SUPPORTING INFORMATION

Regio- and diastereoselective transition metal-free hydroalkylation of *N*-allenyl sulfonamides by push-pull 2-alkynylquinoline

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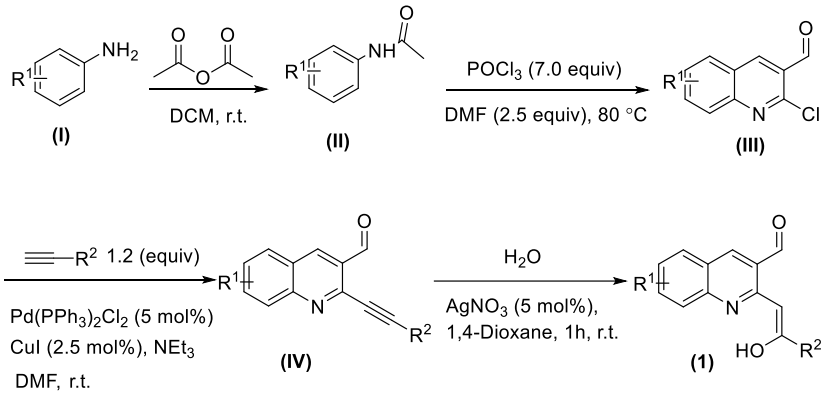
1. Experimental

1.1. General Information

All the required chemicals and solvents in this project were purchased from Sigma-Aldrich, Fluka, and Merck) and were used without further purification. Analytical thin-layer chromatography (TLC) was performed on aluminum-coated plates of silica gel (MERCK, 60 F_{254}) and detected under ultraviolet irradiation (254 nm). Column chromatography separations of products were performed with Merck silica gel 60® (230-400 mesh). Melting points (m. p.) were determined in capillary tubes with an Electrothermal 9100 digital melting point apparatus and are uncorrected. ^{1}H- and ^{13}C NMR spectra were acquired from a Bruker Avance 300 and 400 MHz spectrometer. The chemical shifts (δ) and the coupling constants (J) are reported in ppm and Hz, respectively. The abbreviations of multiplets peak patterns are indicated as follows: *s*, singlet; *d*, doublet; *t*, triplet; *q*, quartet; *m*, multiplet, complex pattern; and *brs*, broad singlet. High-resolution mass spectra (HRMS-ESI) was run on a Waters LCT Premier XE™ TOF (Time of Flight) mass spectrometer in positive ionization mode. Single-crystal X-ray data for compound **3a** was measured at room temperature (298 K) on a Bruker APEX-II Quazar area detector (CCDC: 2175887).

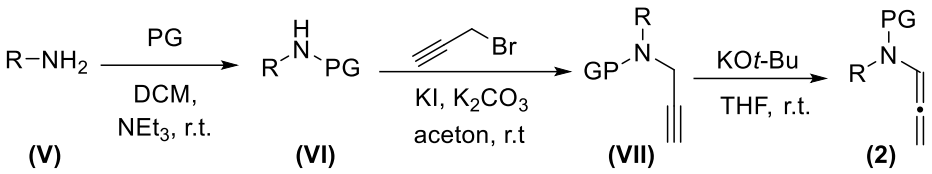
1.2. General Procedure for the Synthesis of (*Z*)-2-(2-hydroxy-2-alkynyl) quinoline-3-carbaldehyde

The (*Z*)-2-(2-hydroxy-2-alkylvinyl)quinoline-3-carbaldehyde was synthesized the same as previously reported procedures:[1]

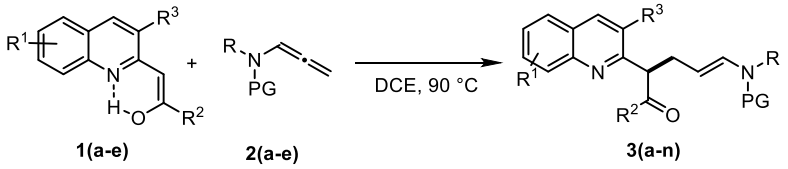


1.3. General Procedure for the Synthesis of *N*-allenyl Sulfonamides

This type of allenamides was synthesized the same as previously reported procedures:[2]



1.4. General Procedure for the Synthesis of the Linear Homoallylic Quinolines



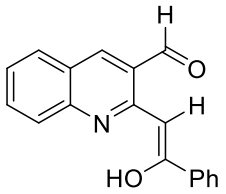
To a sealed tube (Schlenk tube), *N*-allenyl sulfonamides (0.22 mmol, 1.1 equiv.) was added in a solution of (*Z*)-2-(2-hydroxy-2-alkynyl)quinoline-3-carbaldehyde (0.2 mmol, 1.0 equiv.) in 2 mL DCE. The reaction mixture was heated at 90 ℃ for 48 h in an oil bath. The mixture was cooled down to room temperature and the solvent was removed under a vacuum. The residue was purified by column chromatography (silica gel), eluting with *n*-hexane and ethyl acetate (5:1) to afford the corresponding linear homoallylic quinolines structures.

1.5. Procedure for the Synthesis of 3a on a Scale of 1 mmol

To a sealed tube (Schlenk tube), 4-Methyl-*N*-phenyl-*N*-(propa-1,2-dien-1-yl) benzene sulfonamide (2a) (314 mg, 1.1 mmol, 1.1 equiv.) was added in a solution of (*Z*)-2-(2-Hydroxy-2-phenylvinyl) quinoline-3-carbaldehyde (1a) (276 mg, 1.0 mmol, 1.0 equiv.) in 6 mL DCE. The reaction mixture was heated at 90 ℃ for 48 h in an oil bath. The mixture was cooled down to room temperature and the solvent was removed under vacuum. The residue was purified by column chromatography (silica gel), eluting with *n*-hexane and ethyl acetate (5:1) to afford the corresponding (E)-*N*-(4-(3-formylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide structures **3a** (Yield 82%).

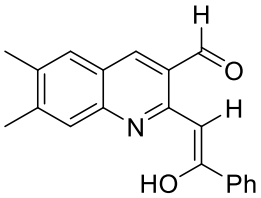
2. Analysis of spectral data

(Z)-2-(2-Hydroxy-2-phenylvinyl)quinoline-3-carbaldehyde (1a)



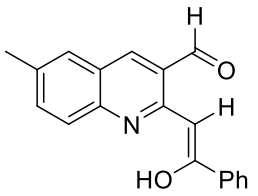
Red solid, (254 mg, Yield 89%, m.p. 155-157 °C), (*n*-hexane/EtOAc = 2:1, R_f= 0.33); 1H NMR (300 MHz, $CDCl_3$) δ 16.21 (*br* s, 1H, -OH), 9.97 (s, 1H, -CHO), 8.09 (s, 1H, H-4 quinoline), 8.01-7.99 (m, 1H, H-Ar), 7.64-7.53 (m, 3H, H-Ar), 7.47-7.42 (*m*, 3H, H-Ar), 7.38 (*d*, *J* = 7 Hz, 1H, H-Ar), 7.37 (s, 1H, =CH), 7.22 (td, *J* = 8.1, 1.5 Hz, 1H, H-Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 185.3, 150.6, 147.9, 147.8, 140.0, 139.1, 129.6, 128.4, 127.1, 126.9, 125.9, 124.0, 121.4, 118.3, 88.5; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{14}NO_2$ 276.1017; Found: 276.1012.

(Z)-2-(2-Hydroxy-2-phenylvinyl)-6,7-dimethylquinoline-3-carbaldehyde (1b)



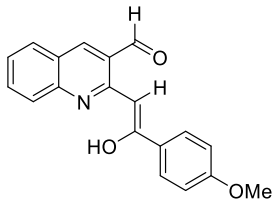
Red solid, (237 mg, Yield 78%, m.p. 172-174 °C), (*n*-hexane/EtOAc = 2:1, R_f= 0.35), ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.35 (*br* s, 1H, -OH), 9.94 (s, 1H, -CHO), 8.04-7.97 (m, 3H, H-Ar), 7.49-7.43 (m, 3H, H-Ar), 7.34 (br s, 1H, H-Ar), 7.29 (br s, 1H, H-Ar), 7.20 (br s, 1H, =CH), 2.35 (s, 3H, Me), 2.27 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 184.1, 150.8, 147.3, 147.2, 145.9, 139.3, 138.7, 133.9, 130.6, 129.0, 128.3, 124.9, 120.1, 118.8, 88.0, 20.8, 19.4; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{18}NO_2$ 304.1332; Found: 304.1335.

(Z)-2-(2-Hydroxy-2-phenylvinyl)-6-methylquinoline-3-carbaldehyde (1c)



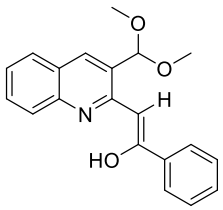
Red solid, (234 mg, Yield 81%, m.p. 163-165 °C), (*n*-hexane/EtOAc = 2:1, R_f= 0.31), ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.43 (*br* s, 1H, -OH), 10.05 (s, 1H, -CHO), 8.13 (s, 1H, H-4 quinoline), 8.05-7.97 (m, 2H, H-Ar), 7.52-7.45 (m, 3H, H-Ar), 7.41-7.36 (m, 4H, H-Ar and =CH), 2.43 (s, 3H, Me).^{13}C NMR (75 MHz, $CDCl_3$) δ 189.6, 184.0, 151.0, 139.1, 138.6, 136.4, 134.2, 130.7, 128.8, 128.3, 126.9, 126.8, 125.9, 121.7, 118.7, 88.3, 21.0; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1181; Found: 290.1178.

(Z)-2-(2-Hydroxy-2-(4-methoxyphenyl)vinyl)quinoline-3-carbaldehyde (1d)



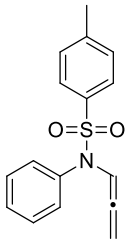
Red solid, (214 mg, Yield 70%, m.p. 97-100 °C), (*n*-hexane/EtOAc = 2:1, R_f= 0.37), ^{1}H NMR (300 MHz, $CDCl_3$) δ 16.10 (*br* s, 1H, -OH), 10.00 (s, 1H, -CHO), 8.15-8.06 (m, 2H, H-Ar), 8.02-7.91 (m, 4H, H-Ar), 7.62-7.52 (m, 3H, H-Ar), 7.37 (br s, 1H, =CH), 3.87 (s, 3H, -OMe); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 185.7, 162.0, 150.0, 149.0, 148.1, 148.0, 140.0, 132.0, 126.1, 123.7, 121.1, 117.9, 113.7, 113.5, 87.8, 55.3; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{19}H_{16}NO_3$ 306.1127; Found: 306.1121.

(Z)-2-(3-(Dimethoxymethyl)quinolin-2-yl)-1-phenylethen-1-ol (1e)



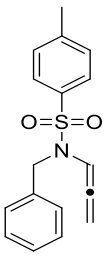
Yellow oil, (173 mg, Yield 54%), (*n*-hexane/EtOAc = 2:1, R_f= 0.41), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 16.57 (s, 1H, -OH), 8.07 (s, 1H, H-4 quinoline), 8.02 – 8.00 (m, 2H, H-Ar), 7.61 (d, *J* = 6.8 Hz, 1H, H-Ar), 7.58 (d, *J* = 6.8 Hz, 1H, H-Ar), 7.56 (d, *J* = 6.6 Hz, 1H, H-Ar), 7.53 (d, *J* = 6.6 Hz, 1H, H-Ar), 7.49 – 7.47 (m, 3H, H-Ar), 6.42 (s, 1H, =CH), 5.51 (s, 1H, -$CH(OMe)_2$), 3.42 (s, 6H, -OCH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.2, 152.5, 140.1, 137.7, 135.2, 131.4, 130.4, 128.3, 128.2, 127.4, 126.8, 123.8, 122.3, 117.9, 98.7, 86.6, 52.6; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$ 322.1431; Found: 322.1434.

4-Methyl-N-phenyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (2a)



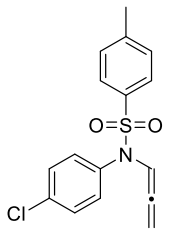
Yellow solid, (265 mg, Yield 93%, m.p. 74-76 ºC), (*n*-hexane/EtOAc = 6:1, R_f= 0.33), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.34-7.28 (m, 5H, H-Ar), 7.14 (t, *J* = 6.3 Hz, 1H, N=CH), 7.04-7.01 (m, 2H, H-Ar), 5.05 (d, *J* = 6.3 Hz, 2H, $=CH_2$), 2.46 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.02, 144.0, 137.2, 135.2, 129.6, 129.5, 128.8, 128.7, 127.7, 102.4, 87.5, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{16}NO_2S$ 286.0890 ; Found: 286.0891.

N-Benzyl-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (2b)



Yellow solid, (222 mg, Yield 74%, m.p. 78-80 ºC), (*n*-hexane/EtOAc = 6:1, R_f= 0.38), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.36-7.25 (m, 7H, H-Ar), 6.84 (t, *J* = 6.2 Hz, 1H, =CH), 5.15 (d, *J* = 6.2 Hz, 2H, $=CH_2$), 4.31 (s, 2H, $-CH_2$), 2.46 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.1, 143.8, 136.1, 135.2, 129.7, 128.3, 127.8, 127.4, 127.2, 100.0, 88.0, 50.0, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{18}NO_2S$ 300.1057; Found: 300.1058.

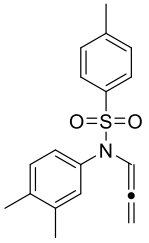
N-(4-Chlorophenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (2c)



Yellow solid, (179 mg, Yield 56%, m.p. 111-113 ºC), (*n*-hexane/EtOAc = 6:1, R_f= 0.31), ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.5 Hz, 2H, H-Ar), 7.30-7.24 (m, 4H, H-Ar), 7.10 (t, *J* = 6.2 Hz, 1H, =CH), 6.93 (d, *J* = 7.5 Hz, 2H, Ar), 5.06 (d, *J* = 6.3 Hz, 2H, $=CH_2$), 2.45 (s, 3H,

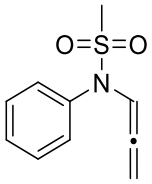
Me).^{13}C NMR (75 MHz, $CDCl_3$) δ 200.8, 144.2, 135.6, 134.9, 134.5, 130.8, 129.6, 129.0, 127.7, 102.3, 87.9, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{16}H_{15}{}^{35}ClNO_2S$ 320.0502; Found: 320.0506.

N-(3,4-Dimethylphenyl)-4-methyl-N-(propa-1,2-dien-1-yl)benzenesulfonamide (2d)



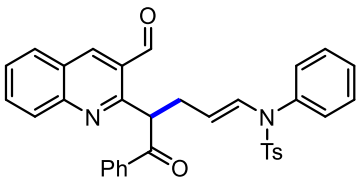
Yellow solid, (197 mg, Yield 63%, m.p. 108-110 ºC), (*n*-hexane/EtOAc = 6:1, R_f= 0.38) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.6 Hz, 2H, H-Ar), 7.28 (d, *J* = 8.6 Hz, 2H, H-Ar), 7.09 (t, *J* = 6.3 Hz, 1H, =CH), 7.01 (d, *J* = 8.1 Hz, 1H, H-Ar), 6.85 (s, 1H, H-Ar), 6.63 (dd, *J* = 8.0, 2.3 Hz, 1H, H-Ar), 5.03 (d, *J* = 6.3 Hz, 2H, $=CH_2$), 2.45 (s, 3H, Me), 2.23 (s, 3H, Me), 2.19 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.1, 143.7, 137.3, 137.2, 135.4, 134.6, 130.7, 130.5, 129.7, 129.6, 129.4, 102.4, 87.3, 21.6, 19.7, 19.5. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{20}NO_2S$ 314.1203; Found: 314.1205.

N-Phenyl-N-(propa-1,2-dien-1-yl)methanesulfonamide (2e)



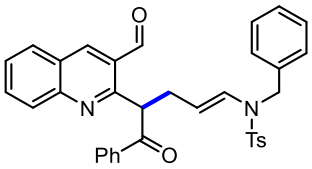
Yellow solid, (168 mg, Yield 80%, m.p. 65-67 ºC), (*n*-hexane/EtOAc = 6:1, R_f= 0.35) ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.40 – 7.36 (m, 3H, H-Ar), 6.98 (t, *J* = 6.3 Hz, 1H, =CH), 5.17 (d, *J* = 6.3 Hz, 2H, $=CH_2$), 3.04 (s, 3H, $-CH_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.9, 137.3, 129.3, 129.2, 128.8, 101.9, 87.8, 38.2; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{10}H_{12}NO_2S$ 210.0581; Found: 210.0584.

(E)-N-(4-(3-Formylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methyl-N-phenylbenzen esulfonamide (3a)



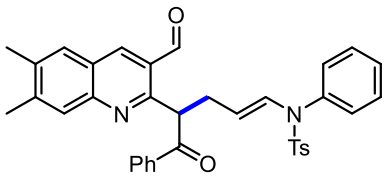
Orange solid, (100 mg, Yield 90%, m.p. 108-110 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.32) ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.17 (s, 1H, -CHO), 8.53 (*br* s, 1H, H-4 quinoline), 8.02 (d, *J* = 8.5 Hz, 1H, H-Ar), 7.92 (d, *J* = 8.1, 1H, H-Ar), 7.88-7.85 (m, 2H, H-Ar), 7.85-7.78 (m, 1H, H-Ar), 7.61 (td, *J* = 8.2, 1.4, 1H, H-Ar), 7.45-7.21 (m, 8H, H-Ar), 7.12 (d, *J*= 8.1, 2H, H-Ar), 6.92 (d, *J* = 14.0 Hz, 1H, =CH-N), 6.78-6.74 (m, 2H, H-Ar), 5.87 (t, *J* = 6.7 Hz, 1H, C(sp^3)-H), 4.51-4.42 (m, 1H, =CH), 2.95-2.82 (m, 2H, -CH_2), 2.39 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 191.8, 157.7, 148.9, 145.6, 143.5, 137.1, 136.5, 135.7, 132.8, 132.4, 130.8, 130.7, 129.9, 129.7, 129.4, 129.3, 128.7, 128.6, 128.4, 127.5, 127.3, 127.1, 125.8, 109.5, 52.7, 31.9, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{34}H_{28}N_2O_4S$ 561.1844; Found: 561.1847.

(E)-N-Benzyl-N-(4-(3-formylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methylbenzene sulfonamide (3b)



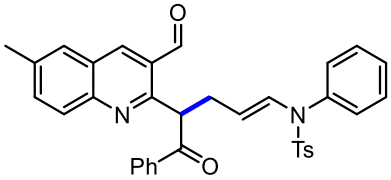
Orange solid, (93 mg, Yield 81%, m.p. 73-75 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.39), ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.94 (s, 1H, -CHO), 8.41 (s, 1H, H-4 quinoline), 8.01 (dd, *J* = 8.1, 1.4 Hz, 1H, H-Ar), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H, H-Ar), 7.90-7.78 (m, 3H, H-Ar), 7.61 (dd, *J* = 8.2, 1.4, 1H, H-Ar), 7.58-7.53 (m, 2H, H-Ar), 7.44 (tt, *J* = 8.3, 2.1 Hz, 1H, H-Ar), 7.38-7.30 (m, 2H, H-Ar), 7.18-7.10 (m, 7H, H-Ar), 6.67 (d, *J* = 14.0, 1H, =CH-N), 5.84 (dd, *J* = 7.9, 5.8 Hz, 1H, C(sp^3)-H), 4.81-4.79 (m, 1H, =CH), 4.33 (d, *J* = 8.7 Hz, 2H, N-CH_2), 2.92-2.77 (m, 2H, -CH_2), 2.38 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 192.0, 157.3, 148.9, 146.0, 143.5, 137.0, 135.7, 135.6, 132.8, 132.7, 132.5, 129.7, 129.6, 128.6, 128.4, 128.3, 127.8, 127.7, 127.5, 127.2, 126.9, 126.8, 125.7, 110.5, 52.9, 49.3, 32.2, 21.5. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_4S$ 575.1992; Found: 575.1996.

(E)-N-(4-(3-Formyl-6,7-dimethylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (3c)



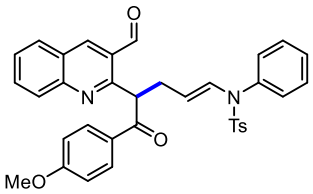
Orange solid, (90 mg, Yield 77%, m.p. 90-93 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.30), ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.15 (s, 1H, -CHO), 8.42 (s, 1H, H-4 quinoline), 7.85 (d, *J* = 8.2 Hz, 2H, H-Ar), 7.82 (br s, 1H, H-Ar), 7.67 (br s, 1H, H-Ar), 7.43-7.39 (m, 3H, H-Ar), 7.34-7.30 (m, 3H, H-Ar), 7.27-7.24 (m, 2H, H-Ar), 7.13 (d, *J* = 8.2, 2H, H-Ar), 6.89 (d, *J* = 13.9 Hz, 1H, =CH-N), 6.75 (d, *J* = 8.2 Hz, 2H, H-Ar), 5.86 (t, *J* = 6.7 Hz, 1H, -C(sp^3)-H), 4.50-4.42 (m, 1H, =CH), 2.95-2.76 (m, 2H, -CH_2), 2.48 (s, 6H, Me), 2.42 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 191.8, 157.0, 144.5, 144.0, 143.5, 137.8, 137.2, 136.6, 135.8, 132.3, 130.6, 130.0, 129.6, 129.4, 129.3, 129.2, 128.8, 128.5, 128.4, 127.7, 127.4, 127.3, 121.7, 109.7, 52.5, 32.2, 21.6, 20.7, 20.0. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{33}N_2O_4S$ 589.2150; Found: 589.2155.

(E)-N-(4-(3-Formyl-6-methylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (3d)



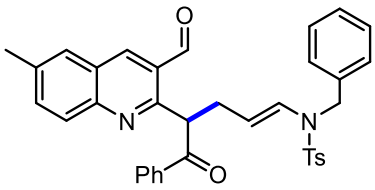
Orange solid, (85 mg, Yield 74%, m.p. 68-70 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.35), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H, -CHO), 8.45 (s, 1H, H-4 quinoline), 7.94 (d, *J* = 8.6 Hz, 1H, H-Ar), 7.87 (d, *J* = 8.6 Hz, 2H, H-Ar), 7.70 (*br* s, 1H, H-Ar), 7.67 (dd, *J* = 8.6, 2.0 Hz, 1H, H-Ar), 7.43 (t, *J* = 7.8 Hz, 1H, H-Ar), 7.39 (d, *J* = 8.1 Hz, 2H, H-Ar), 7.36-7.30 (m, 3H, H-Ar), 7.28-7.24 (m, 2H, H-Ar), 7.12 (d, *J* = 8.1 Hz, 2H, H-Ar), 6.91 (d, *J* = 14 Hz, 1H, =CH-N), 6.76 (d, *J* = 7.0 Hz, 2H, H-Ar), 5.85 (t, *J* = 6.4 Hz, 1H, C(sp^3)-H), 4.51-4.42 (m, 1H, =CH), 2.98-2.80 (m, 2H, -CH_2), 2.58 (s, 3H, Me), 2.41 (s, 3H, Me); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3, 191.9, 156.8, 147.7, 144.9, 143.5, 137.7, 137.1, 136.6, 135.8, 135.2, 132.4, 130.7, 130.0, 129.4, 129.3, 128.8, 128.6, 128.5, 128.4, 127.4, 127.3, 127.1, 125.9, 109.6, 52.6, 32.0, 26.9, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_4S$ 575.1984; Found: 575.1990.

(*E*)-*N*-(4-(3-Formylquinolin-2-yl)-5-(4-methoxyphenyl)-5-oxopent-1-*en*-1-yl)-4-methyl-*N*-phenylbenzenesulfonamide (3e)



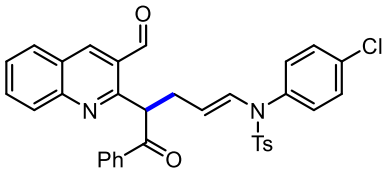
Orange solid, (85 mg, Yield 72%, m.p. 103-105 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.32), ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H, -CHO), 8.55 (s, 1H, H-4 quinoline), 8.07 (d, *J* = 8.2 Hz, 1H, H-Ar), 7.96 (d, *J* = 8.2 Hz, 1H, H-Ar), 7.88 (d, *J* = 8.3 Hz, 2H, H-Ar), 7.87 (t, *J* = 8.6 Hz, 1H, H-Ar), 7.64 (t, *J* = 8.6 Hz, 1H, H-Ar), 7.39 (d, *J* = 8.1 Hz, 1H, H-Ar), 7.32-7.23 (m, 3H, H-Ar), 7.12 (d, *J* = 8.1 Hz, 2H, H-Ar), 6.91 (d, *J* = 14.0 Hz, 1H, =CH-N), 6.82 (d, *J* = 7.9 Hz, 2H, H-Ar), 6.76 (d, *J* = 8.1 Hz, 2H, H-Ar), 5.82 (t, *J* = 7.6 Hz, 1H, C(sp^3)-H), 4.50-4.42 (m, 1H, =CH_2), 3.81 (s, 3H, -OMe), 2.98-2.84 (m, 2H, -CH_2), 2.42 (s, 3H, Me). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 191.7, 163.0, 157.9, 149.0, 145.3, 143.5, 136.6, 135.8, 132.8, 130.8, 130.7, 130.0, 129.8, 129.4, 129.3, 128.8, 128.7, 128.6, 127.5, 127.4, 127.2, 125.8, 113.7, 109.7, 55.4, 52.5, 32.1, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_5S$ 591.1944; Found: 591.1946.

(E)-N-Benzyl-N-(4-(3-formyl-6-methylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methylbenzenesulfonamide (3f)



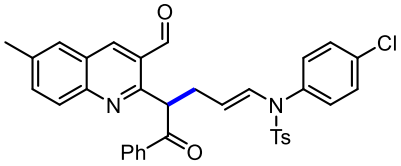
Orange solid, (94 mg, Yield 80%, m.p. 163-165 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.39), ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.92 (s, 1H, -CHO), 8.33 (s, 1H, H-4 quinoline), 7.92 (d, *J* = 8.5 Hz, 1H, H-Ar), 7.84 (d, *J* = 8.5i Hz, 2H, H-Ar), 7.69 (s, 1H, H-Ar), 7.66 (d, *J* = 8.3 Hz, 1H, H-Ar), 7.56 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.44 (t, *J* = 7.4 Hz, 1H, H-Ar), 7.35 (d, *J* = 8.6 Hz, 1H, H-Ar), 7.32 (d, *J* = 8.4 Hz, 1H, H-Ar), 7.19-7.11 (m, 7H, H-Ar), 6.66 (d, *J* = 14.0 Hz, 1H, =CH-N), 5.83 (t, *J* = 8.0, 5.7 Hz, 1H, C(sp^3)-H), 4.88-4.79 (m, 1H, =CH), 4.33 (s, 1H, -CH_2-Ph), 4.32 (s, 1H, -CH_2-Ph), 2.90-2.75 (m, 2H, -CH_2), 2.58 (s, 3H, Me), 2.40 (s, 3H, Me).^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 192.1, 156.4, 147.6, 145.3, 143.5, 137.7, 137.1, 135.8, 135.7, 135.1, 132.5, 129.7, 129.4, 128.5, 128.4, 128.3, 127.7, 127.3, 127.2, 127.0, 126.9, 126.8, 125.8, 110.5, 52.8, 49.3, 32.3, 21.6, 21.5. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{33}N_2O_4S$ 589.2153; Found: 589.2155.

(E)-N-(4-Chlorophenyl)-N-(4-(3-formylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methylbenzenesulfonamide (3g)



Orange solid, (78 mg, Yield 66%, m.p. 173-174 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.34), ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.19 (s, 1H, -CHO), 8.55 (s, 1H, H-4 quinoline), 8.01 (d, *J* = 8.5 Hz, 1H, H-Ar), 7.94 (d, *J* = 8.5 Hz, 1H, H-Ar), 7.90-7.80 (m, 3H, H-Ar), 7.62 (t, *J* = 8.1 Hz, 1H, H-Ar), 7.46-7.30 (m, 5H, H-Ar), 7.21 (d, *J* = 8.3 Hz, 2H, H-Ar), 7.13 (d, *J* = 8.3 Hz, 2H, H-Ar), 6.90 (d, *J* = 14.0 Hz, 1H, =CH-N), 6.71 (d, *J* = 8.6 Hz, 2H, H-Ar), 5.86 (t, *J* = 6.6 Hz, 1H, C(sp^3)-H), 4.56-4.44 (m, 1H, =CH), 3.01-2.78 (m, 2H, -CH_2), 2.40 (s, 3H, Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 191.8, 157.6, 148.9, 145.8, 145.7, 143.8, 137.1, 135.4, 135.1, 134.7, 132.5, 131.3, 131.2, 130.6, 130.4, 129.6, 129.5, 129.4, 128.5, 128.3, 127.3, 127.0, 125.8, 110.1, 52.8, 31.8, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{34}H_{28}{}^{35}ClN_2O_4S$ 595.1452; Found: 595.1454.

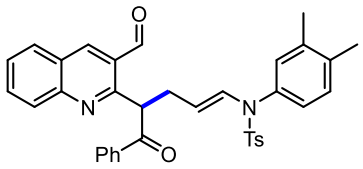
(E)-N-(4-Chlorophenyl)-N-(4-(3-formyl-6-methylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methylbenzenesulfonamide (3h)



Orange solid, (95 mg, Yield 78%, m.p. 91-94 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.37), ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.16 (s, 1H, -CHO), 8.43 (s, 1H, H-4 quinoline), 7.95-7.88 (m, 3H, H-Ar), 7.86 (d, *J* = 8.6 Hz, 2H, H-Ar), 7.67 (br s, 1H, H-Ar), 7.55 (d, *J* = 8.3 Hz, 2H, H-Ar), 7.43-7.37 (m, 6H, H-Ar), 7.13 (d, *J* = 8.2 Hz, 2H, H-Ar), 6.90 (d, *J* = 14.0 Hz, 1H, =CH-N), 5.84 (t, *J* = 6.6 Hz, 1H, C(sp^3)-H), 4.54-4.45 (m, 1H, =CH), 2.97-2.79 (m, 2H, -CH_2), 2.40 (s, 3H, Me), 2.26 (s, 3H, Me); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.3, 192.0, 156.7, 153.4, 143.8, 143.5, 137.7, 137.1, 135.8, 135.6, 135.4, 135.2, 135.1, 135.0, 134.7, 129.6, 129.5, 129.4, 128.4, 128.1, 127.3, 126.9, 113.0, 112.2, 110.2, 52.7, 31.8, 22.7, 21.5. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{30}{}^{35}ClN_2O_4S$ 609.1604; Found: 609.1609.

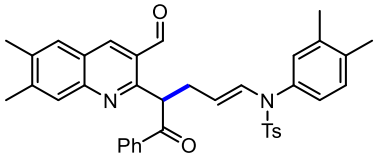
(E)-N-(3,4-Dimethylphenyl)-N-(4-(3-formylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-

methylbenzenesulfonamide (3i)



Orange solid, (90 mg, Yield 77%, m.p. 97-99 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.30), ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.17 (s, 1H, -CHO), 8.53 (s, 1H, H-4 quinoline), 8.03 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.92 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.90-7.79 (m, 5H, H-Ar), 7.60 (t, *J* = 6.9 Hz, 1H, H-Ar), 7.41 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.33 (d, *J* = 8.1 Hz, 1H, H-Ar), 7.10 (d, *J* = 7.9 Hz, 1H, H-Ar), 6.96 (d, *J* = 14 Hz, 1H, =CH-N), 6.95 (br s, 1H, H-Ar), 6.62 (*br* s, 1H, H-Ar), 6.37 (dd, *J* = 8.0, 1.2 Hz, 1H, 1H, H-Ar), 5.87 (t, *J* = 6.6 Hz, 1H, C(sp^3)-H), 4.52-4.42 (m, 1H, =CH), 2.95-2.84 (m, 2H, -CH_2), 2.39 (s, 3H, Me), 2.21 (s, 3H, Me), 2.13 (s, 3H, Me).^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 191.8, 157.8, 149.0, 145.5, 145.4, 143.4, 137.8, 137.4, 137.1, 136.0, 134.0, 132.4, 131.0, 130.9, 130.3, 130.2, 129.9, 129.4, 129.3, 129.2, 128.4, 127.4, 127.1, 126.8, 125.8, 109.2, 52.8, 32.0, 21.6, 19.7, 19.5. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{32}N_2O_4S$ 589.2155; Found: 589.2158.

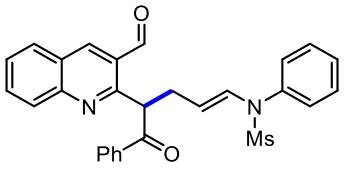
(E)-N-(3,4-Dimethylphenyl)-N-(4-(3-formyl-6,7-dimethylquinolin-2-yl)-5-oxo-5-phenyl pent-1-en-1-yl)-4-methylbenzenesulfonamide (3j)



Orange solid, (74 mg, Yield 60%, m.p. 82-85ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.33), ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.13 (s, 1H, -CHO), 8.39 (s, 1H, H-4 quinoline), 7.85 (d, *J* = 7.2 Hz, 1H, H-Ar), 7.79 (s, 1H, H-Ar), 7.63 (s, 1H, H-Ar), 7.43-7.40 (m, 3H, H-Ar), 7.30 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.28 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.14-7.08 (m, 3H, H-Ar), 6.97 (d, *J* = 8.0 Hz, 1H, H-Ar), 6.88 (d, *J* = 13.9 Hz, 1H, =CH-N), 6.62 (br s, 1H, H-Ar), 6.37 (dd, *J* = 8.0, 1.2 Hz, 1H, H-Ar), 5.85 (t, *J* = 6.9 Hz, 1H, C(sp^3)-H), 4.49-4.42 (m, 1H, =CH_2), 2.95-2.76 (m, 2H, -CH_2), 2.45 (br s, 6H, Me), 2.40 (s, 3H, Me), 2.22 (s, 3H, Me), 2.14 (s, 3H, Me).^{13}C NMR (75 MHz, $CDCl_3$) δ 198.2, 191.7, 157.8, 149.0, 145.5, 145.4, 143.4, 137.8, 137.4, 137.1, 136.0, 134.0, 132.4, 131.0, 130.9, 130.3, 130.2, 129.4, 129.3, 129.2, 128.5, 128.4, 128.3, 127.4, 127.1, 125.8,

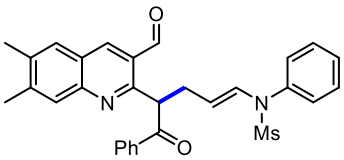
109.2, 52.8, 32.0, 21.6, 21.3, 19.7, 19.5, 18.8. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{38}H_{37}N_2O_4S$ 617.2461; Found: 617.2468.

(E)-N-(4-(3-Formylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-N-phenylmethanesulfonamide (3k)



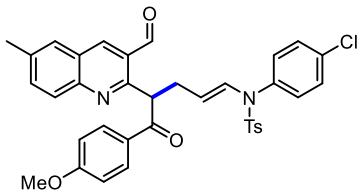
Orange solid, (68 mg, Yield 71%, m.p. 90-93 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.39), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.22 (s, 1H, CHO-), 8.59 (s, 1H, H-4 quinoline), 8.03 (d, *J* = 8.2, 1H, H-Ar), 7.96 (d, *J* = 8.2 Hz, 1H, H-Ar), 7.91 (d, *J* = 8.2 Hz, 2H, H-Ar), 7.82 (td, *J* = 8.4, 1.5 Hz, 1H, H-Ar), 7.62 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.46 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.41-7.34 (m, 5H, H-Ar), 7.16-7.12 (m, 2H, H-Ar), 6.73 (d, *J* = 14.1, 1H, =CH-N), 5.91 (t, *J* = 7.3 Hz, 1H, -C<u>H</u>-CH_2), 4.66 – 4.59 (m, 1H, =C<u>H</u>-CH_2), 3.00-2.82 (m, 2H, -CH_2), 2.85 (s, 3H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 191.8, 157.8, 148.9, 145.6, 137.2, 136.6, 132.9, 132.5, 130.2, 129.8, 129.7, 129.6, 129.0, 128.7, 128.5, 128.4, 127.7, 125.8, 120.8, 109.6, 52.8, 38.7, 31.9; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{28}H_{25}N_2O_4S$ 485.1524; Found: 485.1526.

(E)-N-(4-(3-Formyl-6,7-dimethylquinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-N-phenylmethanesulfonamide (3l)



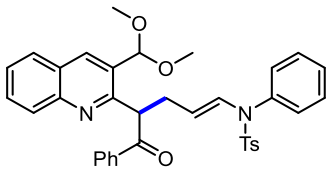
Orange solid, (66 mg, Yield 65%, m.p. 110-112 ºC), (*n*-hexane/EtOAc = 4:1, R_f= 0.35), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.19 (s, 1H, -CHO), 8.45 (s, 1H, H-4 quinoline), 7.87 (d, *J* = 8.4 Hz, 1H, H-Ar), 7.78 (br s, 1H, H-Ar), 7.65 (br s, 1H, H-Ar), 7.45 – 7.37 (m, 4H, H-Ar), 7.36-7.28 (m, 3H, H-Ar), 7.18 – 7.07 (m, 2H, H-Ar), 6.71 (d, *J* = 14.0 Hz, 1H, =CH-N), 5.89 (t, *J* = 7.2 Hz, 1H, -C<u>H</u>-CH_2), 4.66 – 4.58 (m, 1H, =C<u>H</u>-CH_2), 3.08 – 2.94 (m, 1H, =CH-C<u>H</u>$_2$), 2.85 (s, 3H, -SO_2-CH_3), 2.83 – 2.74 (m, 1H, =CH-C<u>H</u>$_2$), 2.45 (s, 3H, -CH_3) 2.46 (s, 3H, -CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 191.9, 157.0, 148.2, 144.6, 144.1, 137.8, 137.2, 136.7, 132.4, 130.1, 129.8, 129.7, 129.0, 128.9, 128.4, 127.7, 126.4, 124.4, 120.8, 109.8, 52.6, 32.1, 22.7, 20.7, 19.9; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{28}N_2O_4S$ 513.1845; Found: 513.1848.

