

Supporting Information

Directing Group Assisted Rhodium Catalyzed *meta*-C–H Alkynylation of Arenes

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1. General Consideration:

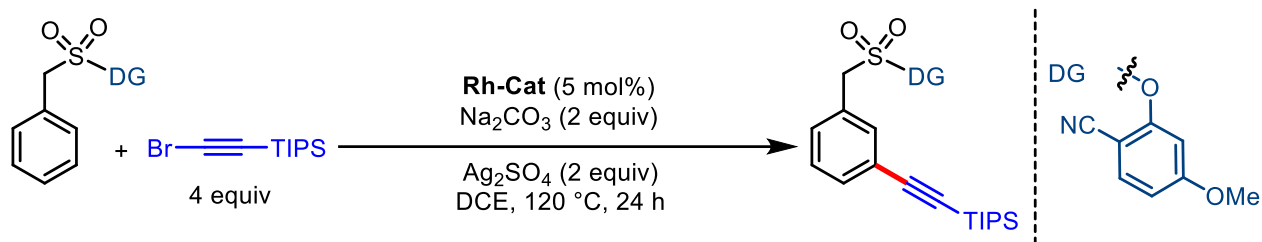
a. Reagents Information. Unless otherwise stated, all the reactions were carried out in screw cap reaction tubes. All the solvents were bought from Aldrich/Alfa Aesar (India)/TCI (India)/Merck in a sure-seal bottle and were used as received.

Chloro(1,5-cyclooctadiene)rhodium(I) dimer, $[\text{Rh}(\text{COD})\text{Cl}]_2$ was bought from TCI (India). Cupric chromite ($\text{Cu}_2\text{Cr}_2\text{O}_5$) is obtained from Sigma Aldrich, silver sulphate is obtained from Merck. All the benzyl chlorides and bromides were bought from Aldrich/Alfa Aesar and (India)/TCI (India)/Spectrochem. For column chromatography, silica gel (100–200 mesh) from SRL Co. was used. A gradient elution using pet ether and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel 60F254).

b. Analytical information. All isolated compounds are characterized by ^1H NMR, ^{13}C NMR spectroscopy. NMR spectra were recorded either on a Bruker 500 or 400 MHz instrument. All ^1H NMR experiments are reported in units, parts per million (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm) in the deuterated solvent, unless otherwise stated. All ^{13}C NMR spectra were reported in ppm relative to CDCl_3 (77.23 ppm), All coupling constants were reported in Hertz (Hz) and all were obtained with ^1H decoupling. High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer.

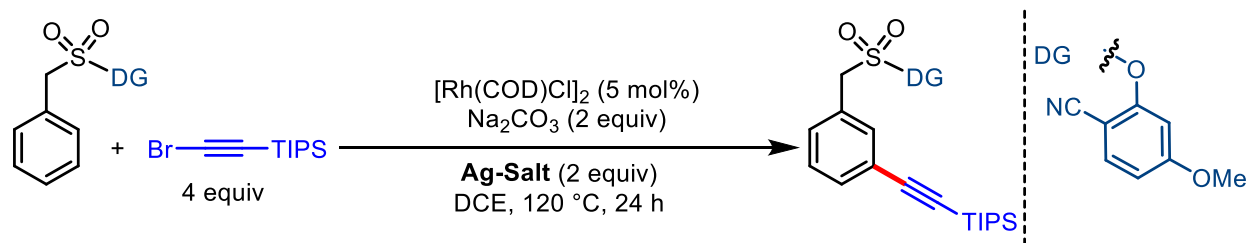
2. Optimization details for rhodium-catalyzed *meta*-C–H alkylation

Table S1. Optimization of Rh-catalyst



Entry	Rh-Catalyst	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	$[\text{RhCp}^*\text{Cl}_2]_2$	n.d.	-
2	$[\text{Rh}(\text{COD})\text{Cl}]_2$	40	10:1
3	$\text{Rh}(\text{OAc})_2$	N.d.	-
4	$\text{Rh}(\text{PPh}_3)_3\text{Cl}$	n.d.	-
5	$[\text{Rh}(\text{COD})(S)\text{-BINAP}]\text{BF}_4$	trace	-
6	Without Rh-catalyst	n.d.	-

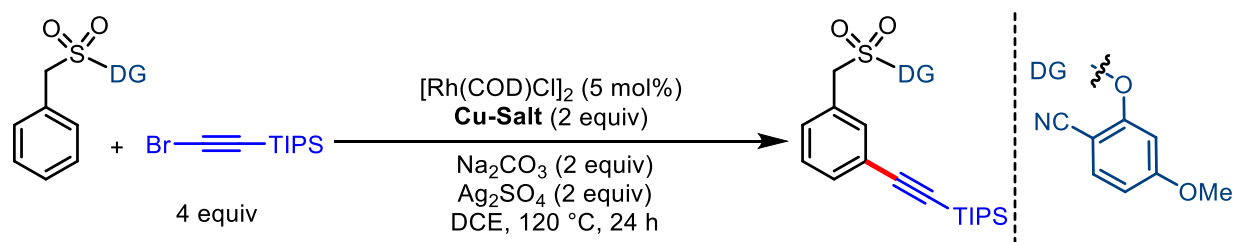
Table S2. Optimization of silver salt



Entry	Ag-salt	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	AgOAc	15	3:1
2	Ag_2CO_3	20	1:1
3	AgTFA	trace	-
4	AgNO_2	trace	-
5	AgNO_3	trace	-

6	AgI	n.d.	-
7	Ag₂SO₄	40	10:1
8	Ag ₂ O	32	3:1
9	AgCN	n.d.	-
10	AgSbF ₆	n.d.	-
11	AgBF ₄	n.d.	-
12	AgPF ₆	n.d.	-

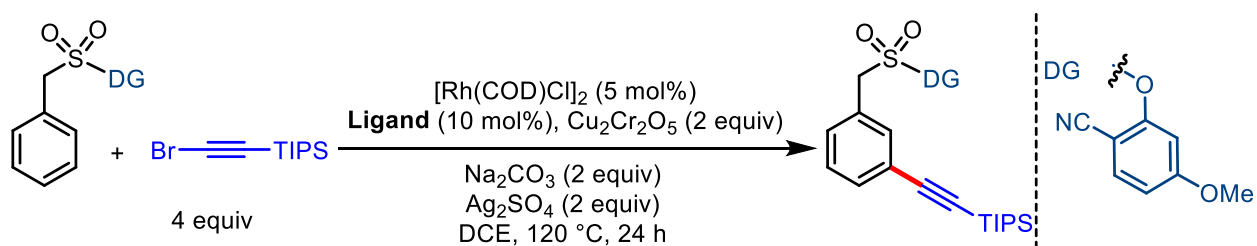
Table S3. Optimization of Cu-salt



Sr. No.	Cu-salt	HPLC yield (%)	Selectivity (<i>m</i> : <i>others</i>)
1	CuCl ₂	39	2:1
2	CuCl	trace	-
3	Cu(TFA) ₂	trace	-
4	Cu(OAc) ₂ ·H ₂ O	20	2:1
5	Cu ₂ O	trace	-
6	CuSCN	trace	-
7	Cu(OTf) ₂	trace	-
8	Cu₂Cr₂O₅	55	10:1
9	CuO	trace	-
10	CuF ₂	26	3:1
11	Cu(NO ₃) ₂ ·3H ₂ O	20	2:1

12	CuBr ₂	25	2:1
13	CuSO ₄	trace	-
14	Cr ₂ O ₃	trace	-
15	CuO + Cr ₂ O ₃ (2:1)	31	10:1

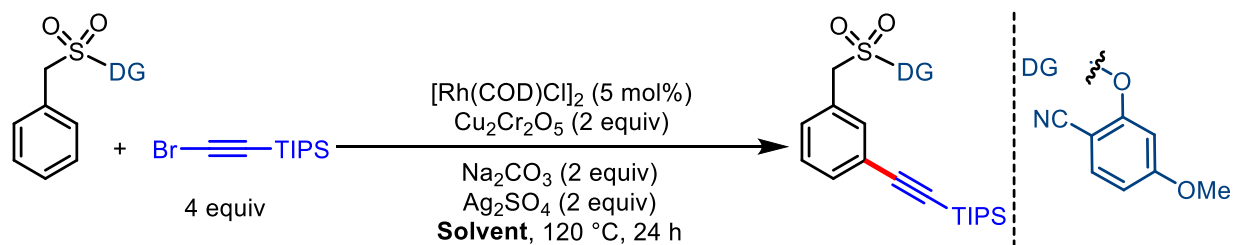
Table S4. Optimization of ligand



Sr. No.	Nitrogen based ligand	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	No Ligand	55	10:1
2	Pyridine	n.d.	-
3	DMAP	n.d.	-
4	Quinoline	trace	-
5	2-Cl-Quinoline	trace	-
6	2,2'-Bipyridine	n.d.	-
7	Phenanthroline	n.d.	-
8	Bathophenanthroline	n.d.	-
9	2,3,8,9-Tetramethyl-1-10-phenanthroline	n.d.	-
10	Trans-1,2-Diaminocyclohexane	n.d.	-
11	<i>N, N</i> -Dimethylethylenediamine	n.d.	-

12	4,7-Dihydroxy-1,10-phenanthroline	n.d.	-
13	4,4'-Di- <i>tert</i> -butyl-2,2'-bipyridyl	trace	-
14	Neocuproin	n.d.	-
15	(+,-)-BINAM	n.d.	-
16	2,2'-Biquinoline	n.d.	-
17	Ethylenediamine	15	3:1

Sr. No.	Phosphine Based Ligand	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	No Ligand	55	10:1
2	PPh ₃	20	-
3	SPhos	10	-
4	XPhos	40	-
5	RuPhos	30	-
6	DavePhos	20	-
7	JohnPhos	20	-
8	CyJohnPhos	15	-
9	MePhos	10	-
10	^t Bu-MePhos	10	-
11	TrippyPhos	15	-
12	XantPhos	18	-
13	S-XylPhos	20	-

Table S5. Optimization of solvent

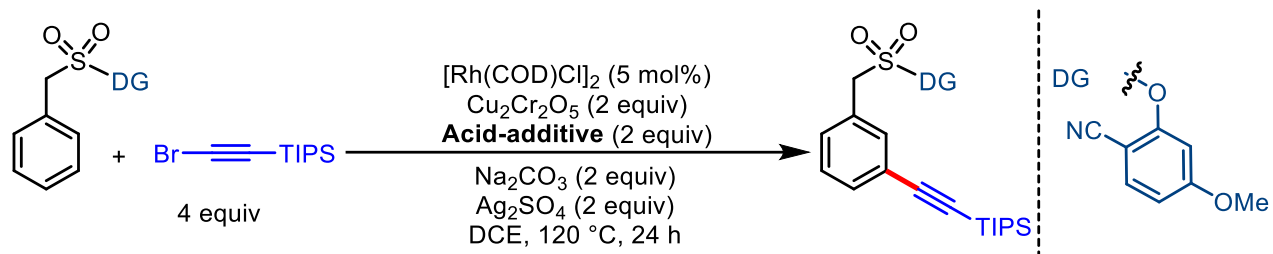
Sr. No.	Solvent	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	DCE	55	10:1
2	DCM	40	8:1
3	CHCl_3	38	8:1
4	CCl_4	n.d.	-
5	HFIP	n.d.	-
6	TFE	trace	-
7	THF	n.d.	-
9	<i>m</i> -Xylene	16	-
8	Toluene	10	-
10	TFT	15	-
11	Benzene	n.d.	-
12	MeOH	trace	-
13	MeCN	n.d.	-
14	PhCN	n.d.	-
15	1,2,3-TCP	n.d.	-
16	NMP	n.d.	-
17	TBME	n.d.	-

18

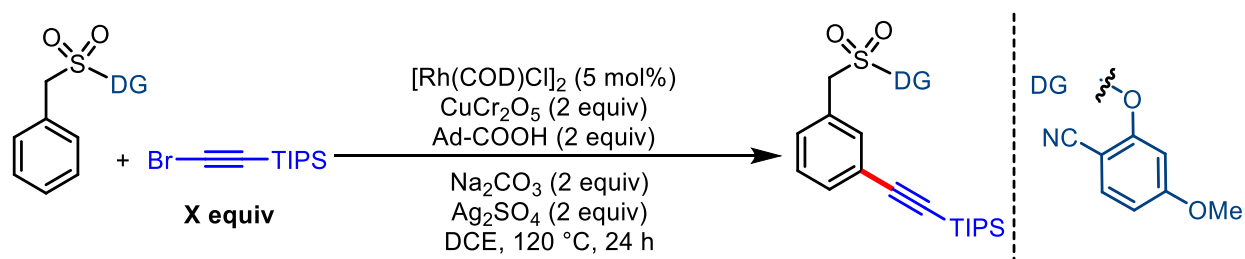
Acetone

n.d.

-

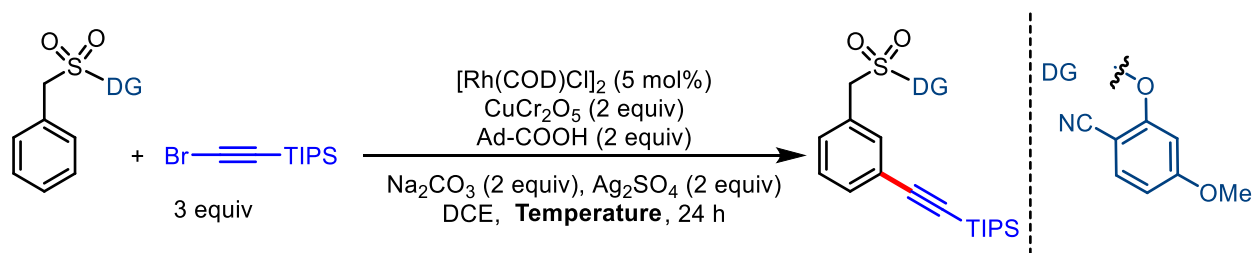
Table S6. Optimization of acid-additive

Sr. No.	Additives	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	TFA	39	6:1
2	AcOH	20	-
3	Pivalic acid	37	3:1
4	Picolinic acid	trace	-
5	Adamantane-1-carboxylic acid	66	10:1
6	Formic acid	trace	-
7	Benzoic acid	12	-
8	Triflic acid	n.d.	-
9	Cyclohexyl-1-carboxylic acid	n.d.	-
10	Propionic Acid	n.d.	-

Table S7. Optimization of alkyne amount

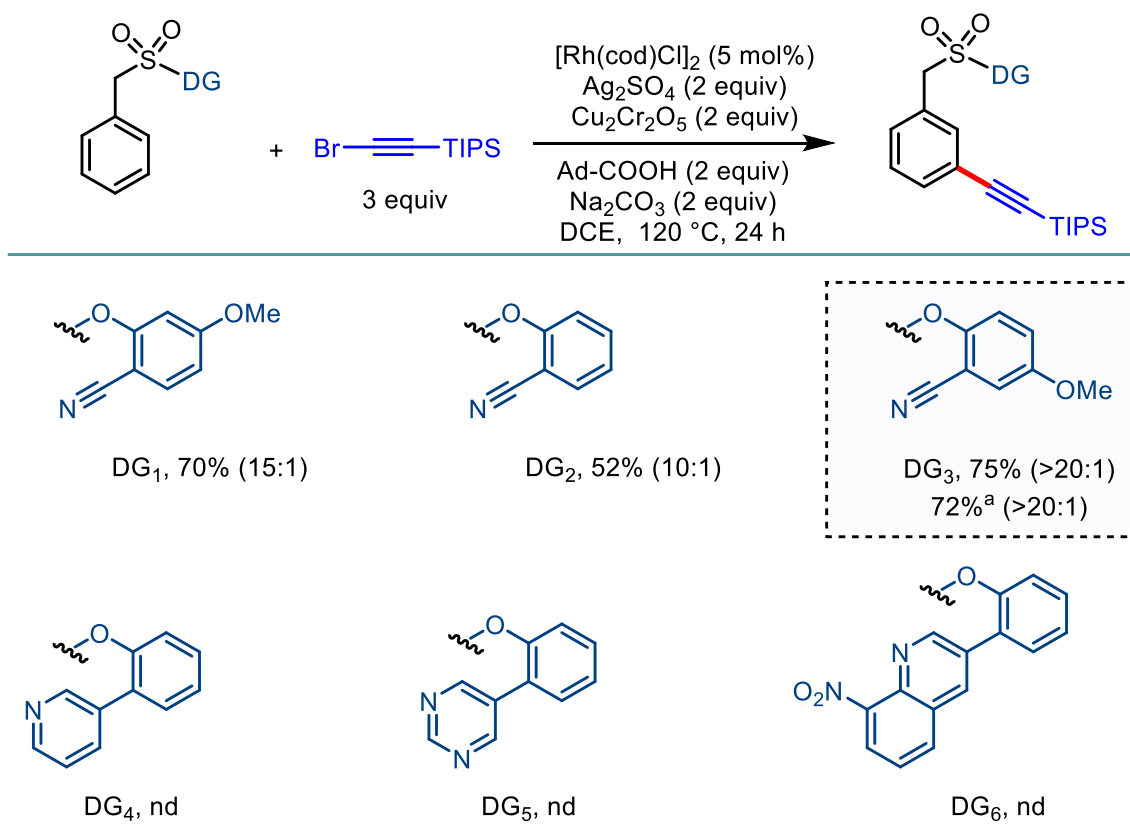
Sr. No.	Alkyne amount (equiv)	HPLC yield (%)	Selectivity (<i>m:others</i>)
1	1	30	-
2	2	35	-
3	2.5	60	10:1
4	3	70	15:1
5	4	66	10:1
6	5	62	8:1

Table S8. Optimization of temperature



Sr. No.	Temperature (°C)	HPLC yield (%)	Selectivity (<i>m: others</i>)
1	80	40	5:1
2	90	45	6:1
3	100	52	8:1
4	110	60	12:1
5	120	70	15:1
6	130	58	15:1

Table S9. Optimization of directing groups (DGs)



meta:others ratio is given in the parenthesis, ^aisolated yield

3. General procedures for the preparation of substrates and coupling partners

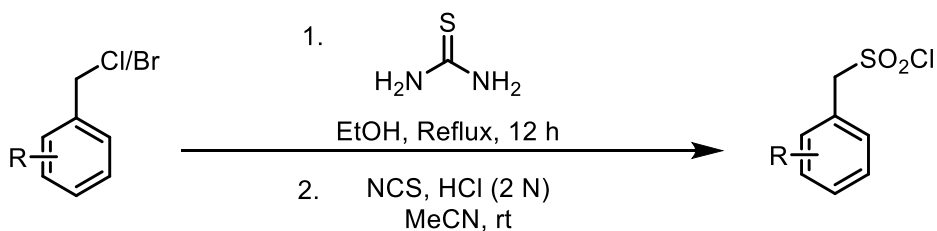
a. Preparation of 2-Hydroxy-5-methoxybenzonitrile (DG₃)¹⁻²



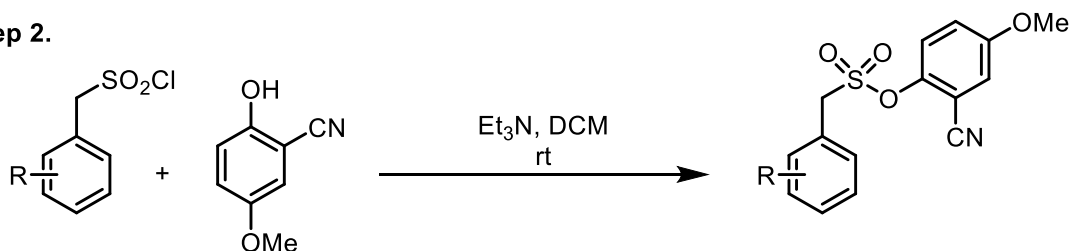
In an oven dried round bottom flask (250 mL), charged with stir-bar, 2-Hydroxy-5-methoxy benzaldehyde (20 mmol) and NaN_3 (3 equiv.) were taken. Acetonitrile (60 mL) was added to it and stirred at room temperature for 15 mins. Then 3 equiv. of triflic acid was added to the mixture in portion with a plastic dropper. After the addition, the reaction was allowed to stir at room temperature for 12 hr. Upon completion the organic solvent was evaporated under reduced pressure. The solid residue was dissolved in ethyl acetate and washed with saturated NaHCO_3 solution (3 times). The organic fraction was then dried over anhydrous Na_2SO_4 and purified through column chromatography using silica gel and petroleum ether/ethyl acetate (80/20, v/v) as the eluent. 1-2 Quantitative conversion; off-white solid.

(b) General procedures A for preparation of sulfonyl ester scaffolds¹⁻²

Step 1.



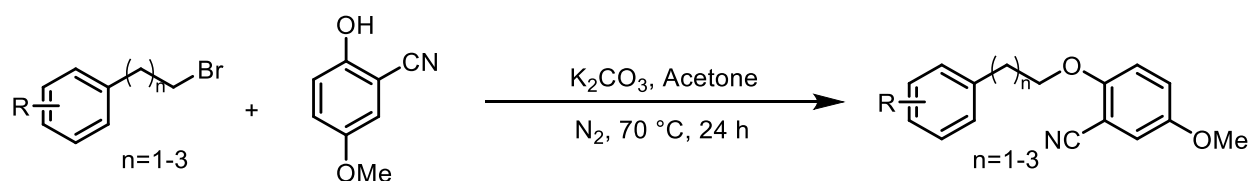
Step 2.



Step 1. An oven dried clean round bottom flask was charged with magnetic stir-bar, substituted benzyl chloride (10 mmol) and thiourea (10 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 obtain white solid thiourea 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 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. The solution was evaporated under reduced pressure to remove the CH₃CN. The remaining aqueous portion was extracted with ethyl acetate. The organic portion was dried over anhydrous Na₂SO₄ and the crude mixture was evaporated and purified by column chromatography using silica gel and ethyl acetate/petroleum ether as the eluent. Quantitative yield.

Step 2. To an ice-cold solution of 2-hydroxy-5-methoxybenzonitrile (5 mmol) and triethylamine (1.5 equiv, 1.04 mL) in 10 mL dichloromethane under nitrogen atmosphere, substituted benzyl sulfonfyl chloride was added portion wise. Stirring was continued for additional 20 minutes, after that the ice bath was removed and the reaction mixture was left for vigorous stirring at room temperature for overnight. CH₂Cl₂ was removed under reduced pressure. The residual was diluted and extracted with ethyl acetate (3 x 20 mL) and brine solution (3 x 10 mL). The organic layer was collected and 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.

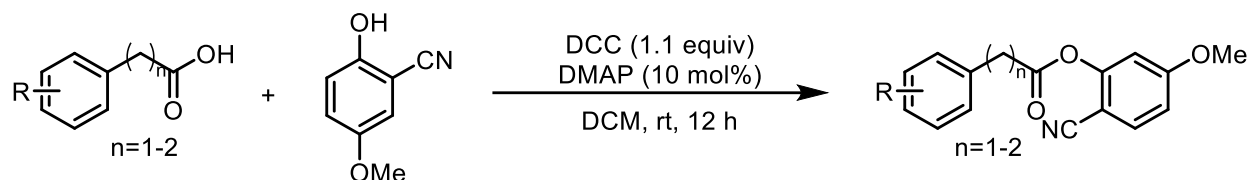
(c) General procedures B for preparation of ether scaffolds³



A clean, oven-dried screw cap reaction tube with previously placed magnetic stir-bar was charged with 2-hydroxy-5-methoxybenzonitrile (1 equiv, 3 mmol), and K₂CO₃ (2 equiv, 6 mmol). The cap was fitted with a rubber septum and the reaction tube was evacuated and back filled with nitrogen and this sequence was repeated three additional times. Now under the positive flow of nitrogen 6

mL acetone was added to the reaction mixture. Then, phenyl alkyl bromide (1.2 equiv, 3.6 mmol) was added by using syringe. The reaction mixture was vigorously stirred at 70 °C for 24 h. Reaction mixture was dried under rotary evaporator. The reaction mixture was extracted thrice with ethyl acetate (3 x 20 mL) and brine solution (3 x 10 mL). The organic layer was collected and dried over anhydrous Na₂SO₄. The solvent was evaporated under reduced pressure. The crude mixture was purified by column chromatography using neutral alumina and ethyl acetate/ petroleum ether (5/95, v/v) as the eluent.

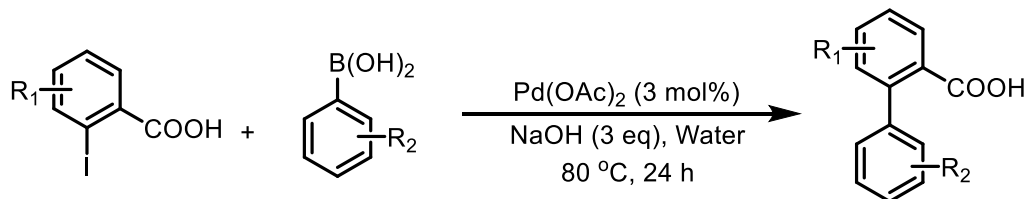
(d). General procedure C for synthesis of carbonyl ester⁴



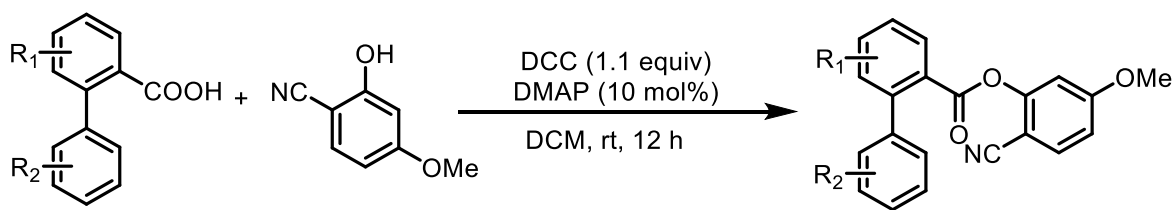
To a stirred solution of carboxylic acid (1 equiv, 10 mmol) and DMAP (1 mmol) in 30 mL anhydrous CH₂Cl₂, 2-hydroxy-4-methoxybenzonitrile (1.5 equiv, 15 mmol) was added. After 15 minute of stirring, DCC (11 mmol) was added to the reaction mixture at 0°C and then allowed to stir overnight at room temperature. Upon completion of reaction, precipitated urea is then filtered off. Filtrate is evaporated and the residue was dissolved in 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.

(e). General procedure D for synthesis of biphenyl carbonyl ester⁵

Step 1:



Step 2:

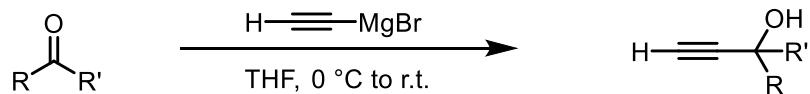


Step 1: A clean, oven-dried screw cap reaction tube with previously placed magnetic stir-bar was charged with 2-iodobenzoic acid derivatives (1 equiv, 3 mmol), corresponding boronic acid (1.2 equiv, 3.6 mmol), sodium hydroxide (3 equiv, 9 mmol) Pd(OAc)₂ (3 mol %) and water 9 mL. The reaction tube was 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. Compound was isolated using was purified by column chromatography on silica gel (eluent: ethyl acetate/petroleum ether).

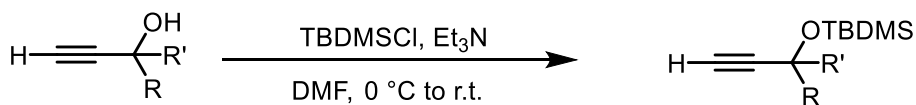
Step 2: To a stirred solution of carboxylic acid (1 equiv, 3 mmol) and DMAP (1 mmol) in 30 mL anhydrous CH₂Cl₂, 2-hydroxy-4-methoxybenzonitrile (1.5 equiv, 4.5 mmol) was added. After 15 minute of stirring, DCC (3.3 mmol) was added to the reaction mixture at 0 °C and then allowed to stir overnight at room temperature. Upon completion of reaction, precipitated urea is then filtered off. Filtrate is evaporated and the residue was dissolved in 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.

(f) General procedure E for synthesis of alkynyl bromide⁶

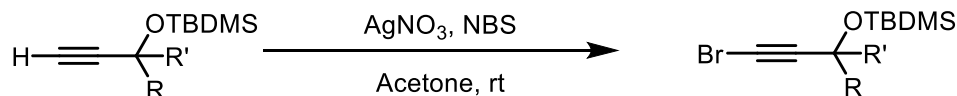
Step 1.



Step 2.



Step 3.

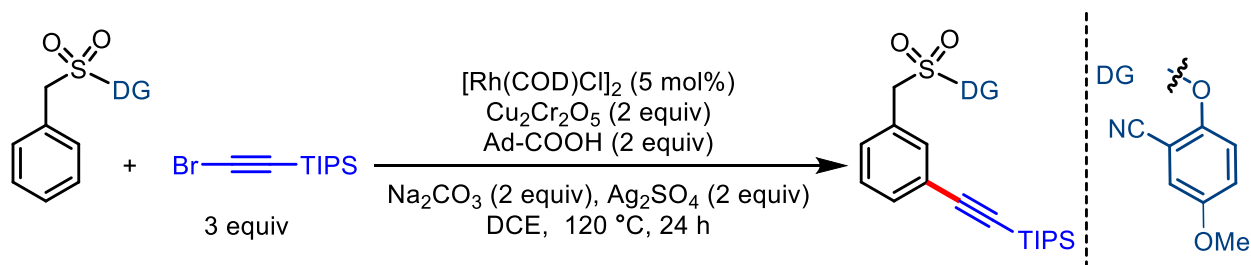


Step 1. To a solution of ketone (10 mmol) in THF (15 mL) kept ice bath ethynylmagnesium bromide (0.5 M in THF, 30 mL, 15 mmol) was added slowly. Upon completion of addition, ice bath was removed and the mixture was stirred for 4 hours at room temperature. The reaction was quenched with 0.5 N HCl (20 mL). The aqueous layer was extracted with ethyl acetate (10 x 3 mL). Combined organic layers were dried with Na₂SO₄ and concentrated in vacuo. Desired propargyl alcohol was used directly without further purification.

Step 2. To a solution of propargyl alcohol (10 mmol) in DMF kept in ice bath triethylamine (1.80 mL, 12.5 mmol) was added then *tert*-Butyldimethylsilyl chloride (TBDMSCl) (1.8 mL, 10 mmol) was added to this solution. After completion of addition, the ice bath was removed. The reaction was stirred for 4 hours at room temperature. The reaction was quenched by sat. aqueous sodium bicarbonate (10 mL). The organic phase was collected and the aqueous layer was further extracted with DCM (10 x 2 mL) twice. The combined organic layers were dried with Na₂SO₄ and concentrated. Crude residue was purified by column chromatography (1% ether in hexane) to give desired silyl ether.

Step 3. In a round bottom flask, wrapped with alumina foil to a solution of alkyne (5 mmol) in acetone (25 mL) *N*-bromo succinimide (0.92 mg, 5.5 mmol) and silver nitrate (84.92 mg, 0.5 mmol) were added at room temperature. The solution was stirred for 4 hours at room temperature in darkness. The reaction was quenched with cold water (5 mL) and extracted with pet ether (10 x 3). The combined organic layers were dried with Na₂SO₄ and concentrated to get desired alkynyl bromide.

(g) General procedure F for rhodium-catalyzed *meta*-alkynylation of arene with protected bromoacetylene



In an oven-dried screw cap reaction tube charged with a magnetic stir-bar sulphonyl ester scaffold (0.1 mmol), [Rh(COD)Cl]₂ (5 mol%, .005 mmol), Cu₂Cr₂O₅ (2 equiv, 0.2 mmol), Ad-COOH (2

equiv, 0.2 mmol), Na₂CO₃ (2 equiv, 0.2 mmol), Ag₂SO₄ (2 equiv, 0.2 mmol) were taken. After that 2 mL DCE was added followed by bromo acetylene (3 equiv) was added with a microlitre pipette under aerobic condition. The tube was tightly capped and placed in a preheated oil bath at 120 °C and the reaction mixture was stirred for 24 h. After completion of the reaction, the reaction mixture was then cooled to room temperature and filtered through a celite pad with ethyl acetate. The filtrate was washed with warm sat. NaHCO₃ solution and then the organic layers are collected and concentrated and the desired *meta*-alkynylated compounds were purified using column chromatography using silica gel and ethyl acetate/petroleum ether as the eluent.

(h) General procedure for different post synthetic application⁶

(i) Procedure for directing group removal of sulfonyl ester scaffolds from alkynylated product:

An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, alkynylated product (**3a**) (0.1 mmol) and 2 mL of THF was added to it. Then 1.2 equiv TBAF was added to the reaction mixture. The reaction mixture was stirred vigorously at room temperature for 12 h. After the completion of the reaction the solvent was removed under reduced pressure. To the reaction mixture, 5 mL of water was added and extracted with ethyl acetate (3 x 10 mL). directing group went to organic layer, the organic layer was dried over Na₂SO₄ and the water part was acidified with 1 mL 2(N) HCl and then dried under reduced pressure. The residue, after evaporating the water completely was washed with MeOH to get the desired alkynylated product (**9**).

(ii) Removal of –SO₂-DG group (modified Julia olefination) from alkynylated product

To a dried round bottom flask equipped with a magnetic stir bar was added 0.3 mL of LDA solution (2M in THF) in 5 mL of dry THF solvent. The solution was cooled to -78 °C. Then a solution in benzaldehyde (0.4 mmol) in dry THF (20 mL) and alkynylated product (**3a**) (0.3 mmol) was added slowly to the LDA/THF solution for 1 h at -78 °C. The reaction mixture was stirred overnight while warming to room temperature. After the reaction mixture was quenched using saturated NH₄Cl solution and extracted with ethyl acetate. Combined organic layers were dried over anhydrous Na₂SO₄. The crude mixture was concentrated under reduced pressure and purified by column

chromatography using silica gel and ethyl acetate/petroleum ether (2/98, v/v) as the eluent to give the desired product (**10**).

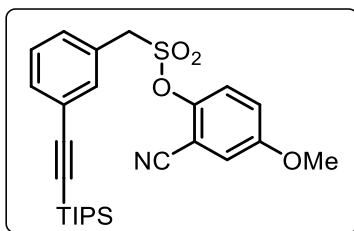
(iii) Synthesis of ketone derivative from alkynylated product from alkynylated product

To a dried reaction tube solution of (**3a**) (0.1 mmol) formic acid (2 mL) was added, then the reaction was stirred vigorously under reflux condition at 100 °C for 1 h. After completion, the reaction mixture was concentrated under reduced pressure. After that, water was added and extracted with dichloromethane (3 x 5 mL). The combined organic phases were dried over Na₂SO₄. Followed by removal of solvent under reduced pressure. The crude product was purified by column chromatography using silica gel and ethyl acetate/petroleum ether (6/94, v/v) as the eluent to give the desired product (**11**).

(iv) Procedure of desilylation of triisopropyl group from alkynylated product

An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, then alkynylated product (**7a**) (0.05 mmol) and 1.5 equiv CsF were added. Then 1 mL of CH₃CN was added. The reaction mixture was stirred vigorously for overnight at room temperature. After the completion of the reaction the solvent was removed under reduced pressure. To the reaction mixture, 5 mL of water was added and extracted with ethyl acetate (3 x 10 mL). The organic layer was dried over Na₂SO₄ followed by removal of solvent under reduced pressure. The desired desilylated product (**12**) was isolated by column chromatography and ethyl acetate/petroleum ether (5/95, v/v) as eluent.

4. Characterization data of product



2-Cyano-4-methoxyphenyl (3-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (**3a**):

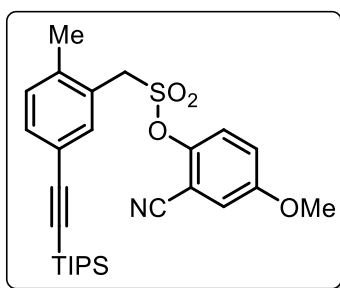
Following the general procedure F, Compound **3a** was obtained from 2-cyano-4-methoxyphenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.58 (s, 1H), 7.52 (d, $J = 7.6$ Hz, 1H), 7.47 (d, $J = 7.9$ Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.31 (d, $J = 9.0$ Hz, 1H), 7.17 – 7.10 (m, 2H), 4.66 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.3, 143.6, 134.5, 133.4, 130.0, 129.2, 126.8, 125.2, 124.8, 120.6, 118.0, 115.12, 108.2, 106.0, 92.3, 58.0, 56.3, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 506.1792 for $(\text{C}_{26}\text{H}_{33}\text{NNaO}_4\text{SSi})$, found 506.1788.

IR (thin film, cm^{-1}): 673, 767, 843, 1031, 1263, 1378, 1493, 1620, 1742, 2155, 2931.



2-Cyano-4-methoxyphenyl (2-methyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (**3b**):

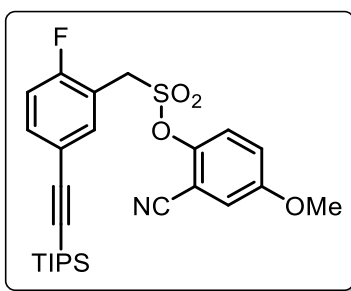
Following the general procedure F, Compound **3b** was obtained from 2-cyano-4-methoxyphenyl 2-methyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: pale yellow oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.55 (d, $J = 1.7$ Hz, 1H), 7.41 (d, $J = 1.8$ Hz, 1H), 7.31 (d, $J = 9.1$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.16 (d, $J = 3.1$ Hz, 1H), 7.12 (dd, $J = 9.1, 3.1$ Hz, 1H), 4.73 (s, 2H), 3.84 (s, 3H), 2.48 (s, 3H), 1.12 (s, 21H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 158.3, 143.5, 139.3, 135.6, 133.5, 131.3, 125.3, 125.2, 122.3, 120.6, 118.0, 115.2, 108.4, 106.2, 91.4, 56.3, 55.5, 19.9, 18.9, 18.5, 11.5, 11.4.

HRMS: [ESI, (+) ve]: calcd. 520.1948 for ($\text{C}_{27}\text{H}_{35}\text{NNaO}_4\text{SSi}$) found 520.1947.

IR (thin film, cm^{-1}): 678, 756, 858, 1033, 1263, 1375, 1620, 1745, 2155, 2920.



2-Cyano-4-methoxyphenyl (2-fluoro-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3c):

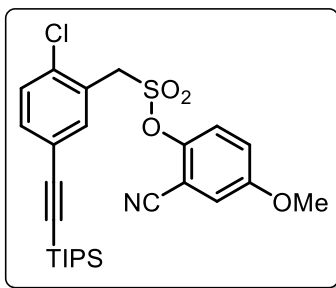
Following the general procedure F, Compound **3c** was obtained from 2-cyano-4-methoxyphenyl 2-fluoro phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: colorless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.64 (dd, $J = 6.8, 1.8$ Hz, 1H), 7.55 – 7.50 (m, 1H), 7.35 (d, $J = 9.0$ Hz, 1H), 7.13 (ddd, $J = 17.9, 11.3, 5.9$ Hz, 3H), 4.73 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 162.2, 160.2, 158.3, 143.4, 136.2 (d, $J = 2.6$ Hz), 135.5 (d, $J = 8.7$ Hz), 125.0, 120.7 (d, $J = 3.9$ Hz), 120.4, 118.0, 116.6, 116.24, 115.0, 114.9, 114.7, 108.4, 105.0, 92.0, 56.3, 51.2(d), 18.9, 17.5 – 17.4, 11.5.

HRMS: [ESI, (+) ve]: calcd. 524.1698 for ($\text{C}_{26}\text{H}_{32}\text{FNNaO}_4\text{SSi}$) found 524.1698.

IR (thin film, cm^{-1}): 673, 767, 1028, 1209, 1376, 1488, 1626, 1736, 2158, 2931.



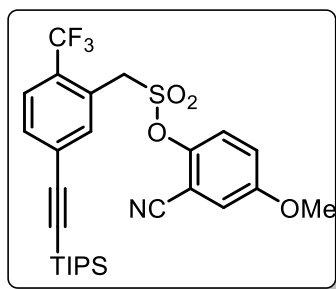
2-Cyano-4-methoxyphenyl (2-chloro-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3d): Following the general procedure F, Compound 3d was obtained from 2-cyano-4-methoxyphenyl 2-chloro phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.69 (d, J = 1.9 Hz, 1H), 7.45 (dd, J = 8.3, 2.0 Hz, 1H), 7.41 (d, J = 8.3 Hz, 1H), 7.34 (d, J = 9.0 Hz, 1H), 7.16 (d, J = 3.0 Hz, 1H), 7.13 (dd, J = 9.0, 3.1 Hz, 1H), 4.89 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 158.3, 143.3, 136.3, 135.7, 134.6, 130.4, 125.3, 125.1, 123.4, 120.6, 118.0, 115.0, 108.4, 104.9, 93.6, 77.5, 76.9, 56.3, 54.9, 18.8, 11.4.

HRMS: [ESI, (+) ve]: calcd. for 540.1402 $\text{C}_{26}\text{H}_{32}\text{ClNO}_4\text{SSiNa}$ found 540.1404

IR (thin film, cm^{-1}): 675, 787, 1038, 1202, 1387, 1495, 1622, 1741, 2155, 2942.



2-Cyano-4-methoxyphenyl (2-trifluoromethyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3e):

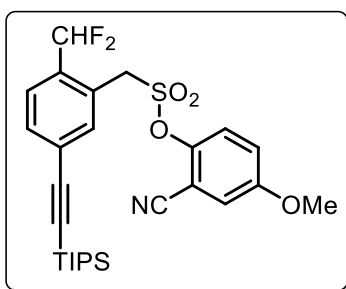
Following the general procedure F, Compound **3e** was obtained from 2-cyano-4-methoxyphenyl 2-trifluoromethyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: brown oil.

^1H NMR (500 MHz, CDCl_3) δ 7.85 (s, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.60 (d, $J = 8.2$ Hz, 1H), 7.36 (d, $J = 9.0$ Hz, 1H), 7.14 (dt, $J = 9.0, 3.0$ Hz, 2H), 4.90 (s, 2H), 3.84 (s, 3H), 1.12 (d, $J = 3.7$ Hz, 21H).

^{13}C NMR (126 MHz, CDCl_3) δ 158.4, 143.2, 136.6, 133.3, 129.9, 129.6, 128.4, 127.2, 127.2, 127.1, 125.2, 125.1, 120.6, 118.1, 114.9, 108.4, 56.3, 54.3, 18.8, 11.4.

HRMS: [ESI, (+) ve]: calcd. 574.1660 for ($\text{C}_{27}\text{H}_{32}\text{F}_3\text{NNaO}_4\text{SSi}$) found 574.1665.

IR (thin film, cm^{-1}): 673, 767, 1031, 1202, 1381, 1497, 1622, 1737, 2155, 2926.



2-Cyano-4-methoxyphenyl (2-difluoromethyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3f):

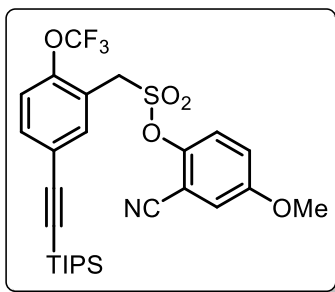
Following the general procedure F, Compound **3f** was obtained from 2-cyano-4-methoxyphenyl 2-difluoromethyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: pale brown oil.

^1H NMR (400 MHz, CDCl_3) δ 7.67 (d, $J = 1.8$ Hz, 1H), 7.53 (dd, $J = 8.5, 1.8$ Hz, 1H), 7.36 (d, $J = 8.8$ Hz, 1H), 7.20 – 7.10 (m, 3H), 6.56 (t, $J = 73.1$ Hz, 1H), 4.78 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

^{13}C NMR (126 MHz, CDCl_3) δ 158.3, 150.1, 143.3, 136.5, 135.2, 125.0, 121.8, 120.6, 119.4, 119.0, 118.1, 116.2, 115.0, 108.3, 104.9, 92.7, 56.3, 52.0, 18.7, 11.5.

HRMS: [ESI, (+) ve]: calcd. 572.1499 for ($\text{C}_{27}\text{H}_{33}\text{F}_2\text{KNO}_4\text{SSi}$) found 572.1499.

IR (thin film, cm⁻¹): 668, 771, 1029, 1209, 1378, 1501, 1627, 1735, 2154, 2956.



2-Cyano-4-methoxyphenyl (2-trifluoromethoxy-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3g):

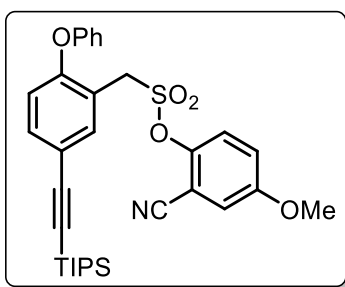
Following the general procedure F, Compound **3g** was obtained from 2-cyano-4-methoxyphenyl 2-trifluoromethoxy phenyl methanesulfonate isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (4:96 v/v); R_f: 0.4 (20% EA-PE); Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 8.6, 2.1 Hz, 1H), 7.34 (d, *J* = 9.1 Hz, 1H), 7.18 – 7.08 (m, 3H), 4.77 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 158.4, 148.0, 136.5, 135.1, 125.0, 123.0, 120.6, 120.0, 119.9, 119.5, 118.1, 115.0, 114.9, 114.9, 114.9, 108.4, 104.6, 93.5, 56.3, 51.9, 18.7, 11.5.

HRMS: [ESI, (+) ve]: calcd. 590.1615 for (C₂₇H₃₂F₃NNaO₅SSi) found 590.1612.

IR (thin film, cm⁻¹): 675, 758, 1029, 1212, 1378, 1489, 1619, 1734, 2155, 2917.



