Supporting Information

Rhodium Catalyzed Template-Assisted Distal *para*-C–H Olefination

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1. General Consideration

1.a. Reagent Information: Unless otherwise stated, all the reactions were carried out under aerobic condition 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 $[Rh(COD)Cl]_2$ was bought from Ark Pharma.Cupric chloride ($CuCl_2$) and vanadium pentoxide (V_2O_5) is obtained from Sigma Aldrich. Palldiumacetate, used for study material preparation, was purchased from Alfa Aesar. All the benzyl chlorides and bromides were bought from Aldrich/Alfa Aesar (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 $60F_{254}$).

1.b. Analytical Information: All isolated compounds are characterized by ^1H NMR, ^{13}C NMR spectroscopy. Copies of the ^1H NMR, ^{13}C NMR can be found in the supporting information. Nuclear magnetic resonance 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), unless otherwise stated, 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.

1.c. Description of Reaction Tube:

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

2. Experimental Section

2.a. Optimization (yields and selectivity is determined by ^{1}H NMR of crude reaction mixture using trimethoxy benzene as internal standard)**:**

Table S1: Initial finding

#	Rh Salt	Oxidant	Ligand	Solvent	Yiled (%) (*p:others*)
1	$[Rh(COD)Cl]_2$	AgOAc	*N*-Ac-Gly-OH	HFIP	nd
2	$[Rh(COD)Cl]_2$	Ag_2CO_3	*N*-Ac-Gly-OH	HFIP	nd
3	$[Rh(COD)Cl]_2$	AgOAc	*N*-Ac-Gly-OH	DCE	nd
4	$[Rh(COD)Cl]_2$	Ag_2CO_3	*N*-Ac-Gly-OH	DCE	nd
5	$[Rh(COD)Cl]_2$	$CuCl_2$	*N*-Ac-Gly-OH	DCE	nd
6	$[Rh(COD)Cl]_2$	CuCl	*N*-Ac-Gly-OH	DCE	nd
7	$[Rh(COD)Cl]_2$	$Cu(OAc)_2$	*N*-Ac-Gly-OH	DCE	nd
8	$[Rh(COD)Cl]_2$	Cu(TFA)	*N*-Ac-Gly-OH	DCE	trace
9	$[Rh(COD)Cl]_2$	Cu(TFA)	-	DCE	trace
10	**$[Rh(COD)Cl]_2$**	**Cu(TFA) & V_2O_5**	**-**	**DCE**	**30 (10:1)**
11	$[RhCp^*Cl]_2$	Cu(TFA)	-	DCE	trace

Table S2: DG optimization

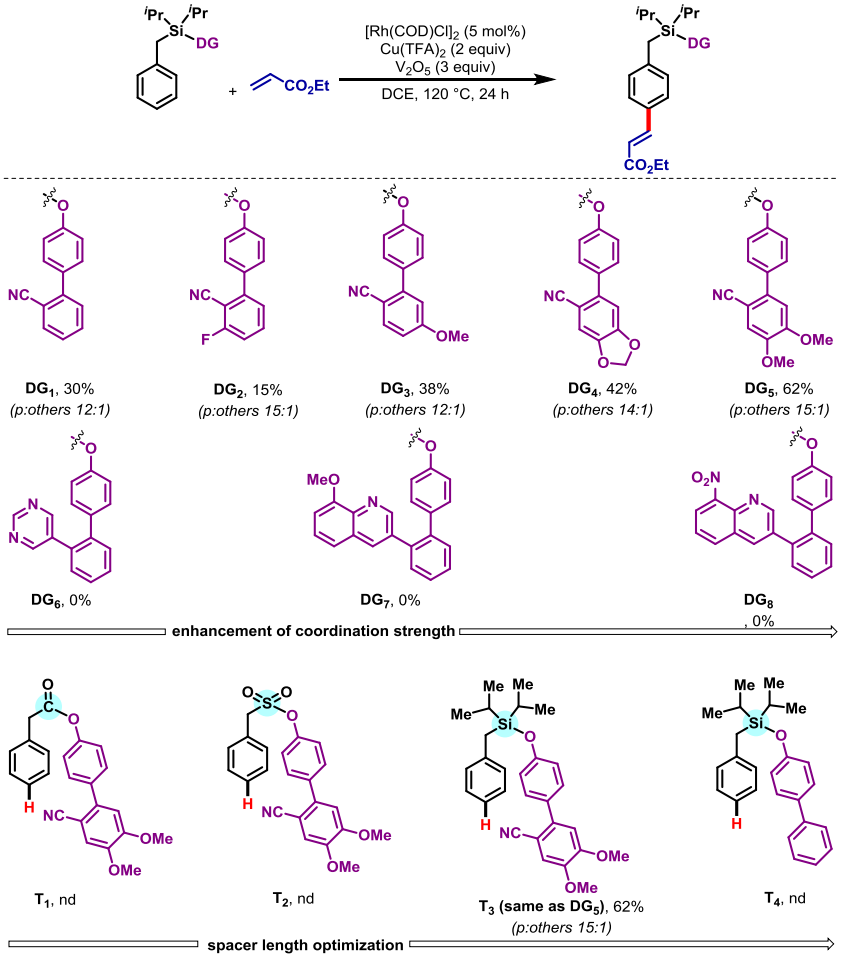
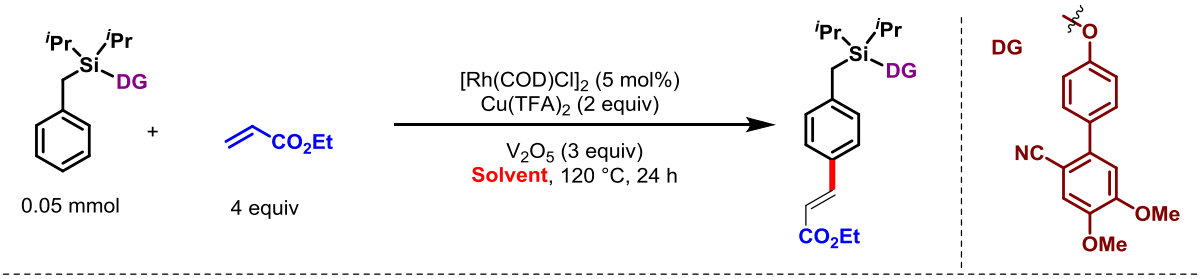


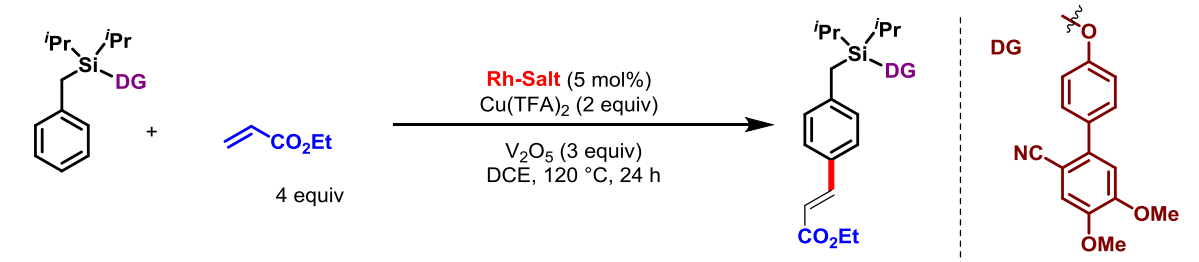
Table S3: Solvent optimization



Sr. No.	Solvents	Yield (%)(*p:others*)
1	**DCE**	**62 (15:1)**
2	DCM	16 (14:1)
3	$CHCl_3$	trace
4	HFIP	nd
5	TFE	nd
6	TFT	nd
7	Toluene	nd
8	*m*-Xylene	nd
9	NMP	nd
10	TBME	nd
11	1,4-Dioxane	trace
12	THF	trace
13	MeOH	nd
14	^{i}PrOH	nd
15	Chlorobenzene	trace
16	TCP	7 (10:1)
17	MeCN	nd
18	PhCN	nd
19	DMF	nd

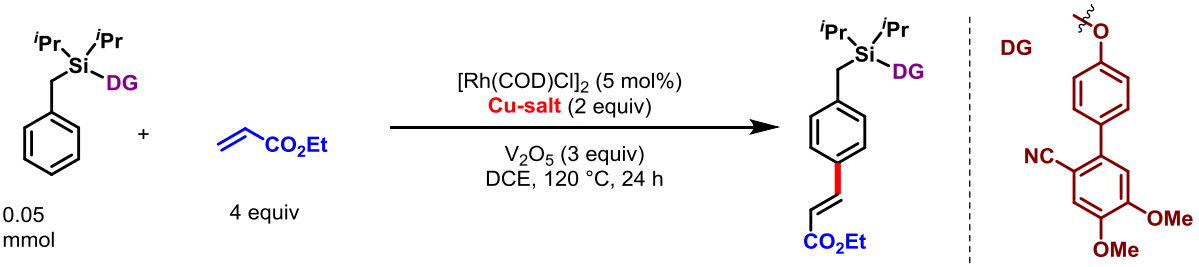
20	DMSO	nd
21	2-Me-THF	nd

Table S4: Rh-Salt Optimization



#	Rh-Salt	Yield (%)(*p:others*)
1	No-Rh cat.	n.d.
2	$[RhCp^*Cl_2]_2$	20 (10:1)
3	**$[Rh(COD)Cl]_2$**	**62 (15:1)**
4	$Rh(OAc)_2$	trace
5	$Rh(PPh_3)_3Cl$	n.d.
6	[Rh(COD)(*S*)-BINAP]BF_4	trace

Table S5: Cu-Salt Optimization

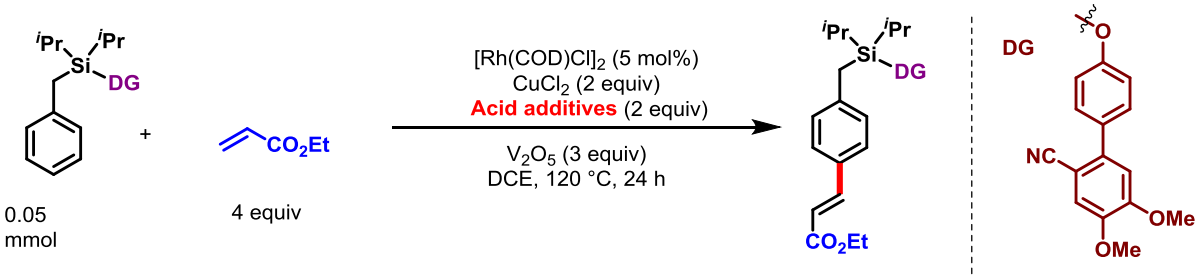


#	Cu-Salt	Yield (%)(*p:others*)
1	No Cu-Salt	20 (13:1)
2	$CuCl_2$	30 (10:1)
3	CuCl	trace

4	**$Cu(TFA)_2$**	**62 (15:1)**
5	$Cu(OAc)_2.H_2O$	24 (7:1)
6	Cu_2O	nd
7	$Cu(OTf)_2$	trace
8	$CuSO_4$	trace

Notably silver salts as oxidant remain ineffective to produce desired product

Table S6: Cu-Salt and Acid Additive Optimization



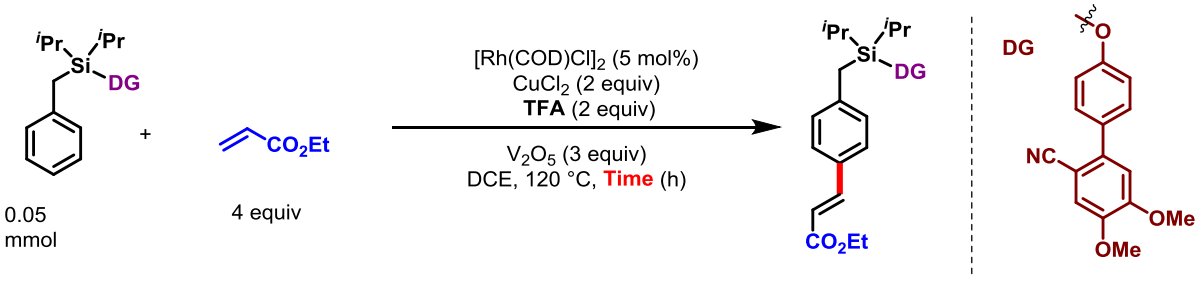
#	Cu-Salt	Acid additives	Yield (%)(*p:others*)
1	$Cu(TFA)_2$	TFA	43 (8:1)
2	$Cu(TFA)_2$	AcOH	40 (10:1)
3	$Cu(TFA)_2$	Piv-OH	26 (12:1)
4	$Cu(TFA)_2$	Adamantane-1-carboxylic acid	55 (16:1)
5	**$CuCl_2$**	**TFA**	**85 (15:1)**
6	$CuCl_2$	AcOH	38 (11:1)
7	$CuCl_2$	Piv-OH	trace
8	$CuCl_2$	Adamantane-1-carboxylic acid	trace
9	$CuCl_2$	-	40
10	$CuCl_2$	TFA	30*

*the reaction was conducted in absence of V_2O_5

Table S7: Temperature Optimization

#	Temperature (°C)	Yield (%)(*p:others*)
1	50	n.d.
2	70	trace
3	80	20 (>20:1)
4	90	26 (18:1)
5	100	35 (16:1)
6	110	72 (15:1)
7	**120**	**85 (15:1)**
8	130	70 (7:1)

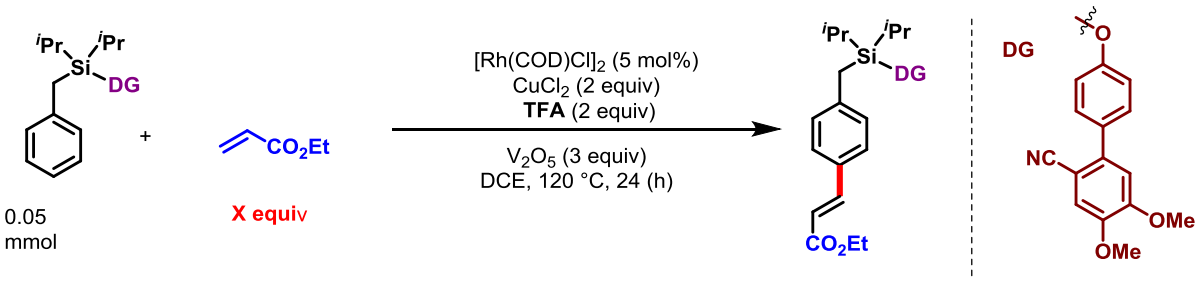
Table S8: Time Optimization



#	Time (h)	Yield (%)(*p:others*)
1	12	60 (18:1)
2	16	68 (18:1)
3	20	76 (16:1)
4	**24**	**85 (15:1)**

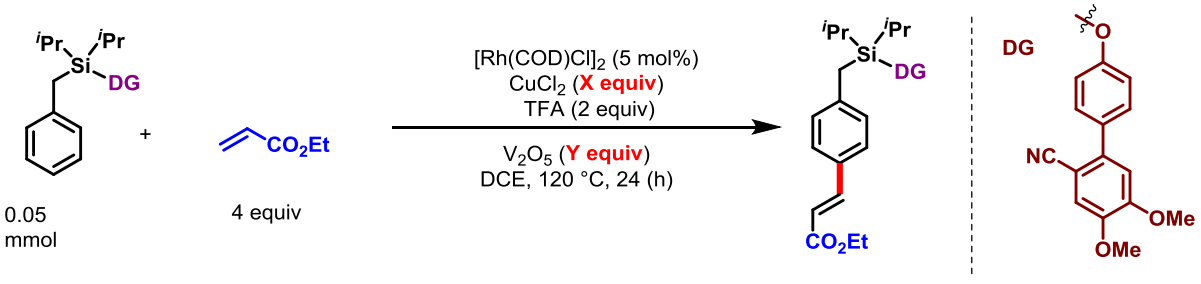
5	36	86 (12:1)
6	48	80 (10:1)

Table S9: Olefin Amount Optimization



#	Olefin amount (equiv.)	Yield (%)(*p:others*)
1	1.0	34 (>20:1)
2	1.5	42 (>20:1)
3	2.0	58 (>16:1)
4	2.5	64 (15:1)
5	3.0	70 (15:1)
6	3.5	77 (15:1)
7	**4.0**	**85 (15:1)**
8	5	84 (10:1)

Table S10: Amount of $CuCl_2$ and V_2O_5 Optimization



#	$CuCl_2$ amount (equiv.)	V_2O_5 amount (equiv.)	Yield (%)(*p:others*)
1	1.0	3.0	52 ((16:1)

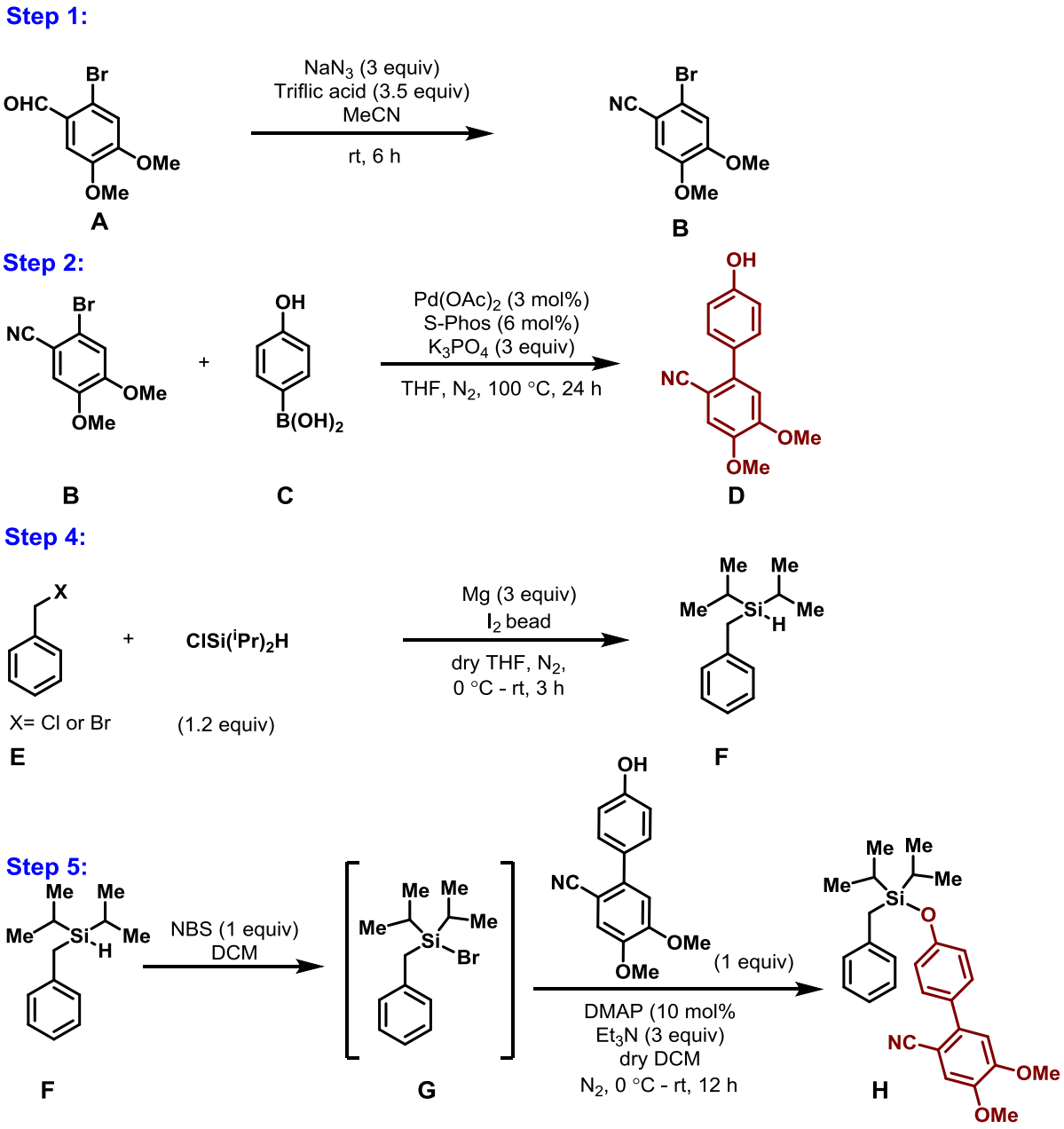
2	1.5	3.0	72 (15:1)
3	**2.0**	**3.0**	**85 (15:1)**
4	2.5	3.0	70 (12:1)
5	3.0	3.0	62 (10:1)
6	2.0	1.0	68 (15:1)
7	2.0	1.5	72 (15:1)
8	2.0	2.0	74 (15:1)
9	2.0	2.5	80 (14:1)
10	2.0	3.5	84 (12:1)
11	2.0	4.0	85 (10:1)

2.b. General Procedure

Procedure A: General Procedure for *para*-Olefination

An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, substrate (0.2 mmol, 1.0 equiv), $[Rh(COD)Cl]_2$ (5mol%, 0.01mmol, 4.9 mg), $CuCl_2$ (0.4 mmol, 2 equiv, 53.6 mg), and V_2O_5 (0.6mmol, 3 equiv, 109.1 mg) were taken. Subsequently, DCE (2 mL), olefin (0.8mmol, 4.0 equiv) and trifluoroacetic acid (0.4 mmol, 4 equiv, 30.6μL) was added.The reaction tube was capped tightly and placed on a preheated 120 °C oil bath. The reaction mixture was stirred vigorously for 24 h. The reaction mixture was then diluted with DCM.10 mL dilute ammonia solution was added to the reaction mixture; the organic part was extracted with DCM and dried over magnesium sulfate. After evaporation of the solvent, the crude mixture was purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether/ethyl acetate as the eluent.

Procedure B: Synthesis of directing group and substrates



Step-1: In an oven dried round bottom flask (250 mL), charged with stir-bar, aldehyde substrate (A) (20 mmol) and NaN_3 (3 equiv.) were taken. MeCN (60 mL) was added to it and stirred at room temperature for 15 mins. 3.5 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 6 hour. Upon completion the reaction was diluted with ethyl acetate and 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.[1] Quantitative conversion; white solid.

Step-2:[2] In an oven dried reaction tube, charged with stir-bar, Pd $(OAc)_2$ (3 mol%), S-phos (6 mol%), **B** (3 mmol), 4-hydroxyphenyl boronic acid (3.5 mmol) and K_3PO_4 (3 equiv.) were added. The reaction tubes were capped with Teflon cap and purged with N_2 using schlenk

line set up. THF was added to the reaction mixture (5 mL) and submerged in a preheated 100 °C oil bath and allowed for vigorous stirring for 24 hours. After 24 hour, reaction mixture was allowed to cool and diluted with EtOAc and extracted with brine solution. The organic layer was dried over $Na_2SO_4$and concentrated by evaporation. Concentrated organic part was purified by column chromatography. Pale yellow crystalline compound was isolated in 75% yields using ethyl acetate and pet ether mixture (20:80) as an eluent.

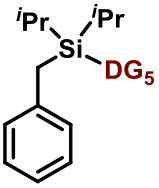
Step 3:[2] In a clean, oven-dried screw cap reaction tube, charged with magnetic stir–bar, activated magnesium turnings (15 mmol, 3 equiv.) and I_2 (one bead) were taken. The reaction tube was evacuated and back filled with nitrogen three times. Dry THF (15 mL) was added to it followed by di-isopropylchlorosilane (6 mmol, 1.2 equiv) in drop wise fashion and stirred at room temperature for 15 mins. A solution of benzyl chloride/bromide (5 mmol) in dry THF (10 mL) was added to the solution drop wise over a period of 15 minutes under ice cold condition. The mixture was vigorously stirred for 3 hours. Upon completion, the reaction mixture was quenched and washed with brine solution (3X10 mL). Aqueous part was washed thrice with ethyl acetate (3X20 mL). The combined organic layer was then dried over anhydrous Na_2SO_4. The compound (**F**) was purified using chromatography [silica gel (60-120/100-200 mesh size)] and petroleum-ether as the eluent. Benzyldiisopropylsilane (**F**) was collected and used for next step.

Step 4:[2] To an ice cold suspension of *N*-bromosuccinimide (5.0mmol, 1.0equiv) in 10 mL dry DCM, benzyldiisopropylsilane (**F**) (5.0mmol, 1.0equiv) was added drop wise under N_2 atmosphere. The reaction was kept on stirring for 3 hours at room temperature. In an another clean round bottomed flask, charged with magnetic stir–bar, 4'-hydroxy-4, 5-dimethoxybiphenyl-2-carbonitrile (**D**) (5 mmol, 1.0equiv) and 4-dimethylaminopyridine (10 mol%) were taken. The set up was evacuated and refilled with N_2. 5 mL dry DCM was added to the mixture followed by triethylamine (15mmol, 3.0equiv) in a drop wise fashion. The entire solution was kept for stirring at room temperature until 4'-hydroxy-4,5-dimethoxybiphenyl-2-carbonitrile gets dissolved completely. The aforementioned solution of benzylbromodiisopropylsilane was added drop wise under the ice-cold condition. The reaction mixture was then stirred overnight at room temperature. Upon completion, the mixture was quenched with water (20 mL) and extracted with ethyl acetate thrice (3X30 mL). The organic layer was combined and dried over anhydrous Na_2SO_4. The final substrate (**H**) was purified through column chromatography using silica gel (60-120/100-200 mesh size) and petroleum-ether/ethyl acetate (90/10, v/v) as the eluent. Isolated compound turned white solid upon drying. Yield: 73%

2.c. Characterization of starting material

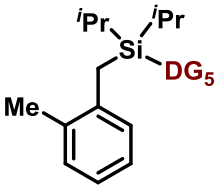
Characterization of starting materials (all the starting material and templates have been prepared by the previous literature report):[3]

4'-((benzyldiisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile:



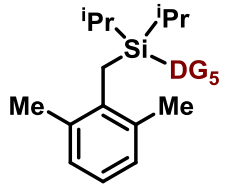
The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (90: 10)
Yield: 73%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.5 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.15 – 7.12 (m, 3H), 7.09 (t, *J* = 7.3 Hz, 1H), 6.90 (s, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.40 (s, 2H), 1.23 (m, 2H), 1.05 (m, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.2, 152.7, 148.2, 140.2, 138.7, 131.4, 130.0, 129.1, 128.5, 124.7, 120.2, 119.5, 115.2, 112.5, 102.3, 56.5, 56.3, 21.2, 17.6, 17.6, 13.1.

4'-((diisopropyl(2-methylbenzyl)silyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile:



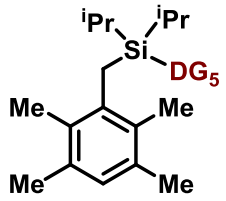
The substrate was prepared following the procedure B.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (90: 10)
Yield: 70%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 10 Hz, 2H), 7.14 (d, *J* = 5 Hz, 1H), 7.11 (s, 1H), 7.08 (t, *J* = 6.6 Hz, 2H), 7.01 (t, *J* = 5 Hz, 1H), 6.87 (s, 1H), 6.69 (d, *J* = 10 Hz, 2H), 3.96 – 3.93 (m, 3H), 3.92 (s, 3H), 2.37 (s, 2H), 2.30 (s, 3H), 1.31 – 1.24 (m, 2H), 1.08 (d, *J* = 10 Hz, 6H), 1.03 (d, *J* = 10 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 152.7, 148.1, 140.2, 137.4, 135.7, 131.2, 130.5, 129.9, 129.4, 125.9, 124.9, 119.9, 119.5, 115.2, 112.5, 102.2, 56.4, 56.3, 20.6, 18.1, 17.7, 17.5, 13.4.

4'-(((2,6-dimethylbenzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



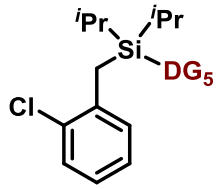
The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether: ethyl acetate (90:10)
Yield: 72%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 1H), 7.00 – 6.90 (m, 3H), 6.88 (s, 1H), 6.73 (d, *J* = 8.4 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.40 (s, 2H), 2.33 (s, 6H), 1.28 – 1.21 (m, 2H), 1.11 – 1.08 (m, 6H), 1.11 – 1.08 (m, 6H), 0.99 – 0.96 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 152.6, 148.1, 140.1, 136.5, 135.4, 131.1, 129.9, 128.2, 124.4, 119.8, 119.3, 115.1, 112.4, 102.2, 56.3, 56.2, 21.5, 17.6, 17.3, 15.8, 14.1.

4'-((diisopropyl(2,3,5,6-tetramethylbenzyl)silyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



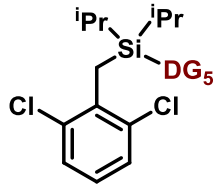
The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (90:10)
Yield: 72%
Physical appearance: White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 6.87 (s, 1H), 6.75 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.48 (s, 2H), 2.20 (s, 6H), 2.18 (s, 6H), 1.28 – 1.19 (m, 2H), 1.11 – 1.07 (m, 6H), 1.00 – 0.95 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 152.7, 148.1, 140.3, 136.2, 133.7, 131.6, 130.9, 129.8, 128.4, 119.8, 119.5, 115.2, 112.5, 102.3, 56.5, 56.3, 21.0, 17.7, 17.5, 17.1, 16.5, 14.2.

4'-(((2-chlorobenzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile:



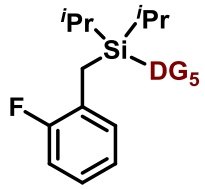
The substrate was prepared following the procedure B.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (88:12)
Yield: 68%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 10 Hz, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.14 – 7.08 (m, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 6.85 (d, *J* = 10 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 2.56 (s, 2H), 1.33 – 1.26 (m, 2H), 1.09 – 1.03 (m, 12H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 152.7, 148.1, 140.1, 137.1, 133.2, 131.3, 130.7, 129.9, 129.6, 126.7, 126.1, 119.9, 119.4, 115.1, 112.4, 102.2, 56.3, 56.2, 18.5, 17.5, 17.4, 13.5.

4'-(((2,6-dichlorobenzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (85:15)
Yield: 68%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 10 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 6.94 (t, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 6.80 (d, *J* = 10 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.75 (s, 2H), 1.41 – 1.33 (m, 2H), 1.11 (d, *J* = 10 Hz 6H), 1.06 (d, *J* = 10 Hz, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 152.7, 148.1, 140.3, 136.8, 134.5, 131.1, 129.8, 128.2, 126.3, 119.8, 119.5, 115.2, 112.5, 102.3, 56.5, 56.3, 18.0, 17.6, 17.5, 14.4.

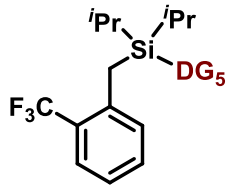
4'-(((2-fluorobenzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile:



The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica

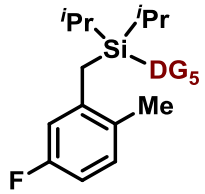
Eluent: petroleum ether:ethyl acetate (88:12)
Yield: 68%
Physical appearance: White solid
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 12 Hz, 2H), 7.19 – 7.11 (m, 2H), 7.09 – 7.03 (m, 1H), 7.01 – 6.94 (m, 2H), 6.90 (s, 1H), 6.87 (d, , *J* = 10 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.38 (s, 2H), 1.29 – 1.21 (m, 2H), 1.10 – 1.02 (m, *J* = 7.3 Hz, 12H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.5 (d, *J* = 243.41), 156.0, 152.6, 148.1, 140.1, 131.3, 131.1 (d, *J* = 4.04), 131.1, 129.9, 126.2 (d, *J* = 8.08), 125.8(d, *J* = 17.17), 123.9 (d, *J* = 3.03), 120.1, 119.4, 115.4, 115.1, 115.1, 112.4, 102.2, 56.3, 56.2, 17.4, 17.4, 13.4, 13.3, 13.2.

4'-((diisopropyl(2-(trifluoromethyl)benzyl)silyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (85:15)
Yield: 68%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.36 (m, 4H), 7.21 – 7.16 (m, 1H), 7.13 (s, 1H), 6.89 (s, 1H), 6.86 (d, *J* = 5.0 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.59 (s, 2H), 1.32 – 1.25 (m, 2H), 1.07 – 1.03 (m, 6H), 0.99 – 0.96 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 156.0, 152.7, 148.2, 140.2, 138.4, 131.6, 131.5, 130.1, 127.9 (q, *J* = 28.98 Hz), 126.4 (q, *J* = 5.88 Hz), 126.1, 124.8, 123.9, 120.1, 119.5, 115.2, 112.5, 102.3, 56.5, 56.3, 17.9, 17.6, 17.4, 13.4.

4'-(((5-fluoro-2-methylbenzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile

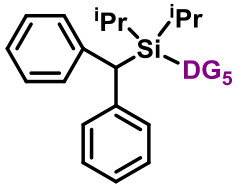


The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (85: 15)
Yield: 69%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 5.7 Hz, 2H), 7.12 (s, 1H), 7.01 (t, *J* = 8.1, 6.4 Hz, 1H), 6.88 (s, 1H), 6.84 (dd, *J* = 10.2, 2.7 Hz, 1H), 6.75 – 6.67 (m, 3H), 3.94 (s, 3H), 3.92 (s,

3H), 2.34 (s, 2H), 2.24 (s, 3H), 1.32 – 1.24 (m, 2H), 1.09 (d, *J* = 7.5 Hz, 6H), 1.04 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 243.18), 155.8, 152.7, 148.1, 140.1, 139.6 (d, *J* = 7.56), 131.5, 131.4, 131.4, 131.2 (d, *J* = 2.52), 129.9, 119.9, 119.4, 115.7 (d, *J* = 21.42), 115.2, 112.5, 111.4 (d, *J* = 20.16), 102.3, 56.4, 56.3, 19.8, 18.5, 17.7, 17.5, 13.4.

4'-((benzhydryldiisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



The substrate was prepared following the procedure **B**.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85: 15)

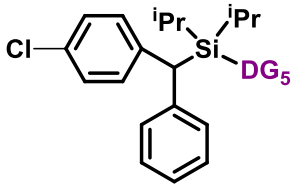
Yield: 75%

Physical appearance: White solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 – 7.48 (m, 4H), 7.41 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.38 (d, *J* = 10.0, 2H), 7.30 – 7.26 (m, 3H), 7.16 (m, 2H), 7.14 (s, 1H), 6.90 (s, 1H), 6.86 (d, *J* = 10.0, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.80 (s, 1H), 1.31 – 1.24 (m, 2H), 0.94 – 0.90 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.1, 152.7, 148.2, 142.7, 142.2, 140.2, 131.4, 130.1, 129.7, 129.2, 128.7, 128.7, 125.8, 125.6, 120.1, 119.5, 115.2, 112.5, 102.4, 56.5, 56.4, 42.9, 18.1, 17.8, 17.8, 17.7, 13.8, 13.3.

4'-((((4-chlorophenyl)(phenyl)methyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



The substrate was prepared following the procedure **B**.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85: 15)

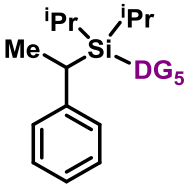
Yield: 72%

Physical appearance: White solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.38 (m, 6H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.14 (s, 1H), 6.90 (s, 1H), 6.87 (d, 10.0 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.77 (s, 1H), 1.31 – 1.24 (m, 2H), 0.97 – 0.87 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 152.7, 148.2, 141.7, 140.9, 140.1, 131.6, 130.9, 130.1, 129.5, 128.8, 128.7, 126.1, 119.9, 119.5, 115.2, 112.5, 102.4, 56.5, 56.3, 42.1, 18.1, 18.1, 17.8, 17.8, 13.8, 13.8.

4'-((diisopropyl(1-phenylethyl)silyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile

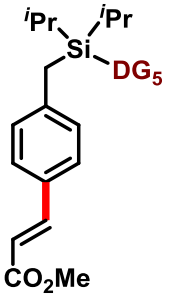


The substrate was prepared following the procedure **B**.
Column material: 100-200 mesh silica
Eluent: petroleum ether:ethyl acetate (85: 15)
Yield: 65%
Physical appearance: White solid
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, 10.0 Hz, 2H), 7.29 – 7.21 (m, 5H), 7.14 (s, 1H), 6.91 (s, 1H), 6.89 (d, 10.0 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.63 (q, *J* = 10.0 Hz, 1H), 1.55 (d, *J* = 7.6 Hz, 2H), 1.38 – 1.32 (m, 1H), 1.25 – 1.17 (m, 1H), 1.11 – 1.00 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 156.4, 152.7, 148.1, 144.9, 140.2, 131.2, 129.9, 128.4, 128.4, 128.2, 127.6, 125.1, 124.8, 120.1, 119.5, 115.1, 112.5, 102.2, 77.5, 77.2, 76.9, 56.4, 56.3, 27.6, 18.1, 18.0, 17.8, 17.8, 17.6, 16.4, 13.1, 12.9.

2.d. Characterization of *para*-olefinated products:

2a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4- yl)oxy)diisopropyl-silyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 75% (*para:others* = 12:1)

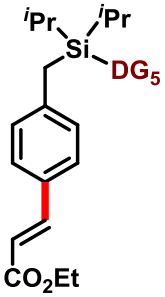
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.38 (dt, *J* = 4.9, 2.8 Hz, 4H), 7.15 – 7.12 (m, 3H), 6.91 – 6.84 (m, 3H), 6.36 (d, 1H), 3.95 (d, *J* = 3.6 Hz, 3H), 3.92 (s, 3H), 3.78 (s, 3H), 2.42 (s, 2H), 1.26 – 1.18 (m, 3H), 1.05 (dd, *J* = 7.4, 2.6 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 156.0, 152.7, 148.2, 145.1, 142.0, 140.1, 131.5, 130.9, 130.1, 129.5, 128.4, 120.1, 119.5, 116.4, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 56.4, 56.3, 51.8, 21.6, 17.6, 17.6, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{32}H_{37}NNaO_5Si$ 566.2333: found: 566.2329.

2b. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)-methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

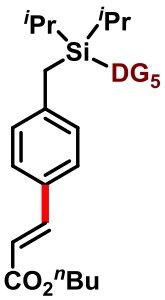
Yield: 78% (*para:others* = 15:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, 1H), 7.41 – 7.36 (m, 4H), 7.16 – 7.12 (m, *J* = 4.1 Hz, 3H), 6.89 (s, 1H), 6.86 (d, 2H), 6.36 (d, 1H), 4.24 (q, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.43 (s, 2H), 1.32 (t, *J* = 9.5, 4.8 Hz, 3H), 1.25 – 1.20 (m, *J* = 14.7, 7.3 Hz, 2H), 1.06 (d, *J* = 2.7 Hz, 6H), 1.04 (d, *J* = 2.6 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 156.0, 152.7, 148.2, 144.8, 141.9, 140.1, 131.5, 131.0, 130.1, 129.5, 128.4, 120.1, 119.5, 116.9, 115.2, 112.5, 102.3, 60.5, 56.5, 56.3, 21.6, 17.6, 17.6, 14.5, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{39}NNaO_5Si$ 580.2490: found: 580.2485.

2c. butyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4yl)oxy)diisopropylsil-yl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure Ain 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

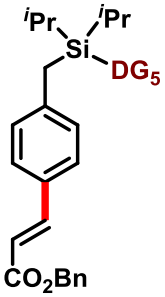
Yield: 74% (*para:others* = 7:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.39 (dt, *J* = 8.5, 2.7 Hz, 4H), 7.13 (d, *J* = 7.7 Hz, 3H), 6.90 – 6.83 (m, 3H), 6.39 – 6.31 (m, 1H), 4.21 – 4.15 (m, 2H), 3.94 (dd, *J* = 13.3, 12.6 Hz, 7H), 2.41 (d, *J* = 8.2 Hz, 2H), 1.71 – 1.64 (m, 3H), 1.42 (dq, *J* = 14.5, 7.3 Hz, 2H), 1.25 – 1.19 (m, 2H), 1.05 (dd, *J* = 7.4, 2.5 Hz, 14H), 0.95 (td, *J* = 7.4, 4.0 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 156.0, 152.7, 148.2, 144.8, 141.9, 140.1, 131.5, 131.0, 130.1, 129.5, 128.3, 120.1, 120.1, 119.4, 116.9, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 64.4, 56.4, 56.3, 30.9, 21.6, 19.4, 17.6, 17.5, 13.9, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{35}H_{43}NNaO_5Si$ 608.2803: found: 608.2796.

2d. benzyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

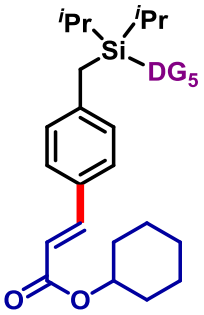
Yield: 71% (*para:others* = 10:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.43 – 7.36 (m, 8H), 7.35 – 7.31 (m, *J* = 7.0, 3.6, 1.4 Hz, 1H), 7.16 – 7.12 (m, *J* = 7.8 Hz, 3H), 6.90 – 6.85 (m, 3H), 6.42 (d, 1H), 5.24 (s, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.43 (s, 2H), 1.26 – 1.19 (m, *J* = 14.1, 6.6 Hz, 2H), 1.06 (d, *J* = 2.5 Hz, 6H), 1.04 (d, *J* = 2.4 Hz, 6H).

^{13}C NMR (126 MHz, CDCl3) δ 167.2, 155.9, 152.7, 148.2, 145.4, 142.1, 140.1, 136.4, 131.5, 130.9, 130.1, 129.5, 128.7, 128.4, 128.4, 128.3, 120.1, 119.5, 116.4, 115.2, 112.5, 102.3, 66.4, 56.4, 56.3, 21.6, 17.6, 17.5, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{41}NNaO_5Si$ 642.2720: found: 642.2720.

2e. cyclohexyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

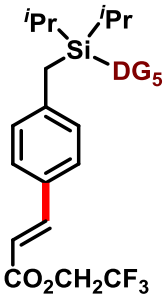
Yield: 77% (*para:others* = 9:1)

^{1}H NMR(500 MHz, $CDCl_3$) δ 8.22 (d, J = 15.9 Hz, 1H), 8.01 – 7.96 (m, 4H), 7.75 – 7.72 (m, 3H), 7.49 (s, 1H), 7.46 (d, J = 10.0 Hz, 2H), 6.96 (d, J = 15.0 Hz, 1H), 5.50 – 5.44 (m, 1H), 4.55 (s, 3H), 4.52 (s, 3H), 3.02 (s, 2H), 2.55 – 2.46 (m, 2H), 2.39 – 2.32 (m, 2H), 2.18 – 2.13 (m, 1H), 2.11 – 1.95 (m, 5H), 1.85 – 1.78 (m, 2H), 1.66 – 1.63 (m, 12H).

^{13}C NMR(126 MHz, $CDCl_3$) δ 166.9, 156.0, 152.7, 148.2, 144.5, 141.8, 140.1, 131.5, 131.1, 130.1, 129.5, 128.3, 120.1, 119.4, 117.5, 115.2, 112.5, 102.4, 77.5, 77.2, 76.9, 72.7, 56.5, 56.3, 31.9, 25.6, 23.9, 21.6, 17.6, 17.6, 13.1 .

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{37}H_{45}NNaO_5Si$ 634.2959: found: 634.2957.

2f. 2,2,2-trifluoroethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

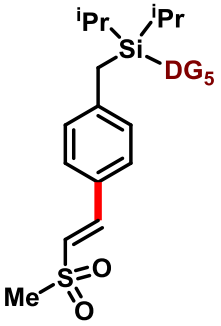
Yield: 69% (*para:others* = 8:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, 1H), 7.40 (m, 4H), 7.15 (dd, *J* = 12.3, 5.5 Hz, 3H), 6.91 – 6.84 (m, 4H), 6.41 (d, 1H), 4.57 (q, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.44 (s, 1H), 1.25 – 1.20 (m, *J* = 14.9, 7.5 Hz, 3H), 1.07 – 1.04 (m, *J* = 7.4, 1.6 Hz, 13H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 156.0, 152.8, 148.3, 147.4, 142.9, 140.1, 131.6, 130.4, 130.1, 129.6, 128.7, 120.1, 119.5, 115.2, 114.5, 112.5, 102.4, 77.5, 77.2, 76.9, 56.5, 56.3, 21.8, 17.6, 17.6, 13.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{36}F_3NNaO_5Si$ 634.2207: found: 634.2209.

2g. (*E*)-4'-((diisopropyl(4-(2-(methylsulfonyl)vinyl)benzyl)silyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile:



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (82:18)

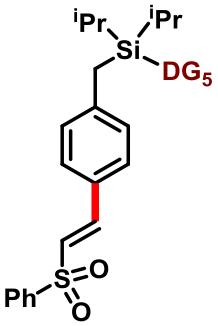
Yield: 48% (*para:others* = 15:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.4 Hz, 1H), 7.37 (t, *J* = 8.3 Hz, 4H), 7.17 – 7.12 (m, 3H), 6.89 (s, 1H), 6.86 – 6.82 (m, 3H), 3.95 (s, 3H), 3.92 (s, 3H), 3.01 (s, 3H), 2.44 (s, 2H), 1.22 (mzz, *J* = 14.8, 6.8 Hz, 4H), 1.07 – 1.03 (m, *J* = 7.2 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 152.8, 148.2, 144.2, 143.5, 140.1, 131.6, 130.1, 129.8, 128.9, 128.6, 124.7, 120.1, 119.5, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 56.5, 56.3, 43.6, 21.8, 17.6, 17.6, 13.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{31}H_{37}NNaO_5SSi$ 586.2054: found: 586.2053.

2h. (*E*)-4'-((diisopropyl(4-(2-(phenylsulfonyl)vinyl)benzyl)silyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (82:18)

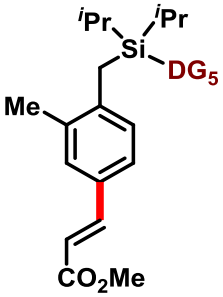
Yield: 62% (*para:others* = 15:1)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, *J* = 7.1, 3.1, 1.8 Hz, 1H), 7.63 (d, *J* = 15.3 Hz, 1H), 7.59 (dd, *J* = 3.8, 2.5 Hz, 1H), 7.55 – 7.51 (m, 1H), 7.38 (d, 1H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.13 (t, *J* = 4.1 Hz, 2H), 6.89 (s, 1H), 6.85 (d, 1H), 6.78 (d, *J* = 15.4 Hz, 1H), 3.96 (s, 1H), 3.93 (s, 2H), 2.43 (s, 1H), 1.24 – 1.16 (m, 1H), 1.05 – 1.03 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.9, 152.8, 148.3, 143.4, 142.9, 141.3, 140.1, 133.4, 131.7, 130.1, 129.7, 129.5, 128.9, 127.8, 125.8, 120.1, 119.5, 115.2, 112.5, 102.4, 77.5, 77.2, 76.9, 56.5, 56.3, 29.9, 21.8, 17.6, 17.6, 13.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{36}H_{39}NNaO_5SSi$ 648.2210: found: 648.2211.

4a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90: 10)

Yield: 72% (*para:others* = 9:1)

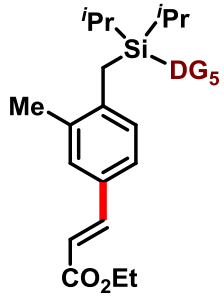
Physical appearance: Colourless viscous compound

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.26 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 7.12 (s, 1H), 6.86 (s, 1H), 6.69 (d, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.78 (s, 3H), 2.40 (s, 2H), 2.30 (s, 3H), 1.32 – 1.23 (m, *J* = 14.6, 7.3 Hz, 2H), 1.09 (d, *J* = 7.4 Hz, 6H), 1.03 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 155.8, 152.7, 148.2, 145.4, 141.0, 140.2, 136.3, 131.4, 131.1, 130.4, 129.9, 129.9, 125.8, 119.9, 119.5, 116.2, 115.2, 112.5, 102.3, 56.5, 56.3, 51.8, 20.6, 18.8, 17.8, 17.5, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{39}NNaO_5Si$ 580.2490: found: 580.2492.

4b. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90: 10)

Yield: 75% (*para:others* = 10:1)

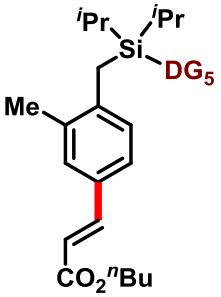
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 13.1 Hz, 1H), 7.31 (d, *J* = 8.6 Hz, 2H), 7.27 (d, *J* = 2.8 Hz, 2H), 7.15 (d, *J* = 8.5 Hz, 1H), 7.12 (s, 1H), 6.86 (s, 1H), 6.70 (d, *J* = 8.6 Hz, 2H), 4.24 (q, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.40 (s, 2H), 2.30 (s, 3H), 1.32 (t, *J* = 7.1, 3.4 Hz, 3H), 1.29 – 1.24 (m, *J* = 15.0, 7.4 Hz, 2H), 1.09 (d, 6H), 1.04 (d, *J* = 7.3, 2.9 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 155.9, 152.7, 148.2, 145.1, 140.9, 140.2, 136.3, 131.4, 131.2, 130.4, 129.9, 129.9, 125.8, 119.9, 119.5, 116.7, 115.2, 112.5, 102.4, 77.5, 77.2, 76.9, 60.4, 56.5, 56.3, 20.6, 18.8, 17.7, 17.5, 14.5, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{34}H_{41}NNaO_5Si$ 594.2646: found: 594.2647.

4c. butyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90: 10)

Yield: 71% (*para:others* = 10:1)

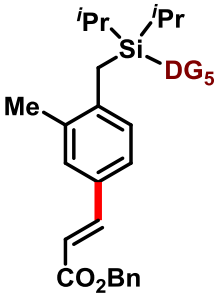
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 16 Hz 1H), 7.33 – 7.30 (m, 2H), 7.28 – 7.26 (m, 2H), 7.16 – 7.14 (m, 1H), 7.12 (s, 1H), 6.86 (s, 1H), 6.71 – 6.68 (m, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.18 (t, *J* = 7.5 Hz 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.40 (s, 2H), 2.30 (s, 3H), 1.70 – 1.64 (m, 2H), 1.47 – 1.39 (m, 2H), 1.30 – 1.24 (m, 2H), 1.09 (d, *J* = 5 Hz, 6H), 1.04 – 1.02 (d, *J* = 10 Hz, 6H), 0.95 (t, *J* = 7.4, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 155.8, 152.7, 148.2, 145.0, 140.9, 140.2, 136.3, 131.4, 131.2, 130.4, 129.9, 129.9, 125.8, 119.9, 119.5, 116.7, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 64.4, 56.5, 56.3, 31.0, 20.6, 19.4, 18.8, 17.7, 17.5, 13.9, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{36}H_{45}NNaO_5Si$ 622.2959: found: 622.2959.

4d. benzyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (87:13)

Yield: 65% (*para:others* = 14:1)

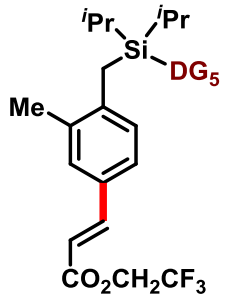
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.65 (d, *J* = 16.0 Hz, 1H), 7.43 – 7.27 (m, 9H), 7.15 (d, *J* = 10.0 Hz, 1H), 7.11 (s, 1H), 6.86 (s, 1H), 6.69 (d, *J* = 10.0 Hz, 2H), 6.42 (d, *J* = 16.0 Hz, 1H), 5.23 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.40 (s, 2H), 2.30 (s, 3H), 1.29 – 1.24 (m, 2H), 1.09 (d, *J* = 7.5 Hz, 6H), 1.03 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 155.8, 152.7, 148.2, 145.7, 141.1, 140.2, 136.4, 136.3, 131.4, 131.1, 130.4, 129.9, 129.9, 128.8, 128.4, 128.3, 125.9, 119.9, 119.5, 116.2, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 66.4, 56.5, 56.3, 20.6, 18.8, 17.7, 17.5, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{39}H_{43}NNaO_5Si$ 656.2803: found: 656.2797.

4e. 2,2,2-trifluoroethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)-3-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90: 10)

Yield: 58% (*para:others* = 10:1)

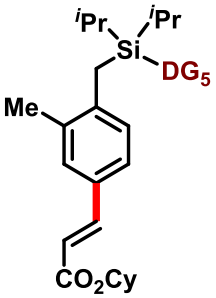
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 15.0 Hz, 1H), 7.33 – 7.28 (m, 4H), 7.17 (d, *J* = 10.0 Hz,1H), 7.12 (s, 1H), 6.86 (s, 1H), 6.71 – 6.69 (d, *J* = 10.0 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 4.56 (qd, *J* = 8.5, 2.7 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.41 (s, 2H), 2.31 (s, 3H), 1.30 – 1.25 (m, 2H), 1.09 (m, 6H), 1.04 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 155.9, 152.7, 148.2, 147.4, 142.9, 140.1, 131.6, 130.5, 130.1, 129.6, 128.7, 120.1, 120.1, 119.5, 115.2, 114.4, 112.5, 102.3, 77.5, 77.2, 76.9, 60.9, 60.6, 60.3, 60.0, 56.4, 56.3, 21.8, 17.6, 17.5, 13.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{34}H_{38}F_3NNaO_5Si$ 648.2471: found: 648.2475.

4f. cyclohexyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90: 10)

Yield: 69% (*para:others* = 15:1)

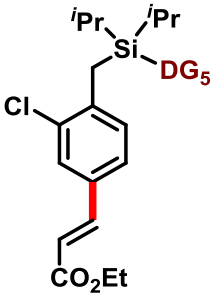
Physical appearance: Colourless viscous compound

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, , *J* = 16.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 4.7 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 2H), 6.86 (s, 1H), 6.69 (d, *J* = 8.0 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.90 – 4.83 (m, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 2.39 (s, 2H), 2.30 (s, 3H), 1.94 – 1.87 (m, 2H), 1.79 – 1.72 (m, 2H), 1.50 – 1.37 (m, 4H), 1.30 – 1.23 (m, 4H), 1.08 (d, *J* = 8.0 Hz, 6H), 1.03 (d, *J* = 8.0 Hz,6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 155.9, 152.7, 148.2, 144.7, 140.8, 140.2, 136.3, 131.4, 131.3, 130.3, 129.9, 129.9, 125.8, 119.9, 119.5, 117.3, 115.2, 112.5, 102.3, 77.6, 77.2, 76.9, 72.7, 56.5, 56.4, 31.9, 25.7, 24.0, 20.6, 18.8, 17.7, 17.5, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{47}NNaO_5Si$ 648.3116: found: 648.3117.

4g. ethyl (*E*)-3-(3-chloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure Ain 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (86:14)

Yield: 64% (*para:others* = 3:1)

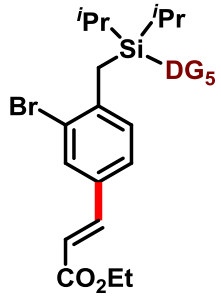
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 16.0, 8.1 Hz, 1H), 7.48 (s, 1H), 7.40 – 7.35 (m, 2H), 7.34 – 7.27 (m, 1H), 7.21 (s, 1H), 7.13 (s, 1H), 6.91 – 6.82 (m, 3H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 6.6, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.58 (s, 2H), 1.35 – 1.28 (m, 5H), 1.10 – 1.03 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 155.9, 152.7, 148.2, 143.3, 140.2, 140.0, 133.9, 132.8, 131.5, 131.1, 130.1, 129.1, 126.3, 120.0, 119.9, 118.4, 115.2, 112.5, 102.4, 77.5, 77.2, 76.9, 60.7, 56.5, 56.4, 19.2, 17.6, 17.5, 14.5, 13.7.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{38}ClNNaO_5Si$614.2105;found: 614.2109

4h. ethyl (*E*)-3-(3-bromo-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (87:13)

Yield: 72% (*para:others* = 8:1)

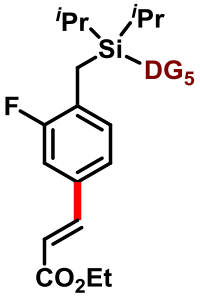
Physical appearance: Colourless viscous compound

^{1}H NMR(500 MHz, $CDCl_3$) δ 7.64 (d, J = 16.0 Hz, 1H), 7.41 – 7.37 (m, 4H), 7.16 – 7.12 (m, 3H), 6.89 (s, 1H), 6.86 (d, J = 8.6 Hz, 2H), 6.36 (d, J = 16.0 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.43 (s, 2H), 1.32 (t, J = 7.5 Hz, 3H), 1.24 – 1.20 (m, 2H), 1.07 – 1.03 (m, 12H).

^{13}C NMR(126 MHz, $CDCl_3$) δ 167.5, 156.1, 152.7, 148.2, 144.9, 141.9, 140.2, 131.6, 131.0, 130.1, 129.5, 128.4, 120.2, 119.5, 116.9, 115.2, 112.5, 102.3, 60.6, 56.5, 56.4, 21.6, 17.6, 17.6, 14.6, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{38}BrNNaO_5Si$: 658.1600 found658.1559.

4i. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-fluorophenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (87:13)

Yield: 64% (*para:others* = 5:1)

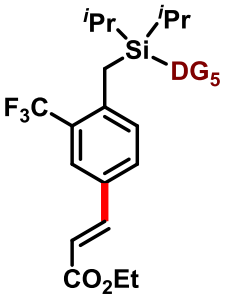
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 16.0 Hz, 1H), 7.40 – 7.36 (m, 2H), 7.32 – 7.24 (m, 1H), 7.20 – 7.11 (m, 3H), 6.92 – 6.83 (m, 3H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.25 (q, , *J* = 6.6 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.40 (s, 2H), 1.32 (t, *J* = 5.0 Hz, 3H), 1.27 – 1.21 (m, 2H), 1.08 – 1.03 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 155.9, 152.7, 148.2, 143.9, 143.7, 140.1, 131.5, 131.5, 130.1, 130.1, 124.2, 120.1, 119.5, 118.3, 115.2, 114.4, 114.2, 112.5, 102.3, 77.5, 77.2, 76.9, 60.7, 56.5, 56.3, 17.5, 17.4, 14.5, 14.0, 13.4.

HRMS (*m/z*): $[M + Na]^+$ calculated for C33H38FNNaO5Si598.2395; found: 598.2393.