(E)-N-(4-Chlorophenyl)-N-(4-(3-formyl-6-methylquinolin-2-yl)-5-(4-methoxyphenyl)-5-oxopent-1-en-1-yl)-4-methylbenzenesulfonamide (3m)



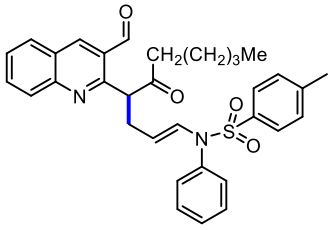
Orange oil, (89 mg, Yield 70%), (*n*-hexane/EtOAc = 4:1, R_f= 0.34), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 1H, -CHO), 8.08 (s, 1H, H-4 quinoline), 7.68 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.61 (br s, 1H, H-Ar), 7.55 – 7.48 (m, 1H, H-Ar), 7.44 (d, *J* = 8.7 Hz, 2H, H-Ar), 7.37 (d, *J* = 6.8 Hz, 2H, H-Ar), 7.24 (d, *J* = 8.1 Hz, 2H, H-Ar), 7.10 (d, *J* = 8.0 Hz, 2H, H-Ar), 6.83 (d, *J* = 14.0 Hz, 1H, =CH-N), 6.75 (d, *J* = 8.6 Hz, 2H, H-Ar), 6.63 (d, *J* = 8.2 Hz, 2H, H-Ar), 5.01 (d, *J* = 6.8 Hz, 1H, -C<u>H</u>-CH_2), 4.73 – 4.60 (m, 1H, =C<u>H</u>-CH_2), 3.70 (s, 3H, O-CH_3), 3.03 – 2.86 (m, 2H, =CH-C<u>H</u>$_2$), 2.55 (s, 3H, -CH_3), 2.40 (s, 3H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 189.4, 162.3, 155.6, 143.7, 136.6, 135.4, 135.2, 134.6, 132.3, 132.2, 131.9, 131.6, 131.3, 131.0, 130.5, 129.6, 129.5, 128.9, 128.5, 127.2, 126.5, 113.7, 113.2, 109.9, 57.5, 55.2, 38.4, 21.7, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{32}{}^{35}ClN_2O_5S$ 639.1707; Found: 639.1711

(E)-N-(4-(3-(Dimethoxymethyl)quinolin-2-yl)-5-oxo-5-phenylpent-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (3n)



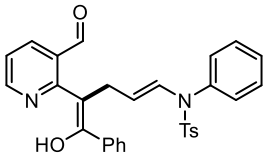
Yellow oil, (49 mg, Yield 41%), (*n*-hexane/EtOAc = 4:1, R_f= 0.30), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 8.32 (s, 1H, H-4 quinoline), 7.95 (d, *J* = 8.1 Hz, 1H, H-Ar), 7.83 (d, *J* = 8.6 Hz, 2H, H-Ar), 7.69 (d, *J* = 8.6 Hz, 1H, H-Ar), 7.52 (d, *J* = 8.6 Hz, 1H), 7.43 – 7.33 (m, 7H, H-Ar), 7.43 – 7.20 (m, 6H, H-Ar), 7.05 (d, *J* = 14.0 Hz, 1H, =CH-N), 6.78 (s, 1H, -C<u>H</u>-O), 5.29 (t, *J* = 6.7 Hz, 1H, -C<u>H</u>-CH_2), 4.53-4.46 (m, 1H, =C<u>H</u>-CH_2), 3.38 (s, 3H, -O-CH_3), 3.35 (s, 3H, -O-CH_3), 2.57 – 2.43 (m, 2H, =CH-C<u>H</u>$_2$), 2.39 (s, 3H, -CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.5, 157.5, 143.5, 137.3, 137.0, 136.6, 132.5, 132.3, 130.7, 129.9, 129.7, 129.4, 129.3, 128.7, 128.6, 128.5, 128.4, 128.3, 127.8, 127.7, 127.3, 126.2, 109.9, 101.9, 54.7, 54.2, 42.3, 32.1, 21.6. HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{36}H_{35}N_2O_5S$ 607.2255; Found: 607.2261.

(E)-N-(4-(3-Formylquinolin-2-yl)-5-oxodec-1-en-1-yl)-4-methyl-N-phenylbenzene sulfonamideb (3o)



Orange oil, (62 mg, Yield 56%), (*n*-hexane/EtOAc = 4:1, R_f= 0.25), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.17 (s, 1H, -CHO), 8.58 (s, 1H, H-4 quinoline), 8.09 (d, *J* = 8.4 Hz, 1H, H-Ar), 7.98 (d, *J* = 8.1 Hz, 1H, H-Ar), 7.88 (dd, *J* = 8.5, 4.5 Hz, 1H, H-Ar), 7.68 (dd, *J* = 8.4, 4.6 Hz, 1H, H-Ar), 7.37 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.31 – 7.24 (m, 3H, H-Ar), 7.11 (d, *J* = 8.5 Hz, 2H, H-Ar), 6.90 (d, *J* = 14.0 Hz, 1H, =CH-N), 6.76 (d, *J* = 8.3 Hz, 2H, H-Ar), 4.93 (dd, *J* = 7.7, 5.9 Hz, 1H, -C<u>H</u>-CH_2), 4.41 – 4.34 (m, 1H, =C<u>H</u>-CH_2), 2.88 – 2.74 (m, 2H, =CH-C<u>H</u>$_2$), 2.41 (s, 3H, =C-C<u>H</u>$_3$), 2.39-2.33 (m, 2H, -CO-CH_2), 1.57 – 1.48 (m, 2H, -CH_2), 1.33-1.12 (m, 4H, -CH_2), 0.82 (t, *J* = 7.0 Hz, 3H, -CH_3); **^{13}C** NMR (101 MHz, $CDCl_3$) δ 208.1, 191.4, 157.6, 149.0, 144.7, 143.5, 136.6, 135.7, 132.9, 130.6, 129.9, 129.5, 129.4, 129.2, 128.9, 128.8, 127.6, 127.3, 125.9, 109.6, 92.9, 57.3, 42.0, 31.2, 31.1, 23.4, 22.5, 21.6, 13.9; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{33}H_{35}N_2O_4S$ 555.2310 Found 555.2314.

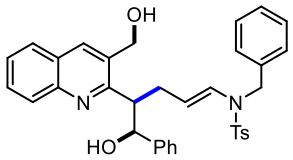
(E)-N-(3-(5-Hydroxy-7-phenyl-5H-pyrano[4,3-b]pyridin-8-yl)prop-1-en-1-yl)-4-methyl-N-phenylbenzenesulfonamide (3p)



Orange solid, (54 mg, Yield 53%, m.p. 79-81 ºC), (*n*-hexane/EtOAc = 3:1, R_f= 0.30), ^{1}H NMR (400 MHz, , DMSO-d_6) δ 16.10 (*br* s, 1H, -OH), 9.36 (s, 1H, -CHO), 9.15 (dd, *J* = 4.3, 1.8 Hz, 1H, H-4 quinoline), 8.60 (dd, *J* = 8.3, 1.8 Hz, 1H, H-Ar), 7.73 (dd, *J* = 8.2, 4.3 Hz, 1H, H-Ar), 7.52-7.44 (m, 5H, H-Ar), 7.38 – 7.31 (m, 7H, H-Ar), 6.82 – 6.75 (m, 2H, H-Ar), 6.61 (d, *J* = 14.1 Hz, 1H, =CH-N), 4.53 (dt, *J* = 13.6, 6.5 Hz, 1H, =CH), 3.85 (d, *J* = 7.6 Hz, 2H, CH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.6, 169.0, 155.8, 154.1, 150.6, 149.7, 143.67, 140.3, 136.7, 135.9, 135.8, 130.2, 130.0, 129.4, 129.1, 128.7, 128.2, 127.4, 122.3, 122.1, 111.5,

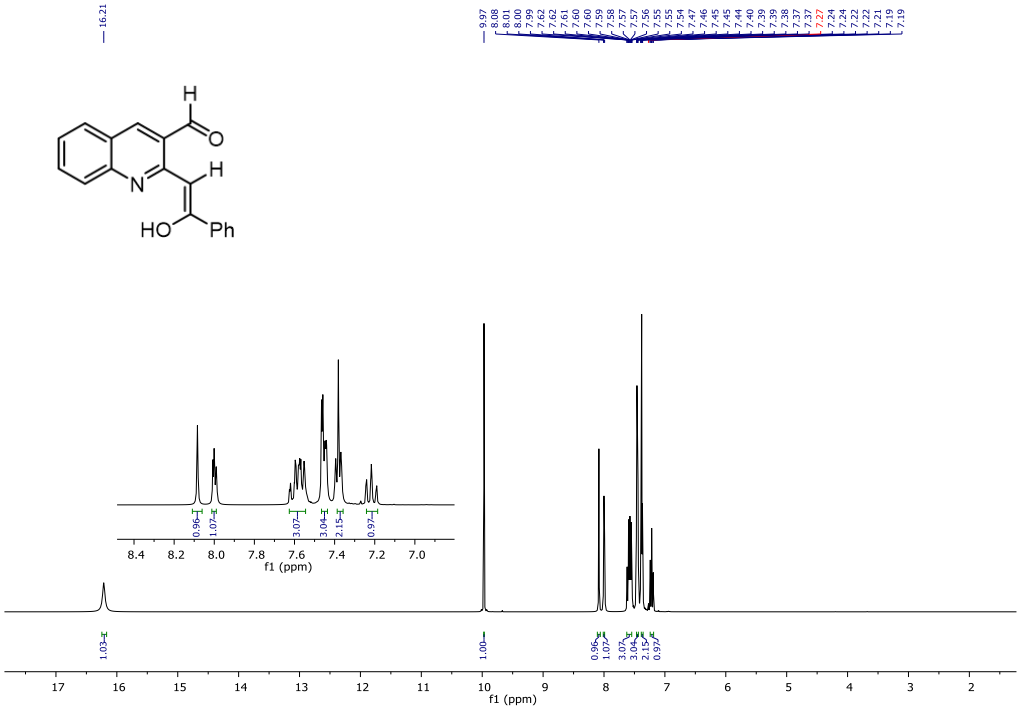
77.3, 27.8, 21.6; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{30}H_{27}N_2O_4S$ 511.1683, Found: 511.1688.

N-Benzyl-N-((4R,5S,E)-5-hydroxy-4-(3-(hydroxymethyl)quinolin-2-yl)-5-phenylpent-1-en-1-yl)-4-methylbenzenesulfonamide (4a)

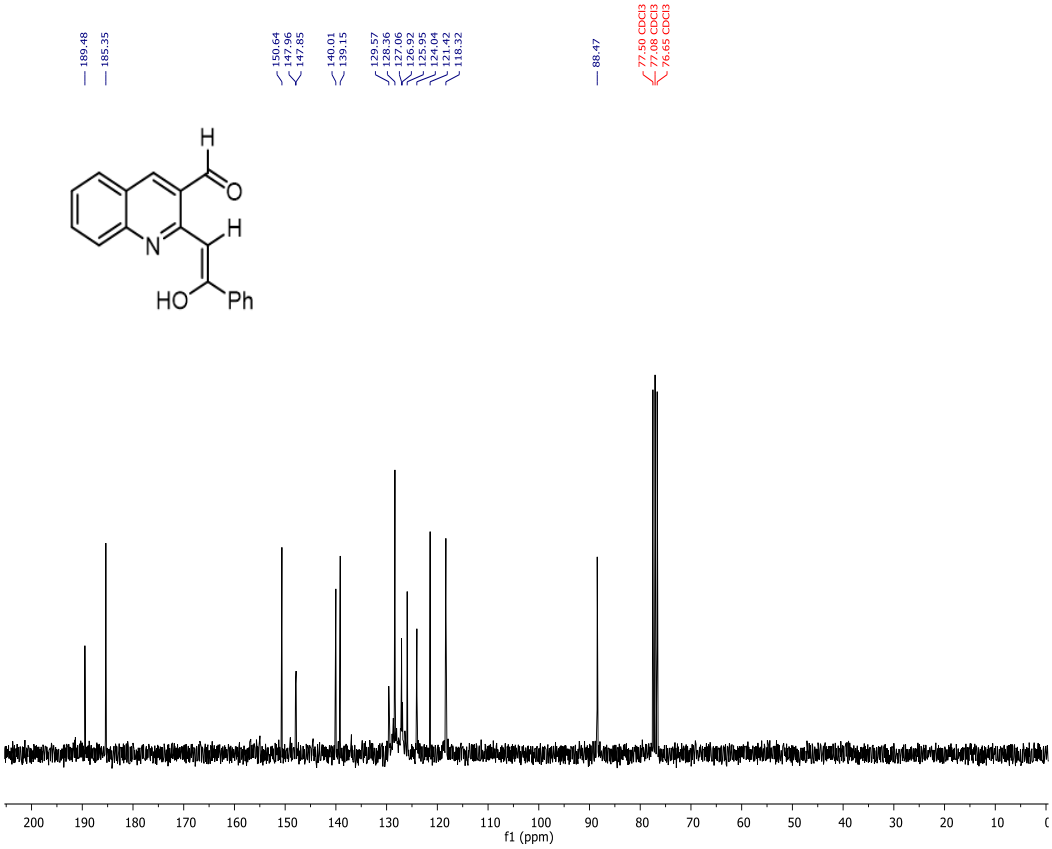


Yellow solid, (82 mg, Yield 72%, m.p. 123-124 ºC), (*n*-hexane/EtOAc = 3:1, R_f= 0.25), (mixture of two diastereomers (50:50); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.74 (m, 5H), 7.67 (br s, 2H), 7.63 – 7.55 (m, 2H), 7.53-7.47 (m, 2H), 7.45-7.40 (m, 3H), 7.41-7.35 (m, 4H), 7.32-7.27 (m, 4H), 7.23-7.15 (m, 4H), 7.13-7.08 (m, 4H), 7.07-7.03 (m, 5H), 7.01-6.93 (m, 3H), 6.19 (t, *J*= 14.0 Hz, 2H), 4.95-4.88 (m, 1H), 4.81 (d, *J* = 14.0 Hz, 1H), 4.76 – 4.49 (m, 3H), 4.47 – 4.19 (m, 6H), 4.17-3.98 (m, 3H), 3.54 – 3.32 (m, 3H), 3.00 – 2.72 (m, 2H), 2.61-2.47 (m, 1H), 2.38 (d, *J* = 4.6 Hz, 6H), 2.37-2.30 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 163.3, 163.6, 146.3, 144.1, 143.7, 143.6, 143.3, 142.4, 136.1, 135.9, 135.8, 135.7, 135.6, 135.5, 135.4, 135.3, 132.6, 132.3, 129.7, 129.6, 129.5, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 127.3, 127.2, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 126.5, 126.4, 125.9, 125.6, 112.7, 111.8, 74.8, 62.4, 62.2, 50.1, 49.5, 49.0, 48.1, 29.7, 28.9, 22.7, 21.5; HRMS-ESI (*m/z*): $[M+H]^+$ calcd for $C_{35}H_{35}N_2O_4S$ 579.2861; Found: 579.2863

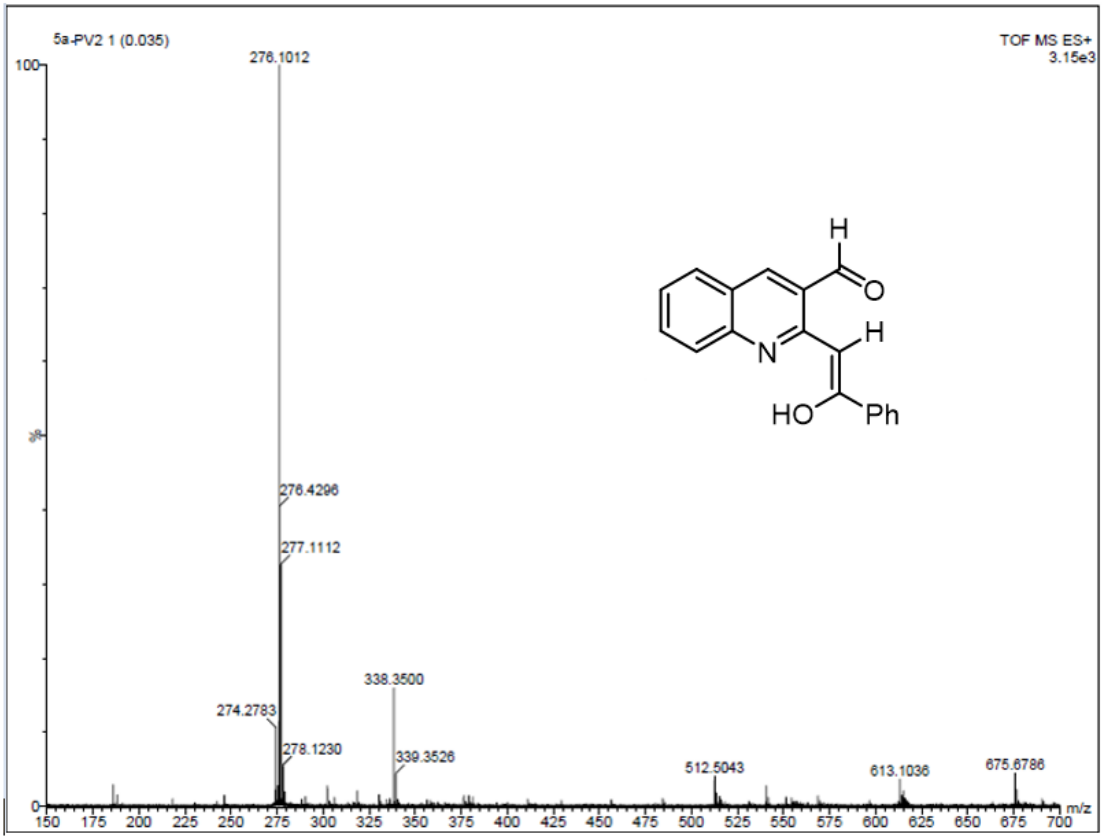
3. ^{1}H NMR, ^{13}C NMR, and HRMS-ESI Spectra



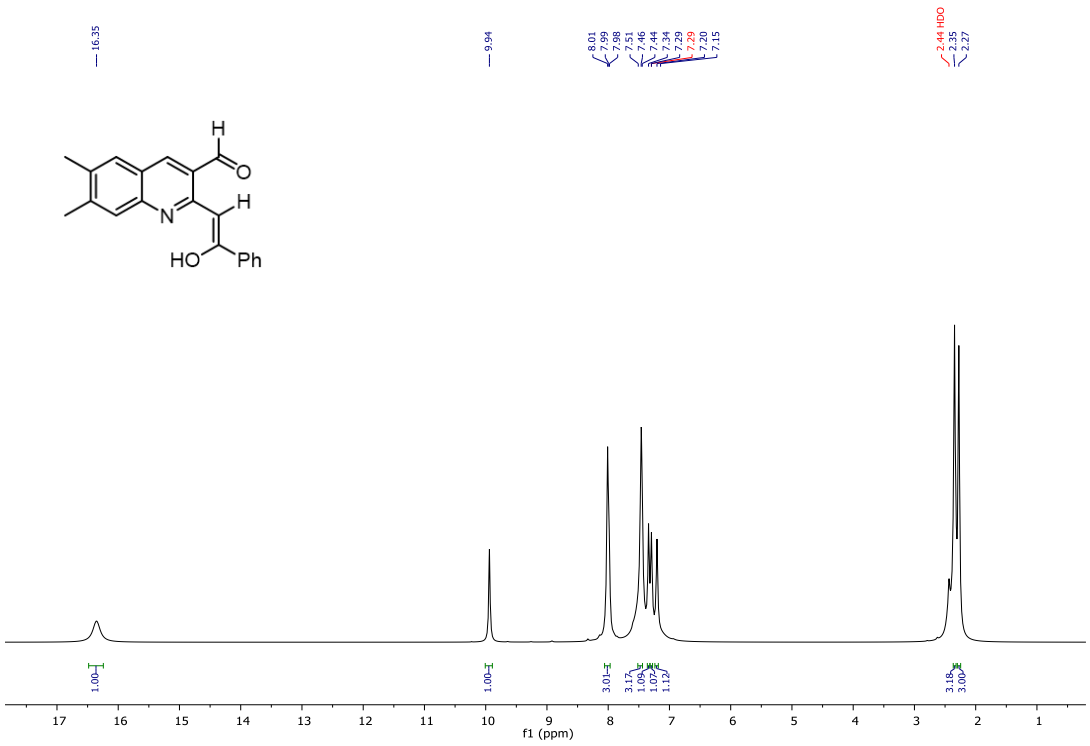
^{1}H-NMR of compound **1a** (300MHz, $CDCl_3$)



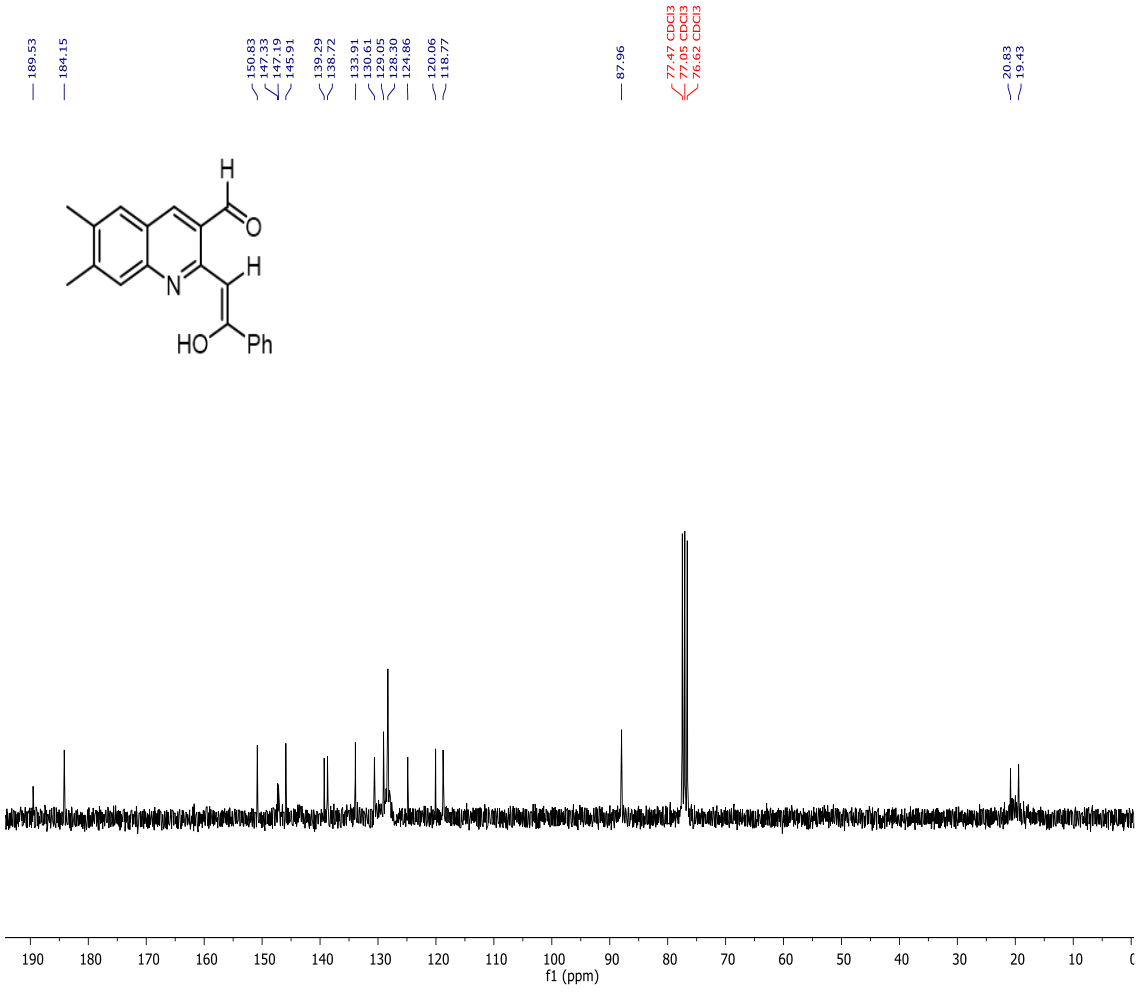
^{13}C-NMR of compound **1a** (75 MHz, $CDCl_3$)



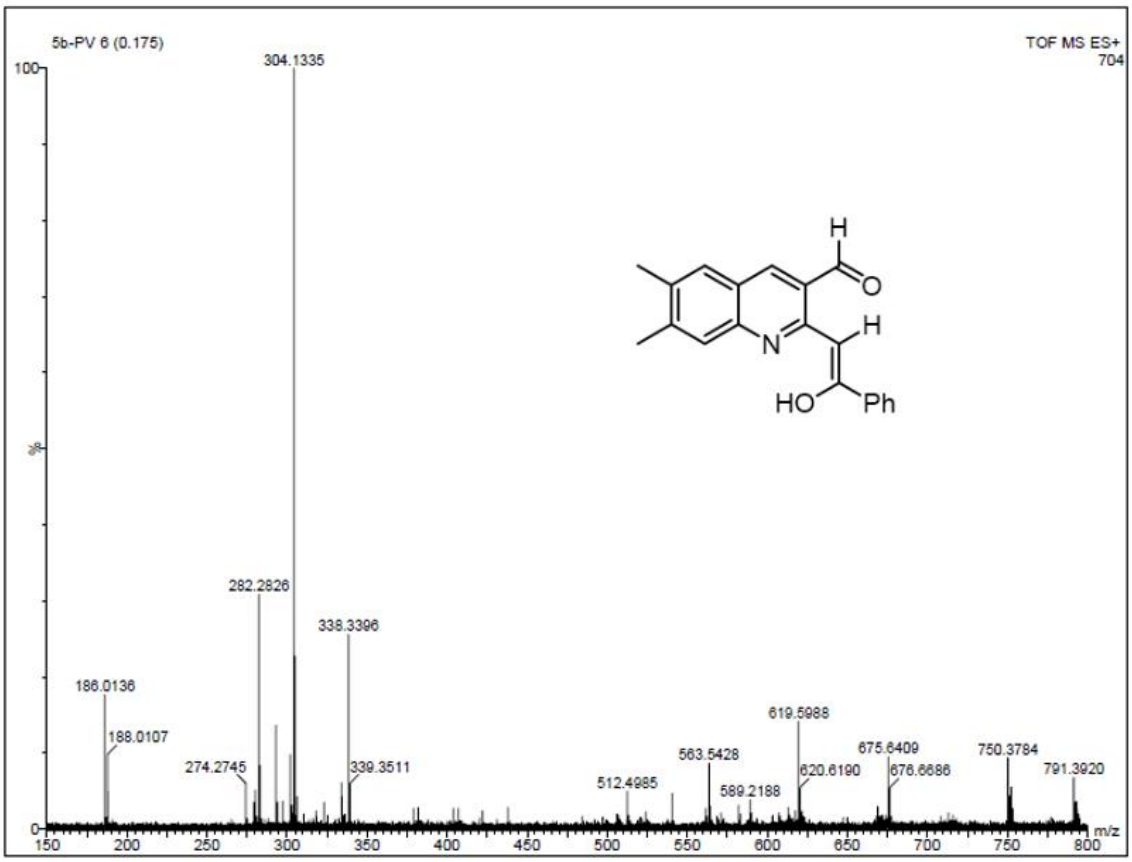
HRMS-ESI of **1a**: $[M+H]^+$ calcd for $C_{18}H_{14}NO_2$ 276.1017



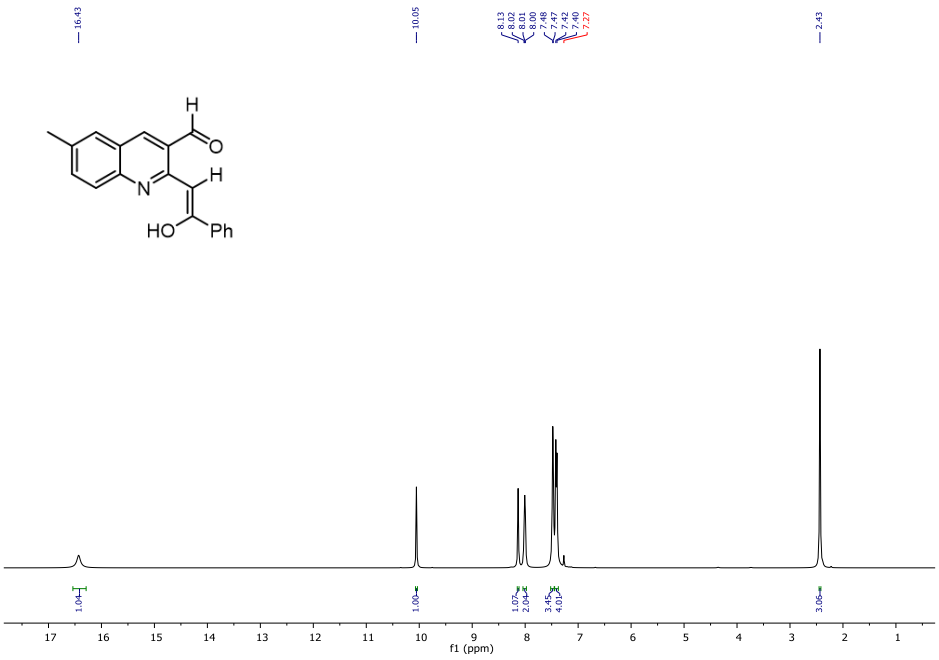
^{1}H-NMR of compound **1b** (300MHz, $CDCl_3$)



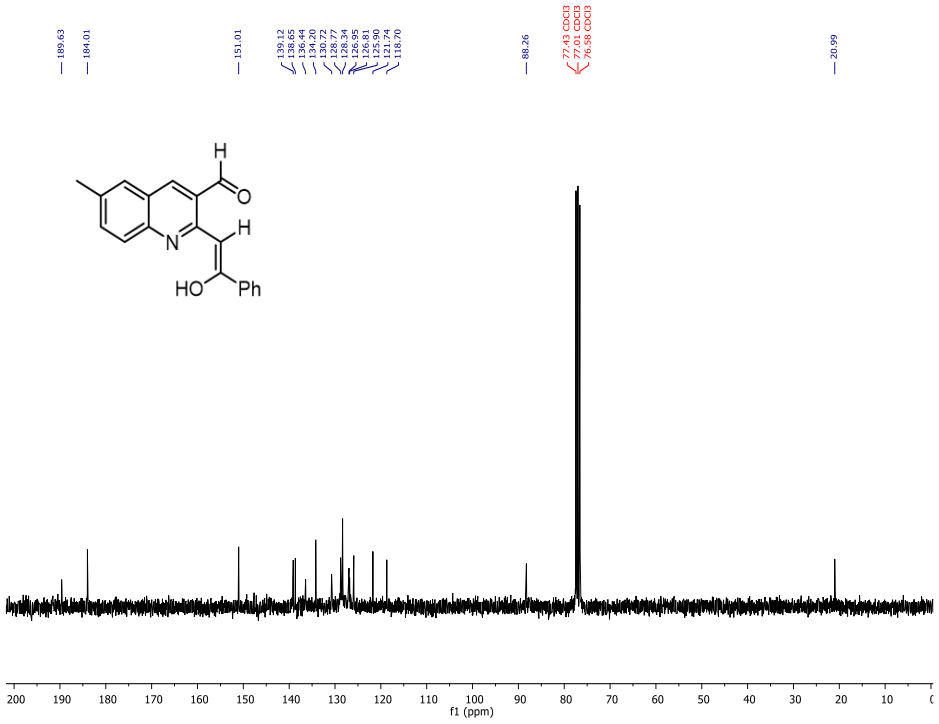
^{13}C-NMR of compound **1b** (75 MHz, $CDCl_3$)



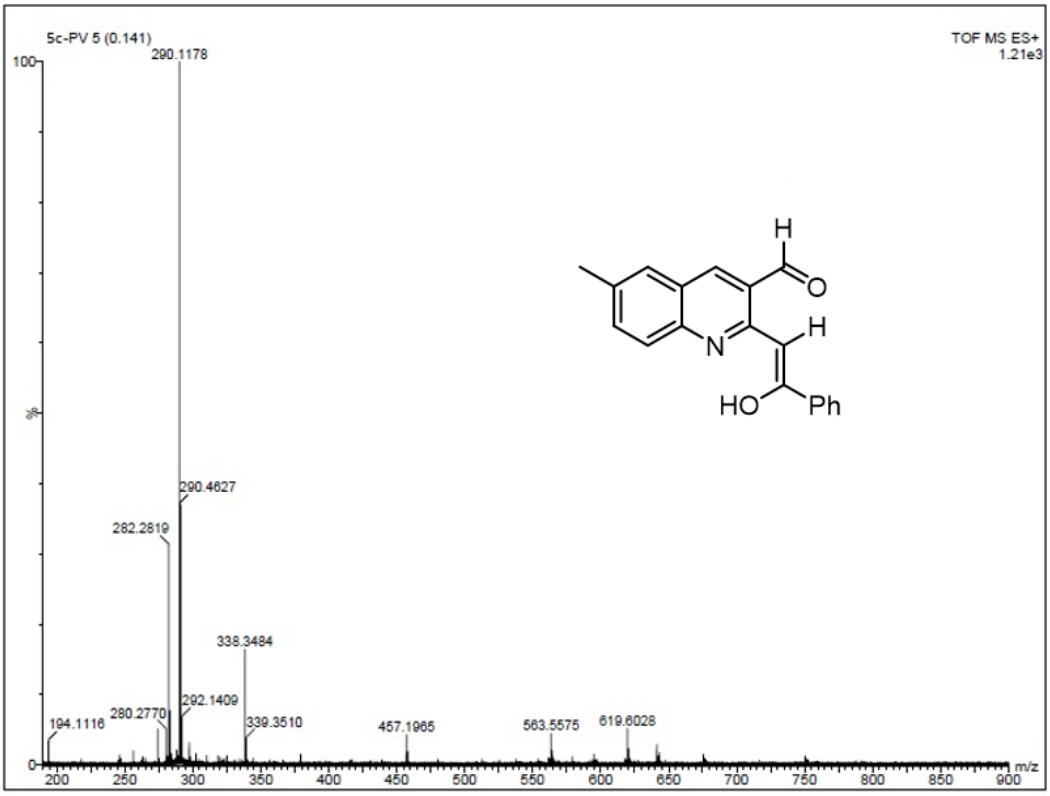
HRMS-ESI of **1b**: $[M+H]^+$ calcd for $C_{20}H_{18}NO_2$ 304.1332



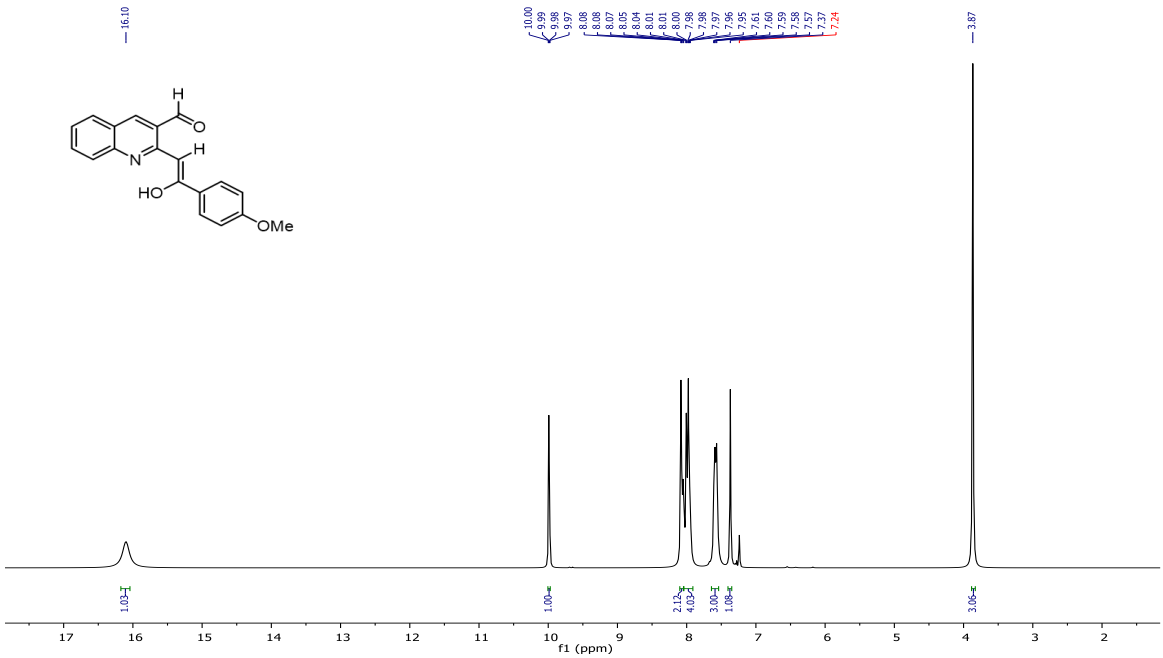
^{1}H-NMR of compound **1c** (300MHz, $CDCl_3$)