2-Cyano-4-methoxyphenyl (2-phenoxy-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3h):

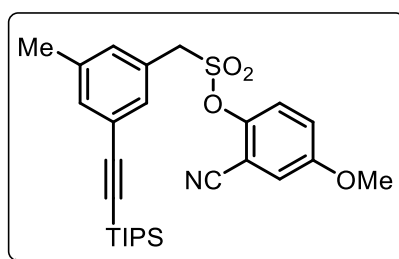
Following the general procedure F, Compound **3h** was obtained from 2-cyano-4-methoxyphenyl 2-phenoxy phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f: 0.4 (20% EA-PE); Appearance: yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.37 – 7.28 (m, 5H), 7.16 – 7.11 (m, 3H), 7.09 (t, *J* = 2.0 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.60 (s, 2H), 3.84 (s, 3H), 1.11 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 158.3, 157.4, 155.2, 143.4, 130.2, 129.8, 129.3, 128.5, 126.3, 125.2, 123.2, 121.4, 120.6, 118.0, 105.2, 93.2, 57.7, 56.3, 18.8, 18.5, 11.4.

HRMS: [ESI, (+) ve]: calcd. 598.2054 for (C₃₂H₃₇NNaO₅Si) found 598.2057.

IR (thin film, cm⁻¹): 676, 844, 999, 1090, 1170, 1221, 1317, 1382, 1486, 1601, 1720, 2157, 2236.



2-Cyano-4-methoxyphenyl (3-methyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (**3i**):

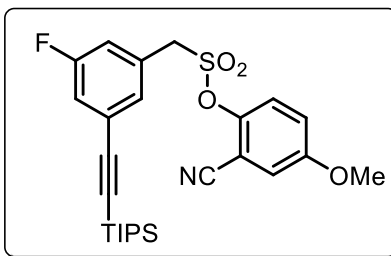
Following the general procedure F, Compound **3i** was obtained from 2-cyano-4-methoxyphenyl 3-methyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f: 0.4 (20% EA-PE); Appearance: brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.38 (s, 1H), 7.33 (d, *J* = 9.1 Hz, 2H), 7.27 (s, 1H), 7.16 (d, *J* = 3.1 Hz, 1H), 7.13 (dd, *J* = 9.0, 3.2 Hz, 1H), 4.62 (s, 2H), 3.84 (s, 3H), 2.35 (s, 3H), 1.12 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 158.2, 143.7, 139.2, 134.0, 131.9, 131.7, 126.6, 125.2, 124.6, 120.7, 118.0, 115.1, 108.2, 106.3, 94.0, 91.6, 90.8, 58.0, 56.3, 21.3, 18.9, 18.6, 11.5.

HRMS: [ESI, (+) ve]: calcd. 520.1948 for (C₂₇H₃₅NNaO₄SSi) found 520.1948.

IR (thin film, cm⁻¹): 677, 757, 858, 1033, 1212, 1263, 1378, 1493, 1620, 1742, 2155, 2866, 2916.



2-cyano-4-methoxyphenyl (3-fluoro-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3j):

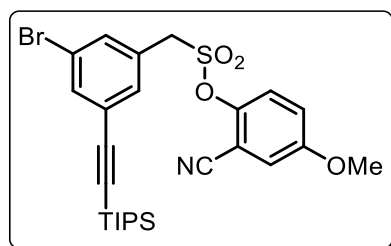
Following the general procedure F, Compound **3j** was obtained from 2-cyano-4-methoxyphenyl 3-fluoro phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f : 0.4 (10% EA-PE); Appearance: yellow liquid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.37 (d, $J = 1.5$ Hz, 1H), 7.34 (dd, $J = 8.6, 0.9$ Hz, 1H), 7.22 (dd, $J = 8.9, 1.5$ Hz, 2H), 7.17 – 7.14 (m, 1H), 7.12 (d, $J = 3.2$ Hz, 1H), 4.64 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 163.5, 161.5, 158.4, 143.4, 130.6, 128.8, 125.2, 120.7, 118.5, 118.3, 118.0, 115.2, 108.2, 93.8, 57.5, 56.3, 18.8, 18.5, 11.4, 0.2.

HRMS: [ESI, (+) ve]: calcd. 524.1698 for $(\text{C}_{26}\text{H}_{32}\text{FNNaO}_4\text{SSi})$ found 524.1698.

IR (thin film, cm^{-1}): 675, 770, 1031, 1209, 1376, 1487, 1626, 1736, 2160, 2964.



2-Cyano-4-methoxyphenyl (3-bromo-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3k):

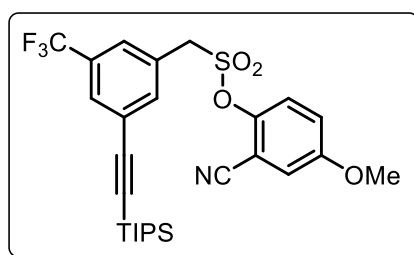
Following the general procedure E, Compound **3k** was obtained from 2-cyano-4-methoxyphenyl 3-bromo phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f: 0.4 (10% EA-PE); Appearance: yellow solid.

¹H NMR (400 MHz, CDCl₃) δ 7.65 (s, 1H), 7.61 (s, 1H), 7.51 (s, 1H), 7.34 (d, *J* = 8.6 Hz, 1H), 7.17 – 7.12 (m, 2H), 4.61 (s, 2H), 3.84 (s, 3H), 1.12 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 158.4, 143.4, 136.0, 133.8, 133.2, 128.7, 126.5, 125.2, 122.8, 120.7, 118.0, 115.2, 108.3, 104.4, 94.2, 57.3, 56.3, 18.9, 11.4.

HRMS: [ESI, (+) ve]: calcd. 584.0897 for (C₂₆H₃₂BrNNaO₄SSi) found 584.0870.

IR (thin film, cm⁻¹): 678, 845, 996, 1030, 1170, 1285, 1382, 1494, 1584, 1733, 2158, 2236, 2866, 2943, 3071.



2-Cyano-4-methoxyphenyl(3-trifluoromethyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate (3l):

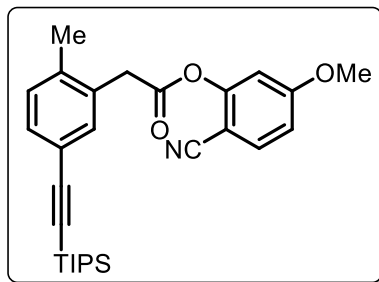
Following the general procedure E, Compound **3l** was obtained from 2-cyano-4-methoxyphenyl 3-trifluoromethyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (3:97 v/v); R_f: 0.4 (20% EA-PE); Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.76 (d, *J* = 6.3 Hz, 1H), 7.70 (s, 1H), 7.35 (dd, *J* = 8.8, 0.6 Hz, 1H), 7.17 – 7.11 (m, 3H), 4.71 (s, 2H), 3.85 (s, 3H), 1.14 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 158.5, 143.4, 137.6, 130.1, 130.1, 130.0, 128.1, 128.1, 127.4, 127.4, 127.4, 127.3, 125.9, 125.7, 125.2, 120.7, 118.0, 115.2, 108.2, 104.3, 94.8, 57.5, 56.3, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 574.1666 for (C₂₇H₃₂F₃NNaO₄SSi) found 574.1660.

IR (thin film, cm⁻¹): 673, 760, 843, 1031, 1202, 1259, 1381, 1497, 1622, 1737, 2155, 2866, 2926.



2-Cyano-5-methoxybenzonitrile 2-(2-methyl-5-((triisopropylsilyl)ethynyl)phenyl)acetate

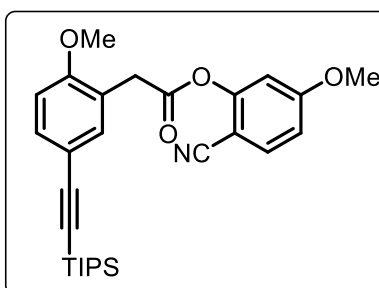
(5a): Following the general procedure F, Compound **5a** was obtained from 2-cyano-5-methoxyphenyl 3-(o-tolyl)acetate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v); R_f: 0.4 (20% EA-PE); Appearance: yellow sticky oil.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.41 (d, *J* = 1.4 Hz, 1H), 7.35 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.95 (s, 2H), 3.84 (s, 3H), 2.41 (s, 3H), 1.12 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 168.7, 164.1, 154.1, 138.0, 134.3, 134.1, 131.8, 131.5, 130.7, 121.7, 115.7, 112.9, 109.1, 106.9, 98.8, 90.4, 56.1, 38.9, 19.9, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 484.2278 for (C₂₈H₃₅NNaO₃Si) found 484.2280.

IR (thin film, cm⁻¹): 676, 774, 883, 1157, 1238, 1478, 1502, 1575, 1613, 1774, 2150, 2726, 2866, 2943.



2-cyano-5-methoxyphenyl 2-(2-methoxy-5-((triisopropylsilyl)ethynyl)phenyl)acetate(5b):

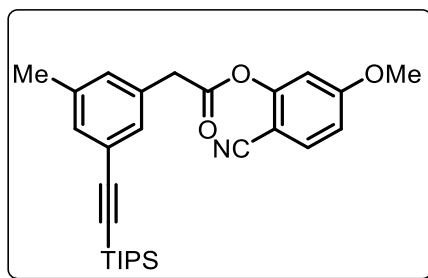
Following the general procedure F, Compound **5c** was obtained from 2-cyano-5 methoxyphenyl 2-(2-methoxyphenyl)acetate, isolated by column chromatography (6:94 v/v), Eluent: ethyl acetate/petroleum ether (9:94 v/v), Appearance: brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, *J* = 5.7, 3.3 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 7.44 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.86–6.78 (m, 2H), 6.76 (d, *J* = 2.4 Hz, 1H), 3.90 (s, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 1.12 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 169.0, 164.0, 158.0, 154.2, 134.9, 134.4, 133.5, 131.1, 129.0, 122.1, 115.9, 112.7, 110.5, 109.2, 106.9, 98.9, 89.1, 56.0, 55.8, 36.1, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 500.2228 for C₂₈H₃₅NO₄SiNa found 500.2225.

IR (thin film, cm⁻¹): 672, 758, 883, 1028, 1108, 1290, 1462, 1502, 1613, 1722, 2149, 2230, 2865, 2930.



2-Cyano-5-methoxybenzonitrile 2-(3-methyl-5-((triisopropylsilyl)ethynyl)phenyl)acetate

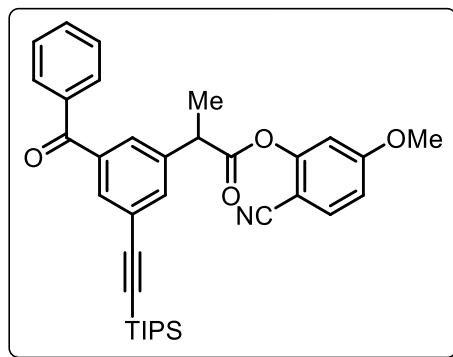
(5c): Following the general procedure F, Compound **5c** was obtained from 2-cyano-5-methoxyphenyl 3-(*o*-tolyl)acetate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v); R_f: 0.4 (20% EA-PE); Appearance: dark brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.29 (s, 1H), 7.19 (s, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.75 (d, *J* = 2.4 Hz, 1H), 3.89 (s, 2H), 3.83 (s, 3H), 2.34 (s, 3H), 1.13 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 168.9, 164.1, 154.6, 138.8, 134.3, 134.2, 132.1, 130.7, 128.8, 124.0, 115.8, 112.6, 109.1, 107.0, 98.9, 90.7, 56.1, 38.8, 21.3, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 484.2278 for (C₂₈H₃₅NNaO₃Si) found 484.2280.

IR (thin film, cm⁻¹): 677, 774, 882, 1160, 1238, 1478, 1500, 1575, 1613, 1774, 2150, 2721, 2873, 2945.



2-cyano-5-methoxyphenyl 2-(3-benzoyl-5-((triisopropylsilyl)ethynyl)phenyl)propanoate (5d):

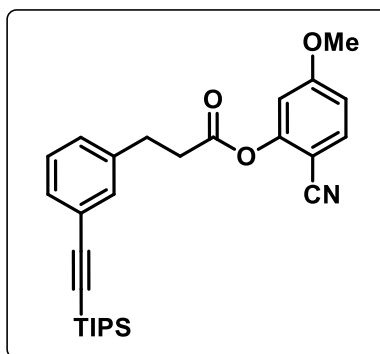
Following the general procedure E, Compound **5d** was obtained from 2-cyano-4-methoxyphenyl 2-(3-benzophenyl)propanoate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.18 – 7.34 (m, 9H), 6.95 – 6.34 (m, 2H), 4.10 (q, *J* = 7.3 Hz, 1H), 3.83 (s, 3H), 1.69 (d, *J* = 7.1 Hz, 3H), 0.88 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 196.9, 171.6, 164.1, 154.0, 142.4, 139.8, 137.5, 134.3, 133.4, 132.9, 130.5, 129.9, 129.2, 129.1, 128.6, 127.8, 121.6, 112.7, 109.0, 104.2, 98.7, 97.3, 56.1, 45.6, 18.6, 14.3, 11.2.

HRMS: [ESI, (+) ve]: calcd. 588.2541 for (C₃₅H₃₉NO₄SiNa) found 588.2539.

IR (thin film, cm⁻¹): 689, 768, 887, 1157, 1238, 1575, 1613, 1787, 2150, 2856, 2948.



2-cyano-5-methoxyphenyl 3-(3-((triisopropylsilyl)ethynyl)phenyl)propanoate (5e):

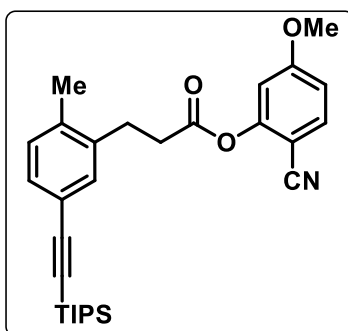
Following the general procedure F, Compound **5e** was obtained from 2-cyano-5-methoxyphenyl 3-phenylpropanoate, isolated by column chromatography (2:98 v/v), Eluent: ethyl acetate/petroleum ether (3:97 v/v), Appearance: pale yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 8.7 Hz, 1H), 7.37 (s, 1H), 7.35 (t, *J* = 1.6 Hz, 1H), 7.33 (t, *J* = 1.7 Hz, 1H), 7.26 – 7.17 (m, 2H), 3.80 (s, 12H), 3.06 (d, *J* = 8.1 Hz, 7H), 2.95 (d, *J* = 8.1 Hz, 4H), 1.11 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 170.19, 164.07, 154.03, 139.93, 134.19, 132.03, 130.45, 128.69, 128.63, 123.96, 115.69, 112.80, 109.05, 107.05, 98.75, 90.75, 56.01, 35.64, 30.57, 18.81, 11.45.

HRMS: [ESI, (+) ve]: calcd. 484.2278 for C₂₈H₃₅NNaO₃Si found 484.2279.

IR (thin film, cm⁻¹): 691, 741, 835, 925, 1110, 1173, 1260, 1513, 1615, 1778, 2152, 2231, 2850, 2957.



2-cyano-5-methoxyphenyl 3-(2-methyl-5-((triisopropylsilyl)ethynyl)phenyl)propanoate (5f):

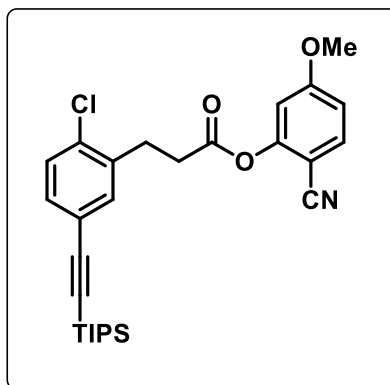
Following the general procedure F, Compound **5f** was obtained from 2-cyano-5-methoxyphenyl 3-(o-tolyl)propanoate, isolated by column chromatography (2:98 v/v), Eluent: ethyl acetate/petroleum ether (3:97 v/v), Appearance: pale yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.33 (s, 1H), 7.27 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 3.08 (t, *J* = 9.4 Hz, 2H), 2.92 (t, *J* = 9.2 Hz, 2H), 2.37 (s, 3H), 1.13 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 170.37, 164.13, 154.11, 138.08, 136.95, 134.24, 132.29, 130.58, 121.53, 115.74, 112.91, 109.07, 107.21, 98.80, 90.04, 56.08, 34.46, 28.18, 19.50, 18.86, 11.51.

HRMS: [ESI, (+) ve]: calcd. 498.2435 for C₂₉H₃₇NO₃SiNa found 498.2433.

IR (thin film, cm⁻¹): 691, 789, 848, 953, 1151, 1158, 1267, 1523, 1636, 1778, 2162, 2272, 2851, 3012.



2-cyano-5-methoxyphenyl 3-(2-chloro-5-((triisopropylsilyl)ethynyl)phenyl)propanoate(5g):

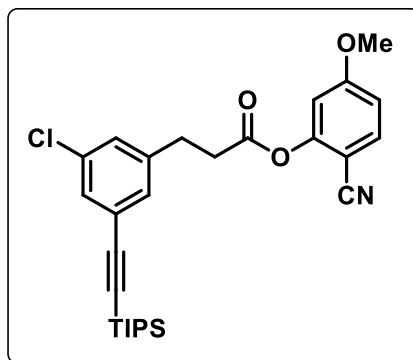
Following the general procedure F, Compound **5g** was obtained from 2-cyano-5-methoxyphenyl 3-(2-chlorophenyl)propanoate, isolated by column chromatography (6:94 v/v), Eluent: ethyl acetate/ petroleum ether (9:94 v/v), Appearance: brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.43 (d, *J* = 1.6 Hz, 1H), 7.30 (t, *J* = 1.4 Hz, 2H), 6.84 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.73 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H), 3.19 (t, *J* = 8.9, 2H), 2.99 (t, *J* = 8.9, 2H), 1.12 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 170.1, 164.1, 154.1, 137.6, 134.3, 134.3, 134.1, 131.9, 129.8, 122.7, 115.7, 112.9, 109.1, 105.8, 98.8, 92.1, 56.1, 33.8, 28.9, 18.8, 11.5.

HRMS: [ESI, (+) ve]: calcd. 518.1889 for C₂₈H₃₄ClNO₃SiNa found 518.1887.

IR (thin film, cm⁻¹): 682, 758, 882, 996, 1111, 1289, 1503, 1572, 1613, 1697, 1773, 2156, 2229, 2864, 2912.



2-cyano-5-methoxyphenyl 3-(3-chloro-5-((triisopropylsilyl)ethynyl)phenyl)propanoate(5h):

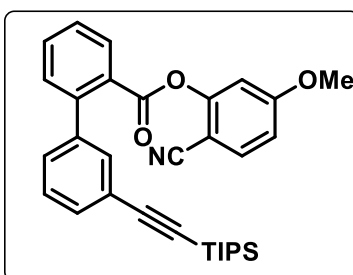
Following the general procedure F, Compound **5h** was obtained from 2-cyano-5-methoxyphenyl 3-(2-chlorophenyl)propanoate, isolated by column chromatography (6:94 v/v), Eluent: ethyl acetate/ petroleum ether (9:94 v/v), Appearance: brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.57 (d, *J* = 8.7 Hz, 1H), 7.33 (t, *J* = 1.7 Hz, 1H), 7.29 – 7.19 (m, 2H), 6.84 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 3.06 (t, *J* = 8.0 Hz, 2H), 2.96 (t, *J* = 8.1, 6.5 Hz, 2H), 1.12 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 169.9, 164.1, 154.0, 141.8, 134.4, 134.3, 130.4, 128.8, 125.5, 115.6, 112.9, 109.0, 105.5, 98.8, 92.5, 56.1, 36.6, 28.0, 18.5, 11.4.

HRMS: [ESI, (+) ve]: calcd. 518.1889 for C₂₈H₃₄ClNO₃SiNa found 518.1887.

IR (thin film, cm⁻¹): 672, 778, 868, 972, 1094, 1293, 1513, 1572, 1613, 1698, 1787, 2157, 2231, 2878, 2950.



2-cyano-5-methoxyphenyl 3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (5i):

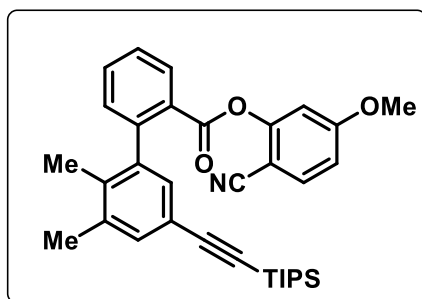
Following the general procedure F, Compound **5i** was obtained from 2-cyano-5-methoxyphenyl [1,1'-biphenyl]-2-carboxylate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v), Appearance: pale yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 8.14 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 10.3 Hz, 3H), 7.51 – 7.46 (m, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.36 (m, 1H), 6.80 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.48 (d, *J* = 2.3 Hz, 1H), 3.80 (s, 3H), 1.11 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 164.07, 163.96, 143.83, 141.28, 141.06, 136.54, 136.19, 135.24, 134.15, 133.11, 132.51, 131.23, 131.20, 130.29, 128.34, 127.99, 127.51, 115.77, 112.89, 108.88, 98.90, 56.06, 20.47, 18.96, 18.92, 16.98, 12.30

HRMS: [ESI, (+) ve]: calcd. 532.2278 for C₃₂H₃₅NO₃SiNa found 532.2276.

IR (thin film, cm⁻¹): 678, 828, 941, 1115, 1160, 1237, 1287, 1503, 1613, 1778, 2152, 2239, 2866, 2943, 3066.



2-cyano-5-methoxyphenyl 2',3'-dimethyl-5'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (5j):

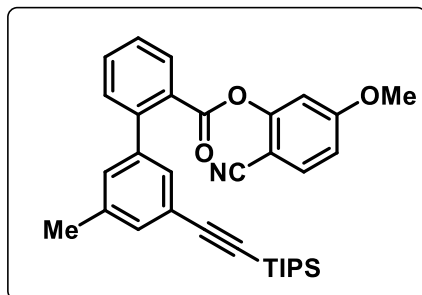
Following the general procedure E, Compound **5j** was obtained from 2-cyano-5-methoxyphenyl 2',3'-dimethyl-[1,1'-biphenyl]-2-carboxylate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v), Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.27 (d, *J* = 7.8 Hz, 1H), 7.64 (t, *J* = 7.5, 1.4 Hz, 1H), 7.53 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.15 (s, 1H), 7.03 (s, 1H), 6.79 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 3.79 (s, 3H), 2.29 (s, 3H), 2.04 (s, 3H), 0.98 (d, *J* = 5.5 Hz, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 164.07, 163.96, 143.83, 141.28, 141.06, 136.54, 136.19, 135.24, 134.15, 133.11, 132.51, 131.23, 131.20, 130.29, 128.34, 127.99, 127.51, 115.77, 112.89, 108.88, 98.90, 56.06, 20.47, 18.96, 18.92, 16.98, 12.30.

HRMS: [ESI, (+) ve]: calcd. 560.2591 for C₃₄H₃₉NO₃SiNa found 560.2589.

IR (thin film, cm⁻¹): 669, 878, 958, 1115, 1158, 1508, 1615, 1783, 2150, 2234, 2874, 2953, 3077.



2-cyano-5-methoxyphenyl 3'-methyl-5'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (5k):

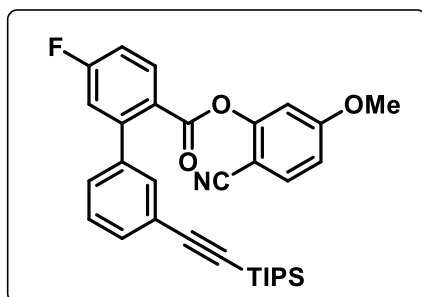
Following the general procedure F, Compound **5k** was obtained from 2-cyano-5-methoxyphenyl 3'-methyl-[1,1'-biphenyl]-2-carboxylate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v), Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 7.7 Hz, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.57 – 7.45 (m, 2H), 7.42 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 9.5 Hz, 2H), 7.21 (s, 1H), 6.80 (dd, J = 8.7, 2.5 Hz, 1H), 6.48 (d, J = 2.5 Hz, 1H), 3.81 (s, 3H), 2.37 (s, 3H), 1.11 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 165.56, 164.12, 154.18, 142.90, 141.28, 138.16, 134.19, 132.60, 131.94, 131.11, 130.82, 129.85, 129.26, 128.92, 127.96, 123.53, 112.94, 108.62, 107.11, 99.11, 90.71, 56.02, 21.37, 18.84, 11.48.

HRMS: [ESI, (+) ve]: calcd. 528.2365 for C₃₂H₃₅FNO₃Si found 528.2364.

IR (thin film, cm⁻¹): 667, 878, 952, 1117, 1158, 1508, 1615, 1783, 2149, 2237, 2868, 2950, 3078.



2-cyano-5-methoxyphenyl 5-fluoro-3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (5l):

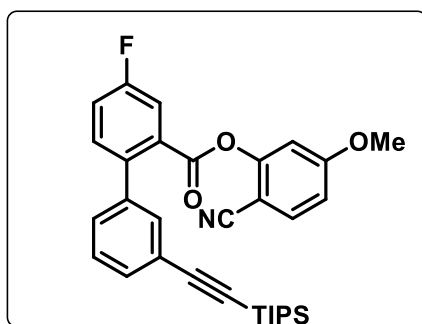
Following the general procedure F, Compound **5l** was obtained from 2-cyano-5-methoxyphenyl 5-fluoro-[1,1'-biphenyl]-2-carboxylate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v), Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, J = 8.7, 5.7 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.39 – 7.36 (m, 1H), 7.24 – 7.18 (m, 1H), 7.14 (dd, J = 9.1, 2.6 Hz, 1H), 6.80 (dd, J = 8.7, 2.4 Hz, 1H), 6.53 (d, J = 2.4 Hz, 1H), 3.81 (s, 3H), 1.12 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 166.19, 164.20, 164.11, 163.65, 154.00, 146.29, 146.20, 140.22, 134.21, 133.89, 133.80, 131.76, 131.73, 128.76, 128.40, 124.71, 124.68, 123.86, 118.62, 118.39, 115.78, 115.30, 115.09, 112.88, 108.74, 106.62, 99.00, 91.51, 56.03, 18.82, 11.45.

HRMS: [ESI, (+) ve]: calcd. 528.2365 for C₃₂H₃₅FNO₃Si m/z found 528.2364.

IR (thin film, cm⁻¹): 677, 835, 881, 944, 1110, 1159, 1233, 1296, 1465, 1503, 1613, 1758, 2156, 2229, 2866, 2943, 3066.



2-cyano-5-methoxyphenyl 4-fluoro-3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (5m):

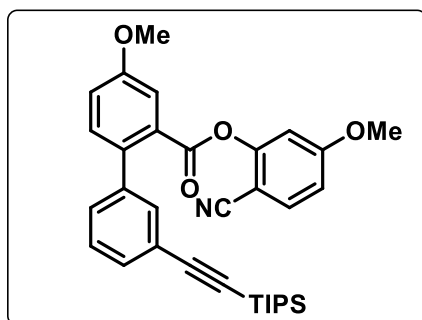
Following the general procedure F, Compound **5m** was obtained from 2-cyano-5-methoxyphenyl 4-fluoro-[1,1'-biphenyl]-2-carboxylate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v), Appearance: dark yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.80 (m, 1H), 7.57 – 7.46 (m, 3H), 7.43 – 7.31 (m, 4H), 6.85 – 6.78 (m, 1H), 6.53 (dd, J = 46.5, 2.4 Hz, 1H), 3.81 (s, 3H), 1.12 (s, 15H), 0.97 (s, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 164.13, 164.10, 163.17, 153.79, 140.53, 140.27, 139.99, 138.96, 138.78, 134.28, 134.22, 133.05, 132.98, 132.04, 131.46, 130.22, 129.76, 129.08, 128.97, 128.39, 127.99, 123.80, 120.10, 119.92, 119.71, 117.97, 117.90, 117.66, 115.64, 113.05, 112.93, 108.89, 108.59, 106.68, 99.00, 98.95, 91.41, 56.04, 18.88, 18.81, 12.26, 11.44.

HRMS: [ESI, (+) ve]: calcd. 528.2365 for C₃₂H₃₅FNO₃Si found 528.2364.

IR (thin film, cm⁻¹): 691, 847, 878, 944, 1110, 1159, 1235, 1286, 1462, 1513, 1623, 1758, 2150, 2231, 2886, 2947, 3066.



2-cyano-5-methoxyphenyl 4-methoxy-3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate (5n):

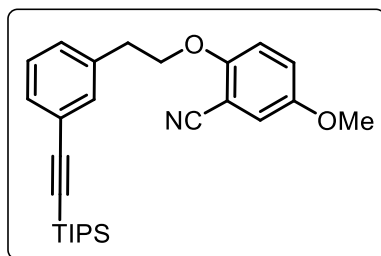
Following the general procedure E, Compound **5n** was obtained from 2-cyano-5-methoxyphenyl 4-methoxy-[1,1'-biphenyl]-2-carboxylate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v), Appearance: brown oil.

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J = 2.8 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 7.49 (s, 1H), 7.48 – 7.43 (m, 1H), 7.35 (dd, J = 5.1, 1.7 Hz, 2H), 7.33 (s, 1H), 7.17 (dd, J = 8.5, 2.8 Hz, 1H), 6.80 (dd, J = 8.7, 2.4 Hz, 1H), 6.48 (d, J = 2.4 Hz, 1H), 3.92 (s, 3H), 3.80 (s, 3H), 1.11 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 165.23, 164.11, 159.22, 154.08, 141.10, 135.23, 134.16, 132.36, 132.24, 131.02, 129.66, 129.26, 128.28, 123.66, 119.22, 115.93, 115.83, 115.18, 112.99, 108.56, 106.97, 99.03, 91.09, 56.05, 55.94, 18.83, 11.47.

HRMS: [ESI, (+) ve]: calcd. 562.2384 for C₃₃H₃₇NO₄SiNa m/z found 562.2382.

IR (thin film, cm⁻¹): 683, 851, 858, 966, 1112, 1153, 1237, 1290, 1467, 1533, 1629, 1755, 2150, 2231, 2886, 3066.



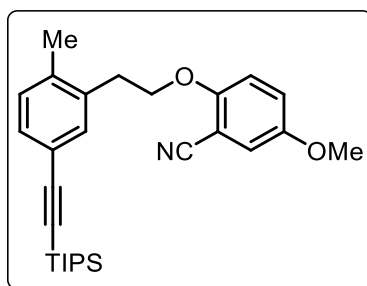
5-Methoxy-2-(3-((triisopropylsilyl)ethynyl)phenethoxy)benzonitrile (7a): Following the general procedure F, Compound **7a** was obtained from 2-phenethoxy-5-methoxybenzonitrile, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.30 (dd, *J* = 15.1, 7.5 Hz, 2H), 7.06 – 7.01 (m, 2H), 6.84 (d, *J* = 10.0 Hz, 1H), 4.18 (t, *J* = 7.0 Hz, 2H), 3.77 (s, 3H), 3.11 (t, *J* = 6.9 Hz, 2H), 1.13 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 155.1, 153.5, 138.0, 132.6, 130.7, 129.8, 128.7, 124.0, 121.0, 117.8, 114.0, 107.2, 102.6, 90.8, 70.4, 56.1, 35.7, 18.9, 11.5

HRMS: [ESI, (+) ve]: calcd. 456.2329 for (C₂₇H₃₅NNaO₂Si) found 456.2332.

IR (thin film, cm⁻¹): 687, 765, 857, 1029, 1265, 1367, 1470, 1582, 1745, 2231, 2866, 2944.



2-(2-Methyl-5-((triisopropylsilyl)ethynyl)phenethoxy)-5-methoxybenzonitrile (7b):

Following the general procedure F, Compound **7b** was obtained from 2-(2-methylphenethoxy)-5-

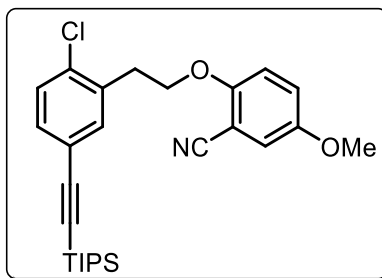
methoxybenzonitrile, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow sticky liquid.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.32 (s, 1H), 7.28 (s, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 7.05 (dt, $J = 7.0, 3.4$ Hz, 2H), 6.88 – 6.83 (m, 1H), 4.17 (t, $J = 7.3$ Hz, 2H), 3.77 (s, 3H), 3.13 (t, $J = 7.3$ Hz, 2H), 2.41 (s, 3H), 1.12 (s, 21H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.1 153.5, 137.7, 136.1, 133.1, 130.8, 130.6, 121.5, 121.0, 117.8, 116.5, 114.0, 107.2, 102.5, 90.1, 69.9, 56.1, 32.8, 19.9, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 448.2665 for ($\text{C}_{28}\text{H}_{38}\text{NO}_2\text{Si}$) found 448.2667.

IR (thin film, cm^{-1}): 678, 756, 858, 1033, 1263, 1375, 1582, 1744, 2157, 2231, 2875, 2947.



2-(2-Chloro-5-((triisopropylsilyl)ethynyl)phenoxy)-5-methoxybenzonitrile (7c):

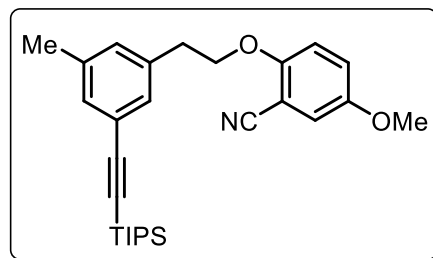
Following the general procedure F, Compound **7c** was obtained from 2-(2-chlorophenoxy)-5-methoxybenzonitrile, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: brown oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.46 (s, 1H), 7.29 (s, 2H), 7.08 – 7.02 (m, 2H), 6.91 – 6.85 (m, 1H), 4.22 (t, $J = 7.3$ Hz, 2H), 3.77 (s, 3H), 3.26 (t, $J = 7.3$ Hz, 2H), 1.12 (s, 21 H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.0, 153.6, 135.4, 135.0, 134.5, 132.0, 129.7, 122.8, 121.0, 118.0, 117.0, 116.3, 114.2, 105.8, 102.7, 92.2, 68.5, 56.2, 33.5, 18.8, 11.5.

HRMS: [ESI, (+) ve]: calcd. 490.1940 for ($\text{C}_{27}\text{H}_{34}\text{ClNO}_2\text{SiNa}$) found 490.1938.

IR (thin film, cm^{-1}): 681, 749, 881, 1042, 1161, 1230, 1384, 1470, 1582, 1734, 2229, 2865, 2941.



2-(3-Methyl-5-((triisopropylsilyl)ethynyl)phenethoxy)-5-methoxybenzonitrile (7d):

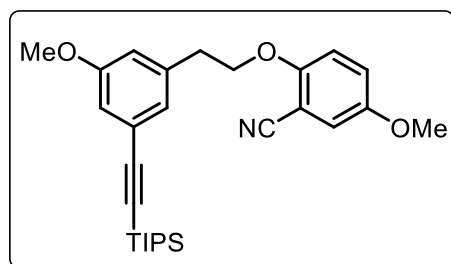
Following the general procedure F, Compound **7d** was obtained from 2-(3-methylphenethoxy)-5-methoxybenzonitrile **1q**, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow liquid.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.19 (s, 2H), 7.14 (s, 1H), 7.06 – 7.02 (m, 2H), 6.84 (d, $J = 10.0$ Hz, 1H), 7.04 (m, 1H), 4.17 (t, $J = 7.0$ Hz, 3H), 3.77 (s, 3H), 3.07 (t, $J = 7.0$ Hz, 2H), 2.33 (s, 3H), 1.13 (s, 21H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.1, 153.4, 138.5, 137.8, 131.3, 130.9, 129.7, 123.7, 121.0, 117.7, 116.5, 114.0, 107.4, 102.5, 90.2, 70.3, 56.1, 35.6, 21.3, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 448.2666 for ($\text{C}_{28}\text{H}_{37}\text{NO}_2\text{Si}$) found 448.2665.

IR (thin film, cm^{-1}): 678, 756, 858, 1031, 1265, 1365, 1581, 1747, 2157, 2238, 2875, 2947.



2-(2-Methoxy-5-((triisopropylsilyl)ethynyl)phenethoxy)-5-methoxybenzonitrile (7e):

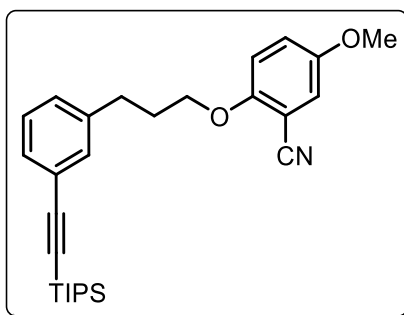
Following the general procedure F, Compound **7e** was obtained from 2-(2-methoxy-5-((triisopropylsilyl)ethynyl)phenethoxy)-5-methoxybenzonitrile, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: brown liquid.

¹H NMR (500 MHz, CDCl₃) δ 7.04 (d, *J* = 6.6 Hz, 2H), 6.98 (s, 1H), 6.89 (s, 2H), 6.84 (d, *J* = 10.1 Hz, 1H), 4.18 (t, *J* = 6.9 Hz, 2H), 3.82 (s, 3H), 3.77 (s, 3H), 3.08 (t, *J* = 6.9 Hz, 2H), 1.13 (s, 21H).

¹³C NMR (126 MHz, CDCl₃) δ 159.7, 155.1, 153.5, 139.5, 125.2, 124.8, 121.0, 117.8, 116.5, 116.0, 115.9, 113.9, 107.0, 102.5, 90.6, 70.3, 56.3, 55.7, 35.8, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 464.2615 for (C₂₈H₃₈NO₂Si) found 464.2619.

IR (thin film, cm⁻¹): 690, 882, 1040, 1155, 1231, 1281, 1463, 1502, 1587, 1732, 2154, 2229, 2866, 2942.



5-Methoxy-2-(3-(3-((triisopropylsilyl)ethynyl)phenyl)propoxy)benzonitrile (7f):

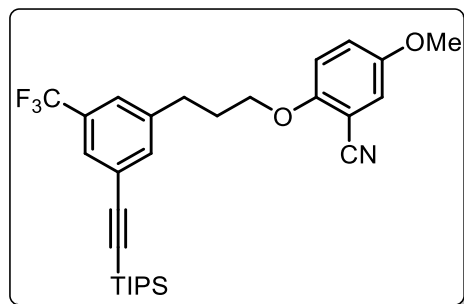
Following the general procedure F, Compound **7f** was obtained from 5-methoxy-2-(3-phenylpropoxy)benzonitrile **1r**, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: pale yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.32 (d, *J* = 7.0 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.1 Hz, 1H), 7.05 (d, *J* = 7.1 Hz, 2H), 6.84 (d, *J* = 10.0 Hz, 1H), 3.98 (dd, *J* = 13.5, 7.4 Hz, 2H), 3.78 (s, 3H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.20 – 2.09 (m, 2H), 1.13 (s, 21H).

¹³C NMR (101 MHz, CDCl₃) δ 155.3, 153.5, 141.4, 132.2, 130.1, 129.0, 128.6, 123.8, 121.1, 117.7, 116.5, 114.1, 107.4, 102.56, 90.4, 68.5, 56.1, 31.8, 30.6, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 448.2666 for (C₂₈H₃₇NO₂Si) found 448.2667.

IR (thin film, cm⁻¹): 688, 745, 855, 1031, 1264, 1362, 1580, 1748, 2153, 2237, 2876, 2951.



5-Methoxy-2-(3-(3-(trifluoromethyl)-5-((triisopropylsilyl)ethynyl)phenyl)propoxy)benzonitrile (7g):

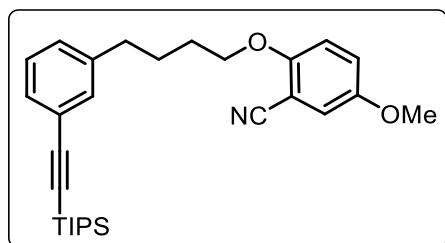
Following the general procedure F, Compound **7g** was obtained from 5-methoxy-2-(3-(3-(trifluoromethyl)-phenyl)propoxy benzonitrile, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow liquid.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.54 (s, 1H), 7.49 (s, 1H), 7.40 (s, 1H), 7.06 (dd, $J = 7.6, 2.7$ Hz, 2H), 6.85 (dd, $J = 7.3, 2.6$ Hz, 1H), 4.00 (t, $J = 6.0$ Hz, 2H), 3.78 (s, 3H), 2.91 (t, $J = 7.6$ Hz, 2H), 2.20 – 2.11 (m, 2H), 1.13 (s, 21H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.1, 153.6, 142.5, 135.5, 131.3, 131.1, 126.8, 126.8, 125.3, 125.3, 124.7, 122.8, 121.1, 117.7, 116.5, 114.1, 105.6, 102.5, 92.7, 68.2, 56.2, 31.7, 30.4, 18.9, 11.5.

HRMS: [ESI, (+) ve]: calcd. 516.2540 for $(\text{C}_{29}\text{H}_{37}\text{F}_3\text{NO}_2\text{Si})$ found 515.2539.

IR (thin film, cm^{-1}): 676, 792, 832, 1039, 1159, 1212, 1416, 1598, 1735, 2150, 2228, 2942.



5-Methoxy-2-(4-(3-((triisopropylsilyl)ethynyl)phenyl)butoxy)benzonitrile (7h):

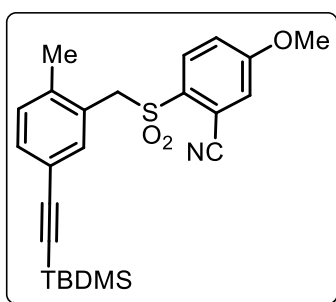
Following the general procedure F, Compound **7h** was obtained from 5-methoxy-2-(4-ethynylphenyl)butoxy)benzonitrile, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: pale yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 7.31 (s, 2H), 7.22 (t, $J = 7.8$ Hz, 1H), 7.14 (dd, $J = 17.0, 7.8$ Hz, 1H), 7.05 (d, $J = 9.2$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 1H), 4.02 (s, 2H), 3.77 (s, 3H), 2.67 (s, 2H), 1.85 (s, 4H), 1.13 (s, 21H).

^{13}C NMR (126 MHz, CDCl_3) δ 155.5, 153.4, 142.3, 132.2, 129.9, 128.8, 128.6, 128.5, 123.7, 121.1, 117.7, 116.6, 114.2, 107.6, 102.6, 90.3, 69.7, 56.2, 35.4, 28.8, 27.6, 18.9, 11.6.

HRMS: [ESI, (+) ve]: calcd. 484.2642 for $(\text{C}_{29}\text{H}_{39}\text{NNaO}_2\text{Si})$ found 484.2642.

IR (thin film, cm^{-1}): 664, 792, 814, 882, 1039, 1159, 1232, 1280, 1416, 1464, 1502, 1598, 1733, 2150, 2228, 2865, 2942.



2-((5-((*tert*-butyldimethylsilyl)ethynyl)-2-methylbenzyl)sulfonyl)-5-methoxybenzonitrile (8a**):**

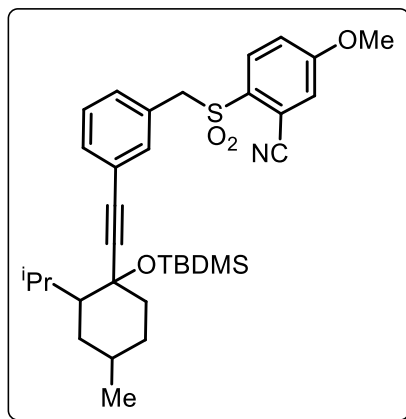
Following the general procedure F, Compound **8a** was obtained from 2-cyano-4-methoxyphenyl 2-methyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow oil.

^1H NMR (500 MHz, CDCl_3) δ 7.54 (d, $J = 1.7$ Hz, 1H), 7.40 (dd, $J = 7.8, 1.7$ Hz, 1H), 7.30 (d, $J = 9.0$ Hz, 1H), 7.20 (d, $J = 7.9$ Hz, 1H), 7.18 – 7.09 (m, 2H), 4.72 (s, 2H), 3.84 (s, 3H), 2.48 (s, 3H), 0.98 (s, 9H), 0.17 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 158.3, 143.4, 139.4, 135.6, 133.4, 131.3, 125.3, 125.2, 122.0, 120.6, 118.0, 115.2, 108.4, 104.8, 93.3, 77.5, 76.9, 56.2, 55.5, 28.0, 26.3, 19.9, 16.9, -4.4.

HRMS: [ESI, (+) ve]: [M+Na]⁺ calculated for C₂₄H₂₉NO₃SSiNa m/z 462.1530 found 462.1528.

IR (thin film, cm⁻¹): 689, 734, 941, 1028, 1161, 1252, 1295, 1503, 1631, 1774, 2142, 2229, 2931.



2-(3-((1-((*tert*-butyldimethylsilyloxy)-2-isopropyl-4-methylcyclohexyl)ethynyl)benzyl)sulfonyl)-5-methoxybenzonitrile (8b**):**

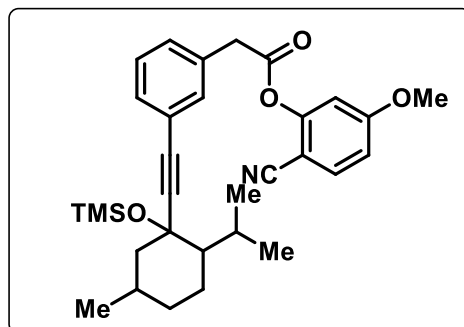
Following the general procedure F, Compound **8b** was obtained from from 2-cyano-4-methoxyphenyl phenyl methanesulfonate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v); R_f : 0.4 (20% EA-PE); Appearance: colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 7.51 (s, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 9.1 Hz, 1H), 7.15 (d, *J* = 3.0 Hz, 1H), 7.12 (dd, *J* = 9.1, 3.1 Hz, 1H), 4.67 (s, 2H), 3.84 (s, 3H), 2.33 (dd, *J* = 14.1, 7.2 Hz, 1H), 2.01 (s, 1H), 1.93 (d, *J* = 2.2 Hz, 1H), 1.72 (d, *J* = 10.6 Hz, 2H), 1.61 (dd, *J* = 13.3, 3.1 Hz, 4H), 1.38 (dd, *J* = 13.0, 3.3 Hz, 3H), 0.96 (d, *J* = 7.0 Hz, 6H), 0.88 (s, 9H), 0.21 (d, *J* = 4.2 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 158.3, 143.6, 135.4, 133.8, 132.5, 130.8, 129.4, 127.1, 125.3, 125.1, 124.7, 120.6, 118.0, 115.2, 108.3, 94.2, 86.4, 73.6, 58.1, 56.3, 54.7, 52.3, 37.3, 35.1, 32.2, 30.7, 29.6, 26.0, 24.3, 22.9, 22.3, 18.4, 17.8, 14.3, 1.2, 0.2, -2.2, -2.7.

