Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

A Novel Sulfonamide Non-Classical Carbenenoid: A Mechanistic Study for the Synthesis of Enediynes

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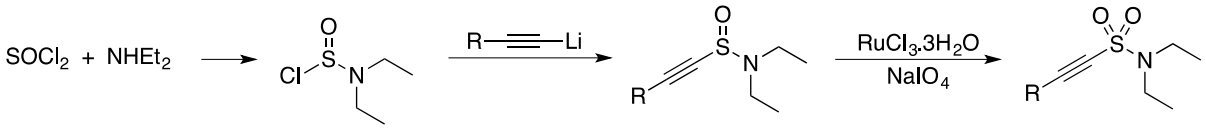
Supporting Information

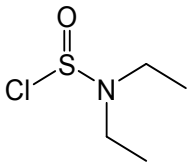
Experimental: General

Reagents and solvents were obtained from commercial sources and used without further modification unless stated otherwise. TLC was performed using Merck Silica plates and compounds visualised by exposure of UV light. Flash column chromatography was carried out using Geduran® silicagel 60 (particle size 40-63 μm). ^{1}H- and ^{13}C-NMR were carried out at the stated field using Bruker AMX-300 MHz, AMX-500 MHz and AMX-600 MHz instruments. Coupling constants were measured in Hertz (Hz) with reference to the deuterated solvent used. Mass spectra were measured on Thermo Finnigan MAT900 XE and Waters LCT Premier XE machines operating in EI, CI and ESI modes. LRMS refers to low-resolution mass spectrometry and HRMS refers to high resolution mass spectrometry. Infrared spectra were recorded using a Bruker Alpha FTIR spectrometer. Distilled THF solvent was dried over CaH_2, distilled and stored over molecular sieves, 4A, 1-2 mm (0.04-0.08 in) beads. (EA:PE) refers to the ethyl acetate:peteroleum ether ratio of the solvent system.

Alkynyl sulfonamides were prepared by known procedures outlined below.[1,2]



Procedure for the synthesis of N,N-diethylsulfurous chloride



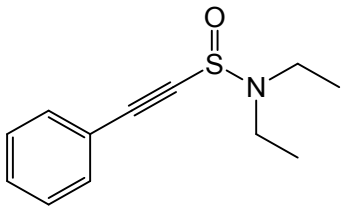
A 500 mL flame-dried flask was charged with thionyl chloride (9.84g, 82.7 mmol, 1.0 eq.) and dry Et_2O (150 mL) under argon. The solution was cooled to -40 ^{o}C and a solution of diethylamine (12.0 g, 164.4 mmol, 2.0 eq.) in dry Et_2O (100 mL) was added dropwise over 2 h whilst the mixture was allowed to stir. The reaction was then warmed to 0 ^{o}C and allowed to stir for a further 1 h. The reaction mixture was then allowed to warm to RT and quickly filtered through a pad of Celite®. The solution was *carefully* concentrated *in vacuo* (while leaving some solvent remaining to avoid explosions on the rotary evaporator apparatus as previously reported when all solvent was removed) to yield a viscous, acrid brown crude product (19.4 g product, containing 8.53 g of desired chloride, 66%). The crude product was quickly stored under argon in a freezer and used without further purification. ^{1}H-NMR (300

MHz, $CDCl_3$) δ_H 3.03 (m, 4 H, NCH_2) 1.47 (t, *J* = 7.3 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (300 MHz, $CDCl_3$) δ_c 42.4, 12.5; no mass ion detected. Data in agreement with literature.[1]

General procedure for the synthesis alkynyl sulfinamides

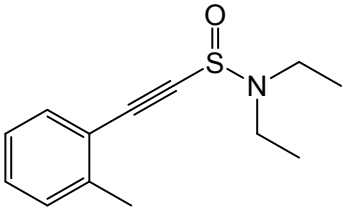
A 100 mL flame-dried flask was charged with aromatic acetylene (1.5 mmol, 1.1 eq.) and dry THF (0.1 M) under argon. The solution was cooled to -78^{o}C and *n*BuLi (2.5 M in hexanes, 1.1 eq.) was added dropwise and allowed to stir for 10 min. *N,N*-diethylsulfurous chloride (1.36 mmol, 1.0 eq.) was then carefully added dropwise and stirred for a further 20 min. The reaction mixture was allowed to warm to RT, diluted with CH_2Cl_2 (200 mL), washed with H_2O (100 mL) then brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude product. Purification *via* flash column chromatography (Petroleum Ether/Ethyl acetate) was carried out to yield the alkynyl sulfinamide product.

***N,N*-diethyl-2-phenylethynesulfinamide**



Yellow oil (74%). *Rf* = 0.18 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.52 (d, *J* = 7.0 Hz, 2 H, Ar*H*), 7.43 (t, *J* = 7.6, Hz, 1 H, Ar*H*), 7.37 (t, *J* = 7.7 Hz, 2 H, Ar*H*), 3.44 (q, *J* = 7.1 Hz, 2 H, NCH_2), 3.37 (q, *J* = 7.0 Hz, 2 H, NCH_2), 1.29 (t, *J* = 7.2 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 132.2 (CH), 130.3 (CH), 128.7 (CH), 120.2 (C_q), 96.4 (C_q), 86.5 (C_q), 42.7 (CH_2), 14.4 (CH_3); ν_{max}/cm^{-1} 2973, 2935, 2871, 2162, 1488, 1443, 1380, 1290, 1178, 1090, 899, 828, 782, 756, 689, 638, 619, 551, 530, 488, 445; LRMS (ES+) *m/z* (%) 277 (7), 267 (5), 265 (8), 263 (3), 238 (4), 224 (7), 223 (19), 222 (100), 214 (3), 209 (2), 192 (9); HRMS (ES+) calc'd for $C_{12}H_{16}NOS$ $(M+H)^+$ 222.0953, found 222.0955. Data in agreement with literature.[2]

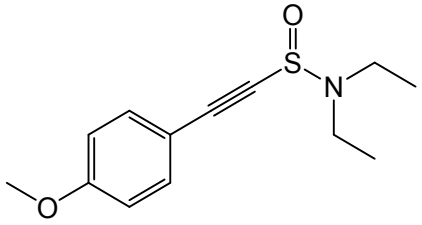
***N,N*-Diethyl-2-(*o*-tolyl)ethynesulfinamide**



Yellow oil (93%). *Rf* = 0.17 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.48 (d, *J* = 7.6 Hz, 1 H, Ar*H*), 7.32 (t, *J* = 7.6 Hz, 1 H, Ar*H*), 7.24 (d, *J* = 7.7 Hz, 1 H, Ar*H*), 7.19 (t, *J* = 7.4 Hz, 1

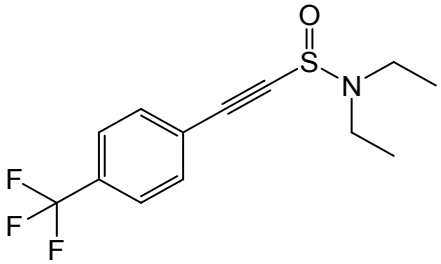
H, Ar*H*), 3.44 (q, *J* = 7.1 Hz, 2 H, NC*H*$_2$), 3.38 (q, *J* = 7.1 Hz, 2 H, NC*H*$_2$), 2.46 (s, 3 H, ArC*H*$_3$), 1.29 (t, *J* = 7.1 Hz, 6 H, NCH$_2$C*H*$_3$); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 141.3 (C_q), 132.7 (CH), 130.4 (CH), 129.8 (CH), 125.9 (CH), 120.1 (C_q), 95.6 (C_q), 90.1 (C_q), 42.6 (CH_2), 20.8 (CH_3), 14.4 (CH_3); ν_{max}/cm^{-1} 3029, 2972, 2933, 2870, 2158, 1604, 1507, 1453, 1407, 1380, 1365, 1345, 1290, 1243, 1222, 1180, 1090, 1007, 926, 898, 842, 815, 782, 762, 708, 652, 590, 530, 474, 449, 411; LRMS (ES+) *m/z* (%) 336 (14), 322 (5), 310 (9), 309 (41), 307 (24), 290 (31), 276 (8), 258 (21), 239 (2), 238 (7), 236 (100), 21 (4), 206 (3), 180 (3), 149 (5), 120 (13); HRMS (ES+) calc'd for $C_{13}H_{18}NOS$ $(M+H)^+$ 236.1109, found 236.1118.

***N*,*N*-Diethyl-2-(4-methoxyphenyl)ethynesulfinamide**



Yellow oil (67%). *Rf* = 0.08 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.46 (d, *J* = 8.3 Hz, 2 H, Ar*H*), 6.88 (d, *J* = 8.4 Hz, 2 H, Ar*H*), 3.84 (s, 3 H, OC*H*$_3$), 3.43 (q, *J* = 7.1 Hz, 2 H, NC*H*$_2$), 3.35 (q, *J* = 7.0 Hz, 2 H, NC*H*$_2$), 1.28 (t, *J* = 7.2 Hz, 6 H, NCH$_2$C*H*$_3$); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 161.2 (C_q), 134.0 (CH), 114.3 (CH), 112.1 (C_q), 97.3 (C_q), 85.3 (C_q), 55.5 (CH_3), 42.7 (CH_2), 14.4 (CH_3); ν_{max}/cm^{-1} 2972, 2934, 2870, 2839, 2549, 2234, 2155, 2051, 2020, 1899, 1602, 1569, 1507, 1461, 1442, 1416, 1380, 1365, 1344, 1293, 1250, 1171, 1087, 1025, 1008, 900, 832, 782, 761, 731, 653, 594, 537, 469, 427; LRMS (CI) *m/z* (%) 371 (5), 323 (11), 285 (4), 253 (16), 252 (100), 203 (17), 179 (10), 121 (6), 120 (9); HRMS (CI) calc'd for $C_{13}H_{18}NO_2S$ $(M+H)^+$ 252.10528, found 252.10534. Data in agreement with literature.[2]

***N*,*N*-Diethyl-2-(4-(trifluoromethyl)phenyl)ethynesulfinamide**



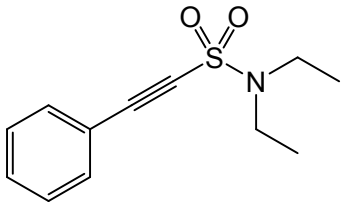
Yellow oil (43%). *Rf* = 0.21 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.63 (m, 4 H, Ar*H*), 3.45 (q, *J* = 7.1 Hz, 2 H, NC*H*$_2$), 3.38 (q, *J* = 7.1 Hz, 2 H, NC*H*$_2$), 1.30 (t, *J* = 7.1 Hz, 6 H, NCH$_2$C*H*$_3$); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 132.5 (CH), 131.9 (q, *J* = 32.8 Hz, C_q), 125.6 (q, *J* = 3.8 Hz, CH), 124.0 (C_q), 123.7 (q, *J* = 272.4 Hz, C_q), 94.2 (C_q), 88.8 (C_q), 42.8 (CH_2), 14.3

(CH_3); ν_{max}/cm^{-1} 2976, 2934, 2873, 2166, 1613, 1458, 1404, 1382, 1318, 1221, 1166, 1124, 1103, 1064, 1013, 927, 901, 839, 783, 759, 736, 657, 645, 598, 566, 645, 598, 566, 524, 464, 443; LRMS (ES+) *m/z* (%) 444 (3), 431 (7), 430 (25), 409 (5), 377 (2), 364 (5), 344 (7), 330 (3), 310 (6), 309 (25), 292 (7), 291 (17), 290 (100), 268 (3), 258 (2); HRMS (ES+) calc'd for $C_{13}H_{15}F_3NOS$ $(M+H)^+$ 290.0826, found 290.0810. Data in agreement with literature.[2]

General procedure for the synthesis alkynyl sulfonamides

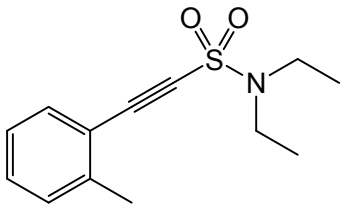
A 50 ml flask was charged with $NaIO_4$ (1.3 eq), H_2O (12 mL) and MeCN (15 mL). The mixture was cooled to 0 °C and stirred until the solid had *completely* dissolved. $RuCl_3.3H_2O$ (1 mmol%) was then added and the reaction mixture was stirred for a further 5 min. A solution of alkynyl sulfinamide (1.00 mmol, 1.0 eq.) in EtOAc (15 mL) was then added in one portion and stirred vigorously until complete consumption of alkynyl sulfinamide had been observed *via* TLC (usually ca. 1 h). The reaction mixture was diluted with CH_2Cl_2 (200 mL), washed with H_2O (100 mL) then brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude product. Purification *via* flash column chromatography (Petroleum Ether/Ethyl acetate) was carried out to yield the alkynyl sulfonamide product.

***N*,*N*-Diethyl-2-phenylethynesulfonamide (2)**



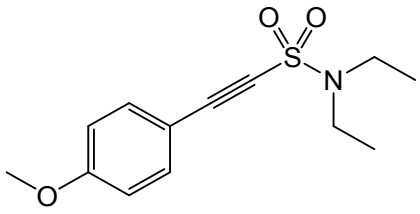
Yellow oil (41%). *Rf* = 0.35 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.54 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.47 (t, *J* = 7.3, Hz, 1 H, Ar*H*), 7.39 (t, *J* = 7.6 Hz, 2 H, Ar*H*), 3.39 (q, *J* = 7.2 Hz, 4 H, NCH_2), 1.30 (t, *J* = 7.2 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 132.6 (CH), 131.0 (CH), 128.8 (CH), 118.7 (C_q), 88.2 (C_q), 83.9 (C_q), 43.0 (CH_2), 13.5 (CH_3); ν_{max}/cm^{-1} 2978, 2939, 2878, 2180,1490, 1468, 1444, 1356, 1298, 1201, 1151, 1098, 1069, 1016, 938, 842, 785, 756, 702, 646, 533; LRMS (ES+) *m/z* (%) 245 (1), 244 (3), 240 (5), 239 (15), 238 (100), 236 (3), 235 (4), 234 (5); HRMS (ES+) calc'd for $C_{12}H_{16}NO_2S$ $(M+H)^+$ 238.0896, found 238.0899. Data in agreement with literature.[2]

***N*,*N*-Diethyl-2-(*o*-tolyl)ethynesulfonamide (25)**



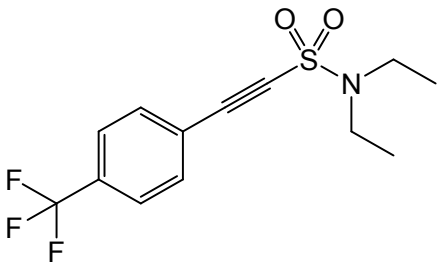
Yellow oil (54%). *Rf* = 0.34 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.50 (d, *J* = 7.7 Hz, 1 H, Ar*H*), 7.36 (t, *J* = 7.6, Hz, 1 H, Ar*H*), 7.26 (d, *J* = 7.8 Hz, 1 H, Ar*H*), 7.21 (t, *J* = 7.6 Hz, 1 H, Ar*H*), 3.39 (q, *J* = 7.2 Hz, 4 H, NCH_2), 2.47 (s, 3 H, ArCH_3), 1.31 (t, *J* = 7.2 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 141.9 (C_q), 133.1 (CH), 131.1 (CH), 130.0 (CH), 126.1 (CH), 118.6 (C_q), 87.5 (C_q), 87.4 (C_q), 43.1 (CH_2), 20.7 (CH_3), 13.5 (CH_3); ν_{max}/cm^{-1}; 2974, 2935, 2874, 2173, 1691,1598, 1483, 1455, 1381, 1355, 1296, 1231, 1200, 1177, 1151, 1111, 1068, 1016, 938, 857, 770, 759, 700, 646, 581, 549, 526, 495, 454, 412; LRMS (ES+) *m/z* (%) 664 (43), 663 (86), 639 (32), 626 (25), 570 (42), 569 (100), 551 (23), 523 (18), 495 (13), 447 (22), 413 (37), 391 (51), 371 (12), 369 (6), 291 (10), 268 (5), 236 (16), 214 (59), 181 (20), 149 (14); HRMS (ES+) calc'd for $C_{13}H_{18}NO_2S$ $(M+H)^+$ 252.1058, found 252.1076.

N,N-Diethyl-2-(4-methoxyphenyl)ethynesulfonamide (33)



Yellow oil (41%). *Rf* = 0.23 (20:80 EA:PE); ^{1}H-NMR 600 MHz, $CDCl_3$) δ_H 7.48 (d, *J* = 8.7 Hz, 2 H, Ar*H*), 6.90 (d, *J* = 8.8 Hz, 2 H, Ar*H*), 3.84 (s, 3 H, OCH_3), 3.37 (q, *J* = 7.2 Hz, 4 H, NCH_2), 1.29 (t, *J* = 7.2 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 161.8 (C_q), 134.4 (CH), 114.5 (CH), 110.4 (C_q), 89.2 (C_q), 82.9 (C_q), 55.6 (CH_3), 43.0 (CH_2), 13.5 (CH_3); ν_{max}/cm^{-1}; 2976, 2937, 2841, 2551, 2174, 2087, 1897, 1602, 1570, 1508, 1463, 1442, 1417, 1383, 1354, 1341, 1295, 1253, 1201, 1174, 1149, 1109, 1067, 1017, 937, 855, 833, 771, 733, 695, 644, 613, 538, 507; LRMS (ES+) *m/z* (%) 269 (8), 268 (100), 252 (6); HRMS (ES+) calc'd for $C_{13}H_{18}NO_3S$ $(M+H)^+$ 268.1007, found 268.1006. Data in agreement with literature.[2]

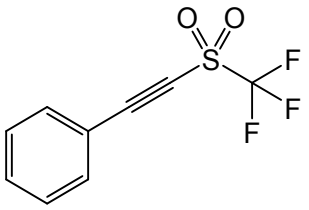
***N,N*-Diethyl-2-(4-(trifluoromethyl)phenyl)ethynesulfonamide (34)**



Yellow oil (38%). *Rf* = 0.47 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H; 7.66 (s, 4 H, Ar*H*), 3.41 (q, *J* = 7.2 Hz, 4 H, NCH_2), 1.31 (t, *J* = 7.2 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (600 MHz,

$CDCl_3$) δ_c 132.9 (CH), 132.7 (q, *J* = 33.0 Hz, C_q), 125.8 (q, *J* = 3.8 Hz, CH), 123.5 (C_q), 122.6 (q, *J* = 272.7 Hz, C_q), 86.0 (C_q), 85.9 (C_q), 43.1 (CH_2), 13.5 (CH_3); ν_{max}/cm^{-1}; 2978, 2939, 2878, 2187, 1613, 1468, 1406, 1384, 1362, 1322, 1240, 1224, 1204, 1158, 1131, 1108, 1067, 1016, 942, 867, 786, 766, 706, 664, 620, 599, 569, 535; LRMS (ES+) *m/z* (%) 323 (5), 308 (12), 307 (25), 306 (100); HRMS (ES+) calc'd for $C_{13}H_{15}F_3NO_2S$ $(M+H)^+$ 306.0775, found 306.0780. Data in agreement with literature.[2]

Procedure for the synthesis of (((trifluoromethyl)sulfonyl)ethynyl)benzene (29)



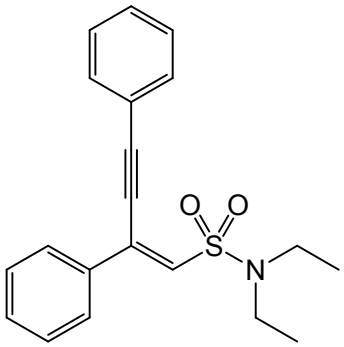
A 100 mL flame-dried flask was charged with a solution of phenylacetylene (0.11 g, 1.08 mmol, 1.0 eq.) in dry Et_2O (10 mL) under argon. The solution was cooled to -78^{o}C and *n*BuLi (0.43 mL of 2.5 M in hexanes, 1.08 mmol, 1.0 eq.) was added dropwise. The mixture was allowed to stir for 30 min. Trifluoromethylsulfonic anhydride (0.34 g, 1.19 mmol, 1.1 eq.) was added dropwise and allowed to stir for a further 20 min. The reaction mixture was allowed to warm to RT, washed with saturated $NaHCO_3$ (10 mL), 1 M HCl (10 mL) then brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude product. Purification *via* flash column chromatography (Petroleum Ether/Ethyl acetate) was carried out to yield the product as a yellow oil (0.11 g, 53%). *Rf* = 0.44 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.71 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.64 (t, *J* = 7.5, Hz, 1 H, Ar*H*), 7.50 (t, *J* = 7.2 Hz, 2 H, Ar*H*); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 133.9 (CH), 133.5 (CH), 129.2 (CH), 119.1 (q, *J* = 323.1 Hz, C_q), 115.9 (C_q), 100.9 (C_q), 77.4 (C_q); ν_{max}/cm^{-1} 3072, 2852, 2175, 2104, 1596, 1489, 1445, 1381, 1219, 1119, 1026, 1000, 926, 863, 759, 686, 595, 561, 535, 504, 458; LRMS (EI) *m/z* (%) 235 (6), 234 (43), 167 (5), 166 (10), 165 (100), 105 (18), 101 (10), 89 (44), 77 (14), 75 (19), 74 (10), 69 (9), 63 (8); HRMS (EI) calc'd for $C_9H_5F_3O_2S$ (M^+) 233.9957, found 233.9956. Data in agreement with literature.[3]

General procedure for the treatment of alkynyl sulfonamides with aromatic acetylene to produce vinylsulfonamides, diynes and enediynes

A 100 mL flame-dried flask was charged with a solution of aromatic acetylene (1.1 eq.) in distilled THF (0.01 M) under argon. The solution was cooled to 0 ^{o}C and *n*BuLi (2.5 M in hexanes, 1.1 eq.) was added dropwise. The mixture was allowed to warm to RT and stirred for a further 10 min. An additional, 100 mL flame-dried flask was charged with a solution of alkynyl sulfonamide (0.15-0.2 mmol, 1.0 eq.) in distilled THF (0.1 M) under argon. The

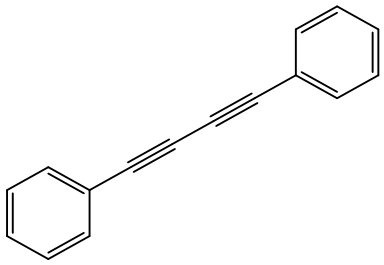
solution was heated to 60 °C and the previously formed lithiated aromatic acetylene solution was added dropwise (addition rate of 0.0025 mmol/min) with constant stirring. The reaction mixture was diluted with CH_2Cl_2 (200 mL), washed with H_2O (100 mL) then brine (100 mL), dried over $MgSO_4$ and concentrated *in vacuo* to yield the crude mixture. Separation *via* flash column chromatography (Petroleum Ether/Ethyl acetate) was carried out to yield the purified products.

(*Z*)-*N*,*N*-Diethyl-2,4-diphenylbut-1-en-3-yne-1-sulfonamide (4)



Yellow oil. *Rf* = 0.30 (20:80 EA:PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.72 (m, 2 H, Ar*H*), 7.62 (m, 2 H, Ar*H*), 7.44 (m, 3 H, Ar*H*), 7.39 (m, 3 H, Ar*H*), 6.88 (s, 1 H, C=C*H*), 3.43 (q, *J* = 7.2 Hz, 4 H, NCH_2), 1.24 (t, *J* = 7.6 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (500 MHz, $CDCl_3$) δ_c 136.2 (C_q), 132.7 (CH), 132.2 (CH), 131.1 (C_q), 130.3 (CH), 129.7 (CH), 128.9 (CH), 128.6 (CH), 127.2 (CH), 122.3 (C_q), 103.6 (C_q), 84.9 (C_q), 41.9 (CH_2), 14.5 (CH_3); ν_{max}/cm^{-1} 3059, 2973, 2929, 2874, 2252, 2211, 1730, 1680, 1598, 1555, 1489, 1444, 1334, 1266, 1200, 1183, 1145, 1017, 934, 910, 815, 758, 735, 692, 648, 653; LRMS (ESI+) *m/z* (%) 868 (2), 763 (1), 701 (100), 644 (1), 460 (2), 340 (58), 267 (1); HRMS (ESI+) calc'd for $C_{20}H_{22}NO_2S$ $(M+H)^+$ 340.1366, found 340.1370.

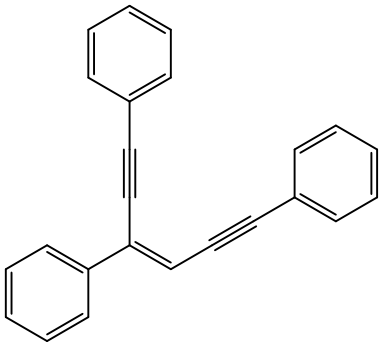
1,4-Diphenylbuta-1,3-diyne (5)



White solid. m.p. 83-87 °C; *Rf* = 0.57 (20:80 EA:PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.54 (d, *J* = 7.6 Hz, 4 H, Ar*H*), 7.36 (m, 6 H, Ar*H*); ^{13}C-NMR (500 MHz, $CDCl_3$) δ_c 132.6 (CH), 129.3 (CH), 128.6 (CH), 121.9 (C_q), 81.6 (C_q), 74.0 (C_q); ν_{max}/cm^{-1} 3047, 2148, 1949, 1879, 1750, 1667, 1591, 1568, 1483, 1438, 1175, 1156, 1066, 1023, 997, 964, 914, 848, 825, 751, 682,

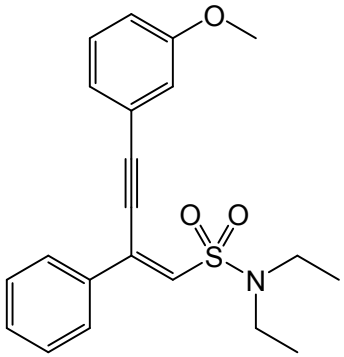
523, 462; LRMS (EI) m/z (%) 204 (3), 203 (9), 202 (100), 200 (17), 150 (3), 101 (6); HRMS (EI) calc'd for $C_{16}H_{10}$ (M^+) 202.0777, found 202.0780.

(*Z*)-Hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (6)



Brown oil. *Rf* = 0.56 (20:80 EA:PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.75 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.61 (m, 2 H, Ar*H*), 7.54 (m, 2 H, Ar*H*), 7.41 (t, *J* = 7.5 Hz, 2 H, Ar*H*), 7.36 (m, 7 H, Ar*H*), 6.58 (s, 1 H, C=C*H*); ^{13}C-NMR (500 MHz, $CDCl_3$) δ_c 136.9 (C_q), 133.5 (CH), 131.9 (CH), 131.7 (CH), 128.9 (CH), 128.8 (CH), 128.7 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 126.2 (CH), 123.5 (C_q), 123.2 (C_q), 113.7 (C_q), 98.5 (C_q), 98.4 (C_q), 89.1 (C_q), 87.7 (C_q); ν_{max}/cm^{-1} 3058, 3031, 2920, 2847, 2198, 2171, 1719, 1676, 1596, 1488, 1443, 1362, 1176, 1069, 914, 843, 756, 690, 529; LRMS (EI) *m/z* (%) 305 (23), 304 (100), 302 (44), 300 (14), 276 (4), 226 (6), 202 (5), 178 (4), 150 (5); HRMS (EI) calc'd for $C_{24}H_{16}$ (M^+) 304.1247, found 304.1246.

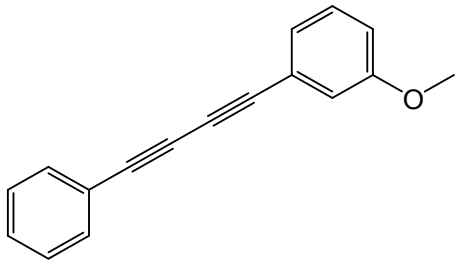
(*Z*)-*N*,*N*-Diethyl-4-(3-methoxyphenyl)-2-phenylbut-1-en-3-yne-1-sulfonamide (13)



Yellow oil. *Rf* = 0.24 (20:80 EA:PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.71 (m, 2 H, Ar*H*), 7.44 (m, 3 H, Ar*H*), 7.29 (t, *J* = 7.8 Hz, 1 H, Ar*H*), 7.21 (d, *J* = 7.6 Hz, 1 H, Ar*H*), 7.13 (m, 1 H, Ar*H*), 6.96 (m, 1 H, Ar*H*), 6.88 (s, 1 H, C=C*H*), 3.83 (s, 3 H, CH_3), 3.42 (q, *J* = 7.2 Hz, 4 H, NCH_2) 1.23 (t, *J* =7.1 Hz, 6 H, NCH$_2$CH_3); ^{13}C-NMR (500 MHz, $CDCl_3$) δ_c 159.5 (C_q), 136.1 (C_q), 132.6 (C_q), 131.2 (CH), 130.3 (CH), 129.7 (CH), 128.9 (CH), 127.2 (CH), 124.7 (CH),123.2 (C_q), 116.7 (CH), 116.4 (CH), 103.5 (C_q), 84.6 (C_q), 55.5 (CH_3), 41.9 (CH_2), 14.5

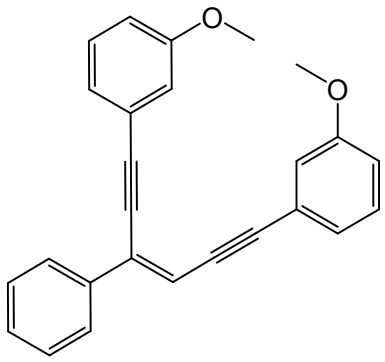
(CH_3); ν_{max}/cm^{-1} 3063, 2928, 2872, 2853, 2204, 1727, 1668, 1596, 1486, 1464, 1429, 1324, 1286, 1262, 1201, 1143, 1040, 1017, 937, 782, 757, 686, 561, 522, 461; LRMS (ES+) *m/z* (%) 371 (5), 370 (100); HRMS (ES+) calc'd for ($C_{21}H_{24}NO_3S$) $(M+H)^+$ 370.1477, found 370.1479.

1-Methoxy-3-(phenylbuta-1,3-diyn-1-yl)benzene (14)



Yellow oil. *Rf* = 0.50 (20:80 EA:PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.53 (dt, *J* = 6.5, 1.7 Hz, 2 H, Ar*H*), 7.35 (m, 3 H, Ar*H*), 7.25 (m, 1 H, Ar*H*), 7.13 (m, 1 H, Ar*H*), 7.05 (s, 1 H, Ar*H*), 6.93 (m, 1 H, Ar*H*), 3.81 (s, 3 H, C*H*$_3$); ^{13}C-NMR (500 MHz, $CDCl_3$) δ_c 159.3 (C_q), 132.6 (CH), 129.6 (CH), 129.3 (CH), 128.5 (CH), 125.2 (CH), 122.8 (C_q), 121.8 (C_q), 117.1 (CH), 116.1 (CH), 83.7 (C_q), 81.5 (C_q), 73.9 (C_q), 73.8 (C_q), 55.4 (CH_3); ν_{max}/cm^{-1} 3060, 2998, 2956, 2924, 2851, 2217, 2189, 2145, 1727, 1670, 1592, 1573, 1485, 1463, 1425, 1342, 1315, 1284, 1251, 1168, 1081, 1042, 993, 916, 870, 855, 780, 755, 685, 580, 563, 526, 467; LRMS (CI) m/z (%) 252 (6), 251 (14), 250 (100), 232 (9); HRMS (CI) calc'd for $C_{17}H_{12}O$ (M^+) 232.0883, found 232.0884.

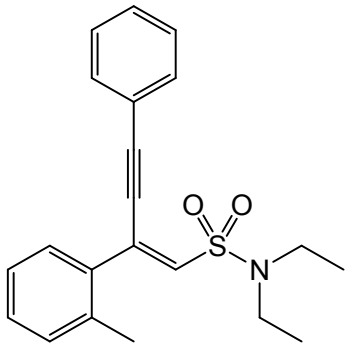
(*Z*)-3,3'-(3-Phenylhexa-3-en-1,5-diyne-1,6-diyl)bis(methoxybenzene) (15)



Yellow oil. *Rf* = 0.34 (20:80 EA:PE); ^{1}H-NMR (500 MHz, $CDCl_3$) δ_H 7.74 (d, *J* = 7.1 Hz, 2 H, Ar*H*), 7.39 (m, 3 H, Ar*H*), 7.24 (m, 3 H, Ar*H*), 7.14 (m, 2 H, Ar*H*), 7.06 (m, 1 H, Ar*H*), 6.91 (m, 2 H, Ar*H*), 6.57 (s, 1 H, C=C*H*), 3.79 (s, 3 H, C*H*$_3$), 3.77 (s, 3 H, C*H*$_3$); ^{13}C-NMR (500 MHz, $CDCl_3$) δ_c 159.5 (C_q), 159.4 (C_q), 136.7 (CH), 135.1 (C_q), 133.7 (C_q), 129.6 (C_q), 129.6 (CH), 129.0 (CH), 128.7 (CH), 126.2 (CH), 124.4 (C_q), 124.3 (CH), 116.4 (CH), 116.2 (CH), 115.6 (CH), 115.5 (CH), 113.8 (CH), 113.7 (CH), 98.5 (C_q), 98.4 (C_q), 97.6 (C_q), 88.7 (C_q), 55.4

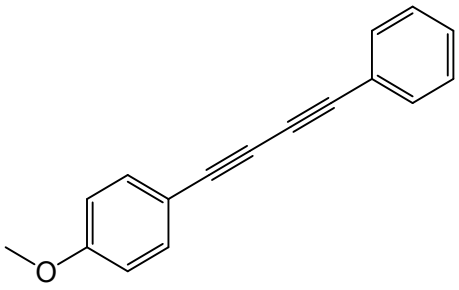
(CH_3), 55.3 (CH_3); ν_{max}/cm^{-1} 3061, 3002, 2958, 2922, 2849, 2835, 2200, 2189, 1724, 1685, 1595, 1575, 1486, 1463, 1450, 1428, 1318, 1285, 1263, 1211, 1175, 1040, 855, 781, 761, 737, 686, 565, 518, 468; LRMS (CI) *m/z* (%) 383 (3), 382 (12), 367 (14), 366 (24), 365 (100); HRMS (CI) calc'd for $C_{26}H_{21}O_2$ $(M+H)^+$ 365.1536, found 365.1537.

(*E*)-*N*,*N*-Diethyl-4-phenyl-2-(*o*-tolyl)but-1-en-3-yne-1-sulfonamide (28)



Colourless oil. *Rf* = 0.31 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.52 (d, *J* = 7.1 Hz, 2 H, Ar*H*), 7.35 (m, 3 H, Ar*H*), 7.30 (m, 1 H, Ar*H*), 7.26 (m, 3 H, Ar*H*), 6.48 (s, 1 H, C=C*H*), 3.43 (q, *J* = 7.2 Hz, 4 H, NCH_2), 2.49 (s, 3 H, ArCH_3), 1.26 (t, *J* = 7.1 Hz, 6 H, NCH_2CH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 137.6 (C_q), 135.7 (C_q), 134.6 (CH), 133.7 (C_q), 132.2 (CH), 131.0 (CH), 129.6 (CH), 129.2 (CH), 128.6 (CH), 128.5 (CH), 126.4 (CH), 122.4 (C_q), 104.1 (C_q), 85.4 (C_q), 41.9 (CH_2), 20.3 (CH_3), 14.6 (CH_3); ν_{max}/cm^{-1} 3048, 2972, 2933, 2873, 2207, 1598, 1562, 1488, 1456, 1443, 1382, 1352, 1332, 1199, 1142, 1069, 1048, 1015, 994, 932, 879, 826, 755, 724, 688, 569, 555, 529, 507, 462, 429; LRMS (ES+) *m/z* (%) 408 (3), 378 (3), 377 (12), 376 (45), 356 (9), 355 (27), 354 (100); HRMS (ES+) calc'd for $C_{21}H_{24}NO_2S$ $(M+H)^+$ 354.1528, found 354.1507.

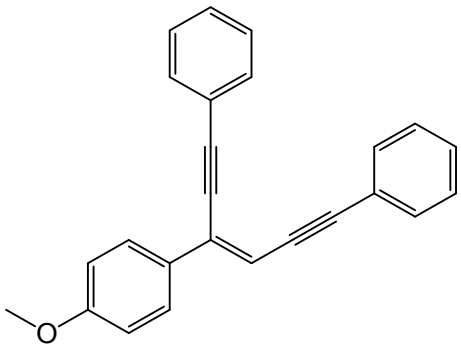
1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (35)



Colourless oil. *Rf* = 0.49 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.53 (d, *J* = 6.6 Hz, 2 H, Ar*H*), 7.48 (d, *J* = 8.6 Hz, 2 H, Ar*H*), 7.35 (m, 3 H, Ar*H*), 6.87 (d, *J* = 8.7 Hz, 2 H, Ar*H*), 3.83 (s, 3 H, OCH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 160.5 (C_q), 134.3 (CH), 132.6 (CH), 129.2 (CH), 128.5 (CH), 122.1 (C_q), 114.3 (CH), 113.8 (C_q), 81.9 (C_q), 81.1 (C_q), 74.3 (C_q), 72.8 (C_q), 55.5 (CH_3); ν_{max}/cm $^{-1}$ 3074, 2953, 2923, 2842, 2541, 2216, 2139, 1976, 1887,

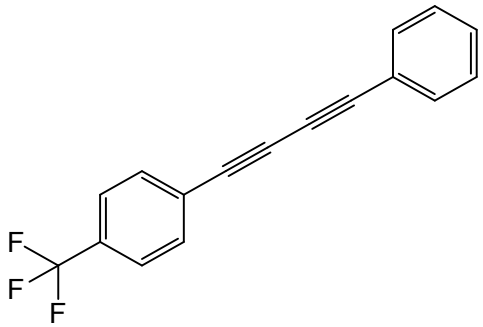
1759, 1599, 1566, 1506, 1487, 1457, 1439, 1344, 1290, 1246, 1170, 1106, 1070, 1026, 952, 939, 918, 827, 757, 732, 689, 643, 616, 532, 491, 443; LRMS (CI) *m/z* (%) 251 (19), 250 (100), 234 (12), 233 (62); HRMS (CI) calc'd for $C_{17}H_{13}O$ $(M+H)^+$ 233.0961, found 233.0960.

(*Z*)-(3-(4-methoxyphenyl)hexa-3-en-1,5-diyne-1,6-diyl)dibenzene (36)



Brown oil. *Rf* = 0.44 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.70 (d, *J* = 8.6 Hz, 2 H, Ar*H*), 7.61 (m, 2 H, Ar*H*), 7.53 (m, 2 H, Ar*H*), 7.38 (m, 3 H, Ar*H*), 7.34 (m, 3 H, Ar*H*), 6.94 (d, *J* = 8.7 Hz, 2 H, Ar*H*), 6.48 (s, 1 H, C=C*H*), 3.86 (s, 3 H, OCH_3); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 160.4 (C_q), 133.0 (C_q), 131.9 (CH), 131.7 (CH), 129.5 (C_q), 128.8 (CH), 128.6 (CH), 128.5 (CH), 128.5 (CH), 127.6 (CH), 123.7 (C_q), 123.3 (C_q), 114.1 (CH), 111.7 (CH), 98.2 (C_q), 97.9 (C_q), 89.4 (C_q), 87.8 (C_q), 55.5 (CH_3); ν_{max}/cm^{-1} 3052, 2954, 2926, 2836, 2199, 2179, 1880, 1726, 1669, 1603, 1577, 1509, 1487, 1460, 1441, 1362, 1304, 1287, 1250, 1177, 1114, 1068, 1030, 913, 823, 754, 689, 605, 527, 448; LRMS (CI) *m/z* (%) 336 (27), 335 (100); HRMS (CI) calc'd for $C_{25}H_{19}O$ $(M+H)^+$ 335.1430, found 335.1431.

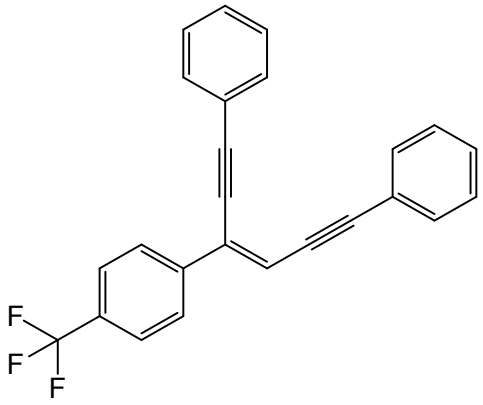
1-(phenylbuta-1,3-diyn-1-yl)-4-(trifluoromethyl)benzene (37)



Yellow oil. *Rf* = 0.66 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.55 (d, *J* = 7.0 Hz, 2 H, Ar*H*), 7.63 (m, 7 H, Ar*H*); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 132.8 (CH), 132.7 (CH), 130.9 (q, *J* = 33.1 Hz, C_q), 129.7 (CH), 128.6 (CH), 125.8 (C_q), 125.5 (q, *J* = 3.8 Hz, CH), 123.9 (q, *J* = 272.6 Hz, C_q), 121.5 (C_q), 83.0 (C_q), 79.9 (C_q), 76.3 (C_q), 73.5 (C_q); ν_{max}/cm^{-1} 2955, 2924, 2853, 2256, 2213, 1916, 1796, 1667, 1612, 1570, 1488, 1462, 1443, 1405, 1317, 1167,

1104, 1064, 1012, 912, 834, 753, 686, 593, 519; LRMS (CI) *m/z* (%) 540 (8), 371 (11), 370 (44), 342 (9), 288 (5), 271 (19), 270 (100), 260 (10), 221 (8).

(Z)-(3-(4-(trifluoromethyl)phenyl)hexa-3-en-1,5-diyne-1,6-diyl)dibenzene (38)



Yellow oil. *Rf* = 0.57 (20:80 EA:PE); ^{1}H-NMR (600 MHz, $CDCl_3$) δ_H 7.85 (d, *J* = 8.2 Hz, 2 H, Ar*H*), 7.67 (d, *J* = 8.2 Hz, 2 H, Ar*H*), 7.61 (m, 2 H, Ar*H*), 7.55 (m, 2 H, Ar*H*), 7.40 (m, 3 H, Ar*H*), 7.37 (m, 3 H, Ar*H*), 6.64 (s, 1 H, C=C*H*); ^{13}C-NMR (600 MHz, $CDCl_3$) δ_c 132.1 (C_q), 131.9 (CH), 131.8 (CH), 131.8 (CH), 131.7 (CH), 130.3 (q, *J* = 31.4 Hz, C_q), 129.1 (CH), 129.0 (CH), 128.6 (CH), 128.6 (CH), 125.7 (q, *J* = 3.4 Hz, CH), 125.0 (C_q), 124.1 (q, *J* = 273.6 Hz, C_q), 123.2 (C_q), 116.1 (C_q), 99.9 (C_q), 99.1 (C_q), 88.7 (C_q), 87.0 (C_q); ν_{max}/cm^{-1} 3079, 3060, 3023, 2954, 2923, 2853, 2183, 1632, 1616, 1597, 1490, 1461, 1443, 1410, 1377, 1324, 1167, 1125, 1069, 1016, 914, 843, 831, 755, 689, 620, 605, 529; LRMS (CI) *m/z* (%) 392 (3), 391 (11), 390 (33), 378 (5), 375 (8), 374 (28), 373 (100), 372 (12), 370 (5), 353 (4), 350 (9), 345 (26), 322 (9); HRMS (CI) calc'd for $C_{25}H_{16}F_3$ $(M+H)^+$ 373.1199, found 373.1199.

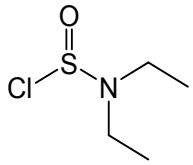
References

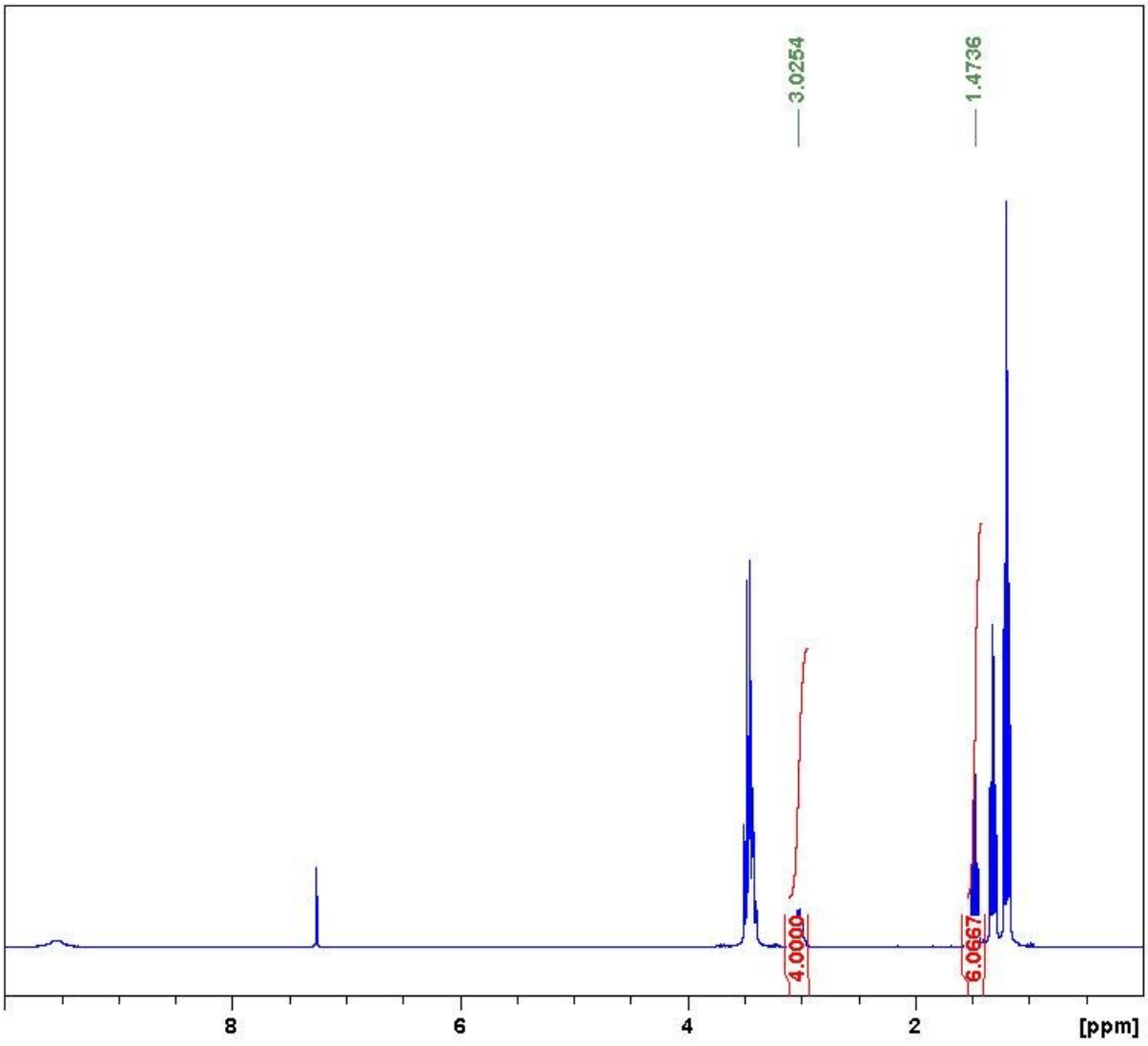
1. Gray, V., **2014**. *New Applications for Sulfur-Based Leaving Groups in Synthesis.* PhD. University College London.

