

Supporting Information

Sulfonylpyrazole and pyrazole directed *ortho*-selective C–H functionalization/alkenylation and desulfenylative olefination of aryl(sulfonyl)pyrazoles

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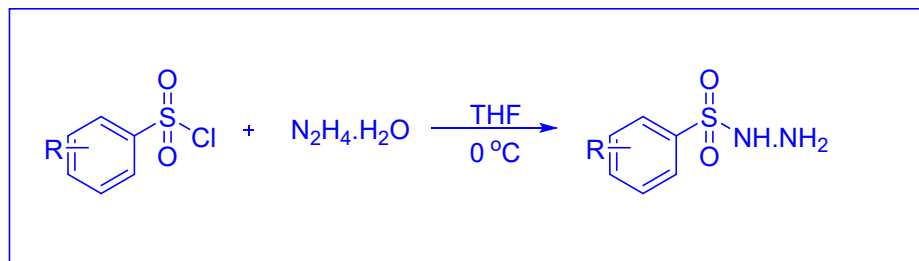
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General experimental section:

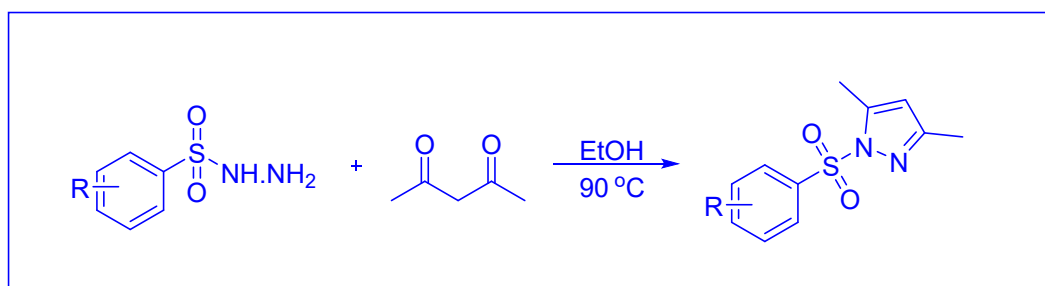
All reactions were performed in oven-dried glass apparatus. Solvents were distilled in the standard way, and commercial reagents were used without any purification. Analytical TLC was performed on 60 F254 plates, and visualized by exposure to ultraviolet light (UV-254 nm). Column chromatography was carried out with silica (60-120, 100-200 mesh). NMR spectra for characterization of compounds were recorded on Bruker Advance DPX FT-NMR 400 MHz instrument (^1H) at 400 MHz and (^{13}C) at 101 MHz respectively. ^{19}F NMR were recorded at 377 MHz. Chemical shifts (δ) are reported in ppm, using the residual solvent peak in CDCl_3 ($\delta\text{H} = 7.26$ and $\delta\text{C} = 77.16$ ppm) and DMSO-d_6 ($\delta\text{H} = 2.50$ and $\delta\text{C} = 39.52$ ppm) as internal reference and coupling constants (J) are given in hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-Resolution Mass Spectra (HRMS) were recorded using Waters XEVO-G2-XS-Q-TOF mass spectrometer. Melting points were recorded on BUCHI melting point M-560.

General Procedure for the synthesis of Sulfonyl hydrazide from Sulfonyl chloride:-



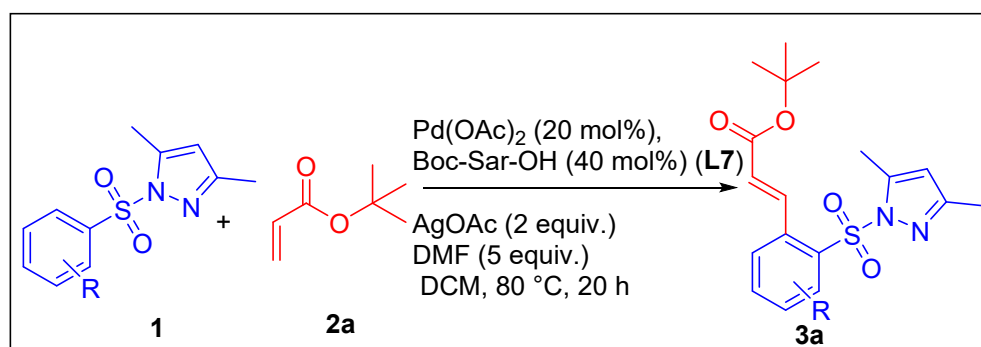
In an round bottom flask, benzenesulfonylchloride (500mg, 2.8mmol, 1.0 equiv) was dissolved in THF and then hydrazine hydrate (0.357 mL 7.14 mmol, 2.5 equiv) was added drop wise at 0 °C. The reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was then cooled to room temperature and extracted with ethyl acetate twice. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The resulting crude residue was used in the further step without any purification.

General Procedure for the synthesis Sulfonyl pyrazole from Sulfonyl hydrazide:-



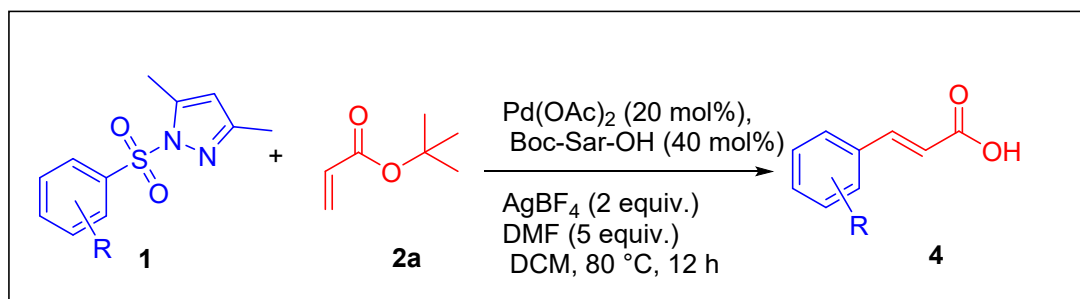
In an round bottom flask, equipped with a magnetic stir bar was added benzenesulfonylhydrazide (500mg, 2.9 mmol, 1.0 equiv), acetylacetone (0.436 mL 4.36 mmol, 1.5 equiv) and ethanol. The reaction mixture was then stirred at 90 °C for 3 h. The reaction mixture was cooled to room temperature and extracted with ethyl acetate twice. The organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated *in vacuo*. The resulting crude residue was subjected to silica gel column-chromatography by using EtOAc/hexane to afford the desired product.

General Procedure for the synthesis of alkenylated sulfonylpyrazole



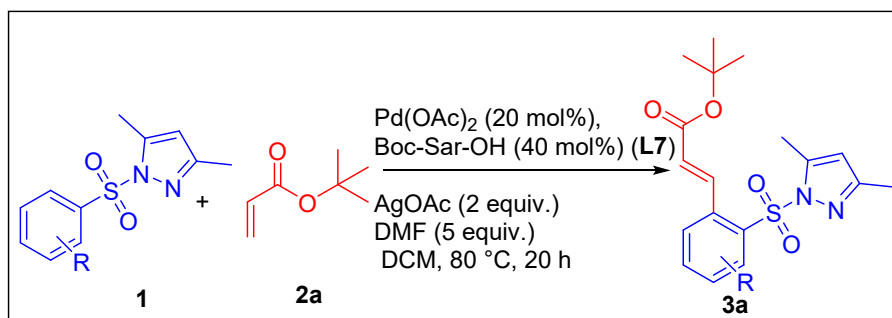
In a round bottom flask, benzenesulfonylpyrazole (100 mg, 0.4 mmol, 1.0 equiv), Pd(OAc)₂ (17.92 mg, 0.08 mmol, 20 mol%), BOC-SAR-OH (29.76 mg, 0.025 mmol, 0.4 equiv), AgOAc (132 mg, 0.8 mmol, 2 equiv.) and DMF (0.144 mL, 2.0 mmol, 5 equiv), *tert*-butyl acrylate (0.234 mL, 0.847 mmol, 2 equiv.) were dissolved in CH₂Cl₂ (2 mL) under air. The reaction mixture was then stirred at 80 °C for 20 h. The reaction mixture was cooled to room temperature and then diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent.

General Procedure for the synthesis of Cinnamic acid



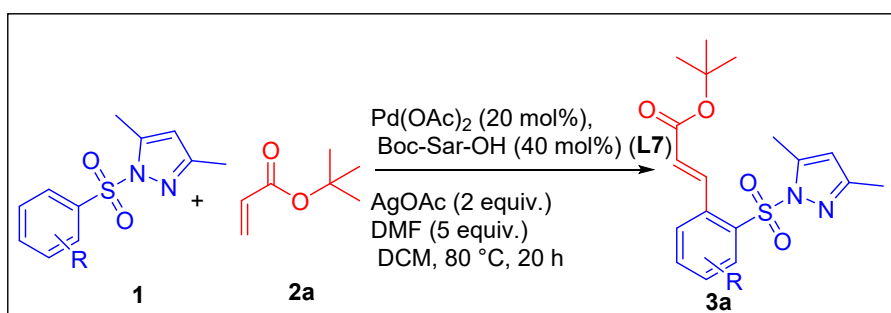
In a round bottom flask, benzenesulfonylpyrazole (100 mg, 0.4 mmol, 1.0 equiv), Pd(OAc)₂ (17.92 mg, 0.08 mmol, 20 mol%), BOC-SAR-OH (29.76 mg, 0.025 mmol, 0.4 equiv), AgBF₄ (155 mg, 0.8 mmol, 2 equiv) and DMF (0.144 mL, 2.0 mmol, 5 equiv), *tert*-butyl acrylate (0.234 mL, 0.847 mmol, 2 equiv.) were dissolved in CH₂Cl₂ (2 mL) under air. The reaction mixture was then stirred at 80 °C for 12 h. The reaction mixture was cooled to room temperature and then diluted with ethyl acetate and filtered through a small pad of Celite. The filtrate was concentrated *in vacuo* and purified by a silica gel packed flash chromatography column, using ethyl acetate/hexane as the eluent.

a) Table S1. Screening of Different Bases and Solvents



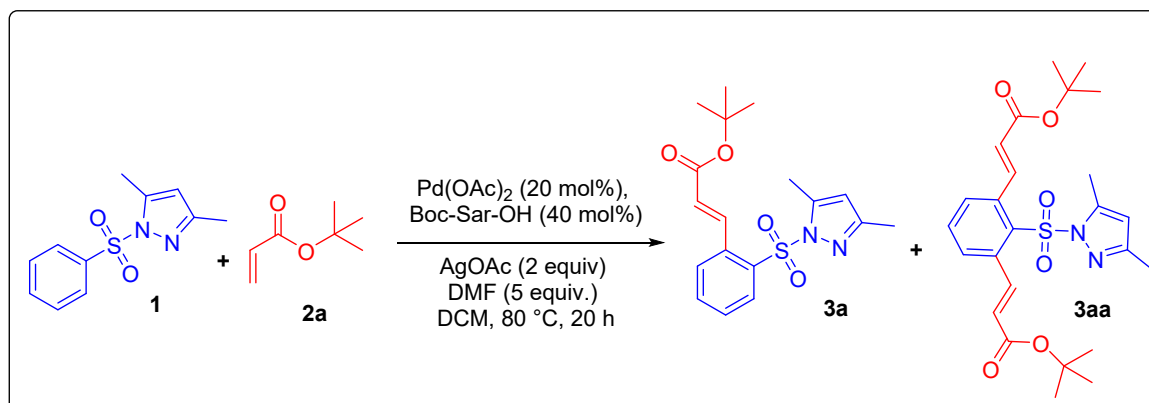
Entry	Catalyst	Temp. (°C)	Ligand	Oxidant	Base	Solvent	Yield (%) ^[b]	
							3a	3aa
1.	Pd(OAc) ₂	80 °C	L7	AgOAc	Na ₂ CO ₃	DCM	Nr	
2.	Pd(OAc) ₂	80 °C	L7	AgOAc	DMF	DMSO	traces	
3.	Pd(OAc) ₂	80 °C	L7	AgOAc	DMF	THF	10	
4.	Pd(OAc) ₂	80 °C	L7	AgOAc	DMF	Toluene	20	
5.	Pd(OAc) ₂	80 °C	L7	AgOAc	DMF	ACN	25	
6.	Pd(OAc) ₂	80 °C	L7	AgOAc	DMF	HFIP	45	
7.	Pd(OAc) ₂	80 °C	L7	AgOAc	DMF	DCE	50	

b) Table S2. Screening of Different Metal Catalysts



Entry	Catalyst	Temp. (°C)	Ligand	Oxidant	Base	Solvent	Yield (%) ^[b]	
							3a	3aa
1.	Cu(OAc) ₂ ·H ₂ O	80 °C	L7	AgOAc	DMF	DCM	nr	
2.	RuCl ₂	80 °C	L7	AgOAc	DMF	DCM	nr	
3.	[RuCl ₂ (p-cymene)] ₂	80 °C	L7	AgOAc	DMF	DCM	nr	
4.	[Rh(1,5-COD)Cl] ₂	80 °C	L7	AgOAc	DMF	DCM	nr	

C) Table S3. Optimization of Equivalence of Acrylate

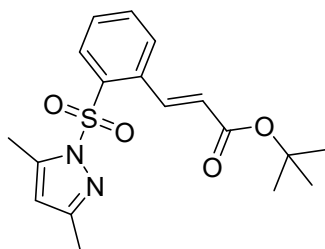


^aReaction conditions: **1** (0.423 mmol, 1 equiv.), **2a** (6 equiv., 1.694 mmol), $\text{Pd}(\text{OAc})_2$ (20 mol %, 0.08 mmol), Boc-Sar-OH (40 mol%, 0.025 mmol), AgOAc (2 equiv., 0.8 mmol), DMF (5 equiv., 2.0 mmol), DCM (4 mL), 80 °C, 20 h. ^b Isolated yields.

Entry	Catalyst	Equiv. 2a	Ligand	Oxidant	Base	Solvent	Yield (%) ^[b]	
							3a	3aa
1.	$\text{Pd}(\text{OAc})_2$	1	L7	AgOAc	DMF	DCM	15	-
2.	$\text{Pd}(\text{OAc})_2$	2	L7	AgOAc	DMF	DCM	35	-
3.	$\text{Pd}(\text{OAc})_2$	3	L7	AgOAc	DMF	DCM	60	traces
4.	$\text{Pd}(\text{OAc})_2$	4	L7	AgOAc	DMF	DCM	70	05
5.	$\text{Pd}(\text{OAc})_2$	5	L7	AgOAc	DMF	DCM	50	40
6.	$\text{Pd}(\text{OAc})_2$	6	L7	AgOAc	DMF	DCM	30	60

Spectroscopic Characterization Data of Compounds:-

tert-butyl (E)-3-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)phenyl)acrylate (3a)



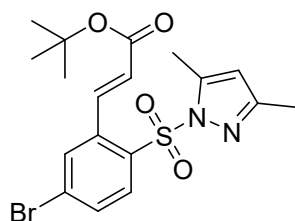
The compound **3a** was purified by column chromatography on silica gel; 108 mg, 70% yield; white solid; m.p. = 113-115 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.24 (dd, *J* = 15.70, 4.63 Hz, 1H), 8.13 (dd, *J* = 7.81, 3.60 Hz, 1H), 7.62-7.51 (m, 3H), 6.11 (dd, *J* = 15.78, 4.85 Hz, 1H), 5.87 (d, *J* = 3.48 Hz, 1H), 2.56 (d, *J* = 4.25 Hz, 3H), 2.13 (d, *J* = 4.17 Hz, 3H), 1.52 (d, *J* = 4.80 Hz, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 165.0, 153.5, 145.2, 139.0, 136.8, 135.3, 134.4, 130.3, 129.6, 129.1, 125.7, 110.2, 81.1, 28.2, 13.9, 13.4 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₂N₂O₄NaS [M+Na]⁺: 385.1198, found: 385.1206.

tert-butyl (E)-3-(5-bromo-2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)phenyl)acrylate(3b)



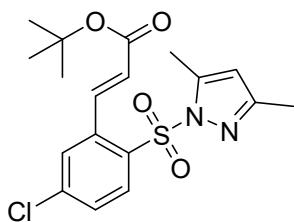
The compound **3b** was purified by column chromatography on silica gel; 89 mg, 63% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 7.84-7.82 (m, 2H), 7.68-7.66 (m, 2H), 7.37 (d, *J* = 16.29 Hz, 1H), 6.06 (d, *J* = 16.20 Hz, 1H), 2.59 (s, 3H), 2.34 (s, 3H), 1.50 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.3, 152.9, 143.7, 136.8, 132.9, 132.5, 130.0, 129.3, 121.1, 117.9, 80.9, 28.2, 14.7, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₂N₂O₄SBr [M+H]⁺: 441.0484, found: 441.0478.

tert-butyl (*E*)-3-(5-chloro-2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)phenyl)acrylate (**3c**)



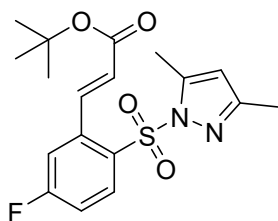
The compound **3c** was purified by column chromatography on silica gel; 94 mg, 64% yield; white solid; m.p. = 115-117 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.93-7.89(m, 2H), 7.52-7.48 (m, 2H), 7.37 (d, *J* = 16.18 Hz, 1H), 6.05 (d, *J* = 16.21 Hz, 1H), 2.59 (s, 3H), 2.33 (s, 3H), 1.50 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.3, 152.8, 143.7, 141.3, 136.2, 132.5, 129.9, 129.3, 121.1, 117.9, 80.9, 28.2, 14.7, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₂N₂O₄SCl [M+H]⁺: 397.0989, found: 397.0984.

tert-butyl (*E*)-3-(2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-5-fluorophenyl)acrylate (**3d**)



The compound **3d** was purified by column chromatography on silica gel; 90 mg, 60% yield; white solid; m.p. = 136-140 °C.

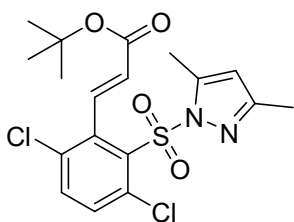
¹H NMR (400 MHz, CDCl₃): δ 8.02-7.99(m, 2H), 7.38 (d, *J* = 16.24 Hz, 1H), 7.24-7.19(m, 2H), 6.06 (d, *J* = 16.24 Hz, 1H), 2.60 (s, 3H), 2.35 (s, 3H), 1.51 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.3, 152.7, 143.7, 132.6, 130.9 (d, *J* = 9.87 Hz), 121.0, 117.8, 117.1, 116.8, 80.9, 28.3, 14.7, 11.7 ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -101.4 (s) ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₂N₂O₄FS [M+H]⁺: 381.1284, found: 381.1281.

tert-butyl (*E*)-3-(3,6-dichloro-2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)phenyl)acrylate (**3e**)



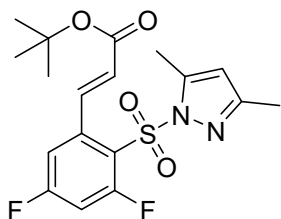
The compound **3e** was purified by column chromatography on silica gel; 88 mg, 62% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, J = 2.48 Hz, 1H), 7.55(dd, J = 8.52, 2.49 Hz, 1H), 7.47-7.41 (m, 2H), 6.10 (d, J = 16.22 Hz, 1H), 2.71 (s, 3H), 2.31 (s, 3H), 1.53 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.3, 153.0, 145.9, 136.8, 135.4, 133.8, 133.2, 132.5, 132.2, 131.1, 121.1, 116.9, 80.9, 28.3, 14.7, 12.2 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₁N₂O₄SCl₂ [M+H]⁺: 431.0599, found: 431.0594.

tert-butyl (*E*)-3-(2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-3,5-difluorophenyl)acrylate (**3f**)



The compound **3f** was purified by column chromatography on silica gel; 85 mg, 58% yield; white solid; m.p. = 128-130 °C.

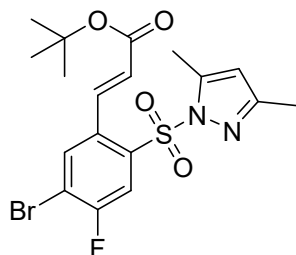
¹H NMR (400 MHz, CDCl₃): δ 8.17-8.12 (m, 1H), 7.43 (d, J = 16.24 Hz, 1H), 7.10-7.06 (m, 1H), 6.94-6.89 (m, 1H), 6.09 (d, J = 16.25 Hz, 1H), 2.67 (s, 3H), 2.31 (s, 3H), 1.52 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.3, 153.0, 145.2, 133.3 (d, J = 11.04 Hz), 132.6, 121.1, 117.4, 112.7, 112.6, 106.4, 106.2, 105.9, 80.9, 28.3, 14.7, 11.7 (d, J = 3.48 Hz) ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -96.4 to -96.5, -103.8 to -103.9 (m) ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₁N₂O₄F₂S [M+H]⁺: 399.1190, found: 399.1183.

tert-butyl(*E*)-3-(5-bromo-2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-4-fluorophenyl)acrylate (**3g**)



The compound **3g** was purified by column chromatography on silica gel; 85 mg, 61% yield; white solid; m.p. = 142-144 °C.

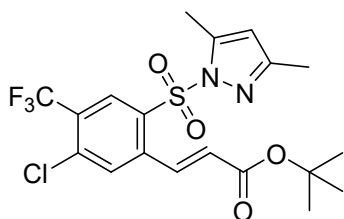
¹H NMR (400 MHz, CDCl₃): δ 7.76-7.71 (m, 2H), 7.65 (d, *J* = 8.29 Hz, 1H), 7.38 (dd, *J* = 16.24, 4.28 Hz, 1H), 6.07 (dd, *J* = 11.86, 4.42 Hz, 1H), 2.60 (s, 3H), 2.35 (s, 3H), 1.50 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.2, 158.9 (d, *J* = 253.72 Hz), 153.3, 143.8, 138.5 (d, *J* = 6.24 Hz), 135.0, 132.3, 124.5 (d, *J* = 4.01 Hz), 121.4, 118.1, 117.2 (d, *J* = 20.77 Hz), 116.2 (d, *J* = 25.95 Hz), 81.0, 28.2, 14.7, 11.7 ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -101.6 (s) ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₁N₂O₄FSBr [M+H]⁺: 459.0389, found: 459.0386.

tert-butyl(*E*)-3-(5-chloro-2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-4-(trifluoromethyl)phenyl)acrylate (**3h**)



The compound **3h** was purified by column chromatography on silica gel; 73 mg, 53% yield; white solid; m.p. = 144-146 °C.

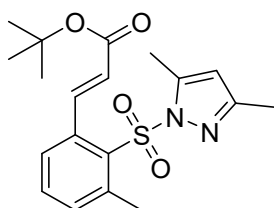
¹H NMR (400 MHz, CDCl₃): δ 8.28 (d, *J* = 2.04 Hz, 1H), 8.09 (dd, *J* = 8.49, 2.23 Hz, 1H), 7.70 (d, *J* = 8.49 Hz, 1H), 7.37 (d, *J* = 16.24 Hz, 1H), 6.07 (d, *J* = 16.22 Hz, 1H), 2.62 (s, 3H), 2.34 (s, 3H), 1.50 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.2, 153.5, 143.9, 139.4, 136.9, 132.9, 132.2, 130.0 (q, *J* = 33.20 Hz), 127.4 (q, *J* = 5.38 Hz), 123.1, 121.6, 120.4, 118.2, 81.0, 28.2, 14.7, 11.7 ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -63.1 (s) ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₁N₂O₄F₃SCl [M+H]⁺: 465.0863, found: 465.0858.

tert-butyl (*E*)-3-(2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-3-methylphenyl)acrylate (**3i**)



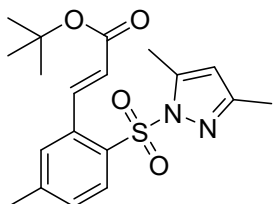
The compound **3i** was purified by column chromatography on silica gel; 107 mg, 71% yield; white solid; m.p. = 136-140°C.

¹H NMR (400 MHz, CDCl₃): δ 7.84 (d, *J* = 8.30 Hz, 2H), 7.37 (d, *J* = 16.13 Hz, 1H), 7.31 (d, *J* = 8.02 Hz, 2H), 6.04 (d, *J* = 16.24 Hz, 1H), 2.58 (s, 3H), 2.41 (s, 3H), 2.34 (s, 3H), 1.49 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.4, 152.3, 145.8, 143.6, 134.9, 130.1, 127.9, 120.6, 117.5, 80.8, 28.2, 21.8, 14.7, 11.6 ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₅N₂O₄S [M+H]⁺: 377.1535, found: 377.1529.

tert-butyl (*E*)-3-(2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-5-methylphenyl)acrylate (**3j**)



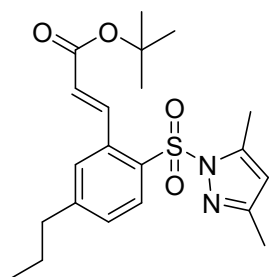
The compound **3j** was purified by column chromatography on silica gel; 106 mg, 70% yield; white solid; m.p. = 136-140 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 8.34 Hz, 2H), 7.38 (d, *J* = 16.22 Hz, 1H), 7.32(d, *J* = 16.08 Hz, 2H), 6.04 (d, *J* = 16.28 Hz, 1H), 2.59 (s, 3H), 2.42 (s, 3H), 2.34 (s, 3H), 1.50 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.4, 152.3, 145.8, 143.6, 135.0, 132.8, 130.1, 127.9, 120.6, 117.6, 80.8, 28.3, 21.8, 14.7, 11.6 ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₅N₂O₄S [M+H]⁺: 377.1535, found: 377.1536.

tert-butyl (*E*)-3-(2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-5-propylphenyl)acrylate (**3k**)



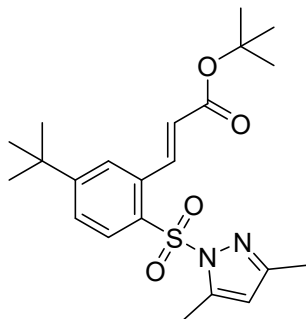
The compound **3k** was purified by column chromatography on silica gel; 98 mg, 67% yield; white solid; m.p. = 85-90 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.86 (d, *J* = 8.26 Hz, 2H), 7.38 (d, *J* = 16.15 Hz, 1H), 7.32 (d, *J* = 8.17 Hz, 2H), 6.05 (d, *J* = 16.33 Hz, 1H), 2.64 (t, *J* = 7.66 Hz, 2H), 2.59 (s, 3H), 2.35 (s, 3H), 1.67-1.61 (m, 2H), 1.50 (s, 9H), 0.93 (t, *J* = 7.32 Hz, 3H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.4, 152.3, 150.4, 143.6, 135.1, 132.8, 129.6, 127.9, 120.6, 117.6, 80.8, 38.1, 28.3, 24.1, 14.7, 13.8, 11.6 ppm

HRMS (ESI) m/z: calcd. for C₂₁H₂₉N₂O₄S [M+H]⁺: 405.1848, found: 405.1845.

tert-butyl (*E*)-3-(5-(*tert*-butyl)-2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)phenyl)acrylate (**3l**)



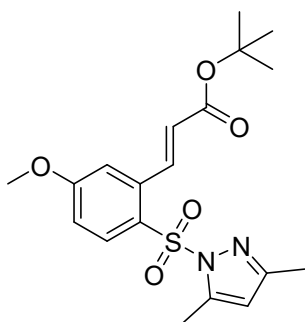
The compound **3l** was purified by column chromatography on silica gel; 98 mg, 68% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 7.88 (d, *J* = 8.67 Hz, 2H), 7.53 (d, *J* = 8.67 Hz, 2H), 7.39 (d, *J* = 16.21 Hz, 1H), 6.05 (d, *J* = 16.46 Hz, 1H), 2.59 (s, 3H), 2.36 (s, 3H), 1.50 (s, 9H), 1.32 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.4, 158.6, 134.8, 132.8, 129.2, 127.7, 126.6, 120.6, 80.8, 35.5, 31.0, 28.3, 14.8, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₂₂H₃₁N₂O₄S [M+H]⁺: 419.2005, found: 419.2000.

tert-butyl (*E*)-3-(2-((3,5-dimethyl-1*H*-pyrazol-1-yl)sulfonyl)-5-methoxyphenyl)acrylate (**3m**)



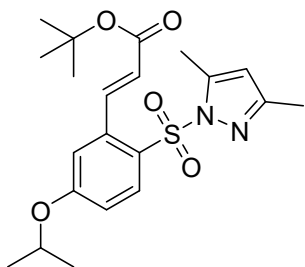
The compound **3m** was purified by column chromatography on silica gel; 98 mg, 68% yield; white semi solid.

¹H NMR (400 MHz, DMSO-*d*₆): δ 8.17 (d, *J* = 15.81 Hz, 1H), 8.01 (d, *J* = 8.96 Hz, 1H), 7.38 (d, *J* = 2.60 Hz, 1H), 7.19 (dd, *J* = 8.97, 2.61 Hz, 1H), 6.49 (d, *J* = 15.67 Hz, 1H), 6.13 (s, 1H), 3.91 (s, 3H), 2.47 (s, 3H), 2.05 (s, 3H), 1.48 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ 165.1, 164.3, 153.0, 144.5, 138.8, 136.6, 132.9, 130.6, 127.7, 125.7, 116.2, 114.6, 110.8, 81.0, 56.6, 28.2, 13.8, 13.2 ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₅N₂O₅S [M+H]⁺: 393.1484, found: 393.1490.

tert-butyl (*E*)-3-(5-isopropoxy-2-((5-methyl-1*H*-pyrazol-1-yl)sulfonyl)phenyl)acrylate (**3n**)



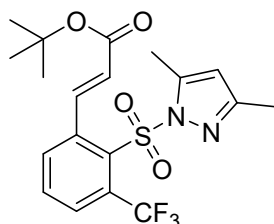
The compound **3n** was purified by column chromatography on silica gel; 98 mg, 69% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 7.89-7.87 (m, 2H), 7.39 (d, *J* = 16.22 Hz, 1H), 6.94-6.92 (m, 2H), 6.04 (d, *J* = 16.21 Hz, 1H), 4.66-4.59 (m, 1H), 2.59 (s, 3H), 2.35 (s, 3H), 1.50 (s, 9H), 1.35 (d, *J* = 6.05 Hz, 6H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.5, 163.0, 152.0, 143.4, 132.9, 130.3, 128.5, 120.4, 117.4, 115.8, 80.8, 70.8, 28.3, 21.9, 14.7, 11.6 ppm

HRMS (ESI) m/z: calcd. for C₂₁H₂₉N₂O₅S [M+H]⁺: 421.1797, found: 421.1789.

tert-butyl(E)-3-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)-3(trifluoromethyl)phenyl)acrylate
(3o)



The compound **3o** was purified by column chromatography on silica gel; 79 mg, 56% yield; white solid; m.p. = 148-150 °C.

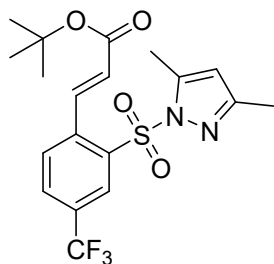
¹H NMR (400 MHz, CDCl₃): δ 8.24-8.21 (m, 1H), 7.91-7.88 (m, 1H), 7.80-7.78 (m, 2H), 7.44 (d, *J* = 16.21 Hz, 1H), 6.09 (d, *J* = 16.27 Hz, 1H), 2.66 (s, 3H), 2.30 (s, 3H), 1.52 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.3, 152.4, 145.1, 136.6, 134.4, 133.2, 132.6 (2C), 128.6 (q, *J* = 6.17 Hz), 128.3, 123.7, 121.0, 117.0, 80.8, 28.3, 14.6, 11.6 ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -58.0 (s) ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₂N₂O₄F₃S [M+H]⁺: 431.1252, found: 431.1242.

tert-butyl(E)-3-(2-((5-methyl-1H-pyrazol-1-yl)sulfonyl)-4-(trifluoromethyl)phenyl)acrylate
(3p)



The compound **3p** was purified by column chromatography on silica gel; 79 mg, 56% yield; white solid; m.p. = 90-92 °C.

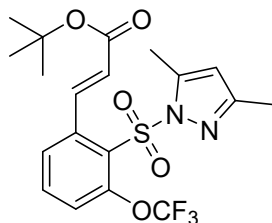
¹H NMR (400 MHz, CDCl₃): δ 8.26 (s, 1H), 8.18 (d, *J* = 7.91 Hz, 1H), 7.91 (d, *J* = 7.82 Hz, 1H), 7.71 (t, *J* = 7.93 Hz, 1H), 7.38 (d, *J* = 16.26 Hz, 1H), 6.07 (d, *J* = 16.23 Hz, 1H), 2.63 (s, 3H), 2.35 (s, 3H), 1.51 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.2, 153.3, 143.9, 139.1, 132.4, 132.3, 132.1, 131.2, 131.1 (d, *J* = 3.48 Hz), 130.4, 125.0 (d, *J* = 3.65 Hz), 121.4, 118.1, 80.9, 28.3, 14.7, 11.7 ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -62.8 (s) ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₂N₂O₄SF₃ [M+H]⁺: 431.1252, found: 431.1245.

tert-butyl(E)-3-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)-3-(trifluoromethoxy)phenyl)acrylate (3q)



The compound **3q** was purified by column chromatography on silica gel; 77 mg, 55% yield; white semi solid.

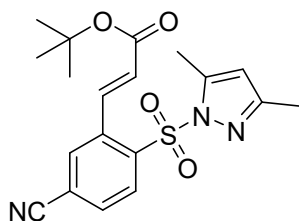
¹H NMR (400 MHz, CDCl₃): δ 8.28-8.25 (m, 1H), 7.74-7.69 (m, 1H), 7.52-7.43 (m, 2H), 7.38 (d, *J* = 8.33 Hz, 1H), 6.12-6.07 (m, 1H), 2.68 (s, 3H), 2.29 (s, 3H), 1.53 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.4, 152.7, 146.5, 145.3, 136.4, 132.4 (d, *J* = 49.08 Hz), 129.7, 126.7, 121.4, 120.9, 119.9 (d, *J* = 2.04 Hz), 118.8, 117.0, 80.9, 28.3, 14.6, 11.6 ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -56.4 (s) ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₂N₂O₅F₃S [M+H]⁺: 447.1202, found: 447.1195.

tert-butyl (E)-3-(5-cyano-2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)phenyl)acrylate (3r)



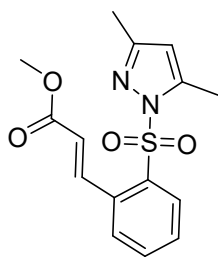
The compound **3r** was purified by column chromatography on silica gel; 77 mg, 52% yield; white solid; m.p. = 175-178 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.09 (d, *J* = 8.66 Hz, 2H), 7.83 (d, *J* = 8.68 Hz, 2H), 7.36 (d, *J* = 16.24 Hz, 1H), 6.06 (d, *J* = 16.26 Hz, 1H), 2.60 (s, 3H), 2.33 (s, 3H), 1.50 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 166.1, 153.5, 143.9, 141.7, 133.2, 132.1, 128.5, 121.6, 130.4, 118.2 (d, *J* = 12.07 Hz), 116.9, 81.0, 28.2, 14.7, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₉H₂₂N₃O₄S [M+H]⁺: 388.1331, found: 388.1334.

methyl (E)-3-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)phenyl)acrylate(3s)



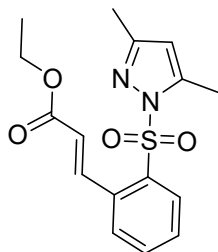
The compound **3s** was purified by column chromatography on silica gel; 128 mg, 74% yield; yellow semi solid.

