Palladium catalyzed remote *meta*-selectiveC–H bond silylation and germanylation

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Supporting Information

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Reagent information. Unless otherwise stated, all reactions were carried out under air in screw cap reaction tubes. Palladium catalysts were got from Johnson Matthey and ligands were purchased from Aldrich and Alfa aesar. For column chromatography, silica gel (60–120 mesh or 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 $60F_{254}$).

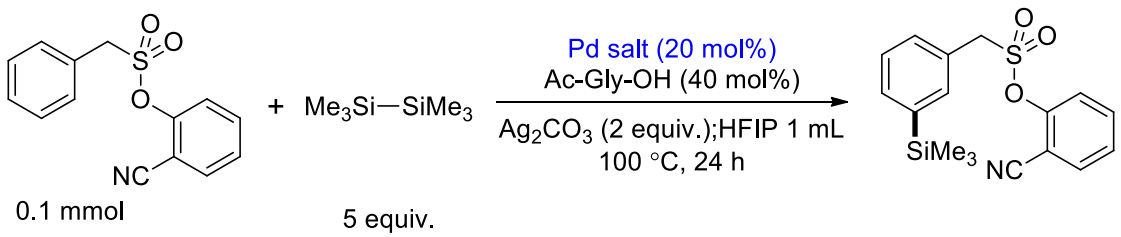
Analytical Information. All isolated compounds were characterized by ^{1}H, ^{13}C, IR spectroscopy, HR-MS. Copies of the ^{1}H-NMR, ^{13}C-NMR can be found in the supporting information. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 and 500 MHz instrument. The references used for the NMR are tetramethylsilane (TMS) or residual solvent for ^{1}H and ^{13}C-NMR. All ^{1}H-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 deuterochloroform (77.2 ppm), unless otherwise stated, and all were obtained with ^{1}H decoupling. For some spectra, a singlet at 0.07 ppm in ^{1}HNMR and a singlet at 1.20 ppm in ^{13}CNMR spectrum is appeared, which is due the tetramethylsilane (TMS). The letter labels of the ^{1}HNMR spectra are as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet, m = multiplet *etc*.Neat infrared spectra were recorded on a Perkin-Elmer spectrum one FT-IR spectrometer. The data was recorded in transmittance mode (%T, cm^{-1}). GCMS analysis was done by Agilent 7890A GC system connected with 5975C inert XL EI/CI MSD (with triple axis detector). High-resolution mass spectra (HRMS) were recorded on a micro-mass ESI TOF (time of flight) mass spectrometer.

Description of Reaction Tube:

Figure S1: Pictorial description of reaction tube: 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) [right]; Thermo Scientific National PTFE/Silicone Septa for Sample Screw Thread Caps (Fisher Scientific Order No. 03394A) [right].

Optimization details for *meta*-C-H silylation of benzyl sulfonate moiety:

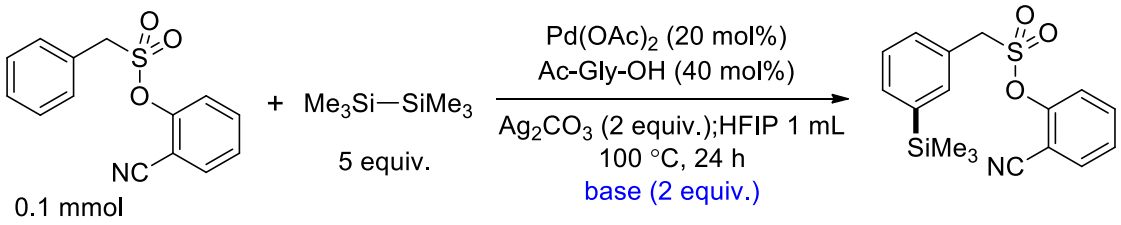
1. Optimization by varying palladium salt



Palladium salt	GC Yield

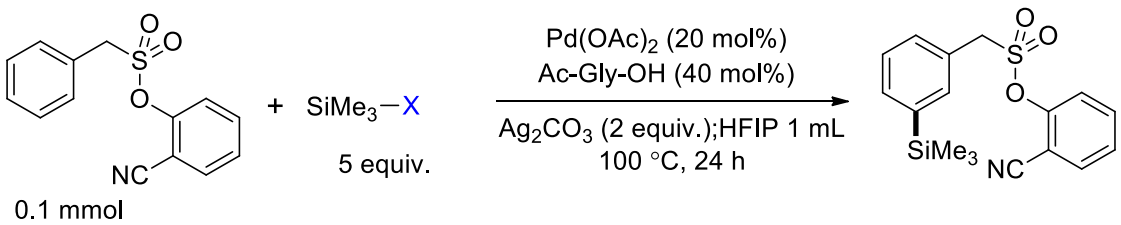
$Pd(OAc)_2$	**11 % mono**
$Pd(OPiv)_2$	9 % mono
$Pd(OCOCF_3)_2$	11 % mono
$Pd(CH_3CN)_2Cl_2$	7 % mono
$Pd(PhCN)_2Cl_2$	9 % mono
$Pd(dppf)_2Cl_2$	5 % mono
$Pd(PPh_3)_2Cl_2$	9 % mono
$Pd(acac)_2$	-
PdO	3 % mono
$PdCl_2$	-
$Pd(COD)Cl_2$	-
$PdSO_4$	-
$Pd_2(DBA)_3$	-
Pd on charcoal	-
No Pd catalyst	-

2. Optimization by varying base



Base	GC Yield
-	**11 % mono**
CsF	-
Na_2CO_3	-
KF	-
K_2CO_3	-
$CsCO_3$	-
$NaHCO_3$	-
Na_2HPO_4	-
K_3PO_4	-
NaH_2PO_4	-
DBU	-
Et_3N	-

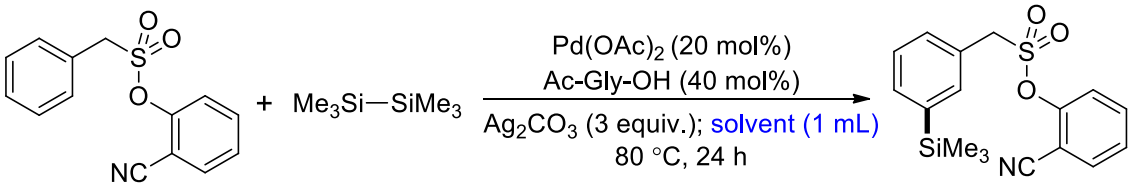
3. Optimization by varying different TMS– source



TMS– source	GC Yield
$(SiMe_3)_2$	**11 % mono**

$Me_3Si—CN$	-
Me_3Si—≡	-
$Me_3Si—CF_3$	-
Me_3Si—=	-
$Me_3Si—OTf$	-
$Et_3Si—H$ + norbornene	No silylated product
$Me_3Si—I$	-

4. Optimization by varying solvent

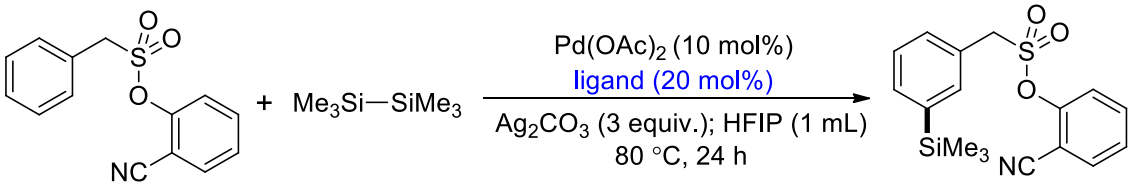


0.1 mmol

5 equiv.

Solvent	GC Yield
HFIP	**15 % mono**
CF_3CH_2OH	11 % mono
^tBuOH	-
DCE	-
DCE+HFIP (1:1)	10 % mono
^{t}amyl alcohol	-
ethanol	-
Polyethylene glycol	-
1,4 dioxane	-
DMF	-
THF	-
isopropanol	-
cyclohexane	-
toluene	-
EtOAc	-
DMSO	-
TFT	-

5. Optimization by varying Palladium salt



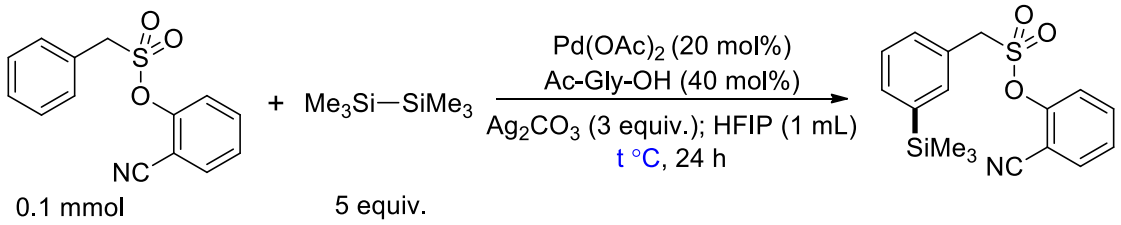
0.1 mmol

5 equiv.

Ligand	GC Yield

Ac-Gly-OH	**16 % mono**
Ac-Leu-OH	17 % mono
Ac-Ala-OH	12 % mono
Ac-Phe-OH	10 % mono
Ac-Val-OH	9 % mono
Ac-Trp-OH	-
Ac-Glu-OH	-
Ac-Met-OH	-
Benzoyl-Gly-OH	2 % mono
Phenyl-Gly-OH	-
Gly-Gly-OH	-
Boc-Gly-OH	-
Fmoc-Gly-OH	-
CBZ-Gly-OH	-
PPh_3	-
1,10 phenanthroline	-
N-Acetyl-2-aminobutyric acid	-
N-Acetylglycine ethyl ester	-
S (+)-2-Aminobutanol	-
N-Methylhydroxyl amine	-
Li-Yu ^{t}Bu Quinoline	7 % mono
Trimethylamine N-oxide	6 % mono
Dimethyl glyoxime	-
2-Methoxy ethylamine	-
2-Picolylamine	-
Diethanolamine	-
2-Hydroxy quinoline	5 % mono
No ligand	Multiple products

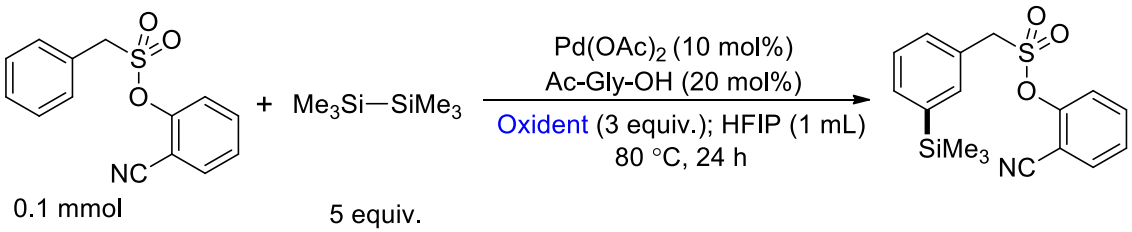
6. Optimization by varying temperature



Reaction Temperature (˚C)	GC Yield
130	5 % mono
120	6 % mono
110	11 % mono
100	10 % mono
90	13 % mono
80	14 % mono
70	15 % mono
75	22 % (19 % mono 3% di)
65	28 % (24 % mono 4 % di)
55	37 % (30 % mono 7 % di)
45	**44 % (36 % mono 8% di)**

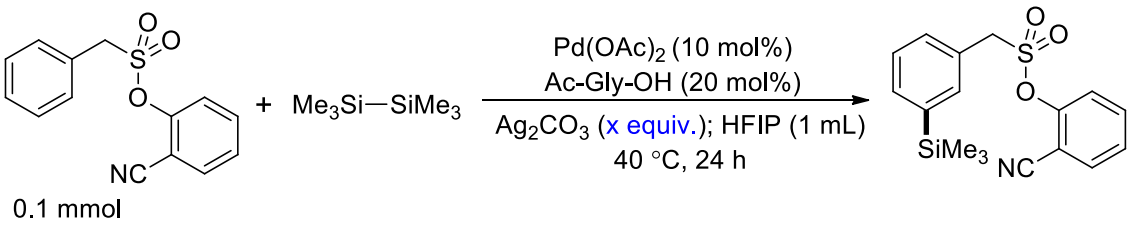
30	27 % (24 % mono 3 % di)

7. Optimization by varying oxidant



Oxidant (temperature)	GC Yield
Ag_2CO_3(80 ˚C)	**16 % mono**
AgOAc (80 ˚C)	11 % mono
Ag_2SO_4 (80 ˚C)	2 % mono
Ag_2O (80 ˚C)	9 % mono
$K_2S_2O_8$ (80 ˚C)	-
$Cu(OAc)_2.H_2O$ (80 ˚C)	10 % mono
$CuCl_2$ (80 ˚C)	-
CuF_2 (80 ˚C)	-
$CuBr_2$ (80 ˚C)	-
CuO (80 ˚C)	-
$CuCO_3$ (80 ˚C)	-
Benzoquinone (80 ˚C)	-
$PhI(OAc)_2$ (80 ˚C)	-
Ag_2CO_3 (45˚C)	**45 % (36 % mono 9 % di)**
AgF (45˚C)	9 % mono
AgBr (45˚C)	-
AgI (45˚C)	-
Ag_2CO_3 (3 equiv.) +$Cu(OAc)_2.H_2O$ (1 equiv.) (45˚C)	14 % mono

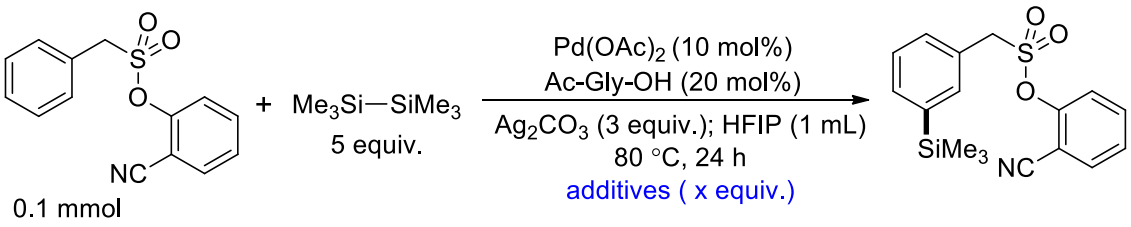
8. Optimization by varying amount of oxidant



Amount of oxidant (equiv.)	GC Yield
1	30 % (26 % mono 4 % di)
2	33 % (28 % mono 5 % di)
3	**45 % (36 % mono 9 % di)**
4	34 % (28 % mono 6 % di)

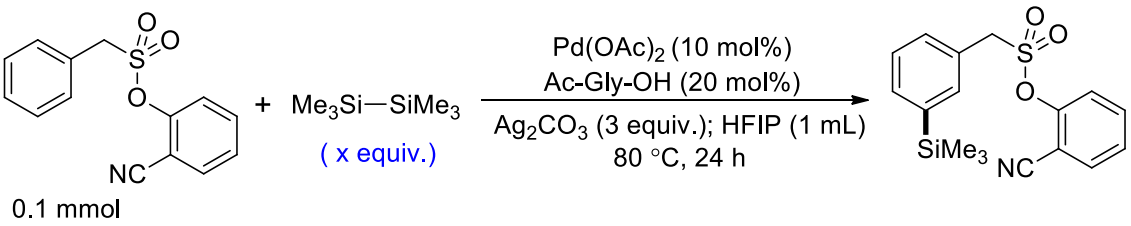
5	40 % (32 % mono 8 % di)

9. Optimization by additives



additives	GC Yield
Norbornene (2 equiv.)	-
TBHP (0.5 M in decane) (2 equiv.)	25 %(21 % mono 4 % di)
DTBP (2 equiv.)	33 %(28 % mono 5% di)
$^{n}Bu_4NBr$ (2 equiv.)	-
PhI(OAc) (2 equiv.)	-
DTBP (2 equiv.)	9 % mono
Na_2CO_3(2 equiv.)	-
NCS(2 equiv.)	-
AIBN (2 equiv.)	-
TEMPO (2 equiv.)	-
$FeCl_3$ (2 equiv.)	-
Benzoquinone (1 equiv.)	-
Acetic anhydride (1 equiv.)	42 %(34 % mono 8% di)
Et_3SiH (1 equiv.)	-
Triflic acid anhydride (1 equiv.)	-
Anhyd. Na_2SO_4 (100 mg)	**50 %(40 % mono 10% di)**
4 Å Molecular sieves (150 mg)	47 %(38 % mono 9 % di)
Styrene (1 equiv.)	-
NFSI (1 equiv.)	8 % mono
CuCN (100 mg)	5 % mono
TBAF (150 mg)	-
Acyl chloride (1 equiv.)	10 % mono
AcOH (1 equiv.)	40 %(31 % mono 8 % di)
AcOH (2 equiv.)	33 %(27 % mono 6 % di)
CaH_2	4 % mono

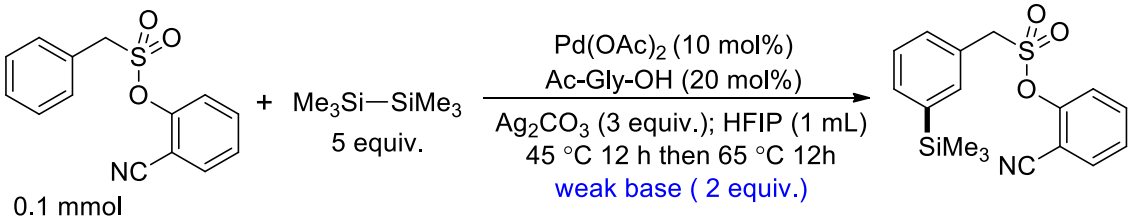
10. Optimization by varying amount of hexamethyldisilane



additives	GC Yield

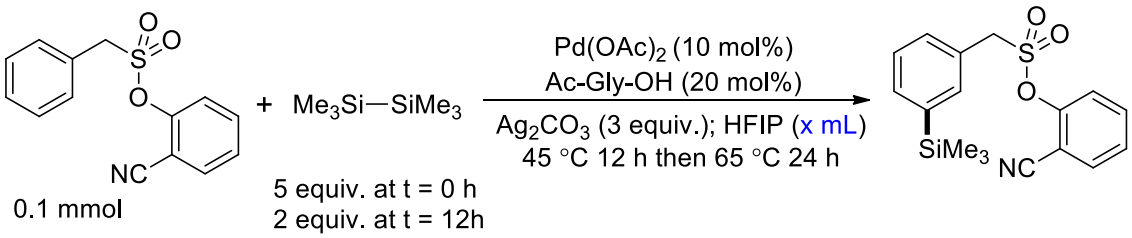
1 equiv.	5 % mono
1.2 equiv.	10 % mono
1.5 equiv.	14 % mono
2 equiv.	17 % mono
2.5 equiv.	28 % (24 % mono 4 % di)
3 equiv.	31 % (28 % mono 5 % di)
4 equiv.	37 % (30% mono 7 % di)
5 equiv.	45 % (36 % mono 9 % di)
6 equiv.	24 % (20 % mono 4 % di)
5 equiv. at t= 0 h then 2 equiv. at t = 12h at 65 ˚C (total time 24 h)	**47 % (38 % mono 9 % di)**
5 equiv. at time t= 0 h and 2 equiv. at t = 24 h at 65 ˚C (total time 36 h)	46 % (37 % mono 9 % di)

11. Optimization by weak base



Weak base	GC Yield
NaCl	41 % (32 % mono 9 % di)
KCl	-
KNO_3	19 % (16 % mono 3 % di)
$NaHSO_4$	24 % (19 % mono 5 % di)
CsCl	-
NaI	-
CuI	-
CuCl	7 % mono
$Bi(NO_3)_3$	-
NaNO2	-
KI	-

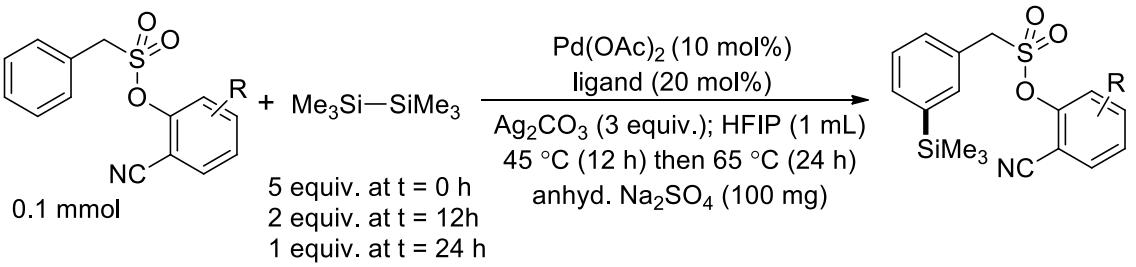
12. Optimization by amount of solvent (HFIP)



Amount of HFIP (x mL)	GC Yield
1	47 % (38 % mono 9 % di)

2	29 % (24 % mono 5 % di)
0.5	46 % (37 % mono 9 % di)
3	28 % (23 % mono 5 % di)

13. Optimization of directing group



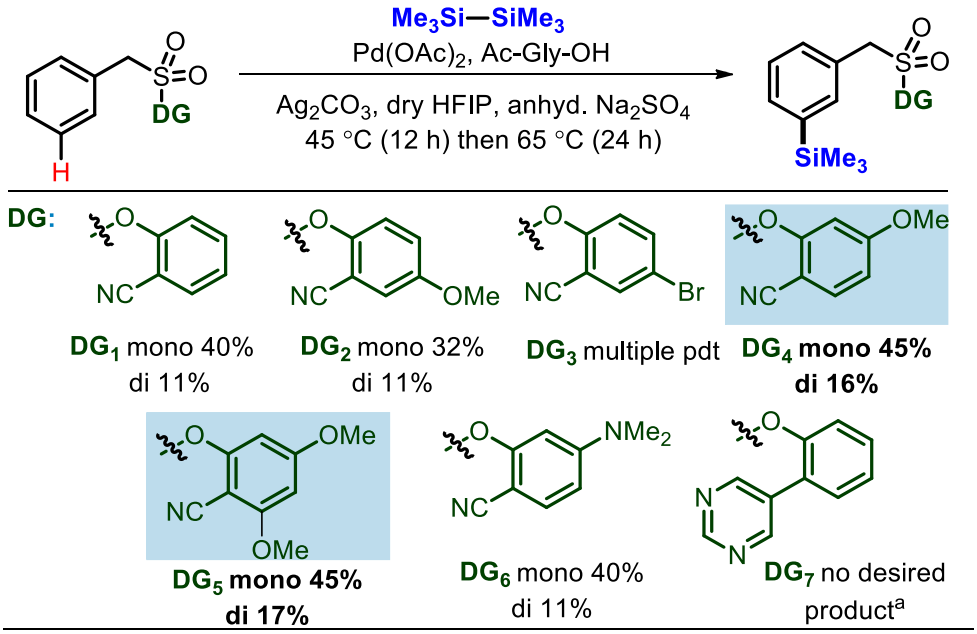
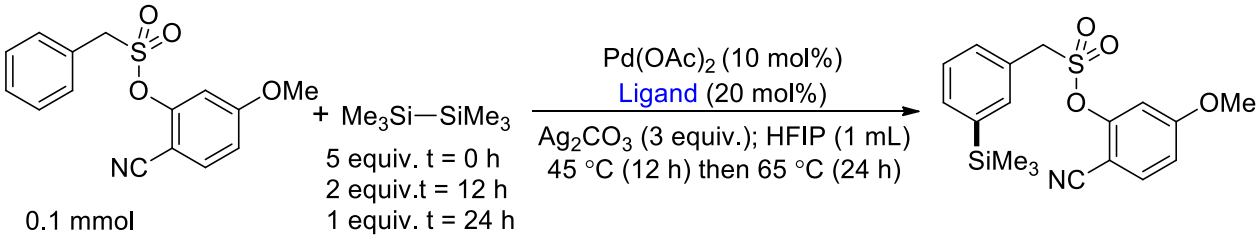
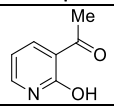


Table S1: Directing group optimization

14. Optimization by varying Ligand

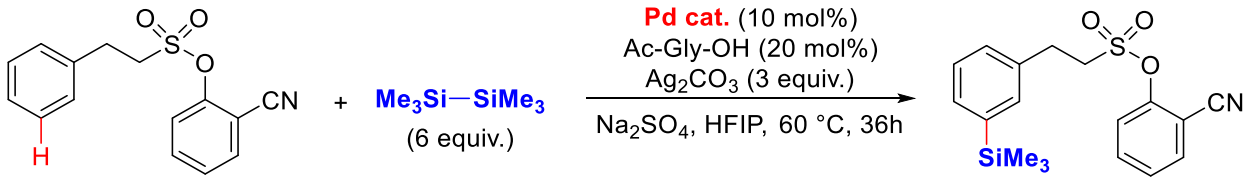


Ligand	Yield
Ac-Gly-OH	**(61 %) 45 % mono 16 % di**
Ac-Leu-OH	(59 %) 44 % mono 15 % di
Ac-Ala-OH	(54 %) 39 % mono 15 % di
Ac-Phe-OH	(46 %) 36 % mono 10 % di
Ac-Val-OH	(34 %) 27 % mono 7 % di
Ac-Trp-OH	-

Ac-Glu-OH	-
Ac-Met-OH	
Benzyloxy-Gly-OH	5 % mono
Piv- Gly-OH	-
Phenyl-Gly-OH	-
Gly-Gly-OH	-
Boc-Gly-OH	-
Fmoc-Gly-OH	-
CBZ-Gly-OH	-
PPh_3	5 % mono
1,10 phenanthroline	-
SiPr	-
Li-Yu-^{t}Bu quinoline	9 %
2-Hydroxy quinoline	
2- Chloro-quinoline	trace
2-Picolyl amine	-
2- Methoxy ethyl amine	-
No ligand	multiple products
8-Aminoquinoline	-
	10 % mono

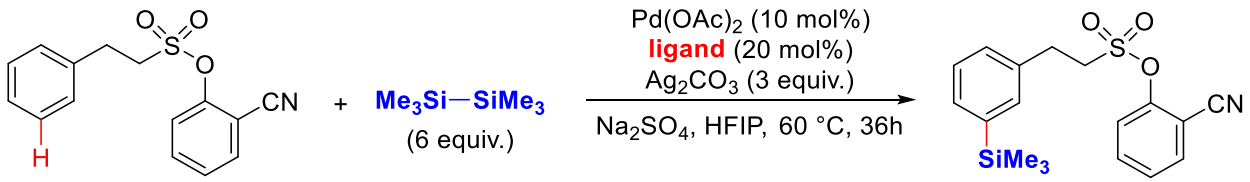
Optimization details for *meta*-C-H silylation of phenethyl sulfonate moiety:

1. Optimization with respect to palladium catalyst:



Pd catalyst	GC Yield
$Pd(OAc)_2$	**47 % (36 % mono+ 11 % di)**
$Pd(OCOCF_3)_2$	8 % mono
$Pd(OCOCMe_3)_2$	11 % mono
$Pd(MeCN)_2Cl_2$	<5 % mono

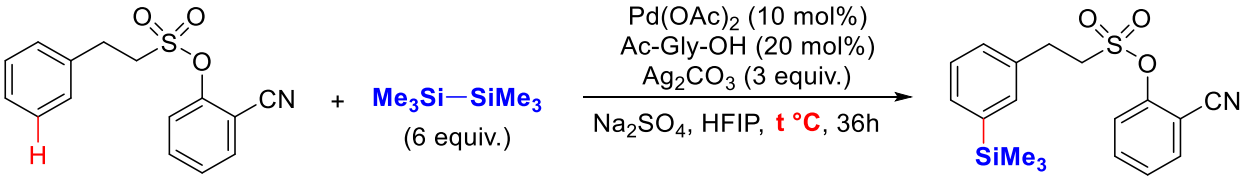
2. Optimization with respect to ligand:



MPAA ligand	GC Yield

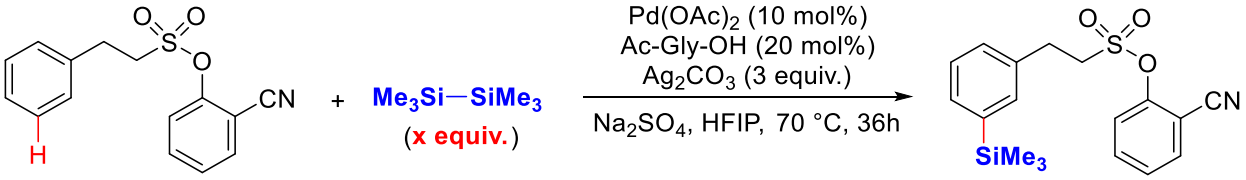
Ac-Gly-OH	**47 % (36 % mono + 11 % di)**
Ac-Ala-OH	34 % (28 % mono+ 6 % di)
Ac-Phe-OH	42 % (35 % mono + 7 % di)
Ac-Val-OH	29 % (25 % mono + 4 % di)

3. Optimization with respect to temperature:



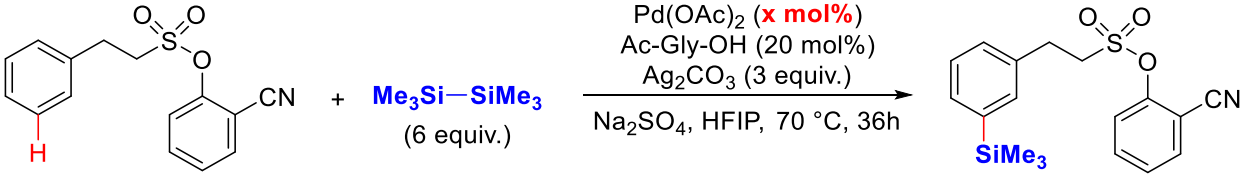
Temp (°C)	GC Yield
50	26 % (21% mono + 5 % di)
60	44 % (35 % mono + 9 % di)
65	48 % (38 % mono + 10 % di)
70	**53 % (41 % mono + 12 % di)**
75	52 % (38 % mono + 13 % di)
80	38 % (31 % mono + 7 % di)
90	17 % mono

4. Optimization with respect to silyl source amount:



Amount of silane (equiv.)	GC Yield
3	21 % mono
4	47 % (38 % mono + 9 % di)
6	**53 % (41 % mono + 12 % di)**
8	44 + 14
5	49 % (39 % mono + 10 % di)

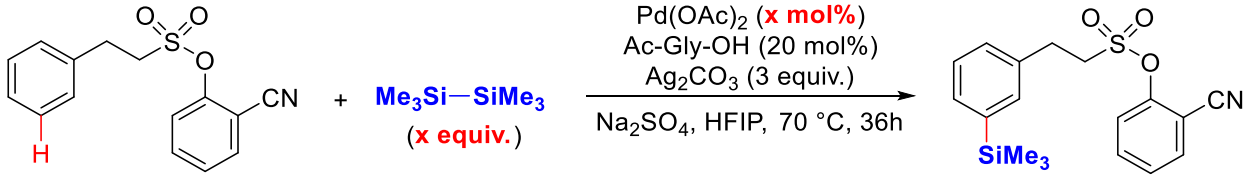
5. Optimization with respect to Pd loading:



Pd loading (mol%)	GC Yield
10	53 % (41 % mono + 12 % di)
15	**64 % (48 % mono + 16 % di)**

20	71 % (53 % mono +18 % di)

6. Optimization with respect to Pd loading and silyl source amount:



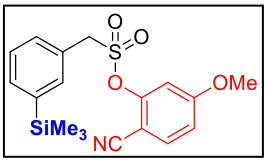
Pd loading (mol%)[a]	Amount of silane (equiv.)[a]	Yield in % (mono + di)
0	2	58 % (44 % mono + 14 % di)
0	4	59 % (45 % mono + 14 % di)
5	**2**	**74 % 54(52) % mono + 20(19)[b] % di**
5	4	75 % (55 % mono + 20 % di)

[a]10 mol% $Pd(OAc)_2$ and 4 equiv. of hexamethyldisilane was used initially and then after 12 h, a second set of $Pd(OAc)_2$ and hexamethyldisilane (mentioned in this table) was added and stirred for next 24 h at 70 °C. [b]Isolated yield in parenthesis.

General Procedure Afor mono silyation through remote *meta* C-H activation of benzylsulfonic acid derivatives:

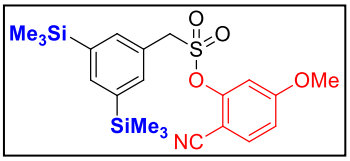
In a clean, oven–dried screw cap reaction tube, with previously placed magnetic stir–bar substrate (0.2 mmol); $Pd(OAc)_2$ (0.1 equiv, 0.02 mmol, 4.5 mg); N-Acetyl-glycine (0.4 equiv, 0.04 mmol, 4.5 mg), Ag_2CO_3 (3 equiv, 0.6 mmol, 166 mg), anhyd. Na_2SO_4 (200mg) were taken. Then hexafluoroisopropanol (1.8 mL) which was previously distilled and collected over activated 4Å molecular sieves was added by syringes. Next, hexamethyldisilane (5 equiv, 1 mmol, 200 µL) was added to mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 45 ˚C. After 12 h of vigorously stirring reaction temperature was increased to 65 ˚C and 2 equiv. of hexamethyldisilane (0.4 mmol, 80 µL) was added to the rection mixture. At time t = 24h, another 1 equiv. of hexamethyldisilane (0.2 mmol, 40 µL) was added to reaction mixture and the mixture was stirred for another 12h at 65 ˚C. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube was washed with 10 mL of dichlorometane. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether-ethyl acetate as eluent.

Characterization data for *meta* C-H activation of benzylsulfonic acid derivatives:

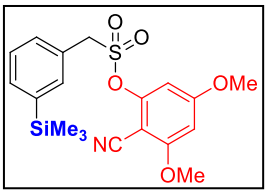


2-Cyano-5-methoxyphenyl (3-(trimethylsilyl)phenyl)methanesulfonate(Table 3, Entry 2a$_{mono}$): White solid. Melting point 87 ˚C.Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 45% (34 mg). R_f = 0.4 (4:1 Pet ether:EtOAc).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (s, 1H, *o*-C_6H_4{3-$SiMe_3$}), 7.60 – 7.55 (m, 2H, *m*-C_6H_3{2-CN,5-OMe} and *p*-C_6H_4{3-$SiMe_3$}), 7.53 – 7.49 (m, 1H, *o*-C_6H_4{3-$SiMe_3$}), 7.41 (t, $^3J_{HH}$ = 7.5 Hz, 1H, *m*-C_6H_4{3-$SiMe_3$}), 6.86 (m, 2H, *o,p*-C_6H_3{2-CN,5-OMe}), 4.72 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 0.28 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 152.1, 142.1, 136.1, 134.7, 134.6, 131.6, 128.6, 125.8, 115.7, 114.0, 109.3, 98.8,

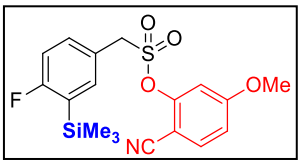
58.9, 56.3, -1.0.HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{21}NO_4SSiNa$: 398.0852, found: 398.0849.



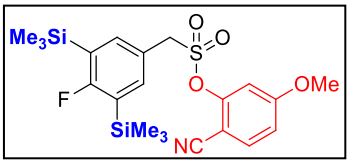
2-Cyano-5-methoxyphenyl (3,5-bis(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2a$_{di}$): White solid. Melting point 111 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 16% (14 mg). R_f = 0.5 (4:1 Pet ether:EtOAc).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (s, 1H, *p*-C_6H_3{3,5-di-$SiMe_3$}), 7.61 (s, 2H, *m*-C_6H_3{3,5 di-$SiMe_3$}), 7.57 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 6.87 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe), 6.84 (d, $^4J_{HH}$ = 2.2 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 4.72 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 0.27 (s, 18H, di-Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (126 MHz, CDCl3) δ 164.2, 152.2, 140.9, 139.4, 136.5, 134.5, 128.3, 127.8, 125.1, 115.7, 113.9, 109.3, 98.8, 59.0, 56.2, -1.0.HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{21}H_{29}NO_4SSi_2Na$: 470.1248, found: 470.1241.



2-Cyano-3,5-dimethoxyphenyl (3-(trimethylsilyl)phenyl)methanesulfonate(Table 1, Entry 2a$_{mono,}$ DG$_5$): White solid. Melting point 83 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 45% (36 mg). R_f = 0.2 (4:1 Pet ether:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H, *o*-C_6H_4{3-$SiMe_3$}), 7.56 (d, $^3J_{HH}$ = 7.3 Hz, 1H, C_6H_4{3-$SiMe_3$}), 7.51 (d, $^3J_{HH}$ = 7.8 Hz, 1H, C_6H_4{3-$SiMe_3$}), 7.41 (d, $^3J_{HH}$ = 7.5 Hz, 1H, C_6H_4{3-$SiMe_3$}), 6.49 (d, $^4J_{HH}$ = 2.1 Hz, 1H, C_6H_2{2-CN, 3,5-di-OMe}), 6.37 (d, $^4J_{HH}$ = 2.1 Hz, 1H, C_6H_3{2-CN, 3,5-di-OMe}), 4.71 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 0.28 (s, 9H, Si(CH_3)$_3$}. ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 152.1, 142.1, 136.1, 134.7, 134.6, 131.6, 128.6, 125.8, 115.7, 114.0, 109.3, 98.8, 58.9, 56.3, -1.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{23}NO_5SSiNa$: 428.0958, found: 428.0952.

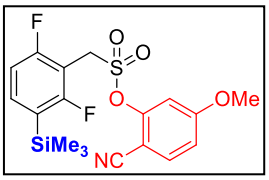


2-Cyano-5-methoxyphenyl (4-fluoro-3-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2b$_{mono}$): Whitish-yellow solid. Melting point 83 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 51% (40 mg). R_f = 0.3 (4:1 Pet ether:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (m, 1H, *m*-C_6H_3{2-CN,5-OMe}), 7.54 – 7.48 (m, *o*-C_6H_3{3-$SiMe_3$, 4-F}), 7.04 (t, $^3J_{HH}$/$^3J_{HF}$ = 8.2 Hz, 1H, *m*-C_6H_3{3-$SiMe_3$, 4-F}), 6.91 – 6.86 (m, 2H, *o,p*-C_6H_3{2-CN,5-OMe}), 4.69 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.32 (d, $^5J_{CF}$ = 0.9 Hz, 9H, Si(CH_3)$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2 (d, $^1J_{CF}$= 245.3 Hz), 164.3, 152.0, 138.2 (d, $^3J_{CF}$ = 12.4 Hz), 134.6, 134.2 (d, $^3J_{CF}$ = 9.3 Hz), 127.9(d, $^2J_{CF}$ = 31.9 Hz), 122.0 (d, $^4J_{CF}$ = 3.2 Hz), 115.7 (d, $^2J_{CF}$ = 27.1 Hz), 115.7, 114.0, 109.3, 98.7, 58.1, 56.3, -1.0.HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{20}NFO_4SSiNa$: 416.0759, found: 416.0766.

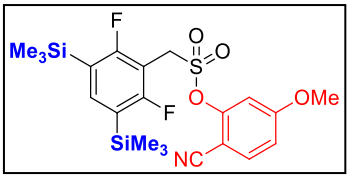


2-Cyano-5-methoxyphenyl (4-fluoro-3,5-bis(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2b$_{di}$): White solid. Melting point 162 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 17% (16 mg). R_f = 0.4 (4:1 Pet ether:EtOAc).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, $^3J_{HH}$ = 9.4 Hz, 1H, *m*-C_6H_3{2-CN,5-OMe}), 7.50 (d, $^3J_{HF}$ = 5.2 Hz, 2H, C_6H_2{3,5-*di*-$SiMe_3$, 4-F}), 6.91 – 6.85 (m, 2H, *o,p*-C_6H_3{2-CN,5-OMe}), 4.69 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.31 (s, 18H, *di*-Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.8 (d, $^1J_{CF}$ =

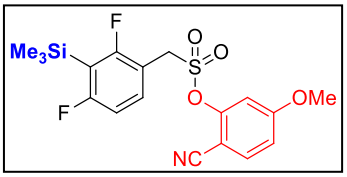
240.0 Hz), 164.3, 152.2, 139.6 (d, $^{3}J_{CF}$ = 13.0 Hz), 134.6, 126.8 (d, $^{2}J_{CF}$ = 37.0 Hz), 121.6 (d, $^{4}J_{CF}$ = 2.8 Hz), 115.7, 113.9, 109.3, 98.8, 58.2, 56.3, -0.9 (d, $^{4}J_{CF}$ = 1.5 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^{+}$: calcd. for $C_{21}H_{28}NFO_4SSi_2Na$: 488.1154, found: 488.1155.



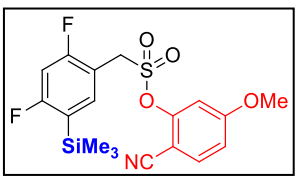
2-Cyano-5-methoxyphenyl (2,6-difluoro-3-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2c$_{mono}$): White solid. Melting point 84 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 61% (50 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.00 (t, J = 8.5 Hz, 1H), 6.95 (d, J = 2.4 Hz, 1H), 6.89 (dd, J = 8.7, 2.4 Hz, 1H), 4.86 (s, 2H), 3.84 (s, 3H), 0.31 (s, 9H).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.48 – 7.42 (m, 1H, C_6H_2{2,6-*di*-F, 3-$SiMe_3$ }), 7.00 (t, $^{3}J_{HH}$/$^{3}J_{HF}$ = 8.5 Hz, 1H, C_6H_2{2,6-*di*-F, 3-$SiMe_3$ }), 6.95 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^{3}J_{HH}$ = 8.7, $^{4}J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.86 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.31 (s, 9H, $Si(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.0 (dd, $^{1}J_{CF}$ = 249.5, $^{3}J_{CF}$ = 5.0 Hz), 164.21, 162.9 (dd, $^{1}J_{CF}$ = 255.8, $^{3}J_{CF}$ = 6.3 Hz), 151.5, 137.64 (dd, J_{CF} = 15.12, J_{CF} = 10.08 Hz), 128.7 (m), 122.7 (dd, $^{2}J_{CF}$ = 32.8, $^{4}J_{CF}$3.8 Hz) , 115.2, 113.9, 111.95 (dd, J_{CF} = 10.2, J_{CF} = 3.8 Hz), 109.2, 103.3 (d, $^{2}J_{CF}$ = 22.7, $^{2}J_{CF}$ = 18.9 Hz), 99.1, 56.2, 46.7, -1.00 (d, $^{4}J_{CF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^{+}$: calcd. for $C_{18}H_{19}NF_2O_4SSi_2Na$: 434.0664, found: 434.0671.



2-Cyano-5-methoxyphenyl (2,6-difluoro-3,5-bis(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2c$_{di}$): White solid. Melting point 98-99 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 15% (14 mg). R_f = 0.5 (4:1 Pet ether:EtOAc). ^{1}HNMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.47 (t, $^{4}J_{HF}$ = 6.9 Hz, 1H, *p*-C_6H_1{2,6-*di*-F, 3,5-*di*-$SiMe_3$), 6.95 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^{3}J_{HH}$= 8.7, $^{4}J_{HH}$= 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.85 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.31 (s, 18H, *di*- $Si(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.4 (d, $^{1}J_{CF}$ = 250.7 Hz), 164.2, 151.7, 142.9 (t, $^{3}J_{CF}$ = 13.9 Hz), 134.7, 129.2 (m), 122.3 (d,J_{CF}= 34.0 Hz), 115.3, 114.0, 109.2, 102.5, 99.1, 56.3, 47.0, -0.9. HRMS (ESI-QTOF) m/z: $[M+Na]^{+}$: calcd. for $C_{21}H_{27}NF_2O_4SSi_2Na$: 506.1060, found: 506.1048.

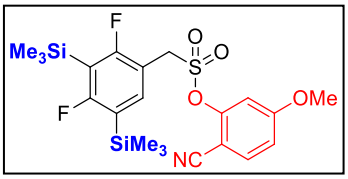


2-Cyano-5-methoxyphenyl (2,4-difluoro-3-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2d$_{mono}$): Off white solid. Melting point 67 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 37 % (30 mg). R_f = 0.4 (4:1 Pet ether:EtOAc).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.57 – 7.53 (m, 1H,*o*-C_6H_2{2,4-*di*-F, 3-$SiMe_3$}), 6.95 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.91 – 6.87 (m, 2H, *p*-C_6H_3{2-CN, 5-OMe} and *m*-C_6H_2{2,4-*di*-F, 3-$SiMe_3$}), 4.74 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.37 (t, J = 1.3 Hz, 8H, $Si(CH_3)_3$).^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 168.1(dd, $^{1}J_{CF}$ = 252 Hz, $^{3}J_{CF}$ = 16.4 Hz) 166.5 (dd, $^{1}J_{CF}$ = 252 Hz, $^{3}J_{CF}$ = 16.4 Hz), 164.3, 151.7, 135.1 (dd, J_{CF} = 12.6 Hz, J_{CF} = 3.8 Hz), 134.7, 115.51, 114.8 (dd, J_{CF}= 35.2, 49.7), 114.0, 112.2 (dd,J_{CF}= 25.2, J_{CF} = 3.8), 109.9 (dd, $^{2}J_{CF}$ = 12.6, $^{4}J_{CF}$ = 3.9), 109.2, 98.8, 56.3, 51.7 (d, $^{3}J_{CF}$ = 3.3 Hz), 0.2 (t, $^{4}J_{CF}$ = 2.9 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^{+}$: calcd. for $C_{18}H_{19}NF_2O_4SSiNa$: 434.0664, found: 434.0664.

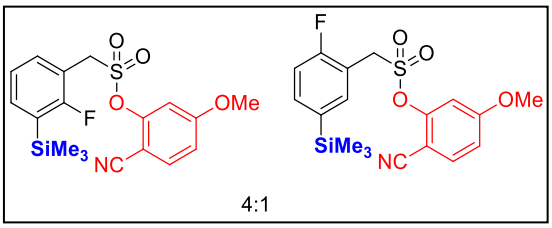


2-Cyano-5-methoxyphenyl (2,4-difluoro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2d$_{mono'}$): Oilly

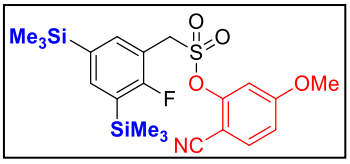
liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 18 % (15 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.54 (dd, $^4J_{HF}$ = 8.8, $^4J_{HF}$ = 6.0 Hz, 1H, *o*-C_6H_2{2,4-*di*-F, 5-$SiMe_3$}), 6.94 (d, $^4J_{HH}$= 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$= 8.7, $^4J_{HH}$=2.3 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 6.85 (dd, $^3J_{HF}$ = 9.8, $^3J_{HF}$ = 8.3 Hz, 1H, *m*-C_6H_2{2,4-*di*-F, 5-$SiMe_3$}), 4.76 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.32 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, CDCl3) δ 168.5 (dd, $^1J_{CF}$ = 252.0 Hz, $^3J_{CF}$ = 11.3 Hz) 164.3, 163.0 (dd, $^1J_{CF}$ = 253.2 Hz, $^3J_{CF}$ = 13.9 Hz) 151.7, 139.3 (dd, $^2J_{CF}$ = 12.6 Hz, $^4J_{CF}$ = 3.8 Hz), 134.7, 123.7 (dd, $^2J_{CF}$ = 32.1 Hz, $^4J_{CF}$ = 3.8 Hz) 115.5, 114.0, 110.1, 109.3, 104.1 (dd, $^2J_{CF}$ = 37.8 Hz, $^2J_{CF}$ = 23.9 Hz) 98.9, 56.3, 51.5 (d, $^3J_{CF}$ = 2.52 Hz) -1.0 (d, $^4J_{CF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NF_2O_4SSi_2Na$: 434.0664, found: 434.0666.



2-Cyano-5-methoxyphenyl (2,4-difluoro-3,5-bis(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2d$_{di}$): White solid. Melting point 125 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 16 % (15 mg). R_f = 0.4 (5:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.54 (dd, $^4J_{HF}$ = 9.0, 6.2 Hz, 1H, *o*-C_6H_1{2,4-*di*-F, 3,5-*di*-$SiMe_3$}), 6.93 (d, $^3J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ =2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.74 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.37 (s, 9H, $Si(CH_3)_3$), 0.30 (d, $^5J_{HF}$ = 0.5 Hz, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.6 (dd, $^1J_{CF}$ = 243.2,$^3J_{CF}$ = 15.1 Hz),166.8 (dd, $^1J_{CF}$ = 250.7, $^3J_{CF}$ = 17.6 Hz), 164.3, 151.9, 140.6 (dd, J_{CF} = 15.2, J_{CF} = 3.8 Hz), 134.7, 123.0 (dd, $^2J_{CF}$ = 38.4, $^4J_{CF}$ = 2.2 Hz), 115.5, 114.0, 109.6 (dd, J_{CF} = 18.9, J_{CF} = 3.8 Hz), 109.2, 98.8, 56.3, 51.9 (d, $^3J_{CF}$ = 2.5 Hz), 0.4 (t, $^4J_{CF}$ = 2.5 Hz), -0.9 (d, $^4J_{CF}$= 1.3 Hz).HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{21}H_{27}NF_2O_4SSi_2Na$: 506.1060, found: 506.1064.

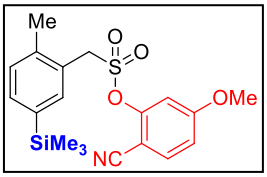


2-Cyano-5-methoxyphenyl (2-fluoro-3-(trimethylsilyl)phenyl)methanesulfonate compound with 2-cyano-5-methoxyphenyl (2-fluoro-5-(trimethylsilyl)phenyl)methanesulfonate (4:1) (Table 3, Entry 2e$_{mono}$): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated as mixture of two compound with 4:1 ratio. Isolated yield: 52% (41 mg). R_f = 0.35 (4:1 Pet ether:EtOAc). For 2-Cyano-5-methoxyphenyl (2-fluoro-3 (trimethylsilyl)phenyl)methanesulfonate:^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.57 (m, 2H, C_6H_3{2-F, 3-$SiMe_3$}, *m*-C_6H_3{2-CN, 5-OMe}), 7.47 (m, 1H, C_6H_3{2-F, 3-$SiMe_3$}), 7.21 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C_6H_3{2-F, 3-$SiMe_3$}), 6.91 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.88 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.79 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 0.32 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.8 (d, $^1J_{CF}$ = 246.9 Hz), 164.3, 151.8, 137.2 (d, $^3J_{CF}$ = 12.6 Hz), 134.7, 134.1 (d, J_{CF}= 2.52 Hz), 127.5 (d, $^2J_{CF}$ = 31.5 Hz), 124.7 (d, J_{CF} = 3.75 Hz), 115.49, 113.96, 113.5 (d, $^2J_{CF}$ = 17.64 Hz), 109.1, 98.9, 56.3, 52.0 (d, $^3J_{CF}$ = 3.78 Hz), -0.9 (d, $^4J_{CF}$ = 1.26 Hz).HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{20}NFO_4SSiNa$: 416.0759, found: 416.0759.

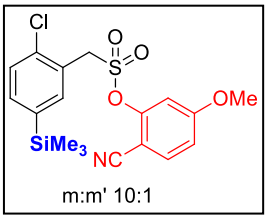


2-Cyano-5-methoxyphenyl (2-fluoro-3,5-bis(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2e$_{di}$): White solid. Melting point 95-96 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as

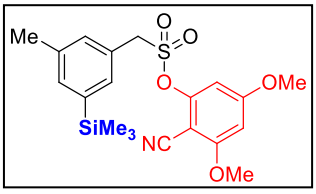
eluent. Isolated yield: 13% (12 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (dd, $^4J_{HF}$ = 7.7, $^4J_{HH}$ = 1.7 Hz, 1H, C_6H_2{2-F, 3,5-*di*-$SiMe_3$}), 7.61 – 7.56 (m, 2H, *m*-C_6H_3{2-CN, 5-OMe} and C_6H_2{2-F, 3,5-*di*-$SiMe_3$}), 6.92 – 6.86 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.80 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 0.33 (d,$^5J_{HF}$ = 0.7 Hz, 9H, $Si(CH_3)_3$), 0.27 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.7 (d, $^1J_{CF}$ = 247.0 Hz), 164.3, 152.0, 142.2 (d, $^3J_{CF}$ = 11.3 Hz), 139.4, 136.9 (d, $^3J_{CF}$ = 5.0 Hz), 134.6, 126.6 (d, $^2J_{CF}$ = 30.2 Hz), 115.5, 114.0, 112.9 (d, $^2J_{CF}$ = 17.6 Hz), 109.2, 98.9, 56.3, 52.2 (d, $^3J_{CF}$ = 2.5 Hz)., -0.87 (d, J = 3.8 Hz).HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{21}H_{28}NFO_4SSi_2Na$: 488.1154, found: 488.1159.



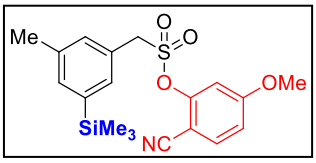
2-Cyano-5-methoxyphenyl (2-methyl-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2f): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 51% (39 mg). R_f = 0.4 (4:1 Pet ether:EtOAc).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.58 (s, 1H, *o*-C_6H_3{2-Me, 5-$SiMe_3$}), 7.47 (dd, $^3J_{HH}$ = 7.5, $^4J_{HH}$ = 1.0 Hz, 1H, *p*-C_6H_3{2-Me, 5-$SiMe_3$}), 7.28 – 7.24 (d, J = 7.5 Hz, 1H, *m*-C_6H_3{2-Me, 5-$SiMe_3$}), 6.89 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 6.82 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 4.81 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 2.49 (s, 3H, CH_3), 0.26 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 152.0, 139.5, 139.0, 137.5, 135.0, 134.6, 130.7, 124.5, 115.7, 114.0, 109.3, 99.0, 56.3, 19.9, -1.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{23}NO_4SSiNa$: 412.1009, found: 412.1021.



2-Cyano-5-methoxyphenyl (2-chloro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2g): Oily liqiud. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent.Isolated as mixture of inseparable meta: meta' isomers in 10:1 ratio. Isolated yield: 43% (35 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, $^4J_{HH}$ = 1.3 Hz, 1H, *o*-C_6H_3{2-Cl, 5-$SiMe_3$}), 7.60 (d, $^3J_{HH}$= 7.9, *m*-C_6H_3{2-CN, 5-OMe}), 7.51 – 7.43 (m, 2H, C_6H_3{2-Cl, 5-$SiMe_3$}), 6.91 – 6.86 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.97 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 0.27 (s, 9H, $Si(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.8, 140.7, 138.2, 136.5, 136.1, 134.7, 129.7, 124.3, 115.5, 114.0, 109.3, 98.9, 56.3, 55.7, -1.1.HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{20}NClO_4SSiNa$: 432.0460, found: 432.0463.

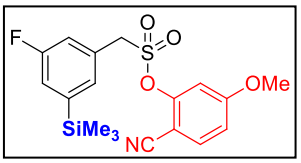


2-Cyano-3,5-dimethoxyphenyl (3-methyl-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2h): White solid. Melting point 129 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 53% (44 mg). R_f = 0.2 (4:1 Pet ether:EtOAc).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H, C_6H_3{3-Me, 5-$SiMe_3$}), 7.35 (s, 1H, C_6H_3{3-Me, 5-$SiMe_3$}), 7.31 (s, 1H, C_6H_3{3-Me, 5-$SiMe_3$}), 6.50 (d, $^4J_{HH}$ = 2.1 Hz, 1H, C_6H_2{2-CN, 3,5-*di*-OMe}), 6.37 (d, $^4J_{HH}$ = 2.1 Hz, 1H, C_6H_2{2-CN, 3,5-*di*-OMe}), 4.68 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3), 0.26 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.0, 163.3, 152.9, 141.8, 138.1, 135.4, 133.2, 132.3, 125.7, 113.4, 100.8, 97.3, 58.9, 56.6, 56.3, 21.5, -1.0.HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{25}NO_5SSiNa$: 442.1115, found: 442.1120.

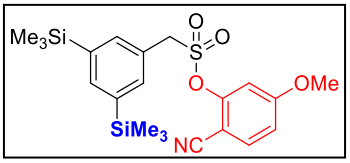


2-Cyano-5-methoxyphenyl (3-methyl-5-(trimethylsilyl)phenyl)methanesulfonate (Entry 2h, DG_4): White solid. Melting point 83 ˚C. Isolated through 100-200 mesh silica gel using pet

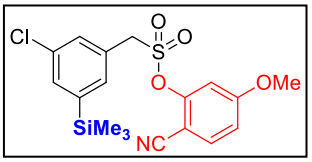
ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 46% (36 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, $^3J_{HH}$ = 9.4 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.41 (s, 1H, C_6H_3{3-Me, 5-$SiMe_3$}), 7.36 (s, 1H, C_6H_3{3-Me, 5-$SiMe_3$}), 7.31 (s, 1H, C_6H_3{3-Me, 5-$SiMe_3$}), 6.90 – 6.84 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.68 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3), 0.26 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 152.1, 141.9, 138.2, 135.5, 134.6, 133.2, 132.3, 125.7, 115.7, 114.0, 109.2, 98.8, 58.9, 56.3, 21.5, -1.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{23}NO_4SSiNa$: 412.1009, found: 412.0995.



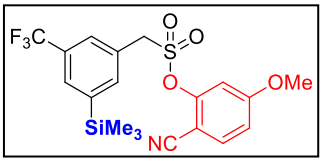
2-Cyano-5-methoxyphenyl (3-fluoro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2i): Brown solid. Melting point 93 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 42% (33 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). Following reaction for 72 h at 46 ˚C, yield 46 % (36 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.4 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.38 (s, 1H, *o*-C_6H_3{3-F, 5-$SiMe_3$}), 7.23 (m, 2H, *o,m* -C_6H_3{3-F, 5-$SiMe_3$}), 6.89 (m,*o,p*-C_6H_3{2-CN, 5-OMe}), 4.71 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.27 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 162.7 (d, $^1J_{CF}$ = 248.8 Hz), 151.9, 145.34 (d, $^3J_{CF}$ = 4.0 Hz), 134.6, 131.7 (d, $^4J_{CF}$= 2.8 Hz), 128.1 (d, $^3J_{CF}$ = 7.1 Hz), 121.2 (d, $^2J_{CF}$= 18.0 Hz), 118.4 (d, $^2J_{CF}$= 22.8 Hz), 115.7, 114.1, 109.4, 98.8, 58.3, 56.3, -1.1.HRMS (ESI-QTOF) m/z: $[M+K]^+$: calcd. for $C_{18}H_{20}NFO_4SSiK$: 432.0498, found: 432.0495.



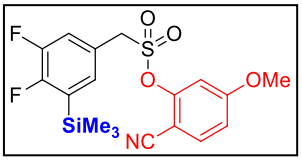
2-Cyano-5-methoxyphenyl (3,5-bis(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2j): White solid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (97:3 v/v) mixture as eluent. Isolated yield: 54% (48 mg). All characterization data are same as **Entry 2a$_{di}$.**



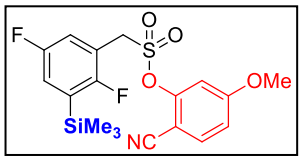
2-Cyano-5-methoxyphenyl (3-chloro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2k): White solid. Melting point 96 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 48% (39 mg). R_f = 0.5 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.52 – 7.47 (m, 3H, C_6H_3{3-Cl, 5-$SiMe_3$}), 6.92 – 6.88 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.68 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.28 (s, 9H, $Si(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.4, 151.9, 144.7, 134.9, 134.6, 134.5, 134.2, 131.3, 127.8, 115.7, 114.1, 109.4, 98.8, 58.2, 56.3, -1.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{20}NClO_4SSiNa$: 432.0463, found: 432.0465.



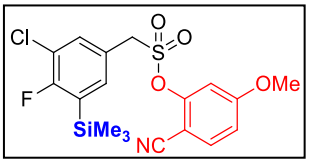
2-Cyano-5-methoxyphenyl (3-(trifluoromethyl)-5-(trimethylsilyl)phenyl)methanesulfonate (Scheme 4, Entry 2l): White solid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 30% (26 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (s, 1H, C_6H_3{3-CF_3, 5-$SiMe_3$}), 7.78 (s, 1H, C_6H_3{3-CF_3, 5-$SiMe_3$}), 7.74 (s, 1H, C_6H_3{3-CF_3, 5-$SiMe_3$}), 7.59 (d, $^3J_{HH}$ = 8.6 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 6.93 – 6.87 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.77 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.32 (s, 9H, $Si(CH_3)_3$).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4, 151.9, 143.9, 139.5, 134.6, 131.1 (q, $^3J_{CF}$ = 3.1 Hz), 131.0 (q, $^2J_{CF}$= 32.3 Hz), 128.2 (q, $^3J_{CF}$= 4.0 Hz), 126.8, 124.1 (d, $^1J_{CF}$ = 274.4 Hz), 115.7, 114.2, 109.4, 98.8, 58.3, 56.3, -1.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{20}NF_3O_4SSiNa$: found: 466.0833.



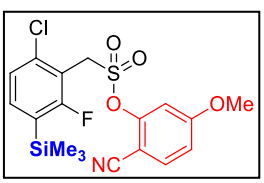
2-Cyano-5-methoxyphenyl (3,4-difluoro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2m): White solid. Melting point 97 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 56 % (46 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$= 8.7 Hz, 1H,*m*-C_6H_3{2-CN, 5-OMe}), 7.36 (m, 1H, C_6H_2{3,4-di-F, 5-$SiMe_3$}),), 7.23 (s, 1H, C_6H_2{3,4-di-F, 5-$SiMe_3$}), 6.93 (d, $^4J_{HH}$= 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$= 8.7 Hz, $^3J_{HH}$= 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.67 (s, 2H,CH_2), 3.86 (s, 3H,OCH_3), 0.35 (s, 9H, $Si(CH_3)_3$).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.4, 154.3 (dd, $^1J_{HF}$= 254.7 Hz, $^2J_{HF}$= 10.1 Hz), 151.8, 151.26 (dd, $^1J_{HF}$= 254.5 Hz, $^2J_{HF}$=17.6 Hz), 134.6, 132.5 (dd, J_{HF}= 11.3 Hz, J_{HF}= 3.8 Hz), 130.8 (d, J_{HF} = 19.0 Hz), 123.0 (dd, J_{HF}= 5.0 Hz, J_{HF}= 3.8 Hz), 121.0 (d, J_{HF} = 18.9 Hz), 115.6, 114.1, 109.5, 98.7, 57.8, 56.3, -1.0 (d, $^4J_{HF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NF_2O_4SSiNa$: 434.0664, found: 434.0664.



2-Cyano-5-methoxyphenyl (2,5-difluoro-3-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2n): White solid. Melting point 87-88 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 51% (42 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.33 – 7.27 (m, 1H, C_6H_2{2,5-*di*-F, 3-$SiMe_3$}), 7.17 – 7.10 (m, 1H, C_6H_2{2,5-*di*-F, 3-$SiMe_3$}), 6.95 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.75 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3), 0.33 (d, J = 0.6 Hz, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 161.5 (d, $^1J_{CF}$ = 244.4 Hz), 158.6 (d, $^1J_{CF}$ = 247.0 Hz), 151.7, 134.7, 130.0 (d, $^2J_{CF}$ = 35.3 Hz), 123.3 (d, $^2J_{CF}$ = 11.3 Hz), 123.1 (d, $^2J_{CF}$ = 12.6 Hz), 120.1 (d, $^2J_{CF}$= 24.0 Hz), 115.4, 114.1, 109.3, 98.9, 56.3, 51.8, -1.1(d, $^4J_{CF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NF_2O_4SSiNa$: 434.0664, found: 434.0669.

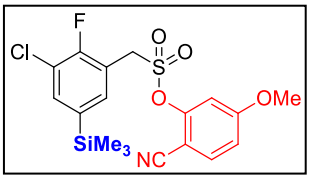


2-Cyano-5-methoxyphenyl (3-chloro-4-fluoro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2o): Whitish-yellow solid. Melting point 94 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 50 % (43 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.55 (m, 2H, *m*-C_6H_3{2-CN, 5-OMe} and *o*-C_6H_2{3-Cl, 4-F, 5-$SiMe_3$}), 7.38 (dd, $^4J_{HH}$/$^4J_{HF}$= 3.9, 2.3 Hz, 1H), 6.93 (d, $^4J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.2 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.66 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3), 0.34 (s, 9H, $Si(CH_3)_3$). ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 162.8 (d, $^1J_{CF}$ = 245.7 Hz), 151.8, 136.2 (d, $^3J_{CF}$ = 11.3 Hz), 134.6, 134.2, 129.6 (d, $^2J_{CF}$ = 31.5 Hz), 123.3 (d, $^3J_{CF}$ = 3.8 Hz), 121.6 (d, $^2J_{CF}$ = 23.9 Hz), 115.6, 114.1, 109.4, 98.7, -1.0 (d, $^4J_{CF}$ = 1.3 Hz).HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NFClO_4SSiNa$: 450.0368, found: 450.0369.

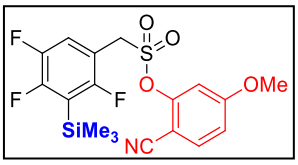


2-Cyano-5-methoxyphenyl (6-chloro-2-fluoro-3-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2p): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 67 % (57 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.39 (dd, $^3J_{HH}$ = 8.0, $^4J_{HF}$ = 5.8 Hz, 1H, *p*- C_6H_2{6-Cl, 2-F, 3-$SiMe_3$}), 7.29 (d, $^3J_{HH}$ = 8.0 Hz, 1H, *m*- C_6H_2{6-Cl, 2-F, 3-$SiMe_3$}), 6.95 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ =2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 5.03 (d, $^4J_{HF}$ = 1.3 Hz, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.32 (d, $^5J_{HF}$ = 0.8

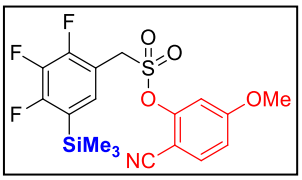
Hz, 9H, Si(CH_3)$_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.4 (d, $^1J_{CF}$ = 248.5 Hz), 164.2, 151.5, 138.0 (d, $^3J_{CF}$ = 3.8 Hz), 137.1 (d, $^3J_{CF}$ = 13.9 Hz), 134.8, 126.1 (d, $^2J_{CF}$ = 37.8 Hz), 125.9 (d, $^4J_{CF}$ = 2.5 Hz), 115.3, 114.0, 113.4 (d, $^2J_{CF}$= 22.7 Hz), 109.3, 99.2, 77.45, 50.2 (d, $^3J_{CF}$ = 2.5 Hz), -1.1 (d, $^4J_{CF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}ClFNO_4SSiNa$: 450.0368, found: 450.0830.



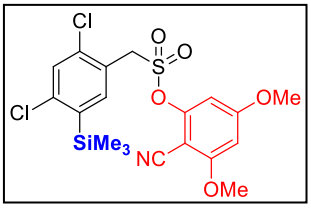
2-Cyano-5-methoxyphenyl (3-chloro-2-fluoro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry2q): Yellow solid. Melting point 82 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 41 % (35 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C$_6H_3${2-CN, 5-OMe}), 7.58 – 7.52 (m, 2H, C$_6H_2${2-F, 3-Cl, 5-SiMe$_3$}), 6.94 ($^4J_{HH}$, J = 2.1 Hz, 1H, *o*-C$_6H_3${2-CN, 5-OMe}), 6.92 – 6.88 (m, 1H, *p*-C$_6H_3${2-CN, 5-OMe}), 4.80 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 0.30 (s, 9H, Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 157.5 (d, $^1J_{CF}$ = 254.5 Hz), 151.7, 138.9 (d, $^3J_{CF}$ = 5.0 Hz), 137.2, 136.1, 134.7, 121.8 (d, $^2J_{CF}$ = 17.6 Hz), 115.5 (d, $^2J_{CF}$ = 13.9 Hz), 115.5, 114.1, 109.3, 98.8, 56.3, 51.9 (d, $^4J_{CF}$ = 3.8 Hz), -1.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NFClO_4SSiNa$: 450.0367, found: 450.0369.



2-Cyano-5-methoxyphenyl (2,4,5-trifluoro-3-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2r): Brown solid. Melting point 105-106 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated as *meta*: other isomer ratio of 8:1. Isolated yield: 45% (39 mg). R_f = 0.3 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C$_6H_3${2-CN, 5-OMe}), 7.41 (m, 1H, C$_6H${2,4,5-tri-F, 3-SiMe$_3$}), 6.97 (d, $^3J_{HH}$ = 2.4 Hz, 1H, *o*-C$_6H_3${2-CN, 5-OMe}), 6.91 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C$_6H_3${2-CN, 5-OMe}), 4.71 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3), 0.40 (t, $^4J_{HH}$ = 1.4 Hz, 9H, Si(CH_3)$_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 159.2 (d, $^1J_{CF}$= 258.3 Hz), 154.8 (d, $^1J_{CF}$= 249.4 Hz), 151.5, 147.2 (d, $^1J_{CF}$= 249.4 Hz), 134.7, 131.1, 121.3 (d, J_{CF} = 10.1 Hz), 115.5, 114.1, 110.1 (d, $^2J_{CF}$= 23.9 Hz), 109.4, 98.8, 56.3, 51.4, 0.12 (t, $^4J_{CF}$ = 2.52 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{18}NF_3ClO_4SSiNa$: 452.0570, found: 452.0573.

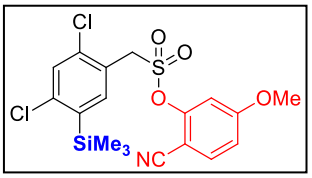


2-Cyano-5-methoxyphenyl (2,3,4-trifluoro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry2s): White solid. Melting point 86 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 41% (35 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, CDCl3) δ 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C$_6H_3${2-CN, 5-OMe}), 7.28 (m, 1H, C$_6H${2,3,4-tri-F, 5-SiMe$_3$}), 6.96 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C$_6H_3${2-CN, 5-OMe} 6.91 (dd, $^3J_{HH}$= 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C$_6H_3${2-CN, 5-OMe}), 4.77 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3), 0.34 (s, 9H, Si(CH_3)$_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.4, 156.1 (d, $^1J_{CF}$ = 252.0 Hz), 151.6, 151.4 (d, $^1J_{CF}$ = 245.7 Hz), 139.9 (d, $^1J_{CF}$ = 277.2 Hz), 134.7, 131.4 (d, J_{CF} = 10.1 Hz), 125.0 (d, $^2J_{CF}$= 27.7 Hz), 115.4, 114.1, 111.8 (d, J_{CF} = 11.3 Hz), 109.4, 98.9, 56.3, 51.5, -1.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{18}NF_3O_4SSiNa$: 452.0570, found: 452.0578.



2-Cyano-3,5-dimethoxyphenyl (2,4-dichloro-5-(trimethylsilyl)phenyl)methanesulfonate (Table 3, Entry 2t): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 33% (31 mg). R_f = 0.2 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, CDCl3) δ 7.64 (s, 1H,

C_6H_2{2,4-di-Cl, 5-$SiMe_3$}), 7.47 (s, 1H, C_6H_2{2,4-di-Cl, 5-$SiMe_3$}), 6.53 (d, $^4J_{HH}$ = 2.1 Hz, 1H,C_6H_2{2-CN, 3,5-di-OMe}), 6.40 (d, $^4J_{HH}$ = 2.0 Hz, 1H, C_6H_2{2-CN, 3,5-di-OMe}), 4.91 (s, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 0.37 (s, 9H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (126 MHz, CDCl3) δ 165.0, 163.4, 152.5, 143.1, 139.8, 139.0, 137.3, 130.6, 123.1, 113.2, 101.0, 97.6, 89.8, 56.7, 56.4, 55.2, -0.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{21}NCl_2O_5SSiNa$: 496.0179, found: 496.0184.

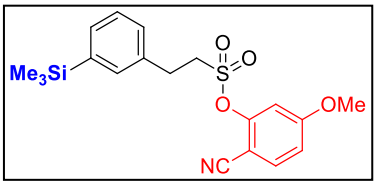


2-Cyano-5-methoxyphenyl (2,4-dichloro-5-(trimethylsilyl)phenyl)methanesulfonate (Entry 2t, DG$_4$): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 25% (22 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 (s, 1H, C_6H_2{2,4-di-Cl, 5-$SiMe_3$}), 7.60 (d, $^3J_{HH}$ = 8.4 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.48 (s, 1H, C_6H_2{2,4-di-Cl, 5-$SiMe_3$}), 6.94 – 6.87 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.92 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.37 (s, 9H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.7, 143.1, 139.8, 139.1, 137.3, 134.7, 130.6, 123.0, 115.5, 114.2, 109.4, 99.0, 56.3, 55.1, -0.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NCl_2O_4SSiNa$: 466.0073, found: 466.0073.

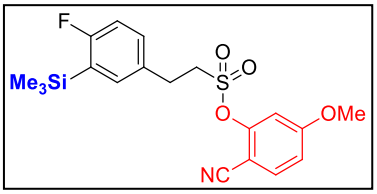
General Procedure Bfor mono silyation through remote *meta* C-H activation of 2-phenylethanesulfonic acid derivatives:

In a clean, oven–dried screw cap reaction tube, with previously placed magnetic stir–bar substrate (0.2 mmol); $Pd(OAc)_2$ (0.1 equiv, 0.02 mmol, 4.5 mg); N-Acetyl-glycine (0.4 equiv, 0.04 mmol, 4.5 mg), Ag_2CO_3 (3 equiv, 0.6 mmol, 166 mg), anhyd. Na_2SO_4 (200mg) were taken. Then hexafluoroisopropanol (1.8 mL) which was previously distilled and collected over activated 4Å molecular sieves was added by syringes. Next, hexamethyldisilane (5 equiv, 1 mmol, 200 µL) was added to mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 70 ˚C. At time t = 24h, another 2 equiv. of hexamethyldisilane (0.4 mmol, 80 µL) and $Pd(OAc)_2$ (0.05 equiv, 0.01 mmol, 2.2 mg) were added to reaction mixture and the mixture was stirred for 12h at 70 ˚C. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube was washed with 10 mL of dichlorometane. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent.

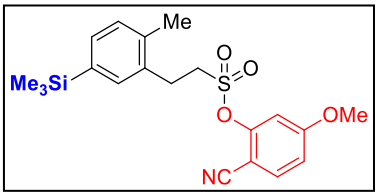
Characterization data for*meta* C-H activation of 2-phenylethanesulfonic acid derivatives:



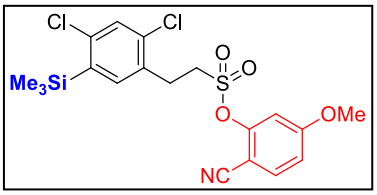
2-Cyano-5-methoxyphenyl 2-(3-(trimethylsilyl)phenyl)ethanesulfonate (Table 4, Entry 3a$_{mono}$): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 52 % (40 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.52 – 7.39 (m, 2H, C_6H_4{3-$SiMe_3$}), 7.36 – 7.31 (m, 1H, C_6H_4{3-$SiMe_3$}), 7.30 – 7.27 (m, 1H, C_6H_4{3-$SiMe_3$}), 7.07 – 7.02 (m, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.91 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.89 (s, 3H, OCH_3), 3.75 – 3.66 (m, 2H, CH_2), 3.41 – 3.33 (m, 2H, CH_2), 0.27 (s, 9H, $Si(CH_3)_3$). ^{13}C {^1H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.5, 141.8, 136.1, 134.7, 133.6, 132.5, 129.1, 128.5, 115.6, 114.0, 109.6, 98.8, 56.3, 53.9, 30.0, -1.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{23}NO_4SSiNa$: 412.1009, found: 412.1022.



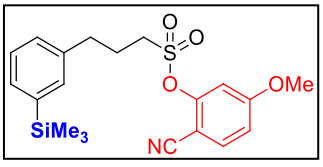
2-Cyano-5-methoxyphenyl 2-(4-fluoro-3-(trimethylsilyl)phenyl)ethanesulfonate (Table 4, Entry 3b$_{mono}$): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 56 % (45 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.30 – 7.22 (m, 2H, C_6H_3{3-SiMe$_3$, 4-F}), 7.04 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.97 – 6.89 (m, 2H, *p*-C_6H_3{2-CN, 5-OMe} and C_6H_3{3-SiMe$_3$, 4-F}), 3.89 (s, 3H, OCH_3), 3.70 – 3.65 (m, 2H, CH_2), 3.37 – 3.32 (m, 2H, CH_2), 0.32 (d, *J* = 0.8 Hz, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.8 (d, $^1J_{CF}$ = 241.4 Hz), 164.3, 151.5, 135.4 (d, $^3J_{CF}$ = 11.8 Hz), 134.6, 132.1 (d, $^4J_{CF}$ = 2.9 Hz), 131.5 (d, $^3J_{CF}$ = 8.9 Hz), 127.2 (d, $^2J_{CF}$ = 31.2 Hz), 115.6, 115.4 (d, $^2J_{CF}$ = 26.5 Hz), 114.0, 109.7, 98.7, 56.3, 54.0, 29.2, -0.9 (d, $^4J_{CF}$ = 1.4 Hz).



2-Cyano-5-methoxyphenyl 2-(2-methyl-5-(trimethylsilyl)phenyl)ethanesulfonate(Table 4, Entry 3c$_{mono}$): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 35 % (28 mg). R_f = 0.4 (4:1 Pet ether:EtOAc).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.39 – 7.32 (m, 2H, C_6H_3{2-Me, 5-SiMe$_3$}), 7.19 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C_6H_3{2-Me, 5-SiMe$_3$}), 7.08 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.92 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.90 (s, 3H, OCH_3), 3.66 (m, 2H, CH_2), 3.43 – 3.37 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 0.27 (s, 9H, $Si(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.5, 138.9, 137.1, 134.7, 134.5, 134.3, 132.8, 130.5, 115.6, 114.0, 109.5, 98.9, 56.3, 52.7, 27.5, 19.4, -0.9. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{25}NO_4SSiNa$: 426.1166, found: 426.1160.

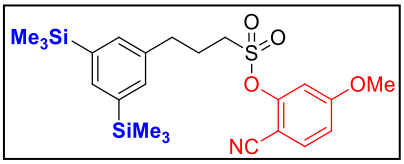


2-Cyano-5-methoxyphenyl 2-(2,4-dichloro-5-(trimethylsilyl)phenyl)ethanesulfonate (Table 4, Entry 3d): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 31% (28 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$= 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.39 (m, 2H, C_6H_2{2,4-di-Cl, 5-SiMe$_3$}), 7.05 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.92 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.89 (s, 3H, OCH_3), 3.73 – 3.68 (m, 2H, CH_2), 3.49 – 3.43 (m, 2H, CH_2), 0.36 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.4, 151.5, 140.8, 138.7, 138.0, 135.7, 134.7, 132.4, 130.2, 115.6, 114.1, 109.6, 98.9, 56.4, 51.7, 27.9, -0.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{21}NCl_2O_4SSiNa$: 480.0230, found: 480.0218.



2-Cyano-5-methoxyphenyl 3-(3-(trimethylsilyl)phenyl)propane-1-sulfonate (Table 4, Entry 4a$_{mono}$): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 45% (36 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.39 (d, $^3J_{HH}$ = 7.2 Hz, 1H,C_6H_4{3-SiMe$_3$}), 7.35 (s, 1H, *2*-C_6H_4{3-SiMe$_3$}), 7.31 (t, $^3J_{HH}$ = 7.4 Hz, 1H, 5-C_6H_4{3-SiMe$_3$}), 7.21 (d, $^3J_{HH}$ = 6.2 Hz, 1H, C_6H_4{3-SiMe$_3$}), 7.02 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7 Hz,$^4J_{HH}$= 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.87 (s, 3H, OCH_3), 3.48 – 3.41 (m, 2H, CH_2), 2.84 (d, $^3J_{HH}$ = 7.5 Hz, 2H, CH_2), 2.45 – 2.35 (m, 2H, CH_2), 0.27 (s, 9H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.6, 141.3, 138.9, 134.7, 133.6,

131.8, 129.1, 128.3, 115.6, 114.0, 109.7, 98.9, 56.3, 51.9, 34.3, 25.4, -0.9. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{25}NO_4SSiNa$: 426.1166, found: 426.1163.

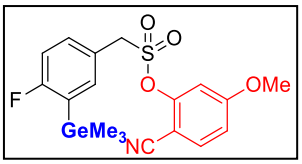


2-Cyano-5-methoxyphenyl 3-(3,5-bis(trimethylsilyl)phenyl)propane-1-sulfonate (Table 4, Entry 4a$_{di}$): White solid. Melting point 89 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (96:4 v/v) mixture as eluent. Isolated yield: 31% (10 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.54 (s, 1H, *p*-C_6H_3{3,5-di-$SiMe_3$}), 7.35 (s, 2H, *o*-C_6H_3{3,5-di-$SiMe_3$}), 7.02 (s, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.93 – 6.87 (m, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.88 (s, 3H, OCH_3), 3.52 – 3.43 (m, 2H, CH_2), 2.85 (t, $^3J_{HH}$ = 6.7 Hz, 2H, CH_2), 2.46 – 2.36 (m, 2H, CH_2), 0.28 (s, 18H, $Si(CH_3)_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.6, 140.3, 138.0, 136.6, 134.6, 134.2, 115.6, 114.0, 109.7, 98.9, 56.3, 52.0, 34.4, 25.5, -0.9.HRMS (ESI-QTOF) m/z: $[M+H]^+$: calcd. for $C_{23}H_{34}NO_4SSi_2$: 476.1742, found: 476.1741.

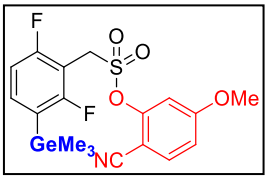
General Procedure C for mono germanylation through remote *meta* C-H activation of benzylsulfonic acid derivatives:

In a clean, oven–dried screw cap reaction tube, with previously placed magnetic stir–bar substrate (0.1 mmol); $Pd(OAc)_2$ (0.1 equiv, 0.01 mmol, 2.2 mg); N-Acetyl-glycine (0.2 equiv, 0.02 mmol, 2.2 mg), Ag_2CO_3 (3 equiv, 0.3 mmol, 83 mg), anhyd. Na_2SO_4 (100 mg) were taken. Then hexafluoroisopropanol (0.9 mL) which was previously distilled and collected over activated 4Å molecular sieves was added by syringes. Next, hexamethyldigermane (4 equiv, 0.4 mmol) was added to mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 45 ˚C. At time t = 24h, another 2 equiv. of hexamethyldigermane (0.2 mmol) and $Pd(OAc)_2$ (0.05 equiv, 0.005 mmol, 1.1 mg) were added to reaction mixture and the mixture was stirred for another 24h at 45 ˚C. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube was washed with 10 mL of dichlorometane. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent.

Characterization data formono germanylation through remote *meta* C-H activation of benzylsulfonic acid derivatives

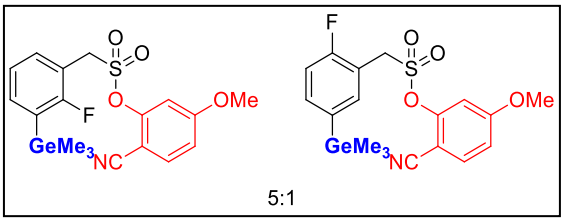


2-Cyano-5-methoxyphenyl (4-fluoro-3-(trimethylgermyl)phenyl)methanesulfonate (Table 6, Entry 5a): White solid. Melting point 83 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 45% (20 mg). R_f = 0.3 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (dd, $^3J_{HH}$ = 8.1, $^5J_{HH}$ = 0.9 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.50 – 7.44 (m, 2H, C_6H_3{4-F, 3-$GeMe_3$}), 7.04 (t, $^3J_{HH/HF}$ = 7.9 Hz, 1H, C_6H_3{4-F, 3-$GeMe_3$}), 6.91 – 6.86 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.69 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.45 (s, 9H, $Ge(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 167.5 (d, $^1J_{CF}$ = 243.0 Hz) 164.3, 152.0, 137.6 (d, $^3J_{CF}$ = 12.6 Hz), 134.6, 133.5 (d, $^3J_{CF}$ = 8.8 Hz), 129.5 (d, $^2J_{CF}$ = 35.3 Hz), 122.1, 115.7, 115.6 (d, $^2J_{CF}$ = 27.7 Hz), 114.0, 109.3, 98.7, 58.1, 56.3, -1.3(d, $^4J_{CF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{20}NFGeO_4SNa$: 462.0204, found: 462.0201.

