

Supplementary Information

Photoinduced *meta*-Selective C–H Oxygenation of Arenes

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1. General Consideration:

Reagent Information. All the reactions were carried out in screw cap reaction tubes under aerobic condition, unless otherwise stated. All the chemicals were purchased from Sigma Aldrich, Alfa Aesar and TCI-India. Solvents were bought from commercial sources and were used without further purification. Silica gel (100–200 mesh) was used for column chromatography obtained from Merck. Petroleum ether and ethyl acetate mixture was used as a gradient elution for column chromatography. A gradient elution using petroleum ether and ethyl acetate was performed, based on Merck aluminum TLC sheets (silica gel 60F254).

Analytical Information. All isolated compounds were characterized by ^1H NMR, ^{13}C NMR spectroscopy, and HRMS. Unless otherwise stated, all Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 MHz and 500 MHz instrument. NMR spectra are reported in parts per million (ppm), and were measured relative to the signals for residual solvent in the deuterated solvent, unless otherwise stated. All NMR analysis were performed with 1,3,5-trimethoxybenzene as the internal standard. All ^{13}C NMR spectra were obtained with ^1H decoupling. High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer. UV/vis absorption spectra were recorded on Agilent Cary 8454 UV-Vis spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in quartz cuvettes (chamber volume = 3.0 mL) fitted with a stopper.

Description of Reaction Tube:



Figure S1. Pictorial description of reaction tube for photoredox acetoxylation: Fisher brand Disposable Borosilicate Glass Tubes (16*125mm) with Threaded End (Fisher Scientific, Order No. 1495935A) [left]; Kimble Black Phenolic Screw Thread Closures with Open Tops (Fisher Scientific Order No. 033407E) [left]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [left].

A custom-made light set-up was used with 4 CFL bulbs arranged around the reaction tubes. A fan attached to the apparatus was used to maintain the temperature at (30-35 °C). For irradiation with CFL bulbs, the reaction tubes were placed between light sources (~ 3 cm distance between the light source and the tube).

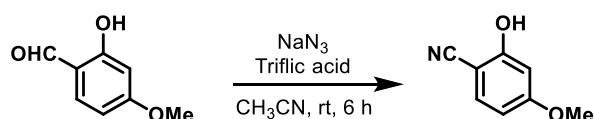


Figure S1: Photograph of the light set used for irradiation of the reaction solutions

2. Preparation of starting materials:

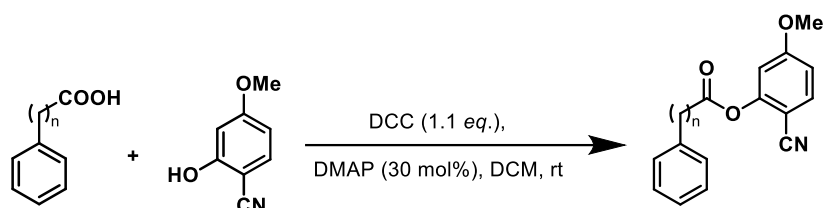
All the starting materials are prepared following our previous literature report (*J. Am. Chem. Soc.* **2022**, *144*, 1929–1940; *Angew. Chem. Int. Ed.* **2017**, *56*, 5272–5276)

2.A. Synthesis of the directing group:



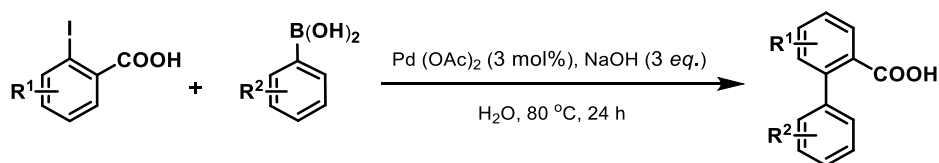
In an oven-dried round bottom flask (250 mL), charged with a stir-bar, corresponding aldehyde (20.0 mmol) and NaN₃ (3.0 equiv.) were taken CH₃CN (60 mL) was added to it and stirred at room temperature for 15 min. After that 3.5 equiv. of triflic acid was added to the mixture in portion wise. After the addition the reaction was allowed to stir at room temperature for 12 h. Upon completion, the solvent was removed under reduced pressure. The solid residue was dissolved in ethyl acetate and washed with saturated NaHCO₃ solution (3 times). The organic fraction was then dried over anhydrous Na₂SO₄ and purified through column chromatography.

2.B. General procedure for synthesis of carbonyl ester of phenylacetic acids:

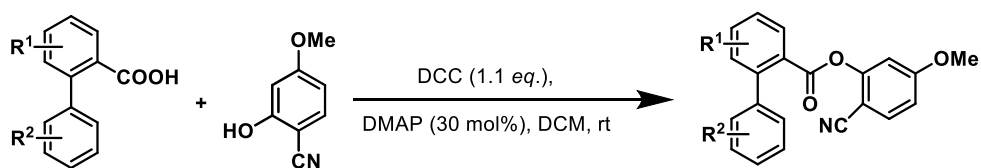


To a stirred solution of carboxylic acid (1 equiv, 5 mmol) and DMAP (0.3 mmol) in 30 mL anhydrous CH_2Cl_2 , 2-hydroxy-4-methoxybenzonitrile (1.5 equiv, 7.5 mmol) was added. After 15 minute of stirring, DCC (5.5 mmol) was added to the reaction mixture at 0°C and then allowed to stir overnight at room temperature. Upon completion of reaction, precipitated urea is then filtered off. Filtrate is evaporated and the residue was dissolved in CH_2Cl_2 and washed with saturated NaHCO_3 solution, and then dried over anhydrous Na_2SO_4 . The solvent is removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to give the desired ester.

2.C. General procedure for synthesis of biphenyl carbonyl ester:



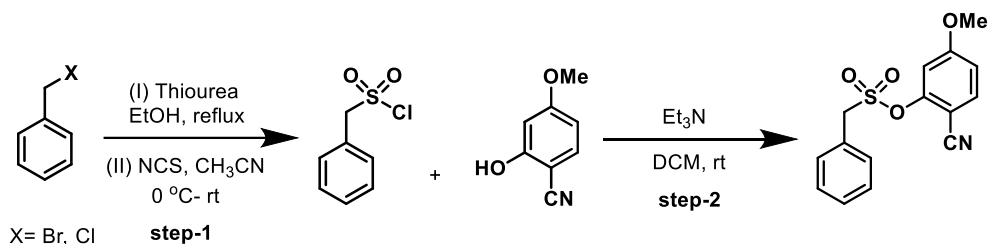
Step 1: A clean, oven-dried screw cap reaction tube with previously placed magnetic stir-bar was charged with 2-iodobenzoic acid derivatives (1 equiv, 3 mmol), corresponding boronic acid (1.2 equiv, 3.6 mmol), sodium hydroxide (3 equiv, 9 mmol) $\text{Pd}(\text{OAc})_2$ (3 mol %) and water 9 mL. The reaction tube was evacuated and back filled with nitrogen and this sequence was repeated three additional times. Then it was placed in preheated oil bath at 80°C for 24 h. After completion of the reaction, the reaction was cooled to room temperature and acidify to 3-4 pH. The resulting mixture was extracted with ethyl acetate and the organic layer was dried Over Na_2SO_4 . The solvent is removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to give the biphenyl acids.



Step 2: To a stirred solution of biphenyl carboxylic acid (1 equiv, 2 mmol) and DMAP (0.3 mmol) in 10 mL anhydrous CH_2Cl_2 , 2-hydroxy-4-methoxybenzonitrile (1.5 equiv, 3.0 mmol)

was added. After 15 minute of stirring, DCC (2.2 mmol) was added to the reaction mixture at 0°C and then allowed to stir overnight at room temperature. Upon completion of reaction, precipitated urea is then filtered off. The filtrate is evaporated and the residue was dissolved in CH₂Cl₂ and washed with saturated NaHCO₃ solution, and then dried over anhydrous Na₂SO₄. The solvent is removed under reduced pressure and the residue was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether) to give the desired ester.

2.D. General synthesis of sulfonyl ester scaffolds:

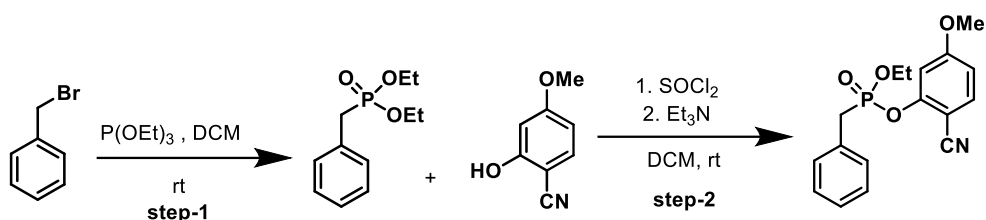


Step 1: Preparation of phenylsulfonyl chloride:

An oven-dried clean round bottom flask was charged with magnetic stir-bar, benzyl chloride/bromide (10.0 mmol) and thiourea (10.0 mmol, 760 mg). 10 mL of absolute ethanol was added and refluxed at 96 °C. After 3 h the reaction was taken out and solvent was evaporated under reduced pressure to obtained white solid thiouric salt. The obtained solid salt was suspended in 14 mL of CH₃CN and 3 mL (2N HCl) was added to it. The mixture was stirred at 0 °C for 15 min. *N*-chlorosuccinimide (NCS) (40.0 mmol; 5.34 g) was added in portion to the suspension in order to obtain a clear solution. The solution was stirred for another 30 min at room temperature. Then the solution was evaporated under reduced pressure to remove the CH₃CN. The remaining aqueous portion was extracted with ethyl acetate and dried over anhydrous Na₂SO₄ and purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether/ ethyl acetate as the eluent.

Step 2: To an ice-cold solution of 2-hydroxy-4-methoxybenzonitrile (5.0 mmol) and TEA (1.5 equiv., 1.04 mL) in 10 mL dichloromethane under nitrogen atmosphere, phenylsulfonyl chloride was added portion wise. Stirring was continued for additional 20 min, after that the ice bath was removed and the reaction mixture was left overnight at room temperature. After completion of the reaction DCM was removed under reduced pressure and the residue was extracted with ethyl acetate (3 x 20 mL). The organic layer was dried over anhydrous Na₂SO₄. After filtration and evaporation of the solvent, the crude mixture was purified by column chromatography using neutral alumina and petroleum ether / ethyl acetate (85/15, v/v) as the eluent.

2.E. General synthesis of Phosphonate ester scaffolds:



Step 1: Preparation of diethyl benzylic phosphonates:

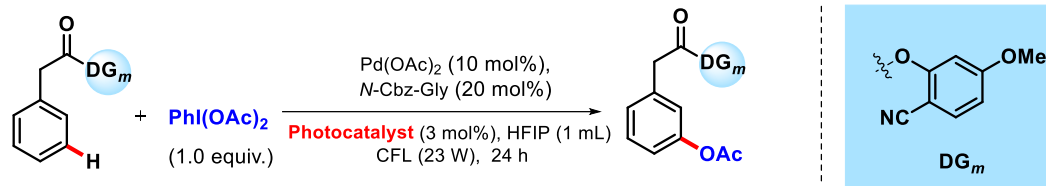
An oven dried clean round bottom flask with magnetic stir-bar was charged with benzyl bromide derivatives (1.0 mmol), P(OEt)₃ (1.2 mmol) and 5 mL of dry DCM and stirred at room temperature in the presence of catalytic amount of ZnI₂ (0.2 mmol). After 6 h the reaction was taken out and evaporated under reduced pressure to obtained crude materials which was then purified by column chromatography as petroleum ether / ethyl acetate as the eluent.

Step 2: Preparation of Phosphonyl chloride:

An oven dried clean round bottom flask was charged with magnetic stir-bar and diethyl benzylic phosphonates, and then SOCl₂ was added as a solvent amount to the reaction mixture and stirred at reflux condition. After 3 h the excess amount of SOCl₂ was removed by rotavapor and the crude phosphonyl chloride derivatives was charged for next step esterification. Under nitrogen atmosphere Et₃N was added to the 2-hydroxy-4-methoxybenzonitrile solution in DCM. The reaction was stirred at 0 °C for 10 mins. Under nitrogen atmosphere Phosphonyl chloride was added to the reaction in portion until effervescence stopped and then transferred to room temperature and stirred overnight. The progress of the reaction was monitored by TLC. Upon completion the reaction was quenched by adding water and the desired compound was extracted with ethyl acetate. Combined organic portion was dried over anhydrous Na₂SO₄. The crude mixture was concentrated under reduced pressure and purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

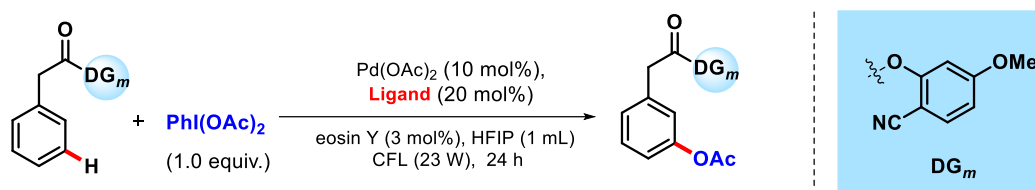
10	Pd(PPh ₃) ₄	trace	-
11	Pd(OAc)₂	51%	>25:1

Table S3: Optimization by varying different photocatalyst:



Entry	Photocatalyst	NMR Yield (%)	<i>meta:others</i>
1	Fluorescein	47	>25:1
2	eosin Y	51	>25:1
3	4-Czipn	35	15:1
4	2,4,6 triphenyl pyroliidinium salt	46	8:1
5	Eosin B	35	20:1
6	1,4 dicyanobenzene	trace	-
7	Rose Bengal	40	18:1
8	Rhodamin B	trace	-
9	Ru(bpy) ₃ Cl ₂	30	7:1
10	Ir[dF(CF ₃)ppy] ₂ (dtbpy))PF ₆	13	17:1

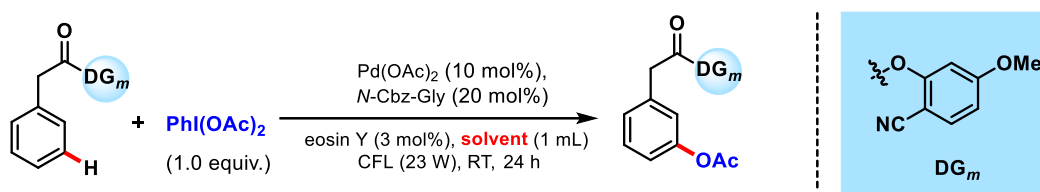
Table S4: Optimization by varying different amino acid ligands:



Entry	Ligand	NMR Yield (%)	<i>meta:others</i>
1	<i>N</i> -Ac-Gly-OH	41	16:1
2	<i>N</i> -Ac-L-Leucine	31	12:1
3	<i>N</i> -Ac-L-Valine	35	10:1
4	<i>N</i> -Ac-DL-2-Phe-Glycine	36	8:1
5	<i>N</i> -Ac-Phe-OH	25	10:1
6	Boc-Gly-OH	38	15:1
7	Fmoc-Gly-OH	40	17:1

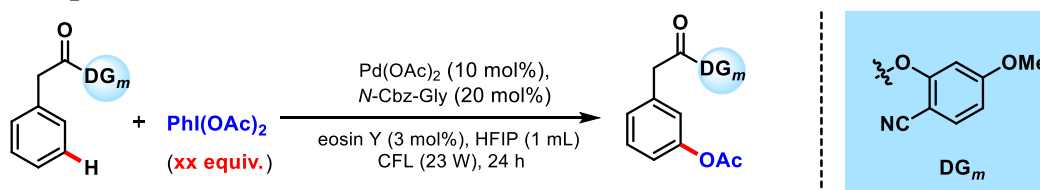
8	CBz-Gly-OH	51	>25:1
9	<i>N</i> -Ac-DL-Tryptophan	16	6:1
10	<i>N</i> -Ac-4-Hydroxy-L-Proline	21	3:1
11	<i>N</i> -Ac-DL-Methionine	19	10:1
12	<i>N</i> -Ac-L-Histidine Monohydrate	13	7:1
13	<i>N</i> -Ac-Glycine Ethyl Ester	58	16:1
14	<i>N</i> -Ac-L-Glutamic Acid	23	11:1
15	2-hydroxy pyridine	18	2:1

Table S5: Optimization by varying different solvents:



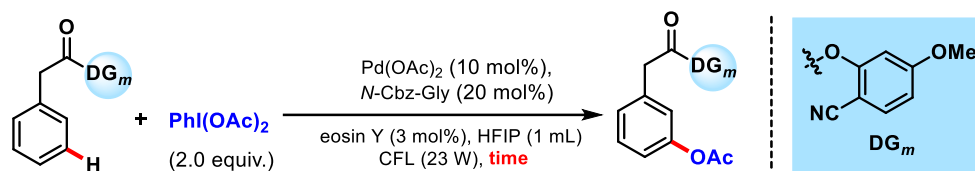
Entry	Solvent	NMR Yield (%)	<i>meta</i> : <i>others</i>
1	HFIP	51	>25:1
2	DCE	n.d	-
3	HFIP+DCE (1:1)	trace	-
4	CH ₃ CN	n.d	-
5	^t Pr-OH	n.d	-
6	MeOH	trace	-
7	1,4 dioxane	n.d.	-
8	THF	n.d.	-
9	TFA	trace	-
10	HFIP+H ₂ O (1:1)	n.d.	-
11	HFIP+TFA (8:2)	15	6:1
12	HFIP+AcOH (8:2)	Multiple product	-
13	TFE	14	>20:1

Table S6: Optimization of amount of PIDA:



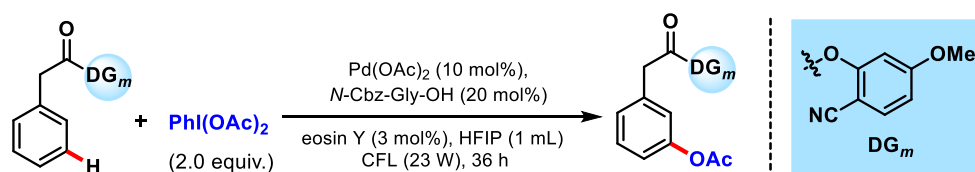
Entry	PIDA amount (equiv.)	NMR Yield (%)	<i>meta:others</i>
1	1	51	>25:1
2	1.5	65	>25:1
3	2	68	>25:1
4	2.5	67	>25:1
5	3	64	>25:1
6	3.5	60	>25:1
7	4	58	>25:1
8	PIDA+Ac ₂ O (1:1) 2	49	>25:1

Table S7: Time optimization:



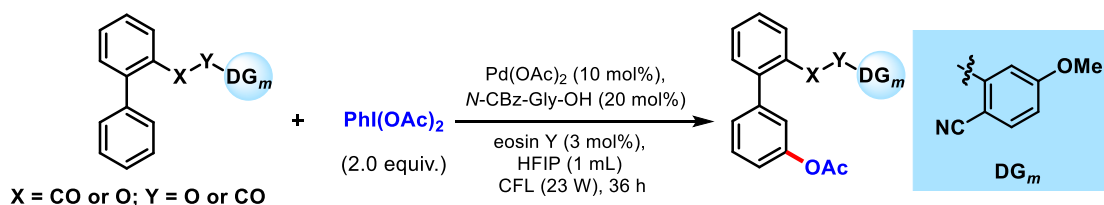
Entry	Time (h)	NMR Yield (%)	<i>meta:others</i>
1	4	14	>25:1
2	8	22	>25:1
3	12	35	>25:1
4	16	47	>25:1
5	20	52	>25:1
6	24	68	>25:1
7	28	72	>25:1
8	32	75	>25:1
9	36	79	>25:1
10	40	78	>25:1
11	44	79	>25:1

4.A. General procedure for *meta*-acetoxylation of phenylacetic acid derivatives:



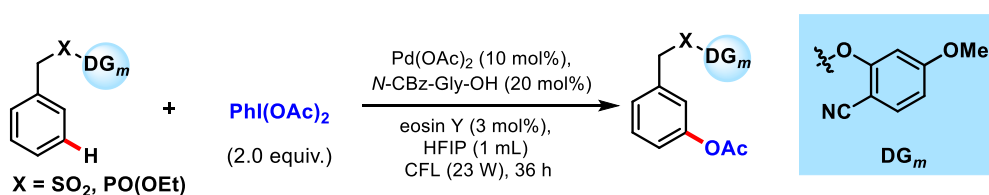
General procedure: In an oven-dried screw capped reaction tube was charged with magnetic stir bar, corresponding ester of phenyl acetic acid (0.1 mmol), Pd(OAc)₂ (10 mol%), *N*-Cbz-Gly-OH (20 mol%), eosin Y (3 mol%), and PhI(OAc)₂ (0.2 mmol, 2 equiv.) in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 3 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 36 h. The temperature was maintained at approximately (30-35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporation under reduced pressure and the crude mixture was purified by column chromatography using silica (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

4.B. General procedure for *meta*-acetoxylation of biphenyl ester/alcohol derivatives:



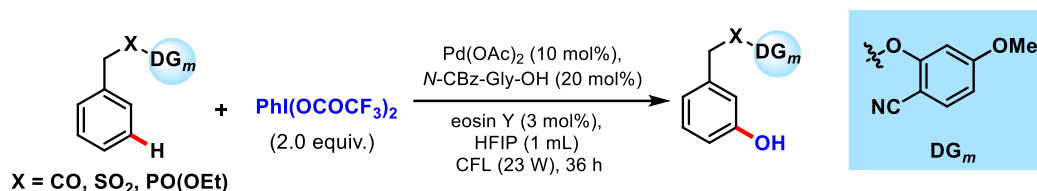
General procedure: In an oven-dried screw capped reaction tube was charged with magnetic stir bar, corresponding biphenyl ester/alcohol (0.1 mmol), Pd(OAc)₂ (10 mol%), *N*-Cbz-Gly-OH (20 mol%), eosin Y (3 mol%), and PhI(OAc)₂ (0.2 mmol, 2 equiv.) in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 3 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 36 h. The temperature was maintained at approximately (30-35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporation under reduced pressure and the crude mixture was purified by column chromatography using silica (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

4.C. General procedure for *meta*-acetoxylation of sulphonyl/phosphonyl ester derivatives:



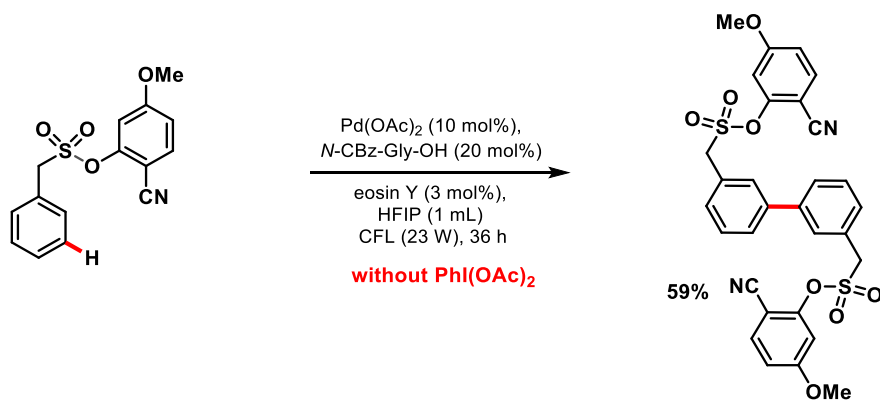
General procedure: In an oven-dried screw capped reaction tube was charged with magnetic stir bar, corresponding sulphonyl/phosphonyl ester (0.1 mmol), Pd(OAc)₂ (10 mol%), *N*-Cbz-Gly-OH (20 mol%), eosin Y (3 mol%), and PhI(OAc)₂ (0.2 mmol, 2 equiv.) in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 3 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 36 h. The temperature was maintained at approximately (30-35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporation under reduced pressure and the crude mixture was purified by column chromatography using silica (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

4.D. General procedure for *meta*-hydroxylation of various arenes derivatives:



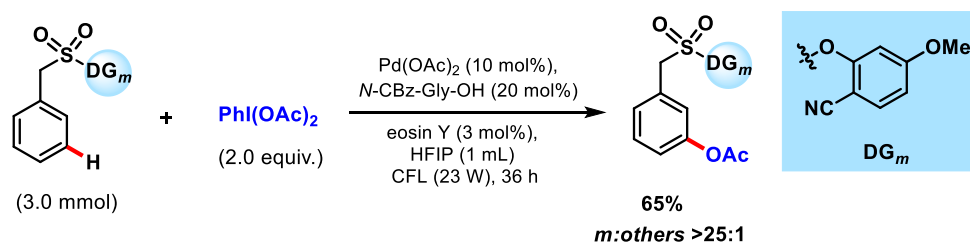
General procedure: In an oven-dried screw capped reaction tube was charged with magnetic stir bar, corresponding sulphonyl/phosphonyl ester (0.1 mmol), Pd(OAc)₂ (10 mol%), *N*-Cbz-Gly-OH (20 mol%), eosin Y (3 mol%), and PhI(OCOCF₃)₂ (0.2 mmol, 2 equiv.) in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 3 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 36 h. The temperature was maintained at approximately (30-35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporation under reduced pressure and the crude mixture was purified by column chromatography using silica (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

4.E. General procedure for *meta-meta* homocoupling:



In an oven-dried screw capped reaction tube was charged with magnetic stir-bar, corresponding sulphonic ester (0.1 mmol), Pd(OAc)₂ (10 mol%), *N*-CBz-Gly-OH (20 mol%) and eosin Y (3 mol%), in 1 mL of 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 5 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 36 h. The temperature was maintained at approximately (30 - 35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporated under reduced pressure and the yield was monitored using ¹H NMR signal in presence of 1,3,5-trimethoxybenzene as internal standard. The spectral data of this compound is correlated with the previous literature report. (*J. Am. Chem. Soc.* **2022**, *144*, 1929–1940).

4.F. General procedure for scaleup reaction:

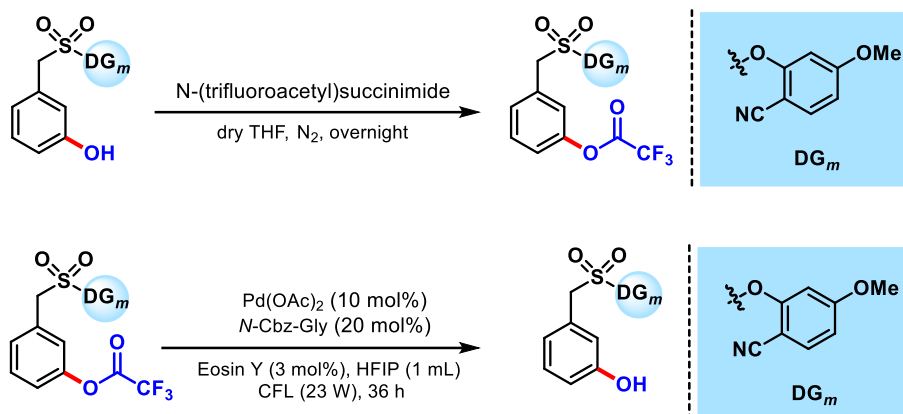


General procedure: In an oven-dried screw capped reaction tube was charged with magnetic stir bar, corresponding sulfonyl ester (3.0 mmol), Pd(OAc)₂ (10 mol%), *N*-Cbz-Gly-OH (20 mol%), eosin Y (3 mol%), and PhI(OAc)₂ (6.0 mmol, 2 equiv.) in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 3 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 36 h. The temperature was maintained at approximately (30-35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporation under reduced pressure and the crude mixture was purified by column chromatography using silica (100-200 mesh size) and petroleum ether / ethyl acetate as the eluent.

5. Identification of intermediate in *meta*-hydroxylation protocol:

In order to confirm the intermediacy of the *meta*-trifluoroacetoxy moiety, the compound was synthesized separately and administered under the optimized condition of *meta*-hydroxylation.

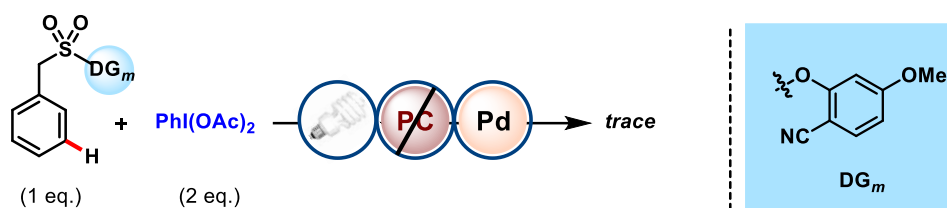
Synthesis of *meta*-trifluoroacetoxy moiety:



The *meta*-hydroxylated compound (0.1 mmol) was dissolved in dry THF (3mL) and *N*-(trifluoroacetyl)succinimide (0.15 mmol) was added to it. The reaction was refluxed overnight under N₂ atmosphere. After the reaction was finished, the precipitated succinimide was filtered off, and solvent was evaporated under reduced pressure forming the trifluoroacetate esters. The crude product was dissolved in diethylether (3 x 5 mL) and filtered to remove the succinimide. The organic part was evaporated to obtain the pure product (yield 88%). The obtained solid compound was directly used under optimized condition (general procedure for *meta*-hydroxylation condition). Formation of hydroxylated product quantitatively confirms the in-situ hydrolysis of trifluoroacetylated product.

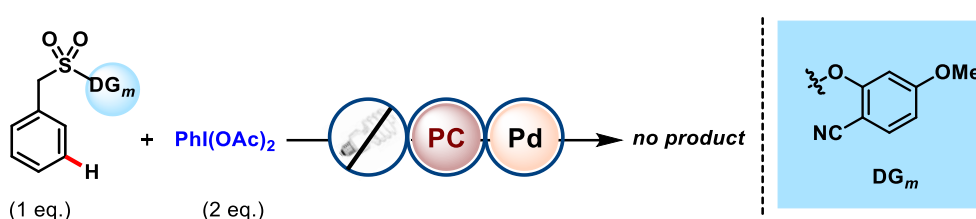
6. Mechanistic Studies:

(I) *Meta*-acetoxylation in the absence of photocatalyst:



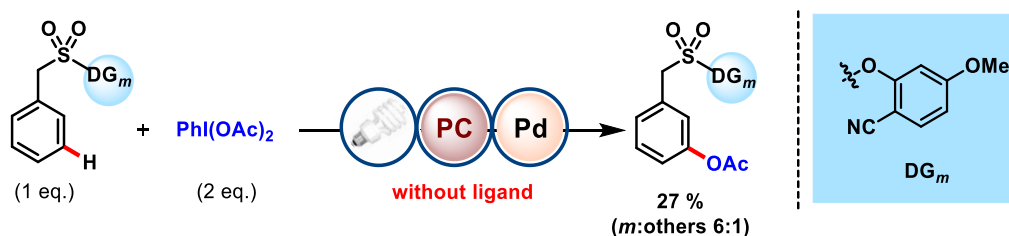
Following the general procedure for *meta*-C–H acetoxylation, the above stated control experiment was performed without photocatalyst in presence of four 23 W house hold CFL bulbs with stirring at (30 - 35 °C) for 36 h.

(II) *Meta*-acetoxylation in the absence of light:



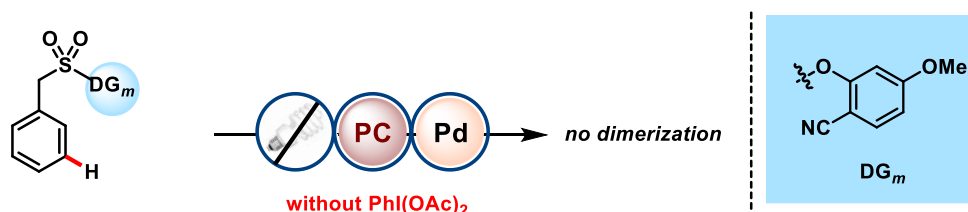
Following the general procedure for *meta*-C–H acetoxylation, the above stated control experiment was performed in absence of CFL bulbs (dark condition) for 36 h.

(III) *Meta*-acetoxylation in the absence of ligand:



Following the general procedure for *meta*-C–H acetoxylation, the above stated control experiment was performed in absence of ligand with four 23 W house hold CFL bulbs with stirring at (30 - 35 °C) for 36 h.

(IV) *Meta-meta* homo-coupling in the absence of light:



Following the general procedure for *meta-meta* homocoupling, the above stated control experiment was performed in absence of CFL bulbs (dark condition) with stirring for 36 h.

From the above control experiment results it was found that light and photocatalyst obligatory for the transformation.

(V) On/Off experiment:

According to the general procedure for *meta*-C–H acetoxylation, a reaction containing TMB (Trimethoxy-benzene) as internal standard was set up and placed in presence of four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature. The reaction was sequentially stirred under visible light irradiation and in the absence of light. Every two hours an aliquot of 50 μ L was removed *via* syringe and analyzed by ^1H NMR spectroscopy. After a total of 16 h the determined yields were plotted against the reaction time.

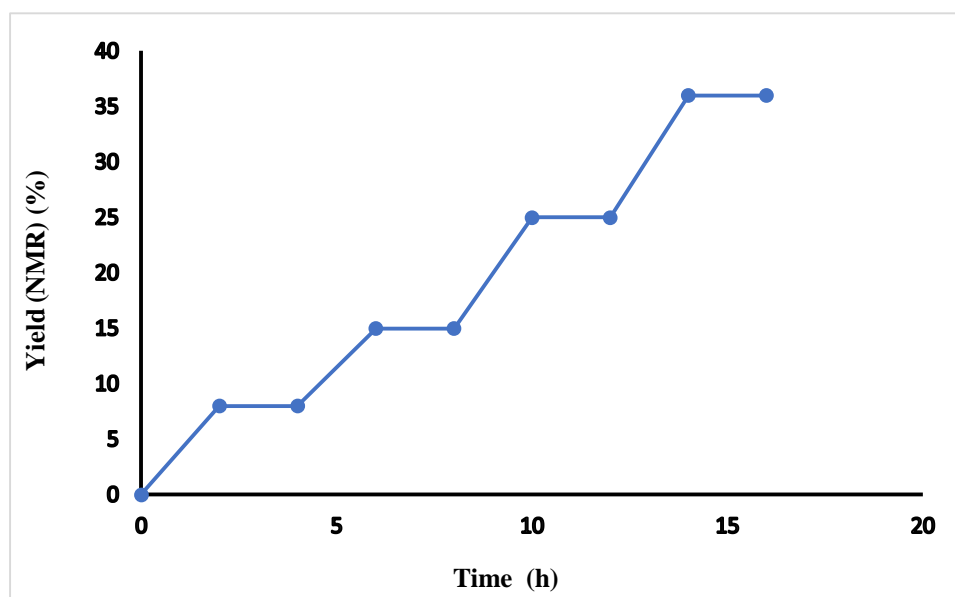
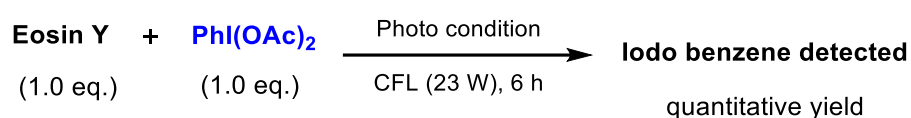


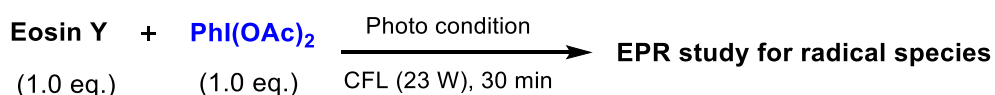
Fig S2: Effect of visible light irradiation

(VI) Detection of radical species in the reaction mixture:



Following the above procedure stated control experiment was performed with four 23 W house hold CFL bulbs with stirring at (30 - 35 $^{\circ}\text{C}$) for 6 h. Formation of iodobenzene in quantitative amount supports the decomposition of PhI(OAc)_2 in presence of eosin Y and visible light.

(VII) EPR Study



The similar control experiment was performed with four 23 W house hold CFL bulbs and after 30 min it is subjected to EPR study. **The EPR experiments show sign of acetate radical in the mixture and proves our mechanistic hypothesis regarding generation of radical to perform meta-acetylation.**

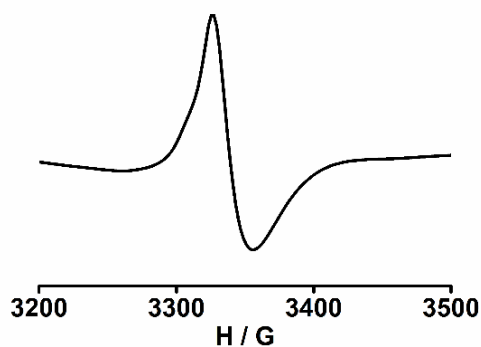
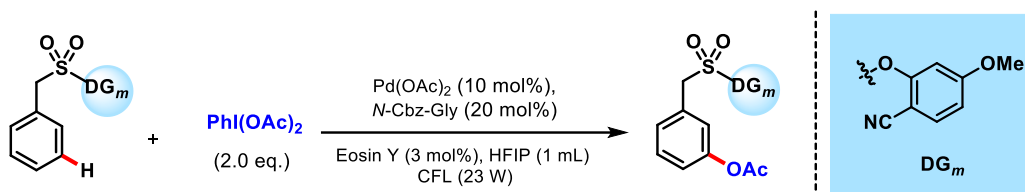


Fig S3: EPR spectra for the mixture of eosin Y, $\text{PhI}(\text{OAc})_2$ in HFIP at 100 K after 30 min of visible light irradiation ($g = 1.993$)



Following the general procedure for *meta*-C–H acetoxylation, the above stated control experiment was performed with four 23 W house hold CFL bulbs for 60 min. to further confirm the formation of acetate radical during the course of the reaction. The similar type of EPR signal was observed as for the above experiment.

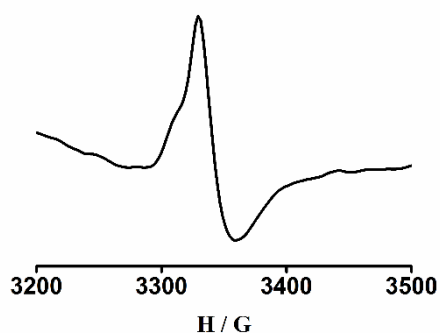
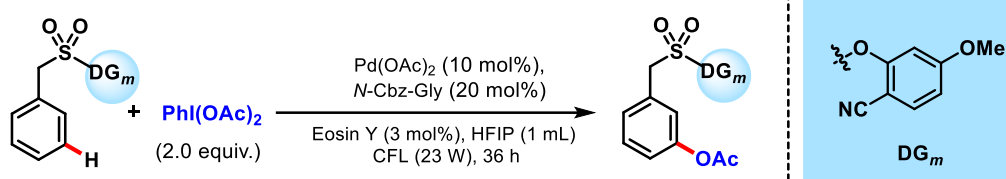


Fig S4: EPR spectra for the mixture of scaffold, ligand, $\text{Pd}(\text{OAc})_2$, eosin Y, $\text{PhI}(\text{OAc})_2$ in HFIP at 100 K after 60 min of visible light irradiation ($g = 2.001$)

Above two EPR experiments suggests the formation of radical species and the transformation proceeds through radical pathway.

(VIII) Effect of radical scavenger:



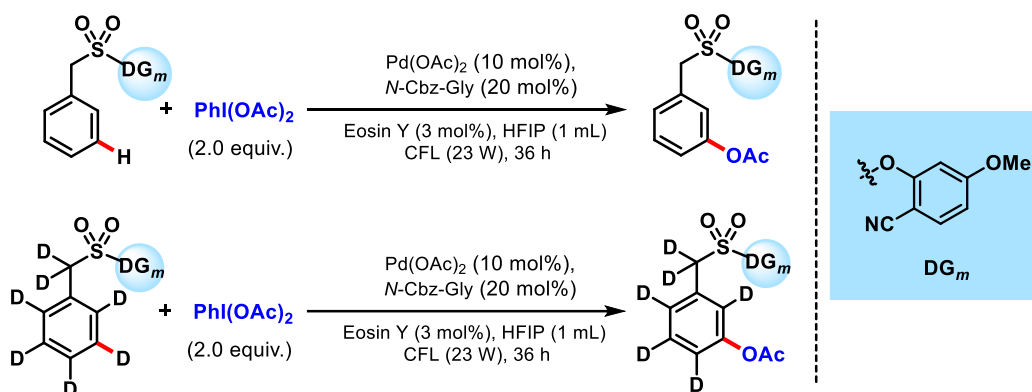
TEMPO (3 eq.), TEMPO = 2,2,6,6-Tetramethylpiperidine-1-oxyl, **no product**

PNB (3 eq.), PNB = Phenyl N-tert-butyl nitron, **no product**

BHT (3 eq.), BHT = Butylated hydroxytoluene, **no product**

Effect on radical scavenger for *meta*-C–H acetoxylation: Following the general procedure for *meta*-C–H olefination, the control experiment was performed with radical inhibitors (0.6 mmol) in presence of four 23 W house hold CFL bulbs with stirring at (30 - 35 °C) for 36 h. **Complete inhibition of the product formation further assures the involvement of radical species in the transformation.**

7. Kinetic isotope effect experiment:



Following the general procedure for *meta*-C–H acetoxylation, the reaction mixture was monitored for 10 to 60 min. After immediately cooling in a dry ice/alcohol bath, the yield of product was determined by crude ¹H NMR using TMB (Trimethoxy benzene) as the internal standard. **Each reaction is performed 3 times and the obtained average yields were plotted as yield [product] vs. time (min).**

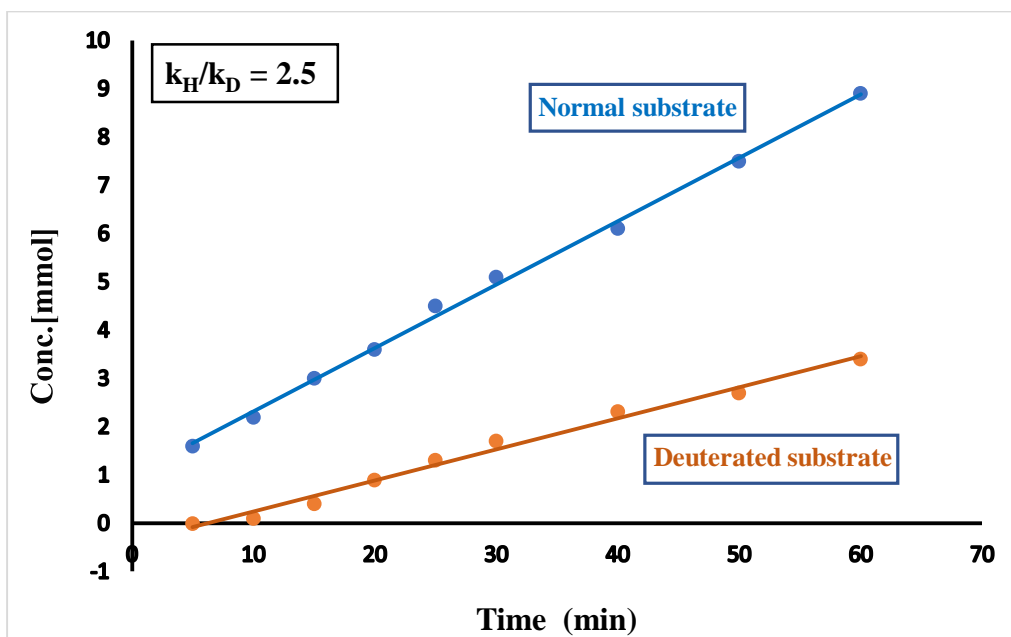


Fig S5: Determination of kinetic isotope effect

Now, Rate = $k \cdot [\text{substrate}]^x [\text{PhI}(\text{OAc})_2]^y$

For run 1, initial rate = Rate 1

So, Rate = $k_H \cdot [\text{substrate}]^x [\text{PhI}(\text{OAc})_2]^y$

or, $0.1314 = k_H \cdot [0.05]^x [0.1]^y$

For run 2, initial rate = Rate 2

So, Rate = $k_D \cdot [\text{deuterated substrate}]^x [\text{PhI}(\text{OAc})_2]^y$

or, $0.0520 = k_D \cdot [0.05]^x [0.1]^y$

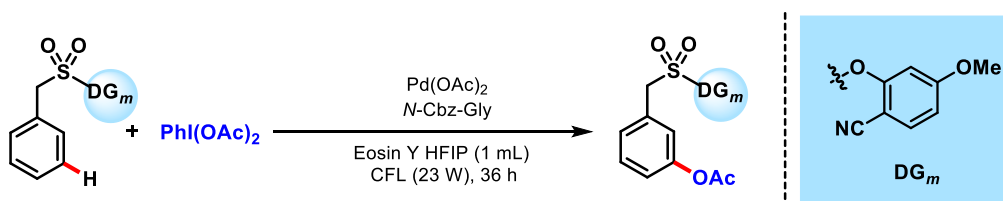
So, $k_H / k_D = \text{Rate 1} / \text{Rate 2}$

or, $k_H / k_D = 0.1314 / 0.0520$

or, $k_H / k_D = 2.5$

The KIE data shown that the C–H cleavage step is the rate-determined step for the *meta* acetoxylation [$K_H/K_D = 2.5$].

8. Order determination for *meta*-C–H acetylation:



We can assume the rate of the reaction is dependent on the concentration of palladium catalyst, scaffold and ligand respectively. **Each reaction is performed 3 times and the obtained average yields were plotted as Conc. [mmol] vs. time (min).**

So, Rate = k. [substrate]^x [ligand]^y [palladium catalyst]^z(1)

8.A. Order determination with respect to scaffold-

Run	scaffold (mmol)	PhI(OAc) ₂ (mmol)	[Pd(OAc) ₂ (mmol)	<i>N</i> -Cbz-Gly (mmol)
1	0.05	0.1	0.005	0.01
2	0.025	0.1	0.005	0.01

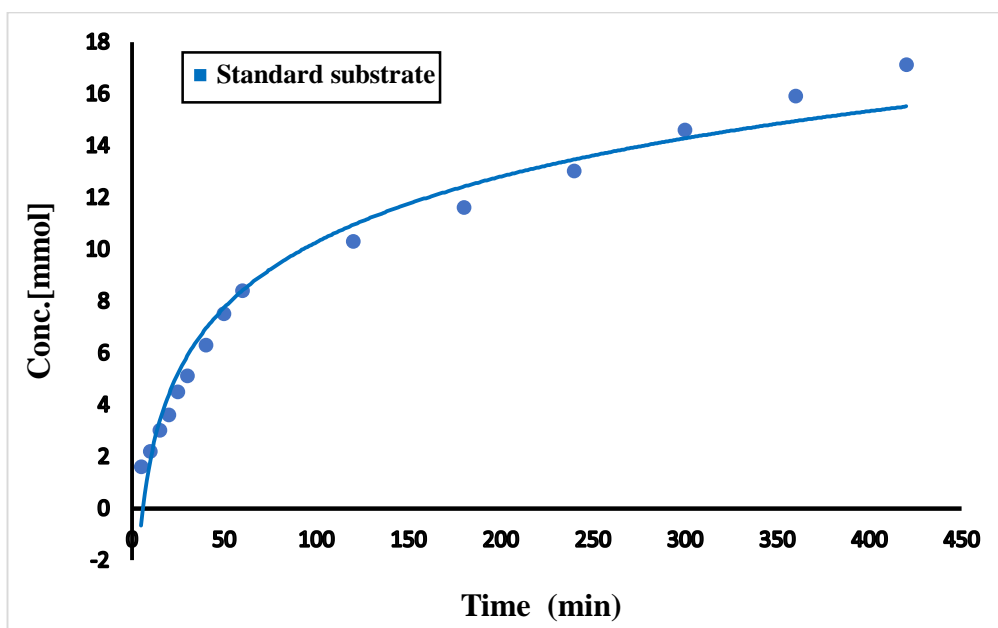


Fig S6. Product formation plot in run 1

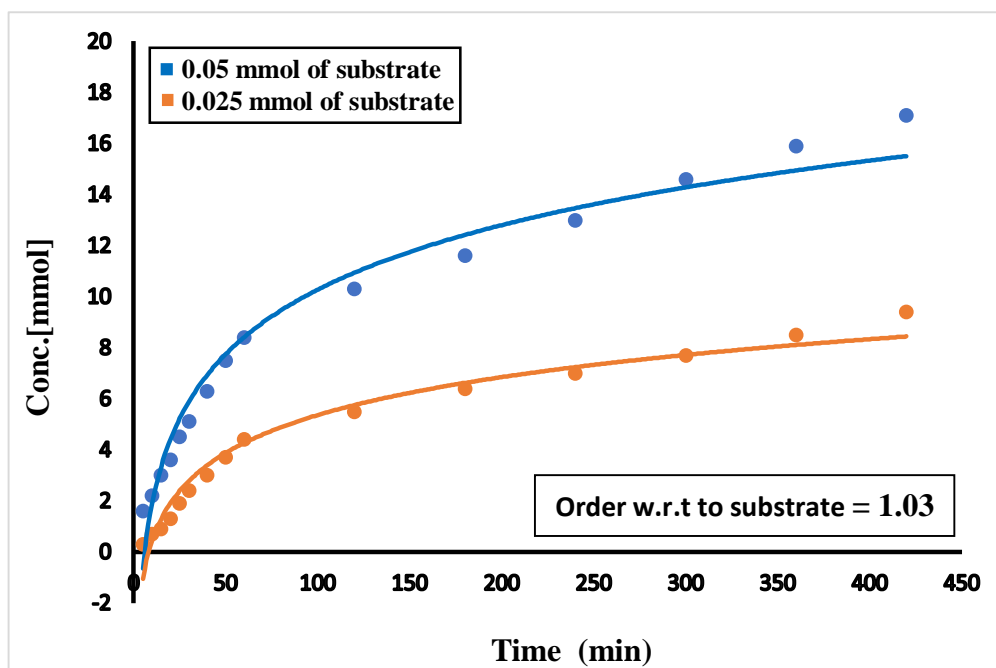


Fig S7. Product formation plot in run 1 and run 2

From the equation (1) we got, Rate = k. [scaffold]^x [ligand]^y

For run 1, initial rate = Rate 1

$$\text{So, Rate 1} = k. [\text{scaffold}]^x [\text{ligand}]^y$$

$$\text{or, } 0.0257 = k. [0.05]^x [0.1]^y \dots\dots\dots(2)$$

For run 2, initial rate = Rate 2

$$\text{So, Rate 2} = k. [\text{scaffold}]^x [\text{ligand}]^y$$

$$\text{or, } 0.0249 = k. [0.025]^x [0.1]^y \dots\dots\dots(3)$$

Hence from equation (2) and (3)

$$\text{We get, } [\text{Rate 1} / \text{Rate 2}] = [0.05 / 0.025]^x$$

$$\text{or, } x = [\log (\text{Rate 1}) - \log (\text{Rate 2})] / [\log (0.05) - \log (0.025)]$$

$$\text{or, } x = [\log (0.0257) - \log (0.0249)] / [\log (0.05) - \log (0.025)]$$

$$\text{or, } x = \mathbf{1.03}$$

So, order with respect to scaffold is ~ 1

8.B. Order determination with respect to ligand *N*-Cbz-Gly

Run	scaffold (mmol)	PhI(OAc) ₂ (mmol)	[Pd(OAc) ₂ (mmol)	<i>N</i> -Cbz-Gly (mmol)
1	0.05	0.1	0.005	0.01
2	0.05	0.1	0.005	0.005

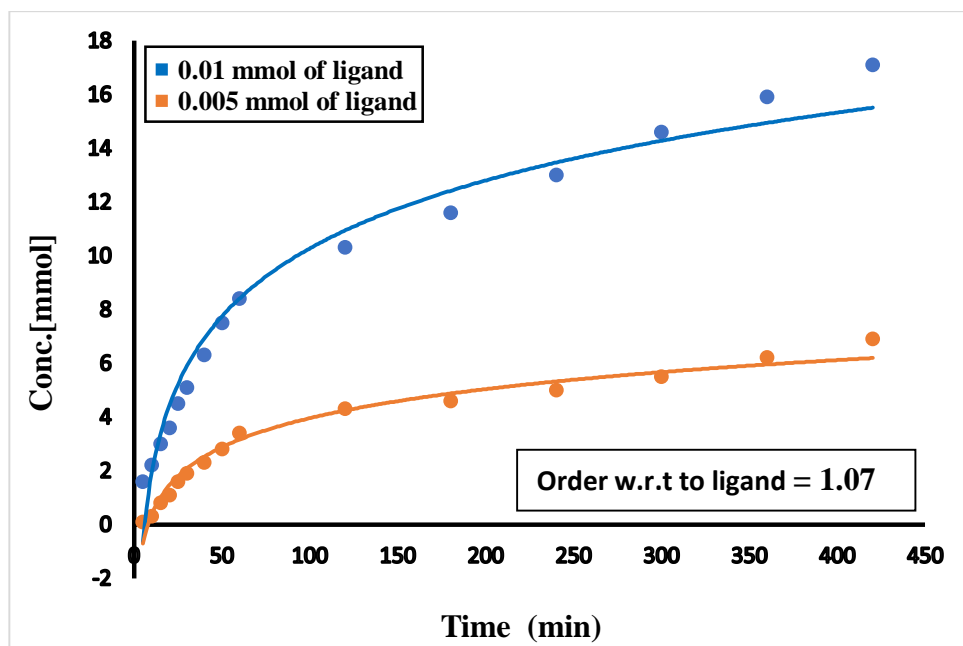


Fig S8. Product formation plot in run 1 and run 3

From the equation (1) we got, Rate = k. [scaffold]^x [ligand]^y

For run 1, initial rate = Rate 1

$$\text{So, Rate 1} = k \cdot [\mathbf{1a}]^x [\mathbf{2a}]^y$$

$$\text{or, } 0.0257 \text{ (mmol}^{-1}\cdot\text{min}^{-1}) = k \cdot [0.05]^x [0.01]^y \quad \dots\dots\dots(2)$$

For run 3, initial rate = Rate 3

$$\text{So, Rate 3} = k \cdot [\mathbf{scaffold}]^x [\mathbf{ligand}]^y$$

$$\text{or, } 0.0239 \text{ (mmol}^{-1}\cdot\text{min}^{-1}) = k \cdot [0.05]^x [0.005]^y \quad \dots\dots\dots(4)$$

Hence from equation (2) and (4)

$$\text{We get, } [\text{Rate 1} / \text{Rate 3}] = [0.01 / 0.005]^y$$

$$\text{or, } x = [\log (\text{Rate 1}) - \log (\text{Rate 3})] / [\log (0.15) - \log (0.01)]$$

$$\text{or, } x = [\log (0.0257) - \log (0.0239)] / [\log (0.15) - \log (0.005)]$$

$$\text{or, } x = \mathbf{1.07}$$

So, order with respect to ligand is ~ 1

8.C. Order determination with respect to palladium catalyst

Run	scaffold (mmol)	PhI(OAc) ₂ (mmol)	[Pd(OAc) ₂] (mmol)	N-Cbz-Gly (mmol)
1	0.05	0.1	0.005	0.01
2	0.05	0.1	0.0025	0.01

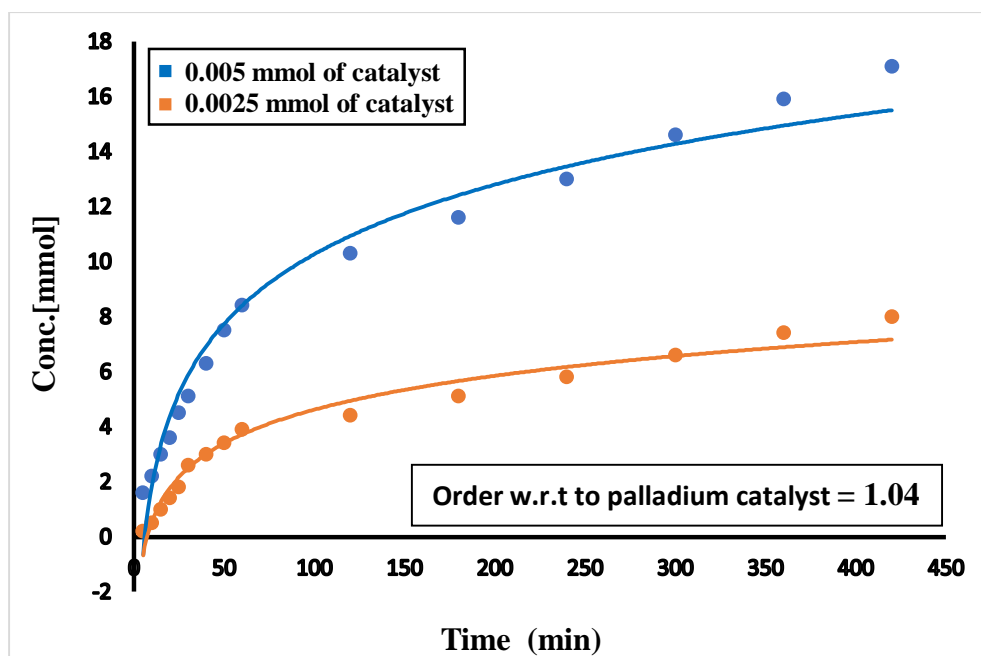


Fig S9. Product formation plot in run 1 and run 4

From the equation (1) we got, Rate = k . [substrate]^x [palladium catalyst]^z

For run 1, initial rate = Rate 1

So, Rate 1 = k. [1a]^x [3a]^z
 or, 0.0257 (mmol⁻¹.min⁻¹) = k . [0.05]^x [0.005]^z(2)

For run 4, initial rate = Rate 4

So, Rate 3 = k. [substrate]^x [palladium catalyst]^z
 or, 0.0246 (mmol⁻¹.min⁻¹) = k . [0.05]^x [0.0025]^z(5)

Hence from equation (2) and (5)

We get, [Rate 1/ Rate 3] = [0.15/ 0.00125]^y

or, x = [log (Rate 1) – log (Rate 3)] / [log (0.005) – log (0.0025)]

or, x = [log (0.0257) – log (0.0246)] / [log (0.005) – log (0.0025)]

or, x = **1.04**

9. A. UV-visible Absorption experiment:

UV/vis absorption spectra were recorded on Agilent Cary 8454 UV-Vis spectrophotometer, equipped with a temperature control unit at 25 °C. The samples were measured in quartz cuvettes (chamber volume = 3.0 mL fitted with a stopper. Following the general procedure for *meta*-C–H acetoxylation, the UV-visible absorption of the reaction mixture was taken separately, along with individual *meta*-scaffold, *meta*-DG, ligand, eosin Y at the standard reaction in HFIP as a solvent. The best fit spectra have taken as reference and plotted in the below graph.

