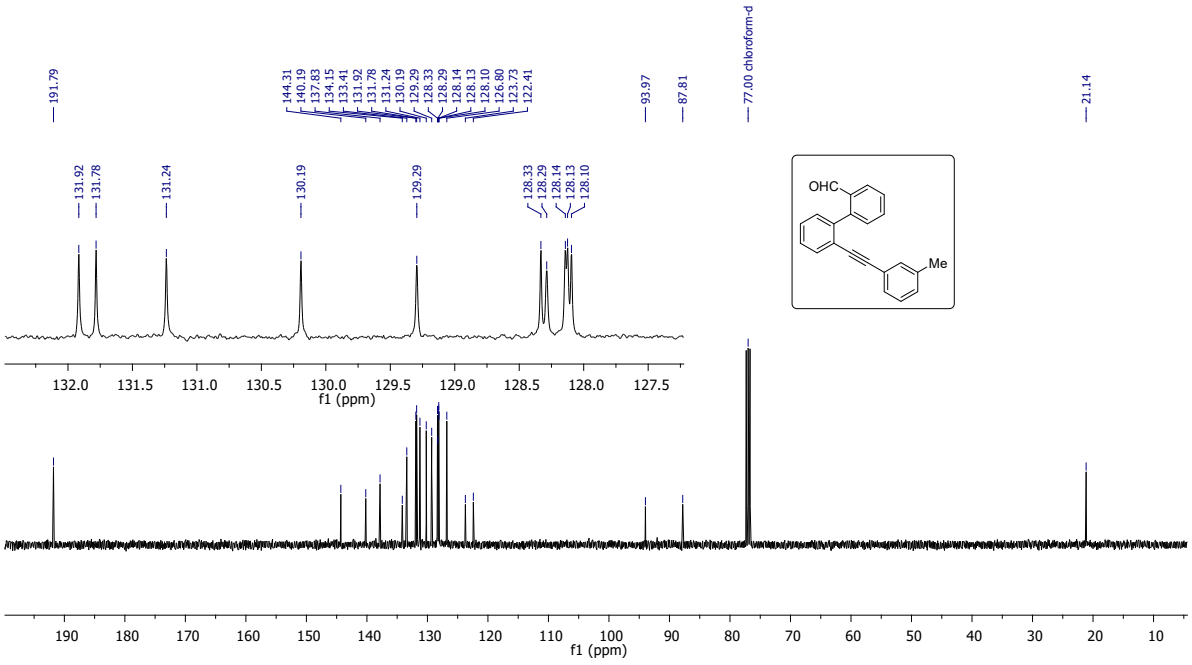
^{1}H NMR (400 MHz) spectrum of **8z** in $CDCl_3$



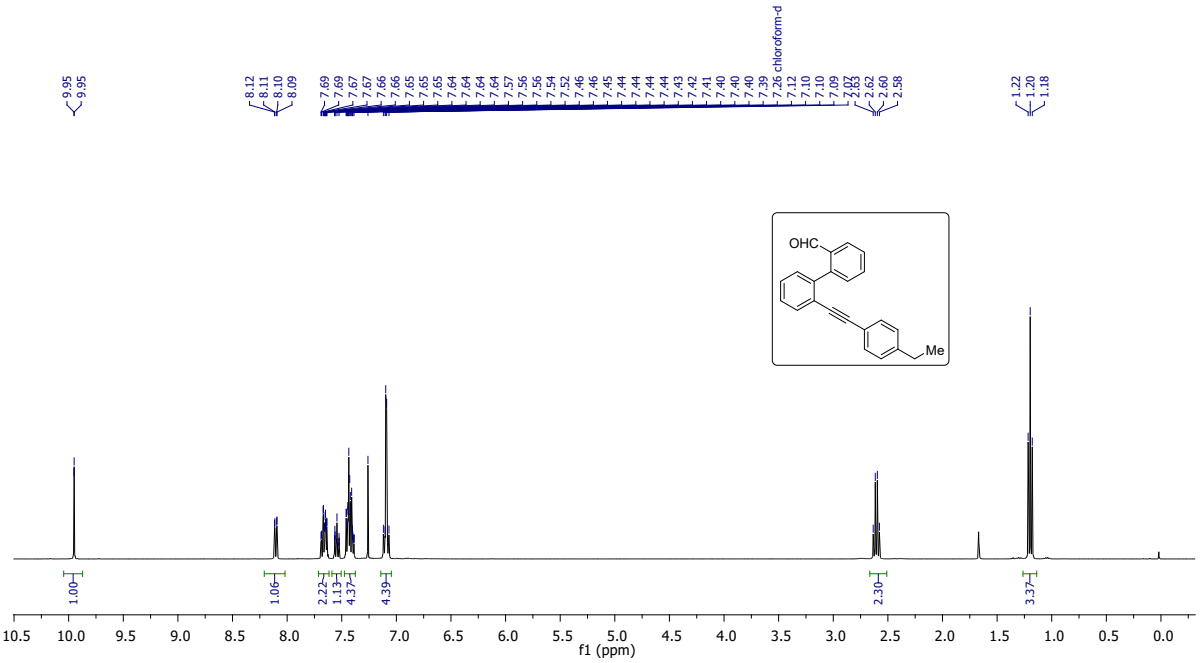
^{13}C{H} NMR (151 MHz) spectrum of **8z** in $CDCl_3$



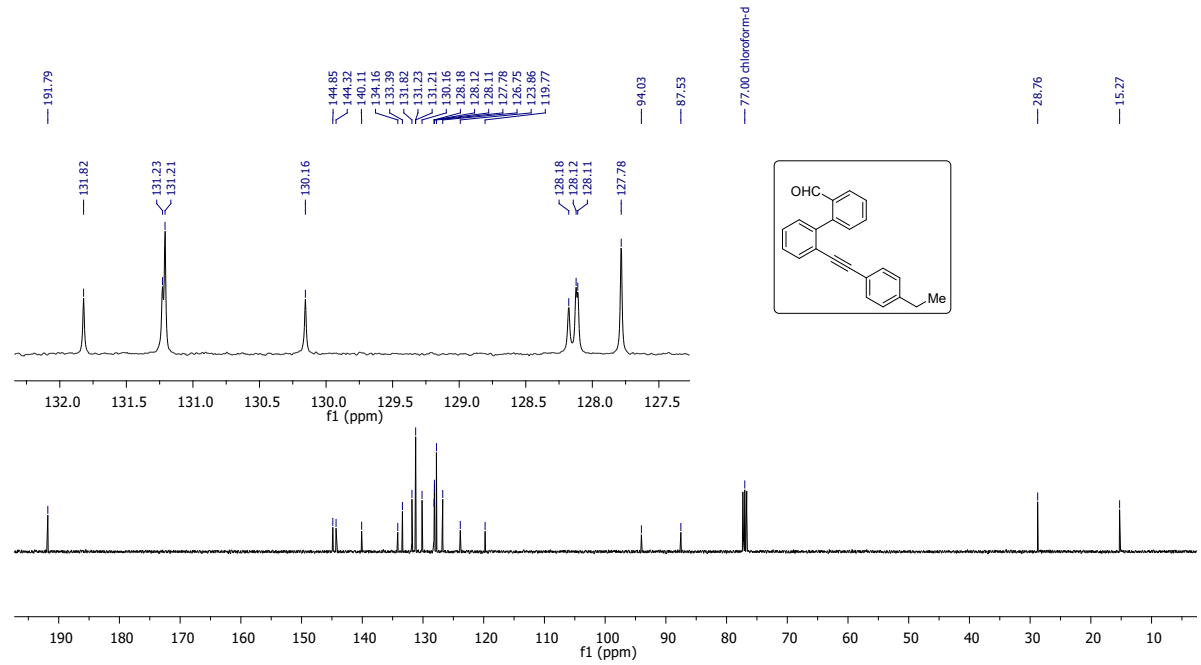
^{1}H NMR (400 MHz) spectrum of **10c** in $CDCl_3$



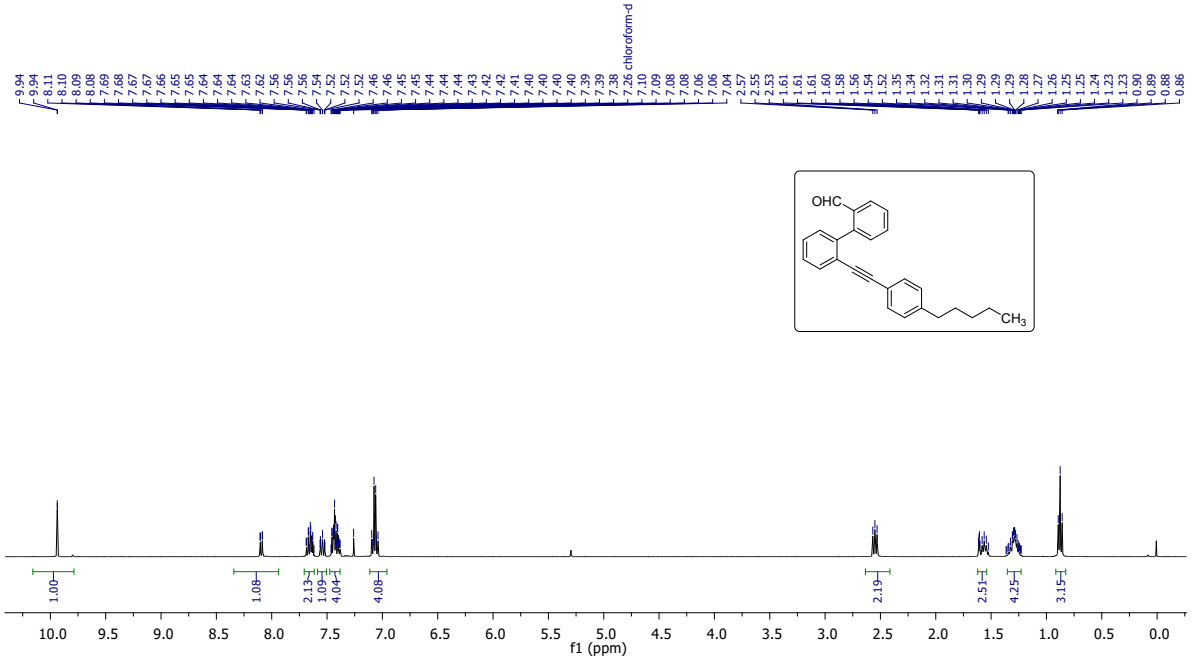
^{13}C{H} NMR (101 MHz) spectrum of **10c** in $CDCl_3$



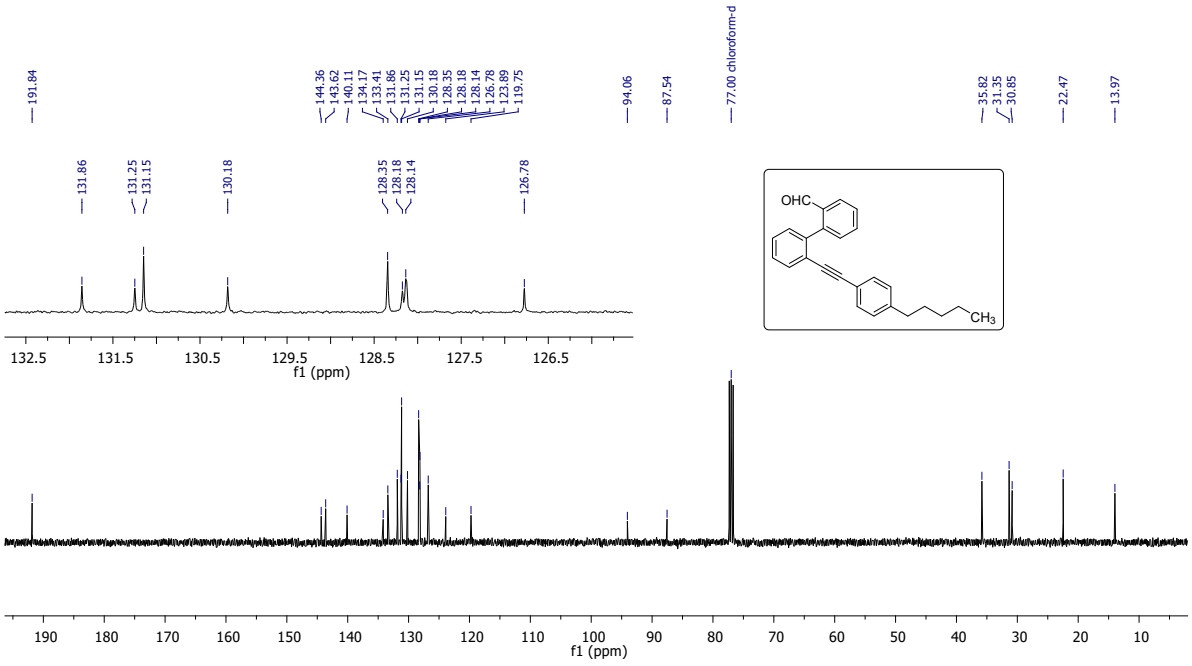
^{1}H NMR (400 MHz) spectrum of **10d** in $CDCl_3$



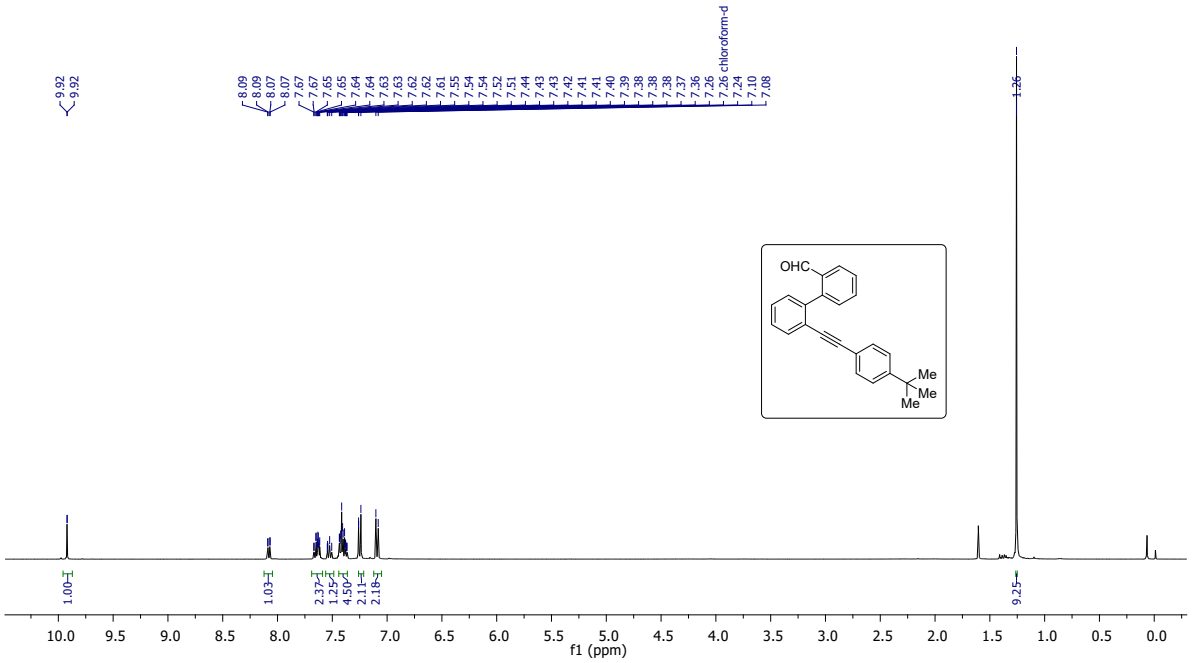
^{13}C{H} NMR (101 MHz) spectrum of **10d** in $CDCl_3$



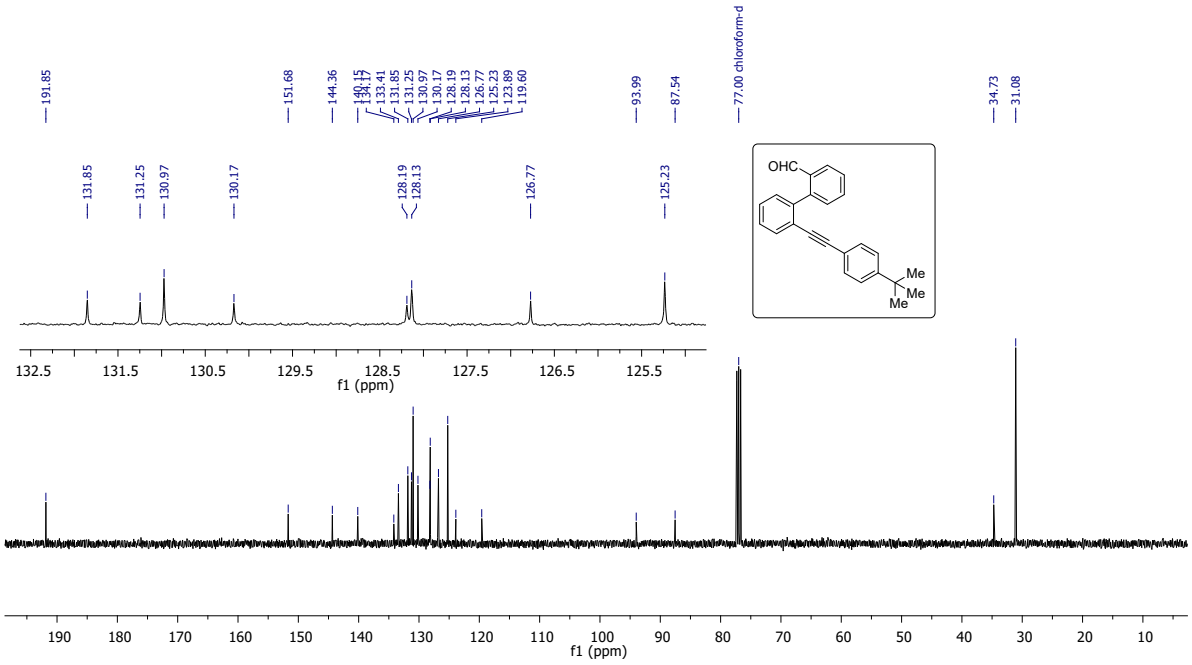
^{1}H NMR (400 MHz) spectrum of **10e** in $CDCl_3$



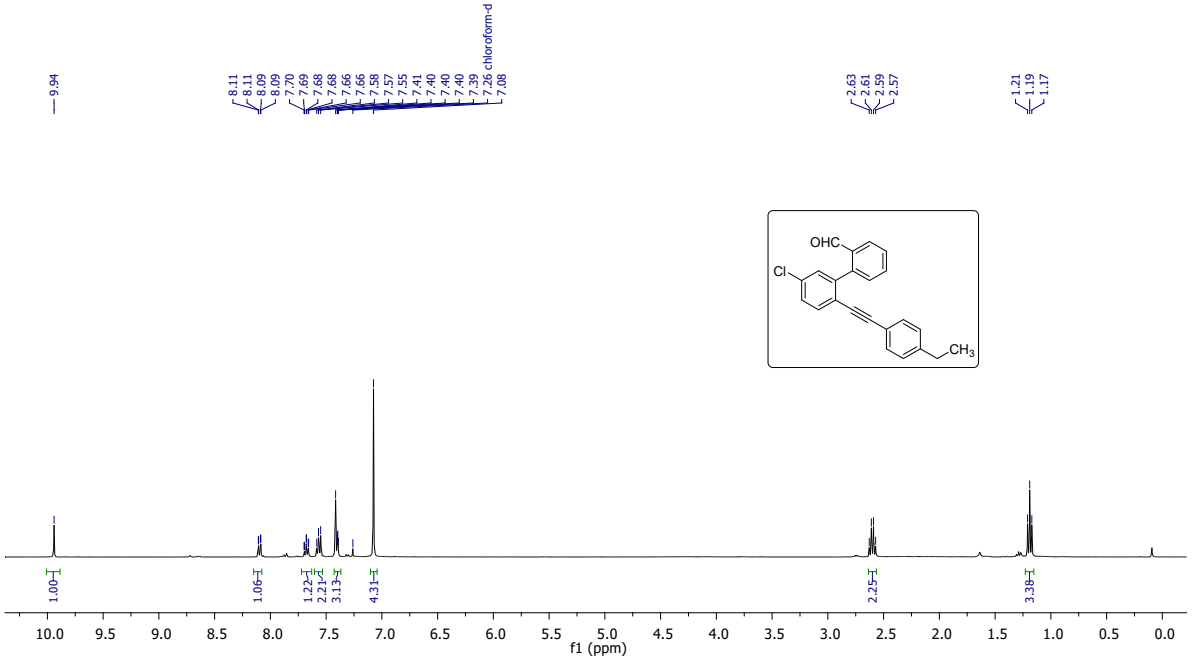
^{13}C{H} NMR (101 MHz) spectrum of **10e** in $CDCl_3$



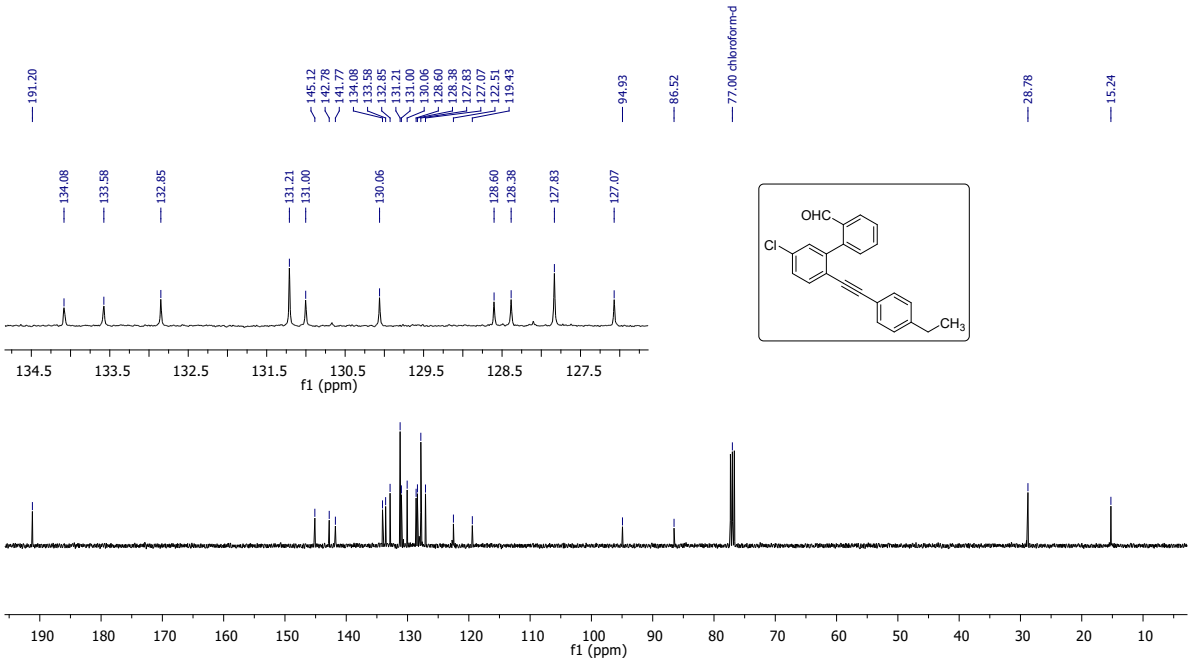
^{1}H NMR (400 MHz) spectrum of **10f** in $CDCl_3$



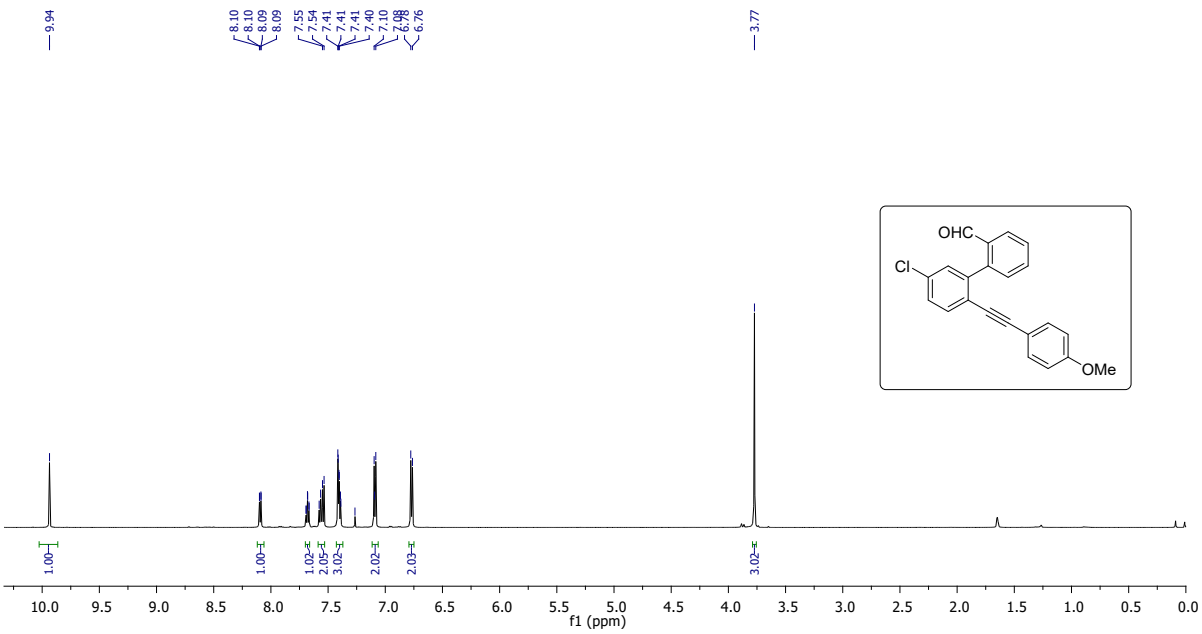
^{13}C{H} NMR (101 MHz) spectrum of **10f** in $CDCl_3$



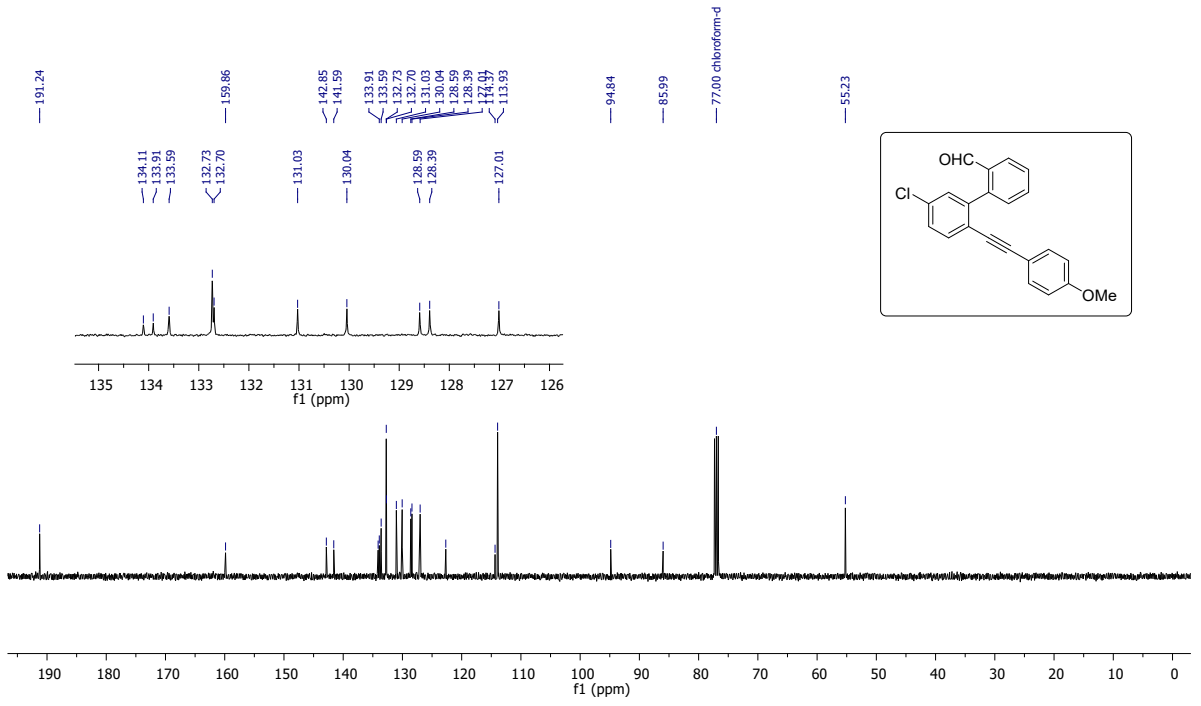
^{1}H NMR (400 MHz) spectrum of **10l** in $CDCl_3$



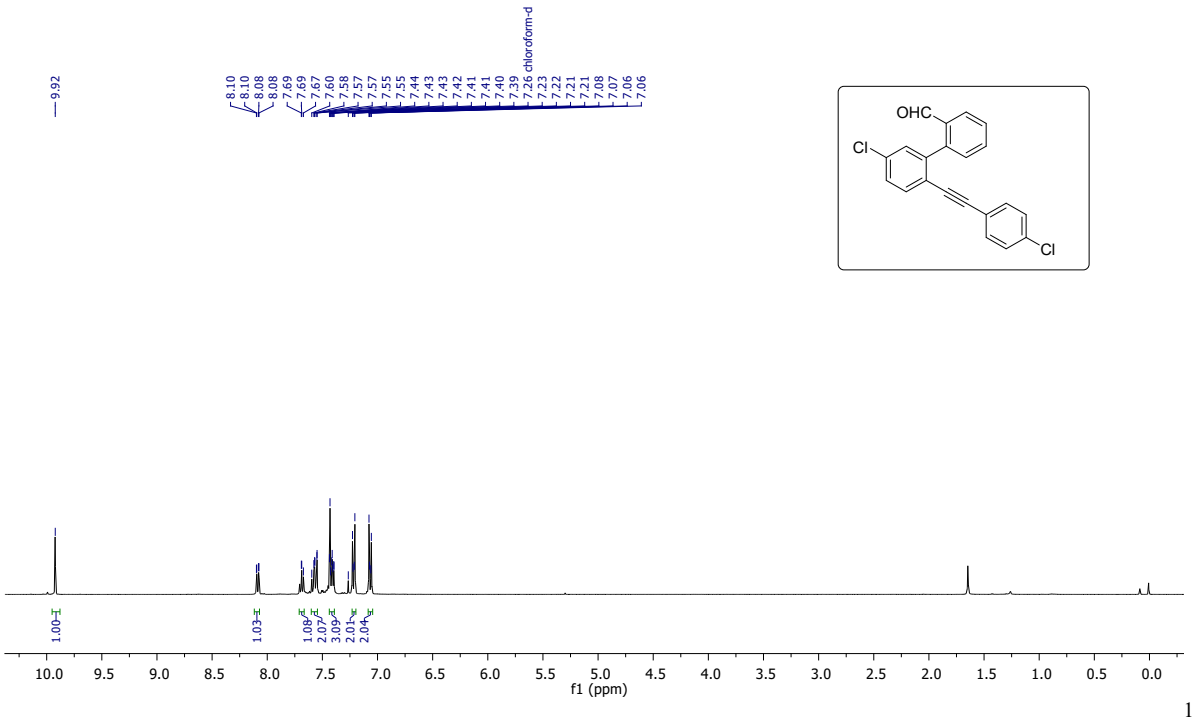
^{13}C{H} NMR (101 MHz) spectrum of **10l** in $CDCl_3$



^{1}H NMR (600 MHz) spectrum of **10m** in $CDCl_3$



^{13}C{H} NMR (101 MHz) spectrum of **10m** in $CDCl_3$



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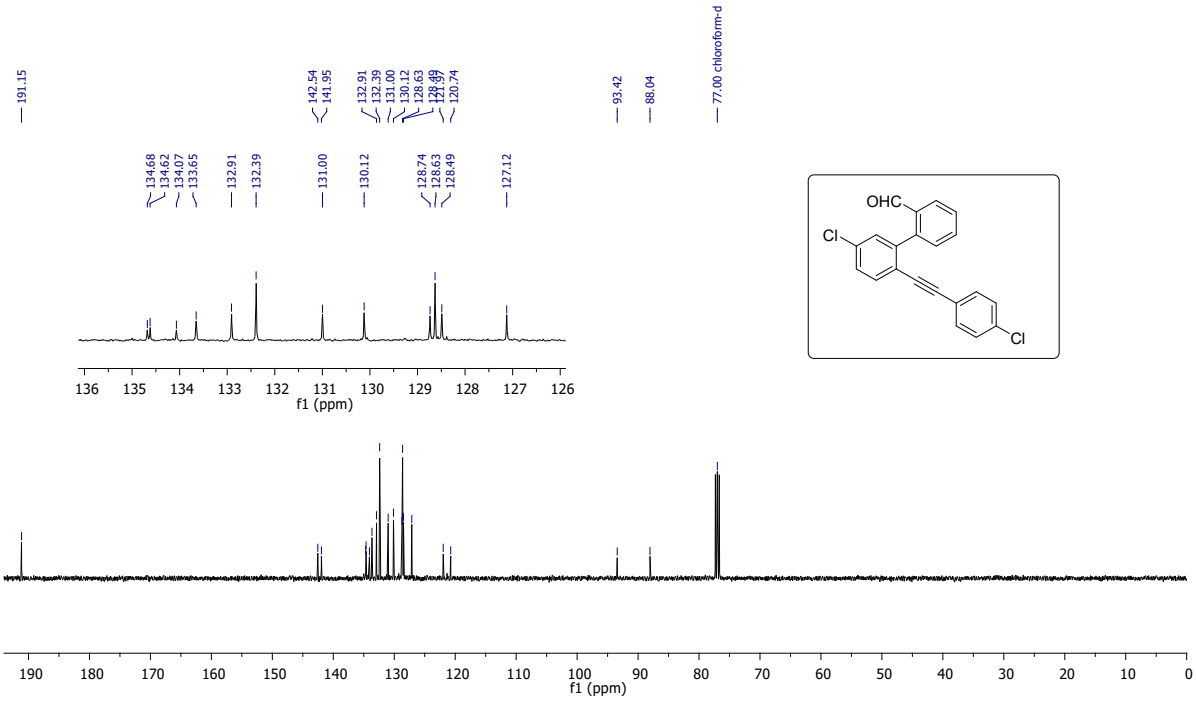
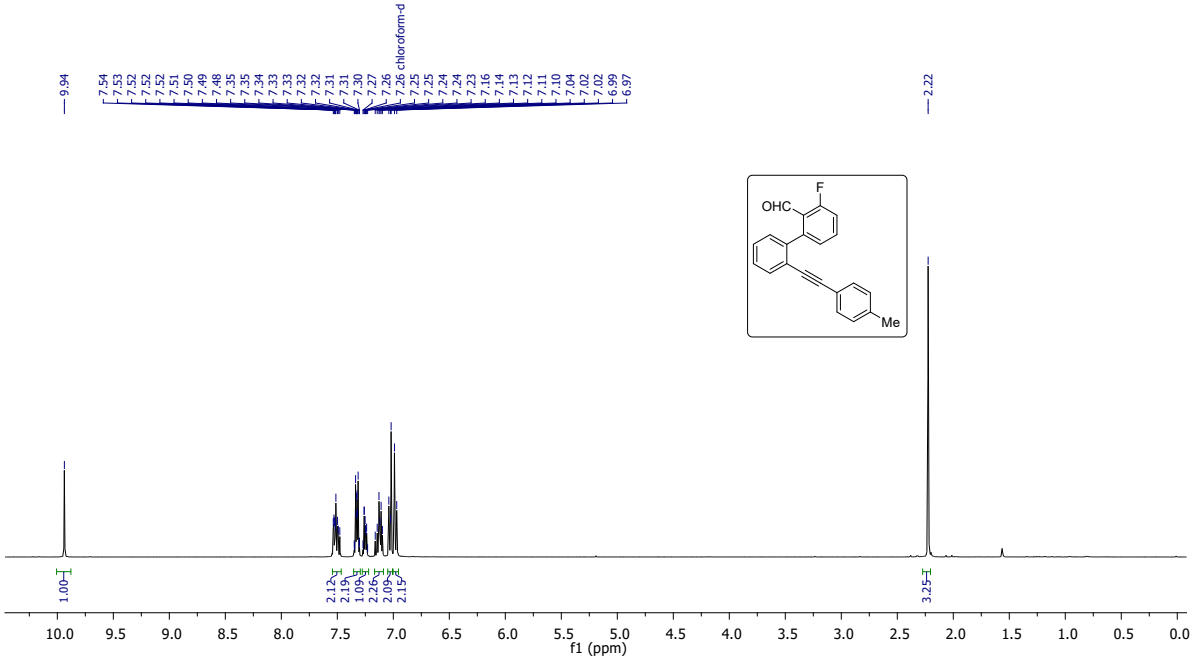
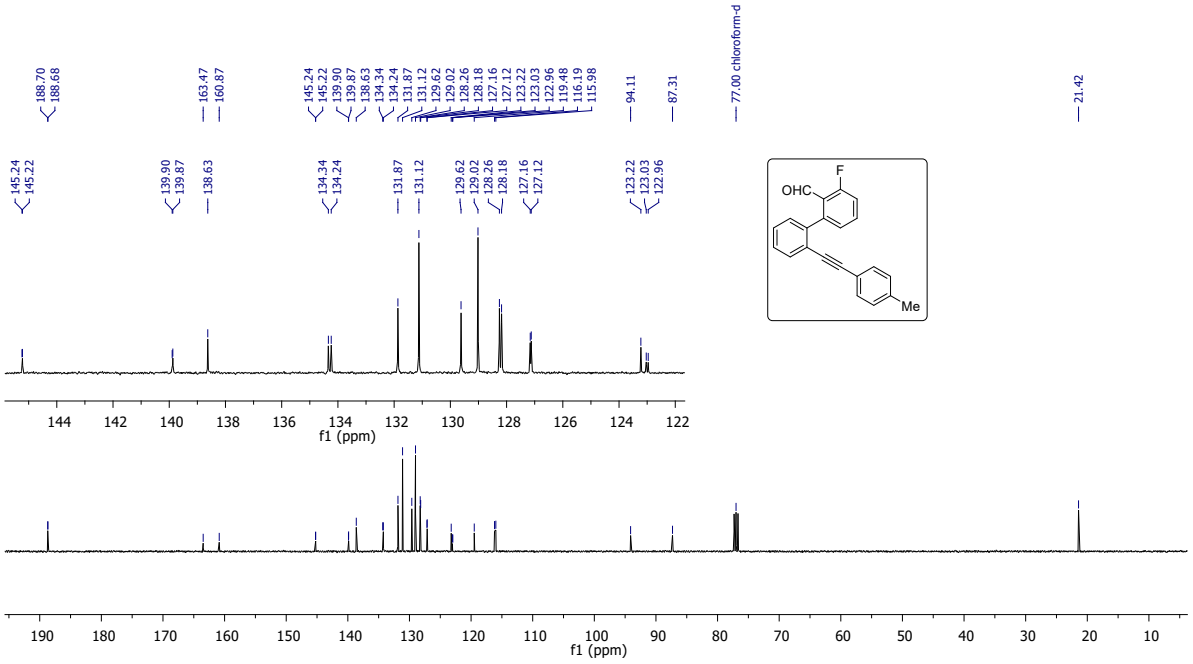
H NMR (400 MHz) spectrum of **10n** in $CDCl_3$



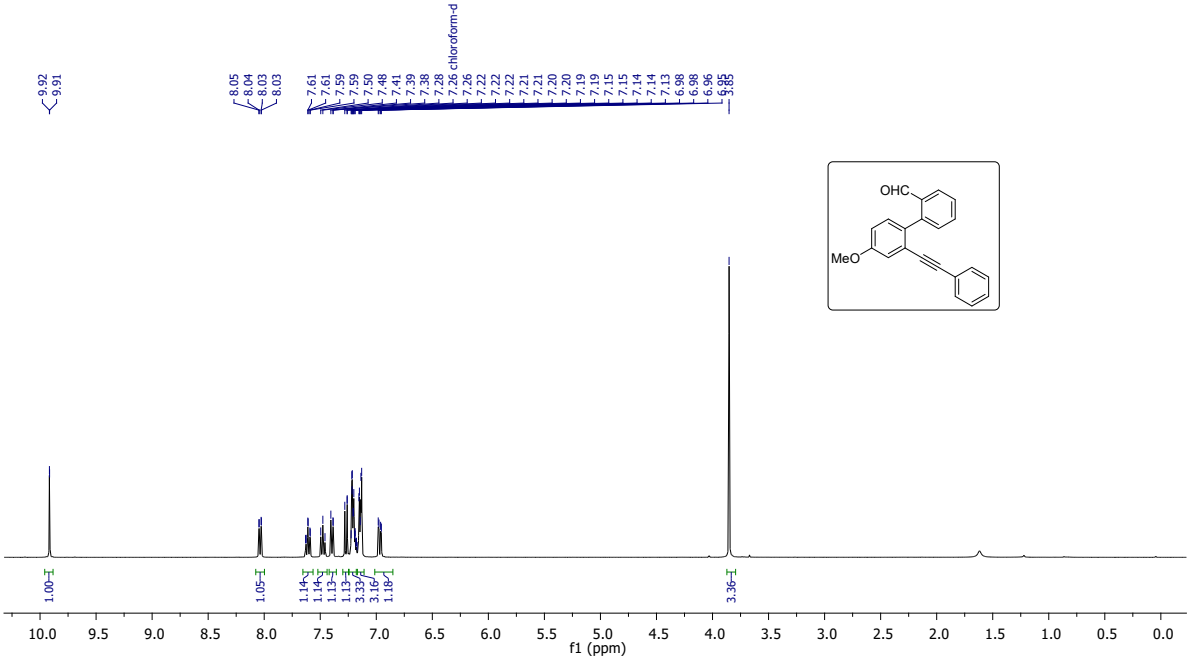
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **10n** in $CDCl_3$



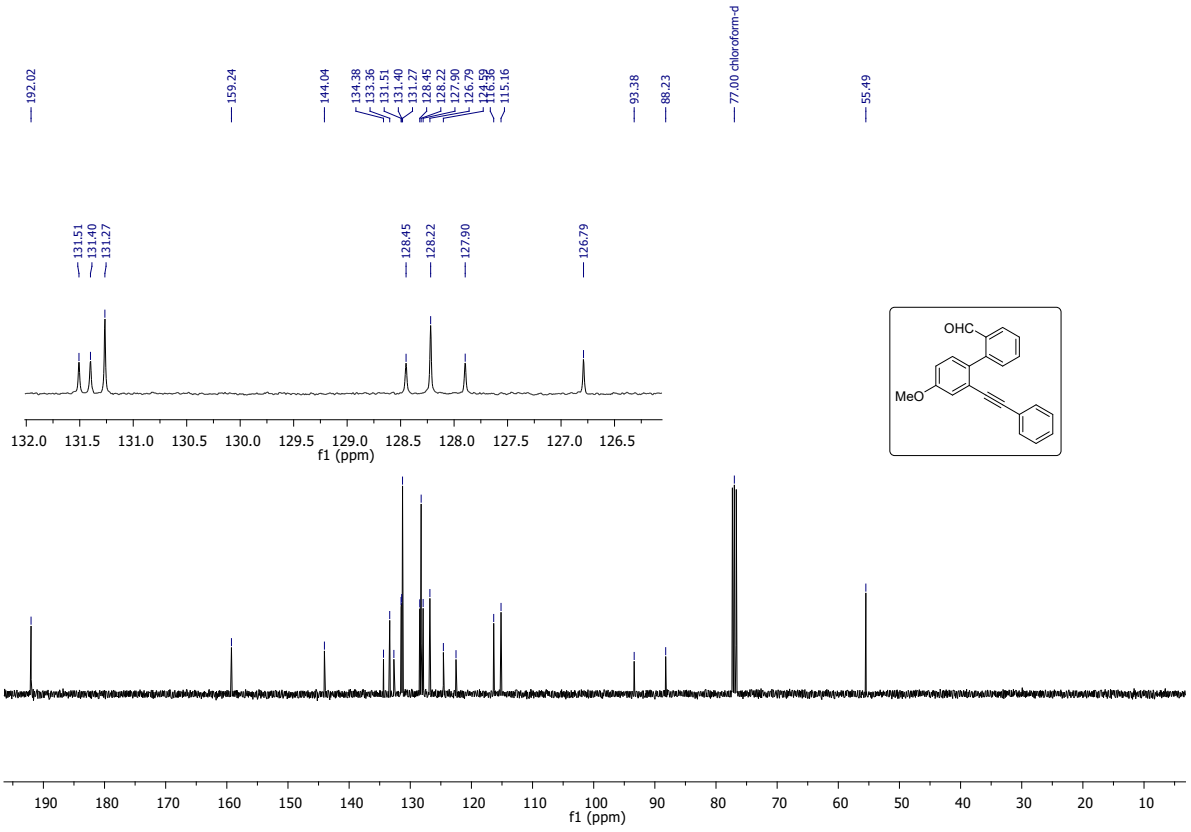
^{1}H NMR (400 MHz) spectrum of **10o** in $CDCl_3$



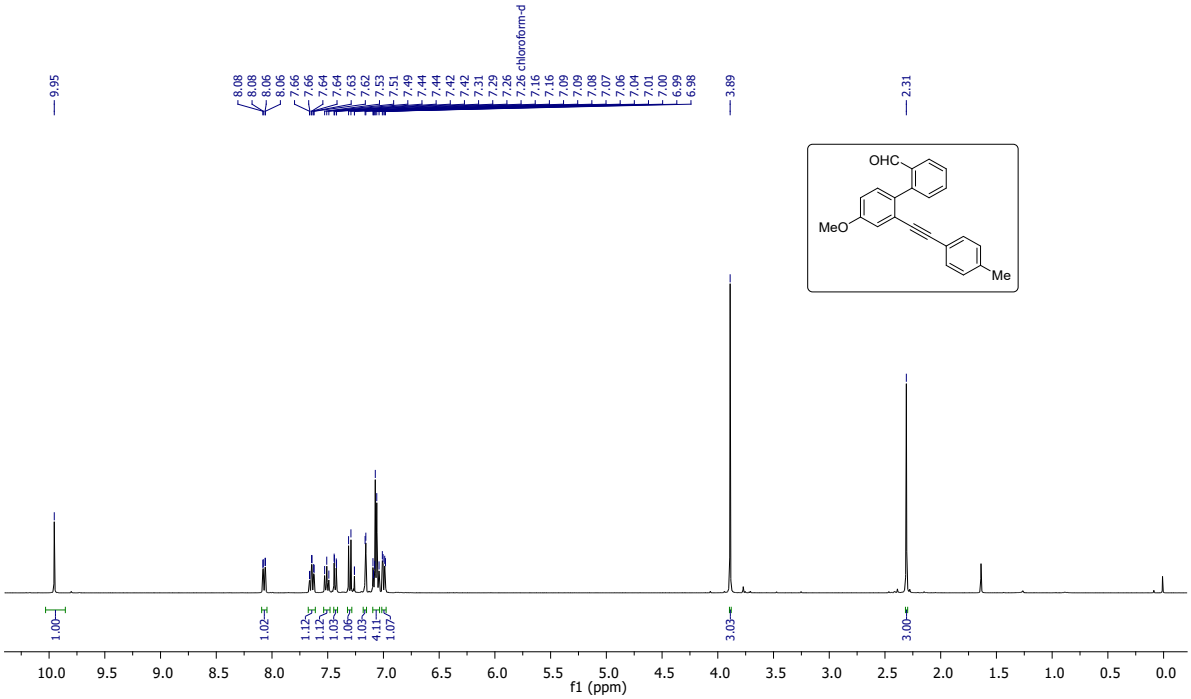
^{13}C{H} NMR (101 MHz) spectrum of **10o** in $CDCl_3$



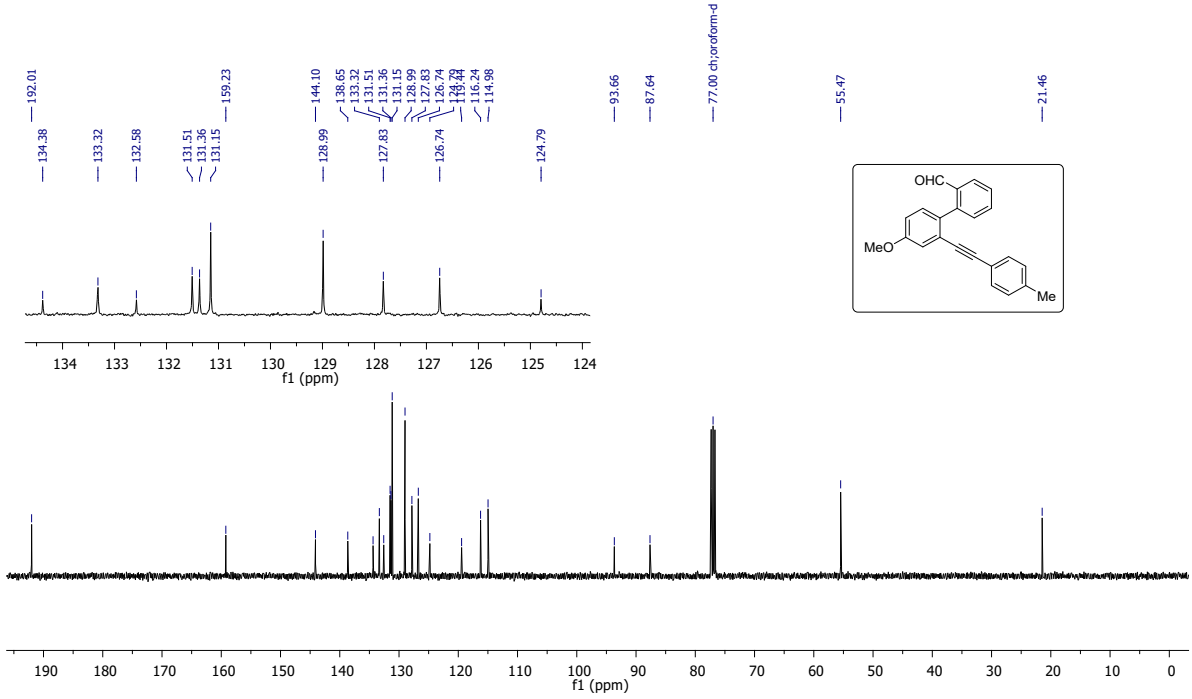
^{1}H NMR (400 MHz) spectrum of **10q** in $CDCl_3$



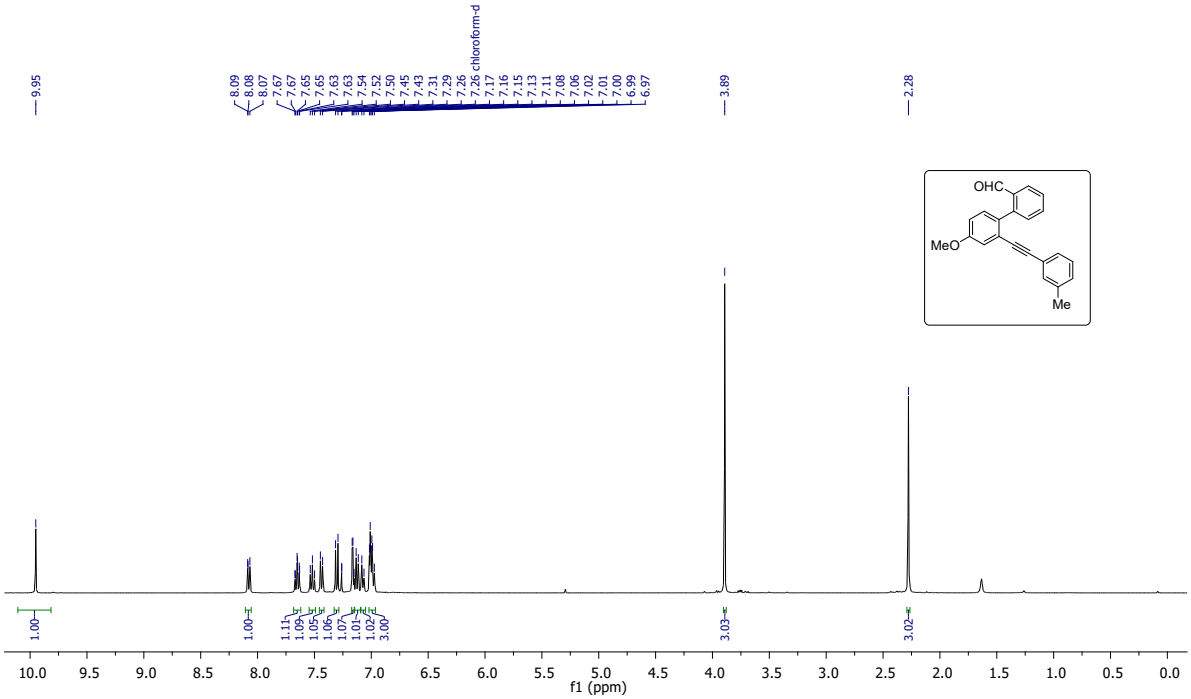
^{13}C{H} NMR (101 MHz) spectrum of **10q** in $CDCl_3$



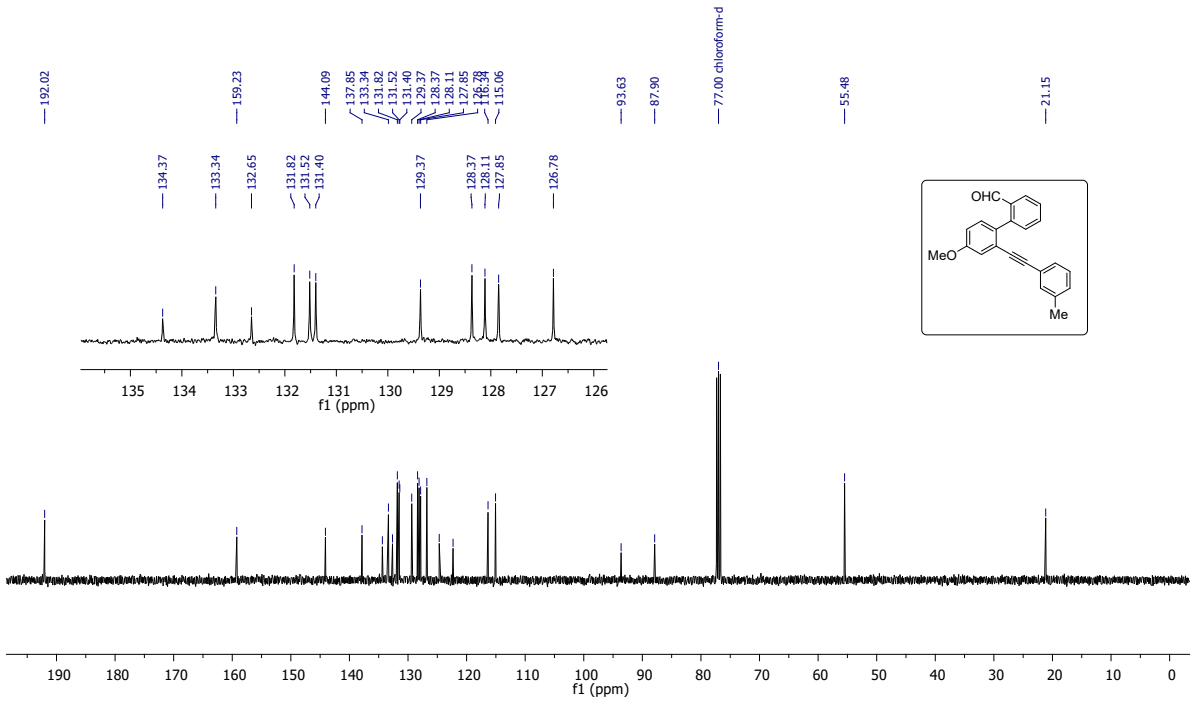
^{1}H NMR (400 MHz) spectrum of **10r** in $CDCl_3$



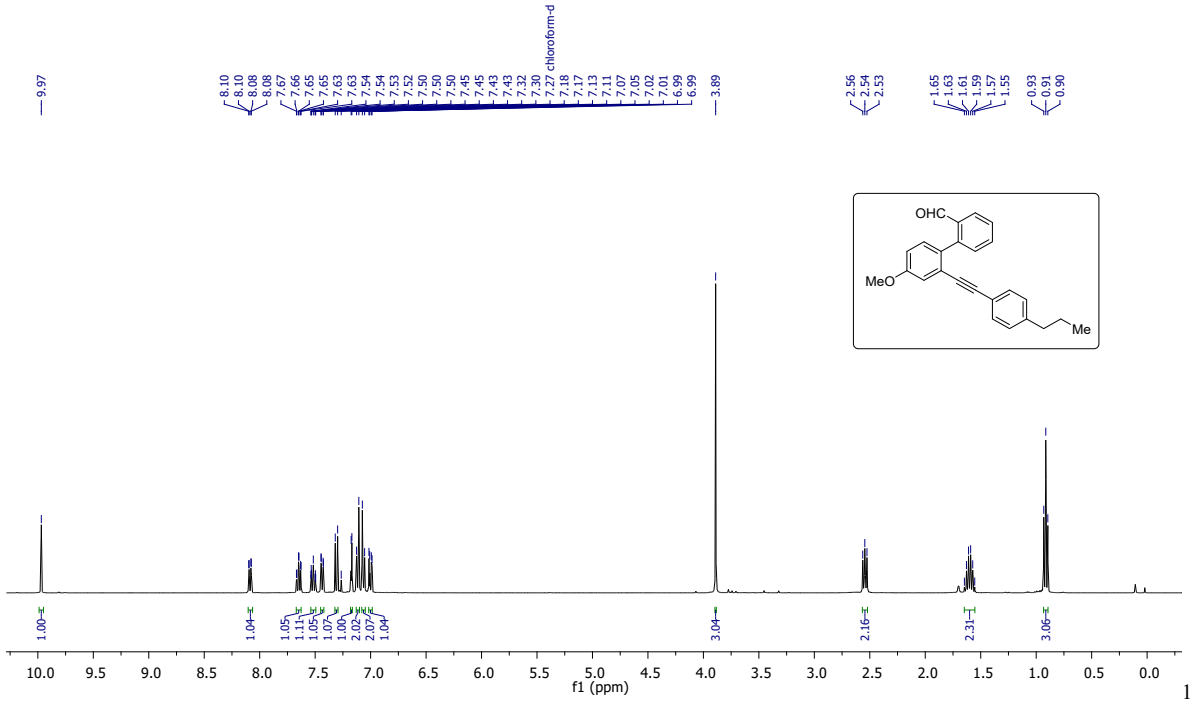
^{13}C{H} NMR (101 MHz) spectrum of **10r** in $CDCl_3$



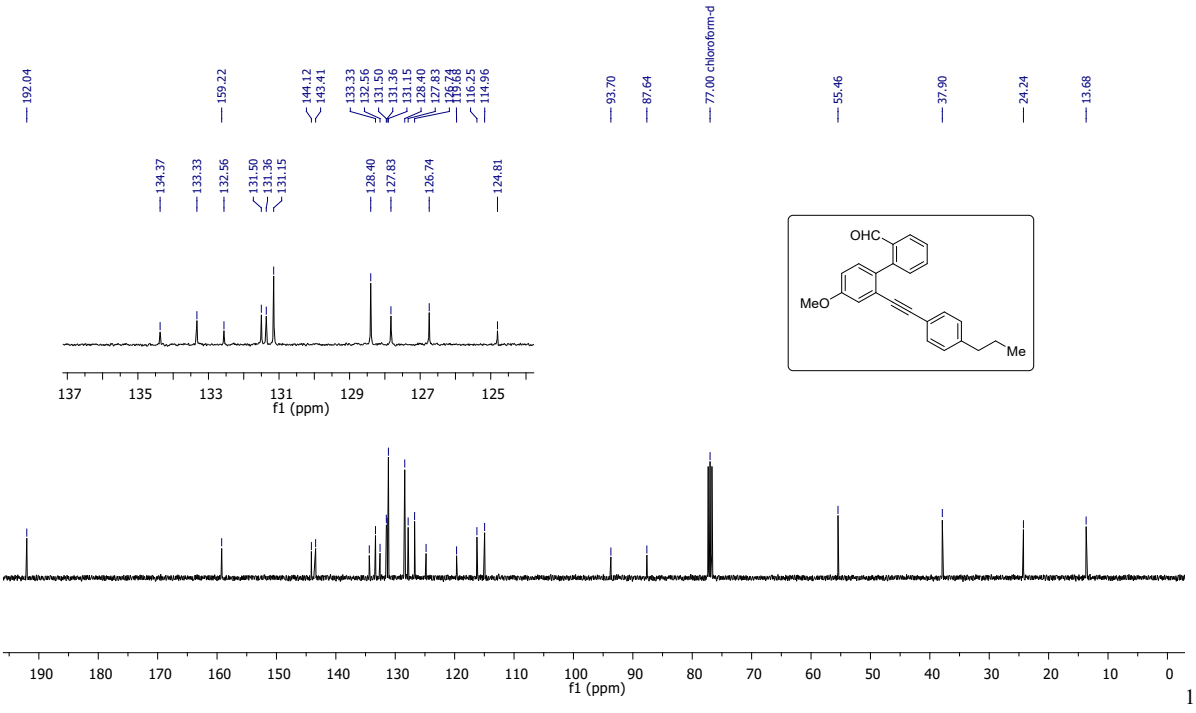
^{1}H NMR (400 MHz) spectrum of **10s** in $CDCl_3$



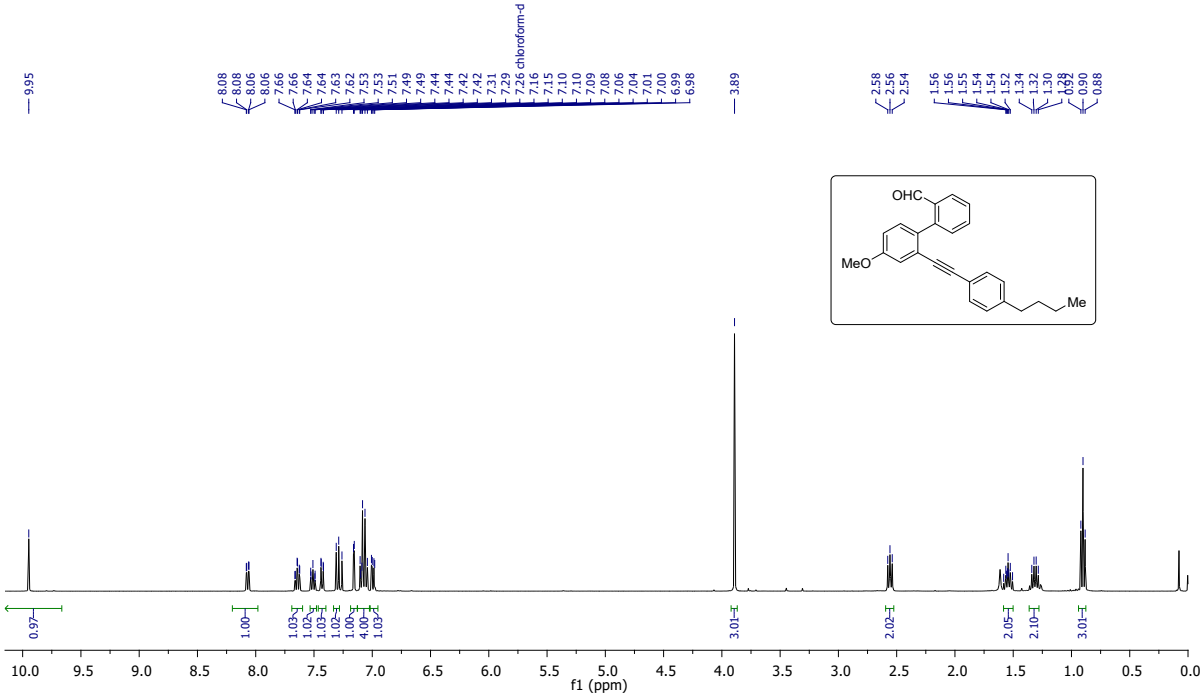
^{13}C{H} NMR (101 MHz) spectrum of **10s** in $CDCl_3$



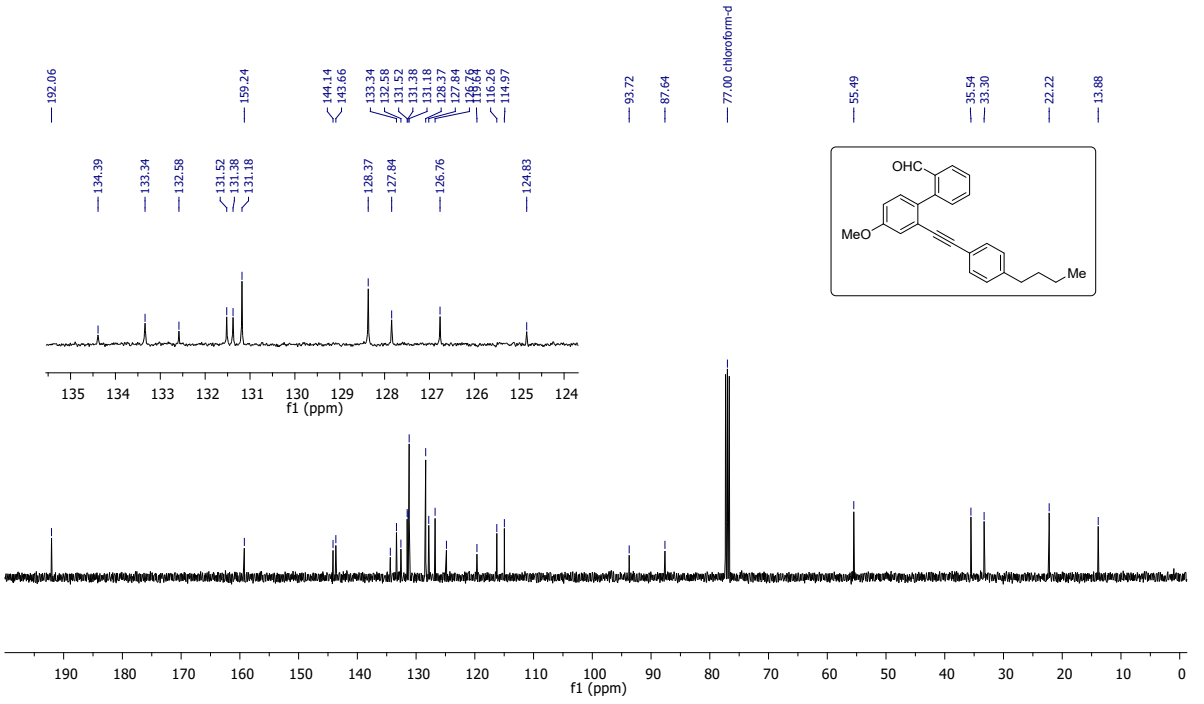
H NMR (400 MHz) spectrum of **10t** in $CDCl_3$



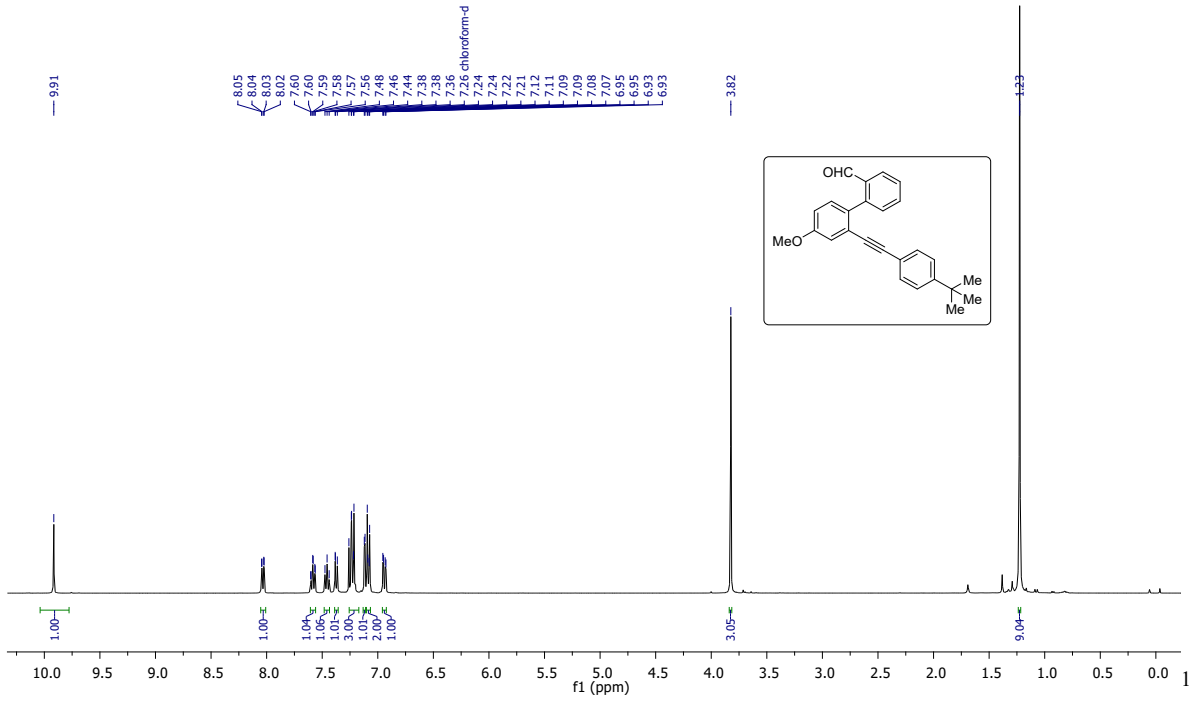
$^{3}C\{H\}$ NMR (101 MHz) spectrum of **10t** in $CDCl_3$



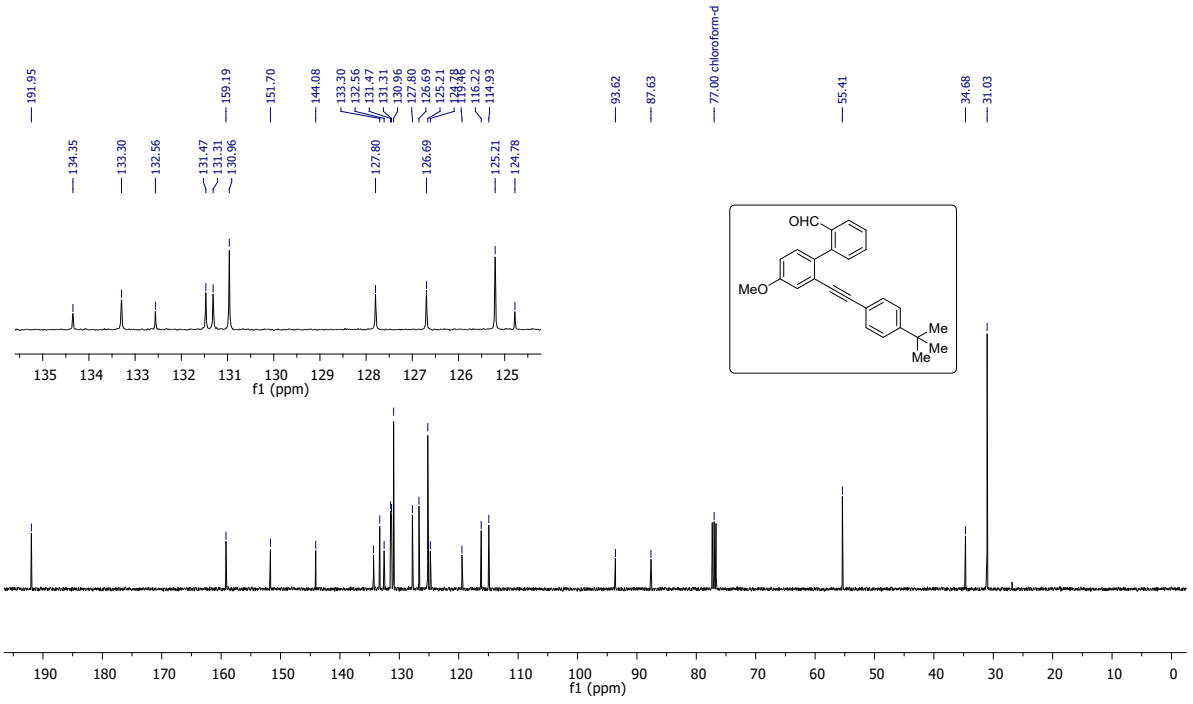
^{1}H NMR (400 MHz) spectrum of **10u** in $CDCl_3$



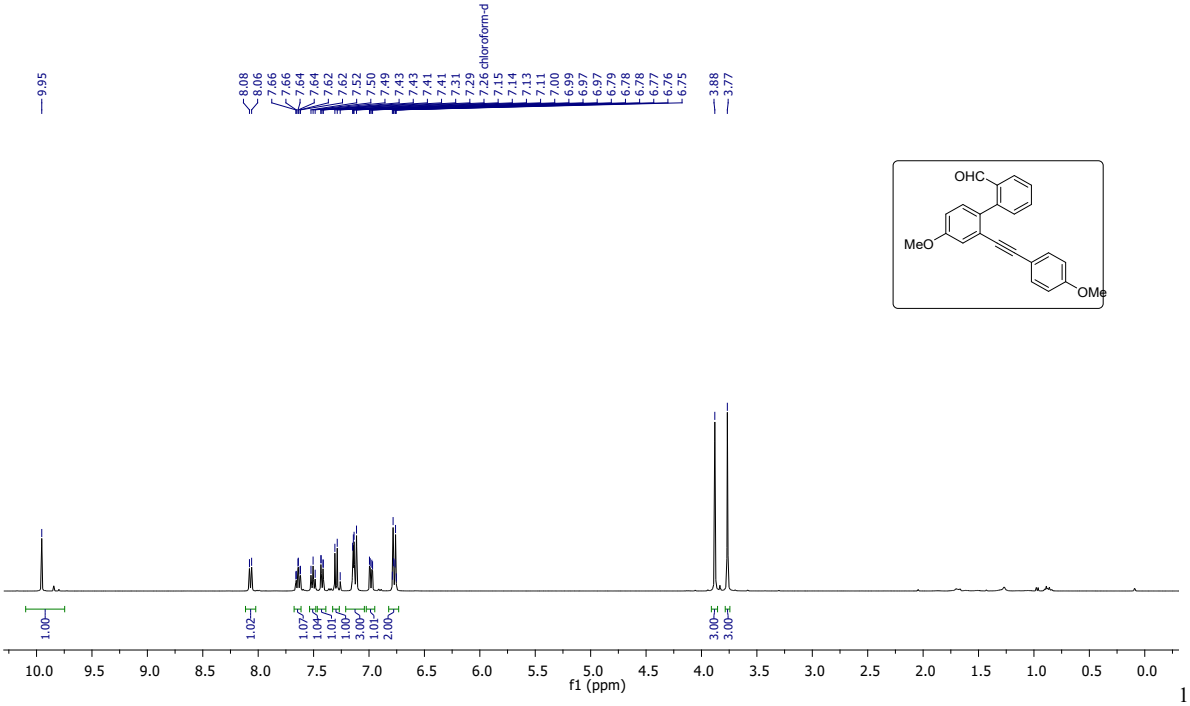
^{13}C{H} NMR (101 MHz) spectrum of **10u** in $CDCl_3$



