Electronic Supplementary Material (ESI) for Chemical Communications.

Remote *meta* C–H Bond functionalization of 2-phenethylsulphonic acid and 3-phenylpropanoic acid derivatives

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Supporting Information

Reagent information. Unless otherwise stated, all reactions were carried out under air in screw cap reaction tubes. All the solvents were bought from Aldrich in sure-seal bottle and were used as received. 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 $60F_{254}$).

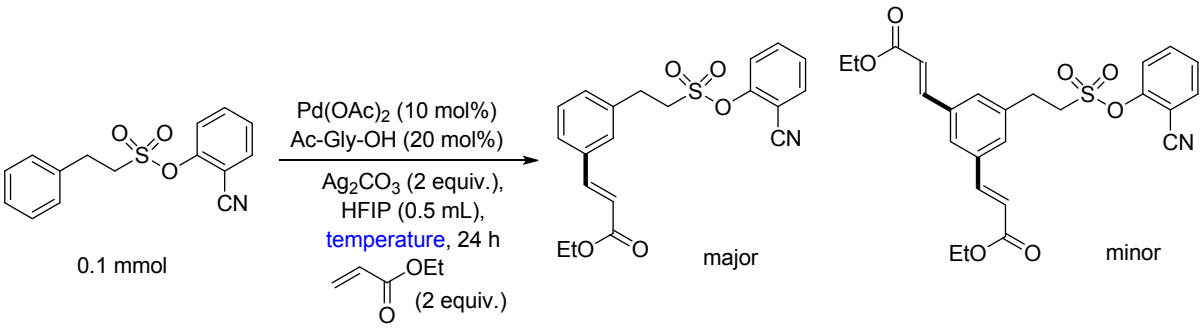
Analytical Information. All isolated compounds were characterized by ^{1}H, ^{13}C, IR spectroscopy, HR-MS. Copies of the ^{1}H-NMR, ^{13}C-NMR can be found in the supporting information. Nuclear Magnetic Resonance spectra were recorded on a Bruker 400 and 500 MHz instrument. The references used for 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. 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:

Fig.1. 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].

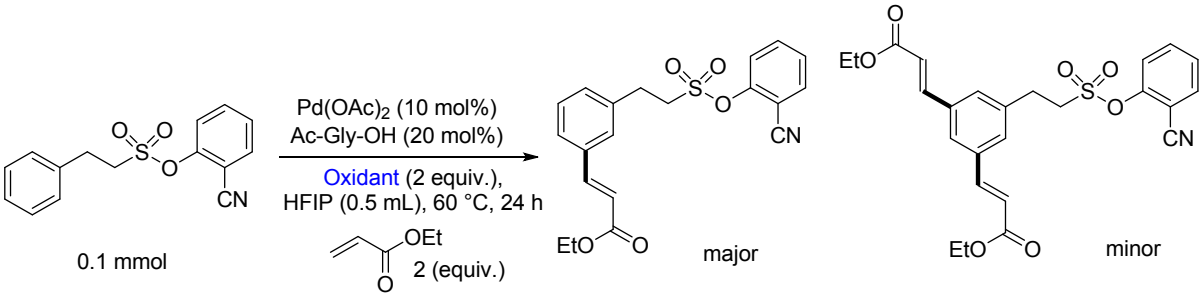
Optimization details for Activation of Remote Meta C-H Bonds of 2 phenylethanesulfonic acid:

1. Optimization by varying temperature



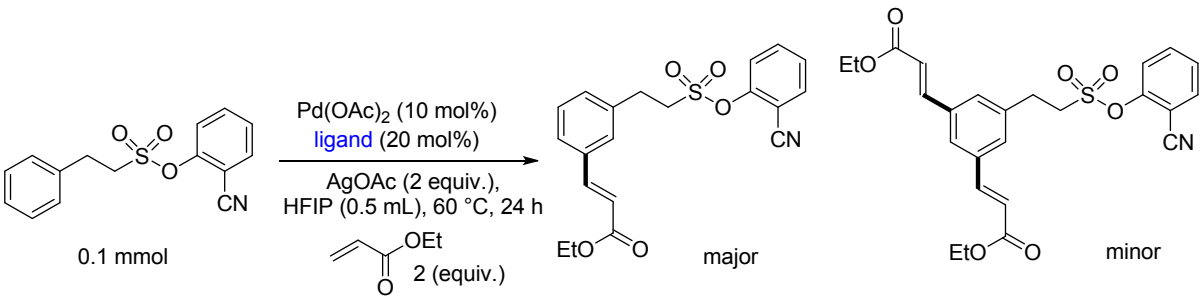
Sr. No.	Temperature (˚C)	Yield on mono olefinated Product (meta:other)	Yield on di olefinated Product
1	50	41% (6:1)	21%
2	60	56% (6:1)	25%
3	70	48% (6:1)	35%
4	80	40% (6:1)	39%
4	90	42% (5:1)	55%

2. Optimization by varying Oxidant



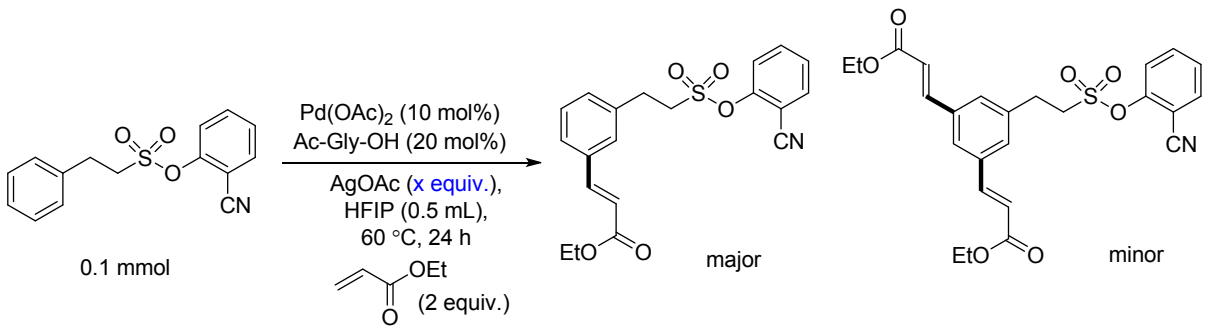
Sr. No.	Oxidant	Yield on mono olefinated Product (meta:other)	Yield on di olefinated Product
1	AgOAc	64% (6:1)	10%
2	Ag_2CO_3	67% (6:1)	25%
3	Ag_2SO_4	12% (2:1)	-
4	$Cu(OAc)_2$	30% (3:1)	-
5	$K_2S_2O_8$	22% (1:1)	-
6	O_2 atmosphere	18% (2:1)	-
7	Benzoquinone	-	-

3. Optimization by varying ligand



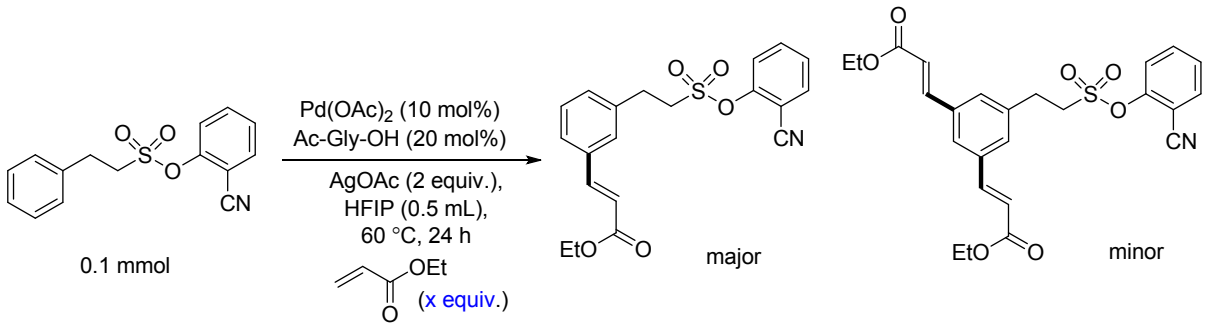
Sr. No.	Ligand	Yield on mono olefinated Product (meta:other)	Yield on di olefinated Product
1	No	20% (3:1)	-
2	Ac-For-OH	67% (8:1)	10%
3	Ac-Gly-OH	64% (6:1)	13%
4	Ac-Phe-OH	61% (4:1)	7 %
5	Ac-Lys-OH	19% (5:1)	-
6	Ac-Gly-Gly-OH	-	-
7	Ac-Ala-OH	58% (4:1)	8%
8	Benzoyl-Gly-OH	-	-
9	Boc-Gly-OH	-	-
10	PPh_3	22% (1:1)	-

4. Optimization by varying amount of oxidant



Sr. No.	Ligand	Yield on mono olefinated Product (meta:other)	Yield on di olefinated Product
1	1 equiv.	55% (6:1)	11%
2	2 equiv.	64% (7:1)	13%
3	3 equiv.	63% (6:1)	19%

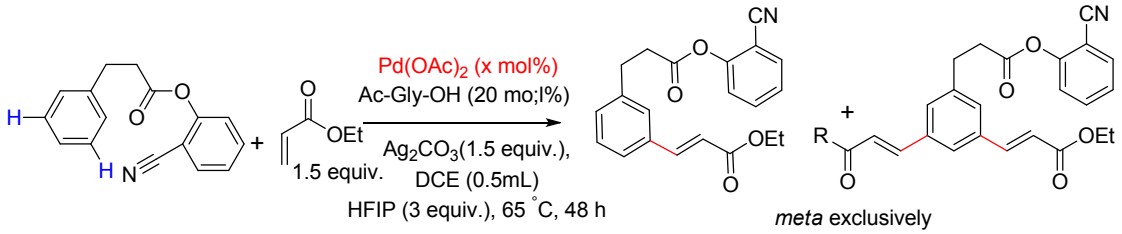
5. Optimization by varying amount of olefin



Sr. No.	Olefin amount	Yield on mono olefinated Product (meta:other)	Yield on di olefinated Product
2	1.5 equiv.	55% (7:1)	11%
3	2 equiv.	66% (7:1)	13%
4	3 equiv.	56% (7:1)	25%

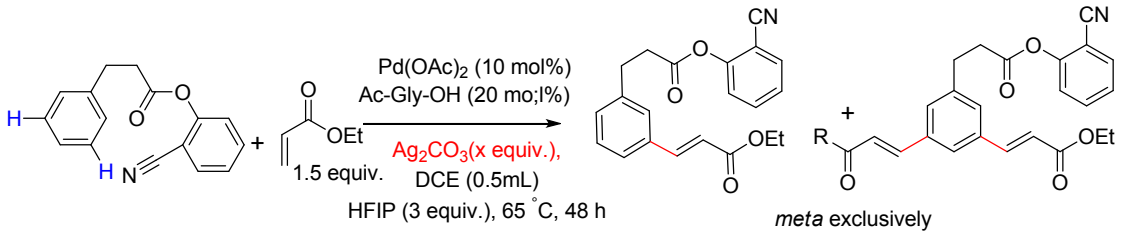
Optimization details for Activation of Remote Meta C-H Bonds of 3-phenylpropanoic acid:

1. Optimization by varying catalyst loading



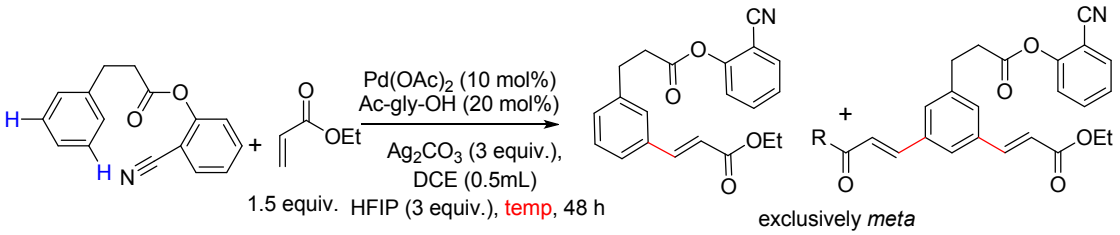
Sr. No.	Pd $(OAc)_2$	Yield (%)	Mono: Di (ratio)
1	10 mol%-	63	8:1
2	7 mol %	57	9:1
3	5 mol%	45	8:1
4	2 mol %	30	10:1
5	1 mol %	14	10:1

2. Optimization by varying amount of oxidant



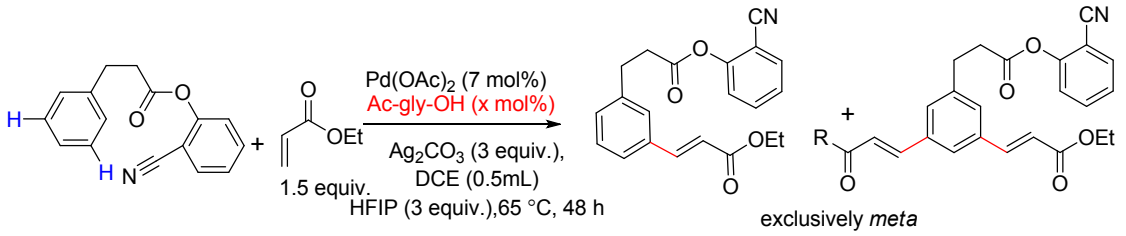
Sr. No.	Ag_2CO_3 (equiv)	Yield (%)	Mono: Di (ratio)
1	1	51	5 : 1
2	1.5	66	8 : 1
3	2.0	65	10 : 1
4	3.0	66	7 : 1

3. Optimization by varying temperature



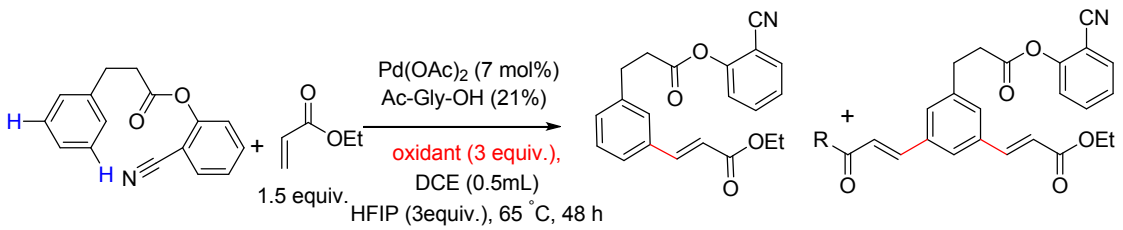
Sr. No.	Temperature (°C)	Yield (%)	Mono: Di (ratio)
1	50	60	9 :1
2	60	66	9:1
3	70	60	6:1
4	80	67	5:1
5	90	68	5:1

4. Optimization by varying ligand amount



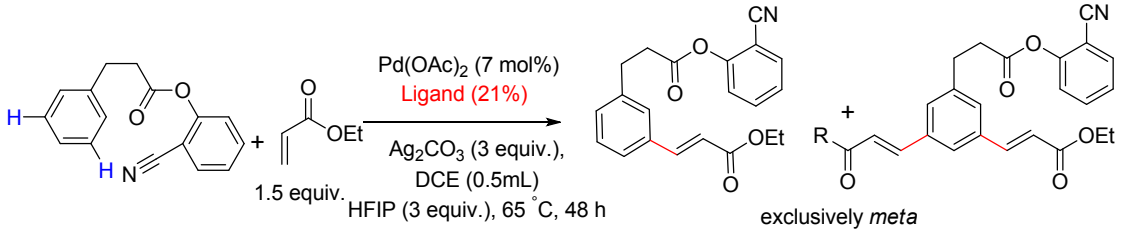
Sr. No.	Ligand (mol %)	Yield (%)	Mono: Di (ratio)
1	14	66	9:1
2	21	69	10 : 1

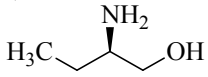
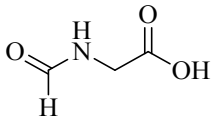
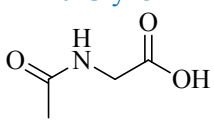
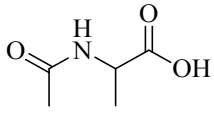
5. Optimization by varying oxidant

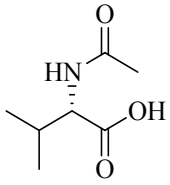
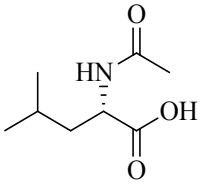
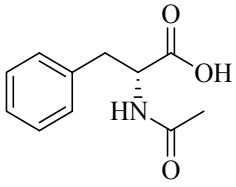
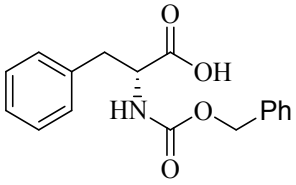
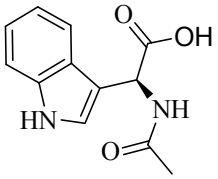
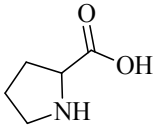


Sr. No.	Oxidant	Yield (%)	Mono: Di (ratio)
1	AgOAc	66	10:1
2	$AgCO_3$	69	10:1
3	AgI	21	-
4	$AgNO_3$	29	-
5	$Cu(OAc)_2$	25	-
6	$K_2S_2O_8$	18	-
7	$PhI(OAc)_2$	19	-
8	BQ	11	-

6. Optimization by varying ligand



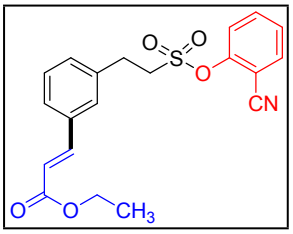
Sr. No.	Ligand	Yield (%)	Mono: Di (ratio)
1	(R)(+) 2-Amino-1-butanol 	-	-
2	Ac-For-OH 	63	8:1
3	Ac-Gly-OH 	71	10:1
4	Ac-Ala-OH 	52	8:1

5	Ac-DL-Val-OH 	39	11:1
6	Ac-Leu-OH 	51	8:1
7	Ac-Phe-OH 	52	8:1
8	Boc-Phe-OH 	-	-
9	Ac-Trp-OH 	-	-
10	D,L-Proline 	-	-
11	No Ligand	-	-

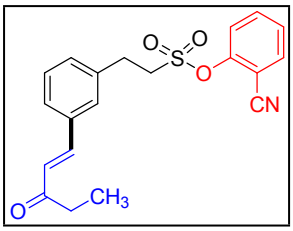
General Procedure A for mono olefination through remote meta C-H activation of 2-phenylethanesulfonic acid:

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-Formyl-glycine (0.4 equiv, 0.04 mmol, 4.1 mg), AgOAc (2 equiv, 0.4 mmol, 46 mg) were taken. Then alkene (2 equiv, 0.4 mmol), hexafluoroisopropanol (0.5mL) were added to this mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 60 ˚C. The reaction mixture was vigorously stirred for 24h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube

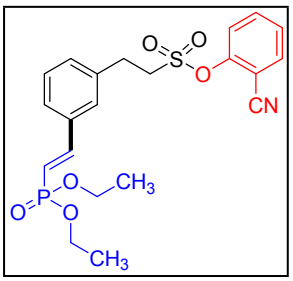
was washed with 10 mL of ethyl acetate. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent.



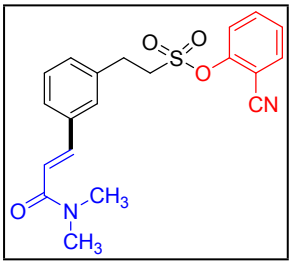
(E)-ethyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (Scheme 3, Entry 2a): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: 66% (50 mg) with 7:1 regioisomeric mixture. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.73 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.70 – 7.63 (m, 2H), 7.56 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H), 7.31 (dt, *J* = 7.6, 1.4 Hz, 1H), 6.45 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 3.76 – 3.67 (m, 2H), 3.47 – 3.35 (m, 2H), 1.34 (t, *J* = 7.1, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.0, 149.9, 144.1, 137.6, 135.4, 134.8, 134.0, 130.5, 129.7, 128.3, 127.7, 127.2, 123.9, 119.1, 115.2, 107.4, 60.8, 53.6, 29.8, 14.5. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{20}H_{19}NO_5SNa$: 408.0876, found: 408.0876.



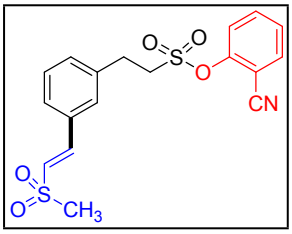
(E)-2-cyanophenyl 2-(3-(3-oxopent-1-en-1-yl)phenyl)ethanesulfonate (Scheme 3, Entry 2b): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 52% (38 mg) with 7:1 regioisomeric mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.70 (m, 1H), 7.70 – 7.64 (m, 1H), 7.58 – 7.50 (m, 2H), 7.48 (s, 1H), 7.47 – 7.41 (m, 2H), 7.40 – 7.34 (m, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 6.76 (d, *J* = 16.0 Hz, 1H), 3.76 – 3.69 (m, 2H), 3.45 – 3.36 (m, 2H), 2.73 – 2.66 (m, 2H), 1.20 – 1.12 (m, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 200.9, 150.0, 141.7, 137.7, 135.7, 134.8, 134.0, 130.6, 129.8, 128.4, 127.7, 127.5, 126.7, 123.9, 115.2, 107.4, 53.8, 34.4, 29.8, 8.4. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{20}H_{19}NO_4SNa$: 392.0927, found: 392.0925.



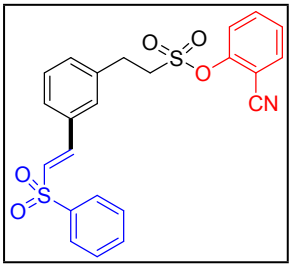
(E)-2-cyanophenyl 2-(3-(2-(diethoxyphosphoryl)vinyl)phenyl)ethanesulfonate (Scheme 3, Entry 2c): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (40:60 v/v) mixture as eluent. Isolated yield: R = 55% (49 mg) with 11:1 regioisomeric mixture. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 – 7.63 (m, 2H), 7.55 – 7.51 (m, 1H), 7.51 – 7.44 (m, 1H), 7.44 – 7.31 (m, 4H), 7.29 (dt, *J* = 7.2, 1.7 Hz, 1H), 6.27 (t, *J* = 17.5 Hz, 1H), 4.16 – 4.07 (m, 4H), 3.83 – 3.60 (m, 2H), 3.55 – 3.22 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (126 MHz, Chloroform-*d*) d 149.8, 148.2 (d; J= 7.6) 137.5, 135.7, 135.6, 134.6, 134.0, 130.5, 129.7, 127.8, 127.7, 127.0, 123.8, 115.1, 114.7 (d, J= 191.5), 107.3, 62.1, 62.1, 53.5, 29.7, 16.5, 16.5. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{21}H_{24}NO_6SPNa$: 427.0954, found: 427.0956.



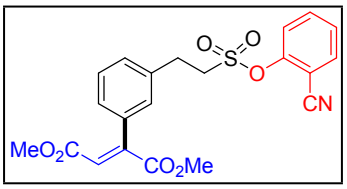
(E)-2-cyanophenyl 2-(3-(3-(dimethylamino)-3-oxoprop-1-en-1-yl)phenyl)ethanesulfonate (Scheme 3, Entry 2d): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (35:65 v/v) mixture as eluent. Isolated yield: R = 51% (39 mg) with 11:1 regioisomeric mixture. ^{1}H NMR (400 MHz, Chloroform-d) d 7.72 (dd, J = 7.8, 1.7 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.55 (dd, J = 8.4, 1.0 Hz, 1H), 7.49 (s, 1H), 7.47 – 7.37 (m, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.27 (d, J = 1.5 Hz, 1H), 6.93 (d, J = 15.4 Hz, 1H), 3.79 – 3.63 (m, 2H), 3.48 – 3.34 (m, 2H), 3.20 (s, 3H), 3.08 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) d 150.0, 141.8, 137.4, 136.4, 134.8, 134.0, 129.8, 129.7, 127.7, 127.6, 127.5, 123.9, 118.3, 115.2, 109.0, 107.4, 53.8, 37.6, 36.1, 29.8. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{20}H_{20}N_2O_4SNa$: 407.1036, found: 407.1034.



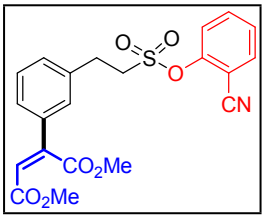
(E)-2-cyanophenyl 2-(3-(2-(methylsulfonyl)vinyl)phenyl)ethanesulfonate (Scheme 3, Entry 2e): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (40:60 v/v) mixture as eluent. Isolated yield: R = 71% (55 mg) with 11:1 regioisomeric mixture. ^{1}H NMR (500 MHz, Chloroform-d) d 7.72 (dd, J = 7.8, 1.7 Hz, 1H), 7.70 – 7.66 (m, 1H), 7.59 (d, J = 15.5 Hz, 1H), 7.54 (dd, J = 8.4, 1.1 Hz, 1H), 7.49 (d, J = 1.4 Hz, 1H), 7.47 – 7.35 (m, 4H), 6.97 (d, J = 15.5 Hz, 1H), 3.86 – 3.64 (m, 2H), 3.50 – 3.34 (m, 2H), 3.03 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-d) d 149.8, 143.4, 138.0, 134.8, 134.0, 133.0, 131.6, 130.0, 128.6, 128.0, 127.7, 127.0, 123.9, 115.2, 107.2, 53.5, 43.4, 29.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{18}H_{17}NO_5S_2Na$: 414.0440, found: 414.0442.



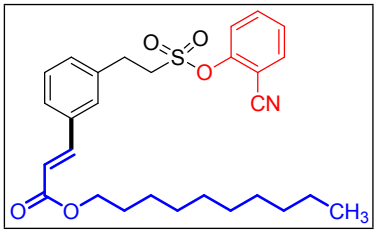
(E)-2-Cyanophenyl 2-(3-(2-(phenylsulfonyl)vinyl)phenyl)ethanesulfonate (Scheme 3, Entry 2f): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (40:60 v/v) mixture as eluent. Isolated yield: R = 65% (58 mg) with 12:1 regioisomeric mixture. ^{1}H NMR (500 MHz, Chloroform-d) d 8.00 – 7.93 (m, 2H), 7.72 (dd, J = 7.7, 1.7 Hz, 1H), 7.70 – 7.61 (m, 3H), 7.59 – 7.53 (m, 3H), 7.46 – 7.42 (m, 2H), 7.41 – 7.33 (m, 3H), 6.90 (d, J = 15.4 Hz, 1H), 3.86 – 3.57 (m, 2H), 3.55 – 3.31 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) d 149.9, 142.0, 140.8, 137.9, 134.8, 134.0, 133.6, 133.3, 131.5, 130.0, 129.6, 128.7, 128.2, 127.9, 127.7, 123.9, 115.2, 107.3, 53.6, 29.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{23}H_{19}NO_5S_2Na$: 476.0597, found: 476.0597.



(Dimethyl 2-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)fumarate (Scheme 3, Entry 2g): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (50:50 v/v) mixture as eluent. Isolated yield: R = 72% (61 mg) with 20:1 regioisomeric mixture. ^{1}H NMR (500 MHz, Chloroform-d) d 7.72 (dd, J = 7.7, 1.7 Hz, 1H), 7.70 – 7.65 (m, 1H), 7.54 (dd, J = 8.4, 1.0 Hz, 1H), 7.43 (td, J = 7.7, 1.1 Hz, 1H), 7.41 – 7.34 (m, 4H), 6.33 (s, 1H), 3.95 (s, 3H), 3.79 (s, 3H), 3.73 – 3.67 (m, 2H), 3.45 – 3.37 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) d 168.3, 165.5, 149.9, 148.5, 137.9, 134.8, 134.1, 134.0, 130.9, 129.9, 127.7, 127.1, 126.0, 123.9, 117.9, 115.1, 107.3, 53.5, 53.0, 52.3, 29.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{21}H_{19}NO_7SNa$: 452.0774, found: 452.0785.



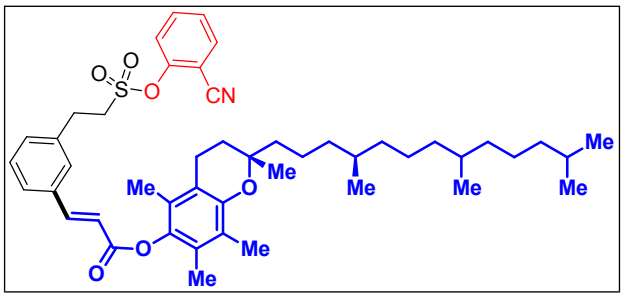
Dimethyl 2-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)maleate (Scheme 3, Entry 2h): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (50:50 v/v) mixture as eluent. Isolated yield: R = 52% (44 mg) with 7:1 regioisomeric mixture. ^{1}H NMR (400 MHz, Chloroform-d) d 7.77 – 7.68 (m, 1H), 7.65 (dd, J = 7.8, 6.2 Hz, 1H), 7.55 (d, J = 8.0 Hz, 1H), 7.49 – 7.39 (m, 1H), 7.36 (dd, J = 13.6, 6.0 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.03 (s, 1H), 3.81 (s, 3H), 3.76 – 3.69 (m, 2H), 3.61 (s, 3H), 3.46 – 3.35 (m, 2H). ^{13}C NMR (126 MHz, Chloroform-d) d 166.7, 165.5, 149.9, 143.9, 136.3, 134.7, 134.6, 134.0, 129.2, 129.1, 128.9, 128.6, 128.0, 127.6, 123.8, 115.1, 107.5, 53.6, 53.2, 52.1, 29.8. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{21}H_{19}NO_7SNa$: 452.0774, found: 452.0770.



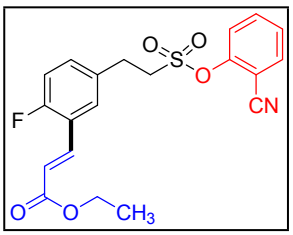
(E)-decyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (Scheme 3, Entry 2i): Oily liquid. Isolated through 100-200 mesh silica gel using pet

ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 61% (60 mg) with 6.5:1 regioisomeric mixture. ^{1}H NMR (400 MHz, Chloroform-d) d 7.73 (dd, J = 7.8, 1.7 Hz, 1H), 7.71 – 7.62 (m, 2H), 7.56 (dd, J = 8.4, 1.2 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.40 – 7.34 (m, 1H), 7.31 (dt, J = 7.5, 1.6 Hz, 1H), 6.46 (d, J = 16.0 Hz, 1H), 4.20 (t, J = 6.7, 2.0 Hz, 2H), 3.80 – 3.66 (m, 2H), 3.46 – 3.08 (m, 2H), 1.70 (p, J = 6.6 Hz, 2H), 1.44 – 1.22 (m, 14H), 0.94 – 0.82 (m, 3H). ^{13}C NMR (126 MHz, Chloroform-d) d 167.1, 149.9, 144.0, 137.6, 135.4, 134.7, 134.0, 130.5, 129.7, 128.3, 127.7, 127.2, 123.9, 119.1, 115.1, 107.4, 65.0, 53.6, 32.0, 29.8, 29.7, 29.5, 29.4, 28.9, 26.1, 22.8, 14.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{28}H_{35}NO_5SNa$: 520.2188, found: 520.2188.

(E)-(2S)-2,5,7,8-tetramethyl-2-((4R)-4,8,12-trimethyltridecyl)chroman-6-yl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (Scheme 3, Entry 2j): Reaction was done following general procedure A using 15 mol% $Pd(OAc)_2$. Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 63% (97 mg) with 6:1 regioisomeric mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J = 16.0 Hz, 1H), 7.75-7.71 (m, 2H), 7.69 – 7.52 (m, 2H), 7.44 – 7.35 (m, 3H), 7.30 – 7.28 (m, 1H), 6.73 (d, J = 16.1 Hz, 1H), 3.77-3.70 (m, J = 7.3, 2H), 3.46 – 3.38 (m, 2H), 2.62 (t, J = 7.0 Hz, 2H), 2.12 (s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.86 – 1.74 (m, 2H), 1.59-1.50 (m, J = 3H), 1.43-1.36 (s, 5H), 1.30 – 1.21 (m, 12H), 1.17-1.06 (m, 7H), 0.84-0.82 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.6, 149.9, 149.6, 145.7, 140.6, 137.7, 135.3, 134.8, 134.7, 134.0, 130.8, 129.8, 129.2, 128.7, 128.5, 127.7, 127.6, 127.5, 127.0, 125.2, 123.9, 123.9, 123.2, 118.2, 117.6, 115.2, 107.4, 75.2, 53.8, 53.7, 39.5, 37.6, 37.6, 37.5, 32.9, 32.9, 29.9, 29.8, 28.2, 25.0, 24.6, 22.9, 22.8, 21.2, 20.8, 19.9, 19.9, 13.2, 12.4, 12.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{47}H_{63}NO_6SNa$: 792.4268, found: 792.4264.

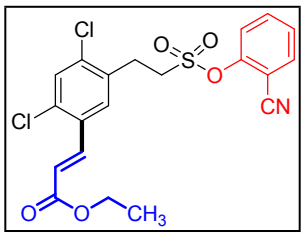


(E)-(8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H cyclopenta[a]phenanthren-3-yl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (Scheme 3, Entry 2k): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 52% (63 mg) with 6:1 regioisomeric mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 16 Hz, 1H), 7.75 – 7.66 (m, 2H), 7.56 (d, J = 8.4 Hz, 1H), 7.53 – 7.47 (m, 2H), 7.47 – 7.38 (m, 2H), 7.35 (q, J = 7.3 Hz, 1H), 7.31 (t, J = 7.6 Hz, 1H), 6.99 – 6.87 (m, 2H), 6.67 – 6.61 (d, J = 16 Hz, 1H), 3.78 – 3.70 (m, 2H), 3.49 – 3.39 (m, 2H), 2.97 – 2.89 (m, 2H), 2.54 – 2.46 (m, 1H), 2.46 – 2.38 (m, 1H), 2.36 – 2.27 (m, 1H), 2.14 (m, 1H), 2.09 – 1.94 (m, 4H), 1.67 – 1.46 (m, 3H), 1.27 (dd, J = 12.3, 5.9 Hz, 2H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 221.1, 165.7, 149.9, 148.8, 145.9, 138.2, 137.7, 137.6, 135.1, 134.8, 134.0, 130.9, 129.9, 128.6, 127.7, 127.4, 126.6, 123.9, 121.8, 119.0, 118.2, 115.2, 107.4, 53.6, 50.6, 48.1, 44.3, 38.2, 36.0, 31.7, 29.8, 29.6, 26.5, 25.9, 21.8, 14.0. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{36}H_{35}NO_6SNa$: 632.2077, found: 632.2079.

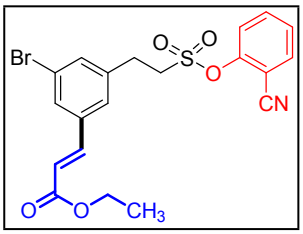


(E)-Ethyl 3-(5-(2-((2-cyanophenoxy)sulfonyl)ethyl)-2-fluorophenyl)acrylate (Scheme 3, Entry 2l): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 62% (50 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 16.3 Hz, 1H), 7.73 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.69 (ddd, *J* = 8.4, 7.6, 1.7 Hz, 1H), 7.55 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.50 – 7.41 (m, 2H), 7.33 –

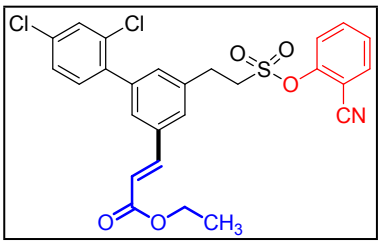
7.27 (m, 1H), 7.08 (dd, *J* = 10.2, 8.5 Hz, 1H), 6.55 (d, *J* = 16.2 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.80 – 3.65 (m, 2H), 3.49 – 3.26 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 160.7 (d, *J* = 252), 149.9, 136.8, 136.8, 134.8, 134.0, 133.1, 133.1, 131.9, 131.8, 129.3, 129.3, 127.7, 124.0, 123.2, 123.1, 121.7, 121.6, 117.1, 116.9, 115.2, 107.3, 60.9, 53.7, 29.2, 14.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{18}NFO_5SNa$: 426.0782, found: 426.0782.



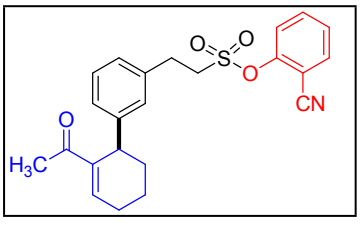
(E)-Ethyl 3-(2,4-dichloro-5-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (Scheme 3, Entry 2m): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 50% (45 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 16.1 Hz, 1H), 7.72 (dd, J= 7.7, 1.6 Hz, 1H), 7.68 – 7.65 (m, 2H), 7.59 – 7.54 (m, 1H), 7.48 (s, 1H), 7.47 – 7.40 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.73 (ddd, *J* = 10.3, 7.7, 5.4 Hz, 3H), 3.49 (ddd, *J* = 10.5, 8.1, 5.4 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, $CDCl^3$) δ 166.4, 149.8, 138.8, 135.9, 134.8, 134.7, 134.0, 133.8, 132.3, 131.1, 129.9, 127.7, 123.9, 122.2, 115.2, 107.4, 61.0, 51.5, 28.0, 14.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{17}NO_5SClNa$: 476.0096, found: 476.0098.



(E)-Ethyl 3-(3-bromo-5-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (Scheme 3, Entry 2n): Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 56% (51 mg) with 5.5:1 regioisomeric mixture. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (dt, *J* = 7.7, 1.8 Hz, 1H), 7.71 – 7.66 (m, 1H), 7.59 – 7.54 (m, 3H), 7.46 – 7.44 (m, 2H), 7.38 (s, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.95 – 3.49 (m, 2H), 3.46 – 3.29 (m, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.6, 149.9, 142.5, 139.6, 137.4, 134.8, 134.0, 133.2, 129.9, 127.8, 127.2, 124.0, 123.6, 120.7, 115.2, 107.4, 61.0, 53.4, 29.5, 14.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{18}BrNO_5SNa$: 485.9981, found: 485.9989. *In this reaction (E)-ethyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate also formed as side product.*



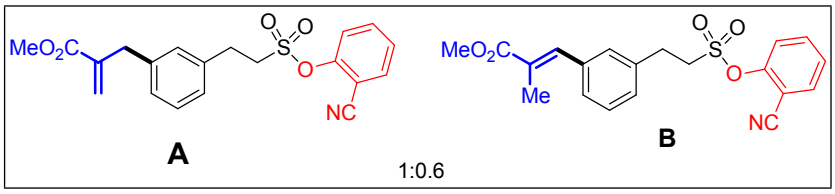
(E)-Ethyl 3-(2',4'-dichloro-5-(2-((2-cyanophenoxy)sulfonyl)ethyl)-[1,1'-biphenyl]-3-yl)acrylate (Scheme 3, Entry 2o): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 58% (61 mg) with 10:1 regioisomeric mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.69 – 7.65 (m, 1H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 7.46 – 7.43 (m, 1H), 7.40 (ddd, *J* = 5.9, 3.5, 1.6 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.29 (dt, *J* = 8.1, 5.3 Hz, 1H), 6.52 – 6.46 (d, *J* = 16.0 Hz, 1H), 4.30 – 4.23 (m, 2H), 3.80 – 3.73 (m, 2H), 3.50 – 3.42 (m, 2H), 1.40 – 1.29 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9, 149.9, 143.6, 139.9, 137.9, 137.7, 135.5, 134.8, 134.5, 134.0, 133.3, 132.1, 131.4, 130.1, 128.2, 127.8, 127.7, 127.6, 123.9, 119.8, 115.2, 107.4, 60.8, 53.6, 29.8, 14.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{26}H_{21}NCl_2O_5SNa$: 552.0410, found: 552.0405.



(R)-2-cyanophenyl 2-(3-(2-acetylcyclohex-2-enyl)phenyl)ethanesulfonate (Scheme 4, Entry 3a): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (65:35 v/v) mixture as eluent. Isolated yield: R = 56% (45 mg) with 7:1 regioisomeric mixture. ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.71 (dd,

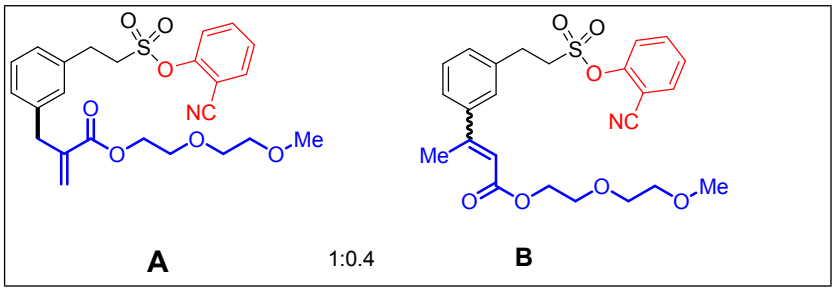
J = 7.8, 1.7 Hz, 1H), 7.66 (ddd, *J* = 8.4, 7.6, 1.7 Hz, 1H), 7.53 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.42 (td, *J* = 7.6, 1.1 Hz, 1H), 7.25 – 7.14 (m, 2H), 7.07 (dt, *J* = 7.6, 1.4 Hz, 1H), 7.02-7.00 (m, 2H), 4.00 (p, *J* = 2.3 Hz, 1H), 3.70-3.66 (m, 2H), 3.44 – 3.16 (m, 2H), 2.51 – 2.37 (m, 1H), 2.35 – 2.27 (m, 1H), 2.25 (s, 3H), 1.95 – 1.82 (m, 1H), 1.80 – 1.69 (m, 2H), 1.61 – 1.39 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.7, 149.9, 146.1, 142.8, 140. 8, 136.5, 134.7, 134.0, 128.9, 128.0, 127.6, 126.9, 126.2, 123.8, 115.1, 107.4, 53.7, 38.3, 31.2, 29.8, 26.2, 25.9, 16.9. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{23}H_{23}NO_4SNa$: 432.1240, found: 432.1237.

Mixture of methyl 2-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)benzyl)acrylate and (E)-methyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)-2-methylacrylate (1:0.6) (Scheme 4, Entry 3b): Oily



liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 50% (38 mg). 1H NMR (500 MHz, CDCl3) δ 7.75 – 7.70 (m, 1H(A) + .6H (B)), 7.67 (m, 1H(A) + .6H (B)), 7.55 (m, 1H(A) + .6H (B)), 7.47 – 7.34 (m, 2H(A) + 1.2H (B)), 7.33 – 7.27 (m, 2H(A) + 1.2H (B)), 7.12 (m1H(A) + .6H (B)+1H (A)), 6.24 (s, 1H(A)), 5.49 (s, 1H(A)), 3.82 (s, 1.6 H(B)), 3.73 (s, 3H(A)), 3.72 – 3.67 (m, 2H(A)+ 1.2H(B)), 3.62 (s, 2H(A)), 3.44 – 3.38 (m, 1.2H(B)), 3.37 – 3.33 (m, 2H(A)), 2.11 (d, J = 1.3 Hz, 1.8H(B)). 13C NMR (126 MHz, CDCl3) δ 169.2, 167.4, 149.9, 139.9, 139.8, 138.5, 137.0, 137.0, 136.8, 134.7, 134.7, 134.0, 129.9, 129.3, 129.2, 129.1, 128.7, 128.6, 128.2, 127.7, 127.6, 126.8, 126.7, 123.9, 123.8, 115.1, 107.5, 53.8, 53.7, 52.3, 52.1, 38.1, 29.8, 29.8, 14.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{19}NO_5SNa$: 408.0876, found: 408.08764.

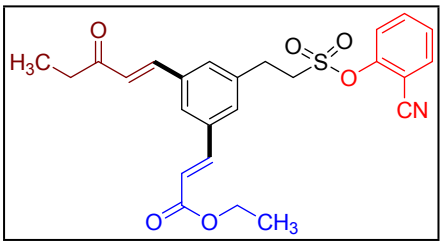
Mixture of 2-(2-methoxyethoxy)ethyl 2-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)benzyl)acrylate and 2-(2-methoxyethoxy)ethyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)but-2-enoate (1:0.4) (Scheme 4, Entry 3c): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 48% (45mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.63



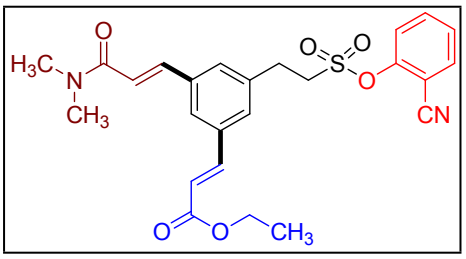
(m, 2H(A) + .8H (B)), 7.61 – 7.49 (m, 1H(A) + .4H (B)), 7.43-7.40 (m, 1H(A) + .4H (B)), 7.31-7.18 (m, 3H(A) + 1.2H (B), 7.17-7.05 (m, 2H(A)+0.4H(B)), 6.29 (s, 1H(A)), 5.50 (s, 1H(A)), 4.42 – 4.34 (m, .8H(B)), 4.34 – 4.24 (m, 2H(A)), 3.85 – 3.29 (m, 15H(A)+5.2H(B)), 2.11 (s, 1.2H(B)). 13C NMR (101 MHz, CDCl3) δ 168.6, 166.9, 149.9, 139.8, 139.8, 138.7, 136.9, 134.8, 134.7, 134.0, 129.9, 129.4, 129.2, 128.7, 128.2, 127.7, 127.6, 127.0, 126.7, 123.8, 115.1, 107.5, 59.2, 53.8, 38.1, 29.8, 14.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{24}H_{27}NO_7SNa$: 496.1400, found: 496.1402.

<u>General Procedure B</u> for sequential di olefination through remote meta C-H activation of 2-phenylethanesulfonic acid : 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-Formyl-glycine (0.4 equiv, 0.04 mmol, 4.1 mg), AgOAc (3 equiv, 0.4 mmol, 66.4 mg) were taken. Then alkene (3 equiv, 0.6 mmol), hexafluoroisopropanol (1 mL) were added to this mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 80 ˚C. The reaction mixture was

vigorously stirred for 48h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube was washed with 10 mL of ethyl acetate. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent.



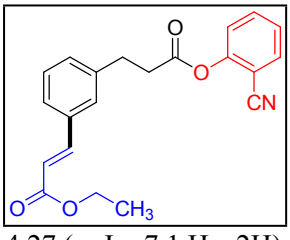
(E)-ethyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)-5-((E)-3-oxopent-1-en-1-yl)phenyl)acrylate (Scheme 5, Entry 4a): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (50:50 v/v) mixture as eluent. Isolated yield: 51% (48 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 1H), 7.71 – 7.68 (m, 1H), 7.68 – 7.62 (m, 1H), 7.59 – 7.56 (m, 1H), 7.55 (s, 1H), 7.50 (s, 1H), 7.50 (s, 1H), 7.48 – 7.41 (m, 2H), 6.79 (d, J = 16.2 Hz, 1H), 6.48 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.78 – 3.70 (m, 2H), 3.47 – 3.39 (m, 2H), 2.75 – 2.64 (m, 2H), 1.34 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.75, 166.8, 149.9, 143.2, 140.8, 138.4, 136.3, 136.2, 134.9, 134.0, 129.8, 129.8, 127.8, 127.3, 127.0, 124.0, 120.1, 115.3, 107.3, 60.9, 53.5, 34.7, 29.7, 14.5, 8.3. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{25}H_{25}NO_6SNa$: 490.1294, found: 490.1297.



(E)-ethyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)-5-((E)-3- (dimethylamino)-3-oxoprop-1-en-1-yl)phenyl)acrylate (Scheme 5, Entry 4b): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (40:60 v/v) mixture as eluent.Isolated yield: 50% (48 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.7, 1.7 Hz, 1H), 7.73 – 7.70 (m, 1H), 7.67 (dd, J = 15.9, 12.3 Hz, 2H), 7.60 – 7.52 (m, 3H), 7.49 – 7.44 (m, 2H), 6.98 (d, J = 15.5 Hz, 1H), 6.50 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.79 – 3.71 (m, 2H), 3.49 – 3.42 (m, 2H), 3.23 (s, 3H), 3.11 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.8, 166.4, 143.7, 141.1, 138.2, 137.1, 136.0, 134.8, 134.0, 129.2, 129.0, 127.7, 126.9, 124.0, 119.9, 119.3, 115.3, 107.3, 60.9, 53.7, 37.7, 36.2, 29.8, 14.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{25}H_{26}N_2O_6SNa$: 505.1403, found: 505.1403.

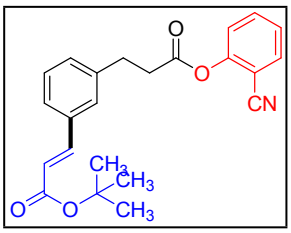
General Procedure C for mono olefination through remote *meta* C-H activation of 3-phenylpropanoic acid:

In a clean, oven–dried screw cap reaction tube, with previously placed magnetic stir–bar substrate (0.2 mmol); $Pd(OAc)_2$ (0.07 equiv, 0.014 mmol, 3.2 mg); N-Acetyl-glycine (0.21 equiv, 0.042 mmol, 4.9 mg), Ag_2CO_3 (2 equiv, 0.4 mmol, 110 mg) were taken. Then alkene (1.5 equiv, 0.3 mmol), dichloroethane (DCE) (1 mL)/ hexafluoroisopropanol (64µL) were added to this mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 65 ˚C. The reaction mixture was vigorously stirred for 48h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube was washed with 10 mL of ethyl acetate. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent.

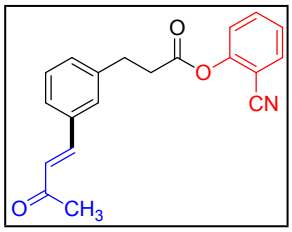


(E)-Ethyl 3-(3-(3-(2-cyanophenoxy)-3-oxopropyl)phenyl)acrylate (Scheme 6, Entry 5a): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (90:10 v/v) mixture as eluent. Isolated yield: R = 68% (47 mg). ^{1}H NMR (500 MHz, CDCl3) δ 7.70 – 7.65 (m, 2H), 7.63 – 7.59 (m, 1H), 7.43 (s, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.30 (d, J = 7.6 Hz, 1H), 7.20 (dd, J = 8.3, 0.5 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 4.27 (q, J = 7.1 Hz, 2H), 3.14 (t, J = 7.6 Hz, 2H), 3.00 (t, J = 11.4, 4.2 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H).