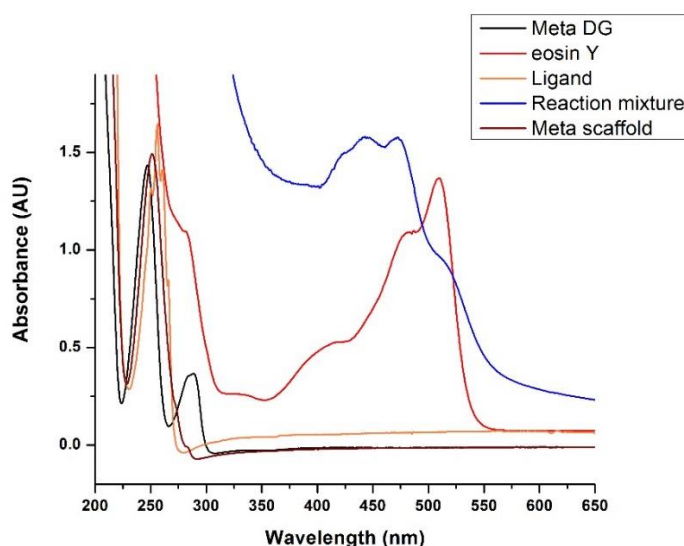


Fig S10: UV-visible absorption spectra of reaction components with reaction mixture

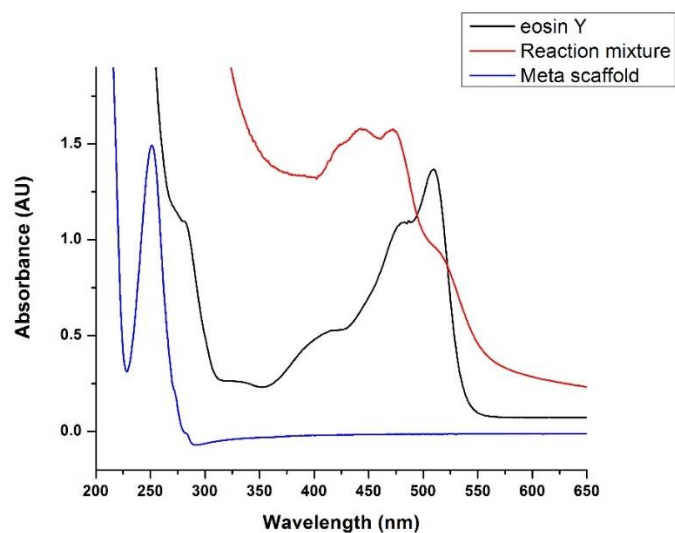


Fig S11: UV-visible absorption spectra of eosin Y, reaction mixture and *meta*-scaffold

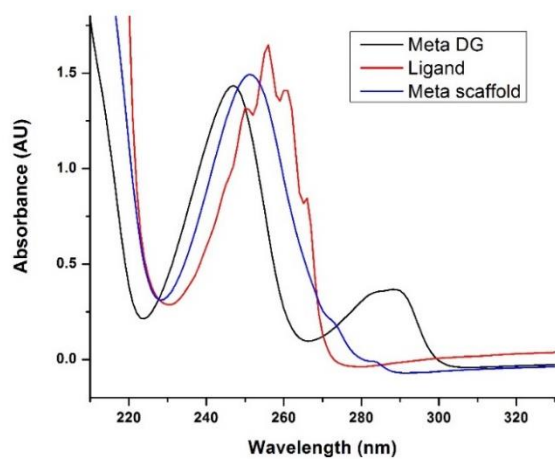


Fig S12: UV-visible absorption spectra of all non-UV component

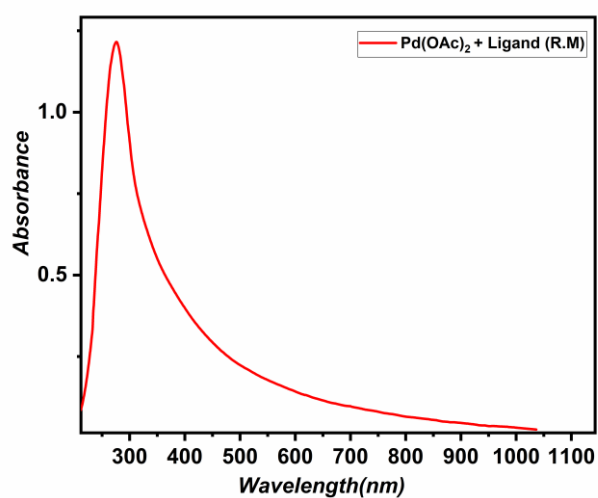


Fig S13. UV/Vis of the Pd(OAc)₂/ligand adduct

According to the UV/vis spectra **Fig S11**: there is a broad signal around the range of 440 to 480 nm. Hence, the species forming in reaction mixture falls in the visible light region and expected to be the light-absorbing species to favour the C–H activation process. Hence, from the present study it may be concluded that for the photo-responsive metallacycle is required and it is a primary requirement for the reaction.

9. B. Fluorescence Quenching Experiments:

Fluorescence quenching experiments were performed on a Horiba Duetta spectrometer and 1 mm High Precision Cell made of quartz from Hellma Analytics. In a typical experiment, a 2.5 μM solution of eosin Y and 0.2 M solution of palladium catalyst and ligand in HFIP was treated with the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. All the reagents were prepared volumetrically in stock solutions. **For case 1**, it was excited at $\lambda = 320$ nm and the luminescence was measured over a range of 400 – 700 nm for pd-ligand reaction mixture and *meta*-scaffold and **for case 2**, it was excited at $\lambda = 500$ nm and the luminescence was measured over a range of 500 – 750 nm for eosin Y and PIDA. It was clearly found that the pd-ligand reaction mixture was quenched by the *meta*-scaffold (Fig. S13, I). In the latter case as well PIDA has quenched the emission of eosin Y photocatalyst (Fig. S13, II). This clearly indicates light has integral role in C–H activation step.

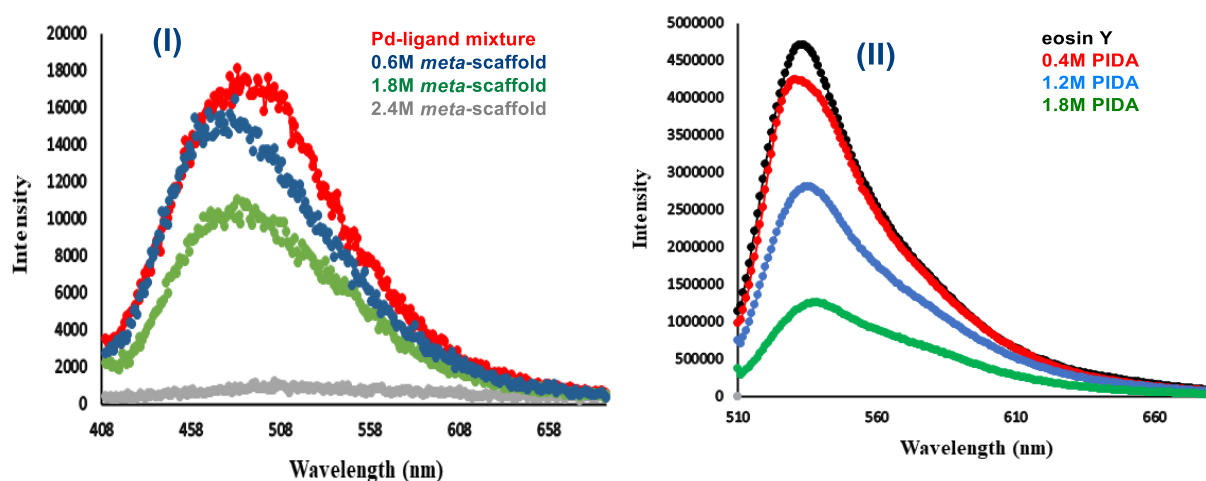


Fig S14. (I) Emission quenching of equimolar mixture of palladium catalyst and ligand by *meta*-scaffold. (II) Emission quenching of eosin Y by PIDA.

10.A. Acetate Monitoring: Upon addition of substrate (1 *eq.*) to the mixture of Pd(OAc)₂ (1 *eq.*), ligand (2.0 *eq.*) and HFIP (2.0 *eq.*), the signal for AcOH intensifies as observed by ¹H

NMR analysis. Notably **same observation was not observed** in absence of ligand signifies that simple Pd(OAc)₂ does not release AcOH in presence of substrate in the similar fashion.

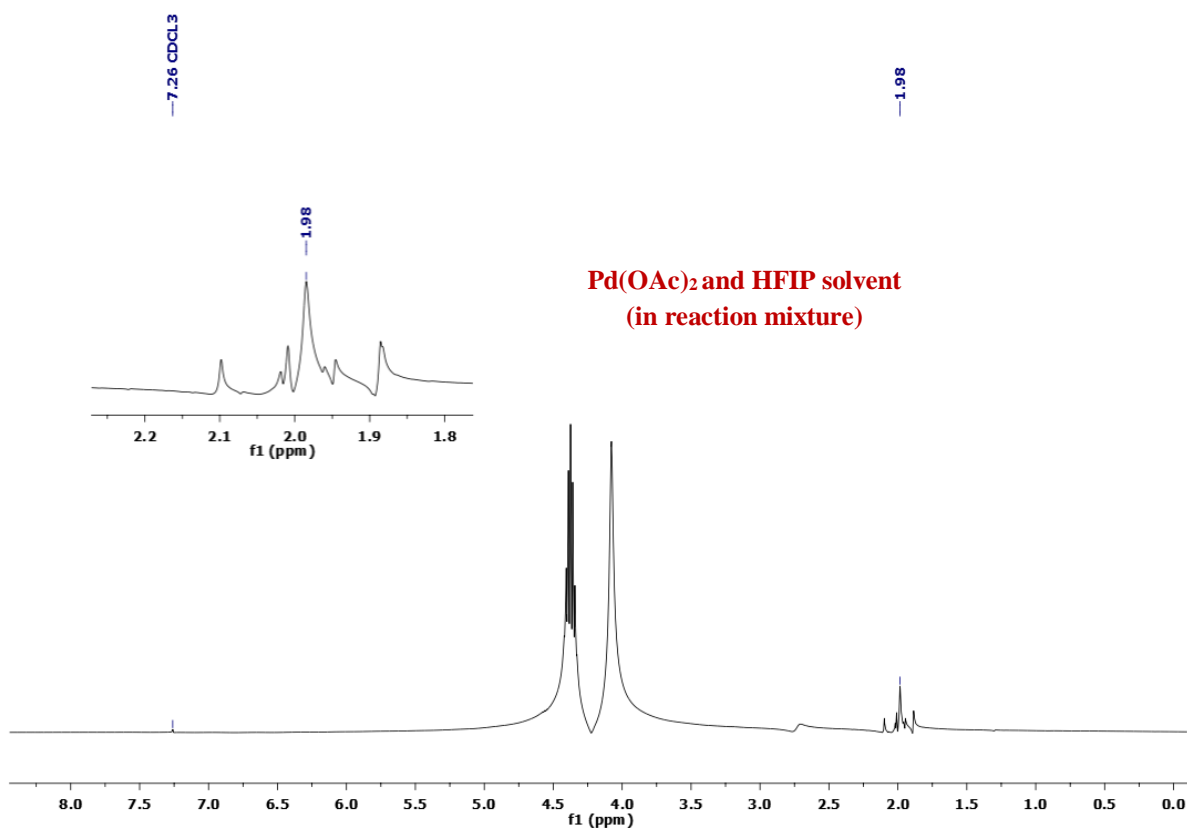
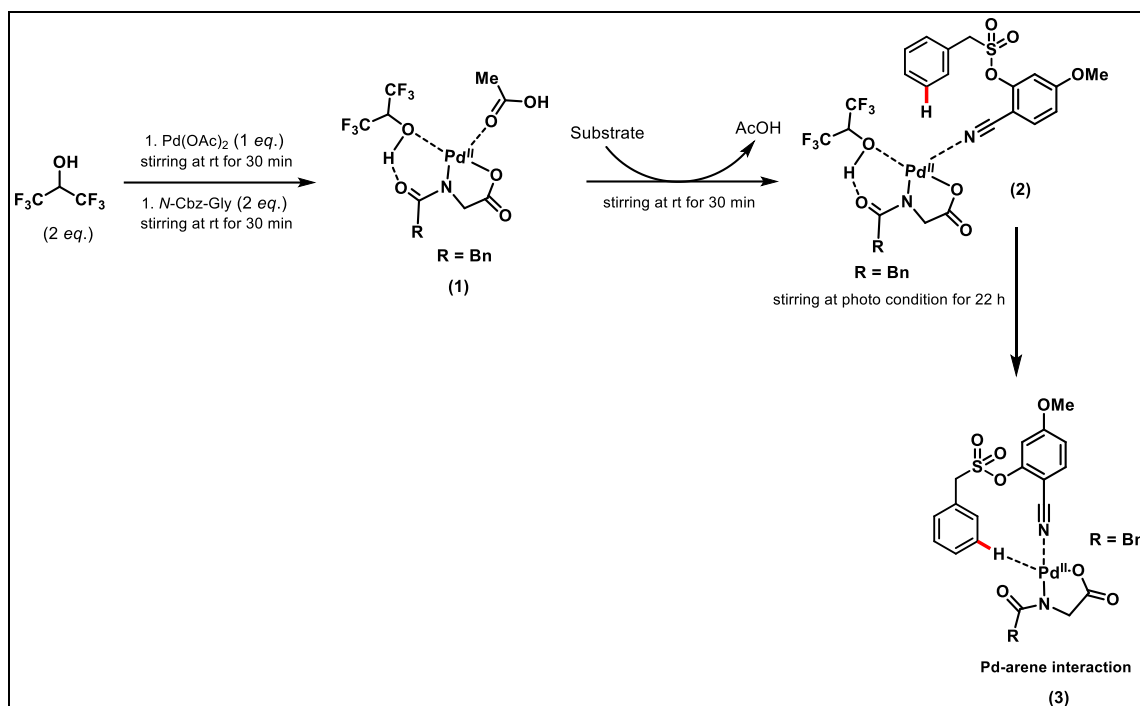


Fig S15. Reaction with Pd(OAc)₂ and HFIP solvent

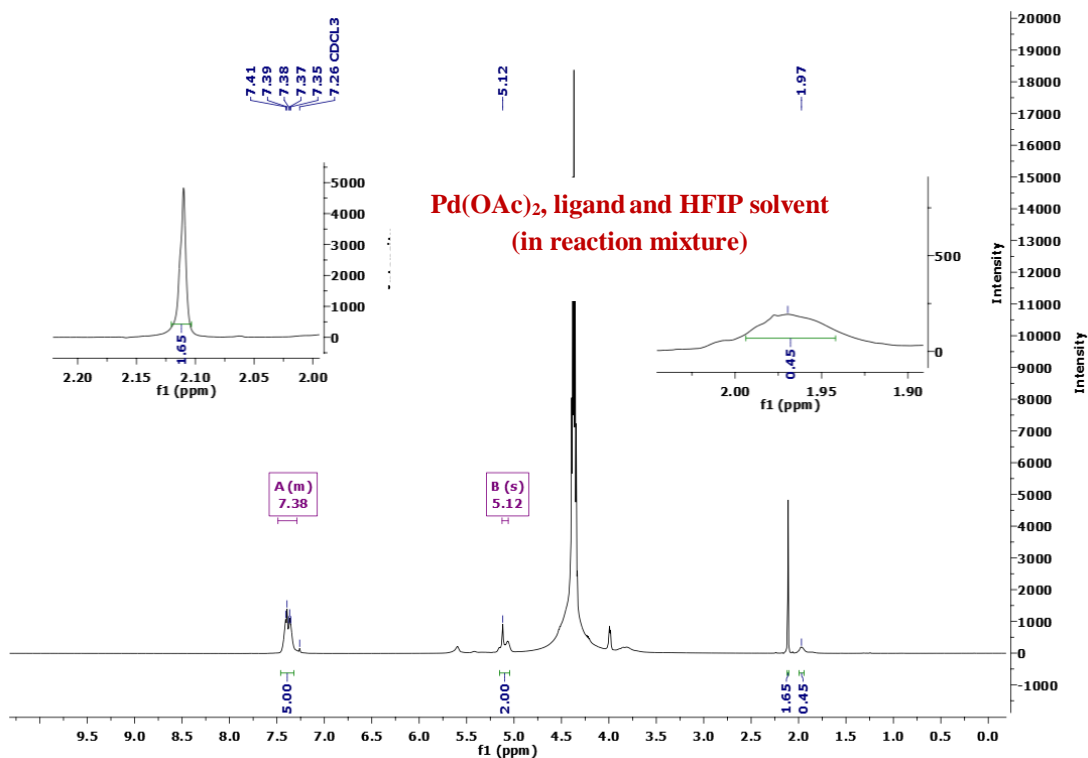


Fig S16. Ligand added in the reaction mixture after 30 min containing Pd(OAc)₂ and HFIP solvent

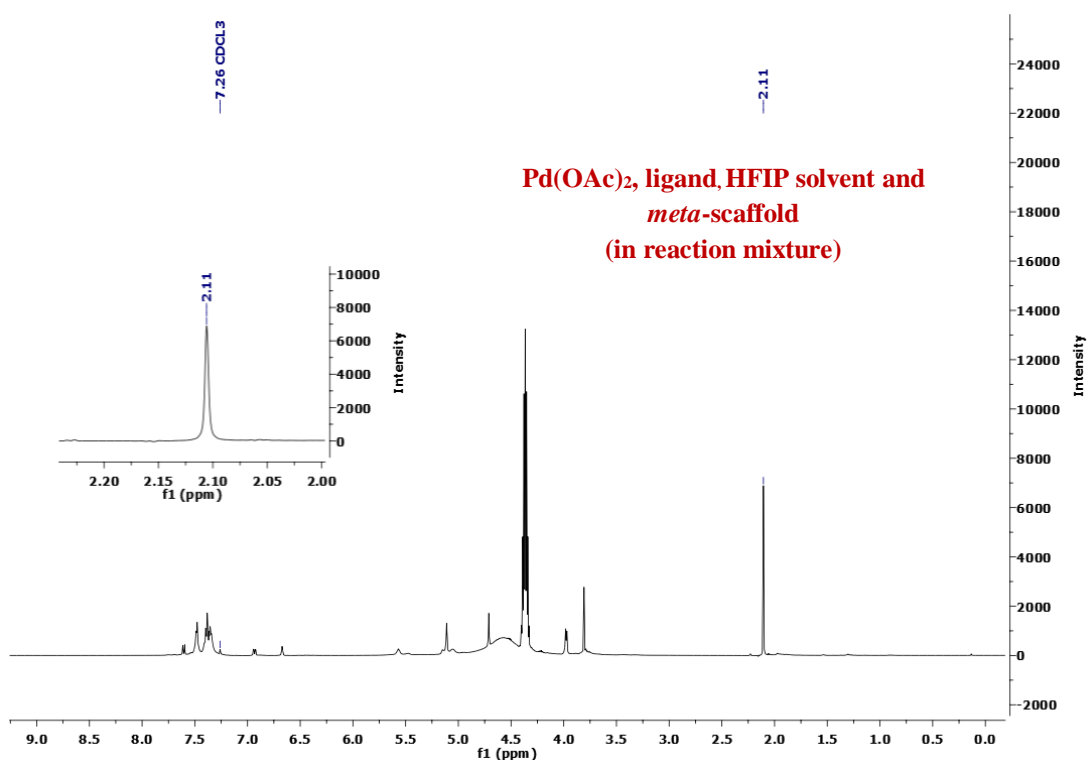


Fig S17. *Meta*-scaffold added in the reaction mixture after 30 min containing Pd(OAc)₂, ligand and HFIP solvent respectively

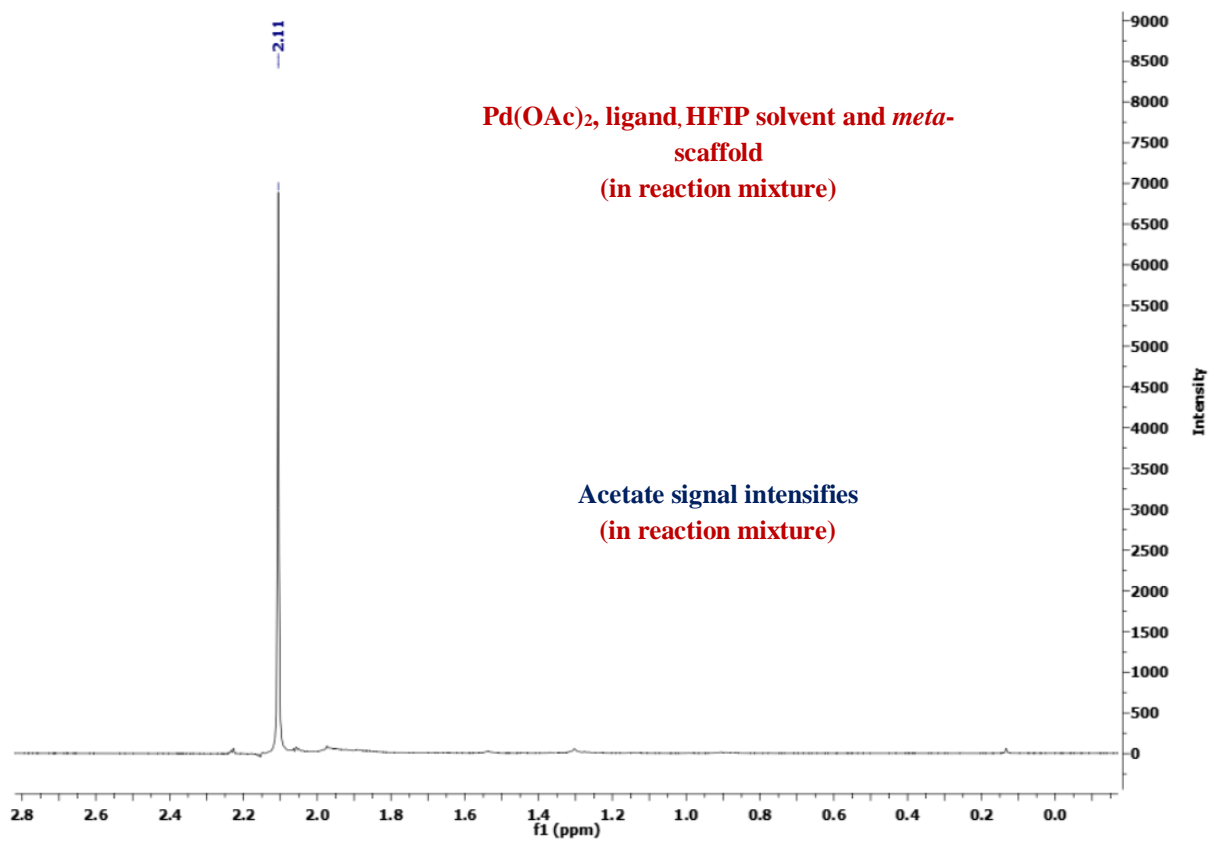
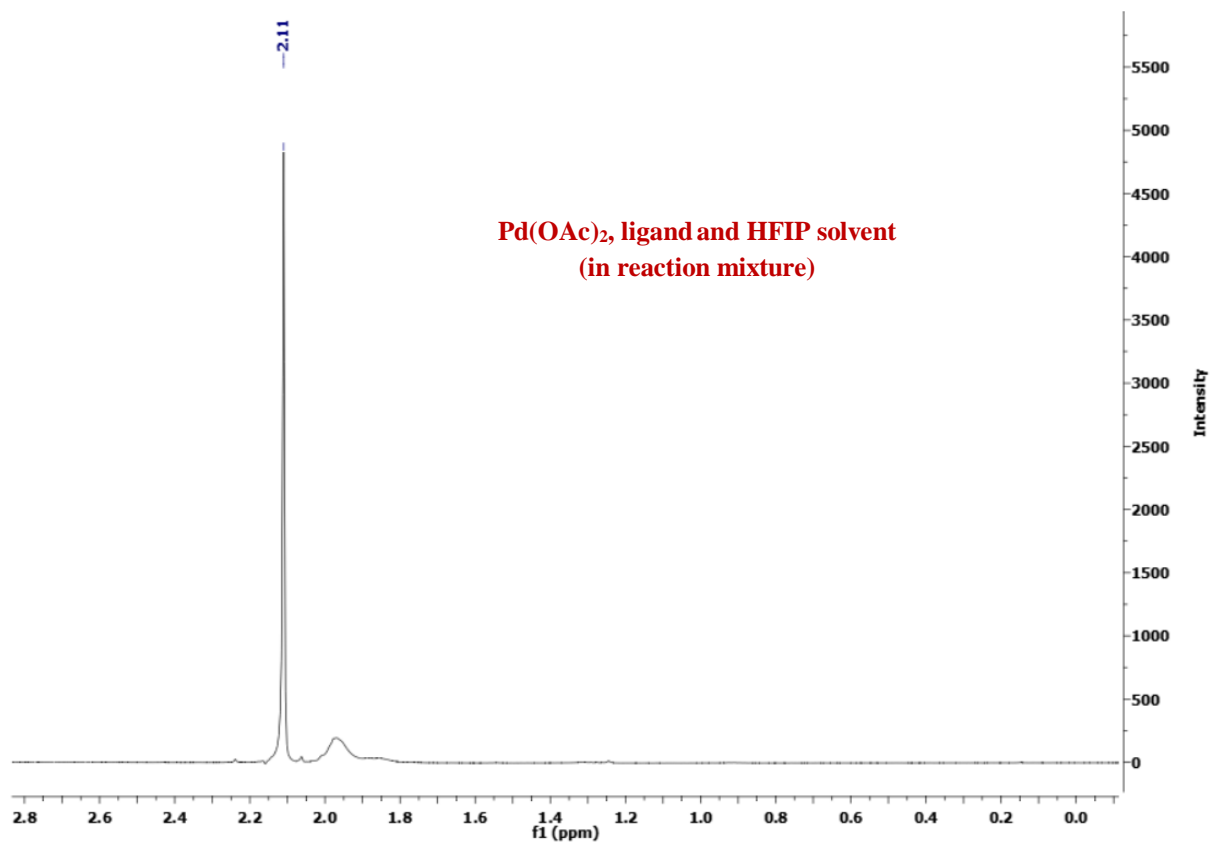


Fig S18. Comparison of acetate intensity before and after adding the *meta*-scaffold

10.B. Role of light in Pd-arene interaction in *meta*-C-H acetoxylation:

In a clean reaction tube HFIP (2 eq.; 6.2 μ L) was added to 510 μ L of CDCl_3 and the $^1\text{H-NMR}$ was recorded. In the same reaction tube, model substrate (0.1 mmol), $\text{Pd}(\text{OAc})_2$ (0.1 mmol) *N*-CBZ-Gly-OH (0.2 mmol) was added and kept under light with stirring for 6 h and after that NMR of the crude reaction mixture was recorded. Again, afterwards the reaction tube was kept for 22 h under irradiation of light. The reaction was cooled in a salted ice-bath to nearly -20°C and kept for 30 mins. Any change of the mixture was monitored by $^1\text{H-NMR}$.

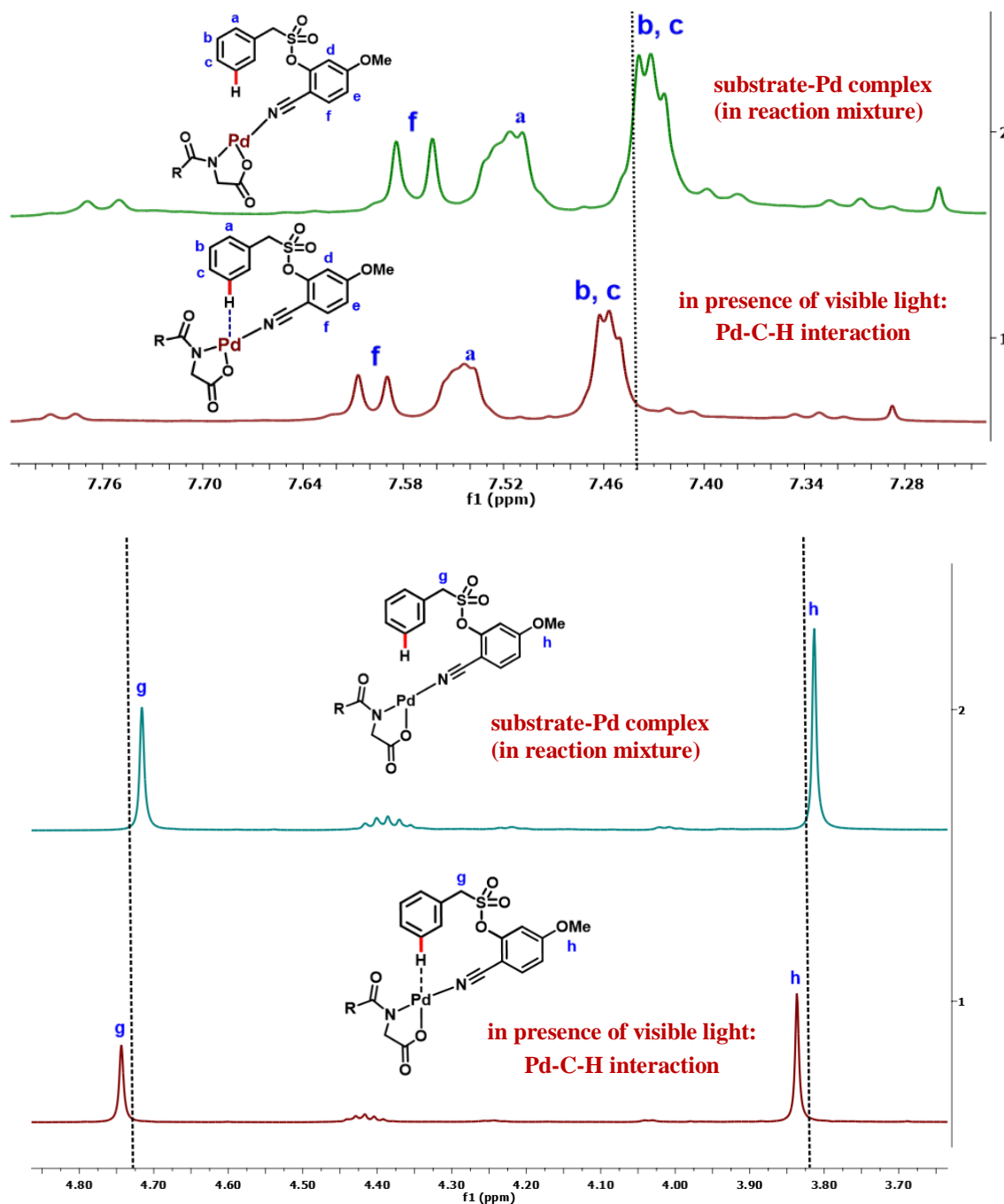


Fig S19. Photoinduced Pd...C-H interaction for *meta*-sulfonyl scaffold

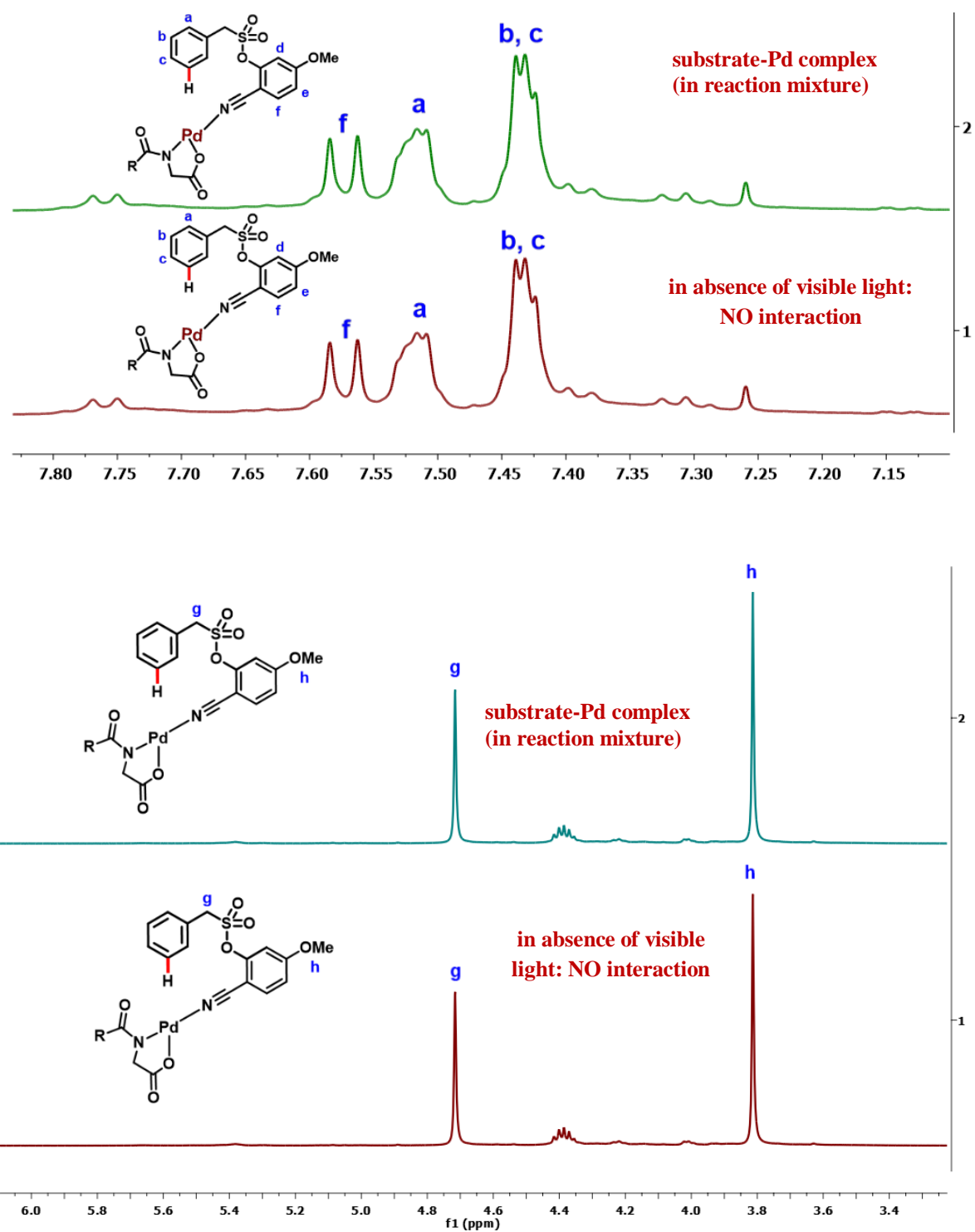


Fig S20. There is no Pd...C-H interaction for *meta*-sulphonyl scaffold in dark condition

10.C. ESI-MS study:

$\text{Pd}(\text{OAc})_2$, substrate, ligand, eosin Y in HFIP was irradiated under visible light stirred for 6 h. After that ESI-MS spectrum was recorded. In mass spectrum, a ligand-Pd-substrate-OAc+Na adduct was appeared as a possible intermediate species with desired isotopic pattern.

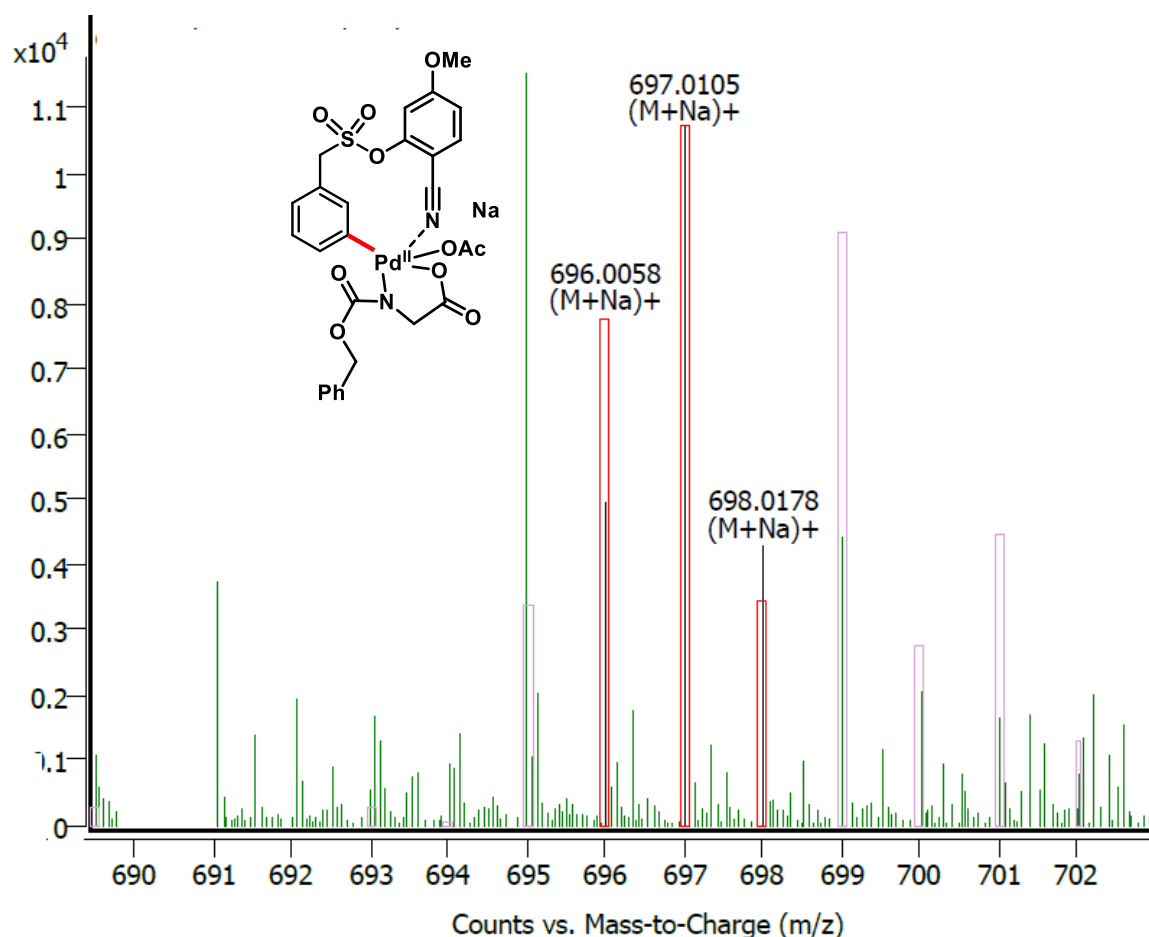



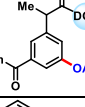

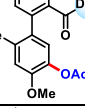


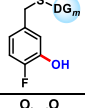


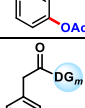
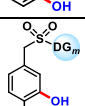
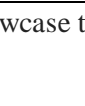


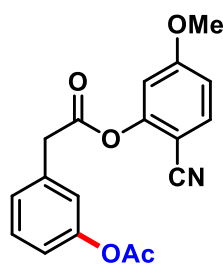
Fig S21: Palladium-Substrate adduct in ESI-MS study in presence of light [**ligand-Pd-substrate-OAc+Na**] $m/z = 697.0083$.

11. Comparison table between photo and thermal condition

Entry	Products	Photoredox	Thermal (80 °C)
1		(<i>m:others</i> >25:1)	(<i>m:others</i> = 5:1)
3		(<i>m:others</i> = 20:1)	(<i>m:others</i> = 2:1) Very poor Yield
14		(<i>m:others</i> >25:1)	(<i>m:others</i> = 2:1) Very poor Yield
17		(<i>m:others</i> >20:1)	(<i>m:others</i> = 3:1)
20		(<i>m:others</i> >25:1)	(<i>m:others</i> = 6:1)
26		(<i>m:others</i> >25:1)	(<i>m:others</i> 3:1)
31		(<i>m:others</i> >25:1)	(<i>m:others</i> = 2:1)
32		(<i>m:others</i> = 15:1)	(<i>m:others</i> = 2:1)
36		(<i>m:others</i> >25:1)	No Reaction
35		(<i>m:others</i> >25:1)	(<i>m:others</i> = 14:1)
37		(<i>m:others</i> >25:1)	(<i>m:others</i> = 15:1)
45		(<i>m:others</i> >25:1)	(<i>m:others</i> = 19:1)
49		(<i>m:others</i> >25:1)	No Reaction
51		(<i>m:others</i> >25:1)	(<i>m:others</i> = 15:1)

TableS8: Comparison table to showcase the superiority of photoinduced protocol over thermal.

12. Characterization data for products.



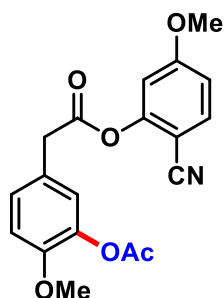
2-Cyano-5-methoxyphenyl 2-(3-acetoxyphenyl)acetate (1)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: Sticky colorless liquid.

Isolated yield: 76% (24.7 mg, 0.076 mmol) (*m*: others >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.7 Hz, 1H), 7.46 – 7.34 (m, 1H), 7.31 – 7.26 (m, 1H), 7.17 (t, *J* = 2.0 Hz, 1H), 7.06 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.76 (d, *J* = 2.5 Hz, 1H), 3.95 (s, 2H), 3.83 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.60, 168.63, 164.14, 154.12, 151.11, 134.28, 134.20, 129.98, 127.25, 122.97, 121.09, 115.71, 113.01, 109.02, 98.77, 56.14, 40.90, 21.33; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₆NO₅ *m/z* 326.1028 and found *m/z* 326.1030.



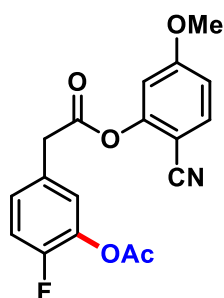
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-methoxyphenyl)acetate (2)

Eluent: ethyl acetate/ petroleum ether (22:78 v/v).

Appearance: Sticky yellow gummy.

Isolated yield: 74% (26.3 mg, 0.074 mmol) (*m*: others >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.21 (m, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.88 (s, 2H), 3.83 (s, 3H), 3.83 (s, 3H), 2.31 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.22, 168.98, 164.13, 154.21, 150.86, 139.97, 134.27, 128.18, 125.14, 124.24, 115.77, 112.99, 112.83, 109.00, 98.77, 56.17, 56.14, 40.21, 20.87; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₉H₁₈NO₆ *m/z* 356.1134 and found *m/z* 356.1140.



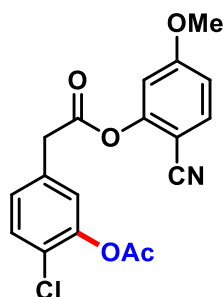
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-fluorophenyl)acetate (3)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: Sticky yellow liquid.

Isolated yield: 69% (23.7 mg, 0.069 mmol) (*m*: others = 20:1)

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.12 (m, 3H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 2H), 3.83 (s, 3H), 2.33 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.55, 168.51, 164.18, 155.05, 154.04, 152.57, 138.40, 138.27, 134.32, 129.21, 129.17, 128.77, 128.47, 128.40, 125.17, 117.27, 117.08, 115.71, 113.01, 109.03, 101.77, 98.72, 56.15, 40.24, 20.71; **¹⁹F NMR** (376 MHz, CDCl₃) δ – 129.68; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₅FNO₅ *m/z* 344.0934 and found *m/z* 344.0940.



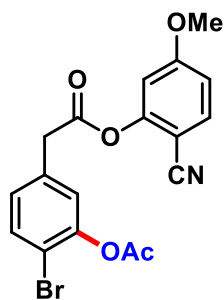
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-chlorophenyl)acetate (4)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless semisolid.

Isolated yield: 72% (25.88 mg, 0.072 mmol) (*m*: others >25:1)

¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.93 (s, 2H), 3.83 (s, 3H), 2.35 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 168.68, 168.30, 164.17, 154.00, 147.29, 134.31, 132.71, 130.73, 128.45, 126.56, 125.10, 115.72, 113.06, 108.99, 98.69, 56.16, 40.35, 20.83; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₅ClNO₅ *m/z* 360.0639 and found *m/z* 360.0645.



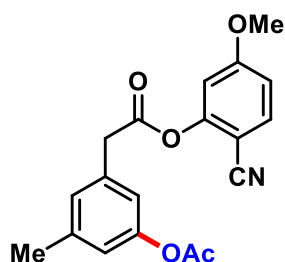
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-bromophenyl)acetate (5)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: whitish solid.

Isolated yield: 65% (26.2 mg, 0.065 mmol) (*m*: others >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.58 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.33 (d, *J* = 2.1 Hz, 1H), 7.30 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.93 – 6.84 (m, 2H), 4.68 (s, 2H), 3.84 (s, 3H), 2.36 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.45, 164.35, 151.68, 148.88, 134.63, 134.19, 130.05, 127.38, 126.59, 118.34, 115.72, 114.21, 109.29, 98.75, 57.74, 56.34, 20.95; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₅BrNO₅ *m/z* 404.0134 and found *m/z* 404.0132.



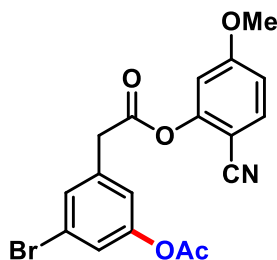
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-5-methylphenyl)acetate (6)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: Sticky yellow liquid.

Isolated yield: 86% (29.15 mg, 0.086 mmol) (*m*: others >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.7 Hz, 1H), 7.12 – 7.04 (m, 1H), 6.96 (s, 1H), 6.87 (s, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 2H), 3.83 (s, 3H), 2.37 (s, 3H), 2.29 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.72, 168.72, 164.11, 154.10, 150.99, 140.29, 134.25, 133.82, 128.10, 121.69, 119.90, 115.71, 112.96, 109.01, 98.72, 56.10, 40.85, 21.43, 21.30; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₉H₁₈NO₅ *m/z* 340.1185 and found *m/z* 340.1190.



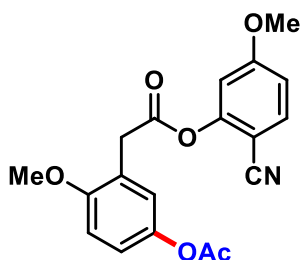
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-5-bromophenyl)acetate (7)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: whitish solid.

