Supporting Information

Gold-Catalyzed 1,2-Acyloxy Migration/Intramolecular Cyclopropanation/Ring Enlargement Cascade: Syntheses of Medium-Sized Heterocycles

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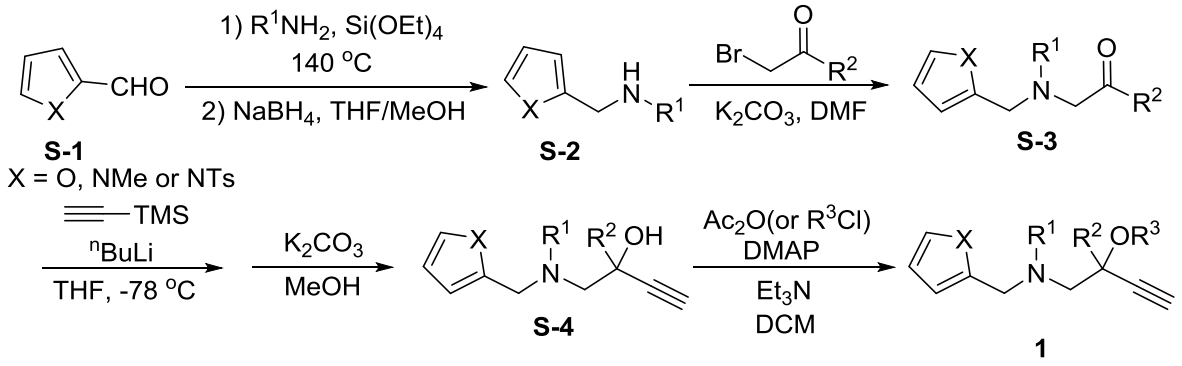
Content

General Remarks.

^{1}H, ^{13}C NMR spectra were recorded on a 400, 100 MHz spectrometer in $CDCl_3$. Internal TMS (δ = 0.0 ppm) was used as the reference for ^{1}H NMR. Infrared spectra were measured on a spectrometer. Mass spectra were recorded by ESI or EI method, and HRMS was measured on Kratos Analytical Concept mass spectrometer (ESI， MALDI or EI). All reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure.

General Procedure for Syntheses of Reaction Substrates and the Spectroscopic Data.

The Syntheses and the Spectroscopic Data of Substrates 1a-1p, 1s-1u, 1z, 10 and 11.



Procedure for the preparation of **1a**: Heating tosylamide (3.42 g, 20 mmol) and furfural (1.92 g, 20 mmol) with $Si(OEt)_4$ (4.58 g, 22 mmol) at 140 °C for 3 h yielded the desired imine after trituration. This imine product was reduced with $NaBH_4$ (0.23 g, 6 mmol) in THF/MeOH (5/1 100 mL) to get sulfonamide **S-2a** (4.72 g, 94% yield) after purified by flash column chromatography (silica gel, PE/EA/DCM = 10/1/10).[1]

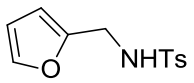
To a stirred solution of **S-2a** (2.51 g, 10 mmol) and K_2CO_3 (1.65 g, 12 mmol) in DMF (20 mL) was added a solution of 2-bromo-1-phenylethanone (2.18 g, 11 mmol) in DMF (20 mL). The reaction mixture was stirred for 3 h. Water was added into the reaction solution and the mixture was extracted with EA for 3 times. The combined organic layers were washed with brine and dried over anhydrous $NaSO_4$. The product **S-3a** (3.10 g, 84%) was purified by flash column chromatography (silica gel, PE/EA = 6/1).