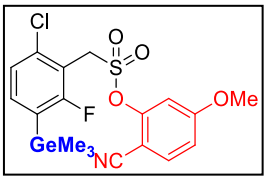


2-Cyano-5-methoxyphenyl (2,6-difluoro-3-(trimethylgermyl)phenyl)methanesulfonate (Table 6, Entry 5b): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate

(94:6 v/v) mixture as eluent. Isolated yield: 45 % (20 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). 1H NMR (500 MHz, CDCl3) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.46 – 7.36 (m, 1H, C_6H_2{2,6-di-F, 3-$GeMe_3$}), 7.00 (t, $^3J_{HH/HF}$ = 8.5 Hz, 1H, C_6H_2{2,6-di-F, 3-$GeMe_3$}), 6.95 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.86 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3), 0.45 (s, 9H, $Ge(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.3 (dd, $^1J_{CF}$ = 247.0 Hz, $^3J_{CF}$ = 6.3 Hz), 164.2, 162.6 (dd, $^1J_{CF}$ = 257.0 Hz, $^3J_{CF}$ = 6.3 Hz), 151.5, 136.9 (dd, $^3J_{CF}$ = 17.6 Hz, $^3J_{CF}$ = 10.1 Hz) 134.8, 124.3 (dd, $^2J_{CF}$ = 25.2 Hz, $^4J_{CF}$ = 3.8 Hz) 115.2, 114.0, 112.0 (dd, $^2J_{CF}$ = 20.2 Hz, $^4J_{CF}$ = 2.5 Hz) 109.2, 103.3 (dd, $^2J_{CF}$ = 23.3 Hz, $^2J_{CF}$ = 19.0 Hz) 99.1, 56.3, 46.9 (t, $^3J_{CF}$ = 2.5 Hz) -1.2 (d, $^4J_{CF}$ = 1.3 Hz). HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NF_2GeO_4SNa$: 480.0109, found: 480.0104.



2-cyano-5-methoxyphenyl (2-fluoro-3-(trimethylgermyl)phenyl)methanesulfonate compound with 2-cyano-5-methoxyphenyl (2-fluoro-5-(trimethylgermyl)phenyl)methanesulfonate (3:1) (Table 6, Entry 5c): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 42% (18 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). Proton NMR of the major product :^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.55 (t, $^3J_{HH}$ = 7.6 Hz, 1H, C_6H_3{2-F, 3-$GeMe_3$}), 7.46 – 7.42 (m, 1H, C_6H_3{2-F, 3-$GeMe_3$}), 7.20 (t, $^3J_{HH}$ = 7.4 Hz, 1H, C_6H_3{2-F, 3-$GeMe_3$}), 6.92 (d, $^4J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.3 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.79 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 0.45 (s, 9H, $Ge(CH_3)_3$).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 166.1, 164.3, 151.9, 136.7, 136.6, 134.7, 133.5, 129.1, 124.8, 115.5, 114.0, 109.1, 98.9, 56.3, 52.1, -1.2, -1.5.



2-Cyano-5-methoxyphenyl (6-chloro-2-fluoro-3-(trimethylgermyl)phenyl)methanesulfonate (Table 6, Entry 5d): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 48% (22 mg). R_f = 0.4 (4:1 Pet ether:EtOAc). with 15:1 meta: other isomer mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$= 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.37 (dd, $^3J_{HH}$ = 7.9, $^4J_{HF}$ = 5.3 Hz, 1H, 4-C_6H_2{2-F, 3-$GeMe_3$, 6-Cl}), 7.28 (d, $^3J_{HH}$ = 8.0 Hz, 1H, 5-C_6H_2{2-F, 3-$GeMe_3$, 6-Cl}), 6.98 – 6.91 (m, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^3J_{HH}$= 8.7, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 5.03 (d, $^4J_{HF}$ = 1.2 Hz, 2H, CH_2), 3.84 (s, 3H. OCH_3), 0.45 (s, 9H, $Ge(CH_3)_3$).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7 (d, $^1J_{CF}$ = 247.0 Hz) 164.2, 151.5, 137.3 (d, J_{CF} = 3.8) 136.6 (d, $^3J_{CF}$ = 13.9 Hz), 134.8, 128.9 (d, $^2J_{CF}$ = 36.5 Hz), 125.9 (J_{CF}, J = 3.8 Hz), 115.3, 114.1, 113.3 ($^2J_{CF}$, d, J = 21.4 Hz), 109.3, 99.2, 56.3, 50.3, -1.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{19}NClFGeO_4SNa$: 495.9810, found: 495.9808.

Reaction with other silylating agents:

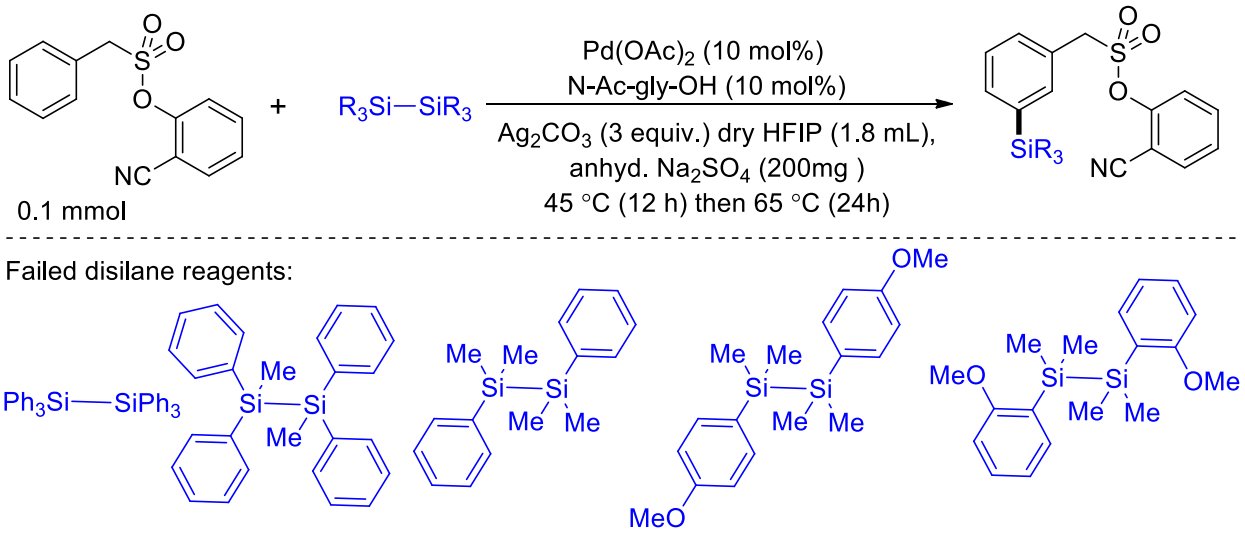
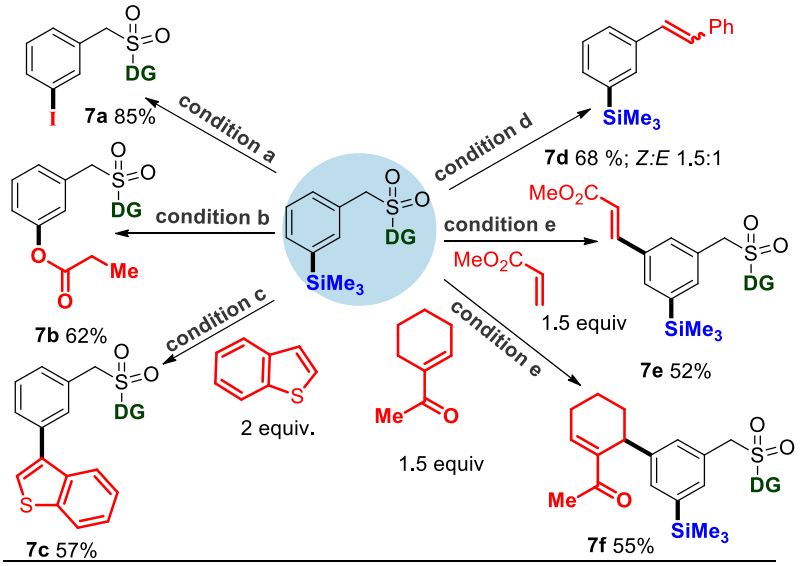


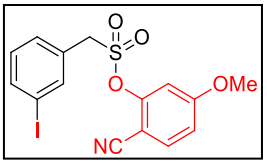
Table S2: Reaction with other disilanes.

Application:

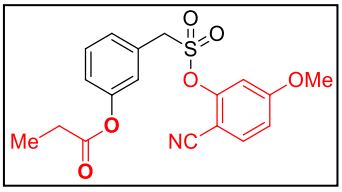


Reaction condition **a:** $AgNO_3$, I_2 MeOH, 70 °C; condition **b**: $Pd(OAc)_2$ (10 mol%), $PhI(OCOCF_3)_2$ (1 equiv.), propanoic acid, 90 °C; condition **c**: $Pd(MeCN)_2Cl_2$ (5 mol%), $CuCl_2$ (1 equiv.), DCE, 70 °C;16h; N_2 atmosphere; **d**: PhCHO, LDA, THF, -78 °C; **e** $Pd(OAc)_2$ (20 mol %), Ac-Gly-OH (20 mol %), Ag_2CO_3 (3 equiv.), HFIP, 70 °C

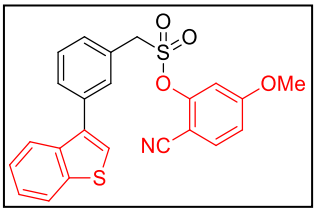
Table S3: Late stage modification of the mono silylated benzyl sulphonate ester.



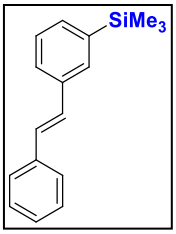
2-Cyano-5-methoxyphenyl (3-iodophenyl)methanesulfonate (Scheme 3, Entry 7a): White solid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (94:6 v/v) mixture as eluent. Isolated yield: 85% (36 mg). R_f = 0.3 (4:1 Pet ether:EtOAc). 1H NMR (400 MHz, CDCl3) δ 7.85 (t, $^4J_{HH}$ = 1.6 Hz, 1H, *o*-C_6H_4{3-I}), 7.79 – 7.73 (m, 1H, C_6H_4{3-I}), 7.61 – 7.56 (m, 1H, *m*-C_6H_3{5-OMe, 2-CN}), 7.51 (dd, J = 7.7, 1.0 Hz, 1H, C_6H_4{3-I}), 7.17 (t, $^3J_{HH}$ = 7.8 Hz, 1H, *m*-C_6H_4{3-I}), 6.92 – 6.86 (m, 2H, *o, p*-C_6H_3{5-OMe, 2-CN}), 4.65 (s, 2H, CH_2), 3.84 (d, $^4J_{HH}$ = 2.9 Hz, 3H, OCH_3).$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 164.3, 151.8, 139.9, 138.8, 134.6, 130.8, 130.5, 128.7, 115.6, 114.1, 109.3, 98.8, 94.6, 57.8, 56.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{15}H_{12}NIO_4SNa$: 451.9425, found: 451.9422.



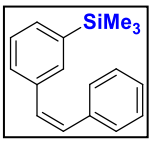
3-(((2-Cyano-5-methoxyphenoxy)sulfonyl)methyl)phenyl propionate (Scheme 3, Entry 7b): Brown solid. Melting point 62 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 62% (23 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 1H*m*-C_6H_3{5-OMe, 2-CN}), 7.47 – 7.41 (m, 1H, C_6H_4{3-$OCOCH_2CH_3$}), 7.38 (dt, $^{3}J_{HH}$ = 7.7, $^{4}J_{HH}$ = 1.3 Hz, 1H, C_6H_4{3-$OCOCH_2CH_3$}), 7.31 – 7.27 (m, 1H, C_6H_4{3-$OCOCH_2CH_3$}), 7.18 (ddd, $^{3}J_{HH}$ = 8.0, $^{4}J_{HH}$ = 2.3, $^{4}J_{HH}$ = 1.3 Hz, 1H, C_6H_4{3-$OCOCH_2CH_3$}), 6.90 – 6.84 (m, 2H, C_6H_3{5-OMe, 2-CN}), 4.71 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 2.65 – 2.54 (m, 2H, CH_2CH_3), 1.29 – 1.22 (m, 3H, CH_2CH_3). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 172.9, 164.3, 151.8, 151.2, 134.6, 130.2, 128.6, 127.9, 124.5, 123.1, 115.6, 114.1, 109.2, 98.8, 58.2, 56.3, 27.9, 9.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{17}NO_6SNa$: 398.0669, found: 398.0666.



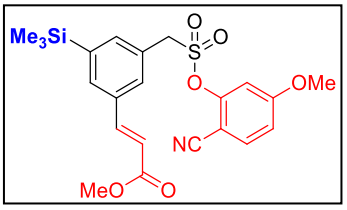
2-Cyano-5-methoxyphenyl (3-(benzo[b]thiophen-3-yl)phenyl)methanesulfonate (Scheme 3, Entry 7c): White solid. Melting point 56 ˚C. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 57% (25 mg). R_f = 0.2 (4:1 Pet ether:EtOAc). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (m, 2H), 7.74 (s, 1H), 7.66 (d, $^{3}J_{HH}$= 6.3 Hz, 1H), 7.61 – 7.53 (m, 3H), 7.45 (d, $^{3}J_{HH}$ = 9.6 Hz, 1H), 7.39 (dd, $^{3}J_{HH}$ = 5.7, 3.6 Hz, 2H), 6.92 (d, $^{4}J_{HH}$ = 2.3 Hz, 1H, *p*-C_6H_3{5-OMe, 2-CN}), 6.88 (dd, $^{3}J_{HH}$ = 8.7, $^{4}J_{HH}$ =2.4 Hz, 1H, *p*-C_6H_3{5-OMe, 2-CN}), 4.79 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 152.0, 140.9, 137.8, 137.1, 134.6, 131.5, 130.4, 130.0, 129.7, 127.1, 124.8, 124.4, 123.2, 122.9, 115.7, 114.1, 109.4, 98.9, 58.8, 56.3. HRMS (ESI-QTOF) m/z: $[M+K]^+$: calcd. for $C_{23}H_{17}NO_4S_2K$: 474.0230, found: 474.0620.



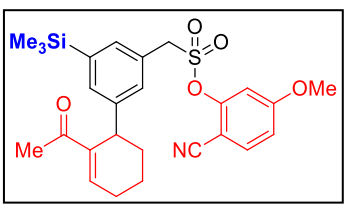
(E)-Trimethyl(3-styrylphenyl)silane (Scheme 3, Entry 7d):oily liquid. Isolated through 100-200 mesh silica gel using pet ether as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (s, 1H, *o*-C_6H_4{3-$SiMe_3$}), 7.52 (dd, $^{3}J_{HH}$= 16.2, $^{3}J_{HH}$ = 7.9 Hz, 3H), 7.43 (d, $^{3}J_{HH}$ = 7.2 Hz, 1H), 7.39 – 7.33 (m, 3H), 7.25 (m, 1H), 7.13 (m, 2H), 0.31 (s, 9H, $Si(CH_3)_3$). ^{13}C {1H} NMR (126 MHz, $CDCl_3$) δ 141.1, 137.6, 136.7, 132.8, 131.9, 129.2, 128.9, 128.8, 128.3, 127.7, 126.9, 126.7, -0.9.



(Z)-Trimethyl(3-styrylphenyl)silane (Scheme 3, Entry 7d):oily liquid. Isolated through 100-200 mesh silica gel using pet ether as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.31 (dd, *J* = 16.2, 7.9 Hz, 1H), 7.28-7.19 (m, 7H), 6.61 (m, 2H), 0.16 (s, 9H, $Si(CH_3)_3$). ^{13}C {1H} NMR (126 MHz, $CDCl_3$) δ 140.3, 137.6, 136.4, 134.2, 132.1, 130.7, 130.4, 129.6, 129.0, 128.4, 127.7, 127.2, -1.1.



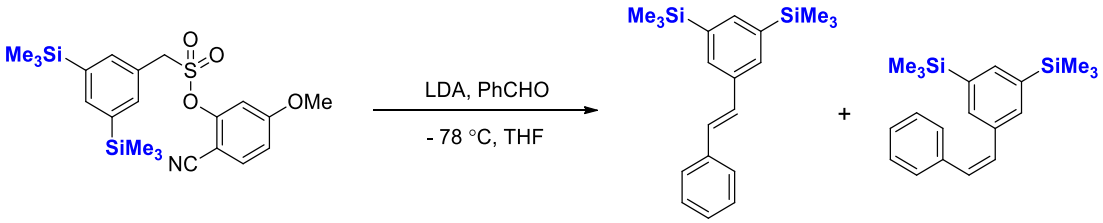
(E)-Methyl 3-(3-(((2-cyano-5-methoxyphenoxy)sulfonyl)methyl)-5-(trimethylsilyl)phenyl)acrylate(Scheme 3, Entry 7e):oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 57% (25 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 1H), 7.68 – 7.65 (m, 2H), 7.63 (s, 1H), 7.59 (dd, $^{3}J_{HH}$ = 9.7, $^{4}J_{HH}$ = 1.4 Hz, 1H), 6.89 (m, 2H, *o,p*-C_6H_3{5-OMe, 2-CN}), 6.50 (d, $^{3}J_{HH}$ = 16.0 Hz, 1H, C*H*), 4.74 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 0.30 (s, 9H, $Si(CH_3)_3$)). ^{13}C{1H} NMR (126 MHz, $CDCl_3$) δ 167.4, 164.3, 151.9, 144.2, 143.2, 137.8, 134.6, 134.4, 130.7, 126.7, 119.1, 114.0, 109.3, 58.5, 56.3, 52.0, -1.1.



2-Cyano-5-methoxyphenyl (6'-acetyl-5-(trimethylsilyl)-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-3-yl)methanesulfonate (Scheme 3, Entry

7f):oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (80:20 v/v) mixture as eluent. Isolated yield: 55 % (55 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.41 (d, *J* = 8.9 Hz, 1H), 7.36 (s, 1H, C_6H_3{3-$SiMe_3$}), 7.19 (t, $^{4}J_{HH}$ = 3.6 Hz, 1H, C_6H_3{3-$SiMe_3$}), 7.14 (s, 1H, C_6H_3{3-$SiMe_3$}), 6.86 (dd, $^{3}J_{HH}$ = 8.7, $^{4}J_{HH}$ = 2.3 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 6.72 (d, $^{4}J_{HH}$ = 2.2 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 4.65 (s, 2H, benzylic-CH_2), 4.05 (br, s, 1H, C*H*), 3.80 (s, 3H. OCH_3), 2.50 – 2.39 (m, 1H, CH_2), 2.35 – 2.25 (m, 1H, CH_2), 2.22 (s, 3H, COCH_3), 1.92 – 1.82 (m, 1H, CH_2), 1.77 – 1.69 (m, 1H, CH_2), 1.64 (s, 1H, CH_2), 1.49 – 1.43 (m, 1H, CH_2), 0.25 (s, 9H, Si(CH_3)$_3$)).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 198.7, 164.2, 152.0, 145.3, 142.9, 141.8, 140.8, 134.5, 133.8, 130.6, 125.3, 115.7, 113.9, 109.2, 98.8, 58.8, 56.2, 38.3, 31.2, 26.2, 25.9, 16.8, -1.0.

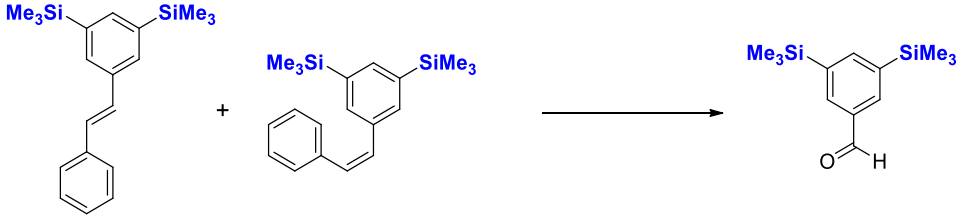
Formal synthesis of TAC 101 (Scheme 4)



In a two neck round bottom flask, dry THF (4 mL) were taken and then LDA (5 equiv., 70 µL) was added to this THF at – 78 ˚C in N_2 atmosphere. After 15 minute of stirring at – 78 ˚C, substrate(0.1 mmol, 47 mg) (diluted in 3 mL THF) was added dropwise by syringe in N_2 atmosphere to the reaction mixture. When the addition of substrate is complete, benzaldehyde (2 equiv. 20 µL) (diluted in 8 mL THF) was added to the reaction mixture by syringe in N_2 atmosphere at – 78 ˚C dropwise. The total reaction mixture was stirred in N_2 atmosphere for overnight. After that the reaction was quenched with brine solution and performed column chromatography to isolate desired product. Total isolated yield of the desired product 55 % (with E:Z 1:1 ratio).

(E)-(5-Styryl-1,3-phenylene)bis(trimethylsilane) (Scheme 4):white solid. Isolated through 100-200 mesh silica gel using pet ether as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 2H, *o*-C_6H_3{3,5-di-$SiMe_3$}), 7.58 – 7.53 (m, 3H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.27 (m, 1H), 7.14 (d, $^{3}J_{HH}$ = 8.8 Hz, 2H), 0.31 (s, 18H, Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 140.1, 137.7, 135.7, 132.3, 129.4, 128.9, 128.9, 128.7, 127.7, 126.7, -0.8.

(Z)-(5-styryl-1,3-phenylene)bis(trimethylsilane) (Scheme 4):white solid. Isolated through 100-200 mesh silica gel using pet ether as eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H, *p*-C_6H_3{3,5-di-$SiMe_3$}), 7.38 (s, 2H, *o*-C_6H_3{3,5-di-$SiMe_3$}), 7.28 (t, *J* = 2.7 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.21 – 7.18 (m, 1H), 6.61 (d, *J* = 8.0 Hz, 2H), 0.16 (s, 18H, Si(CH_3)$_3$). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 139.3, 137.8, 136.9, 135.4, 134.8, 130.9, 130.3, 129.0, 128.4, 127.2, -1.0.

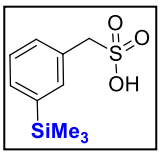


3,5-bis(trimethylsilyl)benzaldehyde: In mortar pestle $KMnO_4$(50 mg), $CuSO_4$ (25 mg), was ground to dust, the 4 µL of H_2O added to in and mixter the mixture properly. The the total mixture was trasfered to a round bottom flask and dichloromrthane (1 mL DCM) was added to it. To the stirred

suspension of the mixture, the substrate diluted in 1 mL DCM was added dropwise. After that, tert-butyl alcohol (13 µL)was added tothis reaction mixture. After that the reaction mixture was refluxed for 5 min, then cooled to room temperature and stirred for 1 h. Then the reaction mixture was filtered through celite and washed with DCM and checked in GCMS. For the deired product [M]+ 250.1.

De-protection of acid moieties and recovery of the directing template (Scheme 5):

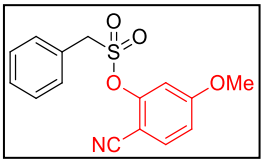
(3-(Trimethylsilyl)phenyl)methanesulfonic acid: In a clean, oven–dried reaction tube, with previously placed magnetic stir–bar, 2-Cyano-5-methoxyphenyl (3-(trimethylsilyl)phenyl)methanesulfonate (0.1 mmol, 37 mg) was taken. Then the 10% KOH in MeOH was added to dissolve it. The reaction mixture was stirred at room temperature till full conversion of starting material. After that, methanol was evaporated to dryness. Then 5mL ethyl acetate was added to the reaction mixture and the reaction mixture was acidified with 2 (N) HCl solution. White solid (3-(trimethylsilyl)phenyl)methanesulfonic acid was isolted. Yield 85%. And the organic portion was dried and concentrated to get pure 2-cyano phenol. **:** ^{1}H NMR (500 MHz, DMSO) δ 7.41 (s, 1H, *o*-C$_6$*H*$_4${3-SiMe$_3$), 7.36 – 7.29 (m, 2H,C$_6$*H*$_4${3-SiMe$_3$)), 7.25 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, *m*-C$_6$*H*$_4${3-SiMe$_3$)), 3.72 (s, 2H, C*H*$_2$), 0.23 (s, 9H, Si(C*H*$_3$)$_3$). ^{13}C {^{1}H} NMR (126 MHz, DMSO) δ 138.7, 135.1, 134.6, 131.1, 130.9, 127.1, 57.6, -1.0.



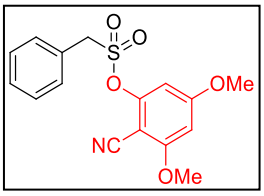
Starting materials

Synthesis of sulphonyl chloride from benzyl chloride: In anoven dried clean round bottom flask charged with magnetic stir-bar, benzyl chloride derivative (100 mmol) and thiourea (100 mmol, 7.6 gm) were taken. Absolute ethanol (100 mL) was added to the reactant mixture and refluxed at 96°C. After 3 h the reaction was taken out and evaporated under reduced pressure to obtained white solid salt. At next step, N-chlorosuccinimide (NCS) (400 mmol; 53.4 gm) was taken in round bottom flask and was suspended in MeCN (100 ML) and 2(N) HCl (20 mL). The reaction mixture was stirred at 0 °C for 15 min. Then, the obtained solid compound was added in portion to the suspension in order to obtain a clear solution. The solution was transferred to room temperature and stirred for another 1 h. The solution was evaporated under reduced pressure to remove the MeCN. The remaining aqueous portion was extracted with ethyl acetate. The organic portion was dried over anhydrous Na_2SO_4 and the crude mixture was evaporated and purified by column chromatography through silica gel (100-200 mesh size) and petroleum ether/ ethyl acetate as the eluent.

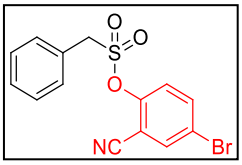
Synthesis of sulphonic ester from sulphonyl chloride: An oven dried clean round bottom flask was charged with magnetic stir-bar and 2-hydroxy-4-methoxy benzonitrile followed by anhyd. DCM. Then under nitrogen atmosphere Et_3N was added to the reaction miture to get a cler solution. After 10 mins, sulphonyl chloride was added in portion and the reaction mixture was transferred to room temperature and stirred overnight. The progress of the reaction was monitored by TLC. Upon completion the reaction was quenched by adding water and the desired compound was extracted with ethyl acetate. Combined organic portion was dried over anhydrous Na_2SO_4. The crude mixture was concentrated under reduced pressure and purified by column chromatography using silica gel (100-200 mesh size) and petroleum ether/ ethyl acetate as the eluent.



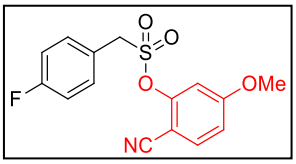
2-Cyano-5-methoxyphenyl phenylmethanesulfonate: White solid. ^{1}H NMR (500 MHz, CDCl3) δ 7.58 (d, $^{3}J_{HH}$ = 8.4 Hz, 1H, *m*-C$_6H_3${2-CN, 5-OMe}), 7.52 (dd, $^{3}J_{HH}$ = 6.2, $^{4}J_{HH}$ = 3.1 Hz, 2H, C$_6H_5$), 7.43 (dd, $^{3}J_{HH}$ = 9.1, 6.0 Hz, 3H, C$_6H_5$), 6.88 (m, 2H, *o,p*-C$_6H_3${2-CN, 5-OMe), 4.72 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3). ^{13}C {1H} NMR (126 MHz, CDCl$_3$) δ 164.2, 151.9, 134.6, 131.3, 129.7, 129.3, 126.5, 115.7, 114.0, 109.2, 98.8, 58.7, 56.3.



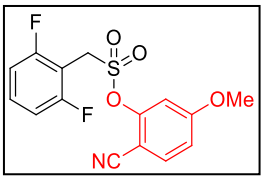
2-Cyano-3,5-dimethoxyphenyl phenylmethanesulfonate: White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.58 – 7.48 (m, 2H, C$_6H_5$), 7.47 – 7.34 (m, 3H, C$_6H_5$), 6.49 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, C$_6H_2${2-CN, 3,5-di-OMe}), 6.38 (d, $^{4}J_{HH}$= 2.1 Hz, 1H, C$_6H_2${2-CN, 3,5-di-OMe}), 4.71 (s, 2H), 3.91 (s, 3H), 3.81 (s, 3H). ^{13}C {1H} NMR (126 MHz, CDCl$_3$) δ 165.0, 163.3, 152.7, 131.3, 129.7, 129.2, 126.6, 113.4, 100.9, 97.4, 89.6, 58.8, 56.7, 56.3.



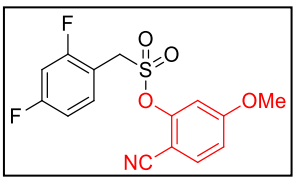
4-Bromo-2-cyanophenyl phenylmethanesulfonate: White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.79 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *m*-C$_6H_3${2-CN, 4-Br}), 7.70 (dd, $^{3}J_{HH}$ = 8.9 Hz, $^{4}J_{HH}$ = 2.4 Hz, 1H, *m*-C$_6H_3${2-CN, 4-Br}), 7.56 – 7.48 (m, 2H, C$_6H_5$), 7.48 – 7.38 (m, 3H, C$_6H_5$), 7.23 (d, *J* = 8.9 Hz, 1H, *o*-C$_6H_3${2-CN, 4-Br}), 4.72 (s, 2H, CH_2). ^{13}C {1H} NMR (101 MHz, CDCl$_3$) δ 149.3, 137.7, 136.2, 131.2, 129.9, 129.3, 126.2, 125.0, 120.4, 113.8, 109.2, 58.8.



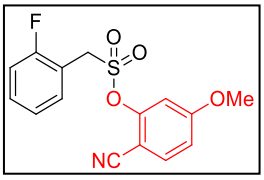
2-Cyano-5-methoxyphenyl (4-fluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (d, *J* = 8.6 Hz, 1H, *m*-C$_6H_3${2-CN, 5-OMe}), 7.54 (m, 2H, C$_6H_4${4-F}), 7.17 – 7.12 (m, 2H, C$_6H_4${4-F}), 6.96 – 6.88 (m, 2H, *o,p*-C$_6H_3${2-CN, 5-OMe}), 4.72 (s, 3H, CH_2), 3.87 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, CDCl$_3$) δ 164.56, 163.6 (d, $^{1}J_{CF}$ = 247.5 Hz) 151.7, 134.6, 133.1 (d, $^{3}J_{CF}$ = 8.7 Hz), 122.4 (d, $^{4}J_{CF}$= 3.7 Hz), 116.3 (d, $^{2}J_{CF}$ = 21.2 Hz), 115.6, 113.9, 109.3, 98.6, 57.7, 56.2.



2-Cyano-5-methoxyphenyl (2,6-difluorophenyl)methanesulfonate: White solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.61 – 7.57 (m, 1H, *m*-C$_6H_3${2-CN, 5-OMe}), 7.43 (tt, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HF}$ =6.4 Hz, 1H, *p*-C$_6H_3${2,6-di-F}), 7.06 – 6.98 (m, 2H, *m*-C$_6H_3${2,6-di-F}), 6.97 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *o*-C$_6H_3${2-CN, 5-OMe), 6.93 – 6.86 (m, 1H, *p*-C$_6H_3${2-CN, 5-OMe}), 4.87 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (101 MHz, CDCl$_3$) δ 164.2, 161.9 (d, $^{1}J_{CF}$ = 246 Hz), 151.3, 134.79, 132.2 (d, $^{3}J_{CF}$ = 10 Hz), 115.2, 114.0, 112.1 (d, $^{2}J_{CF}$ = 25 Hz), 109.2, 104.2, 99.1, 56.3, 46.6.

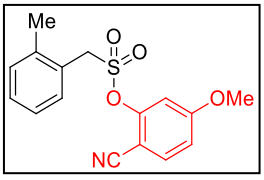


2-Cyano-5-methoxyphenyl (2,4-difluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.66 – 7.52 (m, 2H, *m*-C$_6H_3${2-CN, 5-OMe} and *m*-C$_6H_3${2,4-di-F}), 7.06 – 6.82 (m, 4H, *o,p*-C$_6H_3${2-CN, 5-OMe}, C$_6H_3${2,4-di-F}), 4.76 (s, 2H, CH_2), 3.85 (d, *J* = 4.0 Hz, 3H, OCH_3). ^{13}C {^{1}H} NMR (126 MHz, CDCl$_3$) δ 164.3, 164.1 (dd, $^{1}J_{CF}$ = 252 Hz, $^{3}J_{CF}$ = 11.3 Hz) 162.8 (dd, $^{1}J_{CF}$ = 254.5 Hz, $^{3}J_{CF}$ =12.6 Hz), 151.5, 134.7, 134.0 (dd, $^{3}J_{CF}$ = 8.8 Hz, $^{3}J_{CF}$ = 3.8 Hz), 115.5, 114.0, 112.5 (dd, $^{2}J_{CF}$ = 25.2 Hz,$^{4}J_{CF}$ = 3.8 Hz), 110.4 (dd, $^{2}J_{CF}$ = 15.1 Hz,$^{4}J_{CF}$ = 3.8 Hz), 109.2, 104.8 (t, $^{2}J_{CF}$ =25.2 Hz), 98.7, 56.3, 51.3 (d, $^{3}J_{CF}$ = 2.5 Hz).

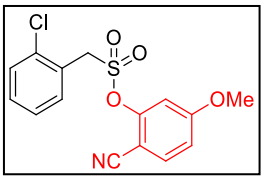


2-Cyano-5-methoxyphenyl (2-fluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 – 7.55 (m, 2H, *m*-C$_6H_3${2-CN, 5-OMe}, and *p*-C$_6H_4${2-F}), 7.46 – 7.39 (m, 1H, *m*-C$_6H_4${2-F}), 7.22 (td, $^{3}J_{HH}$/$^{4}J_{HF}$ = 7.6 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, *o*-C$_6H_4${2-F}), 7.16 (t, $^{3}J_{HH}$ = 9.0 Hz,

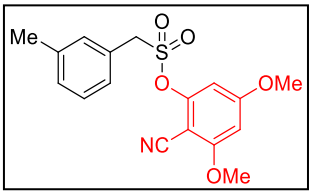
1H, *m*-C_6H_4{2-F}), 6.91 (d, $^4J_{HH}$= 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.88 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.80 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.2, 161.5 (d, $^1J_{CF}$ = 252 Hz), 151.6, 134.7, 133.0 (d, $^4J_{CF}$ = 1.3 Hz), 132.0 (d, $^3J_{CF}$ = 8.8 Hz), 124.95, 124.9 (d, $^3J_{CF}$ = 3.8 Hz), 116.2 (d, $^2J_{CF}$ = 21.4 Hz), 115.5, 114.2 (d, $^2J_{CF}$ = 15.1 Hz), 114.0, 109.2, 98.8, 56.2, 51.7 (d, $^3J_{CF}$ = 3.8 Hz).



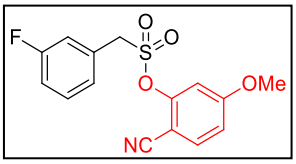
2-Cyano-5-methoxyphenyl o-tolylmethanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.49 (d, $^3J_{HH}$ = 7.6 Hz, 1H, C_6H_4{2-Me}), 7.34 (dd, $^3J_{HH}$ = 10.7 Hz, $^4J_{HH}$ = 4.1 Hz, 1H, C_6H_4{2-Me}), 7.27 (t, $^3J_{HH}$ = 8.1 Hz, 2H, C_6H_4{2-Me}), 6.90 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 6.86 (d, $^3J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 4.81 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 2.51 (s, 3H, CH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.8, 138.9, 134.6, 132.4, 131.3, 130.0, 126.8, 125.0, 115.7, 114.1, 109.3, 99.0, 56.3, 56.1, 19.8.



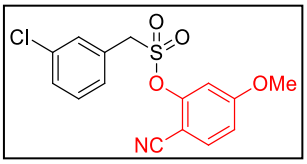
2-Cyano-5-methoxyphenyl (2-chlorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dt, $^3J_{HH}$ = 10.2 Hz, $^4J_{HH}$ = 5.1 Hz, 1H, C_6H_4{2-Cl}), 7.61 – 7.55 (m, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.51 – 7.46 (m, 1H, C_6H_4{2-Cl}), 7.42 – 7.31 (m, 2H, C_6H_4{2-Cl}), 6.92 (d, $^4J_{HH}$= 3.9 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 – 6.85 (m, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.96 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.6, 135.8, 134.7, 133.3, 131.2, 130.4, 127.6, 125.1, 115.5, 114.0, 109.2, 98.9, 56.3, 55.5.



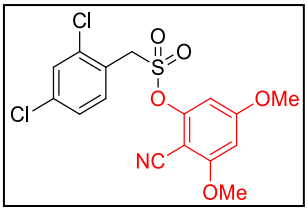
2-Cyano-3,5-dimethoxyphenyl m-tolylmethanesulfonate: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (m,3H, C_6H_4{3-Me}), 7.23 (d, $^4J_{HH}$ = 3.5 Hz, 1H, *o*-C_6H_4{3-Me}), 6.50 (d, $^4J_{HH}$ = 1.7 Hz, 1H, C_6H_2{2-CN, 3,5-di-OMe}), 6.37 (d, $^4J_{HH}$= 1.6 Hz, 1H, C_6H_2{2-CN, 3,5-di-OMe}), 4.67 (s, 2H, CH_2), 3.91 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 2.37 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.0, 163.3, 152.8, 139.1, 131.9, 130.5, 129.1, 128.3, 126.4, 113.4, 100.9, 97.3, 89.6, 58.8, 56.6, 56.3, 21.4.



2-Cyano-5-methoxyphenyl (3-fluorophenyl)methanesulfonate: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.55 (m, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.44 – 7.37 (m, 1H, C_6H_4{3-F}), 7.31 (d, $^3J_{HH}$= 8.1 Hz, 1H, C_6H_4{3-F}), 7.26 – 7.23 (m, 1H, C_6H_4{3-F}), 7.16 – 7.10 (m, 1H, C_6H_4{3-F}), 6.92 – 6.86 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.71 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 162.9 (d, $^1J_{CF}$ = 246 Hz), 151.7, 134.6, 130.8 (d, $^3J_{CF}$ = 8 Hz) 128.6 (d, $^3J_{CF}$ = 8 Hz) 127.0 (d, $^4J_{CF}$ = 3 Hz), 118.2 (d, $^2J_{CF}$ = 23 Hz), 116.8 (d, $^2J_{CF}$ = 21 Hz), 115.6, 114.0, 109.4, 98.7, 58.1, 56.3.

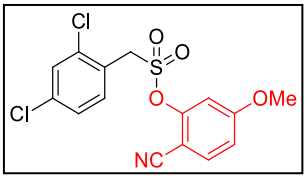


2-Cyano-5-methoxyphenyl (3-chlorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.2 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.52 (s, 1H, 2-C_6H_4{3-Cl}), 7.41 (m, 2H, C_6H_4{3-Cl}), 7.36 (m, 1H, C_6H_4{3-Cl}), 6.95 – 6.84 (m, 2H, *o,p*-C_6H_3{2-CN, 5-OMe}), 4.68 (s, 2H, CH_2), 3.85 (d, *J* = 1.6 Hz, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.7, 135.1, 134.6, 131.2, 130.5, 130.0, 129.5, 128.4, 115.6, 114.1, 109.4, 98.8, 58.0, 56.3.

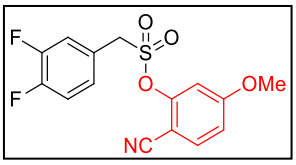


2-Cyano-3,5-dimethoxyphenyl (2,4-dichlorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$= 8.3 Hz, 1H, 6-

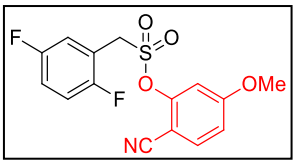
C_6H_3{2,4-di-Cl}), 7.50 (d, $^4J_{HH}$= 1.8 Hz, 1H, 3-C_6H_3{2,4-di-Cl}), 7.34 (dd, $^3J_{HH}$= 8.3 Hz, $^4J_{HH}$ = 1.9 Hz, 1H, 5-C_6H_3{2,4-di-Cl}), 6.54 (d, $^4J_{HH}$= 1.9 Hz, 1H, C_6H_2{2-CN, 3,5-di-OMe}), 6.39 (d, $^4J_{HH}$= 1.8 Hz, 1H, C_6H_2{2-CN, 3,5-di-OMe}), 4.91 (s, 2H, CH_2), 3.92 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 165.0, 163.4, 152.4, 136.7, 136.6, 134.0, 130.3, 128.1, 123.8, 113.3, 100.8, 97.5, 89.6, 56.7, 56.4, 55.1.



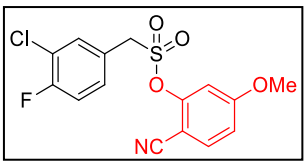
2-Cyano-5-methoxyphenyl (2,4-dichlorophenyl)methanesulfonate: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *m*-C_6H_3{2-CN, 5-OMe} and 6-C_6H_3{2,4-di-Cl}), 7.52 (d, $^4J_{HH}$= 2.1 Hz, 1H, 3-C_6H_3{2,4-di-Cl}), 7.35 (dd, $^3J_{HH}$ = 8.3, $^4J_{HH}$ = 2.1 Hz, 1H, 5-C_6H_3{2,4-di-Cl}), 6.94 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 4.92 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.5, 136.8, 136.6, 134.7, 134.0, 130.4, 128.1, 123.7, 115.5, 114.1, 109.3, 98.8, 56.3, 55.0.



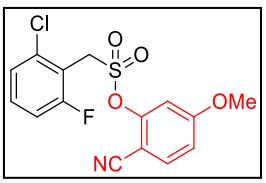
2-Cyano-5-methoxyphenyl (3,4-difluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $^3J_{HH}$ = 7.1 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.41 – 7.35 (m, 1H, C_6H_3{3,4-di-F}), 7.31 – 7.26 (m, 1H, C_6H_3{3,4-di-F}), 7.22 (m, 1H, C_6H_3{3,4-di-F}), 6.93 (d, $^4J_{HH}$= 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.92 – 6.88 (m, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.67 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 152.5, 152.4, 151.6, 151.5, 151.5, 150.4, 150.3, 149.6, 134.6, 127.2, 127.8, 127.7, 123.4, 120.4, 120.3, 118.3, 118.1, 115.6, 114.0, 109.4, 98.6, 57.2, 56.3.



2-Cyano-5-methoxyphenyl (2,5-difluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.34 – 7.28 (m, 1H, C_6H_3{2,5-di-F}), 7.17 – 7.10 (m, 2H, C_6H_3{2,5-di-F}), 6.95 (d, $^4J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.77 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 158.7 (d, $^1J_{HF}$ = 242 Hz) 157.6 (d, $^1J_{HF}$ = 244 Hz), 151.4, 134.7, 119.2 (dd, $^2J_{HF}$ = 25.2 Hz, $^3J_{HF}$= 2.5 Hz), 118.6 (dd, $^2J_{HF}$= 23.9 Hz, $^3J_{HF}$ = 8.8 Hz), 117.4 (dd, $^2J_{HF}$ = 23.9 Hz, $^3J_{HF}$ = 8.8 Hz), 115.7 (dd, $^2J_{HF}$ = 17.6 Hz, $^3J_{HF}$ = 8.8 Hz), 115.4, 114.1, 109.3, 98.9, 56.3, 51.5.

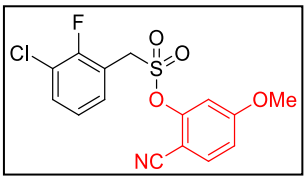


2-Cyano-5-methoxyphenyl (3-chloro-4-fluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 – 7.56 (m, 2H, *m*-C_6H_3{2-CN, 5-OMe} and C_6H_3{3-Cl, 4-F}), 7.43 (ddd, $^3J_{HH}$= 8.4 Hz, $^4J_{HF}$ = 4.4, $^4J_{HH}$ = 2.3 Hz, 1H, C_6H_3{3-Cl, 4-F}), 7.21 (t, $^3J_{HH/HF}$= 8.6 Hz, 1H, C_6H_3{3-Cl, 4-F}), 6.93 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.67 (s, 2H, CH_2), 3.86 (s, 3H, OCH_3).^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 159.1 (d, $^1J_{HF}$= 252 Hz), 151.6, 134.6, 133.4, 133.1, 131.2 (d, $^3J_{HF}$= 7.6 Hz), 130.9 (d, $^3J_{HF}$= 7.6 Hz), 123.6 (d, $^4J_{HF}$= 3.8 Hz) 122.1 (d, $^2J_{HF}$= 18.9 Hz), 117.5 (d, $^2J_{HF}$= 21.4 Hz), 115.7, 114.1, 109.4, 98.7, 57.4, 56.3.

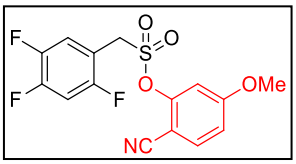


2-Cyano-5-methoxyphenyl (2-chloro-6-fluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.37 (m, 1H, C_6H_3{2-Cl, 6-F}), 7.31 (d, *J* = 8.1 Hz, 1H, C_6H_3{2-Cl, 6-F}), 7.11 (m, 1H, C_6H_3{2-Cl, 6-F}), 6.95 (d, $^4J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.89 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$= 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 5.02 (d, *J* = 1.3 Hz, 2H, CH_2), 3.83 (s, 3H, OCH_3).^{13}C NMR (126 MHz,

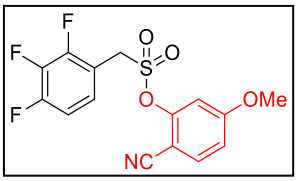
$CDCl_3$) δ 164.2, 162.2 (d, $^1J_{CF}$ = 253 Hz), 151.2, 136.9 (d, $^3J_{CF}$ = 3.8 Hz), 134.7, 132.0 (d, $^3J_{CF}$ = 8.8 Hz), 126.1 (d, $^4J_{CF}$= 3.8 Hz), 115.2, 114.8 (d,$^2J_{CF}$ = 22.7 Hz), 114.3 (d, $^2J_{CF}$ =17.6 Hz), 114.0, 109.3, 99.0, 56.2, 50.0 (d, $^3J_{CF}$ = 2.5 Hz).



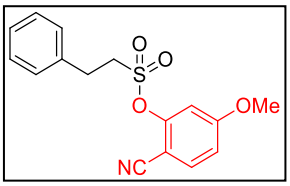
2-Cyano-5-methoxyphenyl (3-chloro-2-fluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, $^3J_{HH}$ = 11.9 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.49 (m, 2H, C_6H_3{2-F, 3-Cl}), 7.21 – 7.14 (m, 1H, C_6H_3{2-F, 3-Cl}), 6.95 (d, $^4J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.90 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.3 Hz, 1H, , *p*-C_6H_3{2-CN, 5-OMe}), 4.81 (s, 2H, CH_2), 3.85 (s, 3H, OCH_3).^{13}C NMR (126 MHz, $CDCl_3$) δ 164.3, 157.2 (d, $^1J_{CF}$ = 253.3 Hz), 151.4, 134.7, 132.5, 131.2 (d, 2.52 Hz), 125.3 (d, $^3J_{CF}$ = 5 Hz), 122.2, 116.0 (d, $^3J_{CF}$ = 13.9 Hz), 115.4, 114.1, 109.3, 98.8, 56.3, 51.7 (d, $^3J_{CF}$ = 2.5 Hz).



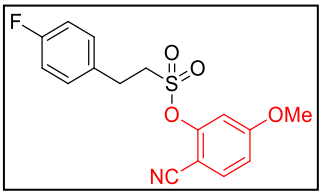
2-Cyano-5-methoxyphenyl (2,4,5-trifluorophenyl)methanesulfonate: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.56 (m, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.51 – 7.40 (m, 1H, C_6H_2{2,4,5-tri-F}), 7.12 – 7.00 (m, 1H, C_6H_2{2,4,5-tri-F}), 6.99 – 6.94 (m, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.92 – 6.85 (m, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.73 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3).



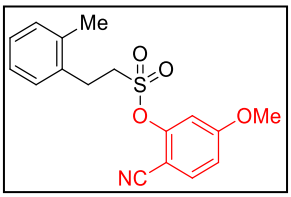
2-Cyano-5-methoxyphenyl (2,3,4-trifluorophenyl)methanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$= 7.0 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.35 (tdd, $^3J_{HH}$ = 7.8, $^4J_{HF}$ =5.5, $^5J_{HF}$ =2.4 Hz, 1H, C_6H_2{2,3,4-tri-F}), 7.11 – 7.04 (m, 1H, C_6H_2{2,3,4-tri-F}), 6.97 (d, $^3J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.91 (dd, $^3J_{HH}$= 8.7 Hz, $^4J_{HH}$=2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 4.77 (s, 2H, CH_2), 3.87 (s, 3H, OCH_3).^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 152.4 (ddd, $^1J_{CF}$ = 254.5 Hz,$^2J_{CF}$ = 9.4 Hz, $^3J_{CF}$ = 3.8 Hz), 151.3, 150.8 (ddd, $^1J_{CF}$ = 254.5 Hz, $^2J_{CF}$ = 11.3 Hz, $^3J_{CF}$ = 3.8 Hz), 140.4 (dt, $^1J_{CF}$ = 254.5 Hz, $^2J_{CF}$ = 15.1 Hz), 134.7, 126.7- 126.6 (m), 115.4, 114.1, 113.2 (dd, $^2J_{CF}$ = 12.6 Hz, $^3J_{CF}$ = 3.8 Hz), 112.1 (dd, $^2J_{CF}$ = 12.6 Hz, $^2J_{CF}$ = 3.8 Hz), 109.3, 98.7, 56.3, 51.2.



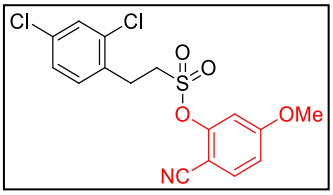
2-Cyano-5-methoxyphenyl 2-phenylethanesulfonate: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.34 (dd, $^3J_{HH}$= 7.7, 6.8 Hz, 2H, C_6H_5), 7.31 – 7.26 (m, 3H, C_6H_5), 7.04 (d, $^4J_{HH}$ = 2.4 Hz, 1H,*o*-C_6H_3{2-CN, 5-OMe}), 6.91 (dd, $^3J_{HH}$ = 8.8, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.87 (s, 3H, OCH_3), 3.74 – 3.67 (m, 2H, CH_2), 3.41 – 3.34 (m, 2H, CH_2). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.2, 151.4, 136.8, 134.6, 129.1, 128.6, 127.4, 115.5, 113.9, 109.6, 98.7, 56.3, 53.7, 29.8.



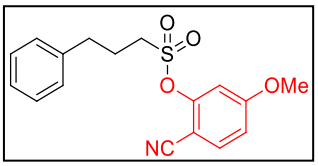
2-Cyano-5-methoxyphenyl 2-(4-fluorophenyl)ethanesulfonate: White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, $^3J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.27 – 7.22 (m, 2H, C_6H_4{4-F}), 7.05 – 6.98 (m, 3H, C_6H_4{4-F} and *o*-C_6H_3{2-CN, 5-OMe}), 6.91 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.87 (s, 3H, OCH_3), 3.70 – 3.65 (m, 2H, CH_2), 3.37 – 3.32 (m, 2H, CH_2). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 164.3, 162.2 (d, $^1J_{CF}$ =246.7 Hz), 151.5, 134.6, 132.6 (d, $^4J_{CF}$ =3.3 Hz), 130.3 (d, $^3J_{CF}$ =8.2 Hz), 116.0 (d, $^2J_{CF}$=21.5 Hz), 115.6, 114.0, 109.7, 98.7, 56.3, 53.8, 29.1.



2-Cyano-5-methoxyphenyl 2-(o-tolyl)ethanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.24 – 7.15 (m, 4H, C_6H_4{2-Me}), 7.06 (d, $^{4}J_{HH}$ = 2.3 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.91 (dd, $^{4}J_{HH}$ = 8.7 Hz, $^{4}J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.89 (s, 3H, OCH_3), 3.71 – 3.60 (m, 2H, CH_2), 3.45 – 3.33 (m, 2H, CH_2), 2.39 (s, 3H, CH_3). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.4, 136.3, 135.0, 134.7, 130.9, 129.2, 127.7, 126.8, 115.5, 113.9, 109.4, 98.8, 56.3, 52.5, 27.3, 19.4.



2-Cyano-5-methoxyphenyl 2-(2,4-dichlorophenyl)ethanesulfonate: White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, $^{3}J_{HH}$ = 8.7 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.41 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, 3-C_6H_3{2,4-di-Cl}), 7.33 (d, $^{3}J_{HH}$= 8.2 Hz, 1H, 6-C_6H_3{2,4-di-Cl}), 7.23 (dd, $^{3}J_{HH}$ = 8.2Hz,$^{4}J_{HH}$ = 2.1 Hz, 1H, 5-C_6H_3{2,4-di-Cl}), 7.04 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.91 (dd, $^{3}J_{HH}$ = 8.8 Hz, $^{4}J_{HH}$ = 2.4 Hz, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.89 (s, 3H, OCH_3), 3.75 – 3.68 (m, 2H, CH_2), 3.50 – 3.43 (m, 2H, CH_2). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.3, 151.4, 134.9, 134.7, 134.4, 133.2, 132.1, 129.9, 127.9, 115.6, 114.1, 109.5, 98.7, 56.4, 51.5, 27.8.



2-Cyano-5-methoxyphenyl 3-phenylpropane-1-sulfonate: Brown solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, $^{3}J_{HH}$= 7.1 Hz, 1H, *m*-C_6H_3{2-CN, 5-OMe}), 7.35 – 7.29 (m, 2H, C_6H_5), 7.25 – 7.18 (m, 3H, C_6H_5), 7.01 (d, $^{4}J_{HH}$ = 2.4 Hz, 1H, *o*-C_6H_3{2-CN, 5-OMe}), 6.91 – 6.87 (m, 1H, *p*-C_6H_3{2-CN, 5-OMe}), 3.87 (s, 3H. OCH_3), 3.47 – 3.38 (m, 2H, CH_2), 2.89 – 2.81 (m, 2H, CH_2), 2.45 – 2.35 (m, 2H, CH_2). ^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 164.2, 151.5, 139.6, 134.6, 128.9, 128.7, 126.8, 115.5, 113.9, 109.6, 98.8, 56.3, 51.7, 34.0, 25.2.

NMR spectra

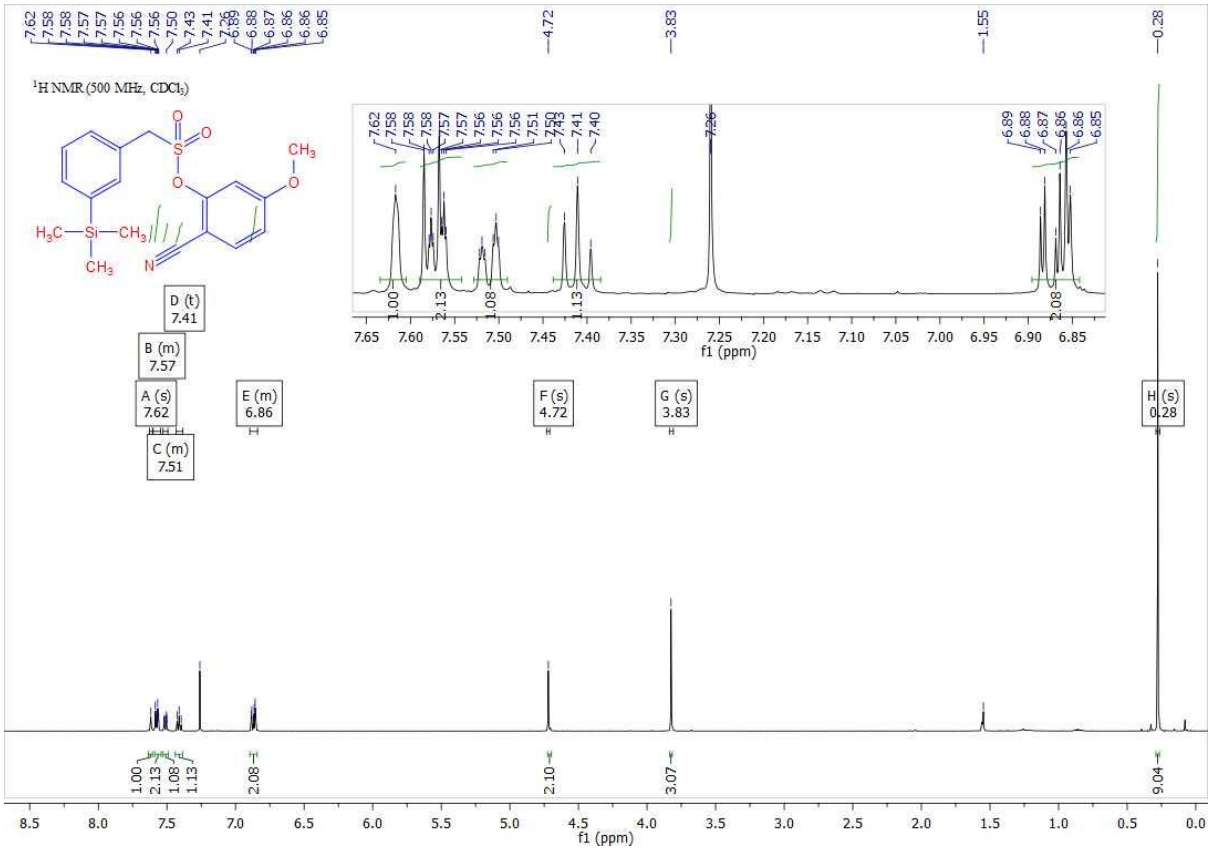


Figure S2: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2a$_{mono}$**

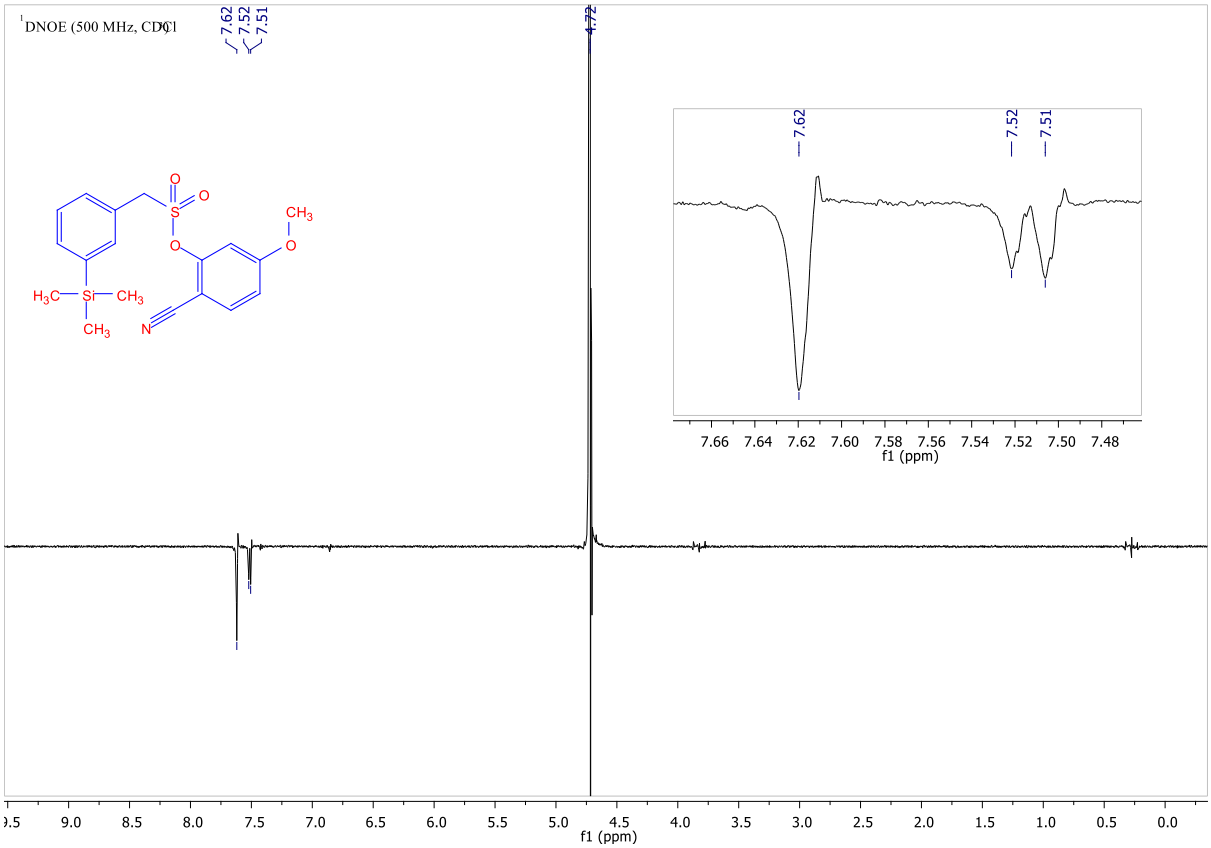


Figure S3: ^{1}DNOE spectrum (500 MHz, $CDCl_3$) of Compound **2a$_{mono}$**

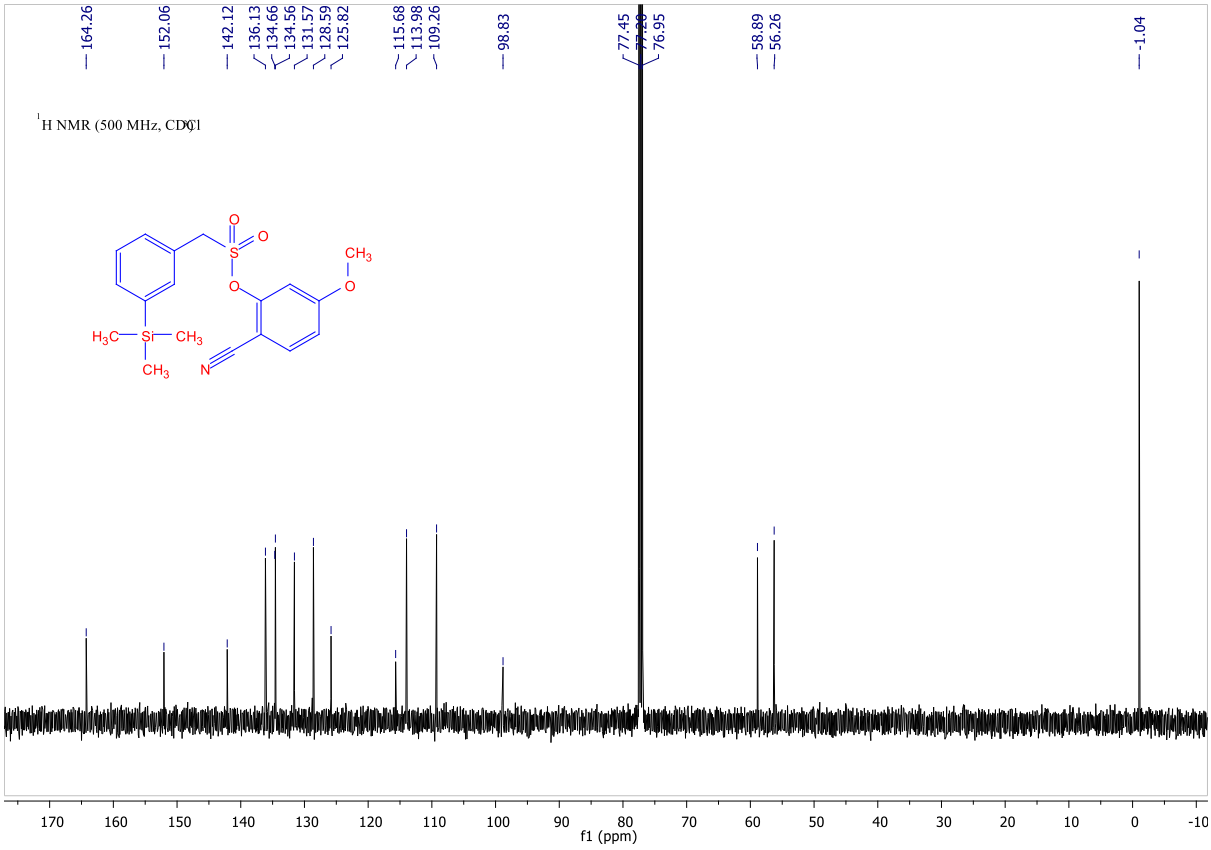


Figure S4: $^{13}C\{^{1}H\}$NMR spectrum (126 MHz, $CDCl_3$) of Compound **2a$_{mono}$**

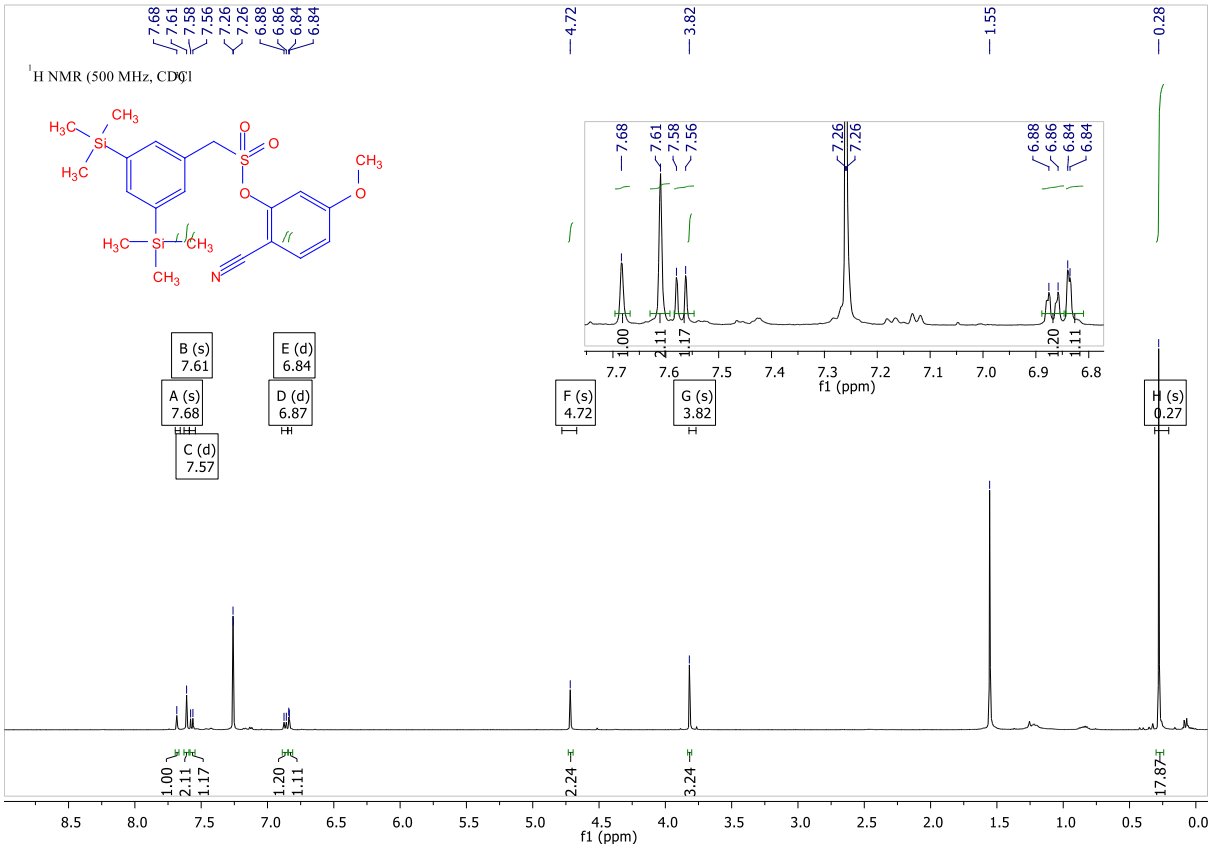


Figure S5: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2a$_{di}$**

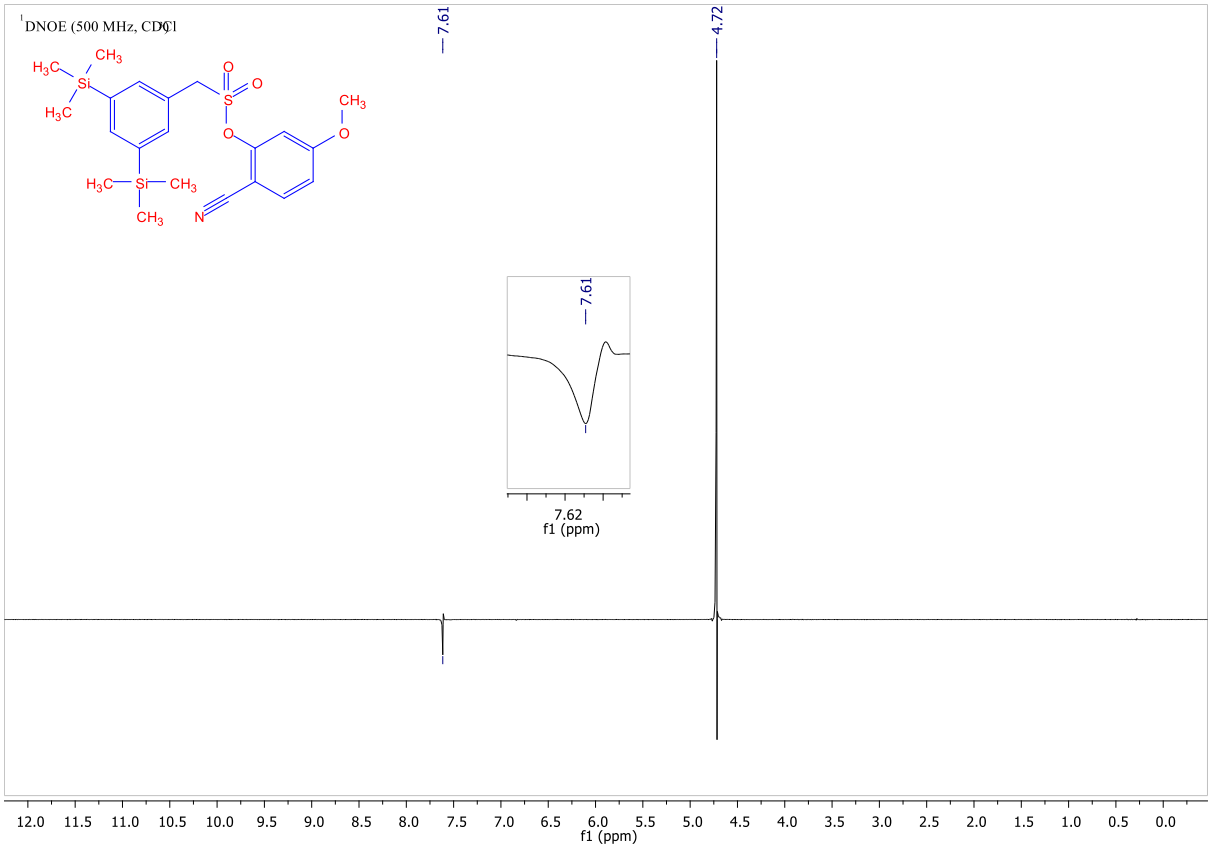


Figure S6: ^{1}D NOE spectrum (500 MHz, $CDCl_3$) of Compound **2a$_{di}$**

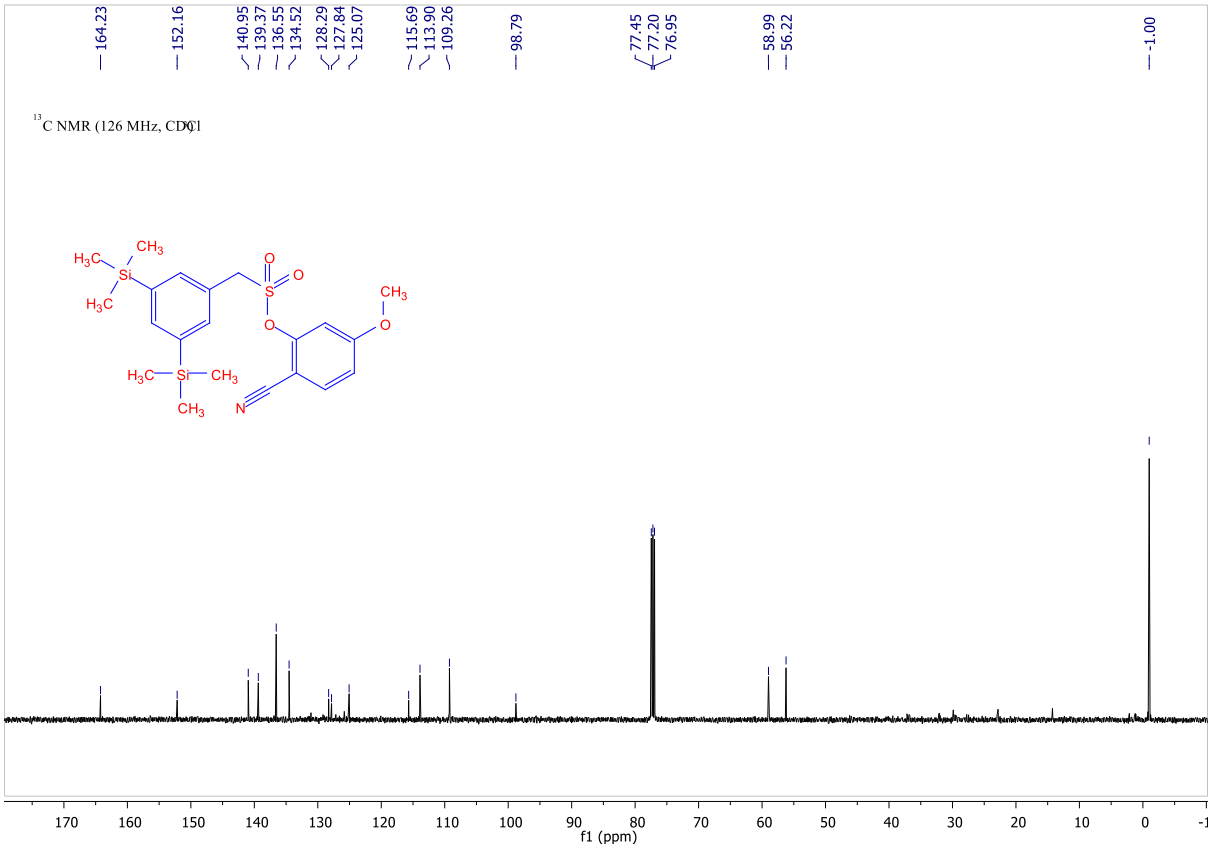


Figure S7: $^{13}C\{^{1}H\}$ NMR spectrum (126 MHz, $CDCl_3$) of Compound **2a$_{di}$**

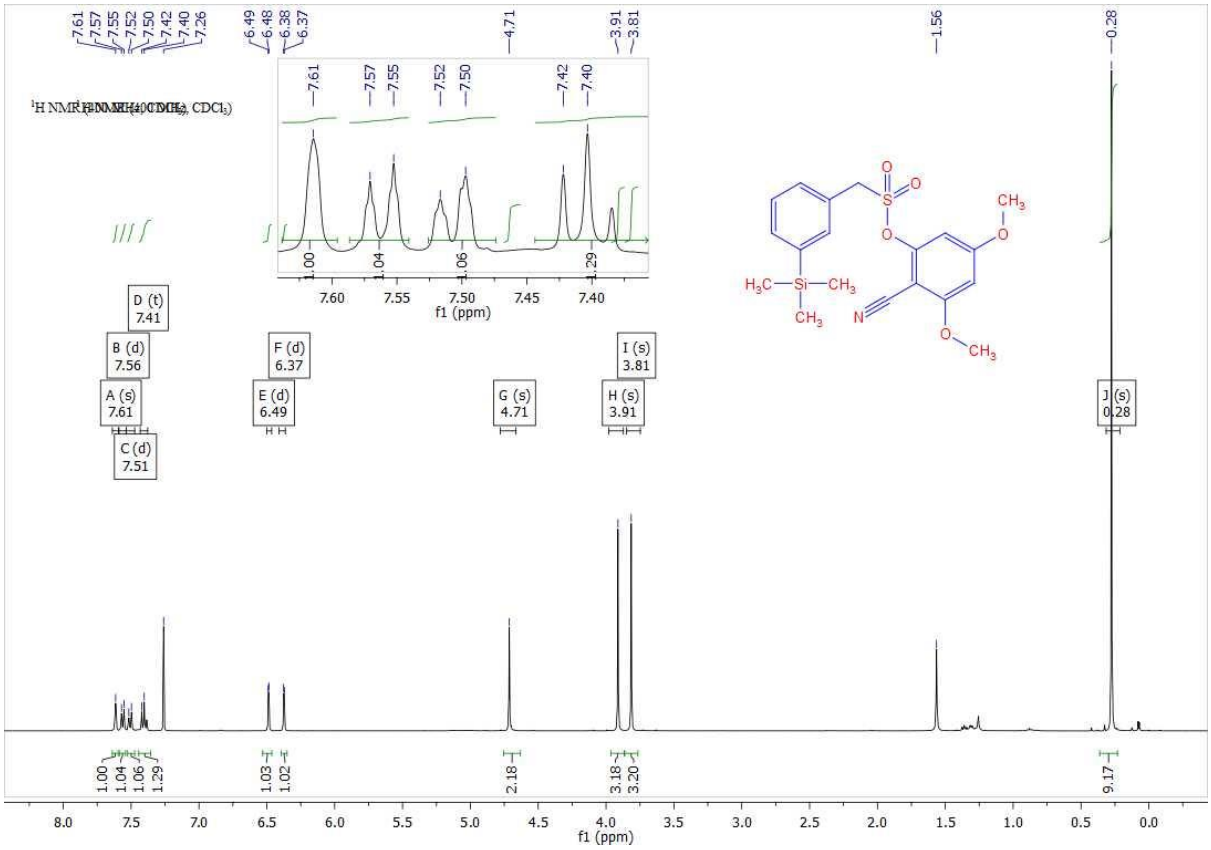


Figure S8: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2a$_{mono}$-DG$_5$**

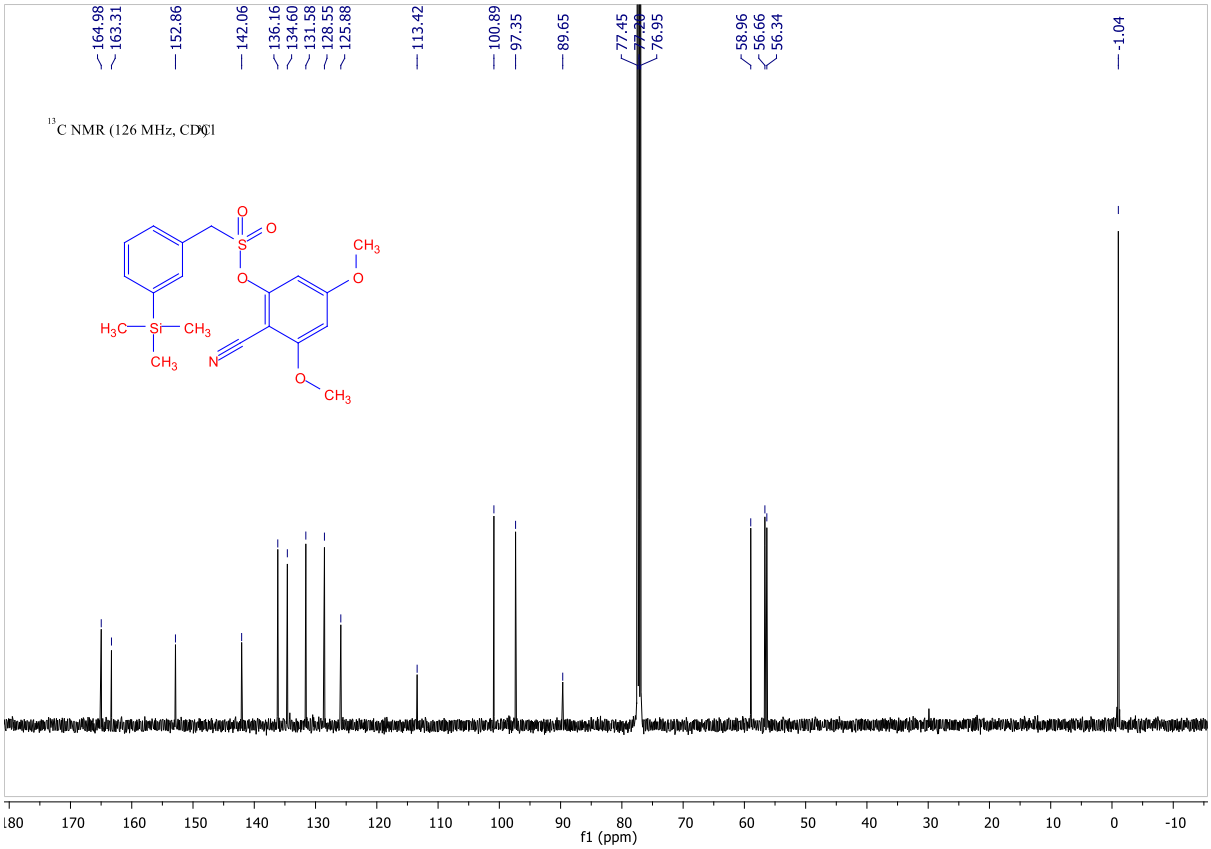


Figure S9: ^{13}C{^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2a$_{mono}$-DG$_5$**