4j. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-(trifluoromethyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (86:14)

Yield: 69% (*para:others* = 7:1)

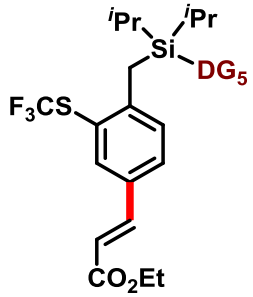
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (s, 1H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.42 – 7.37 (m, 3H), 7.13 (s, 1H), 6.90 – 6.83 (m, 3H), 6.42 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 14.3, 7.2 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.60 (s, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.29 – 1.26 (m, 2H), 1.07 – 1.04 (m, 6H), 0.99 – 0.96 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 155.8, 152.7, 148.2, 143.2, 141.0, 140.1, 132.3, 131.6, 131.3, 130.5, 130.2, 130.1, 120.0, 119.9, 119.5, 118.8, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 60.8, 56.5, 56.3, 18.5, 17.6, 17.3, 14.5, 13.4.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{34}H_{38}F_3NNaO_5Si$ 648.2364: found: 648.2368.

4k. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)-methyl)-3-((trifluoromethyl)thio)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 72% (*para:others* = 17:1)

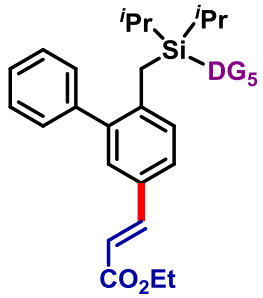
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.61 (d, J = 10.1 Hz, 1H)), 7.51 (dd, J = 8.1, 1.9 Hz, 1H), 7.34 (m, 3H), 7.12 (s, 1H), 6.87 (s, 1H), 6.76 – 6.73 (m, 2H), 6.40 (d, J = 10.1 Hz, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.79 (s, 2H), 1.33 (t, J = 7.1 Hz, 3H), 1.27 (dd, J = 12.7, 5.2 Hz, 2H), 1.08 (d, J = 7.4 Hz, 6H), 1.05 (d,J = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 155.7, 152.7, 148.2, 147.9, 143.1, 140.0, 138.1, 132.5, 131.6, 131.1, 130.2, 130.1, 119.8, 118.7, 115.2, 112.5, 102.3, 60.8, 56.5, 56.3, 20.5, 17.7, 17.5, 14.5, 13.6.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{34}H_{39}F_3NOSSi$: 658.2265: found: 658.2266.

4l. ethyl (*E*)-3-(6-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-[1,1'-biphenyl]-3-yl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 68% (*para:others* = 8:1)

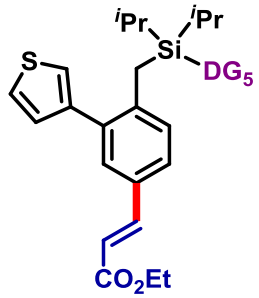
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, 1H), 7.39 – 7.34 (m, *J* = 13.6, 6.5 Hz, 3H), 7.33 – 7.26 (m, *J* = 19.8, 5.7 Hz, 6H), 7.21 (s, 1H), 7.08 (s, 1H), 6.83 (s, 1H), 6.83 (s, 1H), 6.59 (d, *J* = 8.2 Hz, 2H), 6.35 (d, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 2.47 (s, 2H), 1.27 (t, *J* = 7.0 Hz, 3H), 1.05 – 0.99 (m, *J* = 14.4, 7.2 Hz, 2H), 0.84 – 0.78 (m, *J* = 11.6, 7.4 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 155.9, 152.7, 148.2, 144.7, 142.0, 141.5, 140.2, 139.6, 131.3, 131.2, 130.6, 130.5, 129.9, 129.7, 128.6, 127.3, 126.9, 119.9, 119.5, 117.3, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 60.5, 56.5, 56.3, 18.4, 17.4, 17.3, 14.5, 13.2.

HRMS (*m/z*): $[M + H]^+$ calculated for $C_{39}H_{44}NO_5Si$: 634.2989; found: 634.2980.

4m. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-(thiophen-3-yl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 71% (*para:others* = 10:1)

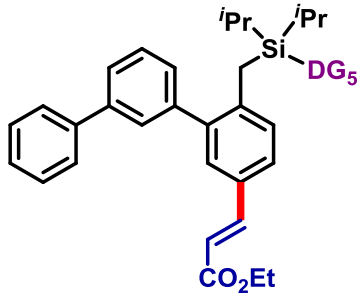
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 15.7 Hz, 1H), 7.34 – 7.27 (m, 5H), 7.18 – 7.16 (m, *J* = 4.6, 1.8 Hz, 2H), 7.12 (s, 1H), 7.00 (s, 1H), 6.88 (s, 1H), 6.63 (d, *J* = 8.5 Hz, 2H), 6.11 (d, *J* = 15.7 Hz, 1H), 4.22 (q, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.39 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.93 (d, 6H), 0.90 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 155.9, 152.7, 148.1, 140.6, 140.2, 137.9, 136.5, 136.3, 133.3, 132.5, 131.3, 130.8, 130.2, 129.9, 129.4, 128.7, 124.9, 119.9, 119.5, 117.4, 115.2, 112.5, 102.3, 60.8, 56.5, 56.3, 18.4, 17.5, 17.4, 14.5, 13.1.

HRMS (*m/z*): $[M + H]^+$ calculated for $C_{37}H_{41}NO_5SSi$: 639.2475; found: 639.2478.

4n. ethyl (*E*)-3-(6-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-[1,1':3',1''-terphenyl]-3-yl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 64% (*para:others* = 5:1)

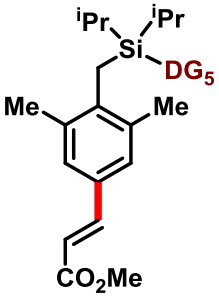
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, 1H), 7.59 – 7.54 (m, *J* = 9.8, 6.8, 1.4 Hz, 4H), 7.49 (t, *J* = 7.1 Hz, 1H), 7.44 – 7.40 (m, *J* = 12.8, 5.5 Hz, 4H), 7.35 – 7.31 (m, 2H), 7.29 (d, 3H), 7.13 (s, 1H), 6.84 (s, 1H), 6.63 (d, 2H), 6.41 (d, 1H), 4.24 (q, 2H), 3.94 (s, 3H), 3.93 (s, 3H), 0.88 (d, *J* = 7.4 Hz, 6H), 0.85 (d, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 155.8, 152.7, 148.1, 144.6, 142.0, 141.9, 141.6, 141.1, 140.1, 139.7, 131.3, 131.3, 130.6, 130.4, 129.9, 128.9, 128.6, 128.6, 127.7, 127.5, 127.4, 127.1, 126.1, 119.9, 119.5, 117.4, 115.2, 112.5, 102.2, 60.5, 56.5, 56.3, 18.6, 17.4, 17.3, 14.5, 13.2.

HRMS (*m/z*): $[M + H]^+$ calculated for $C_{45}H_{48}NO_5Si$: 710.3302 found: 710.3305.

6a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 70% (*para:others* = >20:1)

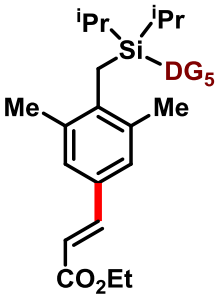
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 16.0 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.14 (s, 2H), 7.11 (s, 1H), 6.85 (s, 1H), 6.74 – 6.70 (m, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 3H), 3.91 (s, 3H), 3.77 (s, 3H), 2.42 (s, 2H), 2.34 (s, 6H), 1.29 – 1.21 (m, 3H), 1.09 (d, *J* = 7.4 Hz, 6H), 1.02 – 0.95 (m, 7H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.0, 155.8, 152.7, 148.1, 145.5, 140.3, 140.1, 136.2, 131.3, 130.5, 129.9, 128.1, 119.7, 119.5, 115.9, 115.2, 112.4, 102.3, 77.5, 77.2, 76.9, 56.4, 56.3, 51.7, 21.5, 17.6, 17.4, 16.6, 14.3.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{34}H_{41}NNaO_5Si$ 594.2646: found: 594.2642.

6b. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 72% (*para:others* = >20:1)

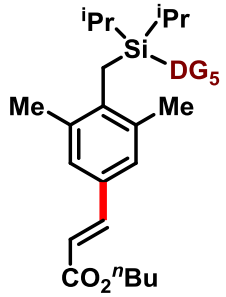
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.31 (d, 2H), 7.15 (s, 2H), 7.12 (s, 1H), 6.86 (s, 1H), 6.72 (d, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.42 (s, 2H), 2.34 (s, 6H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.24 – 1.20 (m, *J* = 9.3, 5.0 Hz, 2H), 1.09 (d, *J* = 7.0 Hz, 6H), 0.97 (d, *J* = 3.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 155.8, 152.7, 148.1, 145.2, 140.2, 140.1, 136.2, 131.3, 130.6, 129.9, 128.1, 119.8, 119.5, 116.4, 115.2, 112.4, 102.3, 77.5, 77.2, 76.9, 60.4, 56.4, 56.3, 21.6, 17.7, 17.4, 16.6, 14.5, 14.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{35}H_{43}NNaO_5Si$ 608.2803: found: 608.2804.

6c. butyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 65% (*para:others* = >20:1)

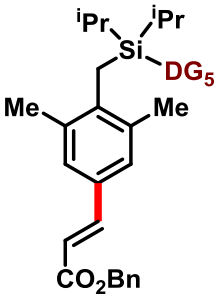
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 16.0 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.15 (s, 2H), 7.11 (s, 1H), 6.85 (s, 1H), 6.74 – 6.70 (m, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.17 (t, *J* = 6.7 Hz, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.42 (s, 2H), 2.34 (s, 6H), 1.69 – 1.64 (m, 2H), 1.46 – 1.38 (m, 2H), 1.25 (td, *J* = 7.3, 3.3 Hz, 2H), 1.09 (d, *J* = 3.1 Hz, 6H), 0.96 (dd, *J* = 7.4, 3.8 Hz, 9H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 155.8, 152.7, 148.1, 145.1, 140.2, 140.1, 136.2, 131.3, 130.6, 129.9, 128.0, 119.8, 119.5, 116.4, 115.2, 112.4, 102.3, 77.5, 77.2, 76.9, 64.4, 56.4, 56.3, 30.9, 21.5, 19.4, 17.6, 17.4, 16.6, 14.2, 13.9.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{37}H_{47}NNaO_5Si$ 636.3116: found: 636.3110.

6d. benzyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 81% (*para:others* = >15:1)

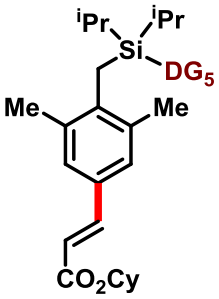
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.42 – 7.34 (m, 5H), 7.34 – 7.30 (m, 3H), 7.15 (s, 2H), 7.11 (s, 1H), 6.86 (s, 1H), 6.73 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.23 (s, 2H), 3.94 (s, 3H), 3.91 (s, 3H), 2.43 (s, 2H), 2.34 (s, 6H), 1.26 – 1.21 (m, 2H), 1.09 (d, *J* = 7.4 Hz, 6H), 0.97 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 155.8, 152.7, 148.2, 145.8, 140.4, 140.1, 136.5, 136.3, 131.3, 130.5, 129.9, 128.7, 128.3, 128.1, 119.8, 119.5, 116.0, 115.2, 112.5, 102.3, 66.3, 56.5, 56.3, 21.6, 17.7, 17.4, 16.7, 14.3.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{40}H_{45}NNaO_5Si$ 670.2959: found: 670.2945.

6e. cyclohexyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 67% (*para:others* = >20:1)

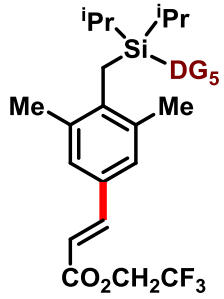
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.15 (s, 2H), 7.11 (s, 1H), 6.85 (s, 1H), 6.73 – 6.71 (m, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 4.88 – 4.83 (m, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 2.42 (s, 2H), 2.33 (s, 6H), 1.89 (dd, *J* = 8.3, 4.2 Hz, 2H), 1.75 (dd, *J* = 8.5, 3.6 Hz, 2H), 1.55 (dd, *J* = 8.9, 3.7 Hz, 1H), 1.50 – 1.45 (m, 2H), 1.44 – 1.35 (m, 3H), 1.25 – 1.21 (m, 2H), 1.08 (d, *J* = 7.4 Hz, 6H), 0.96 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 155.8, 152.6, 148.1, 144.8, 140.1, 140.0, 136.1, 131.3, 130.7, 129.9, 127.9, 119.7, 119.4, 116.9, 115.1, 112.4, 102.2, 77.5, 77.2, 76.9, 72.5, 56.4, 56.3, 31.9, 25.6, 23.9, 21.5, 17.6, 17.3, 16.6, 14.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{39}H_{49}NNaO_5Si$ 662.3272: found: 662.3276.

6f. 2,2,2-trifluoroethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)di-isopropyl-silyl)methyl)-3,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 73% (*para:others* = >20:1)

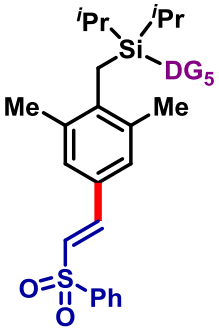
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 16.0 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.17 (s, 2H), 7.12 (s, 1H), 6.86 (s, 1H), 6.74 – 6.71 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.56 (q, *J* = 8.5 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.44 (s, 2H), 2.35 (s, 6H), 1.25 (dd, *J* = 13.7, 6.2 Hz, 2H), 1.10 (d, *J* = 7.4 Hz, 6H), 0.98 (dk, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 155.6, 152.7, 148.2, 147.8, 141.2, 140.1, 136.4, 131.4, 130.1, 129.9, 128.3, 123.4 (q, *J* = 278.4 Hz), 119.7, 119.5, 115.2, 113.9, 112.4, 102.3, 77.5, 77.2, 76.9, 60.4 (q, *J* = 36.5 Hz), 56.4, 56.3, 21.5, 17.6, 17.4, 16.8, 14.3.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{35}H_{40}F_3NNaO_5Si$ 662.2520: found: 662.2524.

6g. (*E*)-4'-(((2,6-dimethyl-4-(2-(phenylsulfonyl)vinyl)benzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (80:20)

Yield: 54% (*para:others* = >20:1)

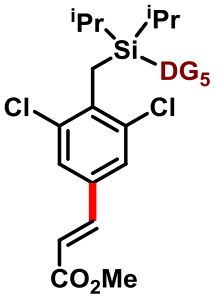
Physical appearance: Colourless viscous compound

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.60 – 7.54 (m, 2H), 7.54 – 7.48 (m, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.12 (s, 1H), 7.11 (s, 2H), 6.86 (s, 1H), 6.86 (s, 1H), 6.77 (d, J = 16 Hz, 1H), 6.72 (d, J = 12.0 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.42 (s, 2H), 2.32 (s, 6H), 1.25 – 1.20 (m, 2H), 1.07 (d, J = 7.3 Hz, 6H), 0.95 (d, J = 7.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.7, 152.7, 148.2, 143.2, 141.6, 141.4, 140.1, 136.5, 133.3, 131.4, 129.9, 129.4, 128.5, 128.5, 127.7, 125.2, 119.7, 119.5, 115.2, 112.45, 102.3, 56.5, 56.3, 21.5, 17.6, 17.4, 16.9, 14.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{43}NNaO_5SSi$676.2529; found:676.2530.

6h. methyl (*E*)-3-(3,5-dichloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 59% (*para:others* = >20:1)

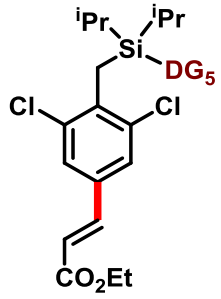
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47 (d, *J* = 16.0 Hz, 1H), 7.37 (s, 2H), 7.31 (d, *J* = 10.0 Hz, 2H), 7.12 (s, 1H), 6.85 (s, 1H), 6.79 (d, *J* = 10.0 Hz, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 3.94 (s, 3H), 3.92 (s, 3H), 3.77 (s, 2H), 2.77 (s, 2H), 1.41 – 1.35 (m, 2H), 1.13 – 1.10 (m, 6H), 1.09 – 1.06 (m, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.1, 155.8, 152.7, 148.1, 142.2, 140.2, 139.1, 134.9, 132.9, 131.2, 129.8, 127.4, 119.7, 119.5, 119.1, 115.2, 112.4, 102.3, 77.5, 77.2, 76.9, 56.5, 56.3, 52.0, 18.7, 17.6, 17.5, 14.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{32}H_{35Cl2}NNaO_5Si$ 634.1550: found: 634.1555.

6i. ethyl (*E*)-3-(3,5-dichloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)-phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 62% (*para:others* = >20:1)

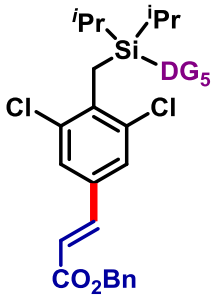
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, 1H), 7.38 (s, 2H), 7.31 (d, 1H), 7.12 (s, 1H), 6.85 (s, 1H), 6.81 – 6.79 (m, 2H), 6.34 (d, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.77 (s, 2H), 1.38 (dd, *J* = 14.9, 7.4 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.12 (d, 6H), 1.07 (d, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 155.9, 152.7, 148.1, 141.9, 140.2, 139.0, 134.9, 132.9, 131.2, 129.9, 127.4, 119.8, 119.7, 119.5, 115.2, 112.4, 102.3, 77.5, 77.2, 76.9, 60.9, 56.5, 56.3, 18.7, 17.6, 17.5, 14.5, 14.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{37}Cl_2NNaO_5Si$ 648.1710: found: 648.1716.

6j. benzyl (*E*)-3-(3,5-dichloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)di-isopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 71% (*para:others* = >20:1)

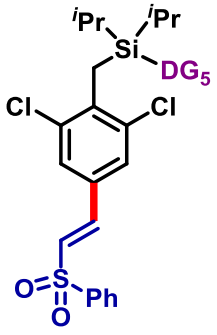
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, 1H), 7.40 – 7.34 (m, 7H), 7.33 – 7.30 (m, 2H), 7.10 (s, 1H), 6.85 (s, 1H), 6.79 (d, 2H), 6.39 (d, *J* = 15.8 Hz, 1H), 5.22 (s, 1H), 3.93 (s, 3H), 3.90 (s, 3H), 2.77 (s, 2H), 1.38 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.11 (d, *J* = 7.5 Hz, 6H), 1.07 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 155.7, 152.7, 148.1, 142.4, 140.1, 139.1, 136.0, 134.9, 132.8, 131.2, 129.8, 128.8, 128.4, 128.3, 127.4, 119.7, 119.5, 119.2, 115.2, 112.4, 102.3, 66.6, 56.4, 56.3, 18.6, 17.6, 17.4, 14.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{39}Cl_2NNaO_5Si$ 710.1867; found: 710.1860.

6k. (*E*)-4'-(((2,6-dichloro-4-(2-(phenylsulfonyl)vinyl)benzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphen-yl]-2-carbonitrile



The compound was synthesized following the general procedure Ain 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (80:20)

Yield: 55% (*para:others* = >20:1)

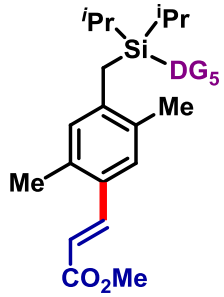
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 15.4 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 2H), 7.26 (s, 1H), 7.13 (s, 1H), 6.85 (s, 1H), 6.81 (d, *J* = 15.4 Hz, 1H), 6.78 (d, *J* = 8.6 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 2.77 (s, 2H), 1.37 (dt, *J* = 14.8, 7.5 Hz, 2H), 1.11 (d, *J* = 7.4 Hz, 6H), 1.06 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 155.7, 152.7, 148.2, 140.5, 140.3, 140.1, 139.7, 135.1, 133.7, 131.3, 130.7, 129.8, 129.6, 128.7, 127.9, 127.9, 119.7, 119.5, 115.3, 112.4, 102.3, 56.5, 56.3, 18.9, 17.6, 17.5, 14.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{36}H_{37}Cl_2NNaO_5SSi$ 716.1436; found: 716.1430.

6l. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 71% (*para:others* = >20:1)

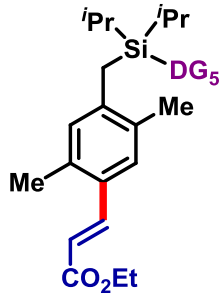
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 15.9 Hz, 1H), 7.32 (d, 2H), 7.30 (s, 1H), 7.12 (s, 1H), 6.95 (s, 1H), 6.86 (s, 1H), 6.72 (d, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 3.78 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H), 1.29 – 1.25 (m, 2H), 1.09 (d, 6H), 1.04 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 168.1, 155.9, 152.7, 148.1, 142.8, 140.6, 140.1, 135.3, 133.7, 131.9, 131.3, 129.9, 129.7, 128.4, 119.9, 119.5, 116.9, 115.2, 112.5, 102.3, 56.5, 56.3, 51.7, 20.2, 19.5, 18.5, 17.7, 17.5, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{35}H_{43}NNaO_5Si$ 608.2803; found: 608.2805.

6m. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2,5-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 70% (*para:others* = >20:1)

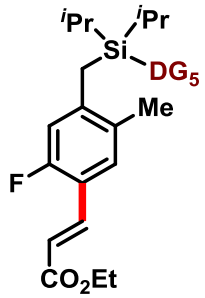
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 15.9 Hz, 1H), 7.34 – 7.30 (m, *J* = 8.6, 1.9 Hz, 3H), 7.12 (s, 1H), 6.95 (s, 1H), 6.86 (s, 1H), 6.72 (d, 2H), 6.30 (d, *J* = 15.9 Hz, 1H), 4.24 (q, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 – 1.23 (m, *J* = 7.4 Hz, 2H), 1.08 (d, *J* = 7.5 Hz, 6H), 1.03 (d, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.7, 155.9, 152.7, 148.1, 142.5, 140.5, 140.1, 135.2, 133.6, 131.9, 131.3, 129.9, 129.8, 128.4, 119.9, 119.5, 117.4, 115.2, 112.4, 102.3, 60.5, 56.4, 56.3, 20.2, 19.5, 18.4, 17.7, 17.5, 14.5, 13.5.

HRMS (*m/z*): $[M + H]^+$ calculated $C_{34}H_{41}NNaO_5Si$ 594.2646; found: 594.2645.

6n. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2-fluoro-5-methylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (86:14)

Yield: 65% (*para:others* = >20:1)

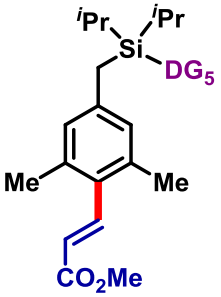
Physical appearance: White solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.2 Hz, 1H), 7.33 (d, *J* = 10.0 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 6.89 – 6.84 (m, 2H), 6.74 – 6.71 (d, *J* = 10.0 Hz, 2H), 6.45 (d, *J* = 16.2, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 3.92 (s, 3H), 2.36 (s, 2H), 2.25 (s, 3H), 1.34 – 1.26 (m, 5H), 1.09 (d, *J* = 5.0 Hz, 6H), 1.04 (d, *J* = 5.0 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 160.9, 158.9, 155.7, 152.7, 148.2, 143.0, 142.9, 140.1, 137.8, 131.9, 131.9, 131.6, 130.6, 130.6, 130.0, 119.8, 119.5, 119.2, 119.2, 118.8, 118.7, 116.5, 116.3, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 60.6, 56.4, 56.3, 19.8, 19.1, 17.7, 17.5, 14.5, 13.5.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{43}NNaO_5SSi$676.2529; found:676.2530.

6o. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)methyl)-2,6-dimethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 56% (*para:others* = >15:1)

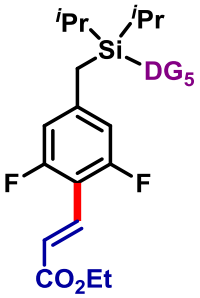
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 16.4 Hz, 1H), 7.39 (d, 2H), 7.13 (s, 1H), 6.89 (s, 1H), 6.87 – 6.85 (m, 2H), 6.81 (s, 2H), 6.05 (d, *J* = 16.4 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.80 (s, 3H), 2.32 (s, 2H), 2.29 (s, 6H), 1.25 – 1.18 (m, *J* = 14.3, 7.3 Hz, 2H), 1.07 (d, *J* = 3.8 Hz, 6H), 1.05 (d, *J* = 3.8 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 156.2, 152.7, 148.2, 143.6, 140.1, 139.4, 137.1, 131.4, 130.1, 130.0, 129.3, 122.4, 120.2, 119.5, 115.2, 112.5, 102.3, 56.5, 56.3, 51.8, 21.4, 20.9, 17.7, 17.6, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{35}H_{43}NNaO_5Si$608.2803; found: 608.2808.

6p. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)methyl)-2,6-difluorophenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

Yield: 63% (*para:others* = >20:1)

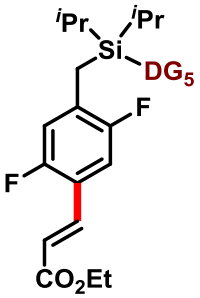
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 16.4 Hz, 1H), 7.41 (d, 2H), 7.13 (s, 1H), 6.90 (s, 1H), 6.88 (d, 2H), 6.68 (d, *J* = 10.0 Hz, 2H), 6.64 (d, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 2.39 (s, 2H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 – 1.22 (m, 2H), 1.07 (d, *J* = 2.1 Hz, 6H), 1.06 (d, *J* = 2.1 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 162.7, 162.6, 160.7, 160.6, 155.7, 152.7, 148.2, 144.7, 144.7, 144.6, 139.9, 131.9, 131.1, 130.2, 122.9, 122.8, 122.8, 120.0, 119.4, 115.2, 112.5, 112.4, 112.2, 108.9, 108.9, 108.8, 102.3, 60.7, 56.4, 56.3, 22.1, 17.6, 17.5, 14.5, 13.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{37}F_2NNaO_5Si$ 616.2301; found: 617.2316.

6q. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsil-yl)methyl)-2,5-difluorophenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 61% (*para:others* = >20:1)

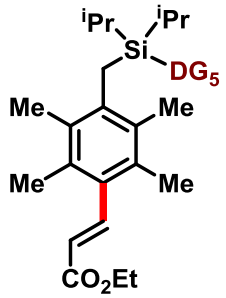
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 16.2 Hz, 1H), 7.39 (d, *J* = 10.0 Hz, 2H), 7.16 – 7.11 (m, 2H), 6.92 – 6.84 (m, 4H), 6.42 (d, *J* = 16.2 Hz, 1H), 4.25 (q, *J* = 6.6 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.37 (s, 2H), 1.32(t, *J* = 7.5 Hz, 2H), 1.26 (m, 3H), 1.07 (d, *J* = 3.2 Hz, 6H), 1.06 (d, *J* = 3.2 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 157.8 (d, *J* = 86.94), 155.9 (d, *J* = 79.38), 155.7, 152.7, 148.2, 140.1, 136.4, 131.7,131.1 (dd, *J* = 21.42, *J* = 8.82), 131.1, 131.0, 130.9 130.1, 120.5 (d, *J* = 6.3), 119.9, 119.4, 117.9 (dd, *J* = 23.94, *J* = 5.04) 115.2, 114.3 (dd, *J* = 25.83, *J* =5.04), 112.5, 102.3, 60.8, 56.5, 56.3, 17.5, 17.4, 14.5, 14.4, 13.4.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{37}F_2NNaO_5Si$ 616.2301: found: 616.2303.

6r. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2,3,5,6-tetramethylphenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (88:12)

Yield: 61%

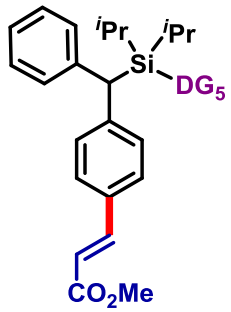
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.3 Hz, 1H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.12 (s, 1H), 6.85 (s, 1H), 6.66 (d, *J* = 8.6 Hz, 2H), 5.82 (d, *J* = 16.3 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 2.52 (s, 2H), 2.24 (s, 6H), 2.17 (s, 6H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.22 (m, *J* = 12.5, 4.9 Hz, 2H), 1.10 (d, *J* = 7.4 Hz, 6H), 0.99 (d, *J* = 7.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.0, 155.9, 152.7, 148.1, 146.7, 140.2, 136.8, 132.0, 132.0, 131.8, 131.1, 129.8, 124.5, 119.7, 119.5, 115.2, 112.5, 102.3, 77.5, 77.2, 76.9, 60.6, 56.5, 56.3, 18.4, 17.7, 17.5, 17.1, 14.5, 14.2.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{37}H_{47}NNaO_5Si$ 636.3121: found: 636.3126.

8a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)(phenyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 78% (*para:others* = 10:1) (mono:di = 5:1)

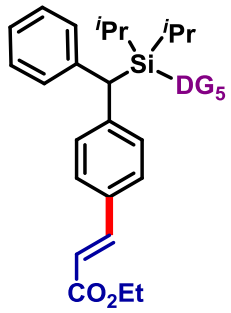
Physical appearance: Colourless viscous compound

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.54 – 7.42 (m, 6H), 7.38 (d, *J* = 8 Hz, 2H), 7.29 (t, *J* = 8 Hz, 2H), 7.18 (t, *J* = 8 Hz, 1H), 7.14 (s, 1H), 6.89 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.82 (s, 1H), 3.79 (s, 3H), 1.32 – 1.27 (m, 2H), 0.95 – 0.90 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 155.9, 152.8, 148.3, 145.2, 144.9, 141.4, 140.1, 132.0, 131.6, 130.1, 130.0, 129.7, 128.8, 128.5, 126.1, 120.0, 119.5, 117.0, 115.2, 112.5, 102.4, 56.5, 56.4, 51.8, 43.0, 18.1, 18.1, 17.8, 13.9.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{38}H_{41}NNaO_5Si$: 642.2646: found: 642.2649.

8b. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)(phenyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 71% (*para:others* = 10:1) (mono:di = 3:1)

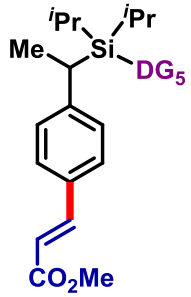
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.52 – 7.47 (m, 4H), 7.44 (d, *J* = 8.3 Hz, 2H), 7.38 (d, 5 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.14 (s, 1H), 6.89 (s, 1H), 6.86 (d, *J* = 10.0 Hz, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 4.24 (q, *J* = 6.6 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.83 (s, 1H), 1.32 (t, *J* = 7.5 Hz, 3H), 1.30 – 1.28 (m, 2H), 0.96 – 0.91 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.4, 155.9, 152.8, 148.3, 145.1, 144.6, 141.5, 140.2, 132.1, 131.7, 130.1, 130.0, 129.7, 128.8, 128.5, 126.1, 120.0, 119.5, 117.5, 115.3, 112.6, 102.4, 60.6, 56.5, 56.4, 43.1, 18.1, 18.1, 17.8, 17.8, 14.5, 14.3, 13.9.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{39}H_{43}NNaO_5Si$: 656.2802: found: 642.2805.

8c. methyl (*E*)-3-(4-(1-(((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)ethyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:1)

Yield: 72% (*para:others* = 9:1)

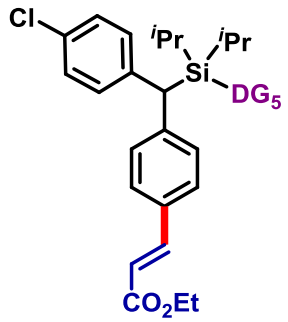
Physical appearance: Colorless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.13 (s, 1H), 6.89 (s, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.39 (d, *J* = 16.0 Hz, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.79 (s, 3H), 2.66 (q, *J* = 5.0 Hz, 1H), 1.54 (d, *J* = 10.0 Hz, 3H), 1.34 (dt, *J* = 14.9, 7.5 Hz, 1H), 1.20 (dt, *J* = 11.5, 7.4 Hz, 1H), 1.07 (dd, *J* = 7.5, 2.5 Hz, 6H), 1.01 (d, *J* = 7.4 Hz, 3H), 0.96 (d, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 156.2, 152.7, 148.2, 145.2, 140.2, 131.4, 131.4, 130.1, 128.8, 128.3, 120.1, 119.5, 116.6, 115.2, 112.5, 102.4, 56.5, 56.4, 51.8, 28.1, 18.2, 18.1, 17.8, 17.8, 16.2, 13.2, 13.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{33}H_{39}NNaO_5Si$: 580.2489: found: 580.2495.

8d. methyl (*E*)-3-(4-((4-chlorophenyl)(((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (84:16)

Yield: 86% (*para:others* = 9:1)

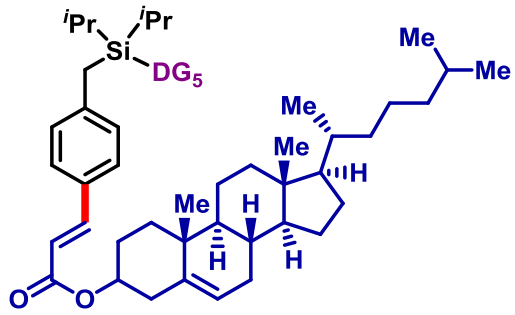
Physical appearance: Colourless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 16.0 Hz, 1H), 7.51 – 7.47 (m, 1H), 7.46 (d, *J* = 4.2 Hz, 2H), 7.44 – 7.38 (m, 4H), 7.27 (s, 1H), 7.25 (s, 1H), 7.14 (s, 1H), 6.89 (s, 1H), 6.86 (d, *J* = 10.0 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 6.6 Hz, 2H), 3.96 (s, 3H), 3.93 (s, 3H), 3.78 (s, 1H), 1.32 (t, *J* = 7.5 Hz, 3H), 1.29 – 1.26 (m, 2H), 0.96 – 0.90 (m, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.3, 155.7, 152.7, 148.3, 144.8, 144.5, 140.2, 140.0, 132.3, 131.9, 131.8, 130.9, 130.8, 130.2, 129.9, 128.9, 128.6, 125.7, 119.9, 119.5, 117.7, 115.2, 112.5, 102.4, 60.6, 56.5, 56.4, 42.2, 18.1, 18.0, 17.8, 17.8, 14.5, 13.9, 13.8.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{39}H_{42}ClNNaO_5Si$: 690.2413 found: 690.2415.

8e. (*E*)-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 3-(4-(((2'-cyanobiphenyl-4-yloxy)diisopropylsilyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 68%(*para:others* = 10:1)

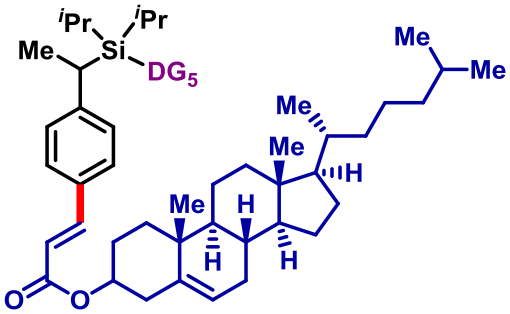
Physical appearance: Colorless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 15.9 Hz, 1H), 7.40 – 7.36 (m, 4H), 7.15 – 7.12 (m, 3H), 6.89 (s, 1H), 6.86 (d, *J* = 8.6 Hz, 2H), 6.35 (d, *J* = 16.0 Hz, 1H), 5.40 (d, *J* = 4.0 Hz, 1H), 4.73 (s, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 2.42 (s, 2H), 2.39 (d, *J* = 7.3 Hz, 2H), 2.04 – 1.78 (m, 6H), 1.55 – 1.42 (m, 6H), 1.24 – 1.08 (m, 10H), 1.08 – 1.03 (m, *J* = 9.4, 6.7 Hz, 17H), 1.02 – 0.97 (m, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88 – 0.84 (m, 7H), 0.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 156.1, 152.8, 148.2, 144.7, 141.9, 140.2, 139.9, 131.6, 131.1, 130.1, 129.5, 128.4, 122.9, 120.2, 119.5, 117.4, 115.2, 112.5, 102.4, 74.1, 56.9, 56.5, 56.4, 56.4, 50.3, 42.5, 39.9, 39.7, 38.5, 37.3, 36.9, 36.4, 36.0, 32.1, 32.1, 28.5, 28.2, 28.1, 24.5, 24.0, 23.0, 22.8, 21.6, 21.3, 19.6, 18.9, 17.6, 17.6, 13.2, 12.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{58}H_{79}NNaO_5Si$: 920.5625 found: 920.5630.

8f. (*E*)-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 3-(4-(((2'-cyanobiphenyl-4-yloxy)diisopropylsilyl)ethyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 61% (*para:others* = 9:1)

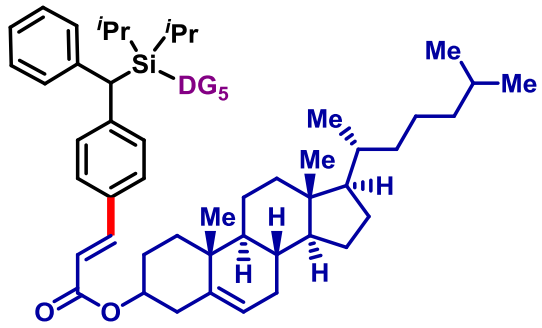
Physical appearance: Colorless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 15.9 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.38 (d, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 7.13 (s, 1H), 6.89 (s, 1H), 6.86 (d, 2H), 6.37 (d, 1H), 5.40 (d, *J* = 3.9 Hz, 1H), 4.78 – 4.69 (m, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.66 (q, *J* = 7.4 Hz, 1H), 2.39 (d, *J* = 7.2 Hz, 2H), 2.06 – 1.80 (m, 6H), 1.71 – 1.42 (m, 13H), 1.23 – 1.11 (m, 7H), 1.09 – 1.04 (m, 11H), 1.03 – 0.99 (m, 6H), 0.96 (d, *J* = 7.5 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.89 – 0.85 (m, 7H), 0.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 156.2, 152.7, 148.2, 147.9, 144.7, 140.2, 139.9, 131.5, 131.4, 130.0, 128.7, 128.2, 122.8, 120.0, 119.5, 117.5, 115.2, 112.5, 102.3, 74.1, 56.9, 56.5, 56.3, 50.2, 42.5, 39.9, 39.7, 38.5, 37.2, 36.8, 36.4, 35.9, 32.1, 32.1, 28.4, 28.2, 28.1, 28.0, 24.5, 24.0, 23.0, 22.8, 21.2, 19.5, 18.9, 18.1, 18.0, 17.9, 17.8, 16.1, 13.2, 13.1, 12.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{59}H_{81}NNaO_5Si$: 934.5782 found: 934.5788.

8g. (*E*)-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 3-(4-(((2'-cyanobiphenyl-4-yloxy)diisopropylsilyl)(phenyl)methyl)phenyl)acrylate



The compound was synthesized following the general procedure A in 0.2 mmol scale.

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 59% (*para:others* = 8:1)

Physical appearance: Colorless viscous compound

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, *J* = 15.9 Hz, 1H), 7.52 – 7.46 (m, 4H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.5 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.14 (s, 1H), 6.89 (s, 1H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 5.39 (d, *J* = 4.1 Hz, 1H), 4.79 – 4.69 (m, 1H), 3.96 (s, 3H), 3.93 (s, 3H), 3.82 (s, 1H), 2.39 (d, *J* = 7.5 Hz, 2H), 2.04 – 1.82 (m, 6H), 1.75 – 1.63 (m, 4H), 1.60 – 1.43 (m, 7H), 1.20 – 1.07 (m, 7H), 1.04 (d, *J* = 5.6 Hz, 4H), 0.92 (dd, *J* = 14.6, 7.5 Hz, 17H), 0.86 (dd, *J* = 6.6, 2.2 Hz, 7H), 0.68 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 155.9, 152.8, 148.2, 144.9, 144.5, 141.8, 140.2, 139.9, 132.2, 131.6, 130.1, 129.9, 129.7, 128.8, 128.5, 126.1, 122.9, 120.0, 119.5, 117.9, 115.2, 112.5, 102.4, 74.2, 56.9, 56.5, 56.4, 50.3, 43.0, 42.5, 39.9, 39.7, 38.5, 37.3, 36.9, 36.4, 36.0, 32.1, 32.1, 29.9, 28.5, 28.2, 28.1, 24.5, 24.0, 23.0, 23.0, 22.8, 21.3, 19.6, 18.9, 18.1, 18.1, 17.8, 17.8, 13.9, 12.1.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{64}H_{83}NNaO_5Si$: 996.5938found: 934.5792.

2.e. Removal of directing group:

Method 1: In a clean, oven-dried screw cap reaction tube with previously placed magnetic stir–bar, compound **2a** (278 mg, 0.5 mmol) was dissolved in 10 mL of THF, a solution of 1M TBAF (1.0 mL, 2.0 eq.) in THF was added drop wise at RT. The solution was stirred for 3 hours at room temperature. After completion of reaction, solvent was evaporated to dryness, and the residue was purified by chromatography using silica gel.

9. Ethyl (*E*)-3-(p-tolyl)acrylate:[4]

Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (98:2)

Yield: 92%

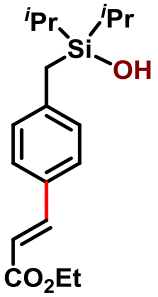
Physical appearance: Colorless liquid

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 16.0 Hz, 1H), 7.41 (d, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 8.0 Hz, 2H), 2.36 (s, 3H), 1.33 (t, *J* = 8.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 144.7, 140.7, 131.9, 129.7, 128.2, 117.3, 77.6, 77.2, 76.9, 60.5, 21.5, 14.5.

Method 2: In a clean, oven-dried screw cap reaction tube with previously placed magnetic stir–bar, compound 2a (111 mg, 0.2 mmol) and p-toluenesulfonic acid (10 mol%) were dissolved in 3 mL of EtOH and 1 mL H_2O (EtOH/H_2O: 3/1). The solution was stirred at 110 °C for 16 hours. After being stirred, reaction mixture was removed from oil-bath and kept at room temperature. Ethanol was removed under reduced pressure and aqueous part was extracted by EtOAc. Organic part was evaporated to dryness and the residue was purified by column chromatography silica gel.

11. Ethyl (E)-3-(4-((hydroxydiisopropylsilyl)methyl)phenyl)acrylate:



Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (95:5)

Yield: 82%

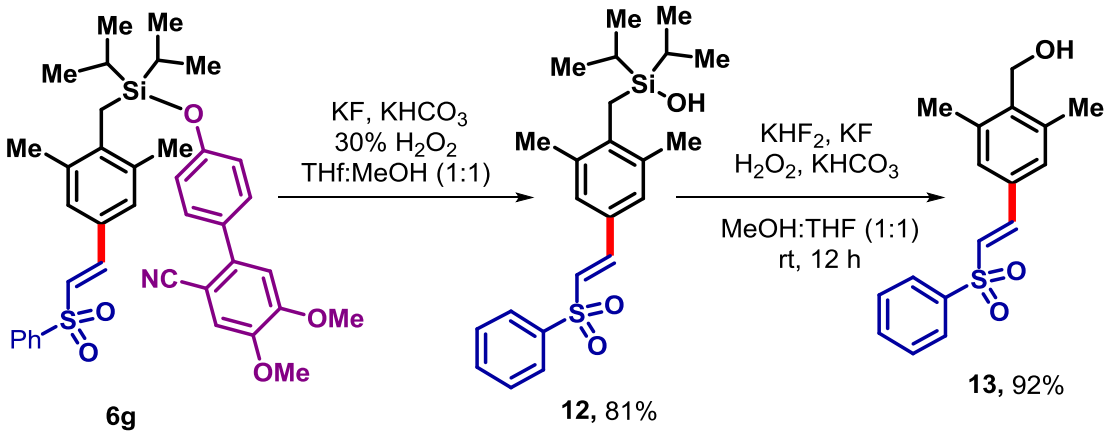
Physical appearance: Crystalline white solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 16.0 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 2.24 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.03 – 0.98 (m, *J* = 10.8, 5.5 Hz, 14H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.5, 144.9, 142.8, 130.9, 129.2, 128.5, 116.8, 60.6, 22.2, 17.5, 17.4, 14.6, 12.9.

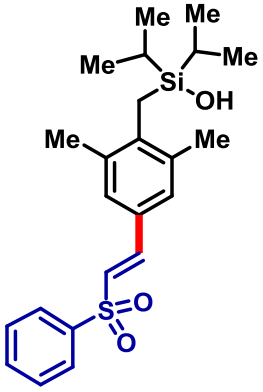
HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{18}H_{28}NaO_3Si$ 343.1700: found: 343.1694.

Diversification of *para*-olefinated products: Preparation of *para*-olefinated benzyl alcohol



Procedure: Procedure modified from literature:[12] The *para*-olefinated product **6g** (0.2 mmol) was added to a mixture of KF (0.4 mmol) and $KHCO_3$ (0.4 mmol) in MeOH (0.5 mL) and THF (0.5 mL). 30% H_2O_2 in THF (4 mmol) was added to the reaction mixture and stirred at 60 °C for 12 h. After being cooled to room temperature, the reaction mixture was treated with H_2O (2 mL). The mixture was then extracted with EtOAc (20 mL) and the combined organic phase was dried over Na_2SO_4 and removal of solvents under reduced pressure afforded the silanol in quantitive amount. The silanol derivative was dissolved in THF:MeOH (2 mL:2 mL). KHF_2 (125 mg, 1.6 mmol), KF (23 mg, 0.4 mmol), H_2O_2 (30% in THF, 0.15 mL, 1.6 mmol), and $KHCO_3$ (160 mg, 1.6 mmol) were added, and the mixture was stirred at room temperature for 12 h. The reaction was quenched with saturated solution of Na_2SO_3 and the resulting mixture was extracted with EtOAc (20 mL, then 2 x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude benzyl alcohol derivative (**12**) was further purified by column chromatography.

12. (*E*)-(2,6-dimethyl-4-(2-(phenylsulfonyl)vinyl)benzyl)diisopropylsilanol



Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (93:7)

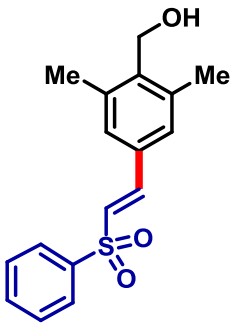
Yield: 81%

Physical appearance: White solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.62 – 7.51 (m, 4H), 7.11 (s, 2H), 6.75 (d, *J* = 15.3 Hz, 1H), 2.31 (s, 6H), 2.25 (s, 2H), 1.03 (d, *J* = 6.5 Hz, 6H), 1.00 – 0.95 (m, 2H), 0.91 (d, *J* = 6.4 Hz, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 143.3, 142.2, 141.5, 136.4, 133.3, 129.5, 128.5, 128.2, 127.8, 125.1, 21.5, 17.5, 17.5, 17.3, 14.0.

13. (*E*)-(2,6-dimethyl-4-(2-(phenylsulfonyl)vinyl)phenyl)methanol



Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (93:7)

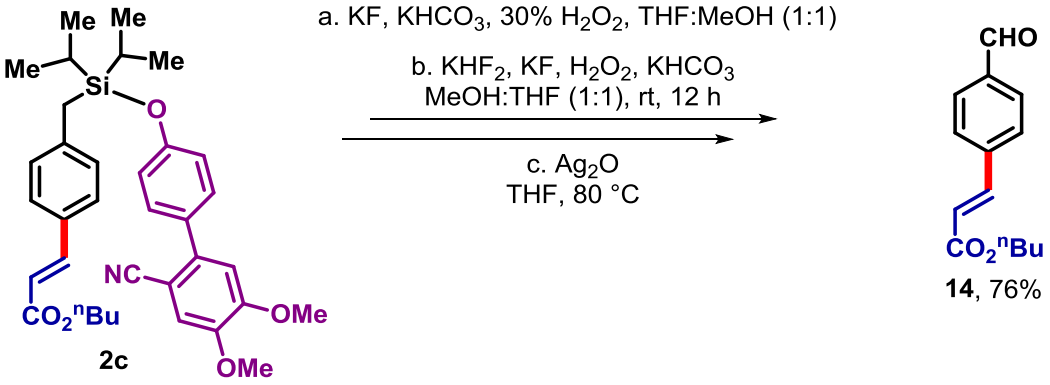
Yield: 92%

Physical appearance: White solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.6 Hz, 2H), 7.63 – 7.58 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.13 (s, 2H), 6.98 (s, 1H), 6.78 (d, *J* = 15.3 Hz, 1H), 2.84 (s, 1H), 2.27 (s, 6H), 2.18 (s, 2H).

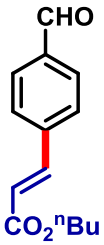
^{13}C NMR (126 MHz, $CDCl_3$) δ 143.2, 141.3, 139.5, 137.5, 135.9, 133.4, 129.5, 128.0, 127.8, 125.8, 125.7, 77.5, 77.2, 76.9, 49.7, 20.7.

Diversification of *para*-olefinated products: Preparation of *para*-olefinated benzaldehyde



Procedure: As stated above the para-olefinated product **2c** was treated with **condition a** and **condition b** to produce the corresponding benzyl alcohol. The benzyl alcohol was then oxidized to benzaldehyde derivative **14** using silver oxide. In a closed cap reaction tube the benzyl alcohol (0.1 mmol) and Ag_2O (34 mg, 0.15 mmol) was taken and dissolved in THF (1 mL). the reaction mixture was stirred at 80 °C for overnight. The resulting reaction mixture was taken out and cooled to room temperature. Then the reaction mixture was filtered the celite pad and purified by column chromatography.

14. butyl (*E*)-3-(4-formylphenyl)acrylate



Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (90:10)

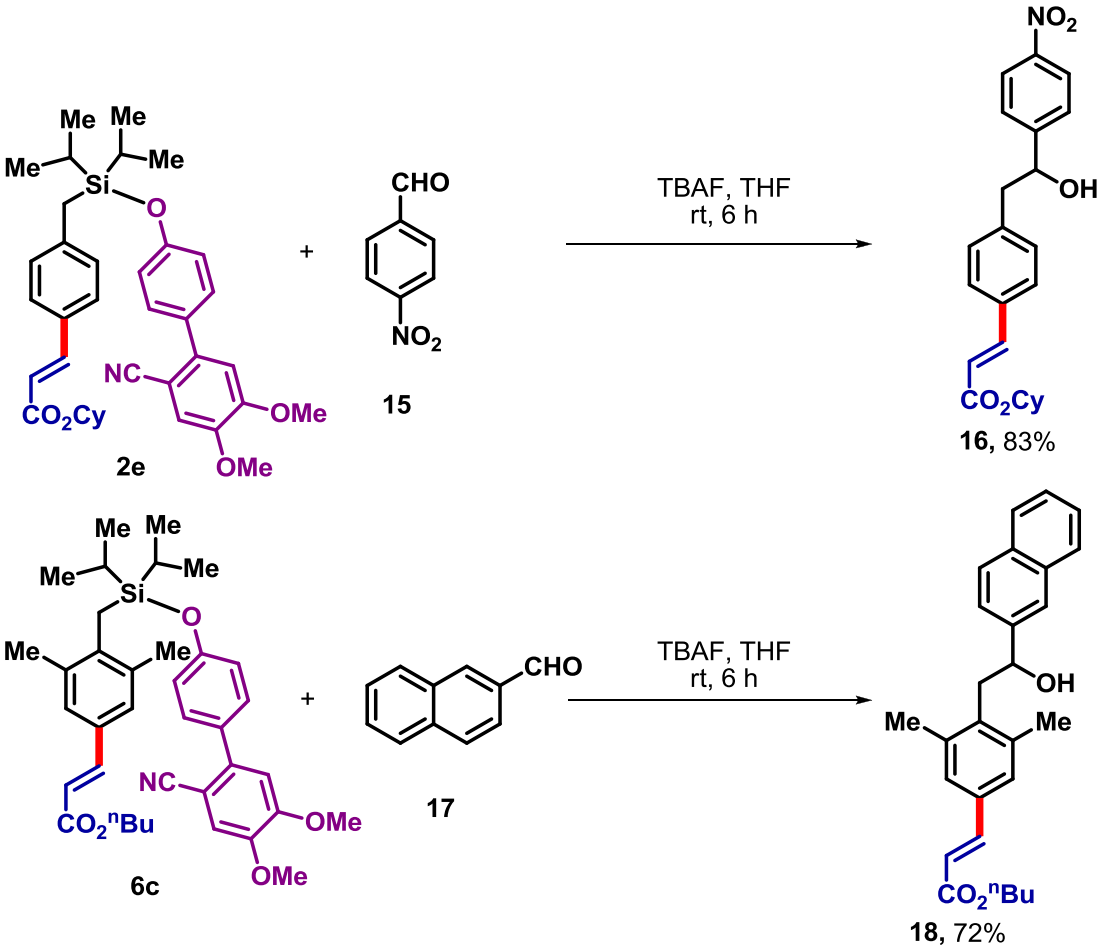
Yield: 76%

Physical appearance: White solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.03 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.73 – 7.66 (m, *J* = 12.4 Hz, 3H), 6.55 (d, *J* = 8.7 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 1.73 – 1.67 (m, 2H), 1.48 – 1.41 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

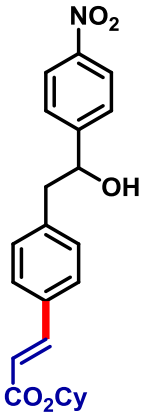
^{13}C NMR (126 MHz, $CDCl_3$) δ 191.7, 166.7, 143.0, 140.4, 137.4, 130.4, 128.7, 121.8, 77.5, 77.2, 76.9, 65.0, 30.9, 19.4, 13.9.

Diversification of *para*-olefinated products: Nucleophilic addition of silyl motif to aldehyde



Procedure modified from literature:[5] In a closed cap reaction tube, para-olefinated product (0.2 mmol, 1.0 equiv.) and corresponding aryl aldehyde (0.24 mmol, 1.2 equiv.) were dissolved in THF (1 mL). To the reaction mixture TBAF (1 (M) solution in THF, 0.2 mmol, 1 equiv) was added. The reaction mixture was stirred at room temperature for 12 hour. The reaction mixture was then extracted with ethyl acetate (20 mL, then 2 x 10 mL). were dried over Na_2SO_4 and concentrated by rotary evaporation. The crude benzyl alcohal derivatives (**16** and **18**) were further purified by column chromatography.

16. cyclohexyl (*E*)-3-(4-(2-hydroxy-2-(4-nitrophenyl)ethyl)phenyl)acrylate



Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 83%

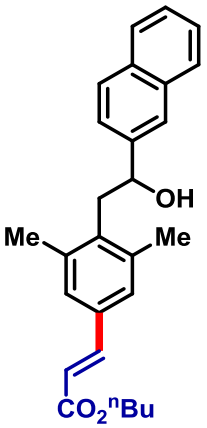
Physical appearance: Crystalline yellow solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 16.0 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.40 (d, *J* = 16.0 Hz, 2H), 5.04 (t, *J* = 5.7 Hz, 1H), 4.92 – 4.85 (m, 1H), 3.10 – 2.97 (m, 2H), 2.28 (s, 1H), 1.96 – 1.87 (m, 2H), 1.80 – 1.73 (m, 2H), 1.60 – 1.55 (m, 1H), 1.53 – 1.45 (m, 2H), 1.45 – 1.36 (m, 2H), 1.34 – 1.27 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 160.0, 147.6, 143.9, 139.3, 133.6, 130.3, 128.5, 126.9, 123.9, 119.1, 74.4, 73.0, 46.0, 31.9, 25.6, 24.0.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{23}H_{25}NNaO_5$ 418.1625: found: 418.1624.

18. butyl (*E*)-3-(4-(2-hydroxy-2-(naphthalen-2-yl)ethyl)phenyl)acrylate



Column material: 100-200 mesh silica

Eluent: petroleum ether:ethyl acetate (85:15)

Yield: 72%

Physical appearance: Crystalline white solid

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.79 (m, 4H), 7.61 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.46 (m, 3H), 7.21 (s, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.09 (dd, *J* = 8.1, 5.0 Hz, 1H), 4.20 (t, *J* = 6.7 Hz, 2H), 3.26 (dd, *J* = 13.9, 8.8 Hz, 1H), 3.07 (dd, *J* = 13.9, 4.9 Hz, 1H), 2.36 (s, 6H), 2.02 (s, 1H), 1.72 – 1.66 (m, 2H), 1.49 – 1.40 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 167.6, 144.8, 141.9, 138.3, 138.1, 133.5, 133.2, 132.8, 128.5, 128.3, 128.2, 127.9, 126.5, 126.1, 124.3, 123.9, 117.7, 74.4, 64.6, 39.9, 31.0, 20.7, 19.4, 13.9.

HRMS (*m/z*): $[M + Na]^+$ calculated for $C_{27}H_{30}NaO_3$ 425.2087: found: 425.2087.

2.f. Kinetic Experiment:

Table S11: Kinetic experiment

	Substrate	Olefin	$[Rh(COD)Cl]_2$	$CuCl_2$+TFA	V_2O_5	DCE
Run 1	**0.1mmol**	0.2mmol	5 mol%	2 equiv	3equiv	1 mL
Run 2	**0.05mmol**	**0.2mmol (4equiv)**	5mol%	2 equiv	3 equiv	1 mL
Run 3	0.05 mmol	**0.3mmol (6equiv)**	5mol%	2 equiv	3 equiv	1 mL
Run 4 (**D_7-1a**)	**0.05 mmol (Deuterated substrate D_7-1a)**	0.2mmol (4equiv)	5mol%	2 equiv	3 equiv	1 mL

*the yield has been determined by 1H NMR of crude reaction mixture using trimethoxy benzene as internal standard

Determination of order with respect to substrate: Comparing Run 1 and Run 2

Run 1: 0.1 mmol of substrate

x_1 – 0.1021

y_1 – 3.4175

x_2 – 0.7448

y_2 – 11.3716

Slope = R_1 = $dy/dx = y_2 - y_1 / x_2 - x_1$

= (11.3716 – 3.4575)/(0.7448 - 0.1021)

= 7.9141/0.6427 = 12.3138

Run 2: 0.05 mmol of substrate

X_1 – 0.0955

Y_1 – 0.5603

X_2 – 0.7179

Y_2 – 4.5374

Slope = R_2 = $dY/dX = Y_2 - Y_1/X_2 - X_1$

= (4.5374 - 0.5603)/(0.7179 - 0.0955)

= 3.9771/0.6224= 6.3899

We know

Rate = $dy/dx = k[substrate]^a[olefin]^b$

Now, $R_1/R_2 = \{dy/dx\}_{run1}/\{DY/DX\}_{run2}$ =

$\{k[substrate]^a{}_{Run1}[olefin]^b{}_{run1}\}/\{k[substrate]^a{}_{run2}[olefin]^b{}_{run2}\}$

At t=0; $[olefin]_{run1} = [olefin]_{run2}$

- $R_1/R_2 = [substrate]^a{}_{run1}/[substrate]^a{}_{run2}$
- $12.3138/6.3899 = [substrate]^a{}_{run1}/[substrate]^a{}_{run2}$
- $1.92 = [substrate]^a{}_{run1}/[substrate]^a{}_{run2}$
- So $[substrate]^a{}_{run1}/[substrate]^a{}_{run2}$ is nearly equal to 2.0

At t=0; $[substrate]^a{}_{run1}/[substrate]^a{}_{run2} = [0.1/0.05]^a = 2^a$

So, $2.0 = 2^a$

log(2) = a*log(2)

So, a = 1.0

Which indicates that the reaction rate with respect to substrate is **one**.