¹H NMR (400 MHz, CDCl₃) : δ 8.00-7.97 (m, 2H), 7.67-7.63 (m, 1H), 7.57-7.53 (m, 2H), 7.48 (d, J = 16.26, 1H), 6.13 (d, J = 16.37 Hz, 1H), 3.78 (s, 3H), 2.62 (s, 3H), 2.35 (s, 3H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.4, 152.4, 144.1, 137.9, 134.6, 134.0, 129.6, 127.9, 118.4, 117.5, 51.9, 14.8, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₅H₁₇N₂O₄S [M+H]⁺:321.0909, found:321.0913.

ethyl (E)-3-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)phenyl)acrylate(3t)



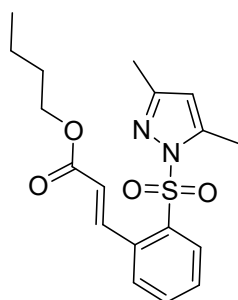
The compound **3t** was purified by column chromatography on silica gel; 96 mg, 68% yield; white solid; m.p. = 138-140 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.00-7.97 (m, 2H), 7.68-7.63 (m, 1H), 7.57-7.53 (m, 2H), 7.48 (d, J =16.25 Hz, 1H), 6.13 (d, J =16.24 Hz, 1H), 4.24 (d, J =7.13 Hz, 2H), 2.62 (s, 3H), 2.36 (s, 3H), 1.32 (t, J =7.11 Hz, 3H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.0, 152.4, 144.0, 137.9, 134.5, 133.8, 129.5, 127.9, 118.9, 117.6, 60.7, 14.7, 14.4, 11.7 ppm

HRMS (ESI) m/z: calcd.for C₁₆H₁₉N₂O₄S [M+H]⁺: 335.1066, found: 335.1072.

butyl (E)-3-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)phenyl)acrylate(3u)



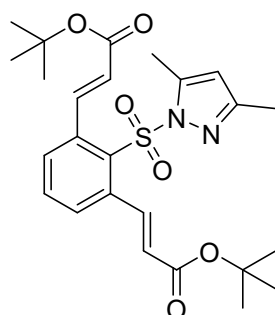
The compound **3u** was purified by column chromatography on silica gel; 153 mg, 62% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 7.98-7.96 (m, 2H), 7.64-7.62 (m, 1H), 7.56-7.52 (m, 2H), 7.47 (d, $J = 16.19$ Hz, 1H), 6.12 (d, $J = 16.25$ Hz, 1H), 4.17 (t, $J = 6.69$ Hz, 2H), 2.61 (s, 3H), 2.35 (s, 3H), 1.69-1.62 (m, 2H), 1.45-1.36 (m, 2H), 0.94 (t, $J = 7.36$ Hz, 3H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.1, 152.4, 143.9, 137.9, 134.5, 133.7, 129.5, 127.9, 118.9, 117.6, 64.6, 30.8, 19.2, 14.7, 13.8, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₃N₂O₄S [M+H]⁺: 363.1379, found: 363.1381.

di-tert-butyl 3,3'-(2-((3,5-dimethyl-1H-pyrazol-1-yl)sulfonyl)-1,3-phenylene)(2E,2'E)-diacrylate (3aa)



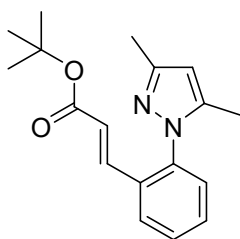
The compound **3aa** was purified by column chromatography on silica gel; 110 mg, 53% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 8.30 (d, $J = 15.75$, 2H), 7.60-7.56 (m, 1H), 7.49 (d, $J = 7.81$, 2H), 6.03 (d, $J = 15.75$, 2H), 5.84 (s, 1H), 2.60 (s, 3H), 2.11 (s, 3H), 1.52 (s, 18H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 165.2, 153.5, 145.2, 141.8, 138.4, 135.1, 133.9, 131.0, 130.8, 125.0, 109.8, 81.0, 28.2, 13.9, 13.4 ppm

HRMS (ESI) m/z: calcd. for C₂₅H₃₃N₂O₆S [M+H]⁺: 489.2059, found: 489.2057.

tert-butyl (*E*)-3-(2-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)acrylate (**4a**)



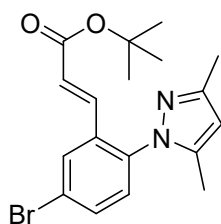
The compound **4a** was purified by column chromatography on silica gel; 128 mg, 74% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 7.59 (d, J = 16.14 Hz, 1H), 7.50-7.46 (m, 2H), 7.41-7.38 (m, 3H), 6.06 (d, J = 16.16 Hz, 1H), 2.43 (s, 3H), 2.38 (s, 3H), 1.54 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.4, 149.2, 140.2, 139.1, 134.9, 129.3, 128.2, 125.3, 116.8, 114.8, 80.3, 28.4, 14.0, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₃N₂O₂ [M+H]⁺: 299.1760, found: 299.1760.

tert-butyl (*E*)-3-(5-bromo-2-(3,5-dimethyl-1*H*-pyrazol-1-yl)phenyl)acrylate (**4b**)



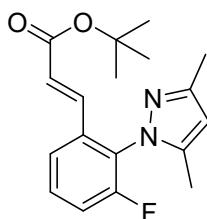
The compound **4b** was purified by column chromatography on silica gel; 101 mg, 67% yield; white semi solid.

¹H NMR (400 MHz, CDCl₃): δ 7.61-7.55 (m, 3H), 7.29 (d, J = 8.64 Hz, 2H), 6.06 (d, J = 16.18 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 1.54 (s, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.3, 149.5, 140.1, 138.2, 134.5, 132.4, 126.6, 121.8, 117.3, 115.2, 80.4, 28.4, 14.0, 11.7 ppm

HRMS (ESI) m/z: calcd. for C₁₈H₂₂N₂O₂Br [M+H]⁺: 377.0865, found: 377.0866.

tert-butyl (*E*)-3-(2-(3,5-dimethyl-1*H*-pyrazol-1-yl)-3-fluorophenyl)acrylate (**4c**)



The compound **4c** was purified by column chromatography on silica gel; 106 mg, 64% yield; white semi solid.

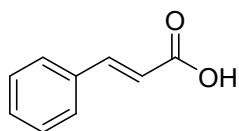
¹H NMR (400 MHz, CDCl₃): δ 7.61-7.56 (m, 1H), 7.45-7.43 (m, 2H), 7.30-7.27 (m, 1H), 7.24-7.21 (m, 1H), 6.06 (dd, *J* = 16.20, 3.33 Hz, 1H), 2.43 (d, *J* = 3.34 Hz, 3H), 2.27 (d, *J* = 1.28 Hz, 3H), 1.54 (d, *J* = 3.35 Hz, 9H) ppm

¹³C{¹H} NMR (101 MHz, CDCl₃): δ 167.3, 158.0, 155.5, 149.9, 142.1, 134.7, 130.6 (d, *J* = 7.74 Hz), 129.1, 127.0 (d, *J* = 11.91 Hz), 125.0 (d, *J* = 3.95 Hz), 117.1, 116.7 (d, *J* = 19.99 Hz), 114.3, 80.3, 28.4, 14.0, 10.9 (d, *J* = 3.91 Hz) ppm

¹⁹F NMR (377 MHz, CDCl₃): δ -121.4 (s) ppm

HRMS (ESI)m/z: calcd. for C₁₈H₂₂N₂O₂F [M+H]⁺: 317.1665, found: 317.1664.

*Cinnamic acid (5a)*¹

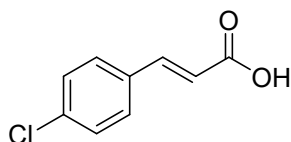


The compound **5a** was purified by column chromatography on silica gel, 110 mg, 53% yield; white semi solid.

¹H NMR (400 MHz, DMSO-*d*₆): δ 7.68-7.66 (m, 2H), 5.78 (d, *J* = 16.03 Hz, 1H), 7.42-7.40 (m, 3H), 6.52 (d, *J* = 16.17 Hz, 1H) ppm

¹³C{¹H} NMR (101 MHz, DMSO-*d*₆): δ 168.2, 144.4, 134.7, 130.8, 129.5, 128.7, 119.8 ppm

(E)-3-(4-chlorophenyl)acrylic acid (5b)

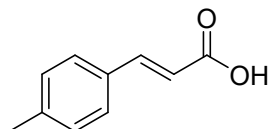


The compound **5b** was purified by column chromatography on silica gel; 110 mg, 53% yield; white semi solid.

¹H NMR (400 MHz, DMSO-d₆): δ 6.83 (d, *J* = 15.99 Hz, 1H), 6.80-6.76 (m, 2H), 6.62-6.58 (m, 2H), 5.68 (d, *J* = 16.00 Hz, 1H) ppm

¹³C{¹H} NMR (101 MHz, DMSO-d₆): δ 161.1, 135.7, 128.1, 125.5, 121.6, 121.1, 111.2 ppm

(E)-3-(*p*-tolyl)acrylic acid (**5c**)

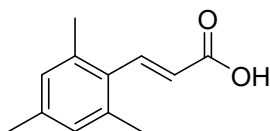


The compound **5c** was purified by column chromatography on silicagel; 45mg, 67% yield; white semi solid.

¹H NMR (400 MHz, DMSO-d₆): δ 7.58-7.53 (m, 3H), 7.23 (d, *J* = 7.96 Hz, 2H), 6.46 (d, *J* = 16.01 Hz, 1H), 2.32 (s, 3H) ppm

¹³C{¹H} NMR (101 MHz, DMSO-d₆): δ 168.1, 144.4, 140.6, 131.9, 129.9, 128.6, 118.5, 21.4 ppm

(E)-3-mesitylacrylic acid (**5d**)

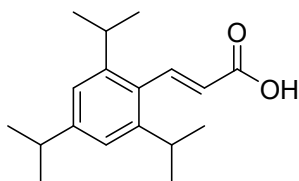


The compound **5d** was purified by column chromatography on silica gel; 46 mg, 70% yield; white semi solid.

¹H NMR (400 MHz, DMSO-d₆): δ 7.67 (d, *J* = 16.36 Hz, 1H), 6.90 (s, 2H), 6.00 (d, *J* = 16.35 Hz, 1H), 2.25 (s, 6H), 2.22 (s, 3H) ppm

¹³C{¹H} NMR (101 MHz, DMSO-d₆): δ 168.0, 142.6, 138.3, 136.9, 131.0, 129.5, 124.4, 21.2 (2) ppm

(E)-3-(2,4,6-triisopropylphenyl)acrylic acid (**5e**)

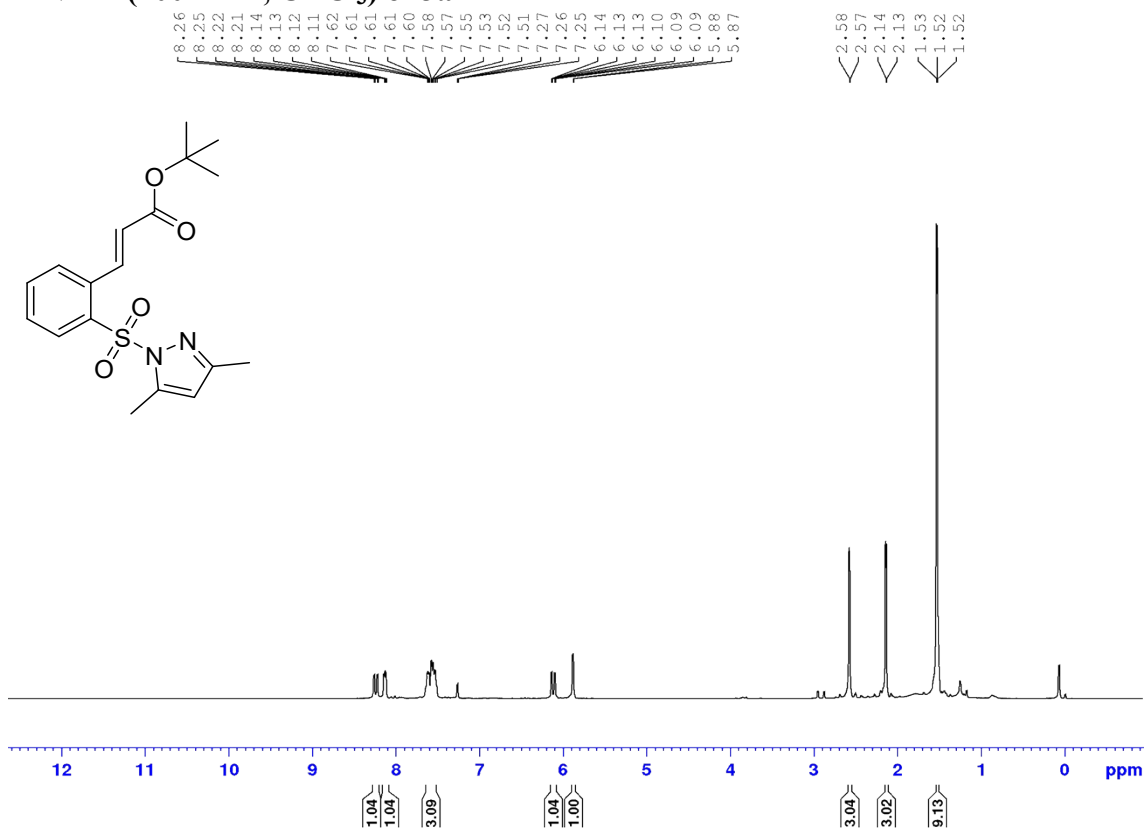


The compound **5e** was purified by column chromatography on silica gel; 55 mg, 72% yield; white semi solid.

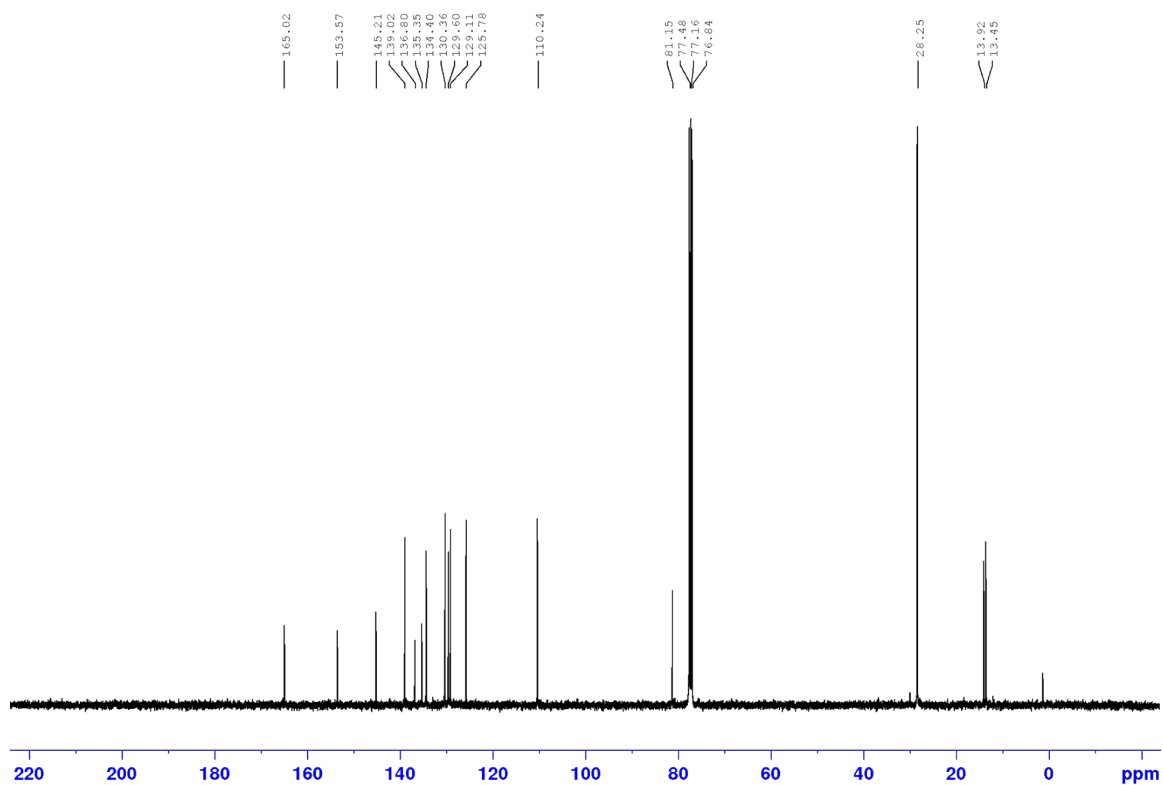
^1H NMR (400 MHz, DMSO- d_6): δ 7.77 (d, J = 16.26 Hz, 1H), 7.03 (s, 2H), 5.85 (d, J = 16.26 Hz, 1H), 3.05-2.98 (m, 2H), 2.89-2.82 (m, 1H), 1.19 (d, J = 6.96 Hz, 6H), 1.14 (d, J = 6.84 Hz, 12H) ppm

$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO- d_6): δ 167.3, 148.8, 146.1, 143.9, 130.5, 125.7, 120.9, 34.0, 30.1, 24.3, 24.1 ppm

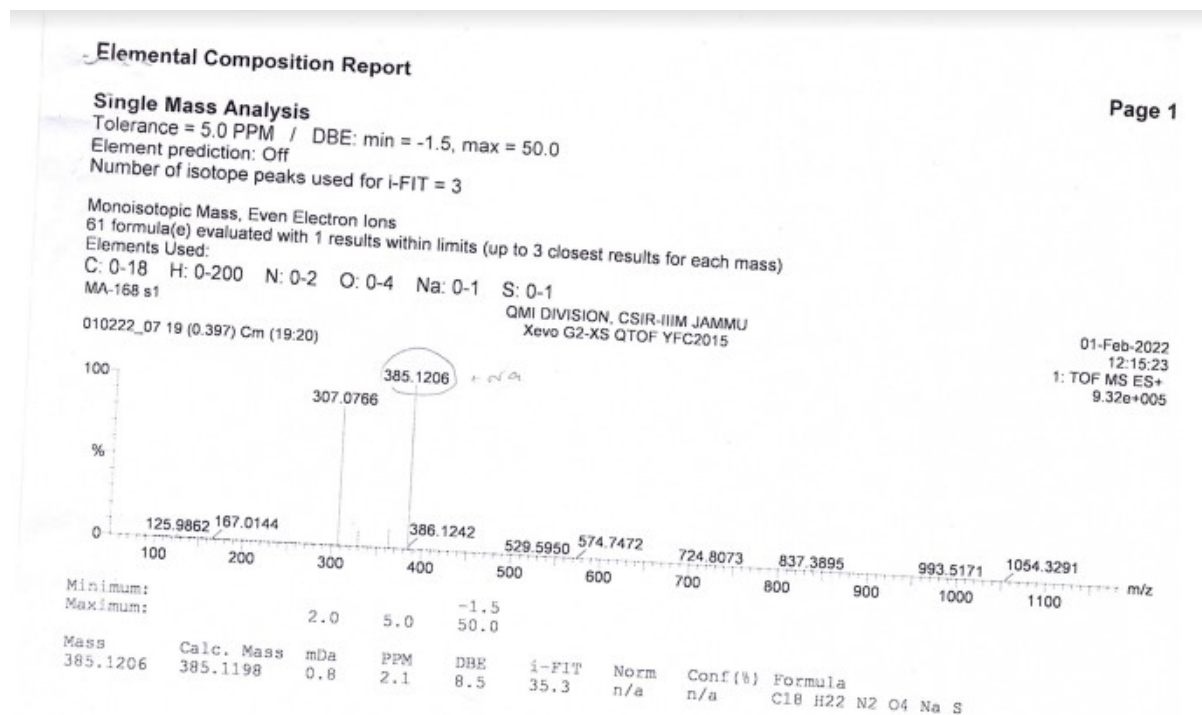
^1H -NMR (400 MHz, CDCl_3) of **3a**



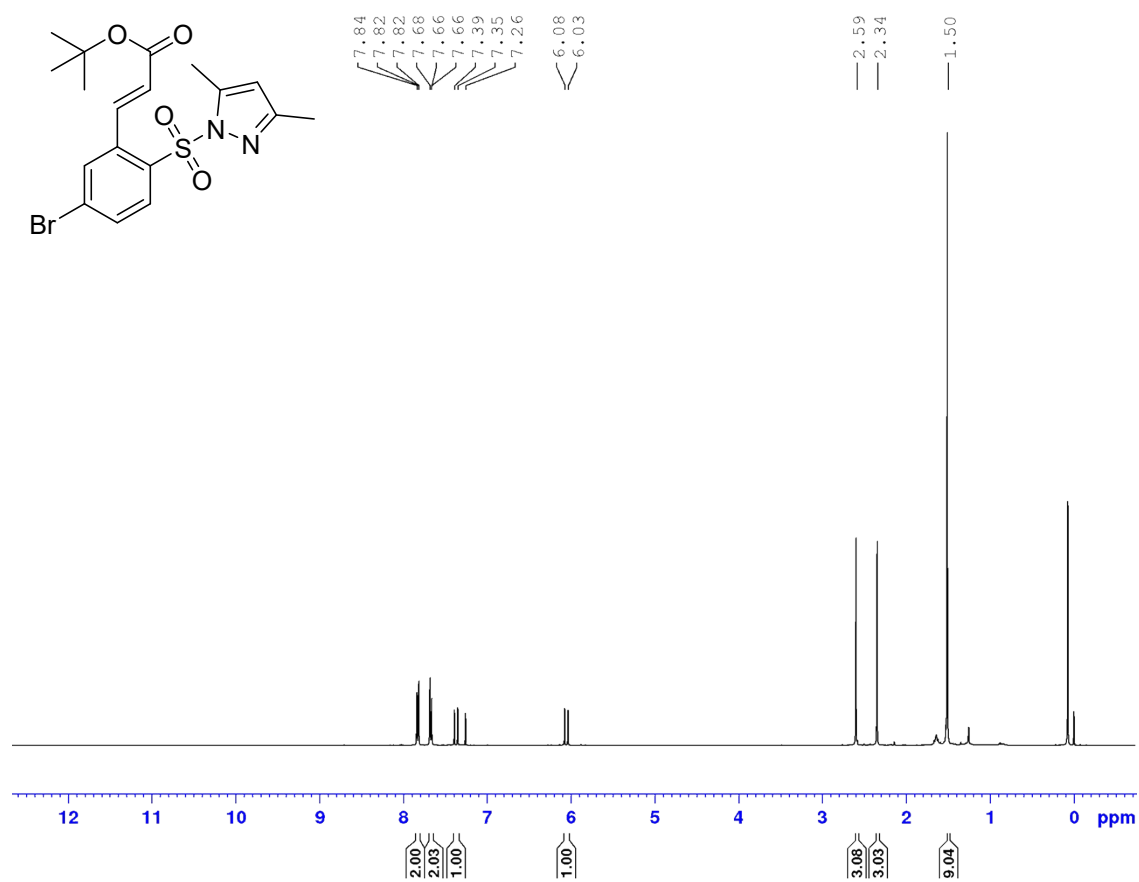
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3a



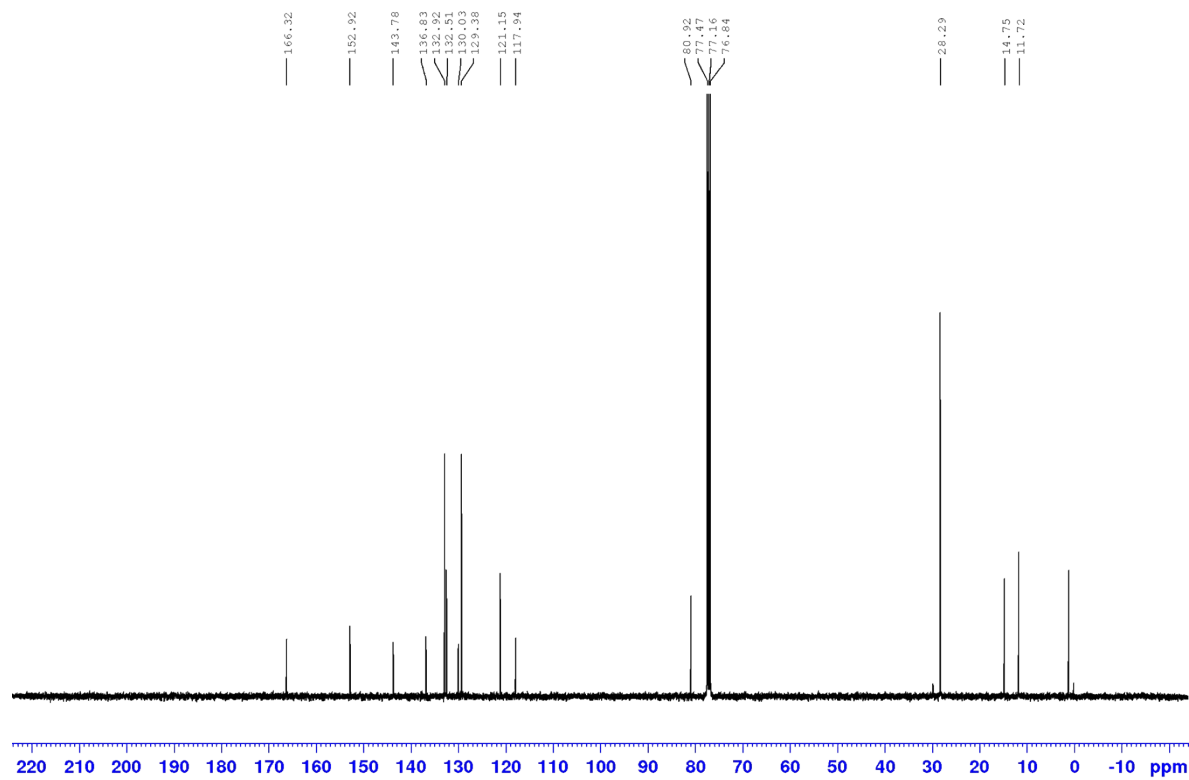
HRMS of 3a



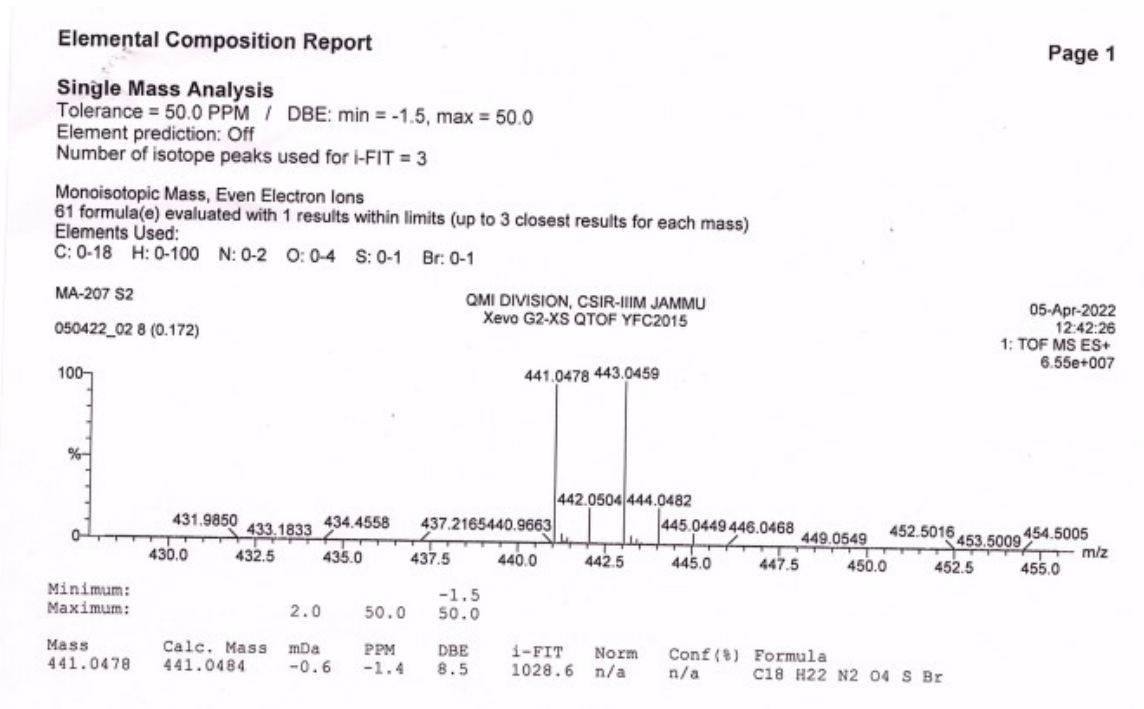
$^1\text{H-NMR}$ (400 MHz, CDCl_3) of **3b**



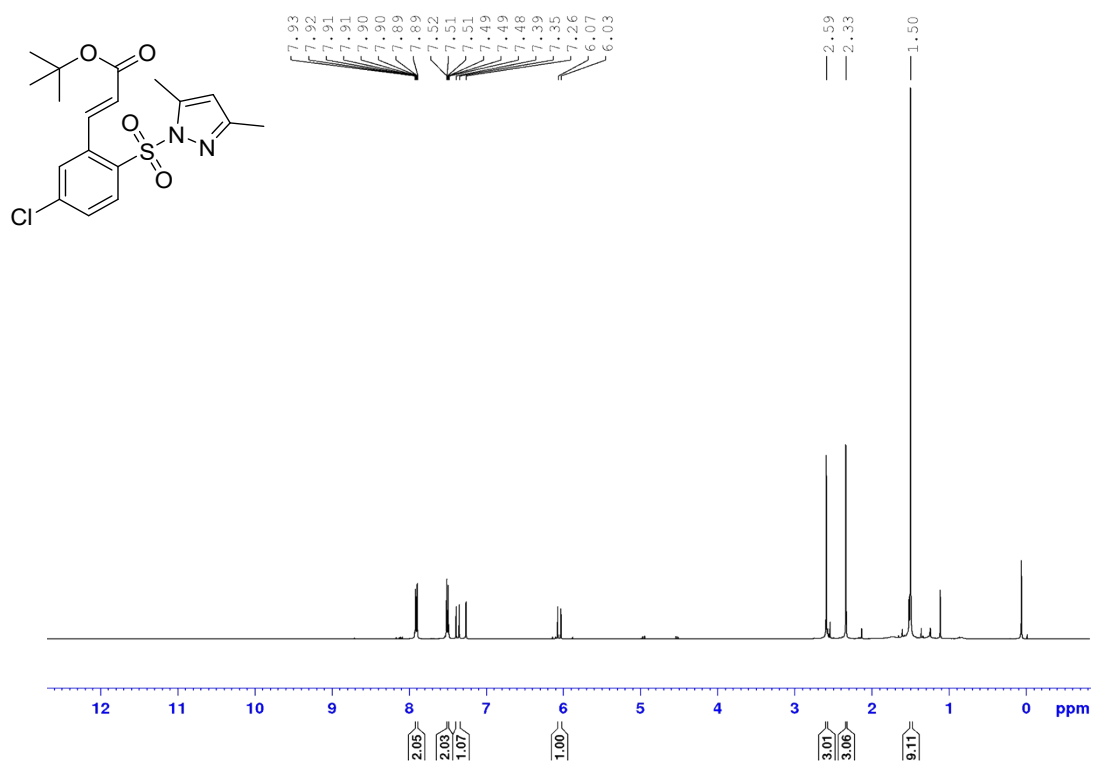
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of **3b**



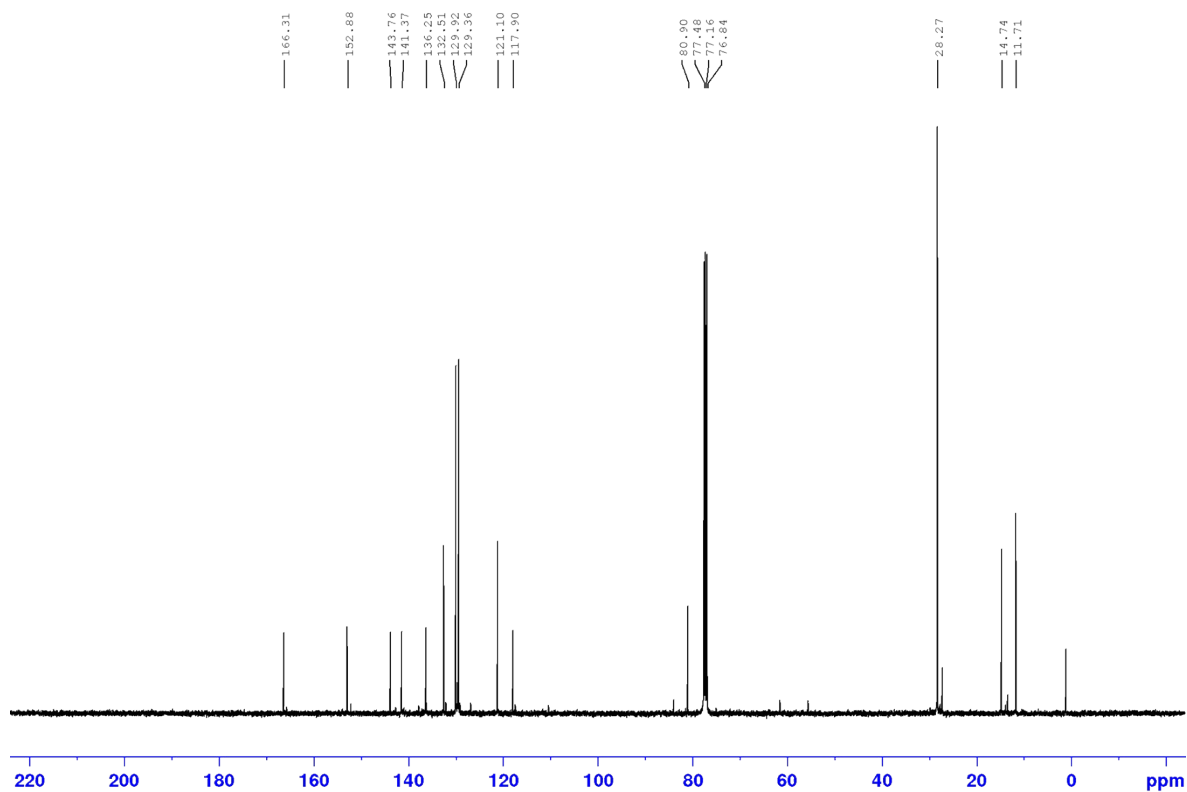
HRMS of 3b



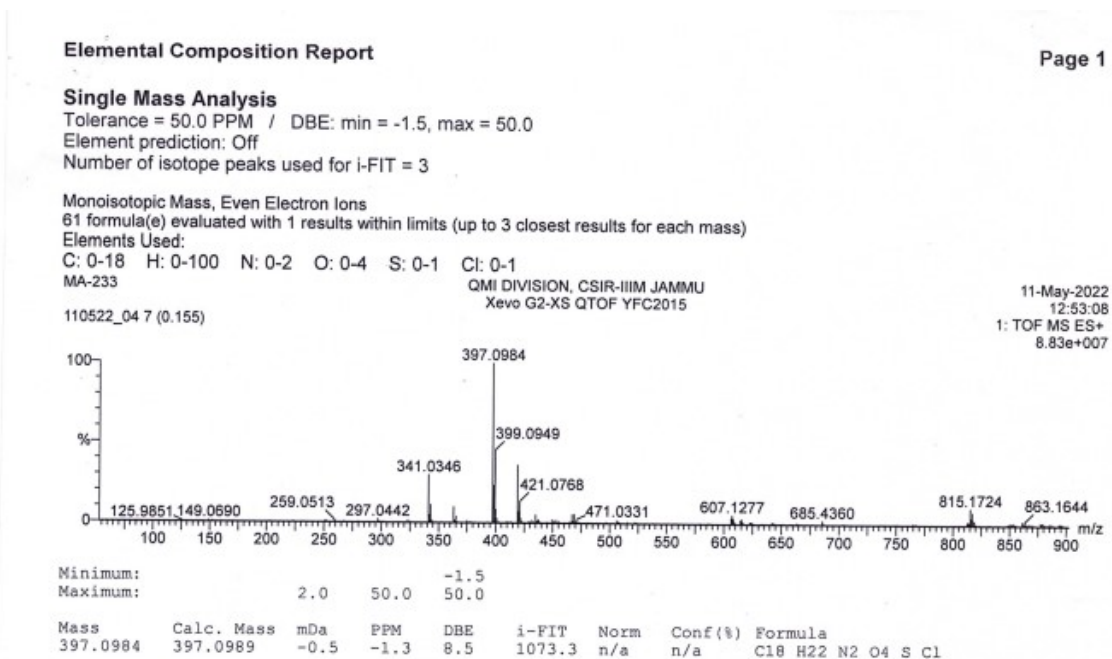
¹H-NMR (400 MHz, CDCl₃) of 3c



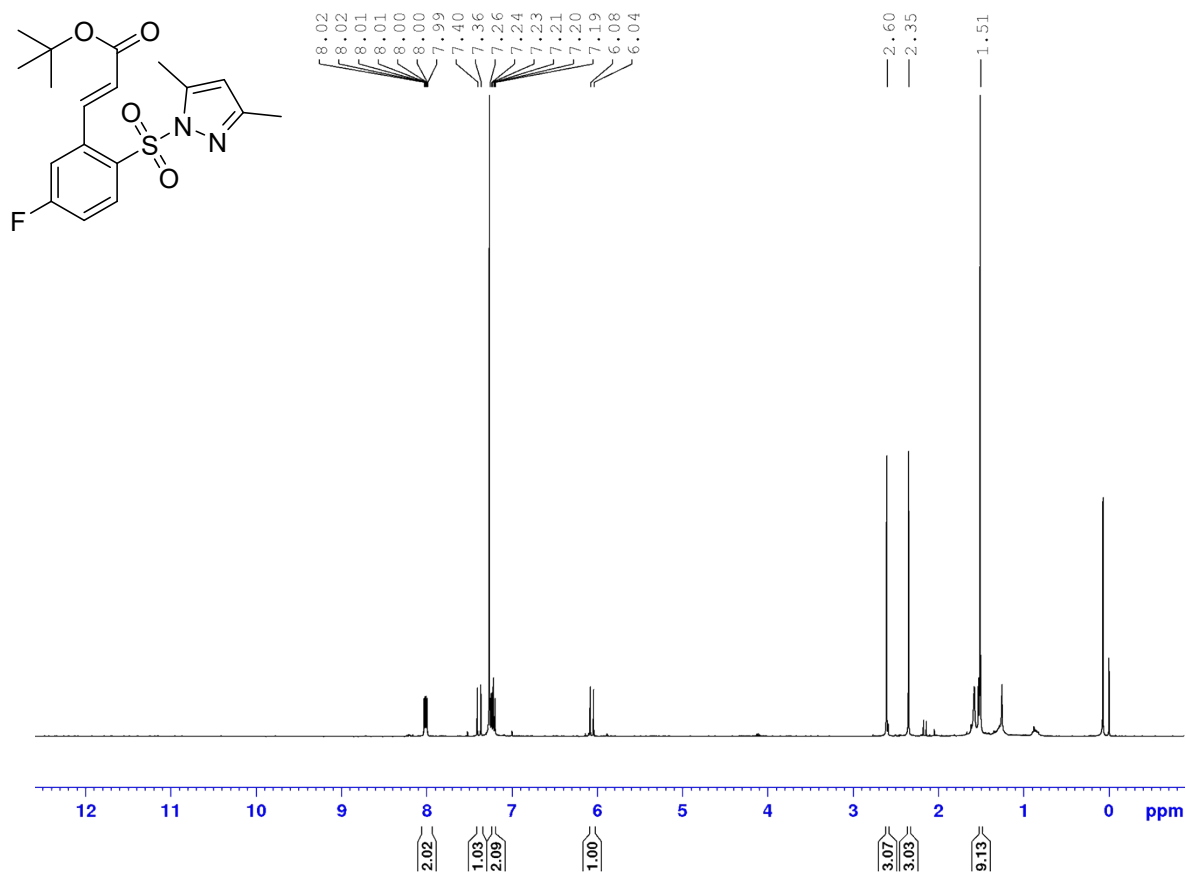
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3c