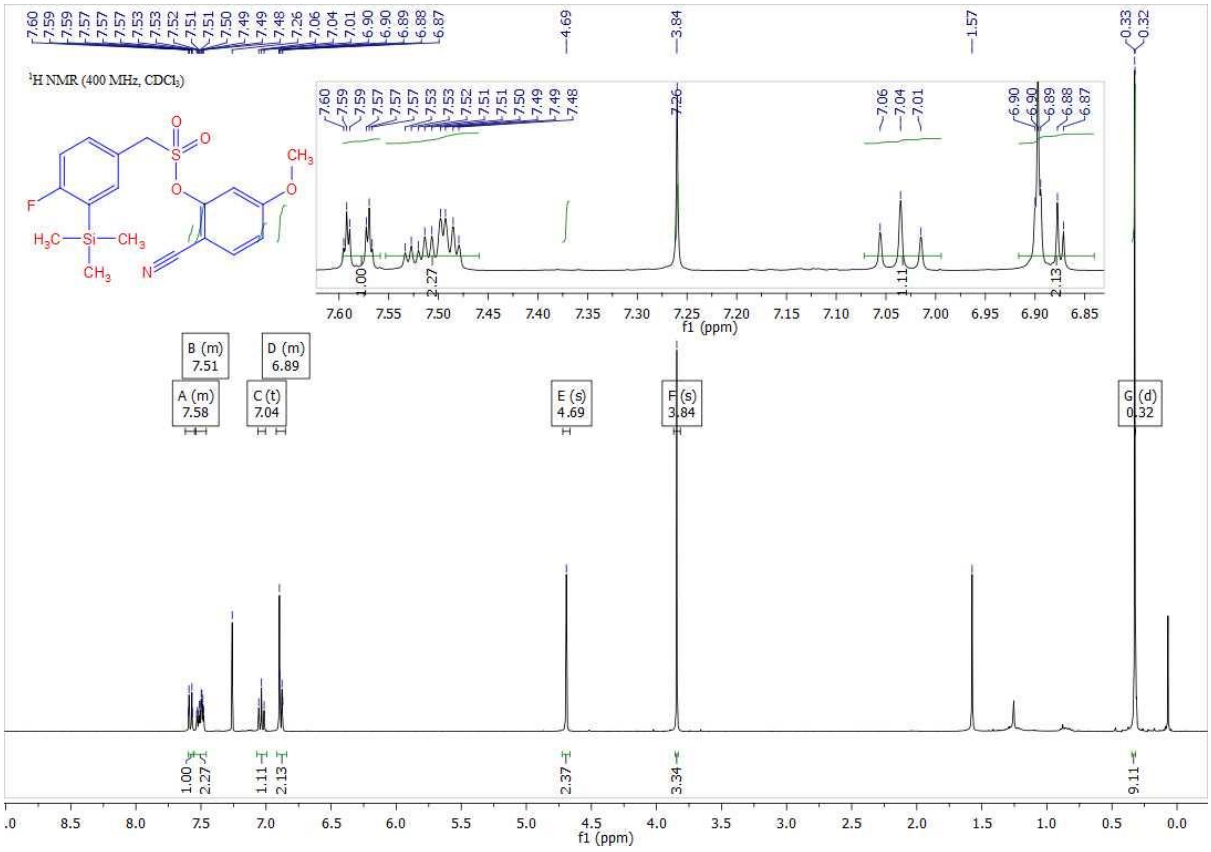


Figure S10: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **2b$_{mono}$**

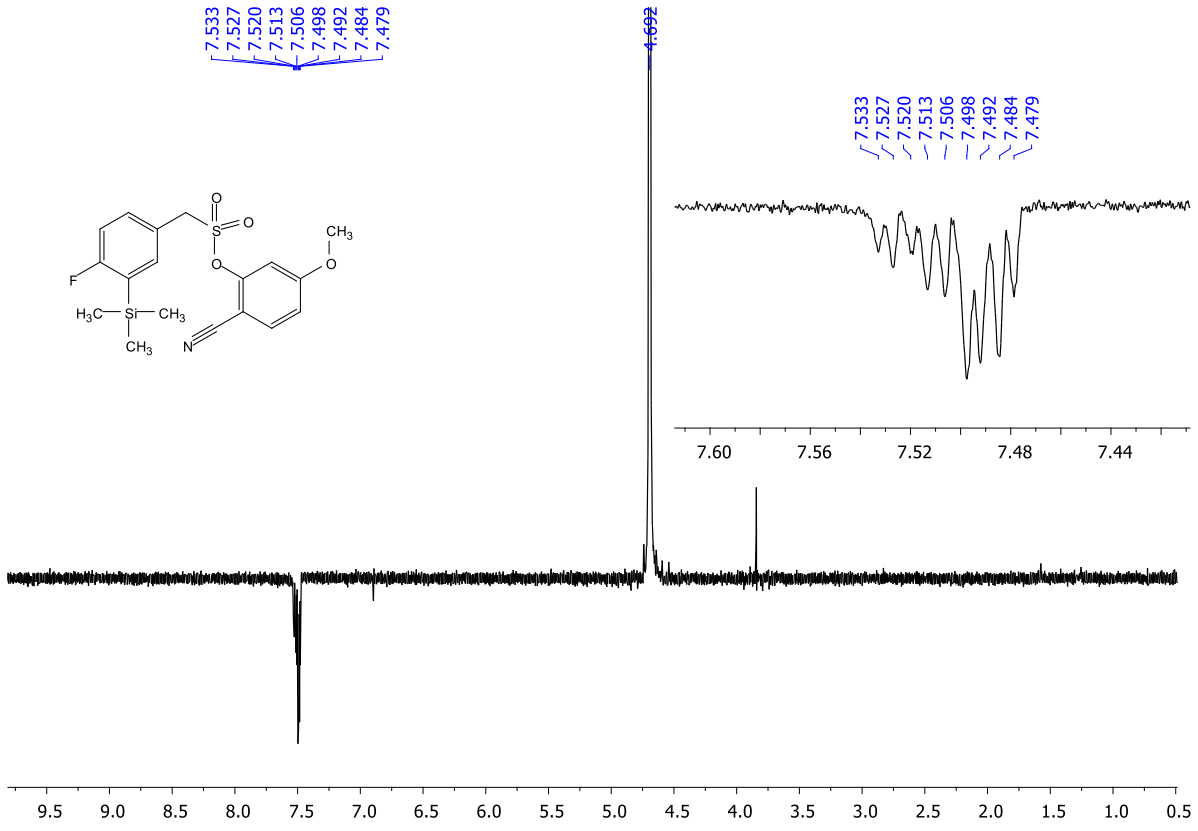


Figure S11: ^{1}D NOE spectrum (400 MHz, $CDCl_3$) of Compound **2b$_{mono}$**

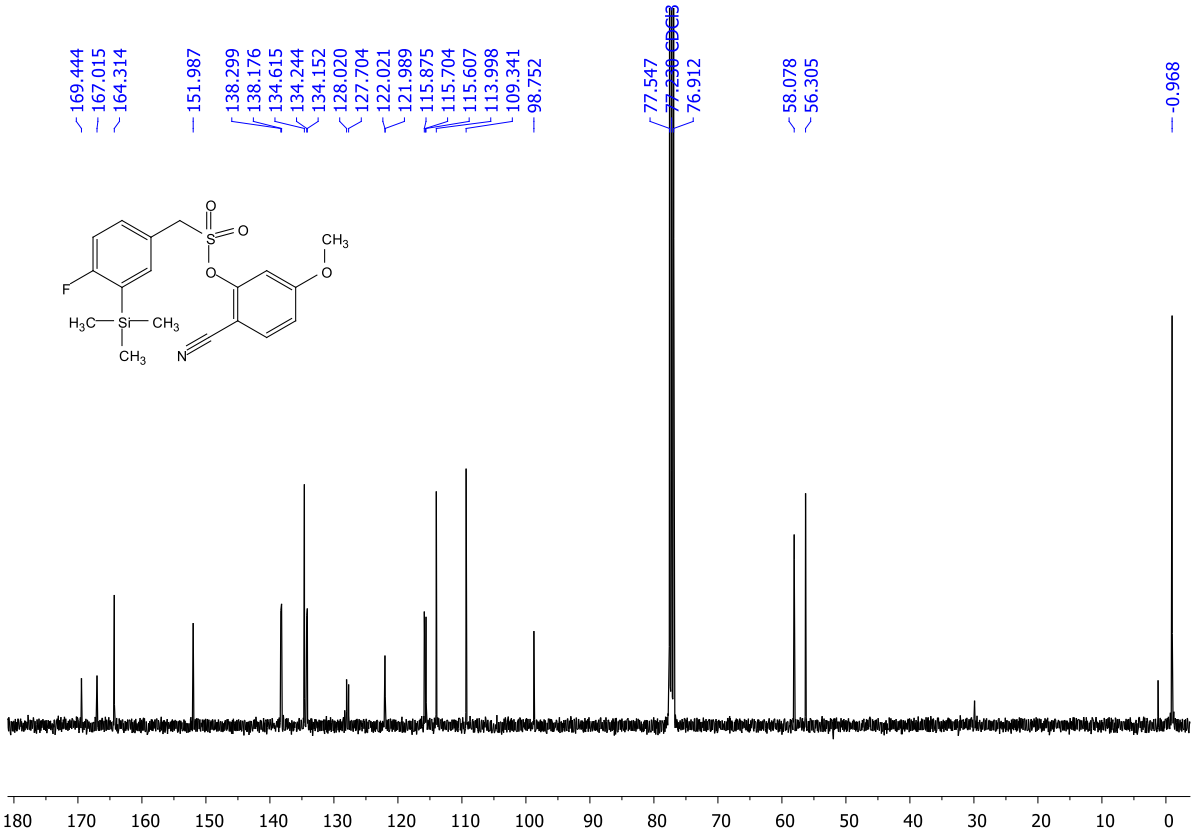


Figure S12: ^{13}C {^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of Compound **2b$_{mono}$**

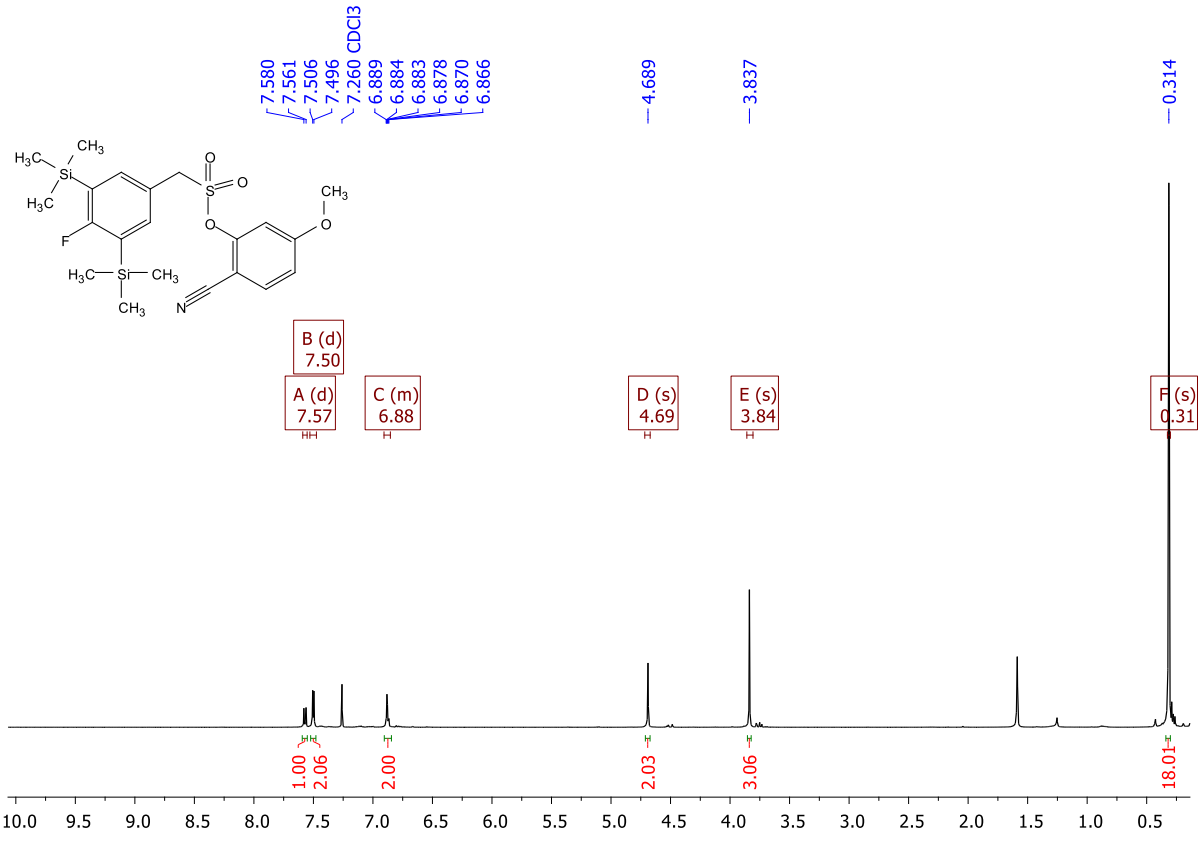


Figure S13: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2b$_{di}$**

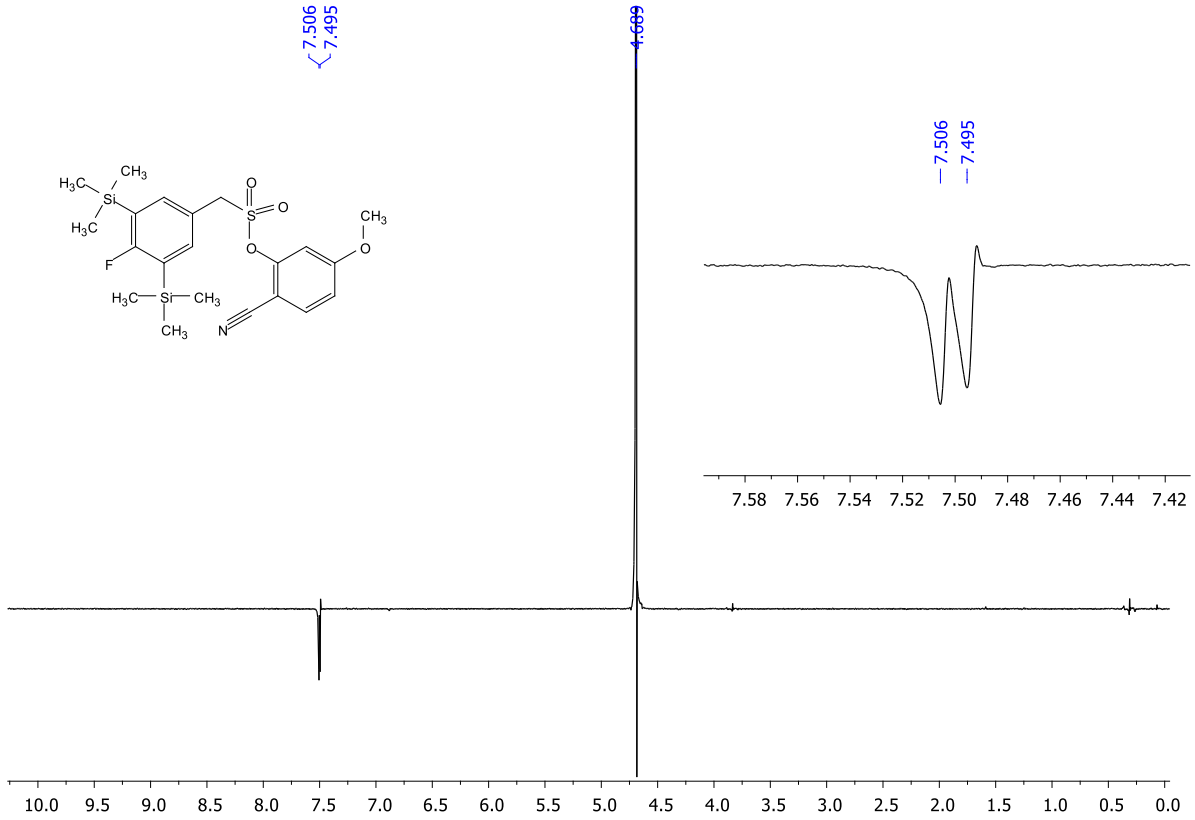


Figure S14: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2b$_{di}$**

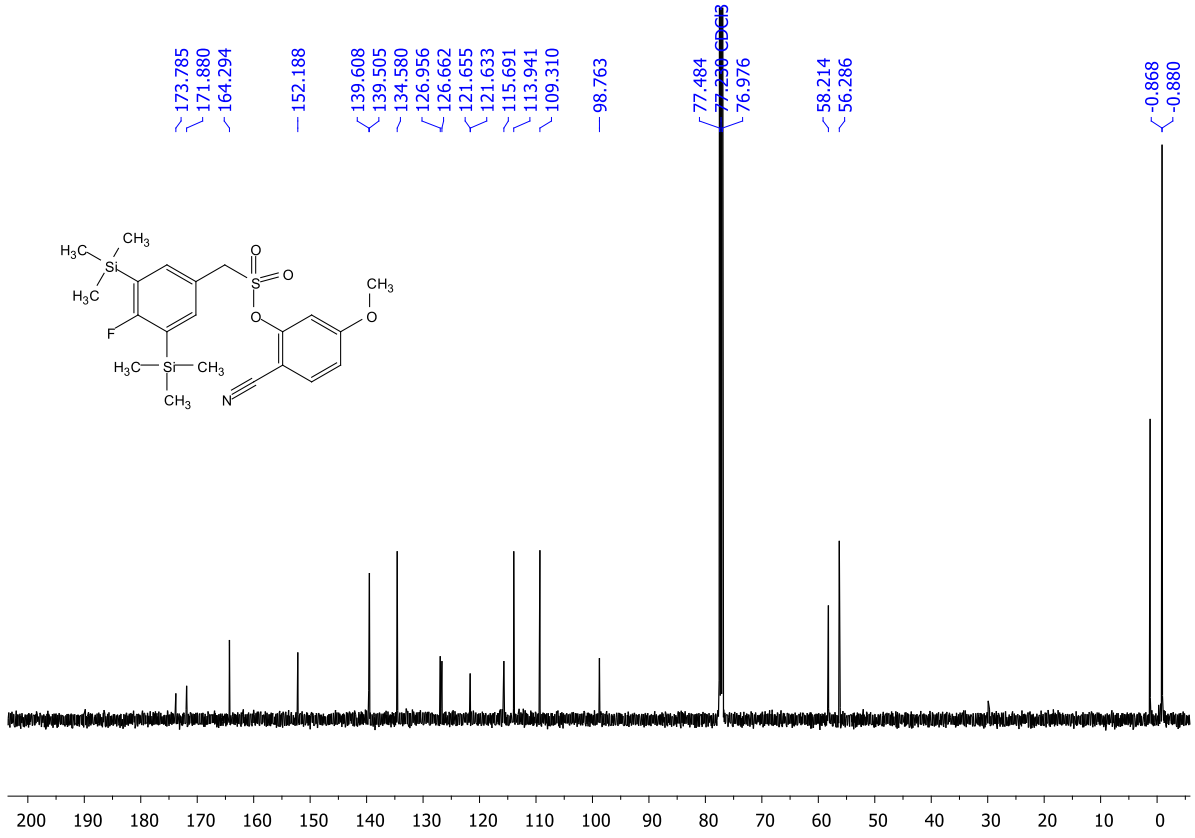


Figure S15: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2b$_{di}$**

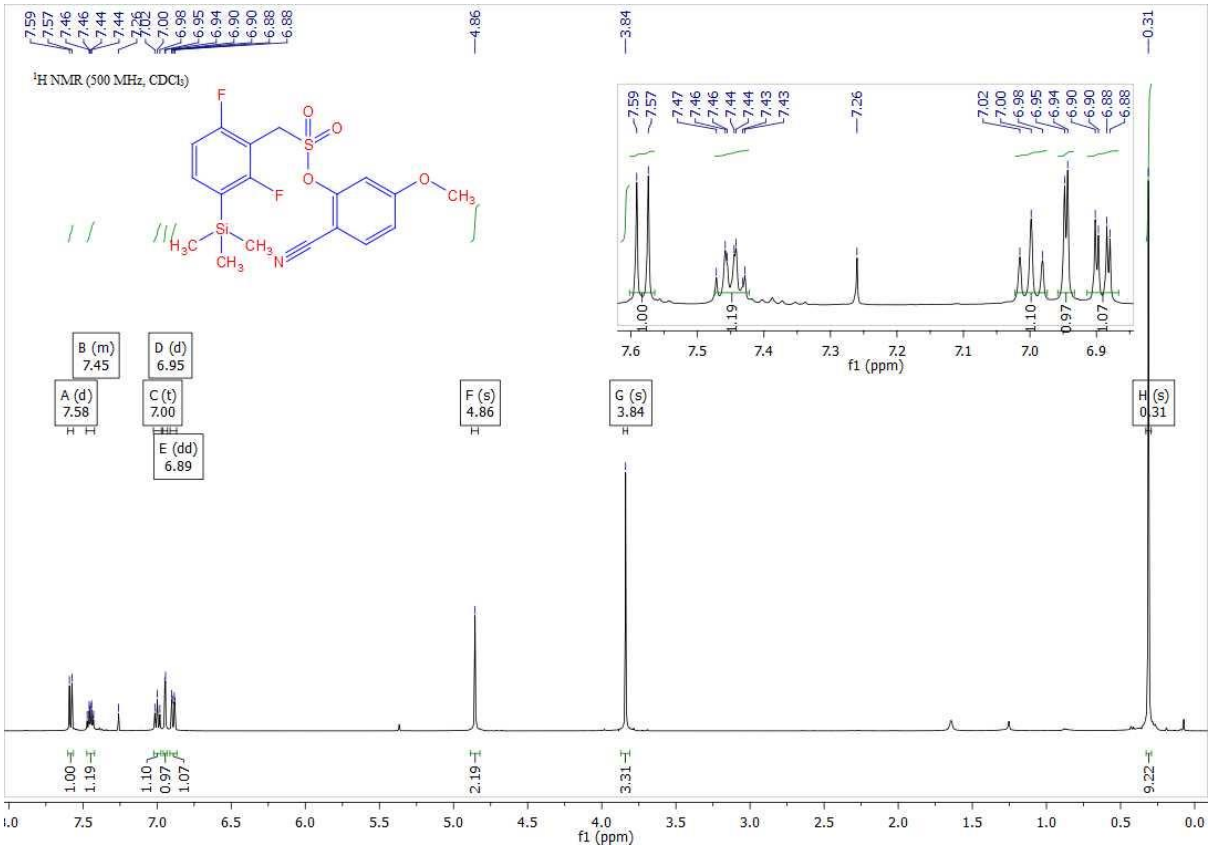


Figure S16: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2c$_{mono}$**

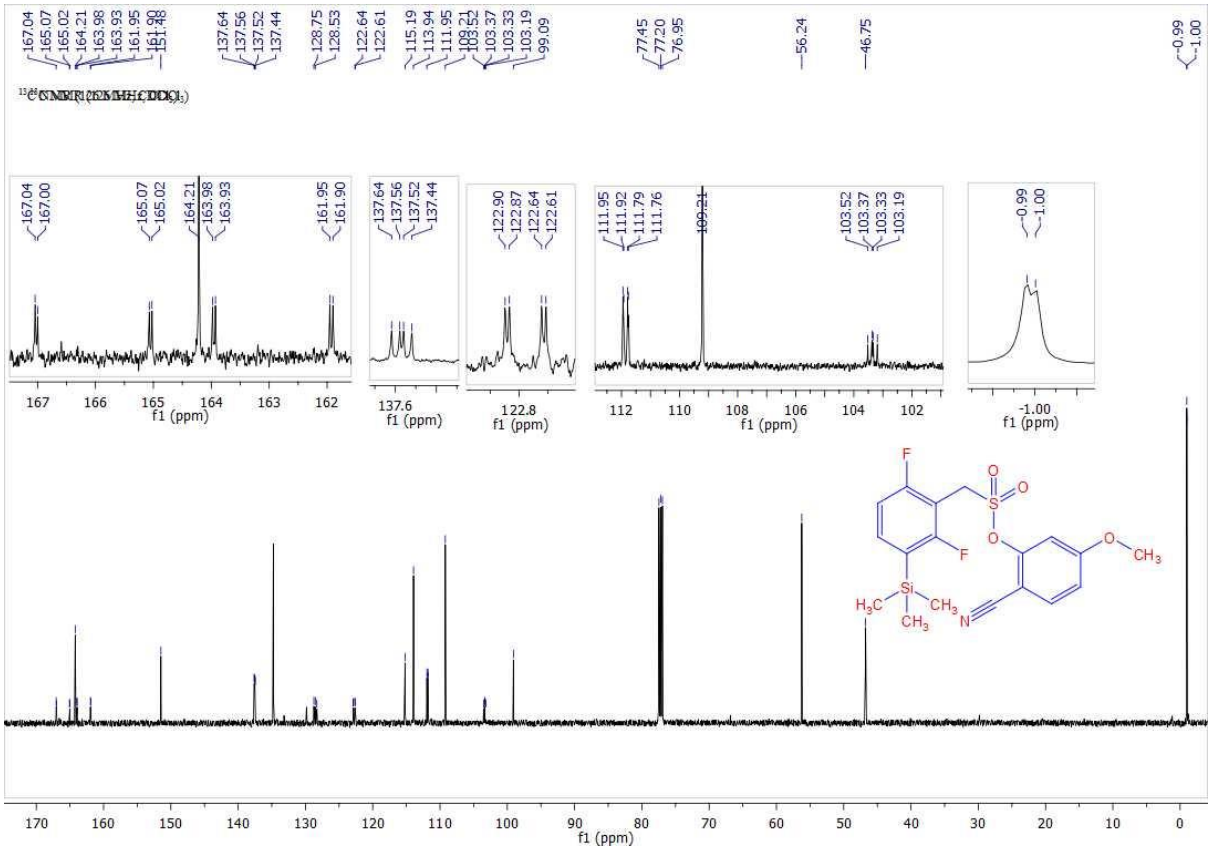


Figure S17: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2c$_{mono}$**

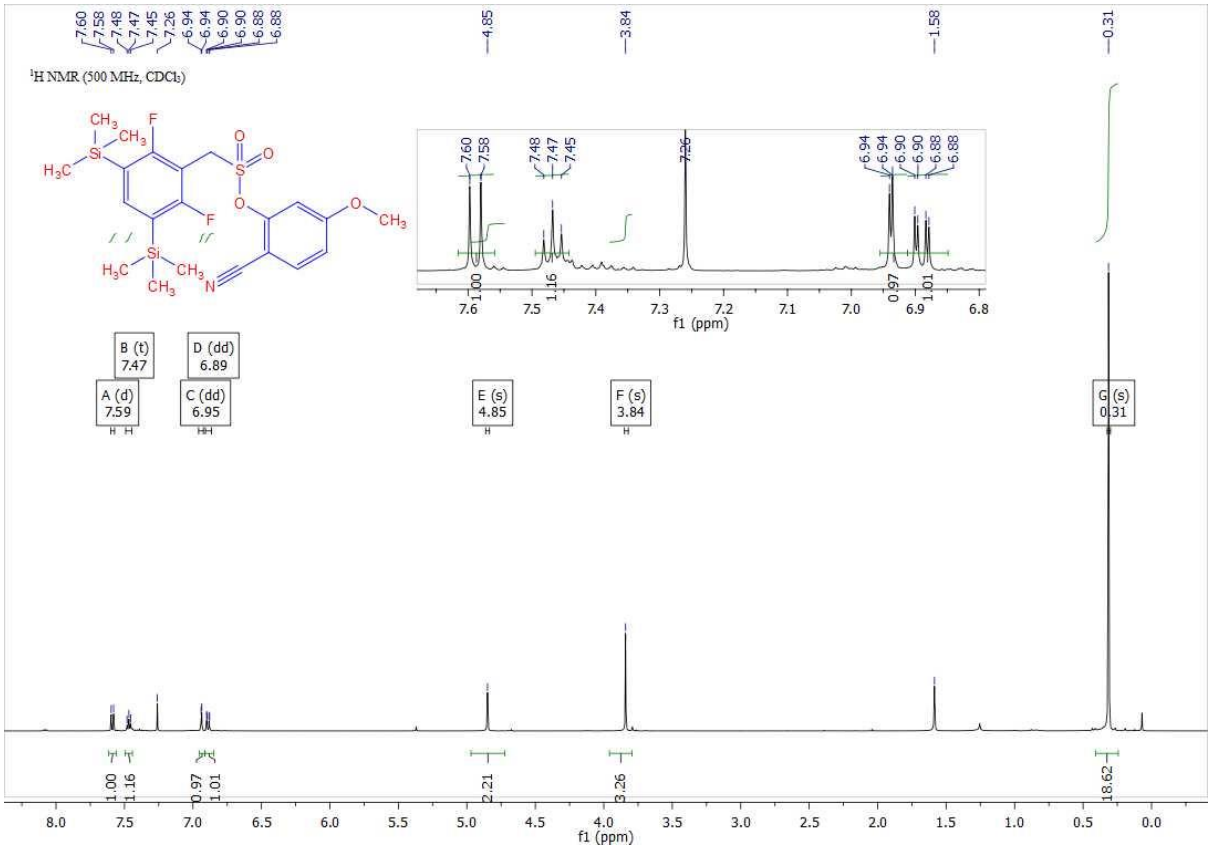


Figure S18: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2c$_{di}$**

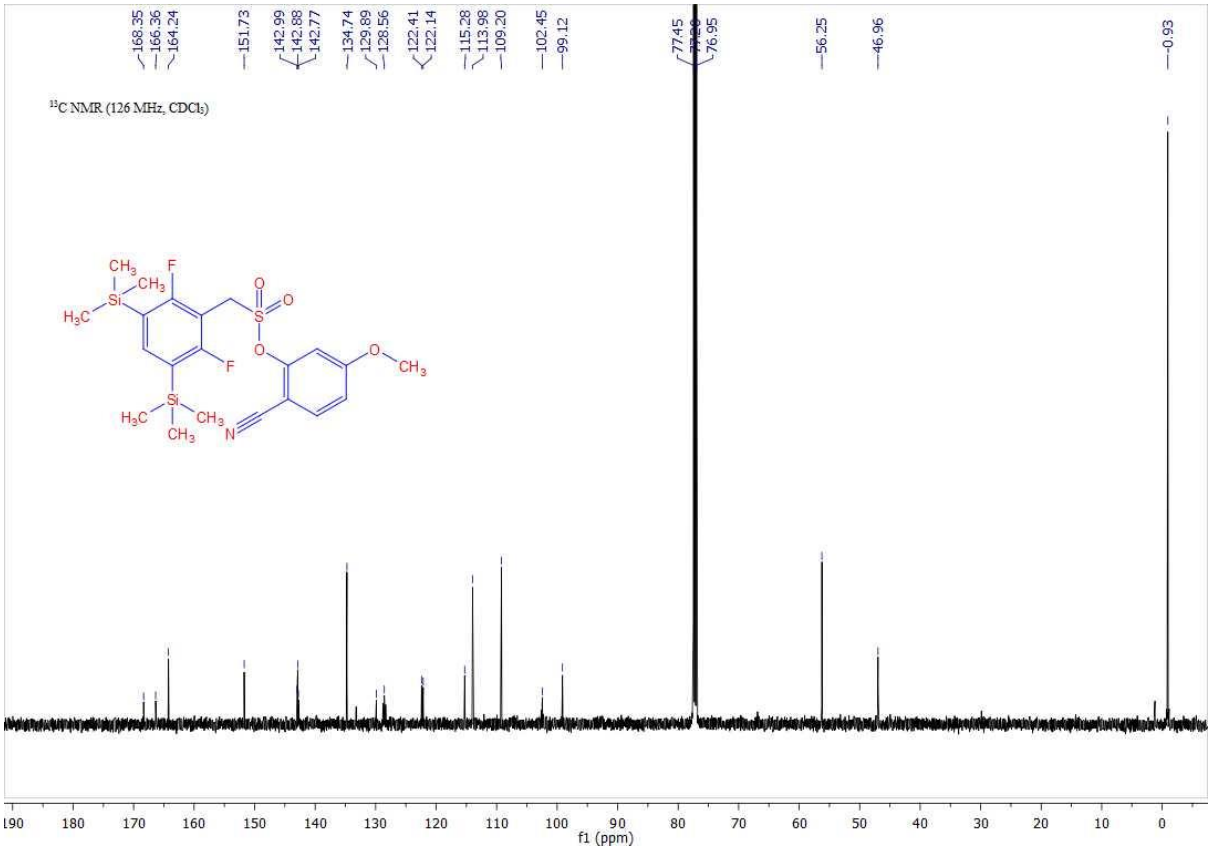


Figure S19: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2c$_{di}$**

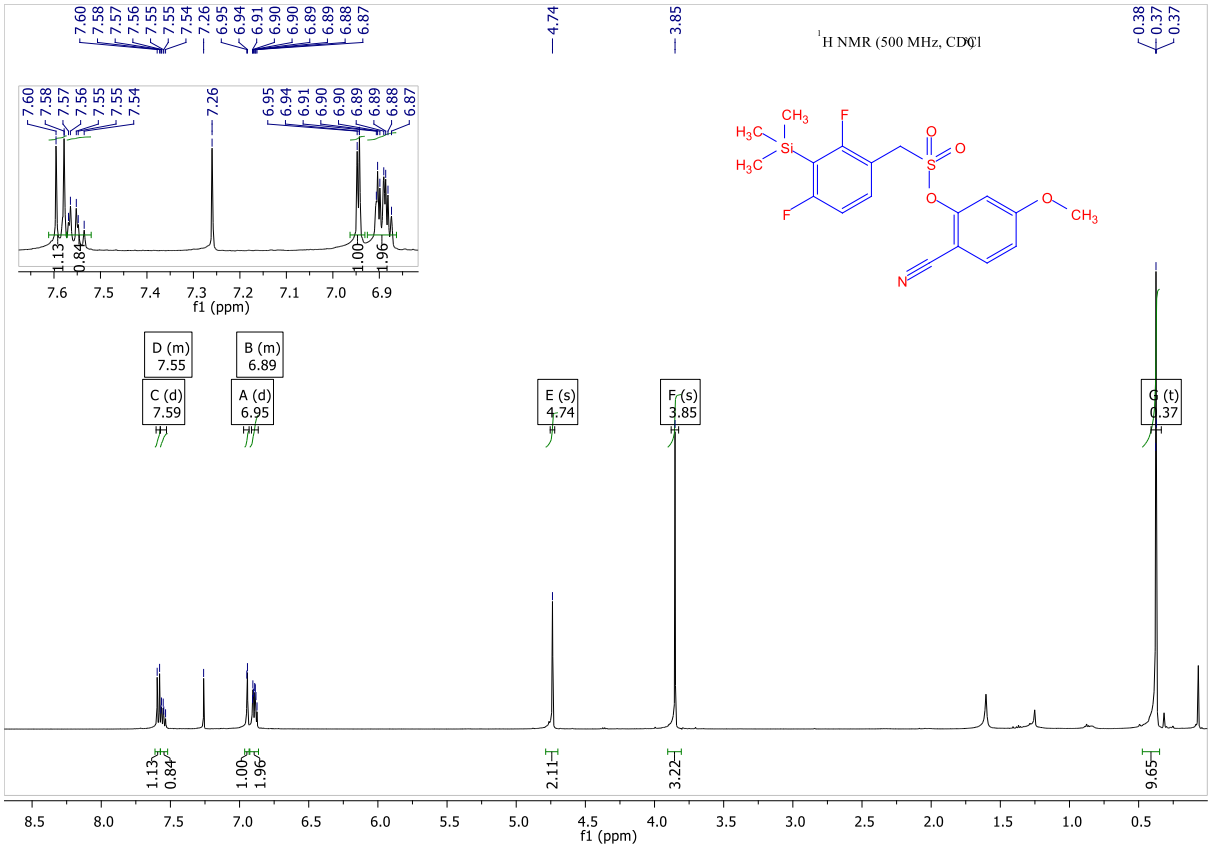


Figure S20: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2d$_{mono}$**,

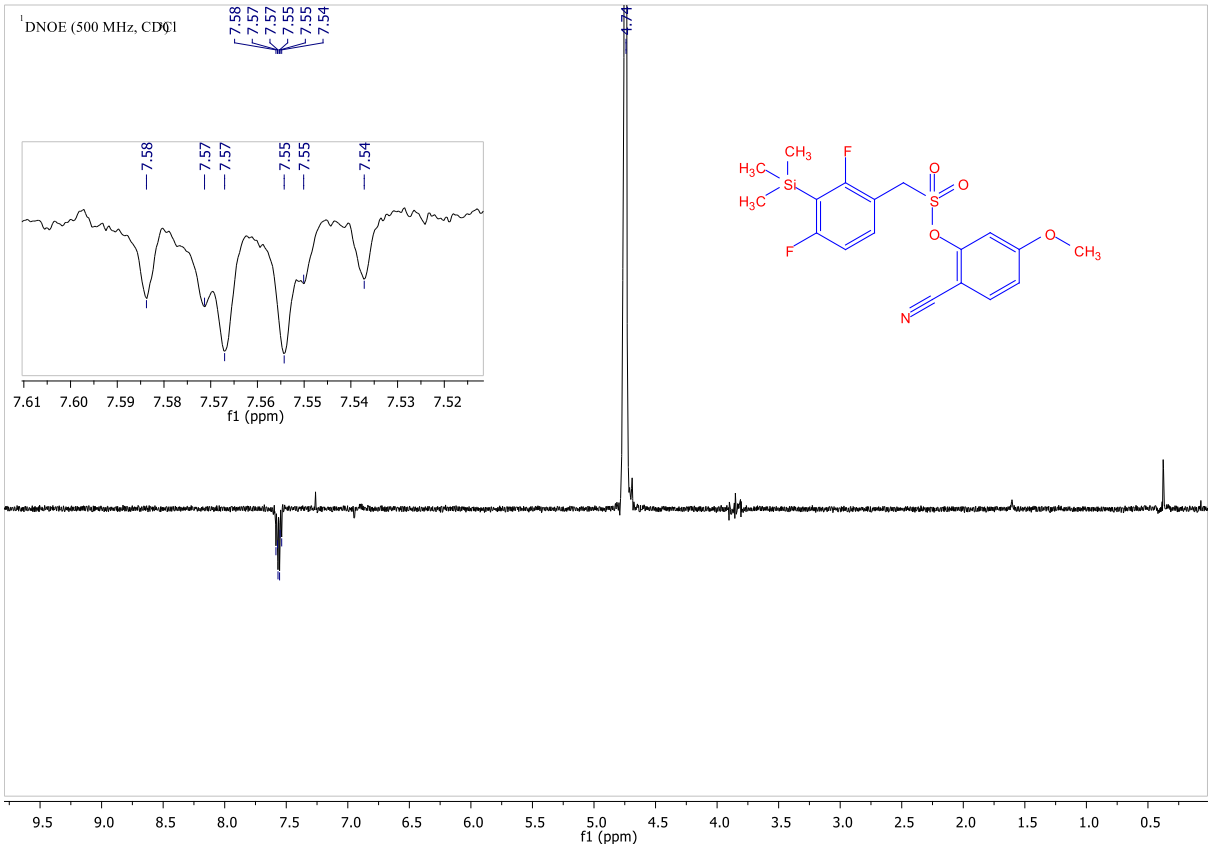


Figure S21: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2d$_{mono}$**,

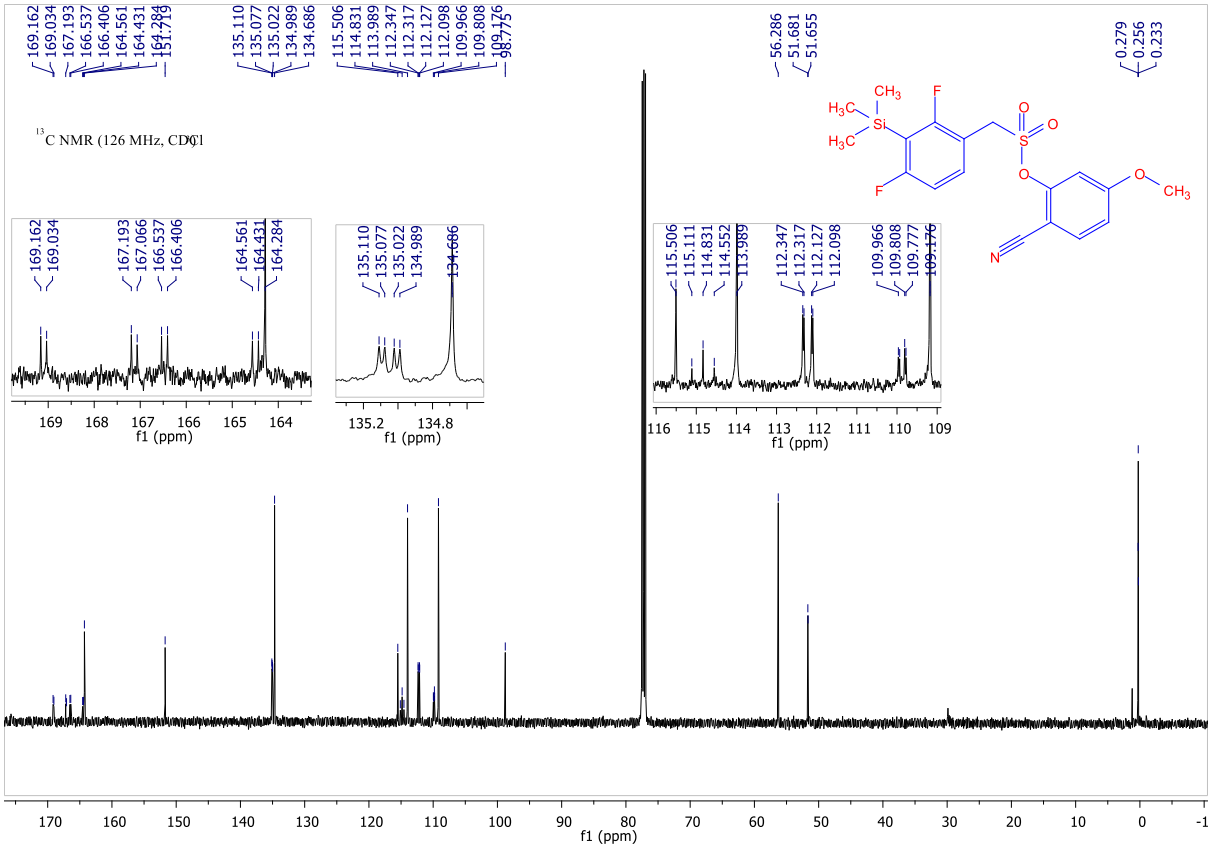


Figure S22: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2d$_{mono}$'**

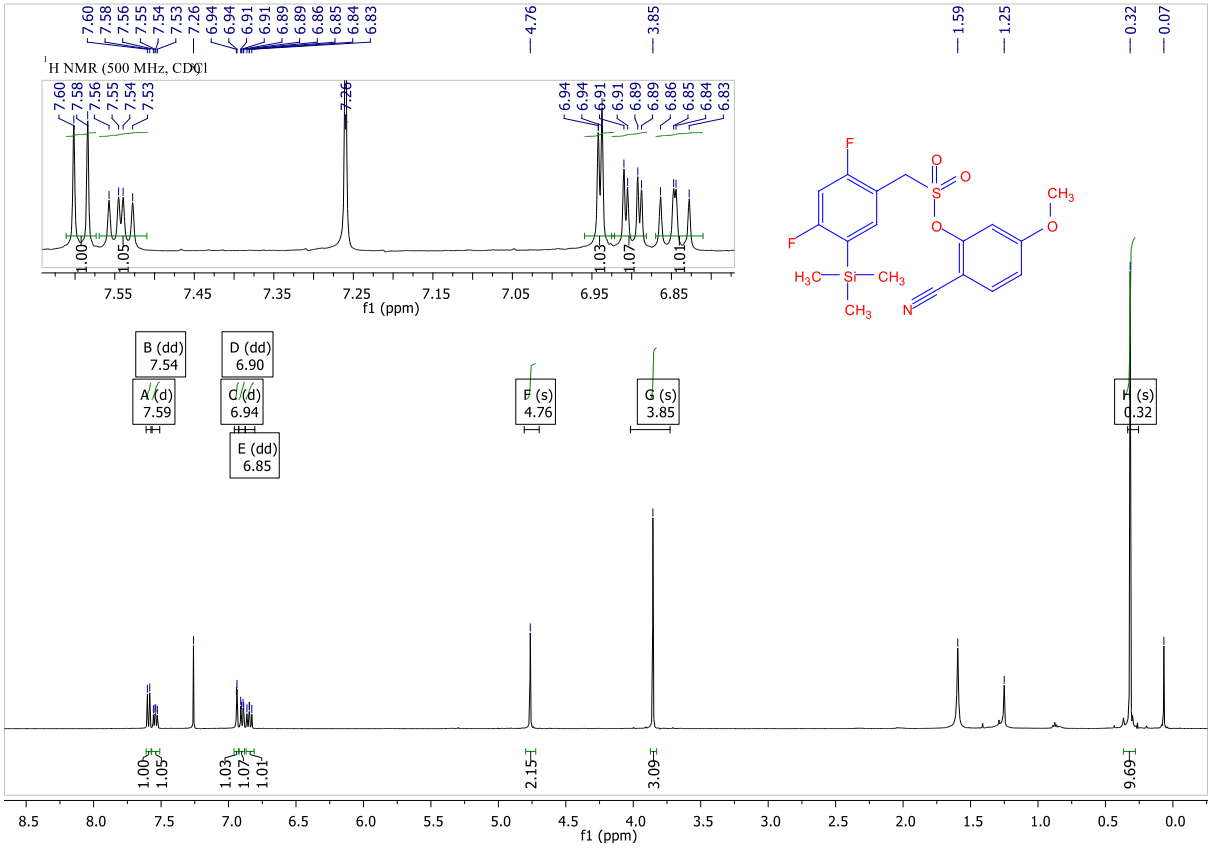


Figure S23: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2d$_{mono}$"**

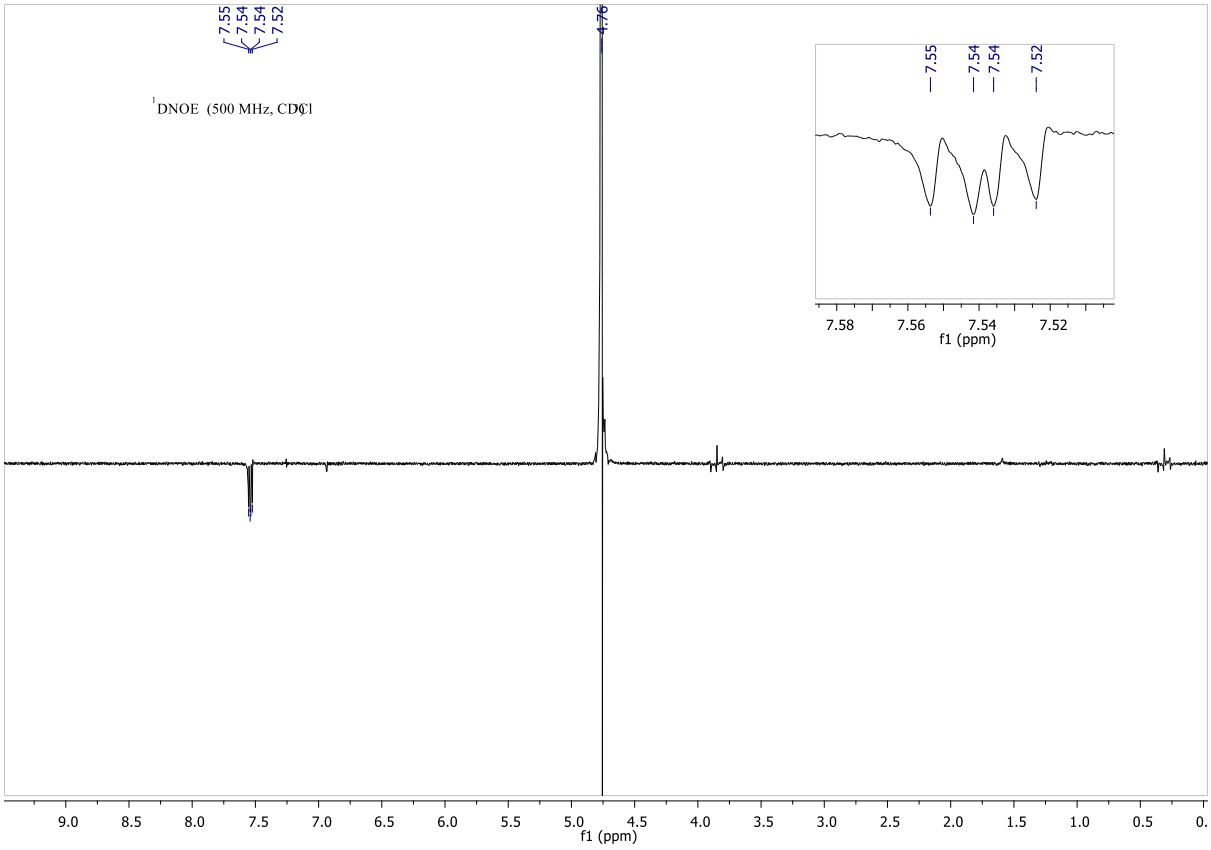


Figure S24: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2d$_{mono}$"**

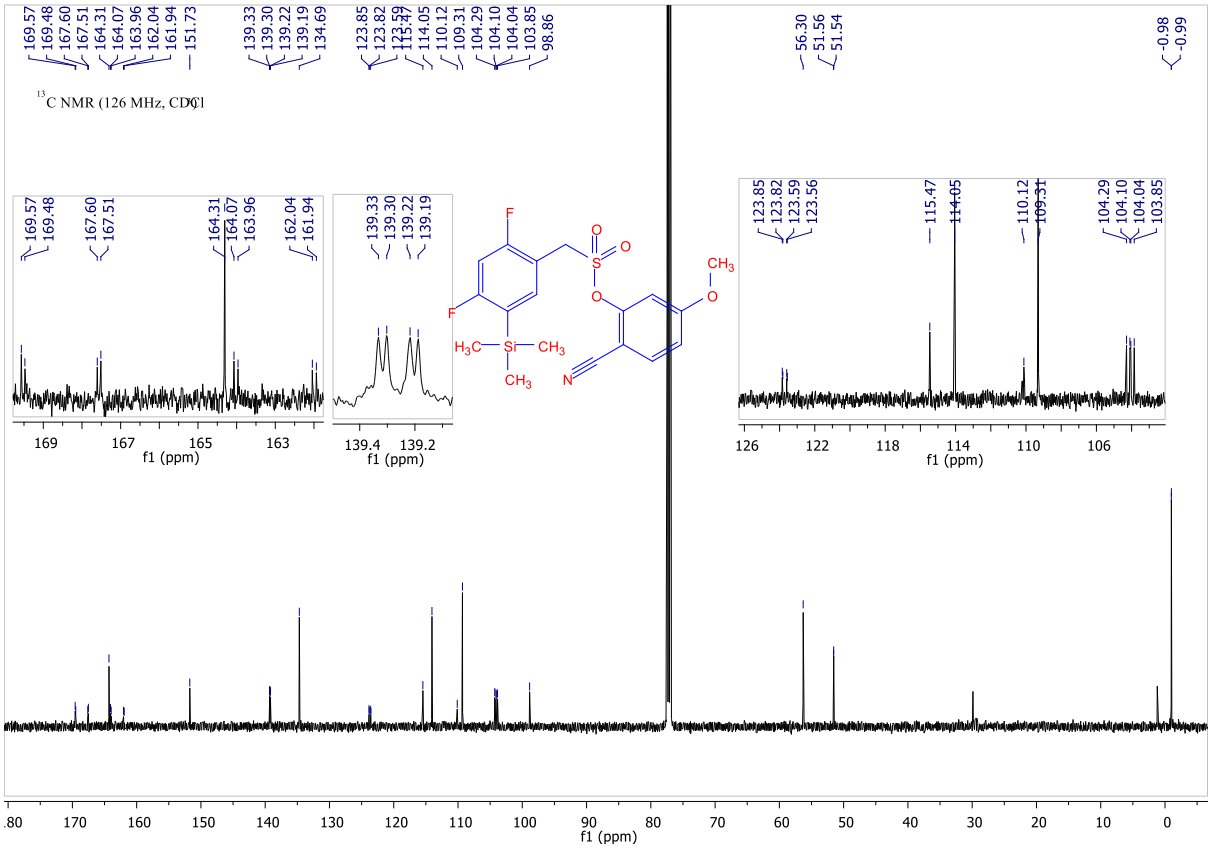


Figure S25: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2d$_{mono}$"**

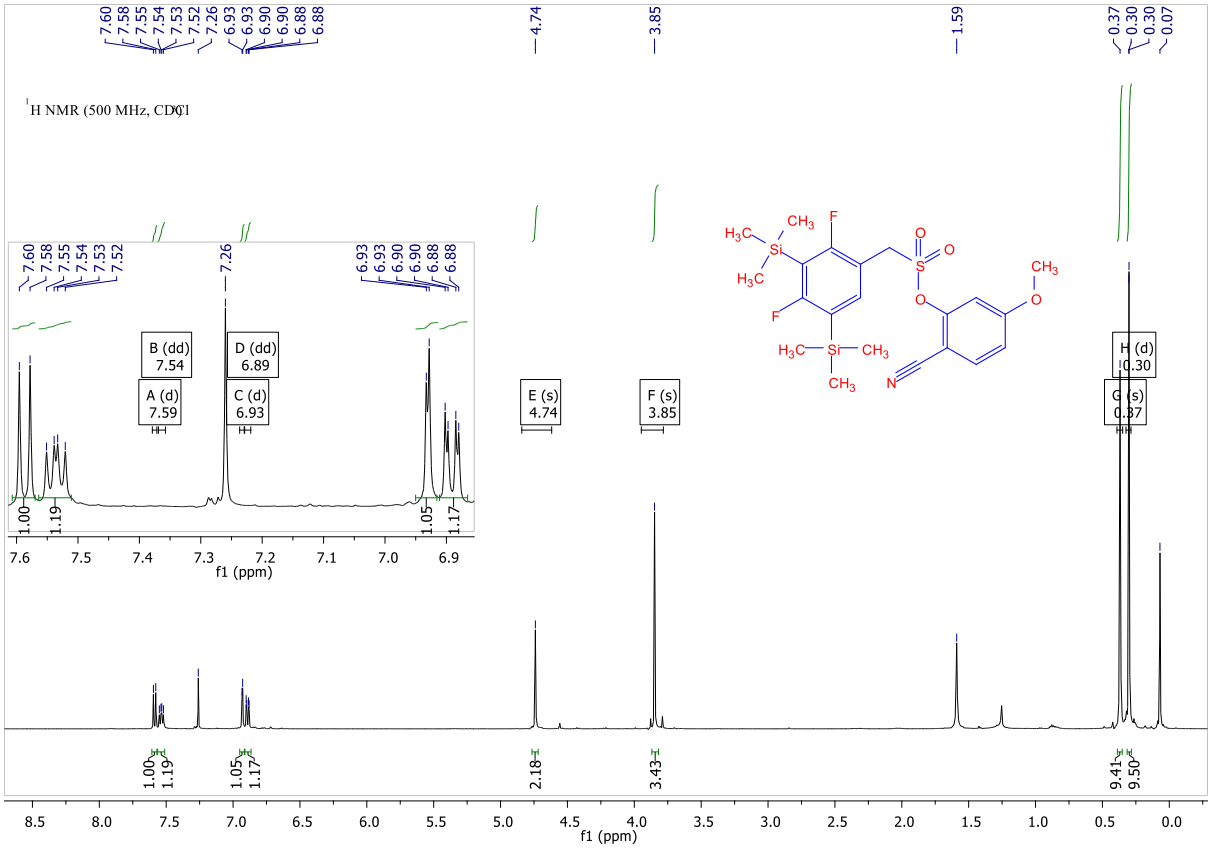


Figure S26: ^{13}C {^{1}H} NMR spectrum (500 MHz, $CDCl_3$) of Compound **2d$_{di}$**

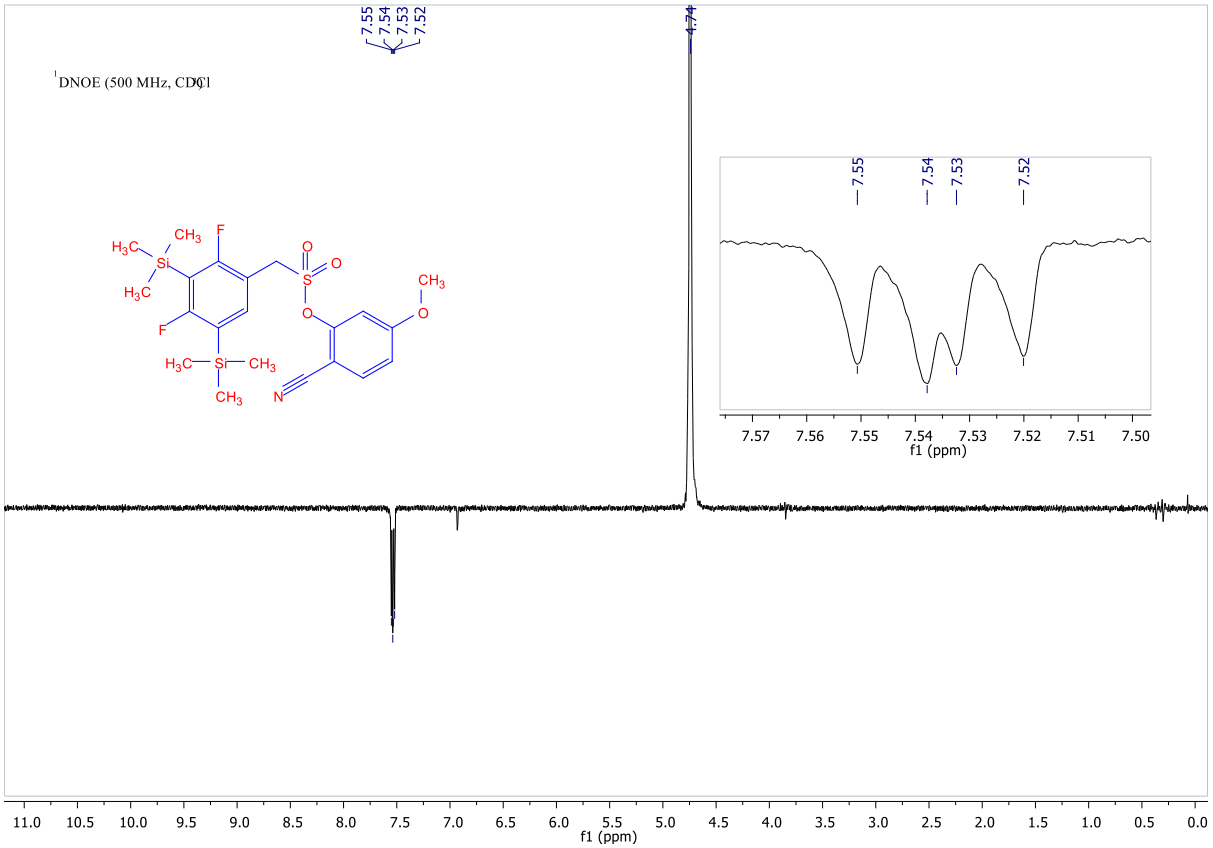


Figure S27: ^{1}D NOE spectrum (500 MHz, $CDCl_3$) of Compound **2d$_{di}$**

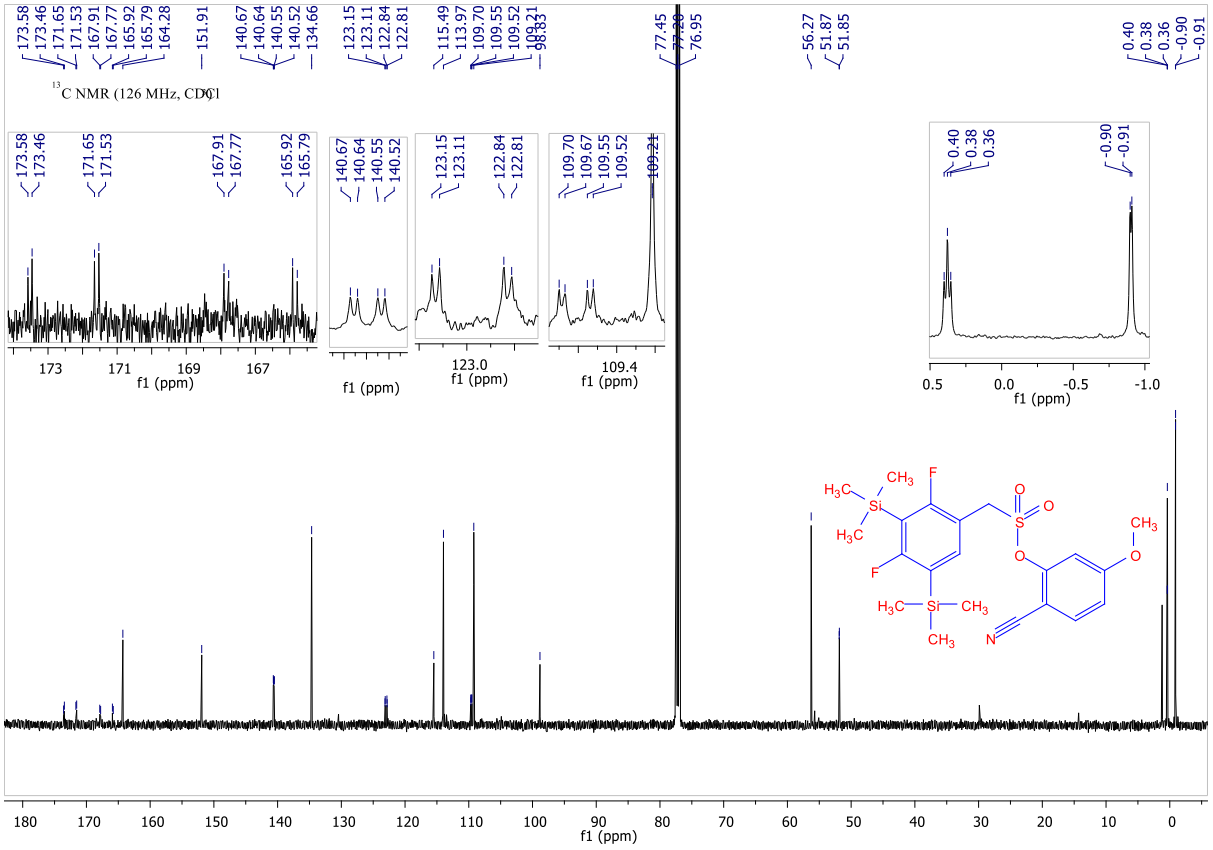


Figure S28: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2d$_{di}$**

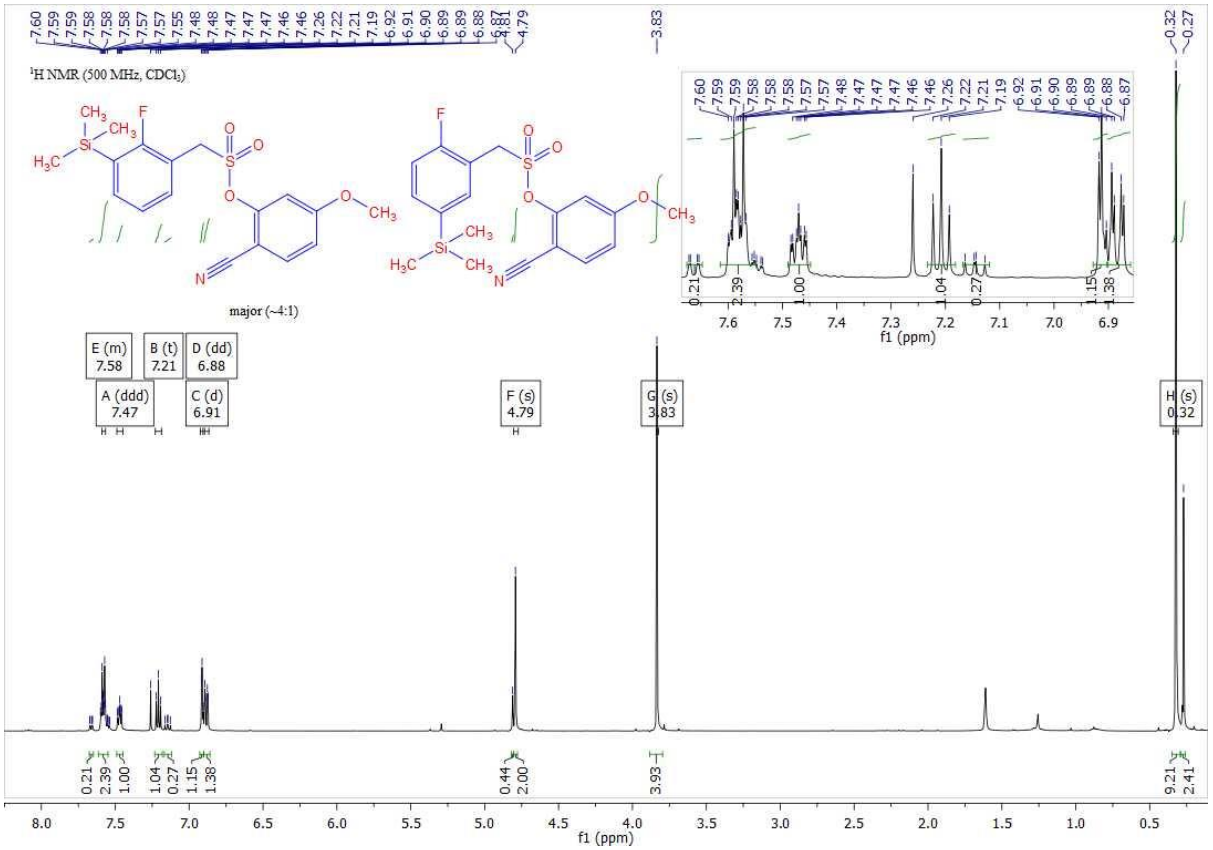


Figure S29: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2e$_{mono}$**

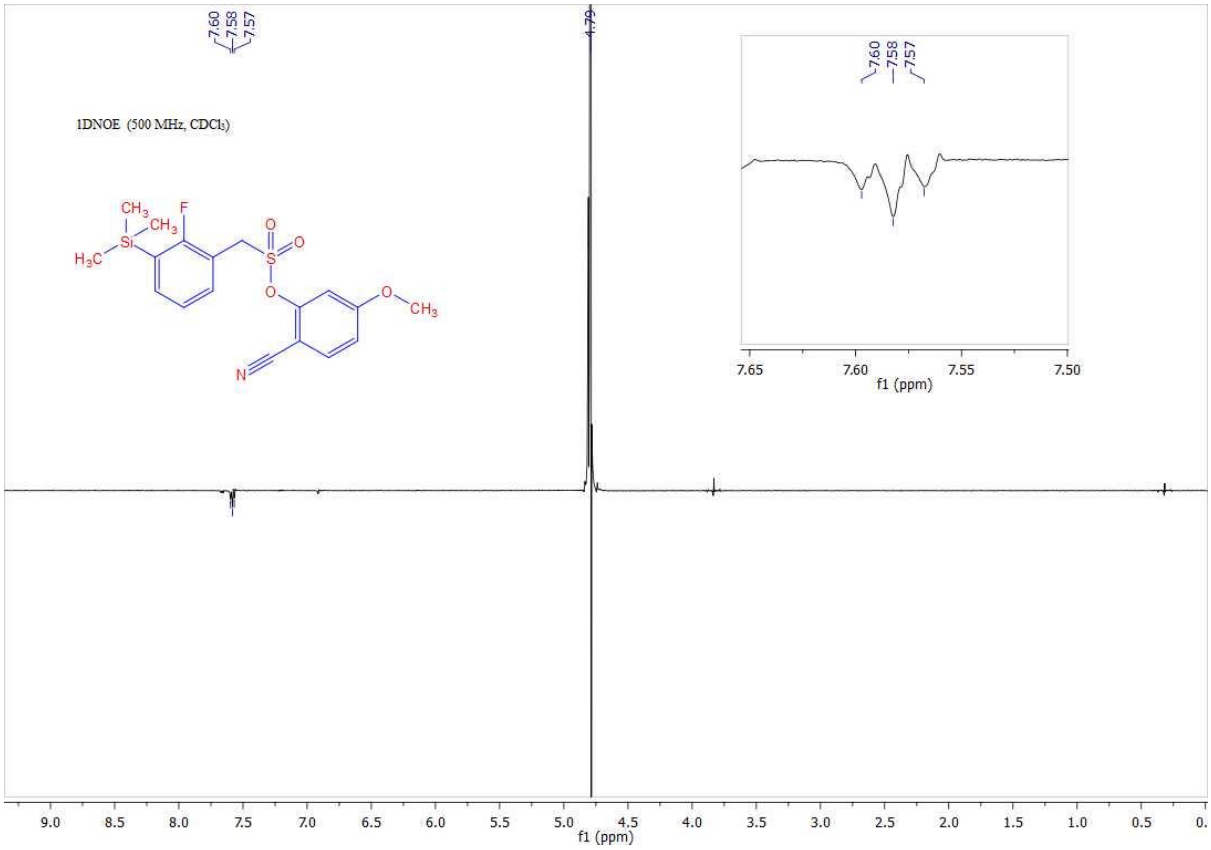


Figure S30: ^{1}D NOE spectrum (500 MHz, $CDCl_3$) of Compound **2e$_{mono}$**

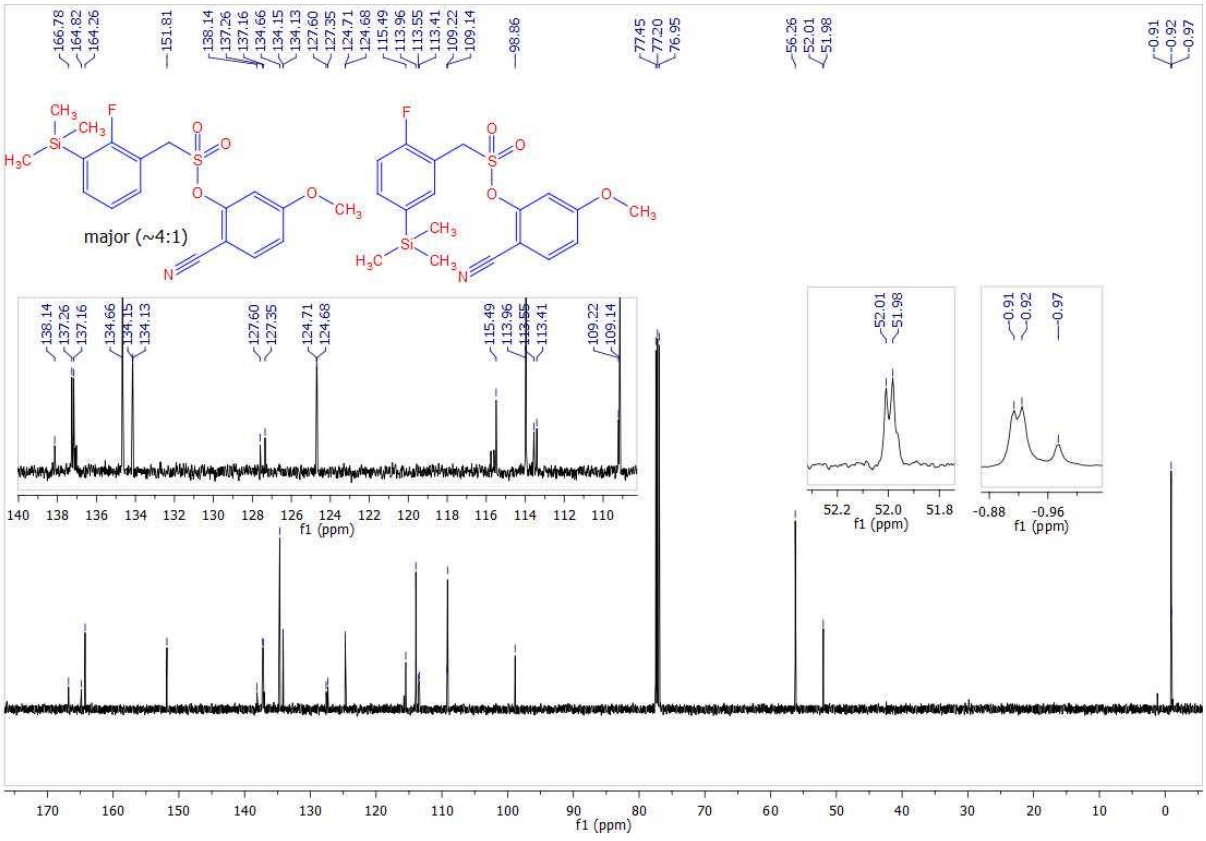


Figure S31: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2e$_{mono}$**

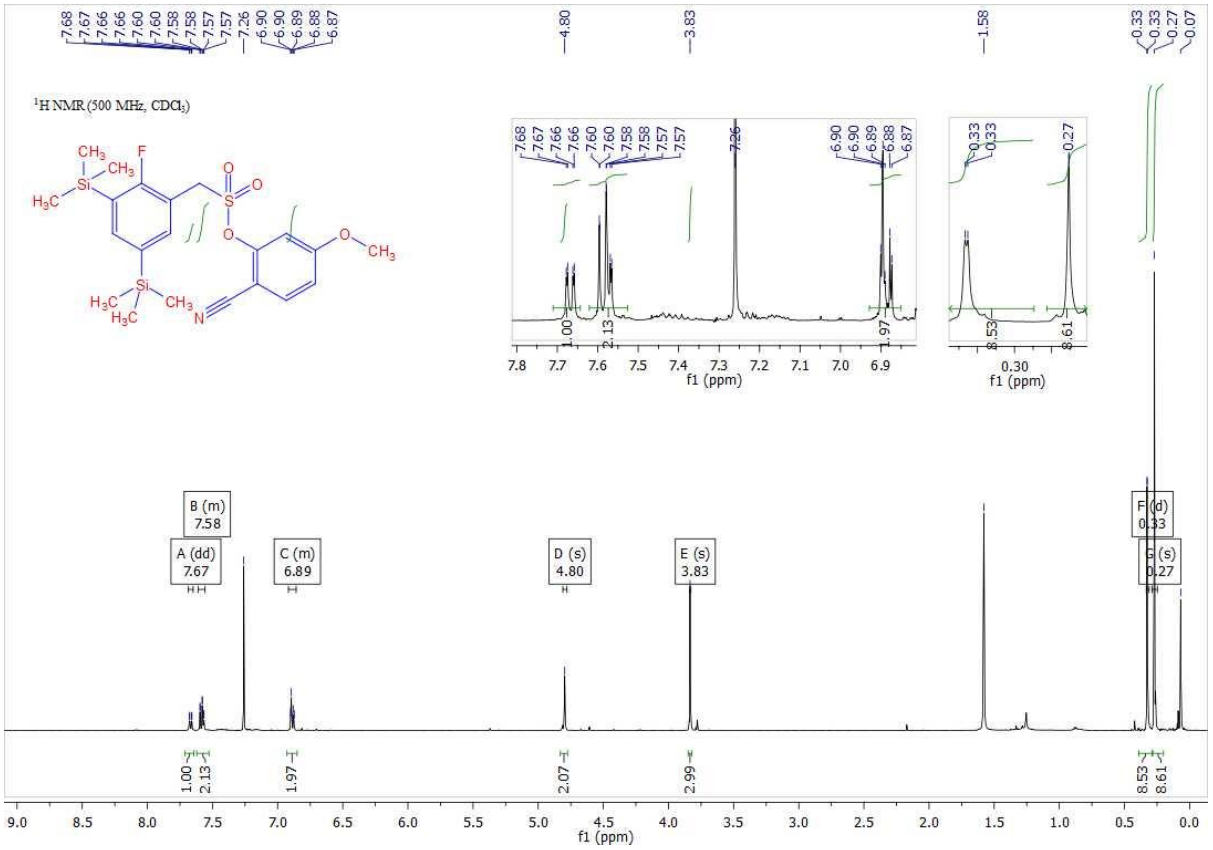


Figure S32: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2e$_{di}$**

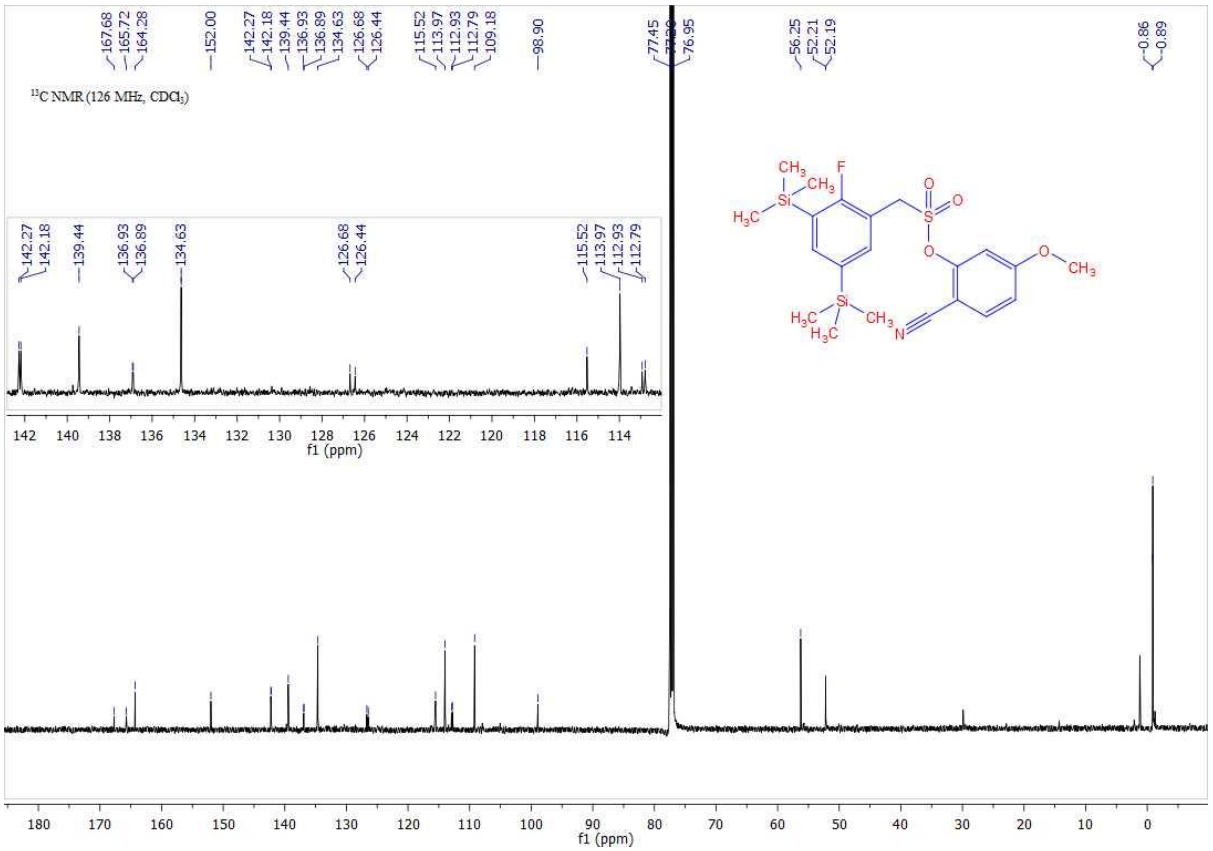


Figure S33: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2e$_{di}$**

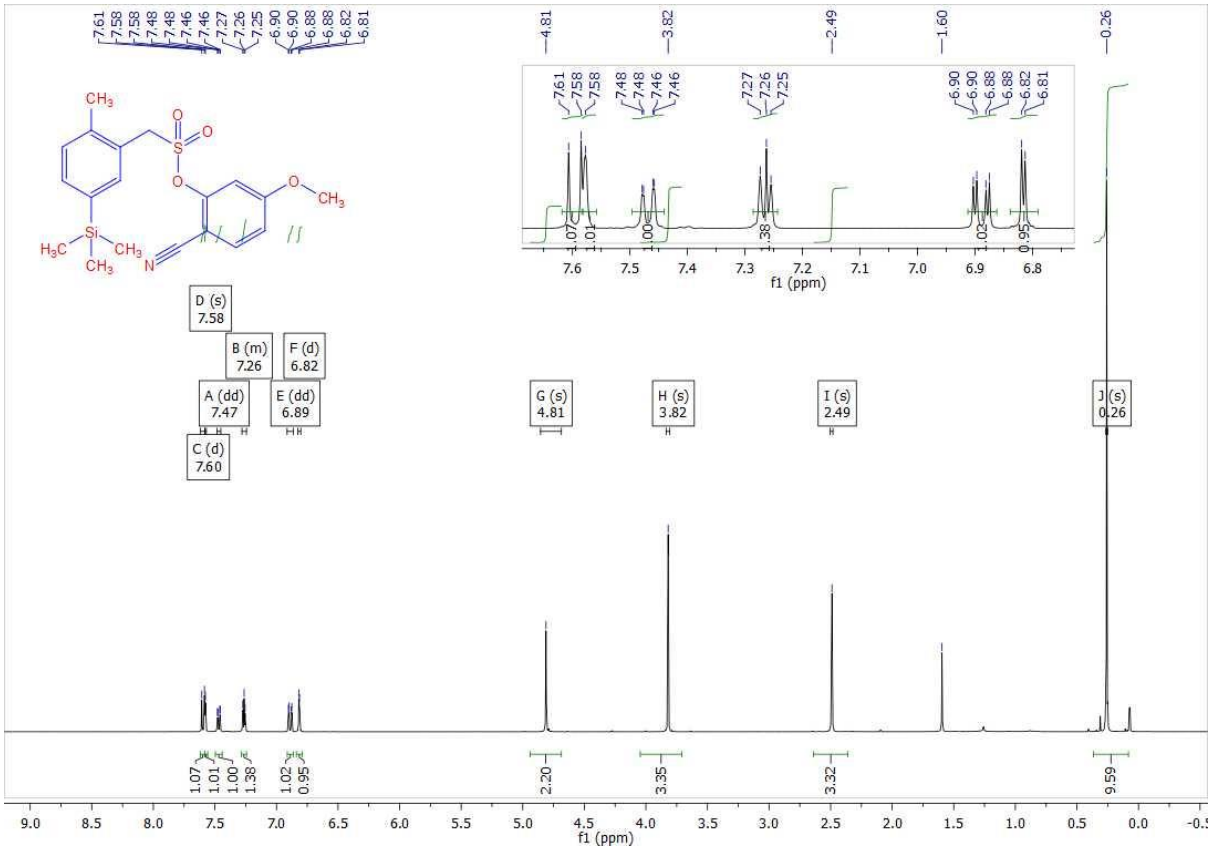


Figure S34: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **2f$_{mono}$**

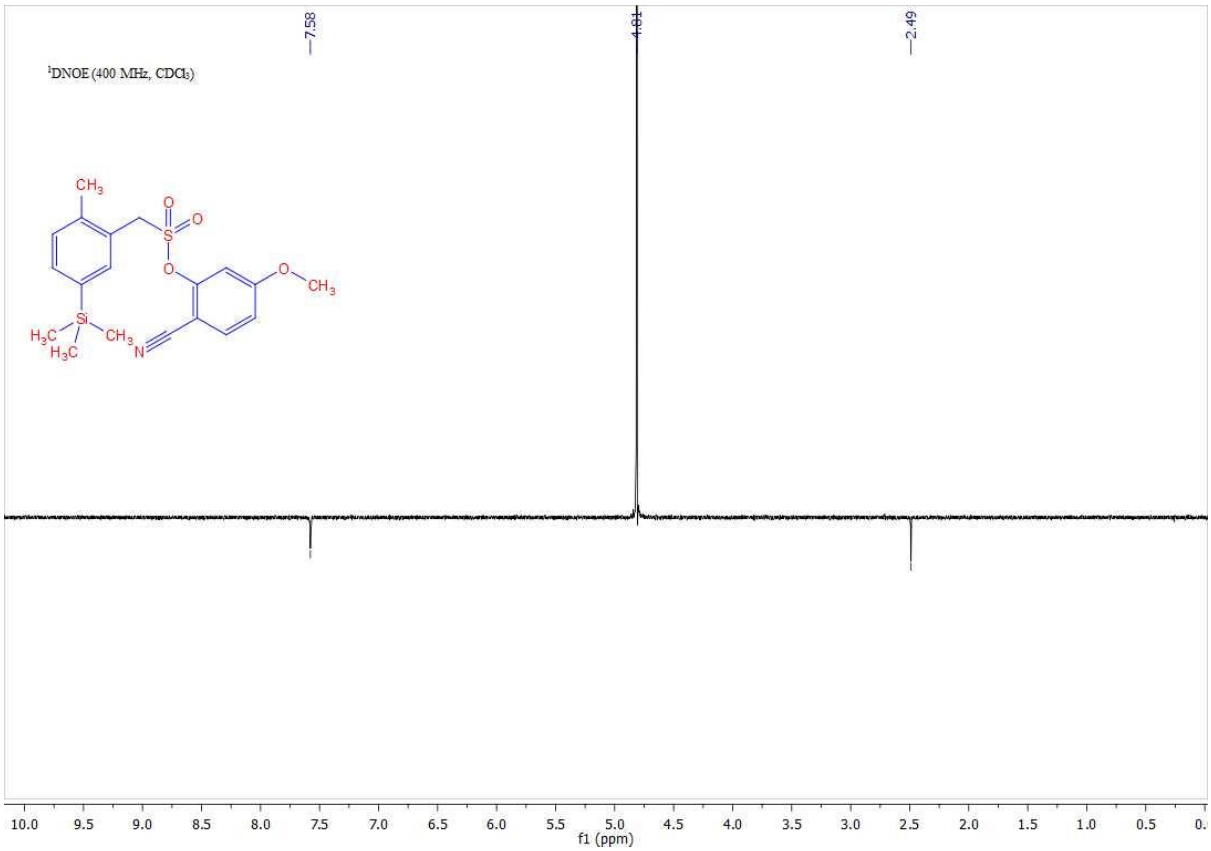


Figure S35: ^{1}D NOE spectrum (400 MHz, $CDCl_3$) of Compound **2f$_{mono}$**

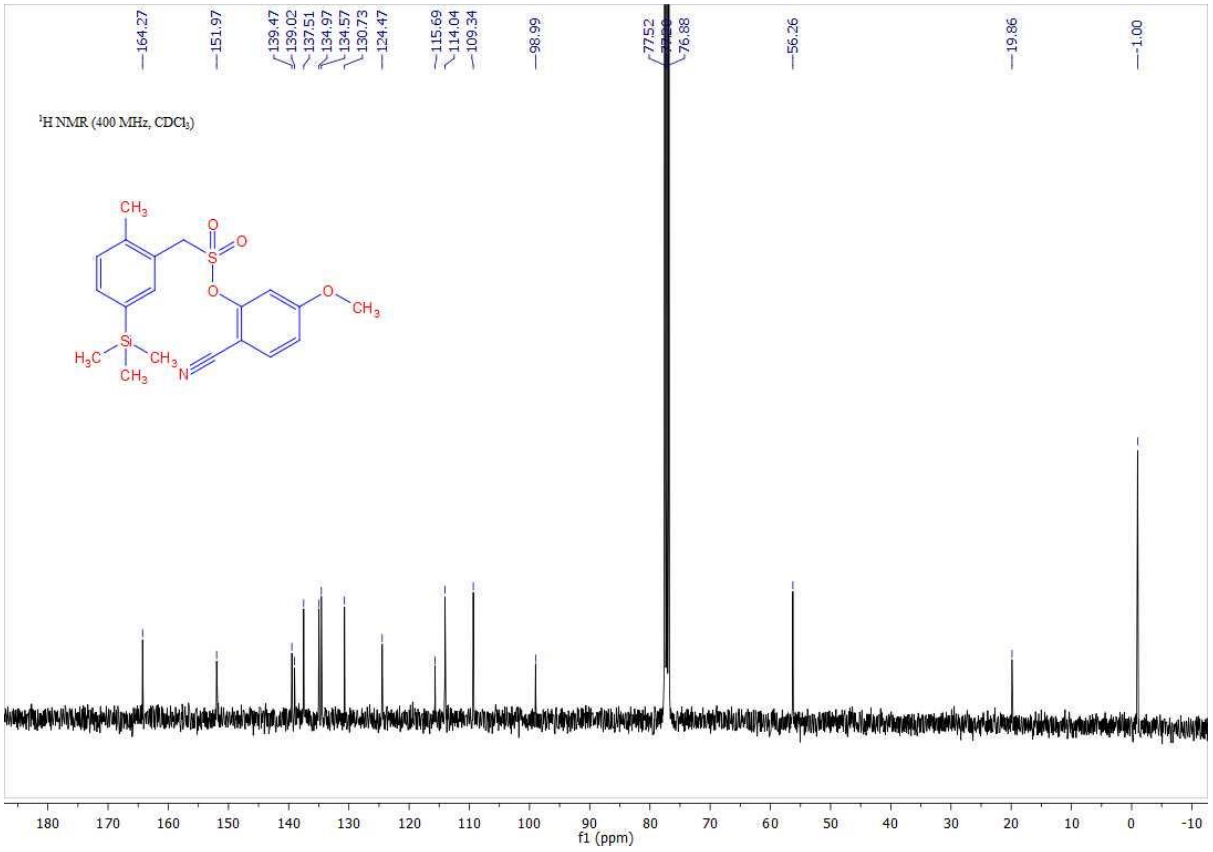


Figure S36: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of Compound **2f$_{mono}$**