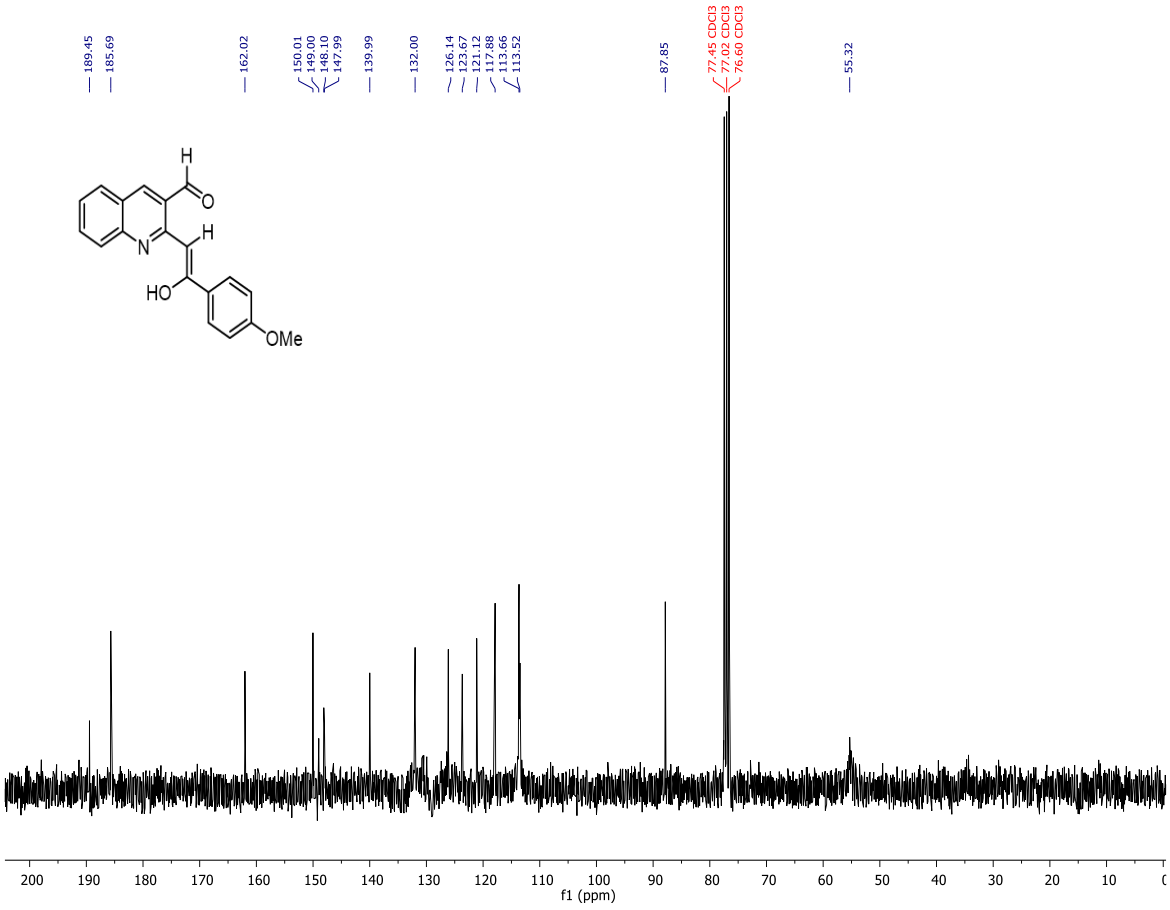
^{13}C-NMR of compound **1c** (75 MHz, $CDCl_3$)



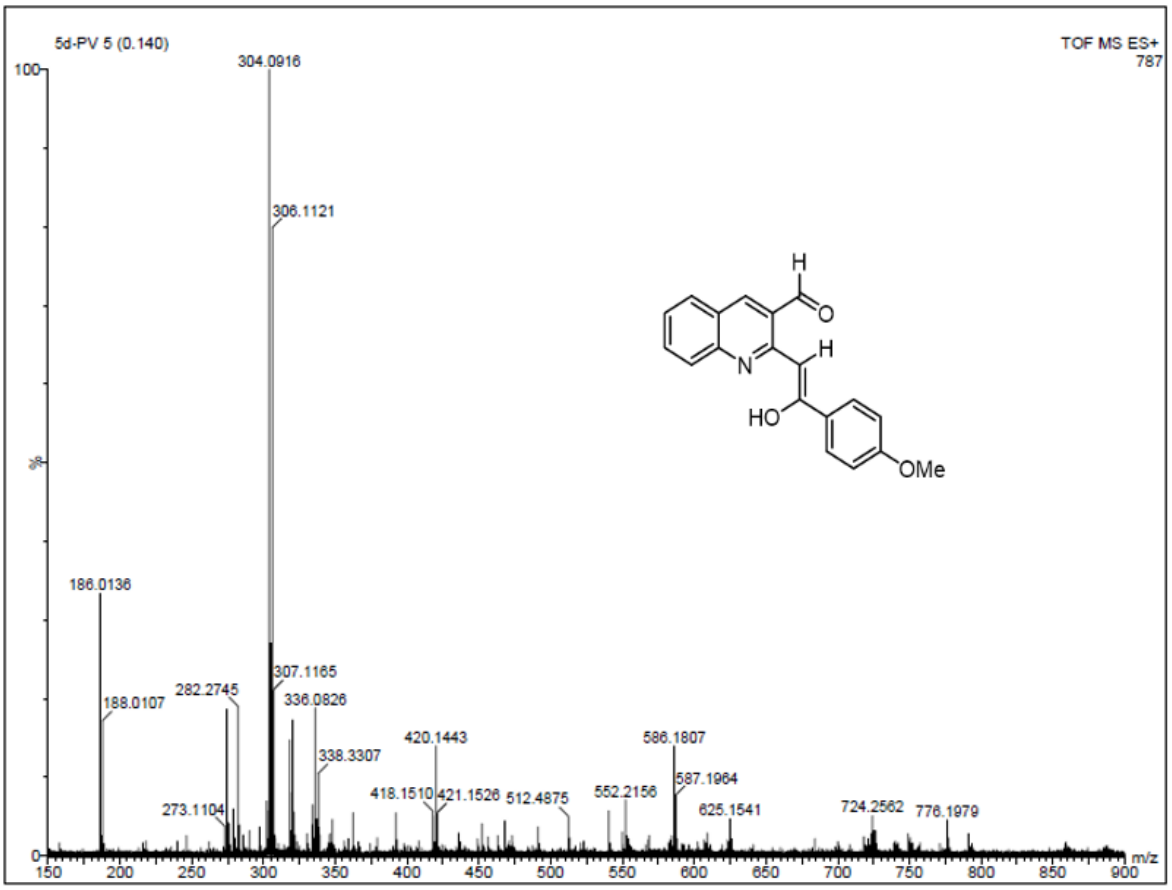
HRMS-ESI of **1c**: $[M+H]^+$ calcd for $C_{19}H_{16}NO_2$ 290.1181



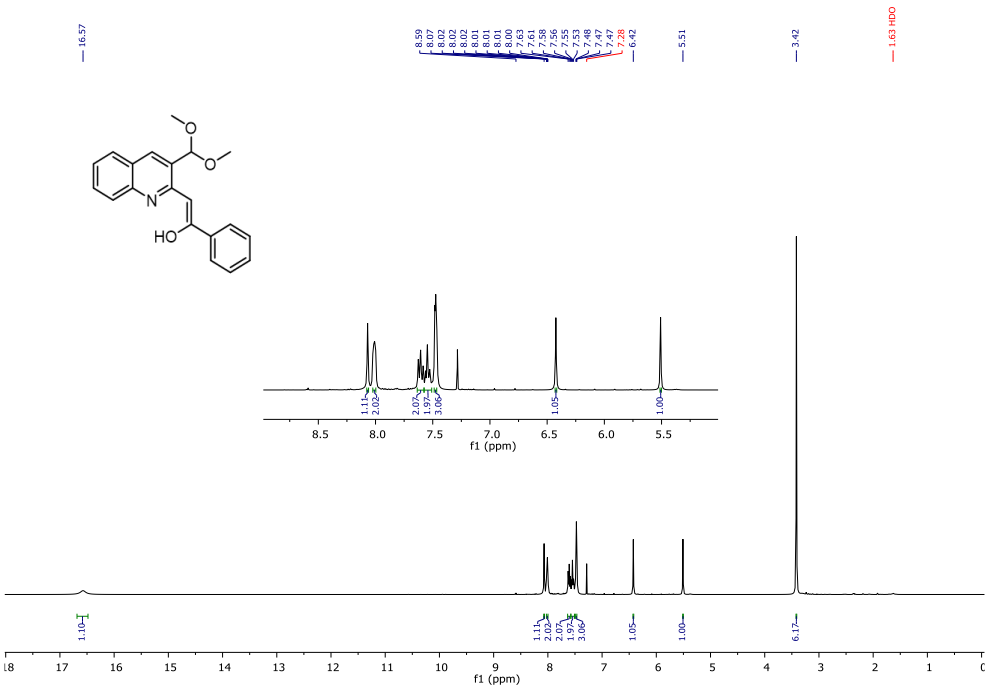
^{1}H-NMR of compound **1d** (300MHz, $CDCl_3$)



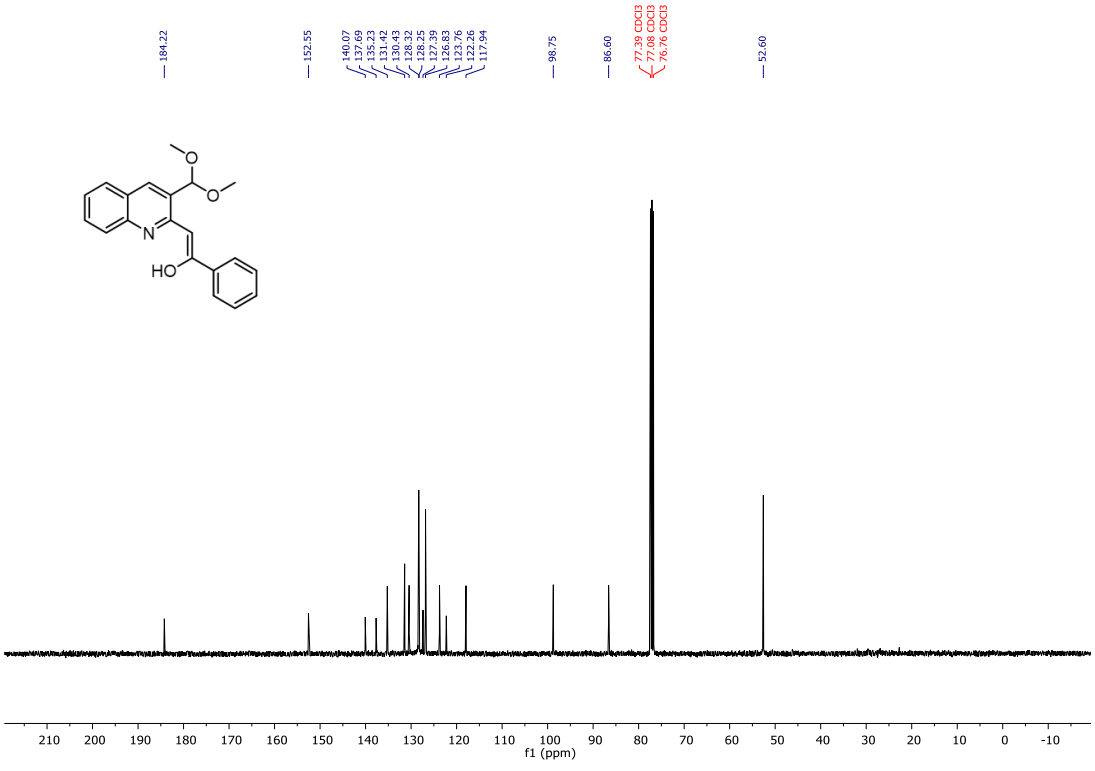
^{13}C-NMR of compound **1d** (75 MHz, $CDCl_3$)



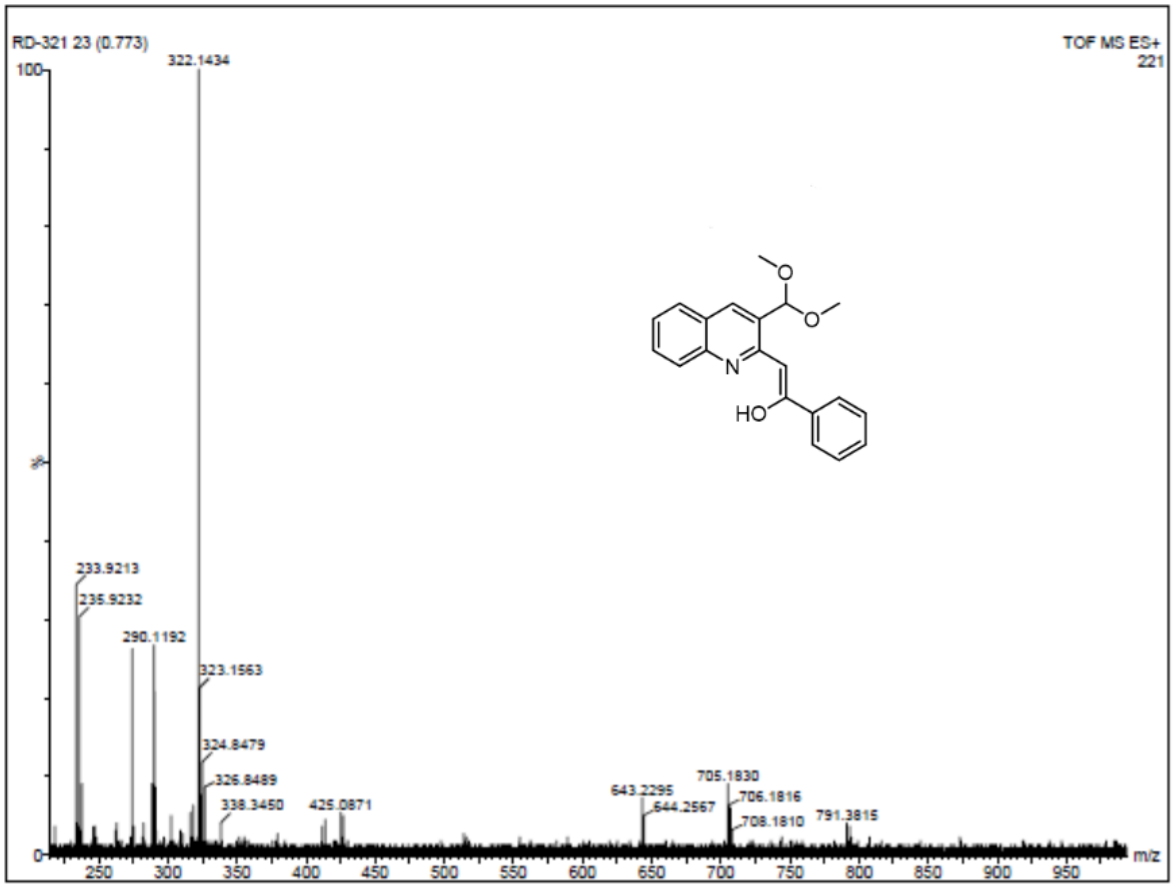
HRMS-ESI of **1d**: $[M+H]^+$ calcd for $C_{19}H_{16}NO_3$ 306.1127



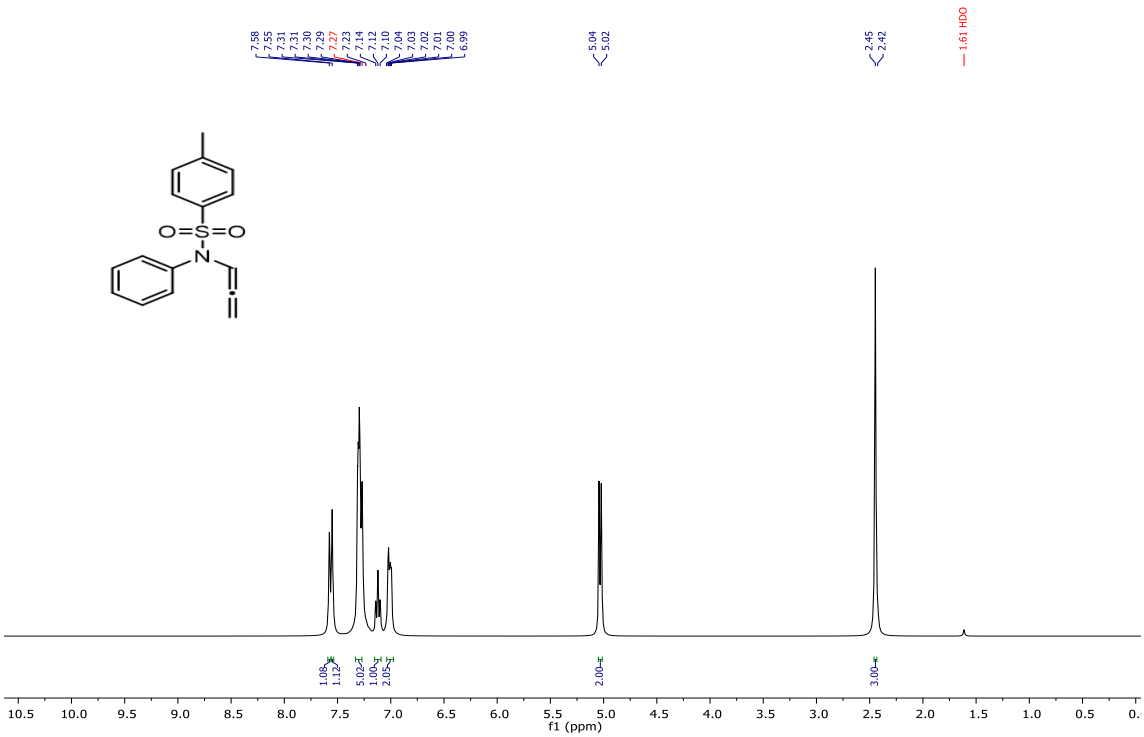
^{1}H-NMR of compound **1e** (400MHz, $CDCl_3$)



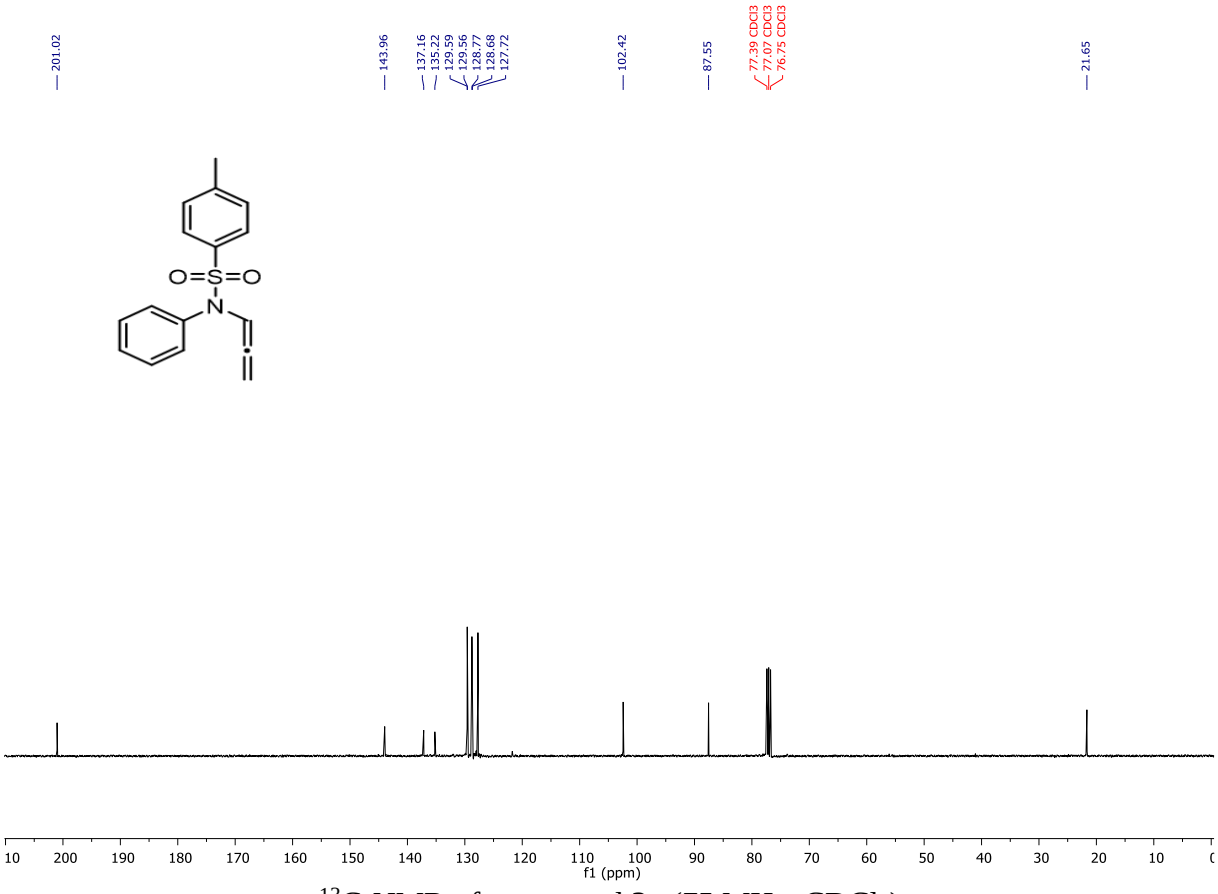
^{13}C-NMR of compound **1e** (101 MHz, $CDCl_3$)



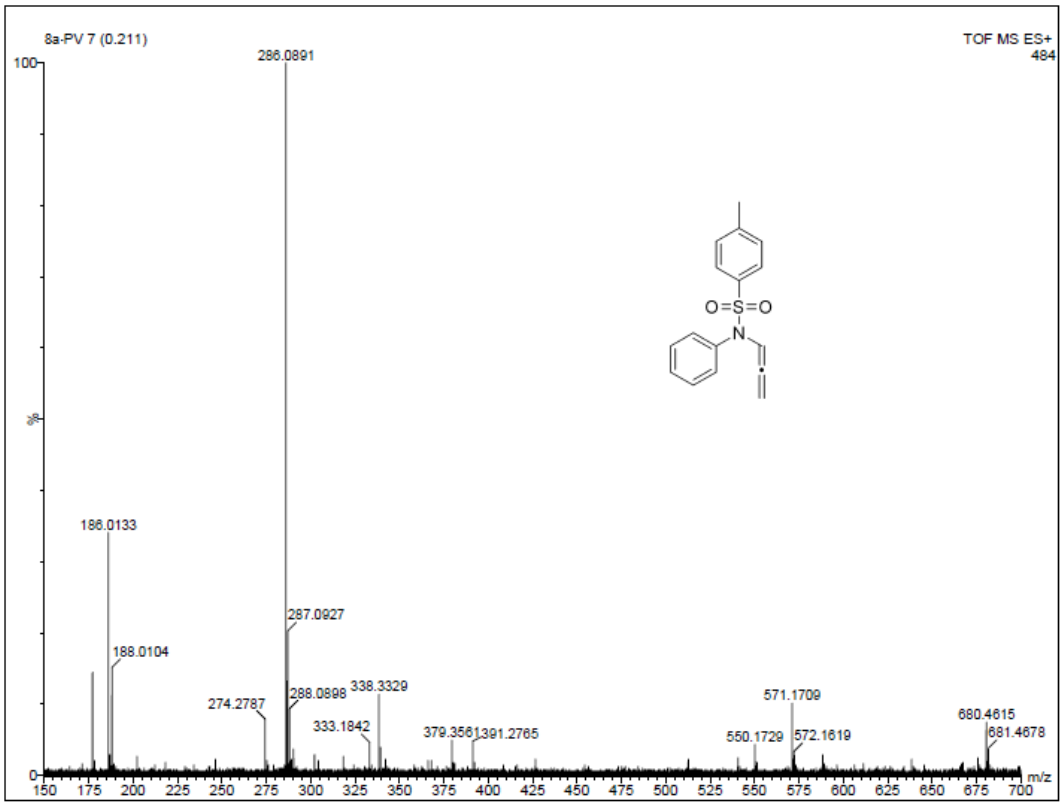
HRMS-ESI of **1e** : $[M+H]^+$ calcd for $C_{20}H_{20}NO_3$ 322.1431



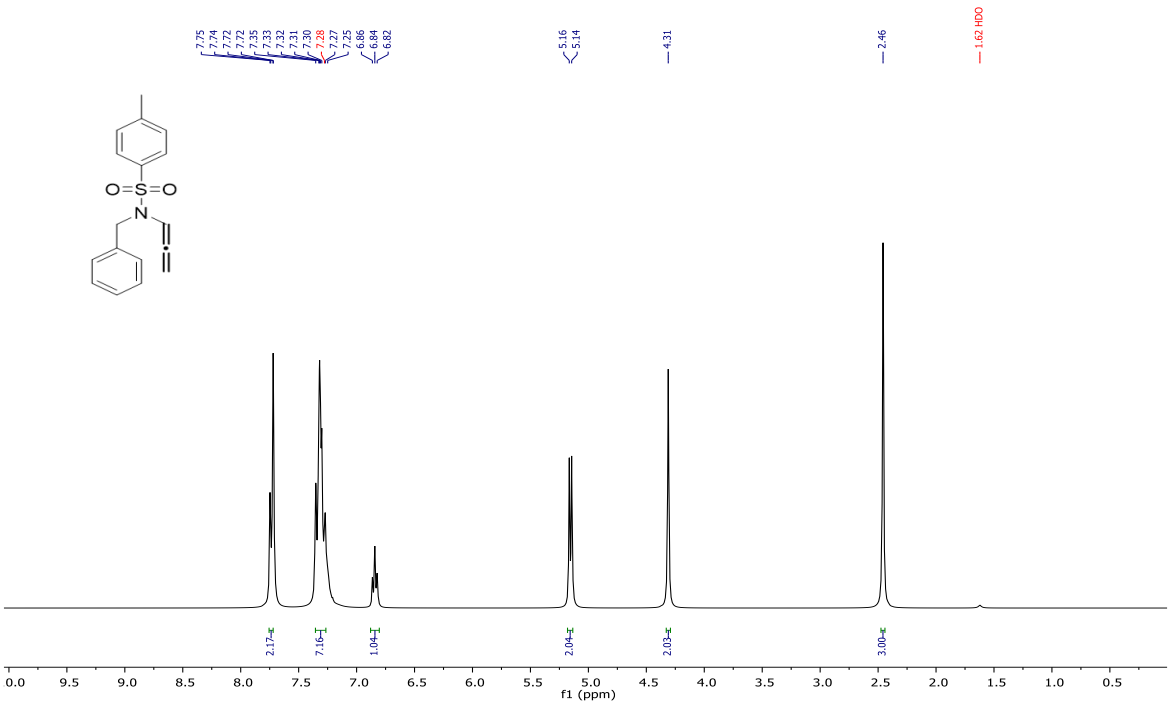
^{1}H-NMR of compound **2a** (300MHz, $CDCl_3$)



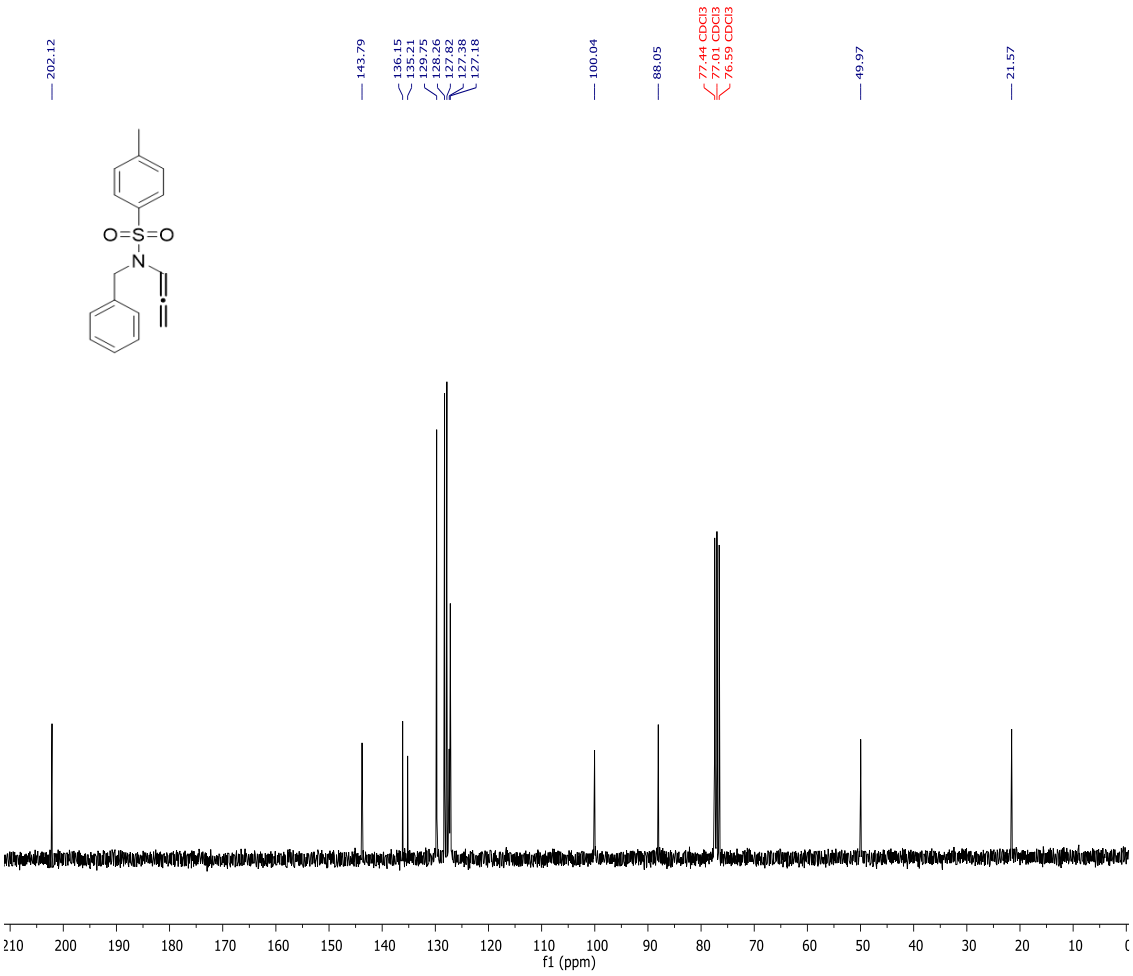
^{13}C-NMR of compound **2a** (75 MHz, $CDCl_3$)



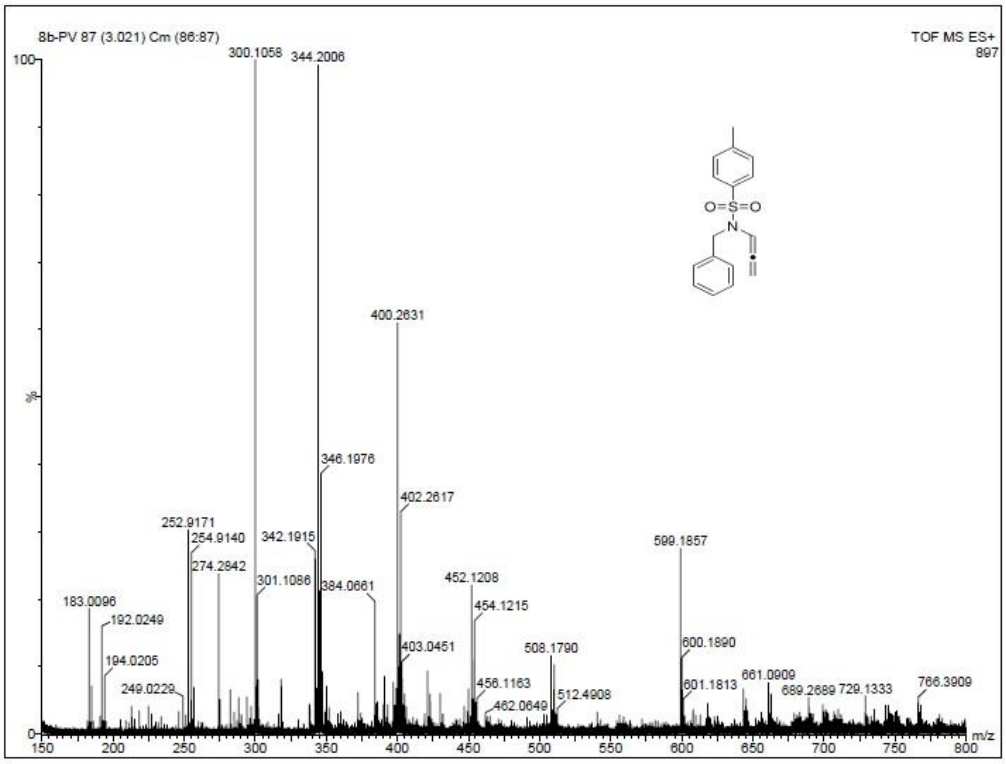
HRMS-ESI of **2a**: $[M+H]^+$ calcd for $C_{16}H_{16}NO_2S$ 286.0890



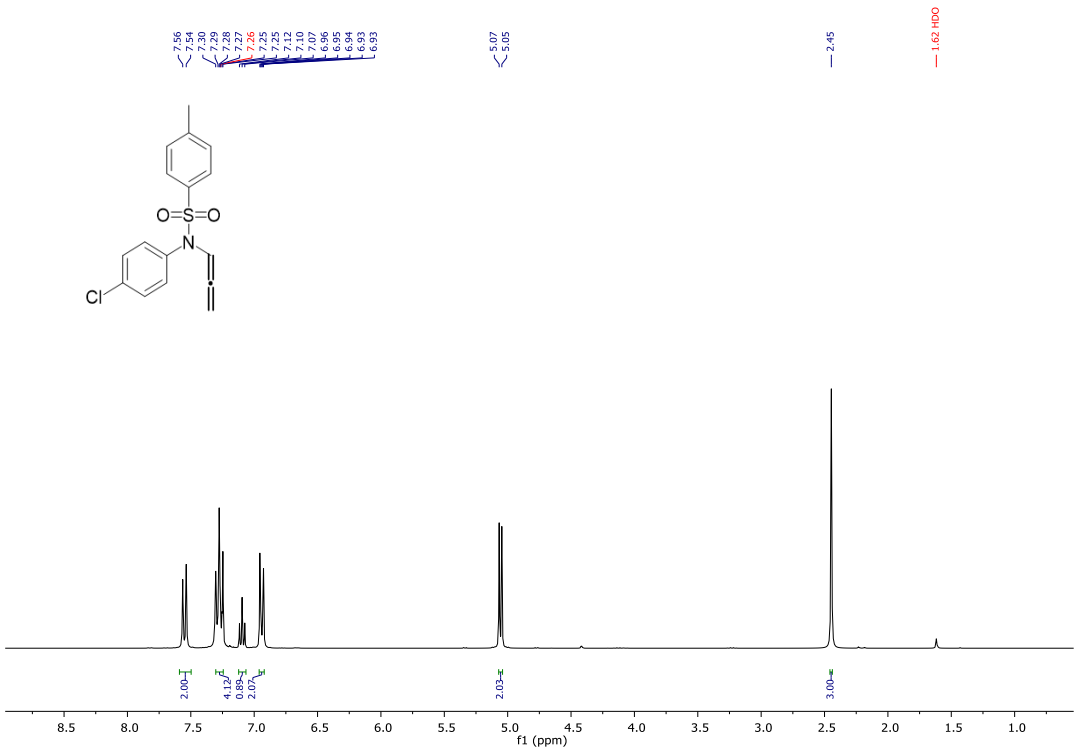
^{1}H-NMR of compound **2b** (300MHz, $CDCl_3$)



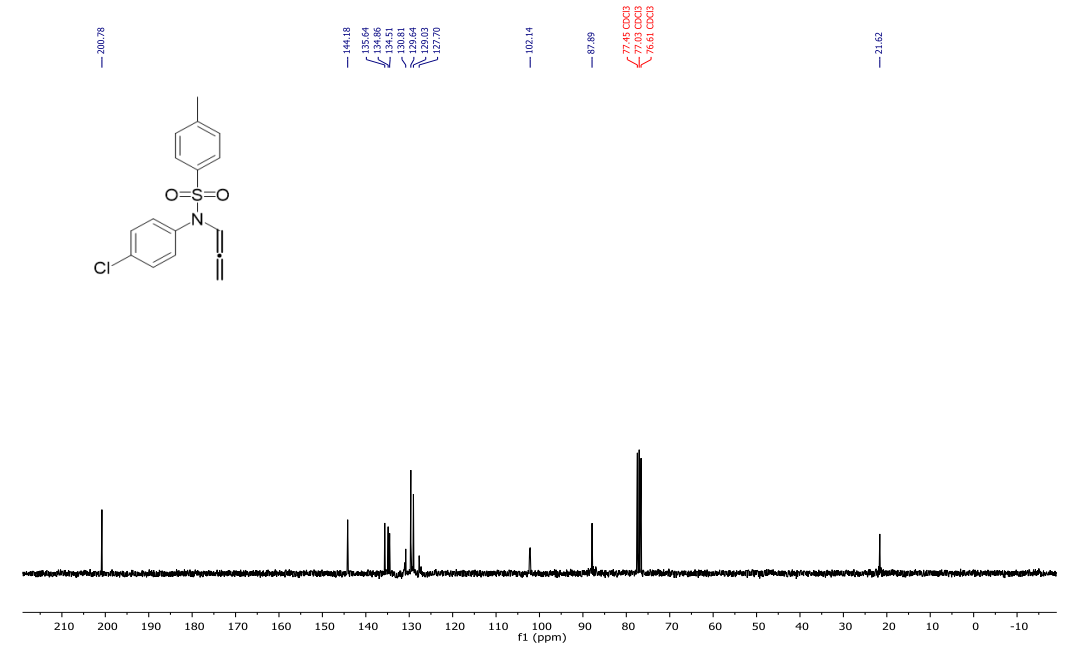
^{13}C-NMR of compound **2b** (75 MHz, $CDCl_3$)