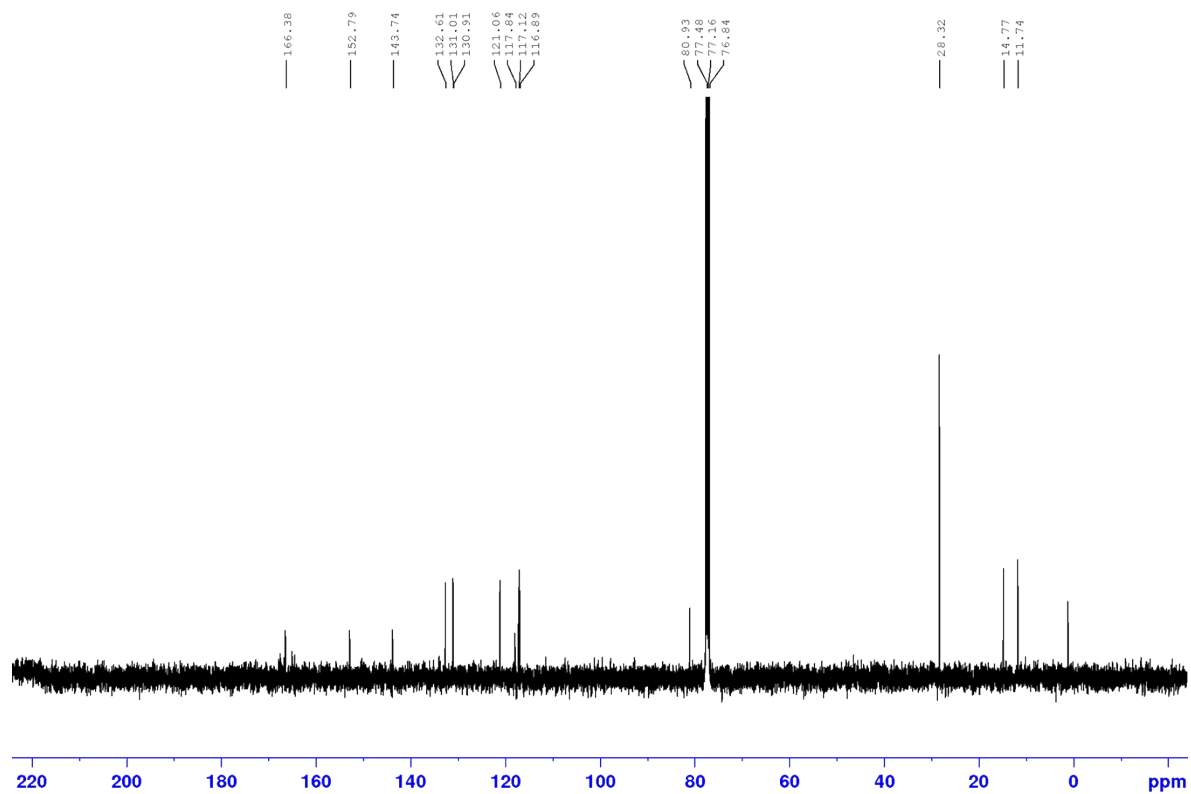
HRMS of 3c



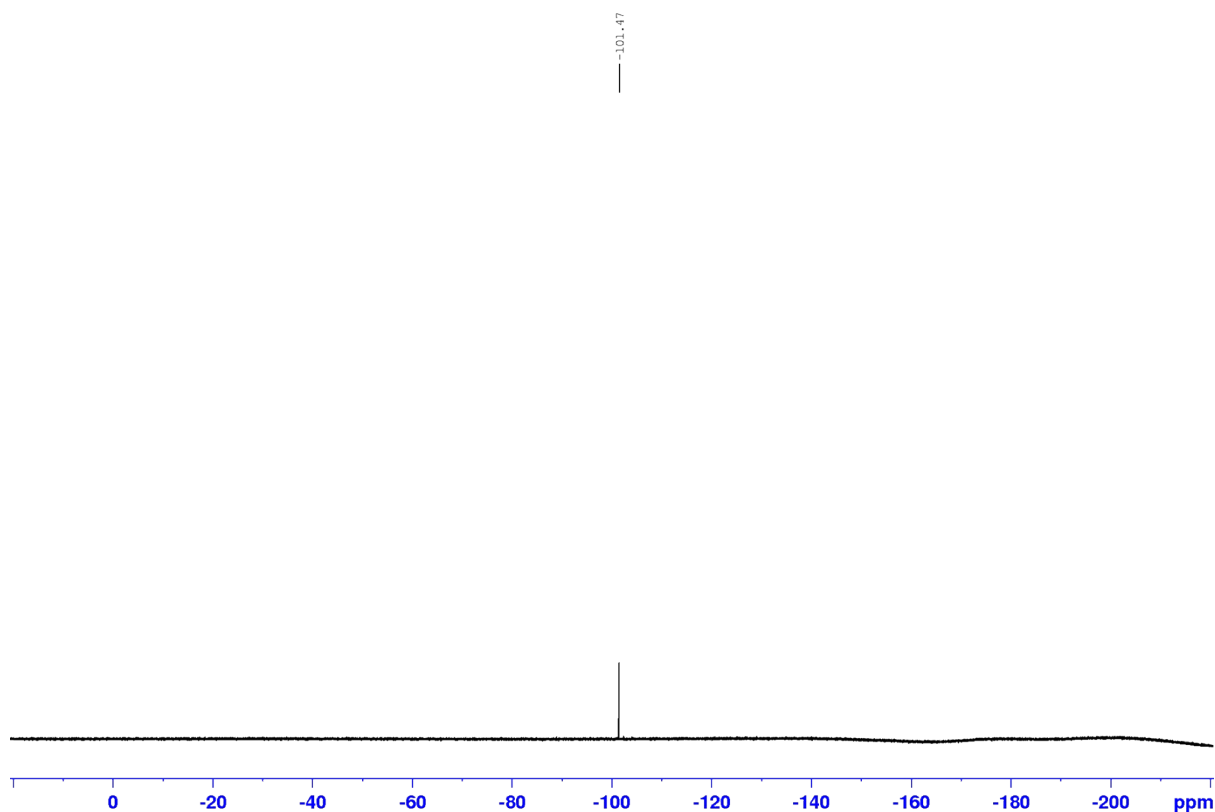
$^1\text{H-NMR}$ (400 MHz, CDCl_3) of 3d



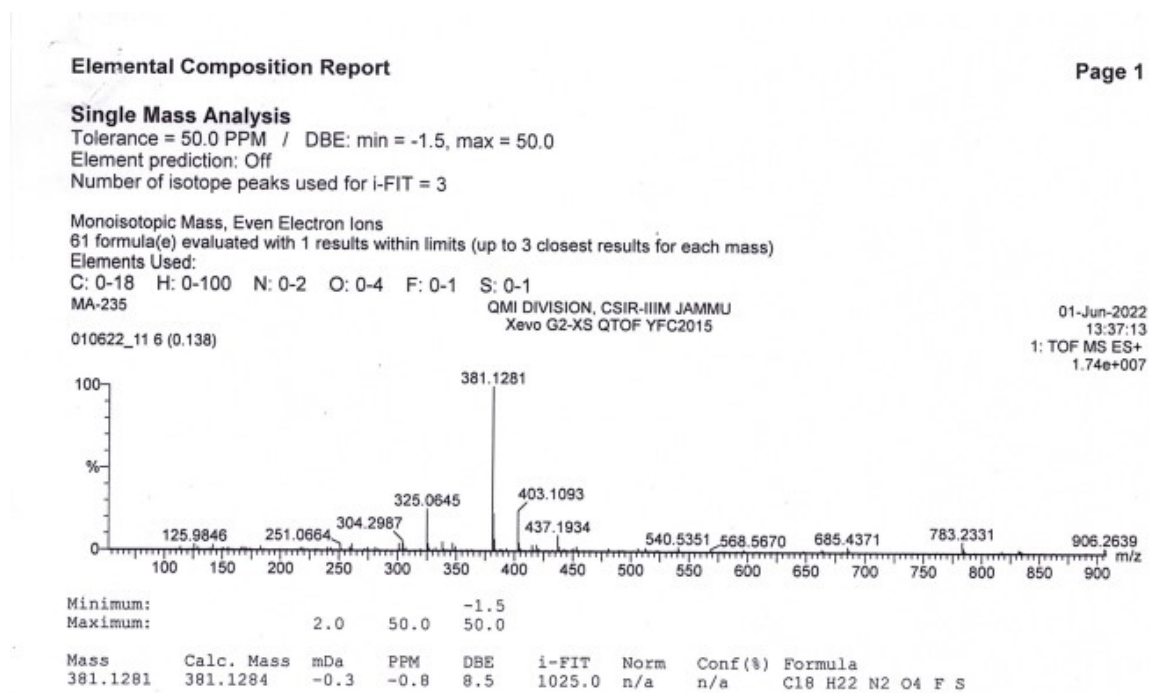
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3d,



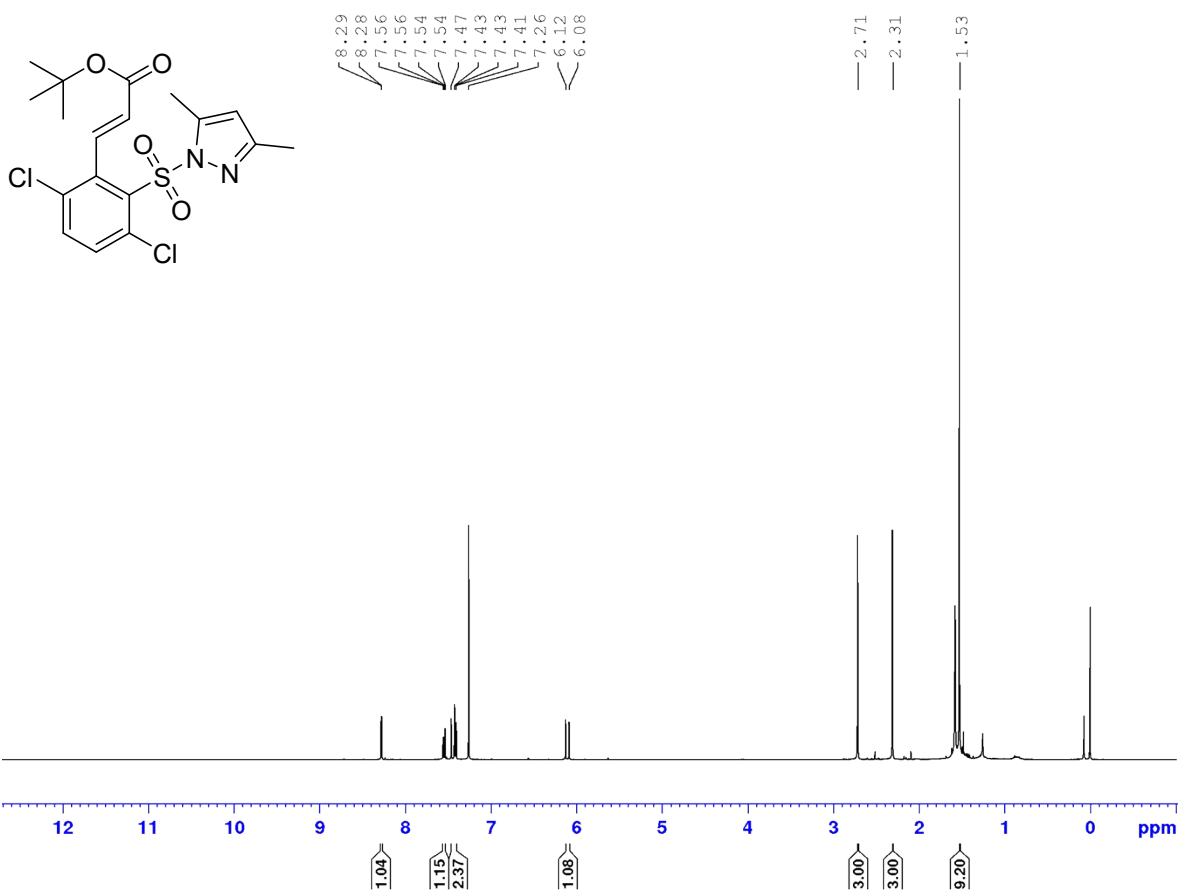
¹⁹F-NMR (377 MHz, CDCl₃) of 3d



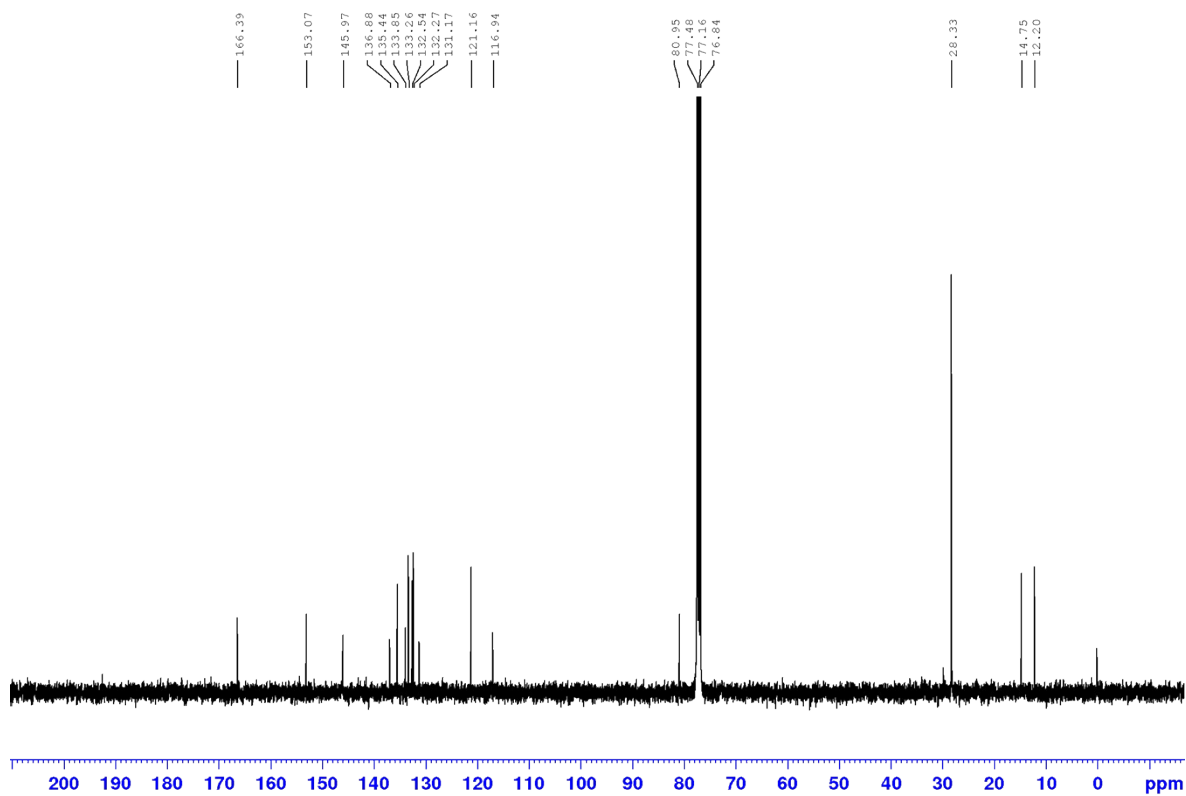
HRMS of 3d



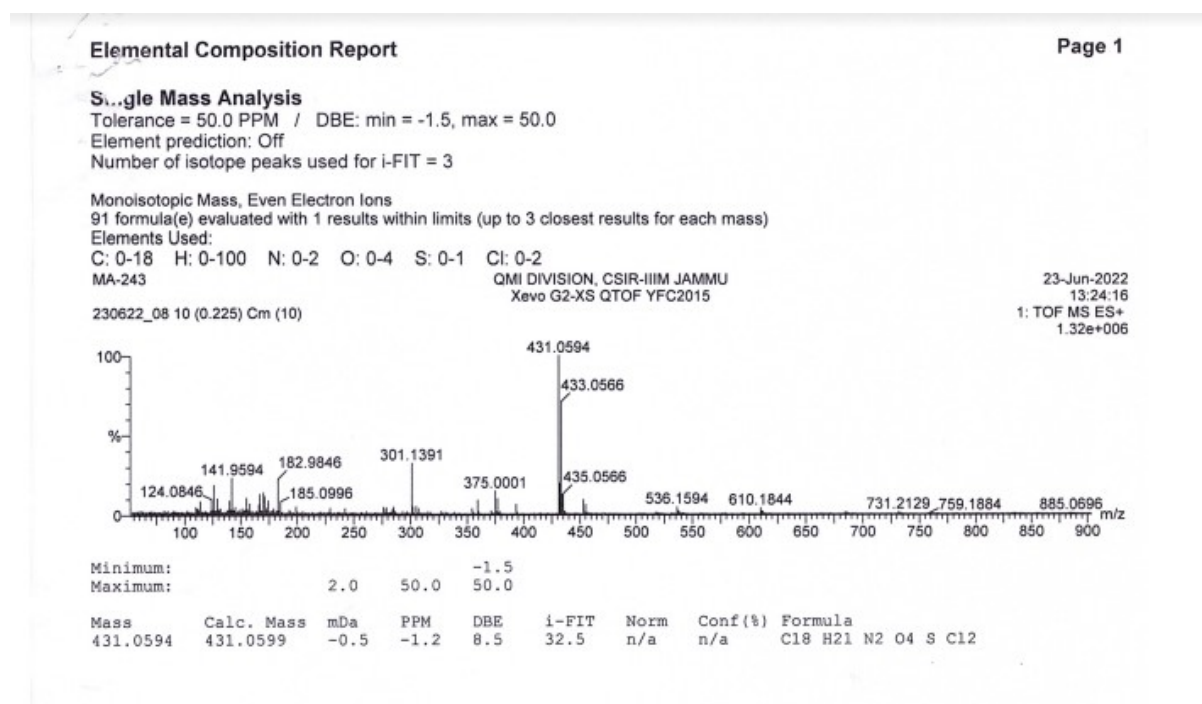
¹H-NMR (400 MHz, CDCl₃) of 3e



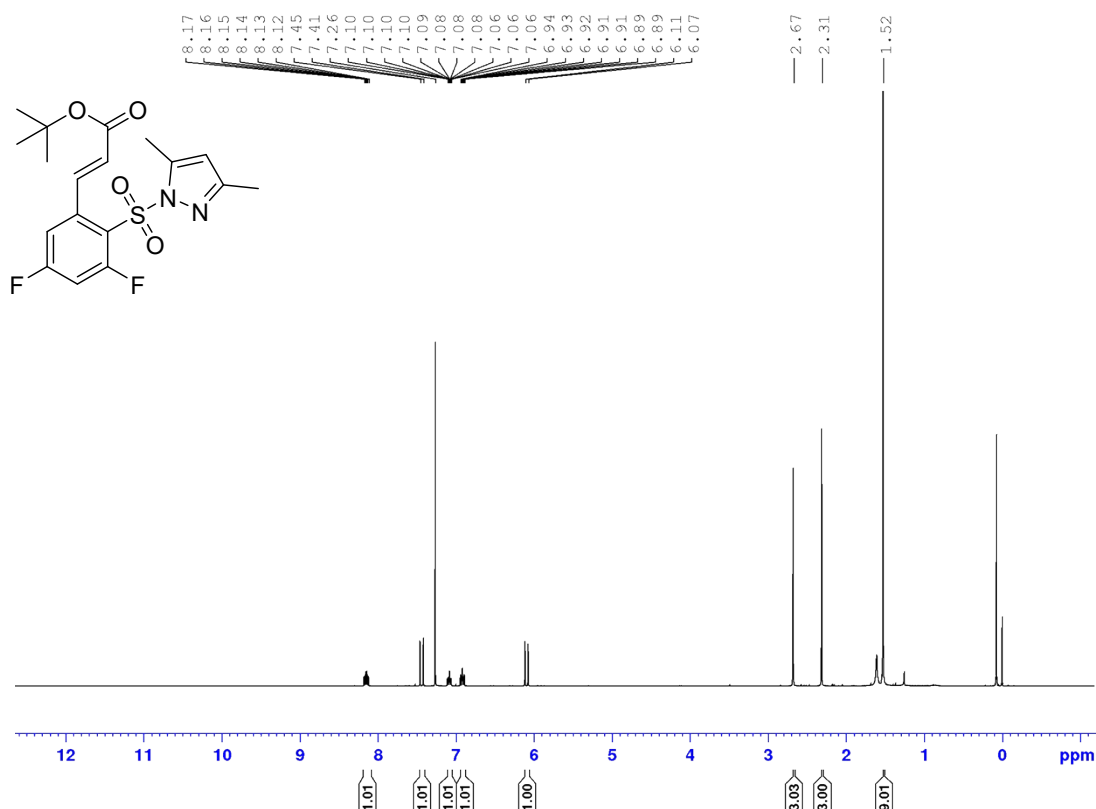
¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3e



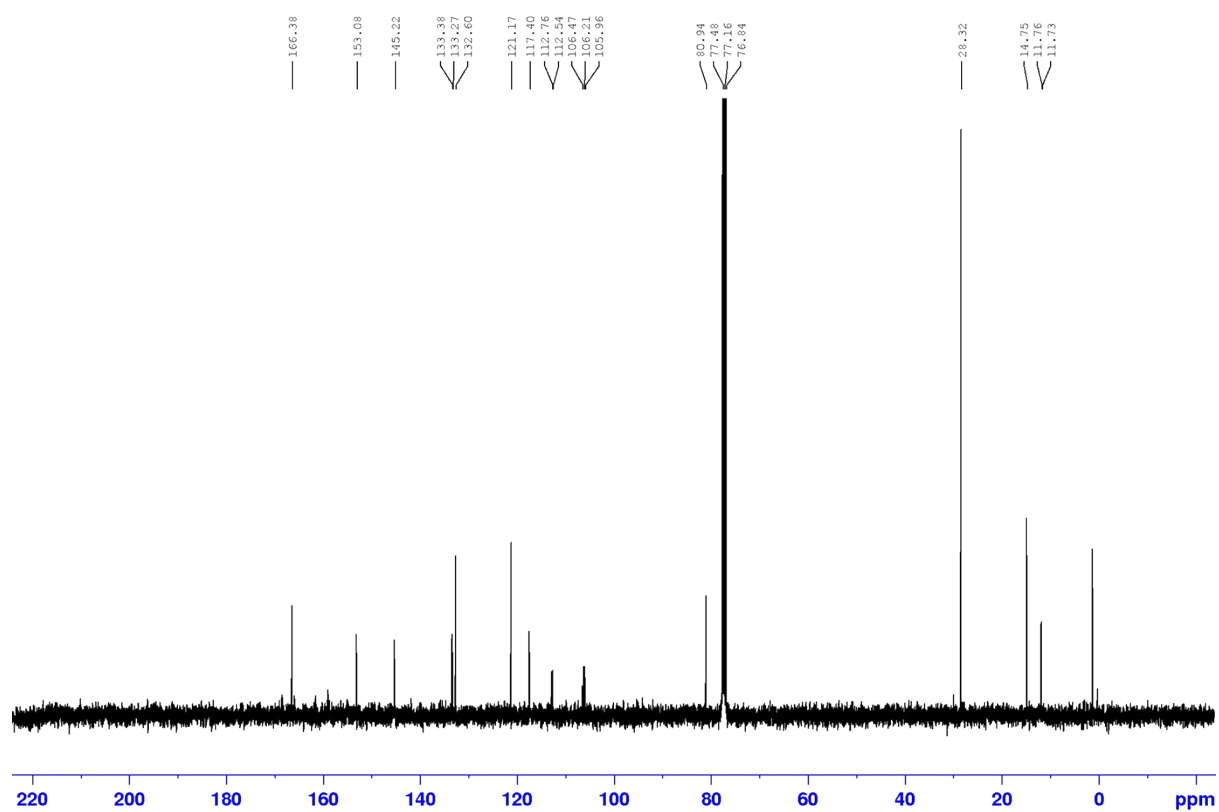
HRMS of 3e



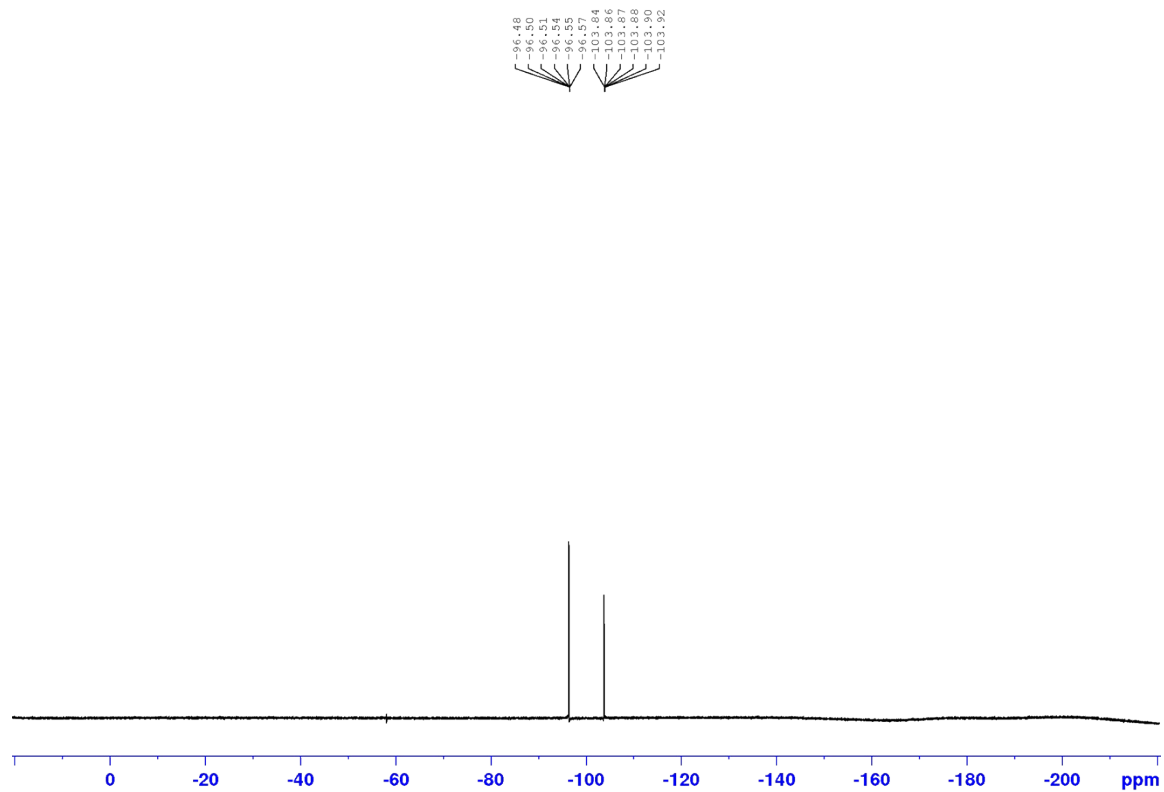
¹H-NMR (400 MHz, CDCl₃) of 3f



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3f



^{19}F -NMR (377 MHz, CDCl_3) of 3f



HRMS of 3f

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

91 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-18 H: 0-100 N: 0-2 O: 0-4 F: 0-2 S: 0-1

MA-242

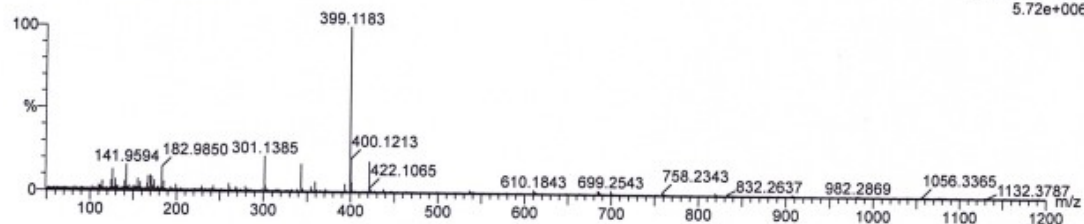
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

240622_11 10 (0.225) Cm (10:12)

24-Jun-2022

13:33:10

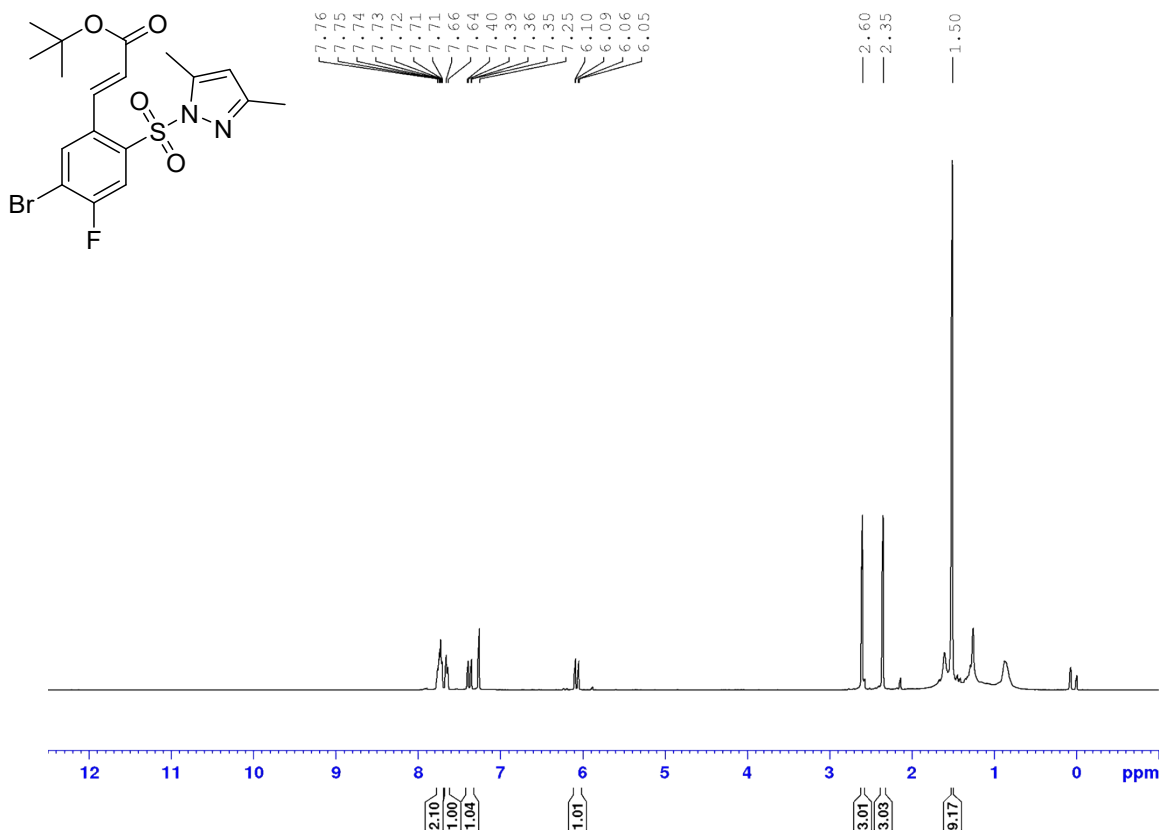
1: TOF MS ES+
5.72e+006



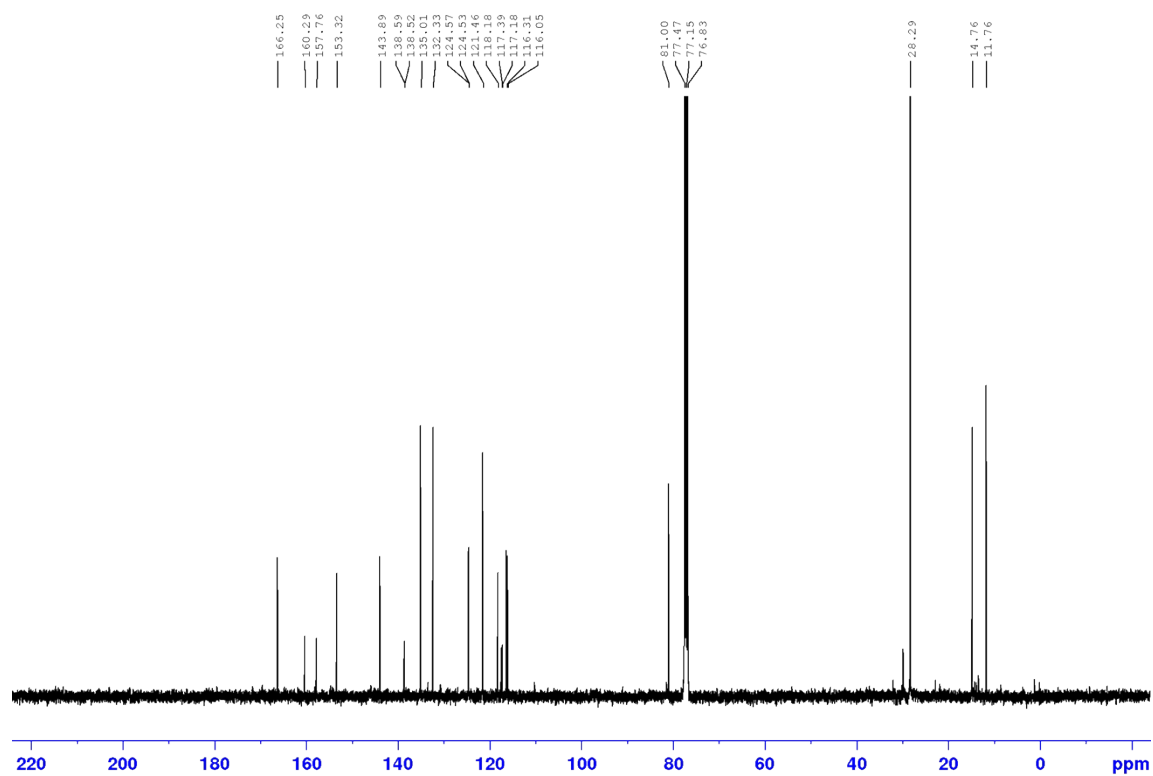
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
399.1183	399.1190	-0.7	-1.8	8.5	42.3	n/a	n/a	C18 H21 N2 O4 F2 S