To a stirred solution of ethynyltrimethylsilane (0.7 mL, 5 mmol) in THF (10 mL) was added $^{n}BuLi$ (2 mL, 5 mmol, 2.5 M in hexane) at -78 °C under Ar atmosphere. The reaction mixture was

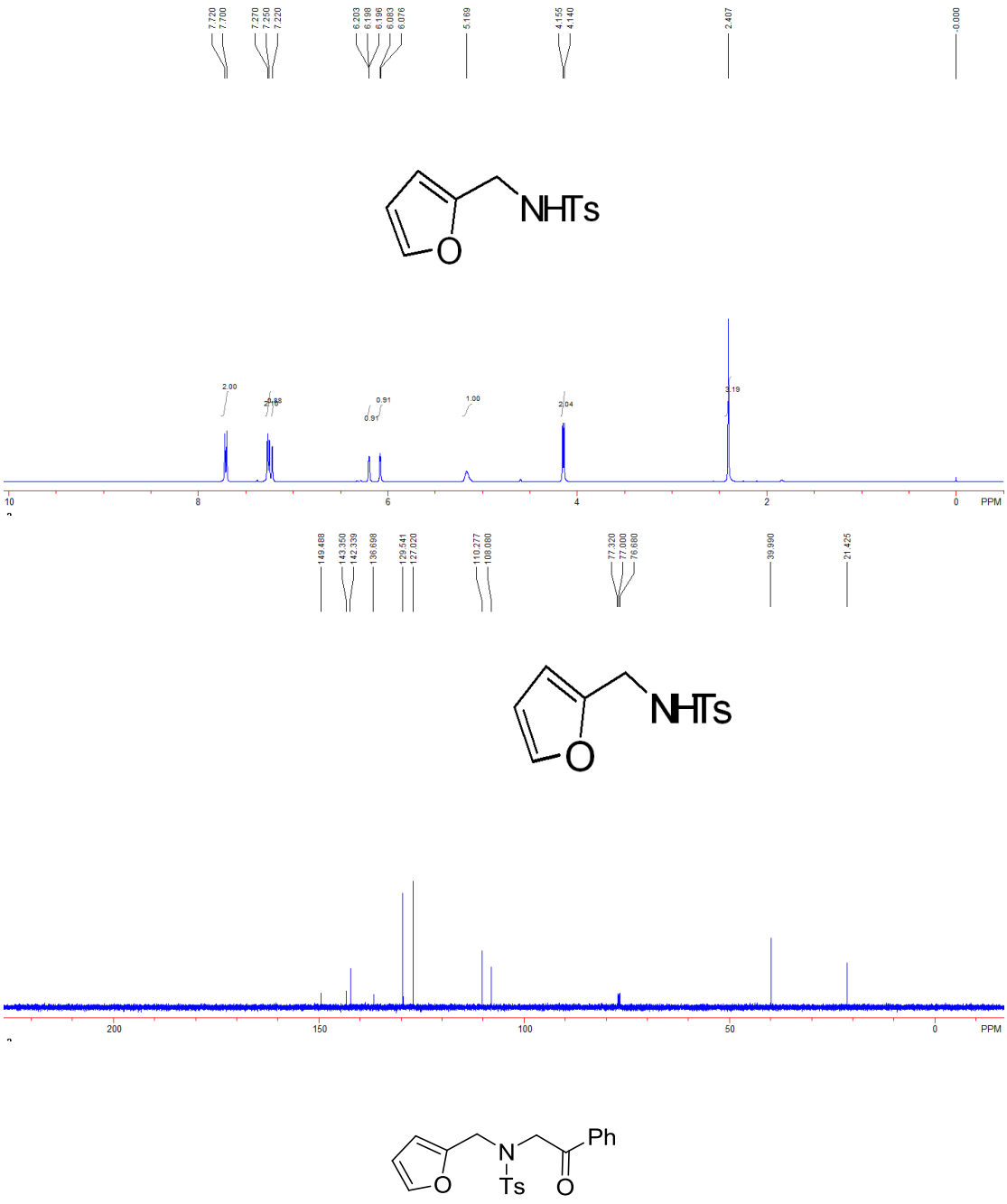
warmed to 0 ^{o}C and stirred for 15 min. A solution of **S-3a** (1.84 g, 5 mmol) in THF (10 mL) was then added at -78 ^{o}C. The reaction was quenched with saturated ammonium chloride and extracted with EA after 2 h. The combined organic layers were washed with brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 6/1) to provide product **S-3a'** (1.42 g) in 61% yield.[2]

A solution of **S-3a'** (0.93 g, 2 mmol) and K_2CO_3 (0.28 g, 2 mmol) in MeOH (10 mL) was stirred for 3 h. The reaction solution was added water and extracted with EA. The combined organic layers were washed with brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 6/1) to provide product **S-4a** (0.78 g) in 99% yield.[2]