H NMR (400 MHz) spectrum of **10v** in $CDCl_3$



$^{13}C\{H\}$ NMR (101 MHz) spectrum of **10v** in $CDCl_3$



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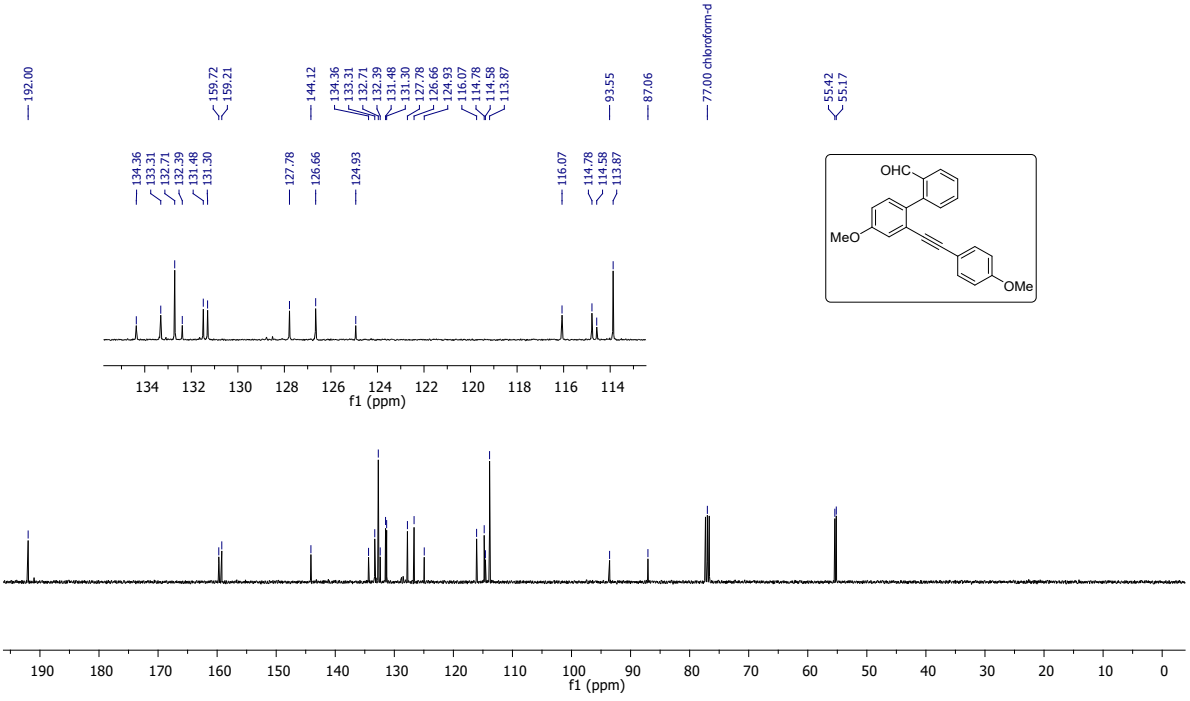
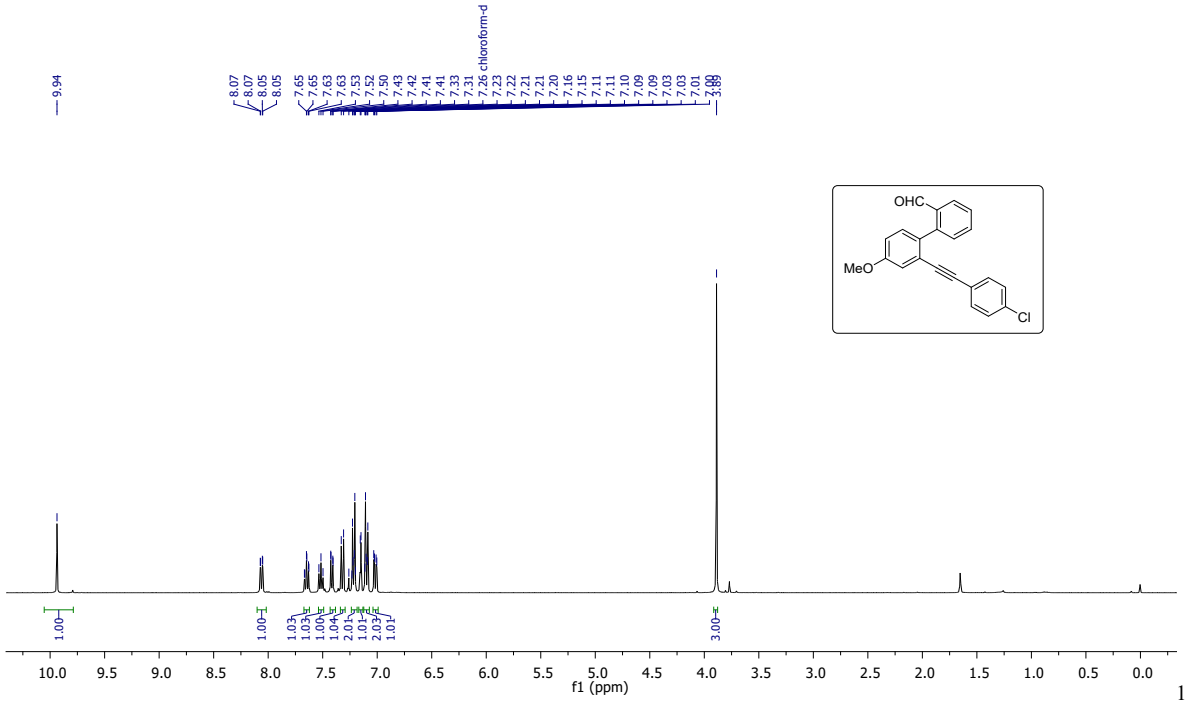
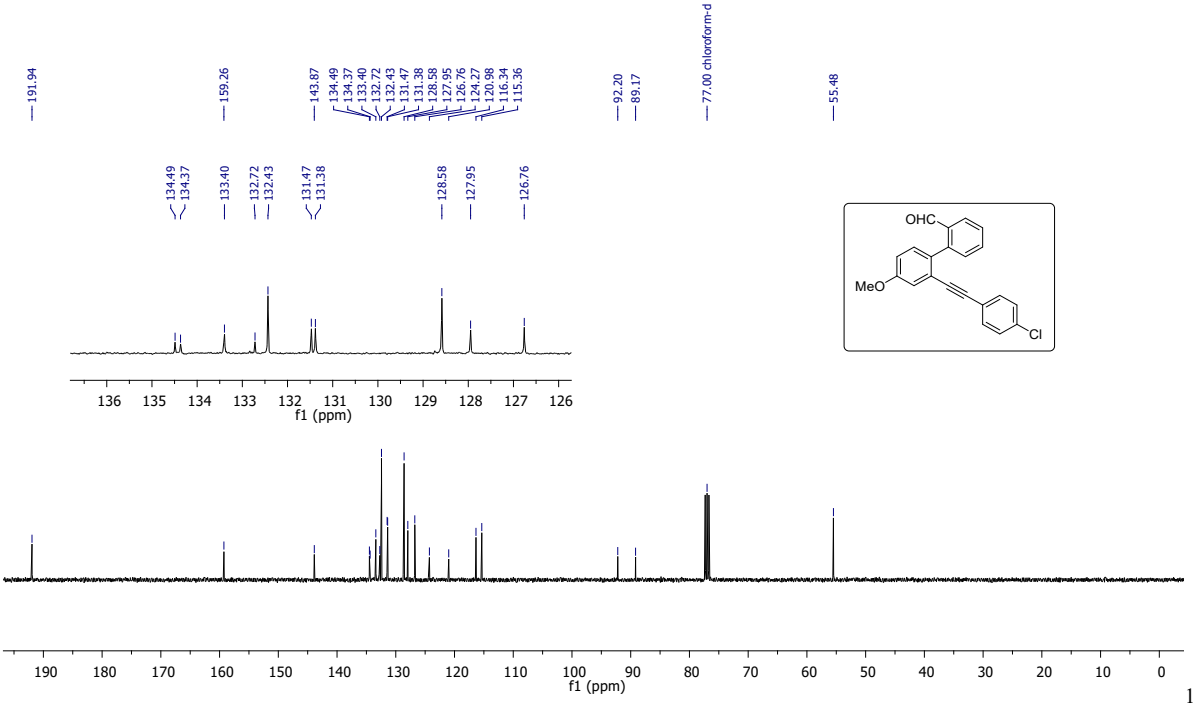
H NMR (400 MHz) spectrum of **10w** in $CDCl_3$



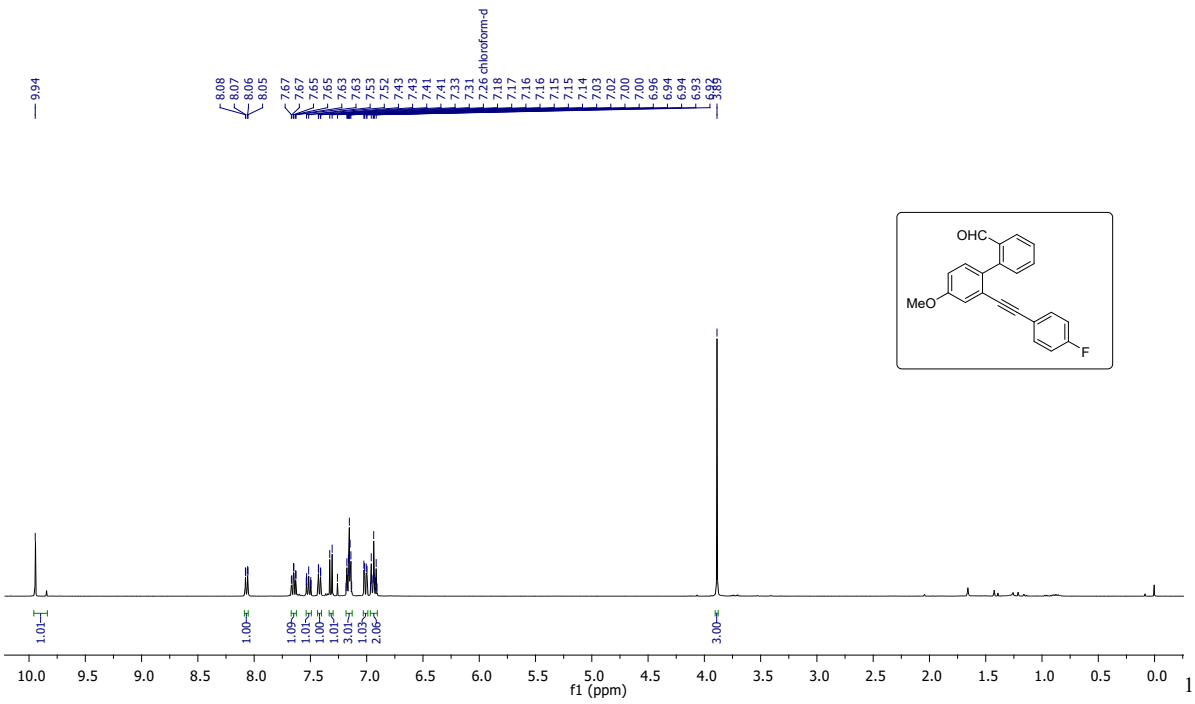
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **10w** in $CDCl_3$



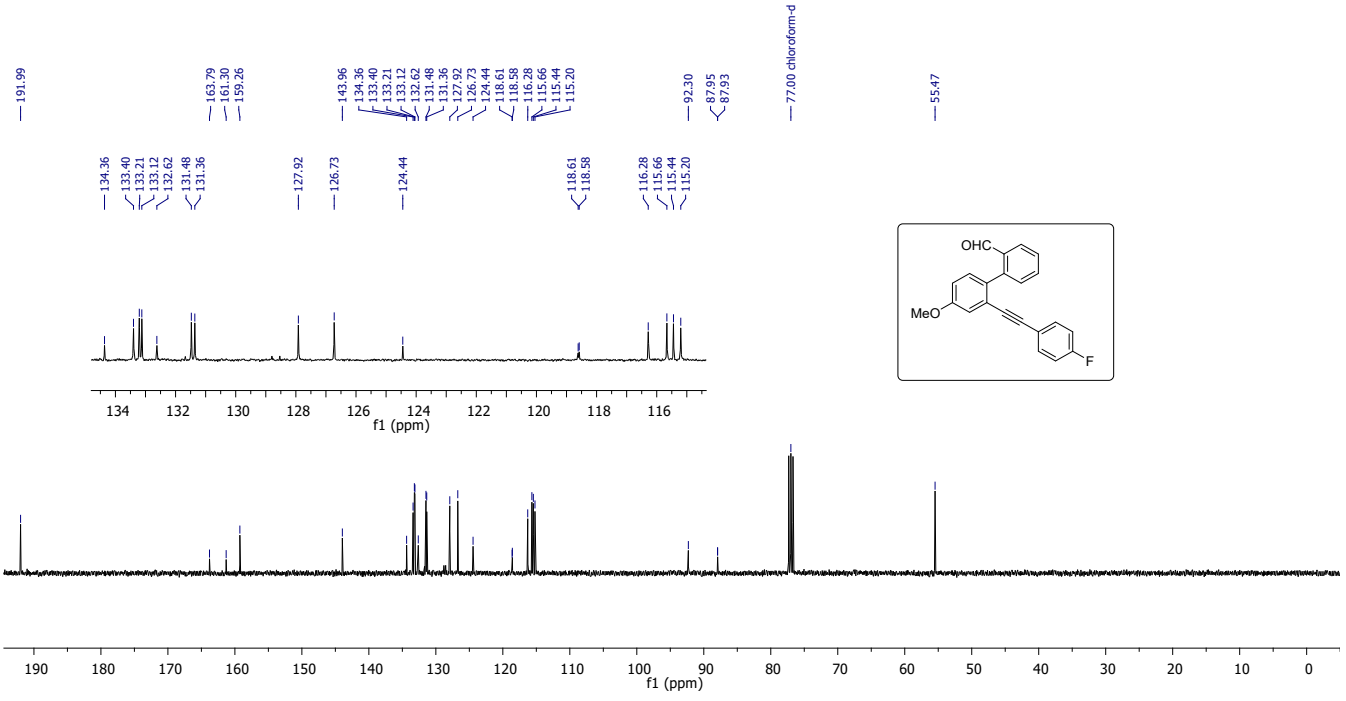
H NMR (400 MHz) spectrum of **10x** in $CDCl_3$



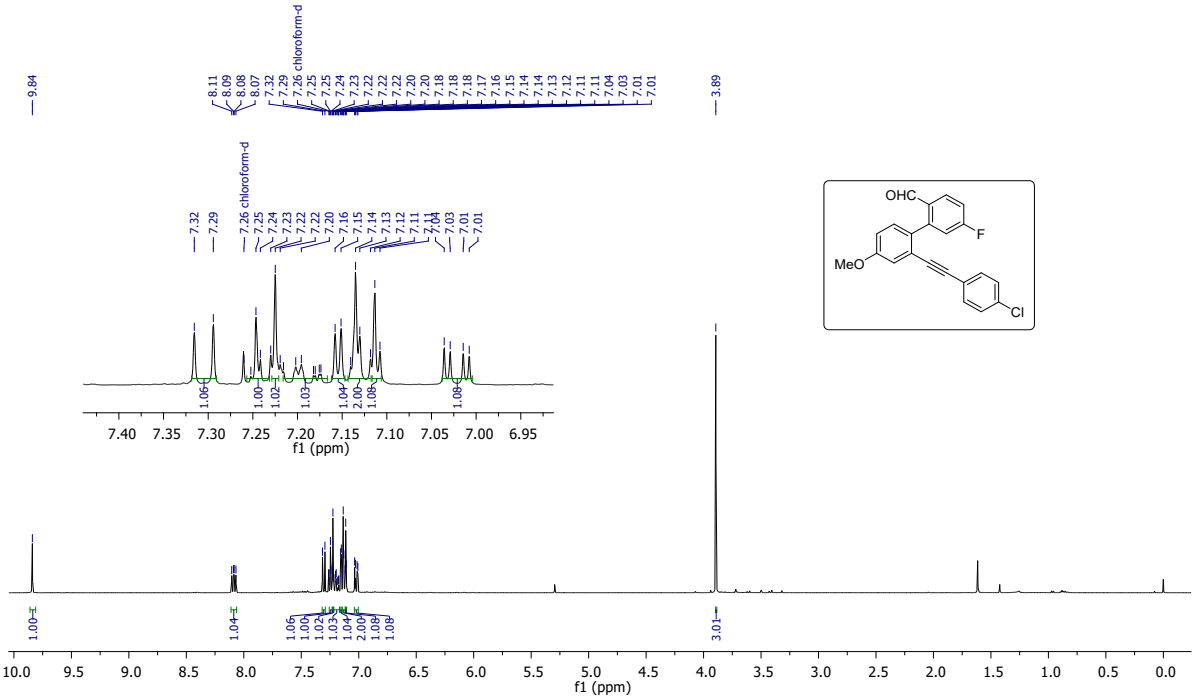
$^{3}C\{H\}$ NMR (101 MHz) spectrum of **10x** in $CDCl_3$



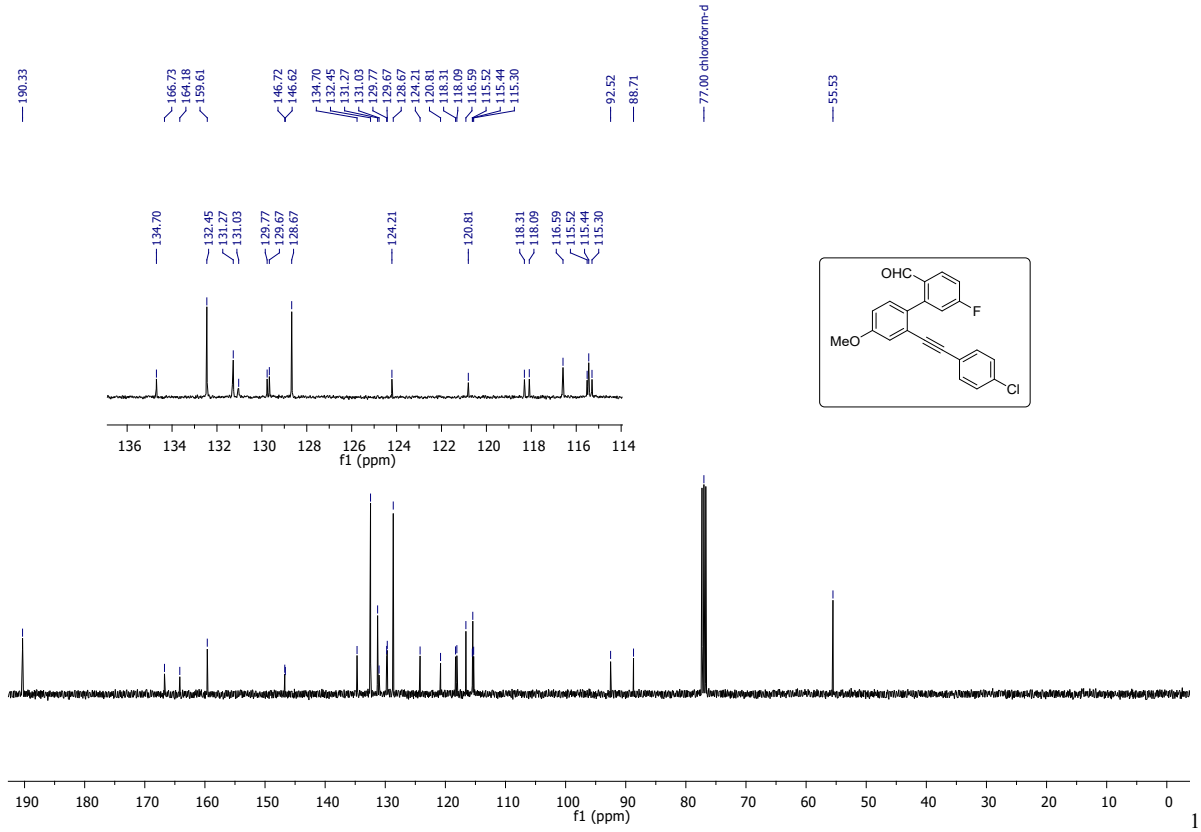
H NMR (400 MHz) spectrum of **10y** in $CDCl_3$



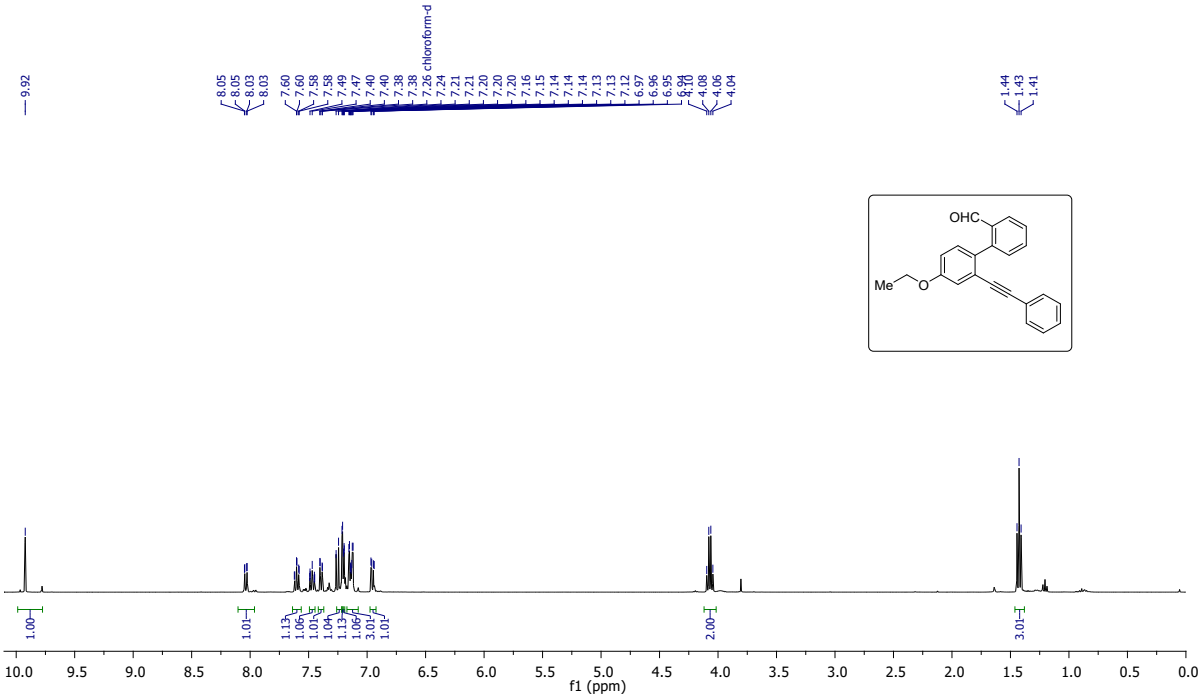
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **10y** in $CDCl_3$



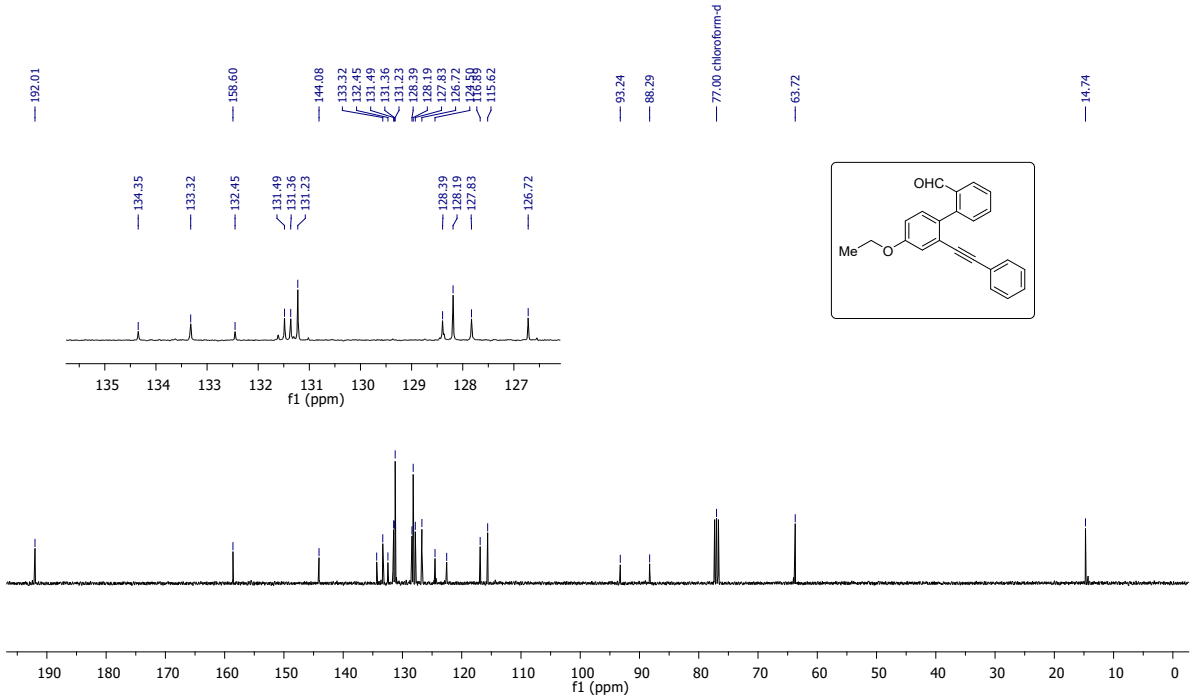
^{1}H NMR (400 MHz) spectrum of **10z** in $CDCl_3$



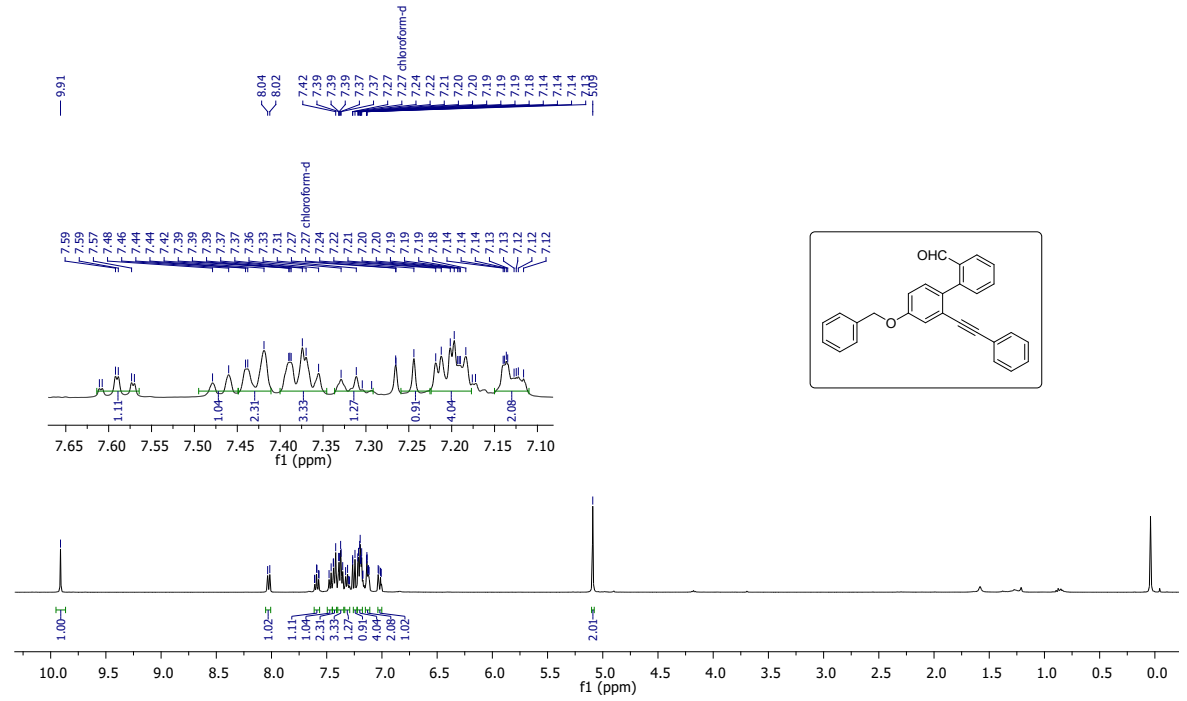
^{3}C{H} NMR (101 MHz) spectrum of **10z** in $CDCl_3$



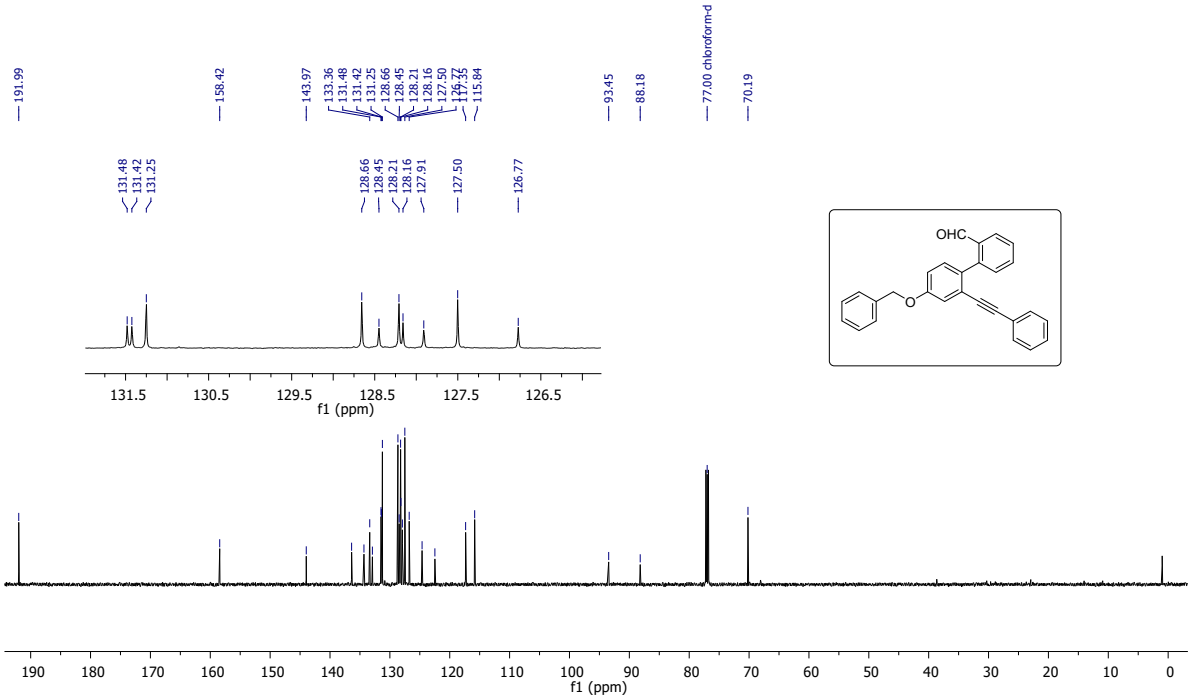
^{1}H NMR (400 MHz) spectrum of **10aa** in $CDCl_3$



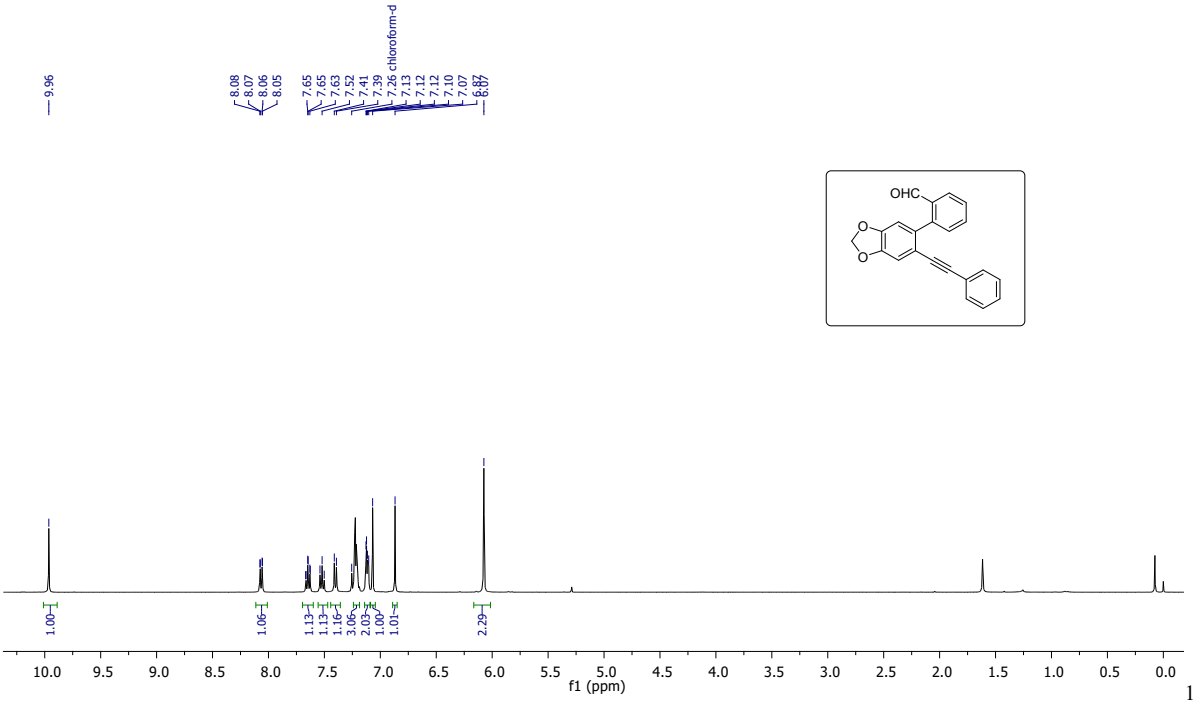
^{13}C{H} NMR (101 MHz) spectrum of **10aa** in $CDCl_3$



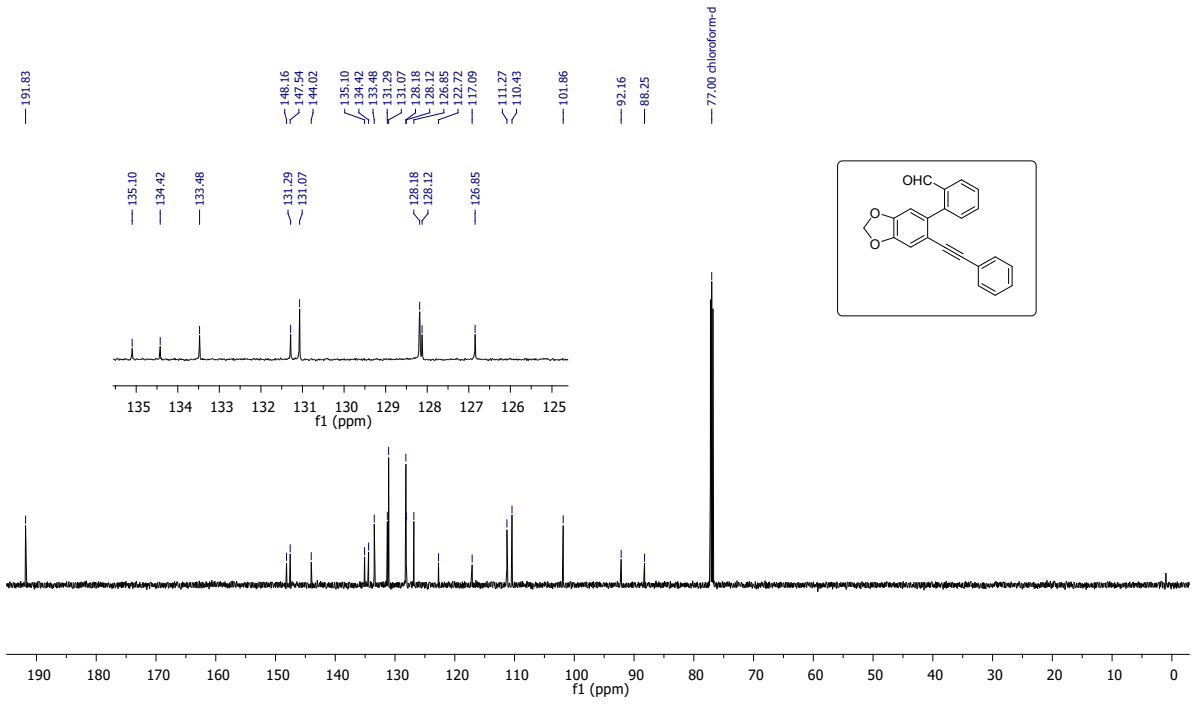
^{1}H NMR (400 MHz) spectrum of **10ab** in $CDCl_3$



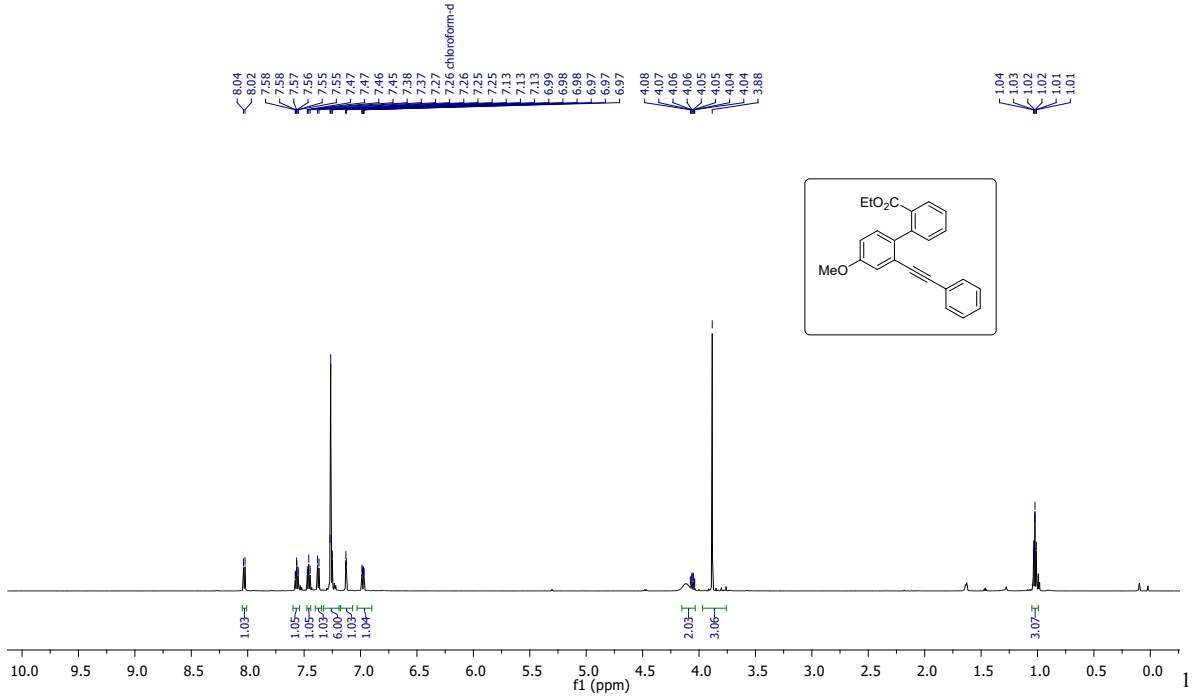
^{13}C{H} NMR (151 MHz) spectrum of **10ab** in $CDCl_3$



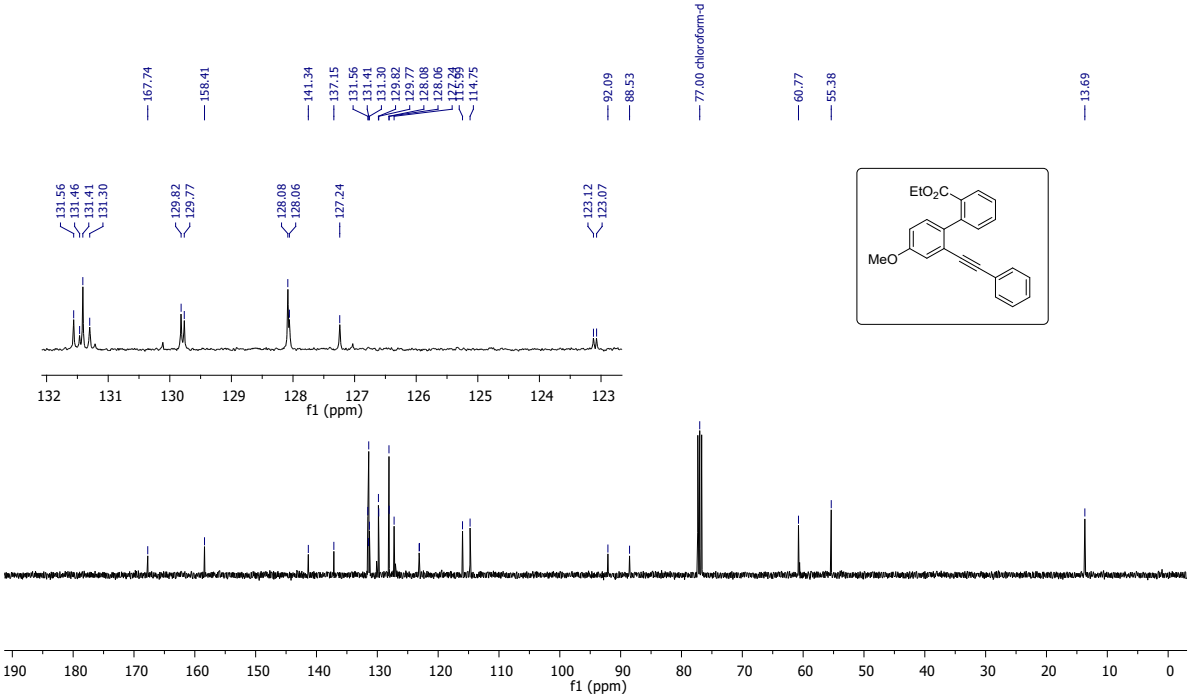
H NMR (400 MHz) spectrum of **10ac** in $CDCl_3$



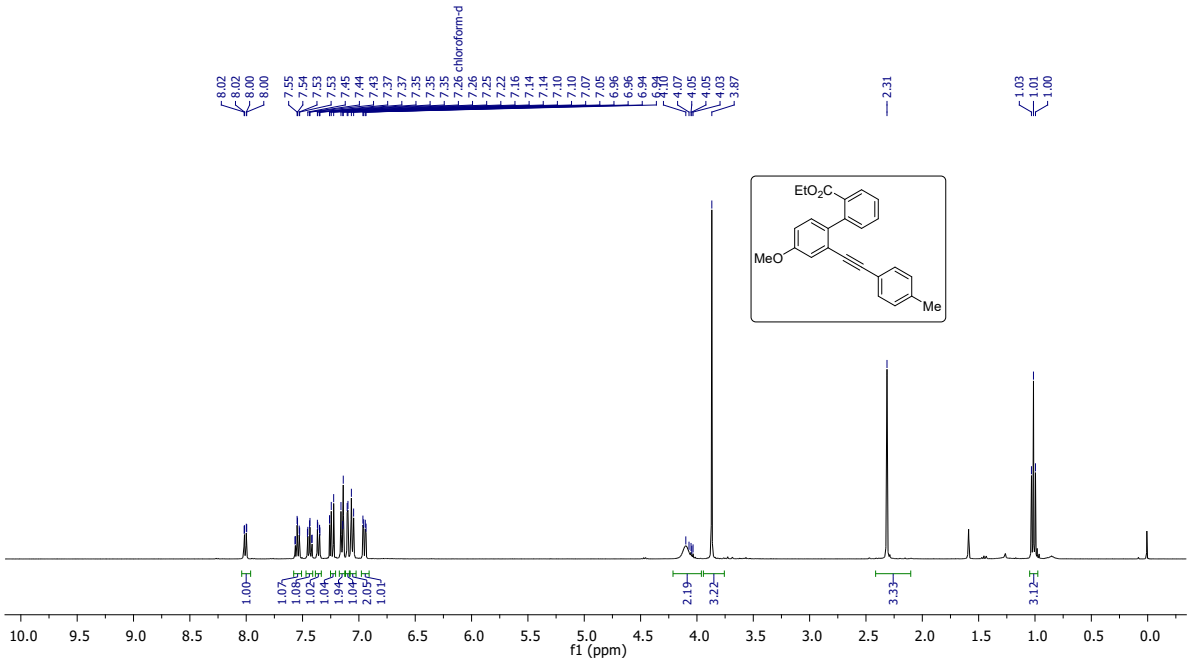
$^{13}C\{H\}$ NMR (151 MHz) spectrum of **10ac** in $CDCl_3$



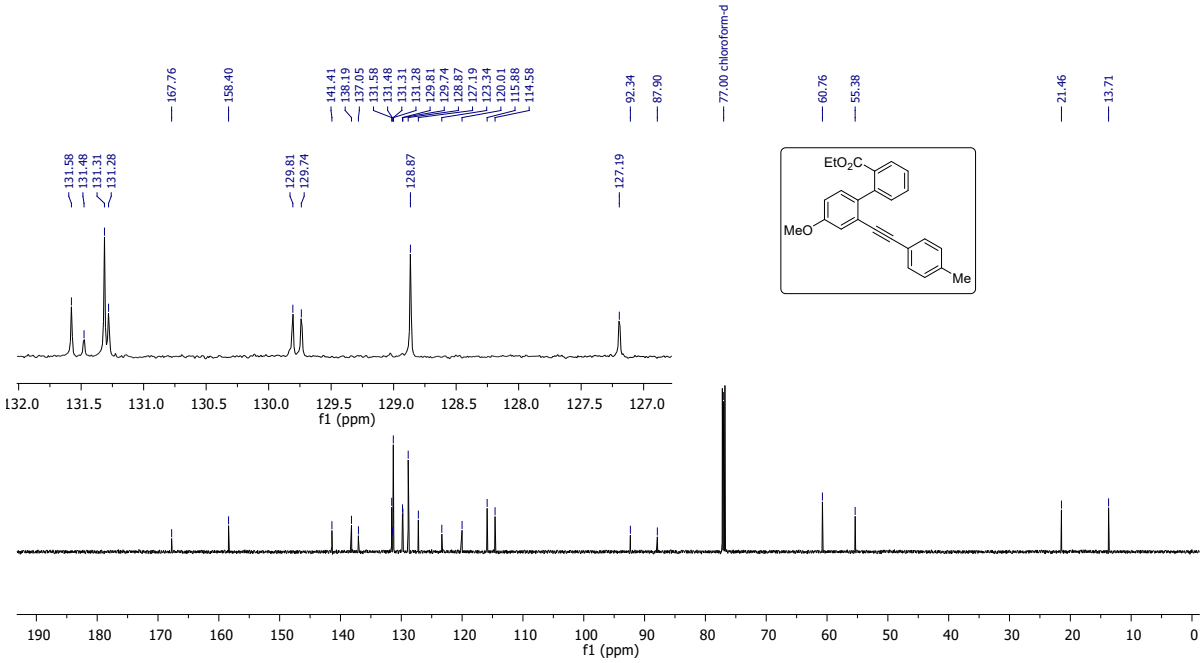
H NMR (600 MHz) spectrum of **11a** in $CDCl_3$



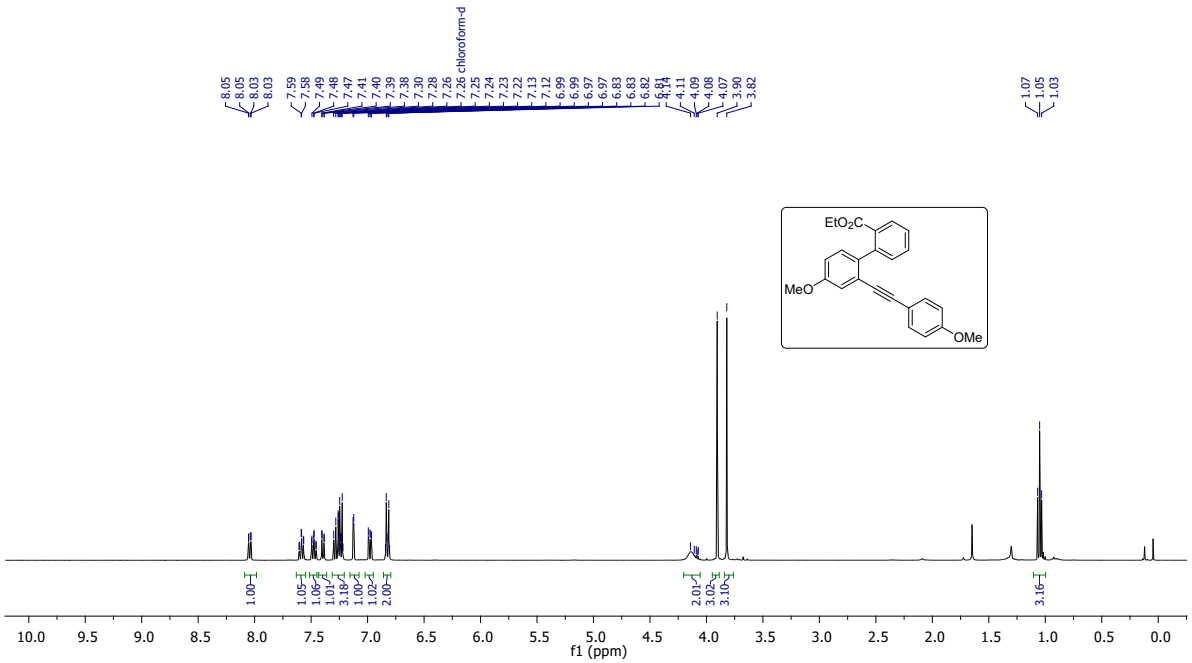
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **11a** in $CDCl_3$



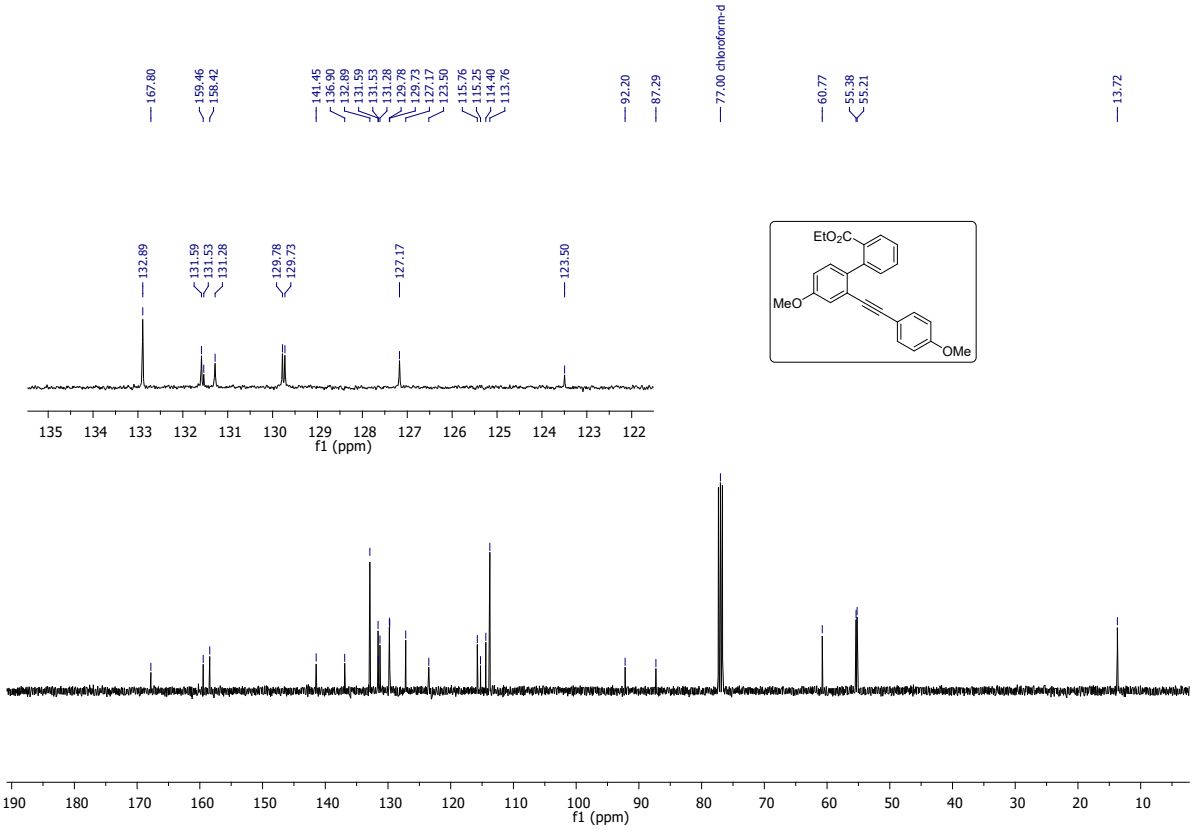
^{1}H NMR (400 MHz) spectrum of **11b** in $CDCl_3$



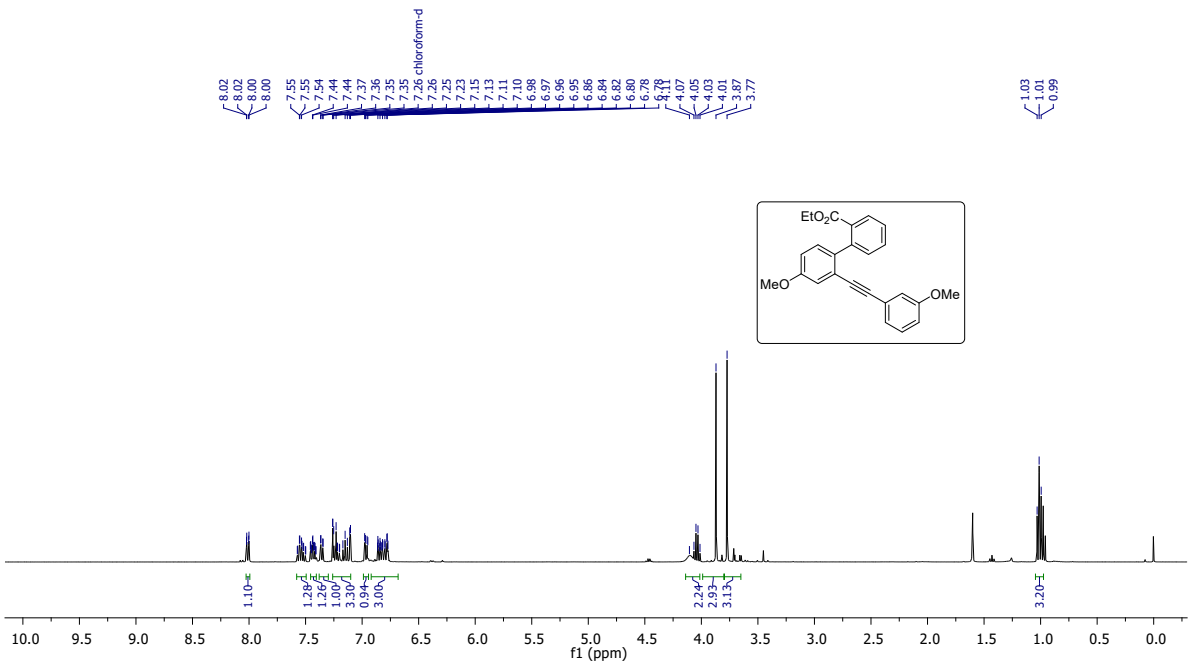
^{13}C{H} NMR (151 MHz) spectrum of **11b** in $CDCl_3$



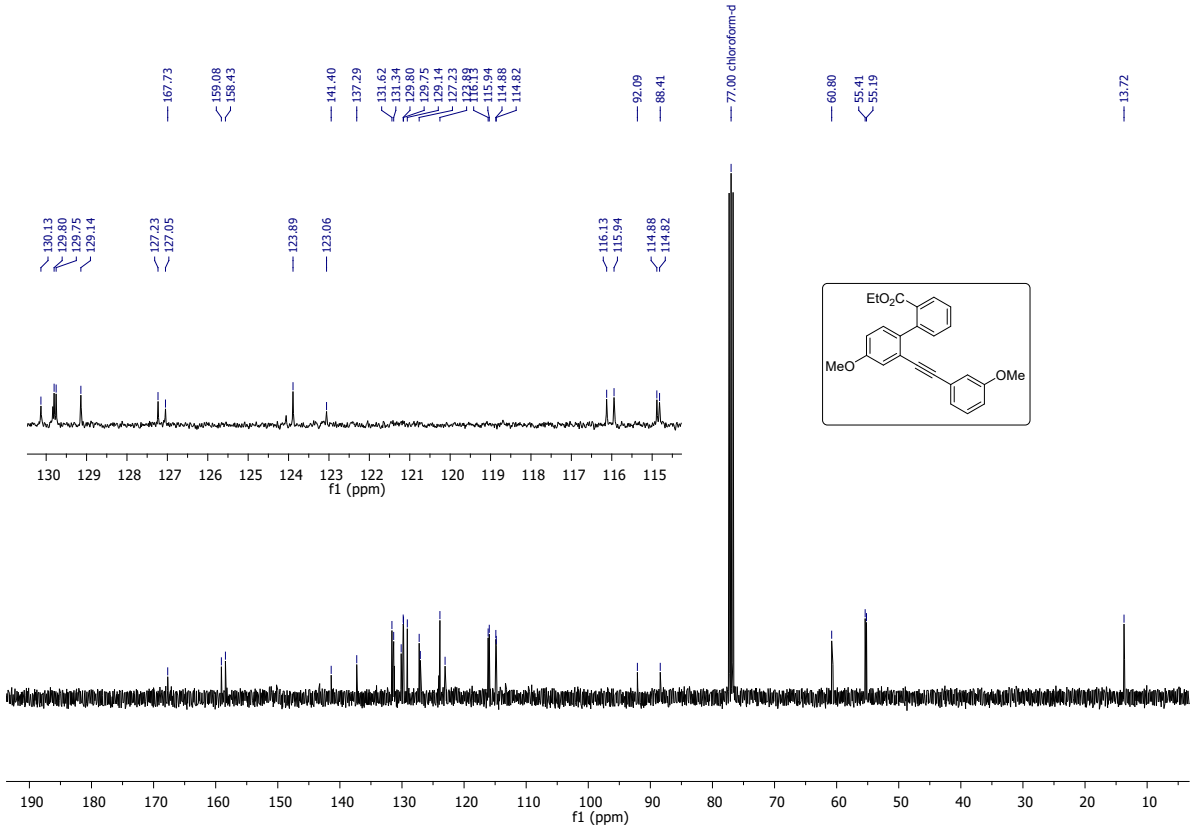
^{1}H NMR (400 MHz) spectrum of **11c** in $CDCl_3$



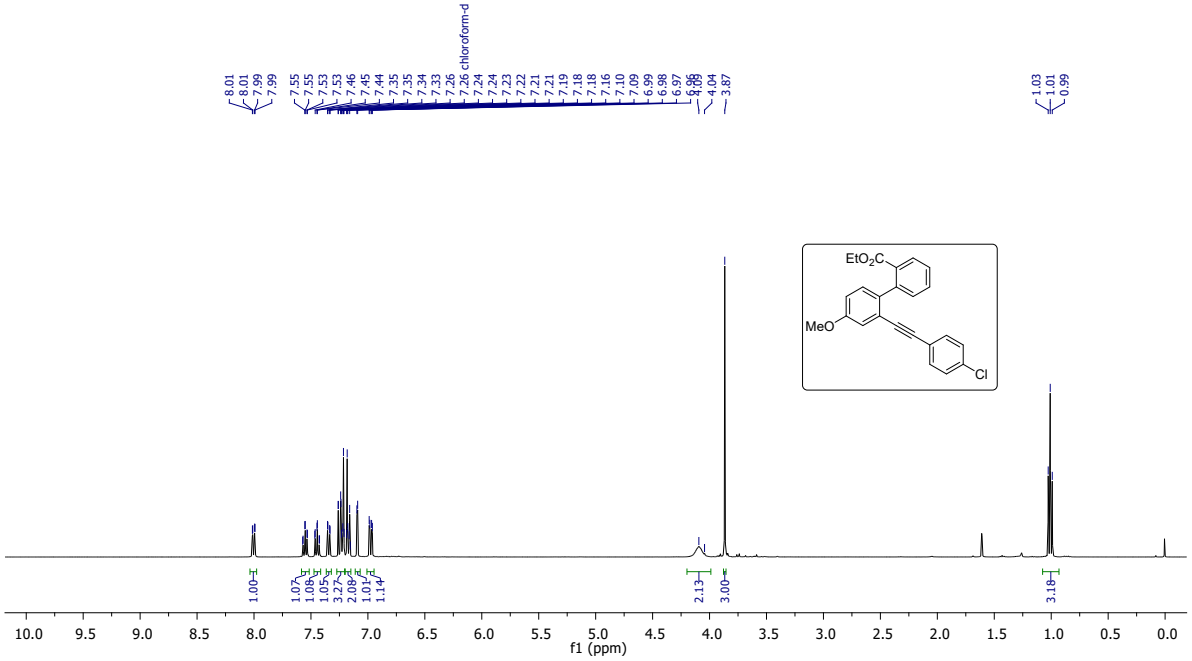
^{13}C{H} NMR (101 MHz) spectrum of **11c** in $CDCl_3$



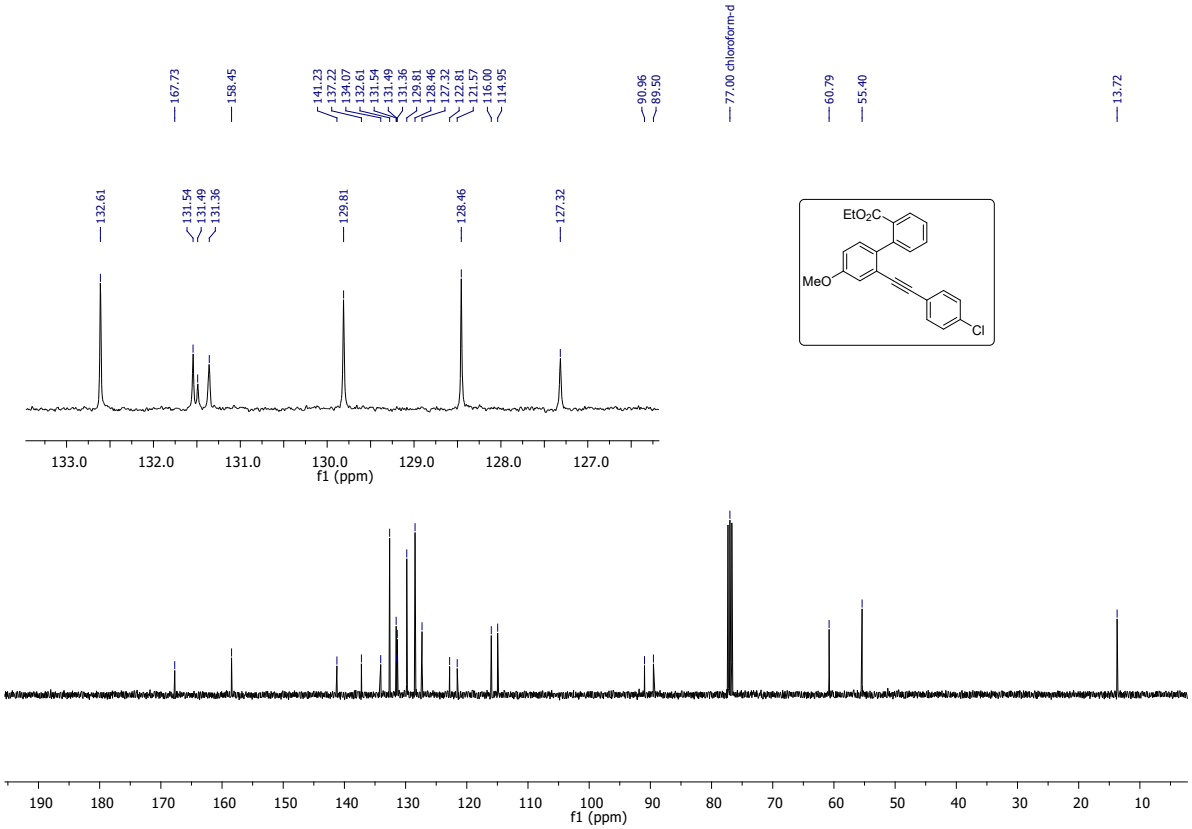
^{1}H NMR (400 MHz) spectrum of **11d** in $CDCl_3$



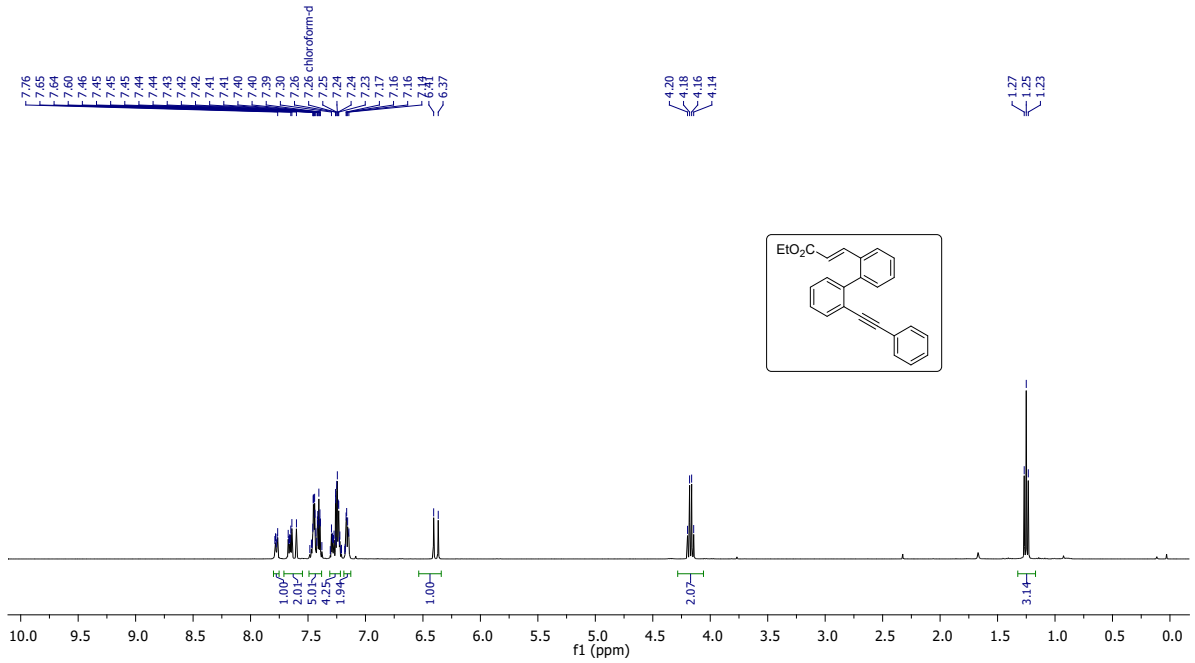
^{13}C{H} NMR (101 MHz) spectrum of **11d** in $CDCl_3$



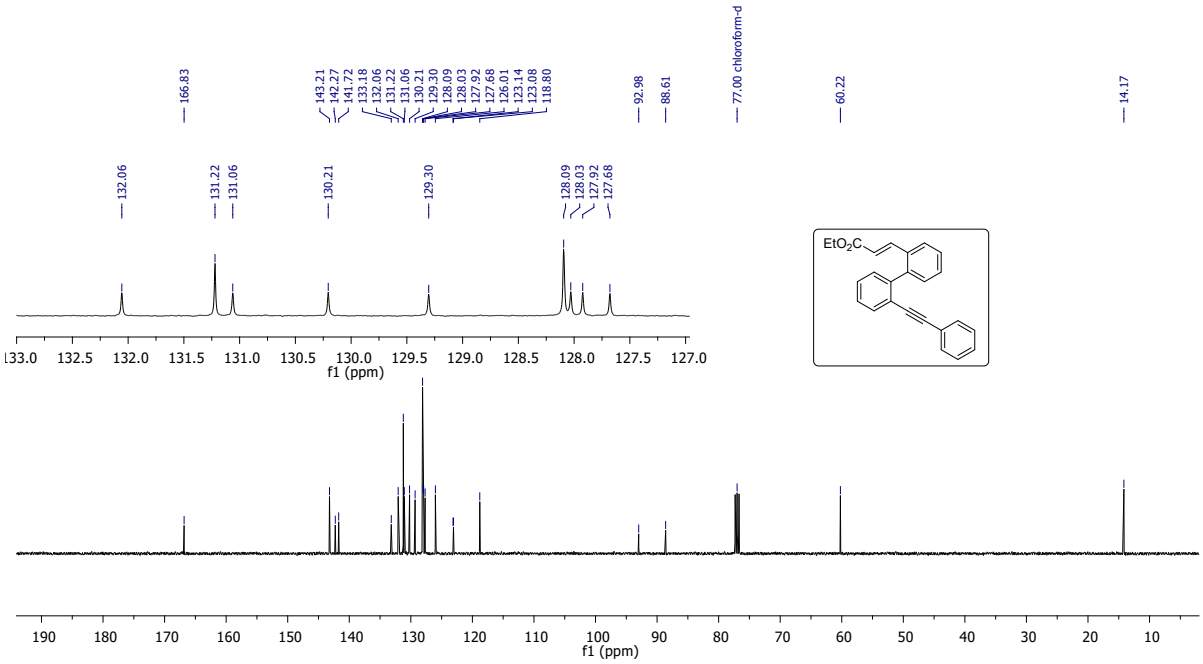
^{1}H NMR (400 MHz) spectrum of **11e** in $CDCl_3$



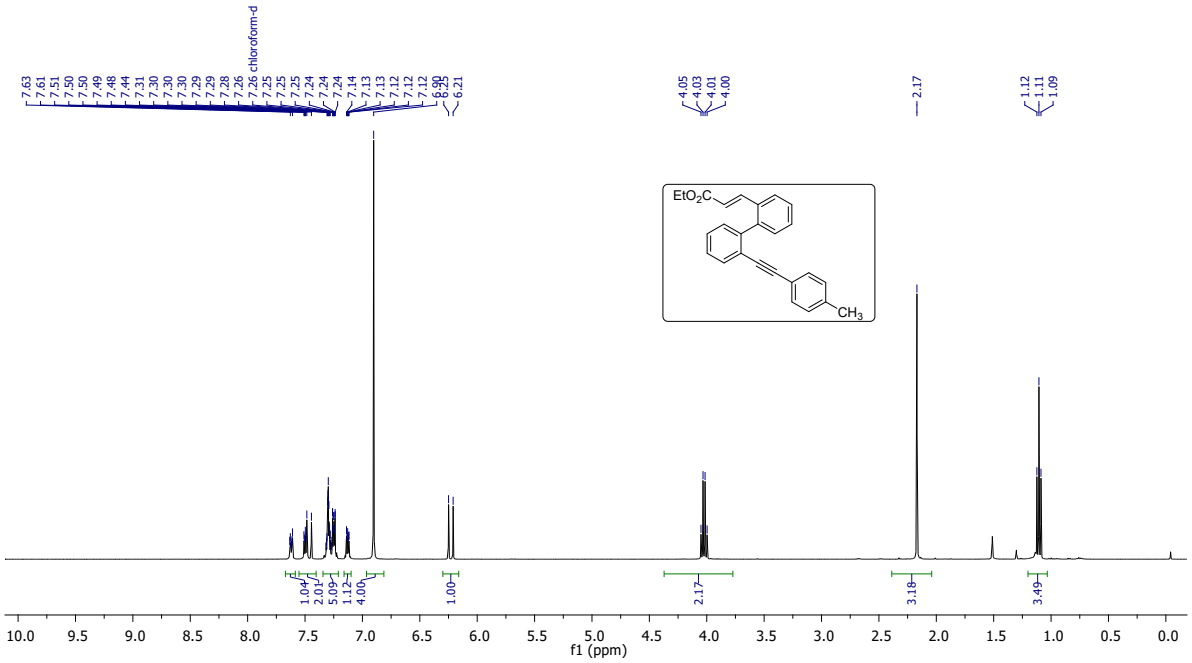
^{13}C{H} NMR (101 MHz) spectrum of **11e** in $CDCl_3$



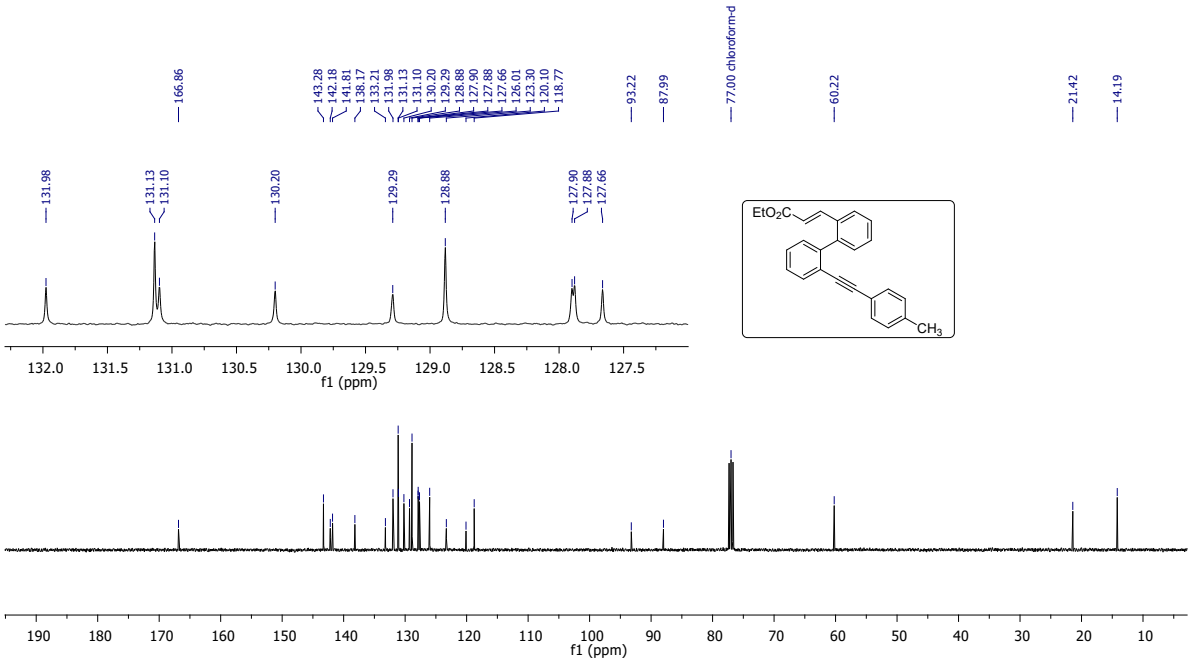
^{1}H NMR (400 MHz) spectrum of **1a** in $CDCl_3$