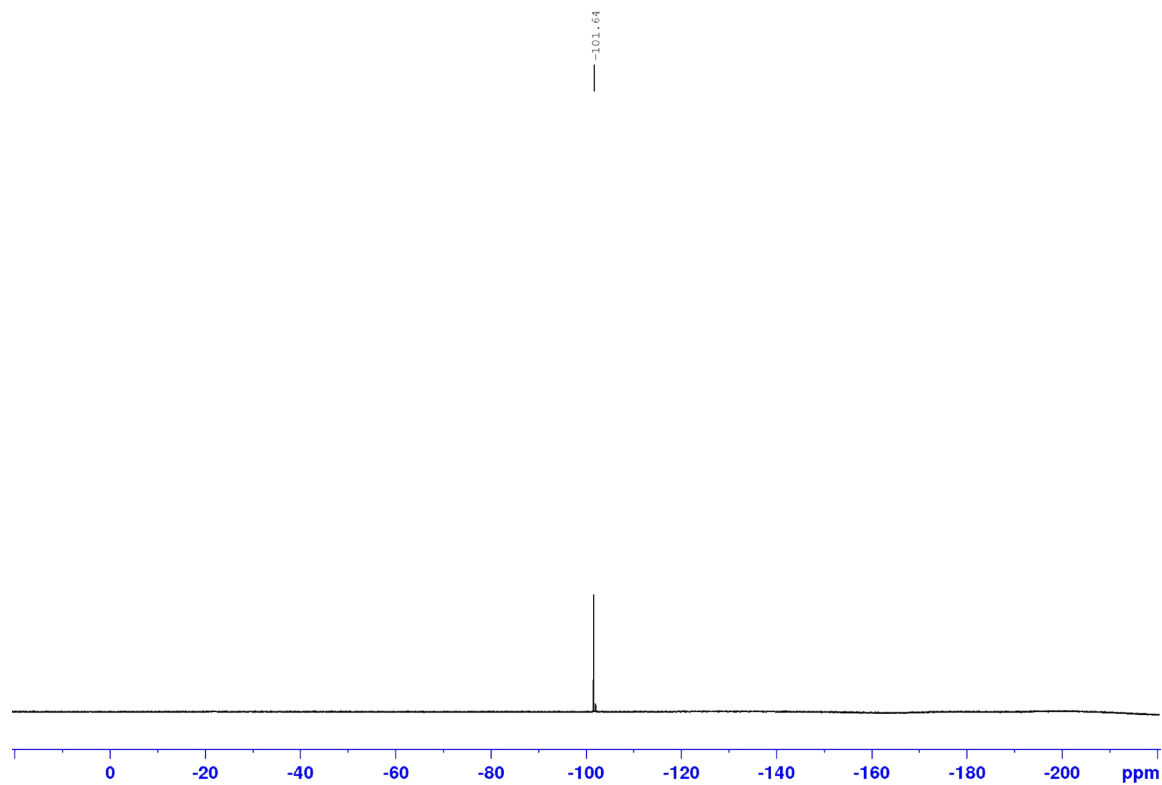
¹H-NMR (400 MHz, CDCl₃) of 3g



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3g



^{19}F -NMR (377 MHz, CDCl_3) of 3g



HRMS of 3g

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

121 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-18 H: 0-100 N: 0-2 O: 0-4 F: 0-1 S: 0-1 Br: 0-1

MA-249

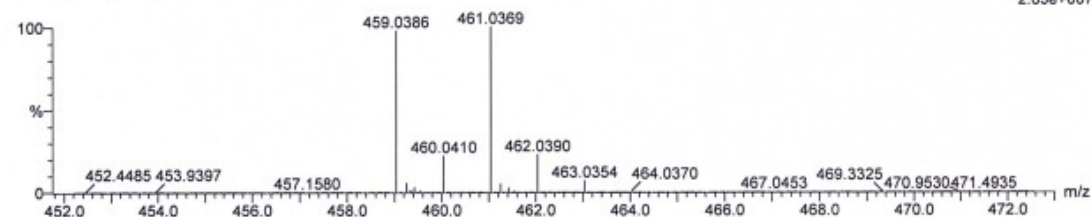
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

18-Aug-2022

11:17:11

180822_06 6 (0.138)

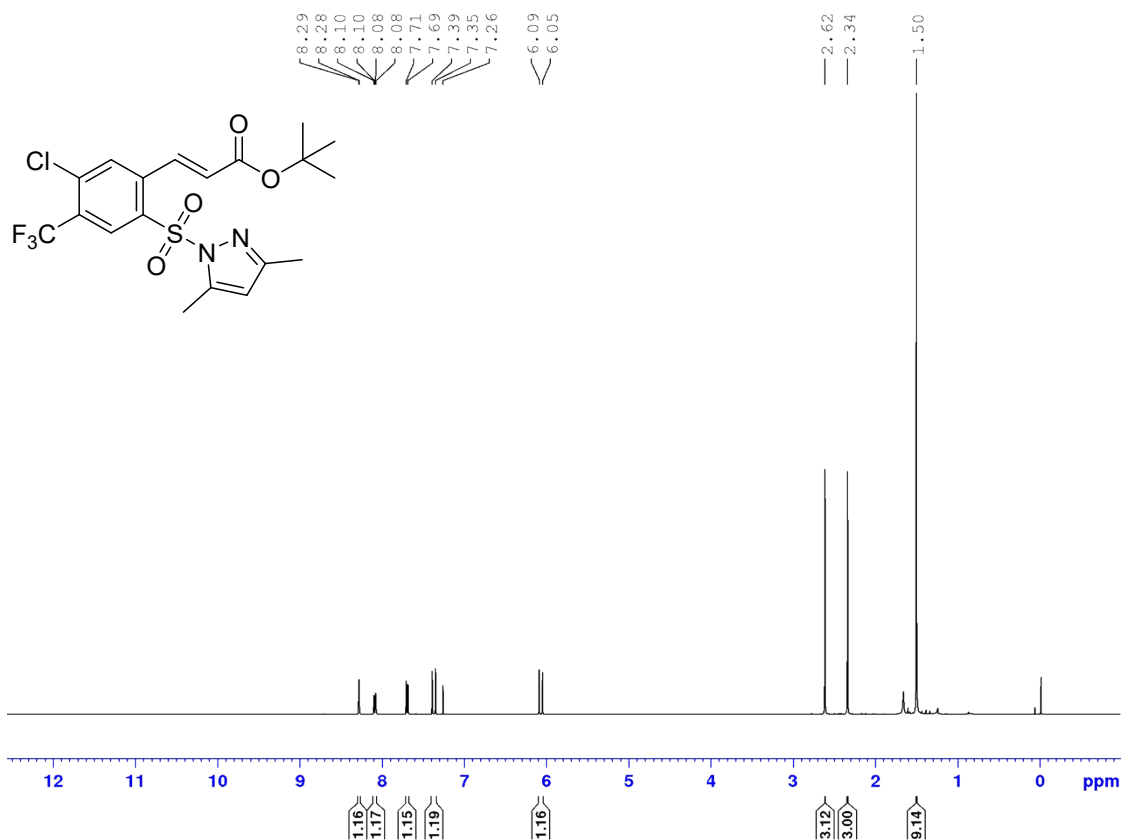
1: TOF MS ES+
2.63e+007



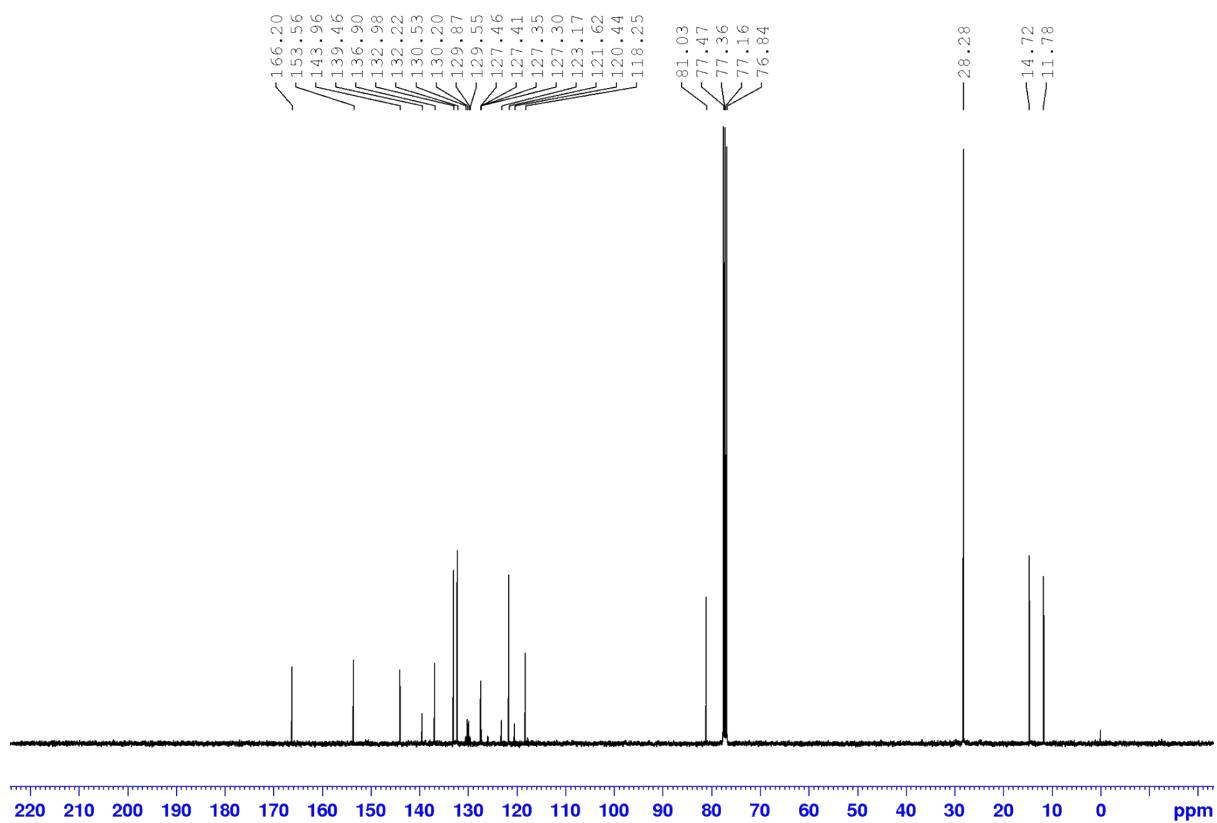
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
459.0386	459.0389	-0.3	-0.7	8.5	866.1	n/a	n/a	C18 H21 N2 O4 F S Br

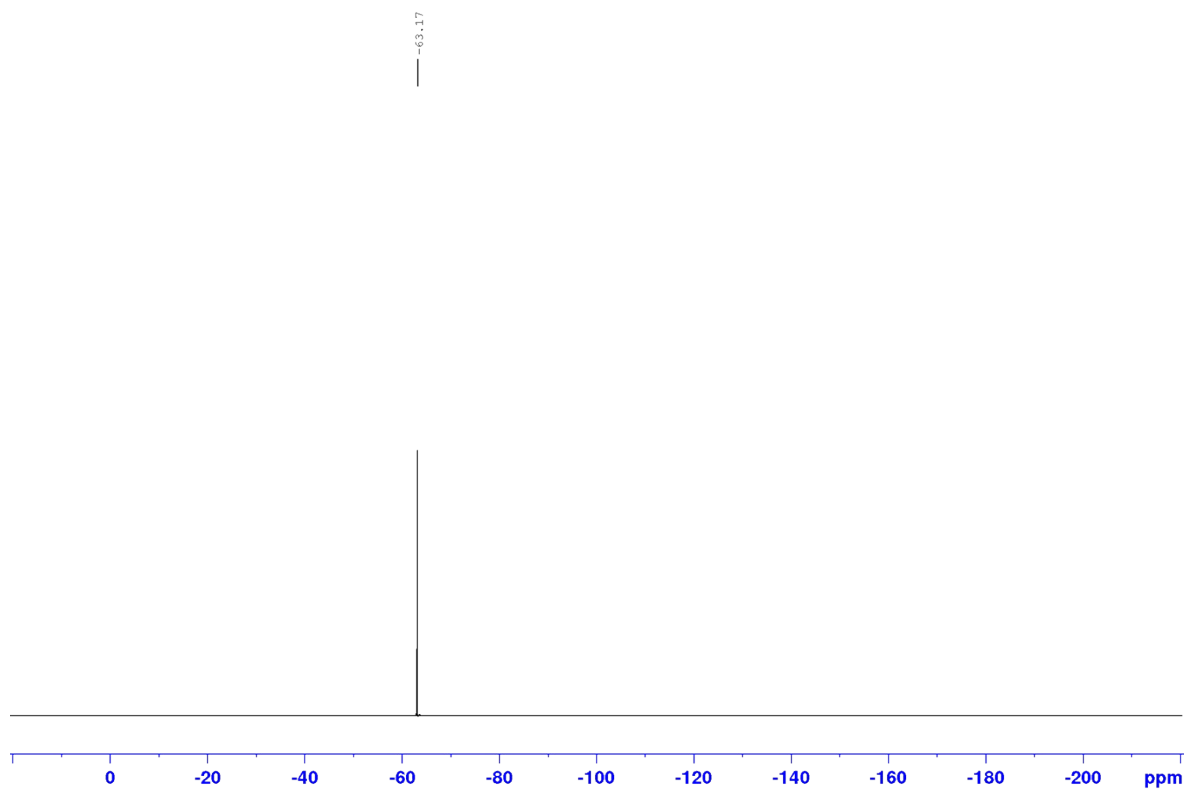
¹H-NMR (400 MHz, CDCl₃) of 3h



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3h



¹⁹F-NMR (377 MHz, CDCl₃) of 3h



HRMS of 3h

Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

241 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

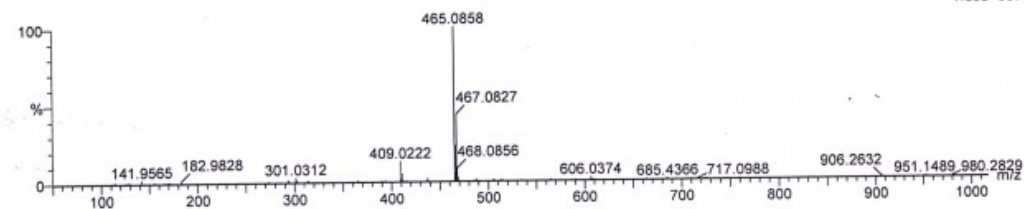
C: 0-19 H: 0-100 N: 0-2 O: 0-4 F: 0-3 S: 0-1 Cl: 0-1

MA-250

QMI DIVISION, CSIR-IIIM JAMMU
 Xevo G2-XS QTOF YFC2015

050822_02 10 (0.225)

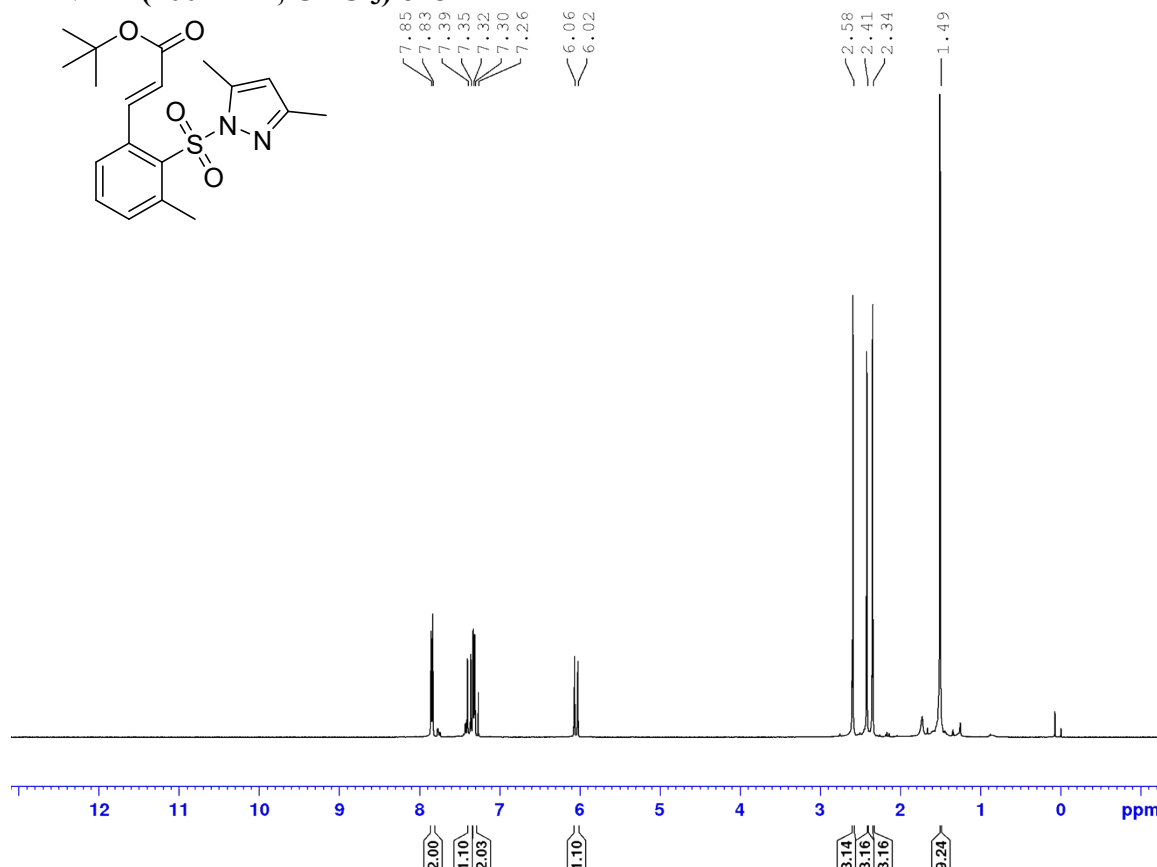
05-Aug-2022
 14:01:53
 1: TOF MS ES+
 1.65e+007



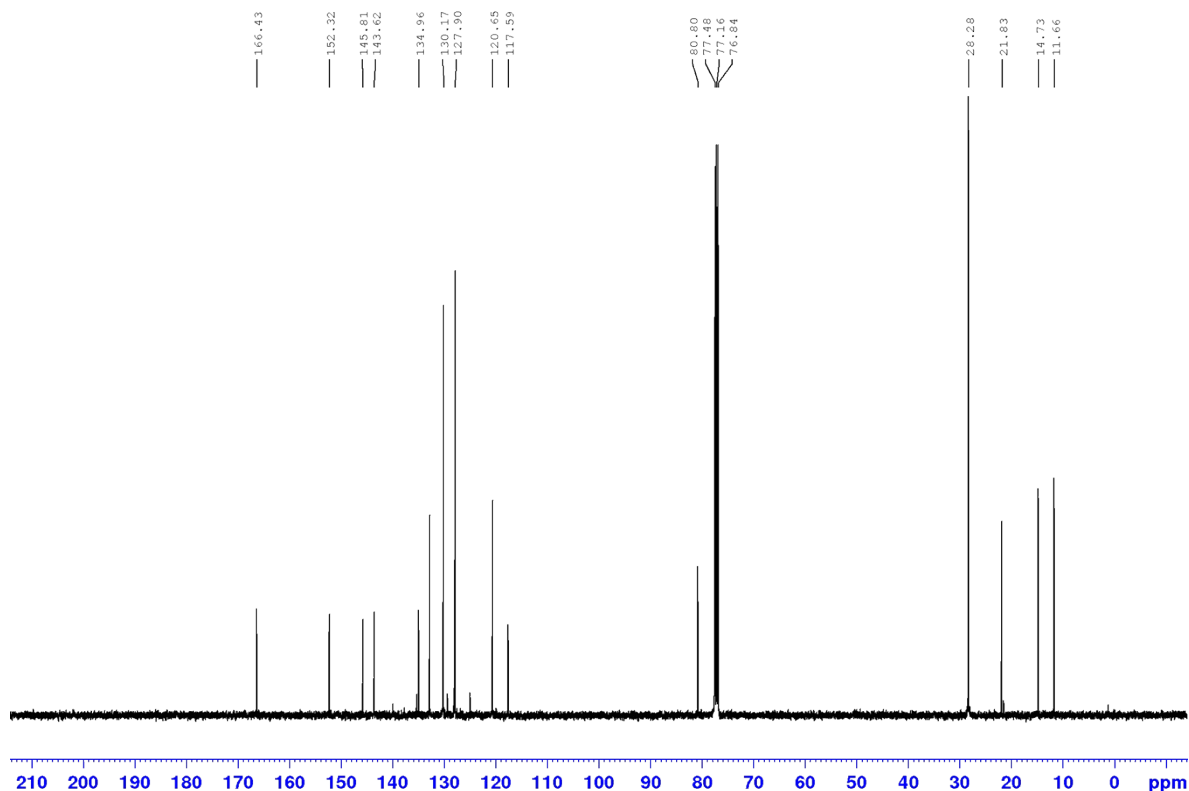
Minimum: -1.5
 Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
465.0858	465.0863	-0.5	-1.1	8.5	735.4	n/a	n/a	C19 H21 N2 O4 F3 S Cl

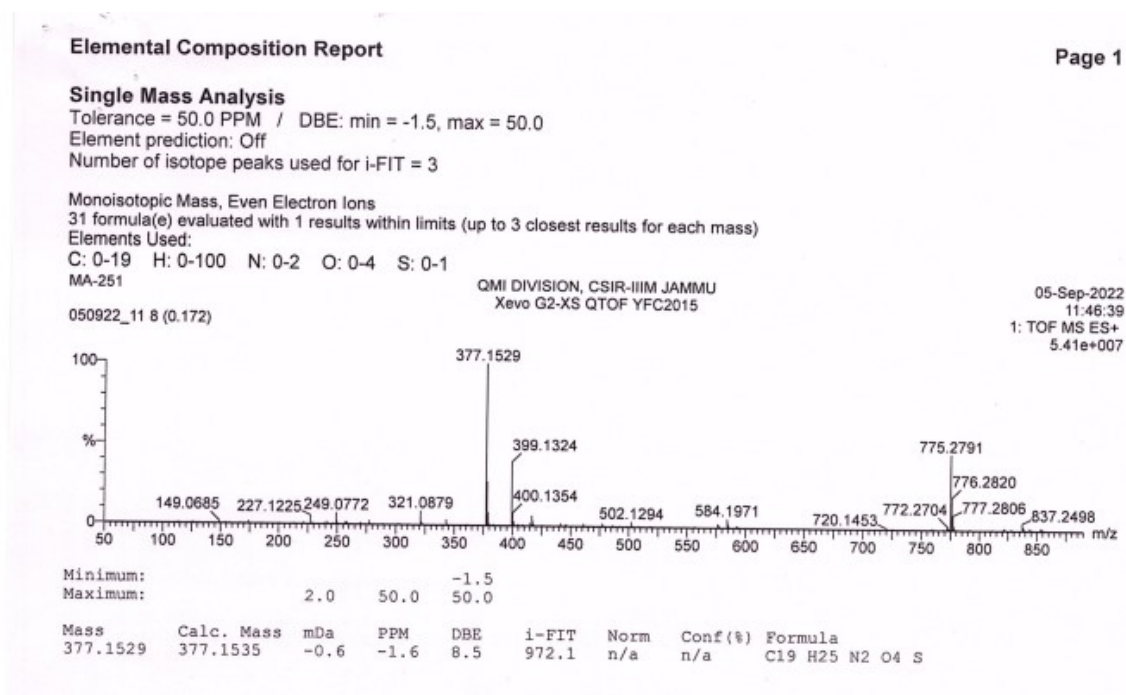
¹H-NMR (400 MHz, CDCl₃) of 3i



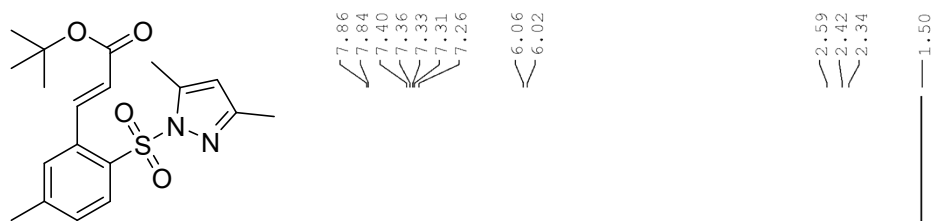
¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3i



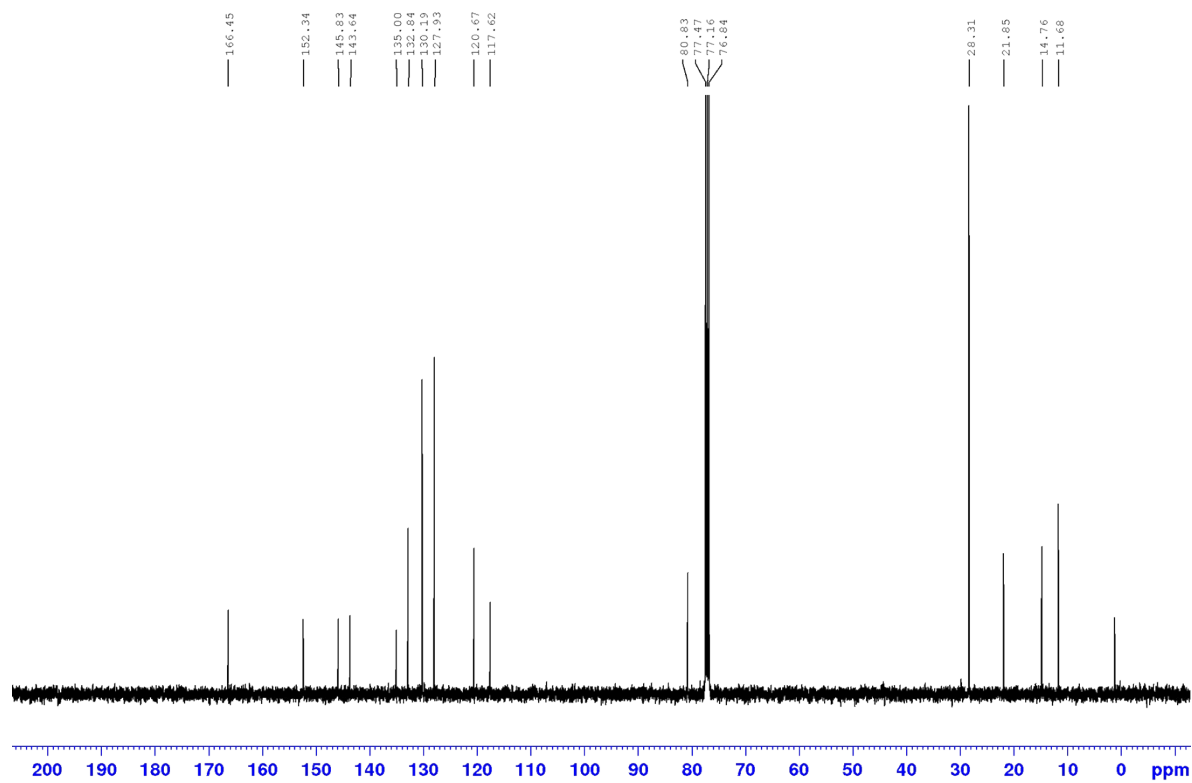
HRMS of 3i



¹H-NMR (400 MHz, CDCl₃) of 3j



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3j



HRMS of 3j

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

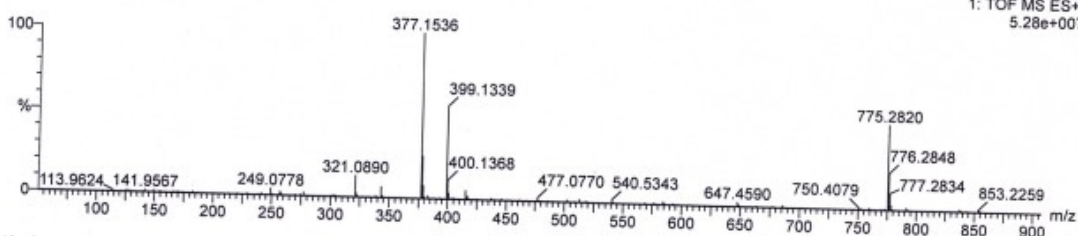
Elements Used:

C: 0-19 H: 0-100 N: 0-2 O: 0-4 S: 0-1

MA-237

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

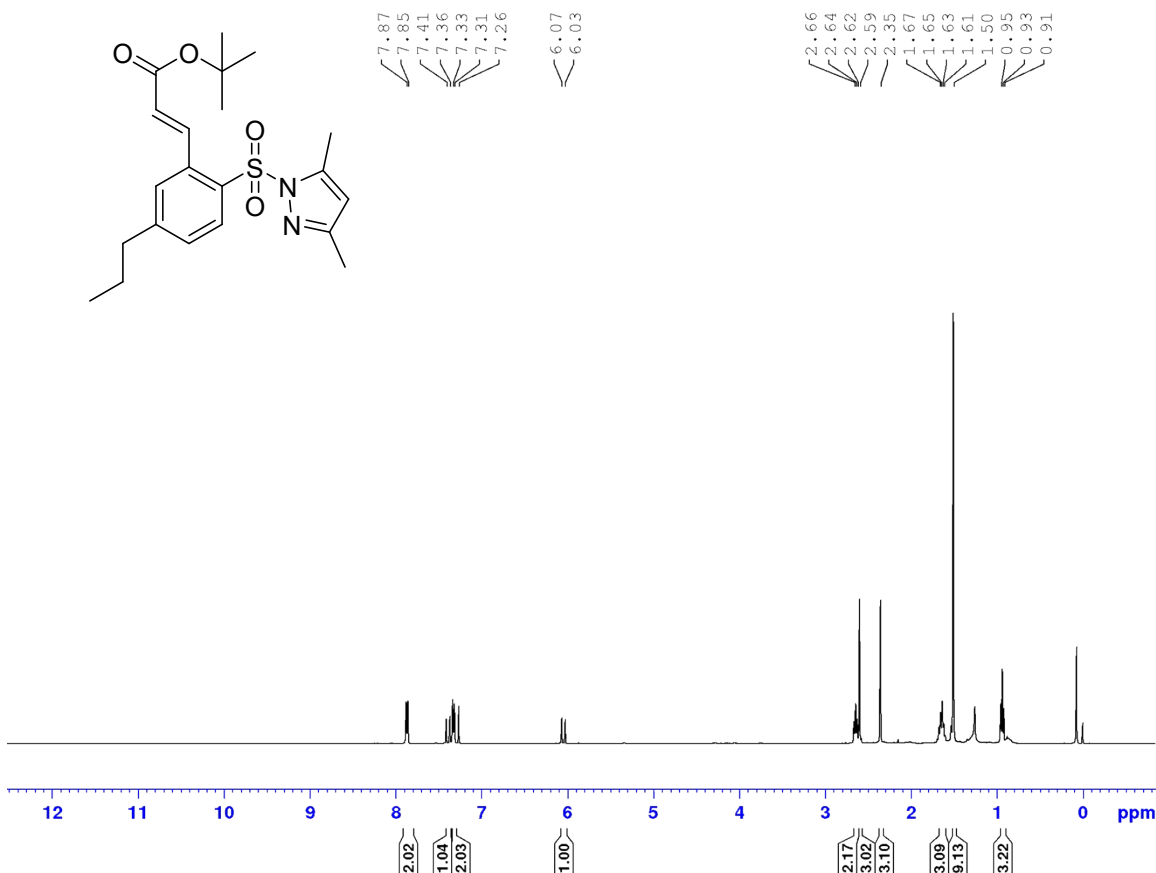
23-May-2022
12:35:48
1: TOF MS ES+
5.28e+007



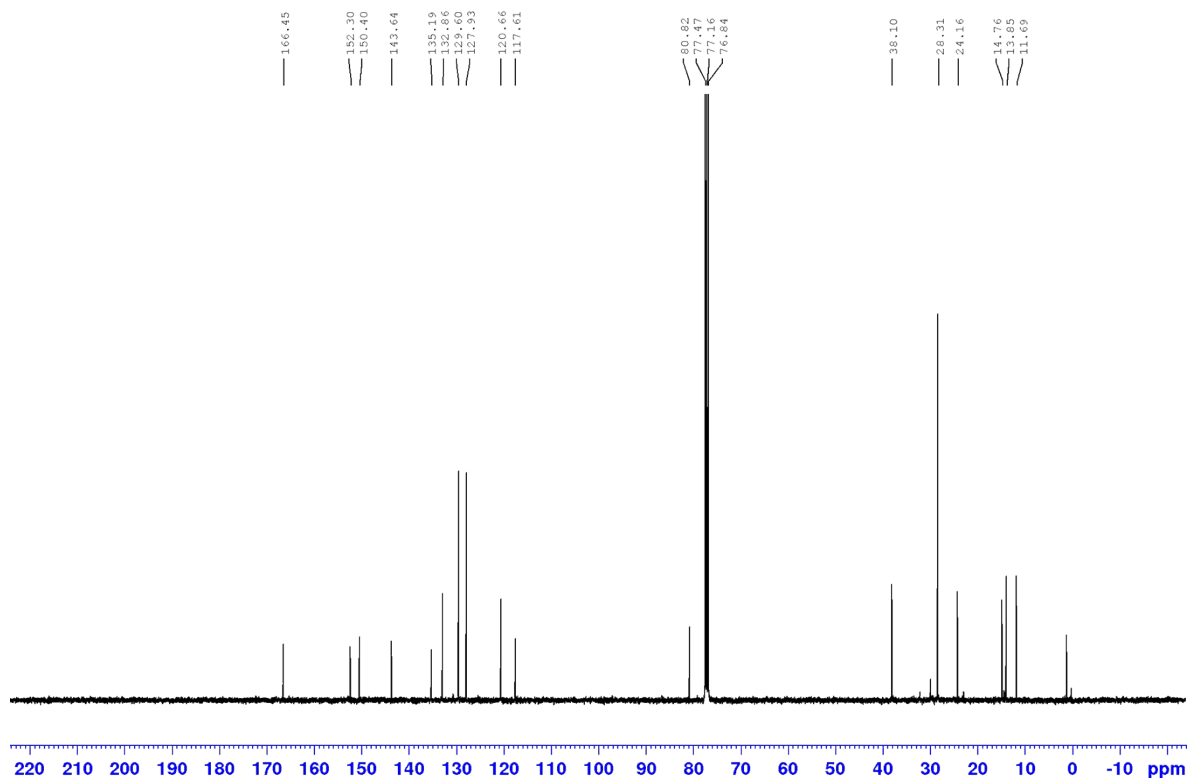
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
377.1536	377.1535	0.1	0.3	8.5	1139.9	n/a	n/a	C19 H25 N2 O4 S

¹H-NMR (400 MHz, CDCl₃) of 3k



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3k



HRMS of 3k

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-21 H: 0-100 N: 0-2 O: 0-4 S: 0-1