Isolated yield: 59% (23.8 mg, 0.059 mmol) (*m*: others = 6:1)

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 1.7 Hz, 1H), 7.26 (d, *J* = 1.0 Hz, 1H), 7.14 (t, *J* = 1.7 Hz, 1H), 6.84 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.76 (d, *J* = 2.3 Hz, 1H), 3.93 (s, 2H), 3.84 (s, 3H), 2.29 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.09, 164.18, 153.95, 151.44, 135.57, 134.32, 130.30, 129.99, 124.64, 122.75, 122.07, 113.13, 109.00, 98.71, 56.18, 40.44, 21.24; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₅BrNO₅ *m/z* 404.0134 and found *m/z* 404.0131.



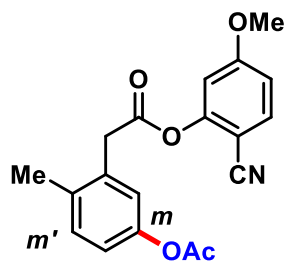
2-Cyano-5-methoxyphenyl 2-(5-acetoxy-2-methoxyphenyl)acetate (8)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: colorless gummy.

Isolated yield: 83% (29.46 mg, 0.083 mmol) (*m*: others >25:1)

¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 8.7 Hz, 1H), 7.06 (d, *J* = 2.9 Hz, 1H), 7.03 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.81 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 3.93 (s, 2H), 3.87 (s, 3H), 3.83 (s, 3H), 2.27 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 170.08, 168.88, 163.99, 155.46, 154.17, 143.96, 134.33, 124.35, 122.75, 121.79, 115.66, 112.71, 111.07, 109.16, 98.81, 56.04, 35.97, 21.23; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₉H₁₈NO₆ *m/z* 356.1134 and found *m/z* 356.1140.



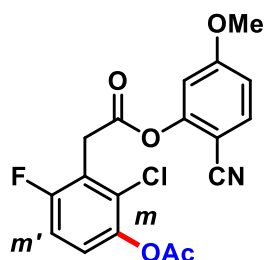
2-Cyano-5-methoxyphenyl 2-(5-acetoxy-2-methylphenyl)acetate (9)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless liquid.

Isolated yield: 74% (25 mg, 0.074 mmol) (*m*: others >25:1) (*m*:*m*' = 12:1)

¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.7 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.09 (d, *J* = 2.5 Hz, 1H), 6.97 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.95 (s, 2H), 3.83 (s, 3H), 2.40 (s, 3H), 2.28 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.78, 168.52, 164.12, 154.07, 149.05, 134.87, 134.29, 132.60, 131.58, 123.52, 121.09, 115.66, 112.98, 109.12, 109.01, 98.80, 56.03, 38.90, 21.25, 19.29; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₉H₁₈NO₅ *m/z* 340.1185 and found *m/z* 340.1179.



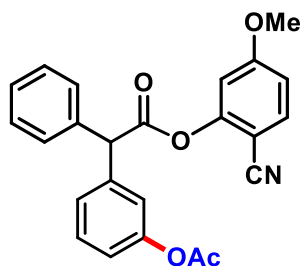
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-2-chloro-6-fluorophenyl)acetate (10)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: Sticky semisolid.

Isolated yield: 67% (25.3 mg, 0.067 mmol) (*m*: others = 22:1) (*m*:*m*' = 6:1)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.7 Hz, 1H), 7.32 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.21 (dd, *J* = 8.8, 7.8 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.7, 2.4 Hz, 1H), 5.02 (d, *J* = 1.7 Hz, 2H), 3.85 (s, 3H), 2.34 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.07, 164.29, 155.29, 152.73, 151.18, 137.68, 137.55, 134.80, 133.66, 128.50, 128.05, 125.99, 125.96, 125.91, 125.87, 115.84, 115.69, 115.23, 114.28, 114.26, 109.40, 109.31, 99.30, 56.32, 50.24, 50.22, 20.63; **¹⁹F NMR** (376 MHz, CDCl₃) δ - 111.08, - 122.19; **HRMS** (ESI-QTOF): [M+Na]⁺ calculated for C₁₈H₁₃ClFNNaO₅ *m/z* 400.0364 and found *m/z* 400.0370.



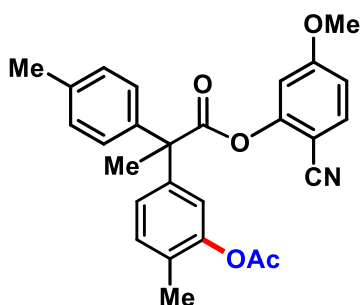
2-Cyano-5-methoxyphenyl 2-(3-acetoxyphenyl)-2-phenylacetate (11)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: Sticky semisolid.

Isolated yield: 62% (24.86 mg, 0.062 mmol) (*m*: others = 18:1)

¹H NMR (400 MHz, CDCl₃) δ 7.55 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.46 – 7.37 (m, 5H), 7.35 – 7.28 (m, 2H), 7.19 (d, *J* = 2.1 Hz, 1H), 7.13 – 7.03 (m, 1H), 6.82 (ddd, *J* = 8.8, 2.5, 0.8 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 5.36 (s, 1H), 3.83 (s, 3H), 2.28 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.87, 169.53, 164.10, 154.01, 151.13, 139.04, 136.98, 134.39, 129.97, 129.16, 128.98, 128.13, 126.53, 122.17, 121.22, 115.69, 113.01, 108.94, 98.86, 56.67, 56.15, 21.35; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₄H₂₀NO₅ *m/z* 402.1341 and found *m/z* 402.1338.



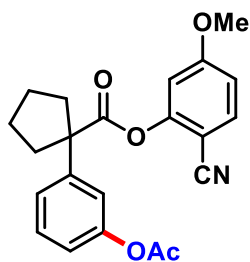
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-methylphenyl)-2-(*p*-tolyl)propanoate (12)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: Sticky semisolid.

Isolated yield: 64% (28.35 mg, 0.064 mmol) (*m*: others = 19:1)

¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.34 – 7.25 (m, 3H), 7.24 – 7.15 (m, 3H), 7.09 (d, *J* = 2.0 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.61 (d, *J* = 2.4 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H), 2.31 (s, 3H), 2.22 (s, 3H), 2.12 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 172.88, 169.32, 164.14, 154.57, 149.37, 142.10, 140.09, 137.25, 134.31, 131.15, 129.47, 129.31, 128.15, 125.83, 122.31, 116.03, 112.90, 108.69, 99.03, 56.47, 56.13, 27.29, 21.21, 21.03, 16.06; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₇H₂₆NO₅ *m/z* 444.1811 and found *m/z* 444.1810.



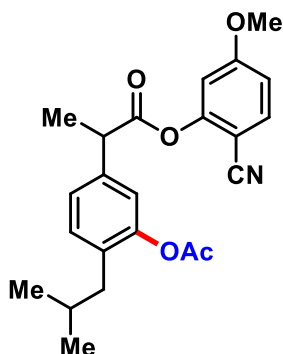
2-Cyano-5-methoxyphenyl 1-(3-acetoxyphenyl)cyclopentane-1-carboxylate (13)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: Sticky colorless gummy.

Isolated yield: 83% (31.5 mg, 0.083 mmol) (*m*: others >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.51 (d, *J* = 8.7 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.22 (td, *J* = 1.8, 1.4, 0.7 Hz, 1H), 7.03 (dt, *J* = 7.0, 2.2 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.54 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H), 2.96 – 2.73 (m, 2H), 2.30 (s, 3H), 2.08 (m, 2H), 2.17 – 2.00 (m, 4H); **¹³C NMR** (101 MHz, CDCl₃) δ 173.35, 169.63, 164.13, 154.39, 150.99, 143.92, 134.15, 129.70, 124.61, 120.89, 120.67, 115.65, 112.97, 108.64, 98.82, 59.51, 56.12, 36.39, 23.79, 21.36; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₂H₂₂NO₅ *m/z* 380.1498 and found *m/z* 380.1493.



2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-isobutylphenyl)propanoate (14)

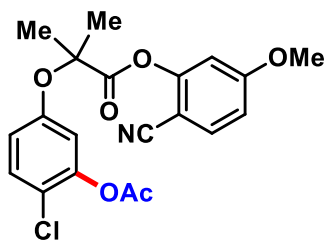
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless semisolid.

Isolated yield: 71% (28 mg, 0.071 mmol) (*m*: others >25:1)

¹H NMR (500 MHz, CDCl₃) δ 7.53 (d, *J* = 8.8 Hz, 1H), 7.39 (d, *J* = 1.7 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.11 (d, *J* = 1.6 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.68 (d, *J* = 2.4 Hz, 1H), 4.02 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 2.39 (d, *J* = 7.2 Hz, 2H), 2.31 (s, 3H), 1.86 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.67 (d, *J* = 7.2 Hz, 3H), 0.90 (dd, *J* = 6.6, 1.2 Hz, 6H); **¹³C NMR** (126 MHz, CDCl₃) δ 171.93, 169.59, 164.14, 154.24, 149.53, 138.07, 134.18, 133.01, 131.68, 129.01, 128.82, 125.40, 121.85, 115.74, 113.12, 108.78, 98.80, 56.14, 45.16, 39.52, 29.32, 22.75, 21.18, 18.46;

HRMS (ESI-QTOF): $[M+Na]^+$ calculated for $C_{23}H_{25}NaNO_5$ m/z 418.1630 and found m/z 418.1630.



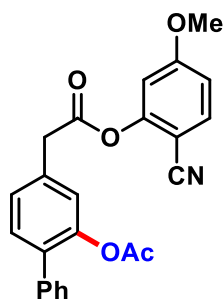
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-4-chlorophenoxy)-2-methylpropanoate (15)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 65% (26.2 mg, 0.065 mmol) (*m*: others >25:1)

1H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 8.7 Hz, 1H), 7.34 (d, J = 8.8 Hz, 1H), 6.87 (dd, J = 3.2, 2.6 Hz, 1H), 6.85 (t, J = 2.9 Hz, 1H), 6.82 (d, J = 2.9 Hz, 1H), 6.58 (d, J = 2.4 Hz, 1H), 3.84 (s, 3H), 2.33 (s, 3H), 1.82 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.62, 168.49, 164.35, 154.75, 153.74, 147.49, 134.35, 130.48, 120.52, 118.25, 115.60, 114.84, 113.52, 108.76, 98.89, 80.19, 56.23, 25.70, 20.87; **HRMS** (ESI-QTOF): $[M+Na]^+$ calculated for $C_{20}H_{18}ClNNaO_6$ m/z 426.0720 and found m/z 426.0725.



2-Cyano-5-methoxyphenyl 2-(2-acetoxy-[1,1'-biphenyl]-4-yl)acetate (16)

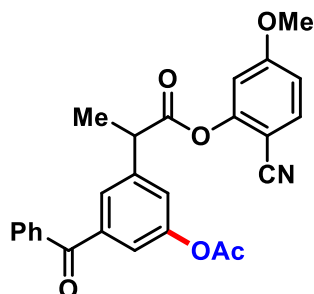
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: Sticky colorless liquid.

Isolated yield: 73% (29.3 mg, 0.073 mmol) (*m*: others >25:1)

1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.54 (m, 3H), 7.50 – 7.42 (m, 3H), 7.31 (t, J = 2.0 Hz, 1H), 7.16 (d, J = 8.6 Hz, 1H), 7.08 (dt, J = 7.3, 2.1 Hz, 1H), 6.83 (dd, J = 8.7, 2.5 Hz, 1H), 6.77 (d, J = 2.6 Hz, 1H), 4.00 (s, 2H), 3.83 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.79, 169.74, 169.12, 169.08, 164.12, 154.20, 151.30, 150.38, 142.47, 139.92, 139.72, 138.63, 134.34, 132.21, 131.86, 130.23, 130.22, 129.96, 129.73, 128.35, 127.78, 127.72,

124.77, 122.10, 120.71, 120.49, 115.77, 112.89, 112.87, 109.11, 109.09, 98.79, 56.13, 40.86, 21.39; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{24}H_{20}NO_5$ m/z 402.1341 and found m/z 402.1345.



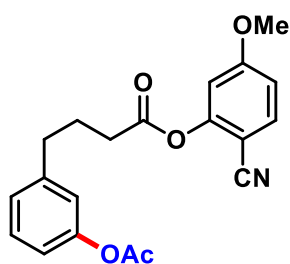
2-Cyano-5-methoxyphenyl 2-(3-acetoxy-5-benzoylphenyl)propanoate (17)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: Sticky colorless liquid.

Isolated yield: 53% (23.5 mg, 0.053 mmol) (*m*: others = >20:1)

1H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.80 (m, 2H), 7.74 (d, $J = 1.7$ Hz, 1H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.54 (d, $J = 8.7$ Hz, 1H), 7.52 – 7.42 (m, 4H), 6.82 (dd, $J = 8.8, 2.5$ Hz, 1H), 6.72 (d, $J = 2.4$ Hz, 1H), 4.12 (t, $J = 7.1$ Hz, 1H), 3.83 (s, 3H), 2.31 (s, 3H), 1.73 (d, $J = 7.3$ Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 195.41, 171.33, 169.34, 164.17, 153.97, 150.93, 141.09, 139.49, 137.21, 134.26, 132.98, 130.30, 128.66, 126.97, 125.30, 123.00, 115.57, 113.16, 108.87, 98.76, 56.18, 45.42, 21.30, 18.53; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{26}H_{22}NO_6$ m/z 444.1447 and found m/z 444.1450.



2-Cyano-5-methoxyphenyl 4-(3-acetoxyphenyl)butanoate (18)

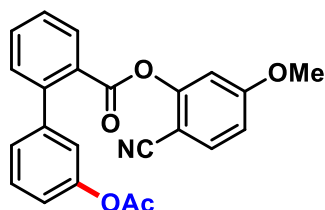
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 68% (24 mg, 0.068 mmol) (*m*: others = 10:1)

1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, $J = 8.7, 0.9$ Hz, 1H), 7.43 – 7.19 (m, 2H), 7.15 – 6.99 (m, 1H), 6.98 – 6.90 (m, 1H), 6.83 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.75 (d, $J = 2.5$ Hz, 1H), 3.84 (s,

3H), 2.77 (t, $J = 7.6$ Hz, 2H), 2.66 (t, $J = 7.4$ Hz, 2H), 2.29 (s, 3H), 2.21 – 2.04 (m, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 170.93, 169.77, 164.14, 154.16, 150.97, 142.90, 138.75, 134.27, 134.08, 129.65, 129.60, 126.26, 121.80, 121.68, 119.50, 115.80, 112.74, 109.21, 101.71, 98.86, 56.07, 34.79, 33.43, 26.13, 21.32; **HRMS** (ESI-QTOF): $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{20}\text{H}_{19}\text{NaNO}_5$ m/z 376.1161 and found m/z 376.1165.



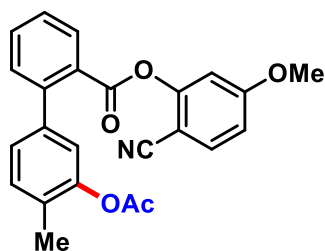
2-Cyano-5-methoxyphenyl 3'-acetoxy-[1,1'-biphenyl]-2-carboxylate (19)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 81% (31.3 mg, 0.081 mmol) ($m:\text{others} = 20:1$)

^1H NMR (500 MHz, CDCl_3) δ 8.17 – 8.12 (m, 1H), 7.63 (td, $J = 7.6, 1.2$ Hz, 1H), 7.56 – 7.50 (m, 2H), 7.43 (dd, $J = 10.3, 6.6$ Hz, 2H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.18 (dd, $J = 4.5, 2.8$ Hz, 1H), 7.11 (dd, $J = 8.1, 1.3$ Hz, 1H), 6.80 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.56 (d, $J = 2.4$ Hz, 1H), 3.82 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 169.51, 165.35, 164.18, 154.19, 150.67, 142.62, 142.57, 134.18, 132.70, 131.23, 130.96, 129.38, 128.92, 128.14, 126.39, 122.20, 120.86, 115.91, 113.14, 108.74, 99.05, 56.11, 21.36; **HRMS** (ESI-QTOF): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{18}\text{NO}_5$ m/z 388.1185 and found m/z 388.1190.



2-Cyano-5-methoxyphenyl 3'-acetoxy-4'-methyl-[1,1'-biphenyl]-2-carboxylate (20)

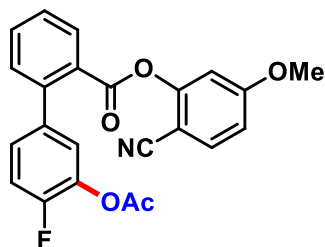
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 76% (30.4 mg, 0.076 mmol) ($m:\text{others} >25:1$)

^1H NMR (400 MHz, CDCl_3) δ 8.13 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.60 (dd, $J = 7.6, 1.4$ Hz, 1H), 7.56 – 7.47 (m, 2H), 7.44 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.29 (d, $J = 7.8$ Hz, 1H), 7.22 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.11 (d, $J = 1.8$ Hz, 1H), 6.80 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.59 (d, $J = 2.4$ Hz, 1H),

3.81 (s, 3H), 2.31 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.25, 165.43, 164.15, 154.22, 149.26, 142.60, 139.96, 134.13, 132.63, 131.29, 131.11, 130.84, 129.58, 128.86, 127.89, 126.50, 122.47, 115.93, 113.17, 108.76, 99.06, 56.05, 21.00, 16.19; HRMS (ESI-QTOF): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{20}\text{NO}_5$ m/z 402.1341 and found m/z 402.1345.



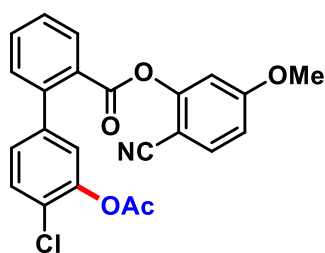
2-Cyano-5-methoxyphenyl 3'-acetoxy-4'-fluoro-[1,1'-biphenyl]-2-carboxylate (21)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: Sticky colorless liquid.

Isolated yield: 68% (27.5 mg, 0.068 mmol) (*m:others* >25:1)

^1H NMR (400 MHz, CDCl_3) δ 8.28 – 8.15 (m, 1H), 7.75 – 7.63 (m, 1H), 7.62 – 7.53 (m, 2H), 7.46 (dd, $J = 7.7, 1.3$ Hz, 1H), 7.37 – 7.23 (m, 3H), 6.86 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.65 (d, $J = 2.4$ Hz, 1H), 3.87 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.38, 165.09, 164.23, 155.11, 154.14, 152.63, 141.98, 137.96, 137.83, 137.75, 137.71, 134.25, 132.84, 131.36, 131.13, 128.73, 128.26, 127.56, 127.49, 124.42, 116.69, 116.51, 115.91, 113.15, 108.77, 99.02, 56.10, 20.70; ^{19}F NMR (376 MHz, CDCl_3) δ -130.03; HRMS (ESI-QTOF): $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{23}\text{H}_{16}\text{FNNaO}_5$ m/z 428.0910 and found m/z 428.0914.



2-Cyano-5-methoxyphenyl 3'-acetoxy-4'-chloro-[1,1'-biphenyl]-2-carboxylate (22)

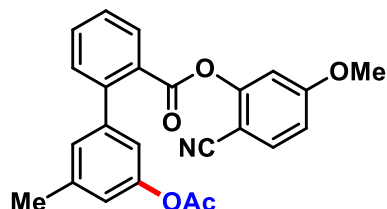
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: whitish solid.

Isolated yield: 72% (30.3 mg, 0.072 mmol) (*m:others* >25:1)

^1H NMR (400 MHz, CDCl_3) δ 8.20 – 8.10 (m, 1H), 7.63 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.57 – 7.51 (m, 2H), 7.49 (d, $J = 8.2$ Hz, 1H), 7.43 – 7.41 (m, 1H), 7.32 – 7.24 (m, 1H), 7.22 (d, $J = 2.1$ Hz, 1H), 6.82 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.59 (d, $J = 2.5$ Hz, 1H), 3.83 (s, 3H), 2.34 (s, 3H); ^{13}C

NMR (101 MHz, CDCl₃) δ 168.56, 165.00, 164.23, 154.11, 146.85, 141.78, 141.08, 134.21, 132.91, 131.24, 131.18, 130.15, 128.60, 128.44, 127.54, 126.46, 124.30, 115.93, 113.33, 108.64, 98.98, 56.13, 20.83; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₃H₁₇ClNO₅ m/z 422.0795 and found m/z 422.0799.



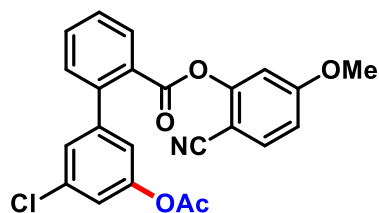
2-Cyano-5-methoxyphenyl 3'-acetoxy-5'-methyl-[1,1'-biphenyl]-2-carboxylate (23)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 86% (34.5 mg, 0.086 mmol) (*m*:others = 20:1)

¹H NMR (400 MHz, CDCl₃) δ 8.12 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.62 (td, *J* = 7.6, 1.4 Hz, 1H), 7.56 – 7.48 (m, 2H), 7.44 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.98 (s, 1H), 6.92 (d, *J* = 1.4 Hz, 1H), 6.80 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.58 (d, *J* = 2.4 Hz, 1H), 3.82 (s, 3H), 2.40 (s, 3H), 2.27 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.59, 165.45, 164.14, 154.18, 150.55, 142.68, 142.22, 139.61, 134.14, 132.58, 131.12, 130.80, 128.92, 127.97, 127.10, 121.48, 119.23, 115.89, 113.09, 108.70, 99.00, 56.04, 21.53, 21.31; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₄H₂₀NO₂ m/z 402.1341 and found m/z 402.1345.



2-Cyano-5-methoxyphenyl 3'-acetoxy-5'-chloro-[1,1'-biphenyl]-2-carboxylate (24)

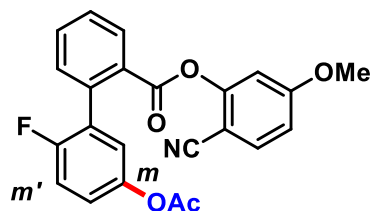
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: whitish gummy.

Isolated yield: 68% (28.6 mg, 0.068 mmol) (*m*:others = 5:1)

¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.64 (td, *J* = 7.6, 1.5 Hz, 1H), 7.59 – 7.49 (m, 2H), 7.42 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.29 (t, *J* = 1.7 Hz, 1H), 7.14 (t, *J* = 2.0 Hz, 1H), 7.10 (dd, *J* = 2.1, 1.5 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.65 (d, *J* = 2.5 Hz, 1H), 3.84 (s, 3H), 2.28 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.04, 164.94, 164.22, 154.14, 154.11, 150.98, 146.64, 143.57, 141.61, 141.43, 140.20, 134.45, 134.24, 134.18, 132.95,

132.92, 131.27, 131.22, 131.10, 130.46, 128.63, 128.47, 128.45, 126.73, 126.34, 123.63, 121.37, 120.86, 115.85, 113.36, 113.29, 108.61, 108.50, 98.92, 56.12, 21.25; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{23}H_{17}ClNO_5$ m/z 422.0795 and found m/z 422.0790.



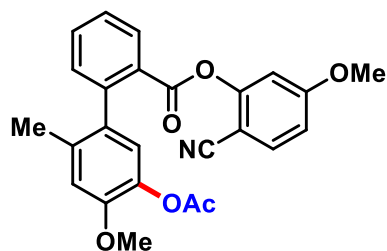
2-Cyano-5-methoxyphenyl 5'-acetoxy-2'-fluoro-[1,1'-biphenyl]-2-carboxylate (25)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 71% (28.7 mg, 0.071 mmol) ($m:others >25:1$) ($m:m' = 1:1$)

1H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, $J = 7.8$ Hz, 1H), 7.73 – 7.63 (m, 1H), 7.63 – 7.52 (m, 2H), 7.44 (ddd, $J = 7.7, 2.5, 1.3$ Hz, 1H), 7.30 – 7.19 (m, 1H), 7.17 – 7.10 (m, 1H), 7.10 – 7.04 (m, 1H), 6.85 – 6.73 (m, 2H), 3.85 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.53, 168.37, 164.32, 164.15, 164.13, 158.19, 155.76, 154.21, 154.16, 152.43, 149.96, 146.65, 136.66, 136.54, 134.26, 134.11, 133.31, 133.25, 131.94, 131.92, 131.23, 131.21, 130.33, 130.19, 129.65, 129.47, 129.04, 128.86, 128.76, 128.33, 128.15, 128.13, 124.33, 124.28, 123.93, 123.89, 123.34, 122.55, 122.46, 116.09, 115.84, 115.74, 113.16, 112.84, 109.16, 109.00, 98.90, 98.74, 56.11, 56.09, 21.24, 20.69; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -119.94, -119.96, -131.66, 131.68; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{23}H_{17}FNO_5$ m/z 406.1091 and found m/z 406.1095.



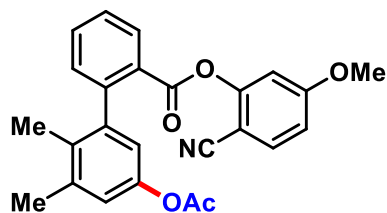
2-Cyano-5-methoxyphenyl 5'-acetoxy-4'-methoxy-2'-methyl-[1,1'-biphenyl]-2-carboxylate (26)

Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: colorless solid.

Isolated yield: 77% (33.5 mg, 0.077 mmol) ($m:others >25:1$)

^1H NMR (500 MHz, CDCl_3) δ 8.20 (dd, $J = 7.9, 1.4$ Hz, 1H), 7.67 – 7.57 (m, 1H), 7.55 – 7.45 (m, 2H), 7.33 (dd, $J = 7.7, 1.3$ Hz, 1H), 6.87 (s, 1H), 6.85 (s, 1H), 6.78 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.51 (d, $J = 2.4$ Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 2.27 (s, 3H), 2.15 (s, 3H); **^{13}C NMR** (126 MHz, CDCl_3) δ 169.26, 164.72, 164.14, 154.16, 150.21, 142.42, 137.21, 134.65, 134.02, 133.11, 132.82, 131.65, 130.89, 129.03, 127.87, 123.32, 115.80, 113.84, 113.21, 108.71, 98.87, 56.03, 55.98, 20.82, 20.29; **HRMS** (ESI-QTOF): $[\text{M}+\text{Na}]^+$ calculated for $\text{C}_{25}\text{H}_{21}\text{NNaO}_6$ m/z 454.1267 and found m/z 454.1270.



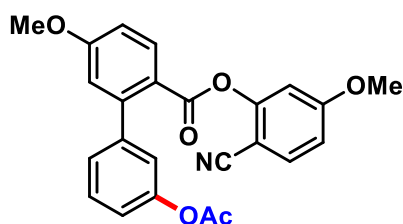
2-Cyano-5-methoxyphenyl 5'-acetoxy-2',3'-dimethyl-[1,1'-biphenyl]-2-carboxylate (27)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 85% (35.4 mg, 0.085 mmol) (m :others >22:1)

^1H NMR (400 MHz, CDCl_3) δ 8.21 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.63 (td, $J = 7.5, 1.4$ Hz, 1H), 7.56 – 7.48 (m, 2H), 7.33 (dd, $J = 7.5, 1.4$ Hz, 1H), 6.89 (d, $J = 2.5$ Hz, 1H), 6.82 – 6.74 (m, 2H), 6.49 (d, $J = 2.5$ Hz, 1H), 3.80 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 2.01 (s, 3H); **^{13}C NMR** (101 MHz, CDCl_3) δ 169.80, 164.54, 164.14, 154.18, 147.84, 143.45, 141.98, 138.26, 134.08, 132.88, 132.20, 131.31, 130.93, 128.71, 127.92, 122.09, 119.68, 115.82, 113.17, 108.75, 98.94, 56.07, 21.30, 20.83, 16.57; **HRMS** (ESI-QTOF): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{25}\text{H}_{22}\text{NO}_5$ m/z 416.1498 and found m/z 416.1496.



2-Cyano-5-methoxyphenyl 3'-acetoxy-5-methoxy-[1,1'-biphenyl]-2-carboxylate (28)

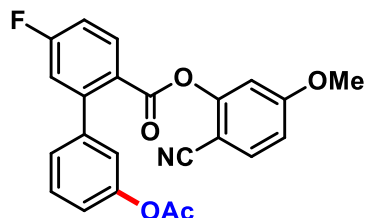
Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 72% (30 mg, 0.072 mmol) (m :others = 16:1)

^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 2.7$ Hz, 1H), 7.53 (d, $J = 8.7$ Hz, 1H), 7.41 (t, $J = 7.9$ Hz, 1H), 7.35 (d, $J = 8.5$ Hz, 1H), 7.30 – 7.23 (m, 1H), 7.19 – 7.12 (m, 2H), 7.08 (ddd, $J =$

8.1, 2.3, 1.0 Hz, 1H), 6.80 (dd, $J = 8.7, 2.5$ Hz, 1H), 6.57 (d, $J = 2.4$ Hz, 1H), 3.92 (s, 3H), 3.82 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.52, 165.18, 164.18, 159.28, 154.16, 150.65, 142.37, 135.02, 134.14, 132.42, 129.79, 129.30, 126.57, 122.35, 120.53, 119.15, 115.94, 115.29, 113.19, 108.69, 98.99, 56.13, 55.96, 21.37; HRMS (ESI-QTOF): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{24}\text{H}_{20}\text{NO}_6$ m/z 418.1291 and found m/z 418.1288.



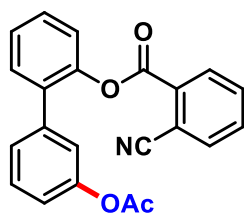
2-Cyano-5-methoxyphenyl 3'-acetoxy-5-fluoro-[1,1'-biphenyl]-2-carboxylate (29)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless gummy.

Isolated yield: 78% (31.6 mg, 0.078 mmol) (m :others = 20:1)

^1H NMR (400 MHz, CDCl_3) δ 8.20 (dd, $J = 8.7, 5.7$ Hz, 1H), 7.53 (d, $J = 8.7$ Hz, 1H), 7.44 (t, $J = 7.9$ Hz, 1H), 7.28 (ddd, $J = 7.7, 1.7, 1.1$ Hz, 1H), 7.21 (ddd, $J = 8.7, 7.8, 2.6$ Hz, 1H), 7.19 – 7.09 (m, 3H), 6.80 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.60 (d, $J = 2.4$ Hz, 1H), 3.82 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.45, 166.20, 164.19, 163.65, 154.08, 150.68, 146.04, 145.95, 141.40, 134.20, 133.92, 133.83, 129.51, 126.12, 124.85, 124.82, 122.03, 121.34, 118.68, 118.46, 115.89, 115.38, 115.16, 113.10, 108.85, 98.97, 56.12, 21.33; ^{19}F NMR (376 MHz, CDCl_3) δ -105.16; HRMS (ESI-QTOF): $[\text{M}+\text{H}]^+$ calculated for $\text{C}_{23}\text{H}_{17}\text{FNO}_5$ m/z 406.1091 and found m/z 406.1095.



3'-Acetoxy-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (30)

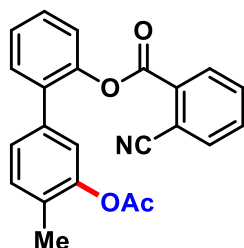
Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: brown gummy.

Isolated yield: 68% (24.2 mg, 0.068 mmol) (m :others = 12:1)

^1H NMR (400 MHz, CDCl_3) δ 8.08 – 8.02 (m, 1H), 7.85 – 7.78 (m, 1H), 7.73 – 7.62 (m, 2H), 7.52 – 7.41 (m, 2H), 7.40 – 7.31 (m, 4H), 7.23 (td, $J = 1.7, 1.0$ Hz, 1H), 7.02 (ddd, $J = 7.5, 2.4, 1.7$ Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.47, 162.72, 150.72, 147.53, 138.86, 135.10, 134.15, 133.31, 132.78, 131.85, 131.60, 131.19, 130.27, 129.53, 129.25,

127.05, 126.63, 123.06, 122.56, 121.03, 117.43, 113.49, 21.26; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{22}H_{16}NO_4$ m/z 358.1079 and found m/z 358.1085.



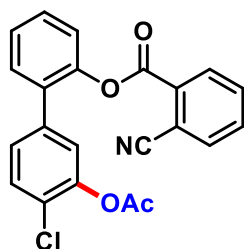
3'-Acetoxy-4'-methyl-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (31)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless liquid.

Isolated yield: 75% (27.8 mg, 0.075 mmol) (*m:others* >25:1)

1H NMR (400 MHz, $CDCl_3$) δ 8.12 – 7.99 (m, 1H), 7.87 – 7.77 (m, 1H), 7.73 – 7.62 (m, 2H), 7.50 – 7.40 (m, 2H), 7.39 – 7.30 (m, 2H), 7.27 – 7.23 (m, 1H), 7.21 (dt, $J = 7.9, 0.6$ Hz, 1H), 7.18 (d, $J = 1.7$ Hz, 1H), 2.27 (s, 3H), 2.14 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.18, 162.75, 149.33, 147.51, 136.29, 135.08, 134.08, 133.27, 132.80, 131.91, 131.63, 131.28, 131.23, 129.73, 128.98, 127.00, 126.71, 123.04, 122.76, 117.49, 113.47, 20.92, 16.11; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{23}H_{18}NO_4$ m/z 372.1236 and found m/z 372.1240.



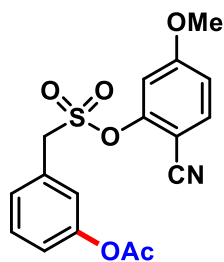
3'-Acetoxy-4'-chloro-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (32)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: whitish solid.

Isolated yield: 66% (25.8 mg, 0.066 mmol) (*m:others* = 15:1)

1H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.04 (m, 1H), 7.87 – 7.80 (m, 1H), 7.74 – 7.65 (m, 2H), 7.53 – 7.37 (m, 4H), 7.37 – 7.32 (m, 1H), 7.32 – 7.27 (m, 2H), 2.31 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 168.46, 162.71, 147.45, 146.99, 137.39, 135.19, 133.46, 133.22, 132.91, 131.94, 131.41, 131.08, 130.39, 129.59, 127.77, 127.18, 126.59, 124.64, 123.19, 117.50, 113.47, 20.76; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{22}H_{15}ClNO_4$ m/z 392.0690 and found m/z 392.0688.



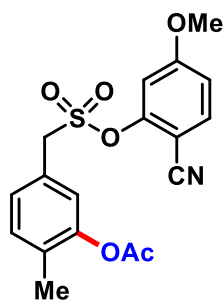
3-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)phenyl acetate (33)

Eluent: ethyl acetate/ petroleum ether (25:750 v/v).

Appearance: colorless gummy.

Isolated yield: 83% (29.9 mg, 0.083 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.66 – 7.52 (m, 1H), 7.51 – 7.36 (m, 2H), 7.29 (s, 1H), 7.18 (dt, *J* = 8.2, 1.8 Hz, 1H), 6.87 (dq, *J* = 4.9, 2.4 Hz, 2H), 4.70 (s, 2H), 3.82 (s, 3H), 2.29 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.28, 164.31, 151.79, 151.21, 134.60, 130.24, 128.67, 128.05, 124.47, 123.11, 115.64, 114.08, 109.28, 98.85, 58.21, 56.29, 21.24; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₇H₁₆NO₆S *m/z* 362.0698 and found *m/z* 362.0690.



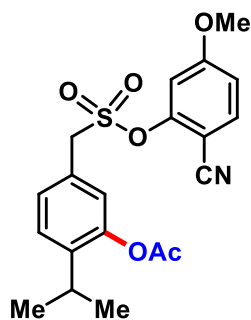
5-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-2-methylphenyl acetate (34)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: colorless gummy.

Isolated yield: 73% (27.4 mg, 0.073 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.52 (m, 1H), 7.36 – 7.27 (m, 2H), 7.21 (d, *J* = 1.5 Hz, 1H), 6.94 – 6.83 (m, 2H), 4.67 (s, 2H), 3.82 (s, 3H), 2.32 (s, 3H), 2.20 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.17, 164.27, 151.82, 149.75, 134.64, 132.23, 131.95, 128.85, 125.27, 124.86, 124.76, 115.70, 114.10, 109.23, 98.81, 58.00, 56.36, 56.19, 20.92, 16.33, 16.23; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₈NO₆S *m/z* 376.0855 and found *m/z* 376.0860.



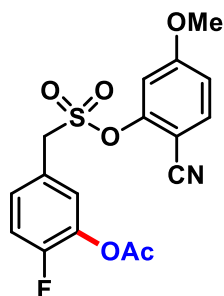
5-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-2-isopropylphenyl acetate (35)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: Sticky colorless liquid.

Isolated yield: 68% (27.4 mg, 0.068 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 9.4 Hz, 1H), 7.36 (d, *J* = 1.2 Hz, 2H), 7.19 (s, 1H), 6.92 – 6.81 (m, 2H), 4.67 (s, 2H), 3.83 (s, 3H), 3.06 – 3.00 (m, 1H), 2.32 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.59, 164.30, 151.93, 148.55, 142.14, 134.59, 129.15, 127.75, 125.23, 124.91, 115.68, 114.04, 109.26, 98.86, 58.02, 56.29, 27.64, 22.98, 21.10; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₀H₂₂NO₆S *m/z* 404.1168 and found *m/z* 404.1162.



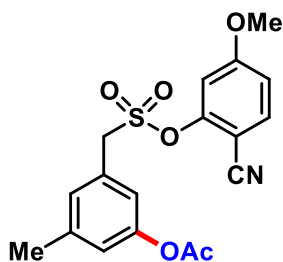
5-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-2-fluorophenyl acetate (36)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 61% (23.1 mg, 0.061 mmol) (*m:others* >25:1)

¹H NMR (500 MHz, CDCl₃) δ 7.65 – 7.51 (m, 1H), 7.48 – 7.28 (m, 2H), 7.21 (dd, *J* = 9.8, 8.4 Hz, 1H), 6.88 (d, *J* = 7.4 Hz, 2H), 4.67 (s, 2H), 3.84 (s, 3H), 2.33 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 168.22, 164.32, 156.10, 154.09, 151.67, 138.68, 138.57, 134.63, 130.17, 130.11, 126.83, 126.82, 123.19, 123.16, 117.69, 117.53, 115.71, 114.10, 109.30, 98.69, 57.60, 56.31, 20.64; **¹⁹F NMR** (471 MHz, CDCl₃) δ -125.93; **HRMS** (ESI-QTOF): [M+Na]⁺ calculated for C₁₇H₁₄FNNaO₆S *m/z* 402.0424 and found *m/z* 402.0428.



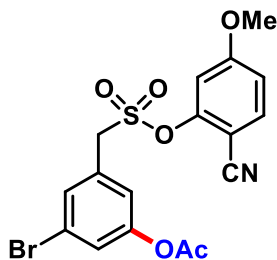
3-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-5-methylphenyl acetate (37)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: colorless gummy.

Isolated yield: 85% (3.8 mg, 0.085 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.19 (dt, *J* = 1.6, 0.8 Hz, 1H), 7.08 (t, *J* = 2.0 Hz, 1H), 6.98 (tt, *J* = 1.6, 0.8 Hz, 1H), 6.94 – 6.80 (m, 2H), 4.66 (s, 2H), 3.83 (s, 3H), 2.37 (s, 3H), 2.28 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.49, 164.28, 151.80, 151.05, 140.72, 134.59, 129.48, 127.58, 123.77, 121.49, 115.66, 114.06, 109.24, 98.78, 58.18, 56.28, 21.40, 21.26; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₈NO₆S *m/z* 376.0855 and found *m/z* 376.850.



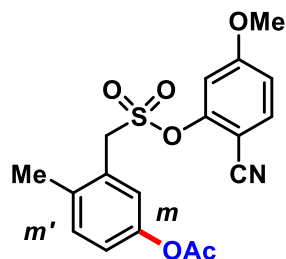
3-Bromo-5-(((2-cyano-5-methoxyphenoxy)sulfonyl)methyl)phenyl acetate (38)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 51% (22.4 mg, 0.051 mmol) (*m:others* = 8:1)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (dt, *J* = 8.8, 1.1 Hz, 1H), 7.53 (t, *J* = 1.6 Hz, 1H), 7.37 (t, *J* = 1.9 Hz, 1H), 7.30 – 7.24 (m, 1H), 6.96 – 6.86 (m, 2H), 4.66 (s, 2H), 3.85 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.91, 164.36, 151.63, 151.51, 134.64, 131.51, 129.48, 126.59, 123.48, 123.03, 115.66, 114.25, 109.36, 98.79, 57.58, 56.35, 21.20; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₇H₁₅BrNO₆S *m/z* 439.9803 and found *m/z* 439.9799.



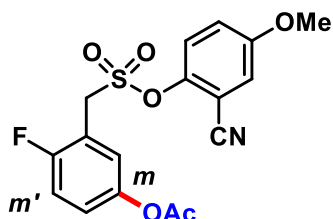
3-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-4-methylphenyl acetate (39)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: colorless gummy.

Isolated yield: 79% (29.6 mg, 0.079 mmol) (*m:others* >25:1) (*m:m'* = 9:1)

¹H NMR (400 MHz, CDCl₃) δ 7.62 – 7.55 (m, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 2.5 Hz, 1H), 7.07 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.94 – 6.74 (m, 2H), 4.76 (s, 2H), 3.82 (s, 3H), 2.47 (s, 3H), 2.28 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.57, 164.31, 151.66, 149.12, 136.41, 134.62, 134.59, 132.13, 126.15, 125.25, 123.19, 115.65, 114.16, 109.36, 98.97, 56.29, 55.83, 21.24, 19.33; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₈NO₆S *m/z* 376.0855 and found *m/z* 376.0850.



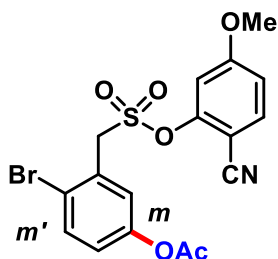
3-(((2-Cyano-4-methoxyphenoxy)sulfonyl)methyl)-4-fluorophenyl acetate (40)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: colorless gummy.

Isolated yield: 74% (28.0 mg, 0.074 mmol) (*m:others* >25:1) (*m:m'* = 1:1)

¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.40 (m, 1H), 7.34 (dt, *J* = 6.1, 1.4 Hz, 1H), 7.32 – 7.30 (m, 1H), 7.30 – 7.27 (m, 2H), 7.24 – 7.20 (m, 2H), 7.19 – 7.15 (m, 2H), 7.13 (d, *J* = 3.0 Hz, 2H), 7.10 (m, *J* = 9.0, 3.1, 1.9 Hz, 4H), 4.80 – 4.70 (m, 3H), 3.82 (s, 6H), 2.31 (d, *J* = 18.2 Hz, 6H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.37, 168.29, 160.17, 158.26, 157.69, 154.57, 152.05, 146.85, 146.82, 143.24, 143.20, 138.85, 138.72, 130.01, 129.99, 125.78, 125.76, 125.62, 125.10, 125.01, 124.92, 124.88, 124.83, 120.56, 118.08, 118.06, 117.09, 116.85, 116.19, 116.06, 115.50, 115.34, 114.94, 108.35, 108.30, 56.25, 51.22, 51.19, 51.14, 51.11, 21.15, 20.64; **¹⁹F NMR** (376 MHz, CDCl₃) δ – 119.12, – 130.24; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₇H₁₅FNO₆S *m/z* 380.0604 and found *m/z* 380.0604.



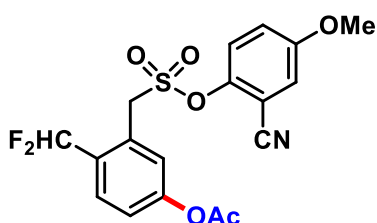
4-Bromo-3-(((2-cyano-5-methoxyphenoxy)sulfonyl)methyl)phenyl acetate (41)

Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: whitish solid.

Isolated yield: 69% (30.3 mg, 0.069 mmol) (*m:others* >25:1) (*m:m'* = 1.7:1)

¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, *J* = 32.0, 8.8 Hz, 2H), 7.51 – 7.41 (m, 1H), 7.10 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.99 – 6.87 (m, 2H), 4.98 (s, 2H), 3.84 (s, 3H), 2.32 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.05, 168.58, 164.31, 151.52, 151.46, 150.26, 149.42, 134.73, 134.70, 134.49, 130.60, 128.90, 128.71, 128.34, 128.08, 126.33, 125.23, 124.88, 122.53, 120.70, 115.52, 114.21, 114.18, 109.24, 98.95, 98.92, 58.04, 57.79, 56.33, 21.23, 20.99; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₇H₁₅BrNO₆S *m/z* 441.2720 and found *m/z* 441.2725.



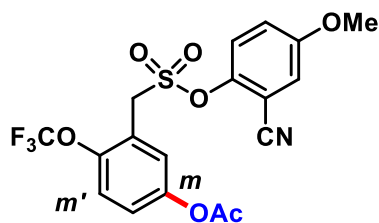
3-(((2-Cyano-4-methoxyphenoxy)sulfonyl)methyl)-4-(difluoromethyl)phenyl acetate (42)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 74% (30.4 mg, 0.074 mmol) (*m:others* >25:1) (*m:m'* = 2:1)

¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 2.7 Hz, 1H), 7.32 (dd, *J* = 8.7, 0.8 Hz, 1H), 7.27 (d, *J* = 8.8 Hz, 1H), 7.19 (dd, *J* = 8.9, 2.8 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.54 (t, *J* = 73.3 Hz, 1H), 4.79 (s, 2H), 3.83 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.29, 158.28, 147.97, 147.84, 143.14, 126.14, 124.91, 124.89, 124.62, 120.77, 120.56, 120.23, 119.04, 118.88, 118.10, 118.08, 116.45, 116.27, 114.99, 108.27, 56.32, 56.28, 56.23, 51.96, 21.22, 21.17; **¹⁹F NMR** (376 MHz, CDCl₃) δ – 80.46, – 80.48; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₆F₂NO₆S *m/z* 412.0666 and found *m/z* 412.0670.



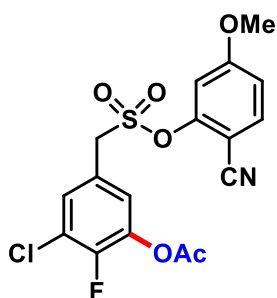
3-(((2-Cyano-4-methoxyphenoxy)sulfonyl)methyl)-4-(trifluoromethoxy)phenyl acetate (43)

Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: Sticky colorless gummy.

Isolated yield: 70% (31.1 mg, 0.070 mmol) (*m:others* >25:1) (*m:m'* = 1.2:1)

¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, *J* = 2.8 Hz, 1H), 7.40 – 7.34 (m, 1H), 7.31 (dd, *J* = 8.8, 0.6 Hz, 1H), 7.23 (dd, *J* = 9.0, 2.8 Hz, 1H), 7.16 – 7.07 (m, 2H), 4.78 (s, 2H), 3.83 (s, 3H), 2.31 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.16, 158.31, 148.76, 145.73, 143.03, 126.17, 124.93, 124.67, 121.32, 120.77, 120.56, 118.10, 114.92, 108.37, 56.20, 51.77, 21.20; **¹⁹F NMR** (376 MHz, CDCl₃) δ – 57.11; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₈H₁₅F₃NO₇S m/z 446.0521 and found m/z 446.0525.



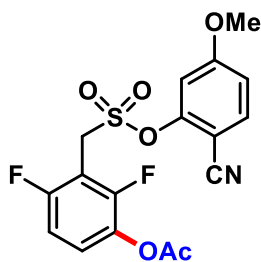
3-Chloro-5-(((2-cyano-5-methoxyphenoxy)sulfonyl)methyl)-2-fluorophenyl acetate (44)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 52% (21.5 mg, 0.052 mmol) (*m:others* = >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.67 – 7.53 (m, 1H), 7.47 (dd, *J* = 6.0, 2.3 Hz, 1H), 7.28 (dd, *J* = 6.2, 2.2 Hz, 1H), 7.06 – 6.80 (m, 2H), 4.64 (s, 2H), 3.86 (s, 3H), 2.35 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 167.86, 164.41, 152.85, 151.60, 150.32, 139.61, 139.48, 134.66, 130.52, 128.77, 128.34, 125.30, 123.38, 123.33, 123.15, 115.69, 114.23, 109.42, 98.74, 57.31, 56.36, 20.60; **¹⁹F NMR** (376 MHz, CDCl₃) δ – 126.46; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₇H₁₄ClFNO₆S m/z 414.0214 and found m/z 414.0220.



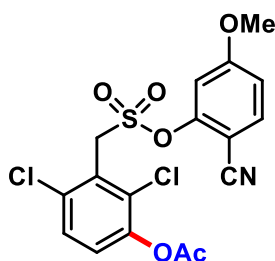
3-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-2,4-difluorophenyl acetate (45)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 74% (29.37 mg, 0.074 mmol) (*m:others* >25:1)

¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 8.7 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.02 (td, *J* = 8.8, 2.0 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.89 (dd, *J* = 8.8, 2.4 Hz, 1H), 4.86 (s, 2H), 3.84 (s, 3H), 2.33 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 168.32, 164.27, 160.02, 159.98, 157.97, 154.42, 154.37, 152.38, 152.33, 151.16, 134.81, 128.76, 128.33, 126.04, 126.02, 125.96, 125.94, 115.17, 114.23, 111.88, 111.84, 111.69, 111.66, 109.30, 105.61, 99.20, 56.32, 46.70, 20.60; **¹⁹F NMR** (471 MHz, CDCl₃) δ -114.08, -124.31, -124.33; **HRMS** (ESI-QTOF): [M+Na]⁺ calculated for C₁₇H₁₃F₂NaNO₆S m/z 420.0329 and found m/z 420.0335.



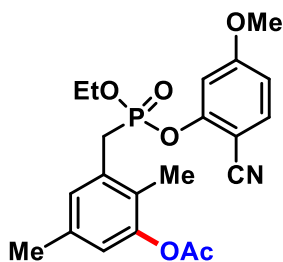
2,4-Dichloro-3-(((2-cyano-5-methoxyphenoxy)sulfonyl)methyl)phenyl acetate (46)

Eluent: ethyl acetate/ petroleum ether (25:75 v/v).

Appearance: whitish solid.

Isolated yield: 78% (33.5 mg, 0.078 mmol) (*m:others* >25:1)

¹H NMR (500 MHz, CDCl₃) δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 8.8 Hz, 1H), 7.21 (d, *J* = 8.8 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.24 (s, 2H), 3.85 (s, 3H), 2.36 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 168.33, 164.29, 151.21, 146.85, 134.78, 134.66, 130.92, 129.20, 125.89, 125.84, 115.34, 114.34, 109.43, 99.29, 56.33, 54.33, 20.80; **HRMS** (ESI-QTOF): [M+Na]⁺ calculated for C₁₇H₁₃Cl₂NaNO₆S m/z 451.9738 and found m/z 451.9740.



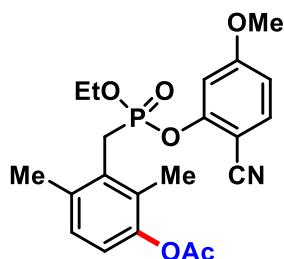
3-(((2-Cyano-5-methoxyphenoxy)(ethoxy)phosphoryl)methyl)-2,5-dimethylphenyl acetate (47)

Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: colorless gummy.

Isolated yield: 75% (31.4 mg, 0.075 mmol) (*m*: others = 20:1)

¹H NMR (400 MHz, CDCl₃) δ 7.46 (d, *J* = 8.7 Hz, 1H), 7.06 (s, 1H), 6.74 (d, *J* = 7.8 Hz, 2H), 6.70 (dd, *J* = 8.7, 2.3 Hz, 1H), 4.16 (dq, *J* = 14.3, 7.1 Hz, 2H), 3.72 (s, 3H), 3.44 (d, *J* = 22.2 Hz, 2H), 2.29 (s, 3H), 2.26 (s, 3H), 2.16 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.48, 164.28, 154.35, 154.28, 149.77, 136.71, 134.19, 130.21, 130.14, 129.86, 129.82, 126.84, 122.18, 122.14, 116.18, 112.27, 106.35, 97.13, 64.06, 64.00, 55.99, 32.28, 31.17, 21.00, 20.92, 16.42, 16.37, 12.61; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₁H₂₅NO₆P *m/z* 418.1419 and found *m/z* 418.1415.



3-(((2-Cyano-5-methoxyphenoxy)(ethoxy)phosphoryl)methyl)-2,4-dimethylphenyl acetate (48)

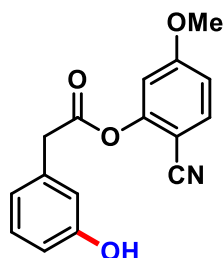
Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: colorless gummy.