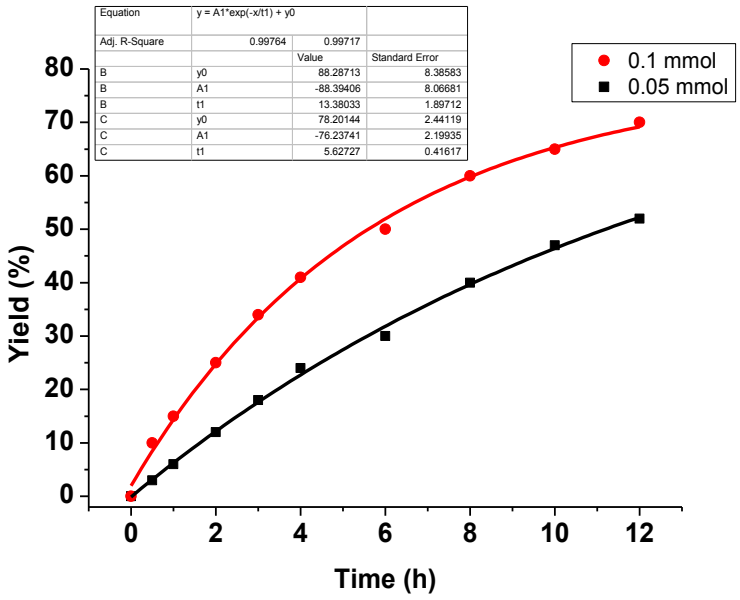


Figure S1: Order determination with respect to the substrate

Determination of order with respect to olefin: Comparing Run 2 and Run 3

Run 2: 0.05 mmol and 4 equiv of olefin

x_1 – 0.1053

y_1 – 0.0198

x_2 – 0.6184

y_2 – 5.5119

Slope = R_2 = $y_2 - y_1 / x_2 - x_1$

= (5.5119 – 0.0198)/(0.6184 - 0.1053)

= 5.4921/0.5131 = 10.7038

Run3: 0.05 mmol and 6 equiv of olefin

X_1 – 0.1123

Y_1 – 0.8362

X_2 – 0.8390

Y_2 – 9.1008

Slope = R_3 = $dY/dX = Y_2 - Y_1 / X_2 - X_1$

= (9.1008 – 0.8362)/(0.8390 - 0.1123)

= 8.2646/0.7267

= 11.37

We know

Rate = dy/dx= $k[substrate]^a[olefin]^b$

Now, $R_3/R_2=\{dY/dX\}_{run3}/\{dy/dx\}_{run2}$ =

$\{k[substrate]^a{}_{Run3}[olefin]^b{}_{run3}\}/\{k[substrate]^a{}_{run2}[olefin]^b{}_{run2}\}$

At t=0; $[ssubstrate]_{run2}=[substrate]_{run3}$

- ⇨ $R_3/R_2 = [olefin]^a{}_{run3}/[olefin]^a{}_{run2}$
- ⇨ $11.37/10.70 = [olefin]^a{}_{run3}/[olefin]^a{}_{run2}$
- ⇨ $1.03 = [olefin]^a{}_{run3}/[olefin]^a{}_{run2}$

At t=0; $[olefin]^a{}_{run3}/[olefin]^a{}_{run2} = [0.3/0.2]^a = 1.5^a$

So, 1.06 which is nearly equal to $1= 1.5^a$

So, log(1.06) = alog(1.5)

=> 0.0253 = a*0.1760

So, a = 0.14, Which indicates that the reaction rate with respect to olefin is zero, i.e. rate is independent on the amount of olefin.

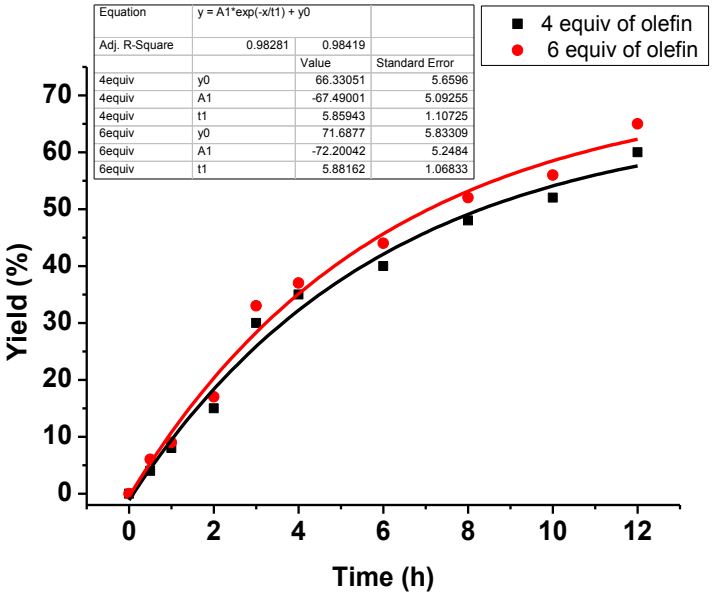


Figure S2: Order determination with respect to the olefin

Determination of k_H/k_D: Comparing Run 2 and Run 4

Run 2: 0.05 mmol and 4equiv of olefin

x_1- 0.3834, y_1- 2.8772

x_2- 1.1783, y_2- 11.4023

$dx = x_2 - x_1 = (1.1783 - 0.3834) = 0.7949$

$dy = y_2 - y_1 = (11.4023 - 2.8772) = 8.5251$

Slope = R_2 = dy/dx = 8.5251/0.7949= 10.7247

Run 4: 0.05 mmol deuterated substrate (D_7-1a)

X_1= 0.2914, Y_1 = 0.8157
X_2= 1.6594, Y_2 = 6.3031
$dX = X_2 – X_1$ = 1.6594 - 0.2914= 1.368
$dY= Y_2 – Y_1$ = 6.3031– 0.8157= 5.4874
R_4 = dY/dX = 5.4874/1.368= 4.0112
We know
Rate = dy/dx= $k[substrate]^a[olefin]^b$
Now, $R_2/R_4 = \{ DY/DX \}_{run2}/\{dy/dx \}_{run4} = \{K_H[substrate]^{a}_{Run2}[olefin]^{b}_{run2}\}/\{K_D[substrate]^{a}_{run4}[olefin]^{b}_{run4}\}$
At t=0; $[olefin]_{run2} = [olefin]_{run4}$ and $[substrate]_{run2} = [substrate]_{run4}$

⇨ $R_2/R_4 = k_H/k_D$= 10.7247/4.0112 = 2.6

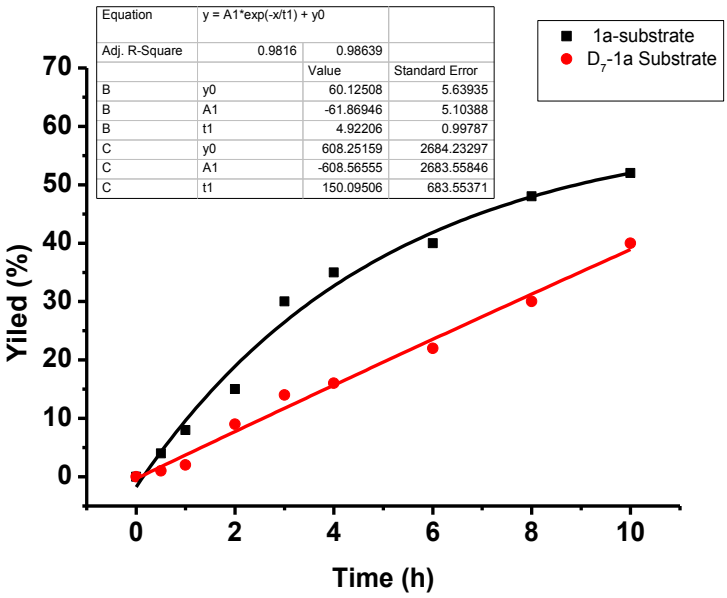


Figure S3: k_H/k_D determination

Intermolecular KIE experiment:

An oven-dried screw cap reaction tube was charged with a magnetic stir-bar, **1a**(0.1 mmol, 45.9 mg), deuterated-**1aD_7-1a** (0.1 mmol, 46.6 mg), olefin (0.8mmol, 4.0 equiv), $[Rh(COD)Cl]_2$ (5mol%), $CuCl_2$ and TFA (2.0 equiv) and V_2O_5 (3 equiv) were taken. Subsequently, DCE (2 mL) was added and the reaction mixture was stirred vigorously for 20 h at 120 °C. The reaction mixture was then diluted with DCM.10 mLdilute ammonia solutionwas added to the reaction mixture; the organic part was extracted with DCM and dried over magnesium sulfate. After evaporation of the solvent, the crude mixture was

purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether/ethyl acetate as the eluent. $\boldsymbol{P_H/P_D}$was calculated from ^{1}H NMR spectrum of the isolated product. From NMR spectrum product distribution $P_H/P_D$was found 2.9.

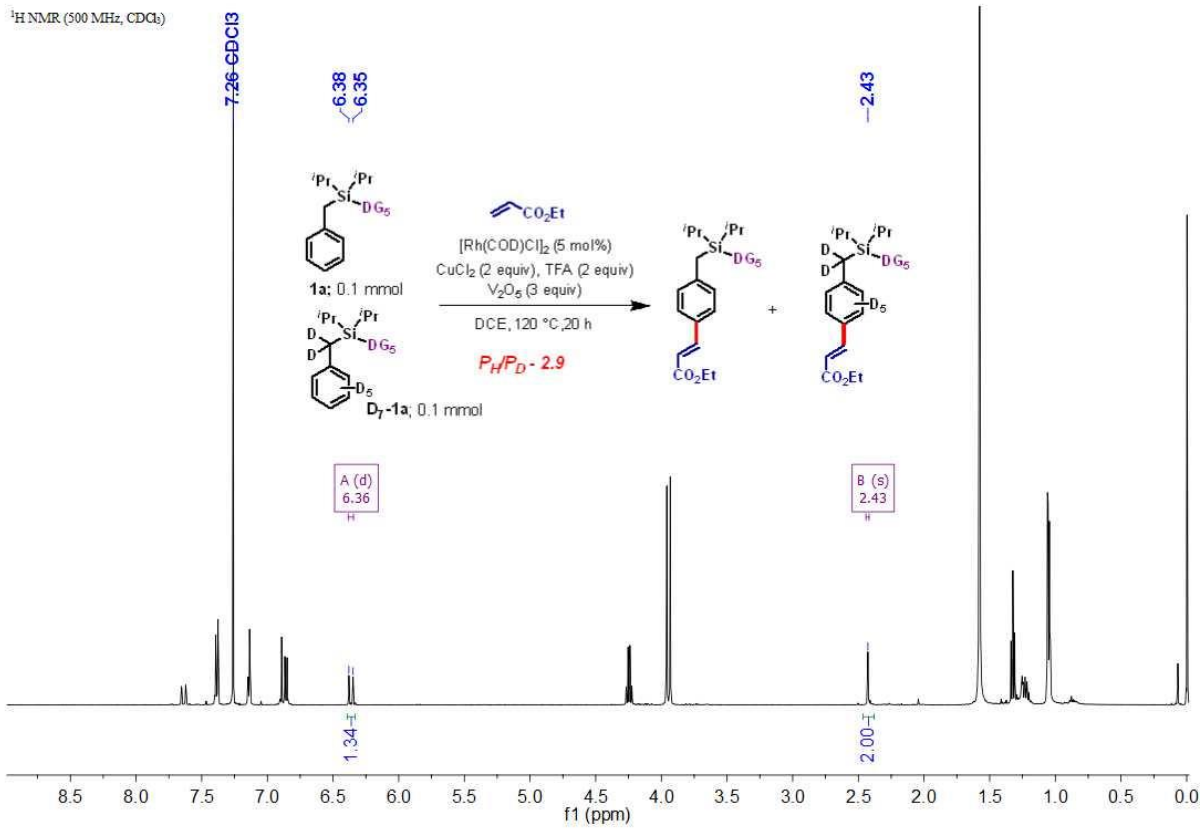


Figure S4: P_H/P_D determination

In this spectrum peak at 2.43 ppm is corresponds to benzylic proton and total integration is 2.0and the doublet at 6.36 ppm coming from the styrenyl proton. Among this 1.34 proton, one proton is coming from compound **2a** is rest 0.34 is the contribution of deutarated substrate **D_7-1a**. And hence $[P_H/P_D]$ = 1/0.34 = 2.9.

3. Computational Study

3a. Analysis of the Origins of Regioselectivity in Rh-Catalyzed C–H Activation

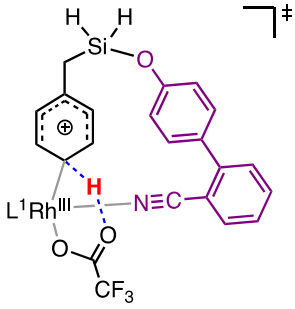
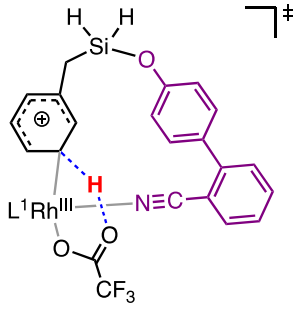
The origins of the *para*-regioselectivity in the Rh-catalyzed C–H activation reaction were explored by performing computations on a series of fragment structures derived from transition states **TS1-*para*** and **TS1-*meta***. The structures are shown in Table S12. Entry A of the table compares the energy (*E*) of the intact**TS1-*para***with that of **TS1-*meta***, showing the former to be 7.7 kcal/mol lower in energy. Entry B showsthe energies of the substrates alone, in the same geometry as found in the TS. The substrate fragment from**TS1-*para*** is 1.0 kcal/mol lower in energy than that from**TS1-*meta***. Entry C shows the $[RhL_n(CF_3CO_2)]^{2+}$unit. This fragment is equienergetic in the two TSs. The results in entries B and C imply that, out

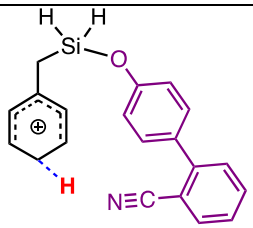
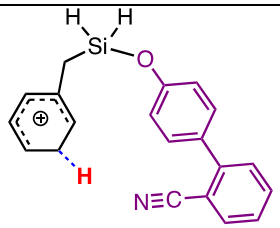
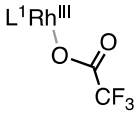
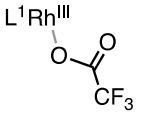
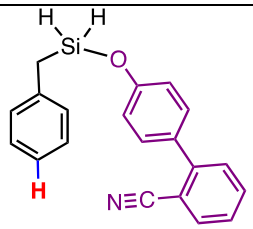
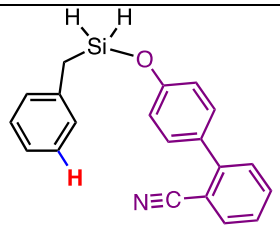
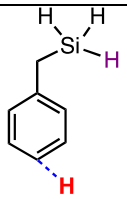
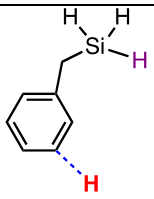
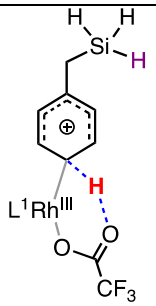
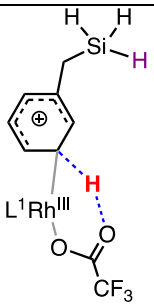
of the total 7.7 kcal/mol energy difference between **TS1-*para*** and **TS1-*meta***, 1.0 kcal/mol is attributable to distortions of the substrate, no differences are ascribable to the $[RhL_n(CF_3CO_2)]^{2+}$unit, and the remainder, 6.7 kcal/mol, is therefore ascribed to differences in the strength of the interaction between the substrate and $[RhL_n(CF_3CO_2)]^{2+}$in the two TSs.

Entry D of the table contains structures wherein the substrate fragment was subjected to a partial optimization, allowing the reacting CH group and the two neighbouring CH groups to relax. For these structures, the *meta*fragment is found to be 0.4 kcal/mol lower in energy than the *para*fragment. This indicates that the conformational preorganization of the DG is approximately equivalent in*meta* vs *para* attack, in fact slightly favoring *meta* attack. Therefore, the origin of the 1 kcal/mol energy difference between the unrelaxed substrate fragments (entry B) must be localized near the site of reactivity rather than within the rest of the scaffold.

In entry E, the substrate has been truncated by replacing the DG with an H atom (positioned at a distance of 1.09 Å from the Si atom). This silylmethylarene fragment is 2.7 kcal/mol lower in energy in the *para* TS than in the *meta* TS. In entry F, the samesilylmethylareneis bound to $[RhL_n(CF_3CO_2)]^{2+}$. This fragment differns by 8.9 kcal/mol between the two TSs, favoring *para*. This result suggests that the main origin of the *para*regioselectivity lies in the interaction between the silylmethylarene moiety and $[RhL_n(CF_3CO_2)]^{2+}$. The silylmethylarene has arenium character in the TS and its interaction with $[RhL_n(CF_3CO_2)]^{2+}$ is enhanced in the *para* TS, becausethe C–Si bond can stabilize the areniumcation, in a variant of theβ-silicon effect.[6]

Table S12. Energy comparison ofstructural fragmentsof**TS1-*para*** and **TS1-*meta***.[a]

Structure	***Para***	***Meta***	**ΔE (*meta* – *para*)**
A.Full TS			7.7

B. Substrate			1.0
C.$[RhL_n(CF_3CO_2)]^{2+}$			0.0
D. Substrate after allowing reacting CH group and two neighbouring CH groups to relax			–0.4
E. Truncated substrate after removal of DG			2.7
F. Truncated substrate bound to RhL_n			8.9

[a]L^1 = COD. ΔE (*meta* – *para*) calculated with M06/6-311+G(d,p)-SDD in SMD dichloroethane (kcal/mol).

3b. Computational Investigations of DG Preorganization inSeveral C–H Activation Mechanisms

Many Rh(III)-catalyzed C–H functionalizations utilize a Rh(III) catalyst precursor such as $[RhCp^*Cl_2]_2$. In the chemistry reported herein, however, the catalyst precursor is a Rh(I) species, $[Rh(COD)Cl]_2$. In our mechanistic study, we therefore considered the possibility that C–H activation may occur either before or after the oxidation of Rh(I) to Rh(III). We performed DFT calculations on three different C–H activation processes, as follows:

Mechanism **1**: A Rh(III)-mediated electrophilic aromatic substitution pathway mediated by $[Rh^{III}(COD)(CF_3CO_2)]^{2+}$

Mechanism **2**: A Rh(I)-mediated concerted metalation–deprotonation pathway mediated by $[Rh^{I}(COD)(CF_3CO_2)]$

Mechanism **3**: A Rh(I)-mediated oxidative addition pathway mediated by [Rh^{I}(COD)Cl].

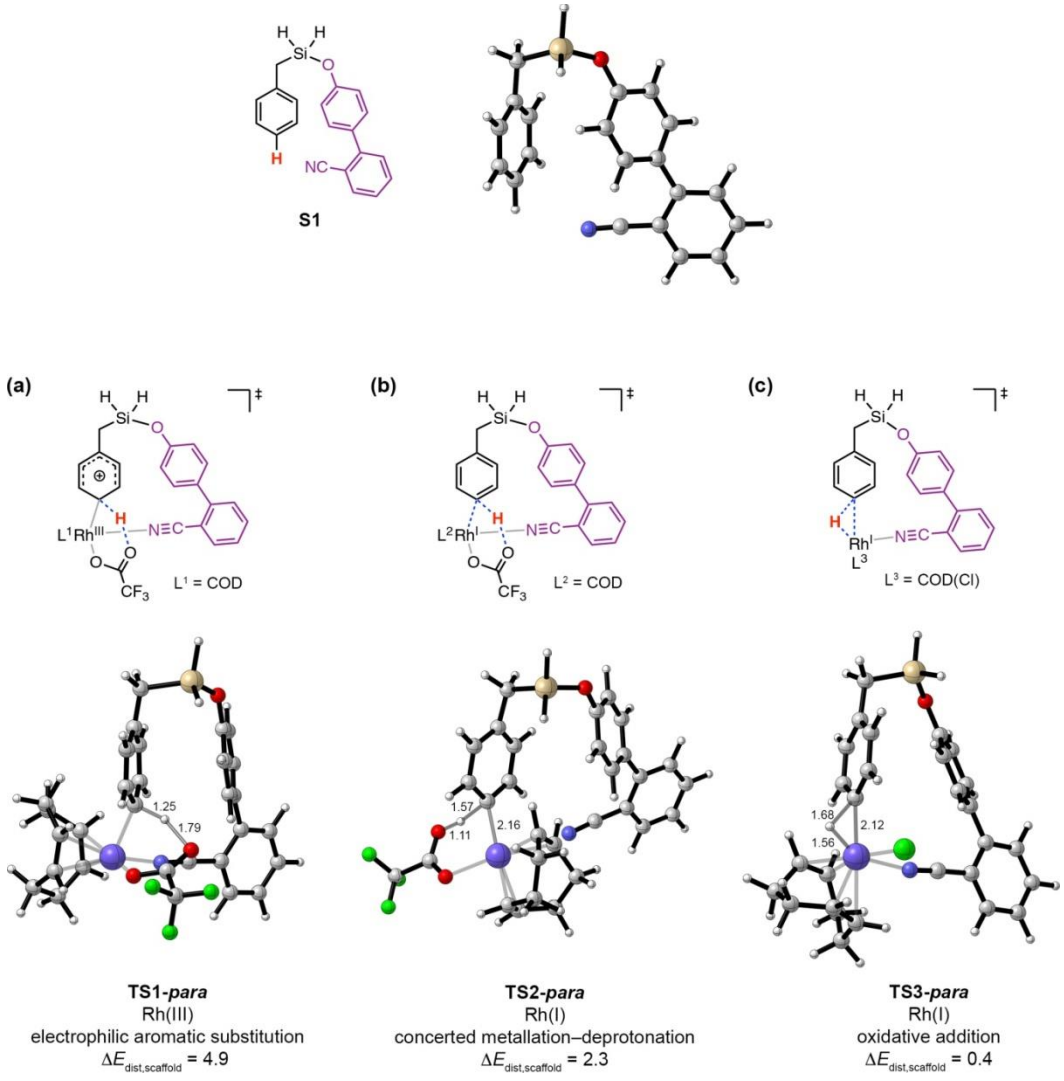


Figure S5. Model substrate **S1** and the transition states for*para*-C–H bond activation of **S1**according to (a) mechanism **1**, (b) mechanism **2**, and (c) mechanism **3**.The energy required to distort the **S1** scaffold into each TS geometry ($\Delta E_{\text{dist,scaffold}}$) is shown. Distances in Å, $\Delta E_{\text{dist,scaffold}}$ in kcal/mol.

A full computational characterization of these three mechanisms will be reported in due course. For the present study, however, we have examined the transition statesfor*para*-C–H bond activation of the model substrate **S1**in each of the three mechanisms **1**–**3**. The transition states, calculated with M06, are shown in Figure S4.

For each TS, a calculation was performed to quantify the amount of conformational reorganization that the substrate undergoes on going from its ground-state geometry to the TS.The atoms of the RhL_n unit were deleted from each TS, leaving the substrate remaining. A

partial geometry optimization was then performed in which the *para*–CH group and the two adjacent CH groups were allowed to relax while holding the remainder of the substrate fixed in the TS geometry. This was done in order to determine the energy associated withthe reorganization of the scaffold,as opposed to the reorganization of the atoms involved in bond-forming and bond-breaking. The energy of the resulting partially-relaxed substrate was calculated with M06/6-311+G(d,p) in SMD dichloroethane. The energies associated with distortion of the scaffold, $\Delta E_{\text{dist,scaffold}}$, are shown in Figure S4.The scaffold distortion energies in **TS1-*para***, **TS2-*para***, and **TS3-*para*** are all small:4.9, 2.3, and 0.4 kcal/mol, respectively, indicating that the preorganization of the DG for distal*para*-C–H activation is quite general for a range of Rh-catalyzed C–H activation mechanisms.

Returning to mechanism **1**,electrophilic aromatic substitution by Rh(III), we also performed calculations todeterminehow the C–H activation barrier is influenced by (a) the nitrile group and (b) the methoxy groups on the DG. Figure S5(a) shows a transition state calculated for the Rh(III)-catalyzed C–H activation wherein the nitrile group is not coordinated to rhodium (**TS1-*para*-2**). This TS is 22.8 kcal/mol higher in energy than the corresponding TS that has the nitrile bound to rhodium (**TS1-*para***).Thus, the coordination of the nitrile to Rh strongly activates the substrate toward C–H activation. Figure S5(b) shows a transition state (**TS1-*para*-3**)corresponding to the C–H activation of a dimethoxy-substituted substrate,**S2**. The barrier for C–H activation of this substrateis 1.6kcal/mol lower than that for the methoxy-free**TS1-*para***, consistent with the greater catalytic activity of the dimethoxy-substituted directing group $\mathbf{DG_5}$ relative to the unsubstituted $\mathbf{DG_1}$.

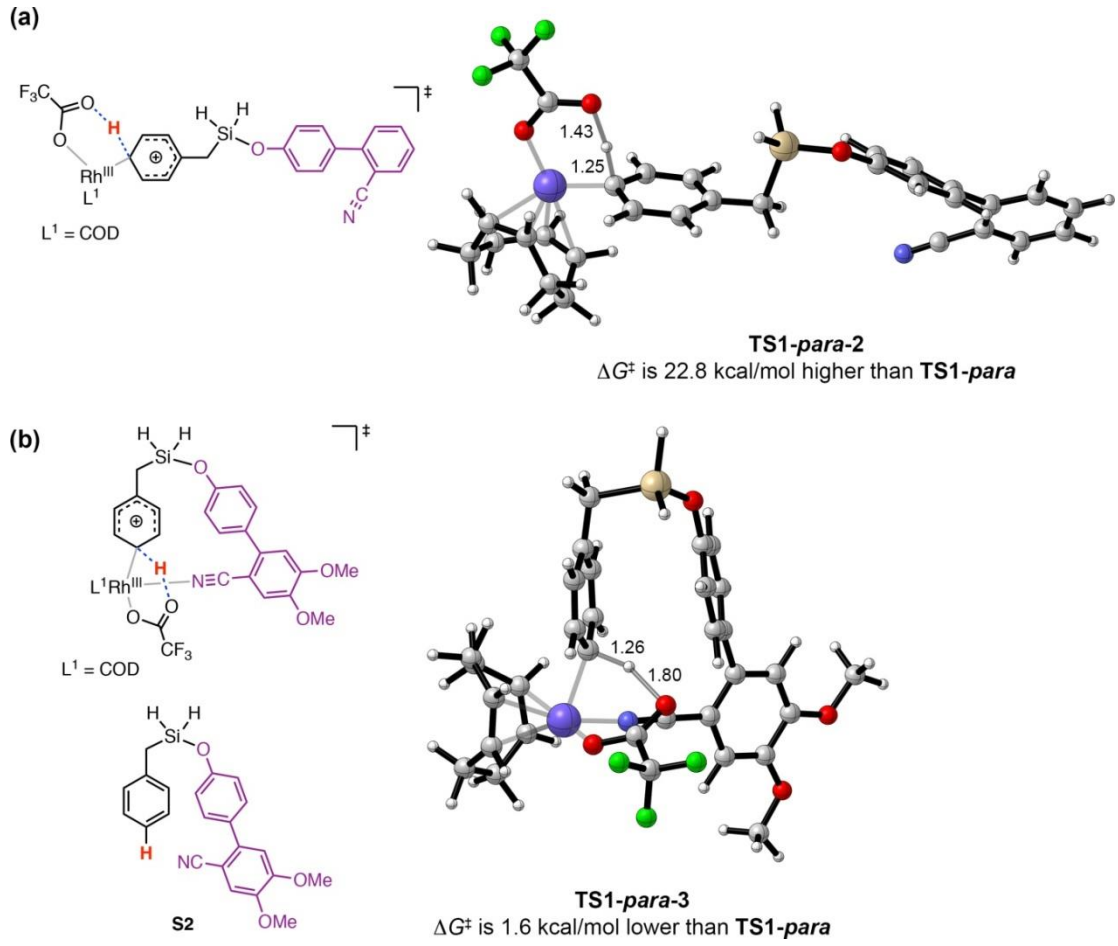


Figure S6. Transition states for *para*-C–H bond activation of (a) the model substrate **S1**without Rh–nitrile coordination, and (b) the dimethoxy-substituted substrate **S2**. Distances in Å, $\Delta G^{\ddagger}$ in kcal/mol.

Computational Methods

Density functional theory calculations were performed in Gaussian 09[7] and Gaussian 16.[8] The M06 functional[9] was used, as has been previously used in other computational studies of Rh-catalyzed C–H activation.[10] For geometry optimizations, a mixed basis set consisting of 6-31G(d,p) on non-metal atoms and LANL2DZ on rhodium was used, in conjunction with the SMD implicit model[11] to simulate the solvent, dichloroethane. Vibrational frequency calculations were performed to characterize each species as a ground state or transition state and to obtain thermochemical quantities.Errors in computed entropies, introduced by the treatment of low frequency modes as harmonic motions, were minimized by use of Truhlar's approximation[12] in which all harmonic frequencies below 100 cm^{-1} were raised to exactly 100 cm^{-1} before evaluation of the vibrational component of the thermal contribution to entropy. Subsequently, single-point energy calculations were performed with M06 using a

mixed basis set consisting of 6-311+G(d,p) on non-metal atoms and SDD on rhodium, in SMD dichloroethane. Gibbs free energies were obtained by adding the thermochemical corrections derived from the M06/6-31G(d,p)-LANL2DZ(SMD) frequency calculations (after application of Truhlar's approximation) to the M06/6-311+G(d,p)-SDD(SMD) single-point energies and are reported at a standard state of 1 mol/L and 298.15 K.

The following section lists the Cartesian coordinates of optimized species along with the following energies (in Hartree):

E: Sum of M06/6-31G(d,p)-LANL2DZ electronic potential energy and free energy of solvation in dichloroethane

G: M06/6-31G(d,p)-LANL2DZ Gibbs free energy in solution at 1 mol/L and 298.15 K after correction of low-frequency vibrational modes

E_{LBS}: Sum of M06/6-311+G(d,p)-SDD electronic potential energy and free energy of solvation in dichloroethane

G_{tot}: Total M06/6-311+G(d,p)-SDD Gibbs free energy in dichlorethaneat 1 mol/L and 298.15 K

Computed Geometries and Energies

S13

C	-1.653563	-2.971560	0.032224
C	-1.623161	-2.181174	-1.113560
C	-2.542075	-1.150200	-1.277412
C	-3.507754	-0.890156	-0.300558
C	-3.537746	-1.698362	0.840802
C	-2.619400	-2.730681	1.006254
C	1.636268	0.951209	0.048536
C	1.282007	2.077380	-0.706442
C	-0.030575	2.515473	-0.767215
C	-1.028195	1.839218	-0.062472
C	-0.689179	0.732324	0.716891
C	0.626719	0.293664	0.760187
C	5.758602	-0.272166	0.218719
C	5.400785	1.070013	0.315796
C	4.066065	1.448718	0.258086
C	3.043201	0.508294	0.099468
C	3.423794	-0.846445	-0.015575
C	4.770892	-1.228260	0.050121
C	2.466202	-1.878280	-0.267416
N	1.731755	-2.752914	-0.491194
C	-4.421113	0.291831	-0.421906
Si	-3.733565	1.779552	0.494952
H	-3.515442	1.436163	1.922694
H	-4.629271	2.948393	0.367257
O	-2.294131	2.307743	-0.184581

H	-0.924511	-3.767838	0.163236
H	-0.870986	-2.361721	-1.878729
H	-2.504457	-0.519824	-2.166218
H	-4.286619	-1.506130	1.609777
H	-2.656289	-3.347875	1.901621
H	2.046754	2.602332	-1.275929
H	-0.308532	3.377401	-1.369004
H	-1.450580	0.192542	1.276716
H	0.865631	-0.571241	1.376582
H	6.801826	-0.571079	0.268435
H	6.167745	1.829326	0.447721
H	3.798087	2.498006	0.360918
H	5.026628	-2.280395	-0.046796
H	-4.580594	0.570553	-1.471499
H	-5.409364	0.081076	0.011716

0 imaginary frequencies
E = -1191.232450
G = -1190.963920
E_{LBS} = -1191.463731
G_{tot} = -1191.195201

$[Rh(COD)(CF_3CO_2)]^{2+}$

Rh	0.396952	-0.054225	0.061793
C	2.173447	0.306583	-1.556173
C	3.327659	-0.601013	-1.372725
C	2.905466	-1.802926	-0.505688
C	2.205468	-1.459775	0.754658
C	2.272927	-0.276975	1.476707
C	3.147682	0.918064	1.275228
C	2.376467	1.942510	0.447502
C	1.809108	1.450553	-0.823629
O	-1.464978	0.612742	-0.710204
C	-2.152412	-0.066770	0.115041
O	-1.617676	-0.760123	0.999847
C	-3.676170	-0.012124	-0.054225
F	-4.083488	1.250203	-0.007559
F	-3.995100	-0.517812	-1.241474
F	-4.282758	-0.704351	0.891880
H	1.513404	0.076945	-2.400419
H	1.102075	2.123974	-1.315162
H	2.267958	-2.483748	-1.082725
H	4.188361	-0.082870	-0.948541
H	3.609320	-0.988618	-2.356835
H	3.801780	-2.393383	-0.251838
H	1.525919	2.357682	1.027906
H	2.975446	2.849703	0.241061
H	4.111999	0.668873	0.828476
H	3.350606	1.357771	2.256607
H	1.625025	-2.265966	1.206916
H	1.640754	-0.242318	2.370958

0 imaginary frequencies
E = -946.885595
G = -946.713694
E_{LBS} = -948.150660
G_{tot} = -947.978759

TS1-*para*

C	-1.341052	-3.328249	-0.317161
C	-1.464547	-2.262029	-1.248590
C	-0.682277	-1.152698	-1.134329

C	0.307357	-1.051002	-0.088275
C	0.517629	-2.211715	0.751997
C	-0.313830	-3.287997	0.663885
Rh	1.970260	0.196370	-0.558481
C	4.056331	-0.796928	-0.737431
C	4.712598	-0.273837	-1.981222
C	3.958438	0.920147	-2.574063
C	2.479648	0.758702	-2.707850
C	1.749726	-0.409081	-2.827626
C	2.292662	-1.793494	-3.088667
C	2.603091	-2.608566	-1.833654
C	3.125335	-1.813540	-0.676457
N	0.502386	1.682140	-0.572571
C	-0.428211	2.375751	-0.545609
O	2.331755	0.331979	1.489218
C	1.463465	0.616938	2.382117
O	0.241121	0.651738	2.303854
C	2.143362	0.906681	3.738603
F	2.810425	-0.174170	4.148516
F	3.014273	1.908464	3.617637
F	1.256851	1.229709	4.667848
H	-0.879010	-0.293212	-1.768571
H	4.457106	-0.442906	0.214557
H	2.977704	-2.251404	0.309966
C	-2.350087	-4.371073	-0.270134
H	-2.252507	-2.310215	-1.997055
H	-0.071309	-0.218606	0.765645
H	1.250829	-2.167131	1.553954
H	-0.230975	-4.106758	1.375358
H	4.136564	1.810624	-1.952715
H	4.823250	-1.075947	-2.716842
H	5.721512	0.058983	-1.718966
H	4.366833	1.180289	-3.562774
H	1.700265	-3.138024	-1.508752
H	3.336939	-3.396162	-2.059704
H	3.177293	-1.705461	-3.727958
H	1.546347	-2.335693	-3.677874
H	1.930496	1.692151	-2.846709
H	0.697167	-0.258834	-3.059243
C	-1.528881	3.273467	-0.589738
C	-1.233520	4.633744	-0.777990
C	-2.263320	5.542906	-0.940886
C	-3.581949	5.093594	-0.930231
C	-3.871968	3.749115	-0.736322
C	-2.862119	2.804396	-0.545590
H	-0.196032	4.955802	-0.806454
H	-2.040112	6.595947	-1.083785
H	-4.395544	5.801945	-1.062484
H	-4.907243	3.418534	-0.700259
C	-3.227467	1.395293	-0.293601
C	-4.182989	0.766318	-1.104438
C	-4.594013	-0.530208	-0.844261
C	-4.062299	-1.223128	0.244132
C	-3.133847	-0.606045	1.082386
C	-2.715478	0.690548	0.802896
H	-4.598265	1.299783	-1.957184
H	-5.322560	-1.028101	-1.479062
O	-4.503560	-2.497020	0.441252
H	-2.735087	-1.131840	1.949444
H	-2.006148	1.174592	1.472708
Si	-3.701751	-3.843233	0.994374

H	-4.713562	-4.906194	1.055760
H	-3.020948	-3.597690	2.282841
H	-1.970958	-5.316191	0.141431
H	-2.855136	-4.532321	-1.228829

This TS was located as the maximum in a plot of ΔG vs C–H distance in the precursor complex (arenium ion) corresponding to a reaction coordinate in which the C–H bond stretches and the proton moves towards the trifluoroacetate oxygen.
0 imaginary frequencies
E = -2138.224828
G = -2137.757646
E_{LBS} = -2139.717803
G_{tot} = -2139.250621

TS1-*meta*

C	-0.053579	-3.736779	1.573572
C	-0.755972	-3.199841	0.476895
C	-0.342975	-1.969264	-0.007474
C	0.739728	-1.257188	0.601896
C	1.428529	-1.856560	1.709416
C	0.993514	-3.063617	2.206296
C	-1.909943	-3.944356	-0.111266
Si	-3.464145	-4.020593	0.971611
O	-4.540833	-2.812999	0.538514
C	-4.210814	-1.521339	0.281974
C	-4.903377	-0.861477	-0.733327
C	-4.577316	0.446047	-1.053007
C	-3.547955	1.116744	-0.379719
C	-2.890802	0.456782	0.664272
C	-3.222404	-0.849035	1.002575
C	-3.182703	2.489985	-0.769174
C	-1.838702	2.873668	-0.978804
C	-1.492062	4.186598	-1.336562
C	-2.488351	5.131507	-1.502005
C	-3.820963	4.764267	-1.321410
C	-4.160602	3.465915	-0.962533
C	-0.794647	1.915693	-0.899252
N	0.082673	1.156454	-0.866648
Rh	1.831025	0.065181	-0.649970
C	1.817872	-0.248146	-2.924949
C	3.150094	0.339291	-3.254670
C	4.343866	-0.212414	-2.461724
C	4.077289	-0.324733	-0.986549
C	3.583373	-1.433441	-0.327805
C	3.218798	-2.749533	-0.943987
C	2.516344	-2.651566	-2.296311
C	1.547143	-1.502906	-2.415824
O	2.329899	1.091059	1.099949
C	1.458205	1.461804	1.949303
O	0.296319	1.073367	2.090020
C	2.017013	2.518434	2.924148
F	2.468710	3.570771	2.243880
F	1.094555	2.929931	3.776838
F	3.032623	1.996570	3.610957
H	4.444721	0.491107	-0.359814
H	3.724852	-1.437328	0.752809
H	-0.891774	-1.509741	-0.828541
H	2.224020	-1.314530	2.212684
H	1.470003	-3.497233	3.080290
H	-0.350210	-4.715132	1.951393

H	3.078499	1.425598	-3.101831
H	4.661588	-1.181968	-2.856739
H	5.182592	0.476964	-2.598098
H	3.325372	0.216225	-4.334364
H	2.580013	-3.293098	-0.238379
H	4.135926	-3.350560	-1.029996
H	3.244427	-2.580469	-3.110961
H	1.957567	-3.577406	-2.466147
H	0.959686	0.348342	-3.239167
H	0.489974	-1.757384	-2.374009
H	-0.446924	4.441787	-1.490850
H	-2.230300	6.150330	-1.774976
H	-4.606249	5.504271	-1.452296
H	-5.202869	3.201062	-0.800298
H	-5.103899	0.947719	-1.862434
H	-5.682141	-1.395991	-1.271274
H	-2.721905	-1.338285	1.838427
H	-2.124630	0.974490	1.241463
H	-4.210365	-5.267880	0.733451
H	-3.061021	-3.897013	2.394157
H	-1.617527	-4.990938	-0.278644
H	-2.187234	-3.535746	-1.091373
H	0.243321	-0.271291	1.211243

This TS was located as the maximum in a plot of ΔG vs C–H distance in the precursor complex (arenium ion) corresponding to a reaction coordinate in which the C–H bond stretches and the proton moves towards the trifluoroacetate oxygen.
1 imaginary frequency
E = -2138.213864
G = -2137.748546
E_{LBS} = -2139.705546
G_{tot} = -2139.240228

TS2-*para*

C	-0.841716	2.052584	1.366300
C	0.010549	0.978608	1.137394
C	1.266393	1.137364	0.522770
C	1.648329	2.461121	0.224434
C	0.787753	3.536157	0.412608
C	-0.485807	3.342453	0.962076
Rh	2.127959	-0.335420	-0.801641
C	0.729176	0.361575	-2.260979
C	1.411048	0.385674	-3.603300
C	2.312300	-0.827216	-3.858670
C	3.036051	-1.264095	-2.605569
C	2.592756	-2.258560	-1.740806
C	1.300563	-3.025104	-1.844341
C	0.097819	-2.151958	-2.216917
C	0.182368	-0.761653	-1.618628
C	-2.305336	-2.517671	0.884028
N	-1.154111	-2.345204	0.906019
H	1.730244	-1.663490	-4.264185
H	3.047522	-0.570360	-4.630439
H	2.021498	1.298675	-3.641408
H	0.663408	0.490040	-4.406985
H	-0.016773	-2.084257	-3.306228
H	-0.814248	-2.635071	-1.844058
H	1.111831	-3.475305	-0.860401
H	1.401788	-3.864480	-2.551279
H	3.333423	-2.693057	-1.064193

```
H     4.086224   -0.973754   -2.528890
H    -0.537083   -0.558497   -0.822763
H     0.365983    1.338067   -1.926144
C    -3.703489   -2.813424    0.888064
H     2.348239    0.470978    1.446816
H     2.636730    2.649524   -0.202231
H     1.091503    4.542612    0.120092
H    -1.816981    1.885675    1.827288
H    -0.322972   -0.019836    1.426074
C    -4.680873   -1.814299    0.696208
C    -6.020192   -2.206704    0.794298
C    -6.378105   -3.522153    1.057511
C    -5.401026   -4.498516    1.230803
C    -4.065277   -4.142880    1.149000
H    -6.794820   -1.459918    0.635045
H    -7.430458   -3.788522    1.117090
H    -5.677688   -5.529525    1.432314
H    -3.282901   -4.883136    1.296361
C    -4.361043   -0.402444    0.399298
C    -3.421372   -0.036464   -0.572689
C    -5.070451    0.616767    1.048679
C    -4.857793    1.950140    0.736004
H    -5.793570    0.357341    1.819569
C    -3.931189    2.296304   -0.247487
H    -5.405799    2.741162    1.242313
C    -3.208910    1.296990   -0.901989
H    -2.872735   -0.805208   -1.116164
H    -2.491509    1.560487   -1.678413
O    -3.804428    3.611744   -0.564508
Si   -2.426784    4.561627   -0.615033
C    -1.472730    4.467137    1.006731
H    -1.538955    4.135264   -1.727642
H    -2.966889    5.912843   -0.877097
H    -0.971882    5.434491    1.150535
H    -2.195091    4.349468    1.826478
O     4.107981   -0.460340    0.208702
C     4.135479   -0.221696    1.414832
O     3.176268    0.217049    2.136895
C     5.433006   -0.436799    2.204071
F     6.382851   -0.956928    1.442931
F     5.212957   -1.255469    3.230132
F     5.861891    0.729098    2.684671
1 imaginary frequency
E = -2138.597866
G = -2138.136824
```

TS3-*para*

```
C    -1.307027    2.824618    1.233049
C    -0.138530    2.075572    1.123146
C     0.501286    1.886661   -0.110119
C    -0.055404    2.549323   -1.216316
C    -1.207502    3.320117   -1.102160
C    -1.864674    3.461385    0.123392
Rh    2.131143    0.540396   -0.272376
C     2.439488    0.140964    1.873749
C     3.127886   -1.183710    2.064448
C     4.222461   -1.504063    1.039089
C     3.946021   -0.953523   -0.339368
C     4.366939    0.279616   -0.780765
C     5.098750    1.319848    0.024884
C     4.571321    1.507375    1.449392
```

```
C    3.069155    1.348585    1.573976
Cl   1.731793    0.276173   -2.672608
C    0.088462   -2.391691   -0.137636
N    0.852119   -1.518737   -0.073090
H    5.194532   -1.133394    1.388062
H    4.327838   -2.592984    0.970725
H    2.359035   -1.963076    2.028106
H    3.542436   -1.216371    3.085167
H    5.057181    0.805868    2.139192
H    4.846702    2.508914    1.798723
H    5.010400    2.272042   -0.512816
H    6.174792    1.084319    0.047505
H    4.339177    0.457554   -1.855258
H    3.591242   -1.654852   -1.095027
H    2.512129    2.258487    1.798339
H    1.438272    0.180462    2.302453
C   -0.807112   -3.502675   -0.194555
H    2.141455    2.098744   -0.396547
H    0.423799    2.455125   -2.187787
H   -1.611578    3.817767   -1.985357
H   -1.798667    2.914374    2.202500
H    0.251264    1.625217    2.033277
C   -2.198133   -3.332352   -0.022109
C   -2.984127   -4.488343   -0.000715
C   -2.425144   -5.749688   -0.159522
C   -1.053117   -5.898457   -0.348358
C   -0.243700   -4.775006   -0.362329
H   -4.060668   -4.386135    0.117781
H   -3.069279   -6.625529   -0.146960
H   -0.617228   -6.884753   -0.479770
H    0.831986   -4.864793   -0.491401
C   -2.820467   -2.003896    0.132660
C   -2.458368   -0.926201   -0.683374
C   -3.817197   -1.795185    1.095385
C   -4.416724   -0.555490    1.249206
H   -4.110906   -2.613999    1.749845
C   -4.036116    0.512308    0.433589
H   -5.180556   -0.390798    2.005292
C   -3.056722    0.317125   -0.541198
H   -1.712468   -1.056966   -1.465918
H   -2.743889    1.134123   -1.187785
O   -4.651224    1.701729    0.640823
Si  -4.610733    3.109694   -0.271999
C   -3.165501    4.197306    0.229763
H   -4.518230    2.755016   -1.709527
H   -5.900687    3.768880    0.022875
H   -3.184437    5.078365   -0.428031
H   -3.337596    4.554087    1.253431
1 imaginary frequency
E = -2072.770140
G = -2072.332453
```

TS1-*para*-2

```
C   11.019850   -1.287974   -0.820350
C   10.962910    0.000279   -0.295261
C    9.738824    0.593356   -0.012751
C    8.534309   -0.076151   -0.242932
C    8.608531   -1.386584   -0.762379
C    9.843383   -1.982332   -1.050850
C    7.249601    0.578484    0.074662
C    7.097779    1.270956    1.283070
```

```
C     5.898822    1.882160    1.611766
C     4.824318    1.815273    0.727118
C     4.962631    1.158220   -0.494460
C     6.166810    0.542635   -0.809831
O     3.667405    2.432163    1.101065
Si    2.118595    2.084721    0.609587
C     1.742105    0.248178    0.973898
C     0.313953    0.031624    0.733302
C    -0.150541   -0.275903   -0.568688
C    -1.493465   -0.399006   -0.807891
C    -2.438881   -0.113670    0.224113
C    -1.969672    0.090511    1.555127
C    -0.620524    0.224214    1.774664
Rh   -4.211013   -0.919004   -0.543576
O    -5.147900    0.978341   -0.566011
C    -4.571637    2.099373   -0.515356
C    -5.525270    3.277549   -0.796937
F    -6.029901    3.147881   -2.022682
C     7.431549   -2.175598   -0.954730
N     6.492455   -2.844990   -1.110230
C    -5.904582   -1.488428    0.687895
C    -4.855730   -1.150153    1.562921
C    -4.075564   -2.157327    2.348342
C    -3.548087   -3.329861    1.522000
C    -3.244594   -2.979197    0.087726
C    -4.119549   -3.125185   -0.972505
C    -5.581053   -3.451319   -0.889456
C    -6.315182   -2.892522    0.343646
O    -3.377419    2.338022   -0.282171
F    -6.531079    3.261563    0.074121
F    -4.904617    4.441464   -0.711830
H    -6.163447   -3.535067    1.217433
H    -7.386859   -2.890135    0.126757
H    -6.057982   -3.066595   -1.799895
H    -5.706426   -4.543340   -0.932922
H    -4.252151   -4.168728    1.532616
H    -2.625751   -3.698836    1.979888
H    -3.251762   -1.661748    2.865892
H    -4.745405   -2.513677    3.146528
H    -4.860503   -0.124514    1.938577
H    -6.598482   -0.689709    0.418976
H    -2.191660   -2.858572   -0.170008
H    -3.688052   -3.136230   -1.975890
H    -2.801838    1.053682   -0.021617
H    -1.848204   -0.642508   -1.813096
H     0.568368   -0.421708   -1.372115
H    -0.259202    0.490775    2.765794
H    -2.666482    0.302688    2.361218
H     2.374504   -0.348502    0.305187
H     2.023338    0.069568    2.018562
H     1.911734    2.315361   -0.838002
H     1.243151    2.939360    1.430089
H     5.771925    2.405227    2.556090
H     4.142135    1.140460   -1.210478
H     7.927433    1.307698    1.986214
H     6.270280    0.049840   -1.774526
H     9.706080    1.608517    0.377025
H    11.880923    0.552366   -0.109675
H     9.862966   -2.996287   -1.441998
H    11.976841   -1.751363   -1.043082
1 imaginary frequency
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E = -2138.181856
G = -2137.721315
E_{LBS} = -2139.674901
G_{tot} = -2139.214360

S14

C	1.514330	2.858456	0.277779
C	1.555154	1.903827	1.290993
C	2.698064	1.133843	1.481593
C	3.818654	1.299497	0.662027
C	3.768317	2.267300	-0.347493
C	2.627625	3.039190	-0.539582
C	-0.265109	-1.096941	-0.220719
C	0.570415	-0.535375	-1.194086
C	1.918781	-0.852606	-1.255953
C	2.467174	-1.720040	-0.310700
C	1.645979	-2.311714	0.647969
C	0.294718	-2.000226	0.690436
C	-4.368108	0.203251	0.005697
C	-3.307197	1.129998	-0.161000
C	-1.999013	0.674008	-0.232957
C	-1.680887	-0.687474	-0.141764
C	-2.739309	-1.592710	0.020534
C	-4.072756	-1.143271	0.093368
C	-2.516264	-3.000498	0.065139
N	-2.367645	-4.155087	0.099905
C	5.017101	0.408250	0.807577
Si	5.064210	-0.953230	-0.489304
H	5.028773	-0.342533	-1.842064
H	6.262419	-1.805031	-0.342556
O	3.792759	-2.029119	-0.295168
H	0.621605	3.463776	0.129091
H	0.691012	1.756715	1.937162
H	2.723664	0.381546	2.269702
H	4.636668	2.410439	-0.991123
H	2.608864	3.787468	-1.329199
H	0.153030	0.156216	-1.924097
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H	2.088312	-2.991968	1.371778
H	-0.326460	-2.440678	1.467906
O	-5.606289	0.732145	0.067049
O	-3.669912	2.421098	-0.228529
H	-1.184280	1.385209	-0.338055
H	-4.864556	-1.876726	0.210359
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H	5.950570	0.977796	0.687201
C	-2.644897	3.391425	-0.355923
C	-6.688086	-0.165574	0.229034
H	-3.146369	4.359660	-0.404430
H	-2.061168	3.241612	-1.273546
H	-1.972158	3.376418	0.512560
H	-7.593026	0.444666	0.249652
H	-6.609966	-0.725026	1.171005
H	-6.752149	-0.874234	-0.607562

E = -1420.163238
G = -1419.833927
E_{LBS} = -1420.454631
G_{tot} = -1420.125320

TS1-*para*-3

C	-2.907043	2.628999	0.410922
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C	-1.325734	2.702917	-1.463913
C	-1.043687	1.380843	-1.290045
C	-1.647190	0.632946	-0.212820
C	-2.666835	1.296480	0.571123
C	-2.322885	4.821053	-0.614576
Si	-1.109363	5.550038	0.686641
O	0.459753	5.219220	0.253836
C	1.115938	4.027920	0.165526
C	2.044580	3.891005	-0.867100
C	2.750956	2.708047	-1.008528
C	2.541028	1.634213	-0.131644
C	1.617961	1.795171	0.908157
C	0.912971	2.983457	1.066812
C	3.362088	0.410236	-0.248877
C	2.828016	-0.890516	-0.299183
C	3.664267	-2.029109	-0.361656
C	5.035060	-1.881632	-0.380341
C	5.588973	-0.571437	-0.353904
C	4.752445	0.536633	-0.291667
C	1.433691	-1.107391	-0.386941
N	0.297530	-1.324981	-0.506849
Rh	-1.783040	-1.475714	-0.517080
C	-1.654755	-2.368260	-2.591855
C	-2.493489	-3.592773	-2.419202
C	-3.880088	-3.367077	-1.804730
C	-3.850066	-2.436929	-0.624545
C	-4.048679	-1.071221	-0.668333
C	-4.320024	-0.247389	-1.890103
C	-3.485390	-0.621025	-3.115912
C	-2.078281	-1.069924	-2.805749
O	5.926063	-2.884982	-0.428572
C	5.424413	-4.209811	-0.426778
O	6.921288	-0.514126	-0.376404
C	7.542354	0.763948	-0.332792
O	-1.951048	-1.664804	1.547498
C	-1.185661	-1.132364	2.419548
O	-0.368674	-0.227675	2.293197
C	-1.417570	-1.751990	3.815059
F	-1.209482	-3.068619	3.779496
F	-0.611578	-1.224332	4.723210
F	-2.678979	-1.541611	4.196972
H	-0.271422	0.918408	-1.897994
H	-3.842196	-2.897823	0.365081
H	-4.295567	-0.606947	0.285612
H	-0.815928	3.278602	-2.233224
H	-0.777142	0.445095	0.679287
H	-3.146421	0.761521	1.385908
H	-3.593047	3.146391	1.078570
H	-1.926783	-4.297601	-1.795283
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H	-4.261558	-4.334307	-1.463698
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H	-4.150278	0.806219	-1.638923
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H     3.210867   -3.014809   -0.405045
H     5.182792    1.532567   -0.235672
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H     2.192134    4.721170   -1.553105
H     0.215663    3.092842    1.896534
H     1.471617    0.998070    1.634157
H    -1.226092    7.013892    0.654021
H    -1.464379    4.959516    1.994094
H    -3.301719    5.185035   -0.273050
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H     7.260154    1.372363   -1.200816
H     7.287128    1.298214    0.590513
H     6.296389   -4.865889   -0.439733
H     4.834336   -4.412388    0.476555
H     4.812161   -4.408117   -1.316170
```

This TS was located as the maximum in a plot of ΔG vs C–H distance in the precursor complex (arenium ion) corresponding to a reaction coordinate in which the C–H bond stretches and the proton moves towards the trifluoroacetate oxygen.