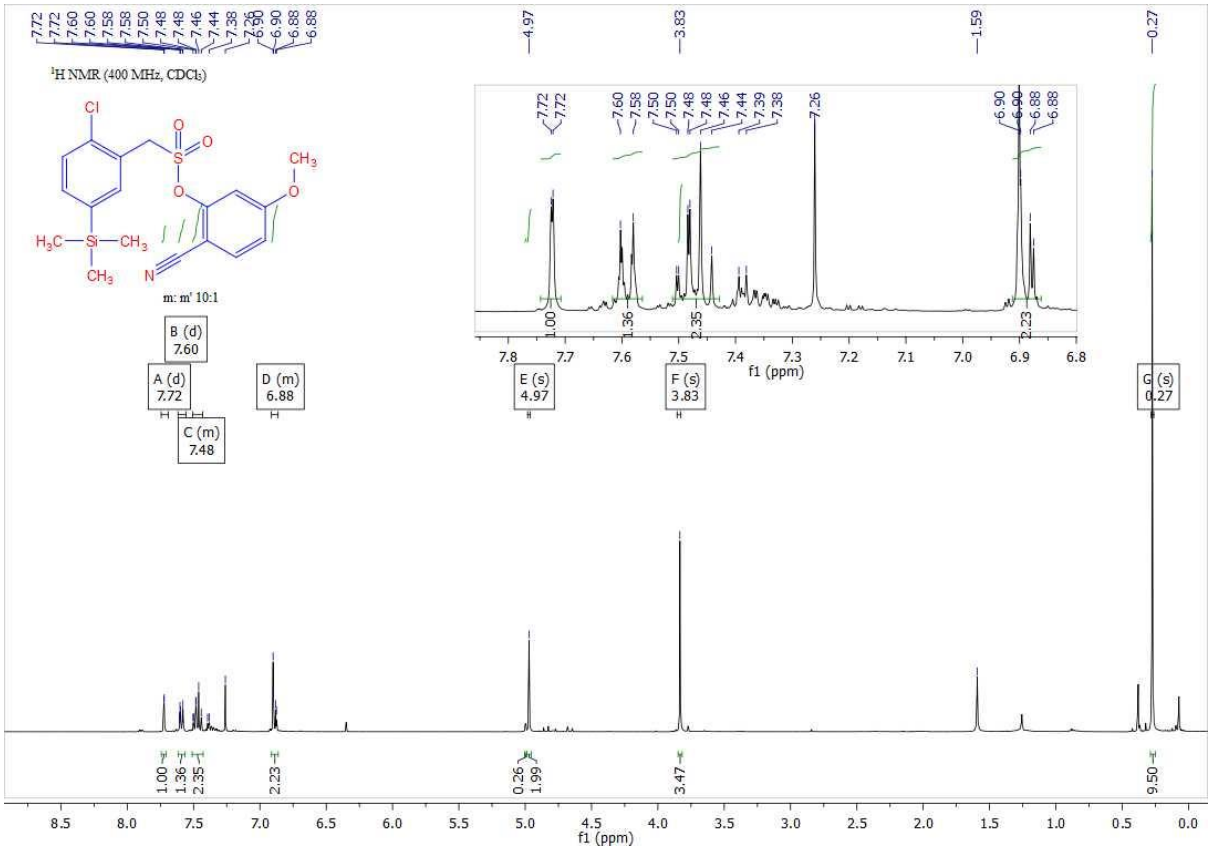


Figure S37: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **2g$_{mono}$**

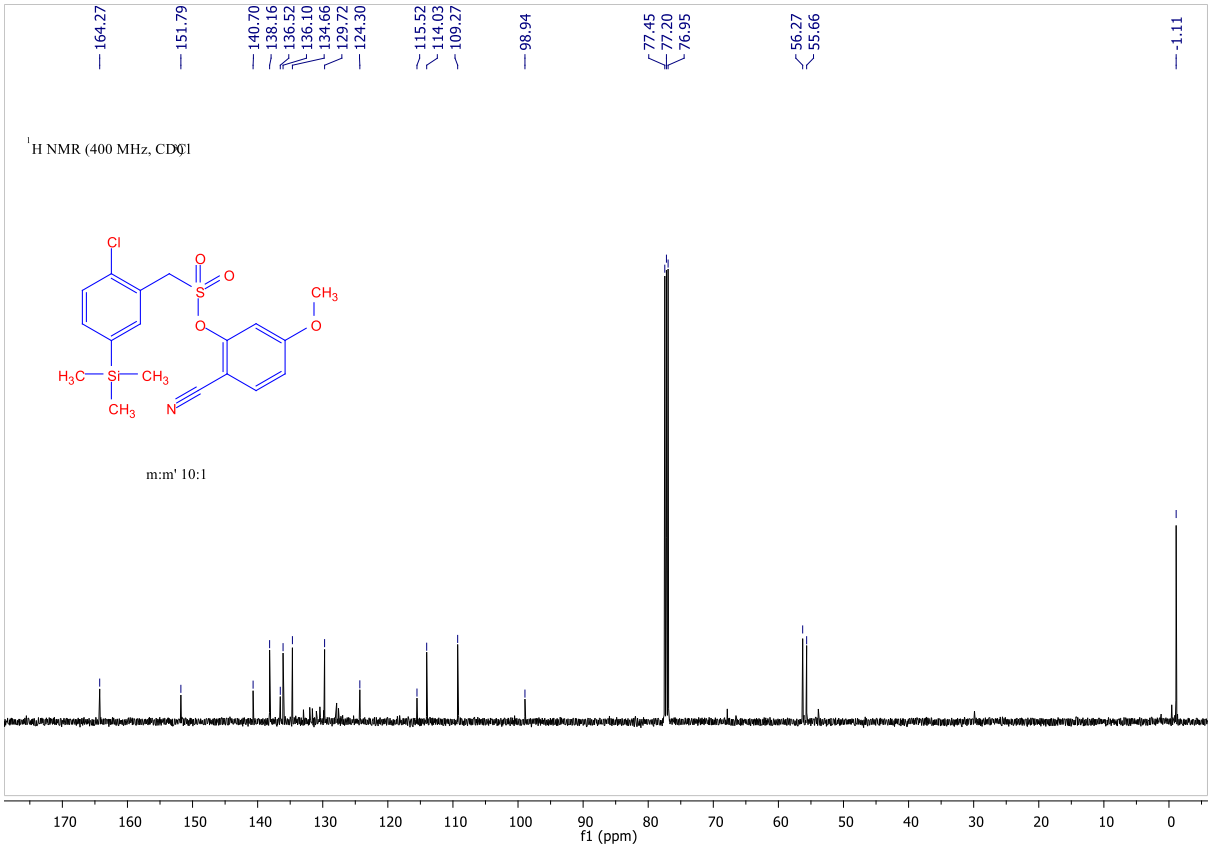


Figure S38: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2g$_{mono}$**

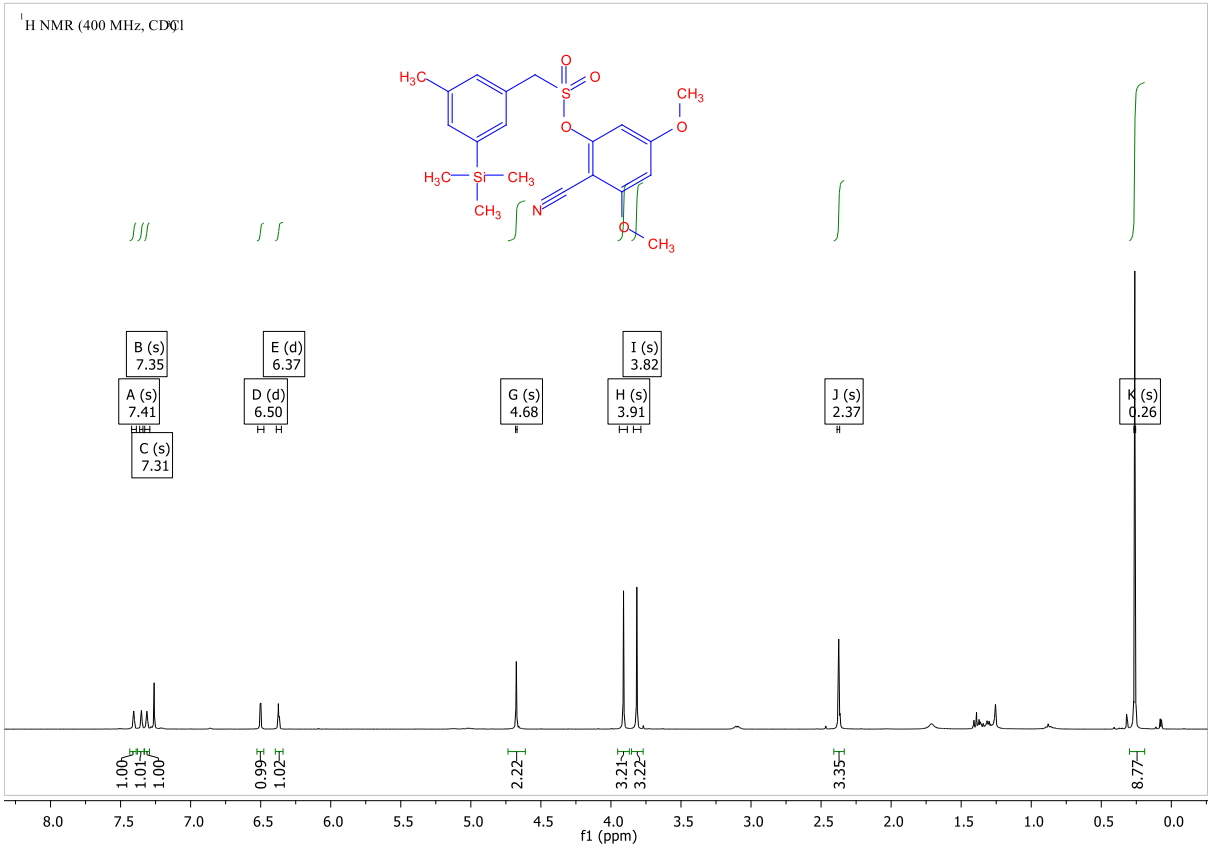


Figure S39: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **2h**

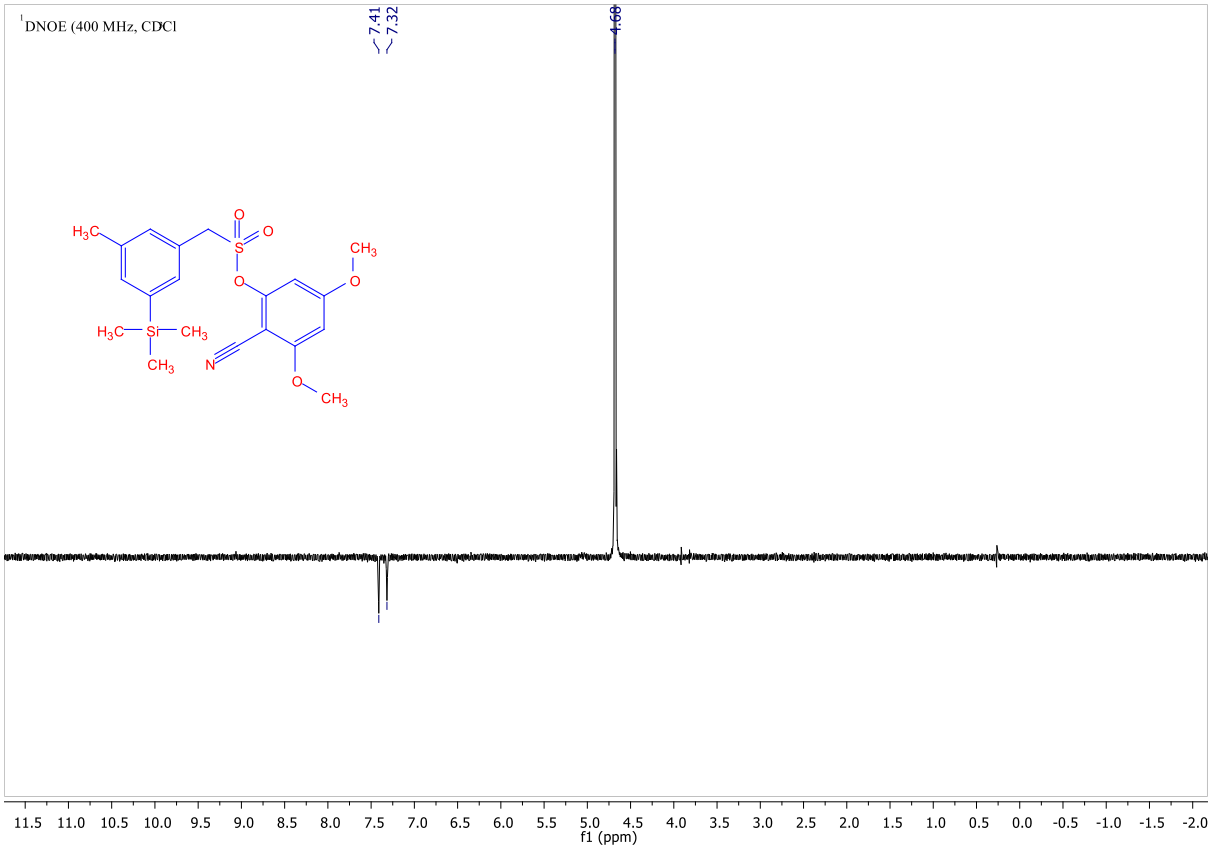


Figure S40: ^{1}D NOE spectrum (400 MHz, $CDCl_3$) of Compound **2h**

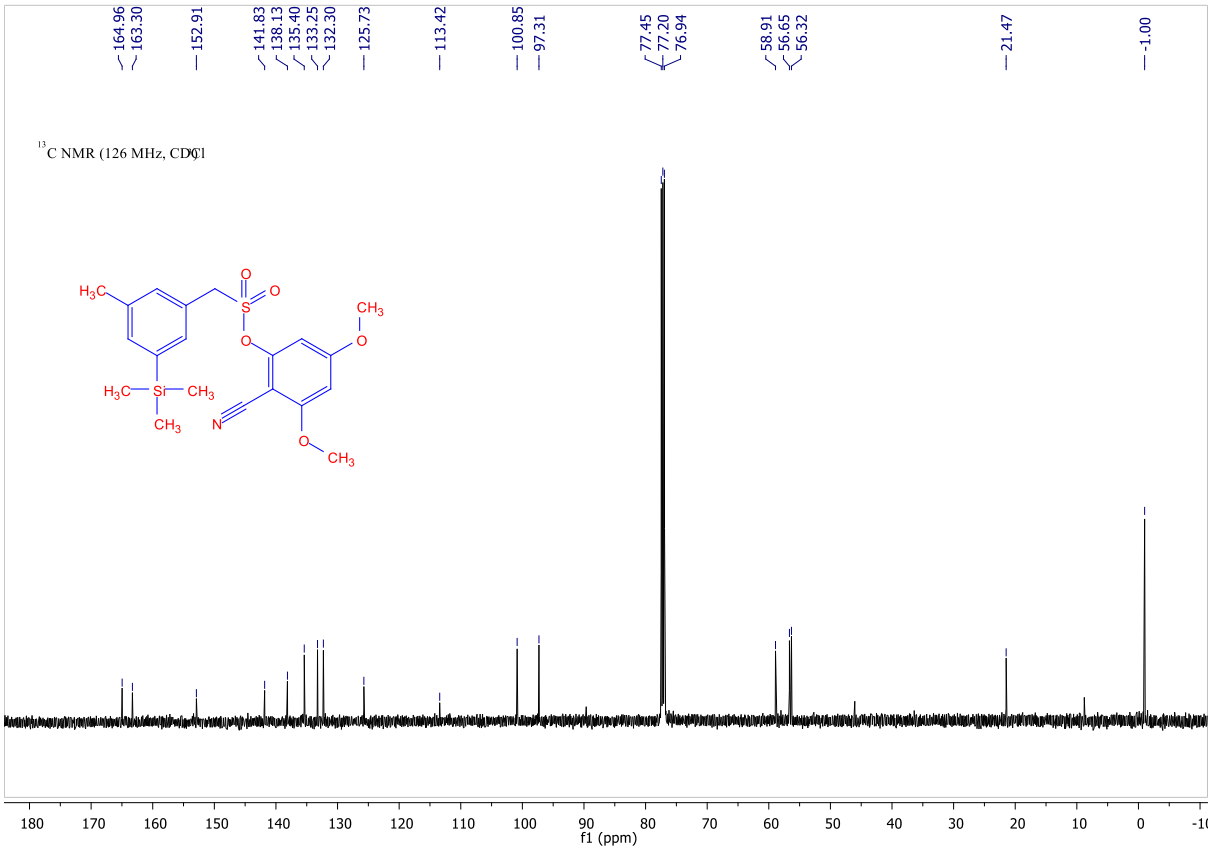


Figure S41: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2h**

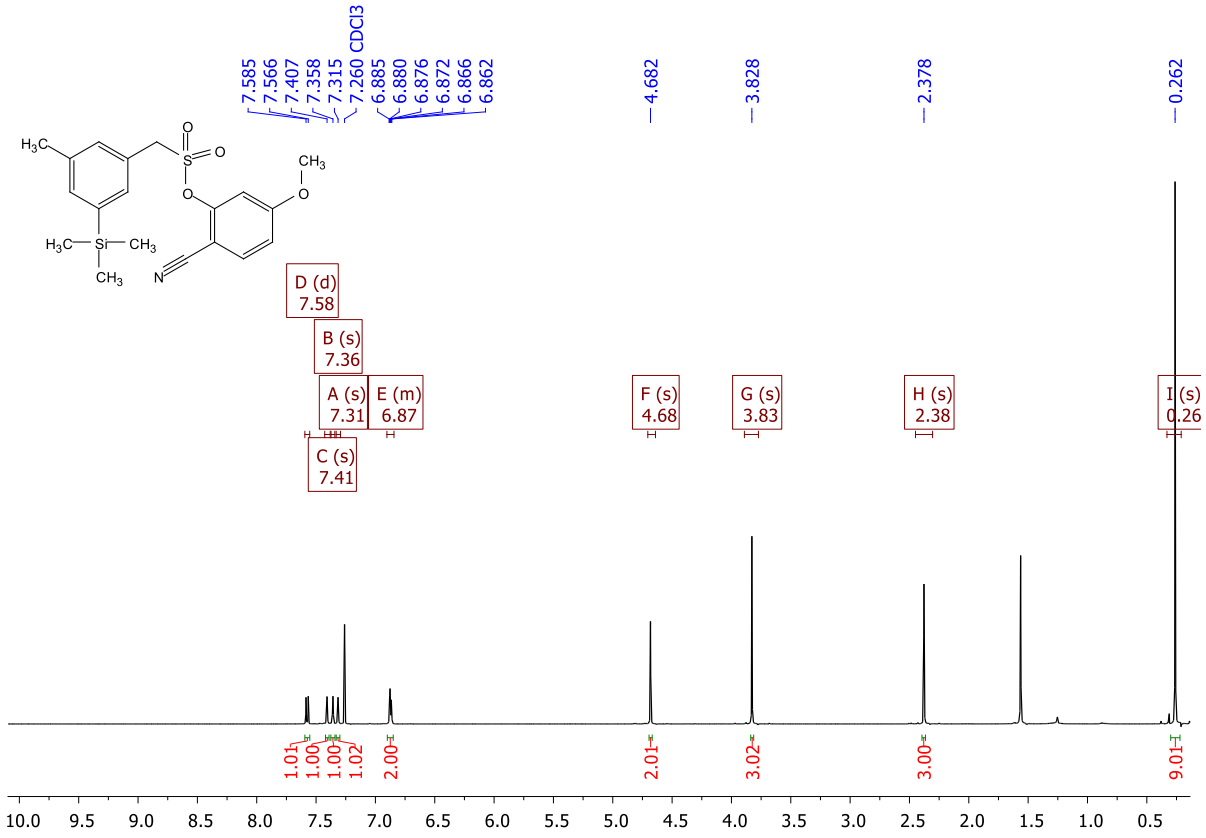


Figure S42: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2h-DG4**

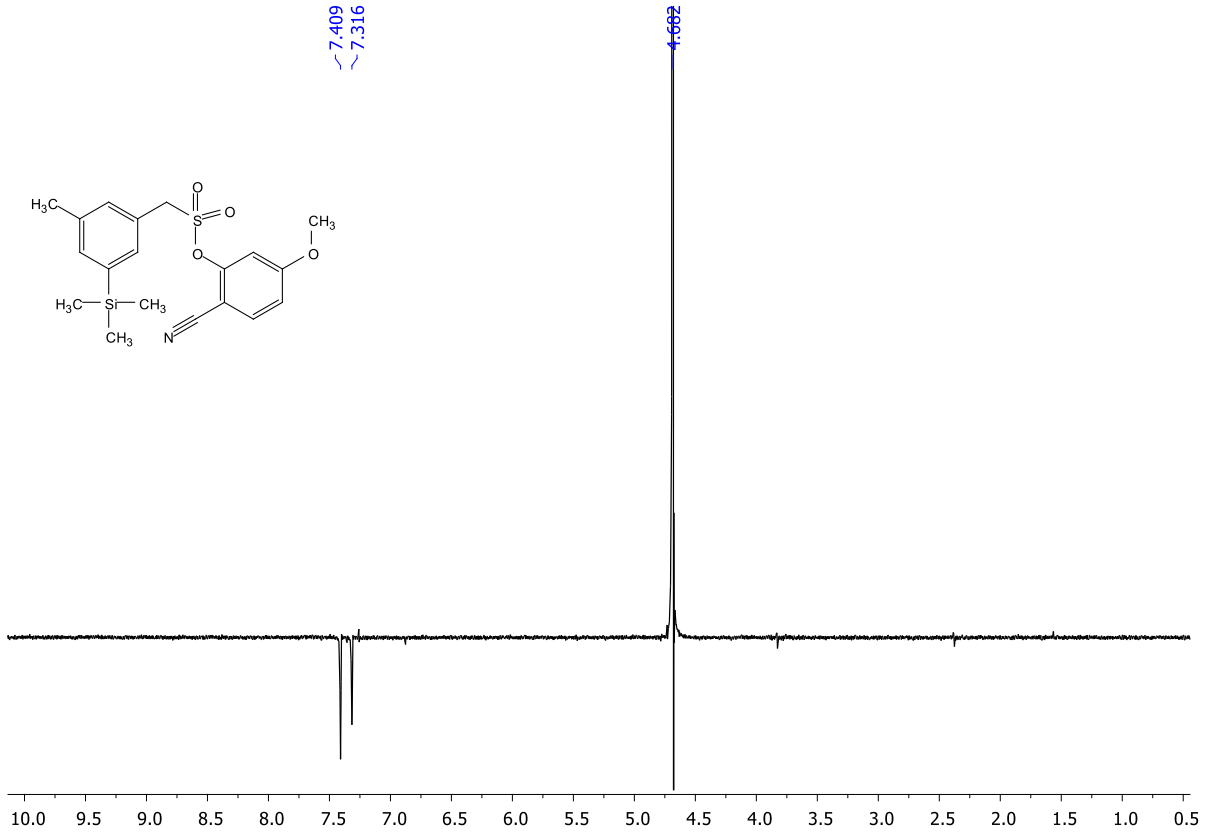


Figure S43: ^{1}D NOE spectrum (500 MHz, $CDCl_3$) of Compound **2h-DG4**

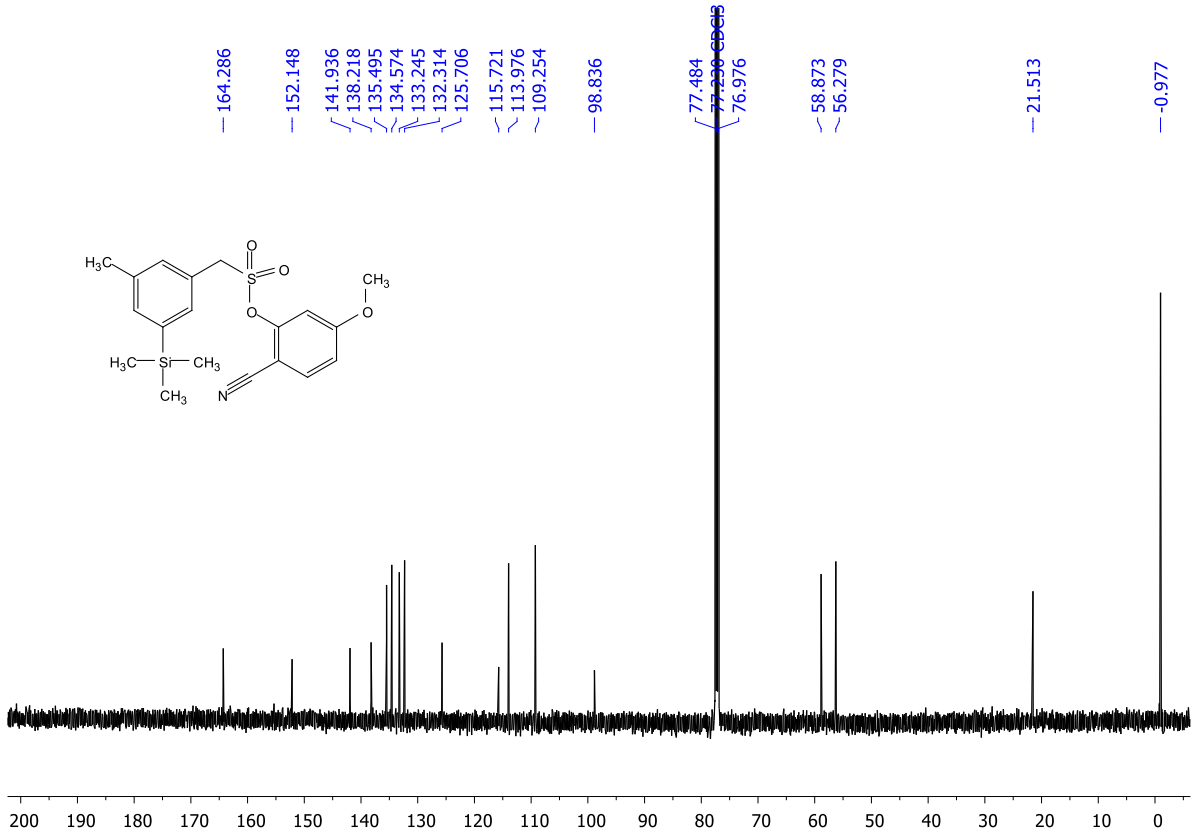


Figure S44: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2h**

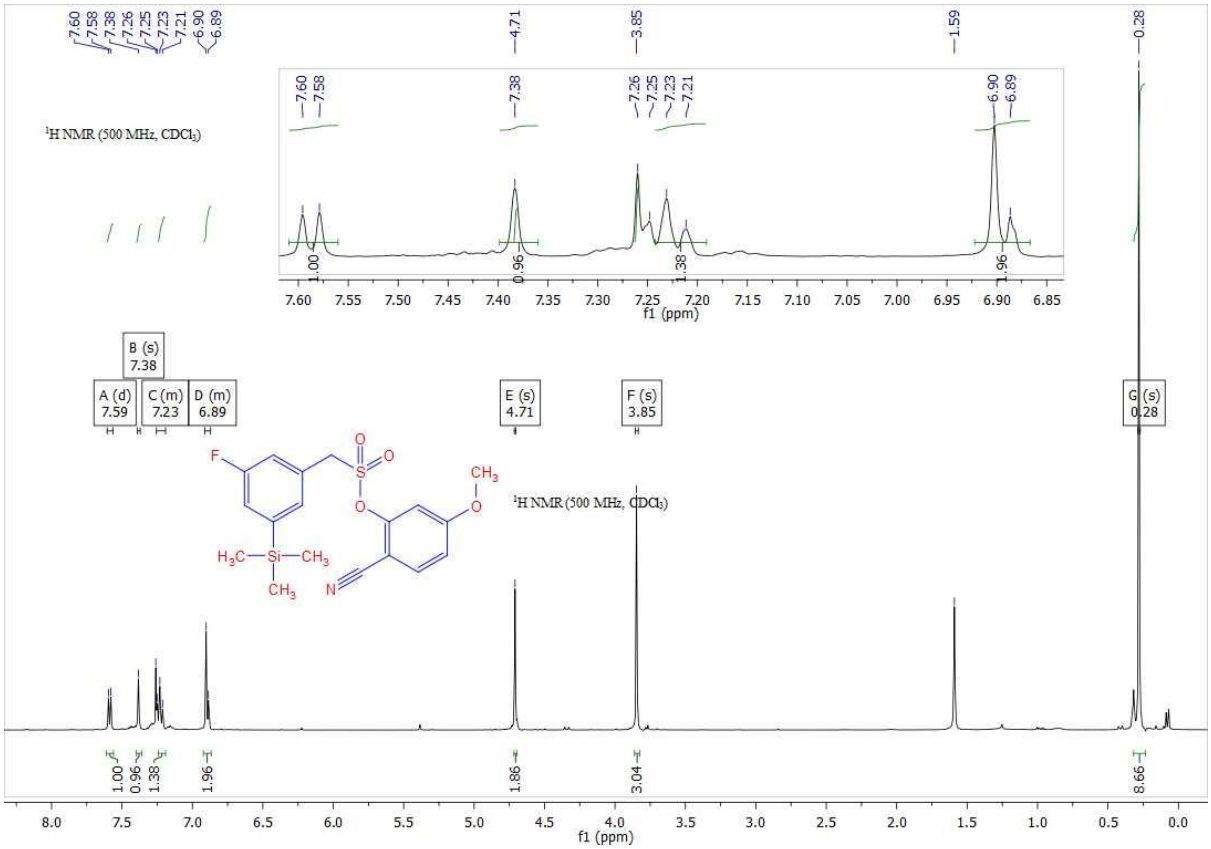


Figure S45: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2i**

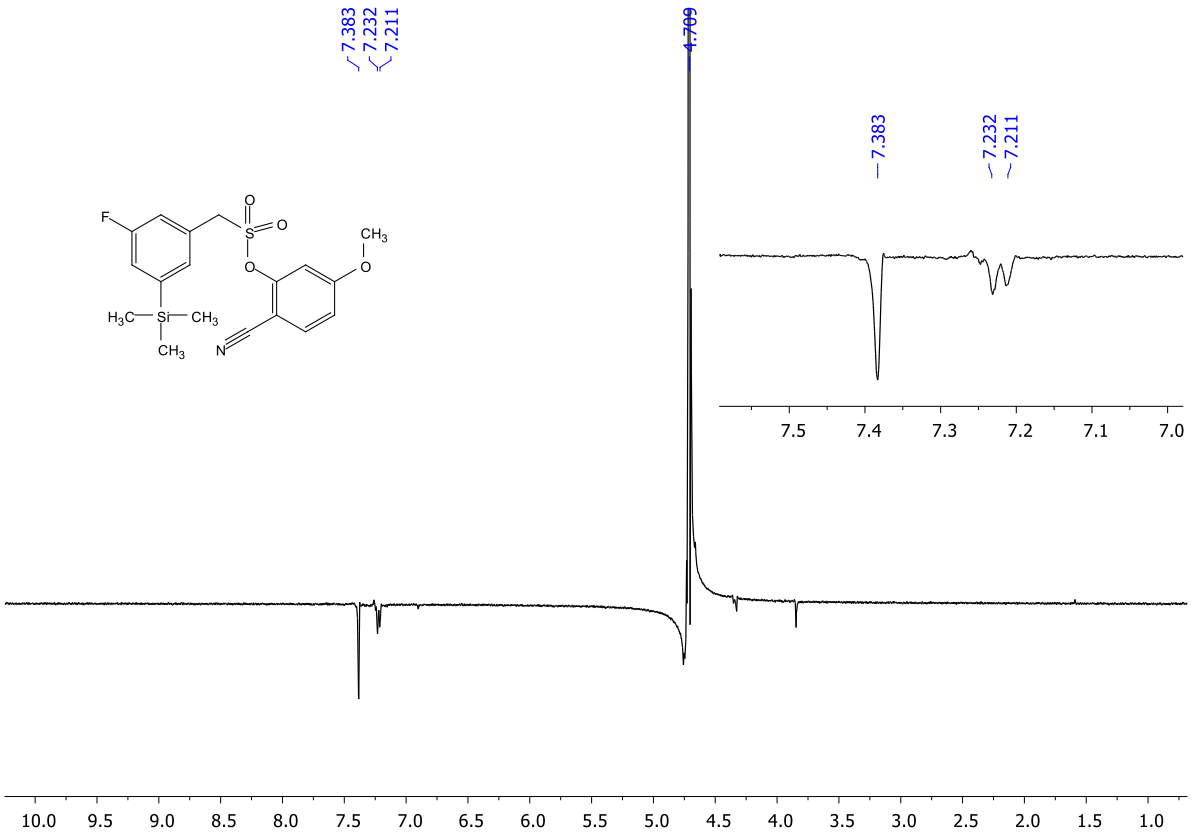


Figure S46: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2i**

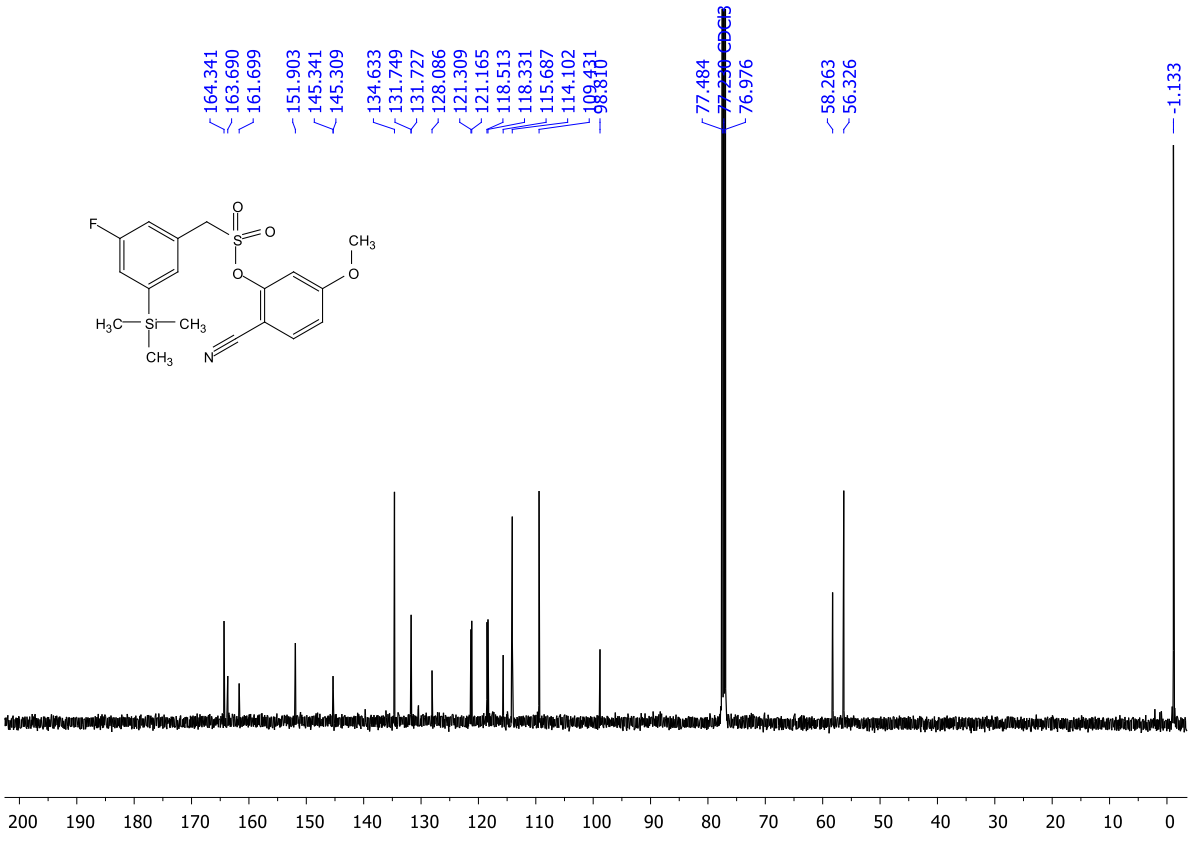


Figure S47: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2i**

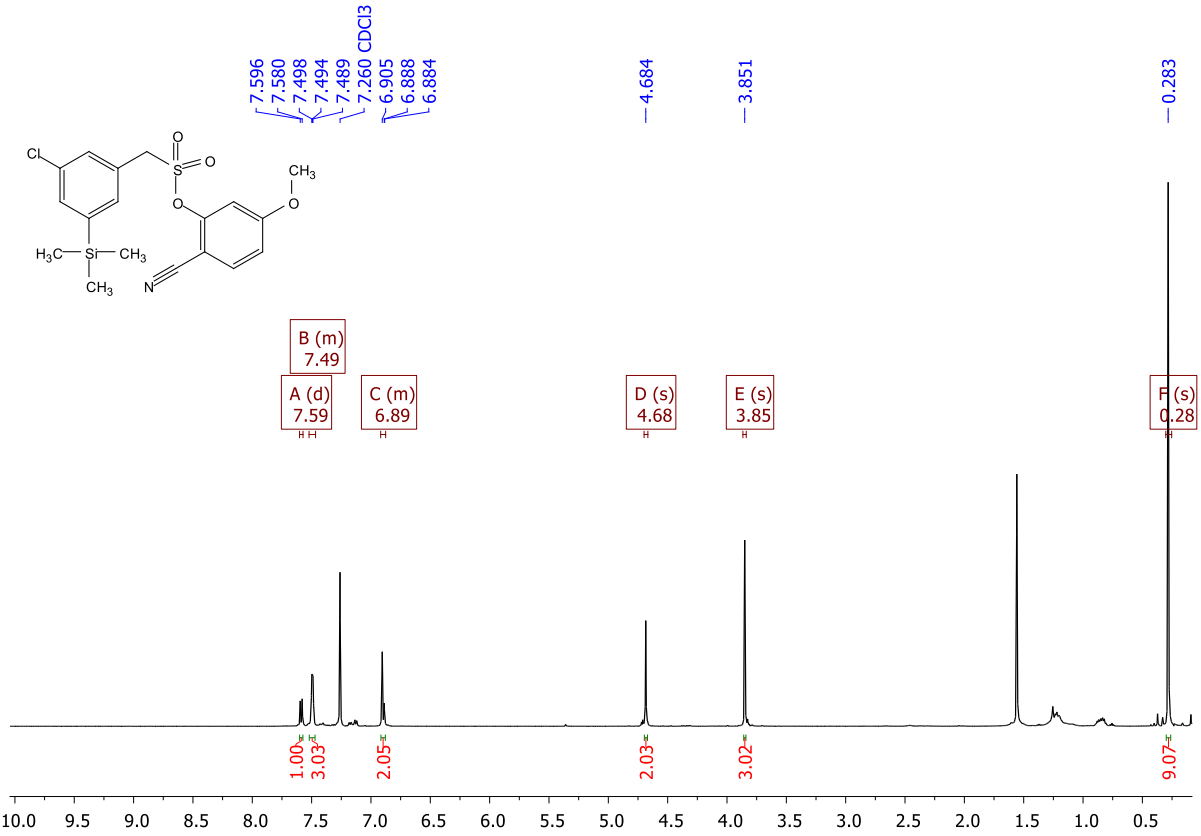


Figure S48: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2k**

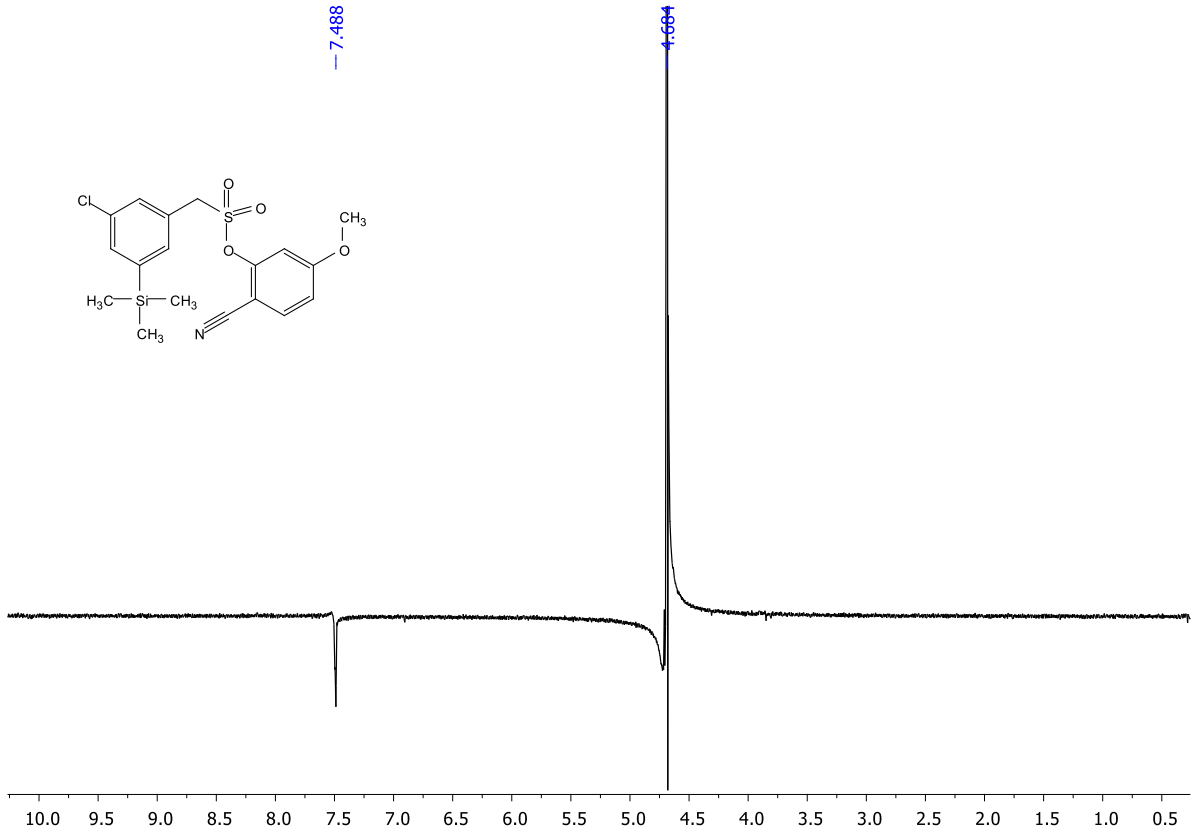


Figure S49: ^{1}D NOE spectrum (500 MHz, $CDCl_3$) of Compound **2k**

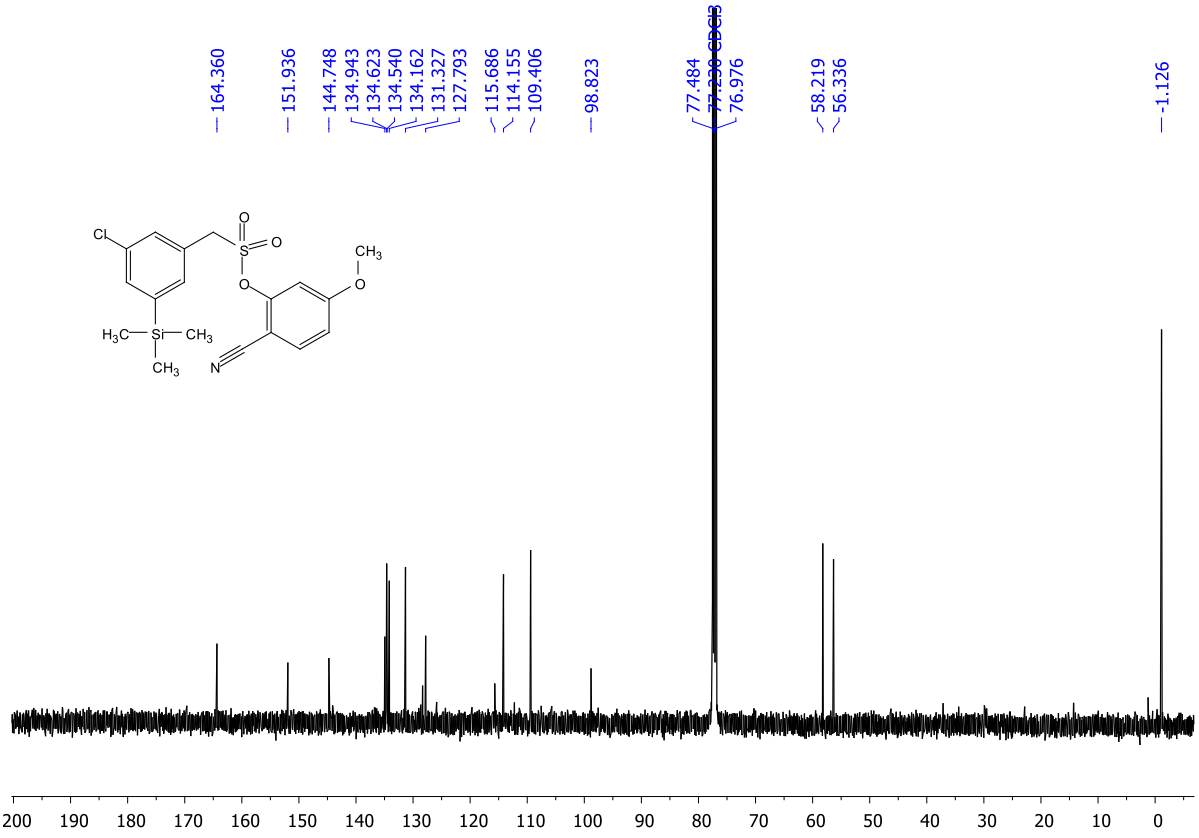


Figure S50: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2k**

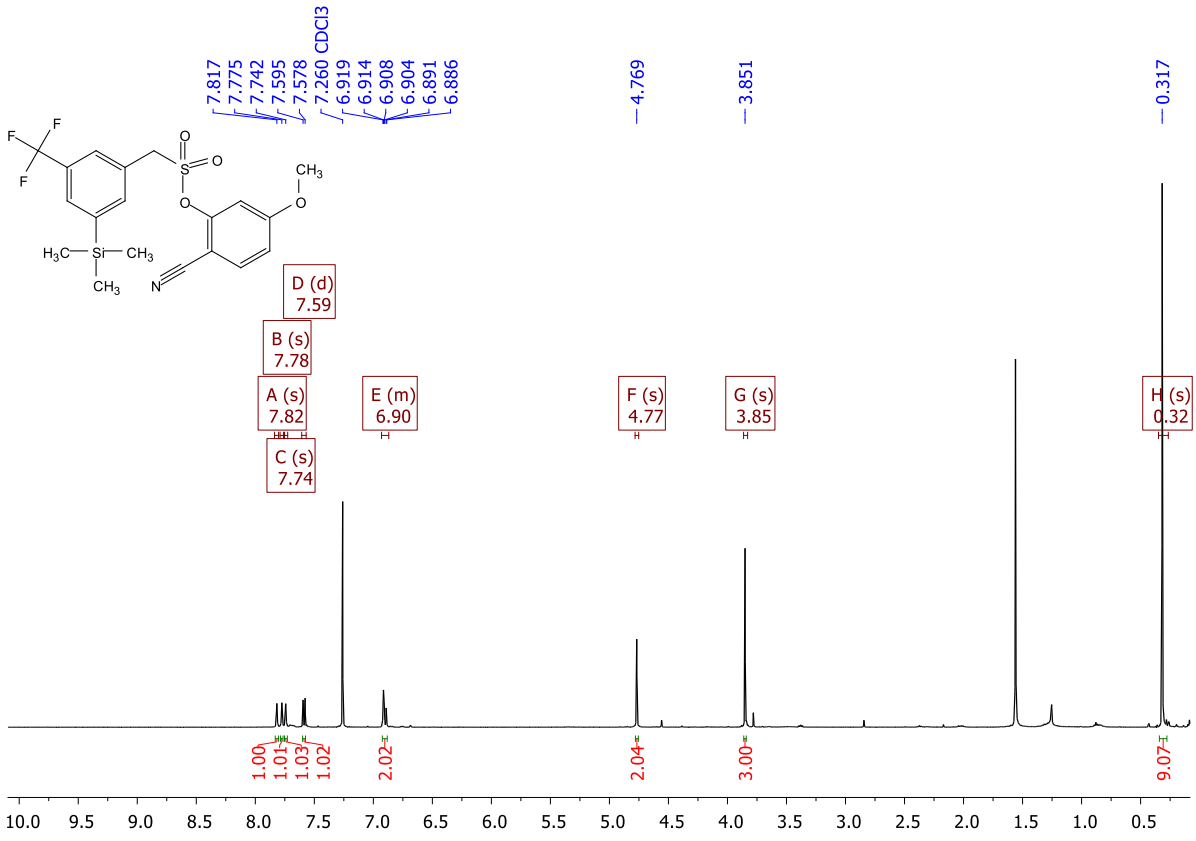


Figure S51: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2l**

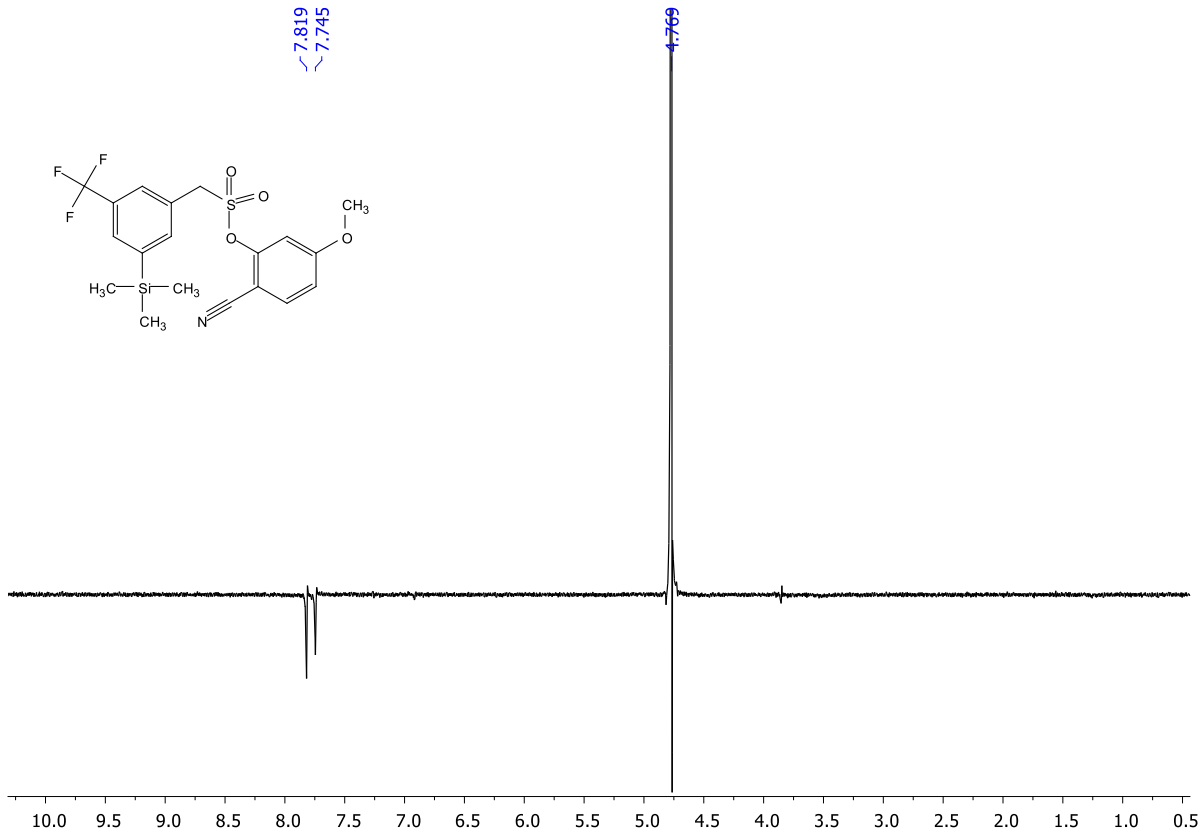


Figure S52: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2l**

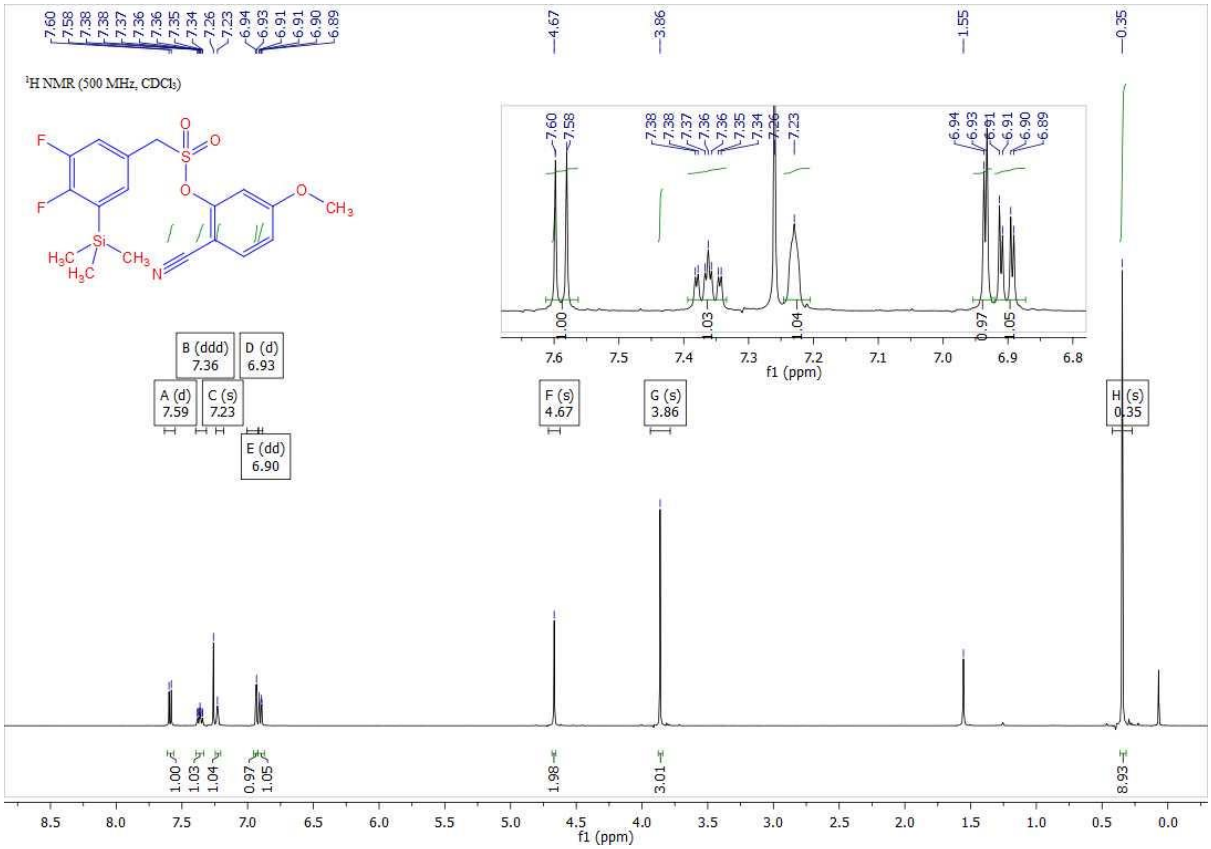


Figure S53: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2m**

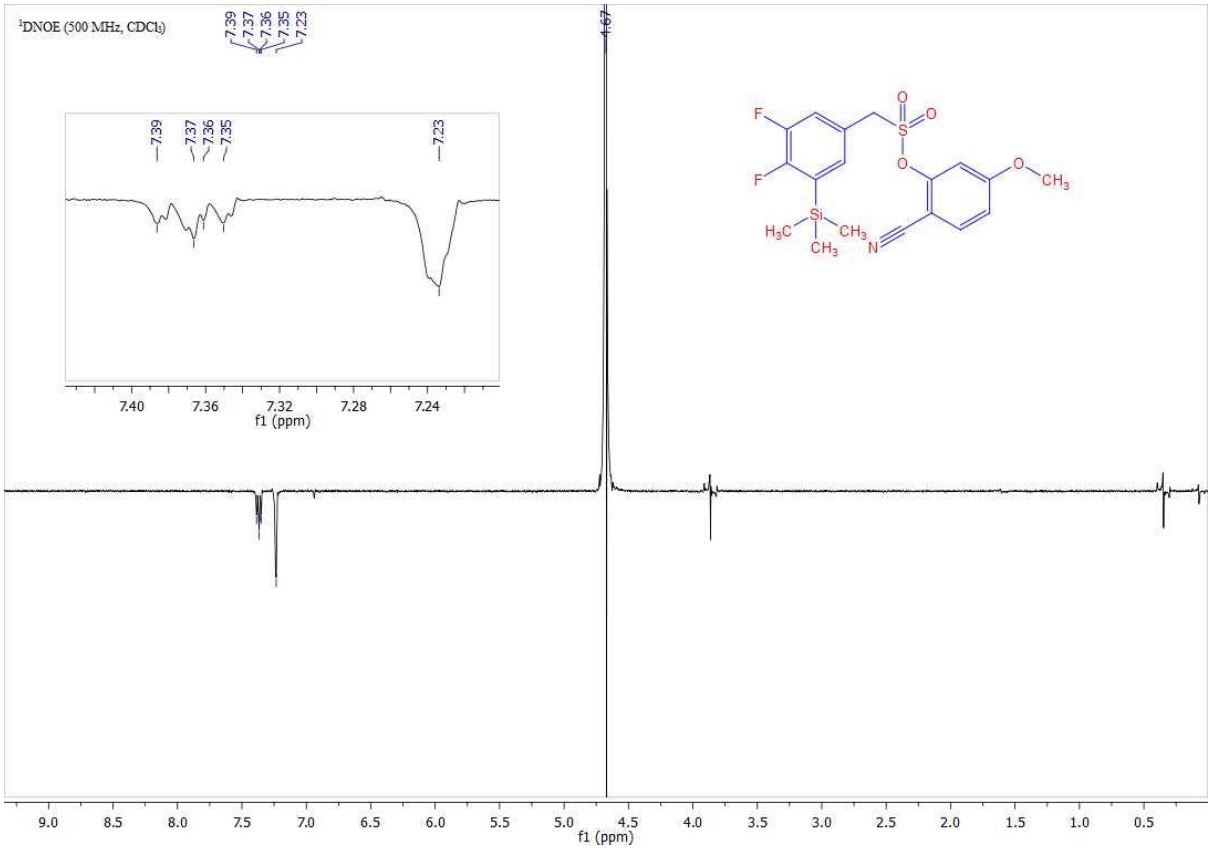


Figure S54: ^{1}D NOE spectrum (500 MHz, $CDCl_3$) of Compound **2m**

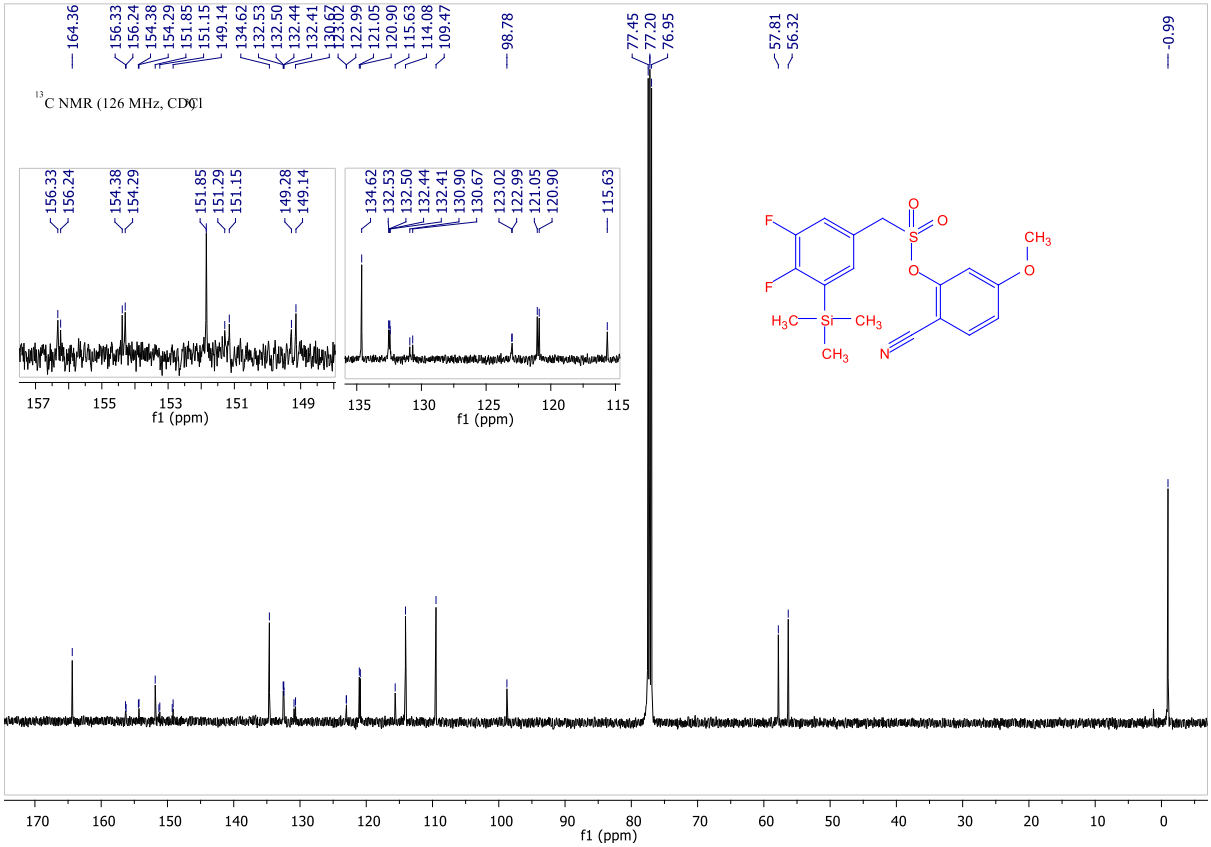


Figure S55: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2m**

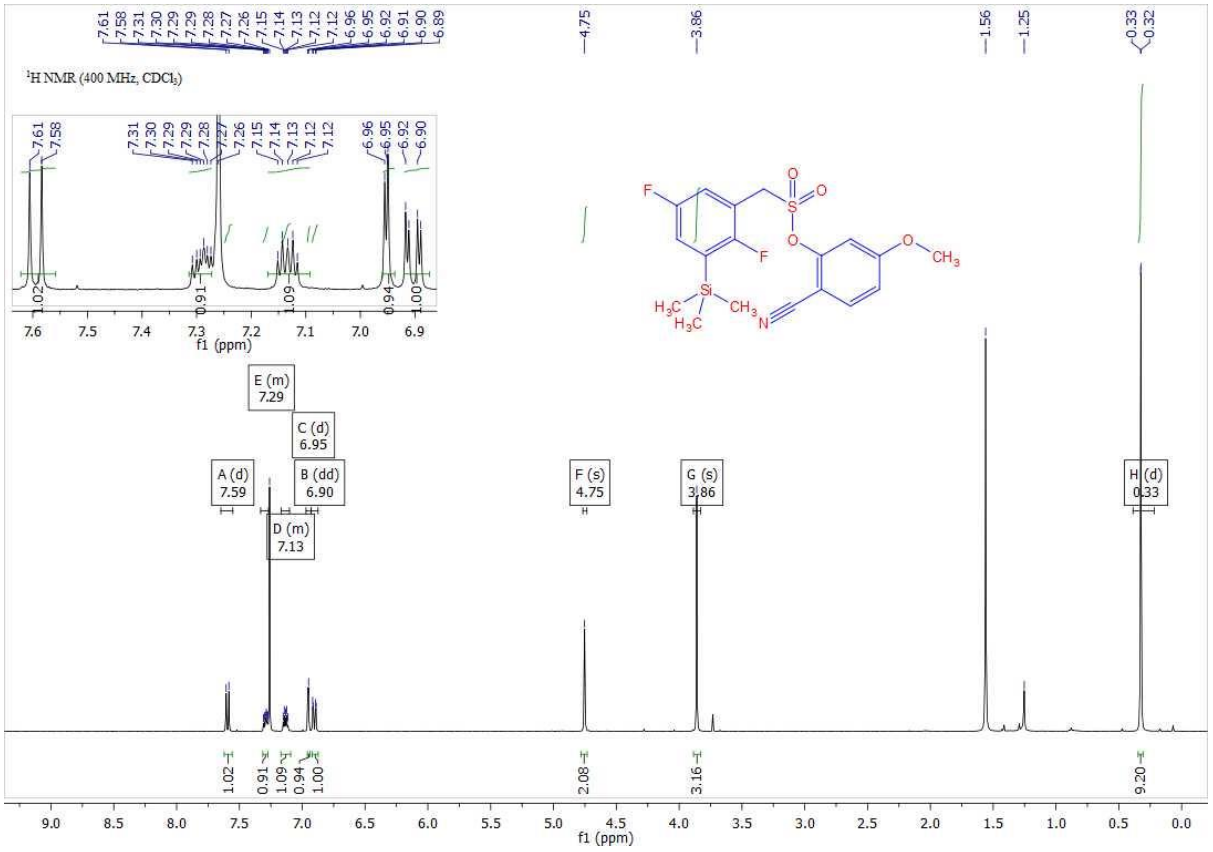


Figure S56: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **2n**

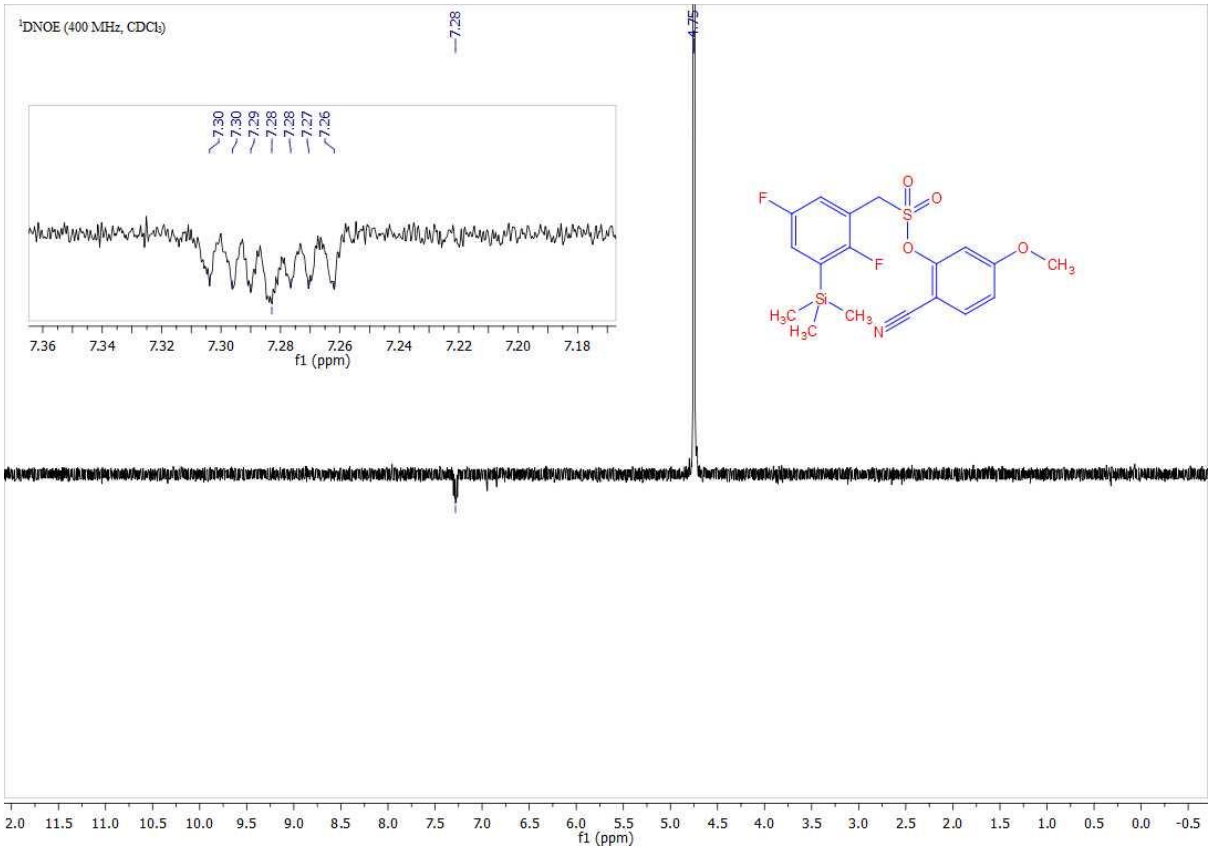


Figure S57: ^{1}D NOE spectrum (400 MHz, $CDCl_3$) of Compound **2n**

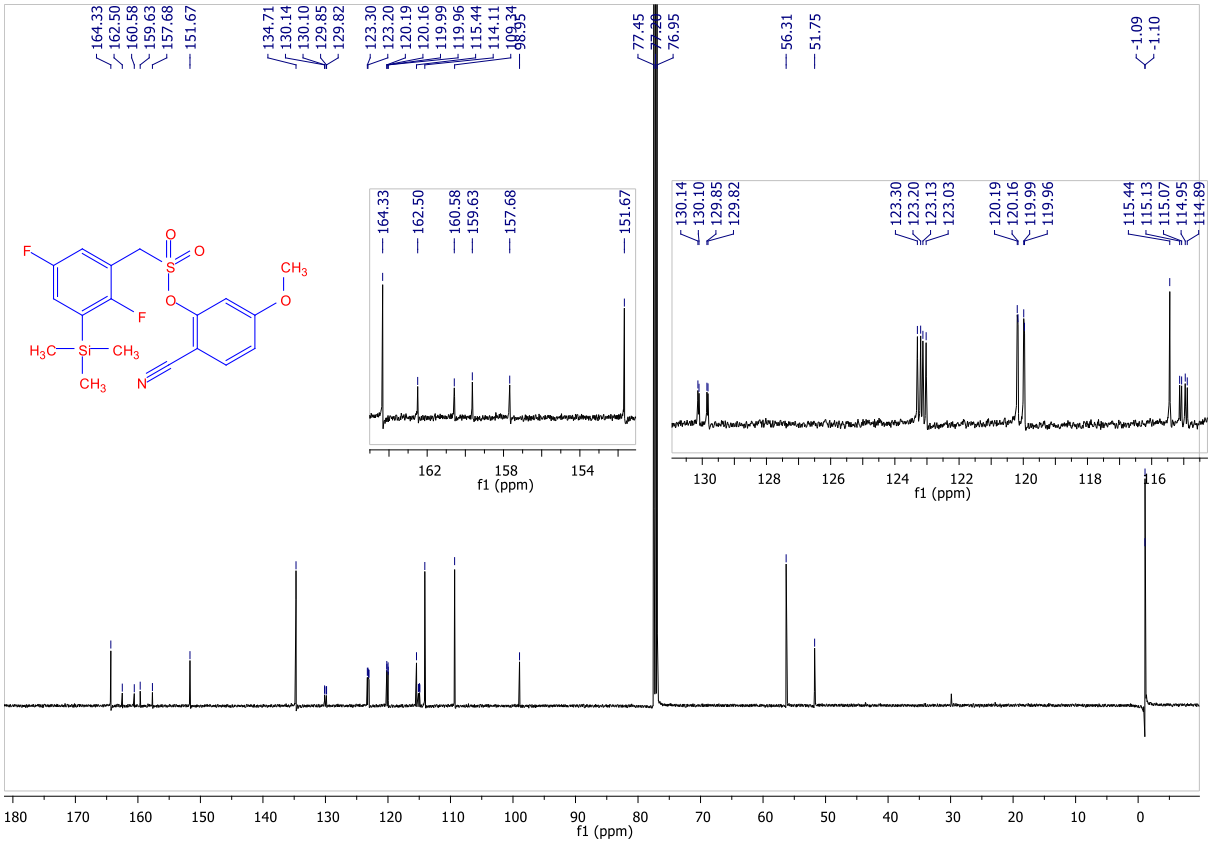


Figure S58: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2n**

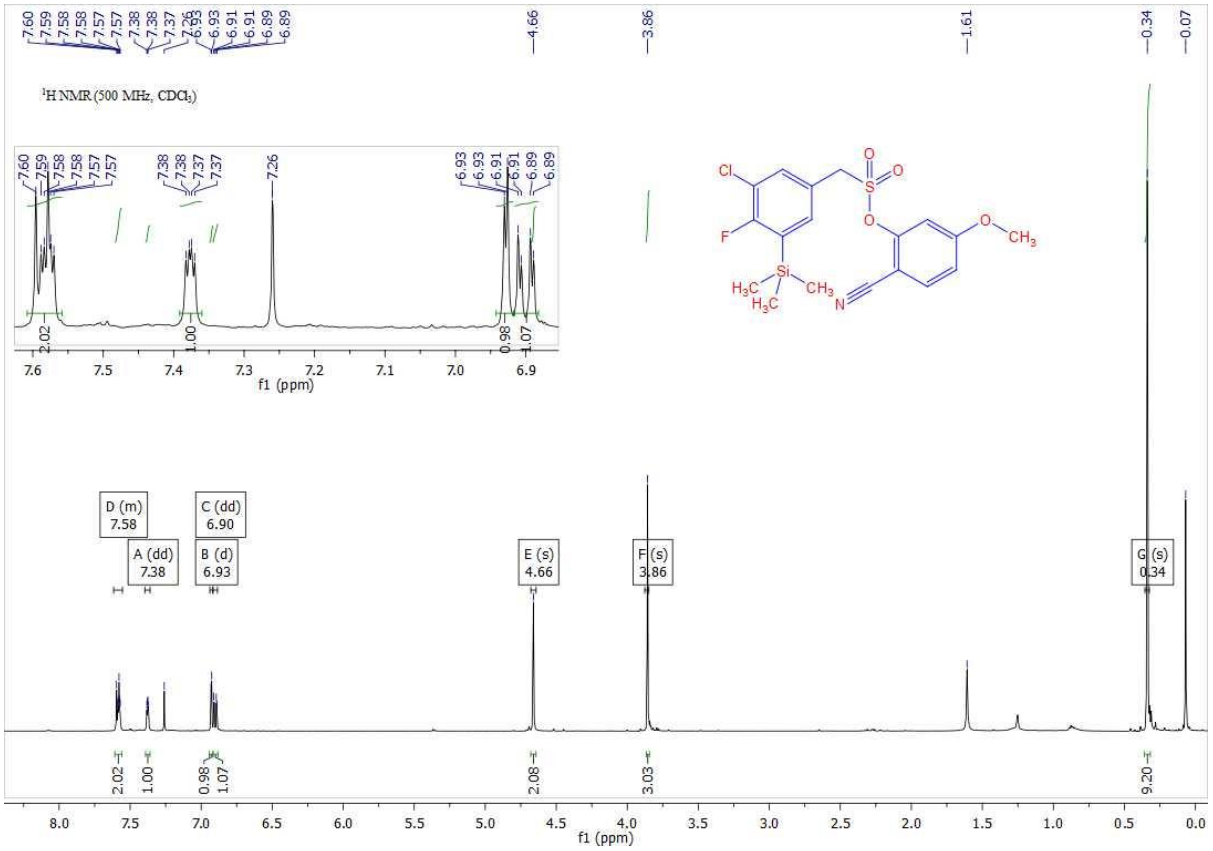


Figure S59: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2o**

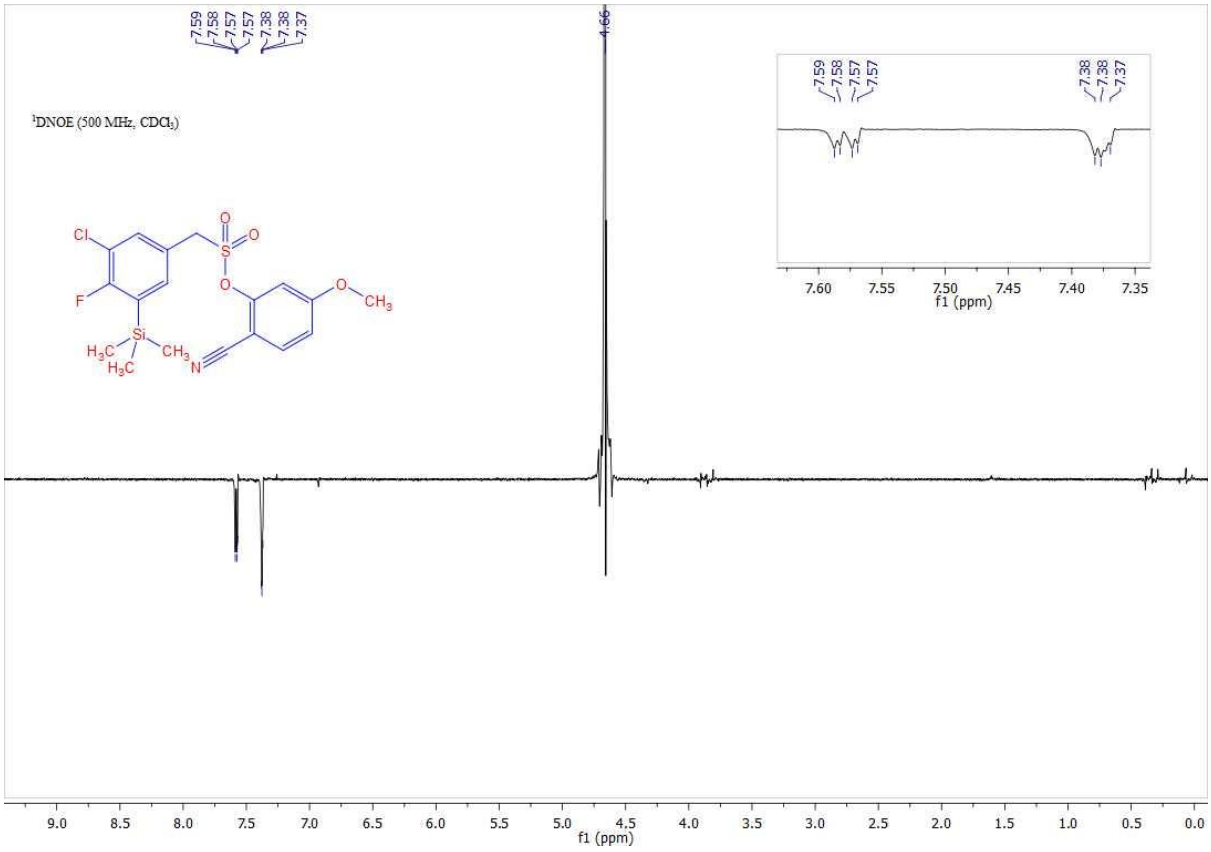


Figure S60: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2o**

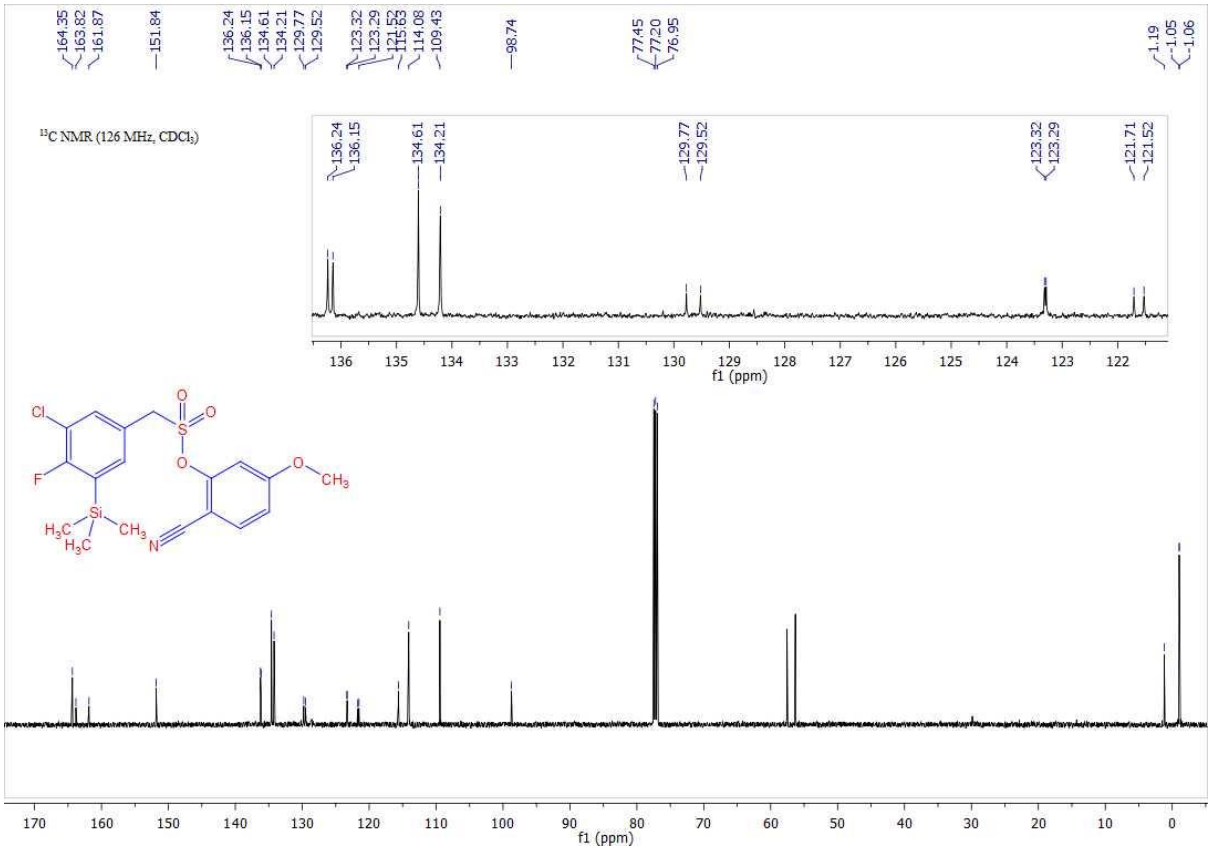


Figure S61: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2o**

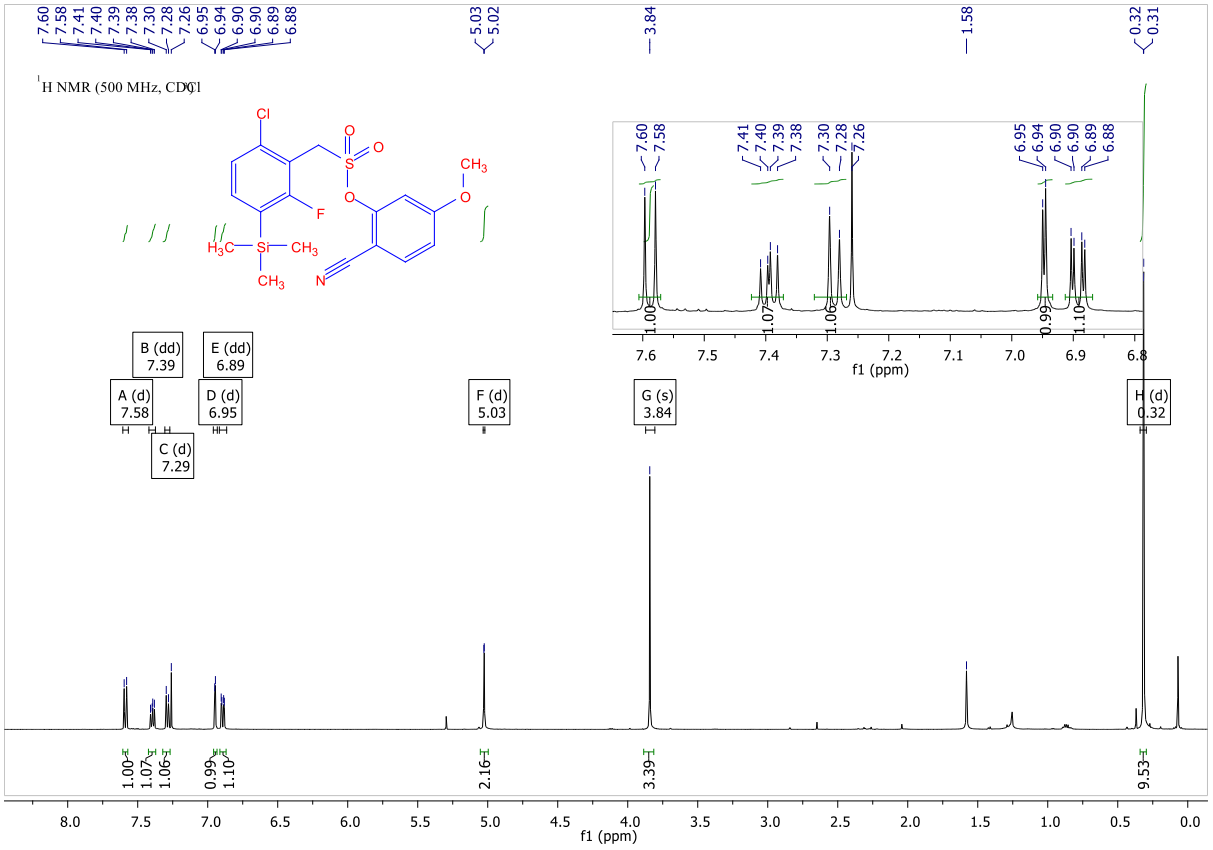


Figure S62: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2p**