Isolated yield: 82% (34.2 mg, 0.082 mmol) (*m*: others >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, *J* = 8.7, 0.9 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 6.85 (dd, *J* = 8.2, 2.8 Hz, 1H), 6.70 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.65 (d, *J* = 1.2 Hz, 1H), 4.51 – 3.96 (m, 2H), 3.70 (d, *J* = 0.7 Hz, 3H), 3.55 (d, *J* = 22.5 Hz, 2H), 2.44 (d, *J* = 1.9 Hz, 3H), 2.29 (s, 3H), 2.24 (d, *J* = 2.0 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.56, 164.28, 154.13, 154.04, 148.03, 147.98, 136.05, 135.99, 134.19, 130.37, 130.31, 129.28,

129.18, 128.83, 128.79, 121.20, 121.16, 116.15, 112.45, 106.45, 106.42, 97.26, 97.20, 64.01, 63.93, 56.01, 29.93, 28.54, 20.97, 20.78, 20.77, 16.37, 16.31, 13.46, 13.44; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{21}H_{25}NO_6P$ m/z 418.1419 and found m/z 418.1426.



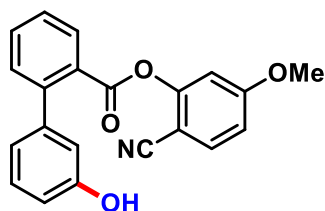
2-Cyano-5-methoxyphenyl 2-(3-hydroxyphenyl)acetate (49)

Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: colorless gummy.

Isolated yield: 73% (207 mg, 0.073 mmol) (m :others >25:1)

1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, J = 8.6 Hz, 1H), 7.22 (t, J = 7.9 Hz, 1H), 6.96 (t, J = 2.1 Hz, 1H), 6.91 (dt, J = 7.5, 1.2 Hz, 1H), 6.85 – 6.78 (m, 3H), 6.14 (s, 1H), 3.88 (s, 2H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.08, 164.23, 156.46, 154.25, 134.34, 134.05, 130.21, 121.79, 116.74, 115.92, 115.16, 112.87, 109.13, 98.33, 56.13, 41.16; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{16}H_{14}NO_4$ m/z 284.0923 and found m/z 284.0922.



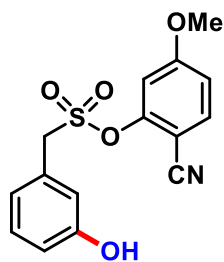
2-Cyano-5-methoxyphenyl 3'-hydroxy-[1,1'-biphenyl]-2-carboxylate (50)

Eluent: ethyl acetate/ petroleum ether (30:70 v/v).

Appearance: sticky colorless gummy.

Isolated yield: 60% (20.7 mg, 0.060 mmol) (m :others = 20:1)

1H NMR (400 MHz, $CDCl_3$) δ 8.04 (dd, J = 8.1, 1.4 Hz, 1H), 7.69 – 7.59 (m, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.36 – 7.28 (m, 2H), 7.12 – 6.96 (m, 2H), 6.88 (ddd, J = 8.2, 2.4, 1.1 Hz, 1H), 6.83 (dd, J = 8.7, 2.4 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 3.83 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.83, 164.54, 156.00, 154.52, 143.39, 141.84, 134.54, 132.58, 131.13, 130.62, 130.05, 129.14, 127.59, 120.53, 116.89, 116.72, 115.37, 113.14, 108.98, 99.19, 56.15; **HRMS** (ESI-QTOF): $[M+H]^+$ calculated for $C_{21}H_{16}NO_4$ m/z 346.1079 and found m/z 346.1085.



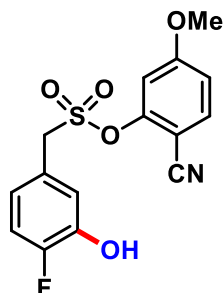
2-Cyano-5-methoxyphenyl (3-hydroxyphenyl)methanesulfonate (51)

Eluent: ethyl acetate/ petroleum ether (35:65 v/v).

Appearance: brown gummy.

Isolated yield: 65% (21 mg, 0.065 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.37 – 7.20 (m, 1H), 7.07 (t, *J* = 2.0 Hz, 1H), 7.03 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.99 – 6.89 (m, 2H), 6.86 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.11 (s, 1H), 4.66 (s, 2H), 3.84 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.41, 156.55, 152.01, 134.71, 130.55, 127.72, 123.37, 118.34, 117.24, 115.93, 113.82, 108.80, 98.11, 58.62, 56.32; **HRMS** (ESI-QTOF): [M+Na]⁺ calculated for C₁₅H₁₃NNaO₅S *m/z* 342.0412 and found *m/z* 342.0415.



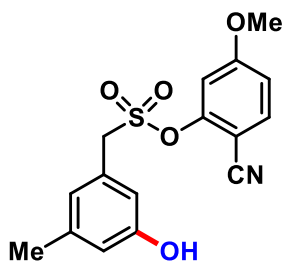
2-Cyano-5-methoxyphenyl (4-fluoro-3-hydroxyphenyl)methanesulfonate (53)

Eluent: ethyl acetate/ petroleum ether (35:65 v/v).

Appearance: whitish solid.

Isolated yield: 61% (20.5 mg, 0.059 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.58 (d, *J* = 8.7 Hz, 1H), 7.21 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.12 (dd, *J* = 10.3, 8.4 Hz, 1H), 7.01 (ddd, *J* = 8.4, 4.4, 2.2 Hz, 1H), 6.95 (d, *J* = 2.4 Hz, 1H), 6.88 (dd, *J* = 8.8, 2.4 Hz, 1H), 5.76 (s, 1H), 4.63 (s, 2H), 3.85 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.39, 153.38, 151.89, 150.98, 144.42, 144.28, 134.69, 123.87, 123.80, 123.22, 123.19, 120.49, 120.46, 116.66, 116.47, 115.82, 113.96, 109.14, 98.45, 58.12, 56.34; **¹⁹F NMR** (376 MHz, CDCl₃) δ – 138.21; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₅H₁₃FNO₅S *m/z* 338.0498 and found *m/z* 338.0493.



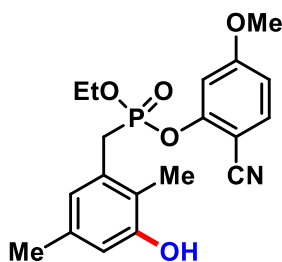
2-Cyano-5-methoxyphenyl (3-hydroxy-5-methylphenyl)methanesulfonate (52)

Eluent: ethyl acetate/ petroleum ether (35:65 v/v).

Appearance: colorless gummy.

Isolated yield: 72% (24 mg, 0.072 mmol) (*m:others* = 20:1)

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.85 (dt, *J* = 8.2, 2.0 Hz, 3H), 6.72 (td, *J* = 1.5, 0.7 Hz, 1H), 5.99 (s, 1H), 4.61 (s, 2H), 3.83 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.39, 156.44, 152.06, 140.87, 134.68, 127.34, 124.23, 117.89, 115.93, 115.44, 113.79, 108.79, 98.13, 58.64, 56.31, 21.46; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₆H₁₆NO₅S *m/z* 334.0749 and found *m/z* 334.0755.



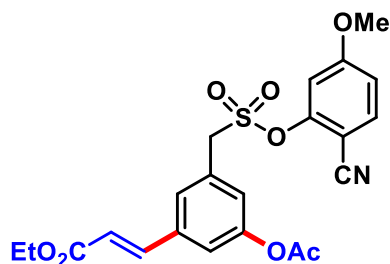
2-Cyano-5-methoxyphenyl ethyl (3-hydroxy-2,5-dimethylbenzyl)phosphonate (54)

Eluent: ethyl acetate/ petroleum ether (40:60 v/v).

Appearance: brown solid.

Isolated yield: 73% (27.5 mg, 0.073 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.46 (dd, *J* = 8.7, 0.9 Hz, 1H), 6.73 (dd, *J* = 2.4, 1.2 Hz, 1H), 6.71 – 6.64 (m, 2H), 6.44 (t, *J* = 2.2 Hz, 1H), 4.28 – 4.11 (m, 2H), 3.69 (s, 3H), 3.42 (d, *J* = 22.0 Hz, 2H), 2.20 (d, *J* = 1.9 Hz, 3H), 2.13 (s, 3H), 1.28 (td, *J* = 7.1, 0.5 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 164.30, 154.86, 154.82, 154.37, 154.28, 136.33, 136.29, 134.18, 129.33, 129.24, 123.88, 123.82, 121.04, 120.97, 116.18, 115.31, 115.27, 112.32, 106.33, 106.30, 97.09, 97.03, 64.10, 64.02, 55.96, 32.29, 30.92, 20.94, 16.43, 16.36, 11.88, 11.86; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₉H₂₃NO₅P *m/z* 376.1314 and found *m/z* 376.1320.



Ethyl (*E*)-3-(3-acetoxy-5-(((2-cyano-5-methoxyphenoxy)sulfonyl)methyl)phenyl)acrylate (55)

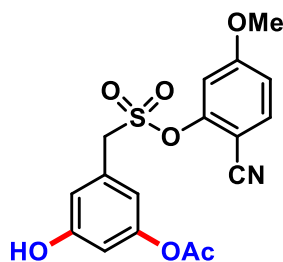
Procedure: In an oven-dried screw capped reaction tube was charged with magnetic stirbar, corresponding sulphonic ester (0.1 mmol), Pd(OAc)₂ (10 mol%), *N*-CBz-Gly-OH (20 mol%), eosin Y (3 mol%), and olefin (0.2 mmol, 2 equiv.) in 1 mL of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) were added. The reaction tube was capped and placed 3 cm away from four 23 W house hold CFL bulbs with stirring (1500 rpm) at room temperature for 28 h. The temperature was maintained at approximately (30-35 °C) through cooling with a fan. Upon completion the mixture was diluted with ethyl acetate and filtered through a celite pad. The filtrate was evaporation under reduced pressure and the crude mixture was purified by column chromatography using silica (100- 200 mesh size) and petroleum ether / ethyl acetate as the eluent.

Eluent: ethyl acetate/ petroleum ether (35:65 v/v).

Appearance: Sticky yellow gummy.

Isolated yield: 75% (34.5 mg, 0.075 mmol) (*m:others* >25:1)

¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.58 (dd, *J* = 8.4, 0.6 Hz, 1H), 7.53 (t, *J* = 1.6 Hz, 1H), 7.32 (dt, *J* = 5.9, 2.0 Hz, 2H), 6.95 – 6.85 (m, 2H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.72 (s, 2H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.84 (s, 3H), 2.32 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 169.18, 166.59, 164.36, 151.71, 151.55, 142.52, 137.09, 134.64, 128.74, 128.19, 125.91, 122.19, 120.87, 115.71, 114.21, 109.38, 98.80, 60.96, 58.02, 56.35, 21.29, 14.47; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₂H₂₂NO₈S m/z 460.1066 and found m/z 460.1070.



3-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)-5-hydroxyphenyl acetate (56)

Procedure: In an oven dried reaction tube, charged with magnetic stir-bar, Pd(OAc)₂ (10 mol%), For-Gly-OH (25 mol%) and *meta*-acetoxyated suphonic ester substrate (0.1 mmol) were added. The hydroxylating agent PhI(TFA)₂ (0.4 mmol) was added to the reaction mixture followed by the HFIP (1 mL). The reaction tube was capped and stirred at room temperature for 15 mins and then placed to a preheated oil-bath at 70 °C for 24 h. Upon completion, the reaction was taken out to cool and diluted with ethyl acetate. The solution was filtered through celite bed. The filtrate was evaporated under reduced pressure and passed through the column for purification. Petroleum ether and ethyl acetate mixture was used as the Eluent.

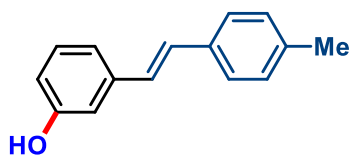
Eluent: ethyl acetate/ petroleum ether (45:55 v/v).

Appearance: brown solid.

Isolated yield: 61% (23.0 mg, 0.061 mmol) (*m:others* = 16:1)

¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 8.7 Hz, 1H), 6.97 (d, *J* = 2.4 Hz, 2H), 6.87 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.81 (d, *J* = 1.8 Hz, 1H), 6.70 (t, *J* = 2.1 Hz, 1H), 6.07 (s, 1H), 4.62 (s, 2H), 3.85 (s, 3H), 2.28 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 169.27, 164.44, 157.35, 152.11, 151.95, 134.73, 128.43, 116.59, 116.14, 113.84, 111.08, 108.69, 58.30, 56.35, 21.33; **HRMS** (ESI-QTOF): [M+Na]⁺ calculated for C₁₇H₁₅NaNO₇S *m/z* 400.0467 and found *m/z* 400.0463.

General Procedure for Julia Olefination Reaction: To a flame dried round bottomed flask equipped with magnetic stir-bar, freshly prepared LDA (2M) and dry THF (6 mL) was added. The solution was cooled to -78 °C. Separately a solution of benzaldehyde and the *meta*-functionalized compound (0.1 mmol) in dry THF (6 mL) was prepared and slowly added to the LDA/THF solution at -78 °C. The reaction mixture was stirred overnight while warmed it to room temperature. Upon completion the reaction was quenched with saturated NH₄Cl solution and extracted with ethyl acetate. The organic portion was dried over anhydrous Na₂SO₄, concentrated under reduced pressure and purified through column chromatography



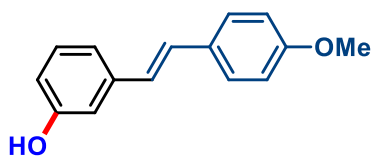
(E)-3-(4-Methylstyryl)phenol (57)

Eluent: ethyl acetate/ petroleum ether (15:85 v/v).

Appearance: colorless gummy.

Isolated yield: 92% (19.3 mg, 0.092 mmol)

¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.24 (dd, *J* = 8.5, 7.3 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.13 – 7.08 (m, 1H), 7.04 (d, *J* = 11.3 Hz, 2H), 7.00 (dd, *J* = 2.8, 1.7 Hz, 1H), 6.75 (ddt, *J* = 7.9, 2.6, 1.3 Hz, 1H), 4.95 (s, 1H), 2.38 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 155.90, 139.50, 137.88, 134.54, 130.06, 129.61, 129.34, 127.41, 126.69, 119.59, 114.68, 114.66, 113.06, 113.04, 21.46; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₅H₁₅O m/z 211.1123 and found m/z 211.1125.



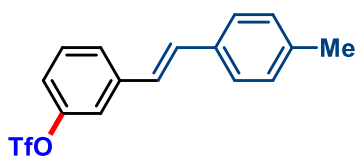
(*E*)-3-(4-Methoxystyryl)phenol (58)

Eluent: ethyl acetate/ petroleum ether (20:80 v/v).

Appearance: colorless solid.

Isolated yield: 90% (20.3 mg, 0.090 mmol)

¹H NMR (400 MHz, CDCl₃) δ 7.44 (d, *J* = 8.6 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.11 – 7.00 (m, 2H), 6.97 (dd, *J* = 2.6, 1.6 Hz, 1H), 6.93 – 6.88 (m, 3H), 6.72 (ddd, *J* = 8.0, 2.5, 0.9 Hz, 1H), 4.87 (s, 1H), 3.83 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 159.60, 156.00, 139.67, 130.21, 130.04, 128.94, 128.01, 126.39, 119.43, 114.48, 114.38, 112.92, 55.56; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₅H₁₅O₂ m/z 227.1072 and found m/z 227.1075.



Procedure: To a solution of (*E*)-3-styrylphenol (1 equiv) in dry dichloromethane anhydrous pyridine (1.5 equiv.) was added at 0 °C and stirred for 15 min, followed by triflic anhydride (2.0 equiv) was added. After allowing the reaction mixture to attain room temperature, the reaction mixture was stirred for overnight. The reaction was quenched with saturated aqueous bicarbonate solution and extracted with DCM. The organic layer was dried over sodium sulfate, concentrated to dryness under reduced pressure, and purified by column chromatography using petroleum ether as eluent. Pure compound was isolated as colorless liquid in 92% yield.

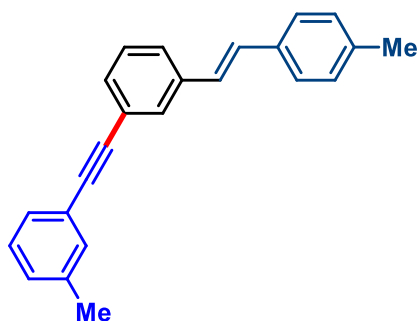
(*E*)-3-(4-Methylstyryl)phenyl trifluoromethanesulfonate (59)

Eluent: ethyl acetate/ petroleum ether (10:80 v/v).

Appearance: whitish solid.

Isolated yield: 95% (32.5 mg, 0.095 mmol)

¹H NMR (400 MHz, CDCl₃) δ 7.50 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.42 (t, *J* = 8.0 Hz, 3H), 7.38 (t, *J* = 2.1 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.17 – 7.12 (m, 1H), 7.11 – 6.96 (m, 2H), 2.38 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 150.26, 140.62, 138.65, 133.83, 131.39, 130.54, 129.74, 126.92, 126.42, 125.66, 119.85, 118.96, 21.52; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₁₆H₁₄F₃O₃S *m/z* 343.0616 and found *m/z* 343.0620.



(E)-1-Methyl-3-((3-(4-methylstyryl)phenyl)ethynyl)benzene (60)

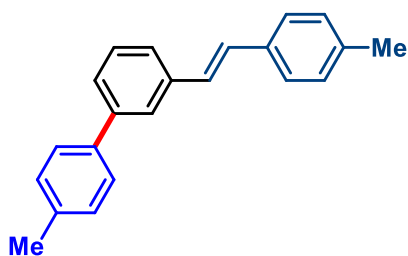
Procedure: Aryl triflate (**59**, 0.1 mmol, 1.0 equiv), 3-ethynyltoluene (0.15 mmol, 1.5 equiv), Pd(OAc)₂ (10 mol%, 0.01 mmol, 2.2 mg), PPh₃ (20 mol%, 0.02 mmol, 5.2 mg) and K₃PO₄ (0.15 mmol, 1.5 equiv, 31.8 mg) was taken in a reaction tube and 2 mL of DMSO was added under N₂ atmosphere. The reaction mixture was stirred for 24 h at 80 °C. After completion of the reaction the reaction mixture was diluted with water and extracted with diethyl ether. The organic layer was washed with brine and dried over Na₂SO₄. Evaporation of the solvent followed by purification have been done by column chromatography and the pure compound (**60**) was isolated as solid using petroleum ether as the eluent.

Eluent: ethyl acetate/ petroleum ether (5:95 v/v).

Appearance: whitish gummy.

Isolated yield: 82% (25.4 mg, 0.082 mmol)

¹H NMR (500 MHz, CDCl₃) δ 7.53 – 7.48 (m, 1H), 7.43 (dd, *J* = 8.0, 1.8 Hz, 4H), 7.40 (dd, *J* = 9.1, 2.3 Hz, 2H), 7.19 (dd, *J* = 7.9, 4.9 Hz, 3H), 7.17 – 7.12 (m, 2H), 7.11 (d, *J* = 5.2 Hz, 1H), 7.06 (s, 1H), 2.38 (s, 3H), 2.38 (s, 3H); **¹³C NMR** (126 MHz, CDCl₃) δ 150.26, 140.62, 138.64, 138.25, 138.00, 137.91, 134.51, 133.84, 132.44, 131.39, 130.62, 130.54, 129.74, 129.65, 129.64, 129.61, 129.43, 128.92, 128.87, 128.48, 127.01, 126.92, 126.72, 126.53, 126.42, 125.66, 123.91, 123.22, 119.84, 118.96, 89.81, 89.19, 21.52, 21.48; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₄H₂₁ *m/z* 309.1643 and found *m/z* 309.1650.



(E)-4'-Methyl-3-(4-methylstyryl)-1,1'-biphenyl (61)

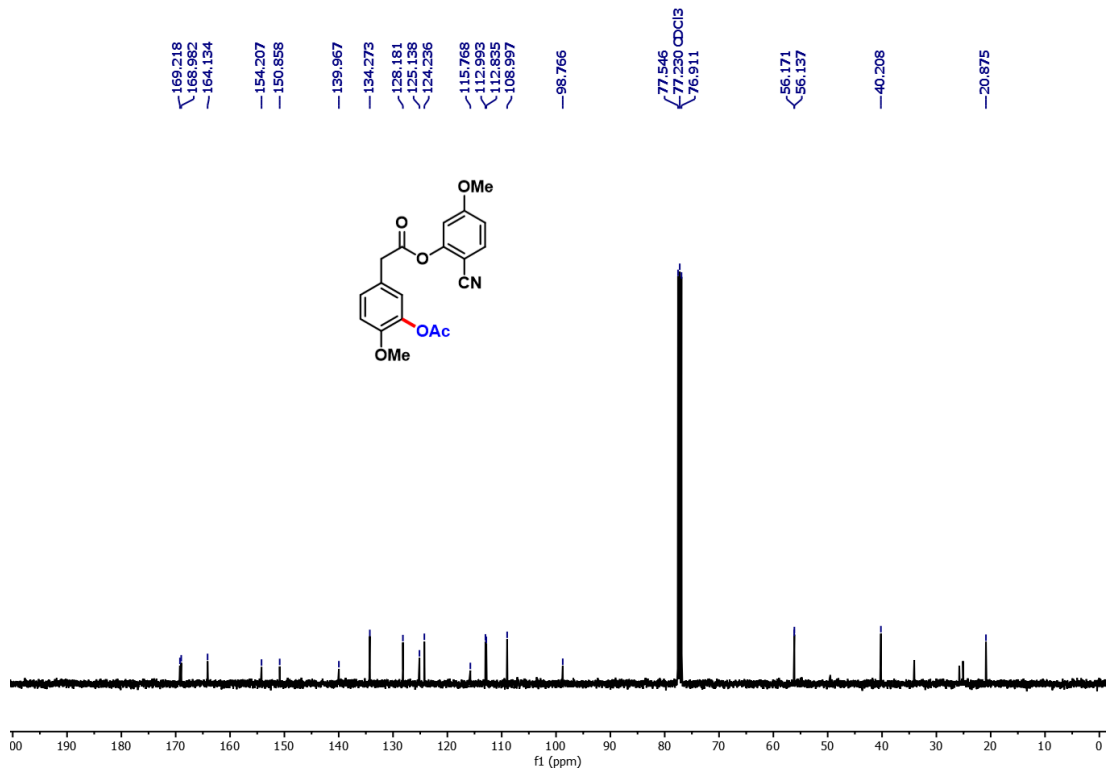
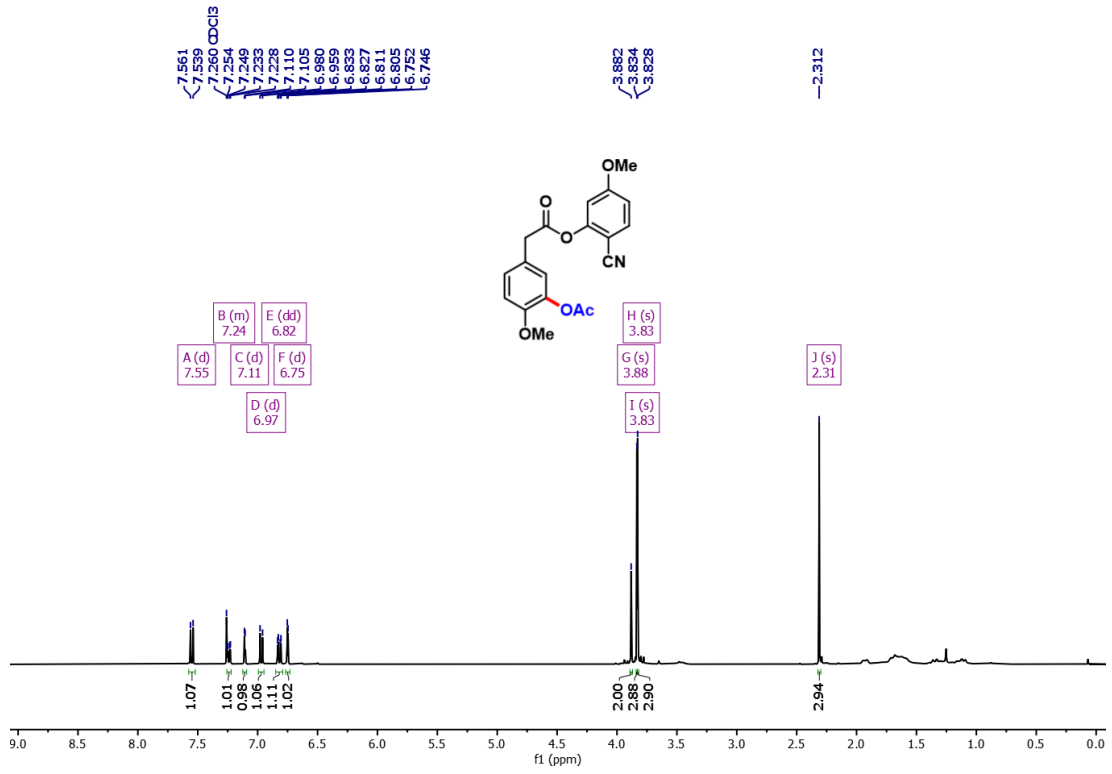
Procedure: In an oven dried reaction tube charged with magnetic stir bar, triflate (**59**, 0.1 mmol, 1.0 equiv), Pd(PPh₃)₂Cl₂ (10 mol%, 0.01 mmol, 7.0 mg), PPh₃ (20 mol%, 0.02 mmol, 5.2 mg), K₂CO₃ (0.2 mmol, 2.0 equiv, 27.6 mg) and aryl boronic acid (0.15 mmol, 1.5 equiv) have been taken. The reaction tube was closed by a screw cap for evacuation and back filled with N₂ for three times. Then 2 mL of dry toluene was added to the reaction mixture and placed in a preheated oil bath at 100 °C. The reaction mixture was stirred vigorously for 24 h. The reaction mixture was allowed to cool to room temperature and filtered through the celite pad. The filtrate was concentrated under reduced pressure and pure product was isolated by column chromatography using petroleum ether as the eluent.

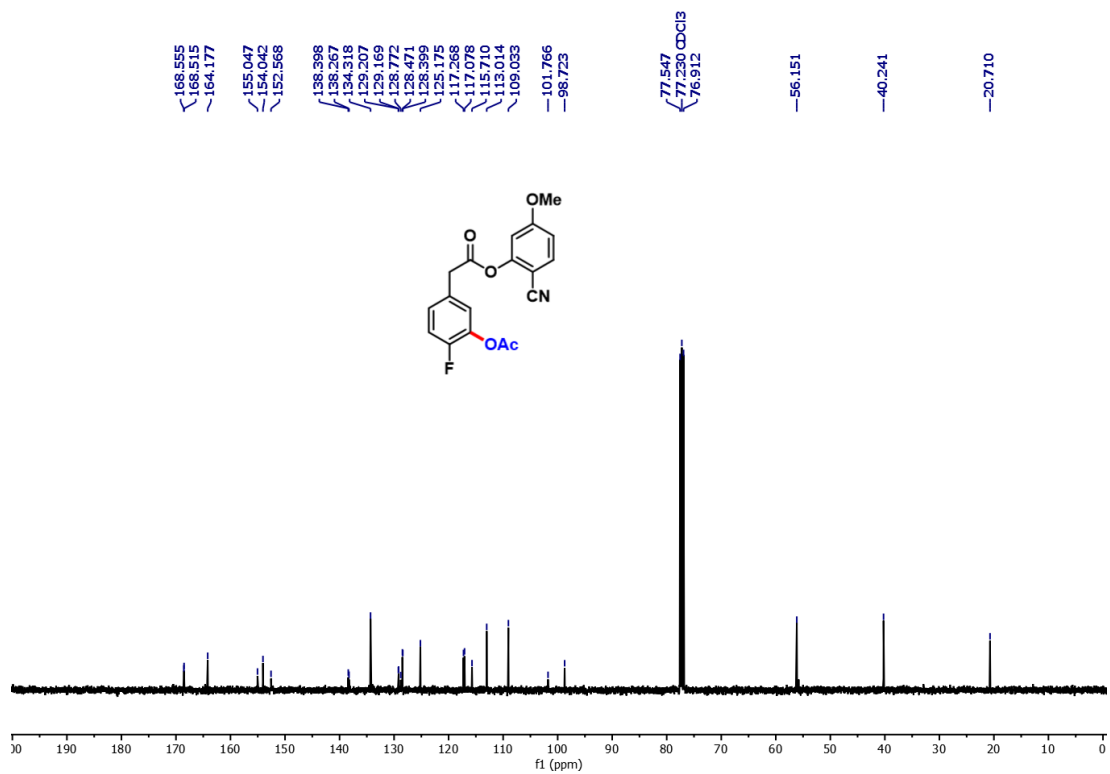
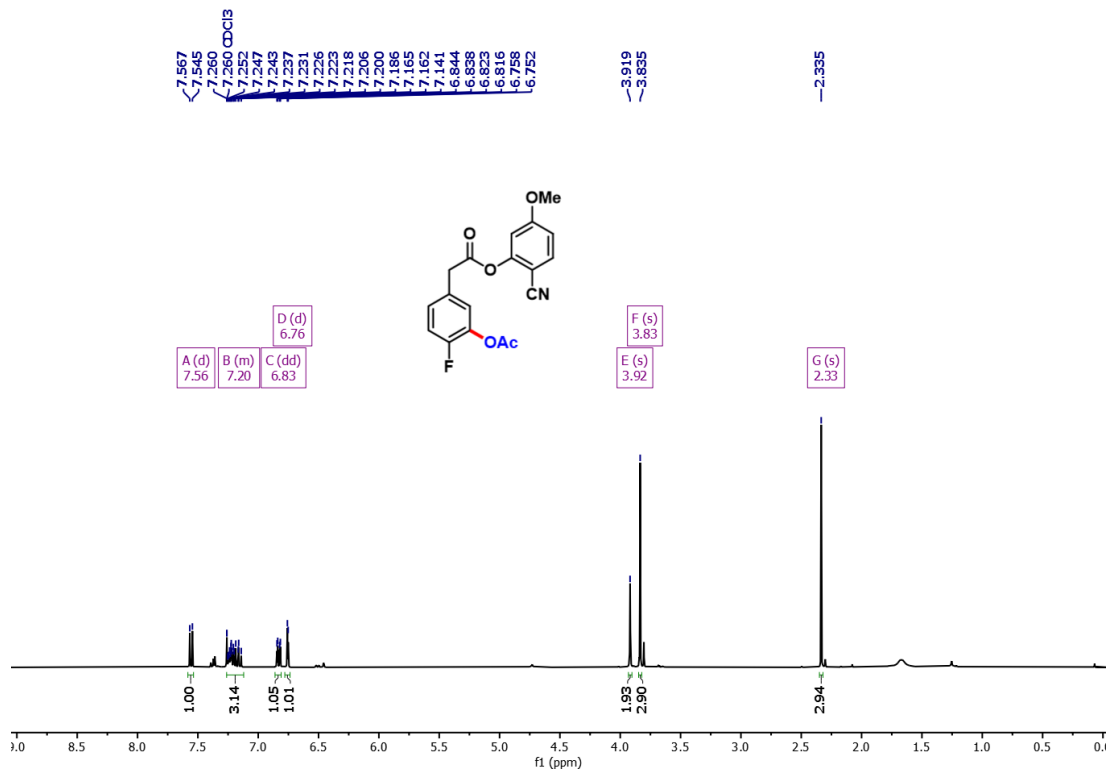
Eluent: ethyl acetate/ petroleum ether (5:95 v/v).

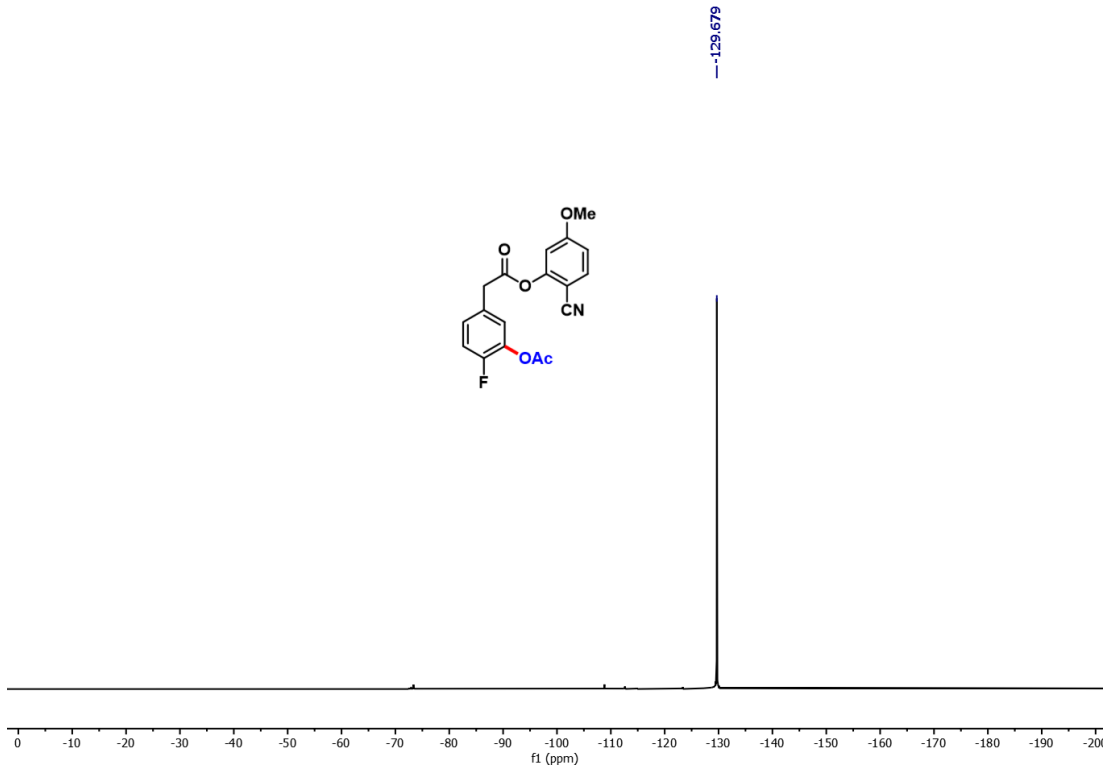
Appearance: colorless liquid.

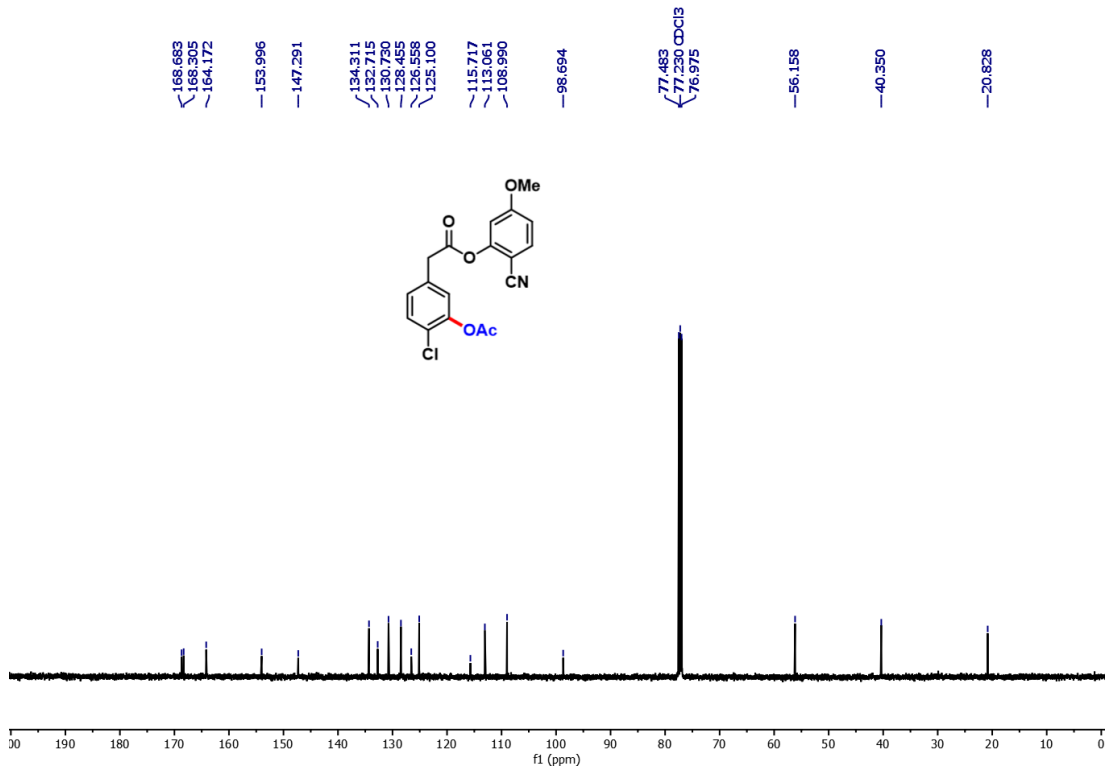
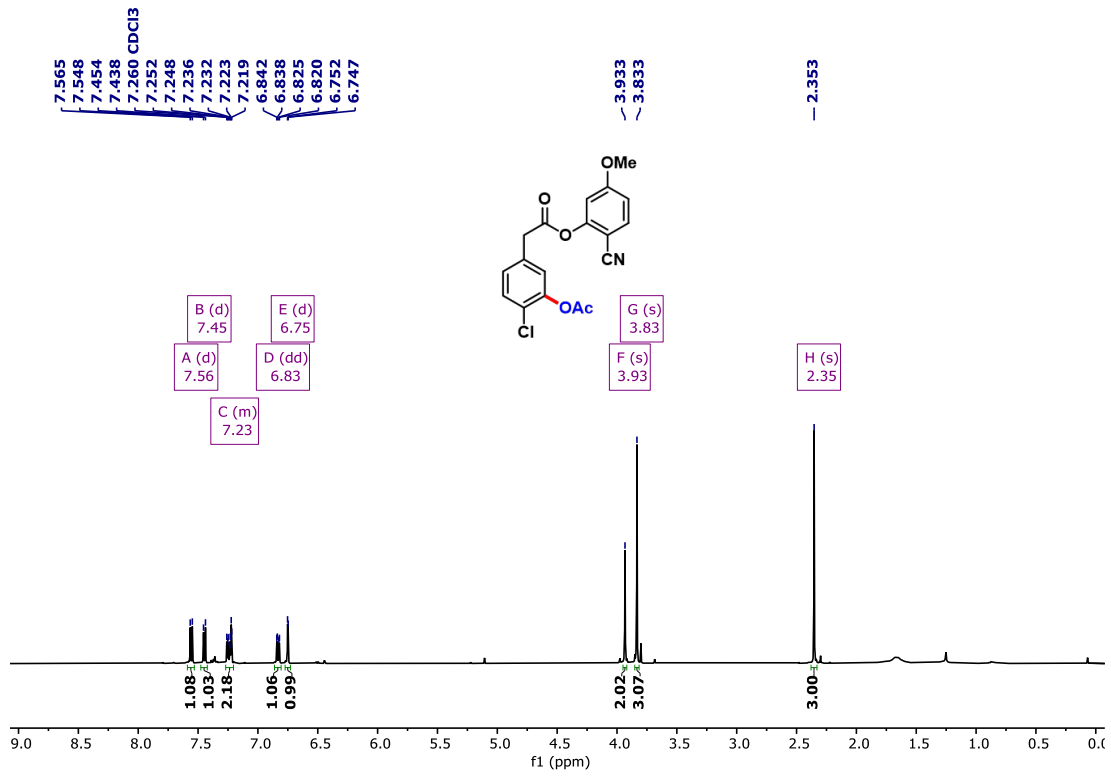
Isolated yield: 87% (27 mg, 0.087 mmol)

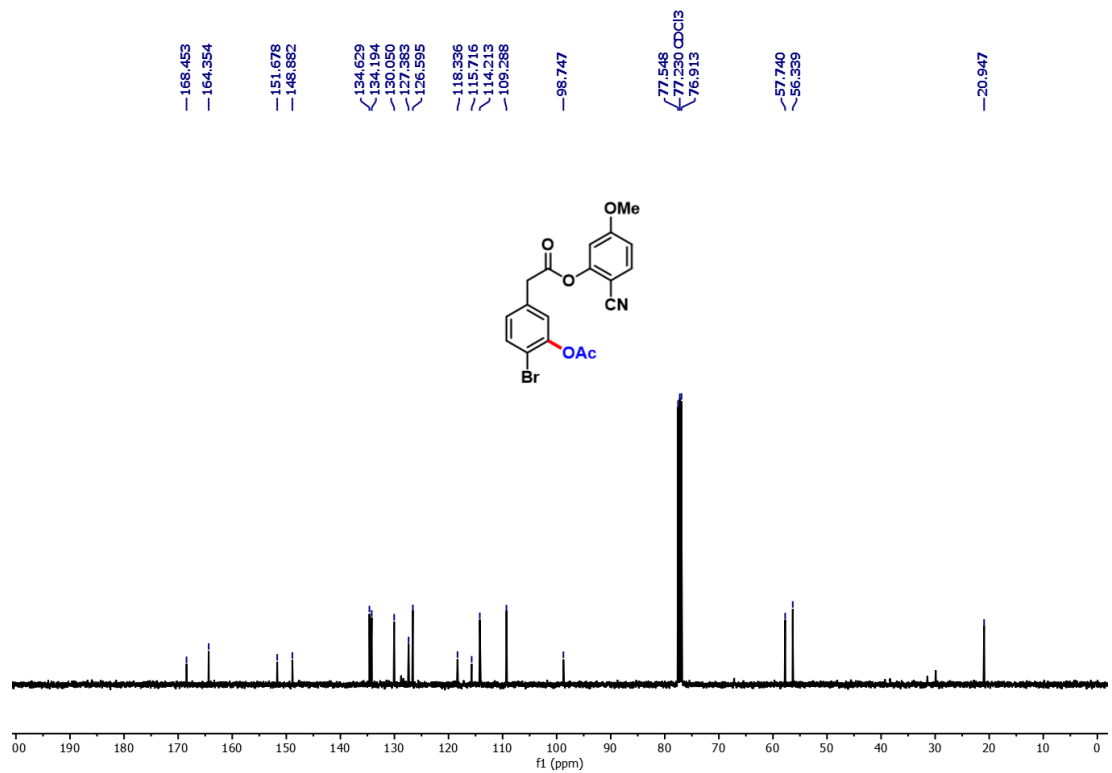
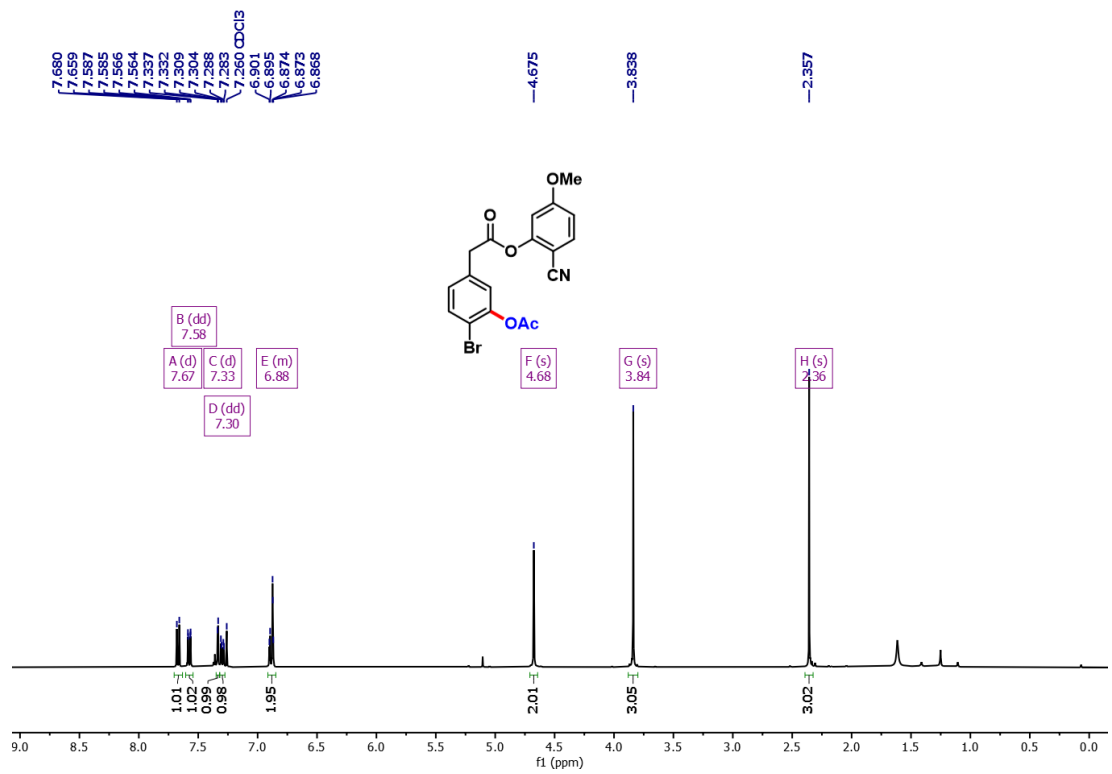
¹H NMR (400 MHz, CDCl₃) δ 7.71 (t, *J* = 1.8 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 2H), 7.50 – 7.41 (m, 5H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.19 (dd, *J* = 7.9, 4.1 Hz, 2H), 7.14 (d, *J* = 2.1 Hz, 2H), 2.42 (s, 3H), 2.38 (s, 3H); **¹³C NMR** (101 MHz, CDCl₃) δ 141.80, 138.48, 138.15, 137.80, 137.37, 134.74, 131.42, 130.54, 129.75, 129.70, 129.63, 129.23, 129.11, 127.89, 127.24, 126.93, 126.68, 126.42, 126.36, 125.69, 125.36, 125.20, 119.85, 118.97, 21.48, 21.34; **HRMS** (ESI-QTOF): [M+H]⁺ calculated for C₂₂H₂₁ m/z 285.1643 and found m/z 285.1640.