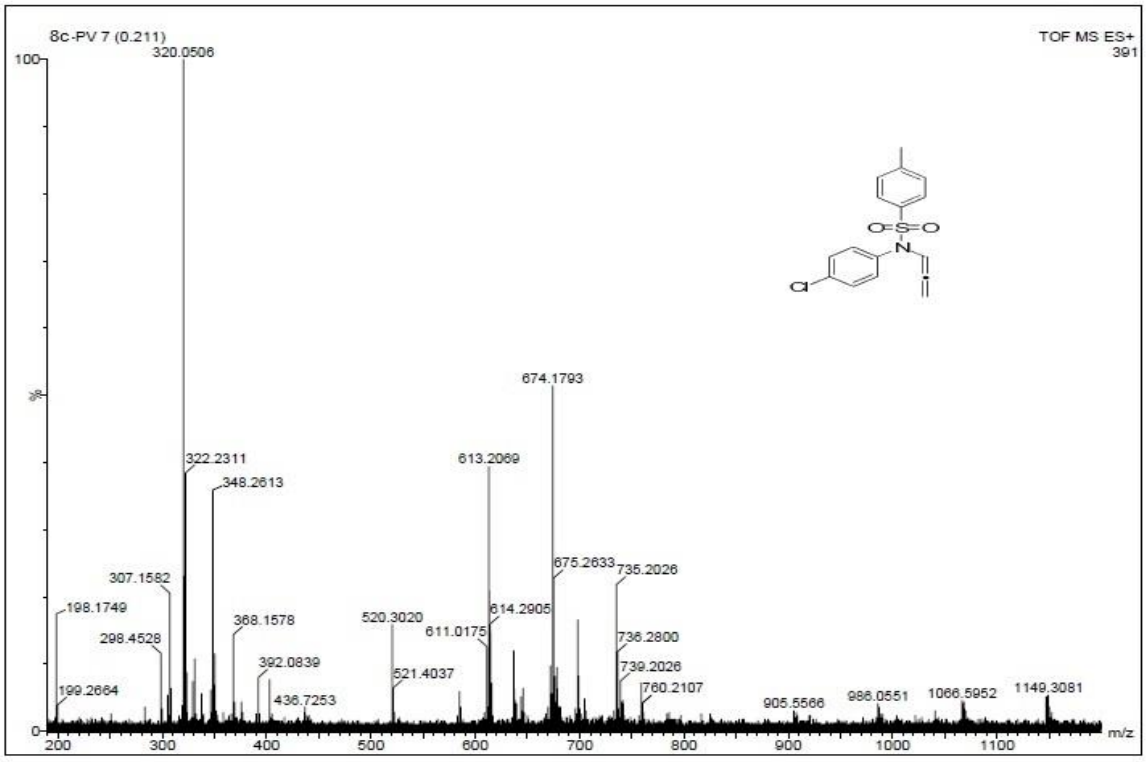
HRMS-ESI of **2b**: $[M+H]^+$ calcd for $C_{17}H_{18}NO_2S$ 300.1057



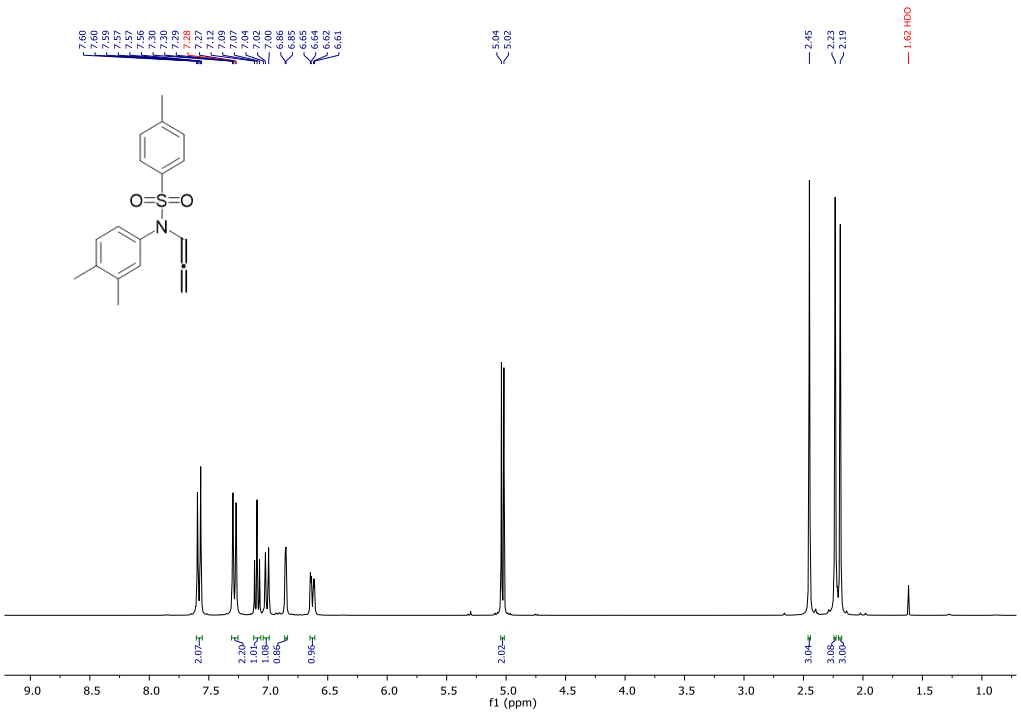
^{1}H-NMR of compound **2c** (300MHz, $CDCl_3$)



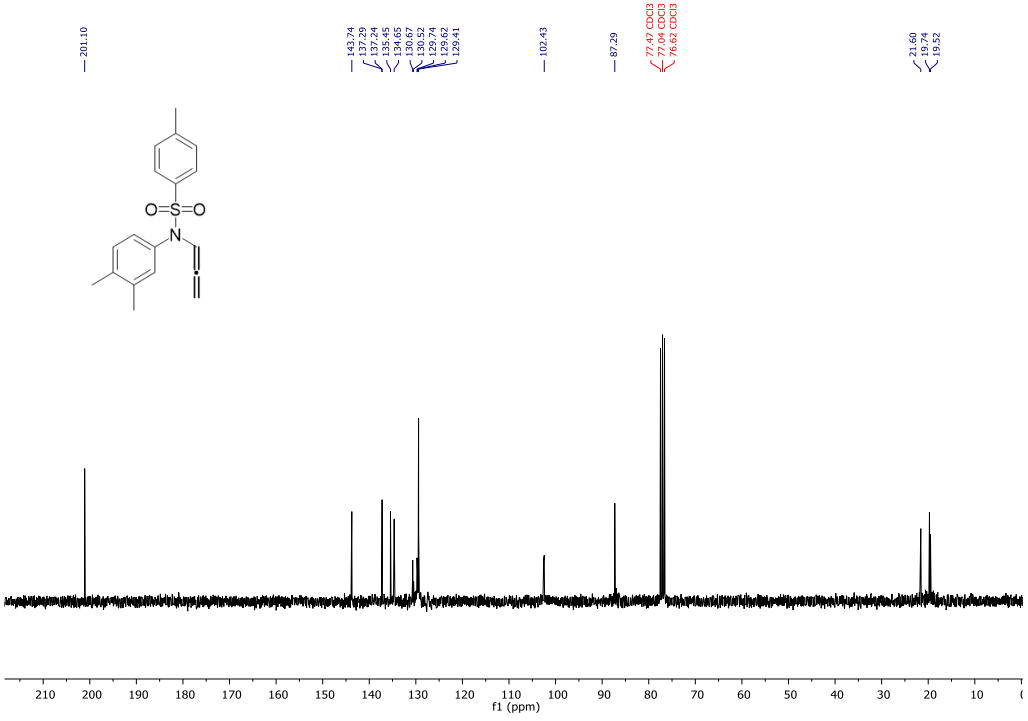
^{13}C-NMR of compound **2c** (75 MHz, $CDCl_3$)



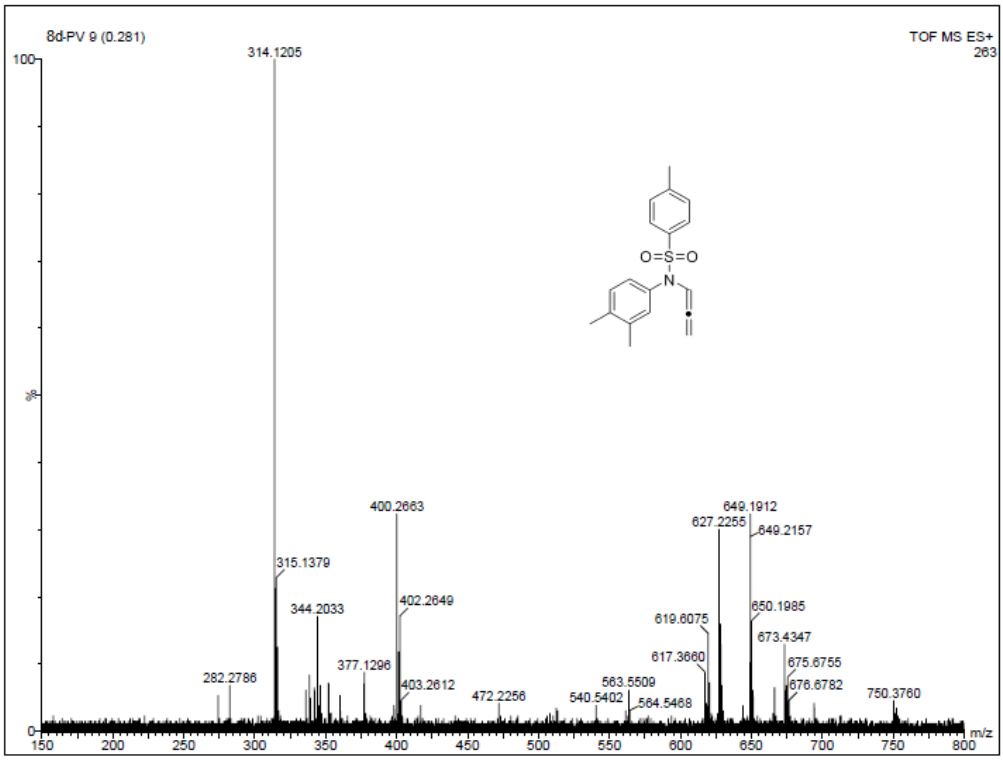
HRMS-ESI of **2c**: $[M+H]^+$ calcd for $C_{16}H_{15}{}^{35}ClNO_2S$ 320.0502



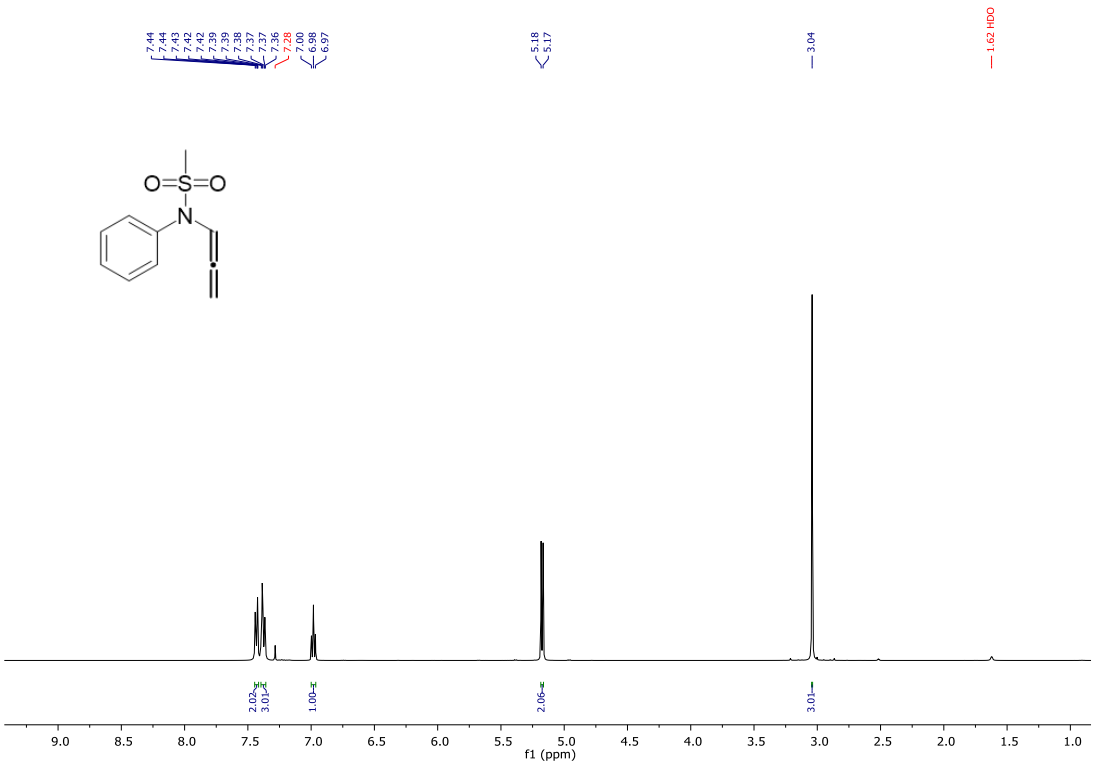
^{1}H-NMR of compound **2d** (300MHz, $CDCl_3$)



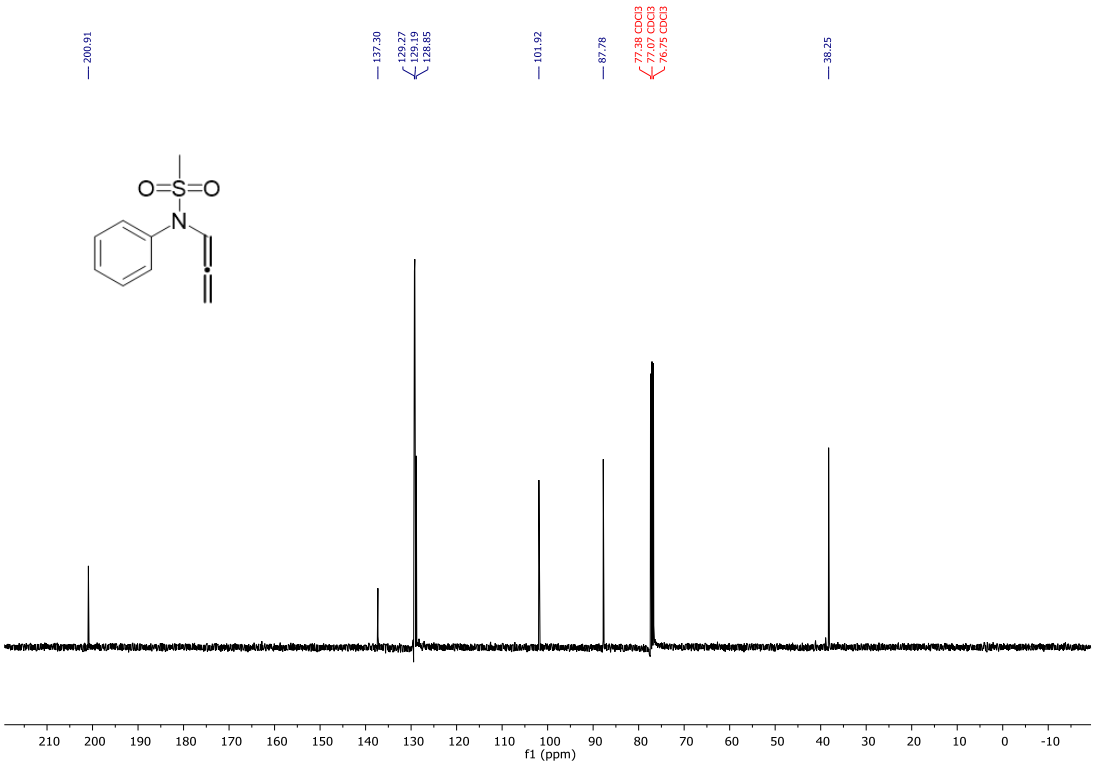
^{13}C-NMR of compound **2d** (75 MHz, $CDCl_3$)



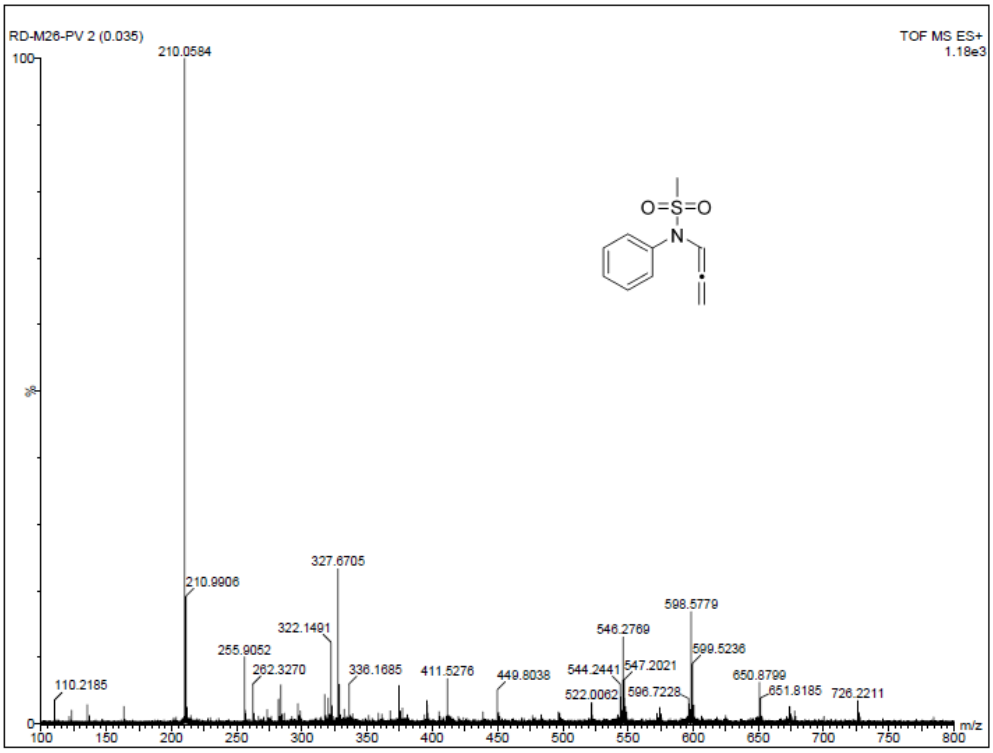
HRMS-ESI of **2d**: $[M+H]^+$ calcd for $C_{18}H_{20}NO_2S$ 314.1203



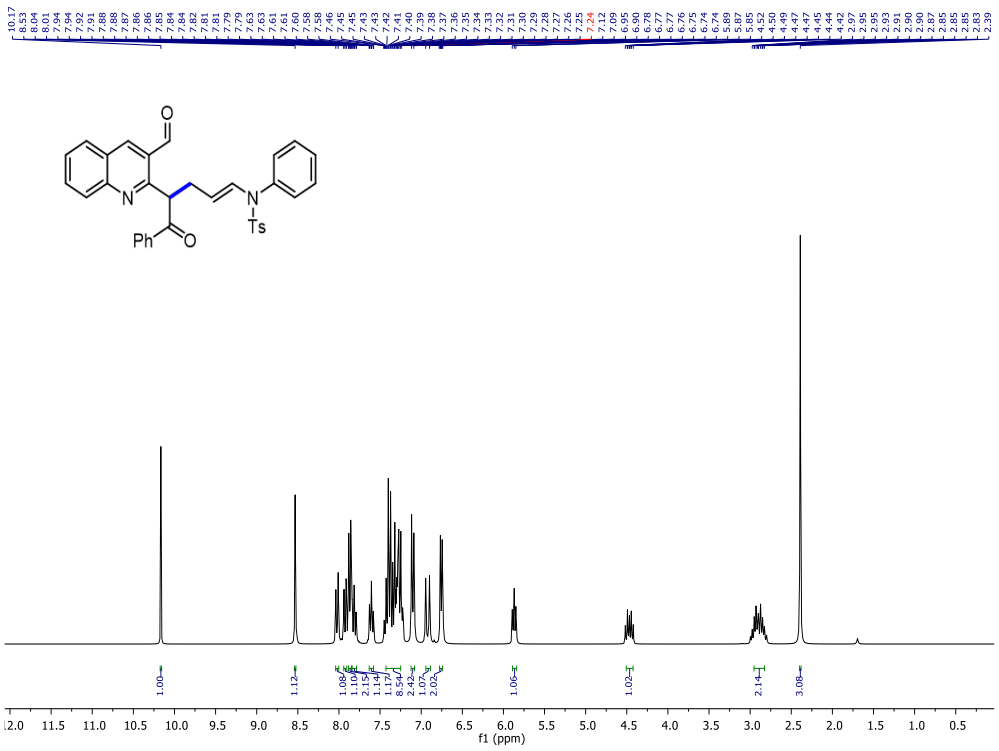
^{1}H-NMR of compound **2e** (400MHz, $CDCl_3$)



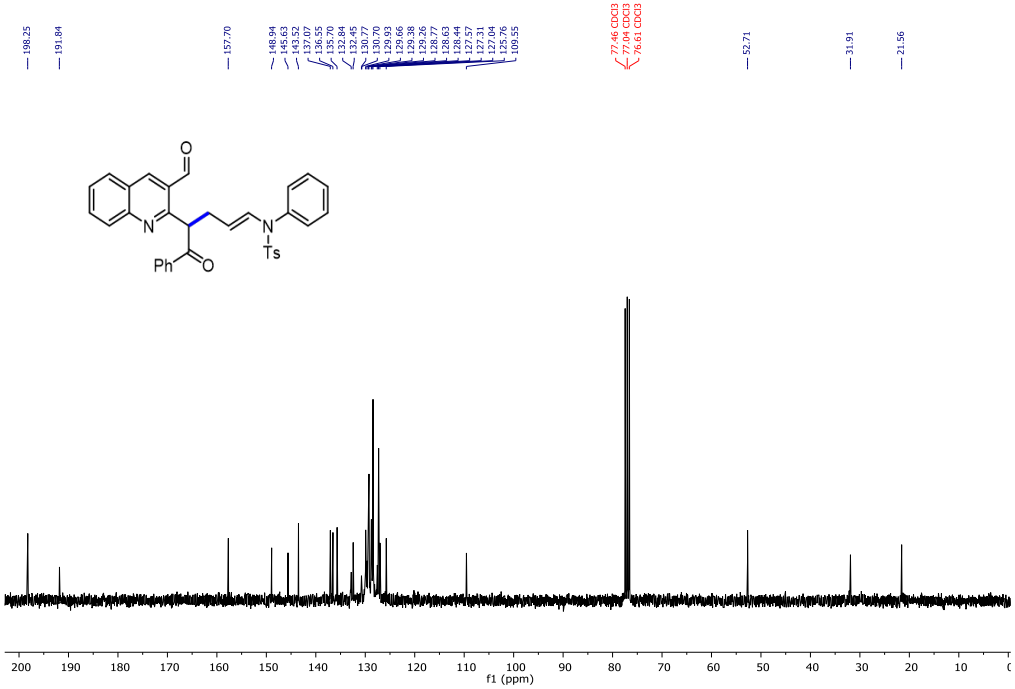
^{13}C-NMR of compound **2e** (101 MHz, $CDCl_3$)



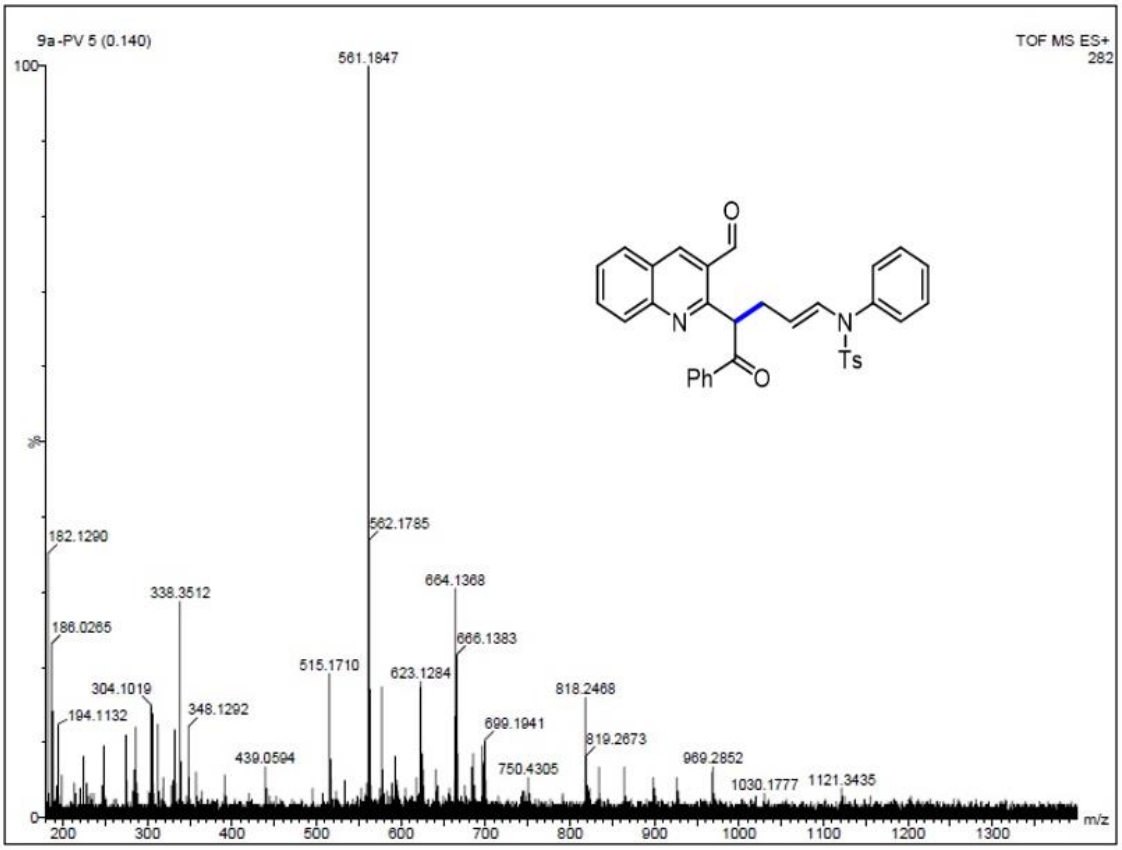
HRMS-ESI of **2e**: $[M+H]^+$ calcd for $C_{10}H_{12}NO_2S$ 210.0581



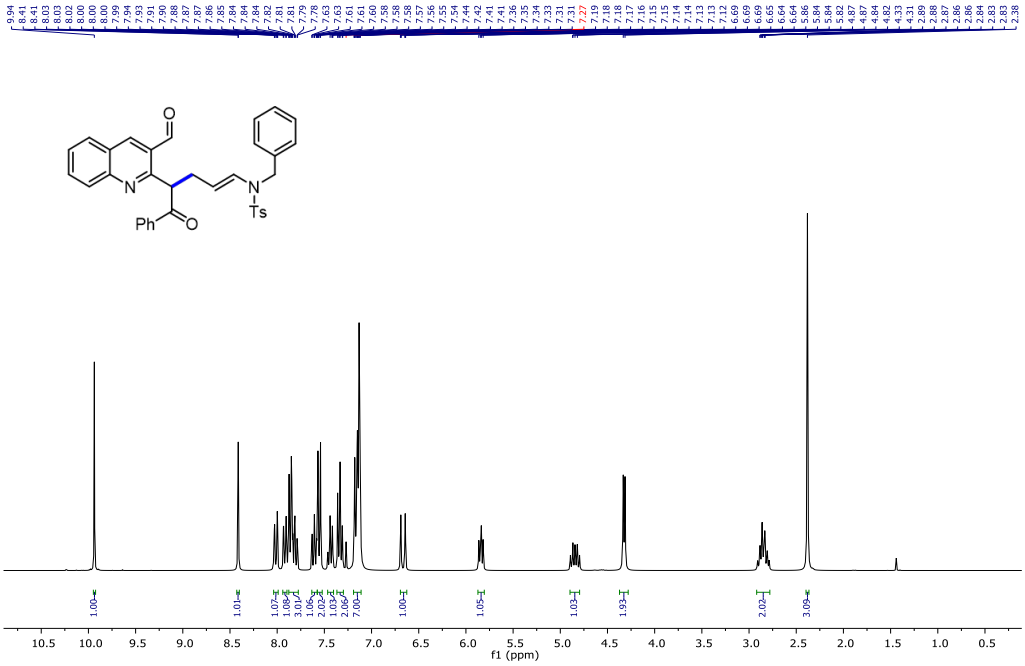
^{1}H-NMR of compound **3a** (300MHz, $CDCl_3$)



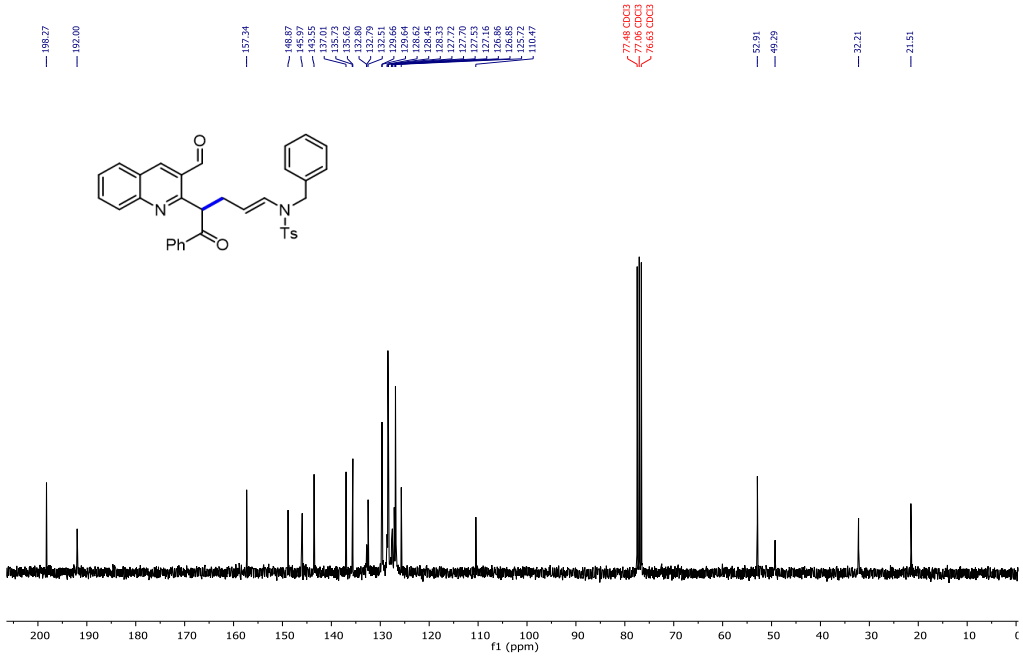
^{13}C-NMR of compound **3a** (75 MHz, $CDCl_3$)



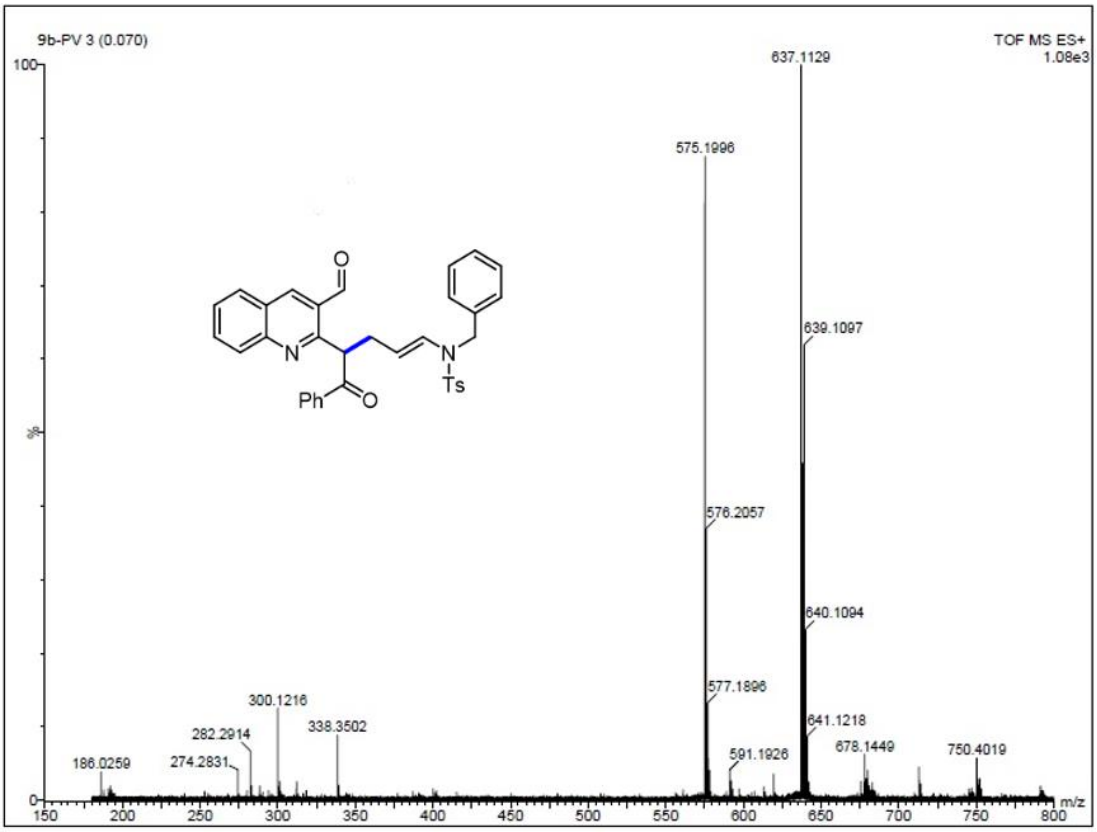
HRMS-ESI of **3a**: $[M+H]^+$ calcd for $C_{34}H_{28}N_2O_4S$ 561.1844



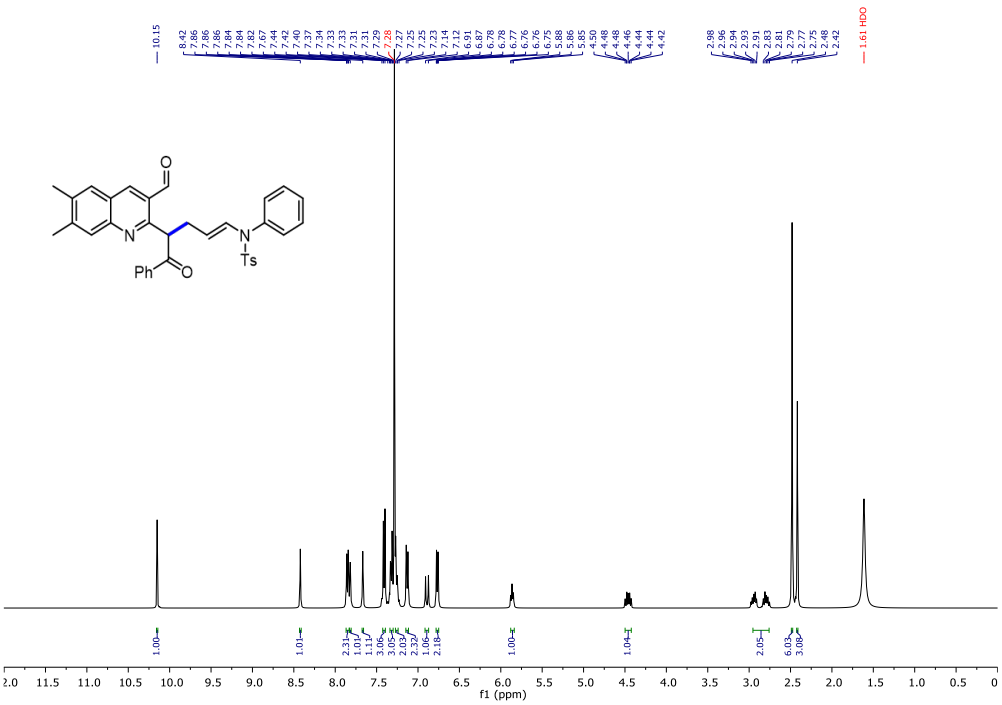
^{1}H-NMR of compound **3b** (300MHz, $CDCl_3$)



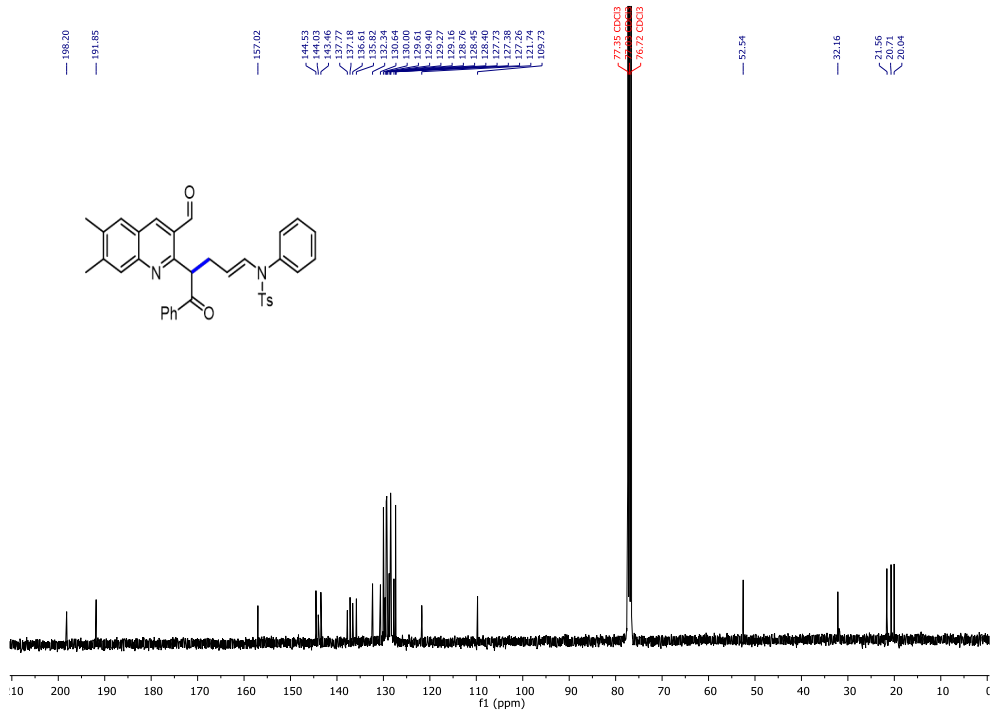
^{13}C-NMR of compound **3b** (75 MHz, $CDCl_3$)