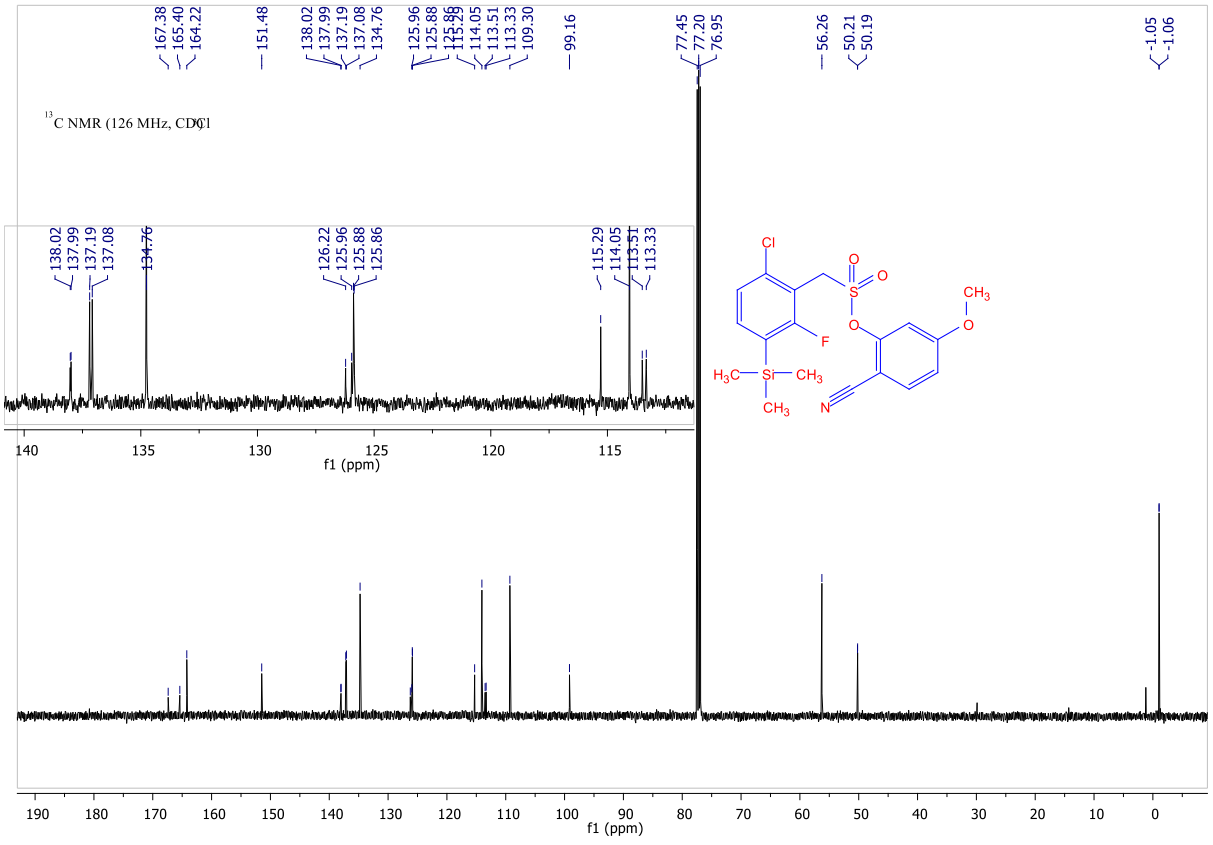


Figure S63: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2p**

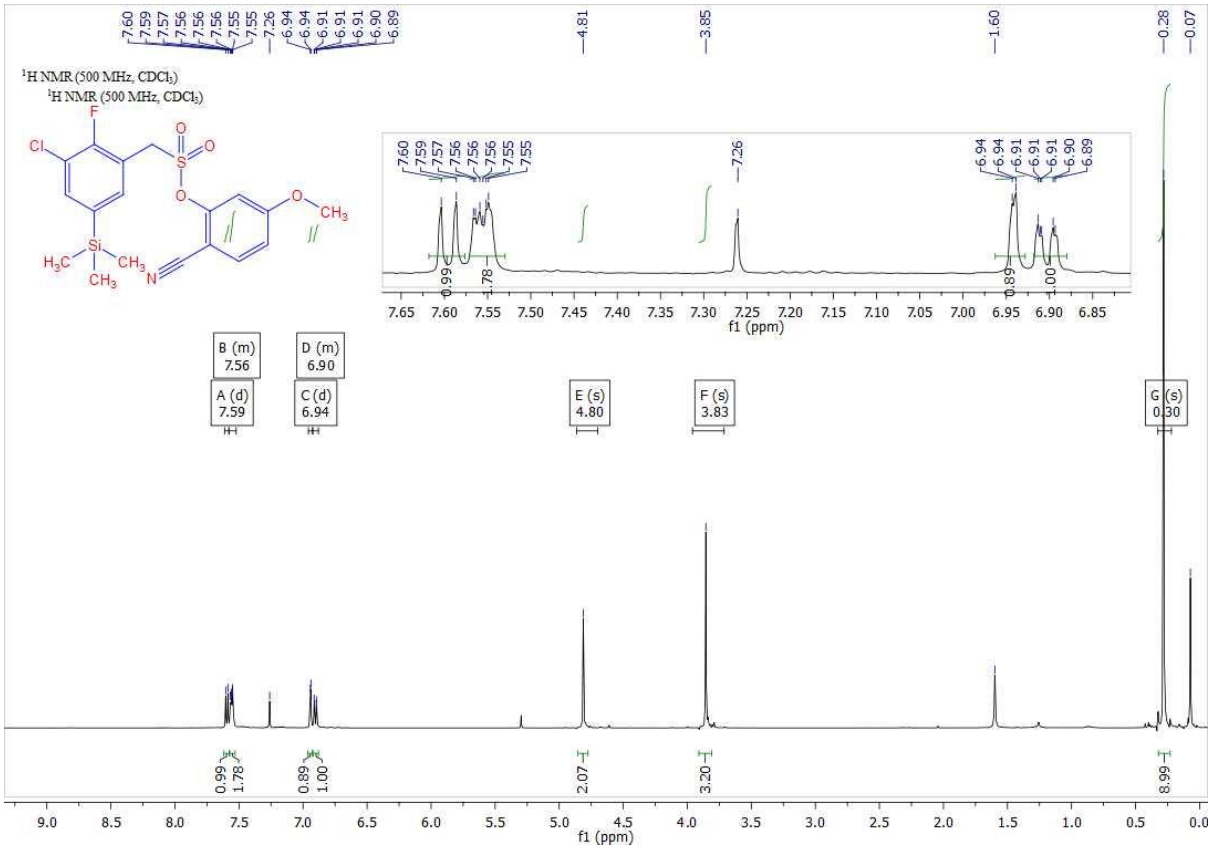


Figure S64: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2q**

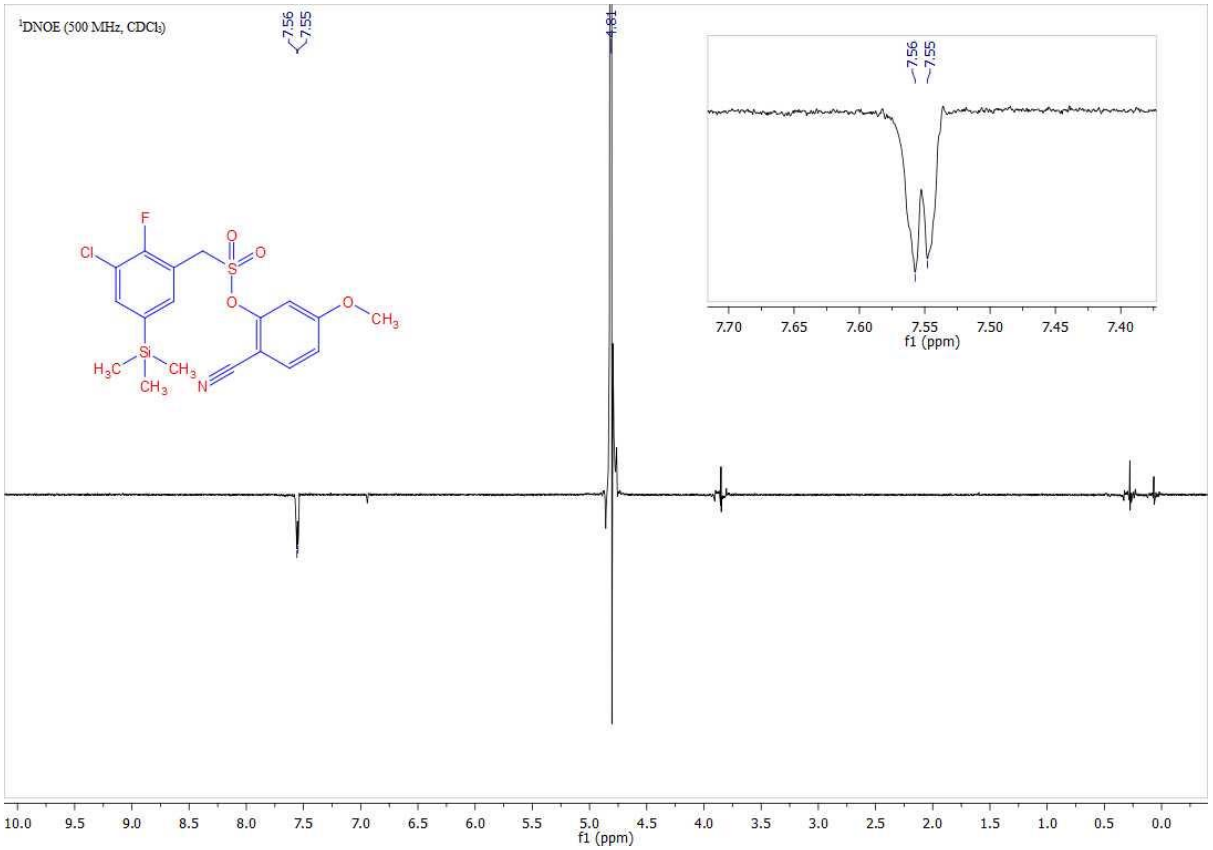


Figure S65: ^{1}D NOE NMR spectrum (126 MHz, $CDCl_3$) of Compound **2q**

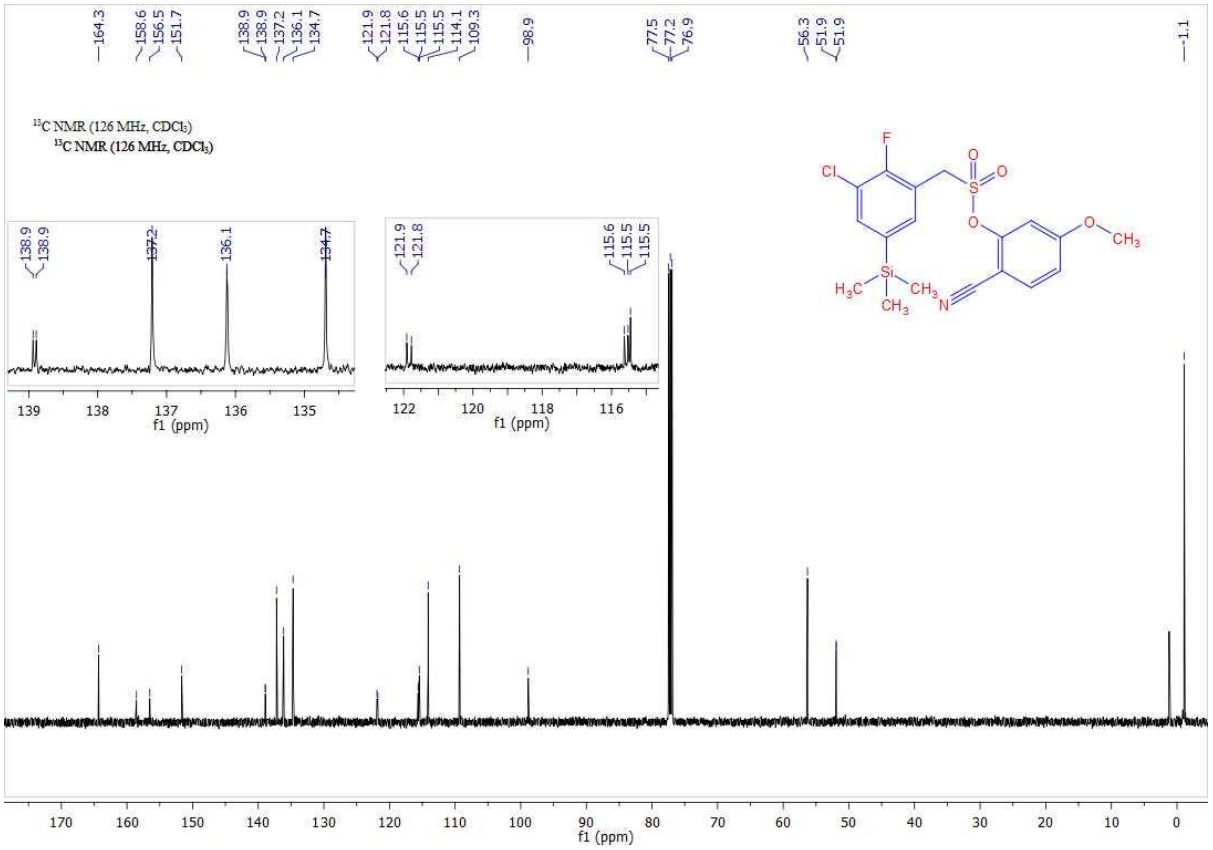


Figure S66: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2q**

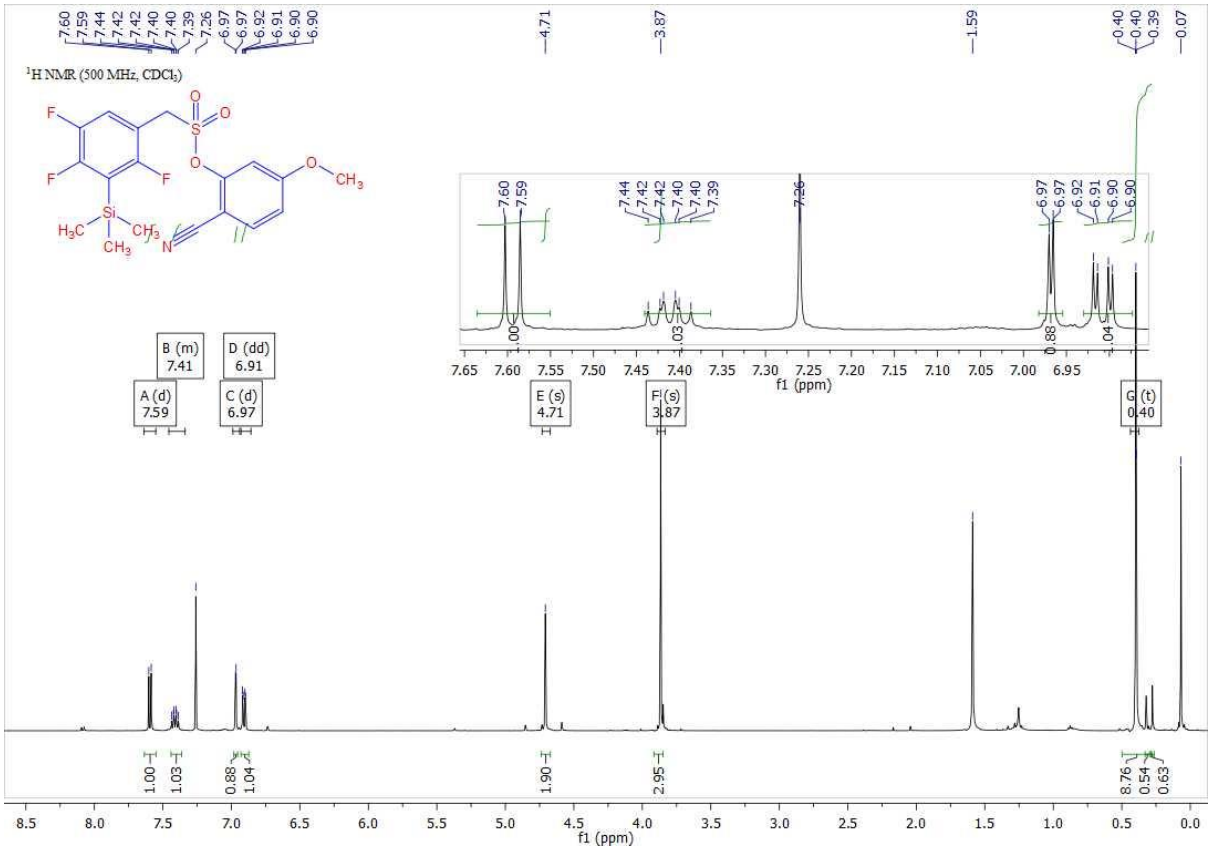


Figure S67: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2r**

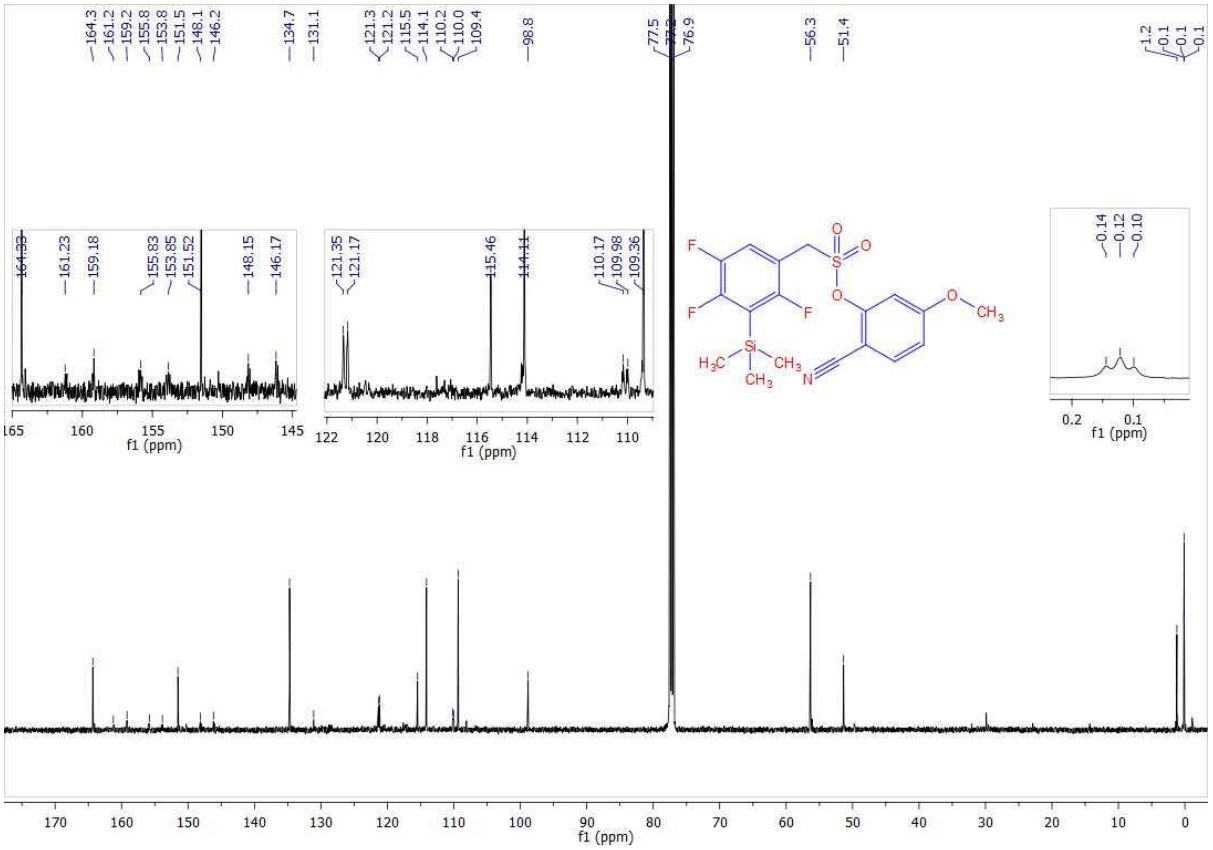


Figure S68: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2r**

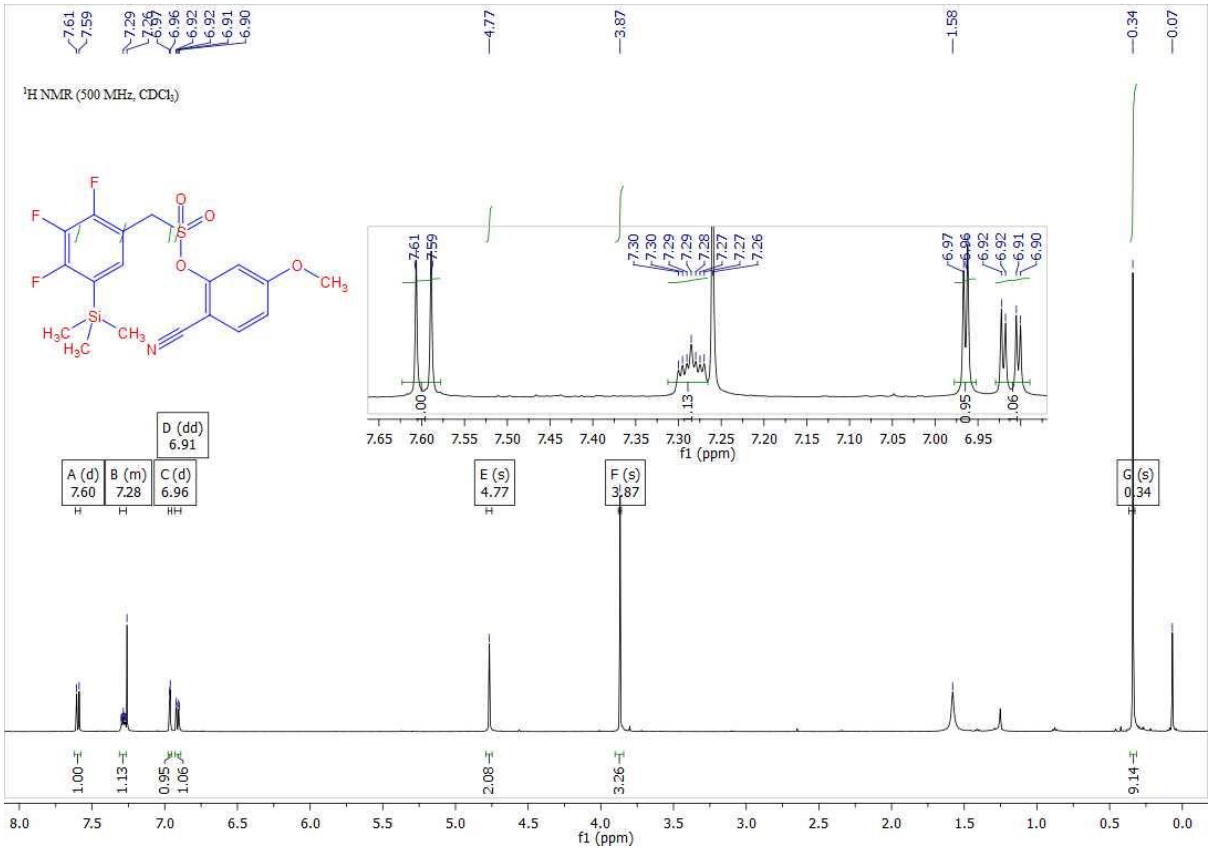


Figure S69: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2s**

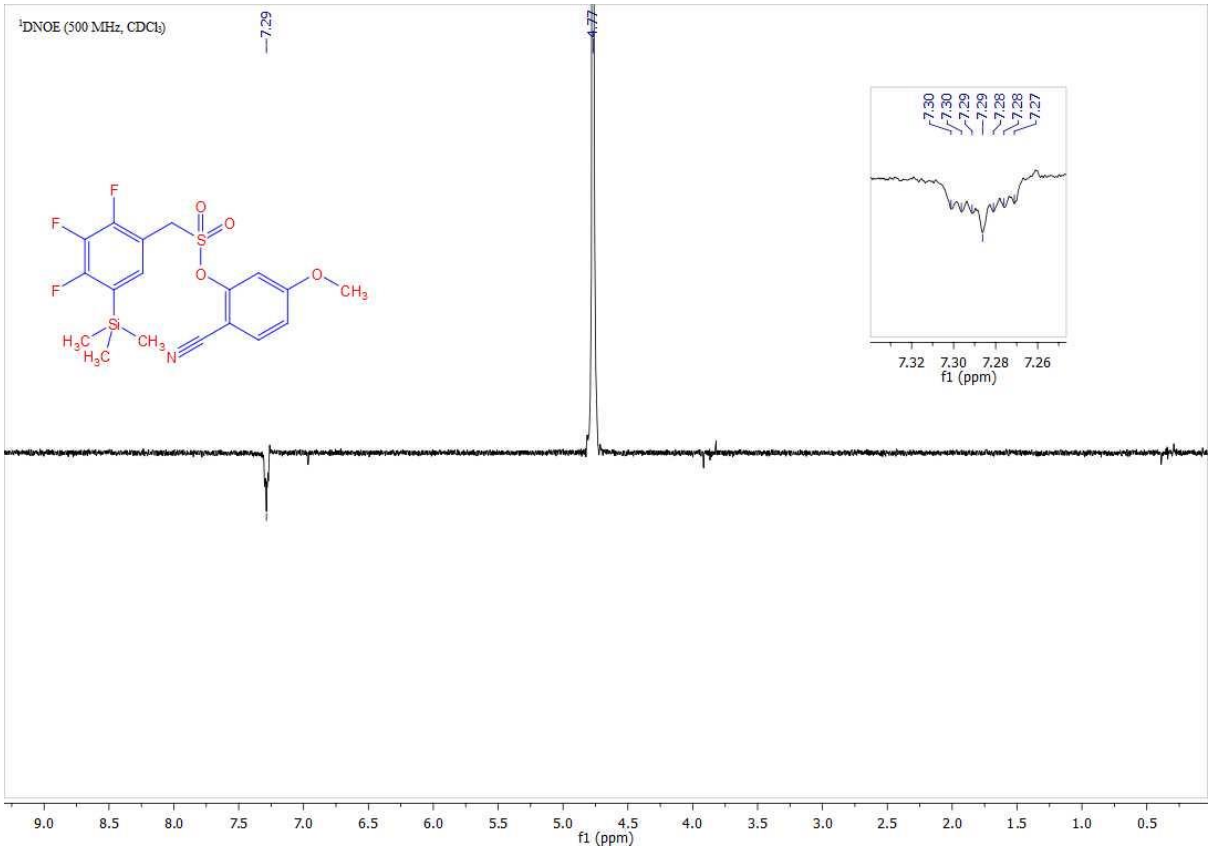


Figure S70: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2s**

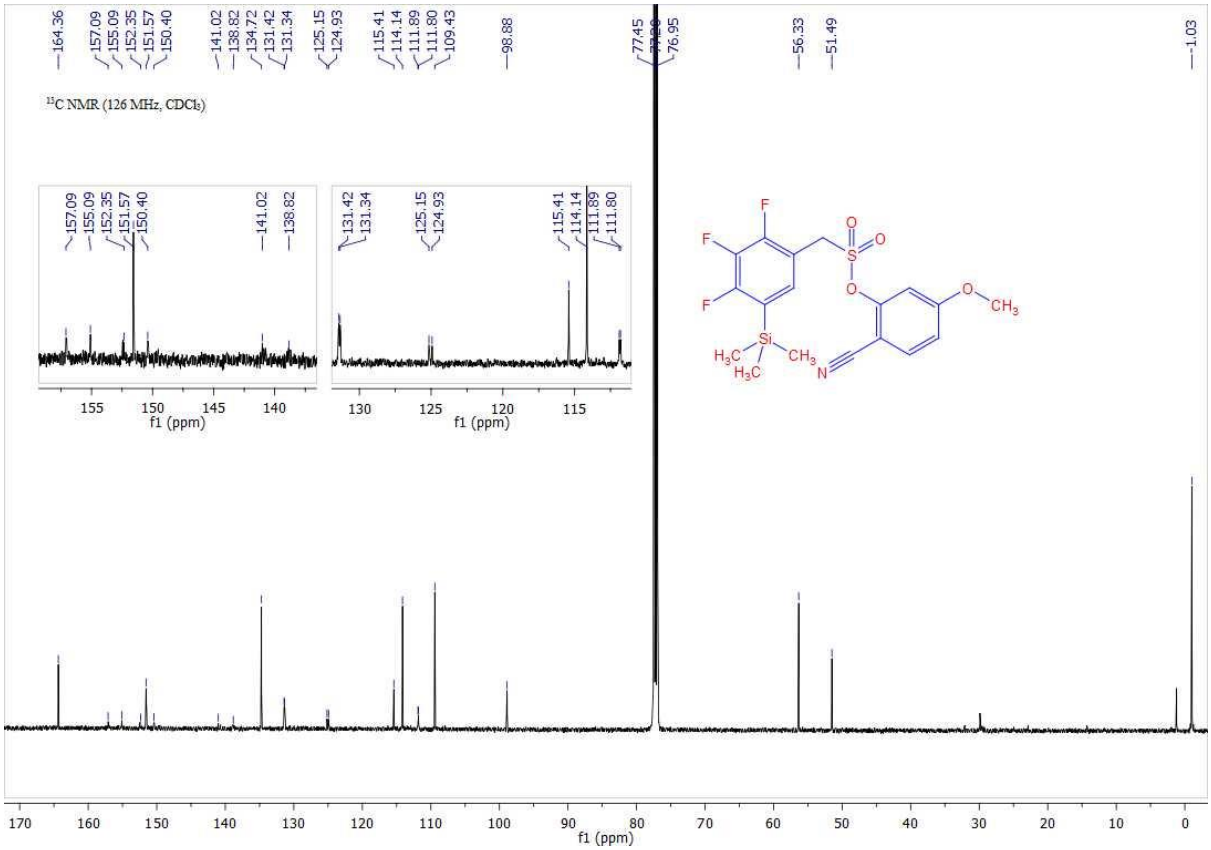


Figure S71: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2s**

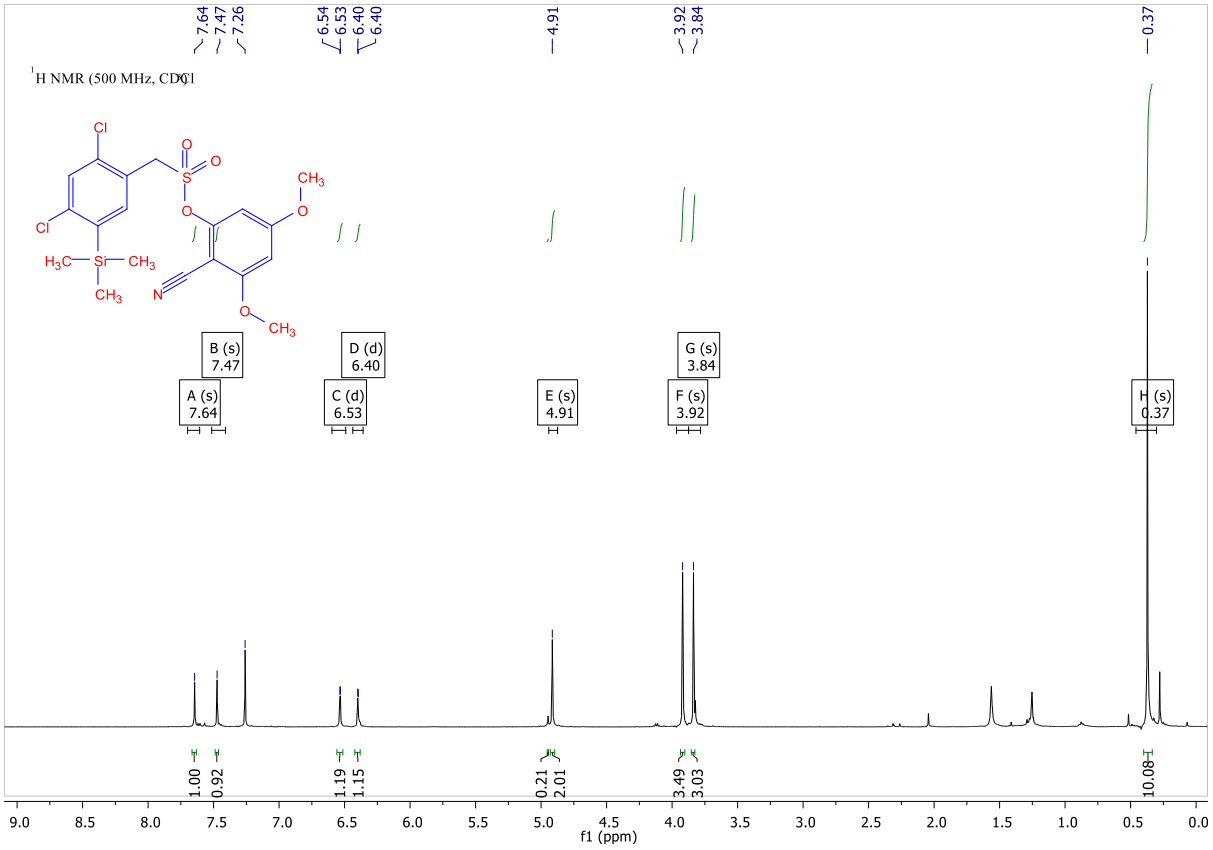


Figure S72: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2t**

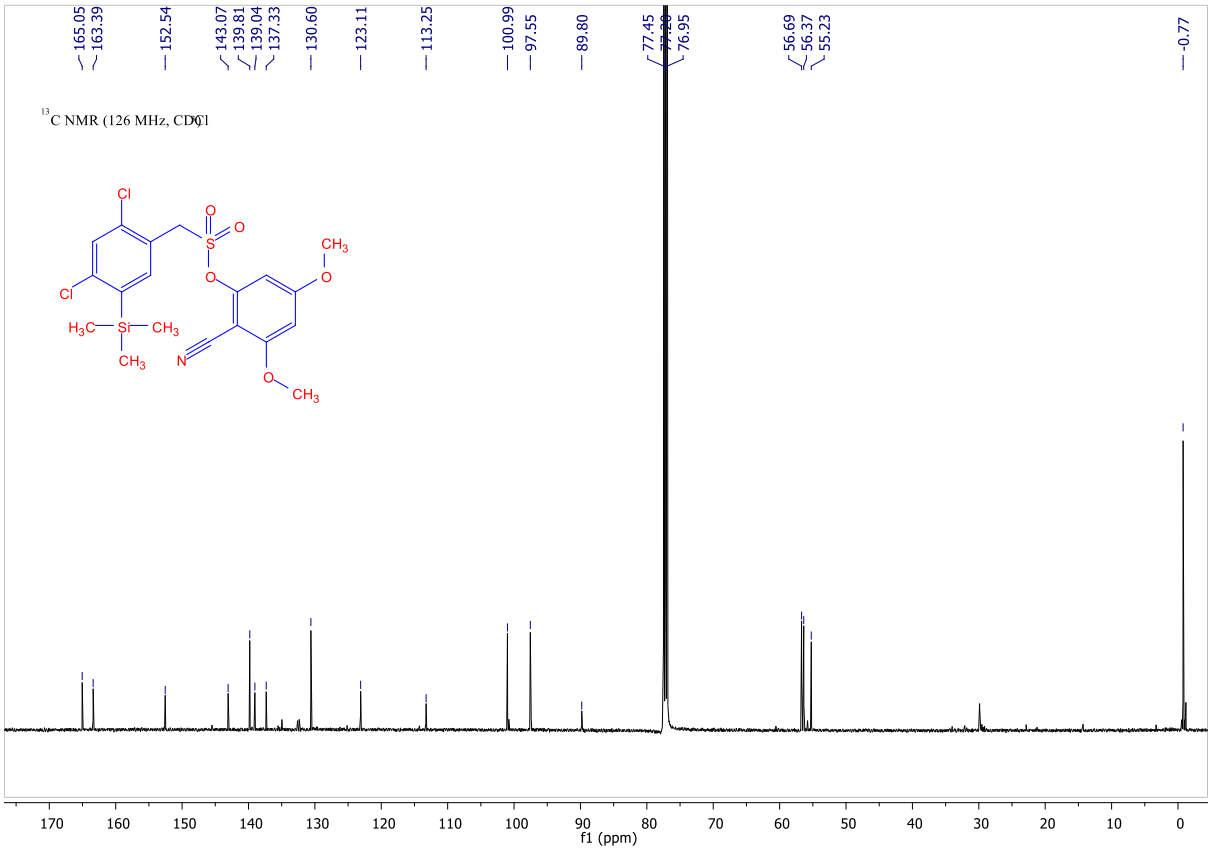


Figure S73: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2t**

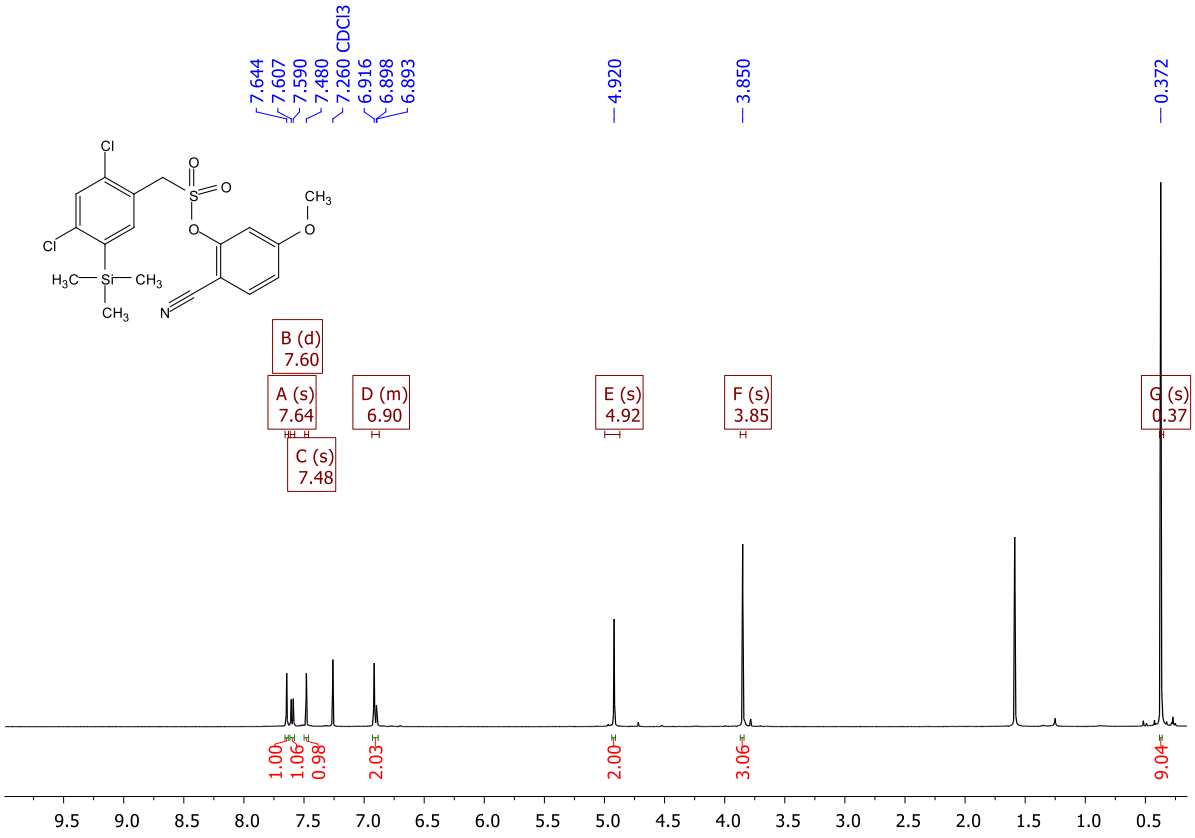


Figure S74: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **2t-DG$_4$**

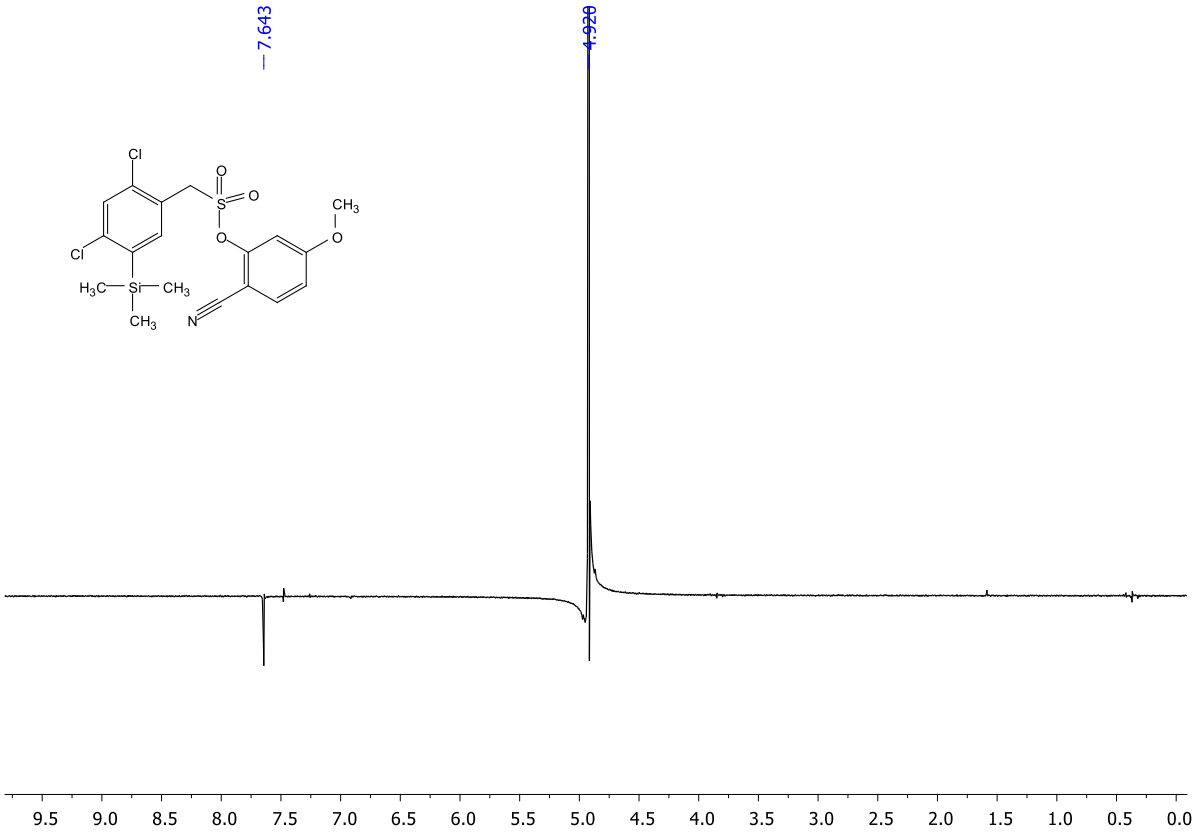


Figure S75: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **2t-DG$_4$**

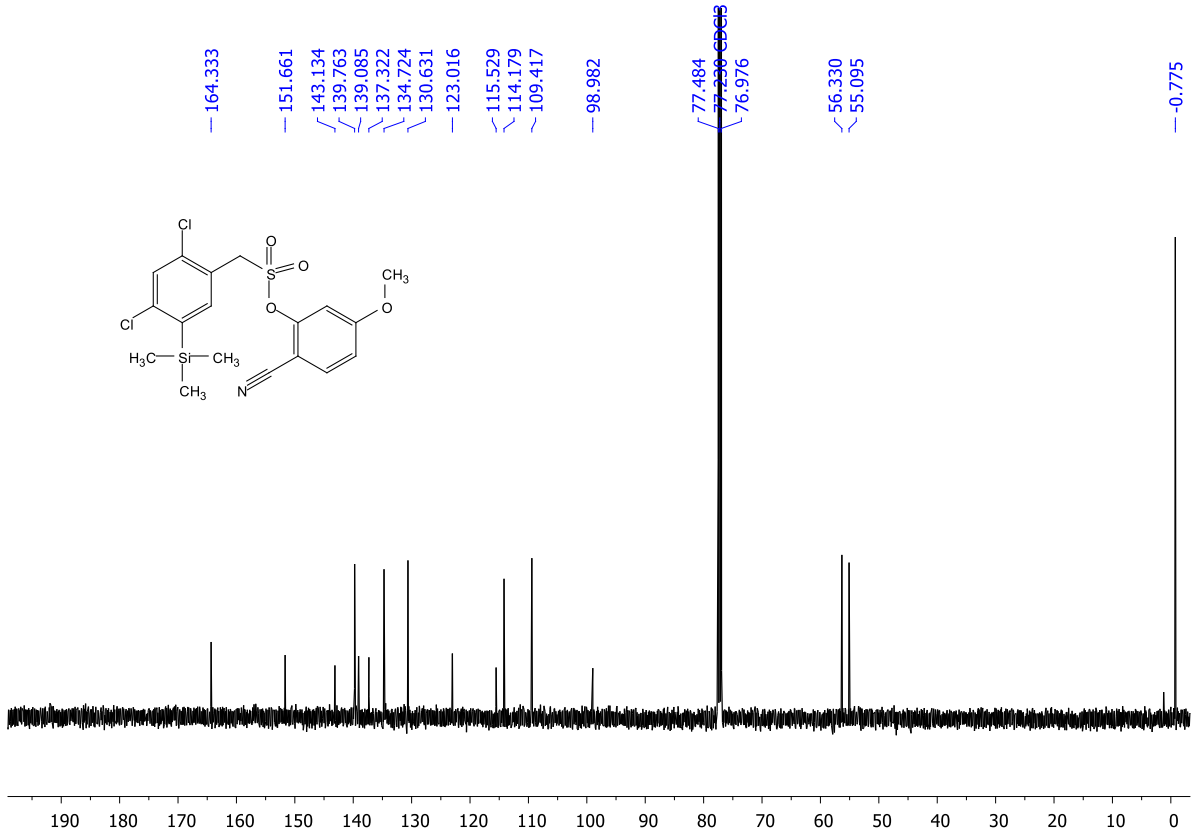


Figure S76: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **2t-DG4**

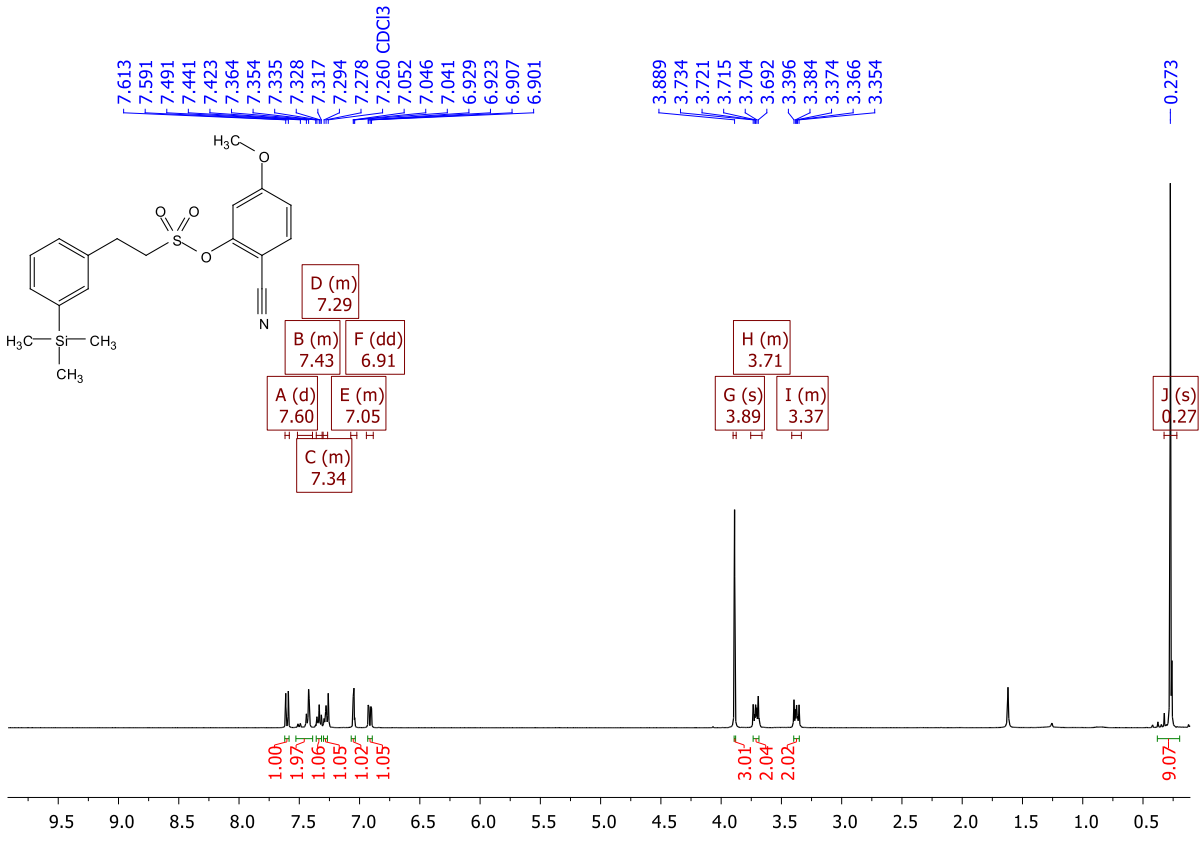


Figure S77: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **3a$_{mono}$**

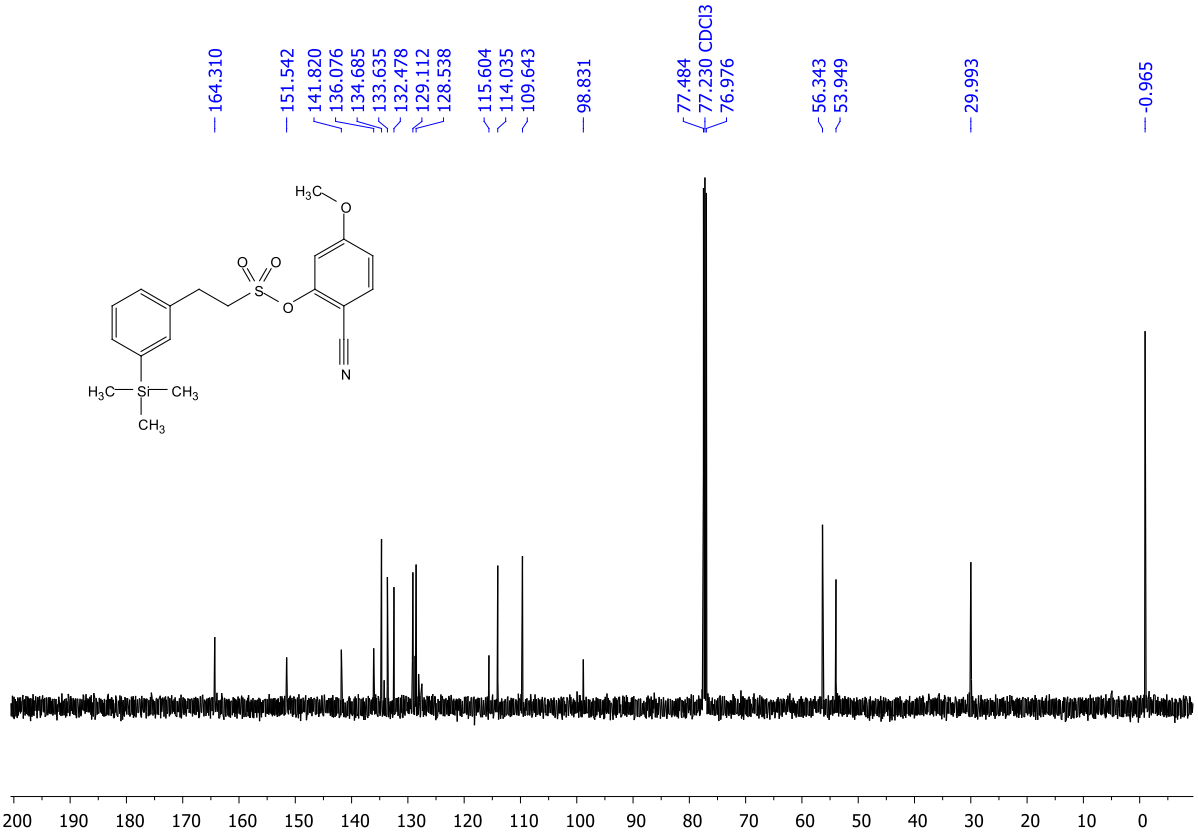


Figure S78: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **3a$_{mono}$**

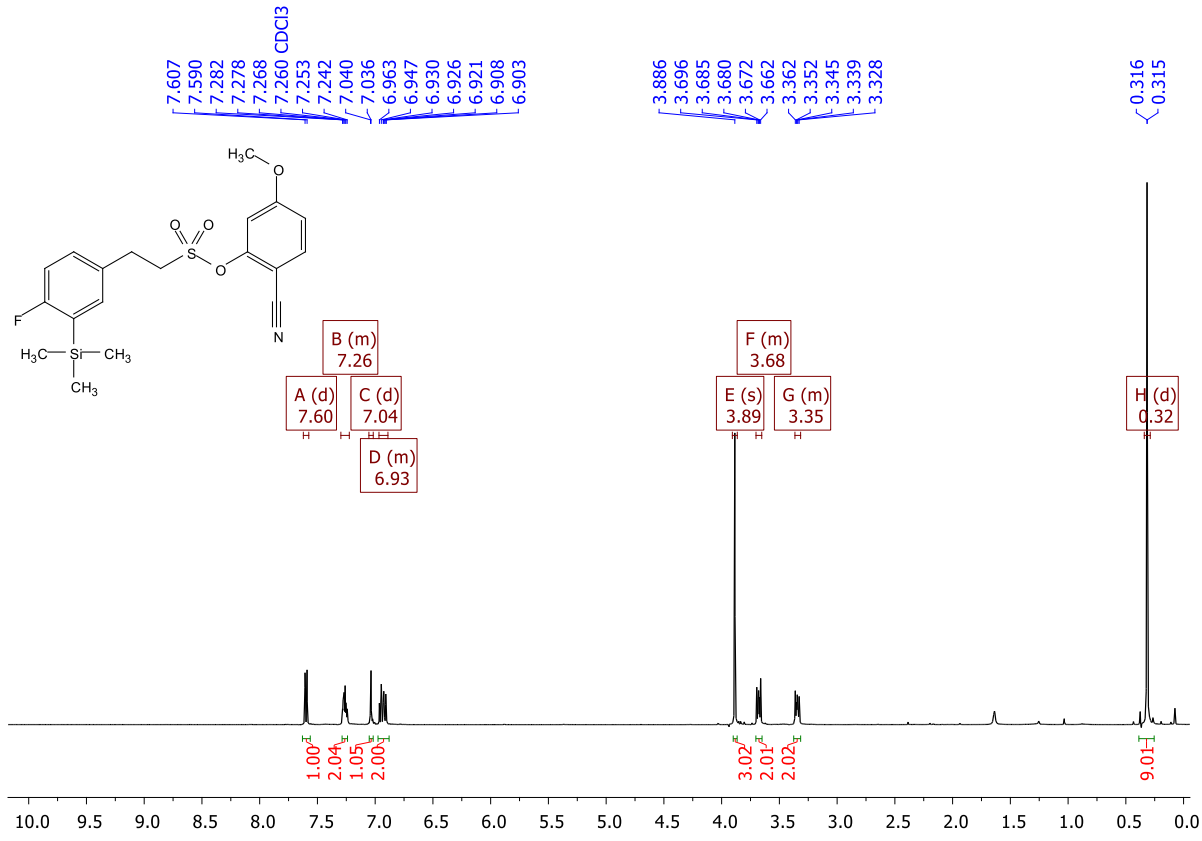


Figure S79: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **3b$_{mono}$**

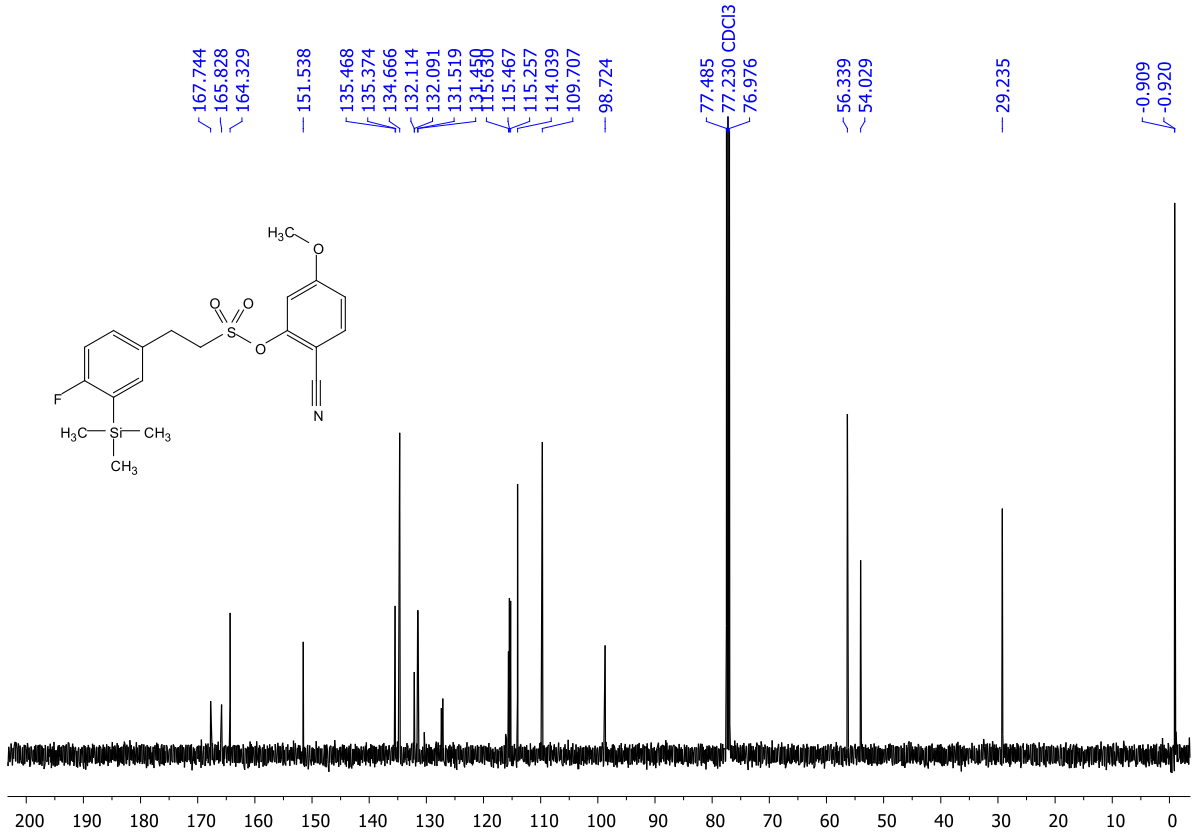


Figure S80: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **3b$_{mono}$**

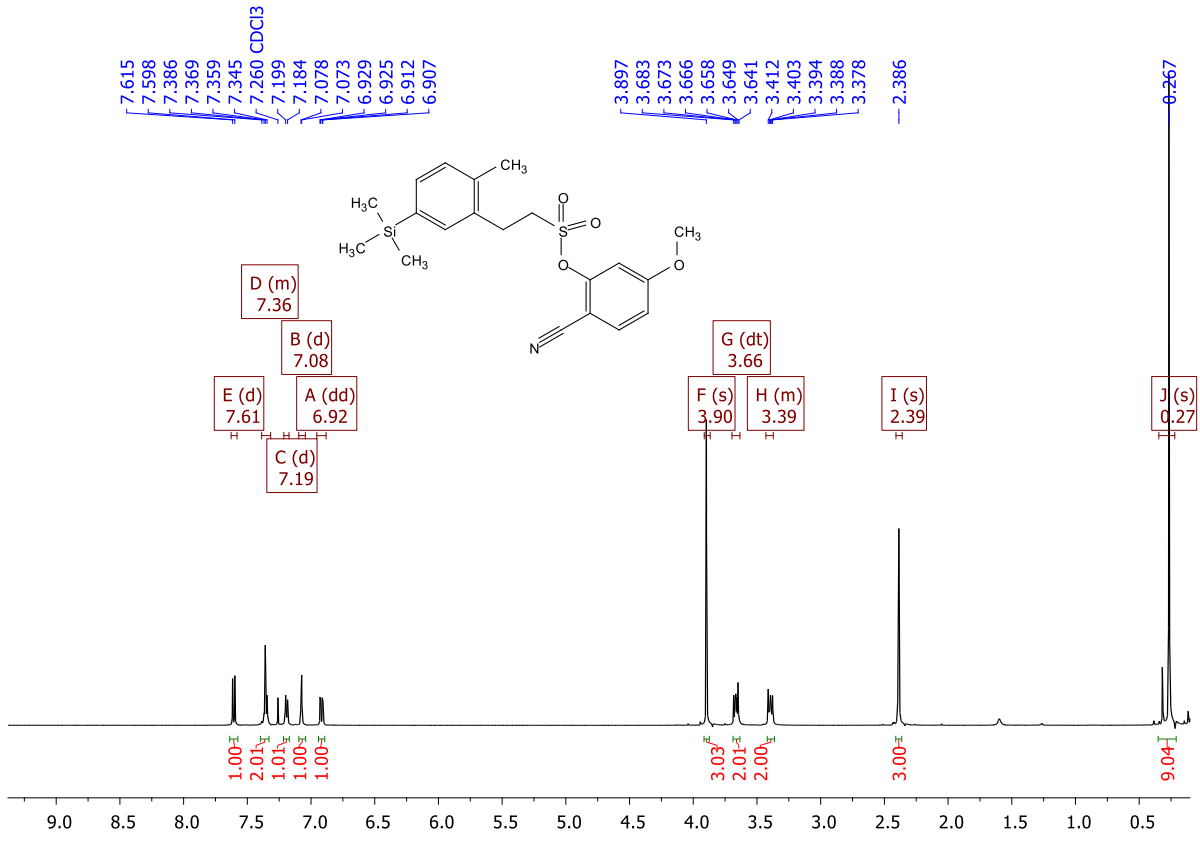


Figure S81: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **3c**

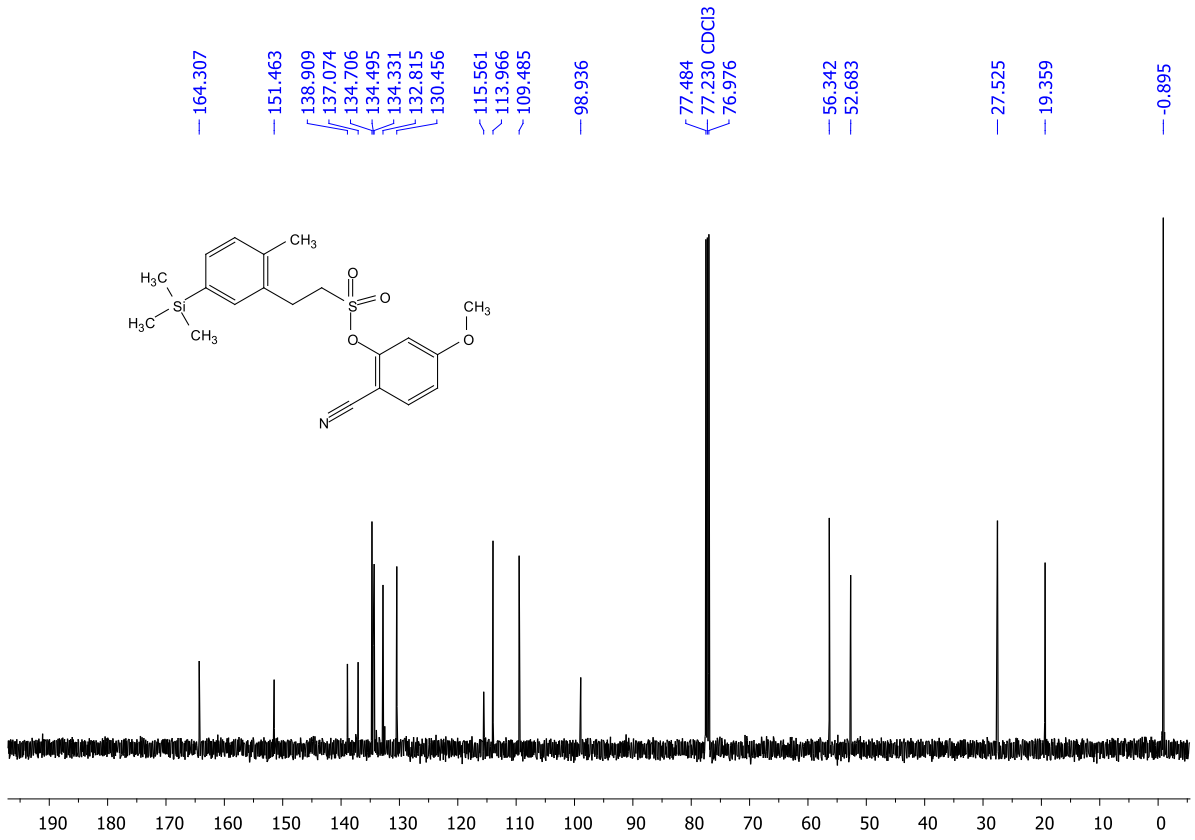


Figure S82: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **3c**

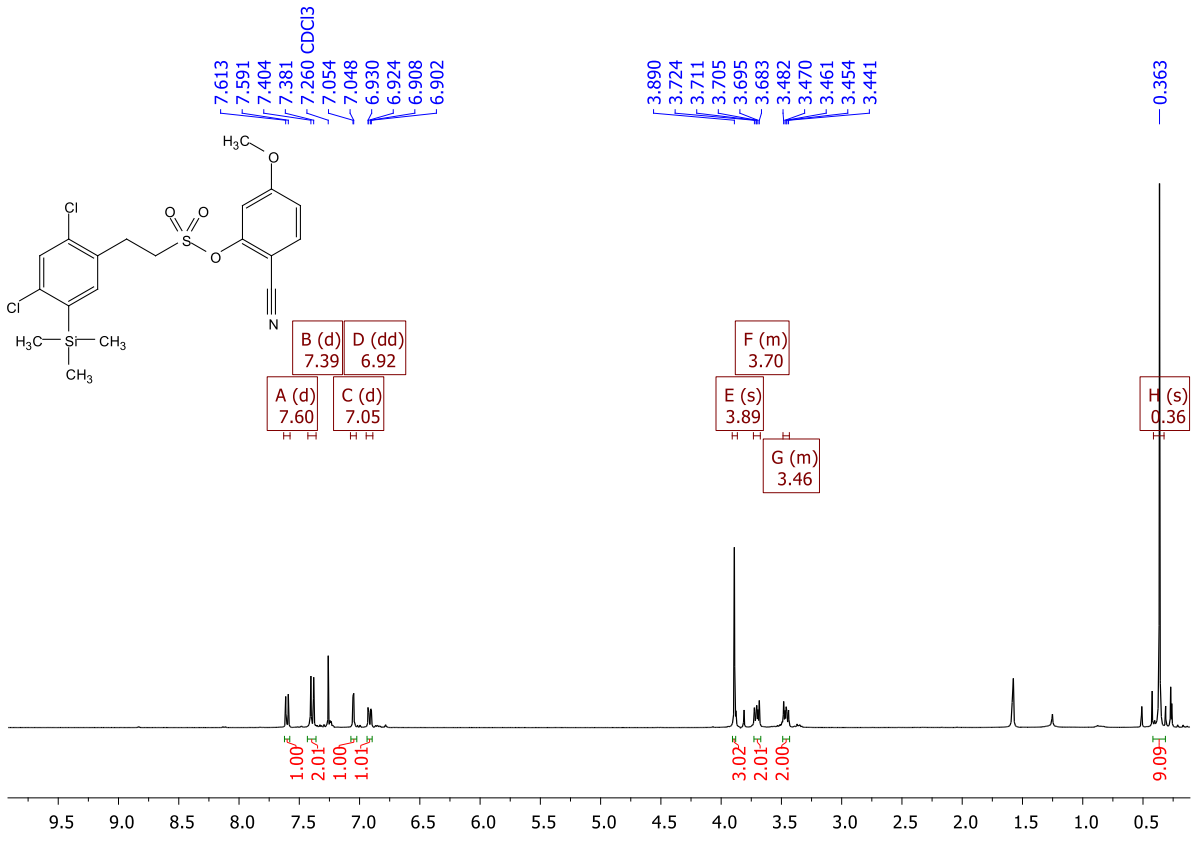


Figure S83: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **3d**

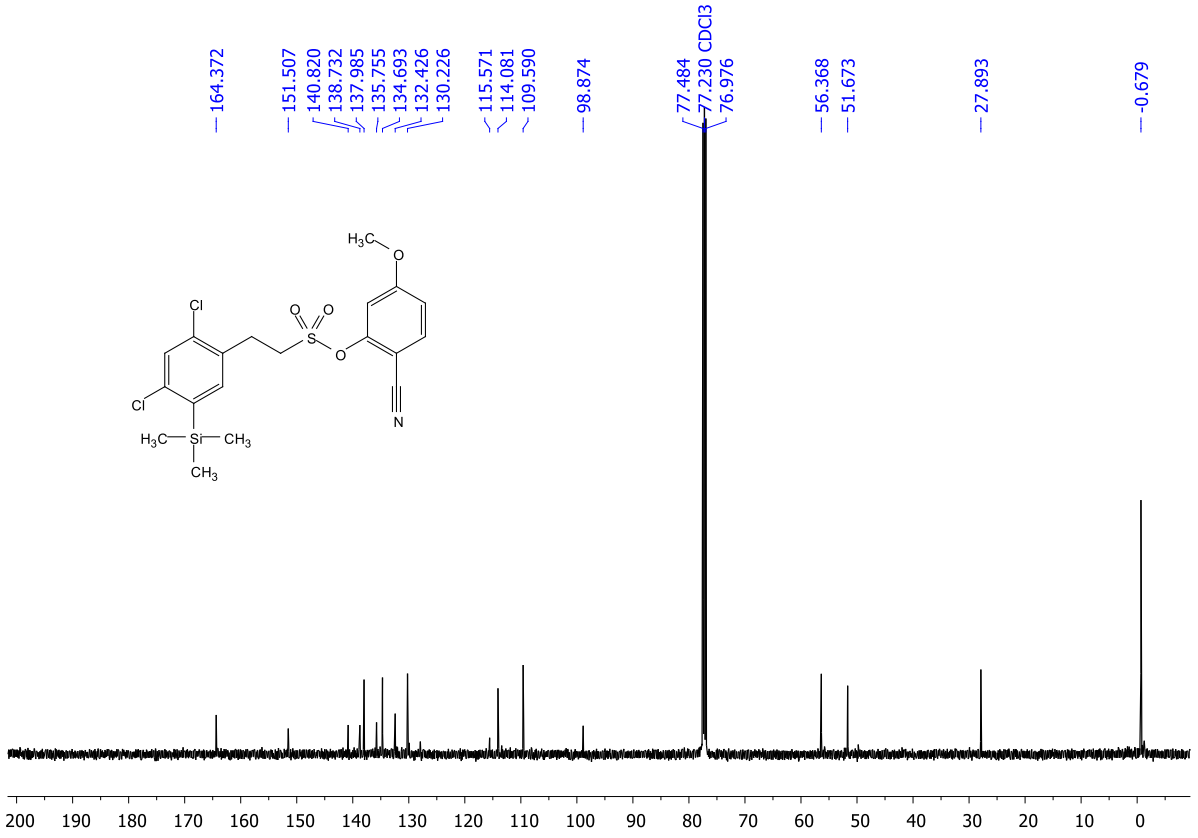


Figure S84: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **3d**

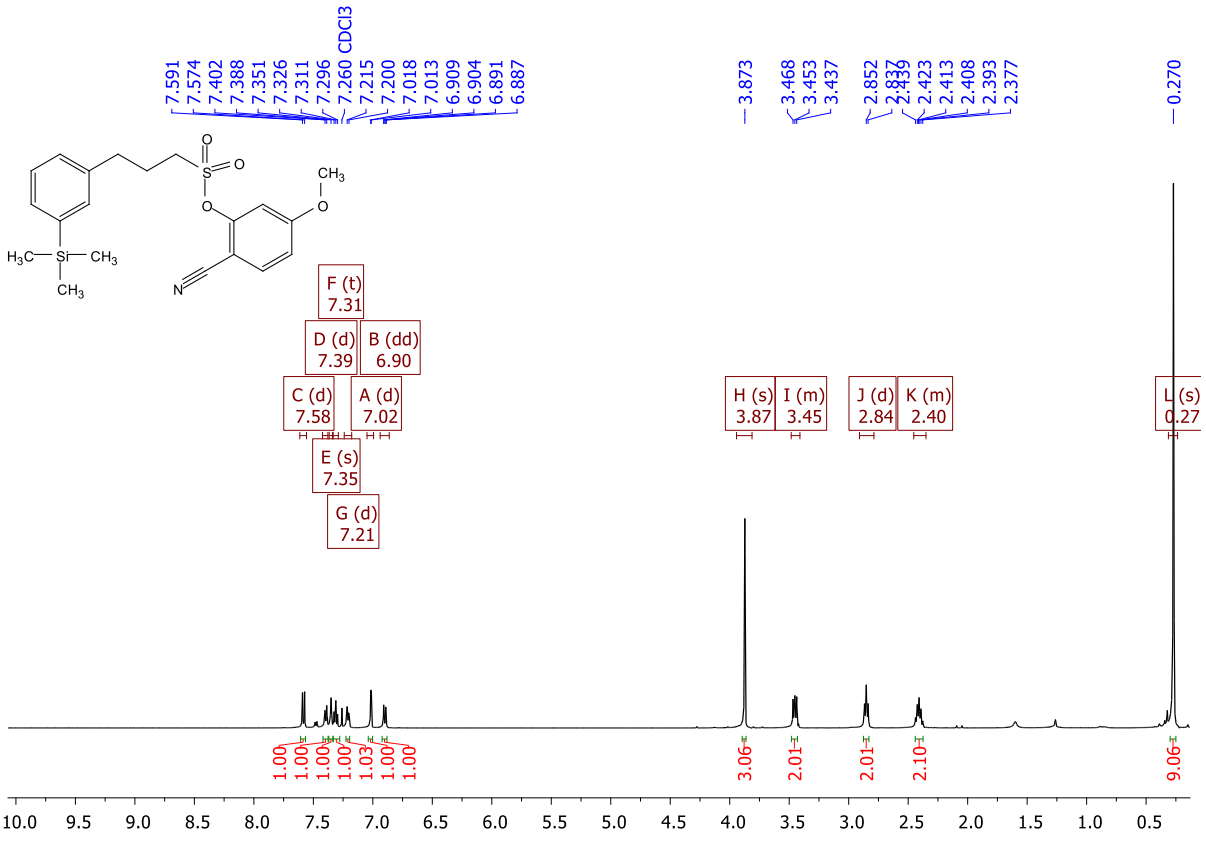


Figure S85: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **4a$_{mono}$**

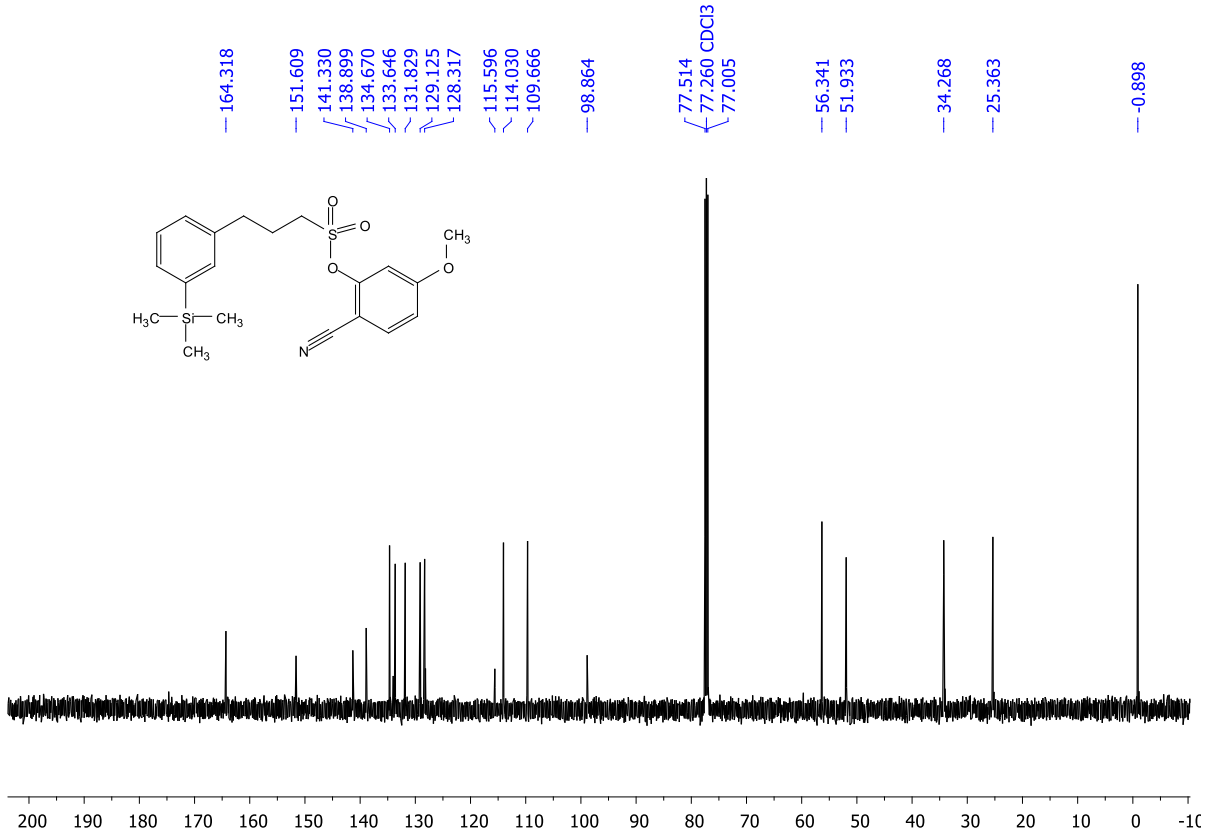


Figure S86: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **4a$_{mono}$**

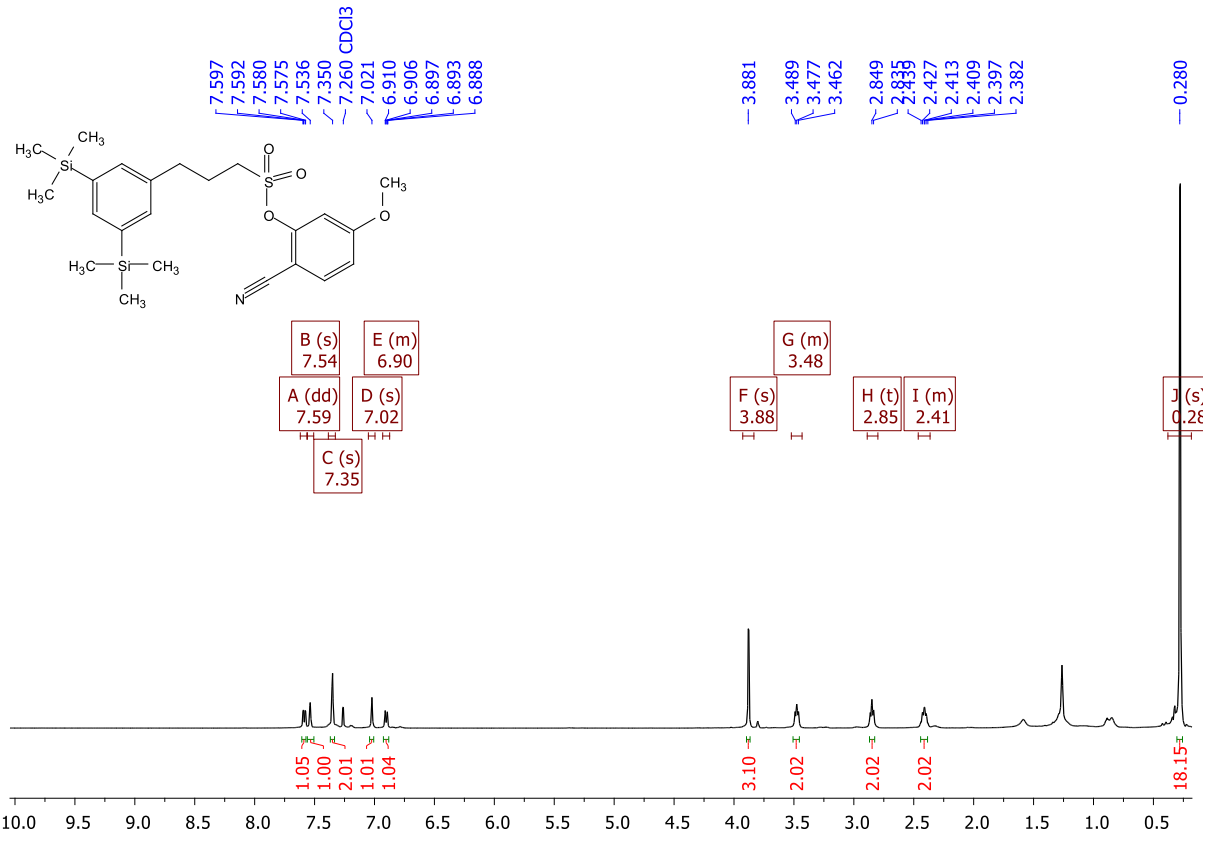


Figure S87: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **4b$_{di}$**