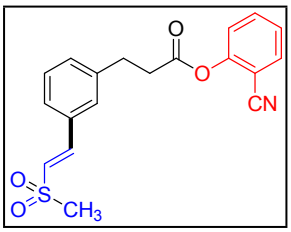
^{13}C NMR (126 MHz, CDCl3) δ 170.3, 167.1, 152.4, 144.6, 140.6, 135.1, 134.2, 133.5, 130.4, 129.4, 128.3, 126.5, 123.4, 118.7, 109.7, 107.3, 60.7, 35.7, 30.7, 14.5. IR (thin film) 595, 828, 876, 1045, 1121, 1218, 1640, 2136, 2365cm^{-1} HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{21}H_{19}NO_4Na$: 372.1206, found: 372.1203.



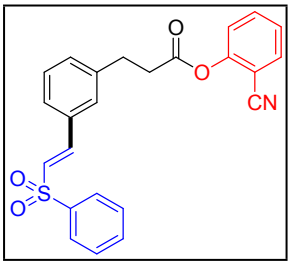
(E)-Tert-butyl 3-(3-(3-(2-cyanophenoxy)-3-oxopropyl)phenyl)acrylate (Scheme 6, Entry 5b): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (90:10 v/v) mixture as eluent. Isolated yield: R = 68% (51 mg) . ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.64 – 7.54 (m, 2H), 7.44 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.19 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.38 (d, *J* = 15.9 Hz, 1H), 3.13 (t, *J* = 8.0 Hz, 2H), 3.00 (ddd, *J* = 8.3, 7.2, 1.1 Hz, 2H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- *d*) δ 170.4, 166.5, 152.4, 143.5, 140.6, 135.2, 134.3, 133.5, 130.2, 129.4, 128.1, 126.6, 126.5, 123.4, 120.6, 115.3, 107.3, 80.7, 35.7, 30.7, 28.4. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{23}H_{23}NO_4Na$: 400.1519, found: 400.1517. IR (thin film) 676, 868, 918, 1118, 1155, 1223, 1449, 1648, 1707, 1773, 2343, 2354 cm^{-1}



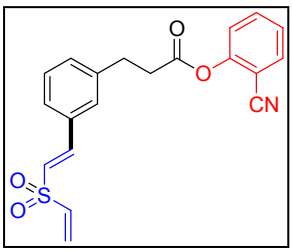
(E)-2-Cyanophenyl 3-(3-(3-oxobut-1-en-1-yl)phenyl)propanoate (Scheme 6, Entry 5c): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (86:14 v/v) mixture as eluent. Isolated yield: R = 66% (42 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61 (td, *J* = 8.0, 1.6 Hz, 1H), 7.51 (d, *J* = 16.3 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.39 – 7.30 (m, 3H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.73 (d, *J* = 16.3 Hz, 1H), 3.14 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 198.7, 170.3, 152.4, 143.5, 140.7, 135.0, 134.3, 133.5, 130.8, 129.5, 128.5, 127.5, 126.7, 126.6, 123.3, 115.3, 107.2, 35.6, 30.6, 27.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{17}NO_3Na$: 342.1100, found: 342.1098. IR (thin film) 682, 774, 1111, 1179, 1216, 1424, 1650, 1776, 1847, 2087, 2345, 2363 cm^{-1}.



(E)-2-Cyanophenyl 3-(3-(2-(methylsulfonyl)vinyl)phenyl)propanoate (Scheme 6, Entry 5d): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 55% (39 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.64 – 7.59 (m, 2H), 7.45 (s, 1H), 7.41 – 7.32 (m, 4H), 7.21 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.94 (d, *J* = 15.6 Hz, 1H), 3.15 (t, *J* = 7.6 Hz, 2H), 3.02 (d, *J* = 9.5 Hz, 5H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.2, 152.4, 144.0, 141.0, 134.3, 133.5, 132.7, 131.6, 129.7, 128.6, 127.2, 126.7, 126.6, 123.3, 115.3, 107.2, 43.5, 35.5, 30.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{17}NO_4SNa$: 378.0770, found: 378.0773.

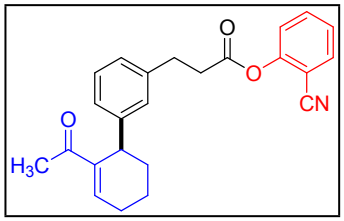


(E)-2-Cyanophenyl 3-(3-(2-(phenylsulfonyl)vinyl)phenyl)propanoate (Scheme 6, Entry 5e): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (65:35 v/v) mixture as eluent. Isolated yield: R = 76% (77 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.99 – 7.92 (m, 2H), 7.70 – 7.52 (m, 6H), 7.43 – 7.31 (m, 5H), 7.22 – 7.16 (m, 1H), 6.89 (d, *J* = 15.4 Hz, 1H), 3.11 (t, *J* = 7.6 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.2, 152.3, 142.5, 140.9, 140.8, 134.3, 133.6, 133.4, 132.9, 131.4, 129.6, 129.5, 128.6, 128.4, 127.8, 127.6, 127.2, 126.6, 123.3, 115.3, 107.1, 35.5, 30.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{24}H_{19}NO_4SNa$: 440.0927, found: 440.0919. IR (thin film) 661, 689, 766, 1004, 1050, 1079, 1261, 1313, 1495, 1898, 2012, 2281, 2381, 2380, 2433, 2521 cm^{-1}.

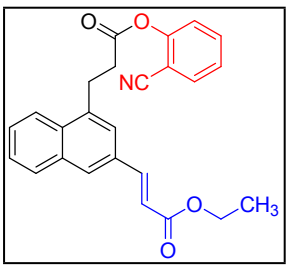


(E)-2-Cyanophenyl 3-(3-(2-(phenylsulfonyl)vinyl)phenyl)propanoate (Scheme 6, Entry 5f): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (65:35 v/v) mixture as eluent. Isolated yield: R = 77% (56 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.68 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.45 – 7.32 (m, 5H), 7.21 (dd, *J* = 8.3, 1.0 Hz, 1H), 6.80 (d, *J* = 15.5 Hz, 1H), 6.67 (dd, *J* = 16.5, 9.8 Hz, 1H), 6.46 (d, *J* = 16.5 Hz, 1H), 6.10 (d, *J* = 9.8 Hz, 1H), 3.13 (t, *J* = 7.6 Hz, 2H), 3.01 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.2, 152.3, 144.5, 141.0, 137.8, 134.3, 133.5, 132.9, 131.7, 129.7, 129.0, 128.7, 127.2, 126.6, 125.8, 123.3, 115.3, 107.2, 35.5, 30.5. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{20}H_{17}NO_4SNa$: 390.0770, found: 390.0774. IR (thin film) 653, 764, 847, 976, 1129, 1216, 1309, 1450, 1488, 1605,1770, 2233 cm^{-1}.

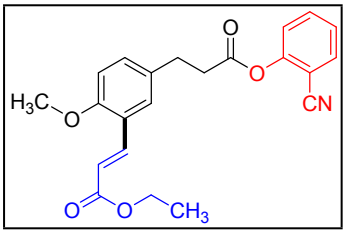
(E)-2-Cyanophenyl 3-(3-(2-(diethoxyphosphoryl)vinyl)phenyl)propanoate (Scheme 6, Entry 5g): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (20:80 v/v) mixture as eluent. Isolated yield: R = 50% (41 mg). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.61 (td, *J* = 8.0, 1.6 Hz, 1H), 7.49 (dd, *J* = 22.5, 17.5 Hz, 1H), 7.41 (s, 1H), 7.39 – 7.28 (m, 4H), 7.20 (d, *J* = 8.3 Hz, 1H), 6.28 (t, *J* = 17.7 Hz, 1H) 4.13 (p, *J* = 7.2 Hz, 4H), 3.13 (t, *J* = 7.6 Hz, 2H), 3.00 (t, *J* = 7.6 Hz, 2H), 1.35 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.3, 152.4, 148.8, 140.6, 134.3, 133.5, 131.0, 130.5, 129.4, 127.8, 126.5, 126.3, 123.4, 118.2, 115.3, 107.2, 62.2, 35.7, 30.7, 16.6. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{22}H_{24}NPO_5Na$: 436.1284, found: 436.1287.



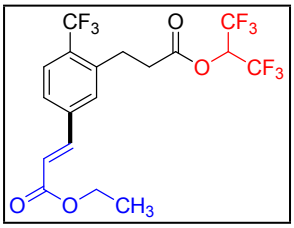
(R)-2-cyanophenyl 3-(6'-acetyl-1',2',3',4'-tetrahydro-[1,1'-biphenyl]-3-yl)propanoate (Scheme 6, Entry 5h): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (85:15 v/v) mixture as eluent. Isolated yield: R = 57% (42 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.61 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 7.32 (td, *J* = 7.7, 1.1 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.14 (m, 2H), 7.07 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.00 (d, *J* = 1.9 Hz, 1H), 6.98 (dt, *J* = 7.6, 1.5 Hz, 1H), 4.00 (t, *J* = 4.4 Hz, 1H), 3.08 (t, *J* = 8.0 Hz, 2H), 3.01 – 2.92 (m, 2H), 2.41 (dq, *J* = 20.0, 4.6 Hz, 1H), 2.34 – 2.24 (m, 1H), 2.22 (s, 3H), 1.87 (dddd, *J* = 13.2, 10.4, 5.7, 4.5 Hz, 1H), 1.81 – 1.72 (m, 1H), 1.58 – 1.46 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.8, 170.6, 152.5, 145.6, 142.3, 141.1, 139.7, 134.3, 133.4, 128.6, 128.0, 126.4, 126.2, 126.1, 123.5, 115.3, 107.2, 38.6, 35.9, 31.4, 31.0, 26.3, 26.0, 17.1. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{24}H_{23}NO_3Na$: 396.1570, found: 396.1570. IR (thin film) 926, 972, 1117, 1219, 1305, 1378, 1455, 1487, 1605, 1664, 1714, 1774, 2233, 2355 cm^{-1}



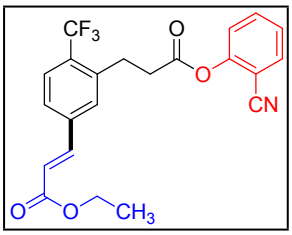
(E)-ethyl 3-(4-(3-(2-cyanophenoxy)-3-oxopropyl)naphthalen-2-yl)acrylate (Scheme 6, Entry 5i): brown solid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (88:12 v/v) mixture as eluent. Isolated yield: R = 62% (49 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.93 – 7.88 (m, 1H), 7.87 (d, *J* = 1.6 Hz, 1H), 7.83 (d, *J* = 16.0 Hz, 1H), 7.70 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.66 – 7.58 (m, 3H), 7.54 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.22 (dd, *J* = 8.4, 1.1 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 3.60 (m, 2H), 3.22 – 2.99 (m, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.5, 167.2, 152.5, 144.6, 136.9, 134.3, 134.1, 133.5, 132.6, 131.8, 129.9, 129.6, 127.9, 126.8, 126.6, 124.0, 123.6, 123.4, 118.8, 115.3, 107.3, 60.7, 35.1, 28.2, 14.5. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{25}H_{21}NO_4Na$: 422.1362, found: 422.1366.



(E)-ethyl 3-(4-(3-(2-cyanophenoxy)-3-oxopropyl)naphthalen-2-yl)acrylate (Scheme 6, Entry 5j): brown solid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (88:12 v/v) mixture as eluent. Isolated yield: R = 52% (39 mg) ^{1}H NMR (500 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 16.2 Hz, 1H), 7.67 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.61 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 7.40 (d, *J* = 2.4 Hz, 1H), 7.33 (td, *J* = 7.7, 1.1 Hz, 1H), 7.26 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.20 (dd, *J* = 8.3, 1.1 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.54 (d, *J* = 16.1 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 3.07 (m, 2H), 2.96 (m, 2H), 1.33 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (126 MHz, Chloroform-*d*) δ 170.4, 167.7, 157.3, 152.4, 140.1, 134.3, 133.5, 132.0, 131.5, 129.0, 126.5, 123.7, 119.2, 115.3, 111.6, 107.2, 60.6, 55.8, 36.0, 30.0, 14.6. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{25}H_{21}NO_4Na$: 422.1362, found: 422.1366.



(E)-Ethyl 3-(3-(3-((1,1,1,3,3,3-hexafluoropropan-2-yl)oxy)-3-oxopropyl)-4-(trifluoromethyl)phenyl)acrylate (Scheme 6, Entry 5k): Oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (97:3 v/v) mixture as eluent. Isolated yield: R = 44% (41 mg). ^{1}H NMR (500 MHz, CDCl3) δ 7.69 – 7.61 (m, 2H), 7.54 – 7.44 (m, 2H), 6.50 (d, J = 16.0 Hz, 1H), 5.78 (p, J = 6.1 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.21 (t, J = 7.8 Hz, 2H), 2.86 (t, J = 7.8 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 169.3, 166.5, 142.4, 138.4, 130.4, 127.3, 126.4, 121.4, 67.5, 67.2, 66.8, 66.5, 66.2, 61.0, 34.6, 27.4, 14.4.

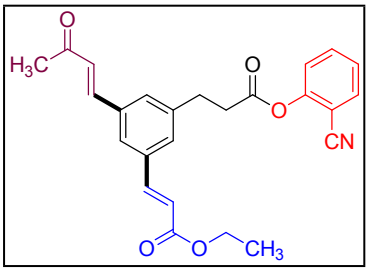


((E)-Ethyl 3-(3-(3-(2-cyanophenoxy)-3-oxopropyl)-4-(trifluoromethyl)phenyl)acrylate (Scheme 6, Entry 5k): Oily liqiud. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (88:12 v/v) mixture as eluent. Isolated yield: R = 24% (20 mg). ^{1}H NMR (400 MHz, CDCl3) δ 7.74 – 7.61 (m, 4H), 7.58 (s, 1H), 7.52 – 7.48 (m, 1H), 7.36 (td, J = 7.7, 1.1 Hz, 1H), 7.31 – 7.24 (m, 1H), 6.52 (d, J = 16.1 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.31 (t, J = 7.7 Hz, 2H), 3.01 (t, J = 7.7 Hz, 2H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, CDCl3) δ 170.0, 166.6, 152.3, 142.6, 138.3, 134.3, 133.5, 130.8, 127.2, 127.1, 126.6, 126.2, 123.3, 121.3, 115.2, 107.3, 61.0, 35.6, 27.7, 14.5. HRMS (ESI-QTOF) m/z: [M+Na]$^{+}$: calcd. for $C_{22}H_{18}F_3NO_4Na$: 440.1080, found: 440.1087.

General Procedure D for sequential di olefination through remote meta C-H activation of 3-phenylpropanoic acid:

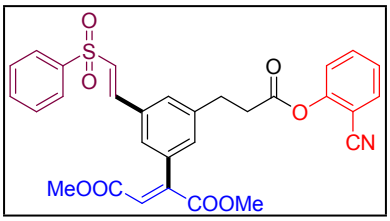
In a clean, oven–dried screw cap reaction tube, with previously placed magnetic stir–bar substrate (0.1 mmol); $Pd(OAc)_2$ (0.1 equiv, 0.01 mmol, 2.2 mg); N-Acetyl-glycine (0.2 equiv, 0.02 mmol, 2.2 mg), Ag_2CO_3 (3 equiv, 0.3 mmol, 83 mg) were taken. Then alkene (2 equiv, 0.2 mmol), hexafluoroisopropanol (0.6 mL) were added to this mixture by syringe. The tube was tightly closed by screw cap and placed in a preheated oil bath at 70 ˚C. The reaction mixture was vigorously stirred for 48h. The reaction mixture was cooled to room temperature and filtered through celite. Reaction tube was washed with 10 mL of ethyl acetate. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent.

(E)-Ethyl 3-(3-(3-(2-cyanophenoxy)-3-oxopropyl)-5-((E)-3-oxobut-1-en-1-yl)phenyl)acrylate (Scheme 7, Entry 6a): oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (70:30 v/v) mixture as eluent. Isolated yield: R = 71% (30 mg) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.65 (m, 2H), 7.62 (ddd, *J* = 8.3, 7.6, 1.7 Hz, 1H), 7.56 (d, *J* = 1.6 Hz, 1H), 7.54 – 7.45 (m,

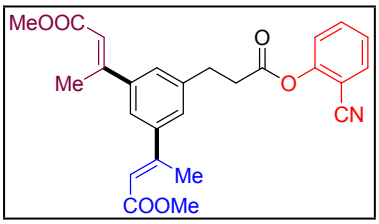


3H), 7.35 (td, J = 7.7, 1.1 Hz, 1H), 7.21 (dd, J = 8.4, 1.0 Hz, 1H), 6.76 (d, J = 16.2 Hz, 1H), 6.48 (d, J = 16.1 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.16 (t, J = 7.5 Hz, 2H), 3.03 (t, J = 7.3 Hz, 2H), 2.40 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.4, 170.1, 166.9, 152.3, 143.6, 142.5, 141.5, 135.8, 134.3, 133.5, 130.0, 129.9, 128.1, 126.6, 126.3, 123.3, 119.8, 115.3, 107.2, 100.1, 60.9, 35.4, 30.5, 28.0, 14.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{25}H_{23}NO_5Na$: 440.1468, found 440.1470. IR (thin film) 765, 981, 1114, 1182, 1450, 1493, 1717, 1771, 2281, 2371, cm^{-1}.

Dimethyl 2-(3-(3-(2-cyanophenoxy)-3-oxopropyl)-5-((E)-2-(phenylsulfonyl)vinyl)phenyl)fumarate (Scheme 7, Entry 6b): oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (55:45 v/v) mixture as eluent. Isolated yield: R = 51% (28 mg) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.92 (m, 2H), 7.71 – 7.60 (m, 4H), 7.60 – 7.53 (m, 2H), 7.47 (s, 1H), 7.43 (m, 2H), 7.34 (td, J = 7.7, 1.1 Hz, 1H), 7.20 (dd, J = 8.3, 1.0 Hz, 1H), 6.92 (d, J = 15.4 Hz, 1H), 6.32 (s, 1H), 3.94 (s, 3H), 3.79 (s, 3H), 3.13 (t, J = 7.5 Hz, 2H), 2.99 (t, J = 7.5, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.0, 168.0, 165.3, 152.2, 147.7, 141.20, 141.2, 140.4, 134.9, 134.4, 133.9, 133.8, 133.5, 130.4, 129.6, 129.4, 129.2, 128.0, 126.7, 125.5, 123.3, 119.0, 115.3, 107.2, 53.2, 52.4, 35.3, 30.5. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{30}H_{25}NO_8SNa$: 582.1193, found: 582.1196.



(2E,2'E)-Dimethyl 3,3'-(5-(3-(2-cyanophenoxy)-3-oxopropyl)-1,3-phenylene)bis(but-2-enoate) (Scheme 7, Entry 6c): oily liquid. Isolated through 100-200 mesh silica gel using pet ether: ethyl acetate (50:50 v/v) mixture as eluent. Isolated yield: R = 55% (25 mg) ^{1}H NMR (500 MHz, CDCl3) δ 7.68 (d, J = 7.1 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.40 (s, 1H), 7.36 (s, 2H), 7.34 (d, J = 7.7 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 6.14 (s, 2H), 3.78 (s, 6H), 3.15 (t, J = 7.7 Hz 2H), 3.02 (t, J = 7.7 Hz, 2H), 2.58 (s, 6H). ^{13}C NMR (126 MHz, CDCl3) δ 170.2, 167.2, 155.5, 152.4, 143.3, 140.6, 134.3, 133.5, 127.2, 126.6, 123.3, 122.9, 117.6, 115.3, 107.2, 51.4, 35.8, 30.9, 18.4. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{26}H_{25}NO_6Na$: 470.1574, found: 470.1570.



General Procedure for sulphonate ester synthesis:

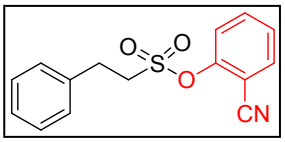
The synthesis was done following the literature procedure with few modifications.

Step 1: In an oven dried 250 mL round bottomed flask the desired benzyl chloride/bromide was added along with thiourea (1.1 eq.). Absolute ethanol was added to it as solvent and refluxed for 12 h. Upon completion the round bottomed flask was cooled and evaporated under reduced pressure yielding white solid compound, which was directly used in the next step.

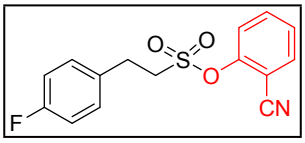
Step 2: N-chlorosuccinimide (4 eq.) was taken in clean round bottomed flask charged with stir-bar. 2(N) HCl was added to it along with MeCN. The reaction mixture was stirred on an ice cooled water bath. The solid salt obtained from the first step was added slowly to this reaction mixture and stirred vigorously. The addition led to an exothermic reaction. However the temperature was maintained below 25 °C. Upon forming a clear solution the mixture was warmed to the room temperature and stirred for 1.5 h. The reaction was evaporated under reduced pressure to remove the acetonitrile. The remaining solution was diluted with water and extracted with ethyl acetate. The organic portion was dried over

anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and purified through column chromatography.

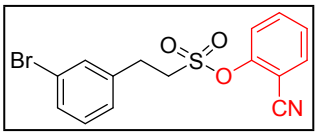
Step 3: In an oven dried round bottomed flask 2-hydroxybenzonitrile was dissolved in dry DCM. Et_3N (3 eq.) was added to the reaction mixture slowly until the clear solution was observed. Benzylsulphonyl chloride was added to the reaction mixture slowly. Upon completion of addition the reaction was stirred at room temperature overnight. Once completed the reaction was quenched with distilled water and extracted with ethyl acetate. The organic portion was dried over anhydrous Na_2SO_4. The solution was concentrated under reduced pressure and purified through column chromatography.



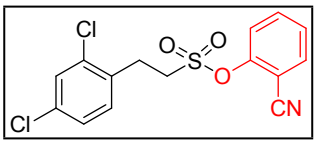
2-Cyanophenyl 2-phenylethanesulfonate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, J = 7.8, 1.4 Hz, 1H), 7.68 (ddd, J = 8.4, 7.6, 1.7 Hz, 1H), 7.56 (dd, J = 8.4, 0.6 Hz, 1H), 7.43 (td, J = 7.7, 1.0 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.29 (d, J = 7.6 Hz, 3H), 3.75 – 3.67 (m, 2H), 3.45 – 3.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.0, 136.8, 134.7, 134.0, 129.2, 128.7, 127.6, 127.5, 123.9, 115.1, 107.5, 53.8, 29.9. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{15}H_{13}NNaO_3S$: 310.0508, found: 310.0501.



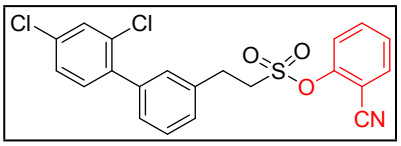
2-Cyanophenyl 2-(4-fluorophenyl)ethanesulfonate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 7.7 Hz, 1H), 7.68 (td, J = 8.1, 0.9 Hz, 1H), 7.55 (d, J = 8.4 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.26 (dd, J = 8.4, 5.3 Hz, 2H), 7.03 (t, J = 8.6 Hz, 2H), 3.83 – 3.56 (m, 2H), 3.47 – 3.28 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.2, 161.2, 149.9, 134.8, 134.0, 132.51, 130.3, 130.3, 127.7, 123.9, 116.1, 116.0, 115.2, 107.4, 53.8, 29.1.



2-Cyanophenyl 2-(3-bromophenyl)ethanesulfonate: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.68 (ddd, *J* = 8.4, 7.7, 1.7 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.46 – 7.39 (m, 3H), 7.24 – 7.20 (m, 2H), 3.73 – 3.67 (m, 2H), 3.40 – 3.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.9, 139.1, 134.7, 134.0, 131.8, 130.7, 127.7, 127.4, 123.9, 123.1, 115.1, 107.4, 53.5, 29.5.



2-Cyanophenyl 2-(2,3-dichlorophenyl)ethanesulfonate ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.68 (ddd, *J* = 8.4, 7.6, 1.7 Hz, 1H), 7.56 (dd, *J* = 8.4, 0.7 Hz, 1H), 7.46 – 7.39 (m, 2H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 8.2, 2.1 Hz, 1H), 3.75 – 3.68 (m, 2H), 3.51 – 3.44 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 149.8, 134.8, 134.7, 134.3, 134.0, 133.1, 132.0, 129.9, 127.9, 127.7, 123.7, 115.1, 107.4, 51.5, 27.8.

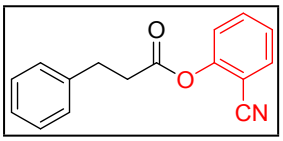


2-Cyanophenyl 2-(2',4'-dichloro-[1,1'-biphenyl]-3-yl)ethanesulfonate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 1.6 Hz, 1H), 7.71 (d, *J* = 1.6 Hz, 1H), 7.70 – 7.64 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 (d, *J* = 1.9 Hz, 1H), 7.45 – 7.38 (m, 3H), 7.34 (m, 1H), 7.32 – 7.27 (m, 1H), 3.82 – 3.69 (m, 2H), 3.48 – 3.41 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.9, 139.1, 138.6, 136.8, 1347, 134.0, 134.0, 133.3, 132.2, 129.9, 129.6, 129.0, 128.5, 128.2, 127.6, 127.4, 123.8, 115.1, 107.4, 53.6, 29.8.

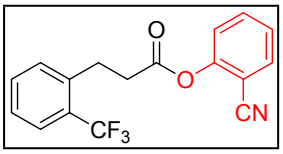
General Procedure for hydrocinamic ester synthesis:

Form corresponding acid chloride: In an oven dried round bottom flask charged with a magnetic sir bar, 2-cyanophenol (2 mmol) was taken. Then dry THF (3 mL) was added to it. The reaction solution was put in ice bath. NaH (2 equiv. 4 mmol) was added to the solution in two portion. When the gas evolution is stopped then acid chloride (1.2 equiv., 2.4 mmol) was dropwise added to the reaction

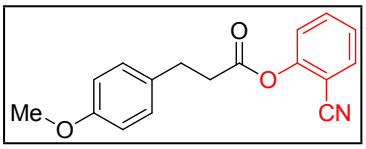
solution with constant stirring at 0˚C temperature. The reaction mixture was stirred at room temperature for overnight. After that, 1 mL water was poured to the reaction mixture. 15 mL ethyl acetate was added and the organic portion was separated by separating funnel. Total organic portion was dried over anhydrous Na_2SO_4 and concentrated in rota vap. The pure ester was isolated trough column chromatography.



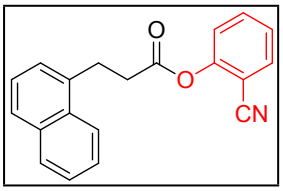
2-Cyanophenyl 3-phenylpropanoate: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 (ddd, *J* = 8.3, 7.7, 1.7 Hz, 1H), 7.38 – 7.30 (m, 3H), 7.30 – 7.26 (m, 2H), 7.23 (dt, *J* = 3.0, 1.8 Hz, 1H), 7.19 (dd, *J* = 8.3, 0.6 Hz, 1H), 3.16 – 3.09 (m, 2H), 3.03 – 2.96 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 170.5, 152.4, 139.9, 134.2, 133.4, 128.8, 128.5, 126.7, 126.5, 123.4, 115.3, 107.2, 35.8, 30.9. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{16}H_{13}NNaO_2$: 274.0838, found: 274.0831.



2-Cyanophenyl 3-(2-(trifluoromethyl)phenyl)propanoate ^{1}H NMR (500 MHz, CDCl3) δ 7.74 – 7.62 (m, 3H), 7.55 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 7.5 Hz, 1H), 7.38 (td, J = 7.6, 3.7 Hz, 2H), 7.30 (s, 1H), 3.33 (t, J = 7.9 Hz, 2H), 3.12 – 2.84 (m, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 170.2, 152.4, 138.6, 134.3, 133.5, 132.3, 131.2, 128.7, 127.0, 126.6, 126.5, 126.4, 123.6, 123.4, 115.3, 107.3, 35.7, 27.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{17}H_{12}NF_3NaO_2$: 342.0712, found: 342.0720.

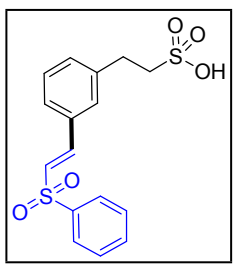


2-Cyanophenyl 3-(4-methoxyphenyl)propanoate ^{1}H NMR (400 MHz, CDCl3) δ 7.67 (dd, J = 7.7, 1.6 Hz, 1H), 7.61 (ddd, J = 8.3, 7.7, 1.7 Hz, 1H), 7.33 (td, J = 7.7, 1.0 Hz, 1H), 7.20 (ddd, J = 9.5, 3.9, 1.8 Hz, 3H), 6.90 – 6.83 (m, 2H), 3.80 (s, 3H), 3.12 – 3.03 (m, 2H), 2.99 – 2.92 (m, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 170.6, 158.5, 152.5, 134.2, 133.5, 132.0, 129.5, 126.4, 123.4, 115.3, 114.2, 107.3, 55.5, 36.2, 30.1.



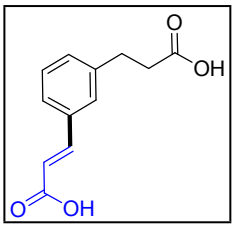
2-Cyanophenyl 3-(naphthalen-1-yl)propanoate ^{1}H NMR (400 MHz, CDCl3) δ 8.13 – 8.05 (m, 1H), 7.89 (dd, J = 8.1, 1.4 Hz, 1H), 7.78 (dd, J = 5.7, 3.8 Hz, 1H), 7.69 (dd, J = 7.7, 1.5 Hz, 1H), 7.67 – 7.59 (m, 1H), 7.58 – 7.55 (m, 1H), 7.51 (ddd, J = 8.0, 6.8, 1.3 Hz, 1H), 7.44 (q, J = 2.6, 2.0 Hz, 2H), 7.35 (tt, J = 7.7, 1.1 Hz, 1H), 7.22 (dd, J = 8.3, 1.0 Hz, 1H), 3.66 – 3.54 (m, 2H), 3.13 (dd, J = 8.7, 7.2 Hz, 2H). ^{13}C NMR (126 MHz, CDCl3) δ 170.7, 152.5, 137.5, 135.9, 134.3, 134.1, 133.5, 131.7, 129.2, 127.7, 126.5, 126.3, 125.9, 125.8, 123.5, 123.4, 107.4, 35.2, 28.1. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{20}H_{15}NNaO_2$: 324.0995, found: 324.0996.

De-protection of acid moieties and recovery of the directing template:



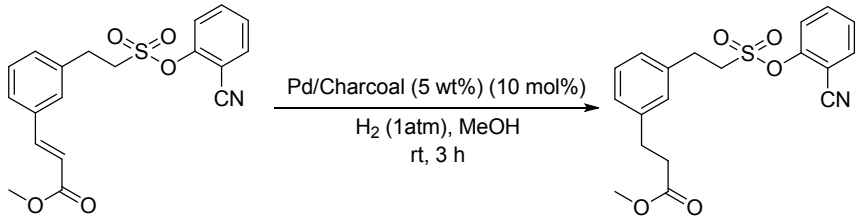
(E)-2-(3-(2-(phenylsulfonyl)vinyl)phenyl)ethanesulfonic acid: In a clean, oven–dried reaction tube, with previously placed magnetic stir–bar, (E)-2-cyanophenyl 2-(3-(2-(phenylsulfonyl)vinyl)phenyl)ethanesulfonate (0.2 mmol, 90 mg) was taken. Then the 10% KOH in MeOH was added to dissolve it. The reaction 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 (E)-2-(3-(2-(phenylsulfonyl)vinyl)phenyl)ethanesulfonic acid was appeared as insoluble part in both the layer. (E)-2-(3-(2-(phenylsulfonyl)vinyl)phenyl)ethanesulfonic acid was isolated through filtration of the total mixture. Yield 97%. And the organic portion was dried and concentrated to get pure 2-cyano phenol. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.96 – 7.89 (m, 2H), 7.76 – 7.70 (m, 1H), 7.69 – 7.60 (m, 5H), 7.53 (dt, *J* = 7.2, 1.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 3.00 –

2.80 (m, 2H), 2.75 – 2.60 (m, 2H), 2.55 – 2.41 (m, 1H). ^{13}C NMR (126 MHz, DMSO) δ 142.1, 142.0, 140.8, 133.5, 132.4, 131.2, 129.6, 129.0, 128.4, 127.9, 127.1, 126.9, 52.6, 31.3.



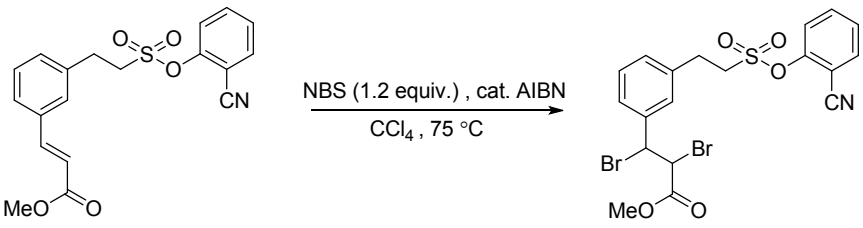
(E)-3-(3-(2-Carboxyethyl)phenyl)acrylic acid: In a clean, oven–dried reaction tube, with previously placed magnetic stir–bar (E)-ethyl 3-(3-(3-(2-cyanophenoxy)-3-oxopropyl)phenyl)acrylate (0.2 mmol, 70 mg) and LiOH.H2O (1.2 mmol) were taken. Then 3 mL MeOH, 2 mL THF, 1 mL H_2O were added to this. The reaction mixture was stirred at room temperature until the reaction was completed. Then the organic solvent was removed in rotavap. Then the remaining portion was washed with ethyl acetate. After that, 2 M HCl solution was added to the aqueous solution to reach the pH 1. Then ethyl acetate was poured to it organic portion was extracted from the aqueous part three times. Total Organic part was with brine solution, dried over Na2SO4, concentrated in rotavap and performed column chromatography to get the desired product. ^{1}H NMR (500 MHz, DMSO) δ 12.27 (s, 1H), 7.59 – 7.53 (m, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.32 (t, J = 7.6 Hz, 1H), 7.29 (m, 1H), 2.85 (t, *J* = 7.6 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 173.8, 167.6, 144.1, 141.7, 134.2, 130.3, 128.9, 128.0, 126.1, 119.1, 35.0, 30.1.

Preparation of methyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)propanoate



In a clean, oven–dried round bottom flask, with previously placed magnetic stir–bar (E)-methyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (0.5 mmol, 185 mg) and Pd/charcoal (10 mol%, 0.05 mmol, 106 mg (5 wt % Pd on charcoal)) were taken. Then the round bottom flask was evacuated and filled with hydrogen gas. Then methanol (30 mL) was added to this mixture by syringe. Then the reaction mixture was vigorously stirred for 3h with continuous flow of hydrogen. After that reaction mixture was filtered through celite. Total organic portion was concentrated and purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent. Isolated yield 97%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 7.7, 1.2 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.58 (d, J = 8.4 Hz, 1H), 7.46 (t, J = 11.1 Hz, 1H), 7.29 (t, J = 9.4 Hz, 1H), 7.17 – 7.12 (m, 3H), 3.75 – 3.66 (m, 5H), 3.41 – 3.34 (m, 2H), 2.97 (t, J = 7.8 Hz, 2H), 2.66 (t, J = 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.3, 149.9, 141.5, 137.0, 134.7, 134.0, 129.3, 128.7, 127.6, 127.4, 126.6, 123.8, 115.1, 107.4, 53.7, 51.8, 35.6, 30.9, 29.8.

Preparation of methyl 2,3-dibromo-3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)propanoate:



In a clean, oven–dried reaction tube, with previously placed magnetic stir–bar (E)-methyl 3-(3-(2-((2-cyanophenoxy)sulfonyl)ethyl)phenyl)acrylate (0.3 mmol, 114 mg) and NBS (1.2 equiv. 0.36 mmol, 63 mg) and catalytic amount AIBN were taken. Then CCl_4 (5 mL) was added to this mixture by syringe.

Then the reaction mixture was vigorously stirred for 24h at 75˚C. After that reaction mixture was was cooled to room temperature and washed with water (10 mL). The total organic portion was dried over anhyd. Na_2SO_4 and concentrated in rota vap. The desired product was purified via column chromatography through silica gel using pet ether- ethyl acetate as eluent (70:30 v/v). Isolated yield 90%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 1H), 7.72 – 7.67 (m, 1H), 7.60 – 7.55 (m, 1H), 7.46 (tdd, J = 7.7, 3.0, 1.1 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 5.37 – 5.33 (m, 1H), 4.89 – 4.85 (m, 1H), 3.92 (s, 3H), 3.78 – 3.72 (m, 2H), 3.48 – 3.41 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 149.9, 138.6, 137.7, 134.7, 134.0, 129.7, 129.7, 128.4, 127.6, 127.2, 123.9, 115.1, 107.4, 53.6, 53.5, 50.30, 46.7, 29.7. HRMS (ESI-QTOF) m/z: $[M+Na]^+$: calcd. for $C_{19}H_{17}Br_2NO_5SNa$: 551.9086, found: 551.9073.

Mass spectrometric studies of the reaction mixture

In an oven dried reaction tube, charged with magnetic stir-bar, $Pd(OAc)_2$ (1 equiv.) , N-For-Gly-OH (2 equiv.), substrate (1 equiv.) and HFIP (1 mL) were added. Then the reaction tube was capped and stirred at room temperature for 15 mins and then placed to a preheated oil-bath at 65 °C. After 5 h of the reaction the reaction mixture was analysed in mass spectrometry.

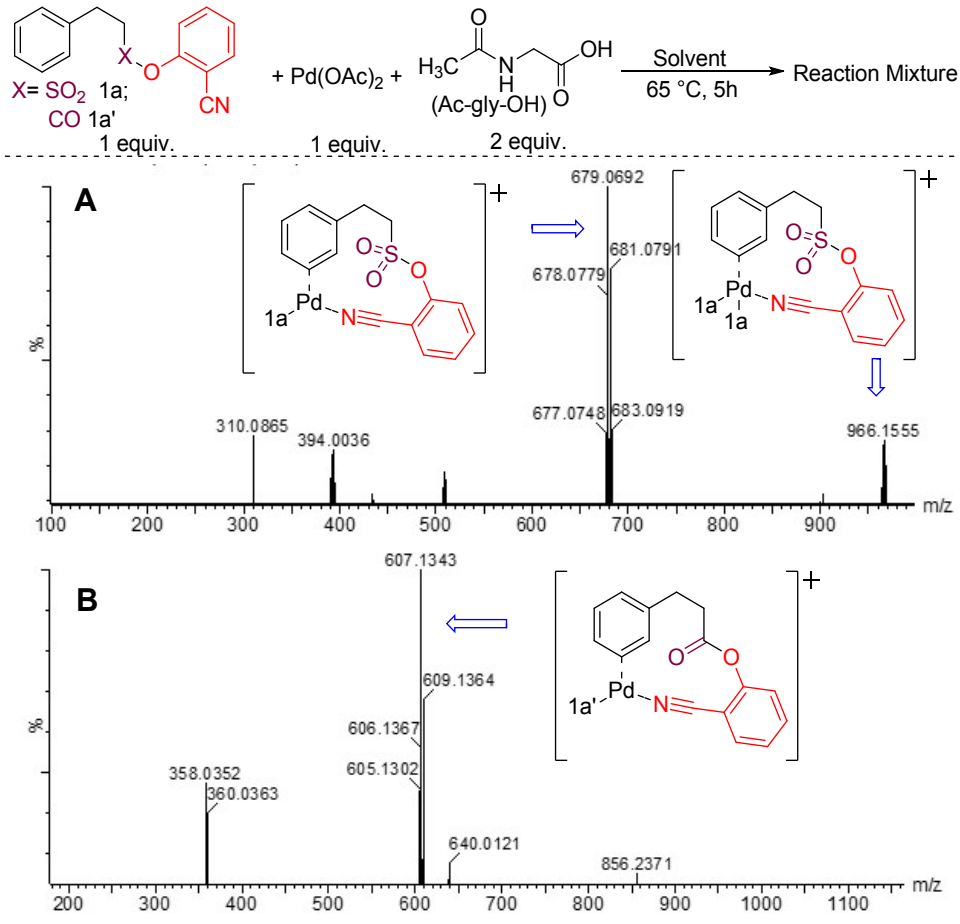


Fig.2. Mass spectrometric studies of the reaction mixture

Determination of order

The order of the reaction with respect to the substrate and olefin was determined using Initial slope method.

Order determination with respect to substrate:

In an oven dried reaction tube, charged with magnetic stir-bar, $Pd(OAc)_2$, N-For-Gly-OH, substrate were added. Olefin (ethyl acrylate) was added to the reaction mixture followed by the HFIP (1 mL). The reaction tube was capped and then placed to a preheated oil-bath at 70 °C. The reaction was stirred vigorously for a definite amount of time and then taken out to cool it to the room temperature. The reaction mixture was diluted with ethyl acetate and equivalent amount of 1,3,5-trimethoxybenzene (external standard) was added to the reaction mixture. 200 µL aliquot was taken out from the mixture, evaporated and dissolved in $CDCl_3$ for NMR study

A	Substrate	olefin	$Pd(OAc)_2$	Ac-For-OH
Red line (run 1)	0.4 mmol	0.4 mmol	0.02 mmol	0.04 mmol
Blue line (run 2)	0.2 mmol	0.4 mmol	0.02 mmol	0.04 mmol

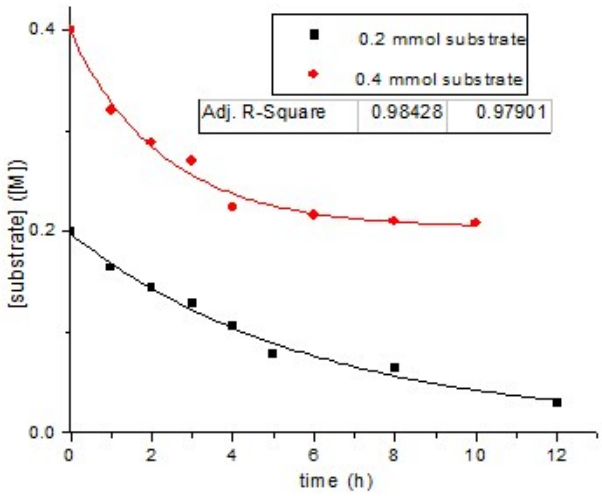


Fig.3. Decay of substrate 1a with respect to time. Reaction was done with 0.2 mmol (red line) and 0.2 mmol (black line) of substrate and 0.4 mmol of ethyl acrylate.

0.4 mmol substrate (run1)

X (concentration axis) = 0.0178937072, Y (time axis) = 0.396134535

X = 0.031210534, Y = 0.395024906

At t=0

Dx= -0.0133

Dy= 0.0011

$\{Dx/dy\}_{run1}$= -0.0833

0.2 mmol substrate (run 2)

X (concentration axis) = **0.0137080927, Y** (time axis) = **0.197826772**

X = 0.0703978785, Y = 0.195998307

At t=0

Dx= -0.0566

Dy= 0.0018

$\{Dx/dy\}_{run2}$ **= -0.0322**

We know

Rate $Dx/dy= k[substrate]^x[olefin]^y$

$\{Dx/dy\}_{run1}/\{Dx/dy\}_{run2} = \{k[substrate]_{run1}^x[olefin]_{run1}^y\}/\{k[substrate]_{run2}^x[olefin]_{run2}^y\}$

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

$2.58 = [substrate]_{run1}^y/[substrate]_{run2}^y$

$At\ t=0;\ [substrate]_{run1}^y/[substrate]_{run2}^y = 2$

$So,\ 2.58 = 2^y$

$0.41 = y \log 2$

$y = 0.41/\log 2$

$= 0.41/0.30 = 1.3 = \sim 1$

Order determination with respect to olefin*:*

In an oven dried reaction tube, charged with magnetic stir-bar, $Pd(OAc)_2$, N-For-Gly-OH, substrate were added. Olefin (phenyl vinyl sulfone) was added to the reaction mixture followed by the HFIP (1 mL). The reaction tube was capped and then placed to a preheated oil-bath at 70 °C. The reaction was stirred vigorously for a definite amount of time and then taken out to cool it to the room temperature. The reaction mixture was diluted with ethyl acetate and equivalent amount of 1,3,5-trimethoxybenzene (external standard) was added to the reaction mixture. 200 µL aliquot was taken out from the mixture, evaporated and dissolved in $CDCl_3$ for NMR study.