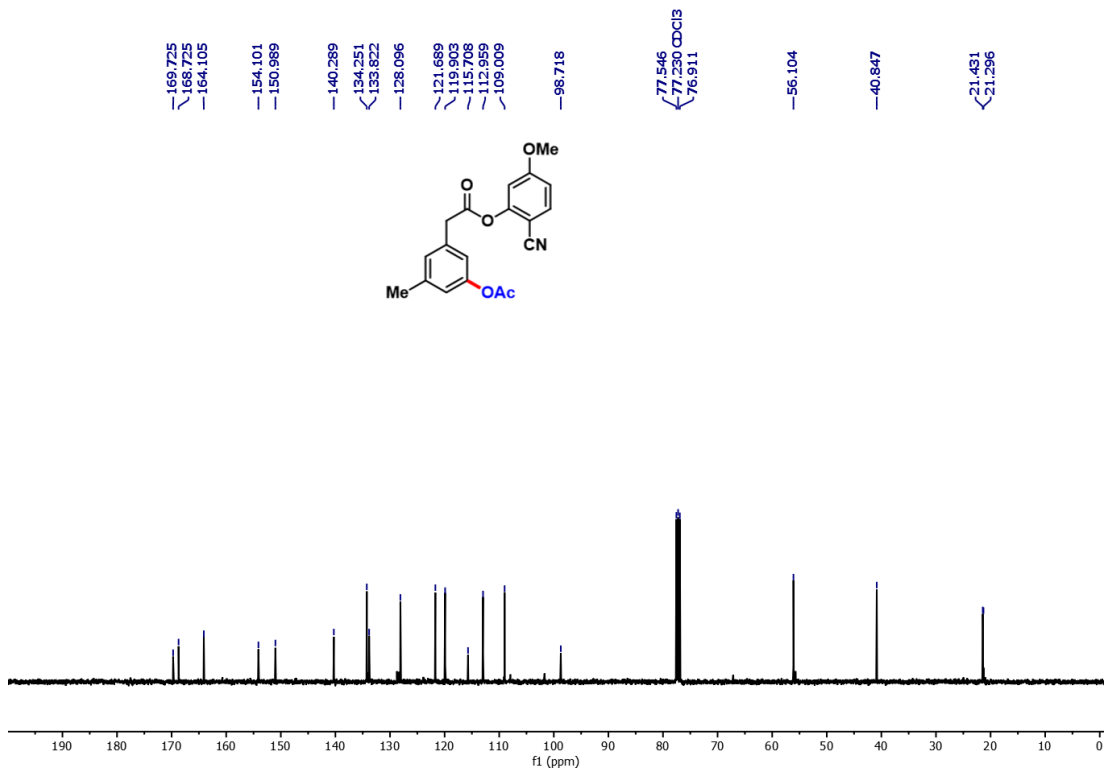
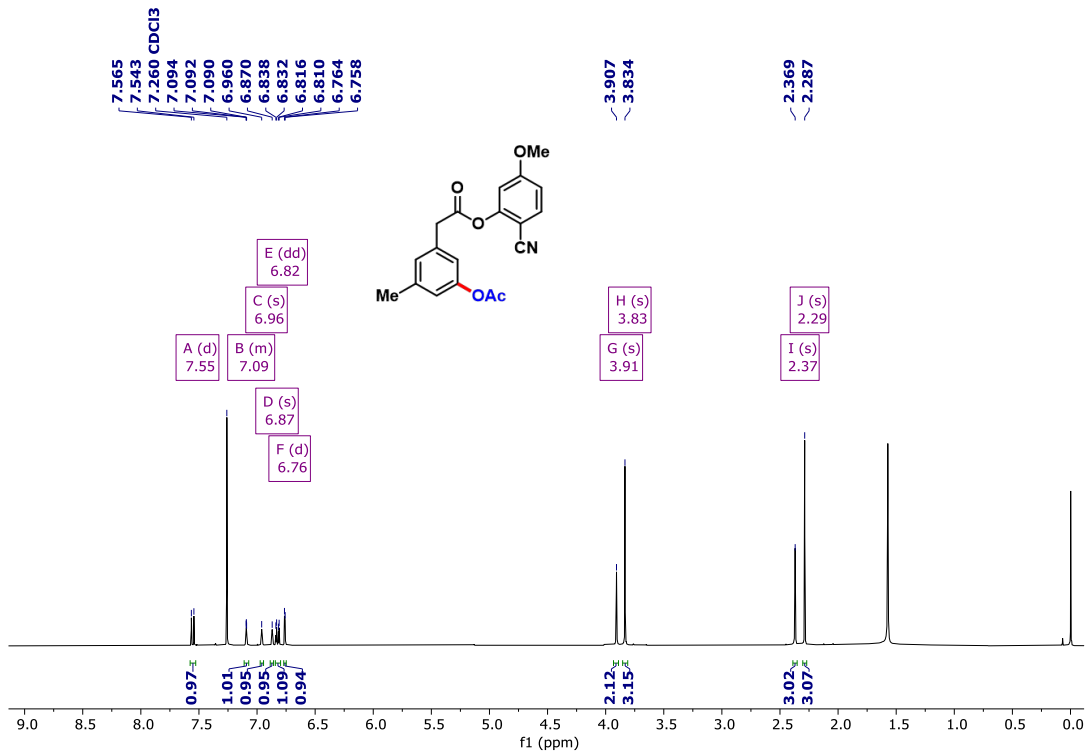


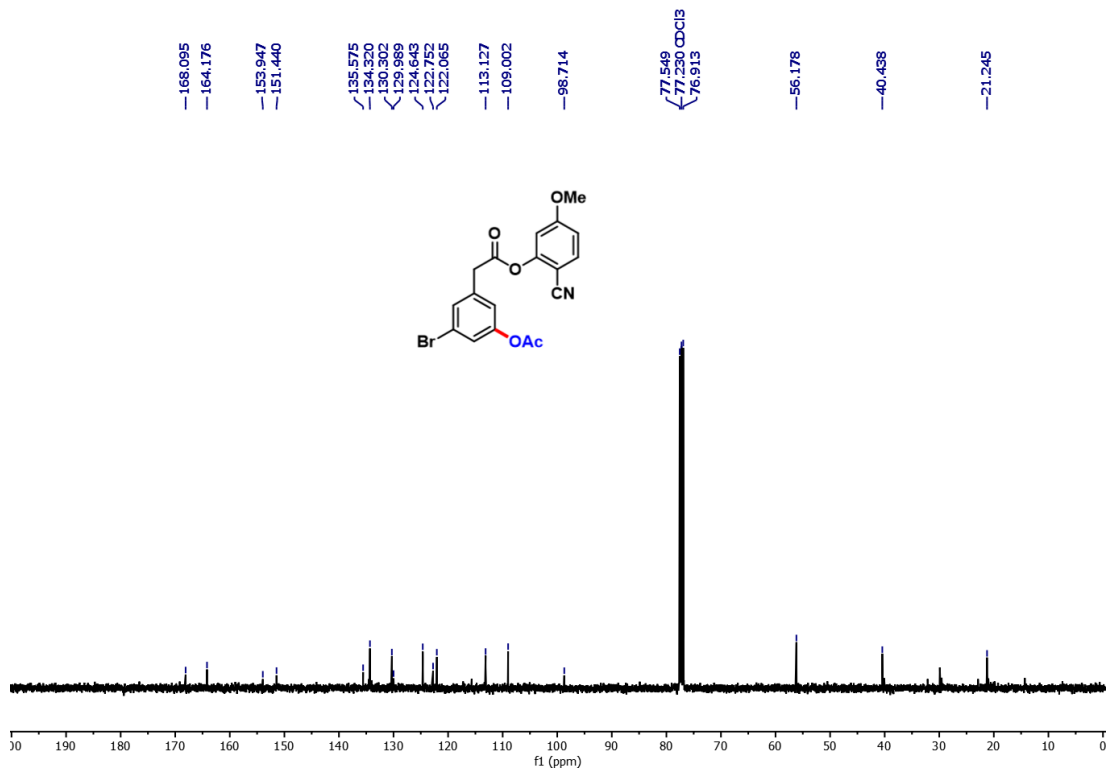
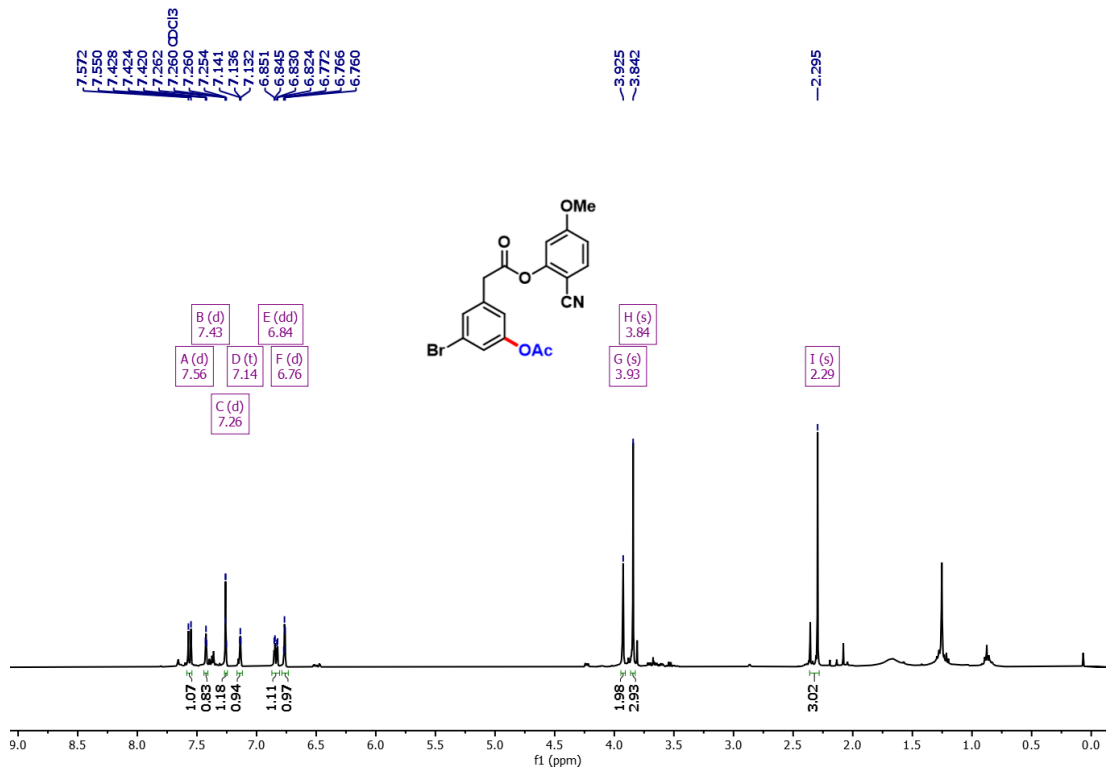


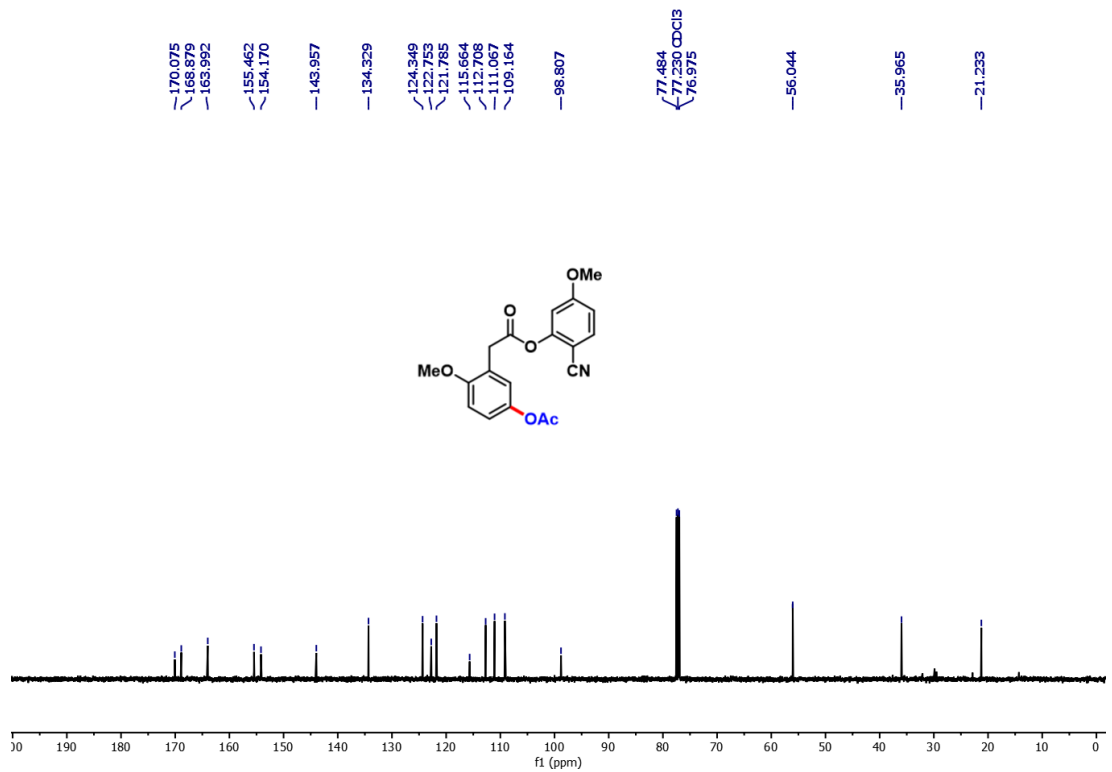
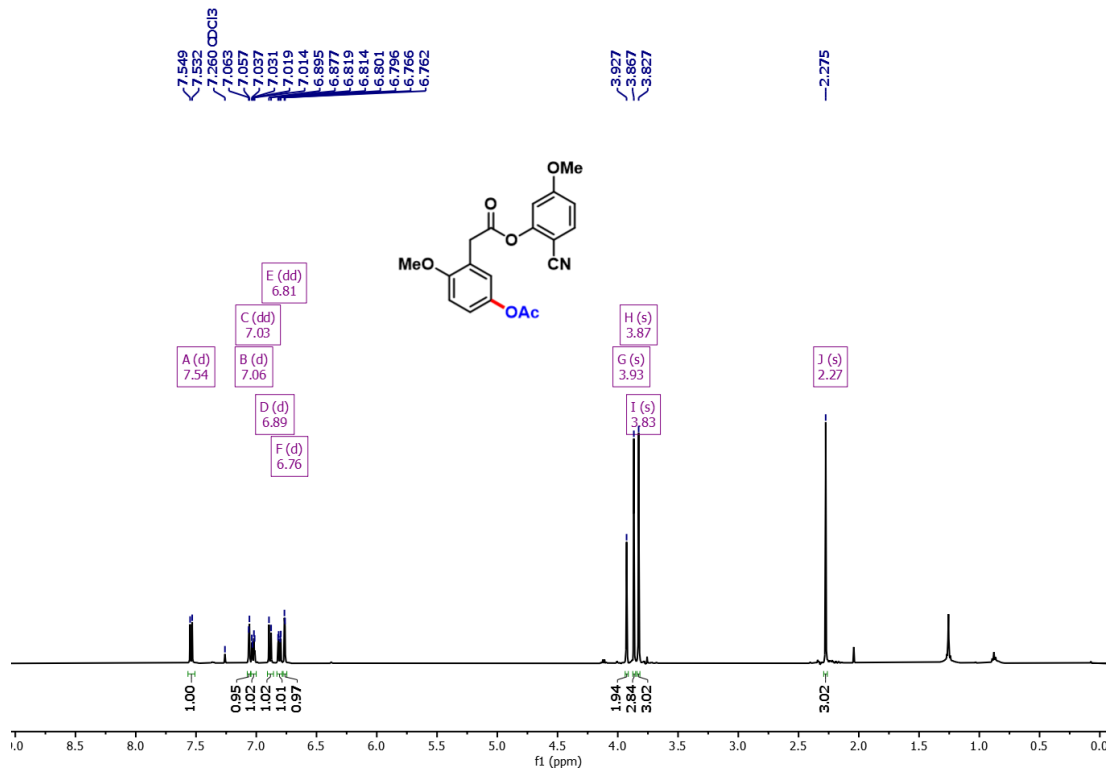


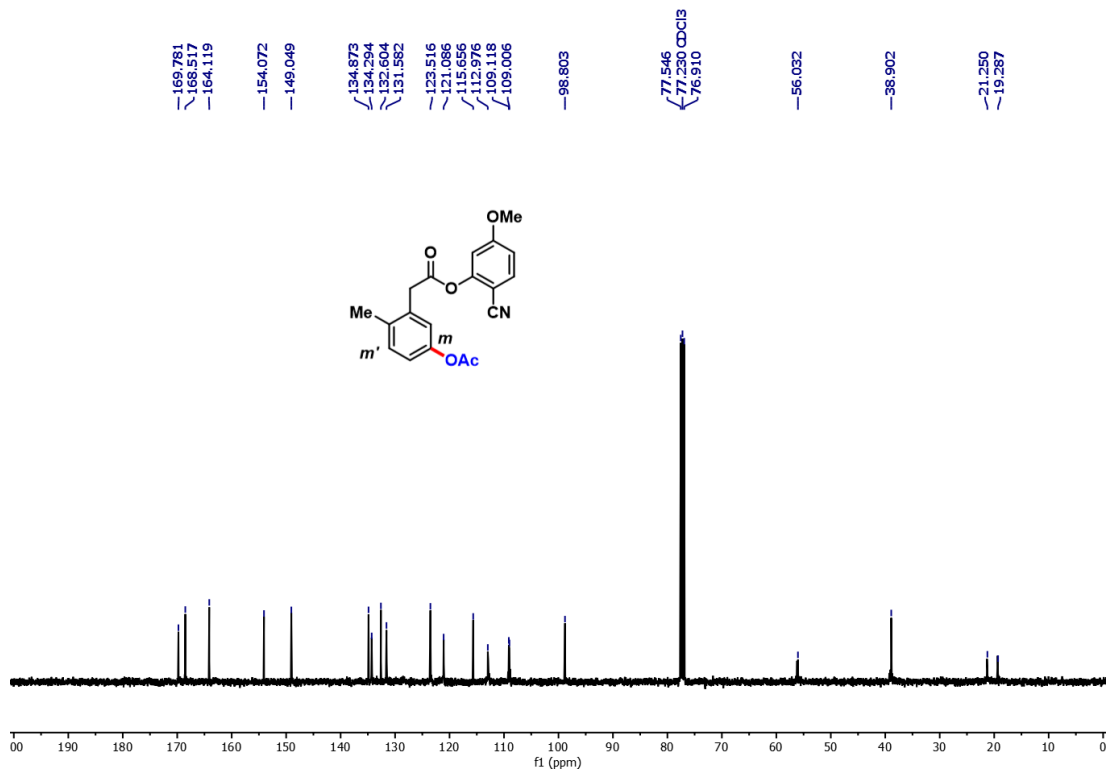
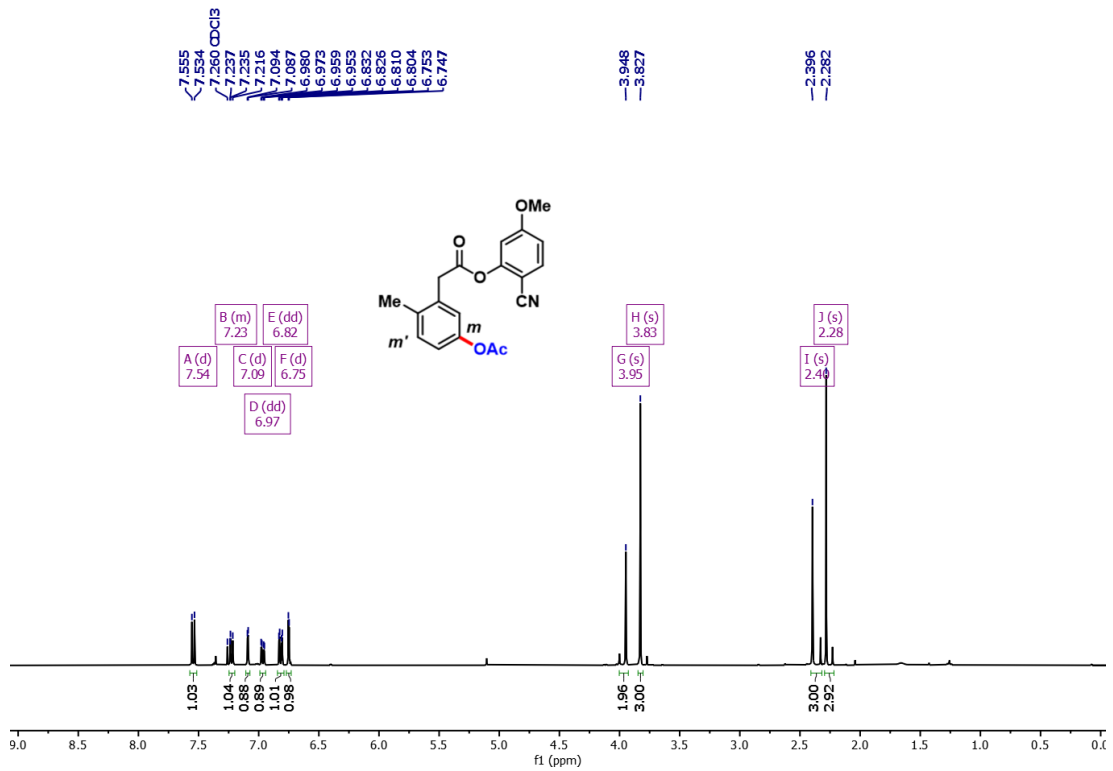


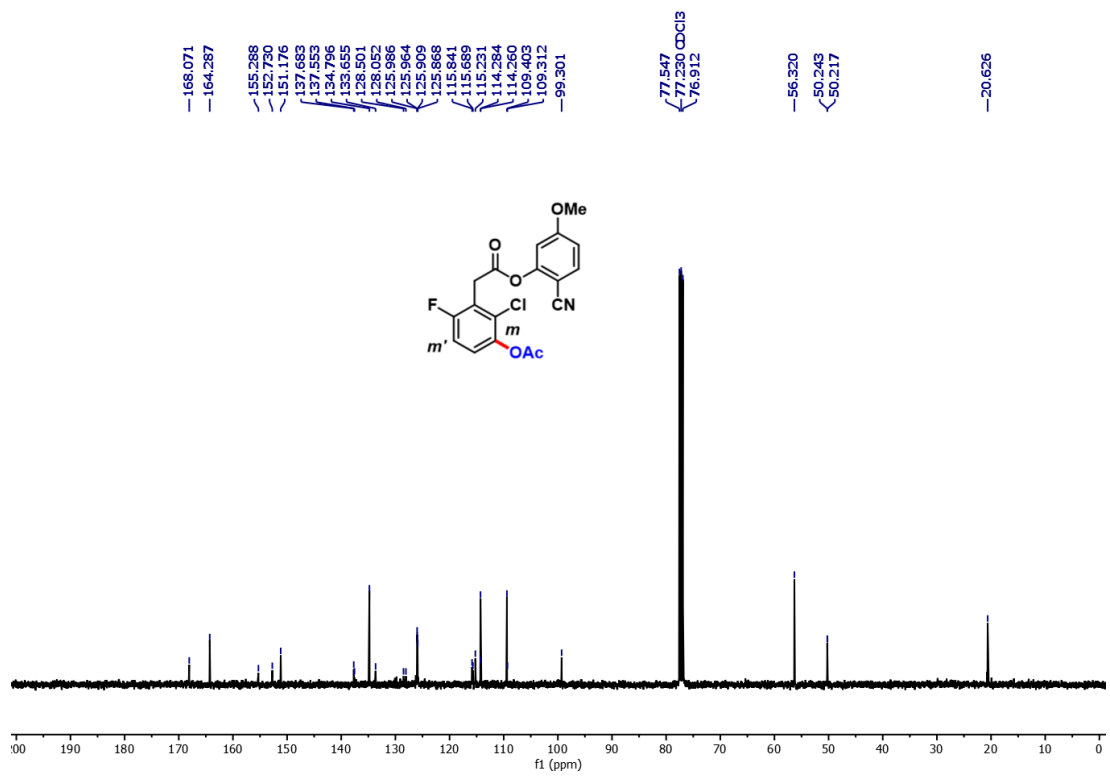
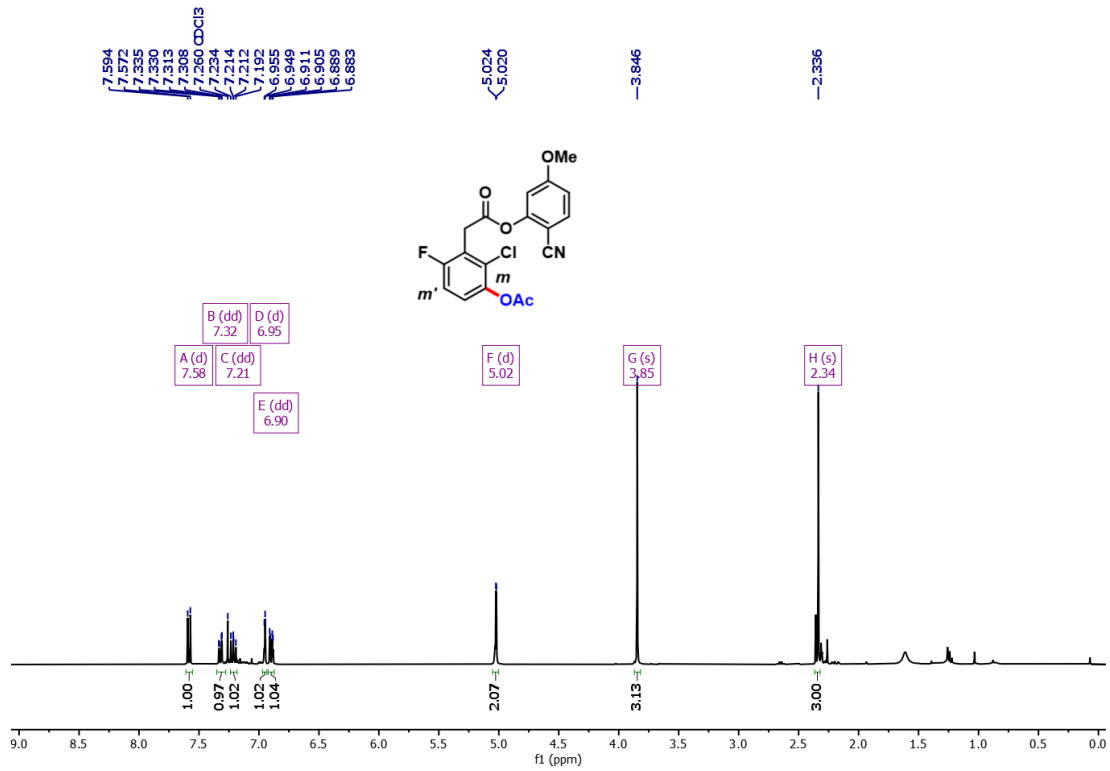


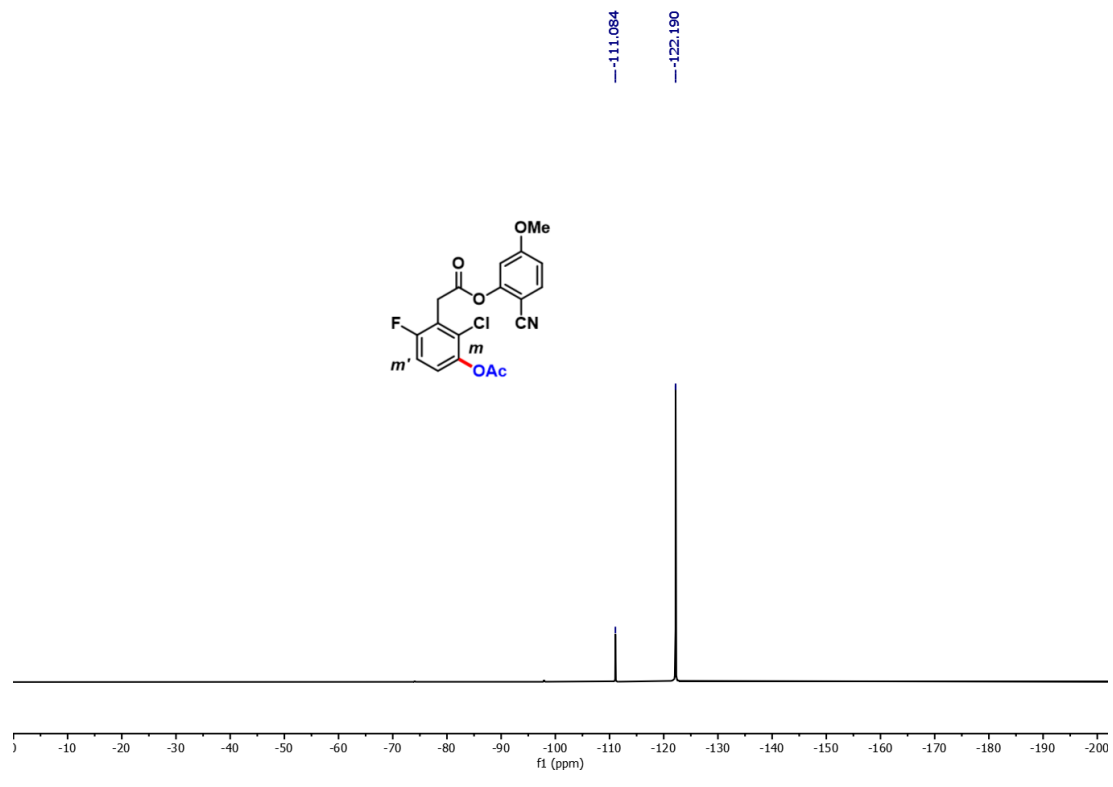


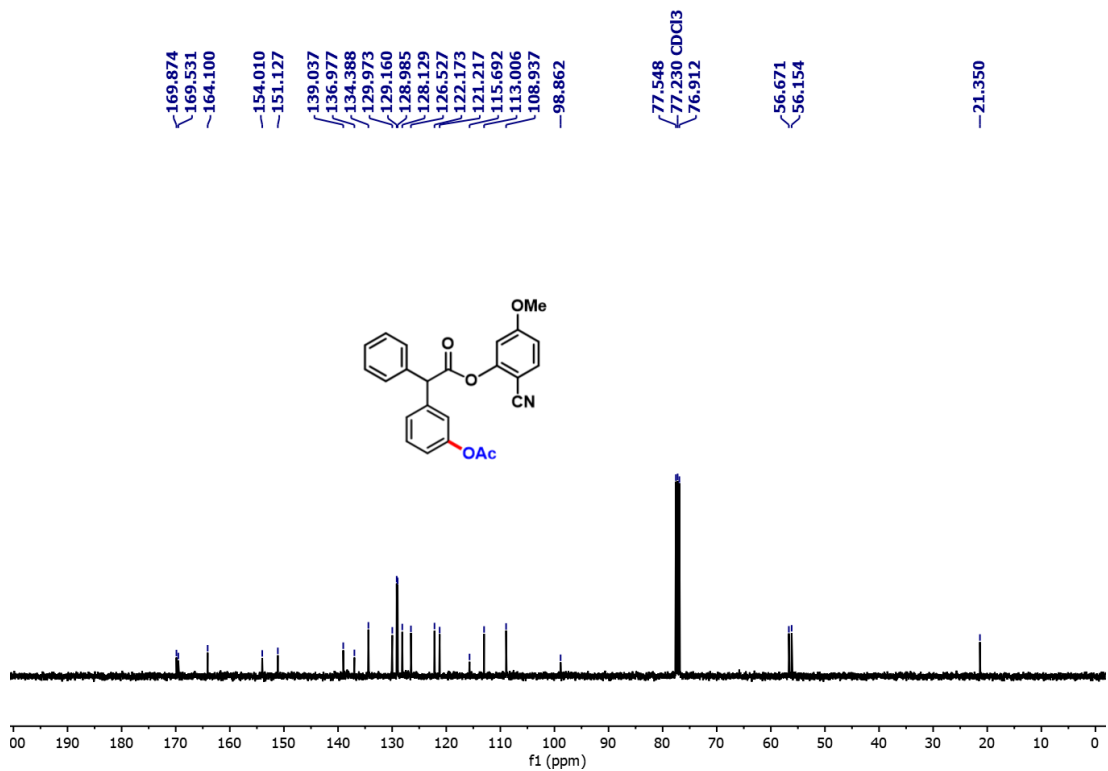
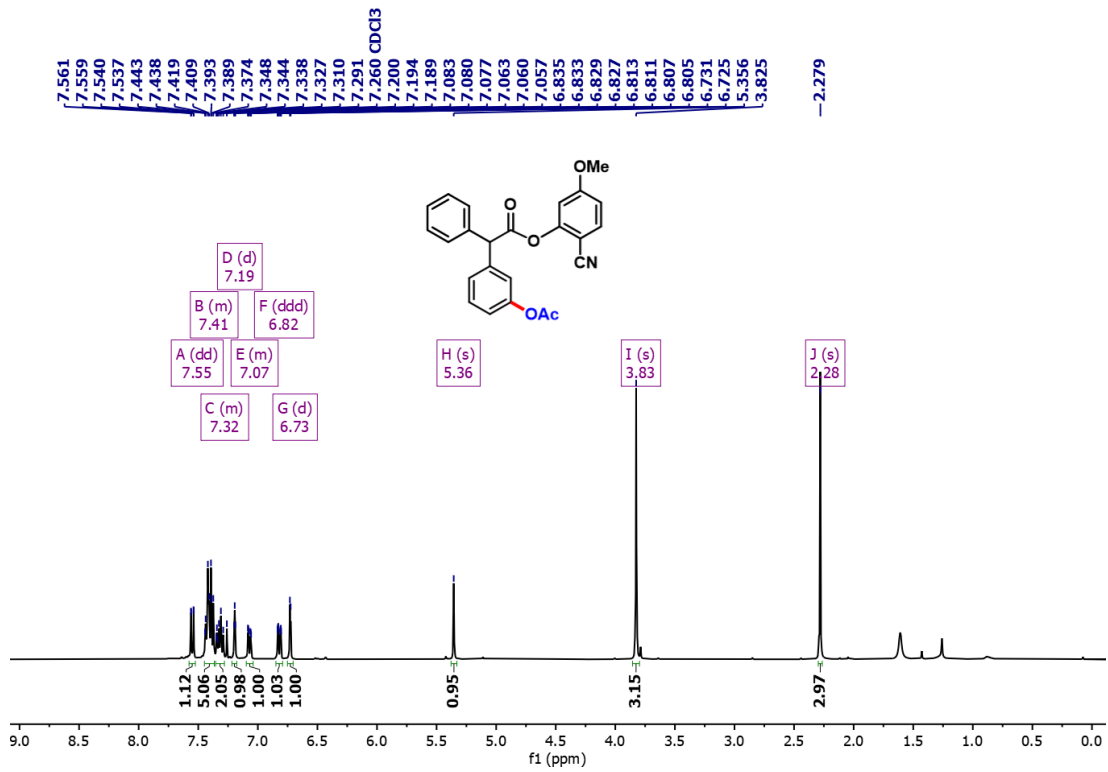


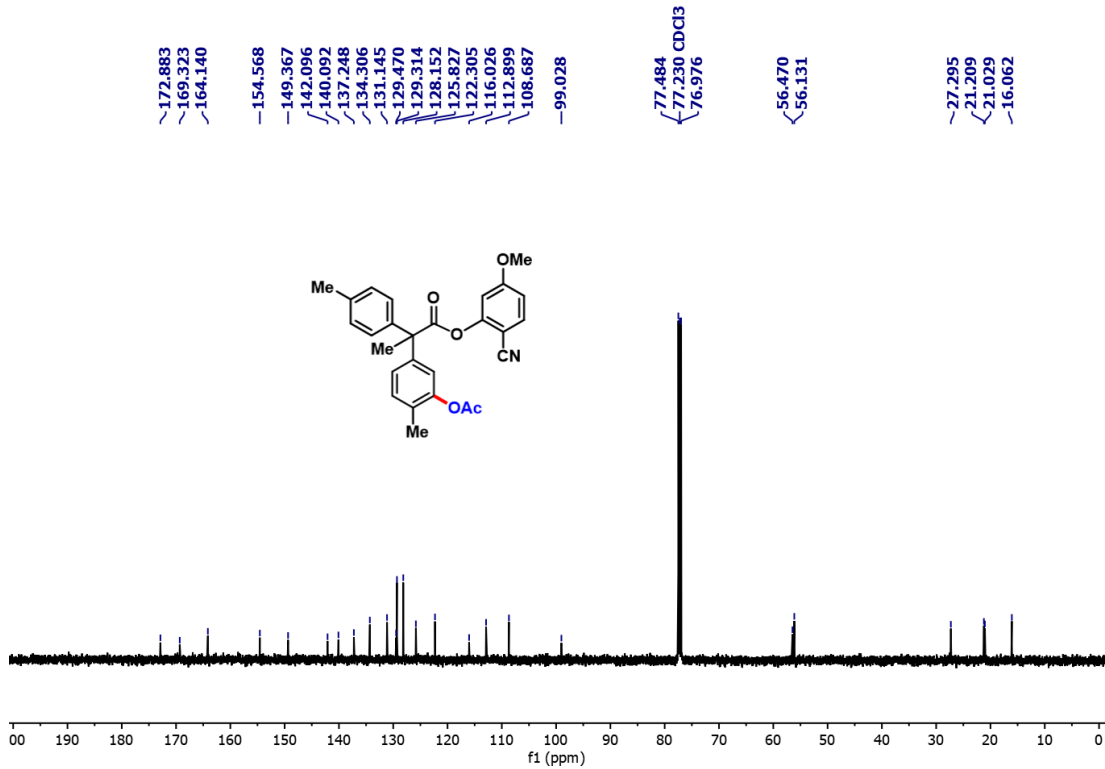
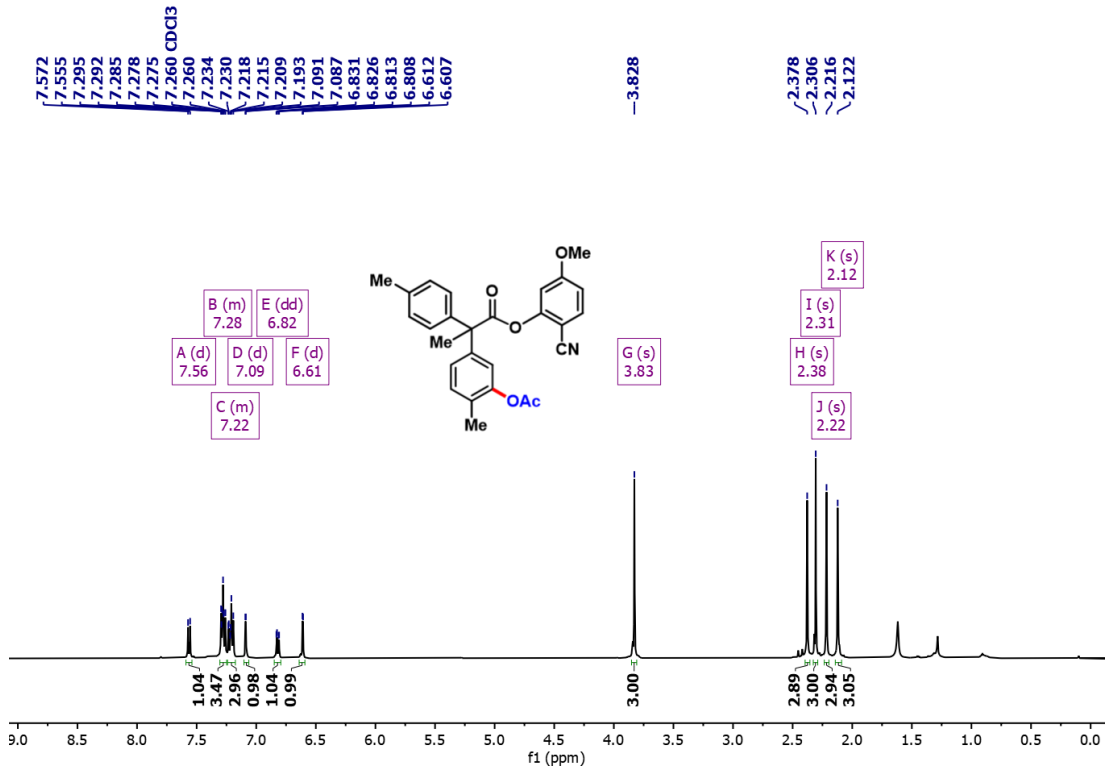


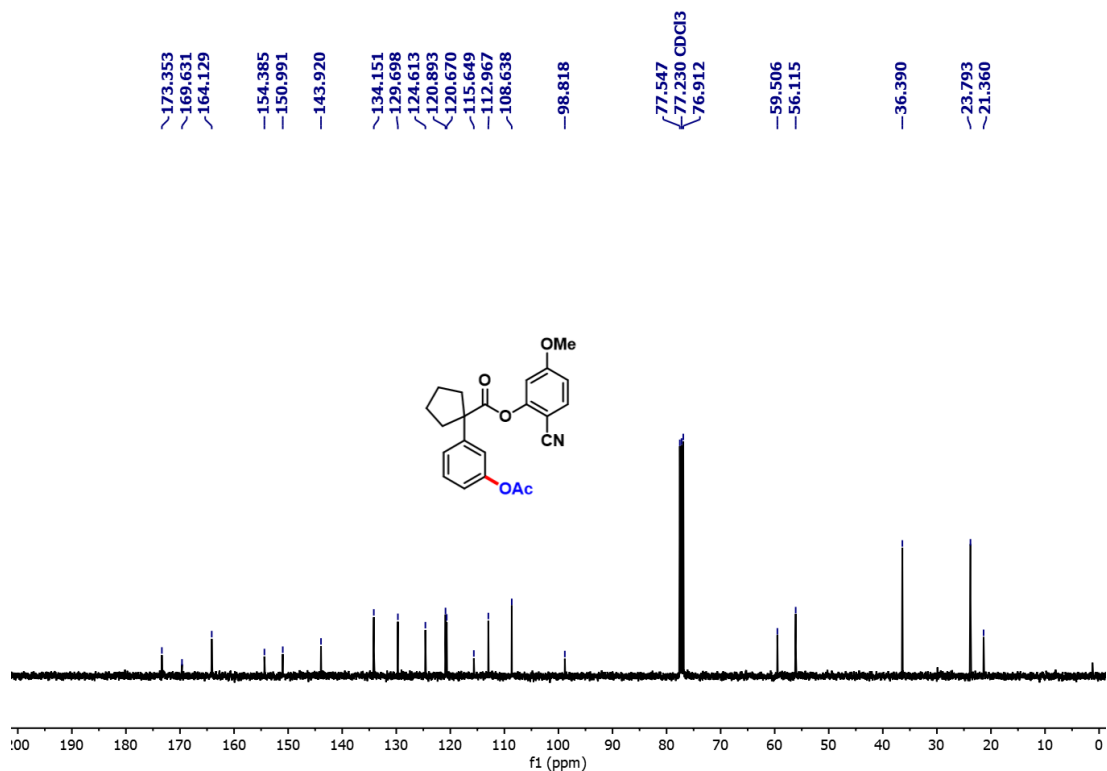
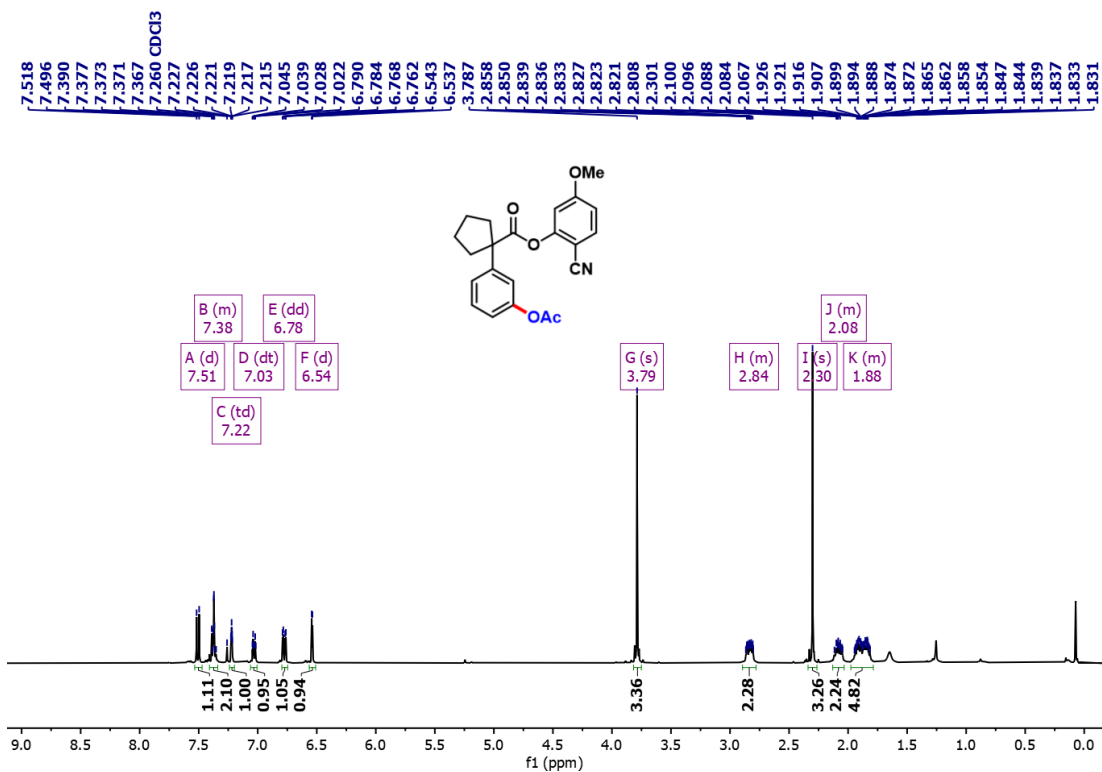


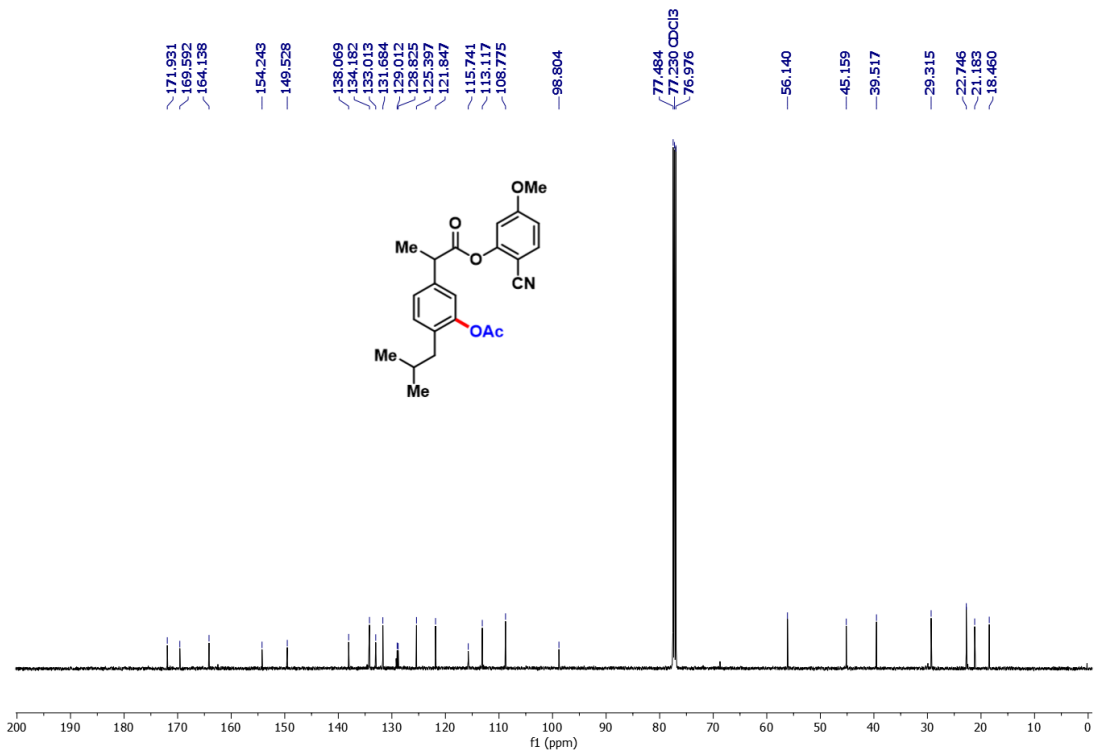
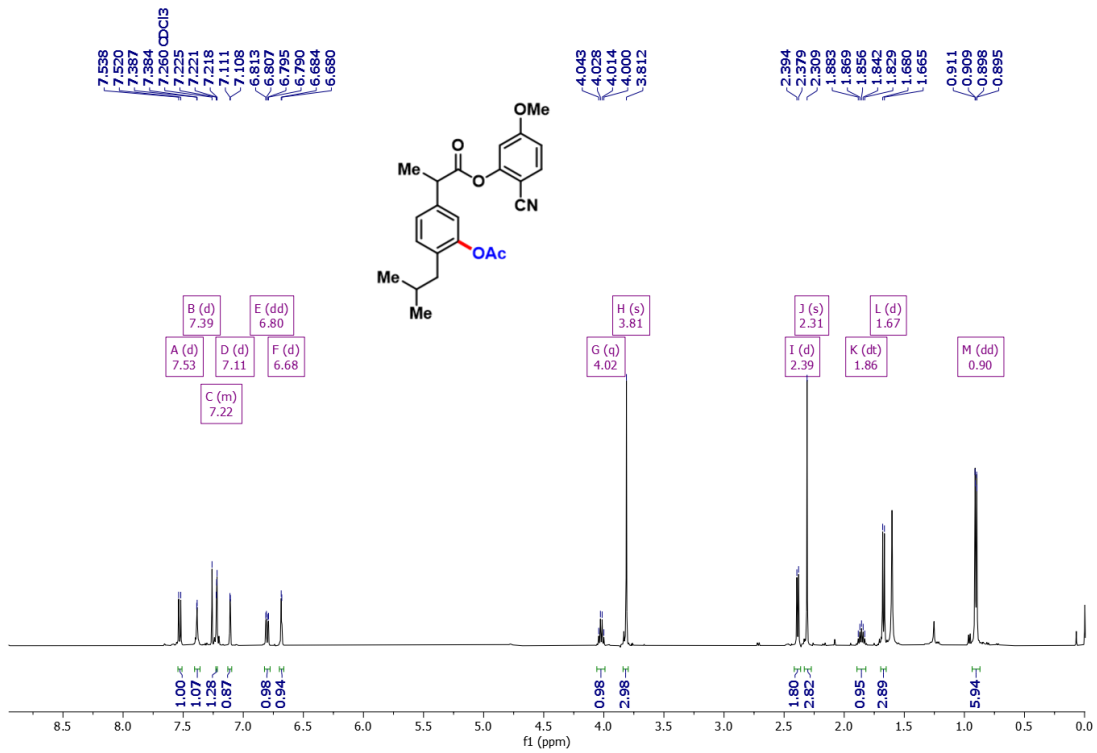


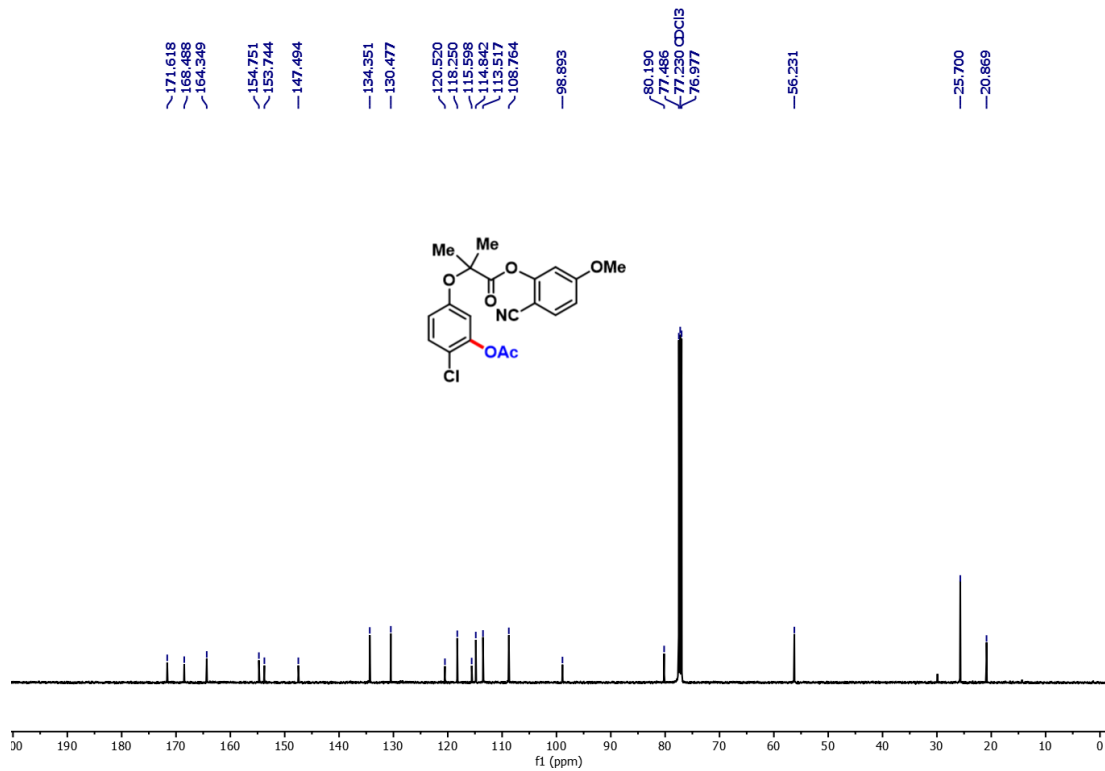
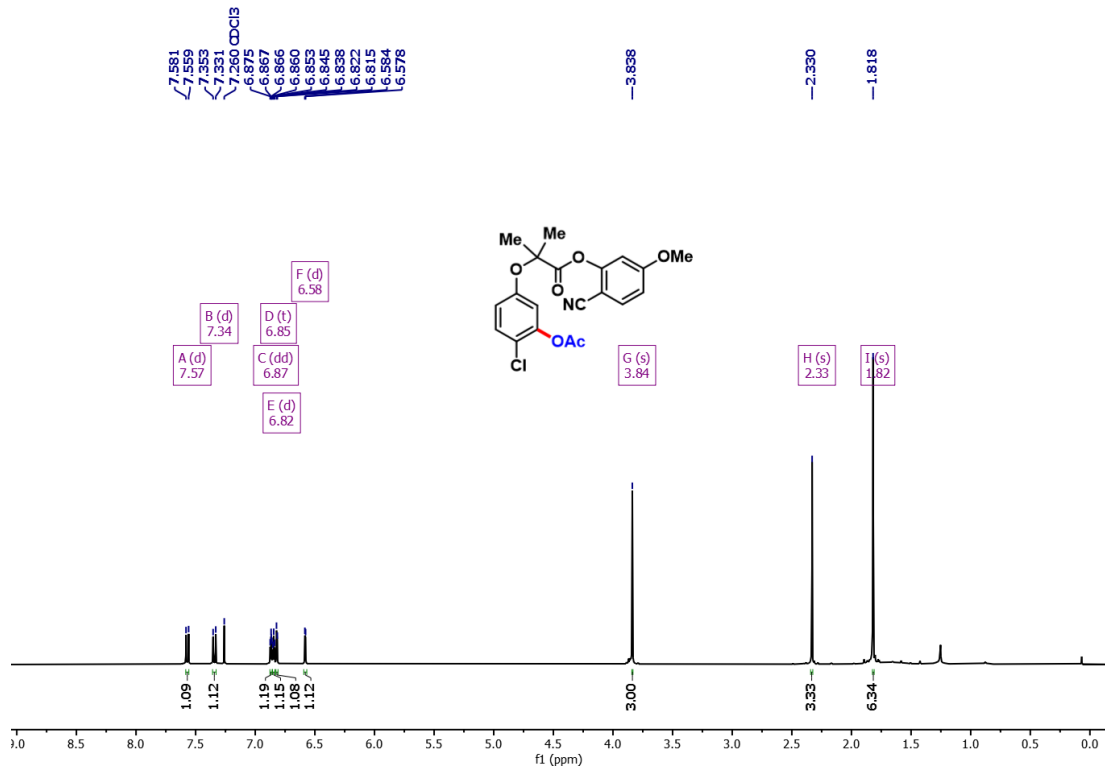