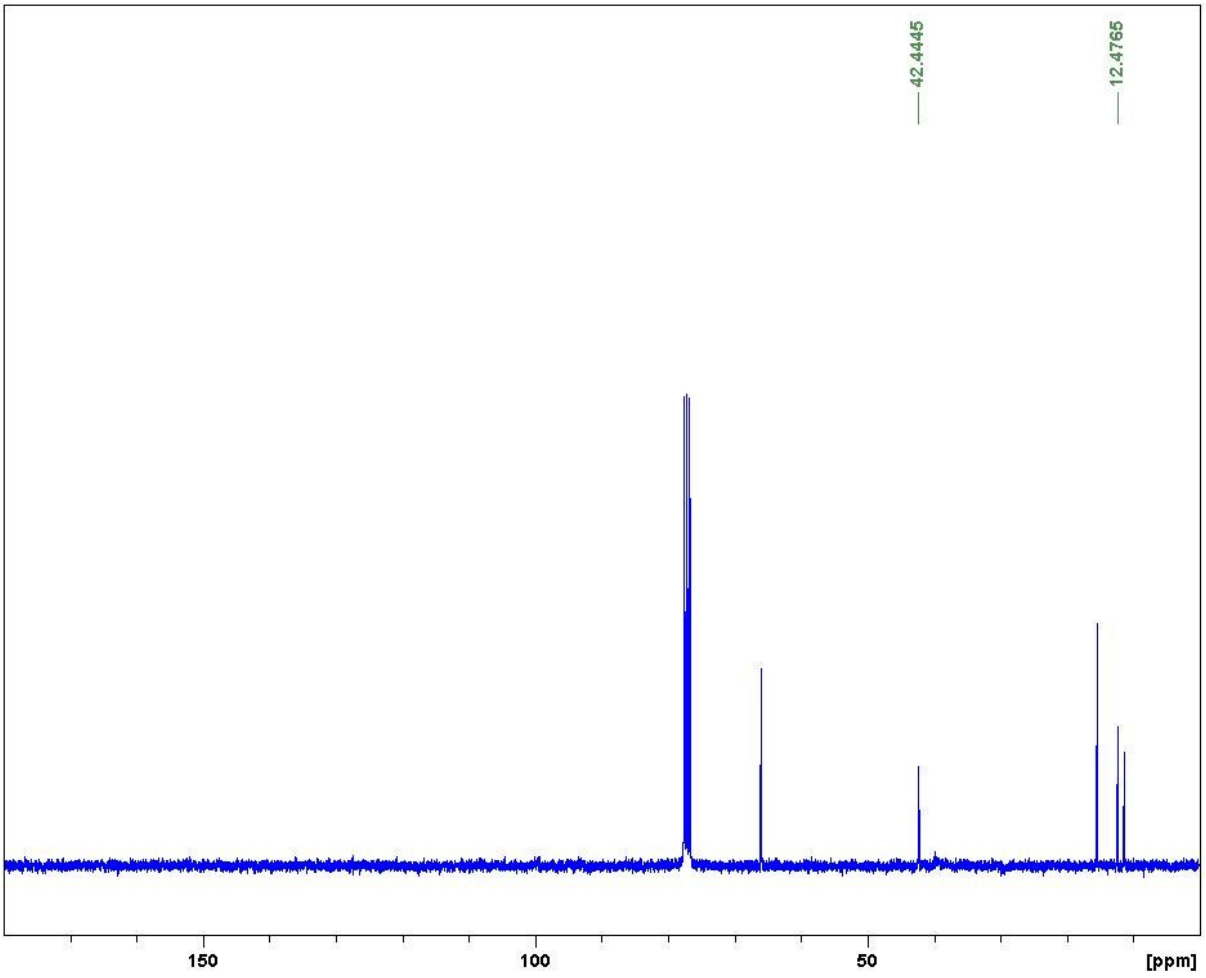
2. Gray, V., Slater, B., Wilden, *J., Chem. Eur. J.*, **2012**, *18*, 15582-15585.

3. Massa, F., Hanack, M., Subramanian, L., *J. Fluorine Chem.*, **1982**, *19*, 601-615.

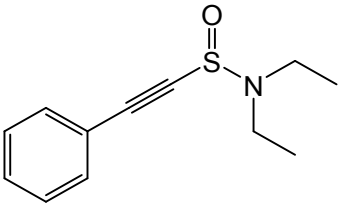
***N,N*-Diethylsulfurous chloride - ^{1}H-NMR and ^{13}C-NMR**

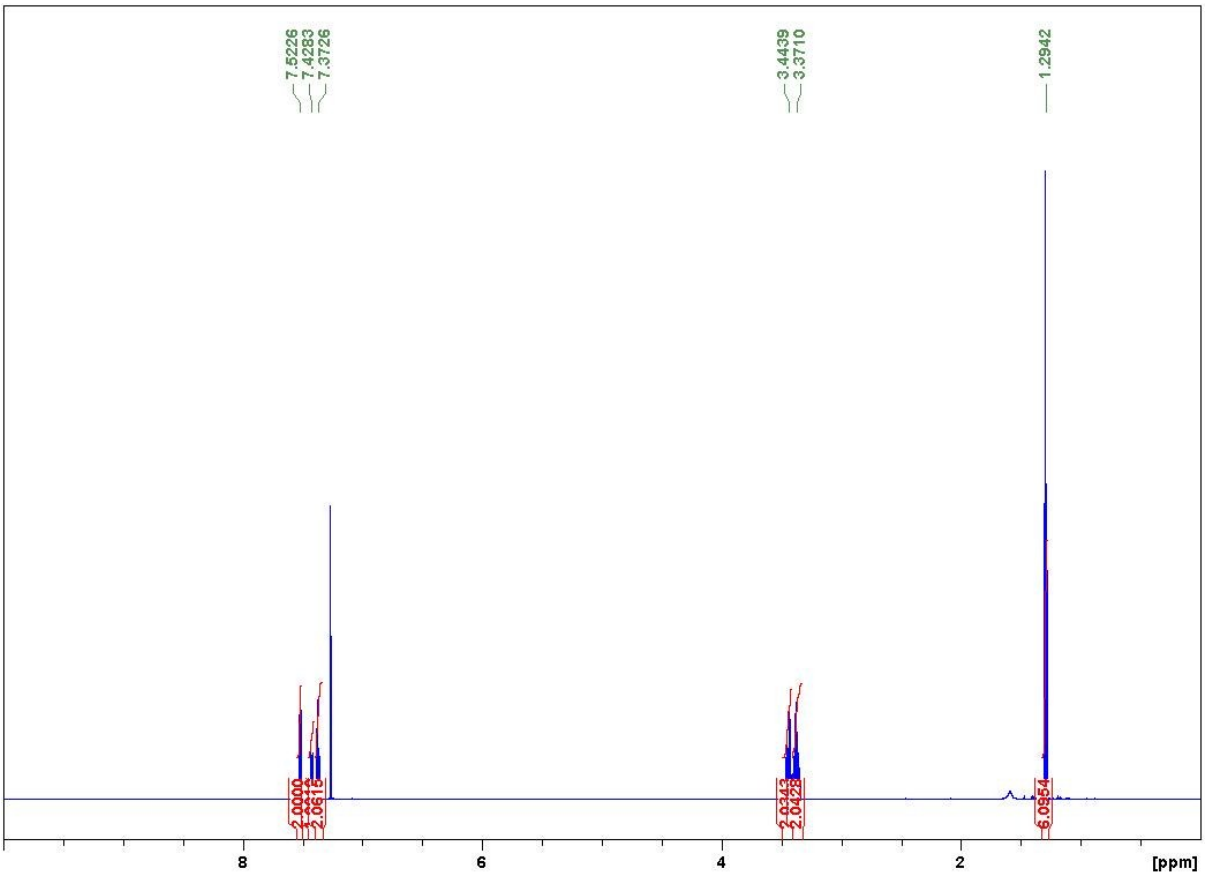


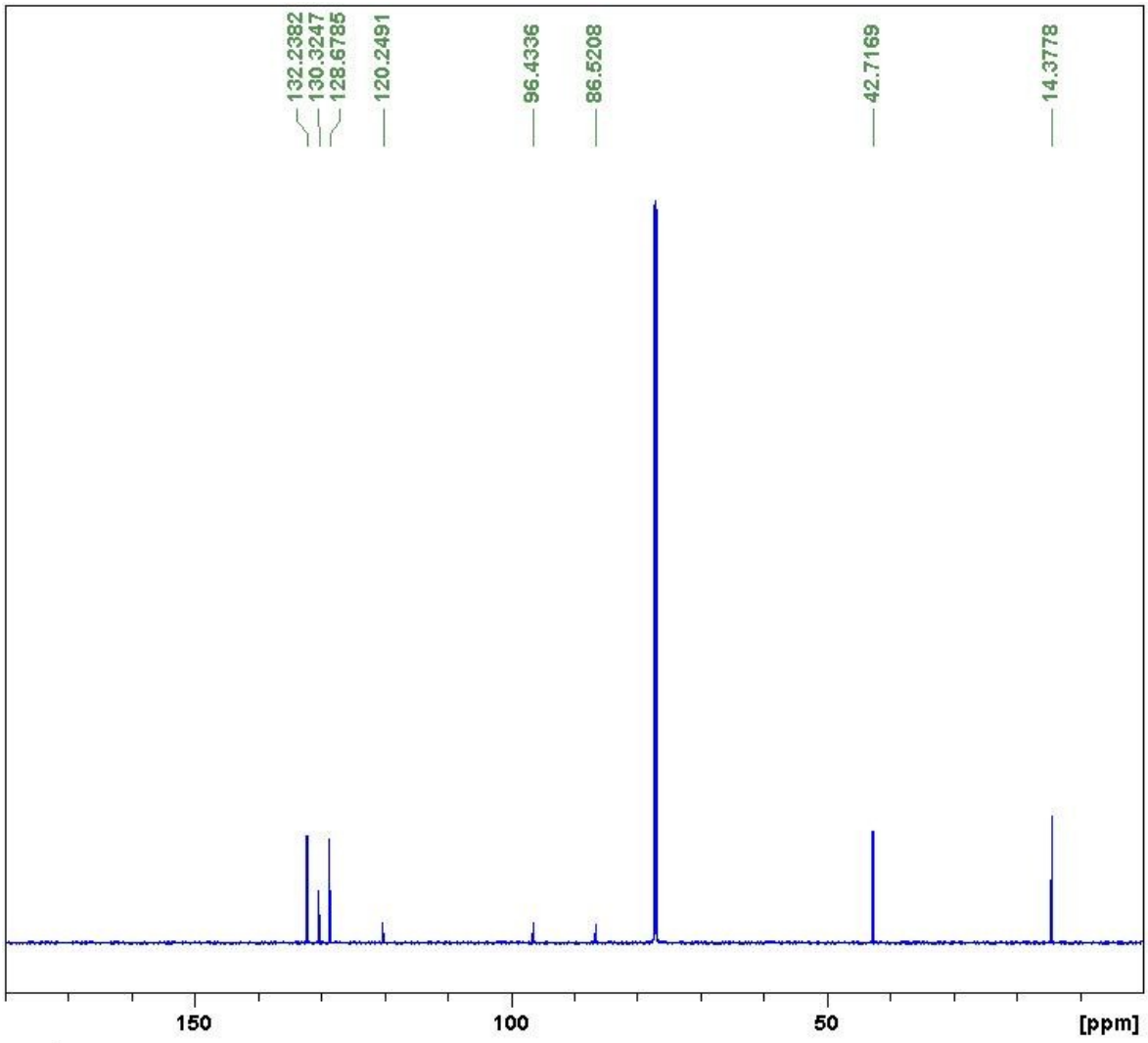


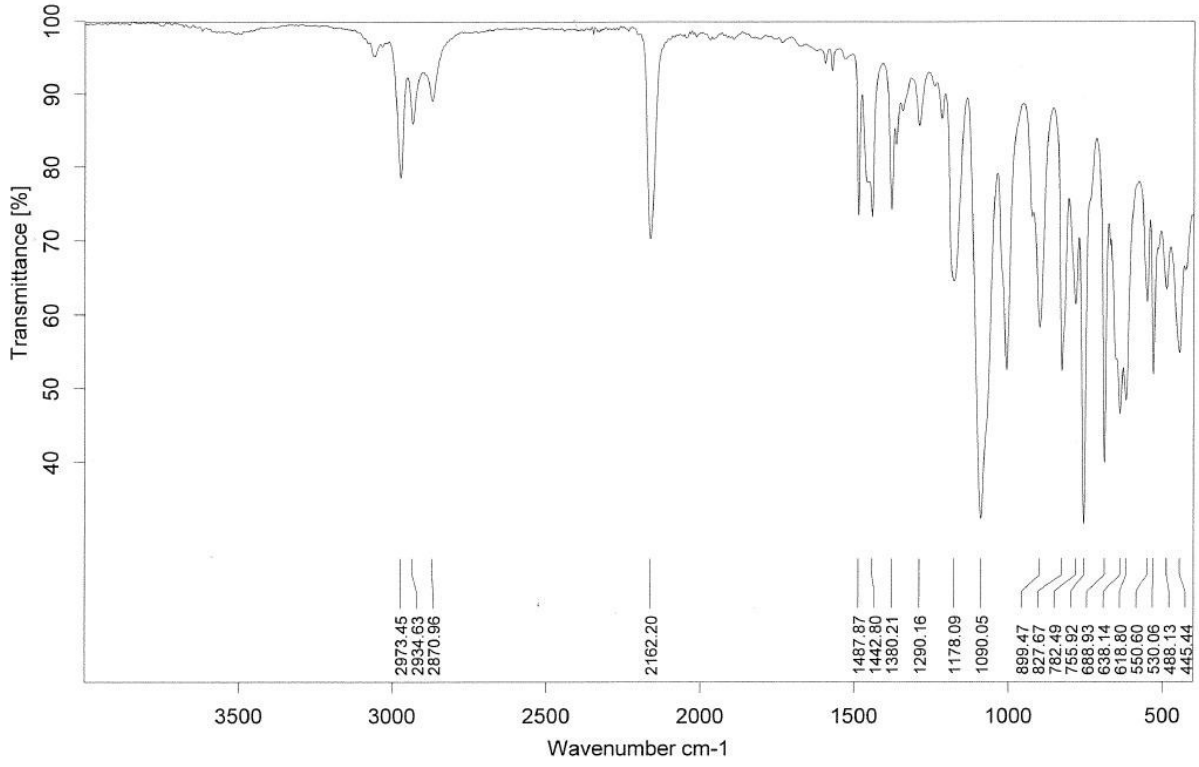

42.4445
12.4765
150
100
50
[ppm]

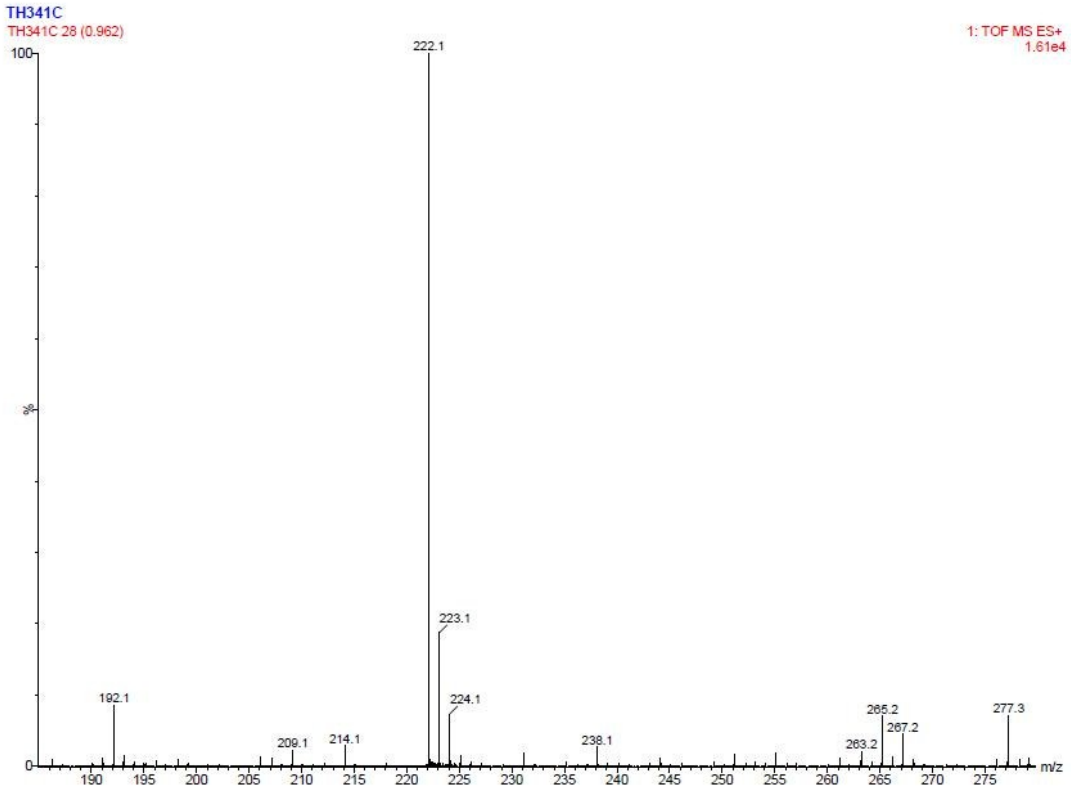
_N_,_N_-Diethyl-2-phenylethynesulfinamide - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

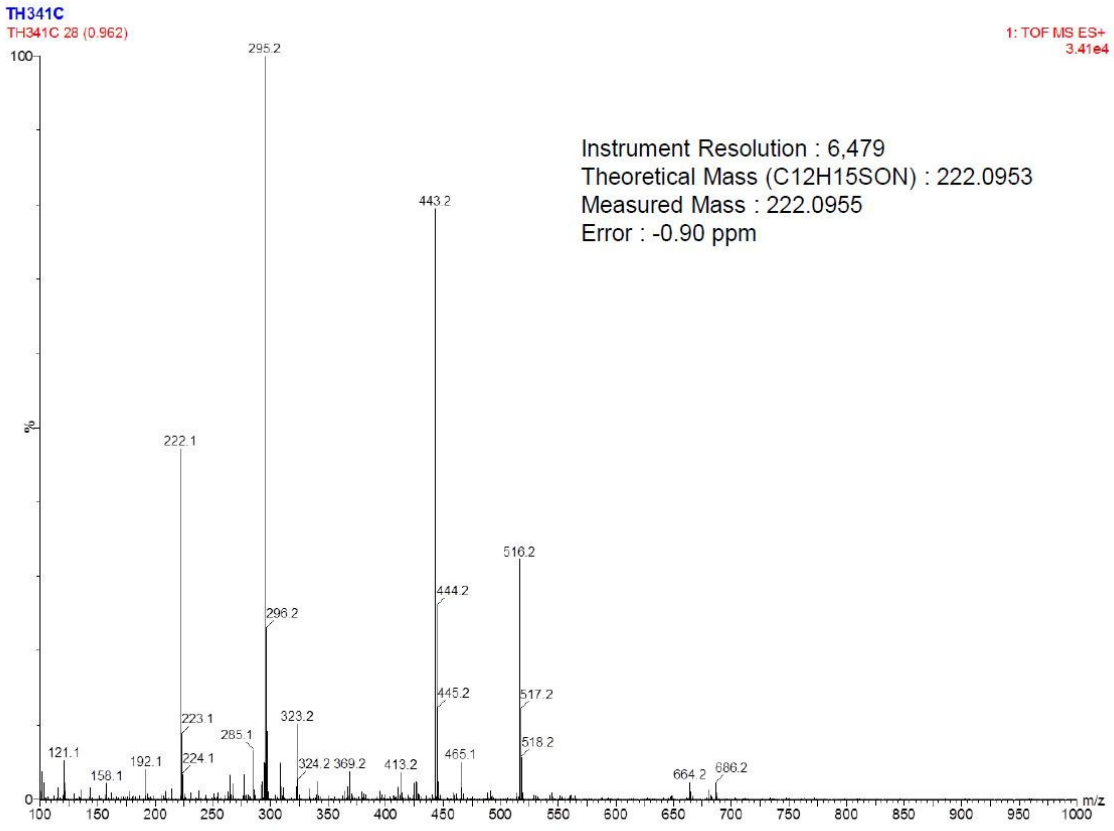




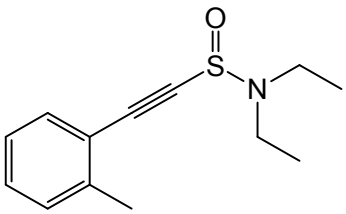

132.2382
130.3247
128.6785
120.2491
96.4336
86.5208
42.7169
14.3778
150
100
50
[ppm]

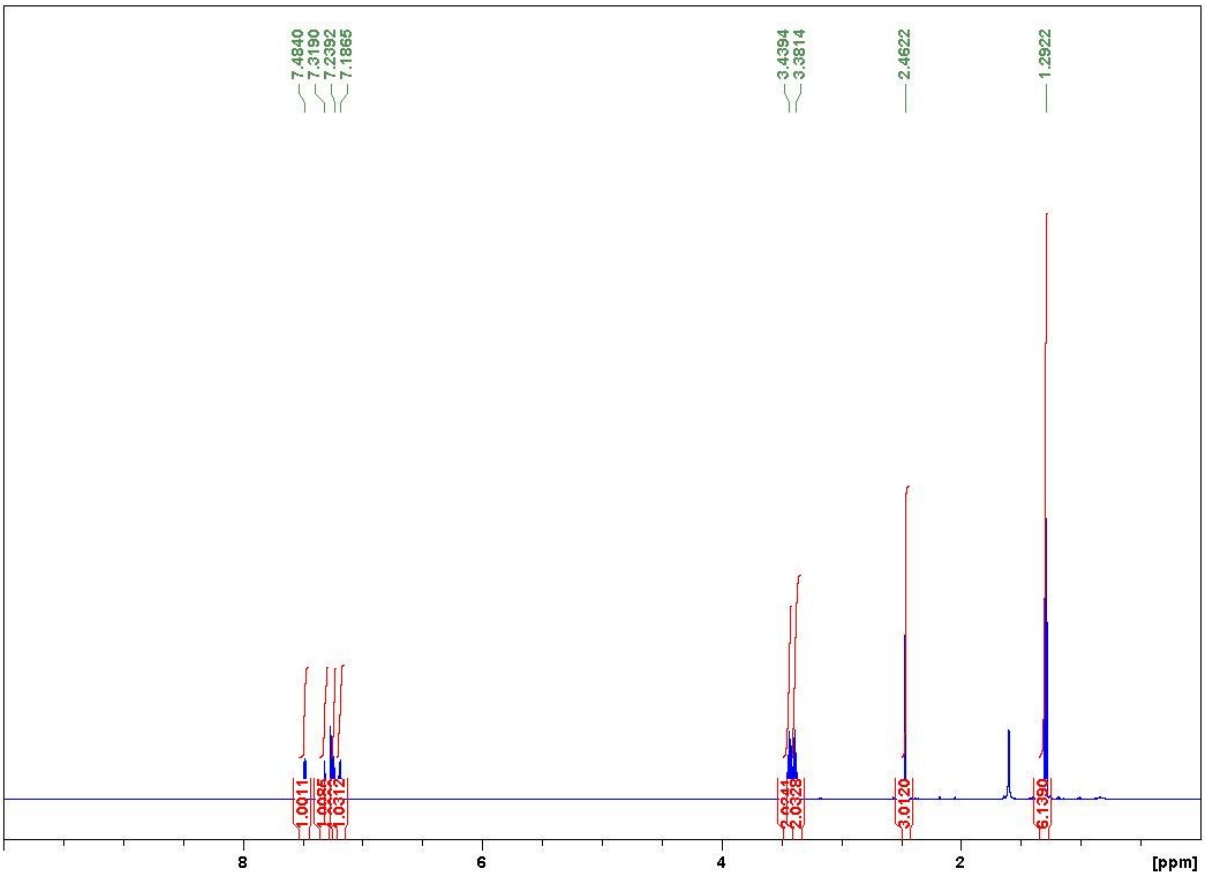

Transmittance [%]
100
90
80
70
60
50
40
2973.45
2934.63
2870.96
2162.20
1487.87
1442.80
1380.21
1290.16
1178.09
1090.05
899.47
827.67
782.49
755.92
688.93
638.14
618.80
550.60
530.06
488.13
445.44
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

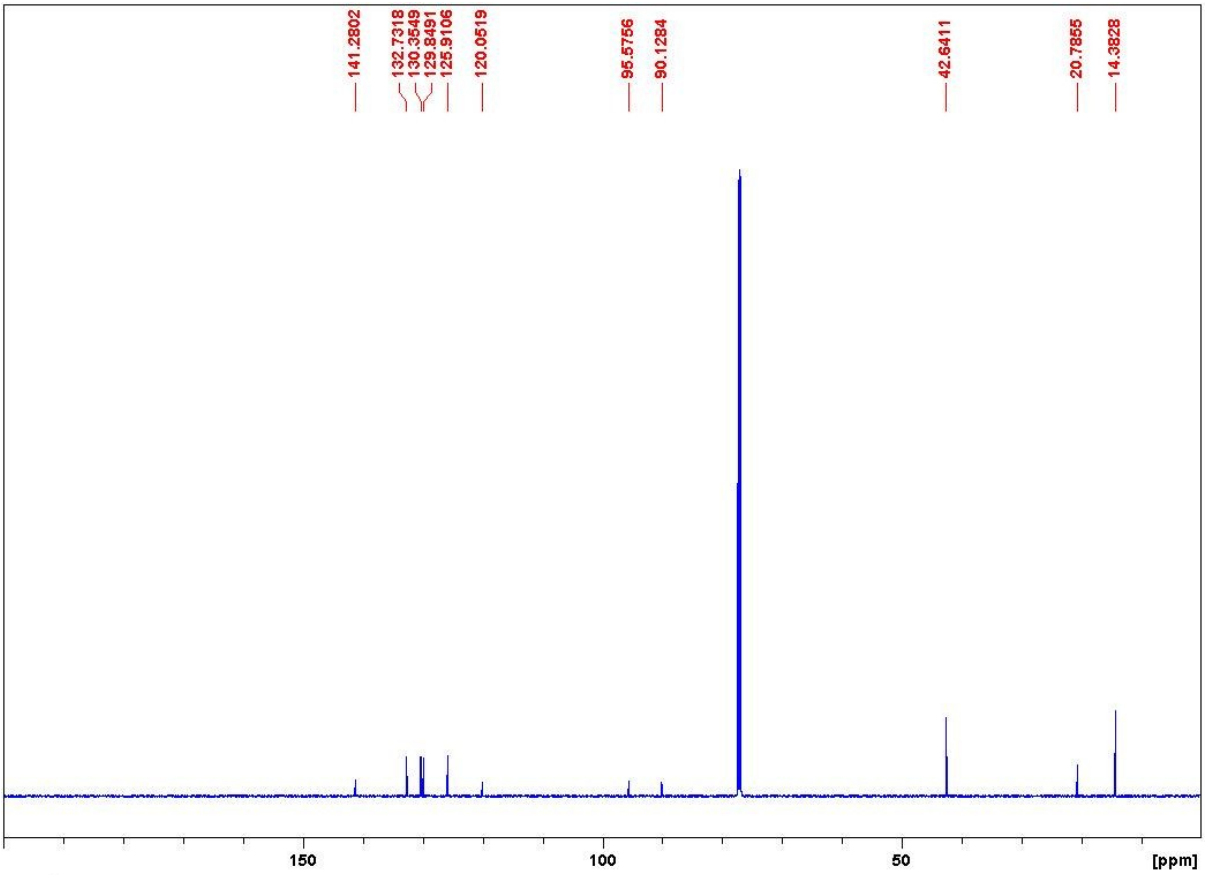

TH341C
TH341C 28 (0.962)
1: TOF MS ES+
1.61e4
100
%
0
222.1
223.1
192.1
224.1
209.1
214.1
238.1
265.2
267.2
263.2
277.3
190 195 200 205 210 215 220 225 230 235 240 245 250 255 260 265 270 275
m/z

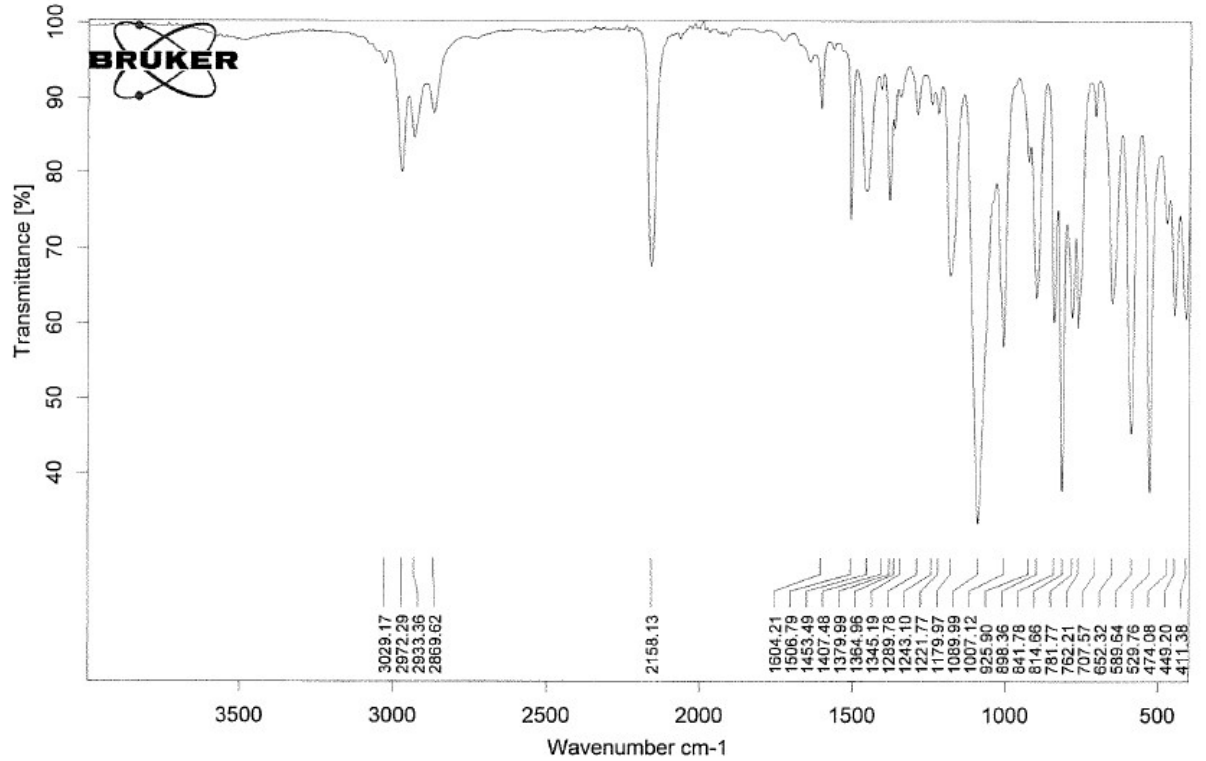

TH341C
TH341C 28 (0.962)
1: TOF MS ES+
3.41e4
100
%
0
295.2
443.2
222.1
516.2
444.2
296.2
445.2
517.2
223.1
323.2
285.1
518.2
121.1
192.1
224.1
324.2 369.2
413.2
465.1
158.1
664.2
686.2
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z
Instrument Resolution : 6,479
Theoretical Mass (C12H15SON) : 222.0953
Measured Mass : 222.0955
Error : -0.90 ppm

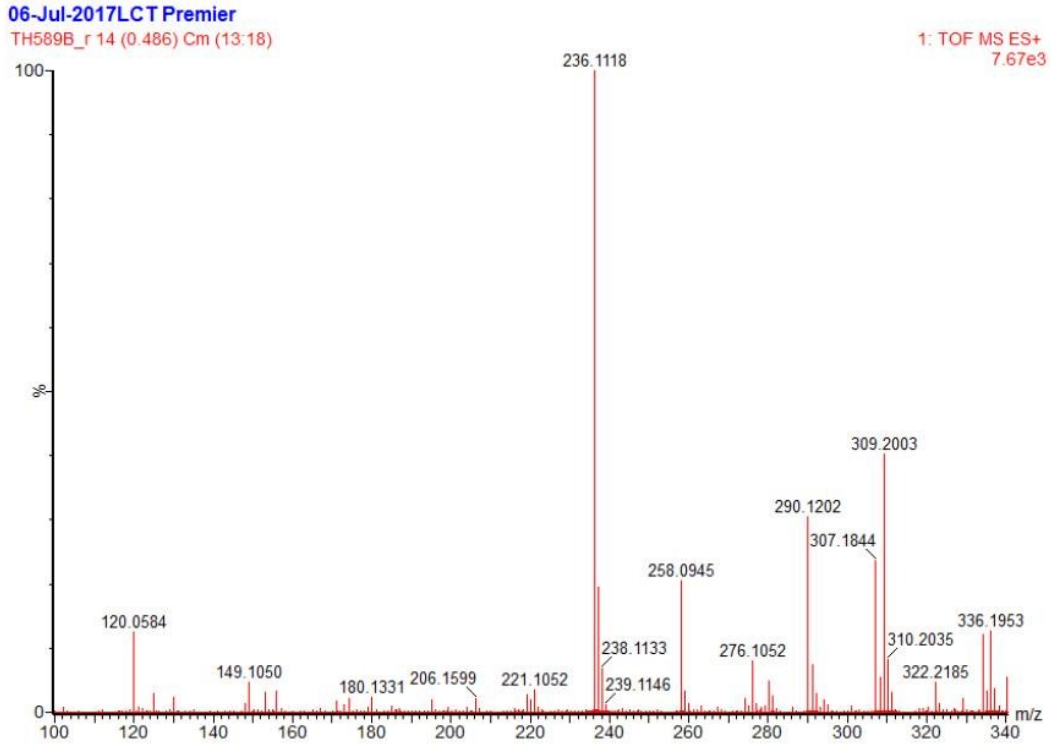
_N_,_N_-Diethyl-2-(_o_-tolyl)ethynesulfinamide (3) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS






141.2802
132.7318
130.3549
129.8491
125.9106
120.0519
95.5756
90.1284
42.6411
20.7855
14.3828
150
100
50
[ppm]


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
3029.17
2972.29
2933.36
2869.62
2158.13
1604.21
1506.79
1453.49
1407.48
1379.99
1364.96
1345.19
1289.78
1243.10
1221.77
1179.97
1089.99
1007.12
925.90
898.36
841.78
814.66
781.77
762.21
707.57
652.32
589.64
529.76
474.08
449.20
411.38
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


06-Jul-2017LCT Premier
TH589B_r 14 (0.486) Cm (13:18)
1: TOF MS ES+
7.67e3
100
%
0
236.1118
309.2003
290.1202
307.1844
258.0945
120.0584
336.1953
310.2035
238.1133
276.1052
322.2185
149.1050
180.1331
206.1599
221.1052
239.1146
m/z
100
120
140
160
180
200
220
240
260
280
300
320
340

UCL Chemistry Mass Spectrometry Facility

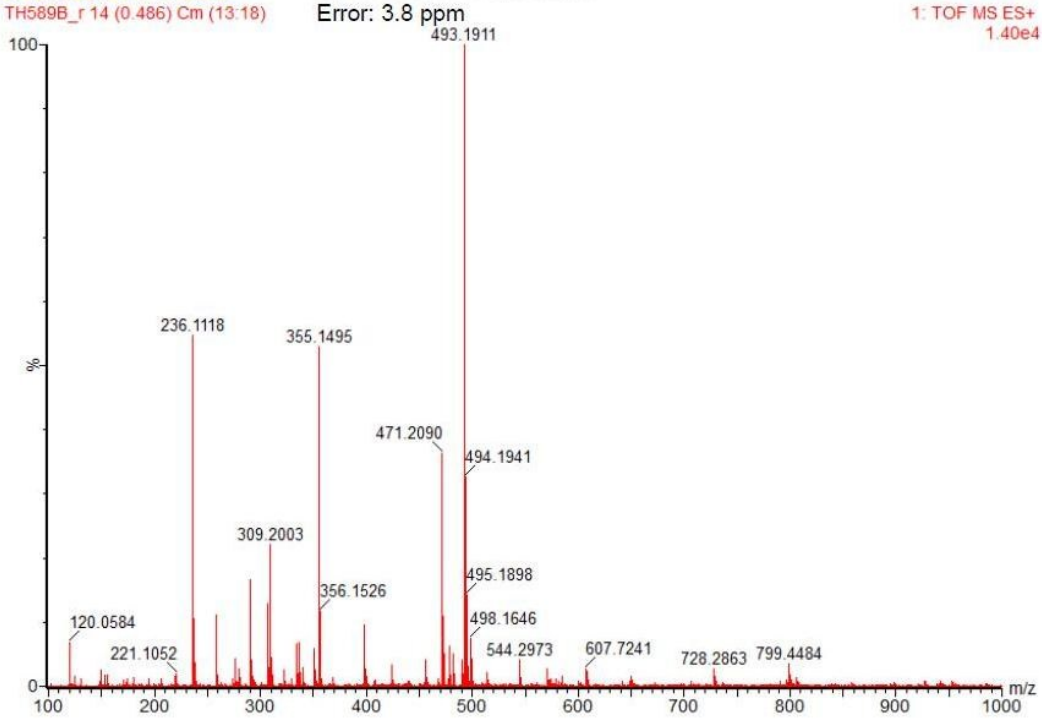
[M+H]+

06-Jul-2017LCT Premier

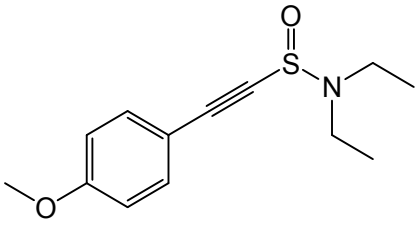
TH589B_r 14 (0.486) Cm (13:18)

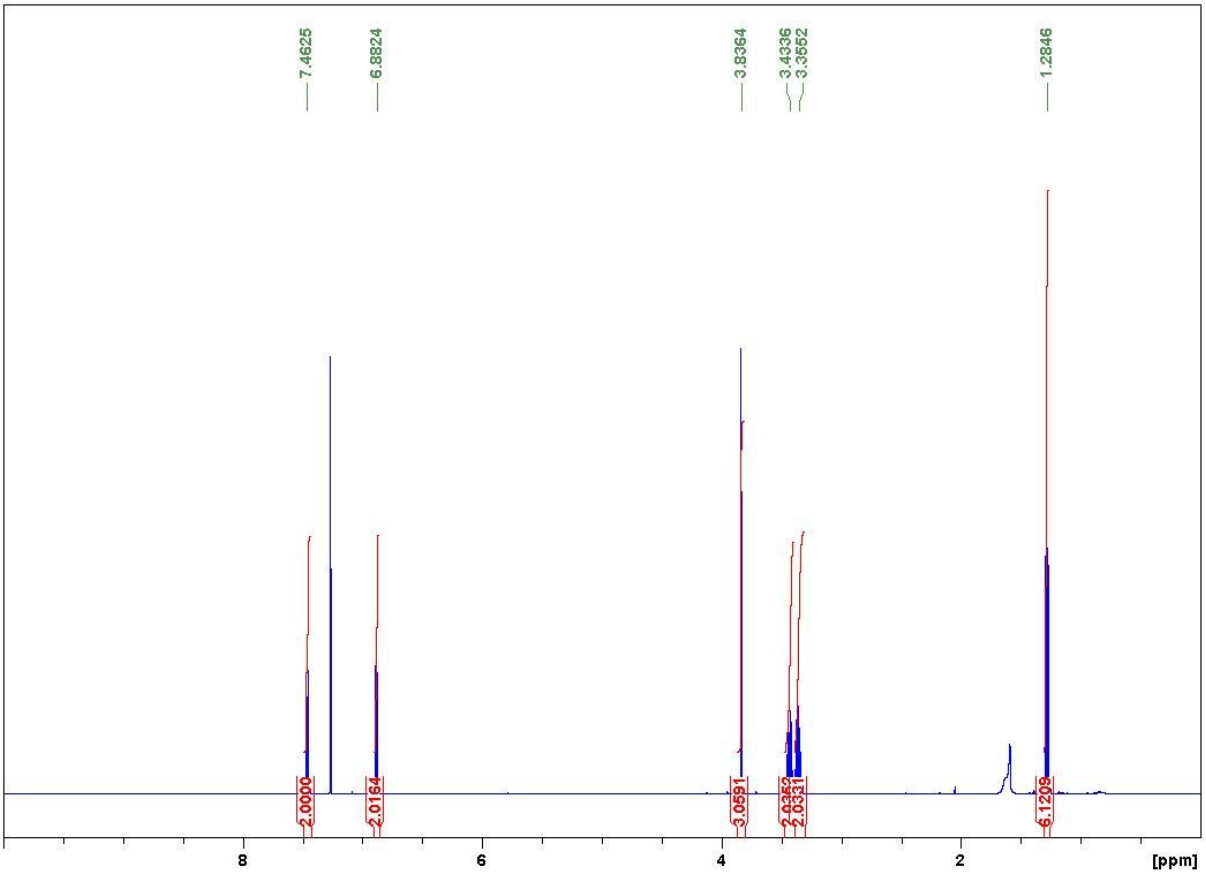
Instrument Resolution: 10,000
Theoretical Mass [C13H18NOS]+:236.1109
Measured Mass : 236.1118
Error: 3.8 ppm

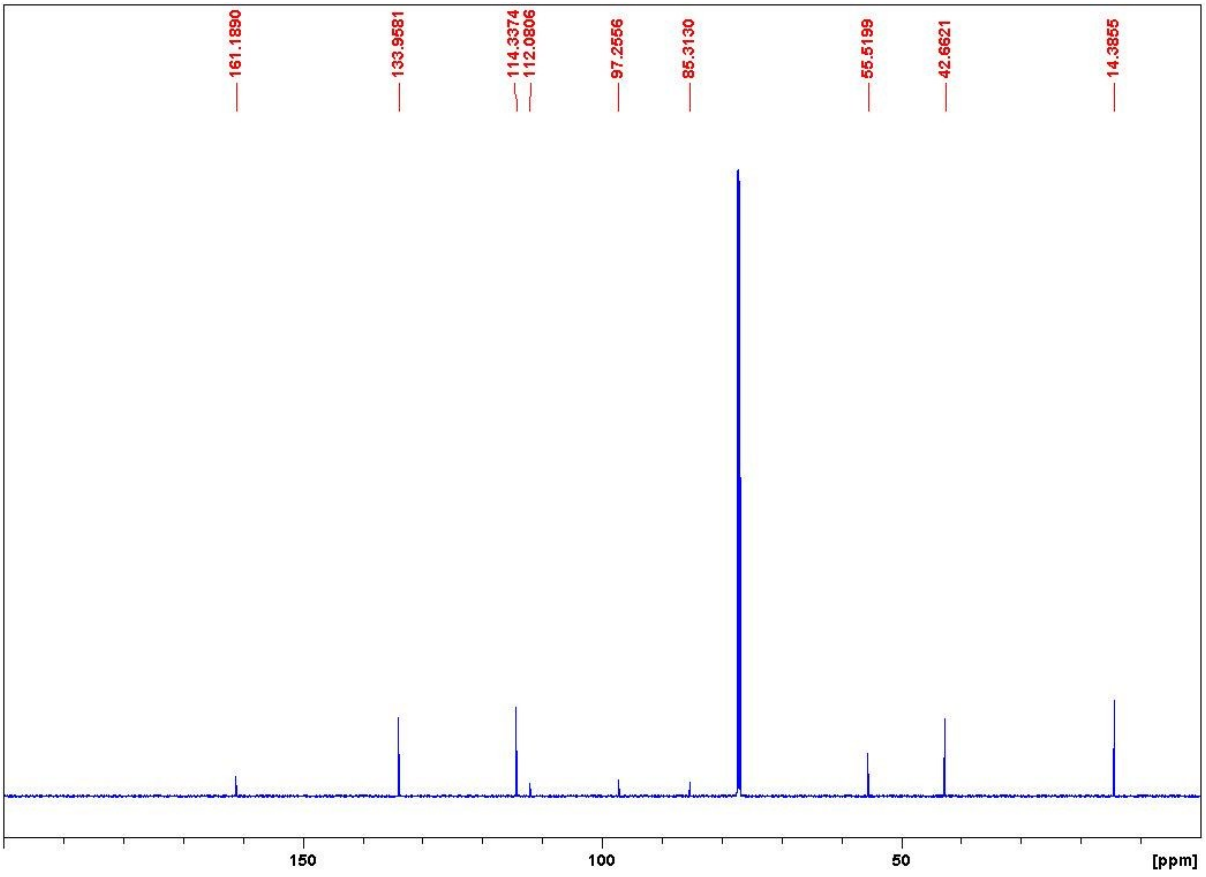
1: TOF MS ES+
1.40e4

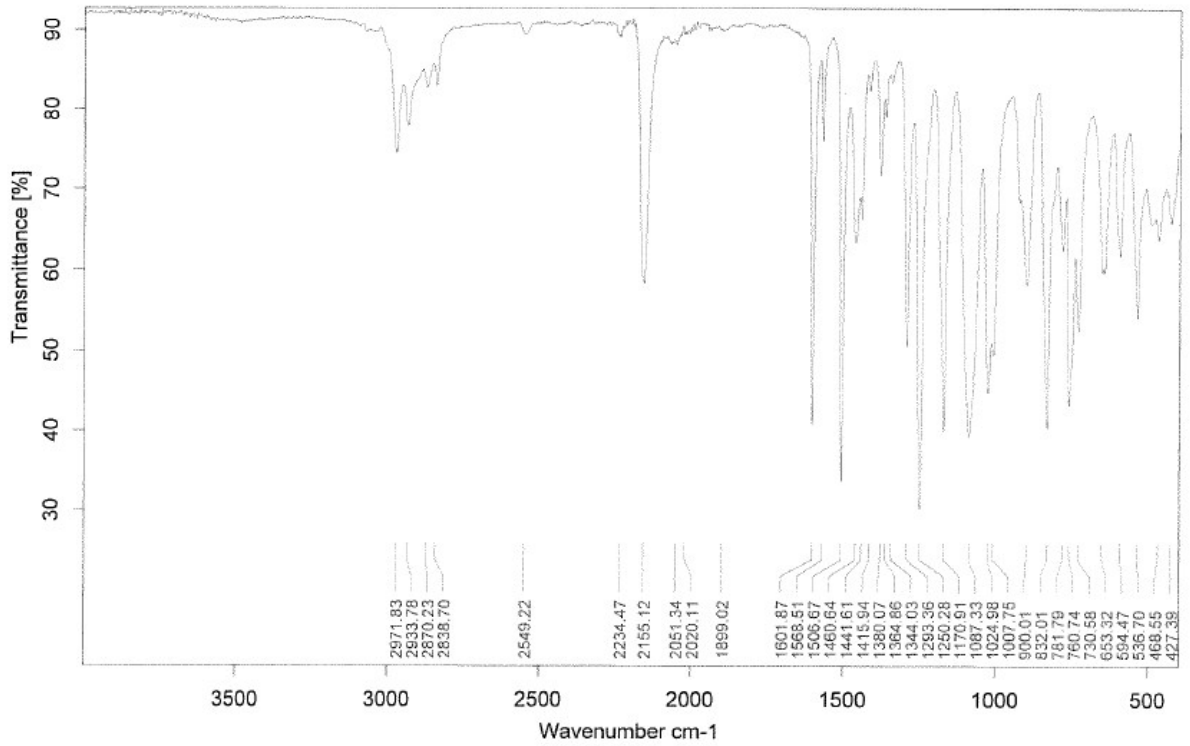


***N*,*N*-Diethyl-2-(4-methoxyphenyl)ethynesulfinamide (4) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS**

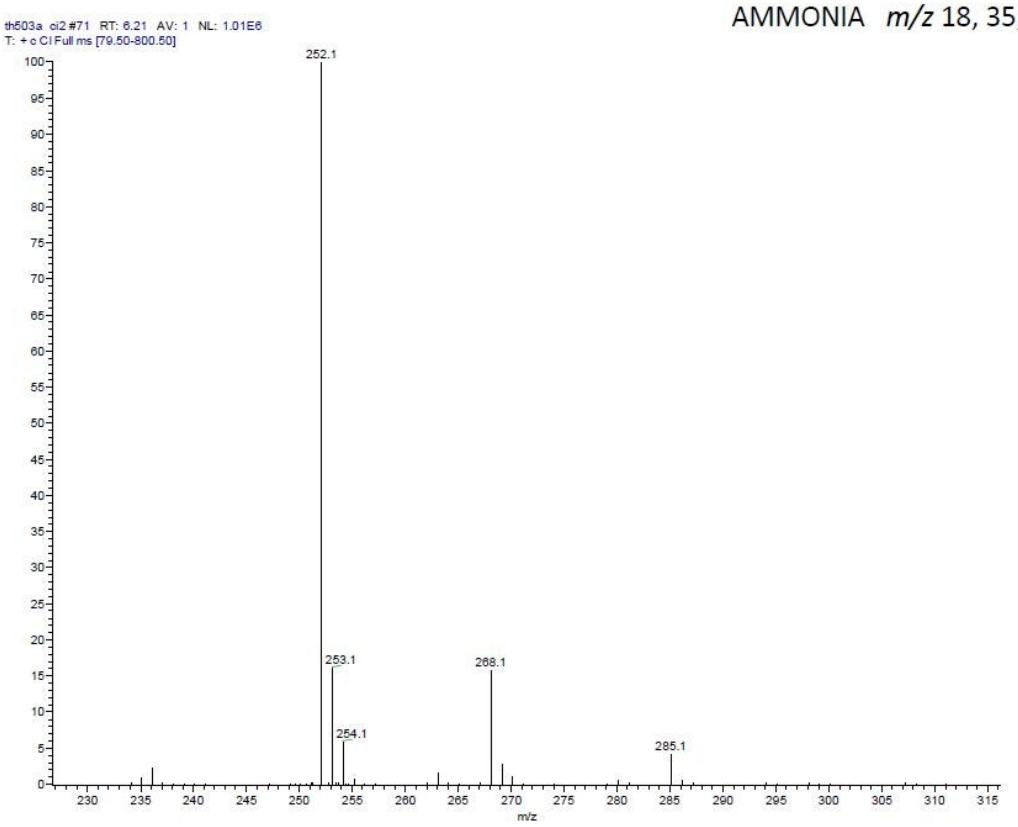




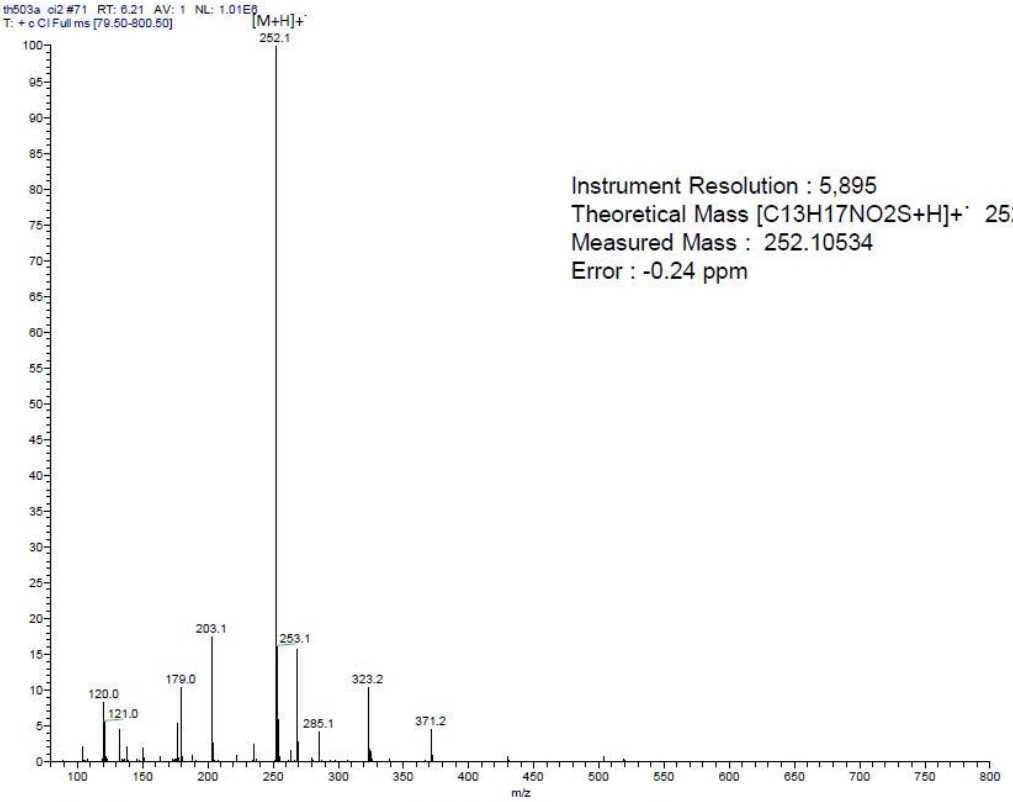

161.1890
133.9581
114.3374
112.0806
97.2556
85.3130
55.5199
42.6621
14.3855
150
100
50
[ppm]