B	Substrate	olefin	$Pd(OAc)_2$	Ac-For-OH
Black line (run 3)	0.2 mmol	0.4 mmol	0.02 mmol	0.04 mmol
Red line (run 2)	0.2 mmol	0.8 mmol	0.02 mmol	0.04 mmol

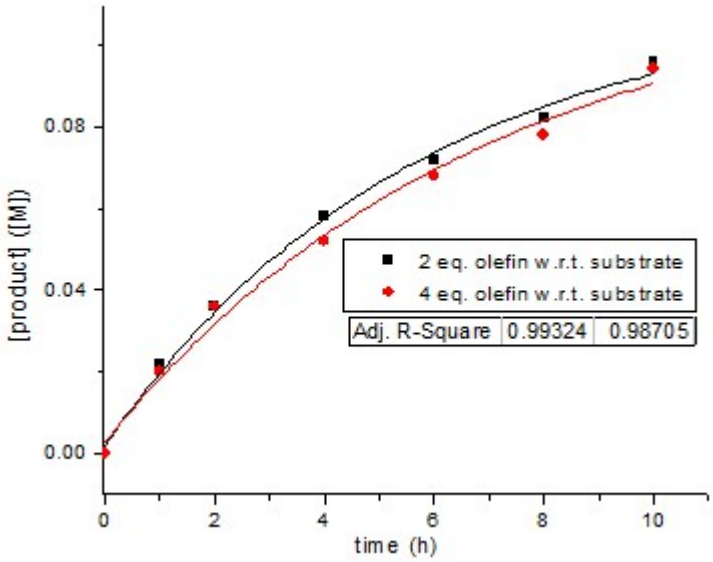
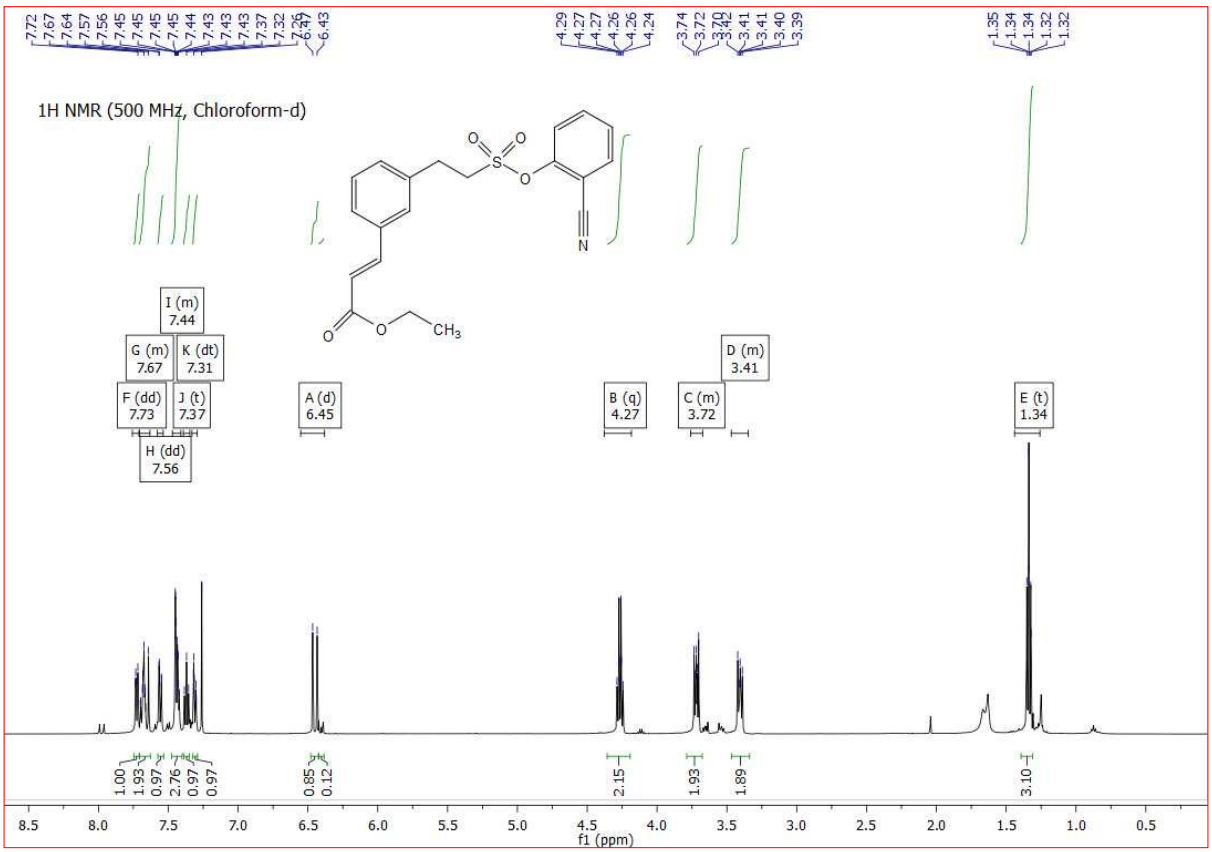


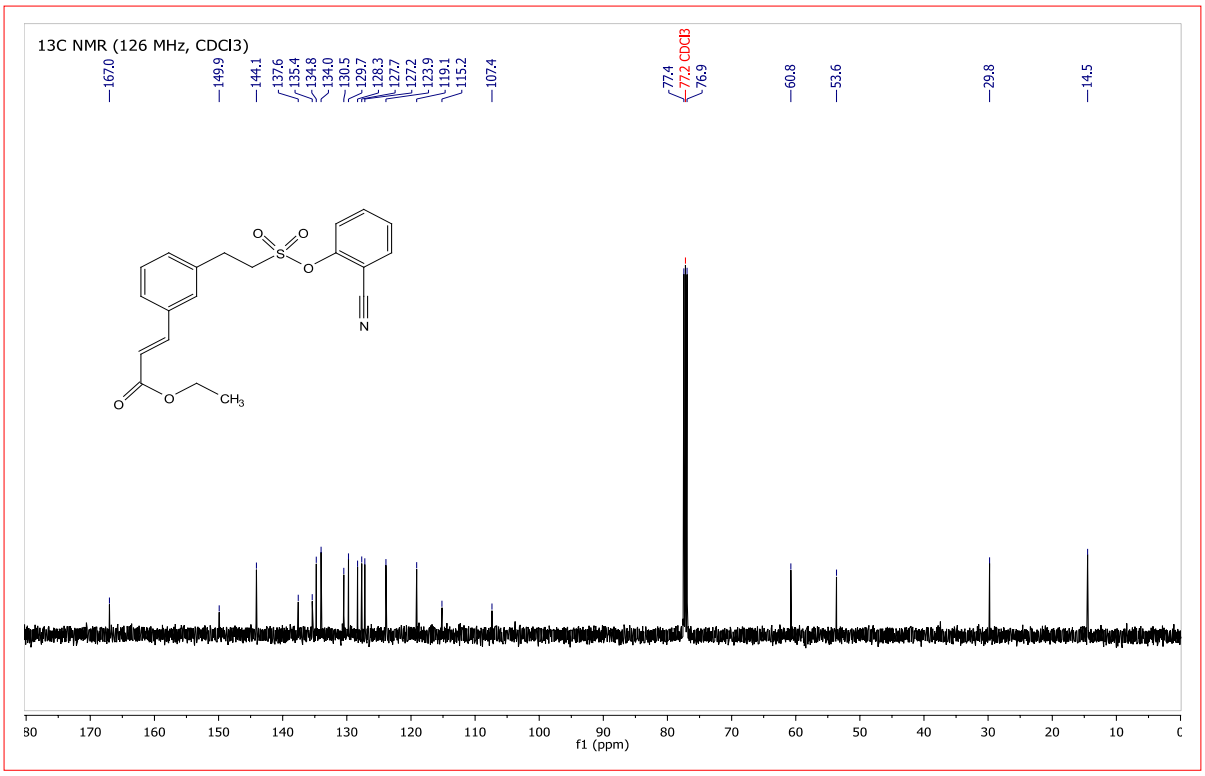
Fig. 4. Overlap of the product growth plot using 2 eq. (black line) and 4 eq. (red line) of olefin with respect to substrate

The overlapping of the rate of the reaction for run 3 and run 4 implies that the rate of the reaction is not dependent on olefin concentration. So x =0