MA-231

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

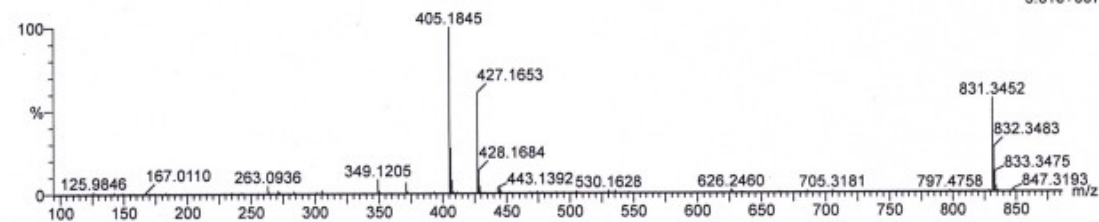
02-May-2022

11:50:25

1: TOF MS ES+

3.61e+007

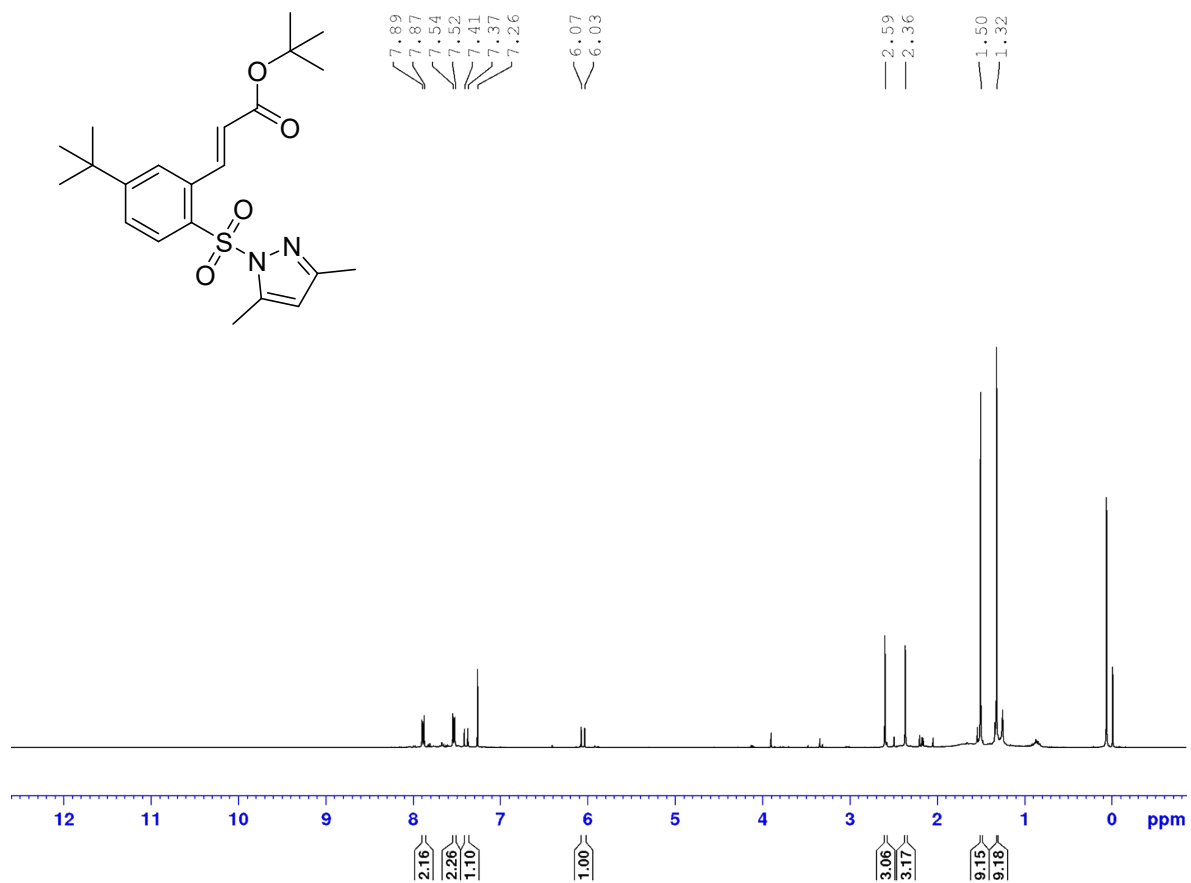
020522_12 8 (0.172)



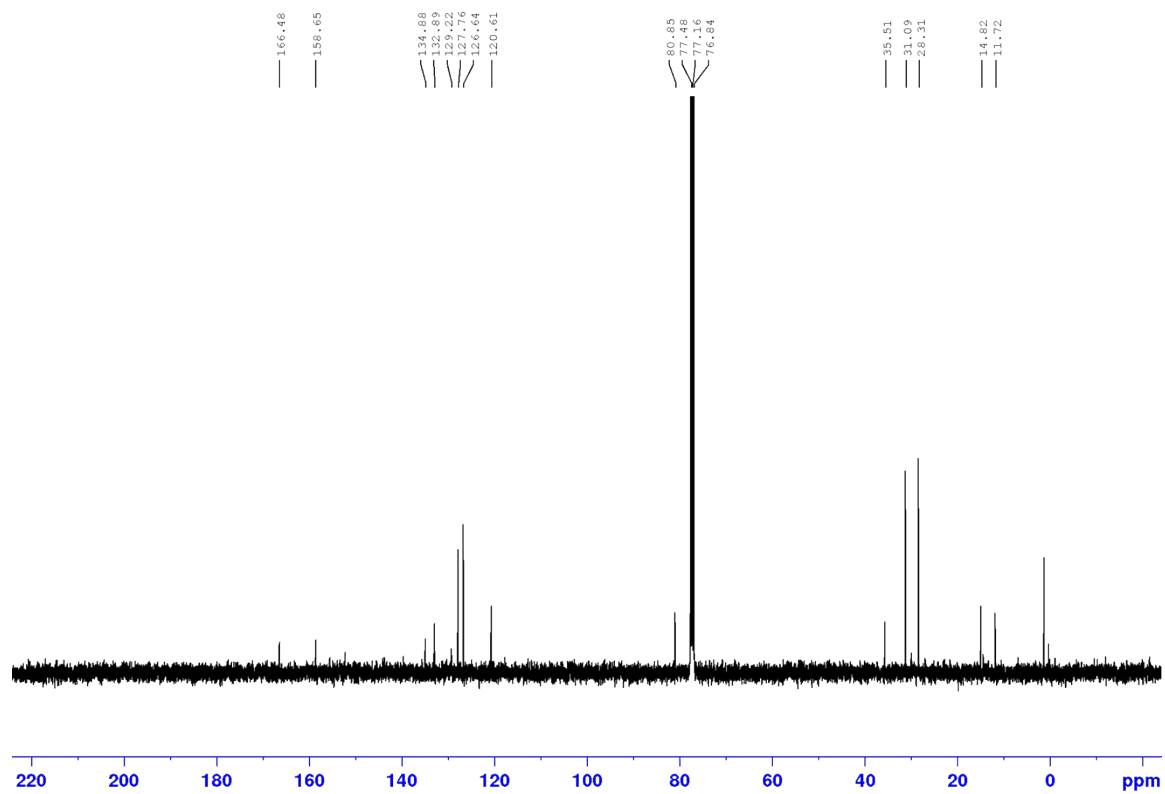
Minimum: -1.5
Maximum: 2.0 20.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
405.1845	405.1848	-0.3	-0.7	8.5	989.2	n/a	n/a	C21 H29 N2 O4 S

¹H-NMR (400 MHz, CDCl₃) of 3l



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 31



HRMS of 31

Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

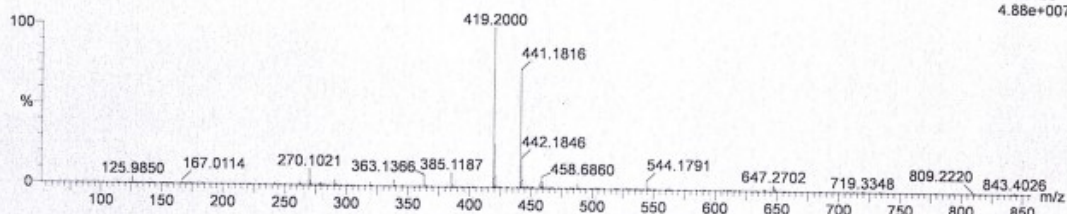
C: 0-22 H: 0-100 N: 0-2 O: 0-4 S: 0-1

MA-206

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

06-Apr-2022
12:16:28
1: TOF MS ES+
4.88e+007

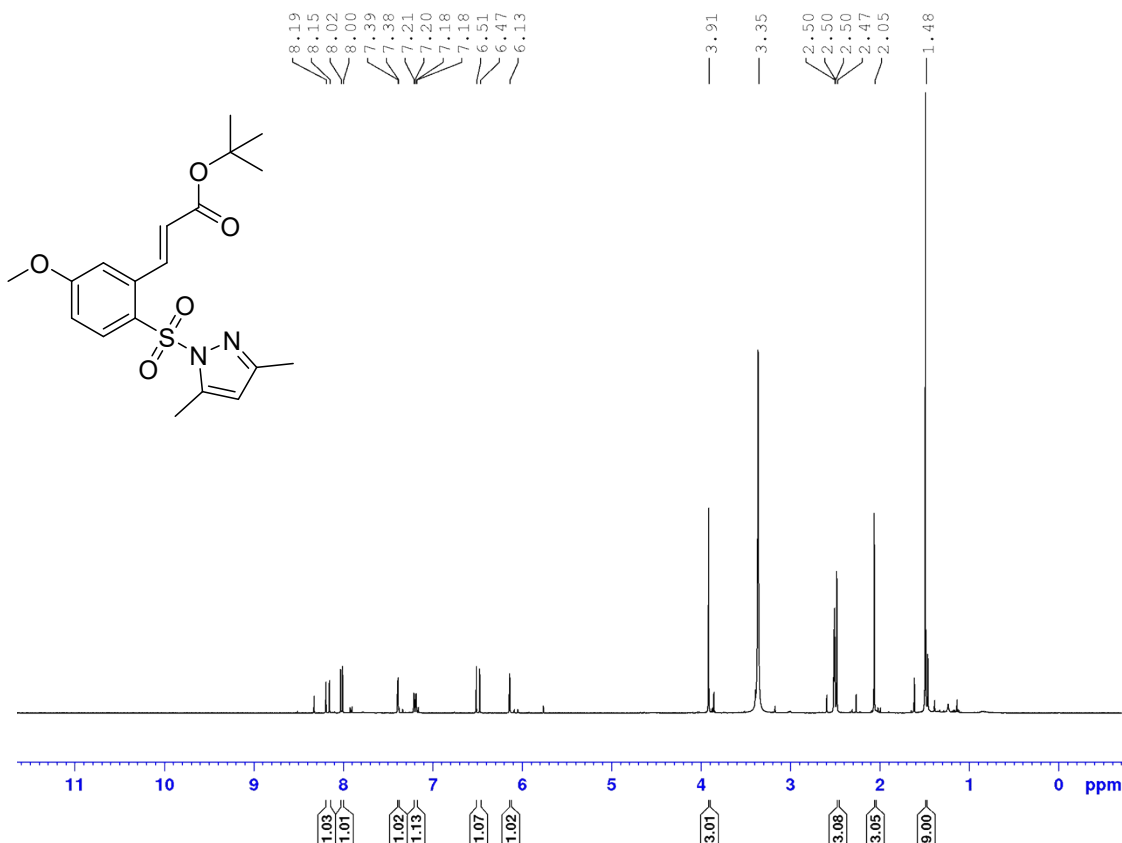
060422_05 7 (0.155)



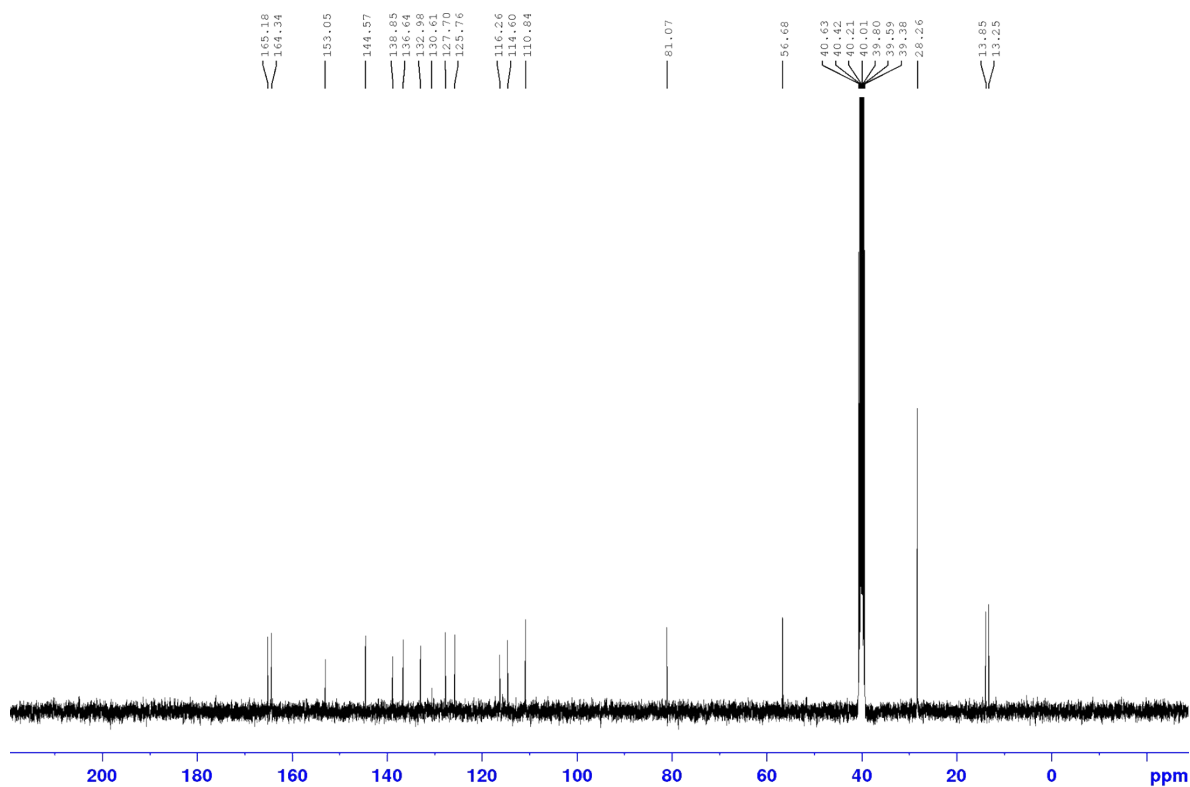
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
419.2000	419.2005	-0.5	-1.2	8.5	1107.8	n/a	n/a	C22 H31 N2 O4 S

¹H-NMR (400 MHz, DMSO-d₆) of 3m



¹³C{¹H}-NMR (101 MHz, DMSO-d₆) of 3m



HRMS of 3m

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

37 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

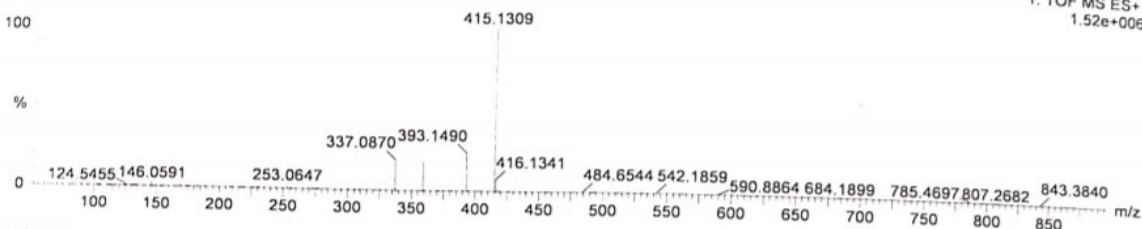
C: 0-19 H: 0-100 N: 0-2 O: 0-5 S: 0-1

MA-172 S2

160222_08 15 (0.310) Cm (15:16)

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

16-Feb-2022
12:28:36
1: TOF MS ES+
1.52e+006

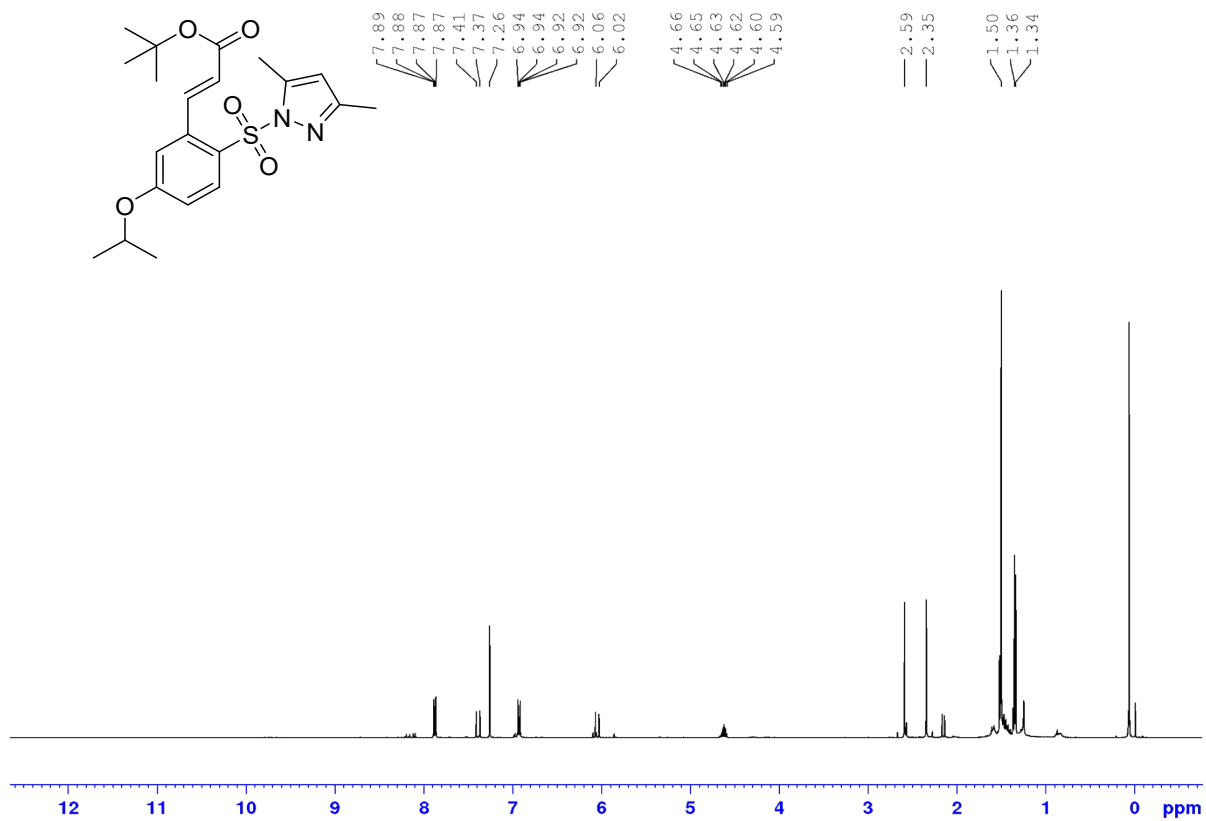


Minimum:

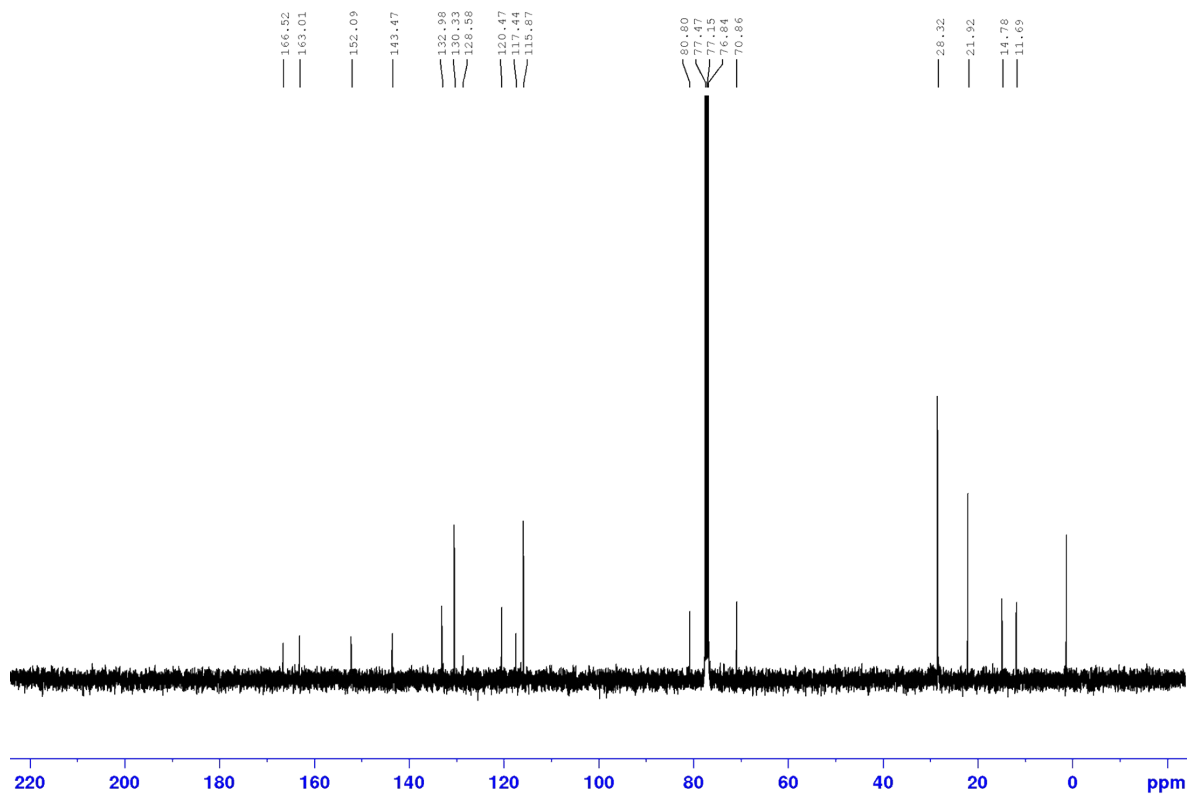
Maximum: 2.0 5.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
393.1490	393.1484	0.6	1.5	8.5	35.0	n/a	n/a	C19 H25 N2 O5 S

¹H-NMR (400 MHz, CDCl₃) of 3n



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3n



HRMS of 3n

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

37 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

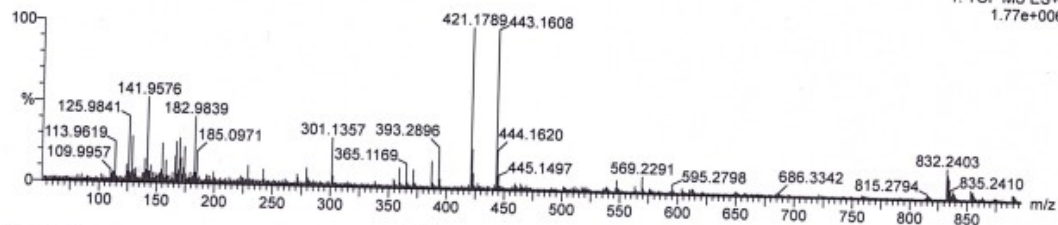
C: 0-21 H: 0-100 N: 0-2 O: 0-5 S: 0-1

MA-232

230522_11 9 (0.208) Cm (9)

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

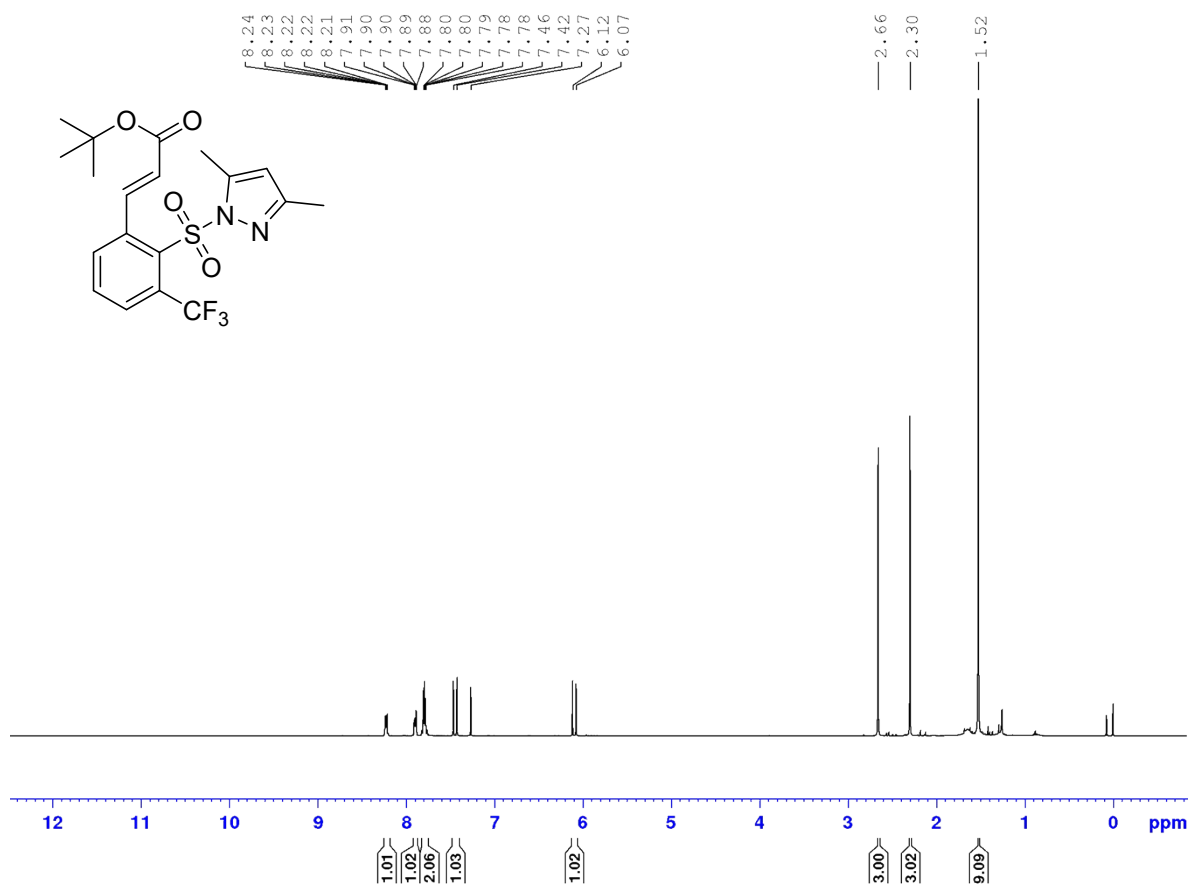
23-May-2022
12:33:14
1: TOF MS ES+
1.77e+006



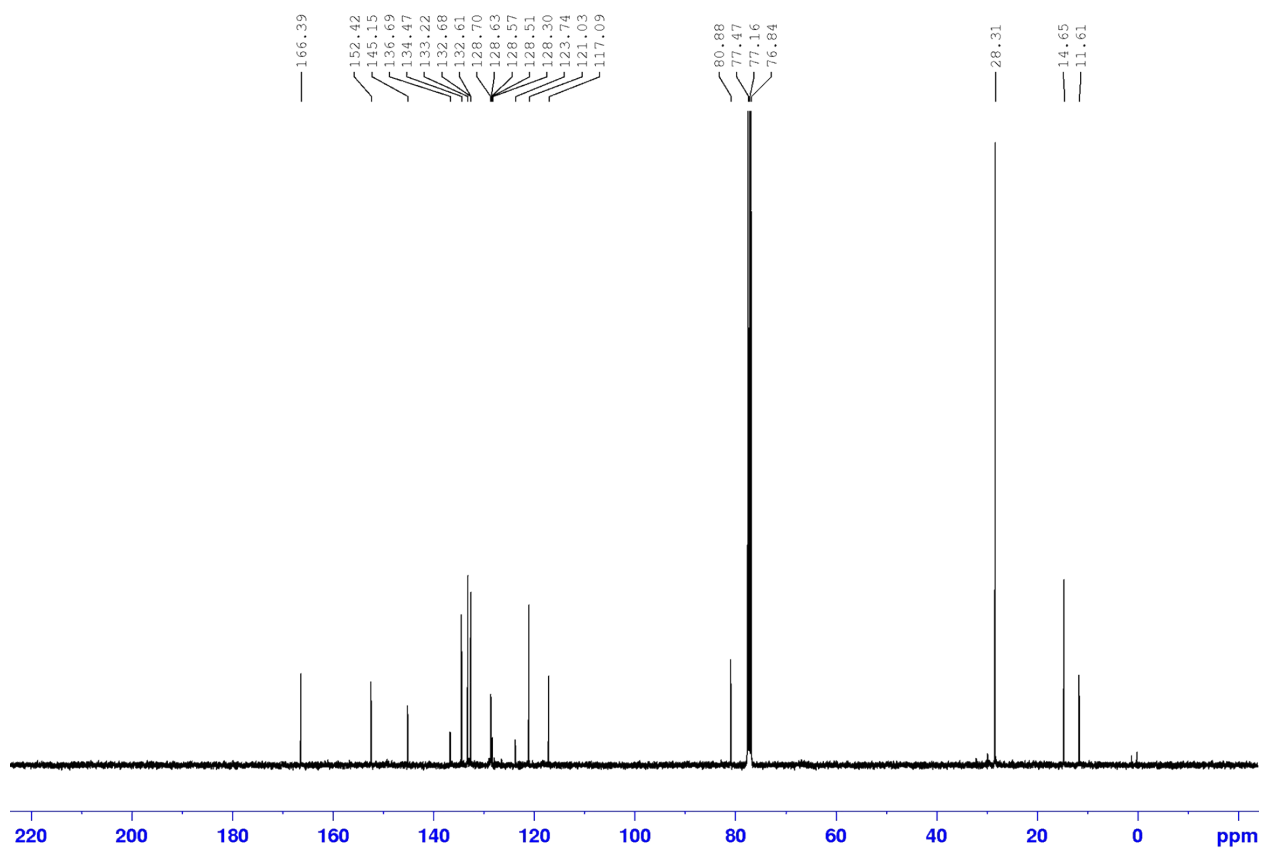
Minimum: -1.5
Maximum: 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
421.1789	421.1797	-0.8	-1.9	8.5	49.7	n/a	n/a	C21 H29 N2 O5 S

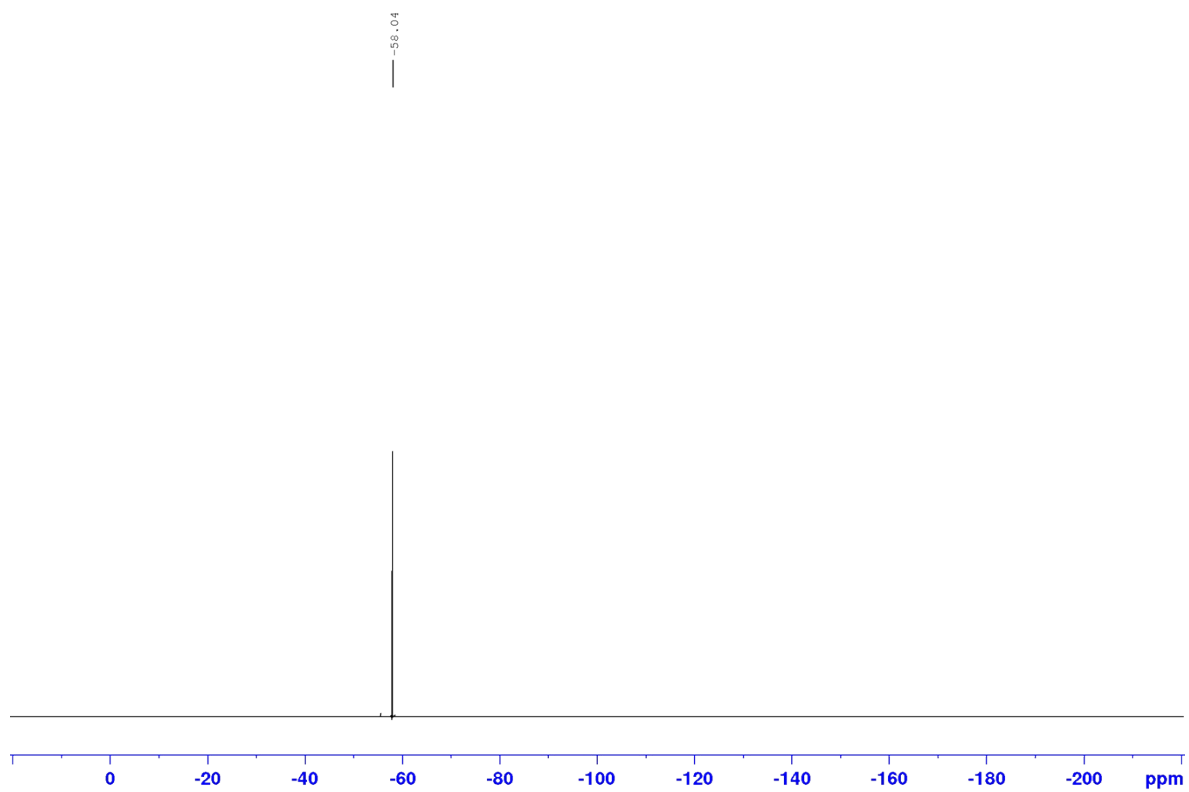
¹H-NMR (400 MHz, CDCl₃) of 3o



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3o



¹⁹F-NMR (377 MHz, CDCl₃) of 30



HRMS of 3o

Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

121 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

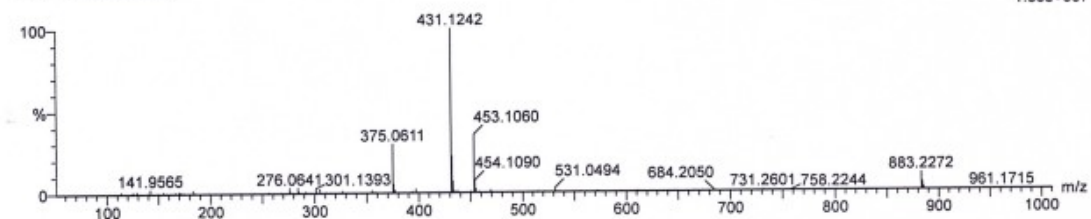
C: 0-19 H: 0-100 N: 0-2 O: 0-4 F: 0-3 S: 0-1

MA-244

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

050822_04 10 (0.225)

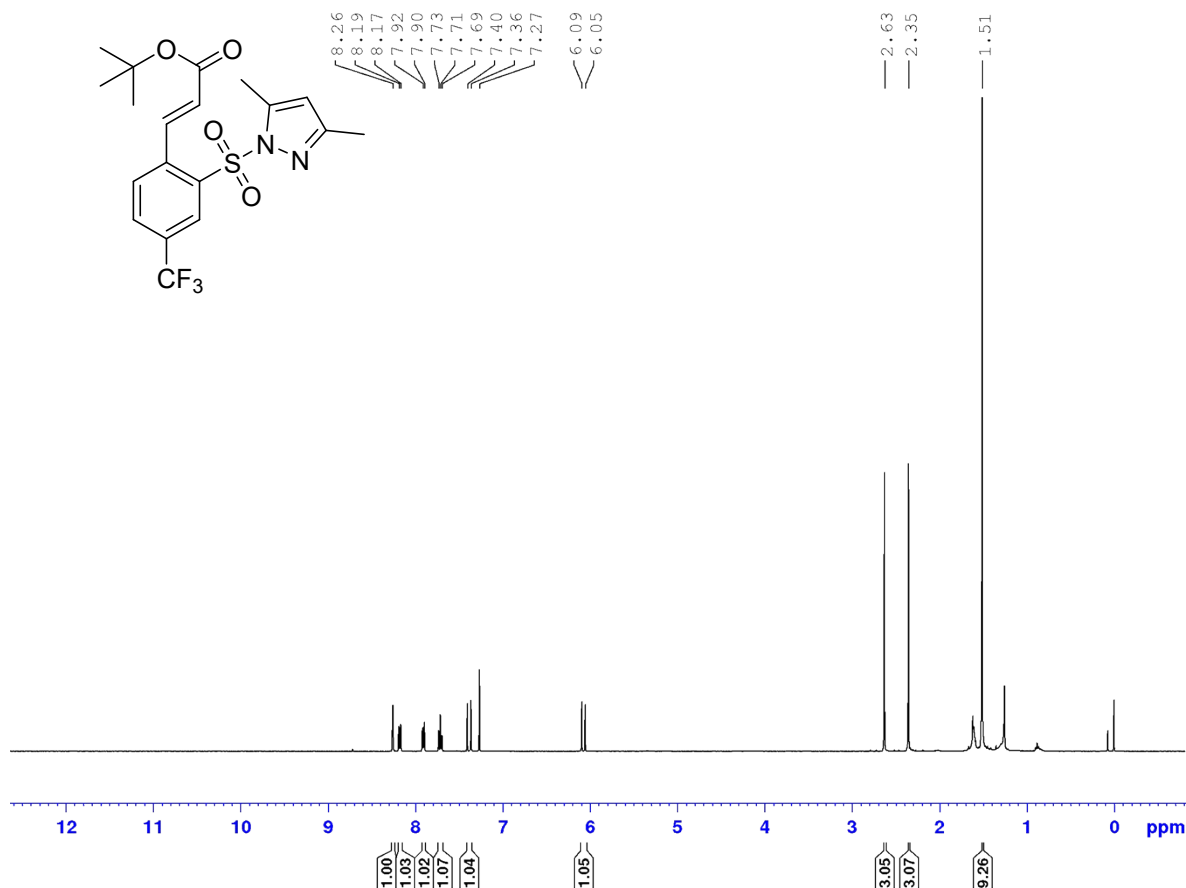
05-Aug-2022
14:07:15
1: TOF MS ES+
1.36e+007