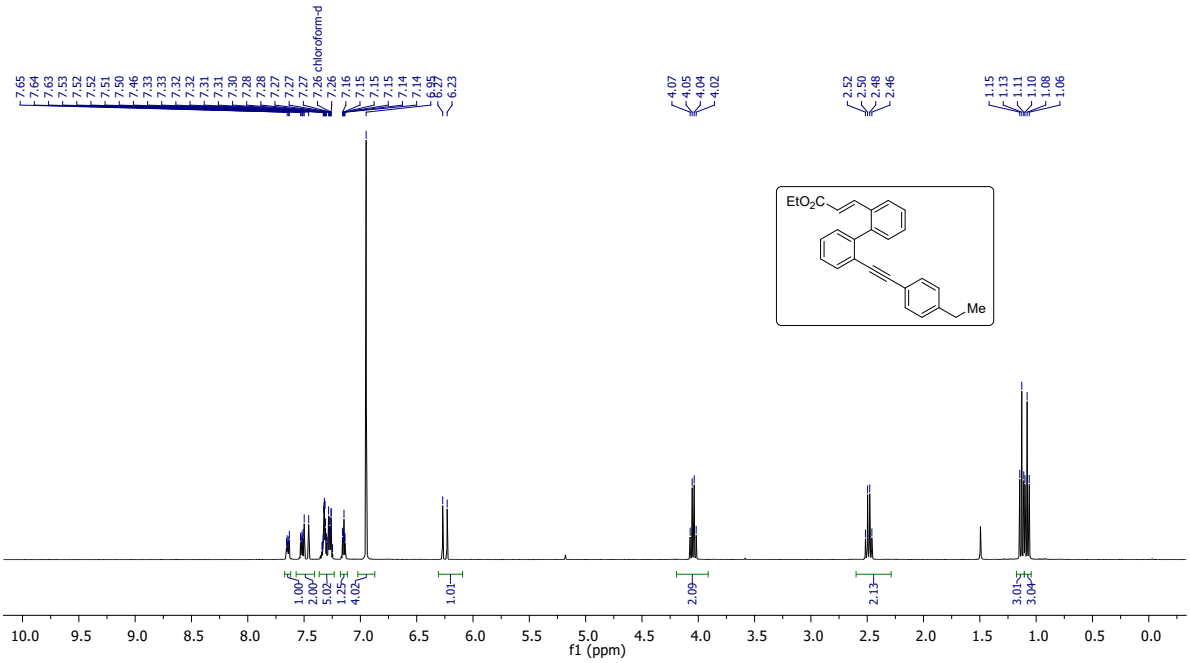
^{13}C{H} NMR (101 MHz) spectrum of **1a** in $CDCl_3$



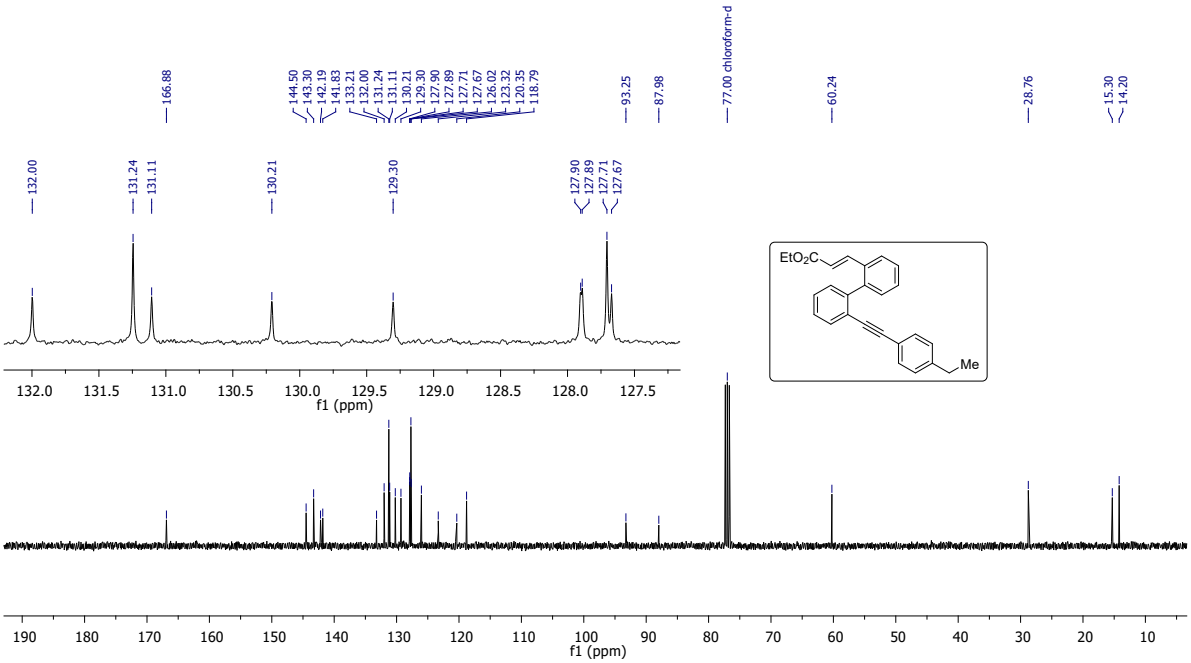
^{1}H NMR (400 MHz) spectrum of **1b** in $CDCl_3$



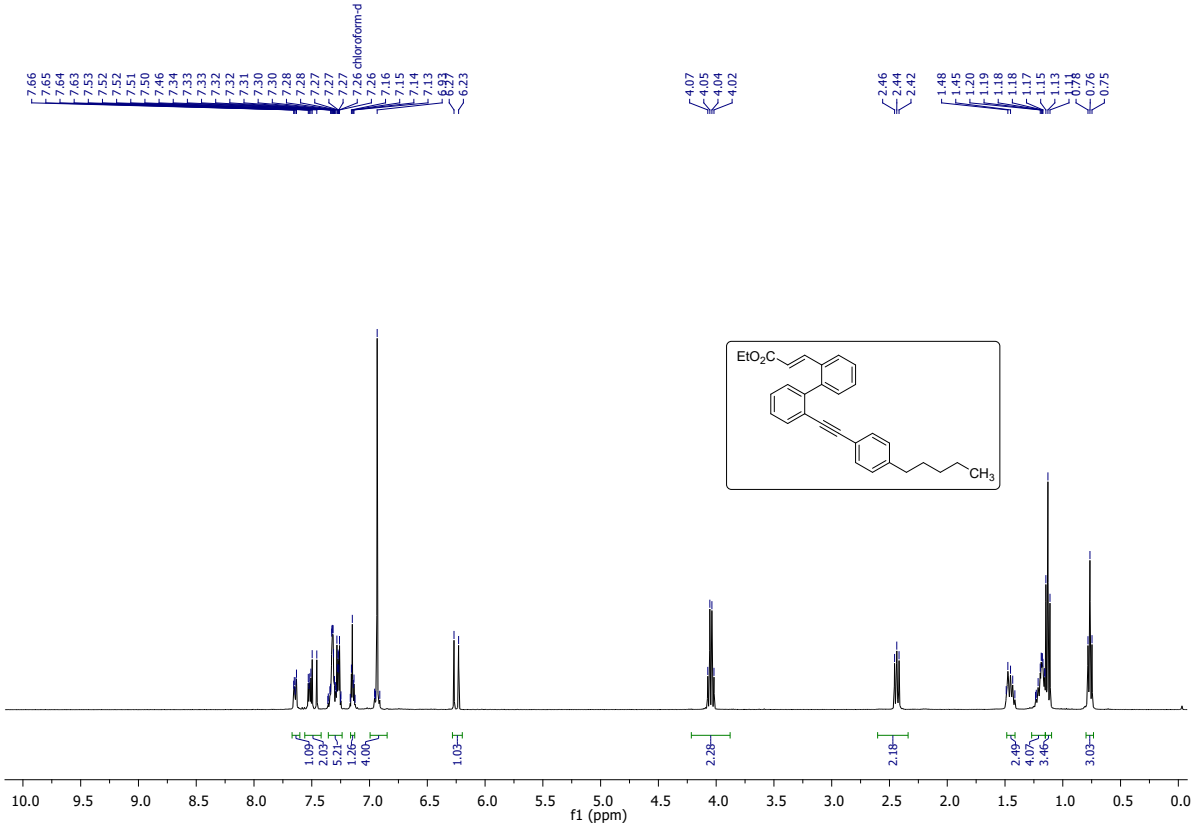
^{13}C{H} NMR (101 MHz) spectrum of **1b** in $CDCl_3$



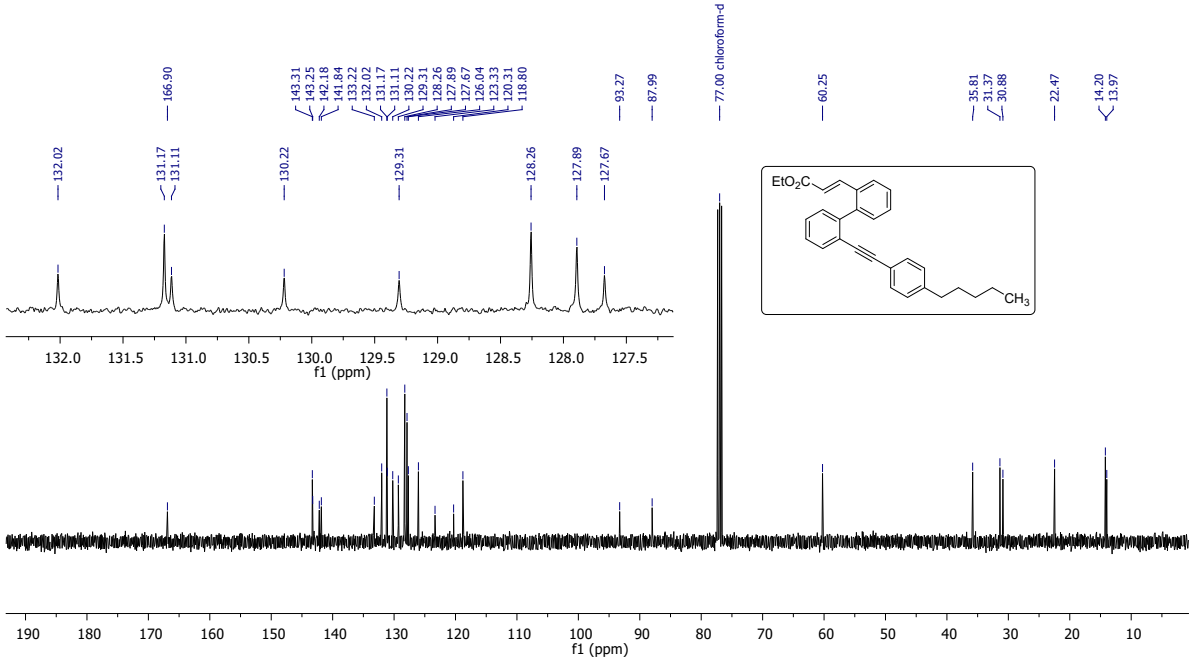
^{1}H NMR (400 MHz) spectrum of **1c** in $CDCl_3$



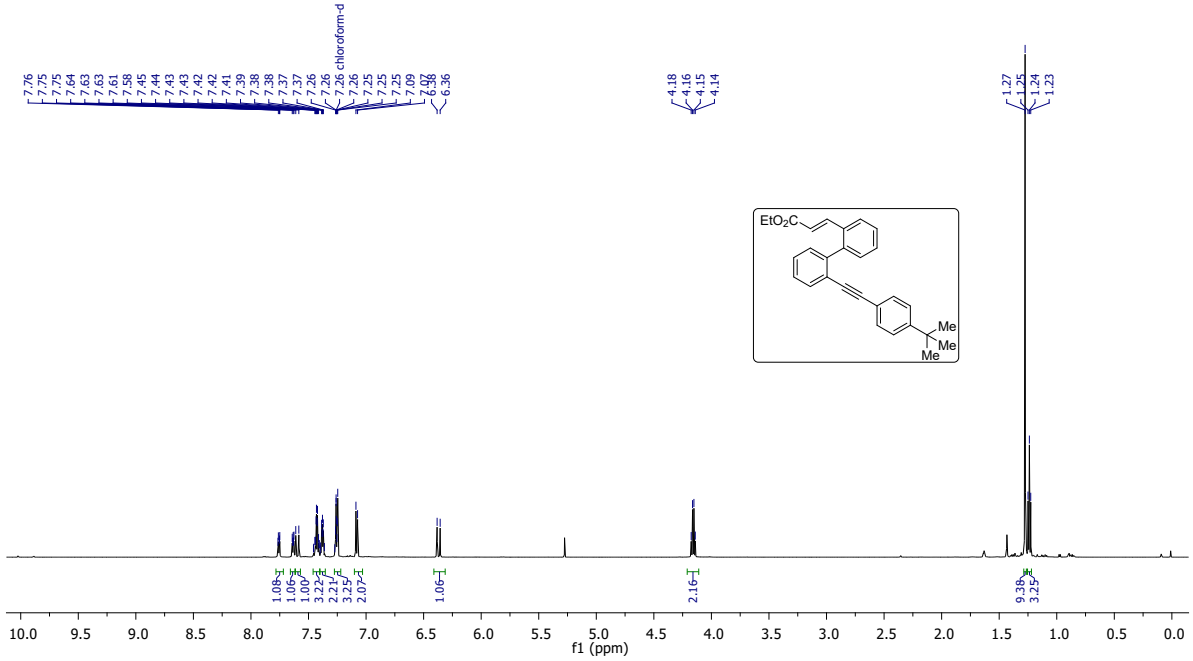
^{13}C{H} NMR (101 MHz) spectrum of **1c** in $CDCl_3$



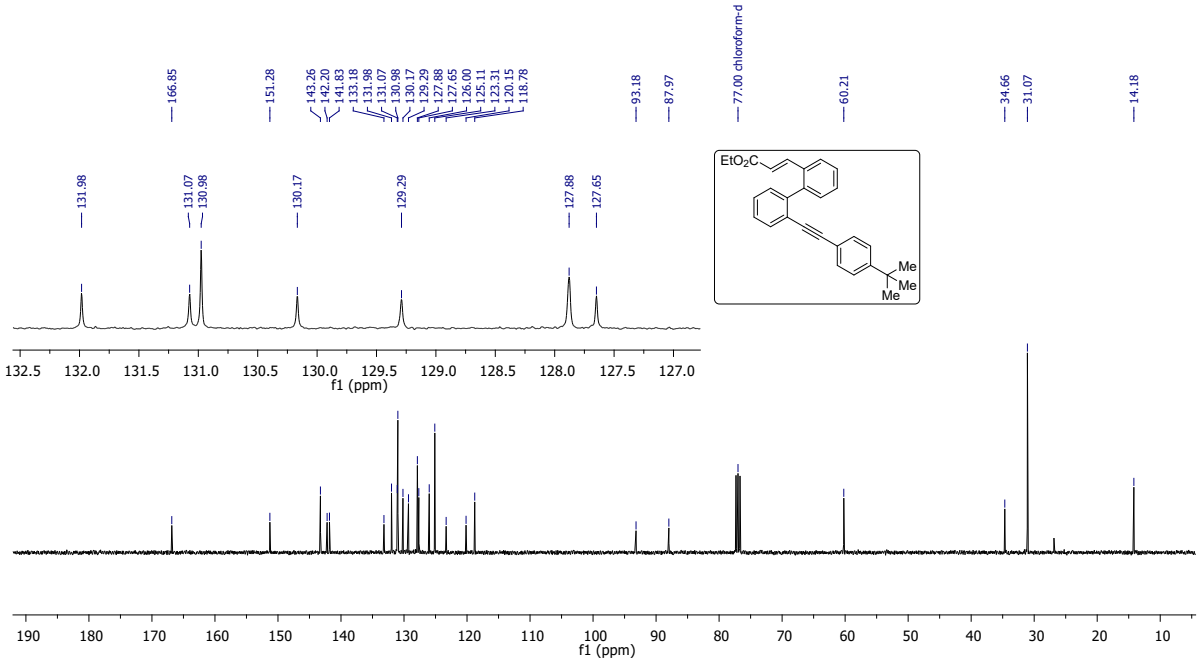
^{1}H NMR (400 MHz) spectrum of **1d** in $CDCl_3$



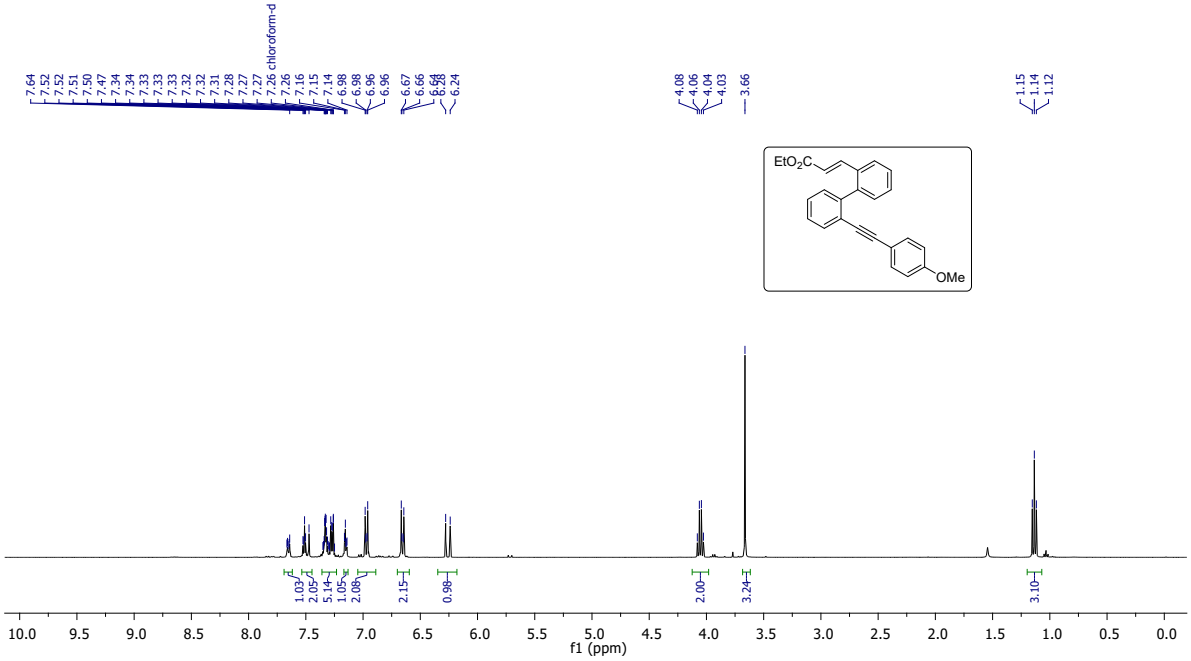
^{13}C{H} NMR (101 MHz) spectrum of **1d** in $CDCl_3$



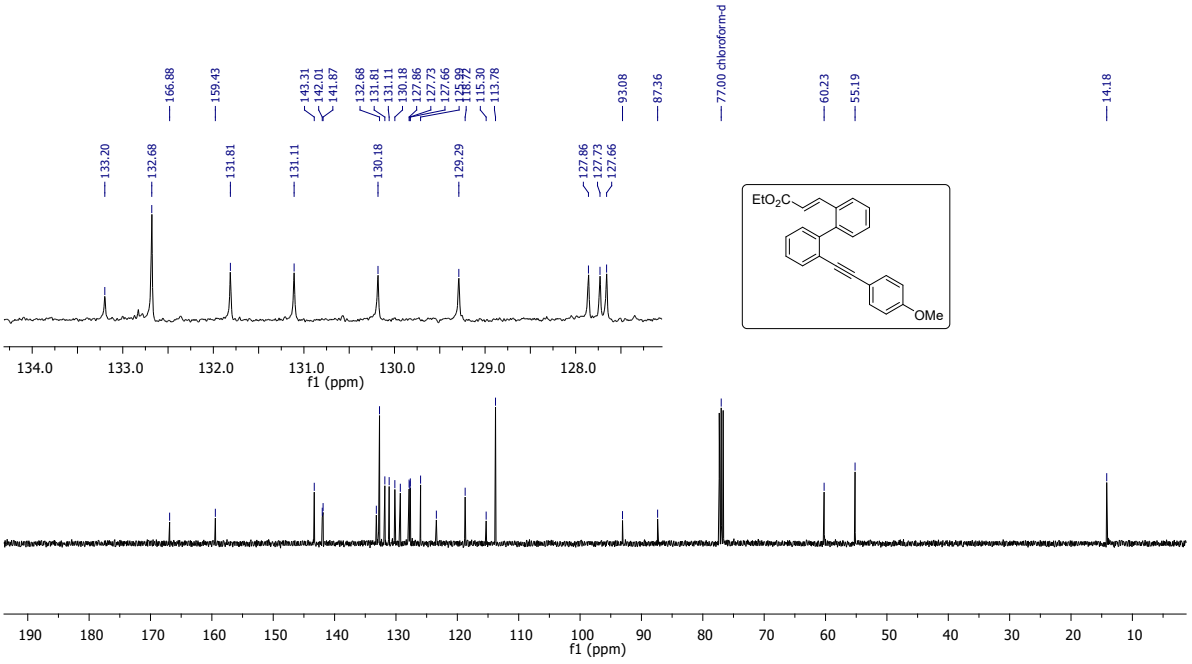
^{1}H NMR (600 MHz) spectrum of **1e** in $CDCl_3$



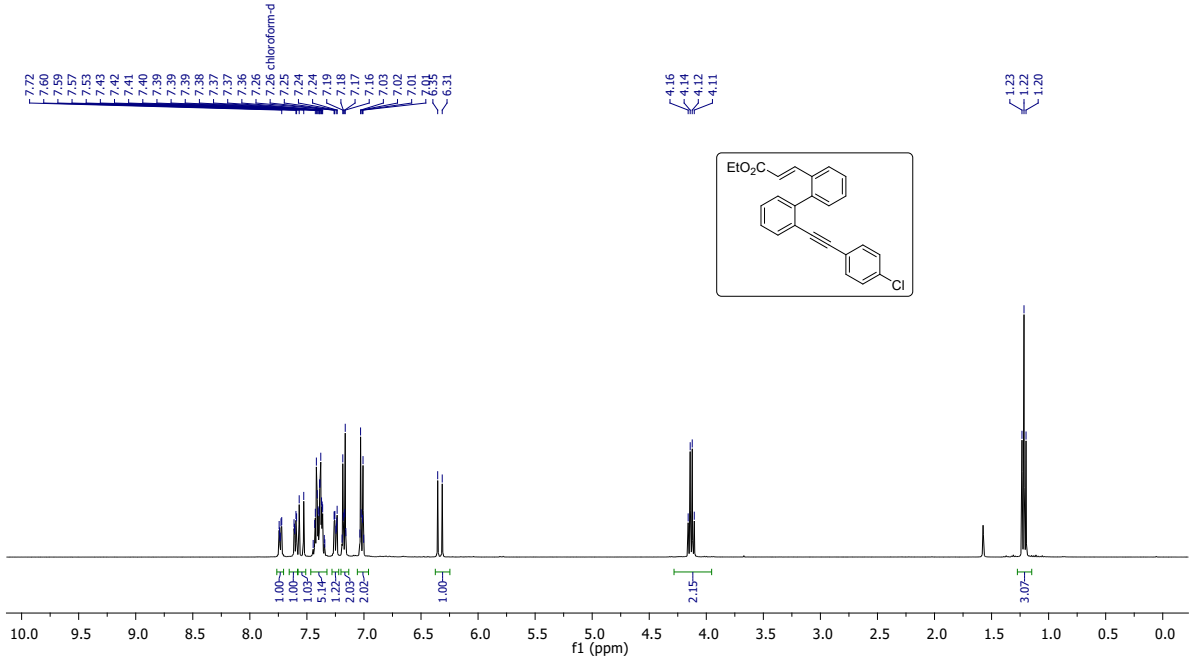
^{13}C{H} NMR (101 MHz) spectrum of **1e** in $CDCl_3$



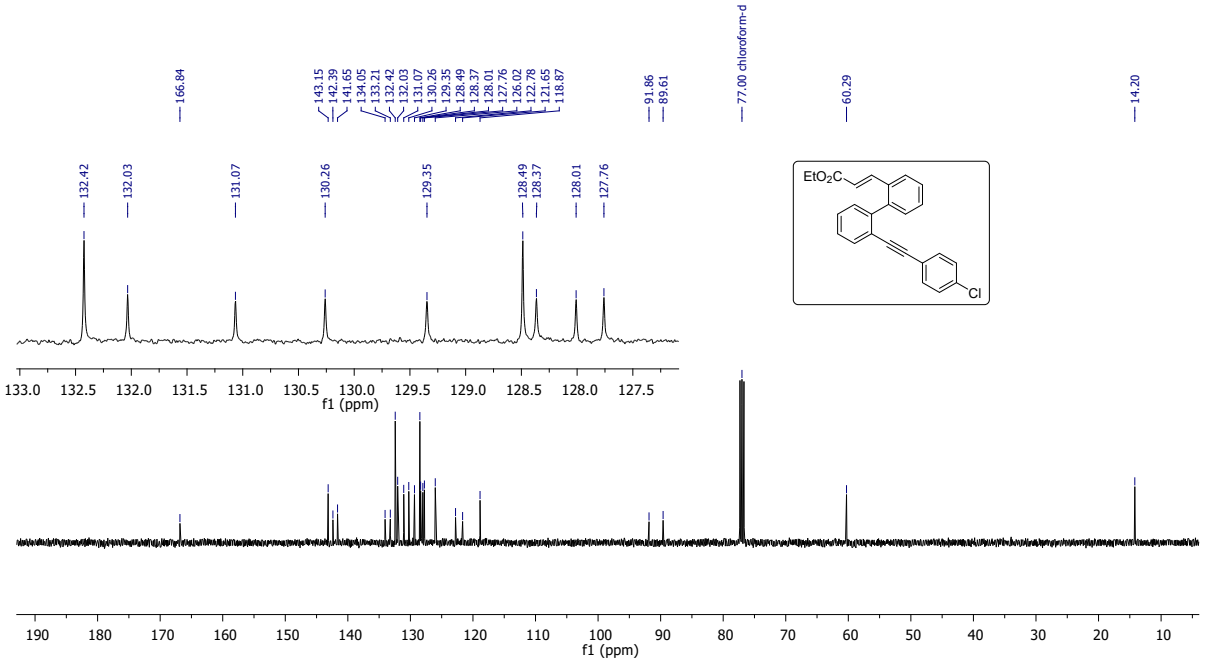
^{1}H NMR (400 MHz) spectrum of **1f** in $CDCl_3$



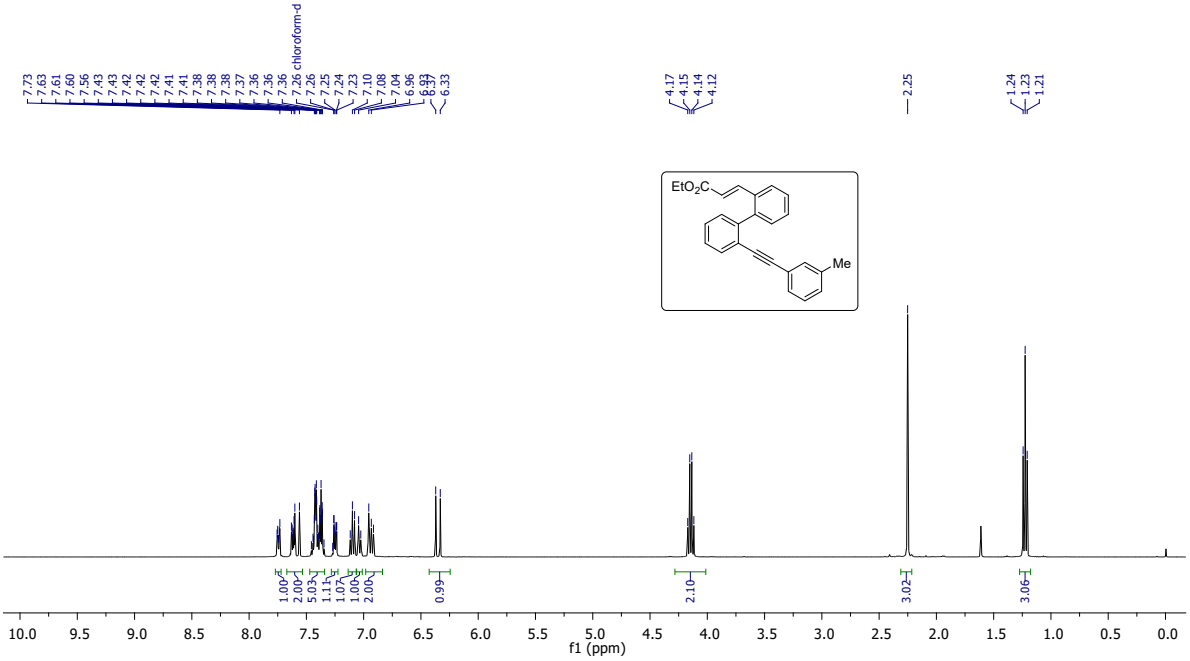
^{13}C{H} NMR (101 MHz) spectrum of **1f** in $CDCl_3$



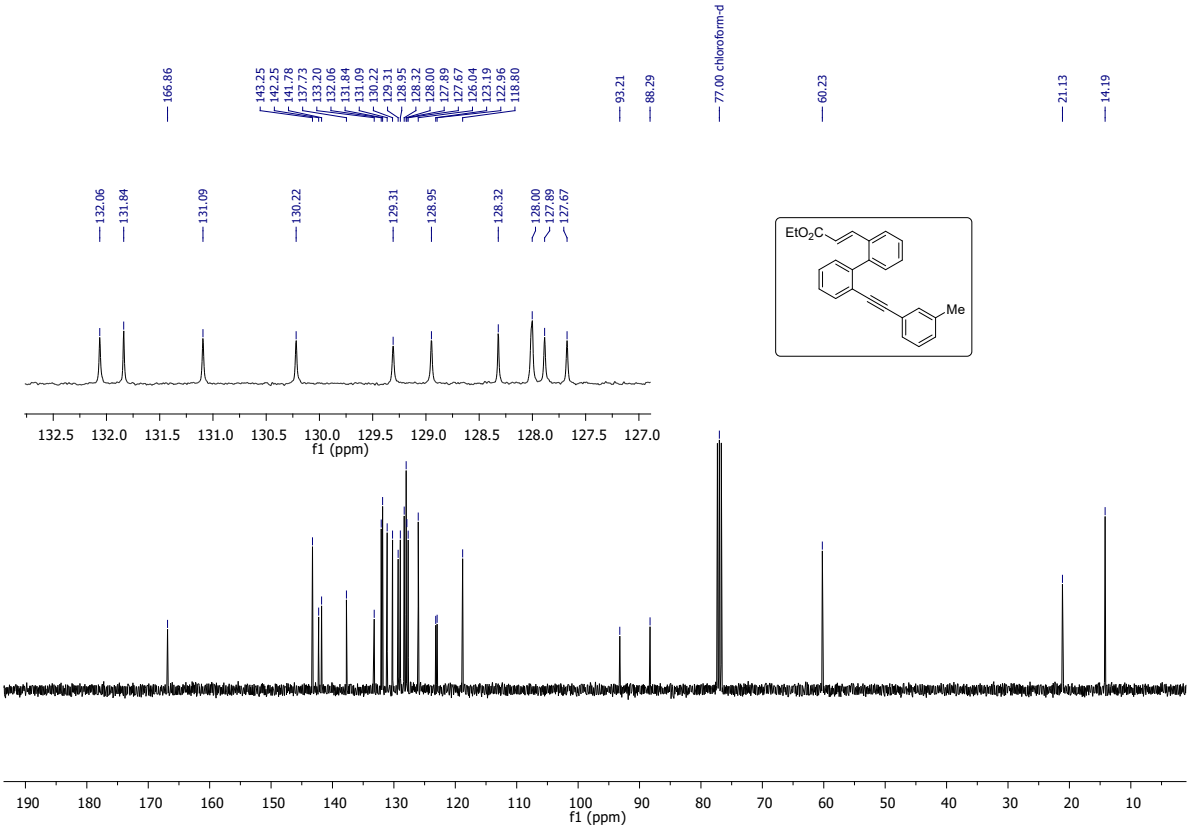
^{1}H NMR (400 MHz) spectrum of **1g** in $CDCl_3$



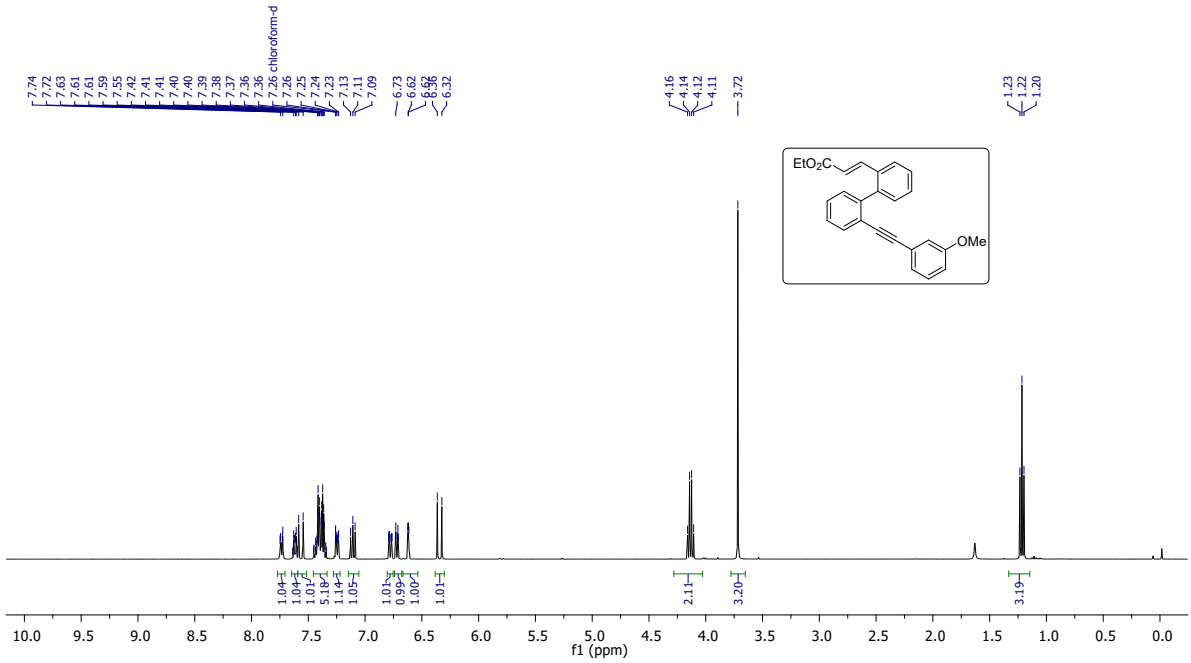
^{13}C{H} NMR (101 MHz) spectrum of **1g** in $CDCl_3$



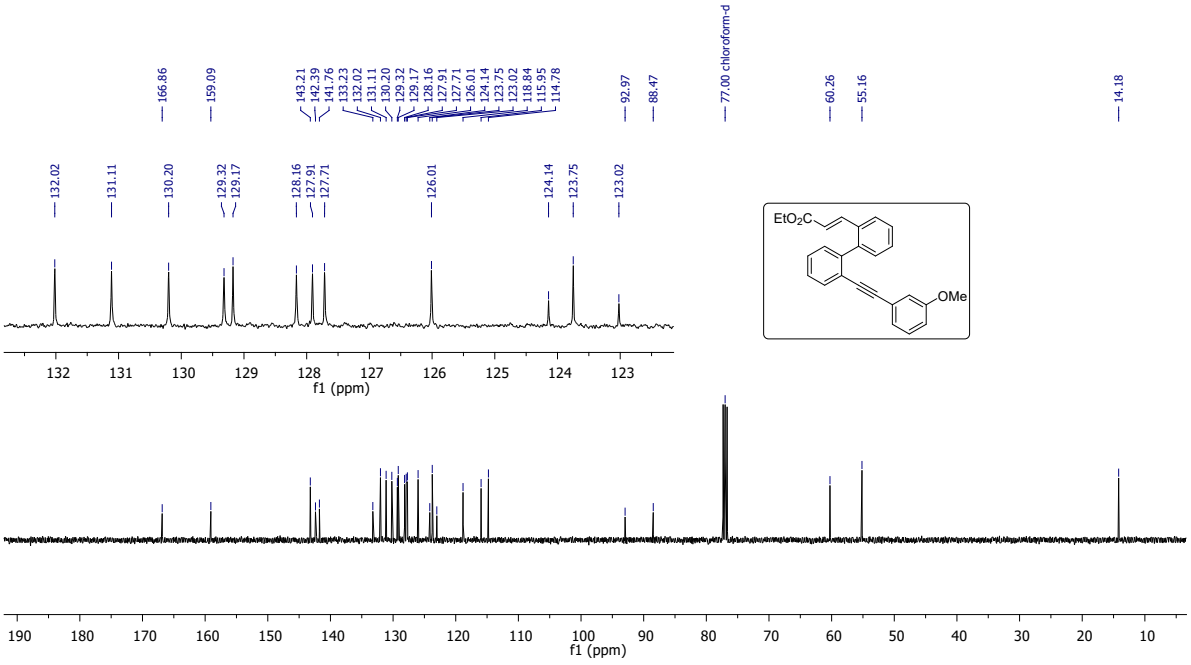
^{1}H NMR (400 MHz) spectrum of **1h** in $CDCl_3$



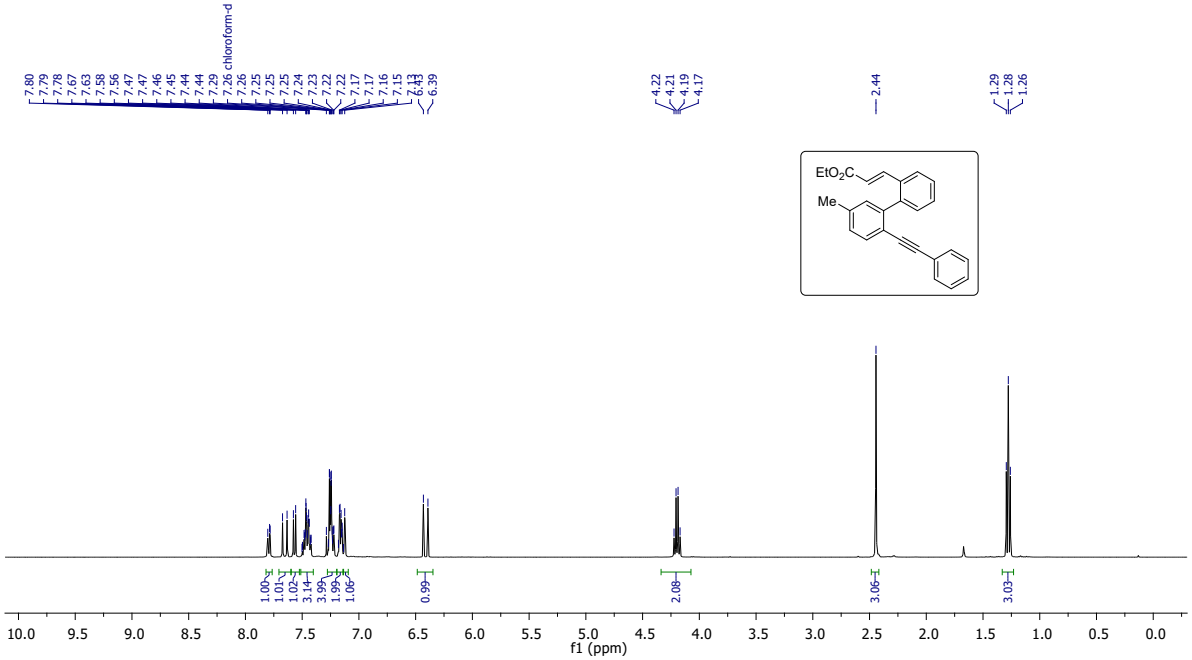
^{13}C{H} NMR (101 MHz) spectrum of **1h** in $CDCl_3$



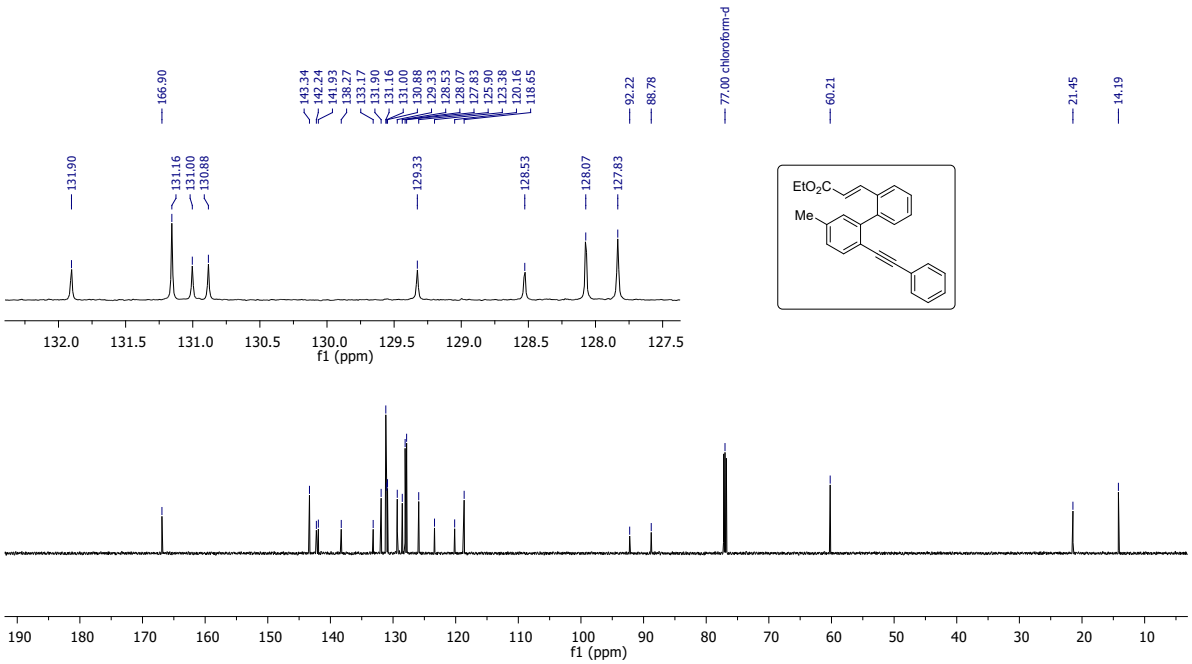
^{1}H NMR (400 MHz) spectrum of **1i** in $CDCl_3$



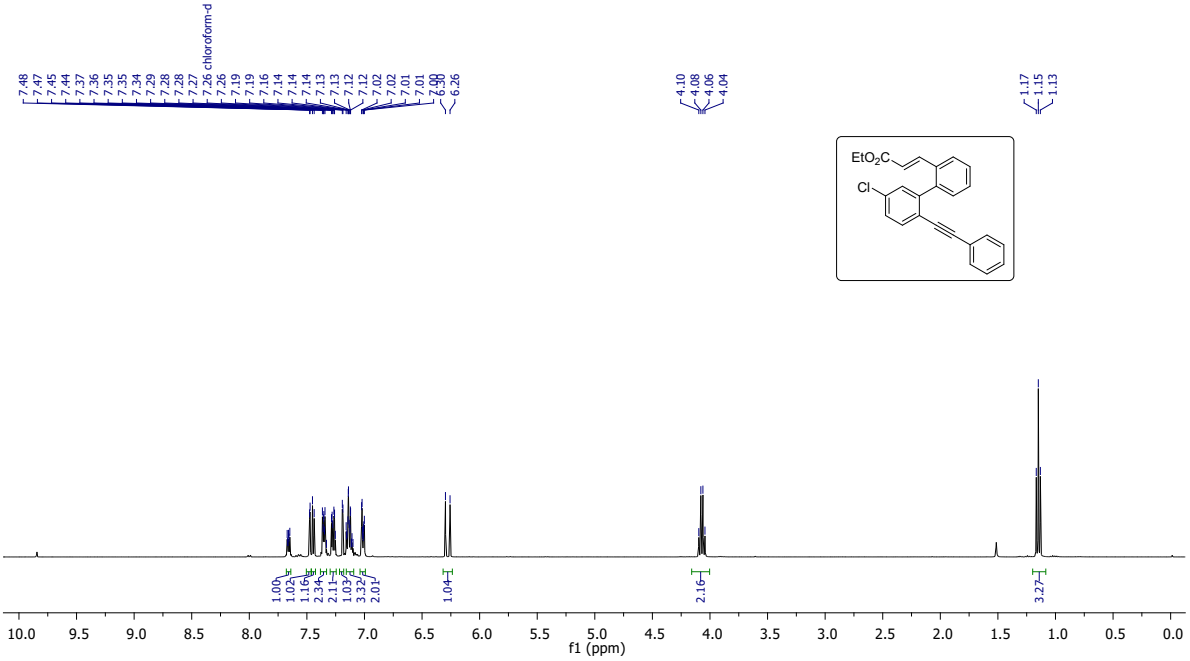
^{13}C{H} NMR (101 MHz) spectrum of **1i** in $CDCl_3$



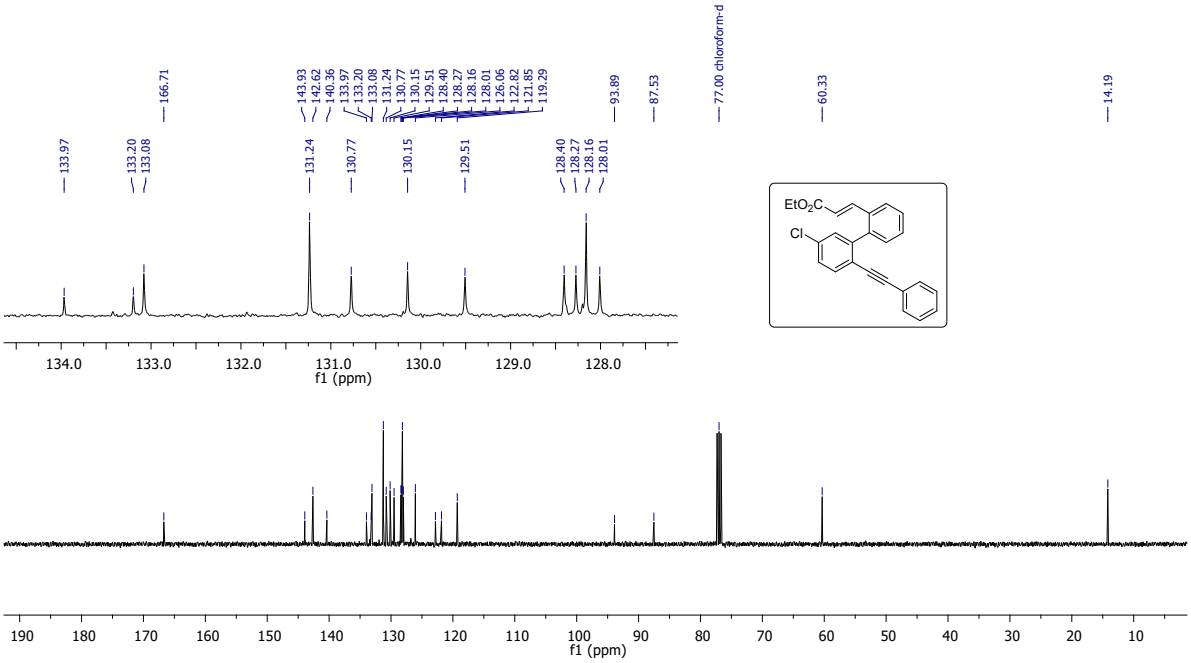
^{1}H NMR (400 MHz) spectrum of **1j** in $CDCl_3$



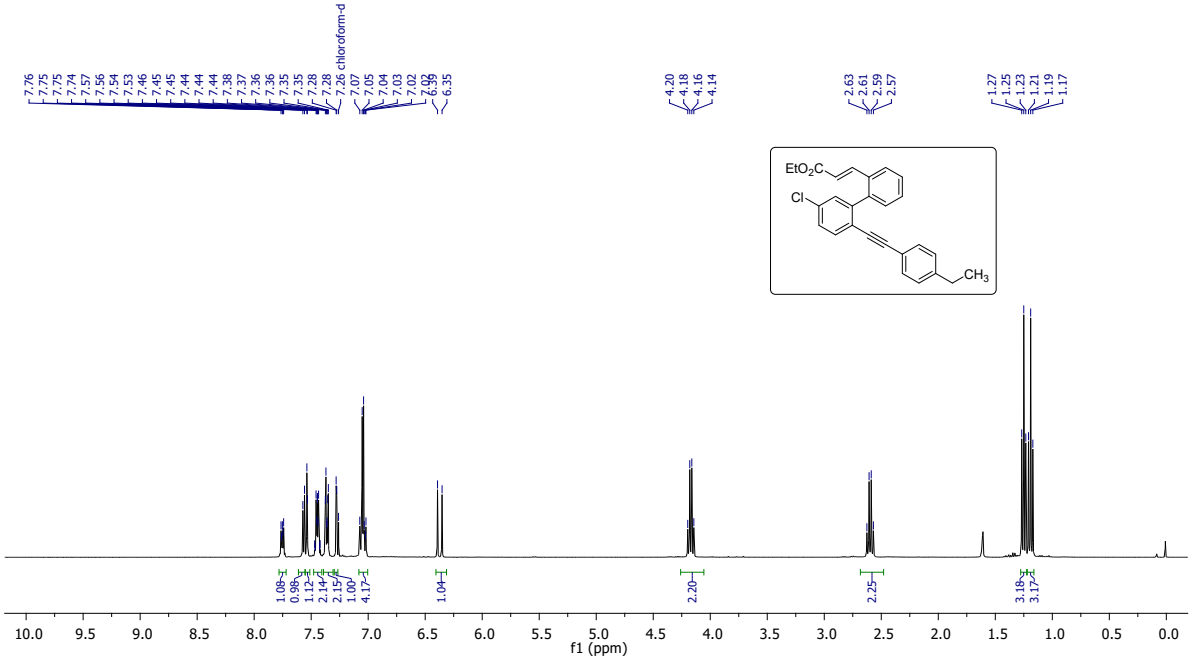
^{13}C{H} NMR (151 MHz) spectrum of **1j** in $CDCl_3$



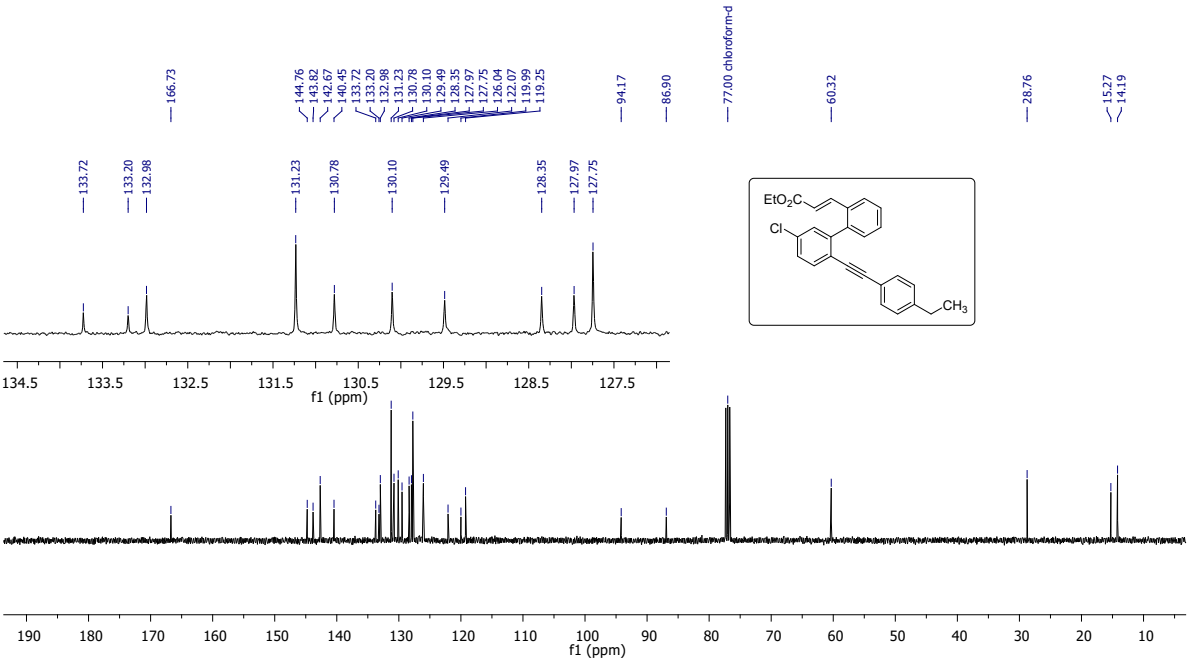
^{1}H NMR (400 MHz) spectrum of **1k** in $CDCl_3$



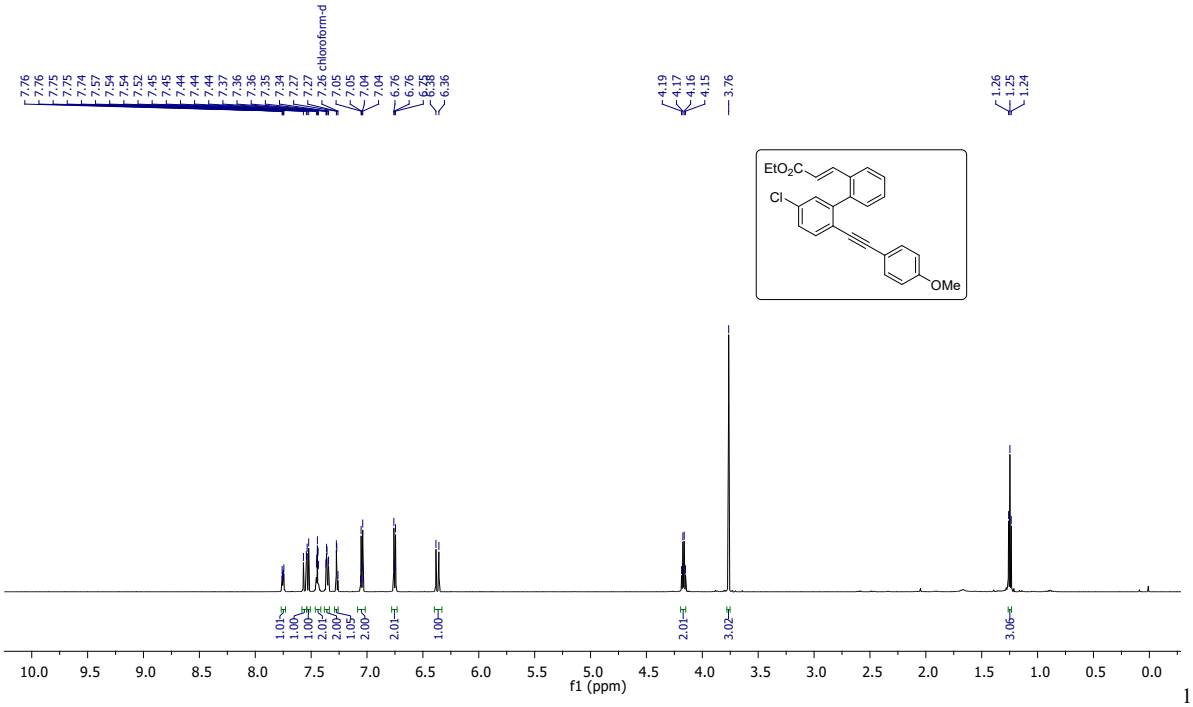
^{13}C{H} NMR (101 MHz) spectrum of **1k** in $CDCl_3$



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



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



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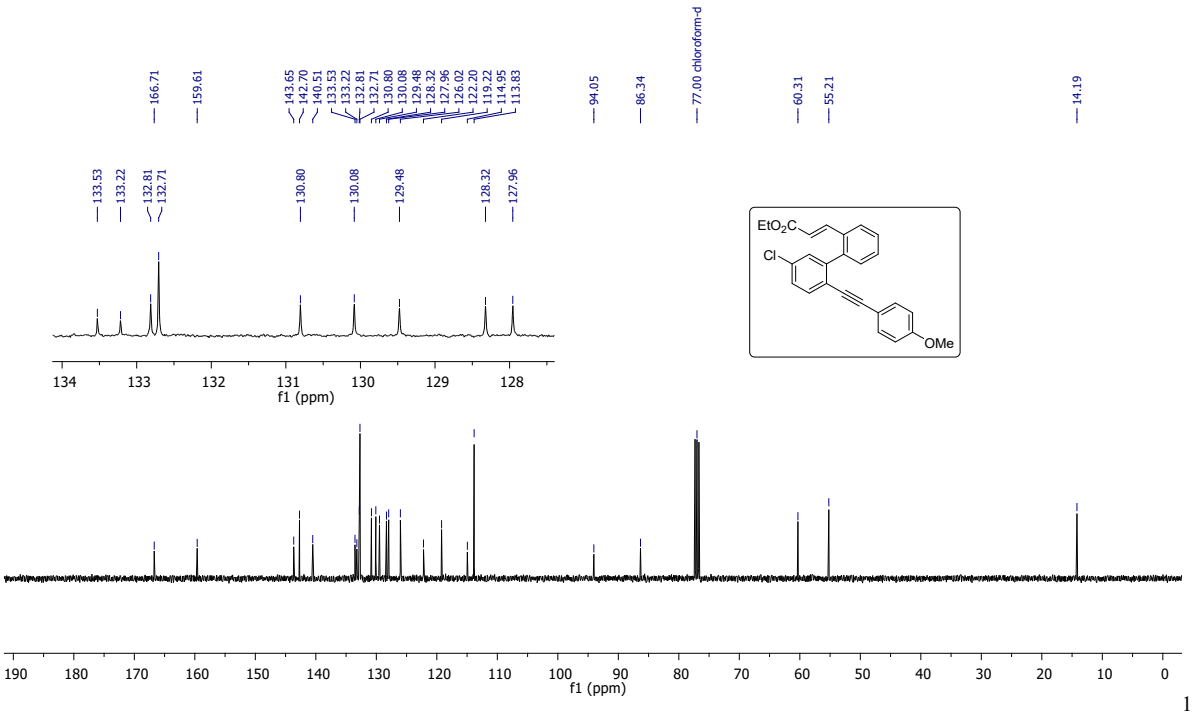
H NMR (400 MHz) spectrum of **1m** in $CDCl_3$



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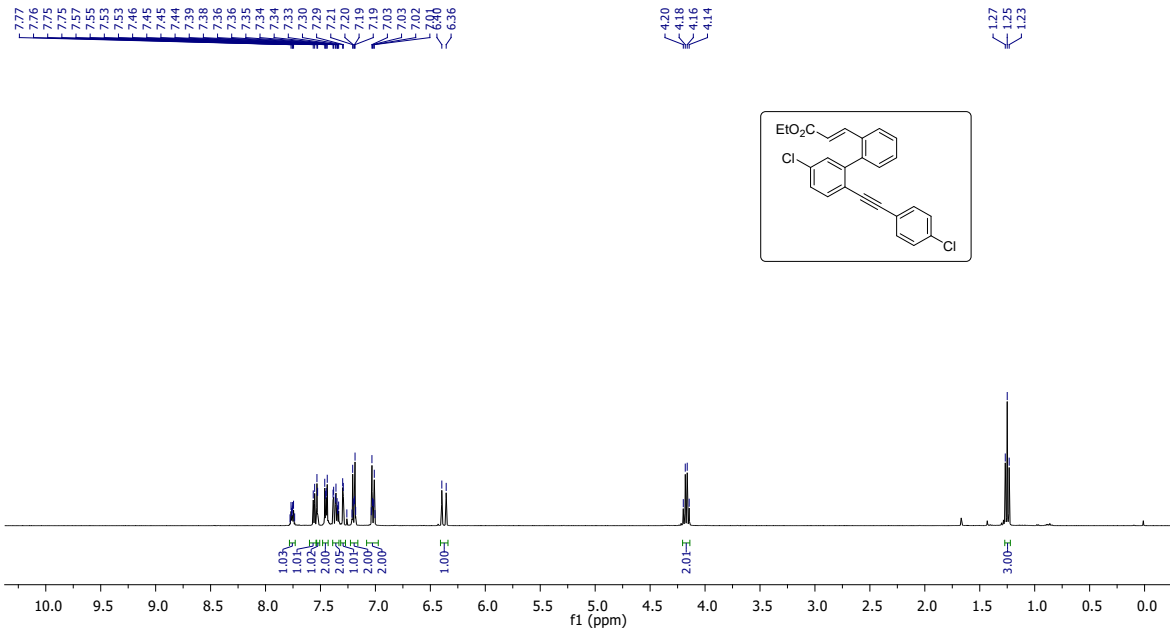
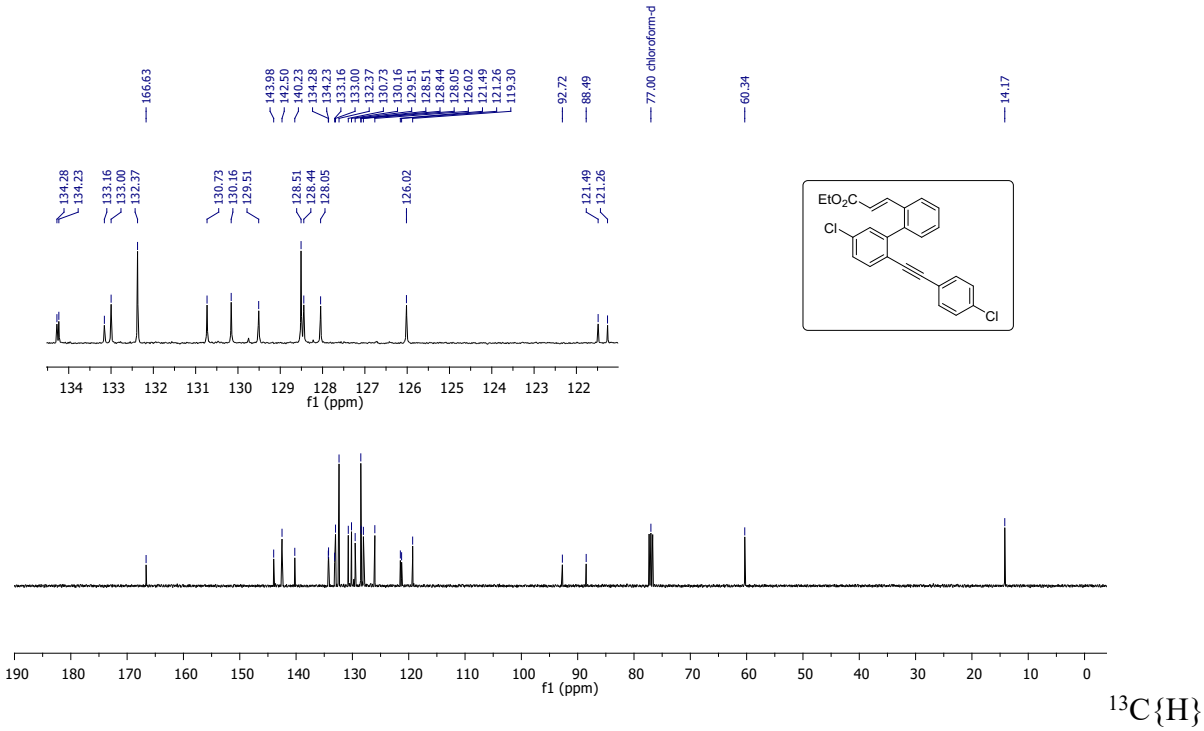
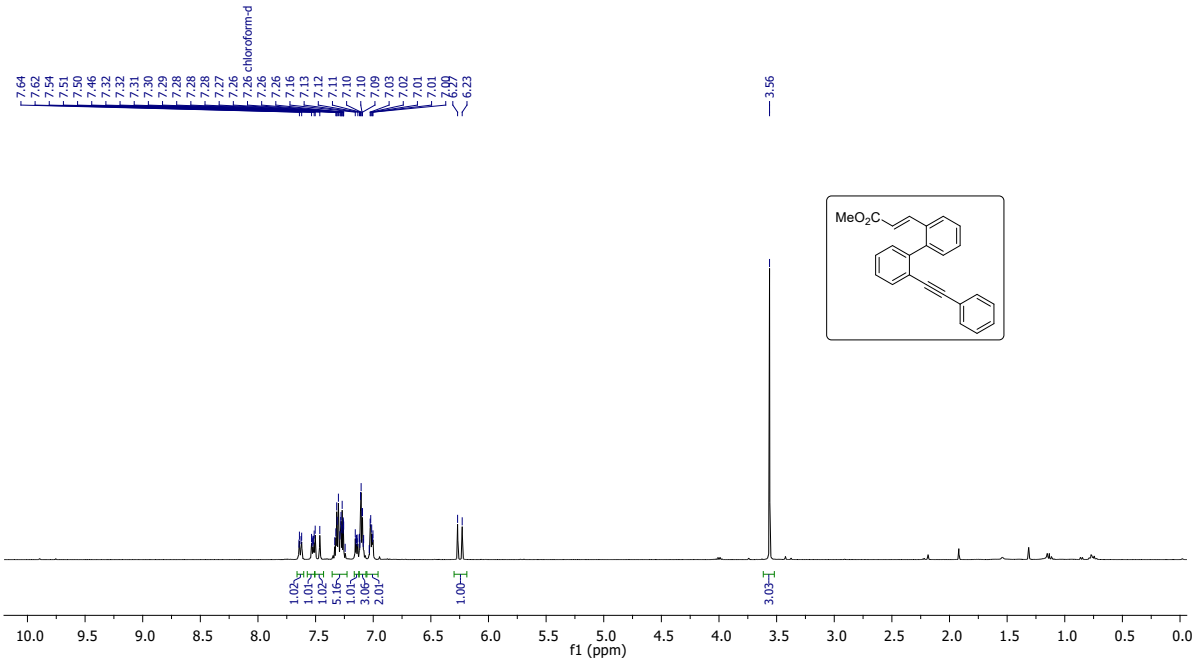
$^{3}C\{H\}$ NMR (101 MHz) spectrum of **1m** in $CDCl_3$



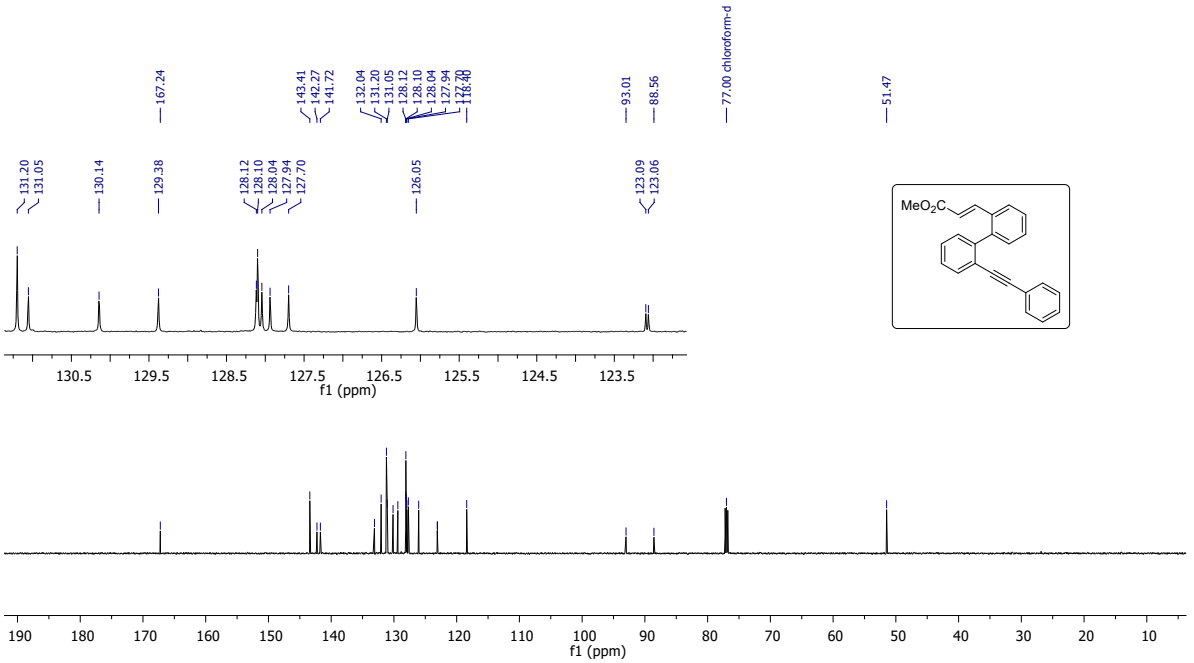
^{1}H NMR (400 MHz) spectrum of **1n** in $CDCl_3$



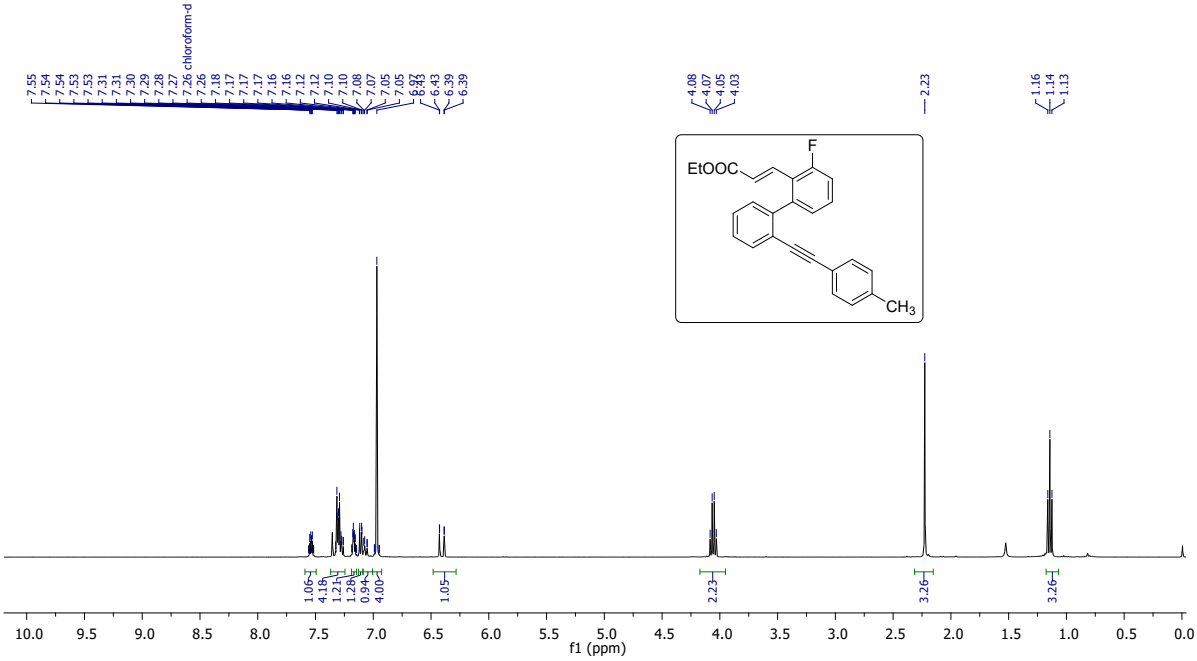
^{13}C{H} NMR (101 MHz) spectrum of **1n** in $CDCl_3$



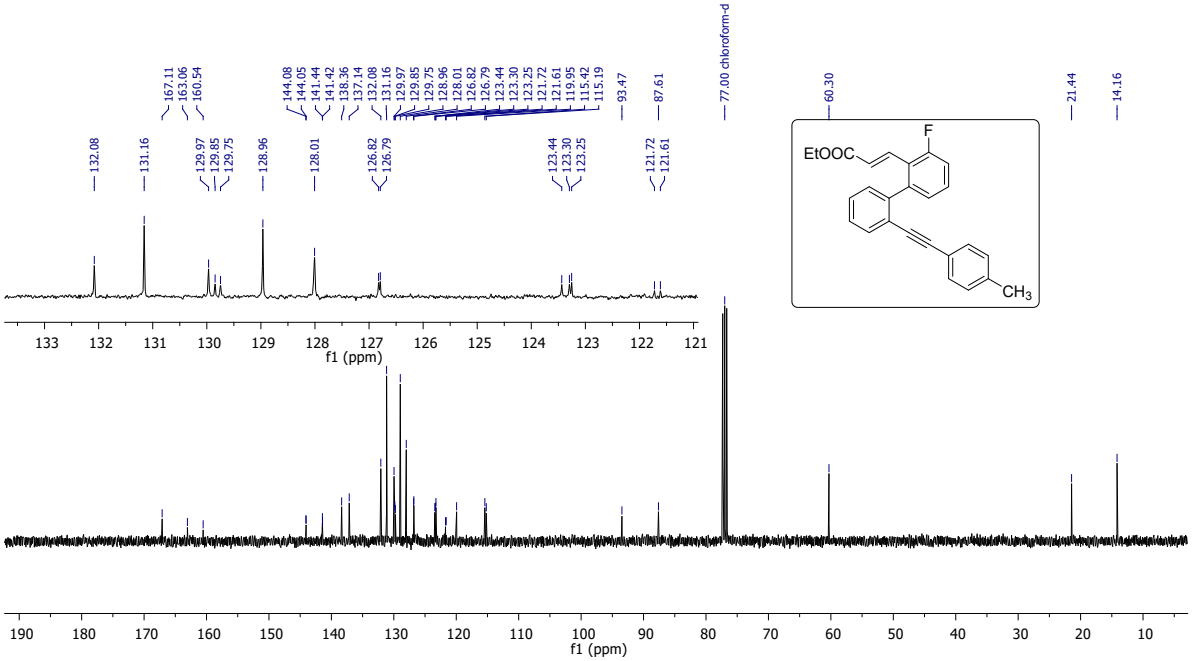
^{1}H NMR (400 MHz) spectrum of **1o** in $CDCl_3$