0 imaginary frequencies

E = -2367.157781

G = -2366.629915

E_{LBS} = -2368.711109

G_{tot} = -2368.183243

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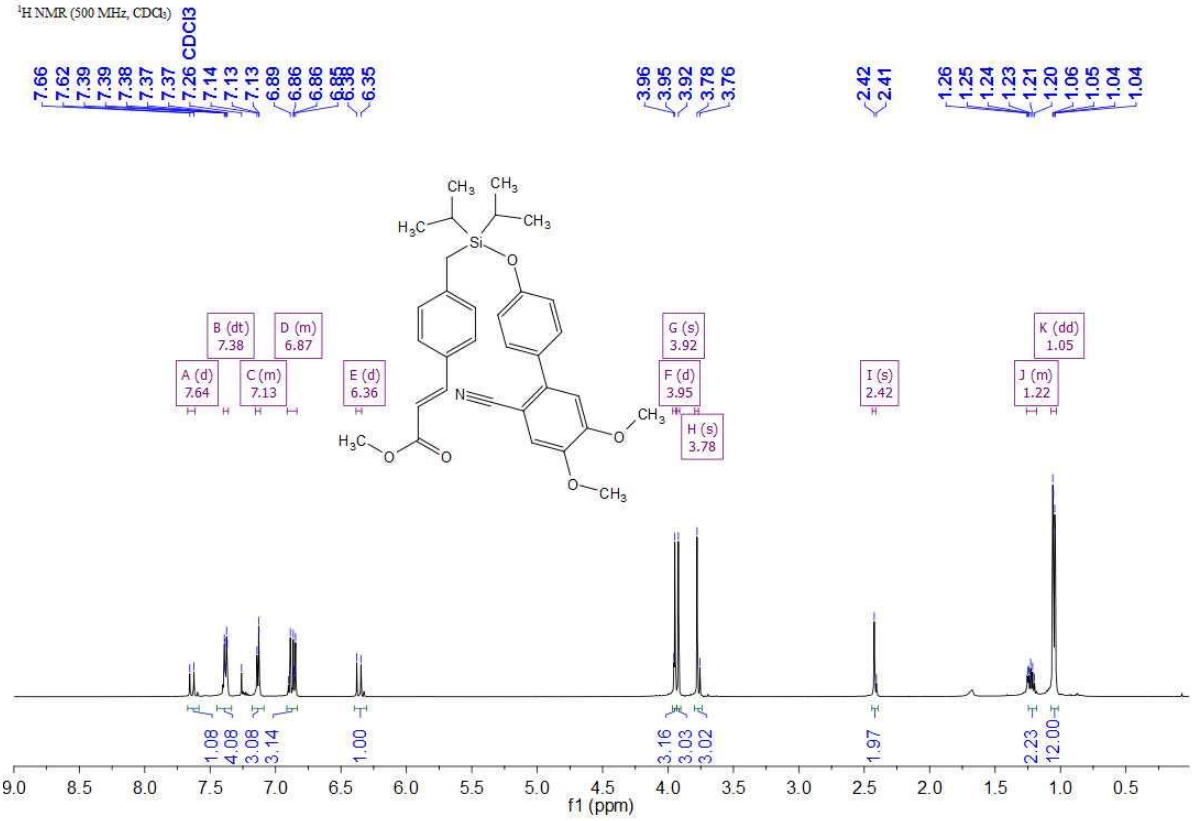
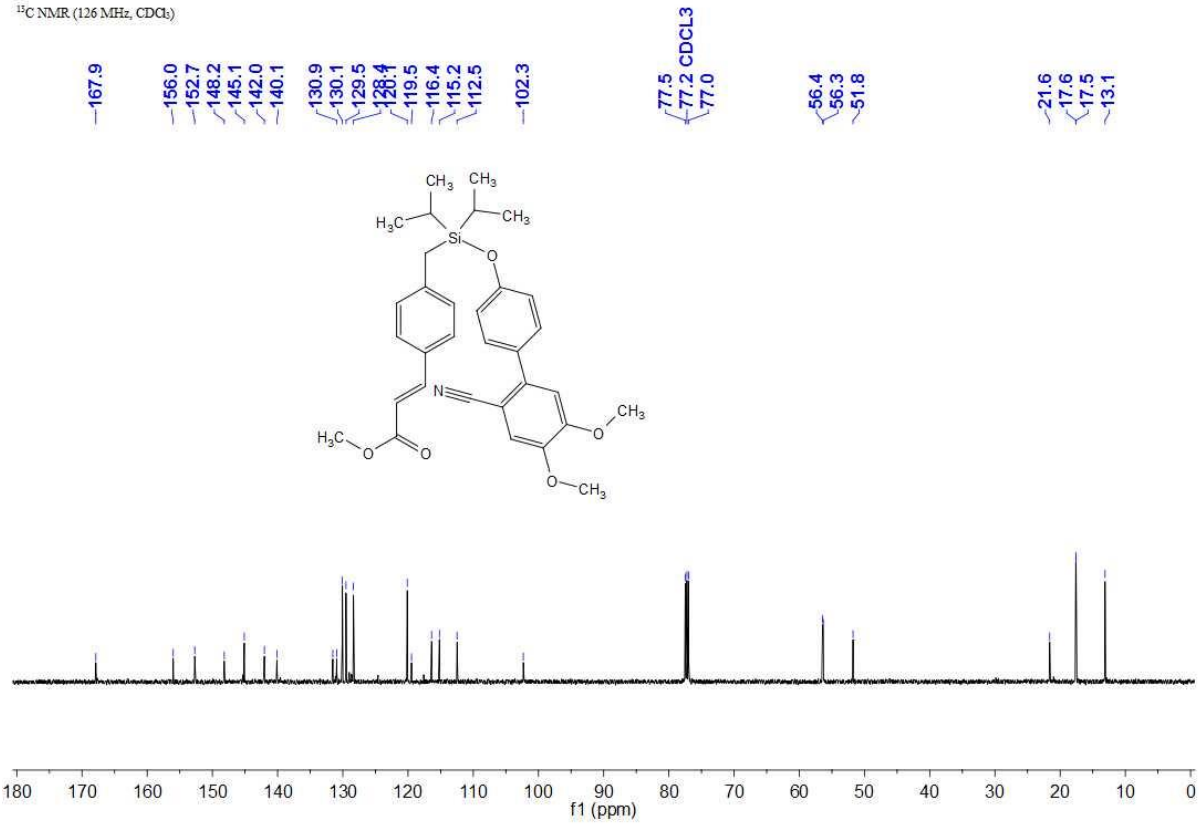
NMR Spectra

2a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4- yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate





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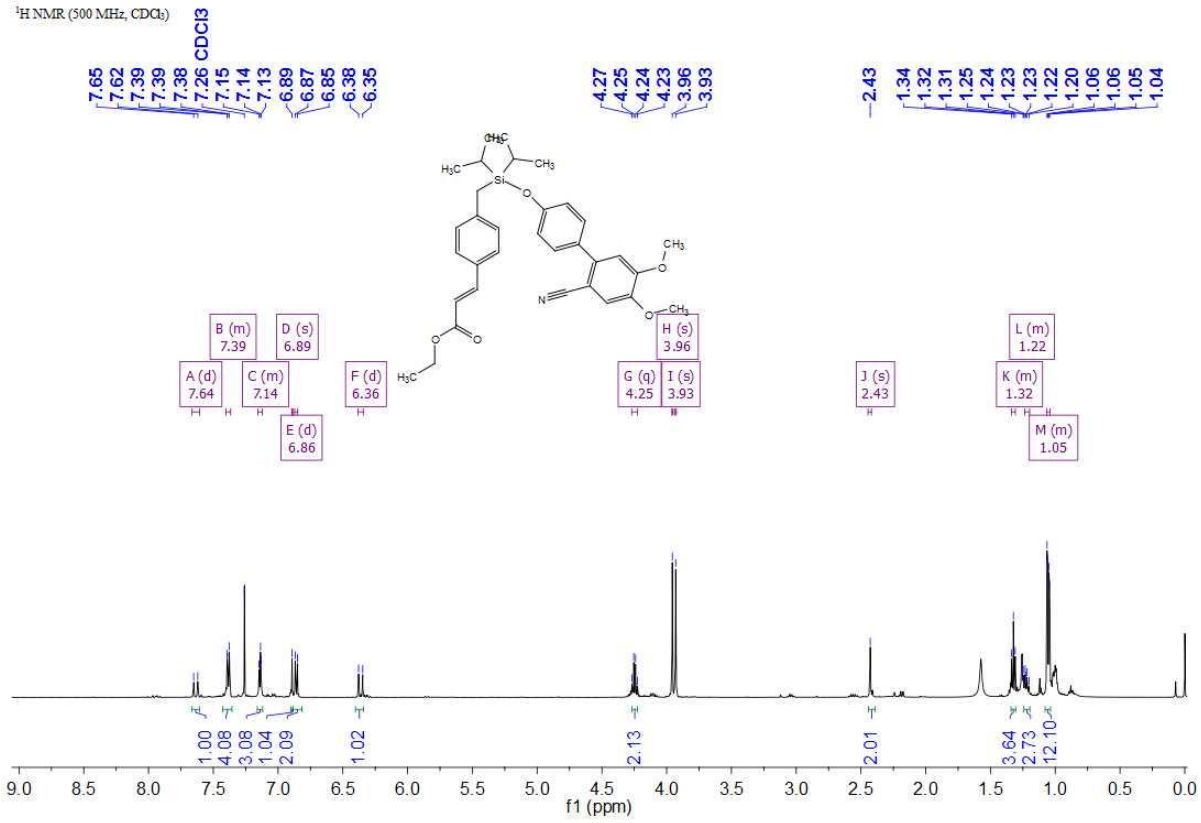
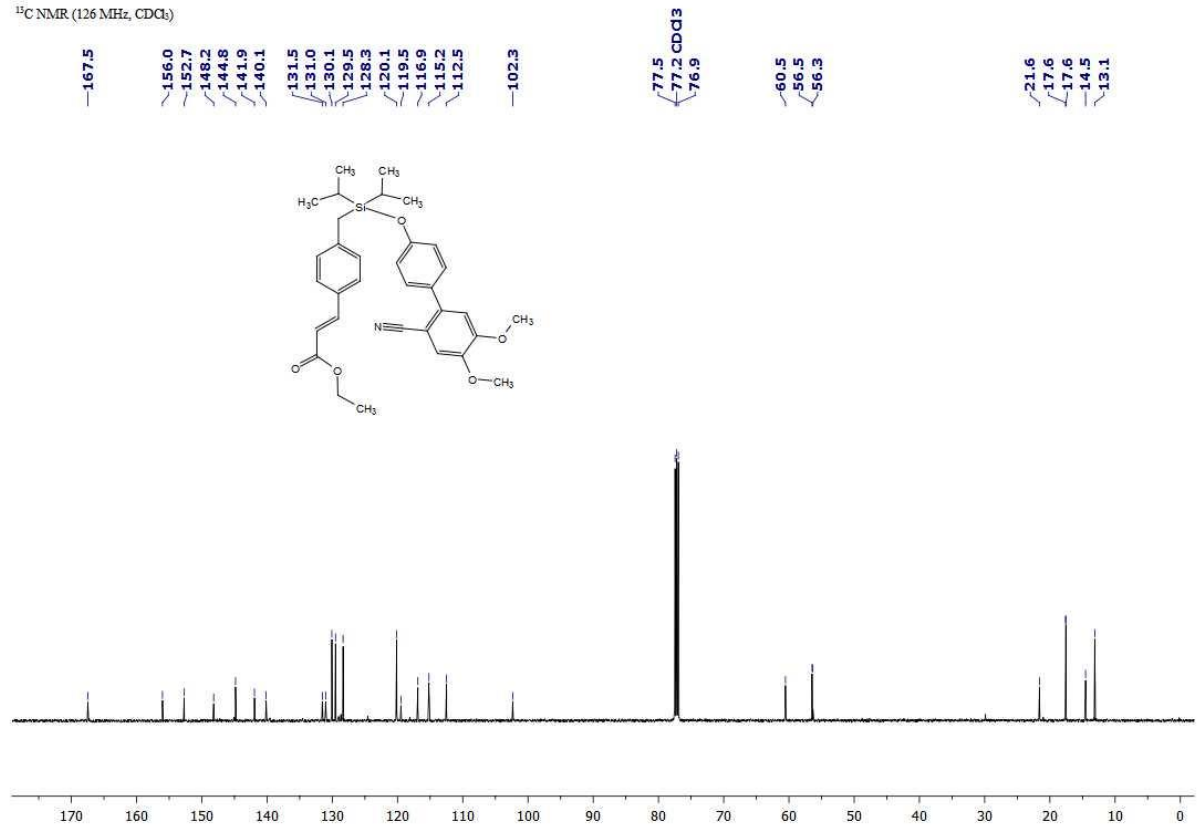
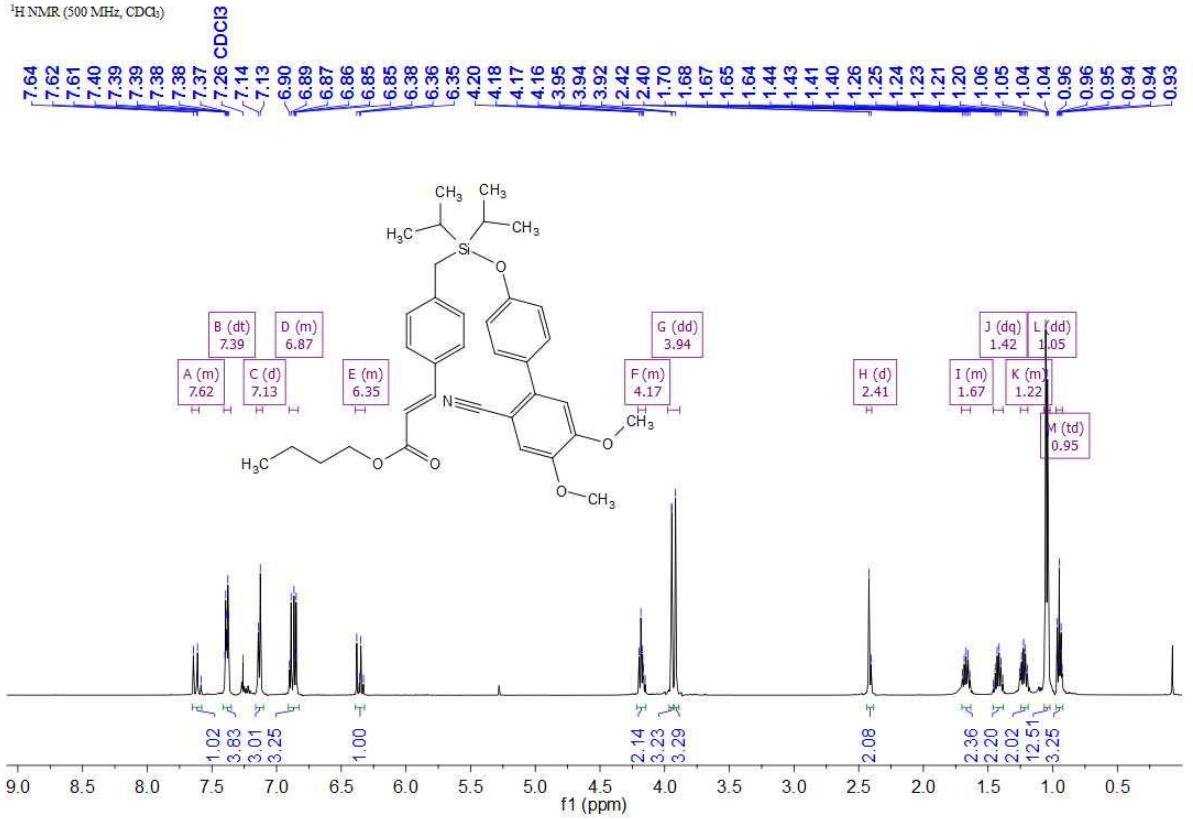
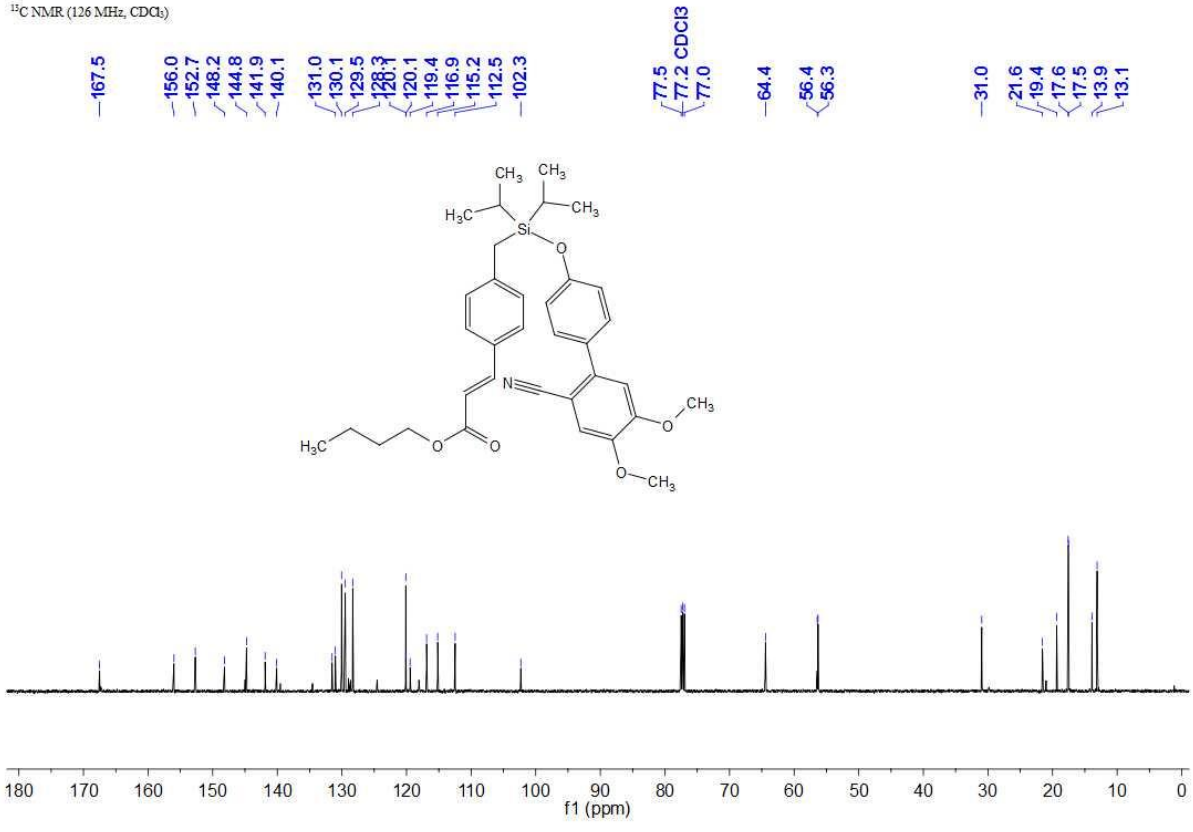


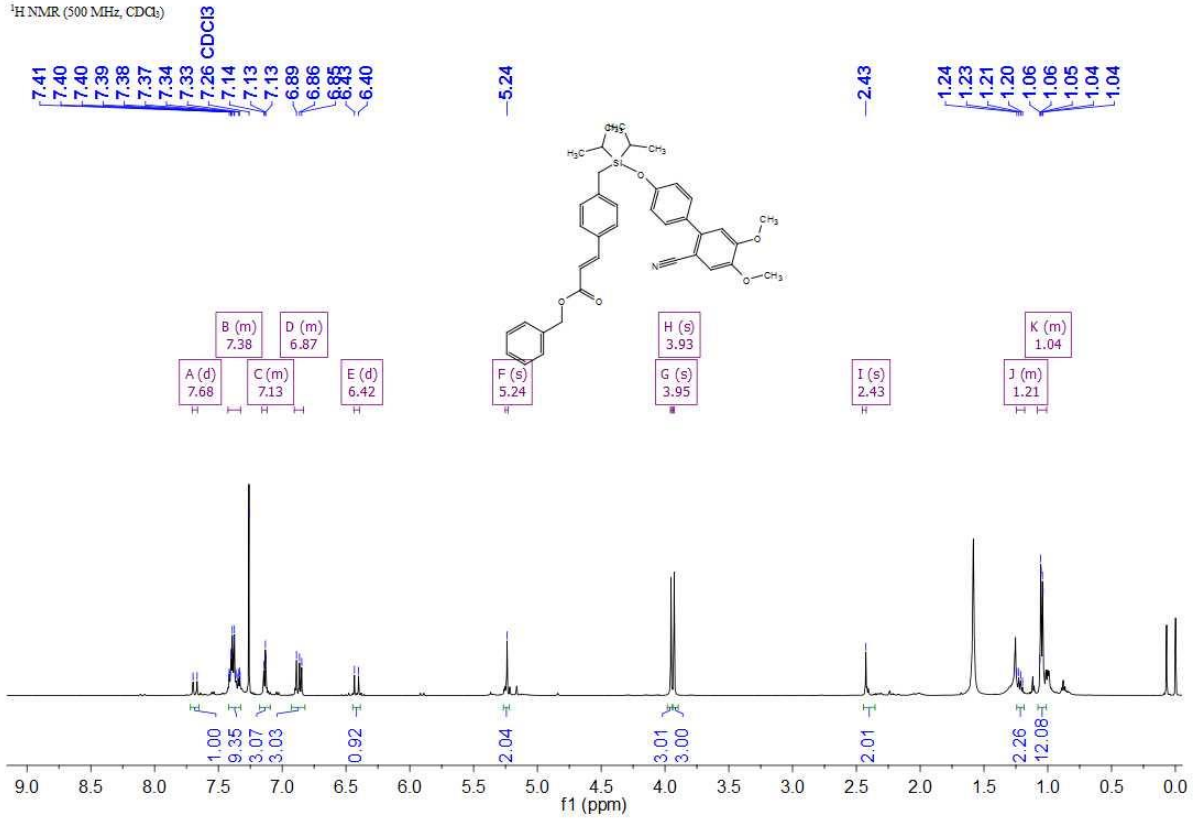


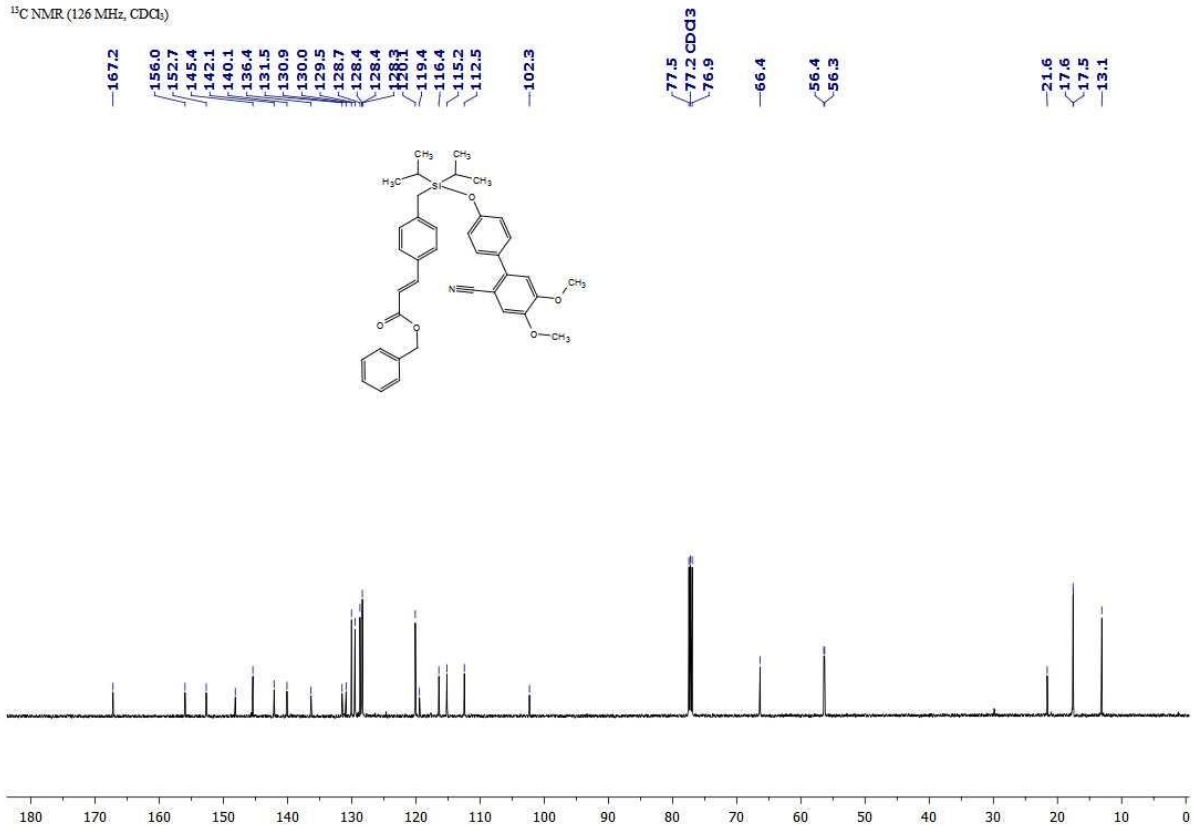
2c. butyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



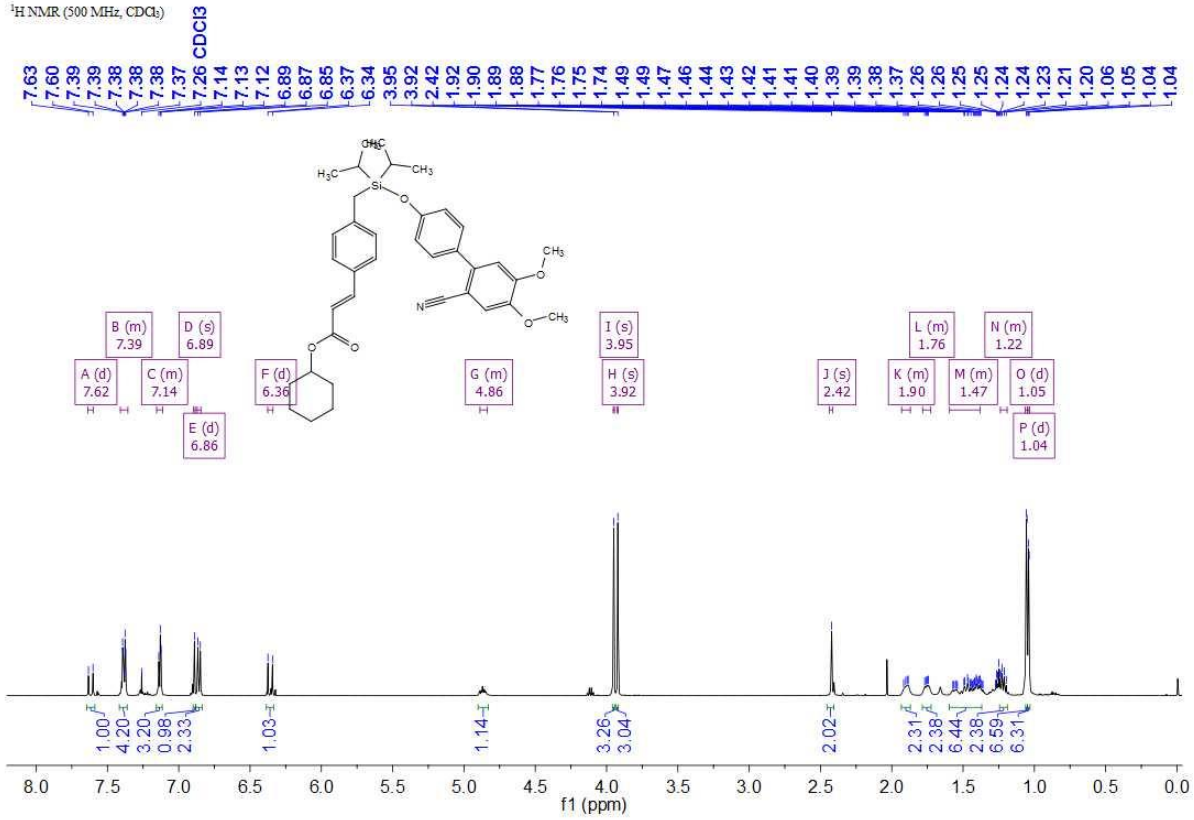


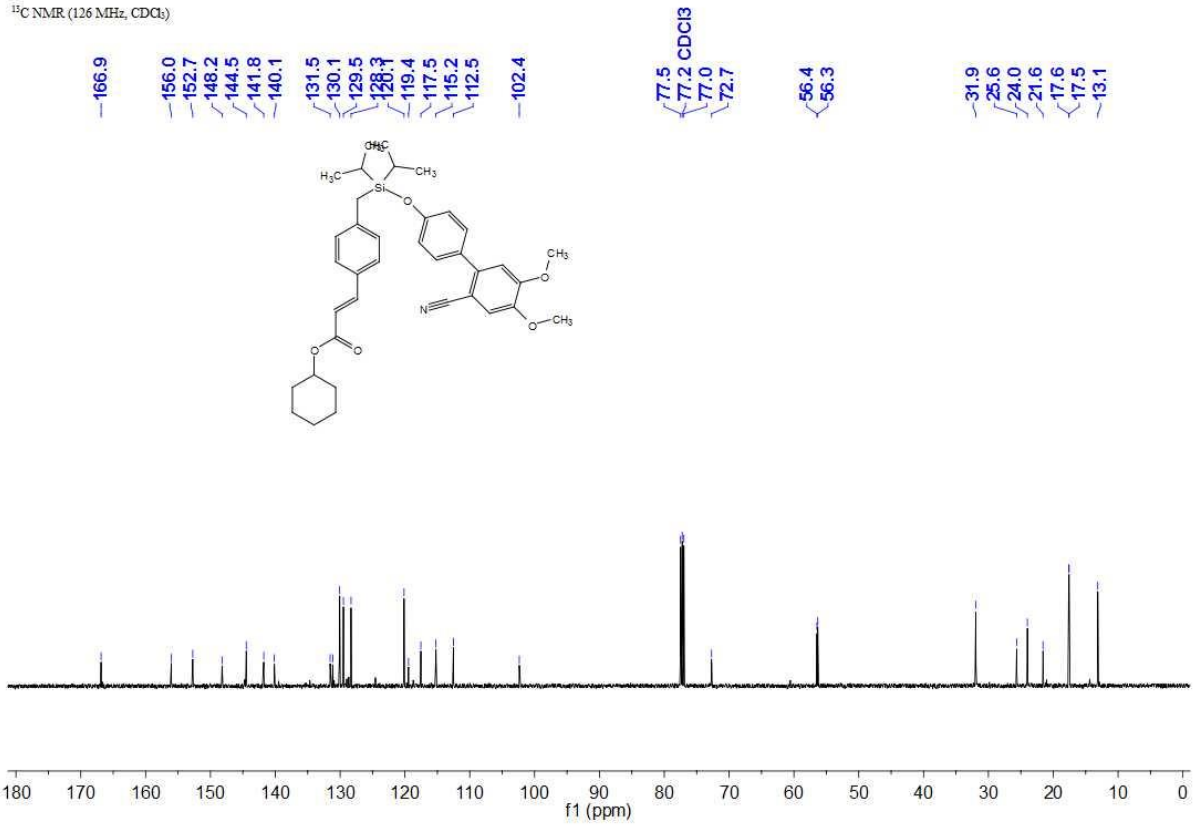
2d. benzyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



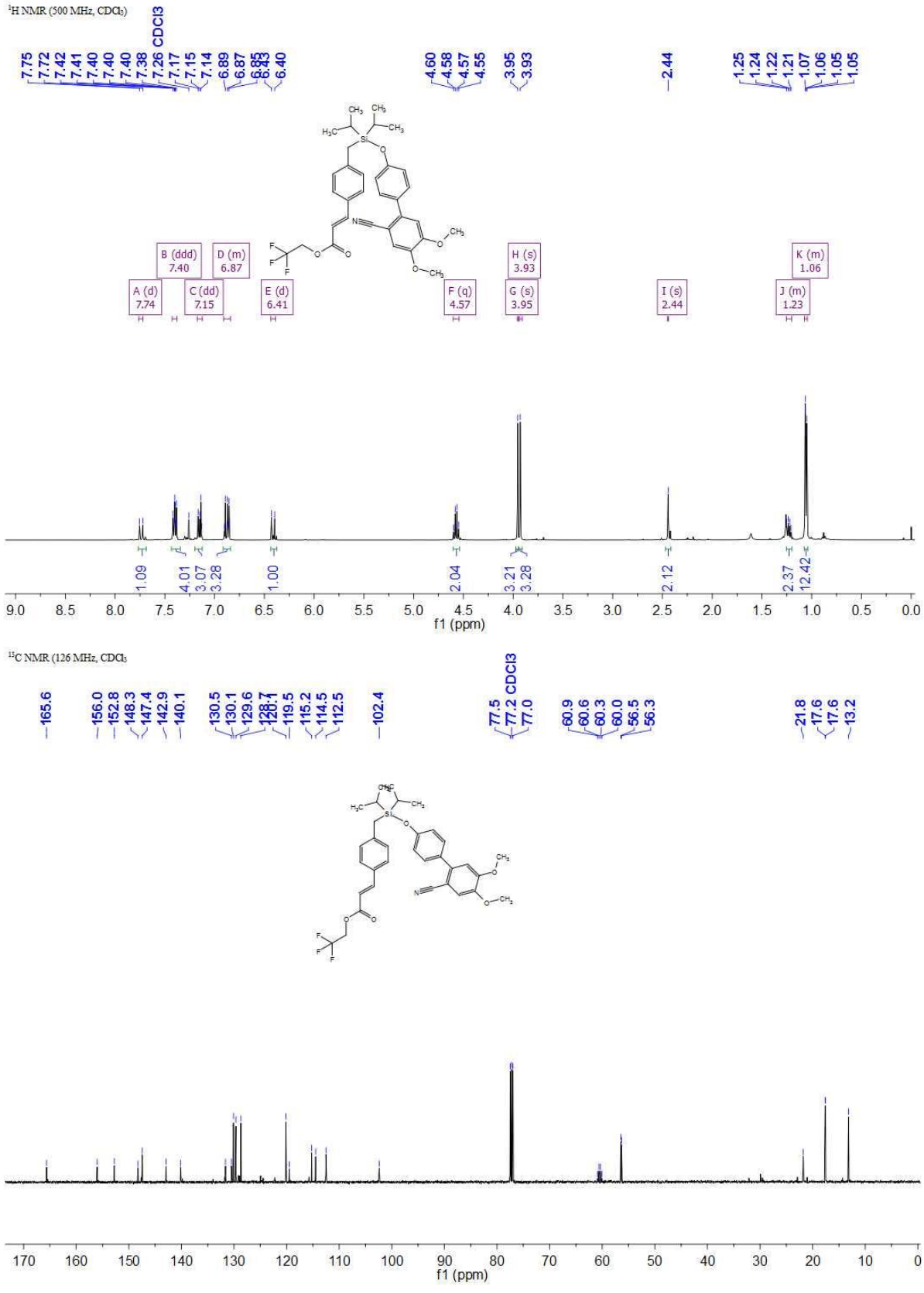


2e. cyclohexyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate





2f. 2,2,2-trifluoroethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)phenyl)acrylate



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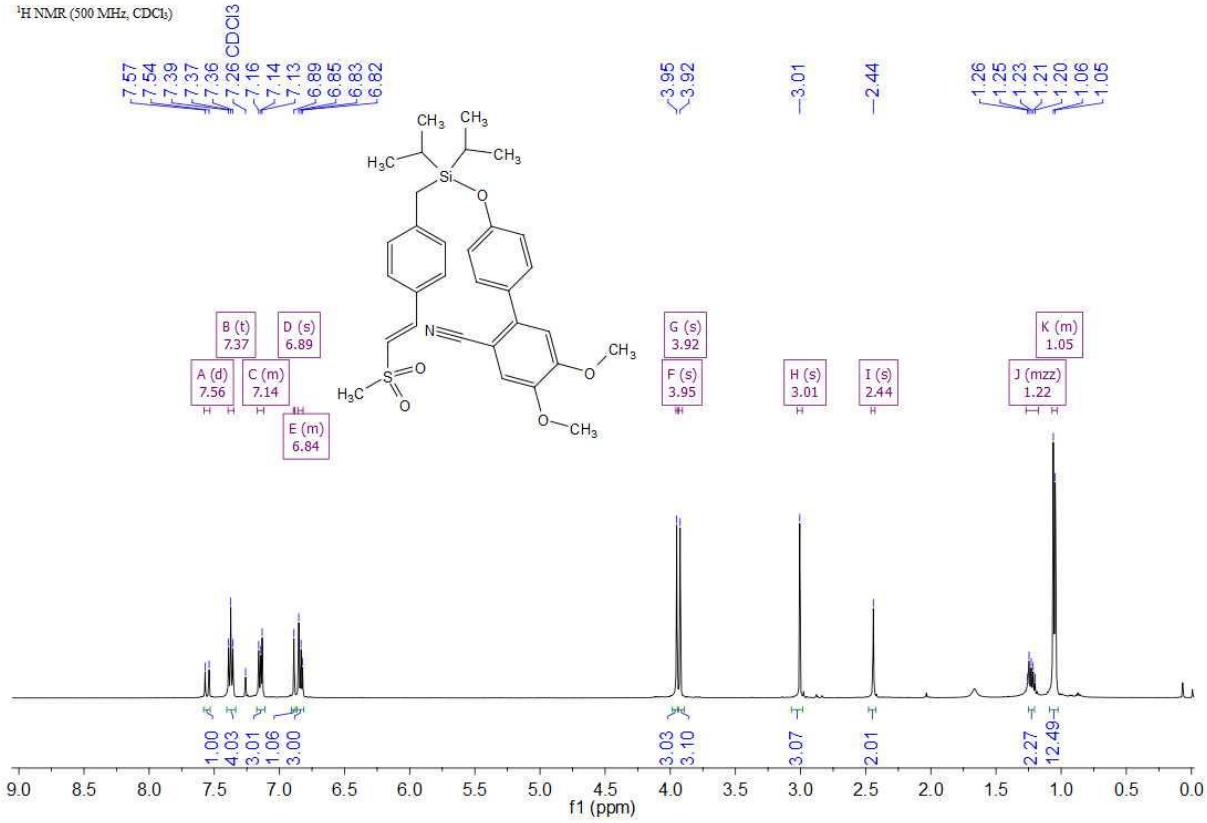

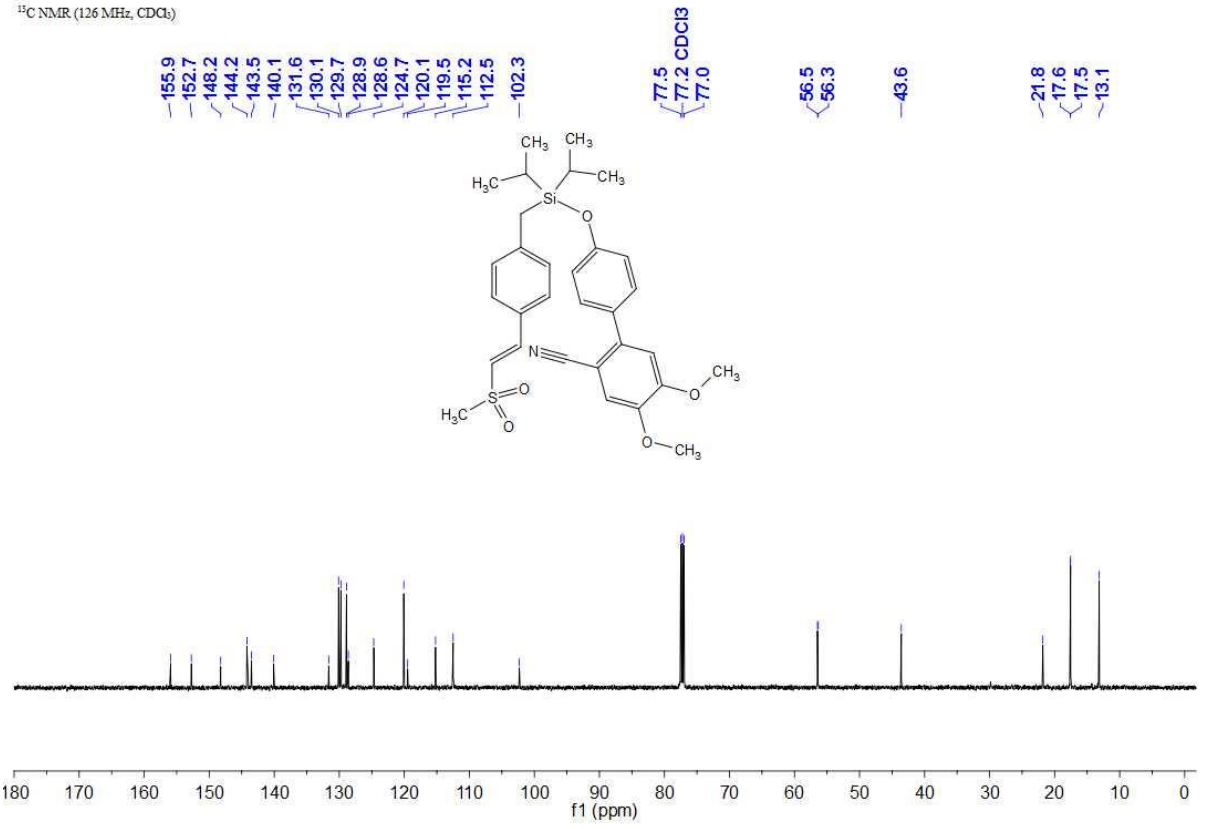

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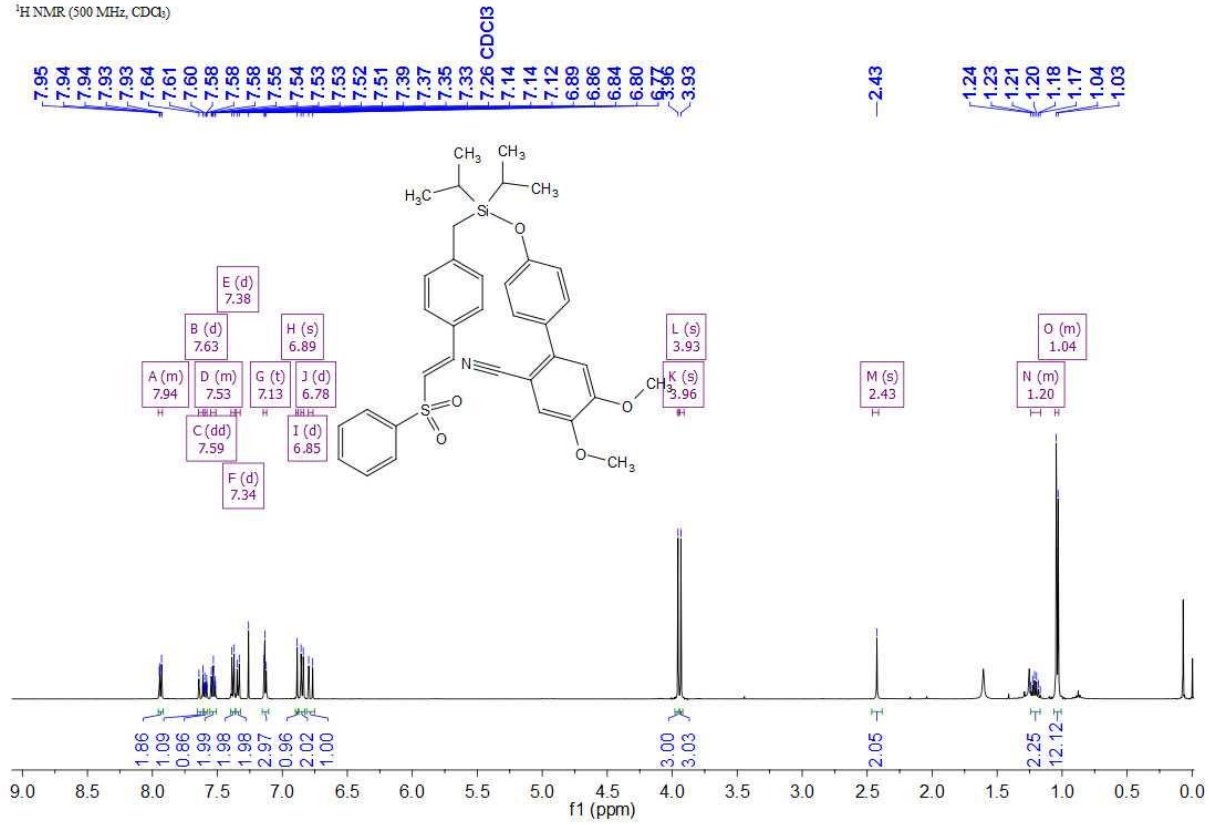
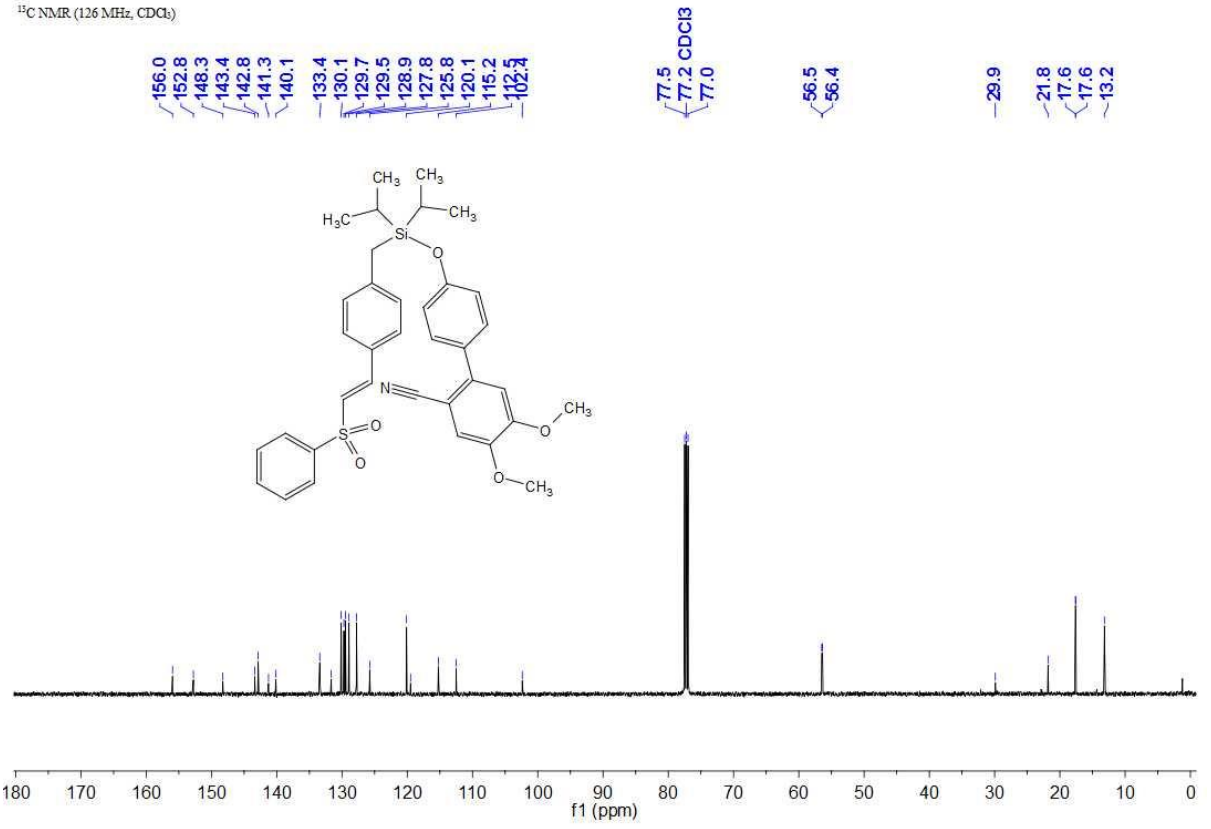
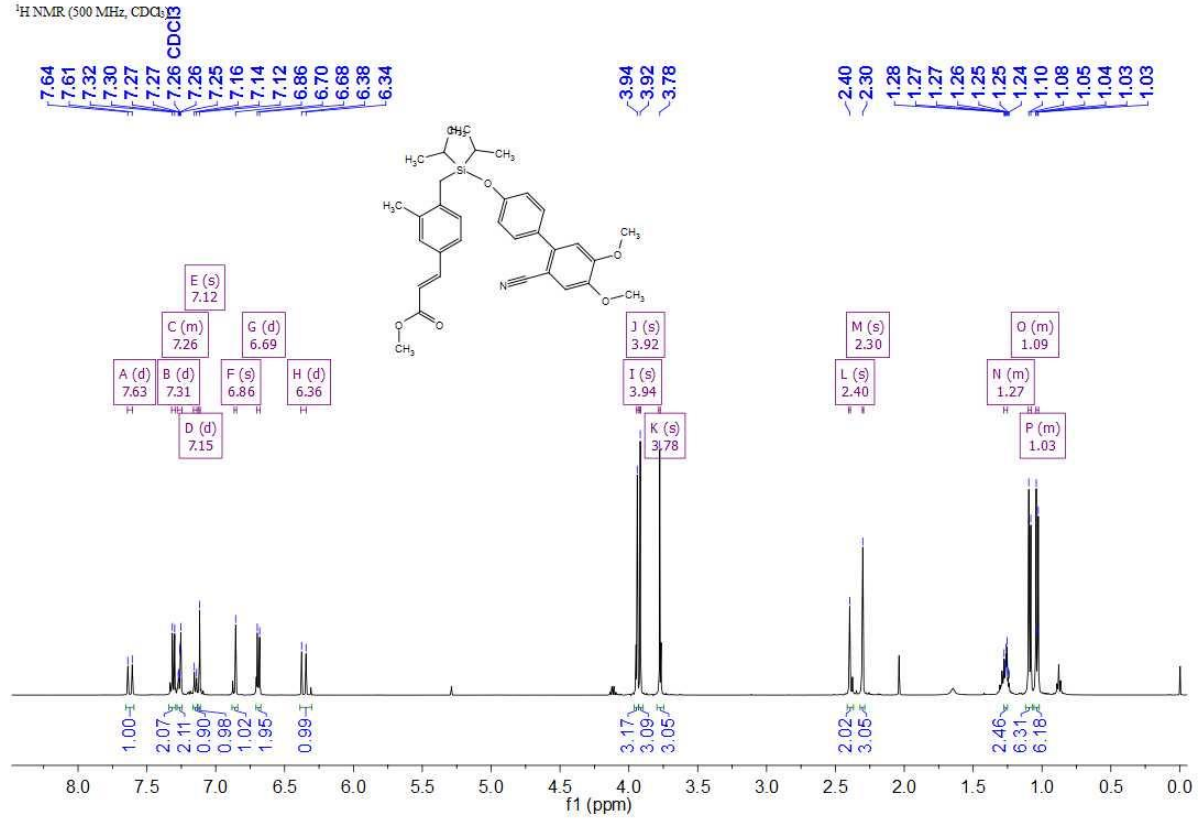
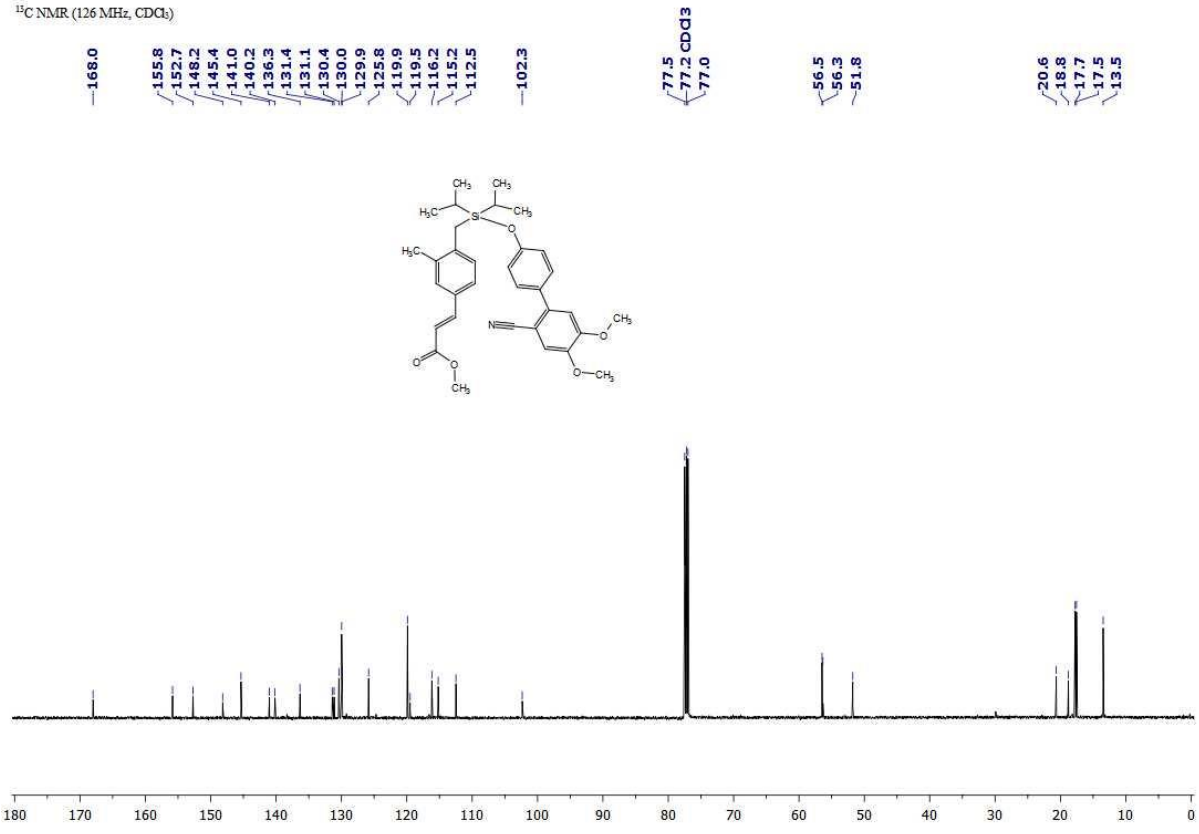




4a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate





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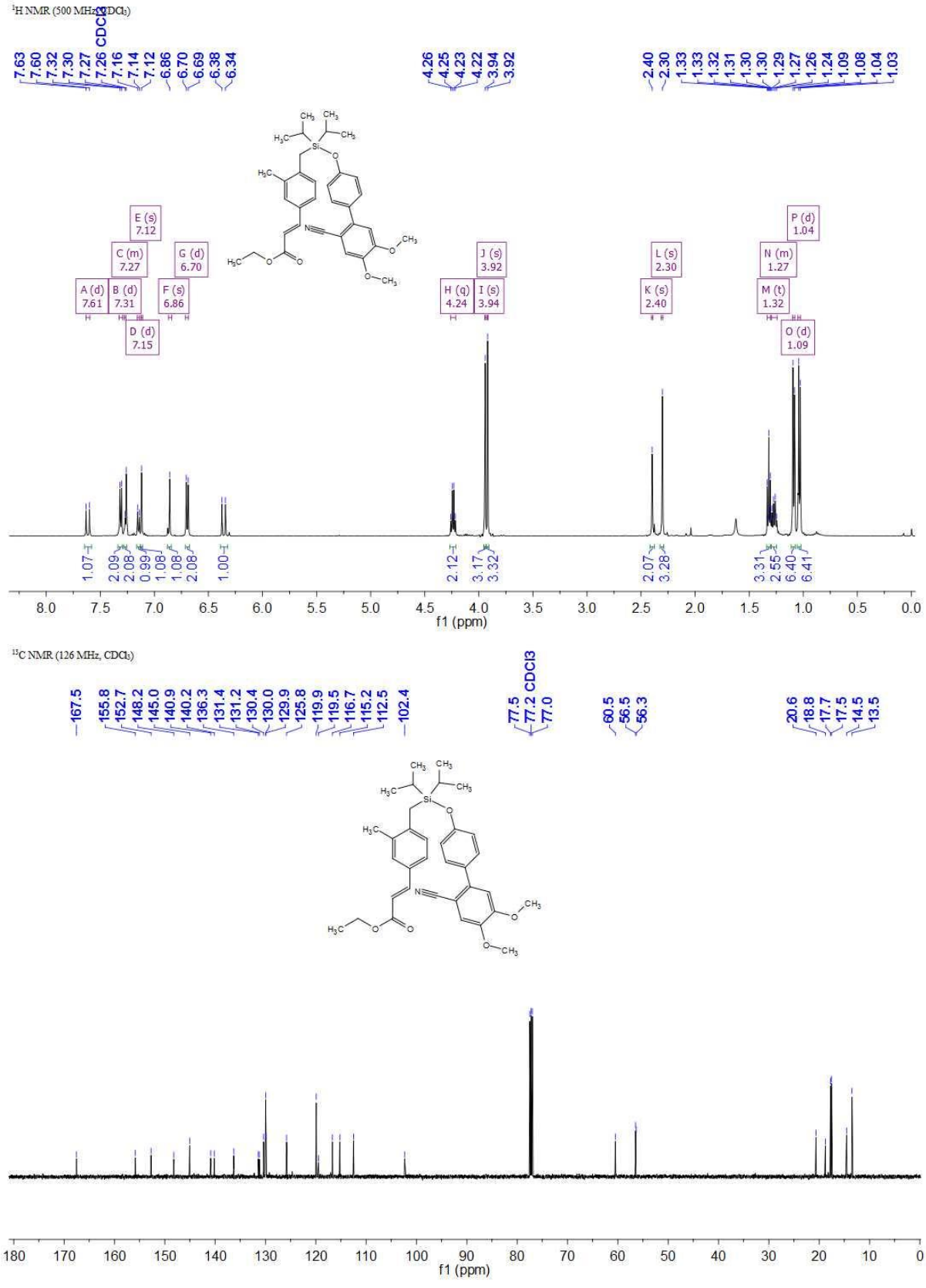
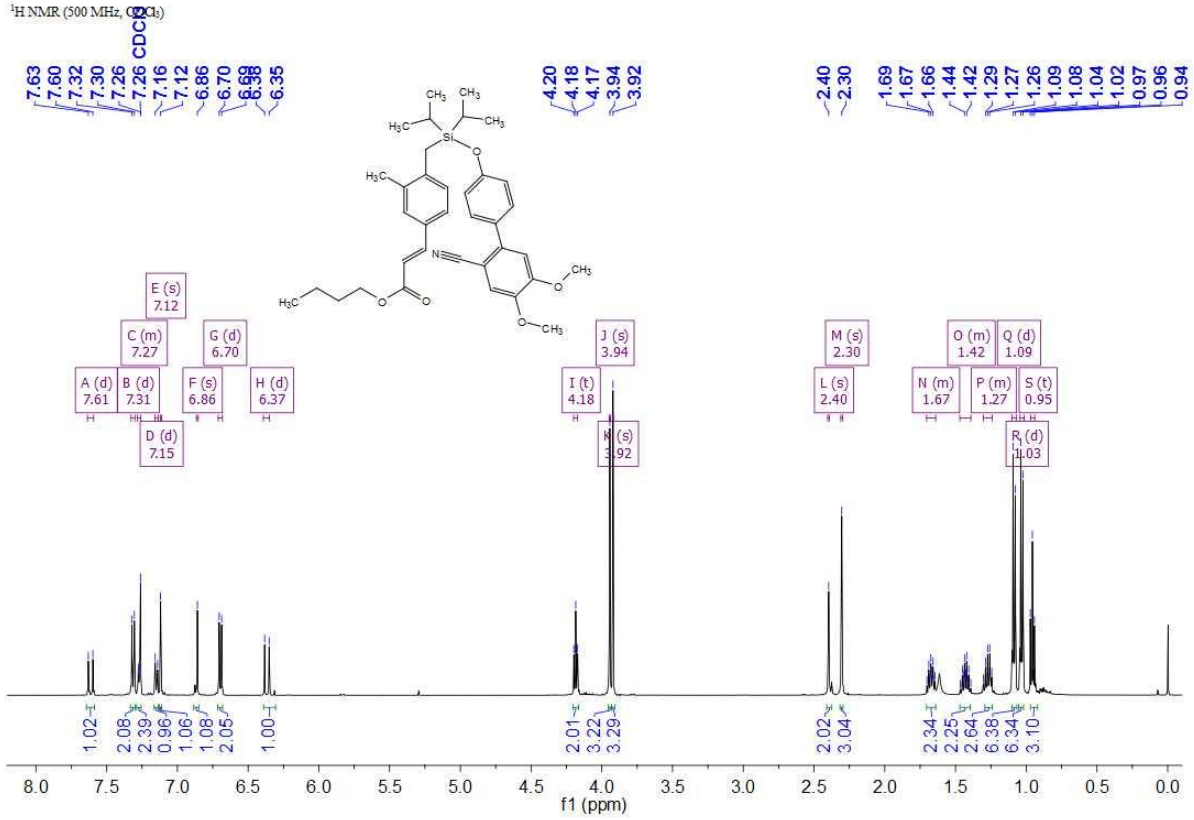
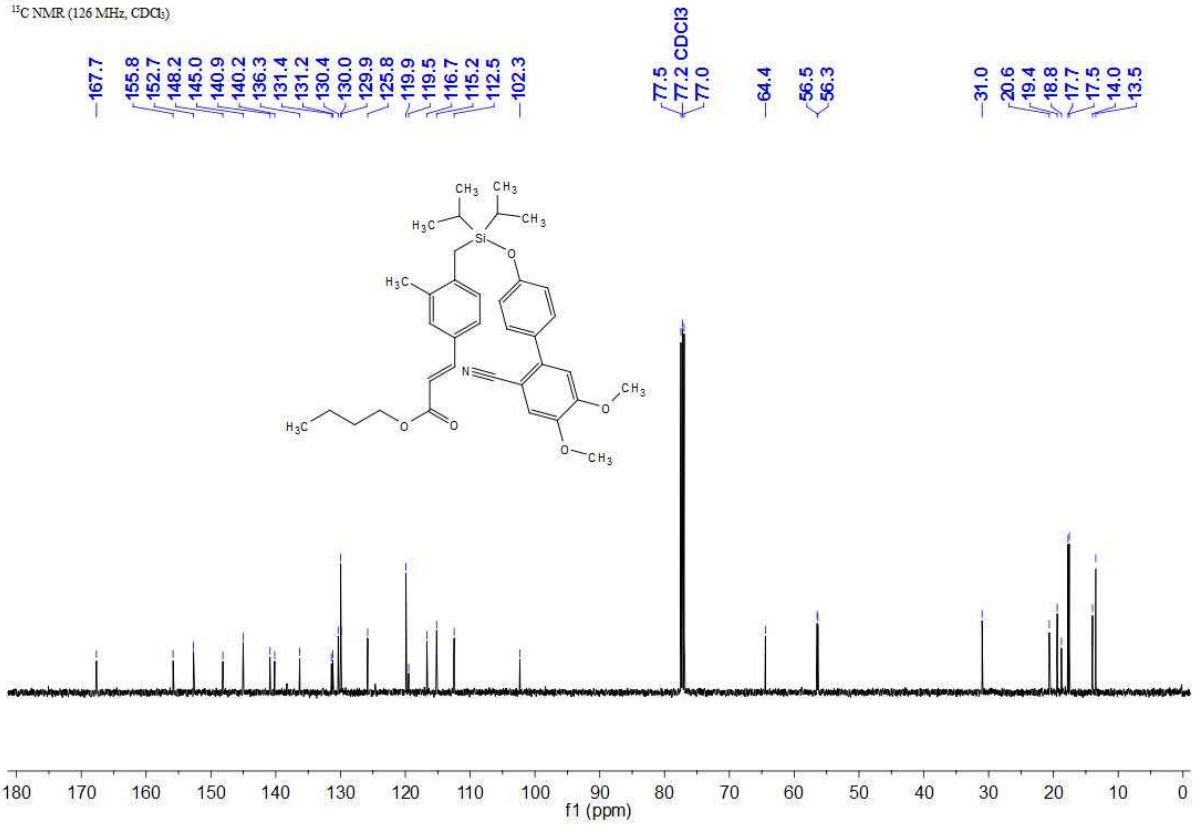
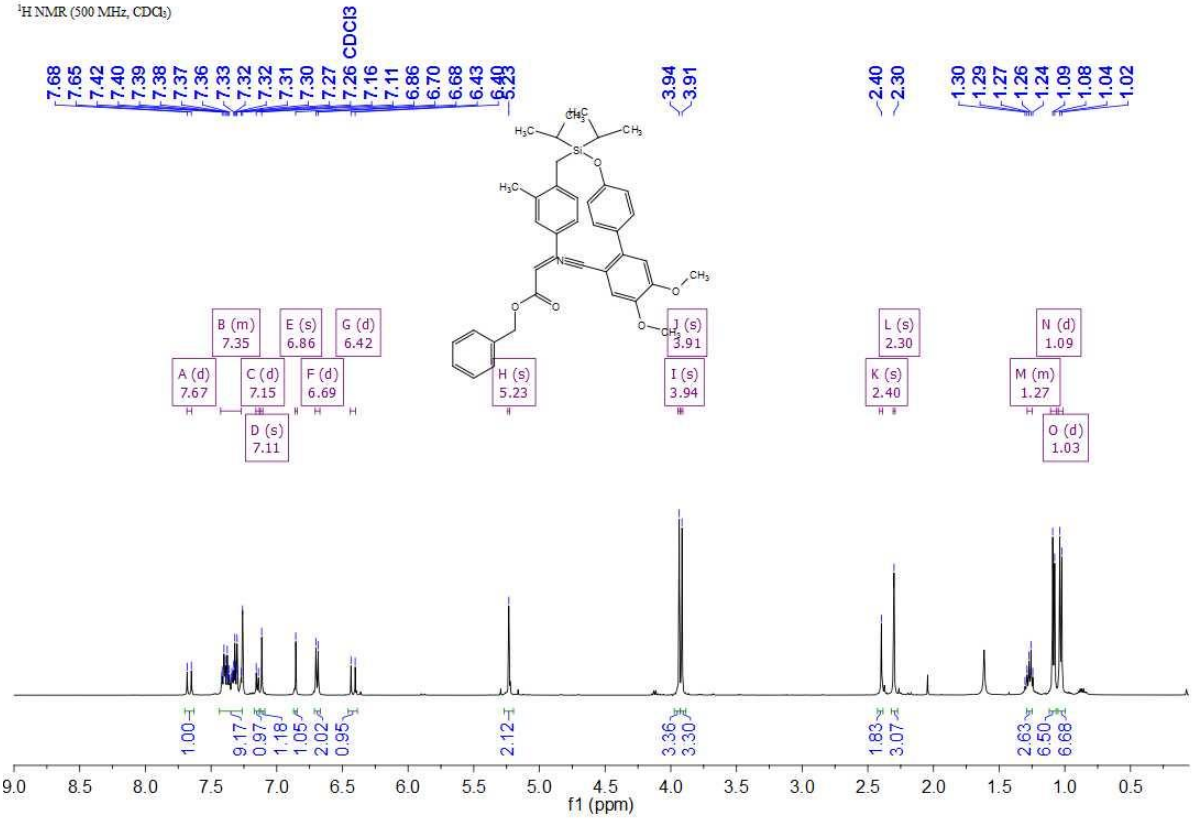