Transmittance [%]
90
80
70
60
50
40
30
2971.83
2933.78
2870.23
2838.70
2549.22
2234.47
2155.12
2051.34
2020.11
1899.02
1601.87
1568.51
1506.67
1460.64
1441.61
1415.94
1380.07
1364.86
1344.03
1293.36
1250.28
1170.91
1087.33
1024.98
1007.75
900.01
832.01
781.79
760.74
730.58
653.32
594.47
536.70
468.55
427.38
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

AMMONIA *m/z* 18, 35, 52

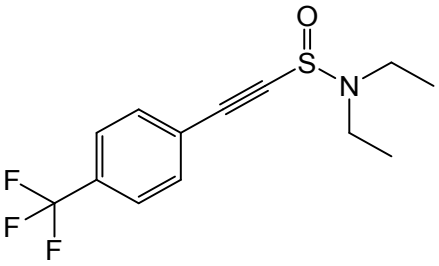


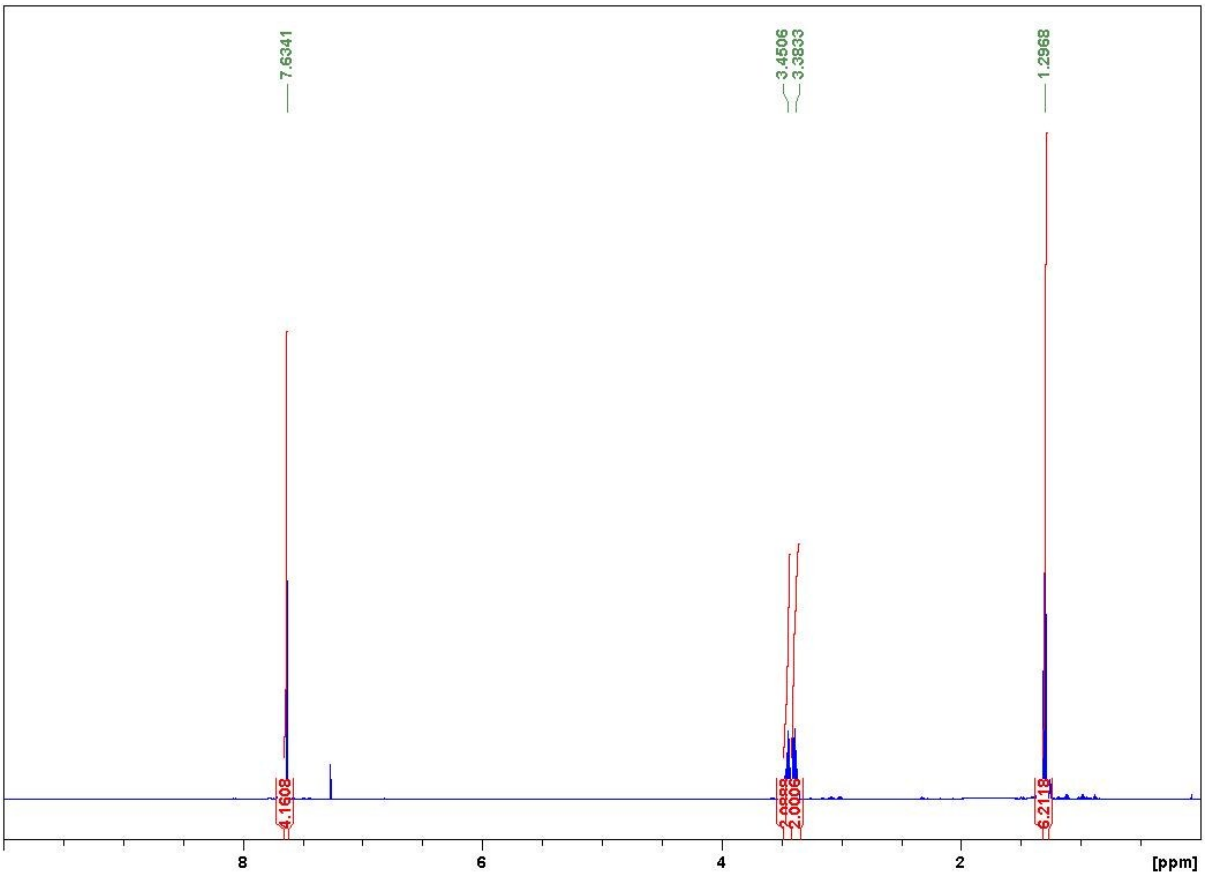
AMMONIA *m/z* 18, 35, 52

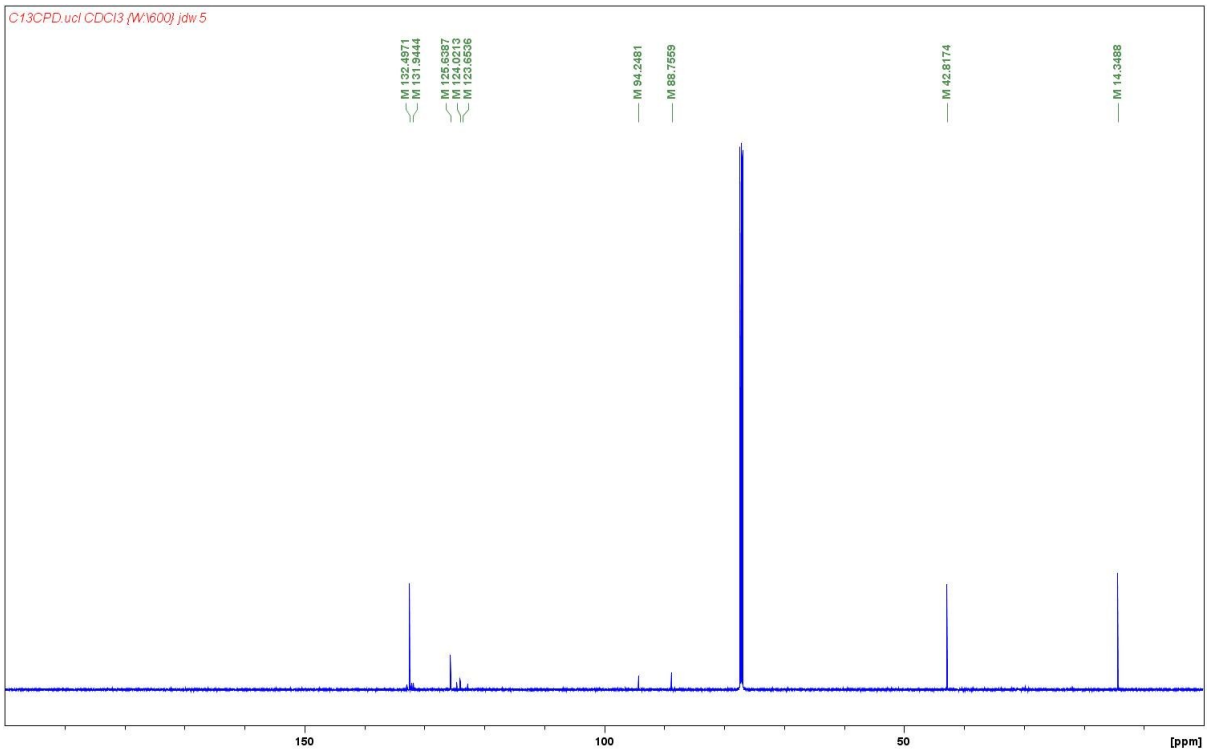


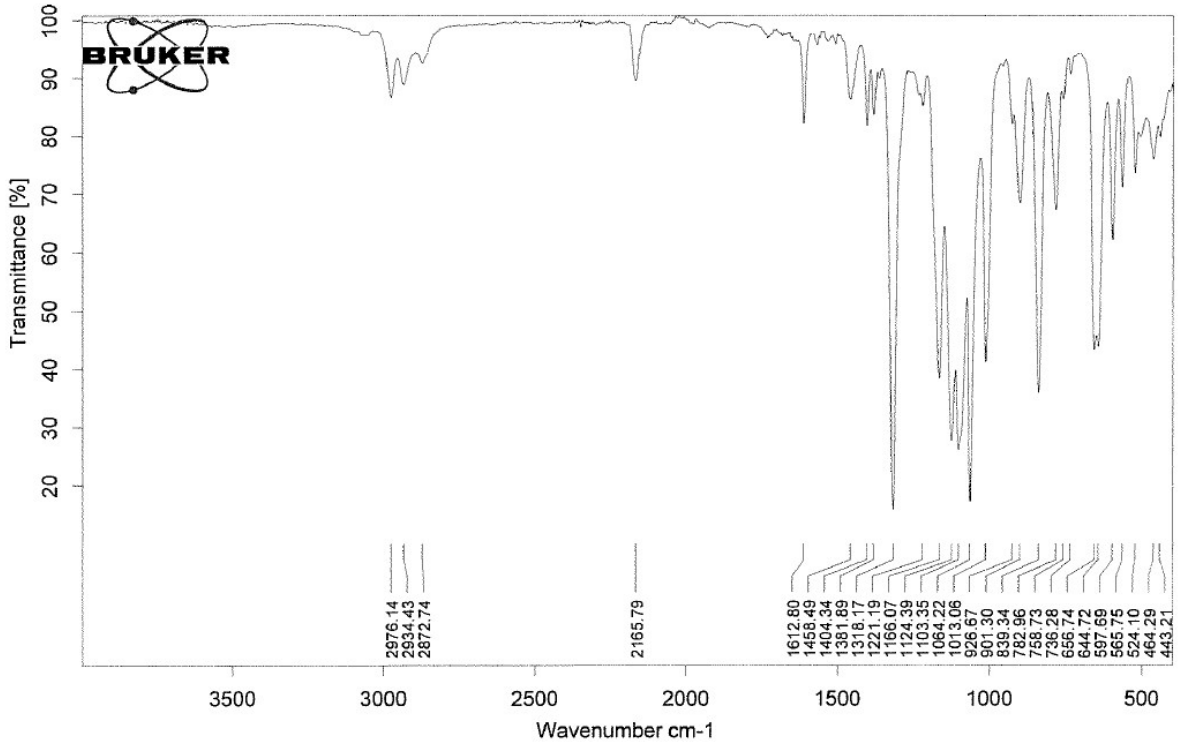
Instrument Resolution : 5,895
Theoretical Mass [C13H17NO2S+H]+˙ 252.10528
Measured Mass : 252.10534
Error : -0.24 ppm

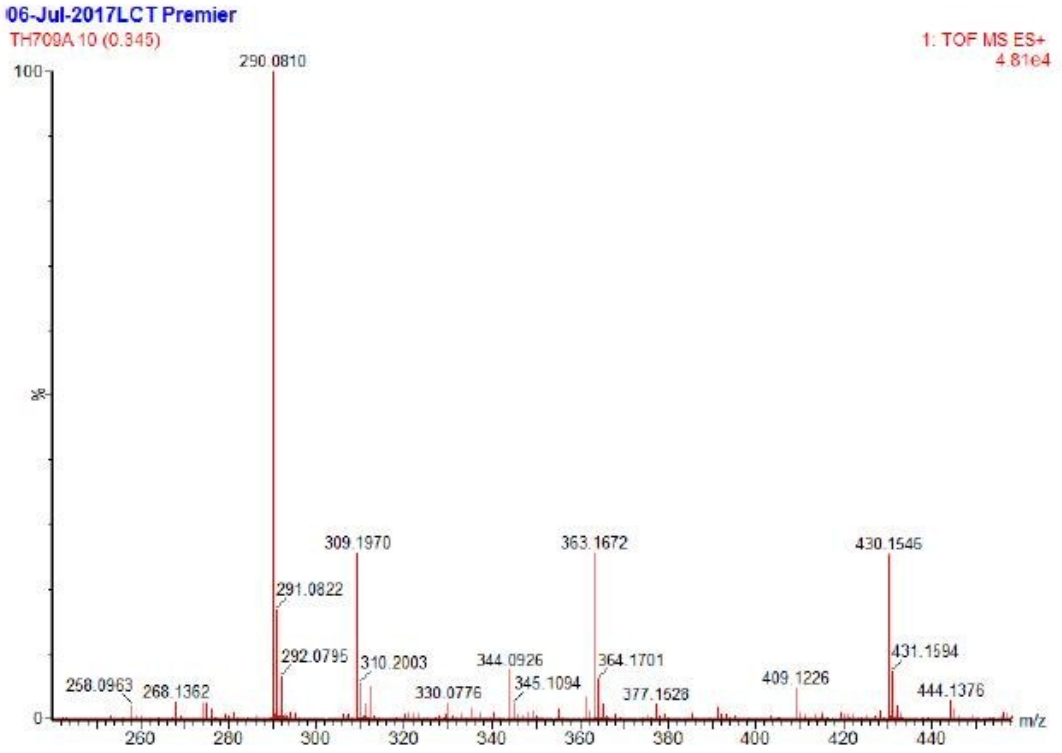
***N*,*N*-Diethyl-2-(4-(trifluoromethyl)phenyl)ethynesulfinamide (5) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS**






C13CPD.ucl CDCl3 {W:\600} jdw 5
M 132.4971
M 131.9444
M 125.6387
M 124.0213
M 123.8536
M 94.2481
M 88.7559
M 42.8174
M 14.3488
150
100
50
[ppm]


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
2976.14
2934.43
2872.74
2165.79
1612.80
1458.49
1404.34
1381.89
1318.17
1221.19
1166.07
1124.39
1103.35
1064.22
1013.06
926.67
901.30
839.34
782.96
758.73
736.28
656.74
644.72
597.69
565.75
524.10
464.29
443.21
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1


06-Jul-2017LCT Premier
TH709A 10 (0.345)
1: TOF MS ES+
4.81e4
100
%
0
290.0810
309.1970
363.1672
430.1546
291.0822
292.0795
310.2003
344.0926
364.1701
431.1594
258.0963
268.1362
330.0776
345.1094
377.1528
409.1226
444.1376
260
280
300
320
340
360
380
400
420
440
m/z

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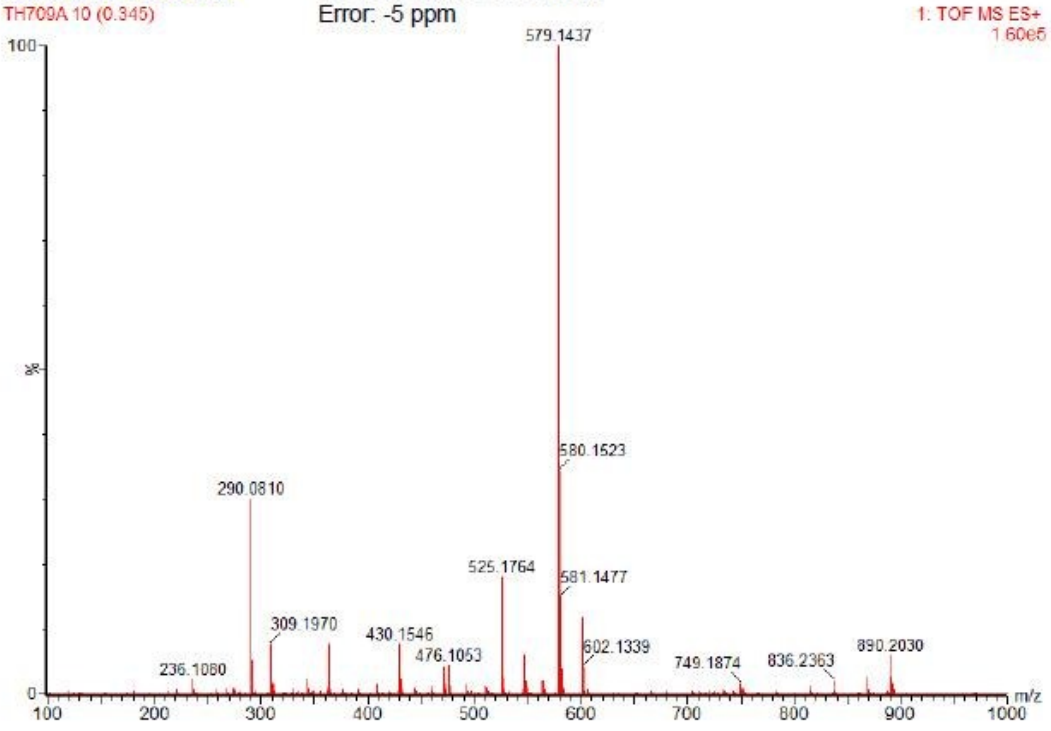
[M+H]+

06-Jul-2017LCT Premier

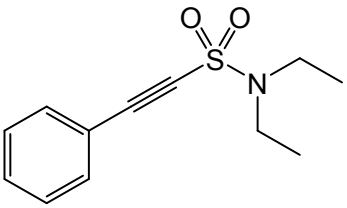
TH709A 10 (0.345)

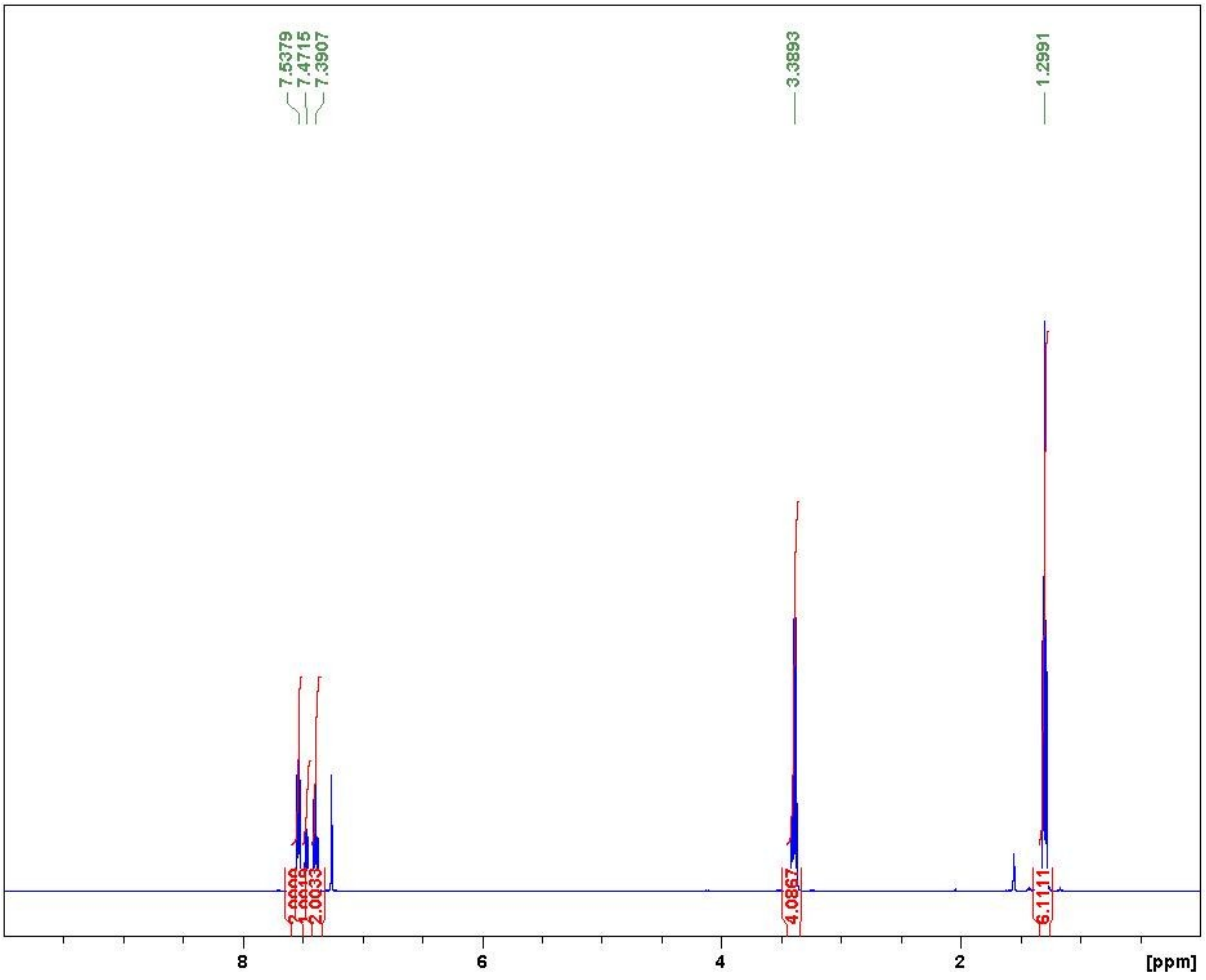
Instrument Resolution: 10,000
Theoretical Mass [C13H15F3NOS]+:290.0826
Measured Mass : 290.0810
Error: -5 ppm

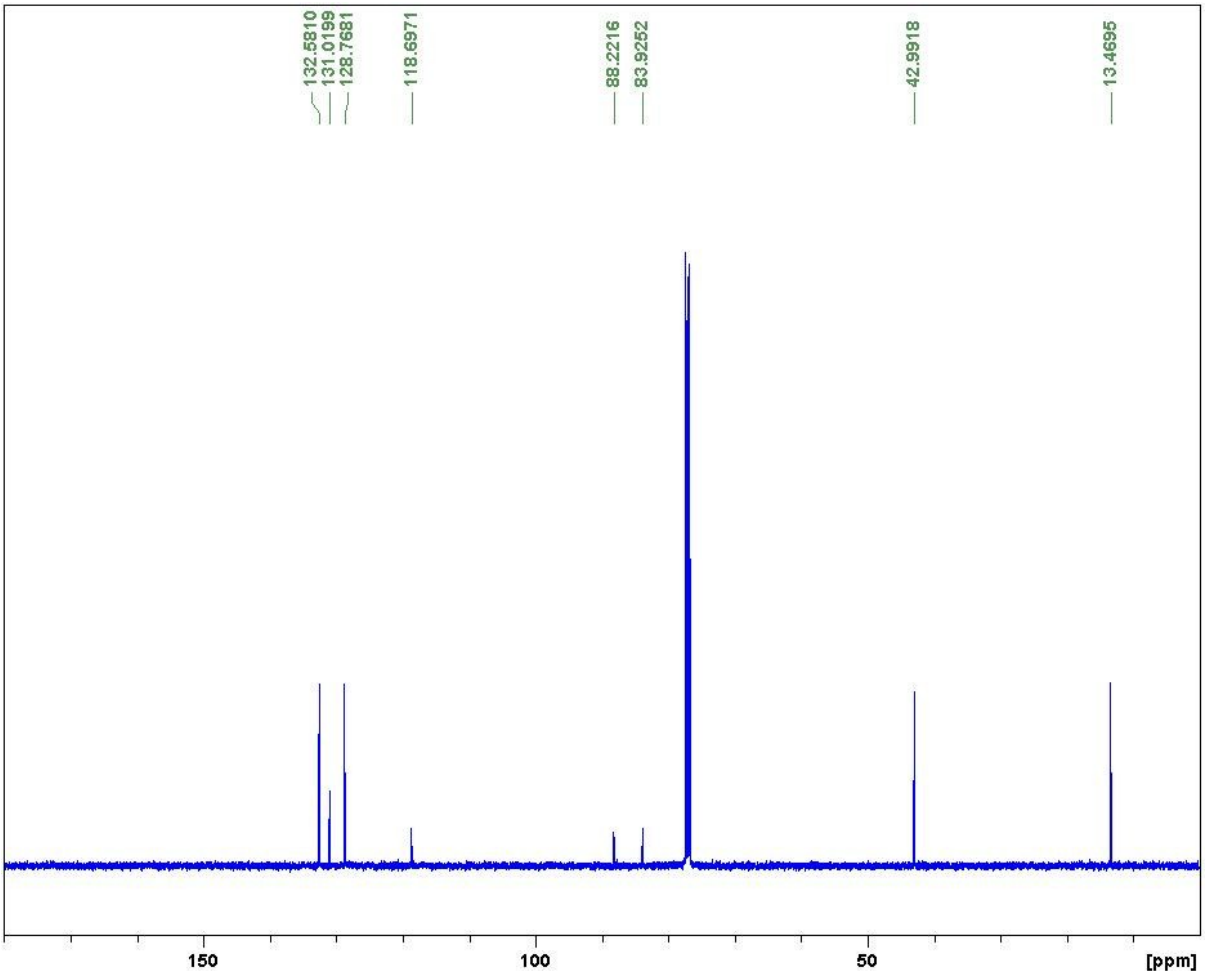
1: TOF MS ES+
1.60e5

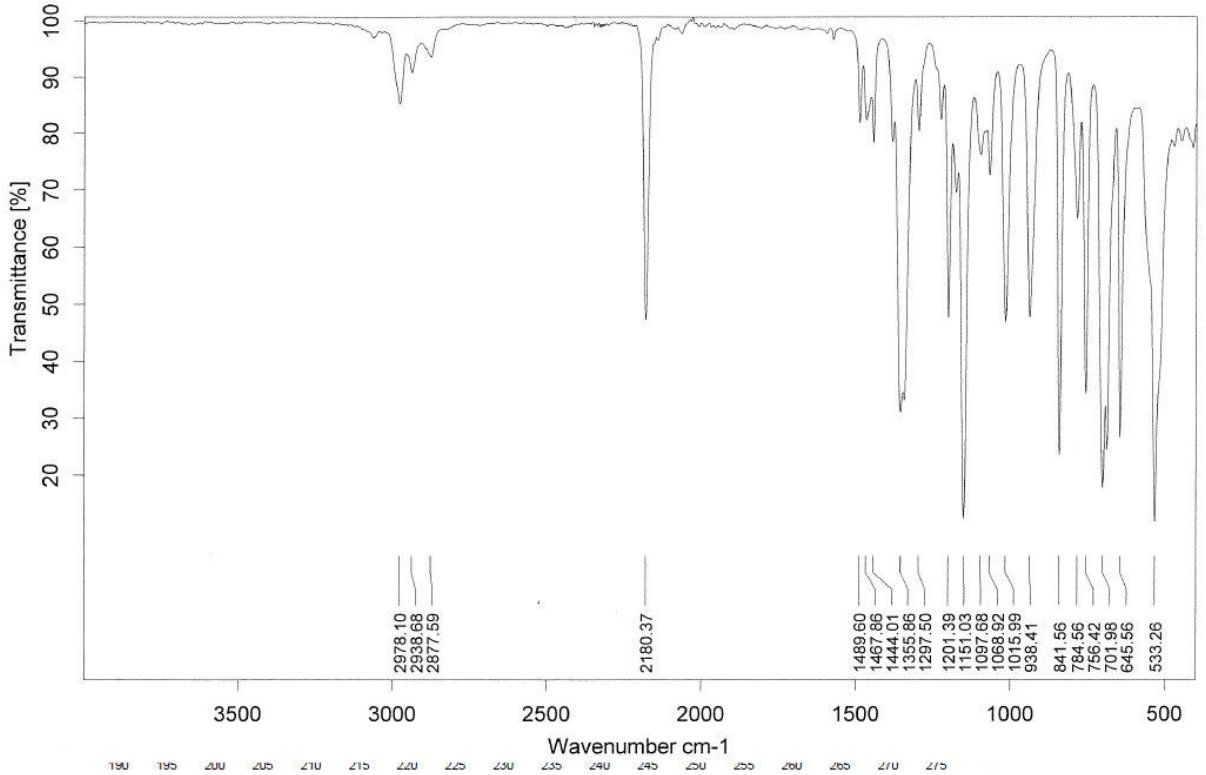


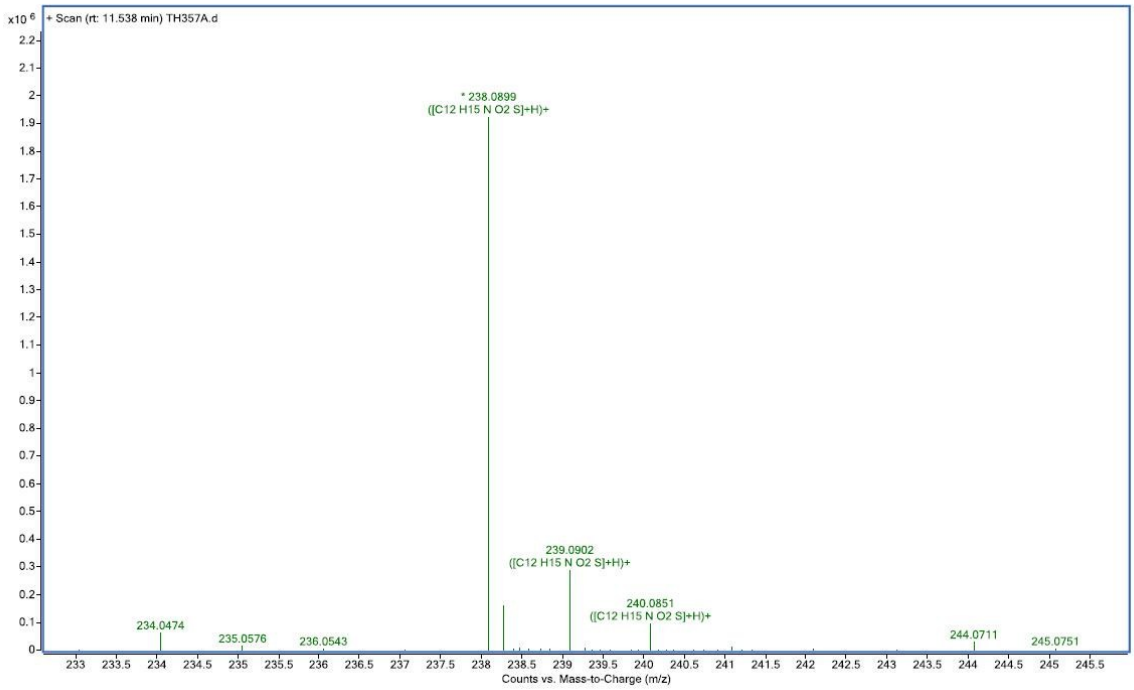
***N*,*N*-Diethyl-2-phenylethyne-1-sulfonamide (2) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS**

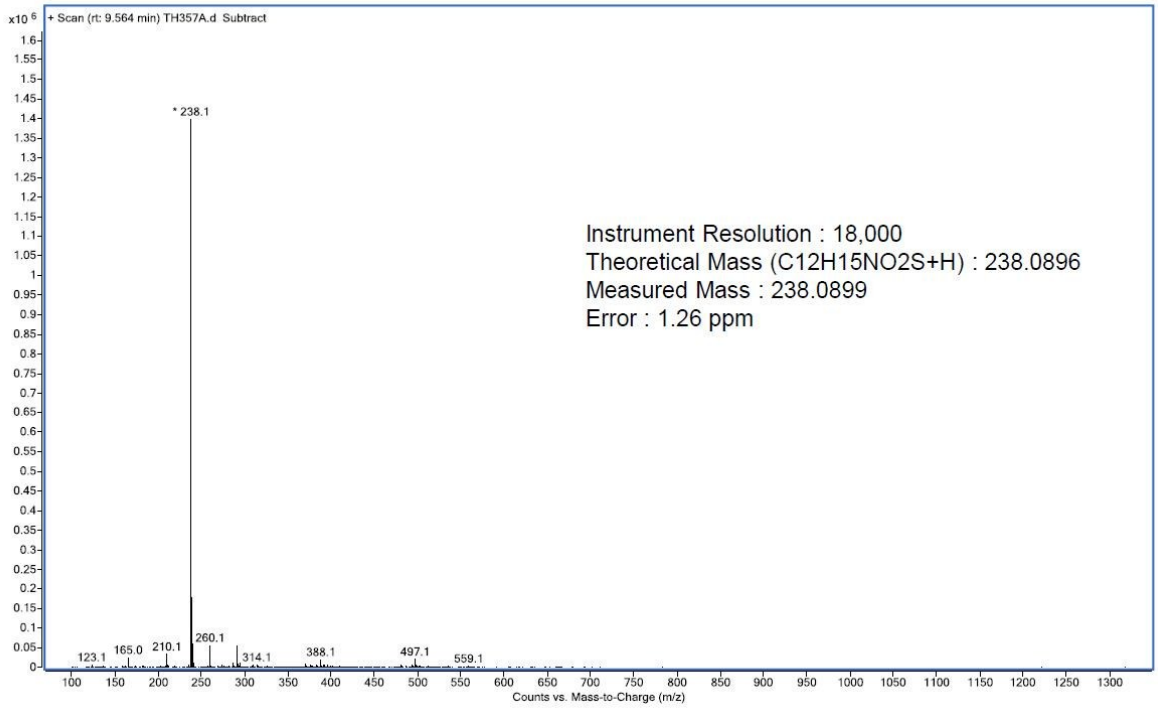





132.5810
131.0199
128.7681
118.6971
88.2216
83.9252
42.9918
13.4695
150
100
50
[ppm]

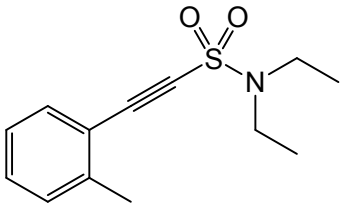

Transmittance [%]
100
90
80
70
60
50
40
30
20
2978.10
2938.68
2877.59
2180.37
1489.60
1467.86
1444.01
1355.86
1297.50
1201.39
1151.03
1097.88
1068.92
1015.99
938.41
841.56
784.56
756.42
701.98
645.56
533.26
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

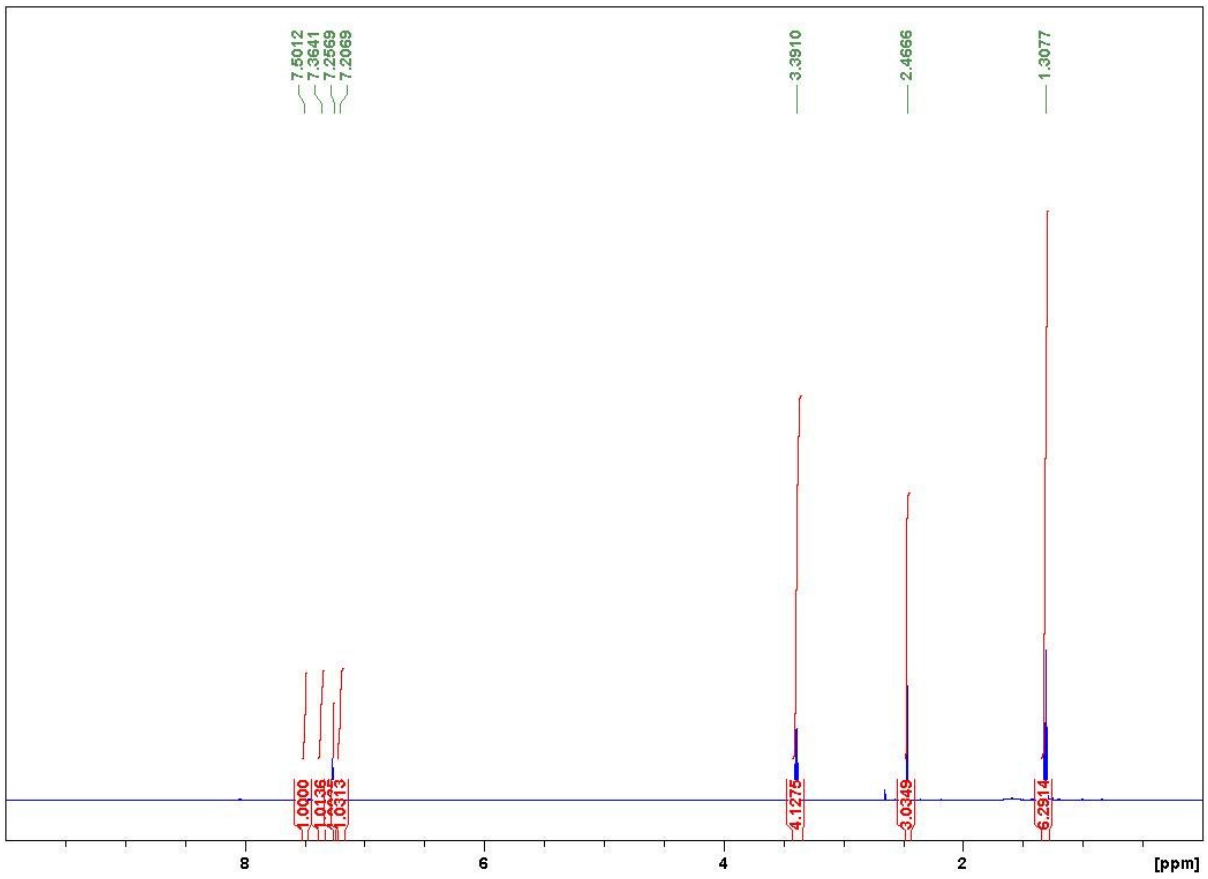


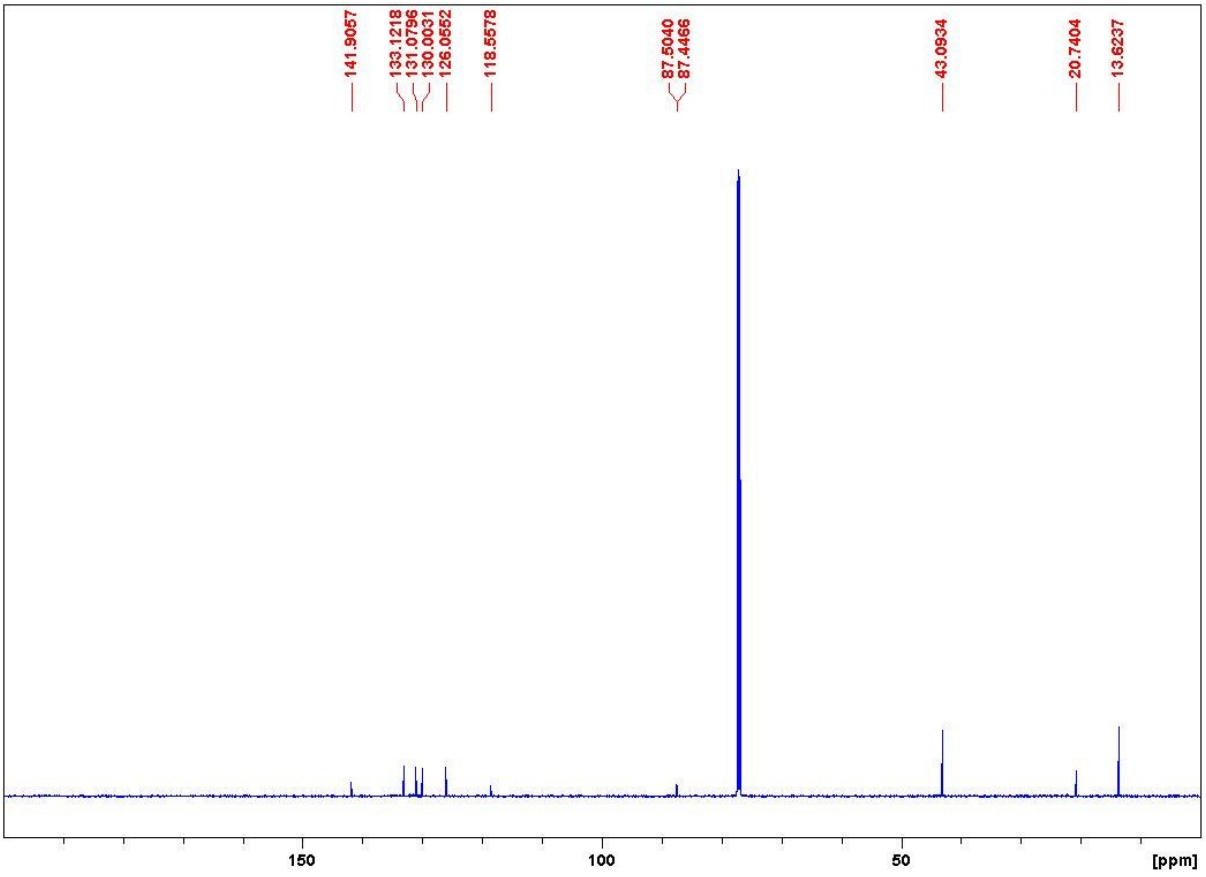


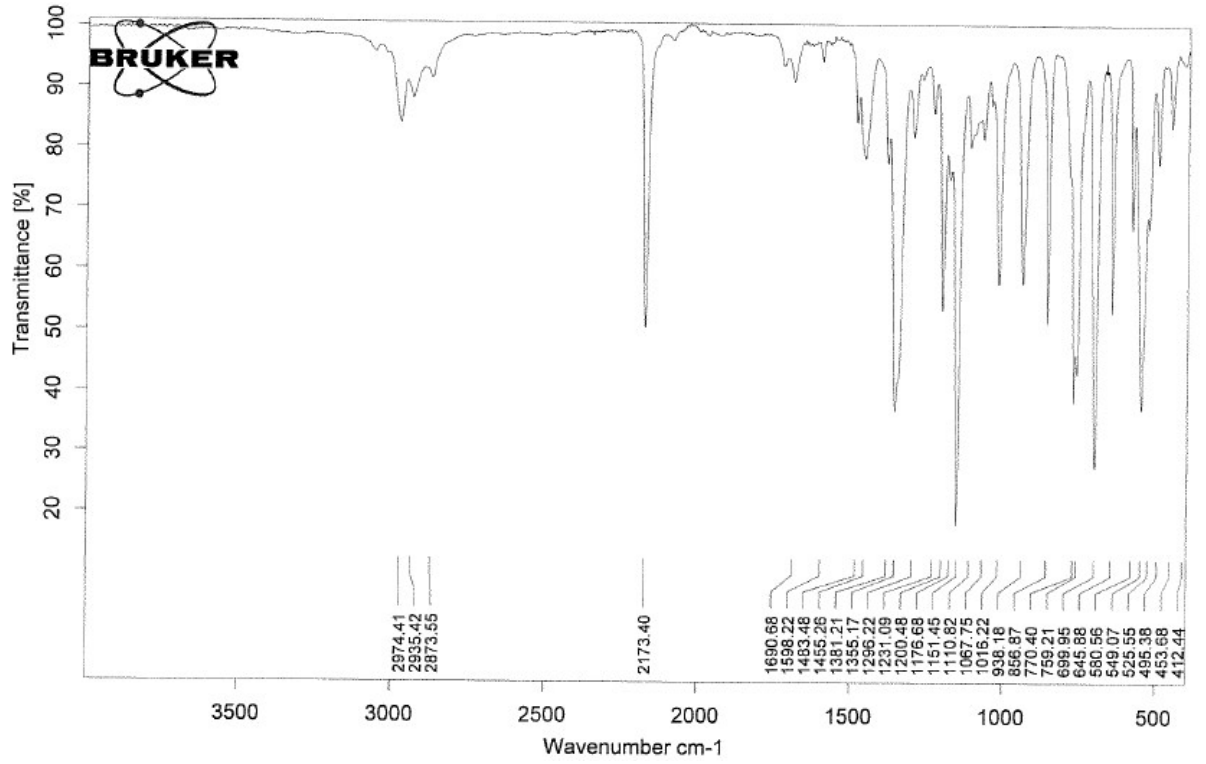
Instrument Resolution : 18,000
Theoretical Mass ($C_{12}H_{15}NO_2S+H$) : 238.0896
Measured Mass : 238.0899
Error : 1.26 ppm

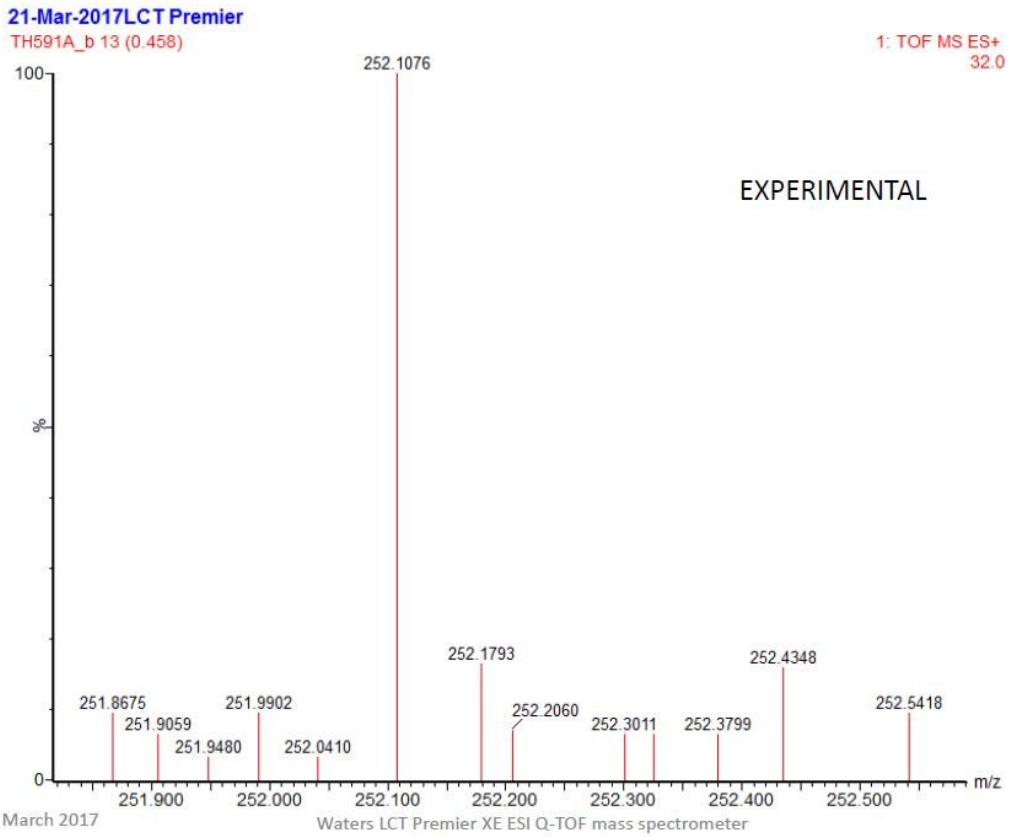
_N_,_N_-Diethyl-2-(_o_-tolyl)ethynesulfonamide (25) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS