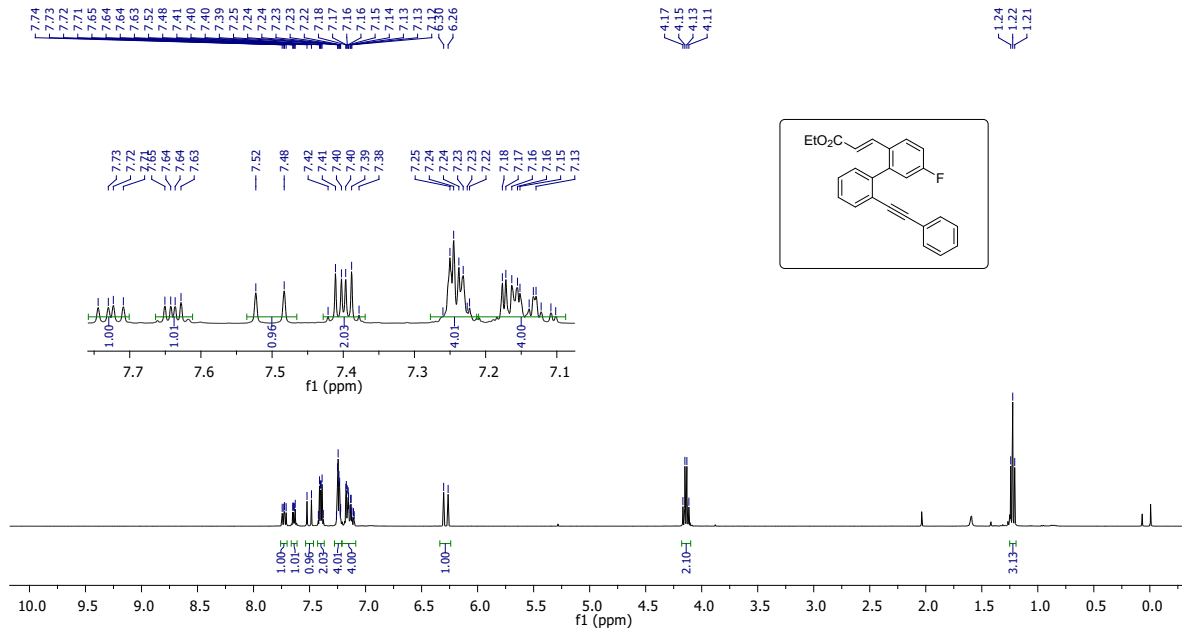
^{13}C{H} NMR (151 MHz) spectrum of **1o** in $CDCl_3$



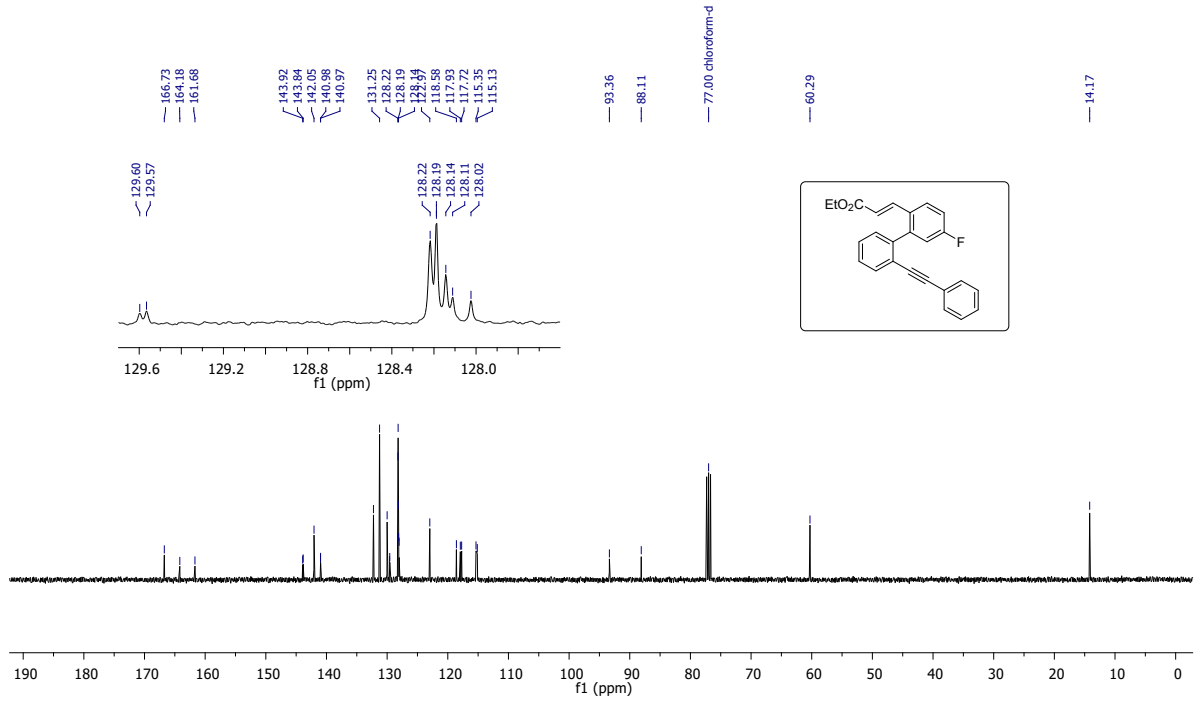
^{1}H NMR (400 MHz) spectrum of **1p** in $CDCl_3$



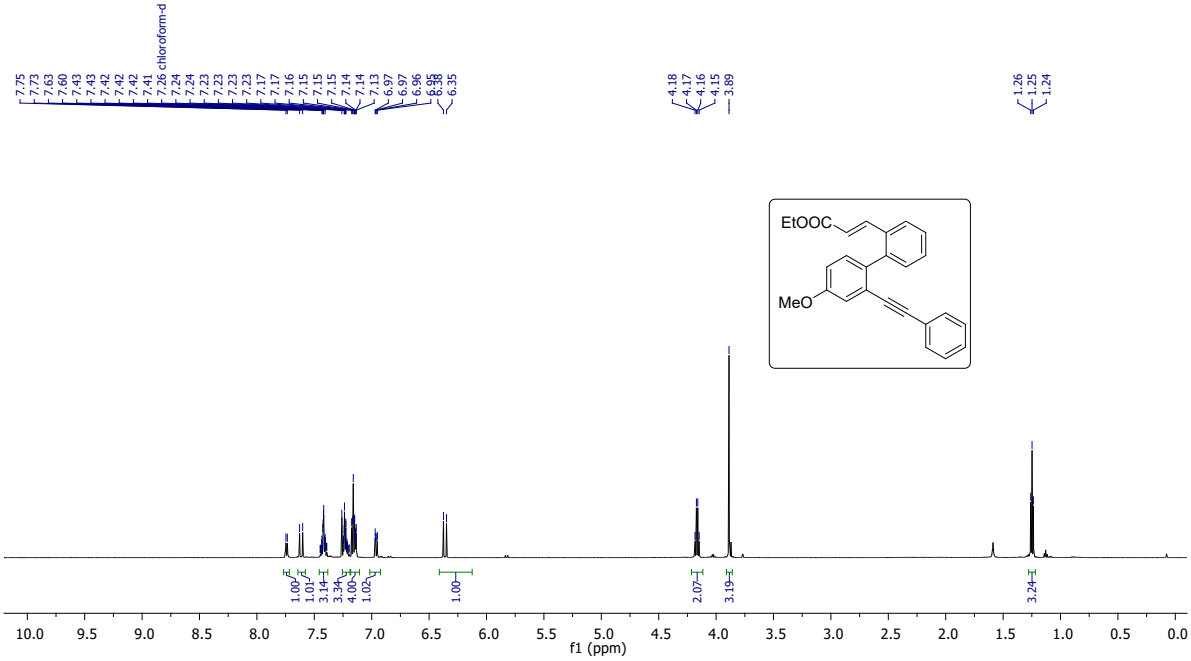
^{13}C{H} NMR (101 MHz) spectrum of **1p** in $CDCl_3$



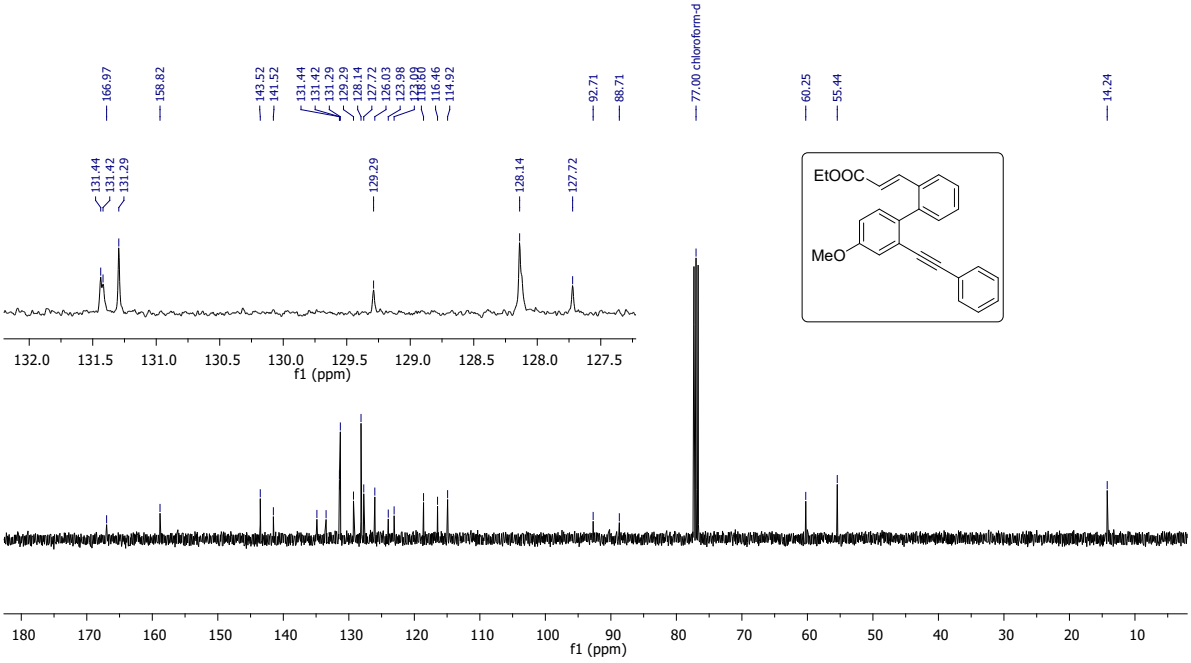
^{1}H NMR (400 MHz) spectrum of **1q** in $CDCl_3$



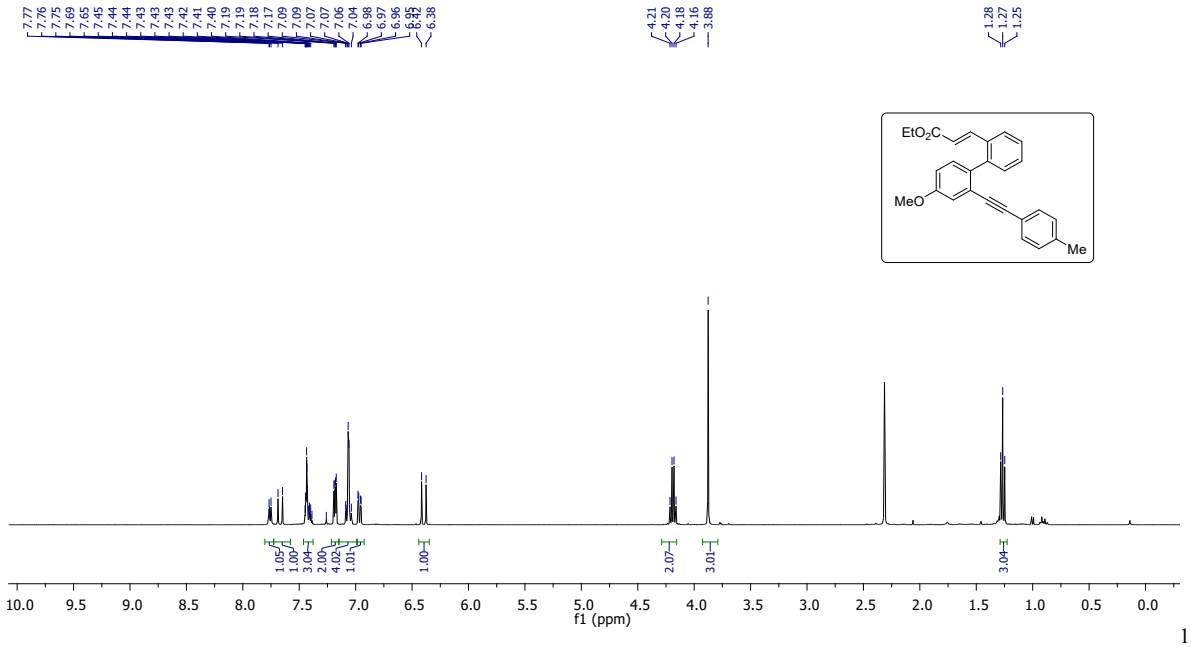
^{13}C{H} NMR (101 MHz) spectrum of **1q** in $CDCl_3$



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



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



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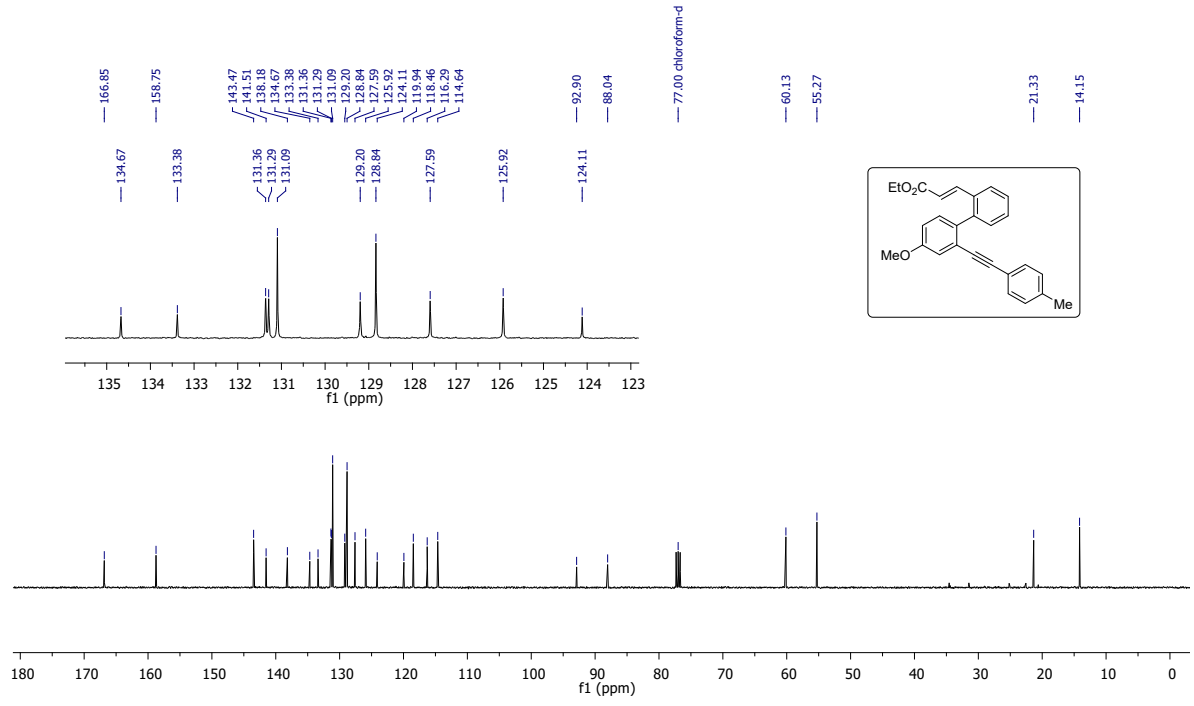
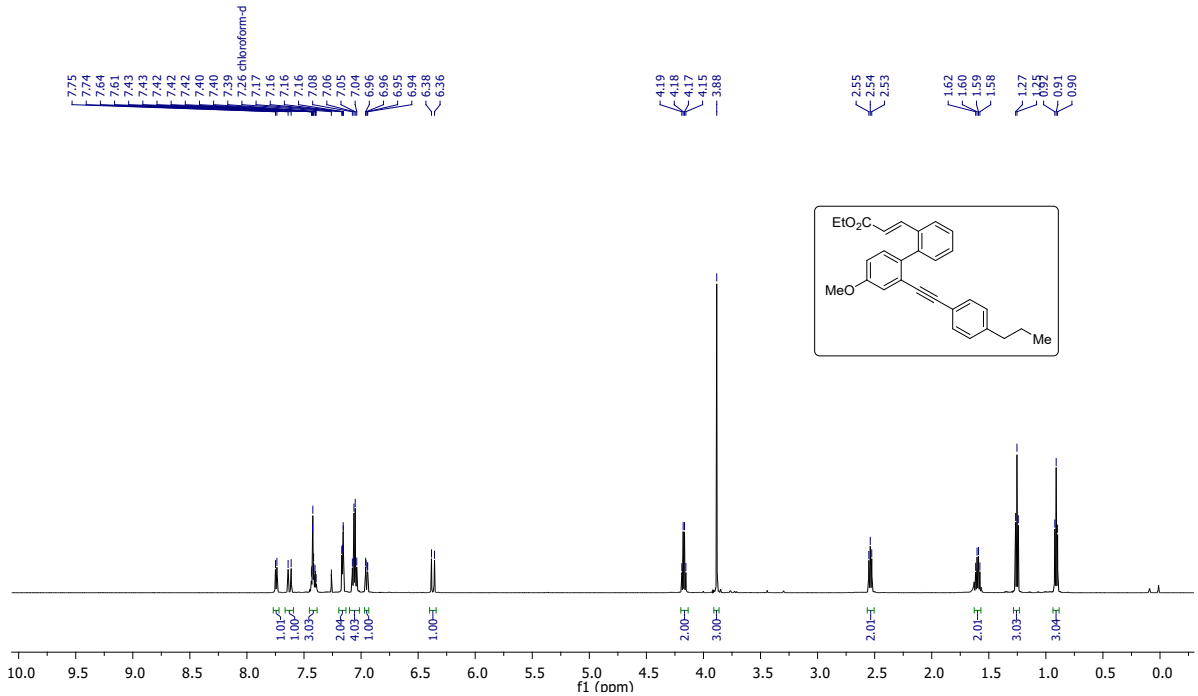
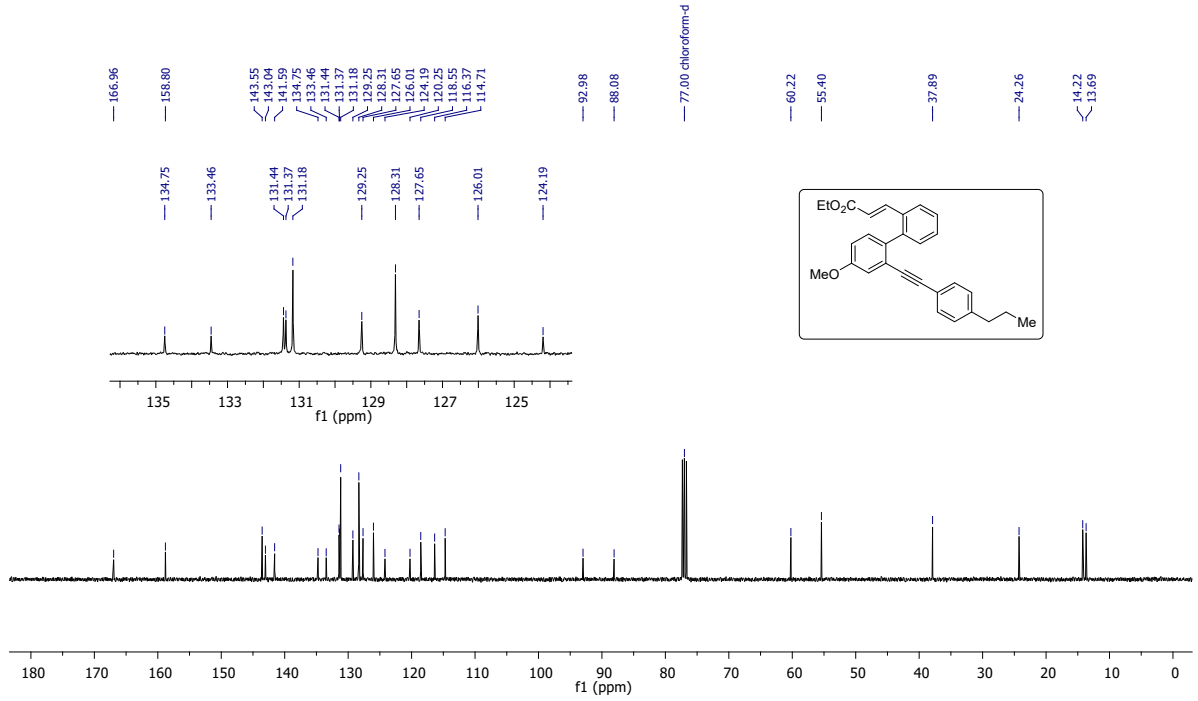
H NMR (400 MHz) spectrum of **1s** in $CDCl_3$



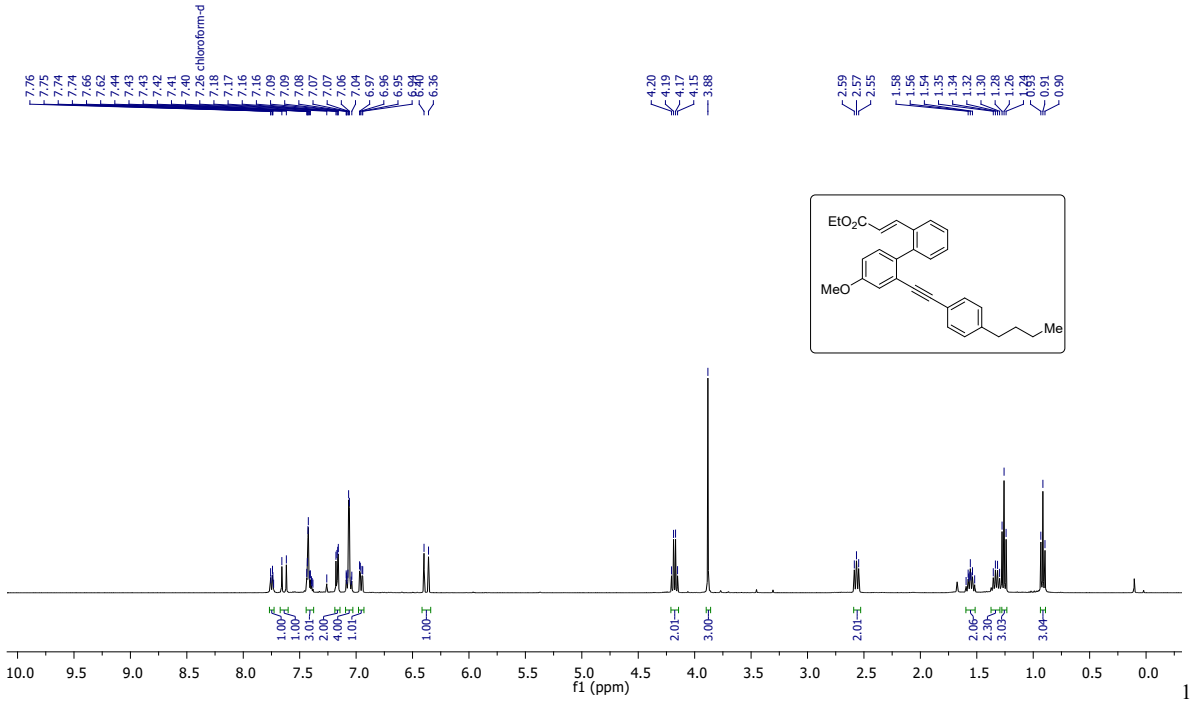
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **1s** in $CDCl_3$



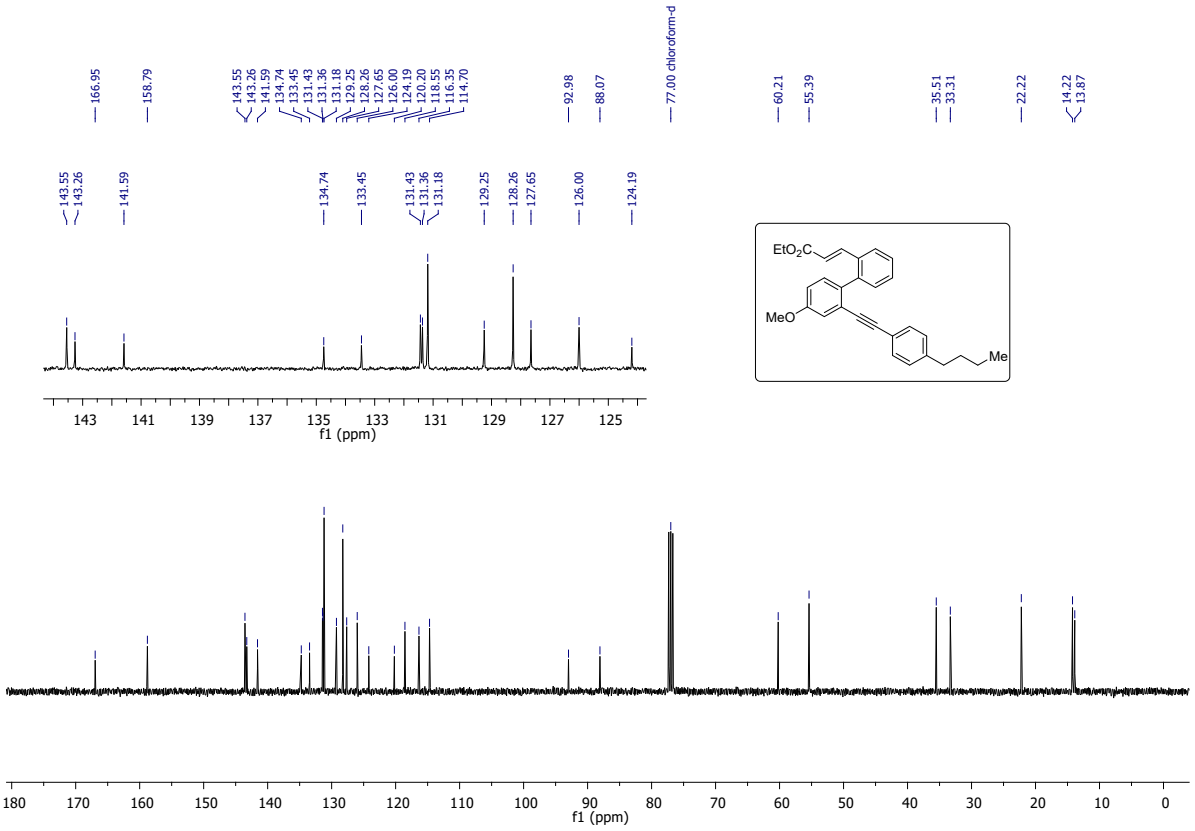
^{1}H NMR (600 MHz) spectrum of **1t** in $CDCl_3$



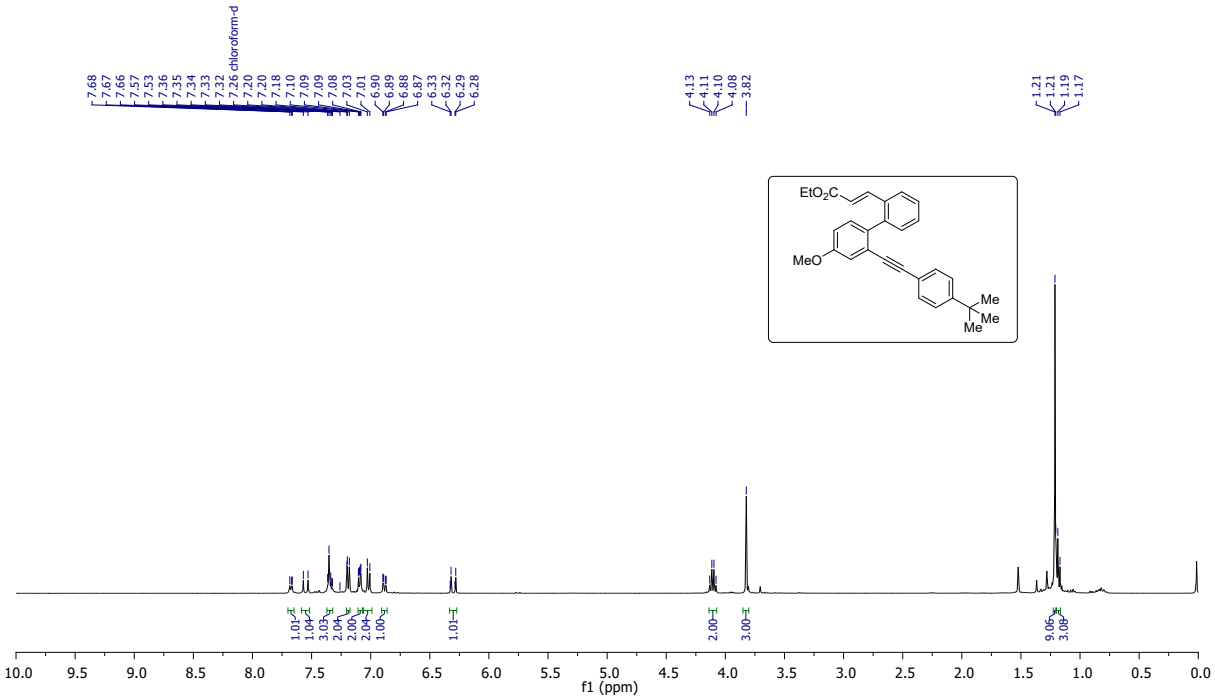
^{13}C{H} NMR (101 MHz) spectrum of **1t** in $CDCl_3$



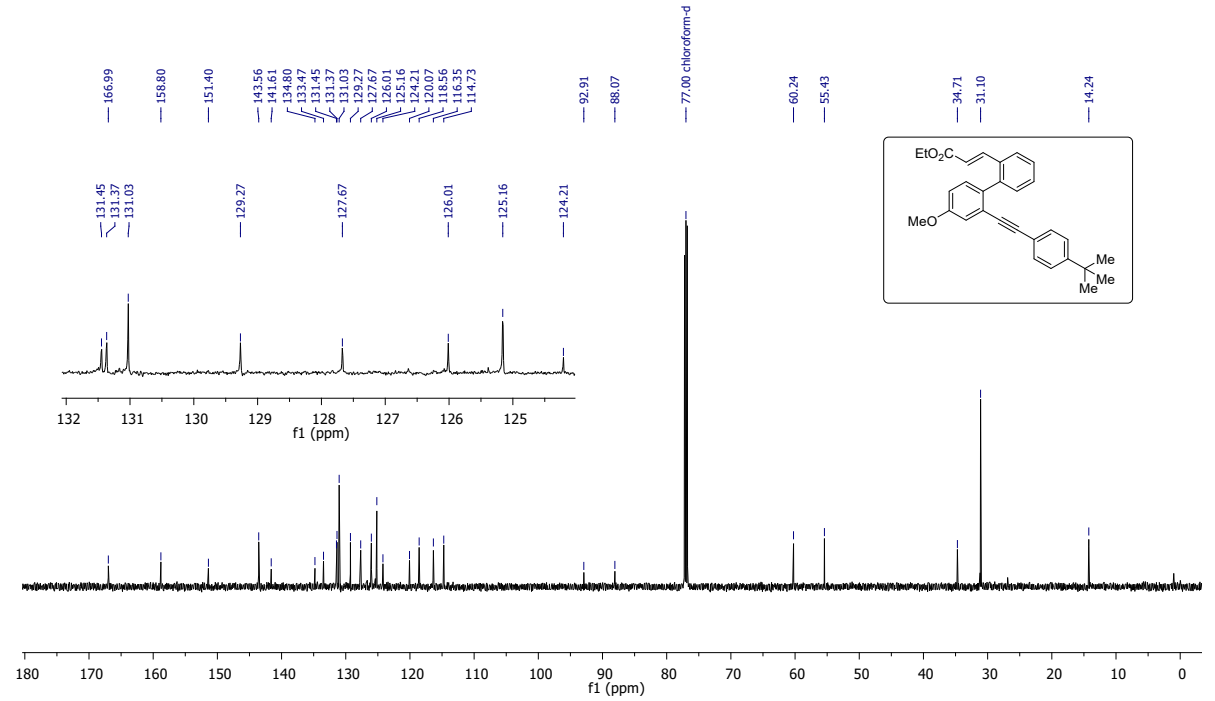
H NMR (400 MHz) spectrum of **1u** in $CDCl_3$



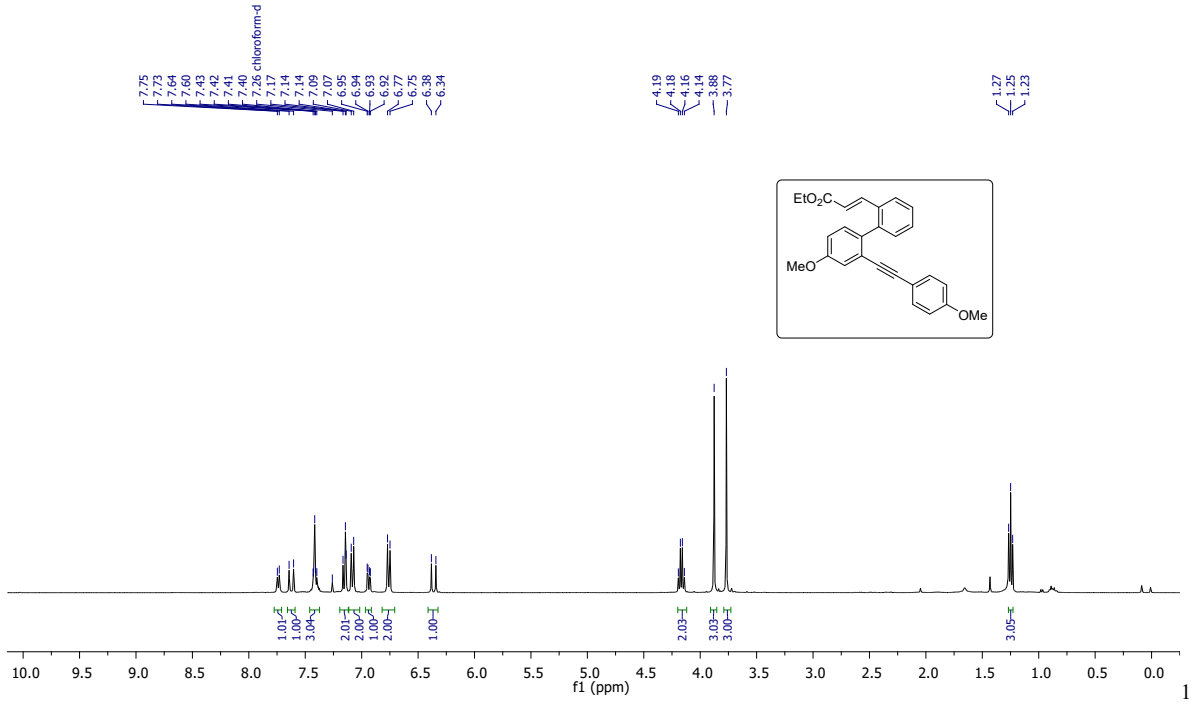
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **1u** in $CDCl_3$



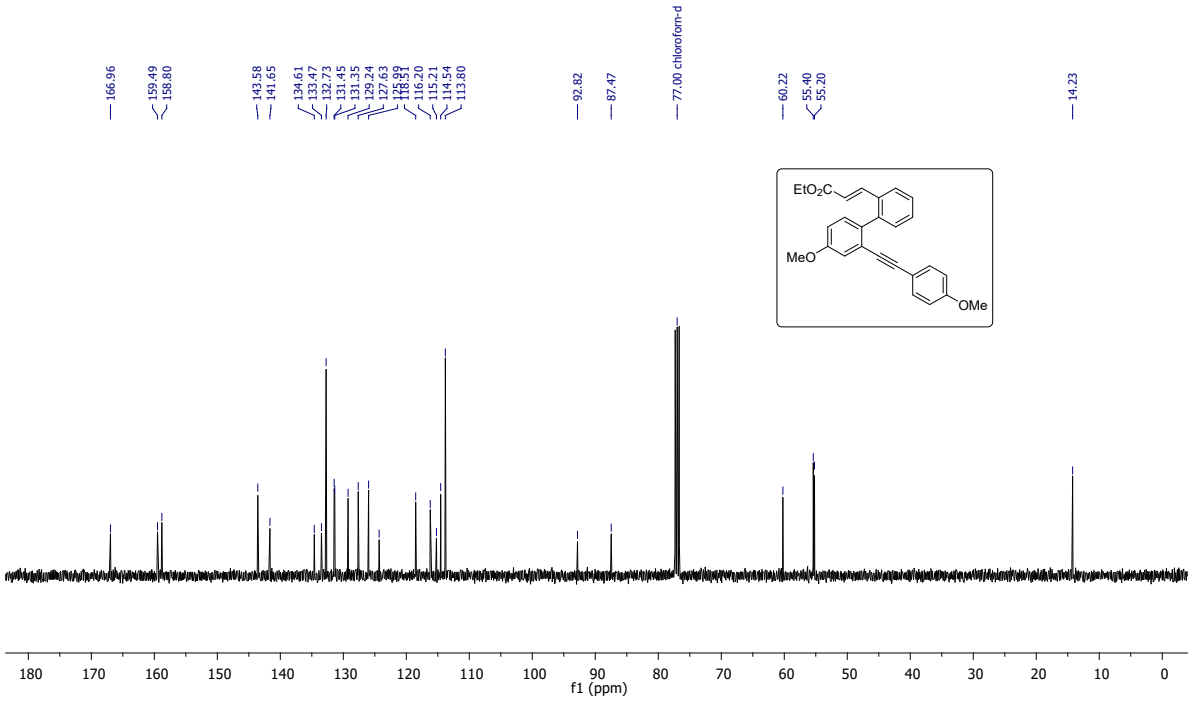
^{1}H NMR (400 MHz) spectrum of **1v** in $CDCl_3$



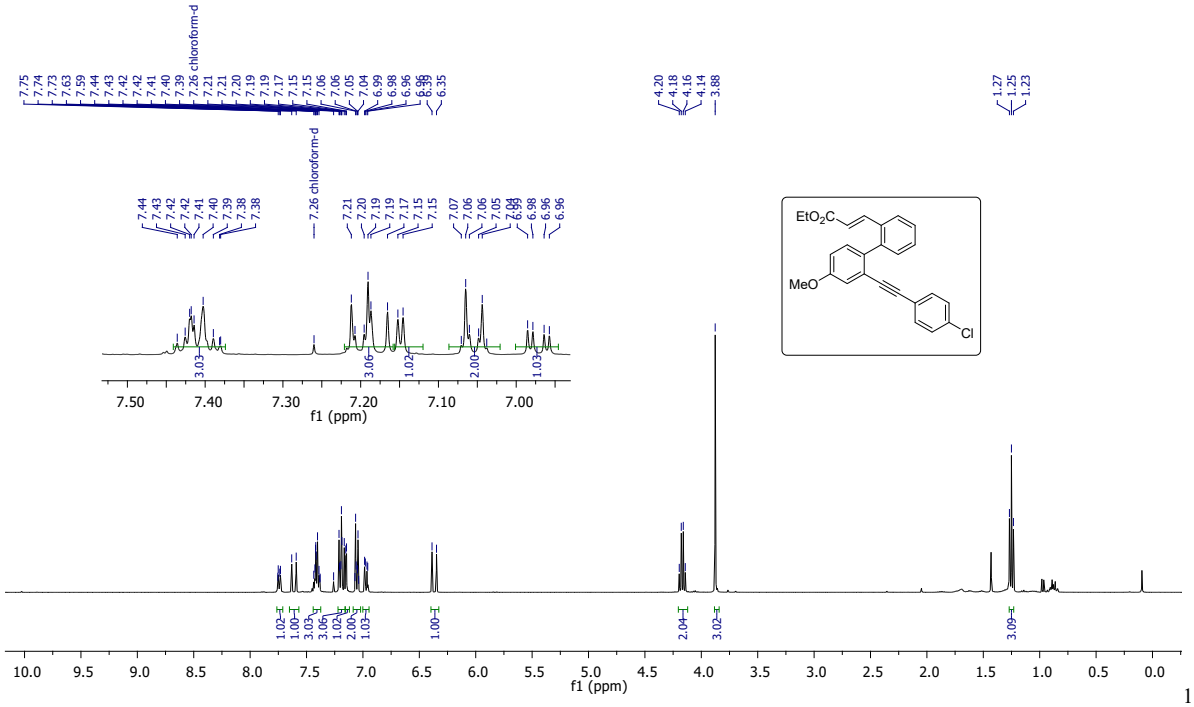
^{13}C{H} NMR (151 MHz) spectrum of **1v** in $CDCl_3$



H NMR (400 MHz) spectrum of **1w** in $CDCl_3$



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



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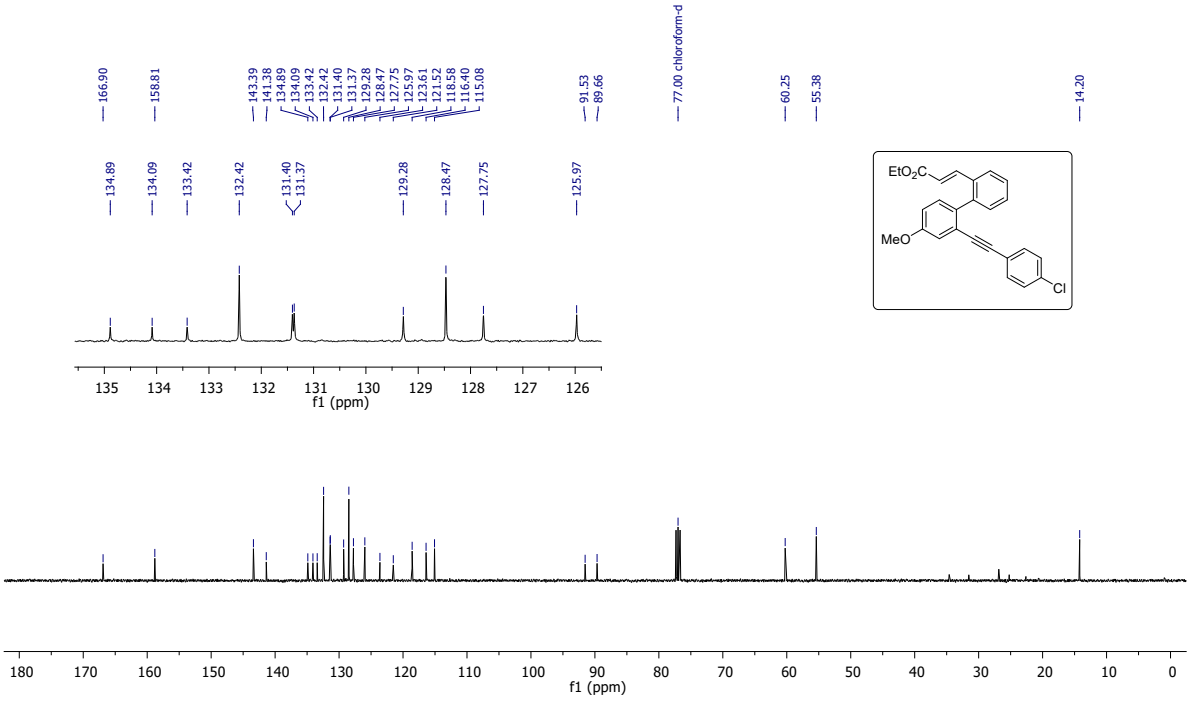
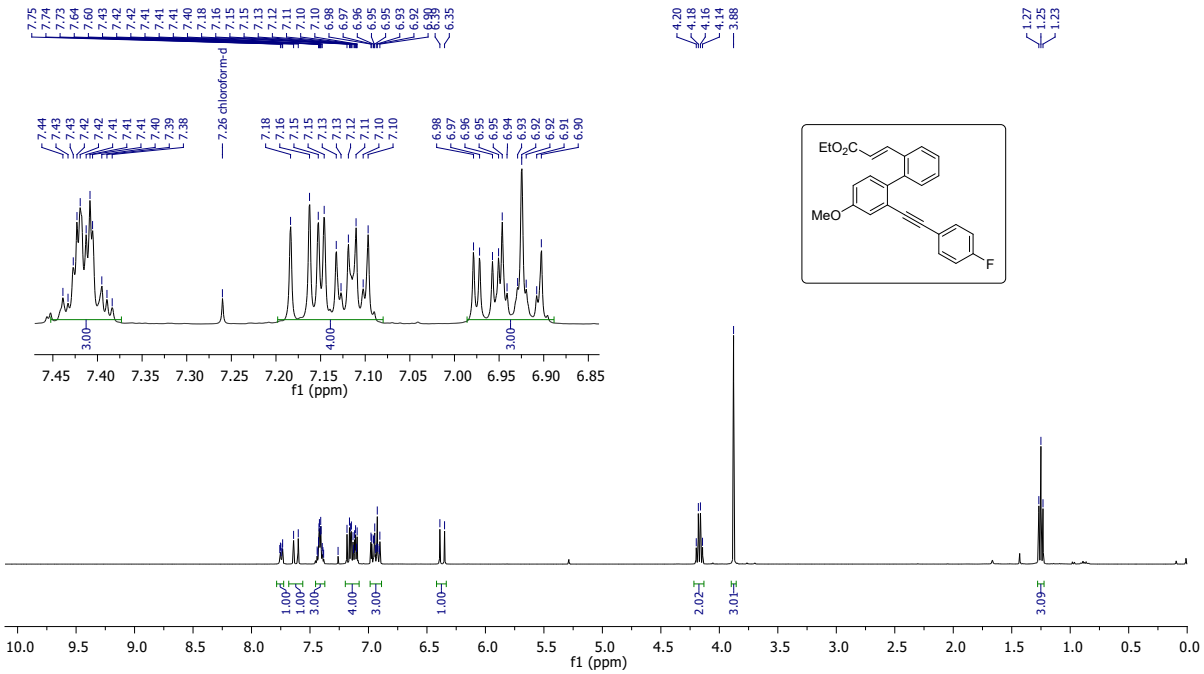
H NMR (400 MHz) spectrum of **1x** in $CDCl_3$

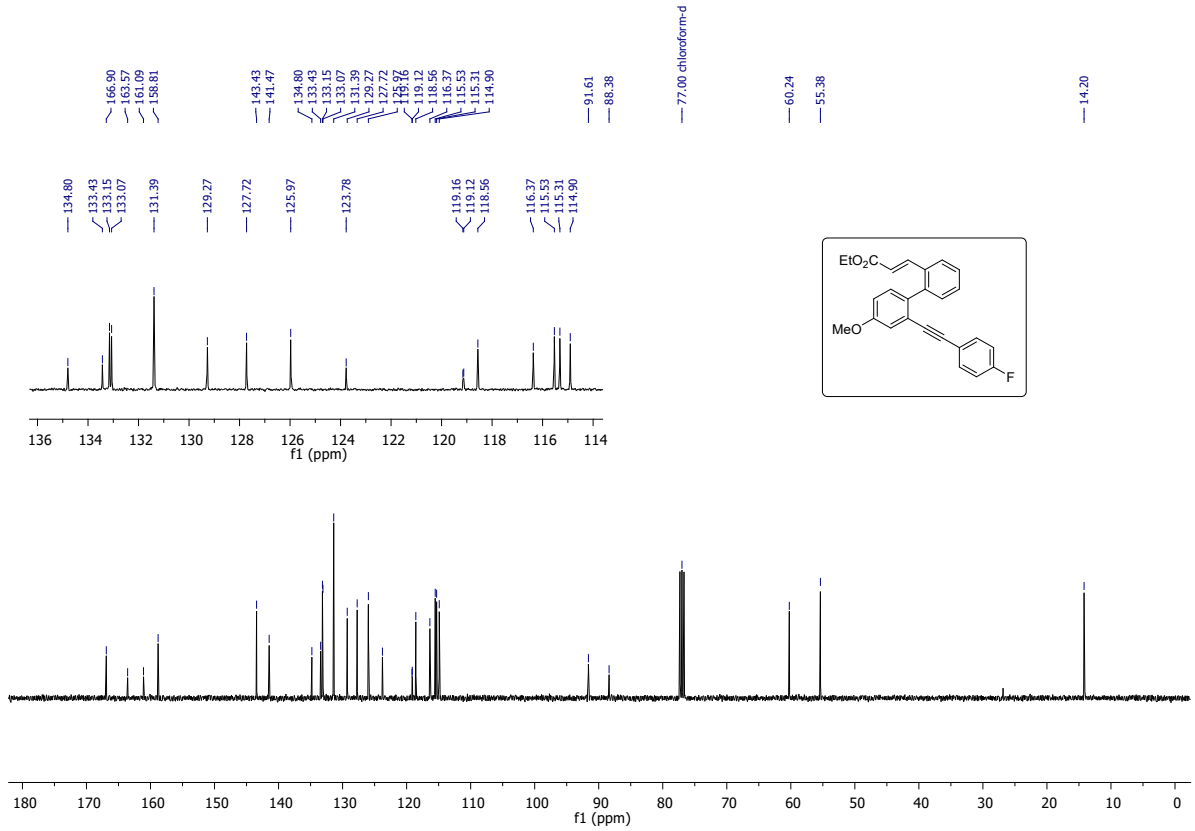


$^{13}C\{H\}$ NMR (101 MHz) spectrum of **1x** in $CDCl_3$

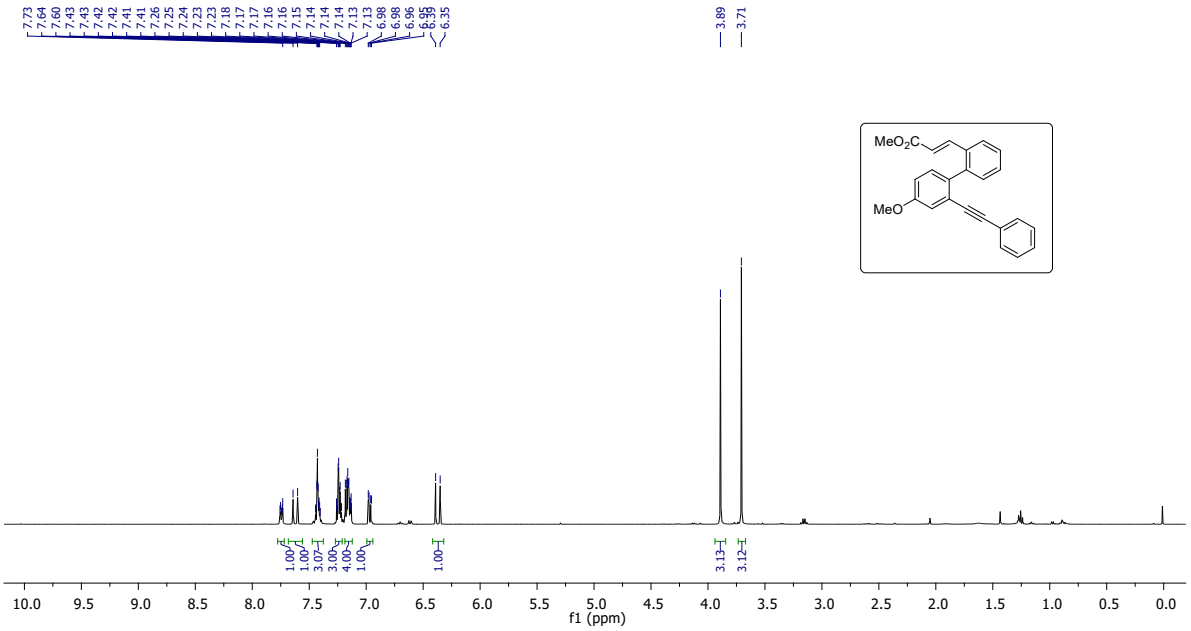
s



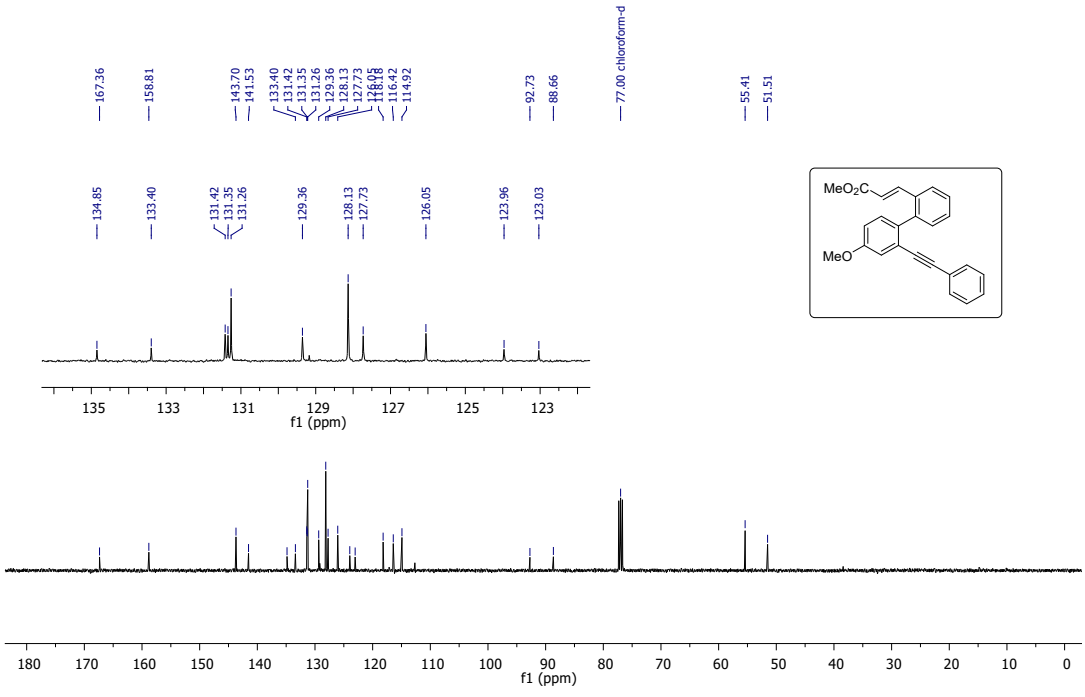
^{1}H NMR (400 MHz) spectrum of **1y** in $CDCl_3$



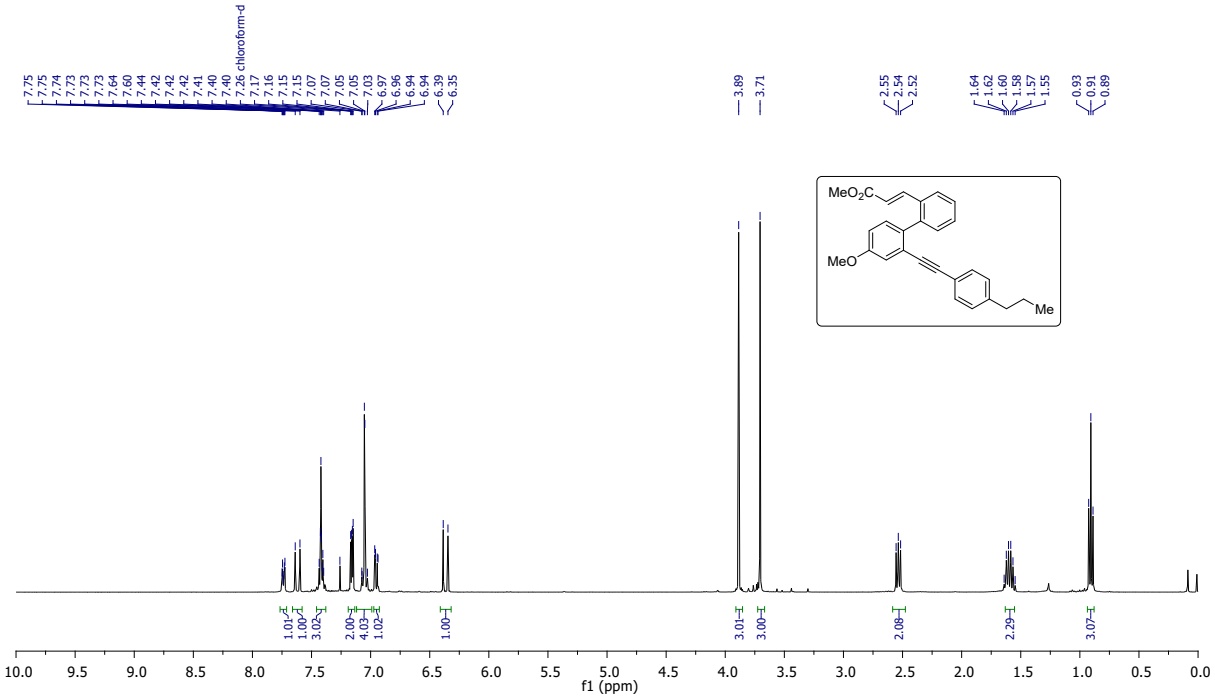
^{13}C{H} NMR (101 MHz) spectrum of **1y** in $CDCl_3$



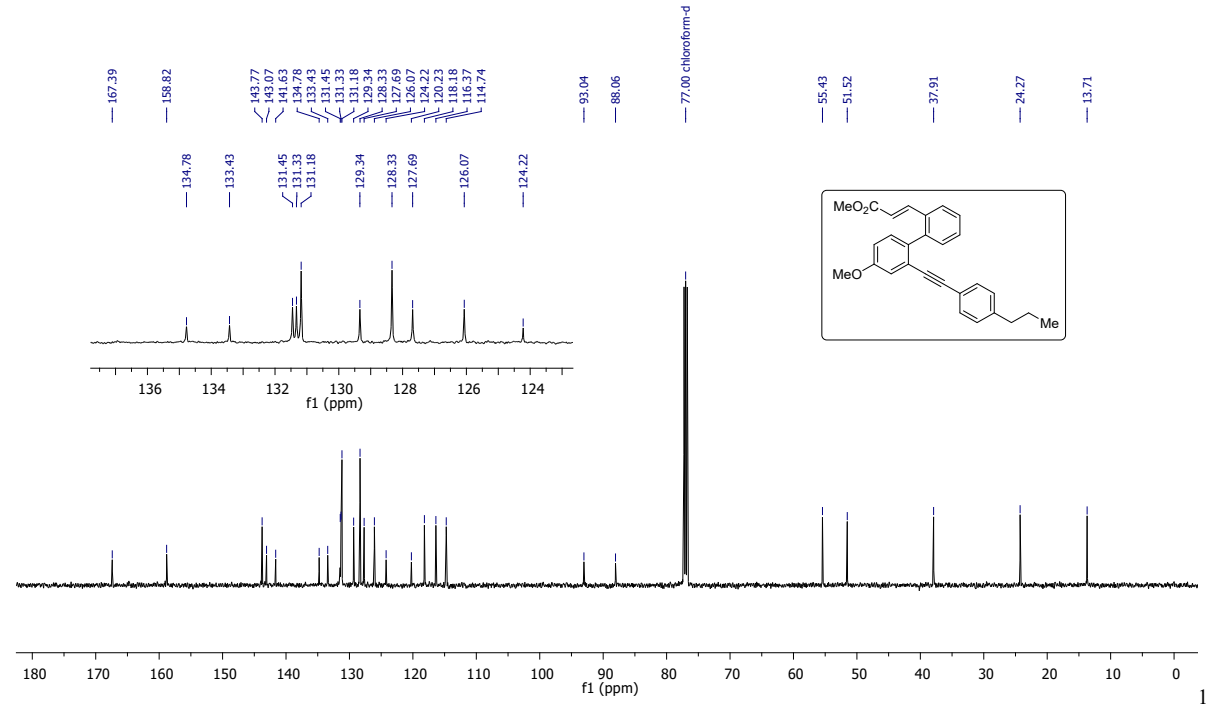
^{1}H NMR (400 MHz) spectrum of **1z** in $CDCl_3$



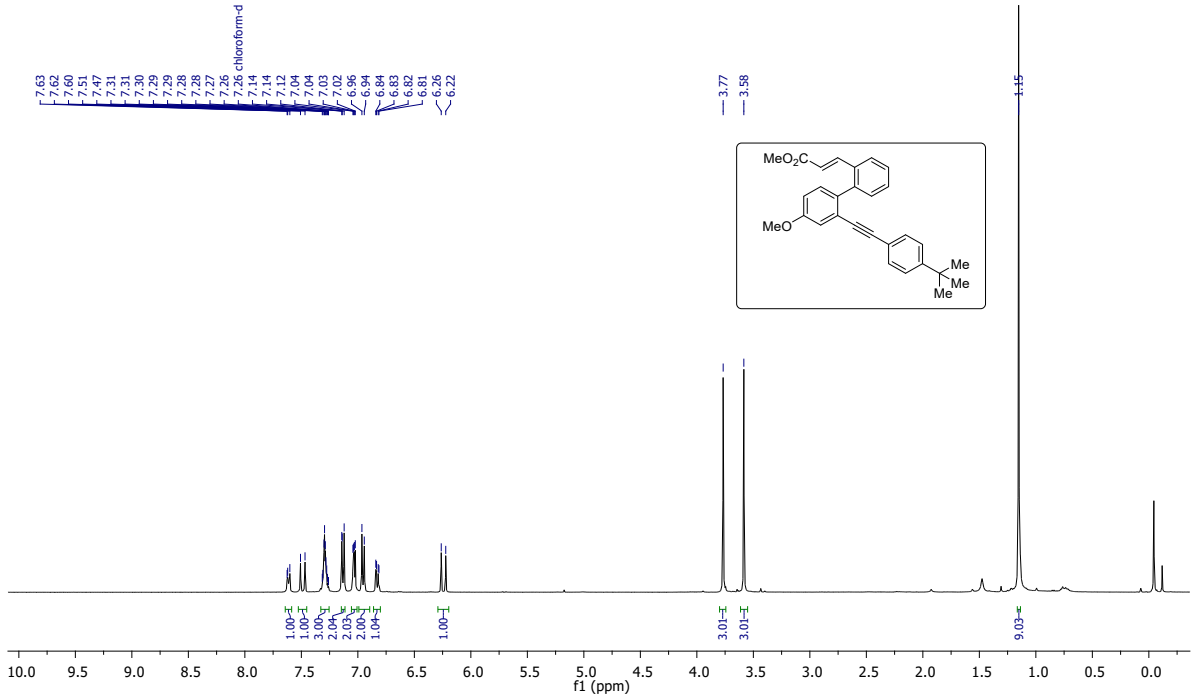
^{13}C{H} NMR (101 MHz) spectrum of **1z** in $CDCl_3$



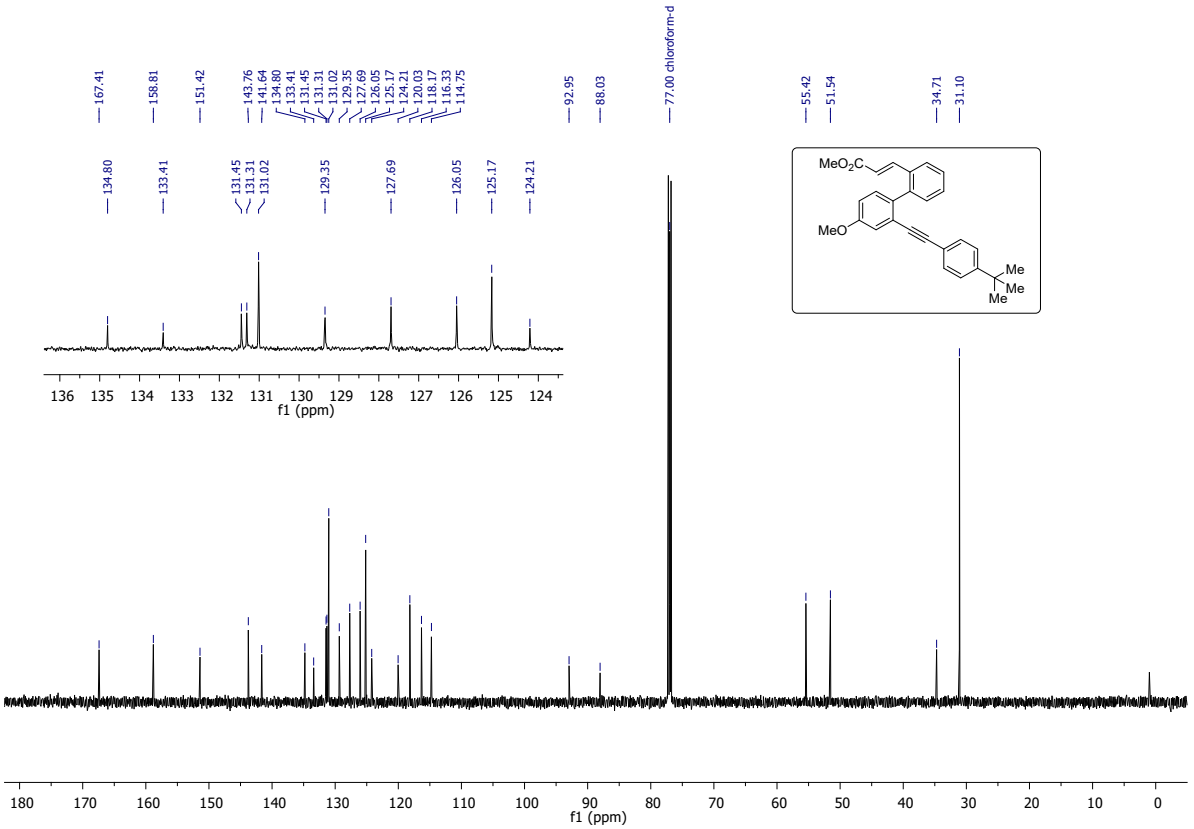
^{1}H NMR (400 MHz) spectrum of **1aa** in $CDCl_3$



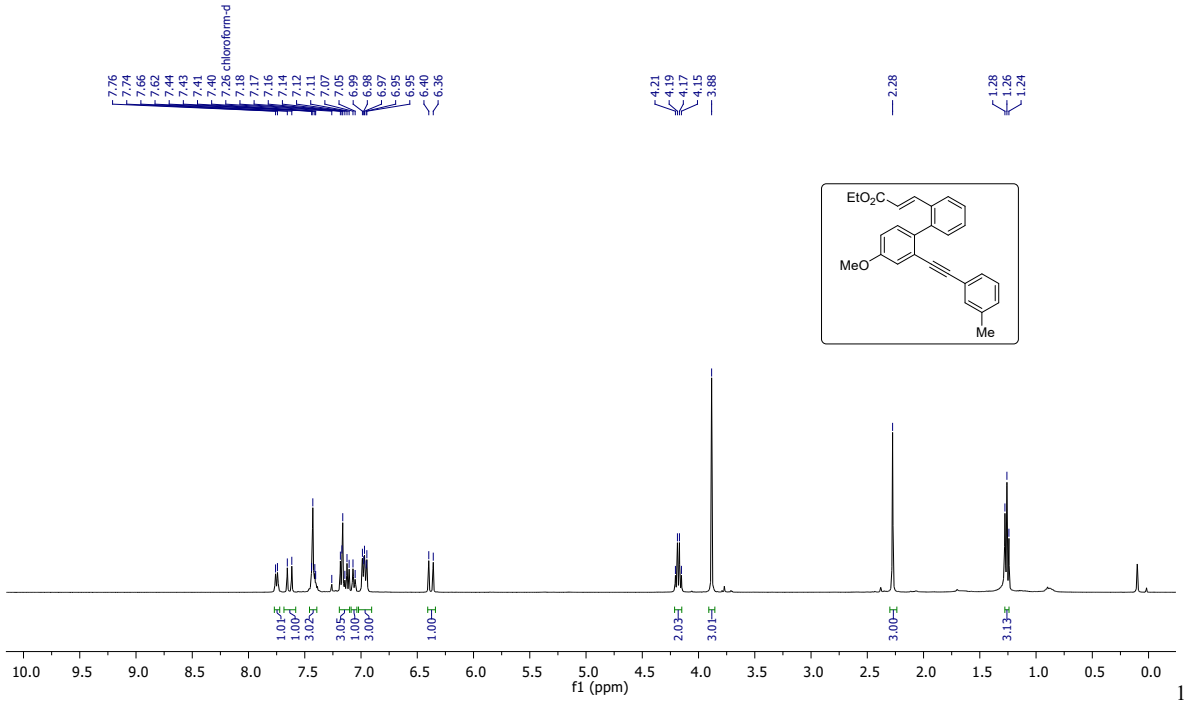
^{3}C{H} NMR (126 MHz) spectrum of **1aa** in $CDCl_3$



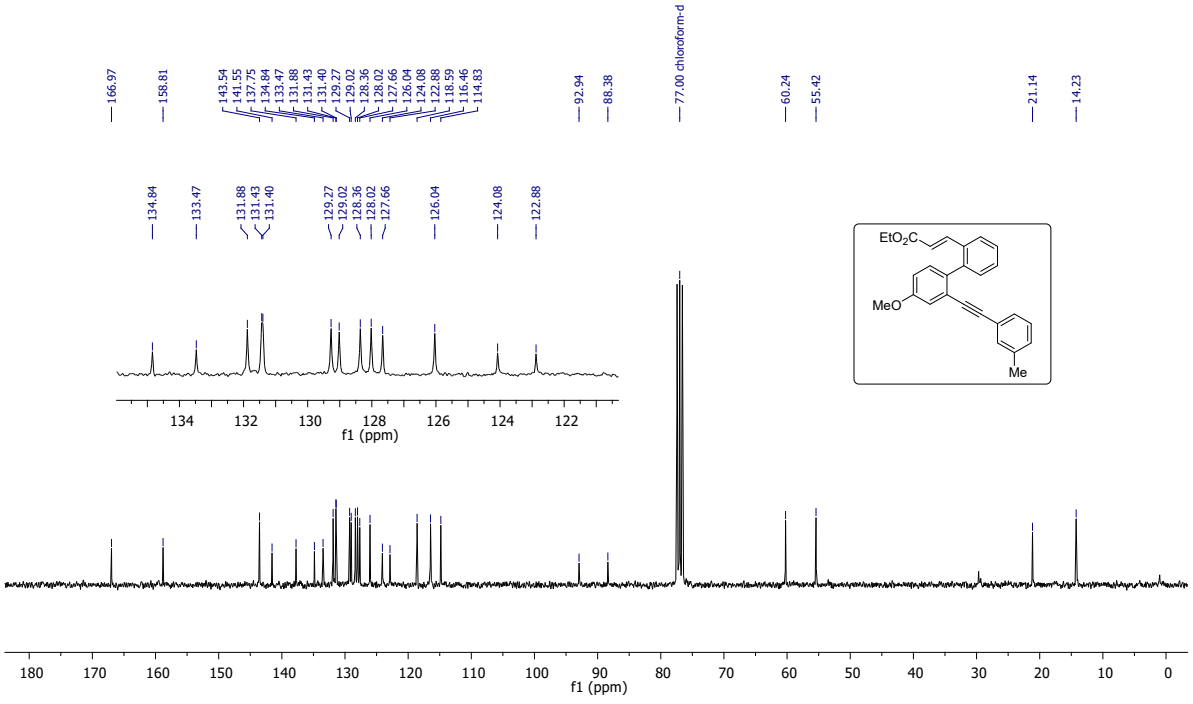
^{1}H NMR (400 MHz) spectrum of **1ab** in $CDCl_3$



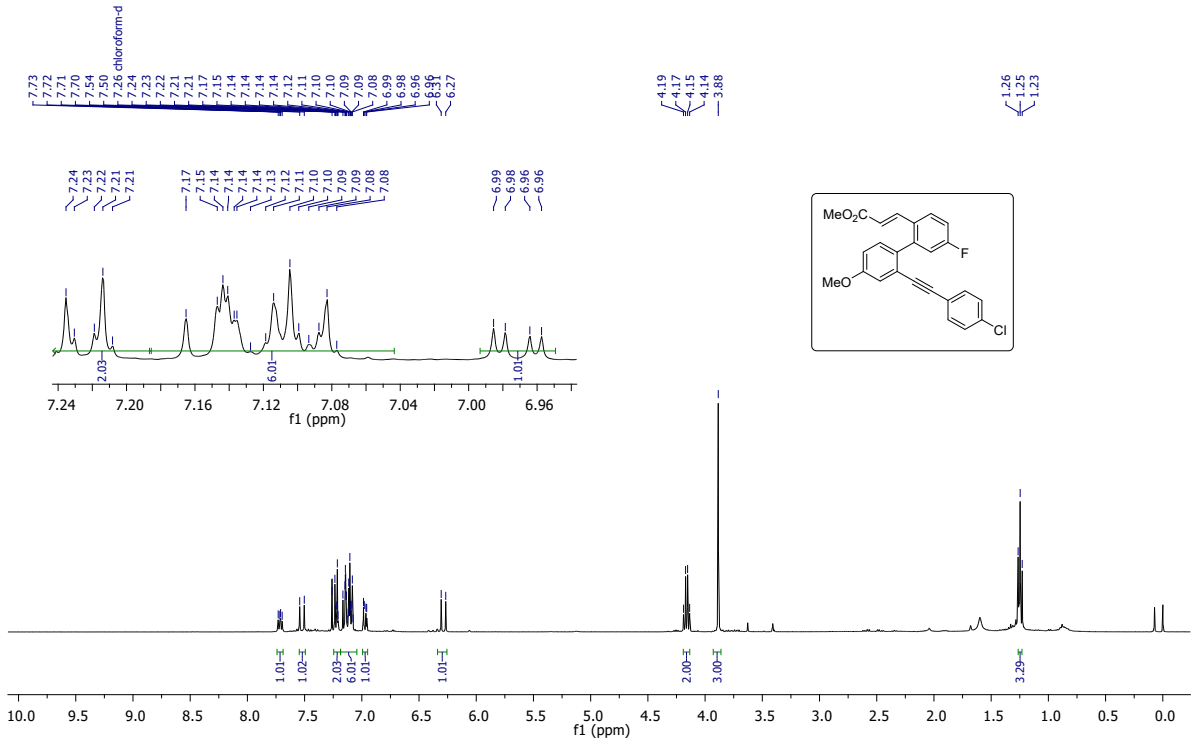
^{13}C{H} NMR (151 MHz) spectrum of **1ab** in $CDCl_3$