HRMS: [ESI, (+) ve]: calcd. 602.2731 for (C₃₅H₄₅NNaO₃Si) found 602.2733.

IR (thin film, cm⁻¹): 675, 751, 849, 937, 1155, 1260, 1513, 1627, 2212, 2851, 2968.



2-cyano-5-methoxyphenyl 2-(3-((2-isopropyl-5-methyl-1-(trimethylsilyloxy)cyclohexyl)ethynyl)phenyl)acetate (8c):

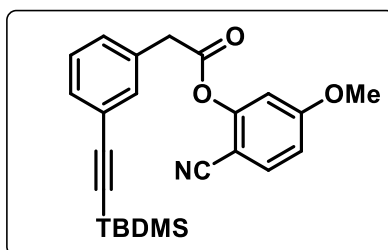
Following the general procedure F, Compound **8c** was obtained from 2-cyano-5-methoxyphenyl 2-phenylacetate, isolated by column chromatography (2:98 v/v), Eluent: ethyl acetate/ petroleum ether (3:97 v/v), Appearance: pale yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.56 (d, *J* = 9.9 Hz, 1H), 7.39 – 7.32 (m, 4H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 3.94 (s, 2H), 3.83 (s, 3H), 2.45 – 2.35 (m, 1H), 2.09 – 1.97 (m, 1H), 1.78 – 1.68 (m, 2H), 1.55 – 1.28 (m, 4H), 1.02 (q, *J* = 13.9, 6.6 Hz, 1H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 6.4 Hz, 3H), 0.21 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 168.79, 164.05, 154.05, 134.27, 132.85, 132.47, 130.84, 129.38, 128.97, 124.08, 115.65, 112.81, 109.05, 98.73, 95.26, 83.89, 73.68, 56.06, 52.14, 50.60, 40.81, 35.13, 28.77, 27.38, 24.24, 22.14, 20.77, 18.58, 1.98.

HRMS: [ESI, (+) ve]: calcd. 540.2541 for C₃₁H₃₉NO₄SiNa found 540.2537.

IR (thin film, cm⁻¹): 687, 747, 843, 933, 1105, 1155, 1263, 1513, 1606, 1783, 2160, 2223, 2847, 2972.



2-cyano-5-methoxyphenyl 2-(3-((tert-butyldimethylsilyl)ethynyl)phenyl)acetate (8d):

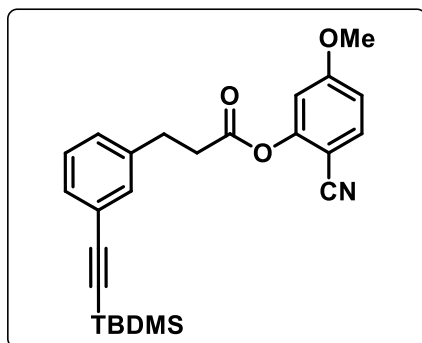
Following the general procedure F, Compound **8d** was obtained from 2-cyano-5-methoxyphenyl 2-phenylacetate, isolated by column chromatography (2:98 v/v), Eluent: ethyl acetate/ petroleum ether (3:97 v/v), Appearance: pale yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.49 (s, 1H), 7.43 (d, *J* = 7.5 Hz, 1H), 7.38 – 7.36 (m, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 3.92 (s, 2H), 3.83 (s, 3H), 1.00 (s, 9H), 0.18 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 168.76, 164.08, 154.09, 134.29, 133.17, 132.79, 131.44, 129.88, 128.92, 123.99, 115.67, 112.92, 109.02, 105.41, 98.77, 93.24, 56.10, 40.83, 26.33, 16.89, -4.43.

HRMS: [ESI, (+) ve]: calcd. 428.1652 for C₂₄H₂₇NO₃SiNa found 428.1651.

IR (thin film, cm⁻¹): 686, 739, 845, 927, 1112, 1175, 1265, 1523, 1616, 1778, 2157, 2231, 2850, 2957.



2-cyano-5-methoxyphenyl 3-(3-((tert-butyldimethylsilyl)ethynyl)phenyl)propanoate (8e):

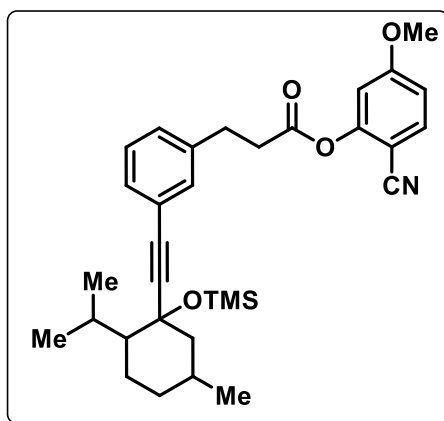
Following the general procedure F, Compound **8e** was obtained from 2-cyano-5-methoxyphenyl 3-phenylpropanoate, isolated by column chromatography (2:98 v/v), Eluent: ethyl acetate/ petroleum ether (3:97 v/v), Appearance: pale yellow oil.

¹H NMR (500 MHz, CDCl₃) δ 7.56 (d, *J* = 8.7 Hz, 1H), 7.38 (s, 1H), 7.35 (d, *J* = 7.3, 1H), 7.27 (s, 1H), 7.25 – 7.23 (m, 1H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 3.84 (s, 3H), 3.08 (t, *J* = 7.8 Hz, 2H), 2.96 (t, *J* = 7.8 Hz, 2H), 0.99 (s, 9H), 0.18 (s, 6H).

^{13}C NMR (126 MHz, CDCl_3) δ 170.24, 164.14, 154.12, 140.00, 134.29, 134.26, 132.11, 130.45, 128.87, 128.84, 128.76, 123.77, 115.73, 112.91, 109.09, 105.77, 98.88, 92.81, 56.09, 35.71, 30.65, 29.89, 26.35, -4.39.

HRMS: [ESI, (+) ve]: calcd. 420.1989 for $\text{C}_{25}\text{H}_{30}\text{NO}_3\text{Si}$ m/z found 442.1988.

IR (thin film, cm^{-1}): 689, 734, 777, 827, 914, 964, 1027, 1110, 1161, 1252, 1295, 1503, 1613, 1774, 2153, 2229, 2857, 2931.



2-cyano-5-methoxyphenyl 3-(3-((2-isopropyl-5-methyl-1-(trimethylsilyloxy)cyclohexyl)ethynyl)phenyl)propanoate (8f):

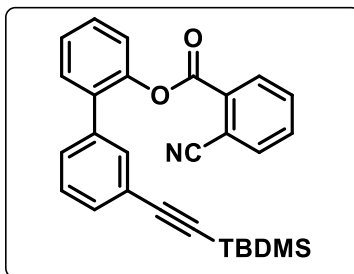
Following the general procedure F, Compound **8f** was obtained from 2-cyano-5-methoxyphenyl 3-phenylpropanoate, isolated by column chromatography (2:98 v/v), Eluent: ethyl acetate/petroleum ether (3:97 v/v), Appearance: pale yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.7$ Hz, 1H), 7.32 – 7.25 (m, 3H), 7.26 – 7.19 (m, 1H), 6.83 (dd, $J = 8.7, 2.4$ Hz, 1H), 6.68 (d, $J = 2.4$ Hz, 1H), 3.84 (s, 3H), 3.10 (t, $J = 8.1$ Hz, 2H), 2.98 (t, $J = 8.1$ Hz, 2H), 2.47 – 2.35 (m, 2H), 2.08 – 1.99 (m, 2H), 1.81 – 1.67 (m, 1H), 1.56 – 1.42 (m, 2H), 1.41 – 1.30 (m, 1H), 1.31 – 1.23 (m, 1H), 0.96 (d, $J = 7.0$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H), 0.88 (d, $J = 6.5$ Hz, 3H), 0.21 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 170.24, 164.08, 154.04, 140.04, 134.24, 131.40, 129.81, 128.79, 128.27, 123.84, 115.71, 112.77, 109.12, 98.78, 94.91, 84.14, 73.67, 56.04, 52.15, 50.64, 35.65, 35.14, 30.60, 28.76, 27.38, 24.24, 22.15, 20.77, 18.59, 1.98.

HRMS: [ESI, (+) ve]: calcd. 554.2697 for $\text{C}_{32}\text{H}_{41}\text{NO}_4\text{SiNa}$ m/z found 554.2695.

IR (thin film, cm^{-1}): 689, 777, 856, 958, 1155, 1276, 1535, 1632, 1781, 2166, 2278, 2891, 3005.



3'-((tert-butyldimethylsilyl)ethynyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate (8g):

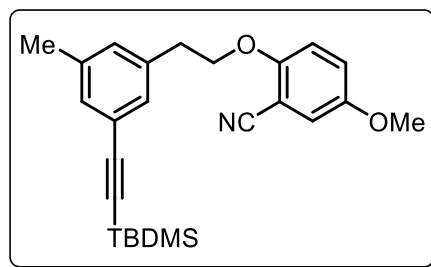
Following the general procedure F, Compound **8g** was obtained from [1,1'-biphenyl]-2-yl 2-cyanobenzoate, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (3:97 v/v), Appearance: light yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 8.09 – 8.02 (m, 1H), 7.86 – 7.78 (m, 1H), 7.70 – 7.62 (m, 2H), 7.62 – 7.57 (m, 1H), 7.49 – 7.39 (m, 3H), 7.41 – 7.31 (m, 3H), 7.29 (dd, $J = 7.7, 0.6$ Hz, 1H), 0.96 (s, 9H), 0.15 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 162.53, 147.51, 137.47, 135.17, 134.17, 133.31, 132.72, 132.71, 131.62, 131.21, 131.08, 129.32, 129.20, 128.49, 127.11, 123.49, 123.05, 117.28, 113.58, 105.45, 92.91, 26.31, 16.86, -4.44.

HRMS: [ESI, (+) ve]: calcd. 460.1703 for $\text{C}_{28}\text{H}_{27}\text{NO}_2\text{SiNa}$ found 460.1701.

IR (thin film, cm^{-1}): 691, 847, 973, 1100, 1237, 1297, 1533, 1635, 1785, 2156, 2234, 2890, 3078.



2-(3-((1-((tert-butyldimethylsilyl)ethynyl)-5-methylphenethoxy)-5-methoxybenzonitrile (8h):

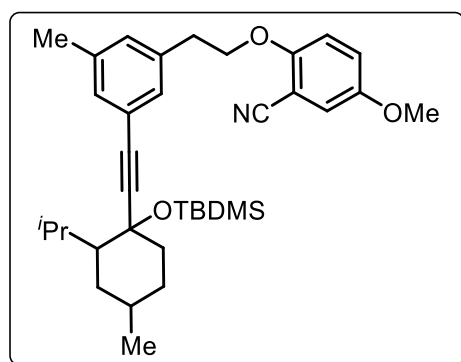
Following the general procedure F, Compound **8h** was obtained from 2-(3-methylphenethoxy)-5-methoxybenzonitrile **1m**, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: brown oil.

¹H NMR (500 MHz, CDCl₃) δ 7.20 (s, 2H), 7.16 (s, 1H), 7.08 – 7.04 (m, 2H), 6.88 – 6.84 (m, 1H), 4.18 (t, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 3.08 (t, *J* = 7.0 Hz, 2H), 2.34 (s, 3H), 1.01 (s, 9H), 0.19 (s, 6H).

¹³C NMR (126 MHz, CDCl₃) δ 155.1, 153.4, 138.5, 137.8, 131.2, 131.0, 129.6, 123.4, 121.0, 117.7, 116.6, 114.8, 113.9, 106.0, 102.5, 92.3, 70.3, 56.2, 35.6, 26.4, 21.3, 14.3, -4.4.

HRMS: [ESI, (+) ve]: calcd. 406.2145 for (C₂₅H₃₁NO₂Si) found 406.2143.

IR (thin film, cm⁻¹): 664, 792, 814, 1159, 1232, 1280, 1464, 1598, 1733, 2141, 2231, 2942.



2-(3-((1-((*tert*-butyldimethylsilyloxy)-2-isopropyl-4-methylcyclohexyl)ethynyl)-5-methylphenethoxy)-5-methoxybenzonitrile (8i**):**

Following the general procedure F, Compound **8i** was obtained from 2-(3-methylphenethoxy)-5-methoxybenzonitrile, isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (20% EA-PE); Appearance: yellow oil.

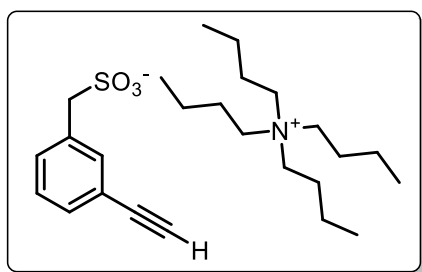
¹H NMR (400 MHz, CDCl₃) δ 7.15 (s, 1H), 7.10 (s, 2H), 7.07 – 7.01 (m, 2H), 6.88 – 6.81 (m, 1H), 4.17 (t, *J* = 6.9 Hz, 2H), 3.77 (s, 3H), 3.08 (t, *J* = 6.9 Hz, 2H), 2.34 (s, 3H), 2.01 (d, *J* = 11.9 Hz, 2H), 1.88 (d, *J* = 8.1 Hz, 1H), 1.71 (d, *J* = 11.4 Hz, 2H), 1.66 – 1.60 (m, 2H), 1.39 (dd, *J* =

13.0, 2.9 Hz, 1H), 1.05 (d, $J = 6.7$ Hz, 1H), 0.97 (d, $J = 6.9$ Hz, 3H), 0.92 (d, $J = 6.5$ Hz, 6H), 0.89 (s, 9H), 0.22 (d, $J = 4.8$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 155.2, 153.5, 138.6, 138.0, 130.6, 130.4, 128.9, 123.7, 121.0, 117.8, 116.5, 114.0, 102.6, 92.5, 87.4, 73.5, 70.4, 56.2, 54.7, 52.4, 35.6, 35.1, 30.7, 29.9, 26.0, 25.8, 24.3, 23.5, 22.3, 21.4, 18.3, 17.9, 14.3, -2.2, -2.7.

HRMS: [ESI, (+) ve]: calcd. 582.3374 for $(\text{C}_{35}\text{H}_{49}\text{NNaO}_3\text{Si})$ found 582.3380.

IR (thin film, cm^{-1}): 678, 748, 847, 933, 1155, 1263, 1513, 1622, 2223, 2847, 2972.



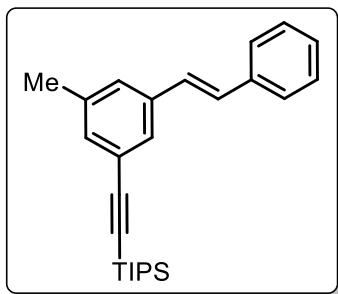
Tetrabutylammonium (3-ethynylphenyl)methanesulfonate (9) Appearance: white solid.

^1H NMR (500 MHz, MeOD) δ 7.28 (s, 1H), 7.16 (d, $J = 7.1$ Hz, 1H), 7.10 (d, $J = 7.5$ Hz, 1H), 7.02 (t, $J = 7.3$ Hz, 1H), 3.78 (s, 2H), 3.17 (s, 1H), 2.99 – 2.90 (m, 8H), 1.38 (dt, $J = 15.6, 8.0$ Hz, 8H), 1.20 – 1.09 (m, 8H), 0.75 (t, $J = 7.3$ Hz, 12H).

^{13}C NMR (126 MHz, DMSO- d_6) δ 136.2, 131.0, 129.50, 128.0, 121.0, 83.8, 80.2, 57.6, 57.0, 39.5, 23.1, 19.3, 13.6.

HRMS: [ESI, (+) ve]: calcd. 438.3036 for $\text{C}_{25}\text{H}_{44}\text{NO}_3\text{S}$ found 438.3035.

IR (thin film, cm^{-1}): 690, 748, 843, 1031, 1215, 1583, 2235, 2856, 2943, 3100.



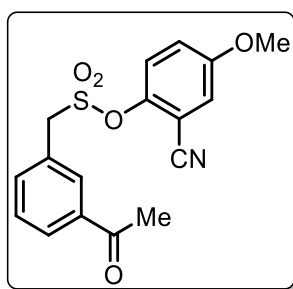
(E)-Triisopropyl((3-methyl-5-styrylphenyl)ethynyl)silane (10) isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (2:98 v/v); R_f : 0.4 (5 % EA-PE), yellow liquid.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.55 (d, $J = 7.9$ Hz, 2H), 7.48 (s, 1H), 7.40 (t, $J = 7.5$ Hz, 2H), 7.33 – 7.28 (m, 2H), 7.25 (s, 1H), 7.14 (d, $J = 16.3$ Hz, 1H), 7.07 (d, $J = 16.3$ Hz, 1H), 2.39 (s, 3H), 1.21 (d, $J = 2.1$ Hz, 21H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 138.4, 137.5, 137.4, 132.0, 129.4, 128.9, 128.1, 127.9, 127.6, 127.5, 126.7, 125.7, 123.9, 107.4, 90.3, 21.4, 18.9, 11.6.

HRMS: [ESI, (+) ve]: calcd. 397.2322 for $\text{C}_{26}\text{H}_{34}\text{SiNa}$ found 397.2322.

IR (thin film, cm^{-1}): 689, 761, 851, 1205, 1350, 1497, 1583, 2120, 2847, 2939, 3280.

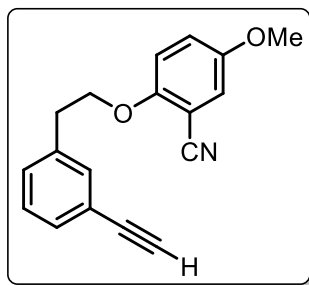


2-Cyano-4-methoxyphenyl (3-acetylphenyl)methanesulfonate (11) isolated by column chromatography (85%), Eluent: ethyl acetate/ petroleum ether (6:94 v/v); R_f : 0.5 (30 % EA-PE), yellow liquid.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.06 (s, 1H), 7.99 (d, $J = 7.8$ Hz, 1H), 7.72 (d, $J = 7.6$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 1H), 7.29 (d, $J = 9.0$ Hz, 1H), 7.11 (dt, $J = 9.1, 2.9$ Hz, 2H), 4.74 (s, 2H), 3.81 (s, 3H), 2.60 (s, 3H). **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) δ 197.5, 158.2, 143.3, 137.9, 135.6, 131.0, 129.6, 129.4, 127.4, 124.9, 120.6, 117.9, 115.1, 108.0, 57.8, 56.2, 26.8.

HRMS: [ESI, (+) ve]: calcd. 368.0563 for $\text{C}_{17}\text{H}_{15}\text{NNaO}_5\text{S}$ found 368.0561.

IR (thin film, cm^{-1}): 691, 758, 840, 914, 1027, 1103, 1166, 1204, 1282, 1359, 1412, 1492, 1583, 1684, 2235, 2844, 2939, 2982, 3070, 3657.



2-(3-Ethynylphenethoxy)-5-methoxybenzonitrile (12) isolated by column chromatography, Eluent: ethyl acetate/ petroleum ether (5:95 v/v); R_f : 0.4 (20 % EA-PE), colorless oil.

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.43 (s, 1H), 7.36 (dd, $J = 14.9, 7.6$ Hz, 2H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.04 (dd, $J = 7.5, 2.7$ Hz, 2H), 6.85 – 6.81 (m, 1H), 4.18 (t, $J = 6.8$ Hz, 2H), 3.76 (s, 3H), 3.11 (t, $J = 6.8$ Hz, 2H), 3.07 (s, 1H).

$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.0, 153.4, 138.2, 132.8, 130.7, 130.3, 128.8, 122.4, 120.9, 117.7, 116.5, 113.9, 102.5, 83.7, 70.1, 56.1, 35.6.

HRMS: [ESI, (+) ve]: calcd. 300.0995 for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{NNa}$ found 300.0991.

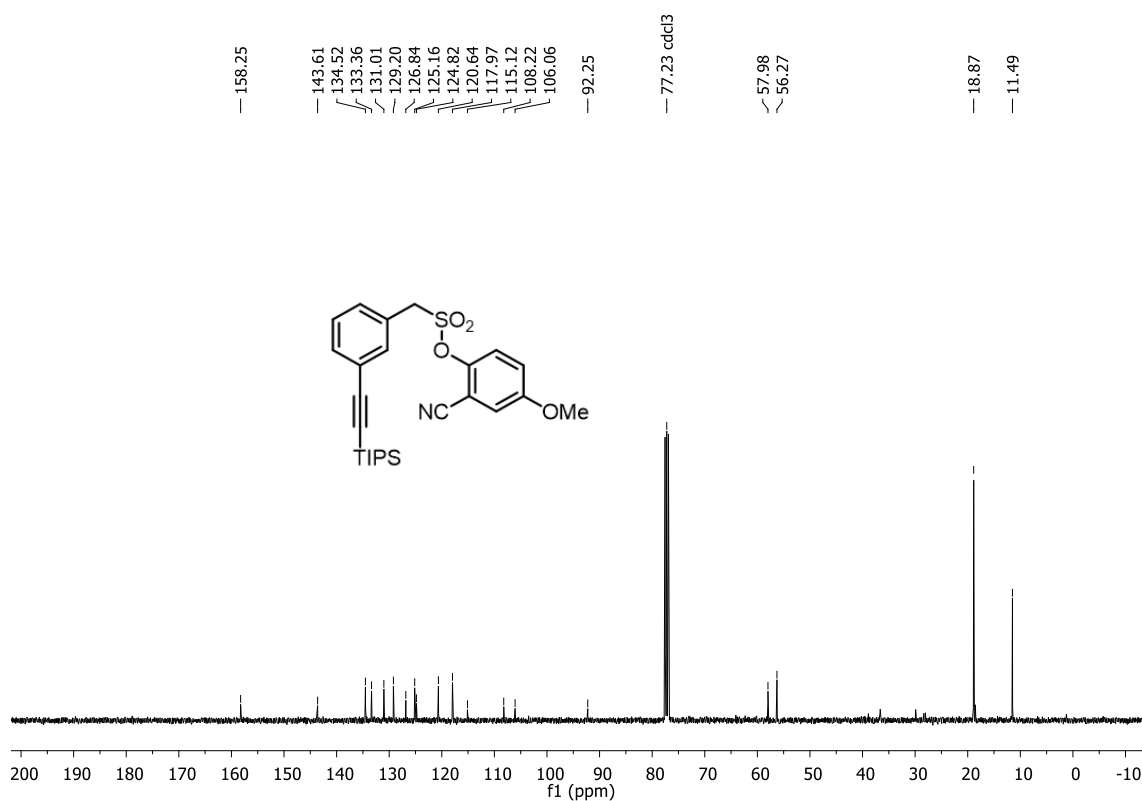
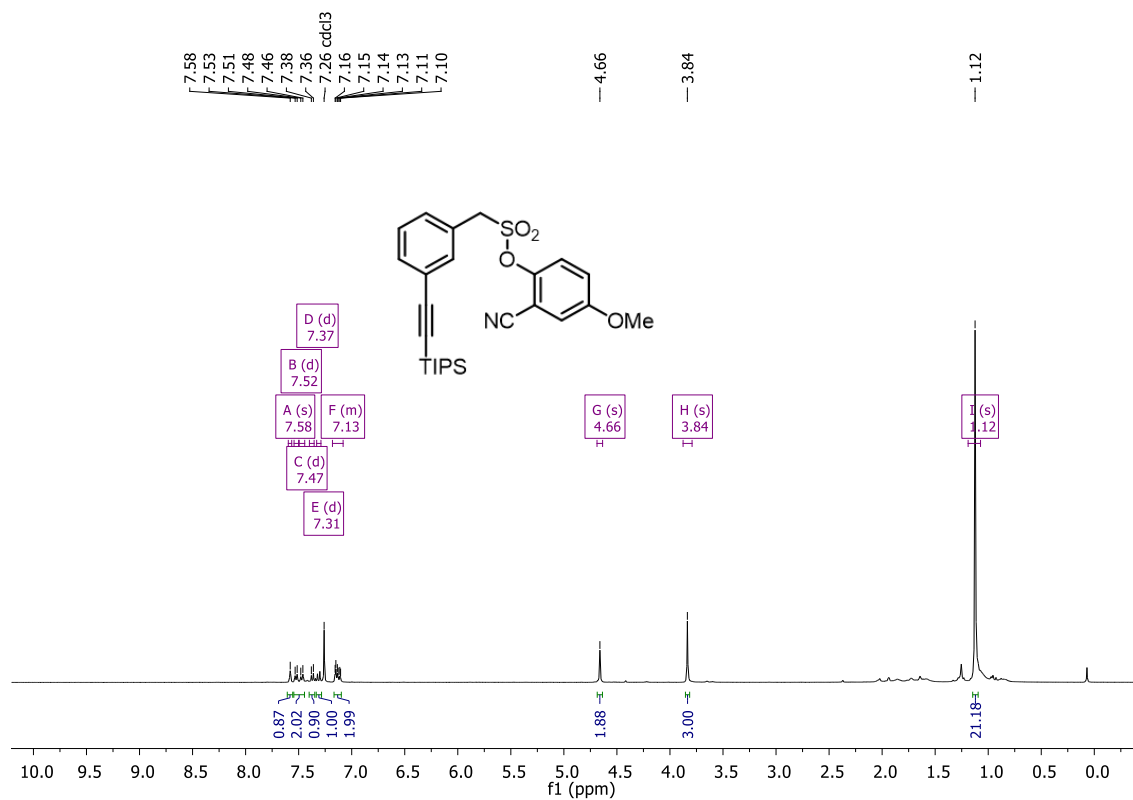
IR (thin film, cm^{-1}): 691, 758, 840, 1027, 1205, 1359, 1492, 1583, 2233, 2847, 2939, 3100.

References

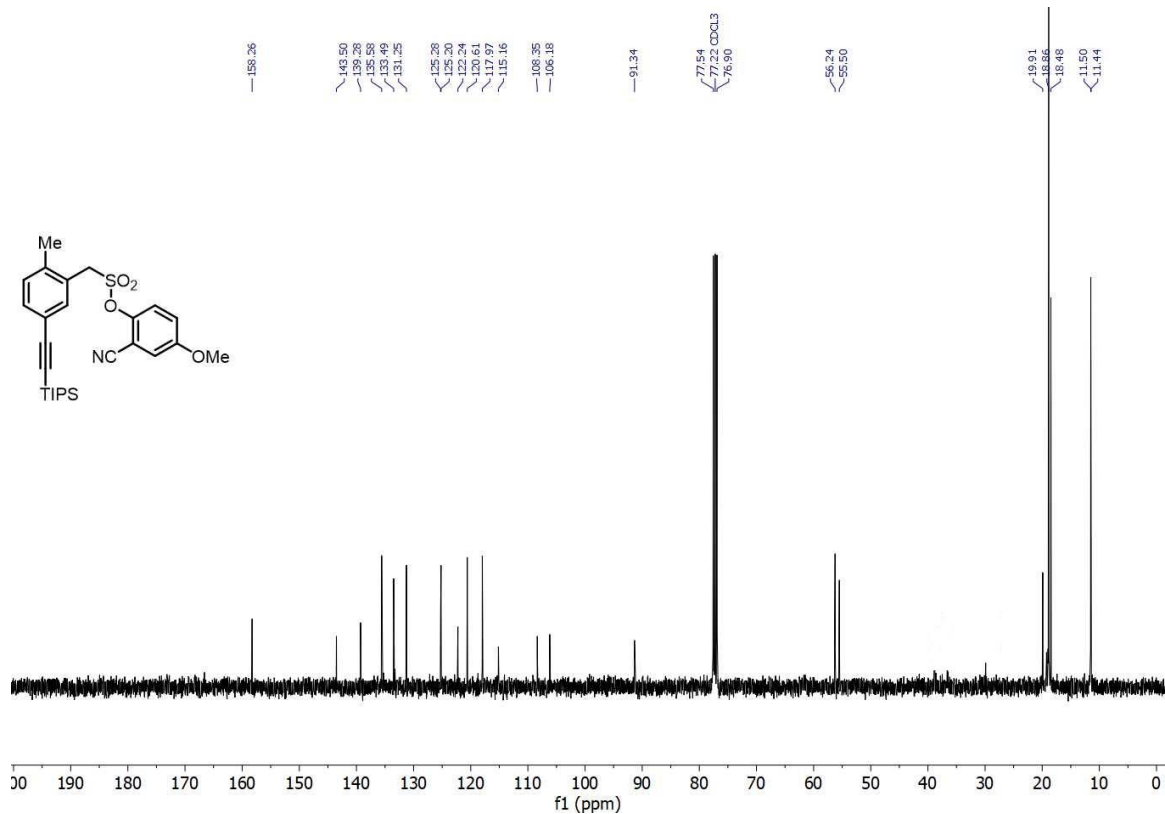
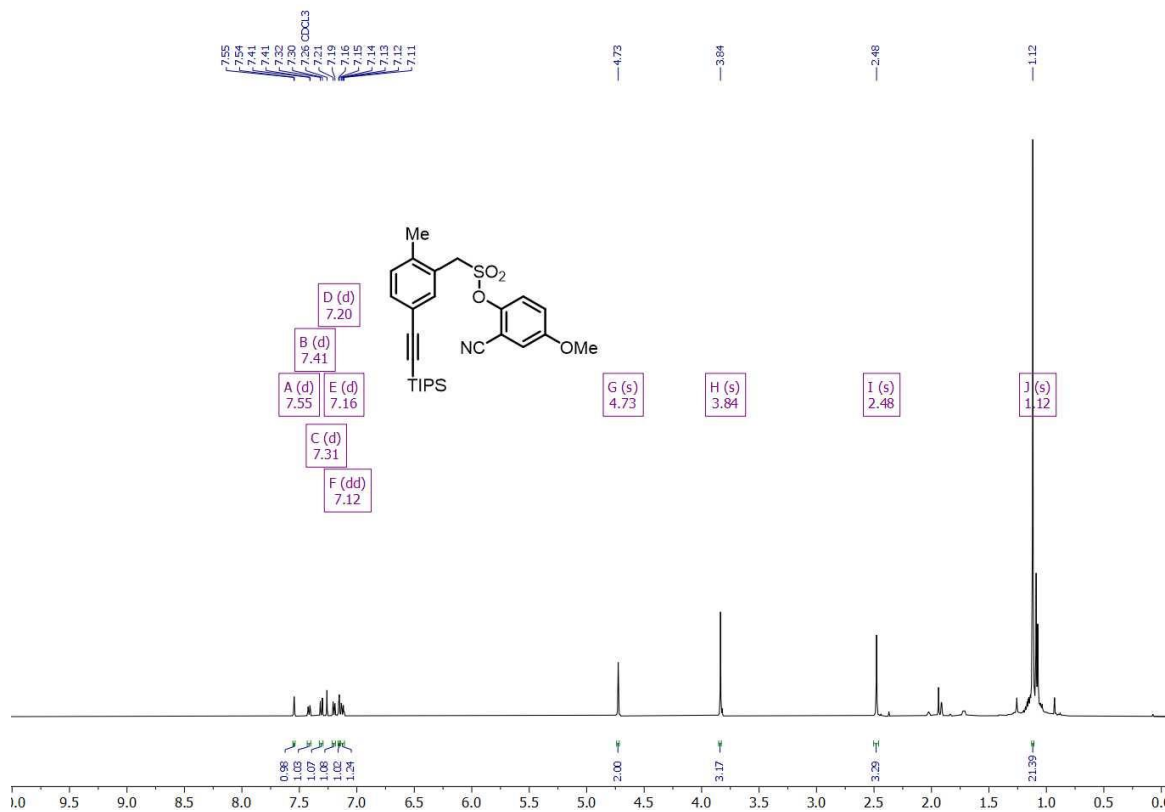
- (1) A. Modak, T. Patra, R. Chowdhury, S. Raul, D. Maiti, *Organometallics*, **2017**, *36*, 2418–2423.
- (2) S. Bag, R. Jayarajan, U. Dutta, R. Chowdhury, R. Mondal, D. Maiti, *Angew. Chem. Int. Ed.* **2017**, *56*, 12538-12542.
- (3) R. Jayarajan, J. Das, S. Bag, R. Chowdhury, D. Maiti, *Angew. Chem. Int. Ed.*, **2018**, *57*, 7659–766.
- (4) M. Bera, A. Maji, S.K. Sahoo, & D. Maiti, *Angew. Chem. Int. Ed.* **2015**, *54*, 8515 –8519.
- (5) a. S. Maity, E. Hoque, U. Dhawa, and D. Maiti, *Chem. Commun.*, **2016**, *52*, 14003-14006. b. H. Li, Subbotina, A. Bunrit, F. Wang, and J. Samec, *Chem. Sci.*, **2019**, *10*, 3681-3686.
- (6) S. Porey, X. Zhang, S. Bhowmick, V. K. Singh, S. Guin, R. S. Paton, D. Maiti, *J. Am. Chem. Soc.* **2020**, *142*, 3762–3774.

NMR SPECTRA

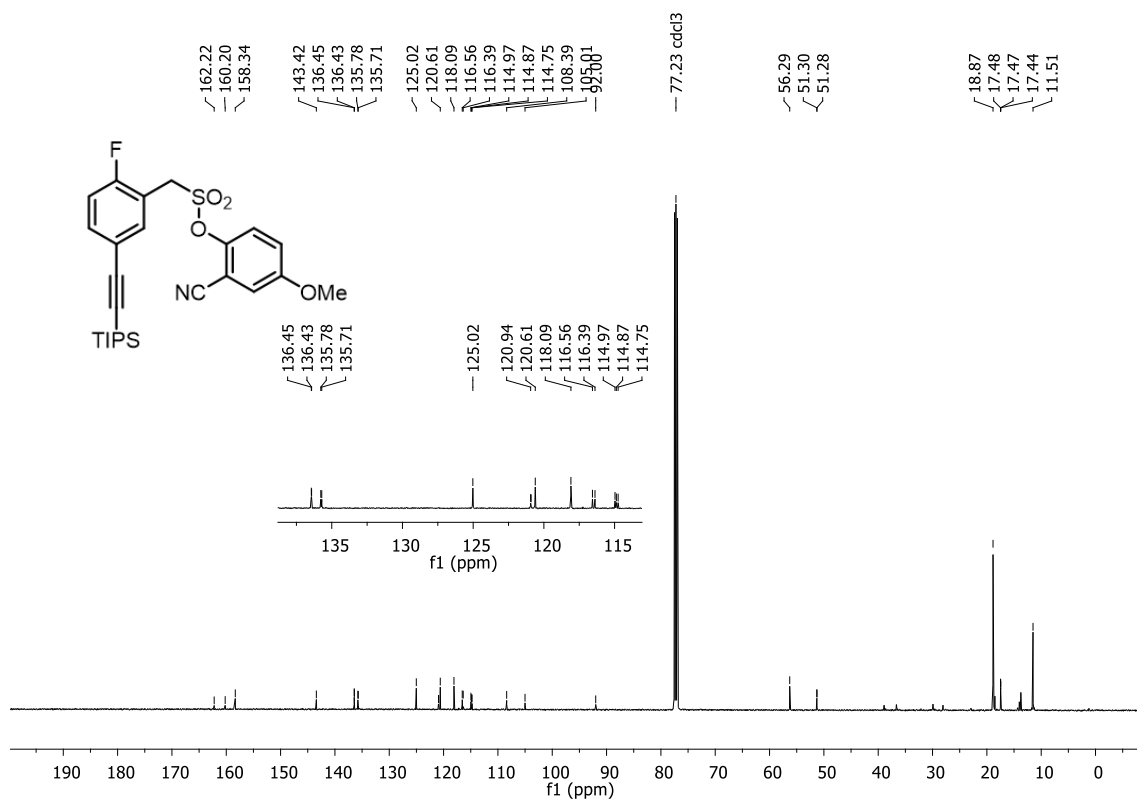
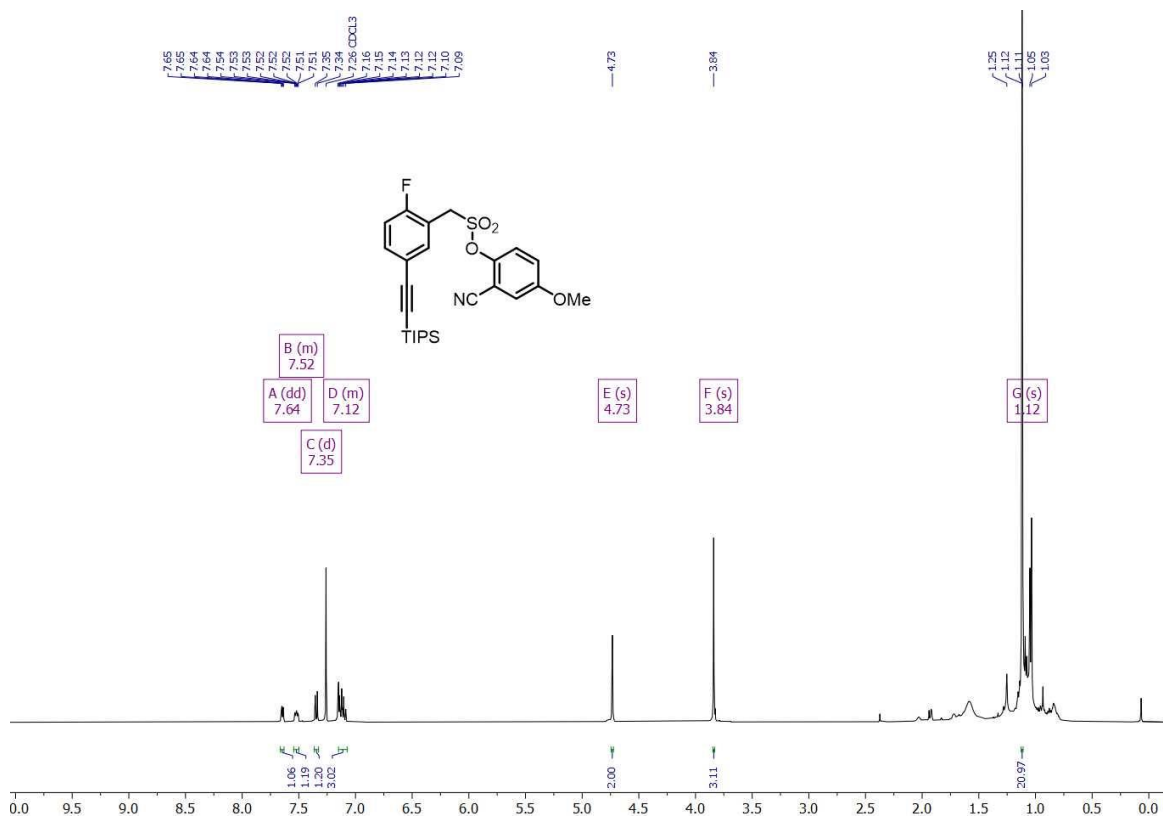
3a. 2-Cyano-4-methoxyphenyl (3-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



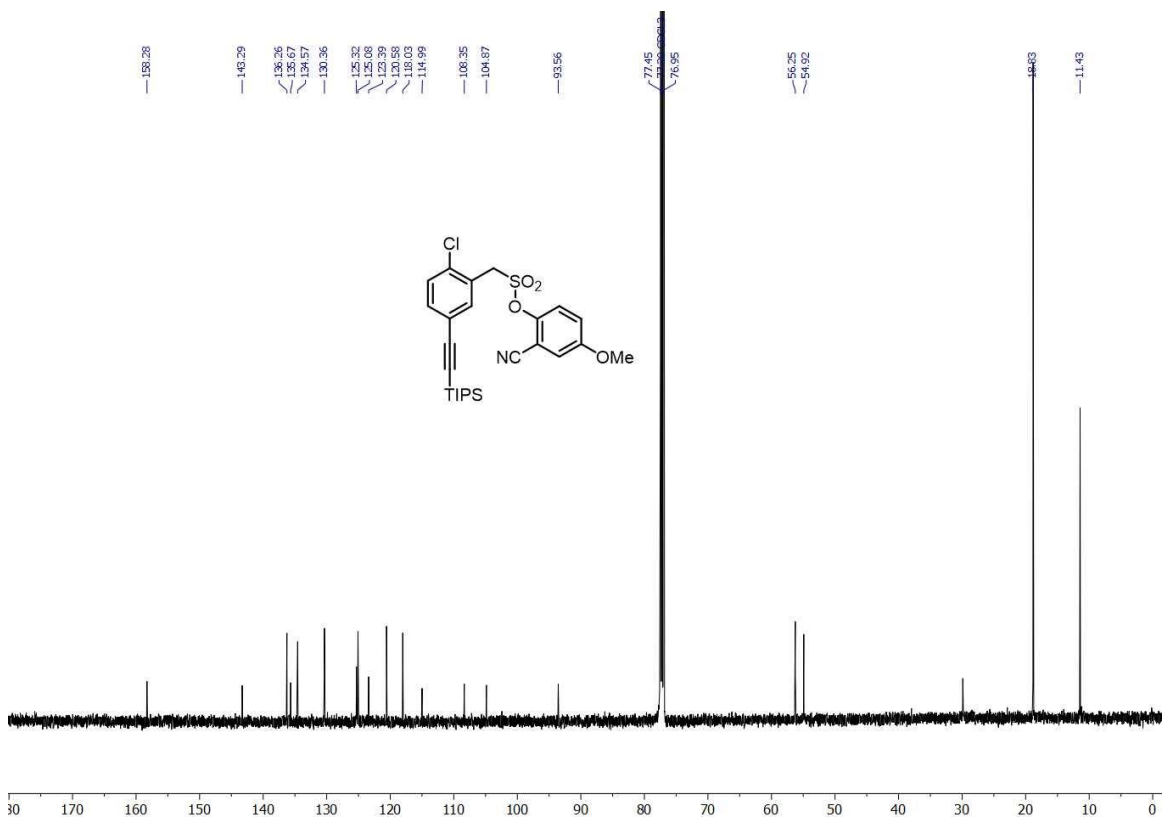
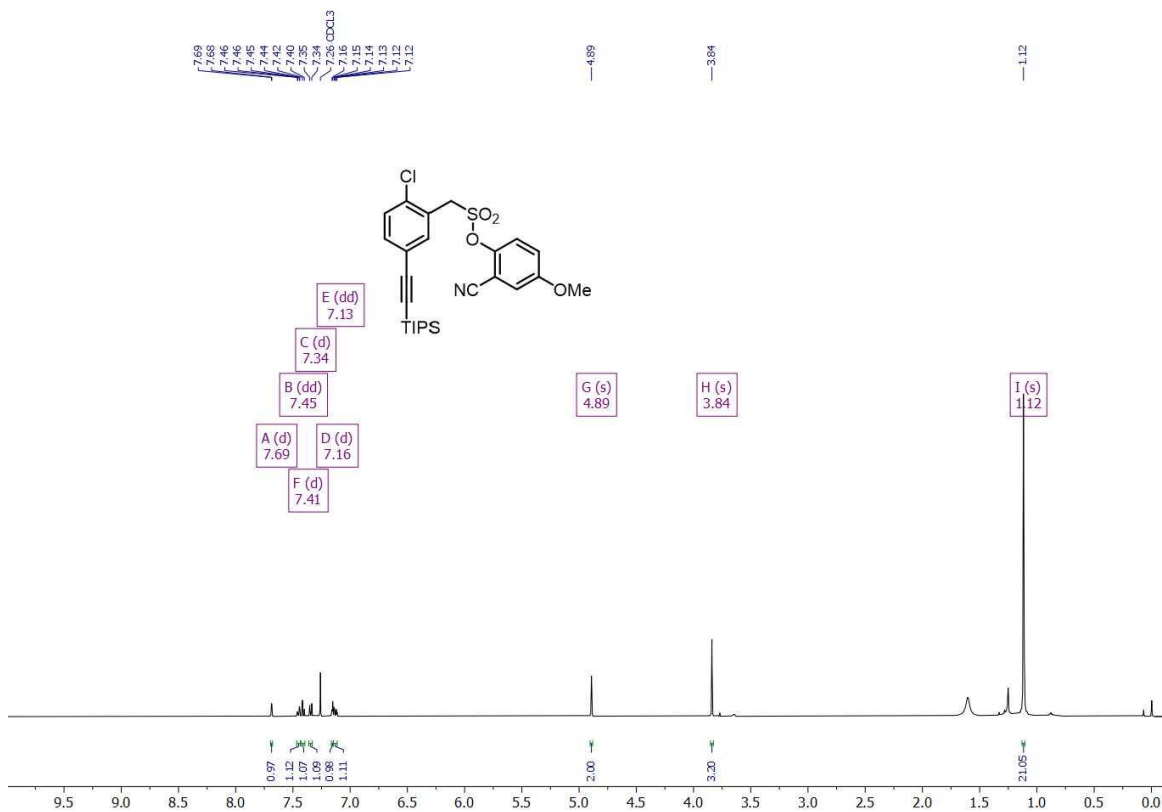
3b. 2-Cyano-4-methoxyphenyl (2-methyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