141.9057
133.1218
131.0796
130.0031
126.0552
118.5578
87.5040
87.4466
43.0934
20.7404
13.6237
150
100
50
[ppm]


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
20
2974.41
2935.42
2873.55
2173.40
1690.68
1598.22
1483.48
1455.26
1381.21
1355.17
1296.22
1231.09
1200.48
1176.68
1151.45
1110.82
1067.75
1016.22
938.18
856.87
770.40
759.21
699.95
645.88
580.56
549.07
525.55
495.38
453.68
412.44
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



EXPERIMENTAL

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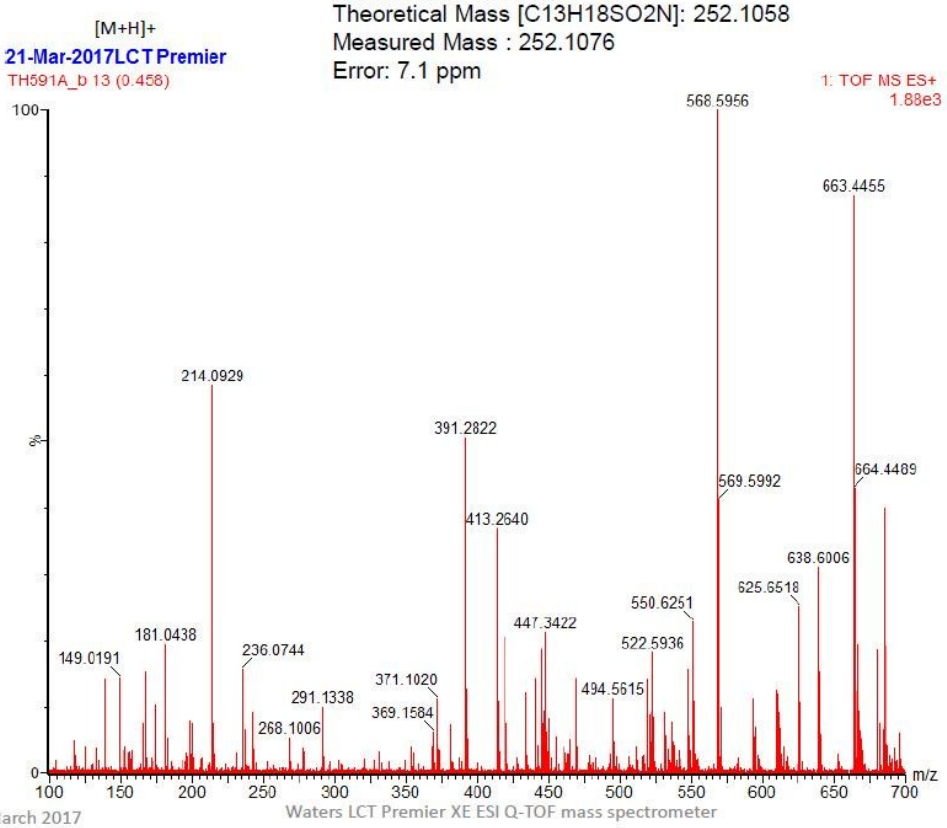
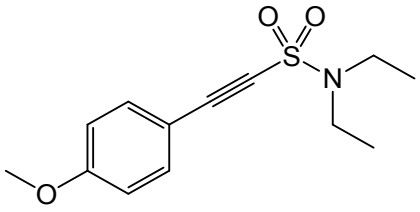
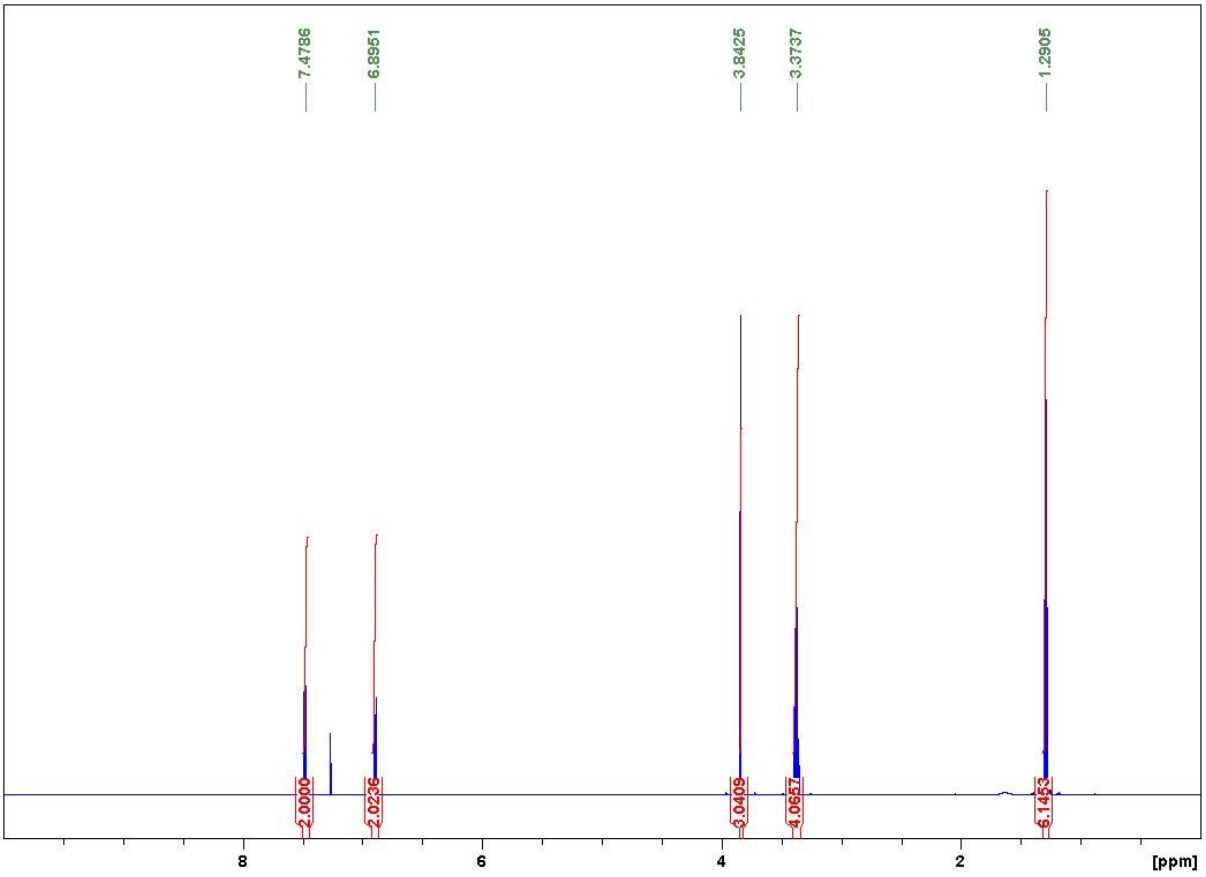
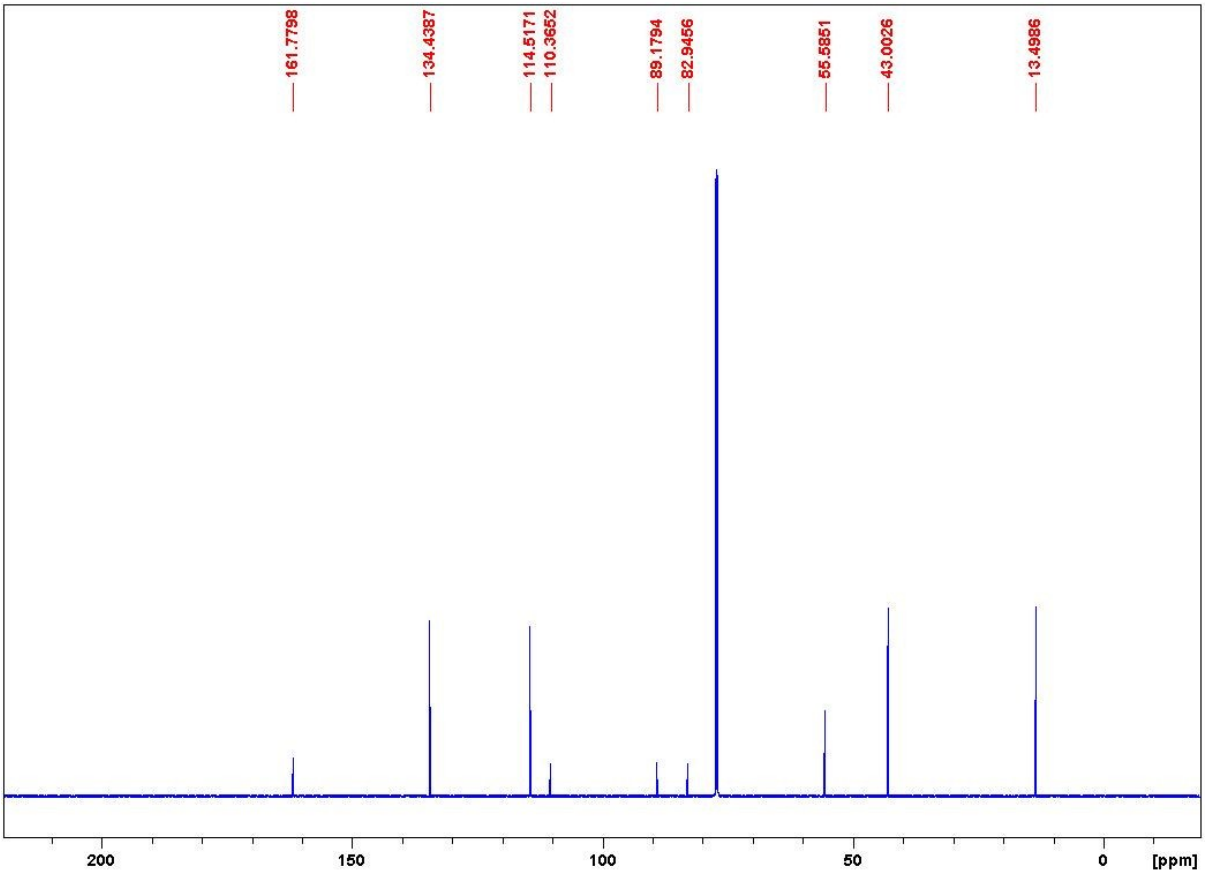
Instrument Resolution : 10,000
Theoretical Mass [C13H18SO2N]: 252.1058
Measured Mass : 252.1076
Error: 7.1 ppm

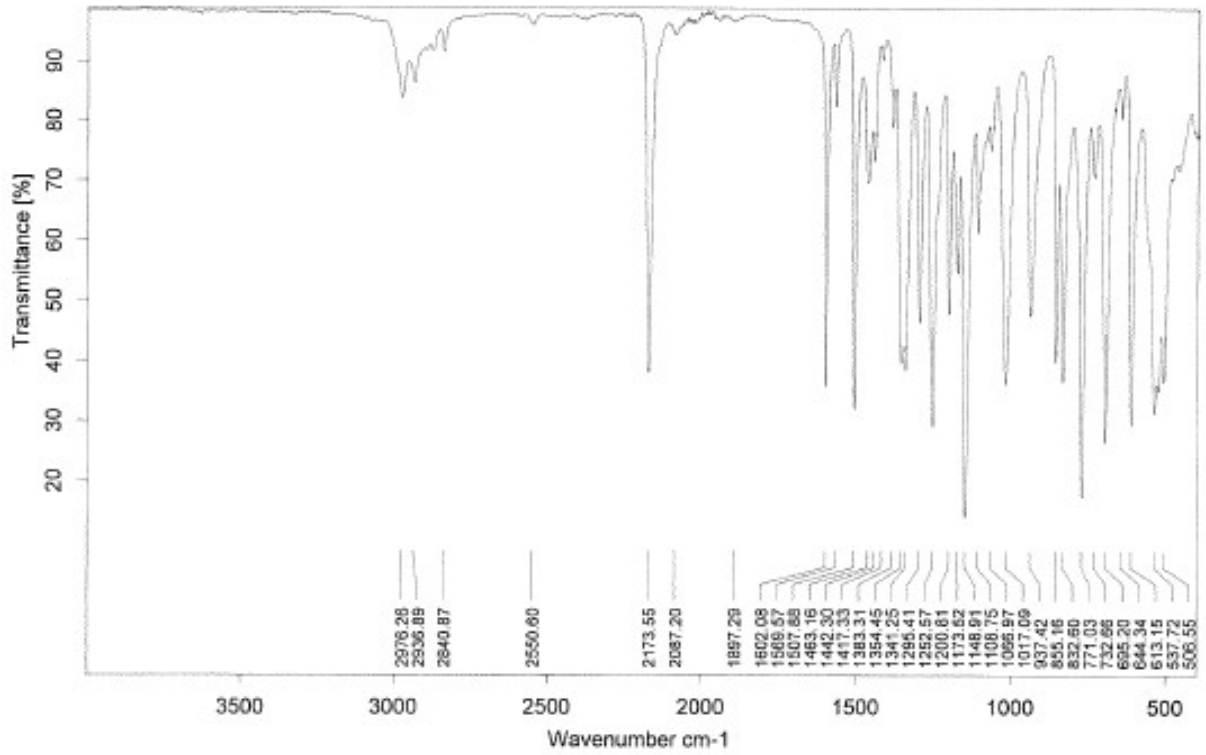


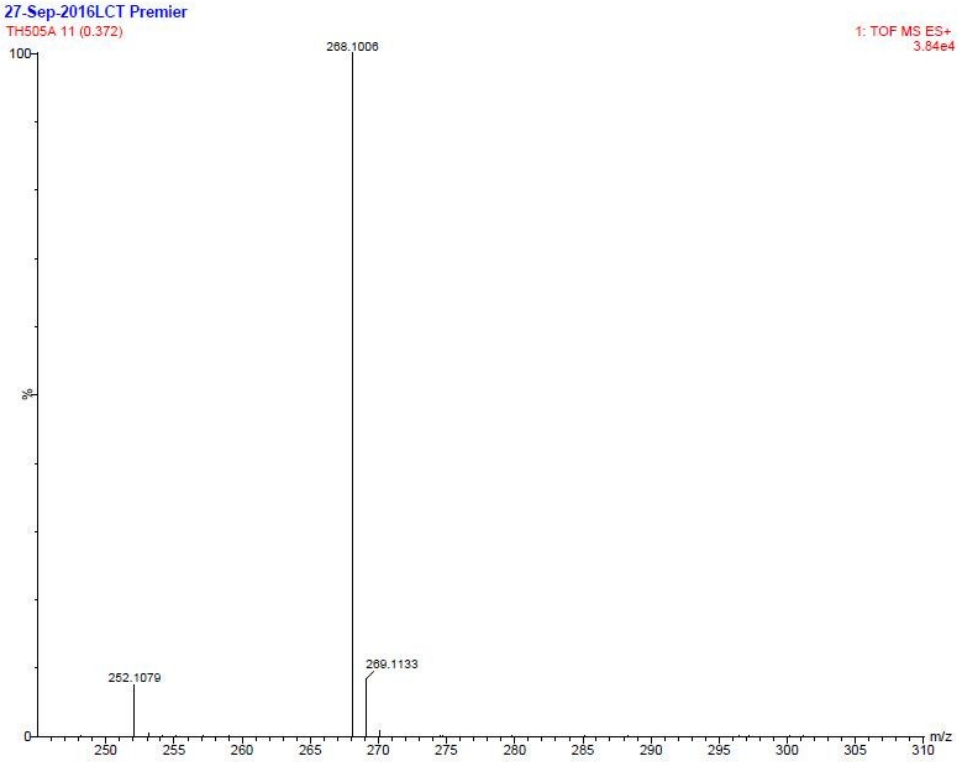
***N*,*N*-Diethyl-2-(4-methoxyphenyl)ethynesulfonamide (33) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS**



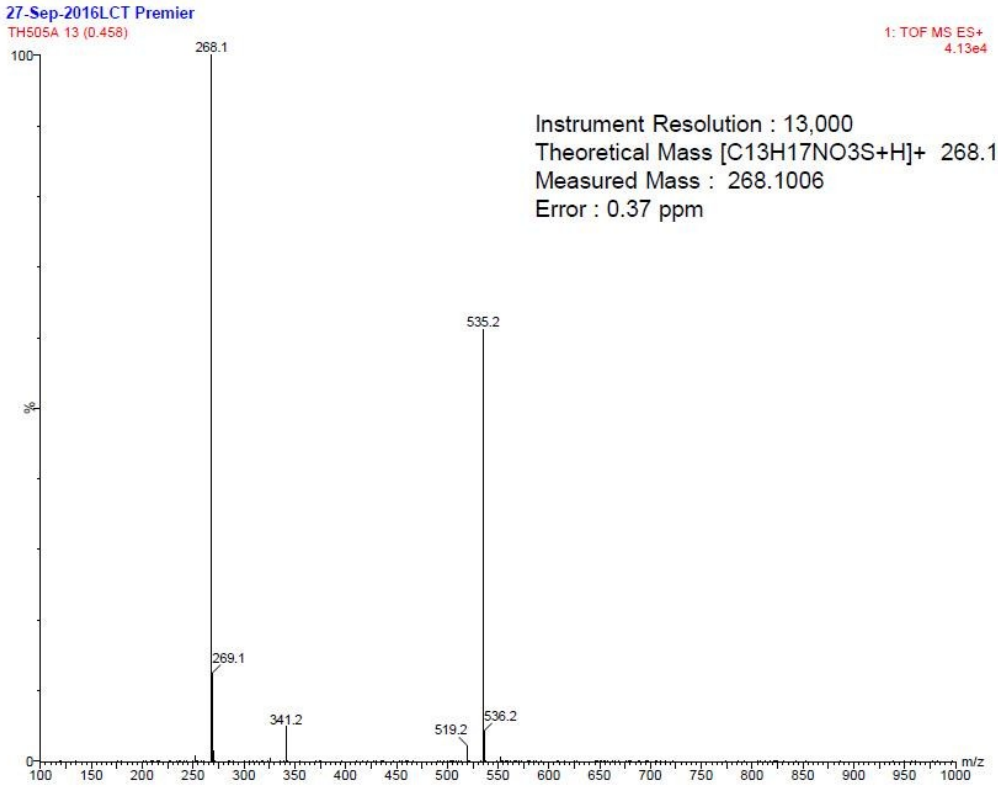



161.7798
134.4387
114.5171
110.3652
89.1794
82.9456
55.5851
43.0026
13.4986
200
150
100
50
0
[ppm]


Transmittance [%]
90
80
70
60
50
40
30
20
2976.28
2936.89
2840.87
2550.60
2173.55
2087.20
1897.29
1602.08
1565.57
1507.88
1463.16
1442.30
1417.33
1383.31
1354.45
1341.25
1295.41
1252.57
1200.81
1173.52
1148.91
1108.75
1066.97
1017.09
937.42
855.16
832.60
771.03
732.66
695.20
644.34
613.15
537.72
506.55
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

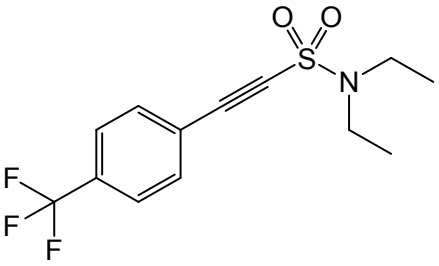

27-Sep-2016LCT Premier
TH505A 11 (0.372)
1: TOF MS ES+
3.84e4
100
%
0
268.1006
269.1133
252.1079
250
255
260
265
270
275
280
285
290
295
300
305
310
m/z

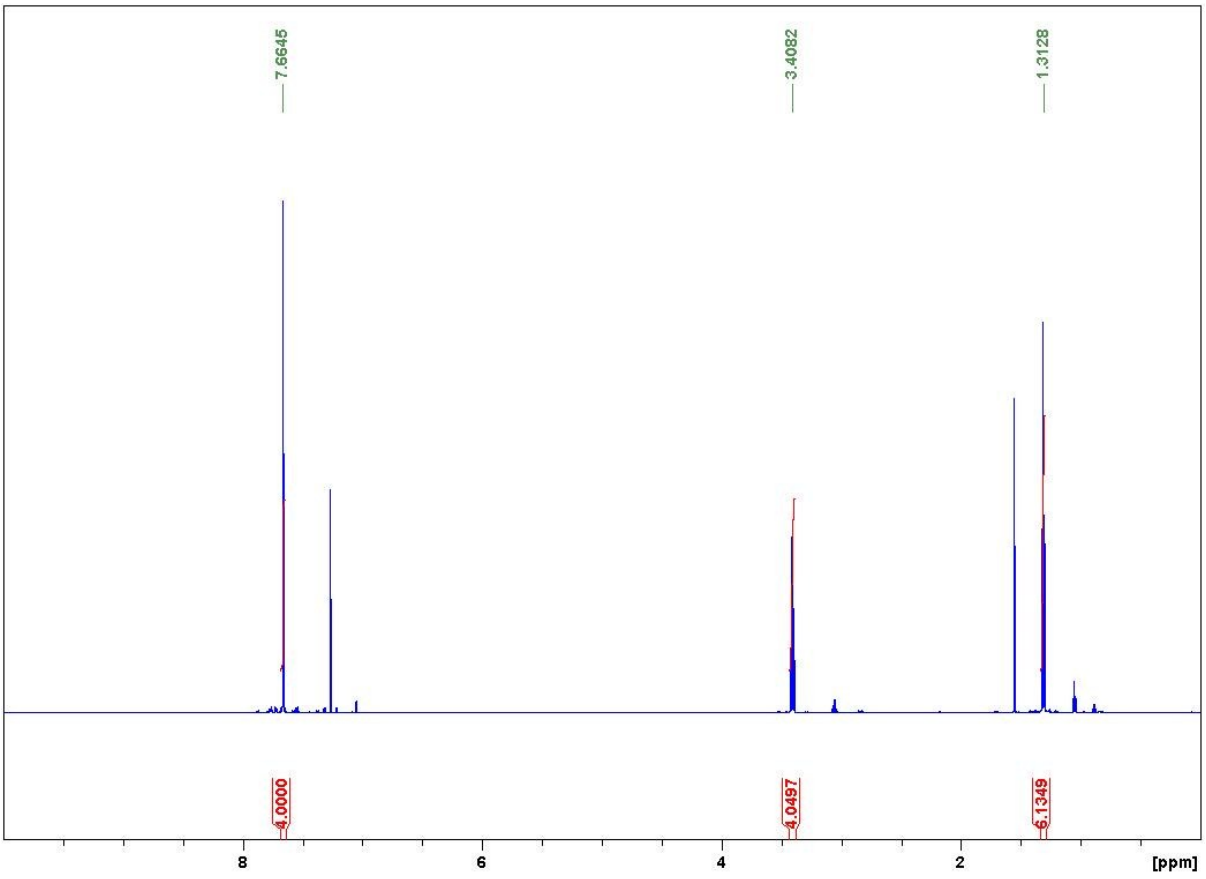
UCL Chemistry Mass Spectrometry Facility

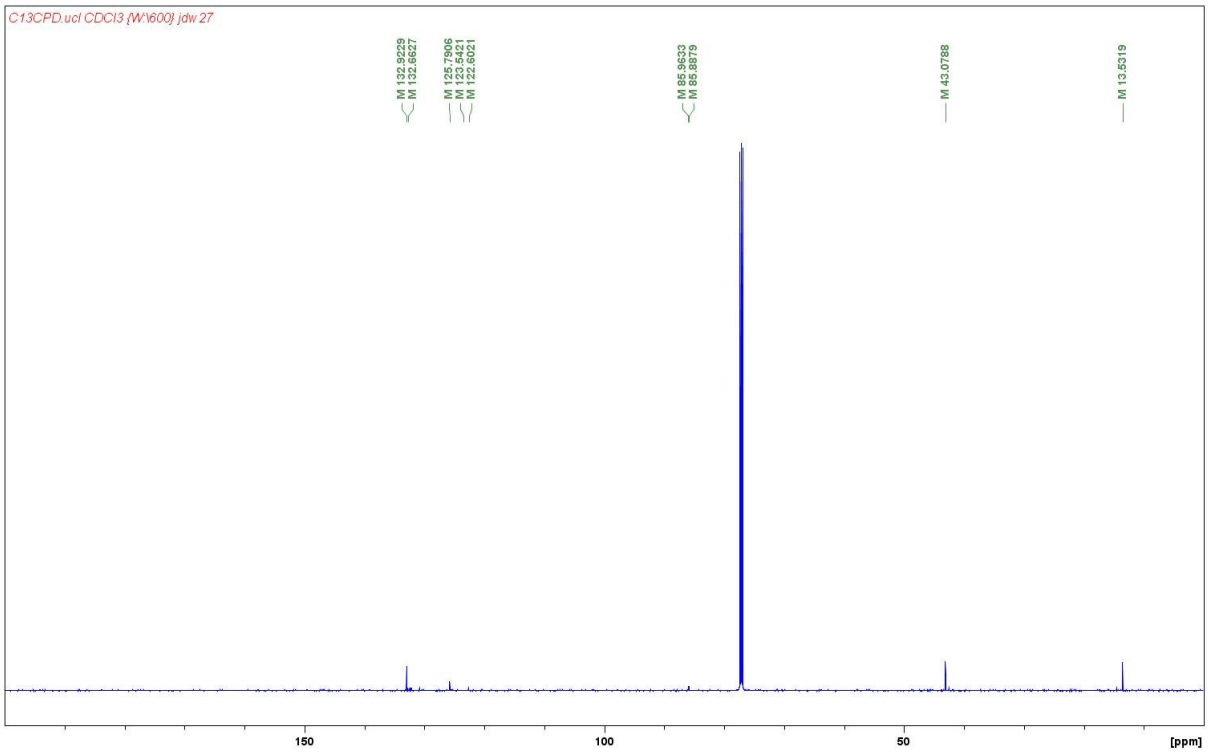


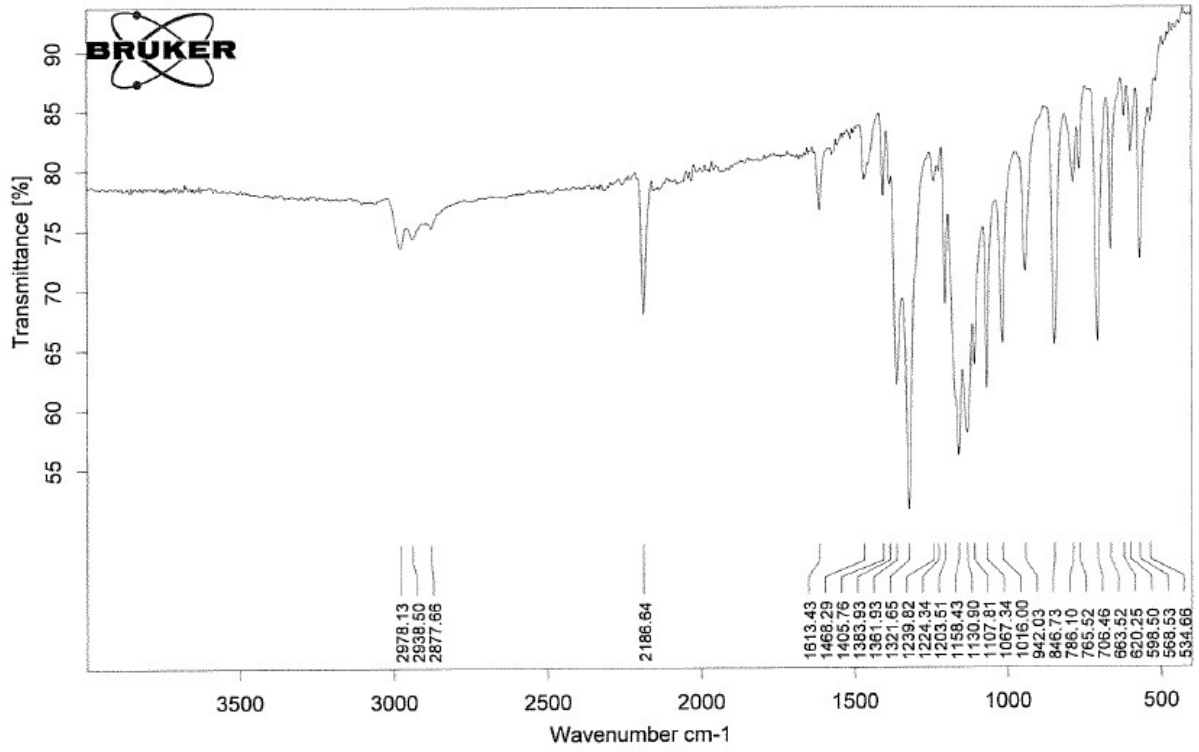
Instrument Resolution : 13,000
Theoretical Mass [C13H17NO3S+H]+ 268.1007
Measured Mass : 268.1006
Error : 0.37 ppm

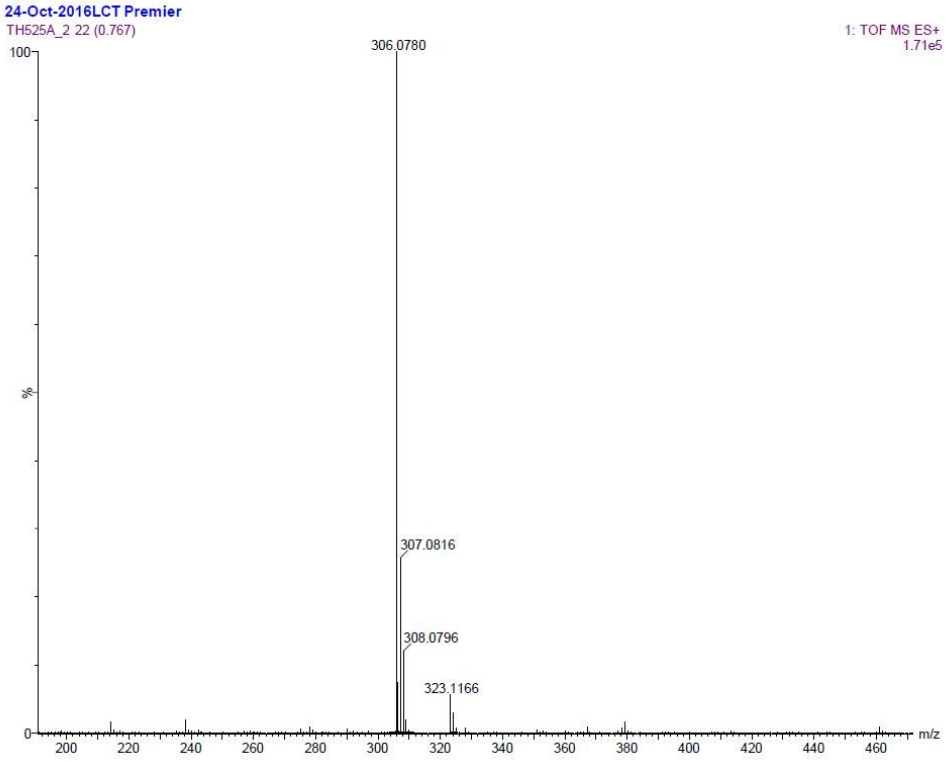
***N*,*N*-Diethyl-2-(4-(trifluoromethyl)phenyl)ethynesulfonamide (34) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS**



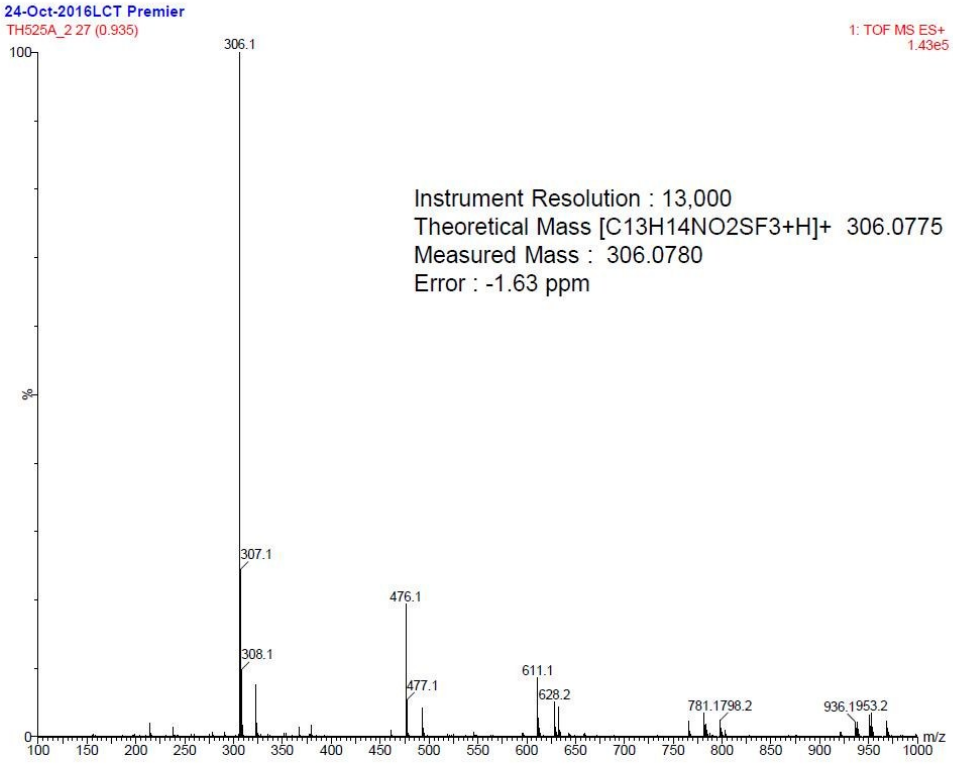



C13CPD.ucl CDCl3 {W:\600} jdw 27
M 132.9229
M 132.6627
M 125.7906
M 123.5421
M 122.6021
M 85.9633
M 85.8879
M 43.0788
M 13.5319
150
100
50
[ppm]

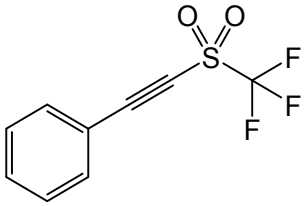

BRUKER
Transmittance [%]
90
85
80
75
70
65
60
55
2978.13
2938.50
2877.66
2186.64
1613.43
1468.29
1405.76
1383.93
1361.93
1321.65
1239.82
1224.34
1203.51
1158.43
1130.90
1107.81
1067.34
1016.00
942.03
846.73
786.10
765.52
706.46
663.52
620.25
598.50
568.53
534.66
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

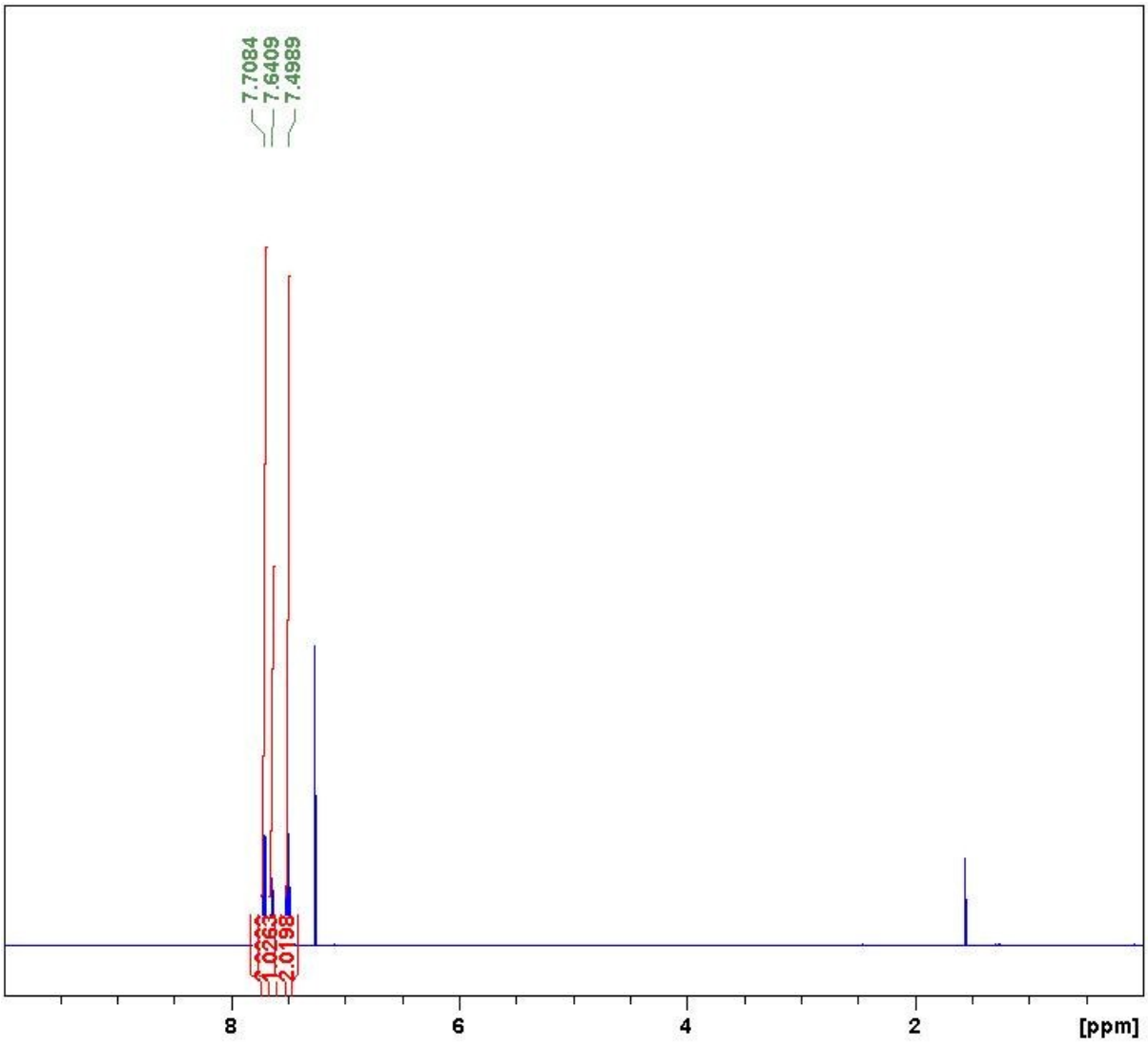

24-Oct-2016LCT Premier
TH525A_2 22 (0.767)
1: TOF MS ES+
1.71e5
306.0780
307.0816
308.0796
323.1166
100
%
0
200
220
240
260
280
300
320
340
360
380
400
420
440
460
m/z

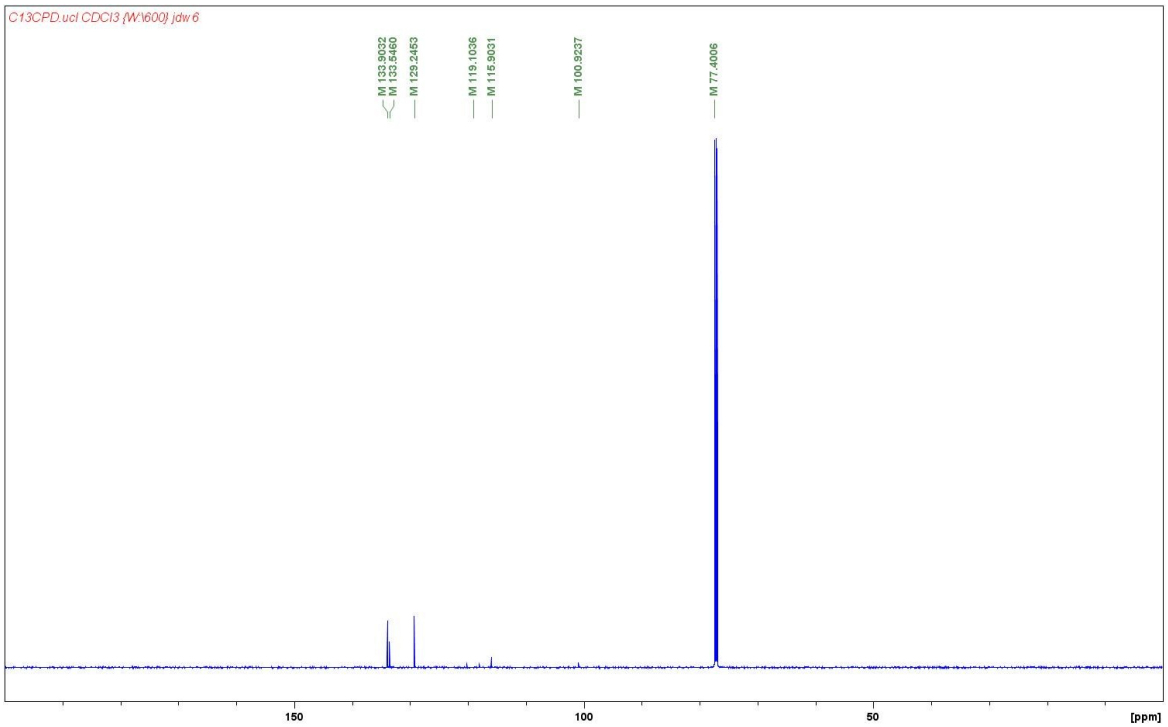
UCL Chemistry Mass Spectrometry Facility

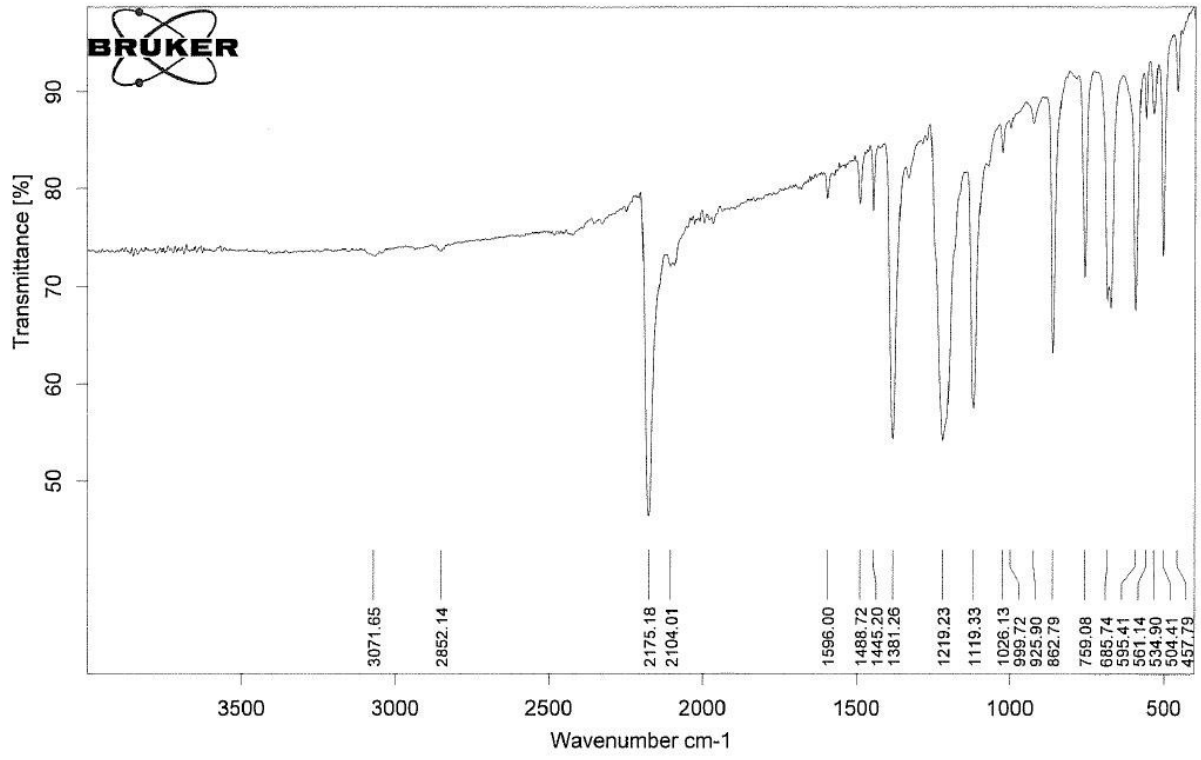


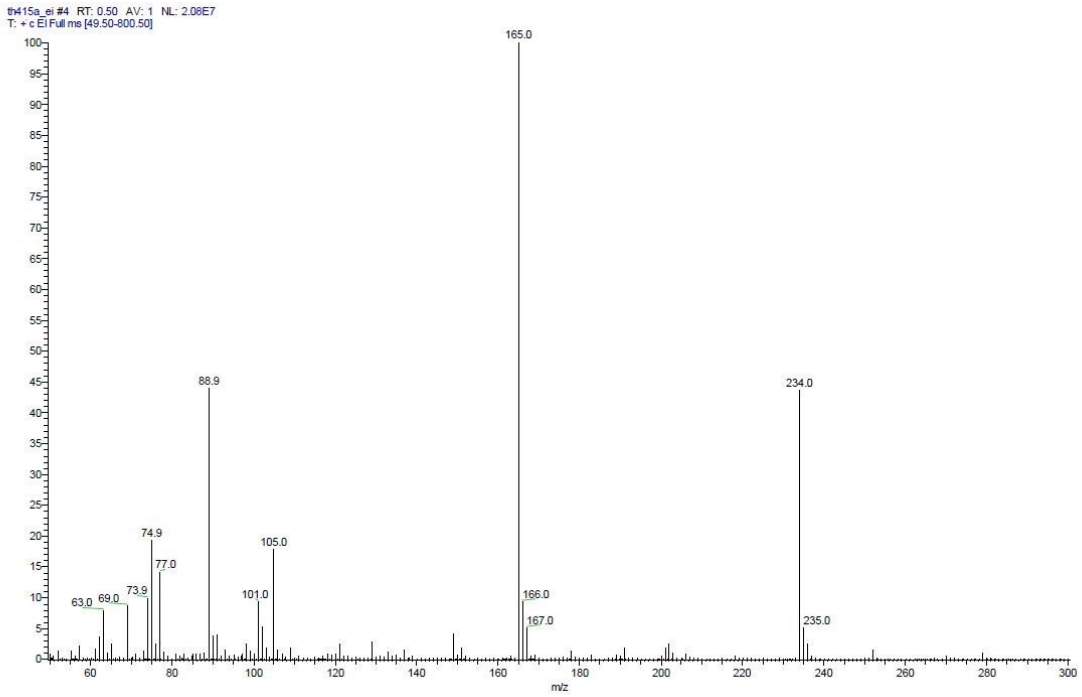
(((Trifluoromethyl)sulfonyl)ethynyl)benzene (29) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

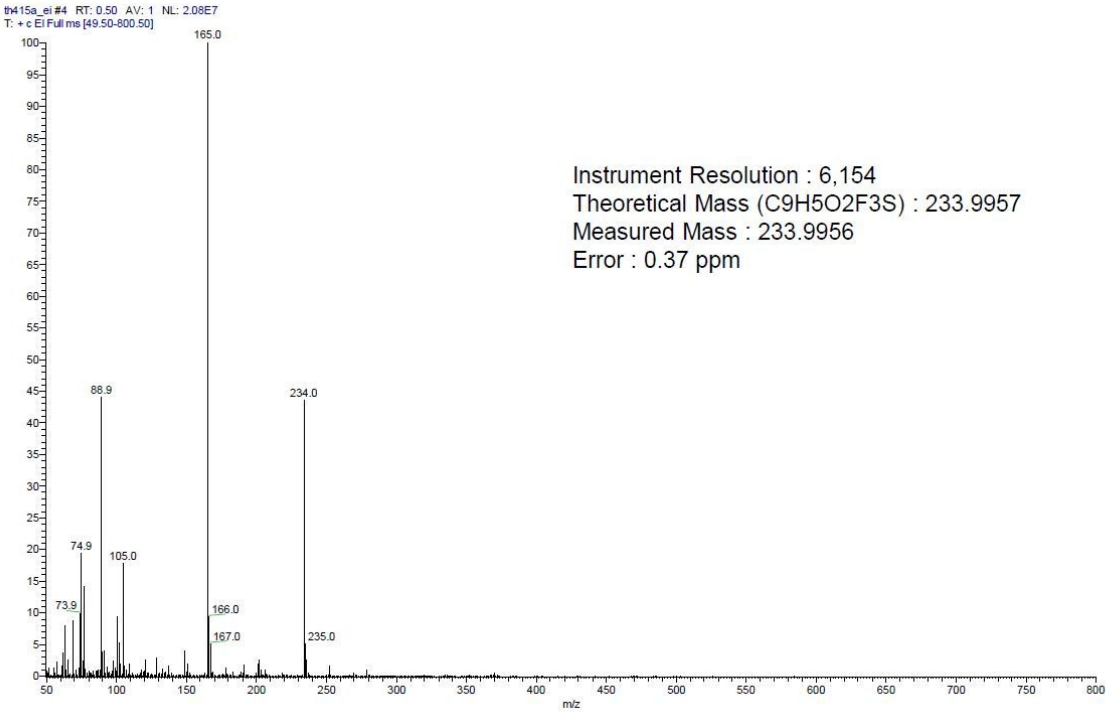





C13CPD.ucl CDCl3 {W:\600} jdw 6
M 133.9032
M 133.6460
M 129.2463
M 119.1036
M 115.9031
M 100.9237
M 77.4006
150
100
50
[ppm]