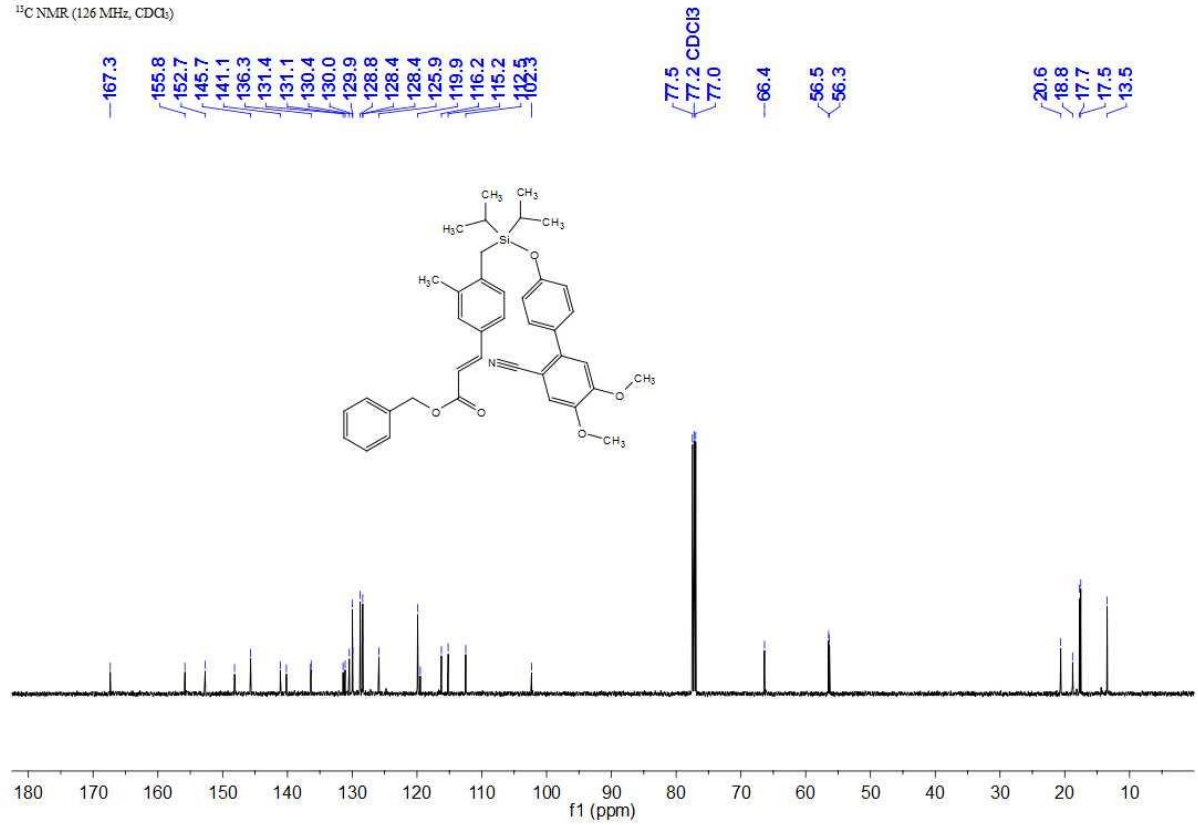
4c. butyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



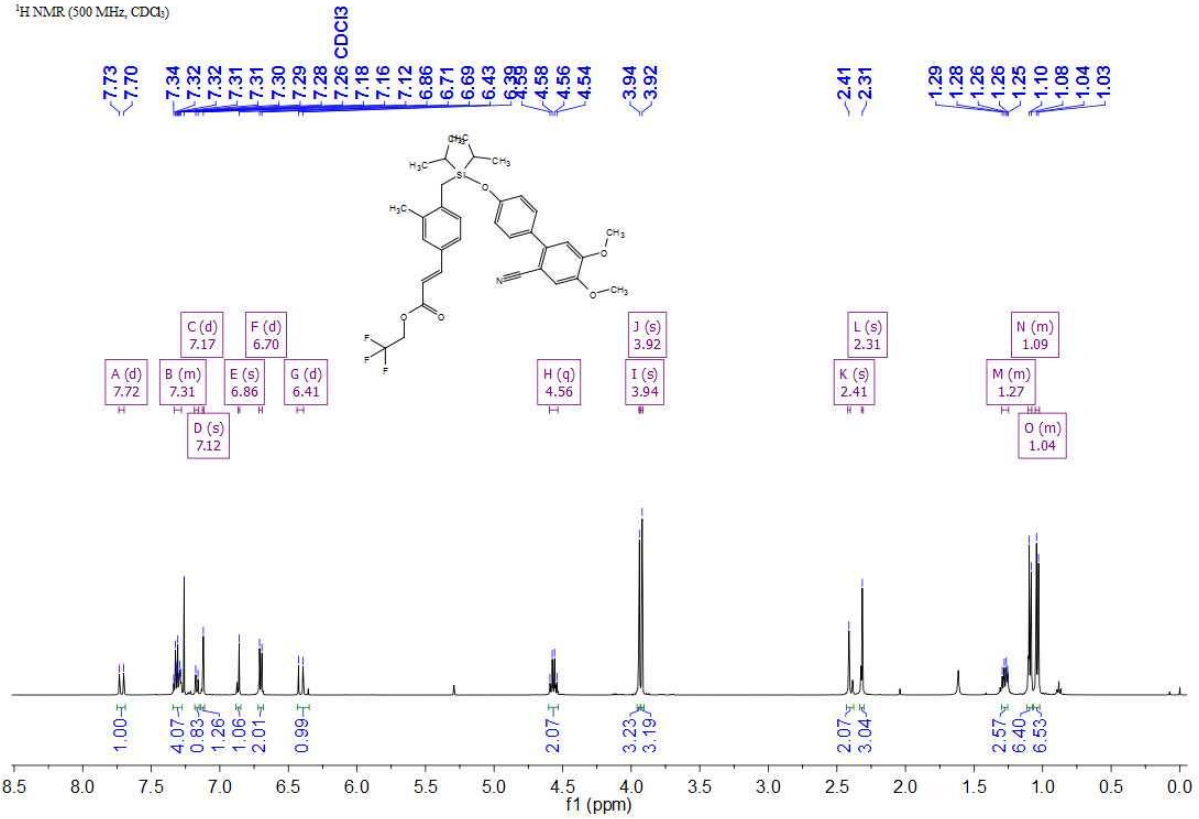


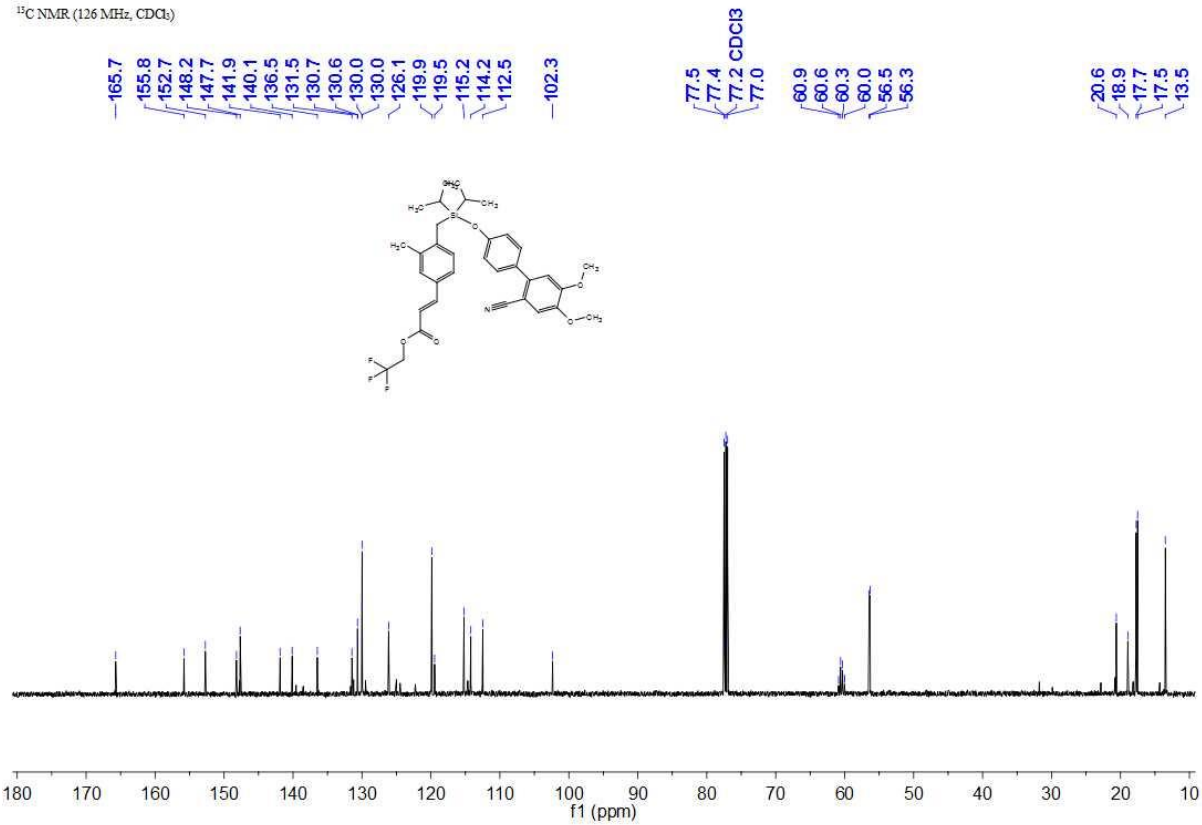
4d. benzyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



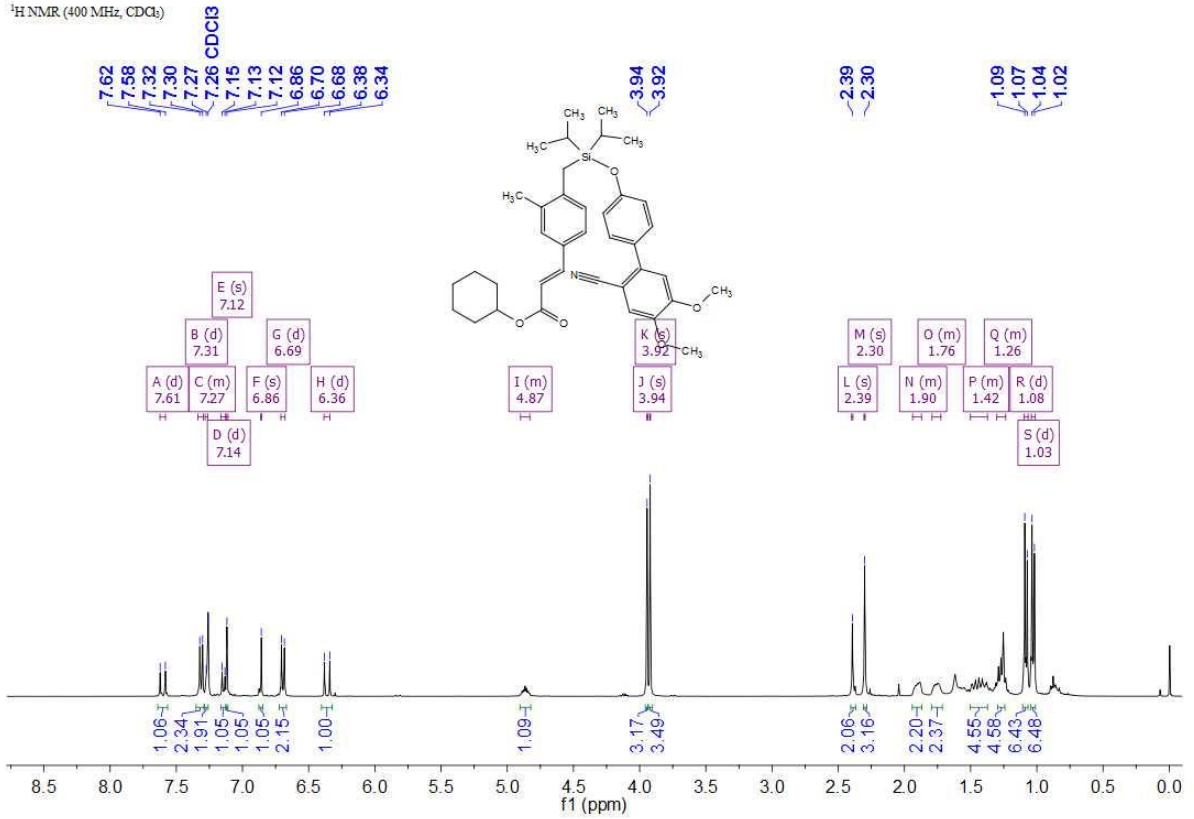


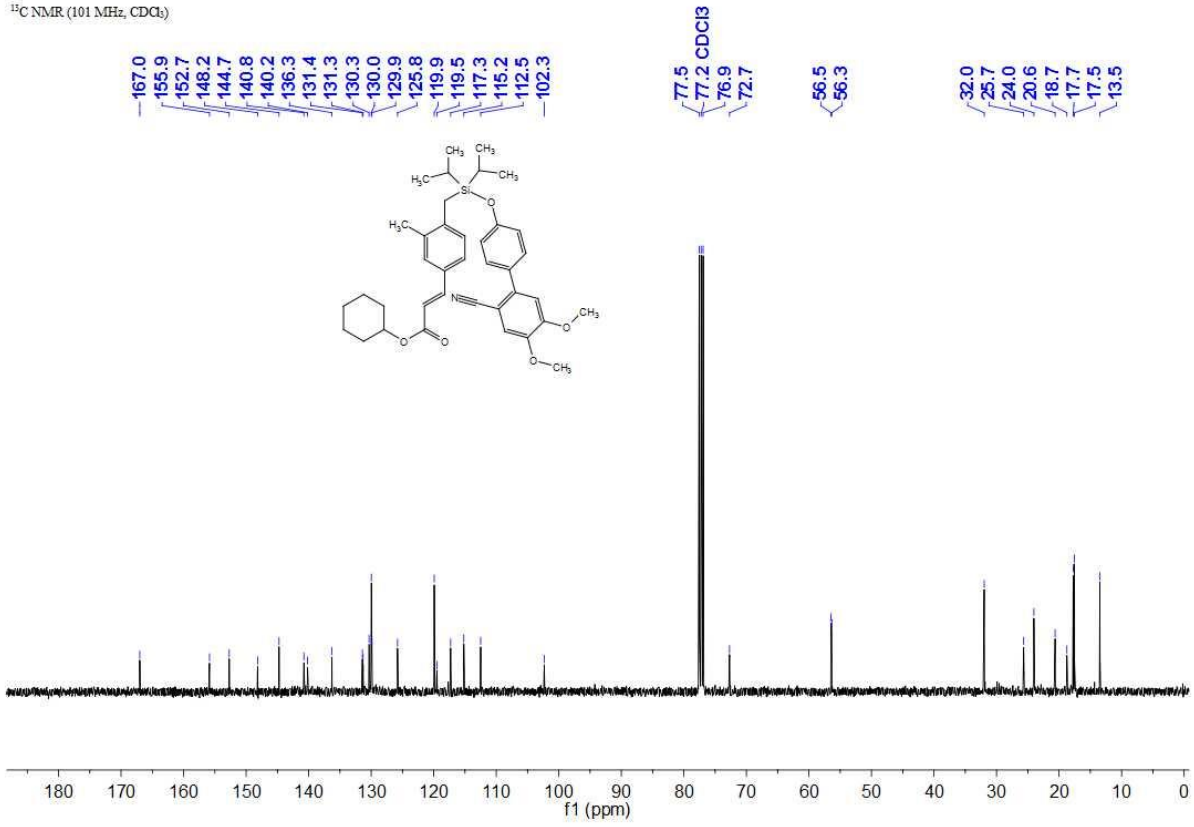
4e. 2,2,2-trifluoroethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)-3-methylphenyl)acrylate



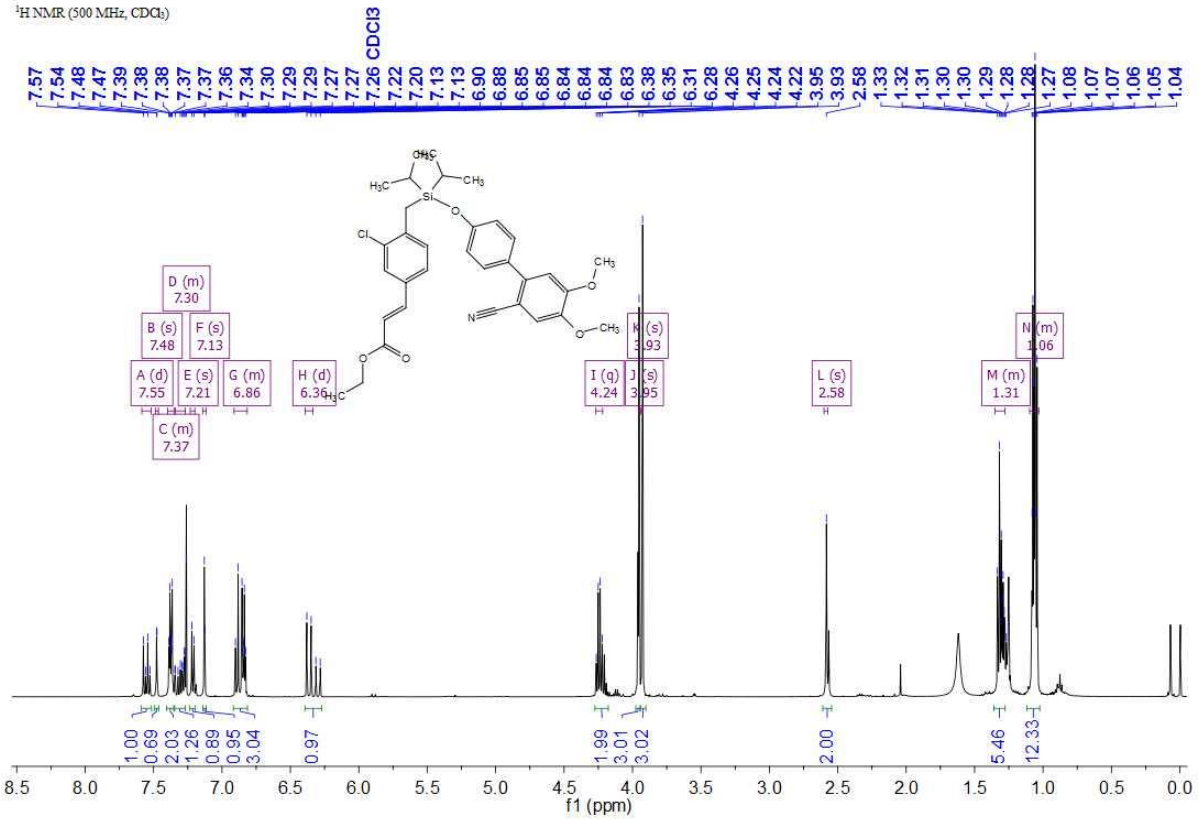


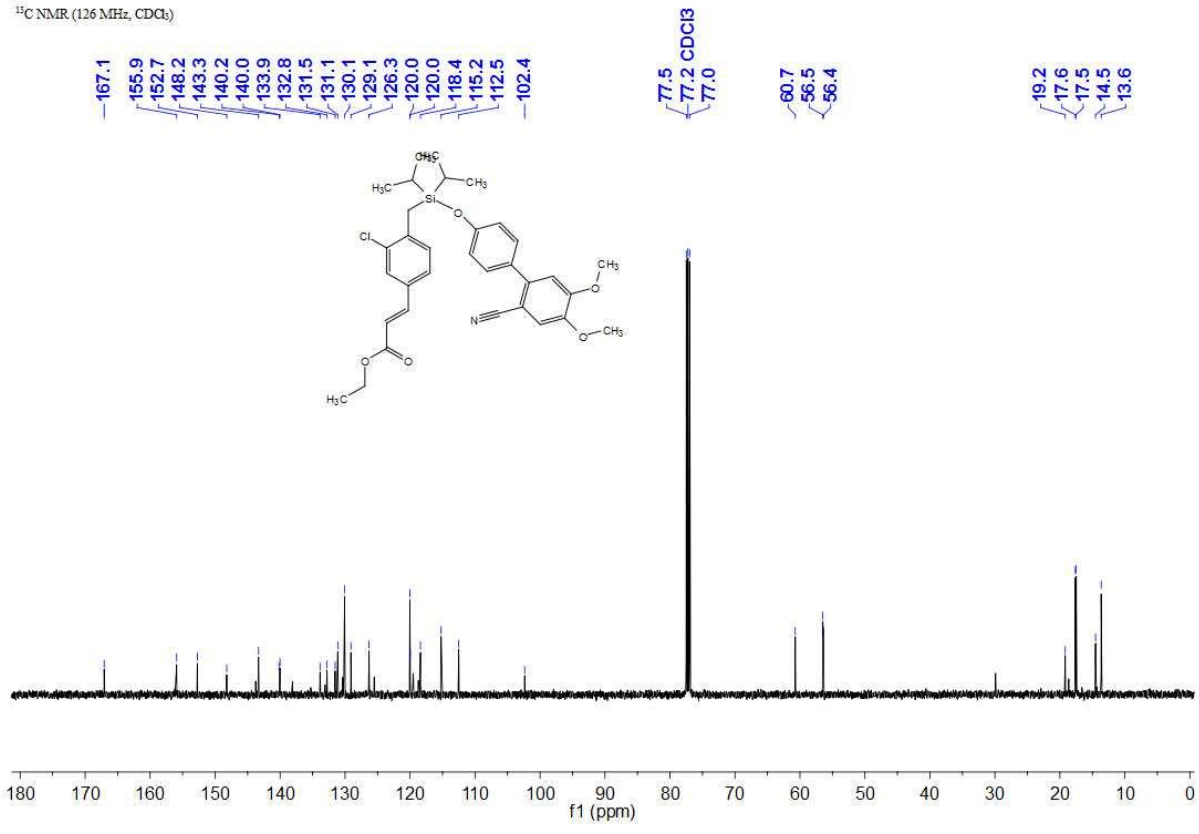
4f. cyclohexyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-methylphenyl)acrylate



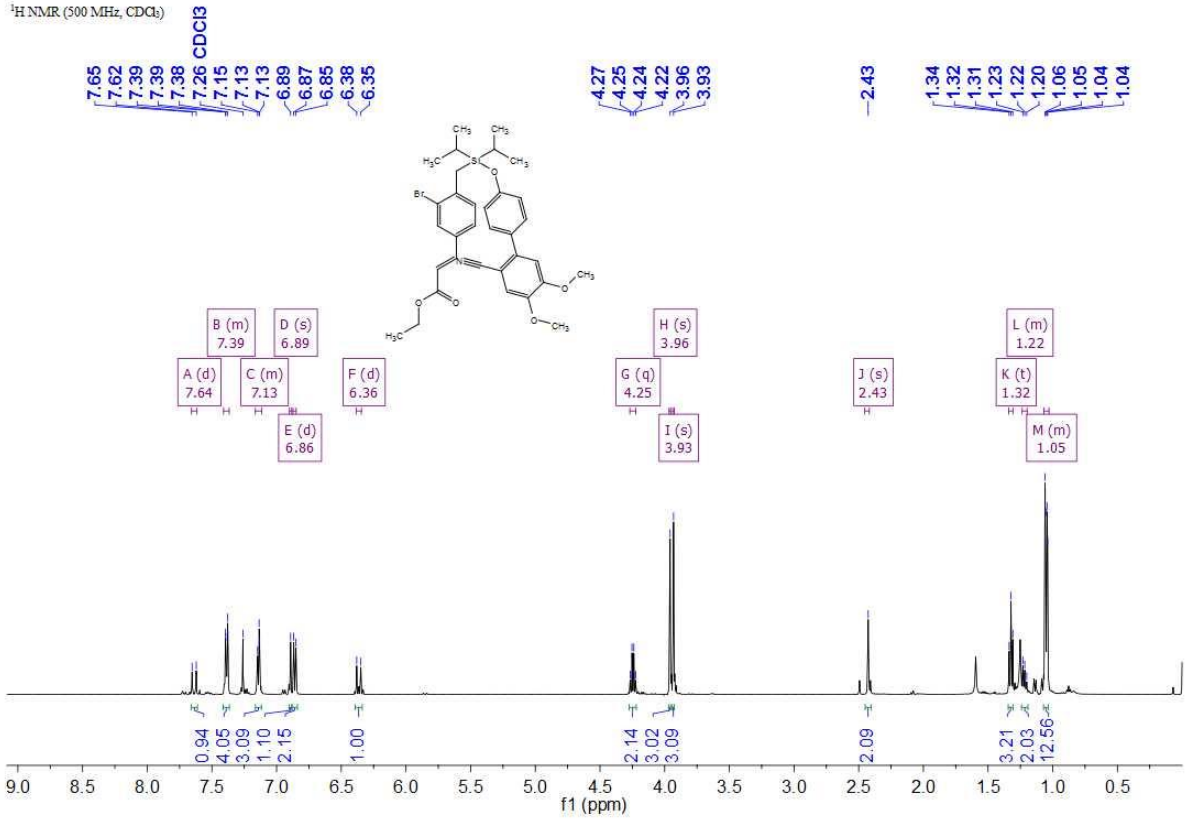


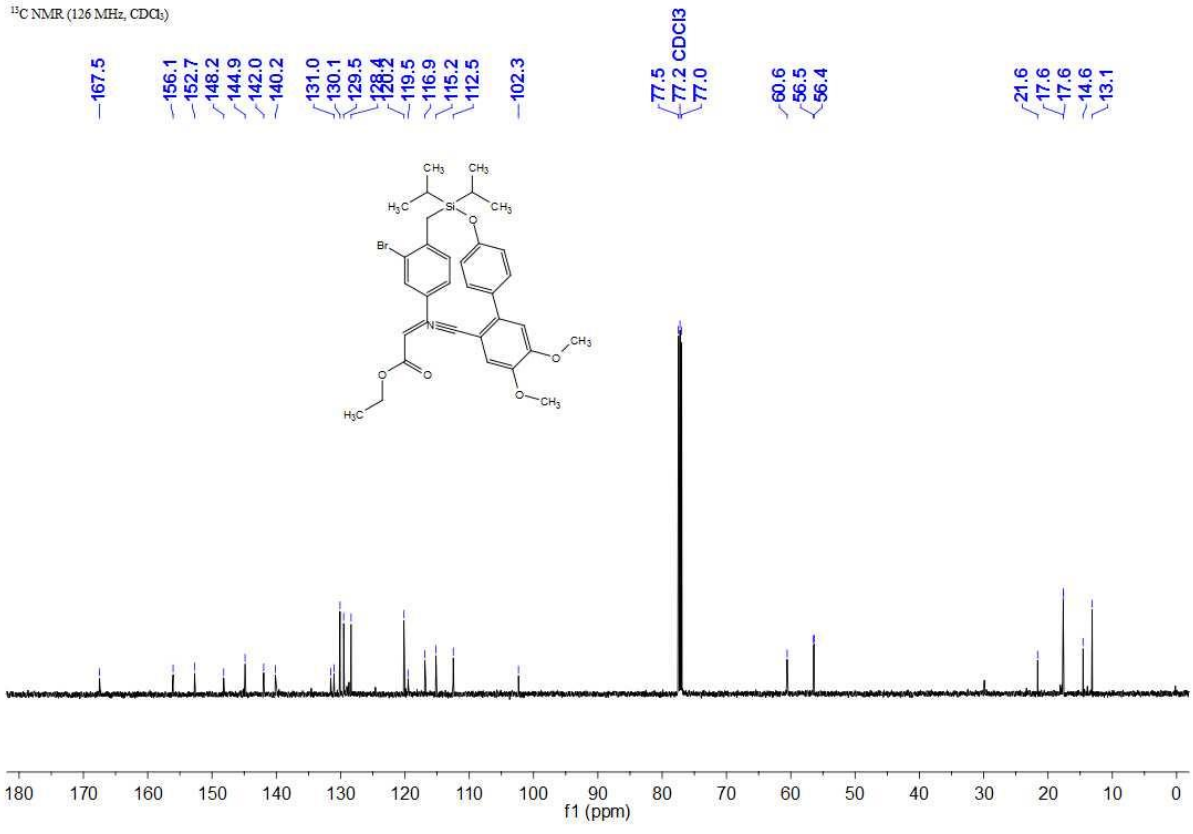
4g. ethyl (*E*)-3-(3-chloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)di-isopropylsilyl)methyl)phenyl)acrylate



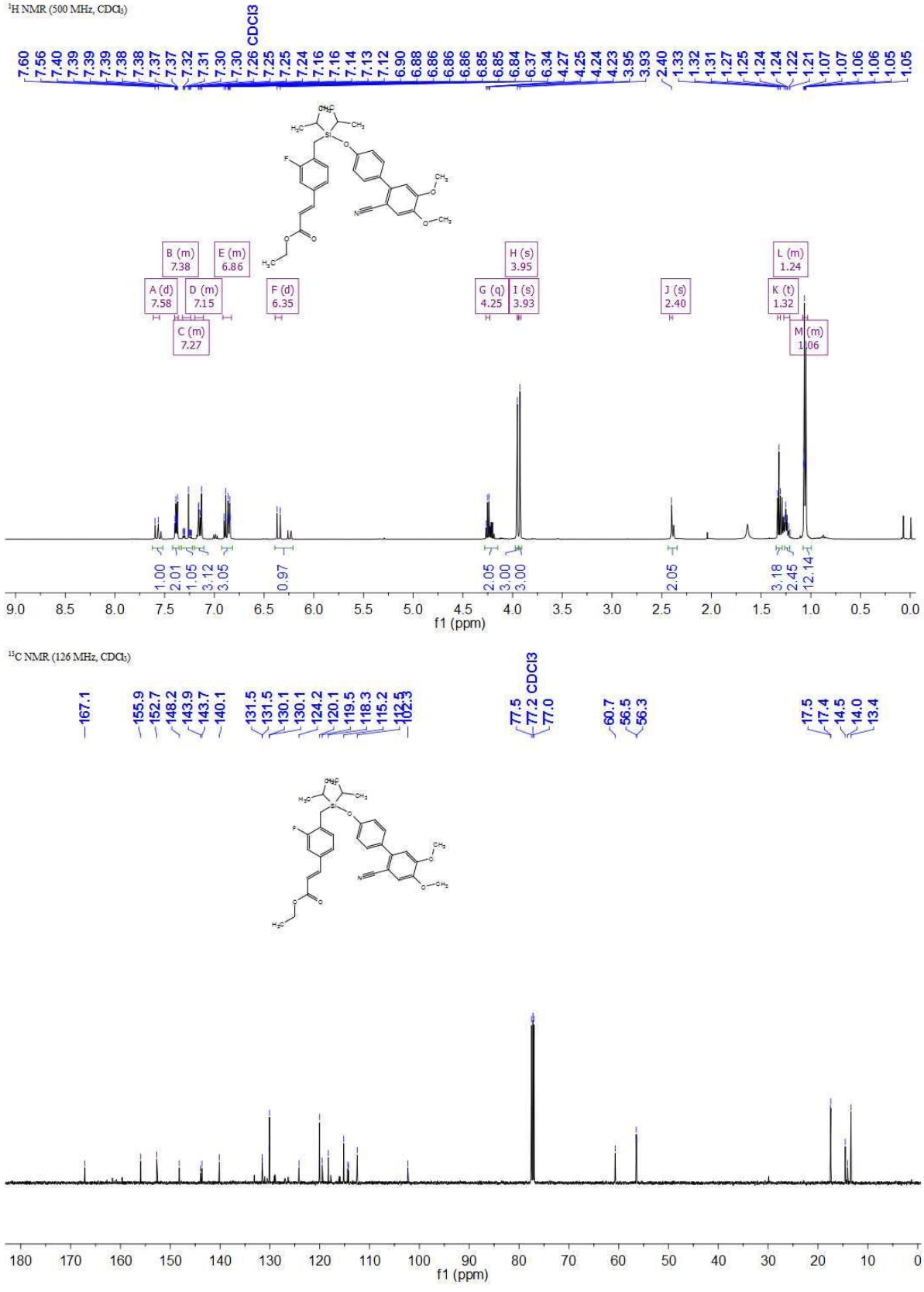


4h. ethyl (*E*)-3-(3-bromo-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate

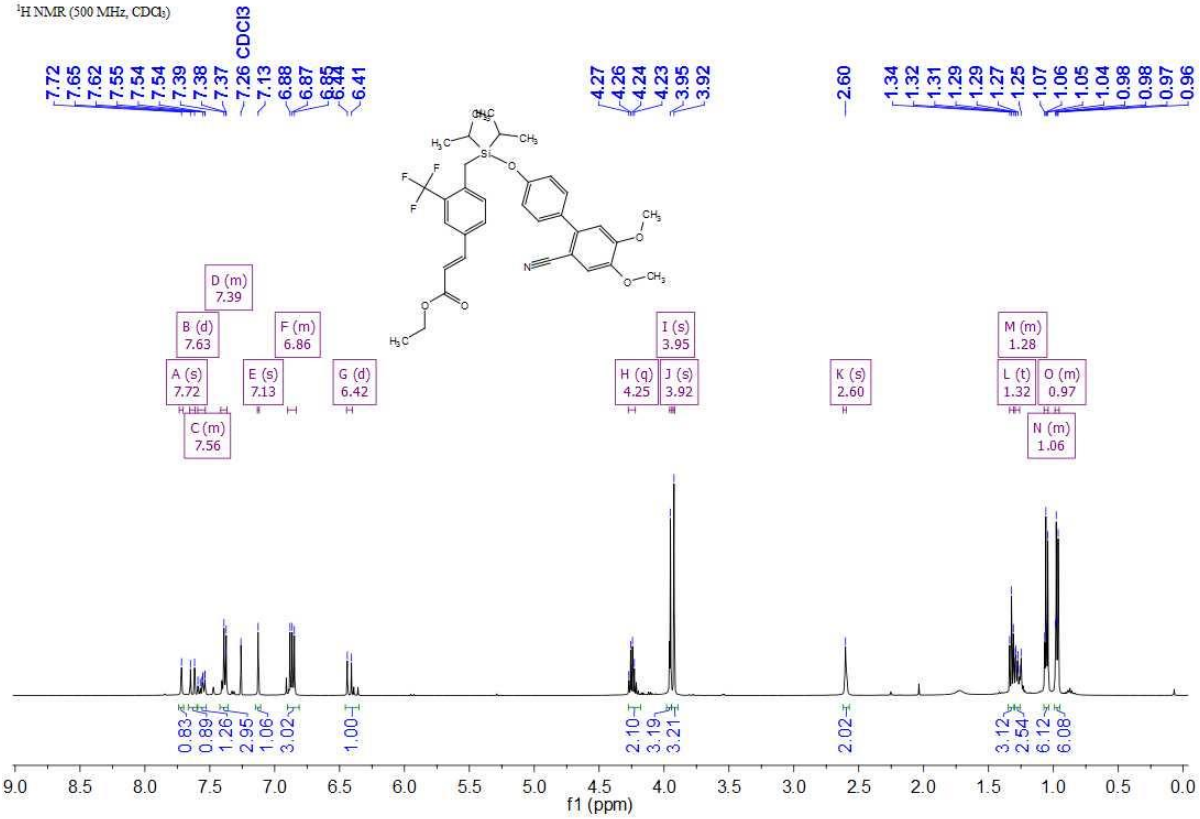


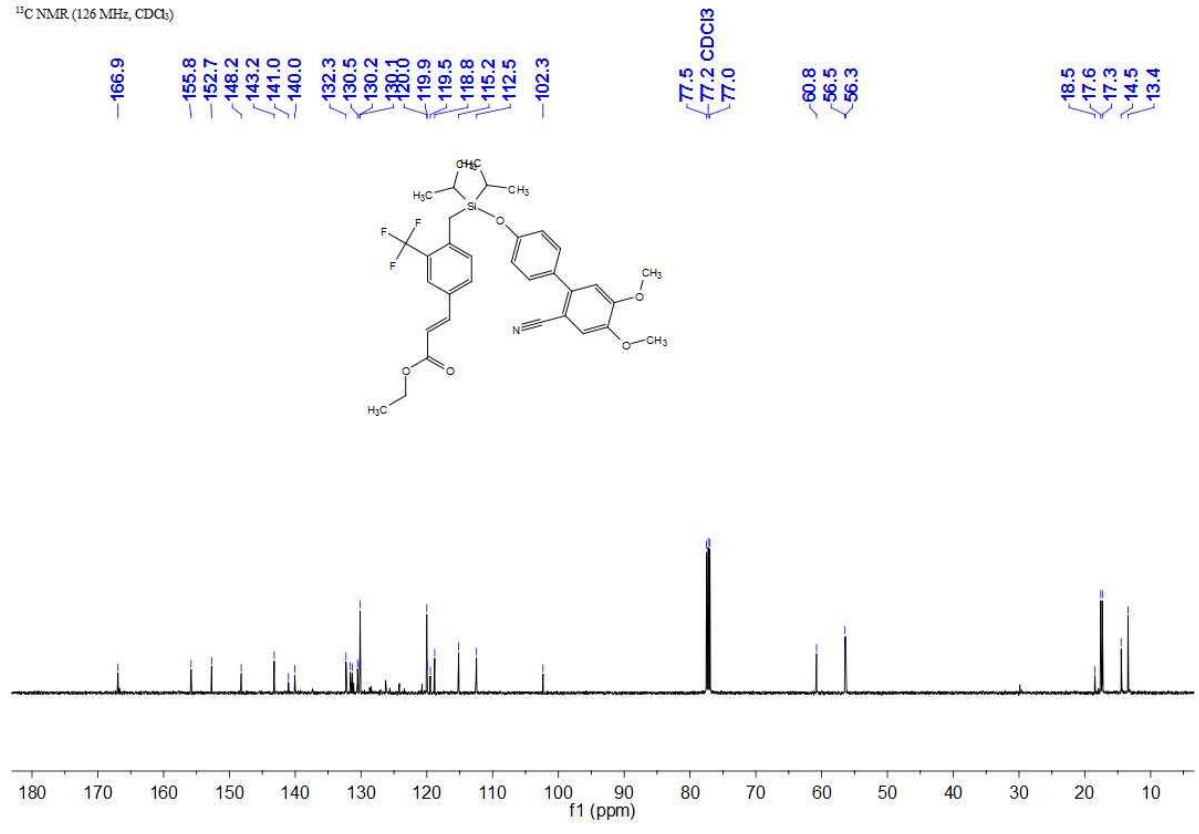


4i. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-fluorophenyl)acrylate

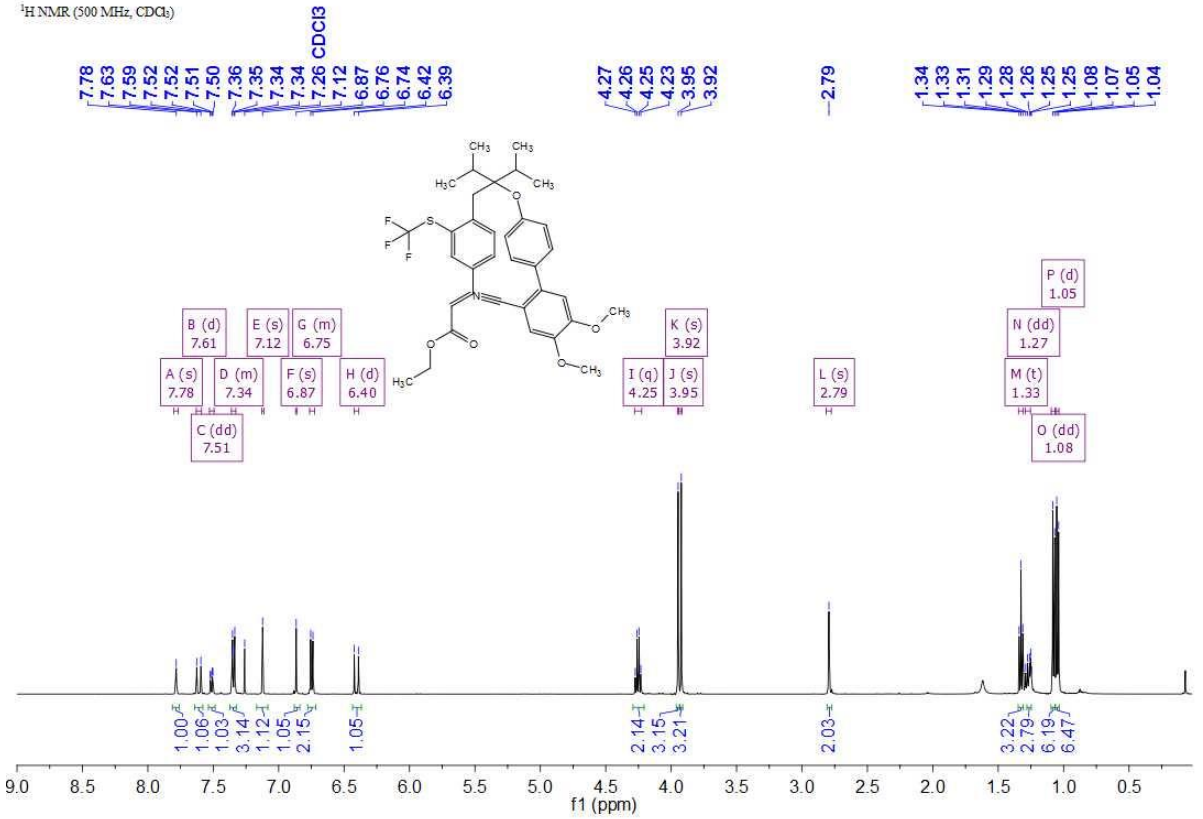


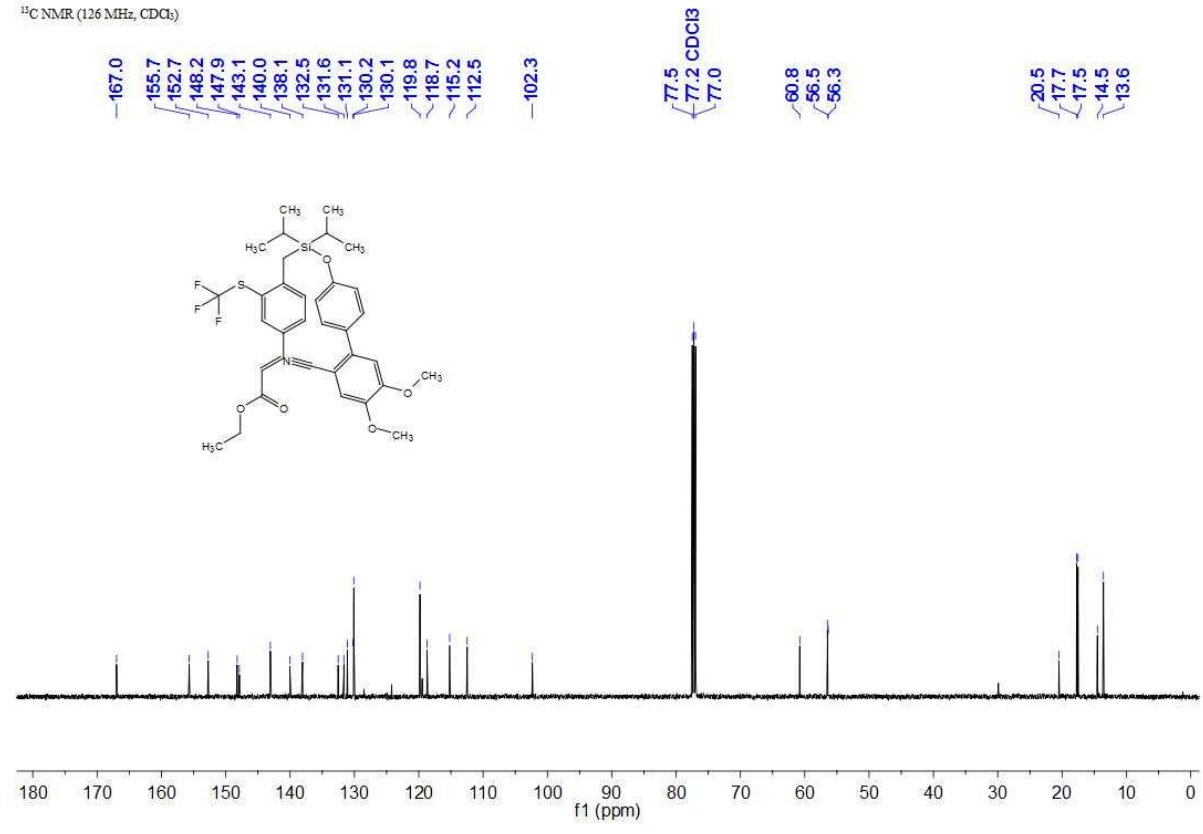
4j. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-(trifluoromethyl)phenyl)acrylate



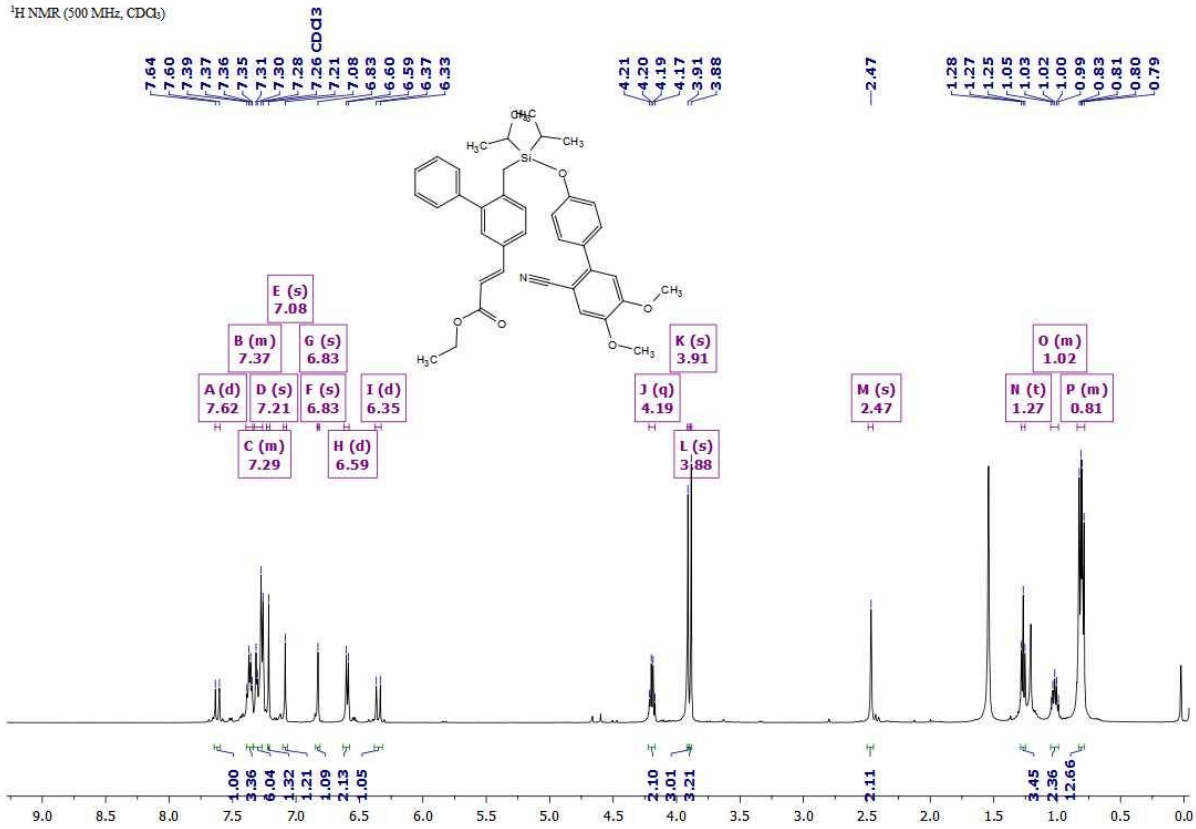


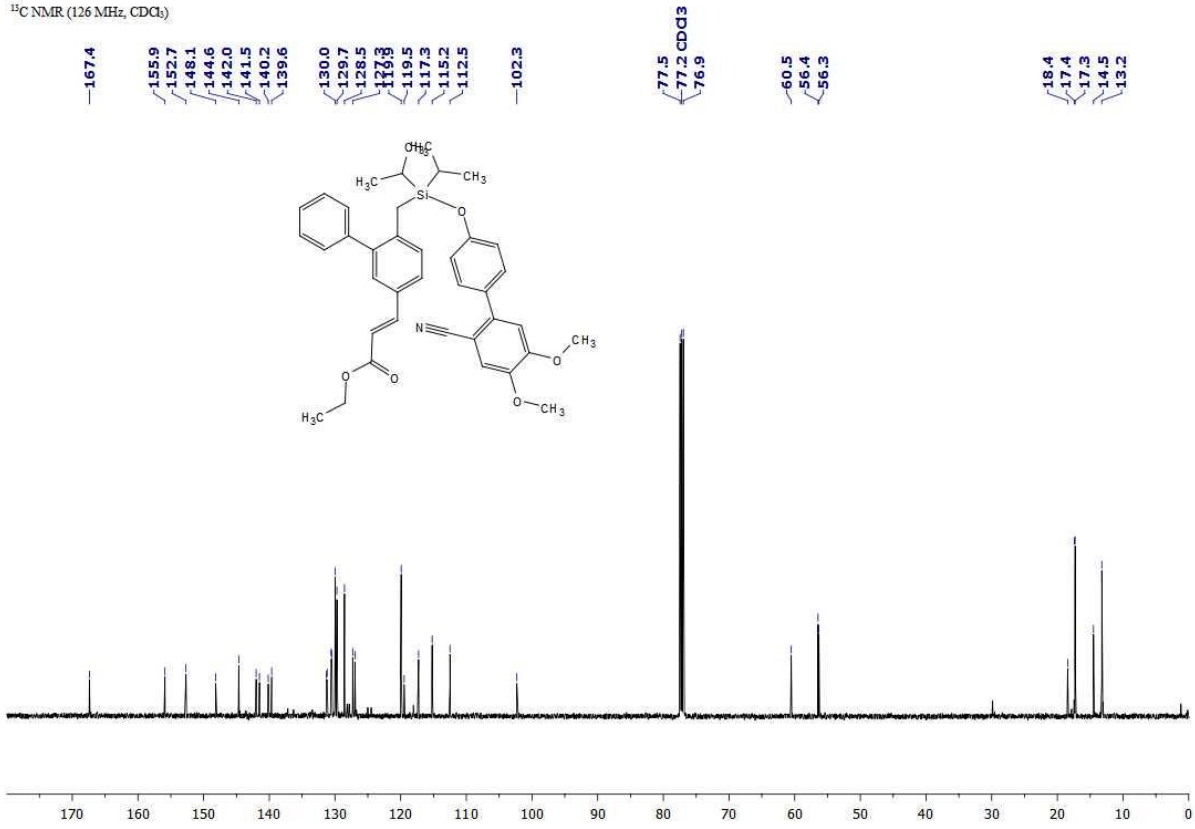
4k. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-(trifluoromethyl)thio)phenyl)acrylate