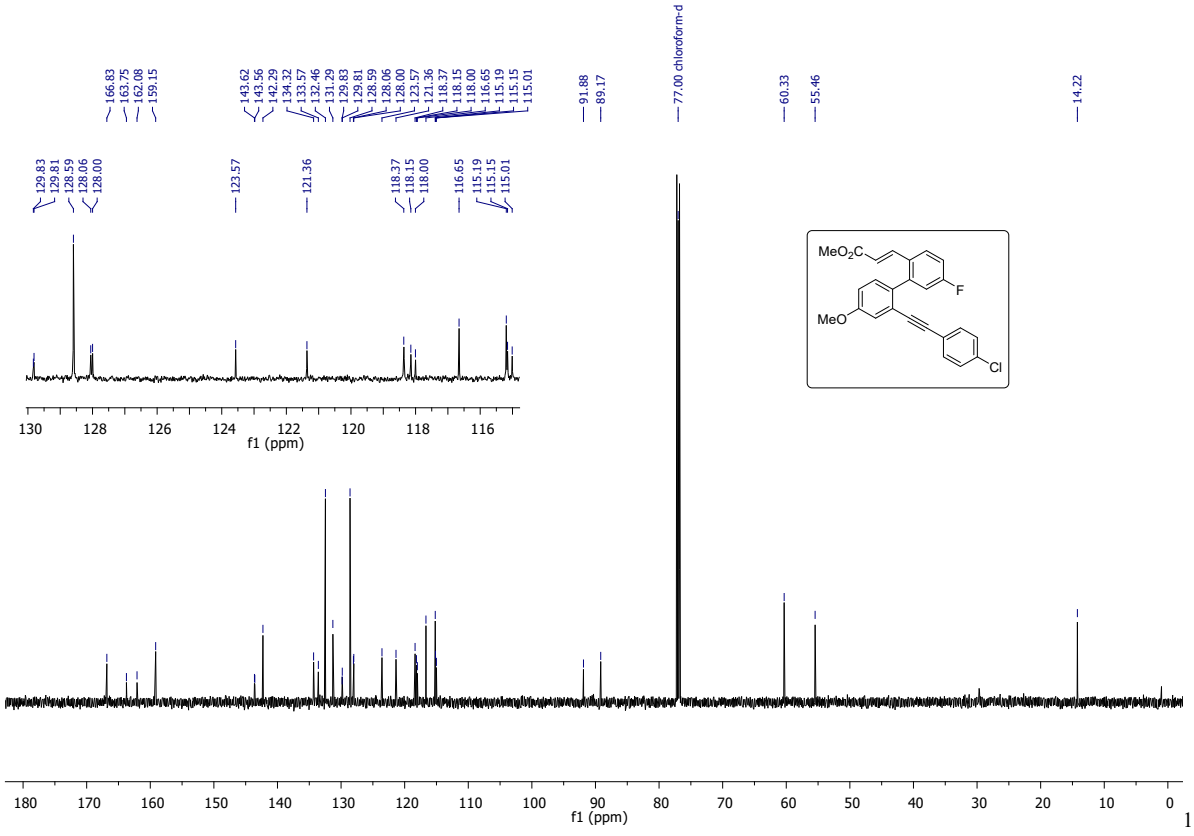
H NMR (400 MHz) spectrum of **1ac** in $CDCl_3$



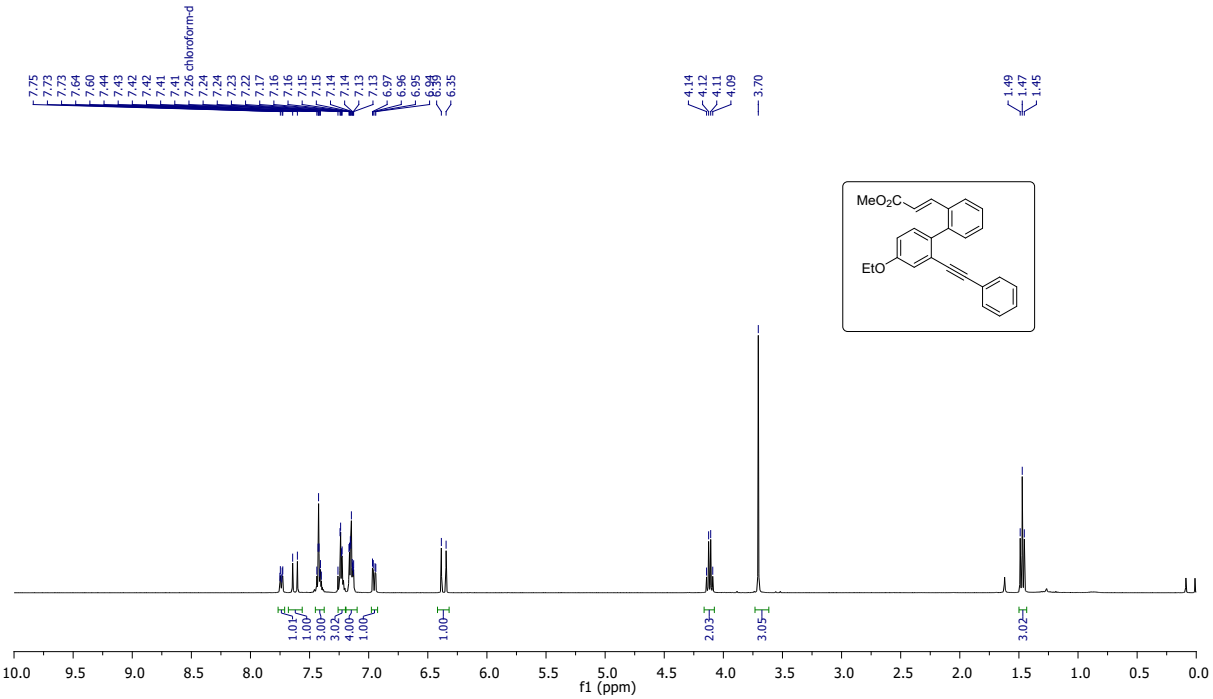
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **1ac** in $CDCl_3$



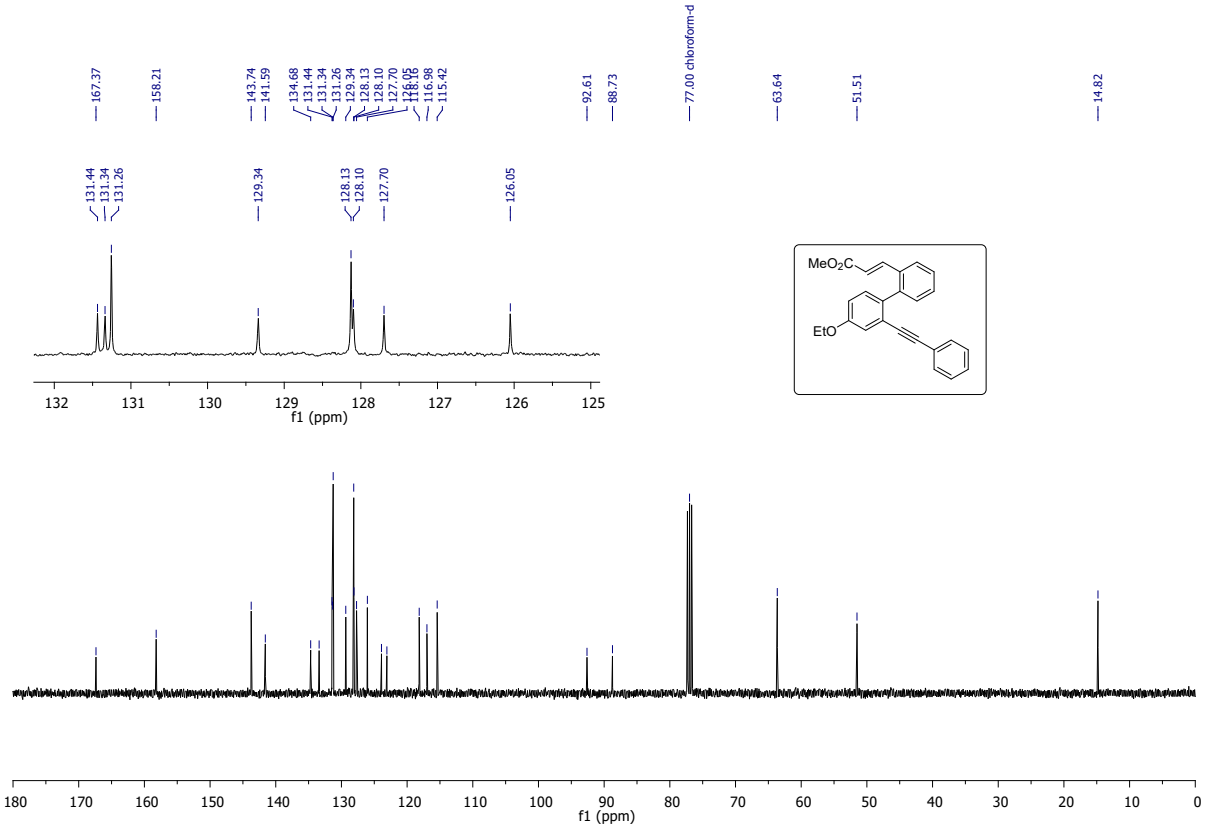
^{1}H NMR (400 MHz) spectrum of **1ad** in $CDCl_3$



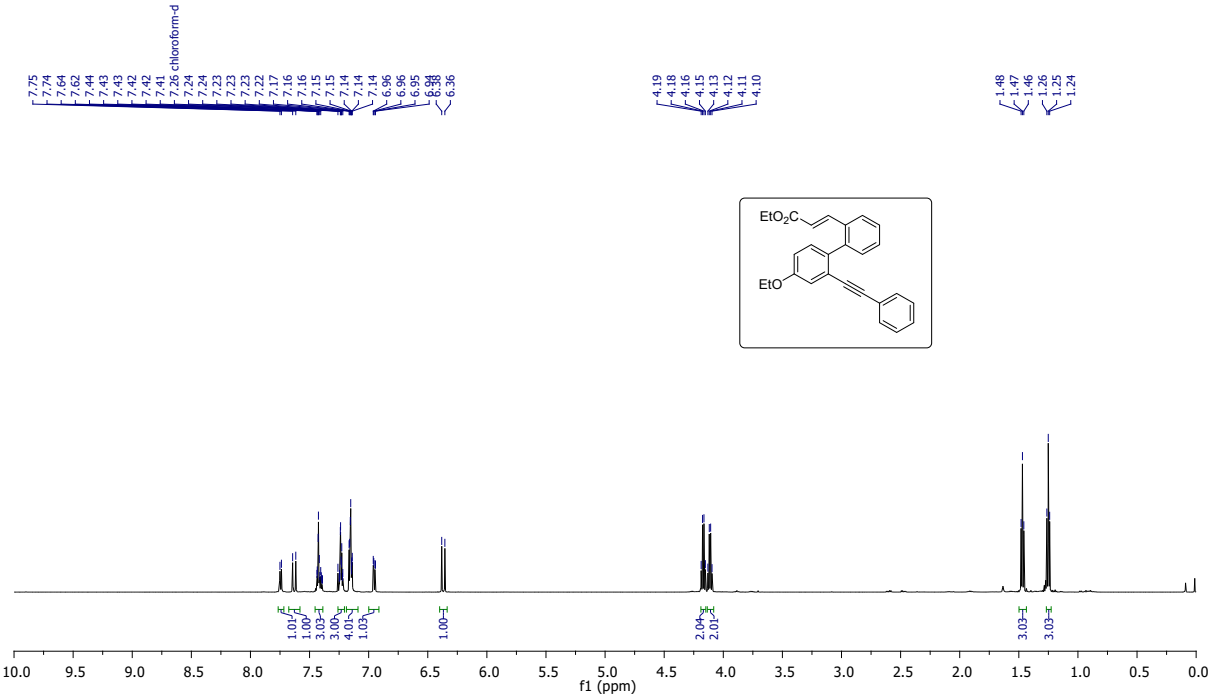
^{3}C{H} NMR (151 MHz) spectrum of **1ad** in CDCl



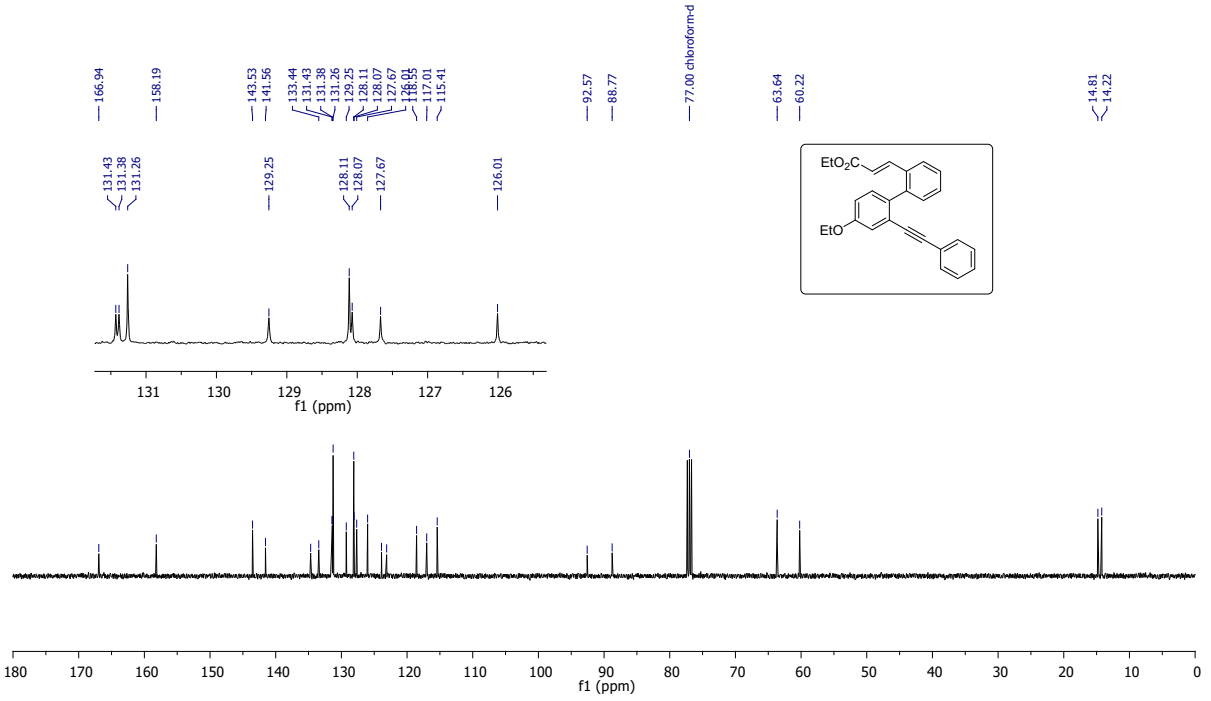
^{1}H NMR (400 MHz) spectrum of **1ae** in $CDCl_3$



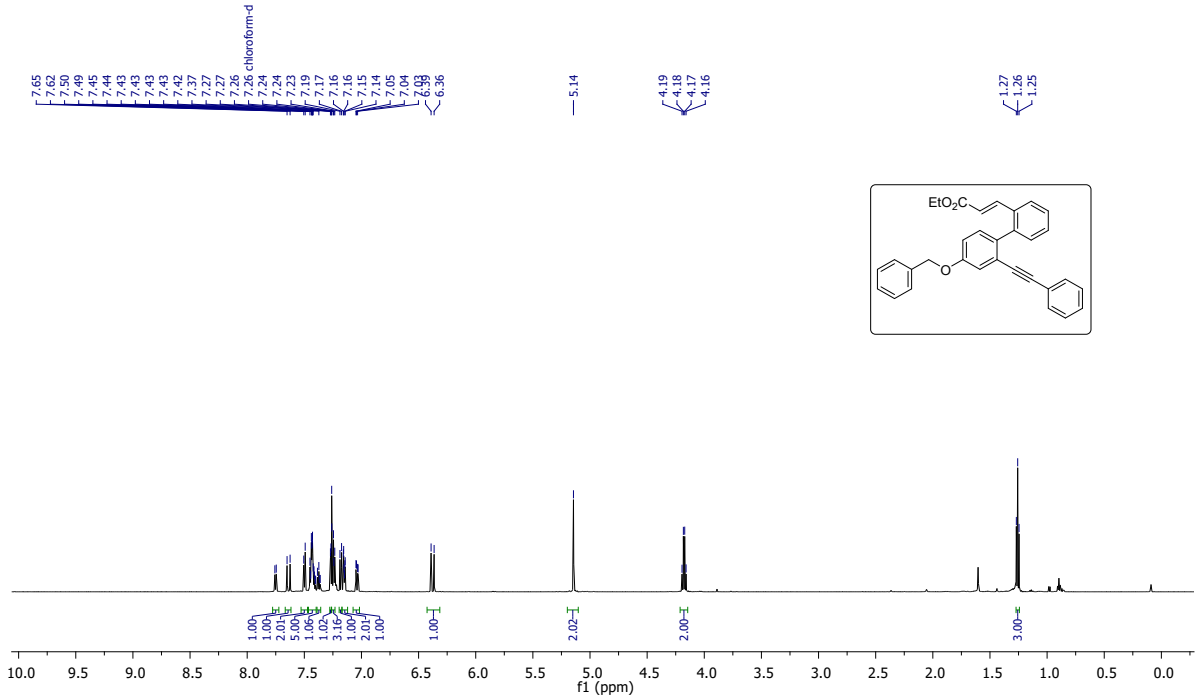
^{13}C{H} NMR (101 MHz) spectrum of **1ae** in $CDCl_3$



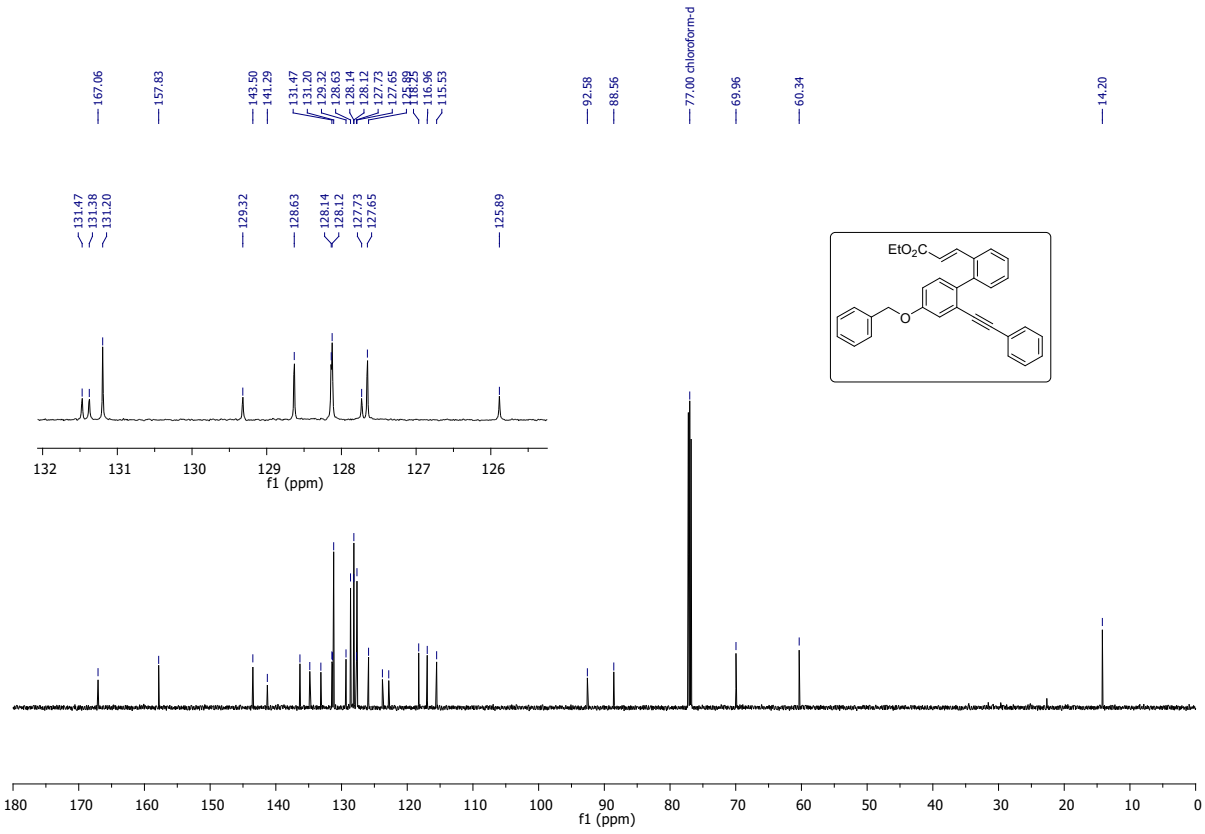
^{1}H NMR (600 MHz) spectrum of **1af** in $CDCl_3$



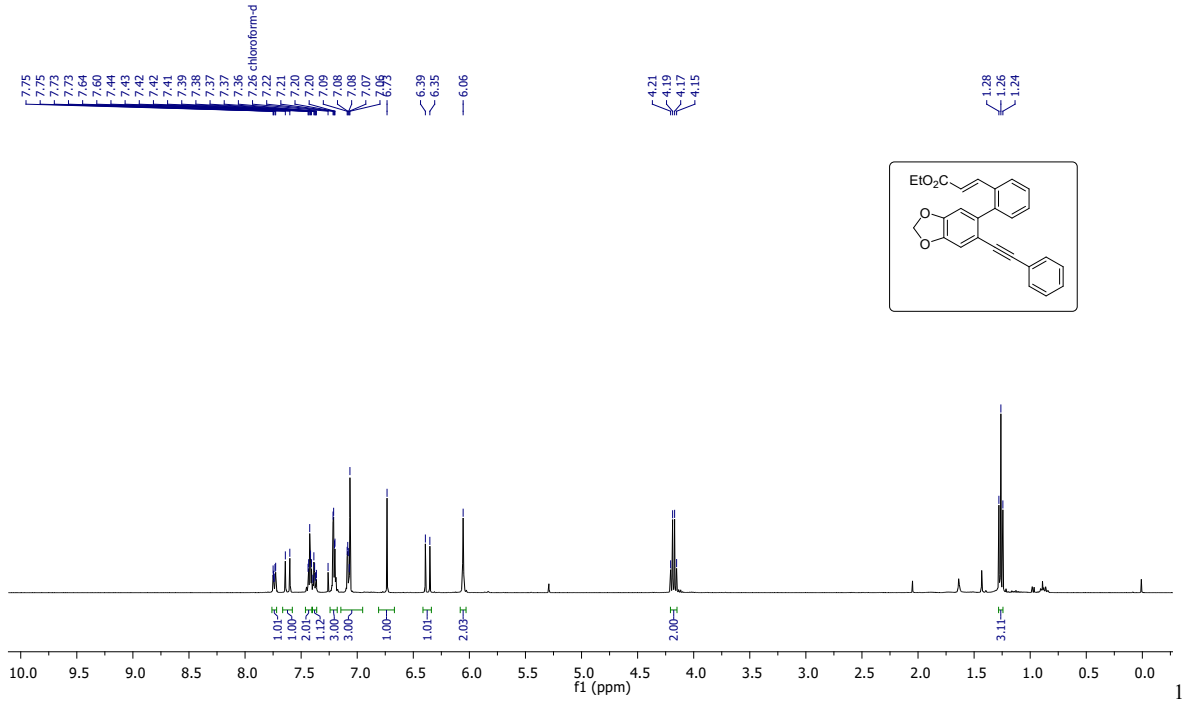
^{13}C{H} NMR (101 MHz) spectrum of **1af** in $CDCl_3$



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

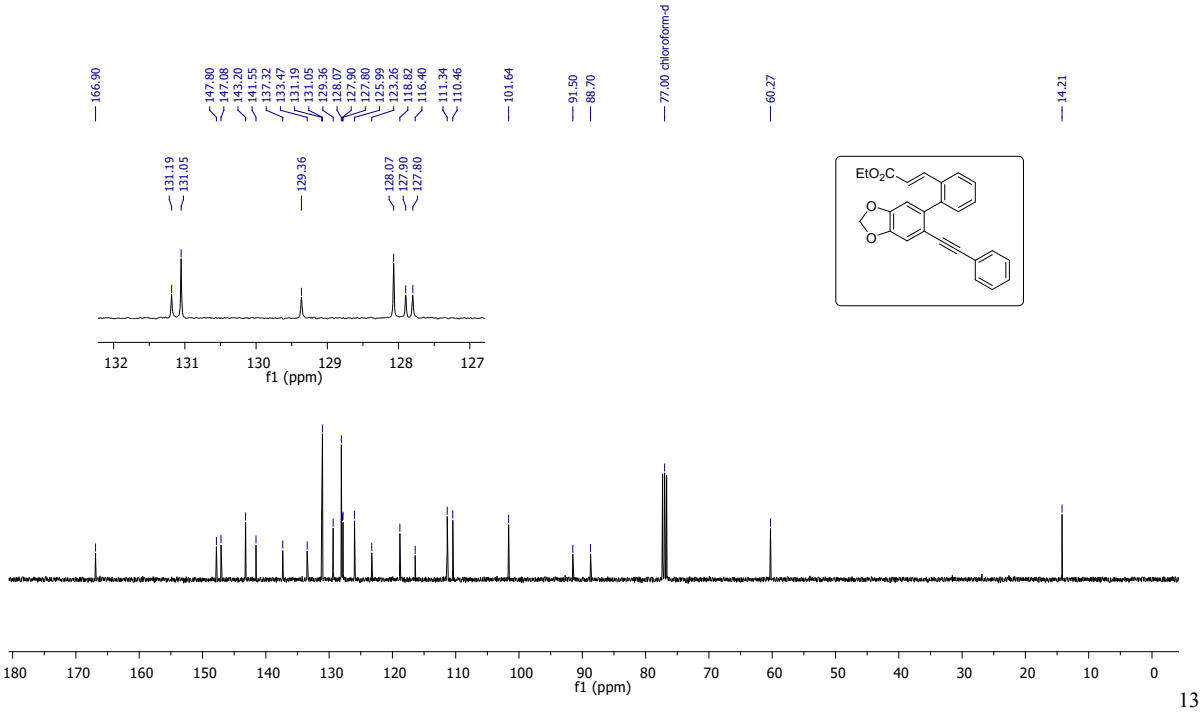


^{13}C{H} NMR (151 MHz) spectrum of **1ag** in $CDCl_3$



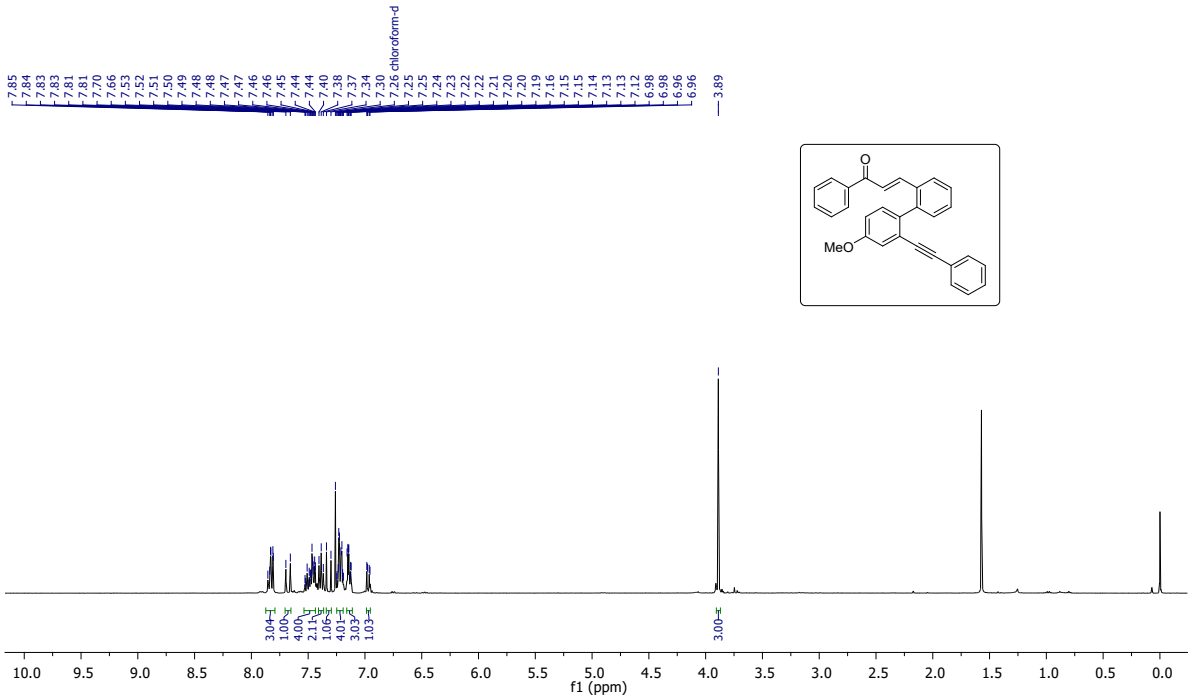
1

H NMR (400 MHz) spectrum of **1ah** in $CDCl_3$

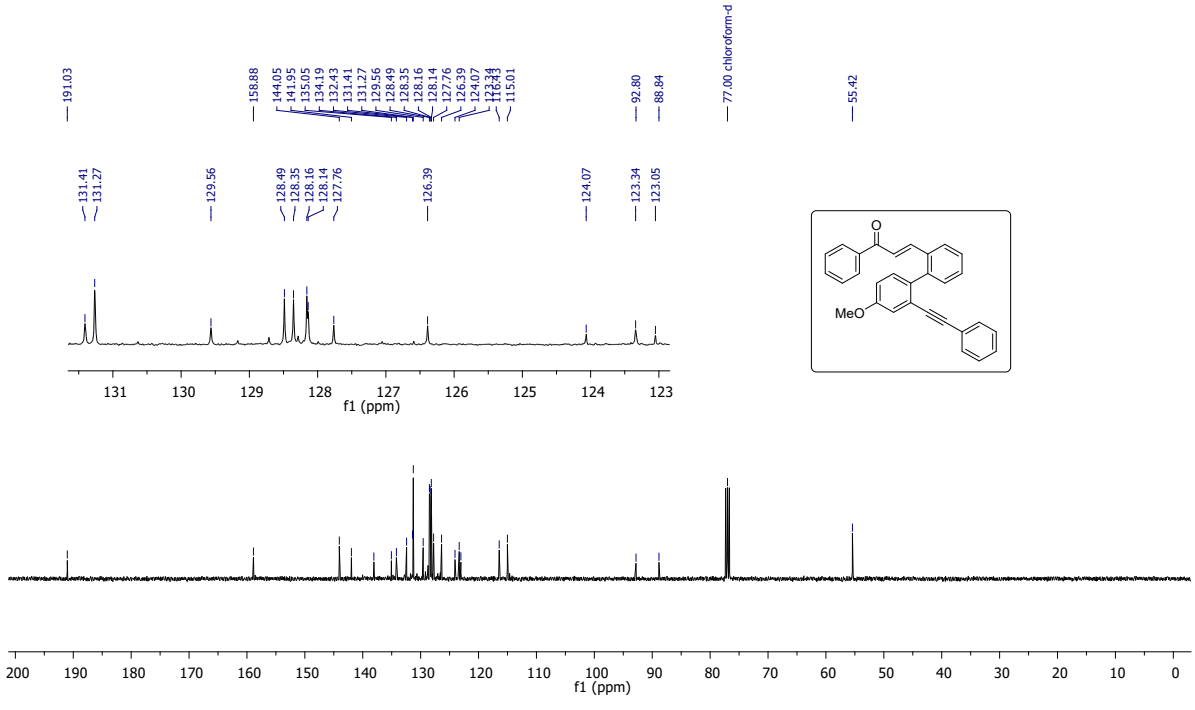


13

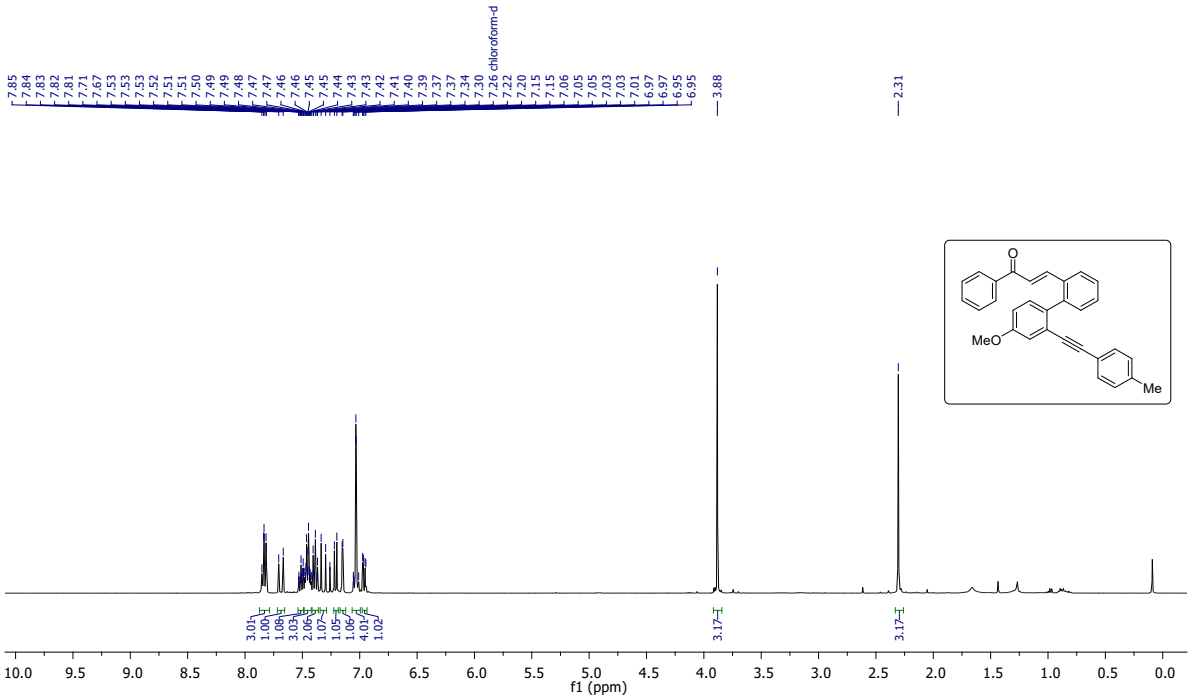
C{H} NMR (101 MHz) spectrum of **1ah** in $CDCl_3$



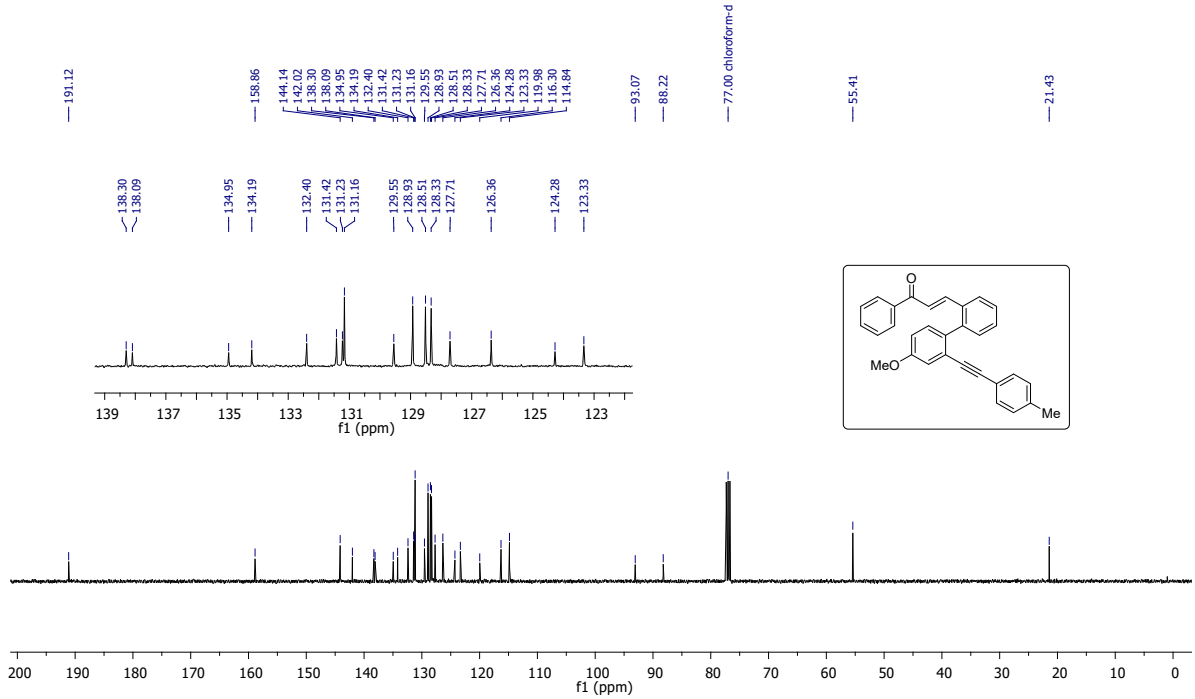
^{1}H NMR (400 MHz) spectrum of **12a** in $CDCl_3$



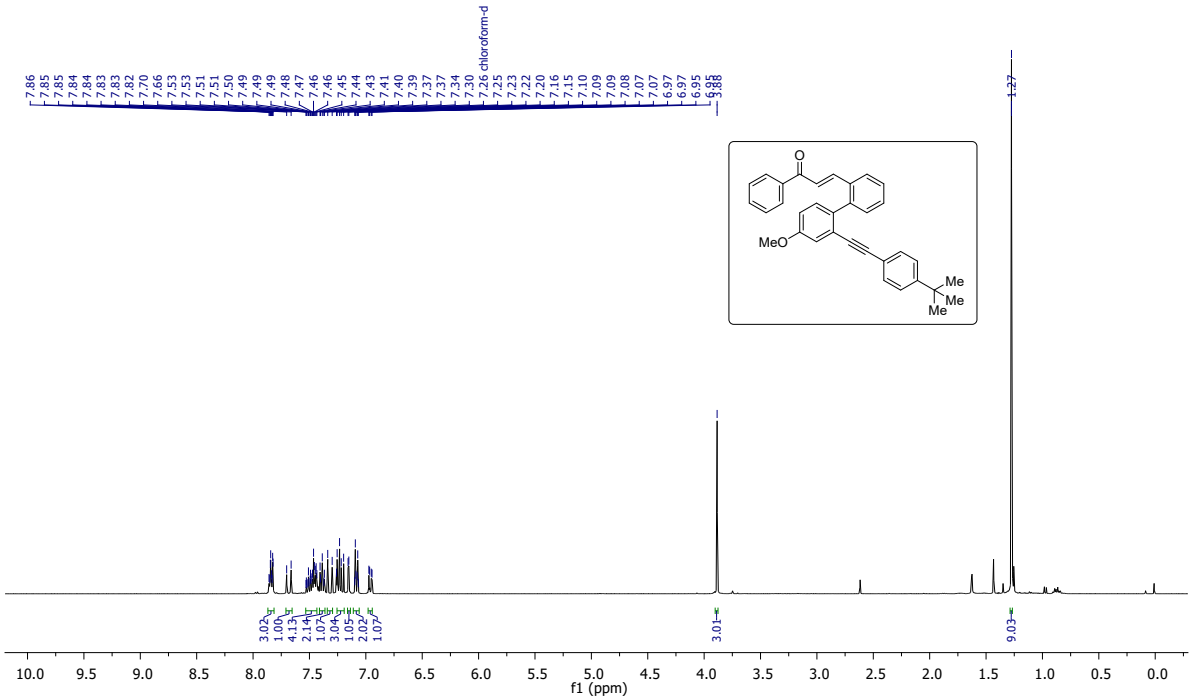
^{13}C{H} NMR (101 MHz) spectrum of **12a** in $CDCl_3$



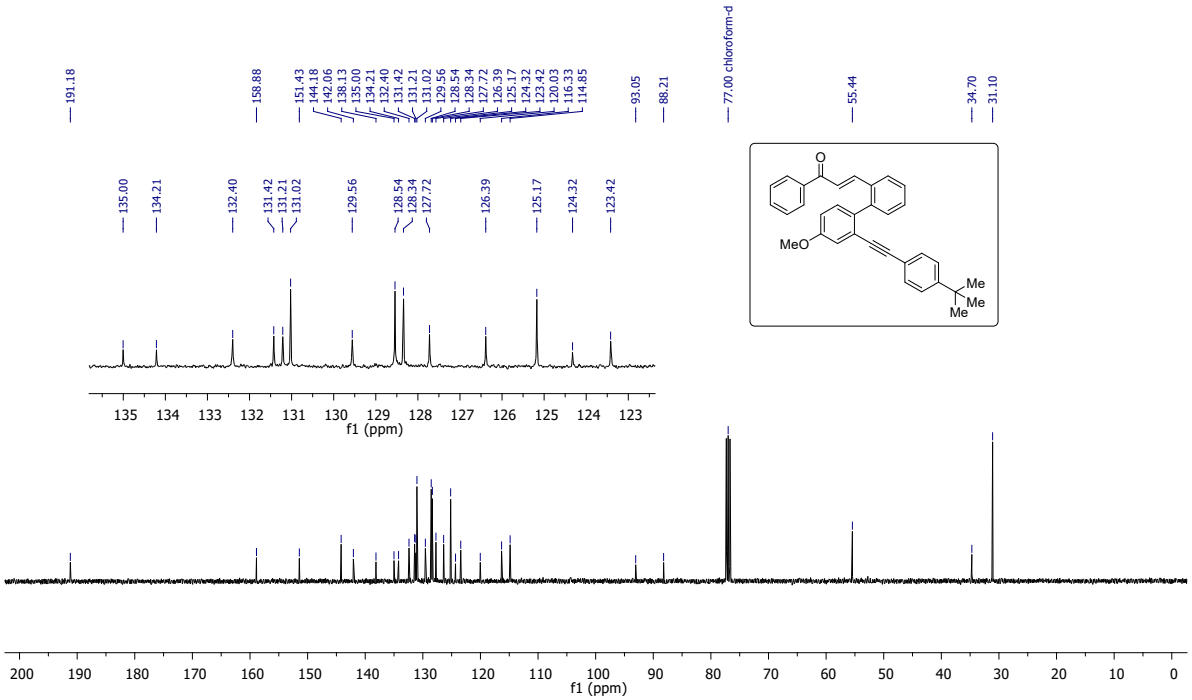
^{1}H NMR (400 MHz) spectrum of **12b** in $CDCl_3$



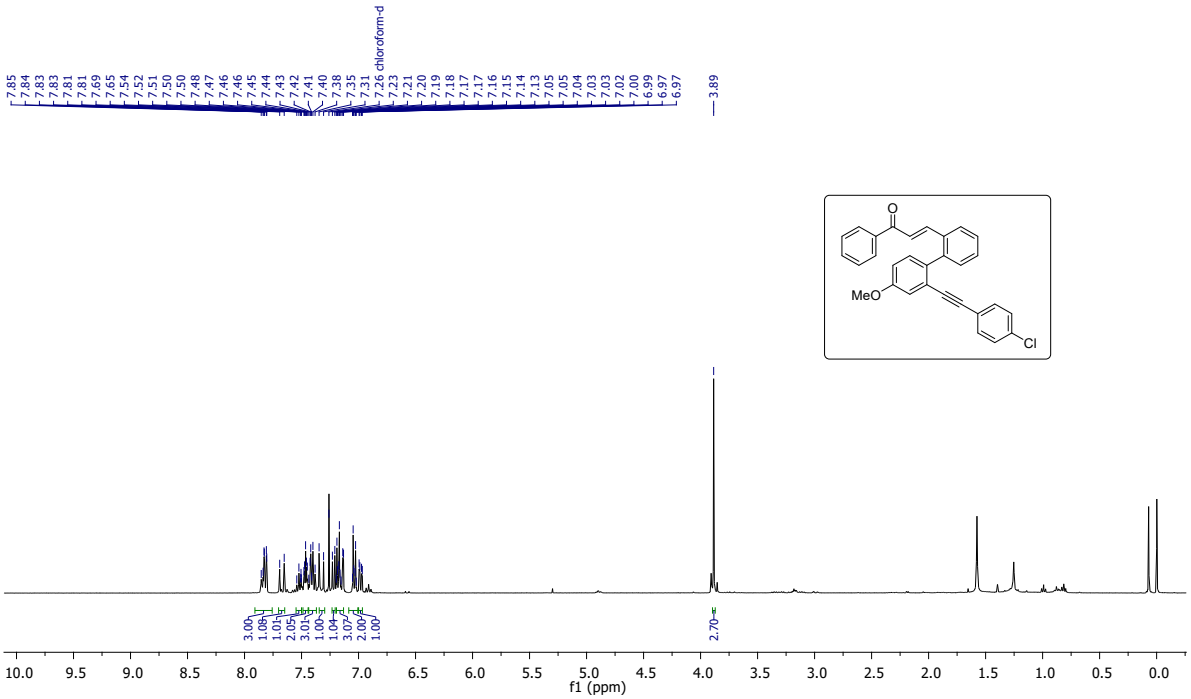
^{13}C{H} NMR (101 MHz) spectrum of **12b** in $CDCl_3$



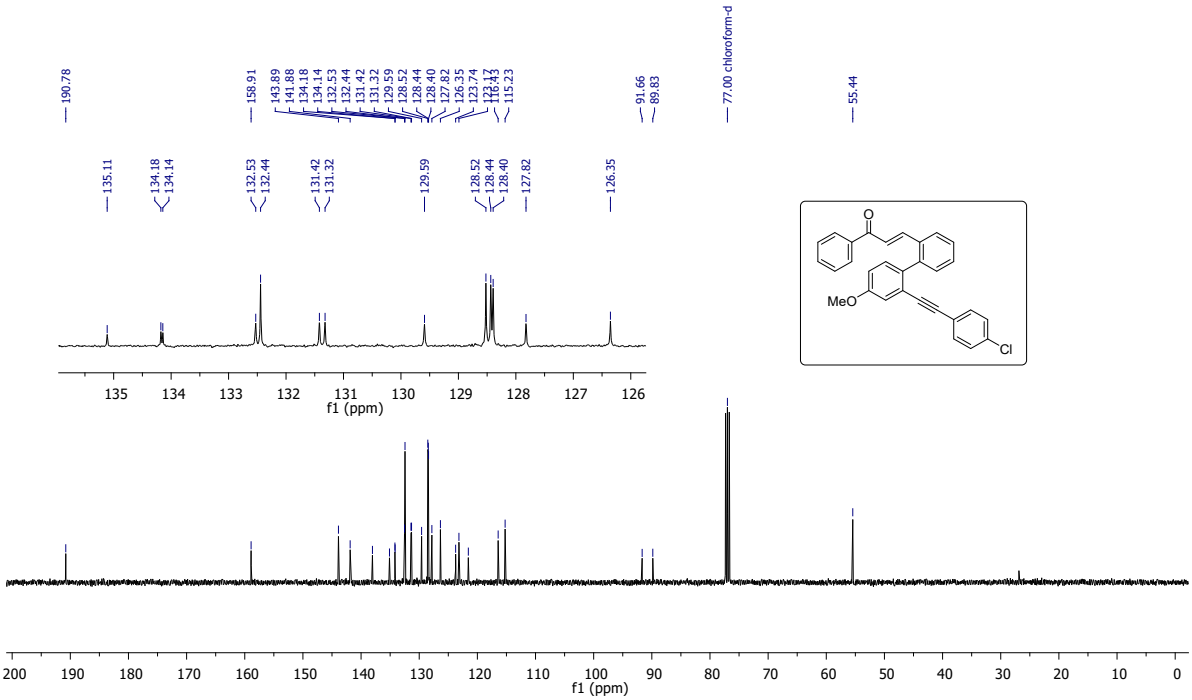
^{1}H NMR (400 MHz) spectrum of **12c** in $CDCl_3$



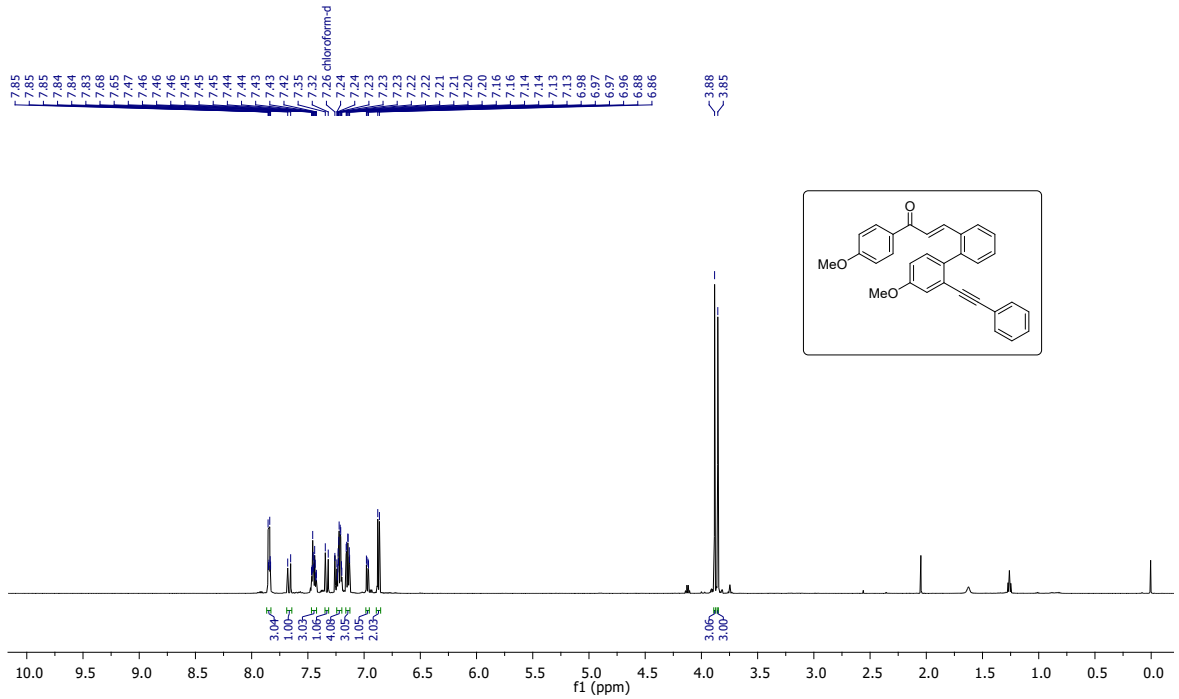
^{13}C{H} NMR (101 MHz) spectrum of **12c** in $CDCl_3$



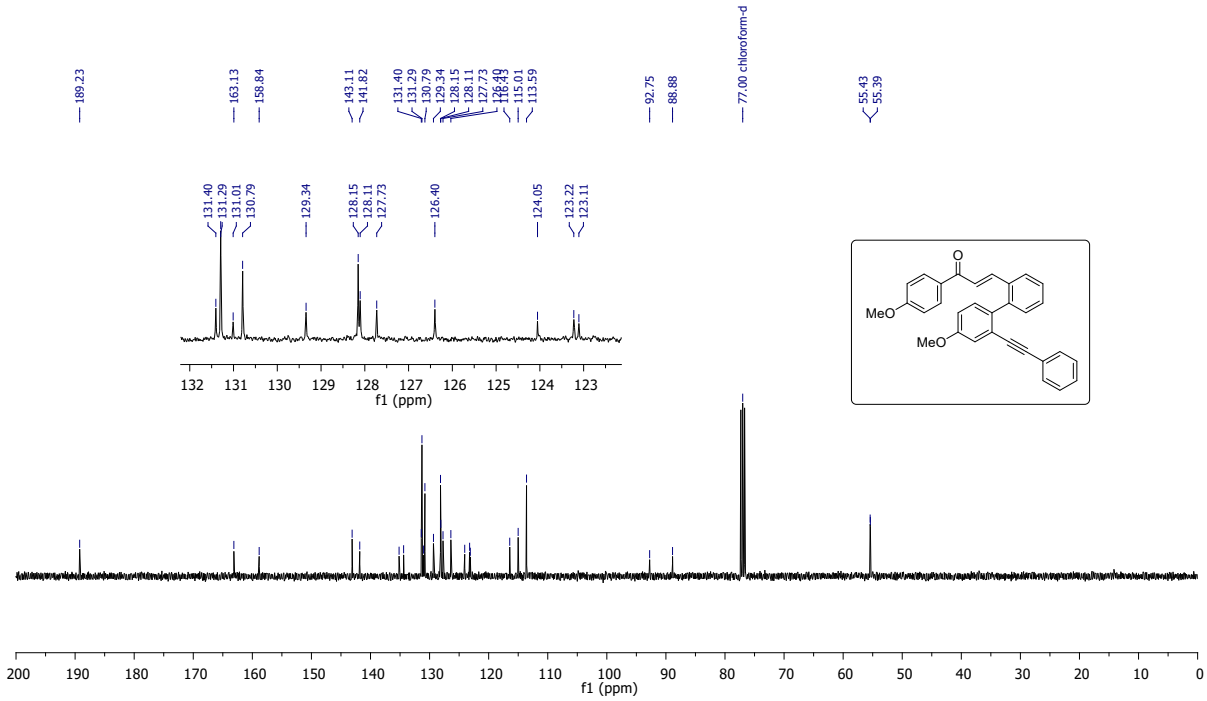
^{1}H NMR (400 MHz) spectrum of **12d** in $CDCl_3$



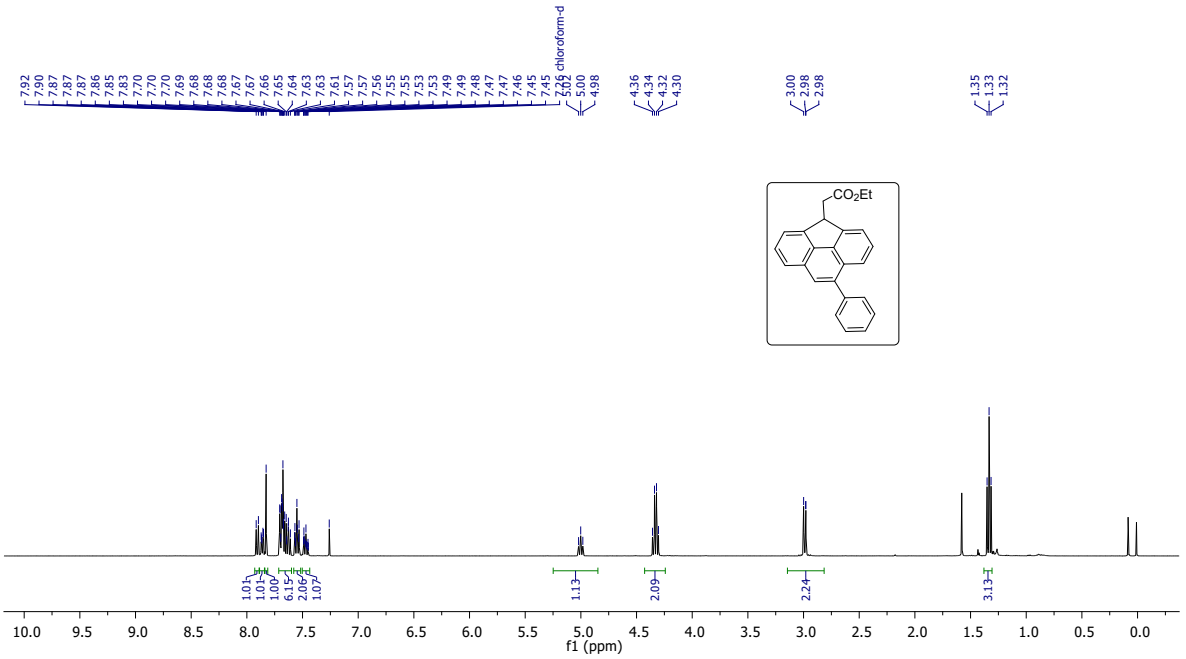
^{13}C{H} NMR (101 MHz) spectrum of **12d** in $CDCl_3$



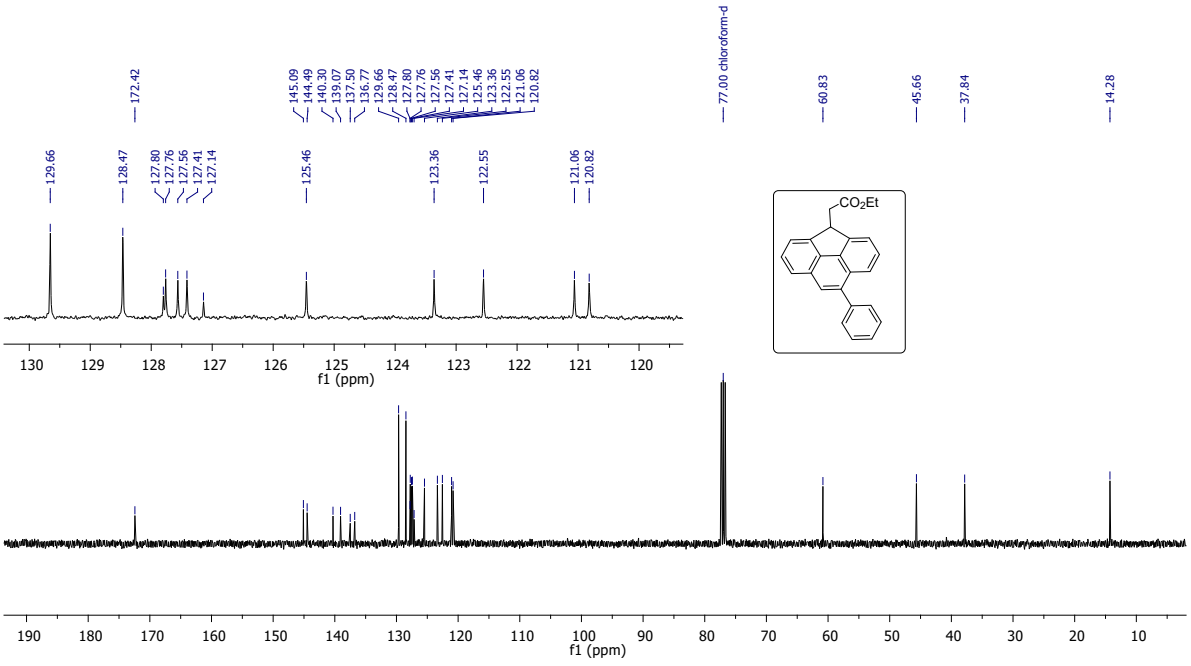
^{1}H NMR (600 MHz) spectrum of **12e** in $CDCl_3$



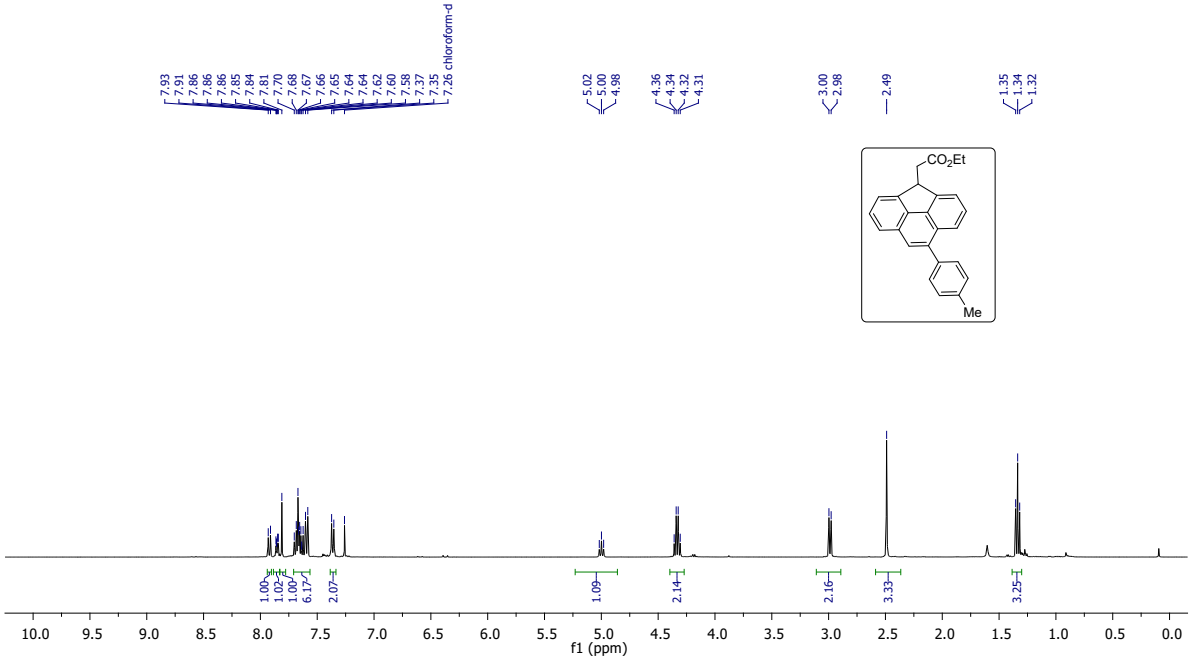
^{13}C{H} NMR (101 MHz) spectrum of **12e** in $CDCl_3$



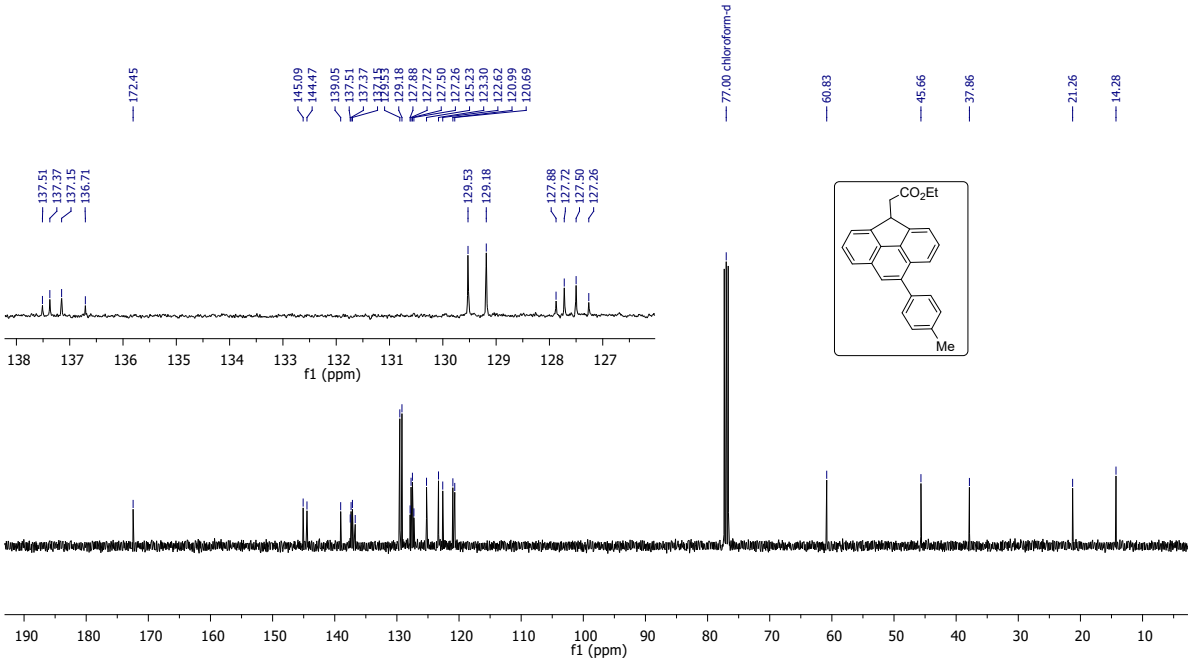
^{1}H NMR (400 MHz) spectrum of **2a** in $CDCl_3$



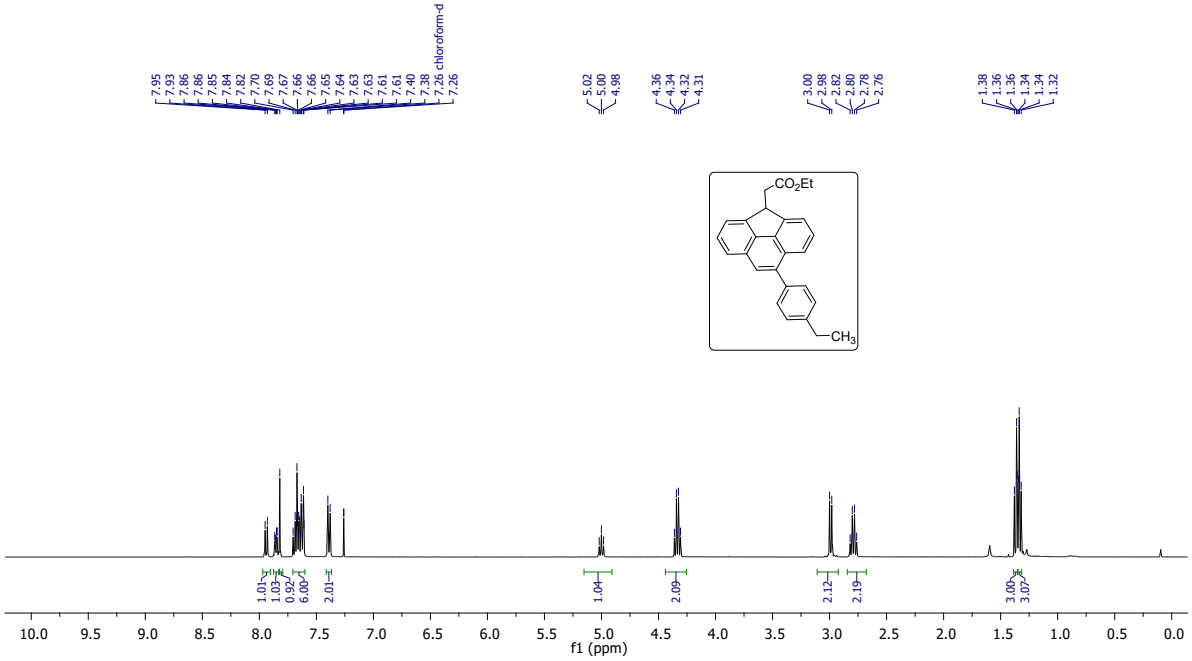
^{13}C{H} NMR (101 MHz) spectrum of **2a** in $CDCl_3$



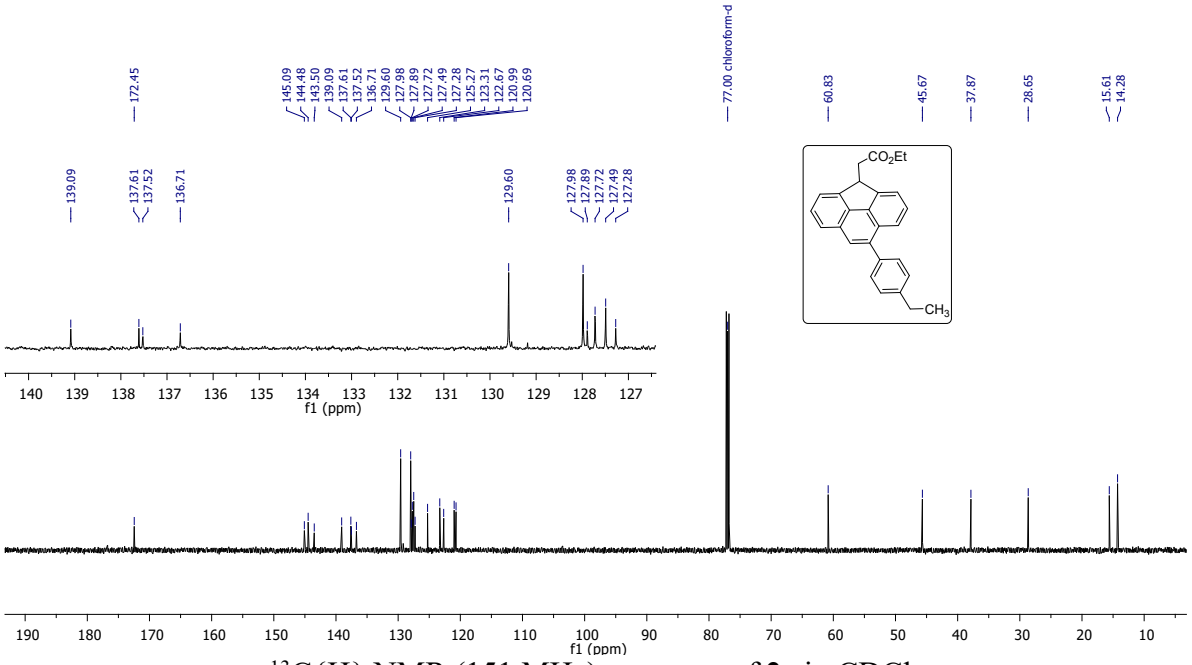
^{1}H NMR (400 MHz) spectrum of **2b** in $CDCl_3$



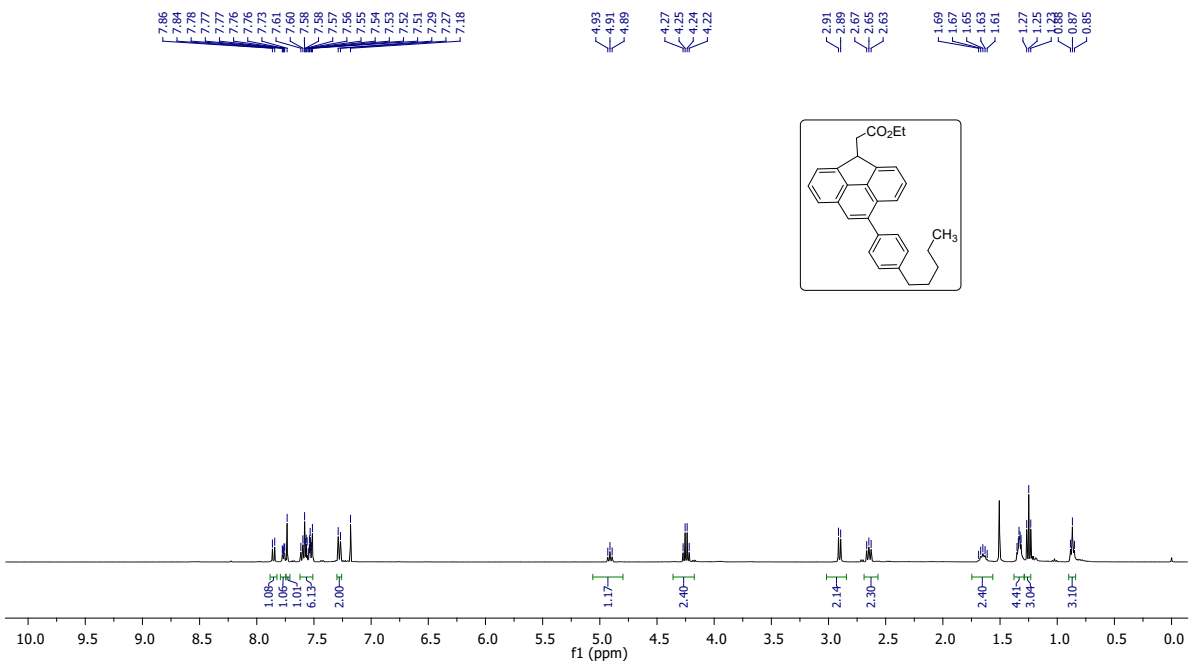
^{13}C{H} NMR (101 MHz) spectrum of **2b** in $CDCl_3$



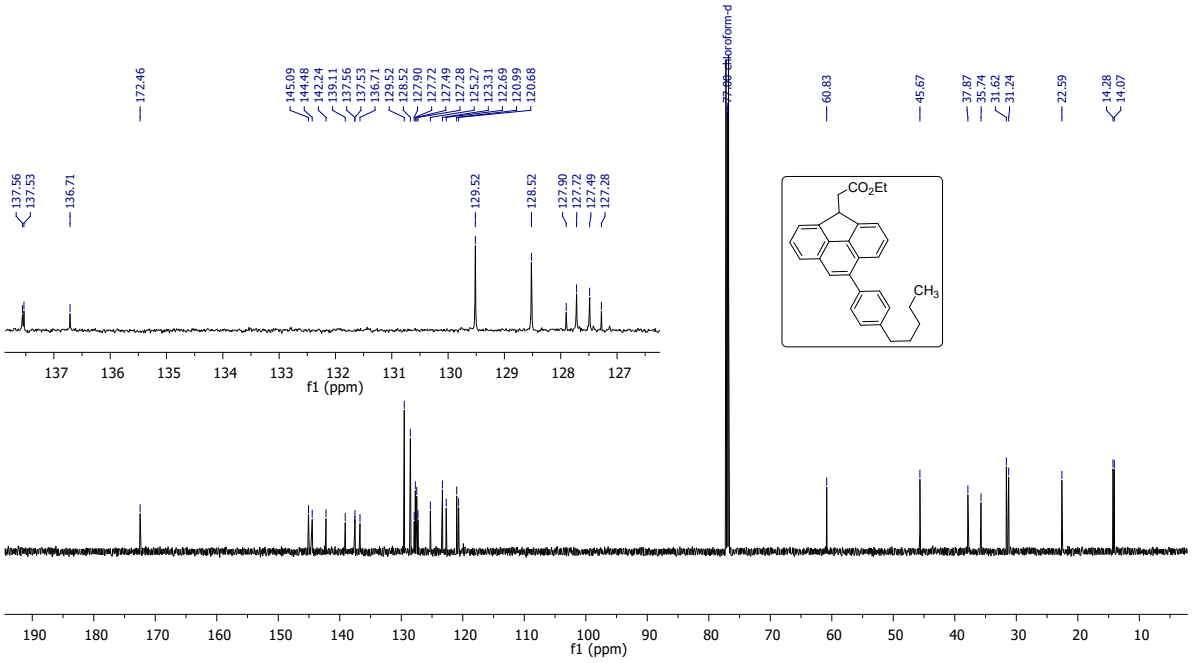
^{1}H NMR (400 MHz) spectrum of **2c** in $CDCl_3$