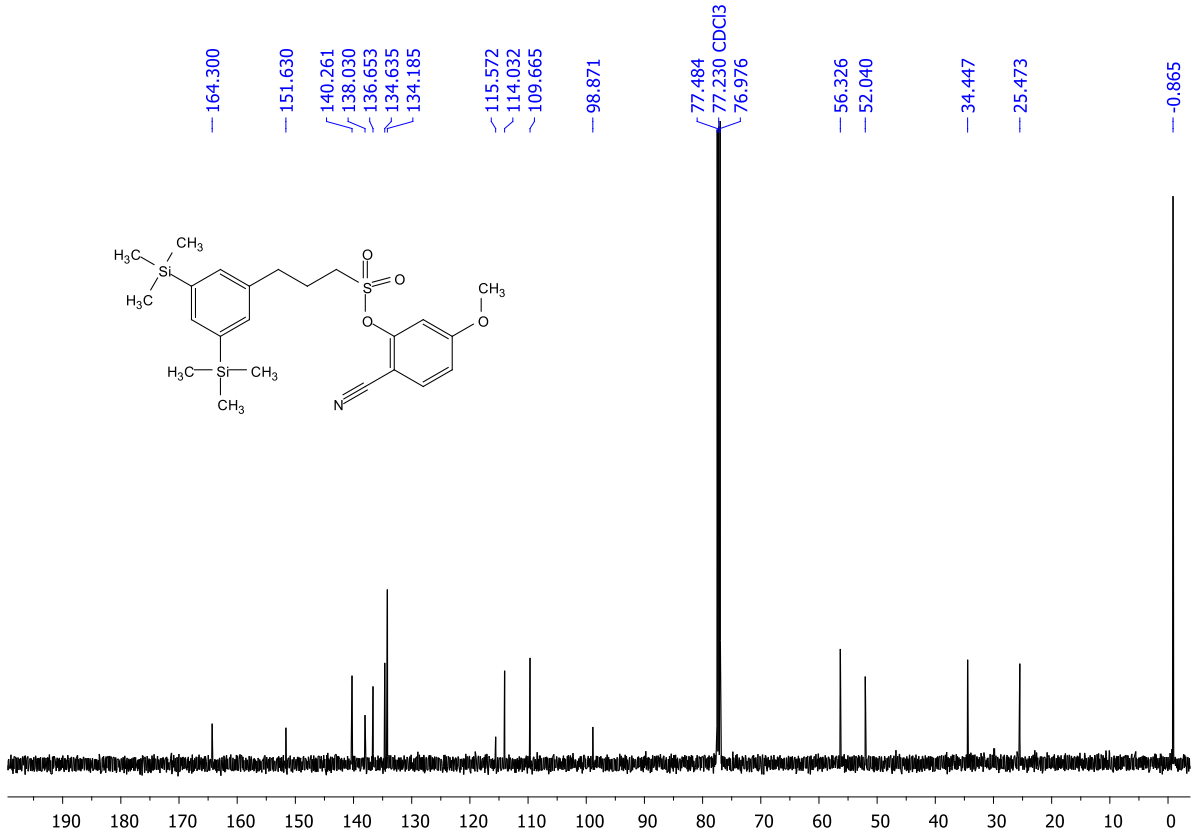


Figure S88: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **4b$_{di}$**

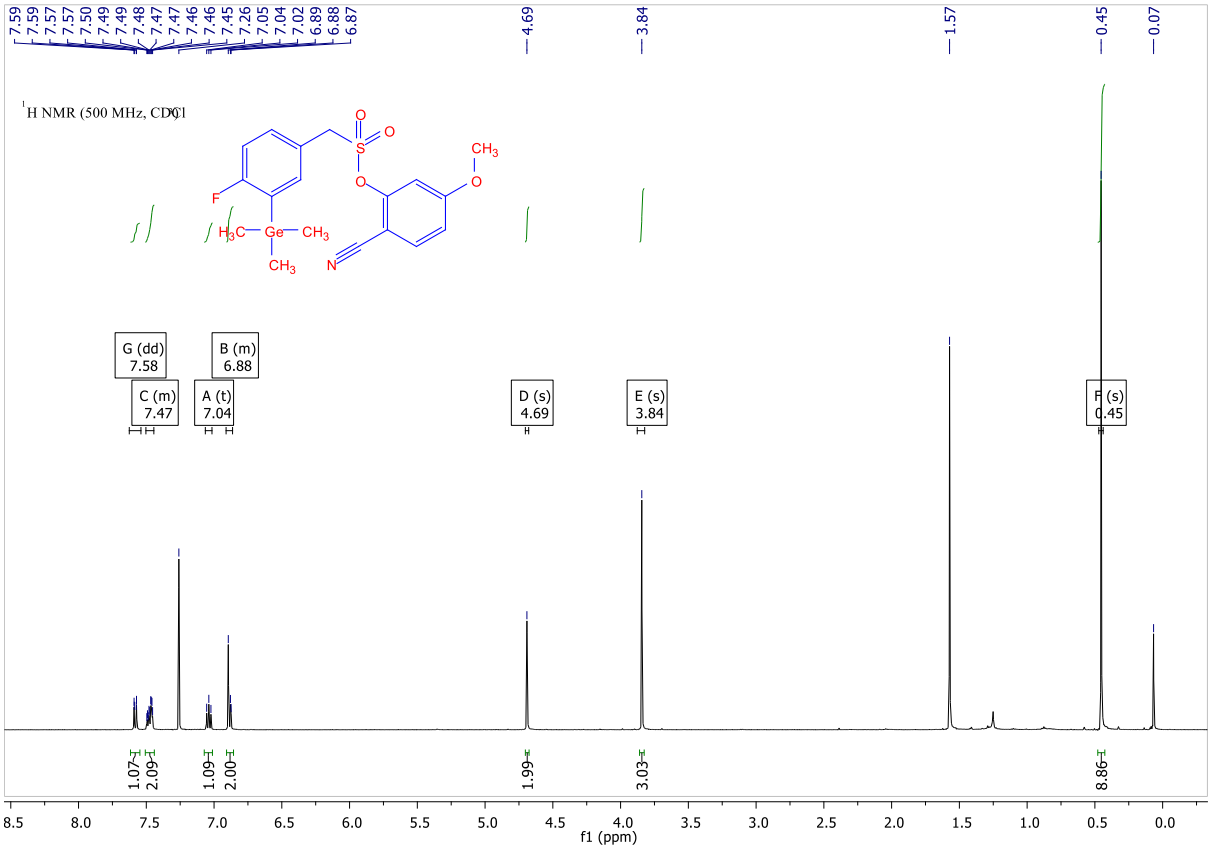


Figure S89: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **5a**

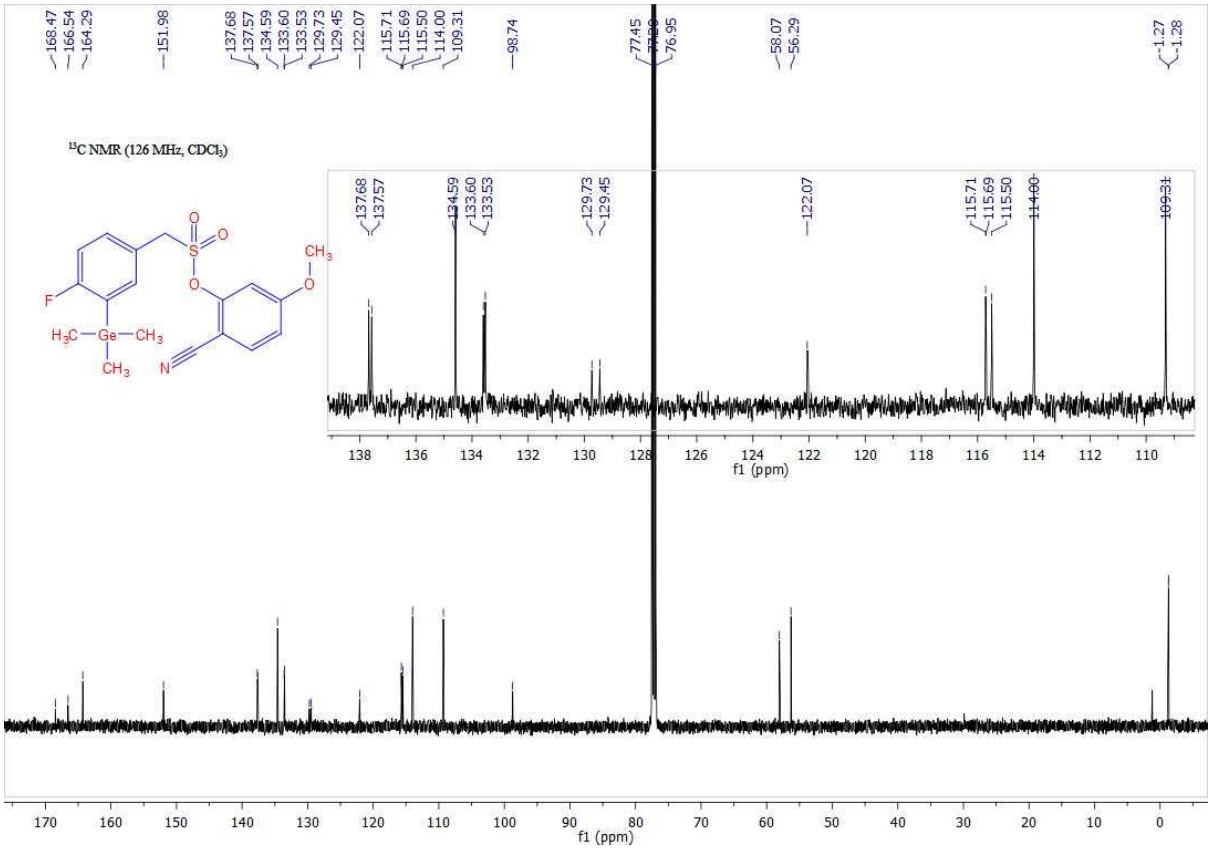


Figure S90: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **5a**

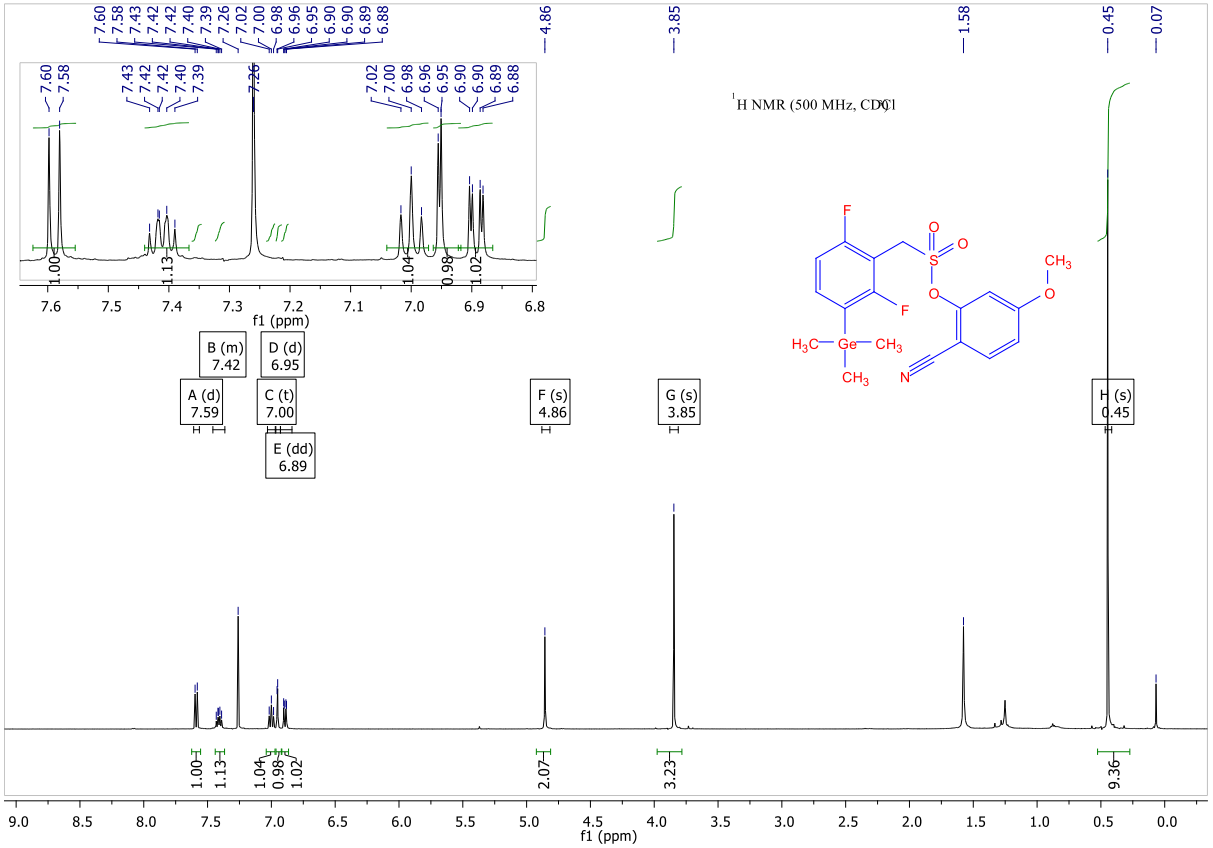


Figure S91: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **5b**

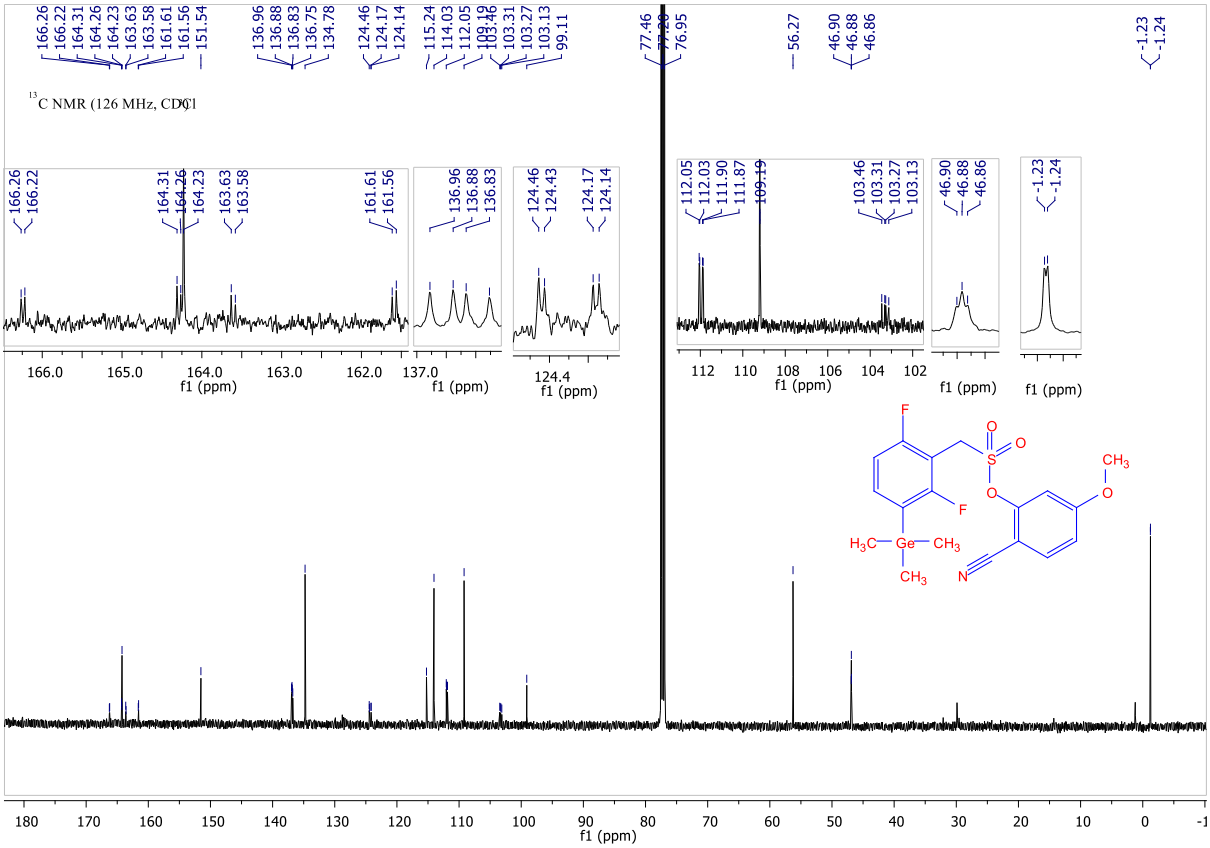


Figure S92: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **5b**

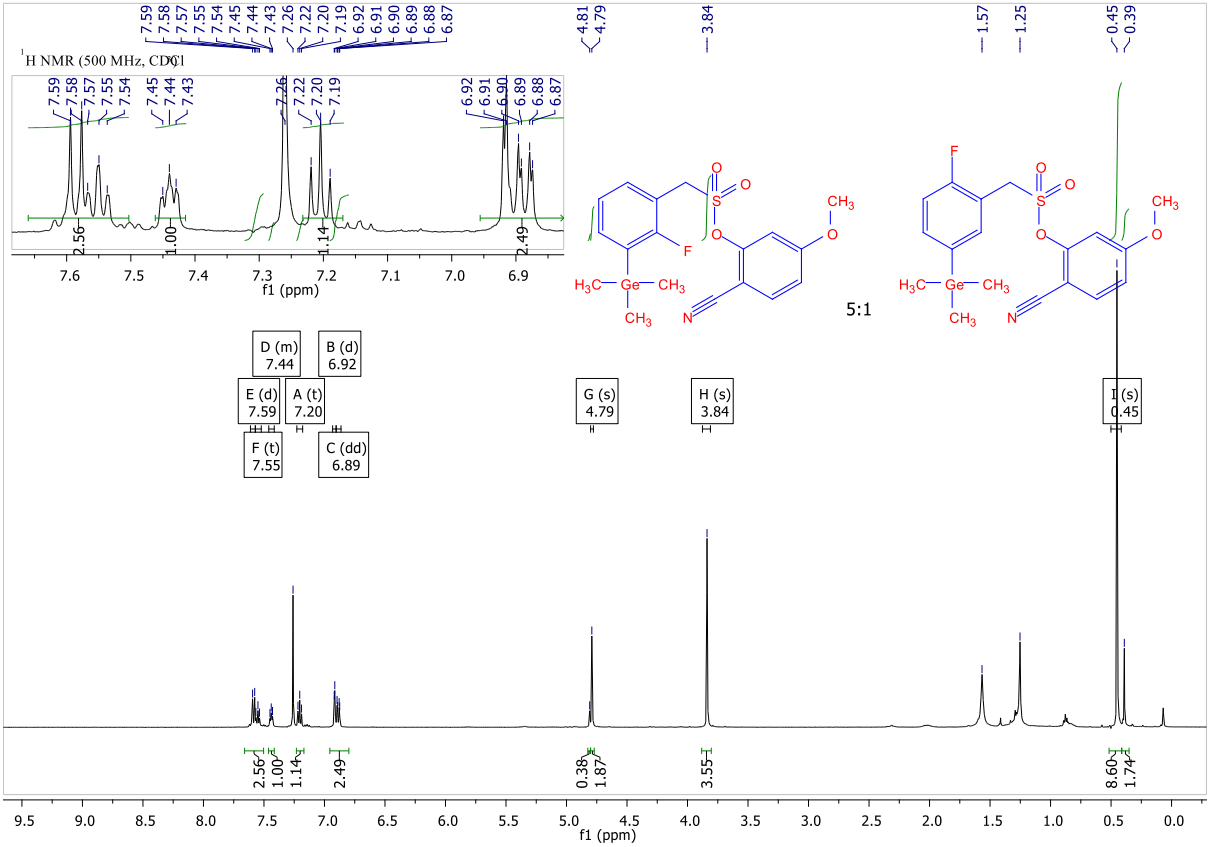


Figure S93: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **5c**

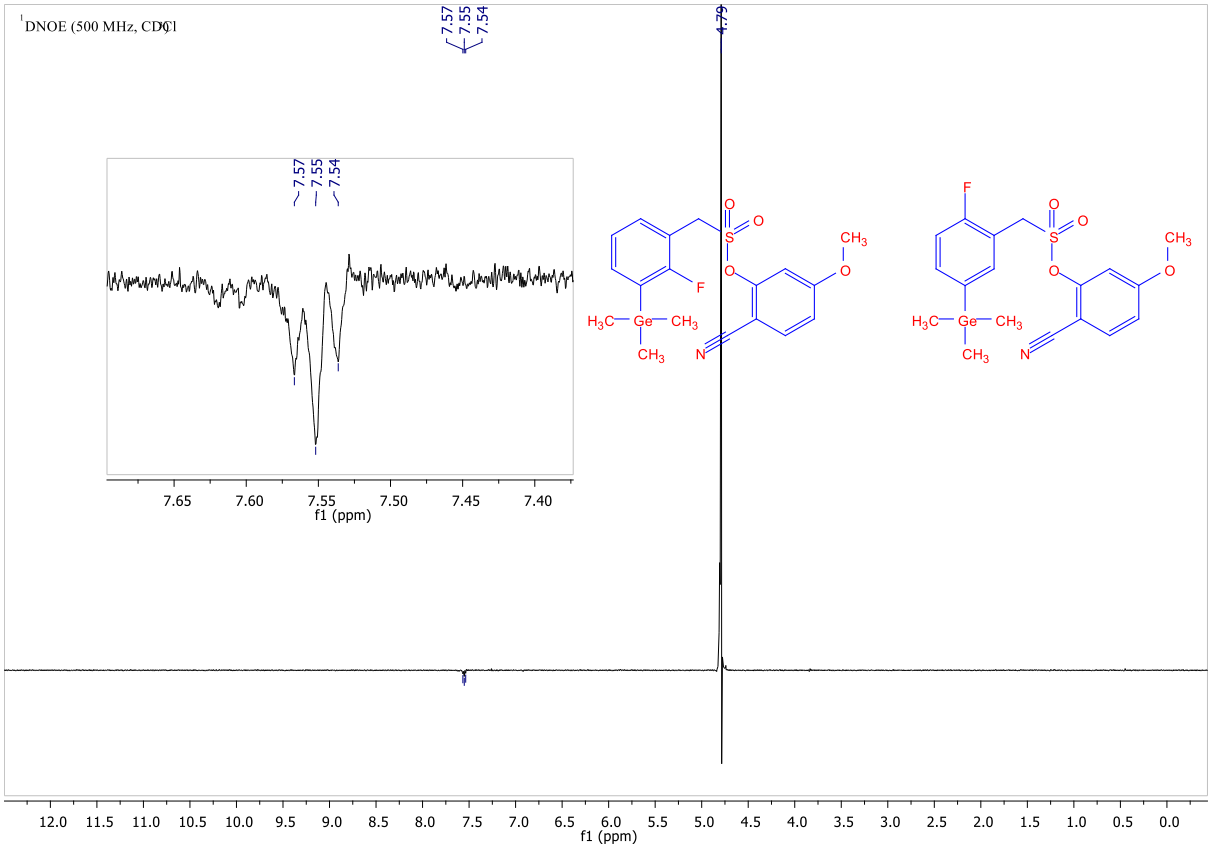


Figure S94: ^{1}D NOE NMR spectrum (500 MHz, $CDCl_3$) of Compound **5c**

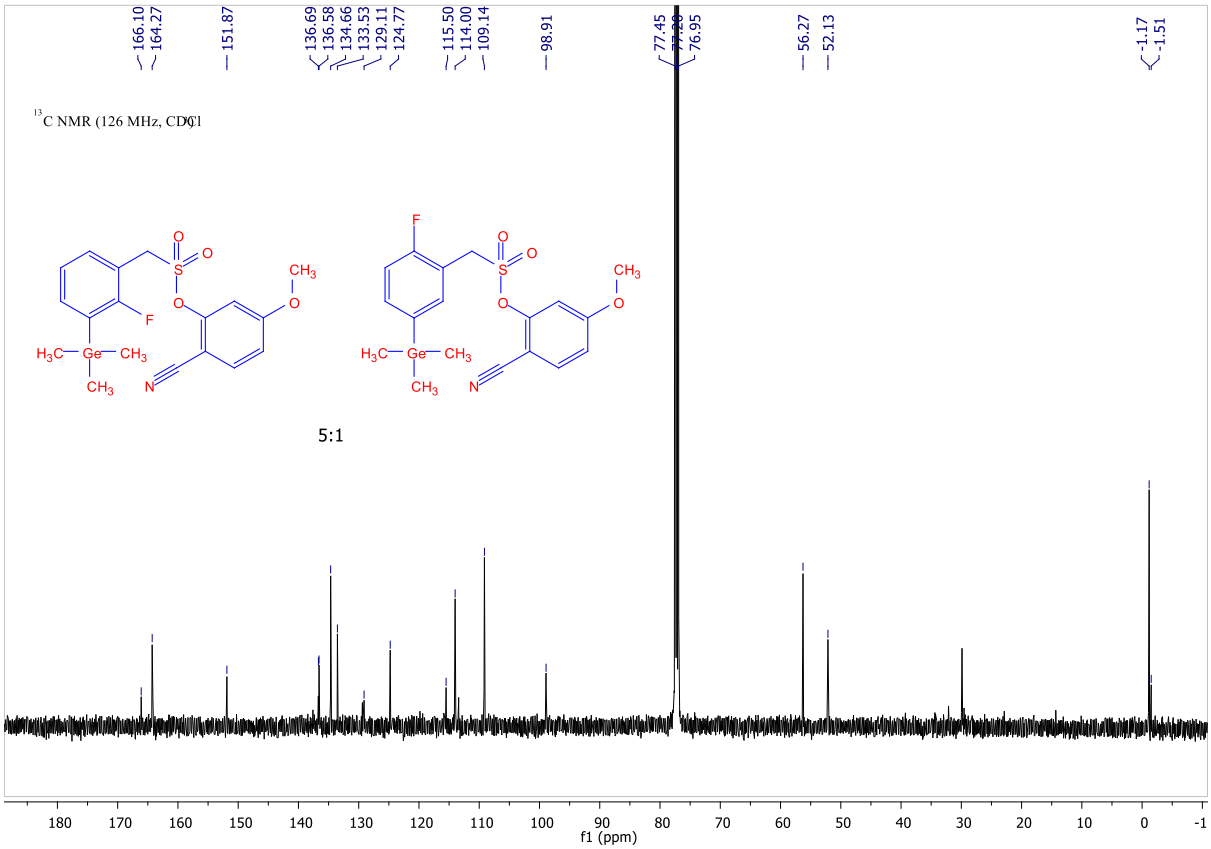


Figure S95: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **5c**

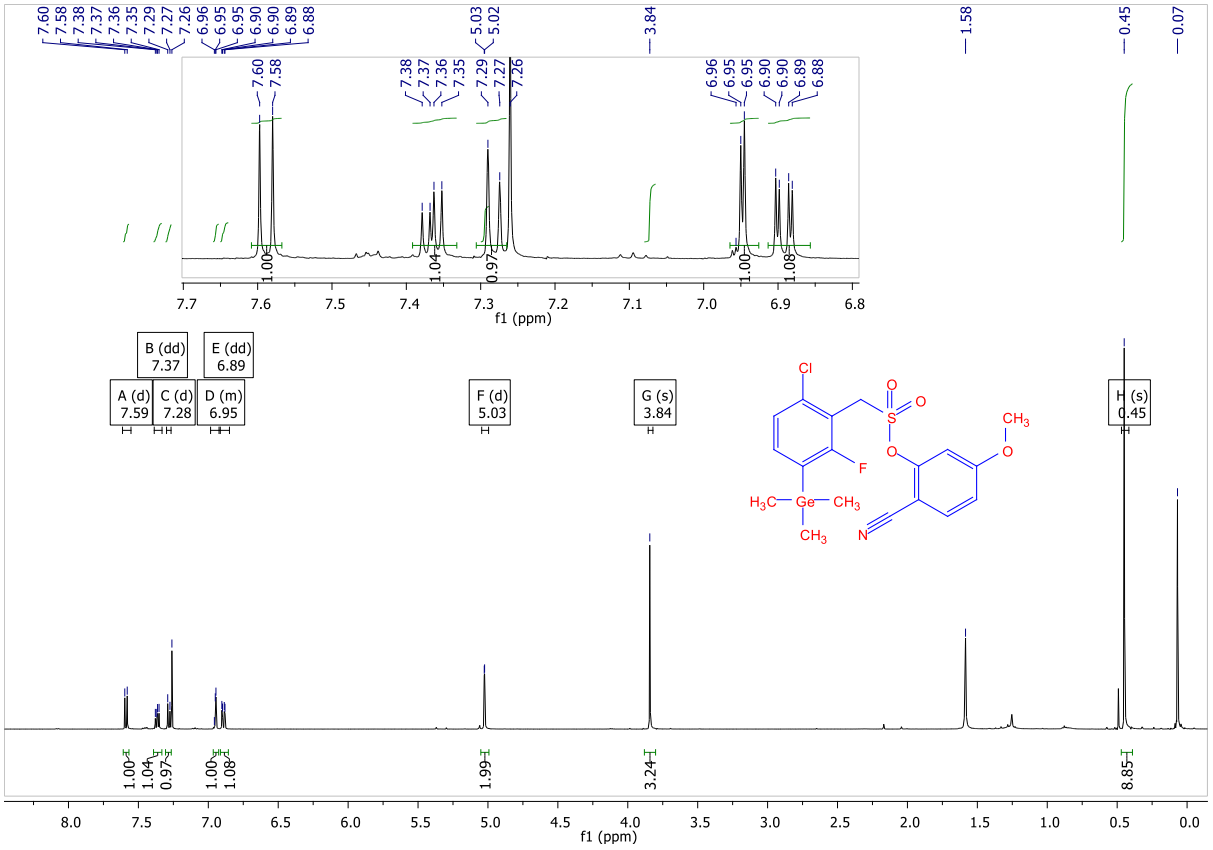


Figure S96: ^{13}C {^{1}H} NMR spectrum (500 MHz, $CDCl_3$) of Compound **5d**

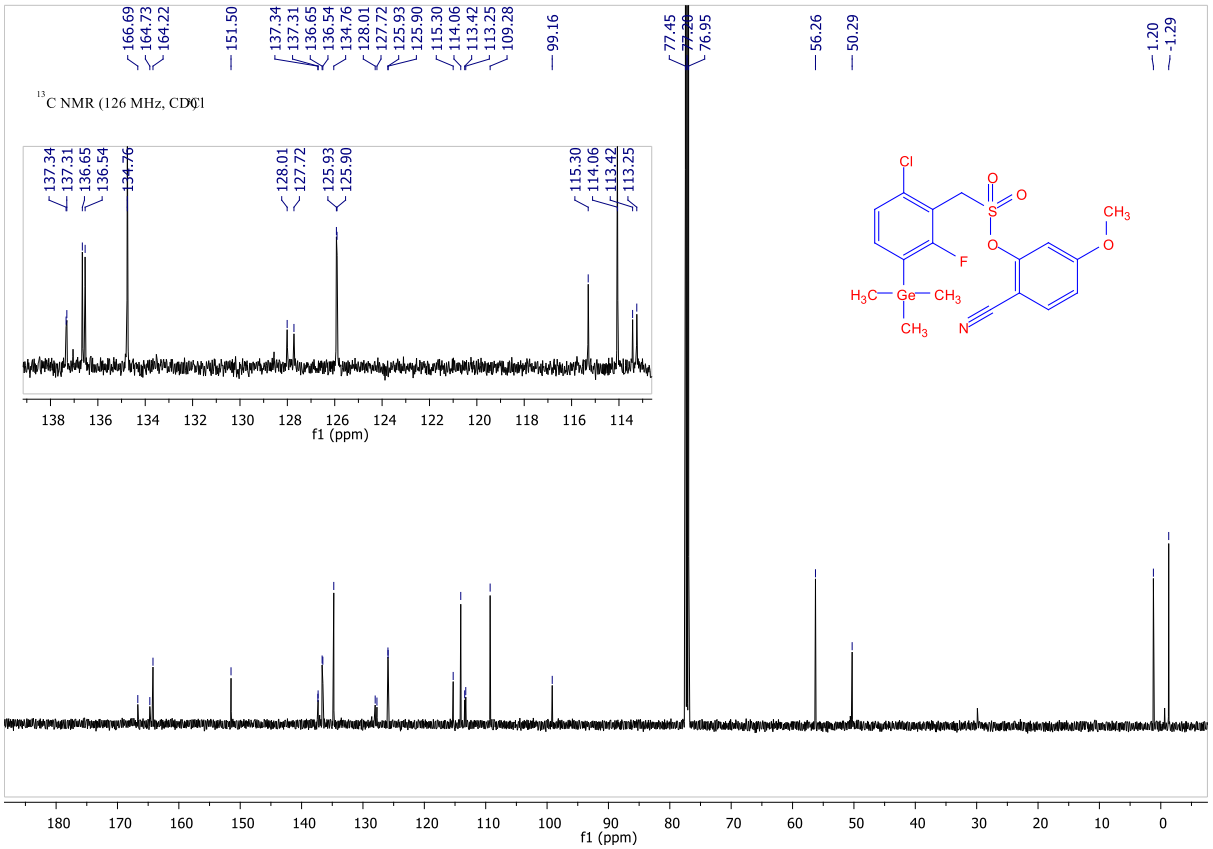


Figure S97: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **5d**

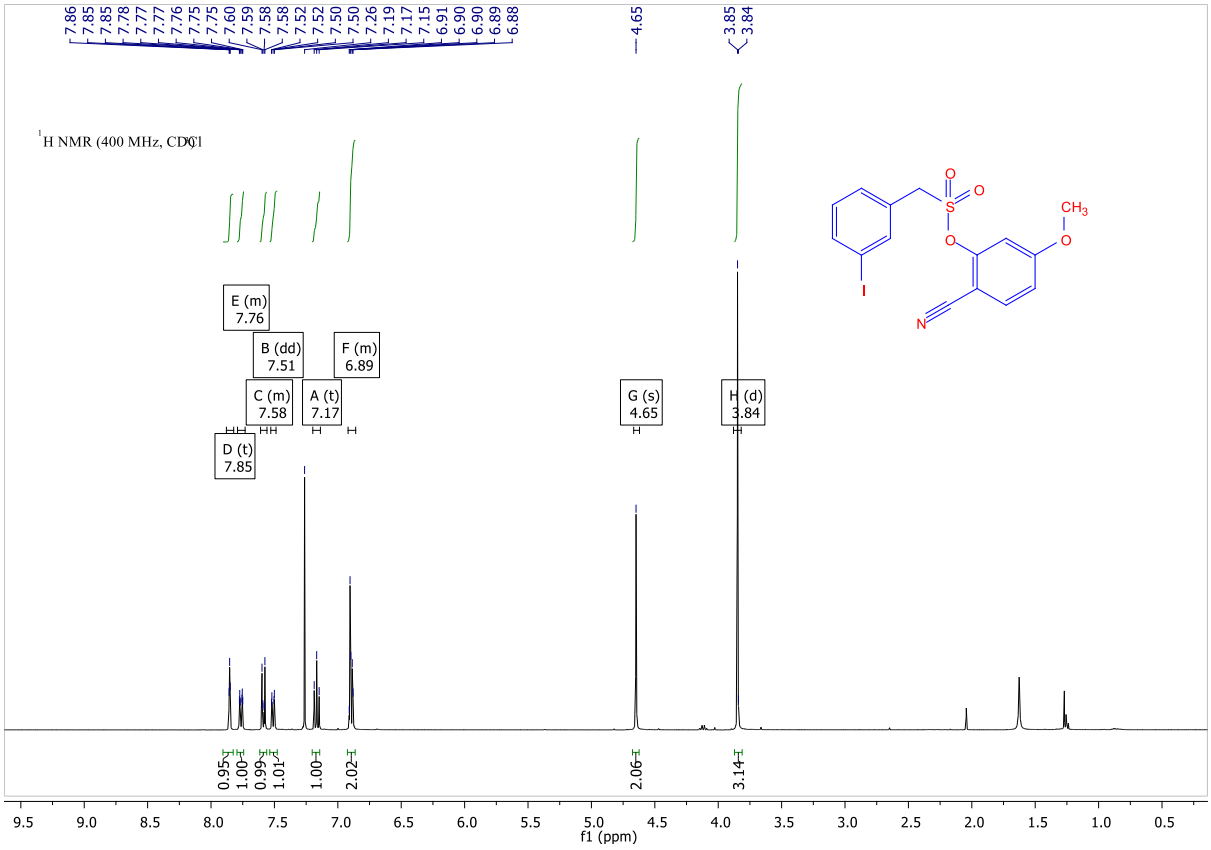


Figure S98: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **7a**

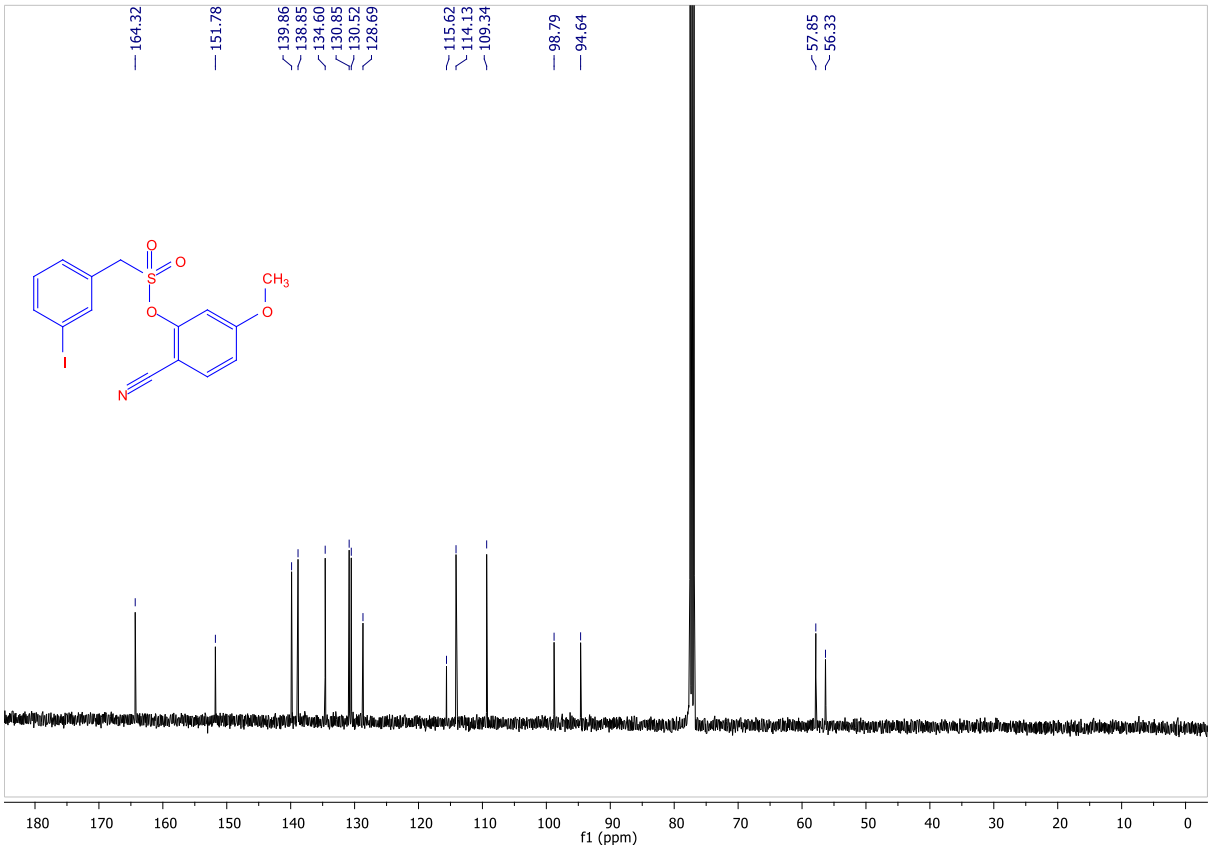


Figure S99: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of Compound **7a**

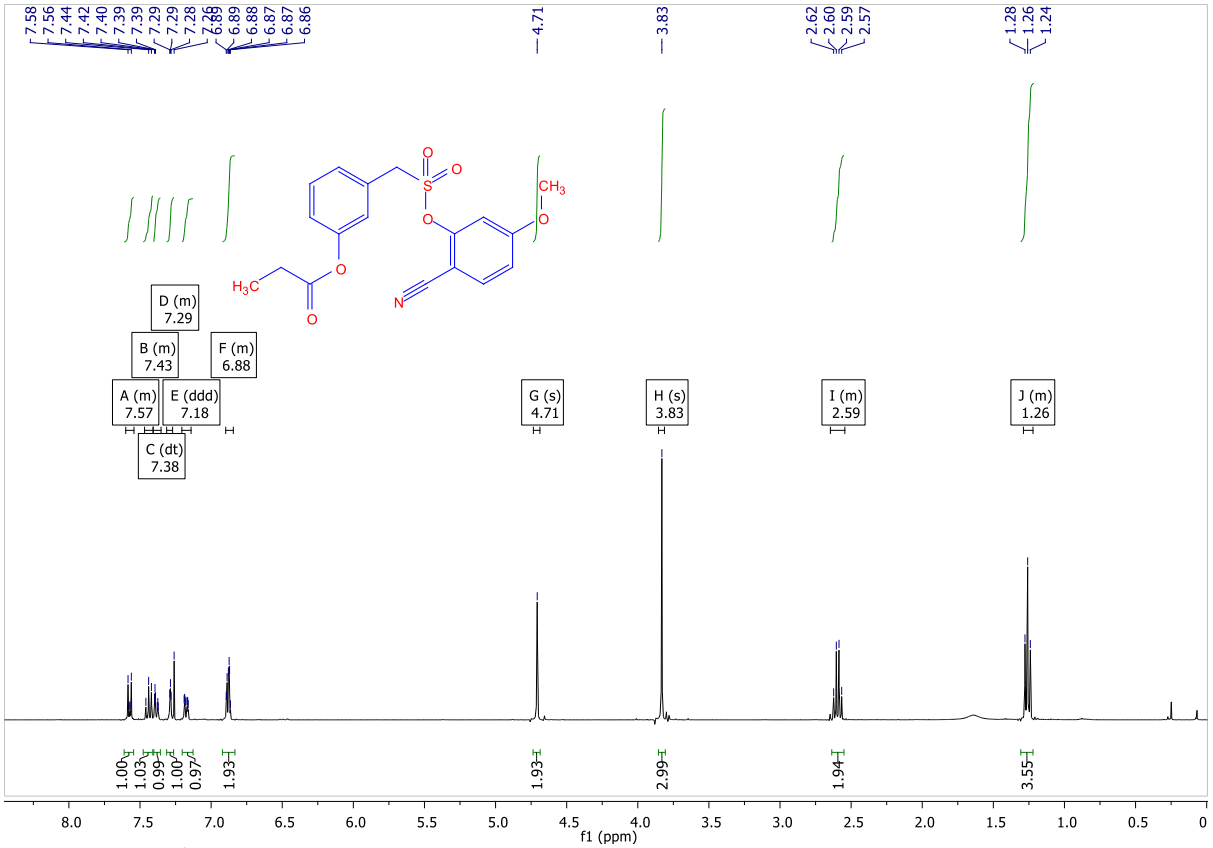


Figure S100: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **7b**

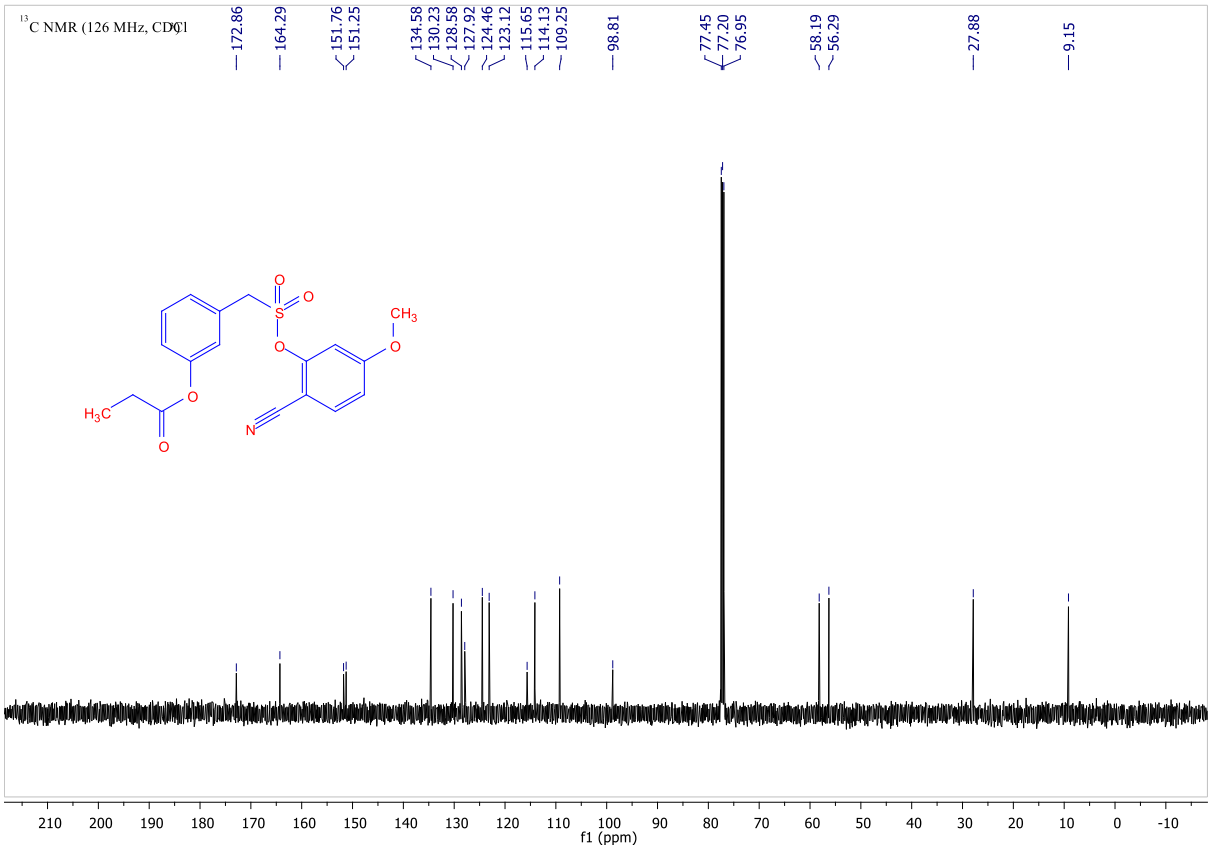


Figure S101: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **7b**

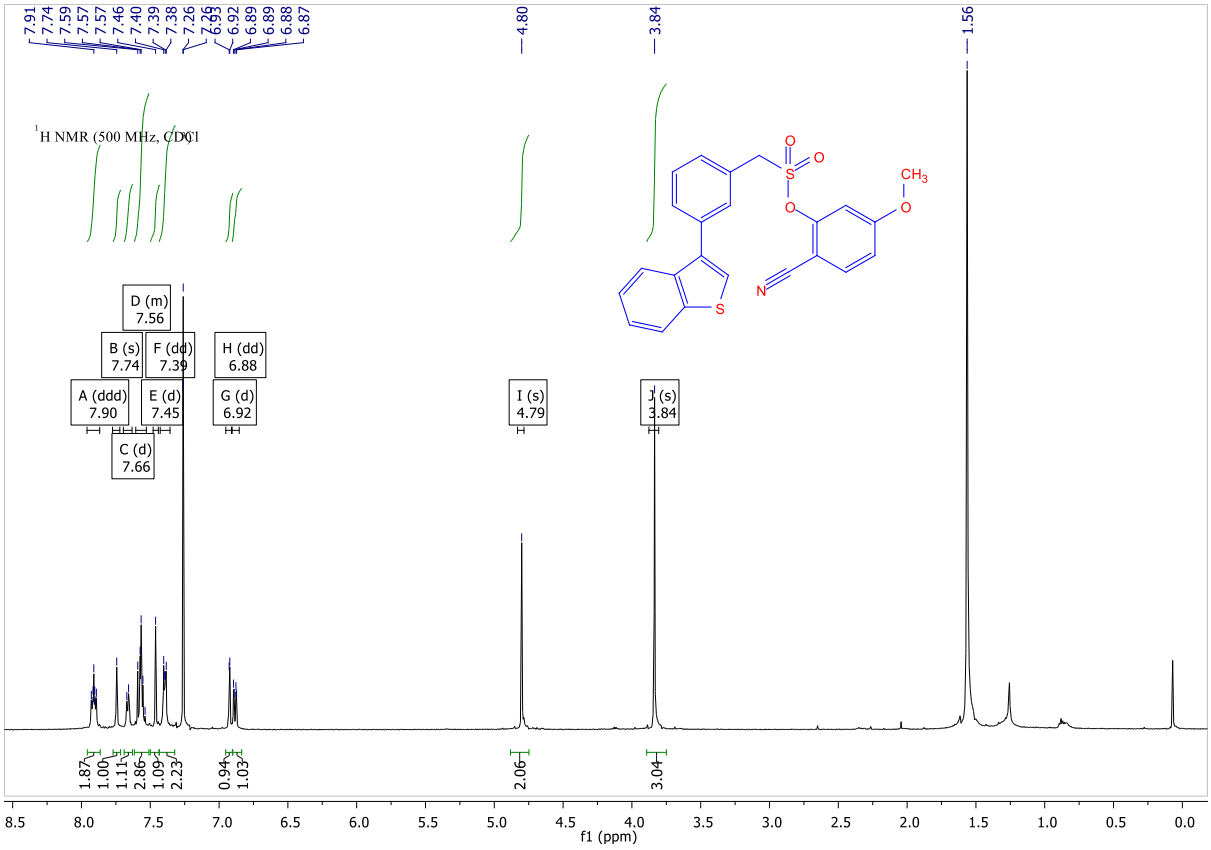


Figure S102: ^{13}C {^{1}H} NMR spectrum (500 MHz, $CDCl_3$) of Compound **7c**

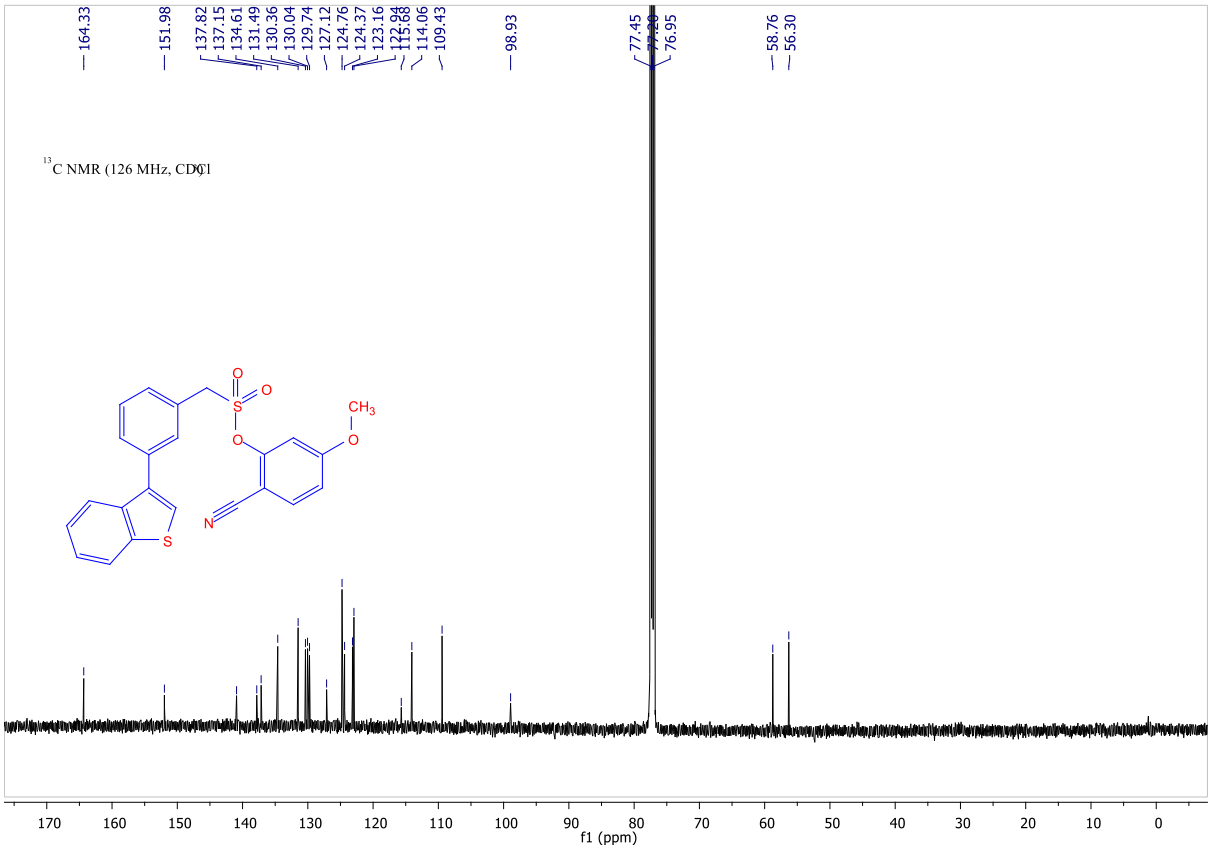


Figure S103: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **7c**

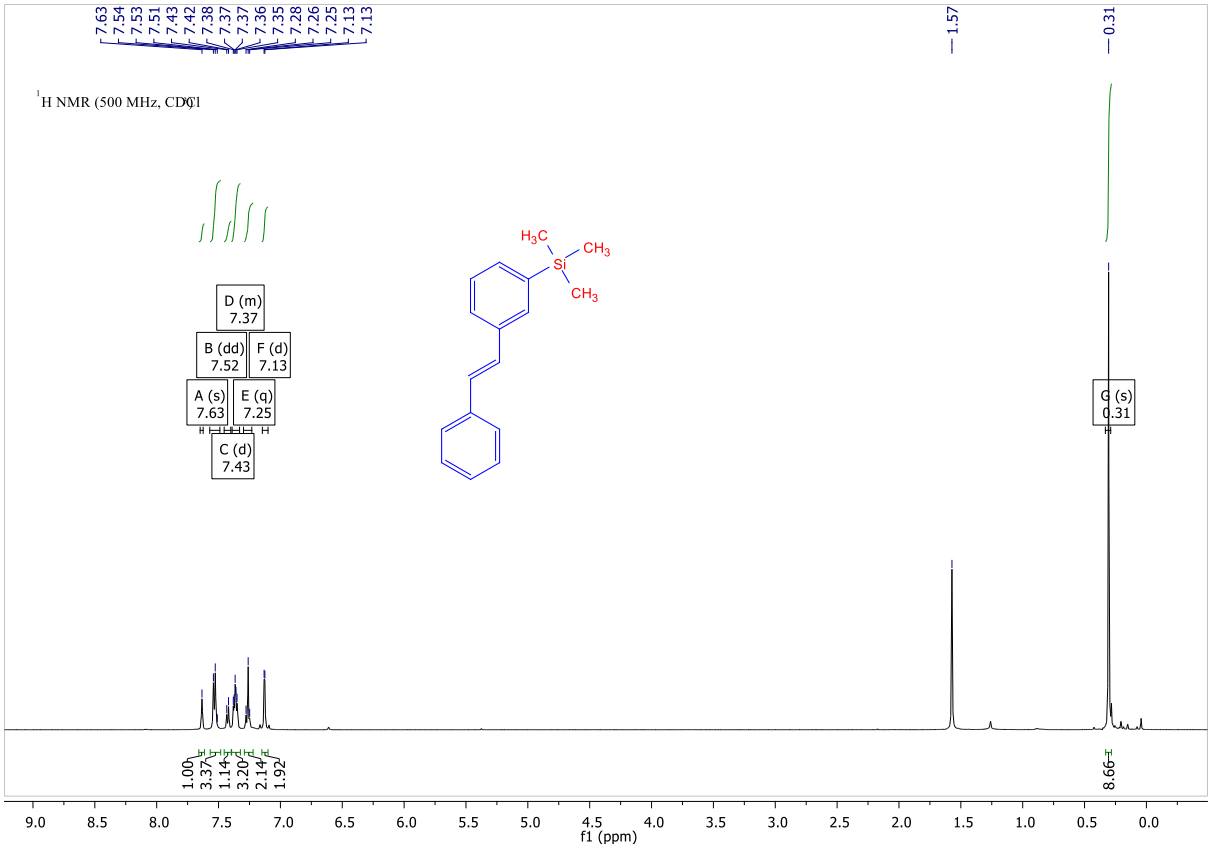


Figure S104: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **7d**

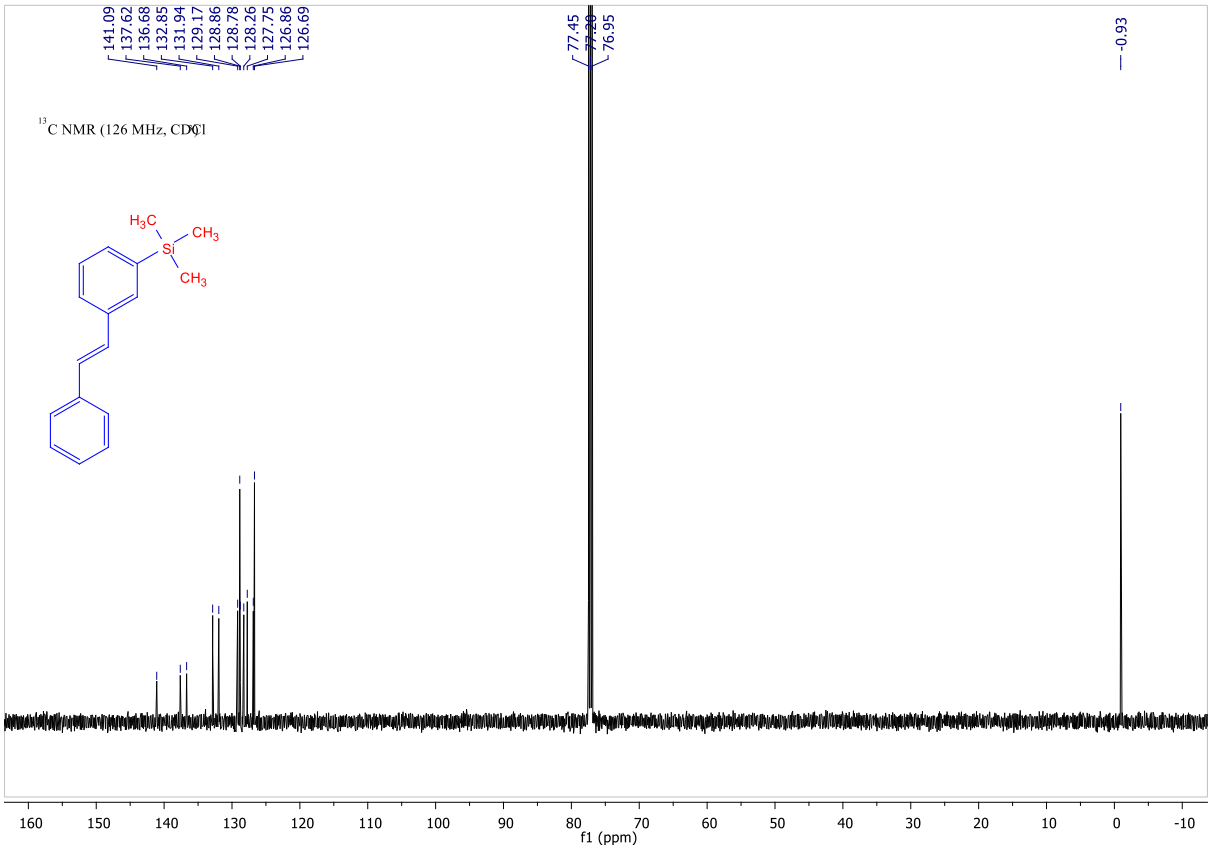


Figure S105: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **7d**

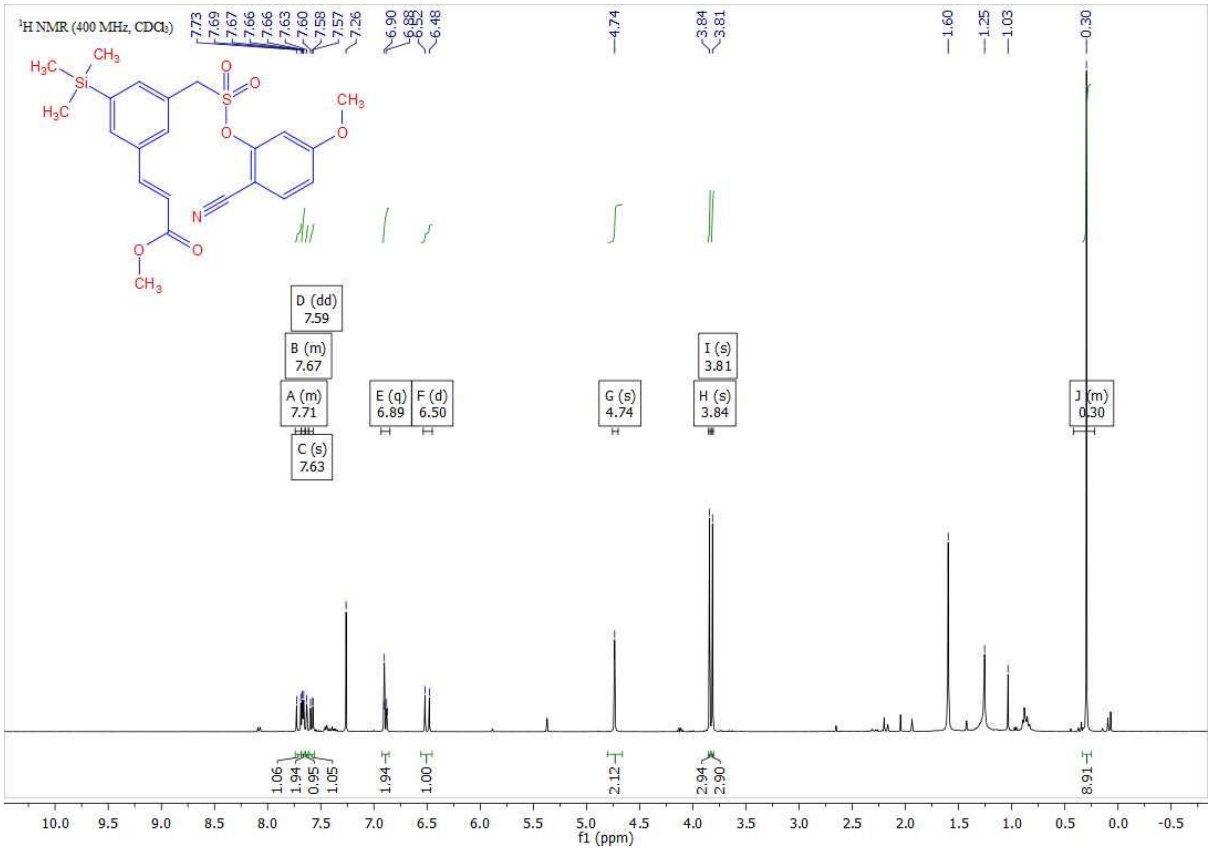


Figure S106: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of Compound **7e**

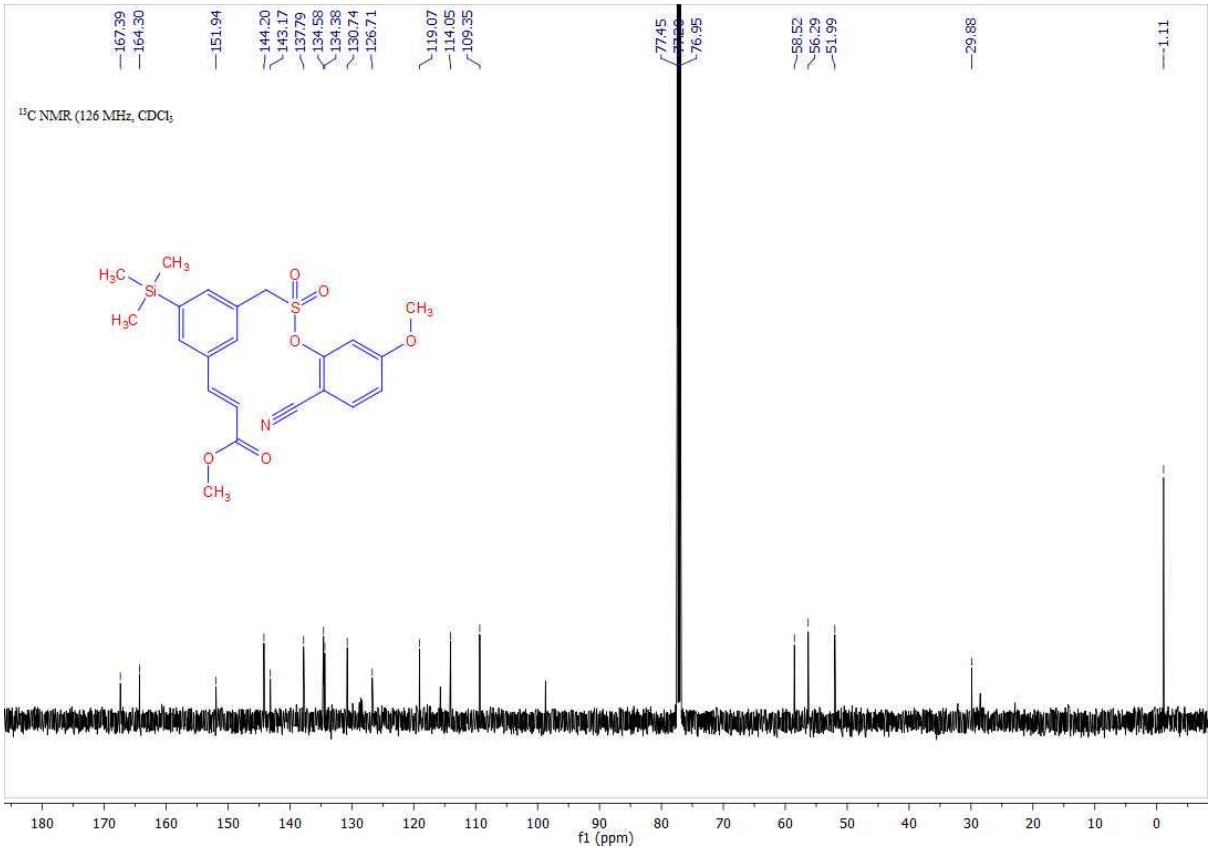


Figure S107: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **7e**

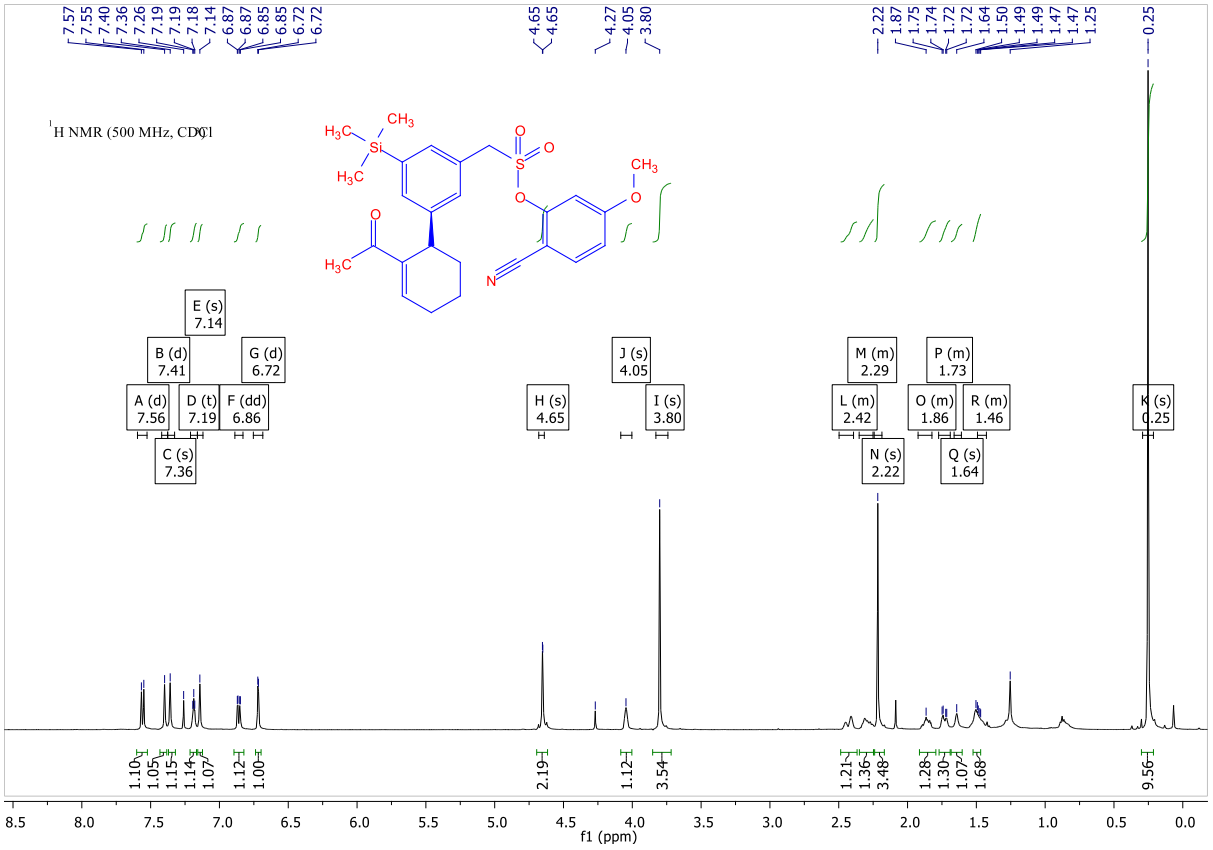


Figure S108: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of Compound **7f**

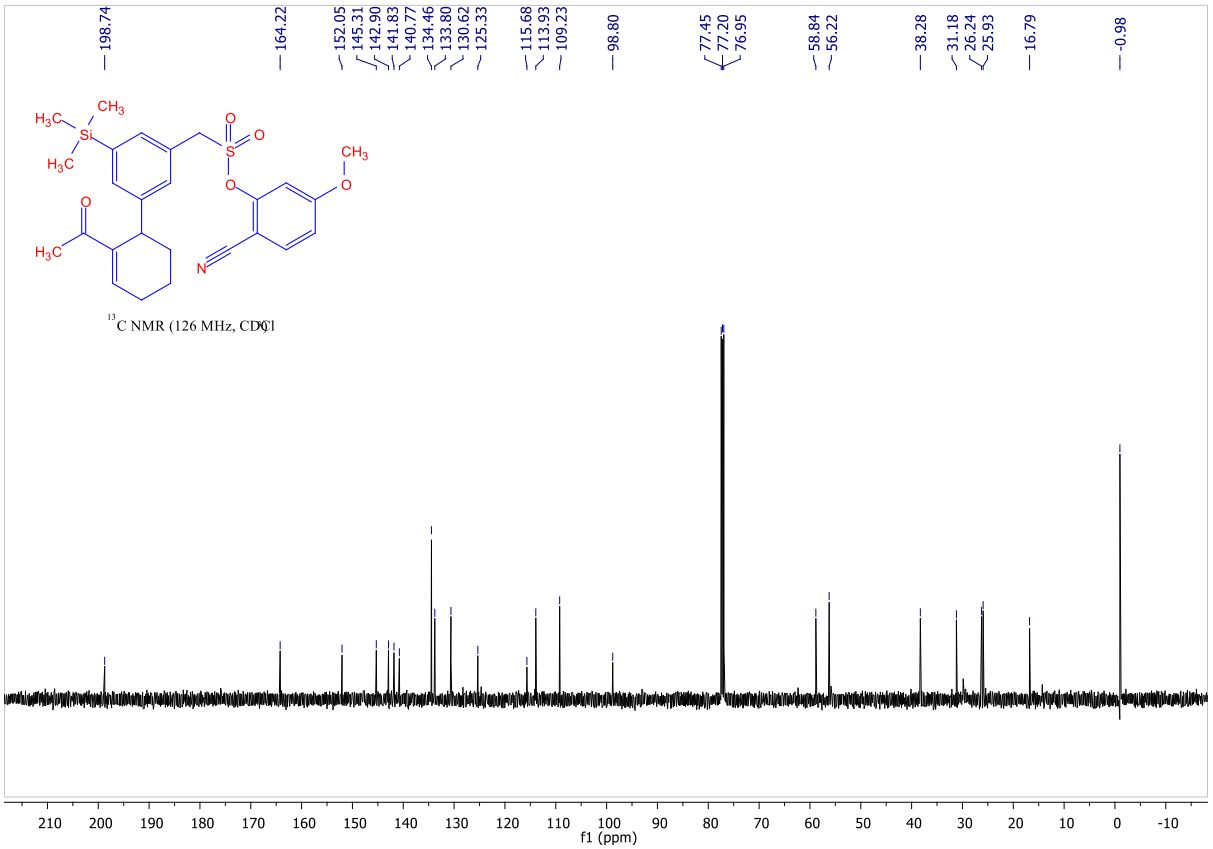


Figure S109: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of Compound **7f**

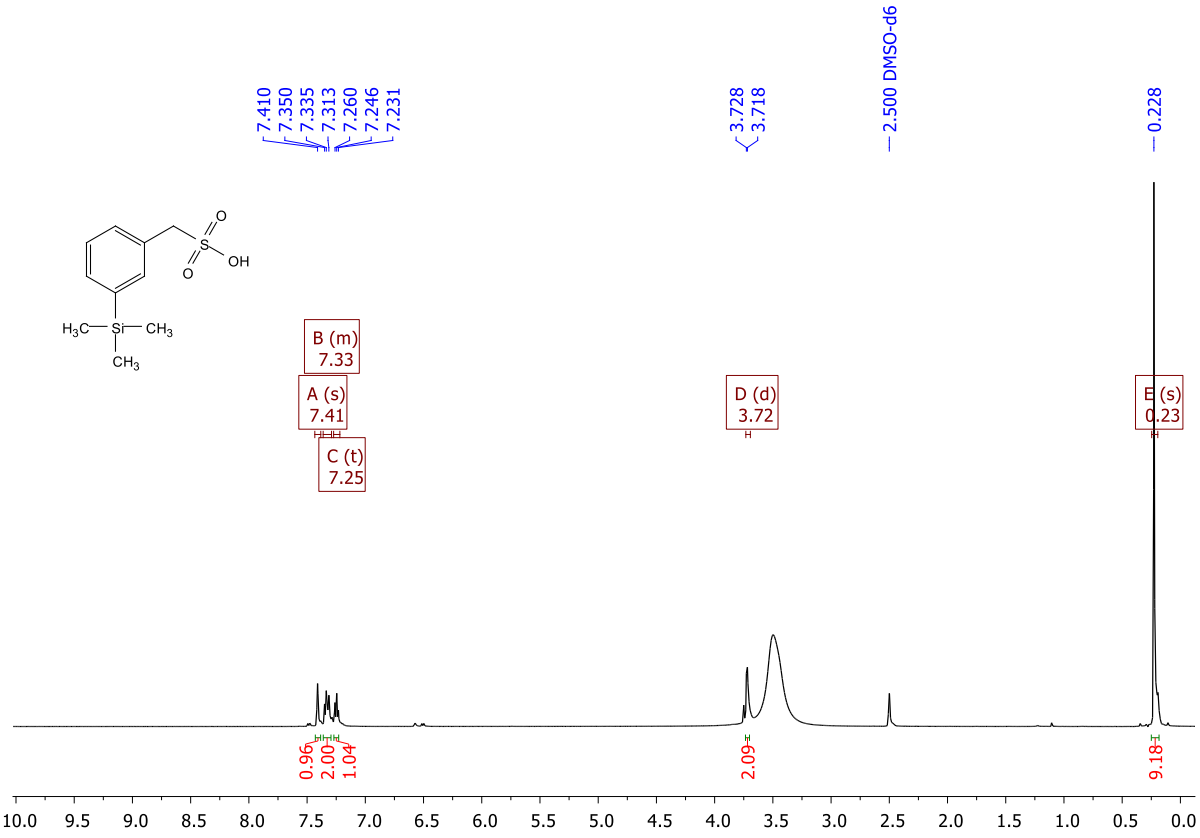


Figure S110: ^{1}H NMR spectrum (126 MHz, DMSO-d^{6}) of (3-(Trimethylsilyl)phenyl)methanesulfonic acid

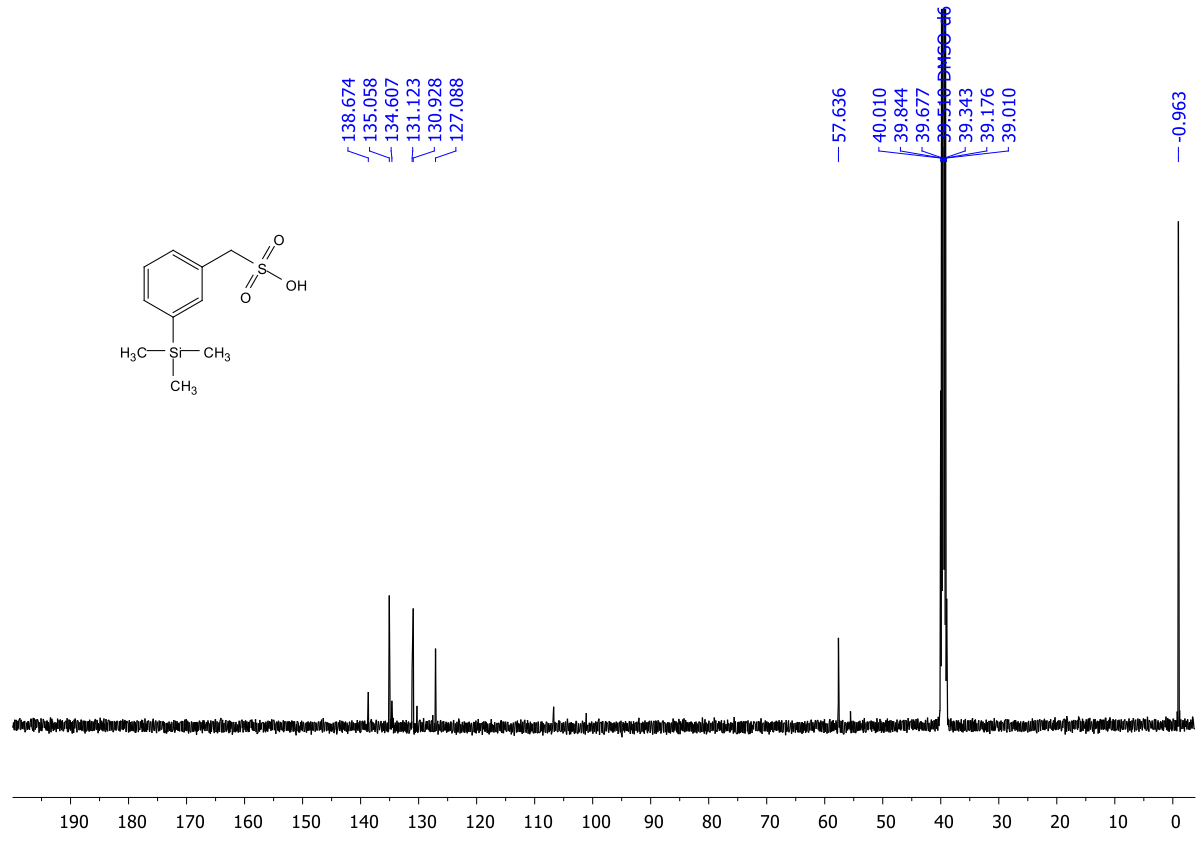


Figure S111: ^{13}C {^{1}H} NMR spectrum (126 MHz, DMSO-d^{6}) of Compound (3-(Trimethylsilyl)phenyl)methanesulfonic acid