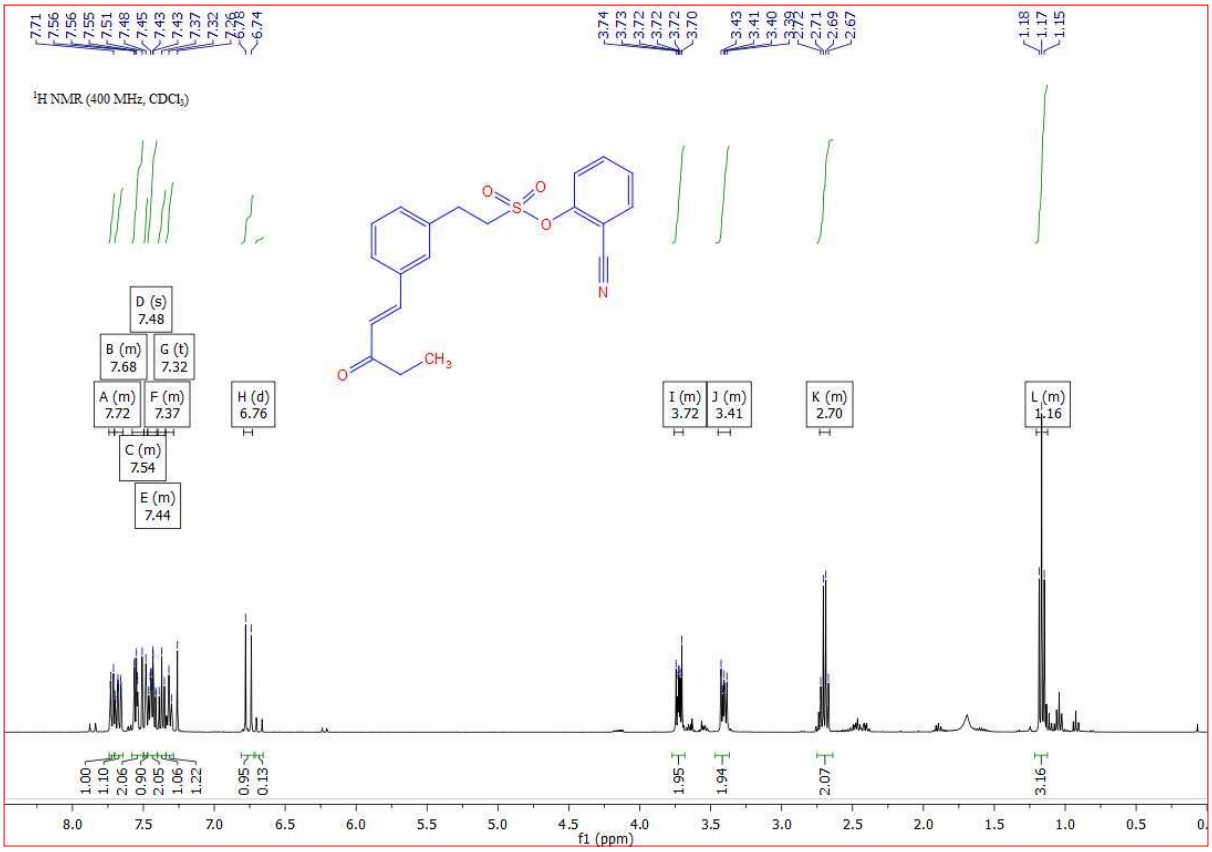
NMR Spectra

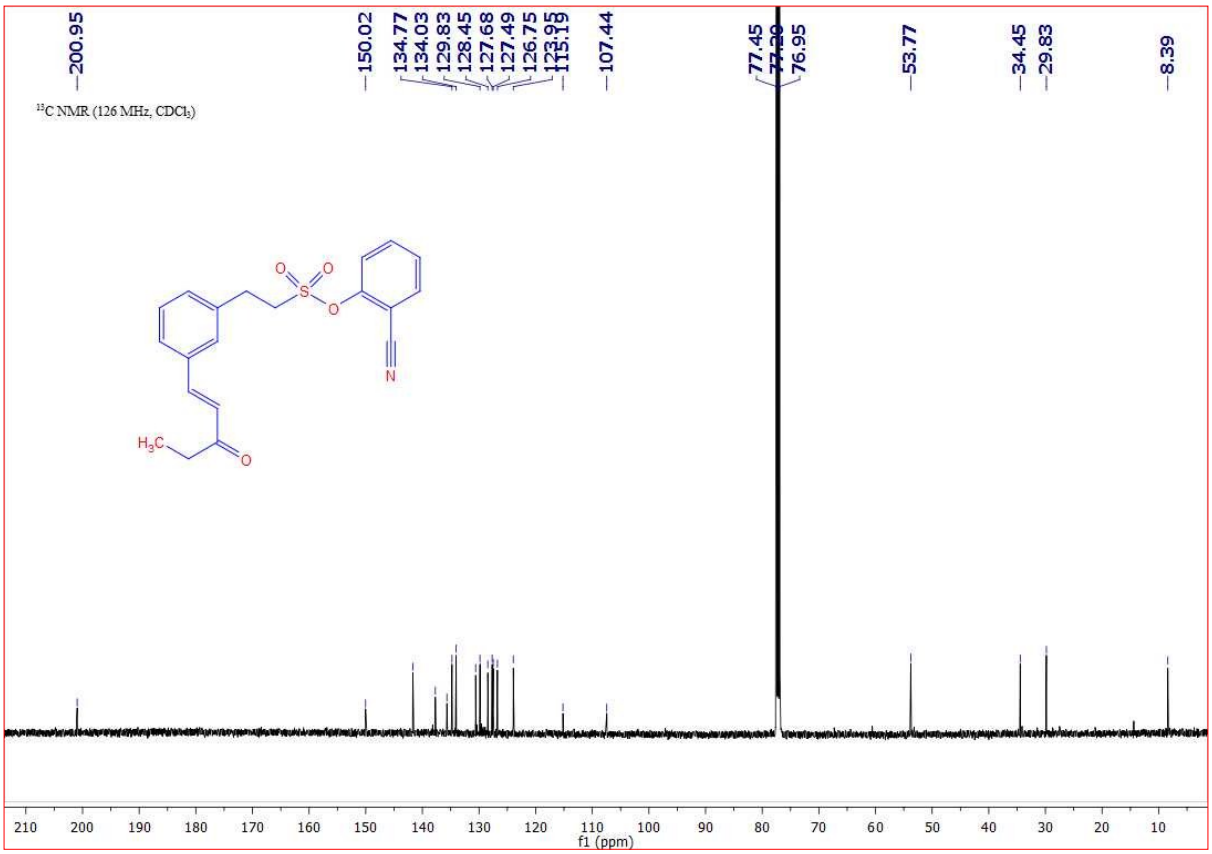
Entry 2a; Scheme 3



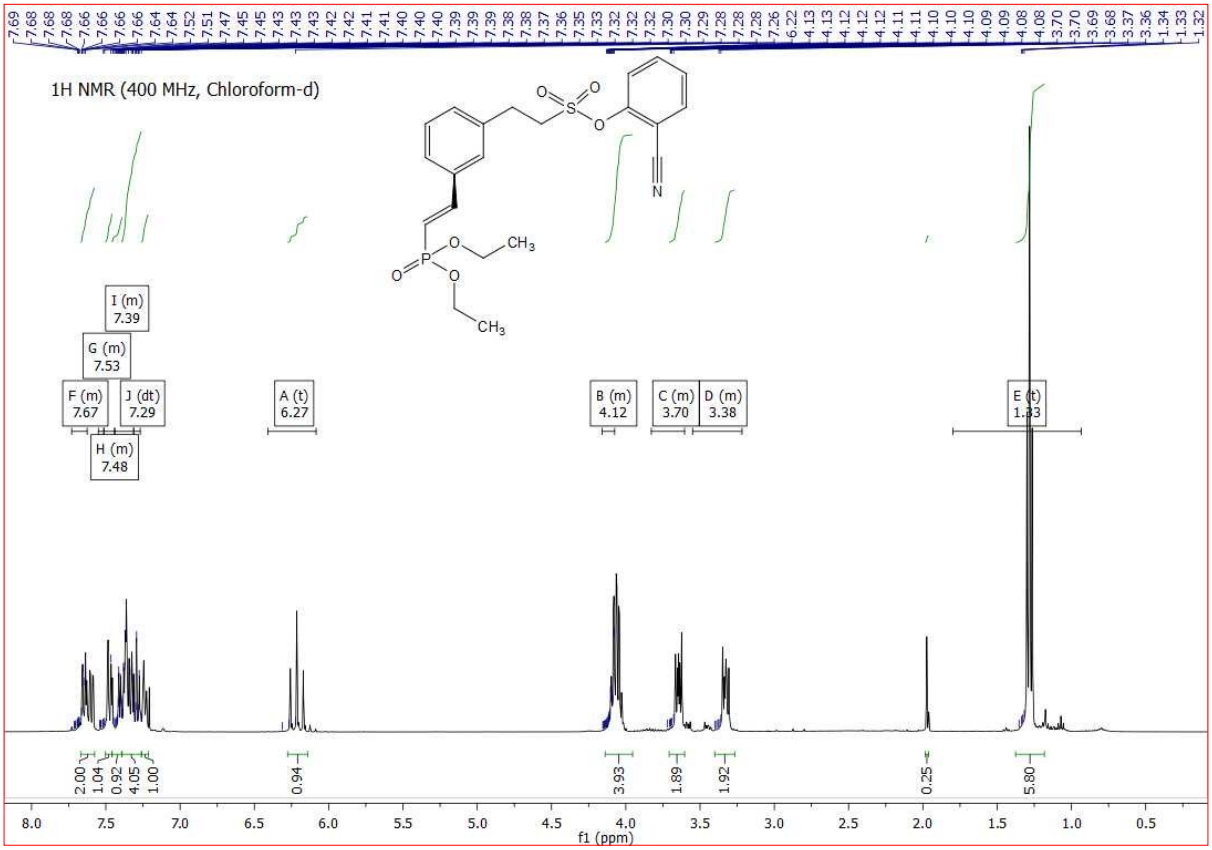


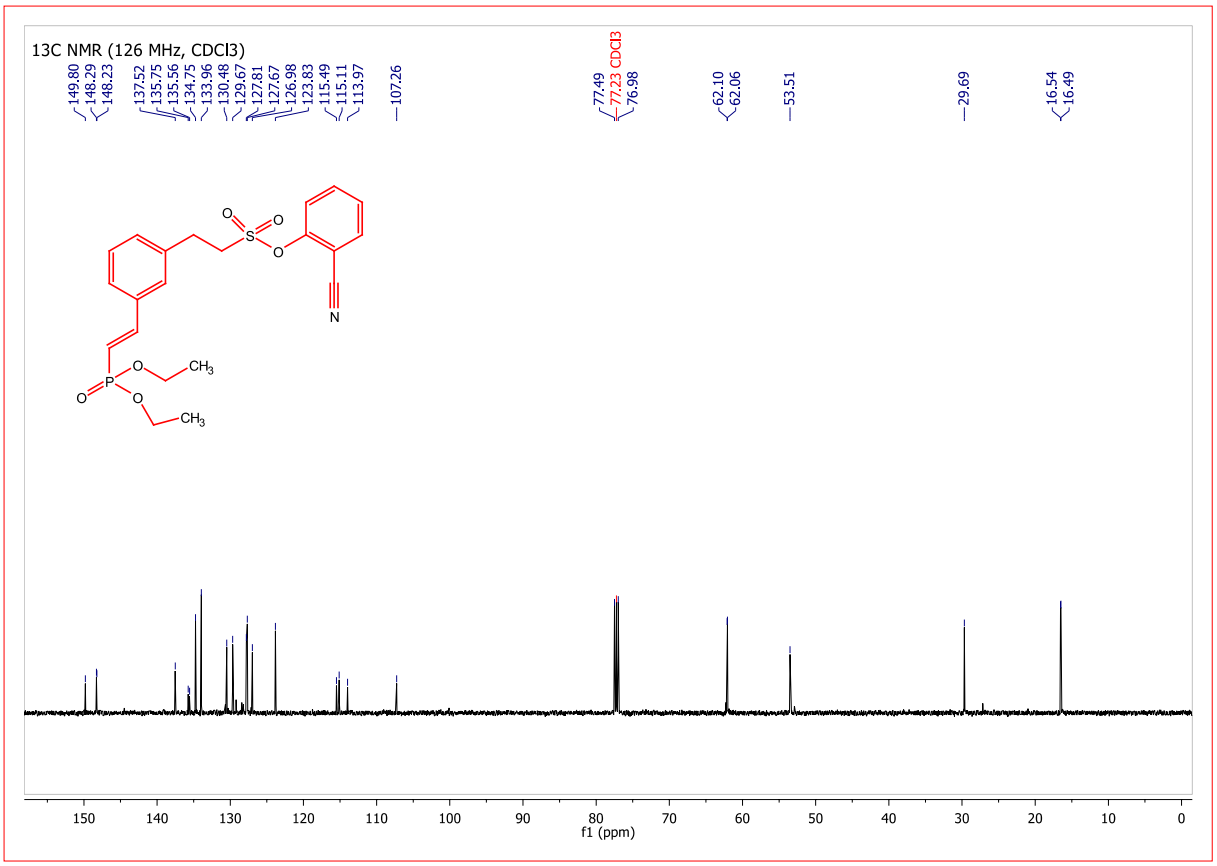
Entry 2b; Scheme 3



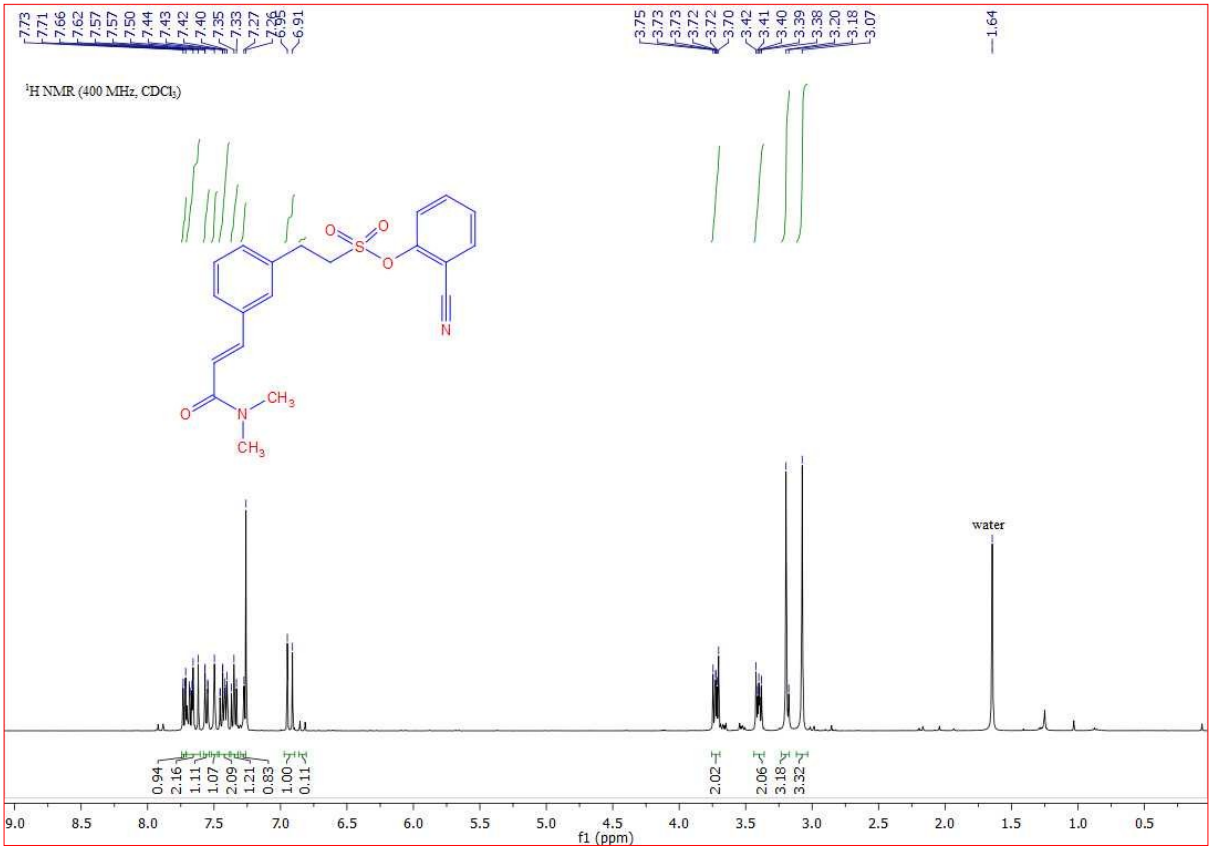


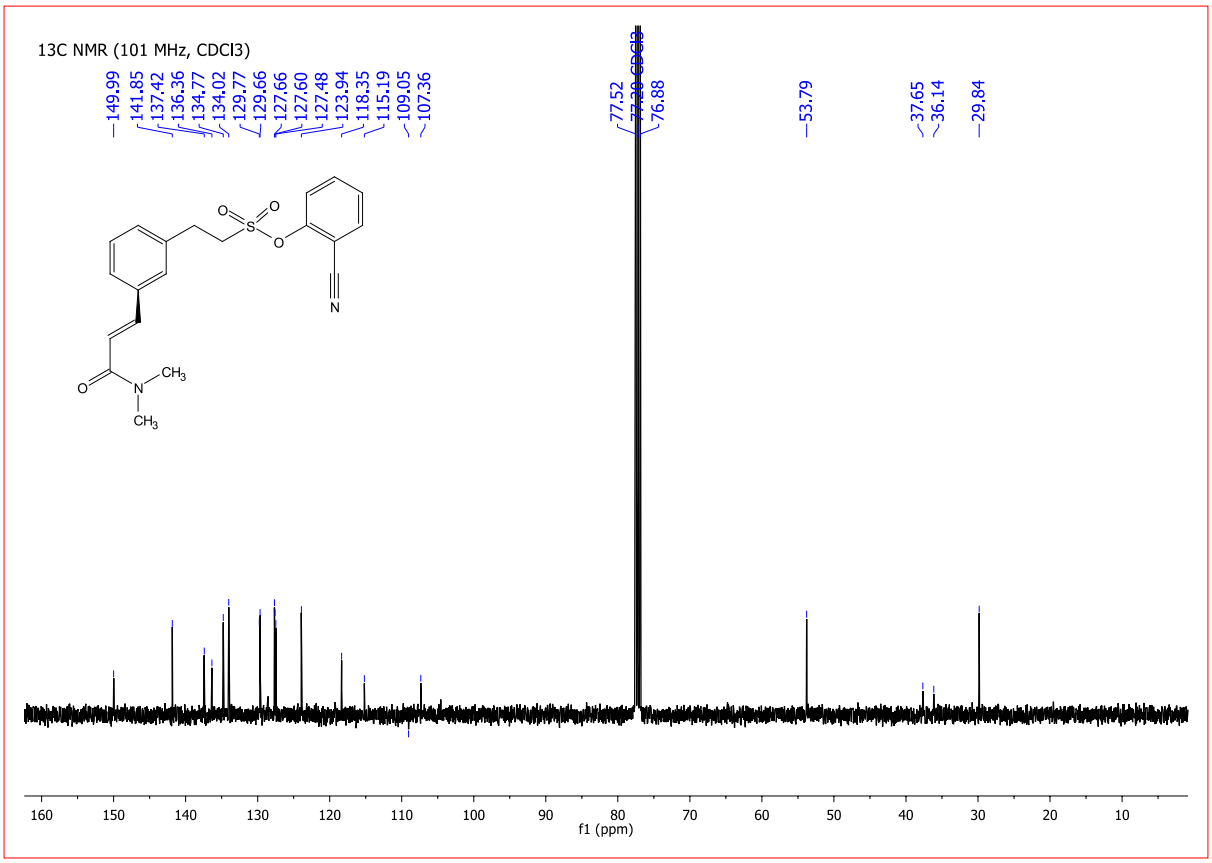
Entry 2c; Scheme 3



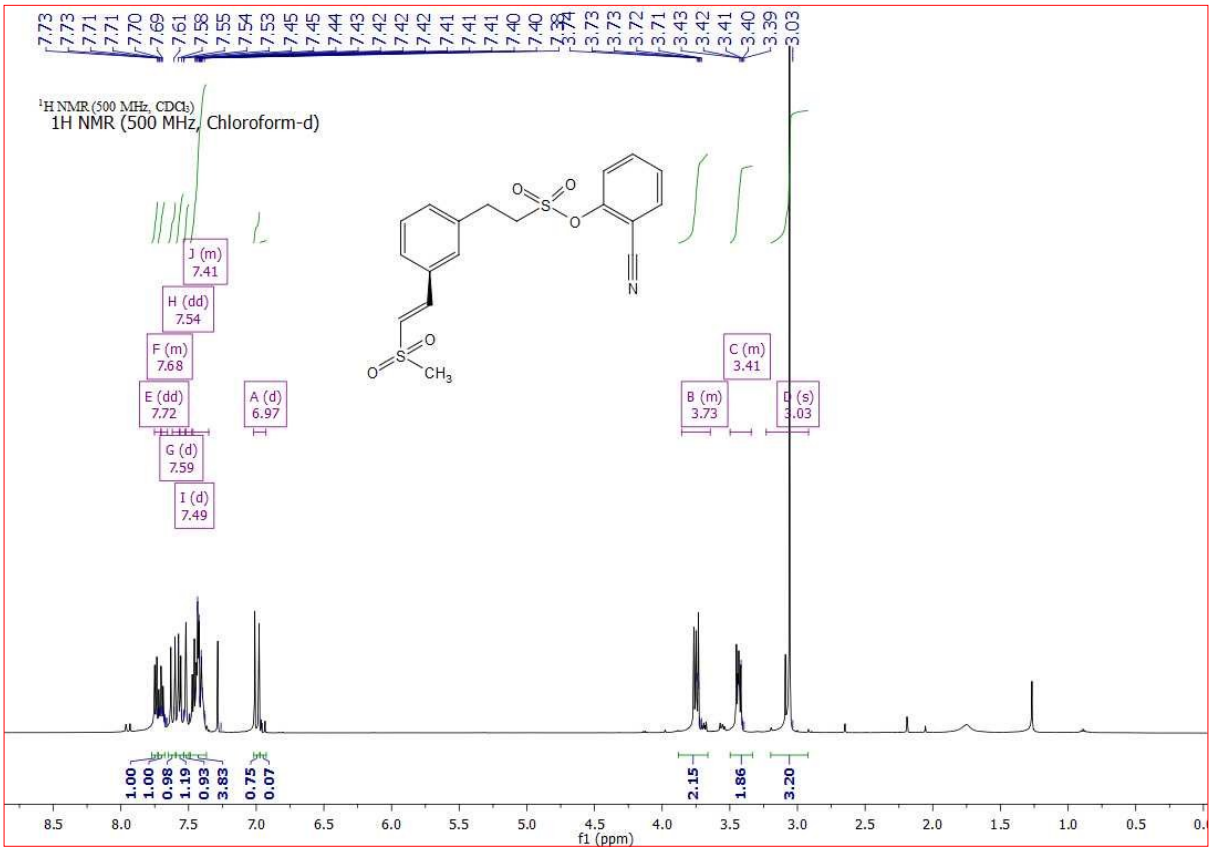


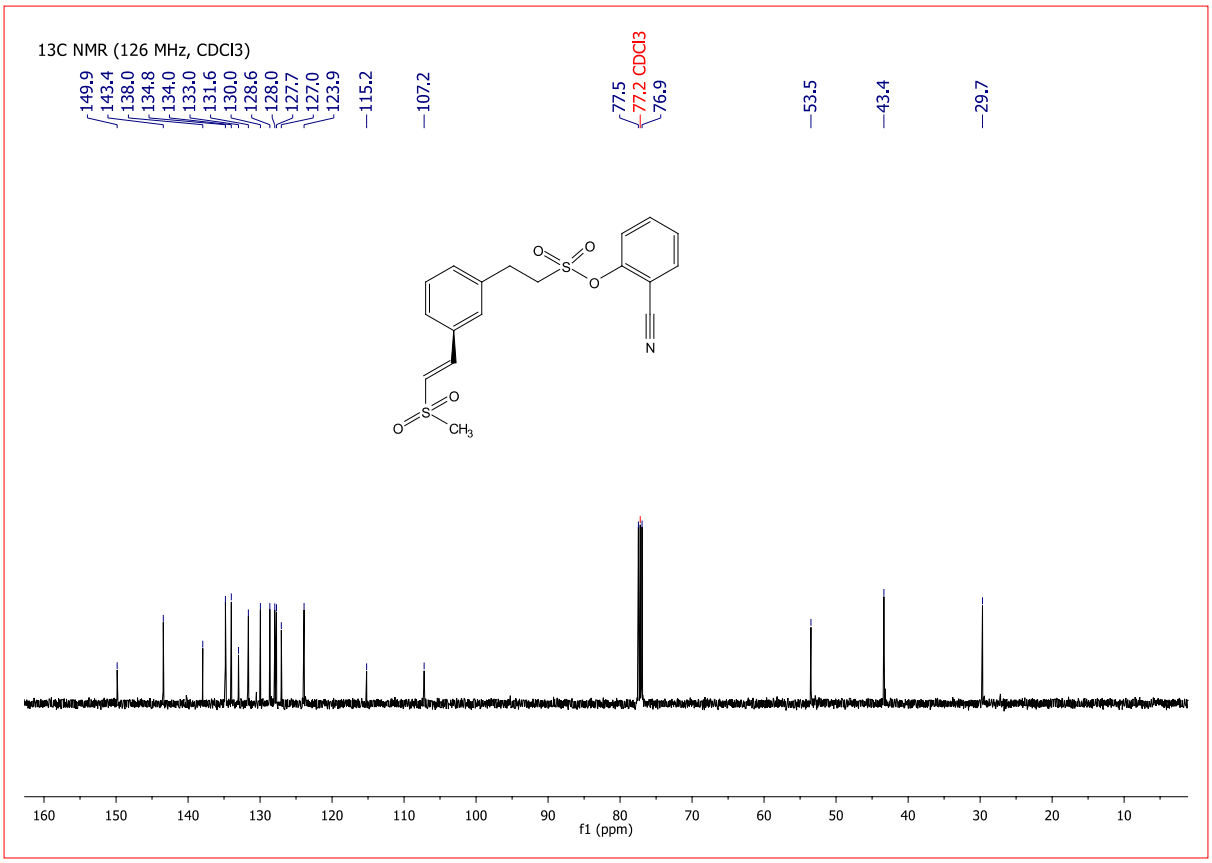
Entry 2d; Scheme 3



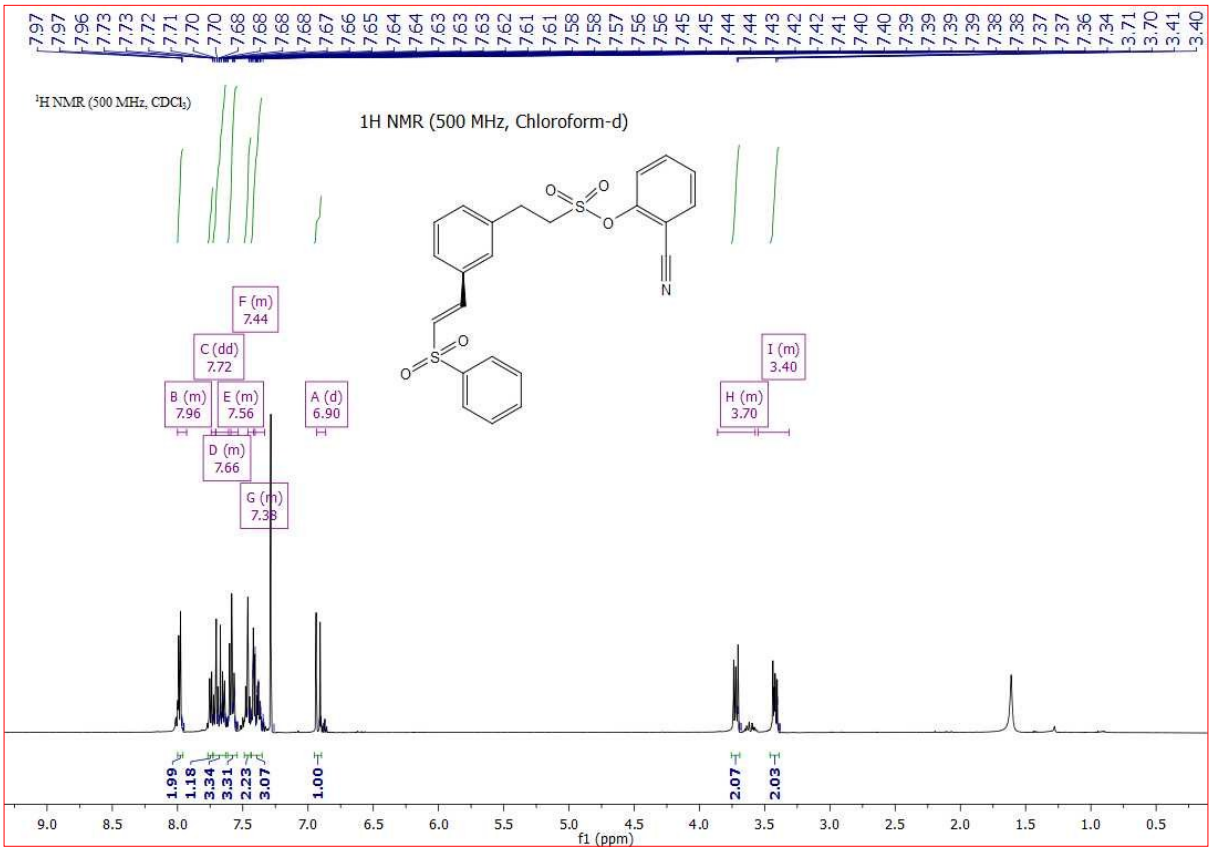


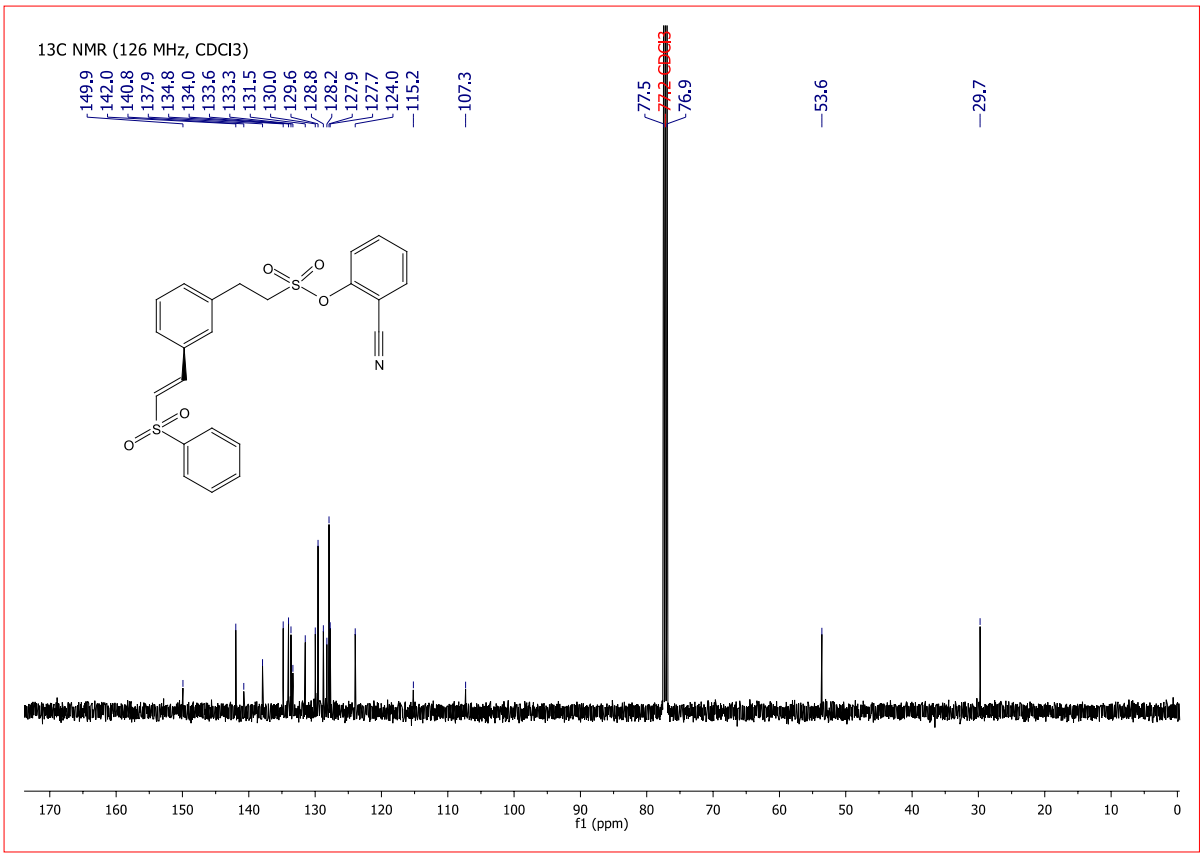
Entry 2e; Scheme 3



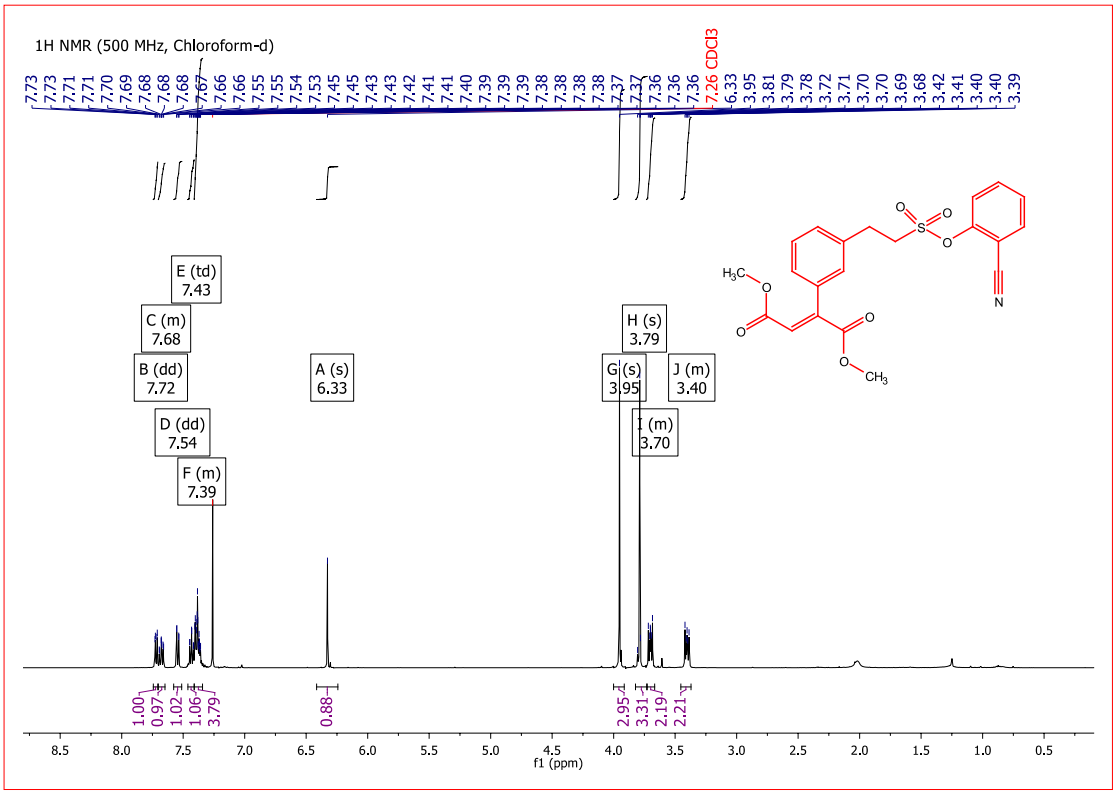


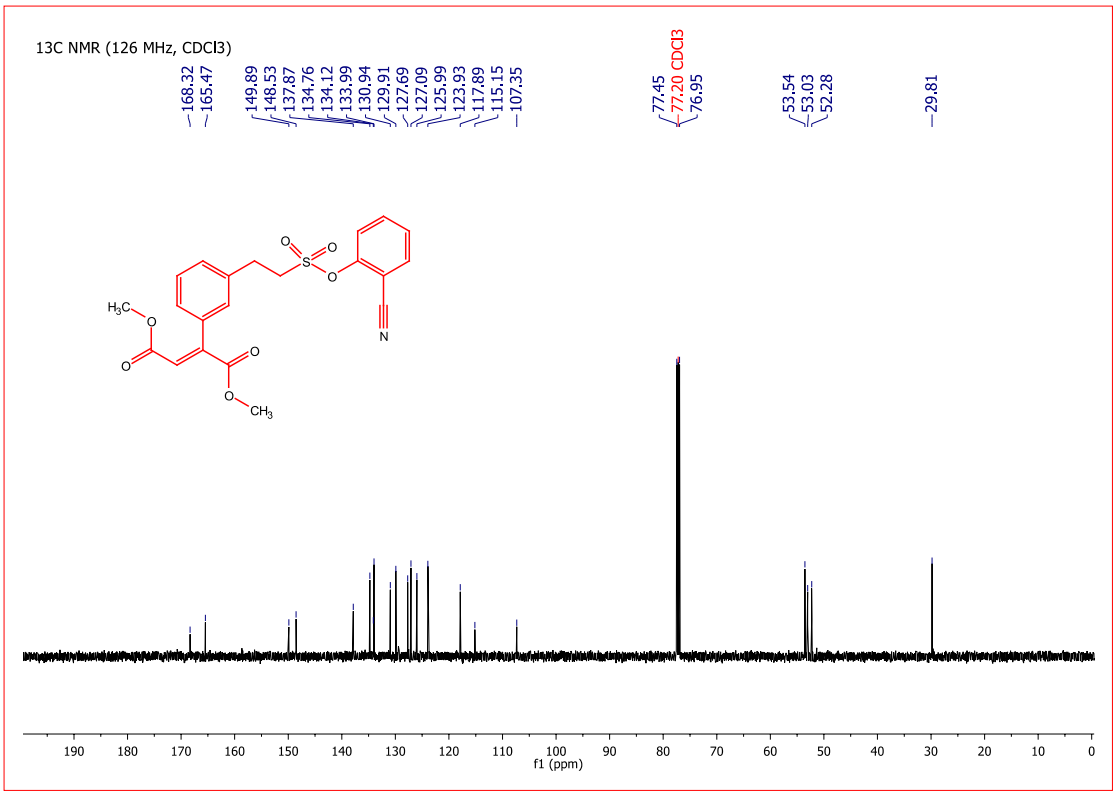
Entry 2f; Scheme 3



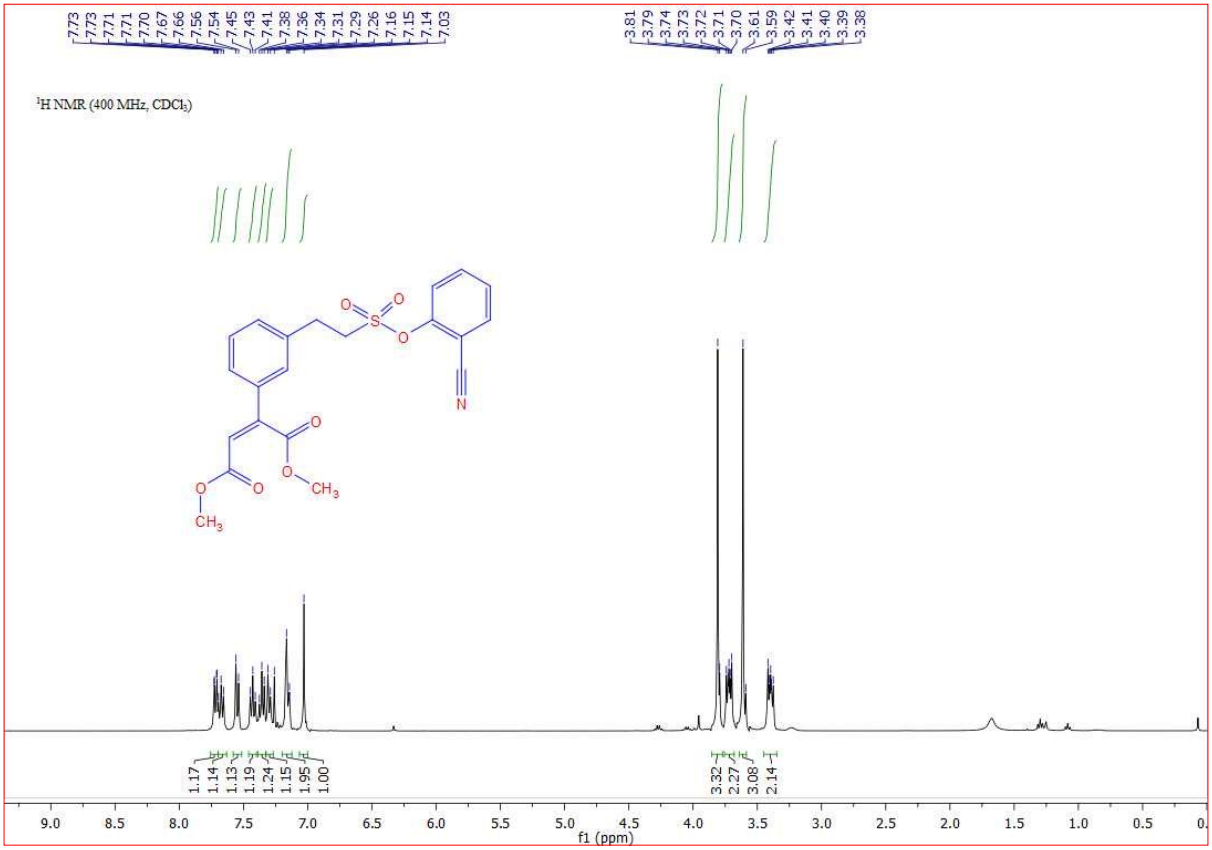


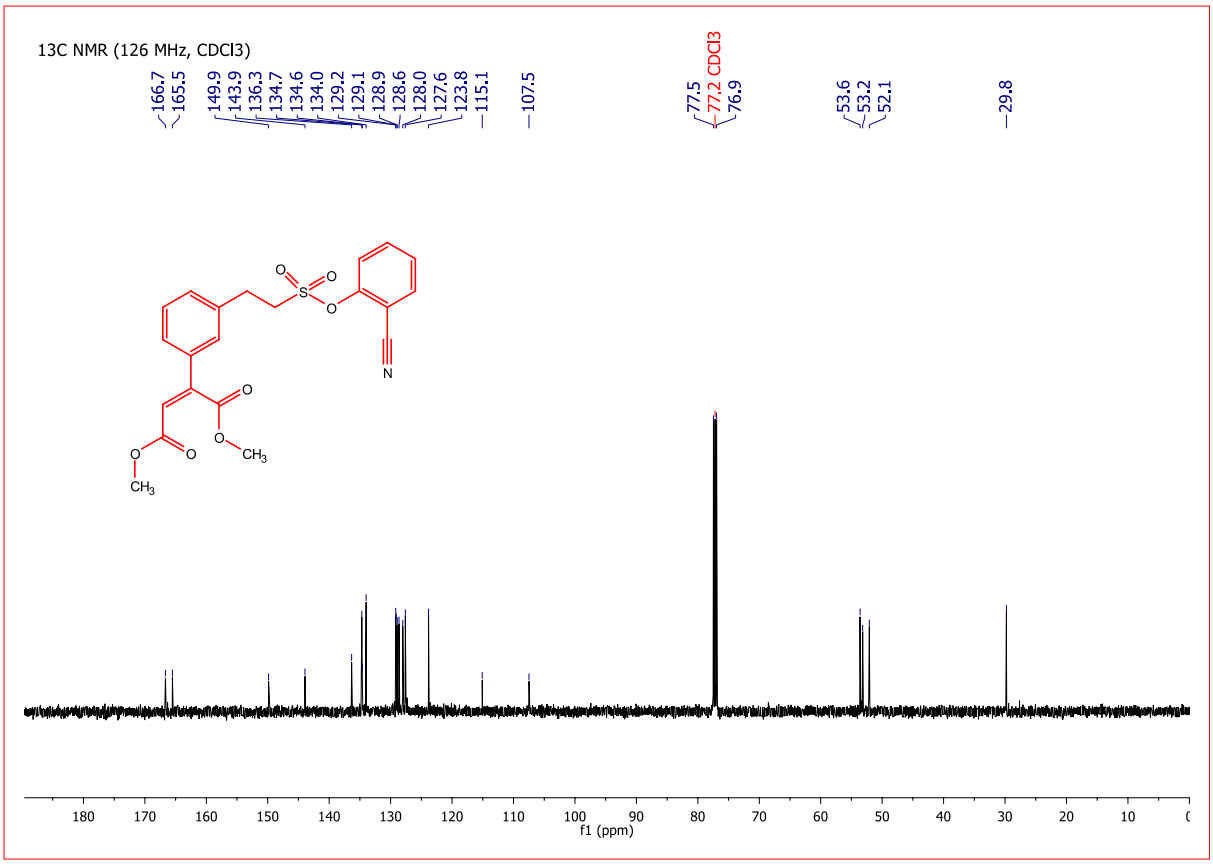
Entry 2g; Scheme 3



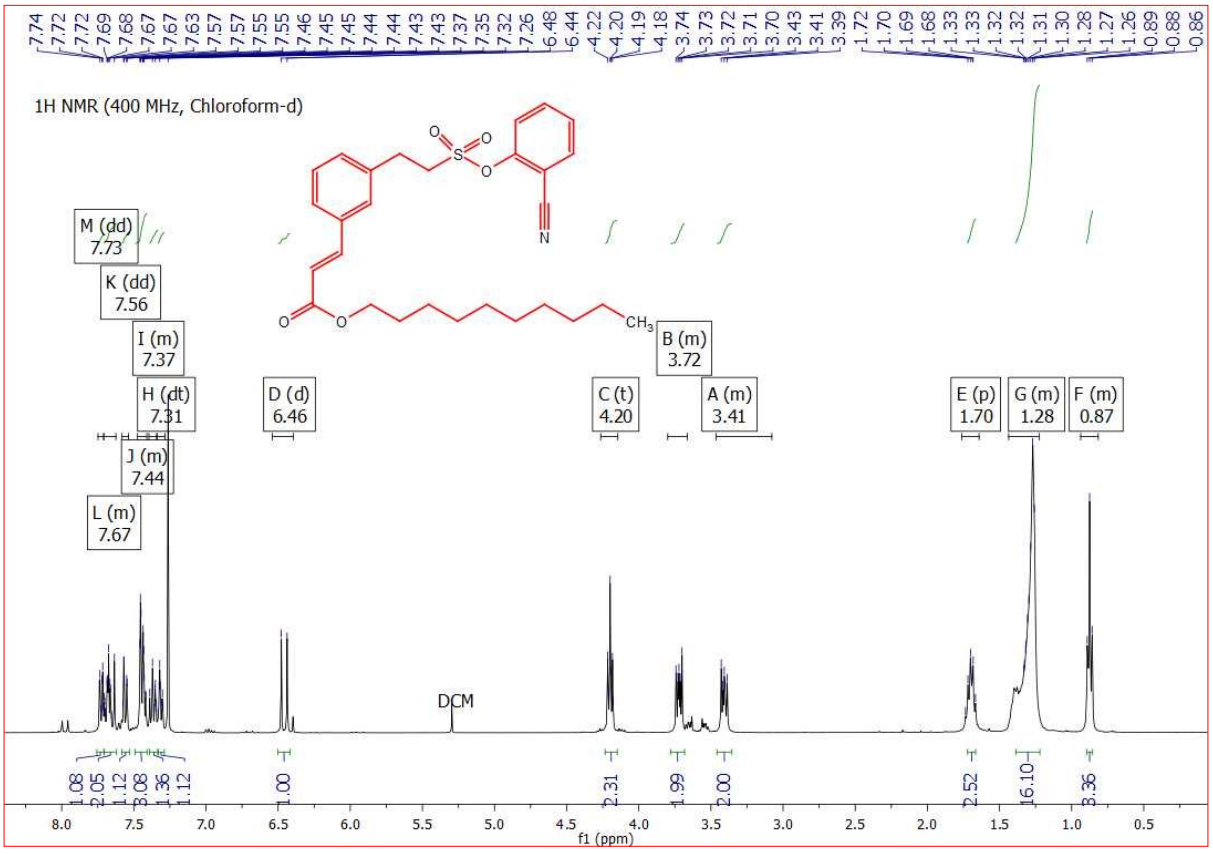


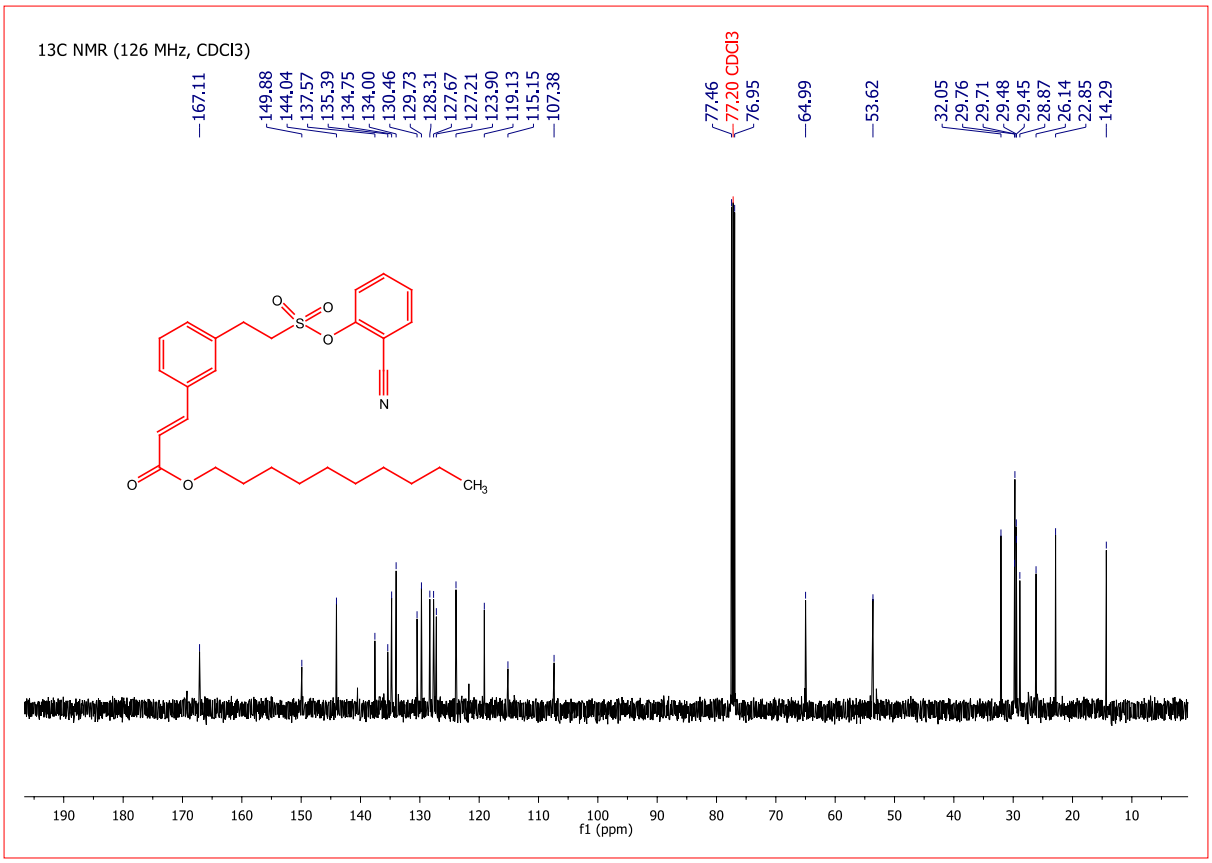
Entry 2h; Scheme 3



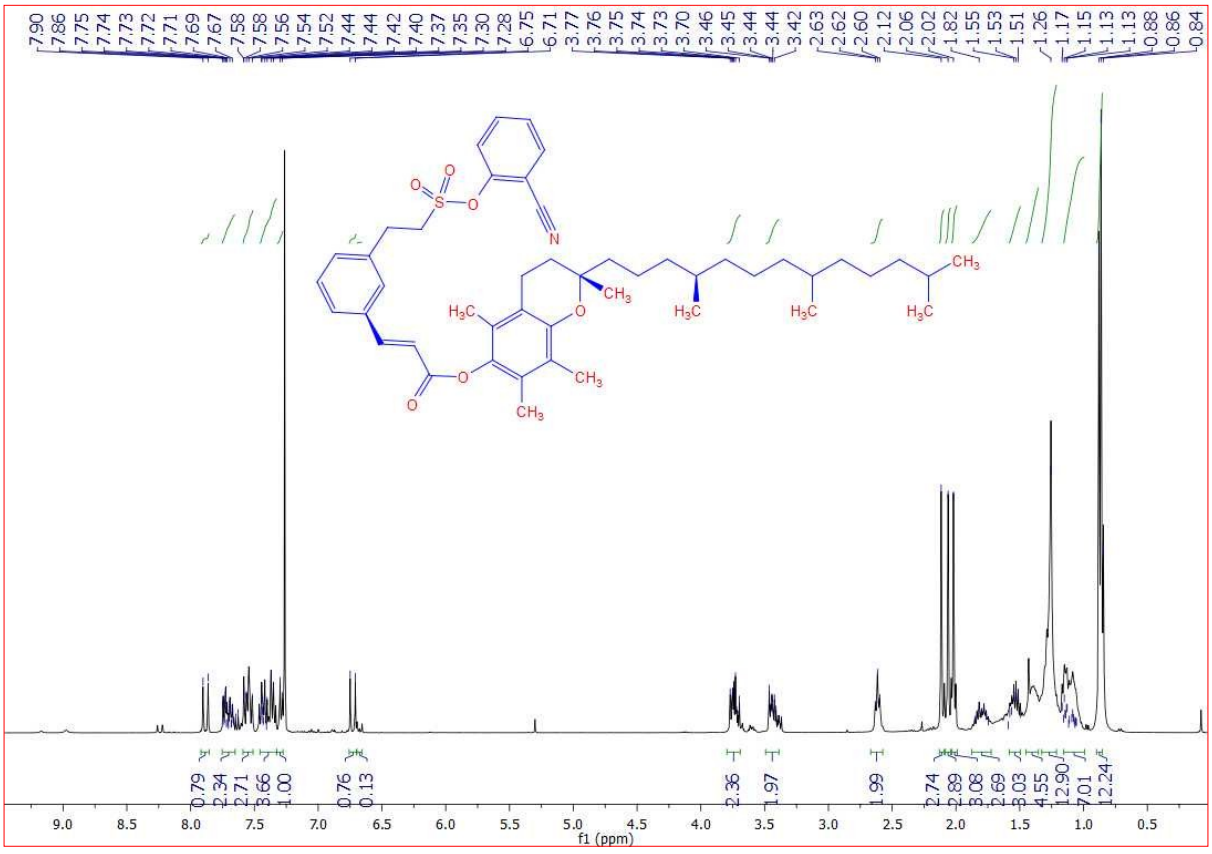


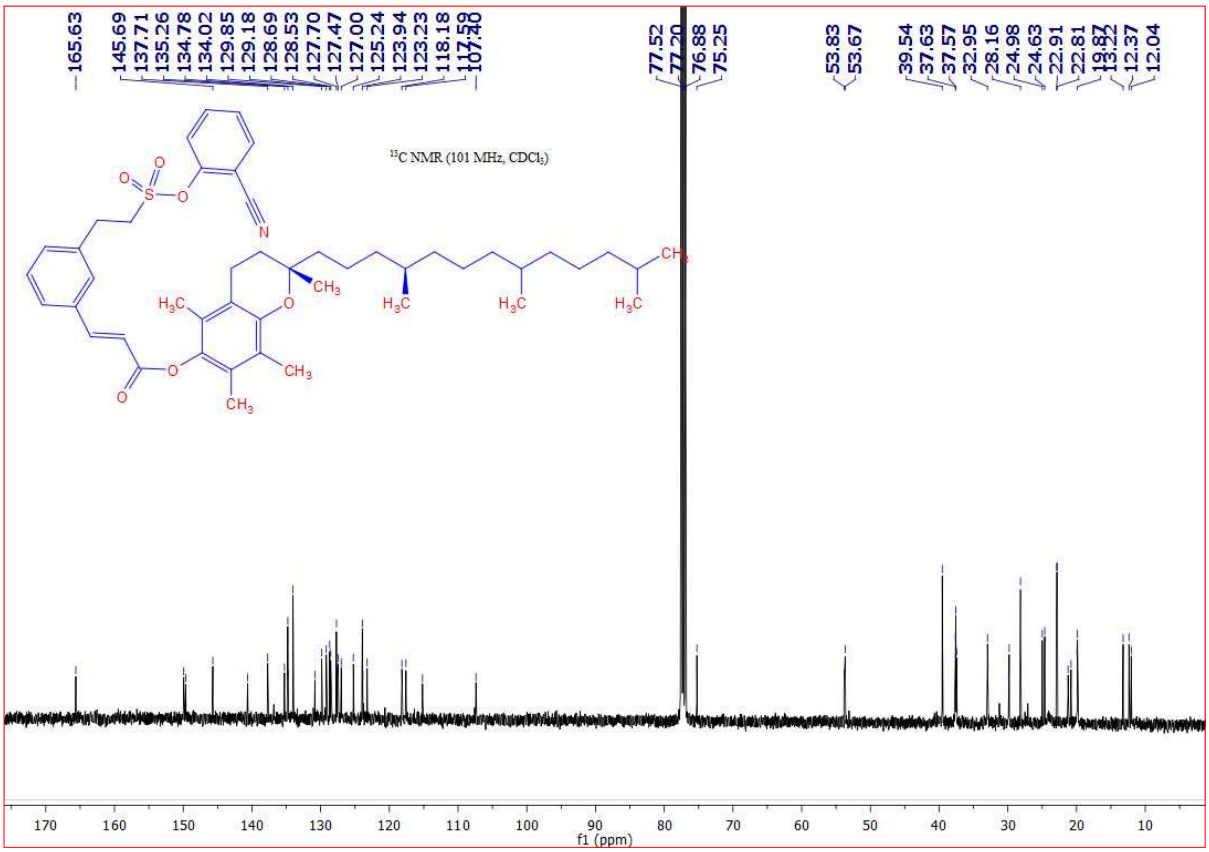
Entry 2i; Scheme 3



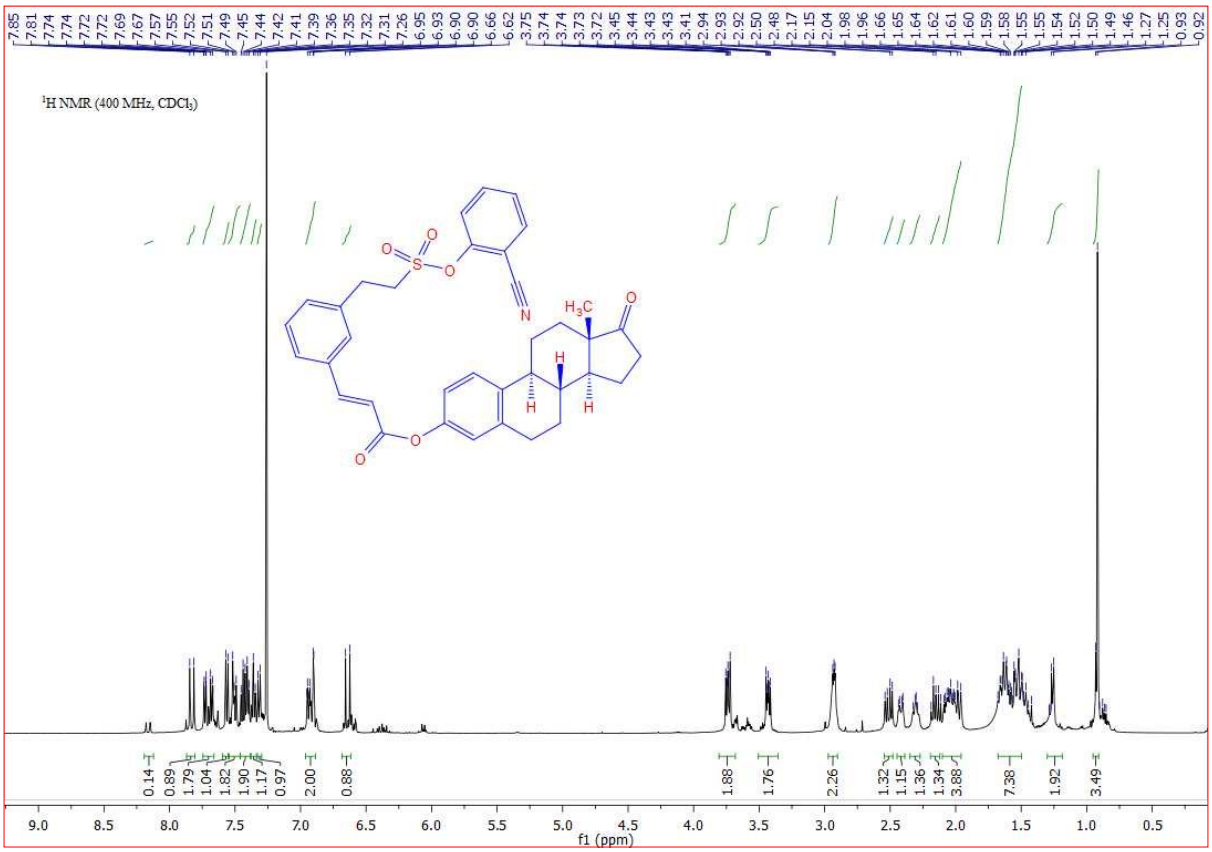


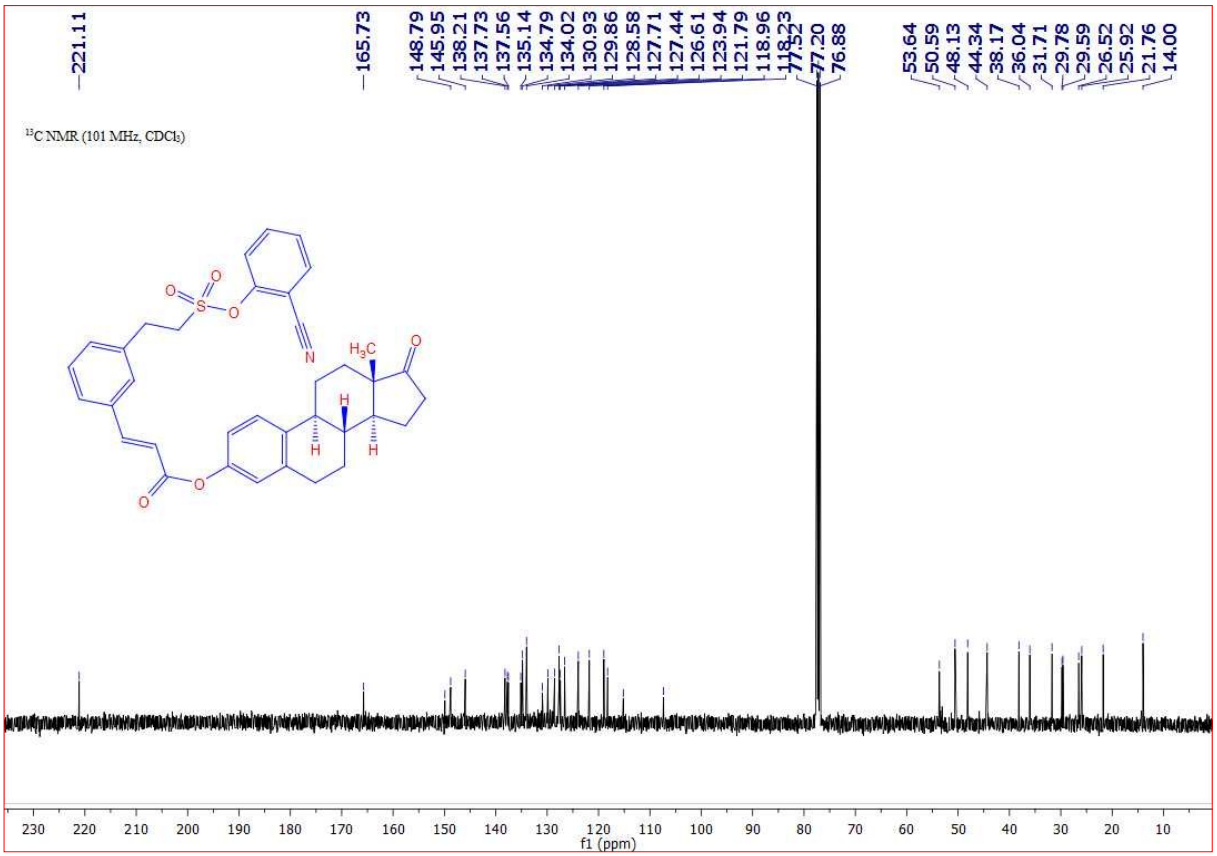
Entry 2j; Scheme 3



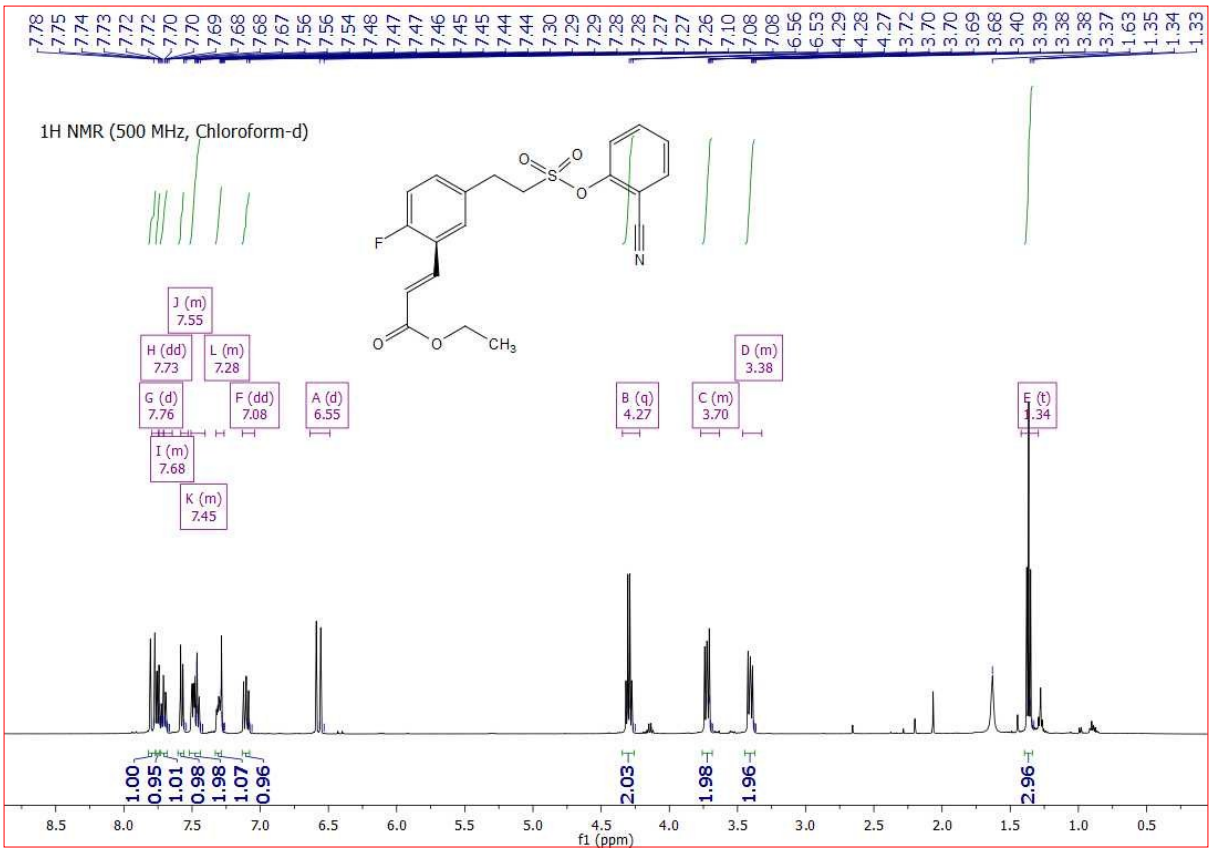


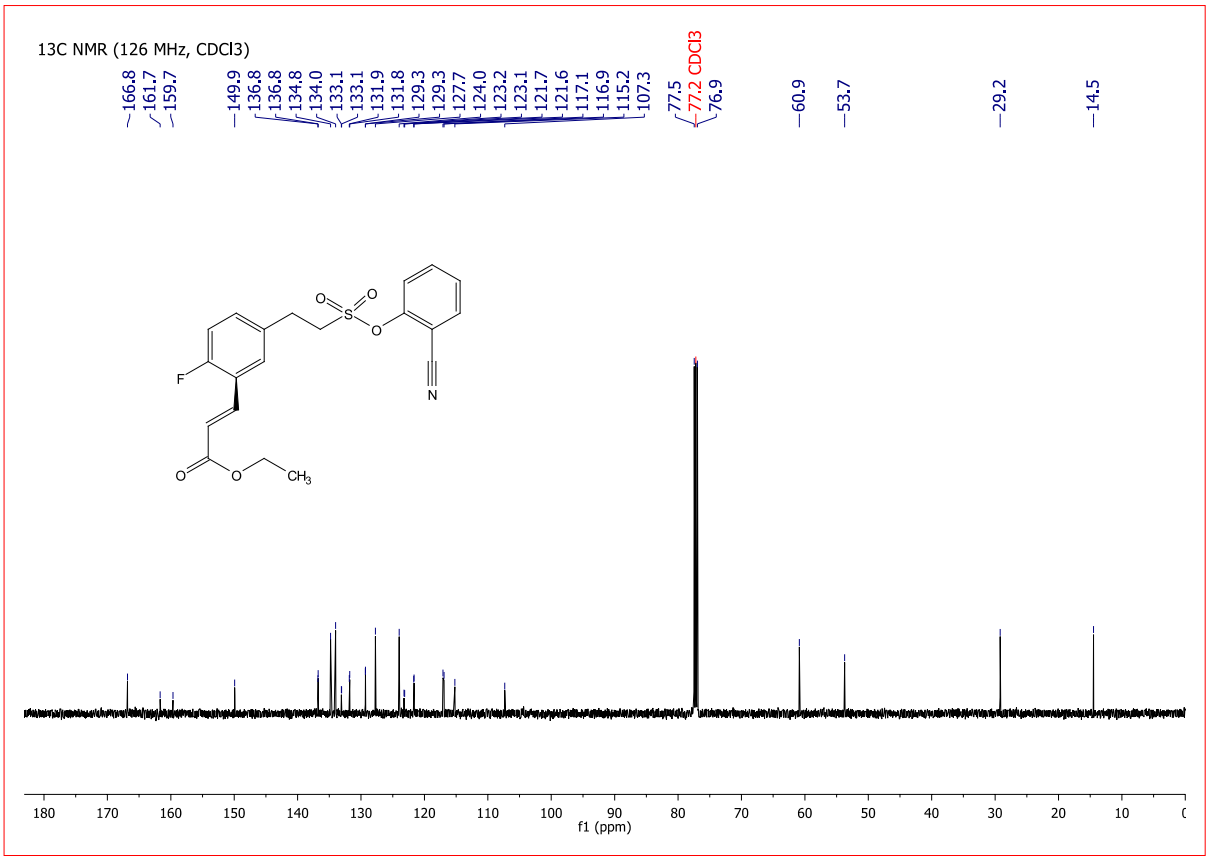