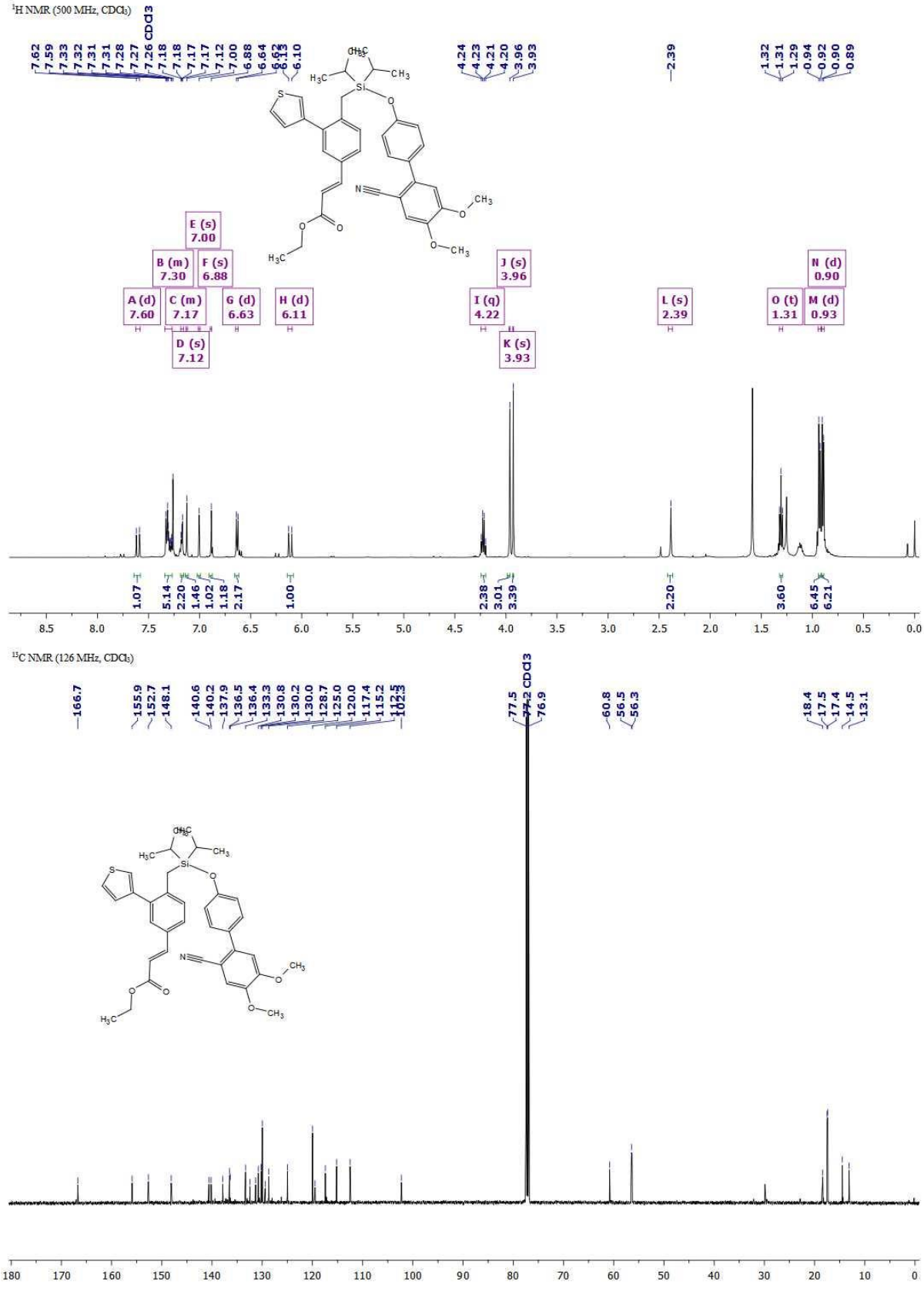


4l. ethyl (*E*)-3-(6-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-[1,1'-biphenyl]-3-yl)acrylate

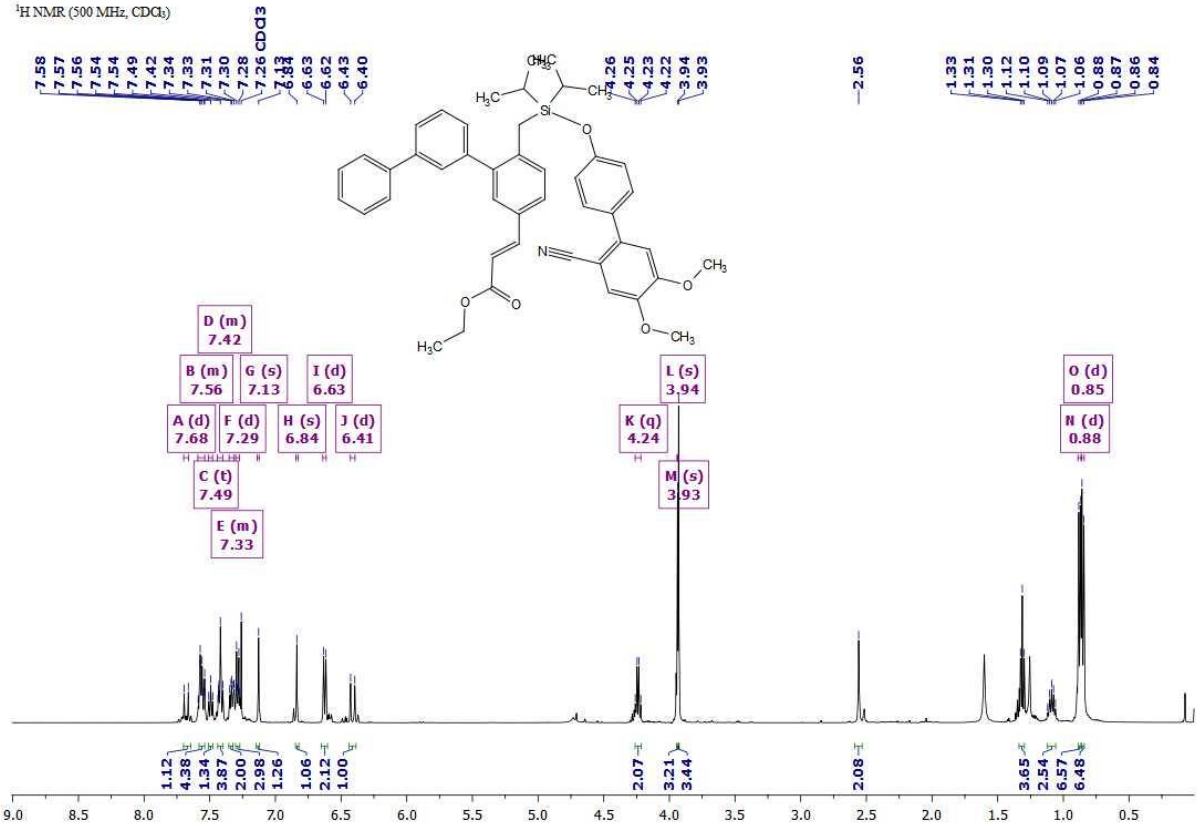


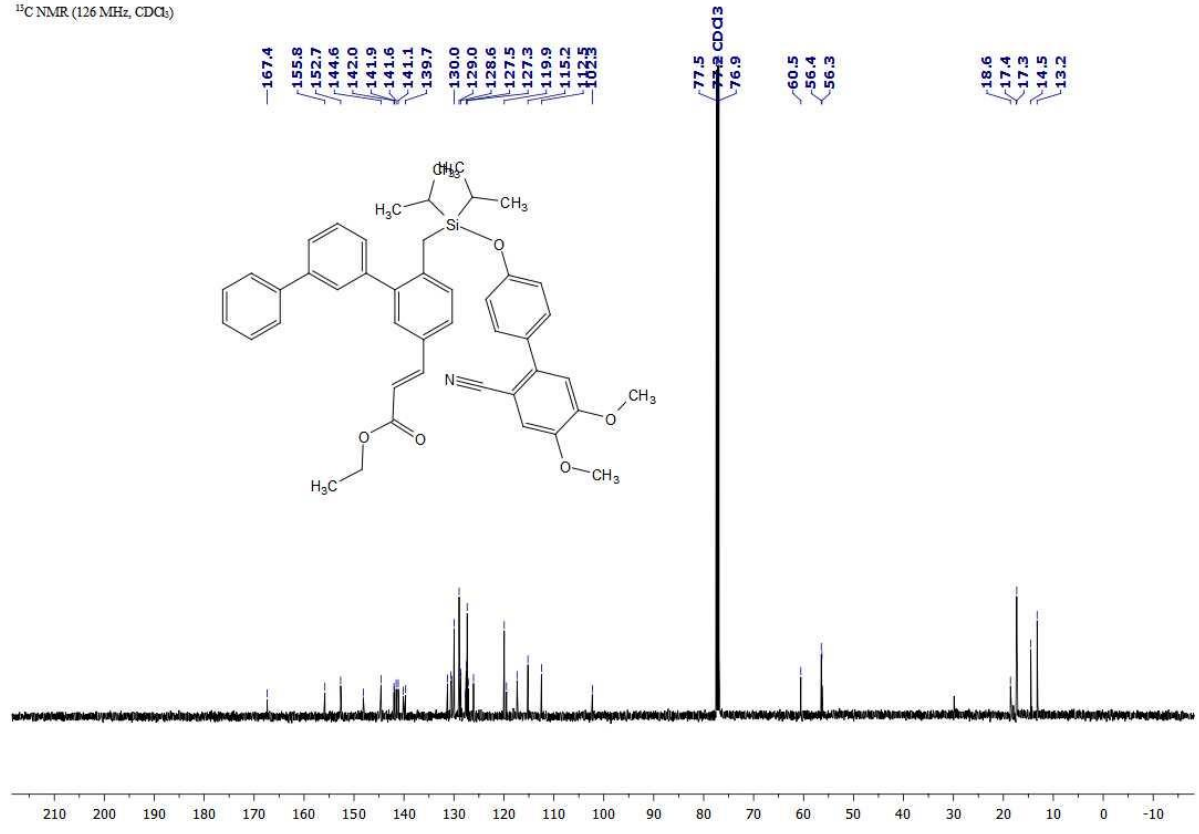


4m. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3-(thiophen-3-yl)phenyl)acrylate

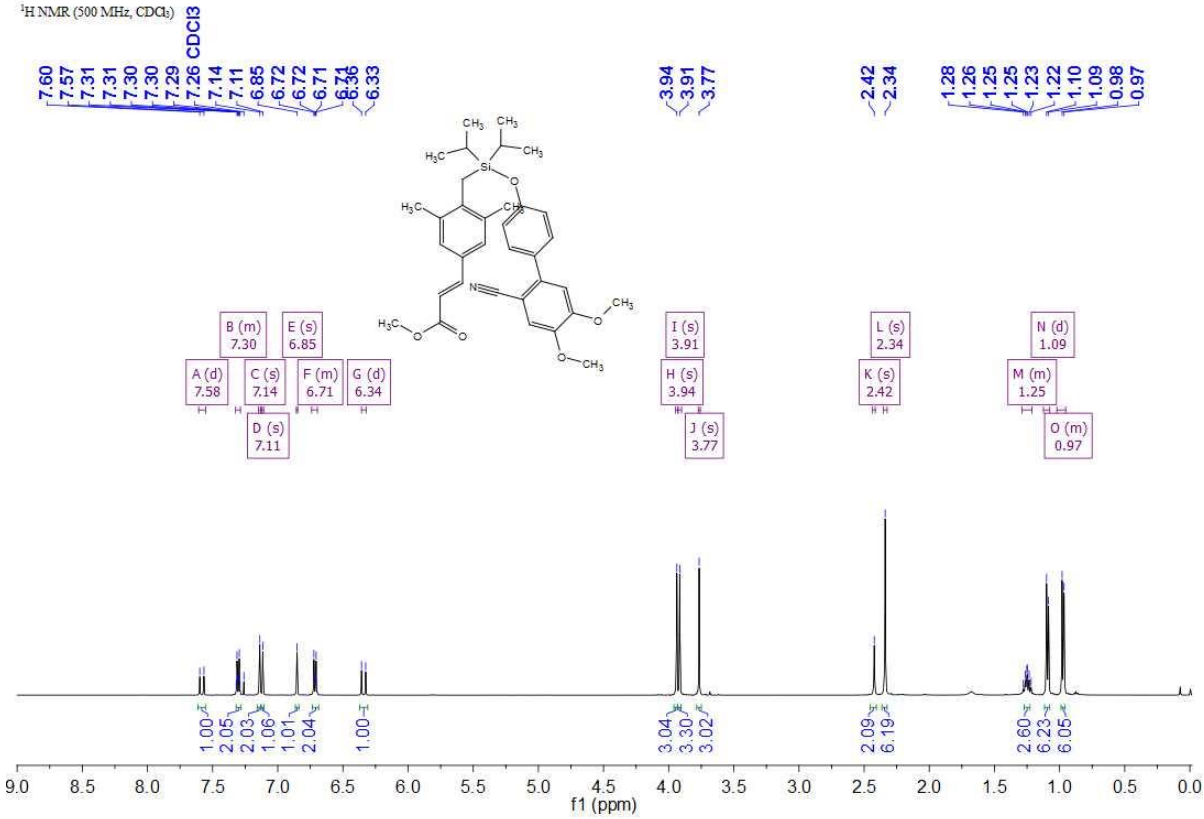


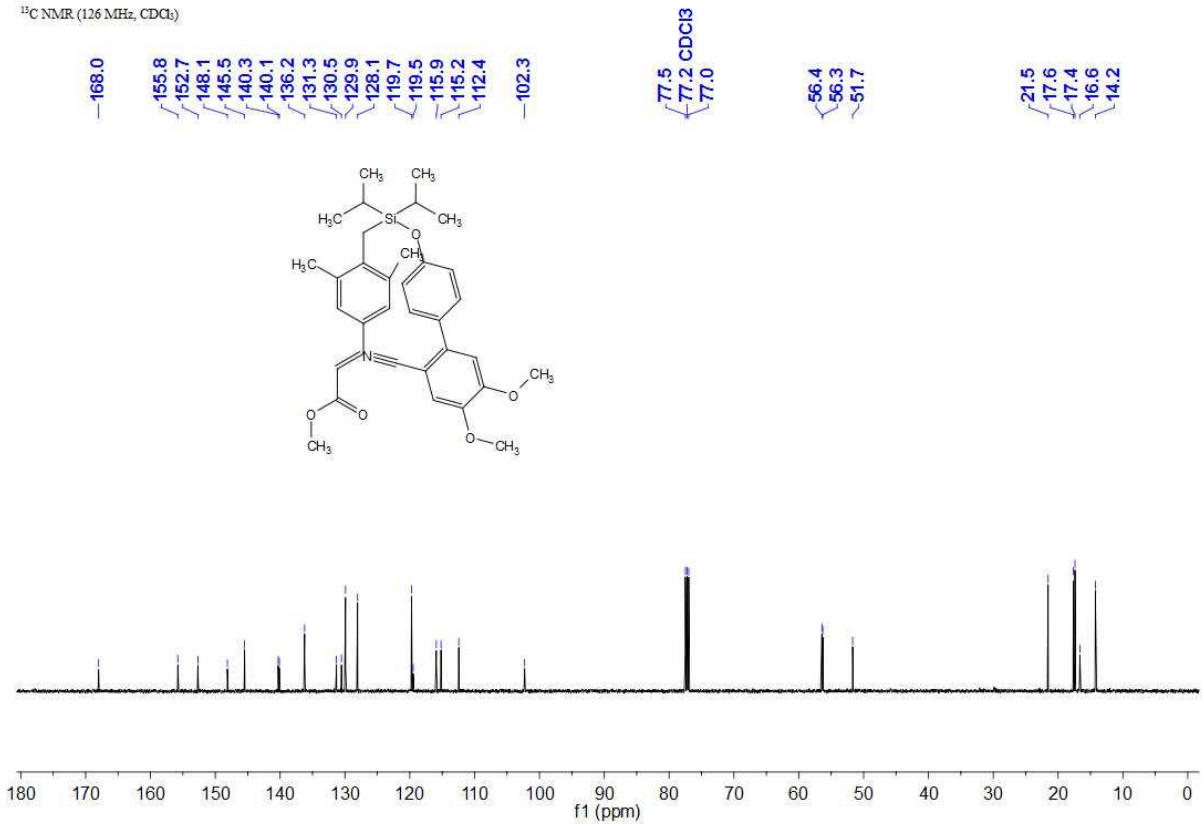
4n. ethyl (*E*)-3-(6-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-[1,1':3',1''-terphenyl]-3-yl)acrylate



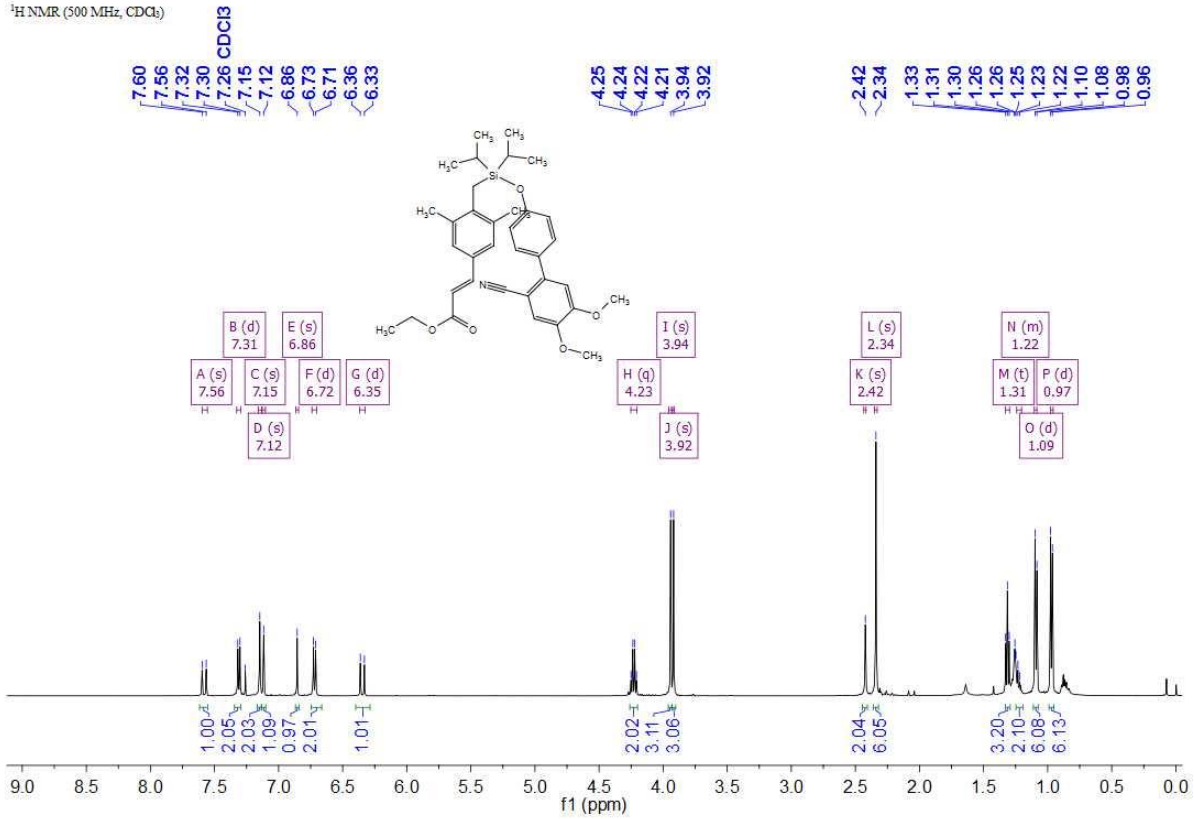


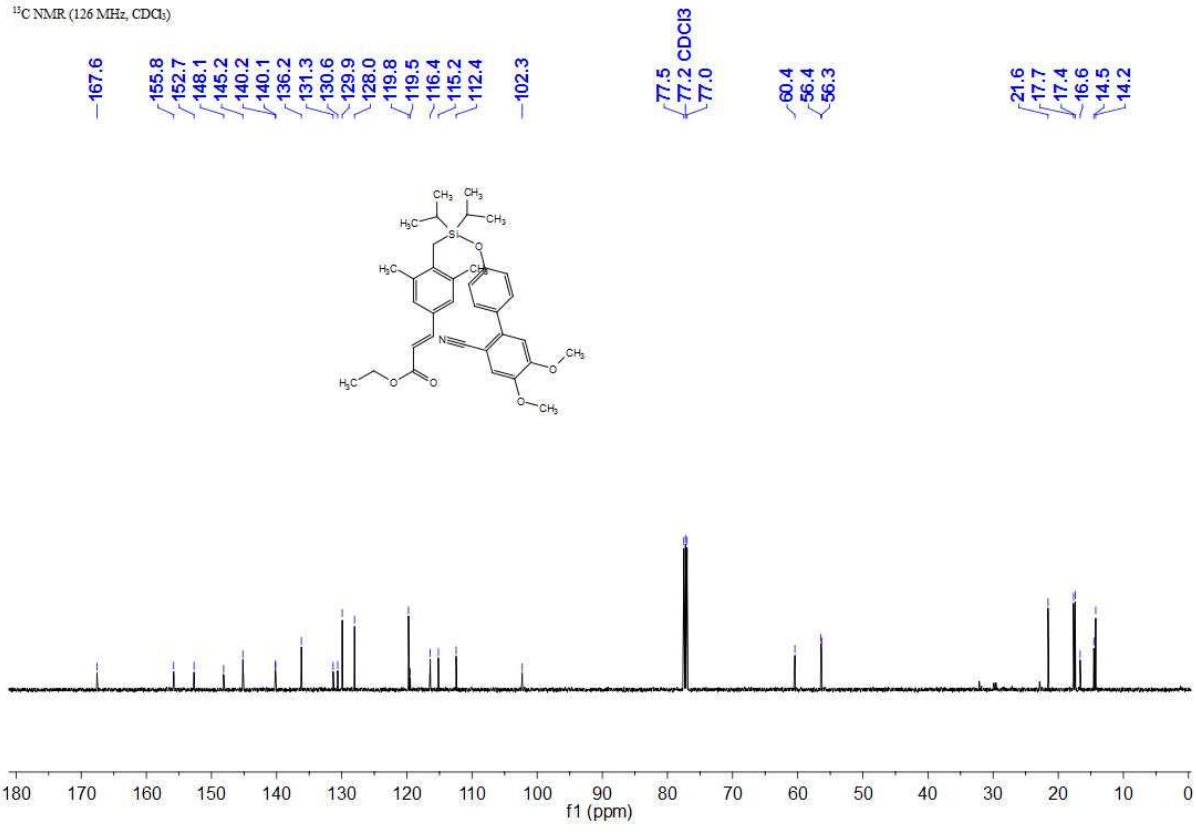
6a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



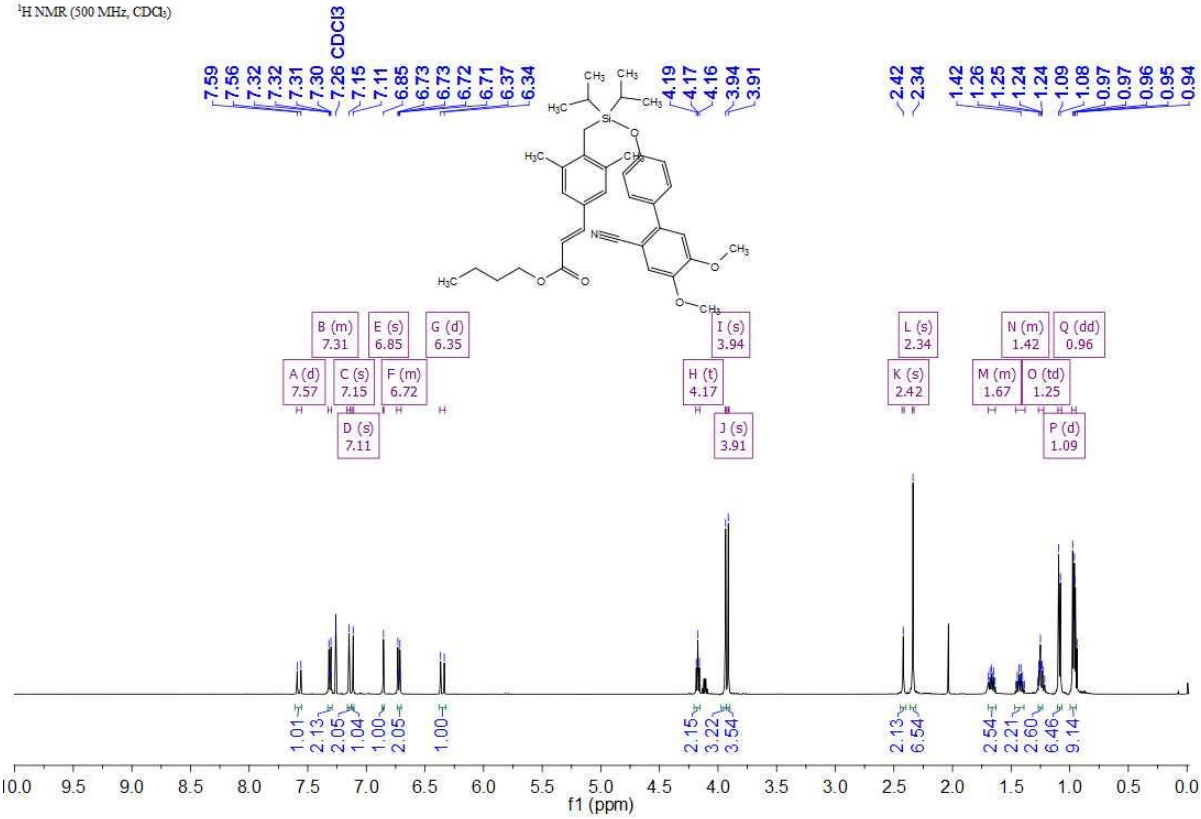


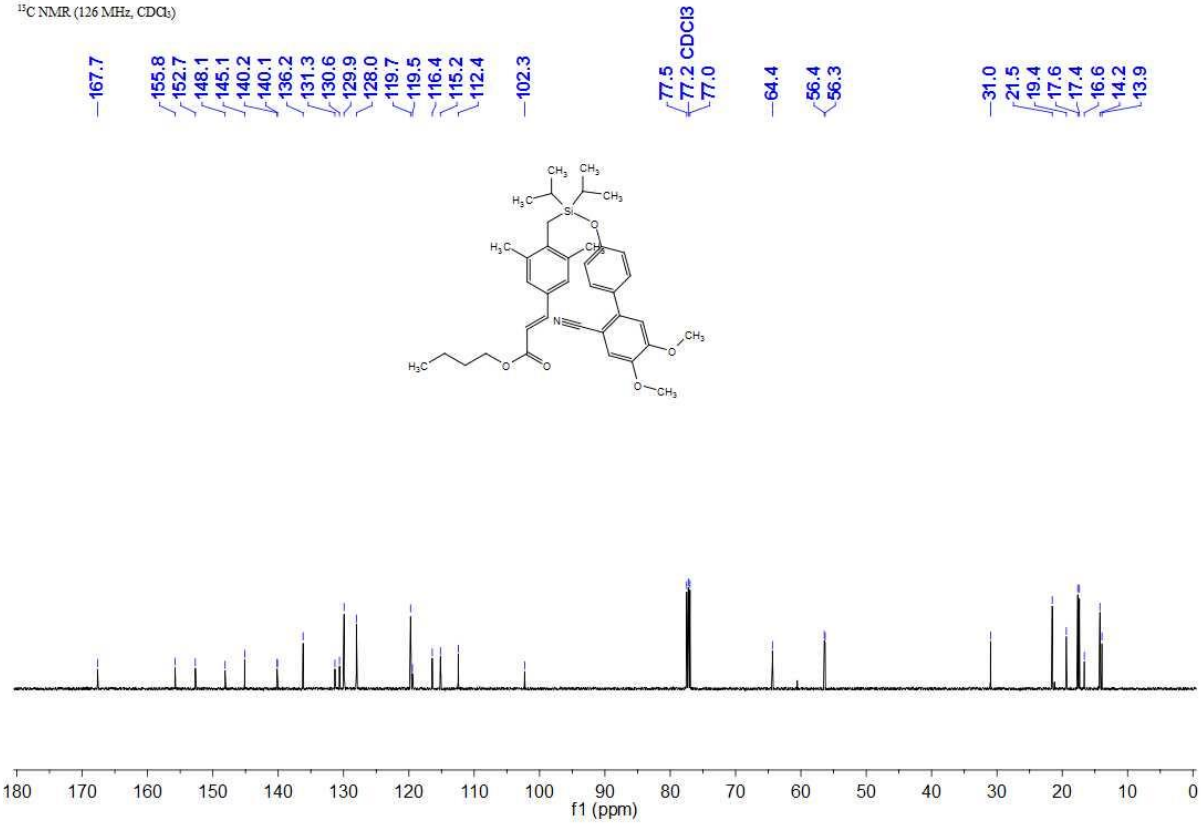
6b. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



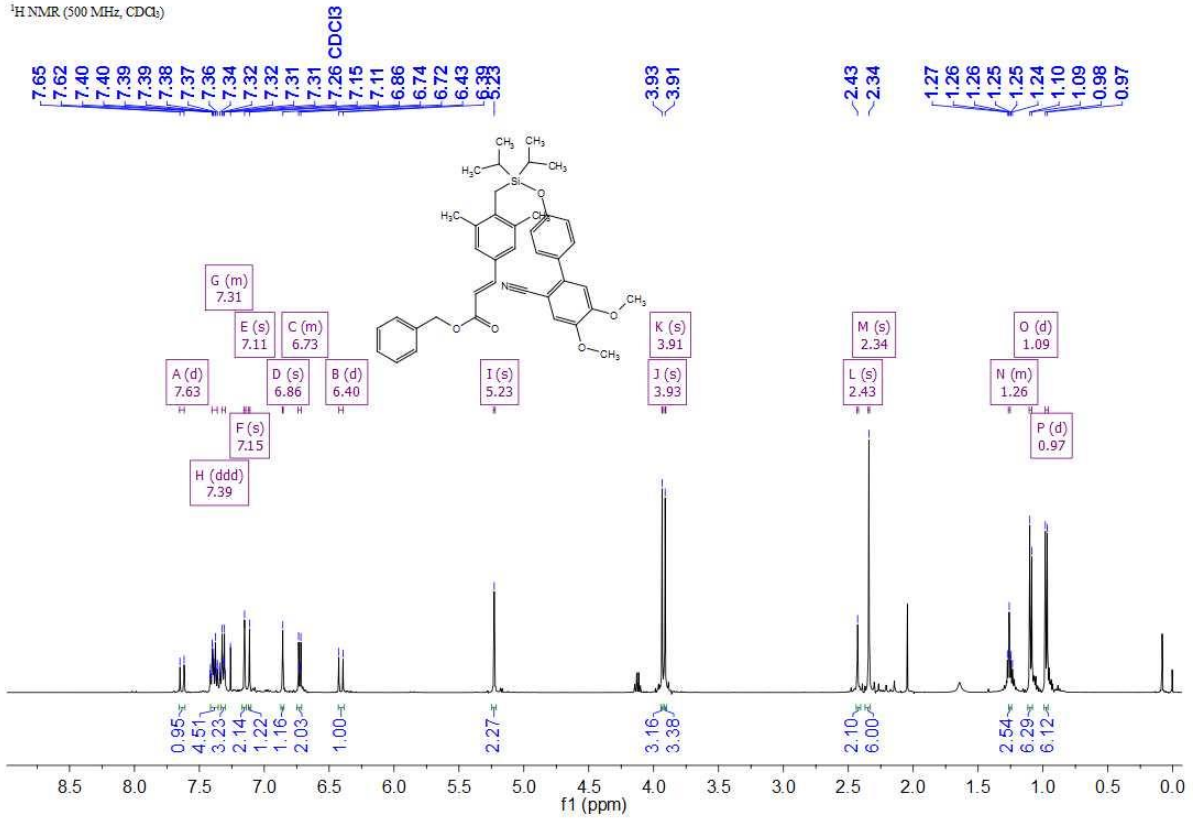


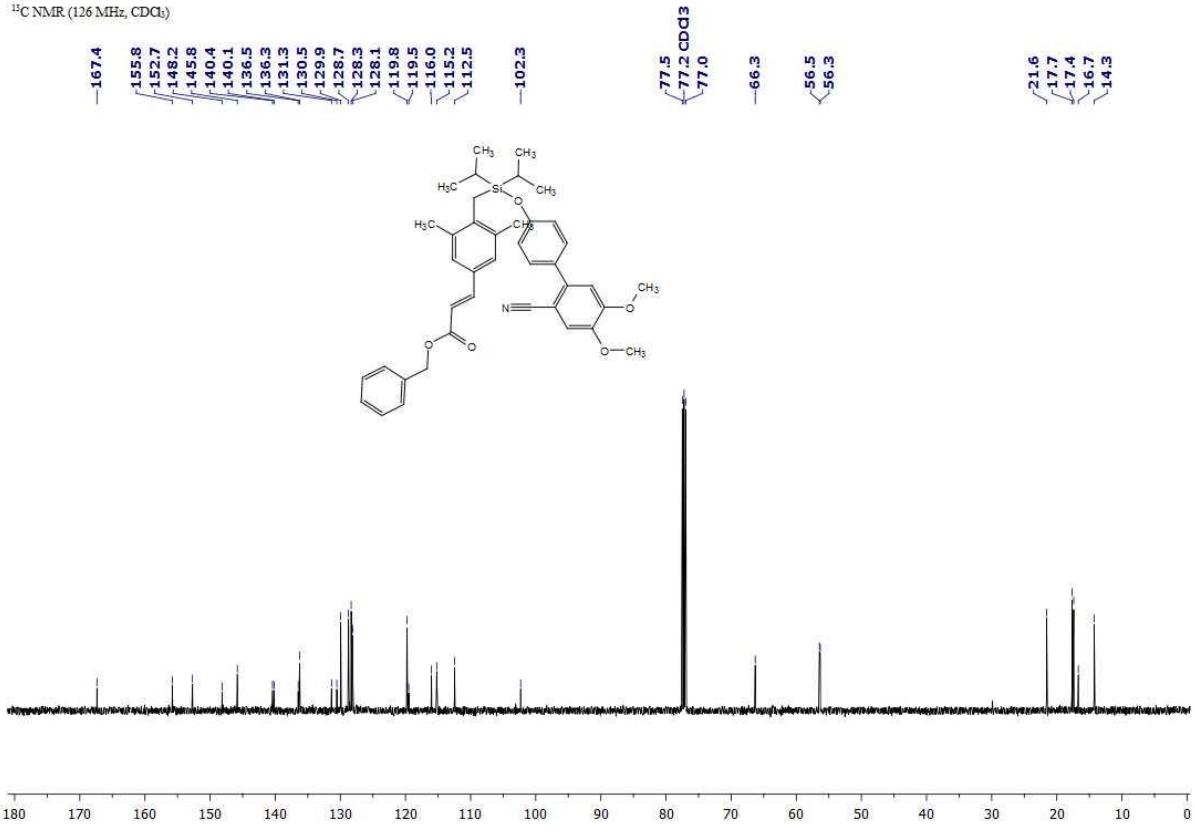
6c. butyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate



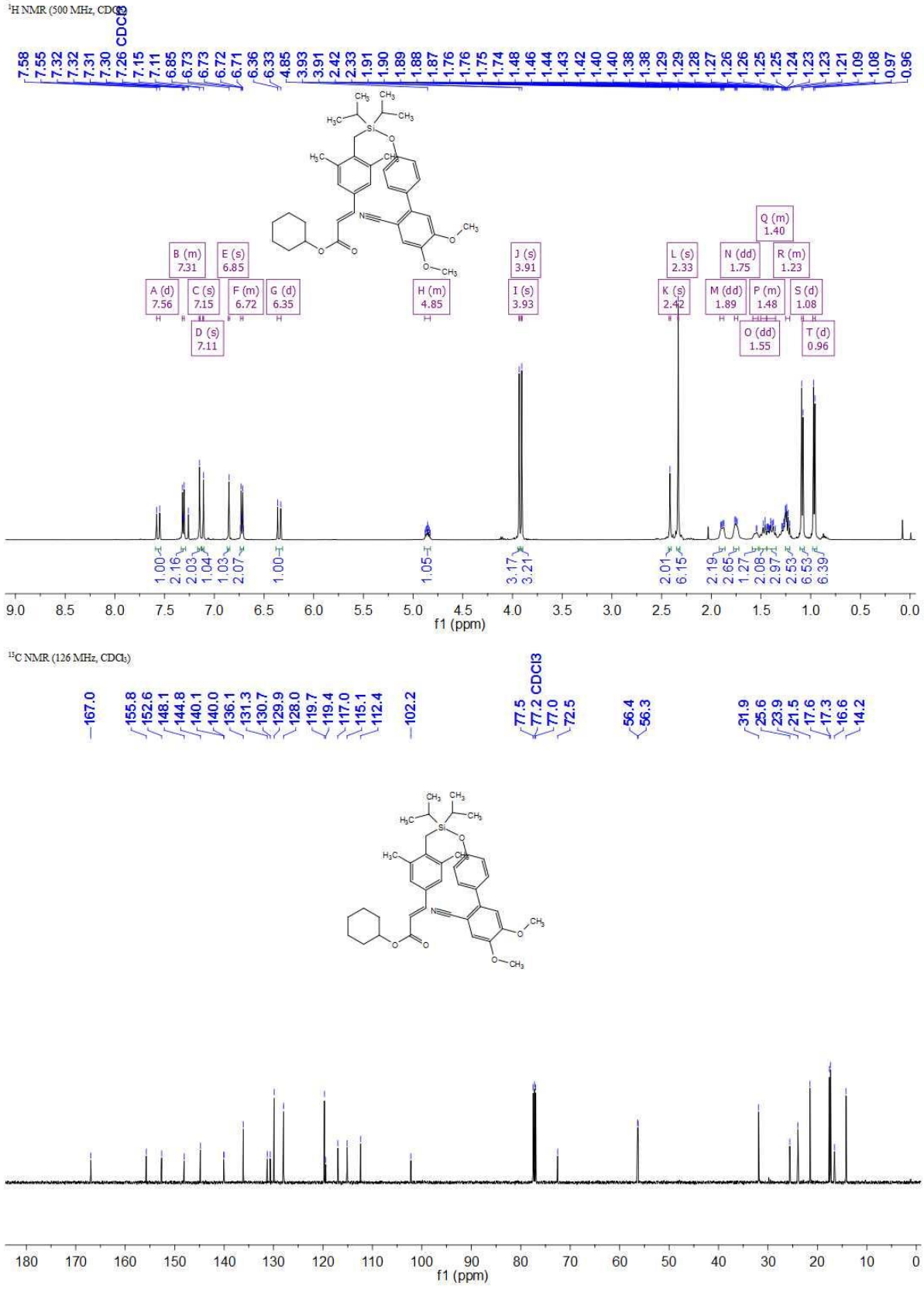


6d. benzyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate

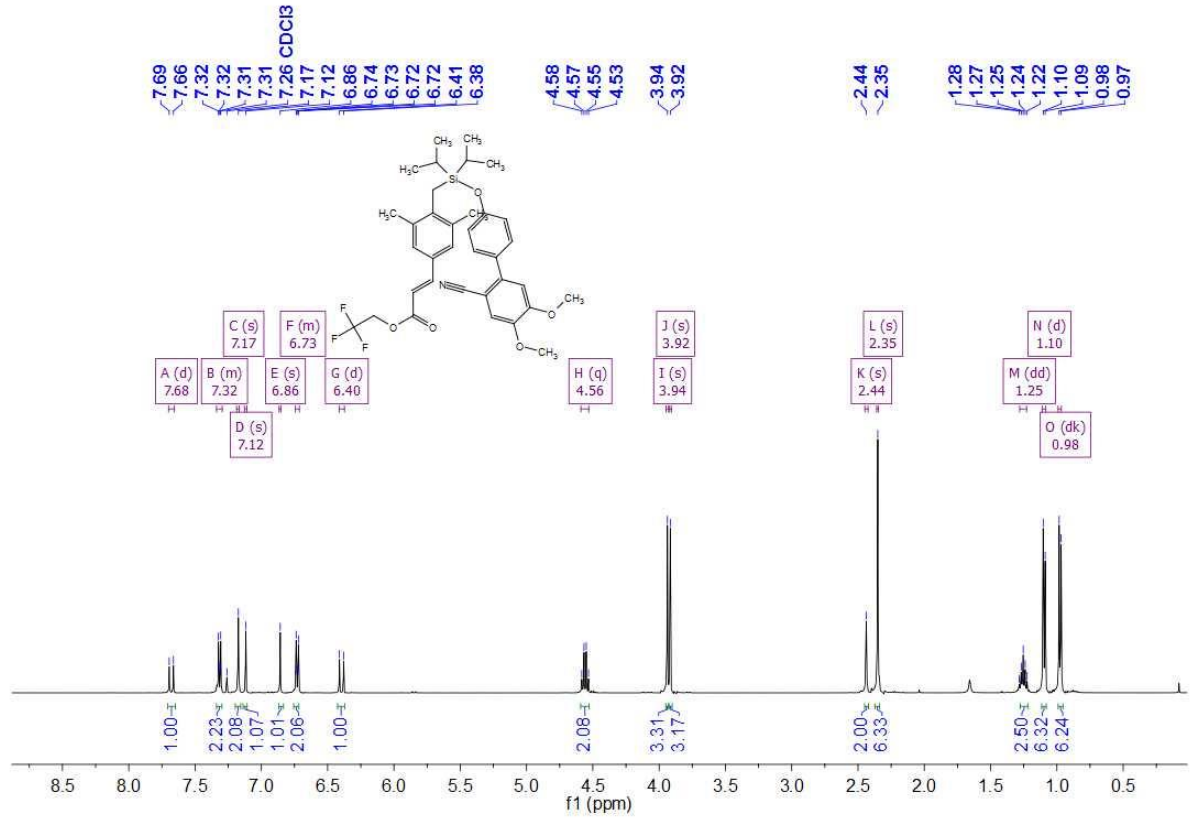


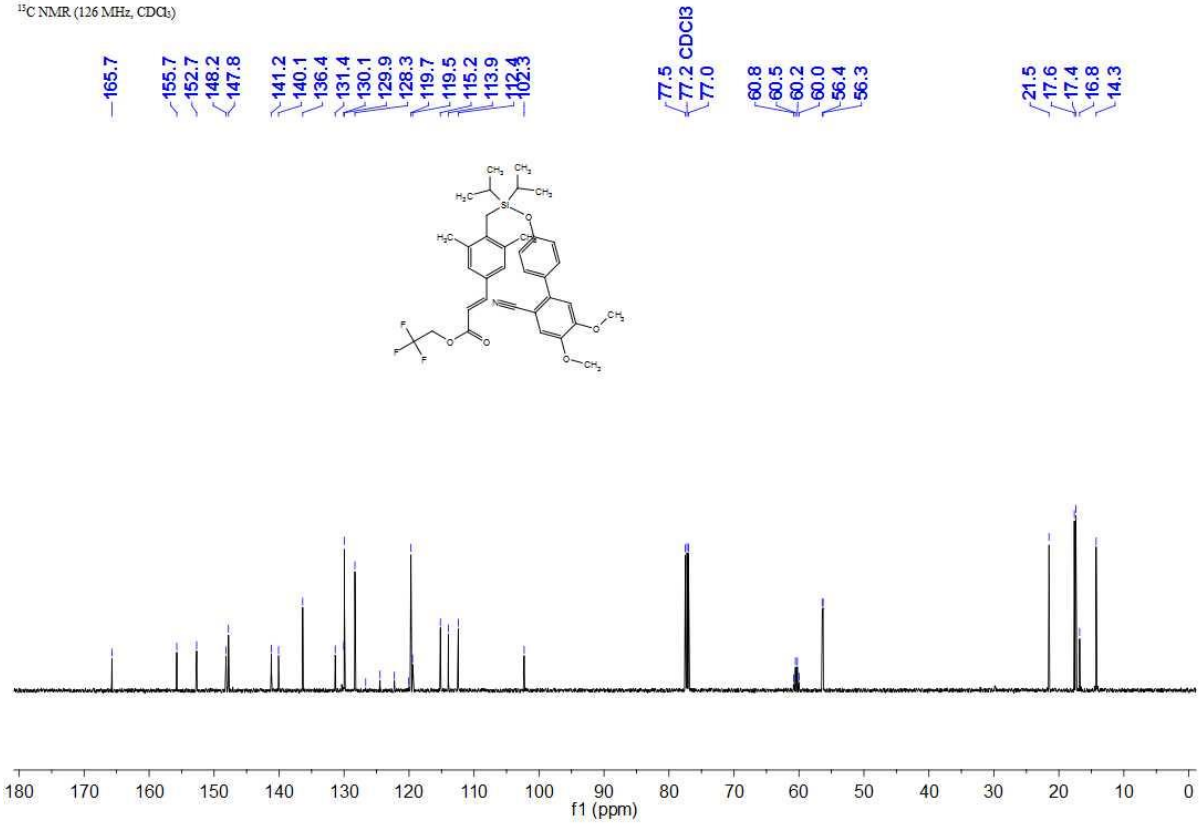


6e. cyclohexyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-3,5-dimethylphenyl)acrylate

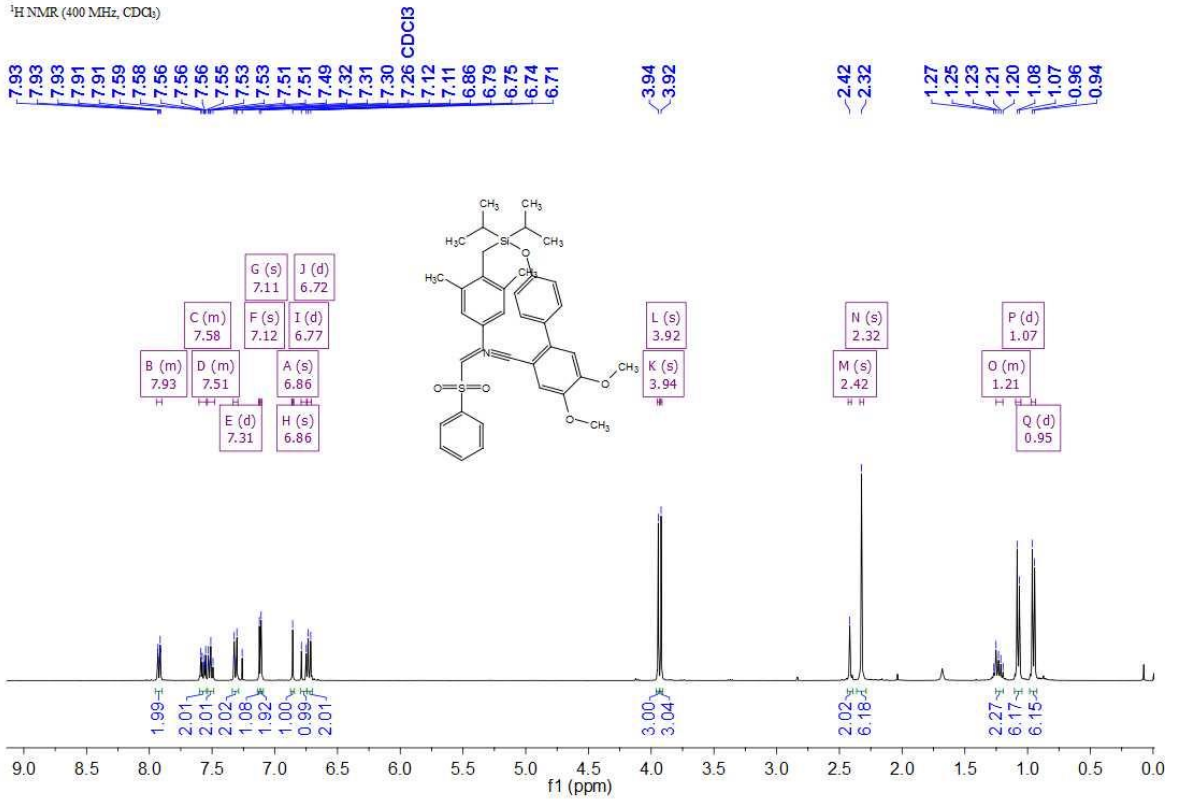


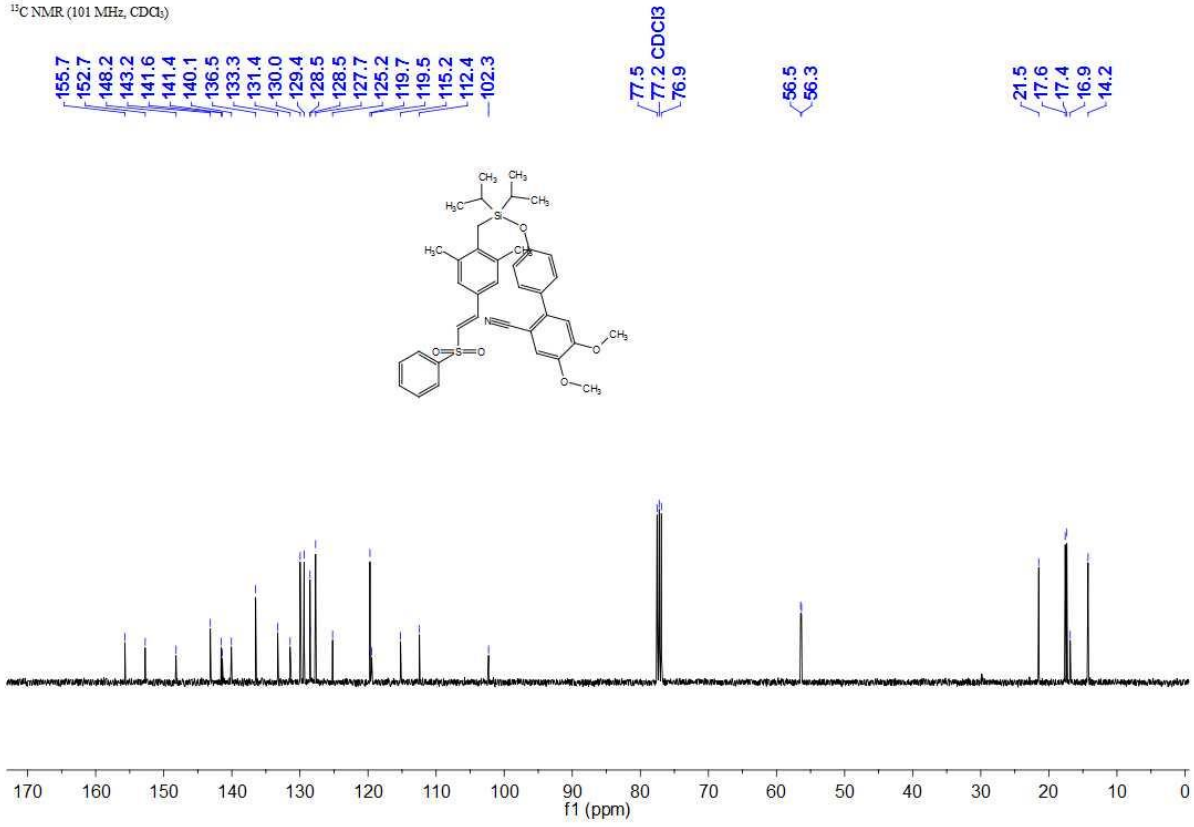
6f. 2,2,2-trifluoroethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)di-isopropyl-silyl)methyl)-3,5-dimethylphenyl)acrylate



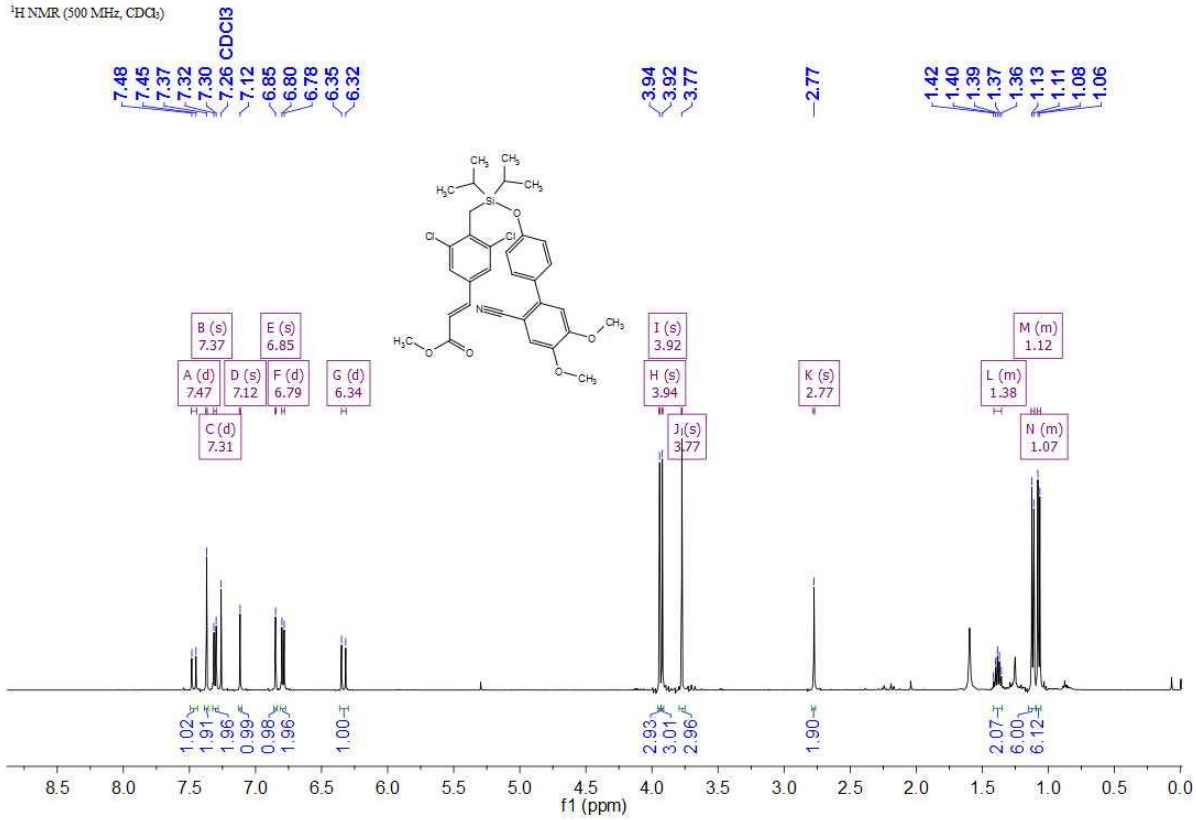


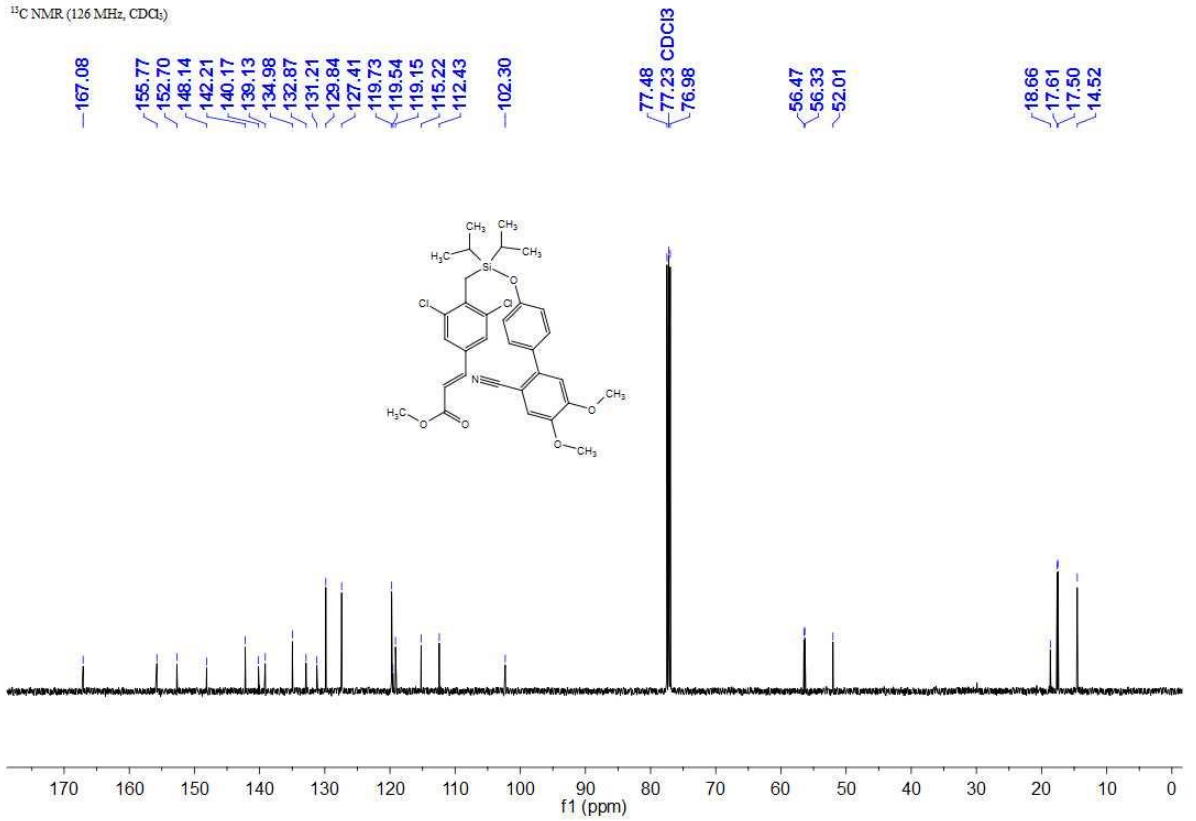
6g. (*E*)-4'-(((2,6-dimethyl-4-(2-(phenylsulfonyl)vinyl)benzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphenyl]-2-carbonitrile