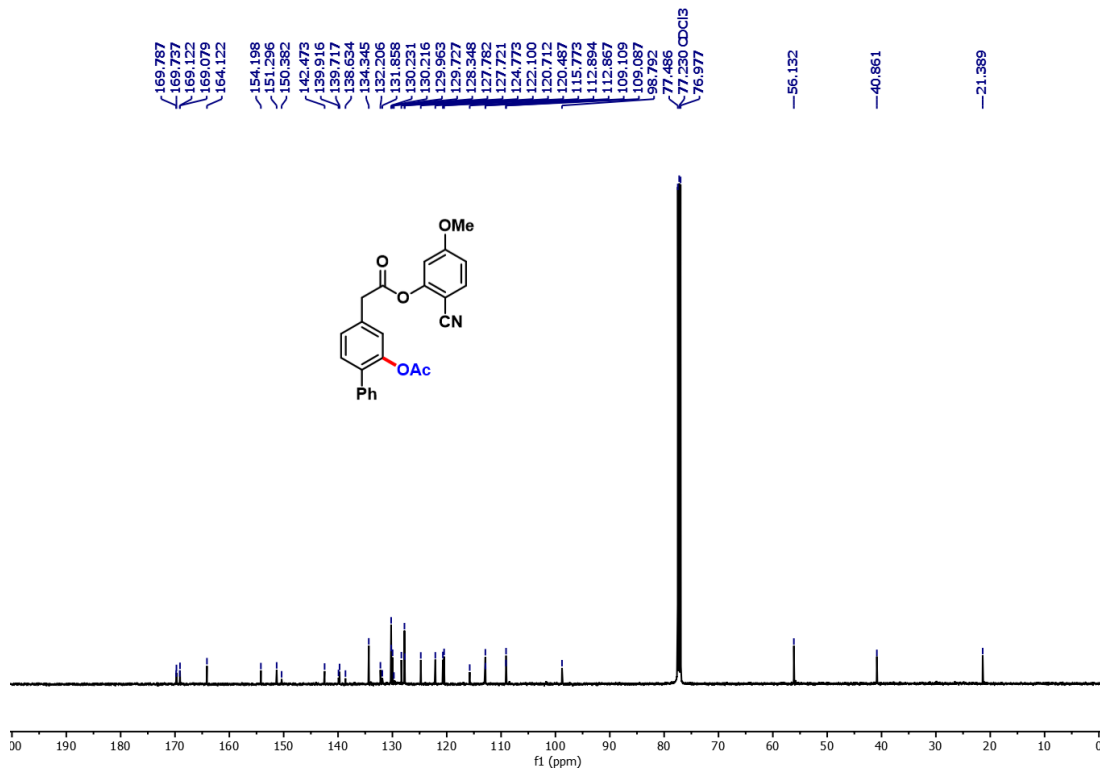
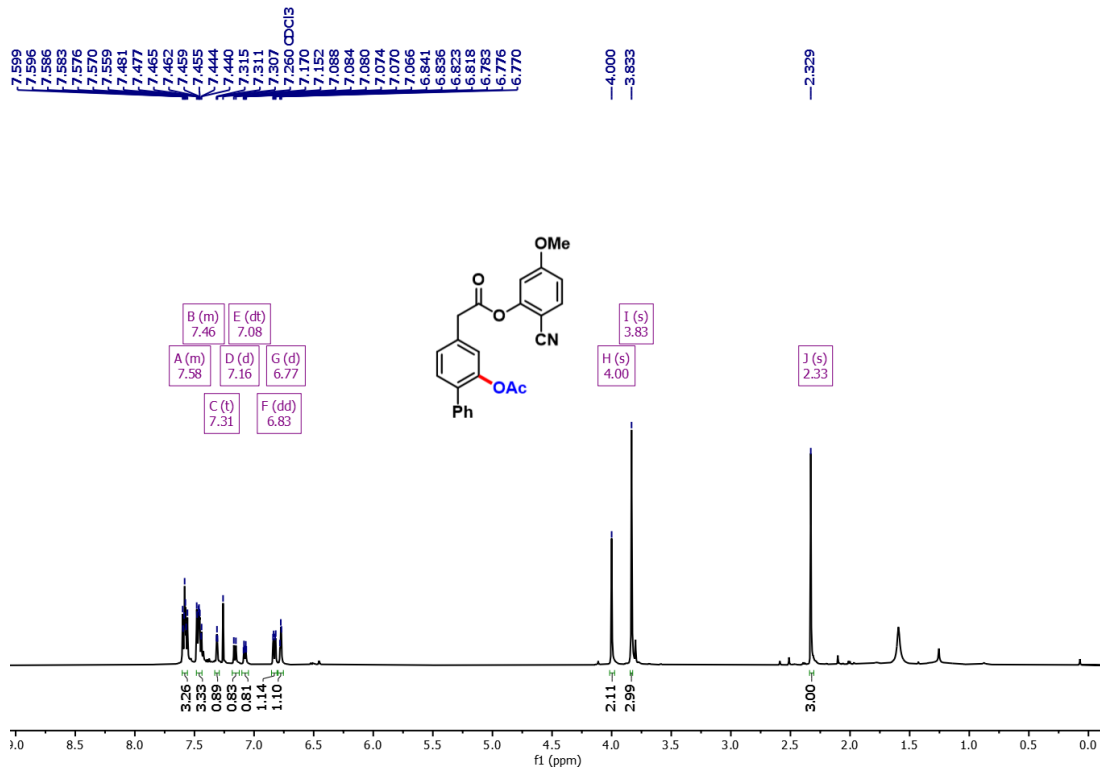


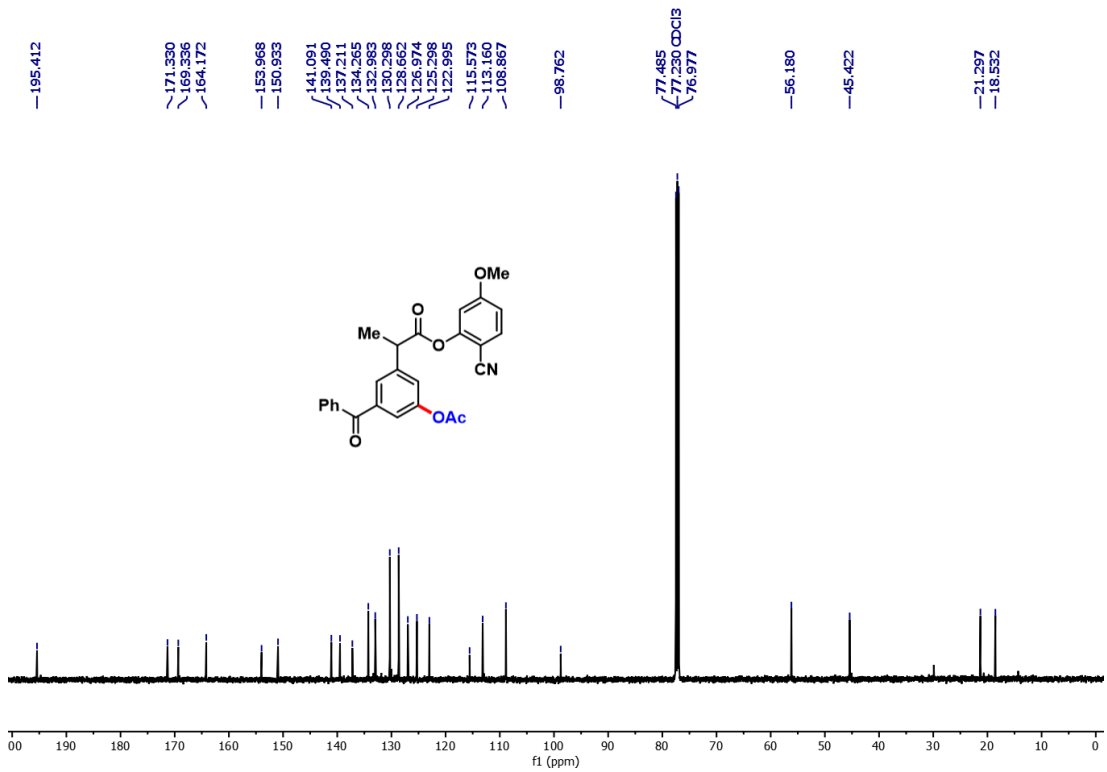
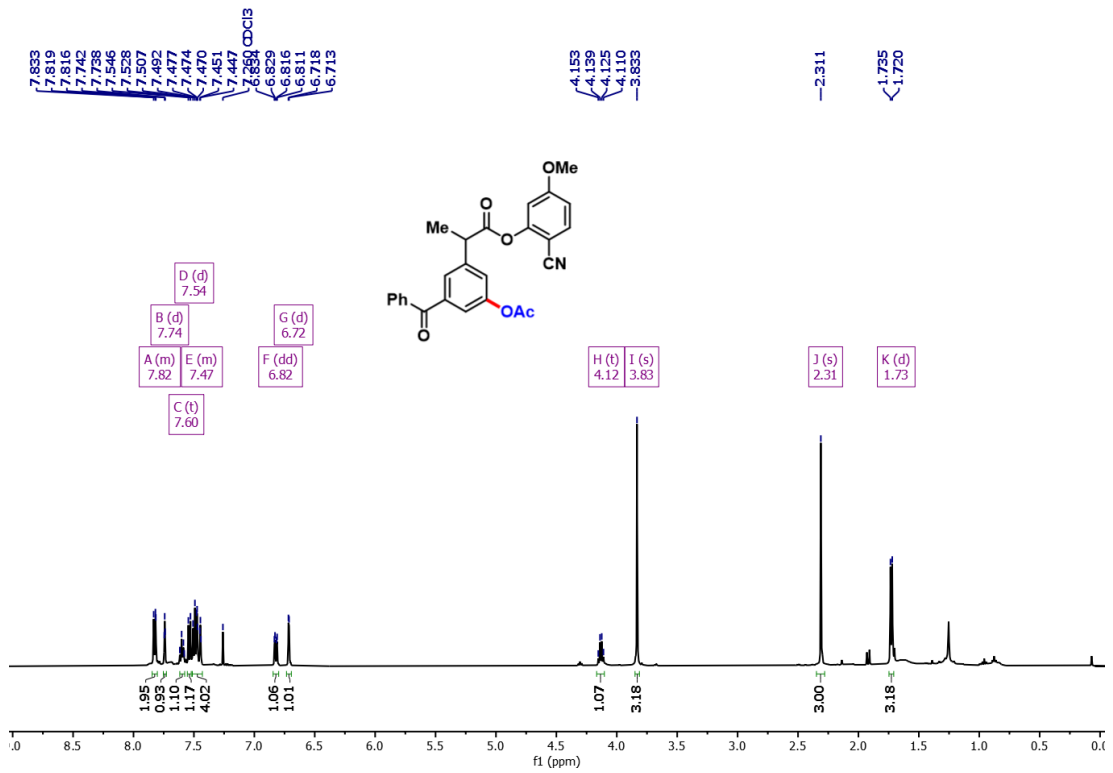


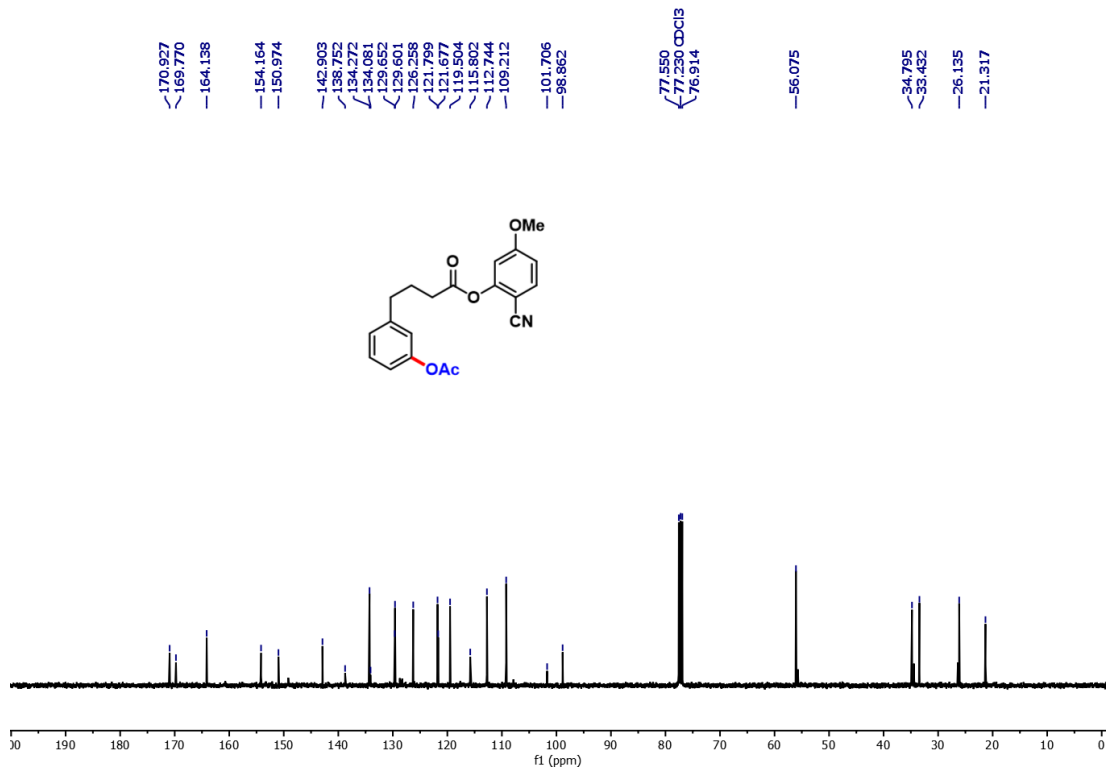
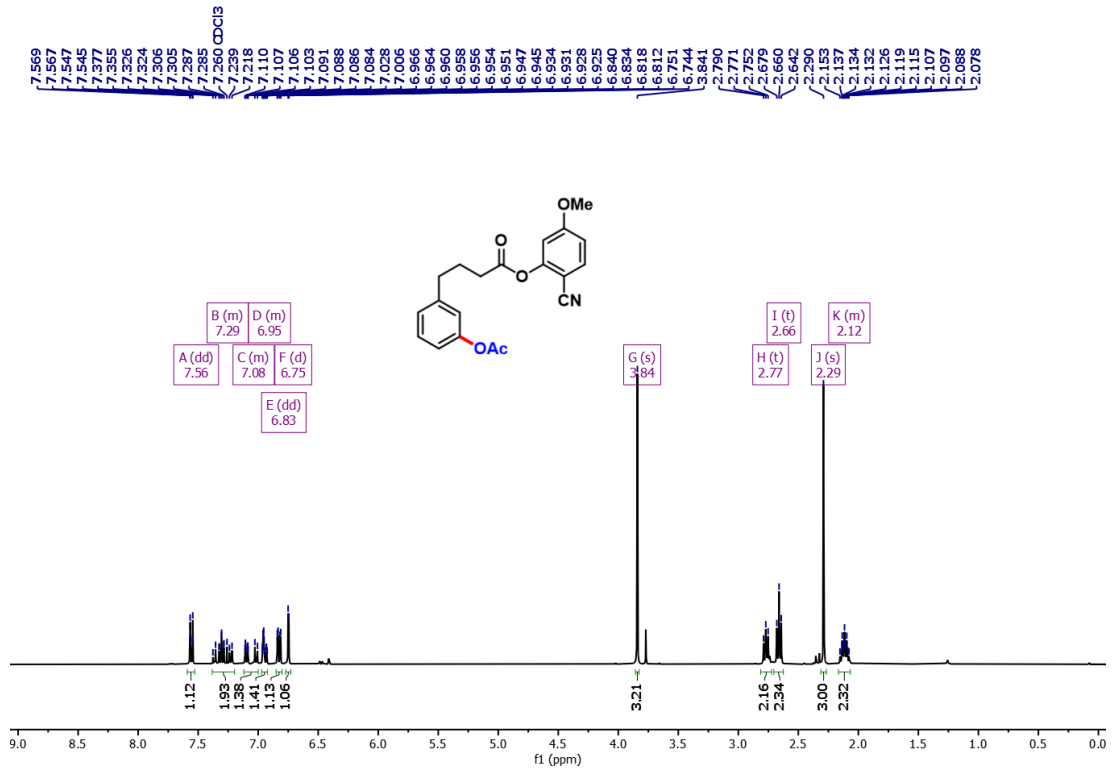


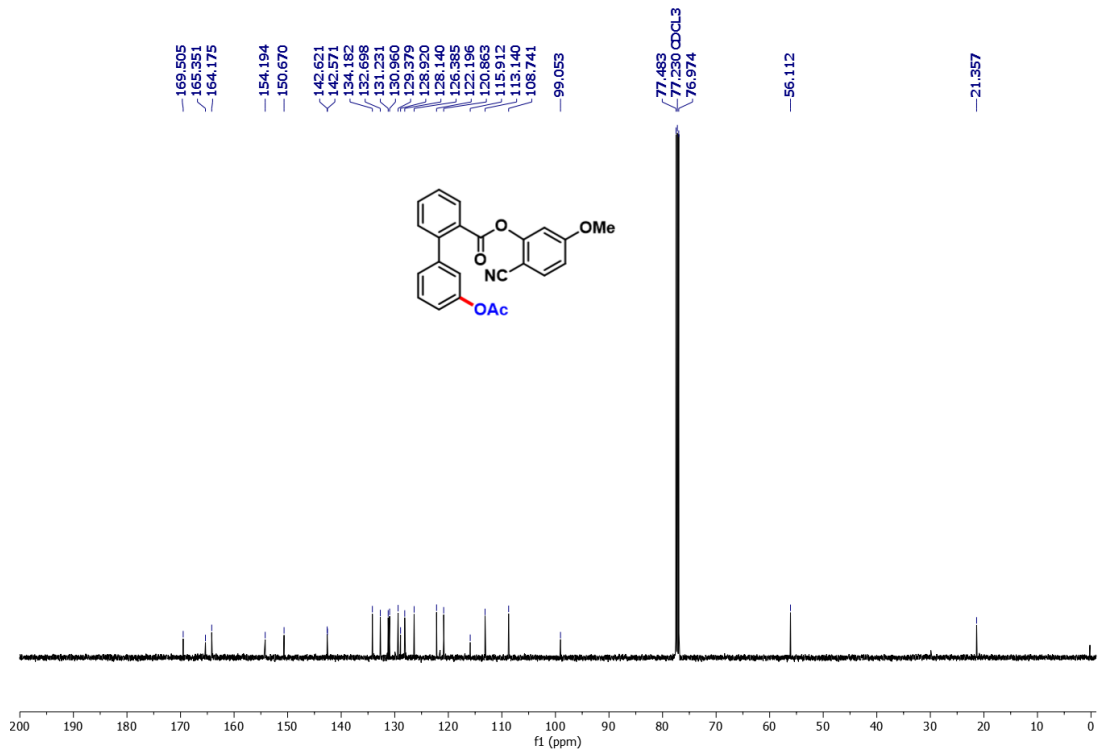
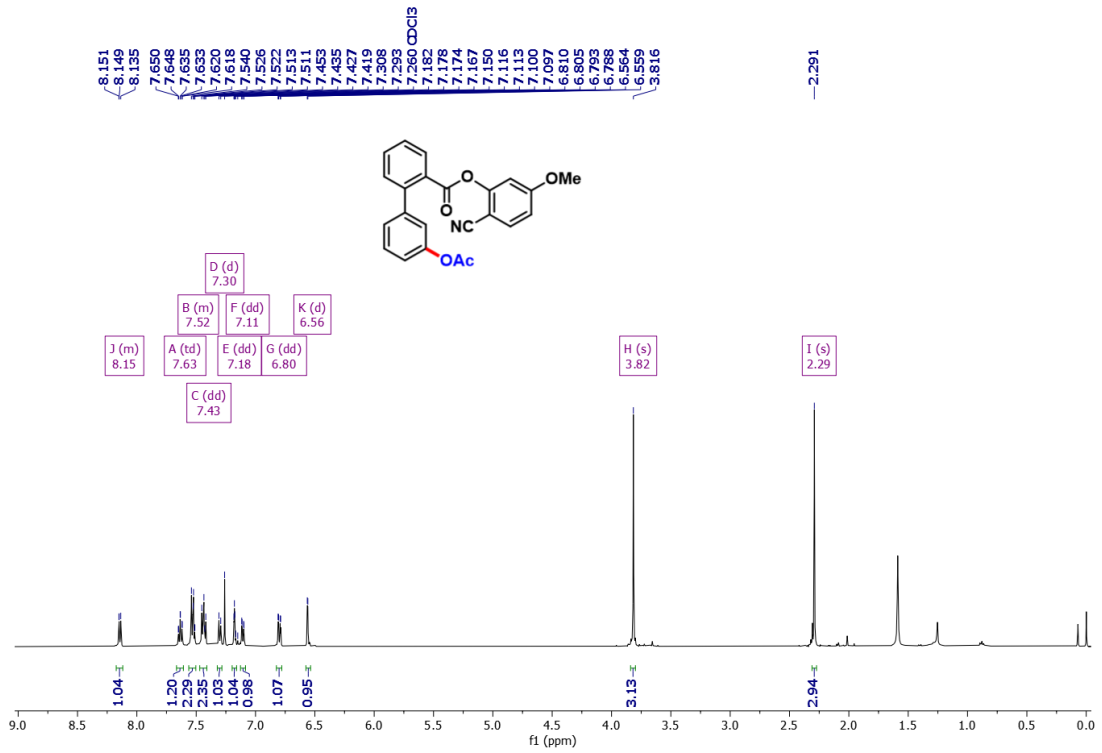


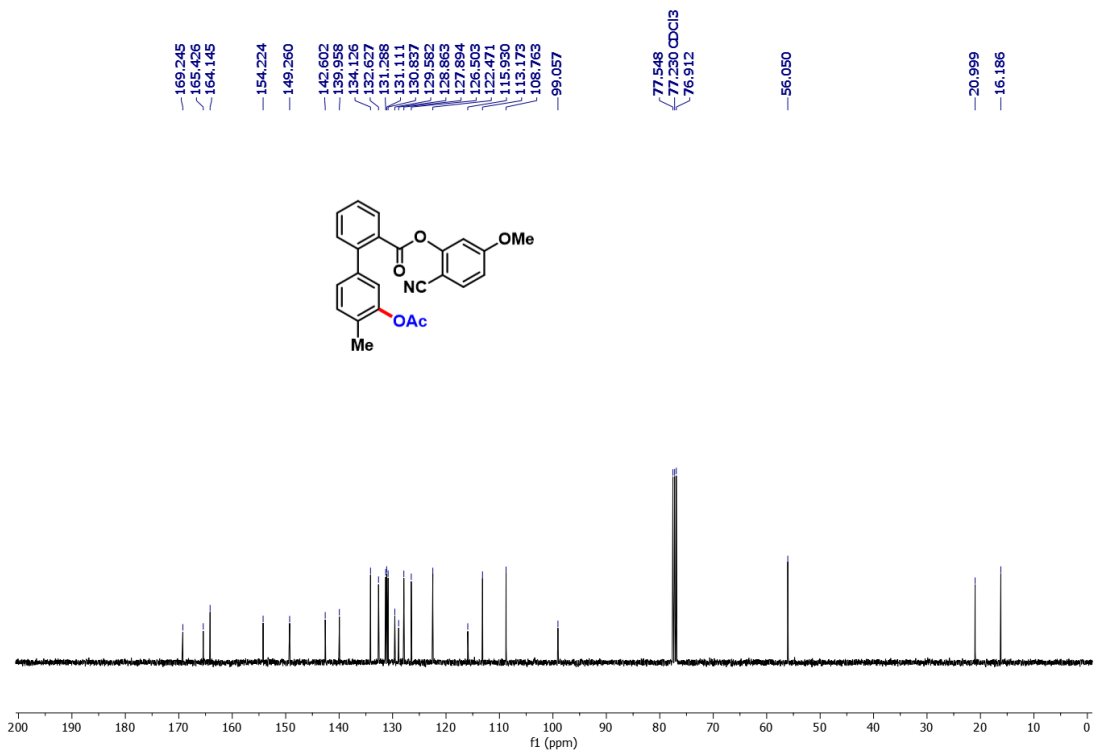
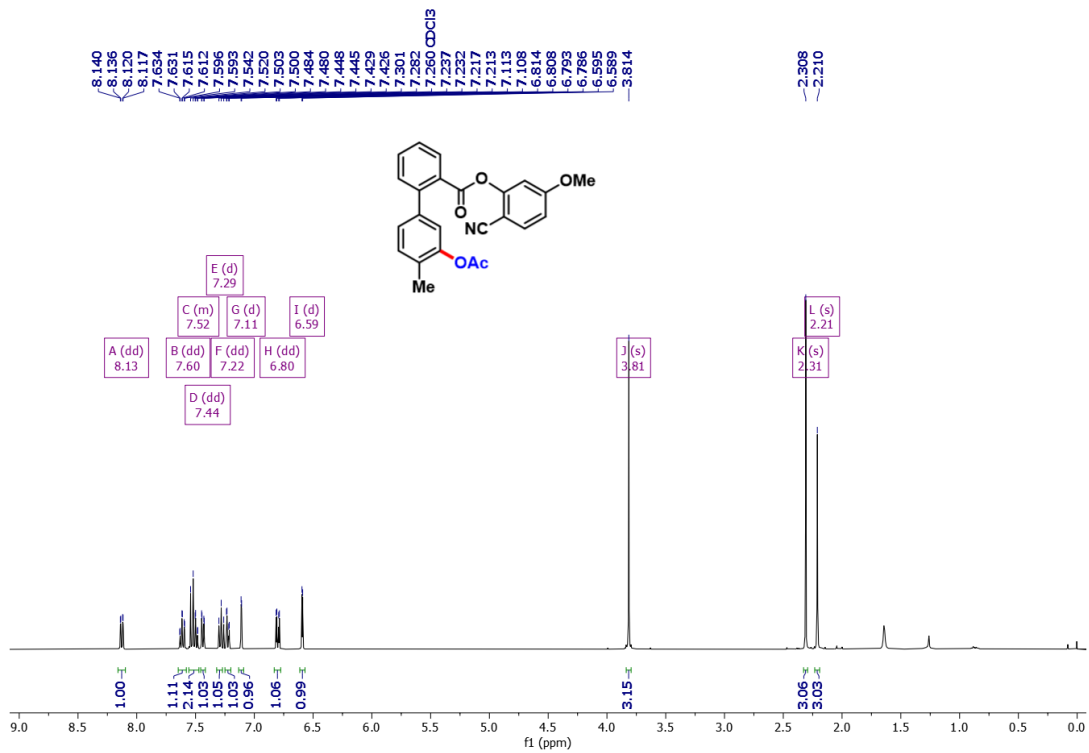


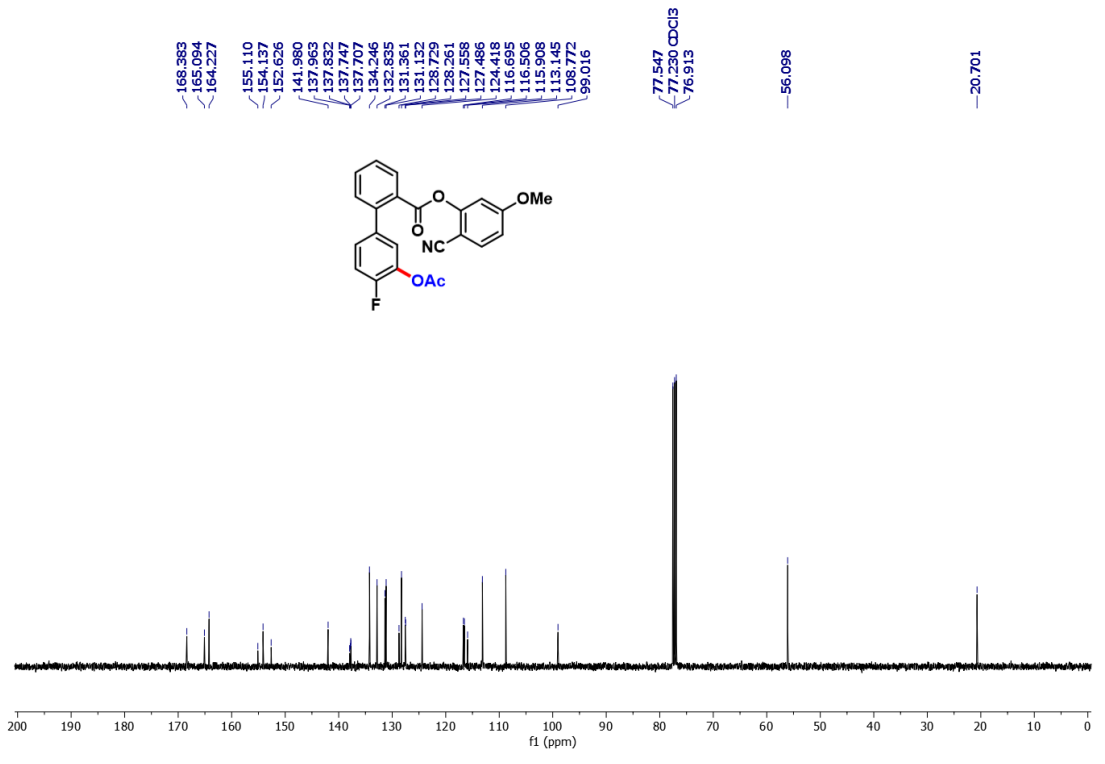
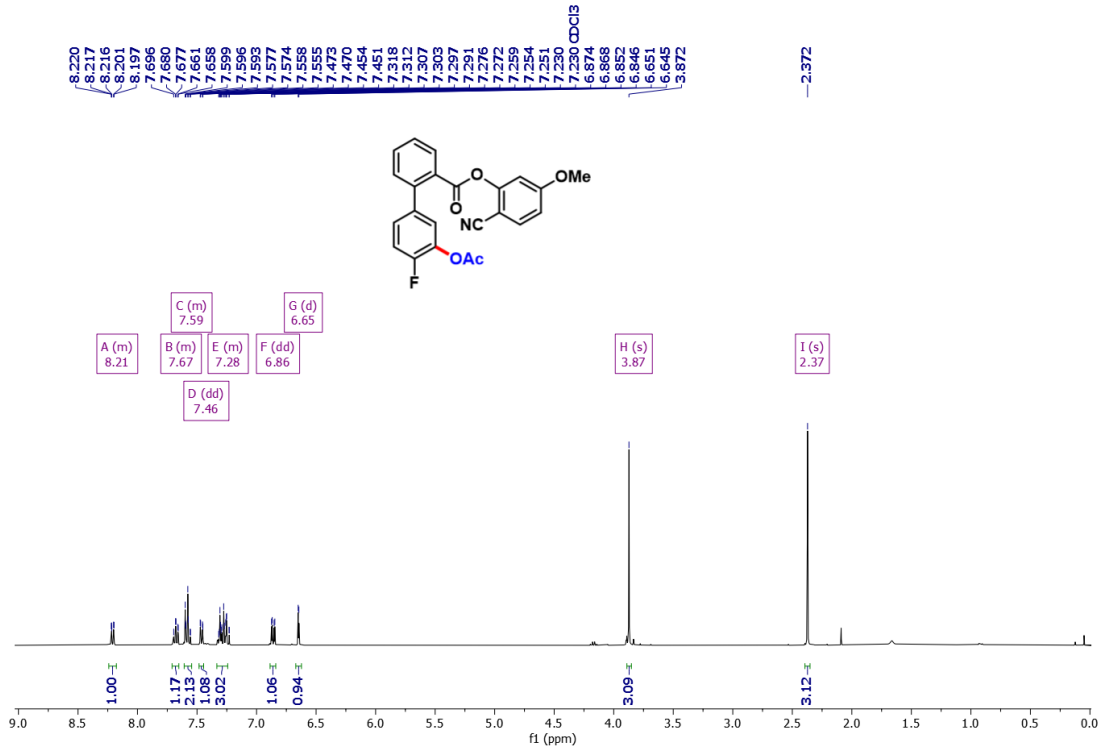


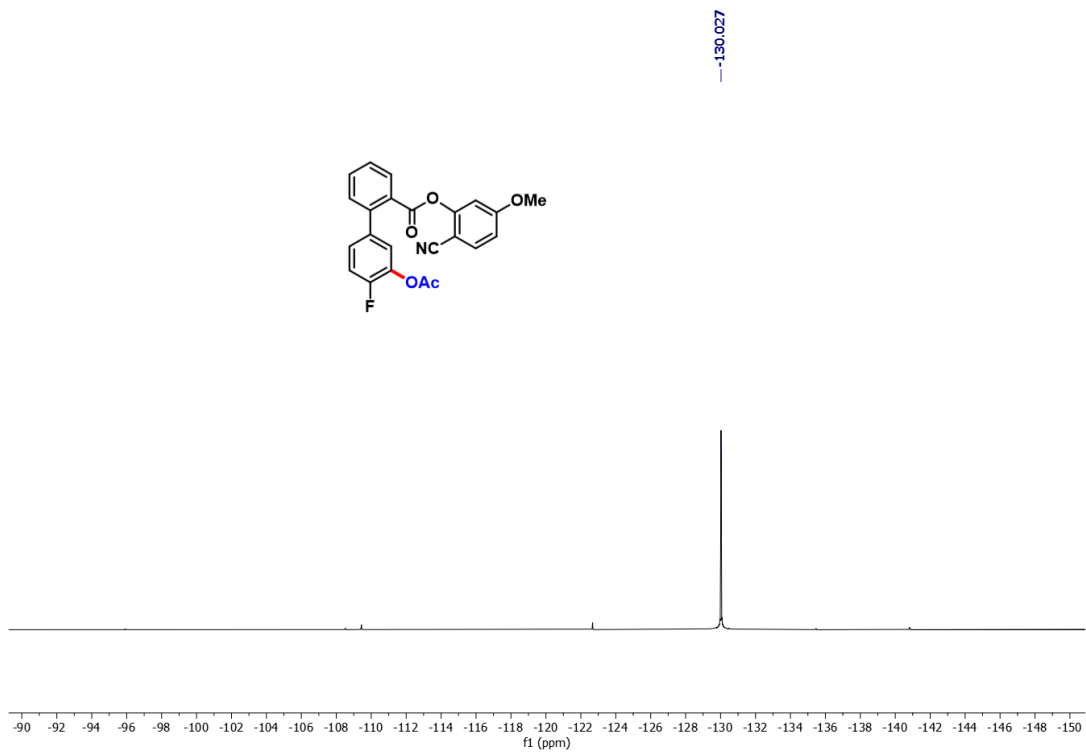


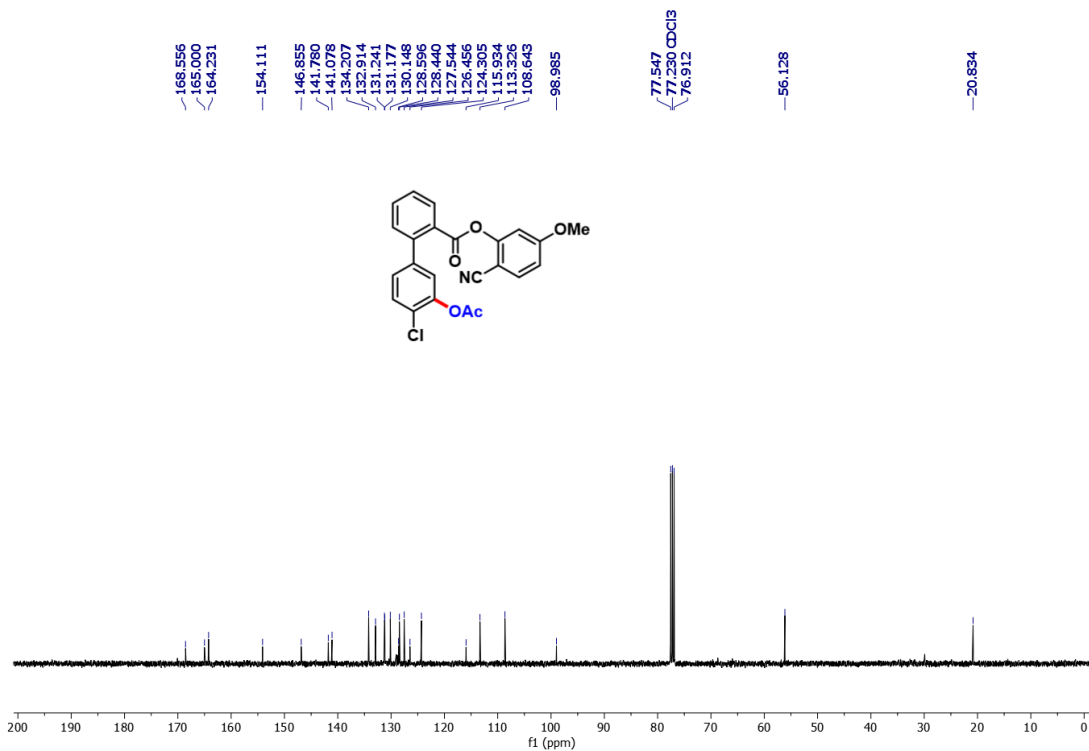
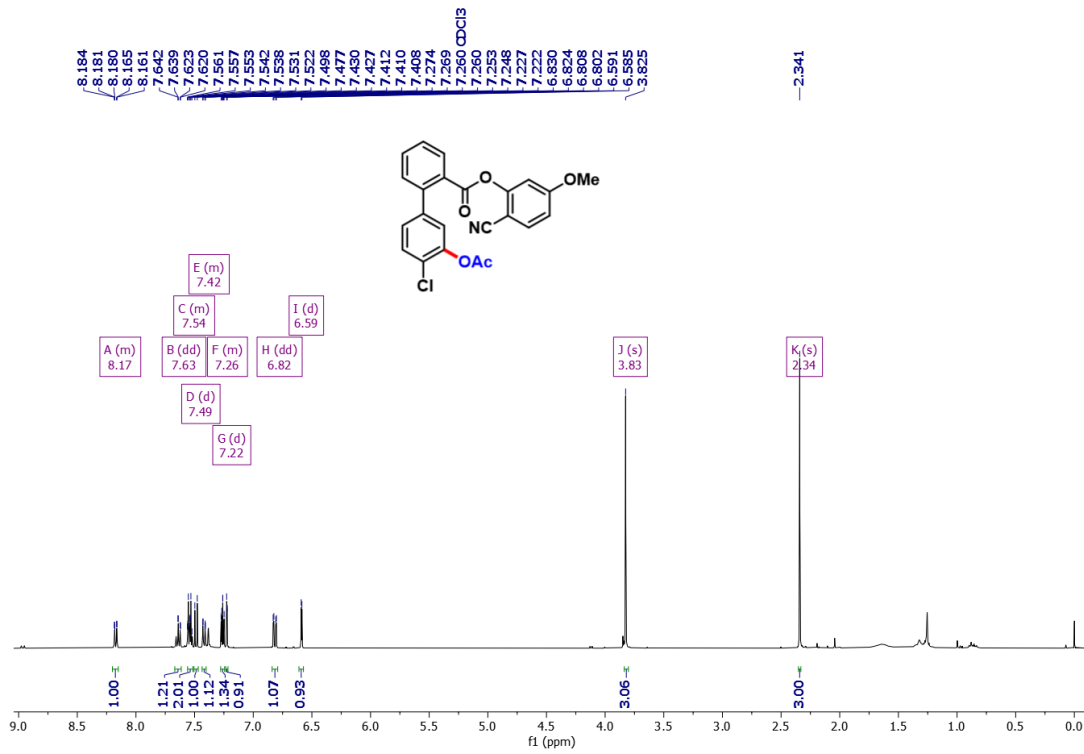


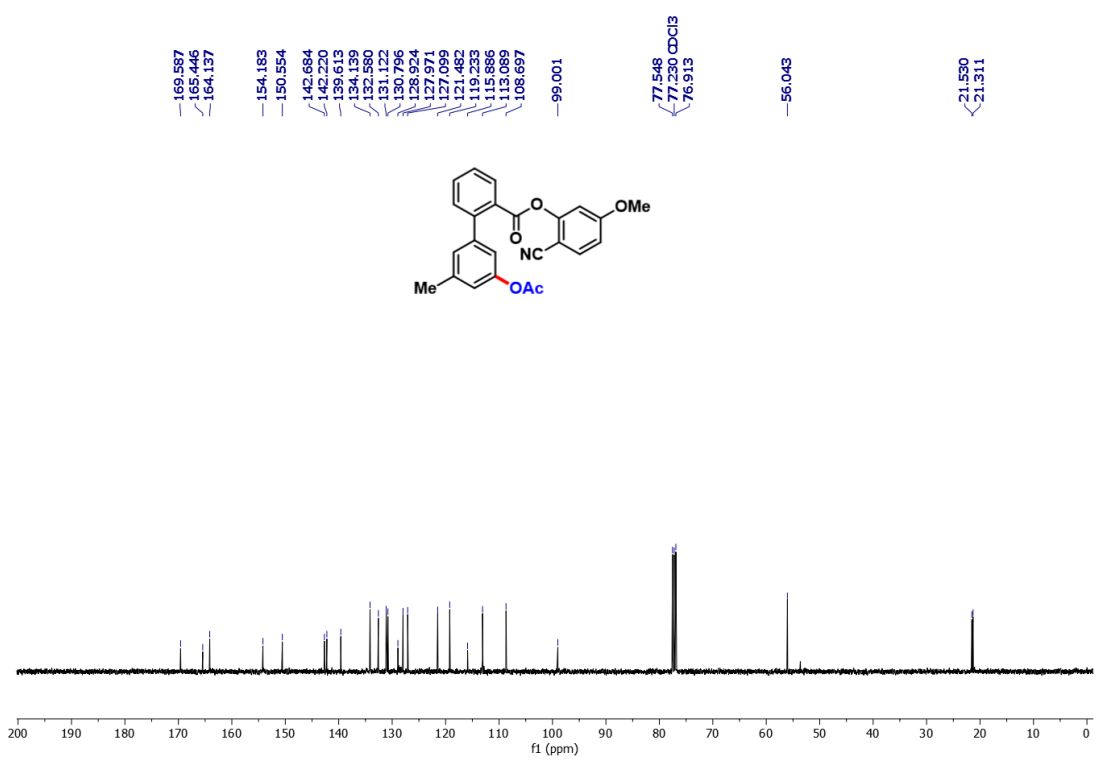
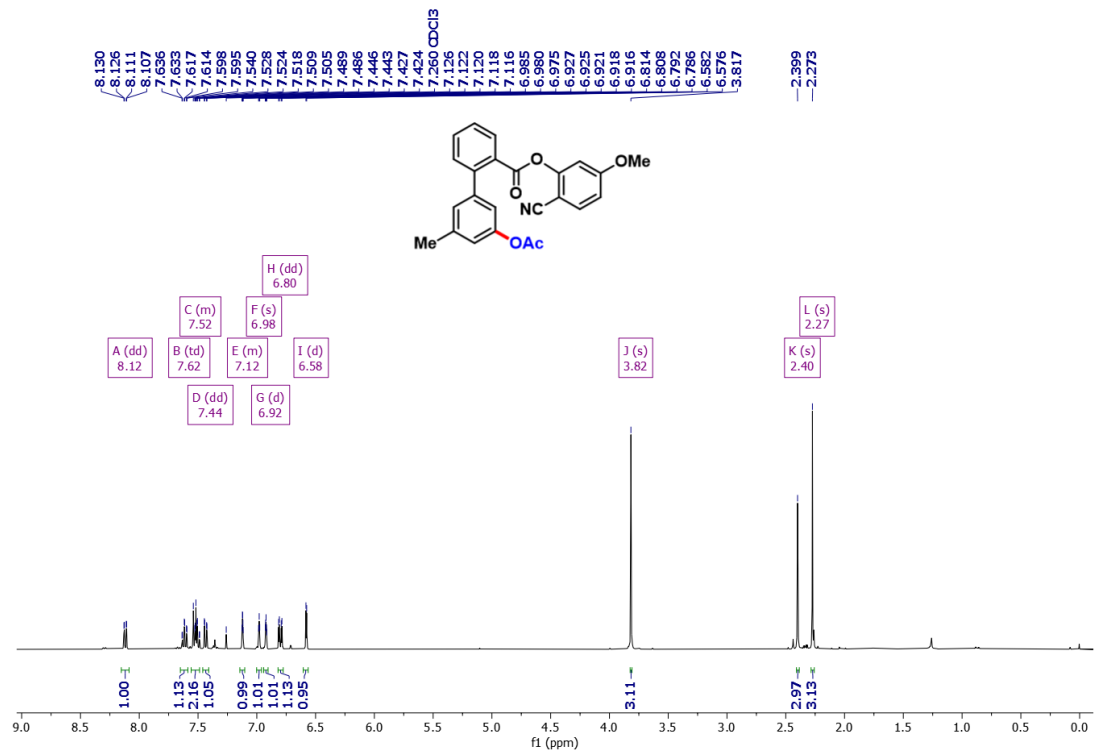


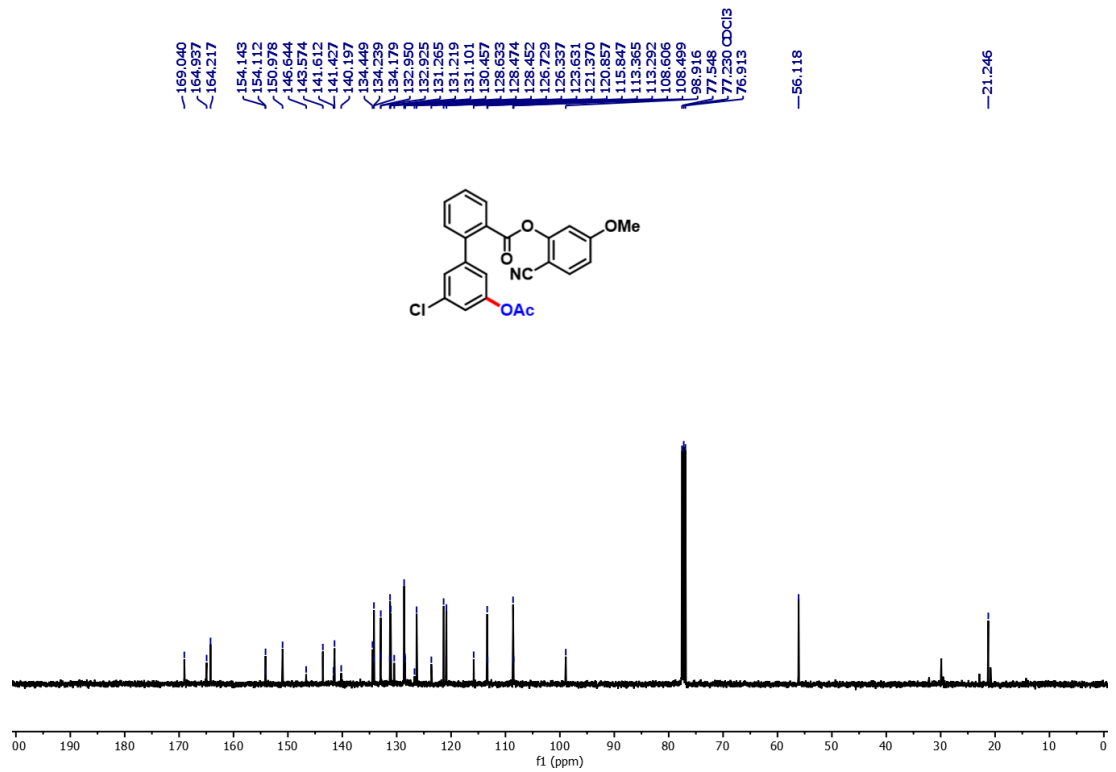
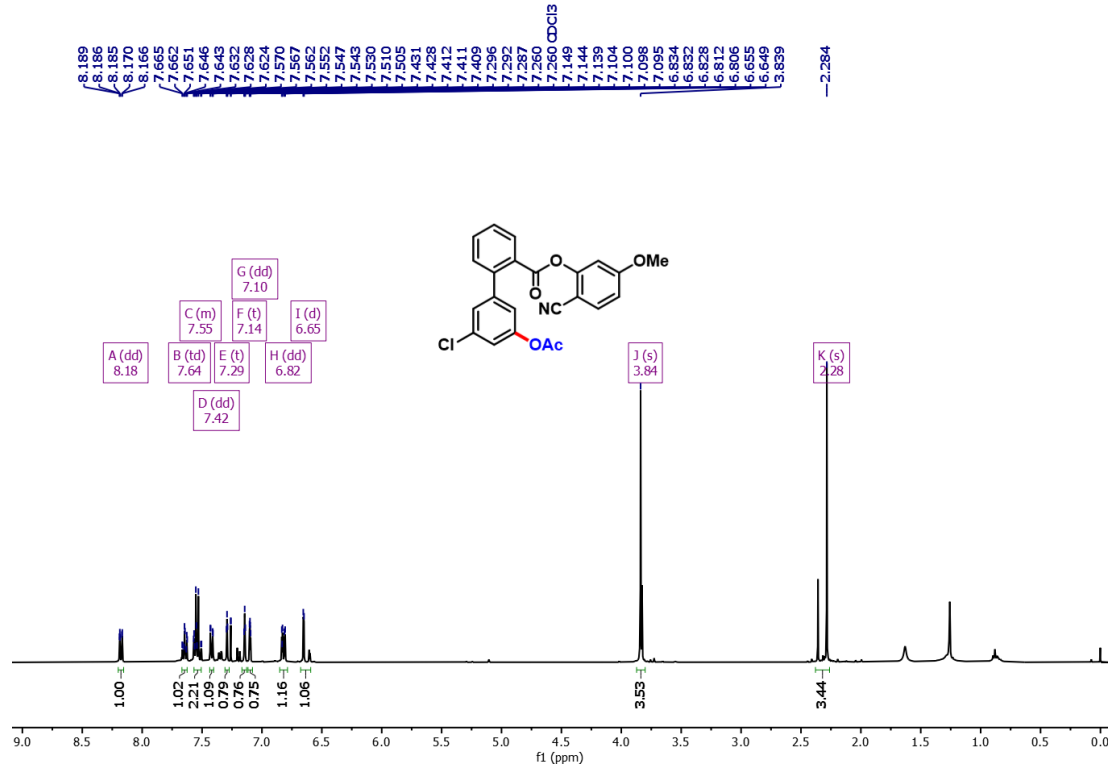


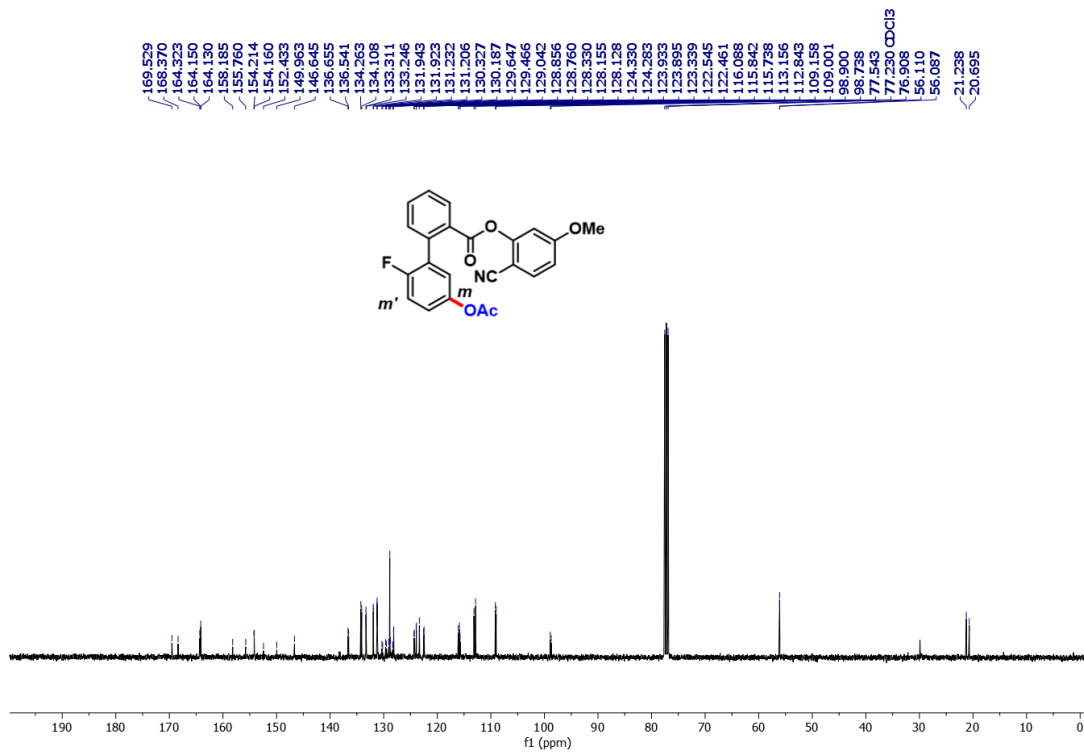
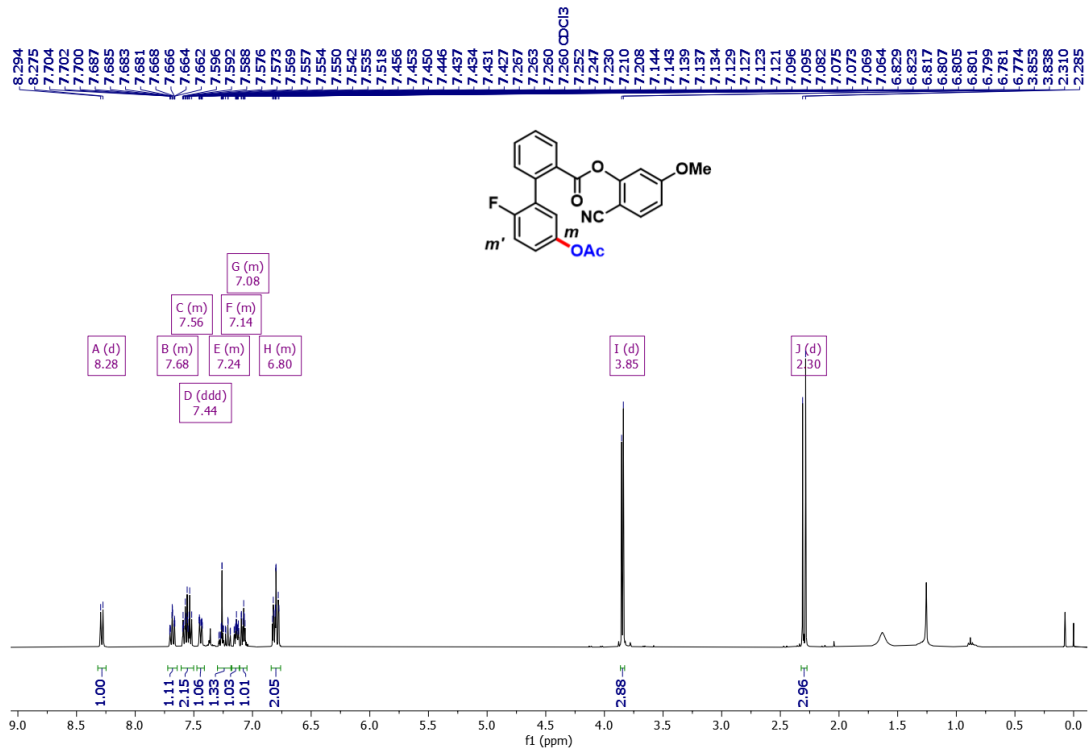