Entry 2k; Scheme 3



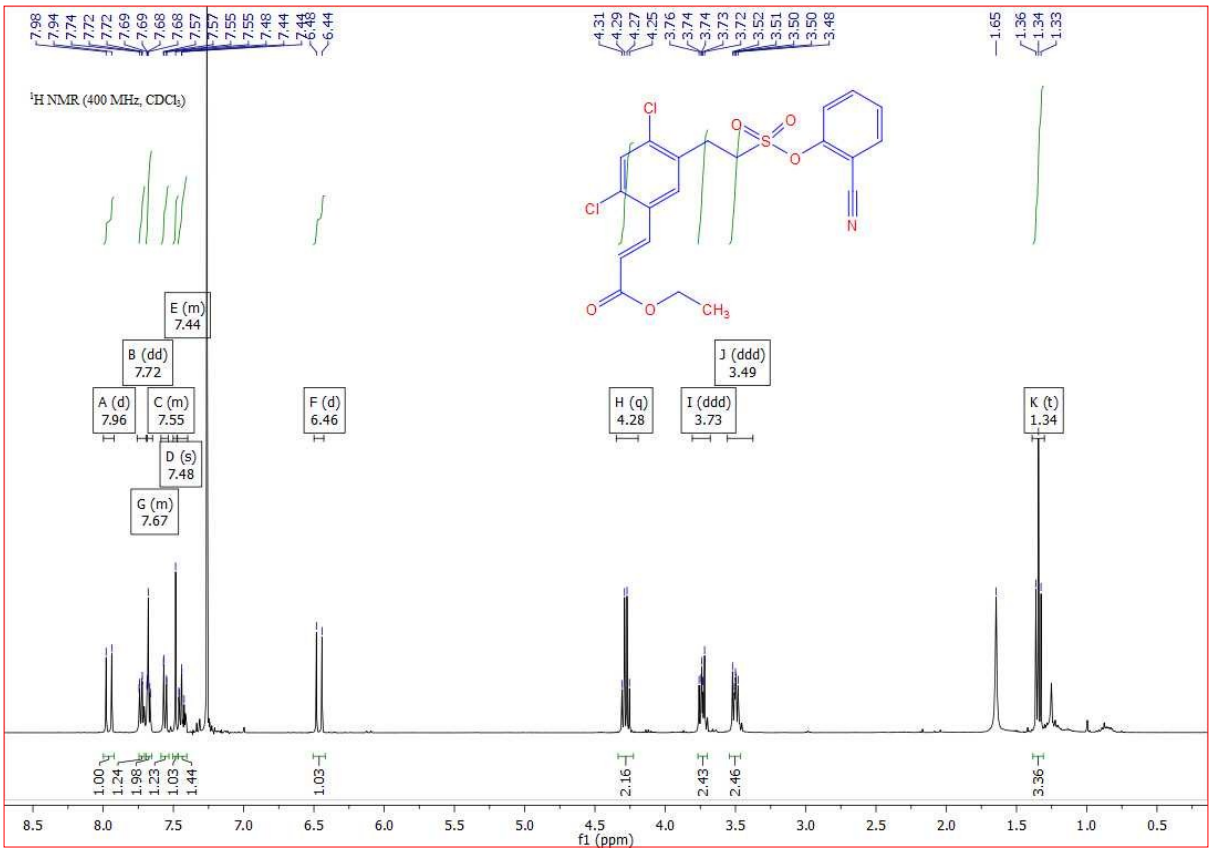


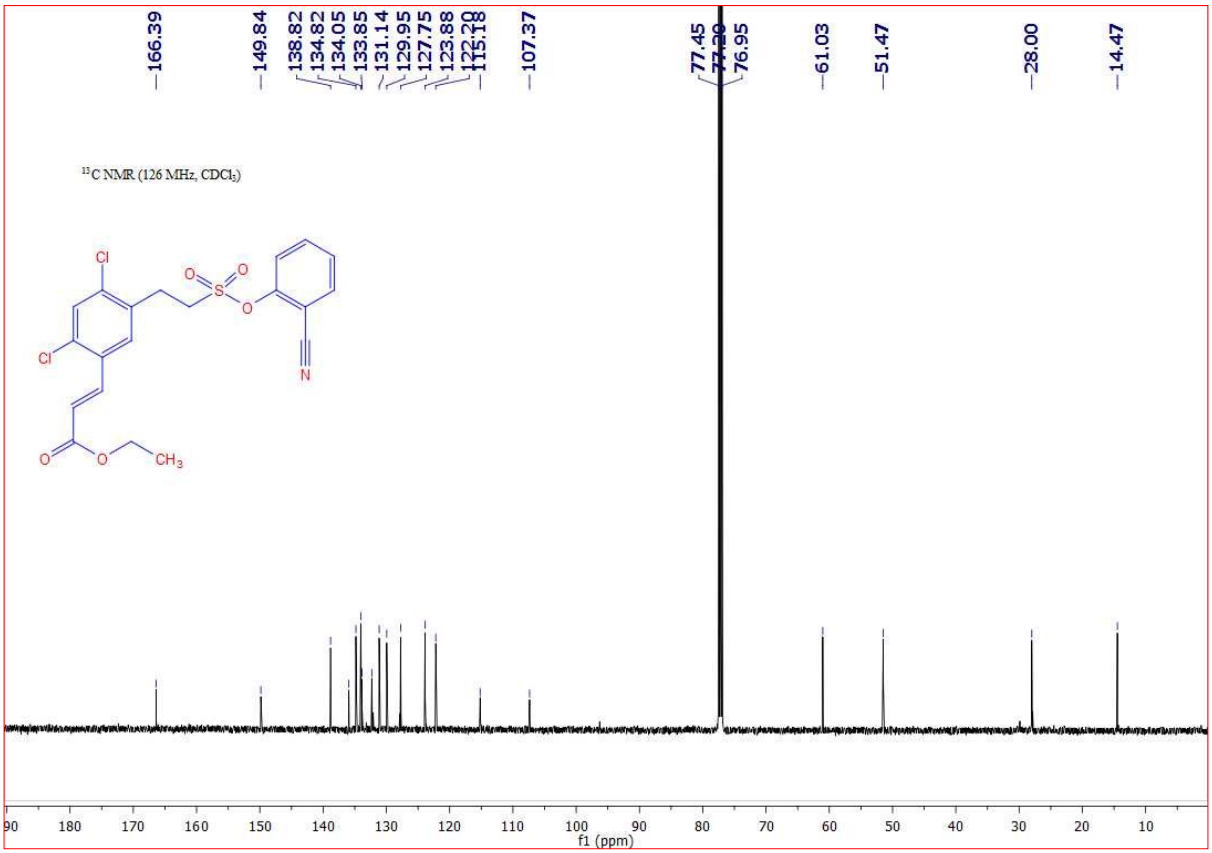
Entry 2l; Scheme 3



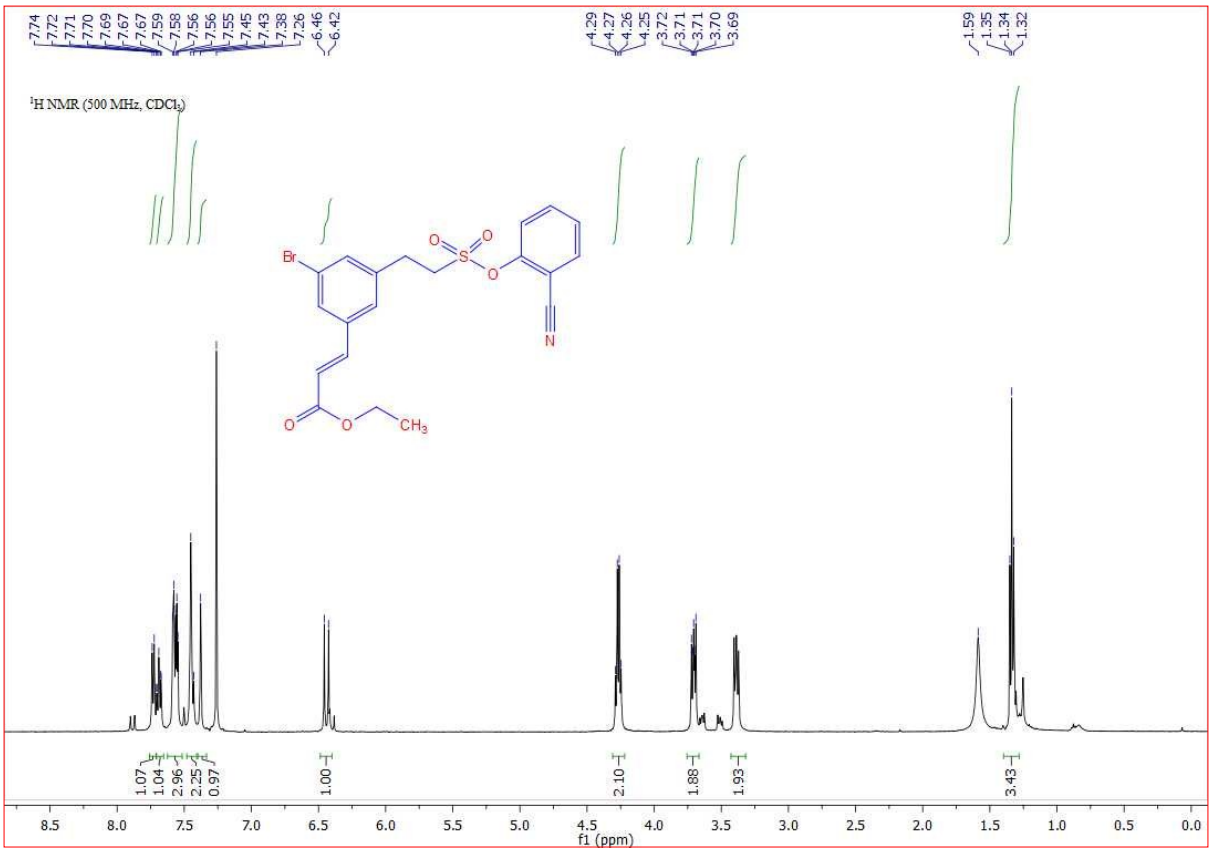


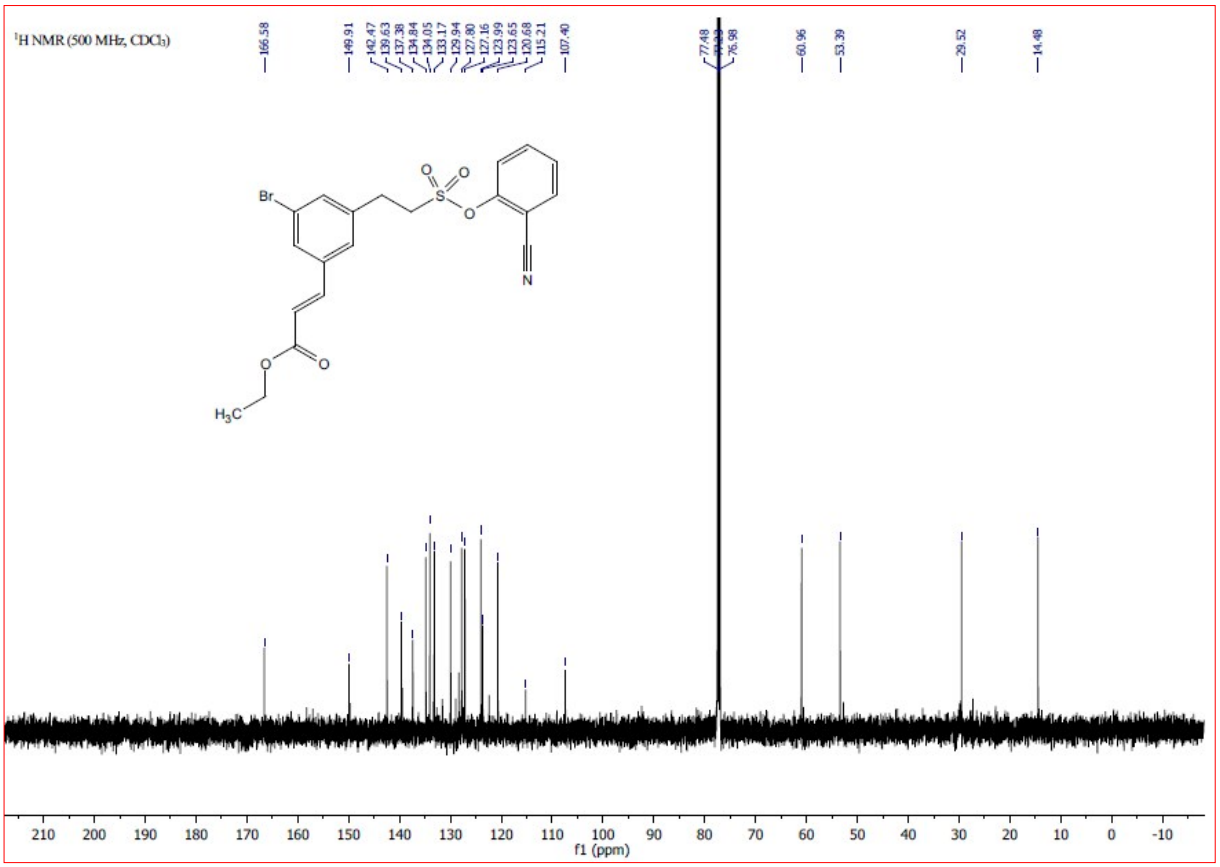
Entry 2m; Scheme 3



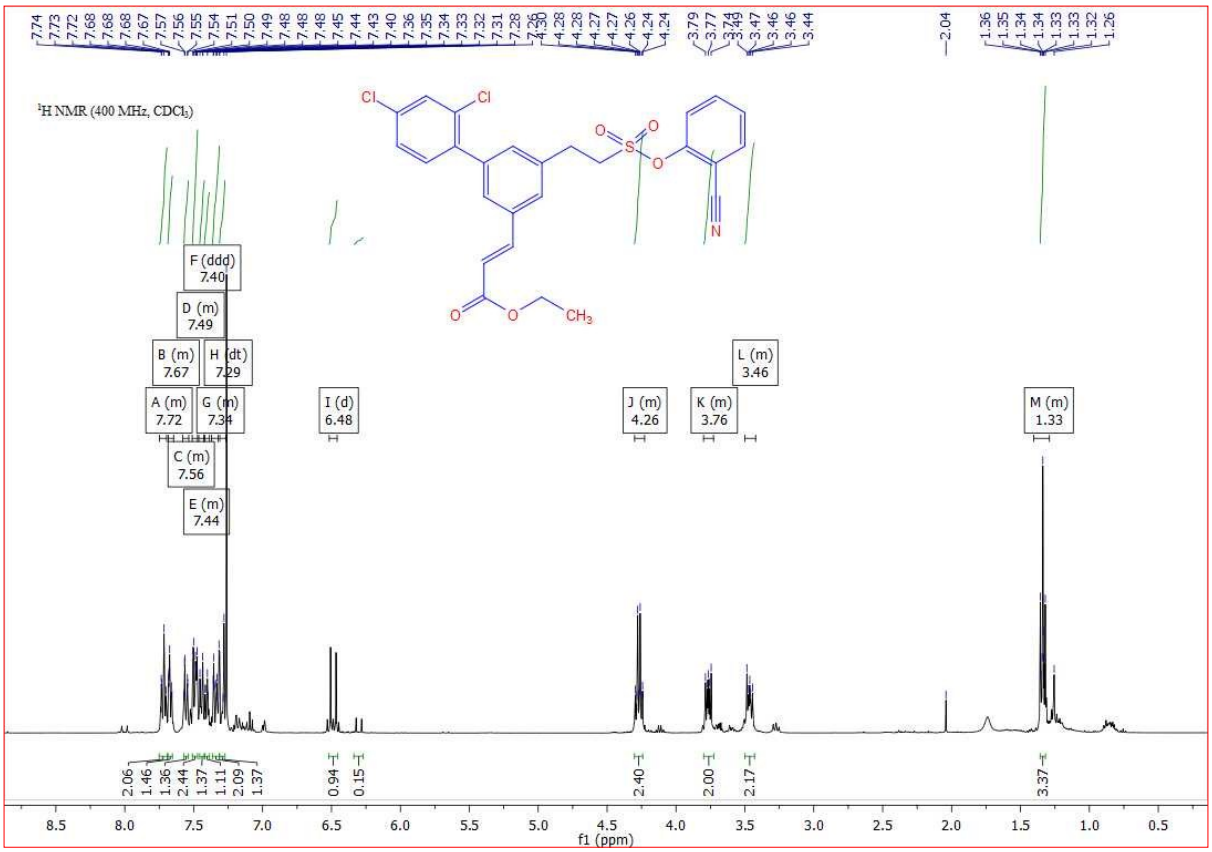


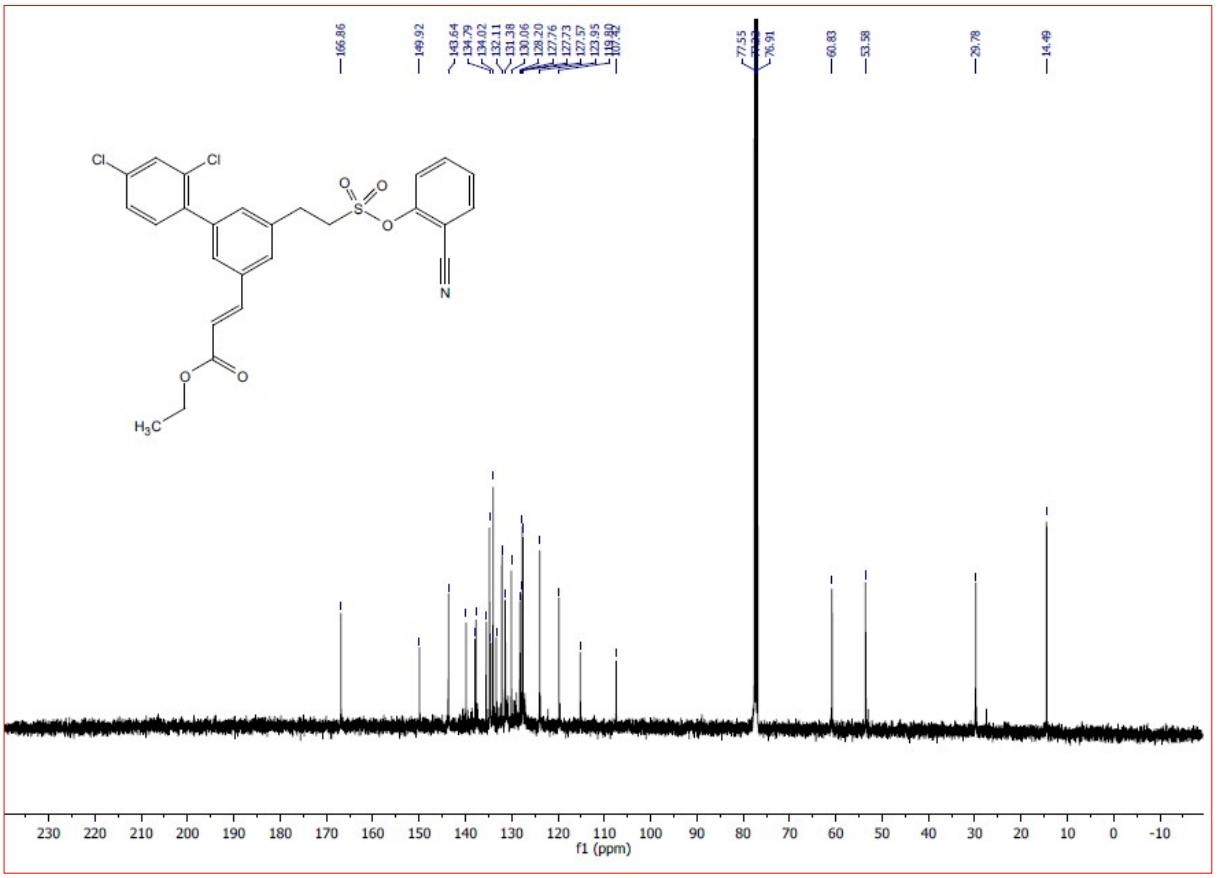
Entry 2n; Scheme 3



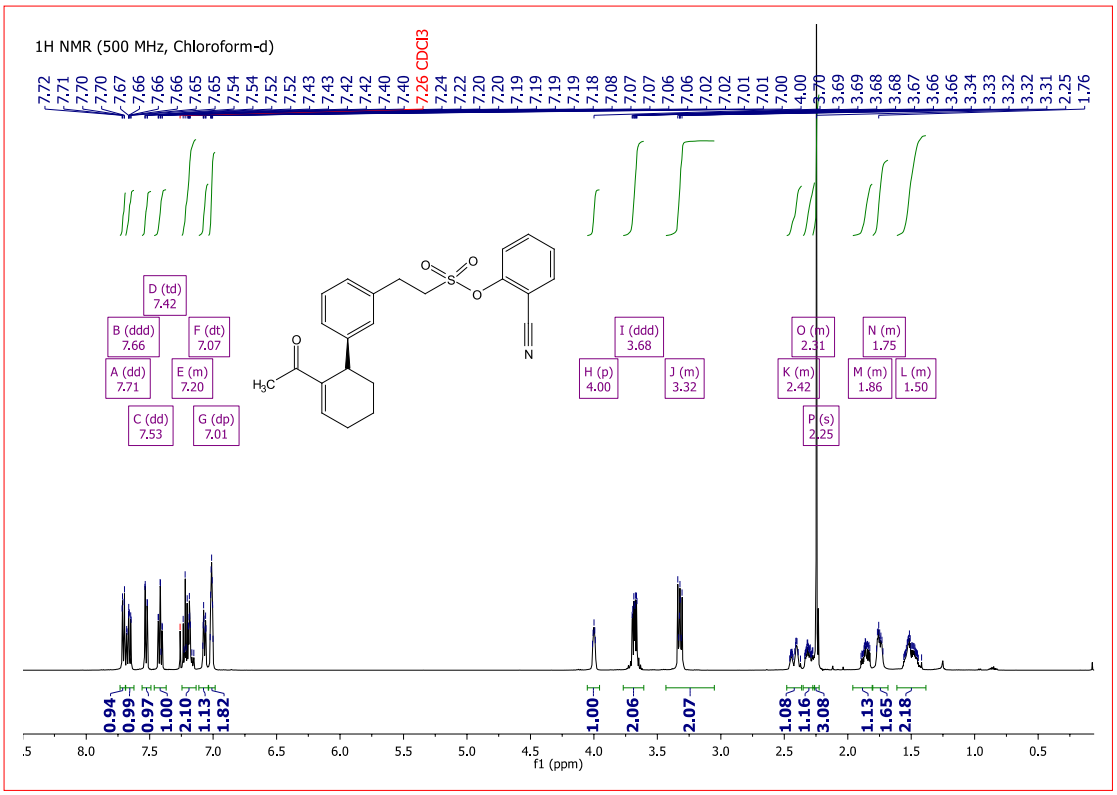


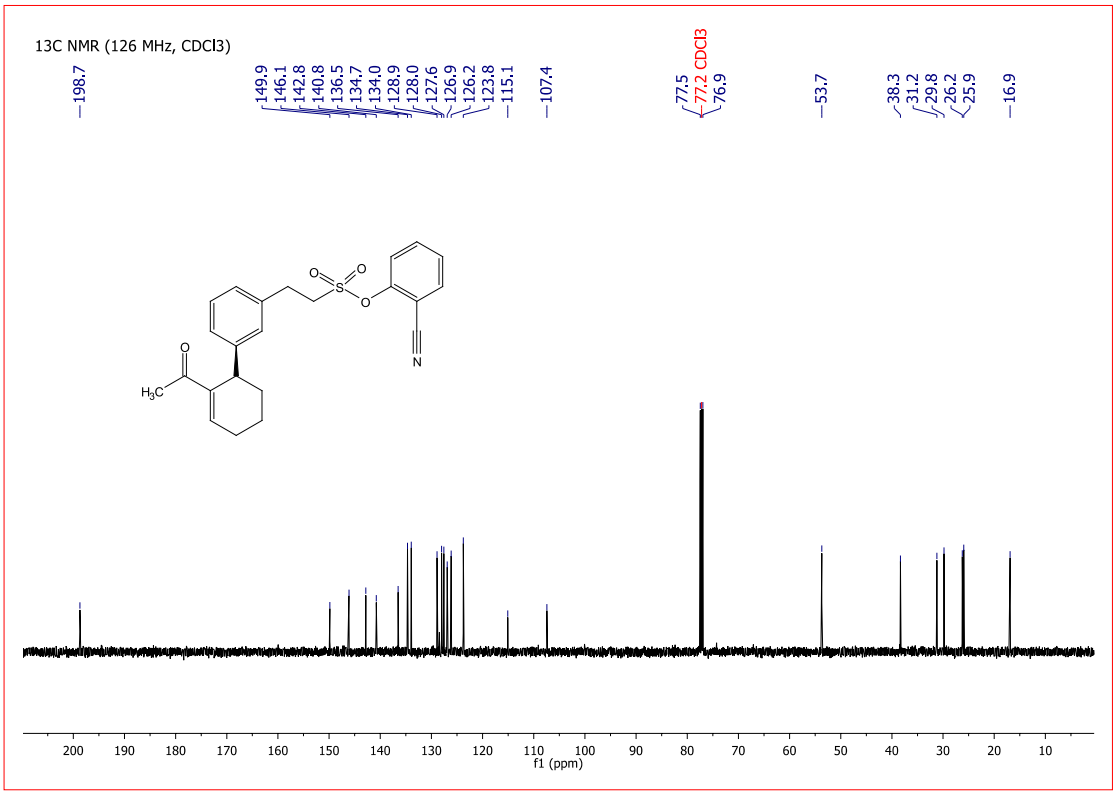
Entry 2o; Scheme 3



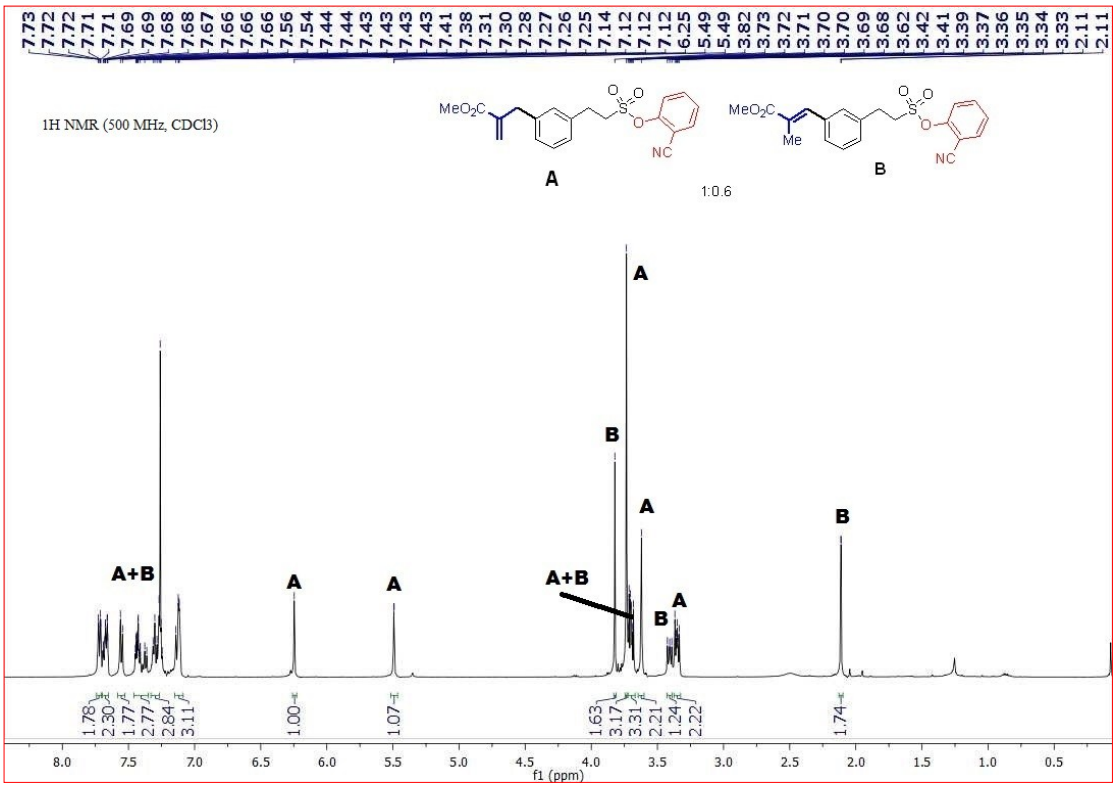


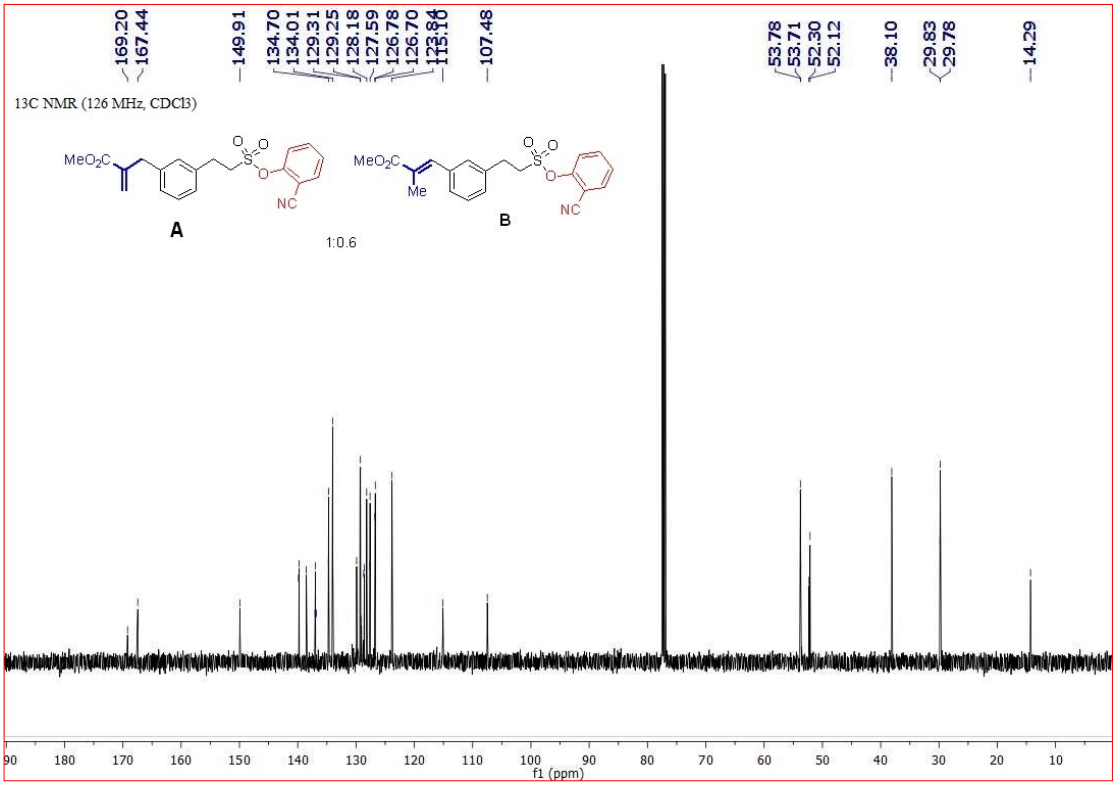
Entry 3a; Scheme 4



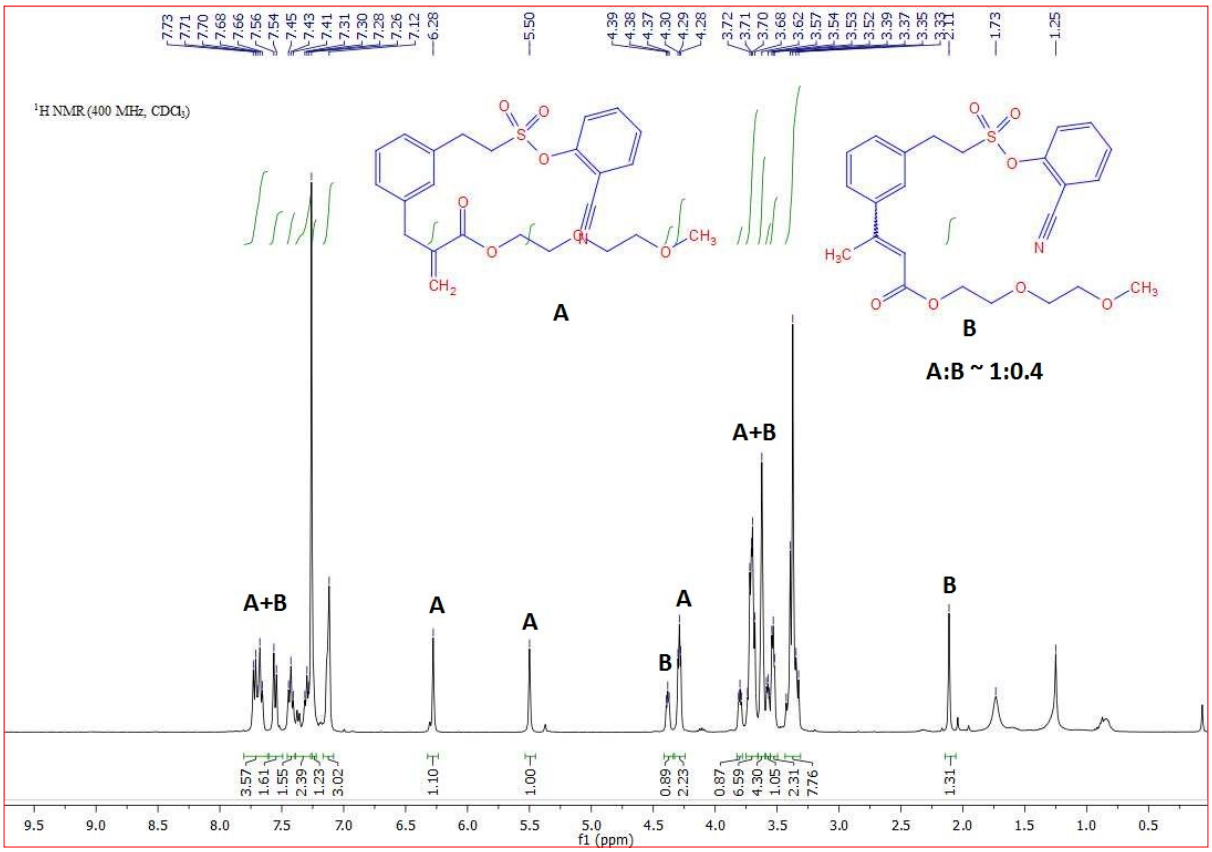


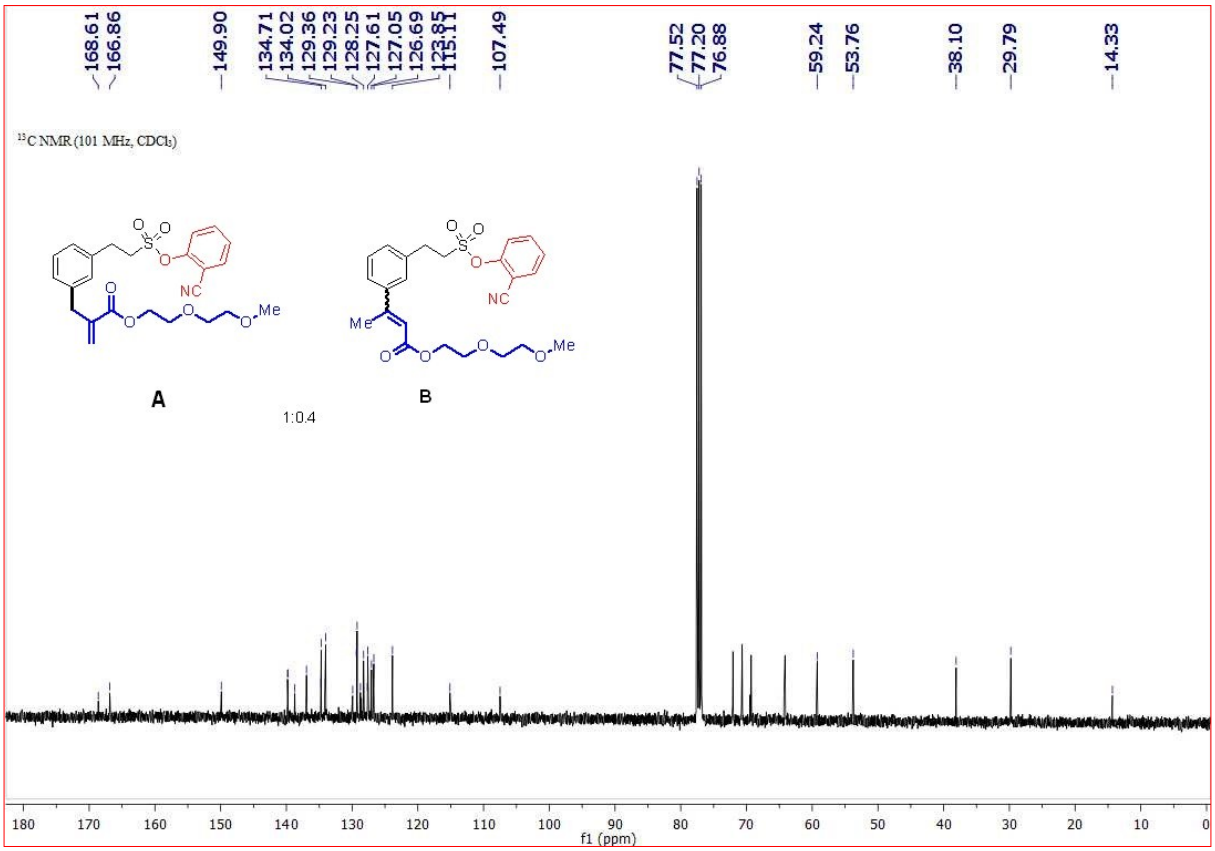
Entry 3b; Scheme 4



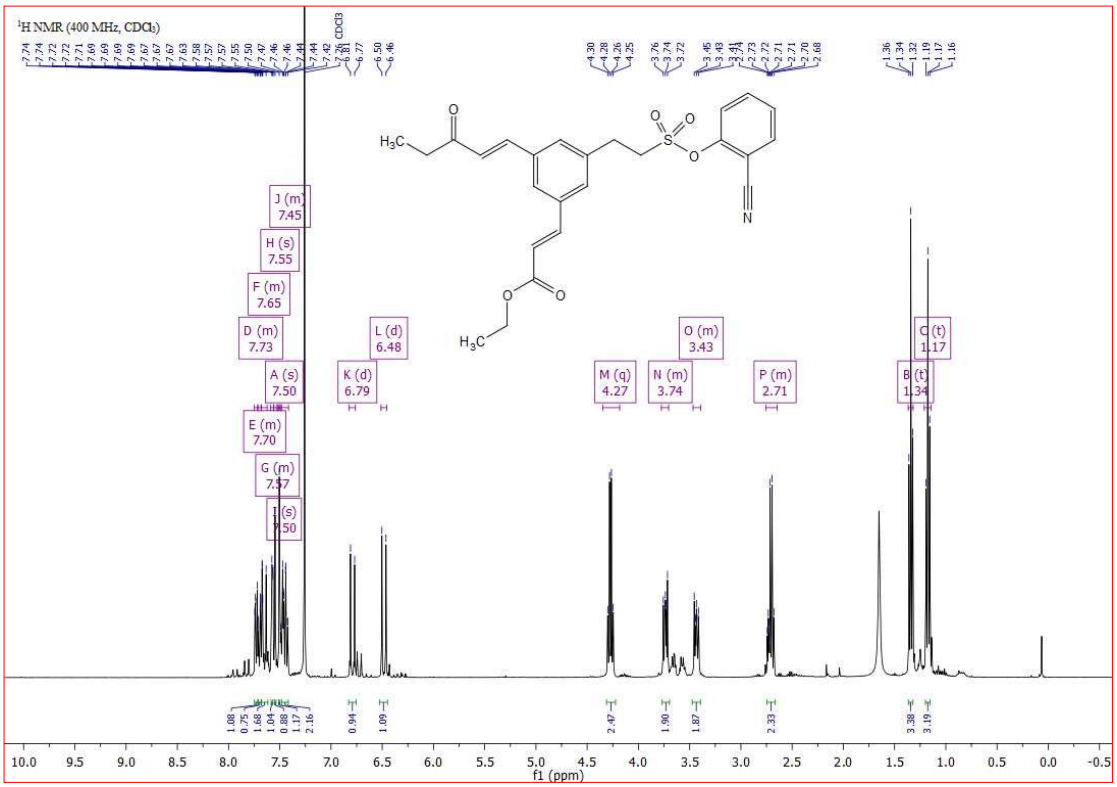


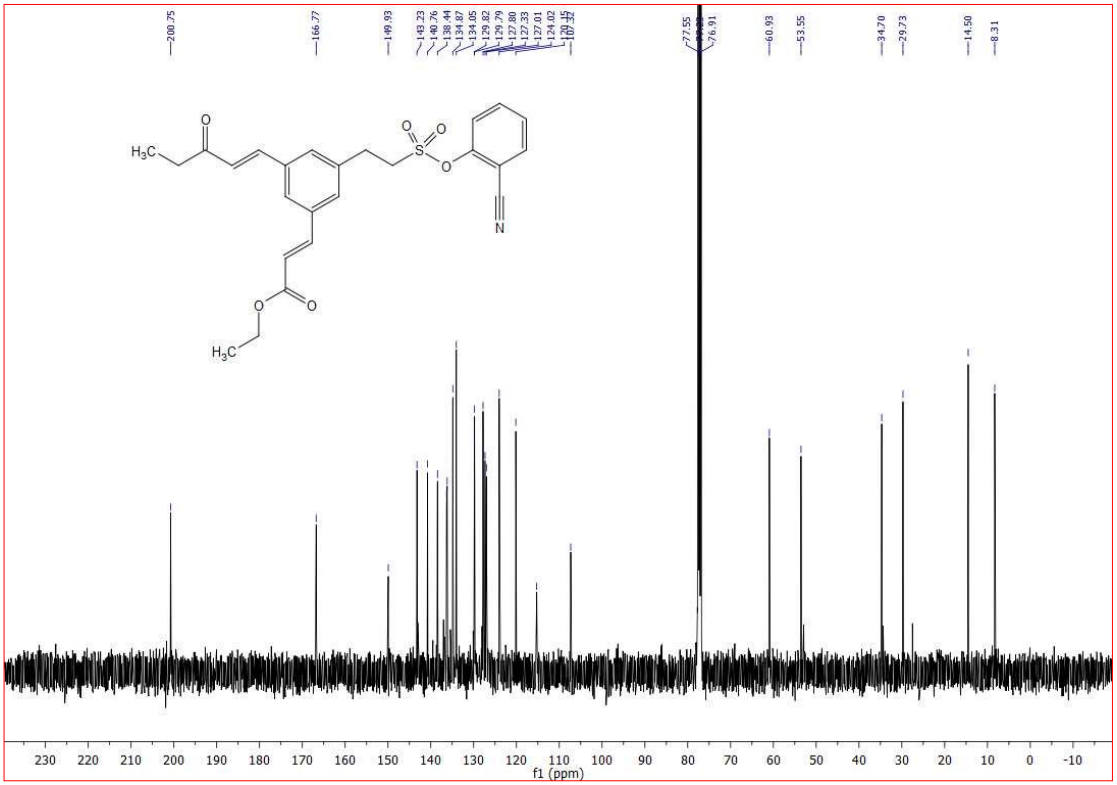
Entry 3b; Scheme 4



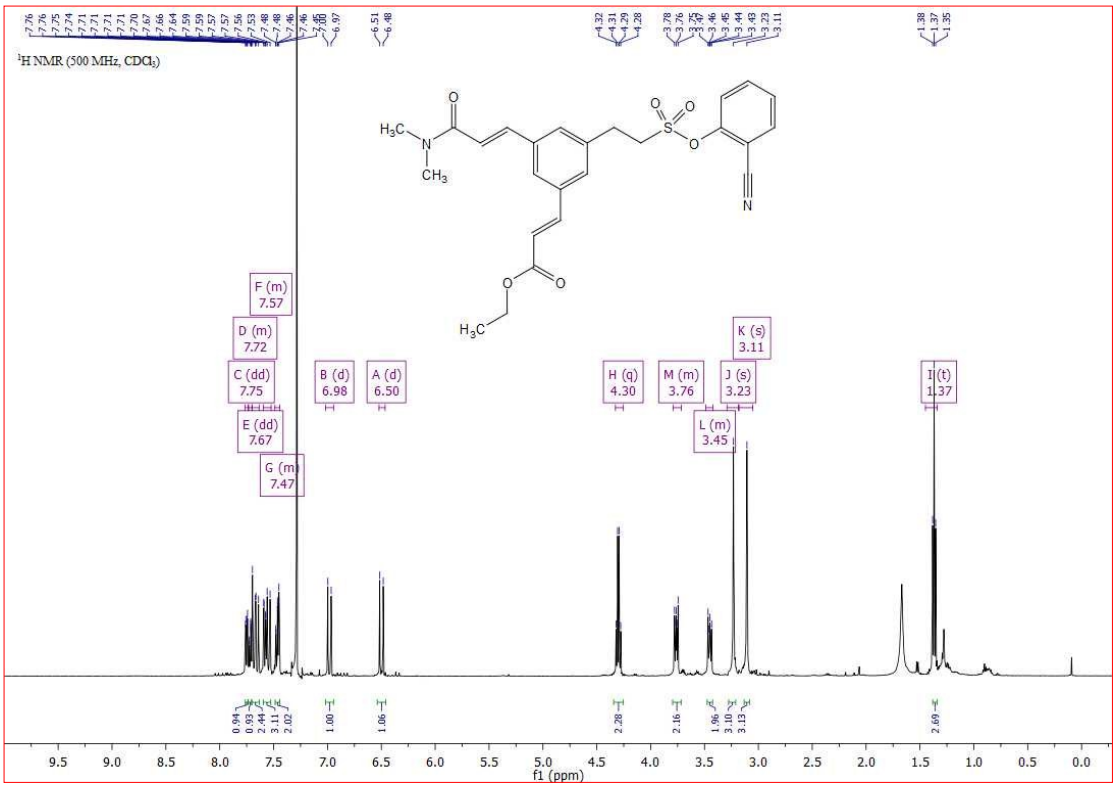


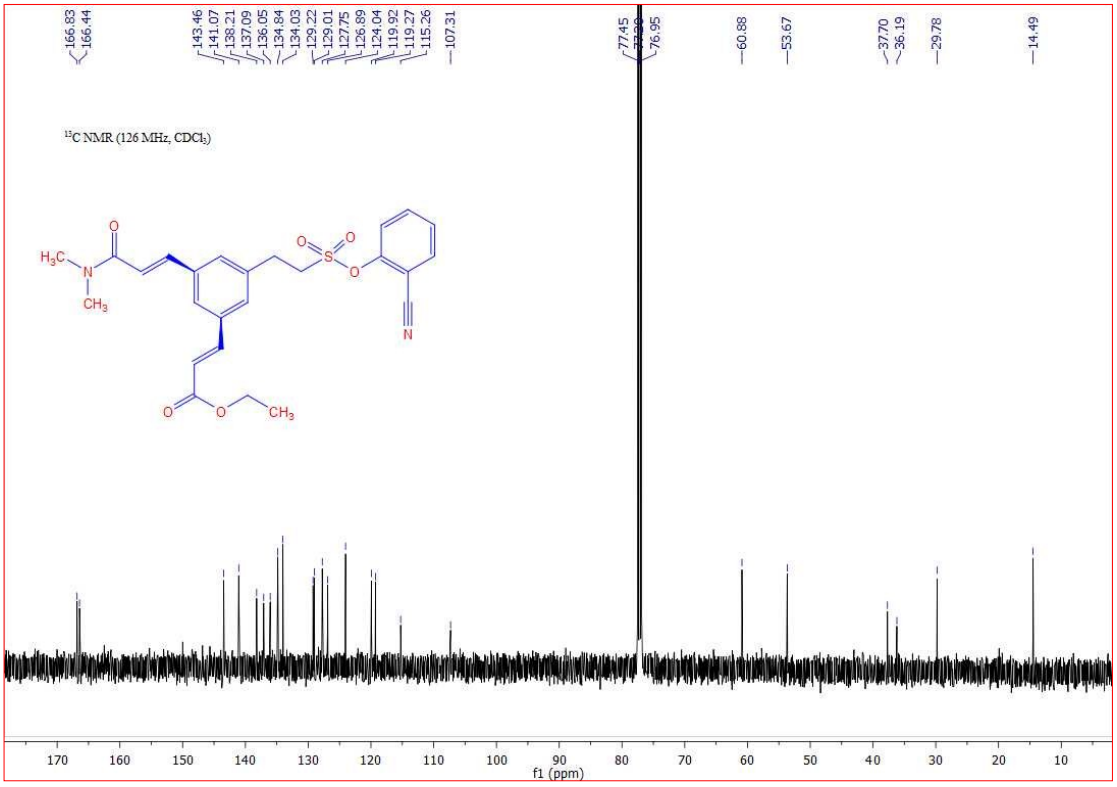
Entry 4a; Scheme 5



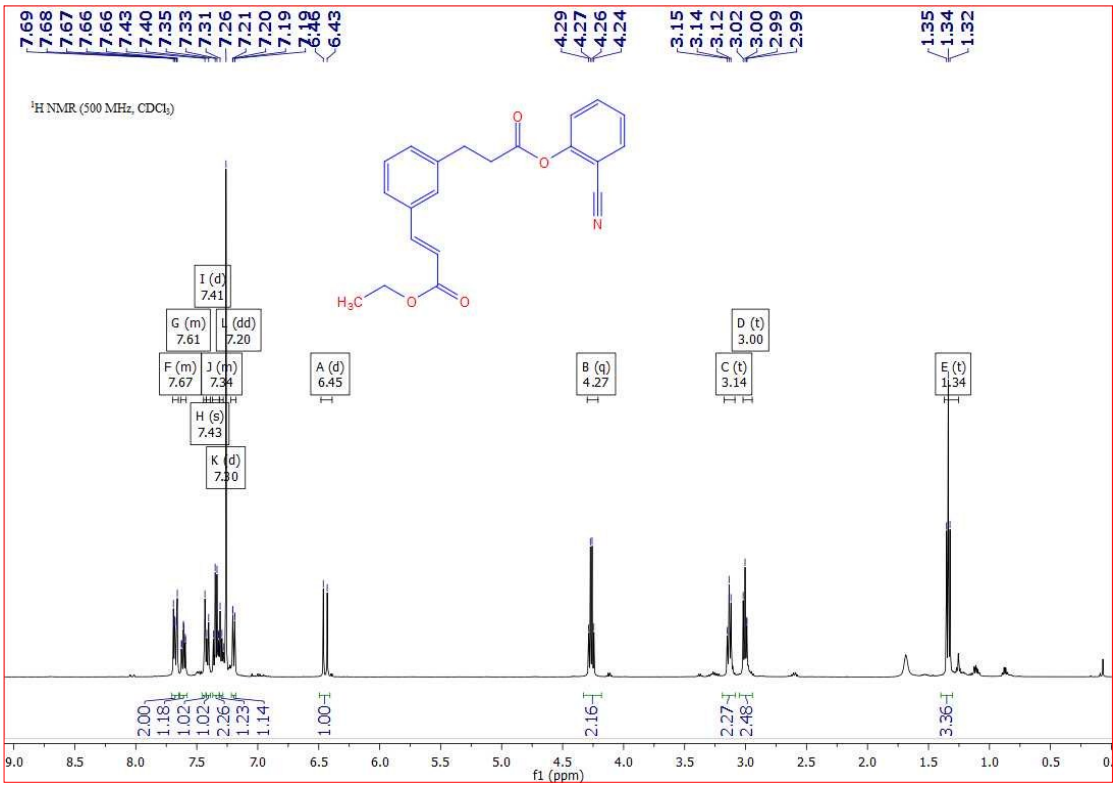


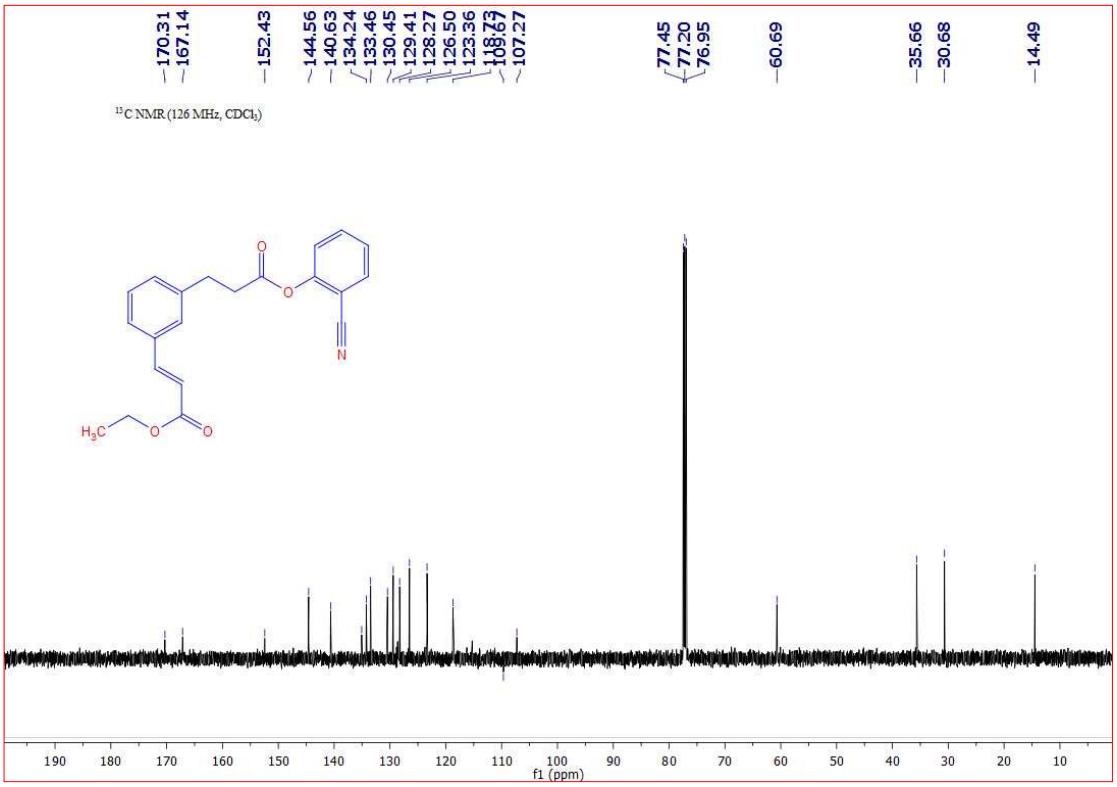
Entry 4b; Scheme 5


^{1}H NMR (500 MHz, $CDCl_3$)
F (m) 7.57
D (m) 7.72
C (dd) 7.75
E (dd) 7.67
G (m) 7.47
B (d) 6.98
A (d) 6.50
H (q) 4.30
M (m) 3.76
J (s) 3.23
L (m) 3.45
K (s) 3.11
I (t) 1.37
f1 (ppm)