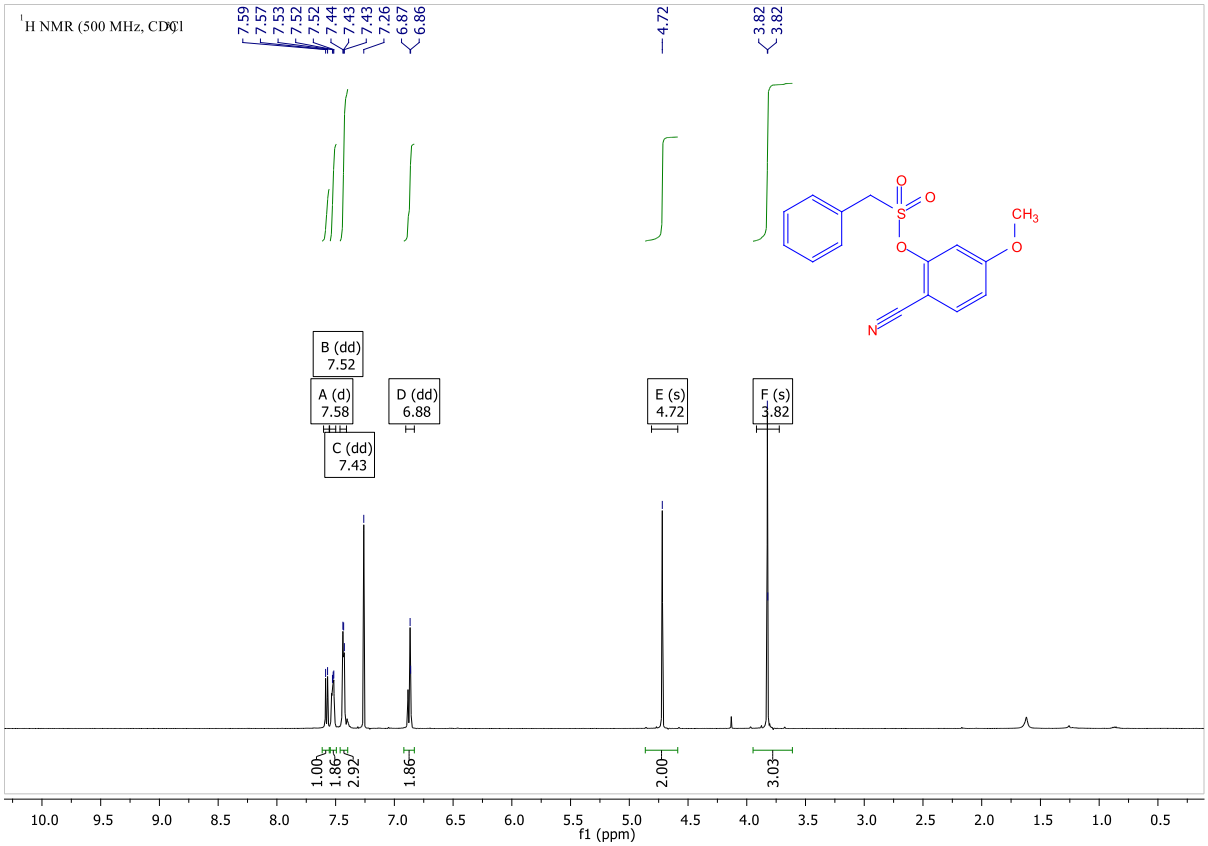


Figure S112: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl phenylmethanesulfonate

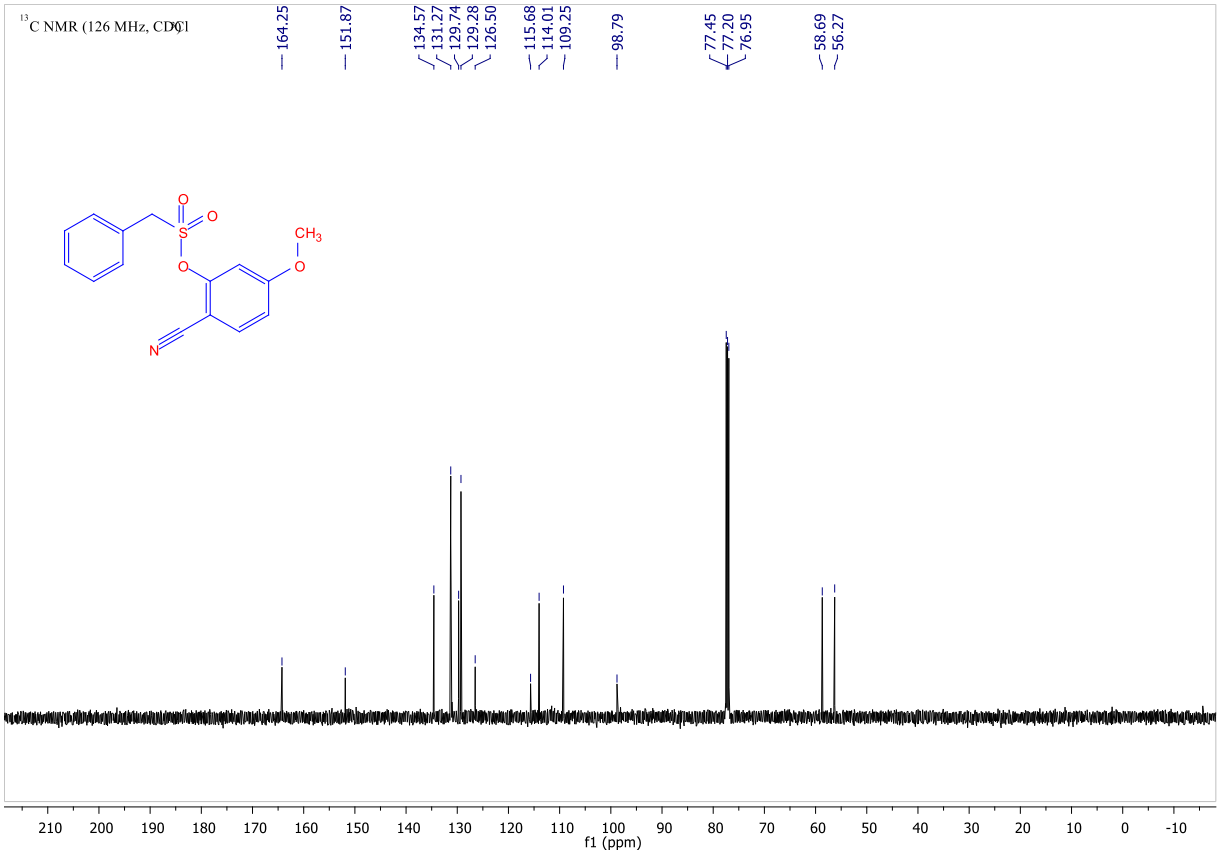


Figure S113: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl phenylmethanesulfonate

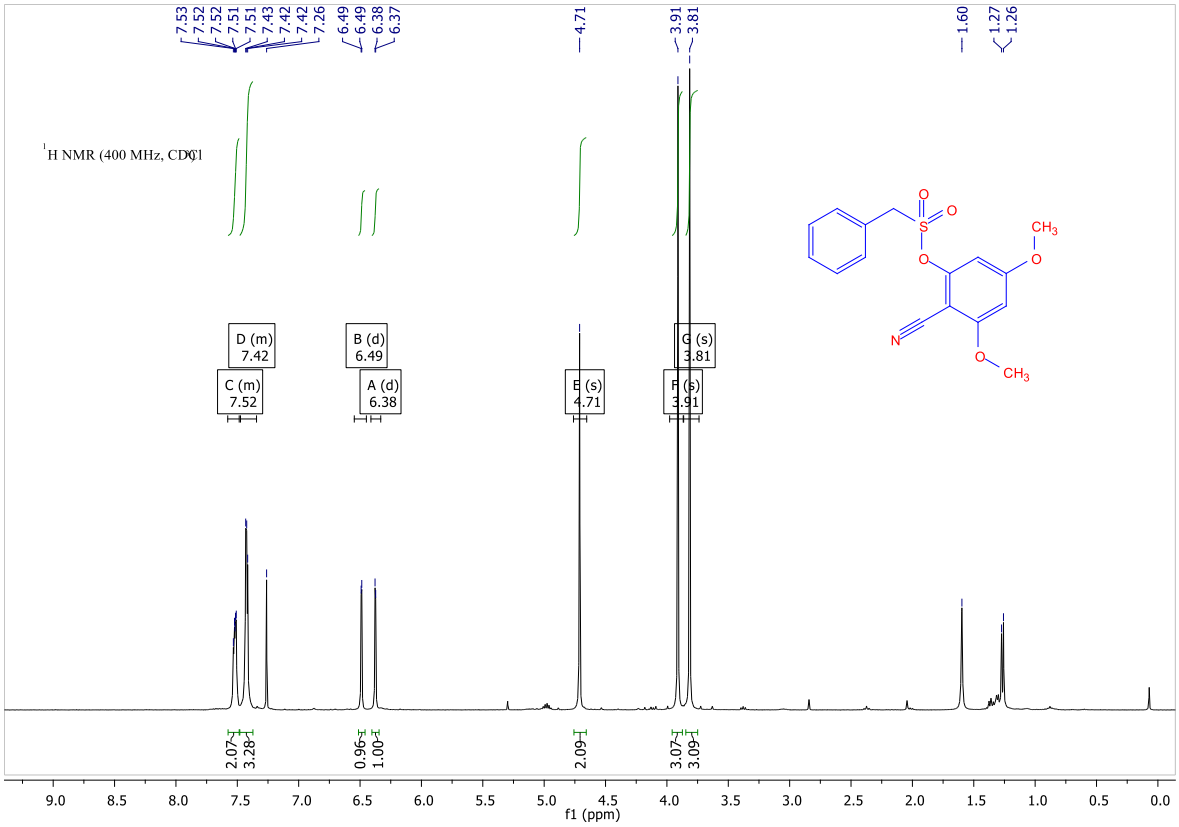


Figure S114: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of2-Cyano-3,5-dimethoxyphenyl phenylmethanesulfonate

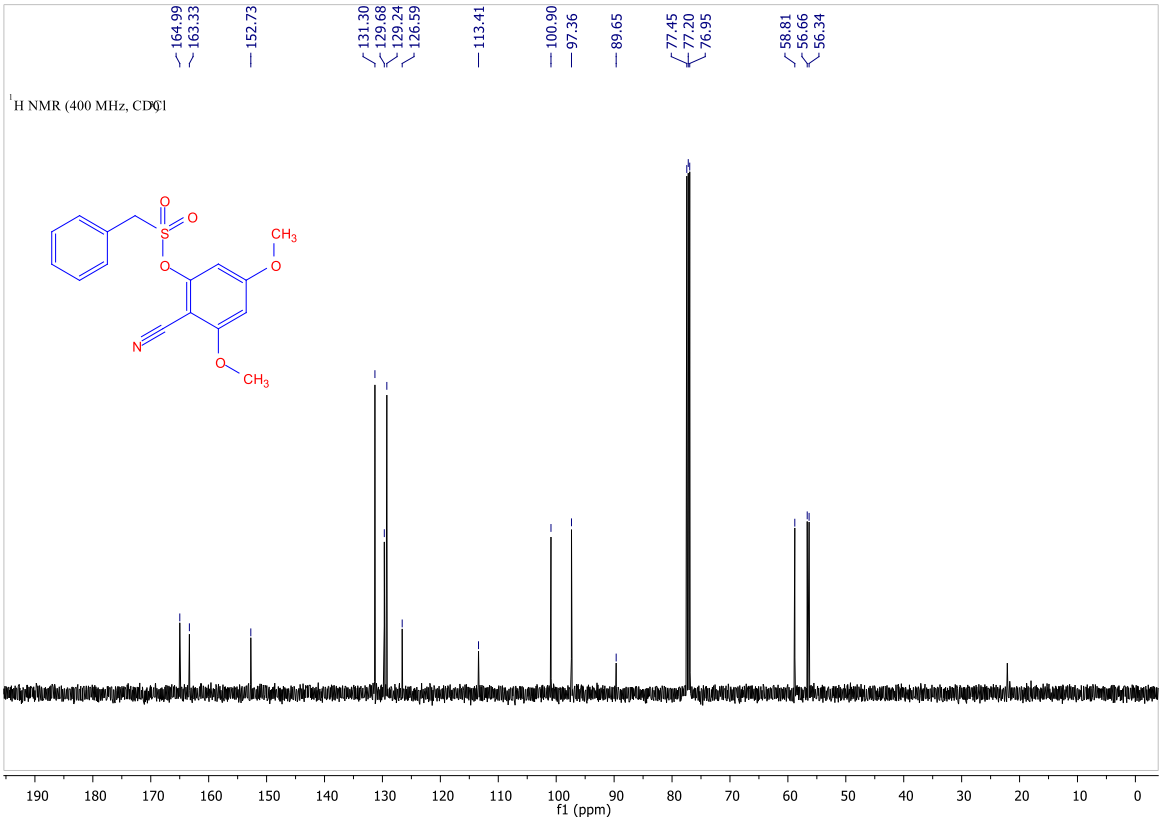


Figure S115: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-3,5-dimethoxyphenyl phenylmethanesulfonate

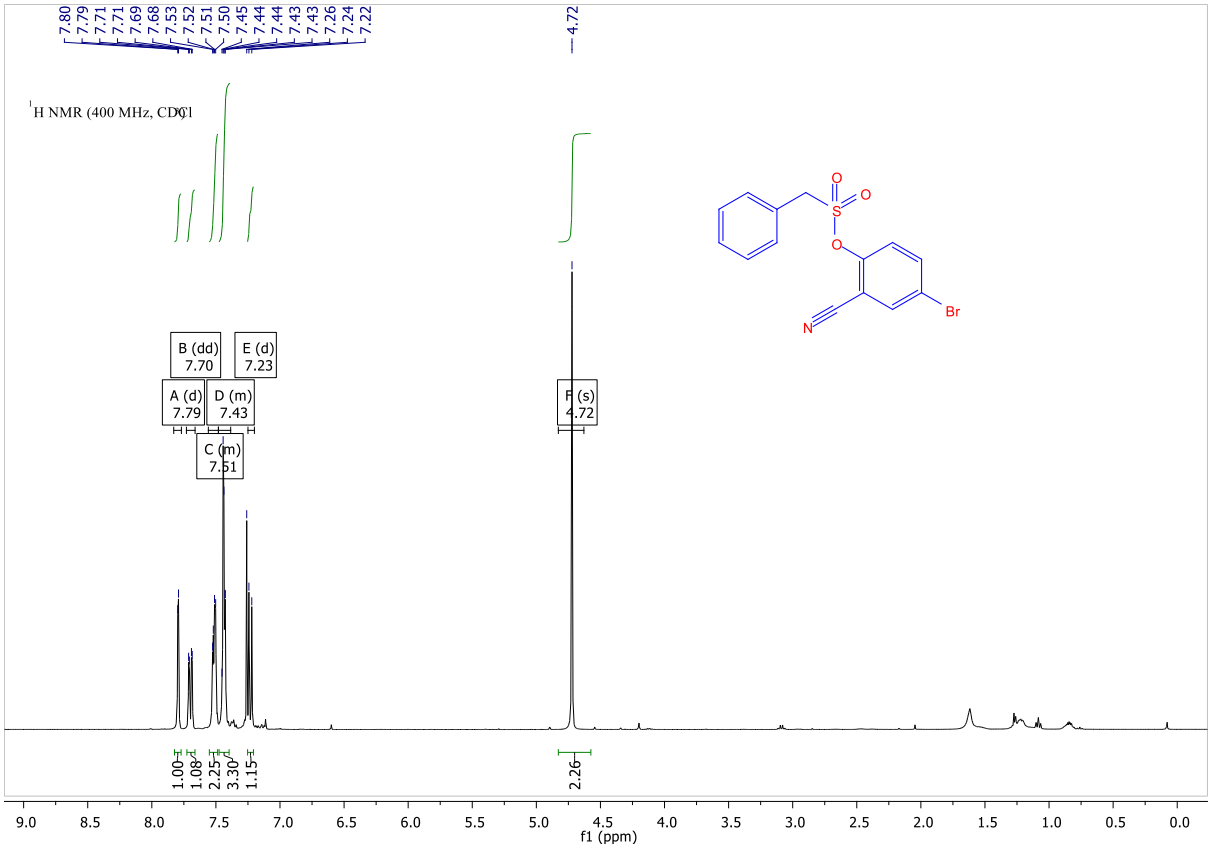


Figure S116: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-Bromo-2-cyanophenyl phenylmethanesulfonate

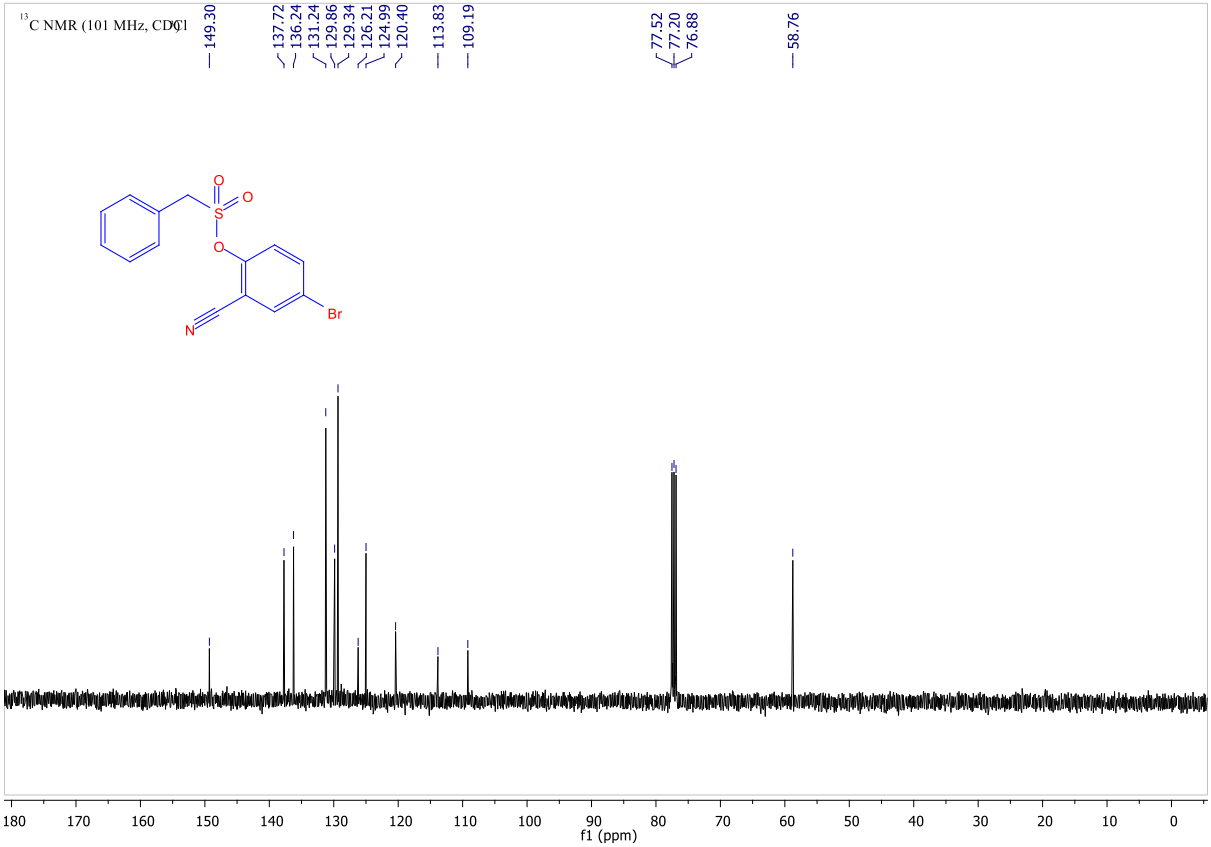


Figure S117: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 4-Bromo-2-cyanophenyl phenylmethanesulfonate

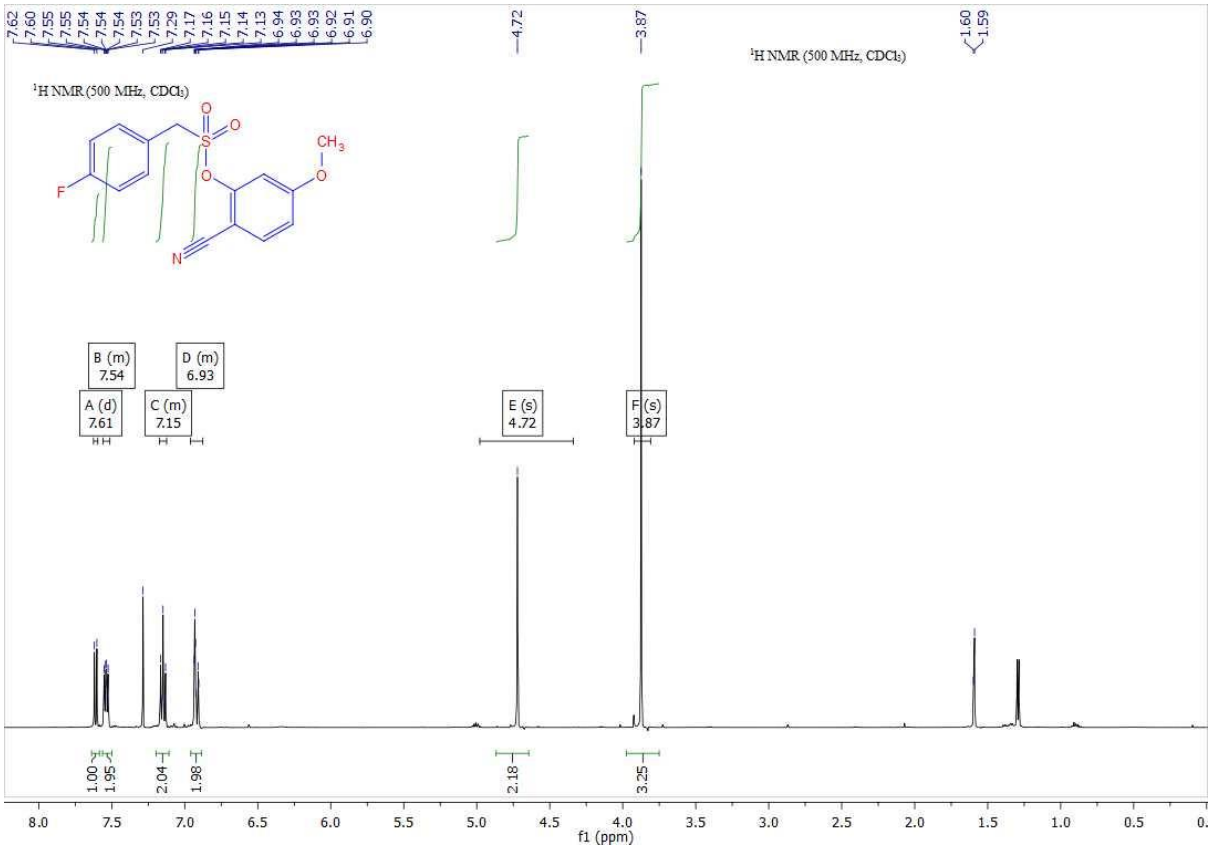


Figure S118: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (4-fluorophenyl)methanesulfonate

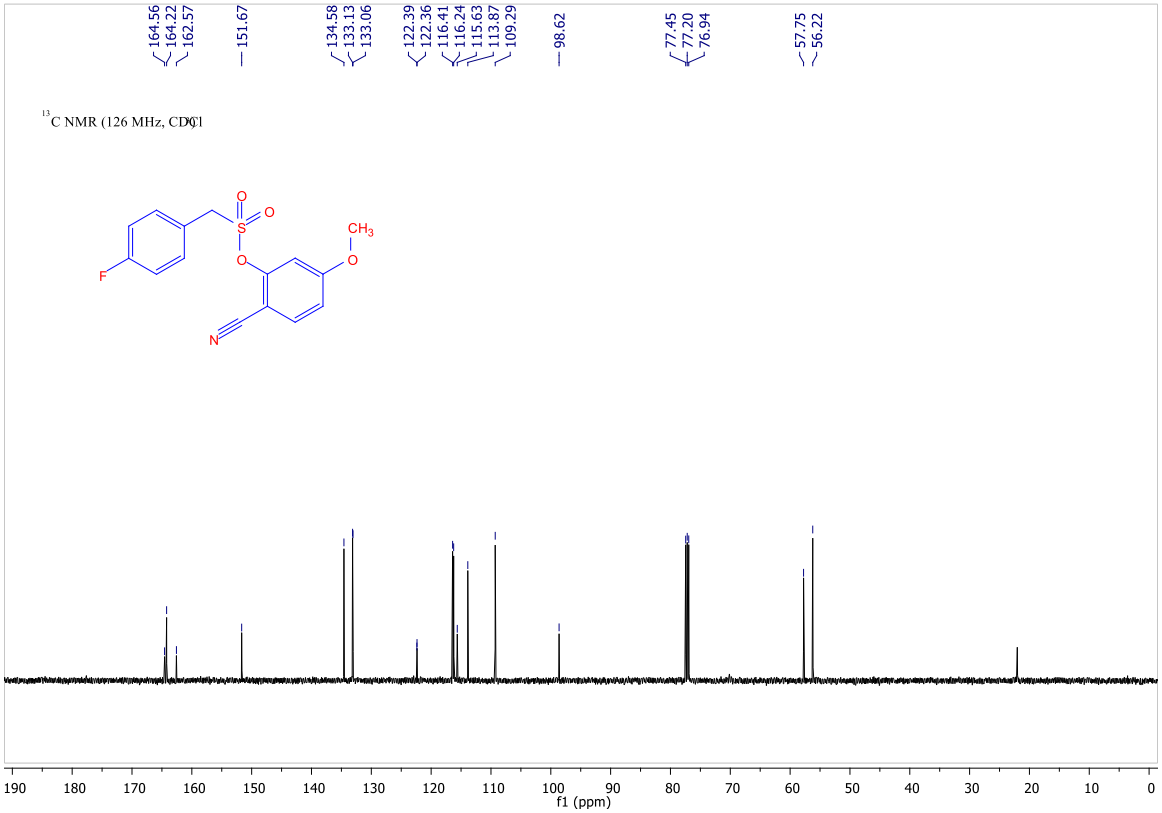


Figure S119: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (4-fluorophenyl)methanesulfonate

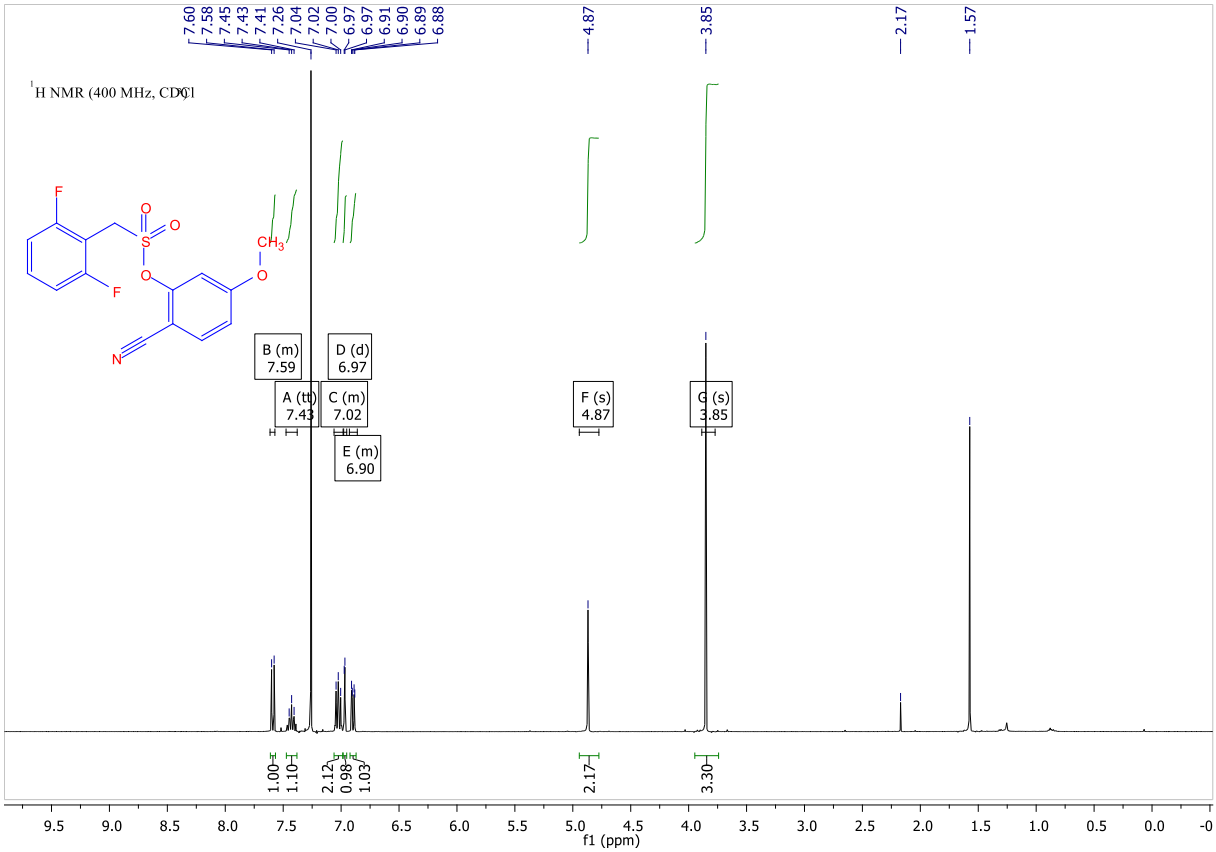


Figure S120: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,6-difluorophenyl)methanesulfonate

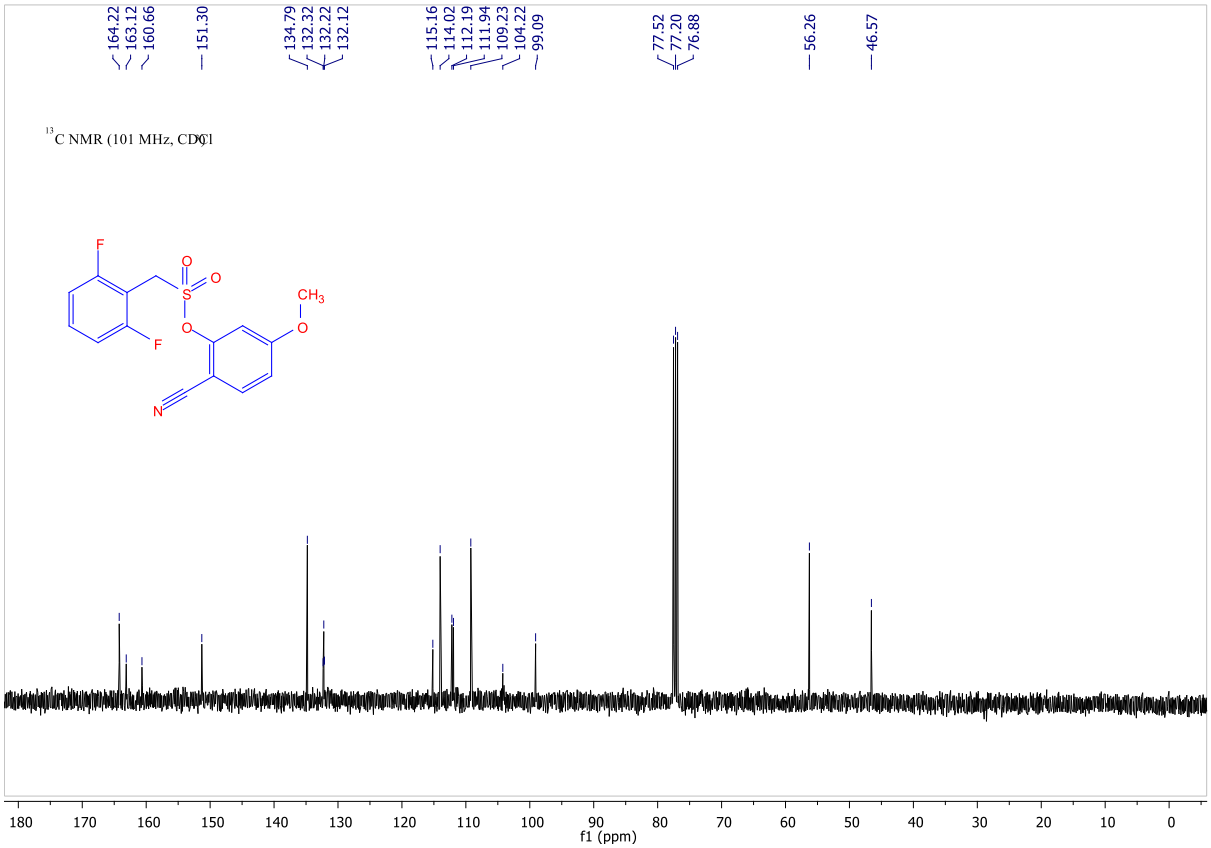


Figure S121: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,6-difluorophenyl)methanesulfonate

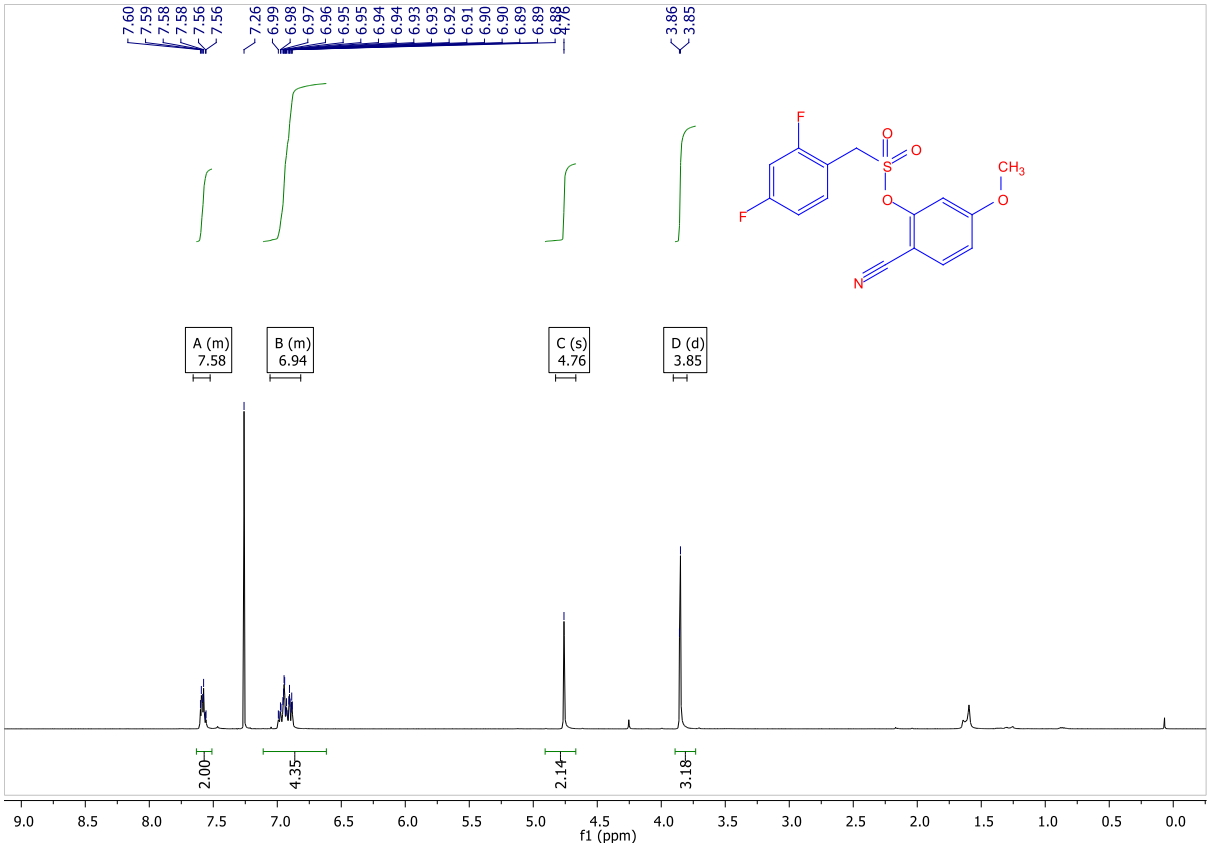


Figure S122: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,4-difluorophenyl)methanesulfonate

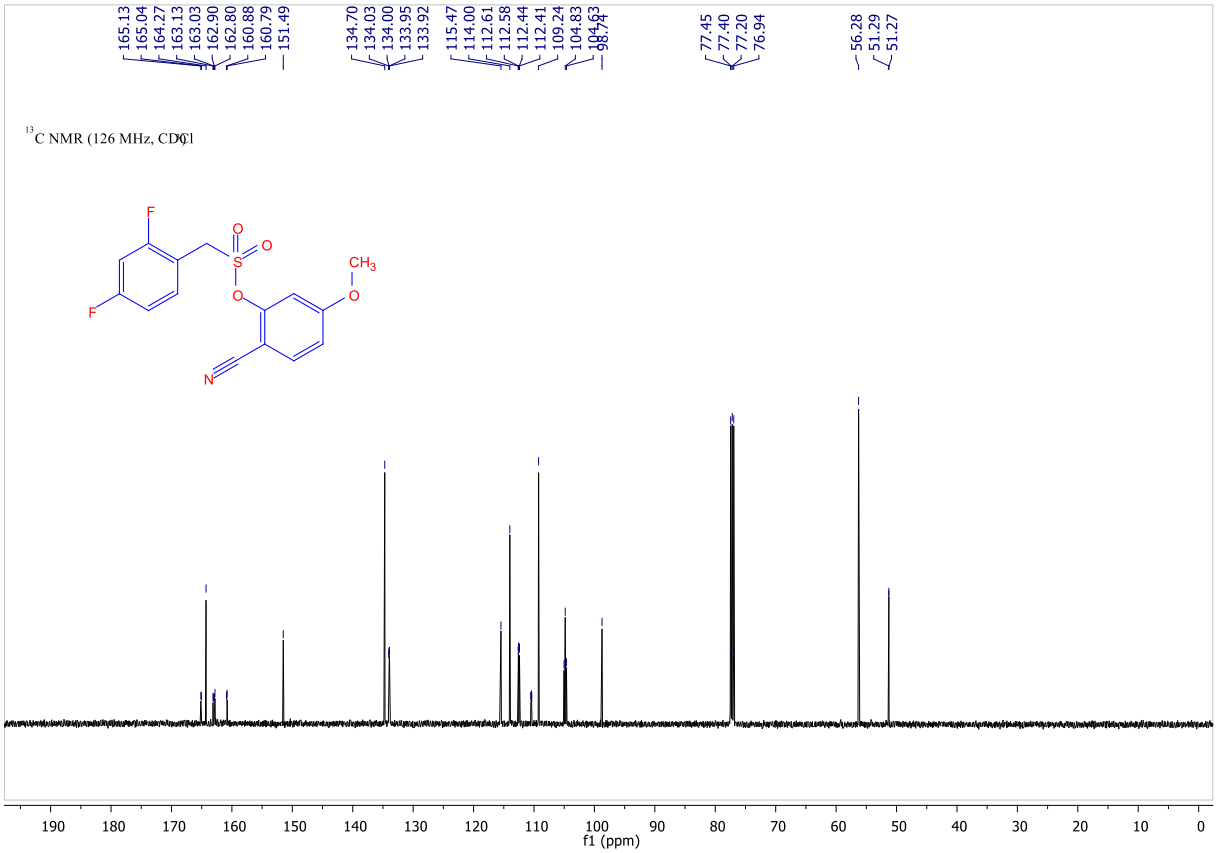


Figure S123: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,4-difluorophenyl)methanesulfonate

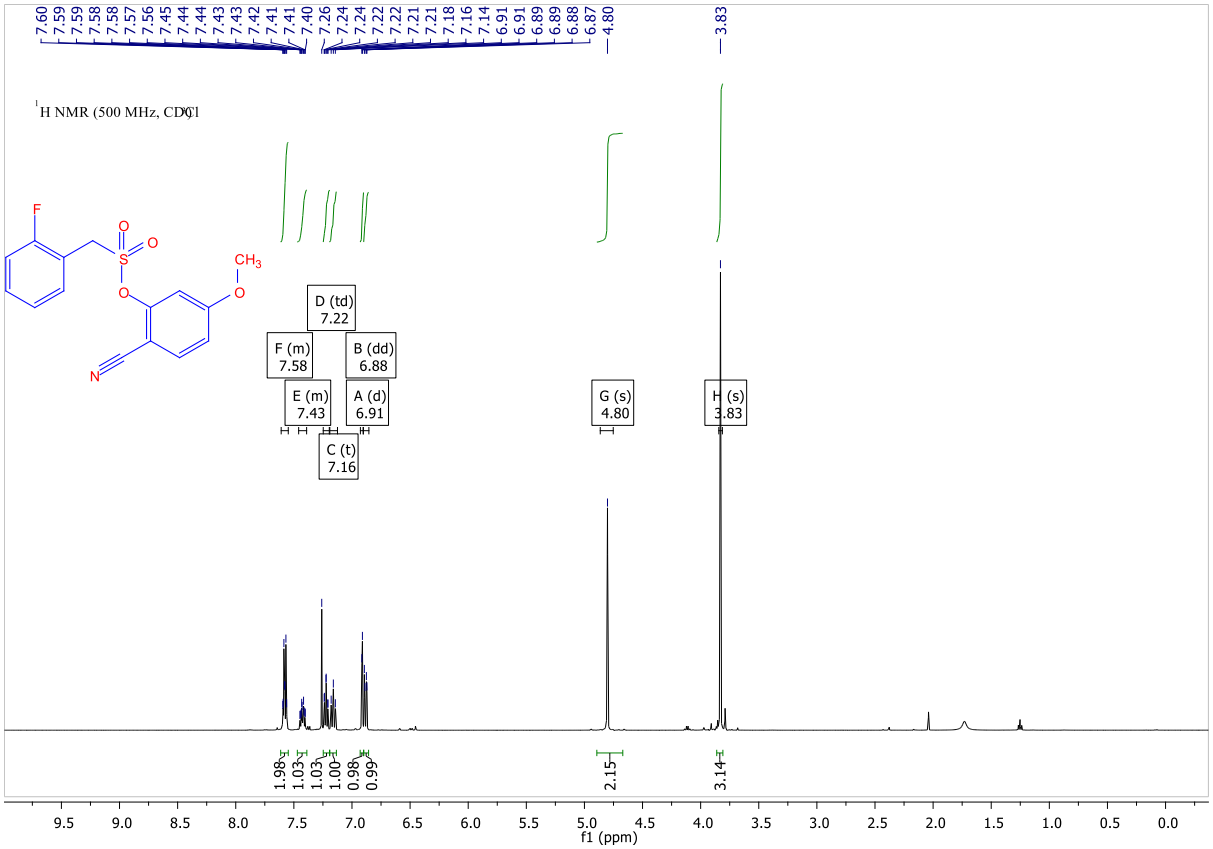


Figure S124: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2-fluorophenyl)methanesulfonate

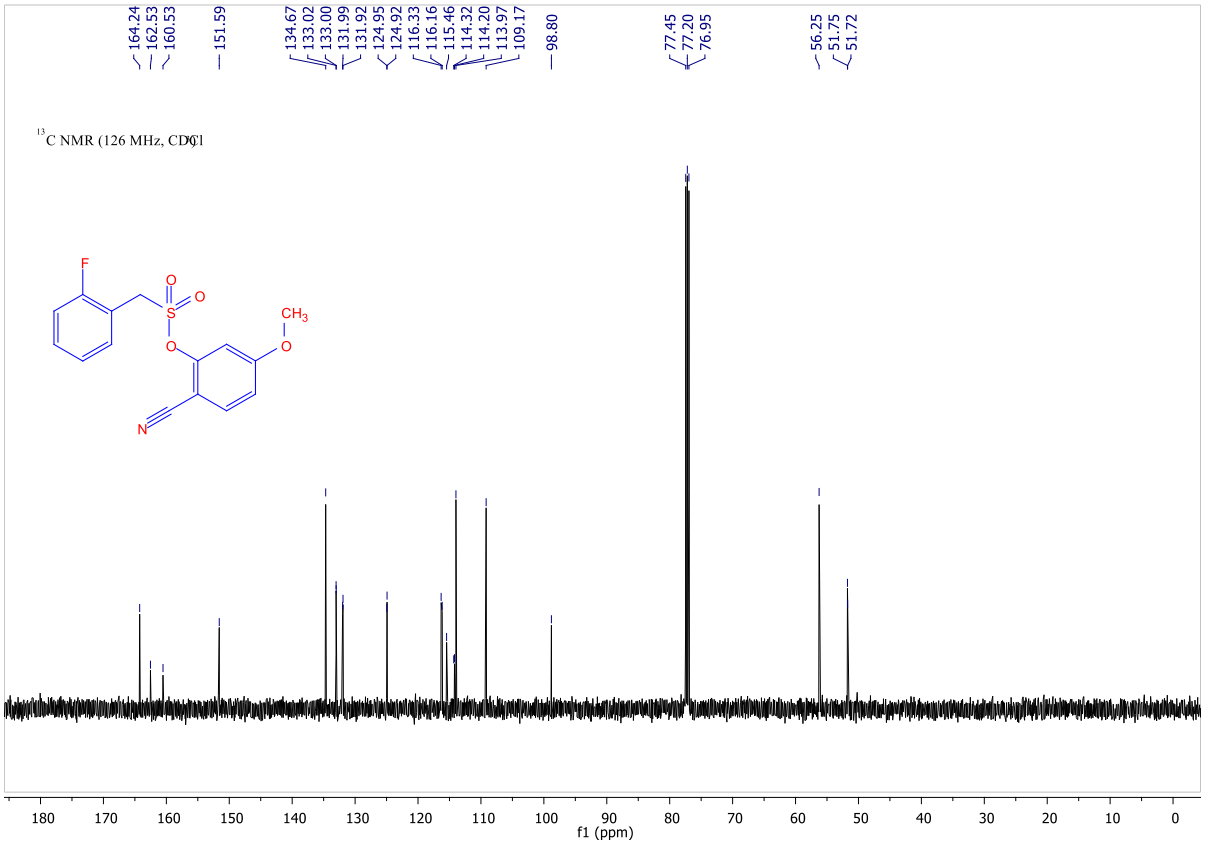


Figure S125: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2-fluorophenyl)methanesulfonate

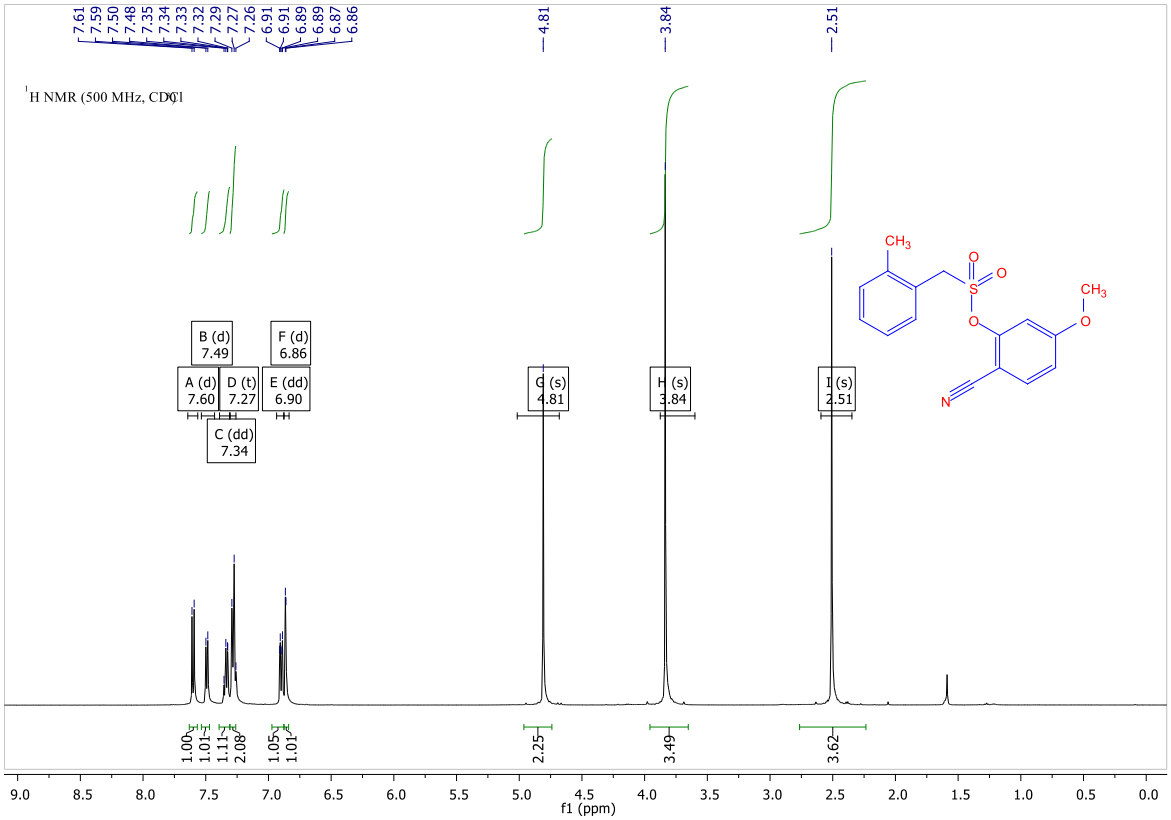


Figure S126: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl o-tolylmethanesulfonate

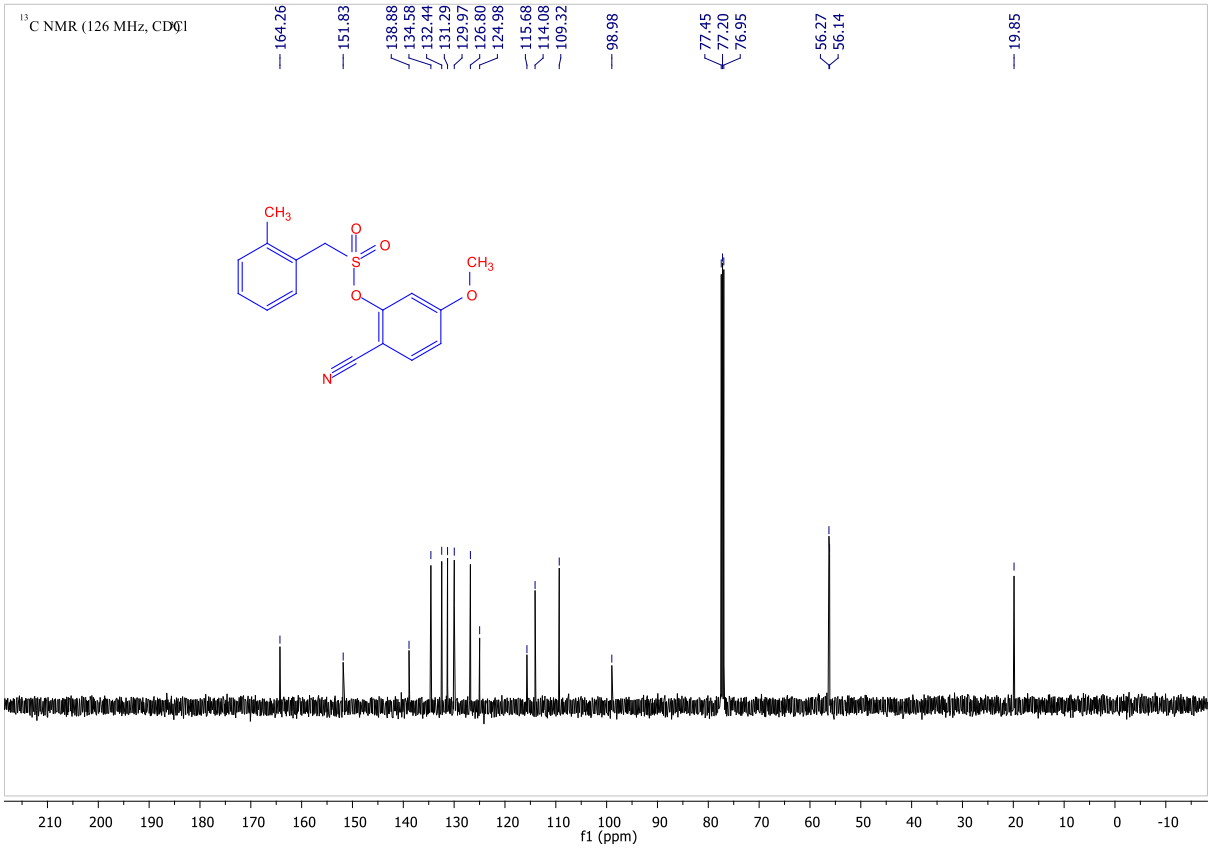


Figure S127: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl o-tolylmethanesulfonate

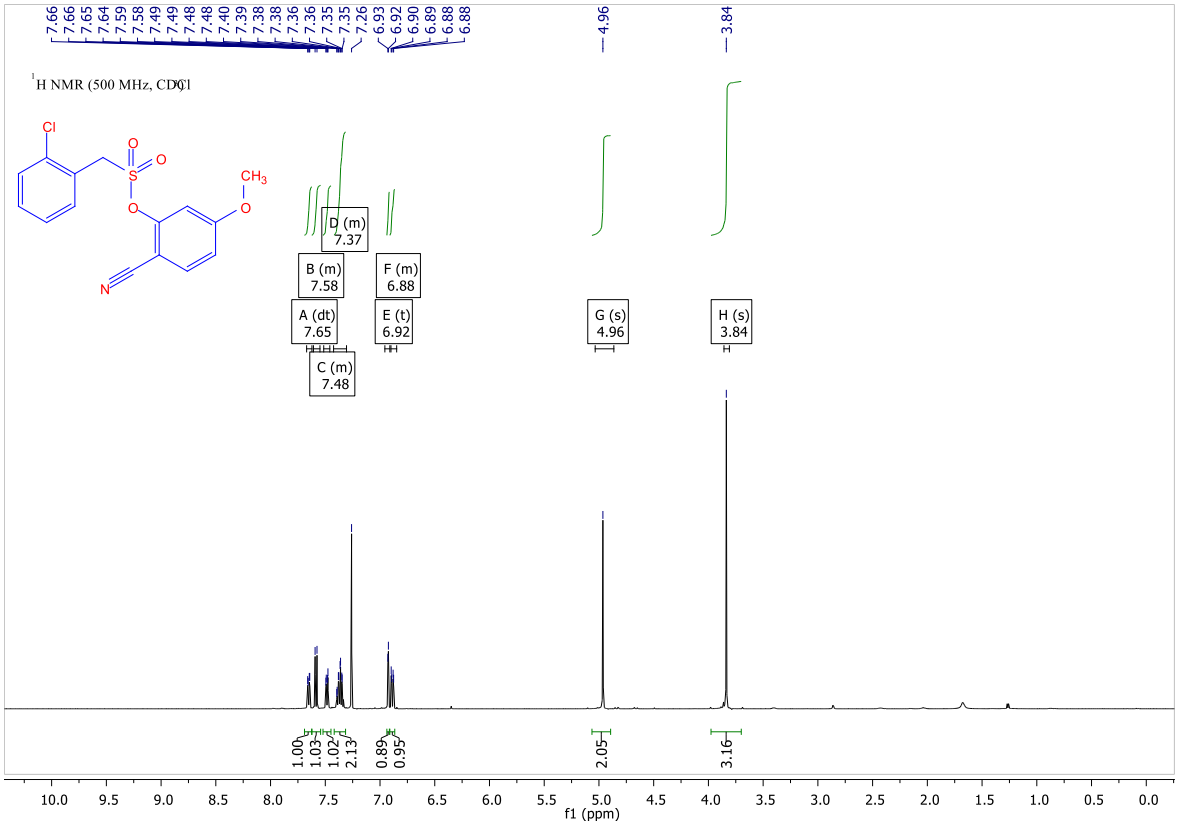


Figure S128: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2-chlorophenyl)methanesulfonate

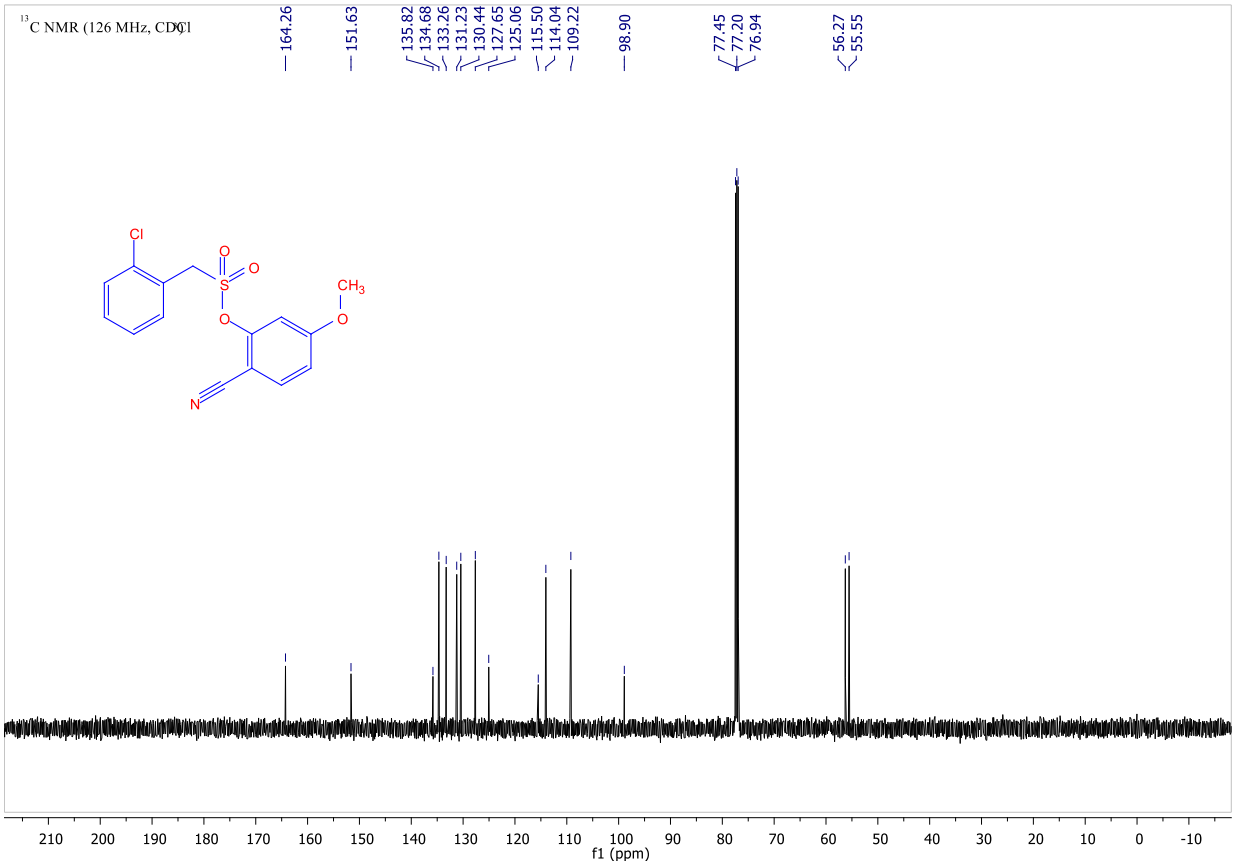


Figure S129: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2-chlorophenyl)methanesulfonate

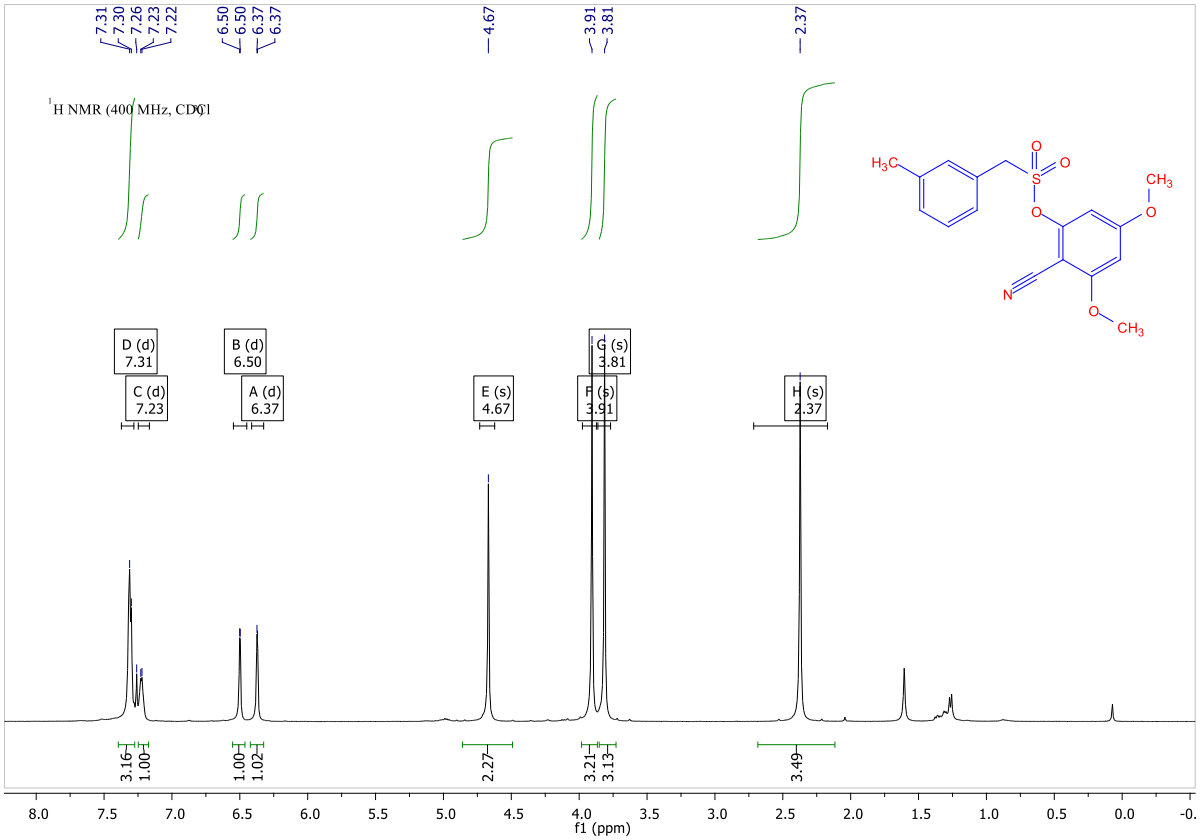


Figure S130: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-3,5-dimethoxyphenyl m-tolylmethanesulfonate

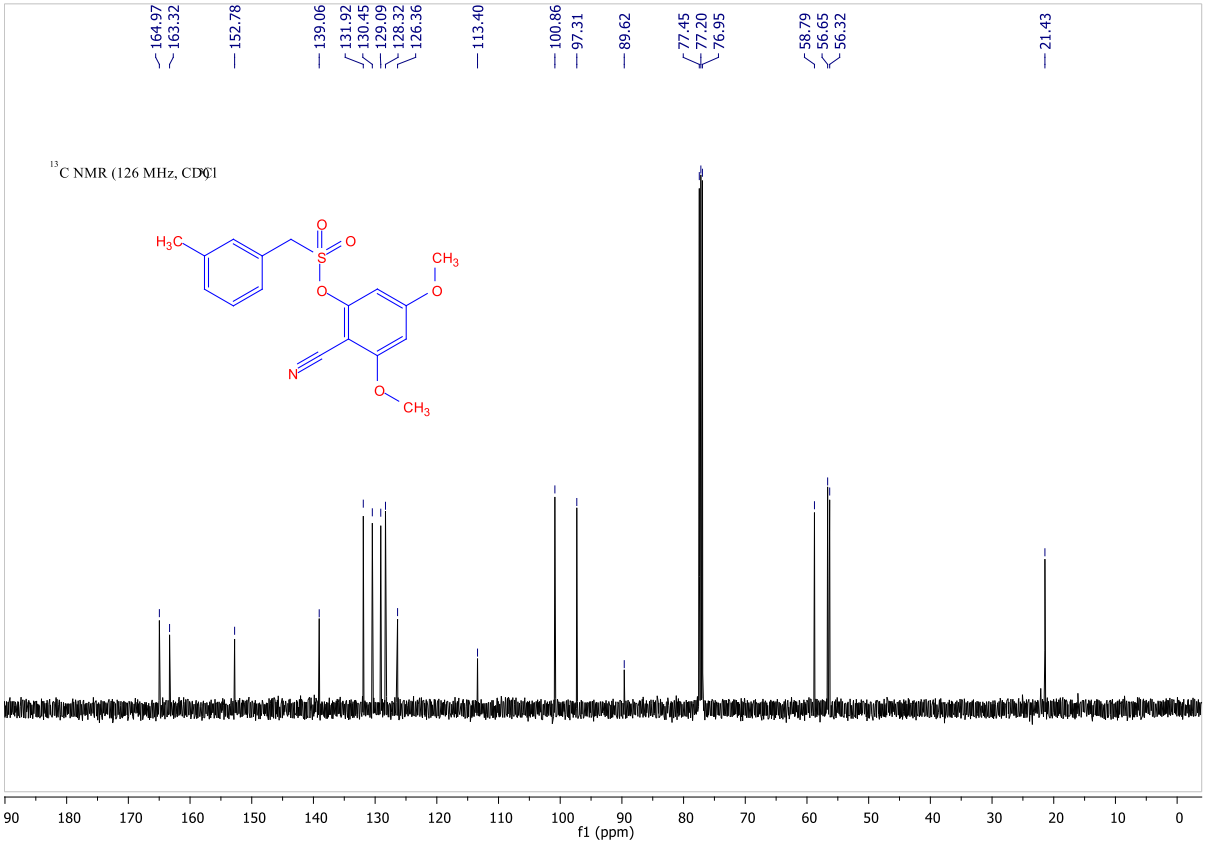


Figure S131: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-3,5-dimethoxyphenyl m-tolylmethanesulfonate

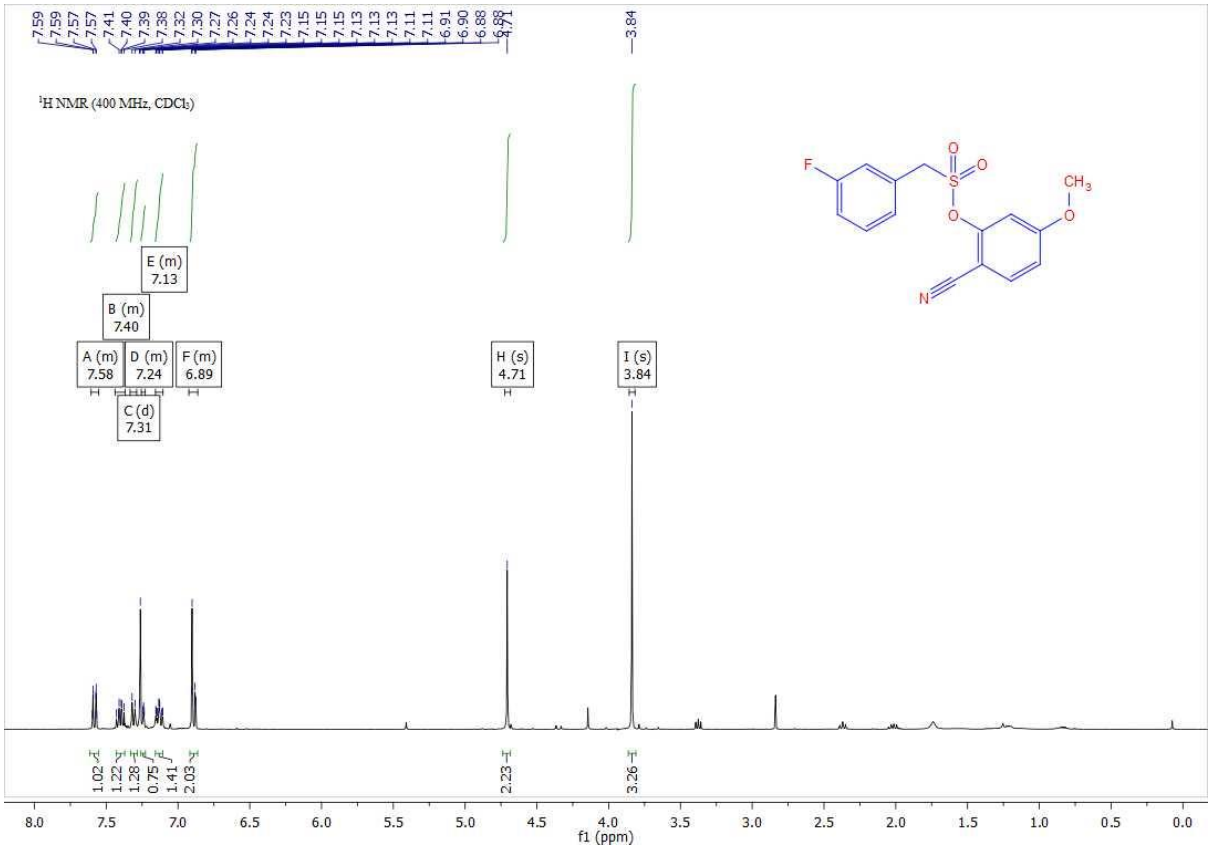


Figure S132: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-fluorophenyl)methanesulfonate

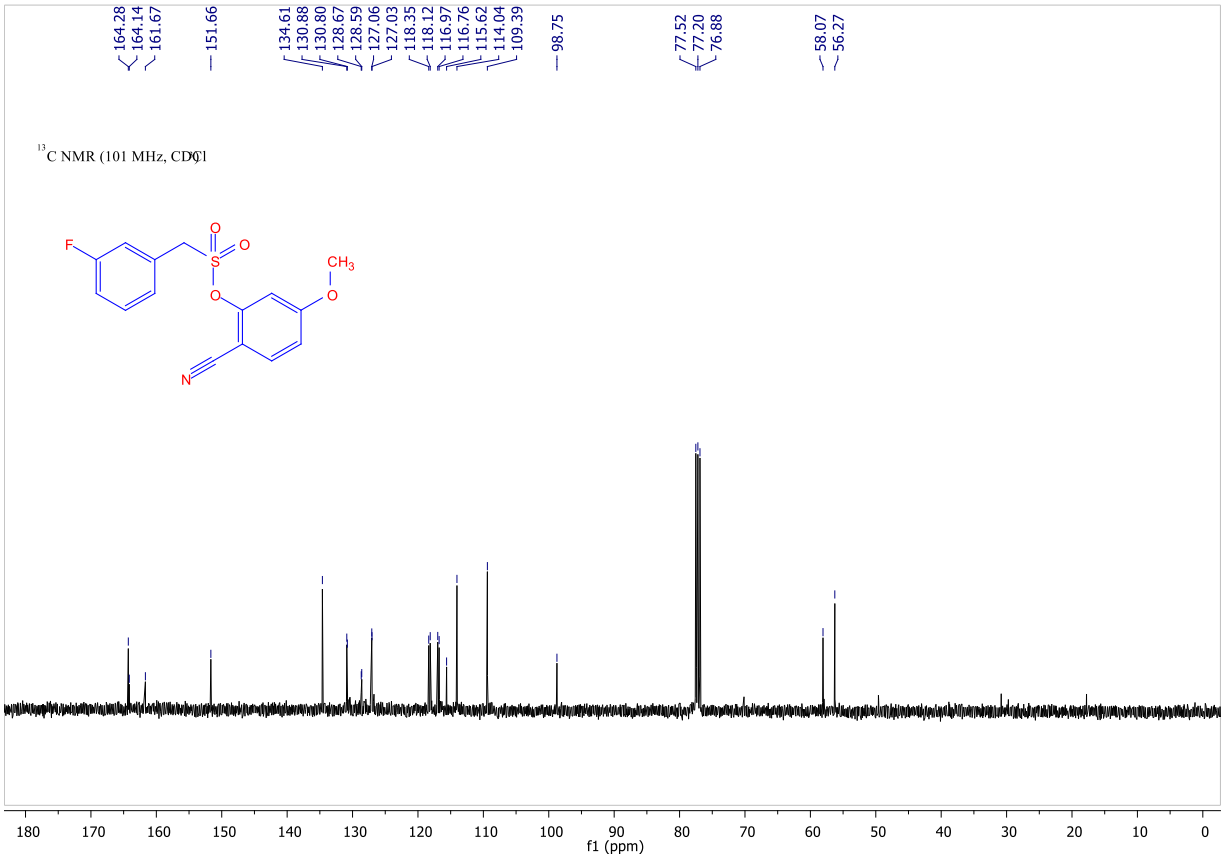


Figure S133: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-fluorophenyl)methanesulfonate

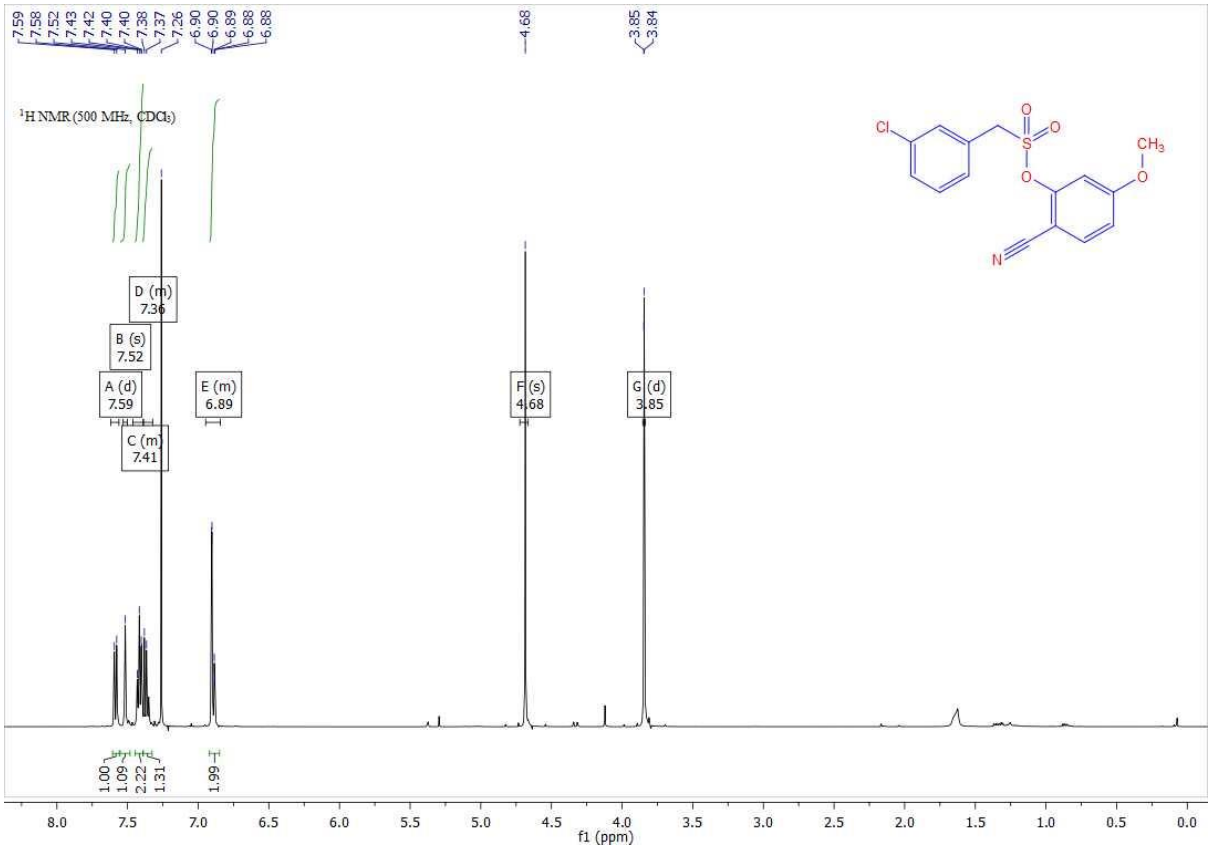


Figure S134: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-chlorophenyl)methanesulfonate

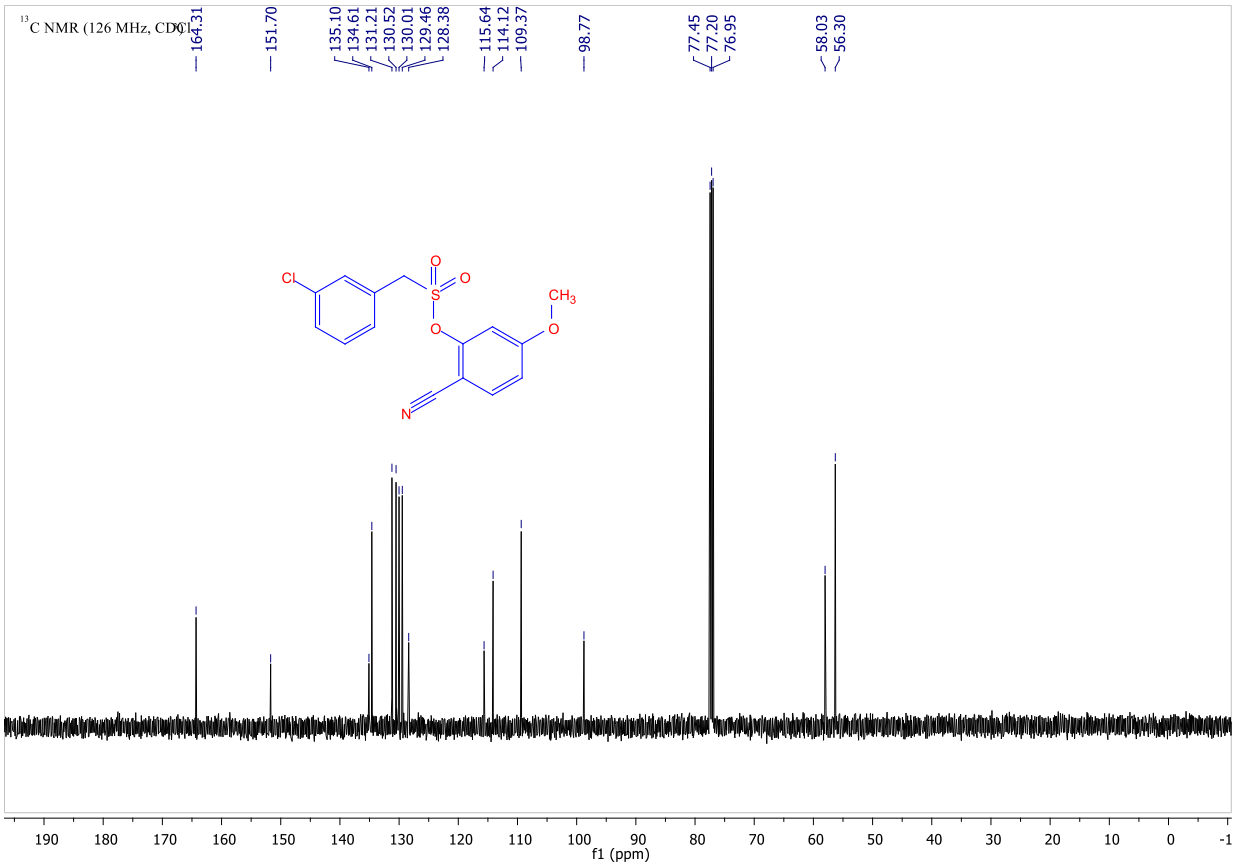


Figure S135: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-chlorophenyl)methanesulfonate

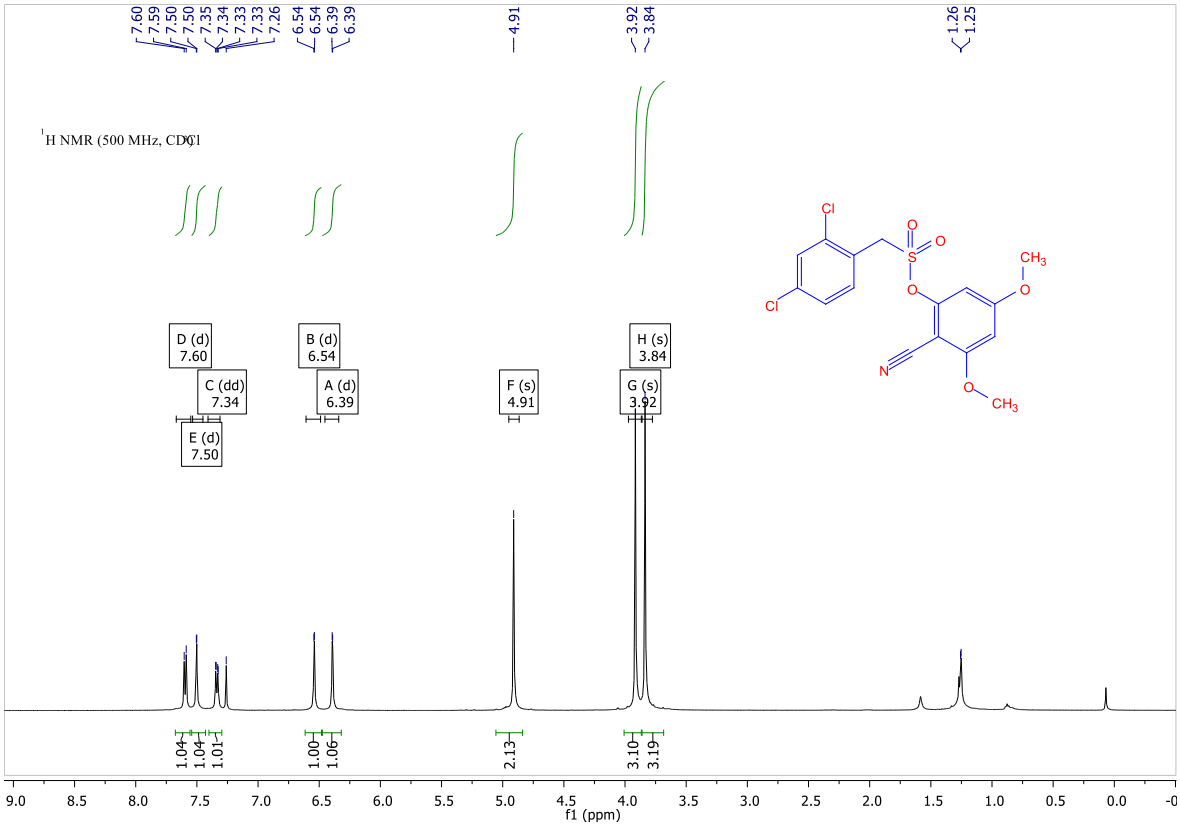


Figure S136: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-3,5-dimethoxyphenyl (2,4-dichlorophenyl)methanesulfonate

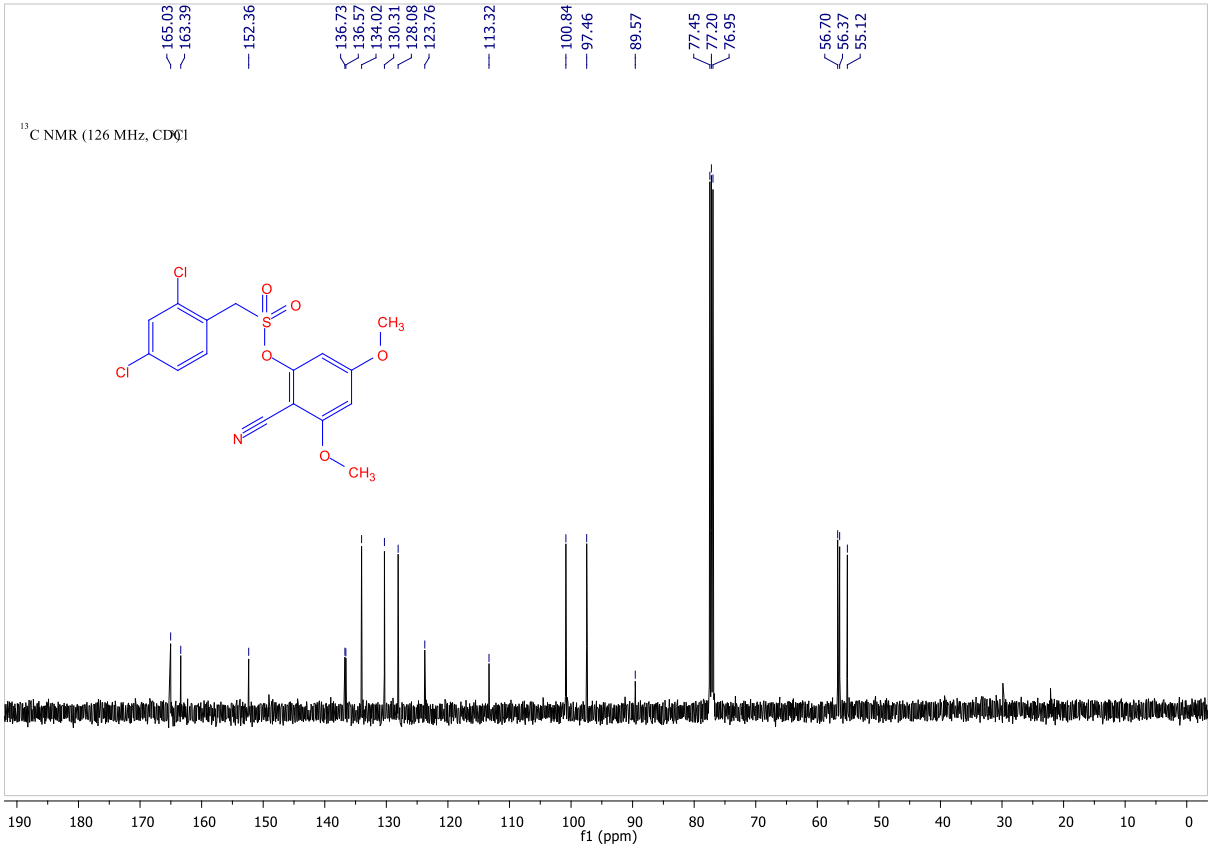


Figure S137: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-3,5-dimethoxyphenyl (2,4-dichlorophenyl)methanesulfonate