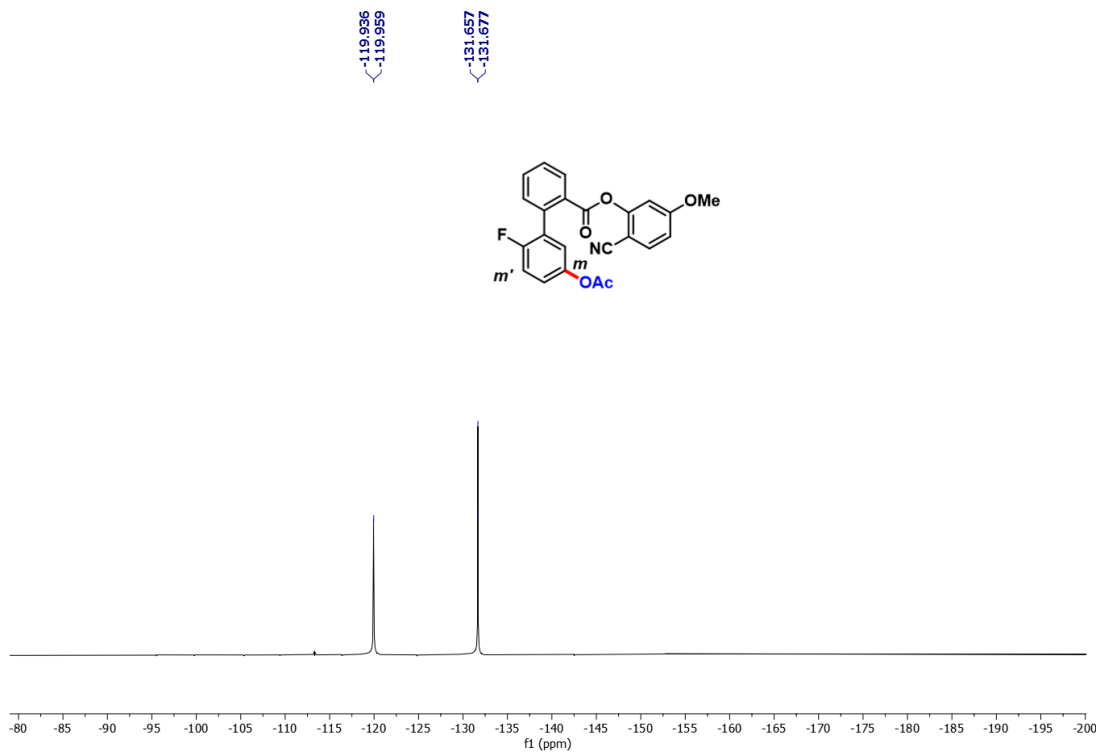


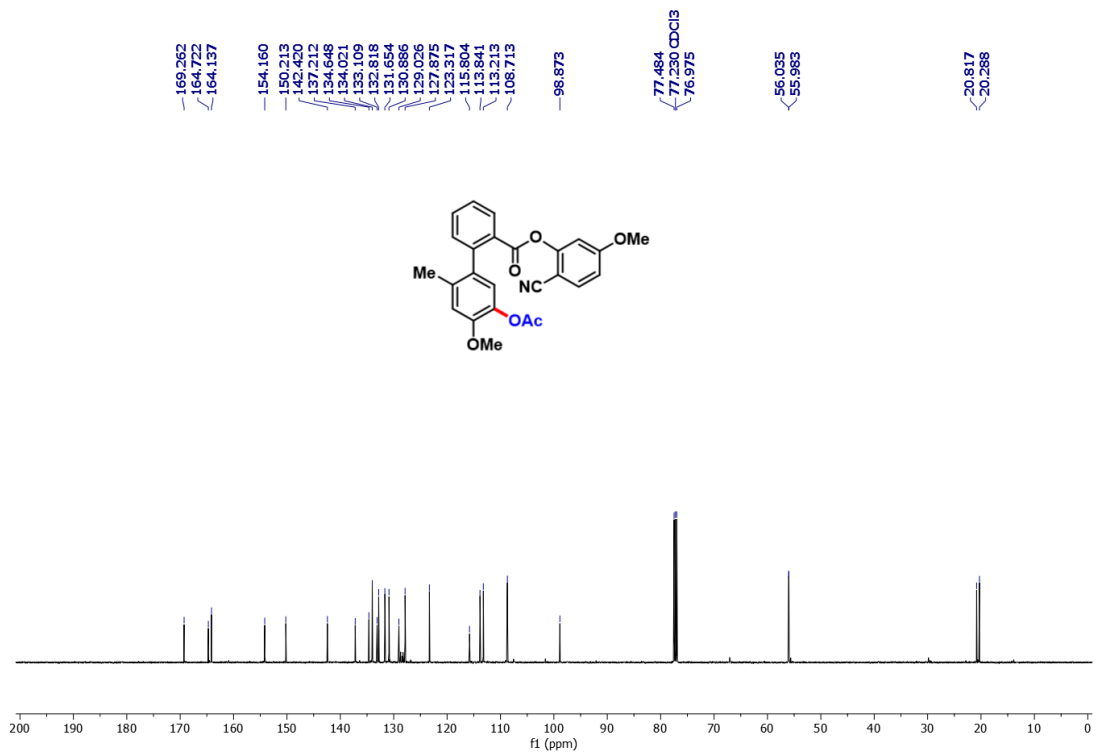
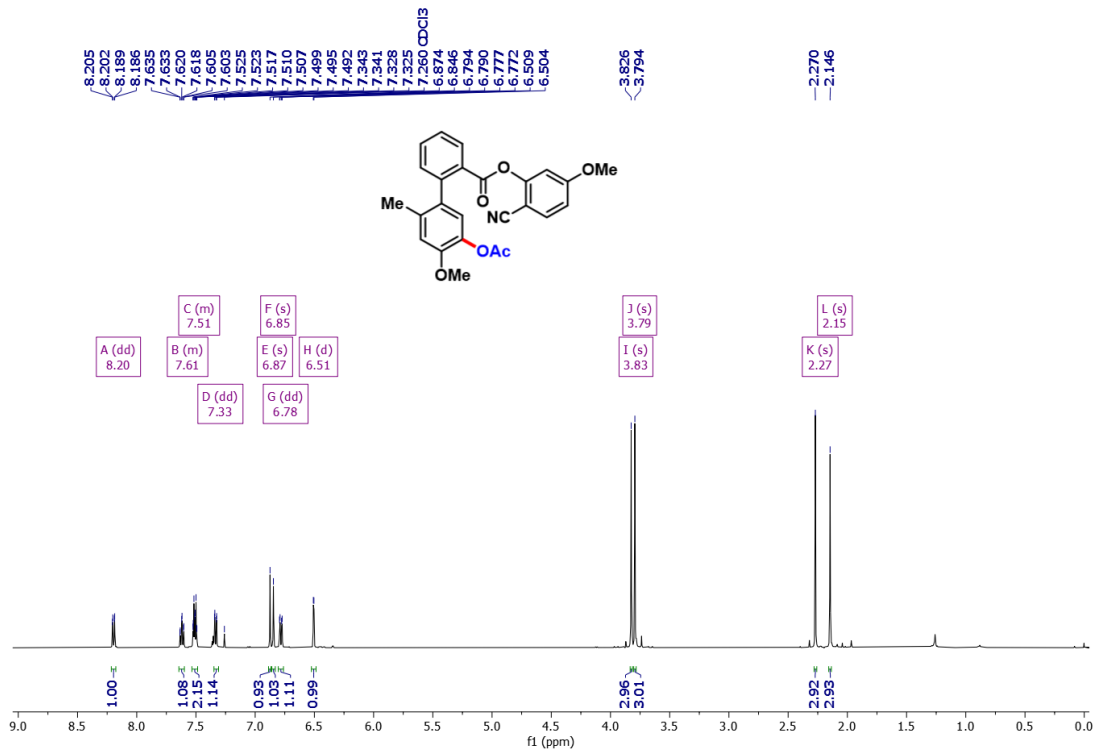


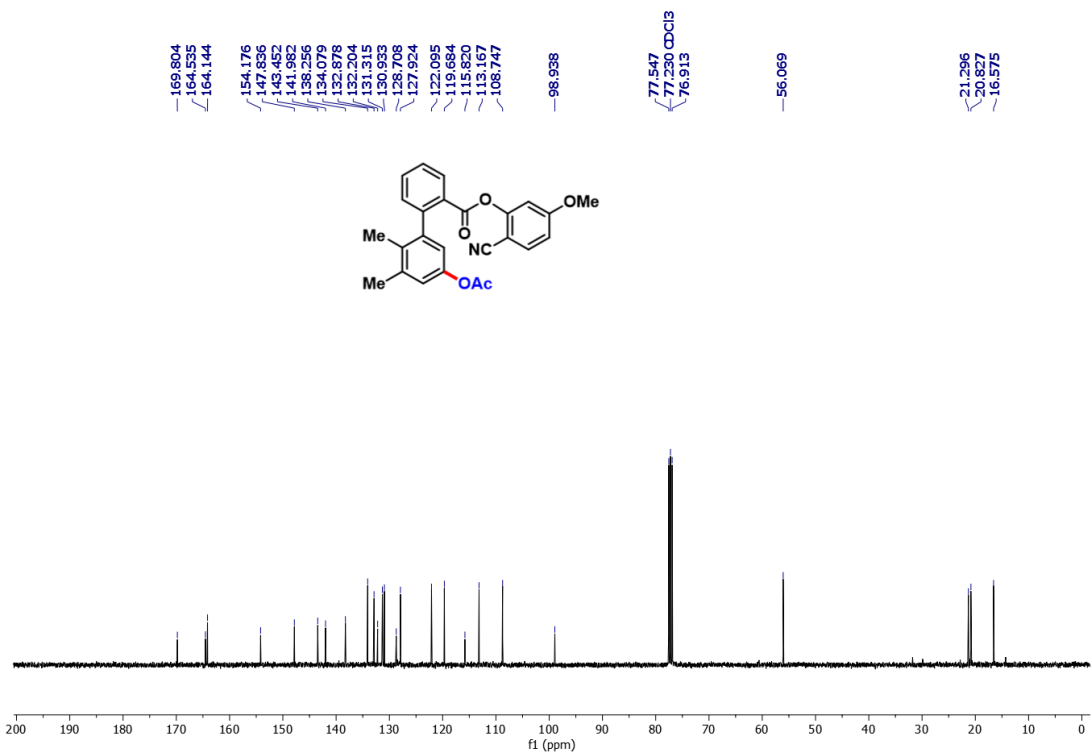
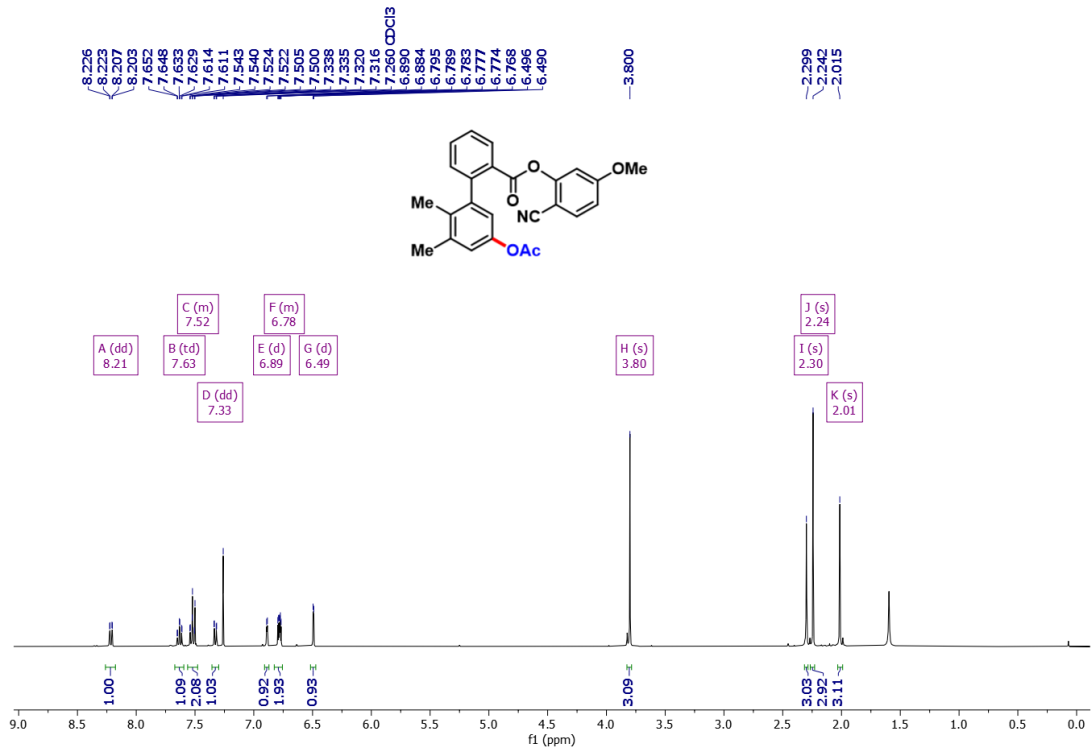


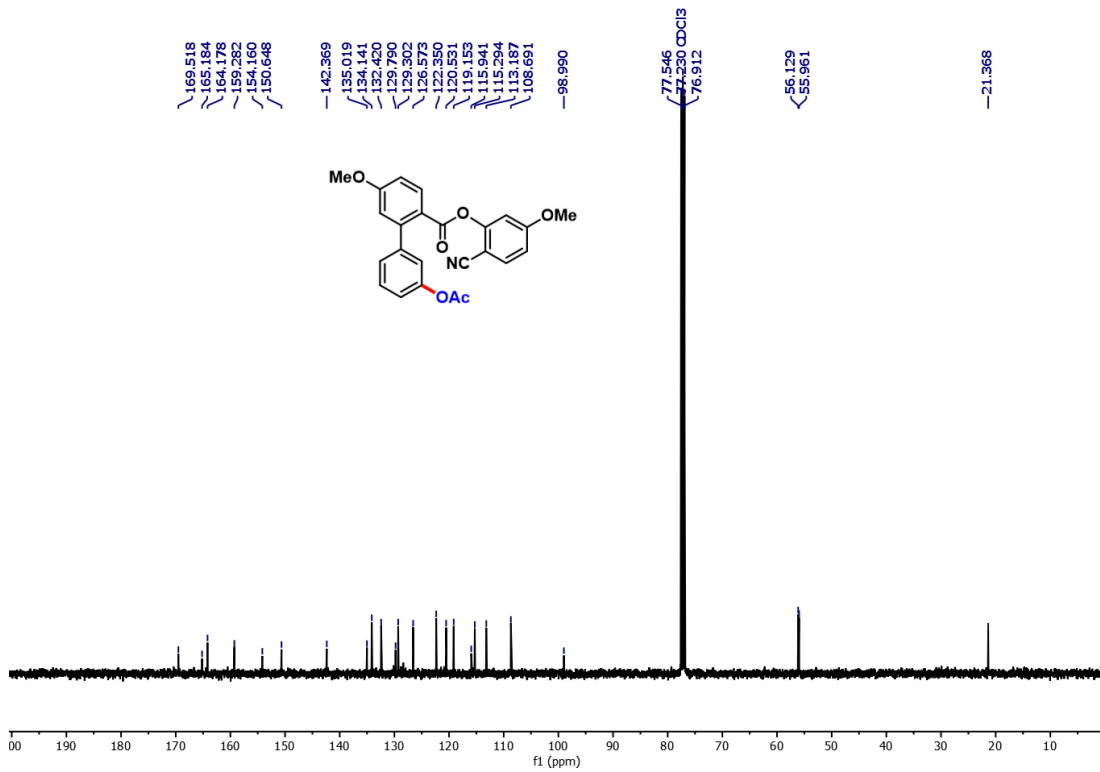
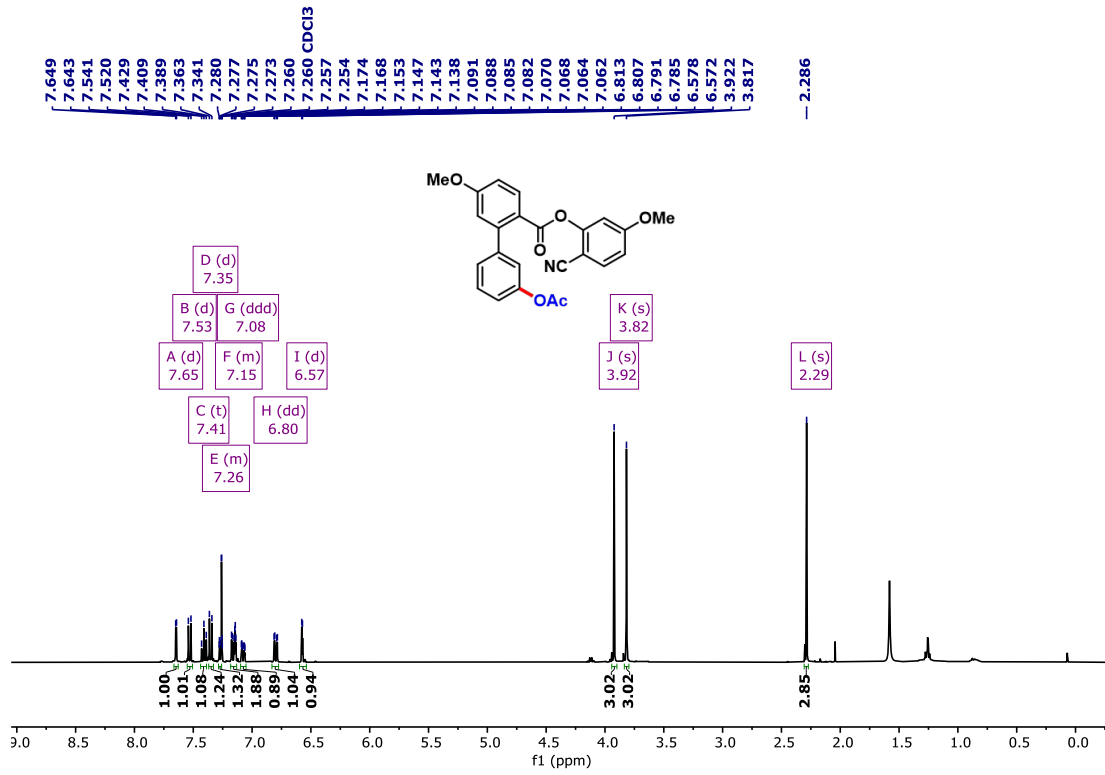


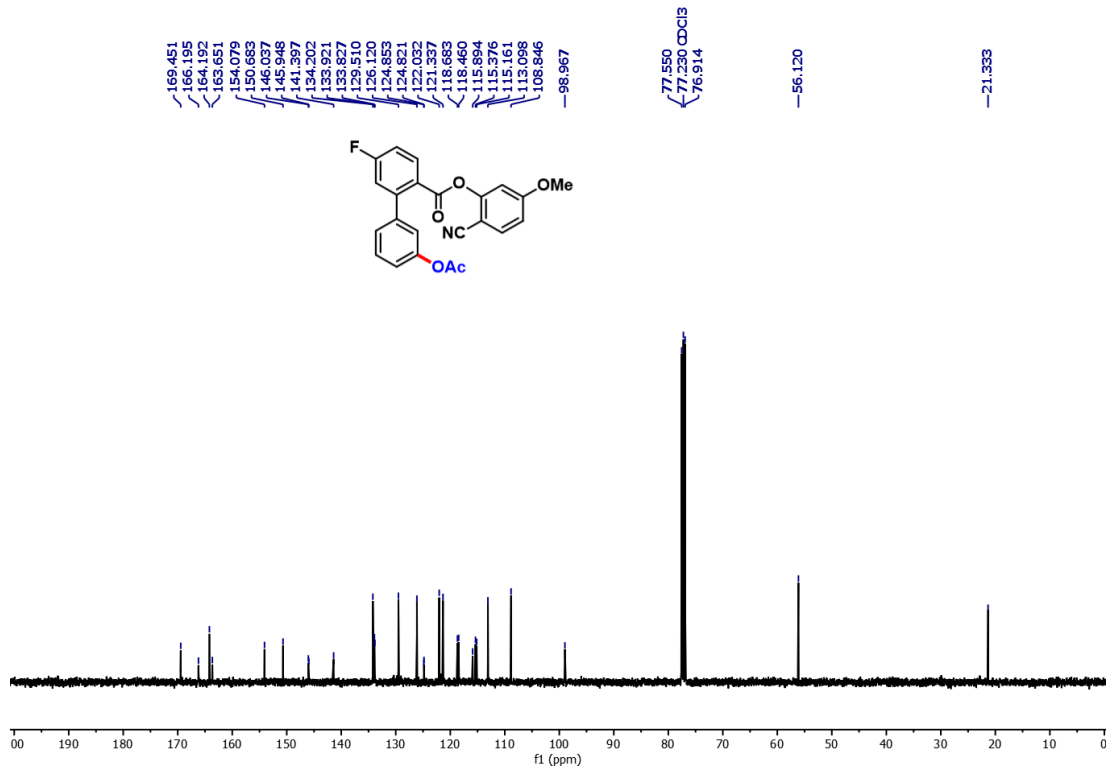
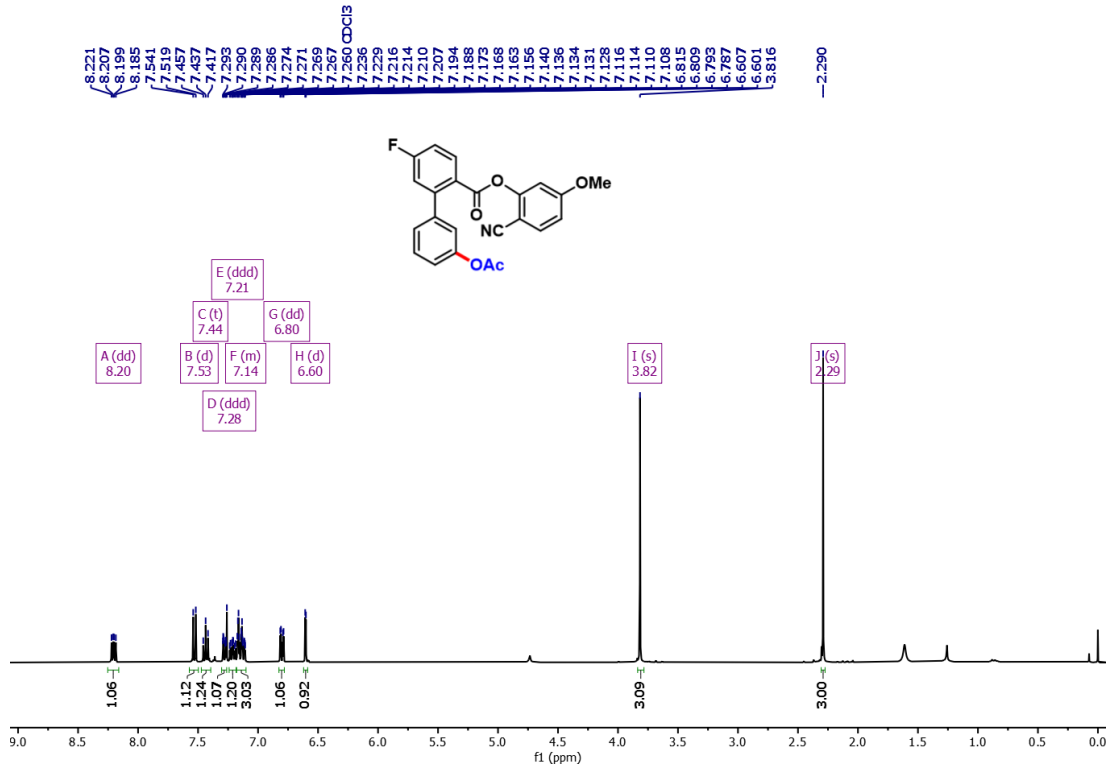




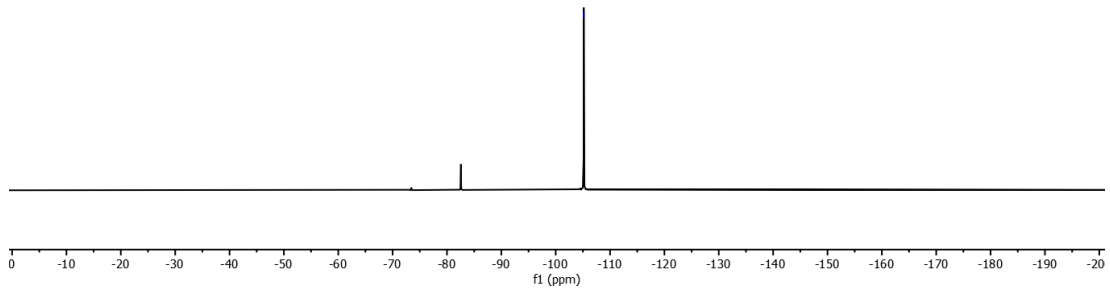
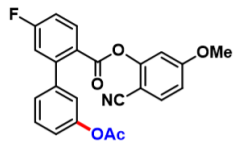


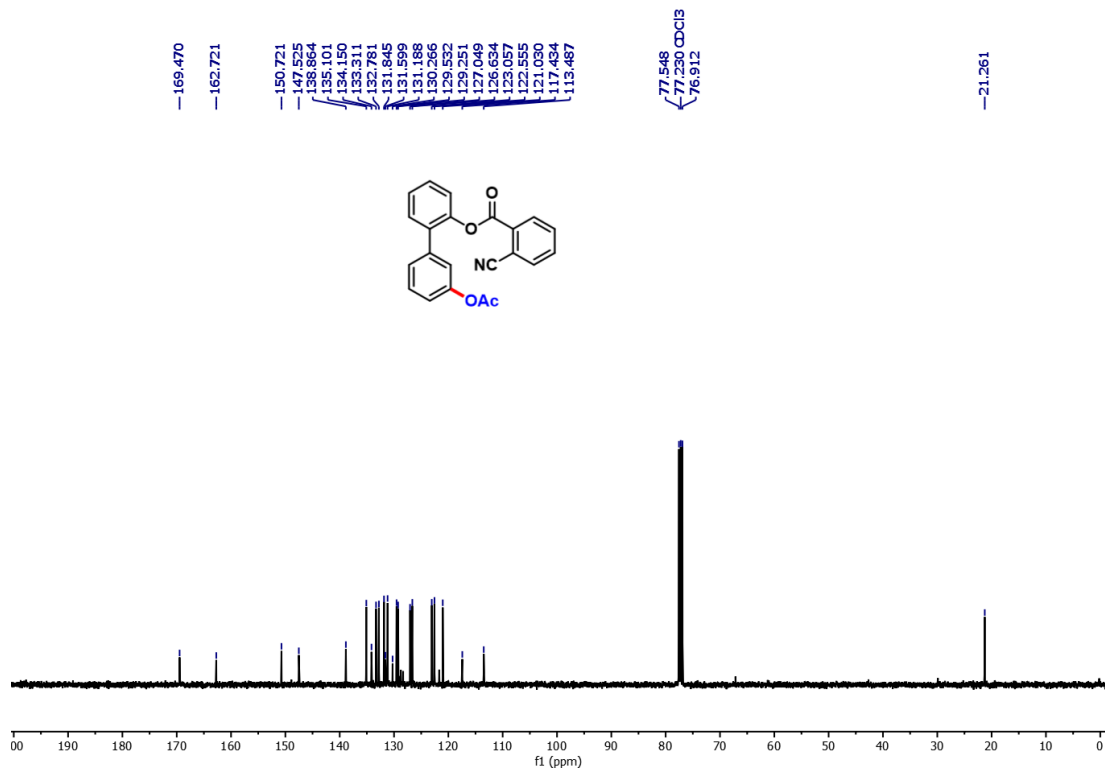
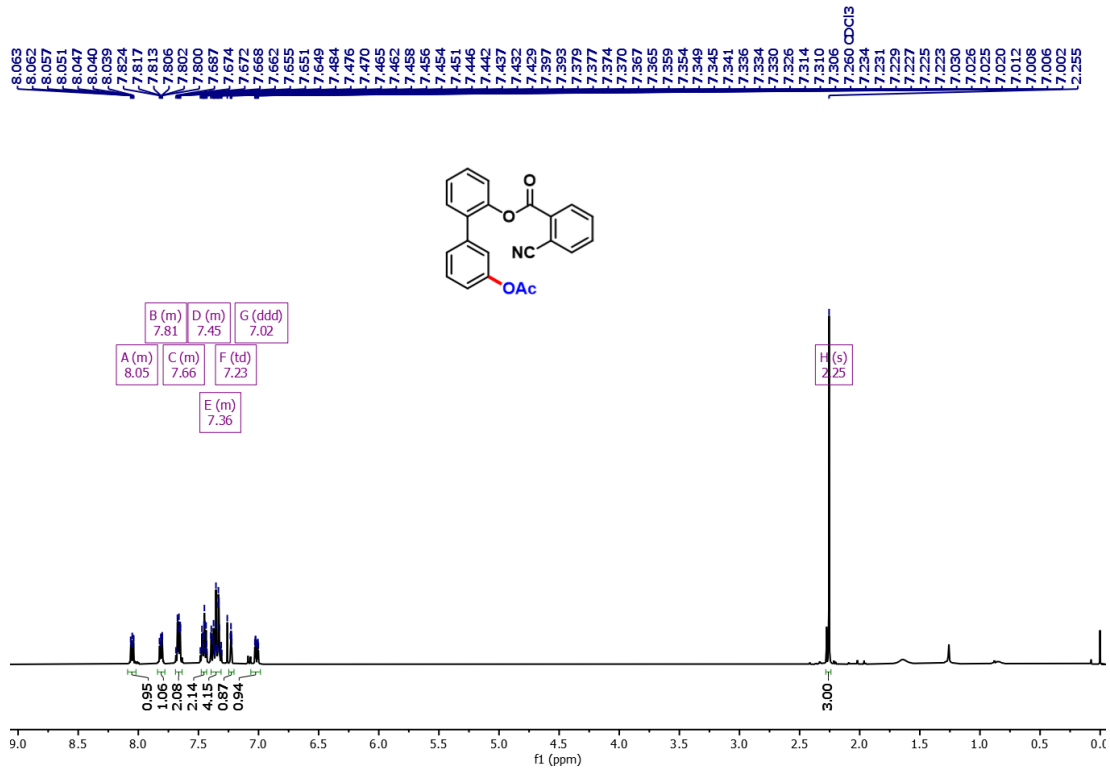


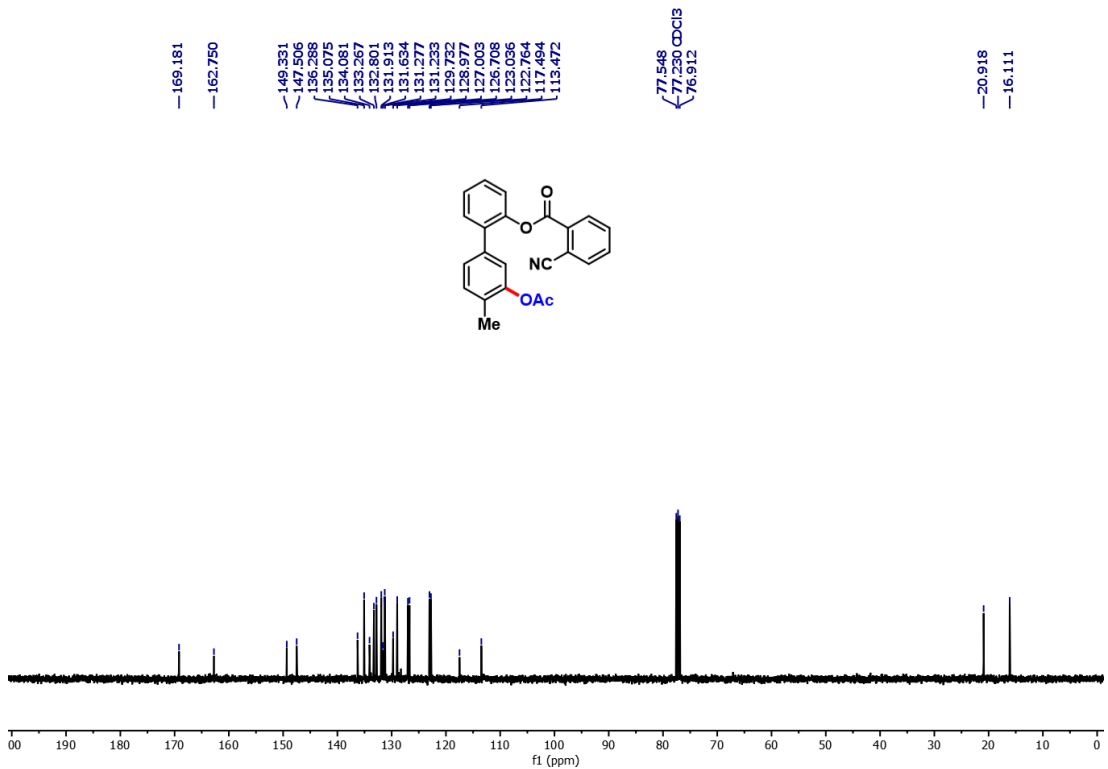
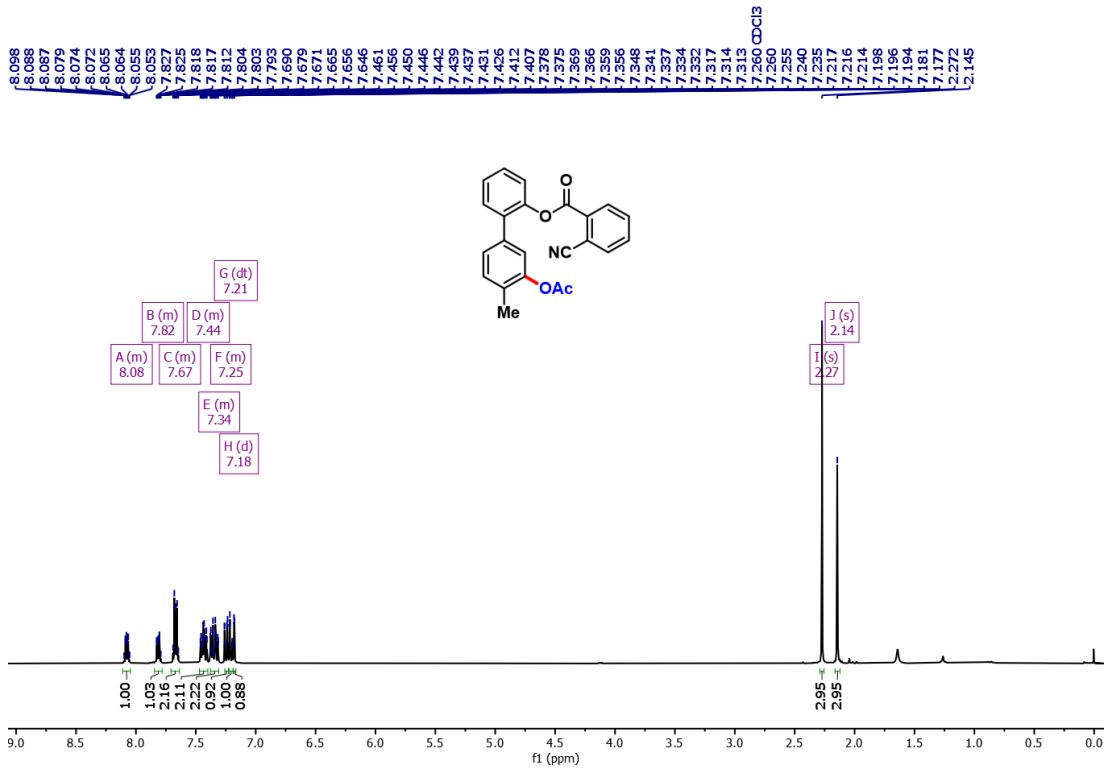


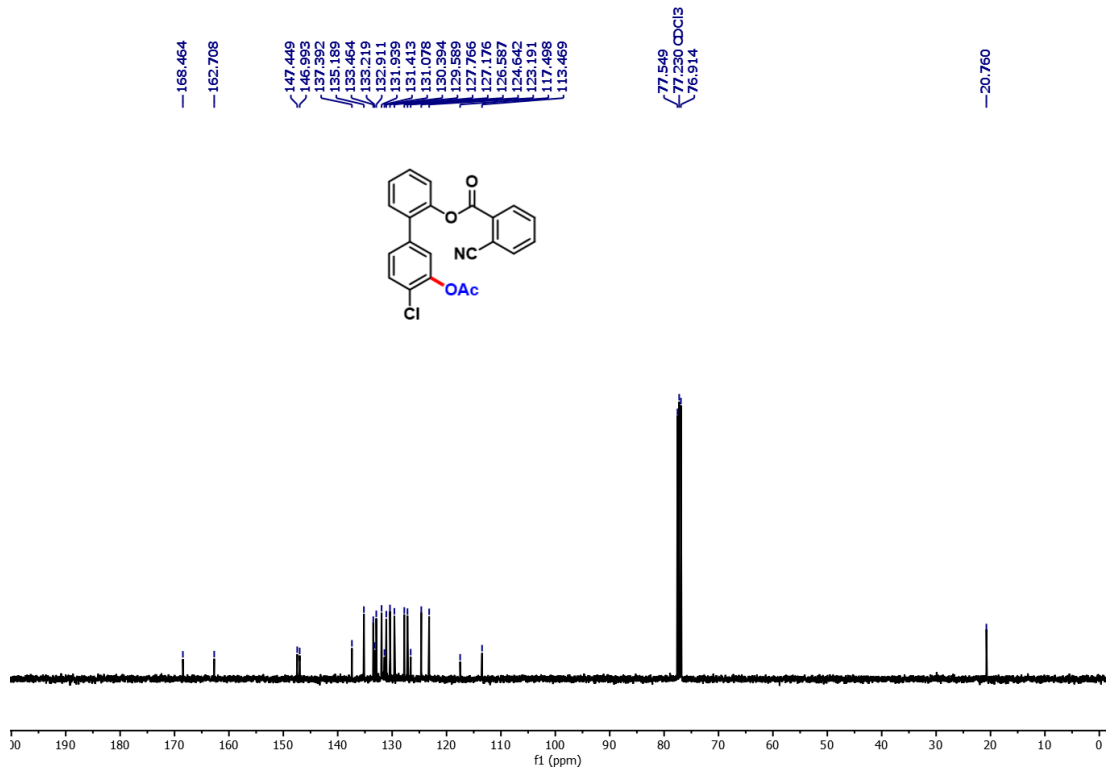
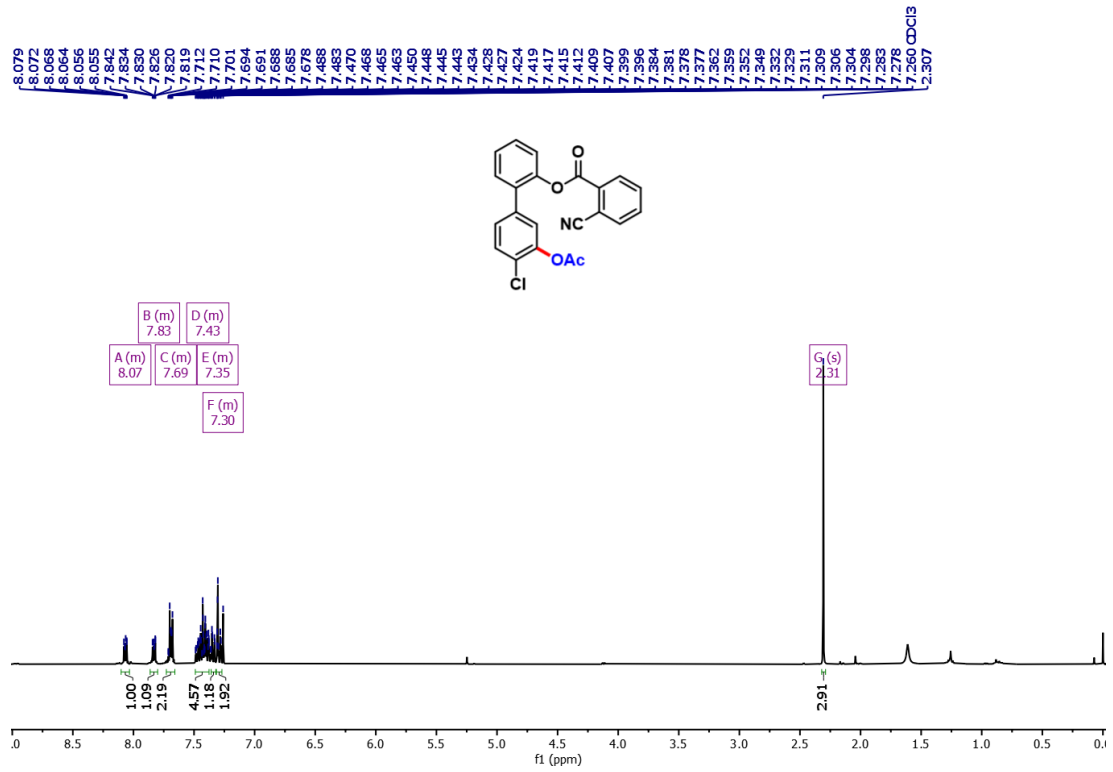


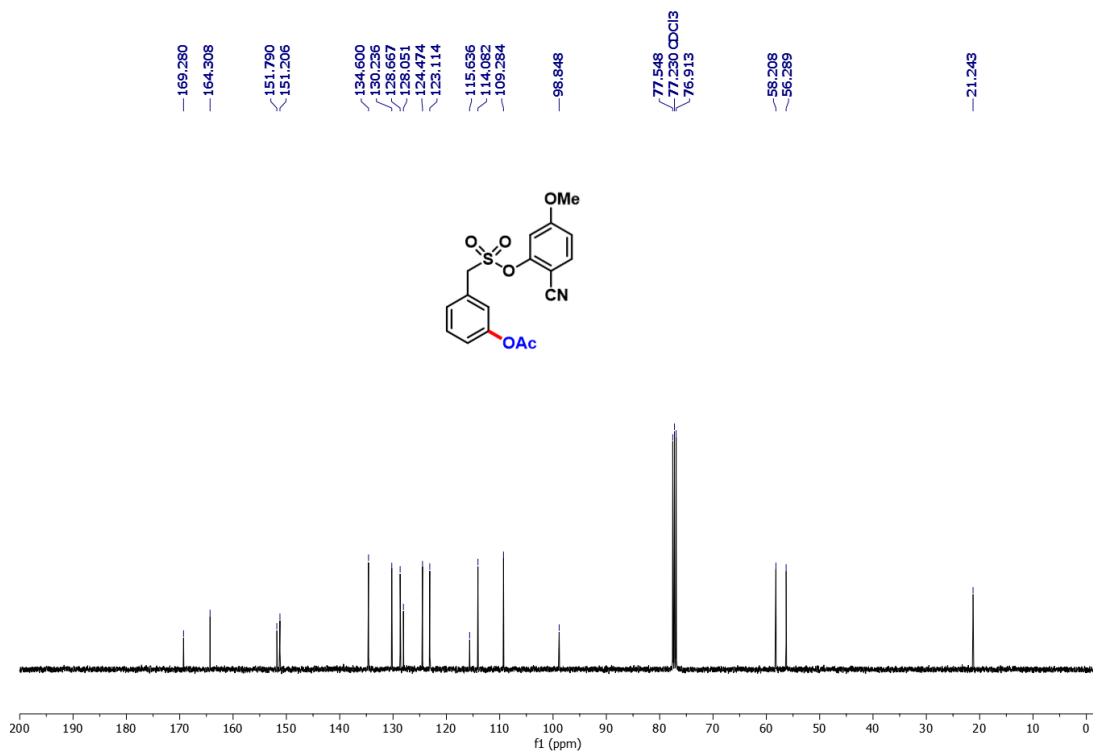
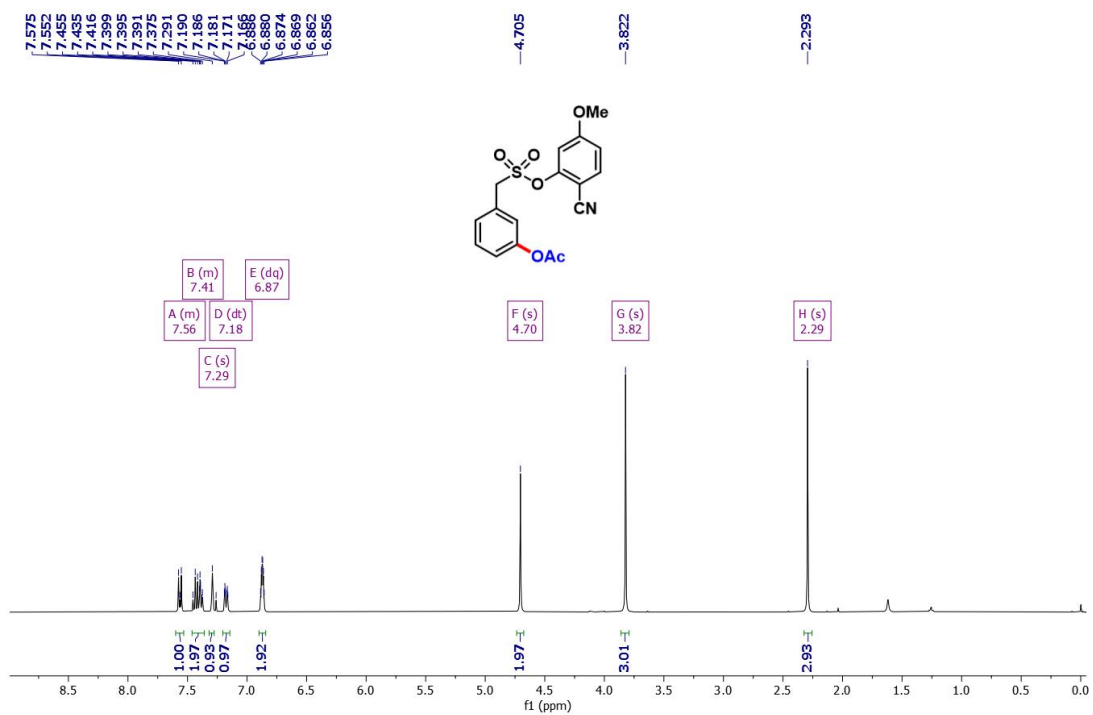
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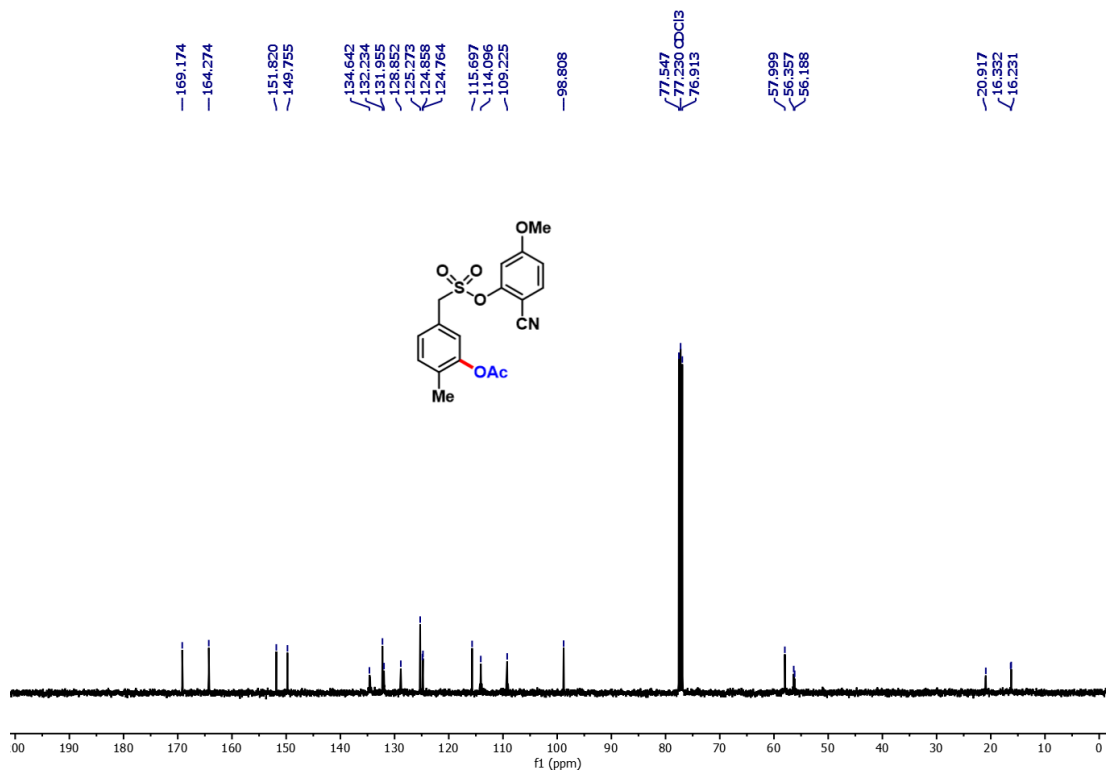
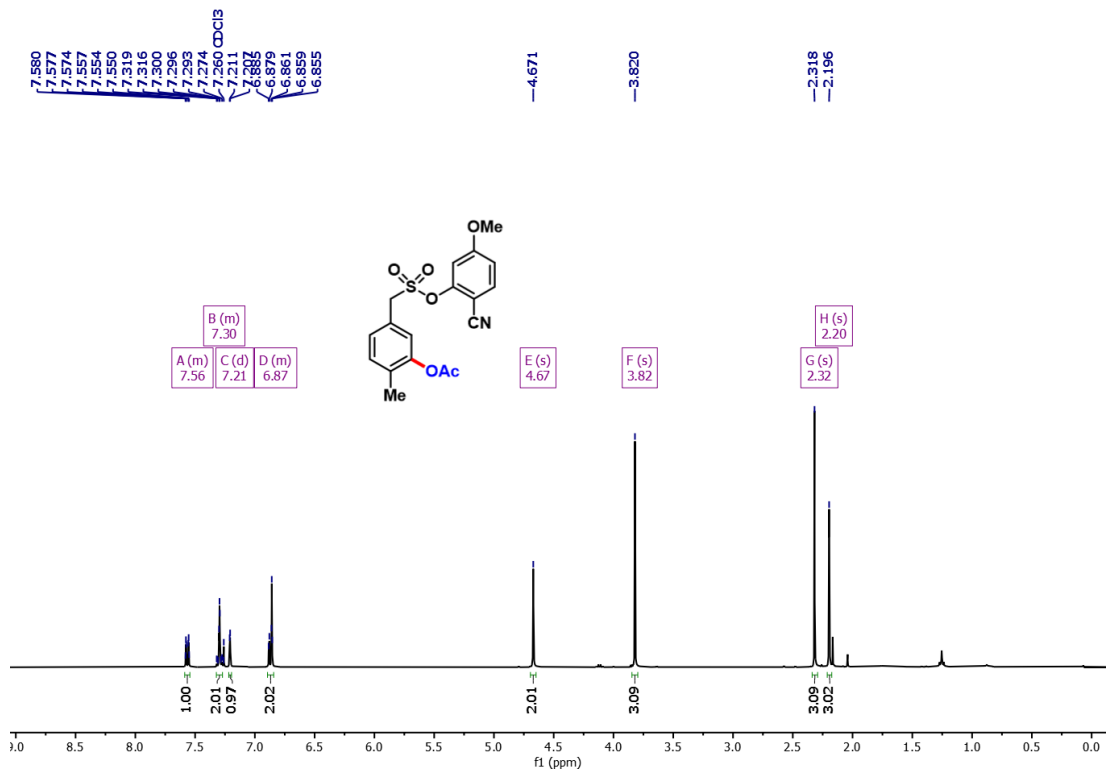