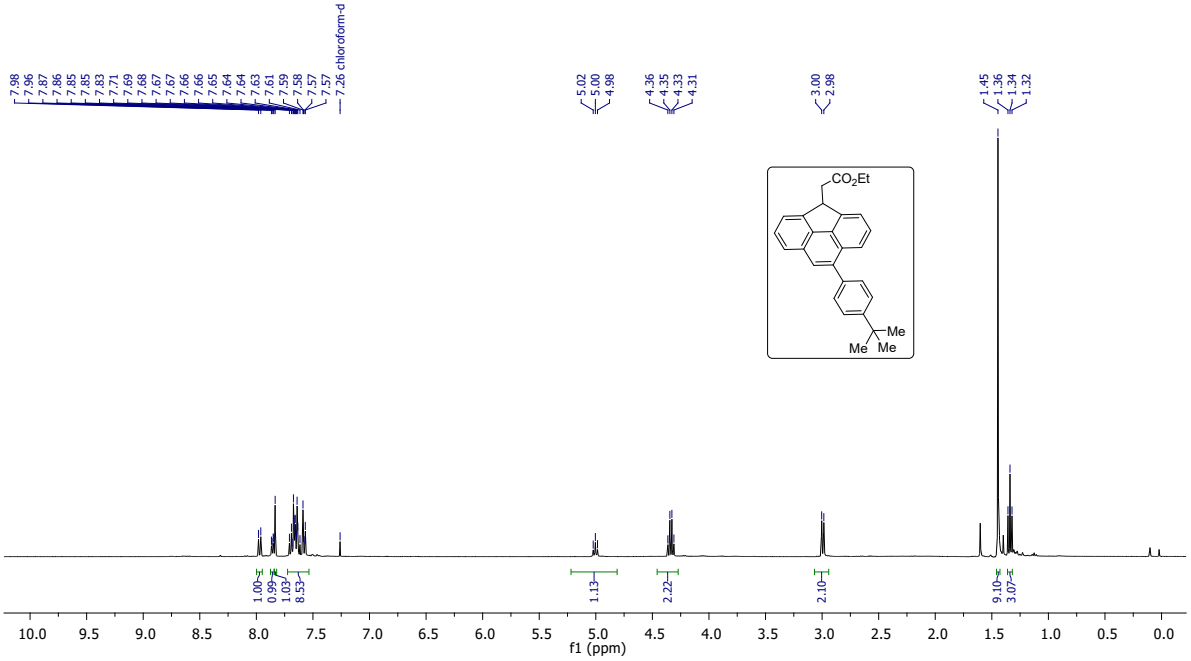
^{13}C{H} NMR (151 MHz) spectrum of **2c** in $CDCl_3$



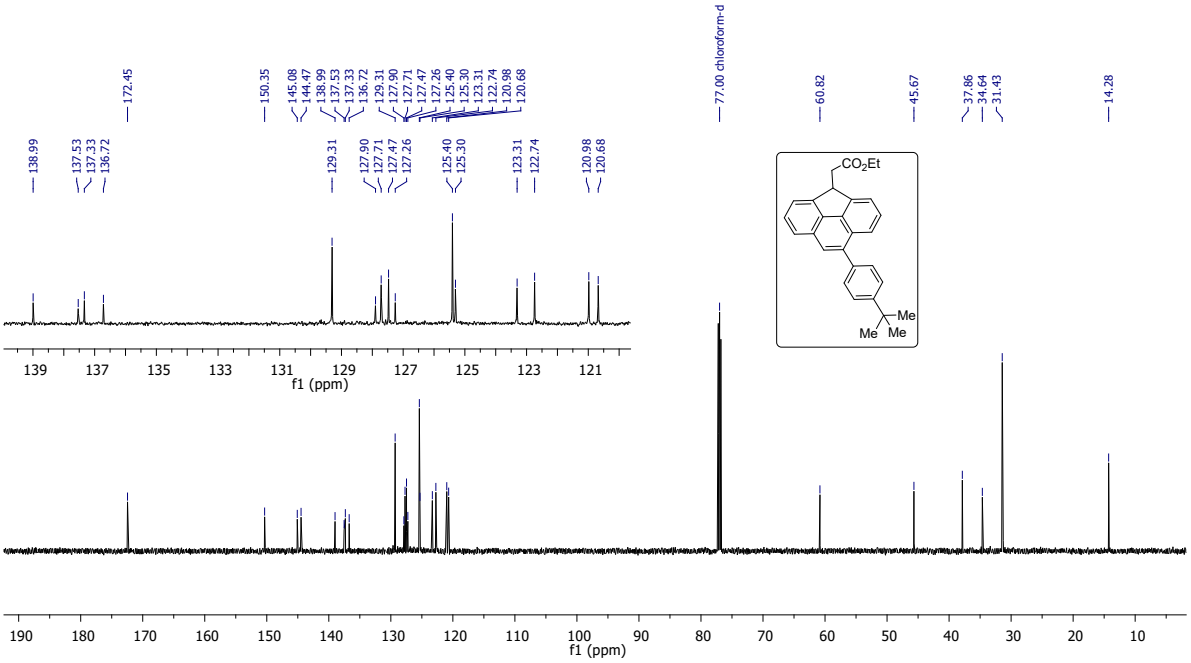
^{1}H NMR (400 MHz) spectrum of **2d** in $CDCl_3$



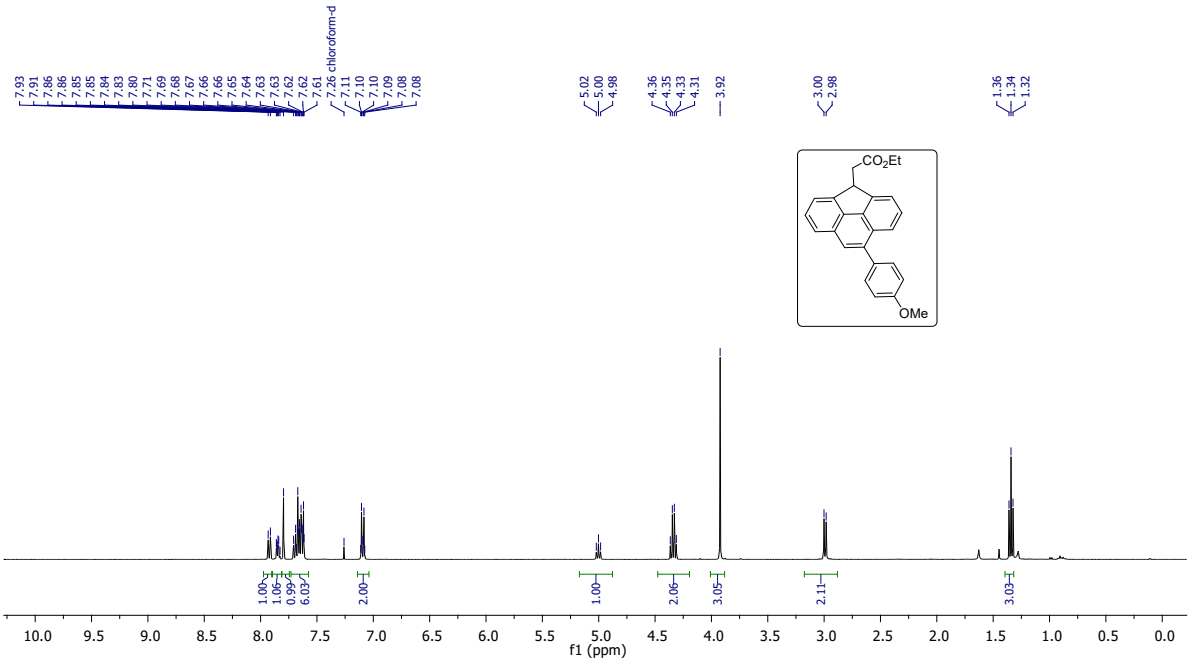
^{13}C{H} NMR (151 MHz) spectrum of **2d** in $CDCl_3$



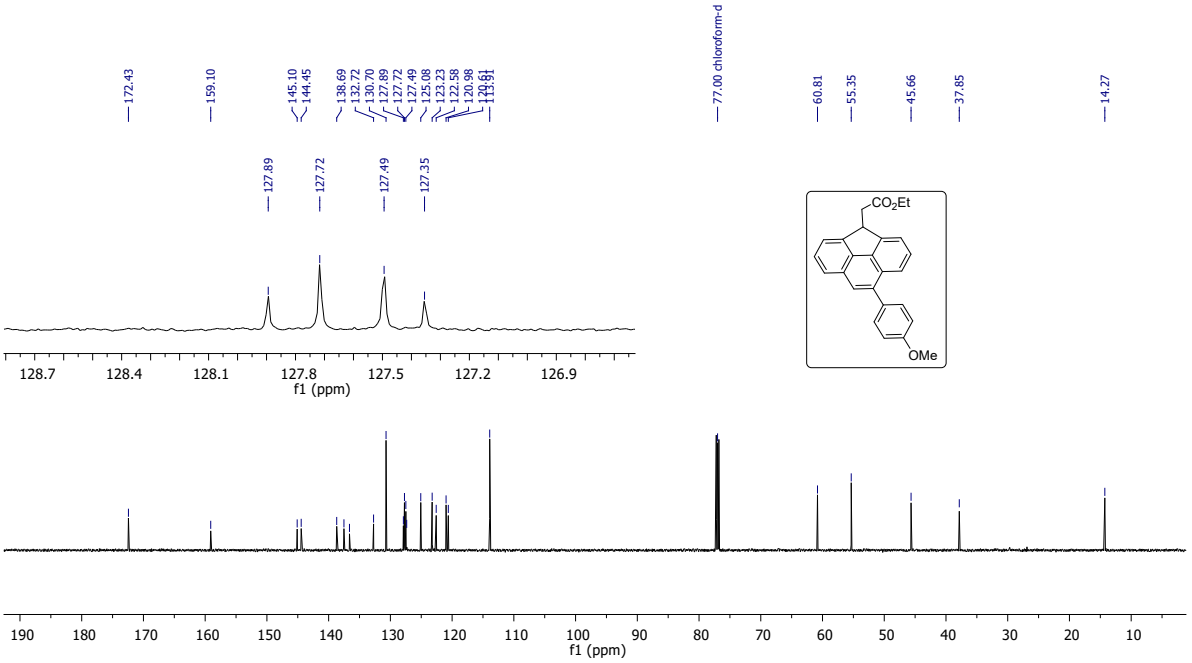
^{1}H NMR (400 MHz) spectrum of **2e** in $CDCl_3$



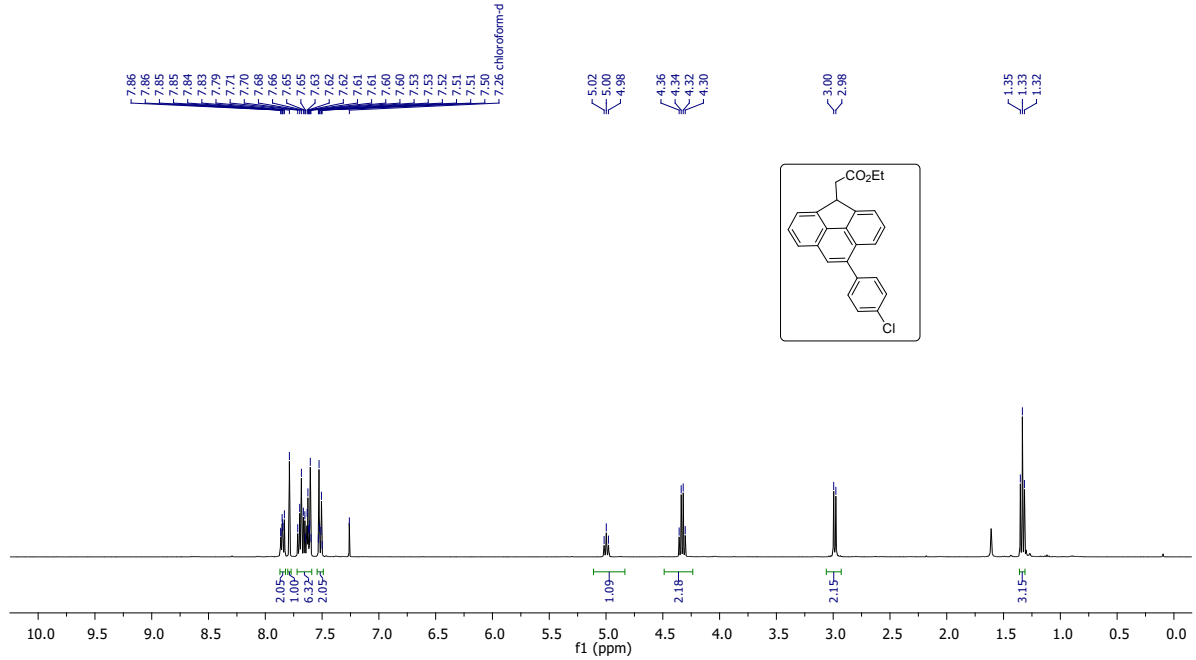
^{13}C{H} NMR (151 MHz) spectrum of **2e** in $CDCl_3$



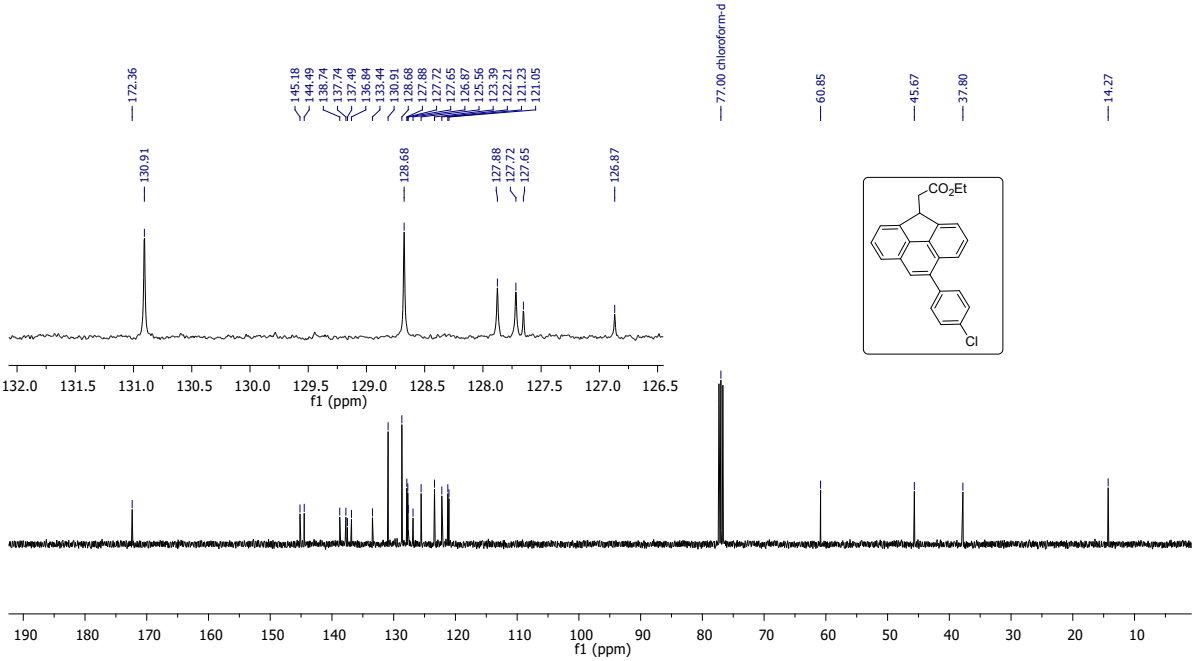
^{1}H NMR (400 MHz) spectrum of **2f** in $CDCl_3$



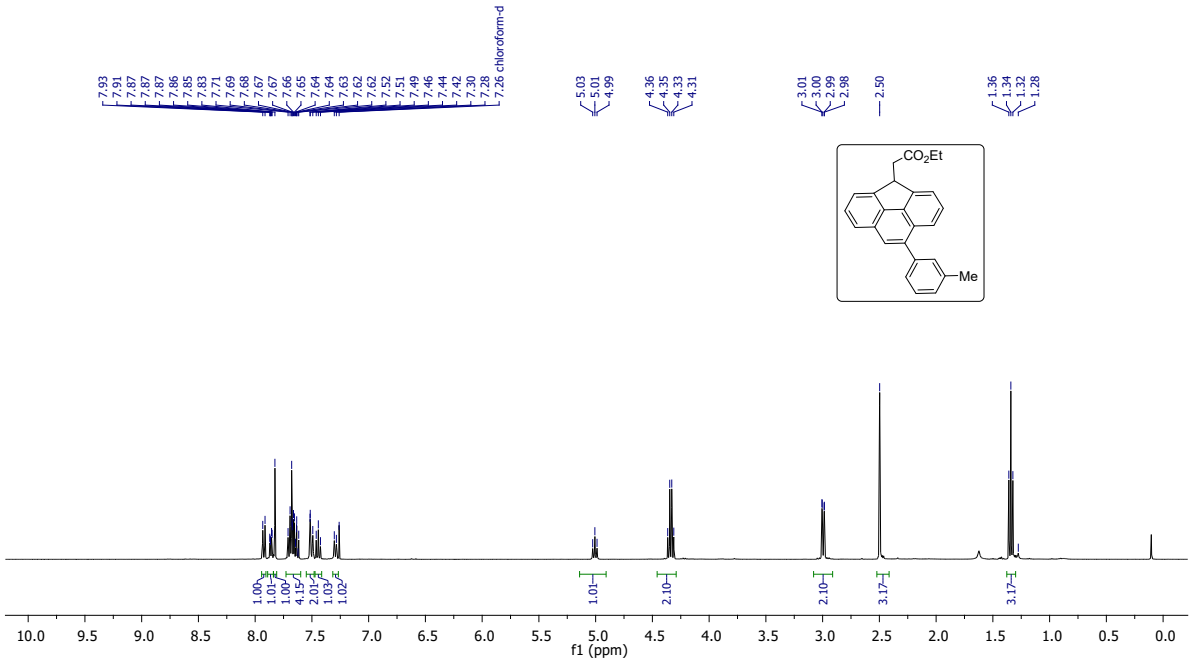
^{13}C{H} NMR (151 MHz) spectrum of **2f** in $CDCl_3$



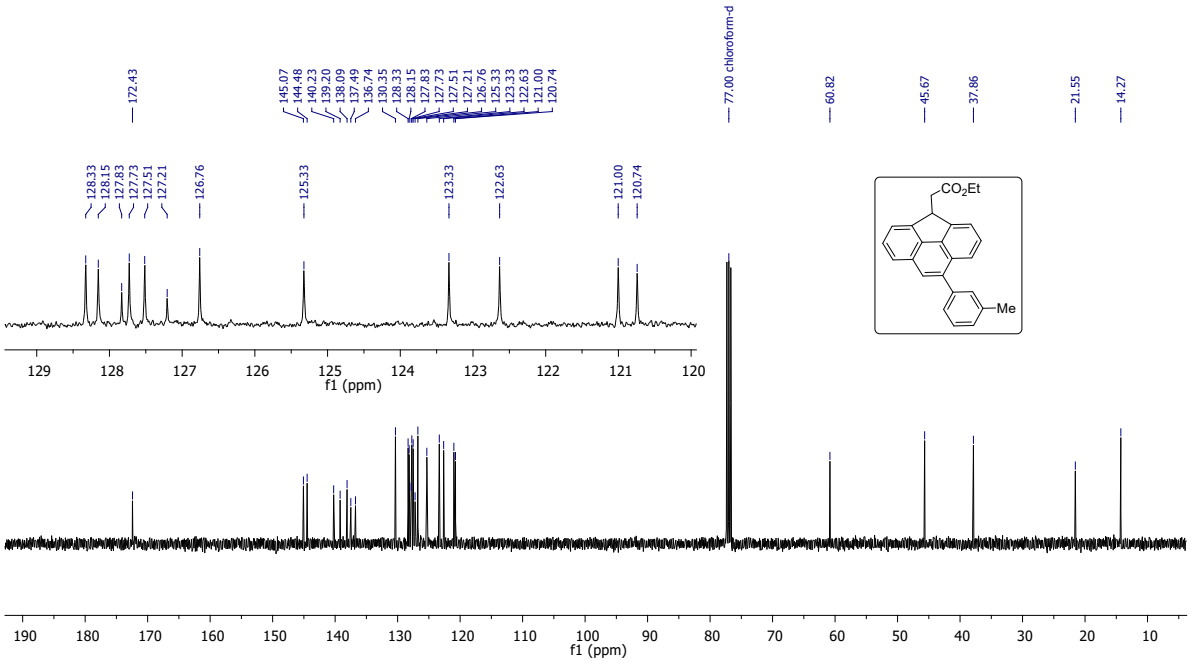
^{1}H NMR (400 MHz) spectrum of **2g** in $CDCl_3$



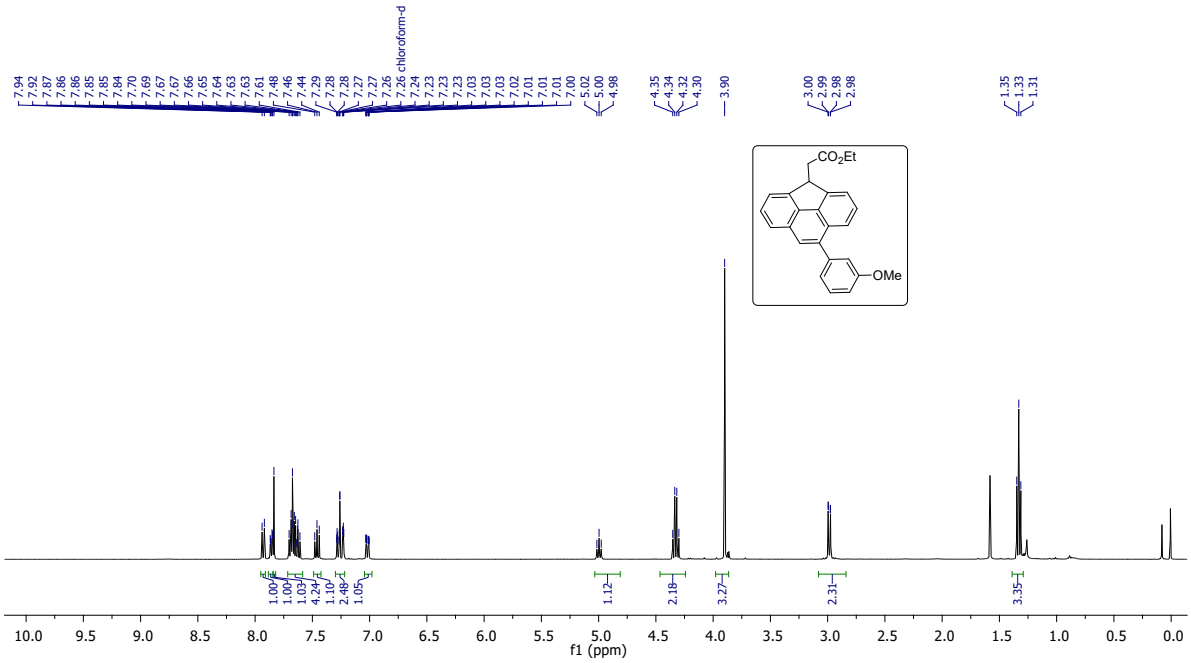
^{13}C{H} NMR (101 MHz) spectrum of **2g** in $CDCl_3$



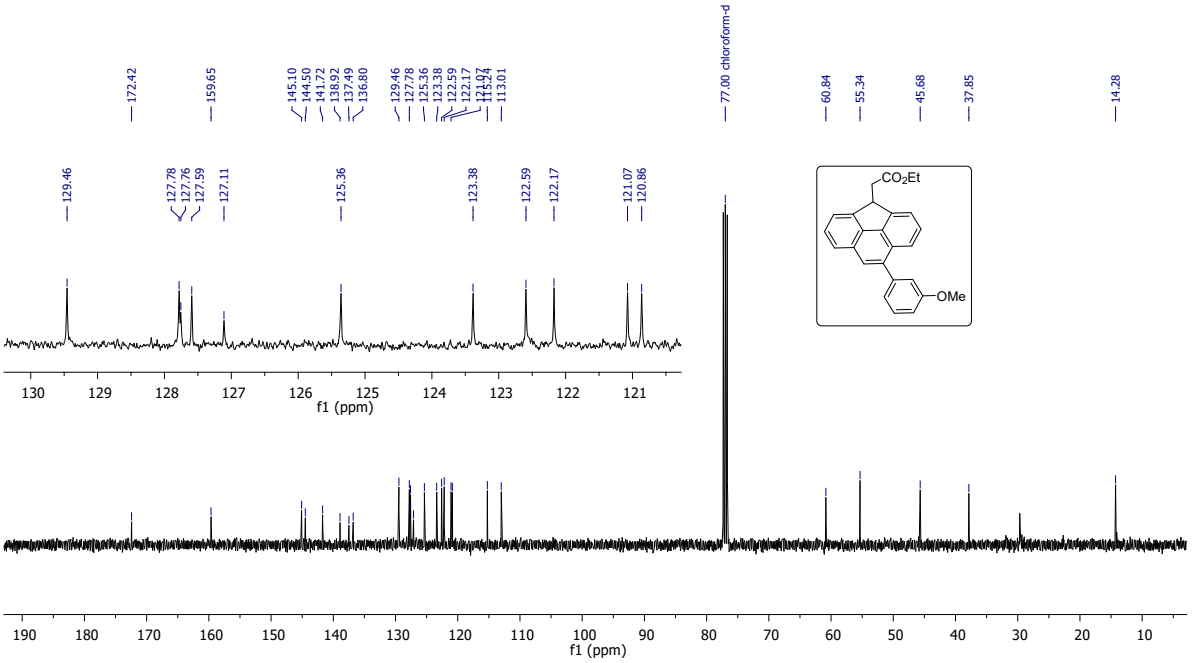
^{1}H NMR (400 MHz) spectrum of **2h** in $CDCl_3$



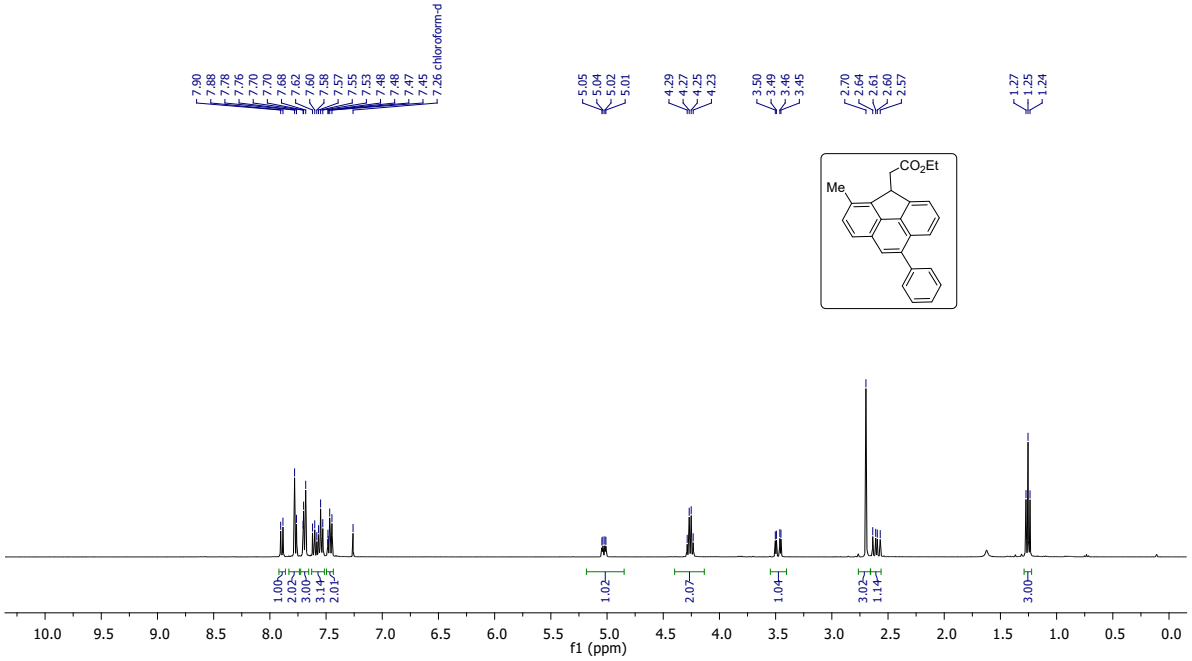
^{13}C{H} NMR (101 MHz) spectrum of **2h** in $CDCl_3$



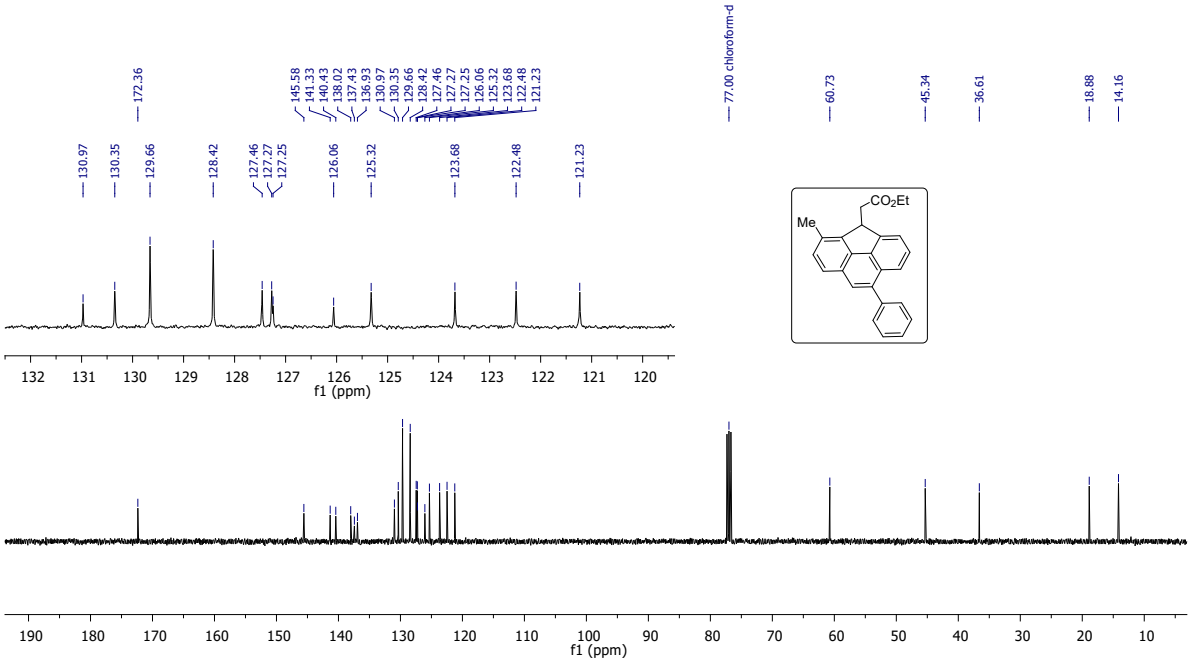
^{1}H NMR (400 MHz) spectrum of **2i** in $CDCl_3$



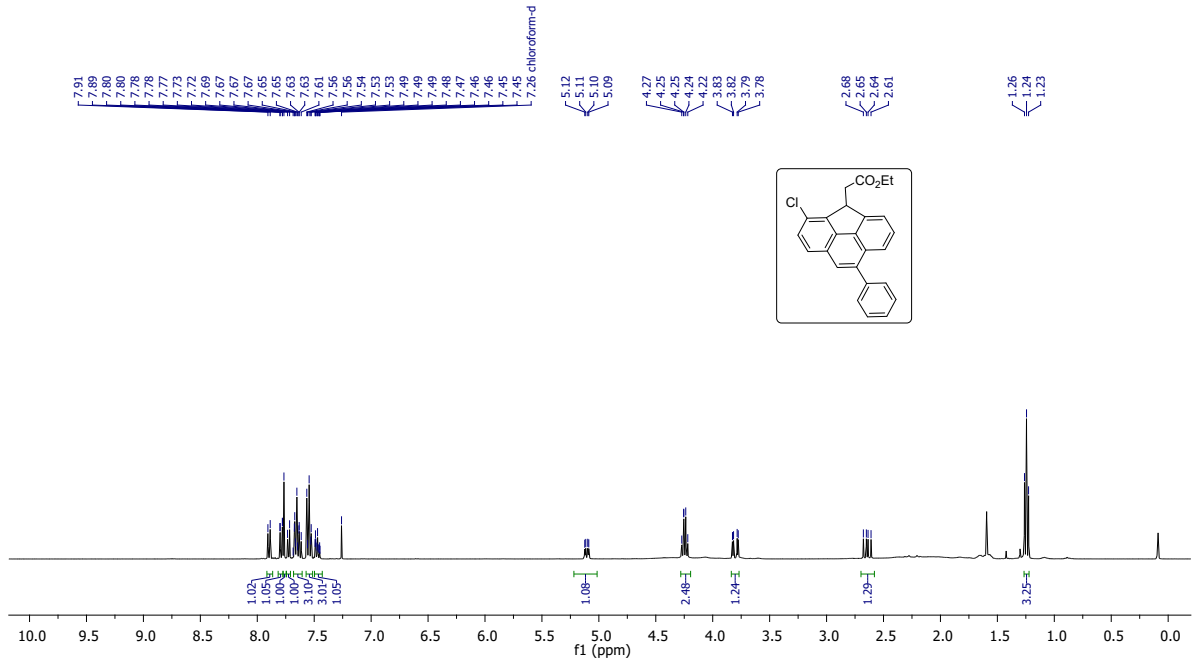
^{13}C{H} NMR (101 MHz) spectrum of **2i** in $CDCl_3$



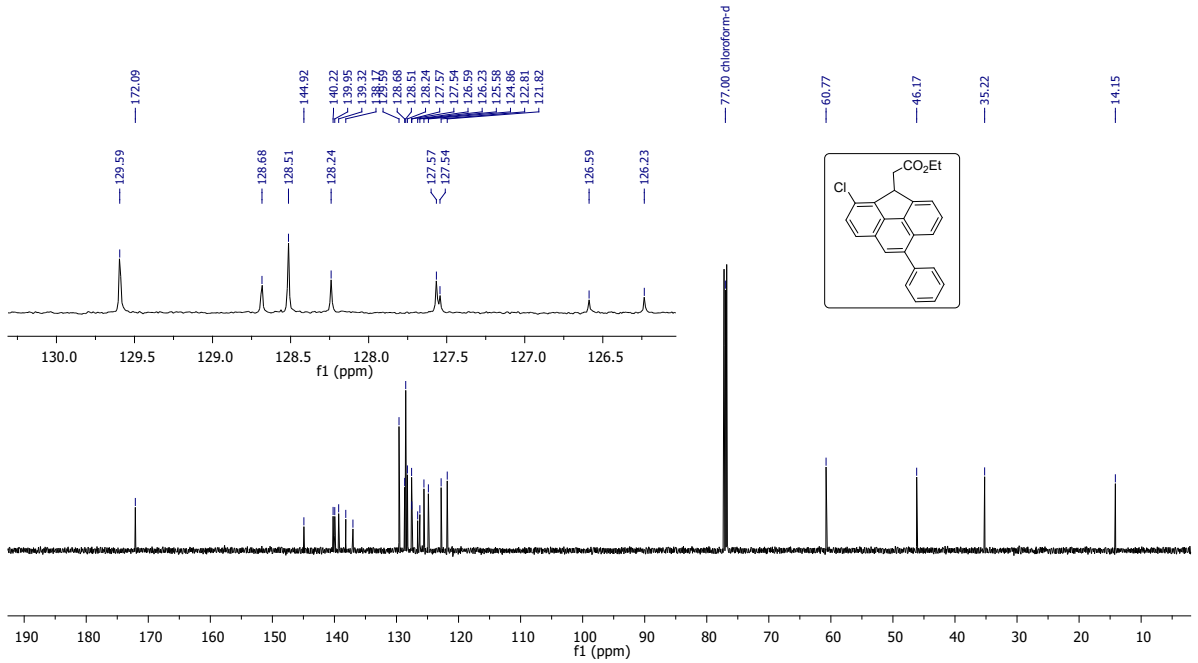
^{1}H NMR (400 MHz) spectrum of **2j** in $CDCl_3$



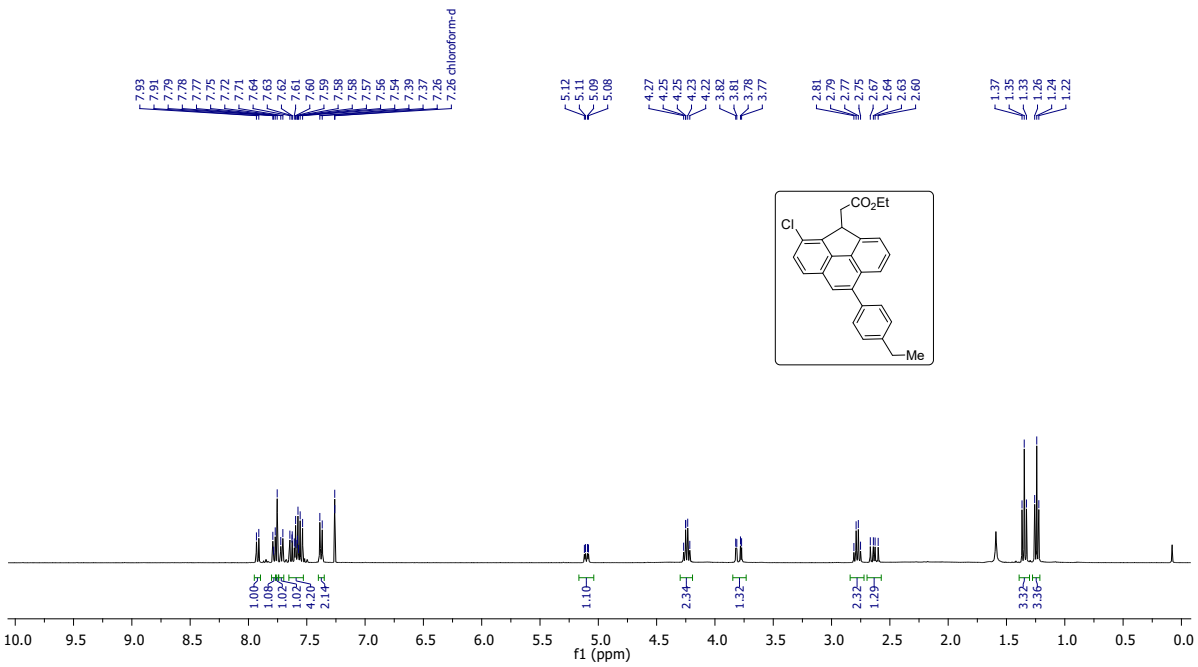
^{13}C{H} NMR (101 MHz) spectrum of **2j** in $CDCl_3$



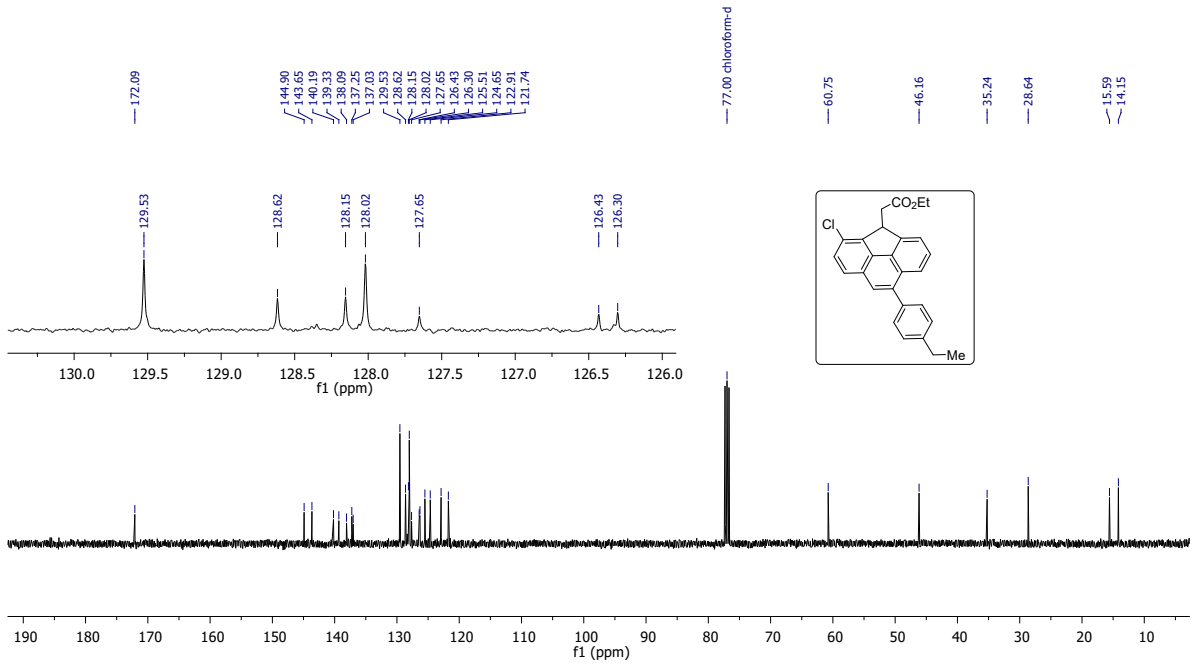
^{1}H NMR (400 MHz) spectrum of **2k** in $CDCl_3$



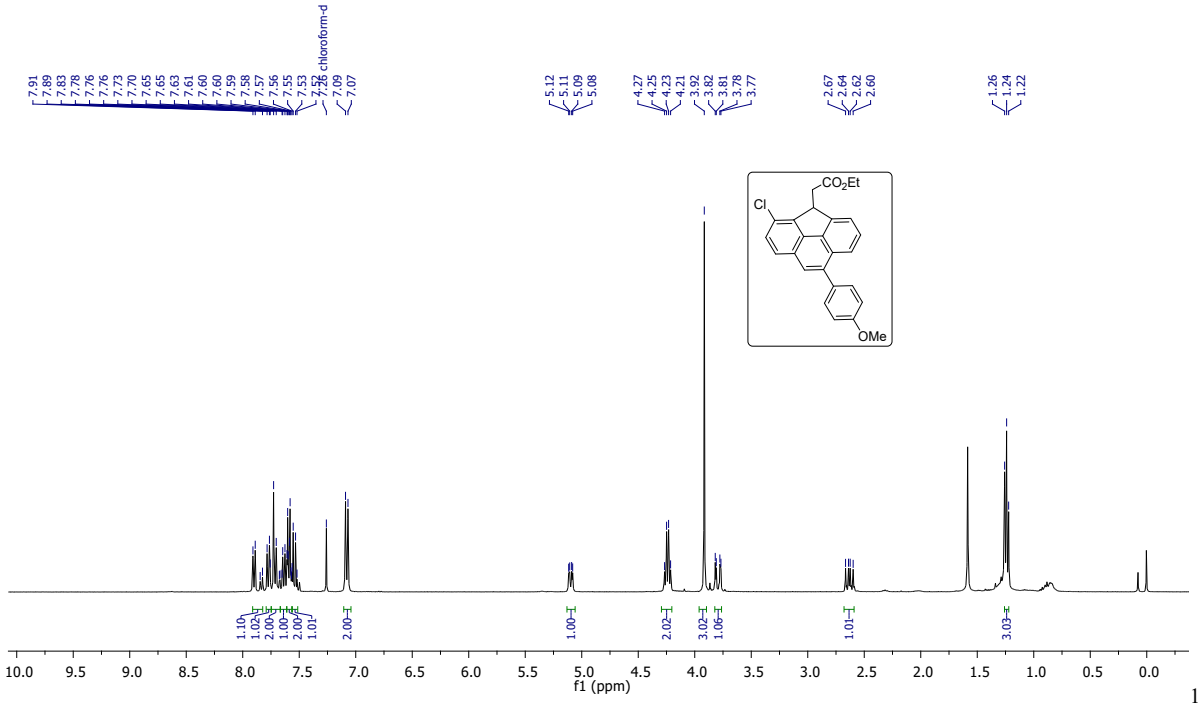
^{13}C{H} NMR (151 MHz) spectrum of **2k** in $CDCl_3$



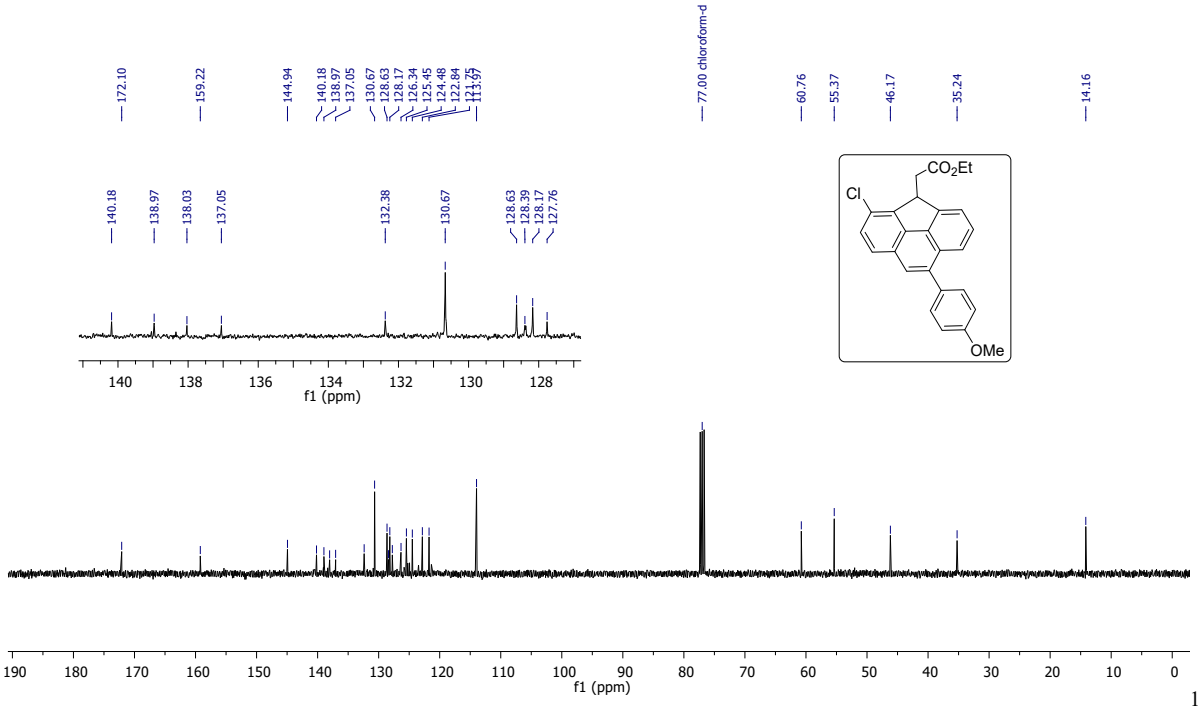
^{1}H NMR (400 MHz) spectrum of **2l** in $CDCl_3$



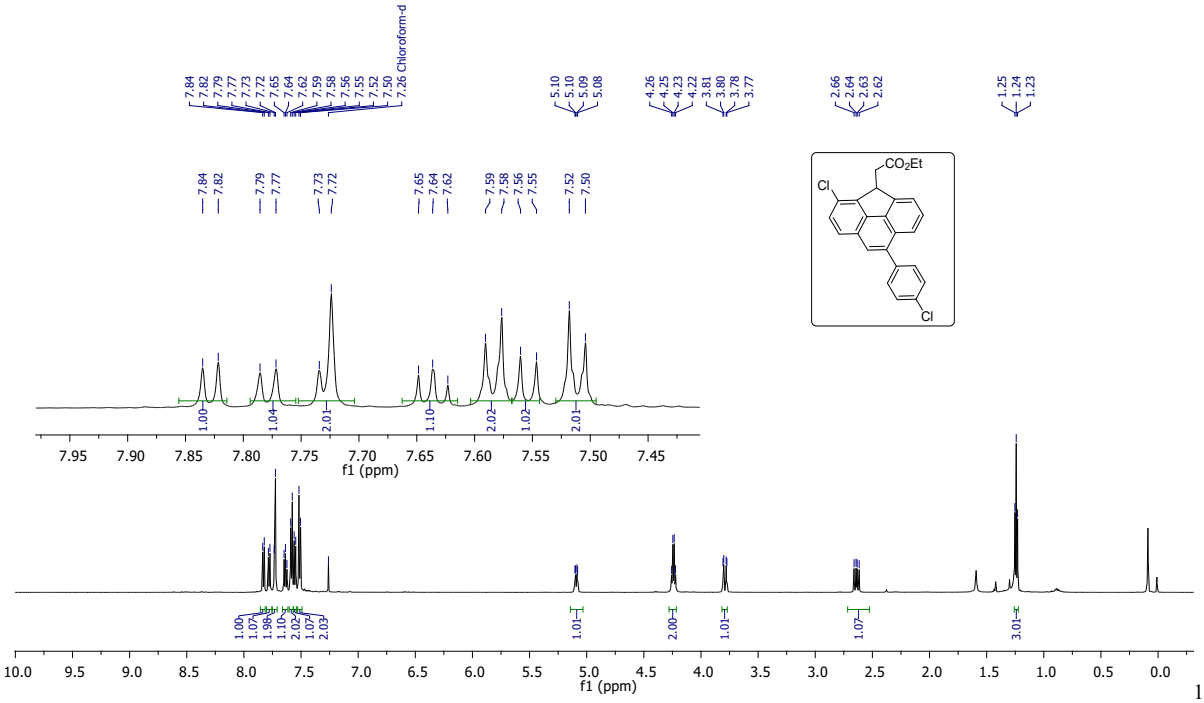
^{13}C{H} NMR (101 MHz) spectrum of **2l** in $CDCl_3$



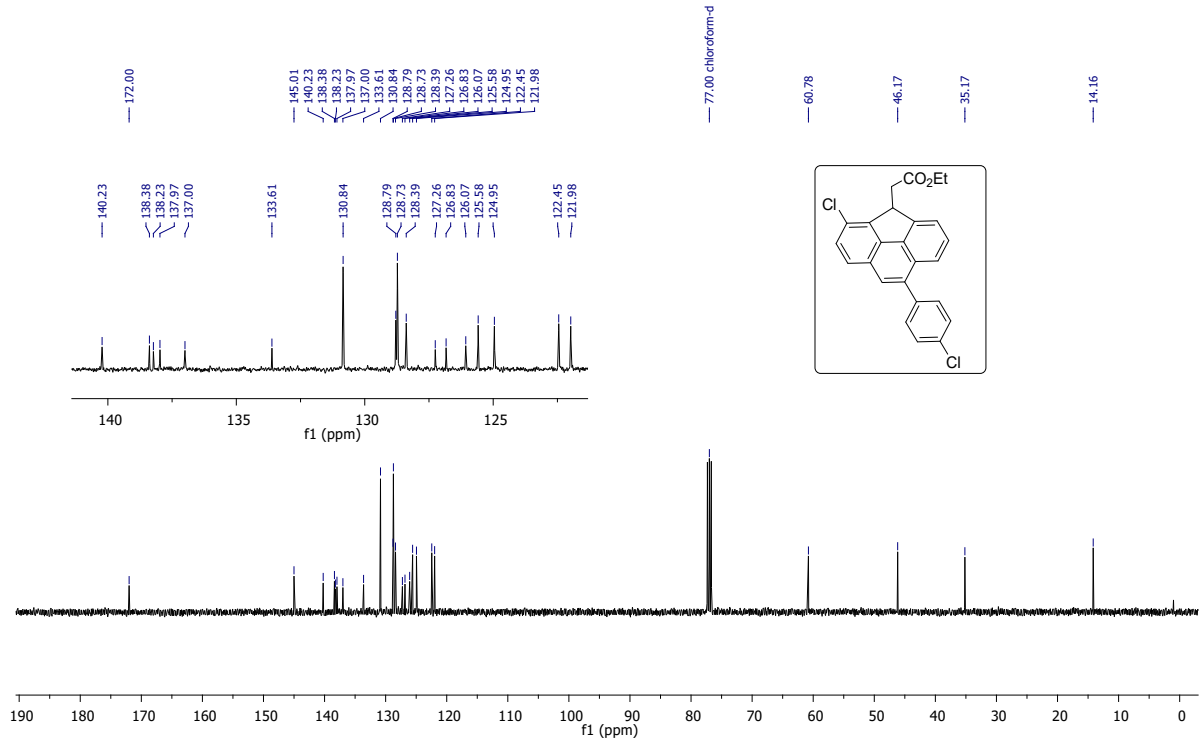
H NMR (400 MHz) spectrum of **2m** in $CDCl_3$



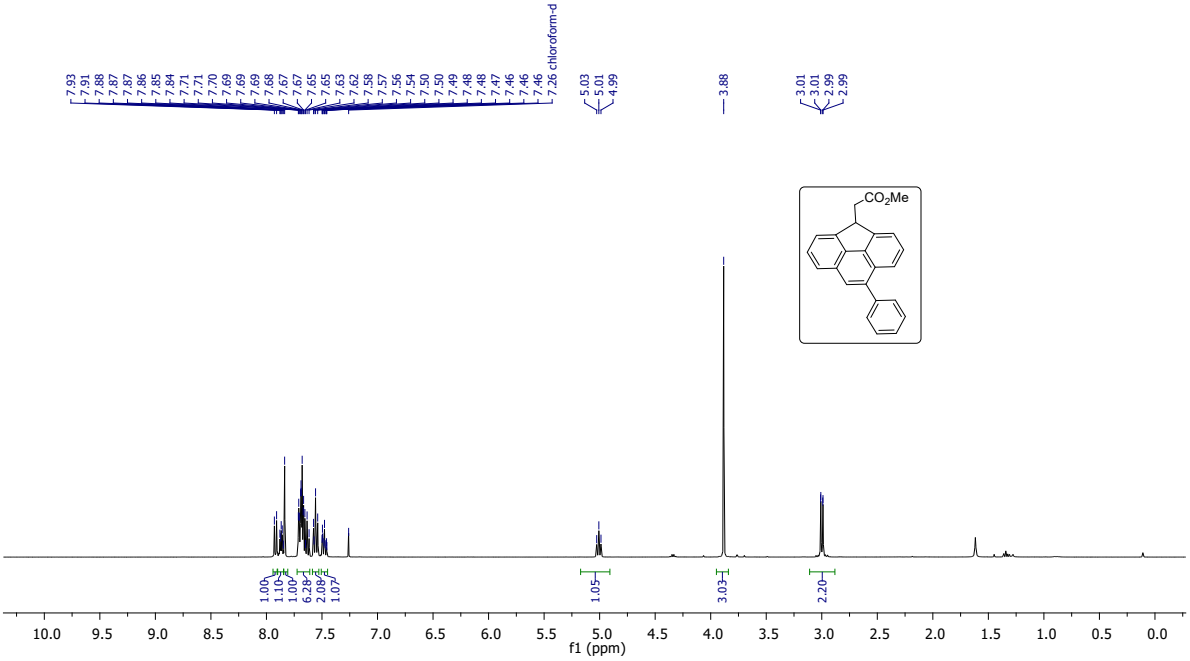
$^{3}C\{H\}$ NMR (101 MHz) spectrum of **2m** in $CDCl_3$



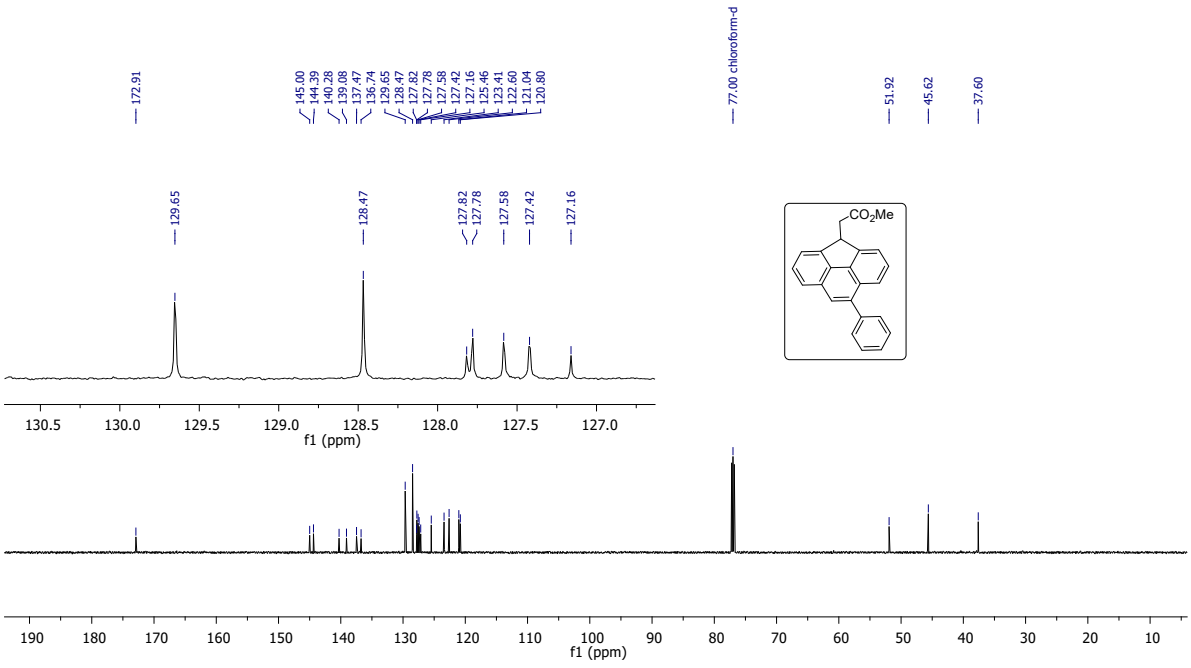
H NMR (600 MHz) spectrum of **2n** in $CDCl_3$



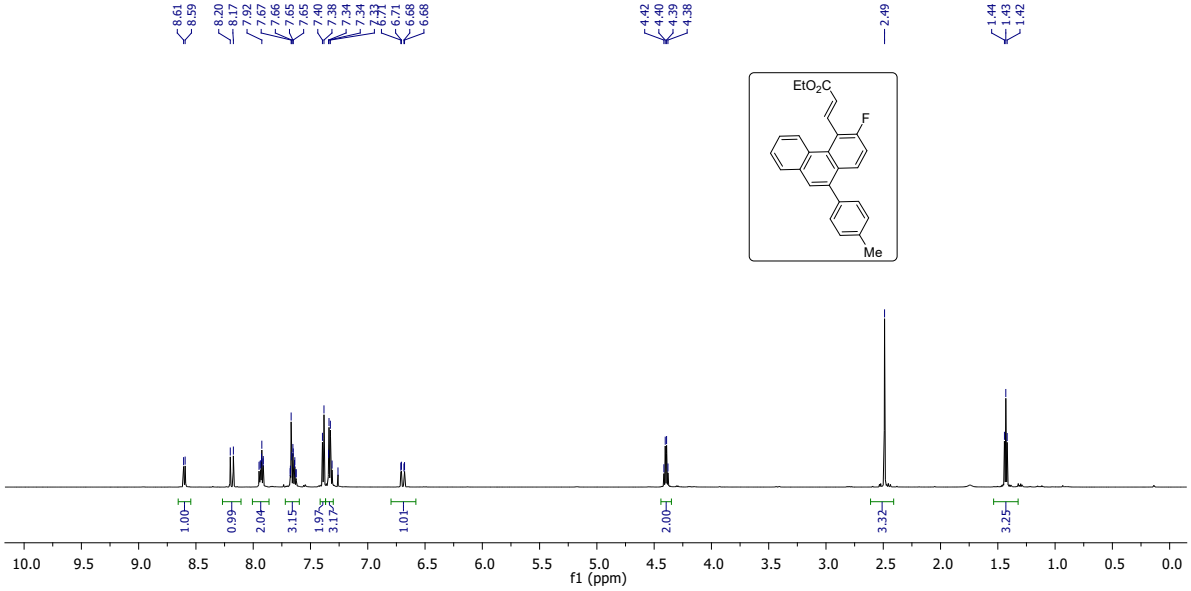
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **2n** in $CDCl_3$



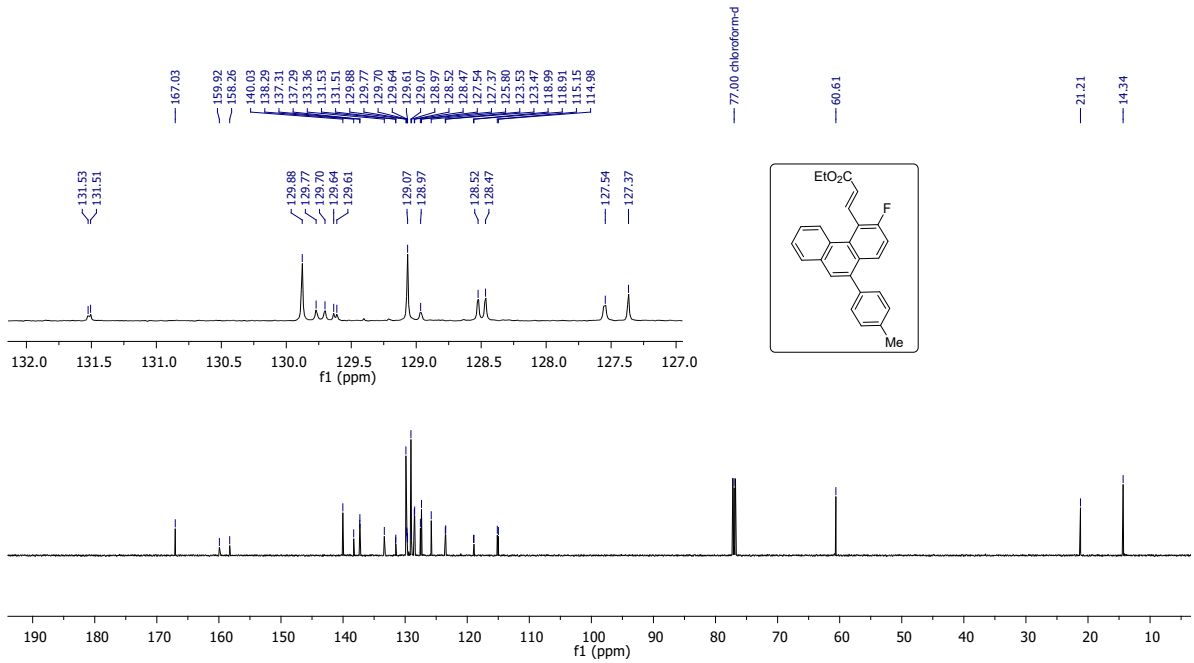
^{1}H NMR (400 MHz) spectrum of **2o** in $CDCl_3$



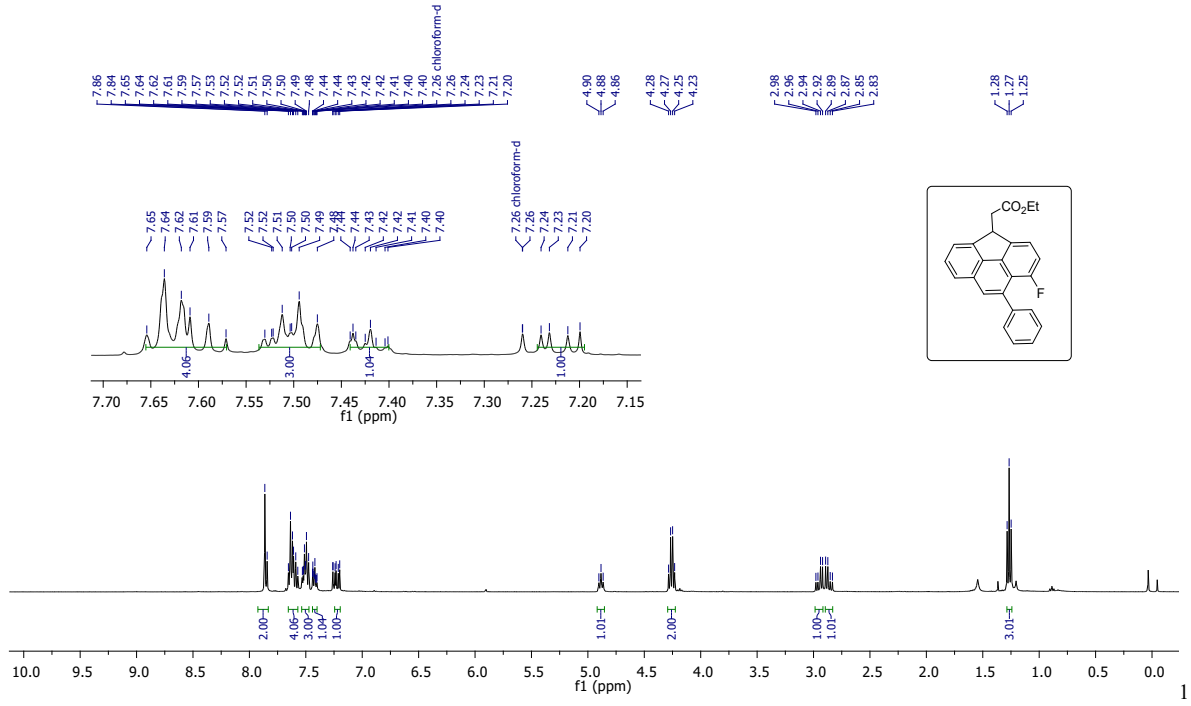
^{13}C{H} NMR (151 MHz) spectrum of **2o** in $CDCl_3$



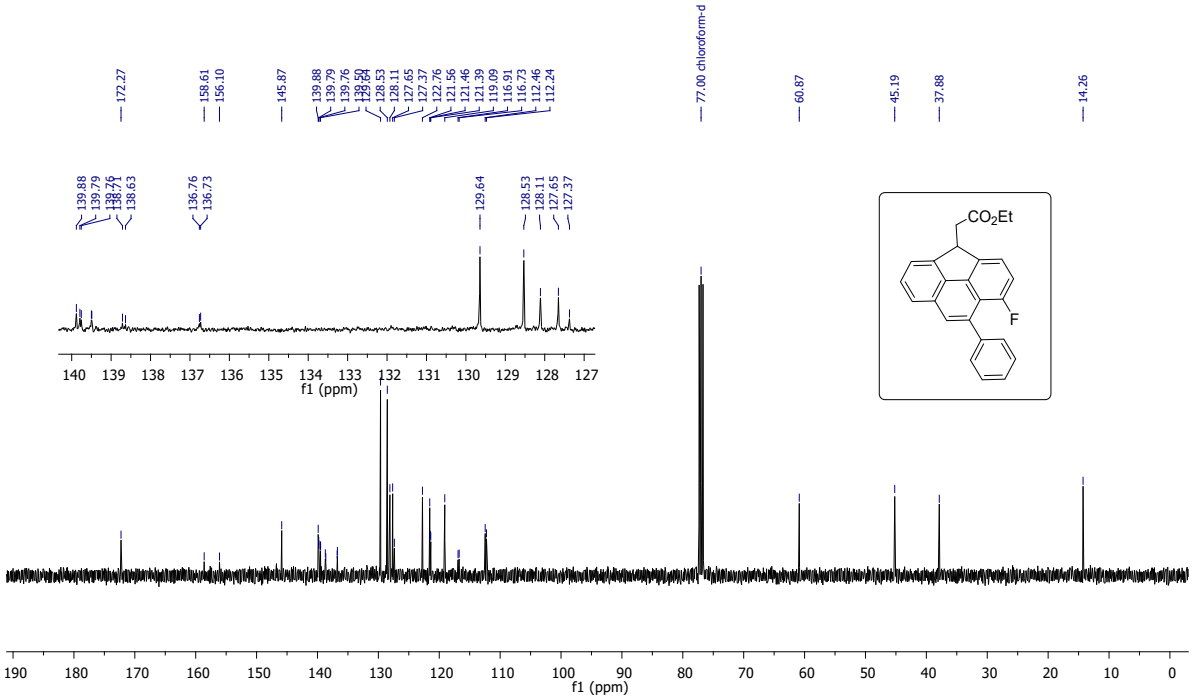
^{1}H NMR (600 MHz) spectrum of **2ip** in $CDCl_3$



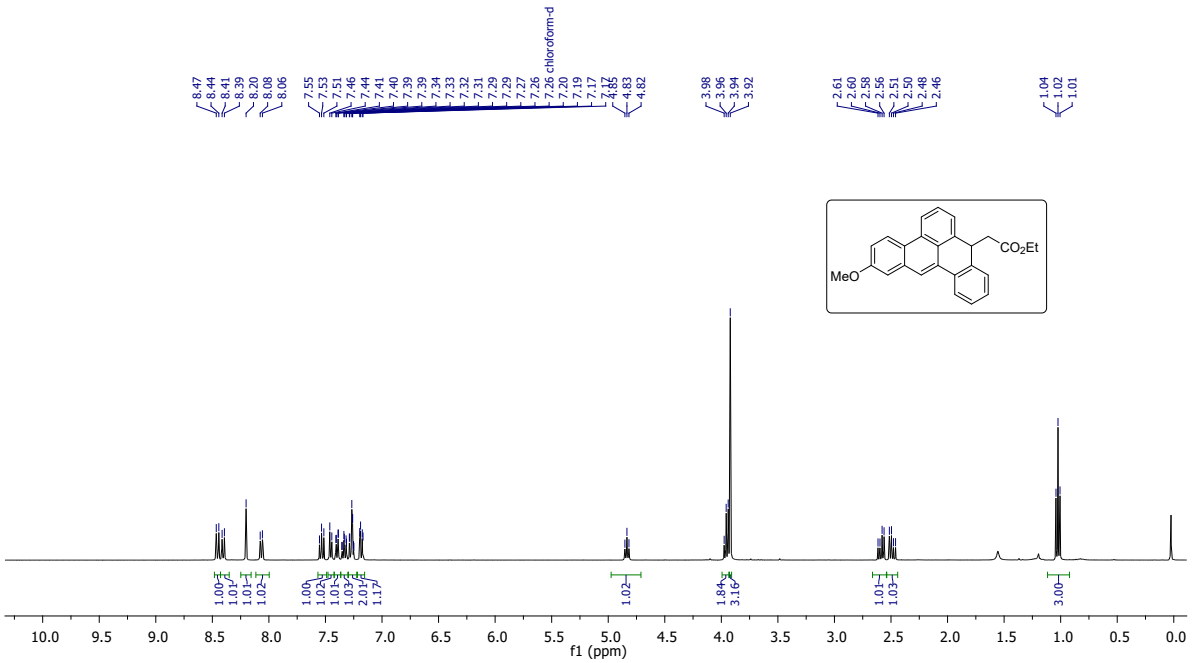
^{13}C{H} NMR (151 MHz) spectrum of **2ip** in $CDCl_3$



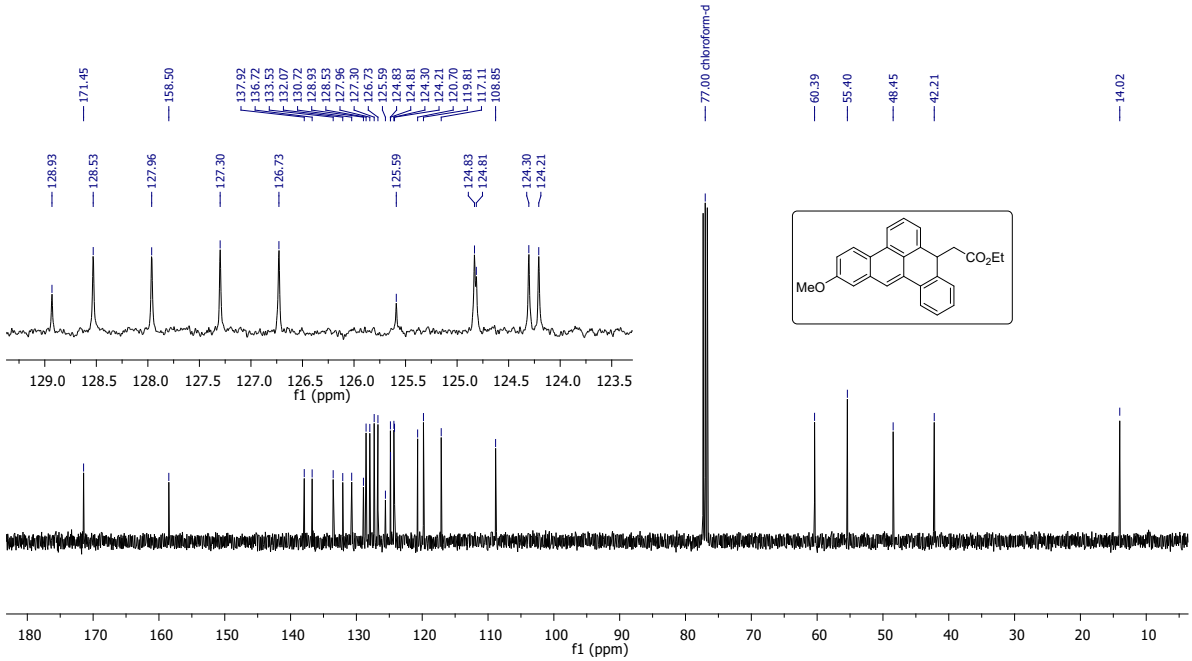
H NMR (400 MHz) spectrum of **2q** in $CDCl_3$



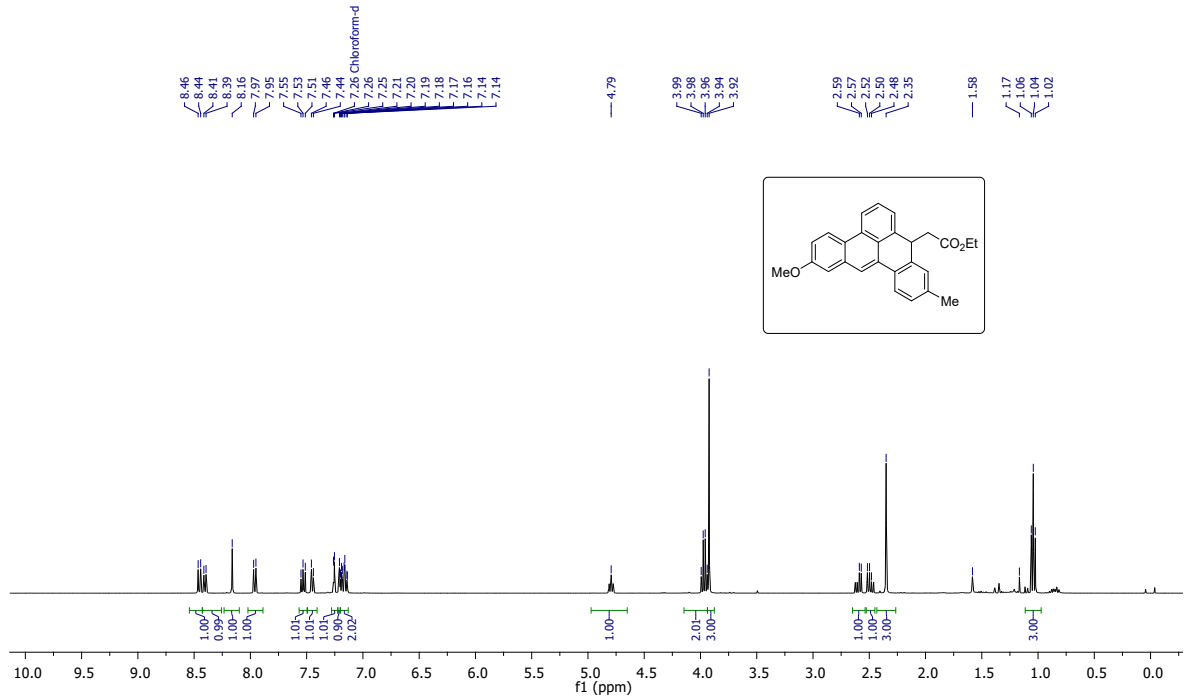
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **2q** in $CDCl_3$