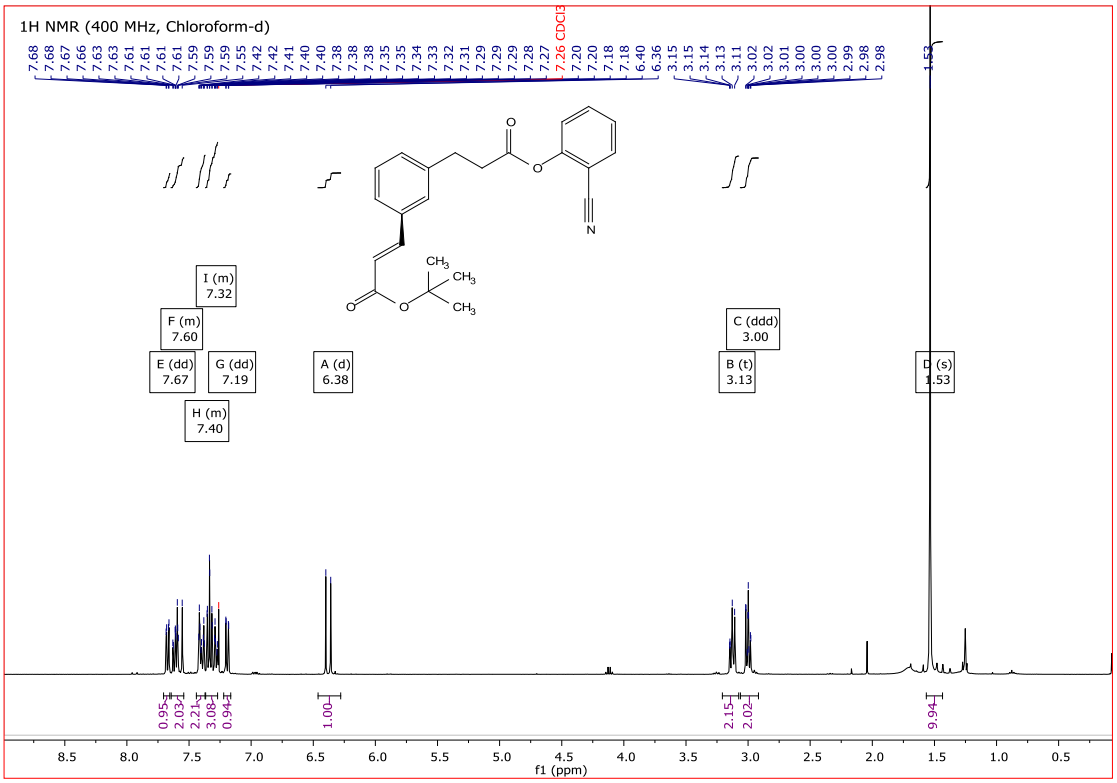

^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

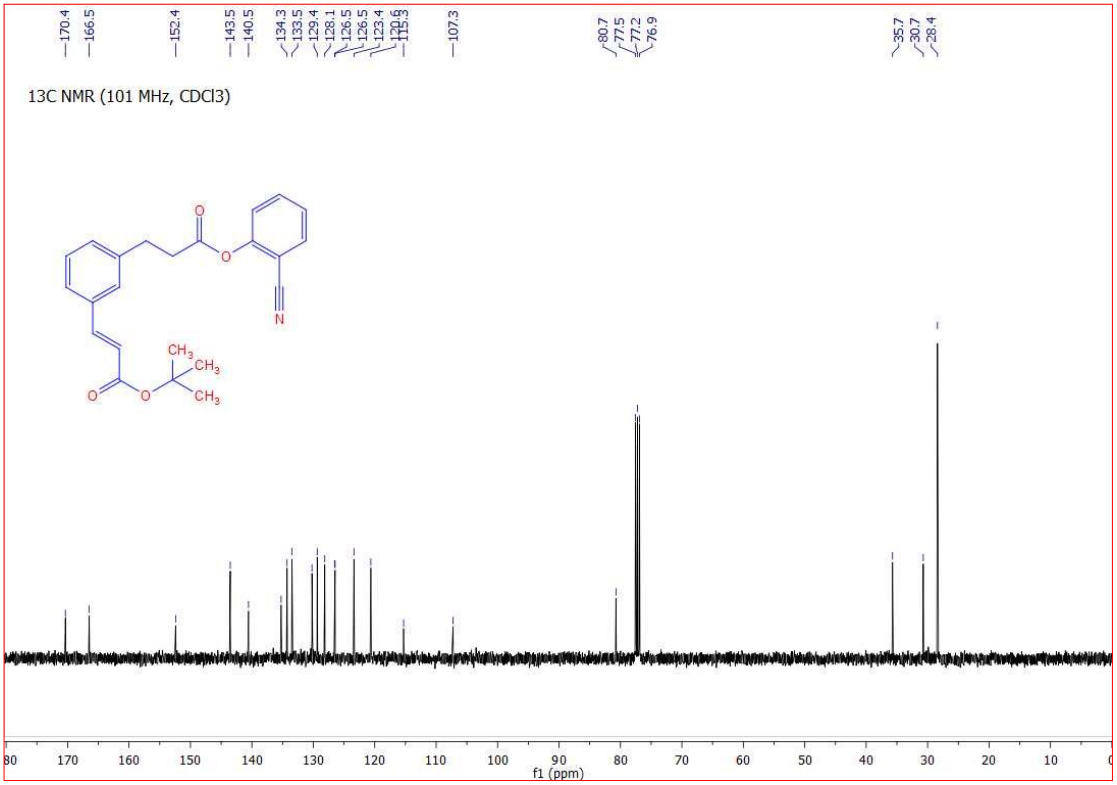
Entry 5a; Scheme 6



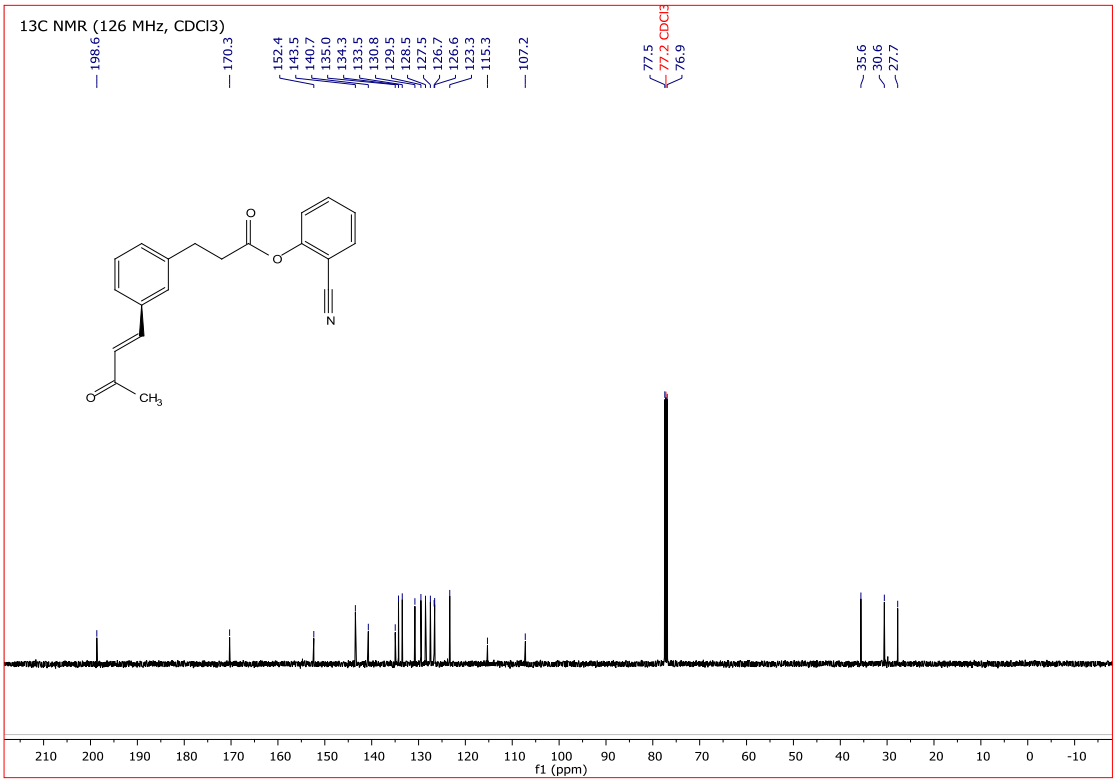


Entry 5b; Scheme 6

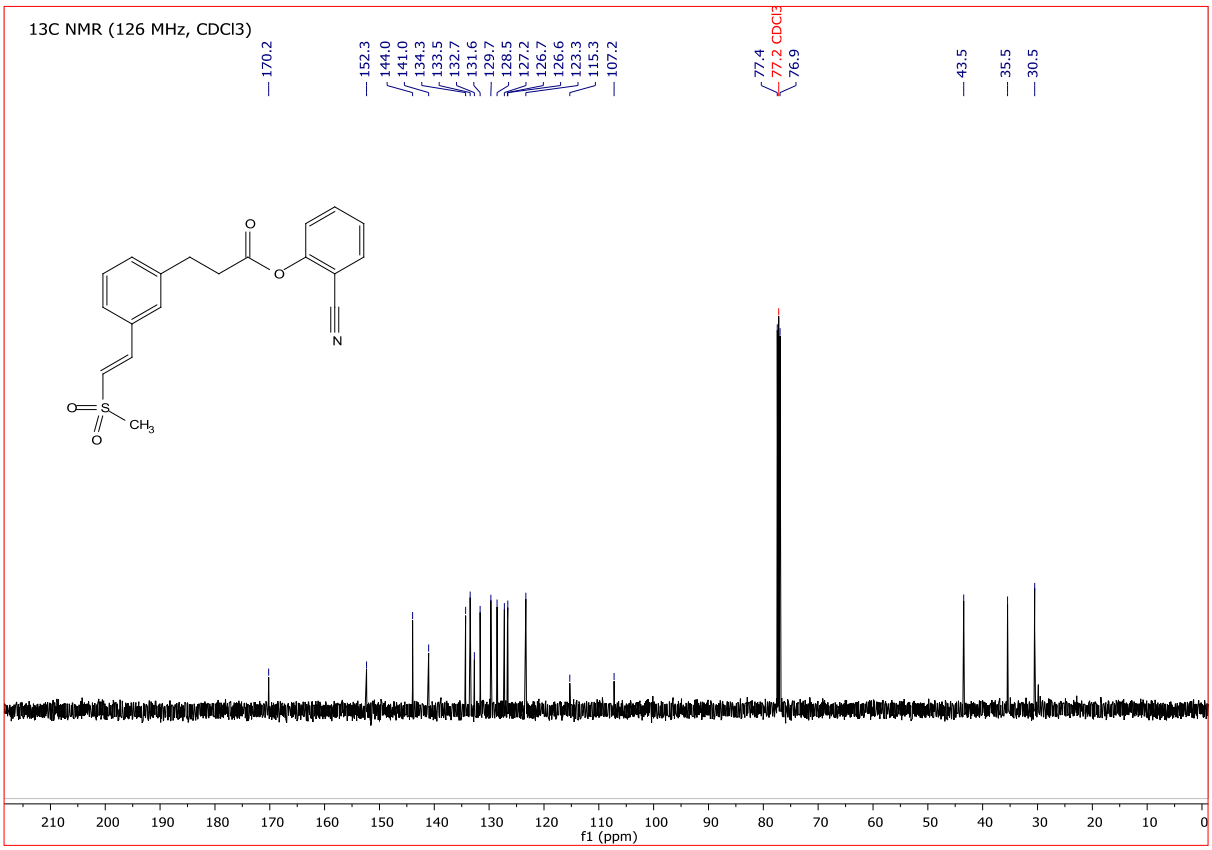




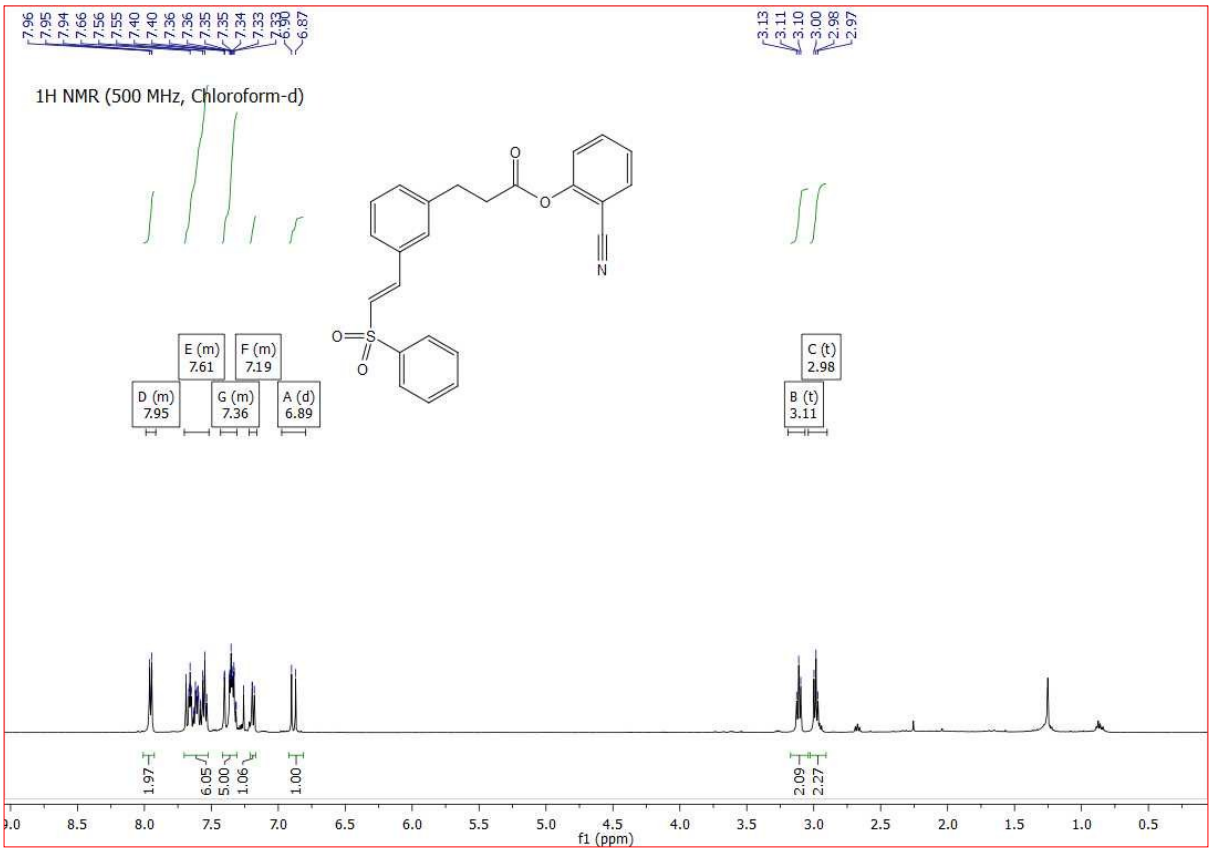
Entry 5c; Scheme 6

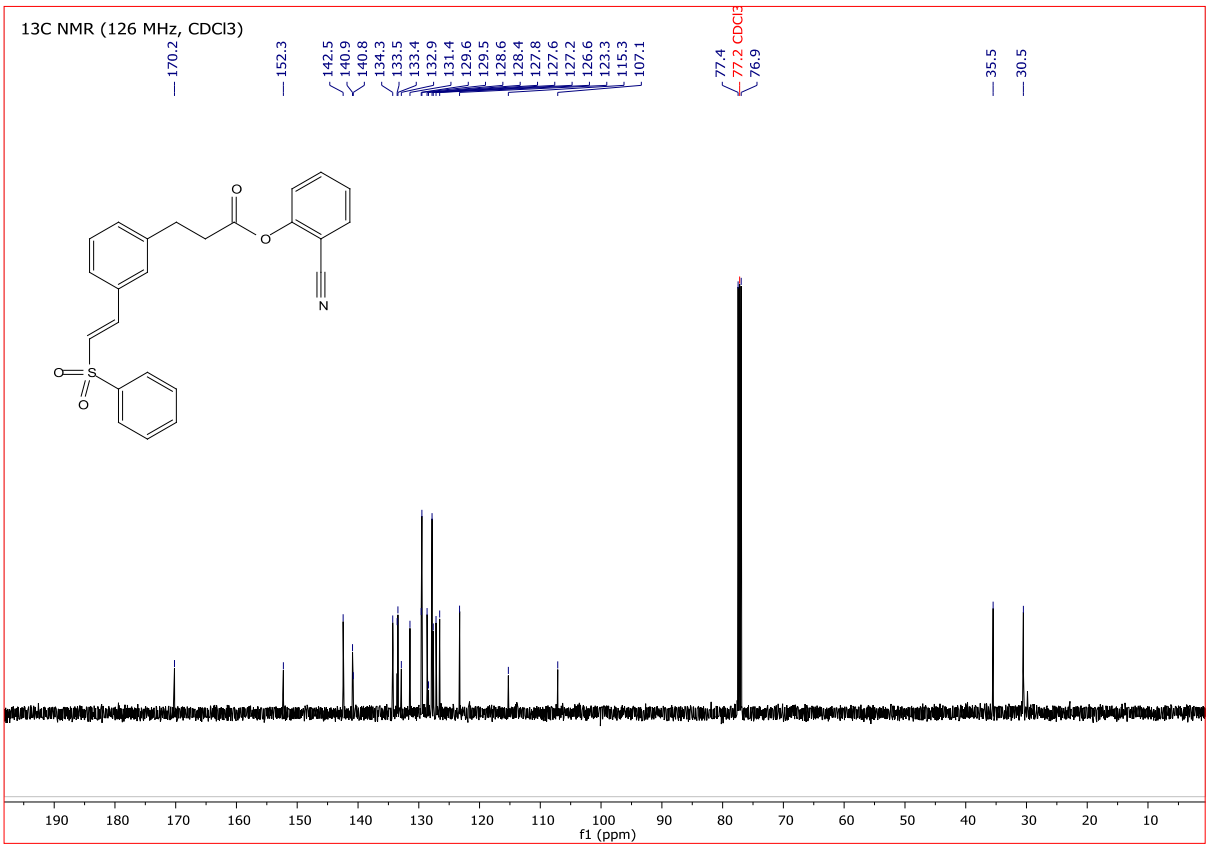


Entry 5d; Scheme 6

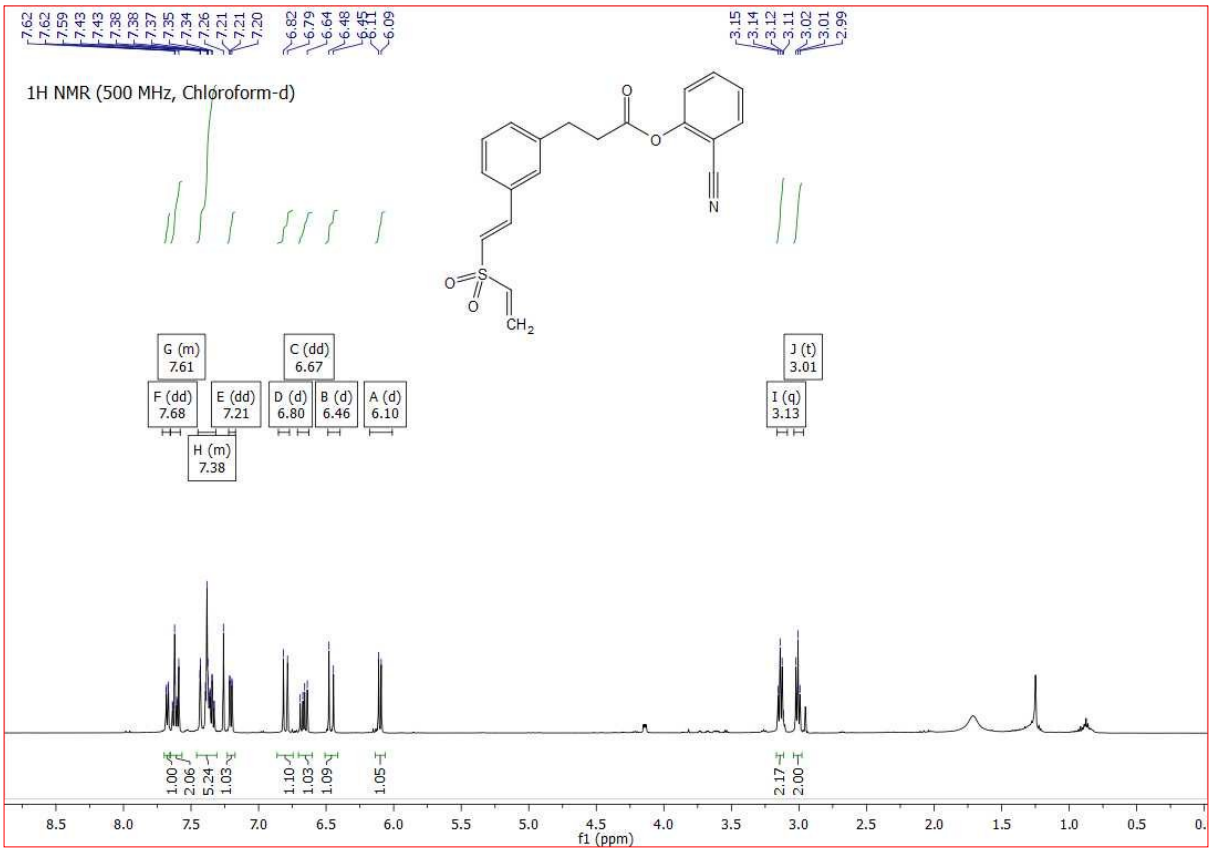


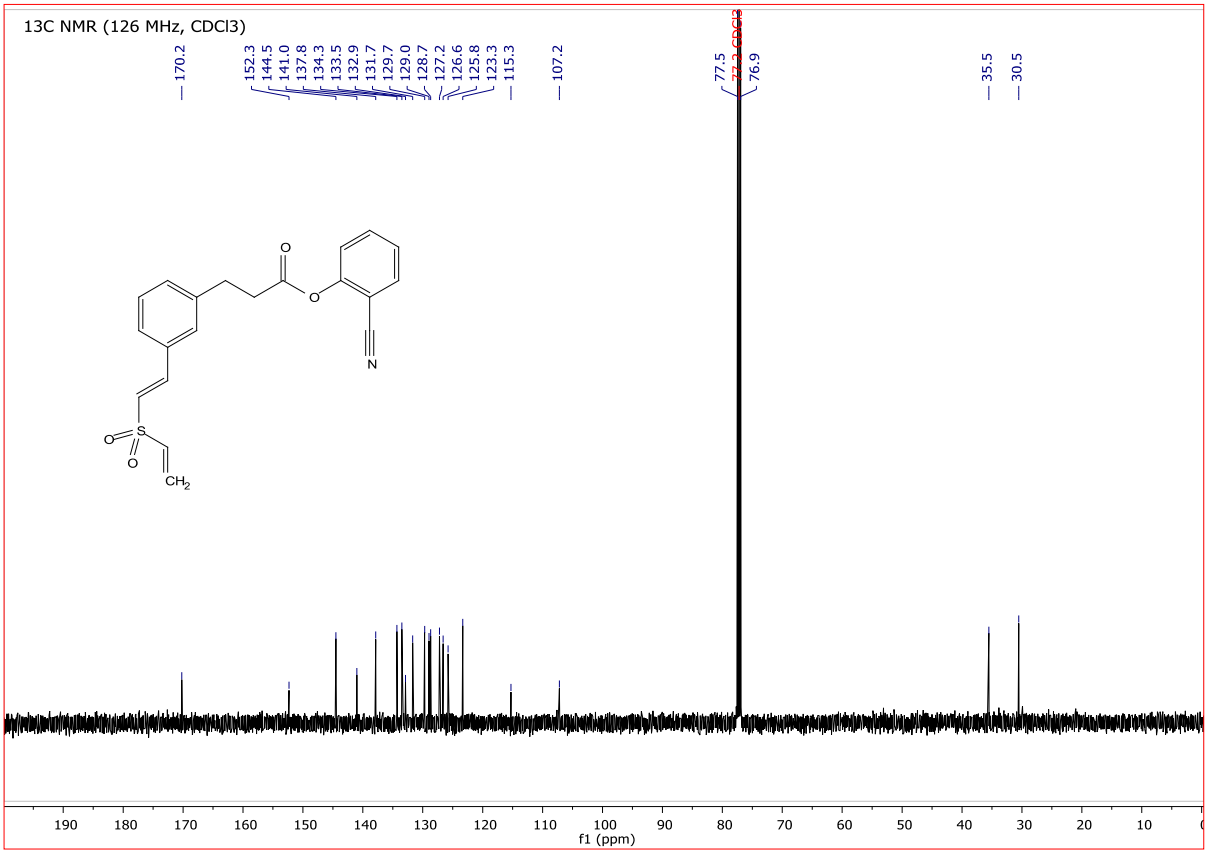
Entry 5e; Scheme 6



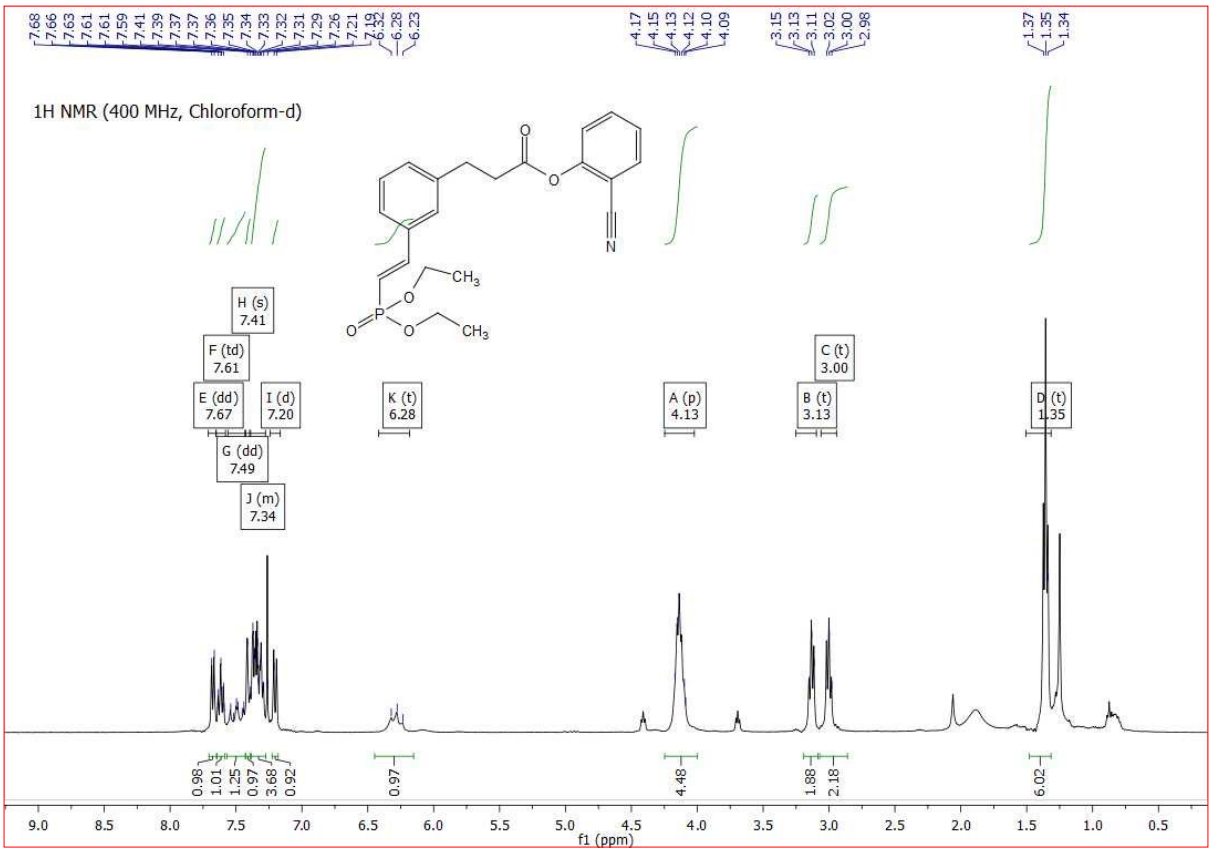


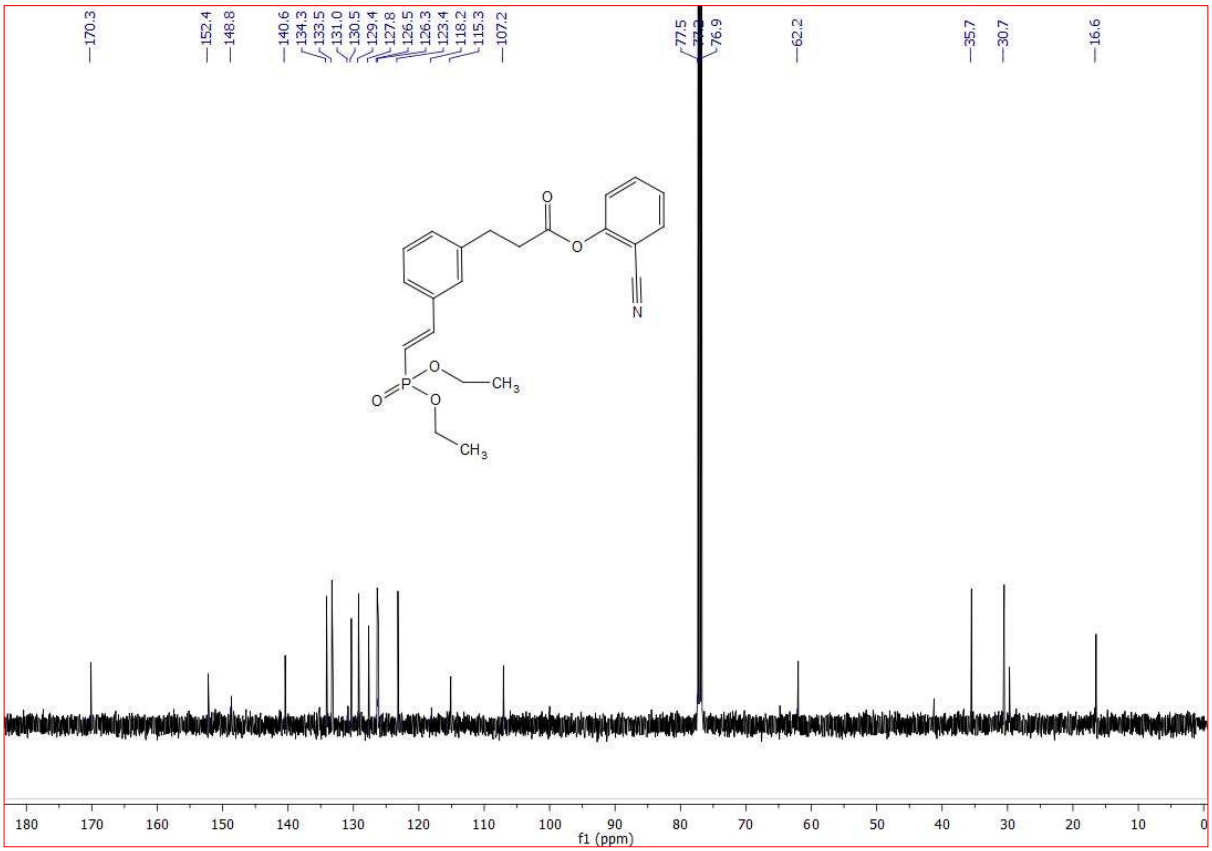
Entry 5f; Scheme 6



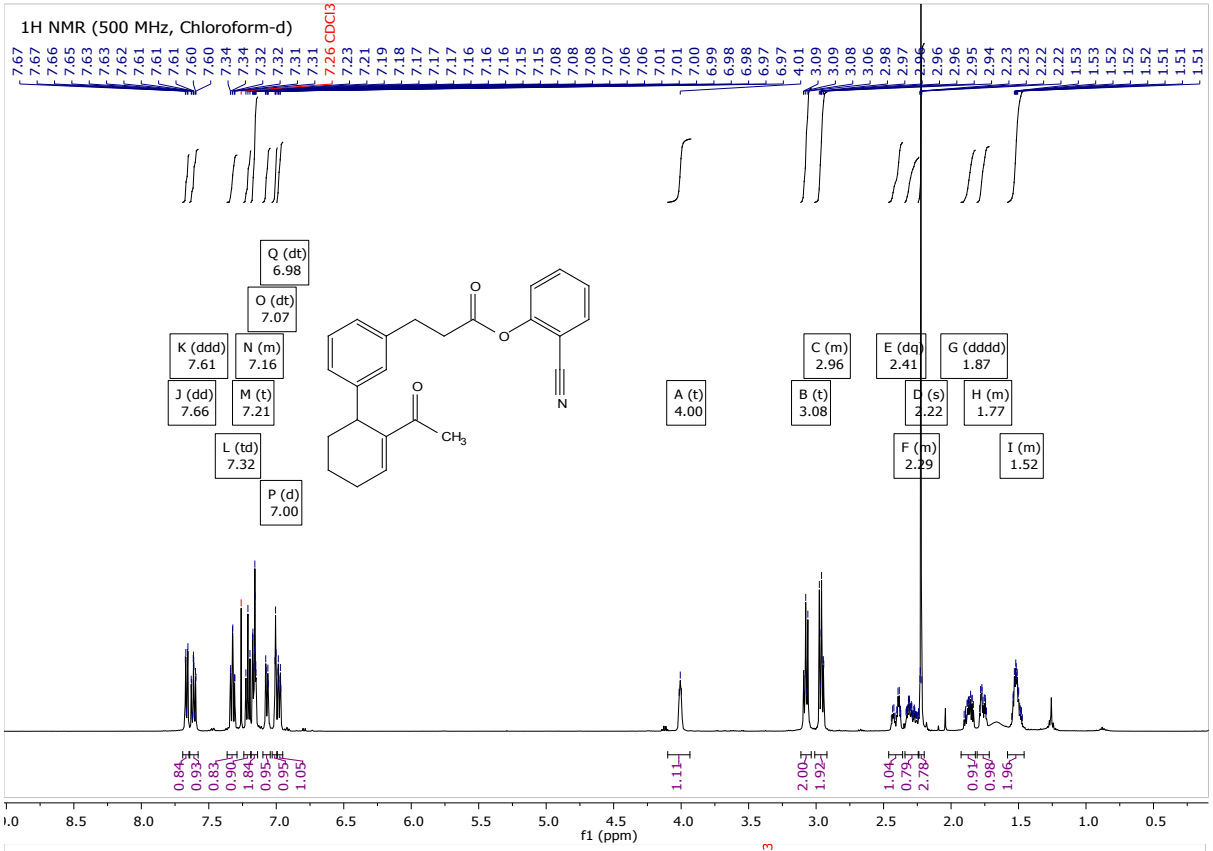


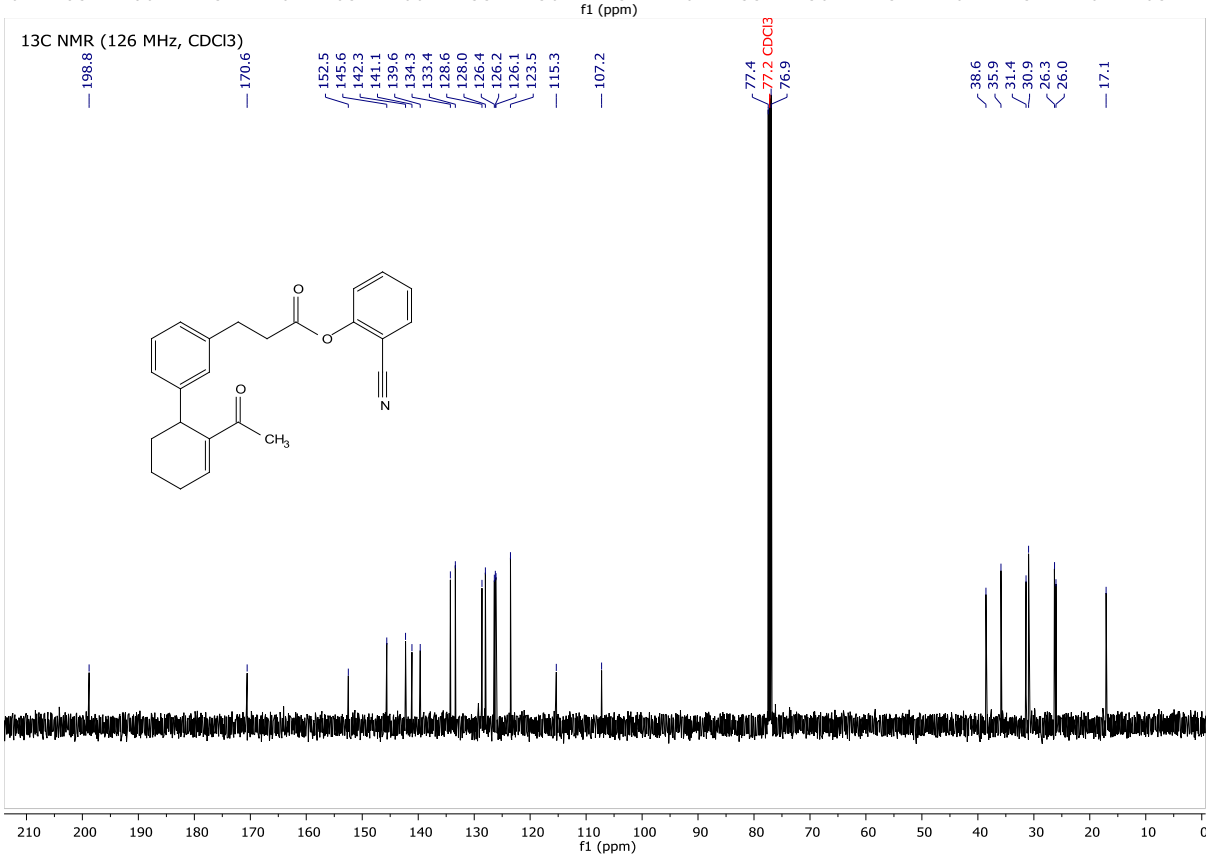
Entry 5g; Scheme 6


1H NMR (400 MHz, Chloroform-d)
H (s) 7.41
F (td) 7.61
E (dd) 7.67
I (d) 7.20
G (dd) 7.49
J (m) 7.34
K (t) 6.28
A (p) 4.13
C (t) 3.00
B (t) 3.13
D (t) 1.35
f1 (ppm)

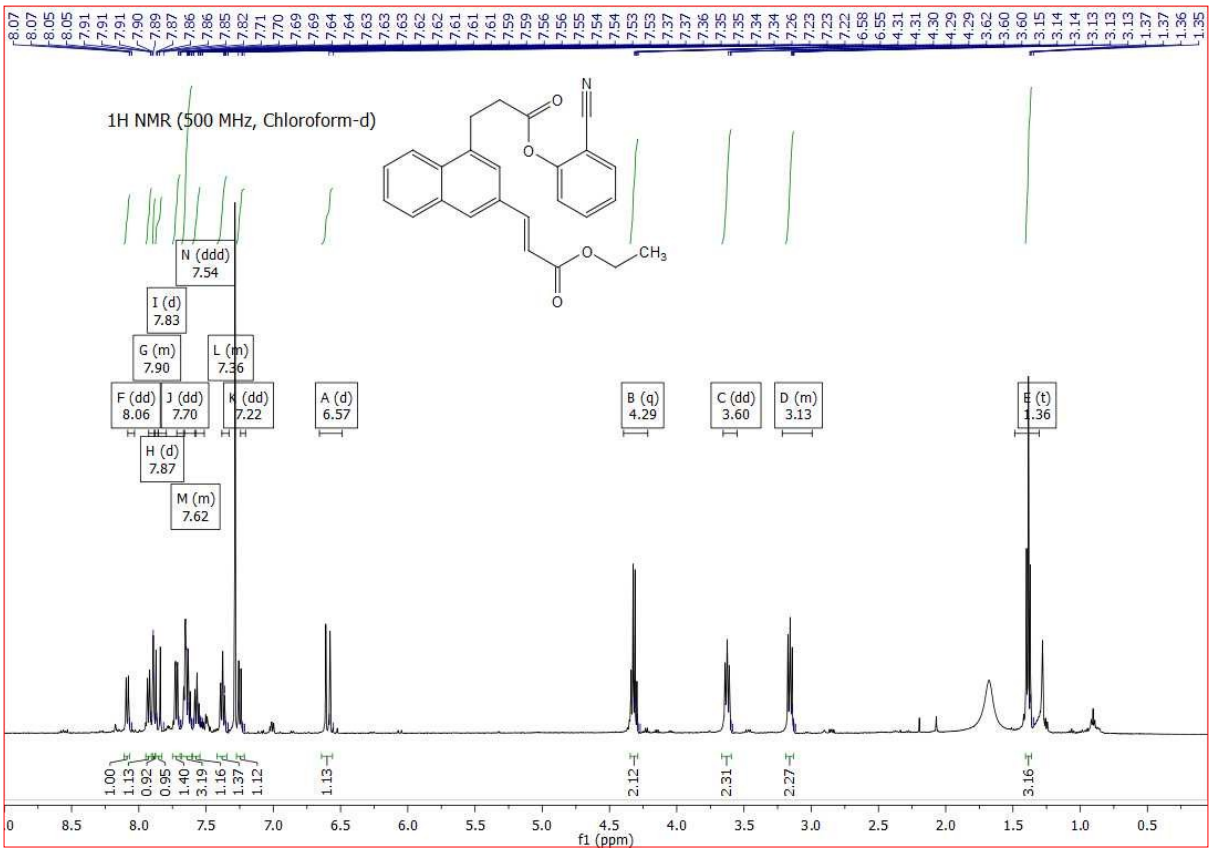

f1 (ppm)

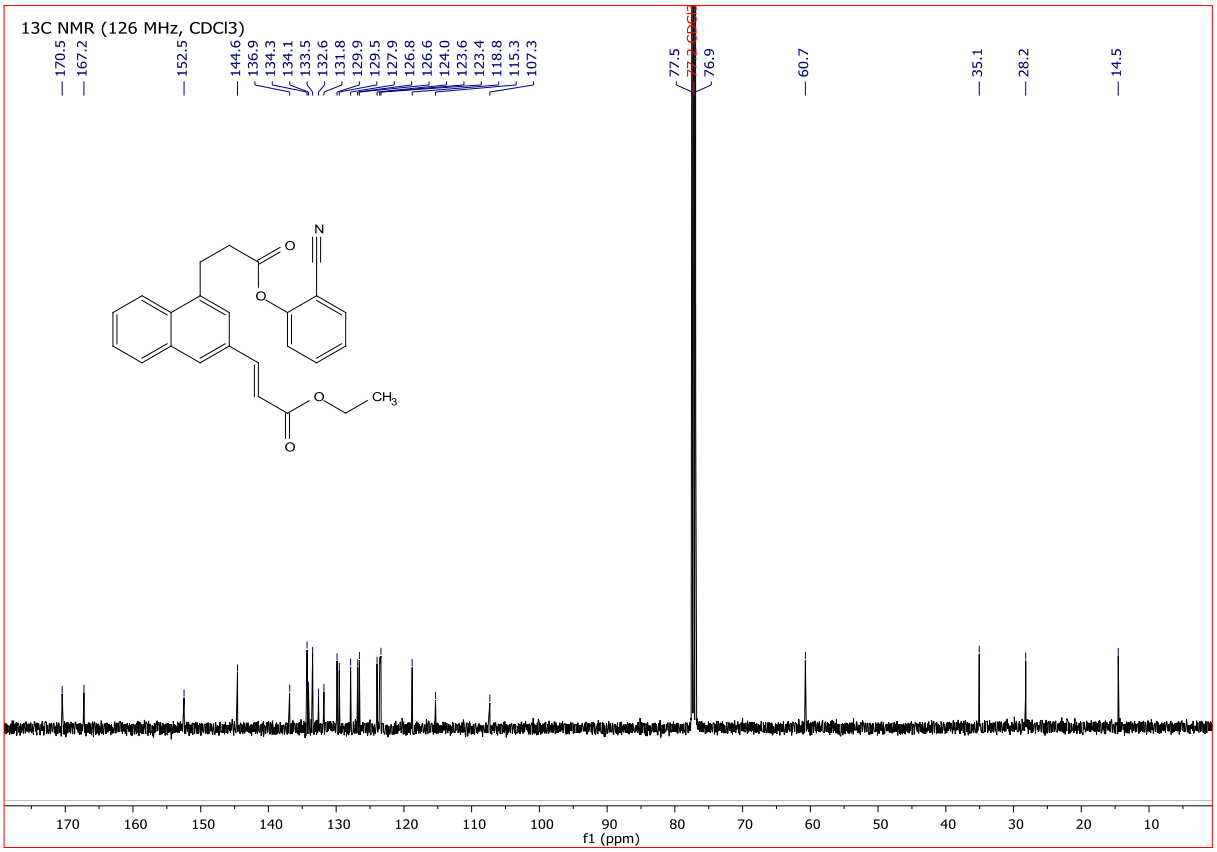
Entry 5h; Scheme 6



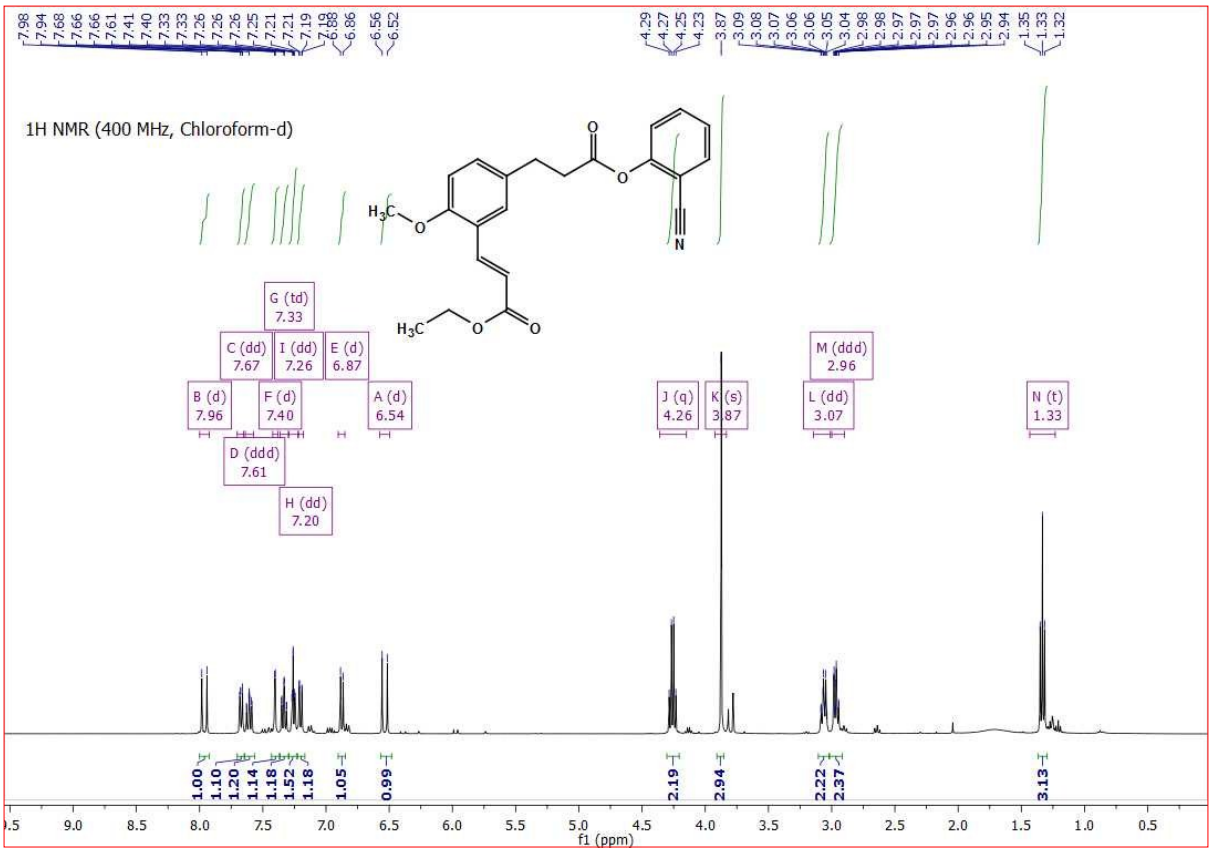


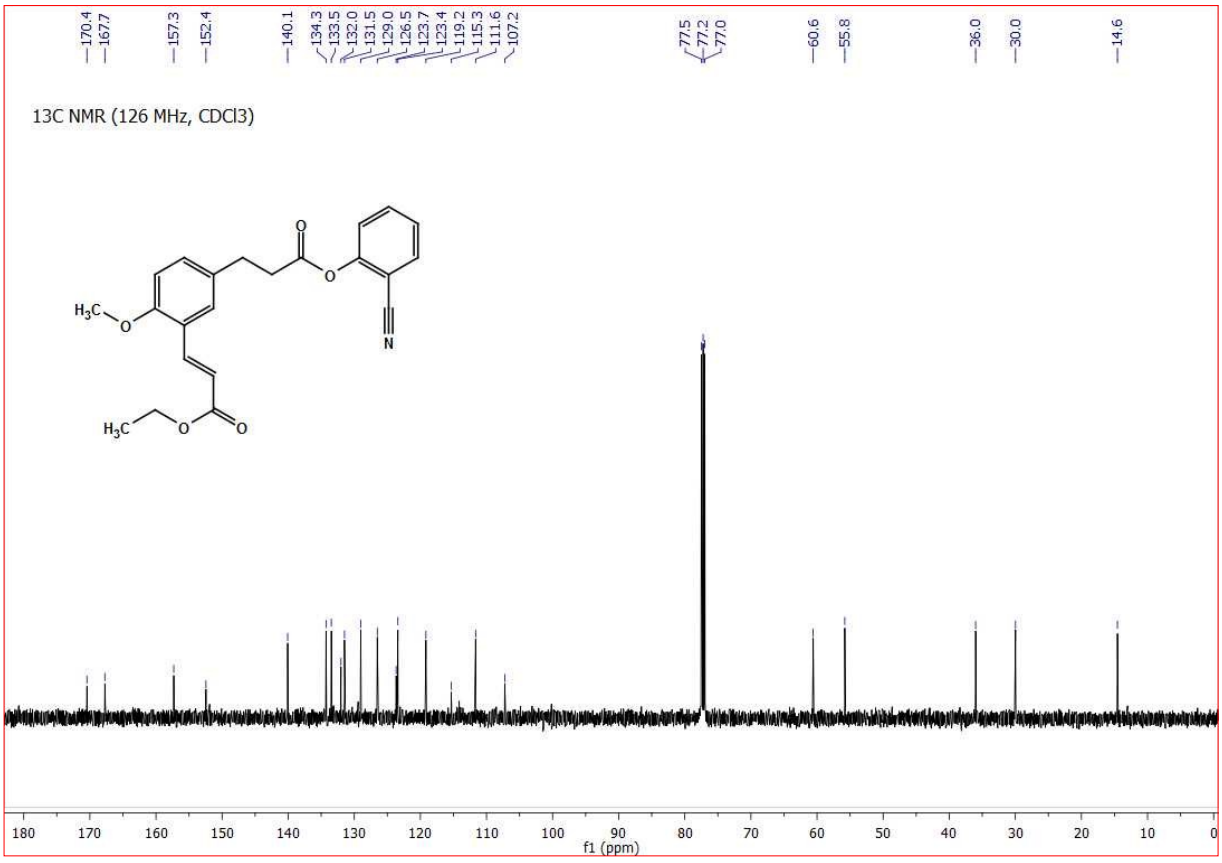
Entry 5i; Scheme 6



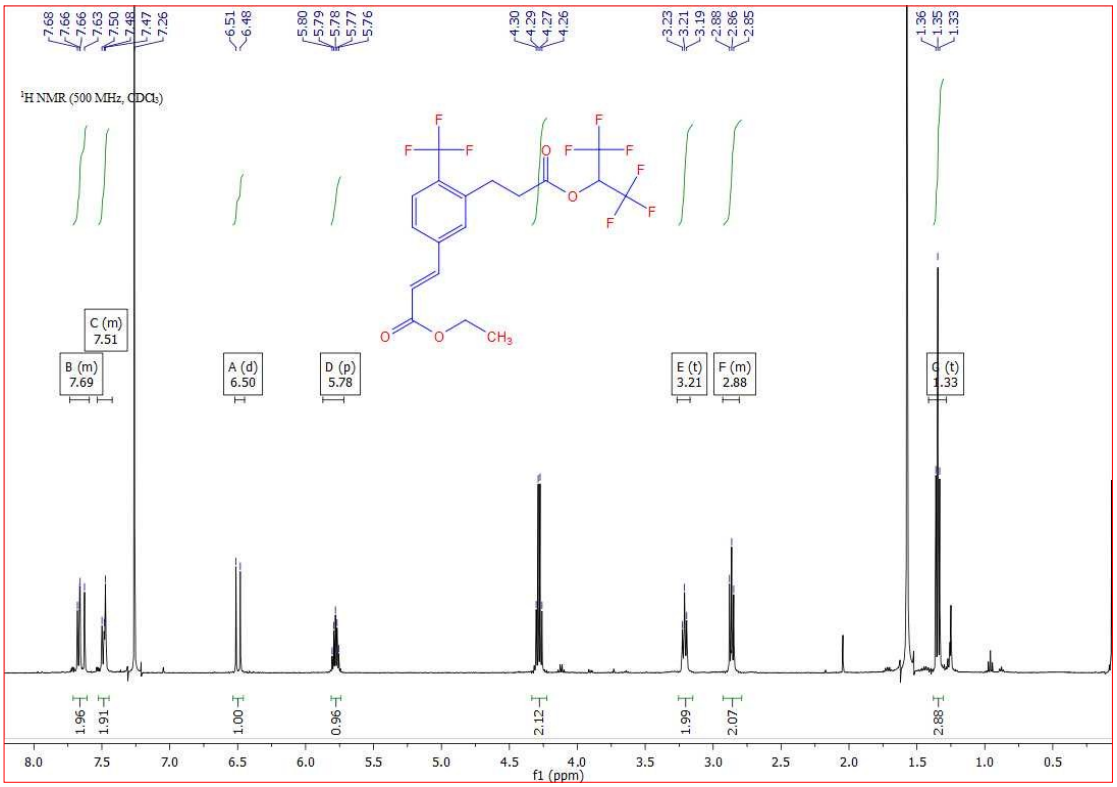


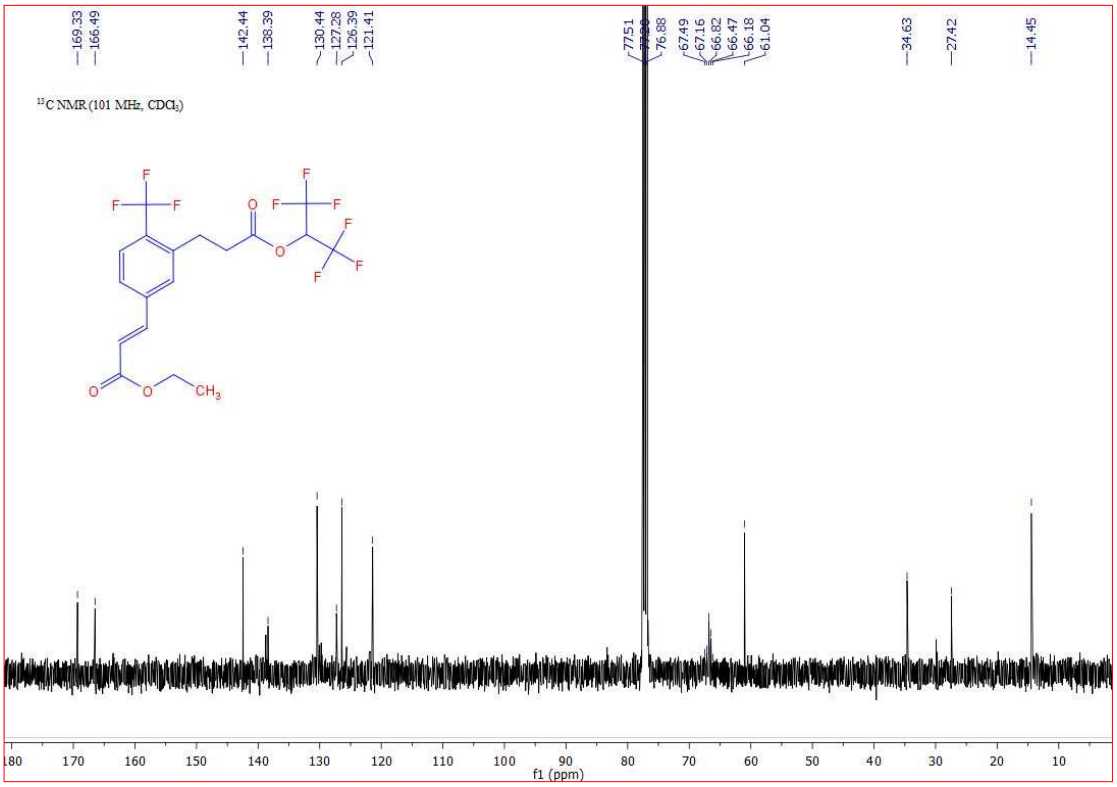
Entry 5j; Scheme 6

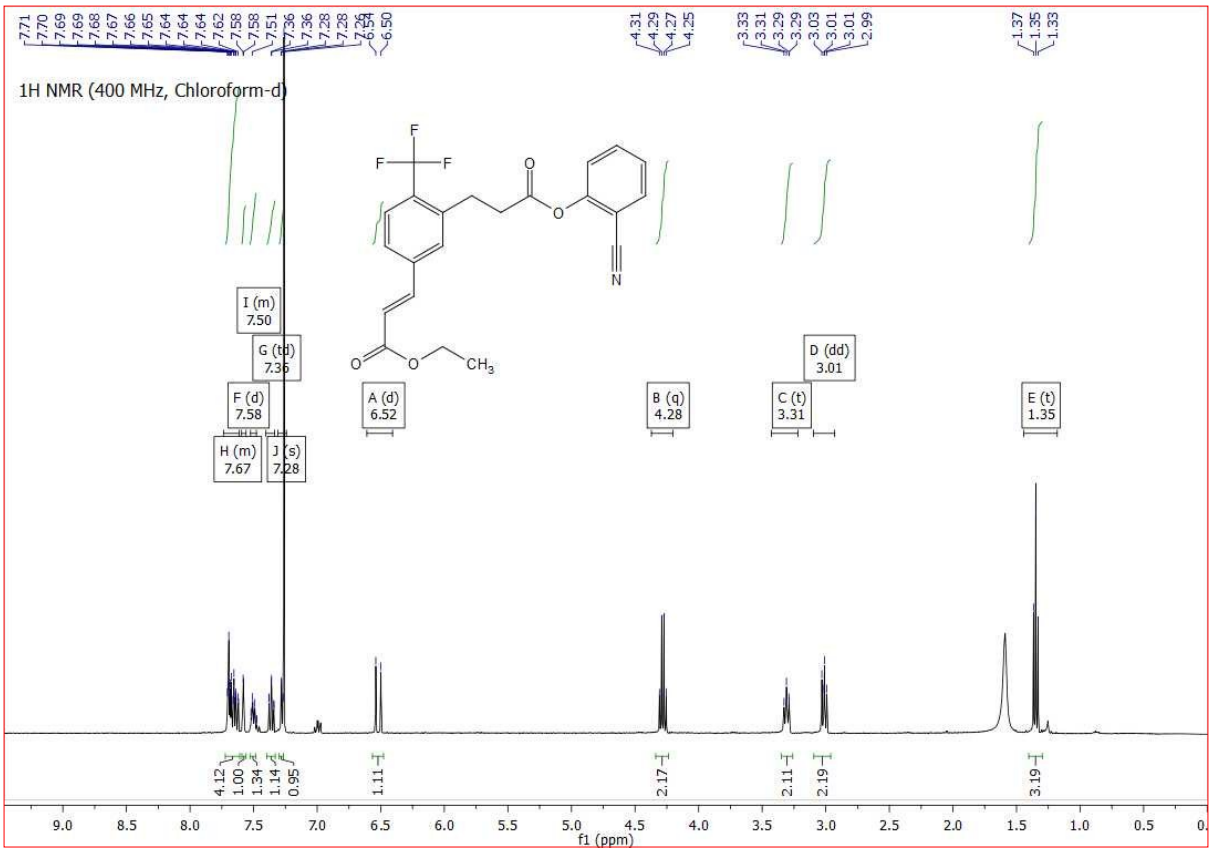

1H NMR (400 MHz, Chloroform-d)
7.98 7.94 7.68 7.66 7.66 7.61 7.41 7.40 7.33 7.26 7.26 7.25 7.21 7.21 7.19 6.88 6.86 6.56 6.52
4.29 4.27 4.25 4.23 3.87 3.09 3.08 3.07 3.06 3.06 3.05 3.04 2.98 2.98 2.97 2.97 2.97 2.96 2.96 2.95 2.94 1.35 1.33 1.32
G (td) 7.33
C (dd) 7.67
I (dd) 7.26
E (d) 6.87
B (d) 7.96
F (d) 7.40
A (d) 6.54
J (q) 4.26
K (s) 3.87
M (ddd) 2.96
L (dd) 3.07
N (t) 1.33
D (ddd) 7.61
H (dd) 7.20
1.00 1.10 1.20 1.14 1.18 1.52 1.18 1.05 0.99 2.19 2.94 2.22 2.37 3.13
f1 (ppm)

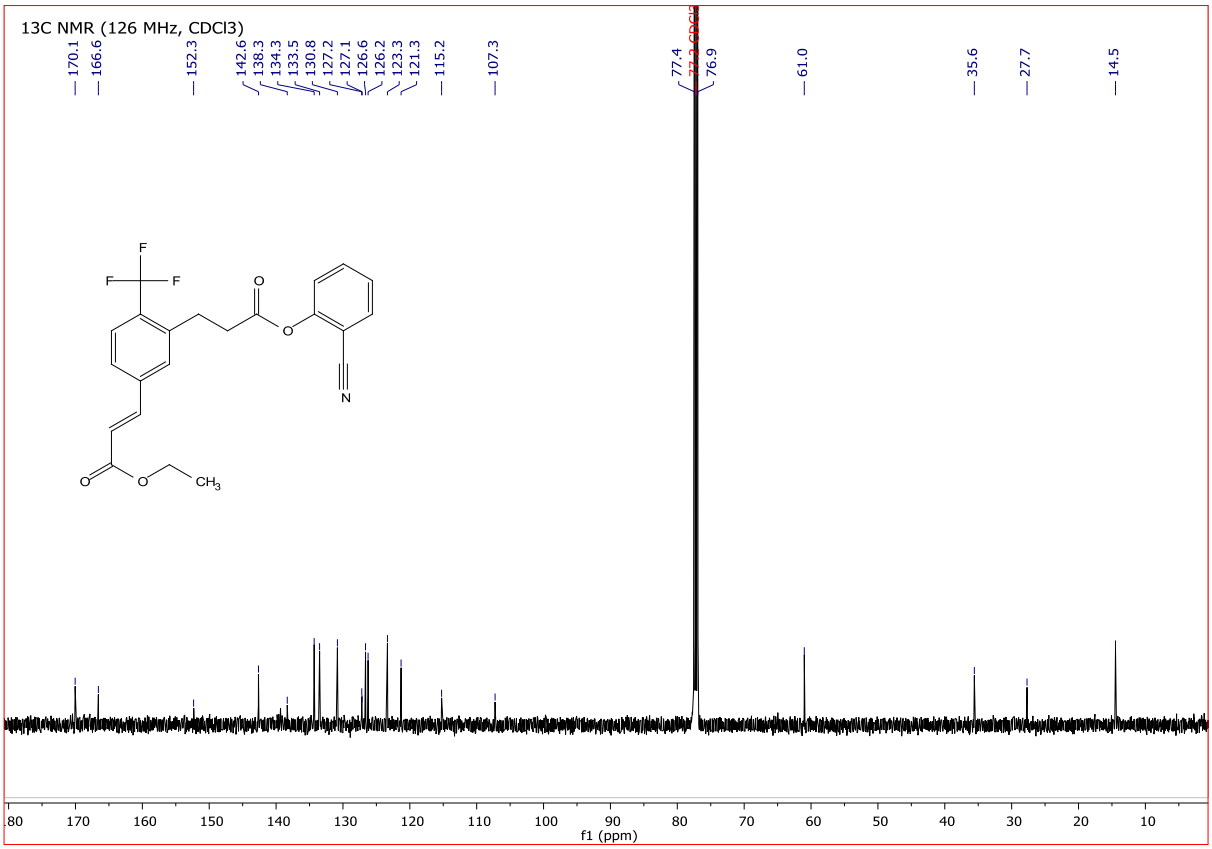

13C NMR (126 MHz, CDCl3)
170.4 167.7 157.3 152.4 140.1 134.3 133.5 132.0 131.5 129.0 126.5 123.7 123.4 119.2 115.3 111.6 107.2
77.5 77.2 77.0 60.6 55.8 36.0 30.0 14.6
f1 (ppm)

Entry 5k; Scheme 6

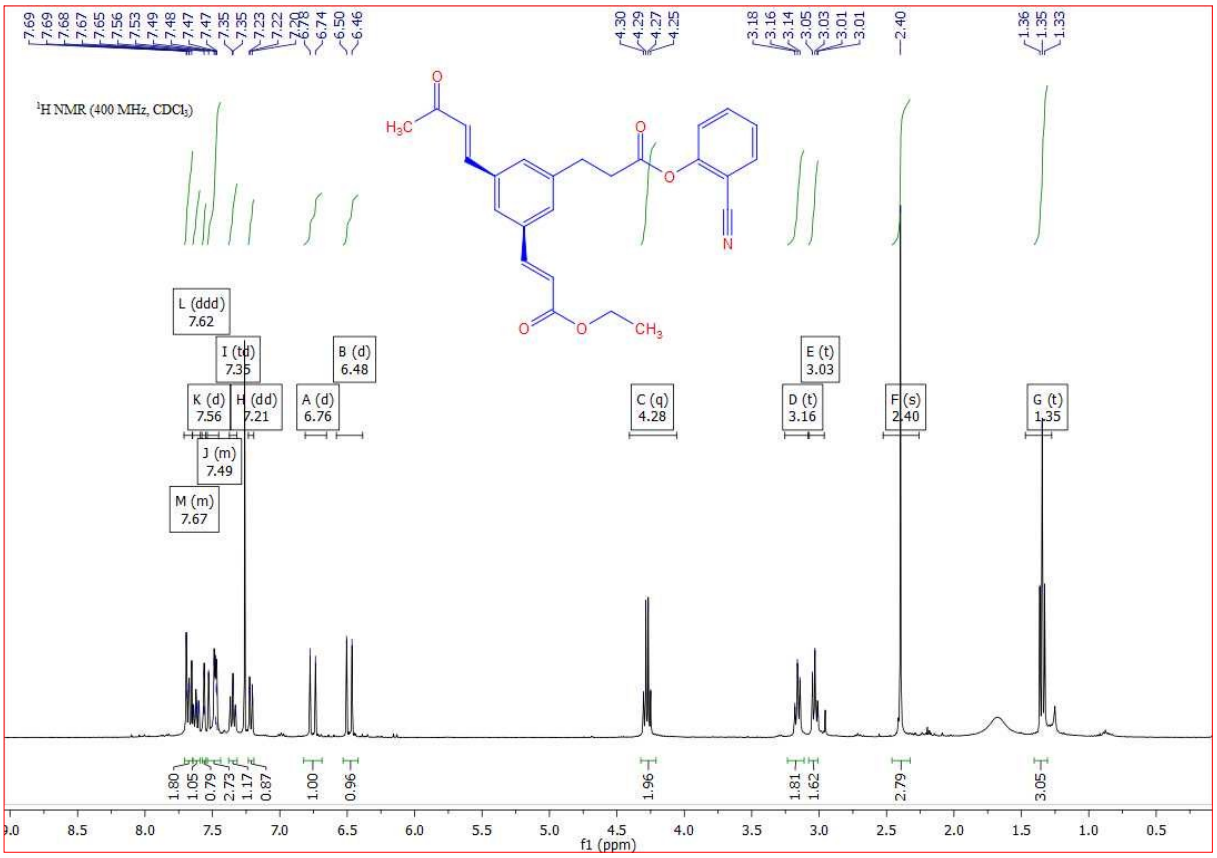


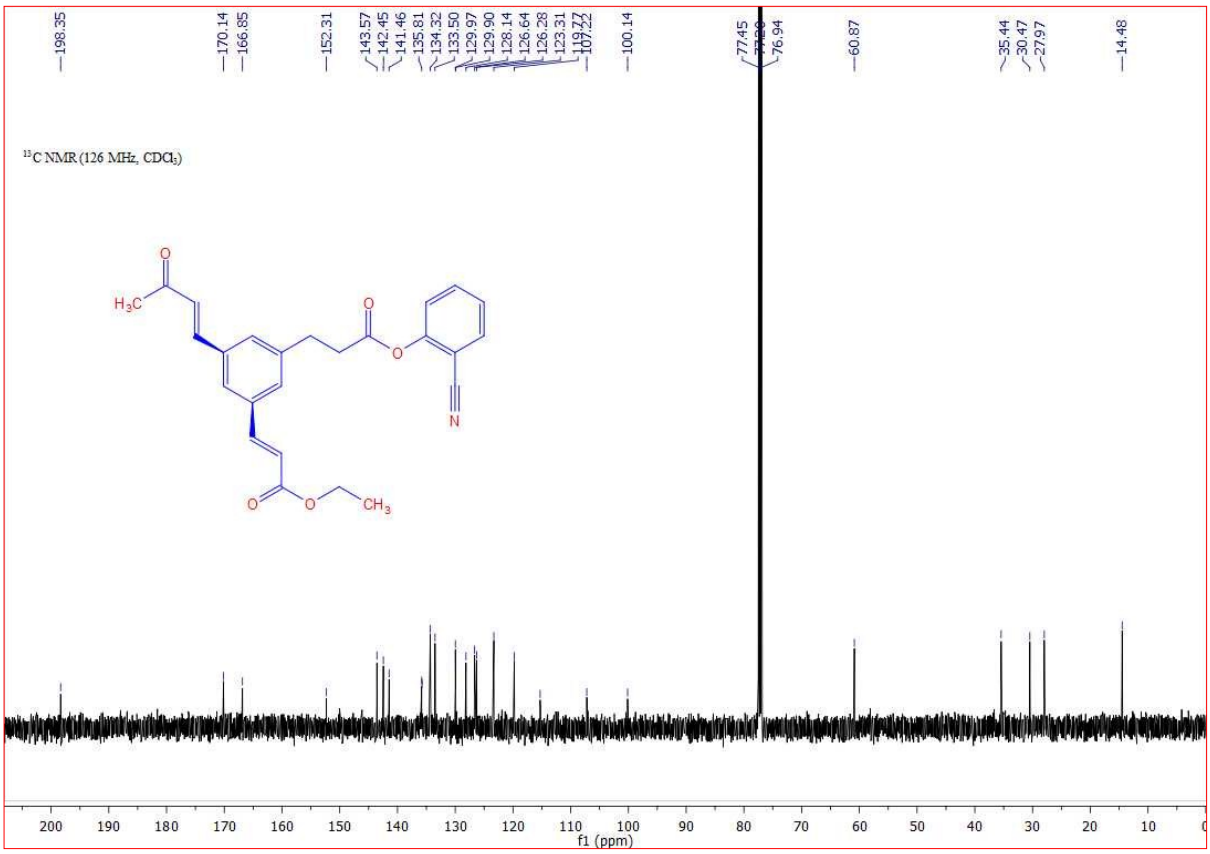



1H NMR (400 MHz, Chloroform-d)
I (m) 7.50
G (td) 7.36
F (d) 7.58
H (m) 7.67
J (s) 7.28
A (d) 6.52
B (q) 4.28
C (t) 3.31
D (dd) 3.01
E (t) 1.35
f1 (ppm)