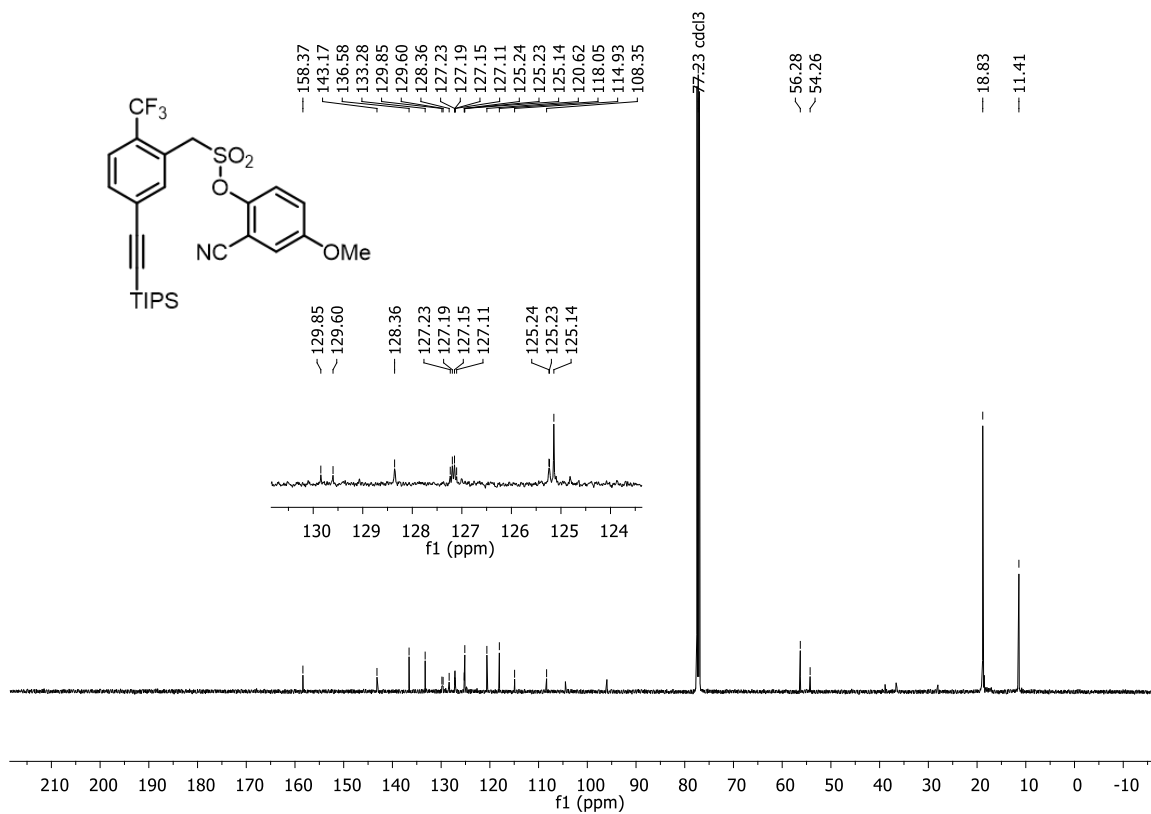
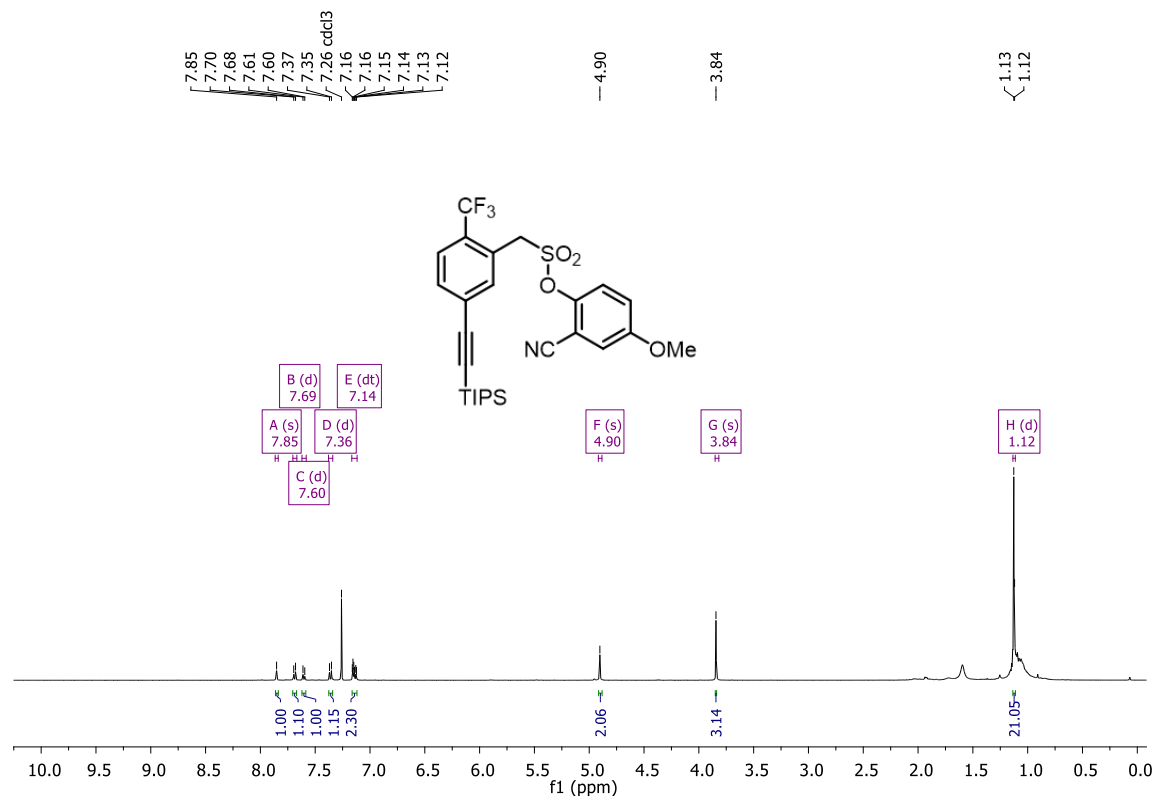
3c. 2-Cyano-4-methoxyphenyl (2-fluoro-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



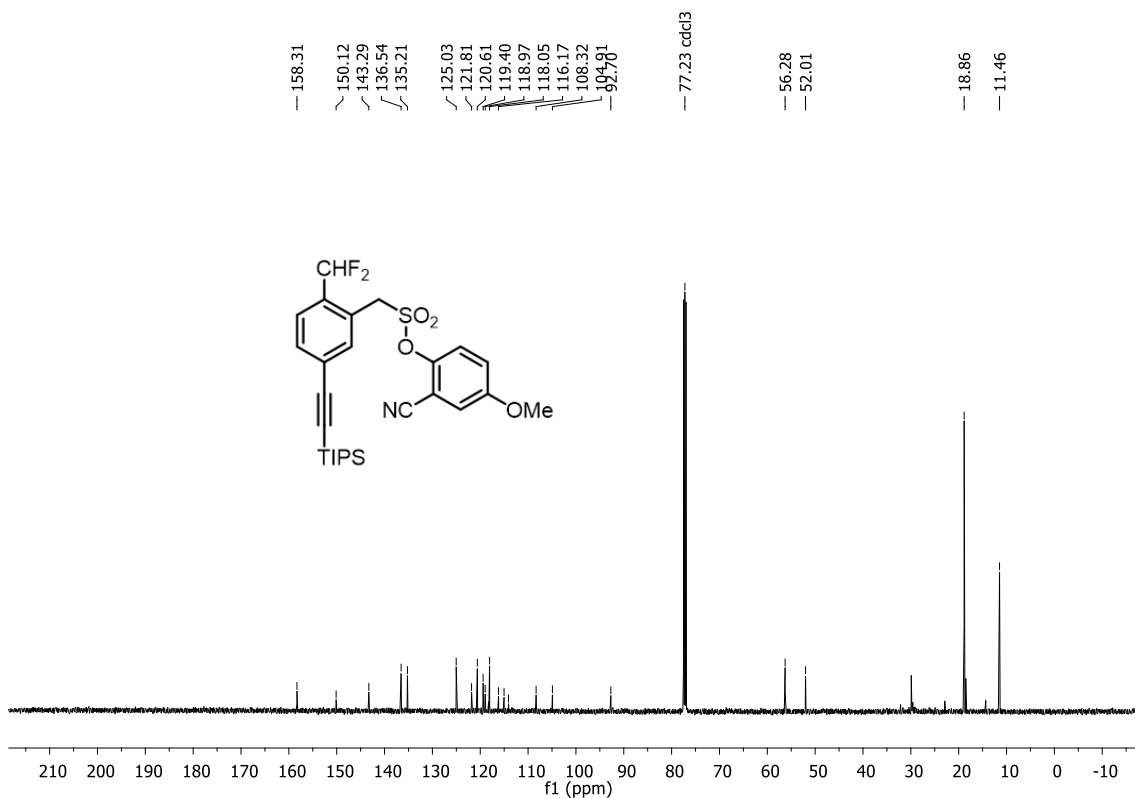
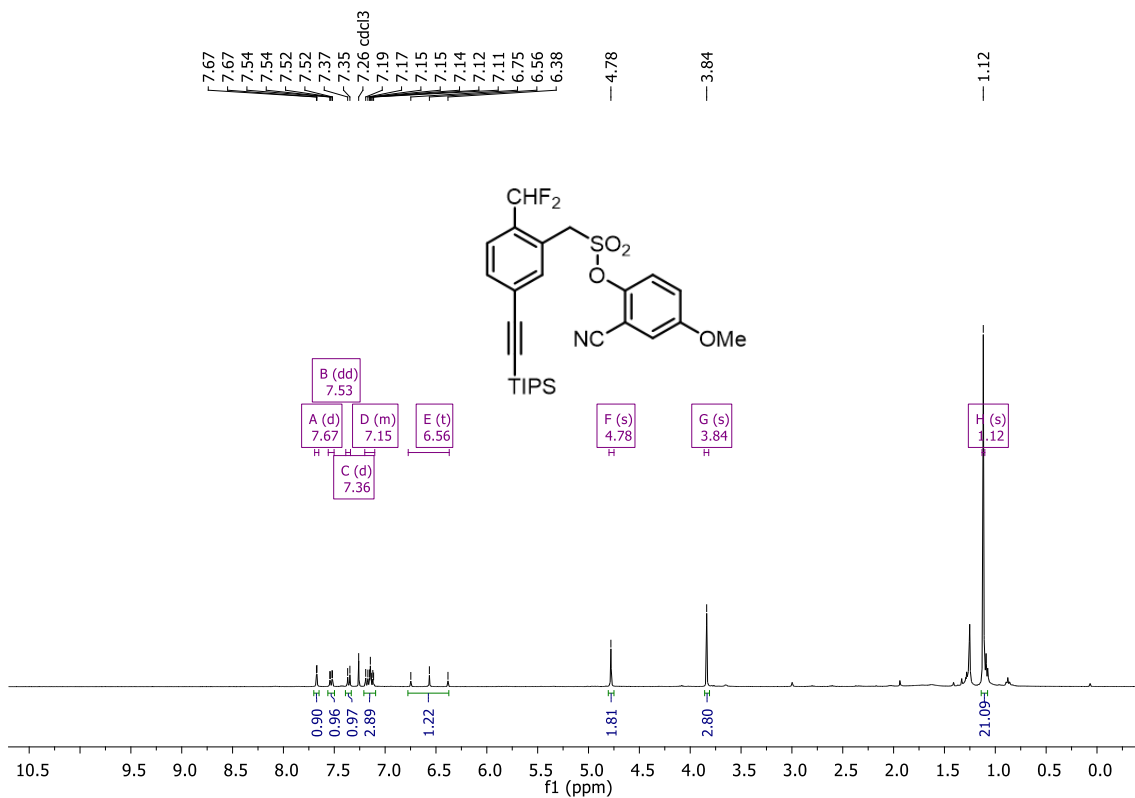
3d. 2-Cyano-4-methoxyphenyl (2-chloro-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



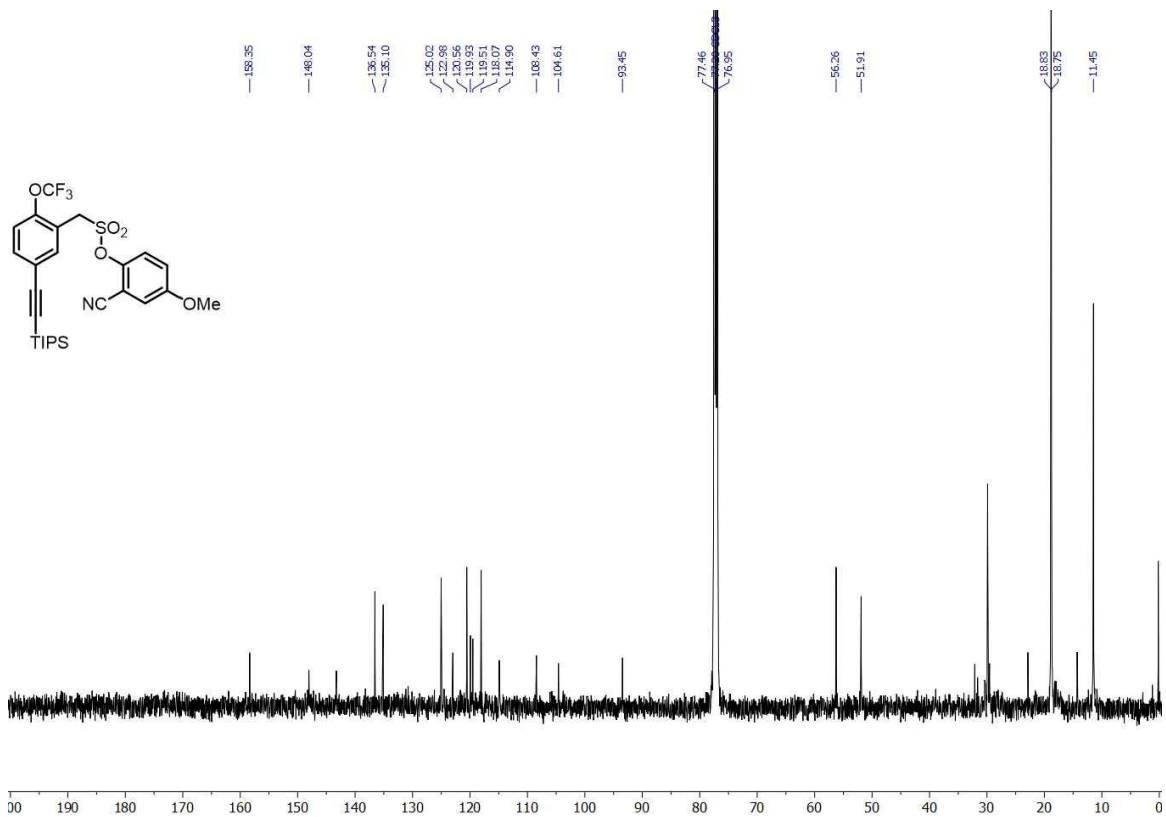
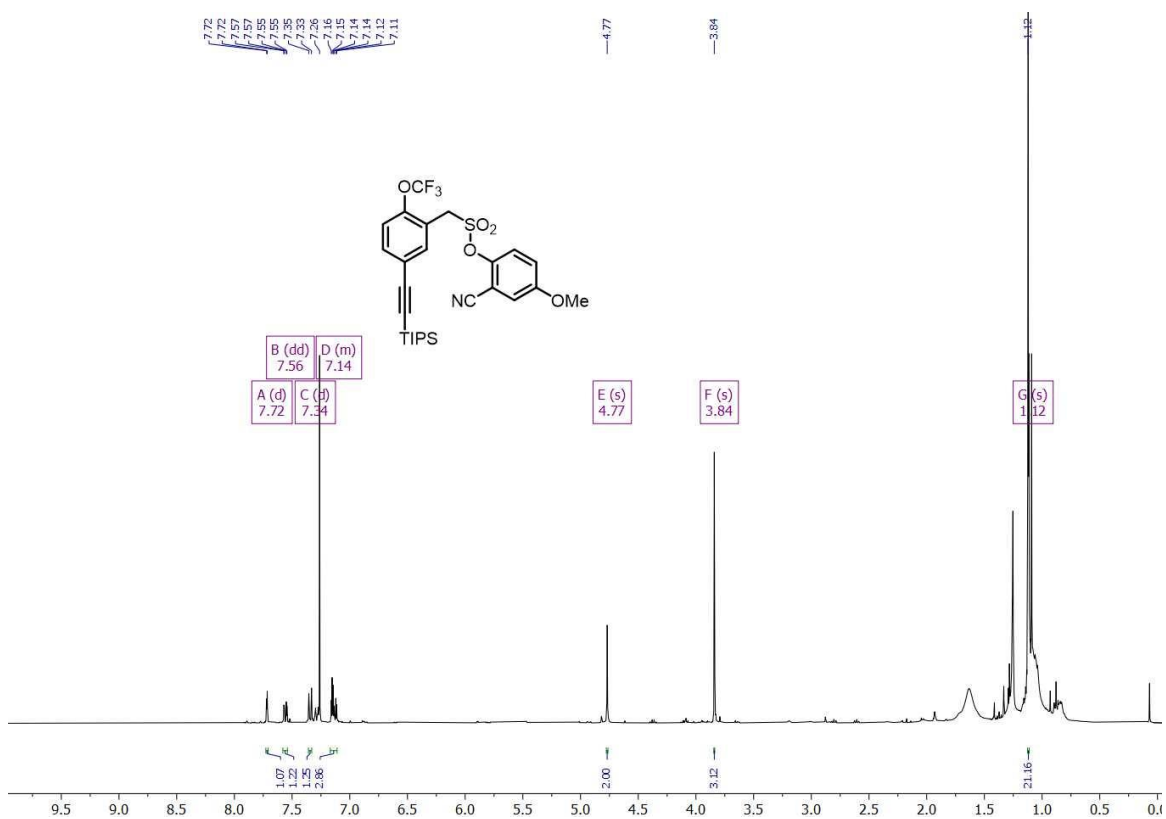
3e. 2-Cyano-4-methoxyphenyl (2-trifluoromethyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



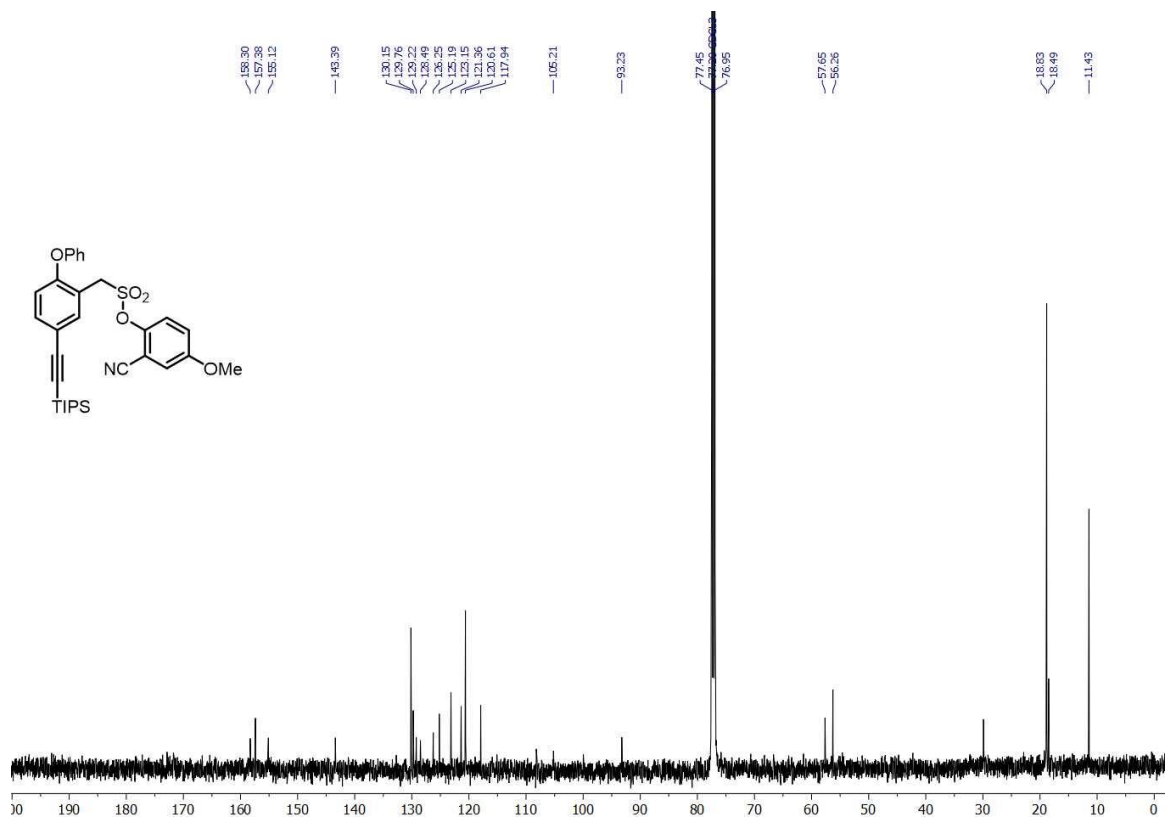
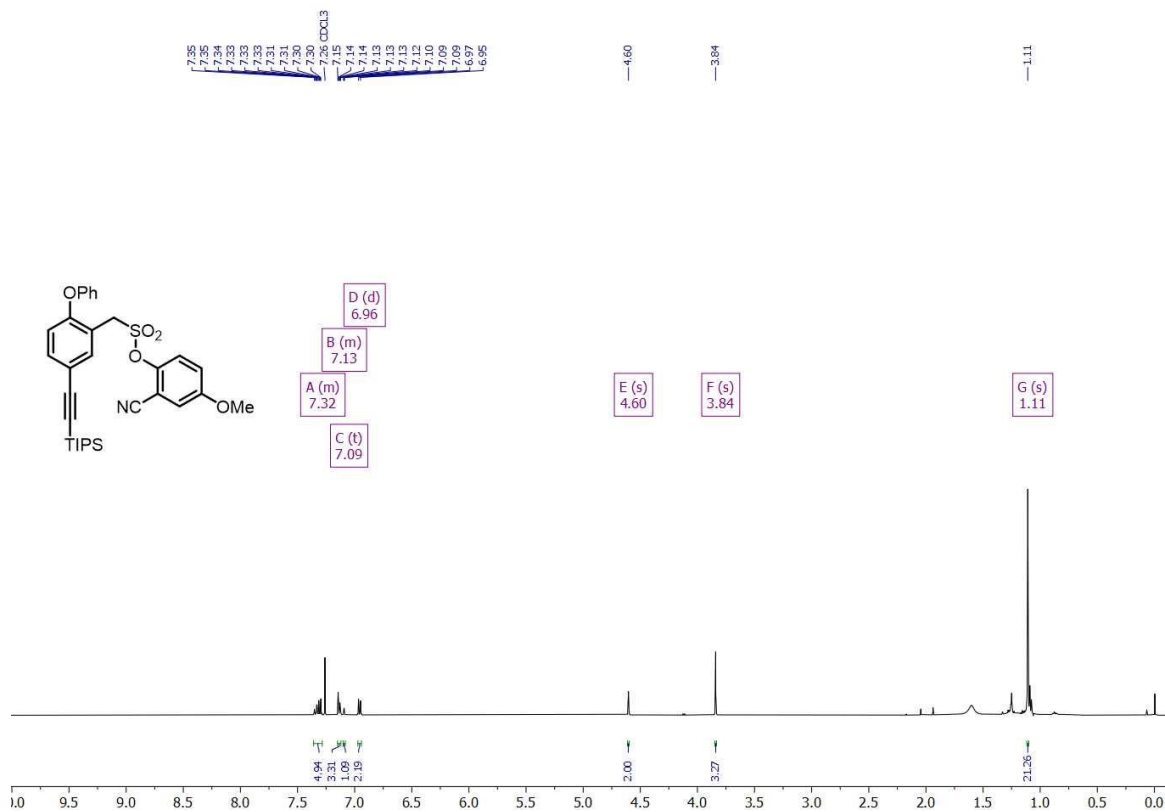
3f. 2-Cyano-4-methoxyphenyl (2-difluoromethyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



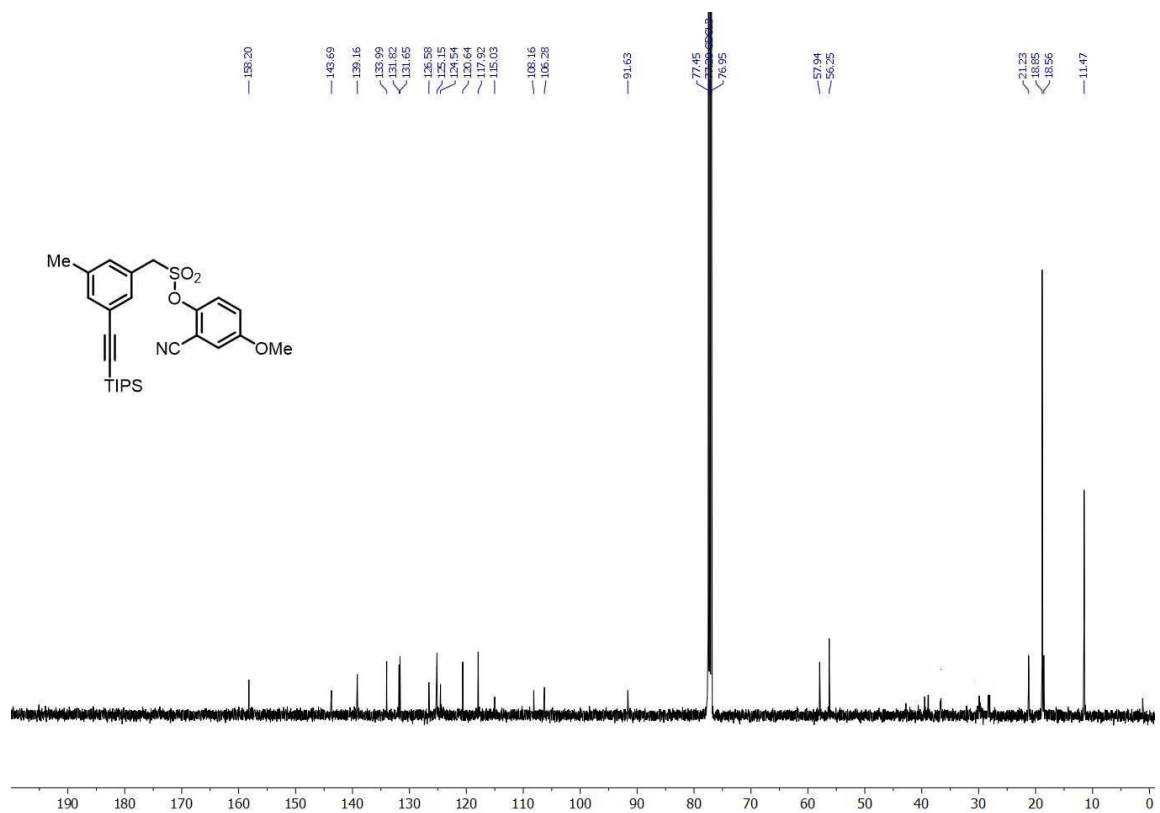
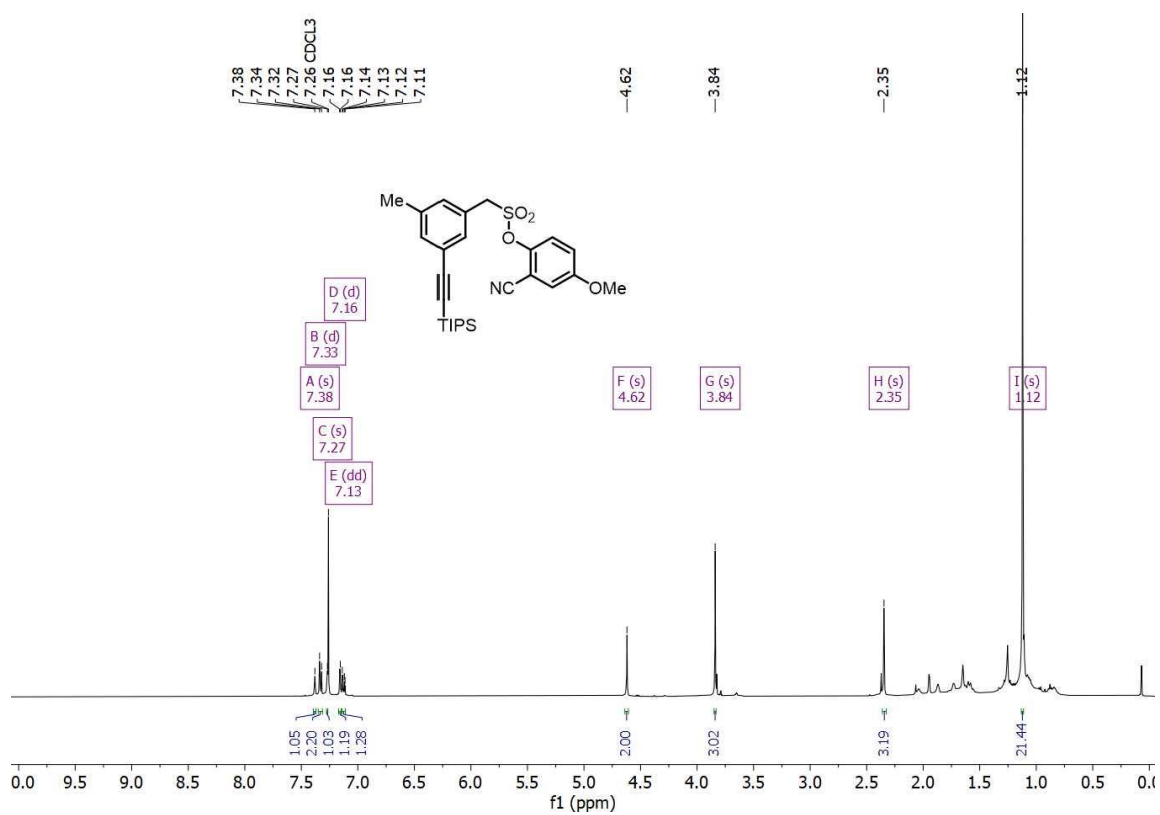
3g. 2-Cyano-4-methoxyphenyl (2-trifluoromethoxy-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



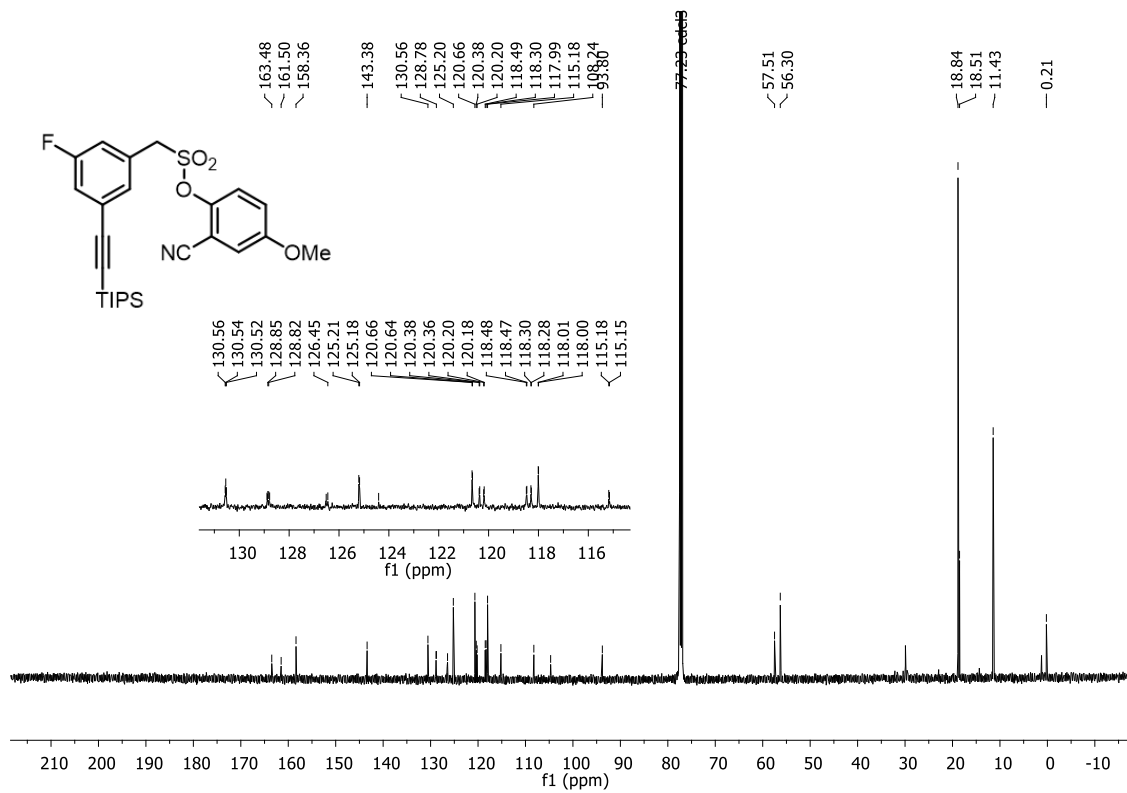
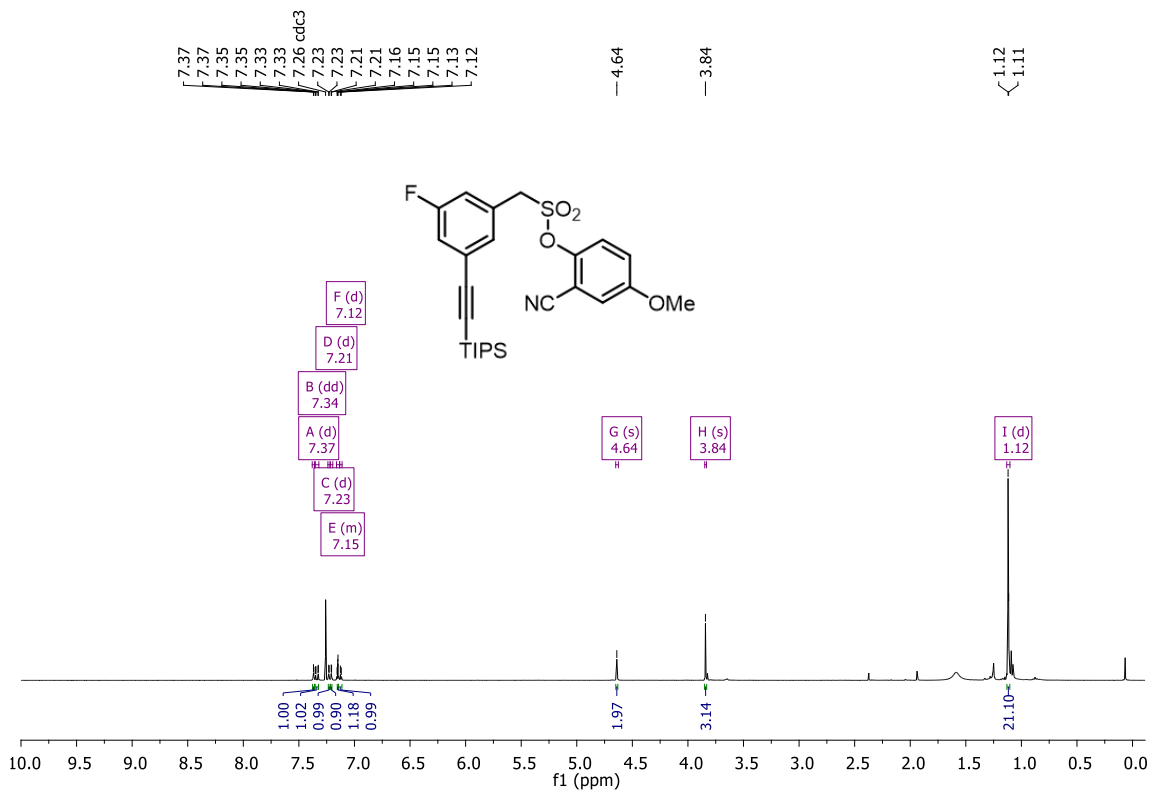
3h. 2-Cyano-4-methoxyphenyl (2-phenoxy-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



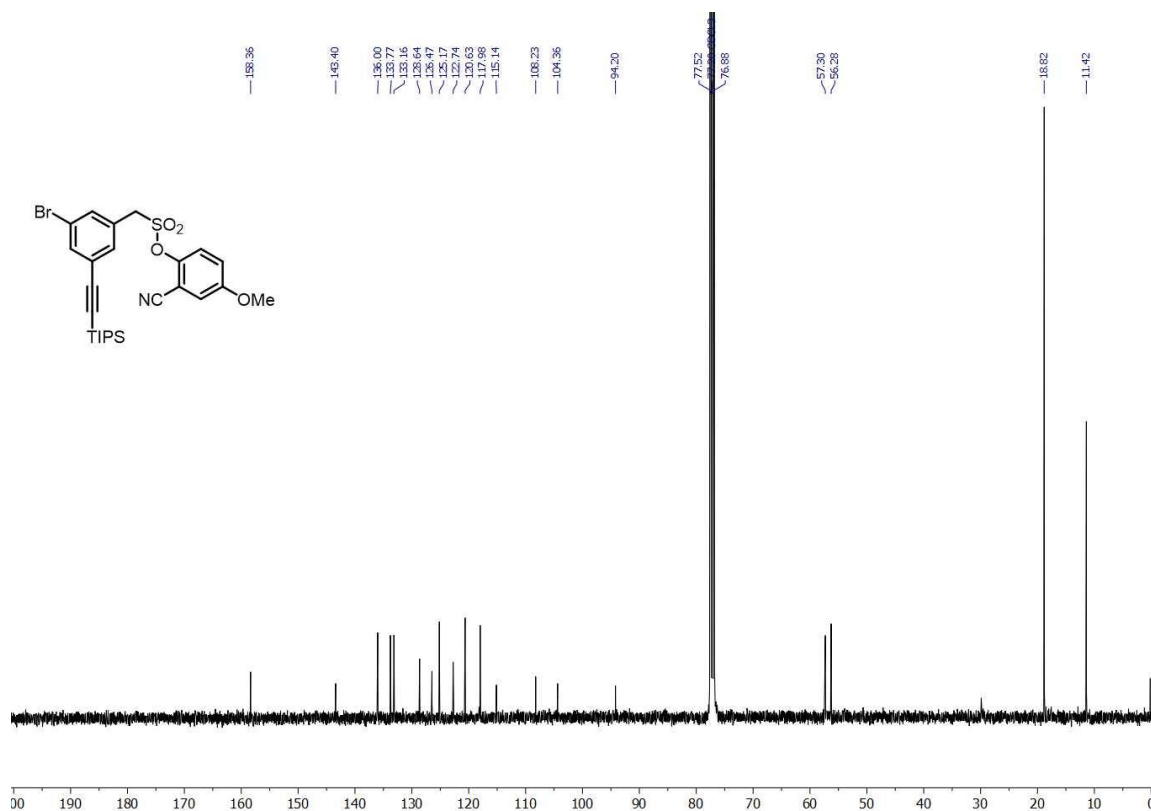
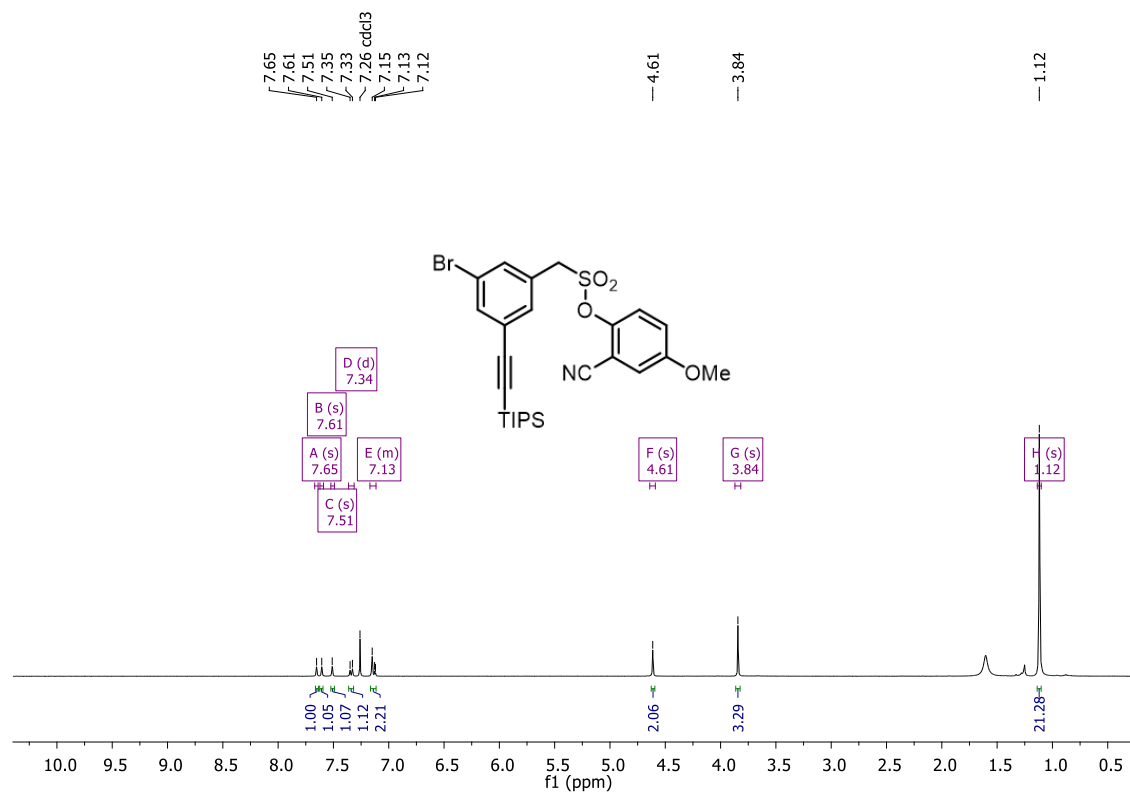
3i. 2-Cyano-4-methoxyphenyl (3-methyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



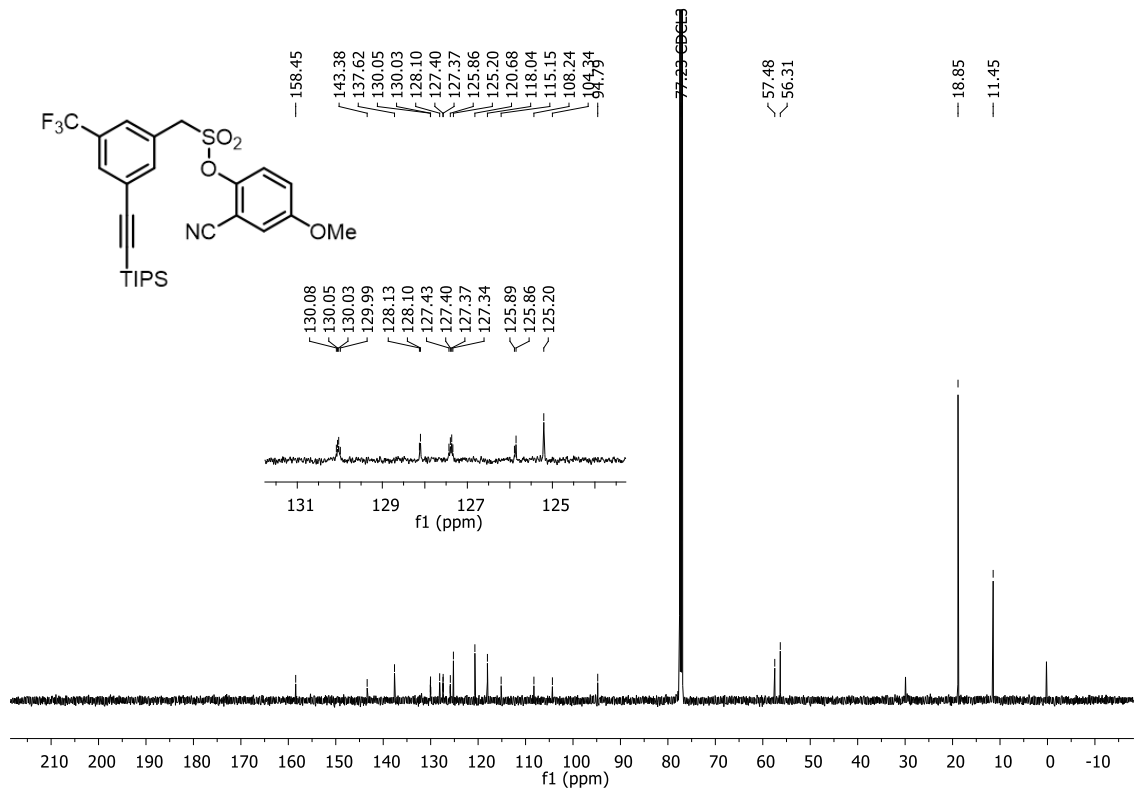
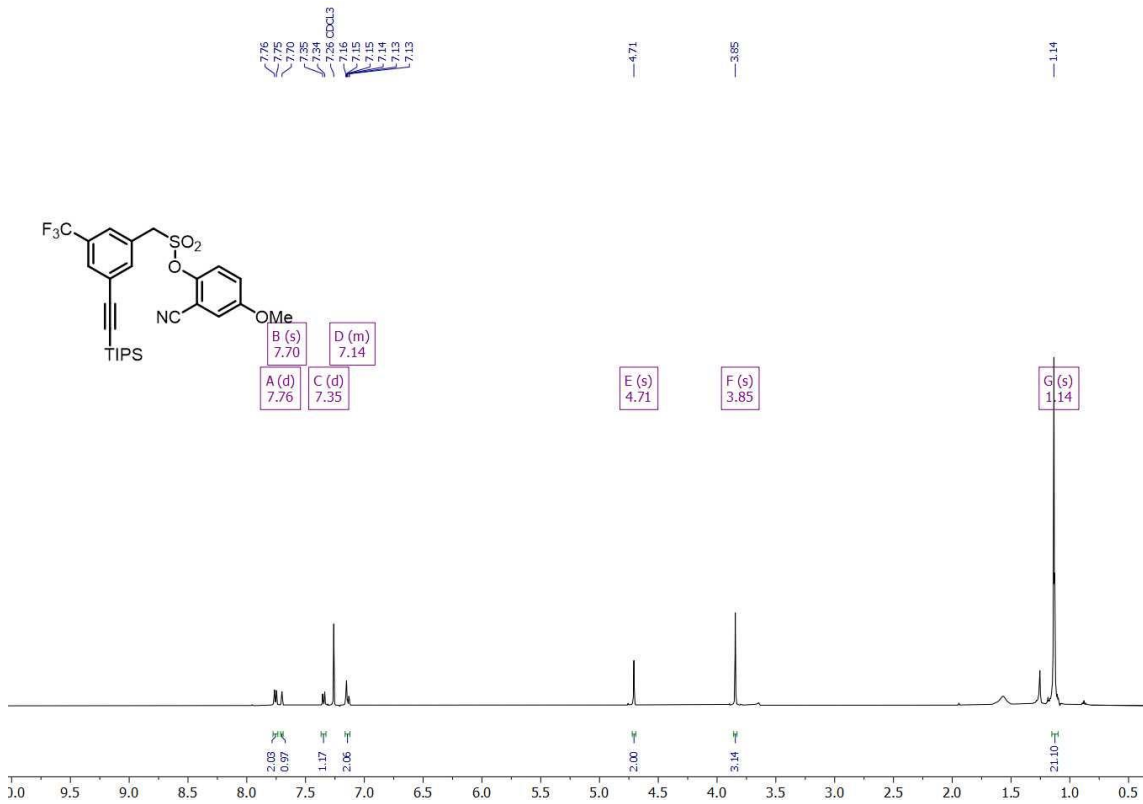
3j. 2-cyano-4-methoxyphenyl (3-fluoro-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