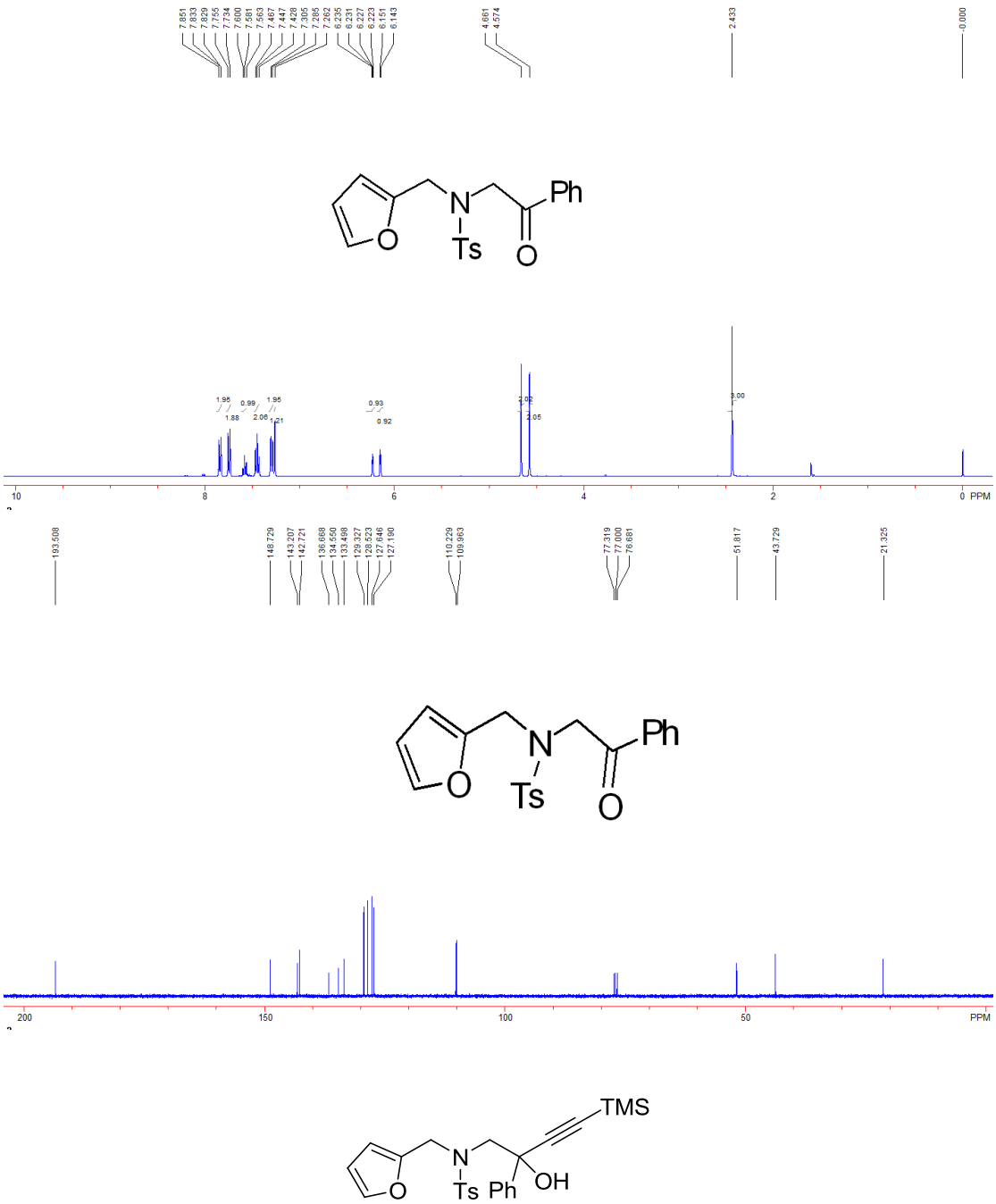
To a solution of **S-4a** (0.78 g, 2 mmol) and DMAP (49 mg, 0.4 mmol) in DCM (15 mL) was added Et_3N (0.5 mL, 4 mmol) at 0 ^{o}C. Then a solution of Ac_2O (0.3 mL, 3 mmol) in DCM (10 mL) was added dropwise. The reaction mixture was stirred overnight. The reaction mixture was washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 6/1) to provide product **1a** (0.79 g) in 90% yield.[2]