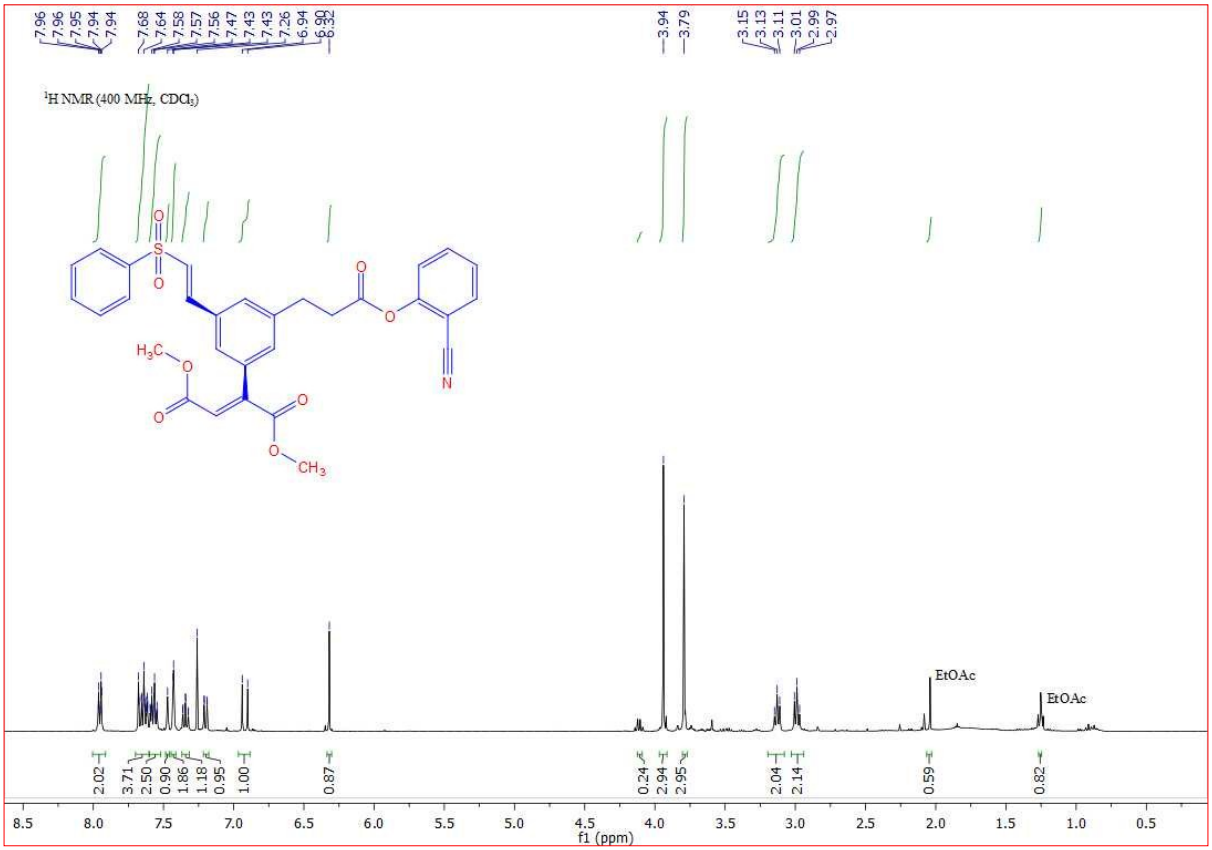

13C NMR (126 MHz, CDCl3)
f1 (ppm)

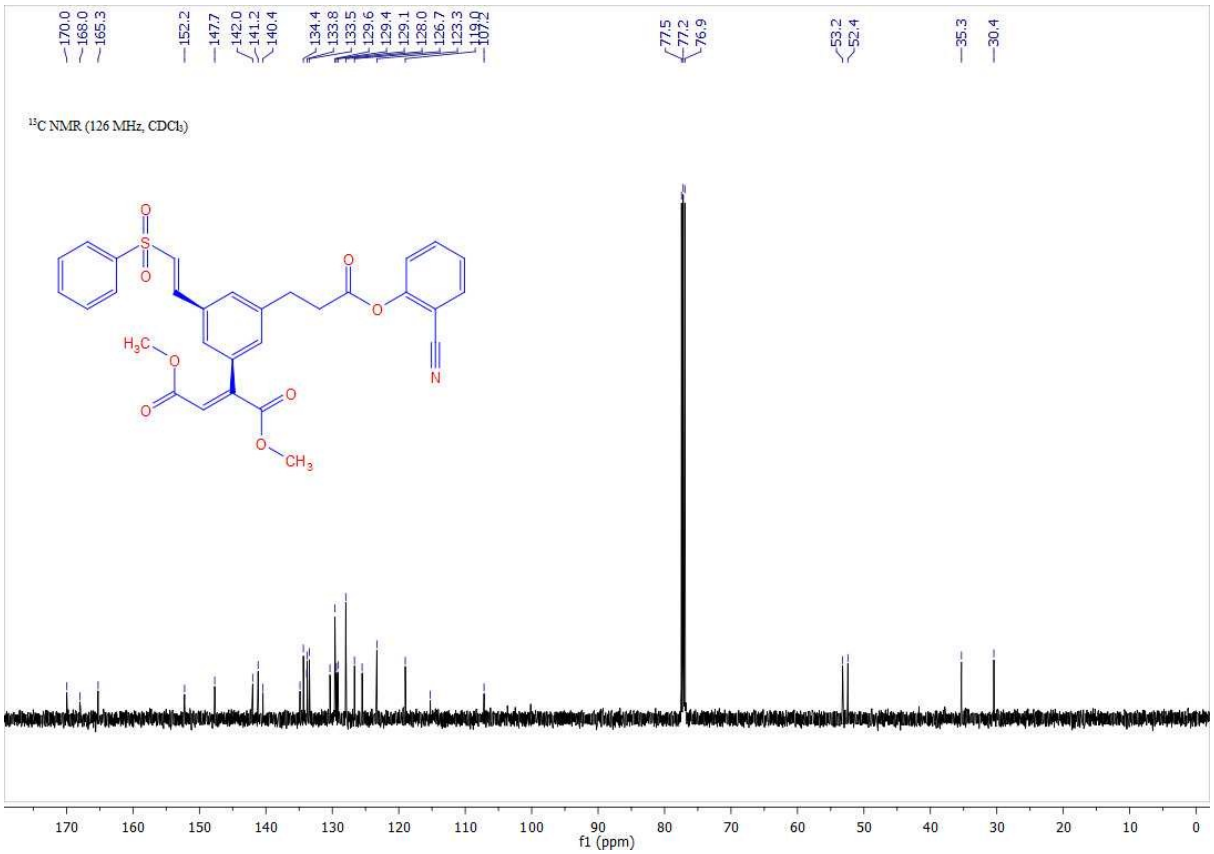
Entry 6a; Scheme 7



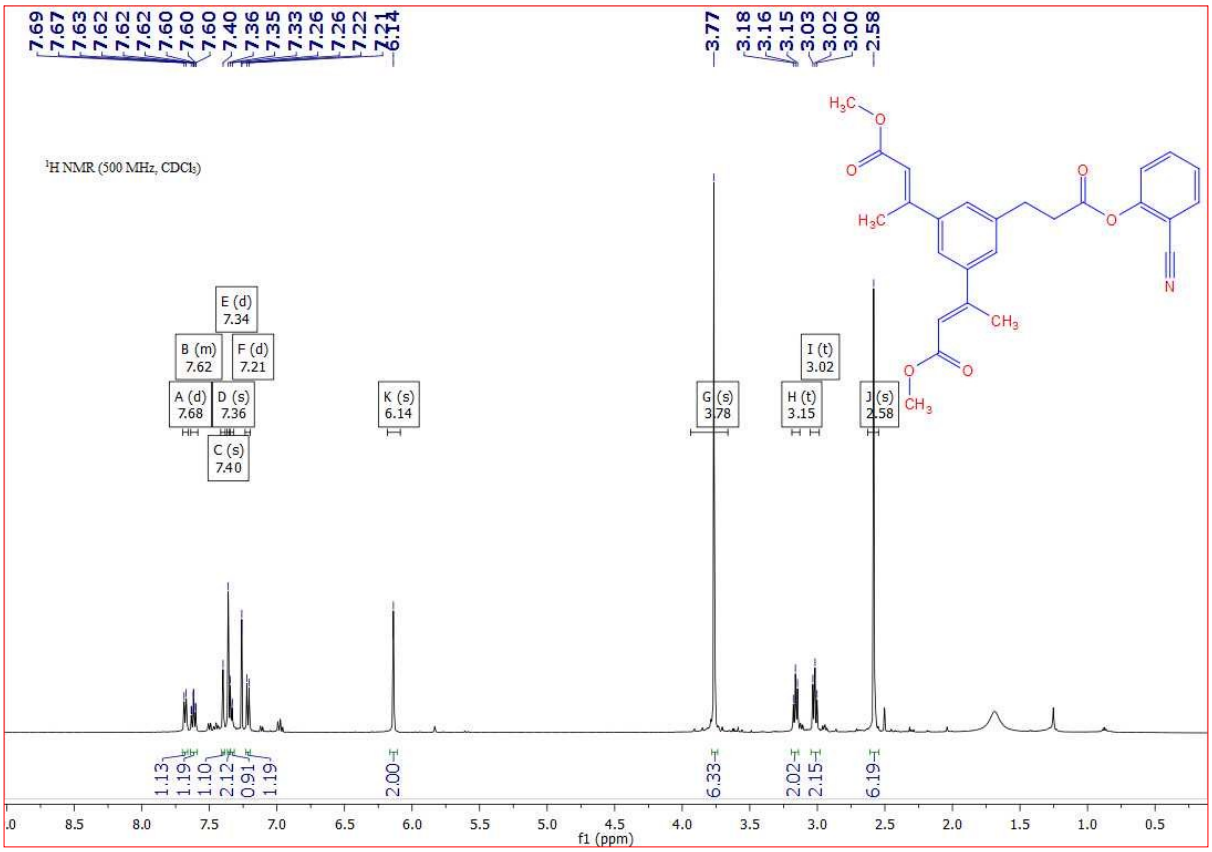


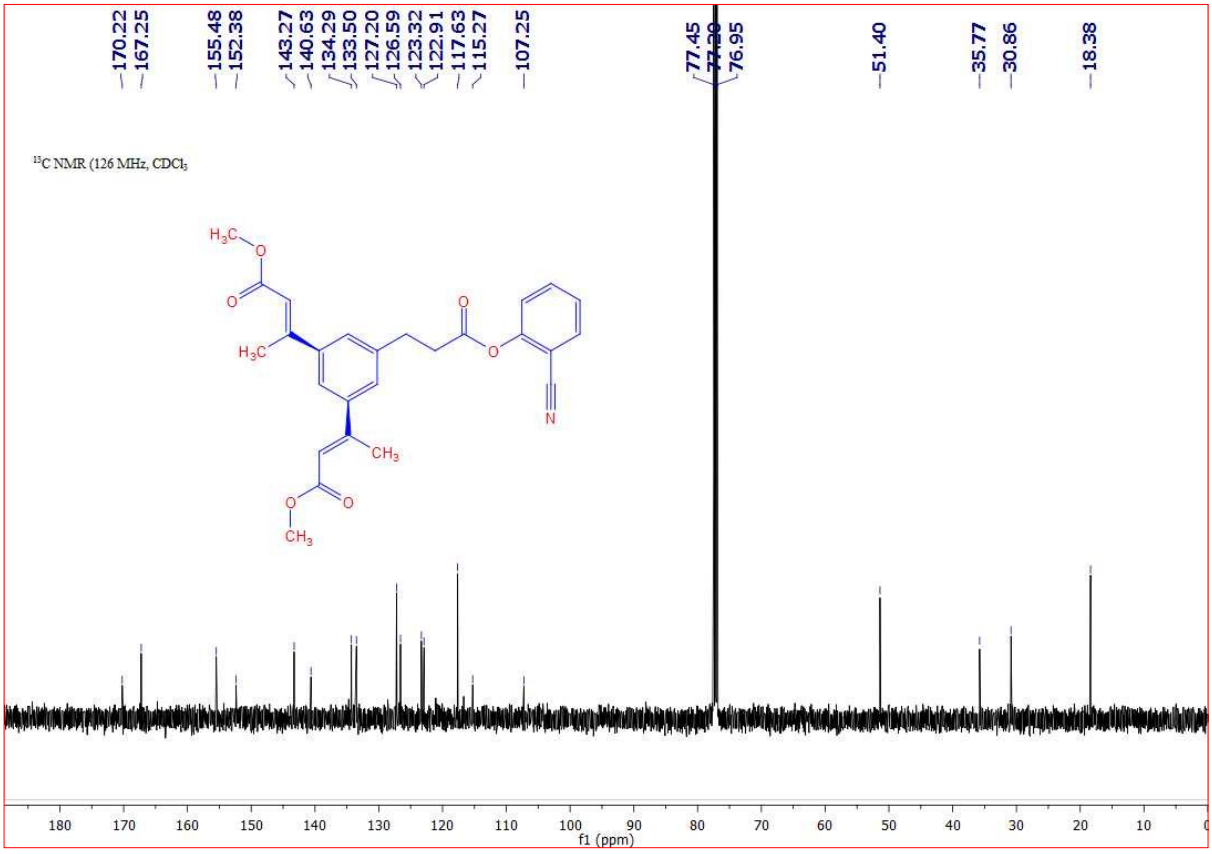
Entry 6b; Scheme 7



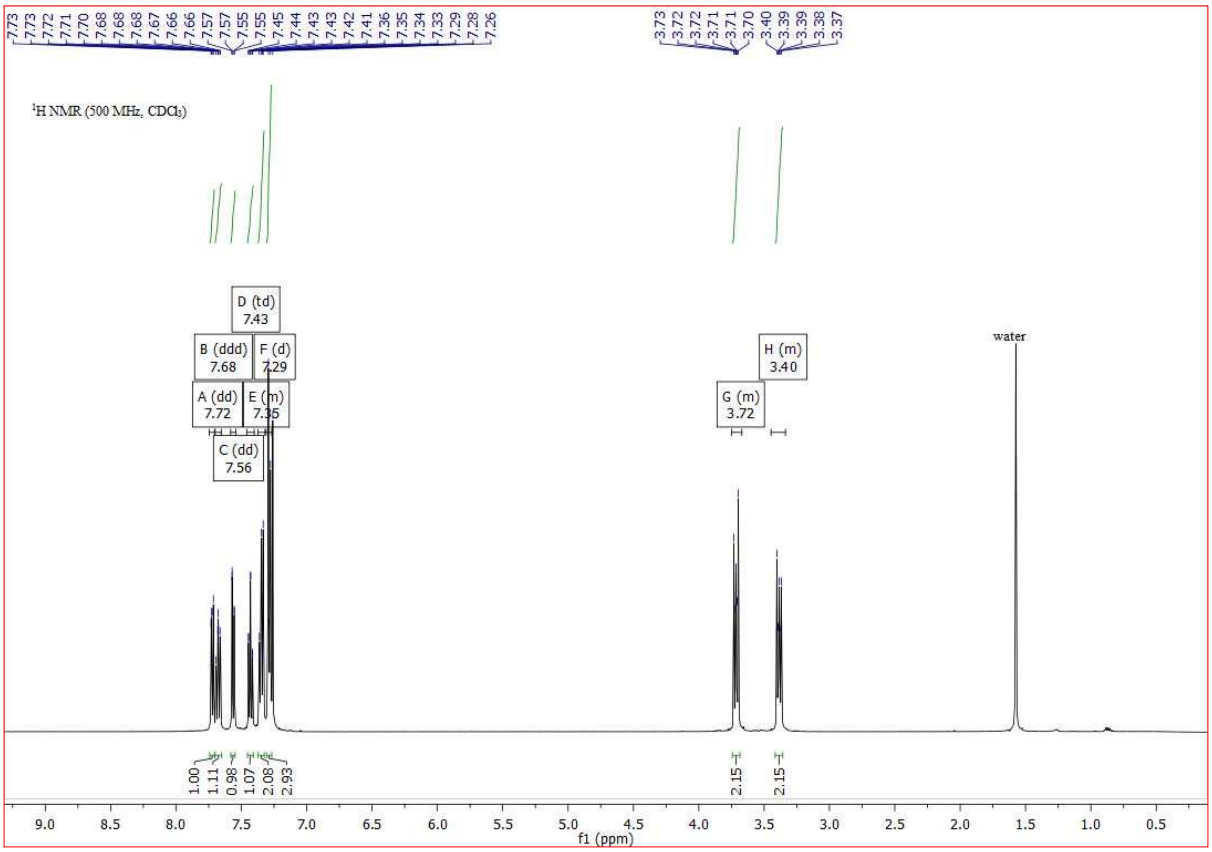


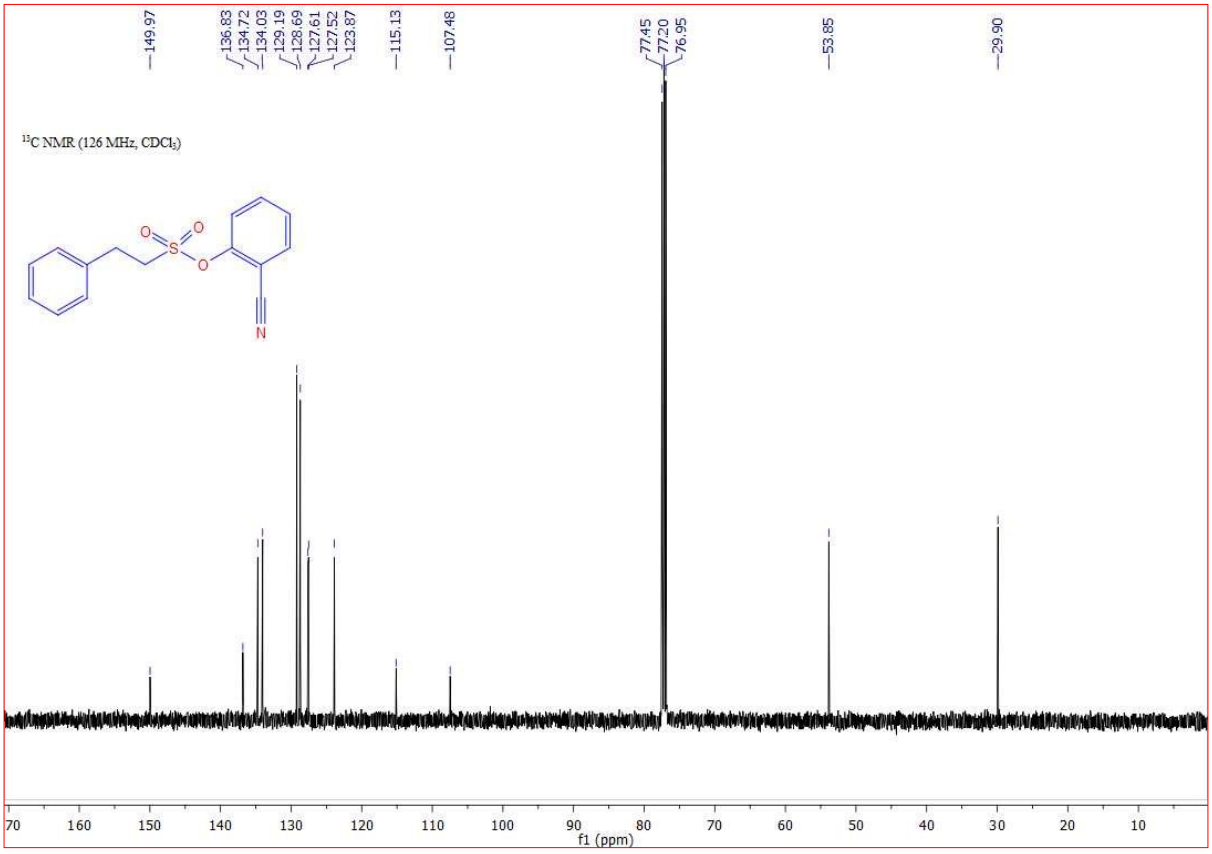
Entry 6c; Scheme 7

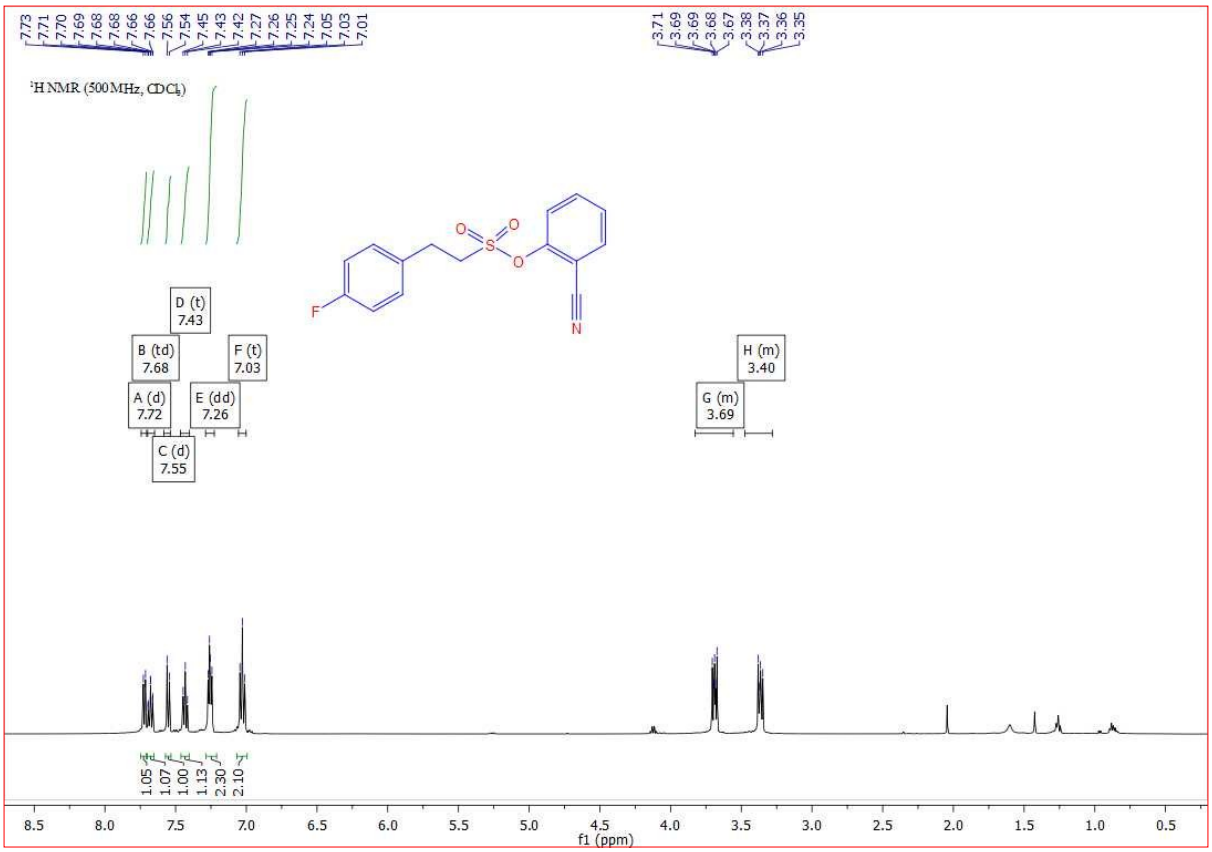


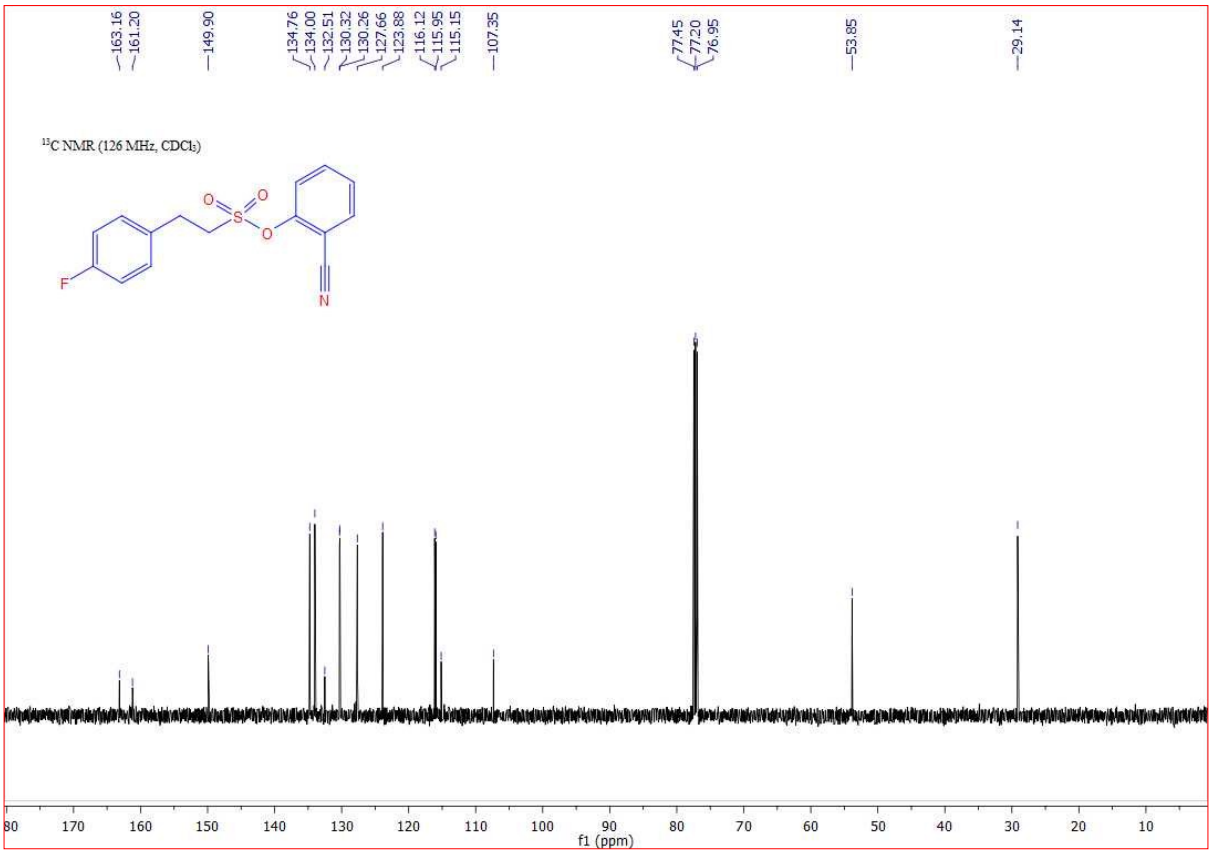


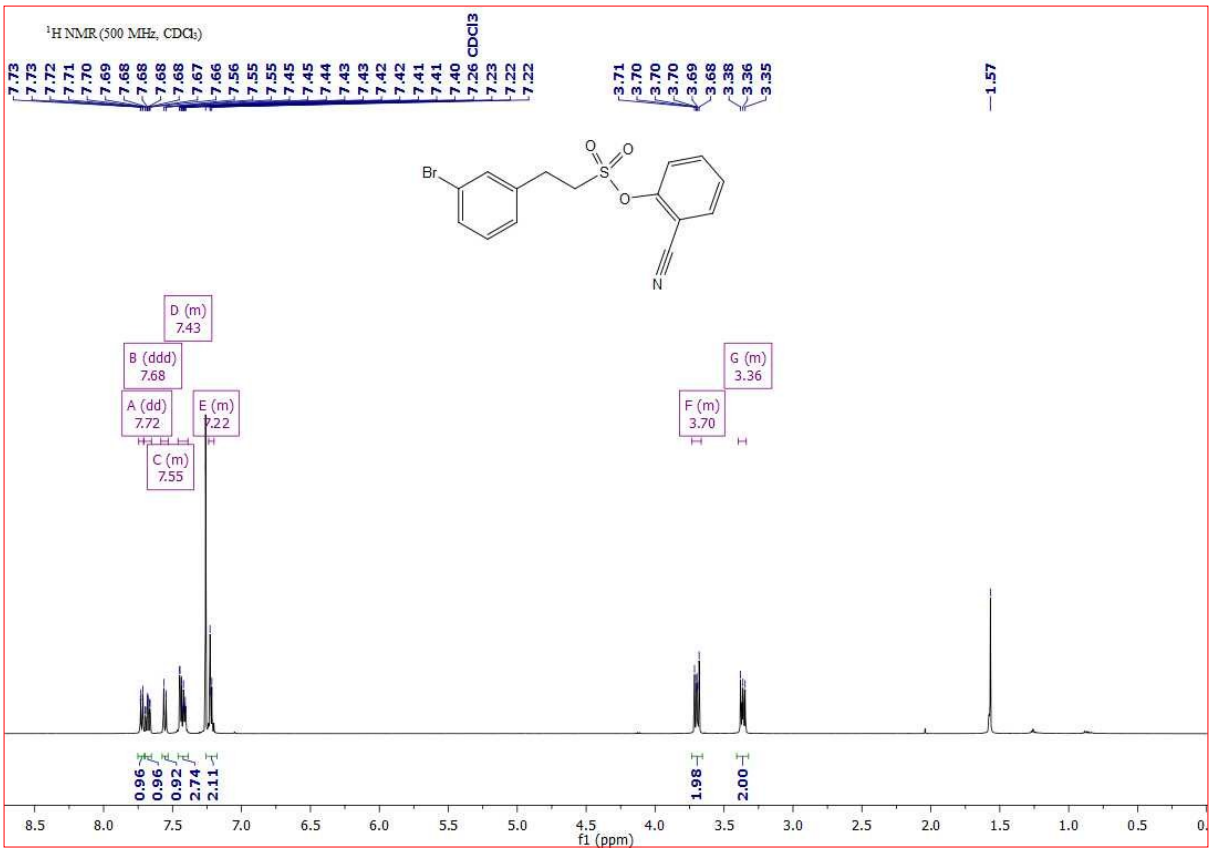
Starting materials:

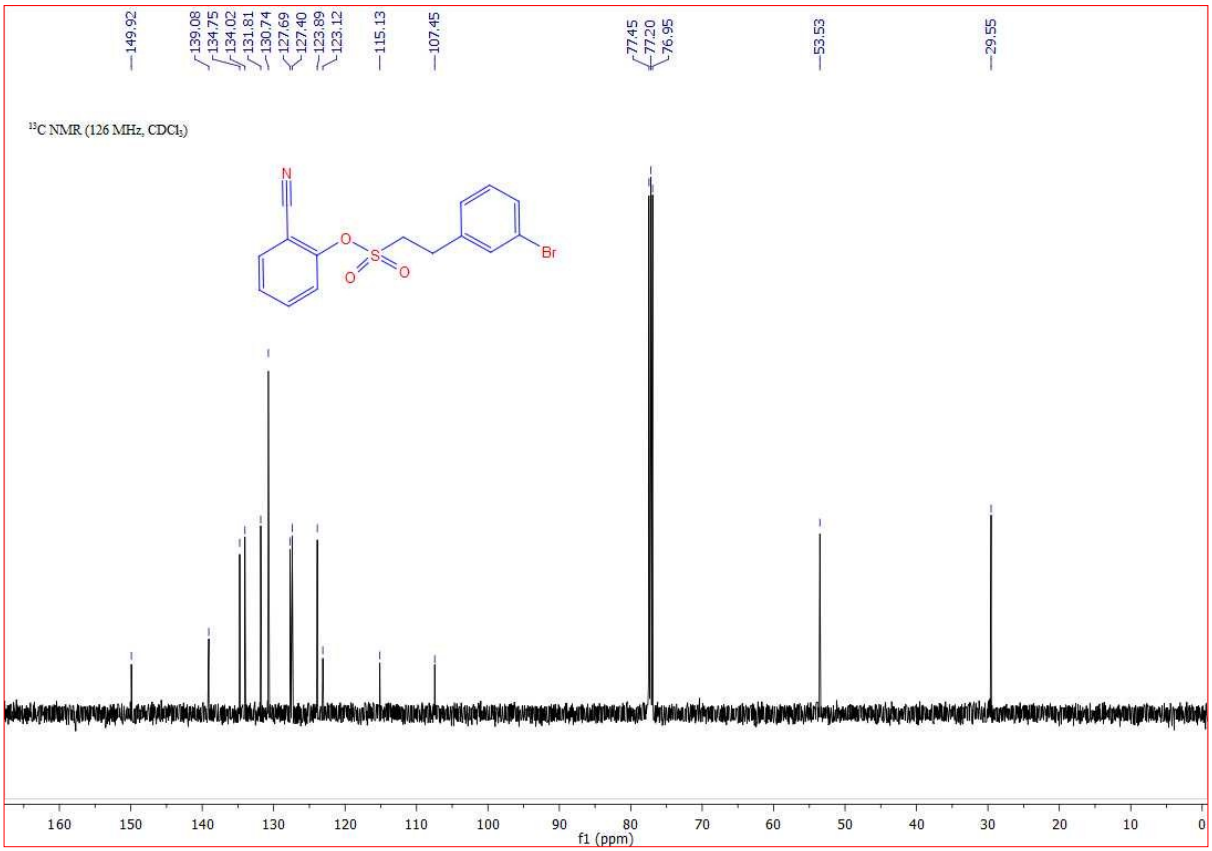


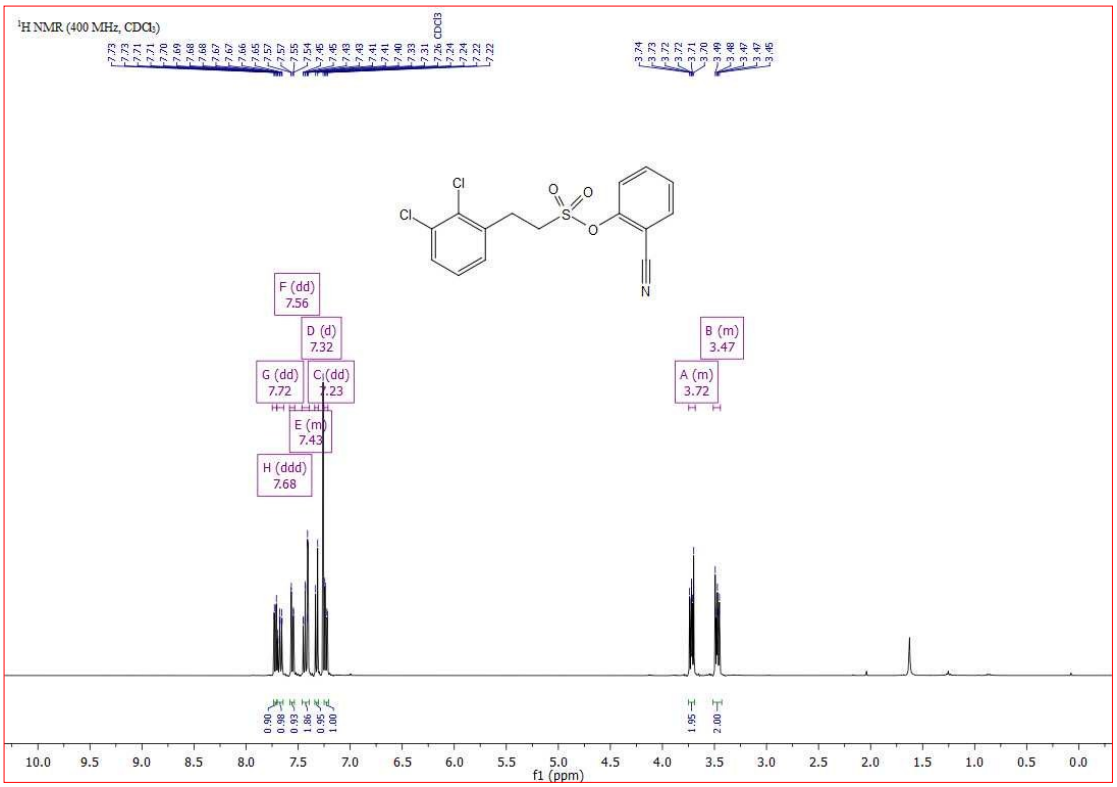


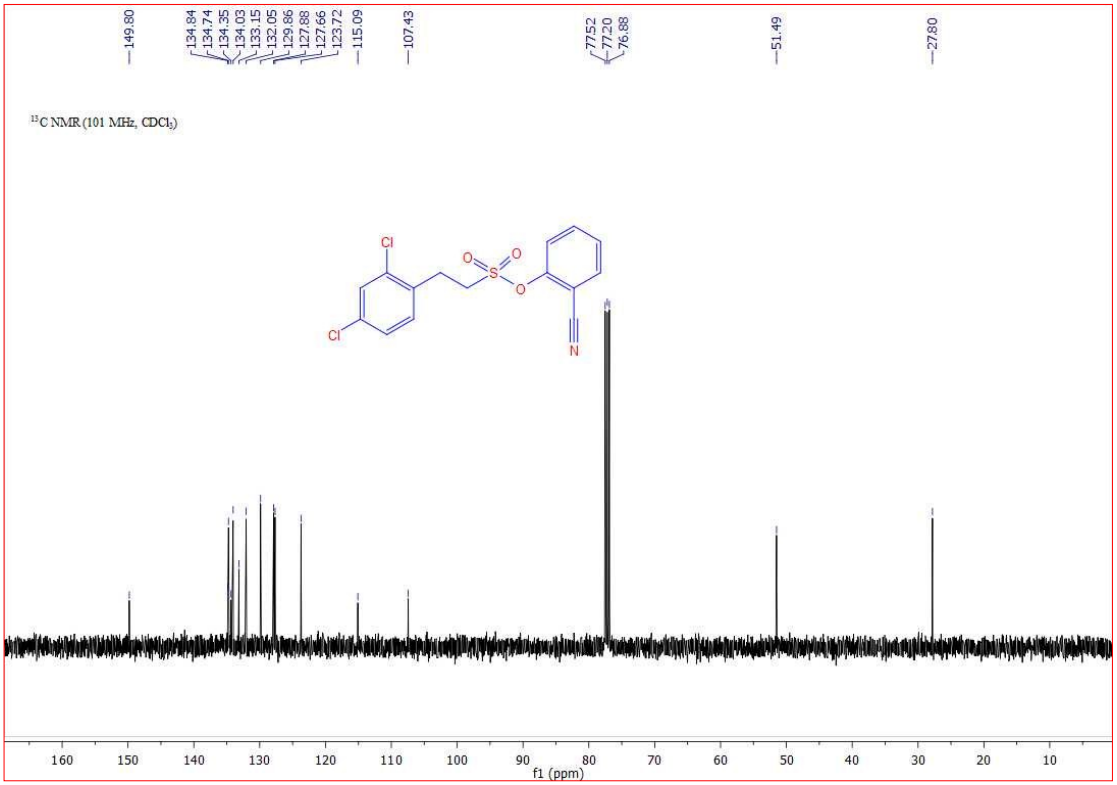

7.73
7.71
7.70
7.69
7.68
7.68
7.66
7.66
7.56
7.54
7.45
7.43
7.42
7.27
7.26
7.25
7.24
7.05
7.03
7.01
3.71
3.69
3.69
3.68
3.67
3.38
3.37
3.36
3.35
¹H NMR (500 MHz, CDCl₃)
D (t)
7.43
B (td)
7.68
F (t)
7.03
A (d)
7.72
E (dd)
7.26
C (d)
7.55
H (m)
3.40
G (m)
3.69
1.05
1.07
1.00
1.13
2.30
2.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

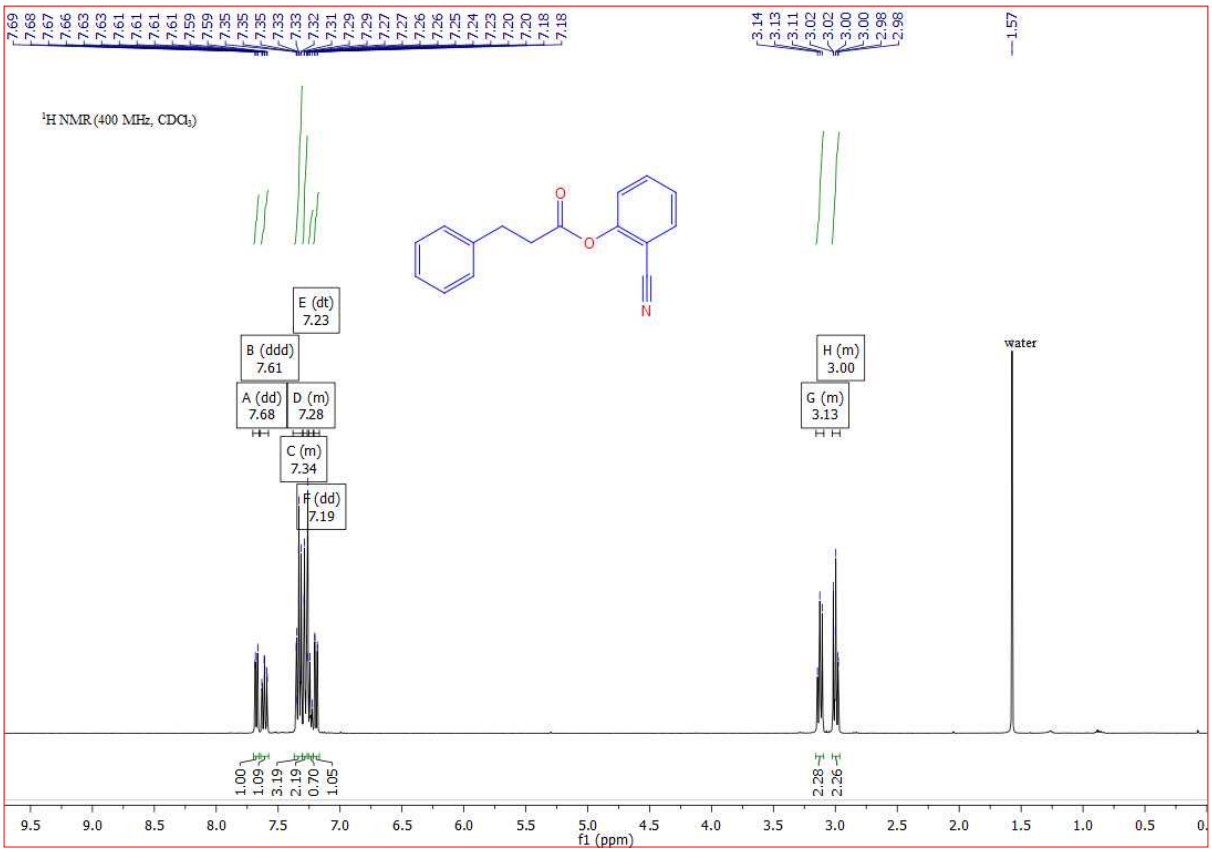

163.16
161.20
149.90
134.76
134.00
132.51
130.32
130.26
127.66
123.88
116.12
115.95
115.15
107.35
77.45
77.20
76.95
53.85
29.14
¹³C NMR (126 MHz, CDCl₃)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

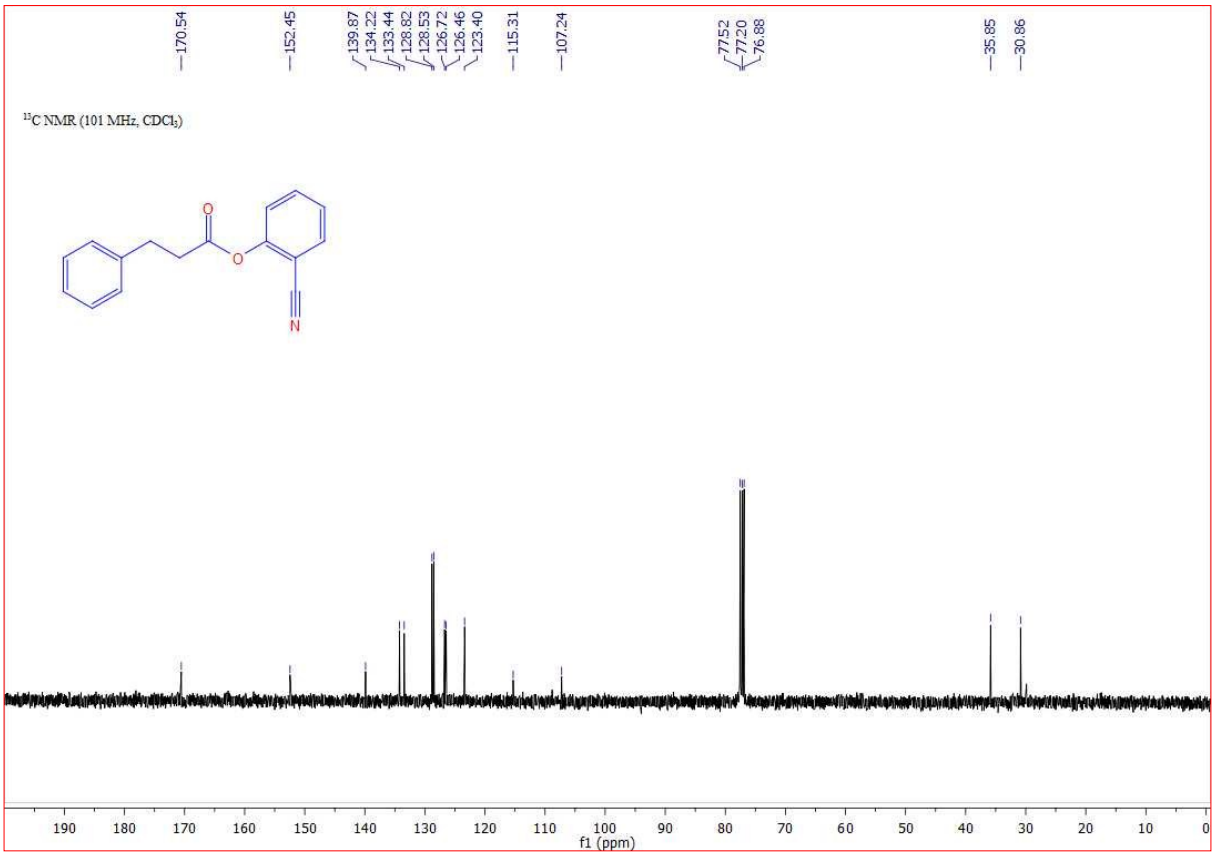

1H NMR (500 MHz, CDCl3)
CDCl3
1.57
D (m) 7.43
B (ddd) 7.68
A (dd) 7.72
E (m) 7.22
C (m) 7.55
G (m) 3.36
F (m) 3.70
0.96
0.96
0.92
2.74
2.11
1.98
2.00
f1 (ppm)