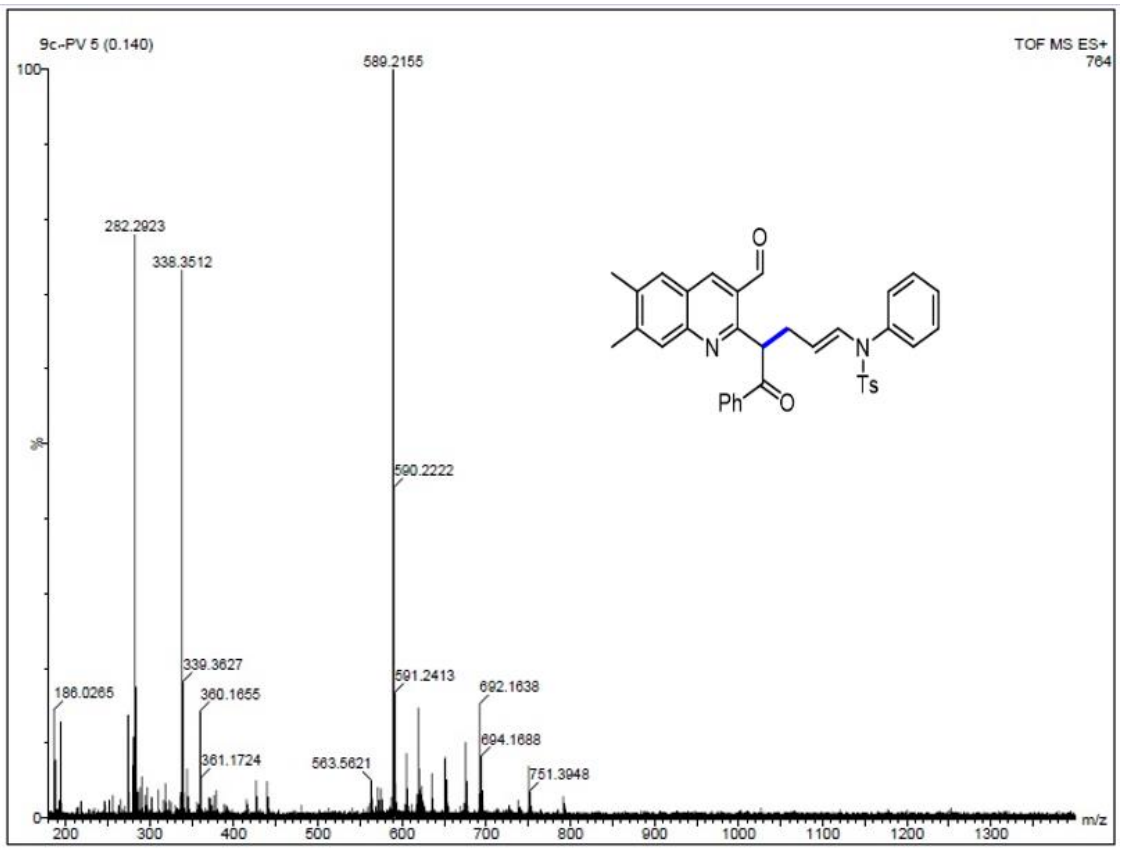
HRMS-ESI of **3b**: $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_4S$ 575.1992



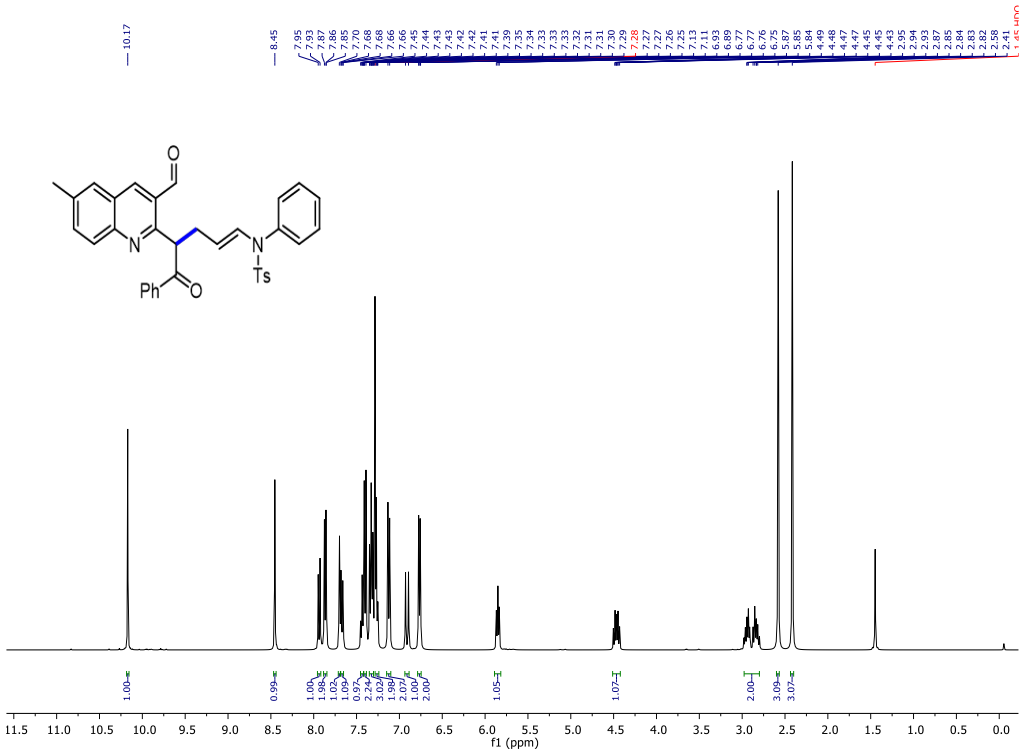
^{1}H-NMR of compound **3c** (300MHz, $CDCl_3$)



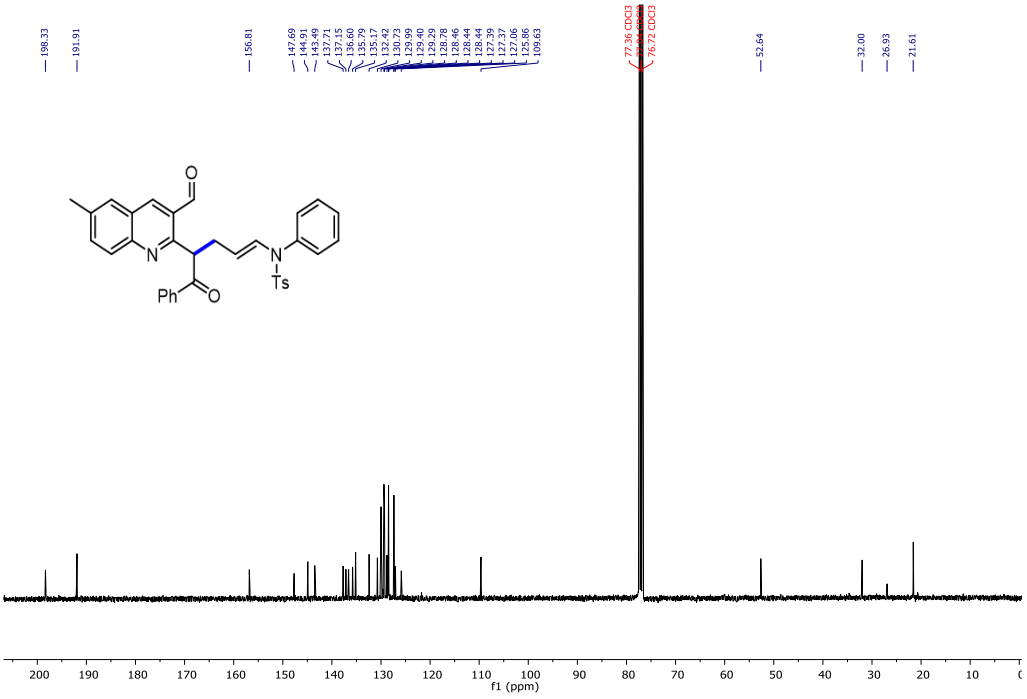
^{13}C-NMR of compound **3c** (75 MHz, $CDCl_3$)



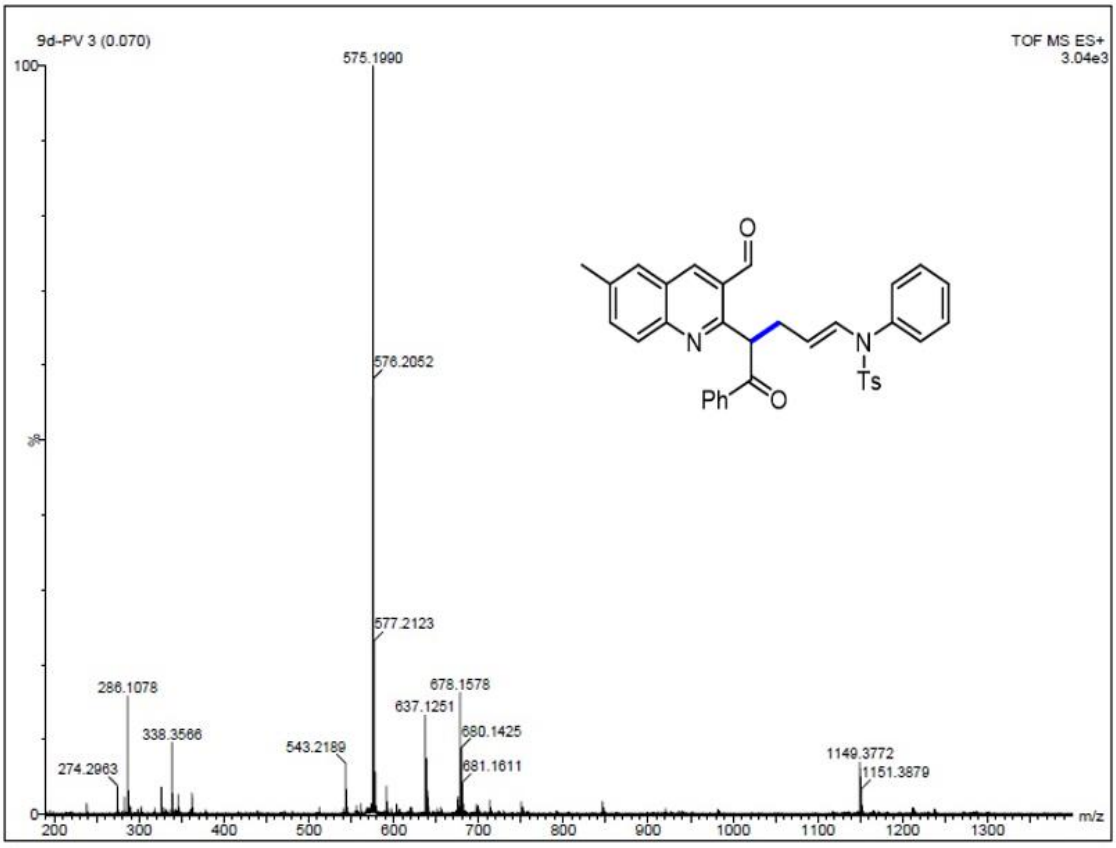
HRMS-ESI of **3c**: $[M+H]^+$ calcd for $C_{36}H_{33}N_2O_4S$ 589.2150



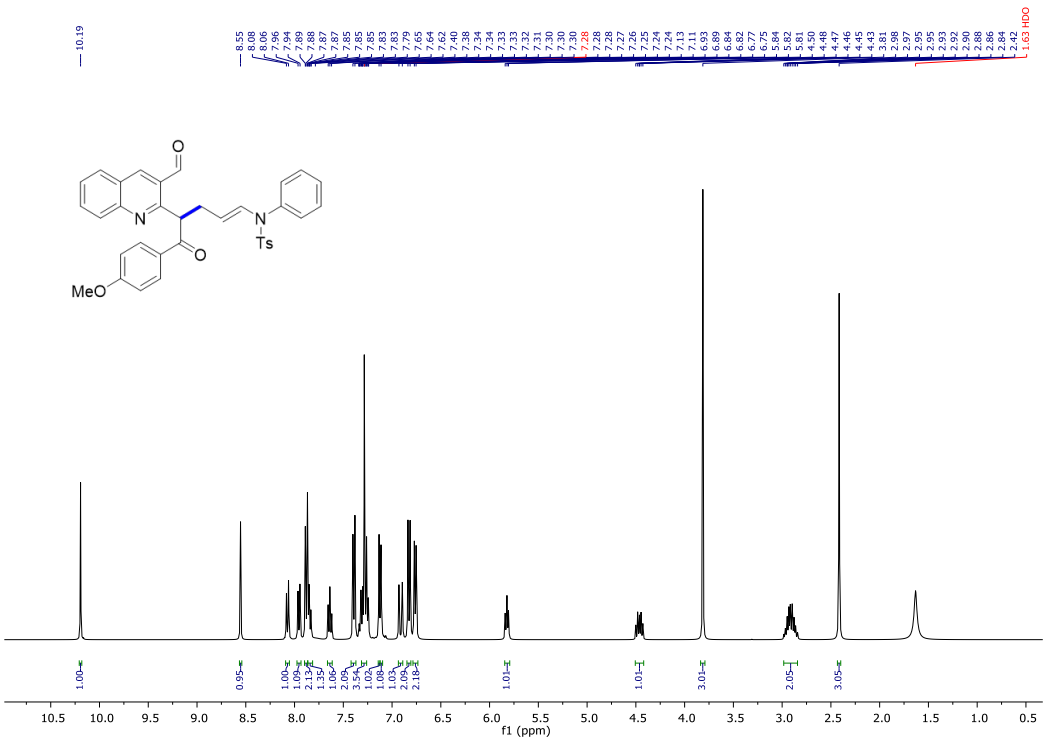
^{1}H-NMR of compound **3d** (400 MHz, $CDCl_3$)



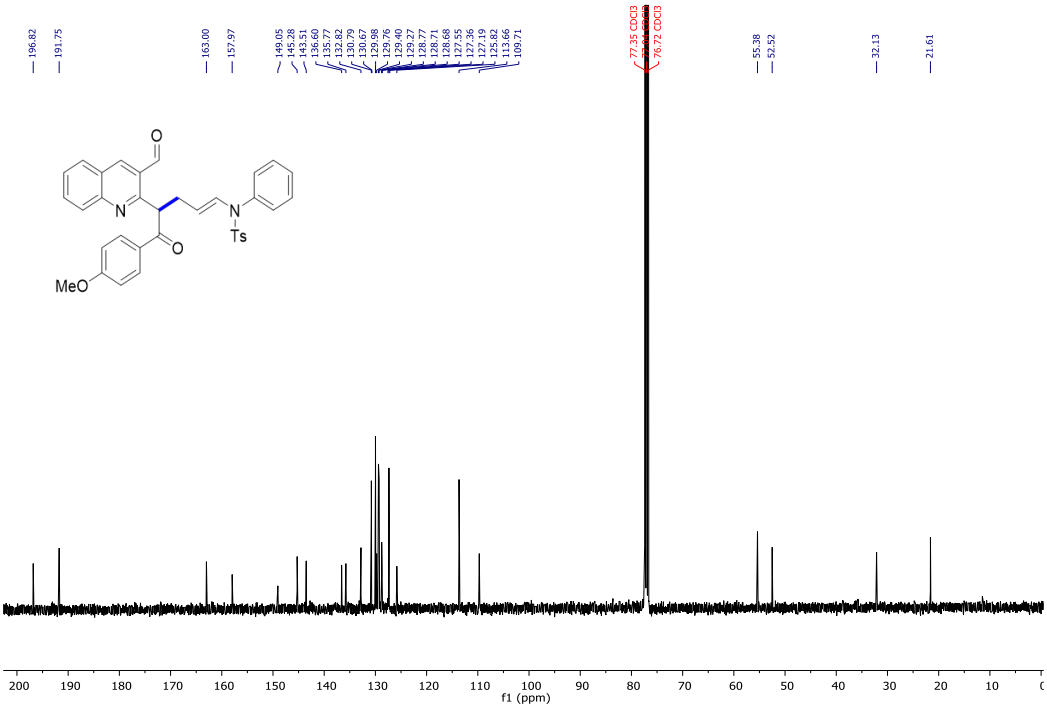
^{13}C-NMR of compound **3d** (101 MHz, $CDCl_3$)



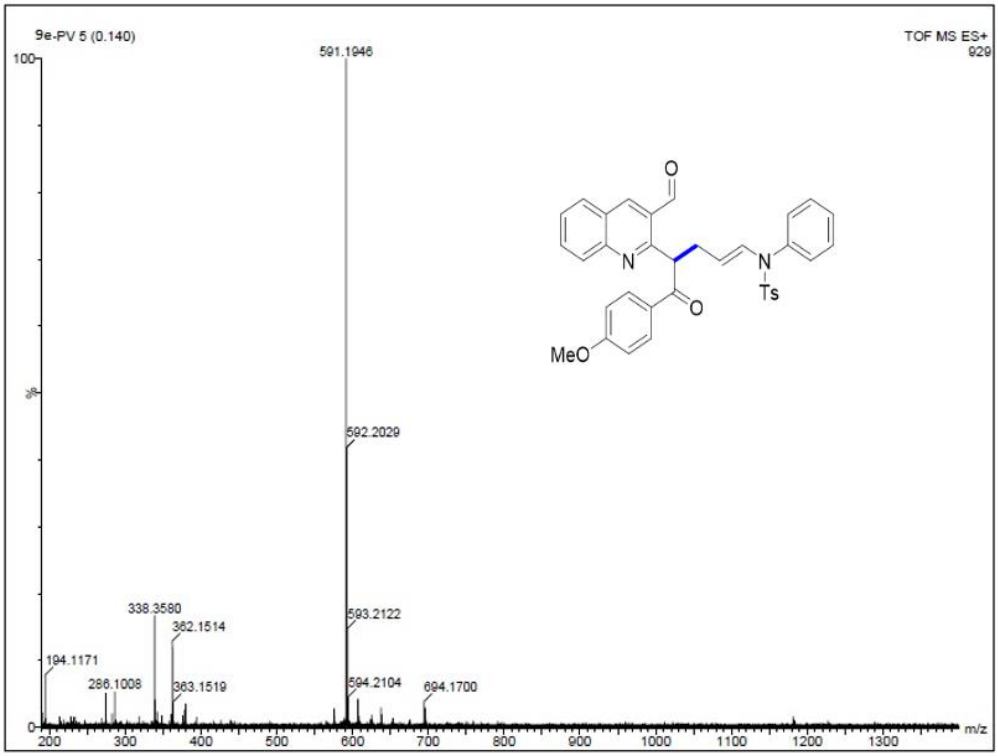
HRMS-ESI of **3d**: $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_4S$ 575.1984



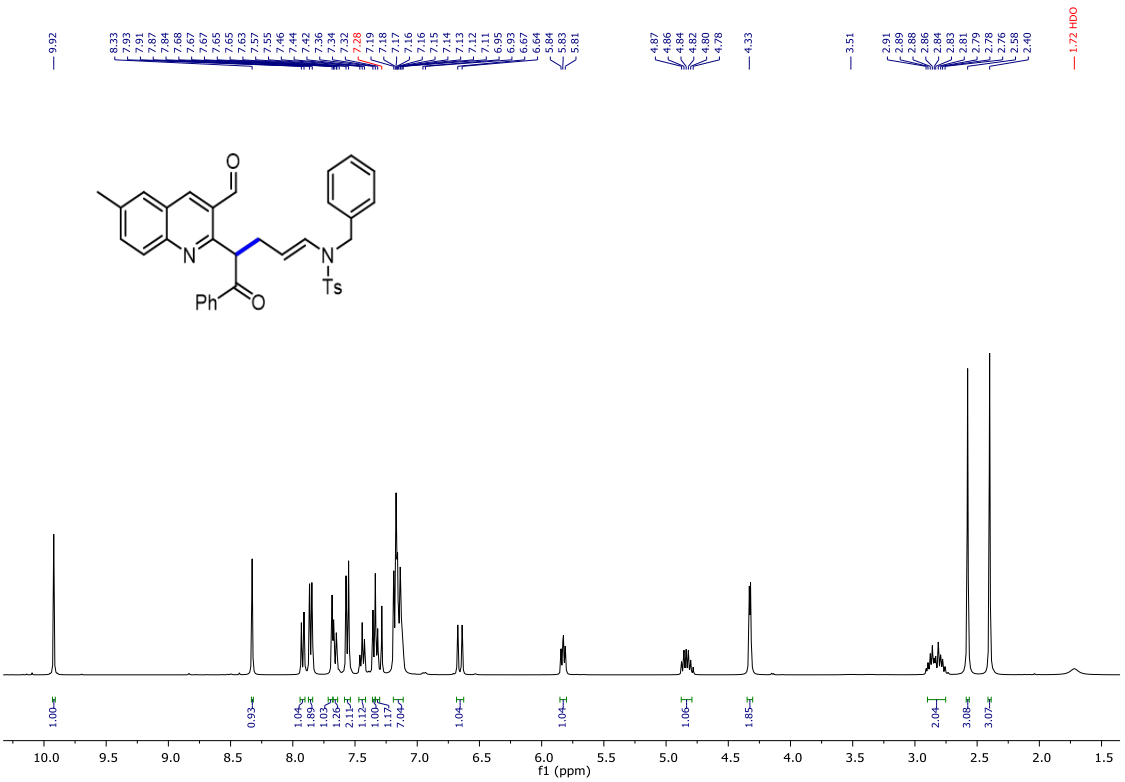
^{1}H-NMR of compound **3e** (400 MHz, $CDCl_3$)



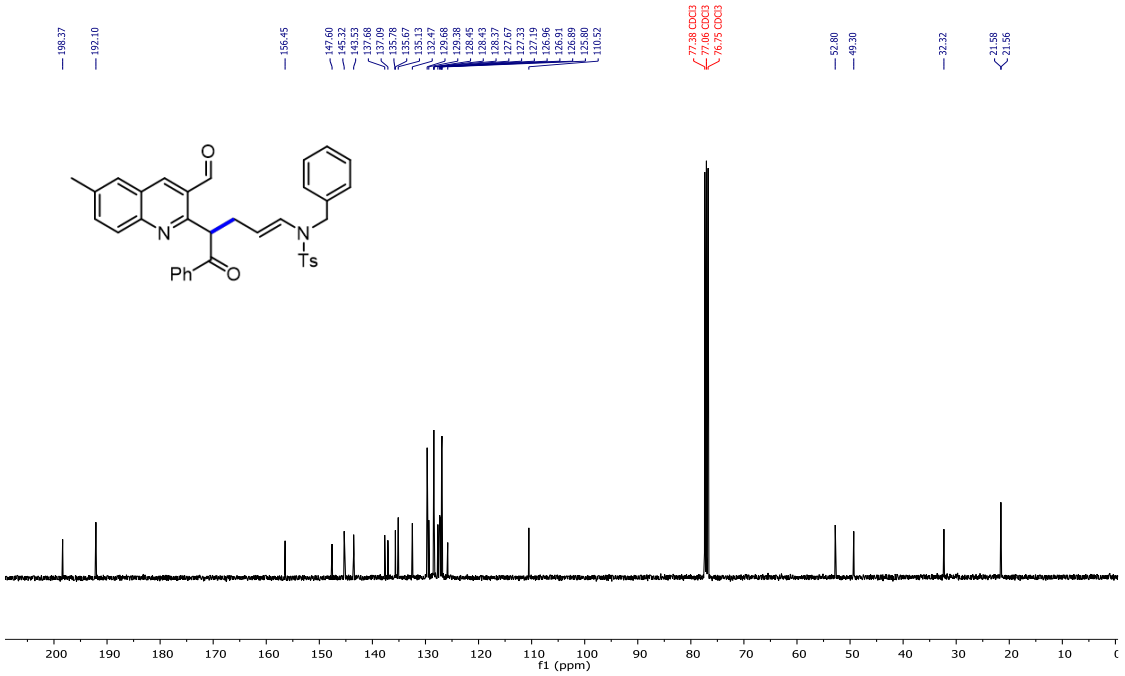
^{13}C-NMR of compound **3e** (101 MHz, $CDCl_3$)



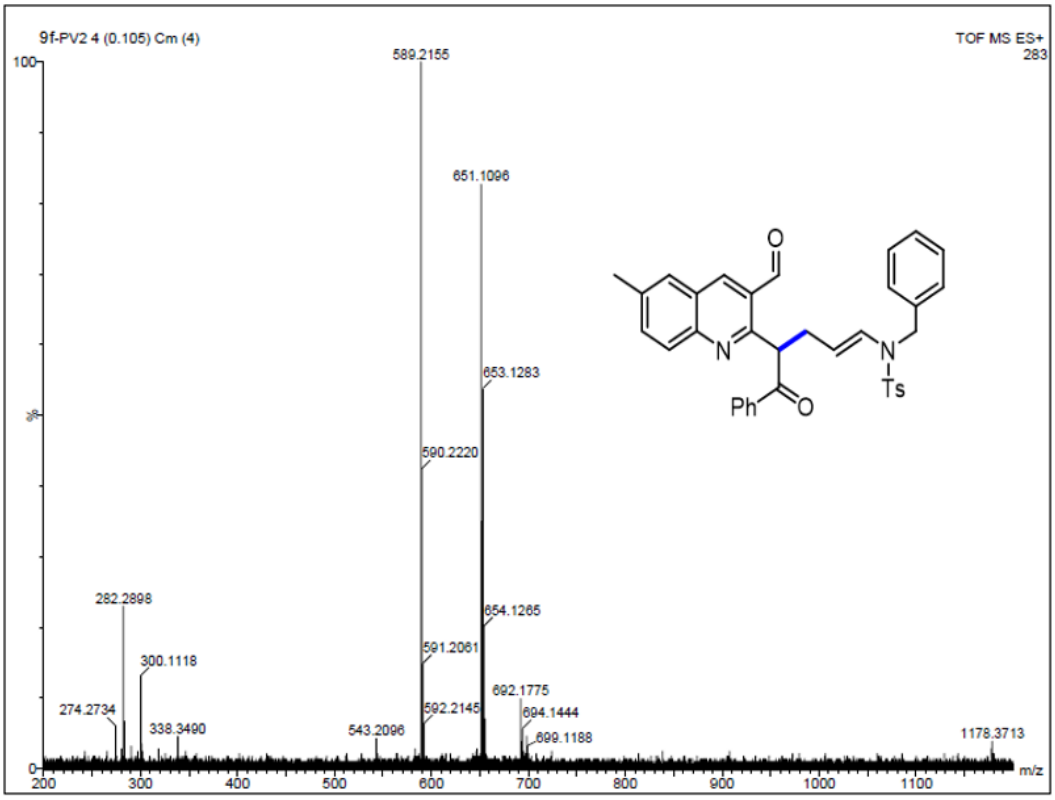
HRMS-ESI of **3e**: $[M+H]^+$ calcd for $C_{35}H_{31}N_2O_5S$ 591.1944



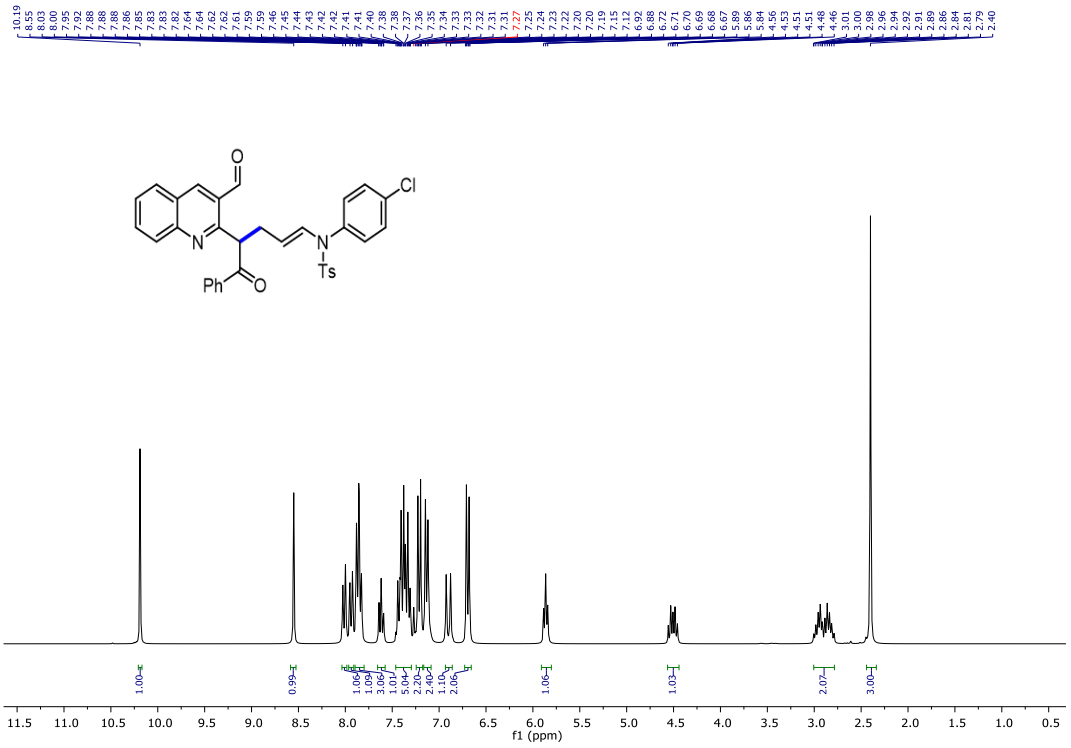
^{1}H-NMR of compound **3f** (400 MHz, $CDCl_3$)



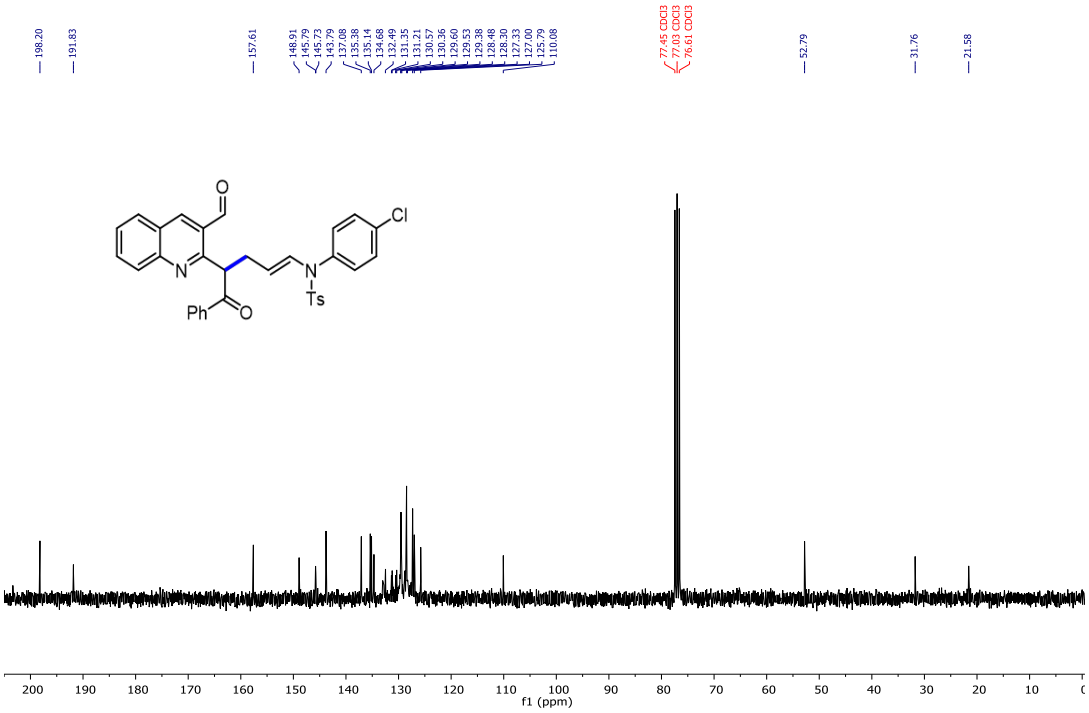
^{13}C-NMR of compound **3f** (101 MHz, $CDCl_3$)



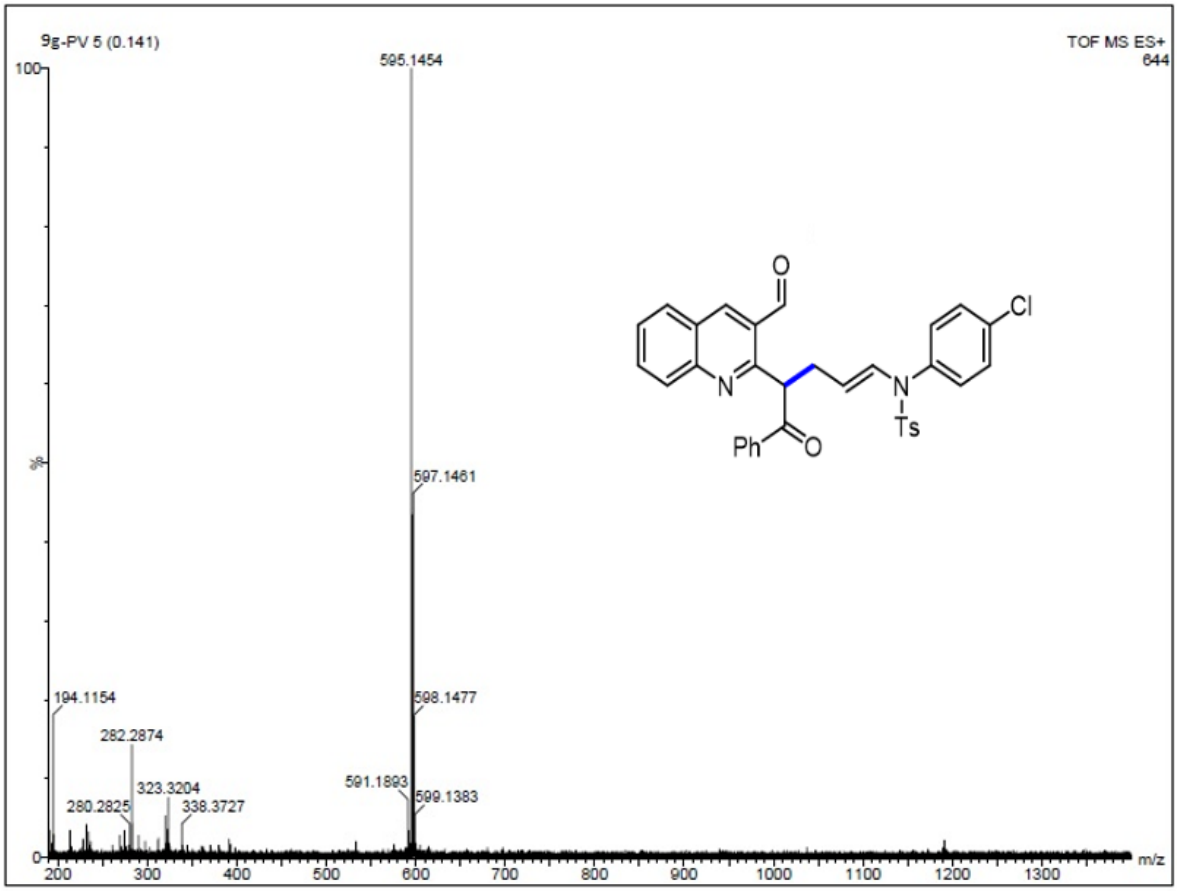
HRMS-ESI of **3f**: $[M+H]^+$ calcd for $C_{36}H_{33}N_2O_4S$ 589.2153



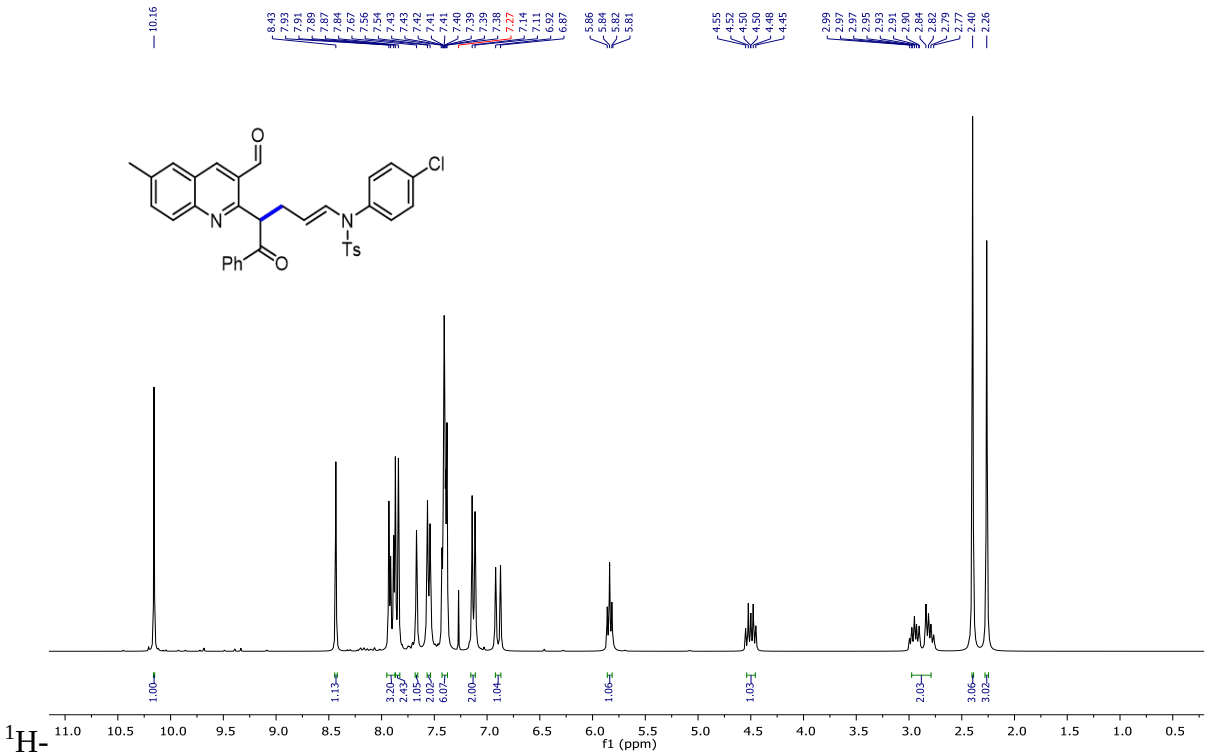
^{1}H-NMR of compound **3g** (300MHz, $CDCl_3$)