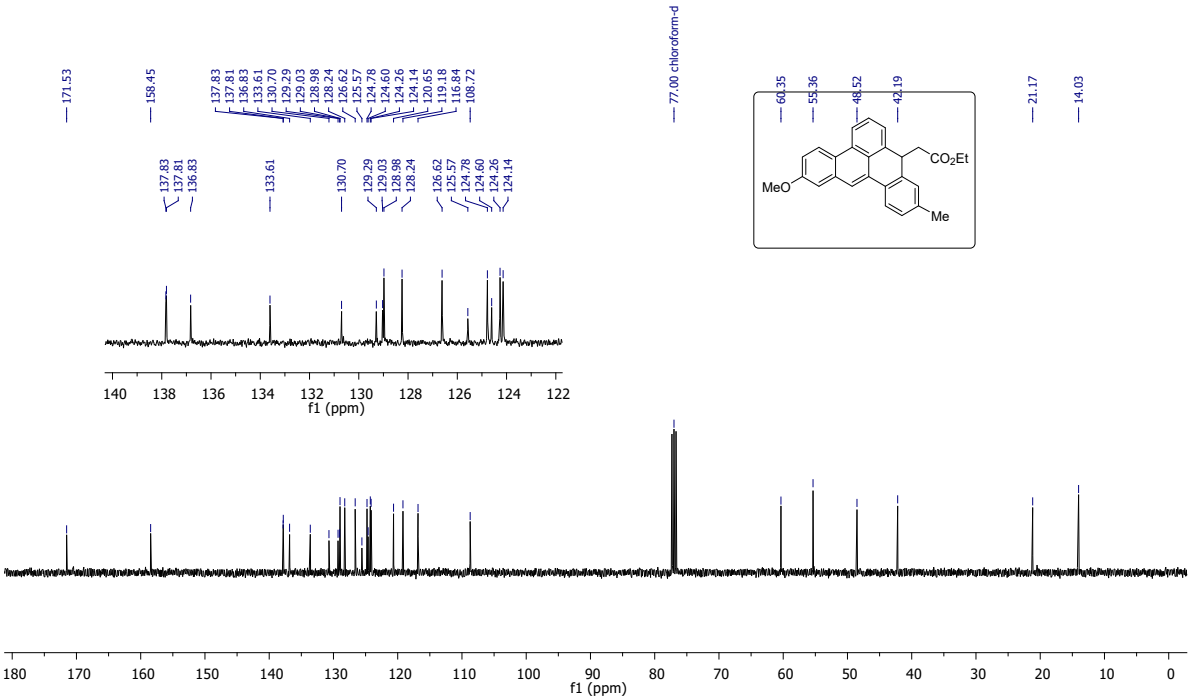
^{1}H NMR (400 MHz) spectrum of **3a** in $CDCl_3$



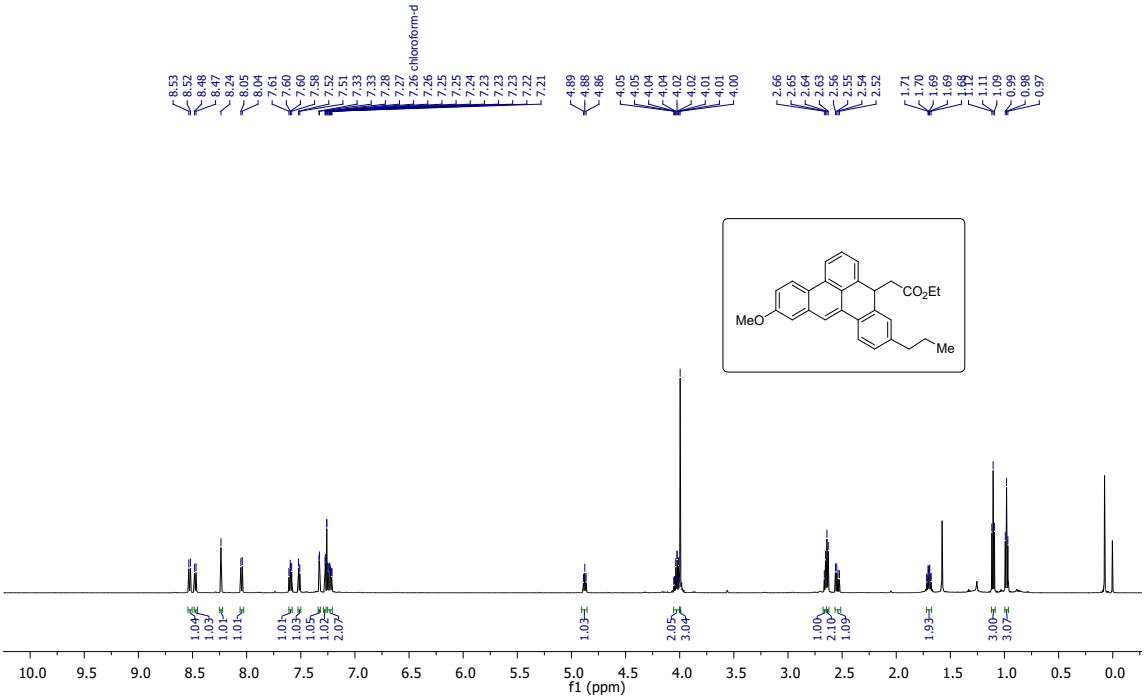
^{13}C{H} NMR (101 MHz) spectrum of **3a** in $CDCl_3$



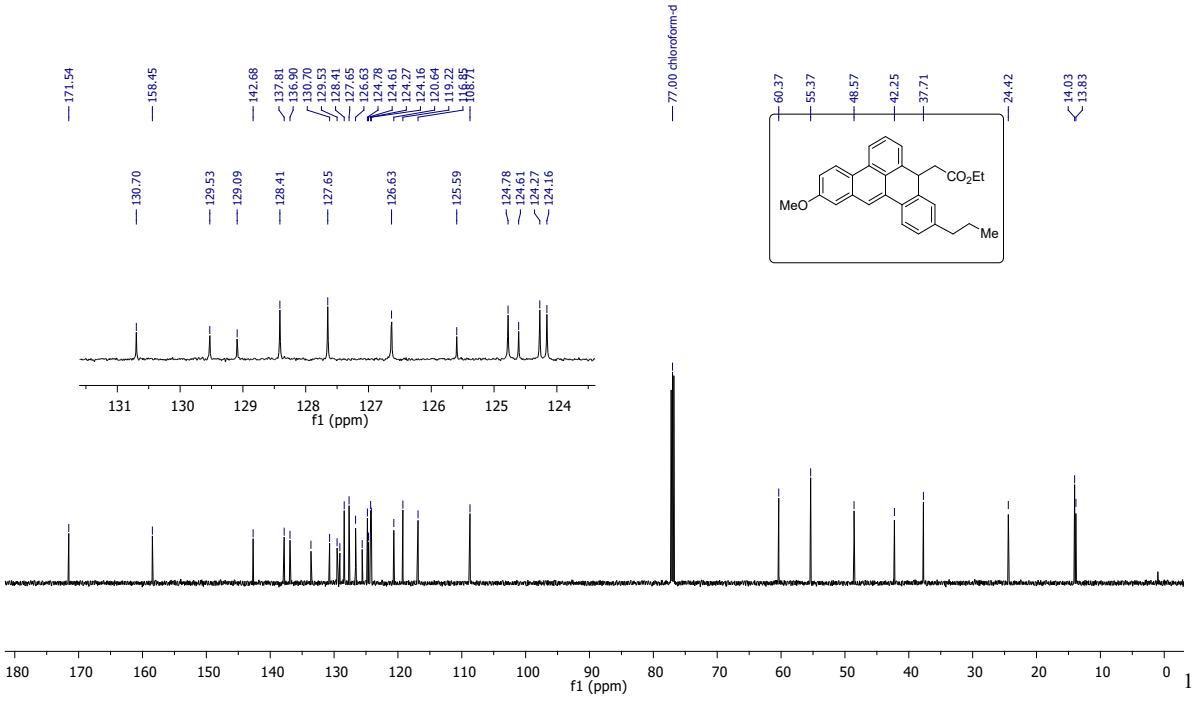
H NMR (400 MHz) spectrum of **3b** in $CDCl_3$



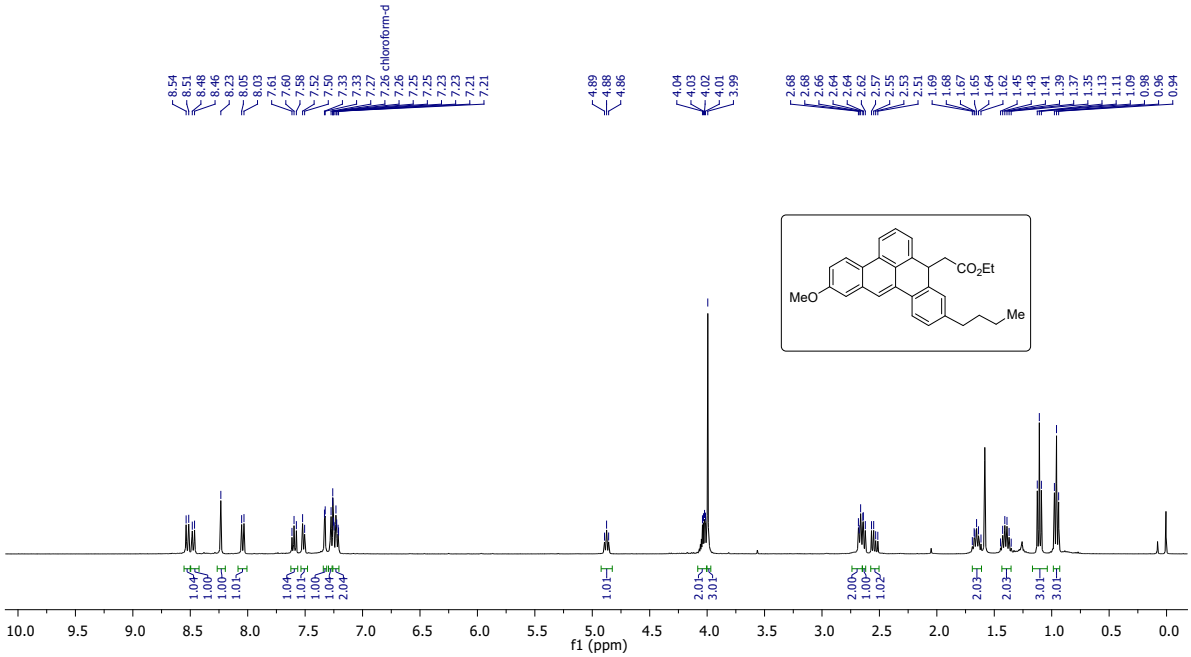
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **3b** in $CDCl_3$



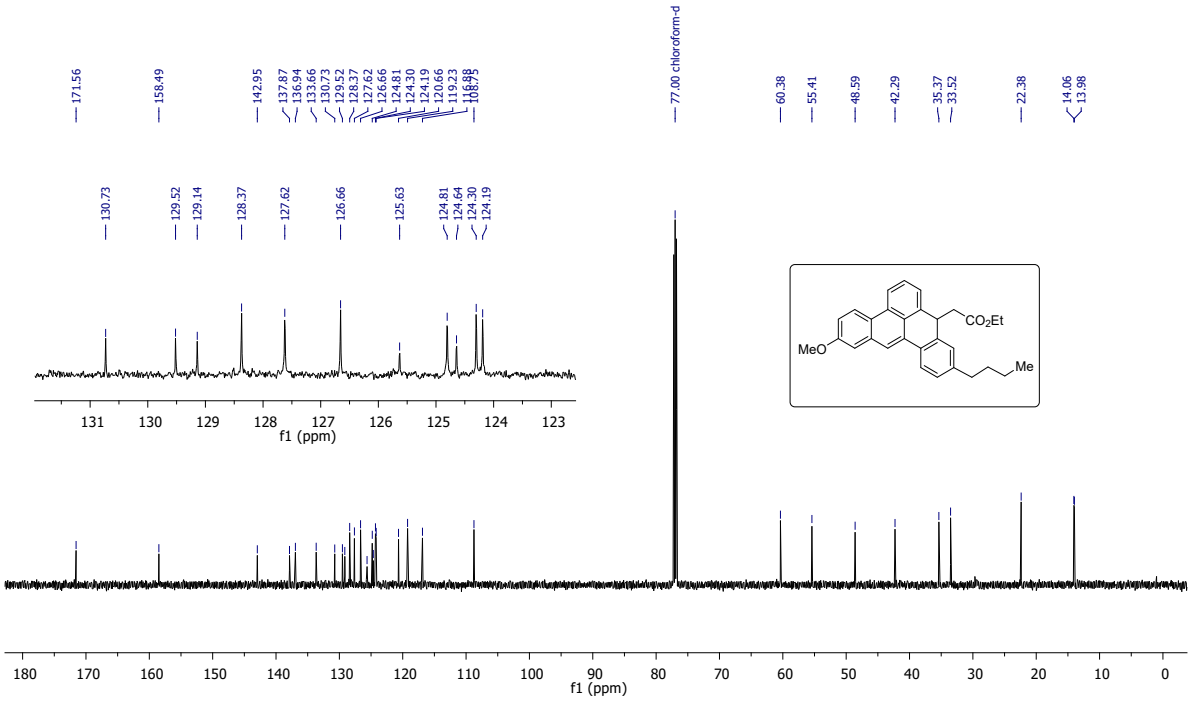
^{1}H NMR (600 MHz) spectrum of **3c** in $CDCl_3$



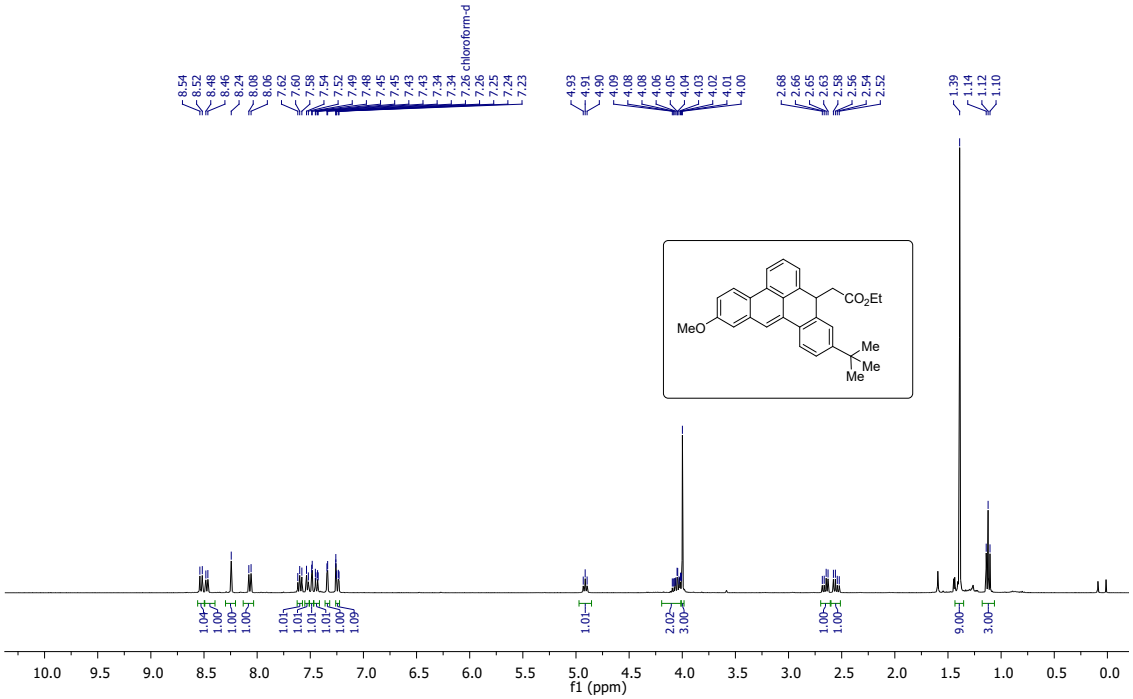
^{3}C{H} NMR (151 MHz) spectrum of **3c** in $CDCl_3$



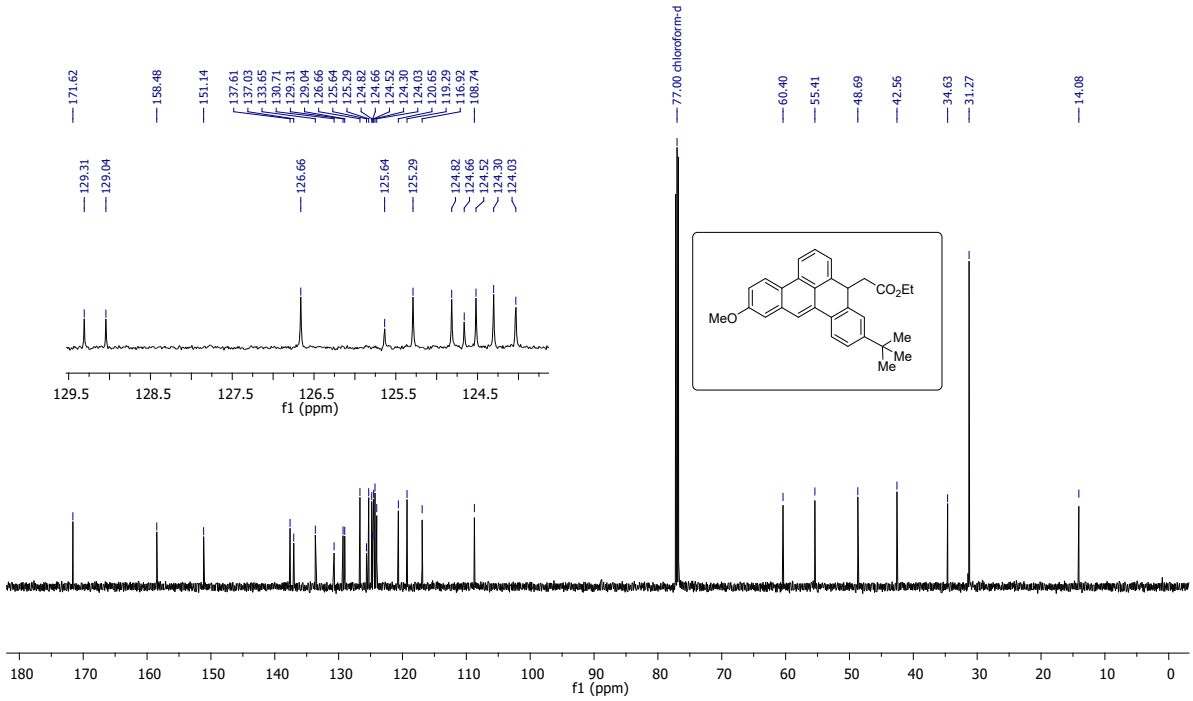
^{1}H NMR (400 MHz) spectrum of **3d** in $CDCl_3$



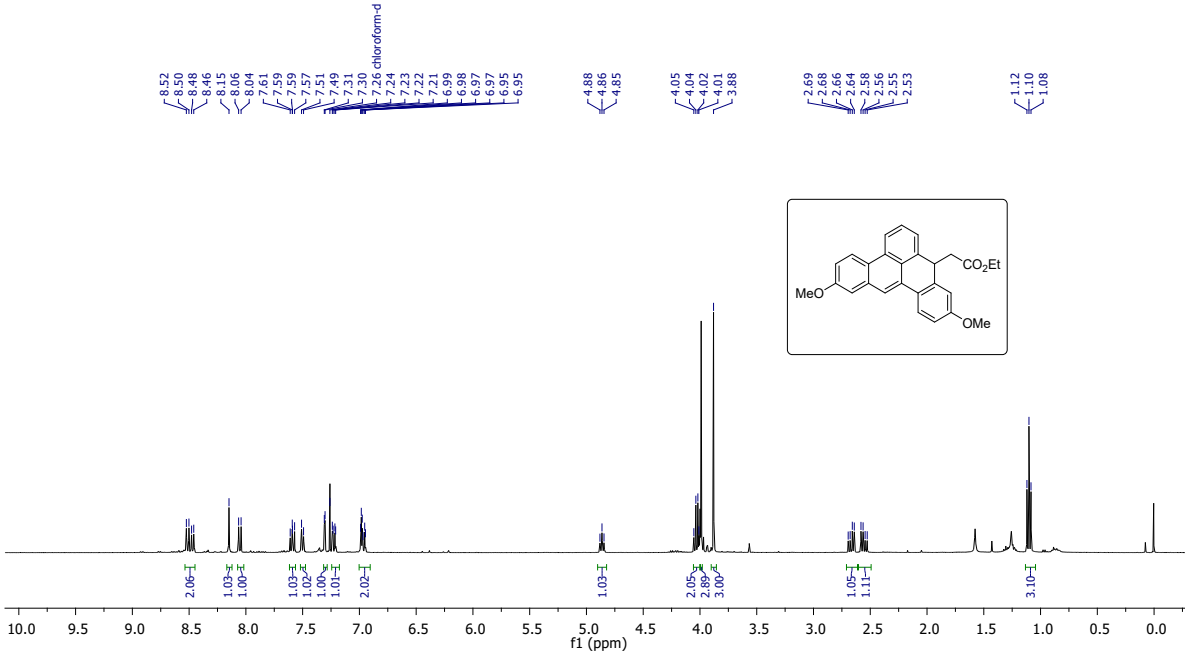
^{13}C{H} NMR (151 MHz) spectrum of **3d** in $CDCl_3$



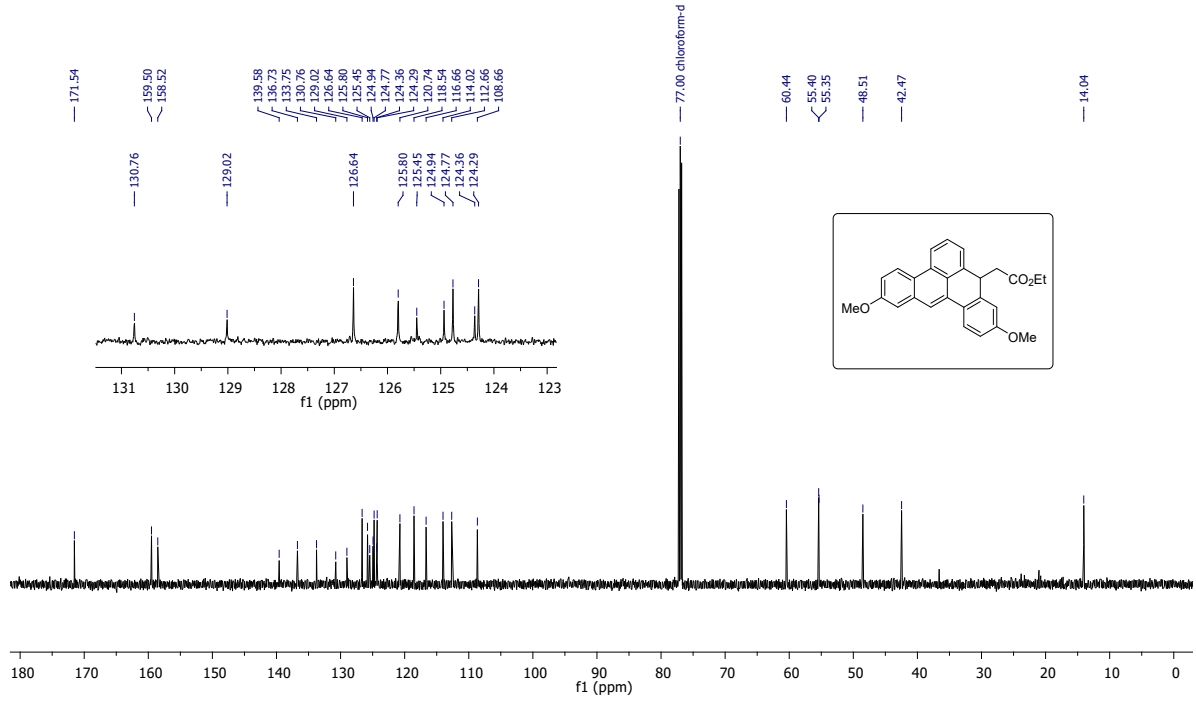
^{1}H NMR (400 MHz) spectrum of **3e** in $CDCl_3$



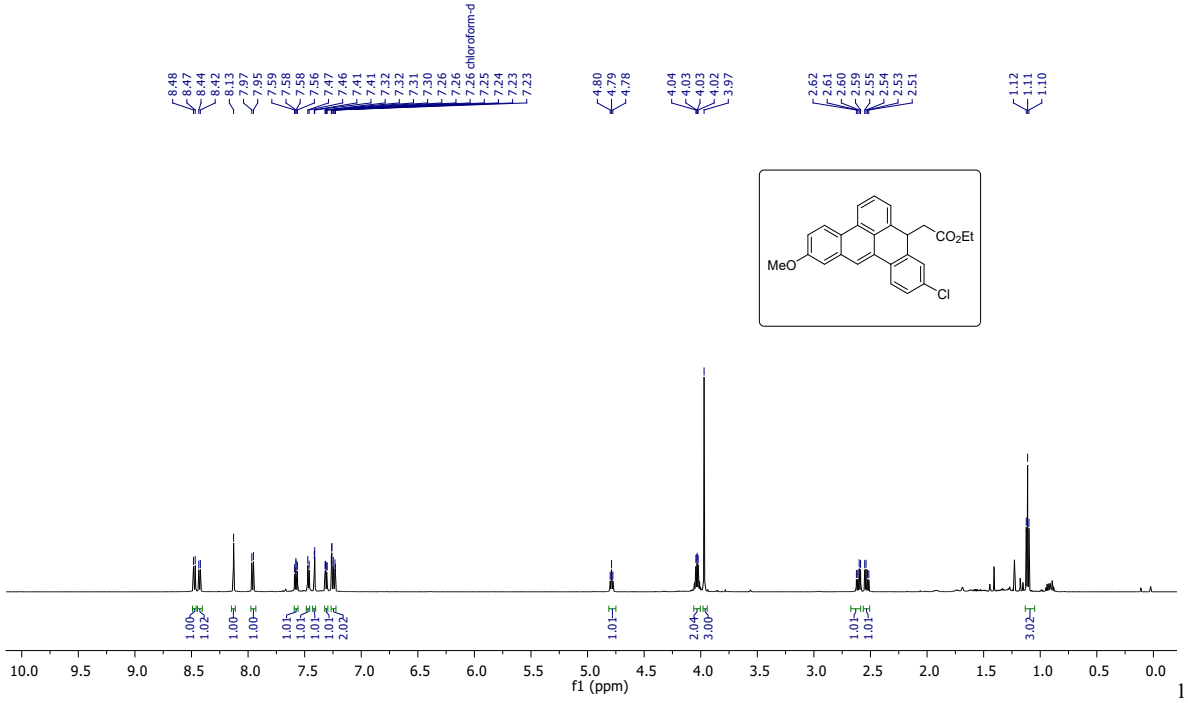
^{13}C{H} NMR (151 MHz) spectrum of **3e** in $CDCl_3$



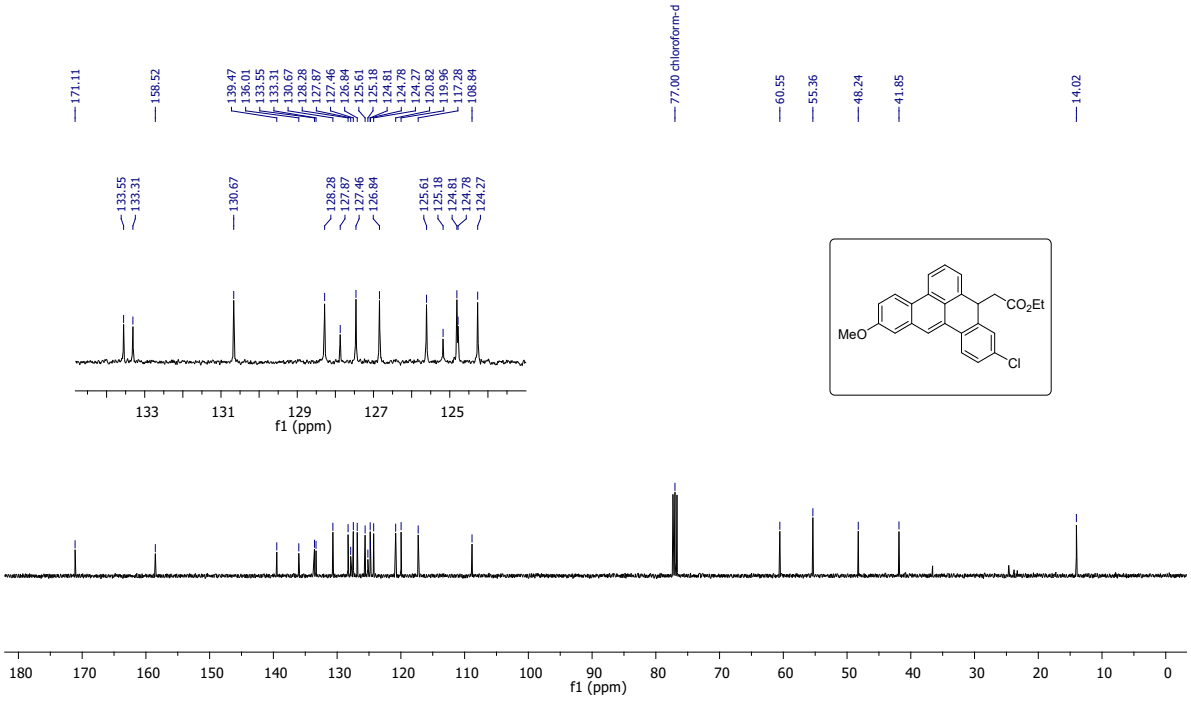
^{1}H NMR (400 MHz) spectrum of **3f** in $CDCl_3$



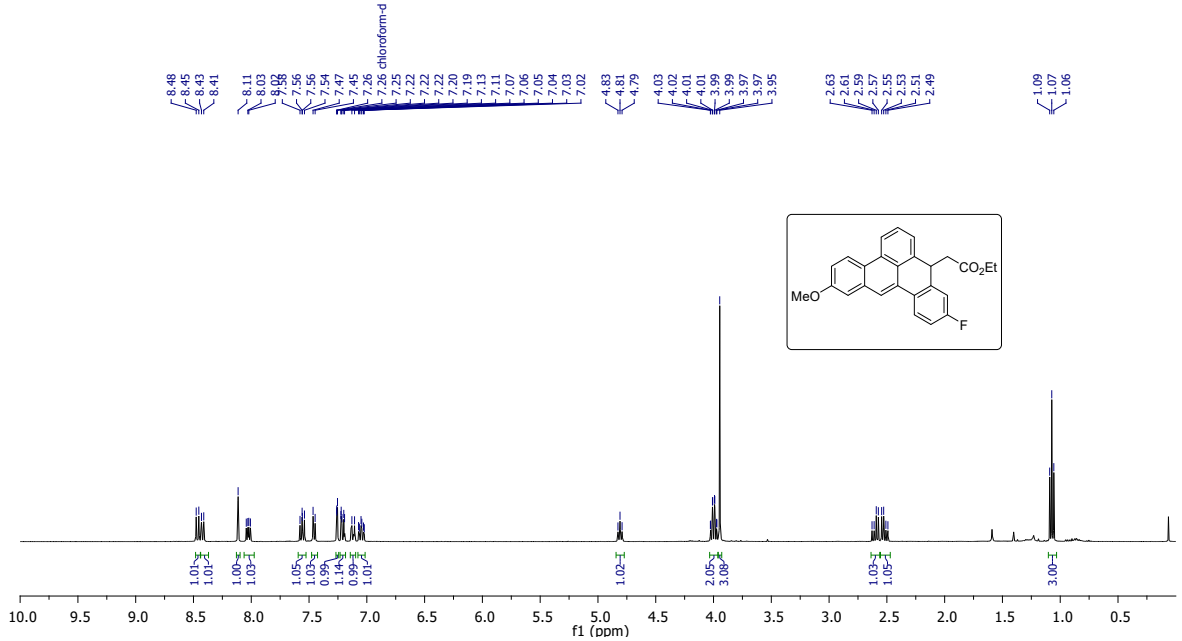
^{13}C{H} NMR (151 MHz) spectrum of **3f** in $CDCl_3$



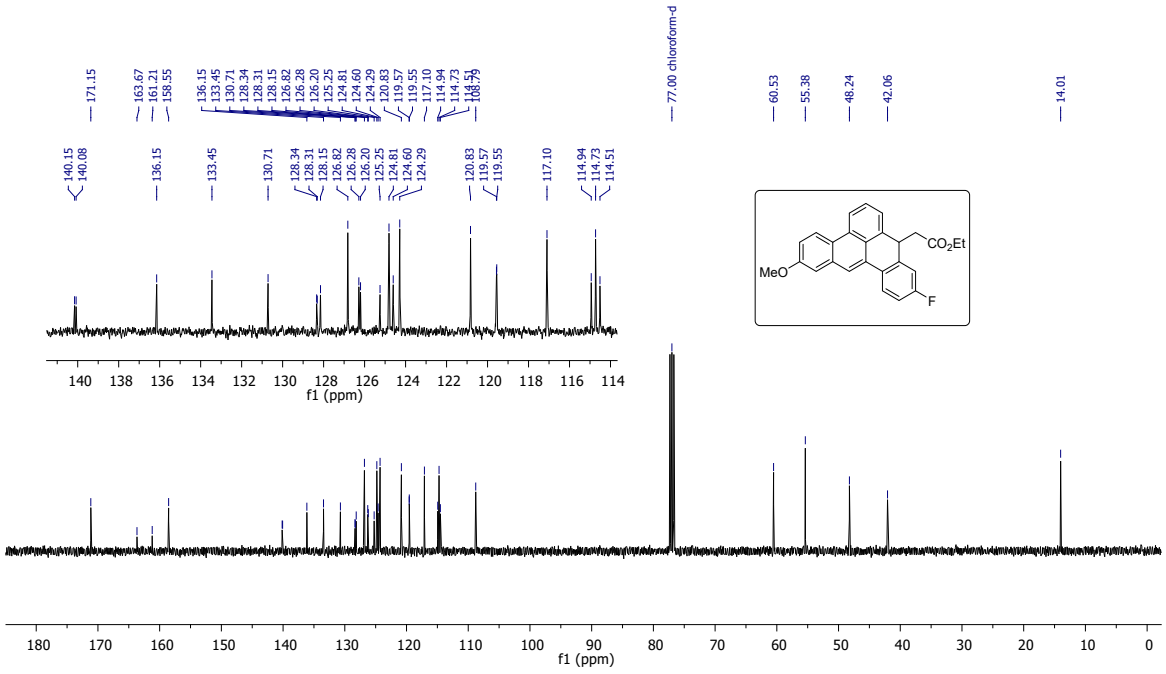
H NMR (600 MHz) spectrum of **3g** in $CDCl_3$



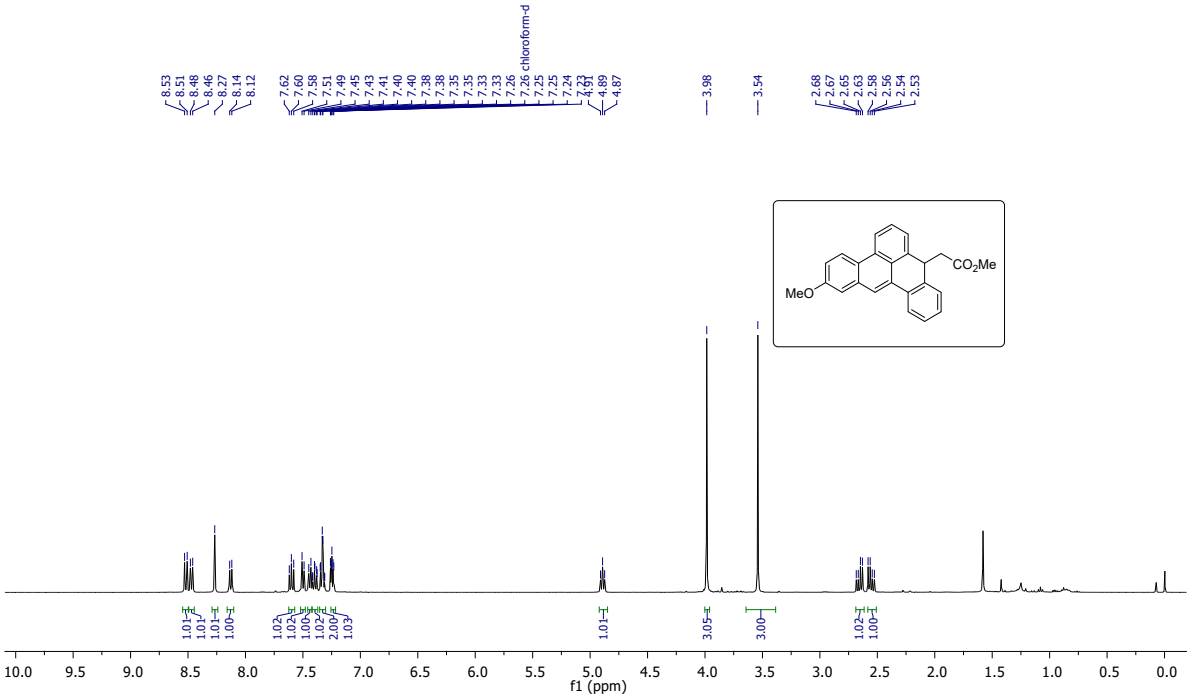
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **3g** in $CDCl_3$



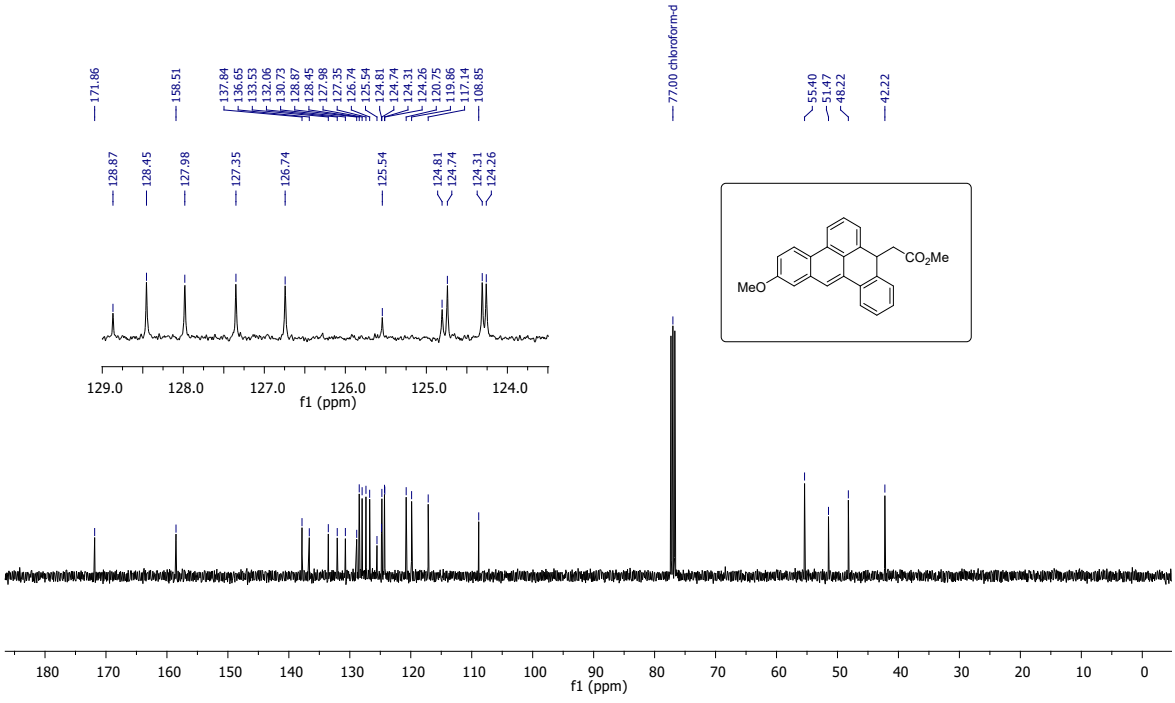
^{1}H NMR (400 MHz) spectrum of **3h** in $CDCl_3$



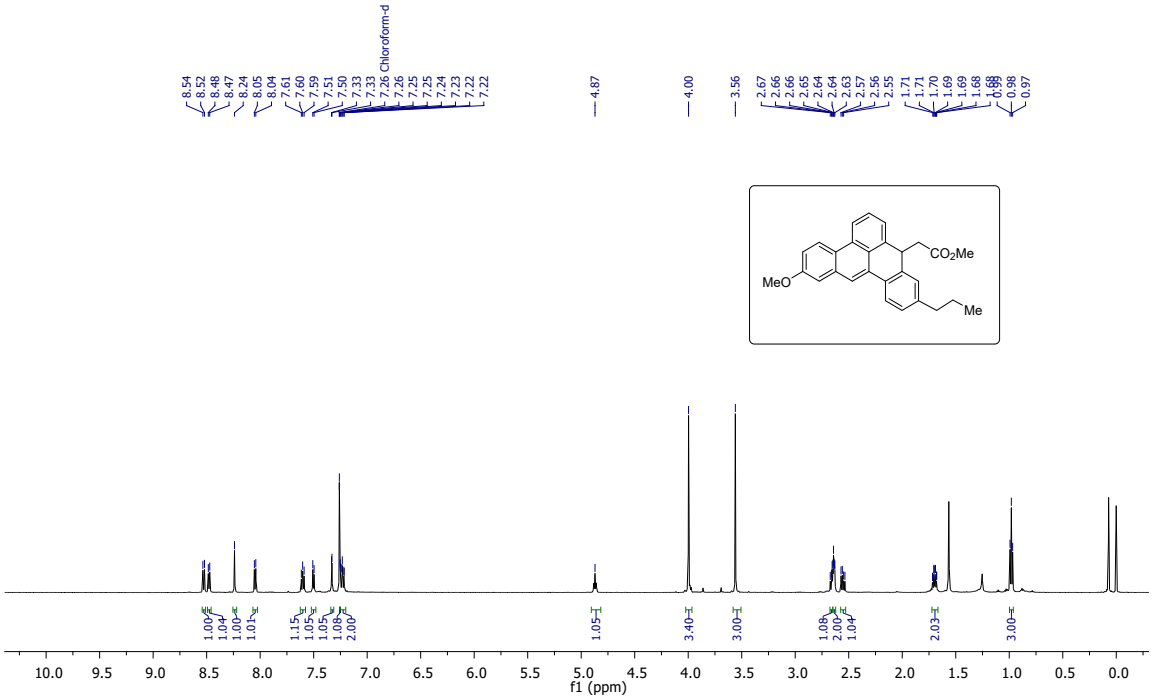
C{H} NMR (101 MHz) spectrum of **3h** in $CDCl_3$



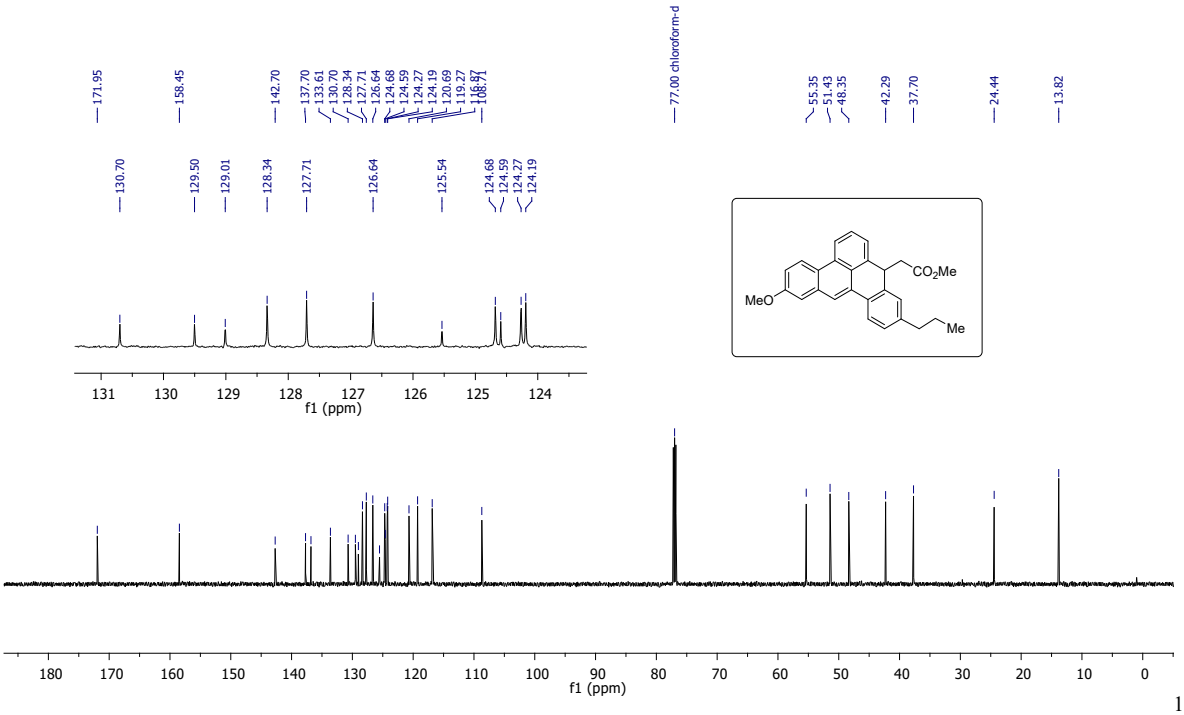
^{1}H NMR (400 MHz) spectrum of **3i** in $CDCl_3$



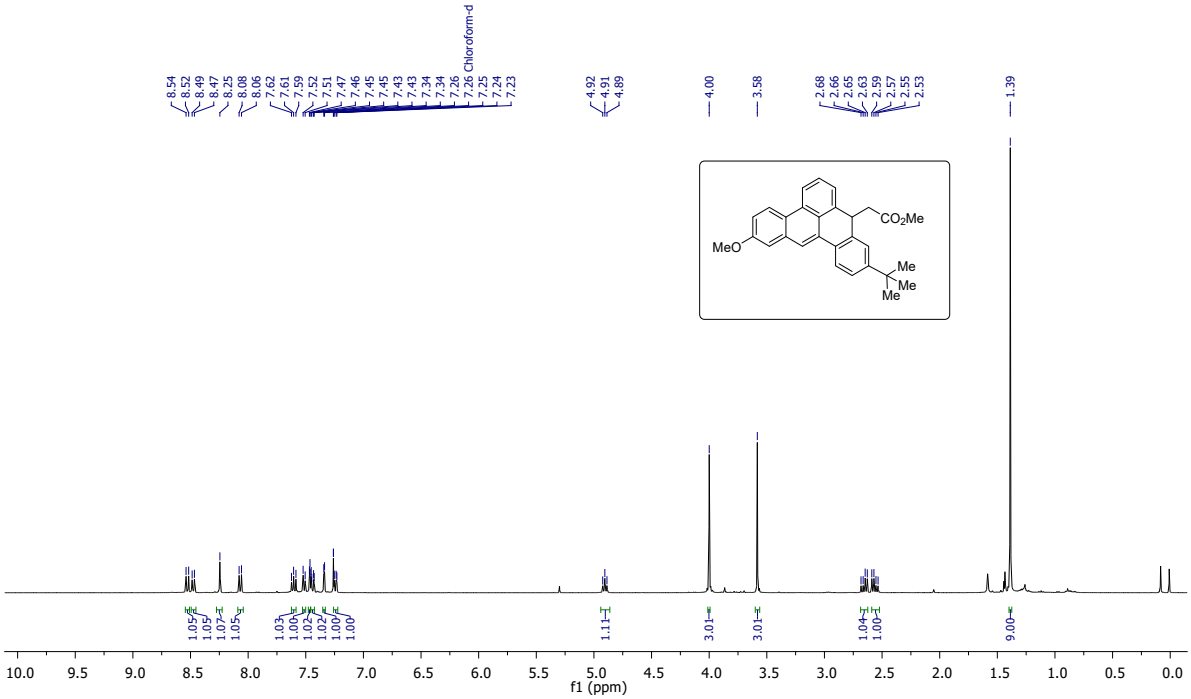
^{13}C{H} NMR (101 MHz) spectrum of **3i** in $CDCl_3$.



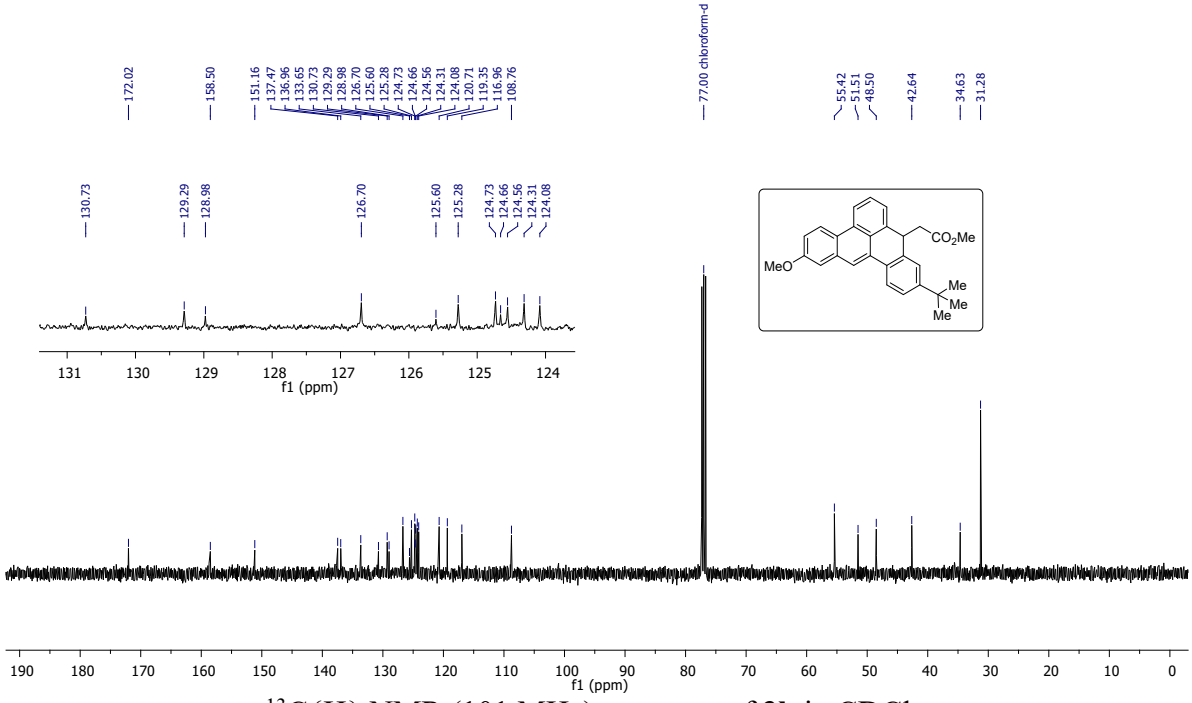
^{1}H NMR (600 MHz) spectrum of **3j** in $CDCl_3$



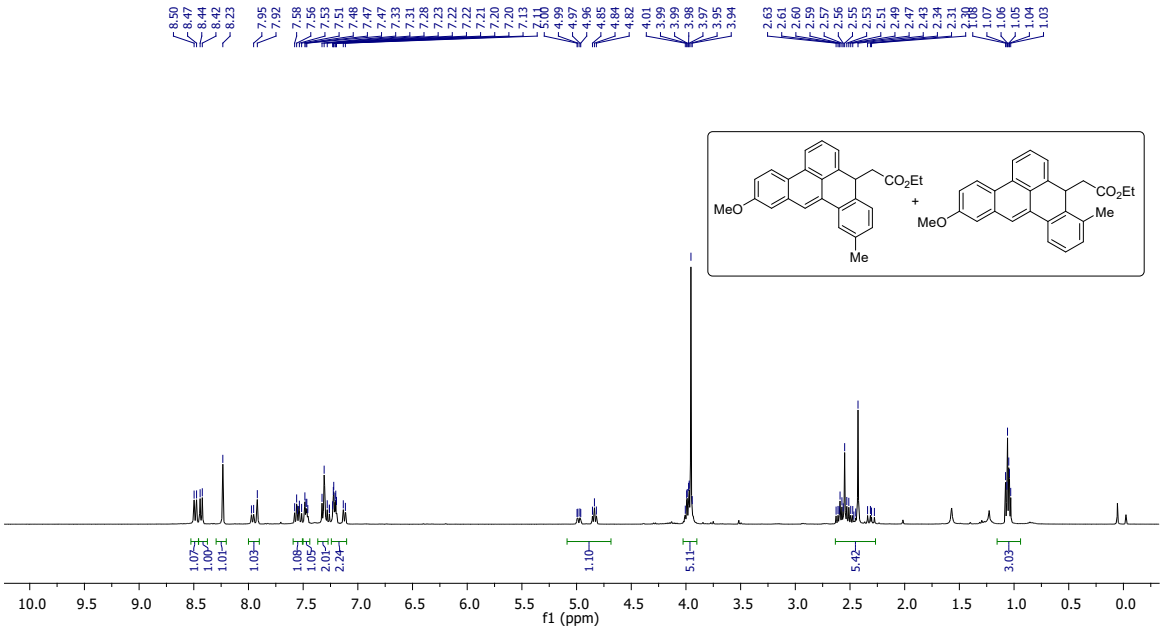
C{H} NMR (151 MHz) spectrum of **3j** in $CDCl_3$



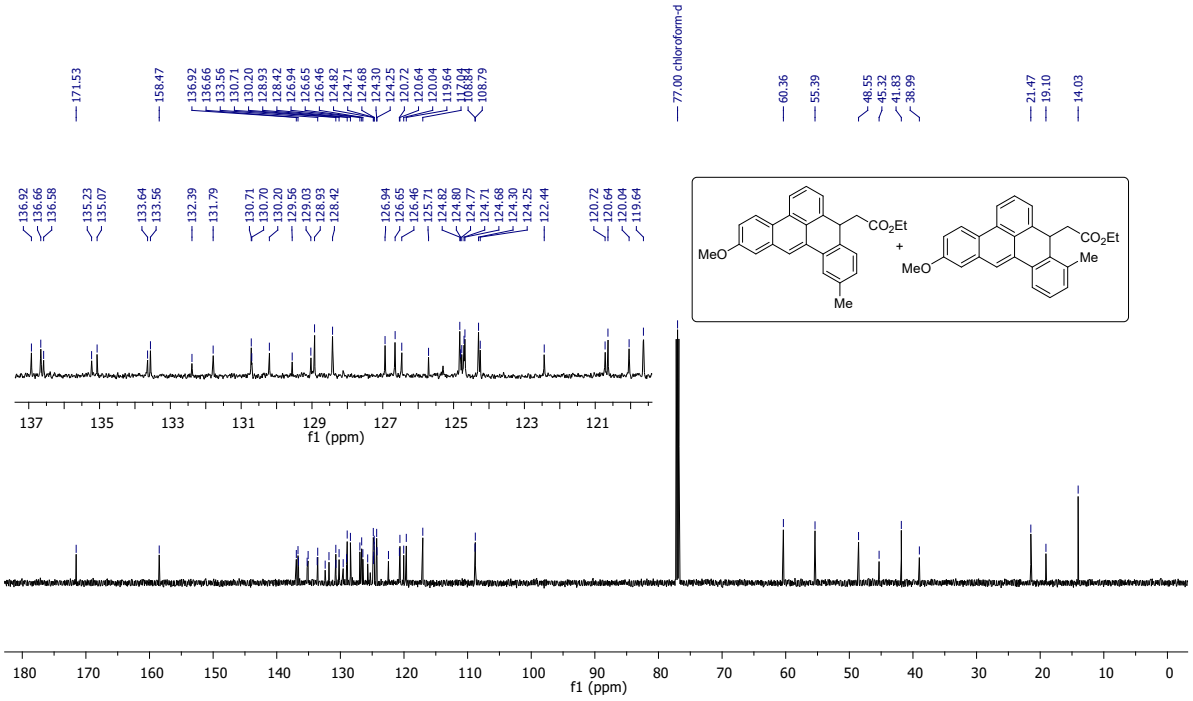
^{1}H NMR (400 MHz) spectrum of **3k** in $CDCl_3$



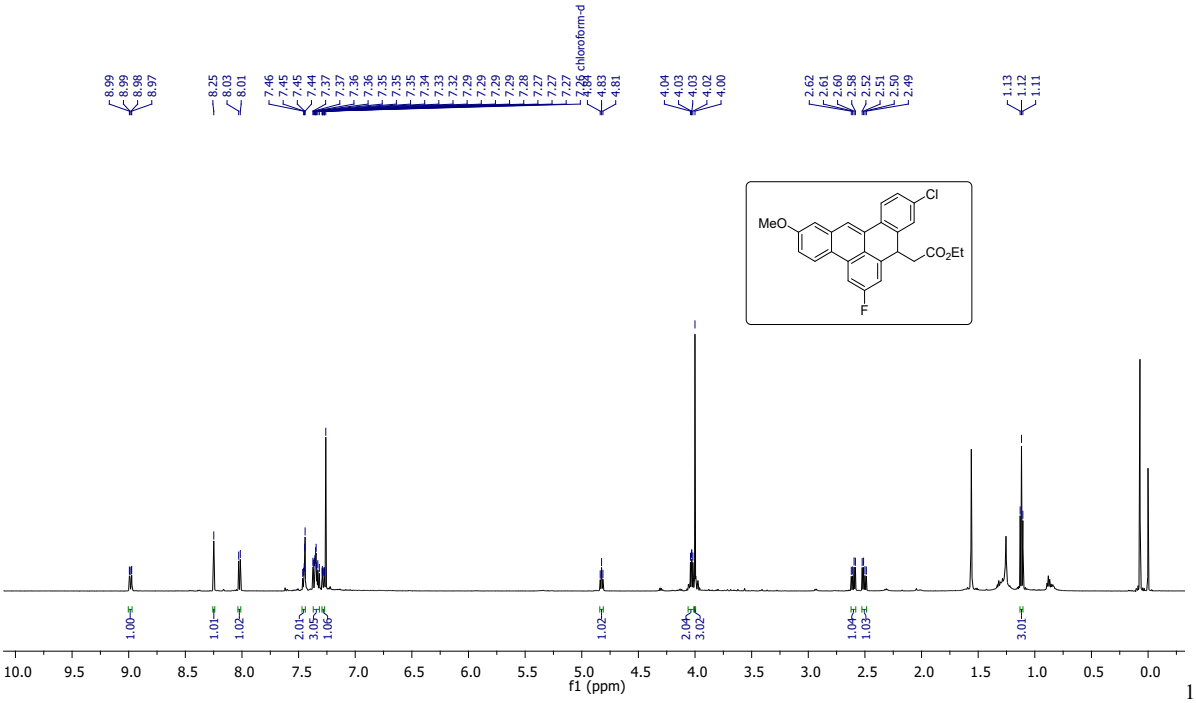
^{13}C{H} NMR (101 MHz) spectrum of **3k** in $CDCl_3$



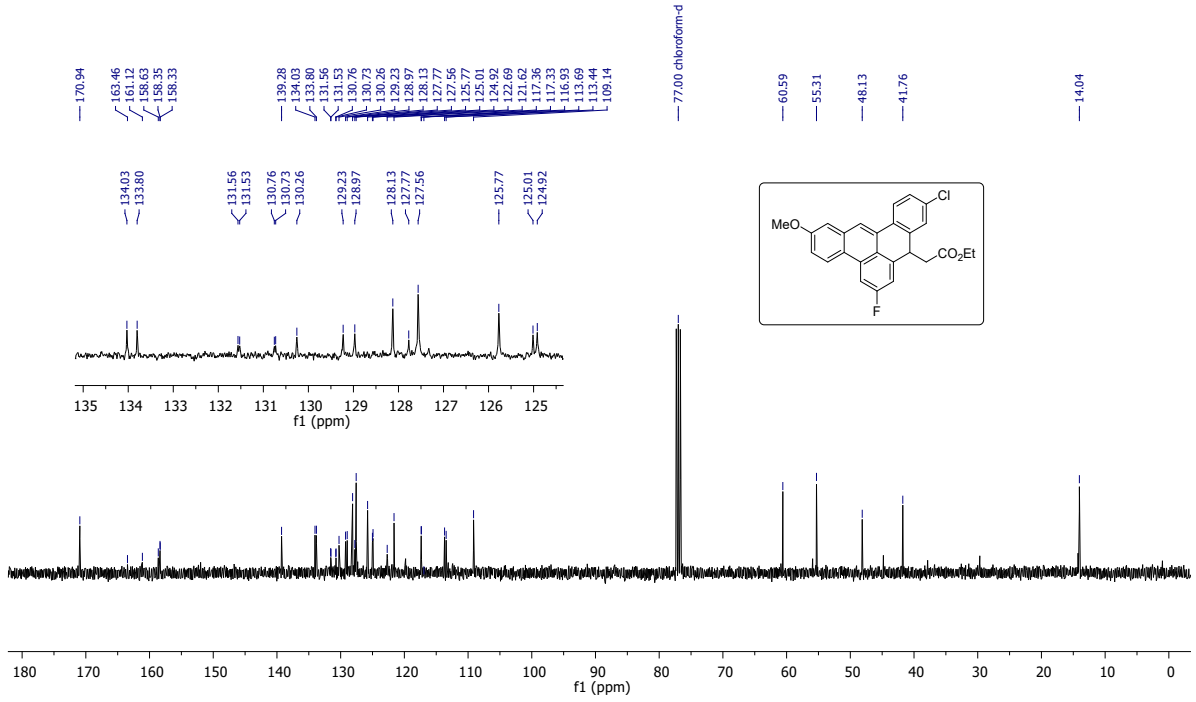
^{1}H NMR (400 MHz) spectrum of **3l** in $CDCl_3$



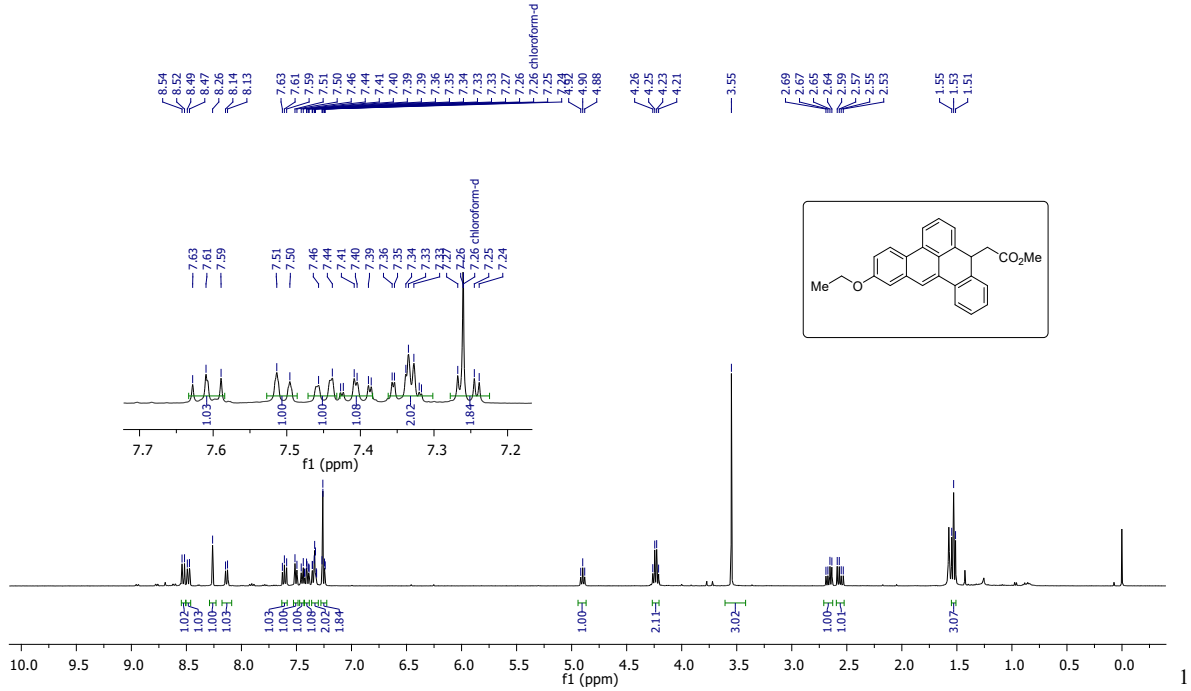
^{13}C{H} NMR (151 MHz) spectrum of **3l** in $CDCl_3$



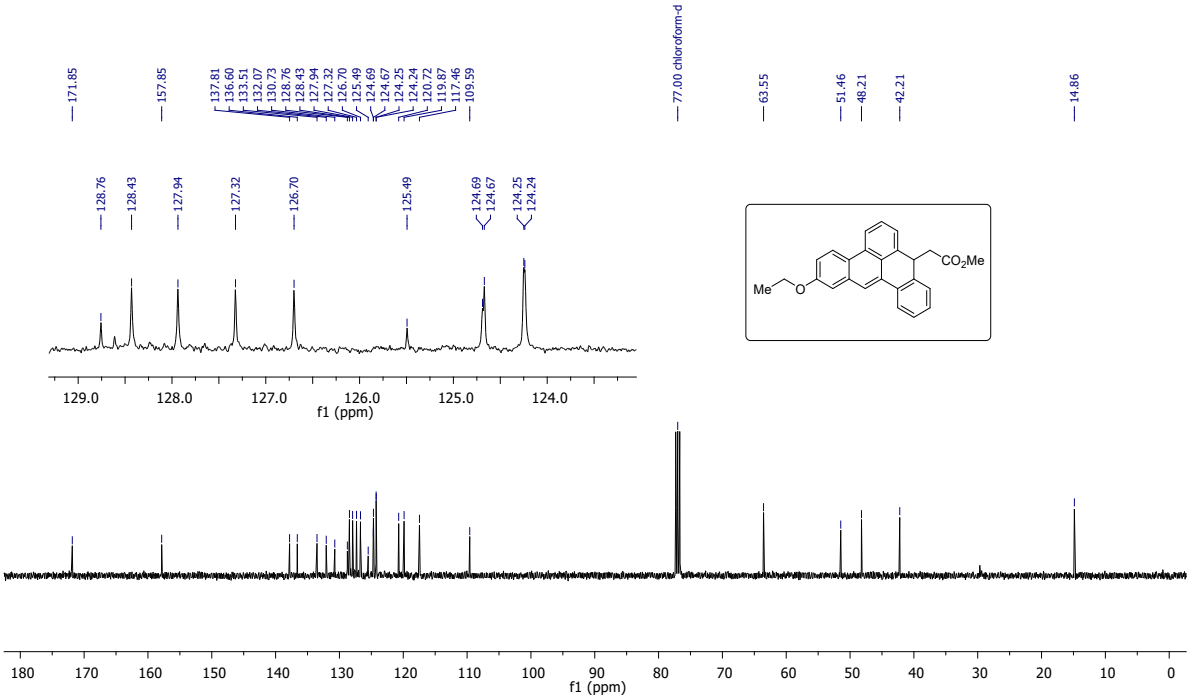
H NMR (600 MHz) spectrum of **3m** in $CDCl_3$



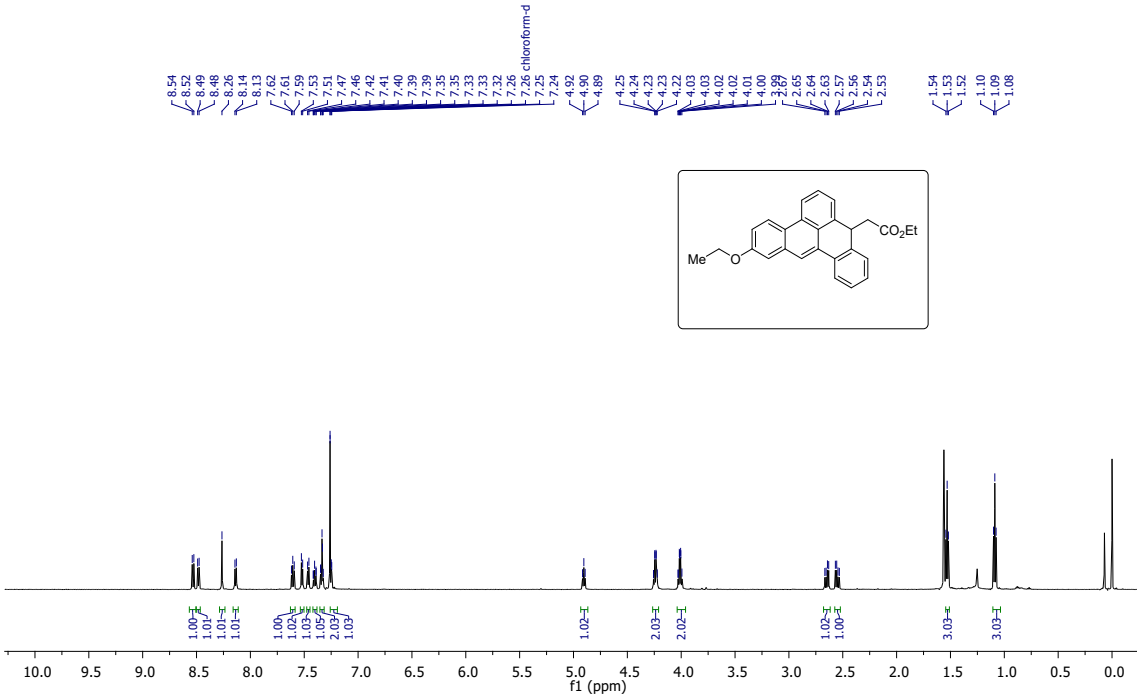
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **3m** in $CDCl_3$



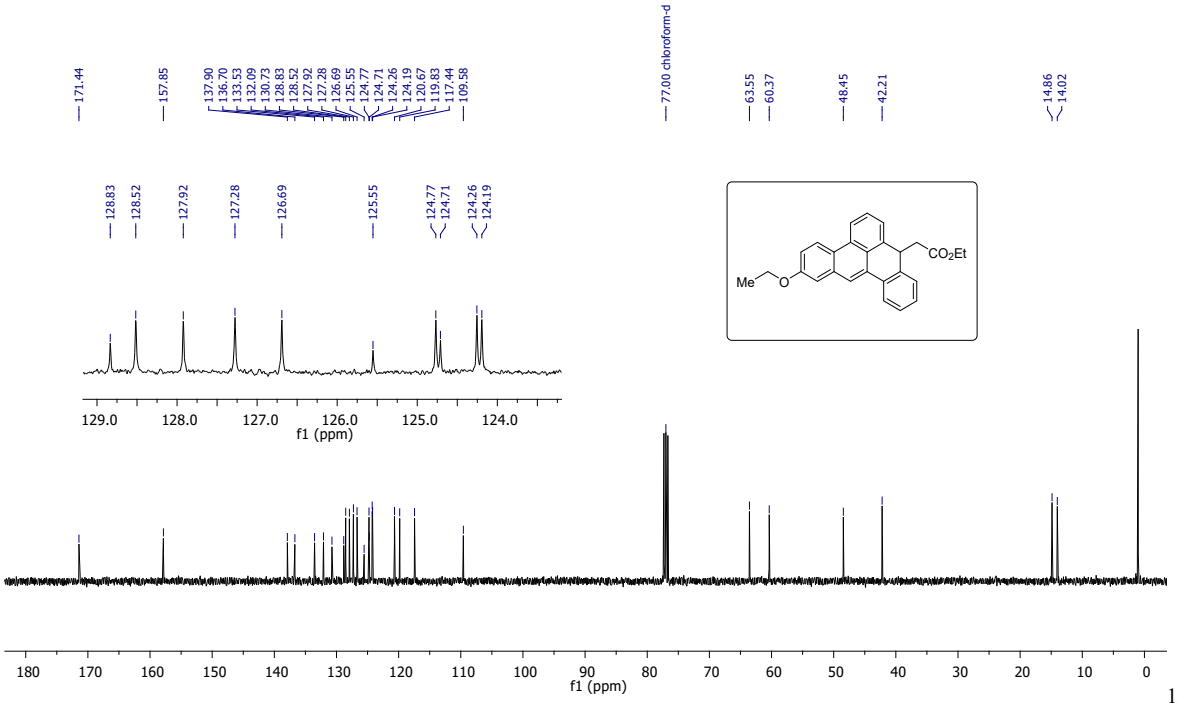
H NMR (600 MHz) spectrum of **3n** in $CDCl_3$



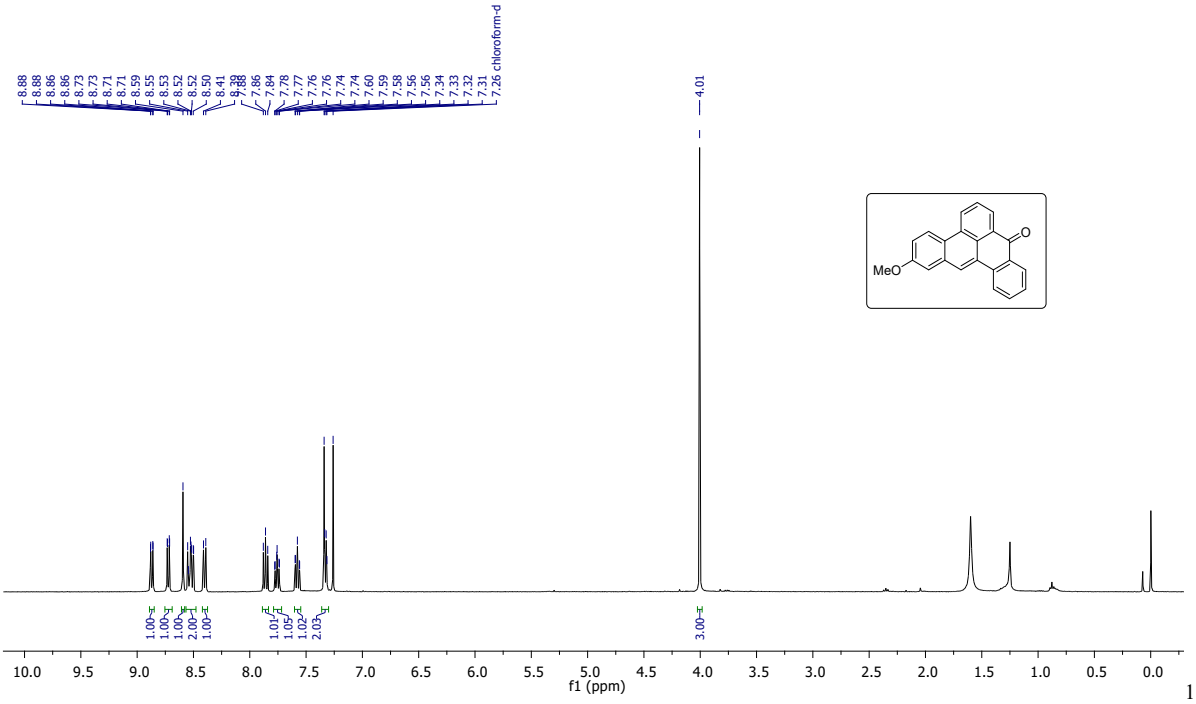
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **3n** in $CDCl_3$