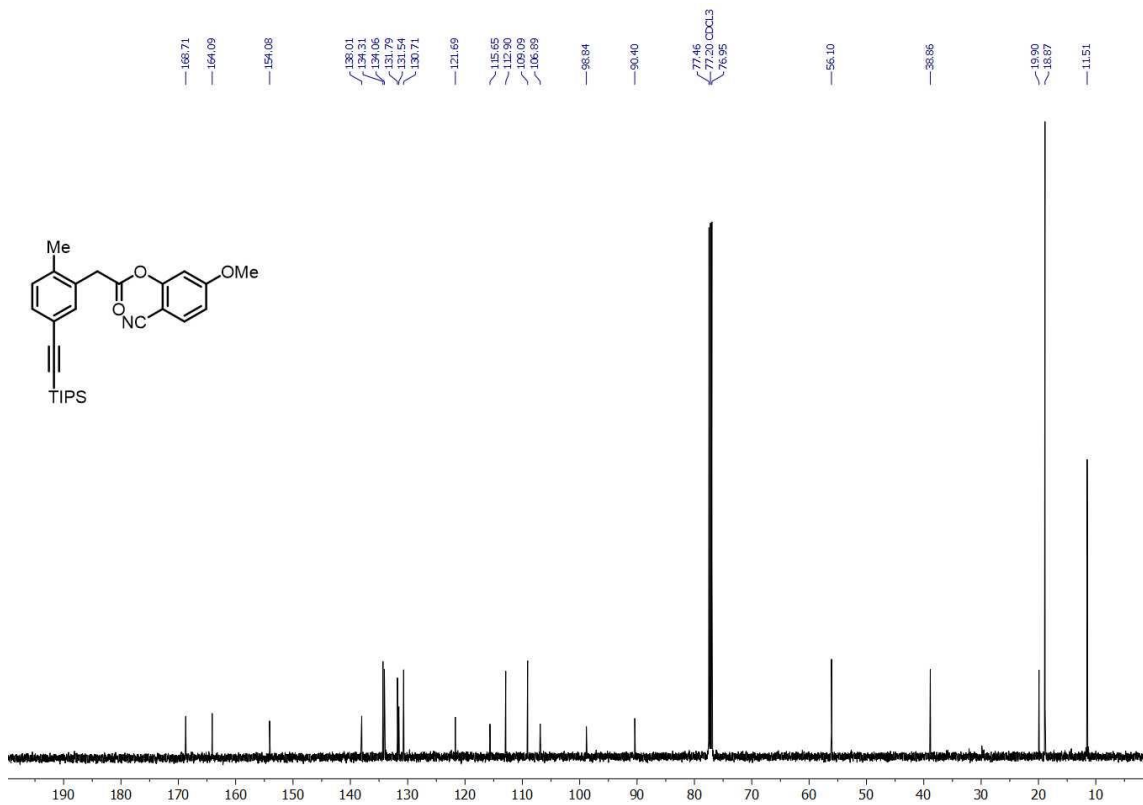
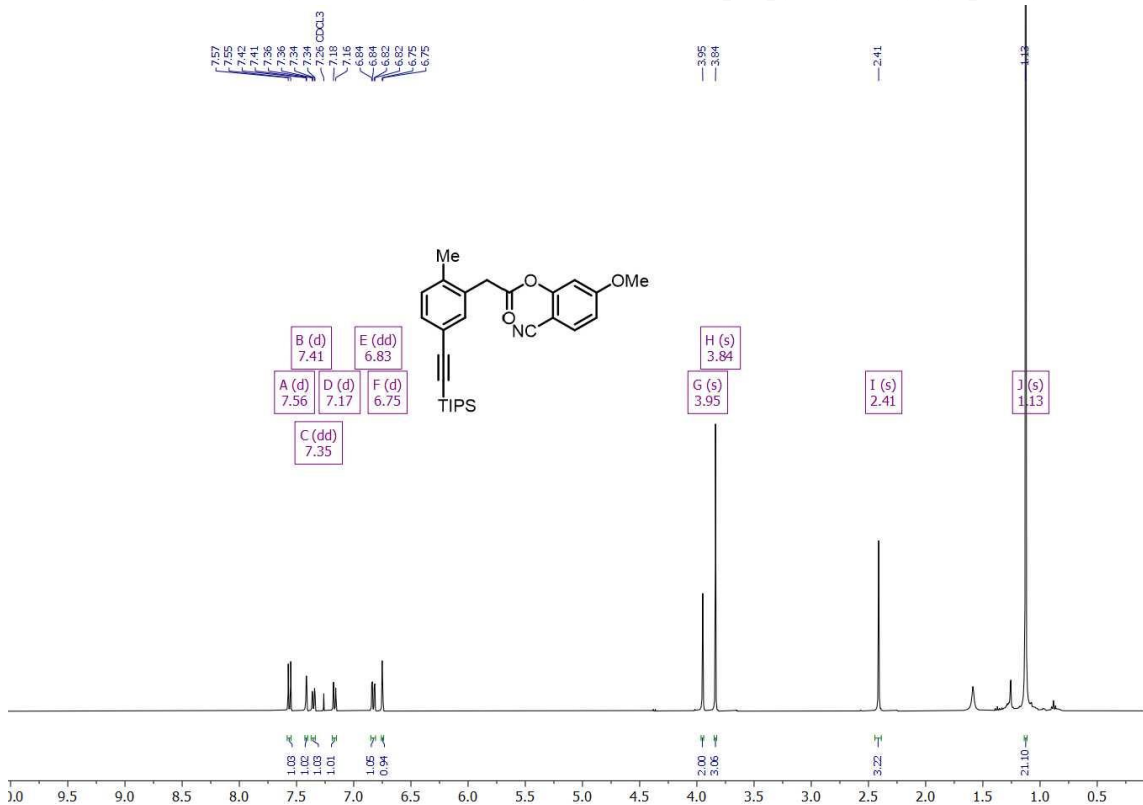
3k. 2-Cyano-4-methoxyphenyl (3-bromo-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



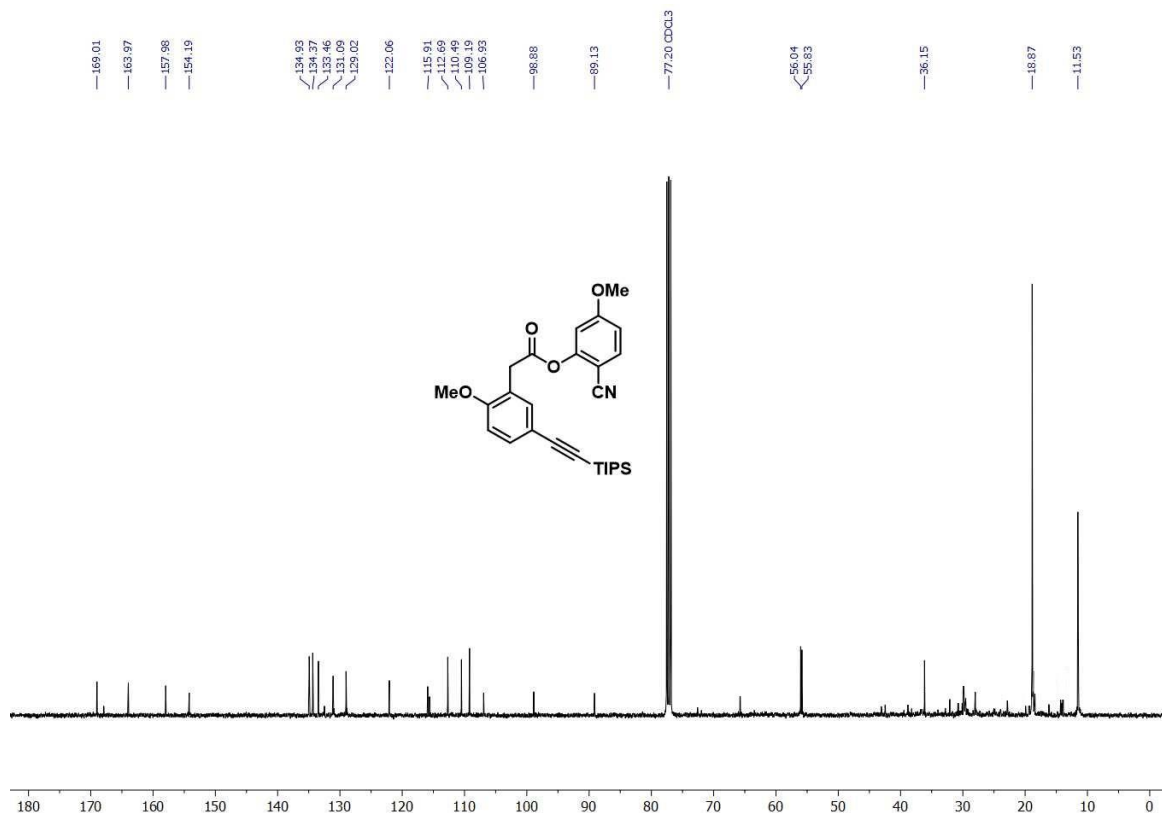
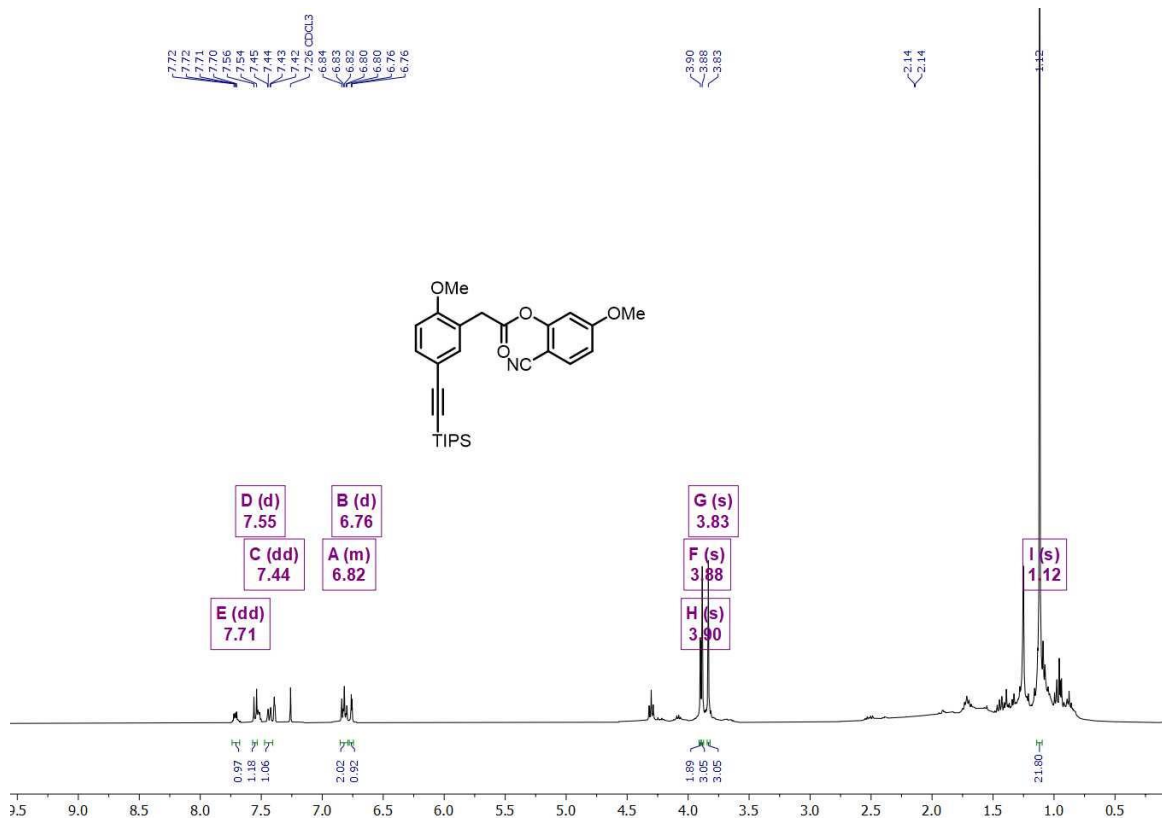
3l. 2-Cyano-4-methoxyphenyl(3-trifluoromethyl-5-((triisopropylsilyl)ethynyl)phenyl)methanesulfonate



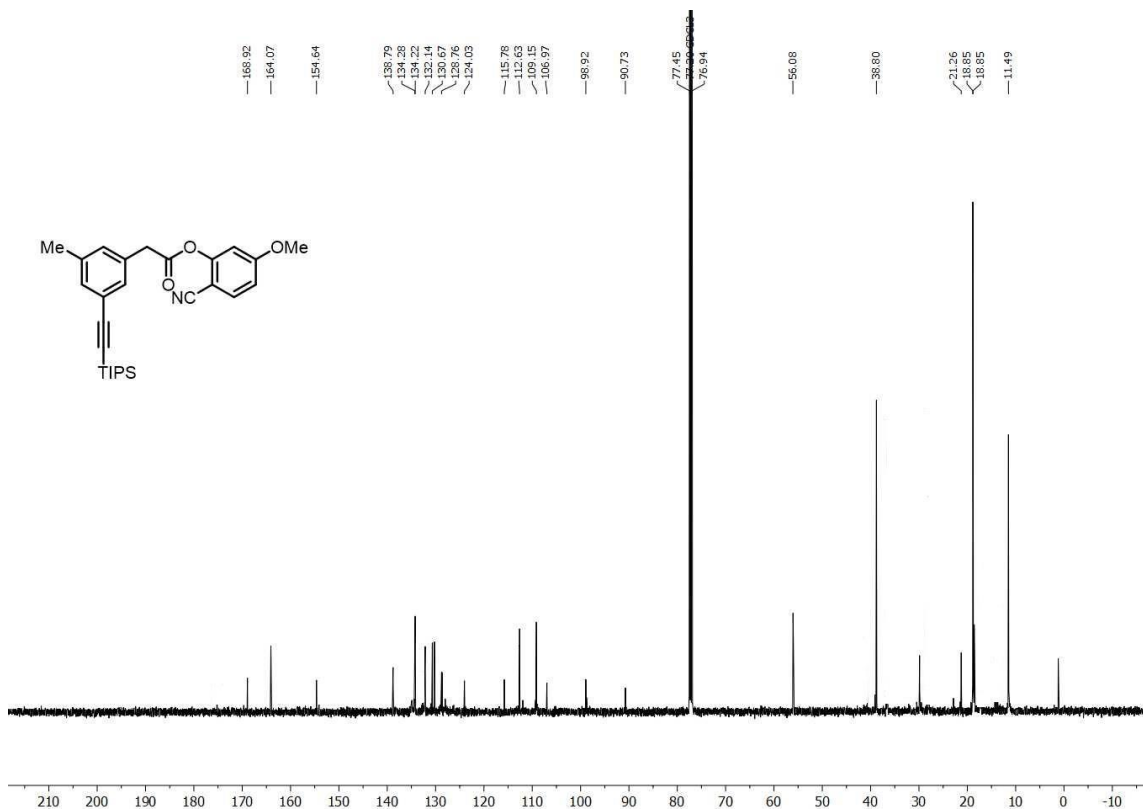
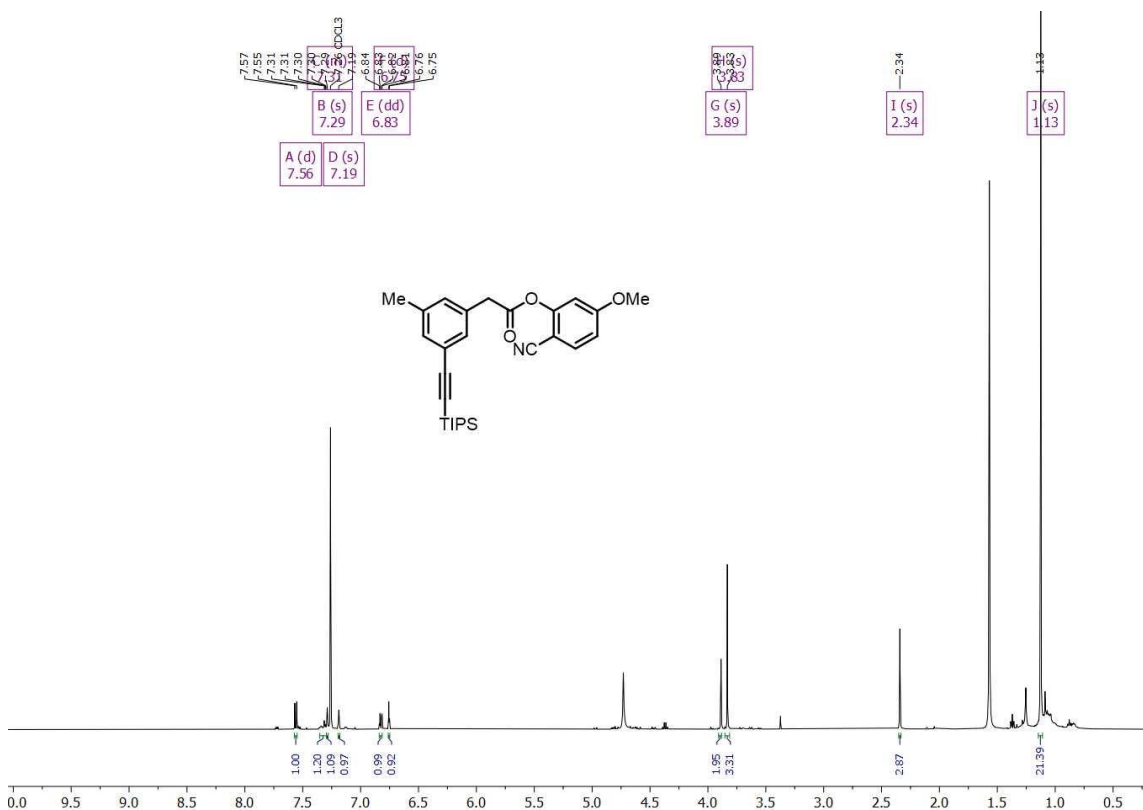
5a. 2-Cyano-5-methoxybenzotrile 2-(2-methyl-5-((triisopropylsilyl)ethynyl)phenyl)acetate



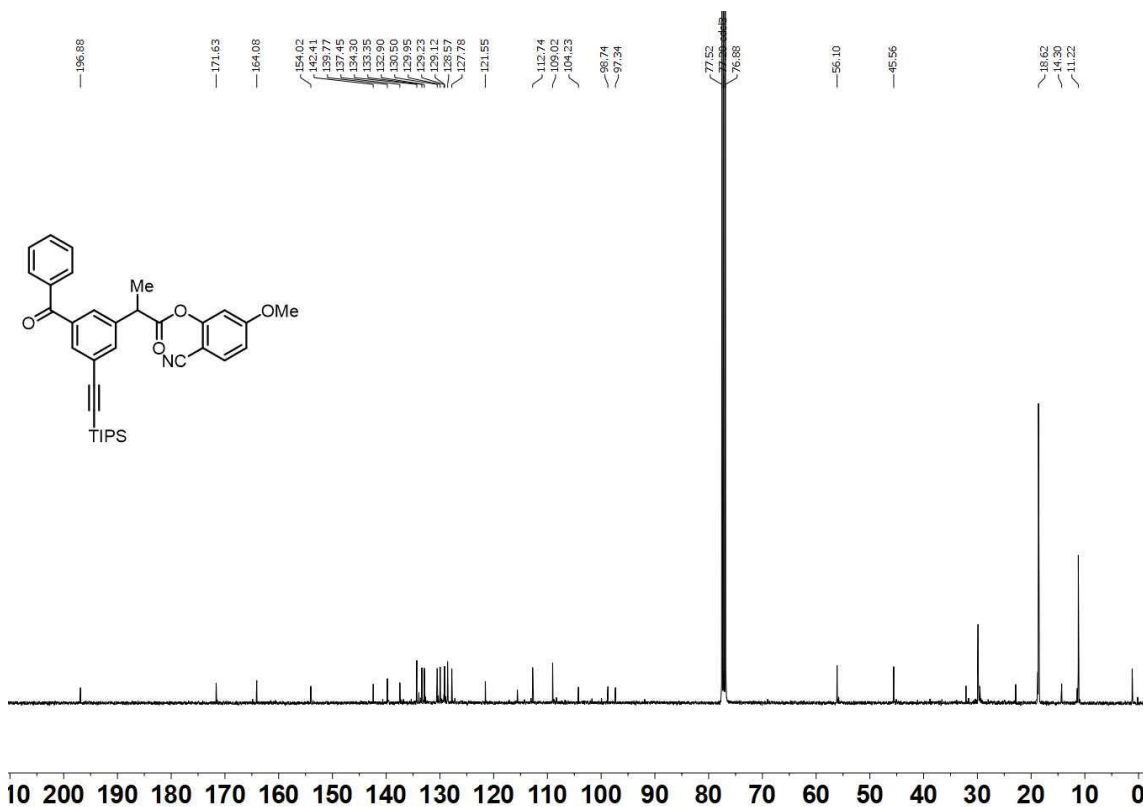
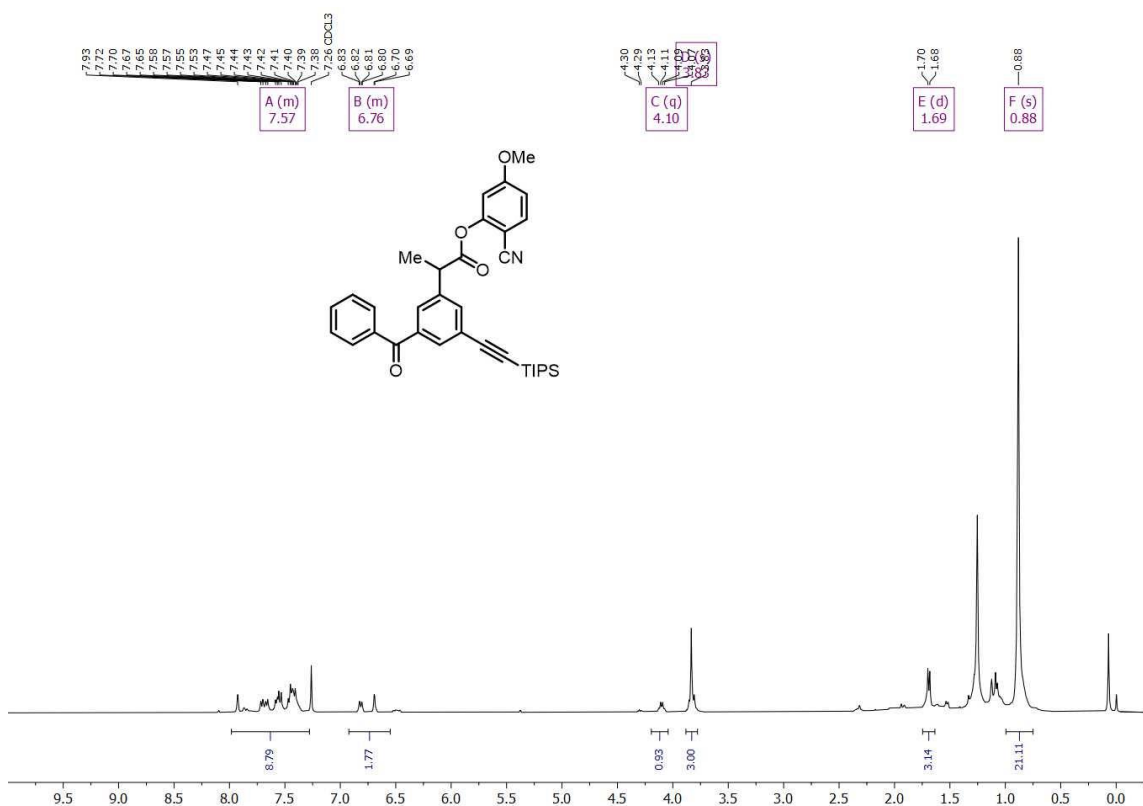
5b. 2-cyano-5-methoxyphenyl 2-(2-methoxy-5-((triisopropylsilyl)ethynyl)phenyl)acetate



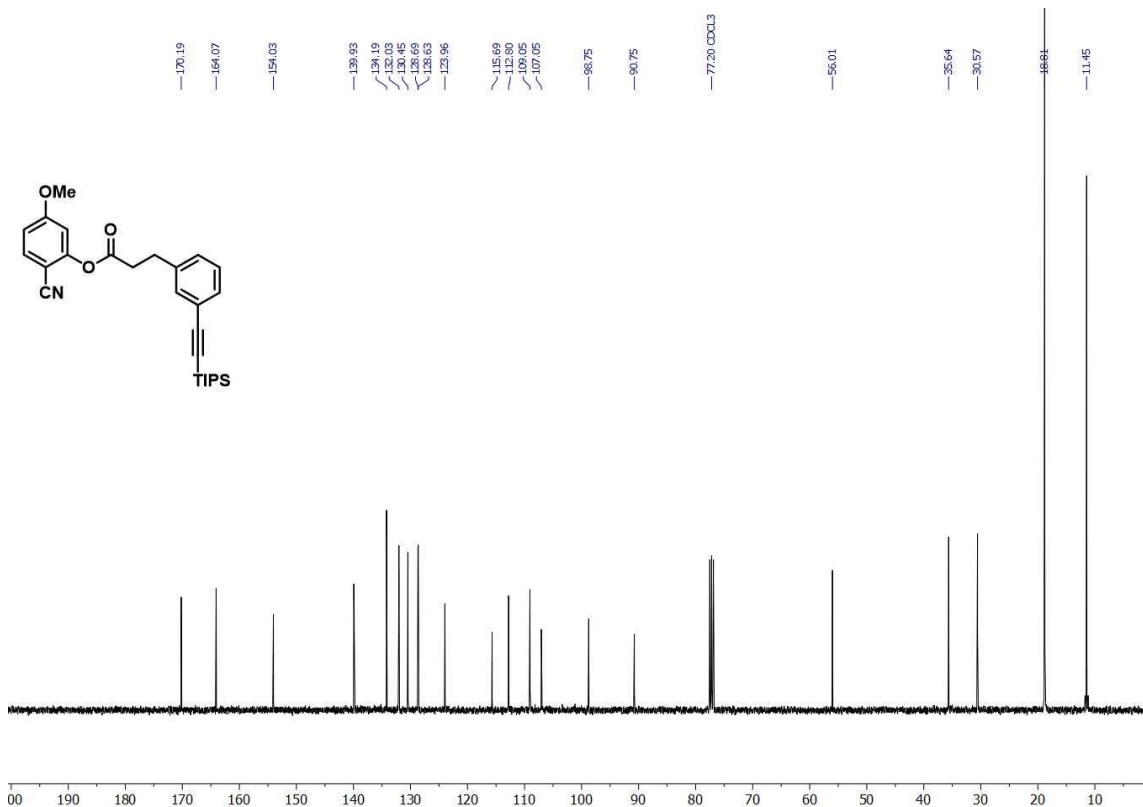
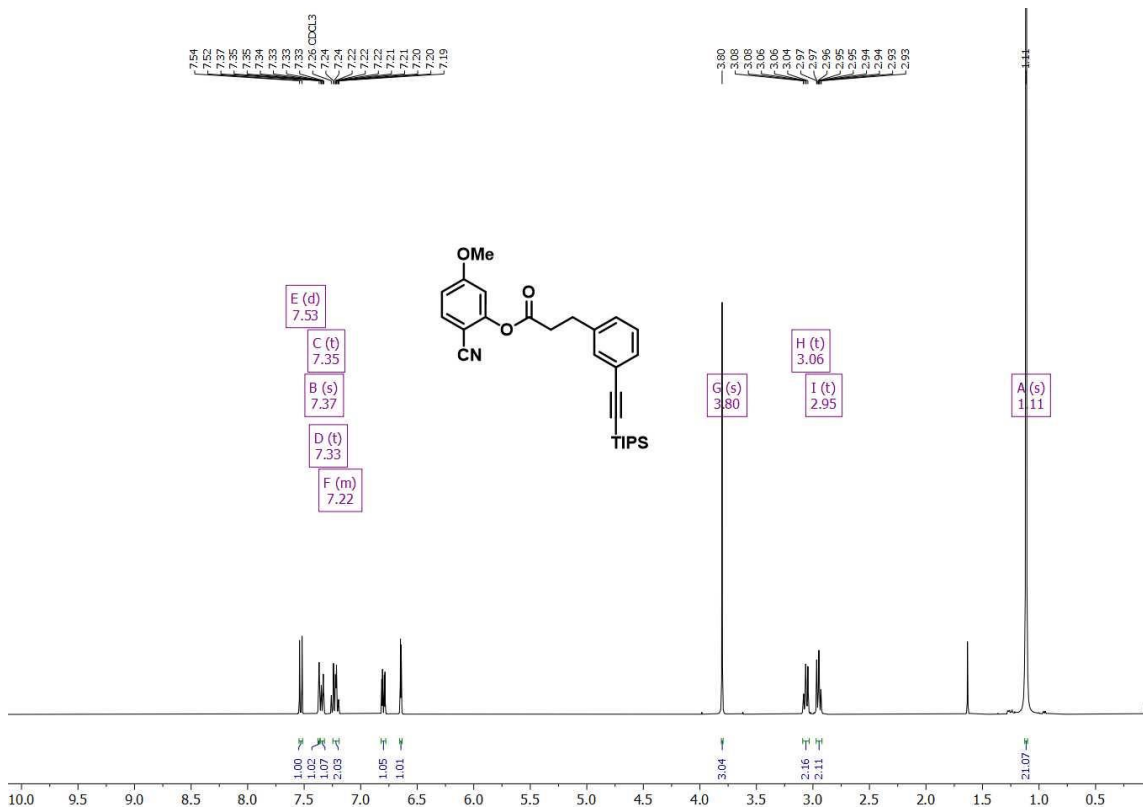
5c. 2-Cyano-5-methoxybenzotrile 2-(3-methyl-5-((triisopropylsilyl)ethynyl)phenyl)acetate



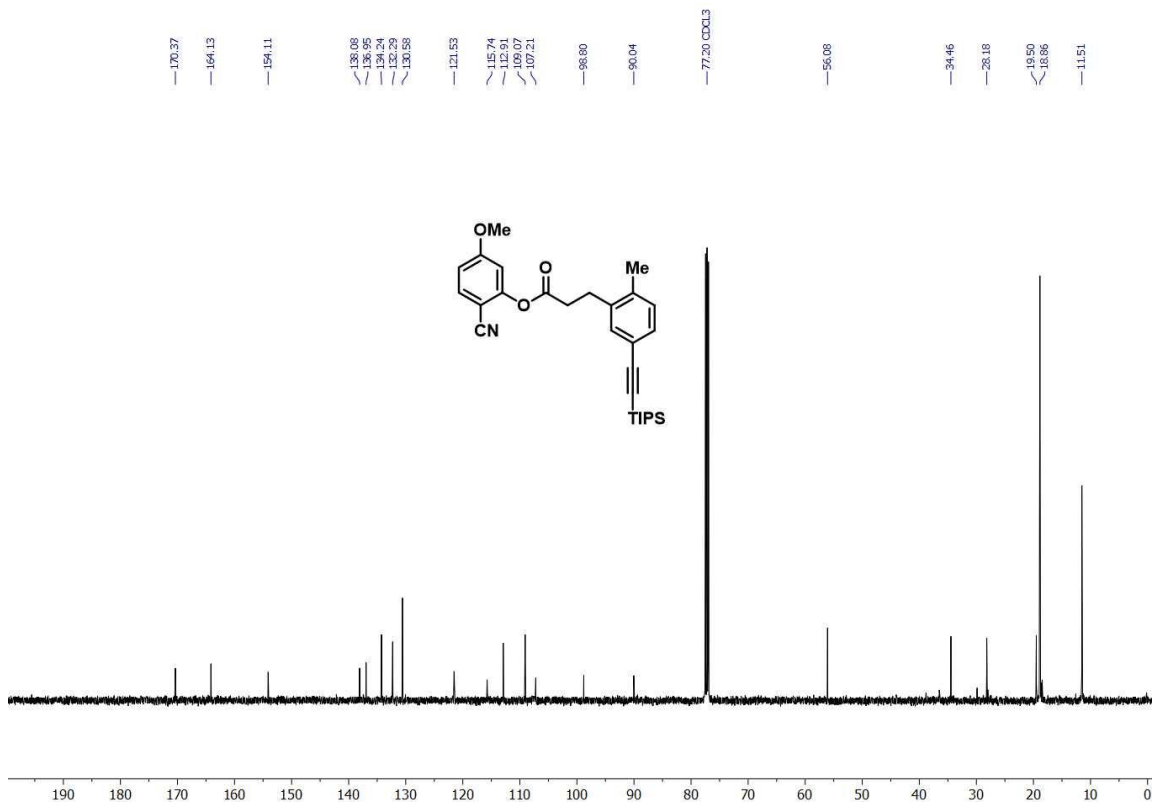
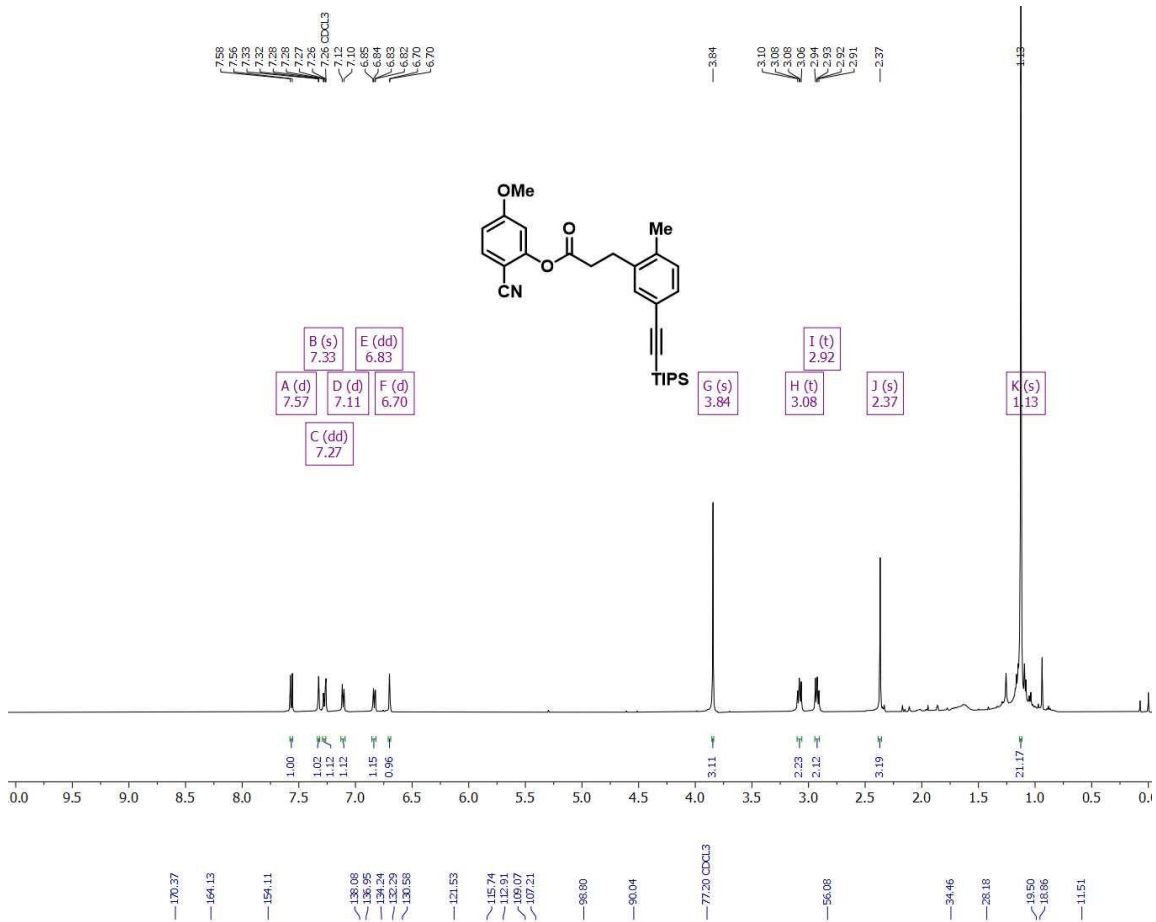
5d. 2-cyano-5-methoxyphenyl 2-(3-benzoyl-5-((triisopropylsilyl)ethynyl)phenyl)propanoate



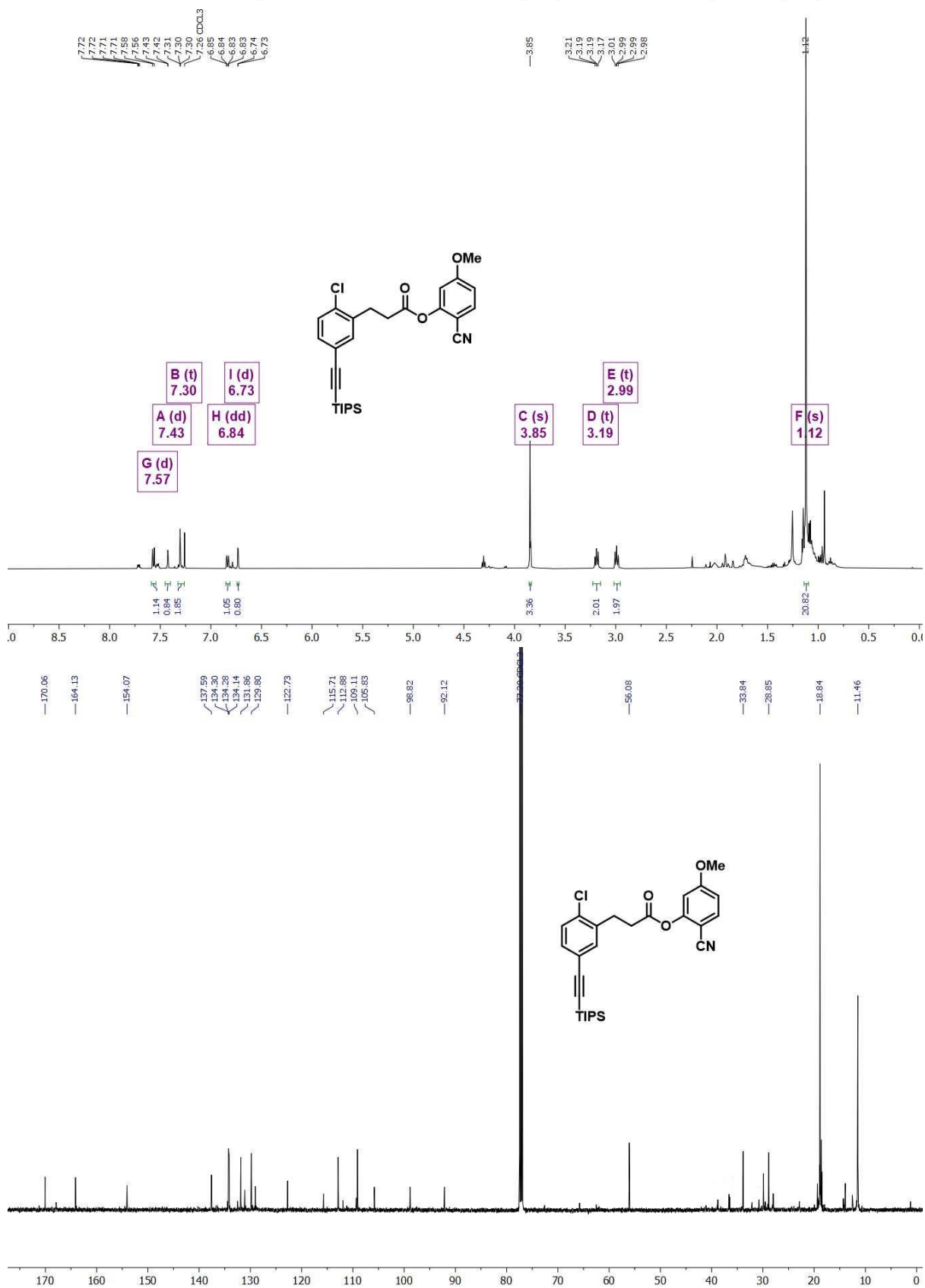
5e. 2-cyano-5-methoxyphenyl 3-(3-((triisopropylsilyl)ethynyl)phenyl)propanoate



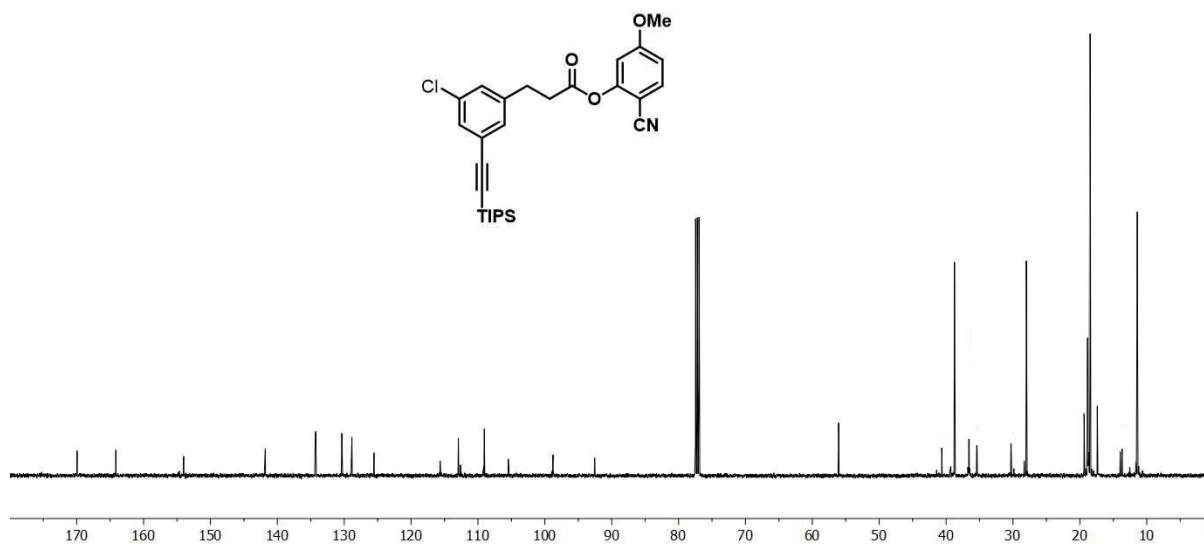
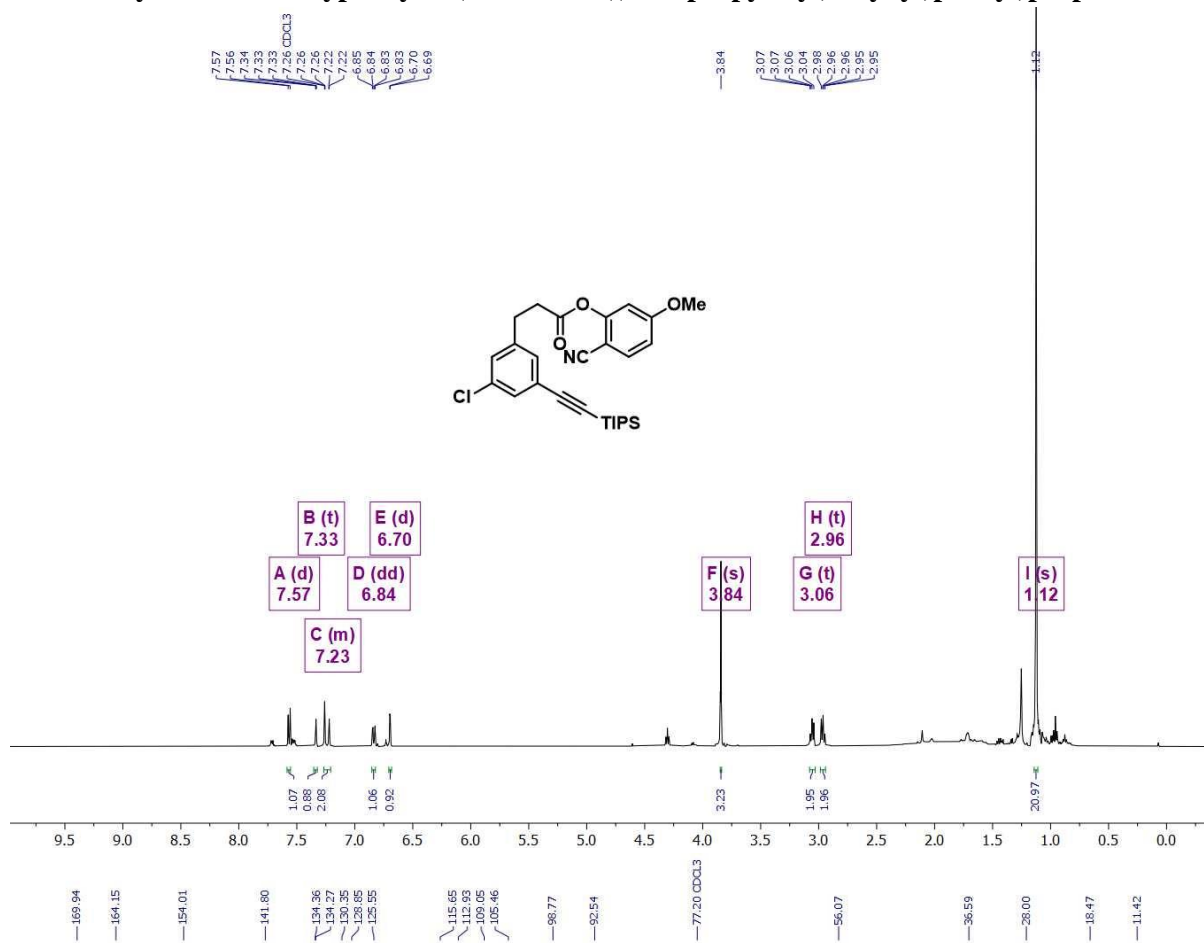
5f. 2-cyano-5-methoxyphenyl 3-(2-methyl-5-((triisopropylsilyl)ethynyl)phenyl)propanoate