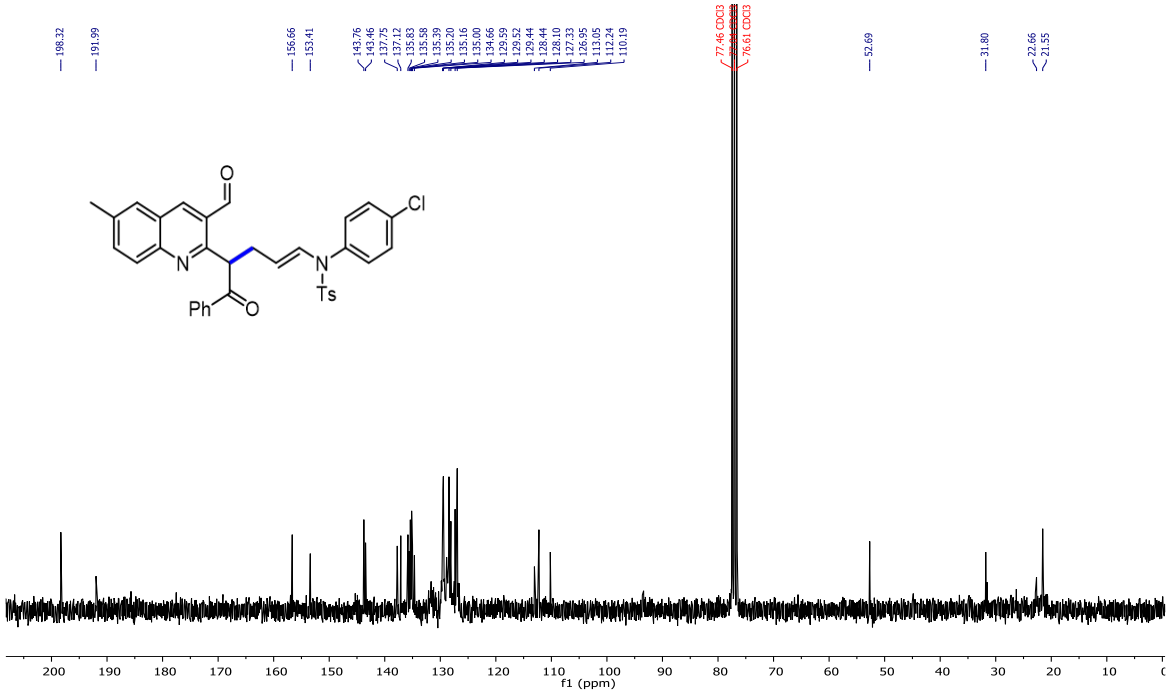
^{13}C-NMR of compound **3g** (75 MHz, $CDCl_3$)



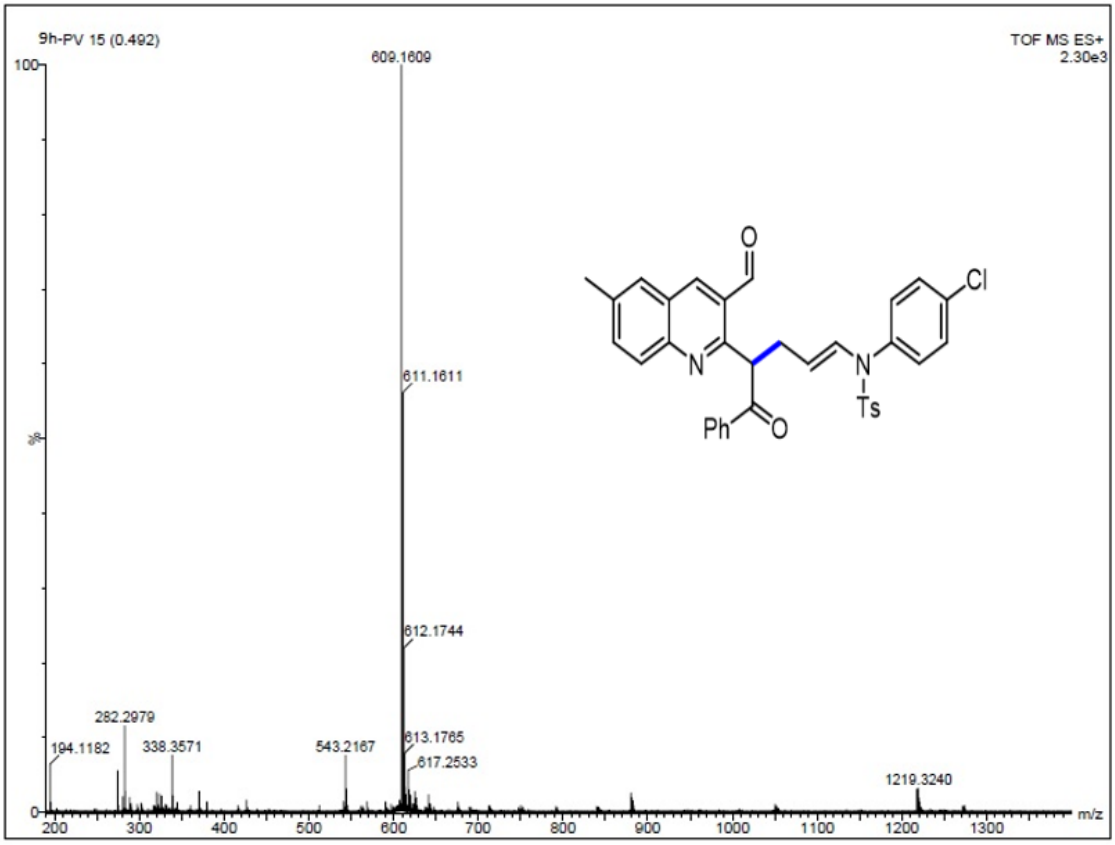
HRMS-ESI of **3g**: $[M+H]^+$ calcd for $C_{34}H_{28}{}^{35}ClN_2O_4S$ 595.1452



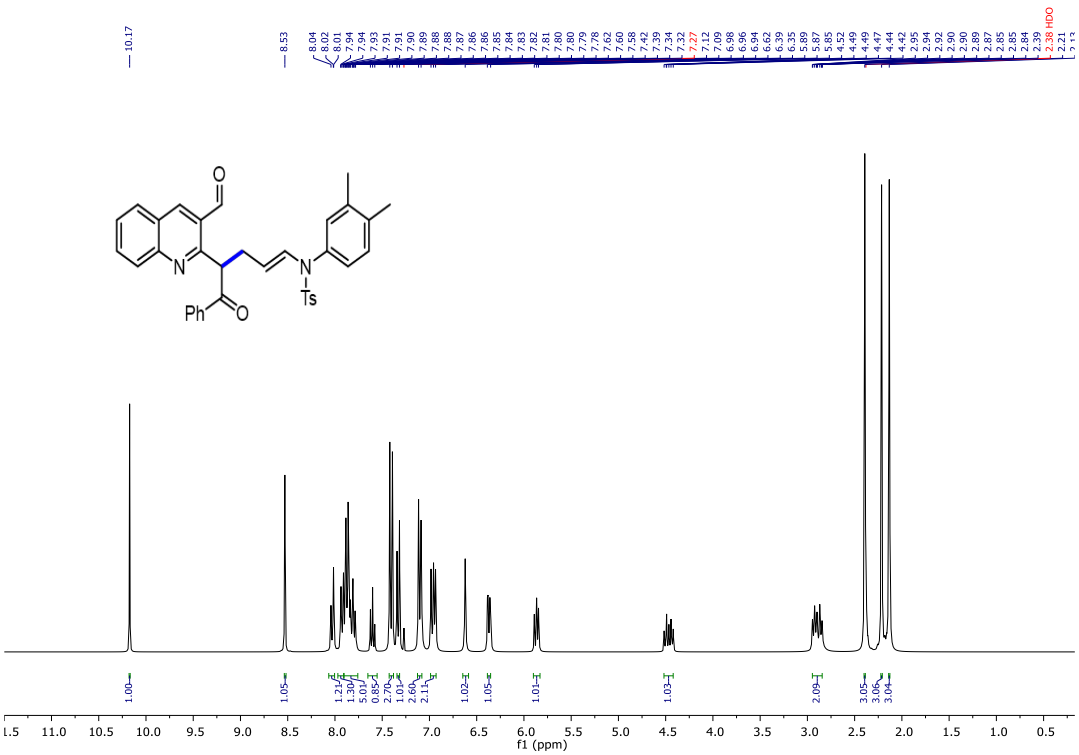
^{1}H-NMR of compound **3h** (300MHz, $CDCl_3$)



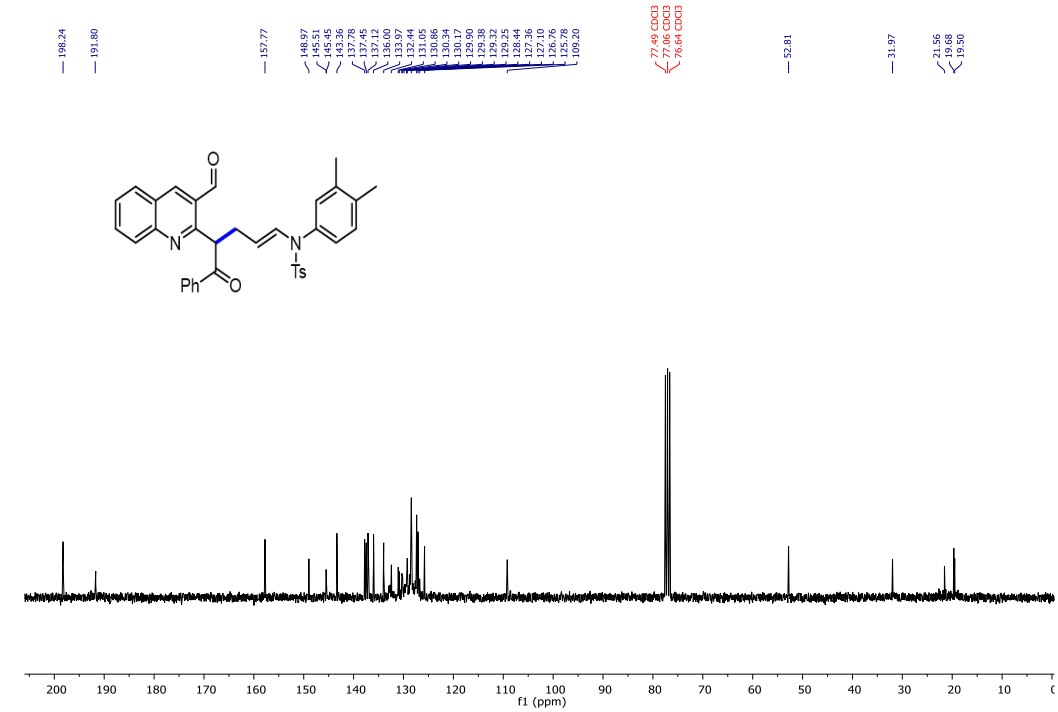
^{13}C-NMR of compound **3h** (75 MHz, $CDCl_3$)



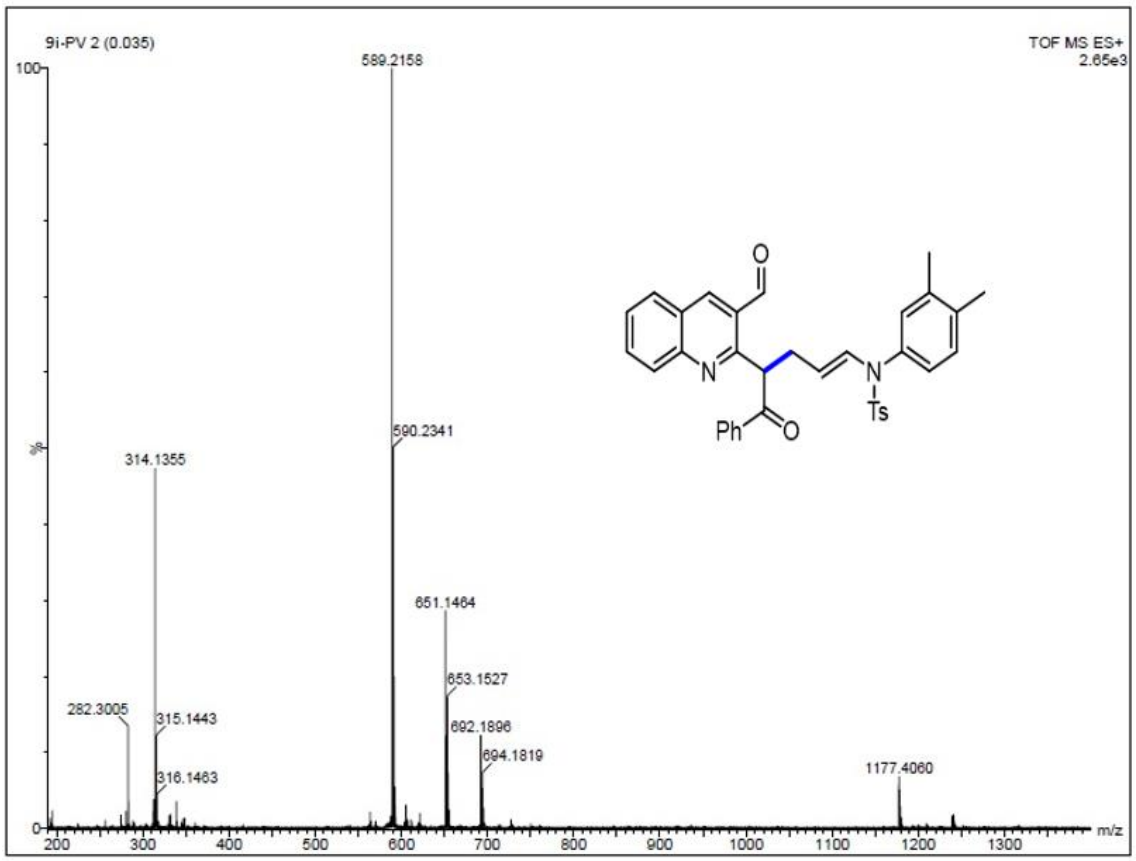
HRMS-ESI of **3h**: $[M+H]^+$ calcd for $C_{35}H_{30}{}^{35}ClN_2O_4S$ 609.1604



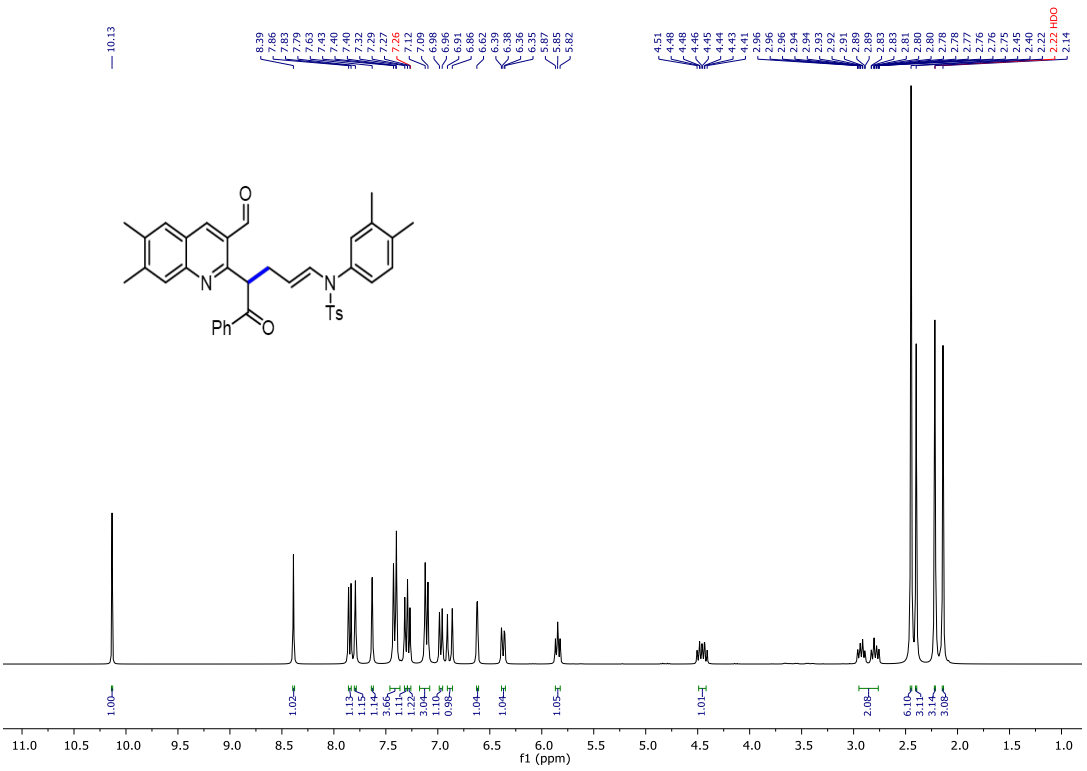
^{1}H-NMR of compound **3i** (300MHz, $CDCl_3$)



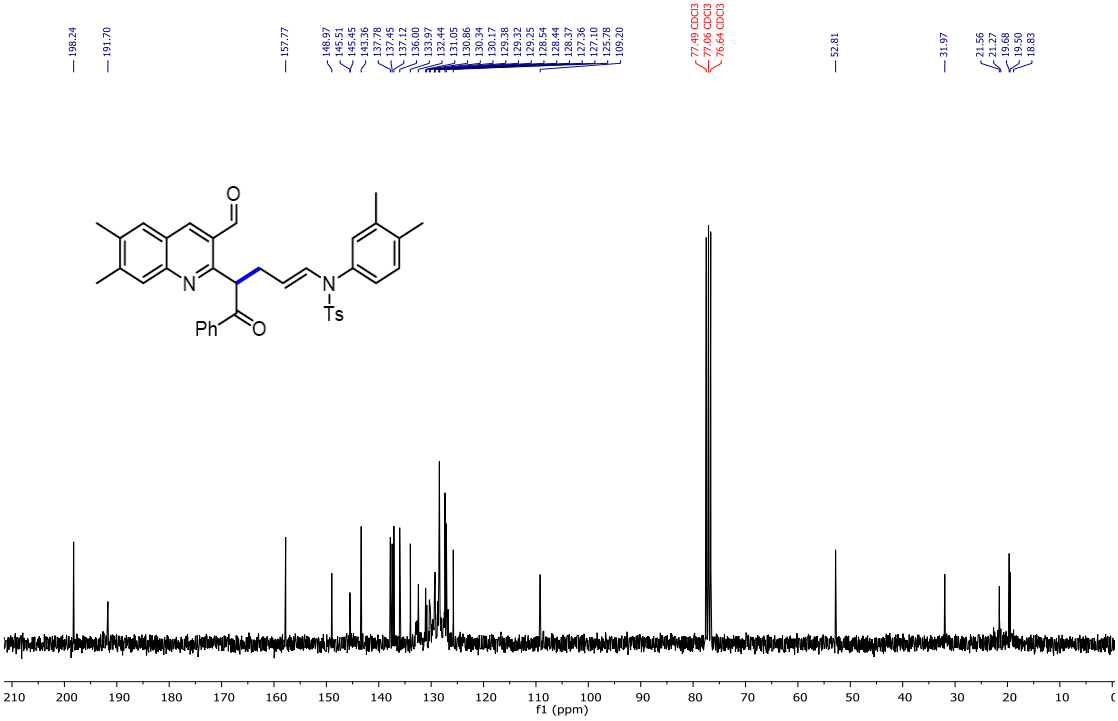
^{13}C-NMR of compound **3i** (75 MHz, $CDCl_3$)



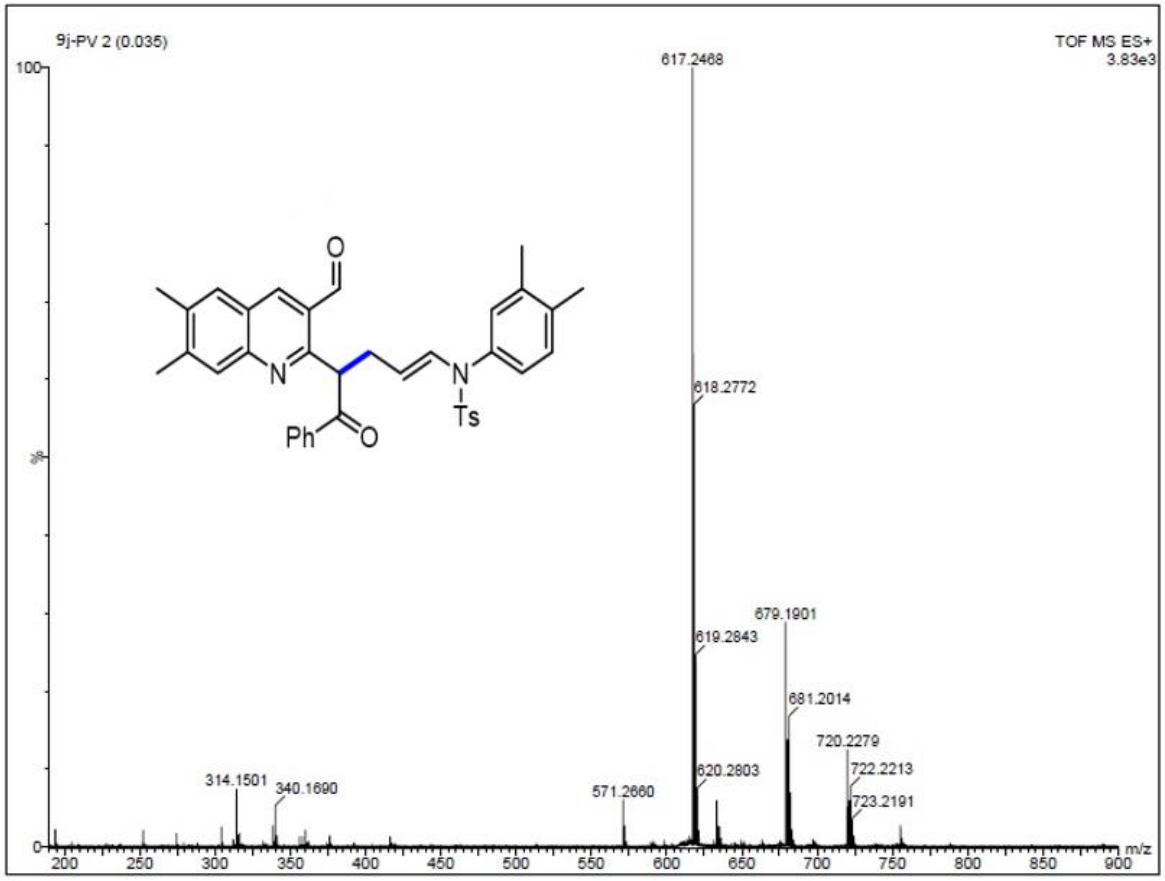
HRMS-ESI of **3i**: $[M+H]^+$ calcd for $C_{36}H_{32}N_2O_4S$ 589.2155



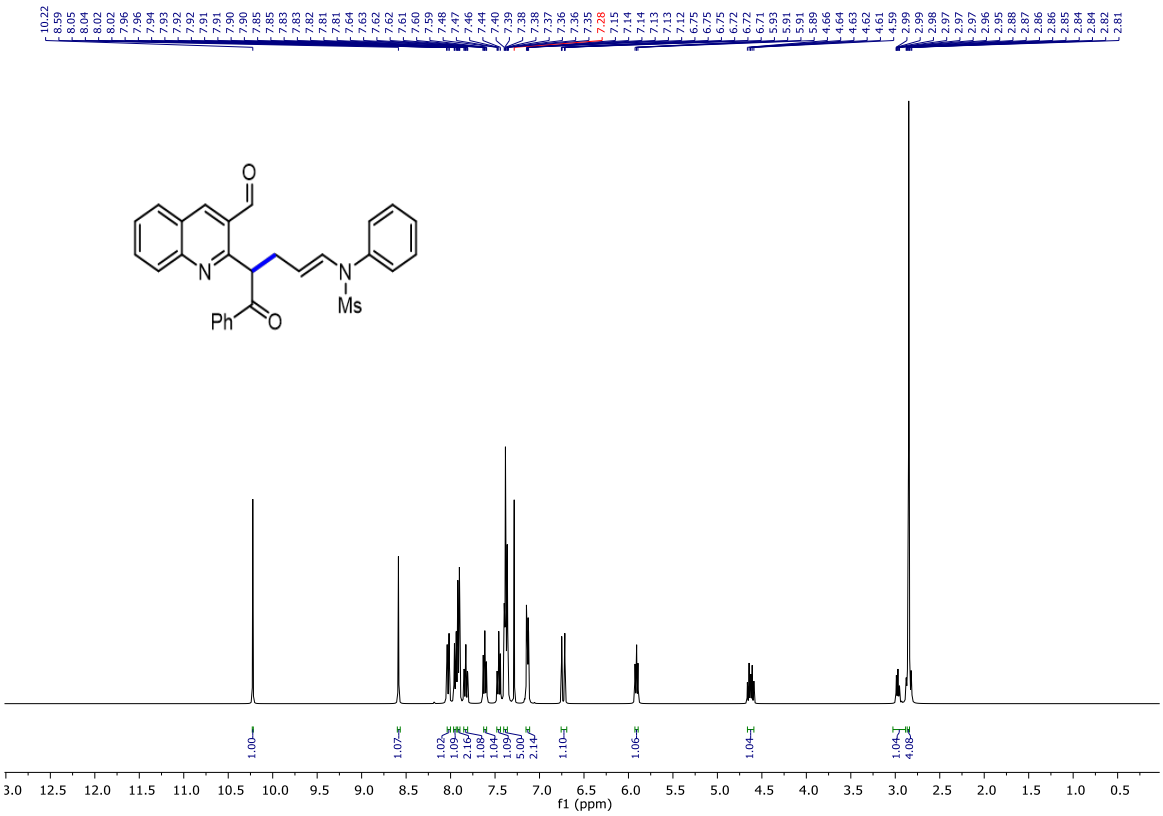
^{1}H-NMR of compound **3j** (300MHz, $CDCl_3$)



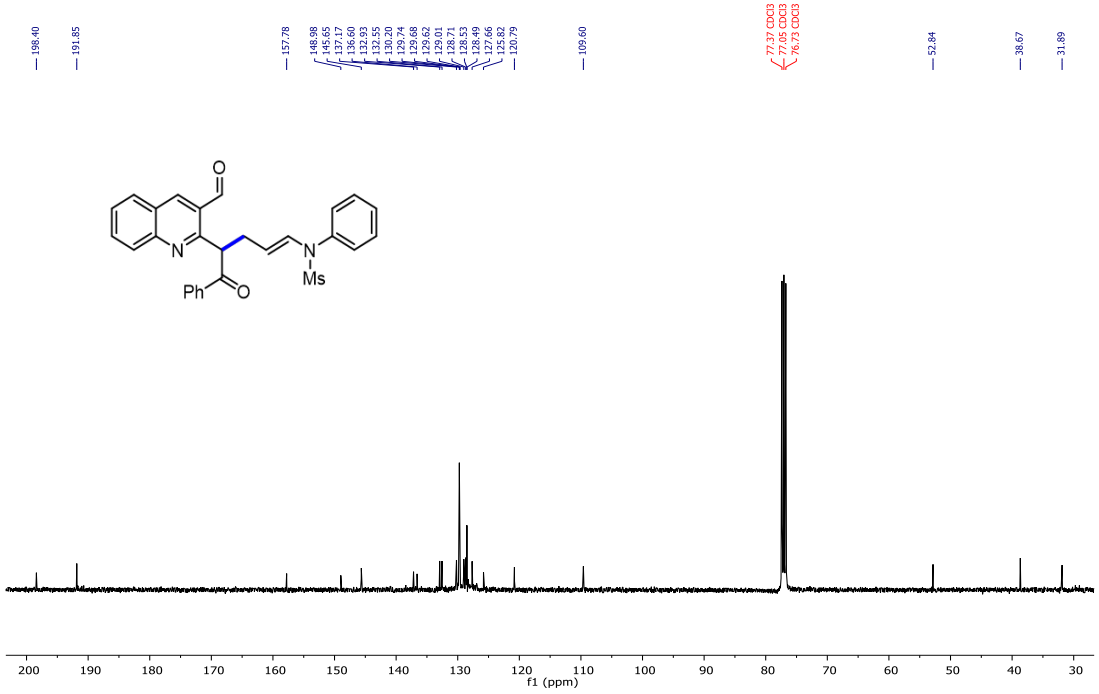
^{13}C-NMR of compound **3j** (75 MHz, $CDCl_3$)



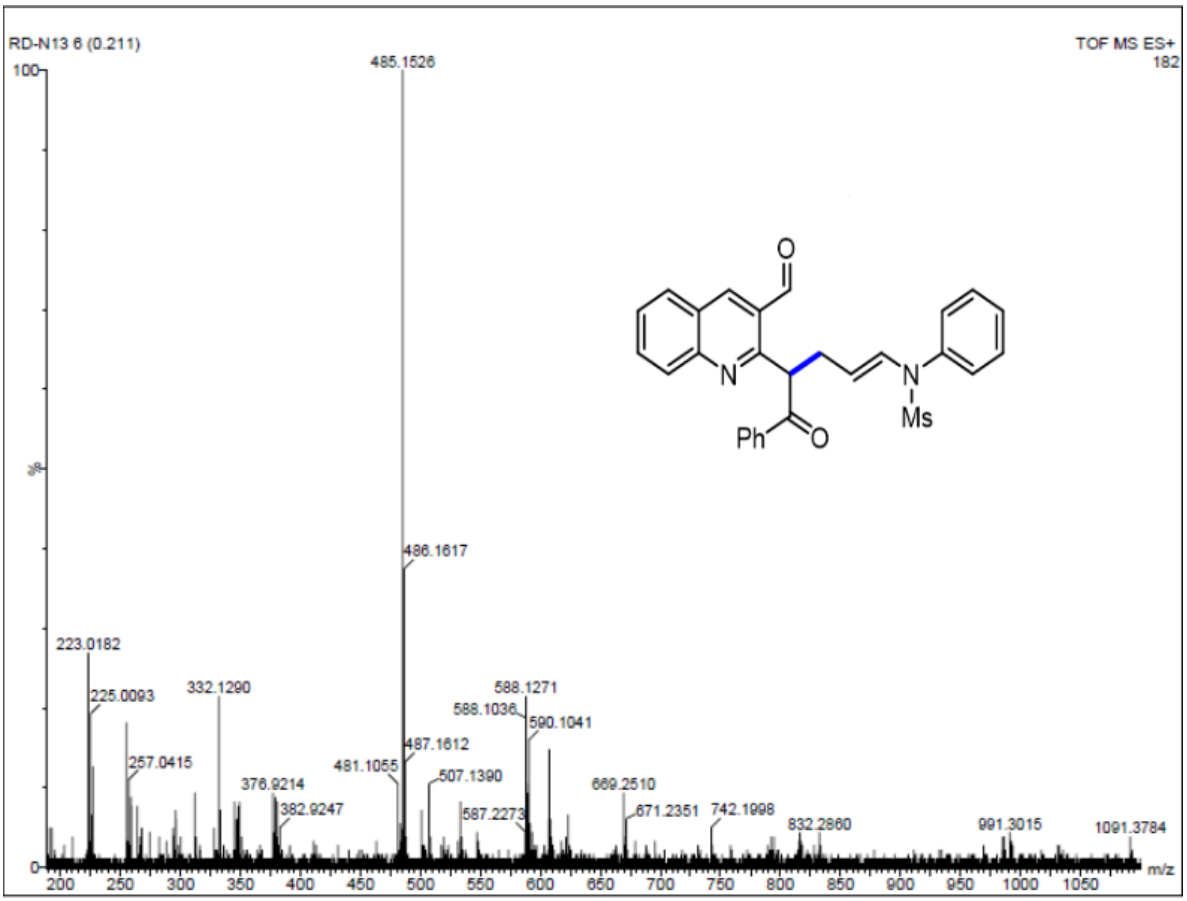
HRMS-ESI of **3j: [**M+H]$^+$ calcd for $C_{38}H_{37}N_2O_4S$ 617.2461



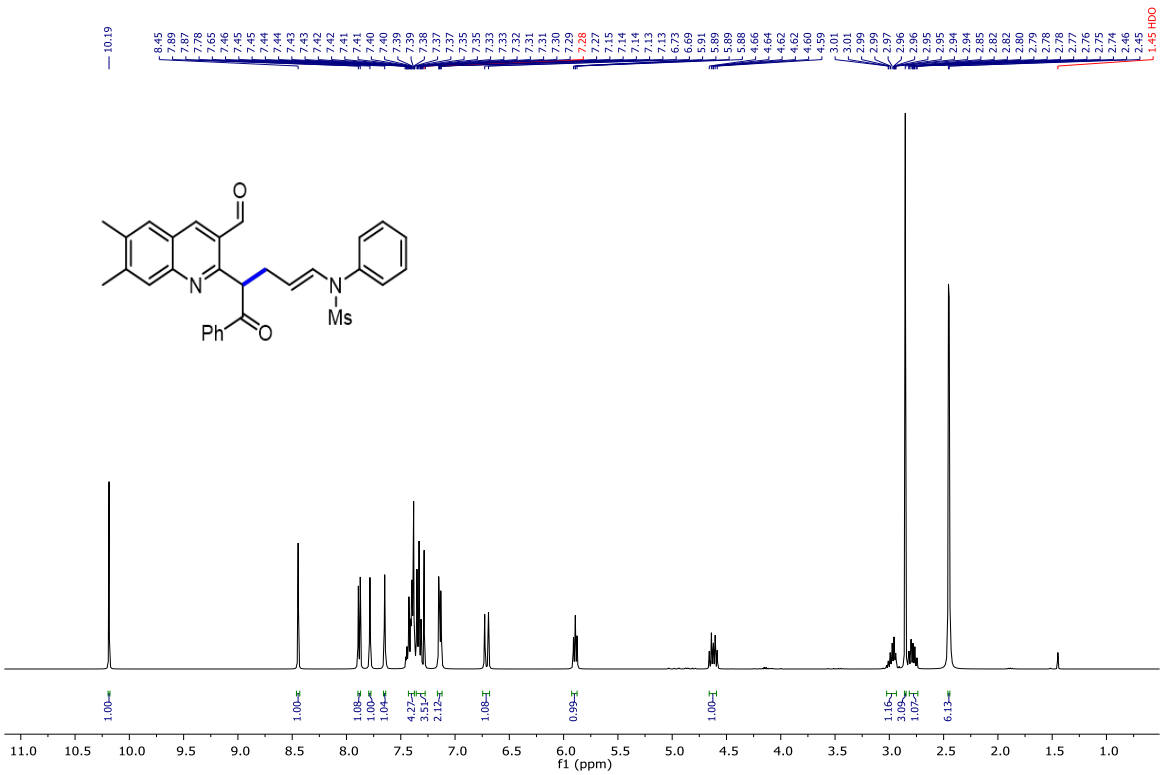
^{1}H-NMR of compound **3k** (400MHz, $CDCl_3$)



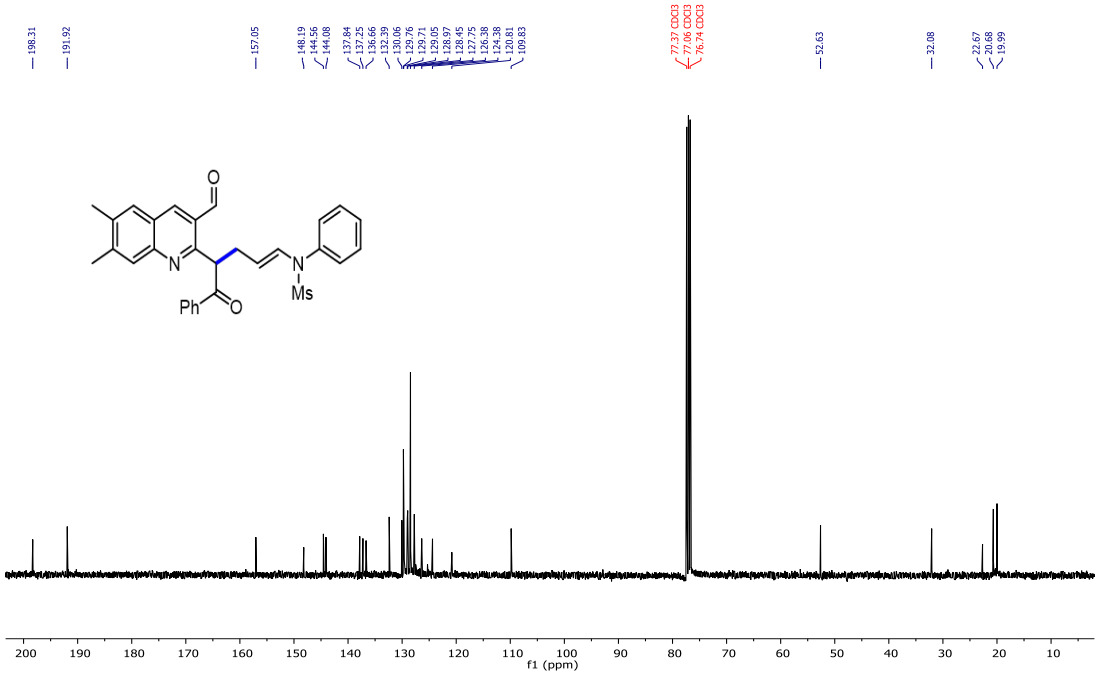
^{13}C-NMR of compound **3k** (101 MHz, $CDCl_3$)