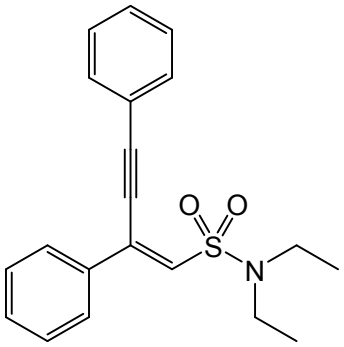

BRUKER
Transmittance [%]
90
80
70
60
50
3071.65
2852.14
2175.18
2104.01
1596.00
1488.72
1445.20
1381.26
1219.23
1119.33
1026.13
999.72
925.90
862.79
759.08
685.74
595.41
561.14
534.90
504.41
457.79
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

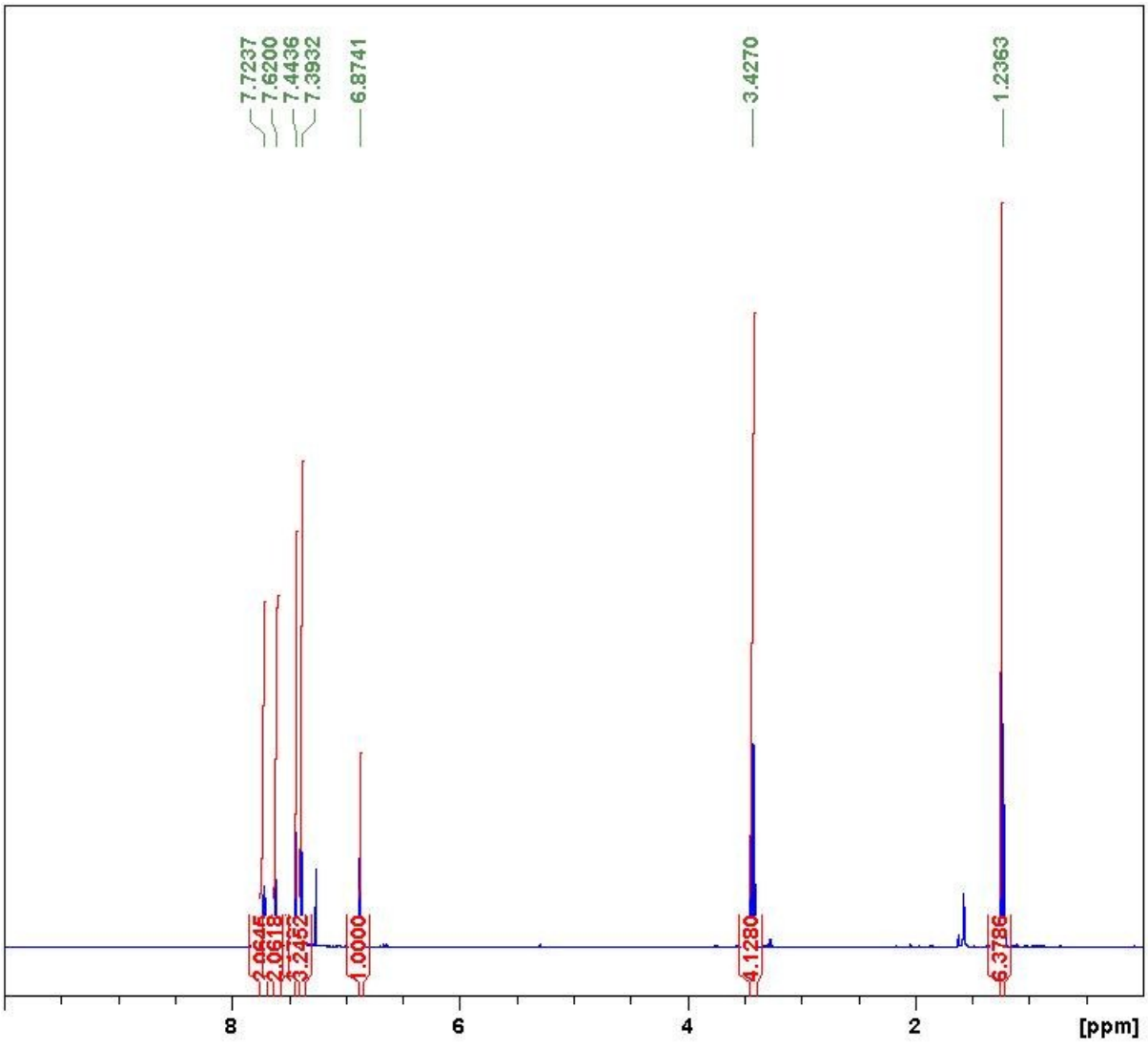


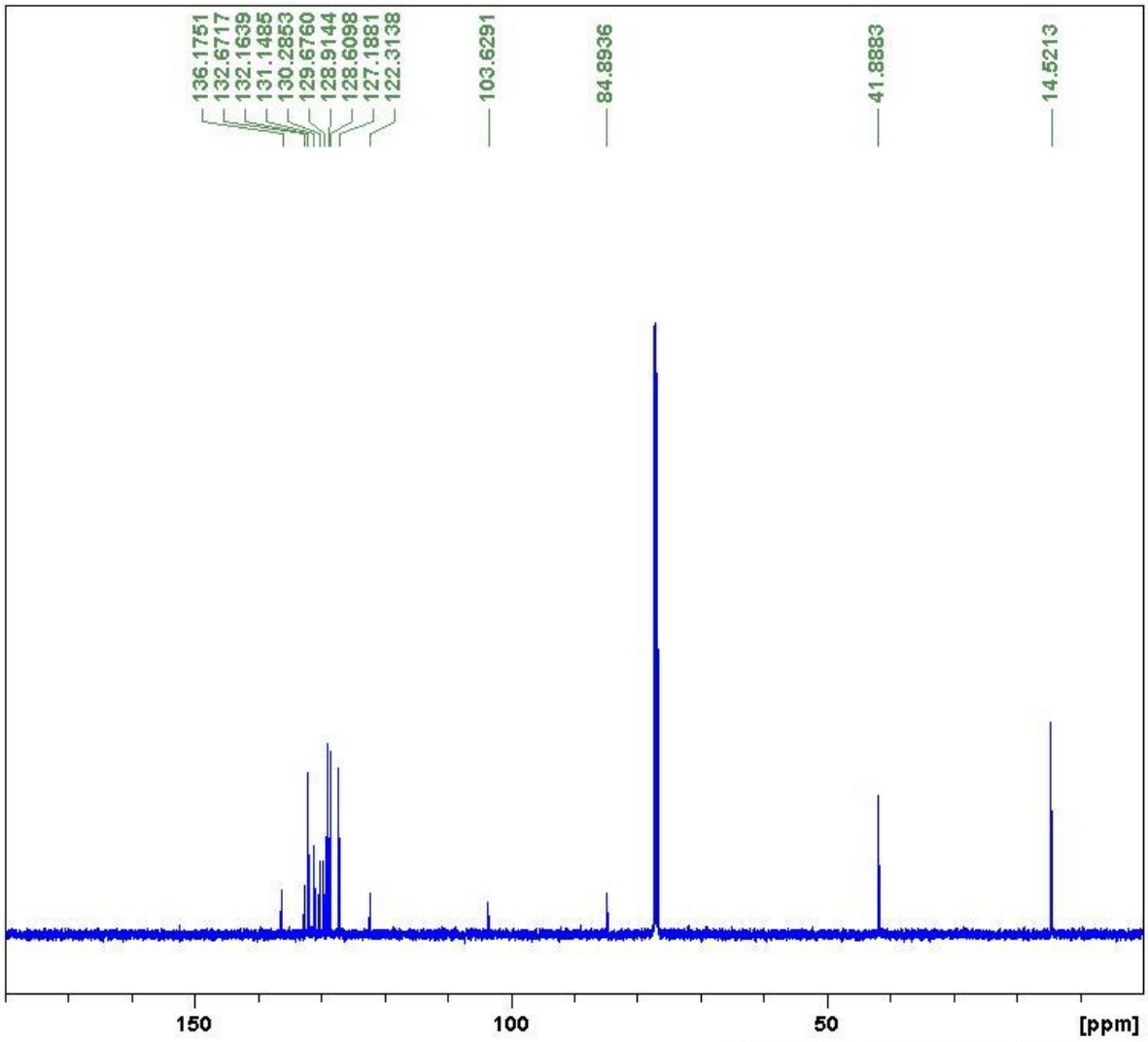


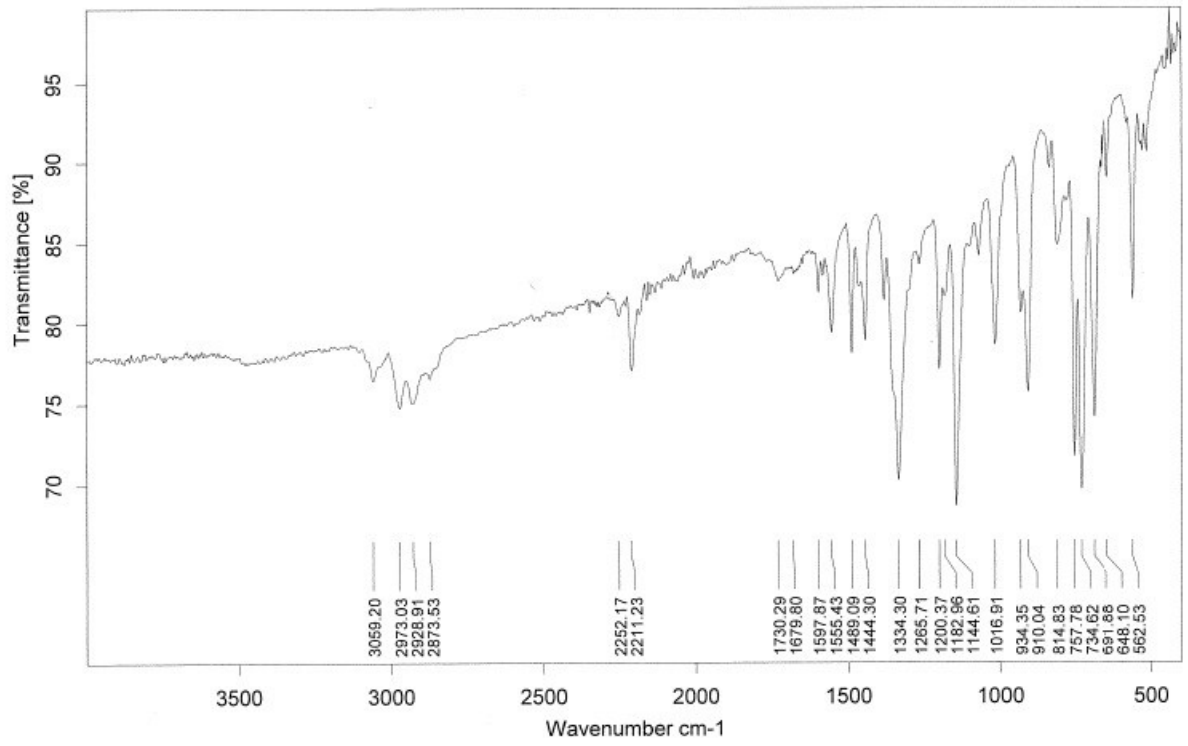
Instrument Resolution : 6,154
Theoretical Mass ($C_9H_5O_2F_3S$) : 233.9957
Measured Mass : 233.9956
Error : 0.37 ppm

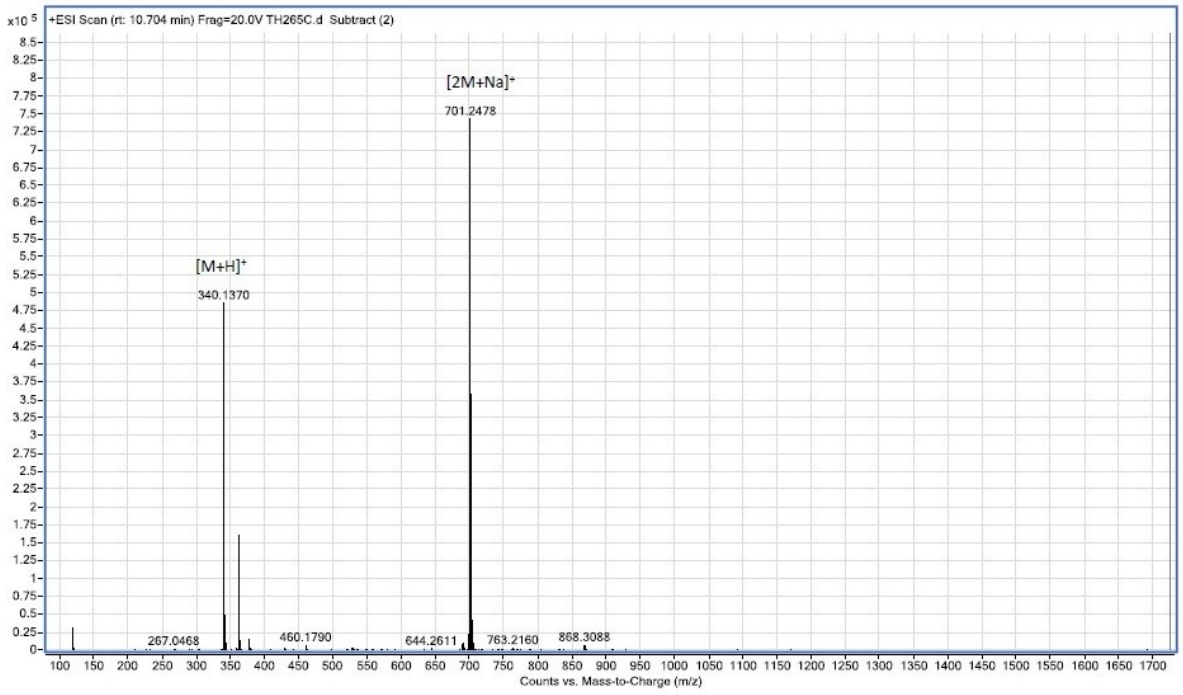
(*Z*)-*N*,*N*-Diethyl-2,4-diphenylbut-1-en-3-yne-1-sulfonamide (4) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

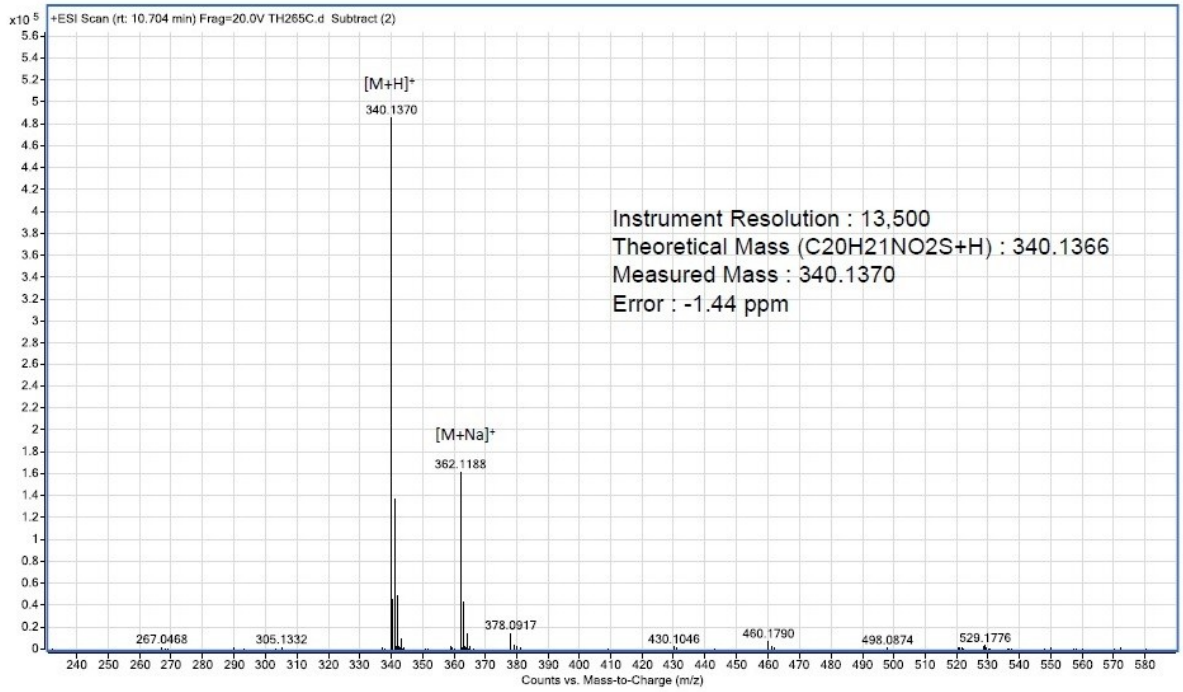




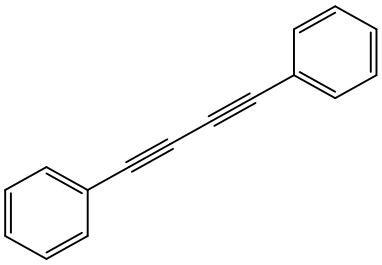

136.1751
132.6717
132.1639
131.1485
130.2853
129.6760
128.9144
128.6098
127.1881
122.3138
103.6291
84.8936
41.8883
14.5213
150
100
50
[ppm]

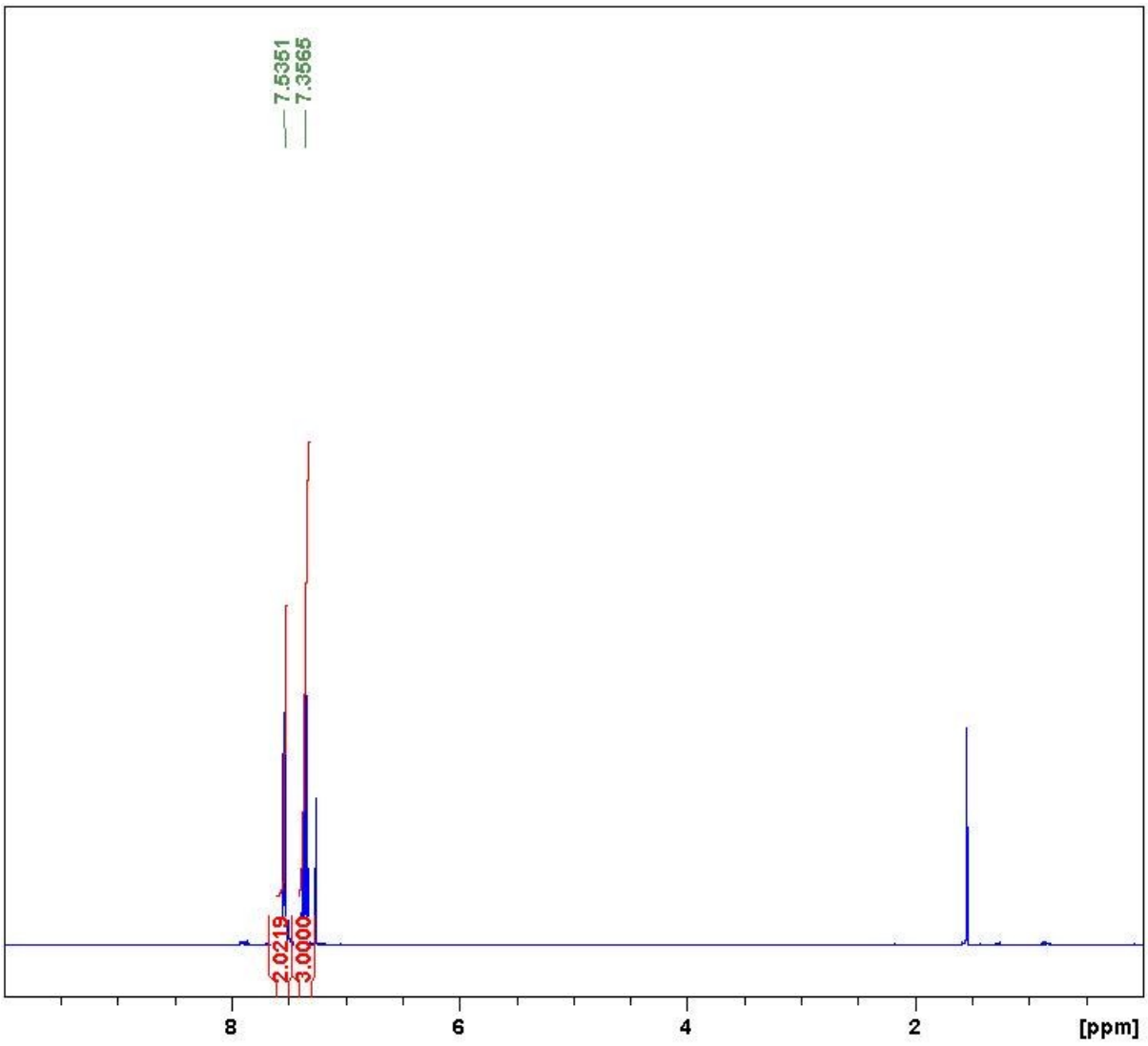

Transmittance [%]
95
90
85
80
75
70
3059.20
2973.03
2928.91
2873.53
2252.17
2211.23
1730.29
1678.80
1597.87
1555.43
1489.09
1444.30
1334.30
1265.71
1200.37
1182.86
1144.61
1016.91
934.35
910.04
814.83
757.78
734.62
691.88
648.10
562.53
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

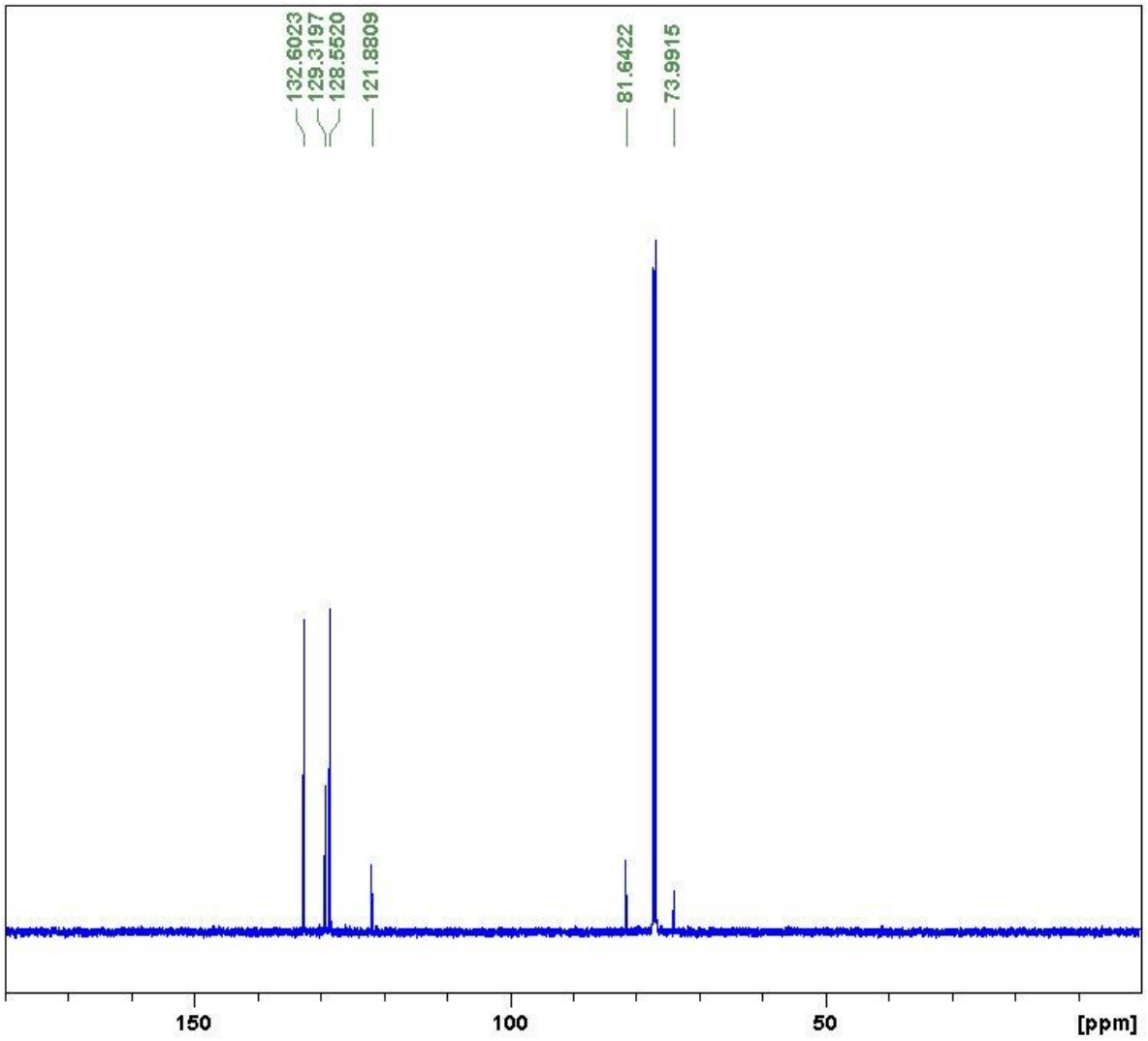

+ESI Scan (rt: 10.704 min) Frag=20.0V TH265C.d Subtract (2)
x10 5
[2M+Na]+
701.2478
[M+H]+
340.1370
267.0468
460.1790
644.2611
763.2160
868.3088
Counts vs. Mass-to-Charge (m/z)

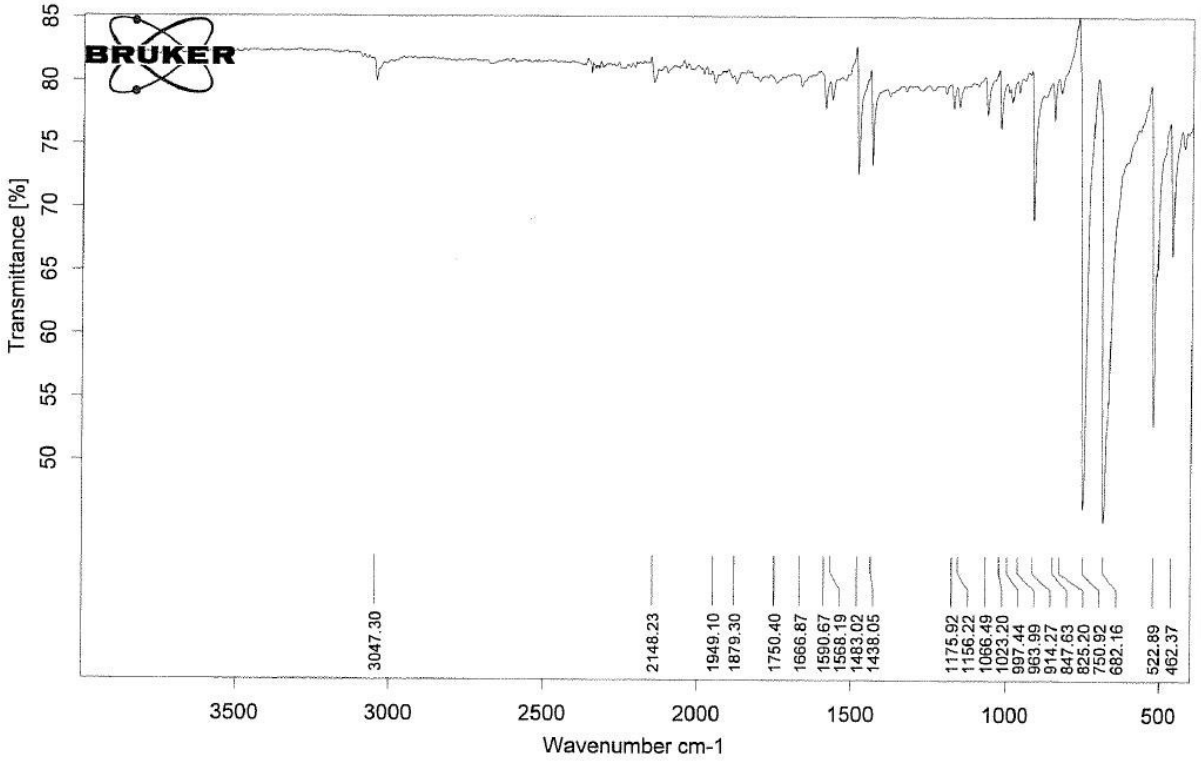

+ESI Scan (rt: 10.704 min) Frag=20.0V TH265C.d Subtract (2)
x10 5
[M+H]+
340.1370
[M+Na]+
362.1188
Instrument Resolution : 13,500
Theoretical Mass (C20H21NO2S+H) : 340.1366
Measured Mass : 340.1370
Error : -1.44 ppm
267.0468
305.1332
378.0917
430.1046
460.1790
498.0874
529.1776
Counts vs. Mass-to-Charge (m/z)

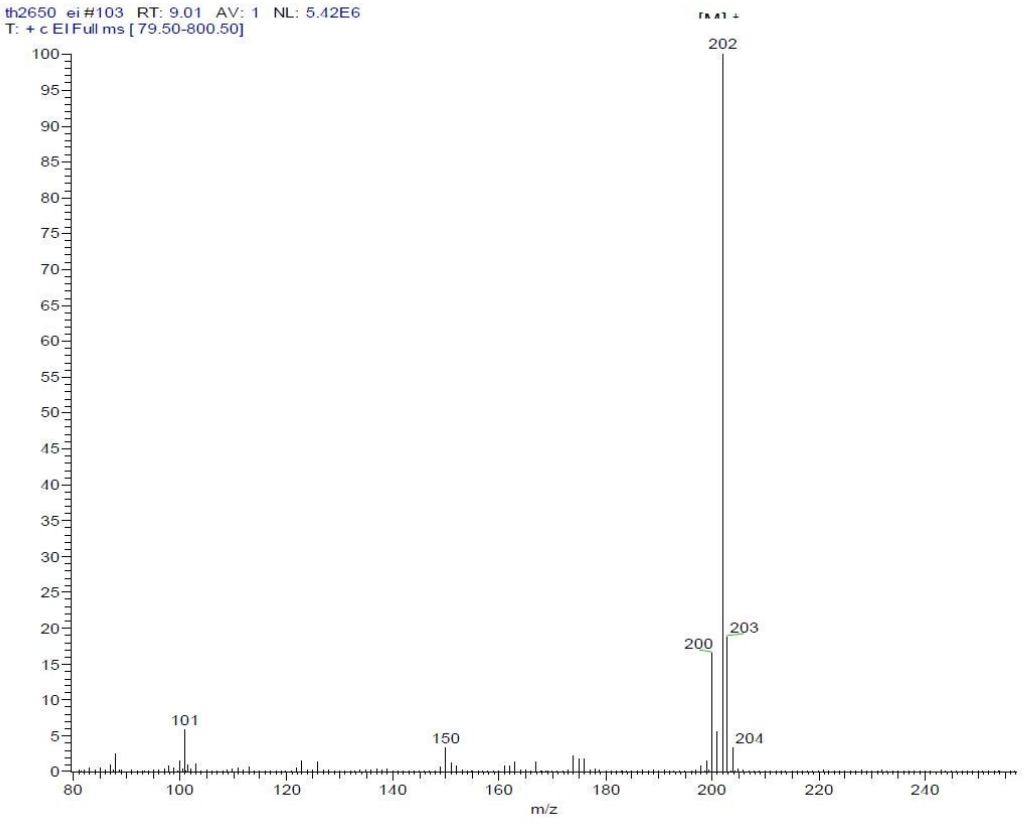
1,4-Diphenylbuta-1,3-diyne (5) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

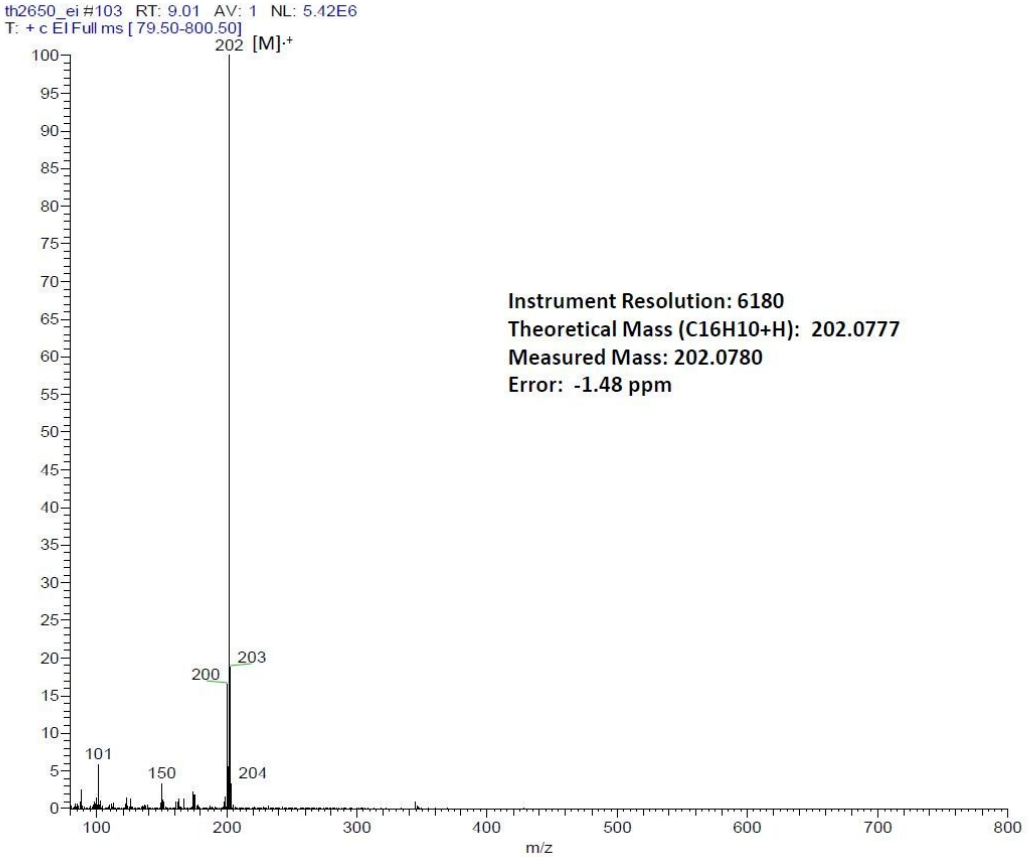





132.6023
129.3197
128.5520
121.8809
81.6422
73.9915
150
100
50
[ppm]

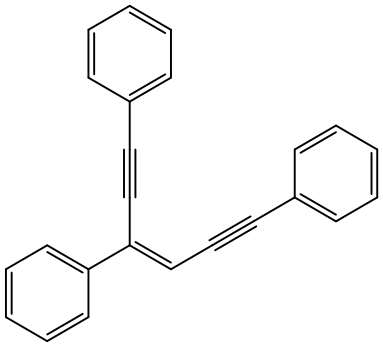

BRUKER
Transmittance [%]
85
80
75
70
65
60
55
50
3047.30
2148.23
1949.10
1879.30
1750.40
1666.87
1590.67
1568.19
1483.02
1438.05
1175.92
1156.22
1066.49
1023.20
997.44
963.99
914.27
847.63
825.20
750.92
682.16
522.89
462.37
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

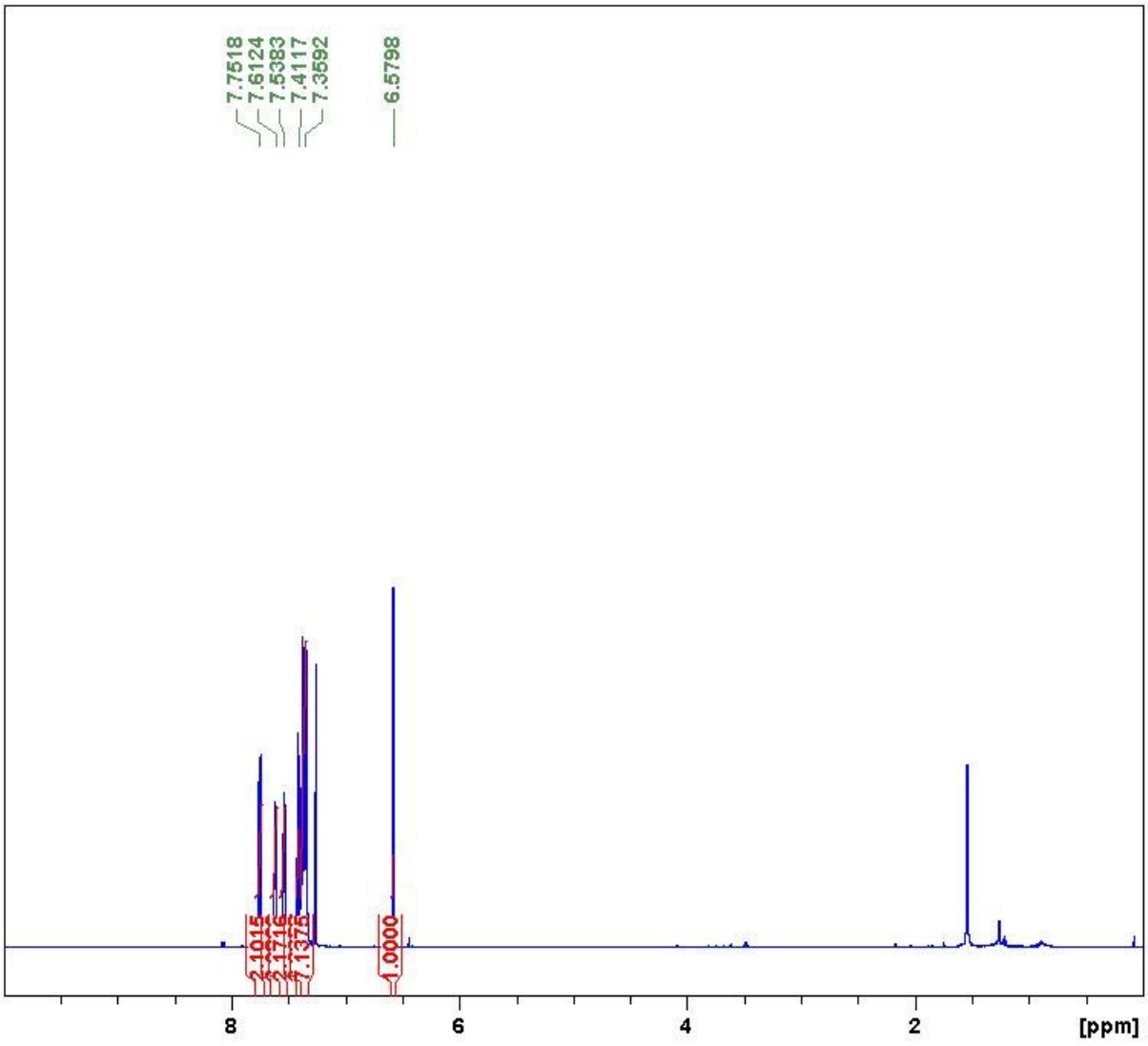


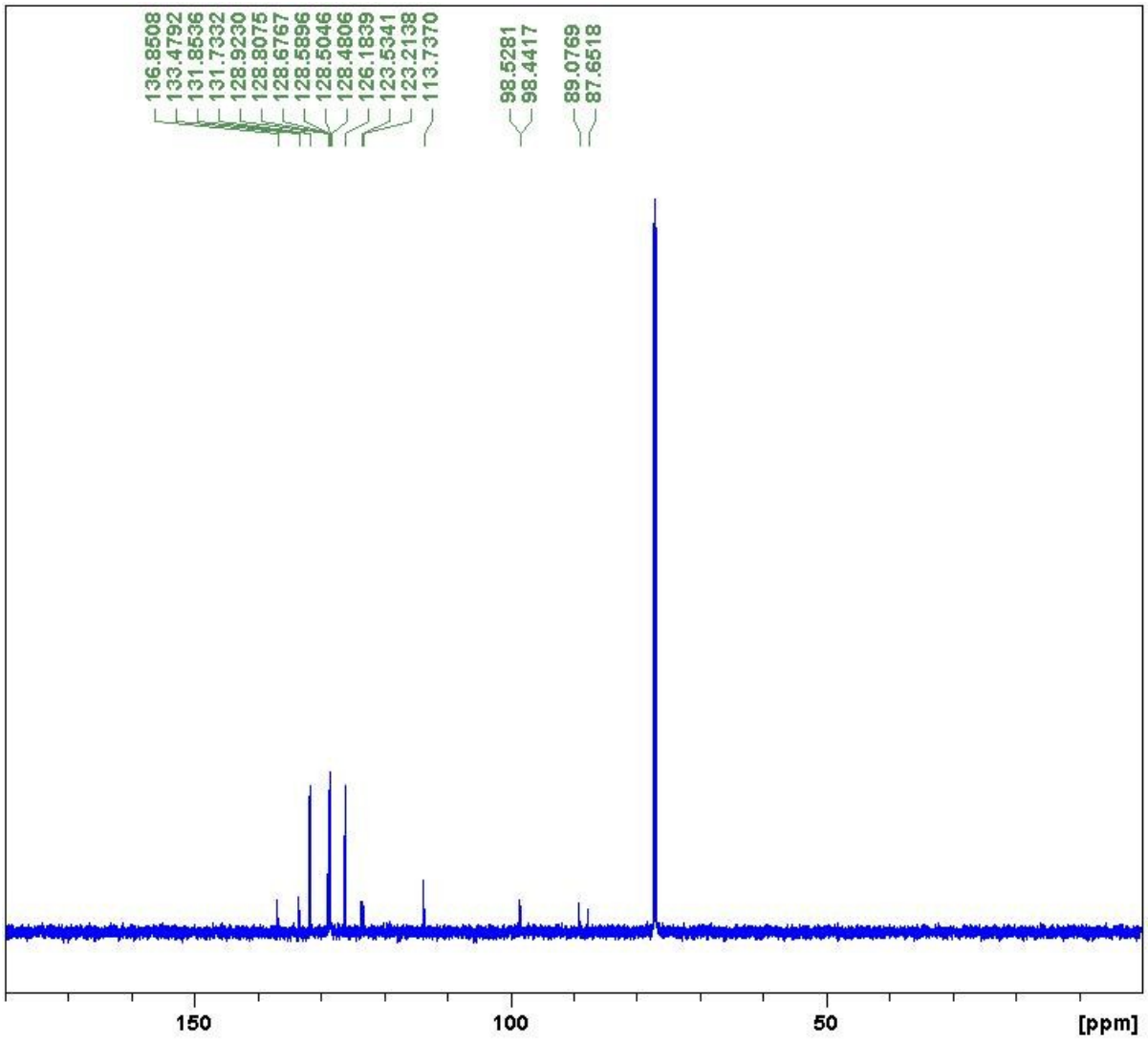


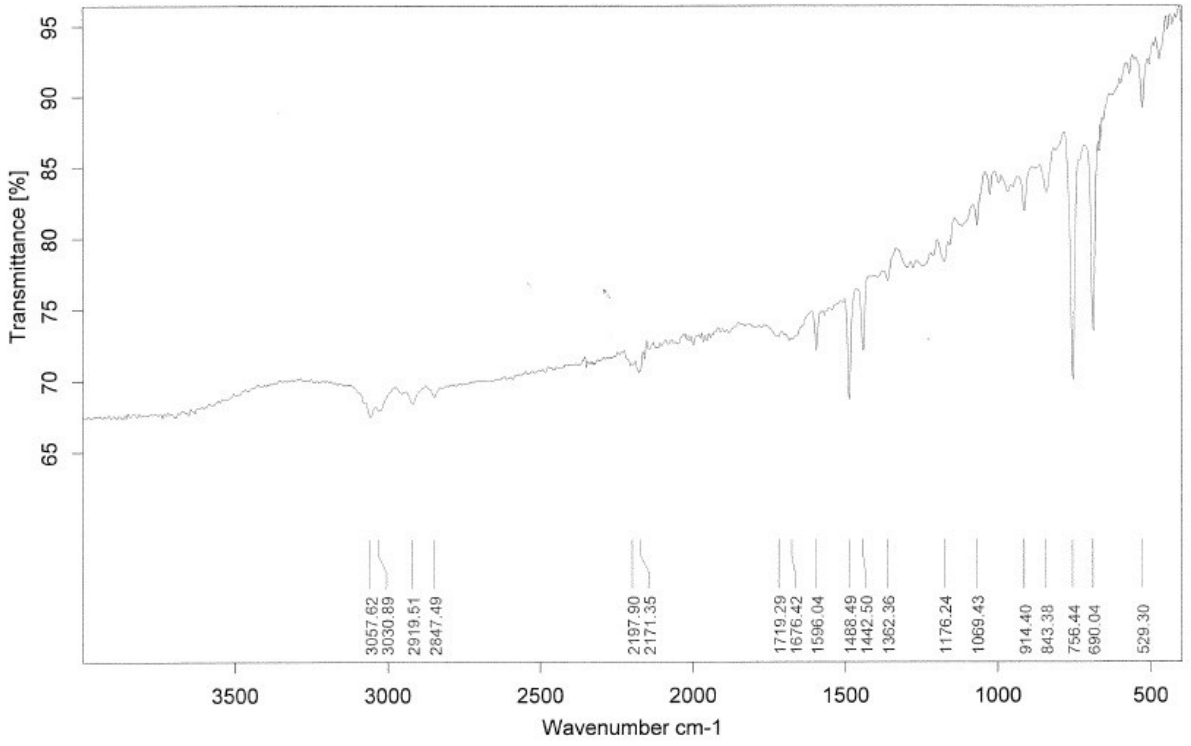
Instrument Resolution: 6180
Theoretical Mass (C16H10+H): 202.0777
Measured Mass: 202.0780
Error: -1.48 ppm

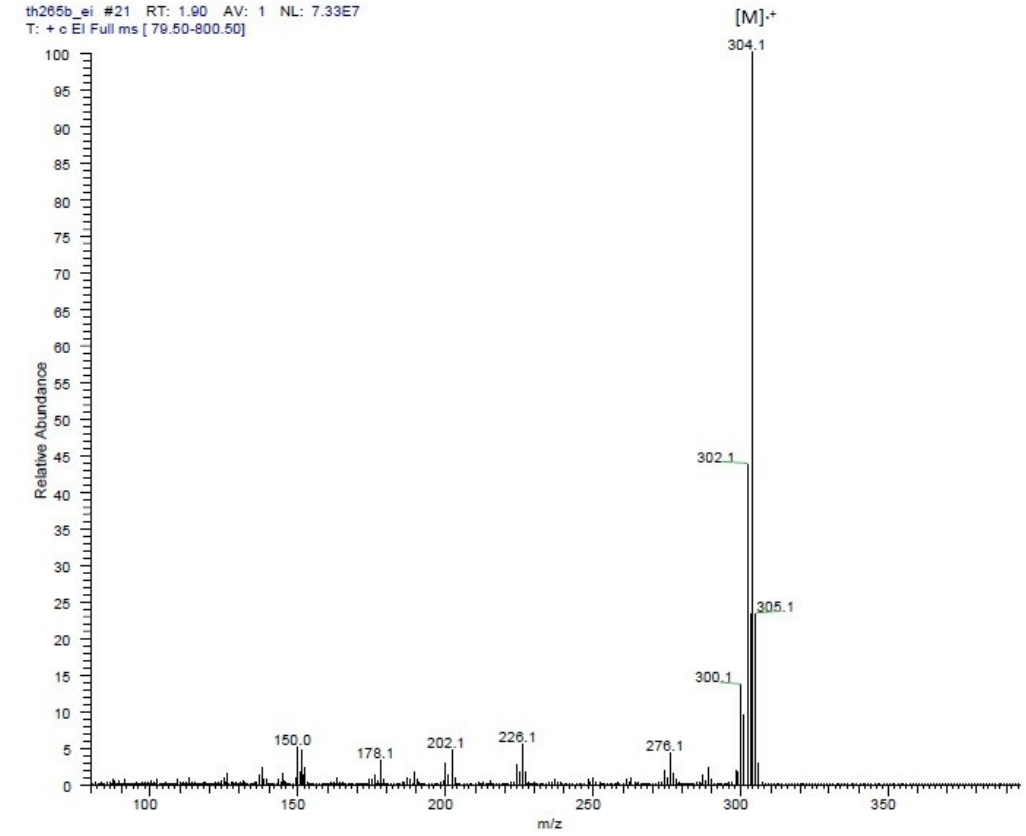
(*Z*)-Hexa-3-en-1,5-diyne-1,3,6-triyltribenzene (6) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