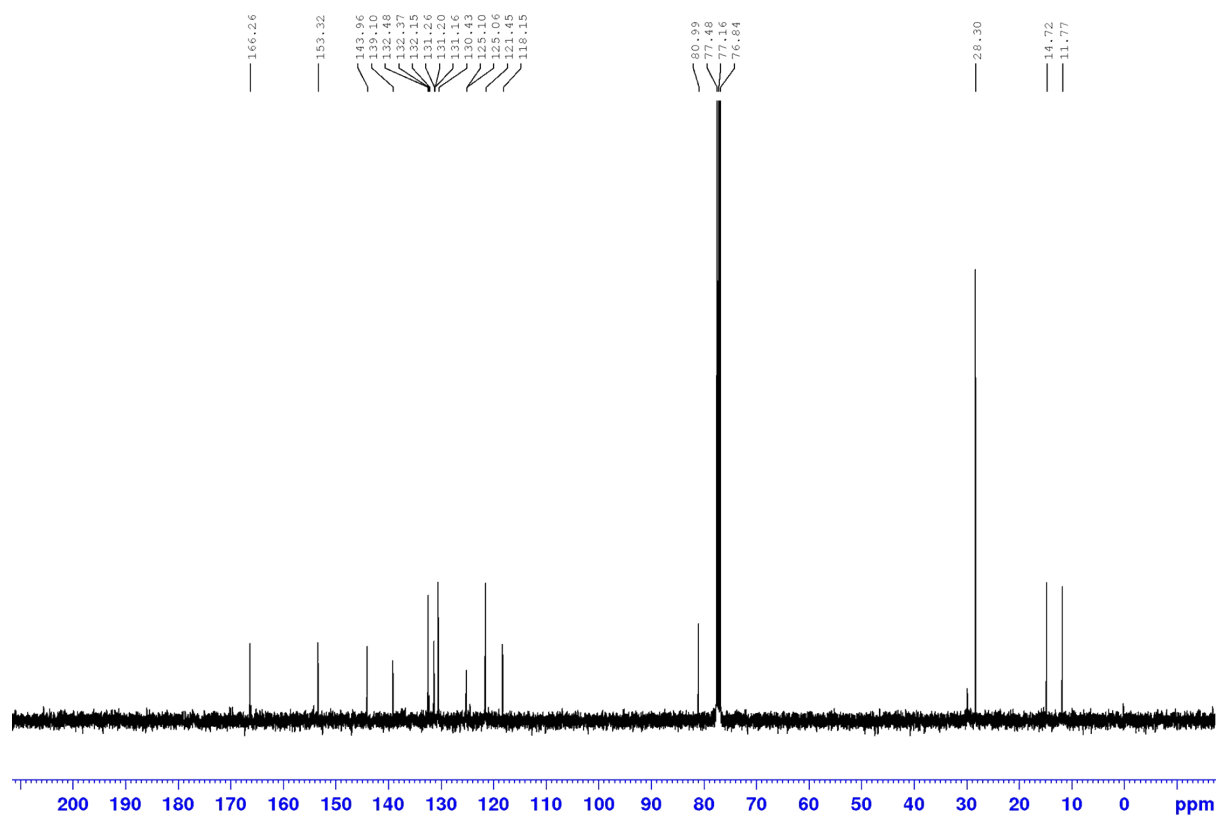
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
431.1242	431.1252	-1.0	-2.3	8.5	777.0	n/a	n/a	C19 H22 N2 O4 F3 S

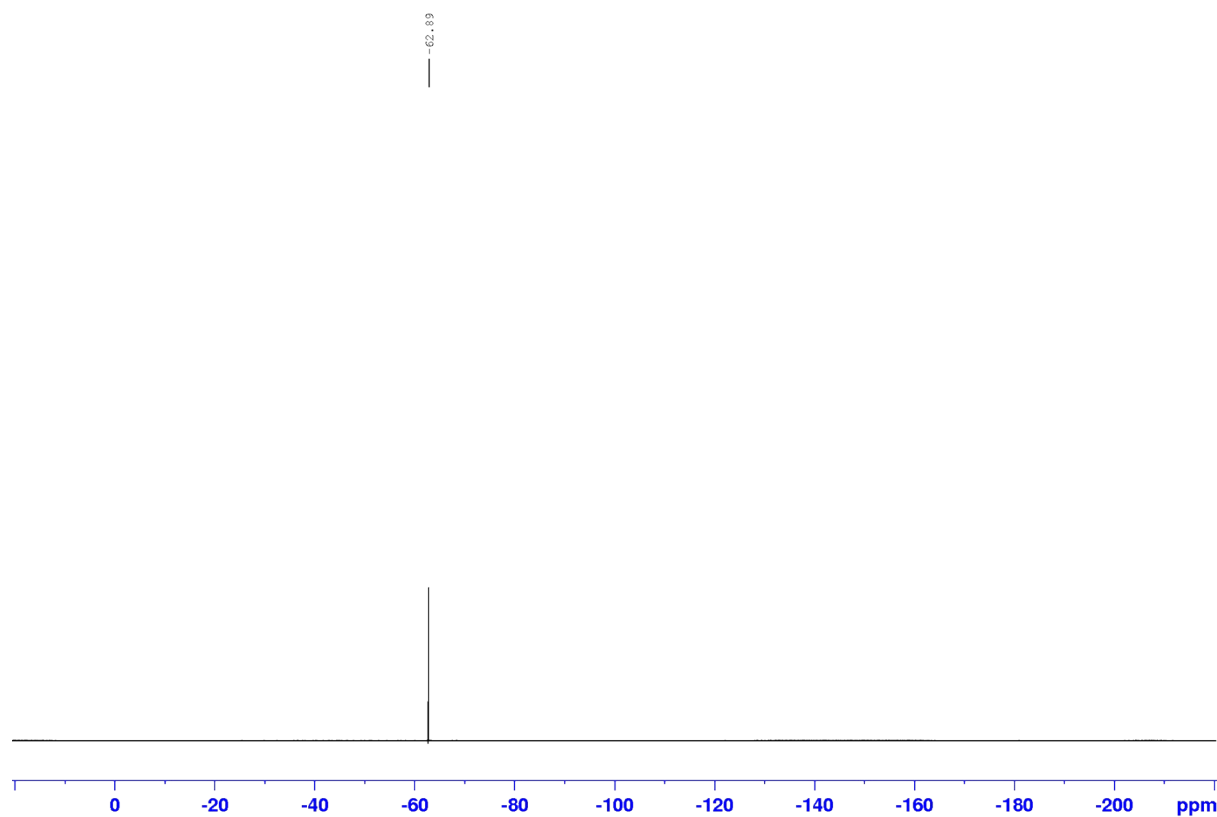
¹H-NMR (400 MHz, CDCl₃) of 3p



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3p



^{19}F -NMR (377 MHz, CDCl_3) of 3p



HRMS of 3p

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

121 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-19 H: 0-100 N: 0-2 O: 0-4 S: 0-1 F: 0-3

MA-241

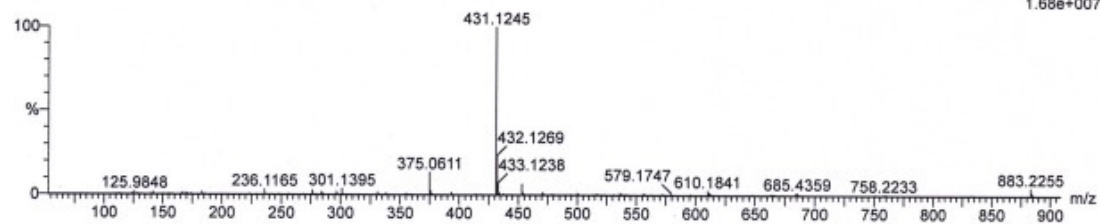
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

17-Jun-2022

13:32:26

1: TOF MS ES+
1.68e+007

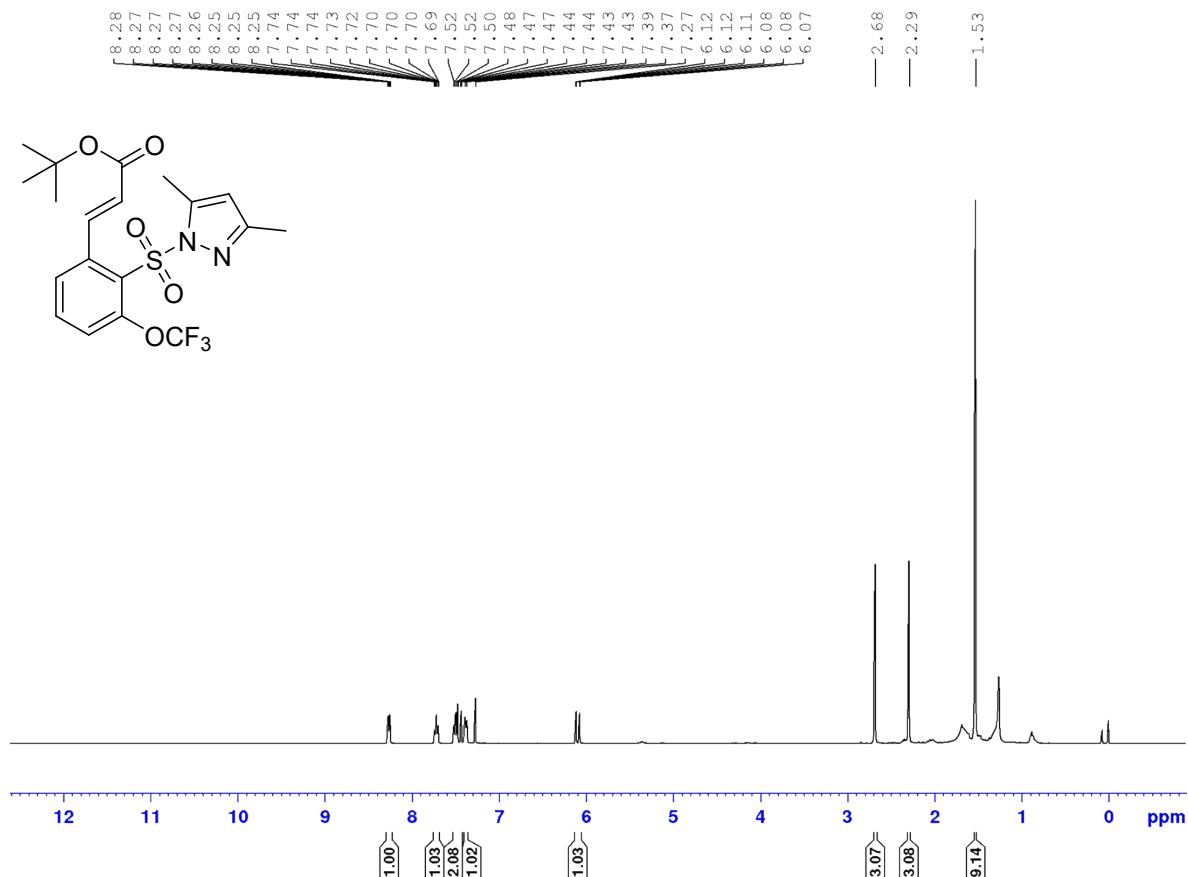
170622_11 8 (0.172)



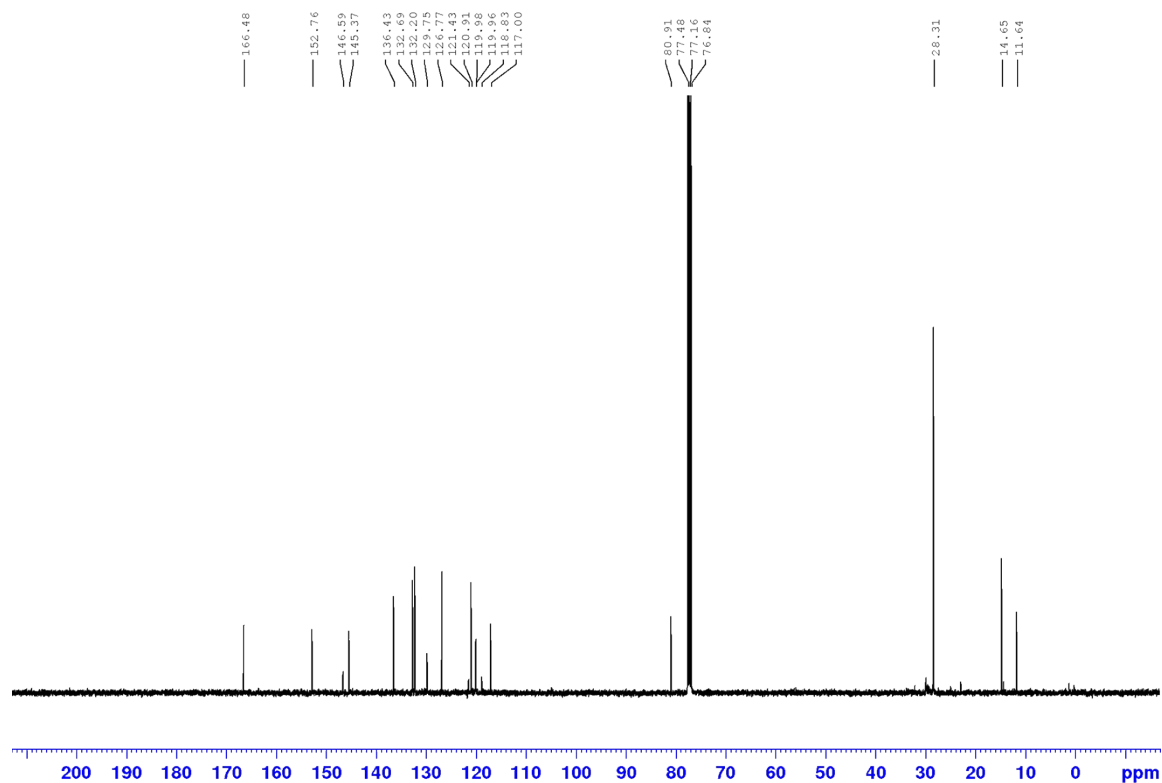
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
431.1245	431.1252	-0.7	-1.6	8.5	863.7	n/a	n/a	C19 H22 N2 O4 S F3

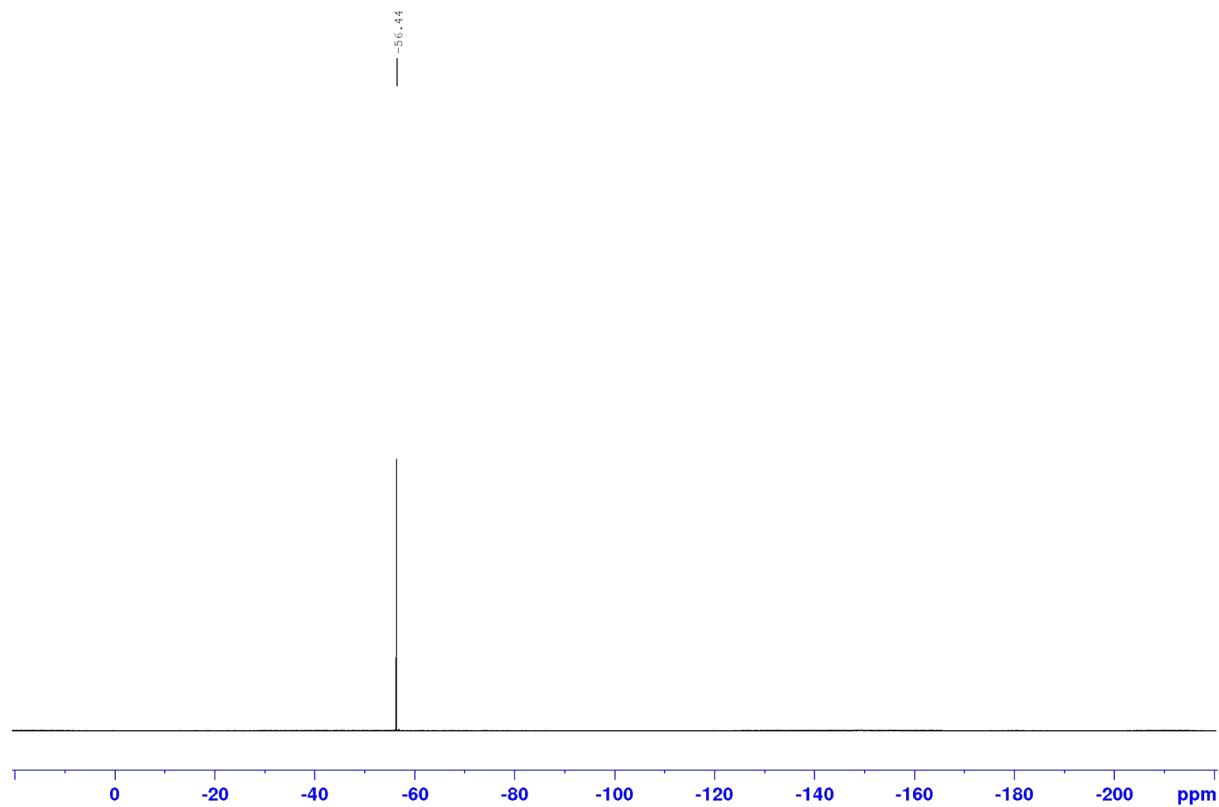
¹H-NMR (400 MHz, CDCl₃) of 3q



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3q



^{19}F -NMR (377 MHz, CDCl_3) of 3q



HRMS of 3q

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

145 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-19 H: 0-100 N: 0-2 O: 0-5 F: 0-3 S: 0-1

MA-248

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

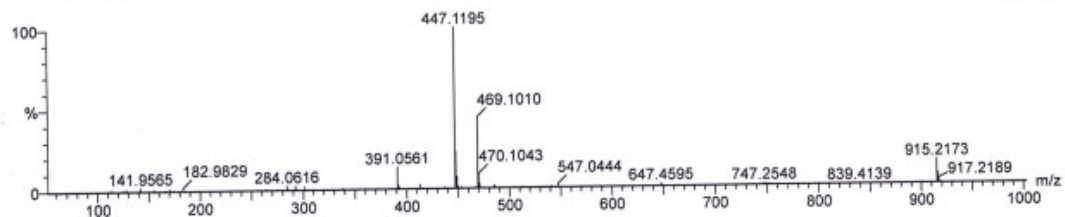
05-Aug-2022

14:04:33

1: TOF MS ES+

1.62e+007

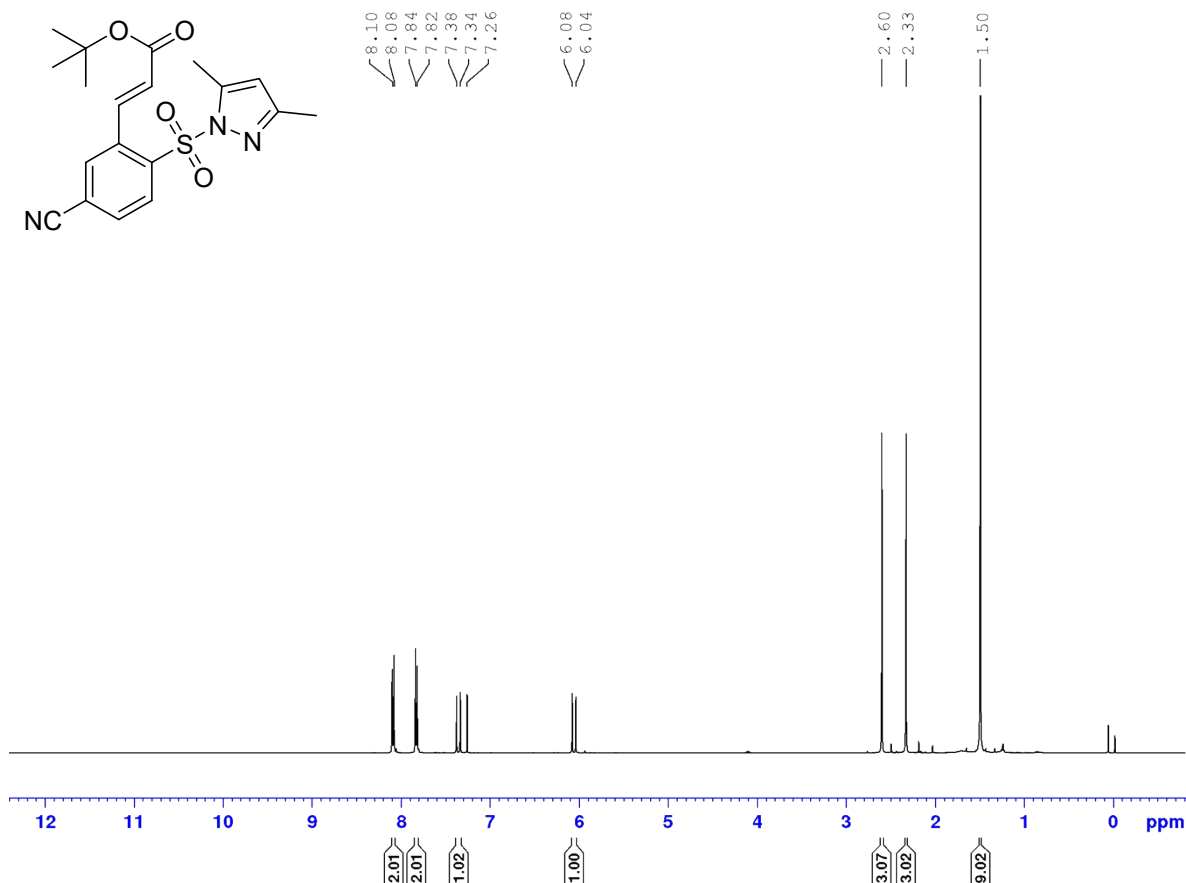
050822_03 9 (0.209)



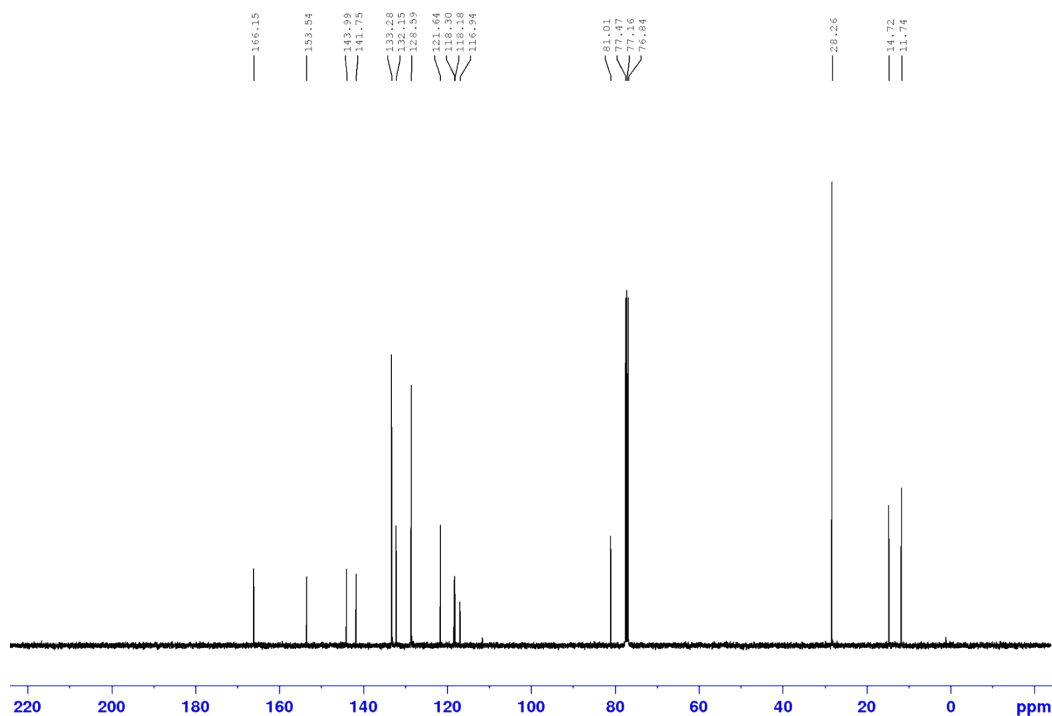
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
447.1195	447.1202	-0.7	-1.6	8.5	768.5	n/a	n/a	C19 H22 N2 O5 F3 S

¹H-NMR (400 MHz, CDCl₃) of 3r



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 3r



HRMS of 3r

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

44 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-19 H: 0-100 N: 0-3 O: 0-4 S: 0-1

MA-238

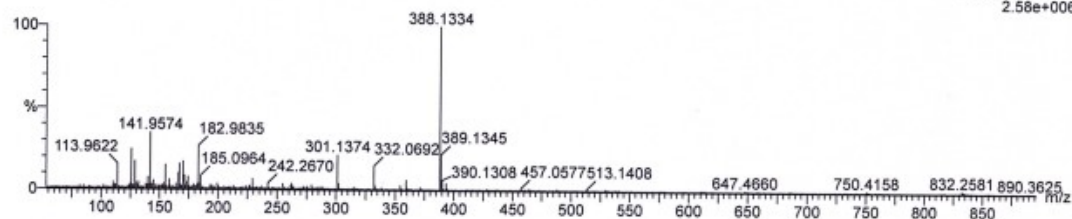
QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

01-Jun-2022

13:39:46

1: TOF MS ES+
2.58e+006

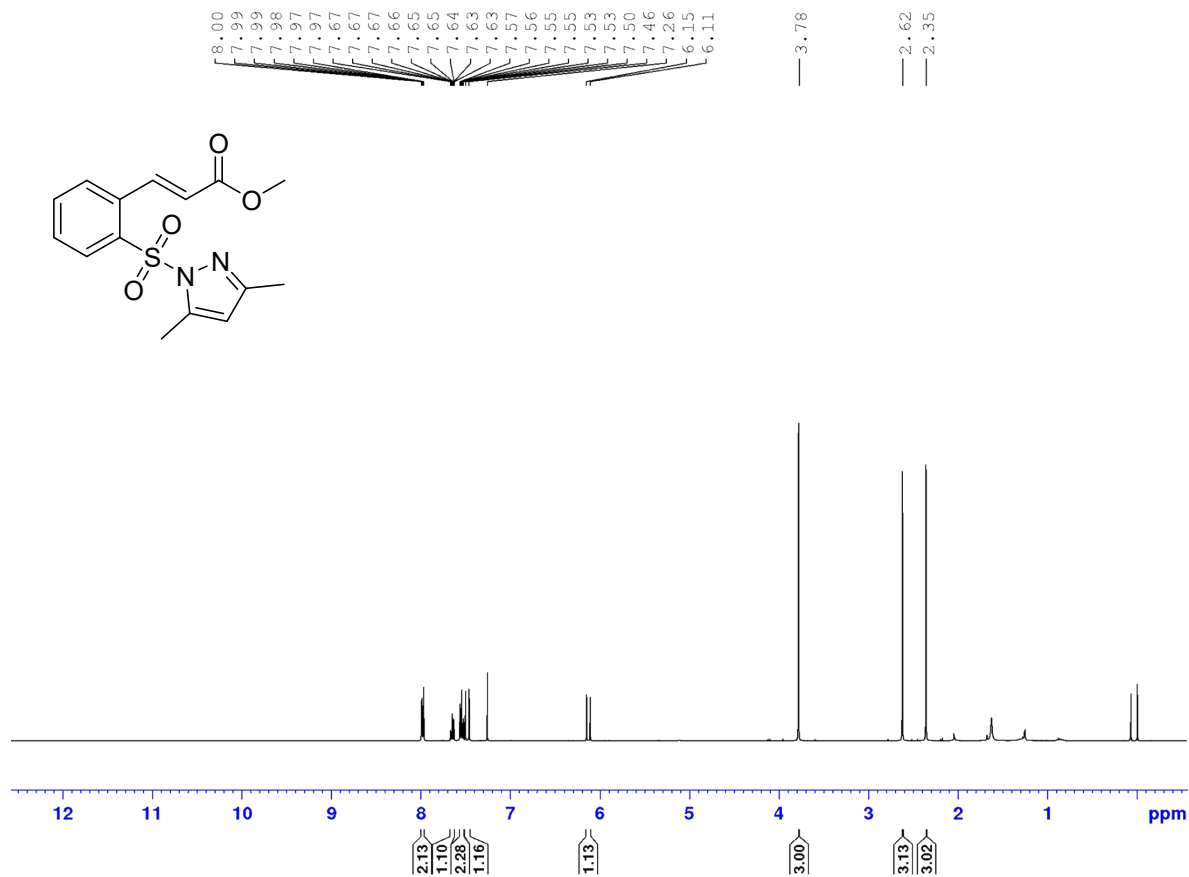
010622_12 16 (0.327) Cm (16)



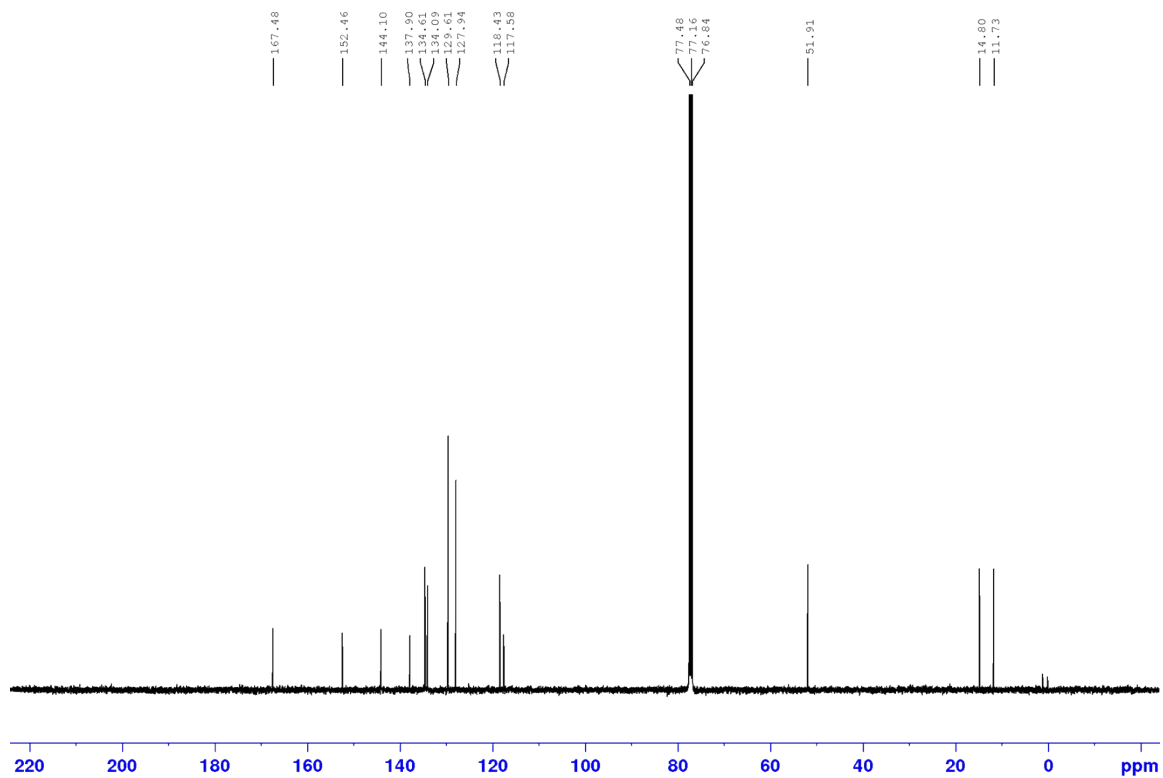
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
388.1334	388.1331	0.3	0.8	10.5	31.3	n/a	n/a	C19 H22 N3 O4 S

^1H -NMR (400 MHz, CDCl_3) of 3s



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3s



HRMS of 3s

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-15 H: 0-100 N: 0-2 O: 0-4 S: 0-1

MA-252

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

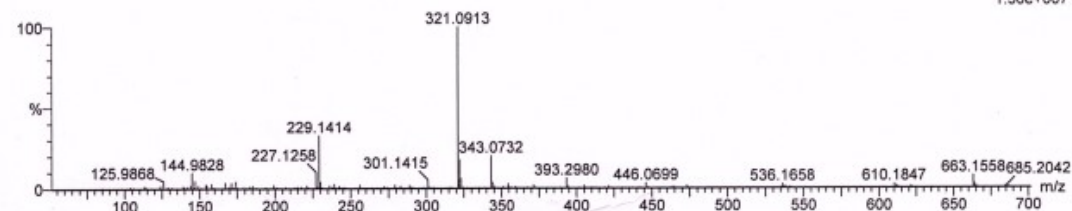
28-Sep-2022

13:03:07

1: TOF MS ES+

1.30e+007

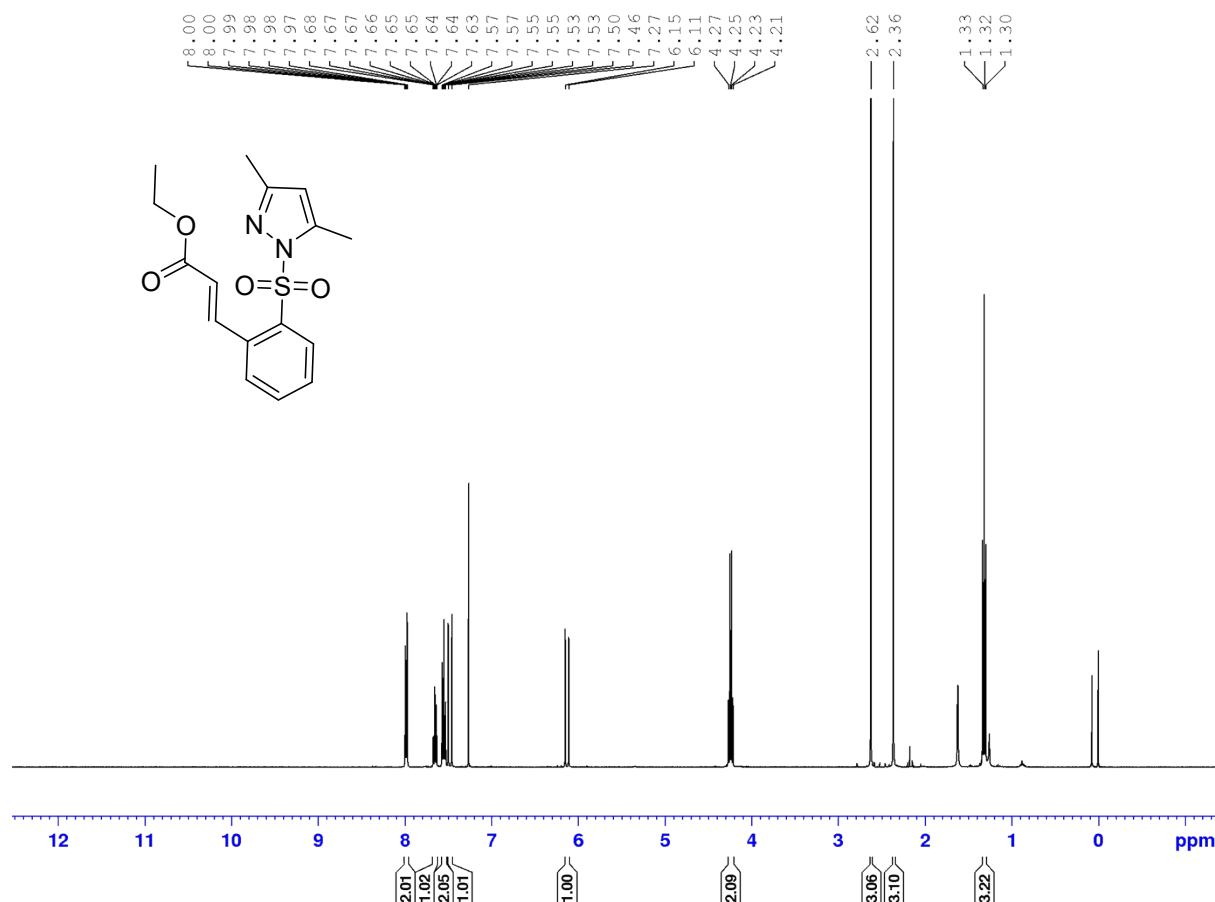
280922_11 9 (0.209)