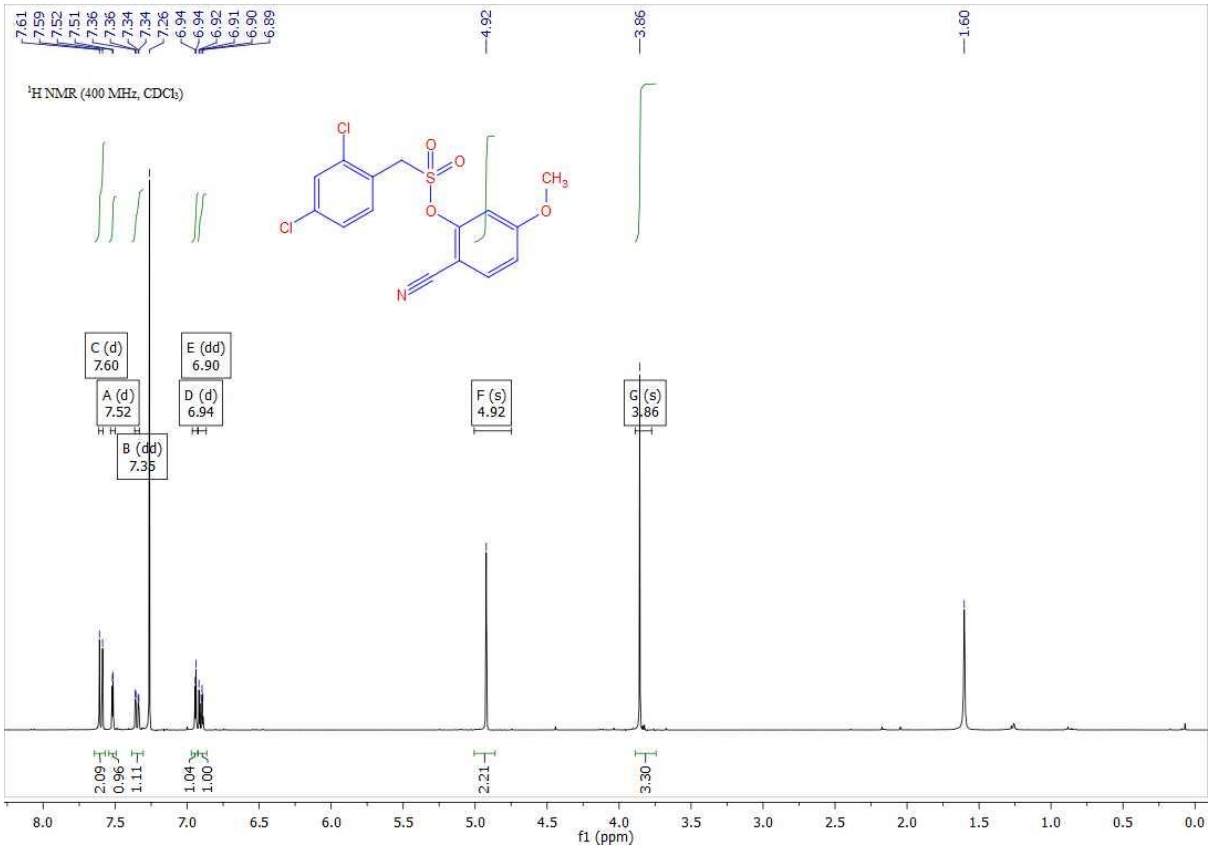


Figure S138: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,4-dichlorophenyl)methanesulfonate

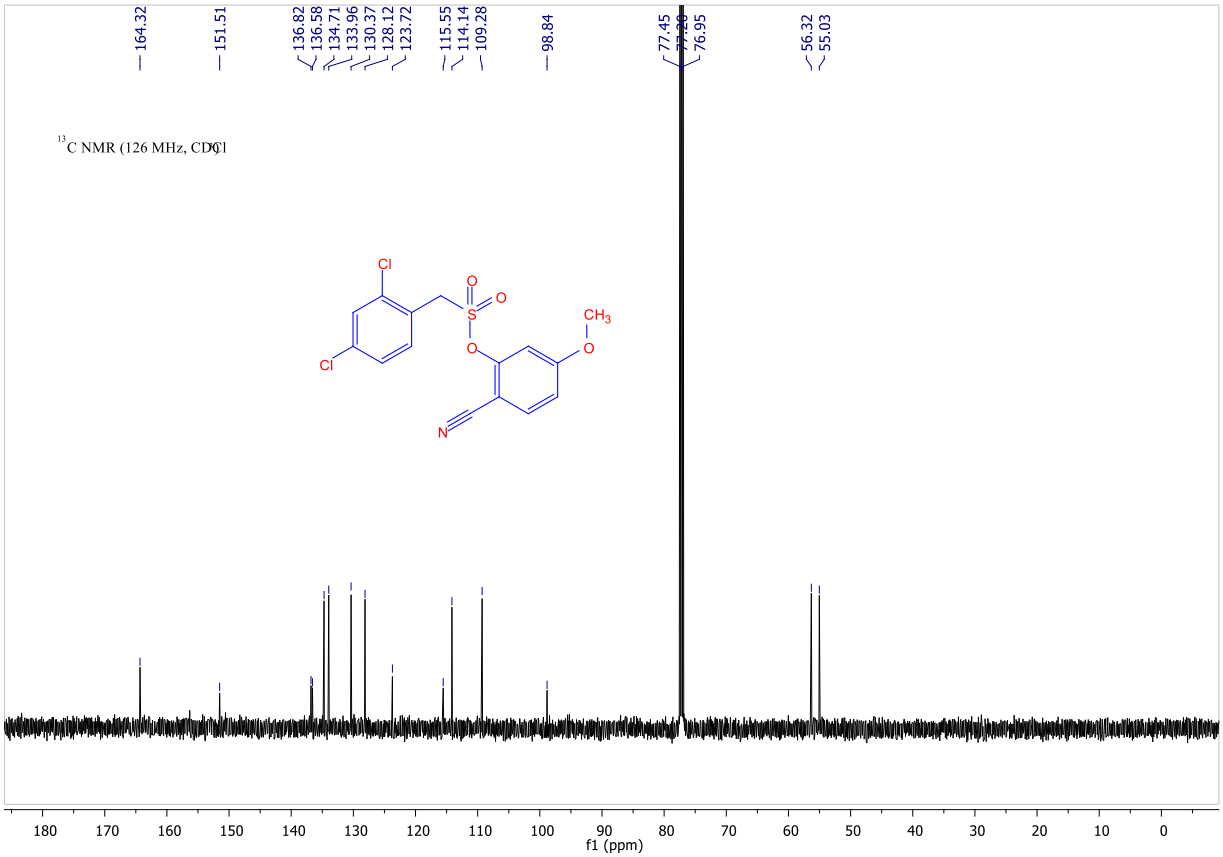


Figure S139: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,4-dichlorophenyl)methanesulfonate

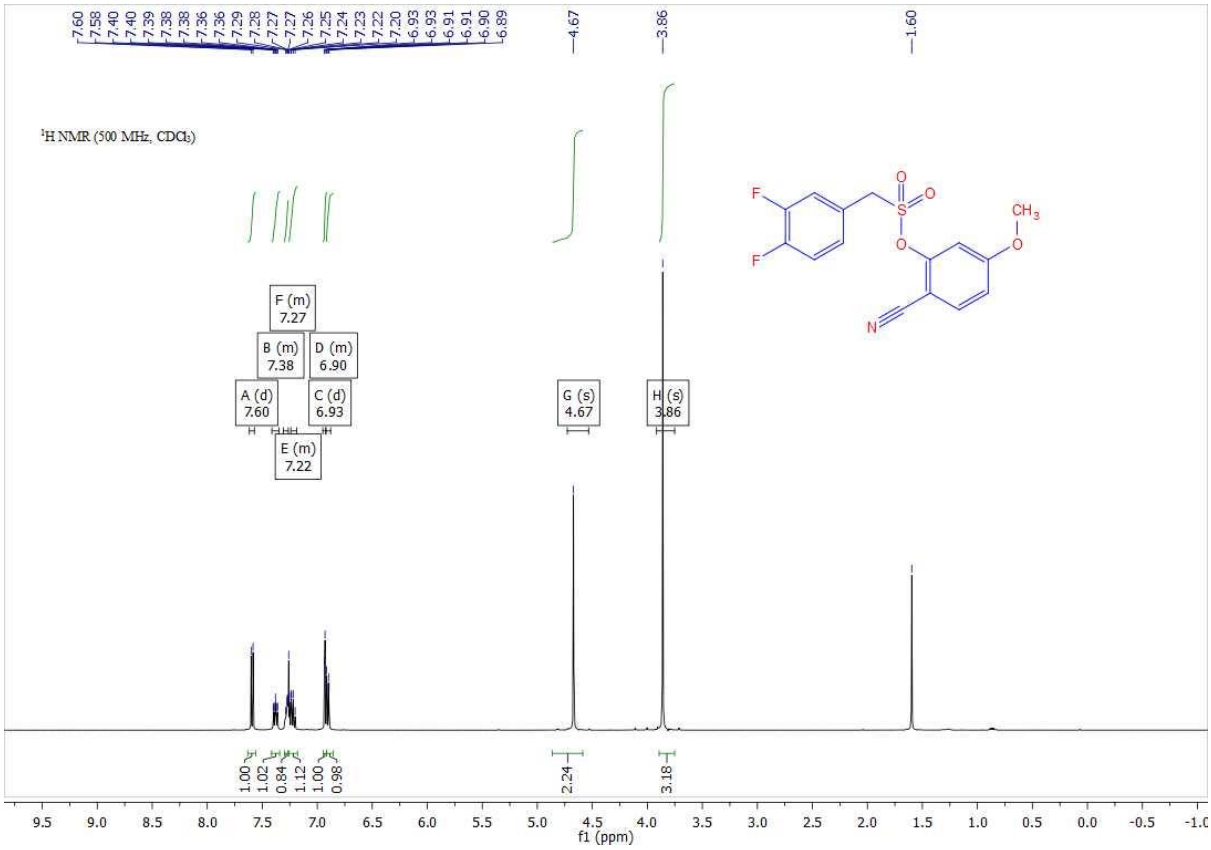


Figure S140: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3,4-difluorophenyl)methanesulfonate

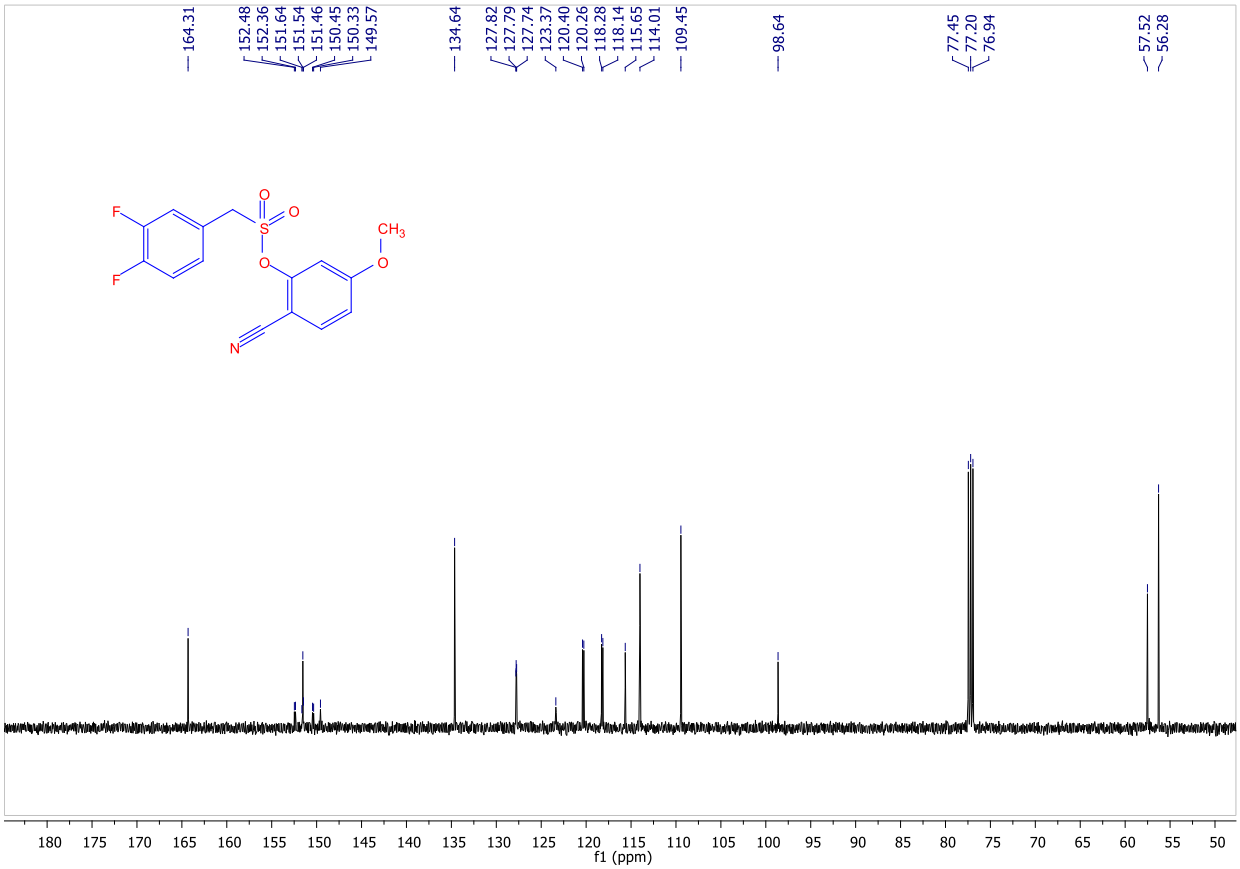


Figure S141: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3,4-difluorophenyl)methanesulfonate

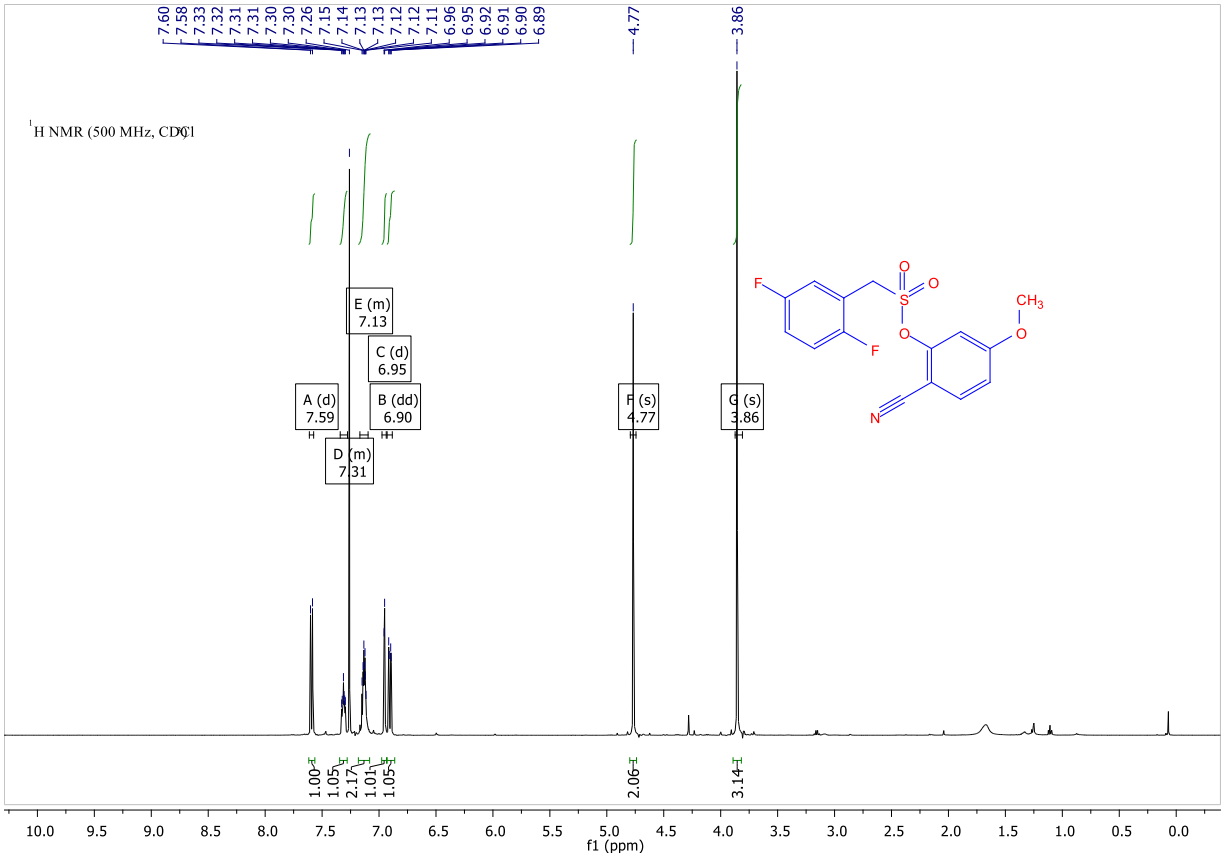


Figure S142: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,5-difluorophenyl)methanesulfonate

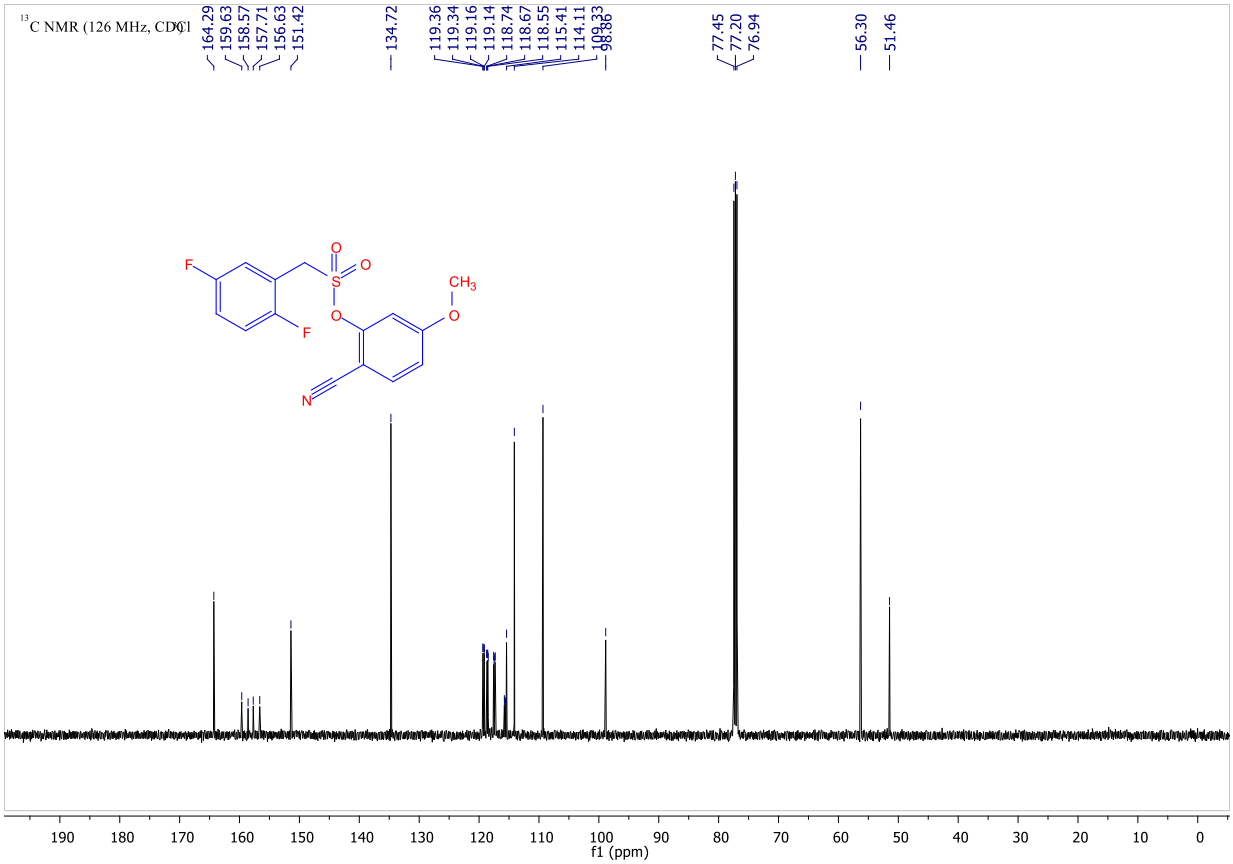


Figure S143: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,5-difluorophenyl)methanesulfonate

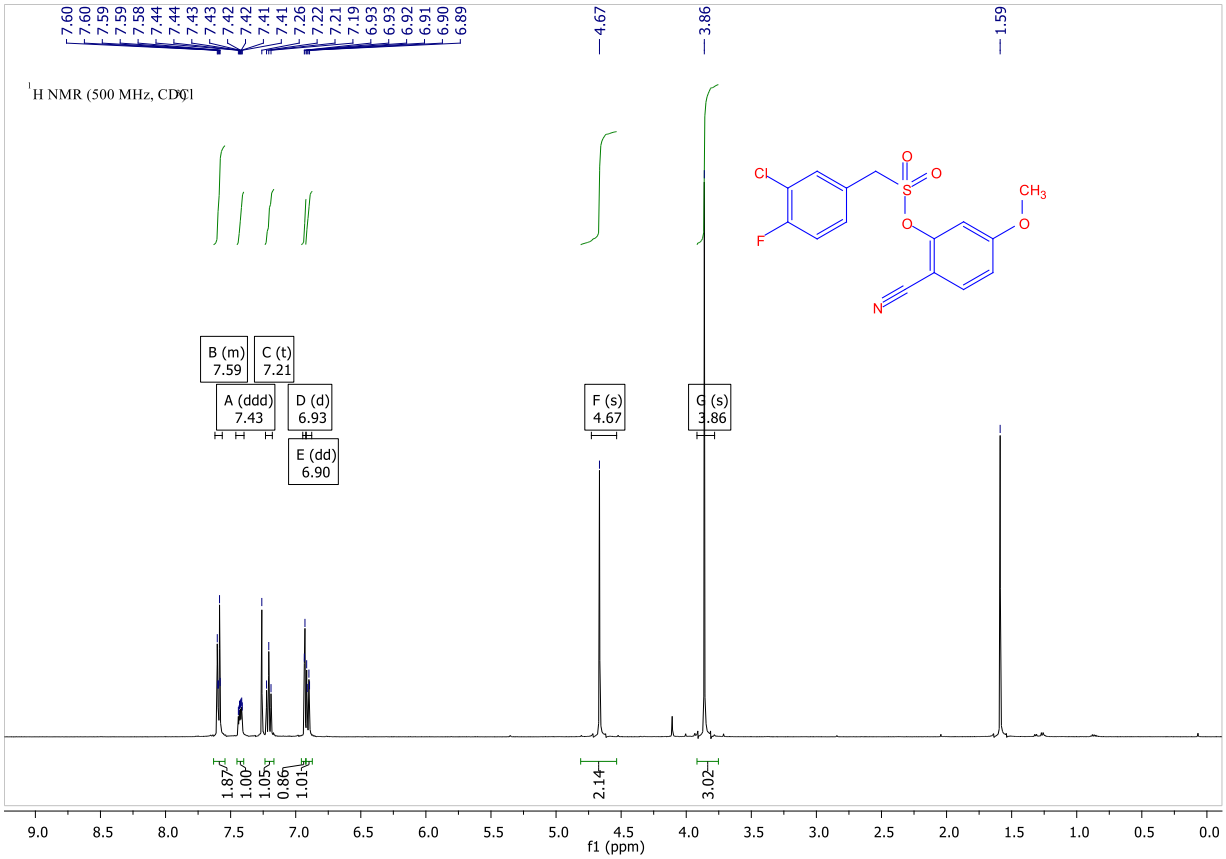


Figure S144: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-chloro-4-fluorophenyl)methanesulfonate

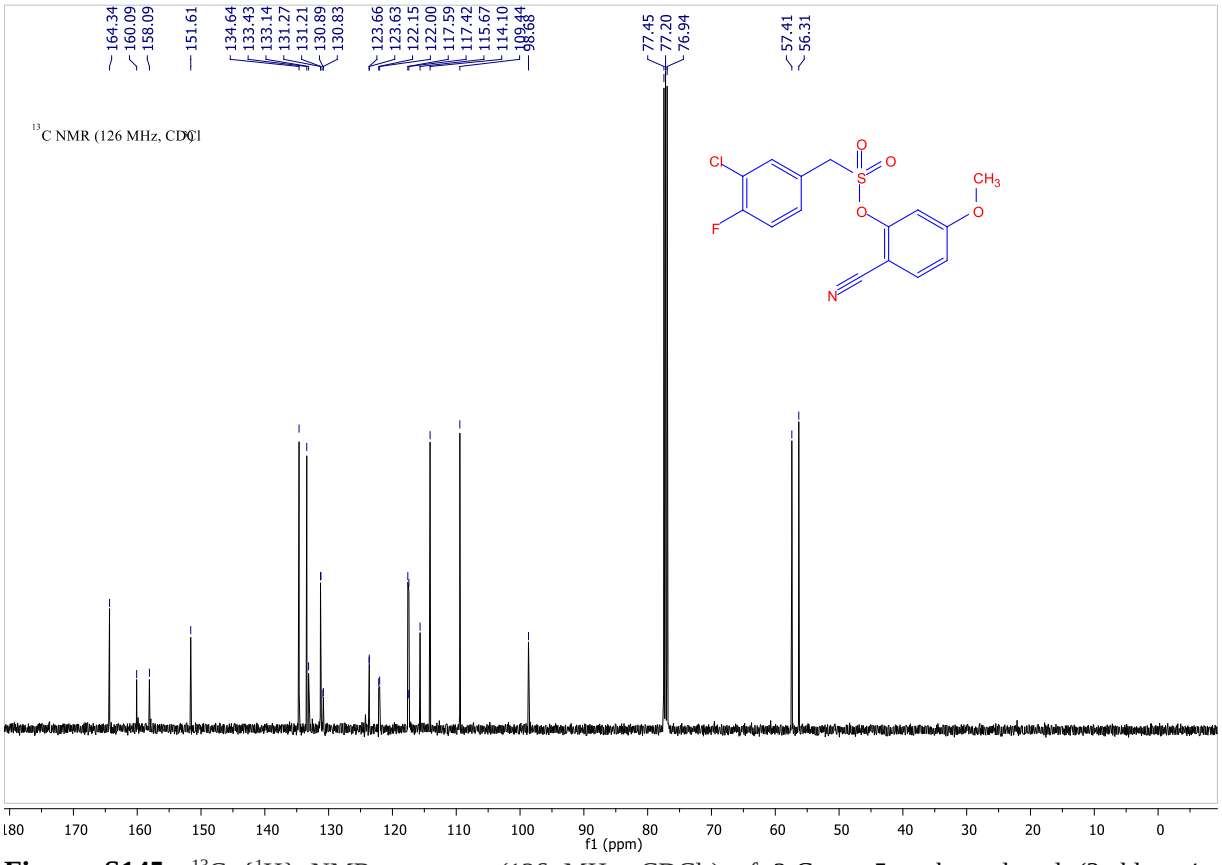


Figure S145: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-chloro-4-fluorophenyl)methanesulfonate

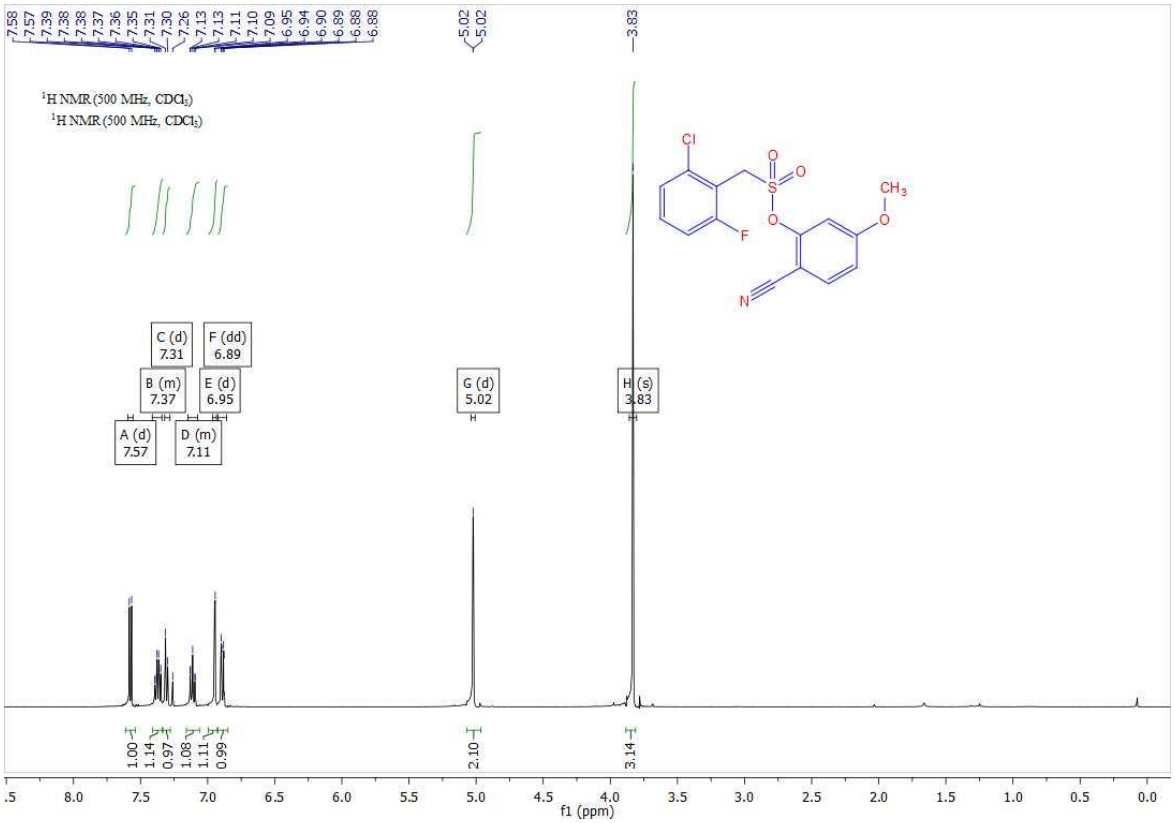


Figure S146: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2-chloro-6-fluorophenyl)methanesulfonate

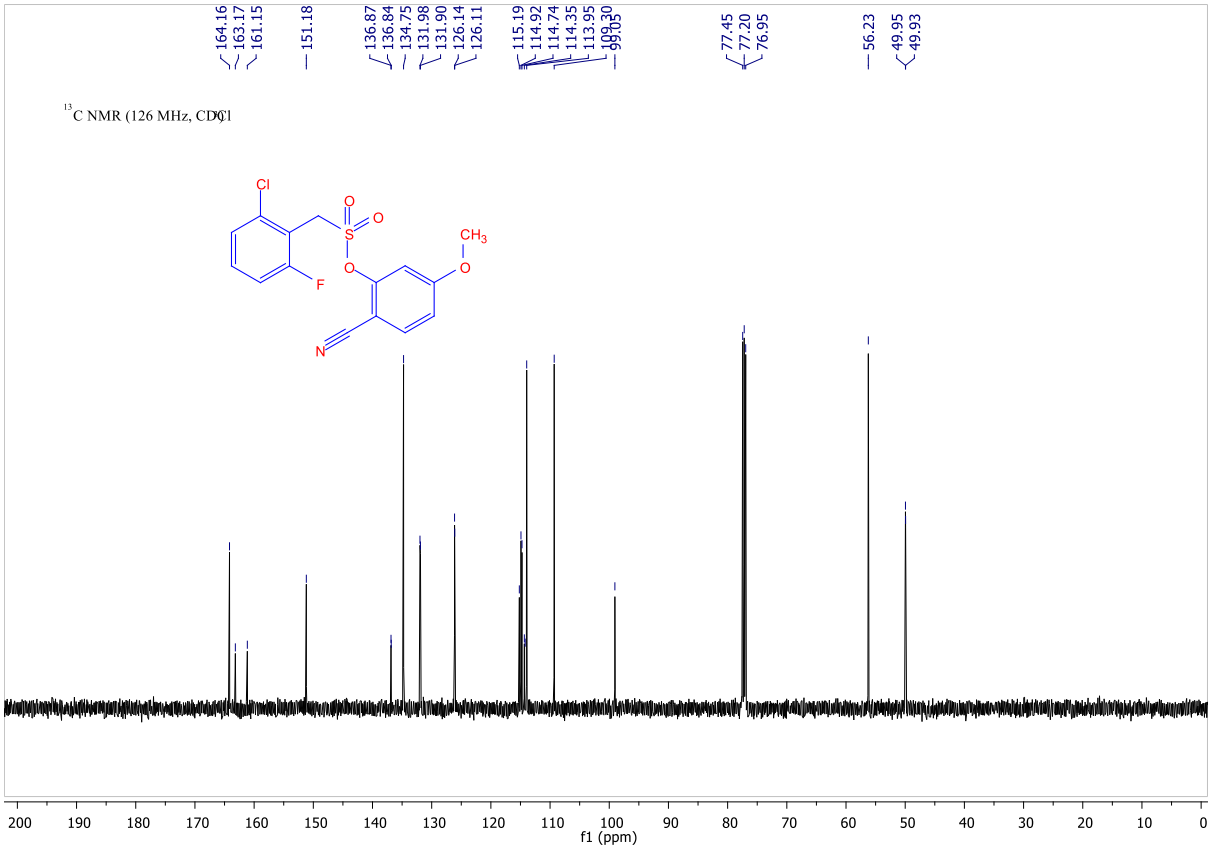


Figure S147: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2-chloro-6-fluorophenyl)methanesulfonate

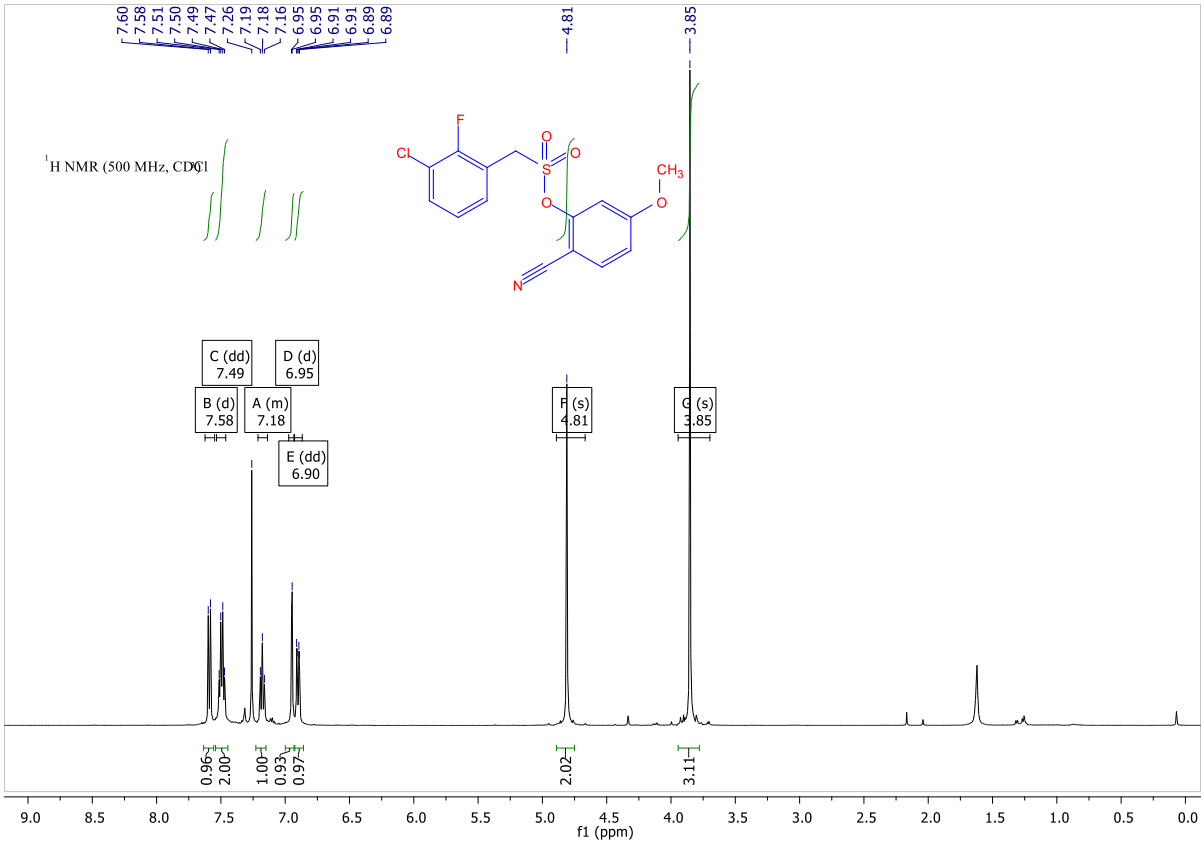


Figure S148: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-chloro-2-fluorophenyl)methanesulfonate

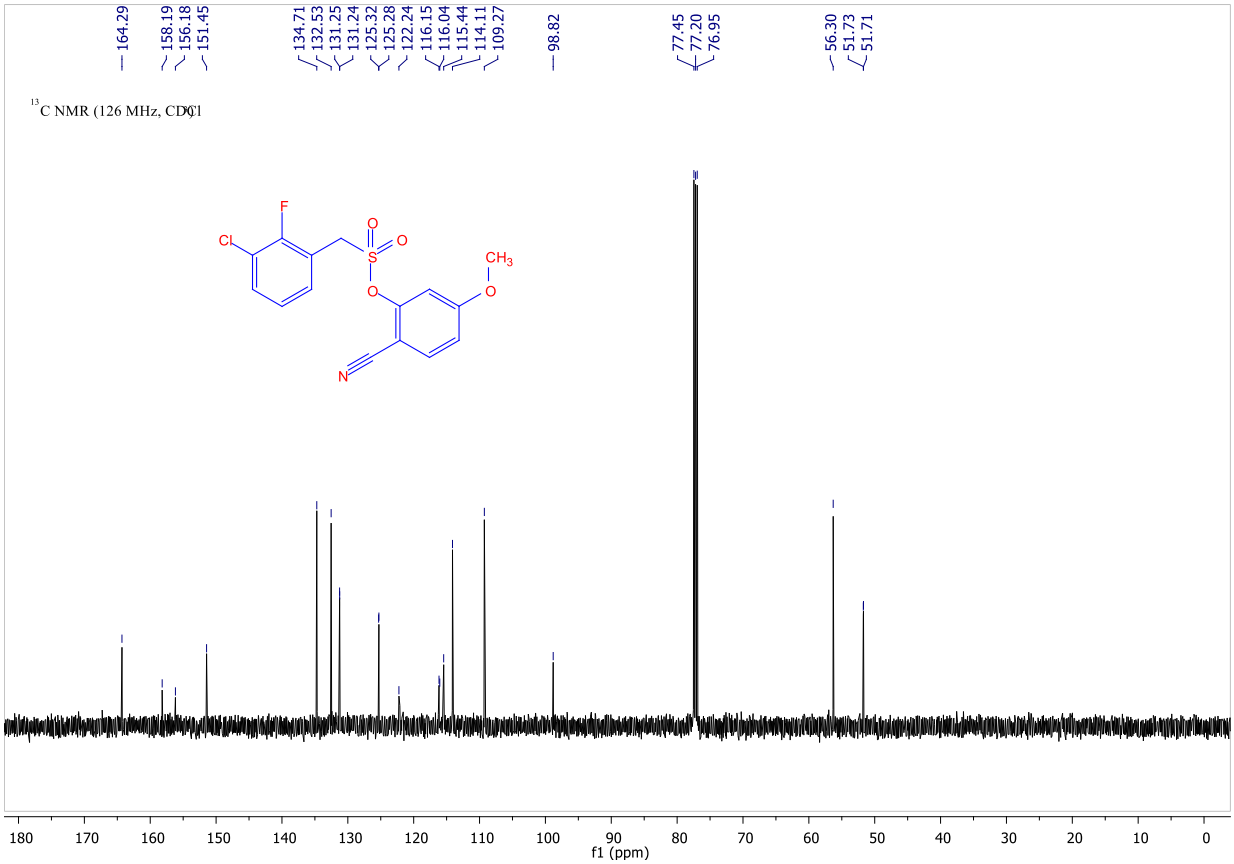


Figure S149: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (3-chloro-2-fluorophenyl)methanesulfonate

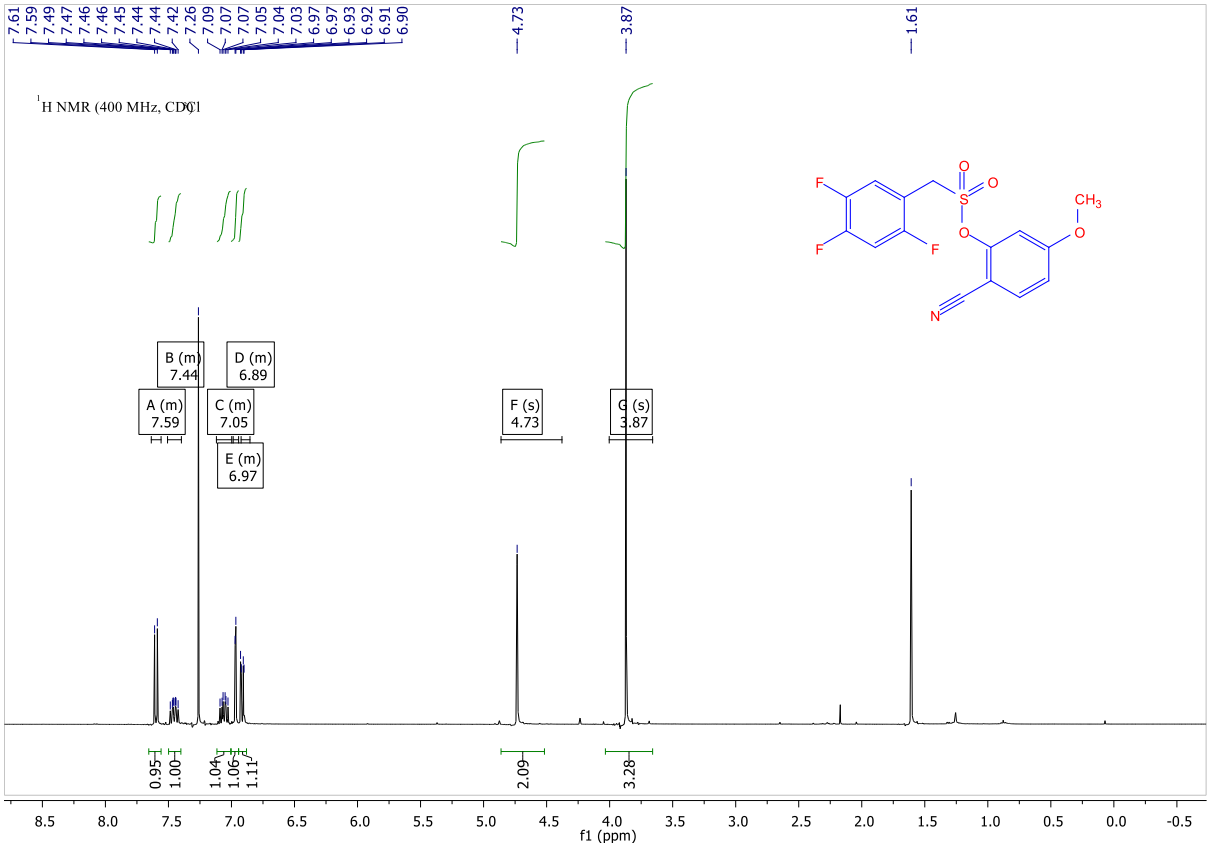


Figure S150: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,4,5-trifluorophenyl)methanesulfonate

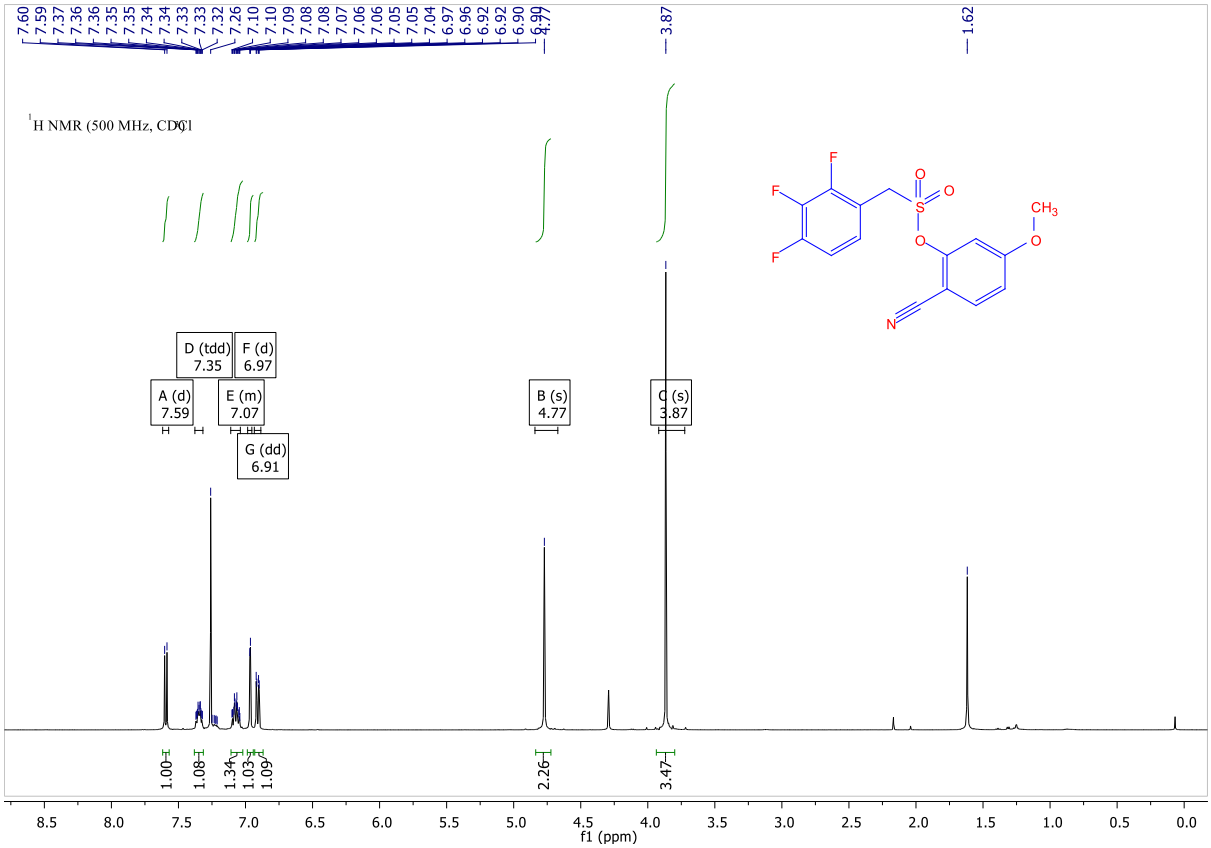


Figure S151: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,3,4-trifluorophenyl)methanesulfonate

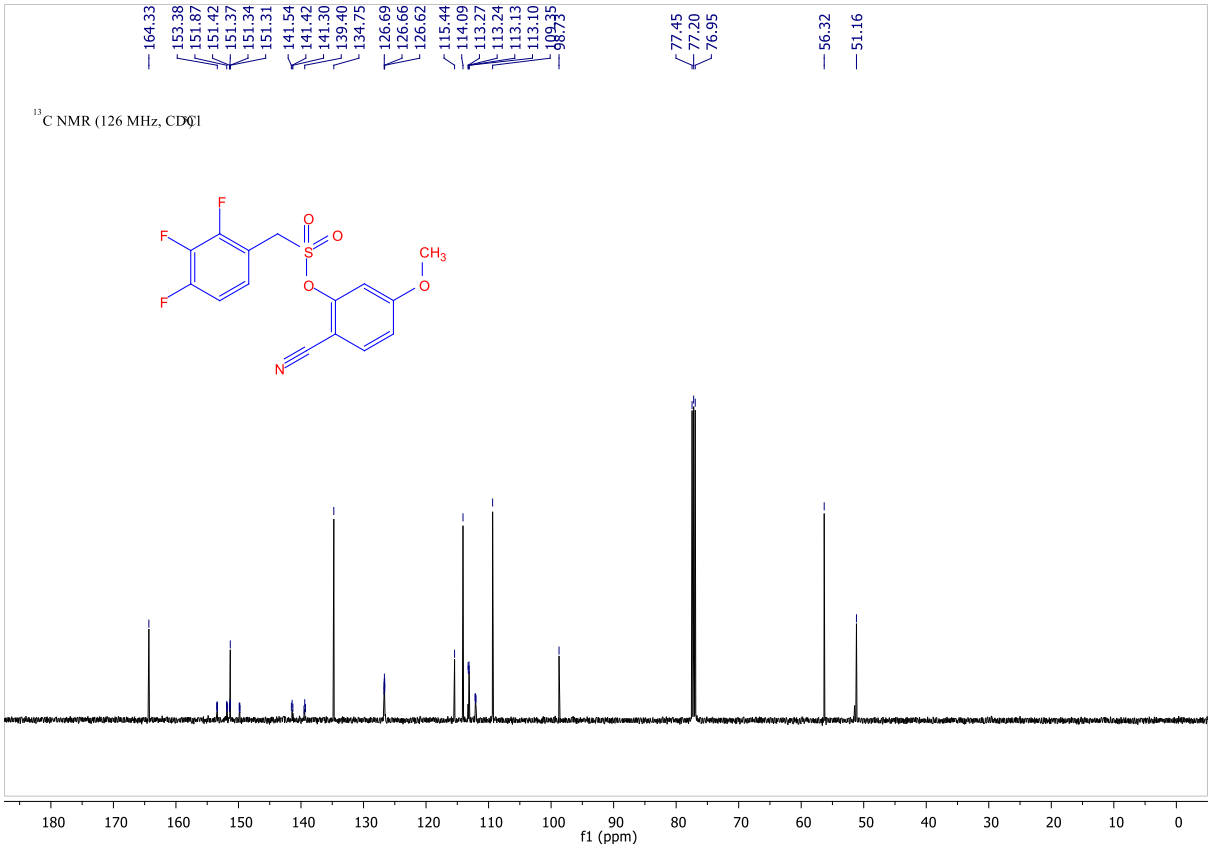


Figure S152: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl (2,3,4-trifluorophenyl)methanesulfonate

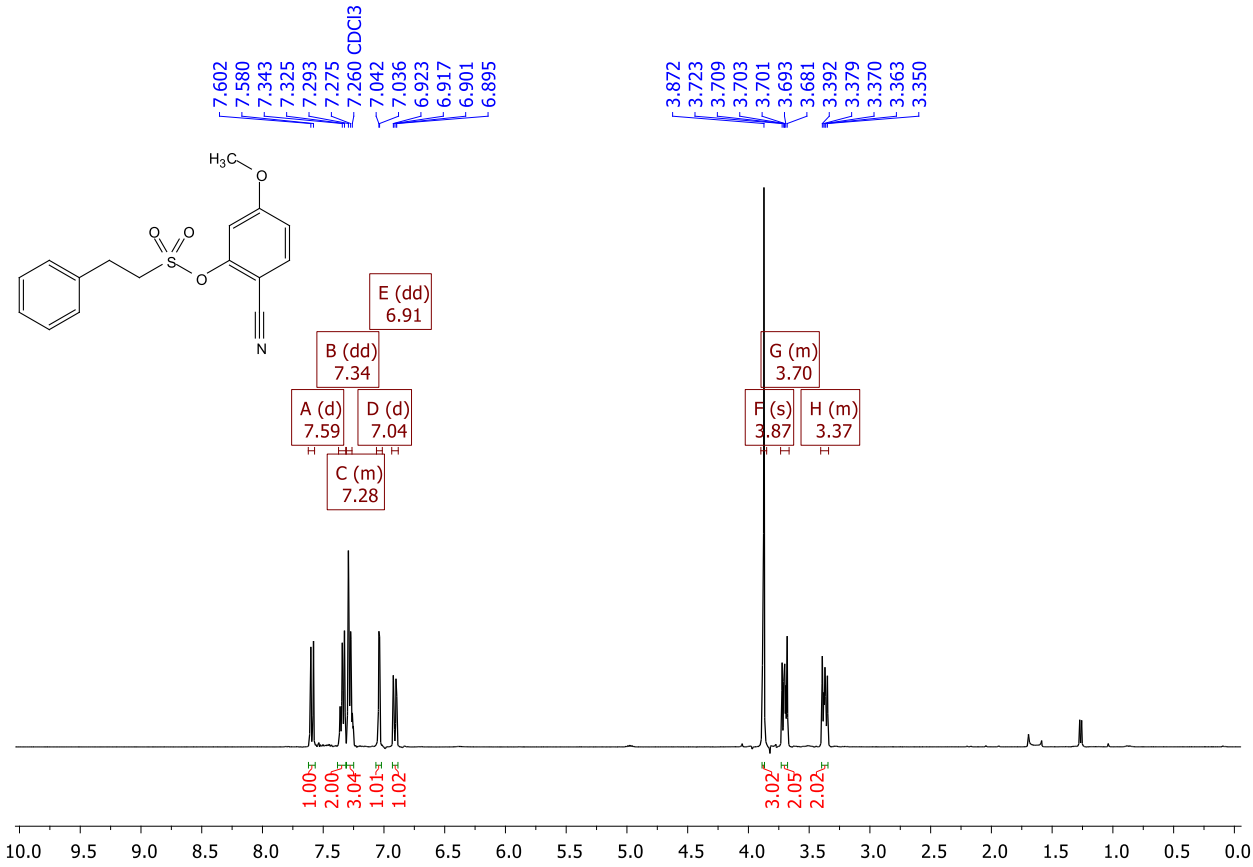


Figure S153: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-phenylethanesulfonate

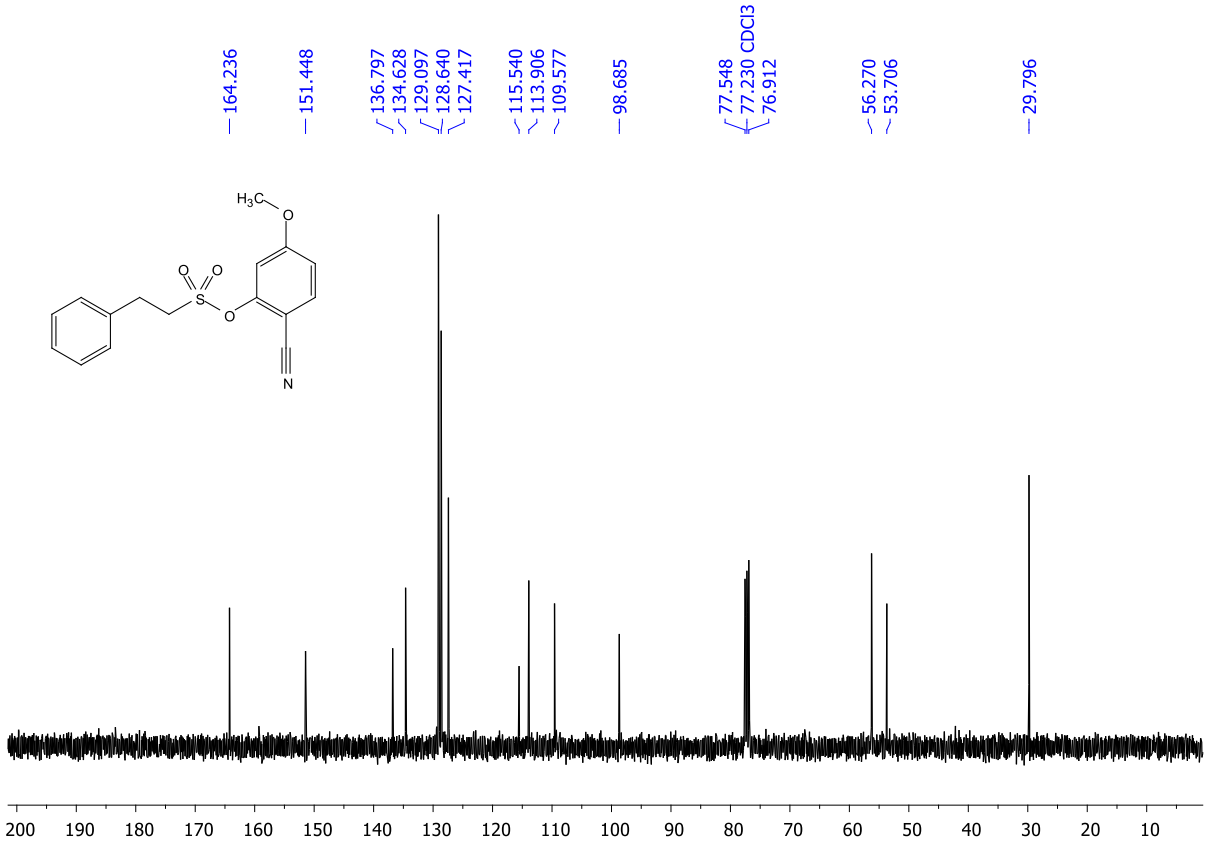


Figure S154: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-phenylethanesulfonate

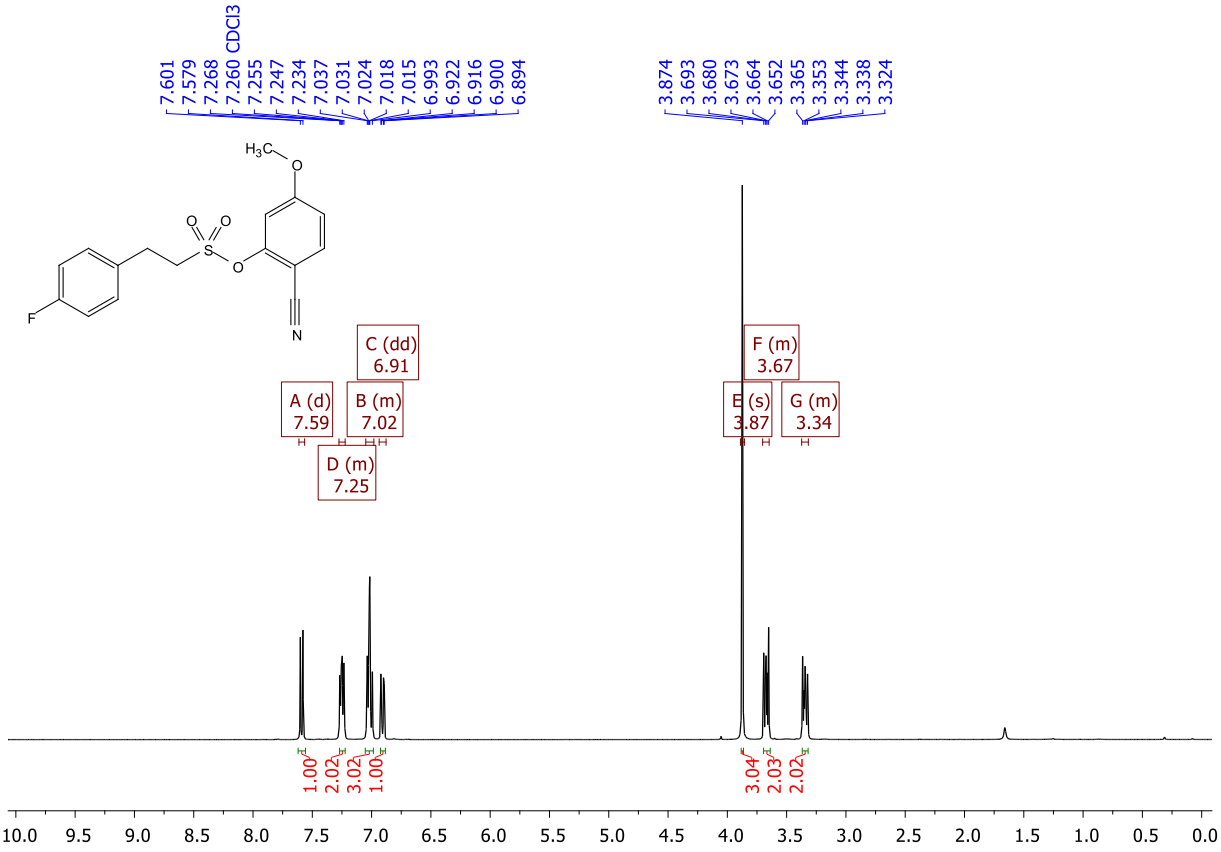


Figure S155: ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-(4-fluorophenyl)ethanesulfonate

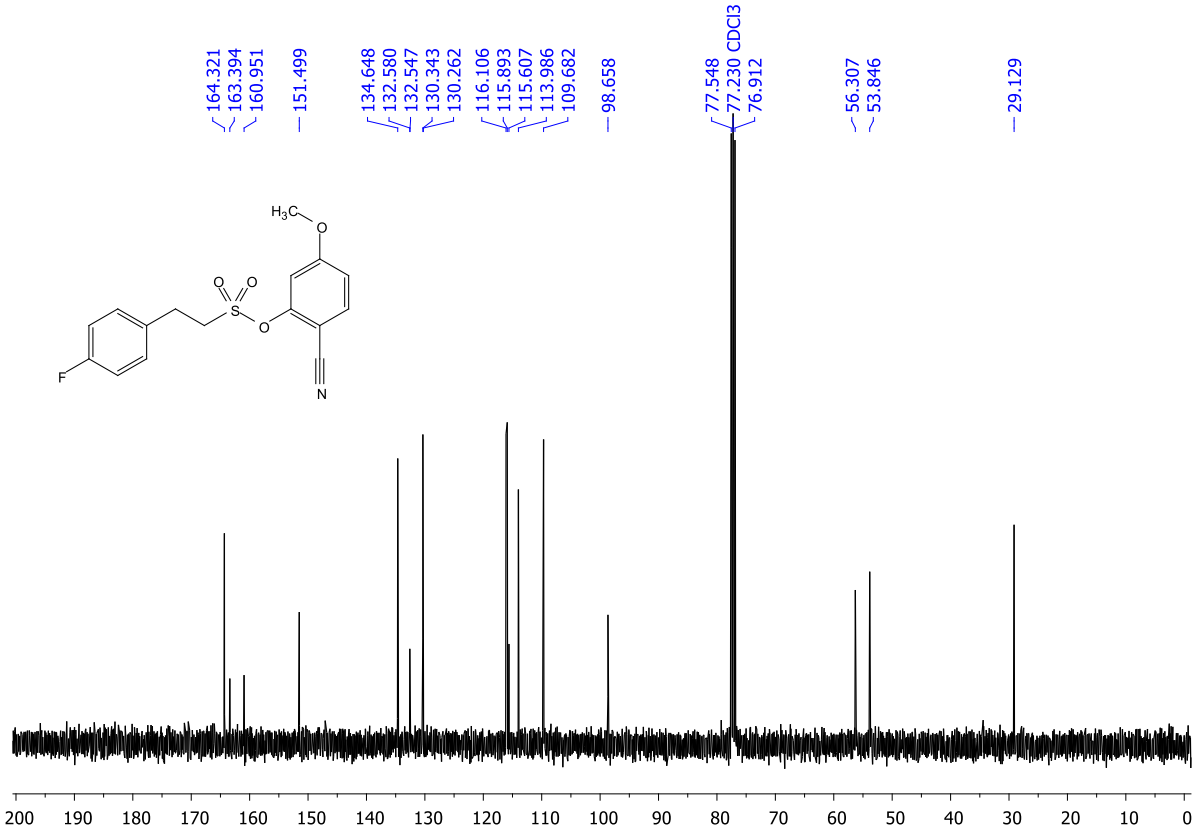


Figure S156: ^{13}C {^{1}H} NMR spectrum (101 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-(4-fluorophenyl)ethanesulfonate

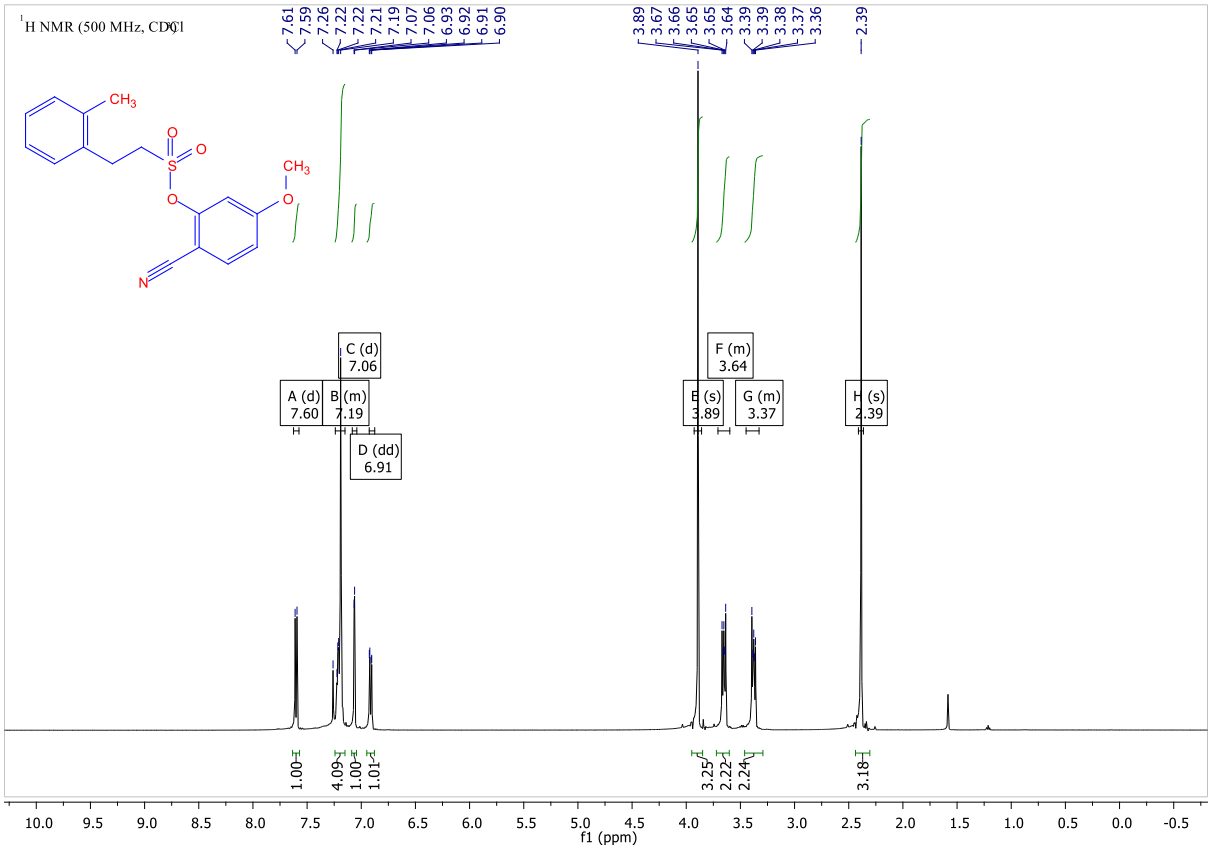


Figure S157: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-(o-tolyl)ethanesulfonate

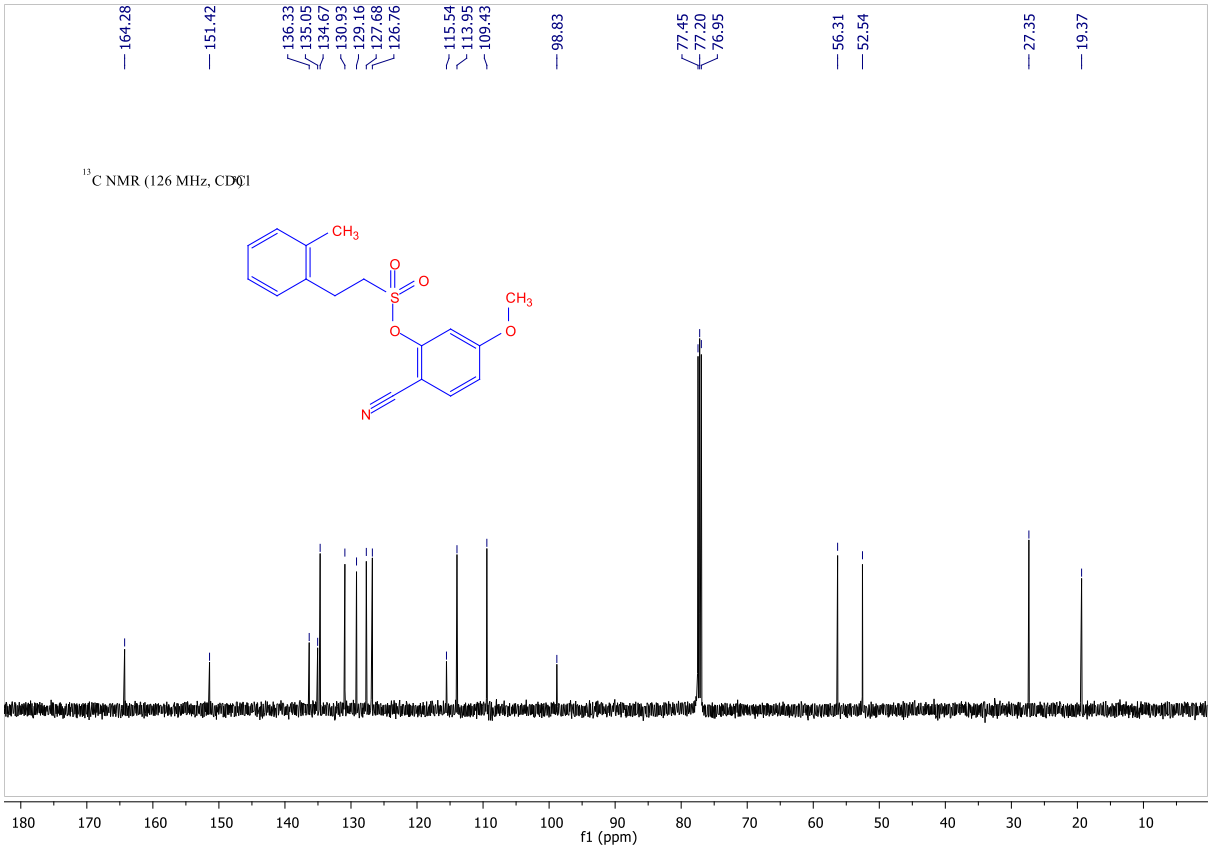


Figure S158: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-(o-tolyl)ethanesulfonate

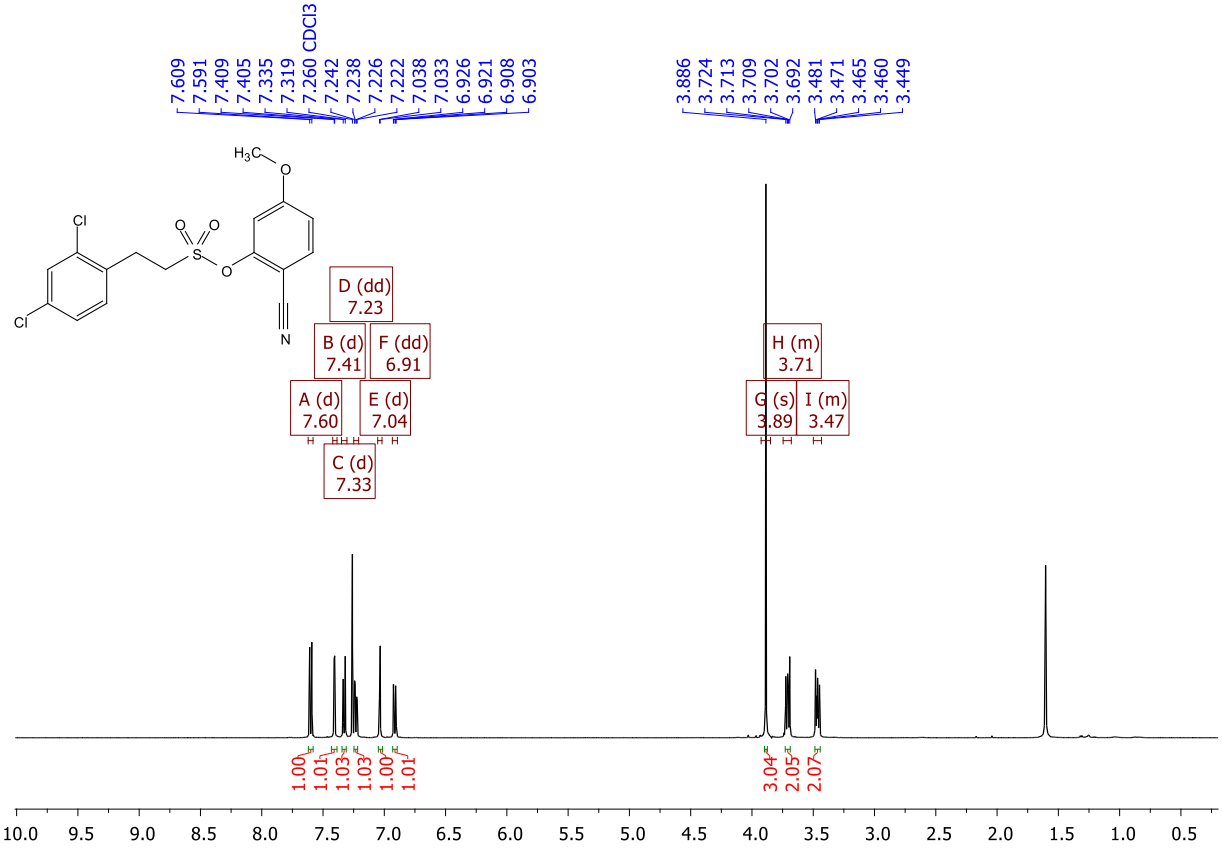


Figure S159: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-(2,4-dichlorophenyl)ethanesulfonate

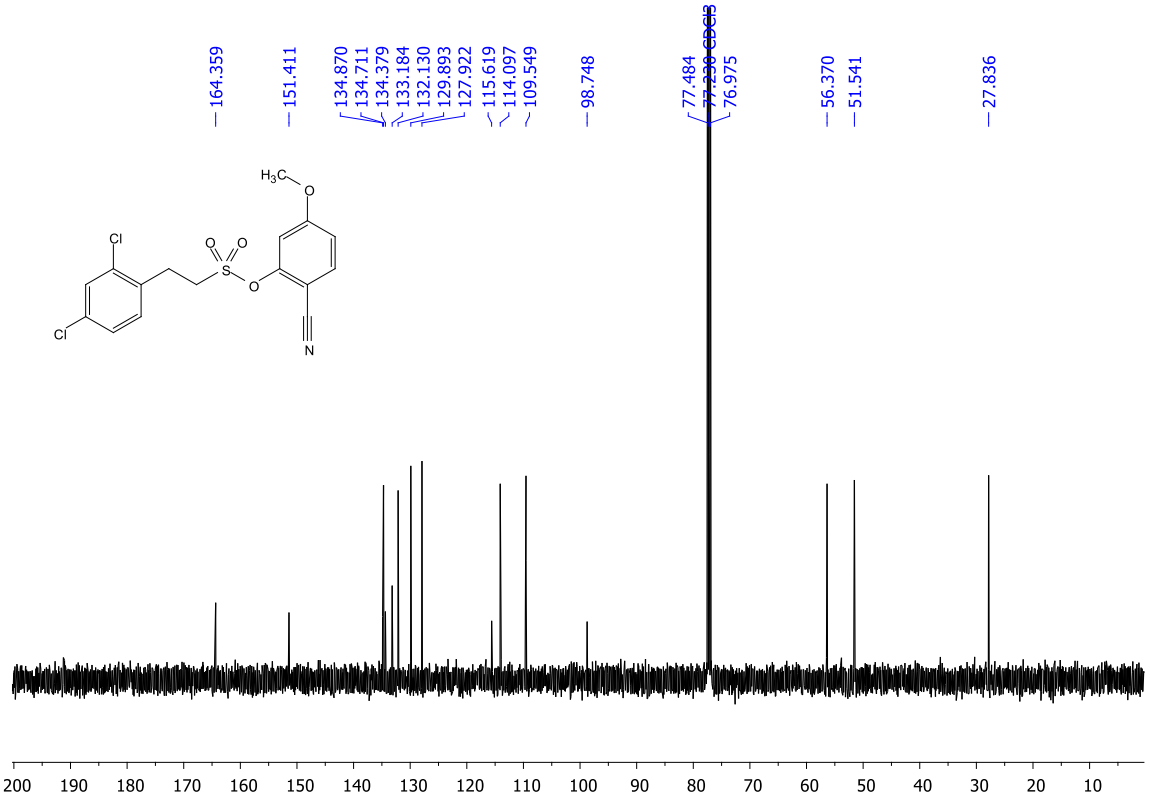


Figure S160: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 2-(2,4-dichlorophenyl)ethanesulfonate

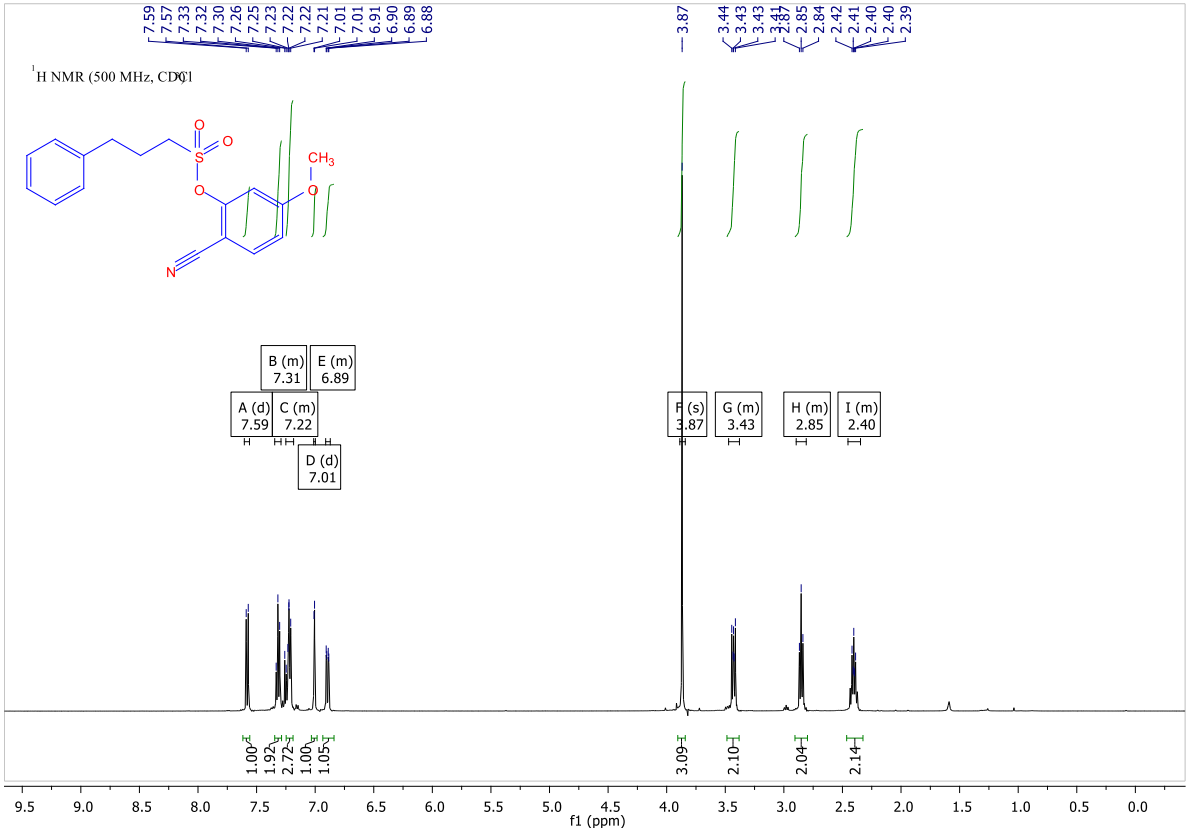


Figure S161: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 3-phenylpropane-1-sulfonate

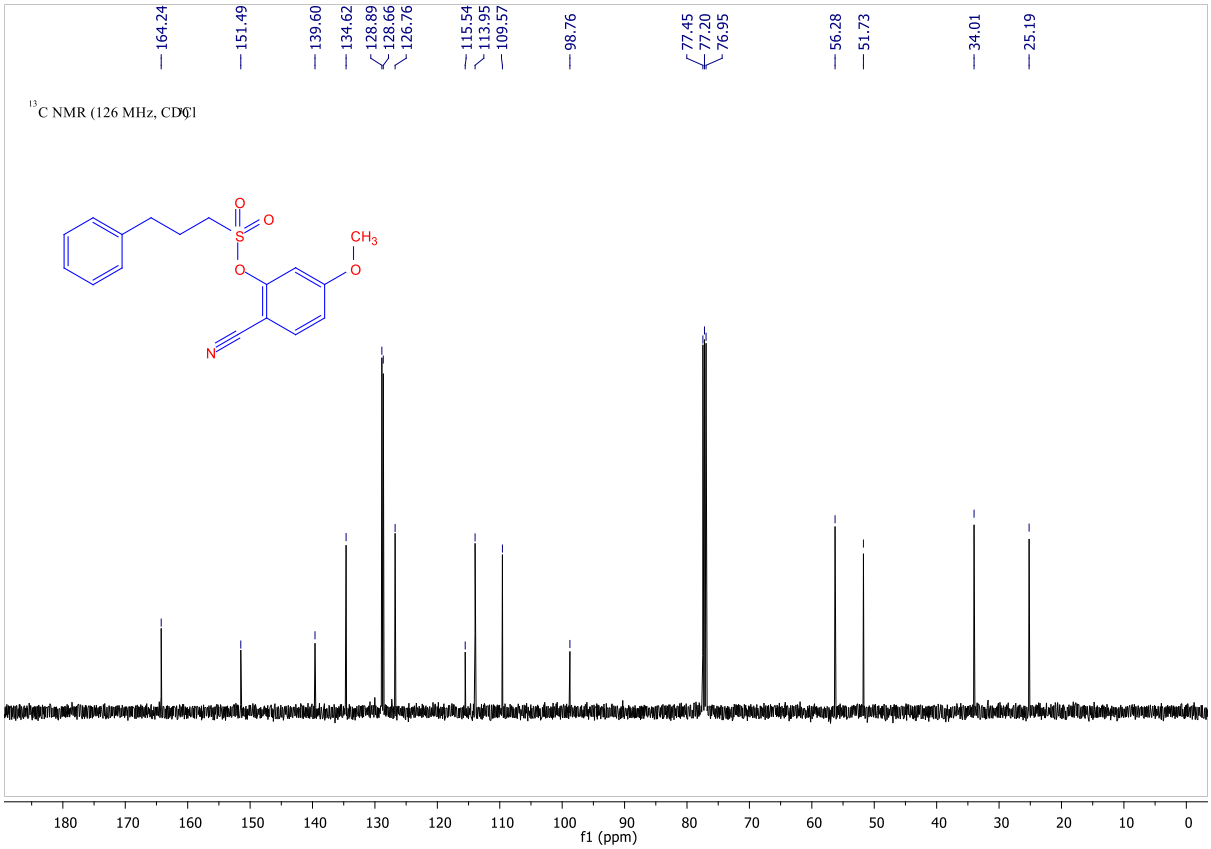


Figure S162: ^{13}C {^{1}H} NMR spectrum (126 MHz, $CDCl_3$) of 2-Cyano-5-methoxyphenyl 3-phenylpropane-1-sulfonate