N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-2a): known compound,[1] a white solid (4.7 g, 94% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.71 (d, 2H, *J* = 8.0 Hz, ArH), 7.26 (d, 2H, *J* = 8.0 Hz, ArH), 7.22 (s, 1H, ArH), 6.20-6.19 (m, 1H, ArH), 6.08 (d, 1H, *J* = 5.6 Hz, ArH), 5.17 (br, 1H, NH), 4.14 (d, 2H, *J* = 6.0 Hz, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.5, 143.3, 142.3, 136.7, 129.5, 127.0, 110.3, 108.1, 40.0, 21.4.

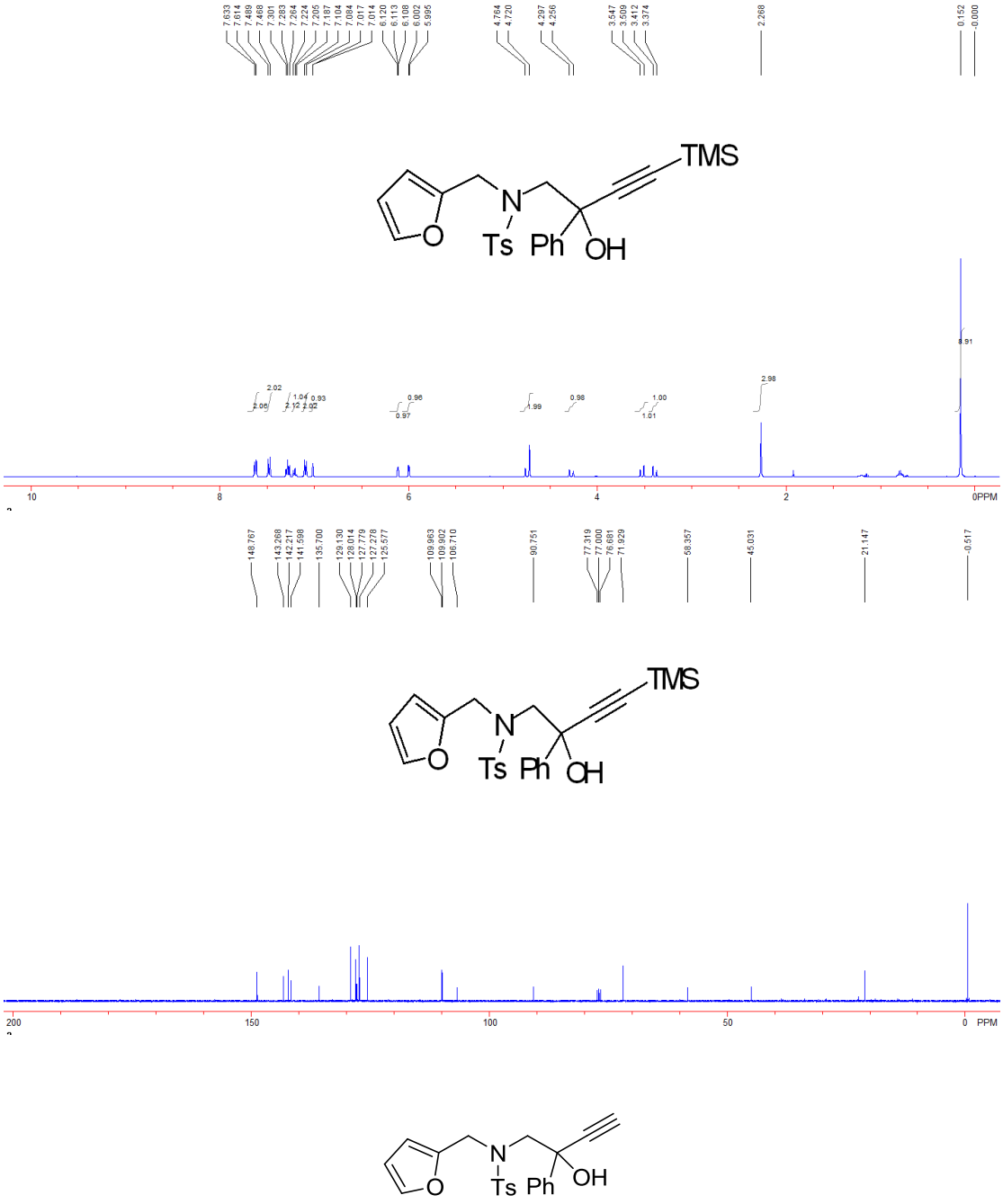


N-(furan-2-ylmethyl)-4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3a): a white solid (3.1 g, 84% yield), mp: 148-150 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.84 (d, 2H, *J* = 8.8 Hz, ArH), 7.74 (d, 2H, *J* = 8.8 Hz, ArH), 7.58 (t, 1H, *J* = 8.0 Hz, ArH), 7.45 (t, 2H, *J* = 8.0 Hz, ArH), 7.29 (d, 2H, *J* = 8.0 Hz, ArH), 7.26 (s, 1H, ArH), 6.23-6.22 (m, 1H, ArH), 6.14 (d, 1H, *J* = 3.2 Hz, ArH), 4.66 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.5, 148.7, 143.2, 142.7, 136.7, 134.5, 133.5, 129.3, 128.5, 127.6, 127.2, 110.2, 110.0, 51.8, 43.7, 21.3; IR (DCM) ν 3065, 2924, 1698, 1335, 1224, 1155, 1092, 911, 813, 734 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{23}N_2O_4S$ $[M + NH_4]^+$ m/z 387.1373, found 387.1374.