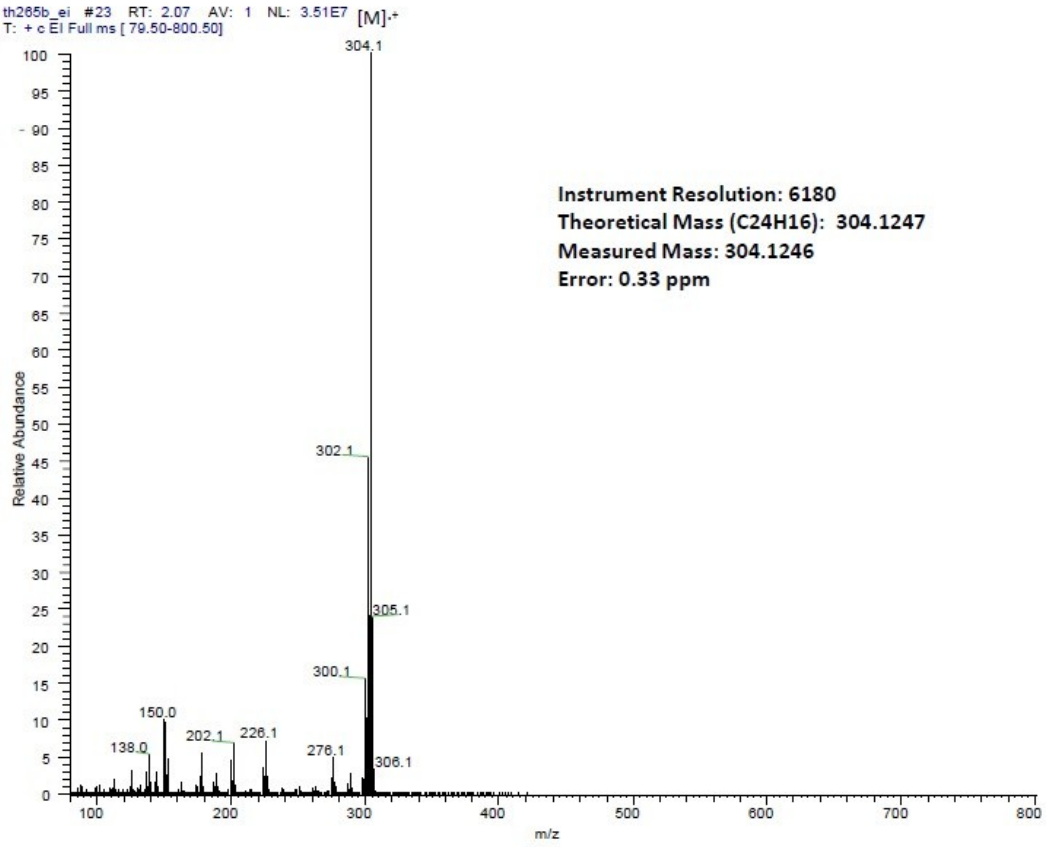





136.8508
133.4792
131.8536
131.7332
128.9230
128.8075
128.6767
128.5896
128.5046
128.4806
126.1839
123.5341
123.2138
113.7370
98.5281
98.4417
89.0769
87.6518
150
100
50
[ppm]

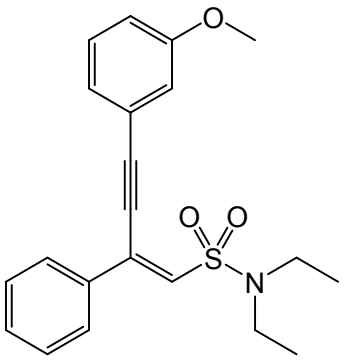

Transmittance [%]
95
90
85
80
75
70
65
3057.62
3030.89
2919.51
2847.49
2197.90
2171.35
1719.29
1676.42
1596.04
1488.49
1442.50
1362.36
1176.24
1069.43
914.40
843.38
756.44
690.04
529.30
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

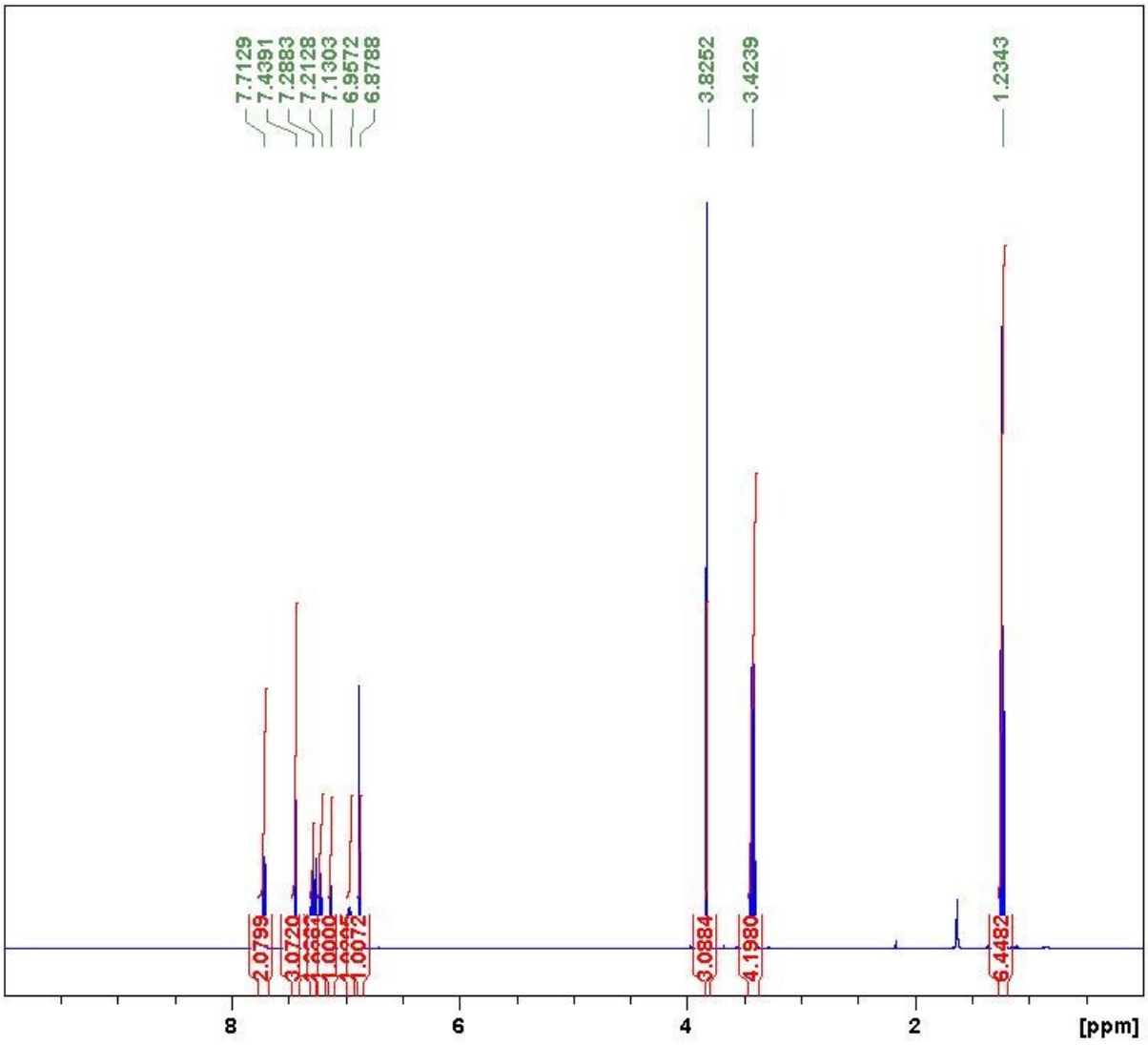


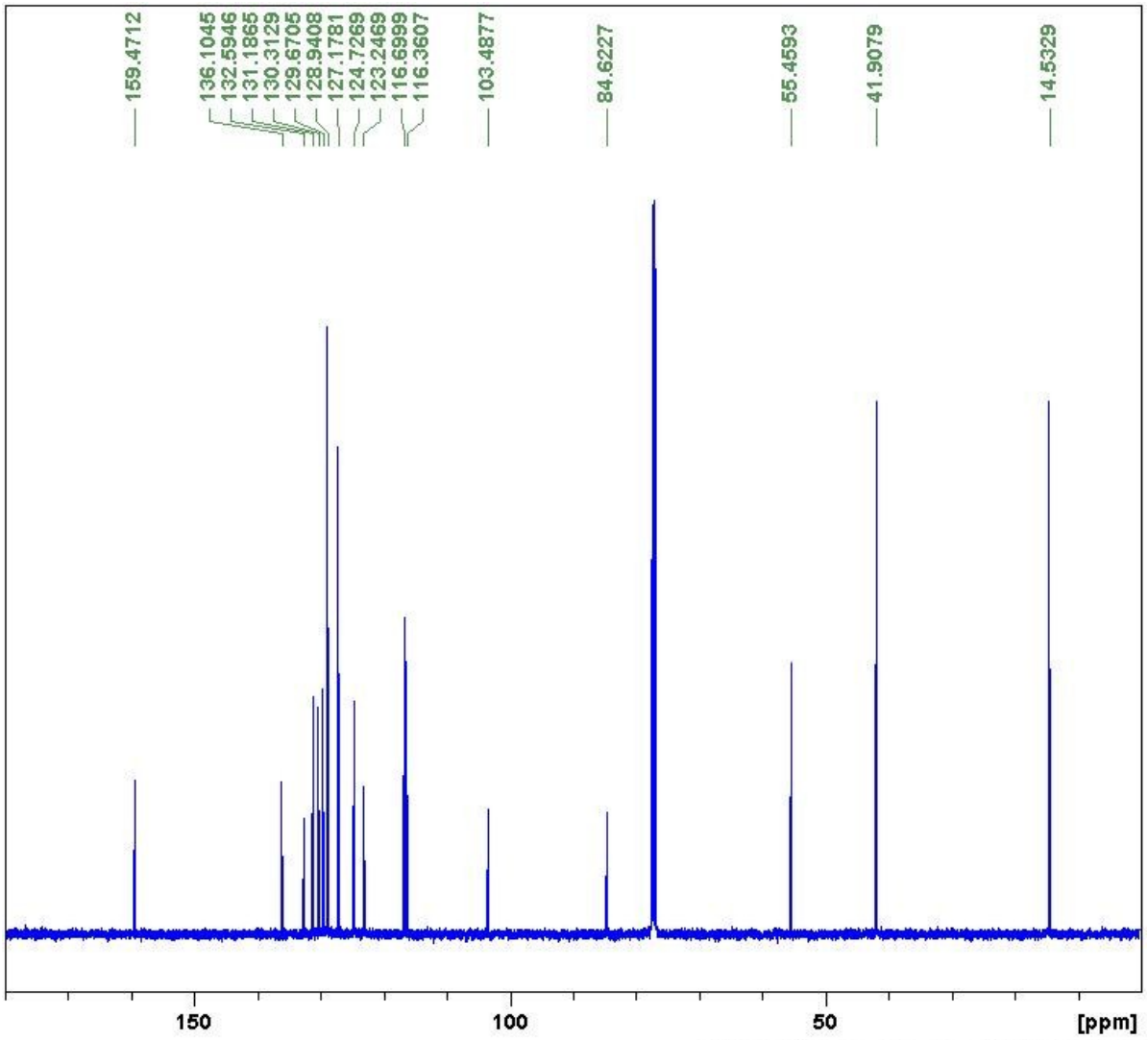


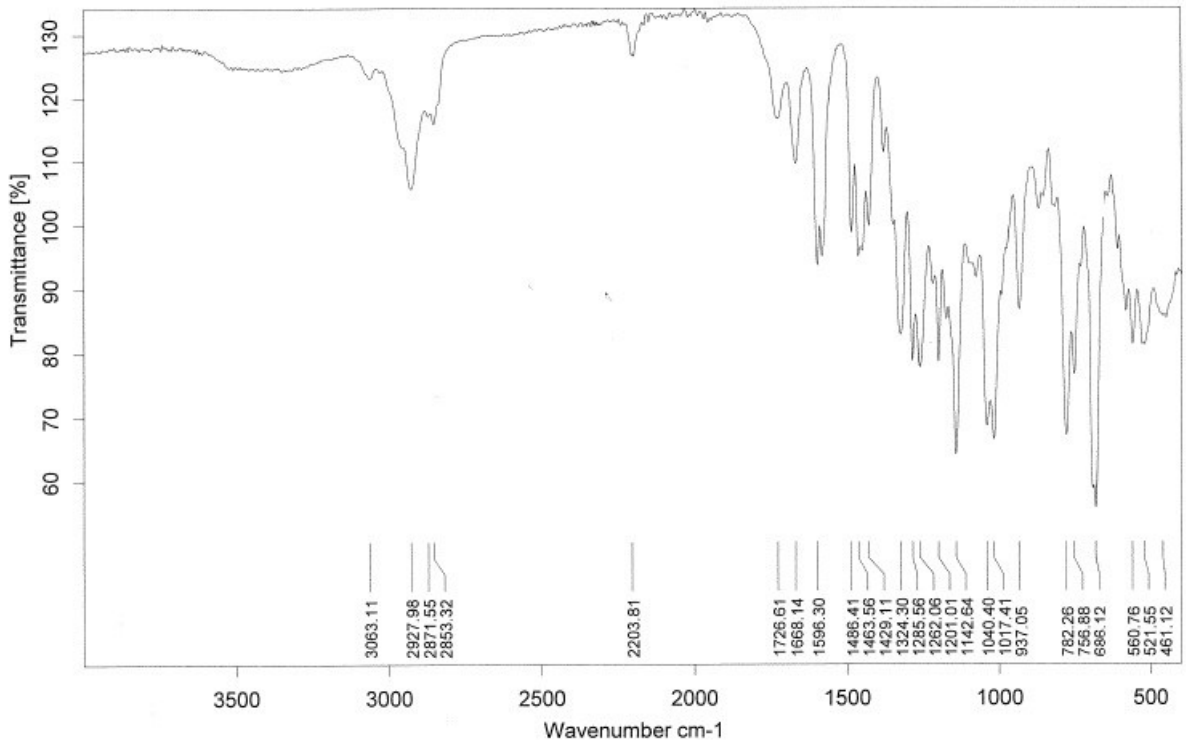
Instrument Resolution: 6180
Theoretical Mass (C24H16): 304.1247
Measured Mass: 304.1246
Error: 0.33 ppm

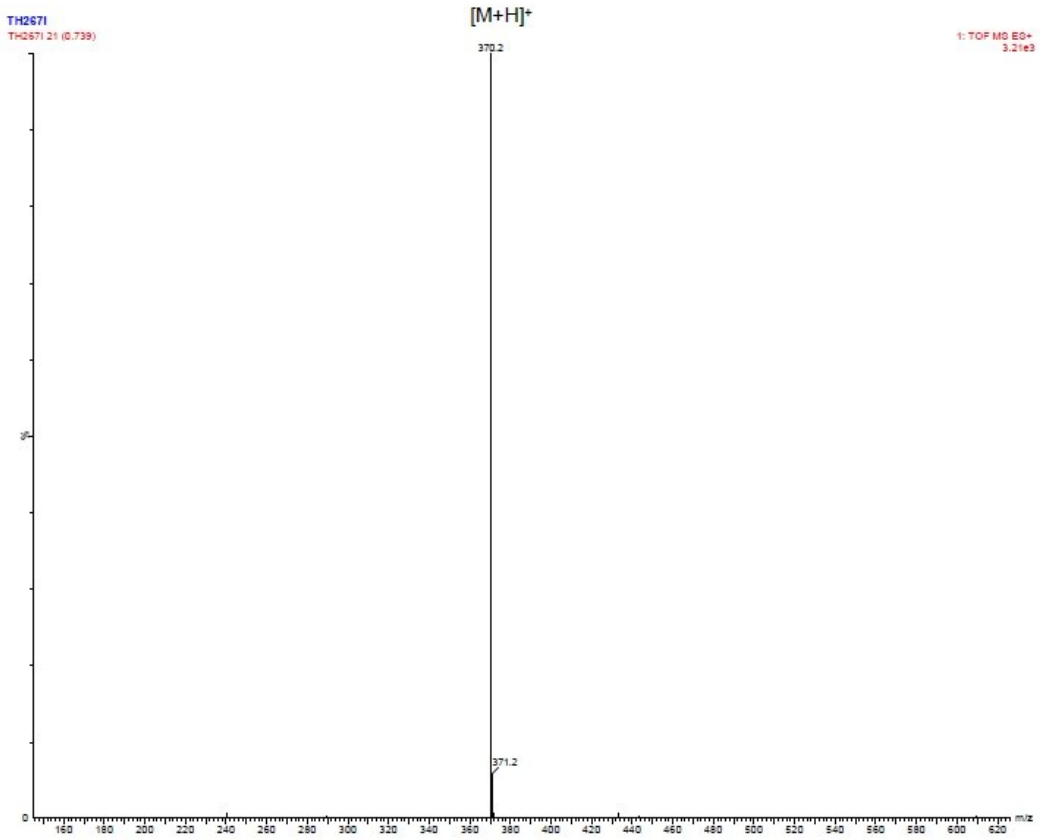
(*Z*)-*N*,*N*-Diethyl-4-(3-methoxyphenyl)-2-phenylbut-1-en-3-yne-1-sulfonamide (13) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

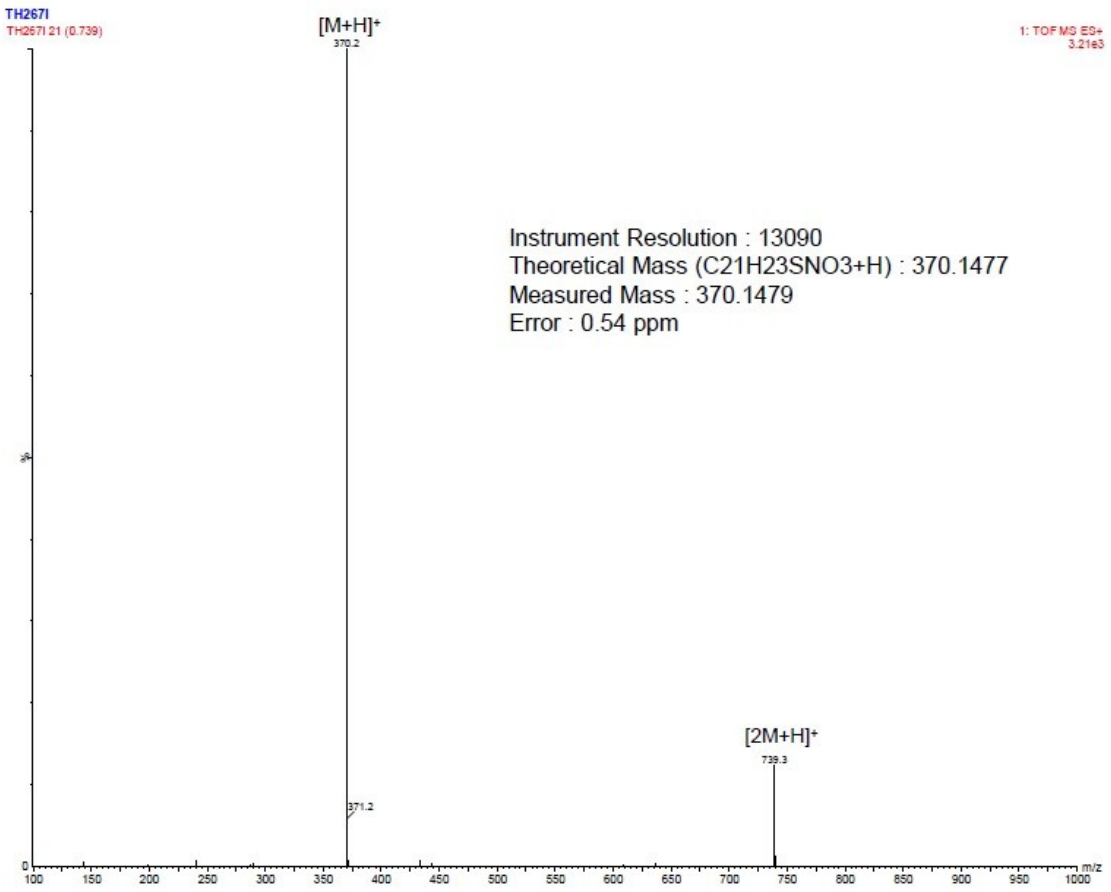




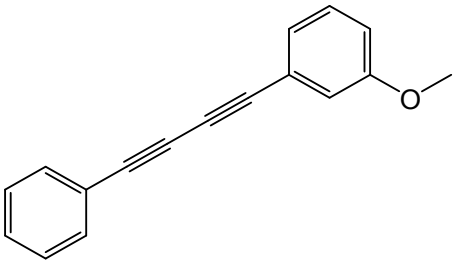

159.4712
136.1045
132.5946
131.1865
130.3129
129.6705
128.9408
127.1781
124.7269
123.2469
116.6999
116.3607
103.4877
84.6227
55.4593
41.9079
14.5329
150
100
50
[ppm]

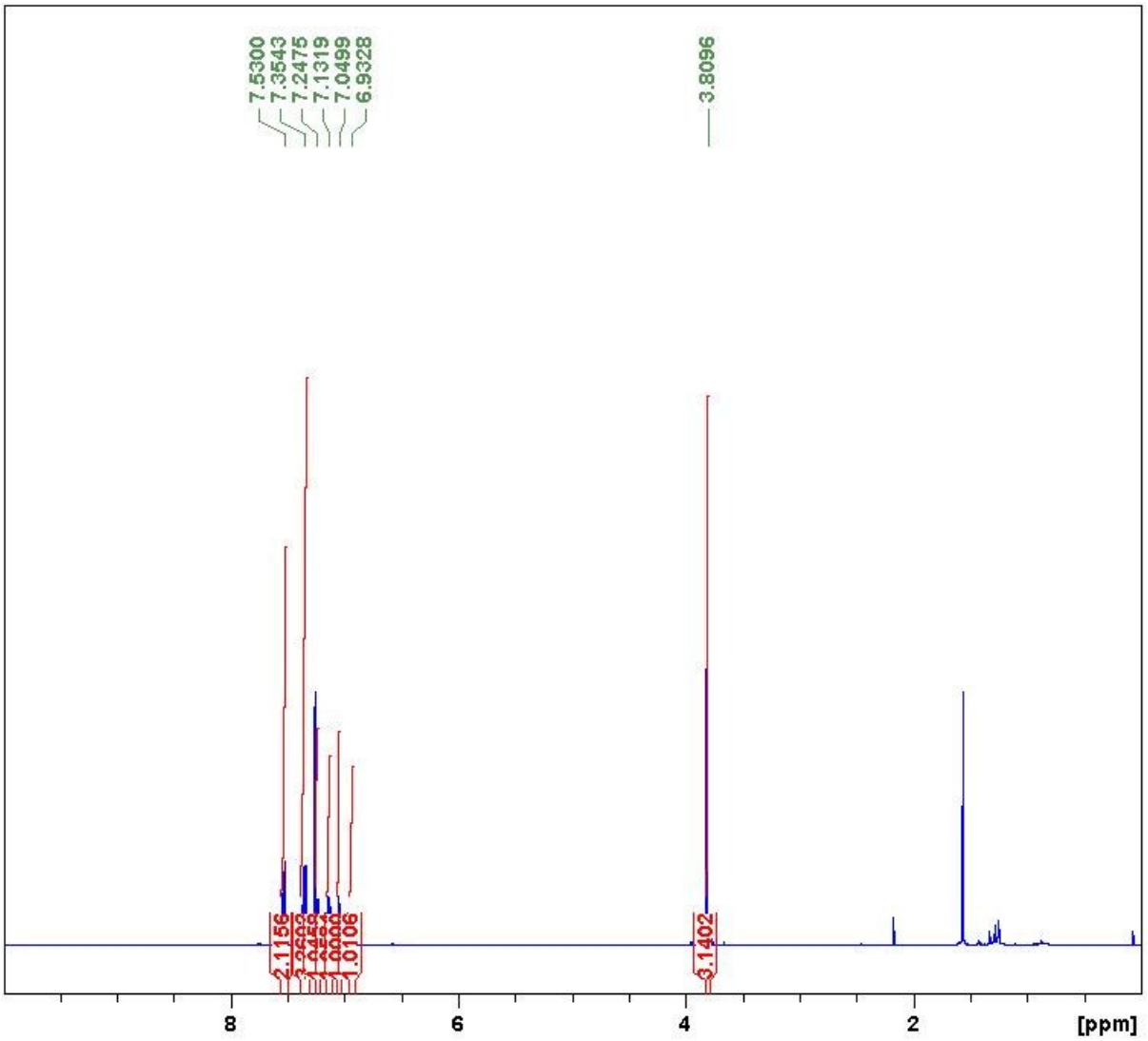

Transmittance [%]
130
120
110
100
90
80
70
60
3063.11
2927.98
2871.55
2853.32
2203.81
1726.61
1668.14
1596.30
1486.41
1463.56
1429.11
1324.30
1285.56
1262.06
1201.01
1142.64
1040.40
1017.41
937.05
782.26
756.88
686.12
560.76
521.55
461.12
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

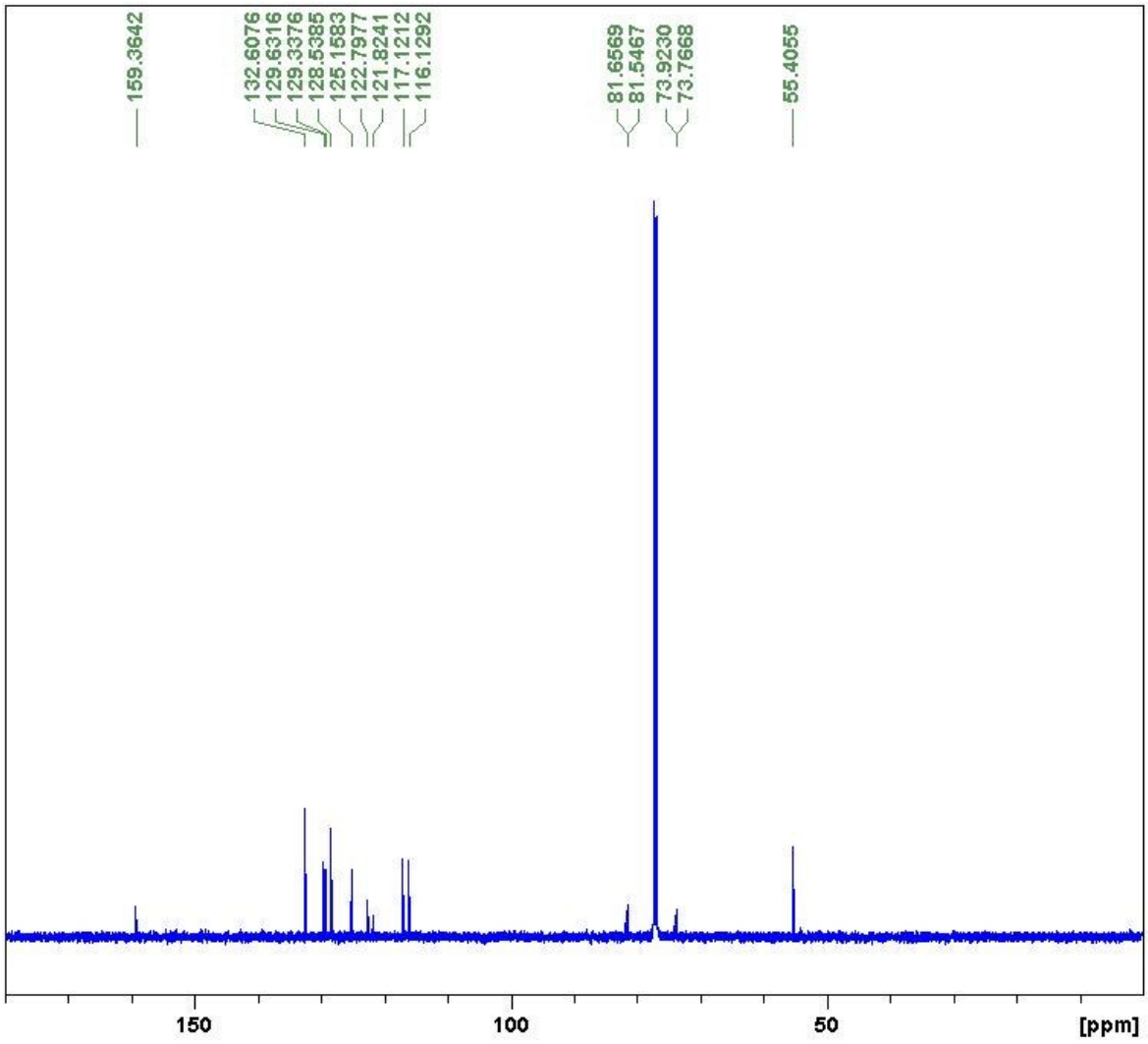

TH267I
TH267I 21 (0.739)
[M+H]+
370.2
1: TOF MS ES+
3.21e3
371.2
%
0
160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600 620
m/z

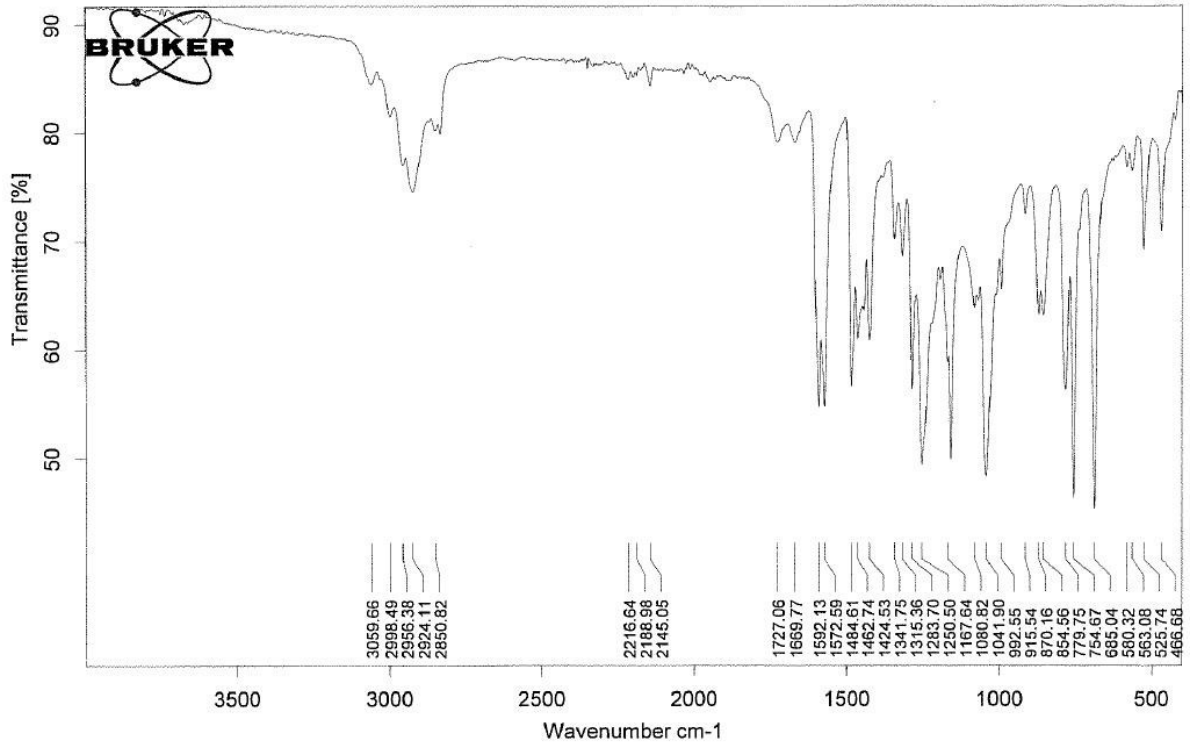

TH267I
TH267I 21 (0.739)
[M+H]+
370.2
1: TOF MS ES+
3.21e3
Instrument Resolution : 13090
Theoretical Mass (C21H23SNO3+H) : 370.1477
Measured Mass : 370.1479
Error : 0.54 ppm
[2M+H]+
739.3
371.2
%
0
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z

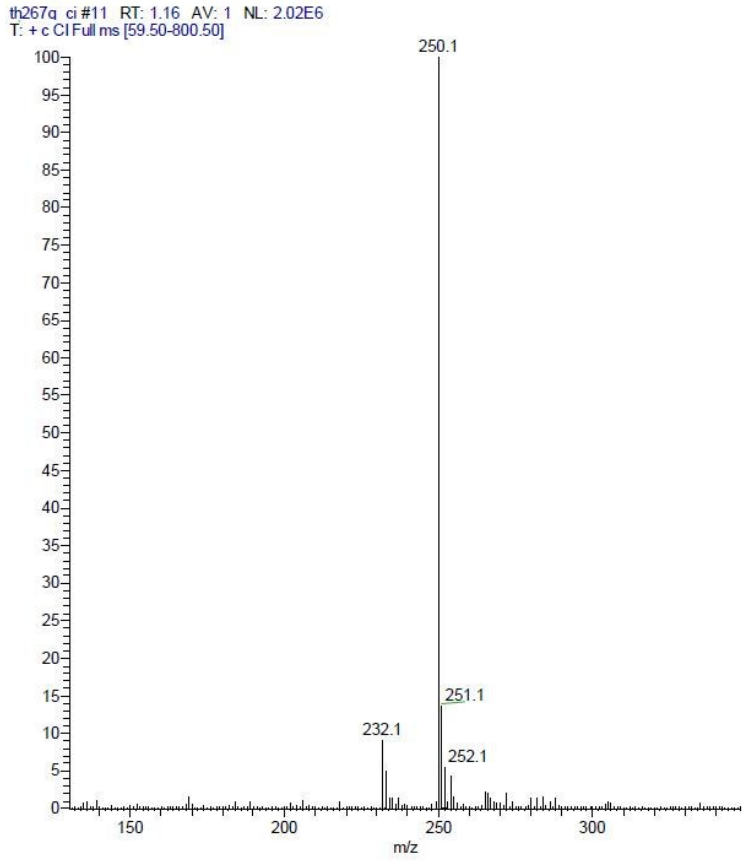
1-Methoxy-3-(phenylbuta-1,3-diyn-1-yl)benzene (14) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

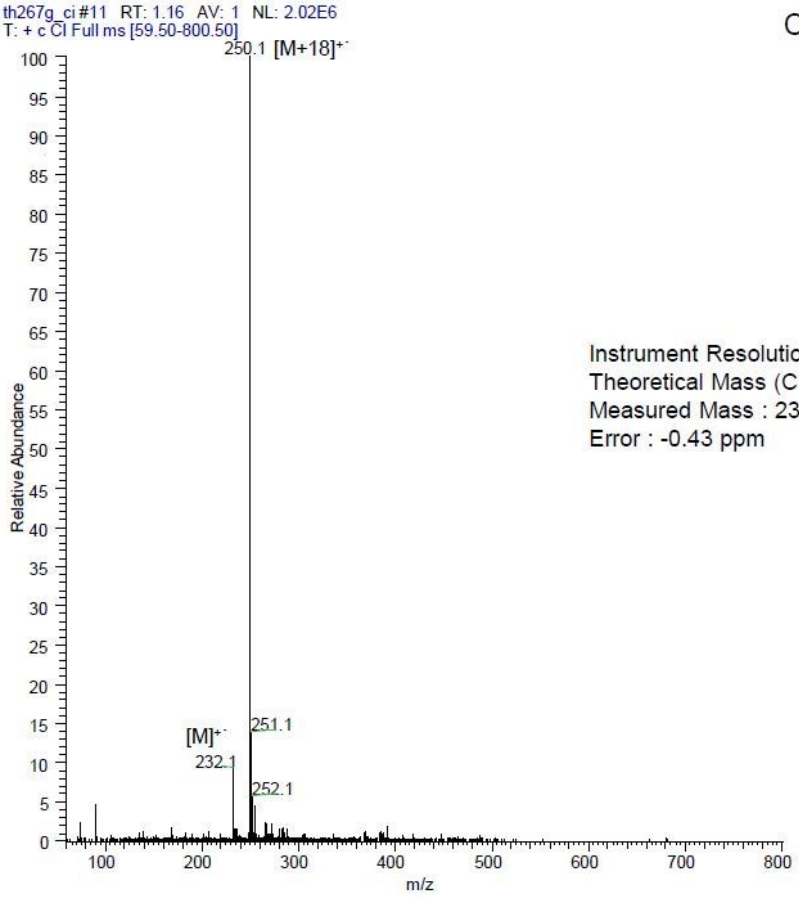





159.3642
132.6076
129.6316
129.3376
128.5385
125.1583
122.7977
121.8241
117.1212
116.1292
81.6569
81.5467
73.9230
73.7668
55.4055
150
100
50
[ppm]


BRUKER
Transmittance [%]
90
80
70
60
50
3059.66
2998.49
2956.38
2924.11
2850.82
2216.64
2188.98
2145.05
1727.06
1669.77
1592.13
1572.59
1484.61
1462.74
1424.53
1341.75
1315.36
1283.70
1250.50
1167.64
1080.82
1041.90
992.55
915.54
870.16
854.56
779.75
754.67
685.04
580.32
563.08
525.74
466.68
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

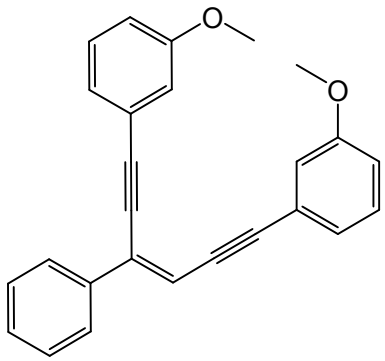


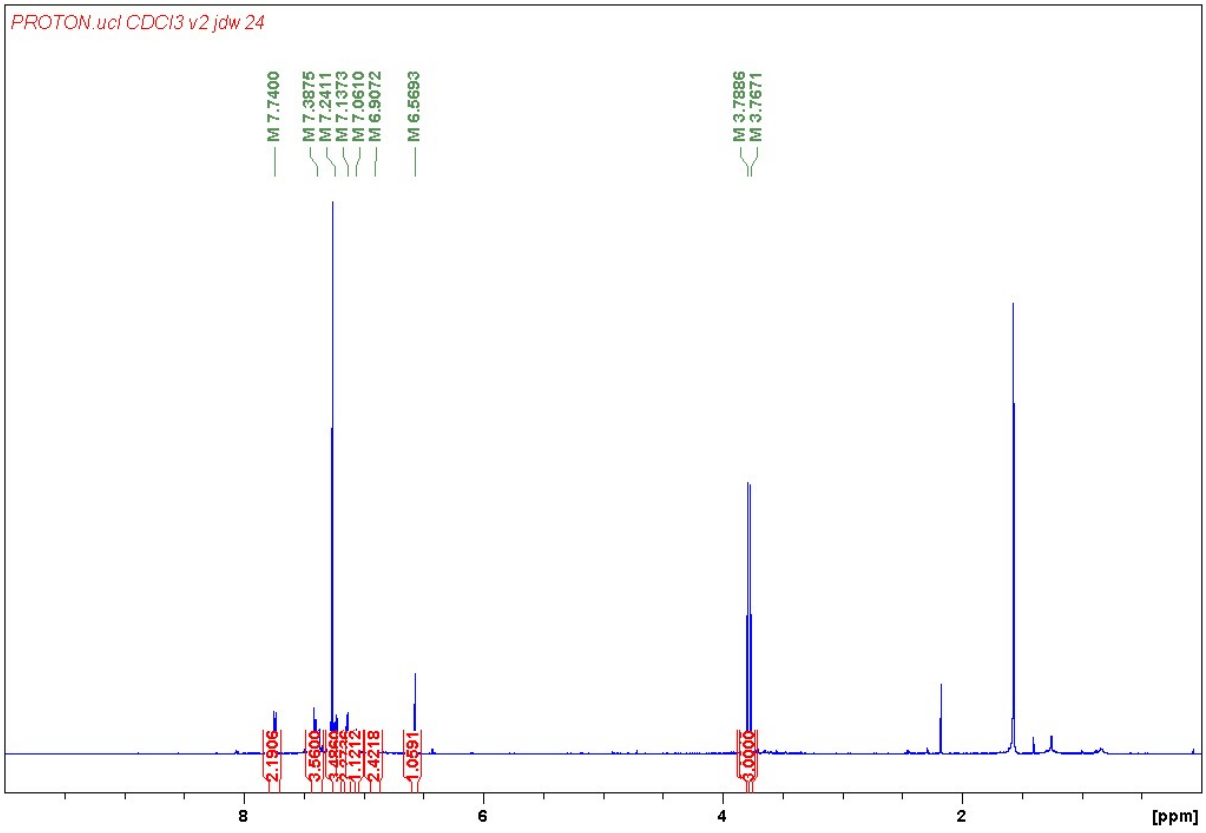


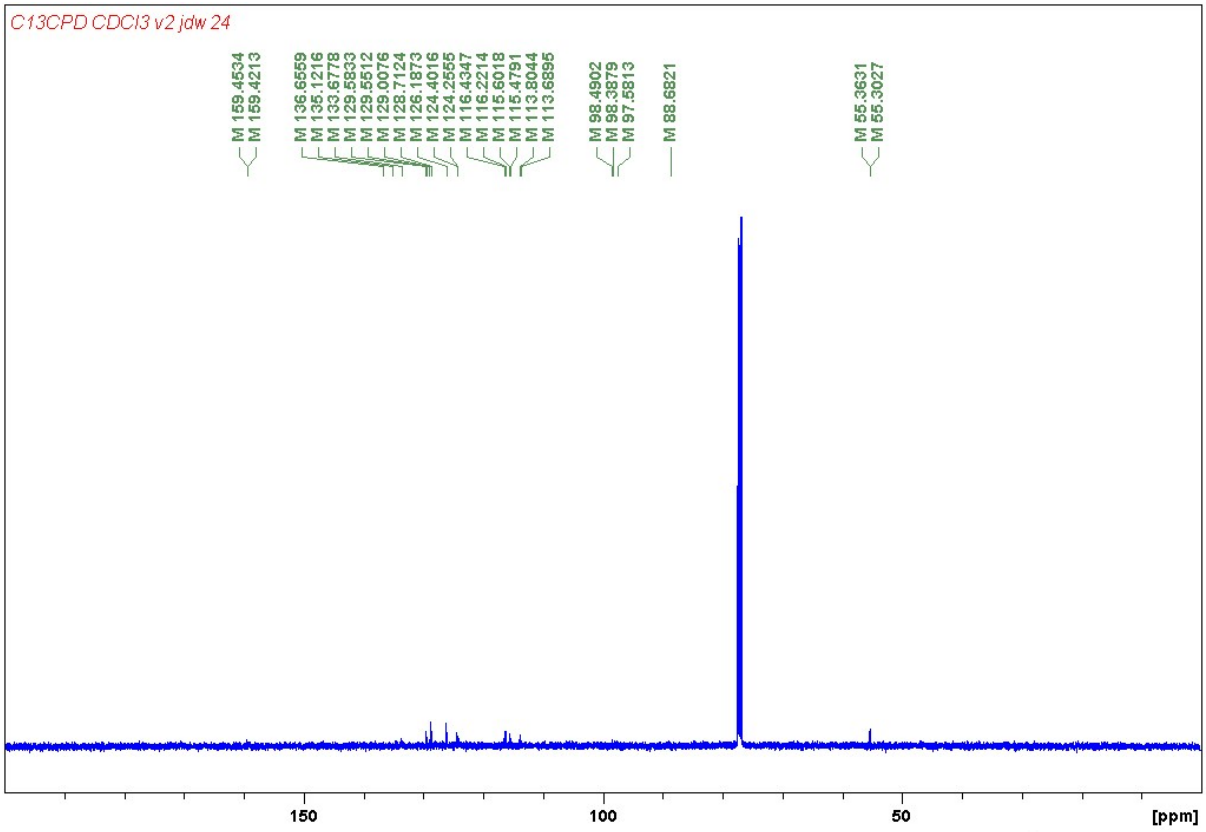
CI Ammonia *m/z* 18, 35, 52

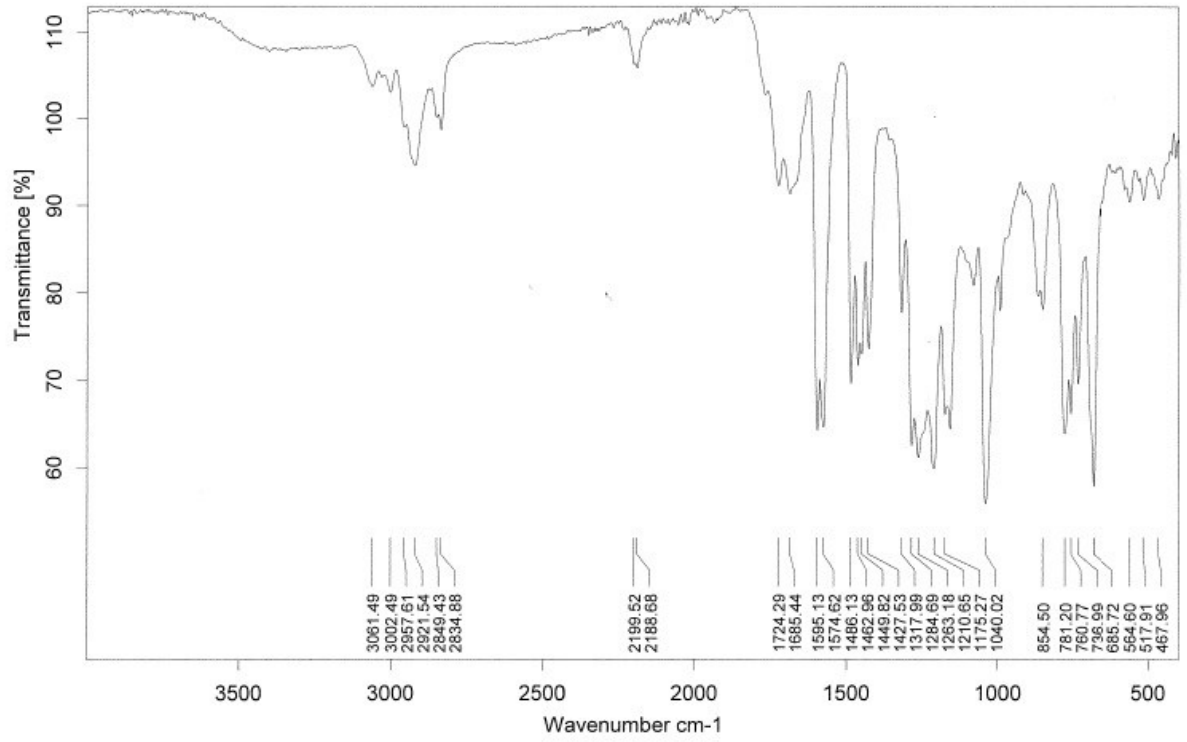
Instrument Resolution : 5890
Theoretical Mass (C17H12O) : 232.0883
Measured Mass : 232.0884
Error : -0.43 ppm

(*Z*)-3,3'-(3-Phenylhexa-3-en-1,5-diyne-1,6-diyl)bis(methoxybenzene) (15) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