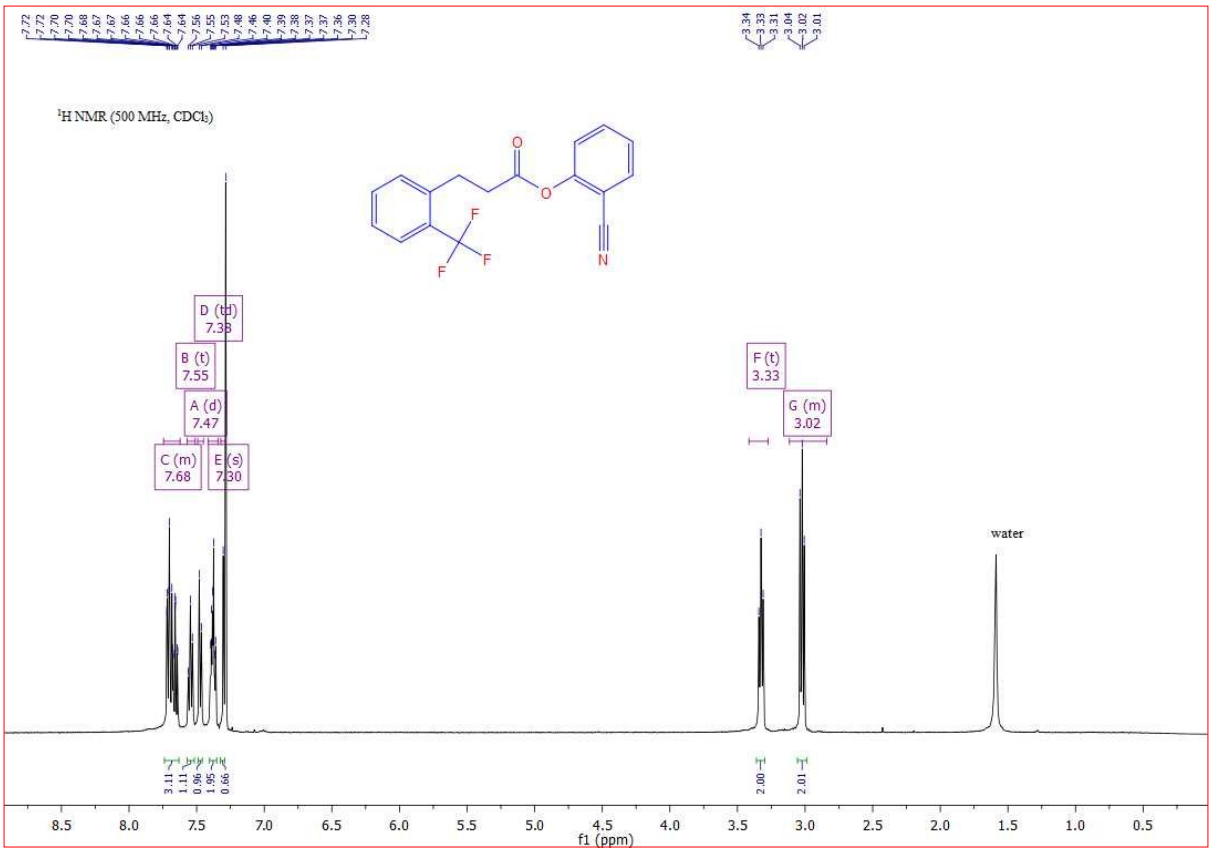

149.92
139.08
134.75
134.02
131.81
130.74
127.69
127.40
123.89
123.12
115.13
107.45
77.45
77.20
76.95
53.53
29.55
13C NMR (126 MHz, CDCl3)
f1 (ppm)

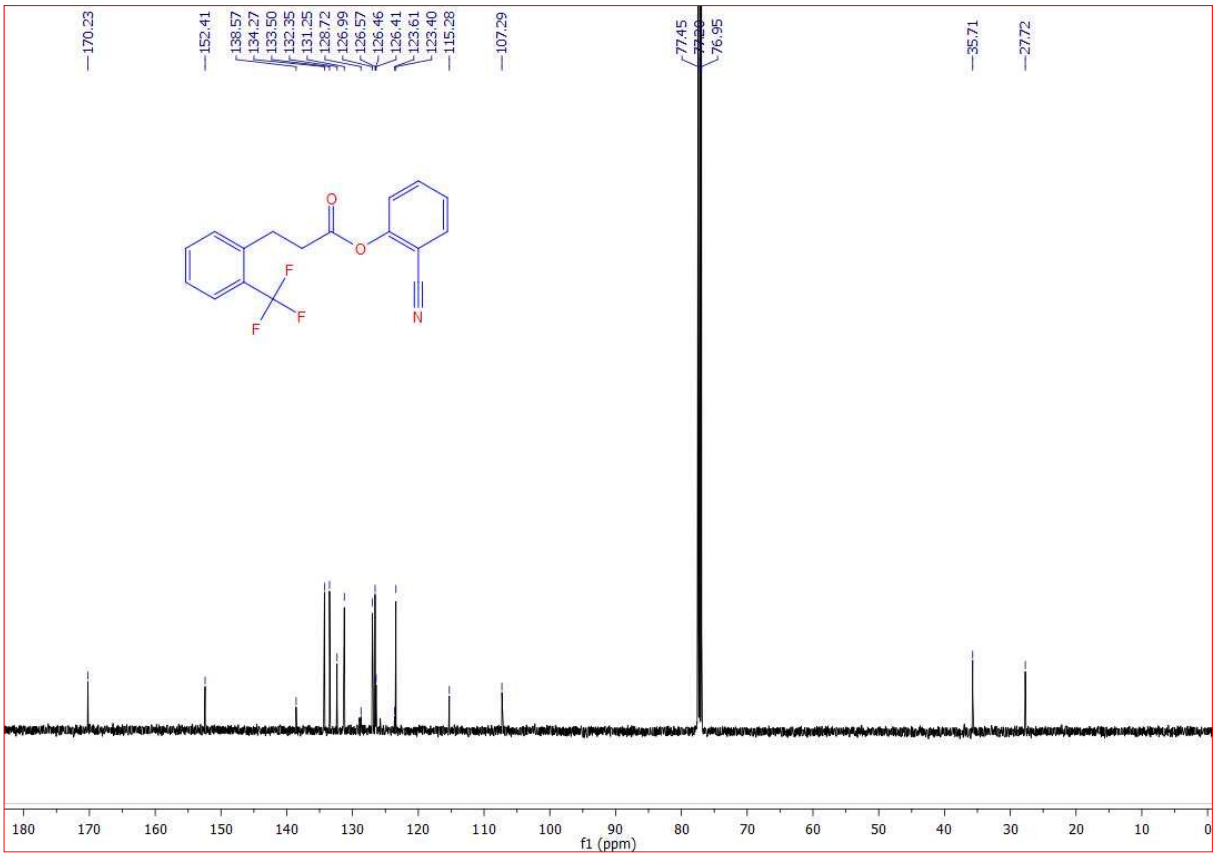

^{1}H NMR (400 MHz, CDCl$_3$)
F (dd) 7.56
D (d) 7.32
G (dd) 7.72
C (dd) 7.23
E (m) 7.43
H (ddd) 7.68
B (m) 3.47
A (m) 3.72
f1 (ppm)

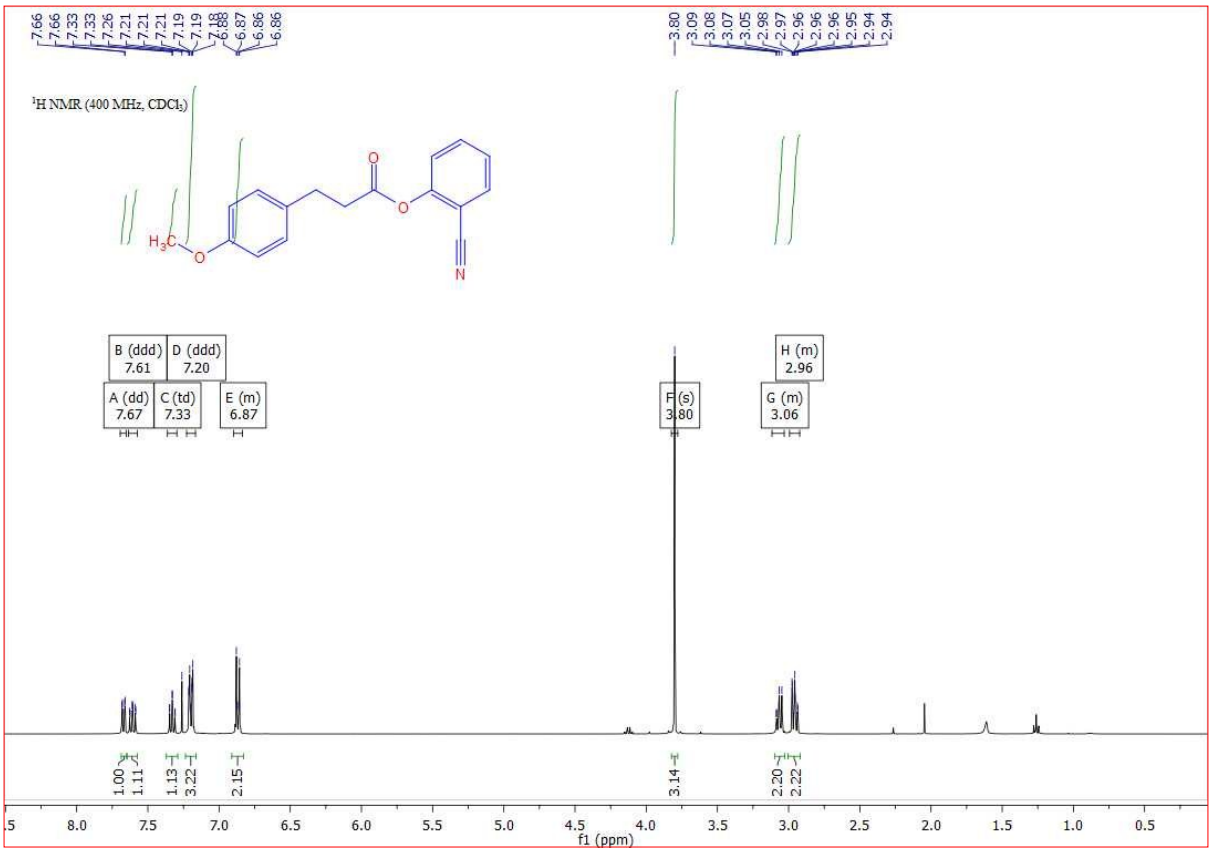

^{13}C NMR (101 MHz, CDCl$_3$)
f1 (ppm)

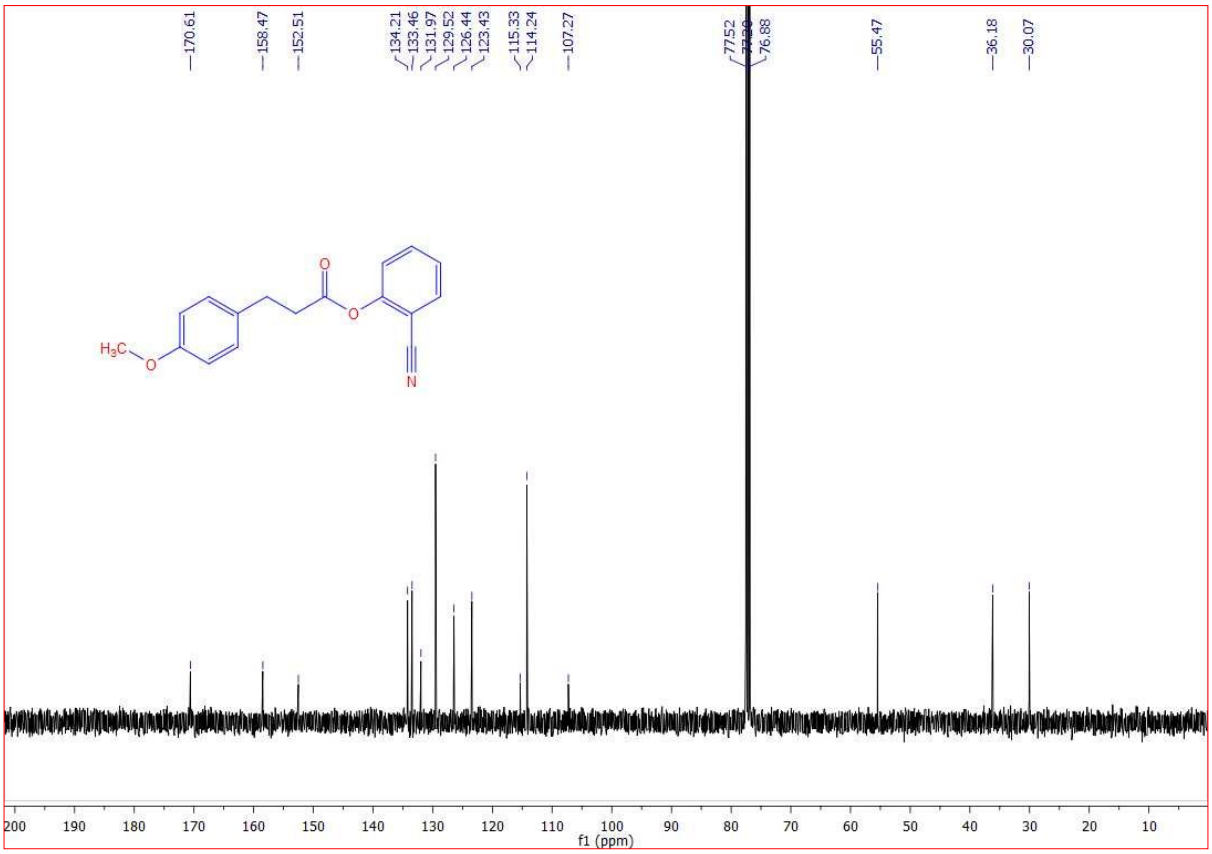

7.69 7.68 7.67 7.66 7.63 7.63 7.61 7.61 7.61 7.61 7.59 7.59 7.35 7.35 7.35 7.33 7.32 7.31 7.29 7.29 7.27 7.27 7.26 7.26 7.25 7.24 7.23 7.20 7.20 7.18 7.18
3.14 3.13 3.11 3.02 3.02 3.00 3.00 2.98 2.98
1.57
^{1}H NMR (400 MHz, CDCl$_3$)
O
O
N
E (dt) 7.23
B (ddd) 7.61
A (dd) 7.68
D (m) 7.28
C (m) 7.34
F (dd) 7.19
H (m) 3.00
G (m) 3.13
water
1.00 1.09 3.19 2.19 0.70 1.05
2.28 2.26
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

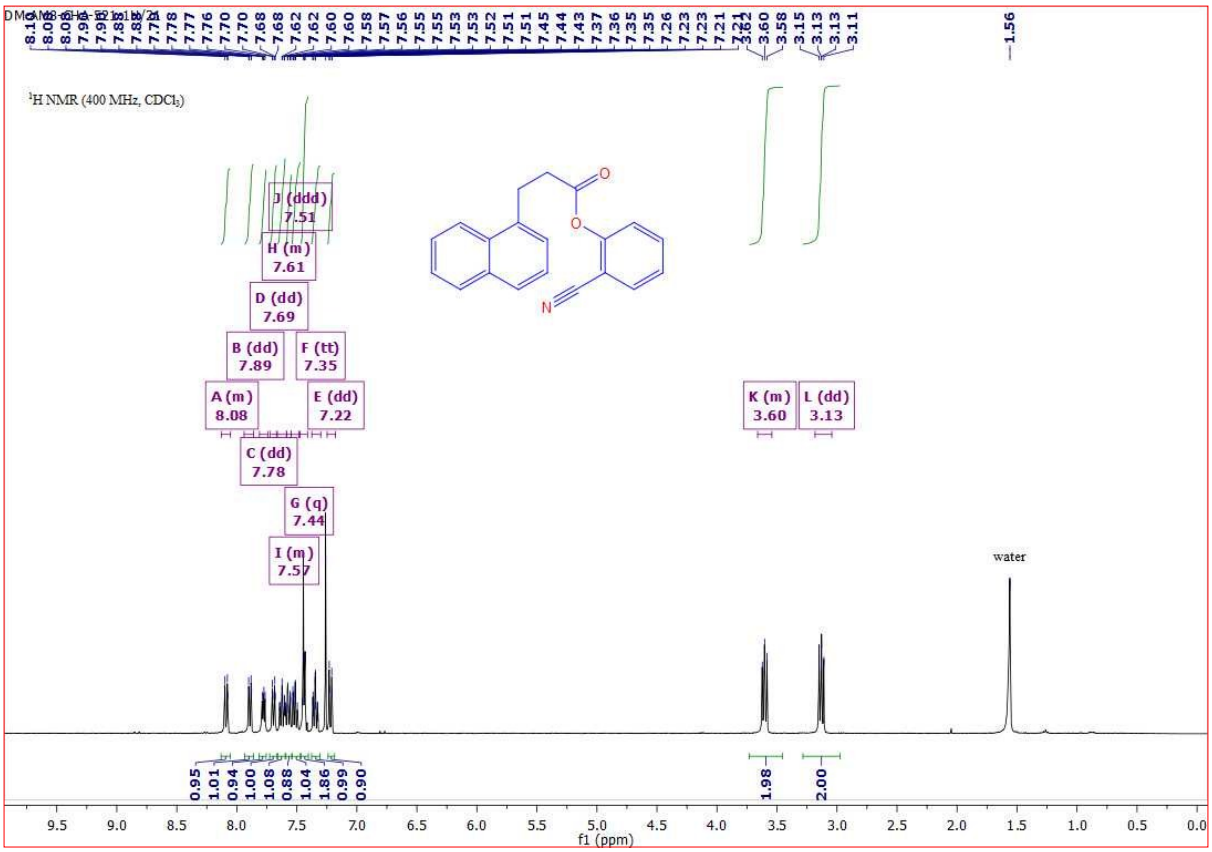

170.54
152.45
139.87
134.22
133.44
128.82
128.53
126.72
126.46
123.40
115.31
107.24
77.52
77.20
76.88
35.85
30.86
^{13}C NMR (101 MHz, CDCl$_3$)
O
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

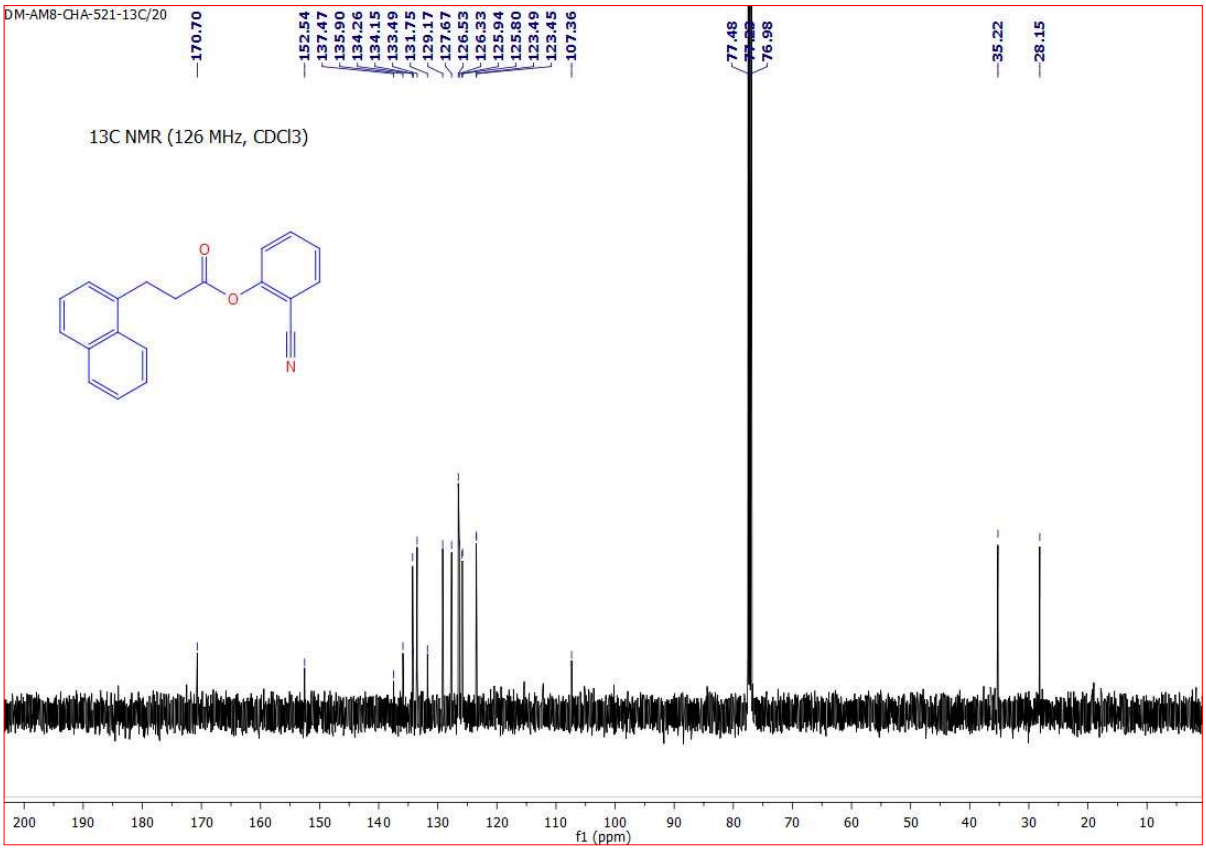

^{1}H NMR (500 MHz, CDCl$_3$)
D (td)
7.38
B (t)
7.55
A (d)
7.47
C (m)
7.68
E (s)
7.30
F (t)
3.33
G (m)
3.02
water
f1 (ppm)


170.23
152.41
138.57
134.27
133.50
132.35
131.25
128.72
126.99
126.57
126.46
126.41
123.61
123.40
115.28
107.29
77.45
76.95
35.71
27.72
f1 (ppm)

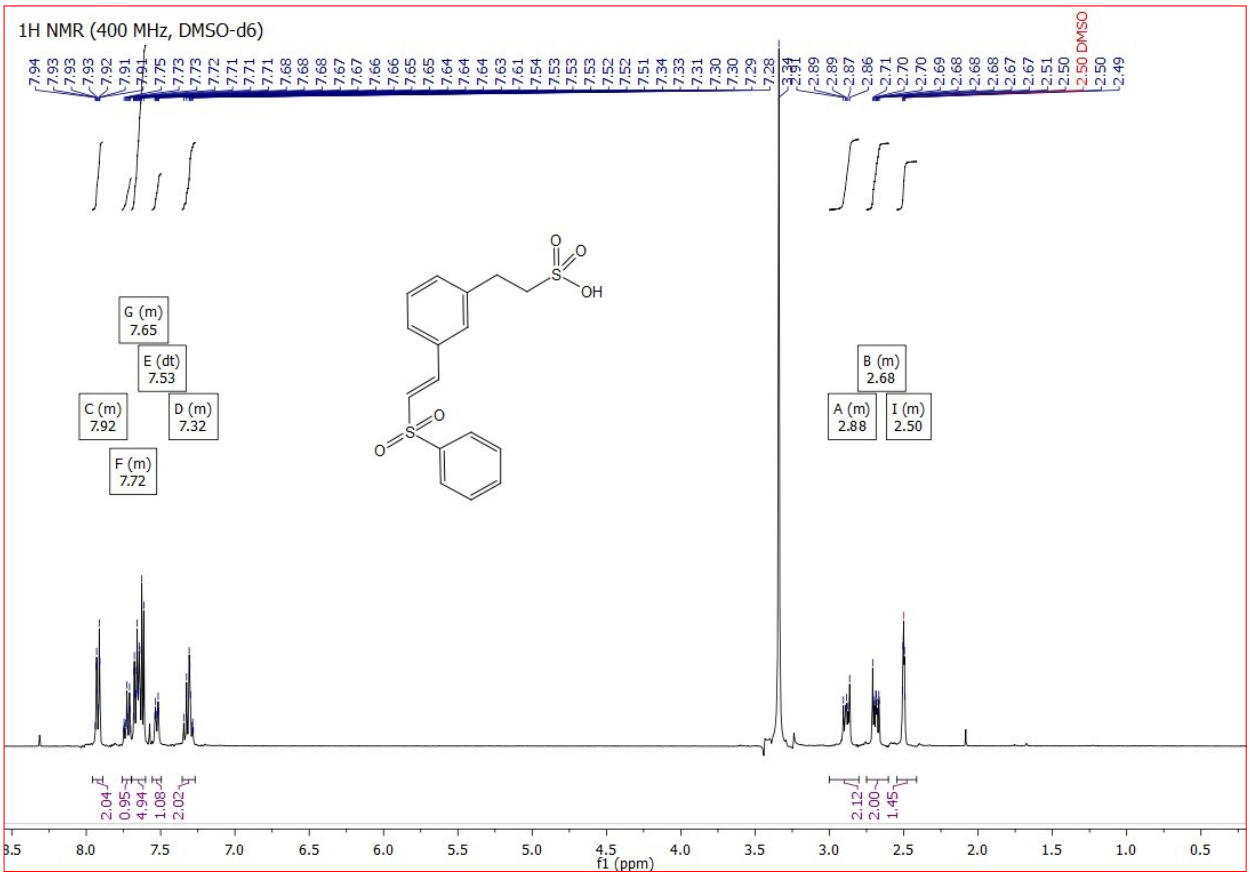

^{1}H NMR (400 MHz, CDCl$_3$)
B (ddd) 7.61
D (ddd) 7.20
A (dd) 7.67
C (td) 7.33
E (m) 6.87
F (s) 3.80
H (m) 2.96
G (m) 3.06
f1 (ppm)

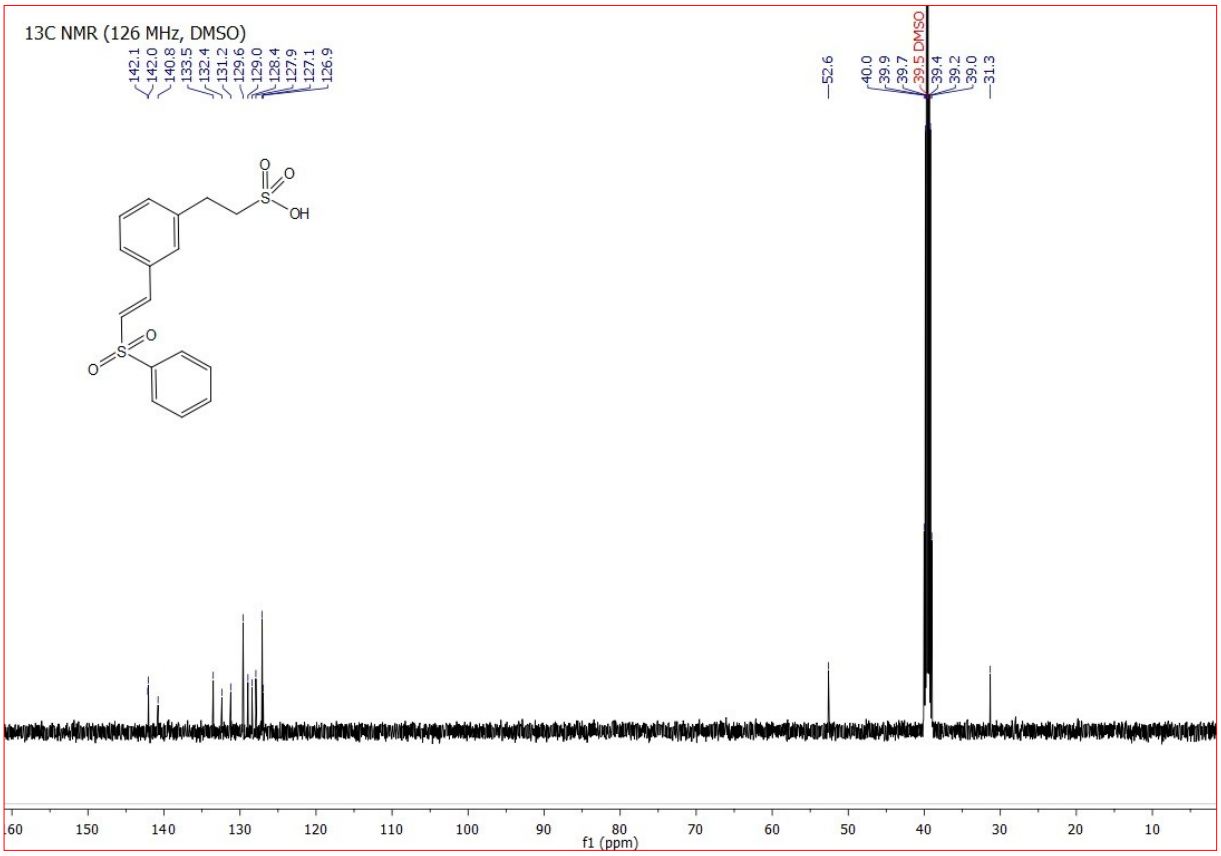

170.61
158.47
152.51
134.21
133.46
131.97
129.52
126.44
123.43
115.33
114.24
107.27
77.52
76.88
55.47
36.18
30.07
f1 (ppm)

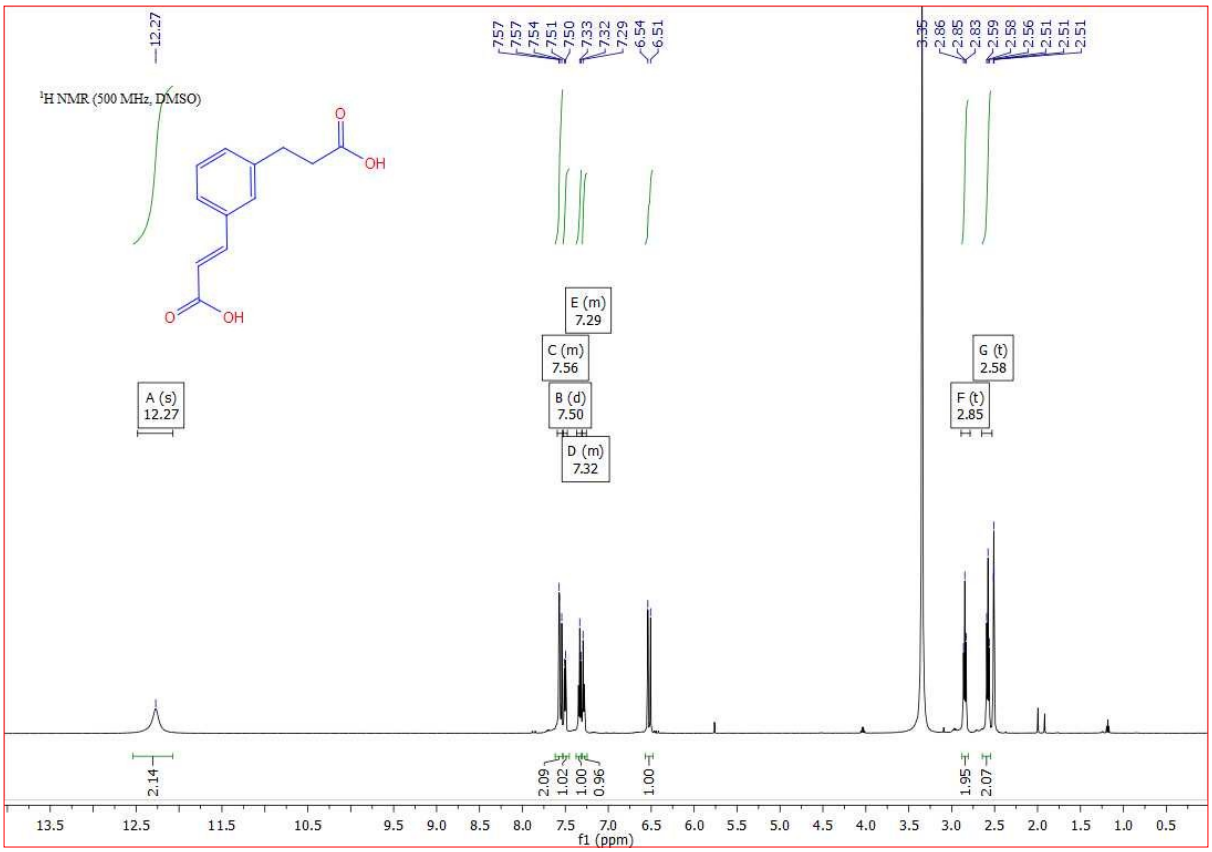

^{1}H NMR (400 MHz, CDCl$_3$)
J (ddd) 7.51
H (m) 7.61
D (dd) 7.69
B (dd) 7.89
F (tt) 7.35
A (m) 8.08
E (dd) 7.22
C (dd) 7.78
G (q) 7.44
I (m) 7.57
K (m) 3.60
L (dd) 3.13
water
0.95
1.01
0.94
1.00
1.08
0.88
1.04
1.86
0.99
0.90
1.98
2.00
f1 (ppm)

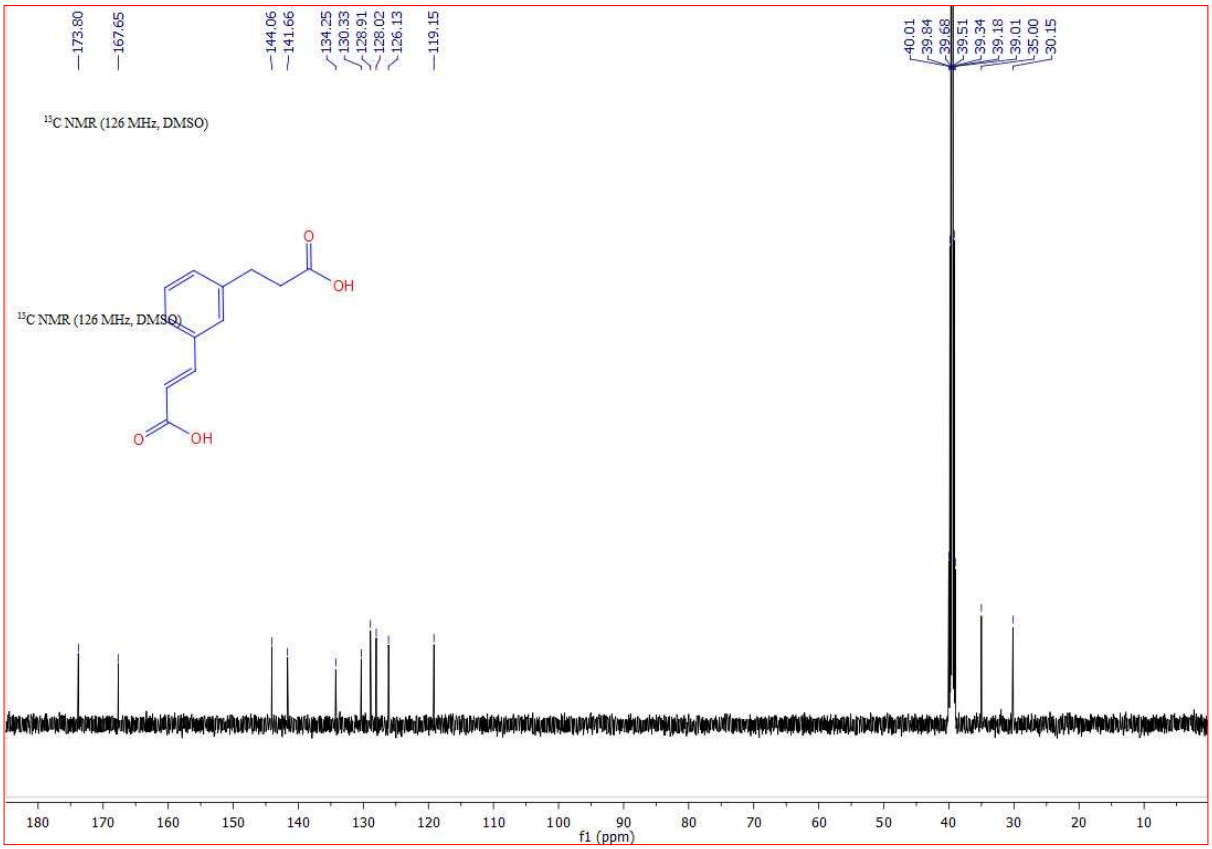

DM-AM8-CHA-521-13C/20
13C NMR (126 MHz, CDCl3)
170.70
152.54
137.47
135.90
134.26
134.15
133.49
131.75
129.17
127.67
126.53
126.33
125.94
125.80
123.49
123.45
107.36
77.48
76.98
35.22
28.15
f1 (ppm)

De-protection of acid moiety; Scheme 8

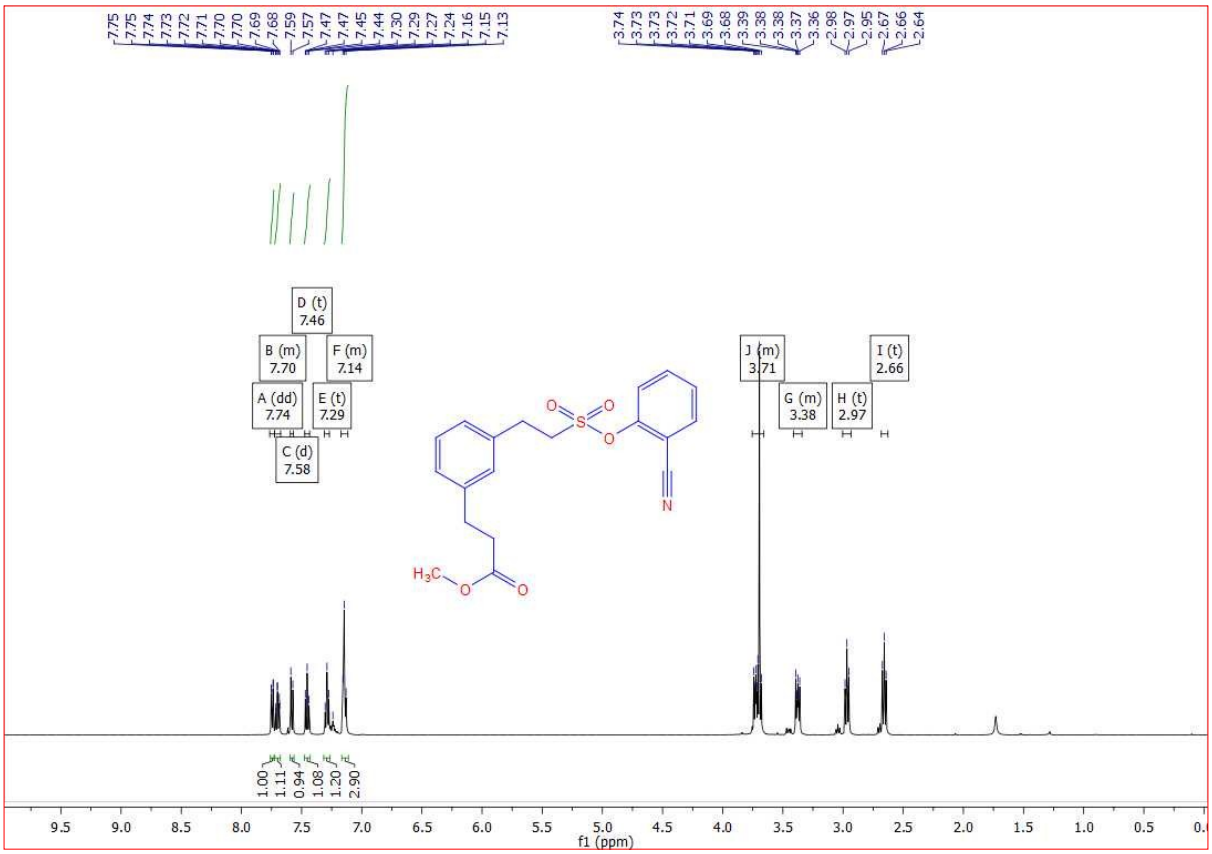


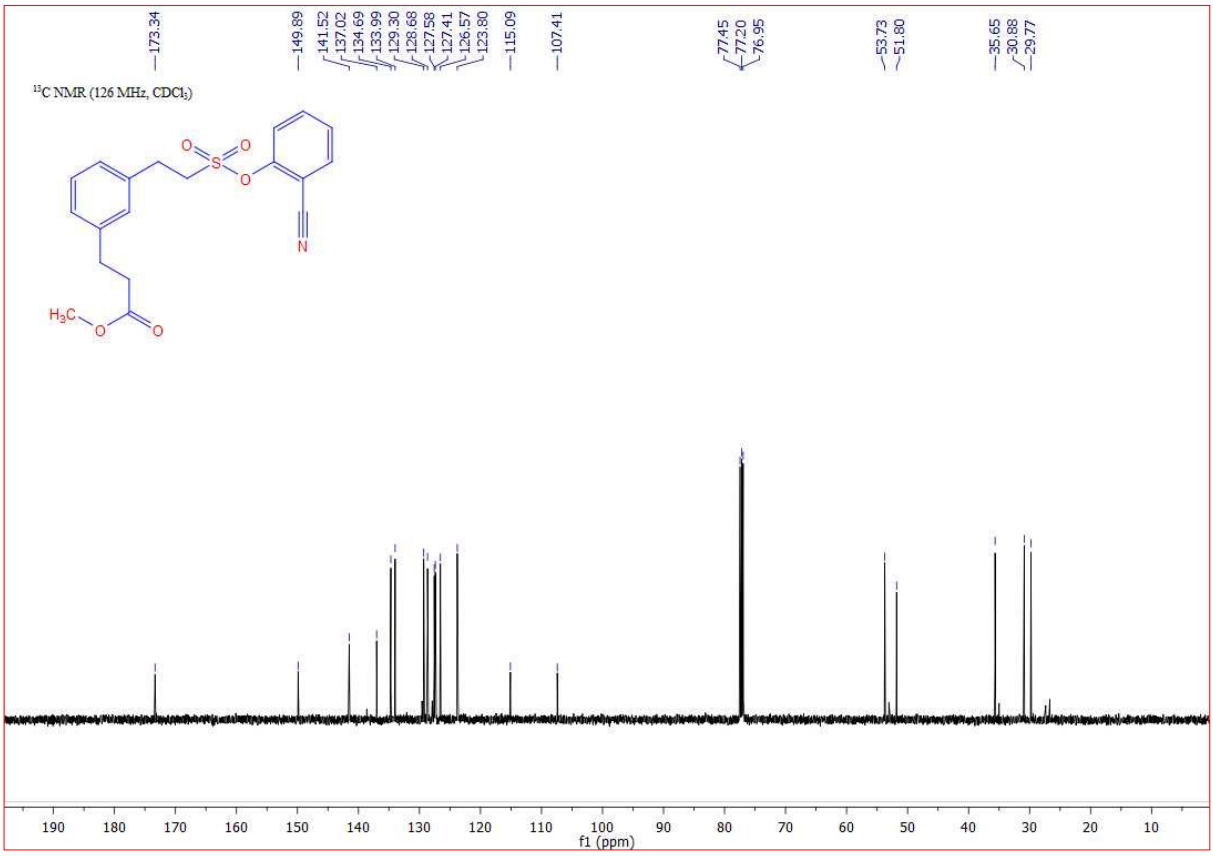


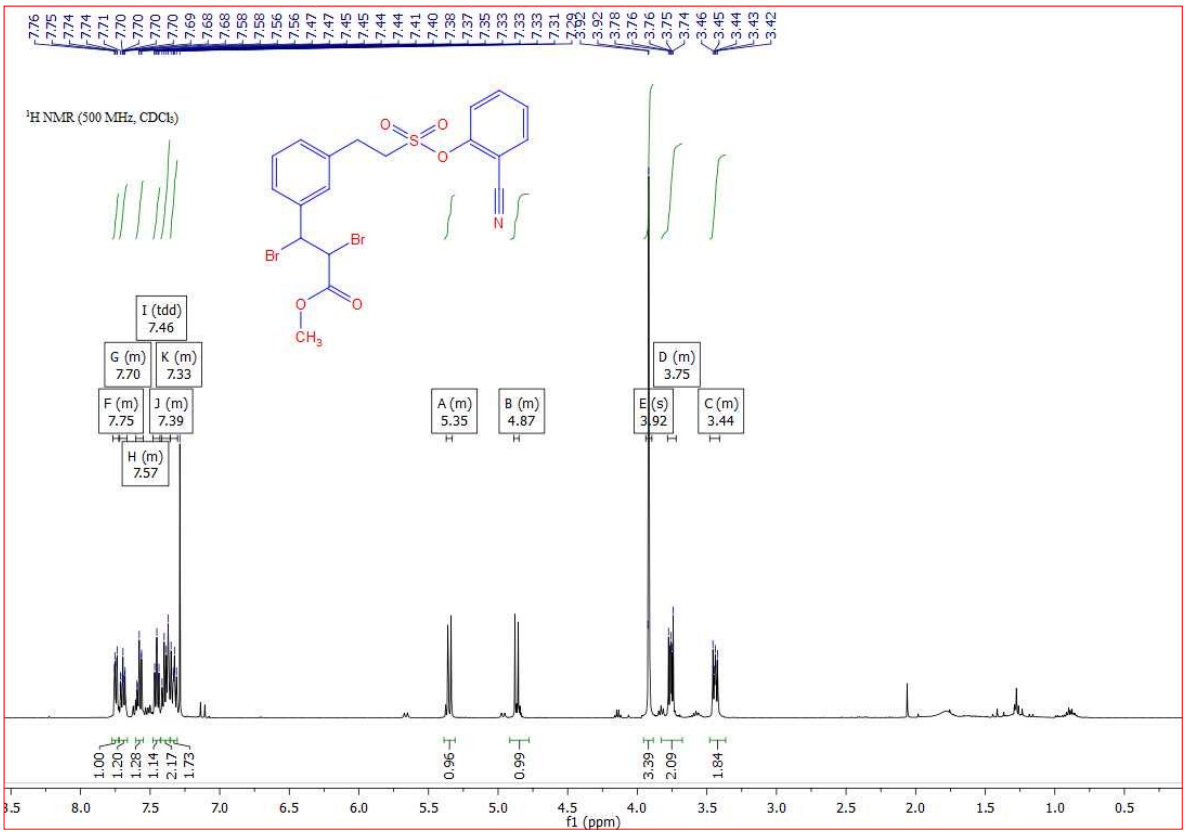

12.27
7.57
7.57
7.54
7.51
7.50
7.33
7.32
7.29
6.54
6.51
3.35
2.86
2.85
2.83
2.59
2.58
2.56
2.51
2.51
2.51
1H NMR (500 MHz, DMSO)
O
OH
O
OH
E (m)
7.29
C (m)
7.56
B (d)
7.50
D (m)
7.32
A (s)
12.27
G (t)
2.58
F (t)
2.85
2.14
2.09
1.02
1.00
0.96
1.00
1.95
2.07
13.5
12.5
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

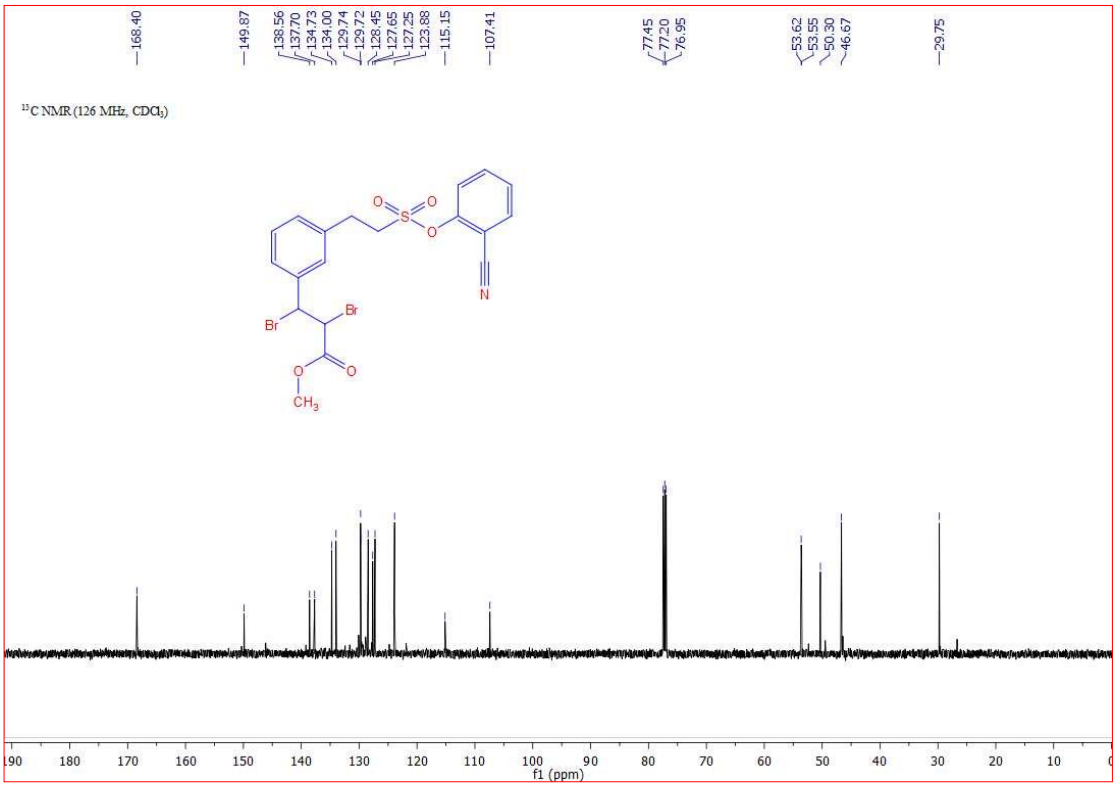

173.80
167.65
144.06
141.66
134.25
130.33
128.91
128.02
126.13
119.15
40.01
39.84
39.68
39.51
39.34
39.18
39.01
35.00
30.15
13C NMR (126 MHz, DMSO)
O
OH
13C NMR (126 MHz, DMSO)
O
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

Scheme 9


D (t) 7.46
B (m) 7.70
F (m) 7.14
A (dd) 7.74
E (t) 7.29
C (d) 7.58
J (m) 3.71
G (m) 3.38
H (t) 2.97
I (t) 2.66
f1 (ppm)


^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)


^{1}H NMR (500 MHz, CDCl$_3$)
I (tdd) 7.46
G (m) 7.70
K (m) 7.33
F (m) 7.75
J (m) 7.39
H (m) 7.57
A (m) 5.35
B (m) 4.87
D (m) 3.75
E (s) 3.92
C (m) 3.44
f1 (ppm)


^{13}C NMR (126 MHz, CDCl$_3$)
f1 (ppm)