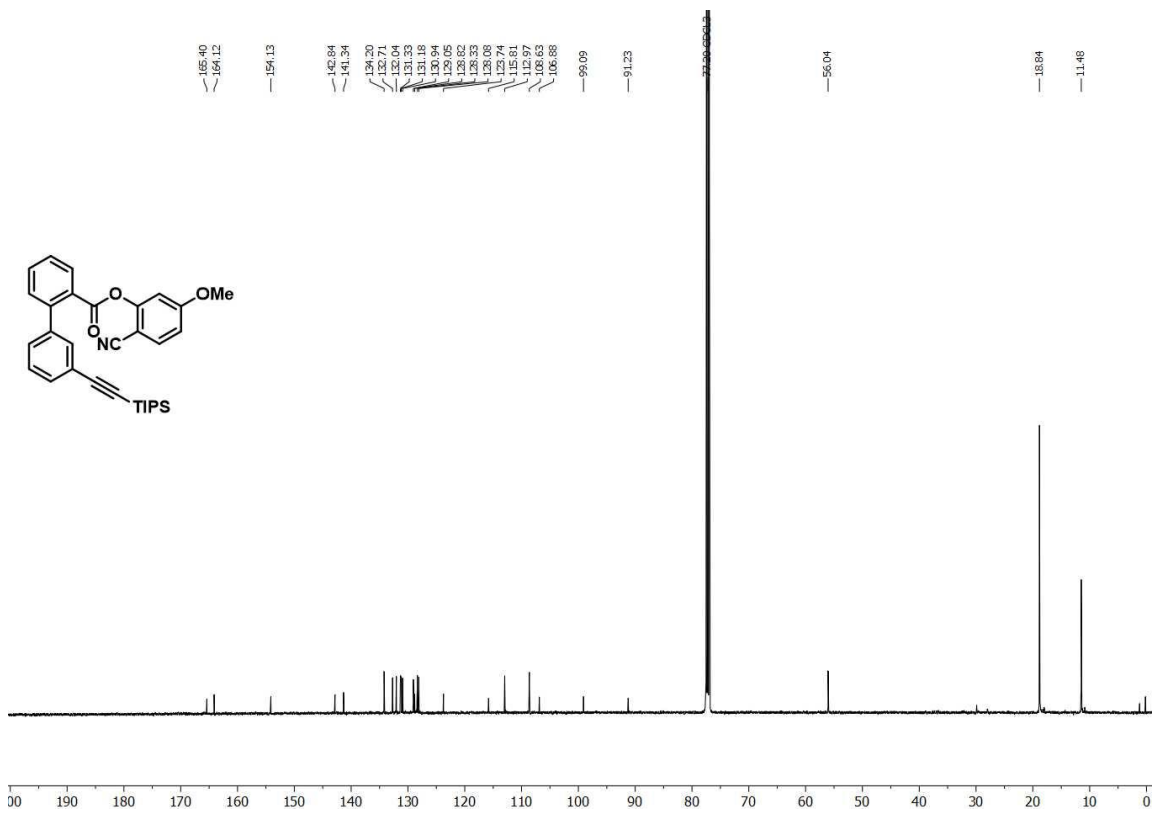
5g. 2-cyano-5-methoxyphenyl 3-(2-chloro-5-((triisopropylsilyl)ethynyl)phenyl)propanoate



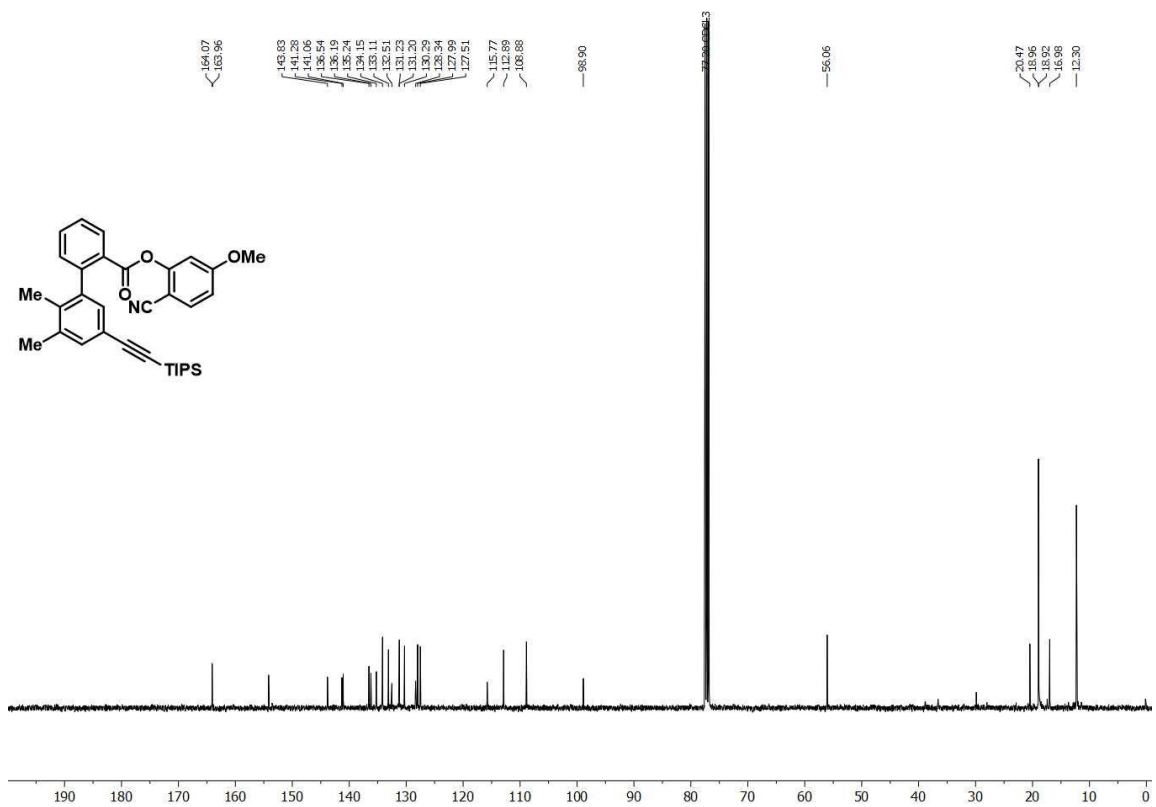
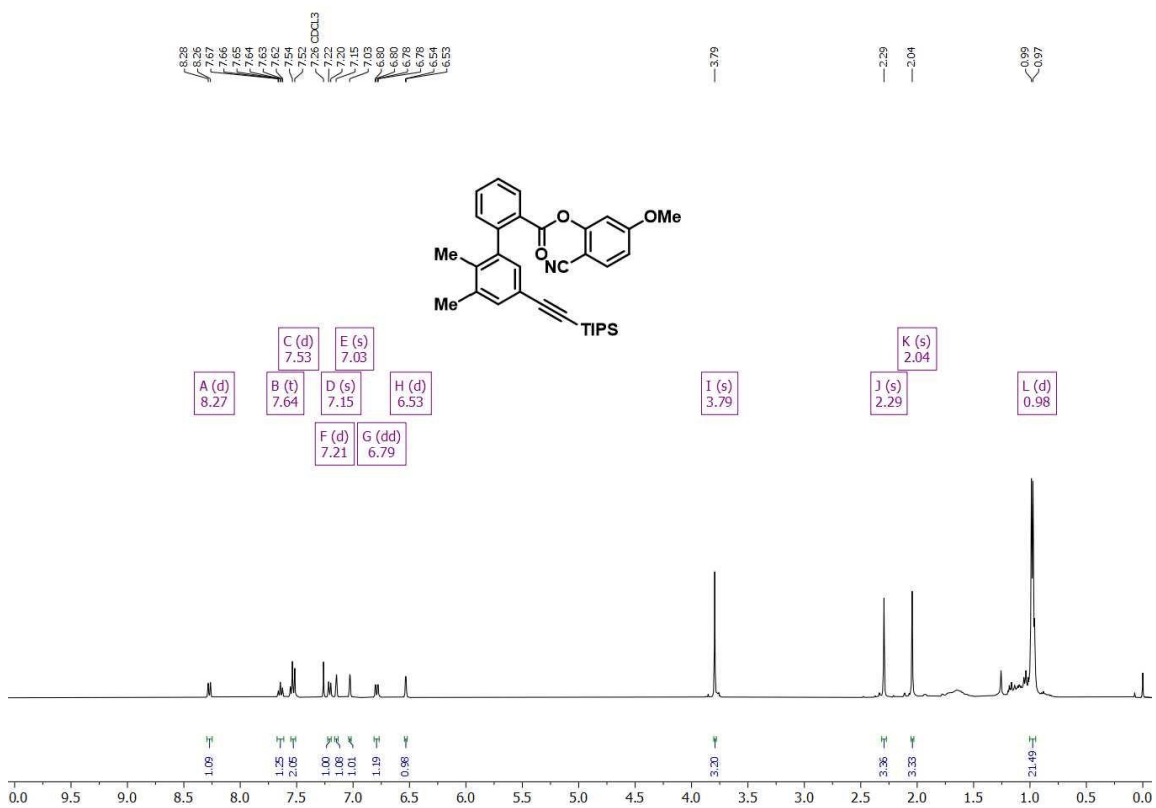
5h. 2-cyano-5-methoxyphenyl 3-(3-chloro-5-((triisopropylsilyl)ethynyl)phenyl)propanoate



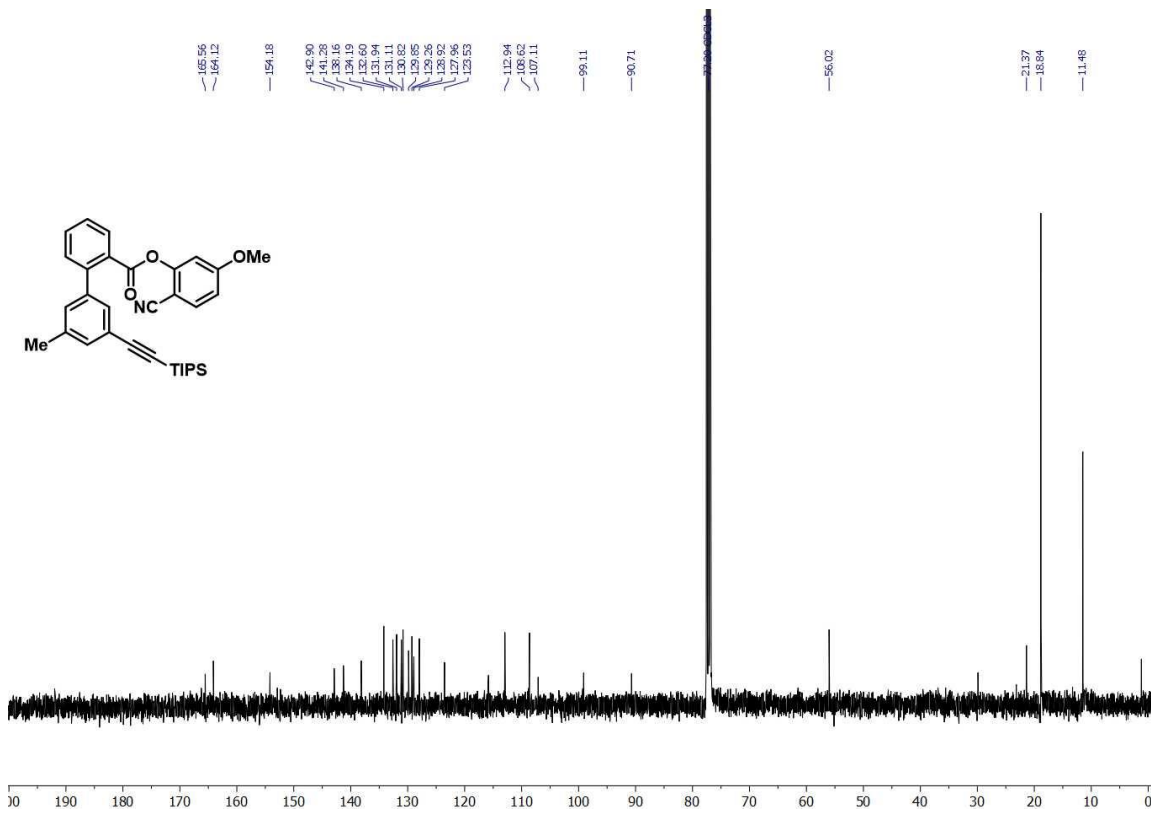
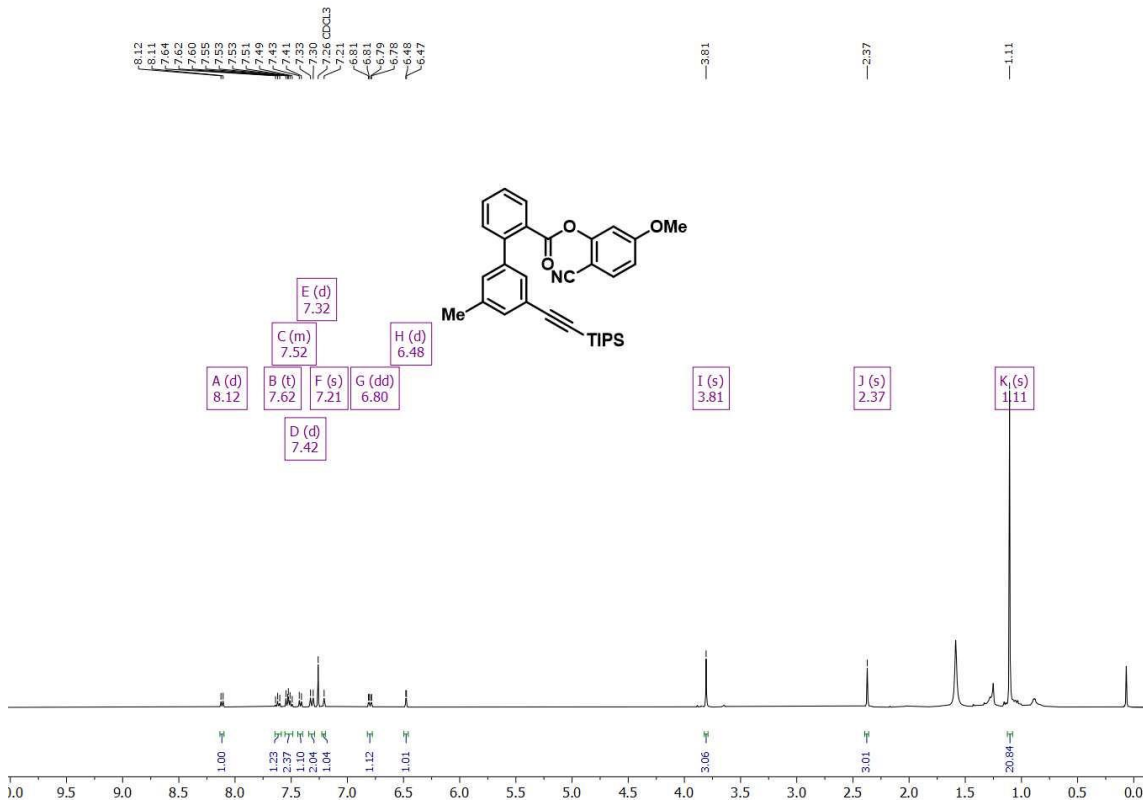
5i. 2-cyano-5-methoxyphenyl 3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate



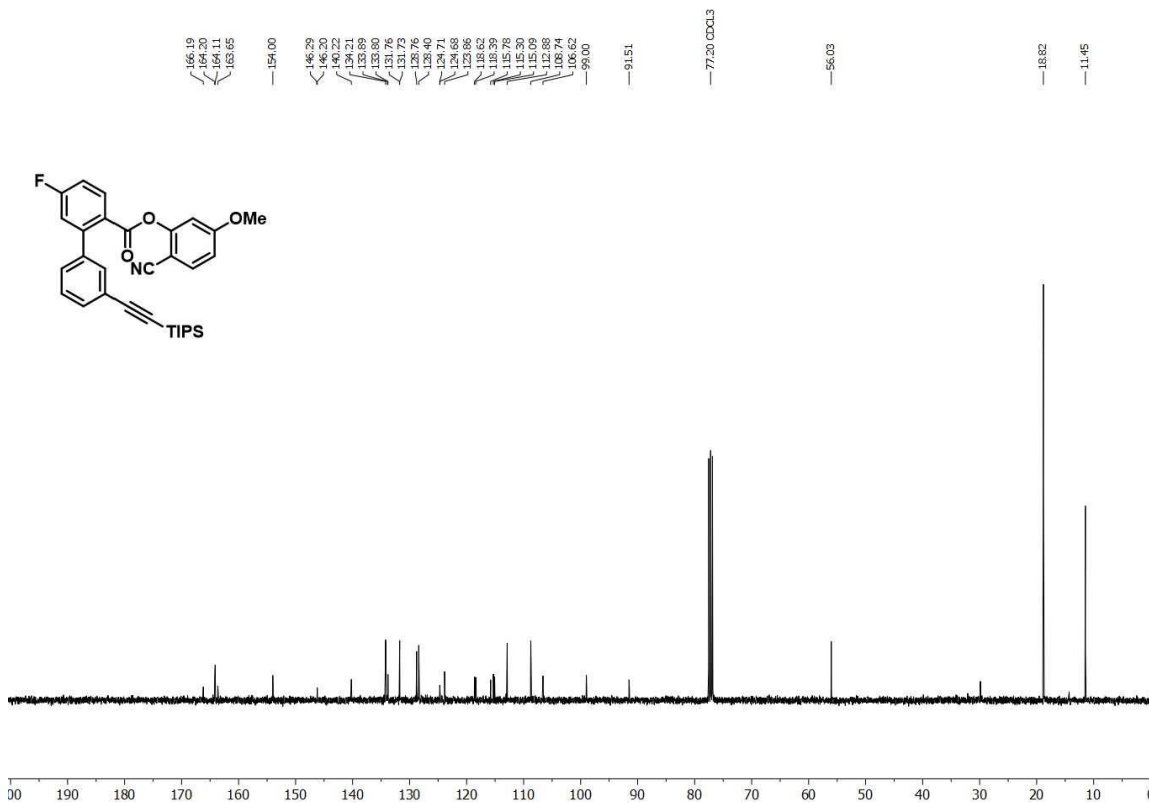
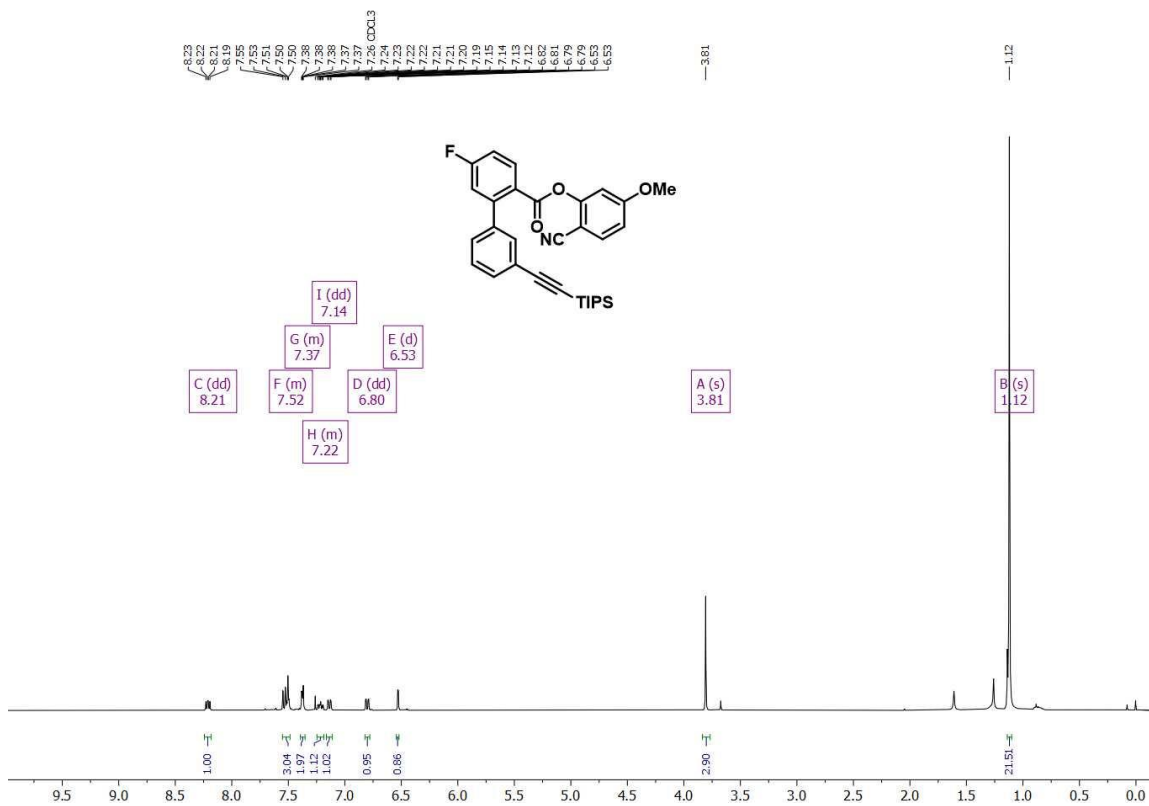
5j. 2-cyano-5-methoxyphenyl 2',3'-dimethyl-5'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate



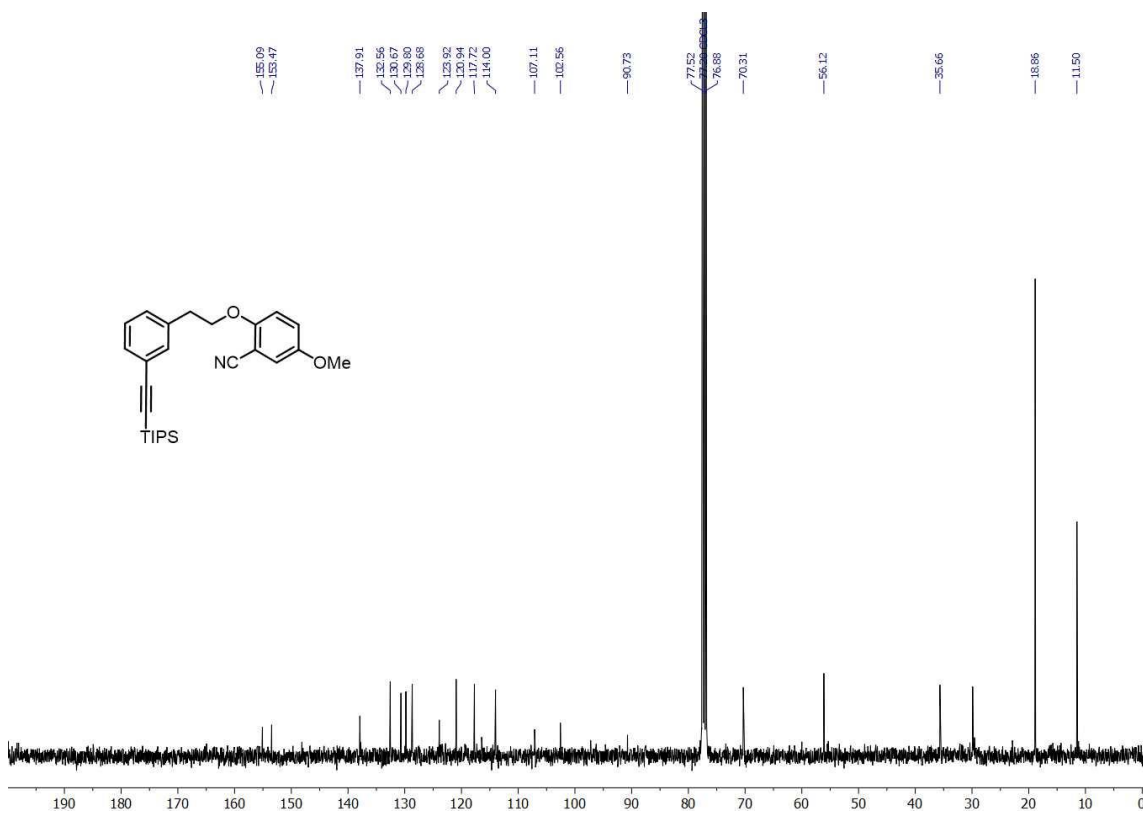
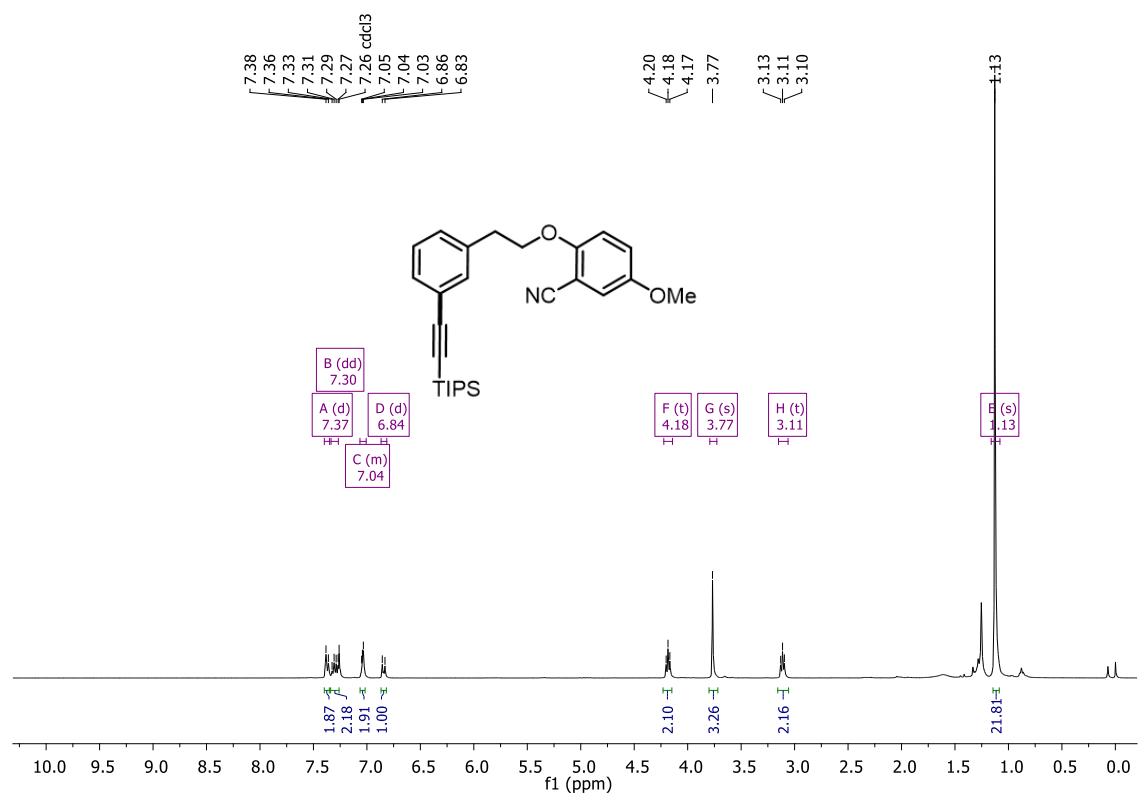
5k. 2-cyano-5-methoxyphenyl 3'-methyl-5'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate



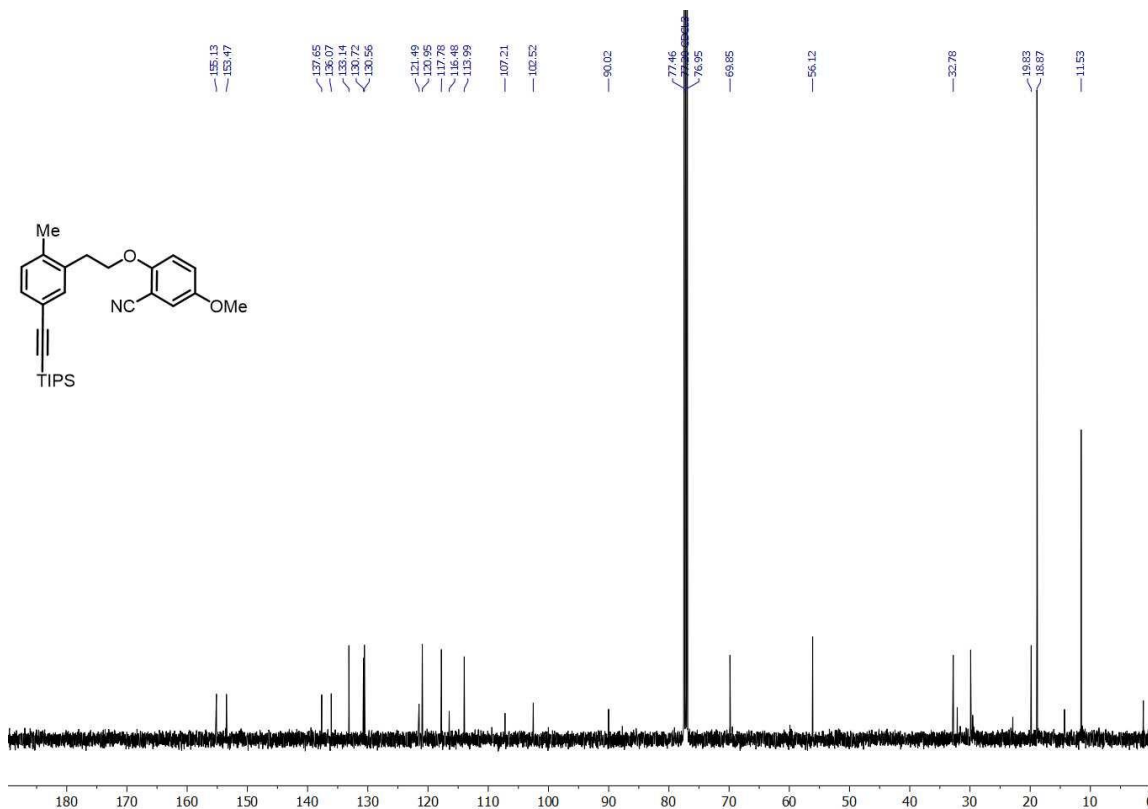
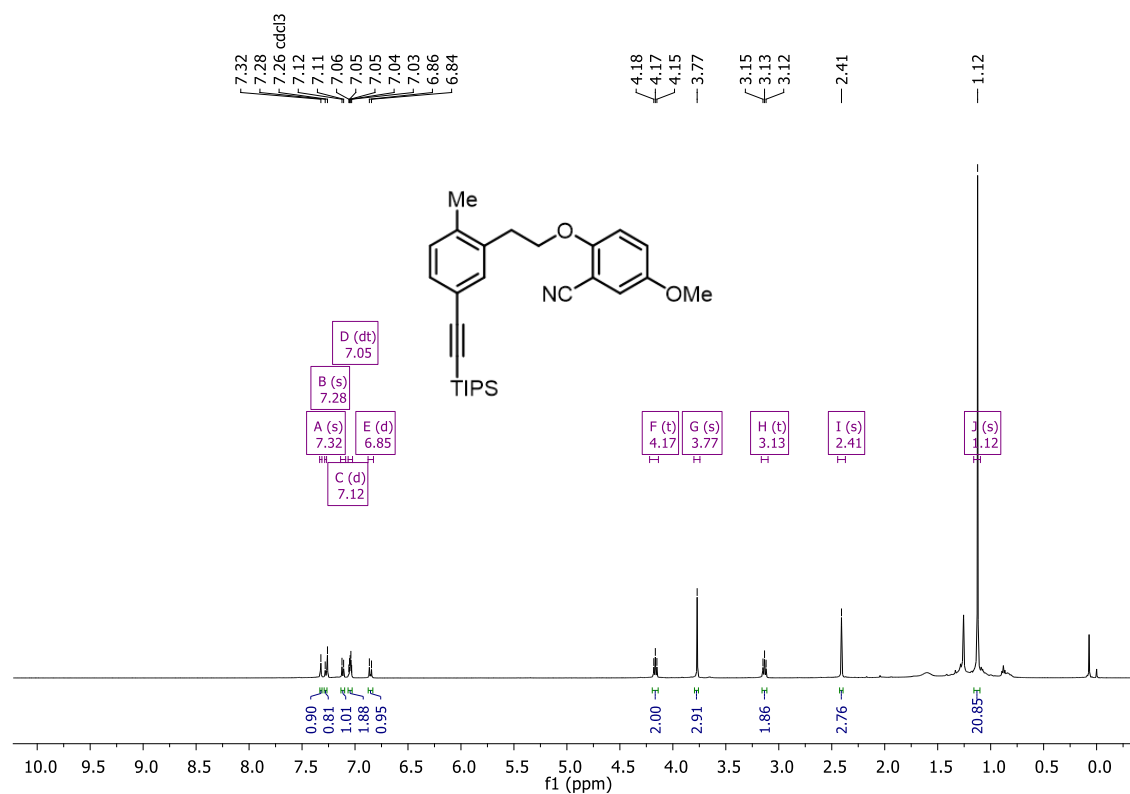
5l. 2-cyano-5-methoxyphenyl 5-fluoro-3'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carboxylate



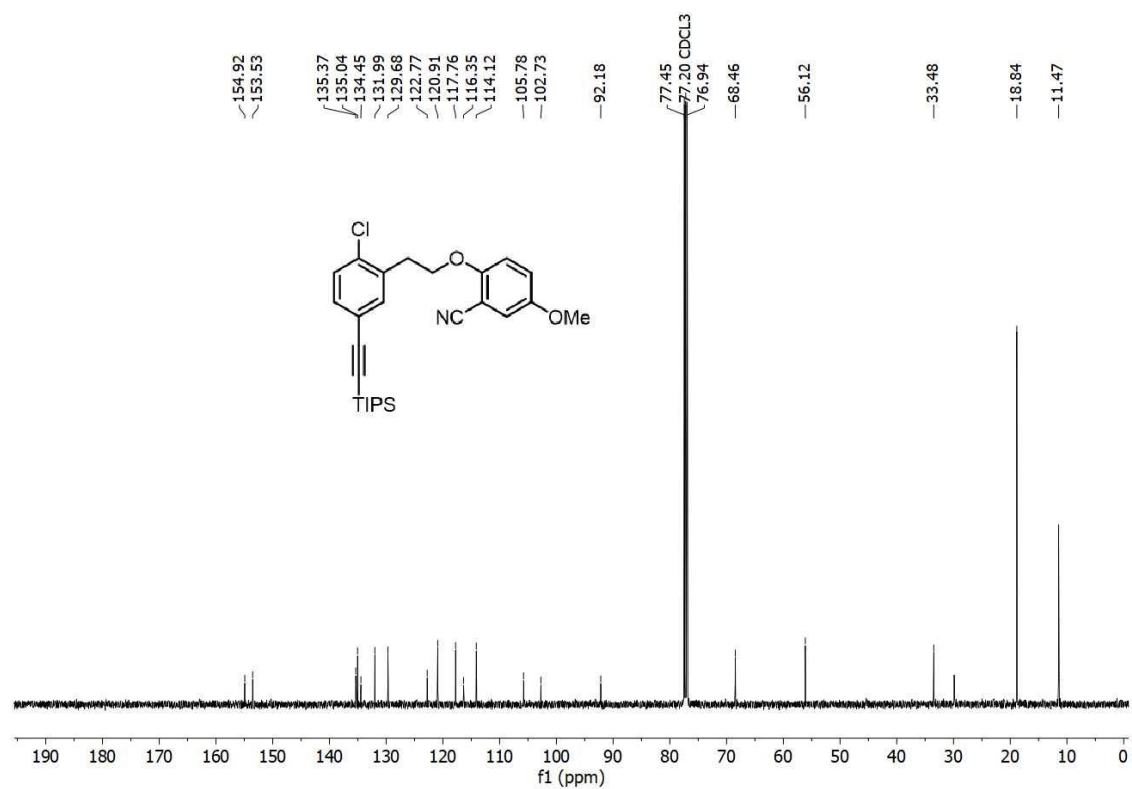
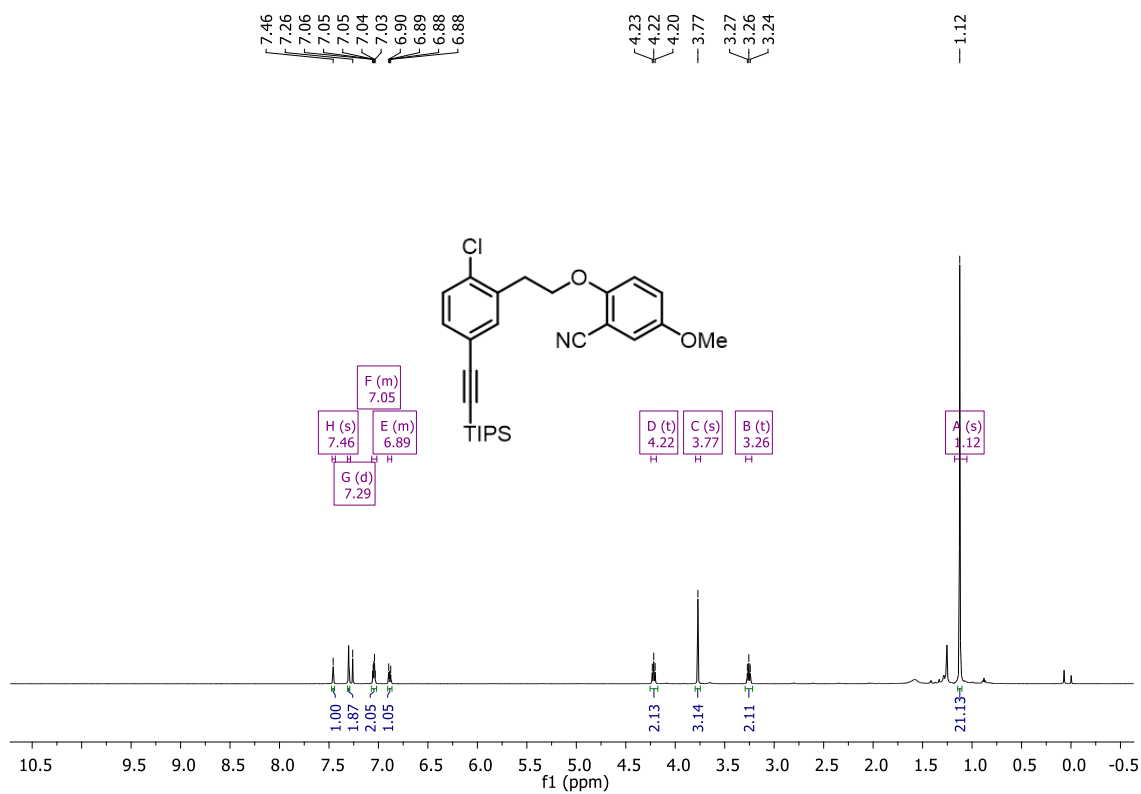
7a. 5-Methoxy-2-(3-((triisopropylsilyl)ethynyl)phenethoxy)benzonitrile



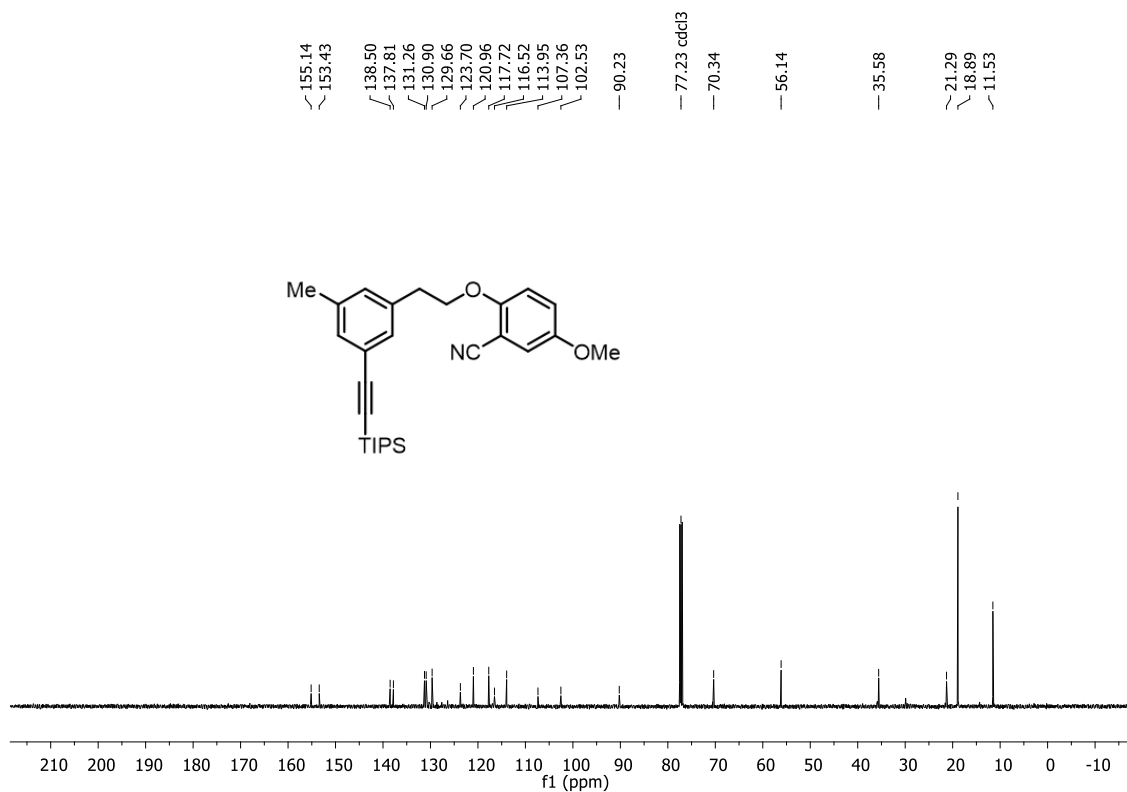
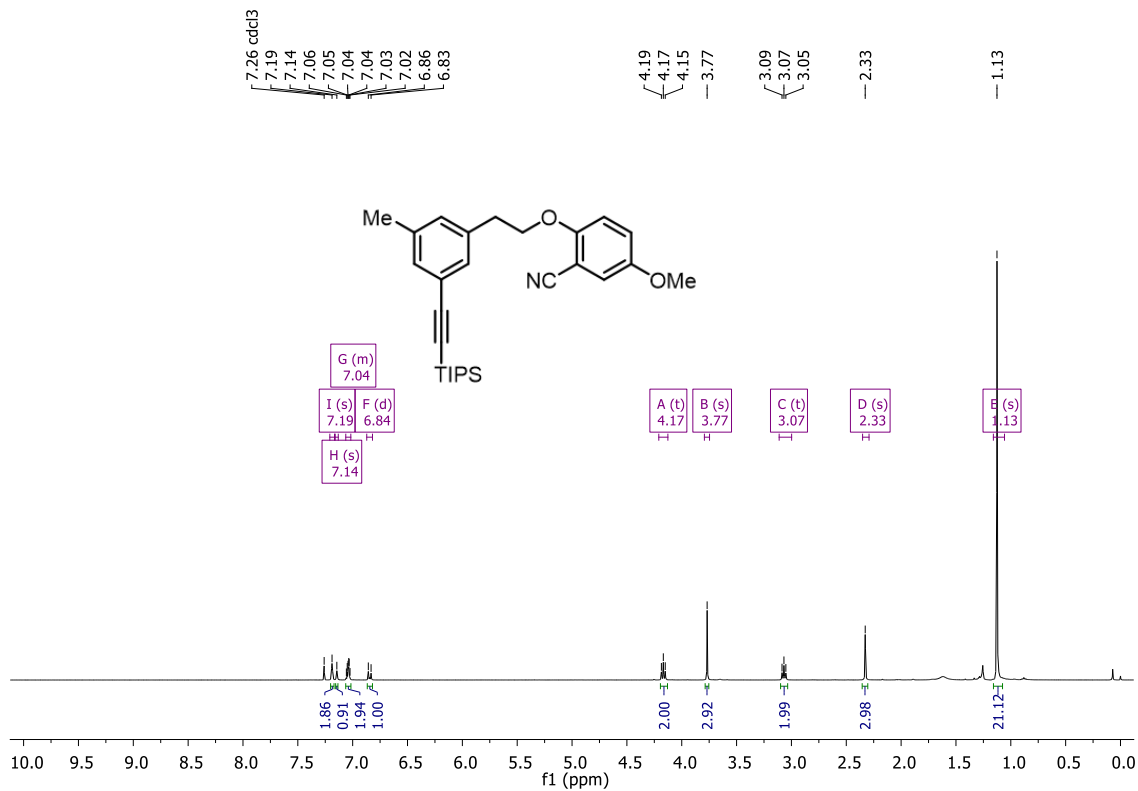
7b. 2-(2-Methyl-5-((triisopropylsilyl)ethynyl)phenoxy)-5-methoxybenzonitrile