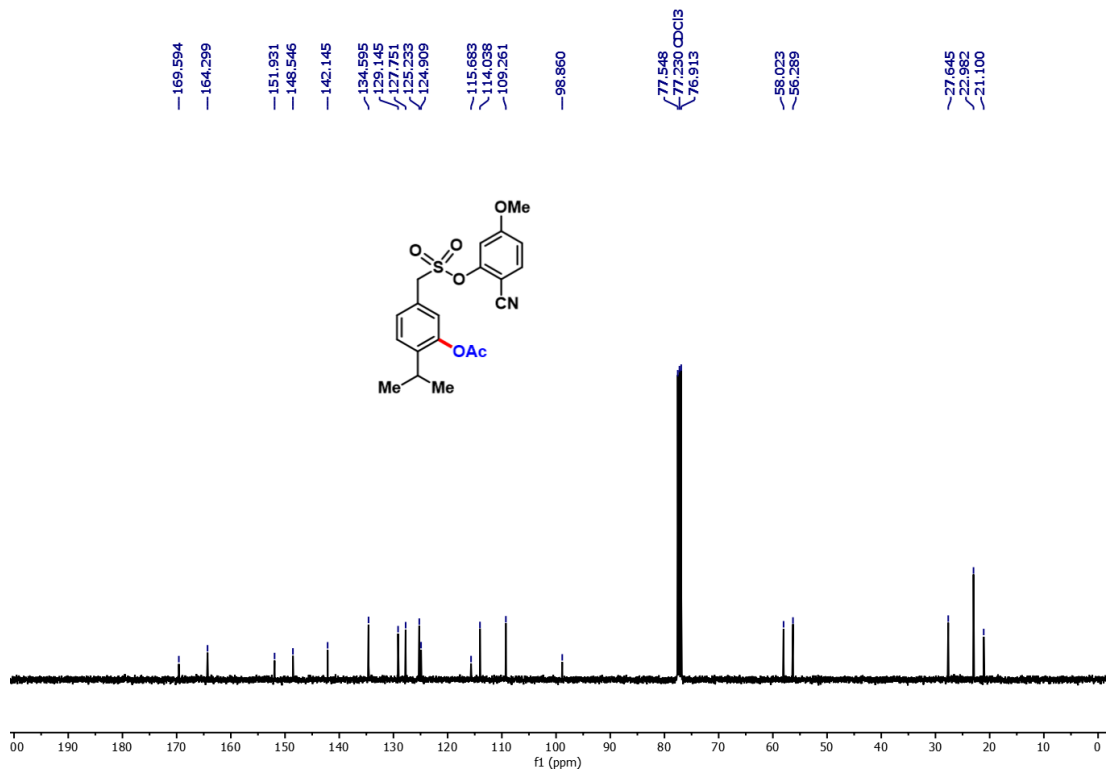
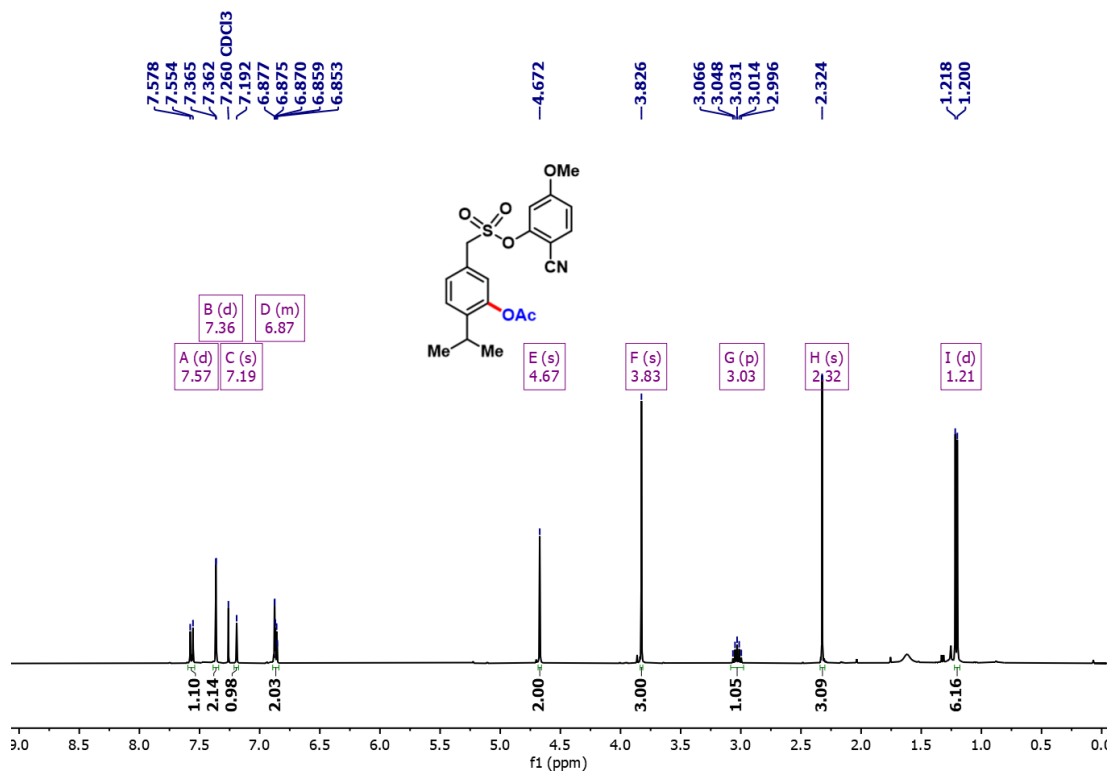


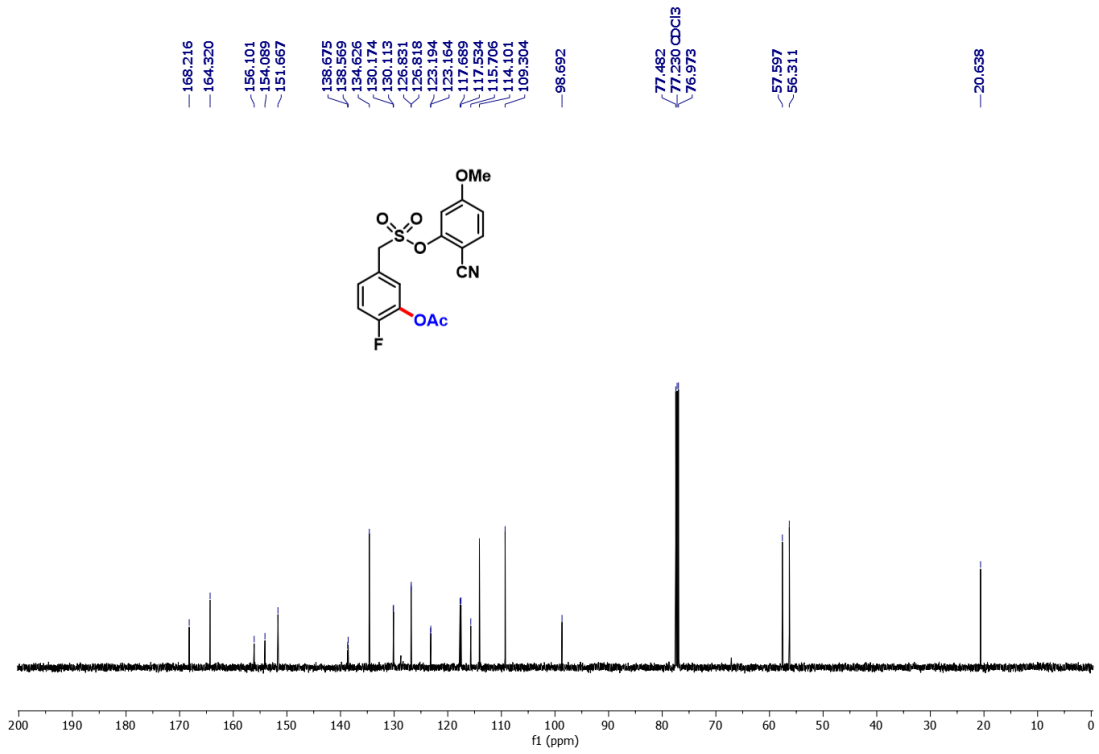
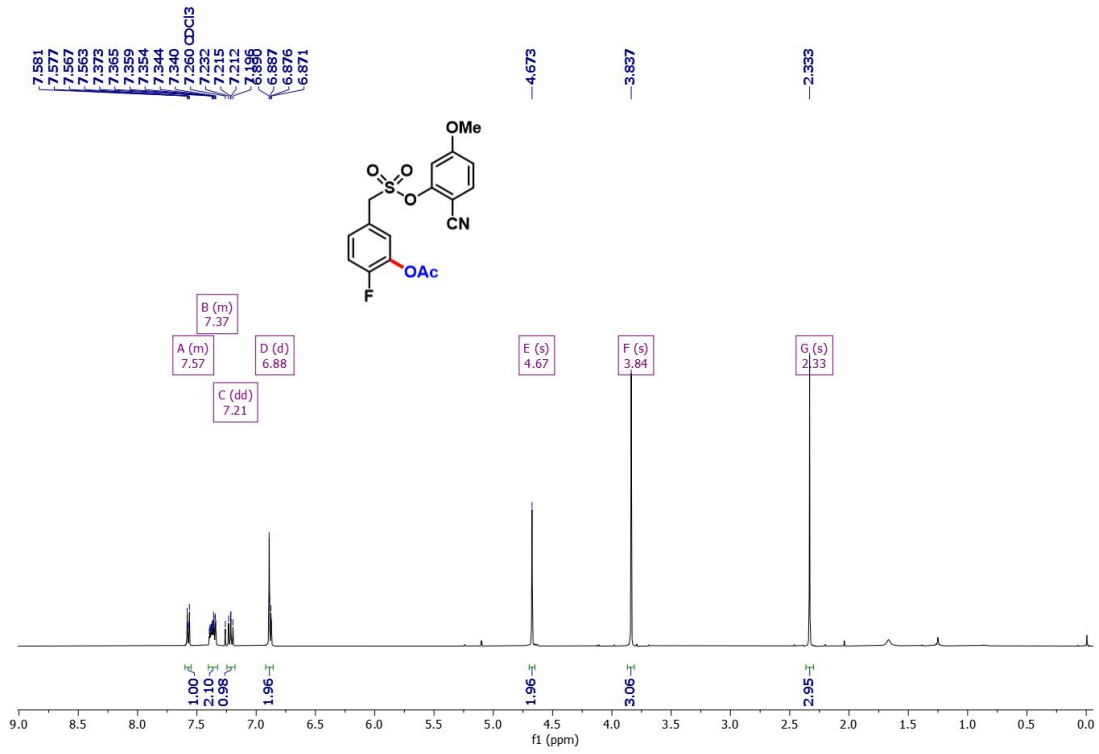




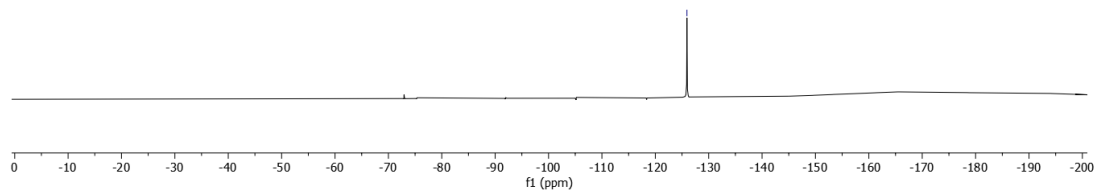


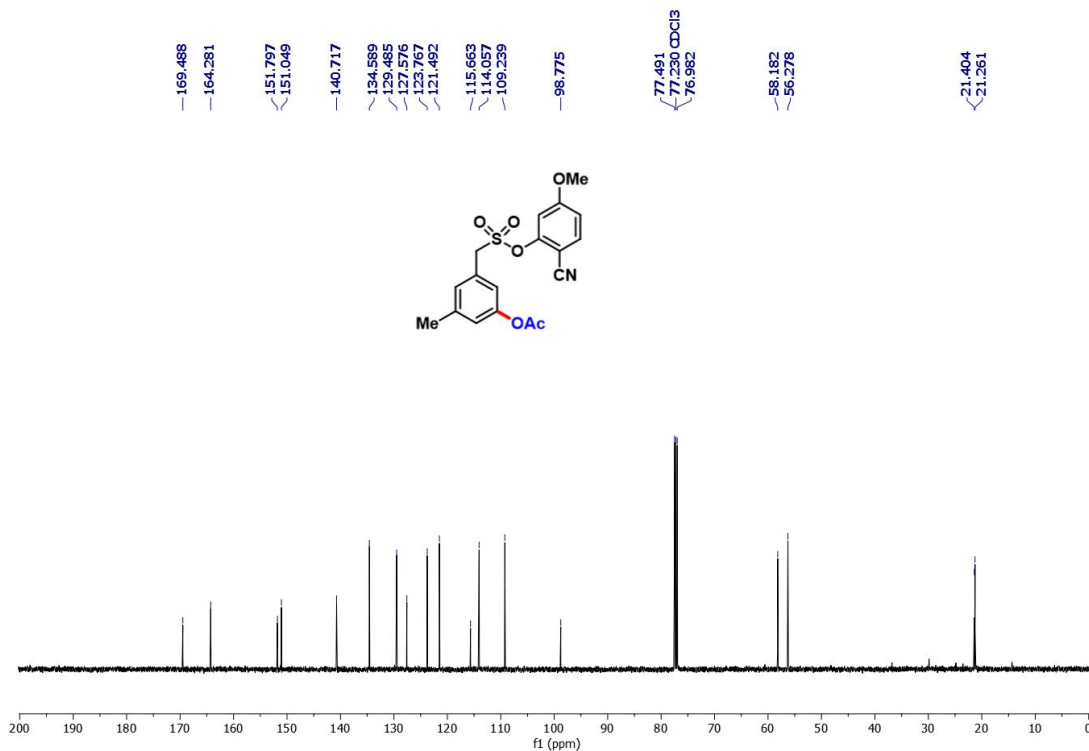
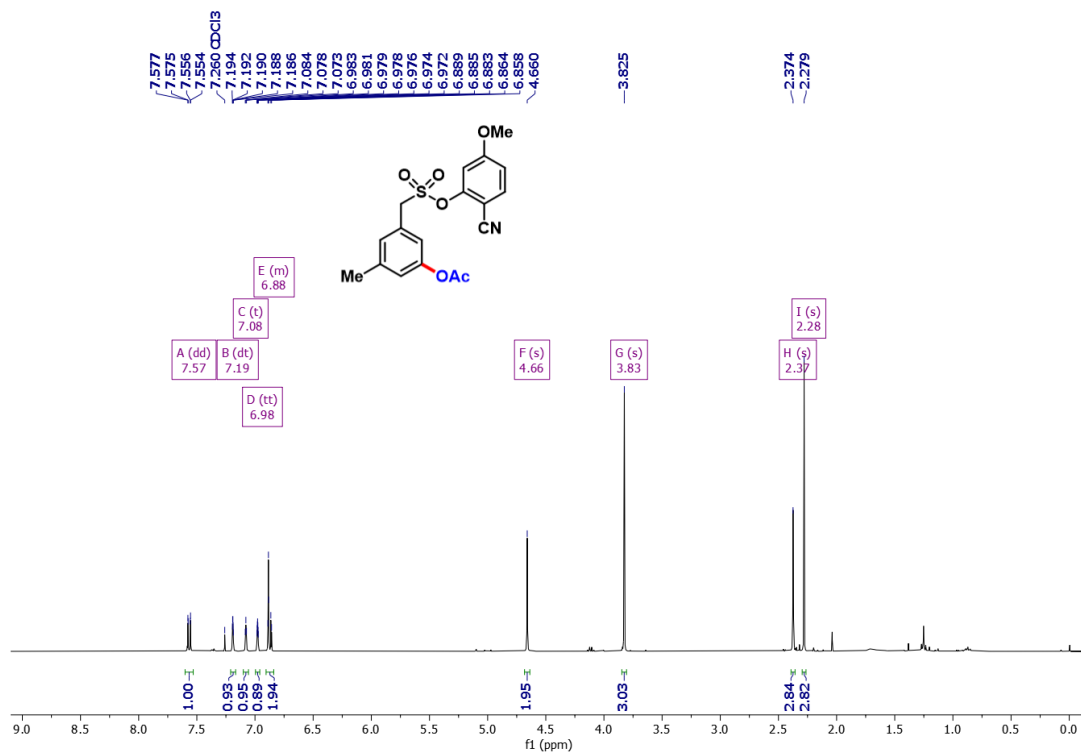


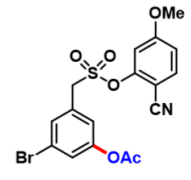
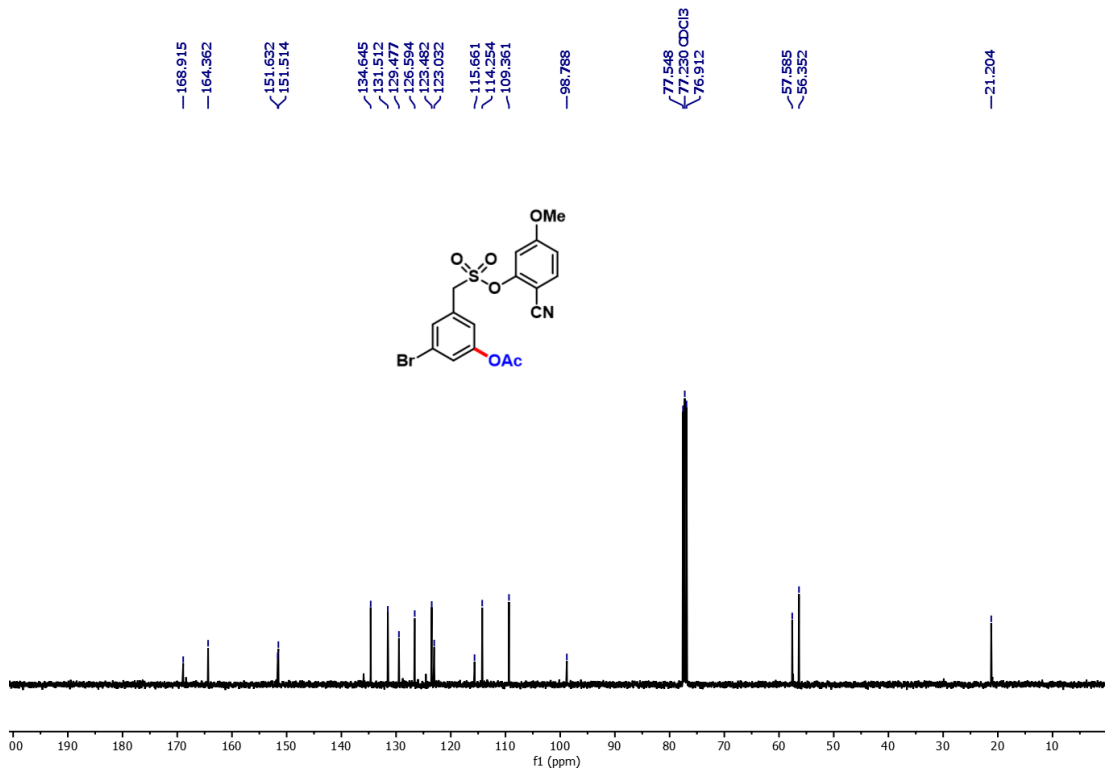
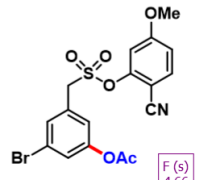
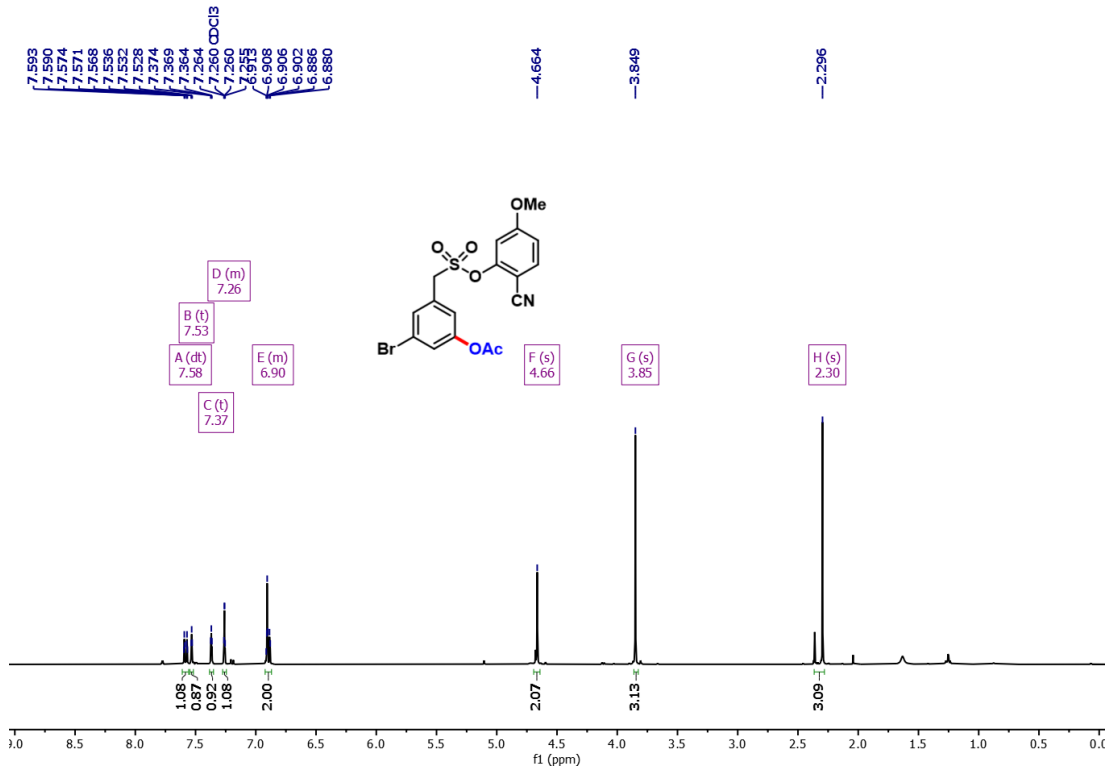


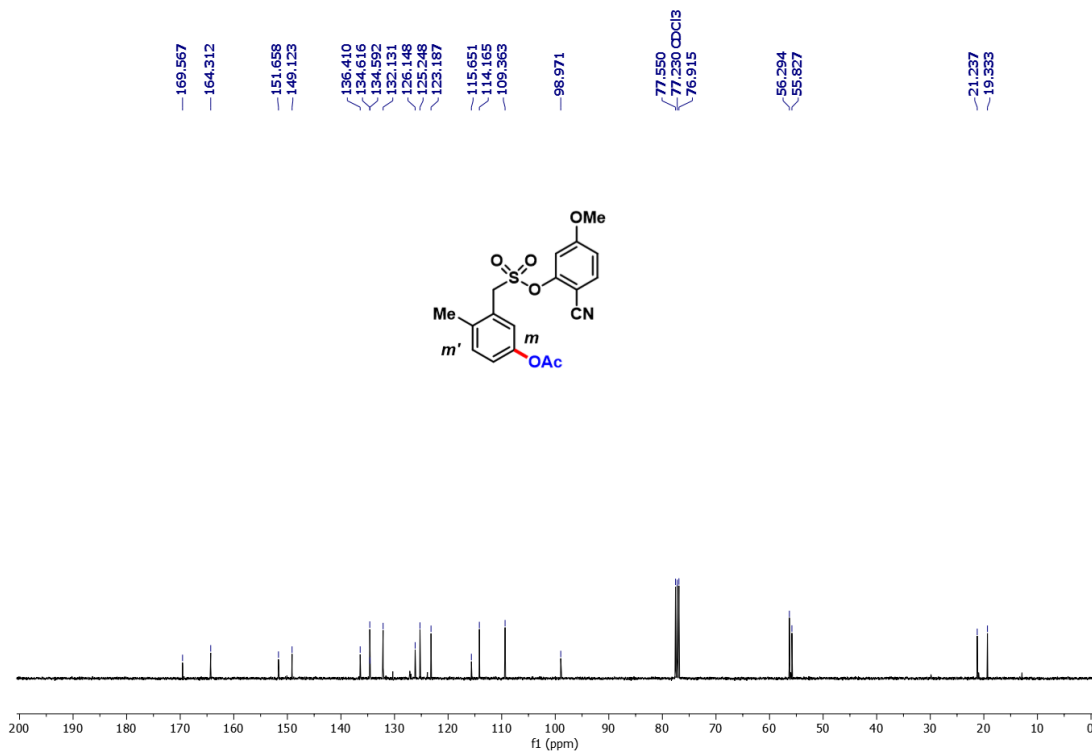
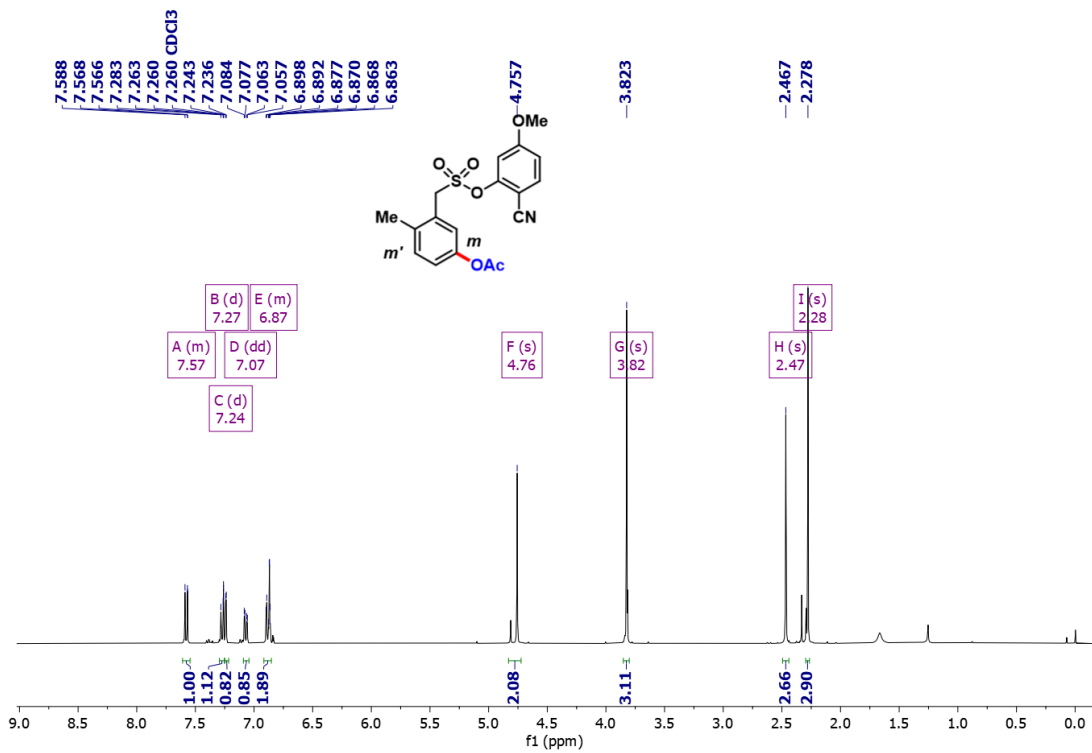


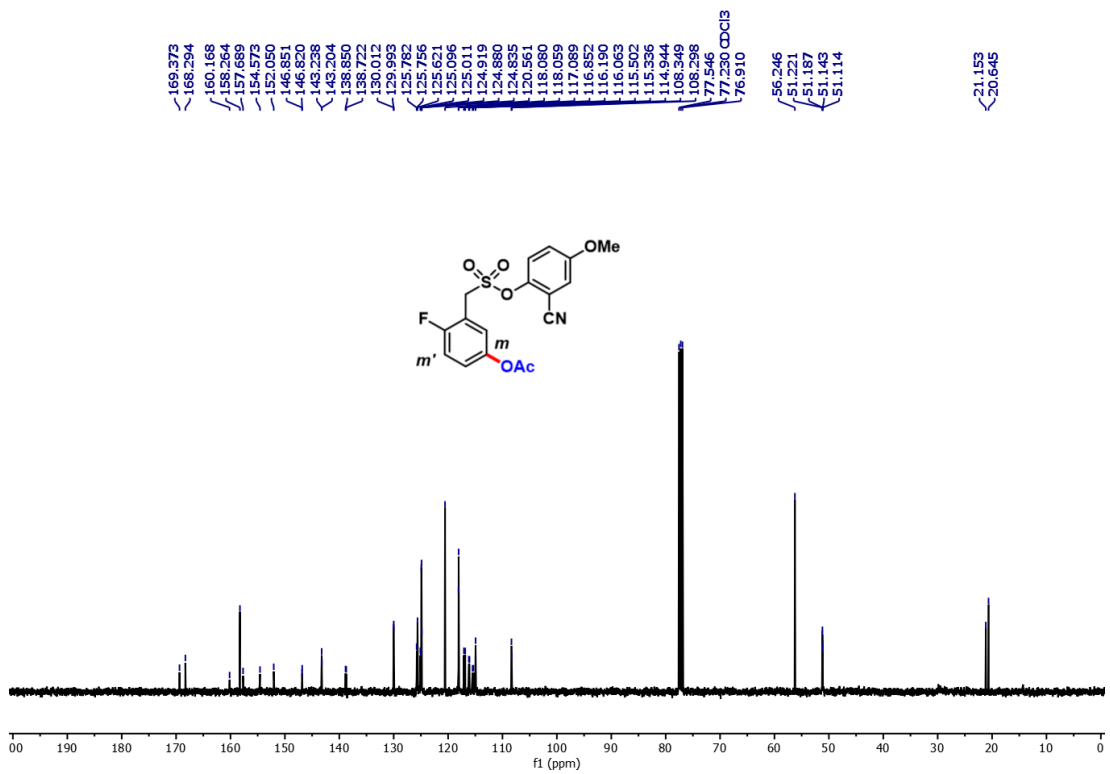
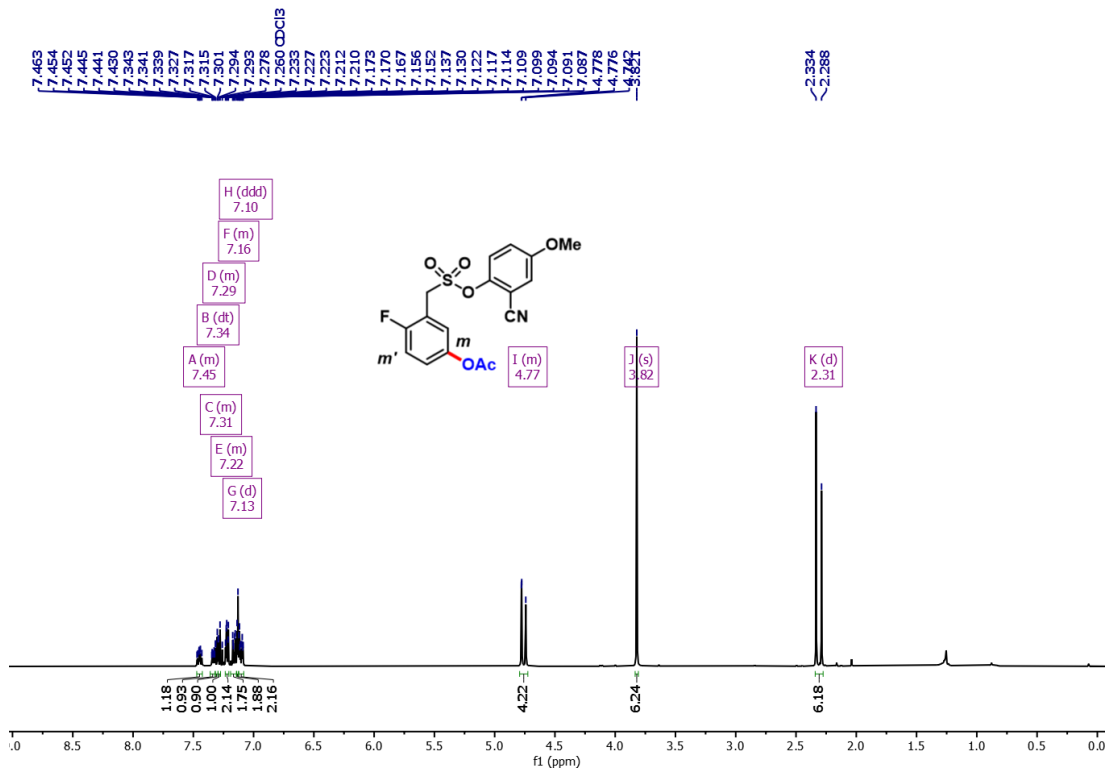
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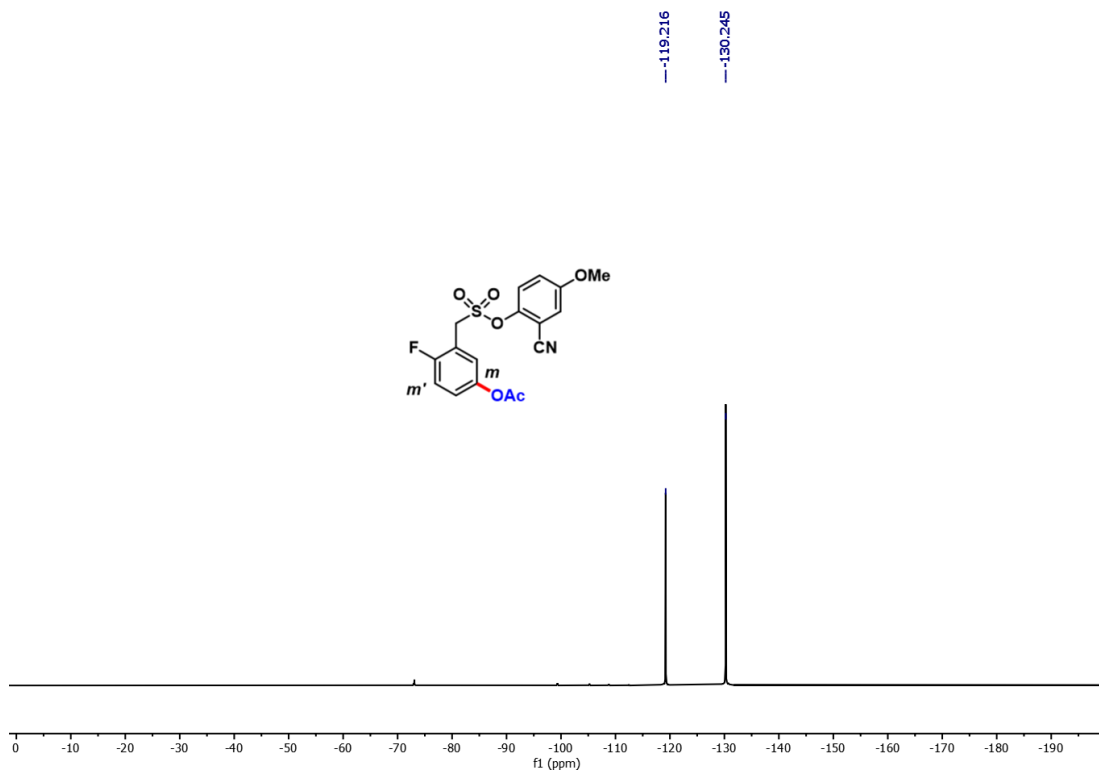


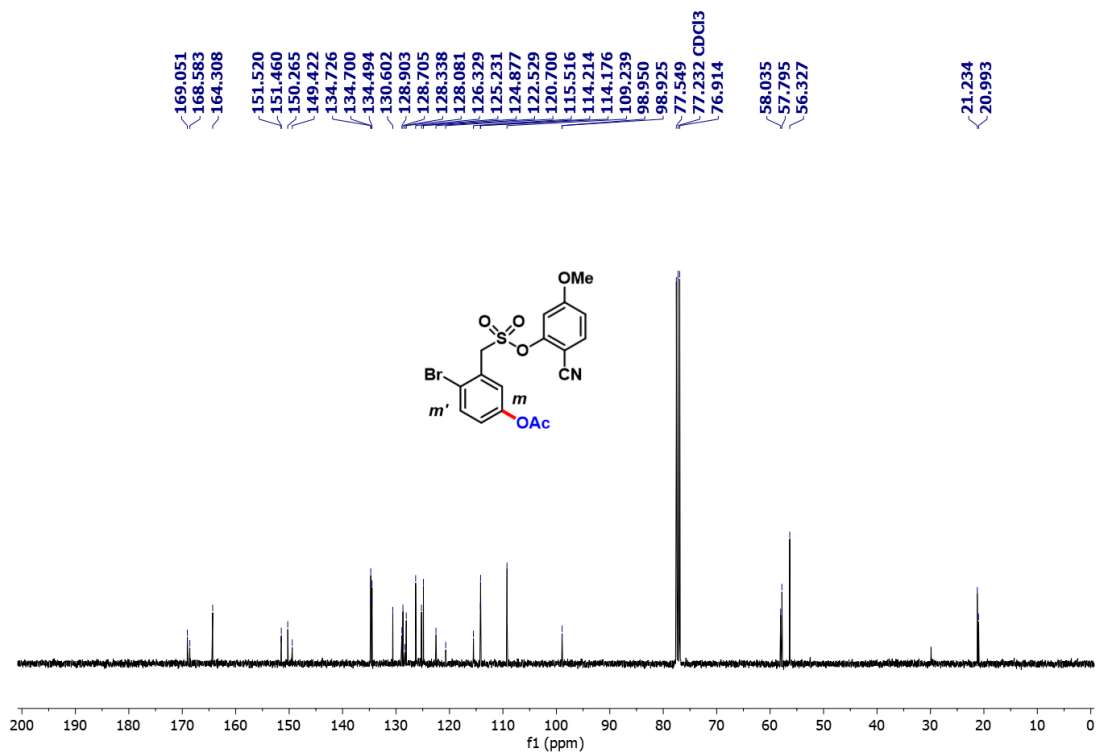
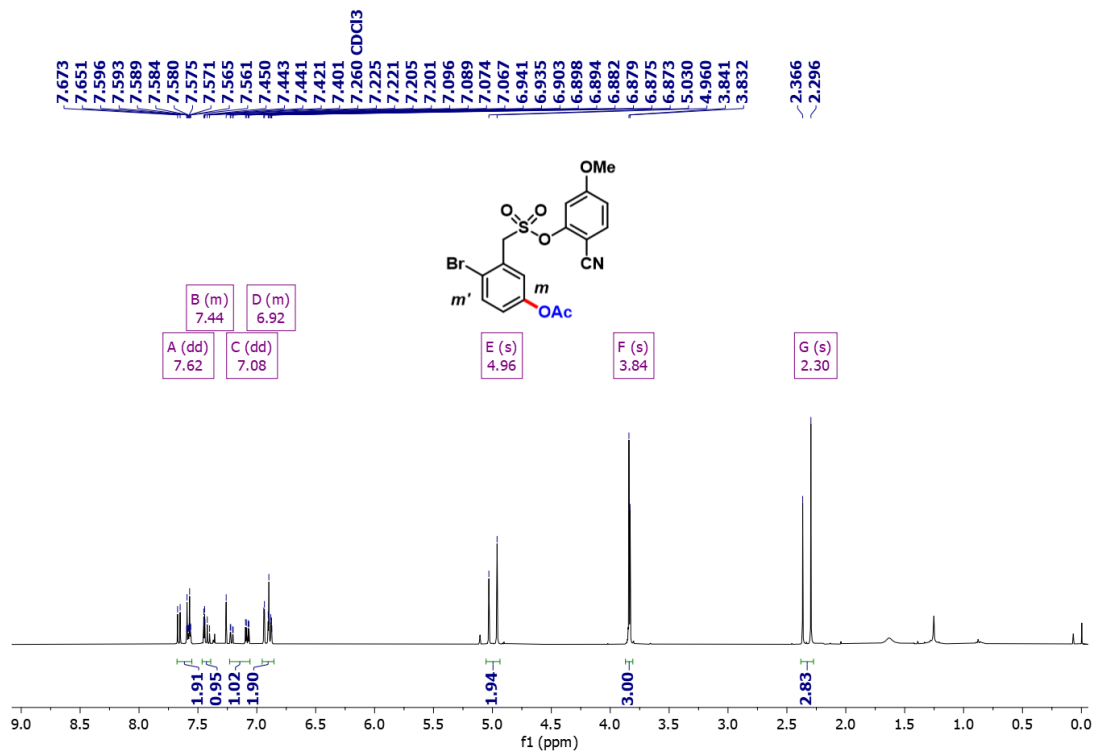


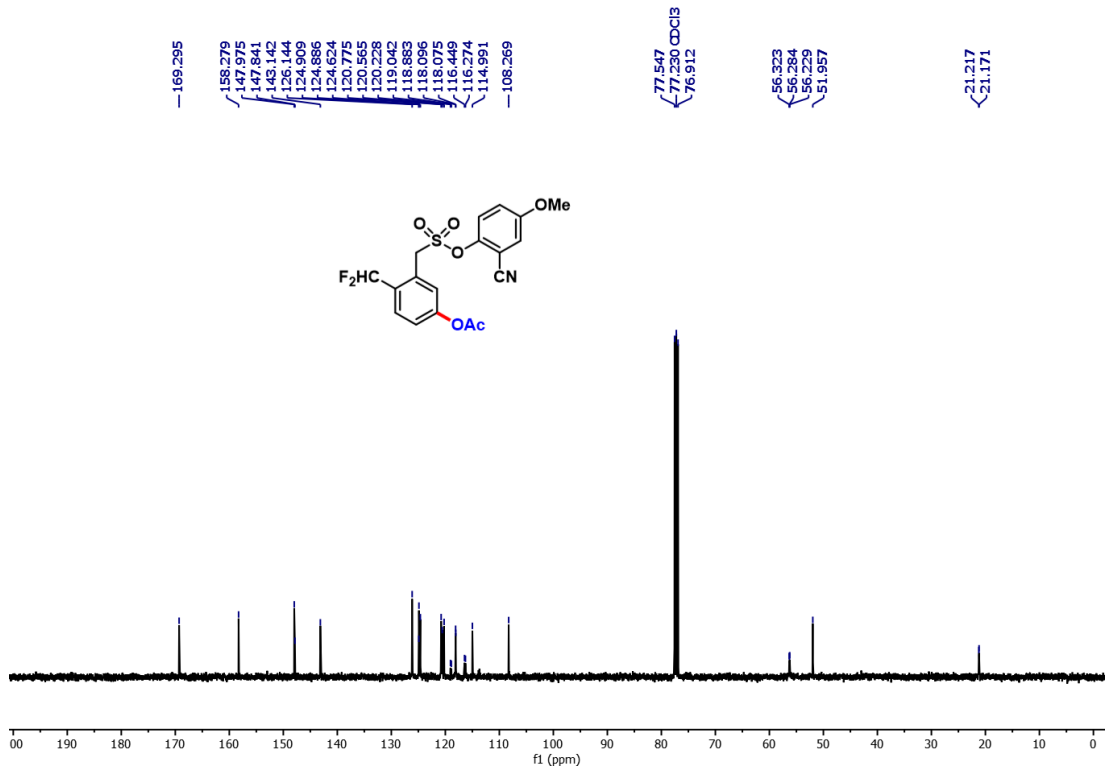
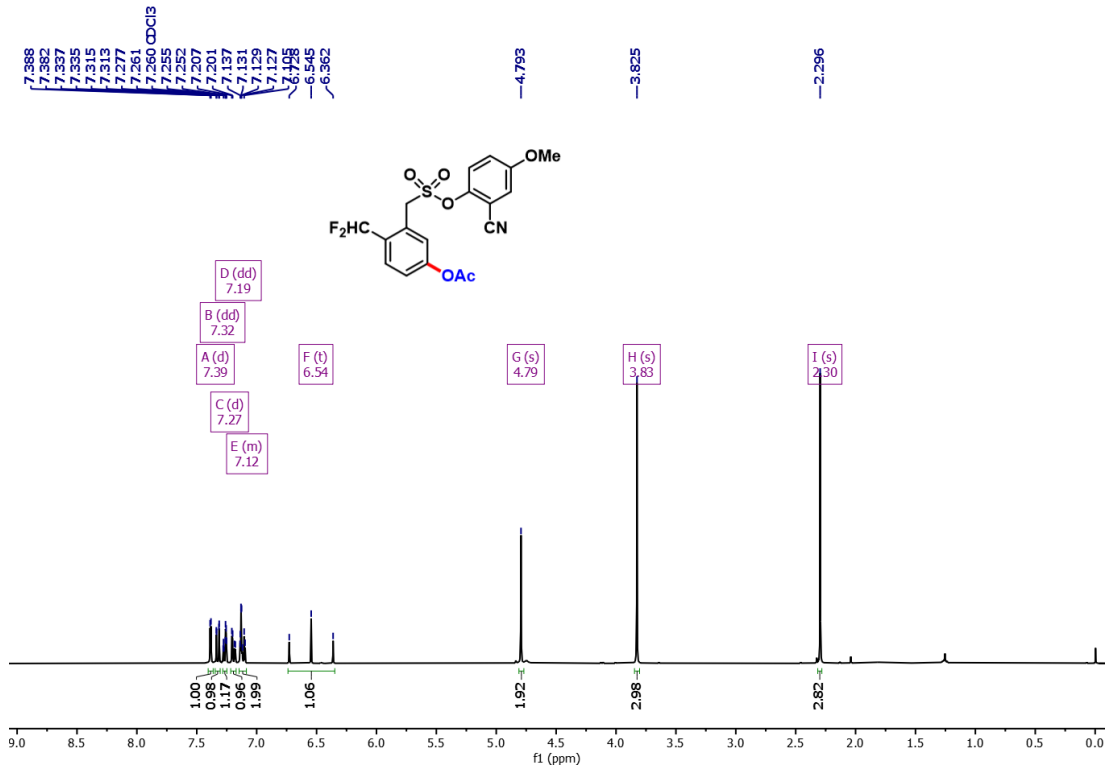




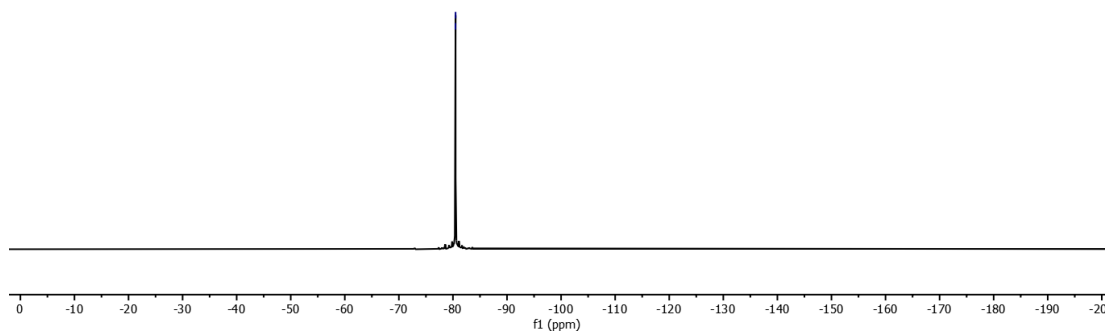
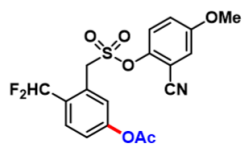


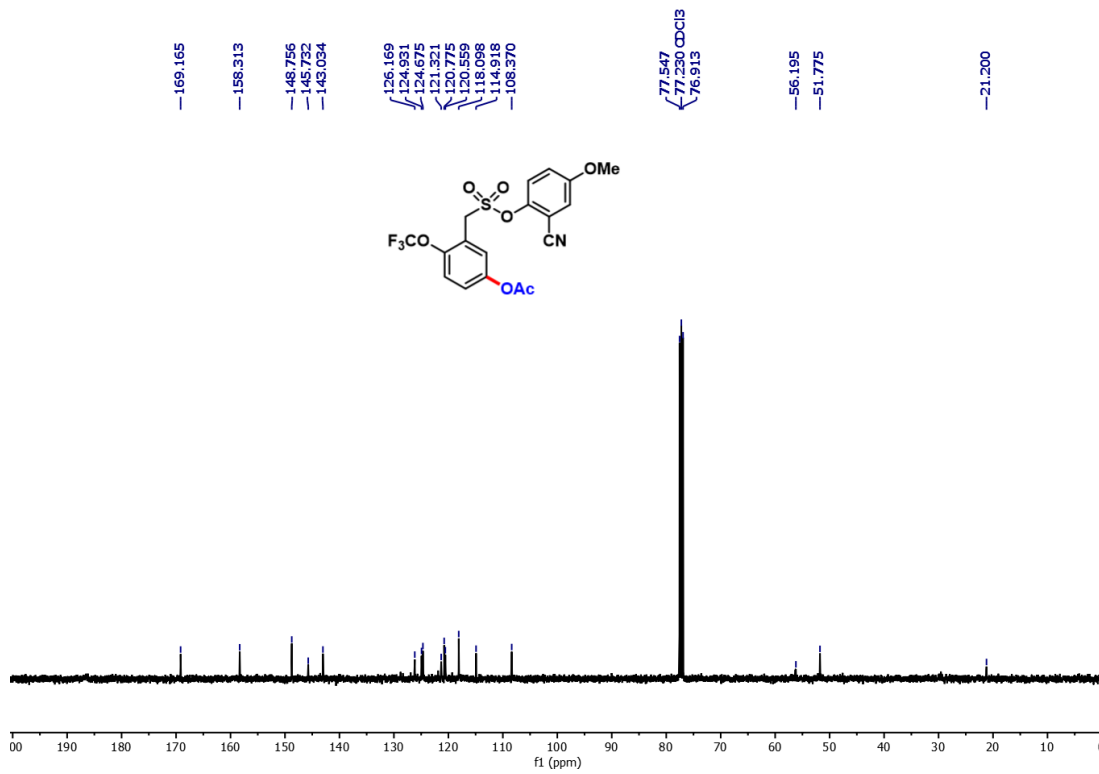
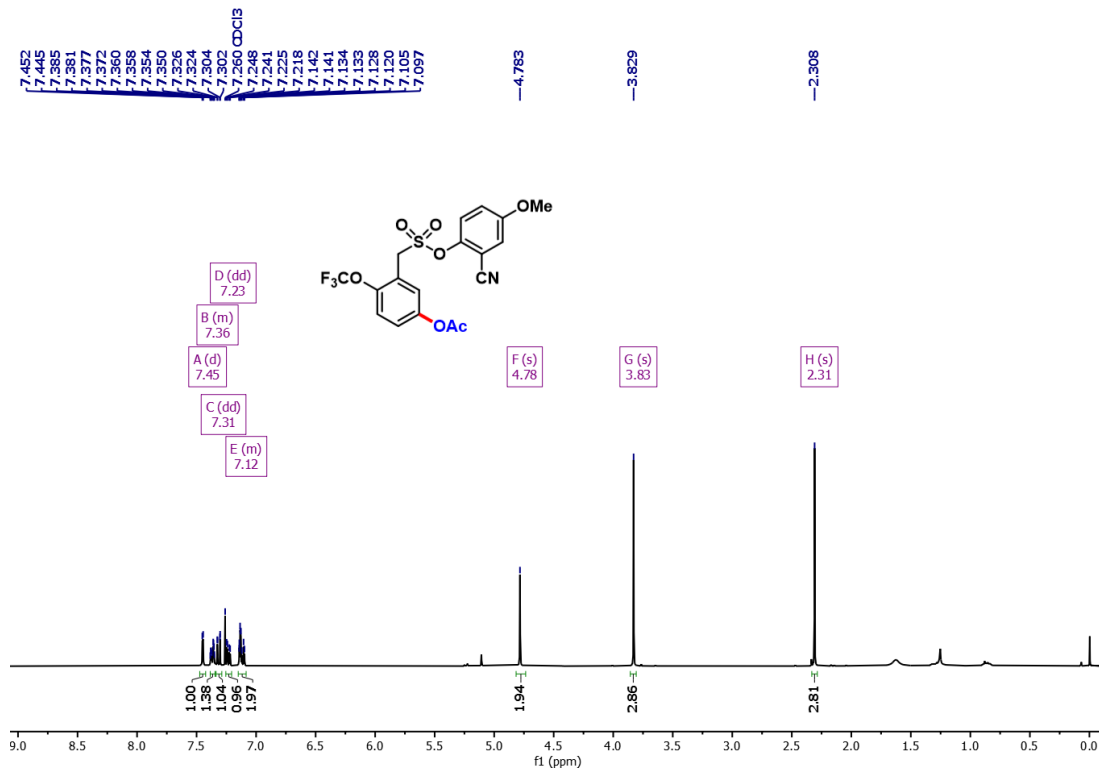






80.455
80.481





-57.106