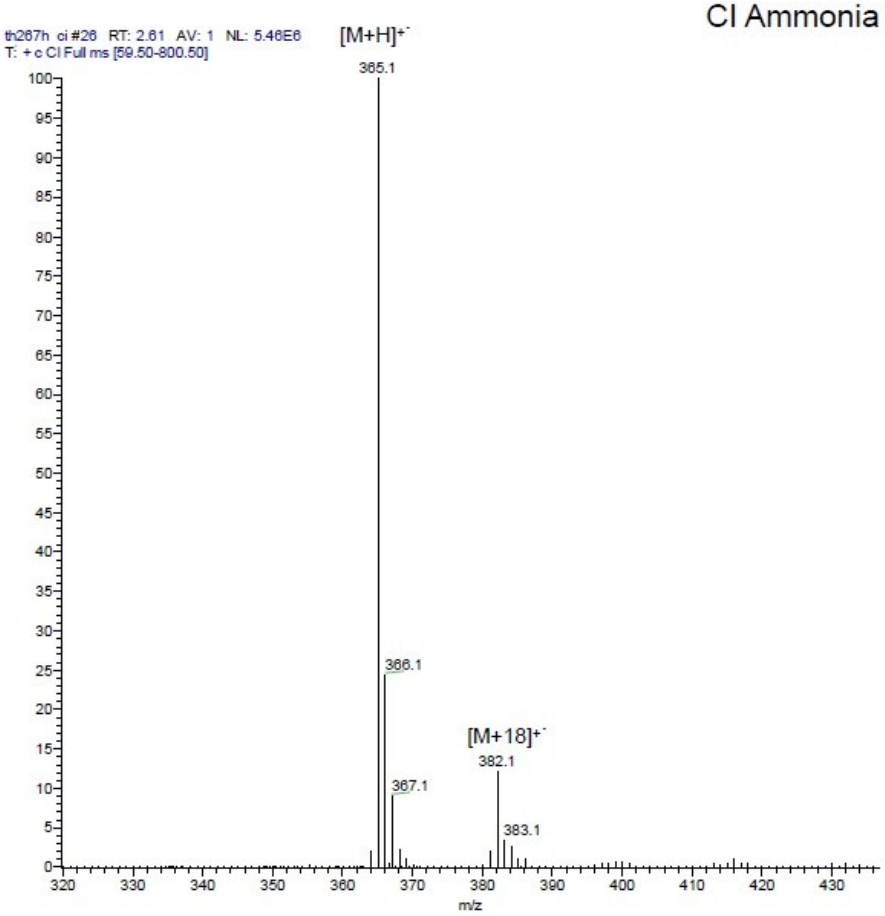




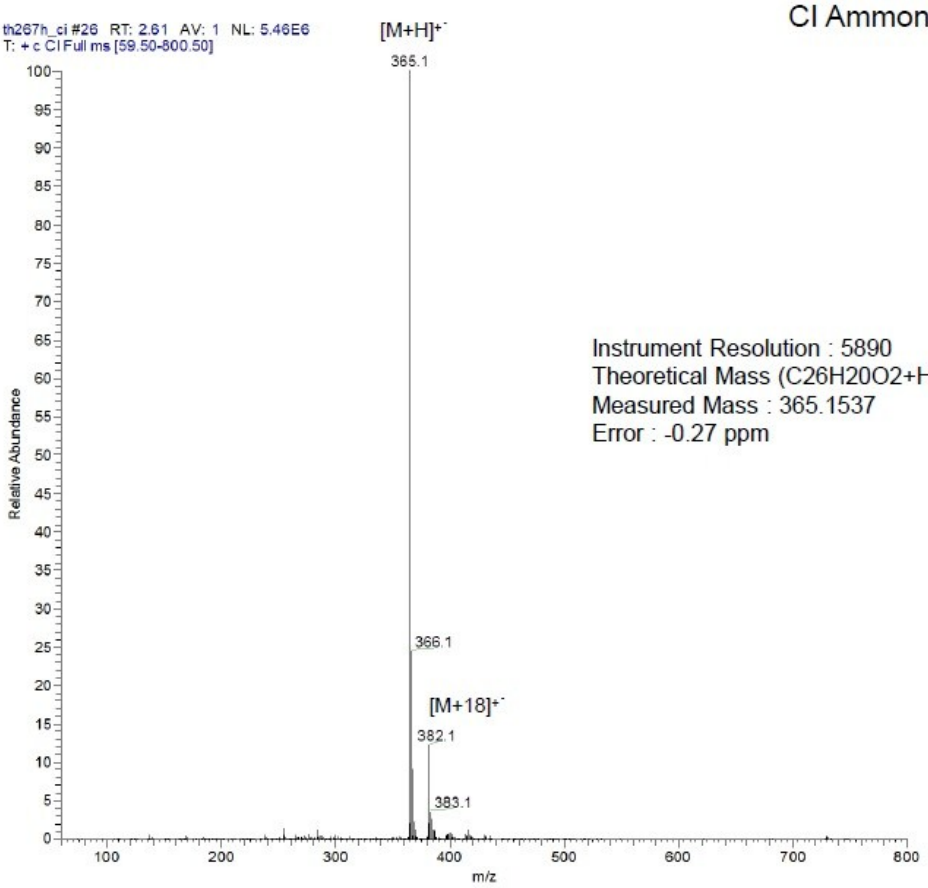

C13CPD CDCl3 v2 jdw 24
M 159.4534
M 159.4213
M 136.6559
M 135.1216
M 133.6778
M 129.5833
M 129.5512
M 129.0076
M 128.7124
M 126.1873
M 124.4016
M 124.2555
M 116.4347
M 116.2214
M 115.6018
M 115.4791
M 113.8044
M 113.6895
M 98.4902
M 98.3879
M 97.5813
M 88.6821
M 55.3631
M 55.3027
150
100
50
[ppm]


Transmittance [%]
110
100
90
80
70
60
3061.49
3002.49
2957.61
2921.54
2849.43
2834.88
2199.52
2188.68
1724.29
1685.44
1595.13
1574.62
1486.13
1462.96
1449.82
1427.53
1317.99
1284.69
1263.18
1210.65
1175.27
1040.02
854.50
781.20
760.77
736.99
685.72
564.60
517.91
467.96
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

CI Ammonia *m/z* 18, 35, 52

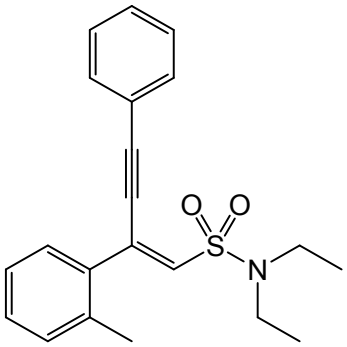


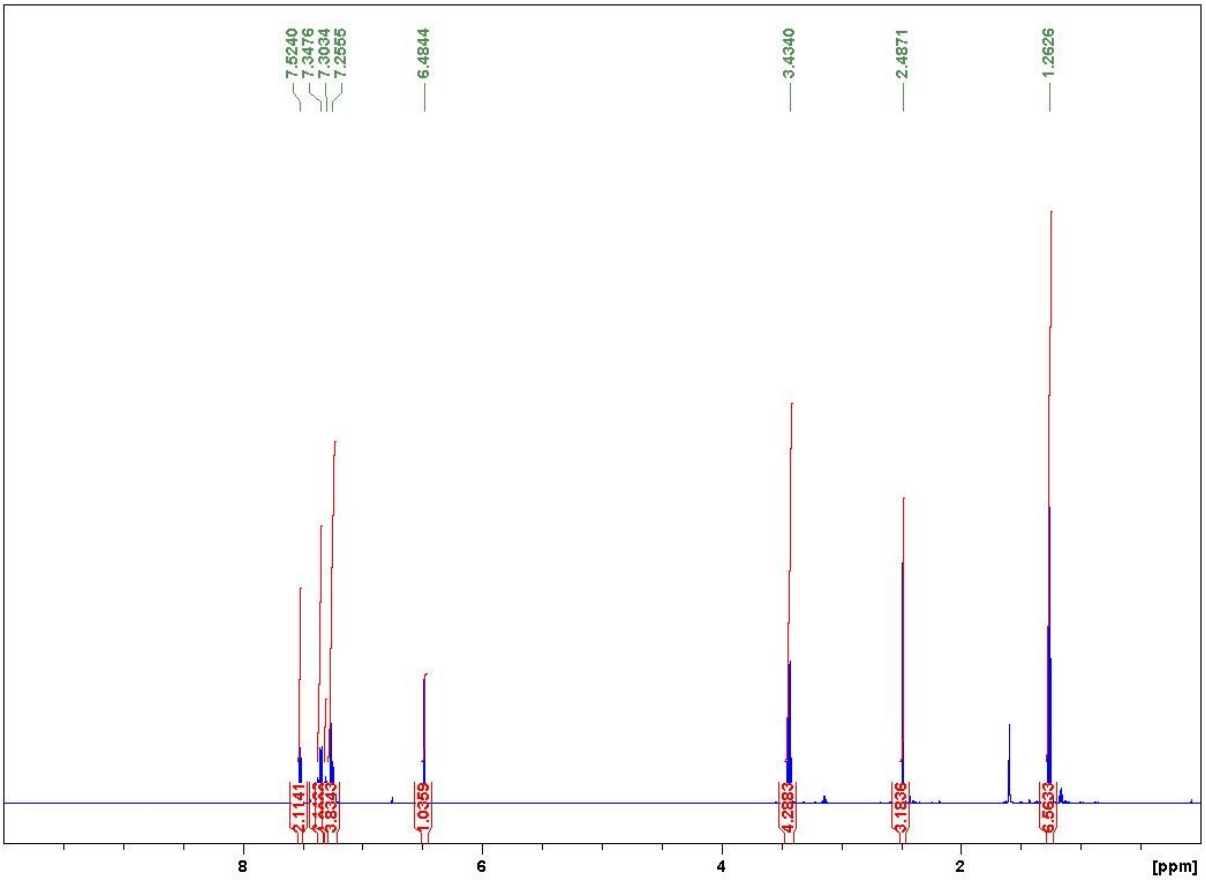
CI Ammonia *m/z* 18, 35, 52

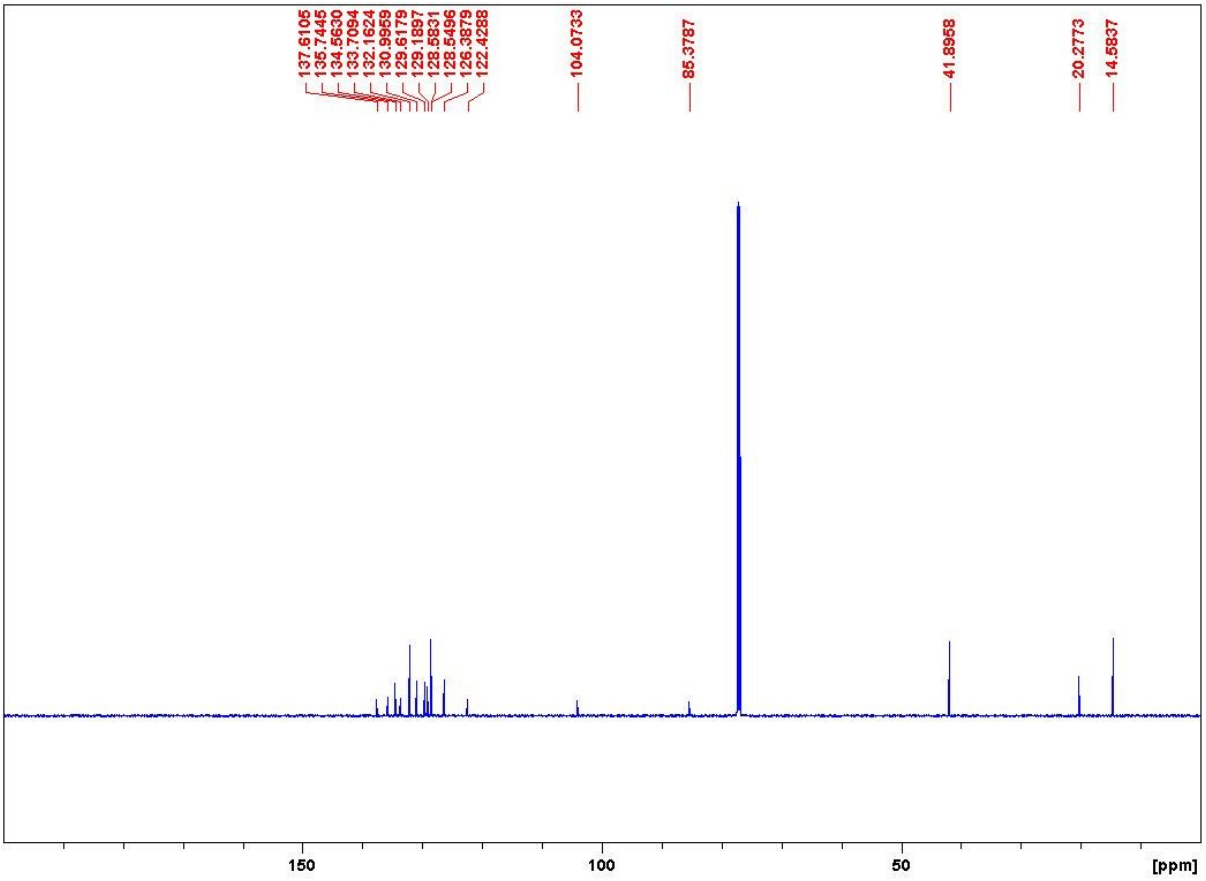


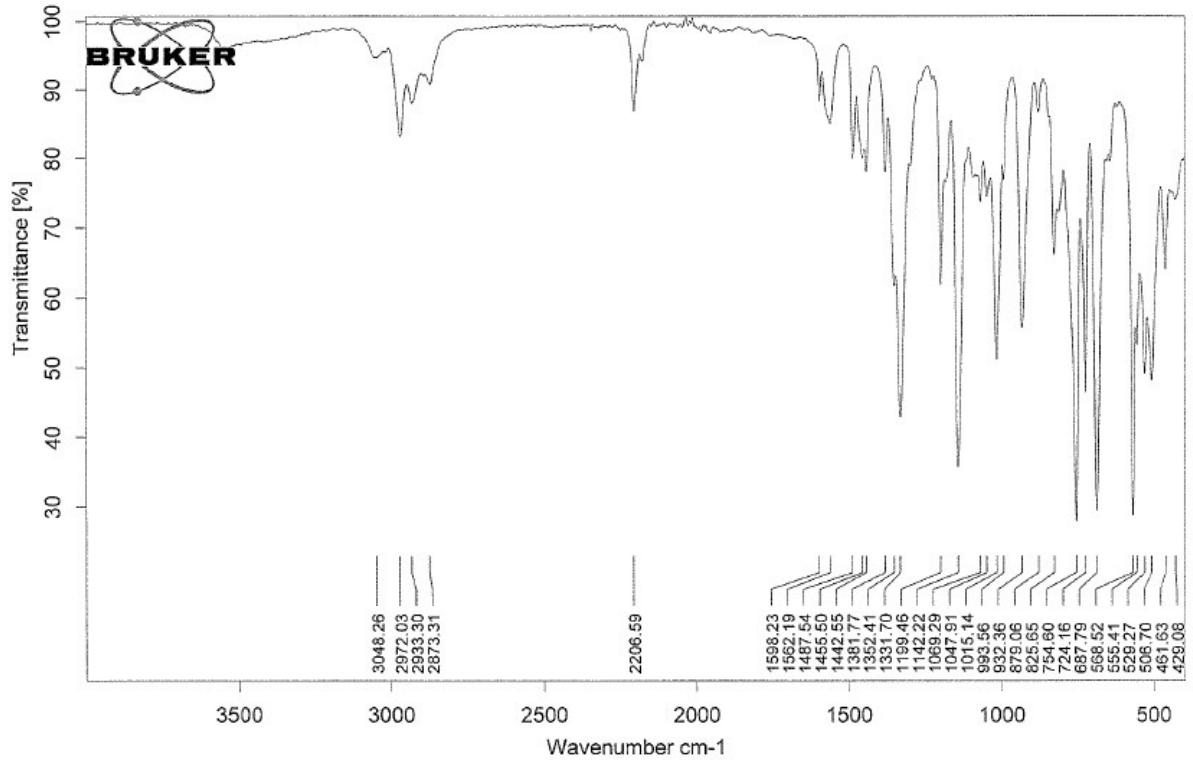
Instrument Resolution : 5890
Theoretical Mass (C26H20O2+H) : 365.1536
Measured Mass : 365.1537
Error : -0.27 ppm

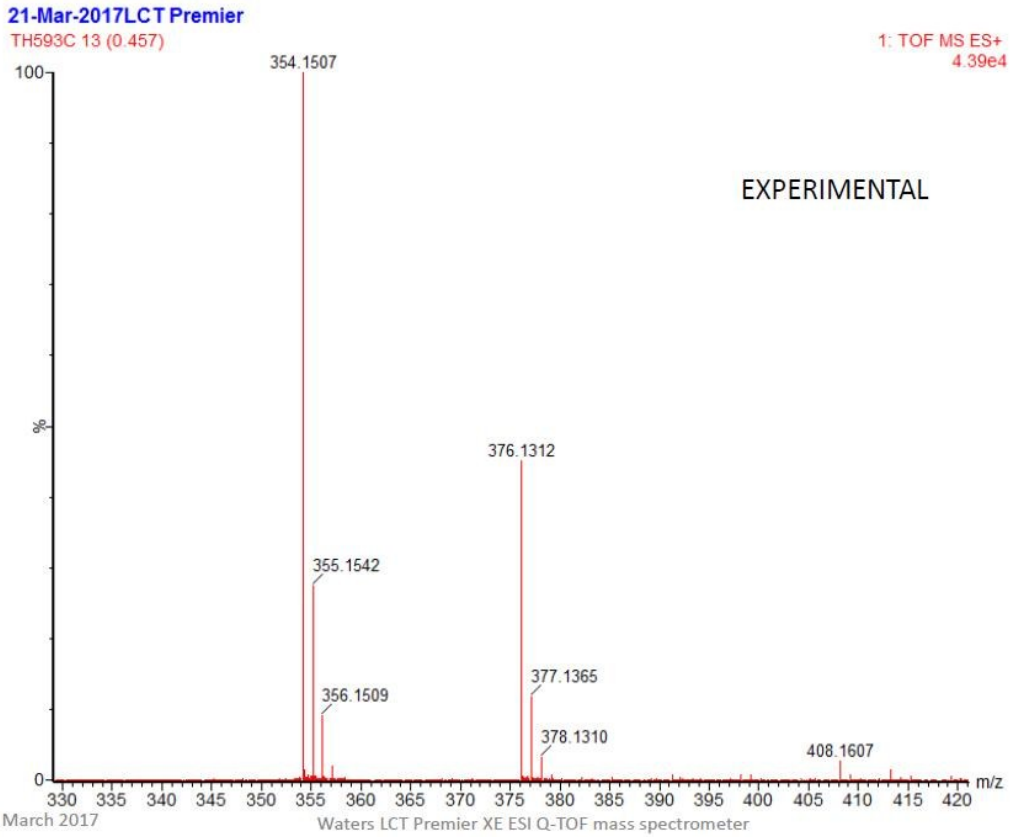
(*E*)-*N*,*N*-Diethyl-4-phenyl-2-(*o*-tolyl)but-1-en-3-yne-1-sulfonamide (28) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS






137.6105
135.7445
134.5630
133.7094
132.1624
130.9959
129.6179
129.1897
128.5831
128.5496
126.3879
122.4288
104.0733
85.3787
41.8958
20.2773
14.5837
150
100
50
[ppm]


BRUKER
Transmittance [%]
100
90
80
70
60
50
40
30
3048.26
2972.03
2933.30
2873.31
2206.59
1598.23
1562.19
1487.54
1455.50
1442.55
1381.77
1352.41
1331.70
1199.46
1142.22
1069.29
1047.91
1015.14
993.56
932.36
879.06
825.65
754.60
724.16
687.79
568.52
555.41
529.27
506.70
461.63
429.08
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



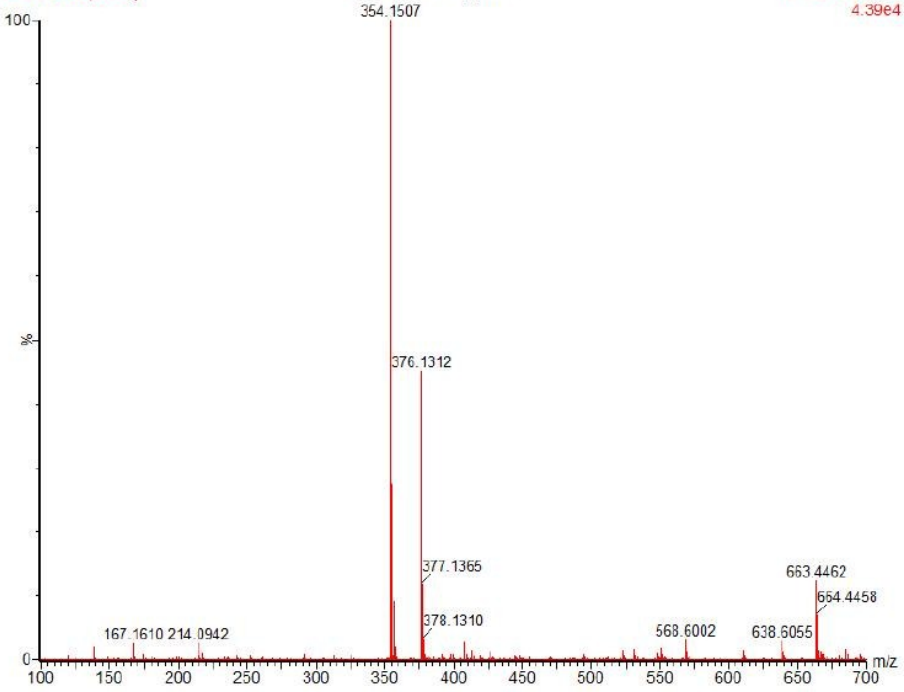
EXPERIMENTAL

UCL Chemistry Mass Spectrometry Facility

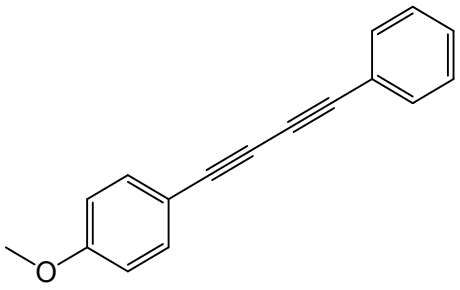
[M+H]+
21-Mar-2017LCT Premier
TH593C 13 (0.457)

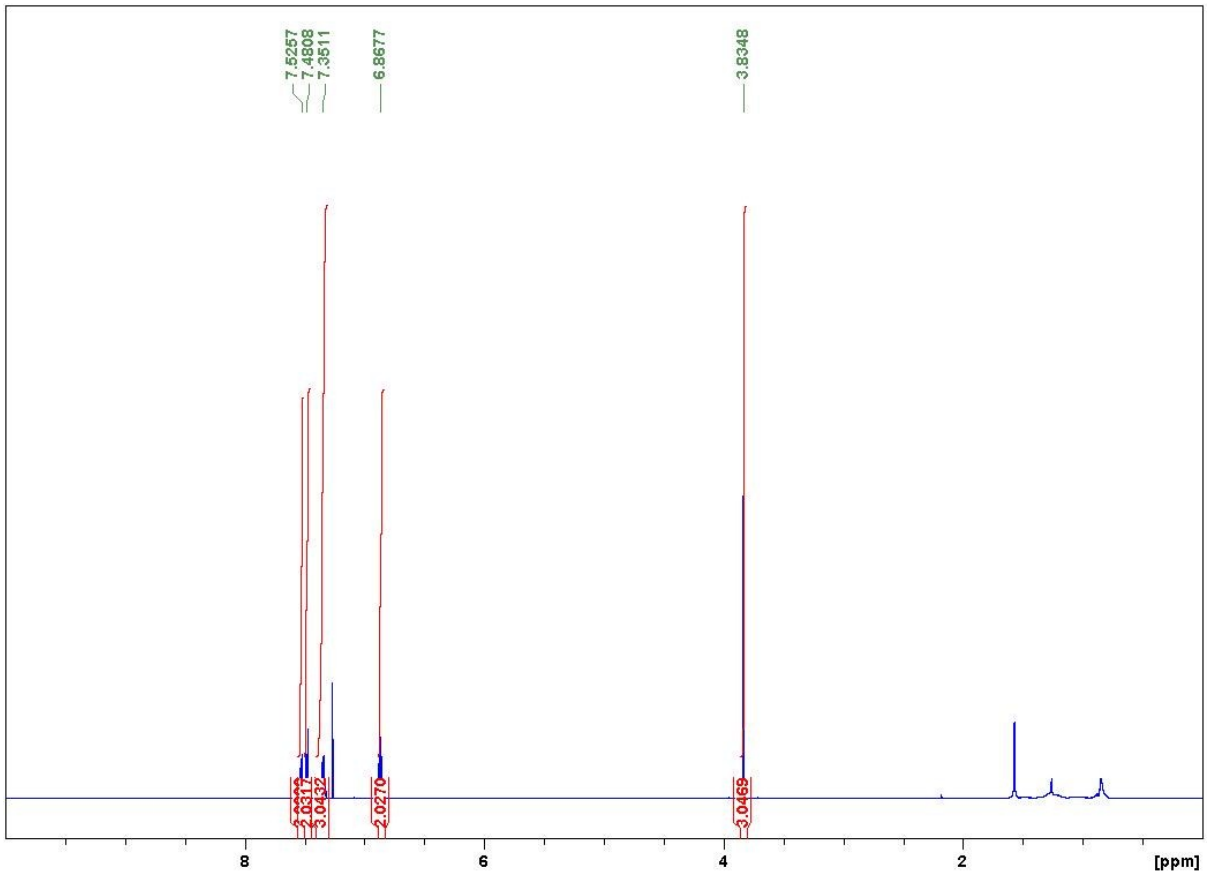
Instrument Resolution : 10,000
Theoretical Mass [C21H24NO2S]+ : 354.1528
Measured Mass : 354.1507
Error : -5.9 ppm

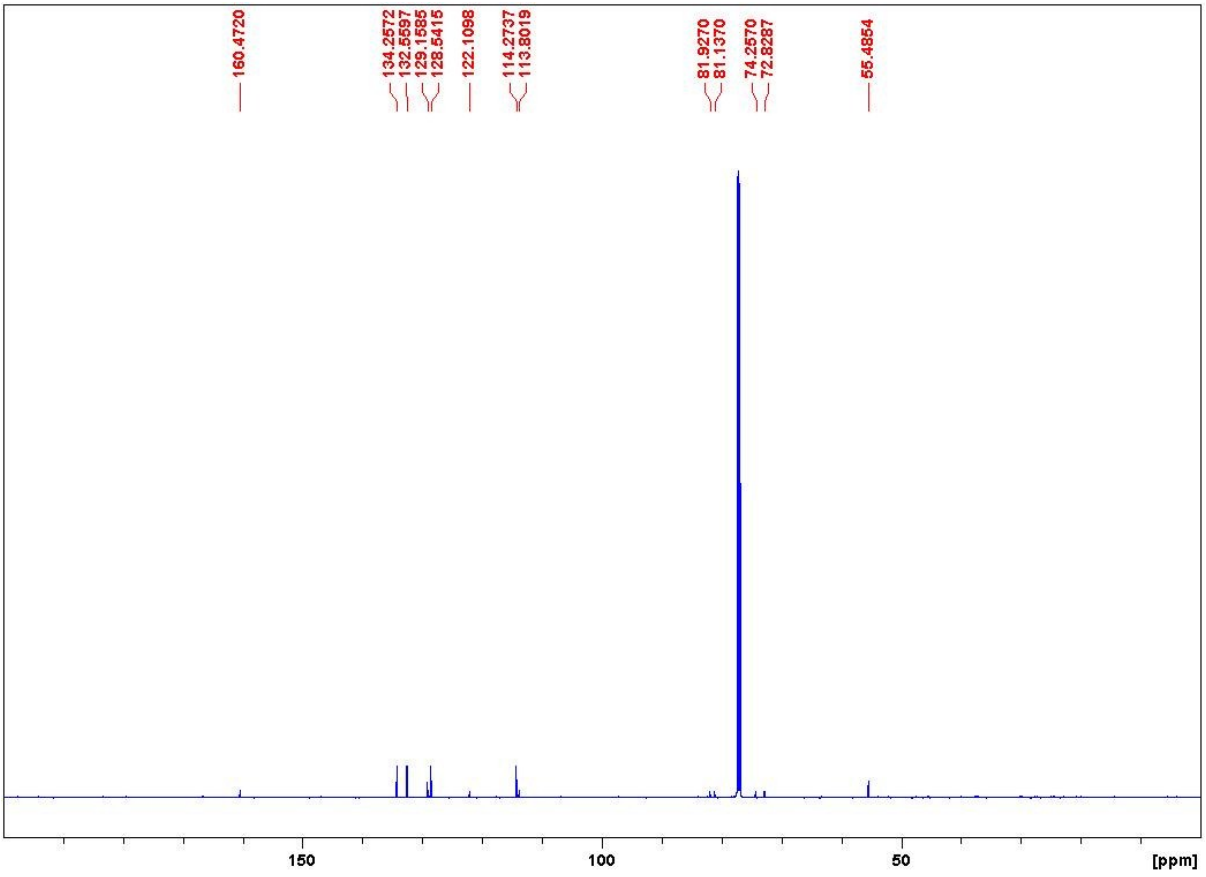
1: TOF MS ES+
4.39e4

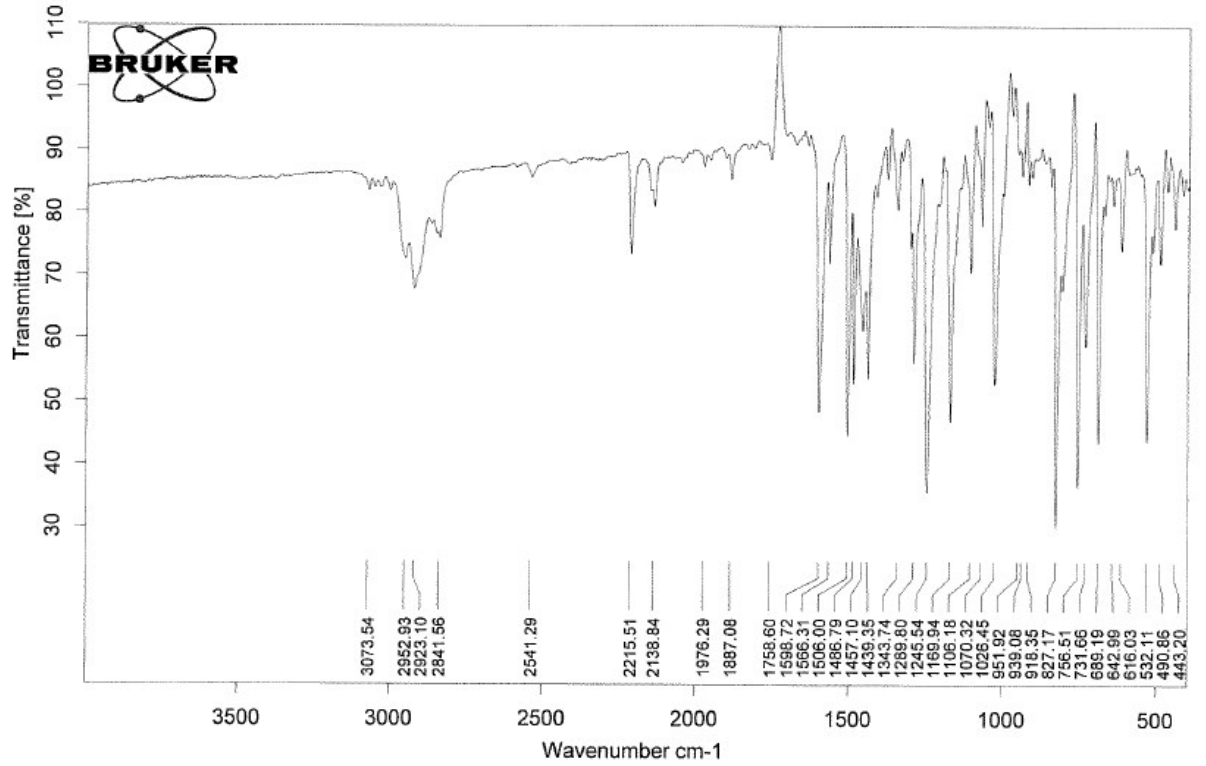


1-methoxy-4-(phenylbuta-1,3-diyn-1-yl)benzene (35) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

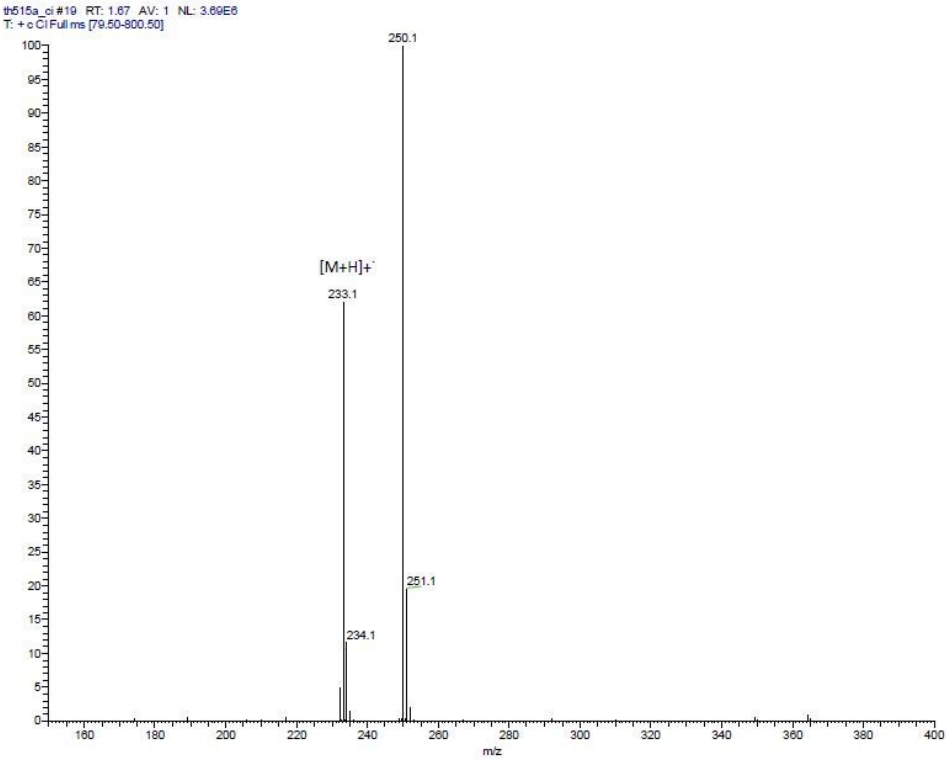




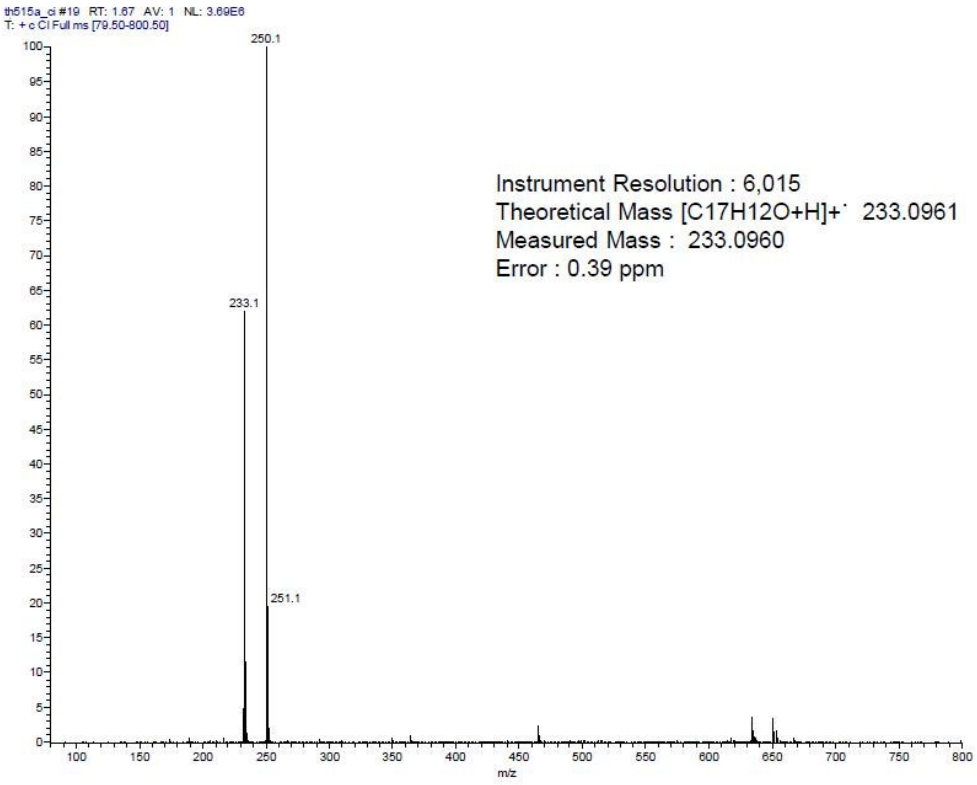

160.4720
134.2572
132.5597
129.1585
128.5415
122.1098
114.4737
113.8019
81.9270
81.1370
74.2570
72.8287
55.4854
150
100
50
[ppm]


BRUKER
Transmittance [%]
110
100
90
80
70
60
50
40
30
3073.54
2952.93
2923.10
2841.56
2541.29
2215.51
2138.84
1976.29
1887.08
1758.60
1598.72
1566.31
1506.00
1486.79
1457.10
1439.35
1343.74
1289.80
1245.54
1169.94
1106.18
1070.32
1026.45
951.92
939.08
918.35
827.17
756.51
731.66
689.19
642.99
616.03
532.11
490.66
443.20
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

AMMONIA *m/z* 18, 35, 52

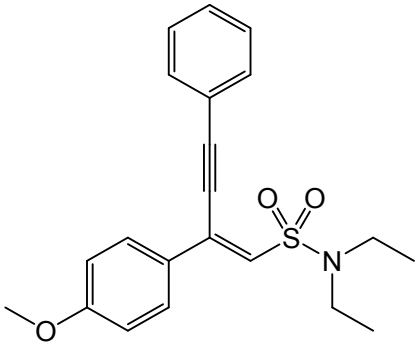


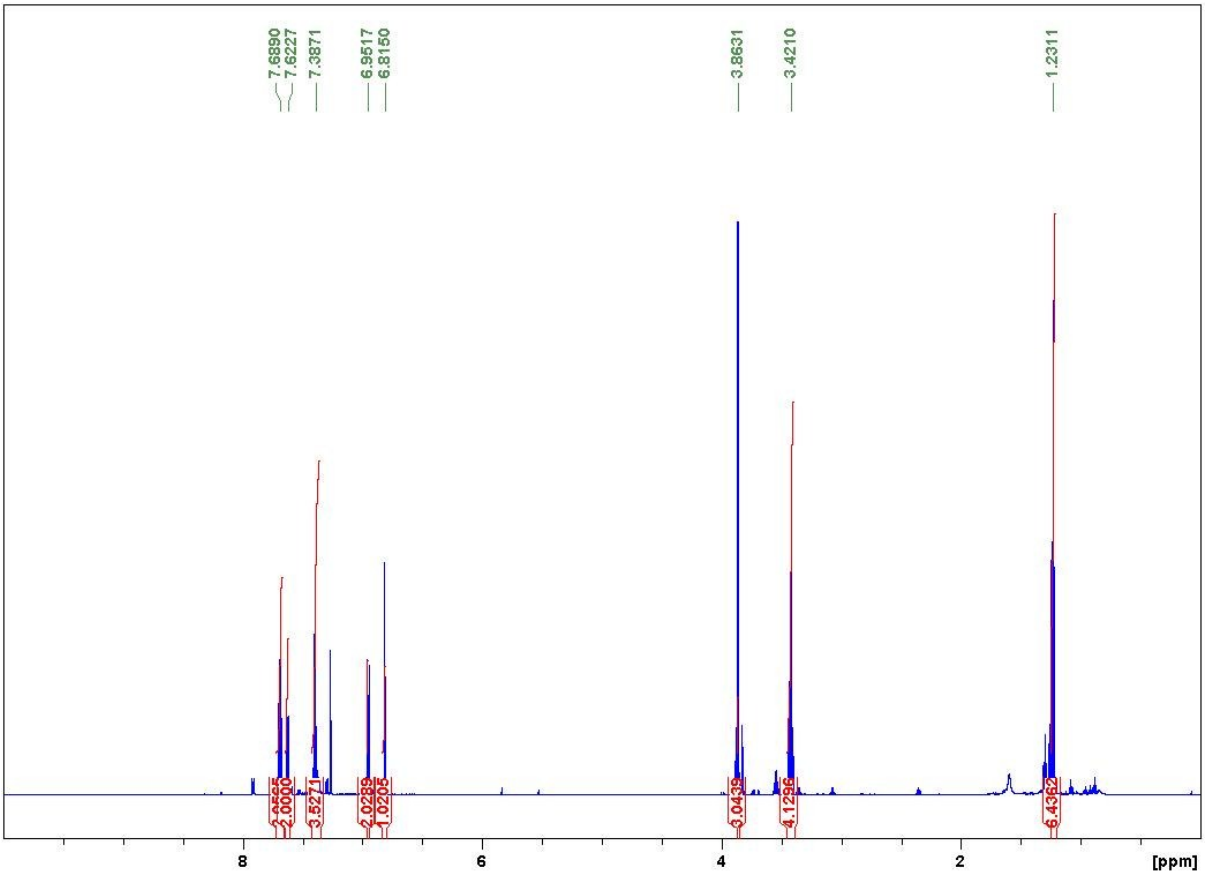
AMMONIA *m/z* 18, 35, 52

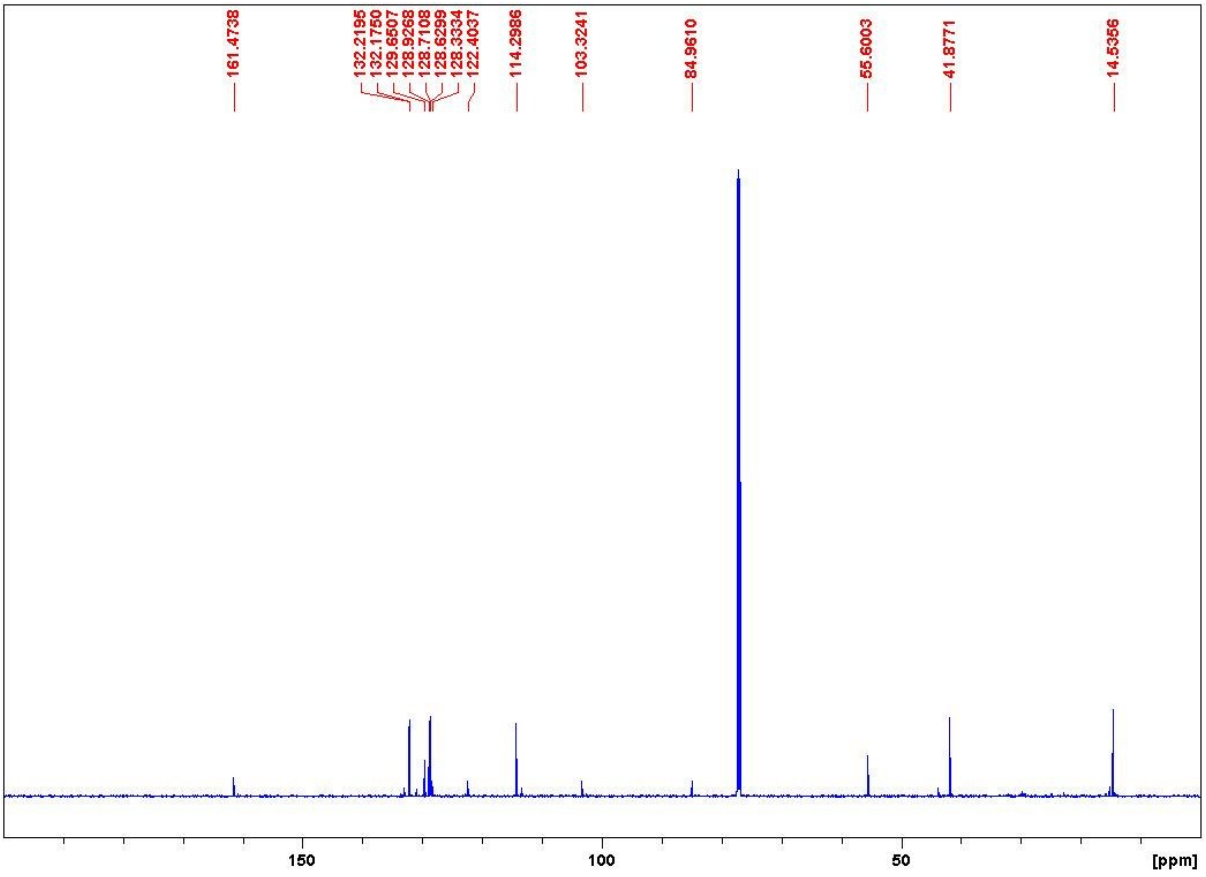


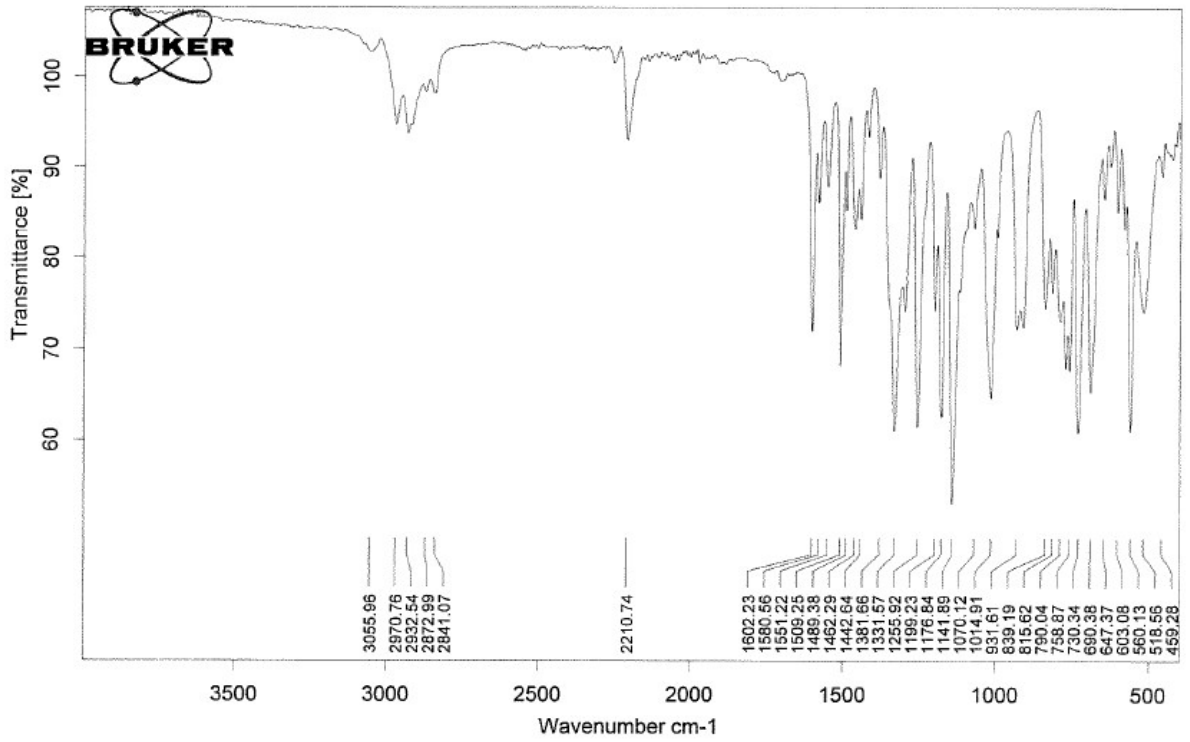
Instrument Resolution : 6,015
Theoretical Mass [C17H12O+H]+˙ 233.0961
Measured Mass : 233.0960
Error : 0.39 ppm

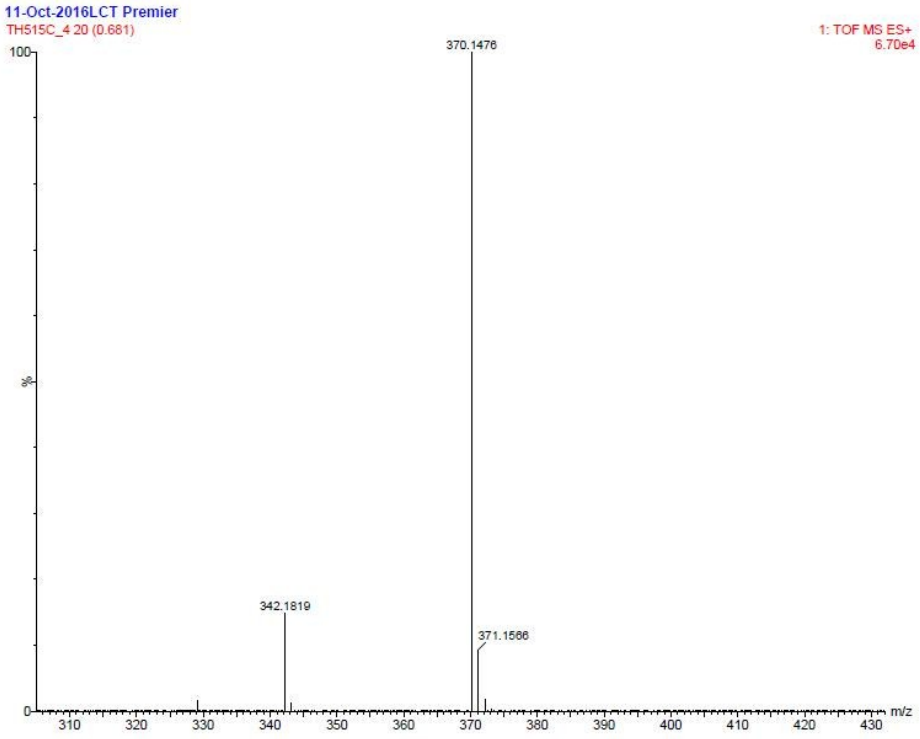
(*Z*)-*N*,*N*-Diethyl-2-(4-methoxyphenyl)-4-phenylbut-1-en-3-yne-1-sulfonamide (36) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