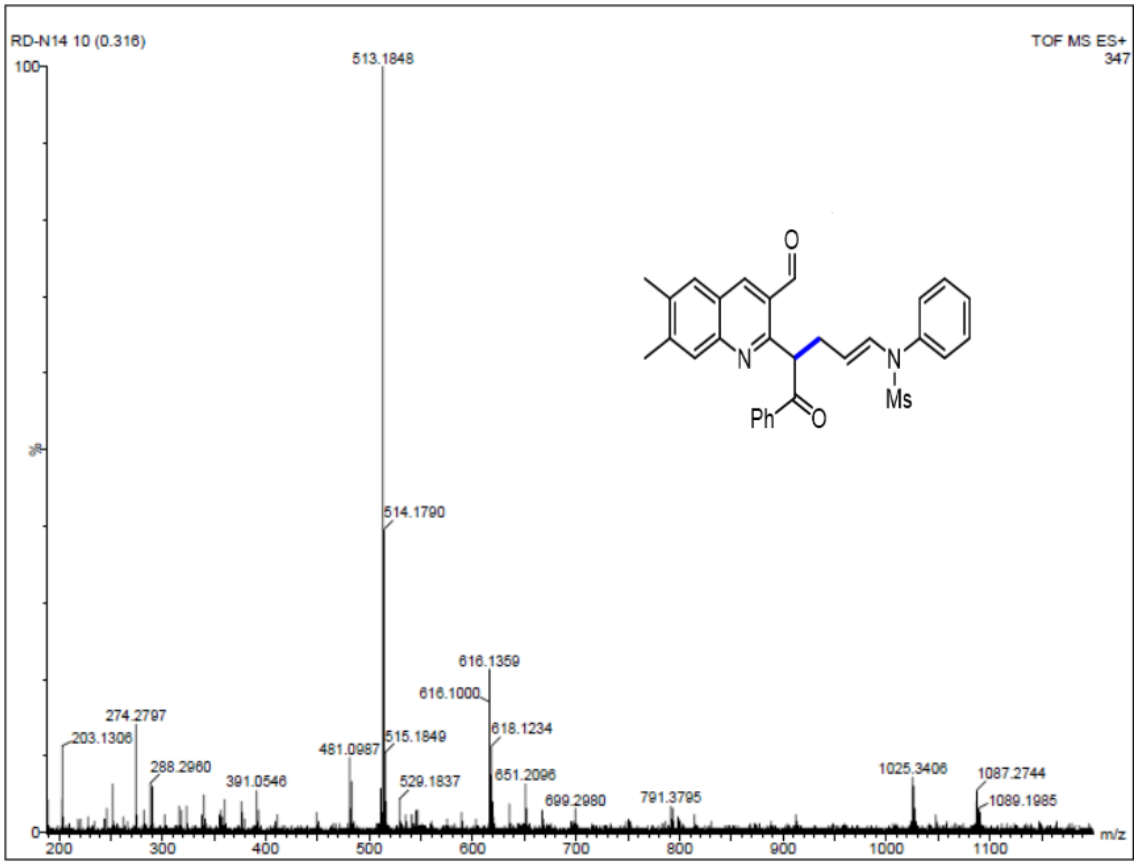
HRMS-ESI of **3k**: $[M+H]^+$ calcd for $C_{28}H_{25}N_2O_4S$ 485.1524



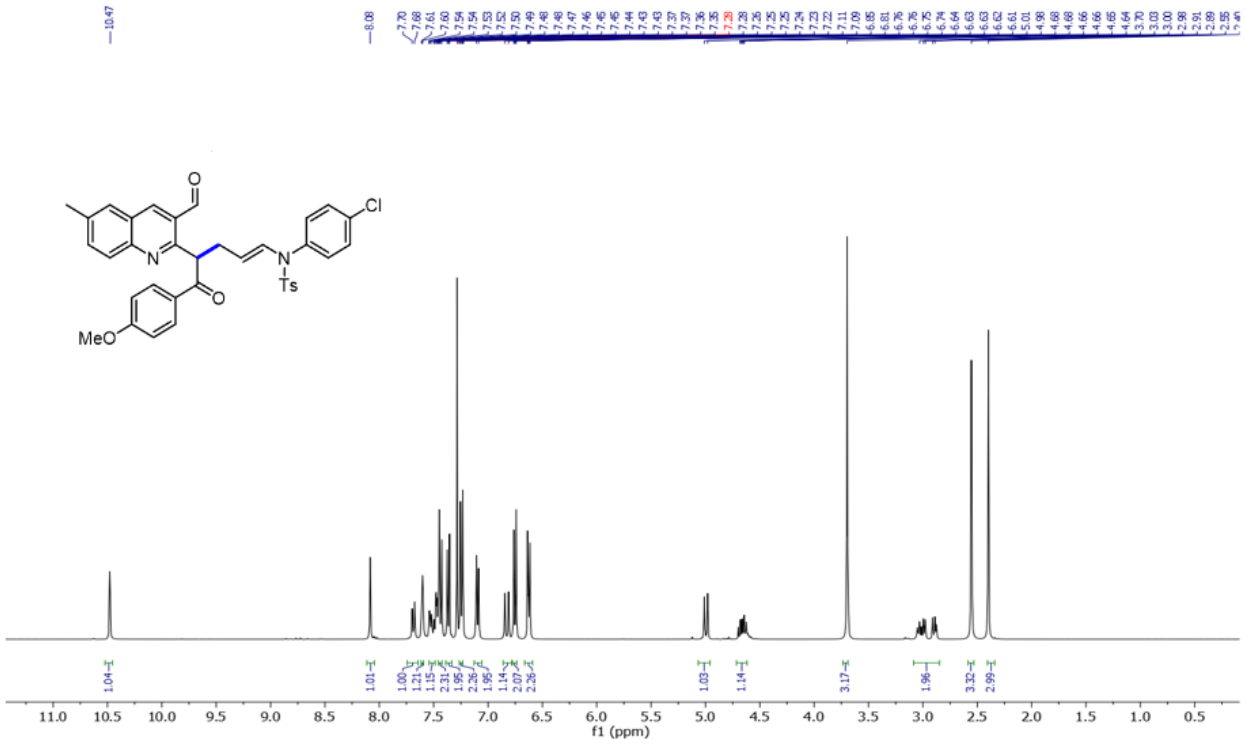
^{1}H-NMR of compound **3l** (400MHz, $CDCl_3$)



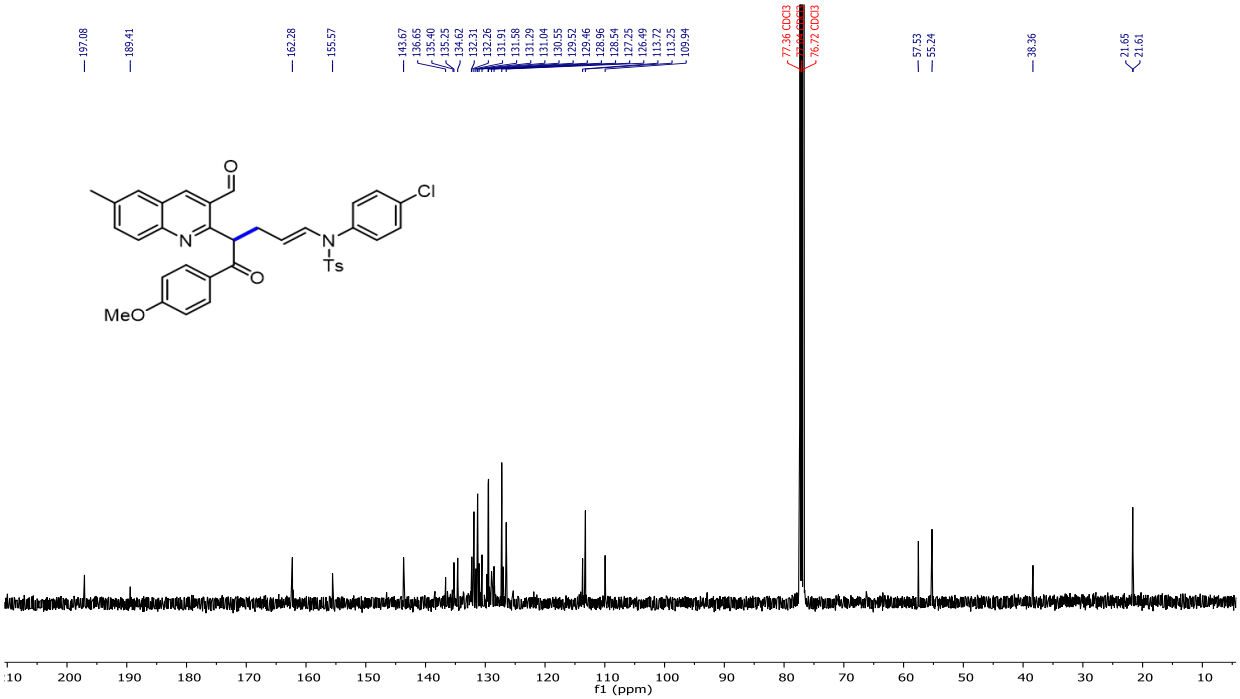
^{13}C-NMR of compound **3l** (101 MHz, $CDCl_3$)



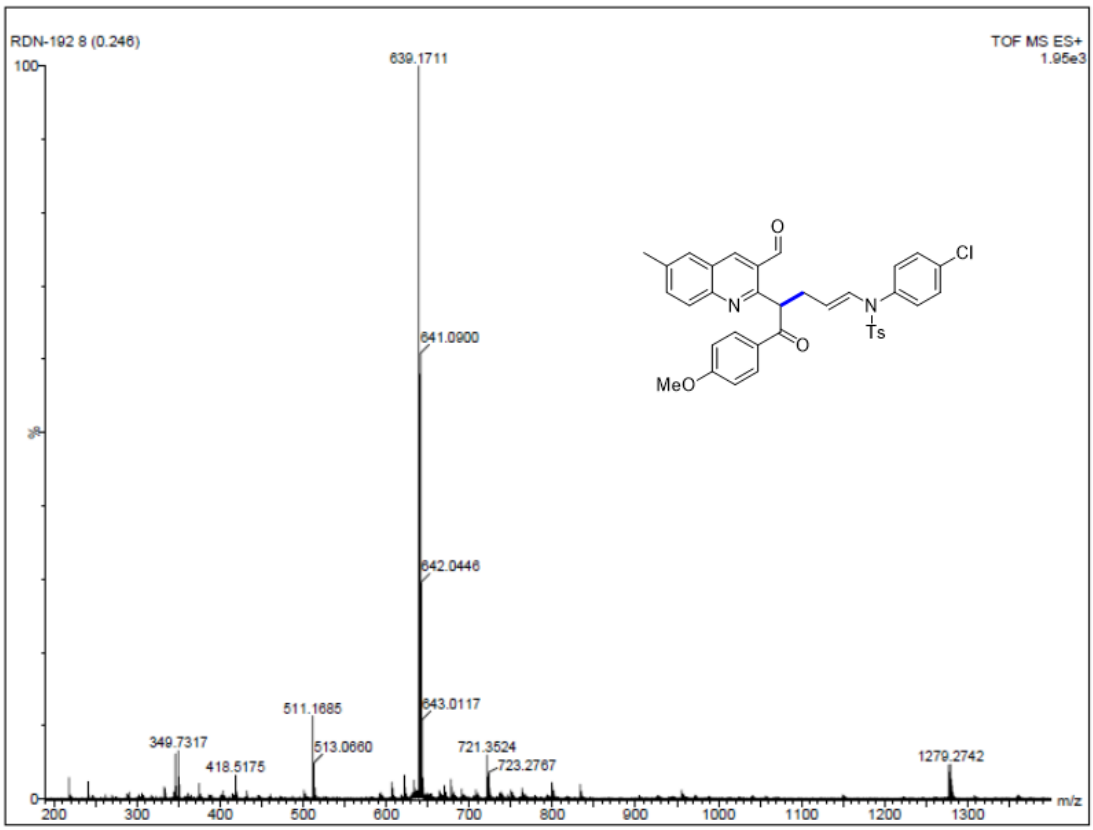
HRMS-ESI of **3l**: $[M+H]^+$ calcd for $C_{30}H_{28}N_2O_4S$ 513.1845



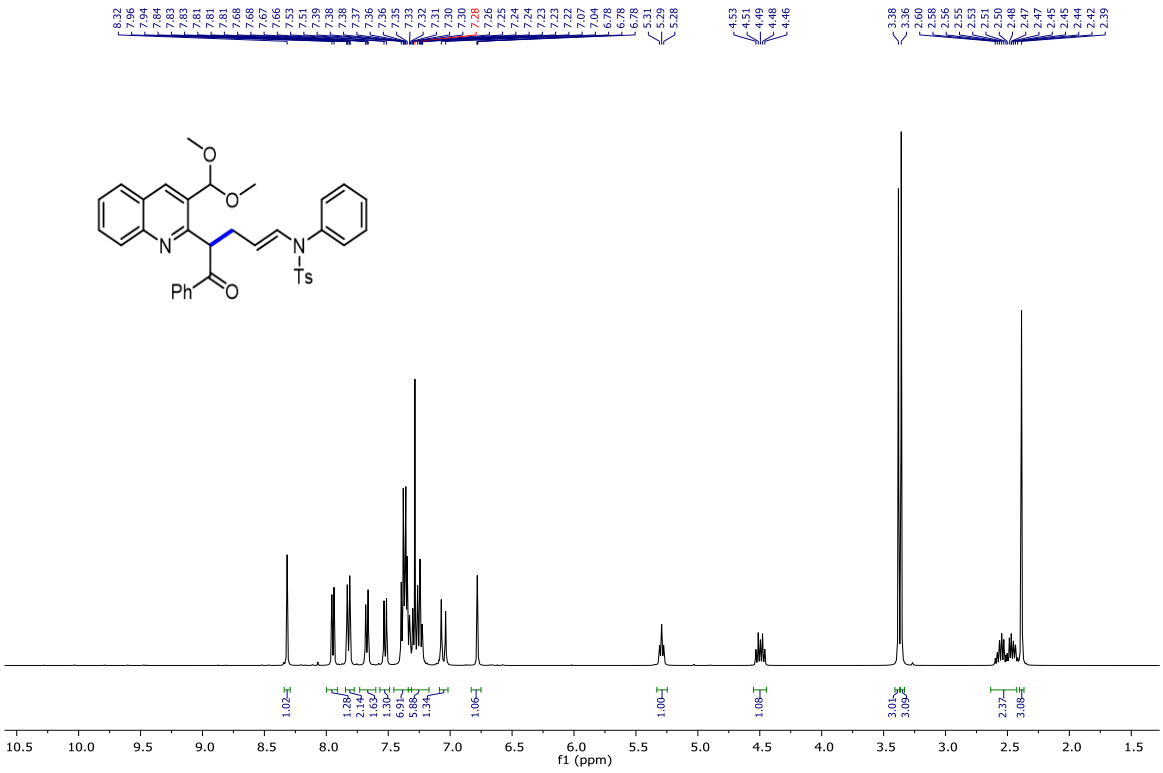
^{1}H-NMR of compound **3m** (400MHz, $CDCl_3$)



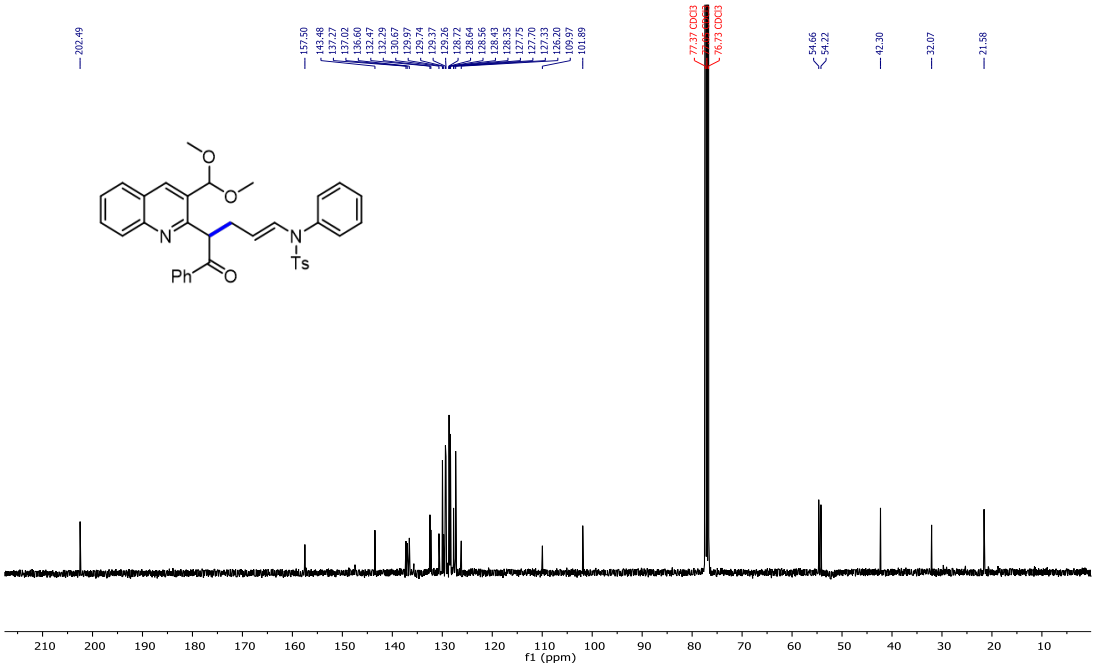
^{13}C-NMR of compound **3m** (101 MHz, $CDCl_3$)



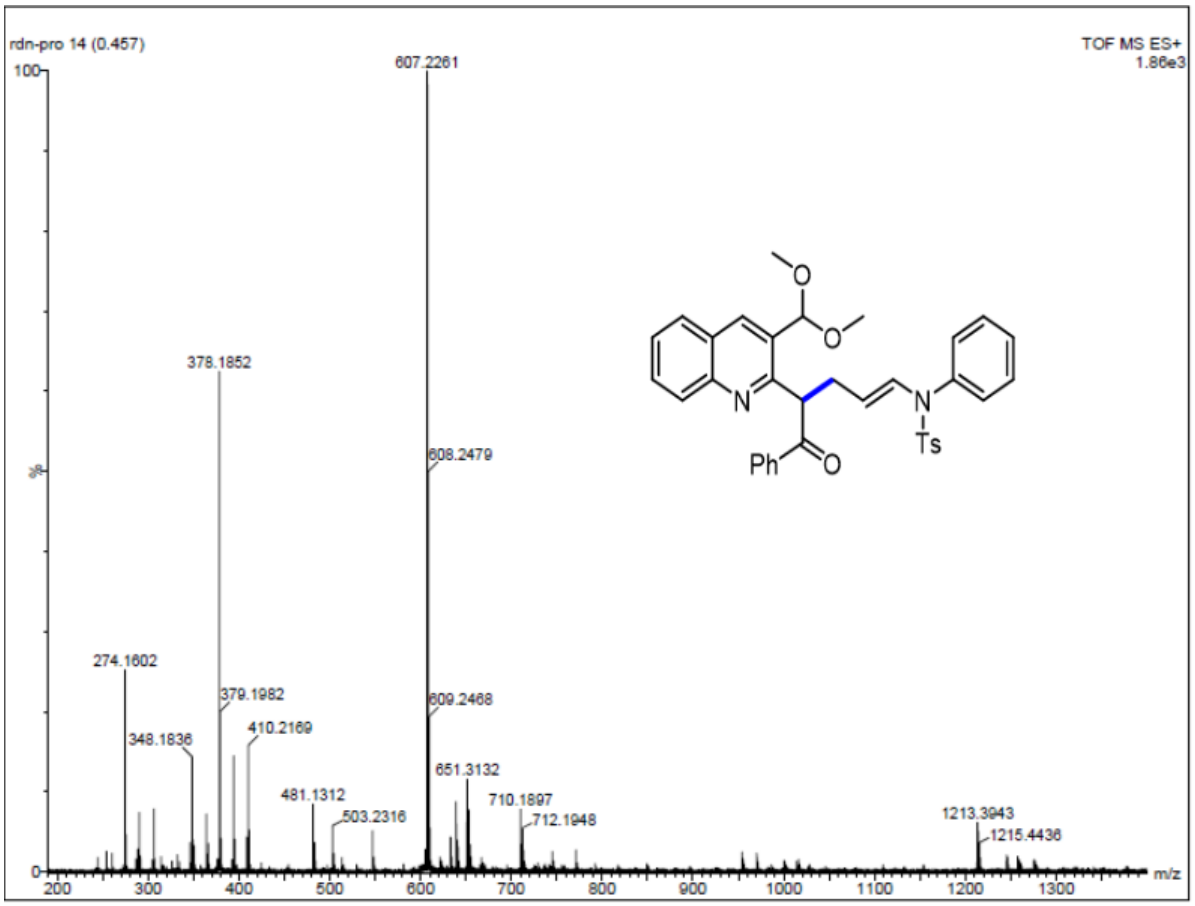
HRMS-ESI of **3m**: $[M+H]^+$ calcd for $C_{36}H_{32}{}^{35}ClN_2O_5S$ 639.1707



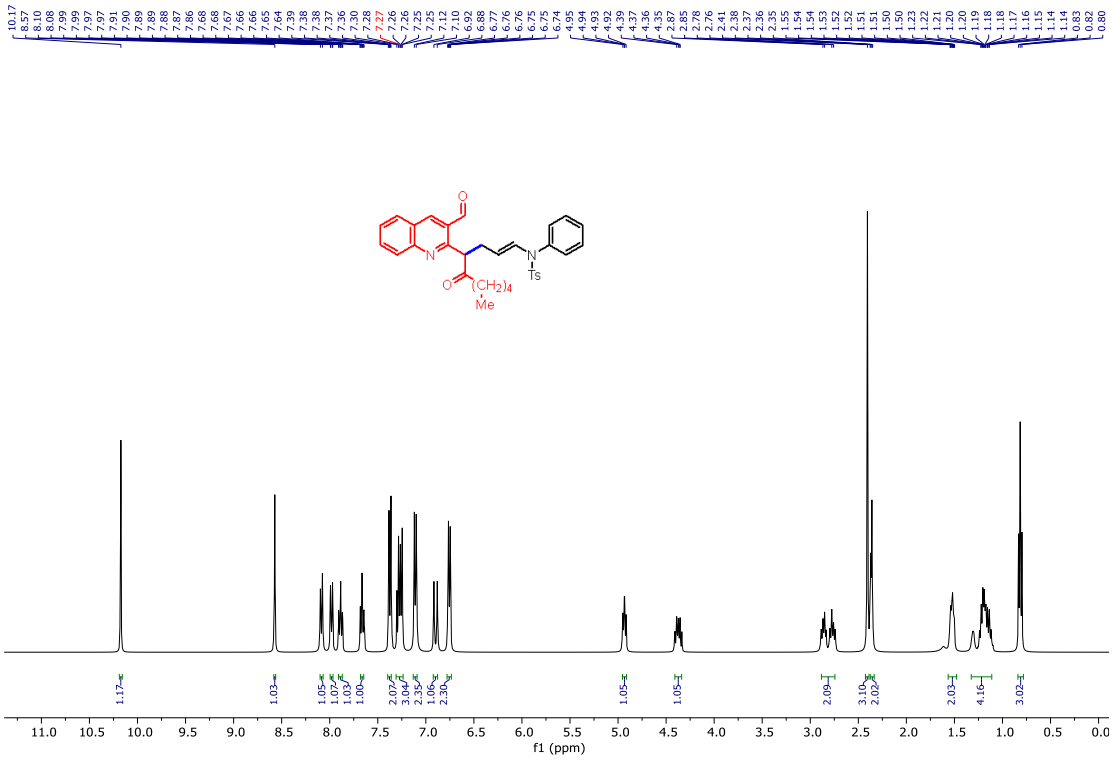
^{1}H-NMR of compound **3n** (400MHz, $CDCl_3$)



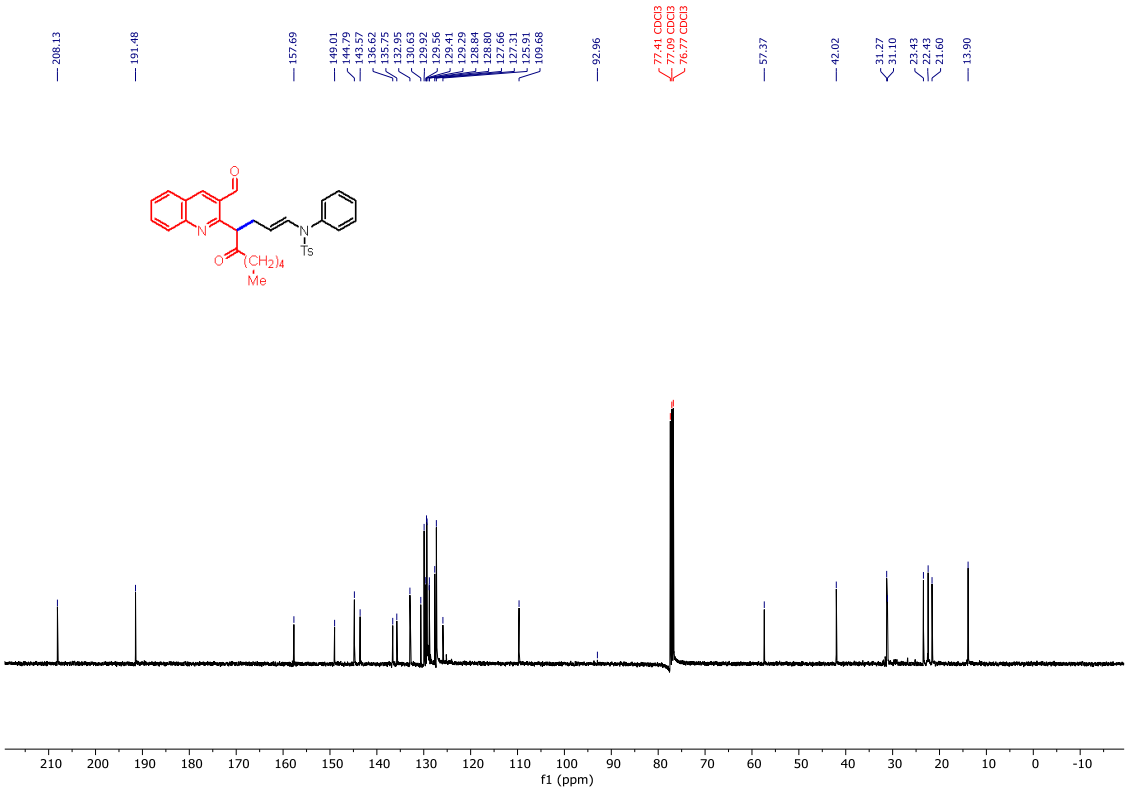
^{13}C-NMR of compound **3n** (101 MHz, $CDCl_3$)



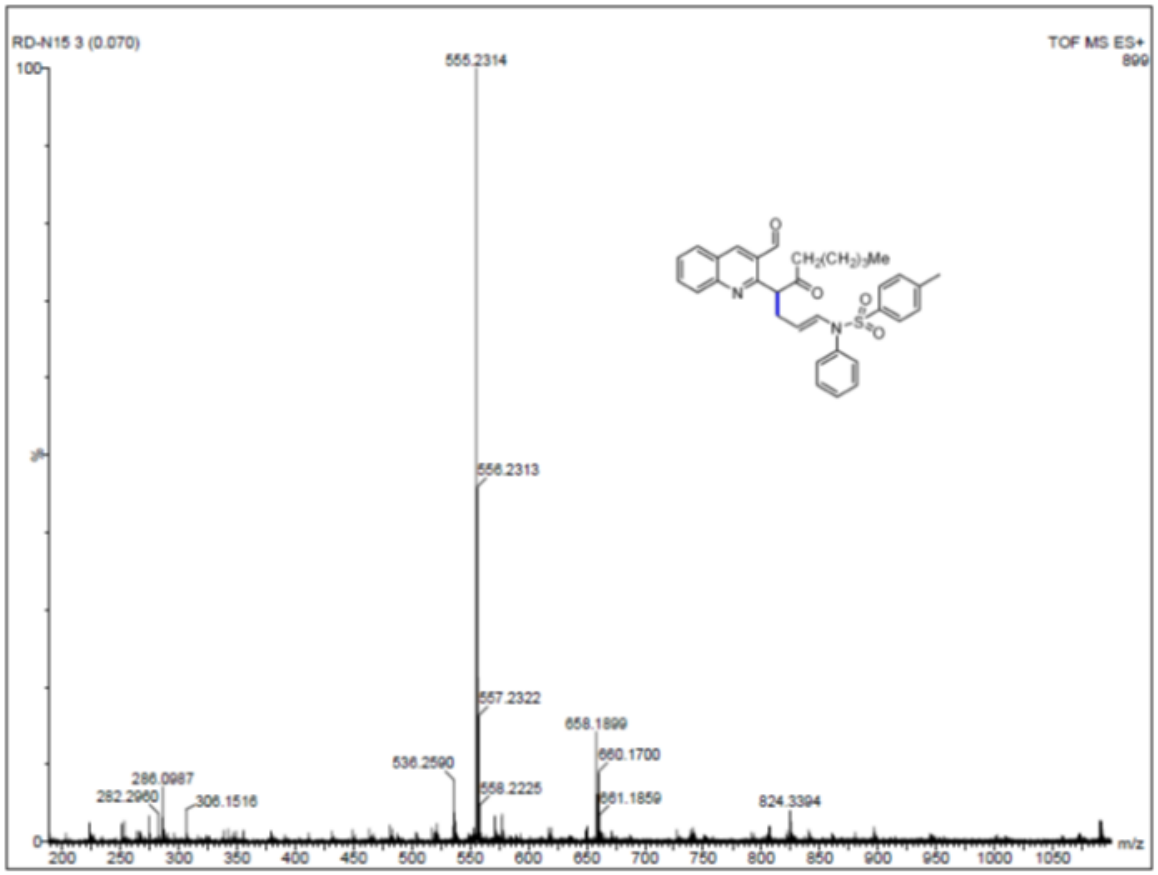
HRMS-ESI of **3n**: $[M+H]^+$ calcd for $C_{36}H_{35}N_2O_5S$ 607.2255



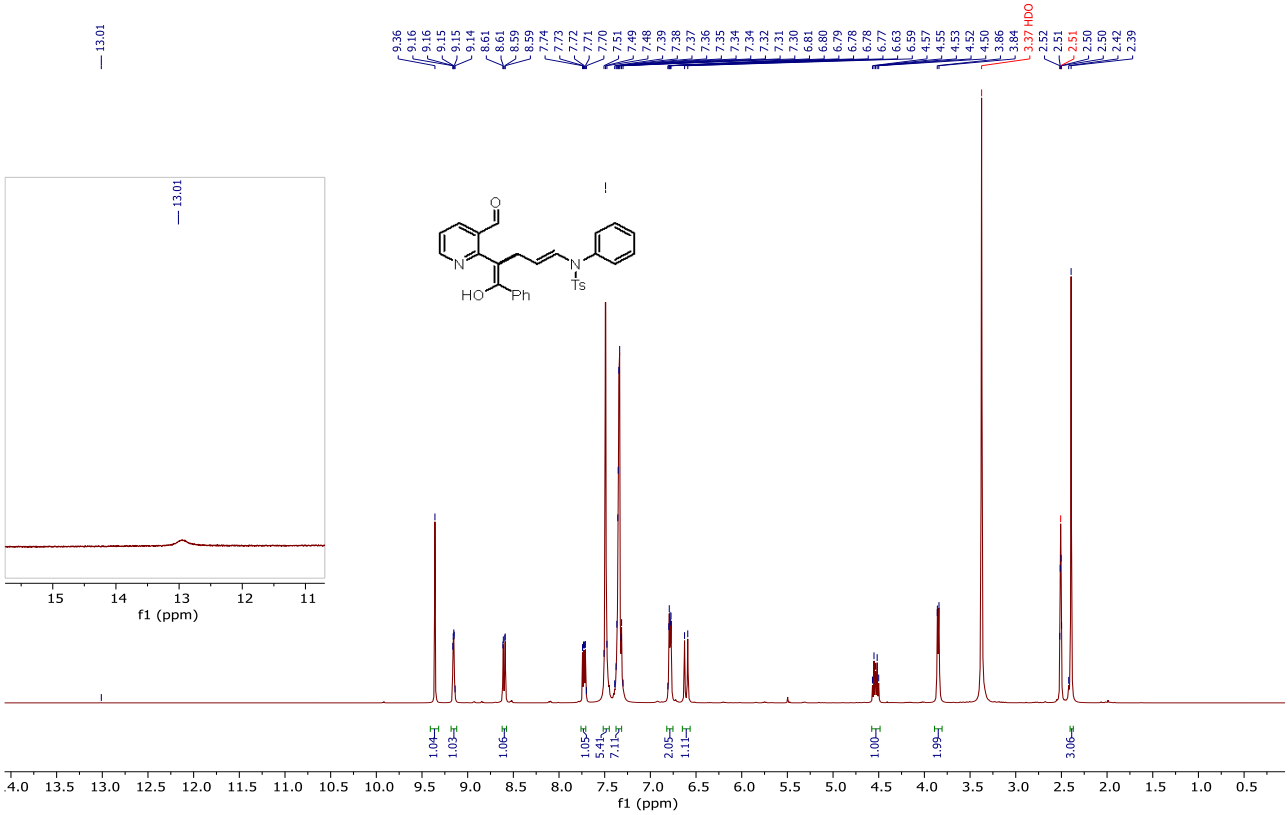
^{1}H-NMR of compound **3o** (400 MHz, $CDCl_3$)



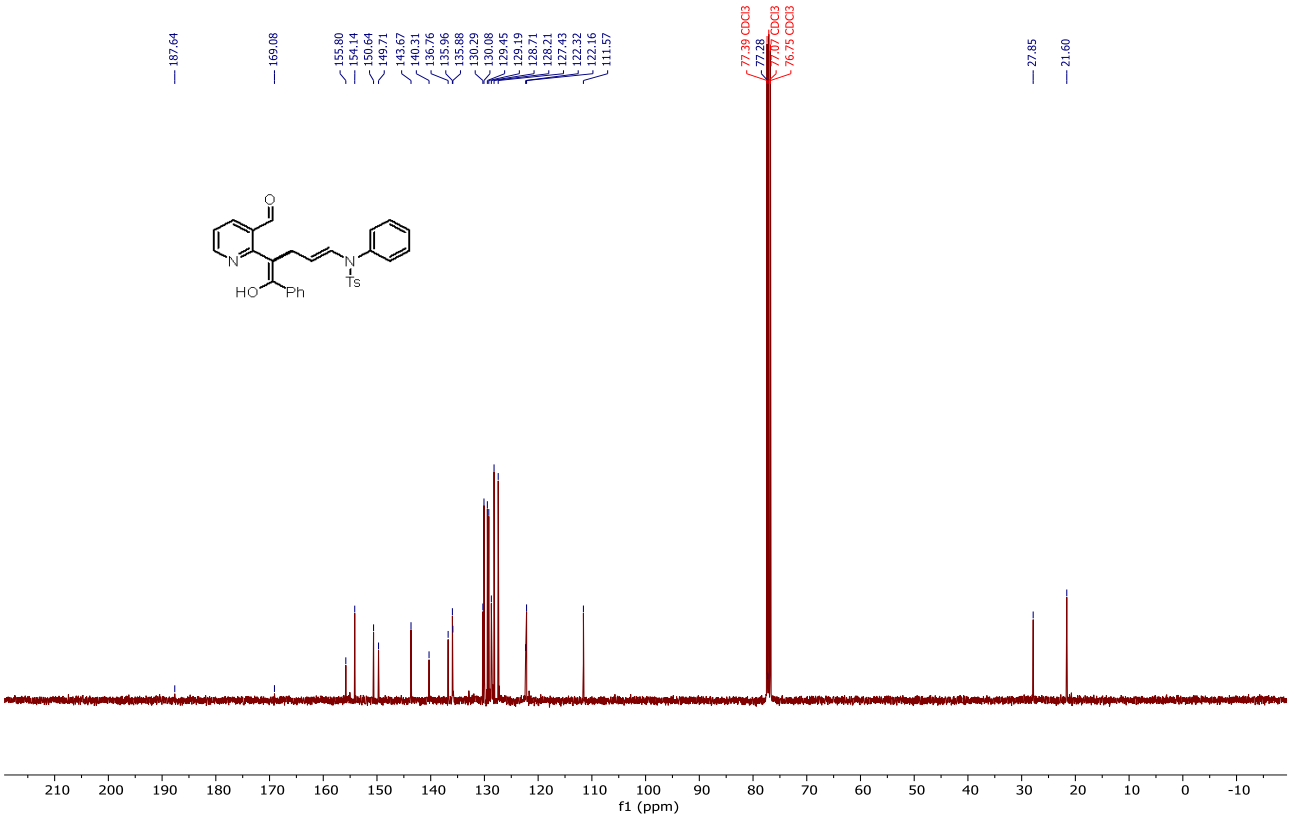
^{13}C-NMR of compound **3o** (101 MHz, $CDCl_3$)