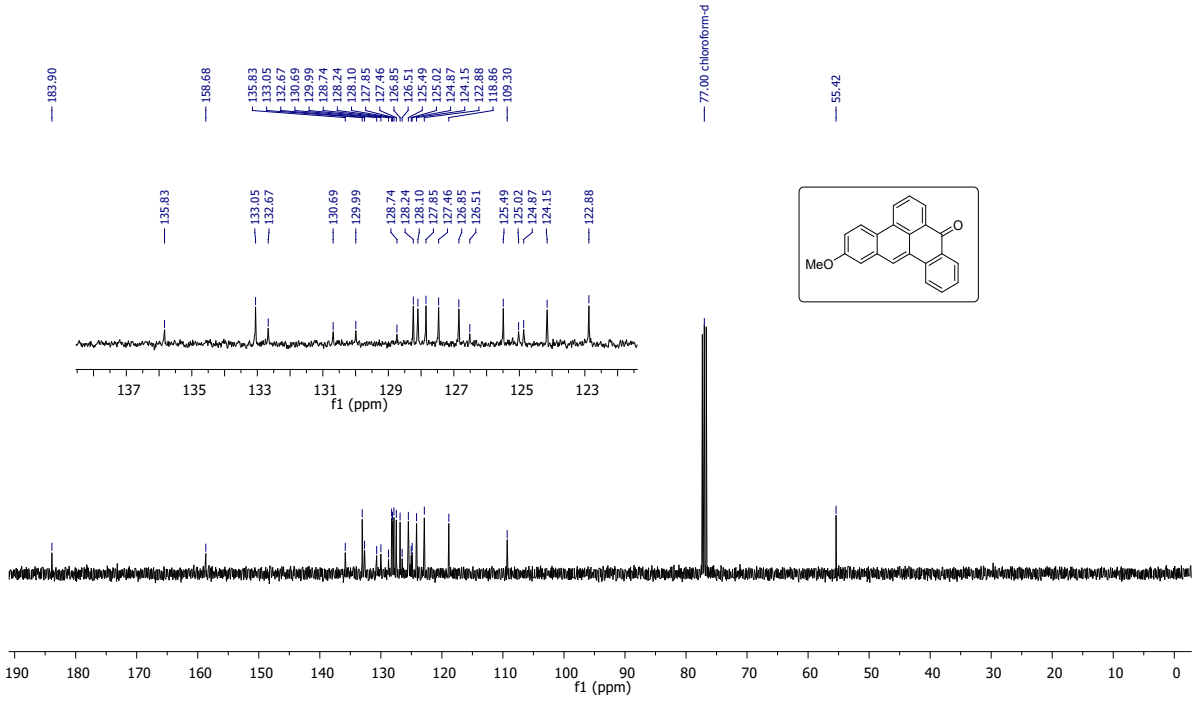
^{1}H NMR (600 MHz) spectrum of **3o** in $CDCl_3$



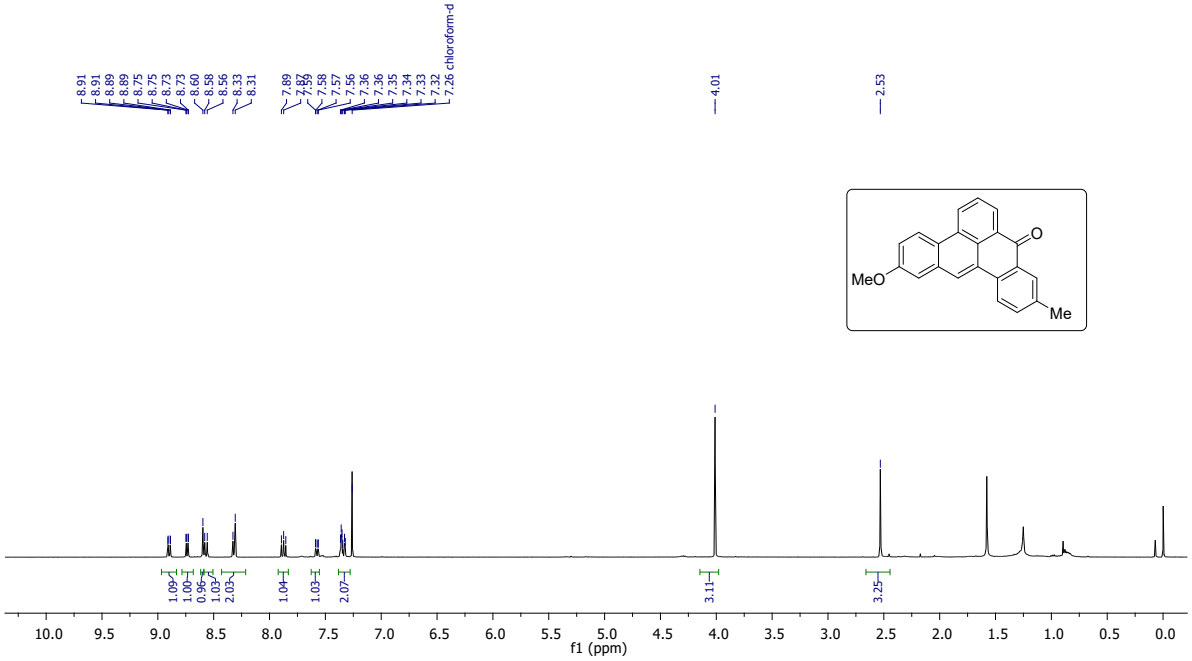
C{H} NMR (101 MHz) spectrum of **3o** in $CDCl_3$



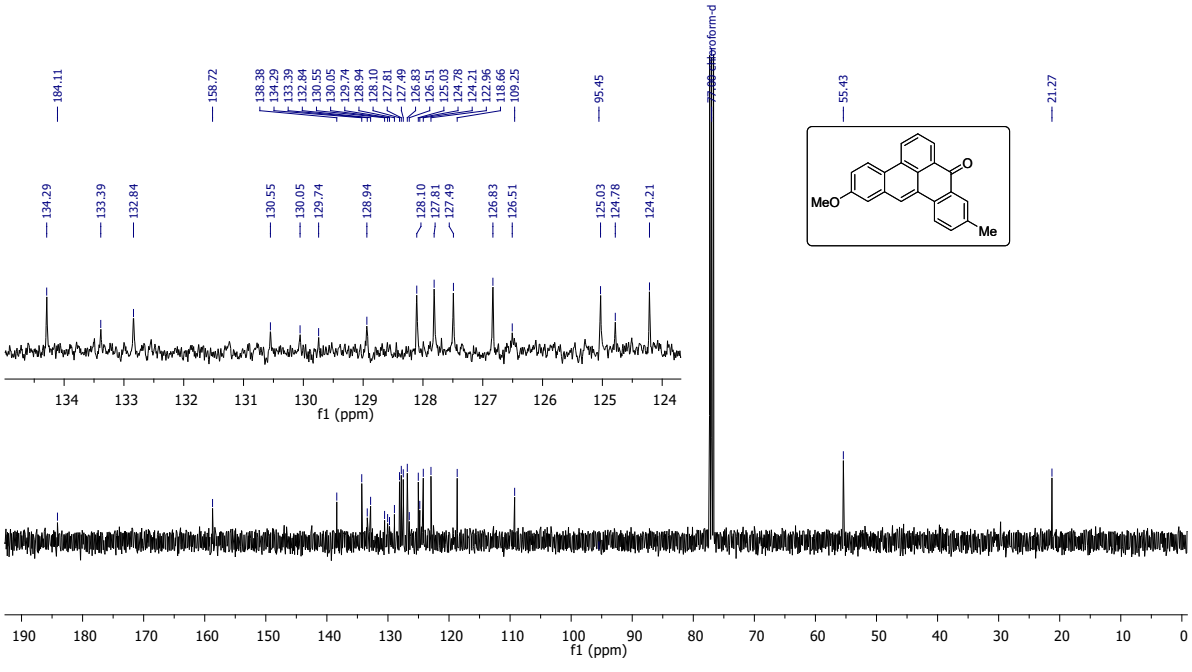
H NMR (400 MHz) spectrum of **4a** in $CDCl_3$



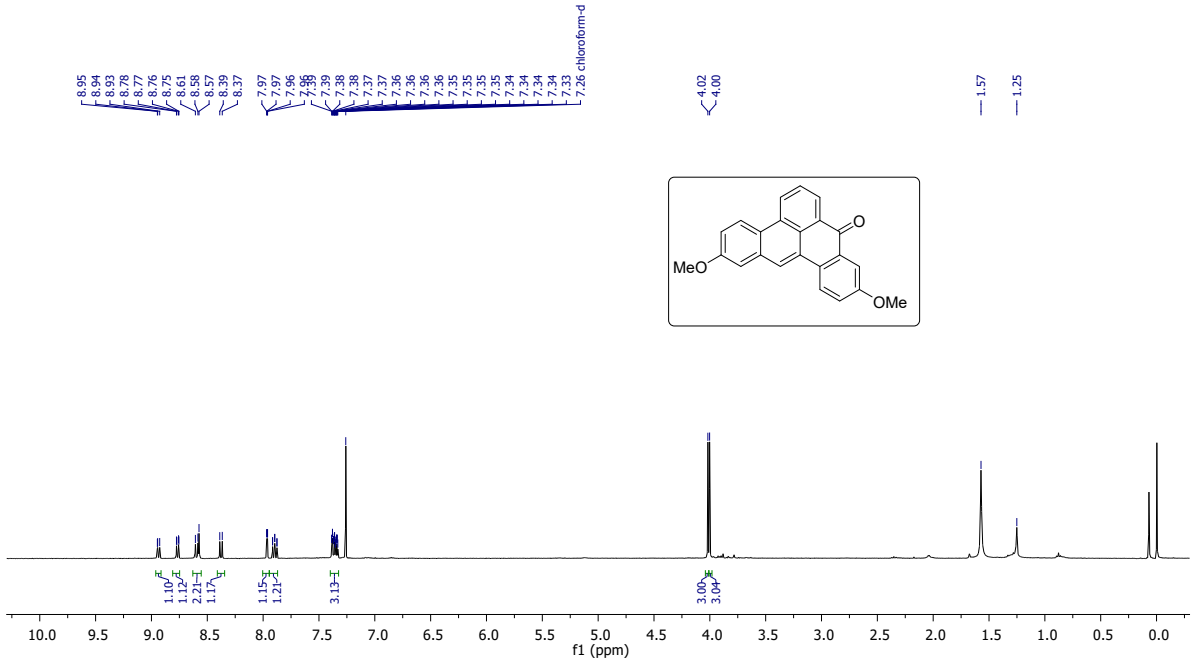
$^{13}C\{H\}$ NMR (101 MHz) spectrum of **4a** in $CDCl_3$



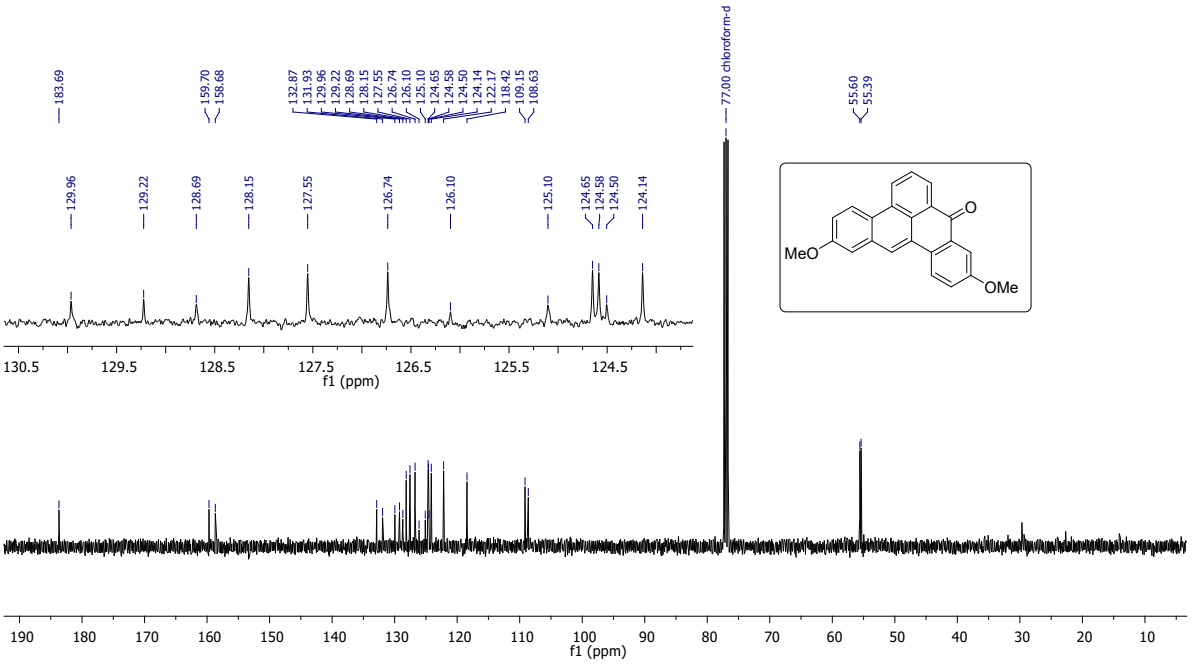
^{1}H NMR (400 MHz) spectrum of **4b** in $CDCl_3$



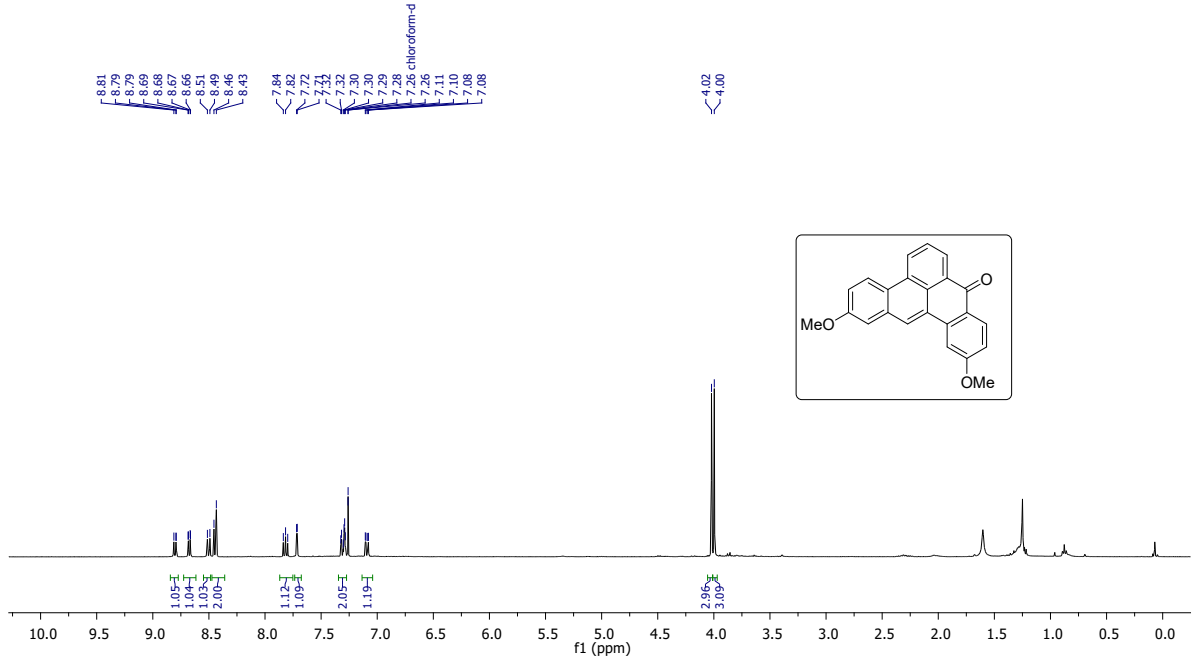
^{13}C{H} NMR (101 MHz) spectrum of **4b** in $CDCl_3$



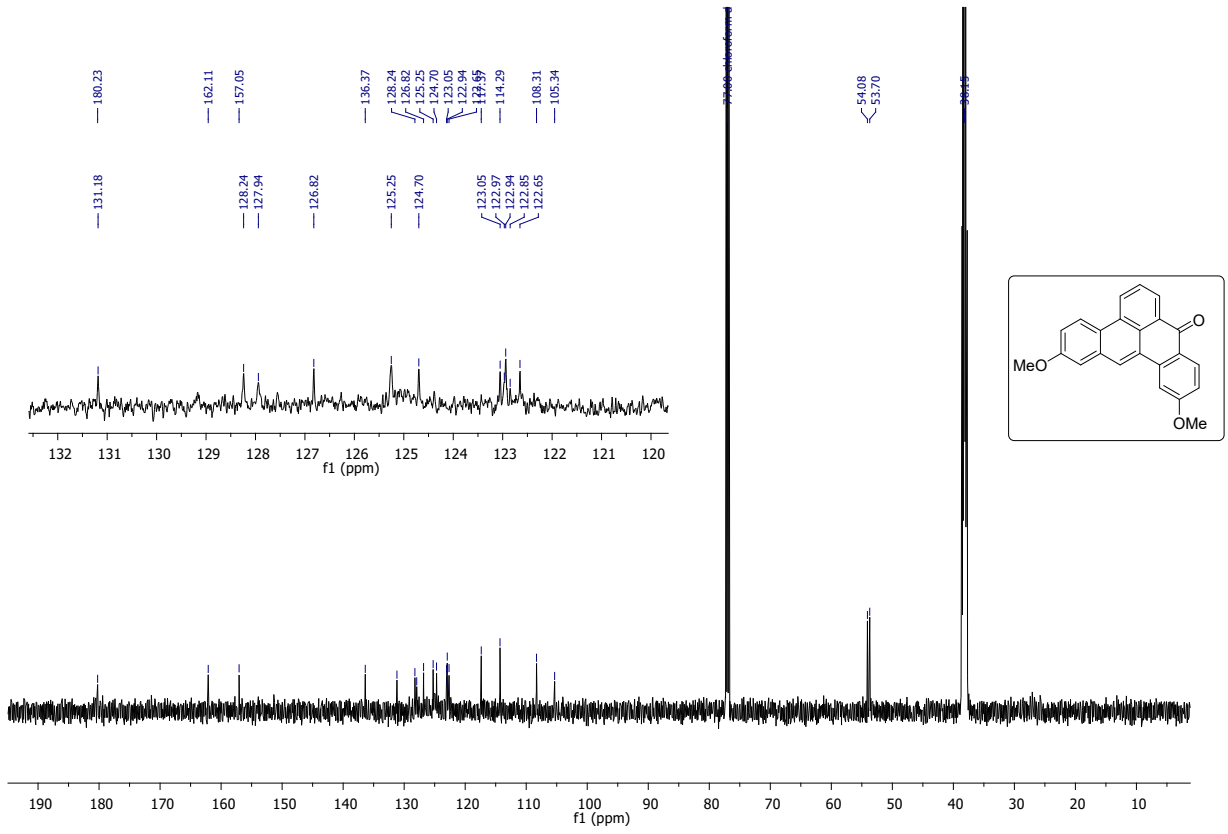
^{1}H NMR (400 MHz) spectrum of **4c** in $CDCl_3$



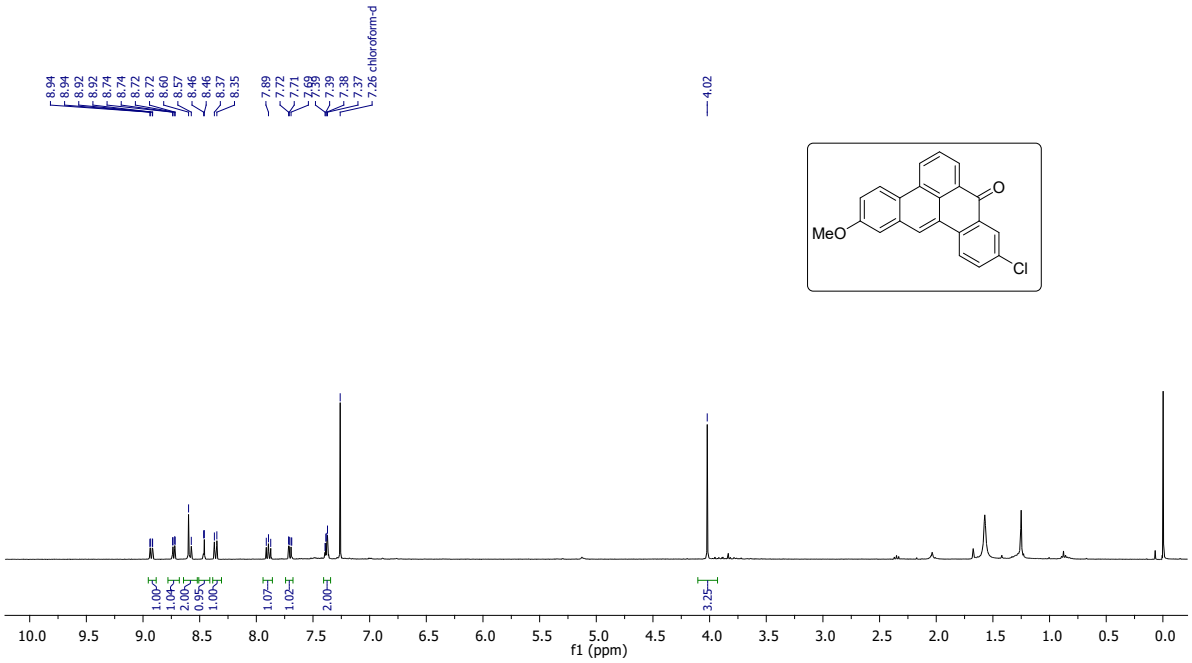
^{13}C{H} NMR (101 MHz) spectrum of **4c** in $CDCl_3$



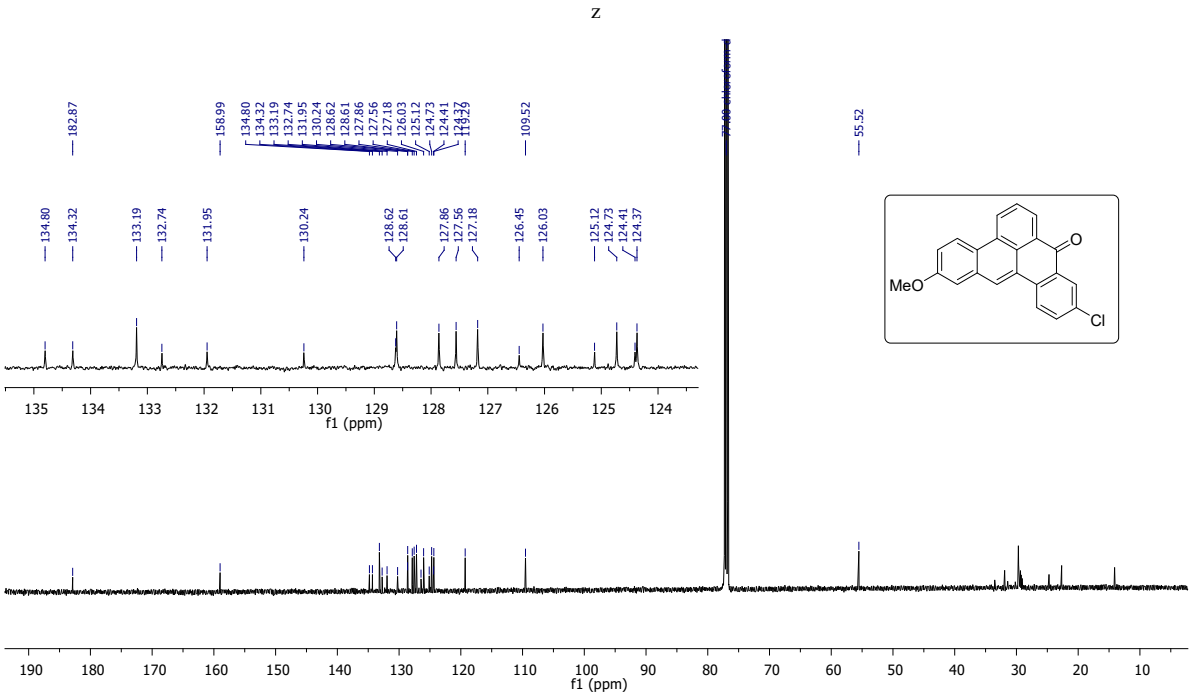
^{1}H NMR (400 MHz) spectrum of **4d** in $CDCl_3$



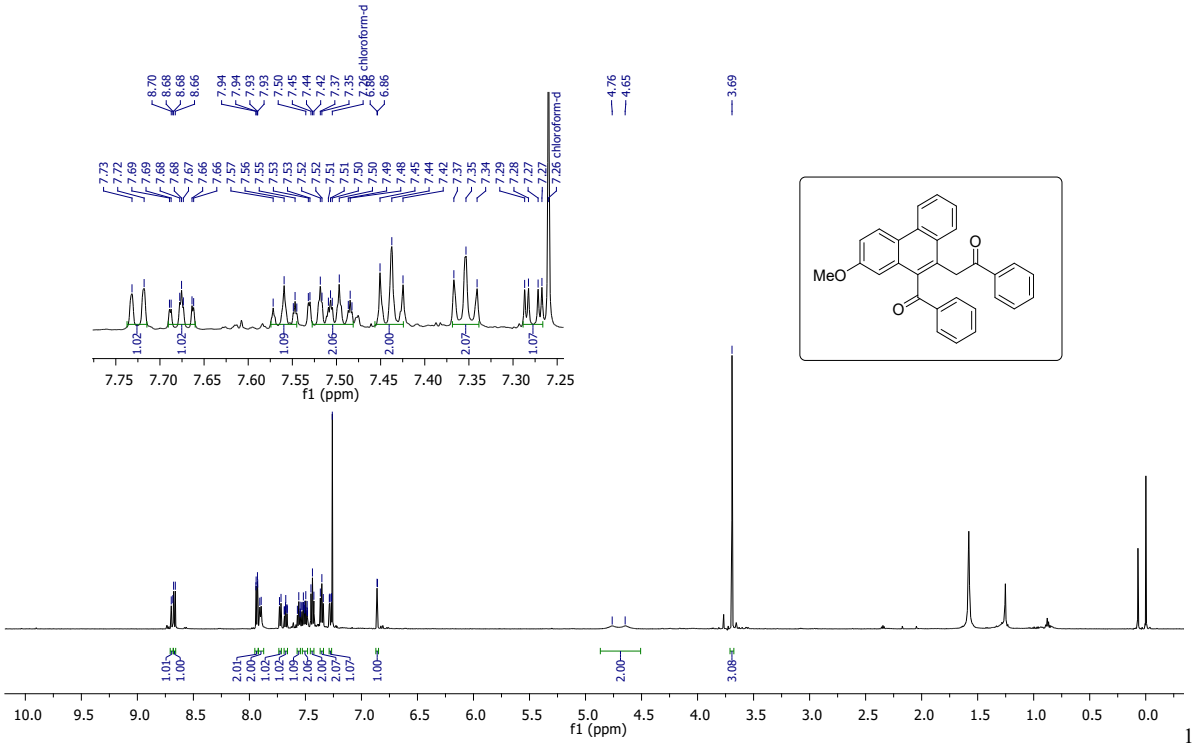
^{13}C{H} NMR (151 MHz) spectrum of **4d** in $CDCl_3$



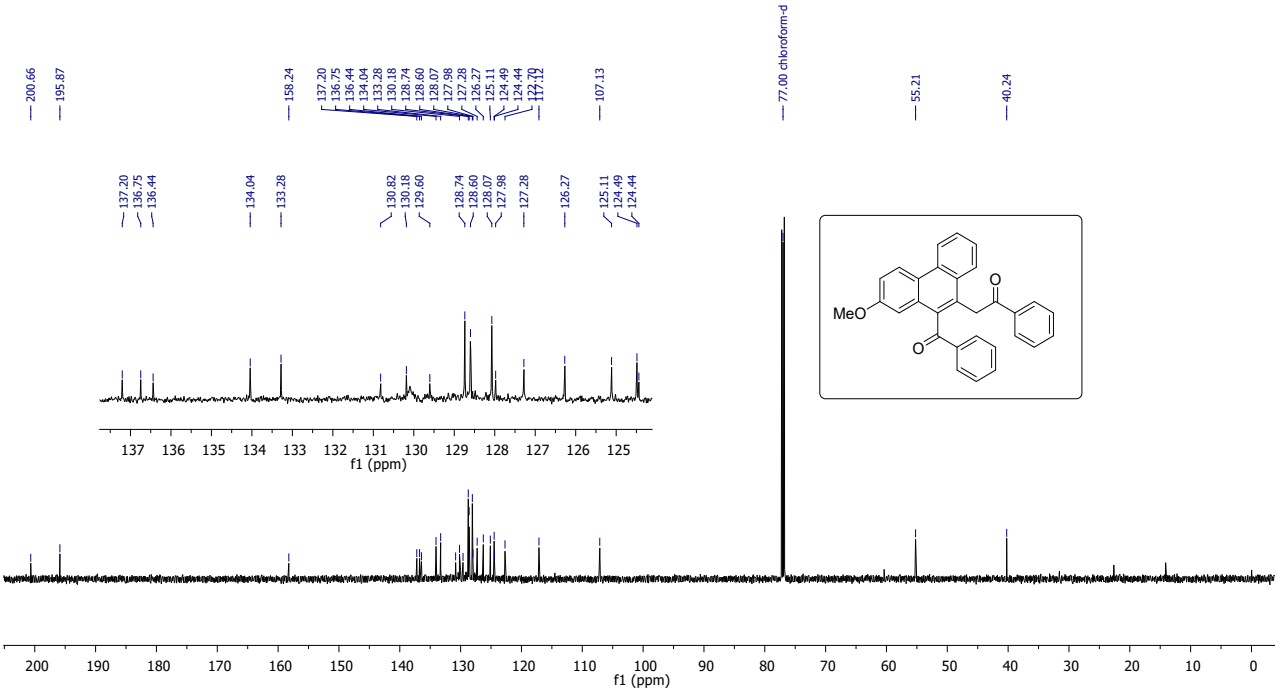
^{1}H NMR (400 MHz) spectrum of **4e** in $CDCl_3$



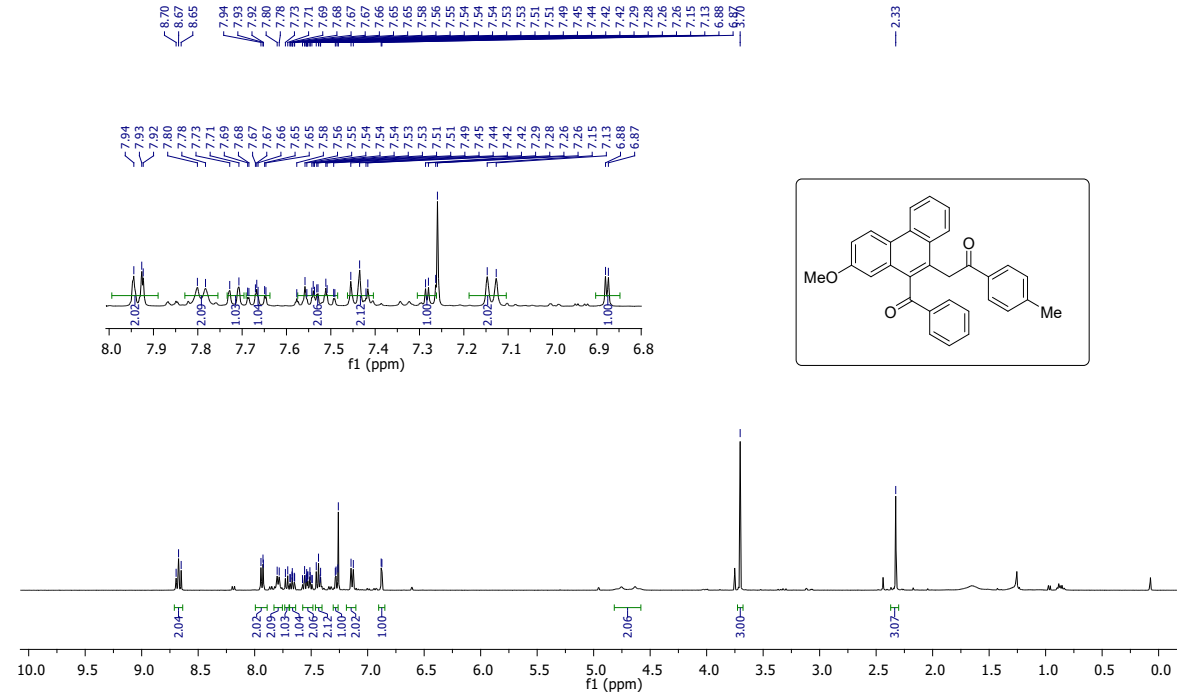
^{13}C{H} NMR (126 MHz) spectrum of **4e** in $CDCl_3$



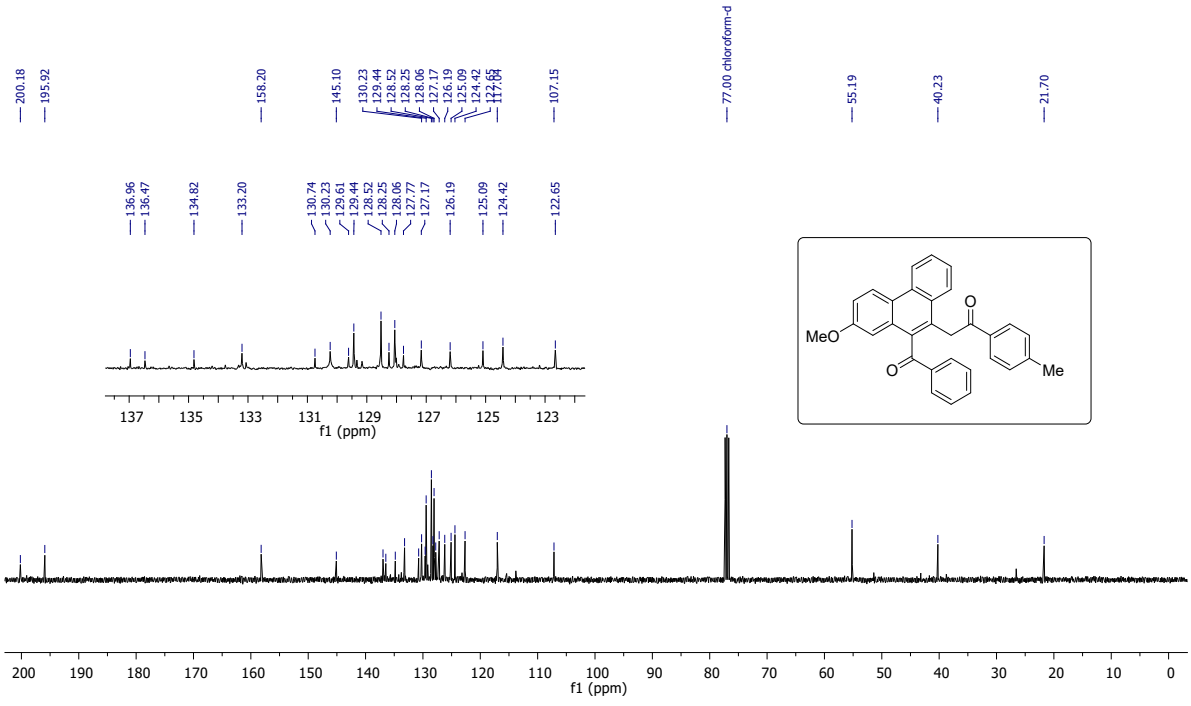
H NMR (600 MHz) spectrum of **5a** in $CDCl_3$



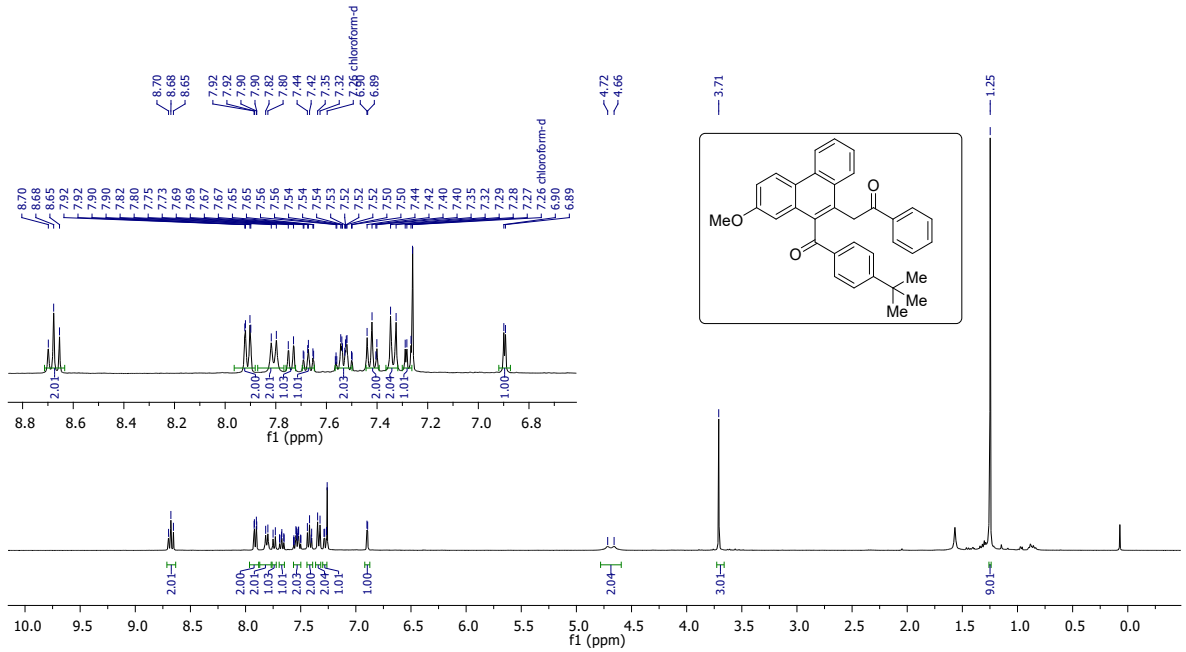
$^{13}C\{H\}$ NMR (151 MHz) spectrum of **5a** in $CDCl_3$



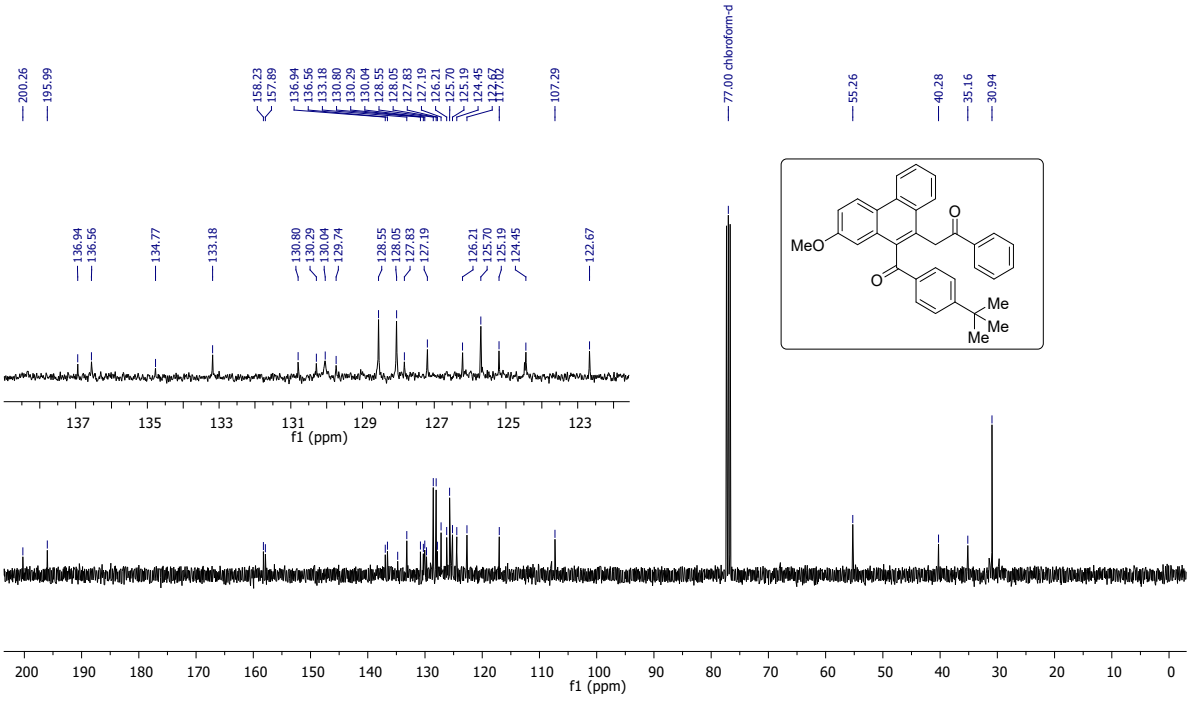
^{1}H NMR (400 MHz) spectrum of **5b** in $CDCl_3$



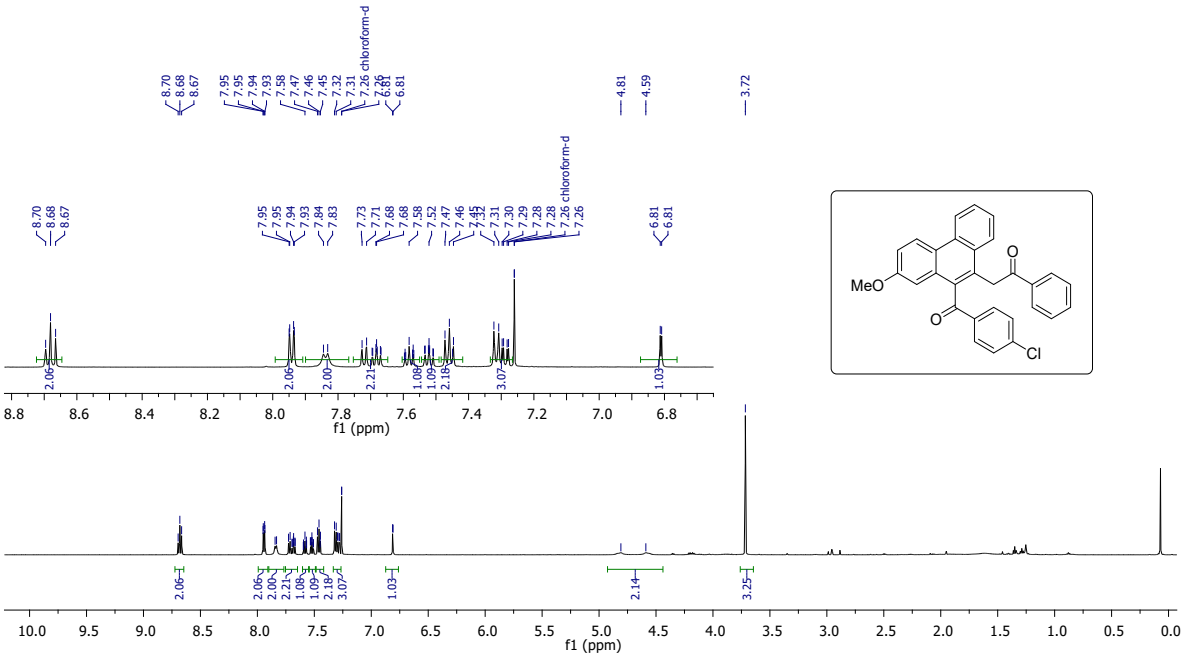
^{13}C{H} NMR (101 MHz) spectrum of **5b** in $CDCl_3$



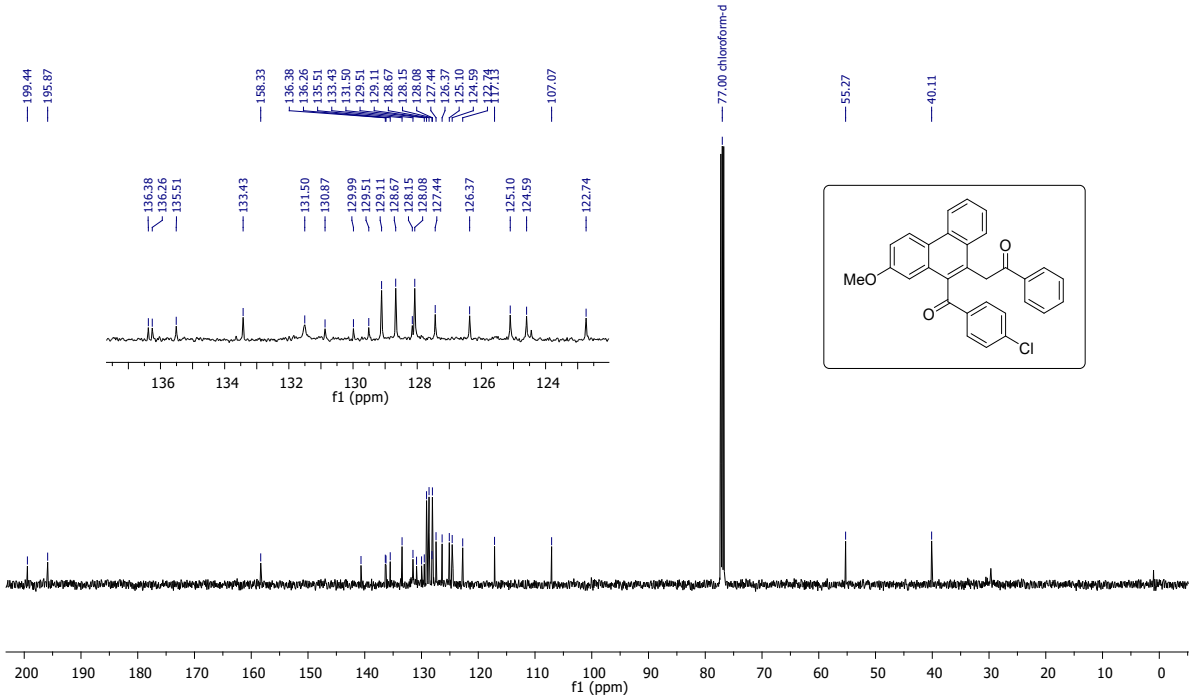
^{1}H NMR (600 MHz) spectrum of **5c** in $CDCl_3$



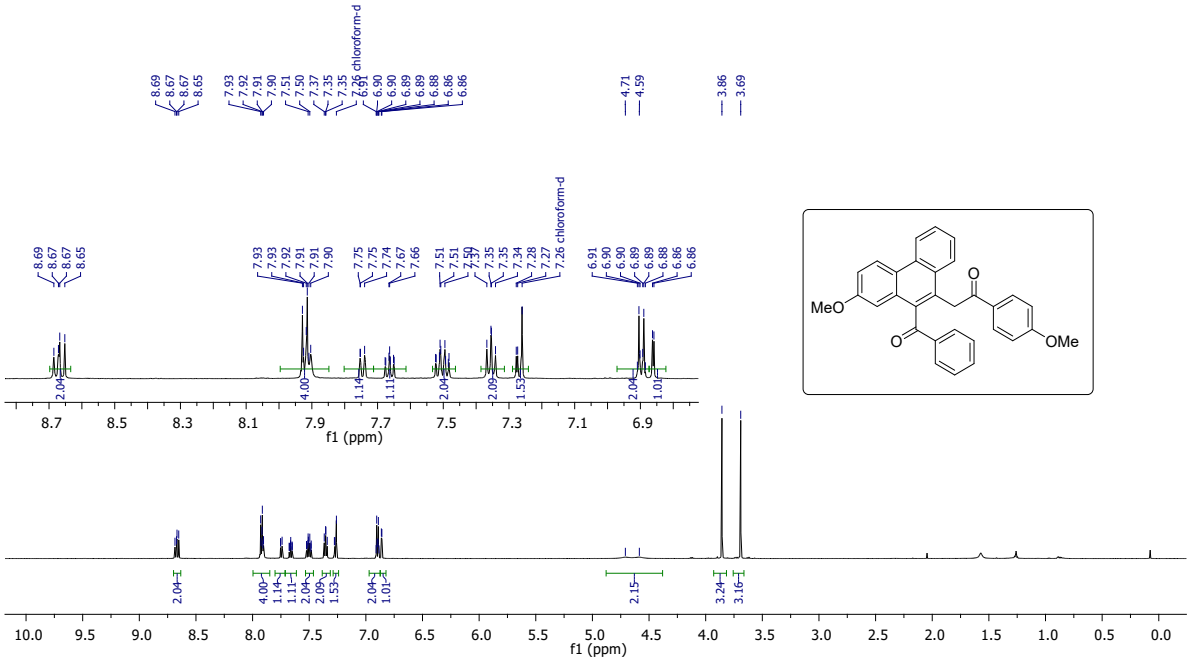
^{13}C{H} NMR (101 MHz) spectrum of **5c** in $CDCl_3$



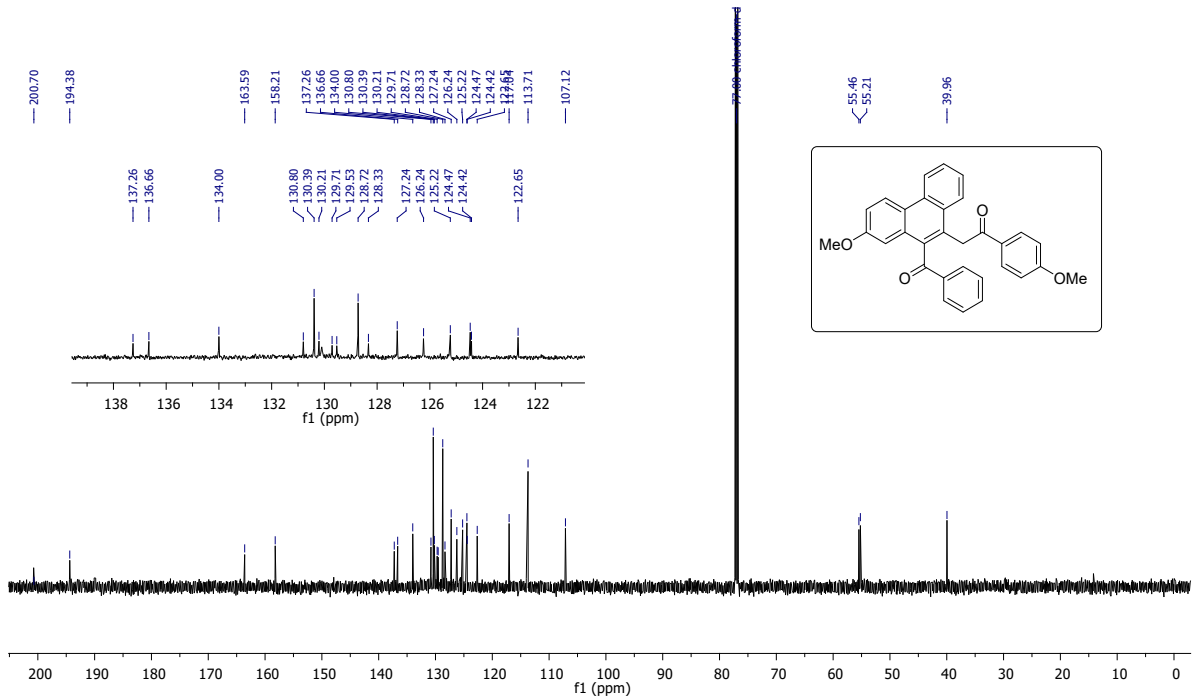
^{1}H NMR (400 MHz) spectrum of **5d** in $CDCl_3$



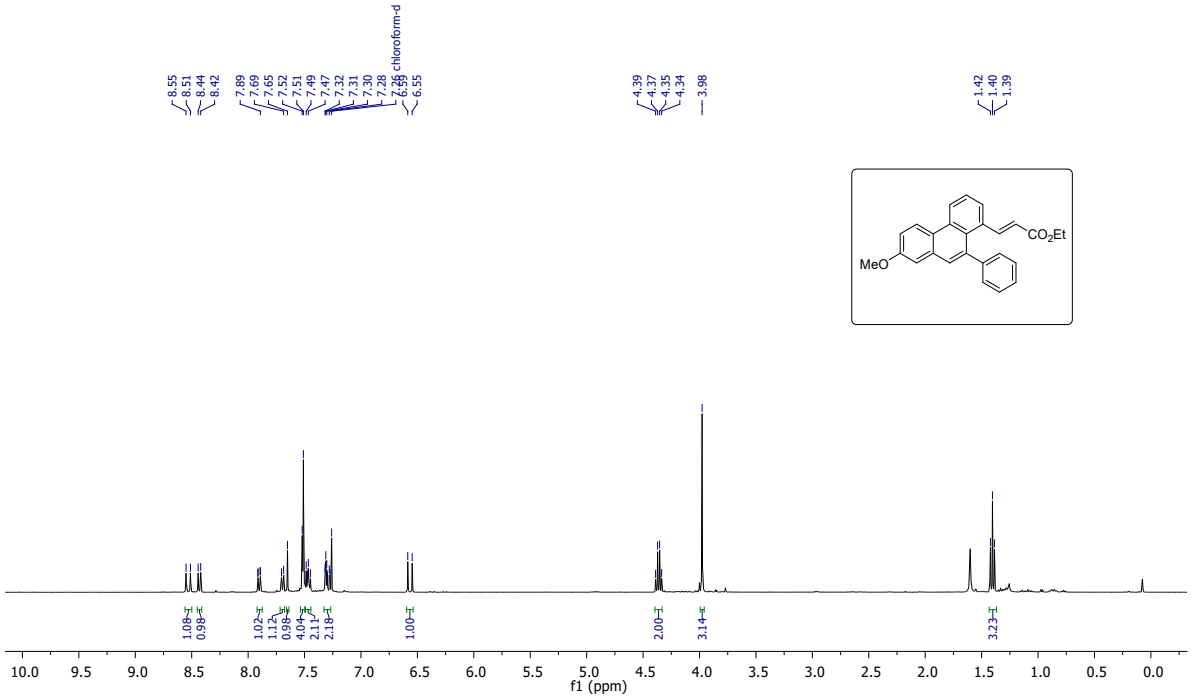
^{13}C{H} NMR (101 MHz) spectrum of **5d** in $CDCl_3$



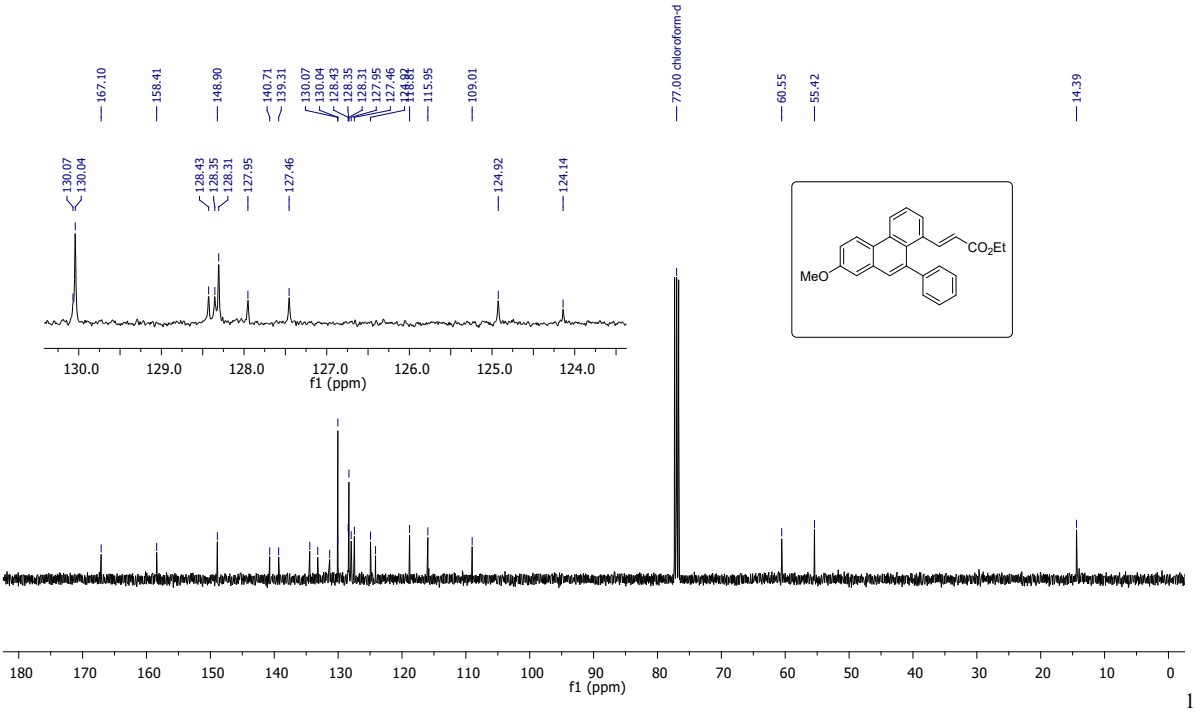
^{1}H NMR (600 MHz) spectrum of **5e** in $CDCl_3$



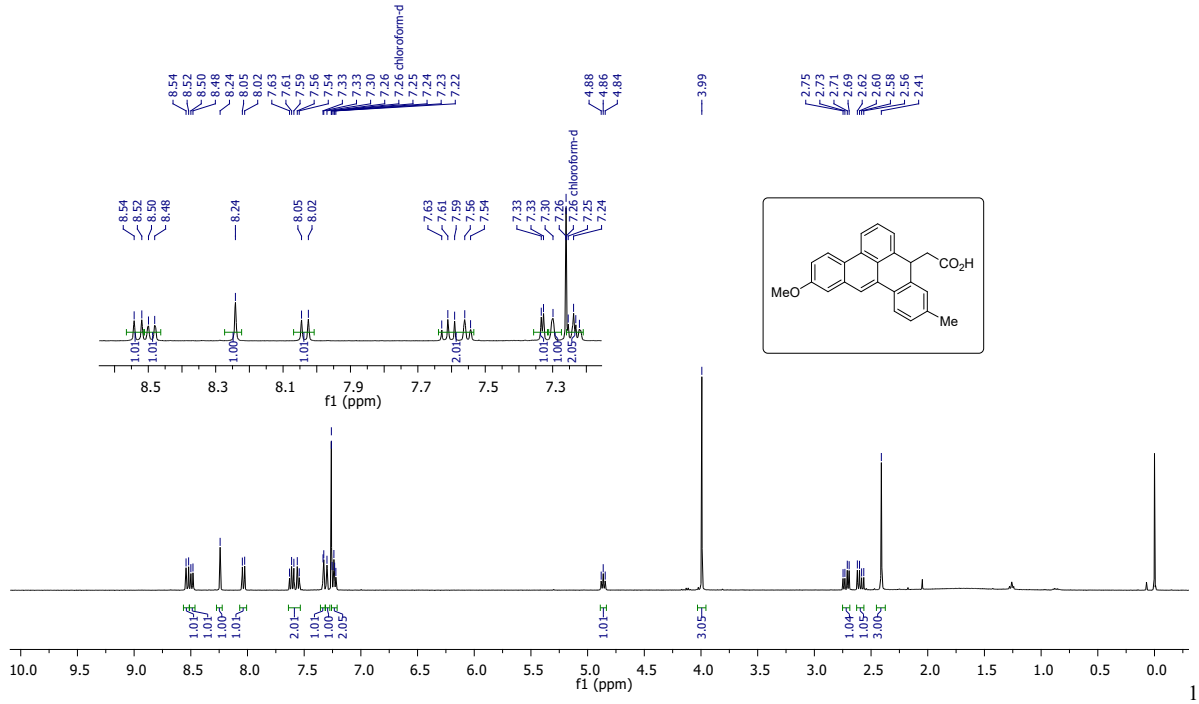
^{13}C{H} NMR (151 MHz) spectrum of **5e** in $CDCl_3$



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

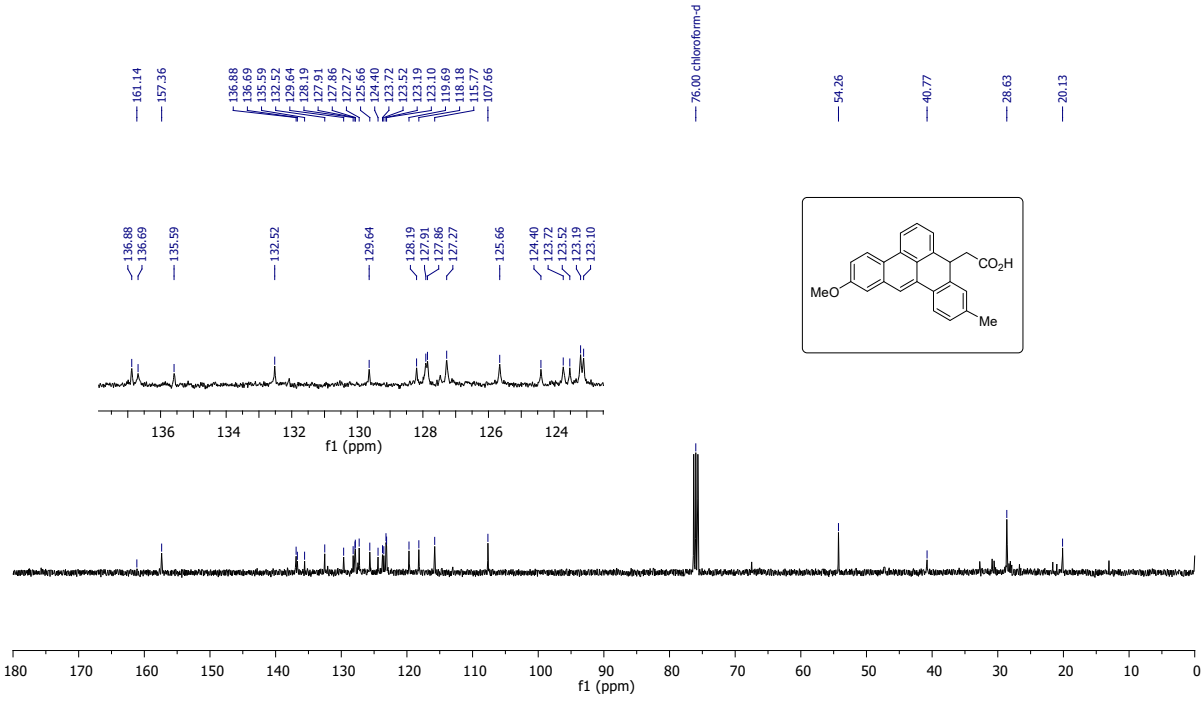


^{3}C{H} NMR (101 MHz) spectrum of **14** in $CDCl_3$



1

H NMR (400 MHz) spectrum of **13** in $CDCl_3$



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

2. X-Ray crystal structure of compound 2n, 13, 4c and 5e:

Crystal of compounds **2n**, **13**, **4c** and **5e** were obtained by dissolving the product in Hexane/CH_2Cl_2 mixture and allowing the solvent to slowly evaporate at room temperature. A suitable crystal was selected and mounted onto the cryoloop on a Bruker APEX-II CCD diffractometer. The crystal was kept at 273.15 K during data collection. Using Olex2,8 the structure was solved with the SHELXT9 structure solution program using Intrinsic Phasing and refined with the SHELXL10 refinement package using Least Squares minimization.

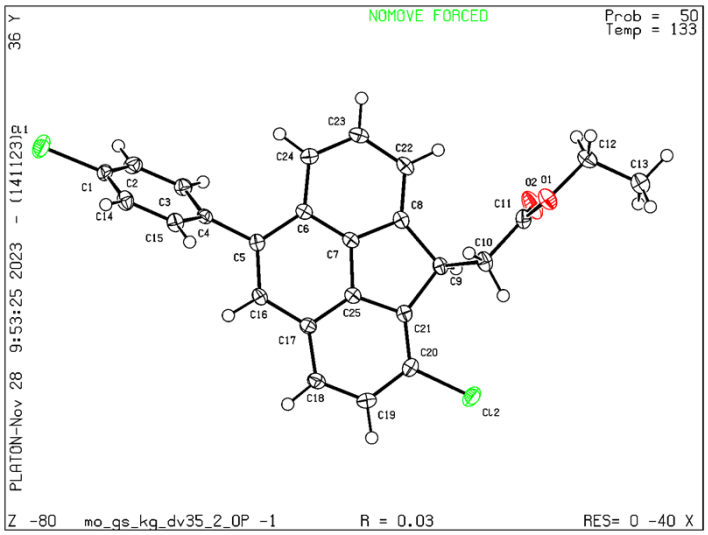


Figure S2: X-ray diagram of compound **2n** with ellipsoid shown at the 50% contour percent probability level (CCDC: 2414274).

Table S10: Crystal data and structure refinement for **2n** (CCDC: 2414274).

Table S10 Crystal data and structure refinement for 2n	
Identification code	**2n**
Empirical formula	$C_{25}H_{18}O_2Cl_2$
Formula weight	421.29
Temperature/K	133.00
Crystal system	triclinic
Space group	P-1
a/Å	9.6407(5)
b/Å	9.9098(5)
c/Å	12.2951(7)
α/°	97.191(2)
β/°	112.732(2)
γ/°	106.874(2)
Volume/Å^3	998.56(9)

Z	2
ρ_{calc}g/cm^3	1.401
μ/mm^{-1}	0.344
F(000)	436.0
Crystal size/mm^3	0.089 × 0.07 × 0.069
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.46 to 54.43
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -15 ≤ l ≤ 15
Reflections collected	30660
Independent reflections	4445 [R_{int} = 0.0564, R_{sigma} = 0.0333]
Data/restraints/parameters	4445/0/263
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0333, wR_2 = 0.0841
Final R indexes [all data]	R_1 = 0.0408, wR_2 = 0.0879
Largest diff. peak/hole / e Å^{-3}	0.33/-0.31

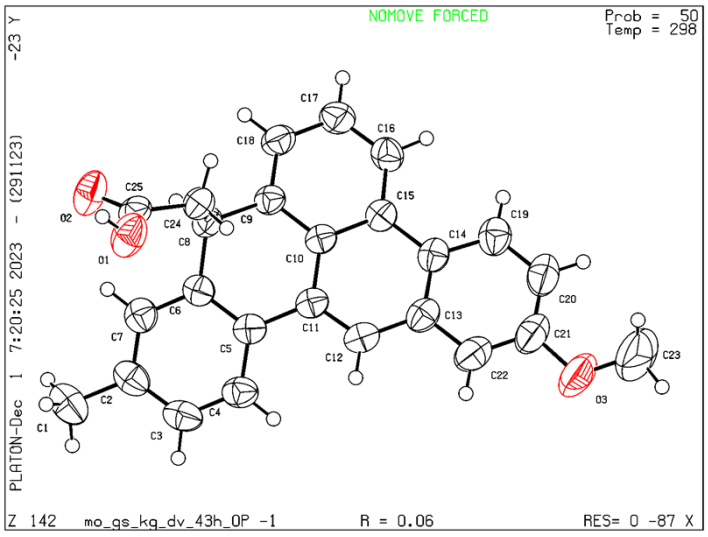


Figure S3: X-ray diagram of compound **13** with ellipsoid shown at the 50% contour percent probability level (CCDC: 2414273).

Table S11: Crystal data and structure refinement for **13** (CCDC: 2414273).

Table S11 Crystal data and structure refinement for 13	
Identification code	**13**
Empirical formula	$C_{25}H_{20}O_3$
Formula weight	368.41
Temperature/K	298
Crystal system	triclinic
Space group	P-1
a/Å	9.1486(5)
b/Å	10.1141(5)
c/Å	11.1933(6)
α/°	76.519(2)

β/°	83.021(2)
γ/°	69.176(2)
Volume/Å^3	940.54(9)
Z	2
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.085
F(000)	388.0
Crystal size/mm^3	0.096 × 0.036 × 0.012
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.402 to 53.458
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14
Reflections collected	9974
Independent reflections	3918 [R_{int} = 0.0393, R_{sigma} = 0.0517]
Data/restraints/parameters	3918/0/255
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0568, wR_2 = 0.1413
Final R indexes [all data]	R_1 = 0.1001, wR_2 = 0.1637
Largest diff. peak/hole / e Å^{-3}	0.26/-0.22

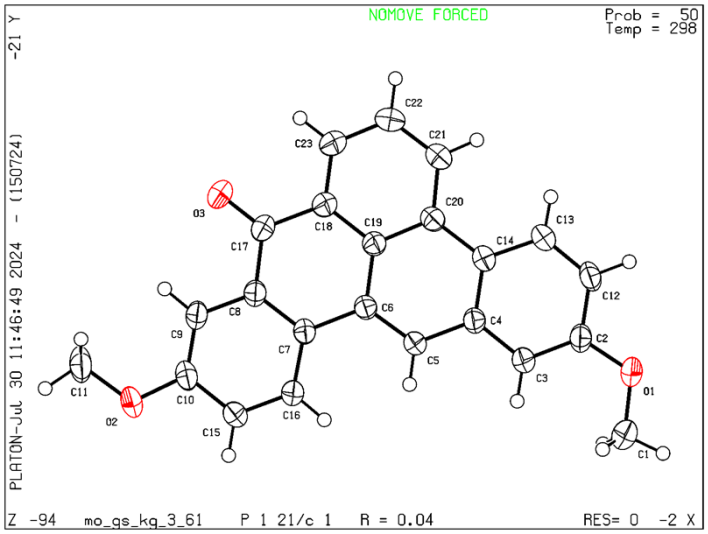


Figure S4: X-ray diagram of compound **4c** with ellipsoid shown at the 50% contour percent probability level (CCDC: 2414272).

Table S12: Crystal data and structure refinement for **4c** (CCDC: 2414272).

Table S12 Crystal data and structure refinement for 4c	
Identification code	**4c**
Empirical formula	$C_{23}H_{16}O_3$
Formula weight	340.36
Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/c$

a/Å	7.961(2)
b/Å	15.645(5)
c/Å	13.670(4)
α/°	90
β/°	105.538(10)
γ/°	90
Volume/Å^3	1640.3(8)
Z	4
ρ_{calc}g/cm^3	1.378
μ/mm^{-1}	0.091
F(000)	712.0
Crystal size/mm^3	0.28 × 0.25 × 0.19
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.208 to 54.386
Index ranges	-10 ≤ h ≤ 9, -20 ≤ k ≤ 20, -17 ≤ l ≤ 17
Reflections collected	26379
Independent reflections	3626 [R_{int} = 0.0525, R_{sigma} = 0.0303]
Data/restraints/parameters	3626/0/237
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1183
Final R indexes [all data]	R_1 = 0.0574, wR_2 = 0.1290
Largest diff. peak/hole / e Å^{-3}	0.22/-0.16

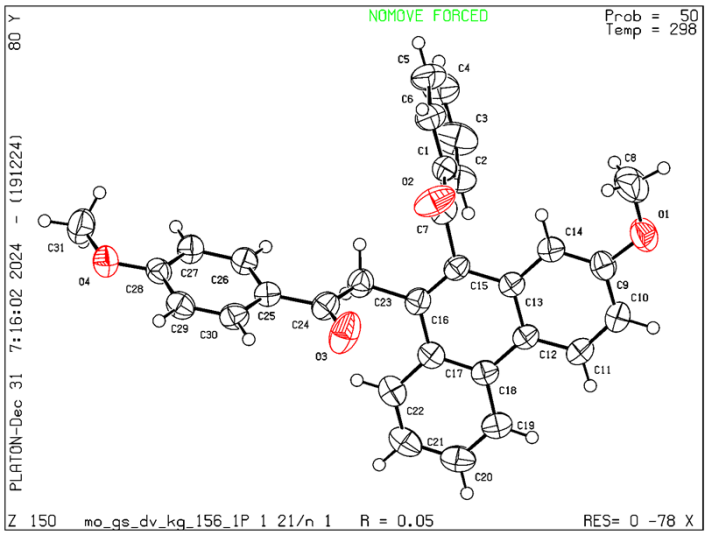


Figure S5: X-ray diagram of compound **5e** with ellipsoid shown at the 50% contour percent probability level (CCDC: 2414271).

Table S13: Crystal data and structure refinement for **5e** (CCDC: 2414271).

Table S13 Crystal data and structure refinement for 5e	
Identification code	**5e**
Empirical formula	$C_{31}H_{24}O_4$
Formula weight	460.50

Temperature/K	298
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.7595(3)
b/Å	14.8506(5)
c/Å	16.2013(6)
α/°	90
β/°	93.2490(10)
γ/°	90
Volume/Å^3	2344.35(14)
Z	4
ρ_{calc}g/cm^3	1.305
μ/mm^{-1}	0.086
F(000)	968.0
Crystal size/mm^3	0.21 × 0.13 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.756 to 54.274
Index ranges	$-12 \leq h \leq 11$, $-17 \leq k \leq 19$, $-20 \leq l \leq 20$
Reflections collected	38656
Independent reflections	5182 [R_{int} = 0.0567, R_{sigma} = 0.0326]
Data/restraints/parameters	5182/0/318
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0461, wR_2 = 0.1087
Final R indexes [all data]	R_1 = 0.0696, wR_2 = 0.1225
Largest diff. peak/hole / e Å^{-3}	0.18/-0.18

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(1) Goel, K.; Satyanarayana, G. Microwave-Assisted Palladium-Catalyzed Crossover-Annulation: Access to Fused Polycyclic Benzofuran Scaffolds. *Org. Lett.* **2025**, *27* (1), 80–85. https://doi.org/10.1021/acs.orglett.4c03917.

(2) Tostado, J.; Milián, A.; Vaquero, J. J.; Fernández-Rodríguez, M. A. Synthesis of Seven- and Eight-Membered Rings by a Brønsted Acid Catalyzed Cationic Carbocyclization of Biphenyl Embedded Enynes. *Org. Lett.* **2024**, *26* (16), 3343–3348. https://doi.org/10.1021/acs.orglett.4c00647.

(3) Milián, A.; García-García, P.; Vaquero, J. J.; Sanz, R.; Fernández-Rodríguez, M. A. Synthesis of Phenanthrene-Based Polycycles by Gold(I)-Catalyzed Cyclization of Biphenyl-Embedded Trienynes. *Advanced Synthesis & Catalysis* **2022**, *364* (22), 3960–3966. https://doi.org/10.1002/adsc.202200887.

(4) Goel, K.; Satyanarayana, G. A Two-Step Access to Fused-/Spiro-Polycyclic Frameworks via Double Heck Cascade and Acid-Driven Processes. *Org. Biomol. Chem.* **2023**, *21* (34), 6919–6925. https://doi.org/10.1039/D3OB01112G.