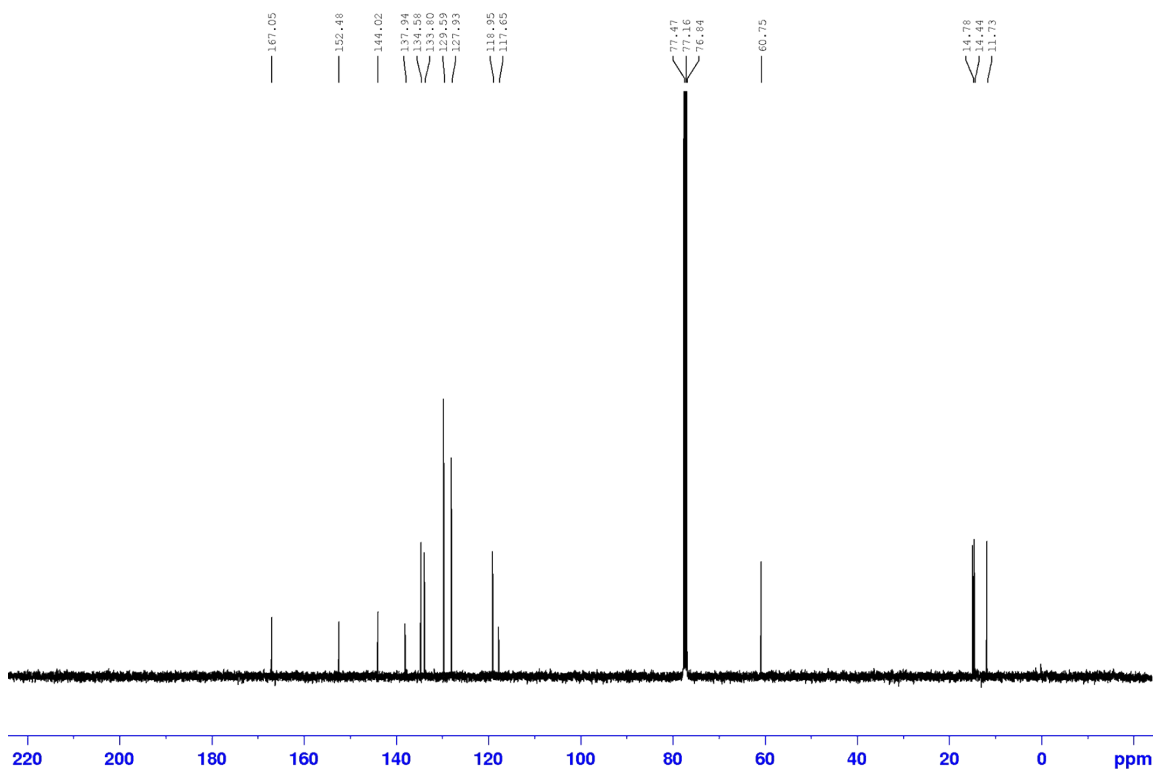
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
321.0913	321.0909	0.4	1.2	8.5	1293.8	n/a	n/a	C15 H17 N2 O4 S

¹H-NMR (400 MHz, CDCl₃) of 3t



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3t



HRMS of 3t

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-16 H: 0-100 N: 0-2 O: 0-4 S: 0-1

MA-EA

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

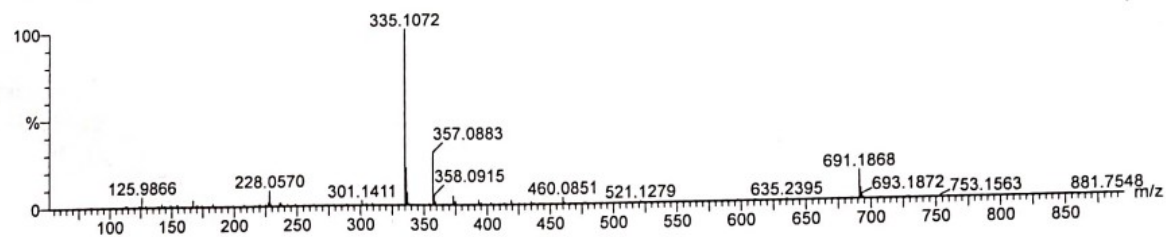
22-Feb-2023

11:17:05

1: TOF MS ES+

1.36e+007

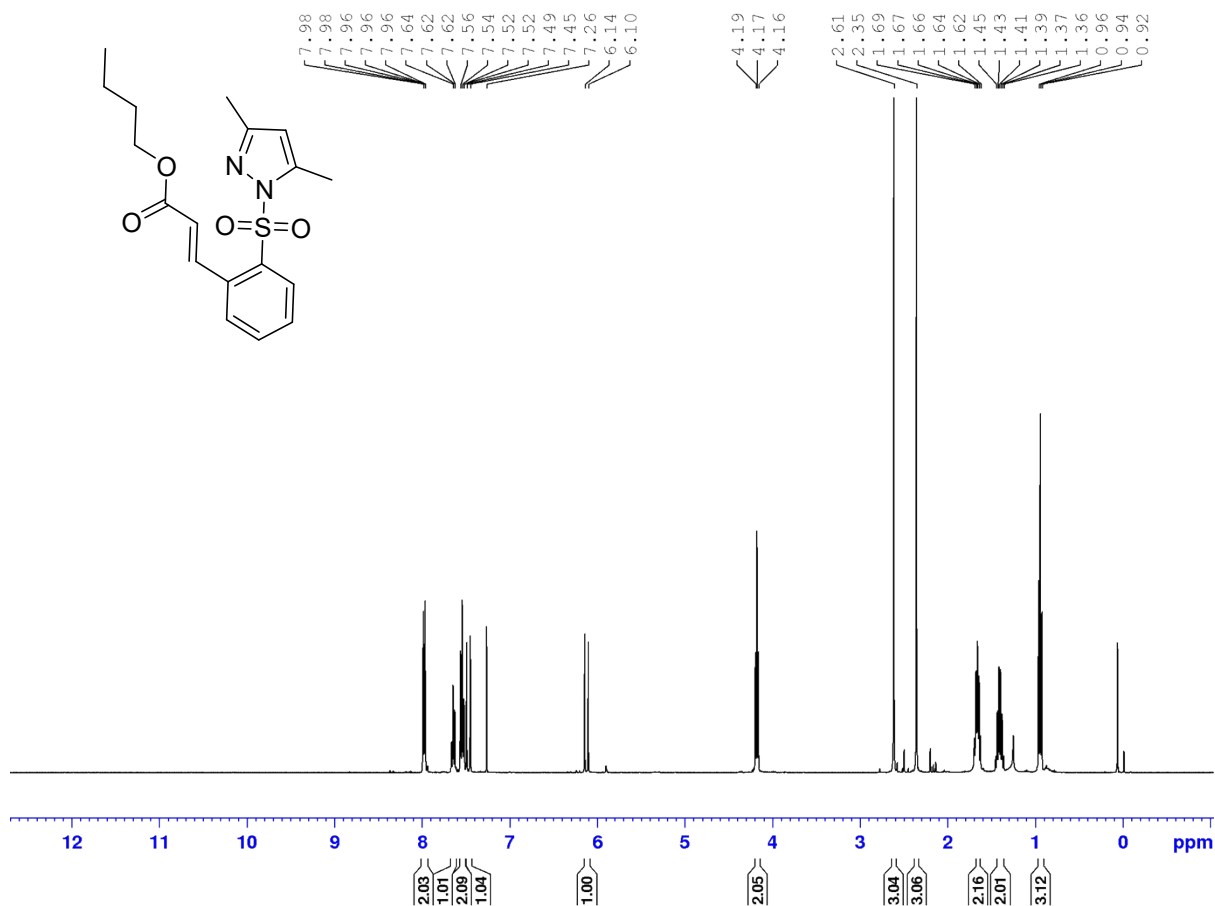
220239 8 (0.172)



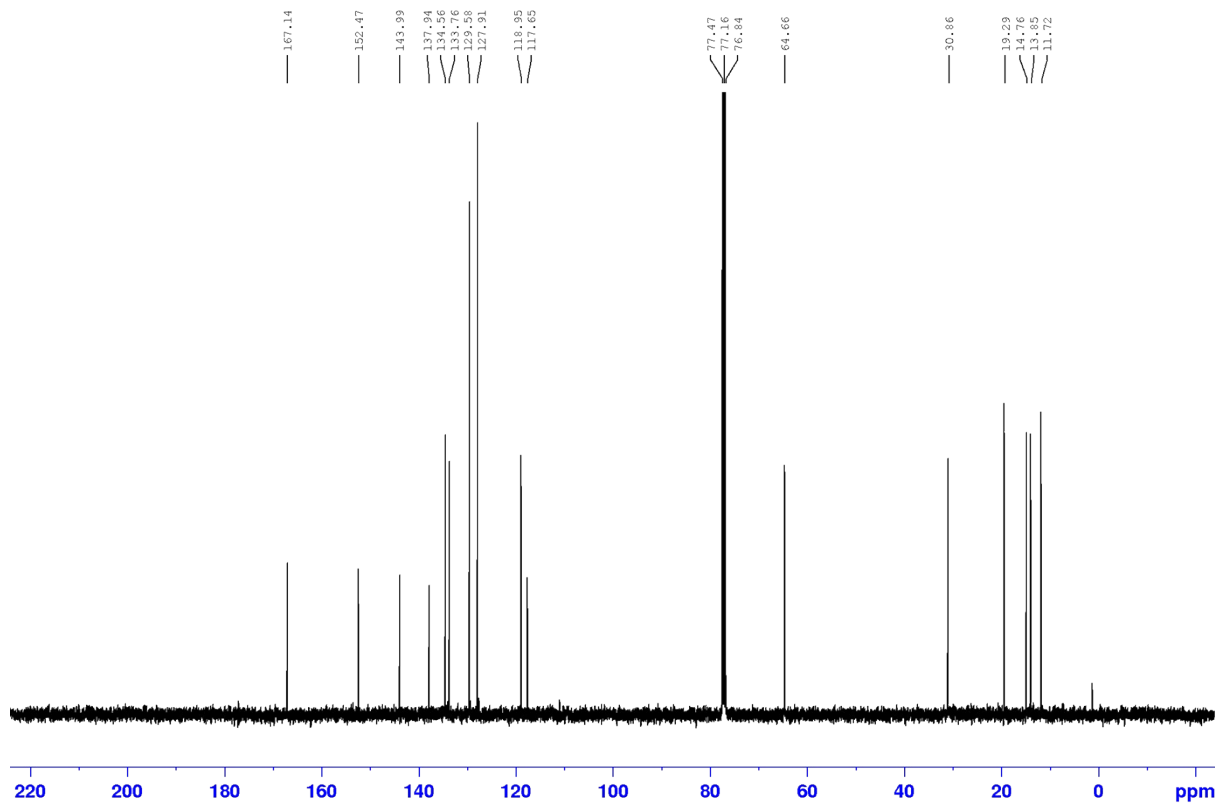
Minimum: -1.5
Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
335.1072	335.1066	0.6	1.8	8.5	1115.3	n/a	n/a	C16 H19 N2 O4 S

¹H-NMR (400 MHz, CDCl₃) of 3u



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3u



HRMS of 3u

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

31 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

C: 0-18 H: 0-100 N: 0-2 O: 0-4 S: 0-1

MA-bu

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

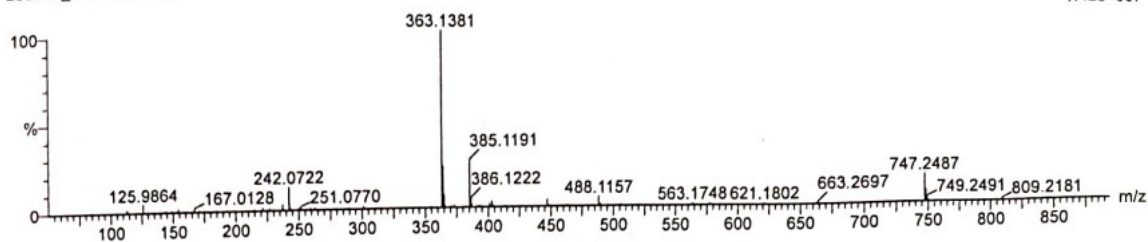
23-Feb-2023

12:20:52

1: TOF MS ES+

1.42e+007

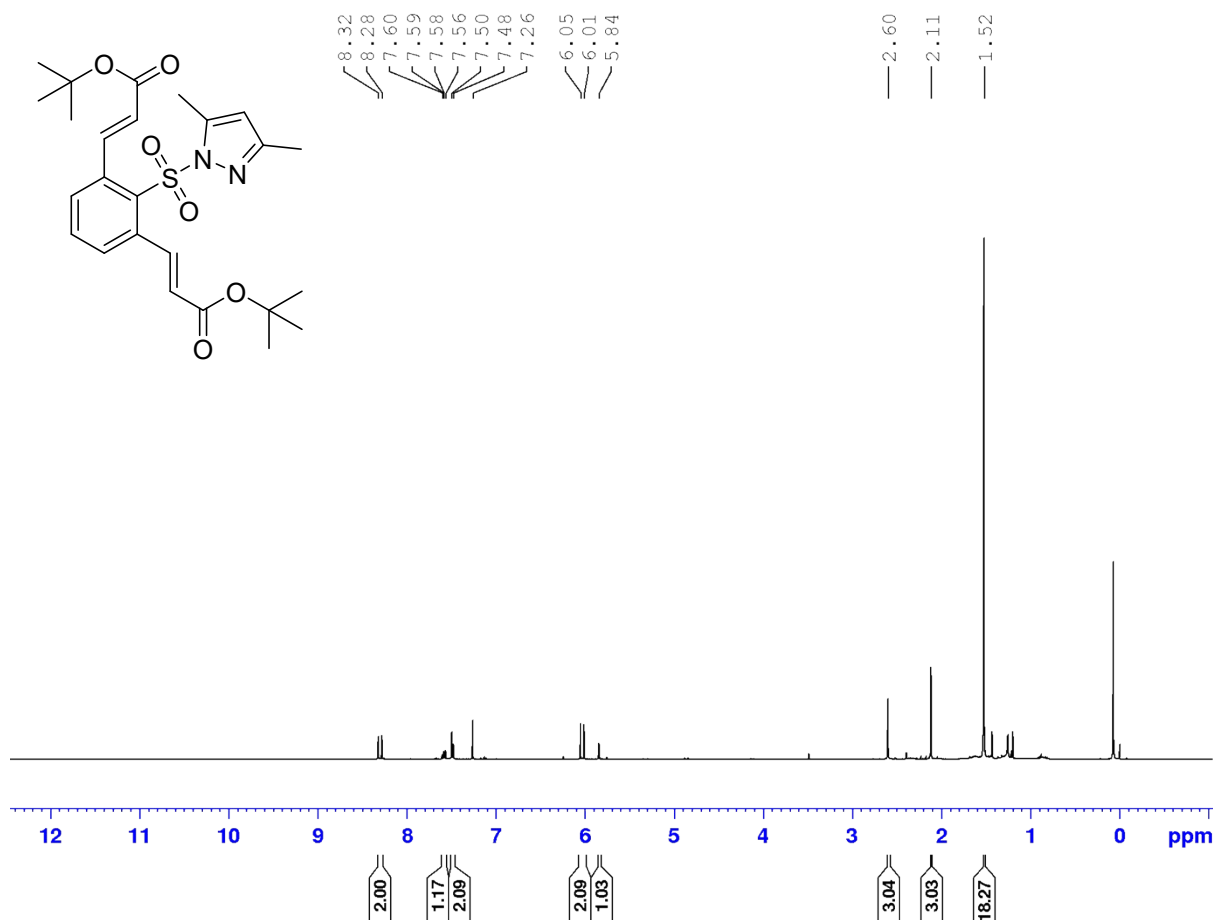
230223_25 31 (0.620)



Minimum: -1.5
Maximum: 2.0 100.0 50.0

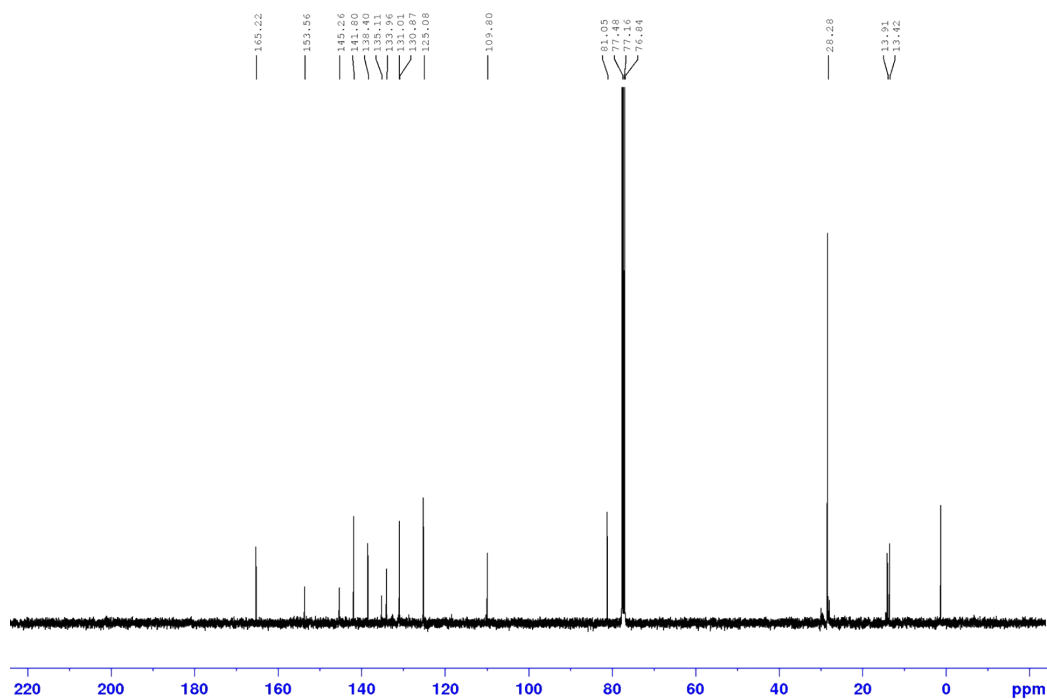
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
363.1381	363.1379	0.2	0.6	8.5	997.5	n/a	n/a	C18 H23 N2 O4 S

¹H-NMR (400 MHz, CDCl₃) of 3aa



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 3aa

S-57



HRMS of 3aa

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

46 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

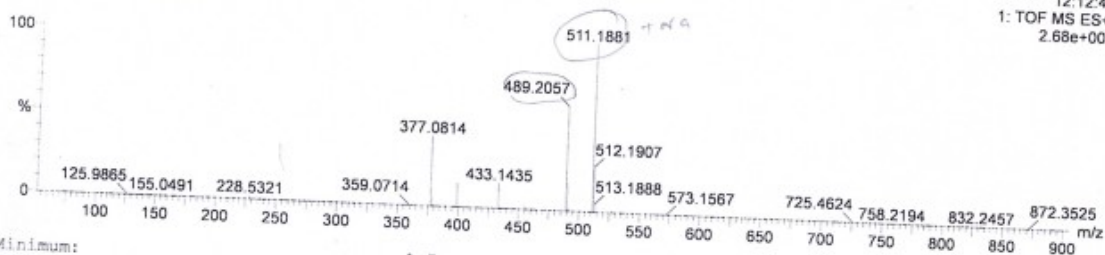
C: 0-25 H: 0-200 N: 0-2 O: 0-6 S: 0-1

MA-168 s2

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

01-Feb-2022
12:12:49
1: TOF MS ES+
2.68e+006

010222_06 8 (0.172) Cm (8)

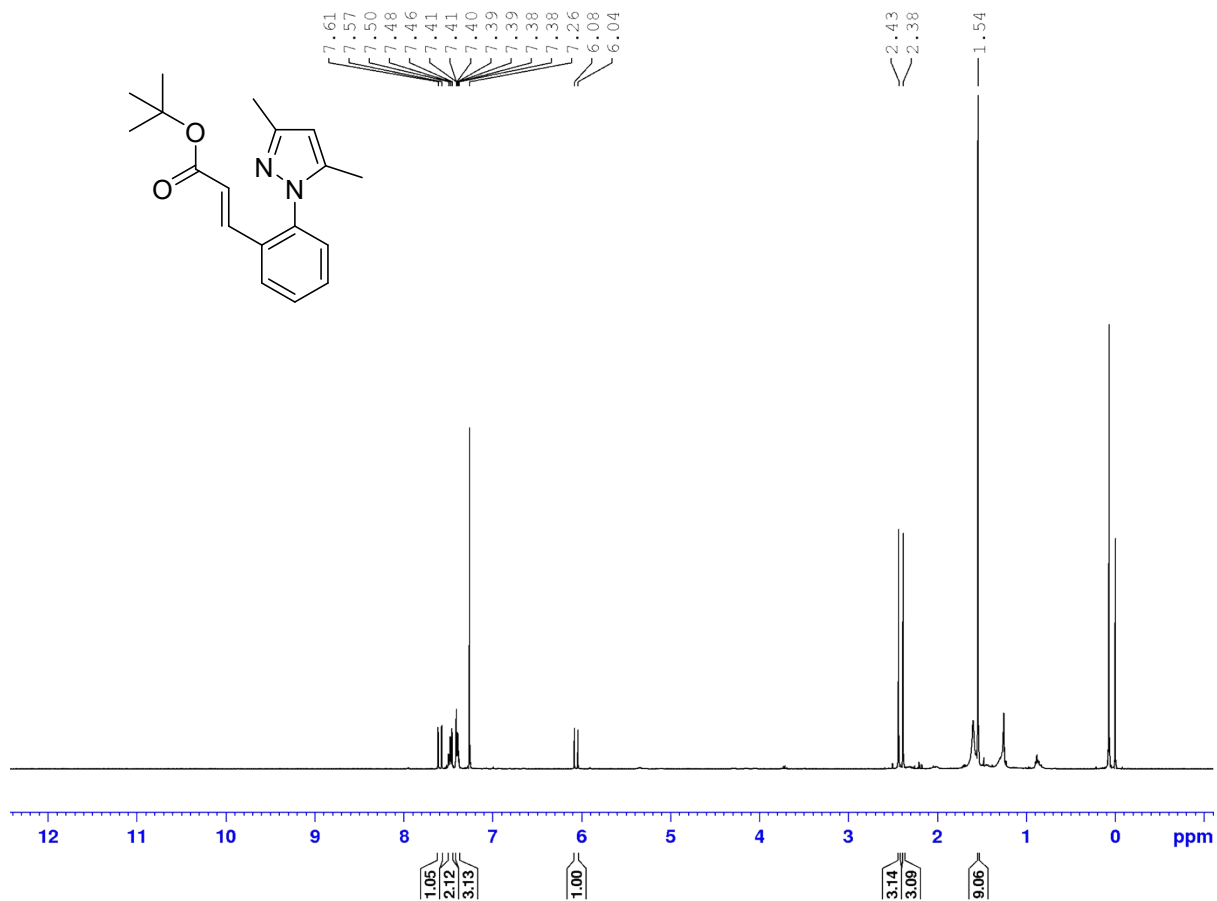


Minimum:
Maximum:

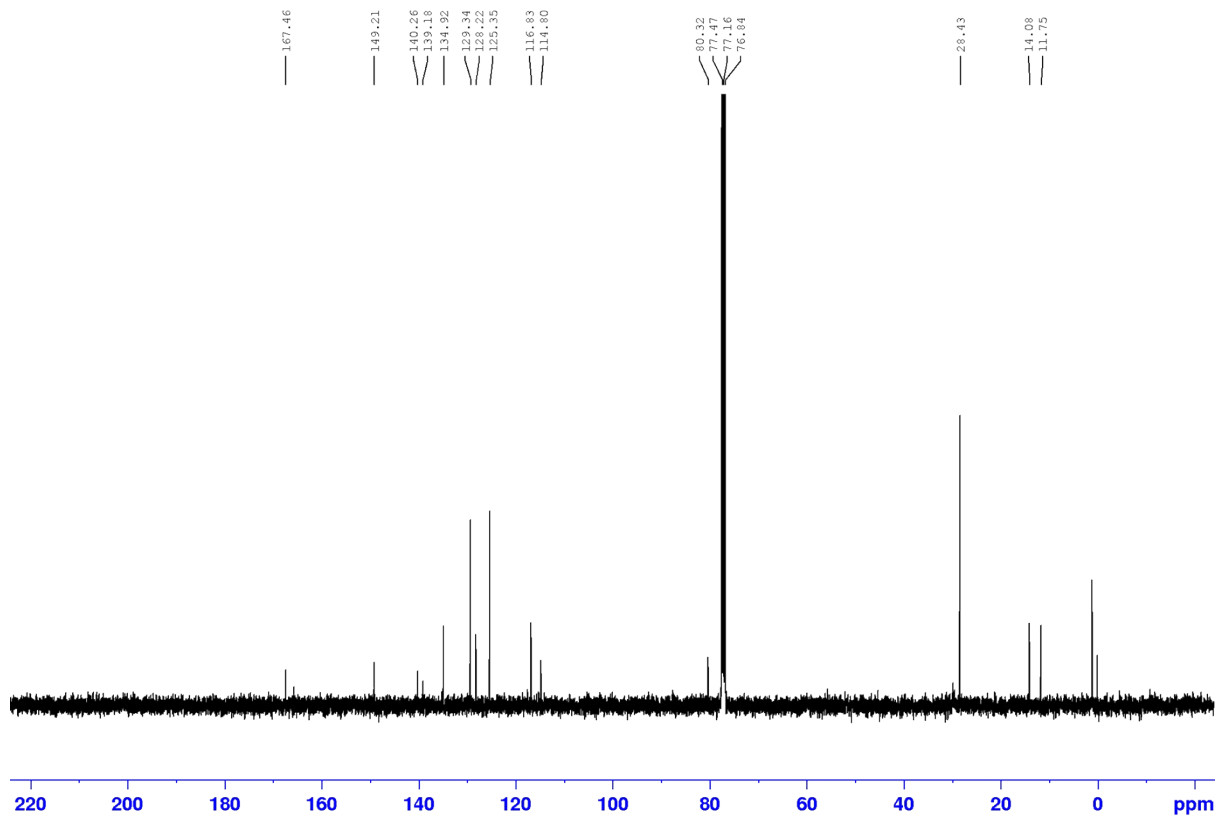
2.0 5.0 -1.5
50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
489.2057	489.2059	-0.2	-0.4	10.5	32.7	n/a	n/a	C25 H33 N2 O6 S

¹H-NMR (400 MHz, CDCl₃) of 4a



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 4a



HRMS of 4a

Elemental Composition Report

Single Mass Analysis

Tolerance = 50.0 PPM / DBE: min = -1.5, max = 50.0
 Element prediction: Off
 Number of isotope peaks used for i-FIT = 3

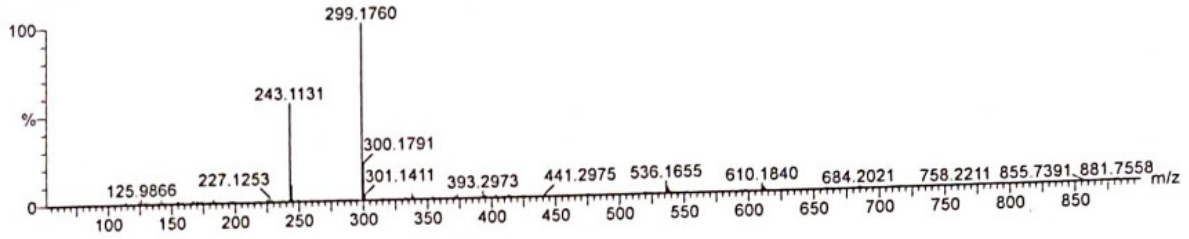
Monoisotopic Mass, Even Electron Ions
 10 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:
 C: 0-18 H: 0-100 N: 0-2 O: 0-2
 MA-PYZ

QMI DIVISION, CSIR-IIIM JAMMU
 Xevo G2-XS QTOF YFC2015

22-Feb-2023
 11:19:38
 1: TOF MS ES+
 1.13e+007

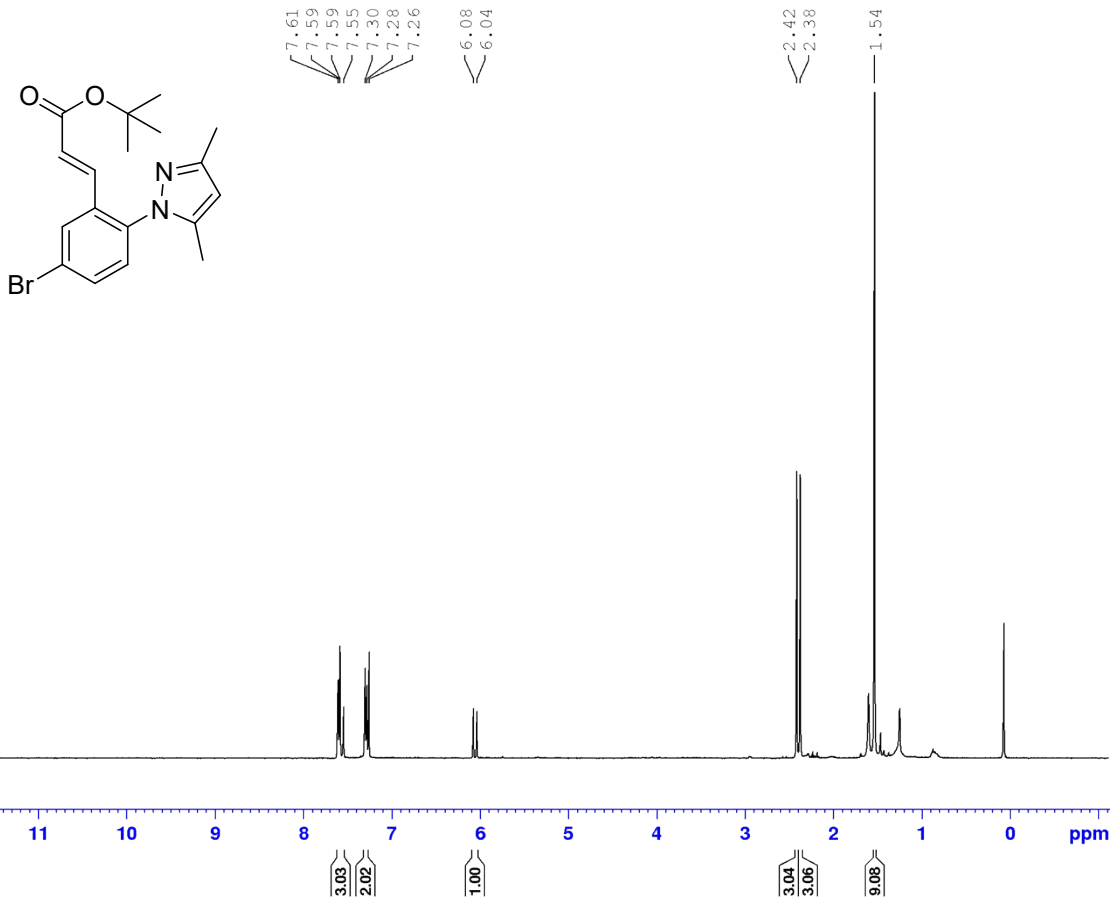
220240 8 (0.172)



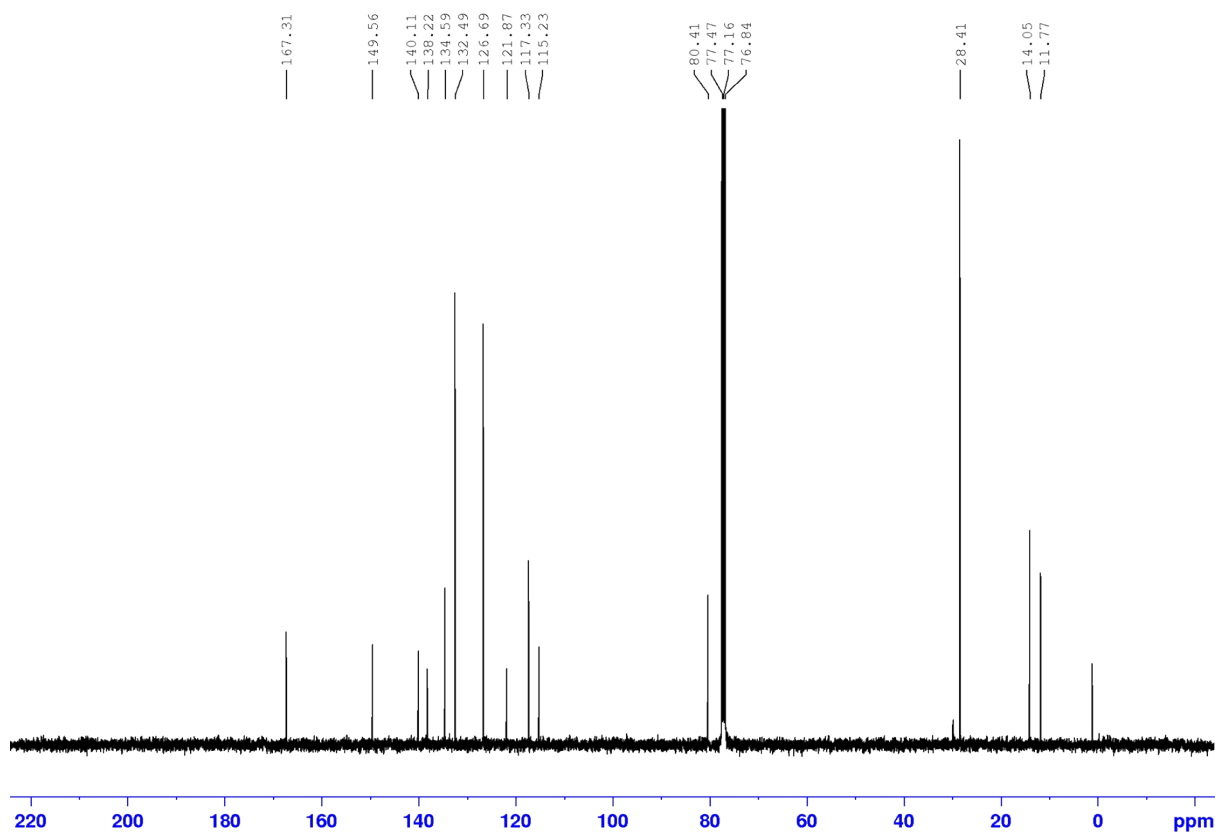
Minimum: -1.5
 Maximum: 2.0 50.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
299.1760	299.1760	0.0	0.0	8.5	1219.8	n/a	n/a	C18 H23 N2 O2

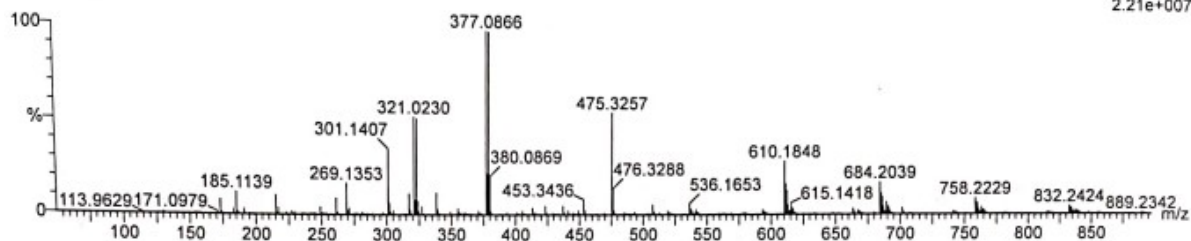
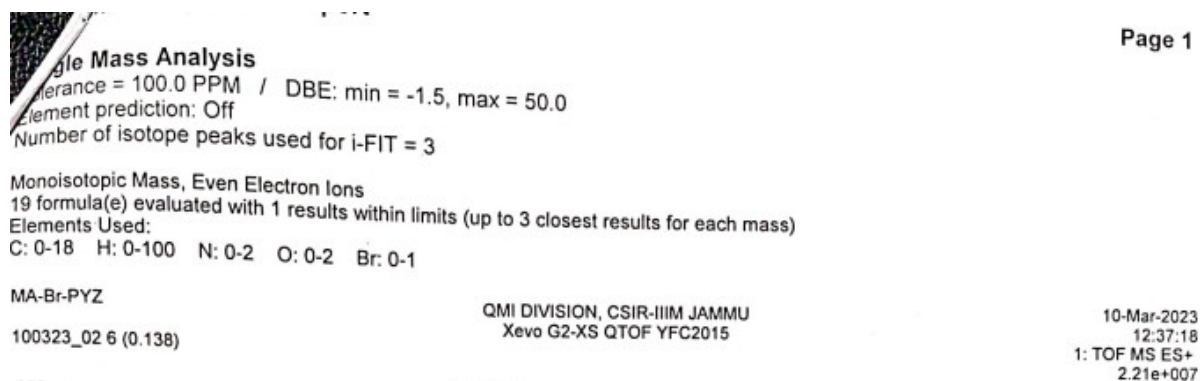
¹H-NMR (400 MHz, CDCl₃) of 4b