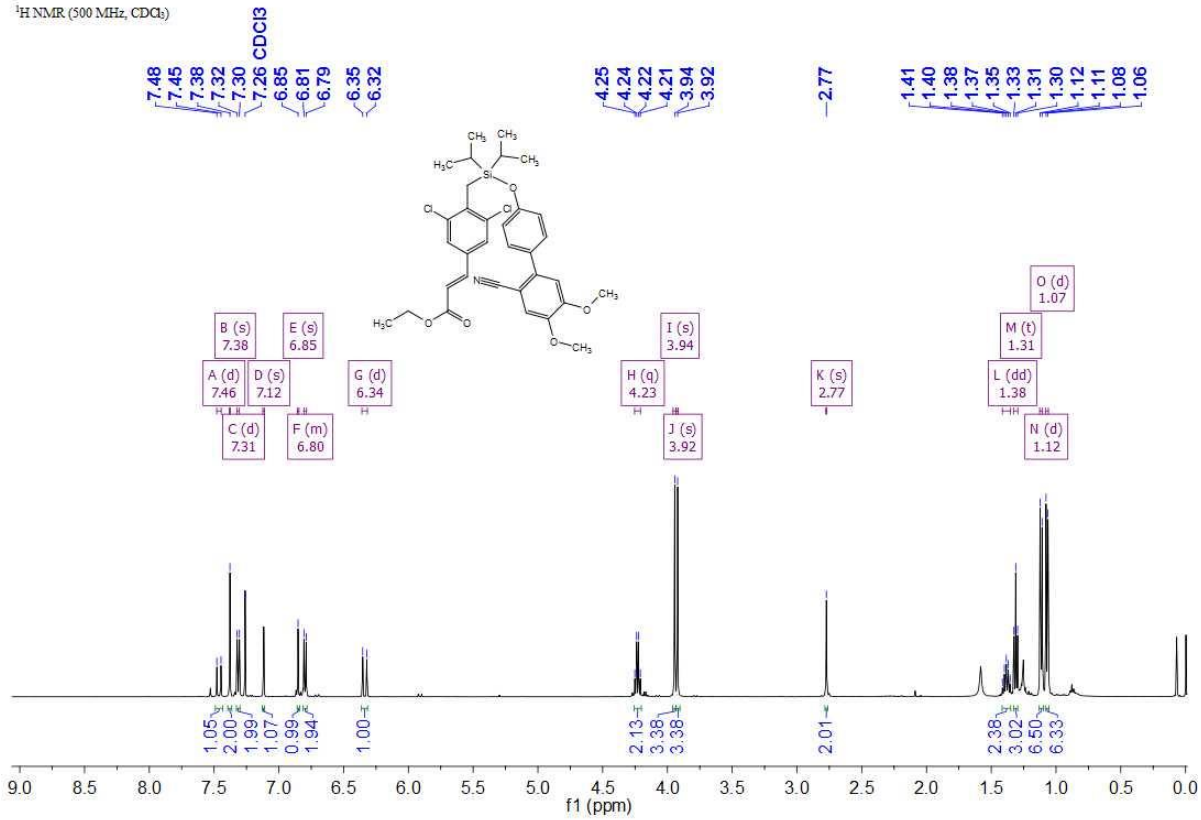


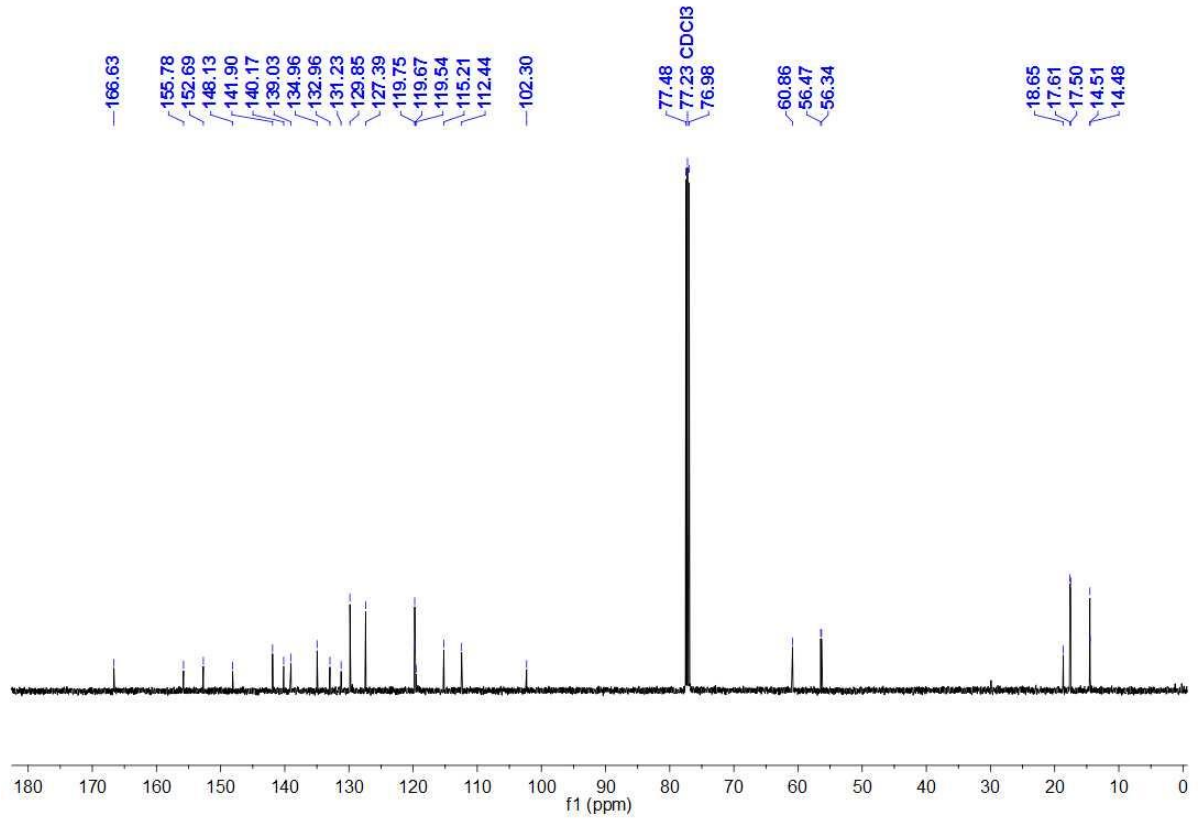
6h. methyl (*E*)-3-(3,5-dichloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)phenyl)acrylate



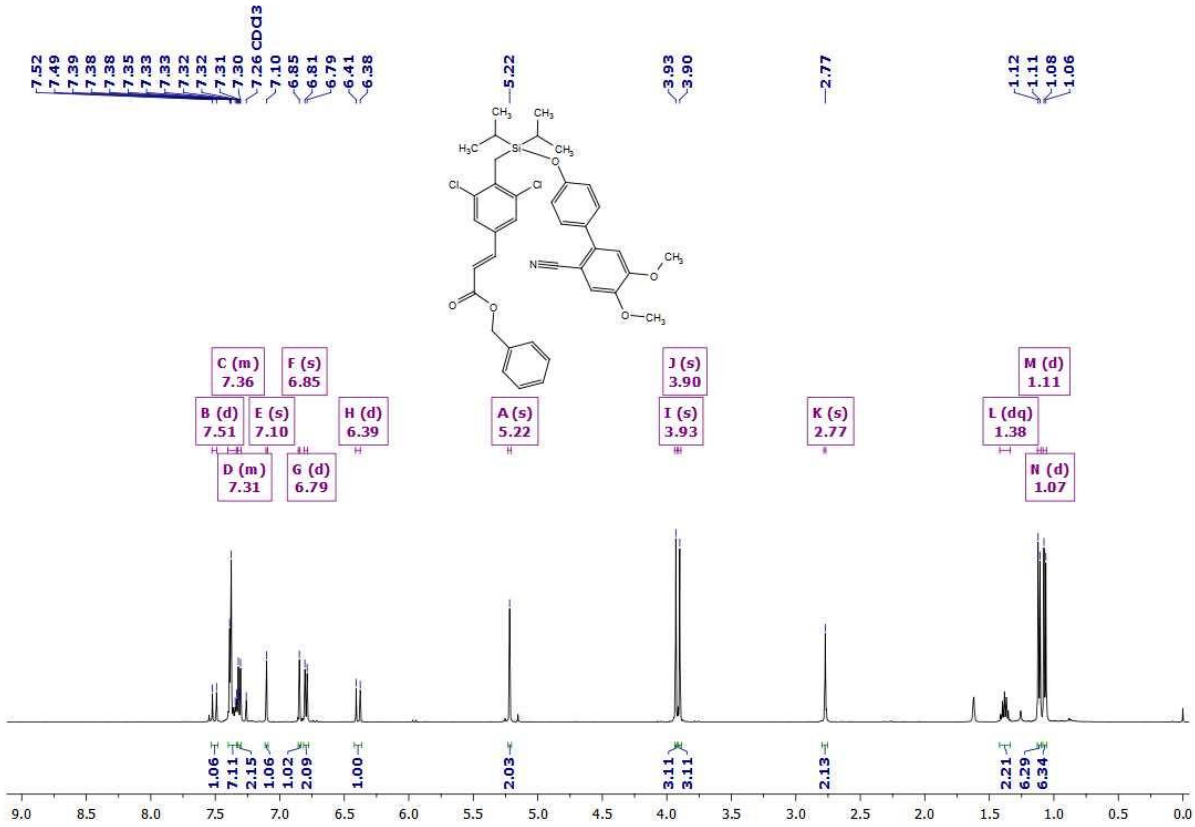


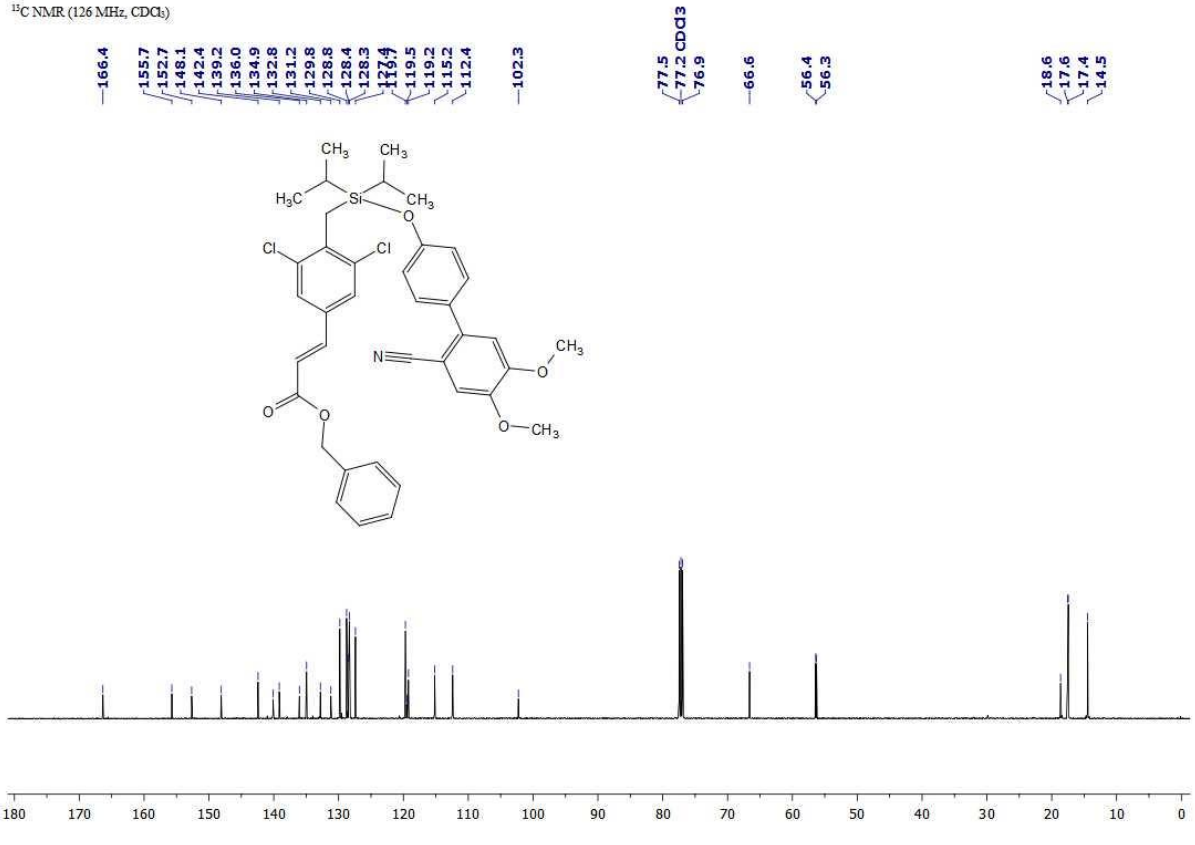
6i. ethyl (*E*)-3-(3,5-dichloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)-diisopropylsilyl)methyl)-phenyl)acrylate



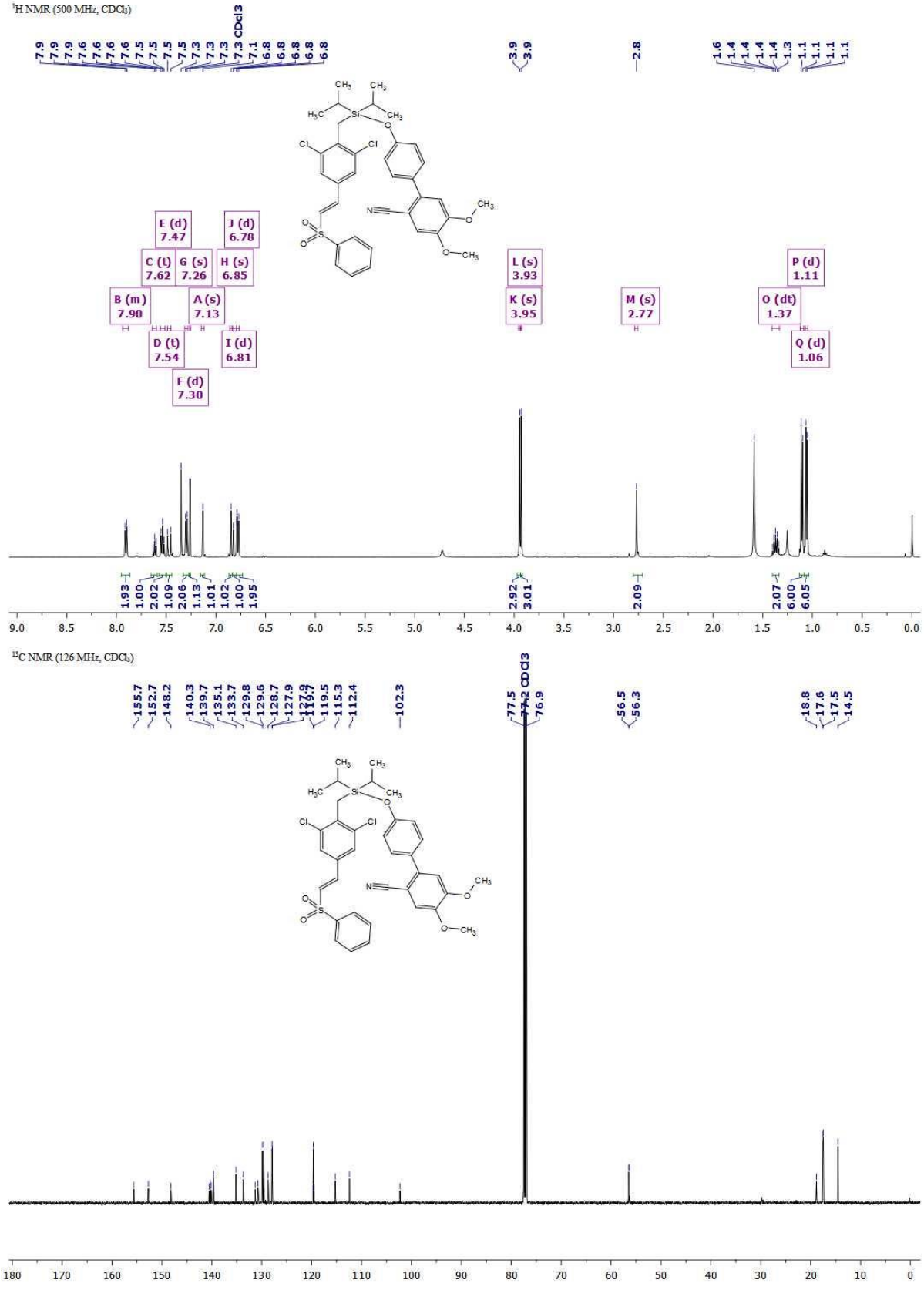


6j. benzyl (*E*)-3-(3,5-dichloro-4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)di-isopropylsilyl)methyl)phenyl)acrylate

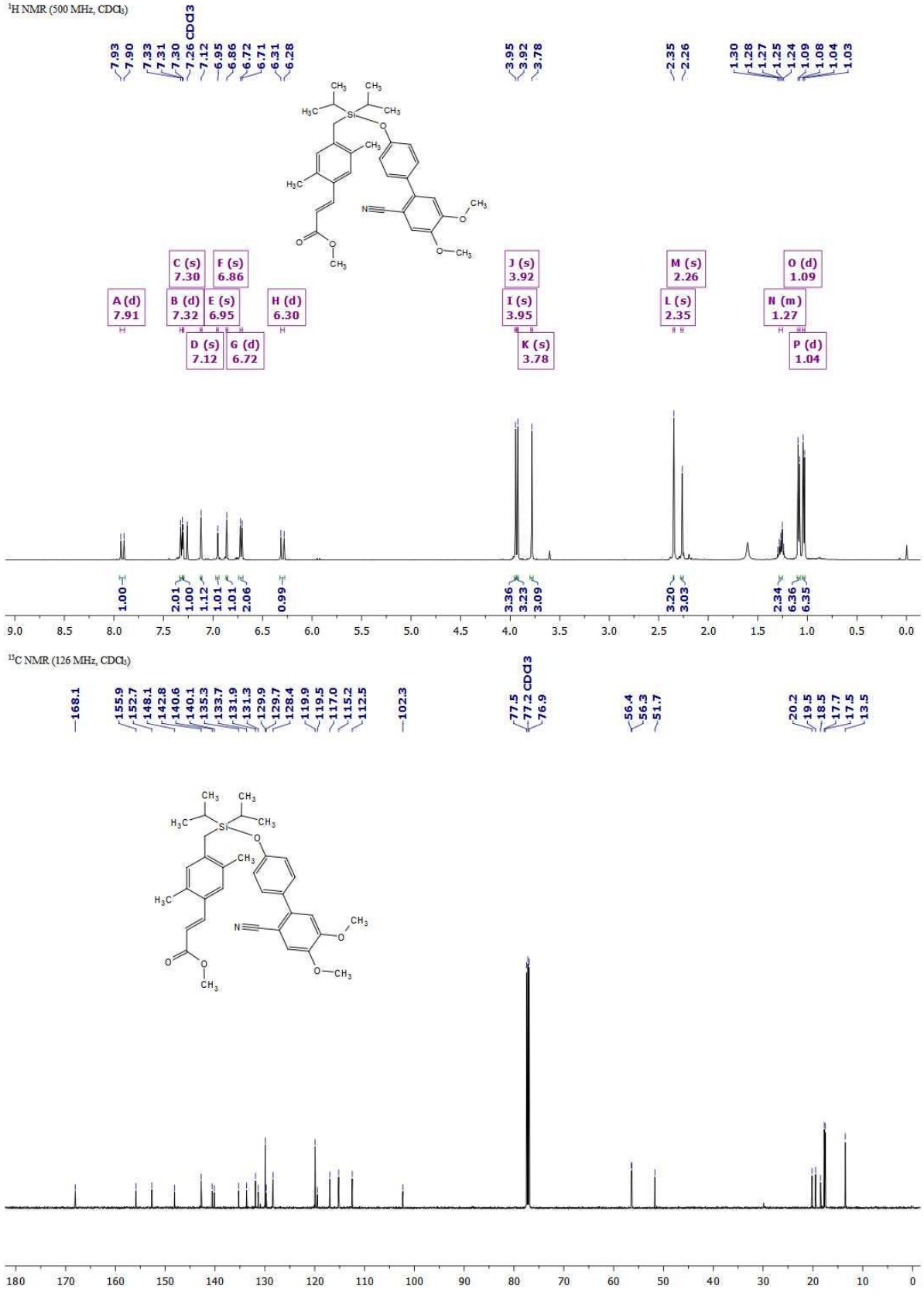




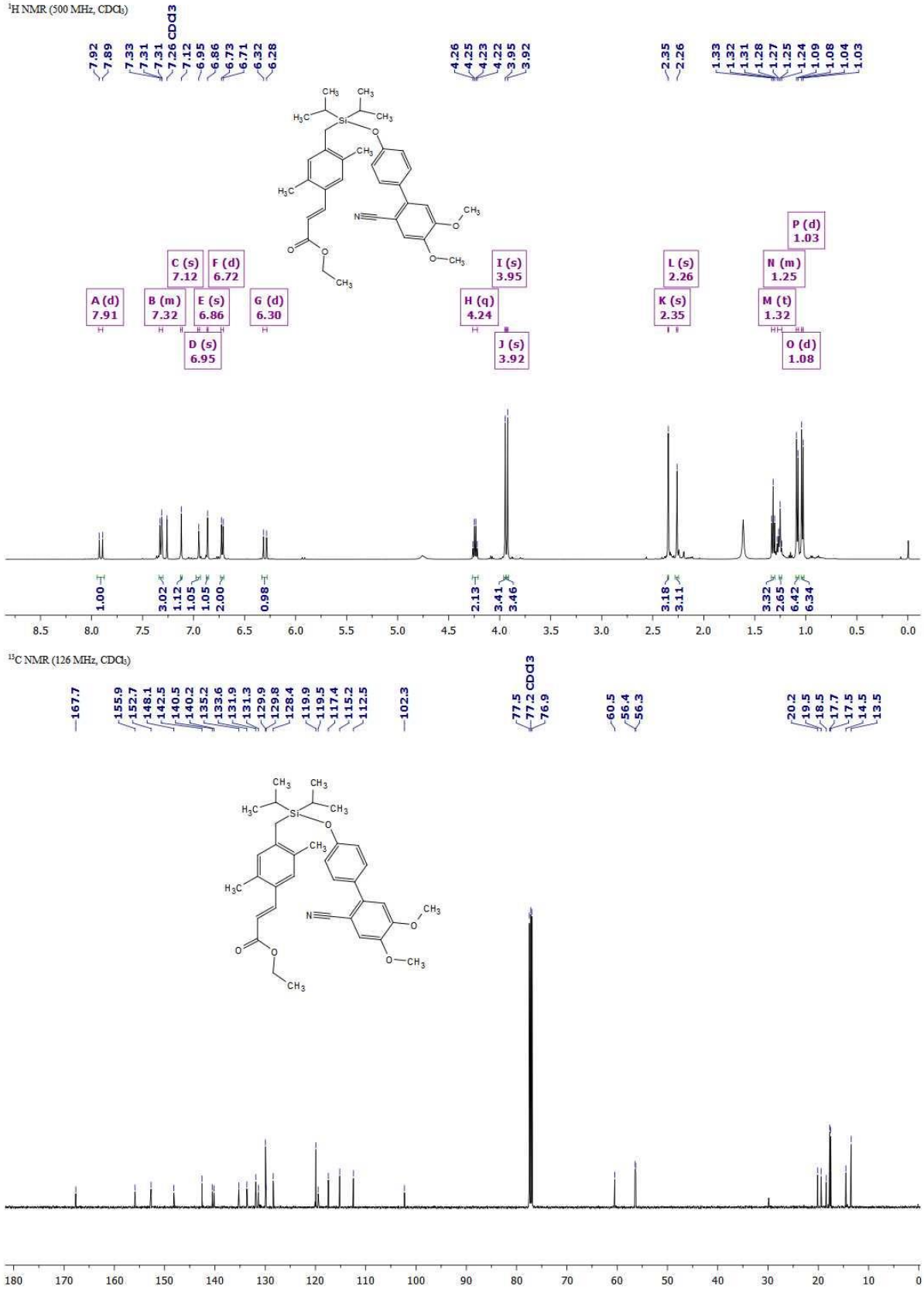
6k. (*E*)-4'-(((2,6-dichloro-4-(2-(phenylsulfonyl)vinyl)benzyl)diisopropylsilyl)oxy)-4,5-dimethoxy-[1,1'-biphen-yl]-2-carbonitrile



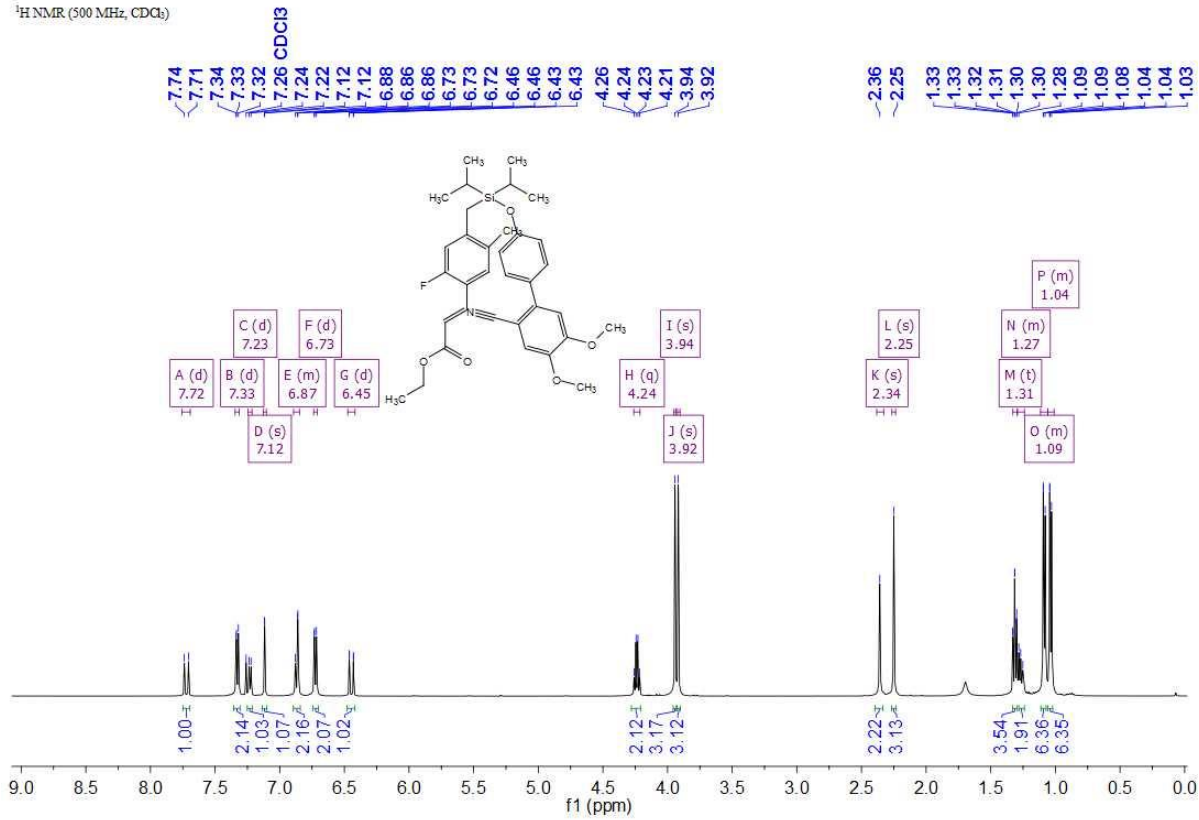
6l. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)methyl)-2,5-dimethylphenyl)acrylate

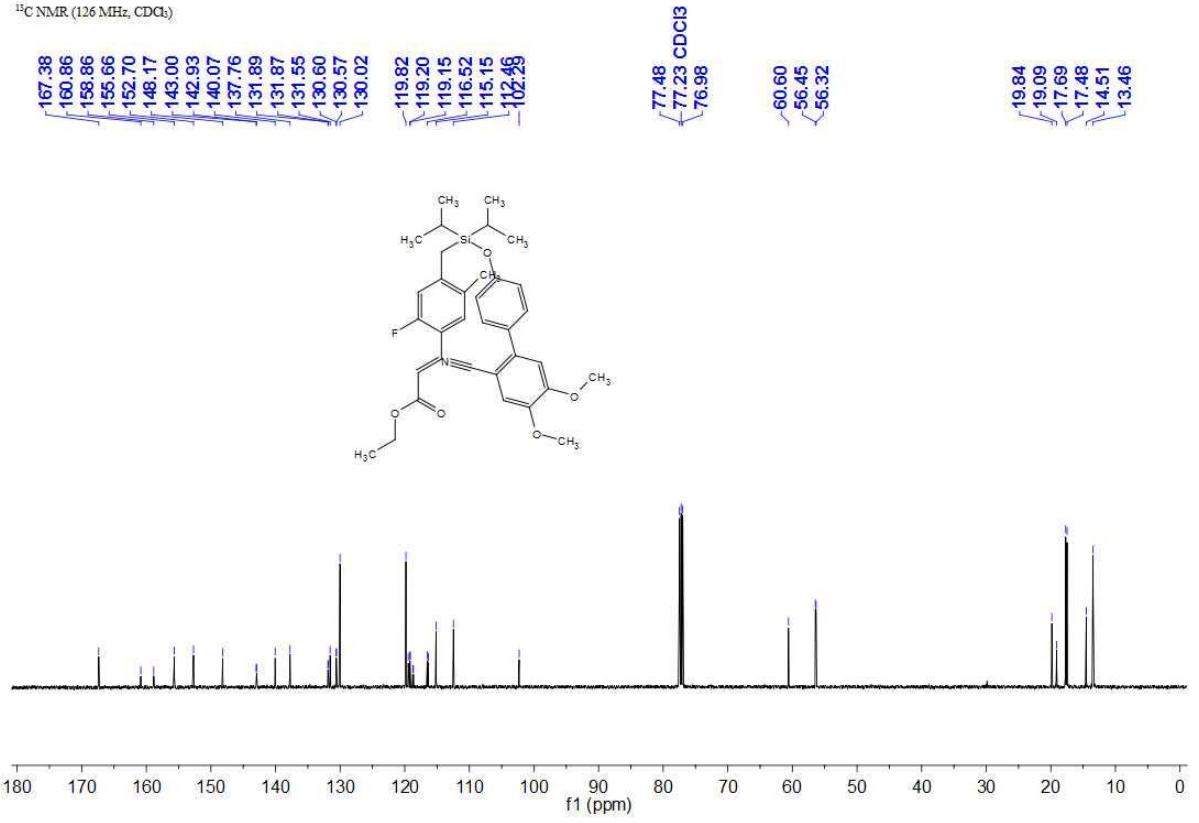


6m. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)methyl)-2,5-dimethylphenyl)acrylate

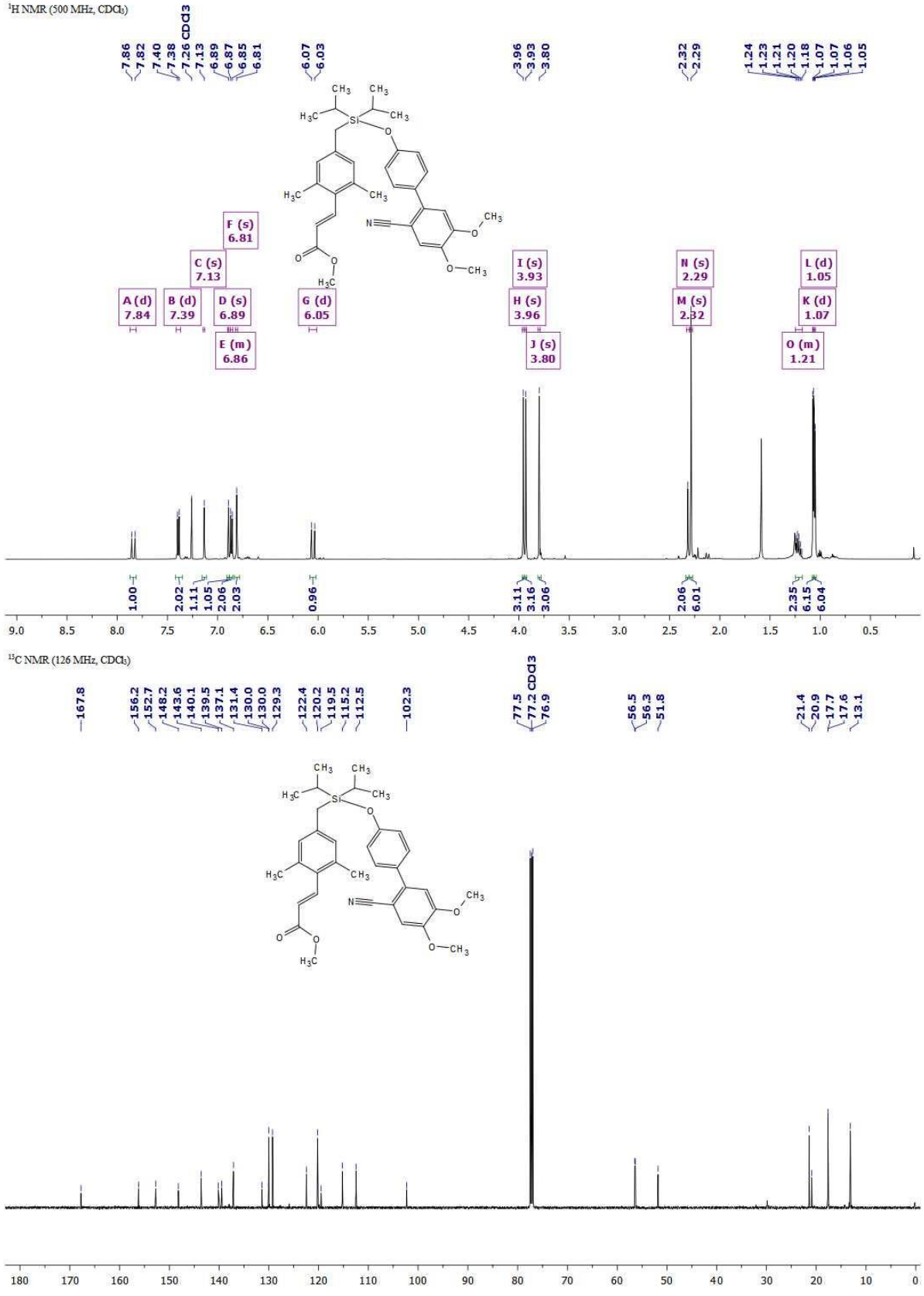


6n. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2-fluoro-5-methylphenyl)acrylate

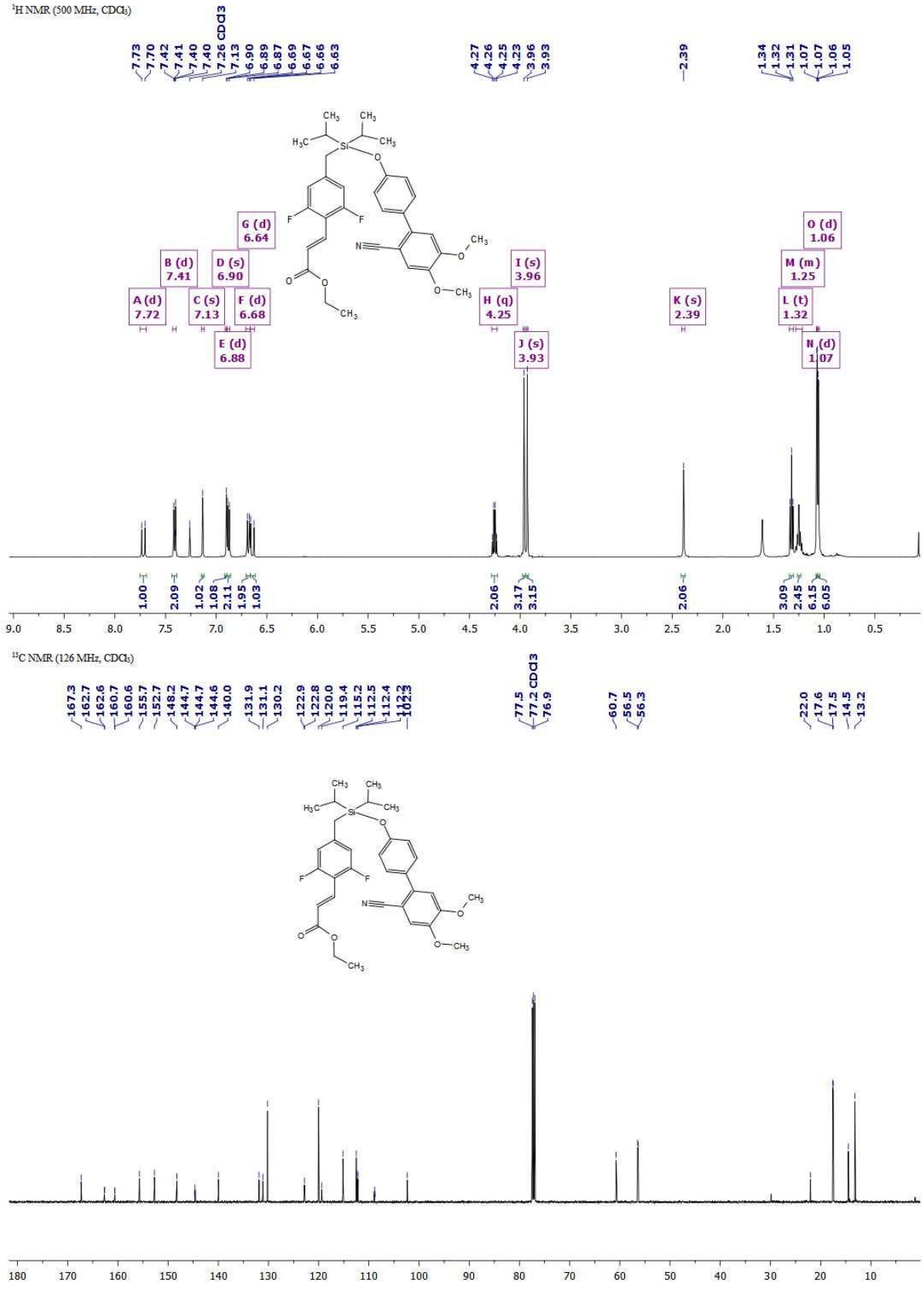




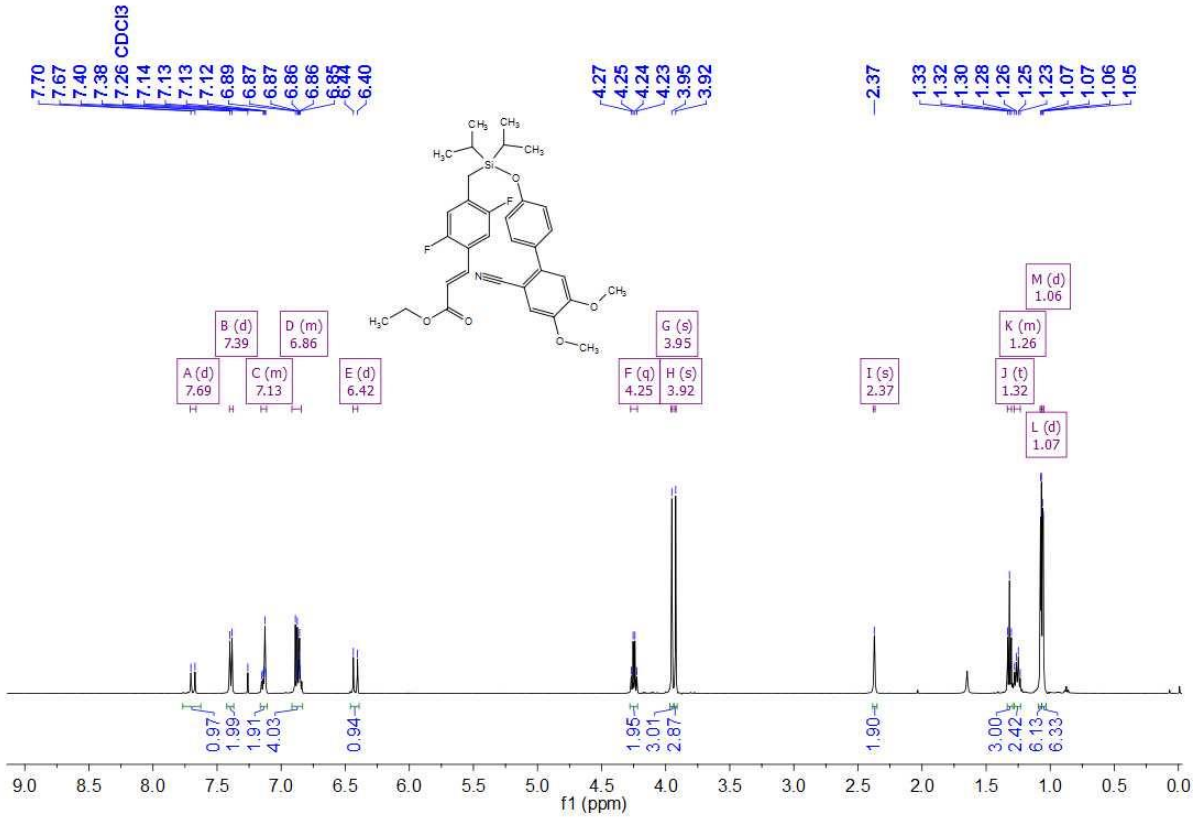
6o. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)methyl)-2,6-dimethylphenyl)acrylate

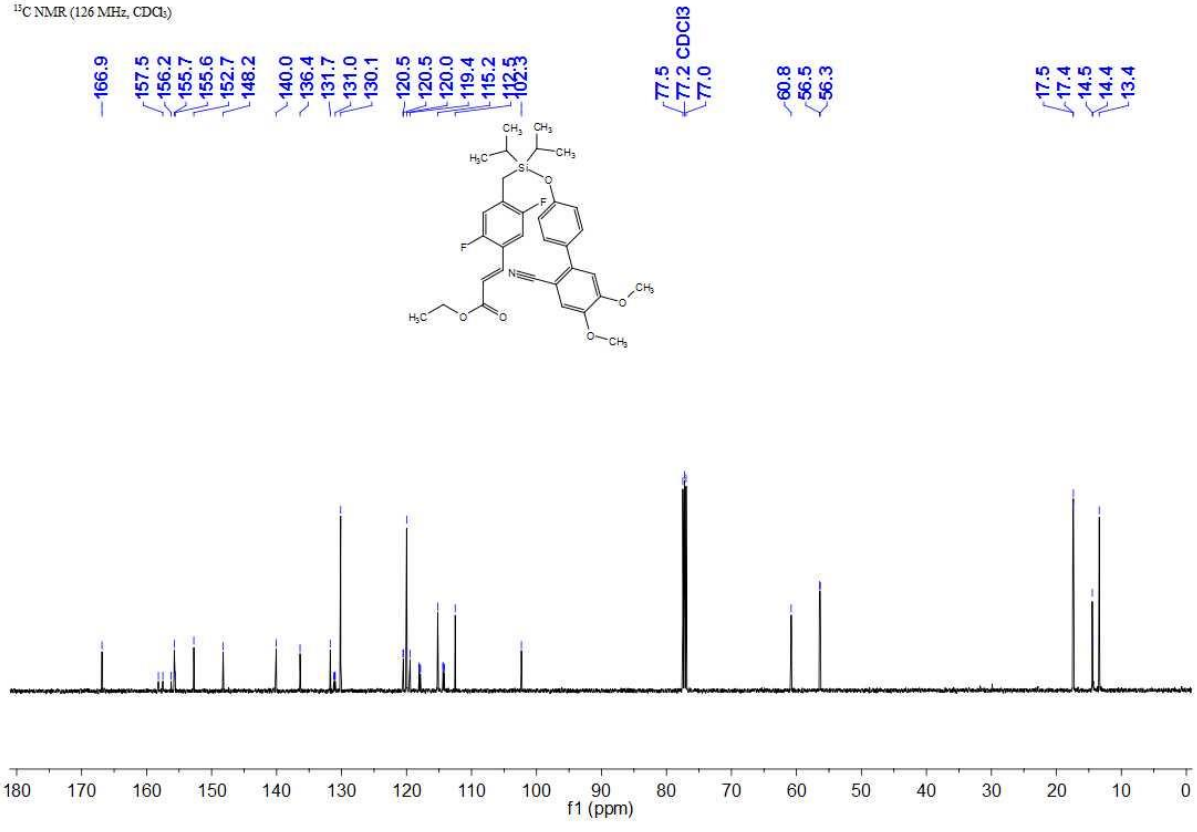


6p. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropyl-silyl)methyl)-2,6-difluorophenyl)acrylate

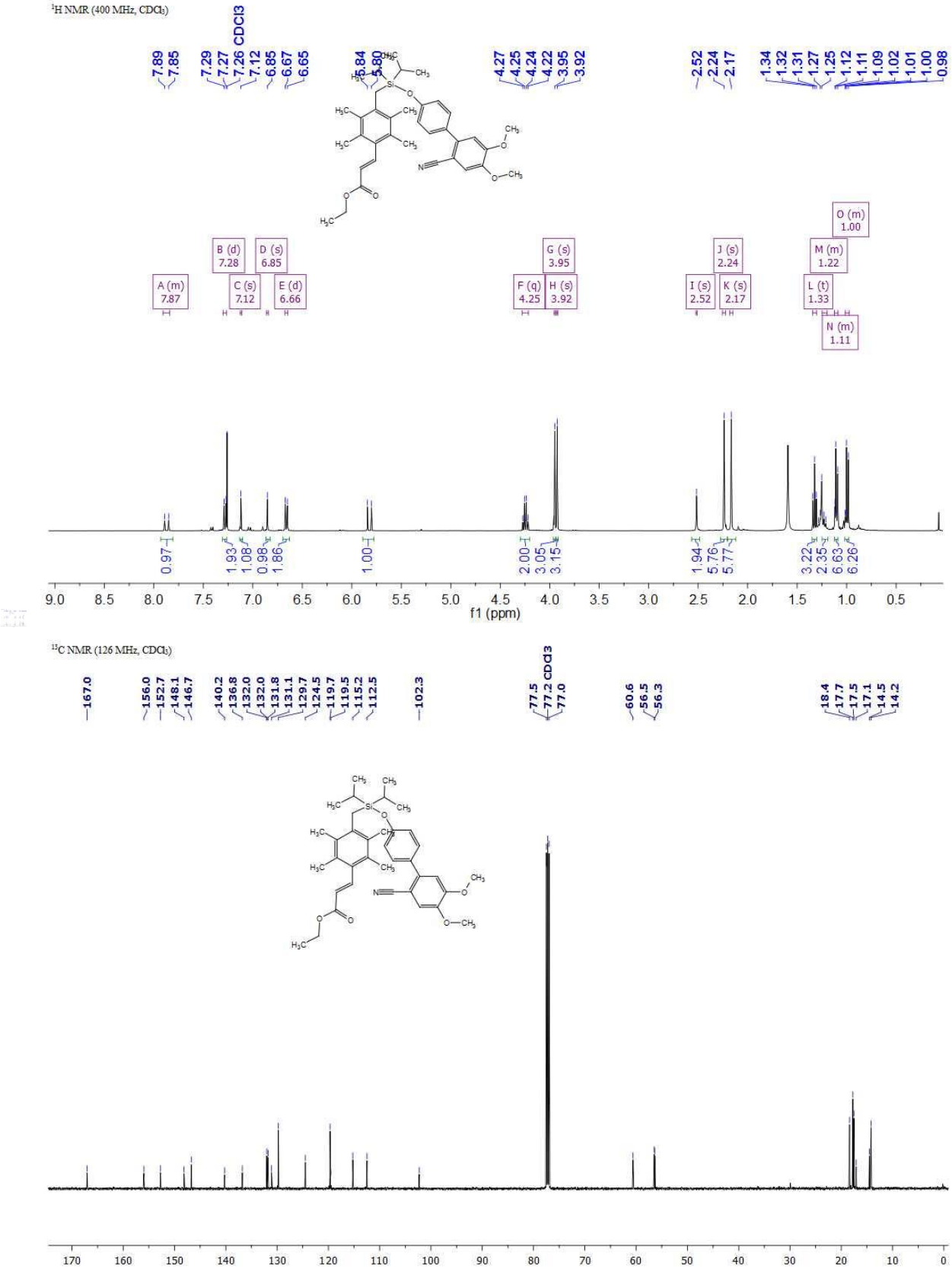


6q. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2,5-difluoro-phenyl)acrylate

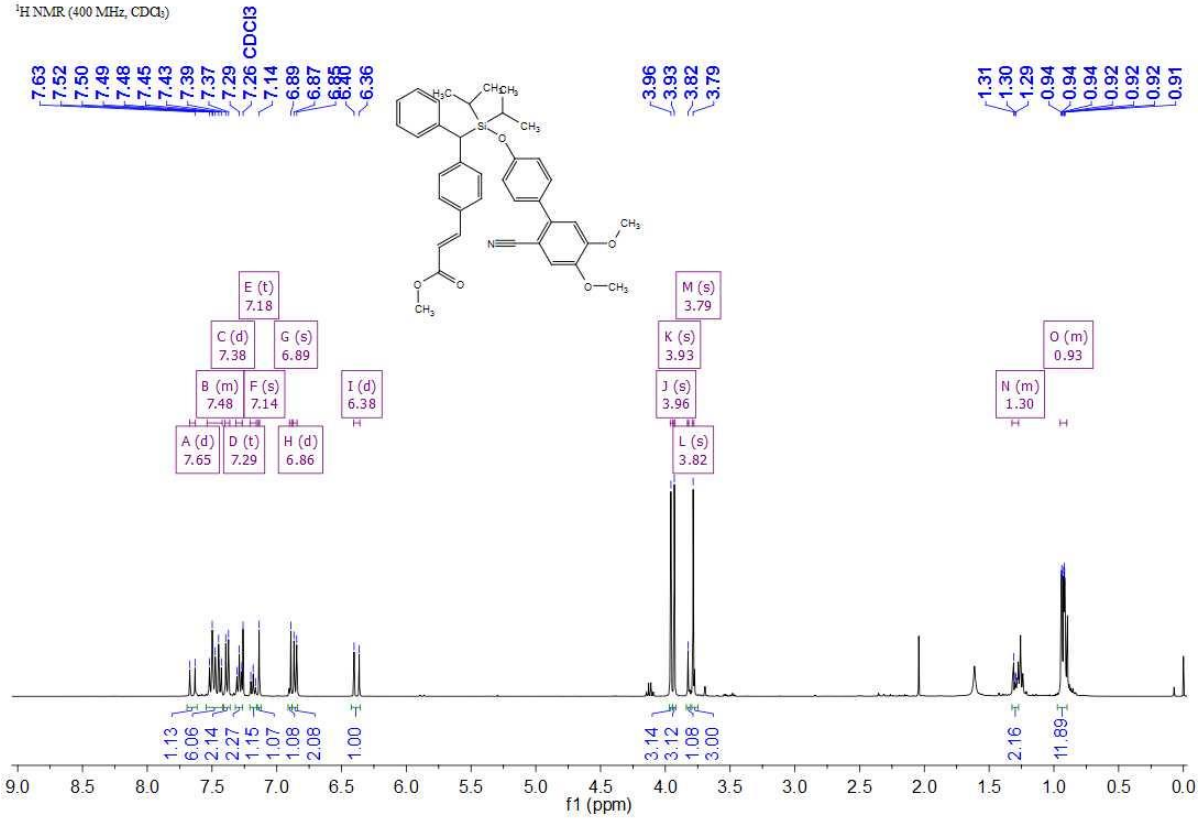


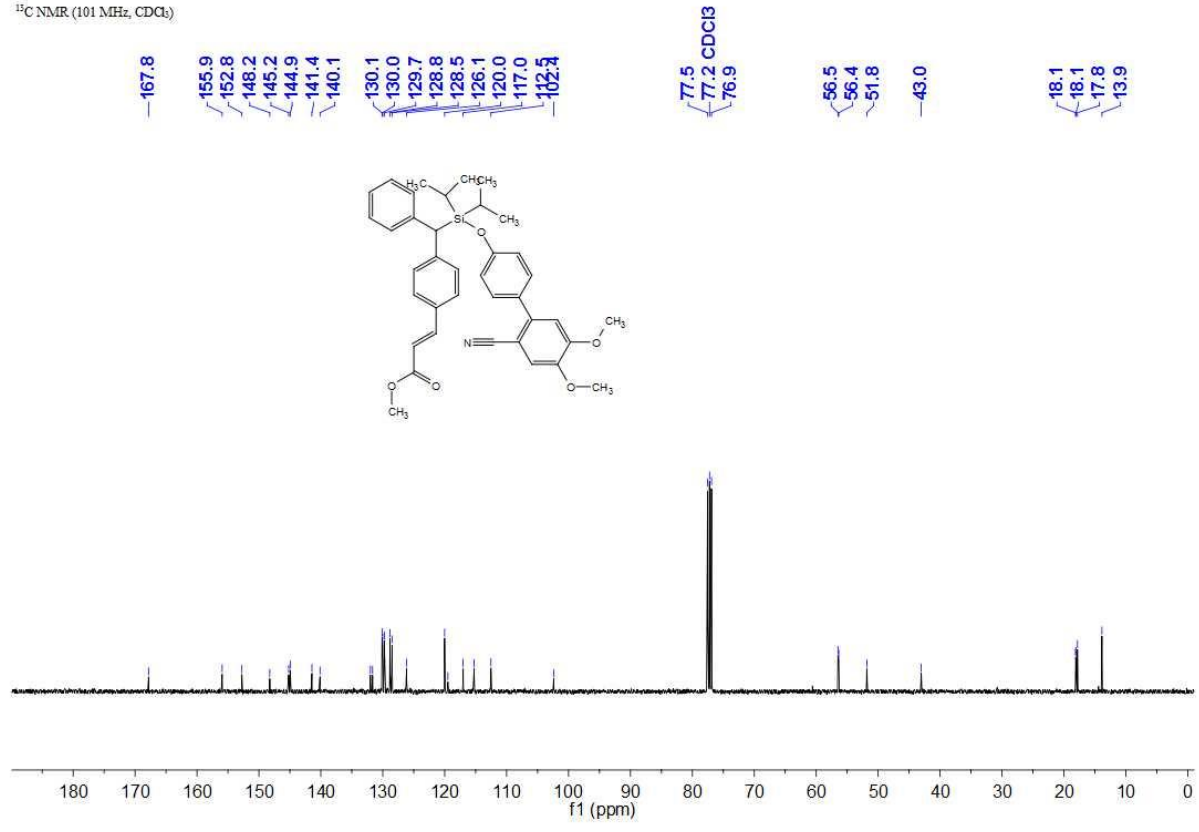


6r. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)-2,3,5,6-tetramethylphenyl)acrylate

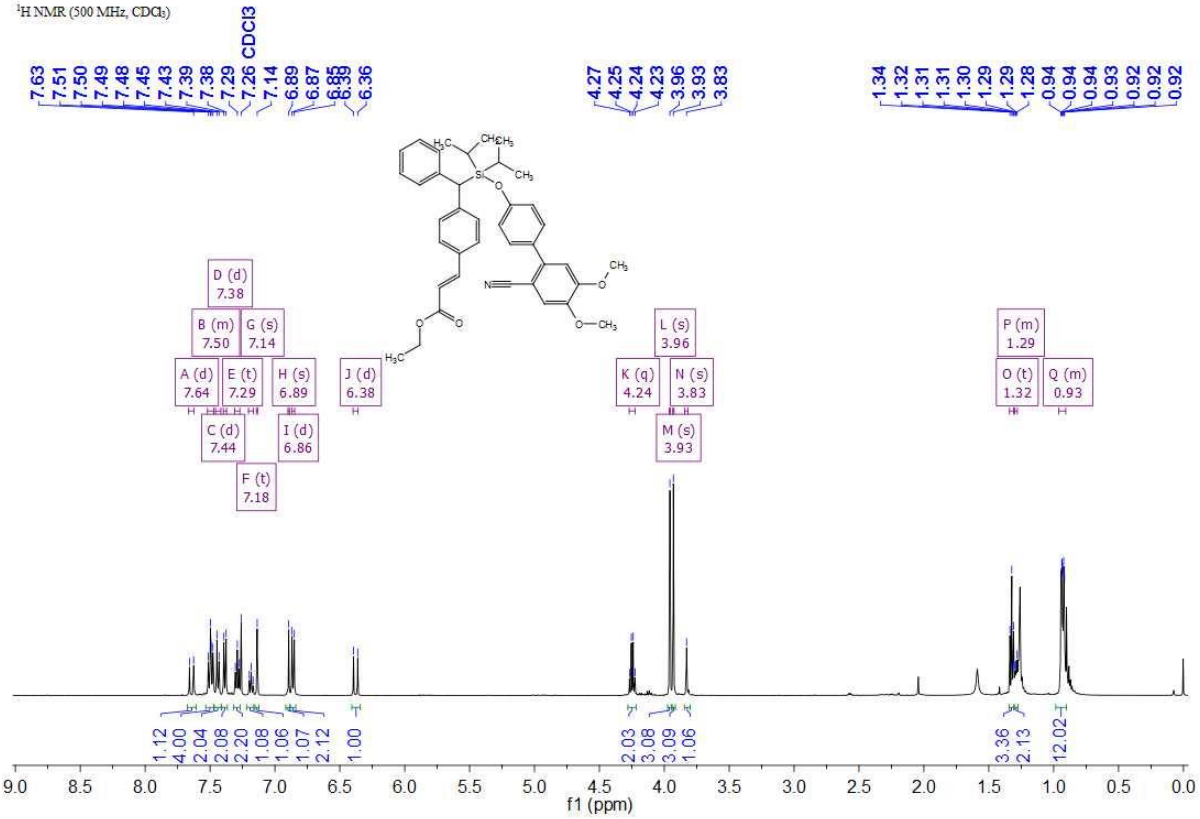


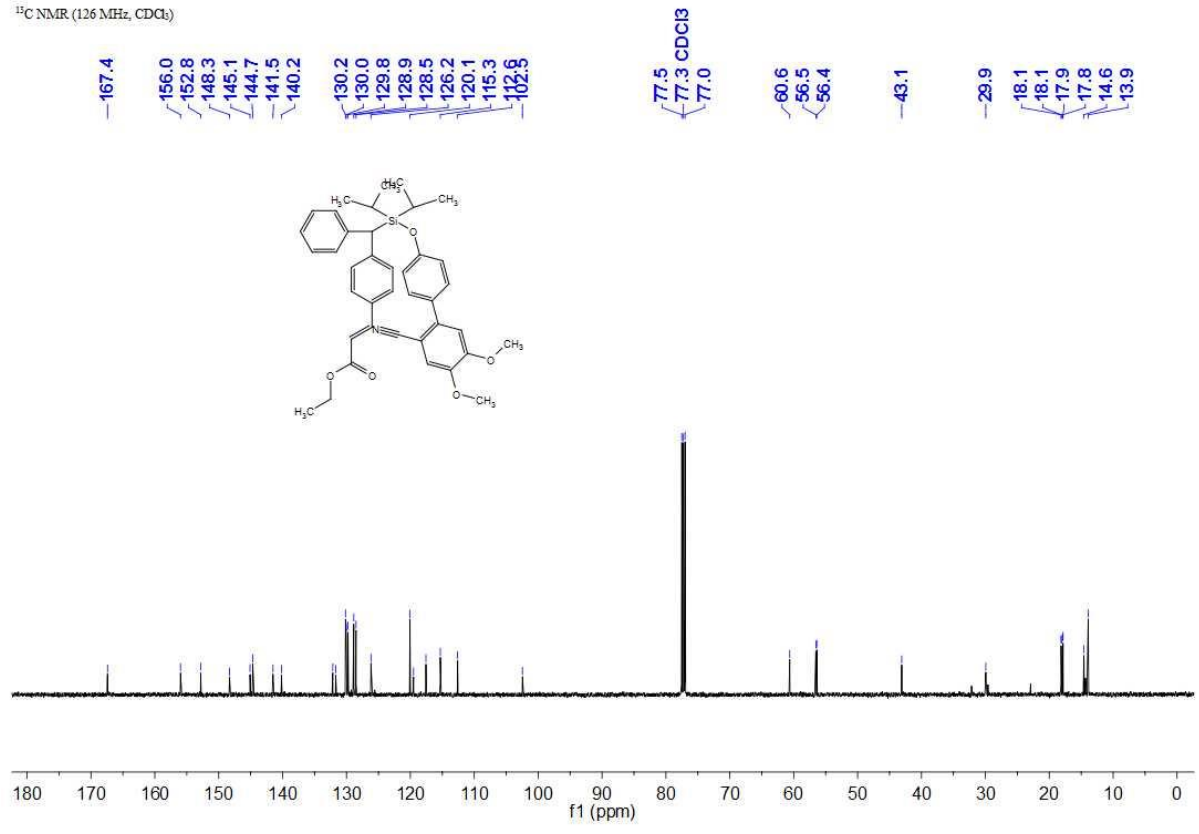
8a. methyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)(phenyl)methyl)phenyl)acrylate