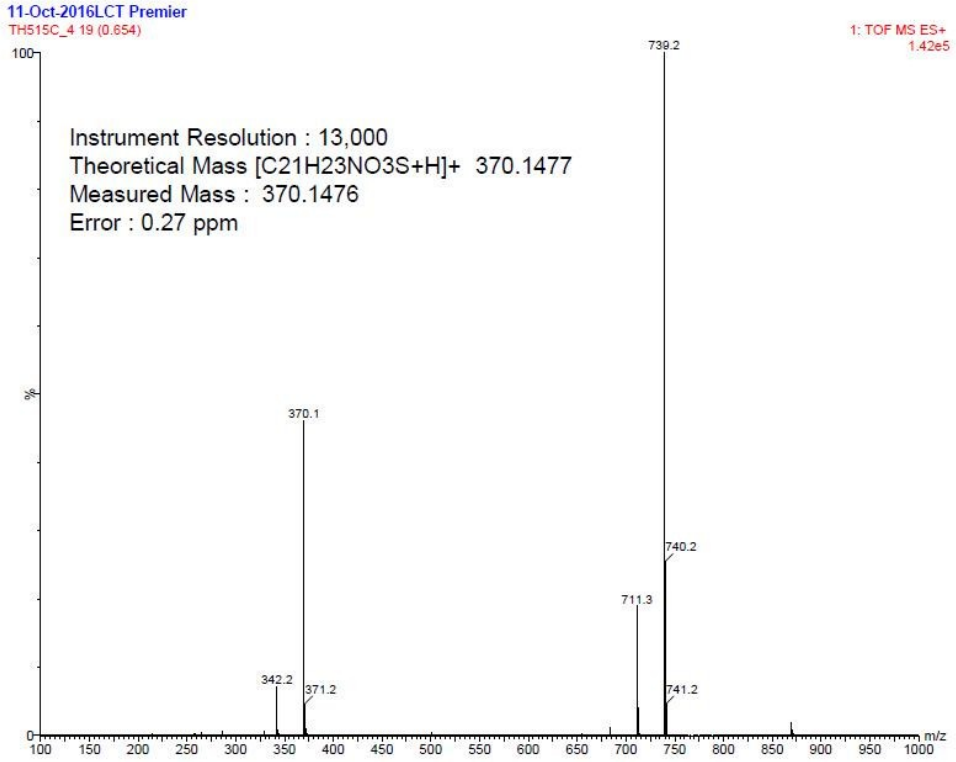




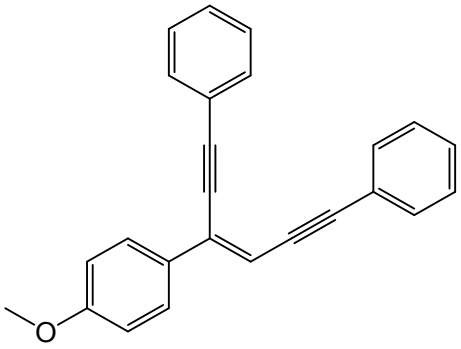

161.4738
132.2195
132.1750
129.6507
128.9268
128.7108
128.6299
128.3334
122.4037
114.2986
103.3241
84.9610
55.6003
41.8771
14.5356
150
100
50
[ppm]

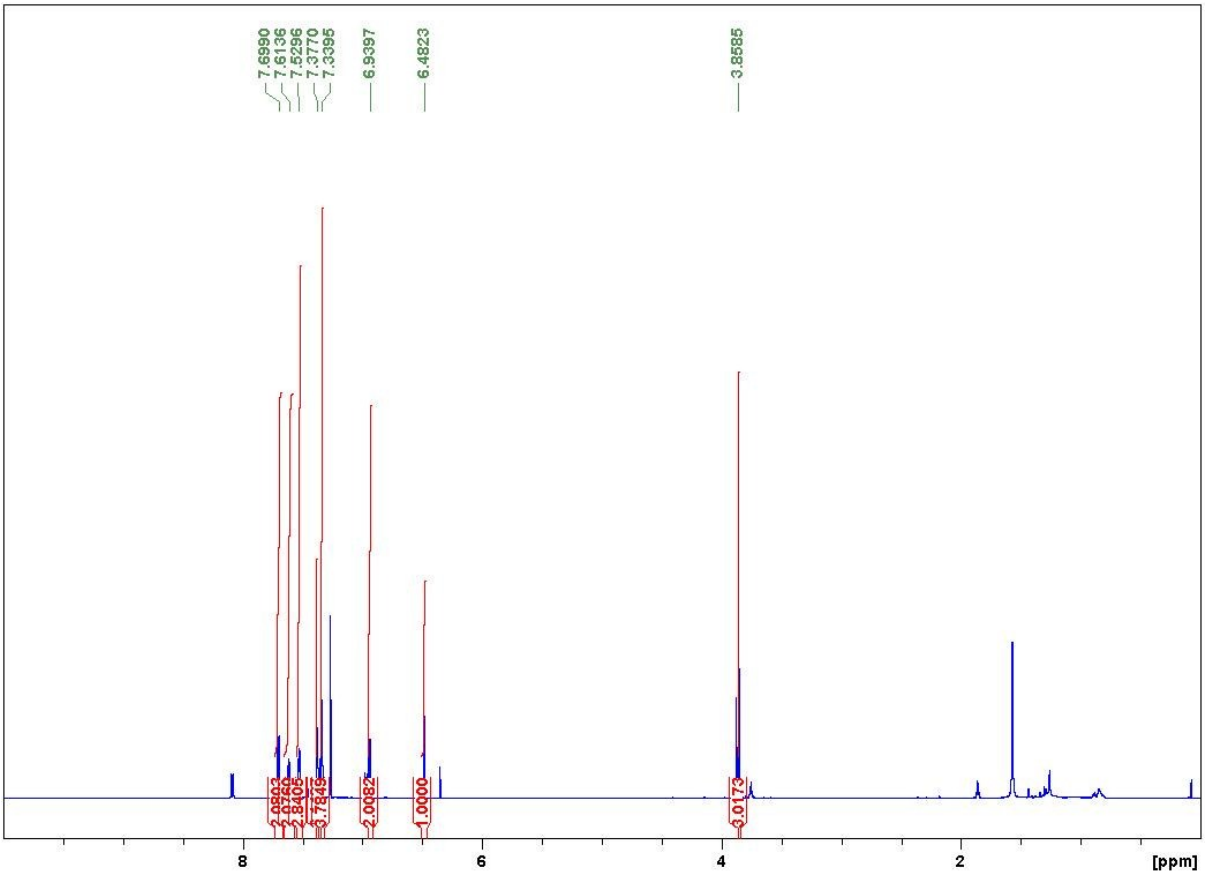

BRUKER
Transmittance [%]
100
90
80
70
60
3055.96
2970.76
2932.54
2872.99
2841.07
2210.74
1602.23
1580.56
1551.22
1509.25
1489.38
1462.29
1442.64
1381.66
1331.57
1255.92
1199.23
1176.84
1141.89
1070.12
1014.91
931.61
839.19
815.62
790.04
758.87
730.34
690.38
647.37
603.08
560.13
518.56
459.28
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

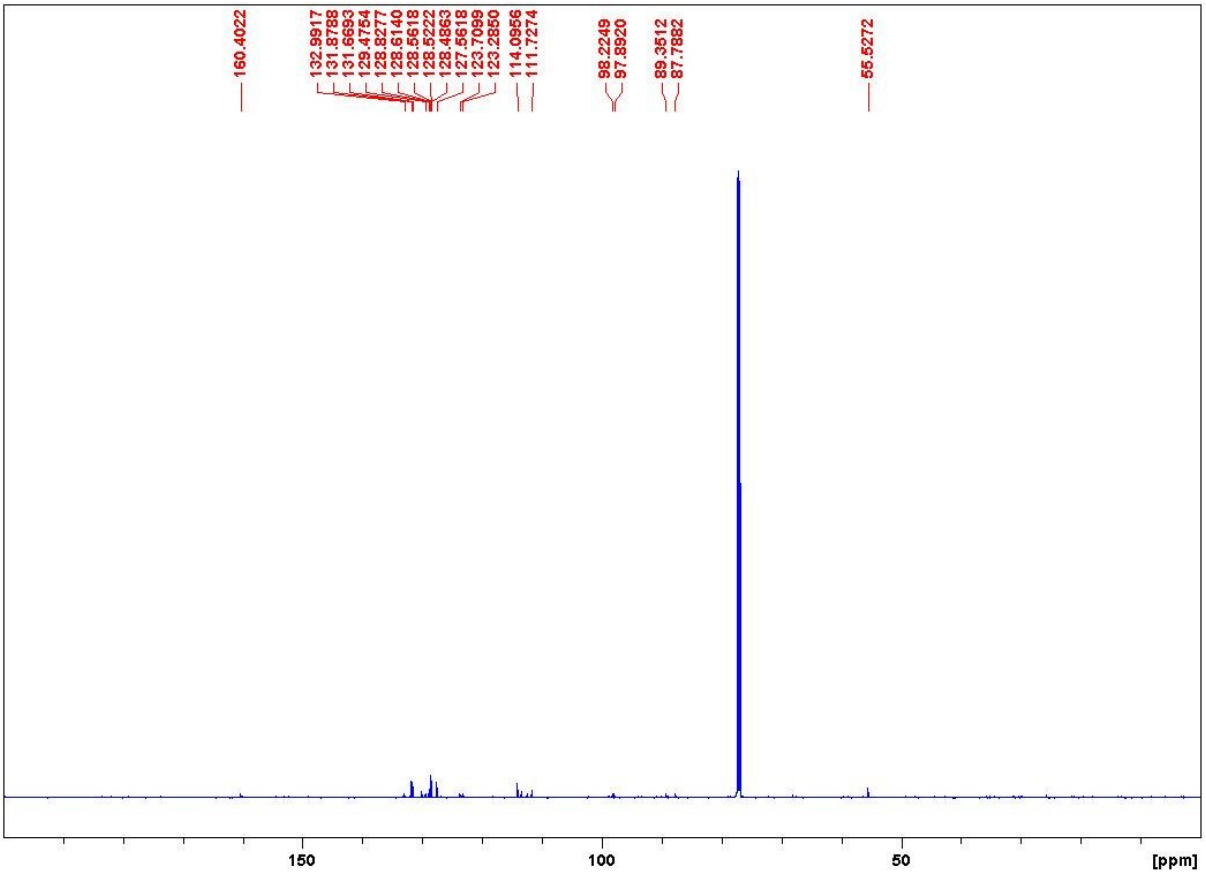

11-Oct-2016LCT Premier
TH515C_4 20 (0.681)
1: TOF MS ES+
6.70e4
100
%
0
370.1476
342.1819
371.1566
310
320
330
340
350
360
370
380
390
400
410
420
430
m/z

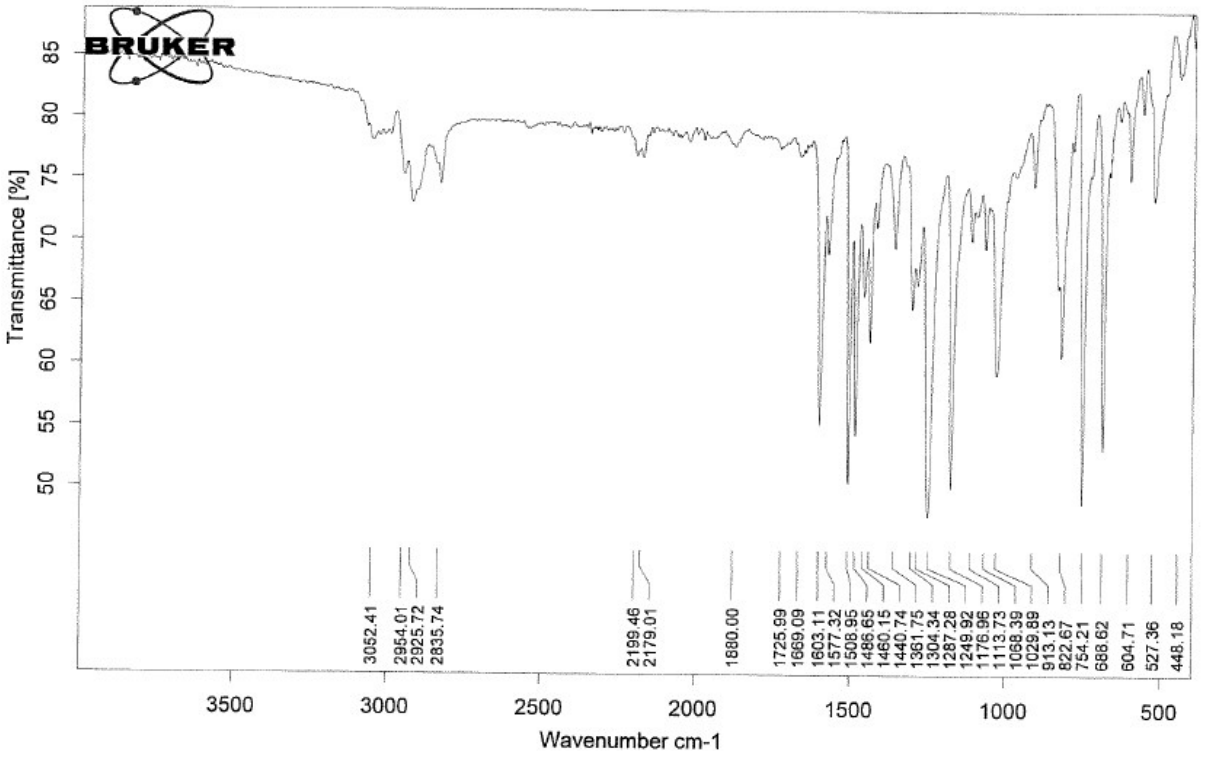

11-Oct-2016LCT Premier
TH515C_4 19 (0.654)
1: TOF MS ES+
1.42e5
100
%
0
Instrument Resolution : 13,000
Theoretical Mass [C21H23NO3S+H]+ 370.1477
Measured Mass : 370.1476
Error : 0.27 ppm
739.2
370.1
740.2
711.3
342.2
371.2
741.2
100 150 200 250 300 350 400 450 500 550 600 650 700 750 800 850 900 950 1000
m/z

(*Z*)-(3-(4-methoxyphenyl)hexa-3-en-1,5-diyne-1,6-diyl)dibenzene (36) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

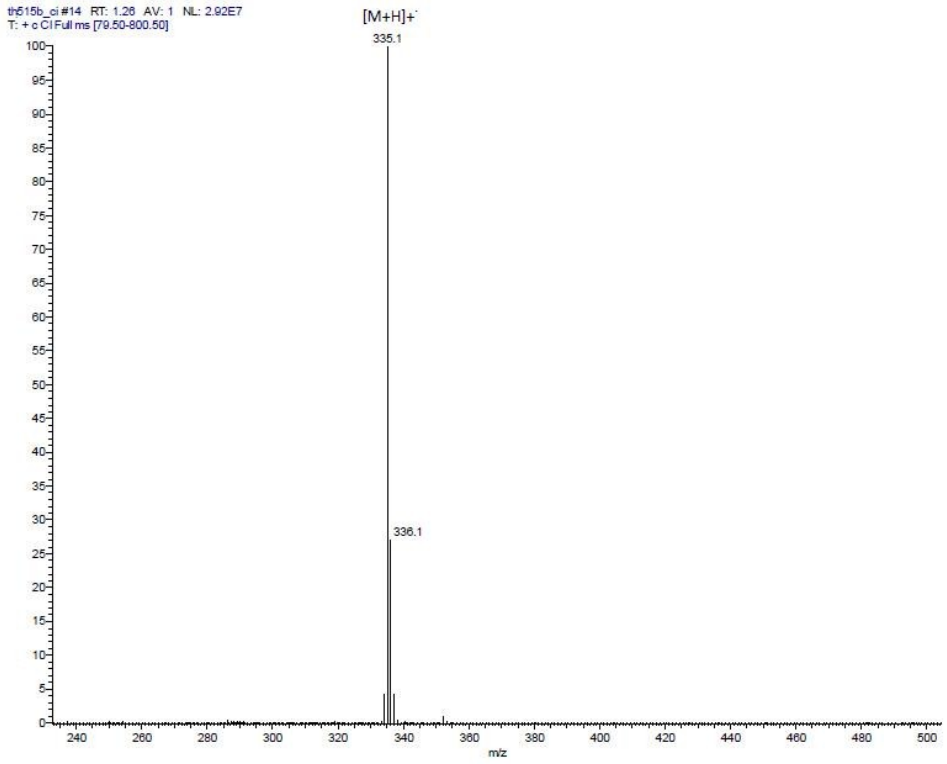




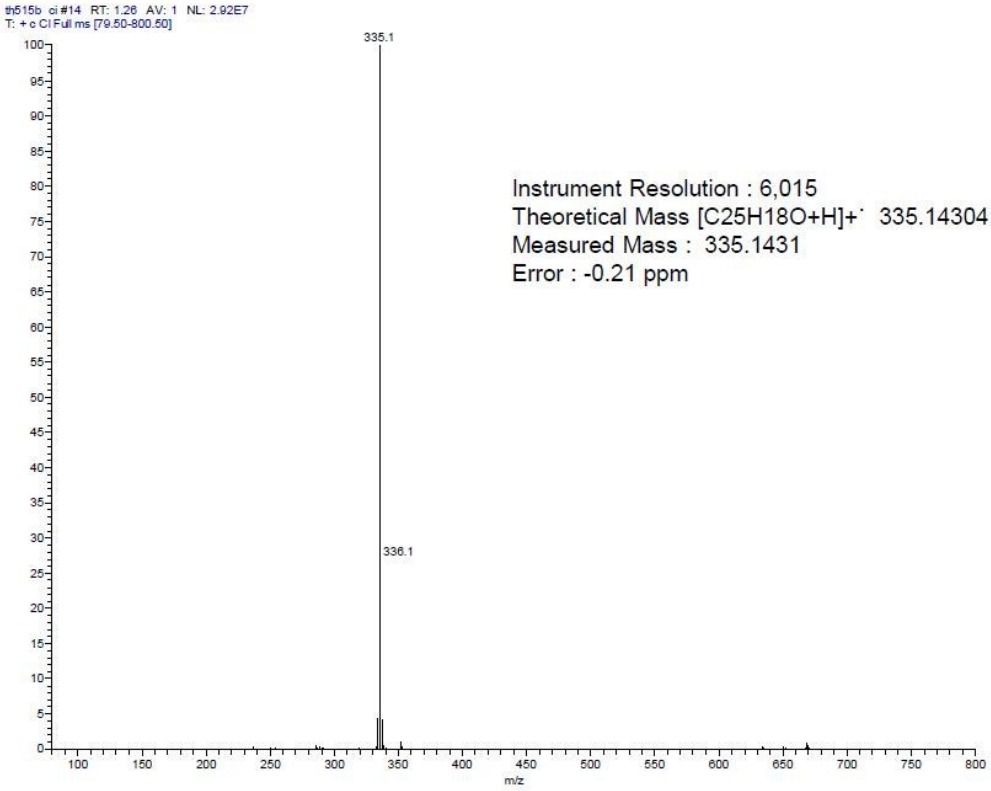

160.4022
132.9917
131.8788
131.6693
129.4754
128.8277
128.6140
128.5618
128.5222
128.4863
127.5618
123.7099
123.2850
114.0956
111.7274
98.2249
97.8920
89.3512
87.7882
55.5272
150
100
50
[ppm]


BRUKER
Transmittance [%]
85
80
75
70
65
60
55
50
3052.41
2954.01
2925.72
2835.74
2199.46
2179.01
1680.00
1725.99
1669.09
1603.11
1577.32
1508.95
1486.65
1460.15
1440.74
1361.75
1304.34
1287.28
1249.92
1176.96
1113.73
1068.39
1029.89
913.13
822.67
754.21
688.62
604.71
527.36
448.18
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

AMMONIA *m/z* 18, 35, 52

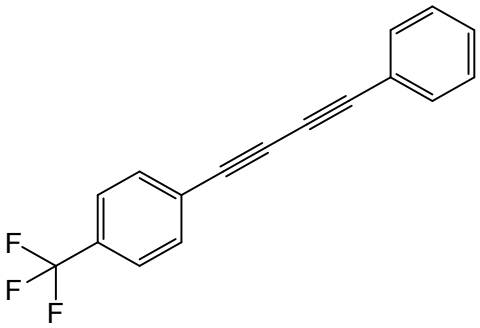


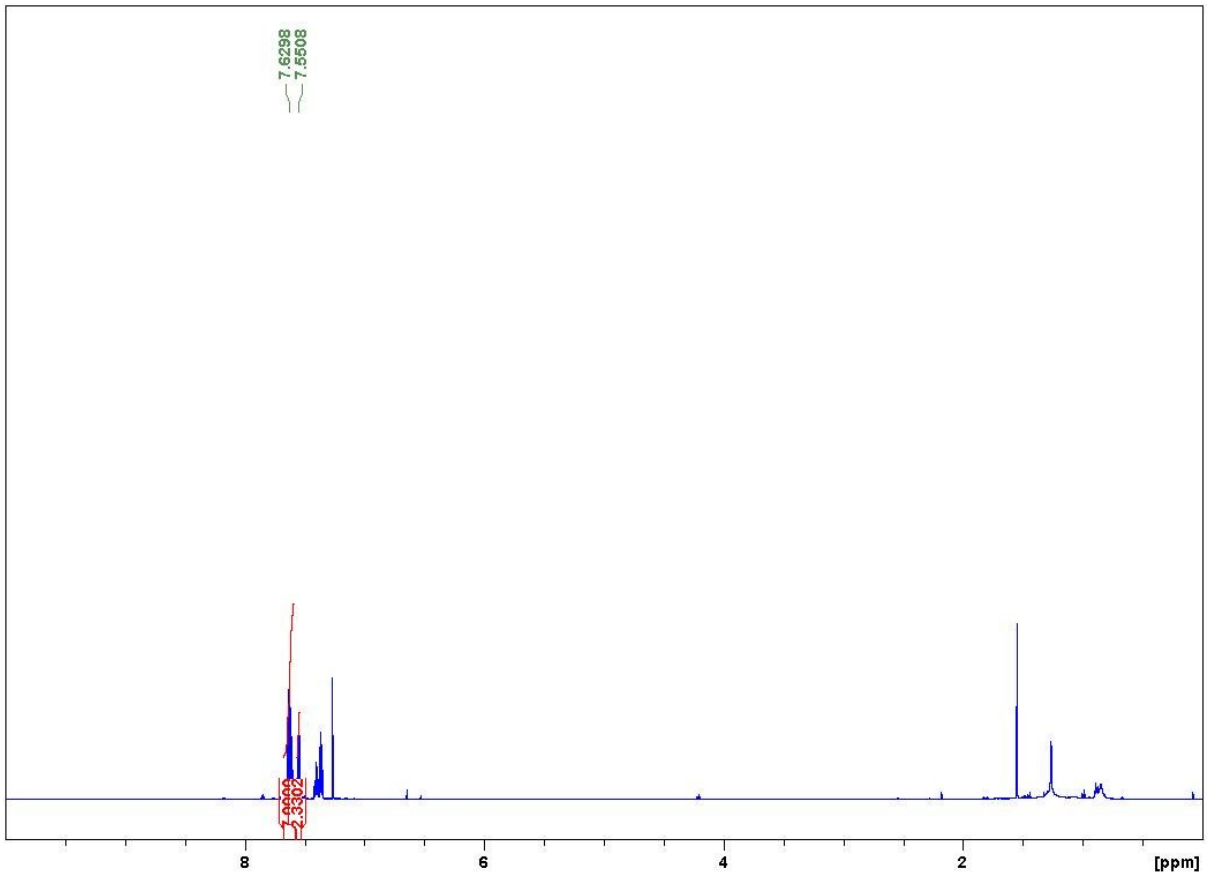
AMMONIA *m/z* 18, 35, 52

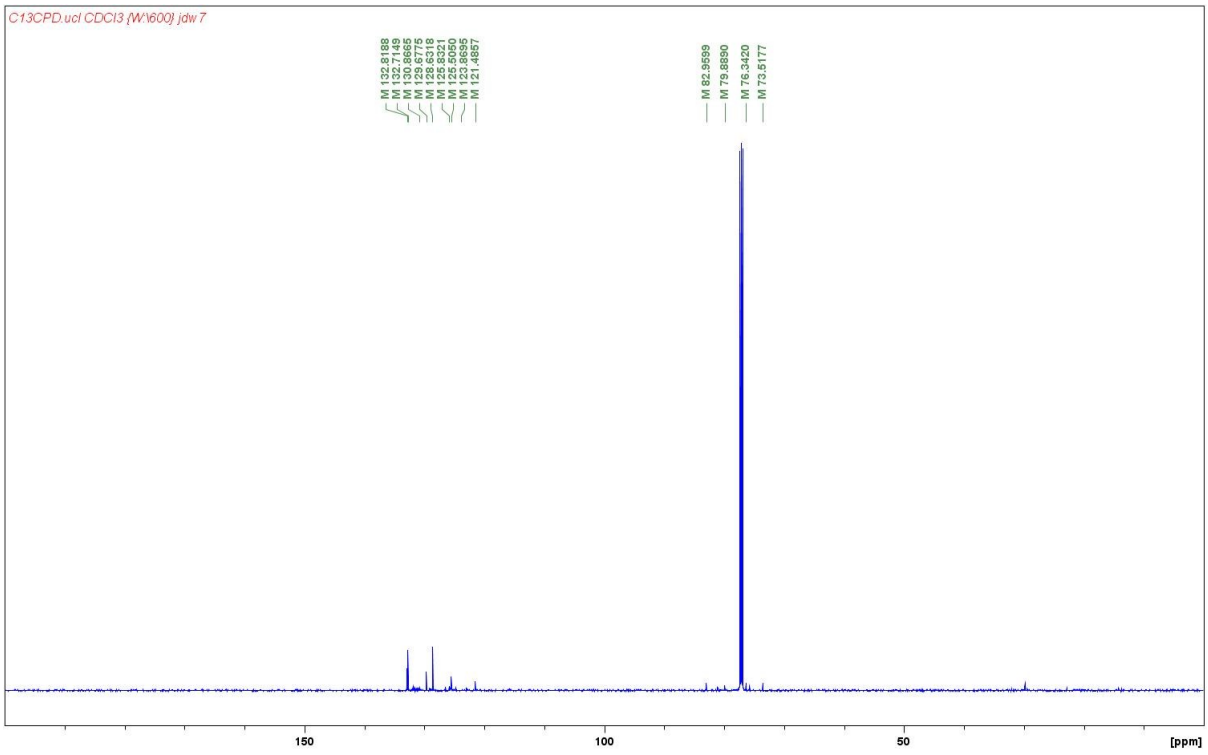


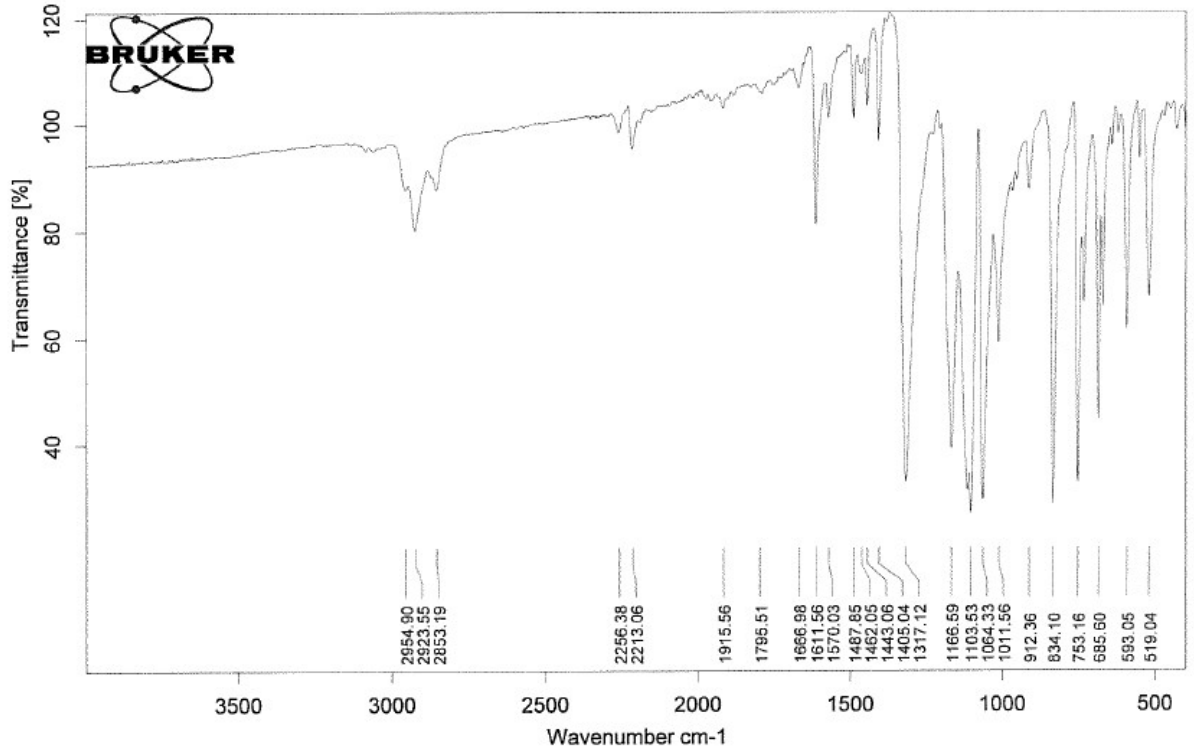
Instrument Resolution : 6,015
Theoretical Mass [C25H18O+H]+˙ 335.14304
Measured Mass : 335.1431
Error : -0.21 ppm

1-(phenylbuta-1,3-diyn-1-yl)-4-(trifluoromethyl)benzene (37) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS

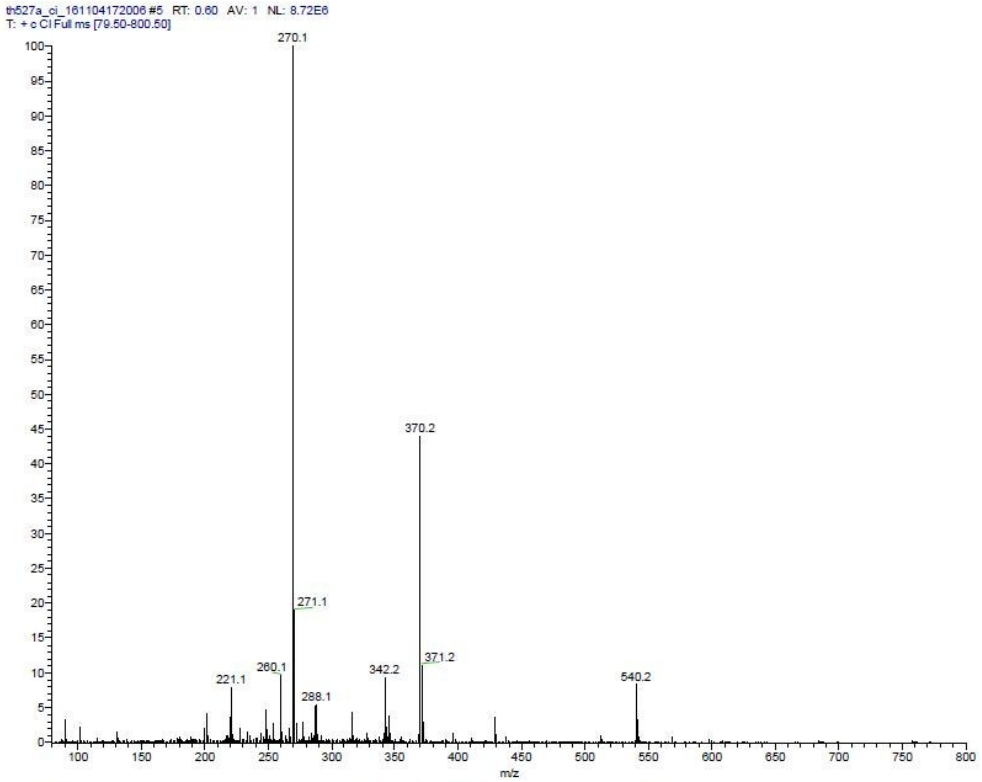




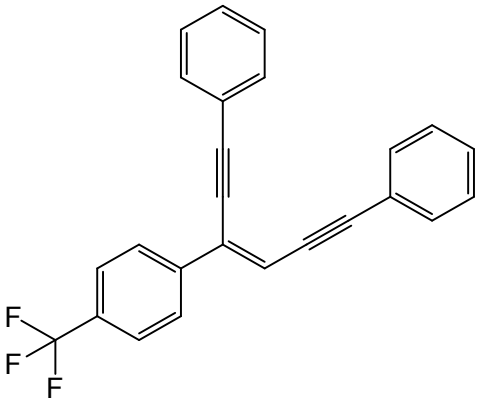

C13CPD.ucl CDCl3 {W:\600} jdw 7
M 132.8188
M 132.7148
M 130.8655
M 129.6775
M 128.6318
M 125.8321
M 125.5050
M 123.8655
M 121.4857
M 82.9599
M 79.8890
M 76.3420
M 73.5177
150
100
50
[ppm]

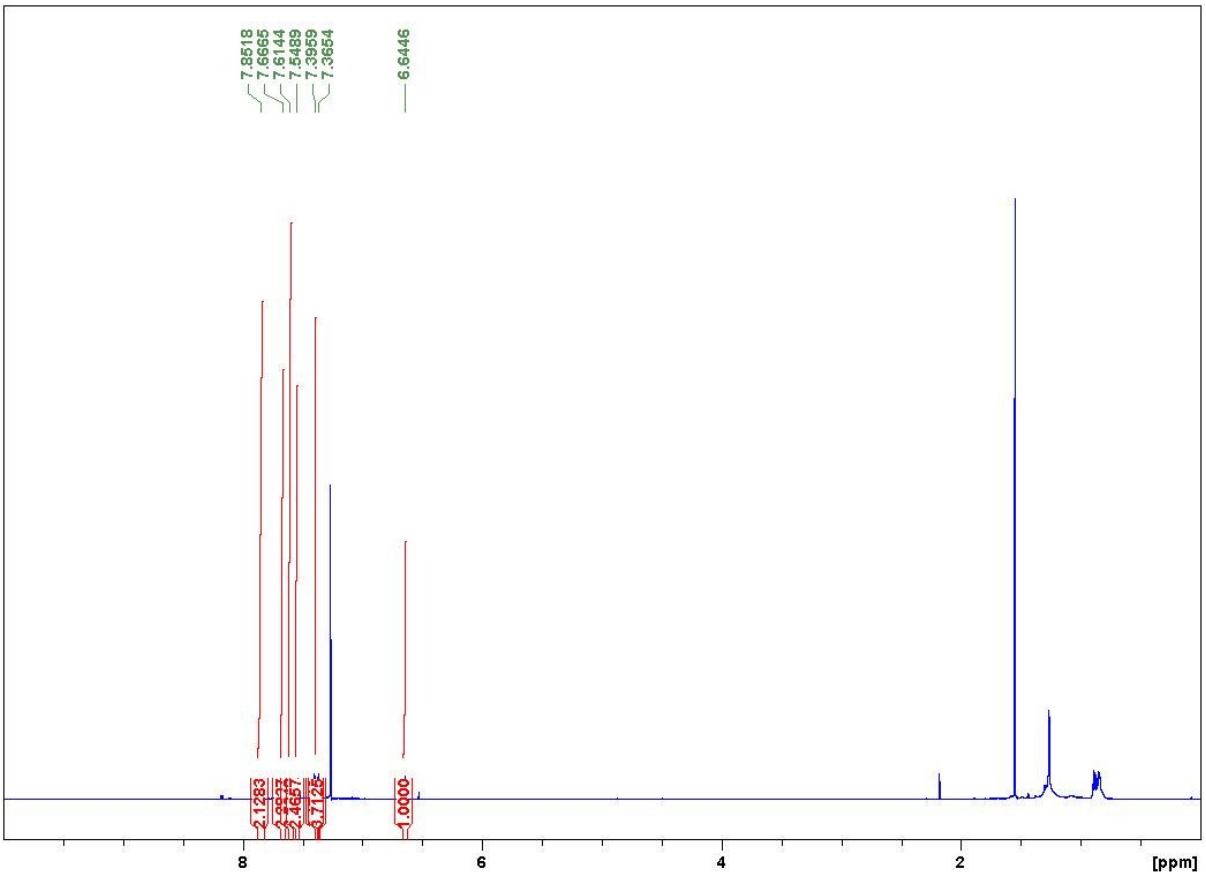

BRUKER
Transmittance [%]
120
100
80
60
40
2954.90
2923.55
2853.19
2256.38
2213.06
1915.56
1795.51
1666.98
1611.56
1570.03
1487.85
1462.05
1443.06
1405.04
1317.12
1166.59
1103.53
1064.33
1011.56
912.36
834.10
753.16
685.60
593.05
519.04
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1

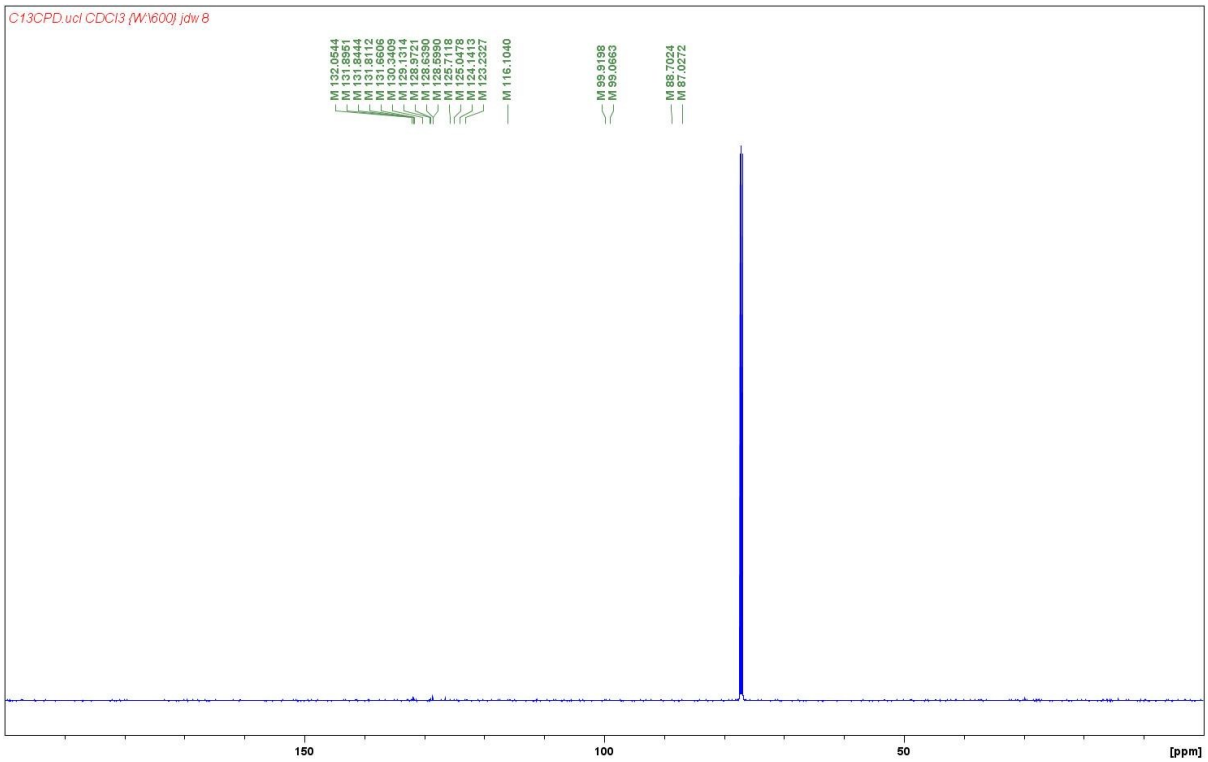
AMMONIA *m/z* 18, 35, 52

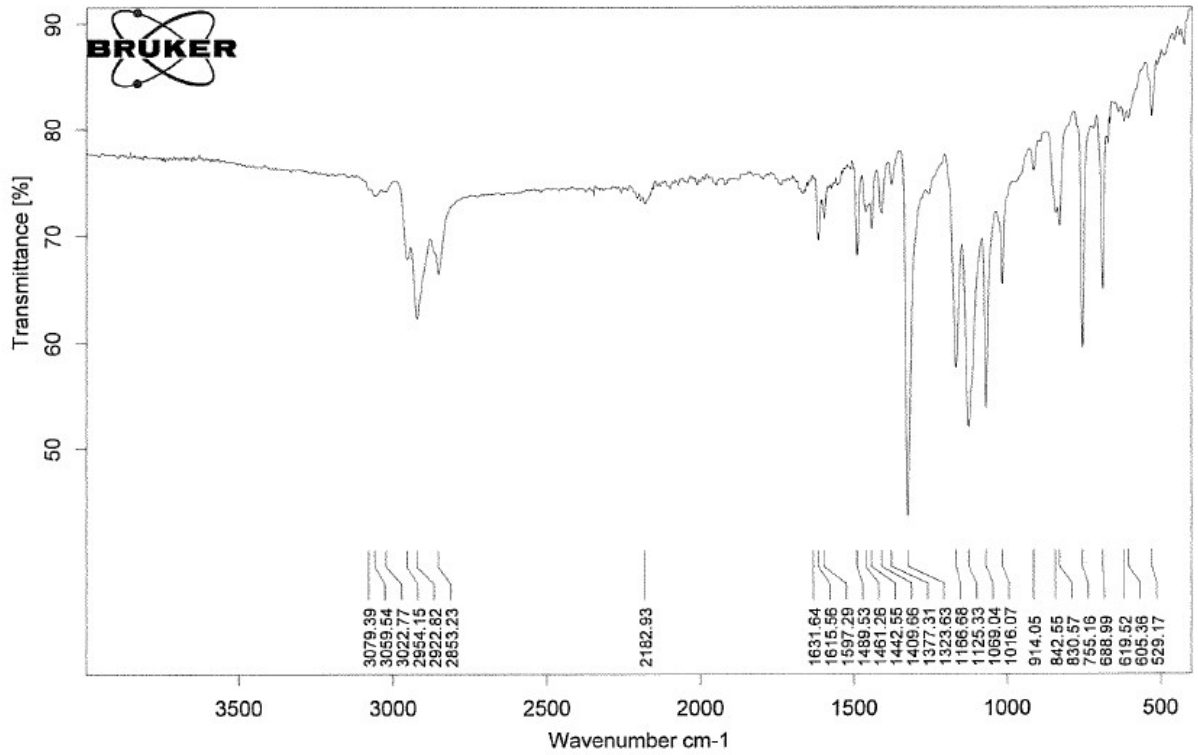


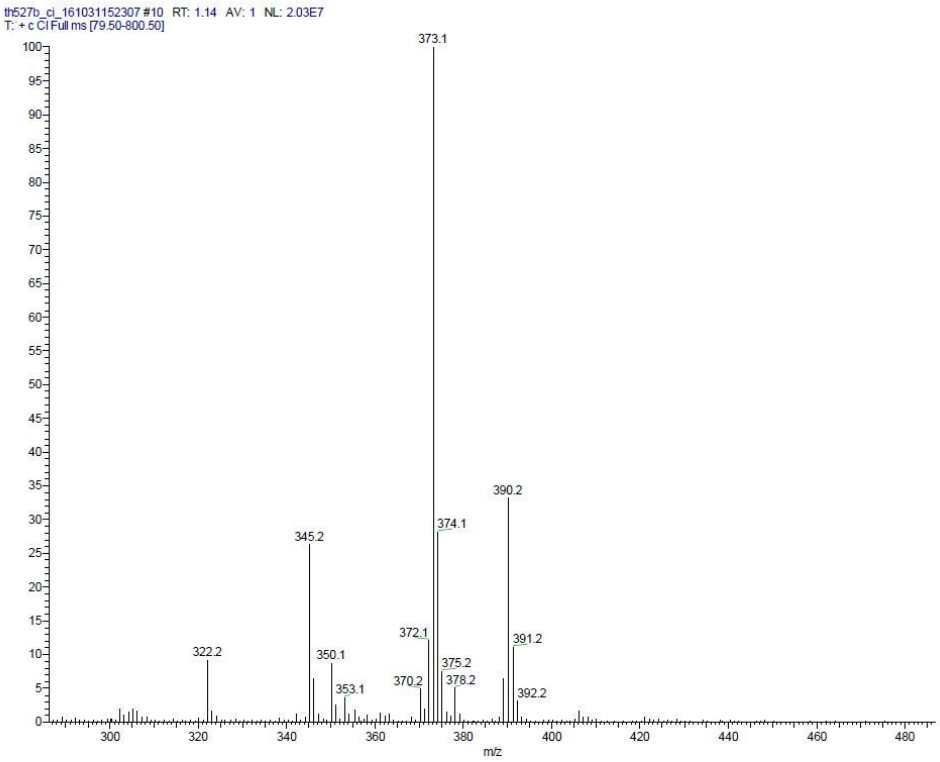
(Z)-(3-(4-(trifluoromethyl)phenyl)hexa-3-en-1,5-diyne-1,6-diyl)dibenzene (38) - ^{1}H-NMR, ^{13}C-NMR, IR, LRMS and HRMS



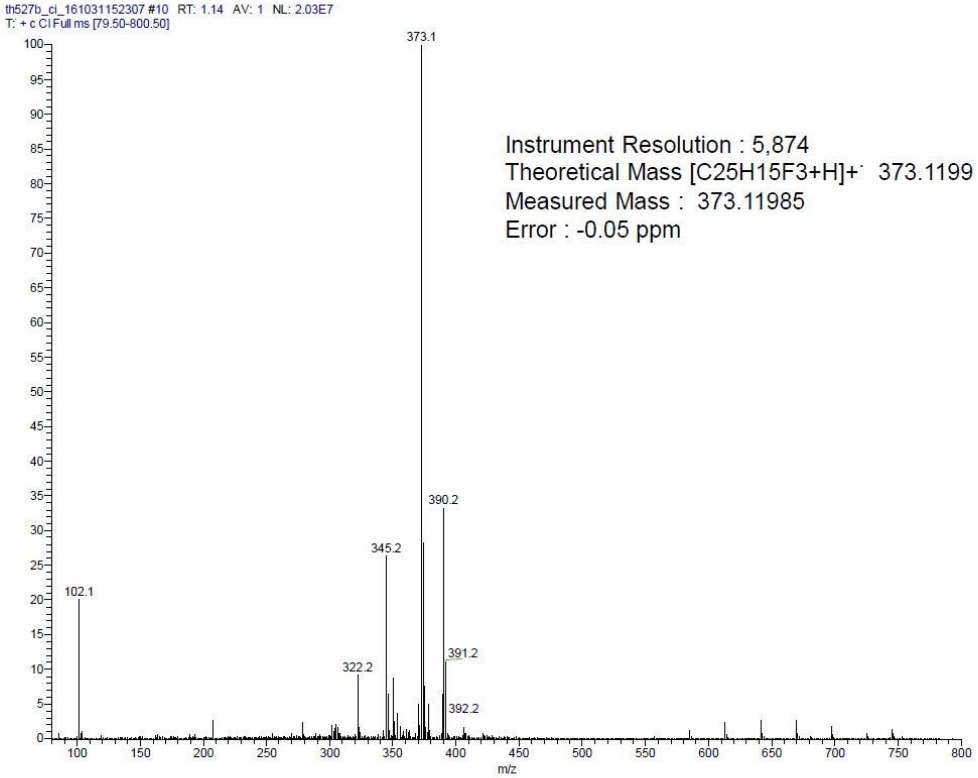



C13CPD.ucl CDCl3 (W:\600) jdw 8
M 132.0544
M 131.8951
M 131.8444
M 131.8112
M 131.6696
M 130.3409
M 129.1314
M 128.9721
M 128.6390
M 128.4690
M 125.7118
M 125.0478
M 124.1413
M 123.2327
M 116.1040
M 99.9198
M 99.0663
M 88.7024
M 87.0272
150
100
50
[ppm]


BRUKER
Transmittance [%]
90
80
70
60
50
3079.39
3059.54
3022.77
2954.15
2922.82
2853.23
2182.93
1631.64
1615.56
1597.29
1489.53
1461.26
1442.55
1409.66
1377.31
1323.63
1166.68
1125.33
1099.04
1016.07
914.05
842.55
830.57
755.16
688.99
619.52
605.36
529.17
3500
3000
2500
2000
1500
1000
500
Wavenumber cm-1



AMMONIA *m/z* 18, 35, 52



Instrument Resolution : 5,874
Theoretical Mass $[C_{25}H_{15}F_3+H]^{+\cdot}$ 373.1199
Measured Mass : 373.11985
Error : -0.05 ppm