¹³C{¹H}-NMR (101 MHz, CDCl₃) of 4b



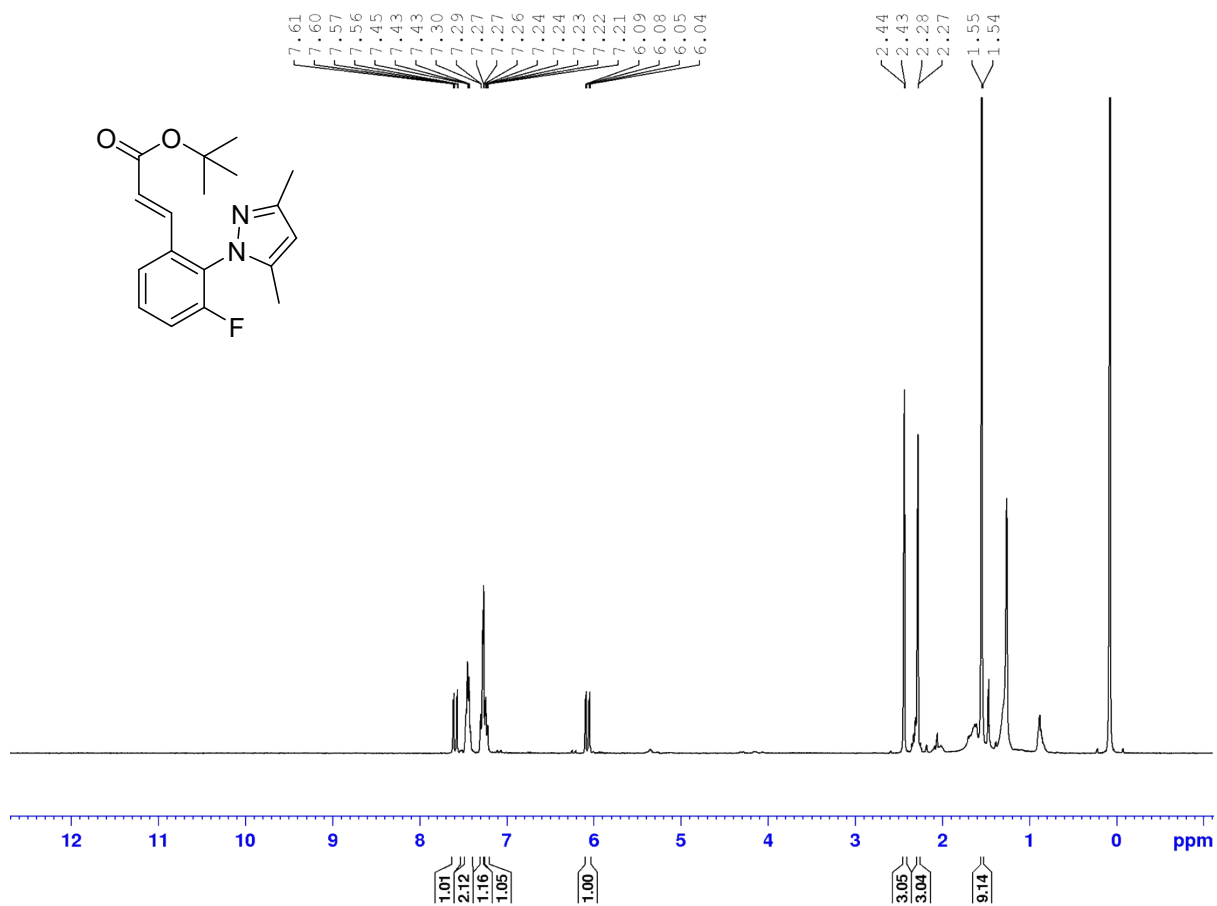
HRMS of 4b



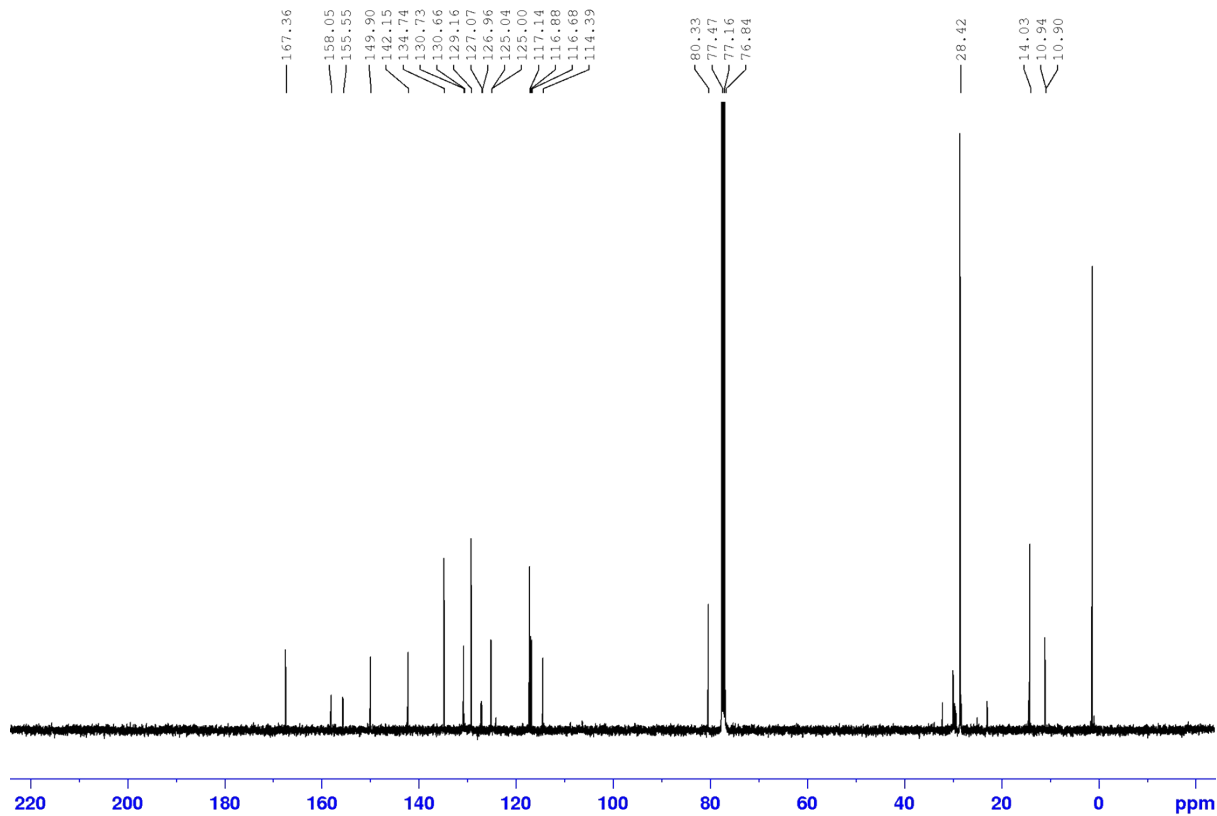
Minimum: -1.5
 Maximum: 2.0 100.0 50.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
377.0866	377.0865	0.1	0.3	8.5	989.7	n/a	n/a	C18 H22 N2 O2 Br

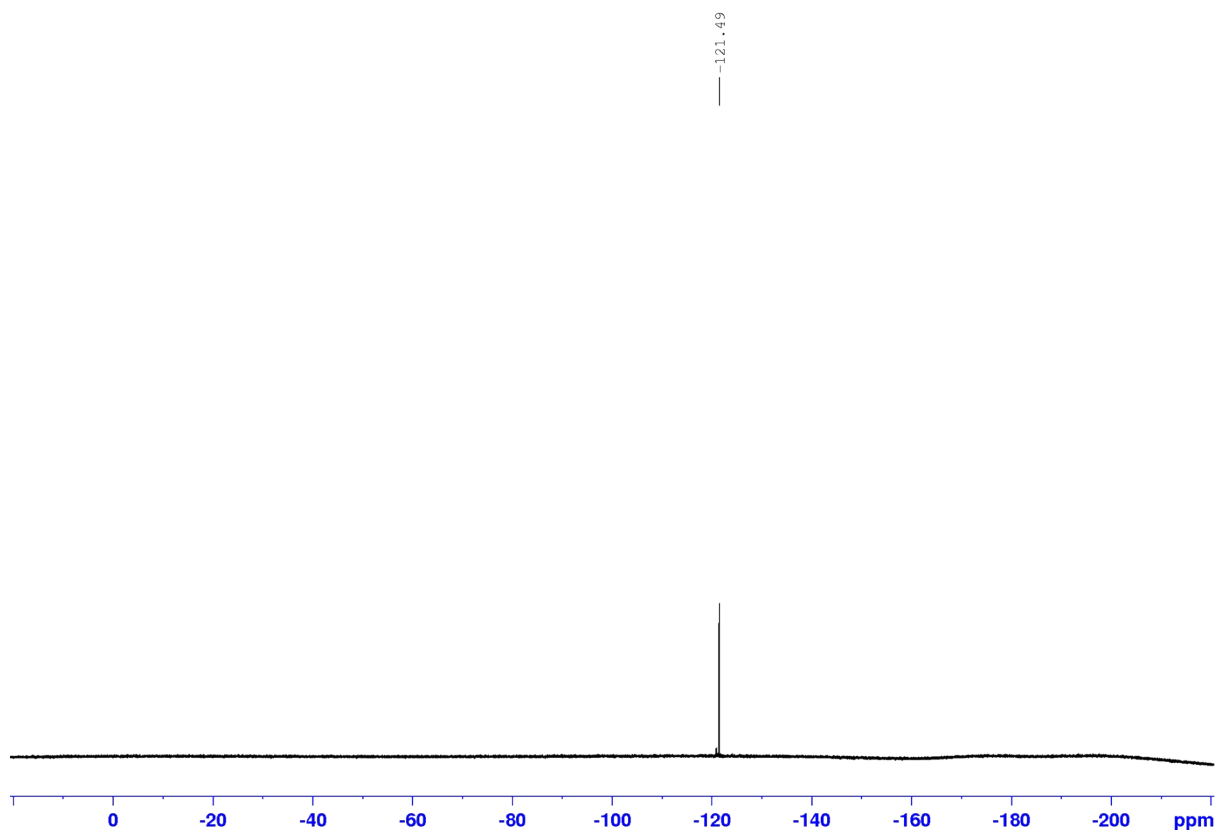
¹H-NMR (400 MHz, CDCl₃) of 4c



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, CDCl_3) of 4c



¹⁹F-NMR (377 MHz, CDCl₃) of 4c



HRMS of 4c

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

19 formula(e) evaluated with 1 results within limits (up to 3 closest results for each mass)

Elements Used:

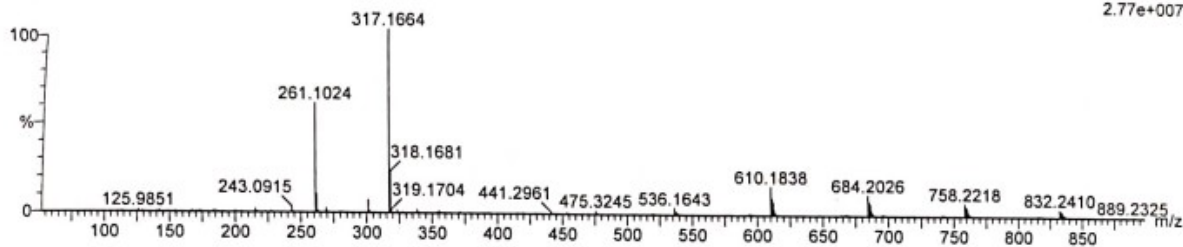
C: 0-18 H: 0-100 N: 0-2 O: 0-2 F: 0-1

MA-2F-PYZ

QMI DIVISION, CSIR-IIIM JAMMU
Xevo G2-XS QTOF YFC2015

10-Mar-2023
12:33:46
1: TOF MS ES+
2.77e+007

100323_03 8 (0.172)



Minimum: -1.5
Maximum: 2.0 100.0 50.0

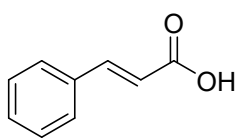
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf (%)	Formula
317.1664	317.1665	-0.1	-0.3	8.5	1188.3	n/a	n/a	C18 H22 N2 O2 F

¹H-NMR (400 MHz, DMSO-d₆) of 5a

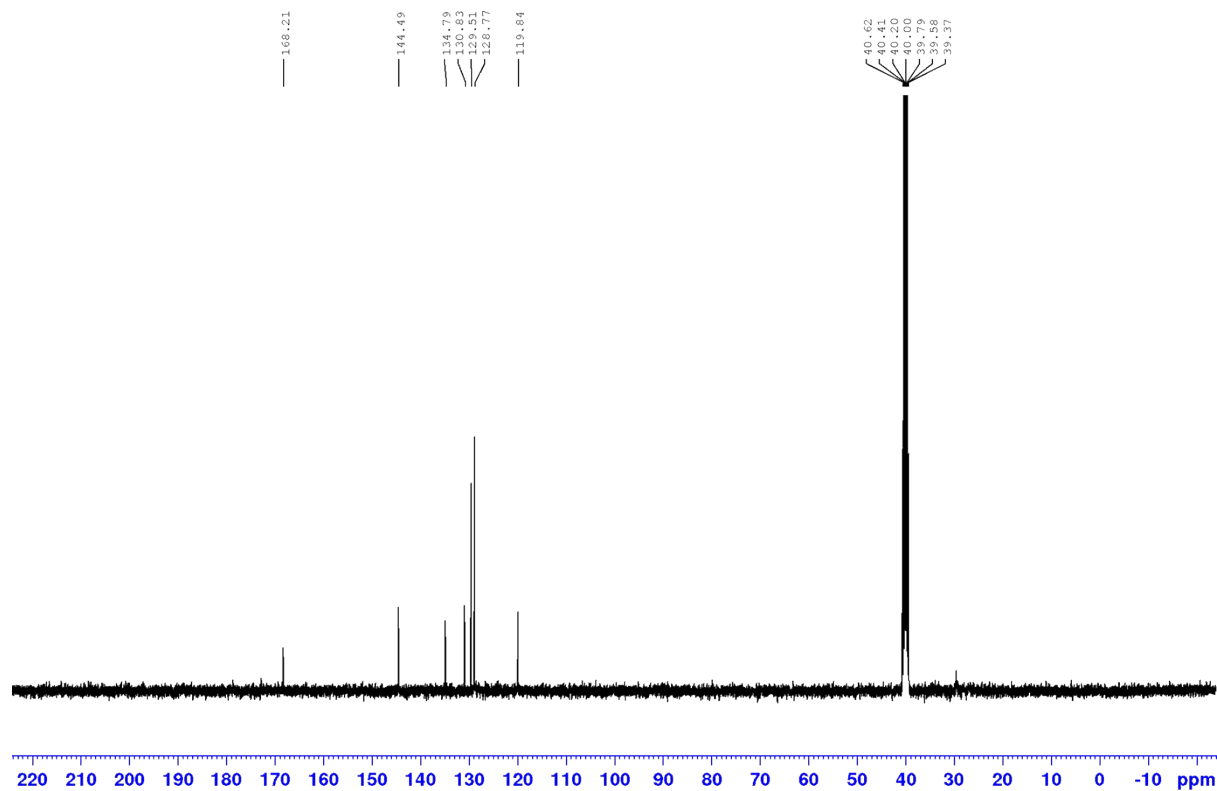
7.68
7.68
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7.60
7.56
7.42
7.41
7.40
6.54
6.50

— 3.47

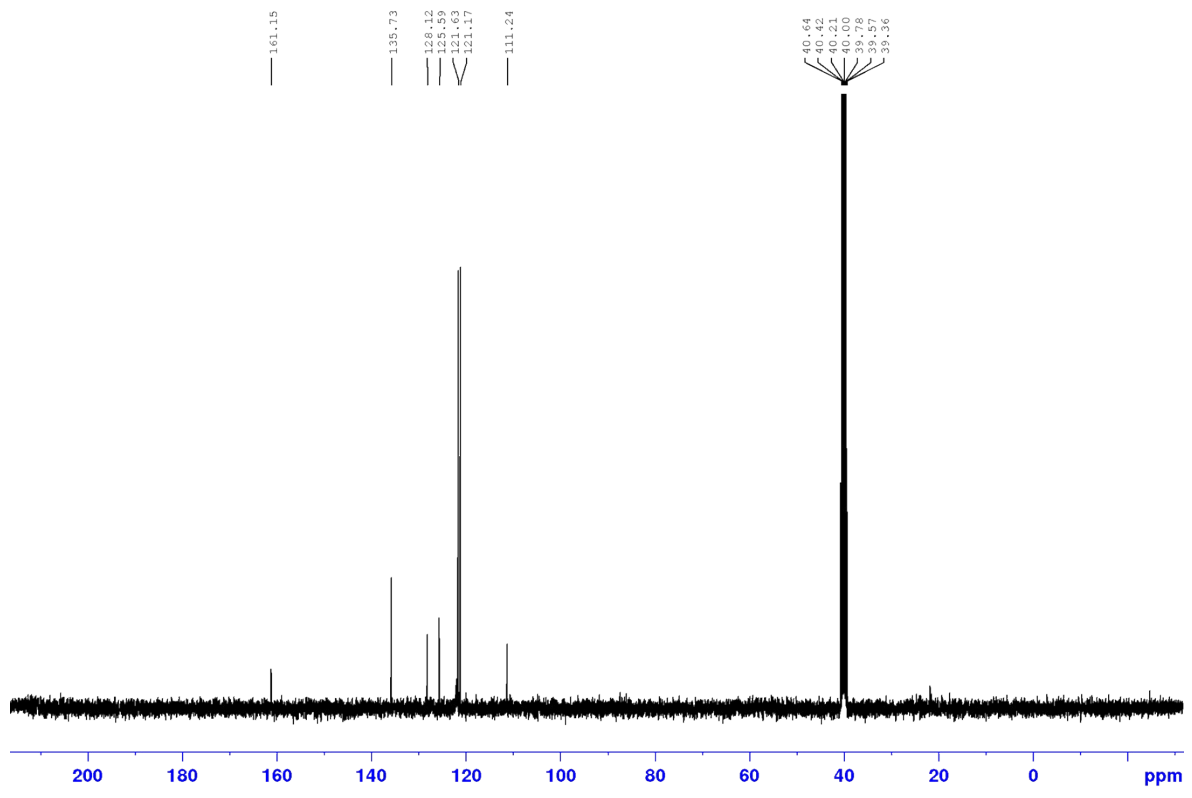
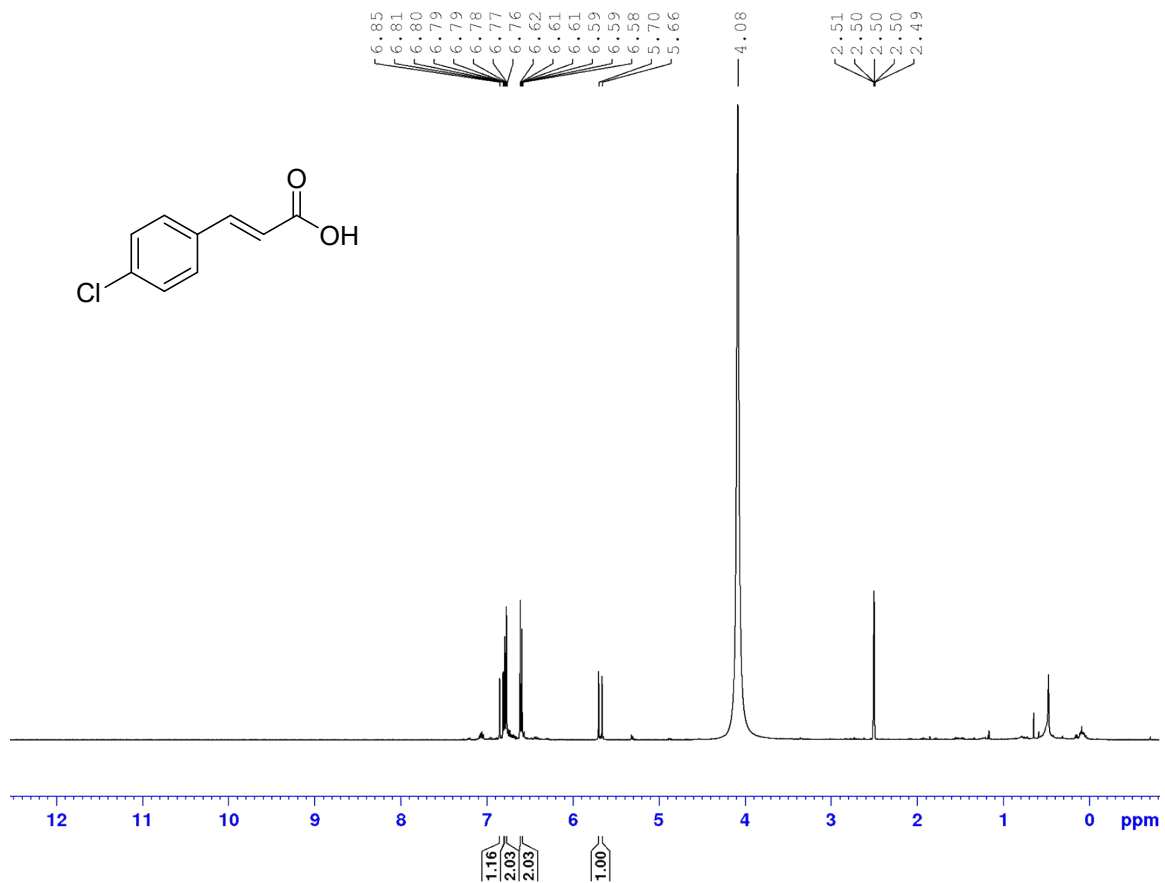
2.50
2.50
2.50



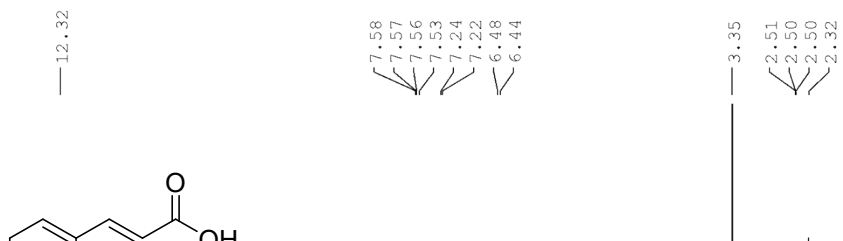
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, DMSO- d_6) of 5a



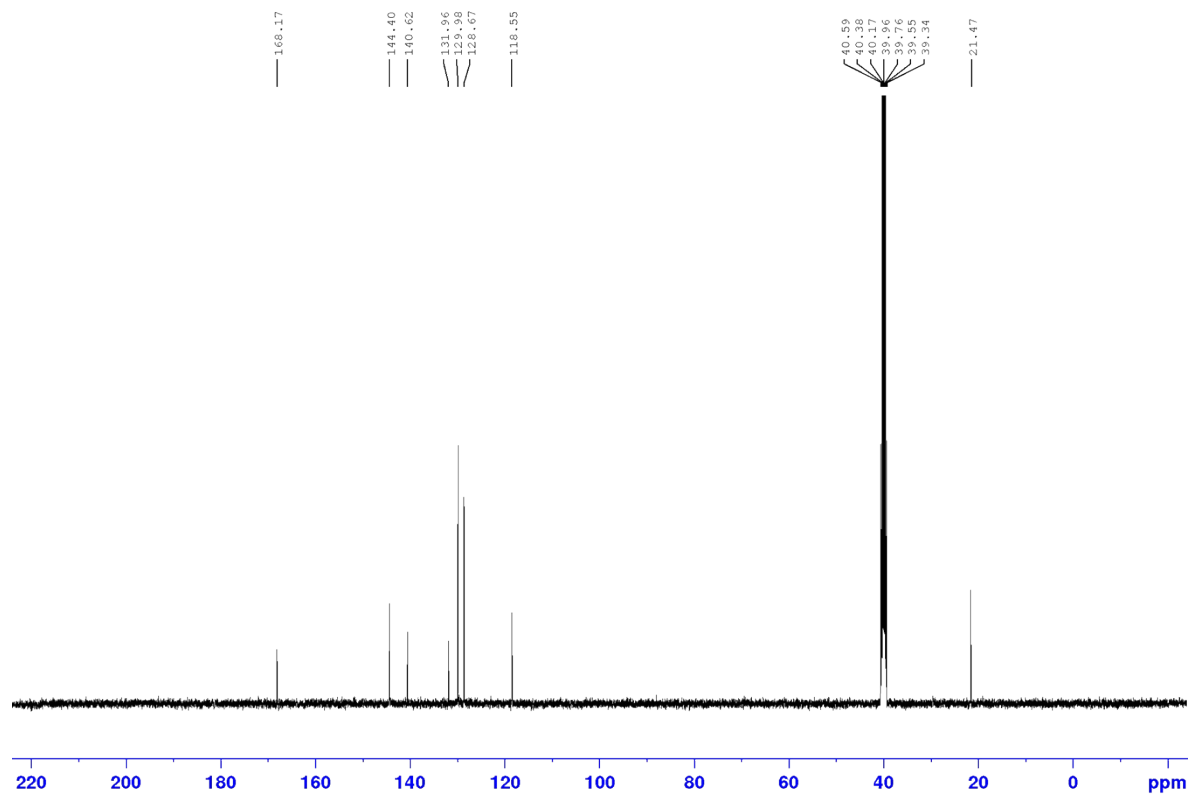
^1H -NMR (400 MHz, DMSO- d_6) of 5b



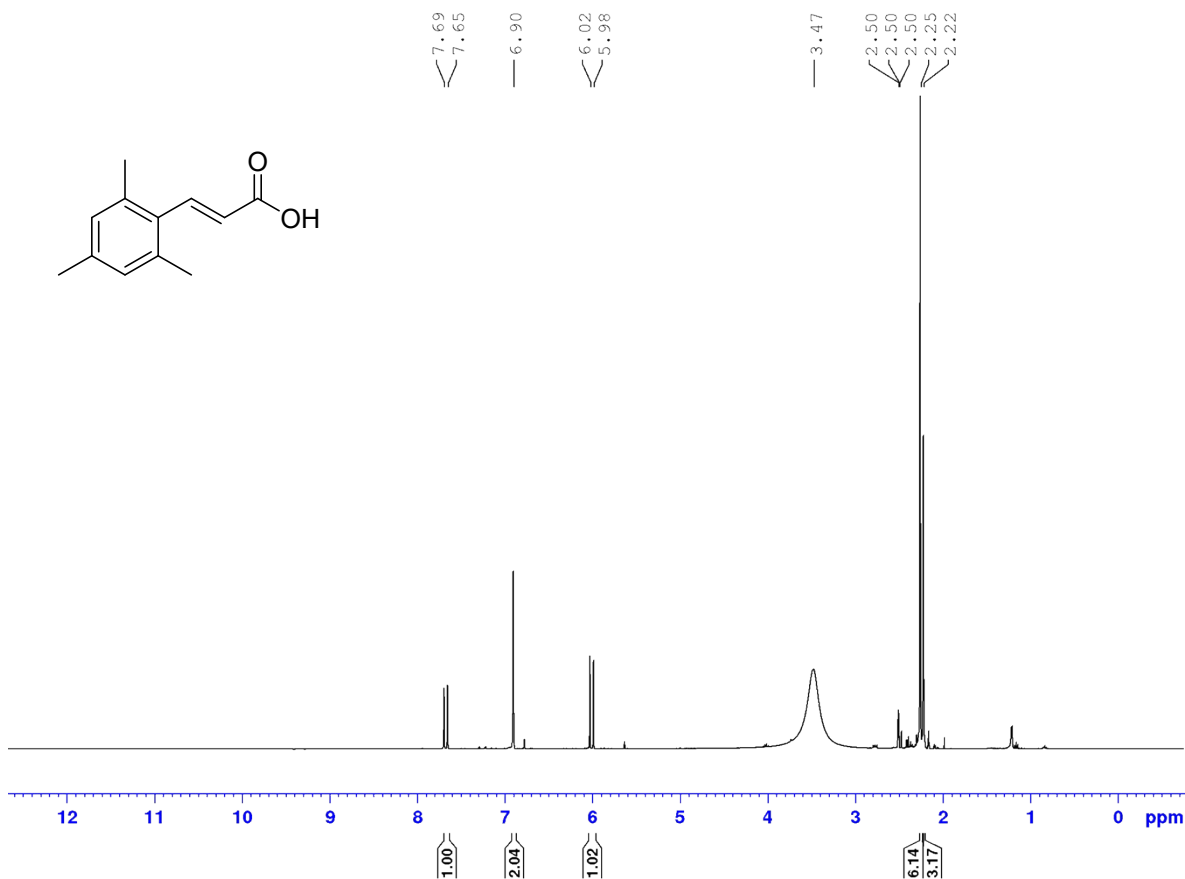
^1H -NMR (400 MHz, DMSO- d_6) of 5c



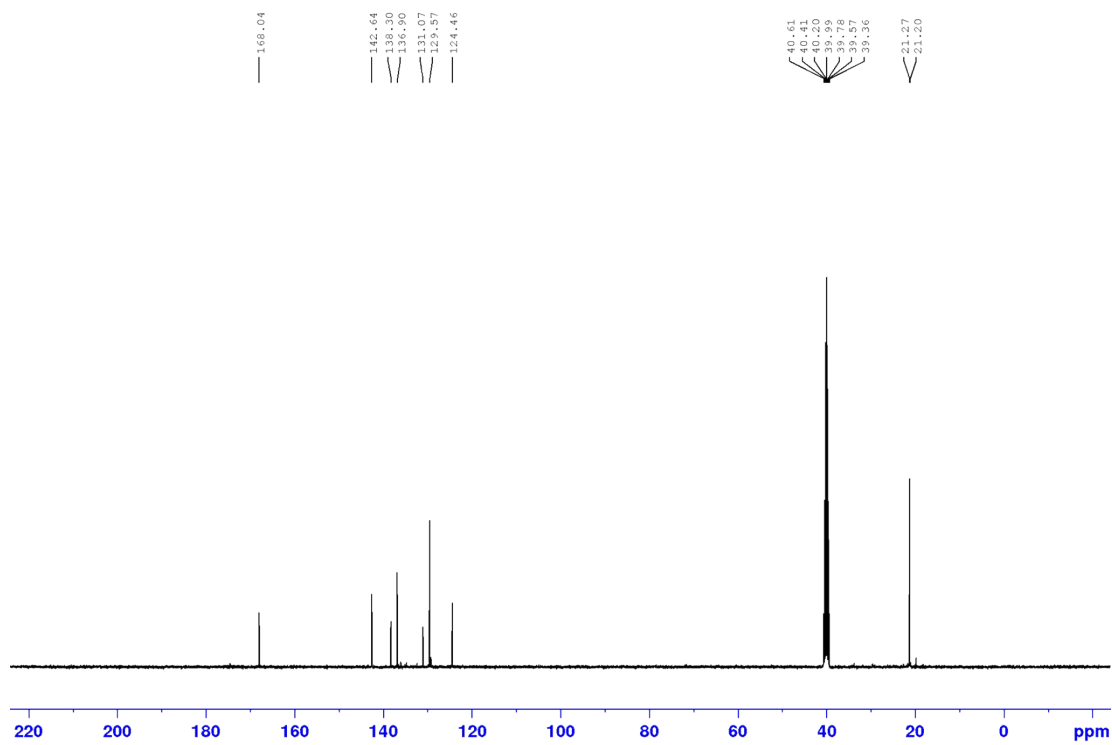
$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, DMSO- d_6) of 5c



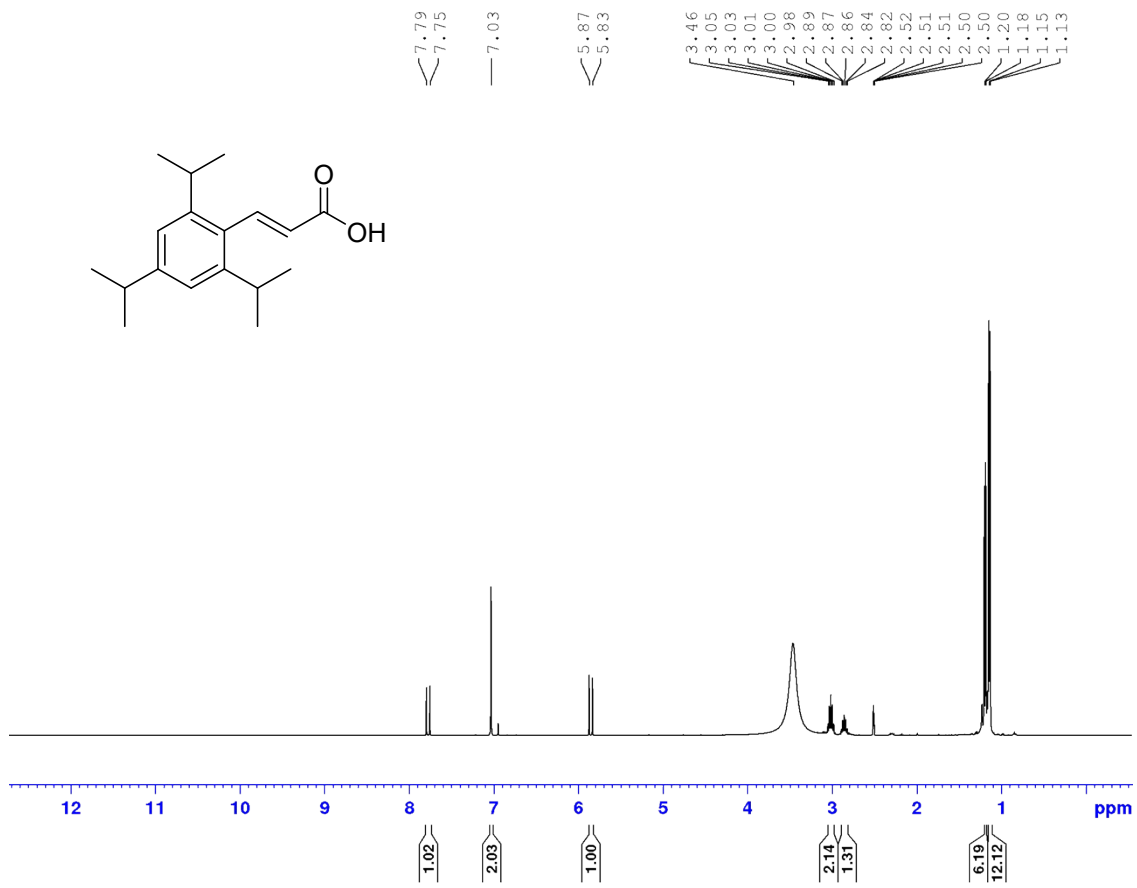
^1H -NMR (400 MHz, DMSO- d_6) of 5d



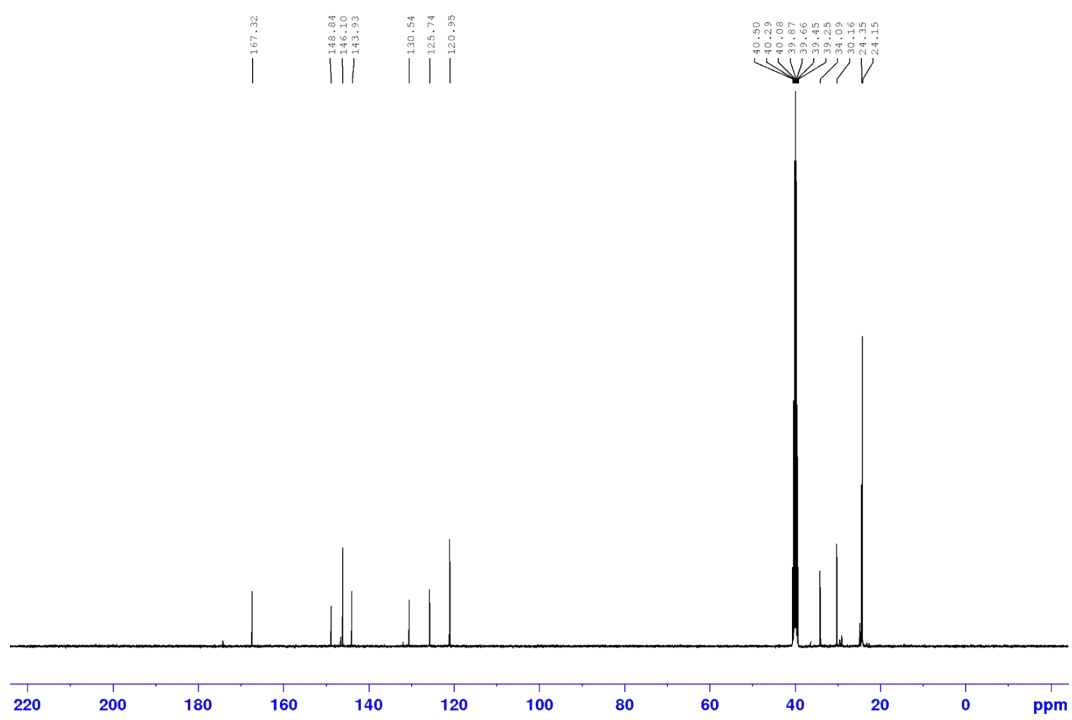
¹³C{¹H}-NMR (101 MHz, DMSO-d₆) of 5d



¹H-NMR (400 MHz, DMSO-d₆) of 5e



$^{13}\text{C}\{^1\text{H}\}$ -NMR (101 MHz, DMSO- d_6) of 5e



References :

1. R. F. Pellon, T. Mamposo, E. Gonzalez and O. Calderon, *Synth. Commun.*, 2000, **30**, 3769-3774.