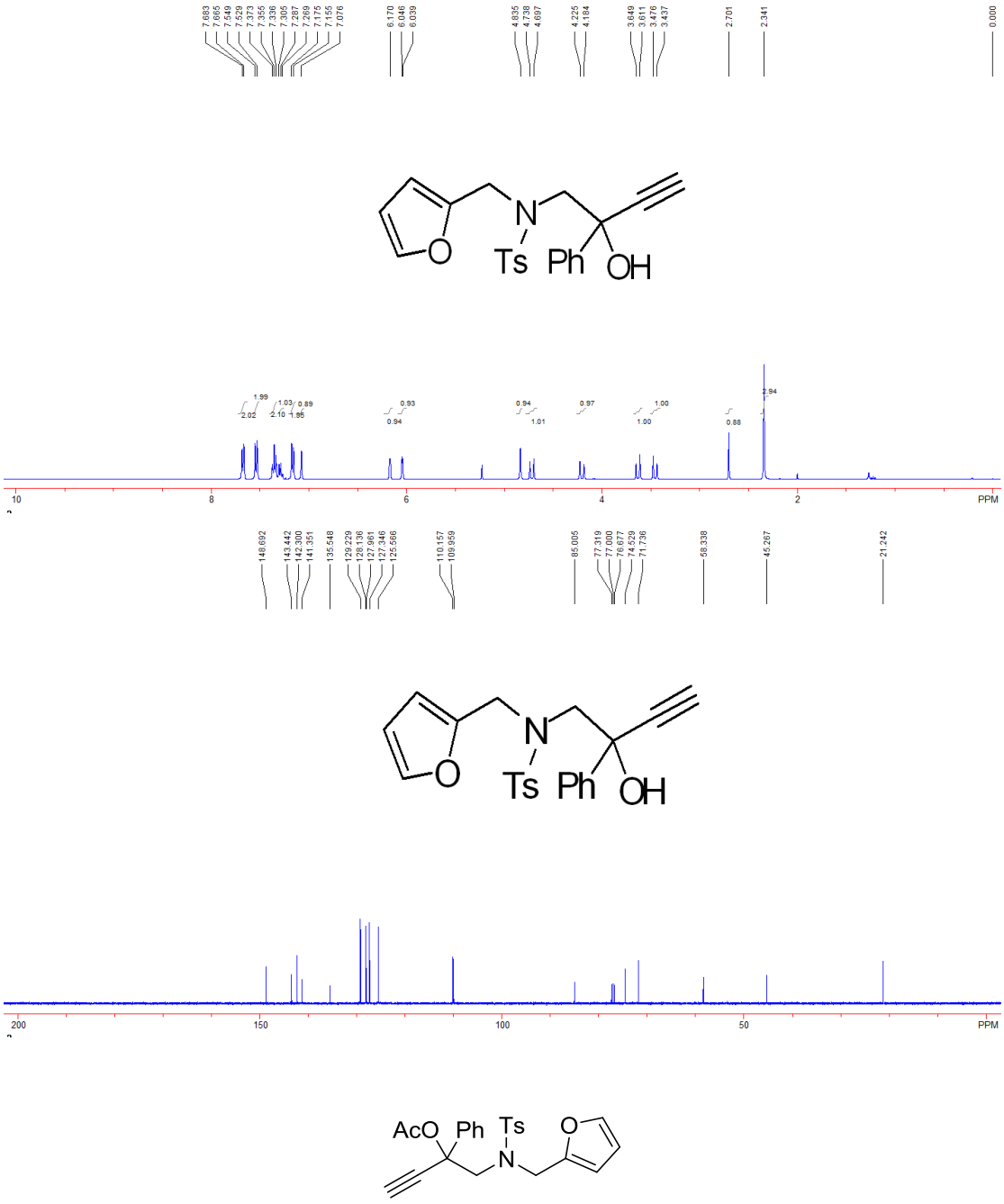
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenyl-4-(trimethylsilyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S-3a'): a colorless oil (1.42 g 61% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.62 (d, 2H, *J* = 7.6 Hz, ArH), 7.48 (d, 2H, *J* = 7.6 Hz, ArH), 7.28 (t, 2H, *J* = 7.6 Hz, ArH), 7.20 (t, 1H, *J* = 7.6 Hz, ArH), 7.09 (d, 2H, *J* = 8.0 Hz, ArH), 7.01 (d, 1H, *J* = 1.2 Hz, ArH), 6.12-6.11 (m, 1H, ArH), 6.00 (d, 1H, *J* = 2.8 Hz, ArH), 4.76-4.72 (m, 2H, OH and CH_2), 4.28 (d, 1H, *J* = 16.4 Hz, CH_2), 3.53 (d, 1H, *J* = 15.2 Hz, CH_2), 3.39 (d, 1H, *J* = 15.2 Hz, CH_2), 2.27 (s, 3H, CH_3), 0.15 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.8, 143.3, 142.2, 141.6, 135.7, 129.1, 128.0, 127.8, 127.3, 125.6, 110.0, 109.9, 106.7, 90.7, 71.9, 58.3, 45.0, 21.1, -0.5; IR (DCM) ν 3457, 2955, 1595, 1331, 1152, 1080, 842 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{33}N_2O_4SSi$ [M +

$NH_4]^+$ m/z 485.1925, found 485.1925.