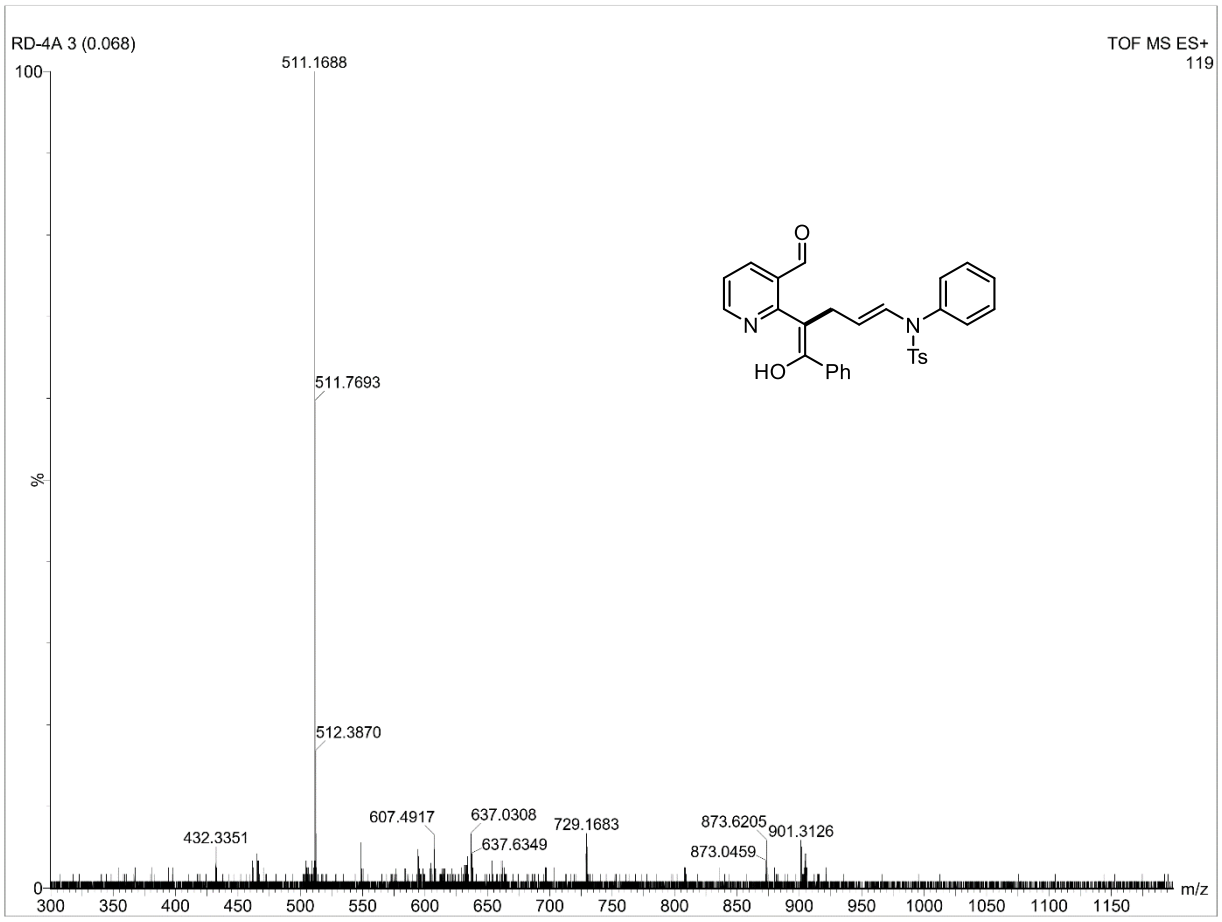
HRMS-ESI of **3o**: $[M+H]^+$ calcd for $C_{33}H_{35}N_2O_4S$ 555.2310



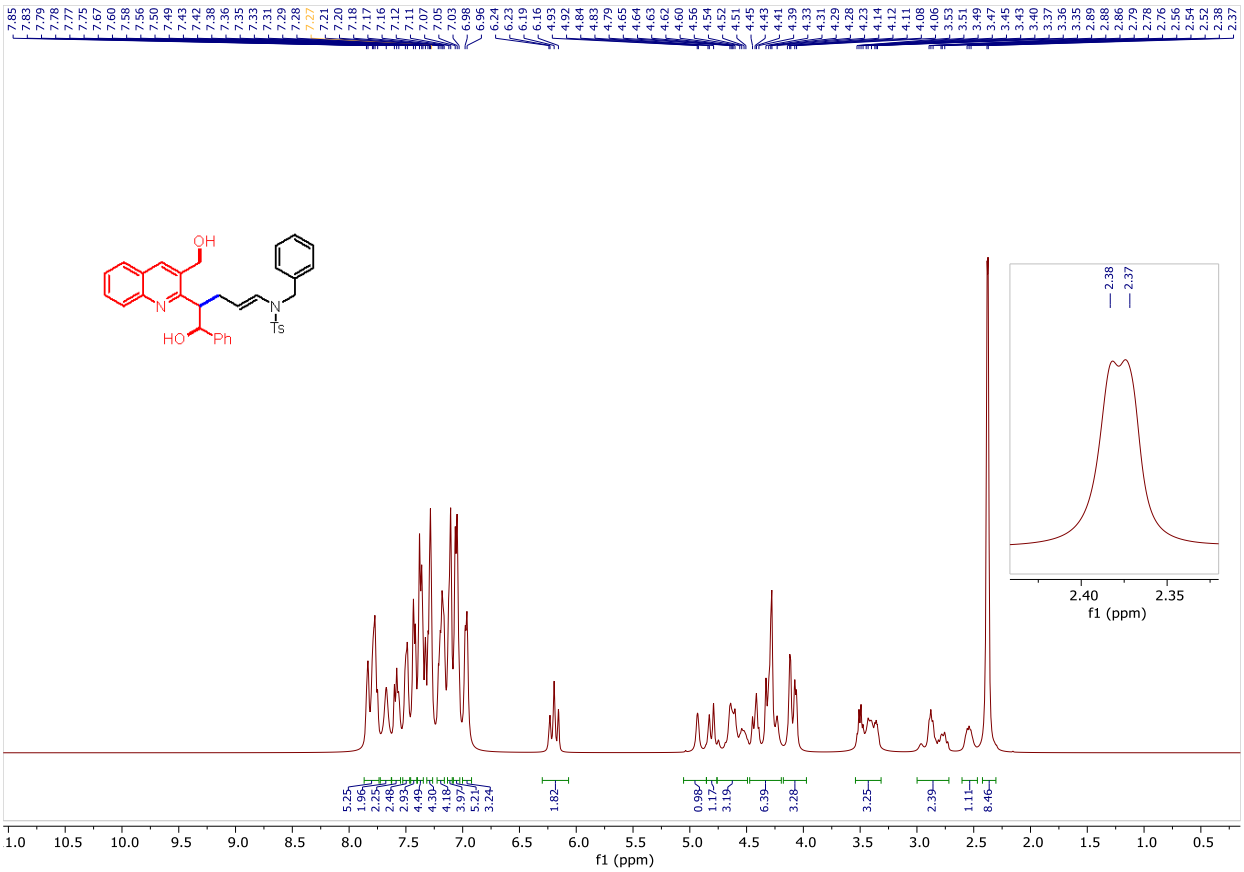
^{1}H-NMR of compound **3p** (400 MHz, DMSO-d_6)



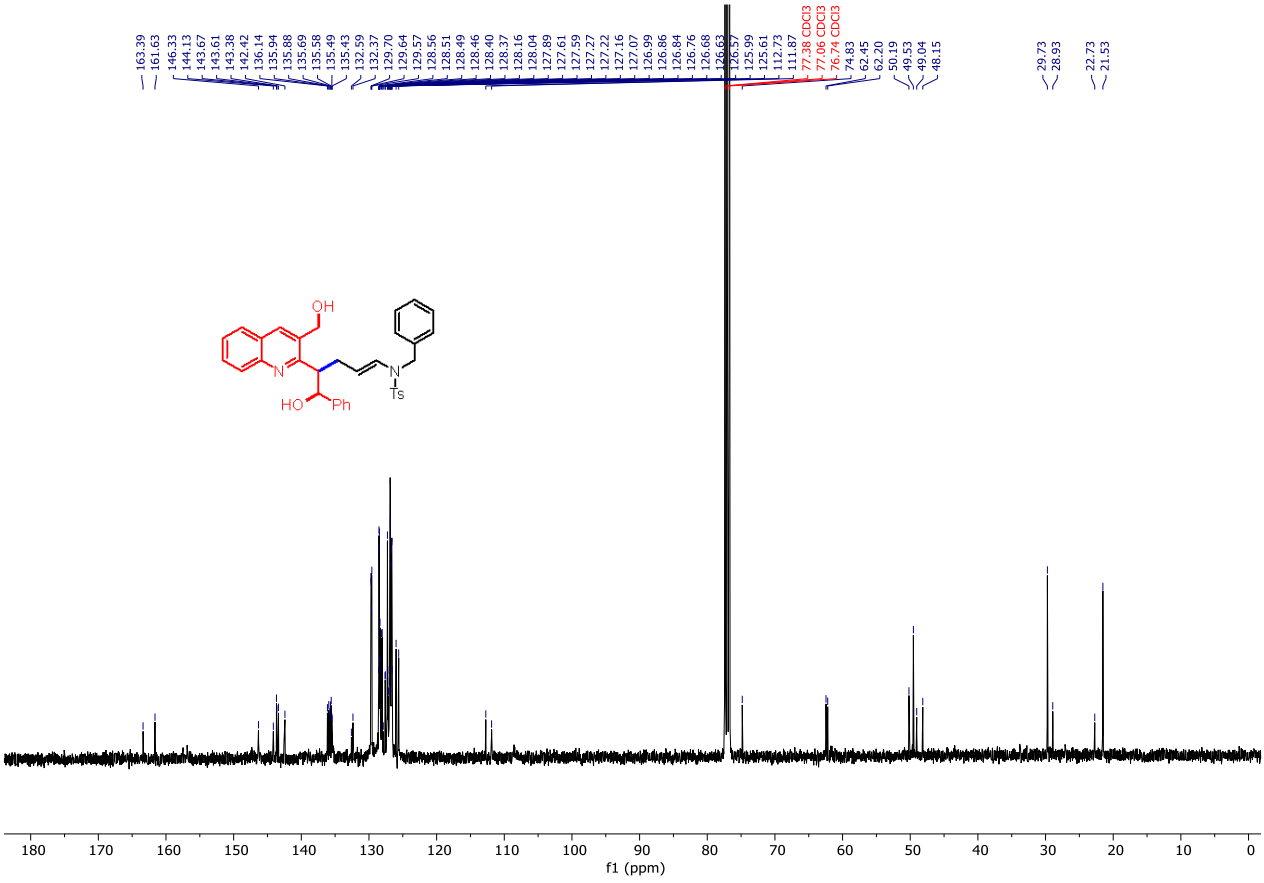
^{13}C-NMR of compound **3p** (101 MHz, $CDCl_3$)



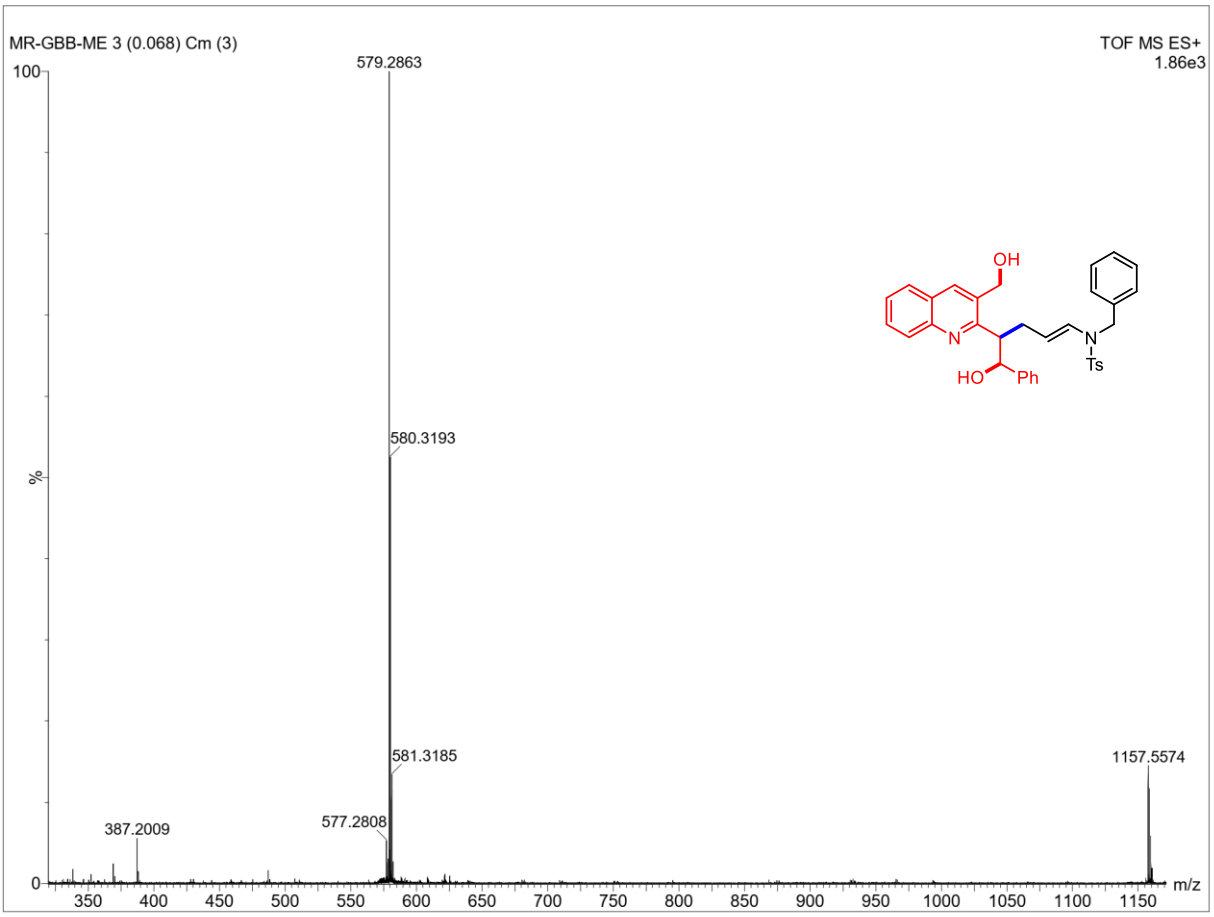
HRMS-ESI of **3p**: $[M+H]^+$ calcd for $C_{30}H_{27}N_2O_4S$ 511.1683



^{1}H-NMR of compound **4a** (400MHz, $CDCl_3$) (mixture of two diastereomers (50:50))



^{13}C-NMR of compound **4a** (101MHz, $CDCl_3$) (mixture of two diastereomers (50:50))



HRMS-ESI of **4a**: $[M+H]^+$ calcd for $C_{35}H_{35}N_2O_4S$ 579.2861(mixture of two diastereomers (50:50))

4. X-ray Crystallographic Analysis

Crystal data and structure refinement for 3a.

Probe : 3a
Sample code : sba180
Operator : F. Rominger
Instrument : Bruker APEX-II Quazar area detector

Table 1: Crystal data and structure refinement for sba180.

Identification code	3a
Empirical formula	$C_{34}H_{28}N_2O_4S$
Formula weight	560.64
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system	orthorhombic
Space group	Pbcn
Z	8
Unit cell dimensions	a = 13.7850(6) Å □ = 90 deg.
	b = 14.0217(7) Å □ = 90 deg.
	c = 29.4717(13) Å □ = 90 deg.
Volume	5696.6(5) $Å^3$
Density (calculated)	1.31 g/cm^3
Absorption coefficient	0.16 mm^{-1}
Crystal shape	brick
Crystal size	0.168 x 0.077 x 0.063 mm^3
Crystal colour	colourless
Theta range for data collection	1.4 to 27.1 deg.
Index ranges	-17□h□16, -17□k□17, -35□l□37
Reflections collected	38791
Independent reflections	6215 (R(int) = 0.0840)
Observed reflections	3596 (I > 2□(I))
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.96 and 0.92
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	6215 / 0 / 371
Goodness-of-fit on F^2	1.01
Final R indices (I>2sigma(I))	R1 = 0.054, wR2 = 0.105
Largest diff. peak and hole	0.24 and -0.34 $eÅ^{-3}$

Table 2: Atomic coordinates and equivalent isotropic displacement parameters ($Å^2$) for sba180. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
C1	0.8667(2)	0.8606(2)	0.7555(1)	0.0292(6)
C2	0.8674(2)	0.8004(2)	0.7124(1)	0.0266(5)
H2	0.9149	0.7472	0.7166	0.032
C3	0.8969(2)	0.8577(2)	0.6701(1)	0.0276(6)

H3A	0.8463	0.9058	0.6632	0.033
H3B	0.9584	0.8919	0.6761	0.033
C4	0.9095(2)	0.7929(2)	0.6301(1)	0.0295(6)
H4	0.9571	0.7441	0.6322	0.035
C5	0.8591(2)	0.7991(2)	0.5923(1)	0.0307(6)
H5	0.8113	0.8478	0.5904	0.037
S1	0.7906(1)	0.7434(1)	0.5127(1)	0.0385(2)
O1	0.8790(2)	0.9462(1)	0.7543(1)	0.0484(5)
N11	0.8709(2)	0.7380(1)	0.5542(1)	0.0335(5)
C11	0.8499(2)	0.8116(2)	0.8001(1)	0.0295(6)
O12	0.8305(1)	0.6902(2)	0.4758(1)	0.0487(5)
C12	0.8154(2)	0.8657(2)	0.8361(1)	0.0404(7)
H12	0.8045	0.9321	0.8322	0.048
O13	0.7670(1)	0.8422(1)	0.5074(1)	0.0475(5)
C13	0.7968(2)	0.8235(2)	0.8776(1)	0.0485(8)
H13	0.7717	0.8607	0.9018	0.058
C14	0.8144(2)	0.7280(2)	0.8838(1)	0.0500(8)
H14	0.8009	0.6991	0.9122	0.060
C15	0.8514(2)	0.6740(2)	0.8489(1)	0.0441(7)
H15	0.8657	0.6085	0.8536	0.053
C16	0.8679(2)	0.7152(2)	0.8067(1)	0.0350(6)
H16	0.8915	0.6773	0.7824	0.042
C21	0.7671(2)	0.7575(2)	0.7059(1)	0.0275(6)
N22	0.6968(1)	0.8203(1)	0.7026(1)	0.0291(5)
C23	0.6028(2)	0.7893(2)	0.6965(1)	0.0299(6)
C24	0.5283(2)	0.8573(2)	0.6936(1)	0.0409(7)
H24	0.5433	0.9234	0.6951	0.049
C25	0.4341(2)	0.8285(2)	0.6885(1)	0.0471(8)
H25	0.3842	0.8750	0.6860	0.057
C26	0.4102(2)	0.7322(2)	0.6870(1)	0.0479(8)
H26	0.3442	0.7136	0.6838	0.057
C27	0.4803(2)	0.6643(2)	0.6899(1)	0.0428(7)
H27	0.4632	0.5986	0.6892	0.051
C28	0.5791(2)	0.6916(2)	0.6940(1)	0.0322(6)
C29	0.6556(2)	0.6271(2)	0.6968(1)	0.0372(7)
H29	0.6423	0.5608	0.6949	0.045
C30	0.7499(2)	0.6568(2)	0.7023(1)	0.0317(6)
O31	0.9110(2)	0.5915(1)	0.7078(1)	0.0507(5)
C31	0.8244(2)	0.5817(2)	0.7039(1)	0.0441(7)
H31	0.8017	0.5179	0.7017	0.053
C41	0.9212(2)	0.6480(2)	0.5605(1)	0.0339(6)
C42	0.8808(2)	0.5781(2)	0.5875(1)	0.0410(7)
H42	0.8199	0.5880	0.6018	0.049
C43	0.9306(2)	0.4930(2)	0.5933(1)	0.0517(8)
H43	0.9034	0.4441	0.6117	0.062
C44	1.0189(3)	0.4788(2)	0.5728(1)	0.0562(9)
H44	1.0525	0.4203	0.5771	0.067
C45	1.0587(2)	0.5489(2)	0.5460(1)	0.0547(9)
H45	1.1195	0.5388	0.5316	0.066
C46	1.0098(2)	0.6347(2)	0.5399(1)	0.0446(7)
H46	1.0373	0.6837	0.5218	0.054
C51	0.6863(2)	0.6843(2)	0.5317(1)	0.0349(6)
C52	0.6747(2)	0.5873(2)	0.5237(1)	0.0454(7)
H52	0.7226	0.5529	0.5073	0.054
C53	0.5929(2)	0.5412(2)	0.5399(1)	0.0490(8)
H53	0.5853	0.4748	0.5346	0.059
C54	0.5221(2)	0.5900(2)	0.5637(1)	0.0477(8)
C55	0.5347(2)	0.6864(2)	0.5715(1)	0.0494(8)
H55	0.4867	0.7208	0.5880	0.059

C56	0.6162(2)	0.7337(2)	0.5557(1)	0.0416(7)
H56	0.6239	0.8000	0.5614	0.050
C58	0.4324(3)	0.5397(3)	0.5805(1)	0.0709(11)
H58A	0.4232	0.5535	0.6128	0.106
H58B	0.4399	0.4707	0.5763	0.106
H58C	0.3758	0.5620	0.5634	0.106

Table 3: Hydrogen coordinates and isotropic displacement parameters ($Å^2$) for sba180.

Atom	x	y	z	U_{eq}
H2	0.9149	0.7472	0.7166	0.032
H3A	0.8463	0.9058	0.6632	0.033
H3B	0.9584	0.8919	0.6761	0.033
H4	0.9571	0.7441	0.6322	0.035
H5	0.8113	0.8478	0.5904	0.037
H12	0.8045	0.9321	0.8322	0.048
H13	0.7717	0.8607	0.9018	0.058
H14	0.8009	0.6991	0.9122	0.060
H15	0.8657	0.6085	0.8536	0.053
H16	0.8915	0.6773	0.7824	0.042
H24	0.5433	0.9234	0.6951	0.049
H25	0.3842	0.8750	0.6860	0.057
H26	0.3442	0.7136	0.6838	0.057
H27	0.4632	0.5986	0.6892	0.051
H29	0.6423	0.5608	0.6949	0.045
H31	0.8017	0.5179	0.7017	0.053
H42	0.8199	0.5880	0.6018	0.049
H43	0.9034	0.4441	0.6117	0.062
H44	1.0525	0.4203	0.5771	0.067
H45	1.1195	0.5388	0.5316	0.066
H46	1.0373	0.6837	0.5218	0.054
H52	0.7226	0.5529	0.5073	0.054
H53	0.5853	0.4748	0.5346	0.059
H55	0.4867	0.7208	0.5880	0.059
H56	0.6239	0.8000	0.5614	0.050
H58A	0.4232	0.5535	0.6128	0.106
H58B	0.4399	0.4707	0.5763	0.106
H58C	0.3758	0.5620	0.5634	0.106

Table 4: Anisotropic displacement parameters ($Å^2$) for sba180. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ (h^2\ a^{*2}\ U_{11} + ... + 2\ h\ k\ a^*\ b^*\ U_{12})$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	0.0245(13)	0.0322(14)	0.0308(14)	-0.0043(11)	-0.0036(11)	-0.0014(11)
C2	0.0281(14)	0.0254(12)	0.0261(13)	0.0005(10)	-0.0007(11)	-0.0017(11)
C3	0.0274(14)	0.0304(13)	0.0251(13)	-0.0005(10)	-0.0013(11)	-0.0031(11)
C4	0.0270(14)	0.0332(13)	0.0282(14)	-0.0005(11)	0.0010(11)	0.0026(11)
C5	0.0330(15)	0.0302(13)	0.0290(14)	0.0002(11)	-0.0006(12)	0.0024(11)
S1	0.0446(4)	0.0454(4)	0.0256(4)	0.0011(3)	-0.0066(3)	0.0011(3)

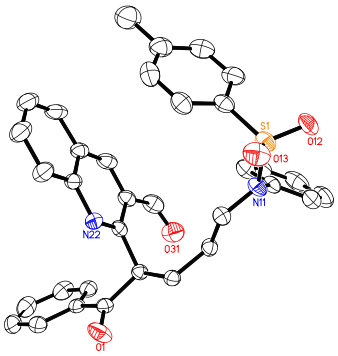
O1	0.0761(15)	0.0320(10)	0.0370(11)	-0.0064(9)	-0.0028(10)	-0.0107(10)
N11	0.0406(13)	0.0369(12)	0.0231(11)	-0.0012(9)	-0.0062(10)	0.0034(10)
C11	0.0230(14)	0.0405(15)	0.0251(14)	-0.0020(11)	-0.0031(11)	-0.0055(11)
O12	0.0514(12)	0.0719(14)	0.0228(10)	-0.0085(9)	-0.0041(9)	0.0029(11)
C12	0.0339(16)	0.0530(17)	0.0342(16)	-0.0072(13)	-0.0023(13)	-0.0063(14)
O13	0.0591(13)	0.0424(11)	0.0409(12)	0.0117(9)	-0.0130(10)	-0.0003(10)
C13	0.0377(17)	0.078(2)	0.0301(16)	-0.0099(15)	0.0037(13)	-0.0089(16)
C14	0.0420(18)	0.079(2)	0.0293(16)	0.0123(16)	-0.0011(14)	-0.0056(17)
C15	0.0374(17)	0.0534(18)	0.0413(18)	0.0157(14)	-0.0073(14)	-0.0017(14)
C16	0.0304(15)	0.0449(16)	0.0298(15)	0.0025(12)	-0.0047(12)	-0.0013(13)
C21	0.0326(15)	0.0293(13)	0.0205(12)	-0.0011(10)	-0.0001(11)	-0.0003(11)
N22	0.0276(12)	0.0289(11)	0.0308(12)	0.0002(9)	-0.0004(9)	-0.0024(9)
C23	0.0289(14)	0.0358(14)	0.0249(14)	-0.0006(11)	-0.0004(11)	-0.0071(12)
C24	0.0304(16)	0.0428(16)	0.0495(18)	0.0003(13)	-0.0008(13)	-0.0015(13)
C25	0.0296(16)	0.0588(19)	0.053(2)	0.0020(15)	-0.0016(14)	-0.0019(14)
C26	0.0321(16)	0.071(2)	0.0404(18)	0.0019(15)	-0.0017(14)	-0.0150(16)
C27	0.0452(18)	0.0500(17)	0.0332(16)	0.0010(13)	-0.0054(14)	-0.0250(15)
C28	0.0343(15)	0.0378(15)	0.0244(14)	0.0024(11)	-0.0035(12)	-0.0082(12)
C29	0.0480(18)	0.0305(14)	0.0331(15)	0.0005(12)	-0.0035(13)	-0.0140(13)
C30	0.0410(16)	0.0254(13)	0.0287(14)	0.0001(11)	-0.0016(12)	-0.0035(12)
O31	0.0476(13)	0.0351(11)	0.0695(15)	-0.0054(10)	-0.0052(11)	0.0062(10)
C31	0.058(2)	0.0269(14)	0.0472(19)	-0.0020(12)	-0.0045(16)	-0.0010(14)
C41	0.0395(16)	0.0382(15)	0.0238(14)	-0.0046(11)	-0.0048(12)	0.0009(13)
C42	0.0488(18)	0.0430(16)	0.0313(16)	-0.0031(13)	-0.0023(14)	-0.0005(14)
C43	0.074(2)	0.0359(16)	0.0449(19)	-0.0026(14)	-0.0150(18)	-0.0011(16)
C44	0.072(2)	0.0453(18)	0.051(2)	-0.0182(16)	-0.0193(19)	0.0193(18)
C45	0.051(2)	0.064(2)	0.049(2)	-0.0227(17)	-0.0040(16)	0.0158(17)
C46	0.0441(18)	0.0550(18)	0.0348(17)	-0.0091(14)	-0.0005(14)	-0.0014(15)
C51	0.0398(16)	0.0362(14)	0.0288(14)	-0.0016(12)	-0.0095(13)	0.0044(13)
C52	0.0432(18)	0.0438(17)	0.0491(19)	-0.0135(14)	-0.0125(15)	0.0060(14)
C53	0.056(2)	0.0395(16)	0.051(2)	-0.0039(14)	-0.0141(17)	-0.0023(15)
C54	0.0504(19)	0.0557(19)	0.0369(17)	0.0066(15)	-0.0082(15)	-0.0098(16)
C55	0.054(2)	0.0551(19)	0.0390(18)	-0.0021(15)	0.0075(15)	0.0051(16)
C56	0.0526(19)	0.0362(15)	0.0360(16)	-0.0012(12)	-0.0026(14)	0.0053(14)
C58	0.072(2)	0.087(3)	0.053(2)	0.0030(19)	0.0019(19)	-0.029(2)

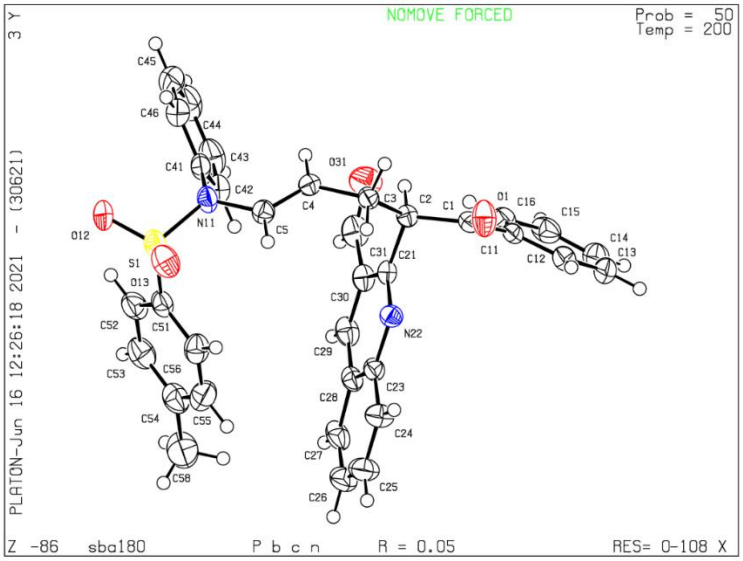
Table 5: Bond lengths (Å) and angles (deg) for sba180.

C1-O1	1.213(3)	C11-C12	1.389(3)
C1-C11	1.502(3)	C12-C13	1.381(4)
C1-C2	1.523(3)	C12-H12	0.9500
C2-C21	1.520(3)	C13-C14	1.374(4)
C2-C3	1.540(3)	C13-H13	0.9500
C2-H2	1.0000	C14-C15	1.375(4)
C3-C4	1.498(3)	C14-H14	0.9500
C3-H3A	0.9900	C15-C16	1.389(4)
C3-H3B	0.9900	C15-H15	0.9500
C4-C5	1.315(3)	C16-H16	0.9500
C4-H4	0.9500	C21-N22	1.313(3)
C5-N11	1.422(3)	C21-C30	1.436(3)
C5-H5	0.9500	N22-C23	1.378(3)
S1-O12	1.4277(19)	C23-C24	1.404(4)
S1-O13	1.4304(19)	C23-C28	1.411(3)
S1-N11	1.653(2)	C24-C25	1.368(4)
S1-C51	1.753(3)	C24-H24	0.9500
N11-C41	1.451(3)	C25-C26	1.391(4)
C11-C16	1.388(3)	C25-H25	0.9500

C26-C27	1.359(4)	C5-N11-C41	118.55(19)
C26-H26	0.9500	C5-N11-S1	118.72(17)
C27-C28	1.420(4)	C41-N11-S1	117.03(16)
C27-H27	0.9500	C16-C11-C12	119.0(2)
C28-C29	1.392(4)	C16-C11-C1	122.8(2)
C29-C30	1.374(4)	C12-C11-C1	118.2(2)
C29-H29	0.9500	C13-C12-C11	120.4(3)
C30-C31	1.472(4)	C13-C12-H12	119.8
O31-C31	1.207(3)	C11-C12-H12	119.8
C31-H31	0.9500	C14-C13-C12	120.2(3)
C41-C46	1.376(4)	C14-C13-H13	119.9
C41-C42	1.380(4)	C12-C13-H13	119.9
C42-C43	1.387(4)	C13-C14-C15	120.2(3)
C42-H42	0.9500	C13-C14-H14	119.9
C43-C44	1.374(4)	C15-C14-H14	119.9
C43-H43	0.9500	C14-C15-C16	120.0(3)
C44-C45	1.375(4)	C14-C15-H15	120.0
C44-H44	0.9500	C16-C15-H15	120.0
C45-C46	1.390(4)	C11-C16-C15	120.1(3)
C45-H45	0.9500	C11-C16-H16	119.9
C46-H46	0.9500	C15-C16-H16	119.9
C51-C56	1.384(4)	N22-C21-C30	122.2(2)
C51-C52	1.389(4)	N22-C21-C2	114.5(2)
C52-C53	1.384(4)	C30-C21-C2	123.3(2)
C52-H52	0.9500	C21-N22-C23	119.5(2)
C53-C54	1.384(4)	N22-C23-C24	118.8(2)
C53-H53	0.9500	N22-C23-C28	122.1(2)
C54-C55	1.383(4)	C24-C23-C28	119.1(2)
C54-C58	1.507(4)	C25-C24-C23	120.1(3)
C55-C56	1.385(4)	C25-C24-H24	120.0
C55-H55	0.9500	C23-C24-H24	120.0
C56-H56	0.9500	C24-C25-C26	121.0(3)
C58-H58A	0.9800	C24-C25-H25	119.5
C58-H58B	0.9800	C26-C25-H25	119.5
C58-H58C	0.9800	C27-C26-C25	120.6(3)
O1-C1-C11	119.9(2)	C27-C26-H26	119.7
O1-C1-C2	121.6(2)	C25-C26-H26	119.7
C11-C1-C2	118.4(2)	C26-C27-C28	119.9(3)
C21-C2-C1	108.63(19)	C26-C27-H27	120.1
C21-C2-C3	110.14(19)	C28-C27-H27	120.1
C1-C2-C3	112.76(19)	C29-C28-C23	116.8(2)
C21-C2-H2	108.4	C29-C28-C27	123.8(2)
C1-C2-H2	108.4	C23-C28-C27	119.3(2)
C3-C2-H2	108.4	C30-C29-C28	121.8(2)
C4-C3-C2	110.57(19)	C30-C29-H29	119.1
C4-C3-H3A	109.5	C28-C29-H29	119.1
C2-C3-H3A	109.5	C29-C30-C21	117.5(2)
C4-C3-H3B	109.5	C29-C30-C31	116.6(2)
C2-C3-H3B	109.5	C21-C30-C31	125.9(2)
H3A-C3-H3B	108.1	O31-C31-C30	127.7(3)
C5-C4-C3	124.3(2)	O31-C31-H31	116.1
C5-C4-H4	117.8	C30-C31-H31	116.1
C3-C4-H4	117.8	C46-C41-C42	121.0(3)
C4-C5-N11	124.6(2)	C46-C41-N11	119.1(2)
C4-C5-H5	117.7	C42-C41-N11	119.9(2)
N11-C5-H5	117.7	C41-C42-C43	118.9(3)
O12-S1-O13	120.67(12)	C41-C42-H42	120.6
O12-S1-N11	106.31(11)	C43-C42-H42	120.6
O13-S1-N11	106.15(11)	C44-C43-C42	120.5(3)
O12-S1-C51	108.20(12)	C44-C43-H43	119.7
O13-S1-C51	107.87(12)	C42-C43-H43	119.7
N11-S1-C51	106.89(11)	C43-C44-C45	120.2(3)

C43-C44-H44	119.9
C45-C44-H44	119.9
C44-C45-C46	119.9(3)
C44-C45-H45	120.1
C46-C45-H45	120.1
C41-C46-C45	119.5(3)
C41-C46-H46	120.3
C45-C46-H46	120.3
C56-C51-C52	119.8(3)
C56-C51-S1	120.0(2)
C52-C51-S1	120.2(2)
C53-C52-C51	119.5(3)
C53-C52-H52	120.3
C51-C52-H52	120.3
C54-C53-C52	121.2(3)
C54-C53-H53	119.4
C52-C53-H53	119.4
C55-C54-C53	118.7(3)
C55-C54-C58	120.4(3)
C53-C54-C58	120.9(3)
C54-C55-C56	120.9(3)
C54-C55-H55	119.5
C56-C55-H55	119.5
C51-C56-C55	119.9(3)
C51-C56-H56	120.0
C55-C56-H56	120.0
C54-C58-H58A	109.5
C54-C58-H58B	109.5
H58A-C58-H58B	109.5
C54-C58-H58C	109.5
H58A-C58-H58C	109.5
H58B-C58-H58C	109.5





sba180: colourless crystal (brick), dimensions 0.168 x 0.077 x 0.063 mm^3, crystal system orthorhombic, space group Pbcn, Z=8, a=13.7850(6) Å, b=14.0217(7) Å, c=29.4717(13) Å, alpha=90 deg, beta=90 deg, gamma=90 deg, V=5696.6(5) $Å^3$, rho=1.307 g/cm^3, T=200(2) K, $Theta_{max}$= 27.071 deg, radiation MoK□, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 5.95and a completeness of 99.3% to a resolution of 0.78 Å, 38791 reflections measured, 6215 unique (R(int)=0.0840), 3596 observed (I > 2□(I)), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.16mm^{-1}, T_{min}=0.92, T_{max}=0.96, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[3], 371 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values R1(F)=0.054, wR(F^2)=0.105 for observed reflections, residual electron density -0.34 to 0.24 e$Å^{-3}$. CCDC 2175887 contains the supplementary crystallographic

data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

Lit. 2: (SHELXT - Integrated space-group and crystal structure determination)
Sheldrick G. M., Acta Cryst. A71 (2015) 3-8.

Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

5. References

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2. Cui, J.; Meng, L.; Chi, X.; Liu, Q.; Zhao, P.; Zhang, D. P.; Chen, L.; Li, X.; Dong, Y.; Liu, H. A palladium-catalyzed regiocontrollable hydroarylation reaction of allenamides with B2pin2/H2O. *Chemical Communications Chem Commun*. **2019**, *55*, 4355-4358.