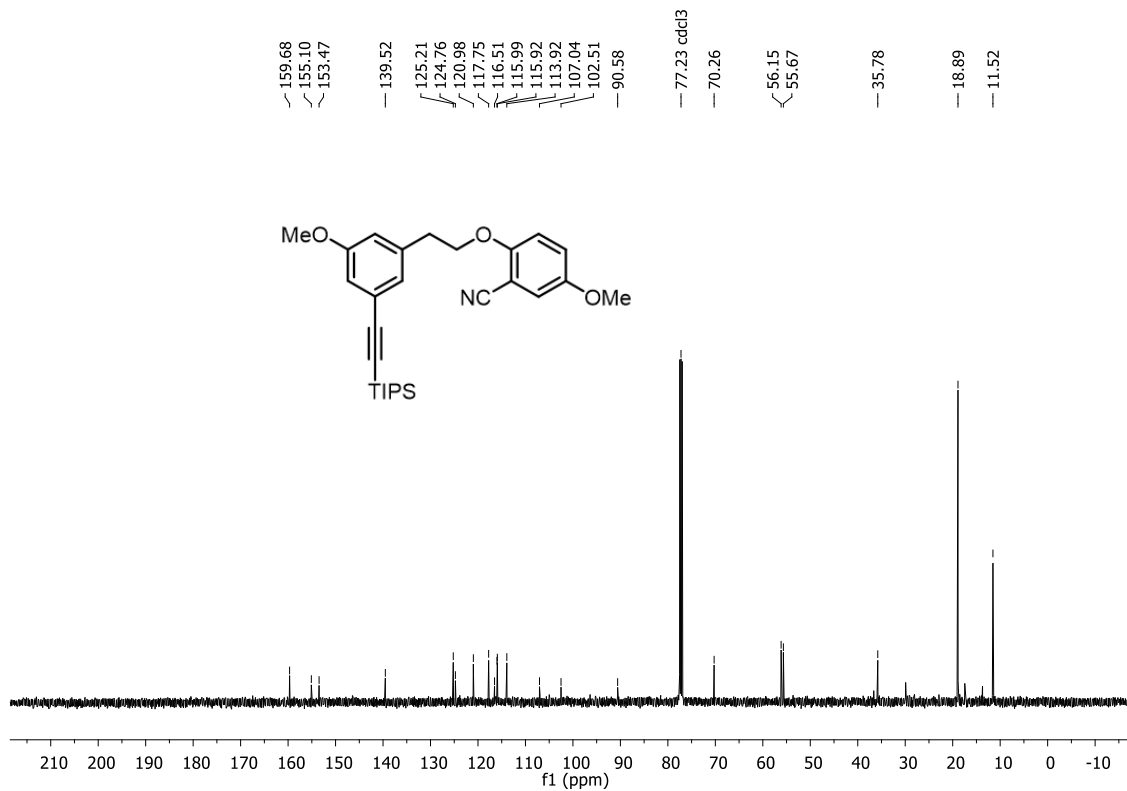
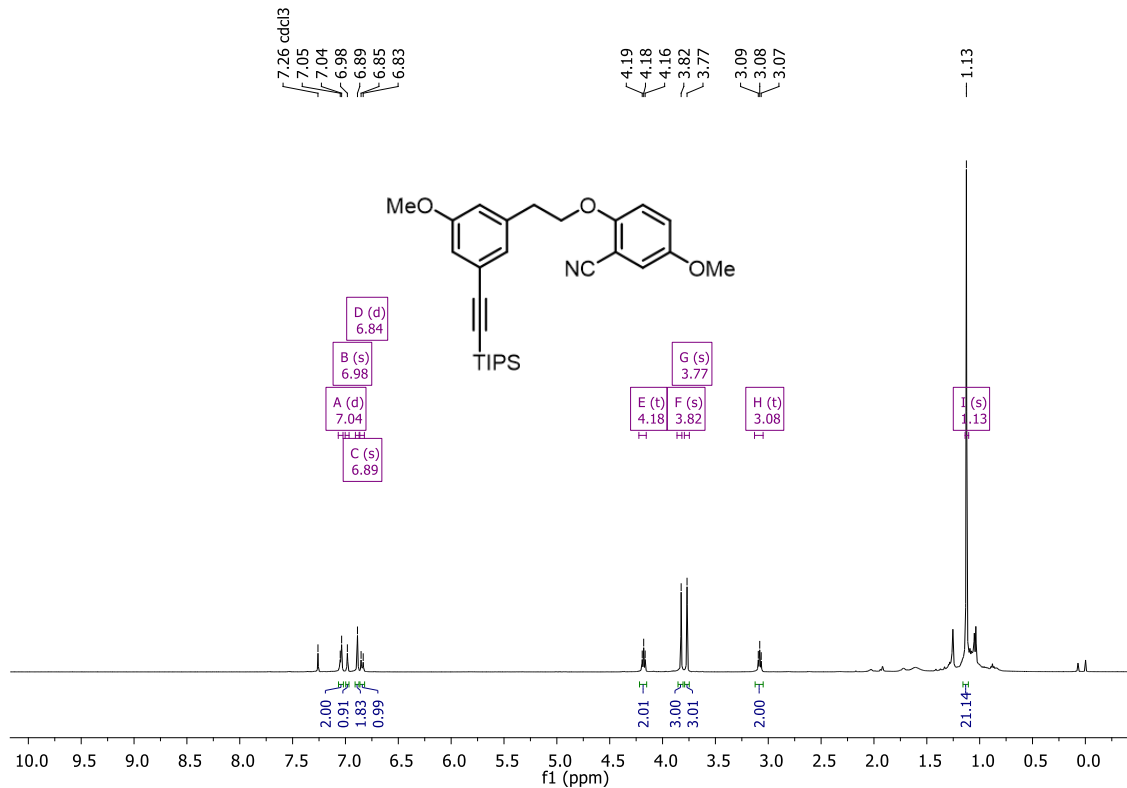
7c. 2-(2-Chloro-5-((triisopropylsilyl)ethynyl)phenethoxy)-5-methoxybenzonitrile



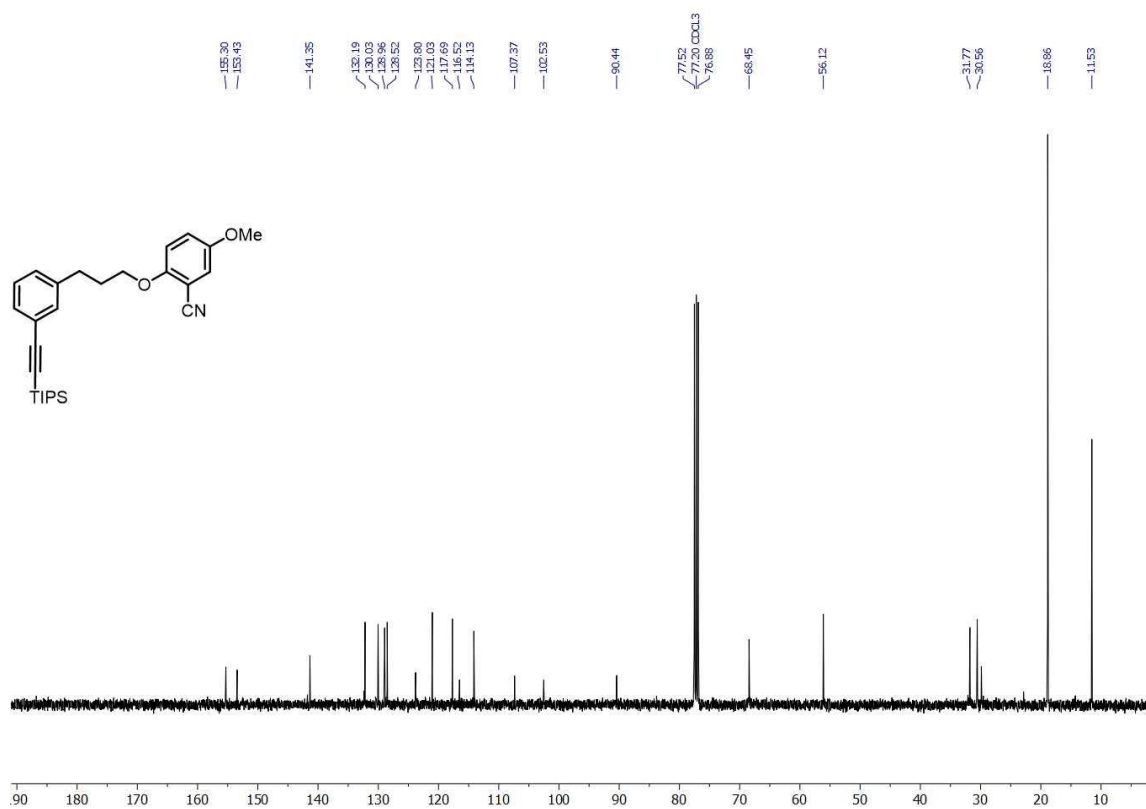
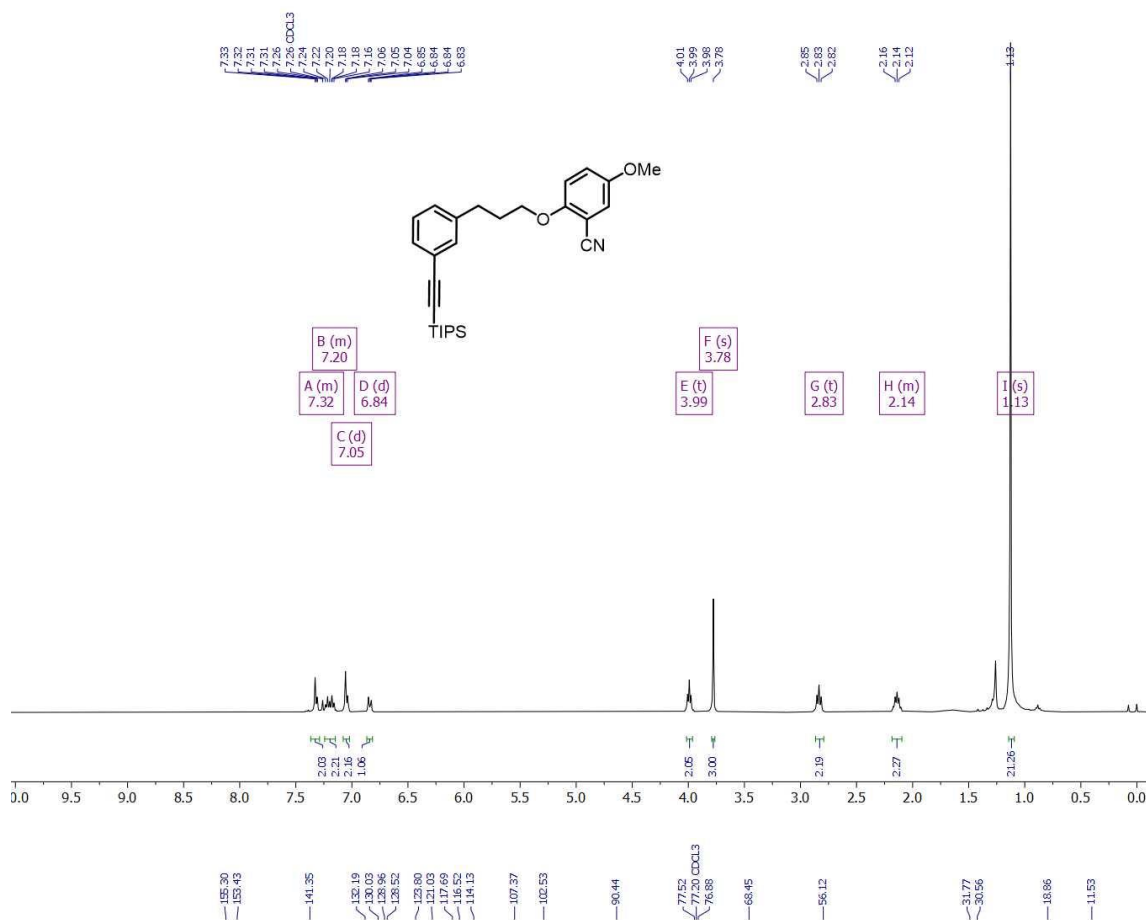
7d. 2-(3-Methyl-5-((triisopropylsilyl)ethynyl)phenethoxy)-5-methoxybenzonitrile



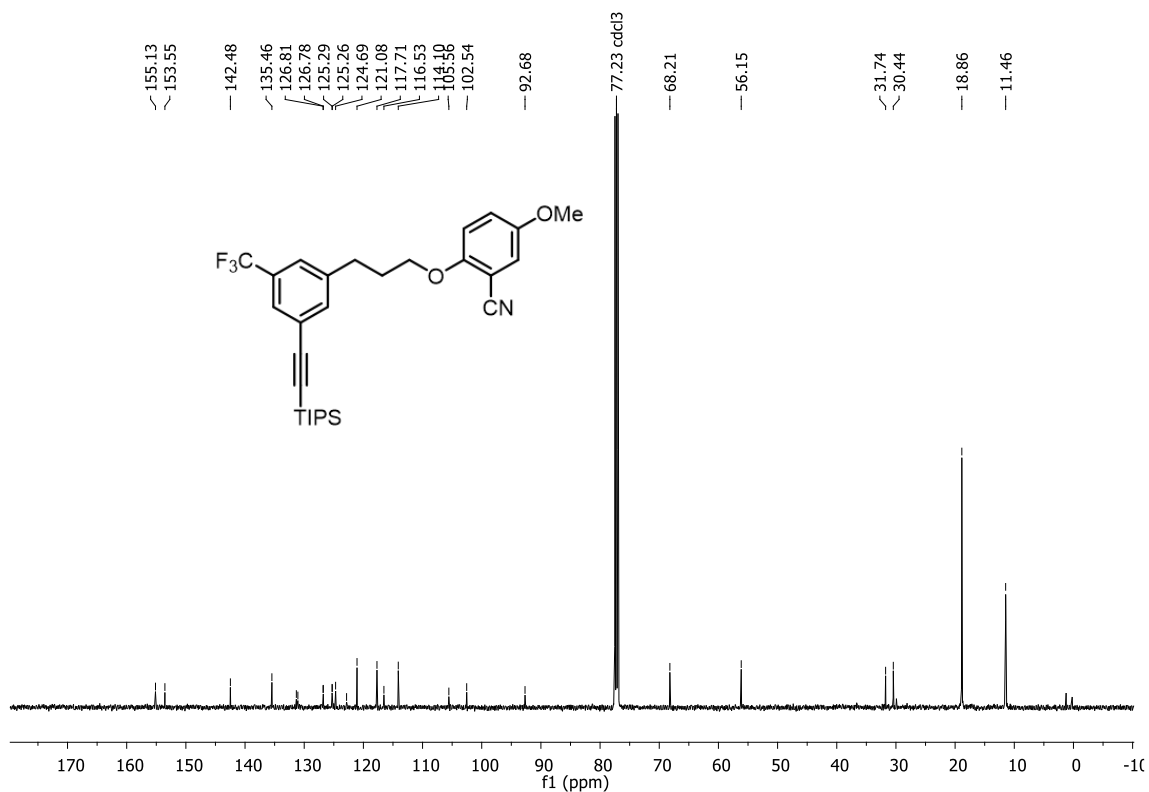
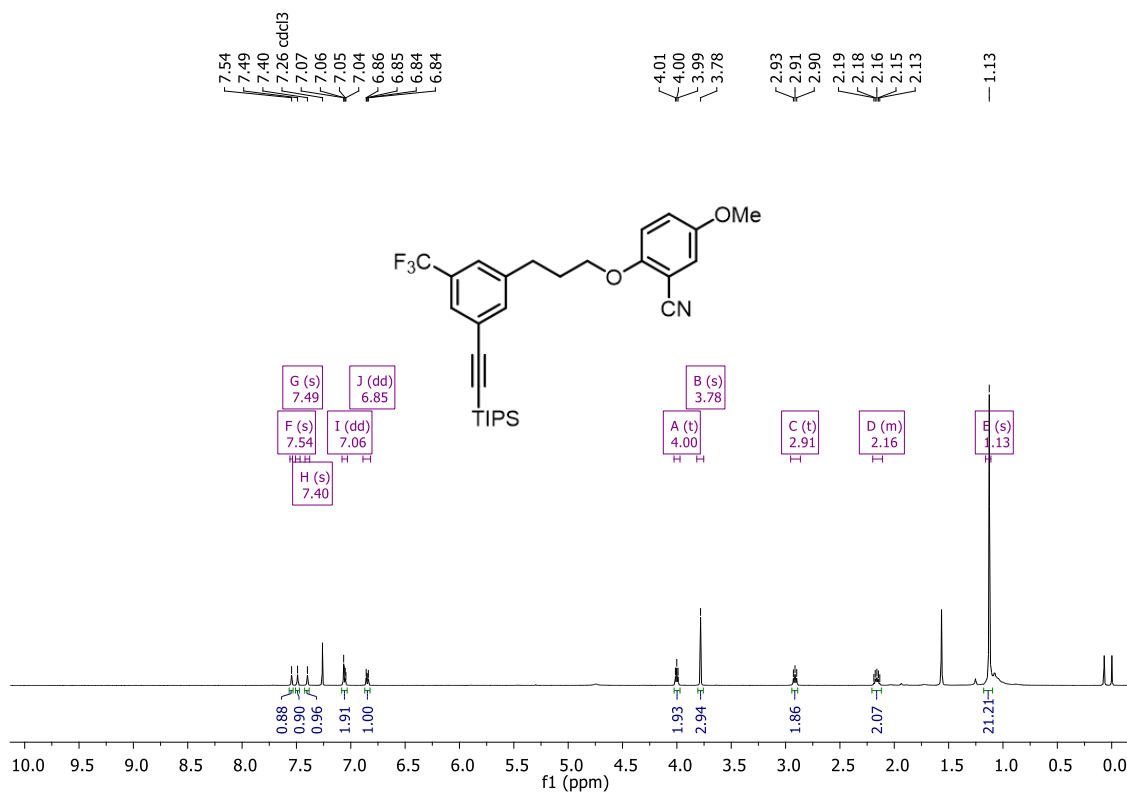
7e. 2-(2-Methoxy-5-((triisopropylsilyl)ethynyl)phenoxy)-5-methoxybenzonitrile



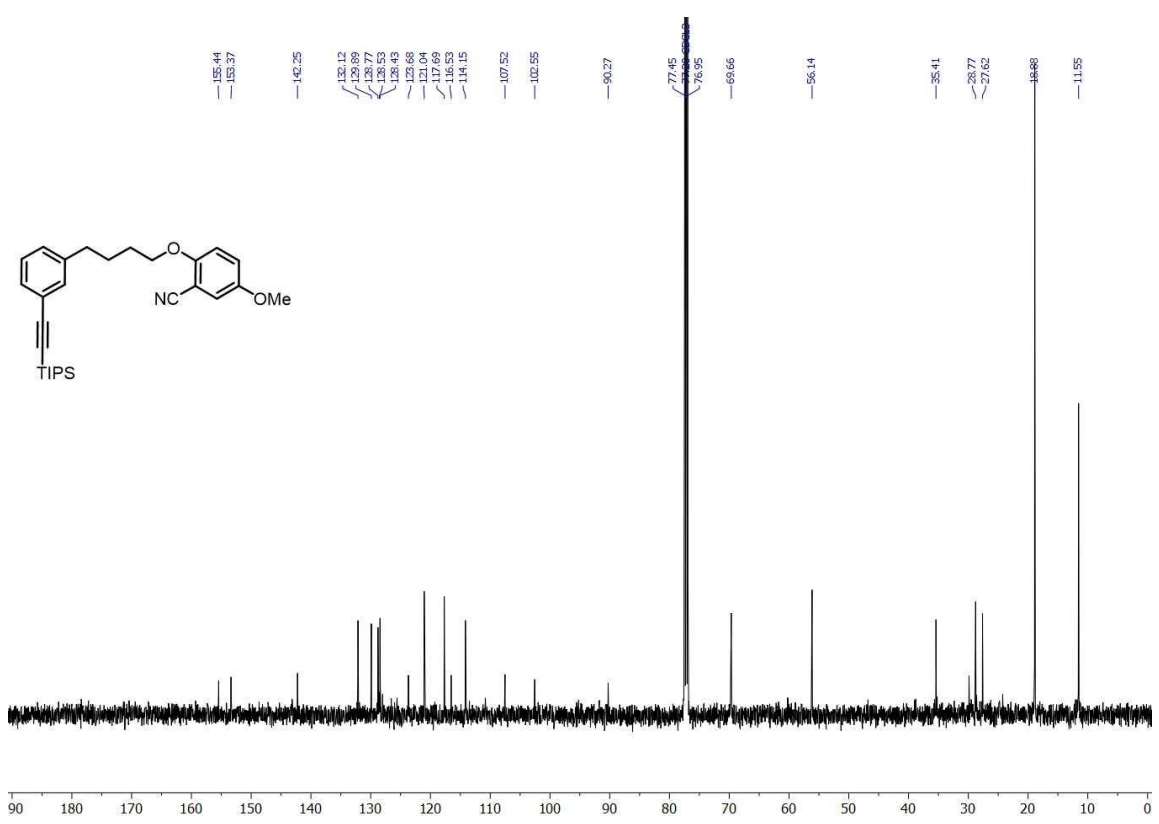
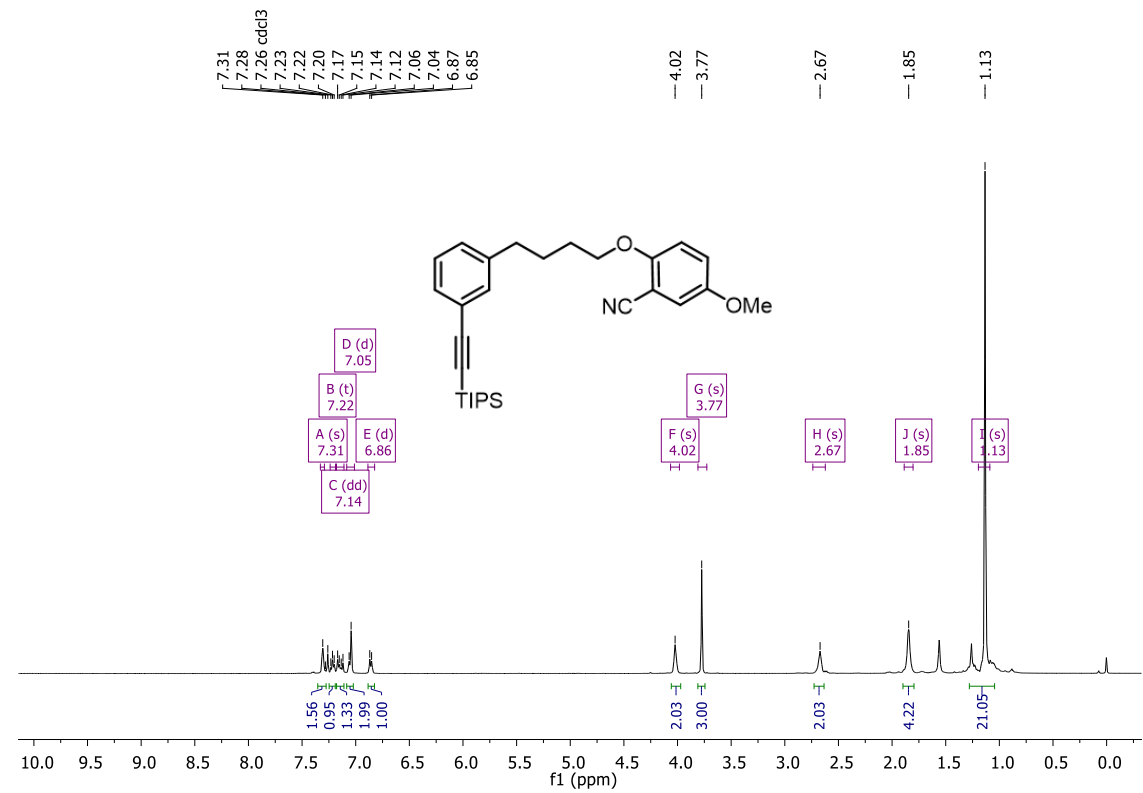
7f. 5-Methoxy-2-(3-(3-((triisopropylsilyl)ethynyl)phenyl)propoxy)benzonitrile



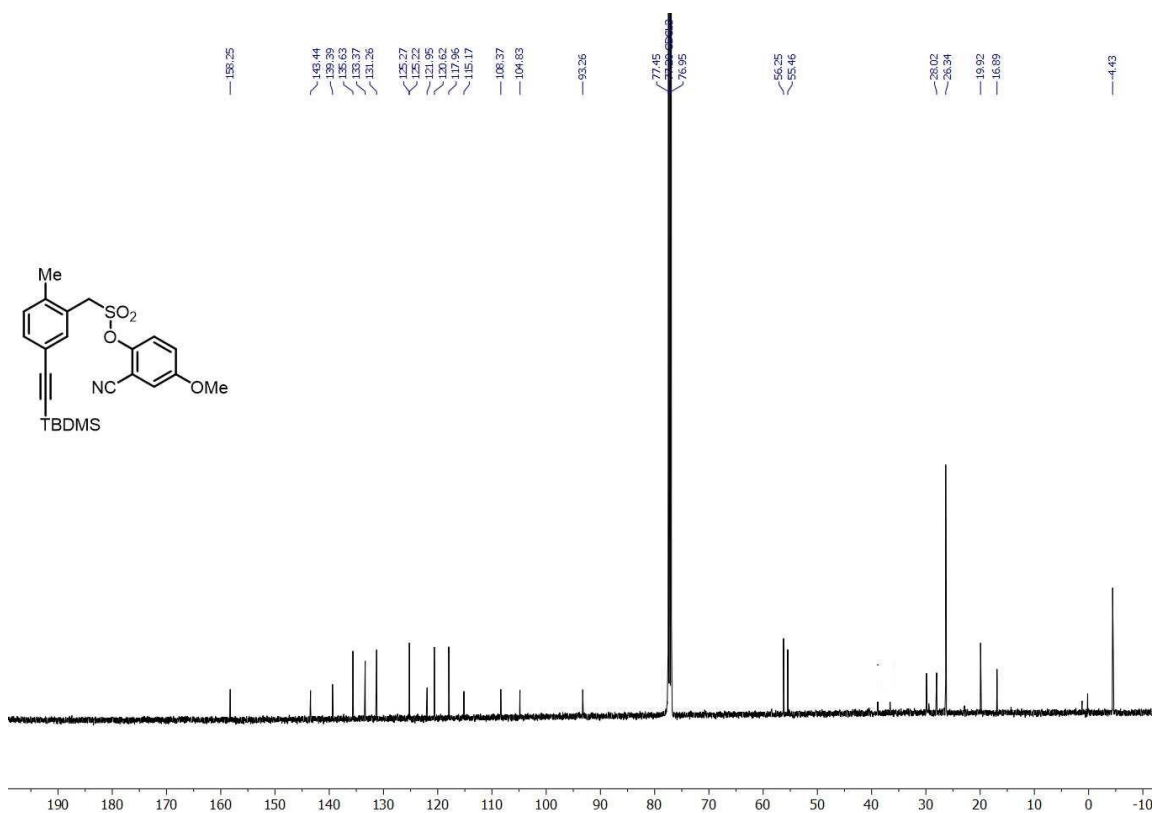
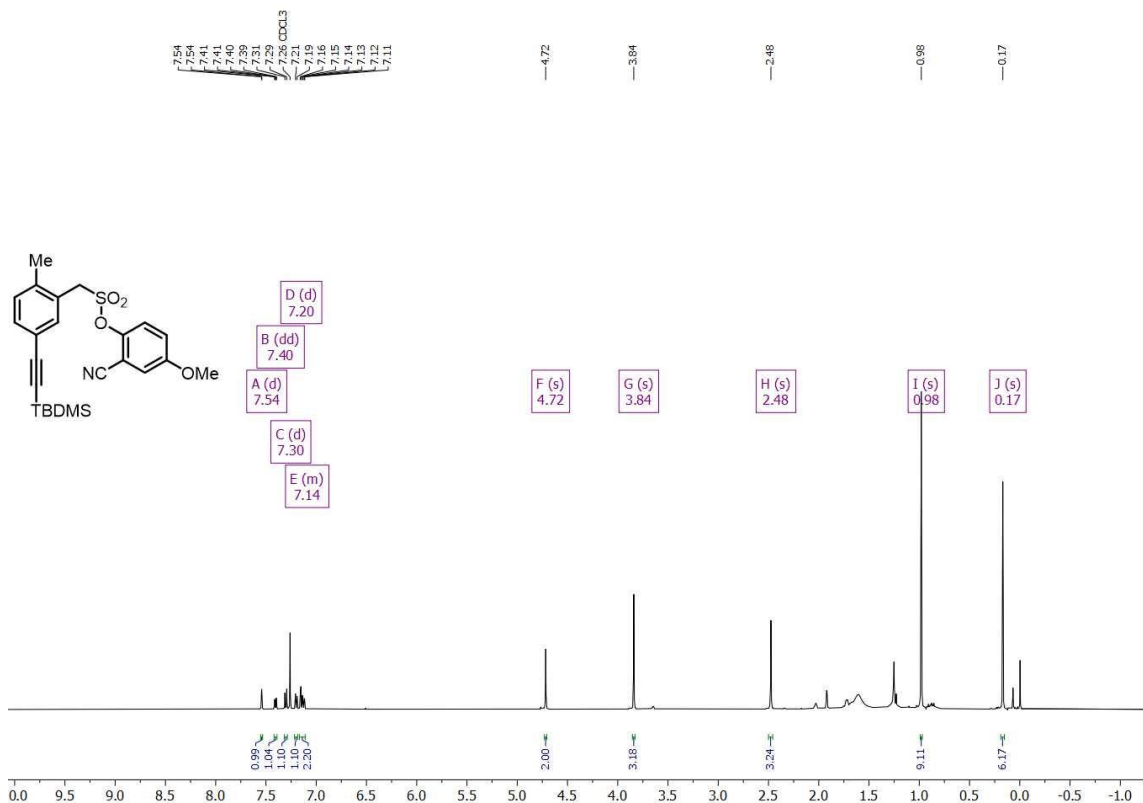
7g. 5-Methoxy-2-(3-(3-(trifluoromethyl)-5-((triisopropylsilyl)ethynyl)phenyl)propoxy)benzonitrile



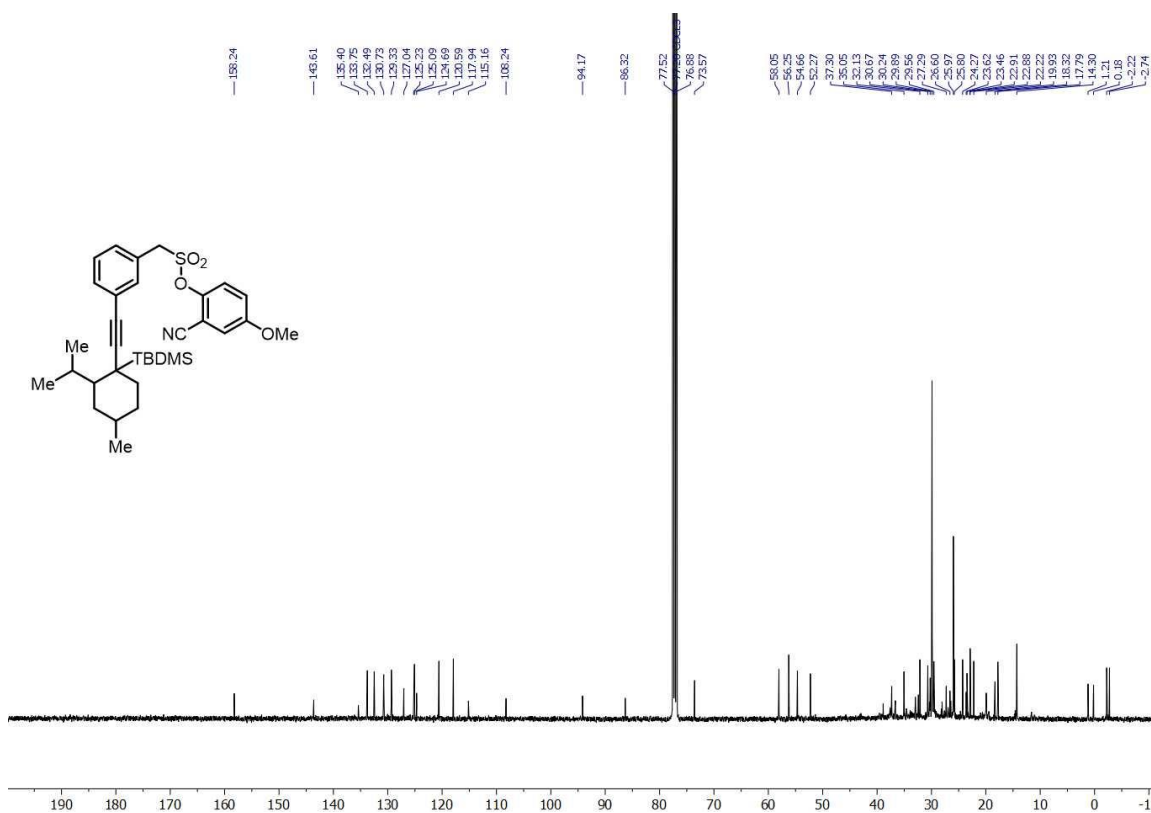
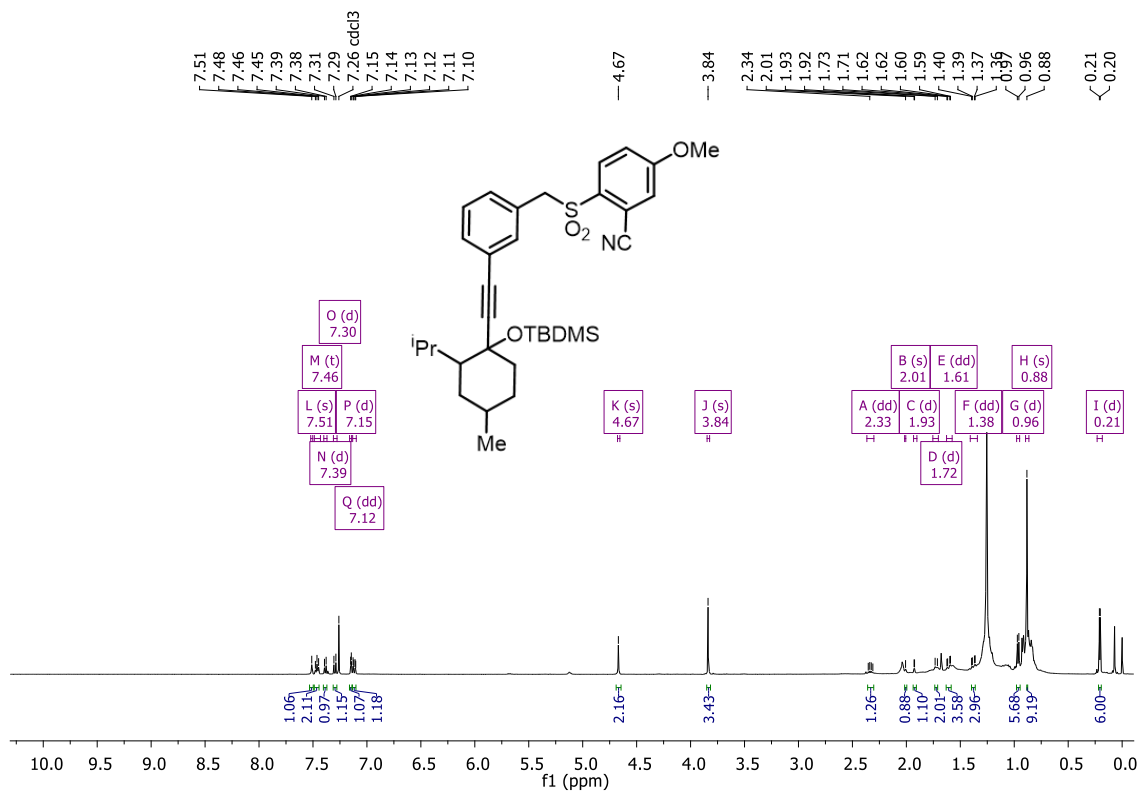
7h. 5-Methoxy-2-(4-(3-((triisopropylsilyl)ethynyl)phenyl)butoxy)benzonitrile



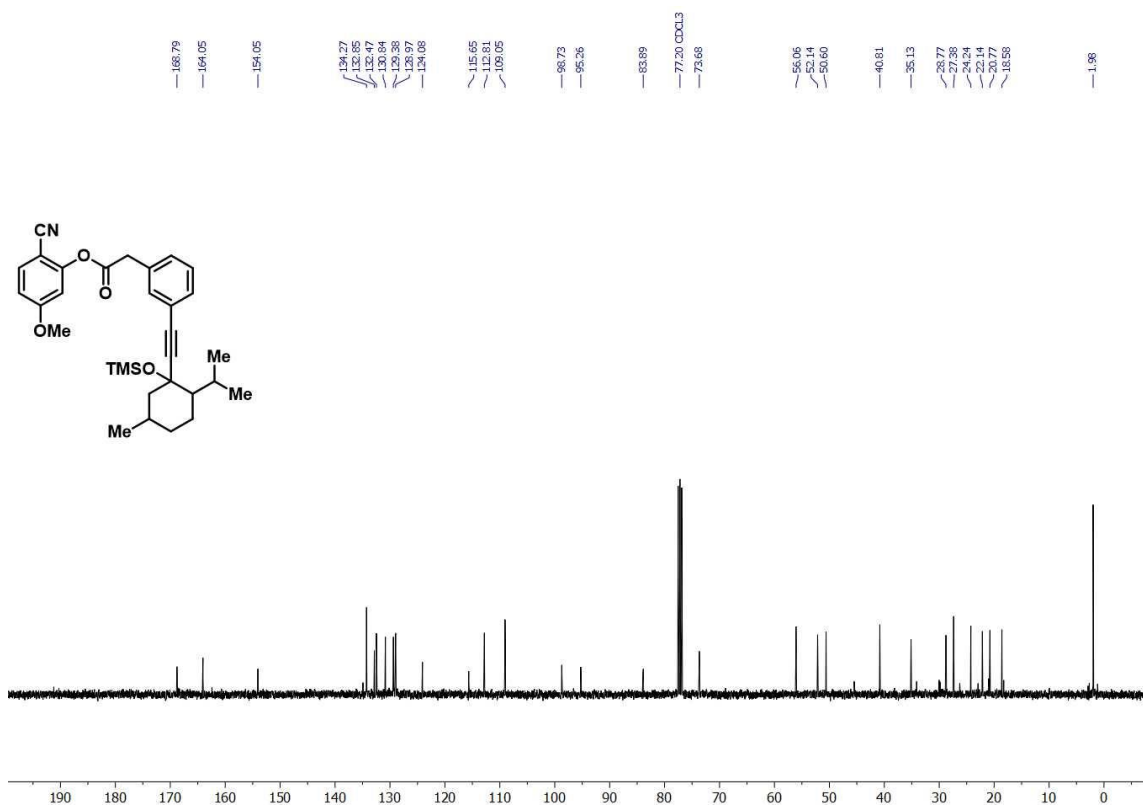
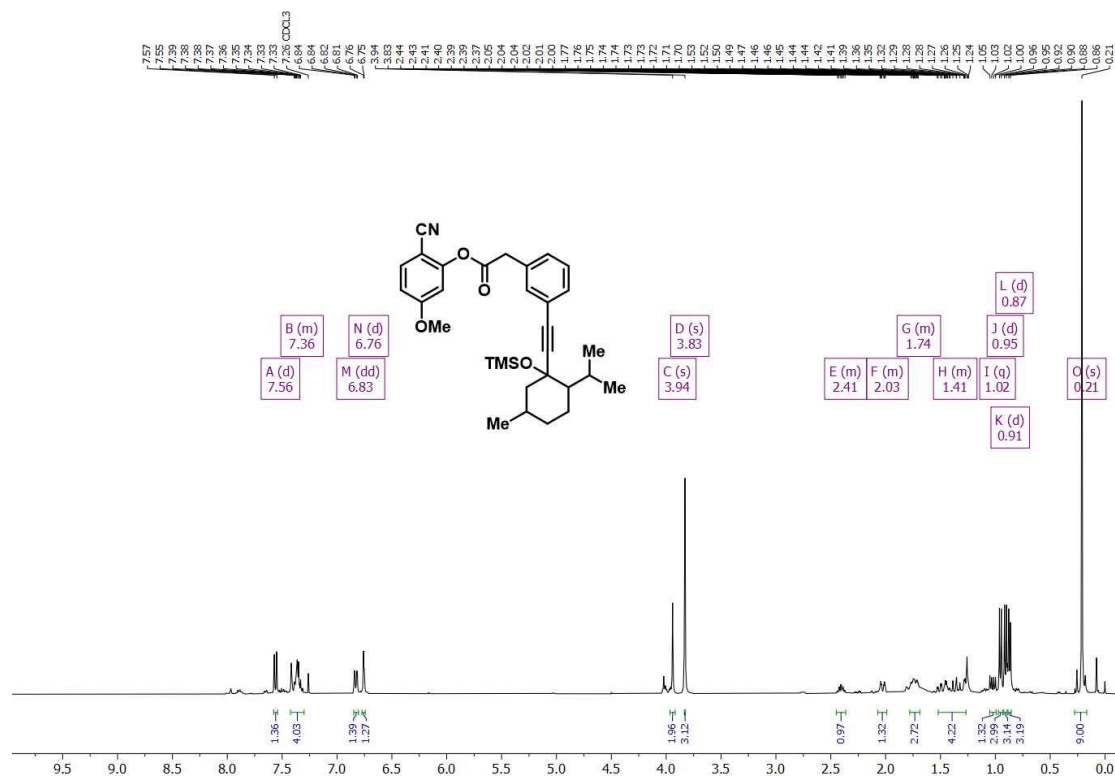
8a. 2-((5-((*tert*-butyldimethylsilyl)ethynyl)-2-methylbenzyl)sulfonyl)-5-methoxybenzonitrile



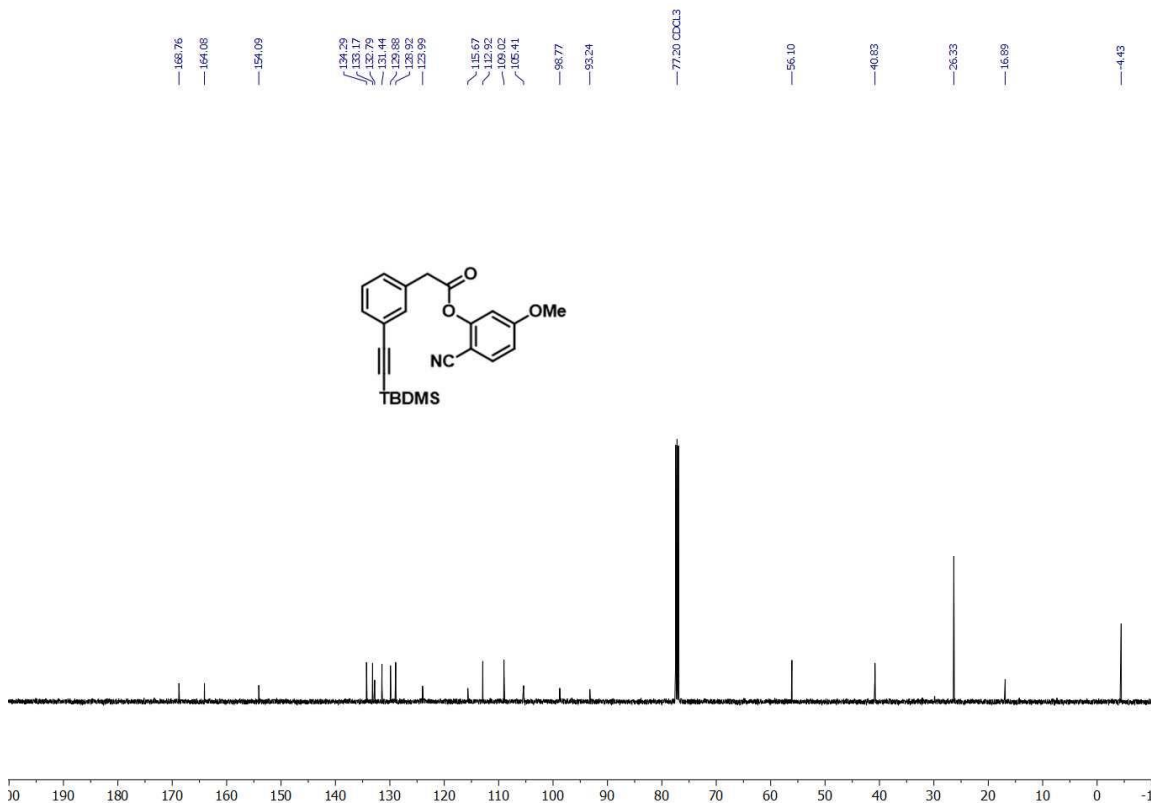
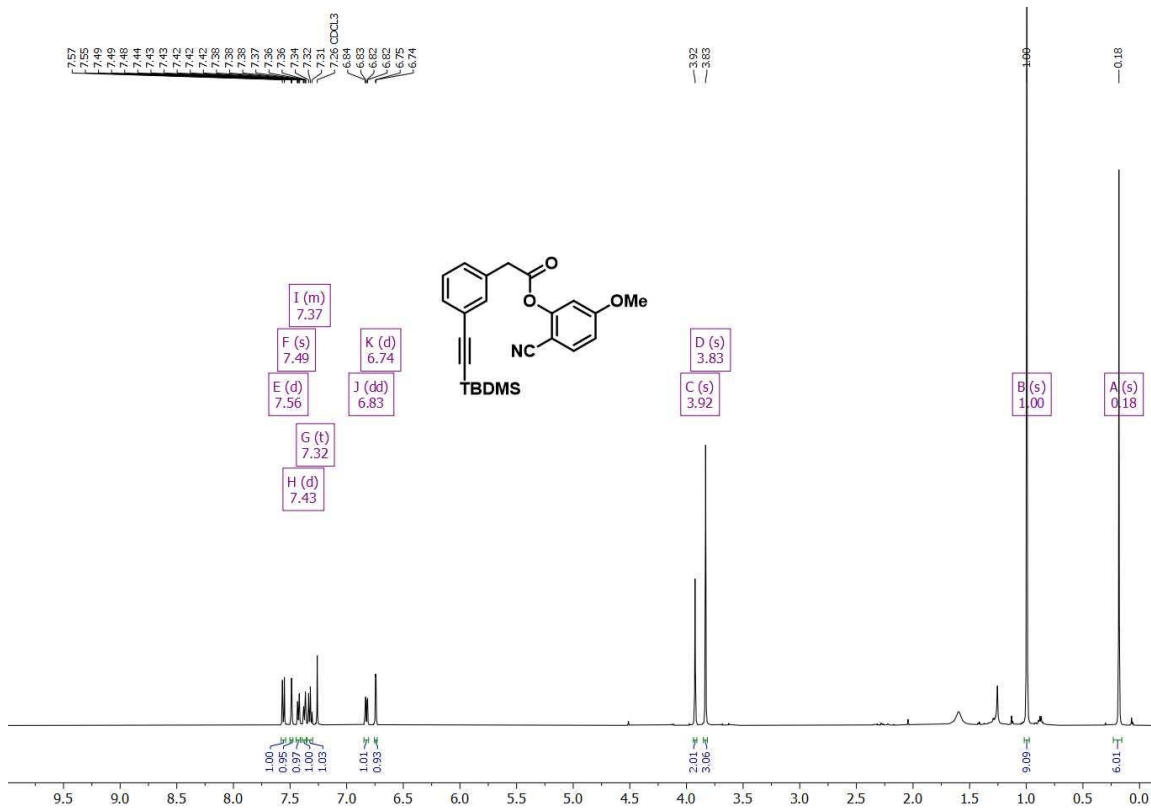
8b. 2-(3-((1-(*tert*-butyldimethylsilyl)oxy)-2-isopropyl-4-methylcyclohexyl)ethynyl)benzyl)sulfonyl)-5-methoxybenzonitrile