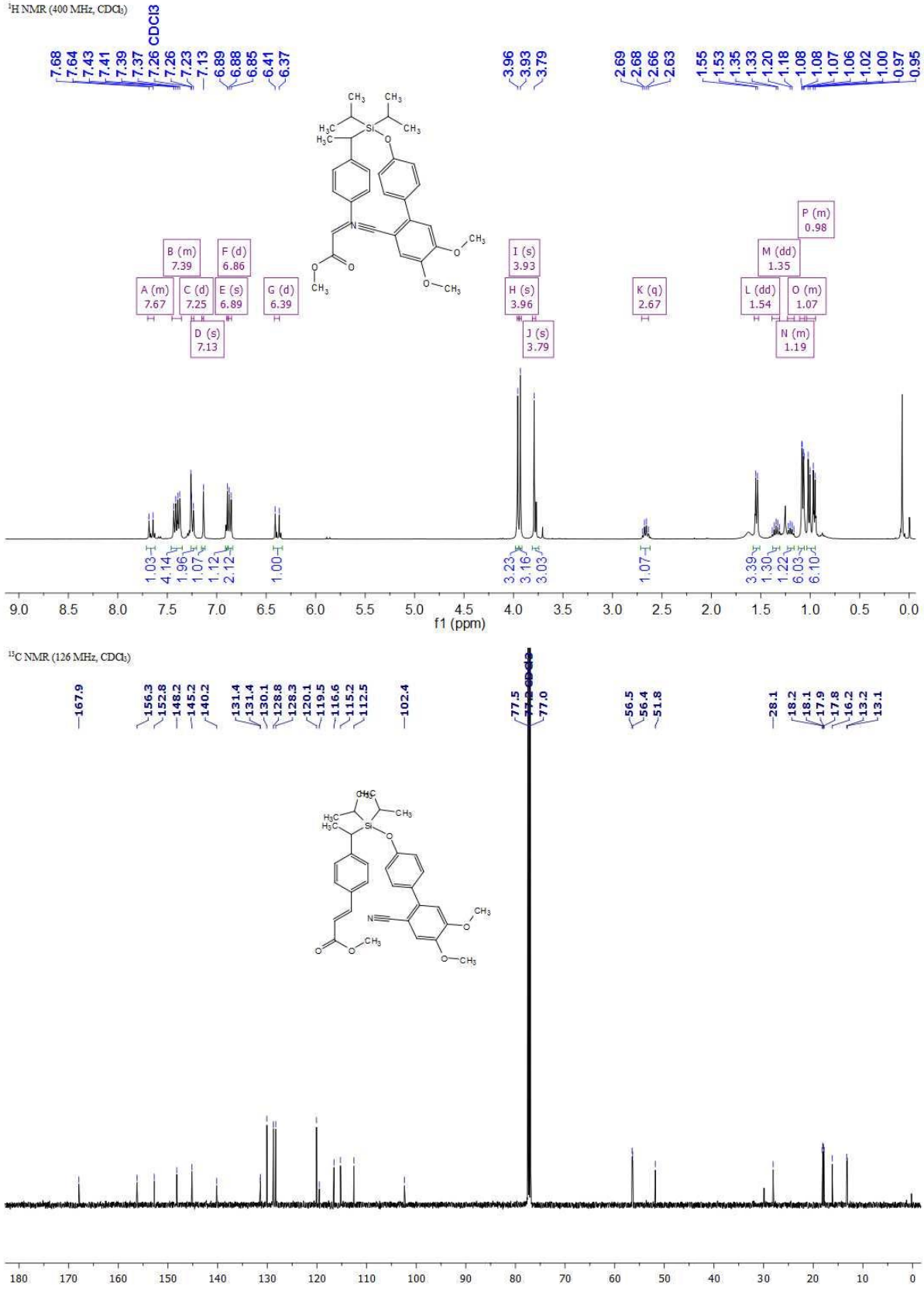


8b. ethyl (*E*)-3-(4-((((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)(phenyl)methyl)phenyl)acrylate

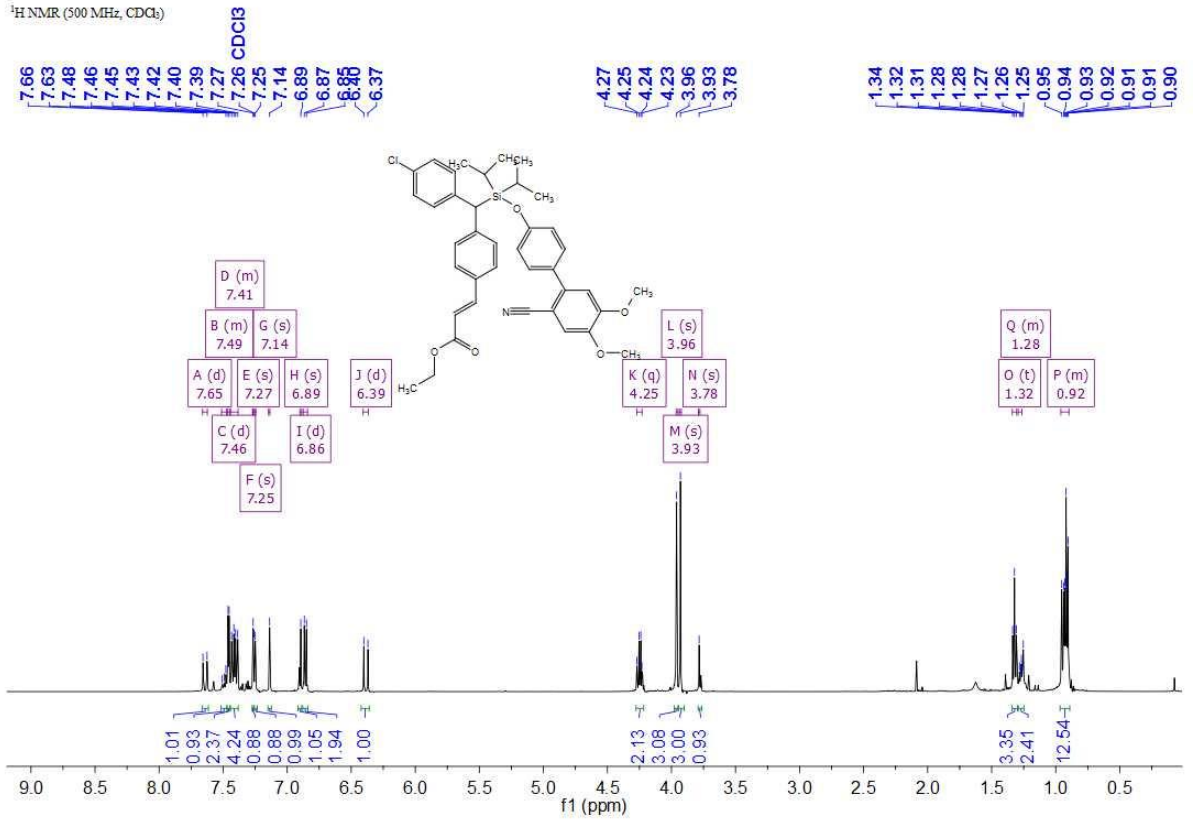


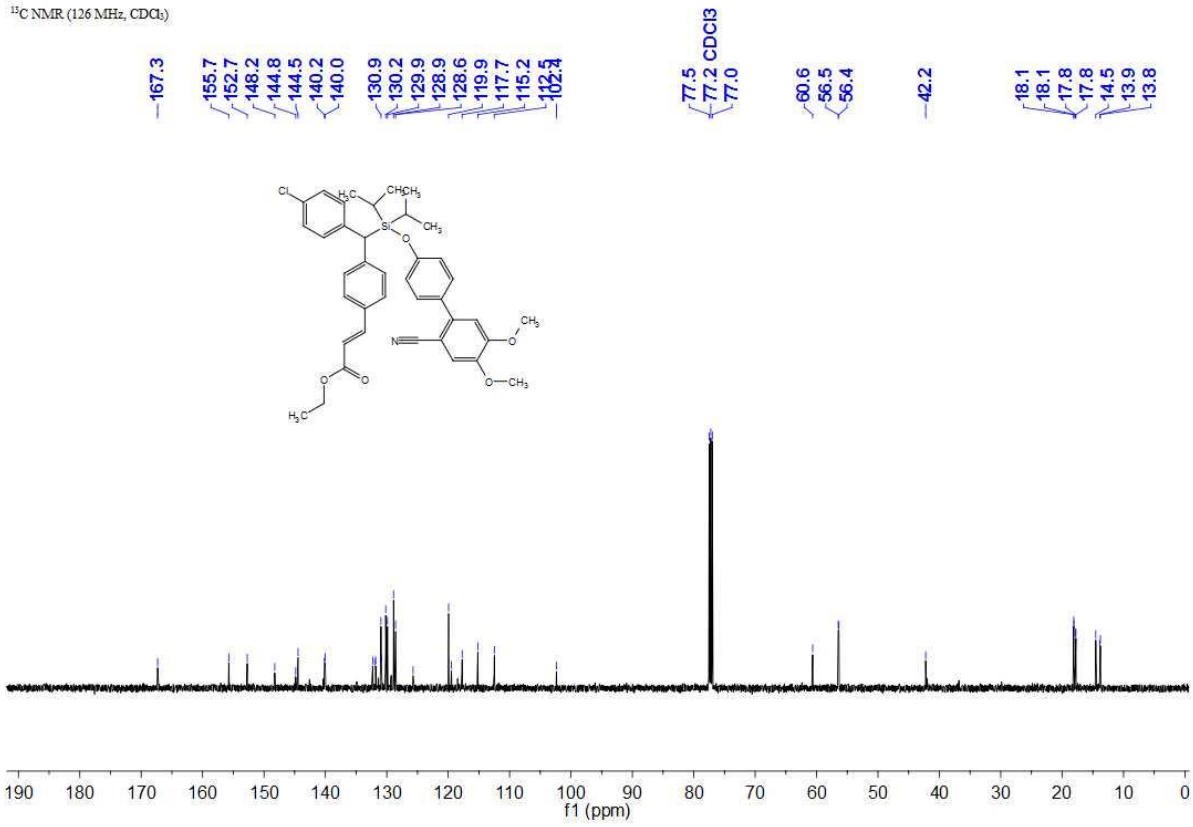


8c. methyl (*E*)-3-(4-(1-(((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)ethyl)phenyl)acrylate

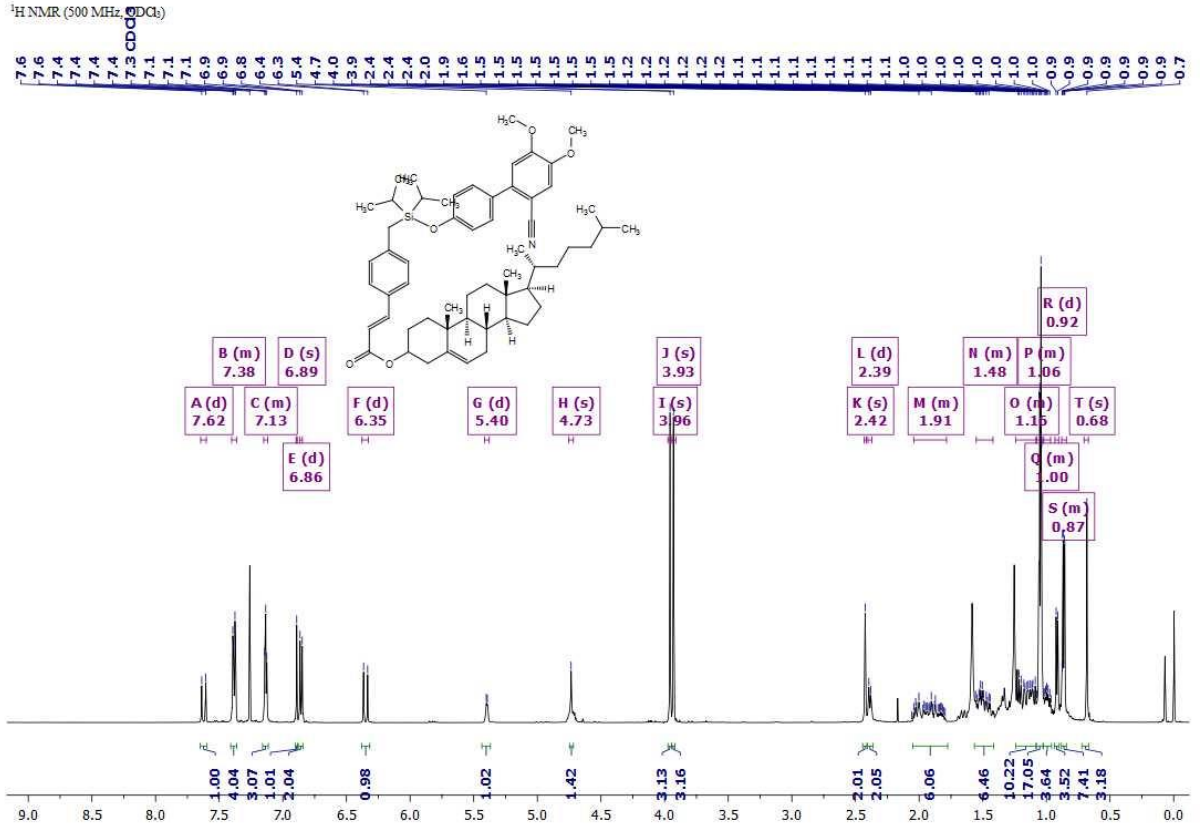


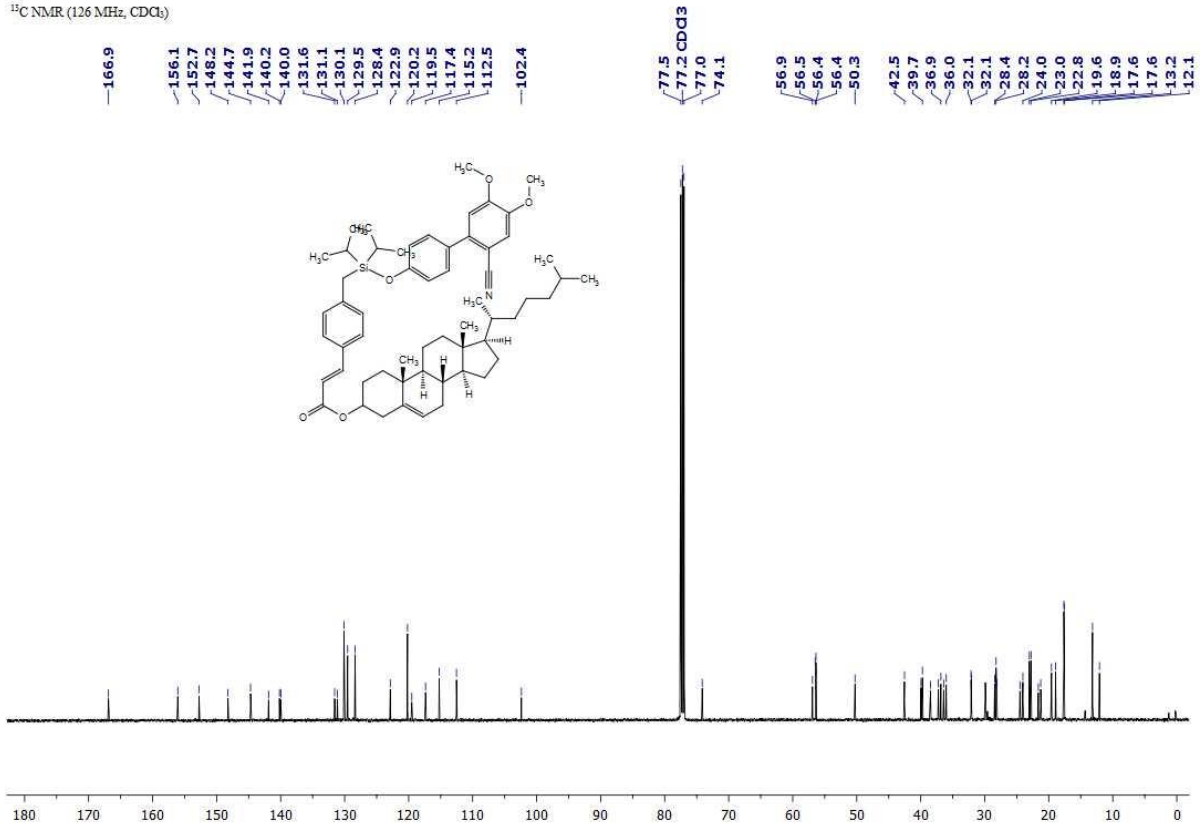
8d. methyl (*E*)-3-(4-((4-chlorophenyl)(((2'-cyano-4',5'-dimethoxy-[1,1'-biphenyl]-4-yl)oxy)diisopropylsilyl)methyl)phenyl)acrylate



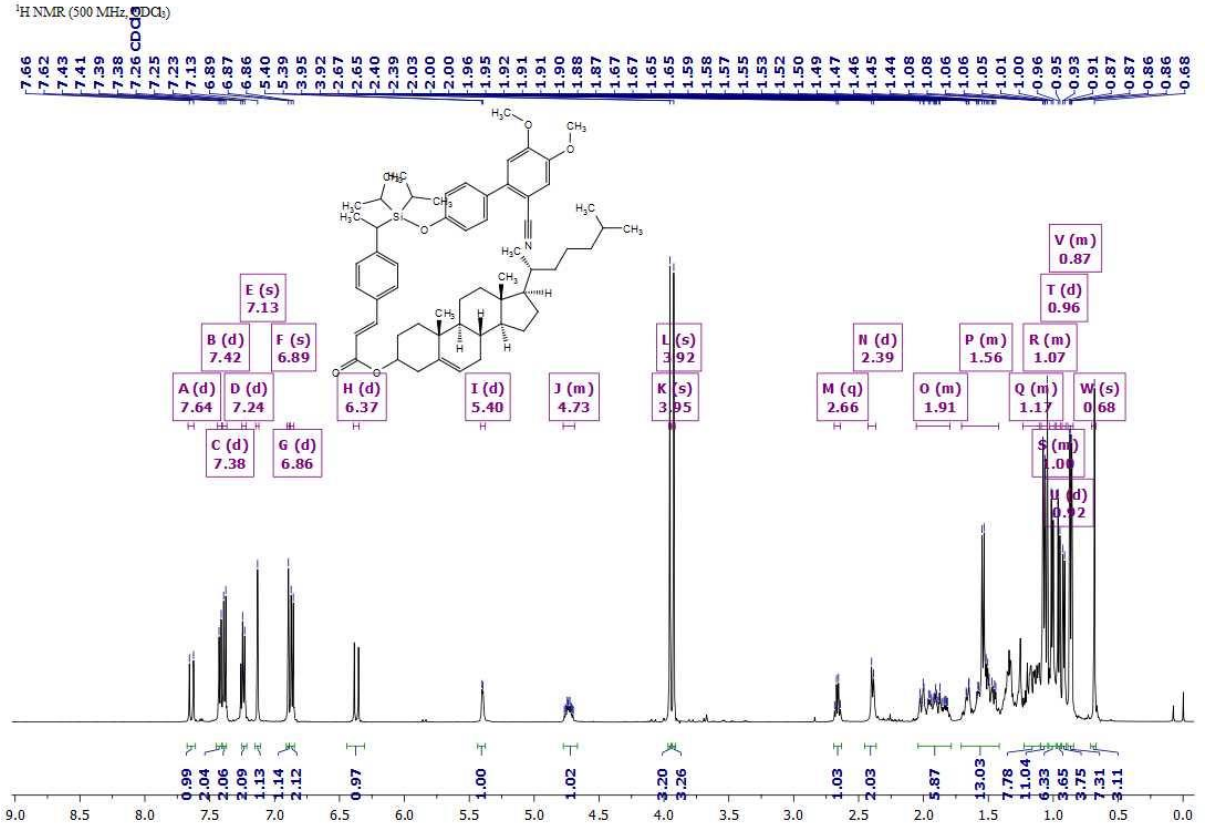


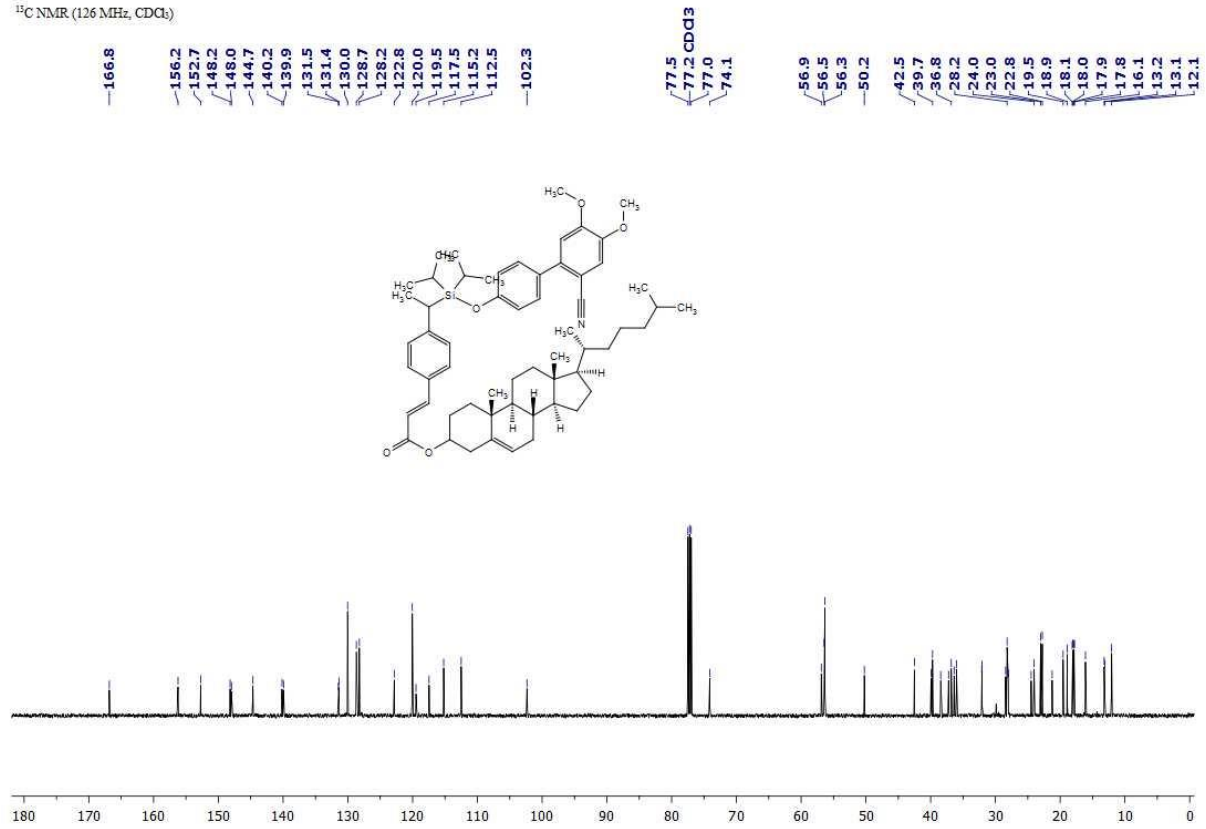
8e. (*E*)-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 3-(4-(((2'-cyanobiphenyl-4-yloxy)diisopropylsilyl)methyl)phenyl)acrylate



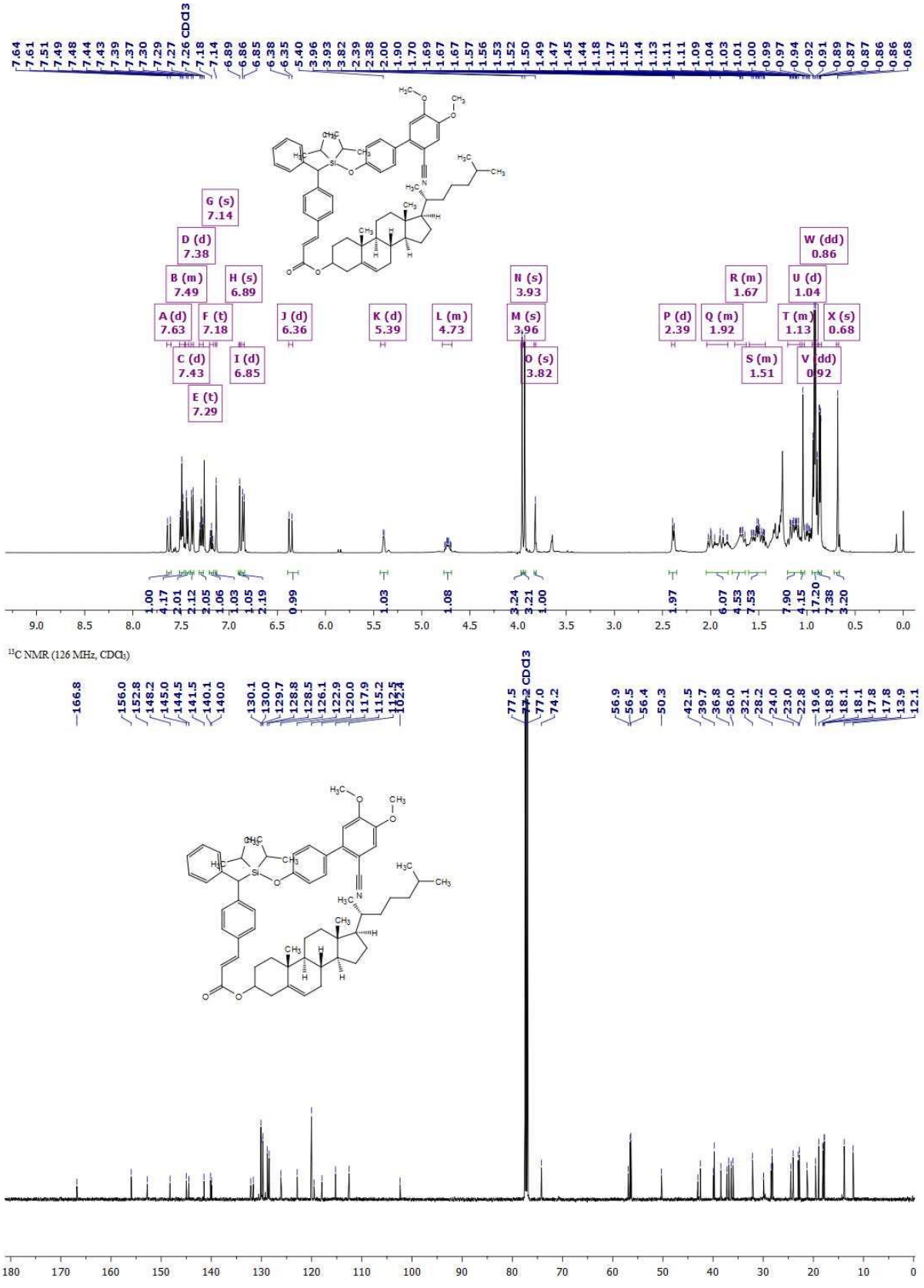


8f. (*E*)-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 3-(4-(((2'-cyanobiphenyl-4-yloxy)diisopropylsilyl)ethyl)phenyl)acrylate

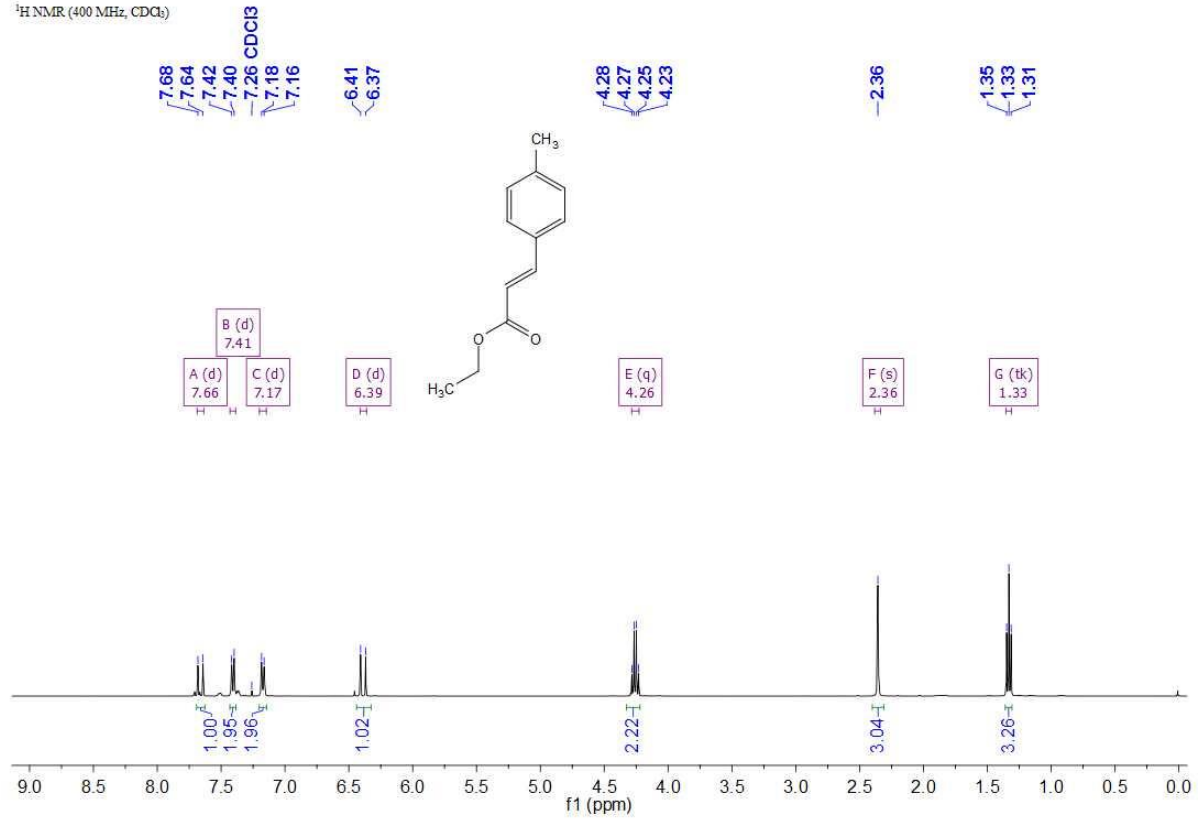


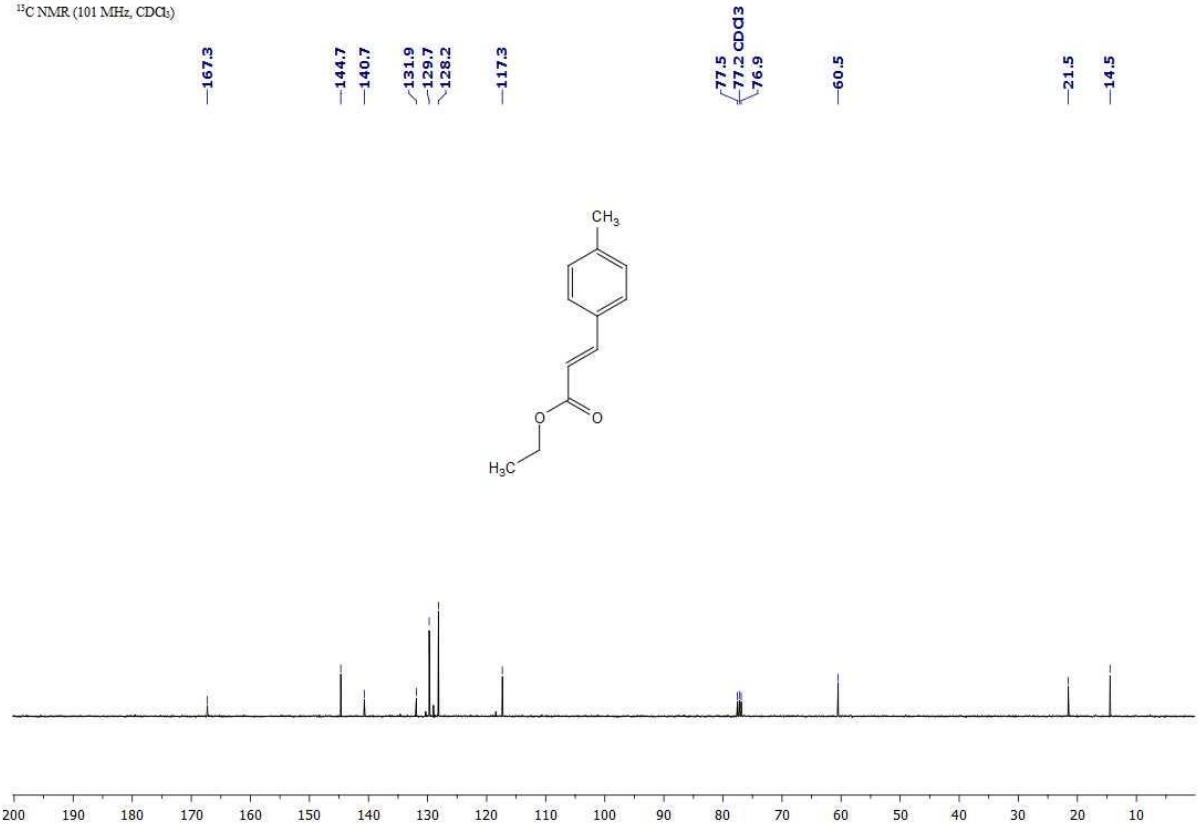


8g. (*E*)-((8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl) 3-(4-(((2'-cyanobiphenyl-4-yloxy)diisopropylsilyl)(phenyl)methyl)phenyl)acrylate

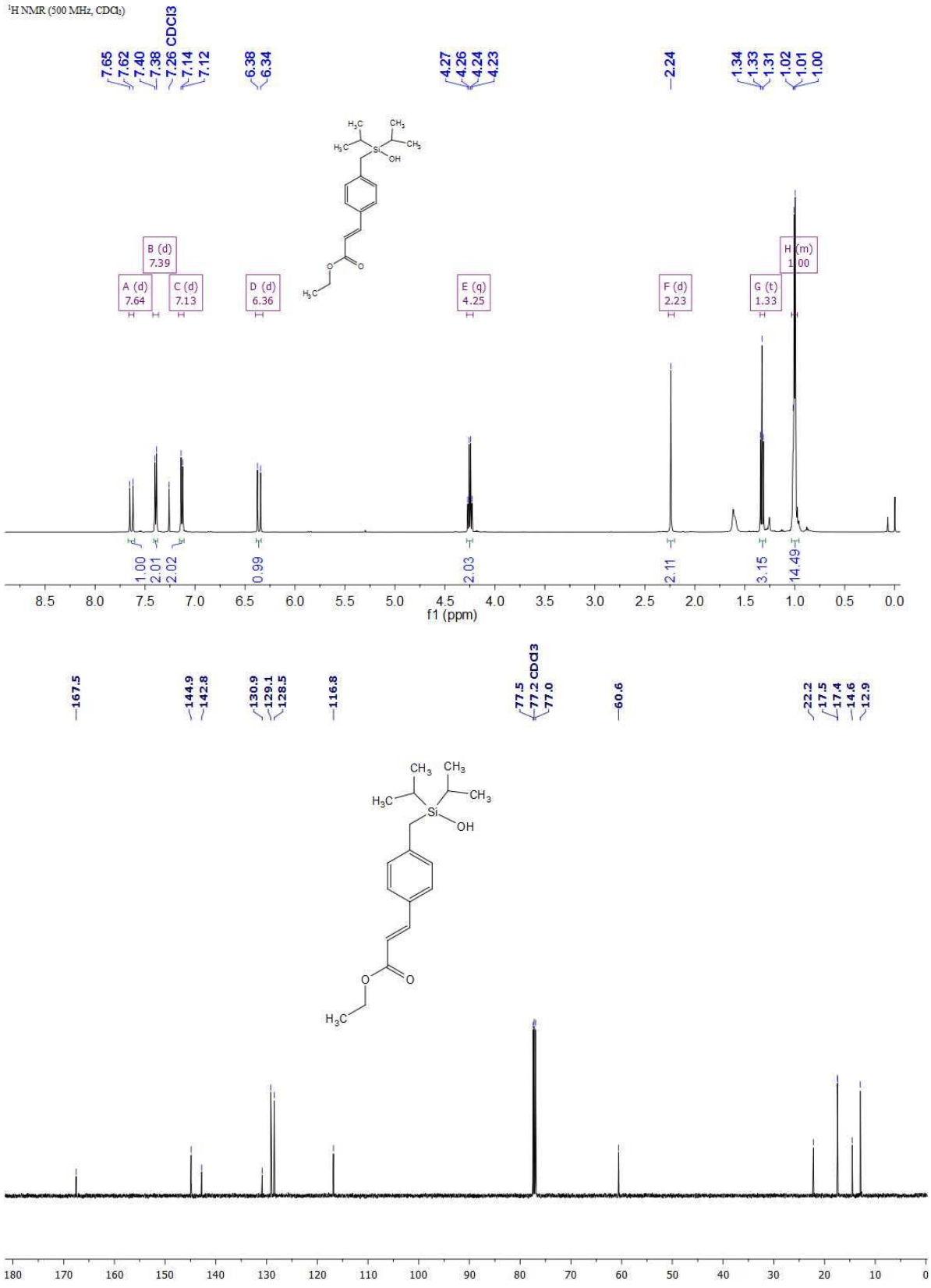


9. Ethyl (*E*)-3-(p-tolyl)acrylate

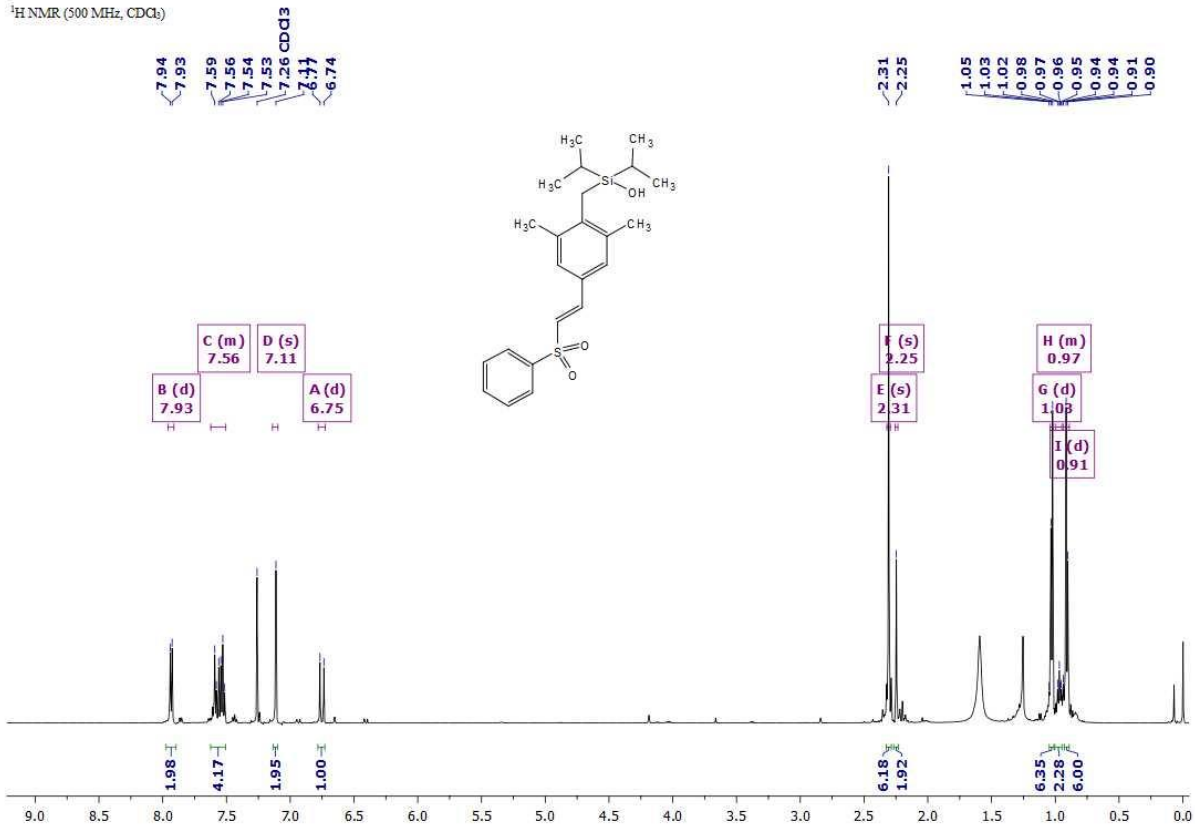


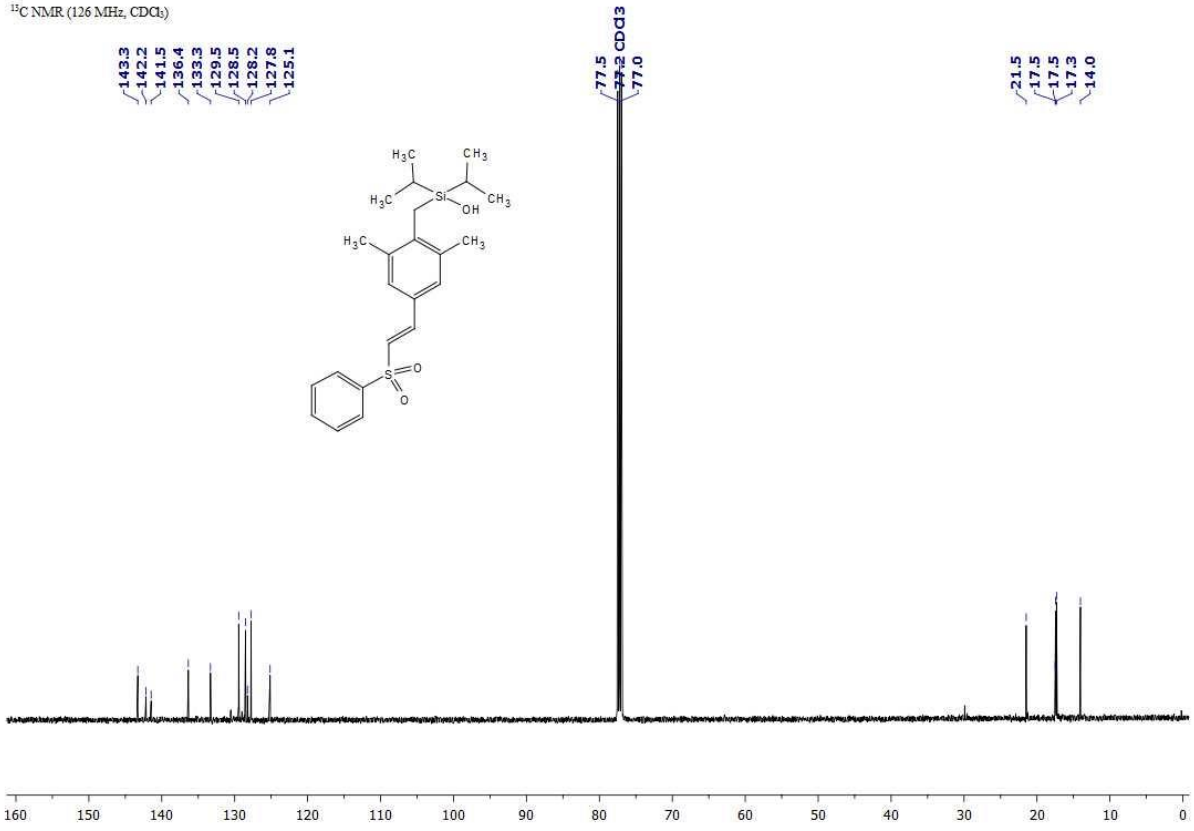


11. Ethyl (E)-3-(4-((hydroxydiisopropylsilyl)methyl)phenyl)acrylate

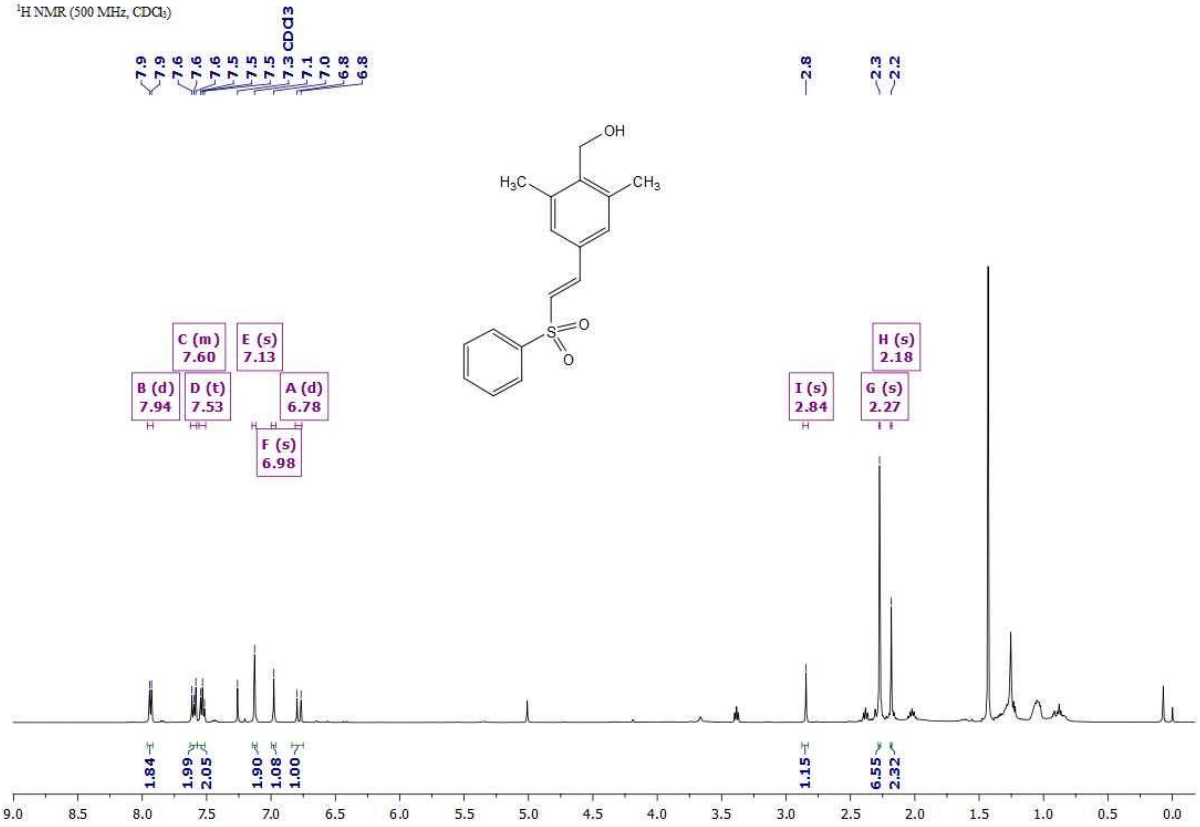


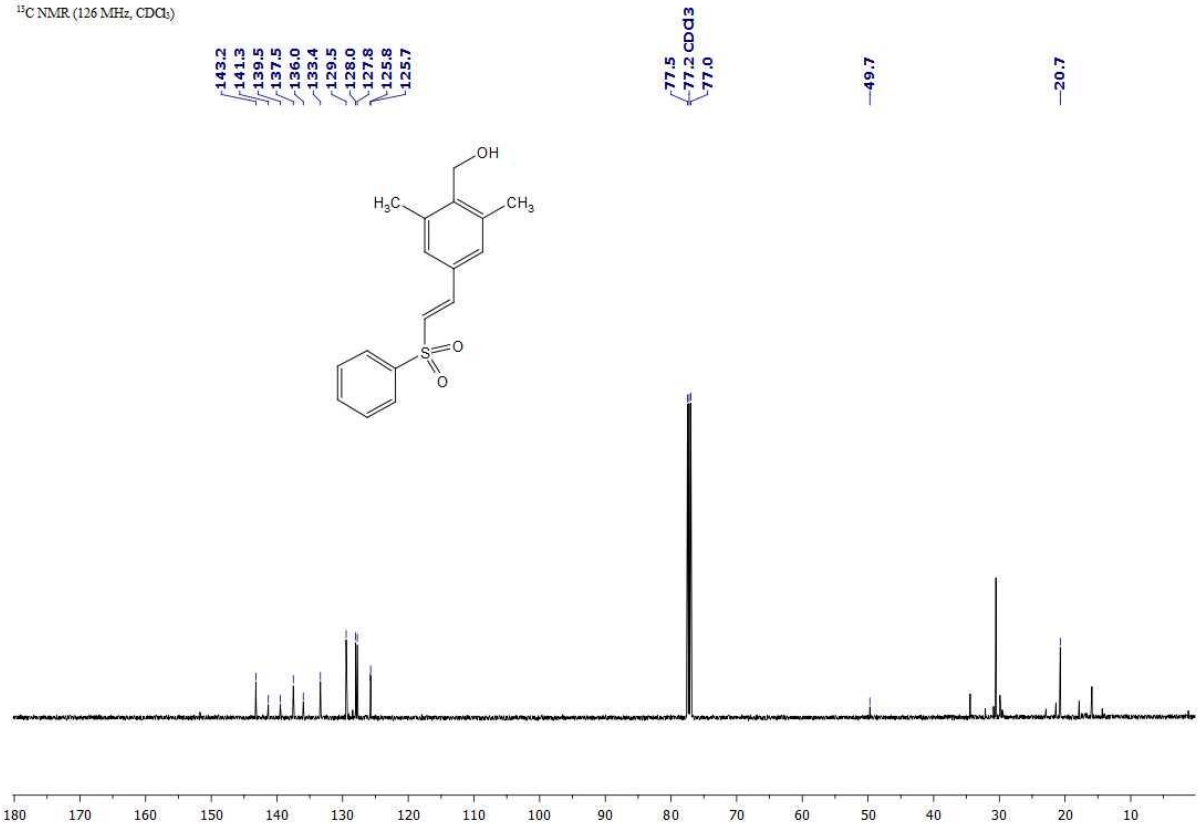
12. (*E*)-(2,6-dimethyl-4-(2-(phenylsulfonyl)vinyl)benzyl)diisopropylsilanol



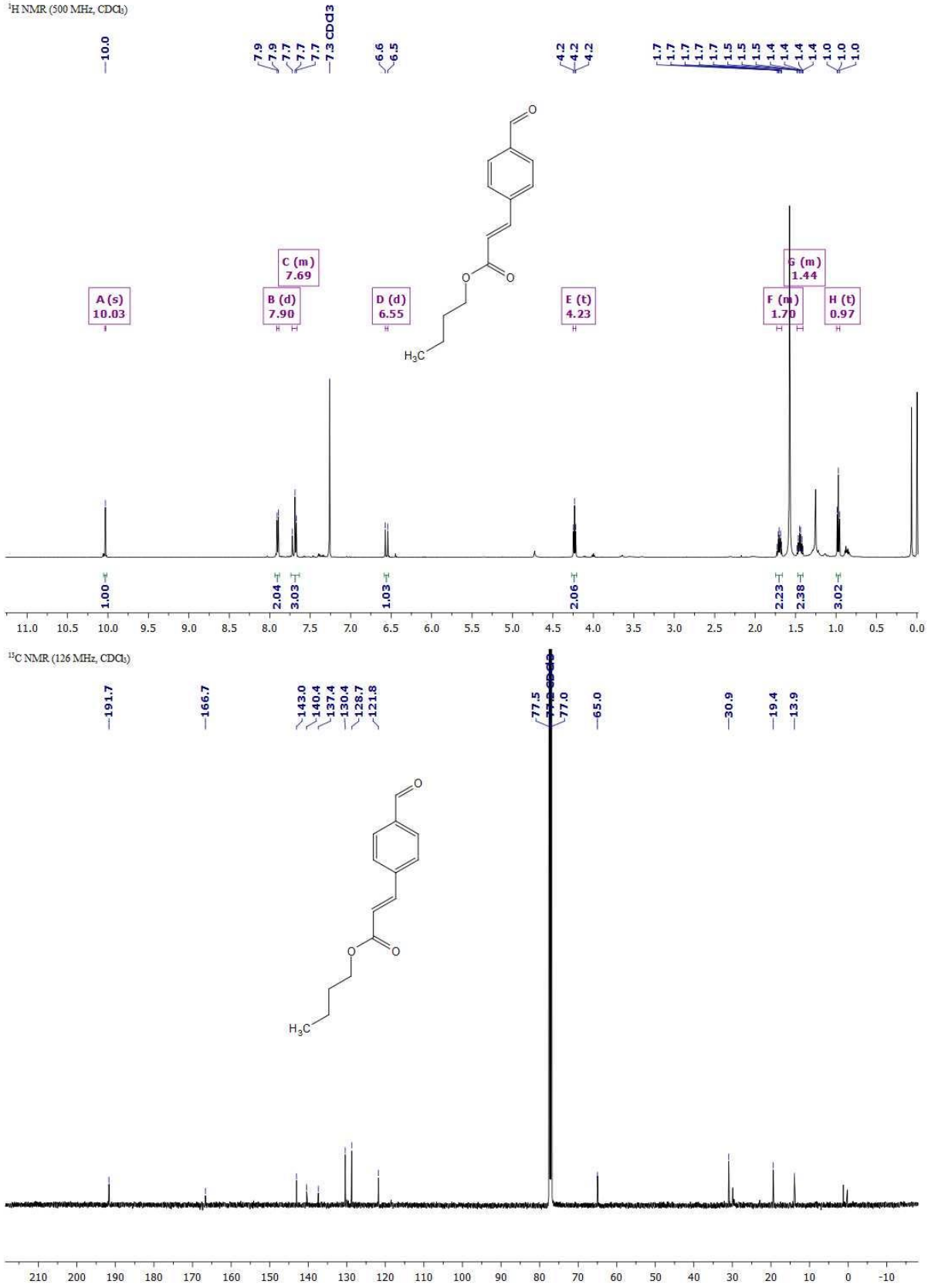


13. (*E*)-(2,6-dimethyl-4-(2-(phenylsulfonyl)vinyl)phenyl)methanol

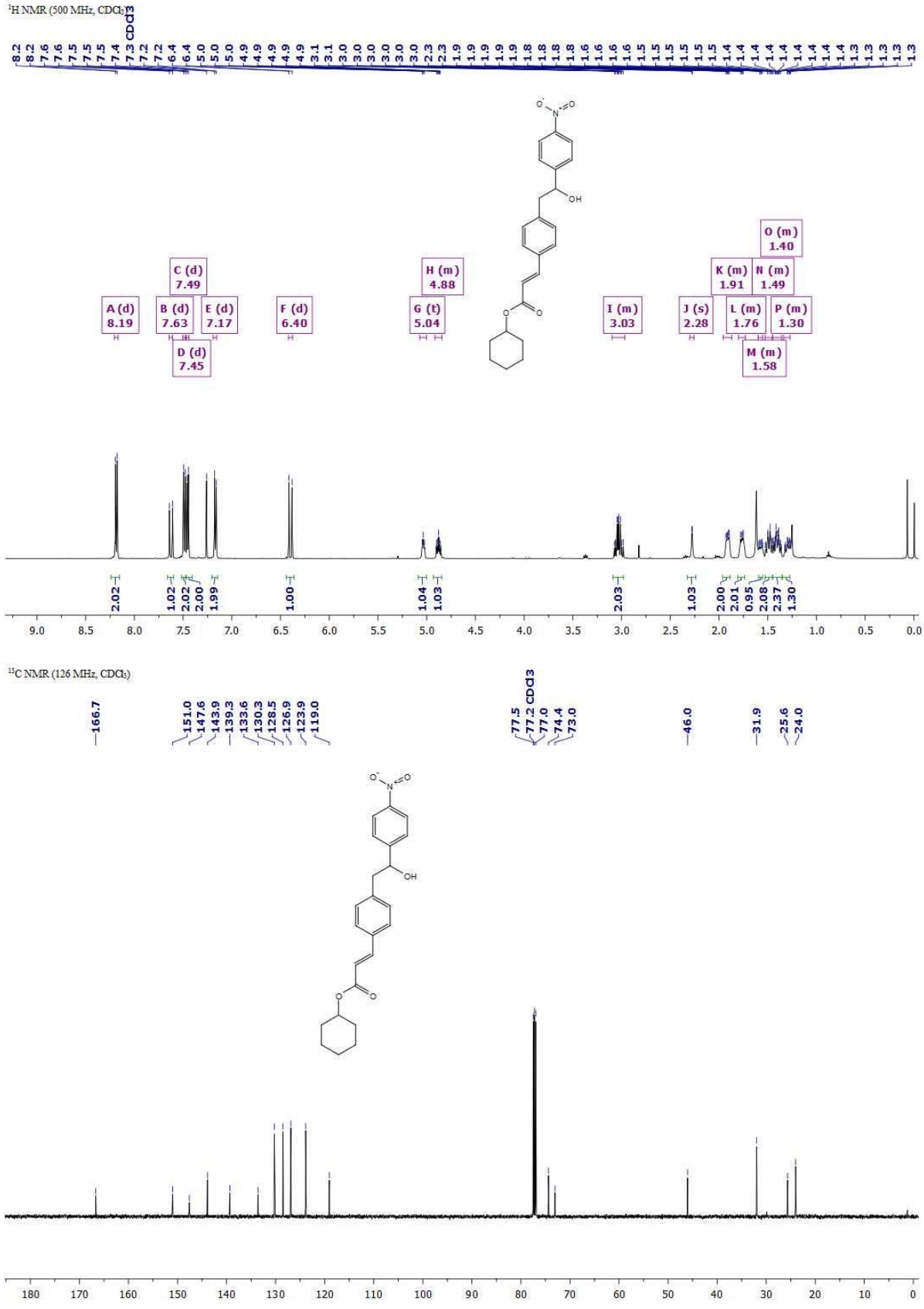




14. butyl (*E*)-3-(4-formylphenyl)acrylate



16. cyclohexyl (*E*)-3-(4-(2-hydroxy-2-(4-nitrophenyl)ethyl)phenyl)acrylate



18. butyl (*E*)-3-(4-(2-hydroxy-2-(naphthalen-2-yl)ethyl)phenyl)acrylate