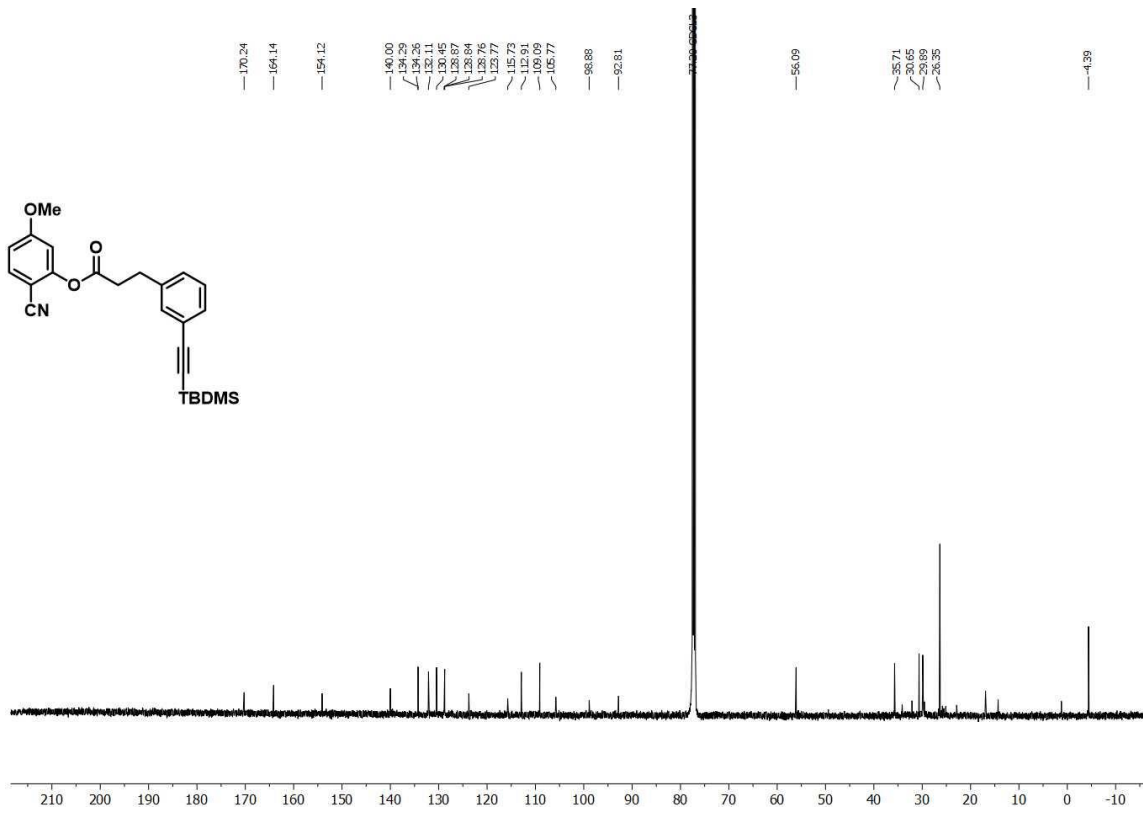
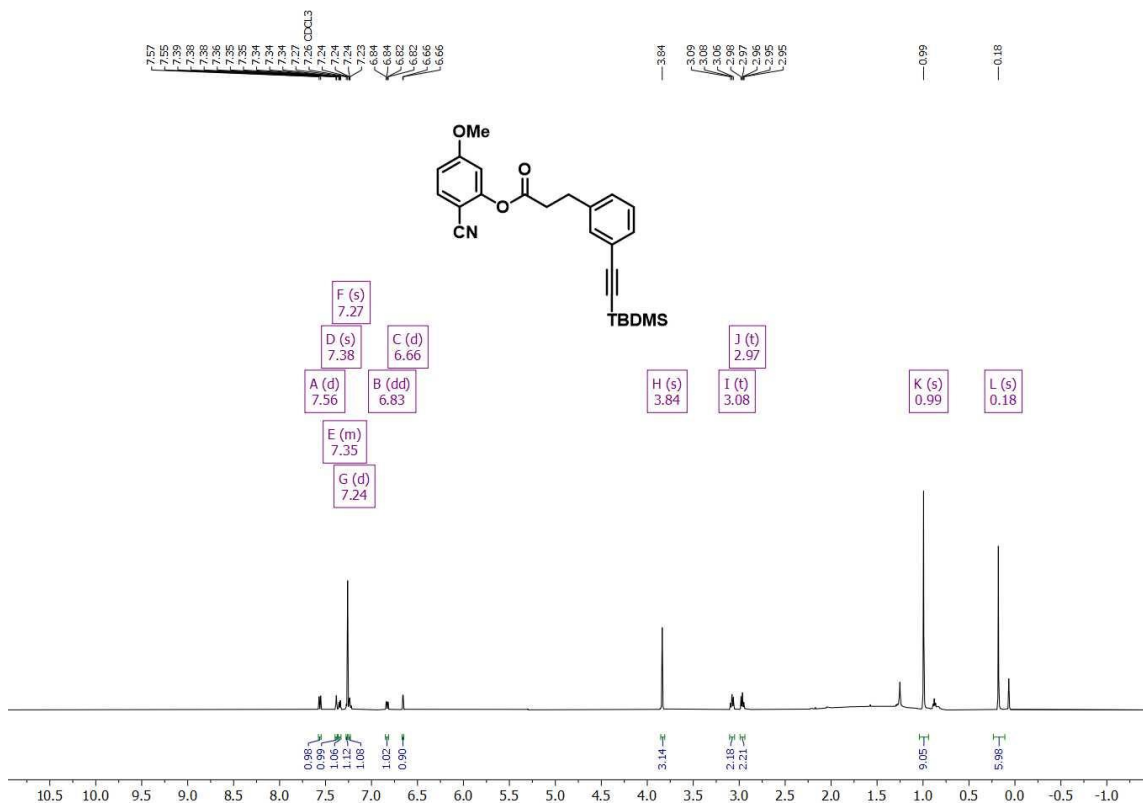
8c. 2-cyano-5-methoxyphenyl 2-(3-((2-isopropyl-5-methyl-1((trimethylsilyl)oxy)cyclohexyl)ethynyl)phenyl)acetate



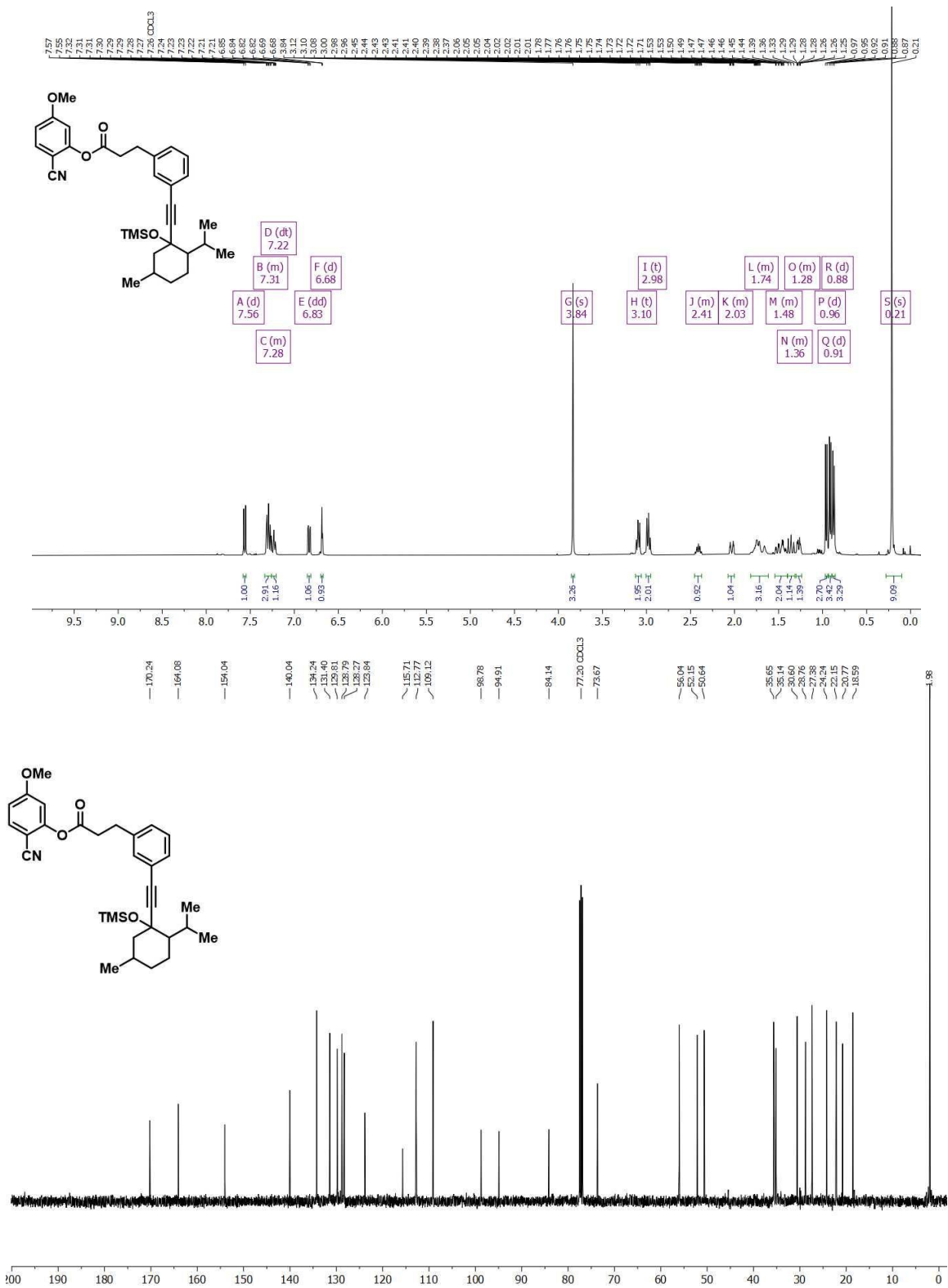
8d. 2-cyano-5-methoxyphenyl 2-(3-((tert-butyldimethylsilyl)ethynyl)phenyl)acetate



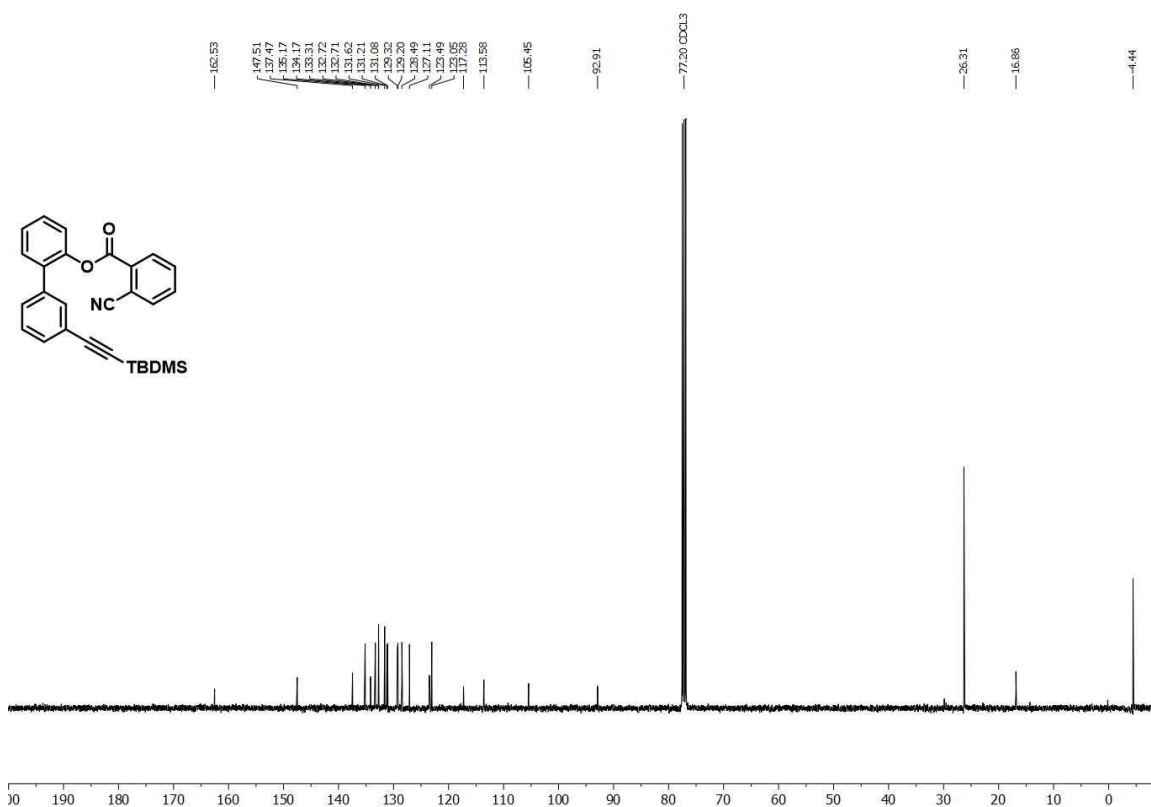
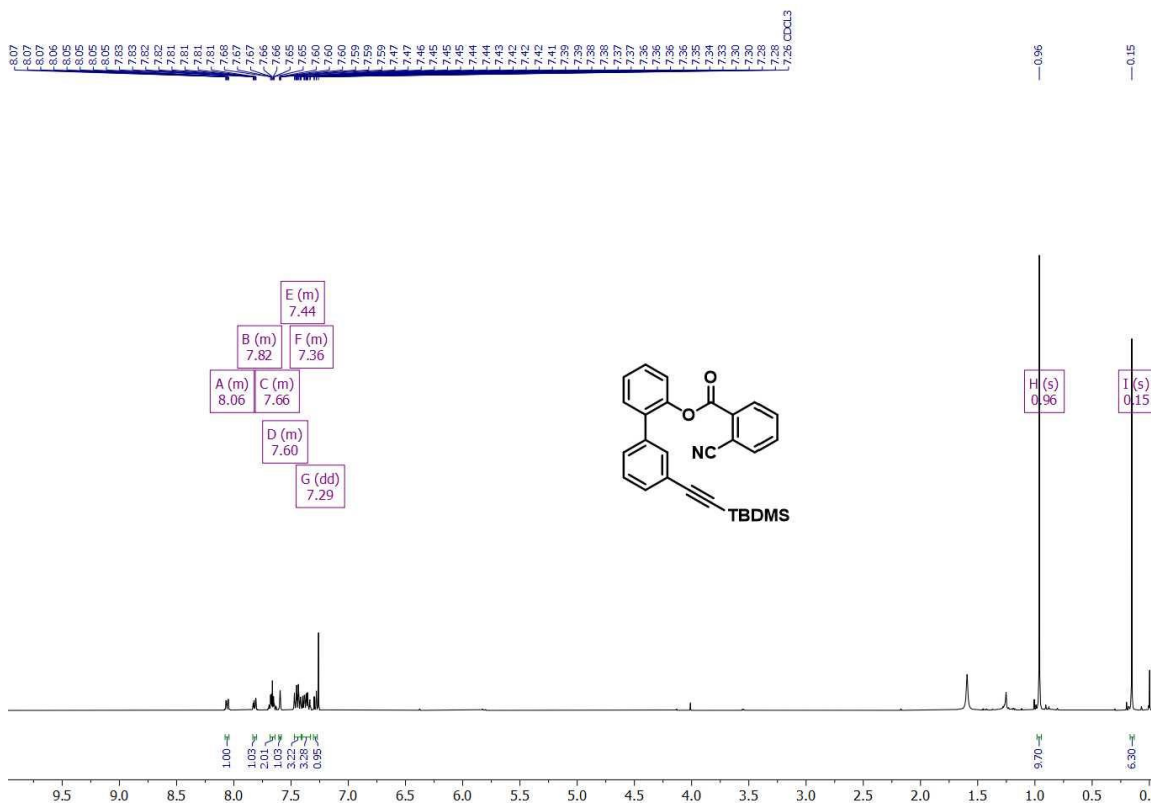
8e. 2-cyano-5-methoxyphenyl 3-(3-((tert-butyldimethylsilyl)ethynyl)phenyl)propanoate



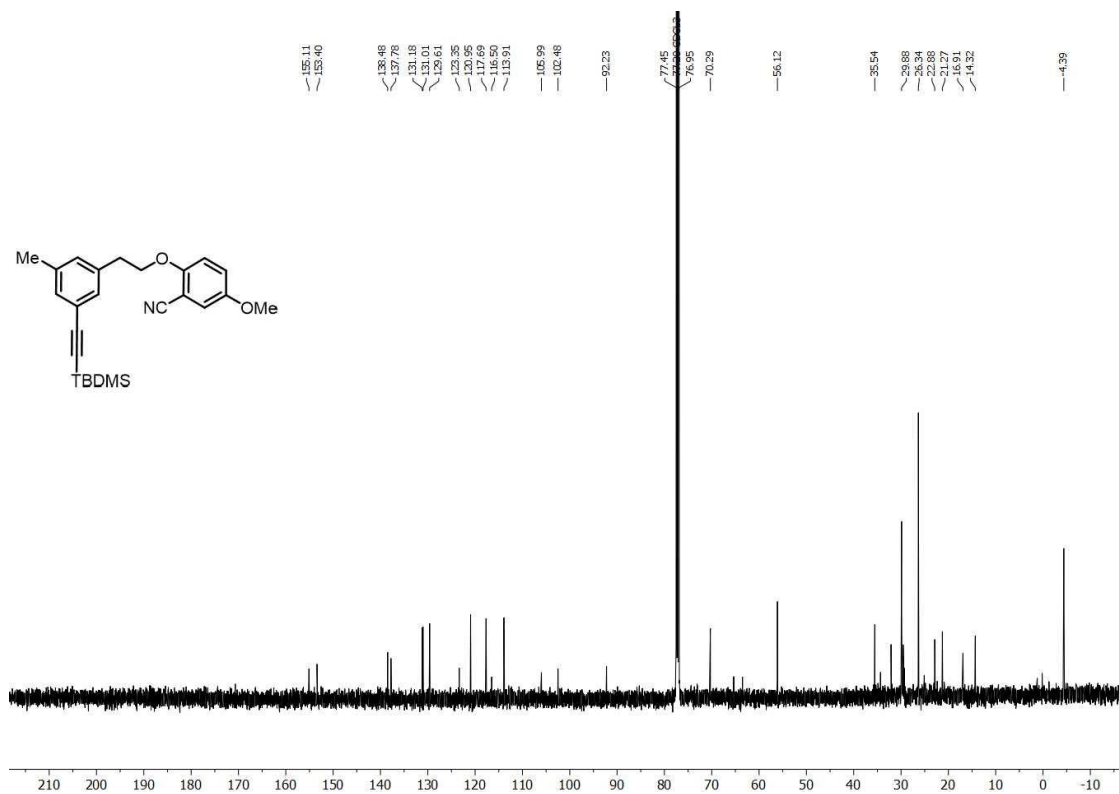
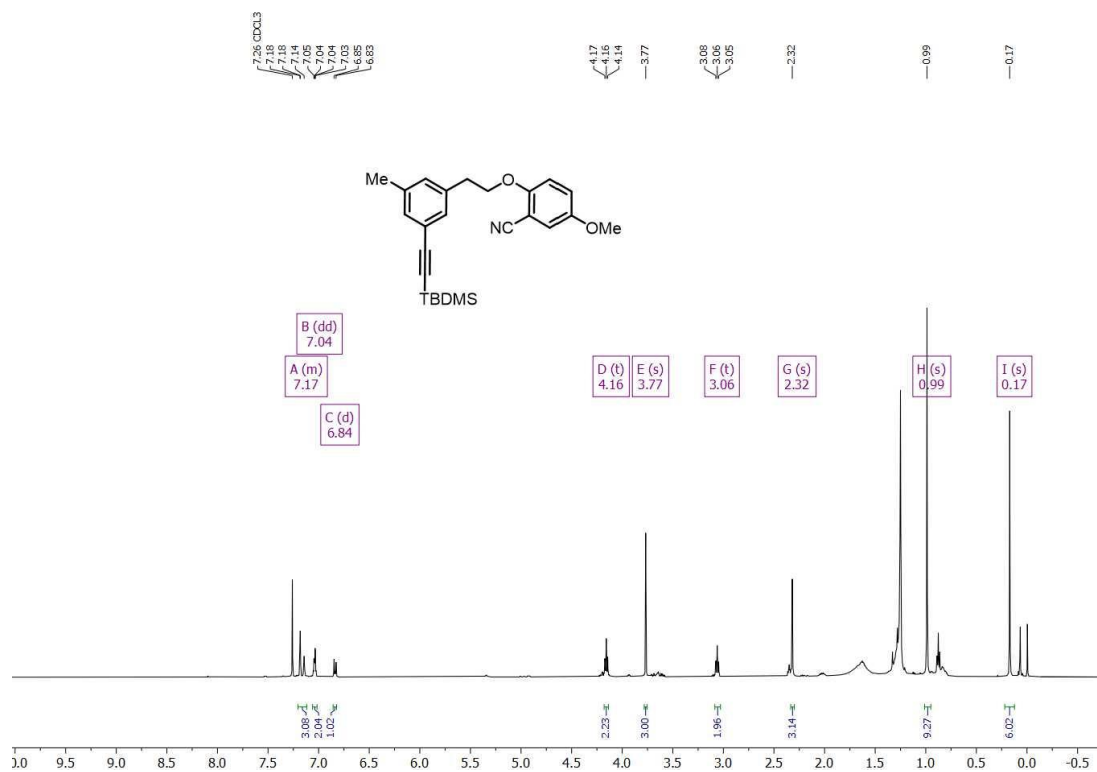
8f. 2-cyano-5-methoxyphenyl 3-(3-((2-isopropyl-5-methyl-1-(trimethylsilyl)oxy)cyclohexyl)ethynyl)phenyl)propanoate



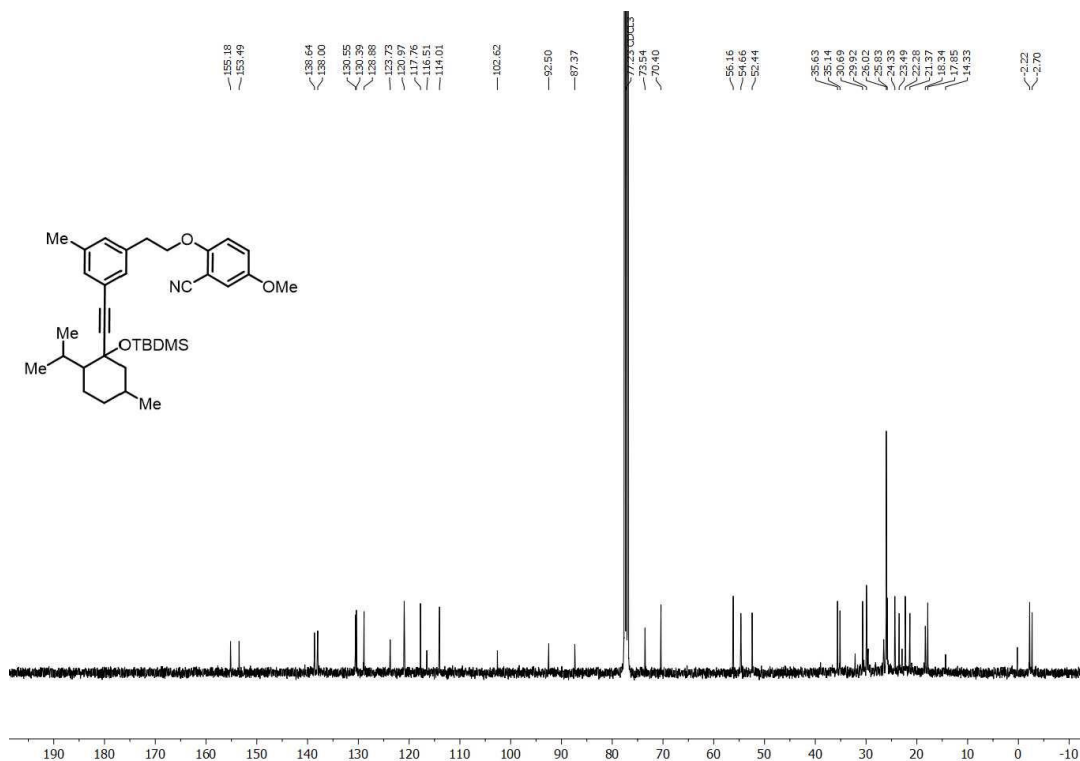
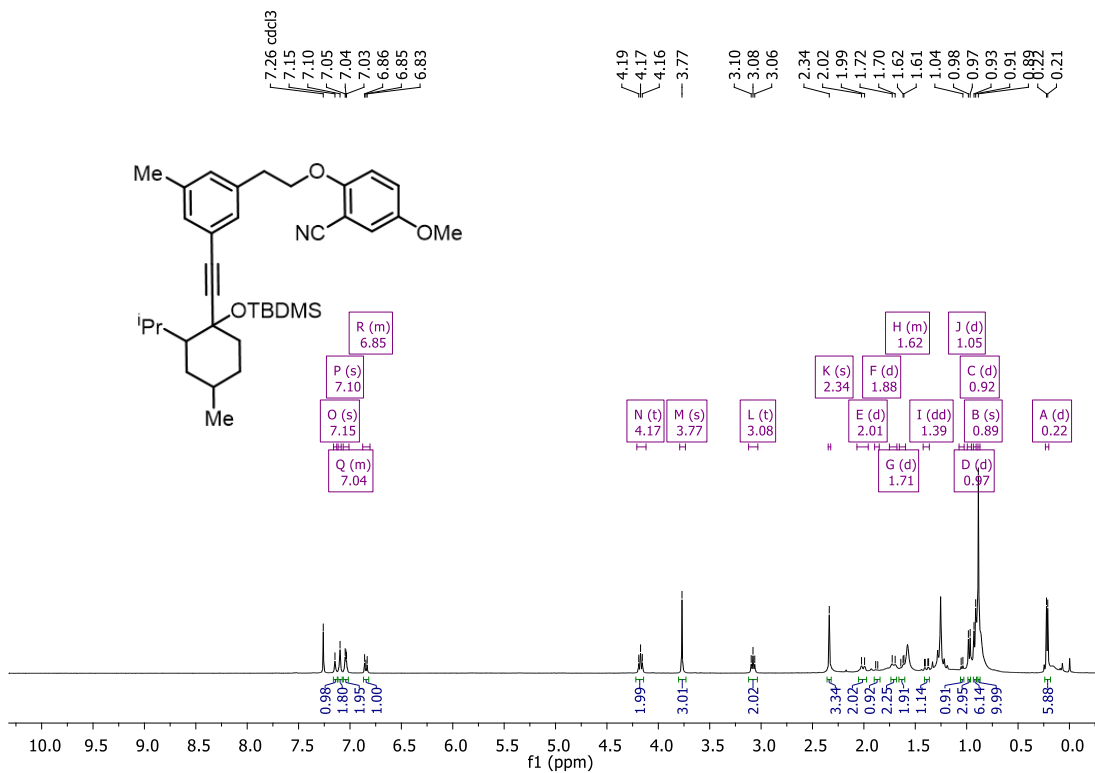
8g. 3'-((tert-butyldimethylsilyl)ethynyl)-[1,1'-biphenyl]-2-yl 2-cyanobenzoate



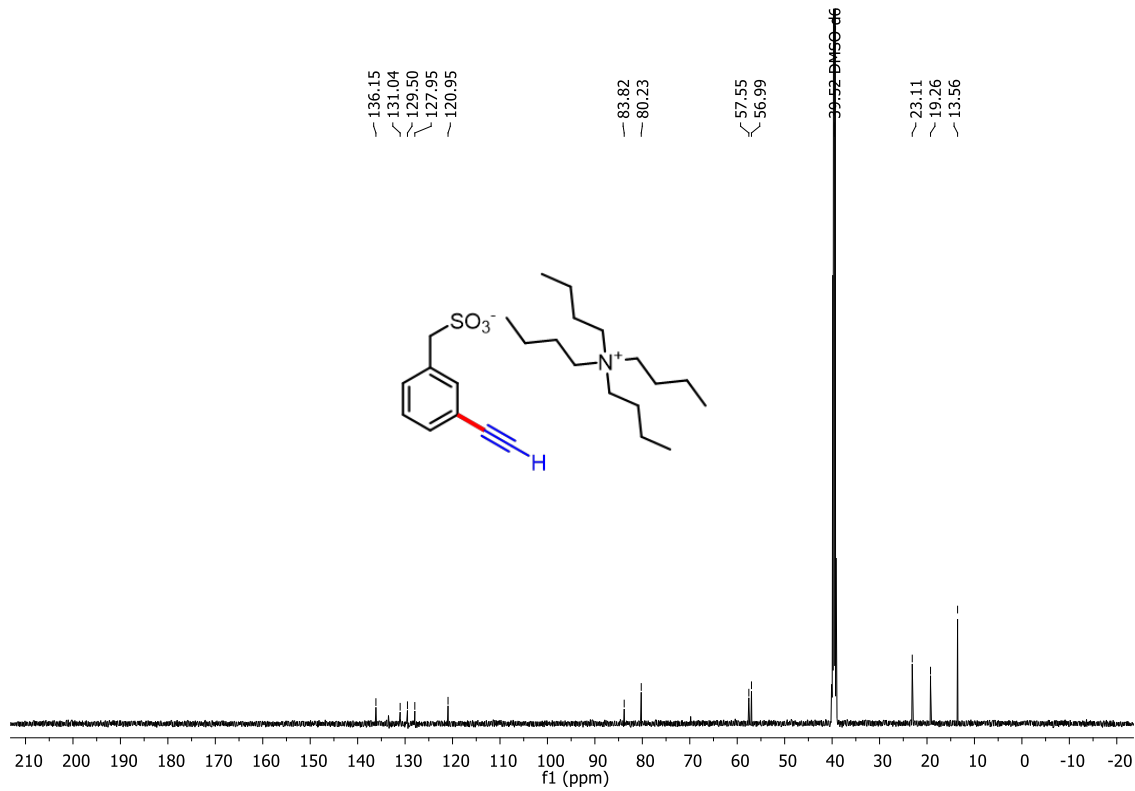
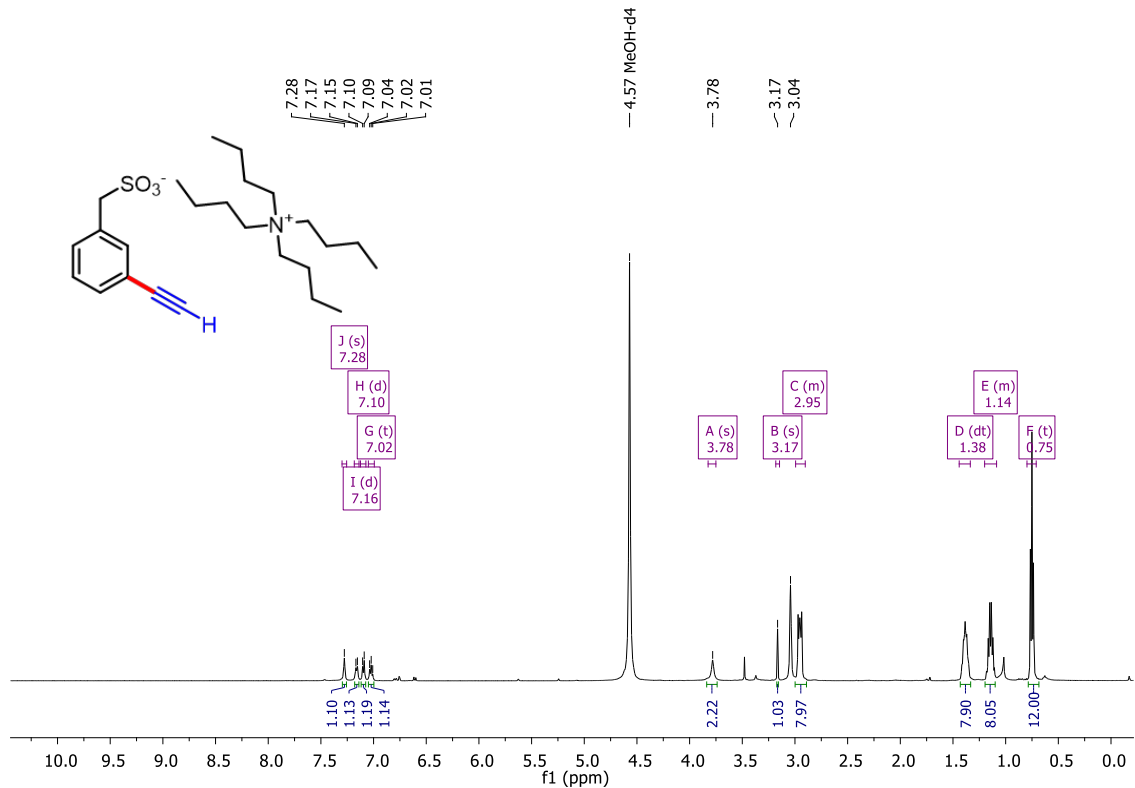
8h. 2-(3-((1-((*tert*-butyldimethylsilyl)ethynyl)-5-methylphenoxy)-5-methoxybenzonitrile



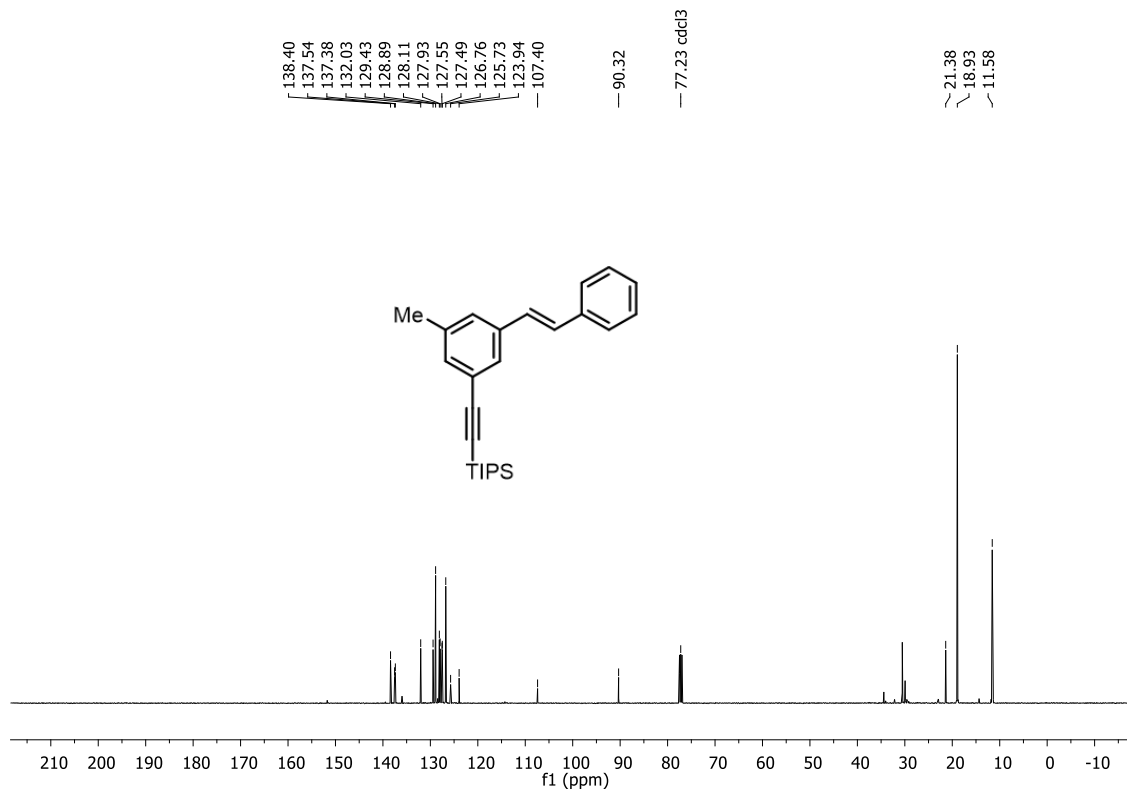
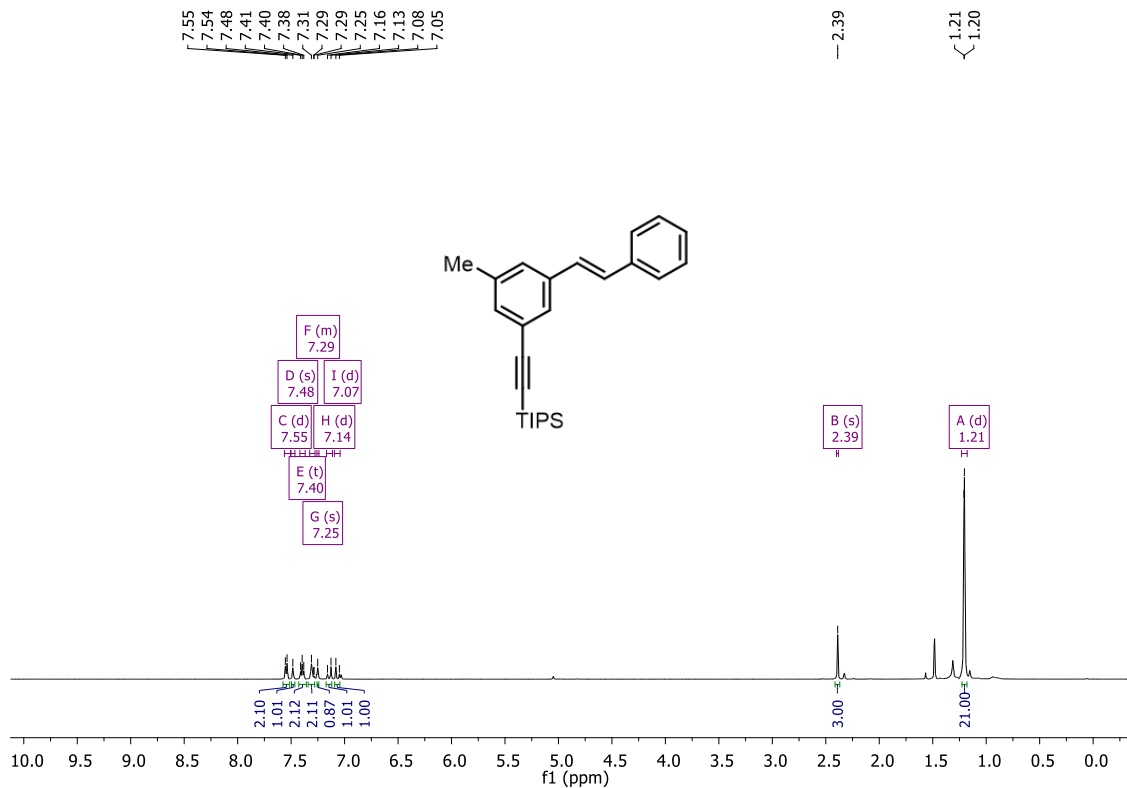
8i. 2-(3-((1-((*tert*-butyldimethylsilyl)oxy)-2-isopropyl-4-methylcyclohexyl)ethynyl)-5-methoxybenzonitrile



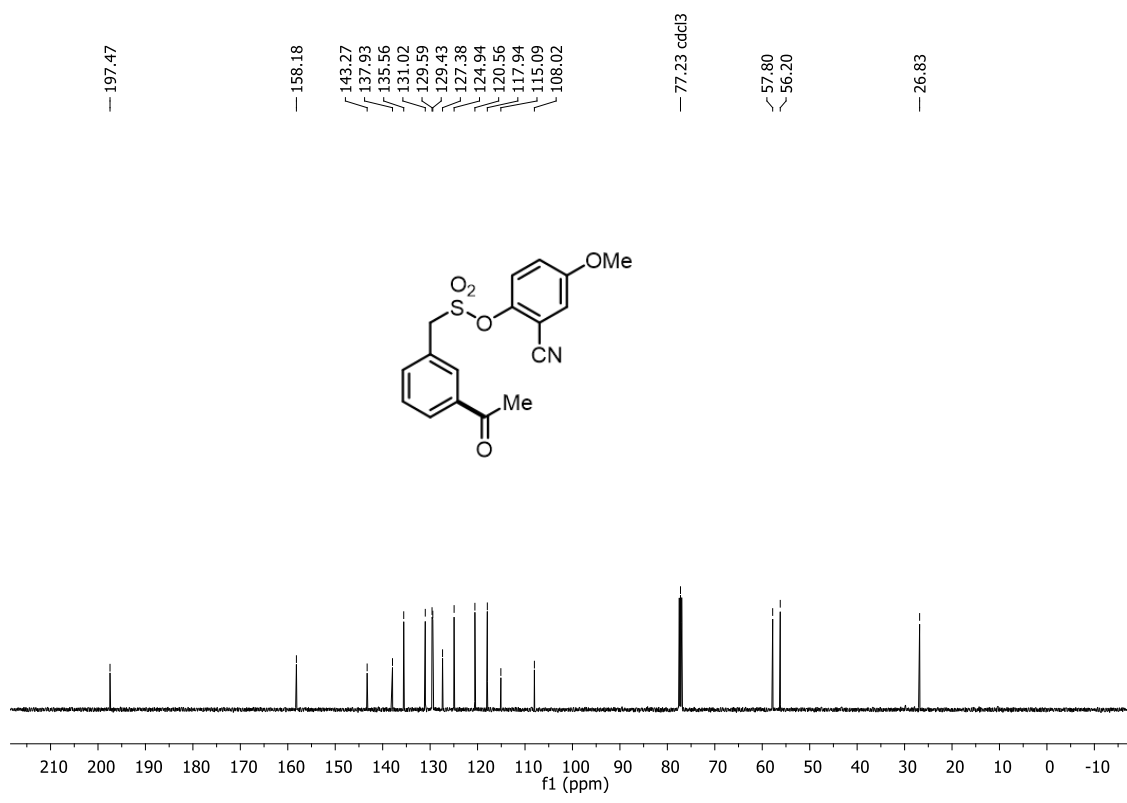
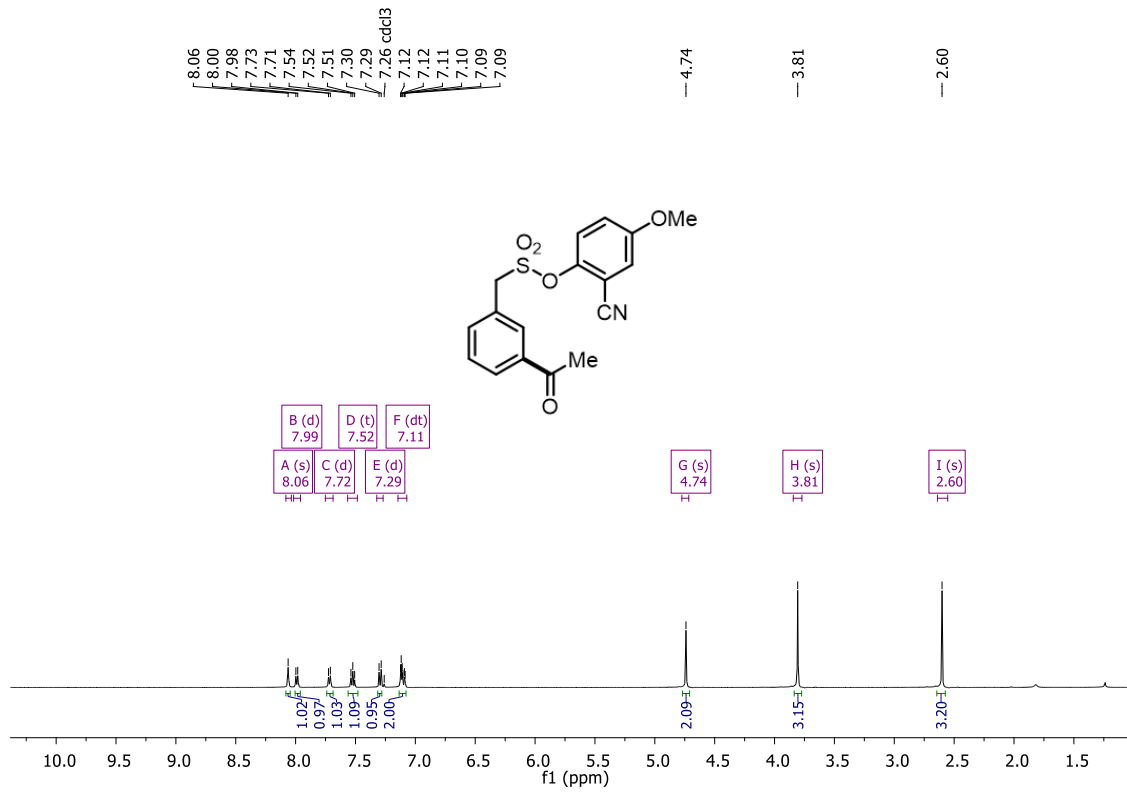
9. Tetrabutylammonium (3-ethynylphenyl)methanesulfonate



10. (*E*)-Triisopropyl((3-methyl-5-styrylphenyl)ethynyl)silane



11. 2-Cyano-4-methoxyphenyl (3-acetylphenyl)methanesulfonate



12. 2-(3-Ethynylphenethoxy)-5-methoxybenzonitrile