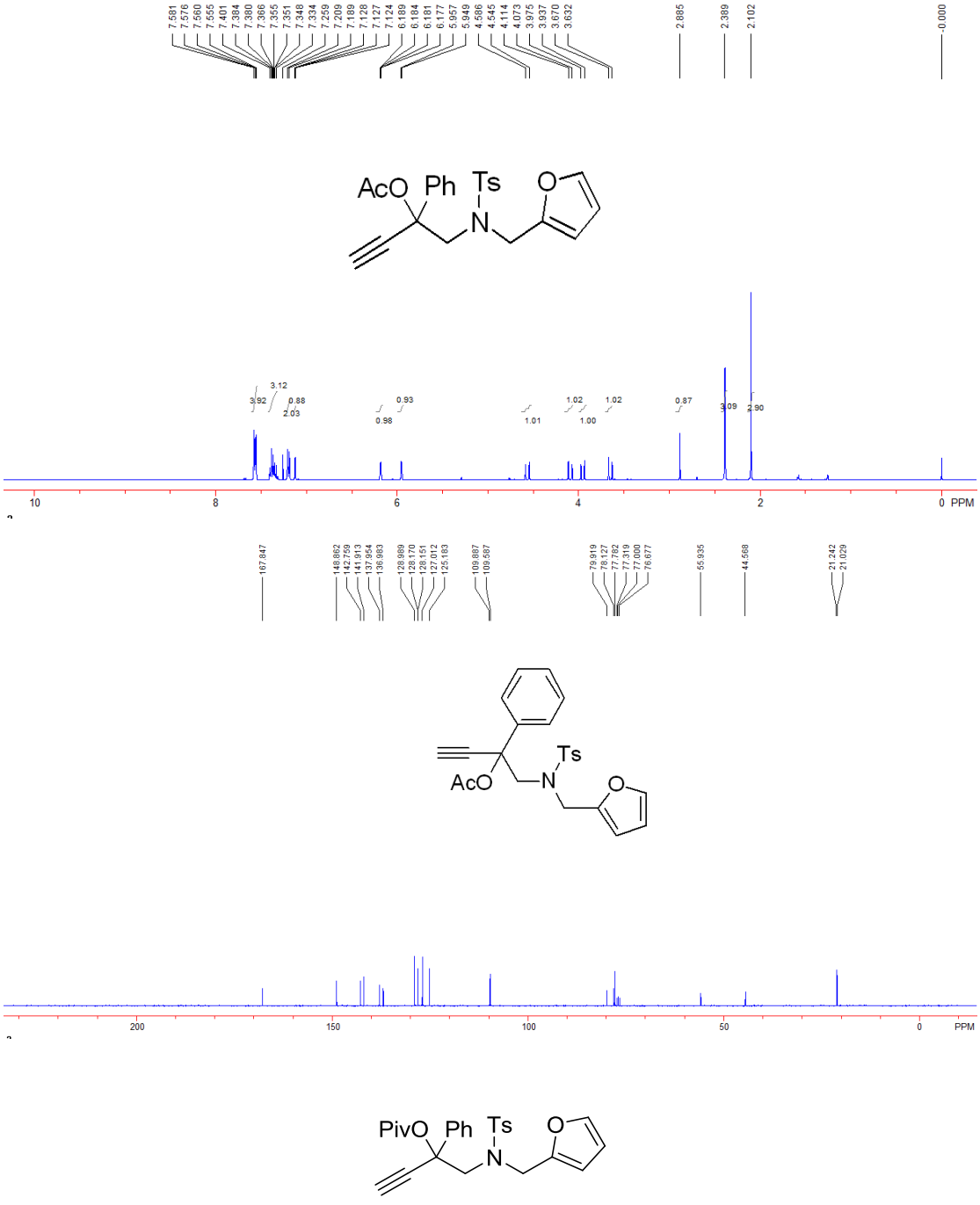
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-4a): a white solid (782 mg, 99% yield), mp: 110-112 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.67 (d, 2H, *J* = 7.2 Hz, ArH), 7.54 (d, 2H, *J* = 8.0 Hz, ArH), 7.34 (t, 2H, *J* = 7.6 Hz, ArH), 7.29 (t, 1H, *J* = 7.2 Hz, ArH), 7.16 (d, 2H, *J* = 8.0 Hz, ArH), 7.08 (s, 1H, ArH), 6.17 (s, 1H, ArH), 6.04 (d, 1H, *J* = 2.8 Hz, ArH), 4.83 (s, 1H, OH), 4.72 (d, 1H, *J* = 16.4 Hz, CH_2), 4.20 (d, 1H, *J* = 16.4 Hz, CH_2), 3.63 (d, 1H, *J* = 15.6 Hz, CH_2), 3.46 (d, 1H, *J* = 15.6 Hz, CH_2), 2.70 (s, 1H, CH), 2.34 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.7, 143.4, 142.3, 141.3, 135.5, 129.2, 128.1, 128.0, 127.3, 125.6, 110.1, 109.9, 85.0, 74.5, 71.7, 58.3, 45.3, 21.2; IR (DCM) ν 3456,

3287, 2360, 1598, 1329, 1151, 1007, 932, 731, 699 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}NNaO_4S$ $[M + Na]^+$ m/z 418.1083, found 418.1084.



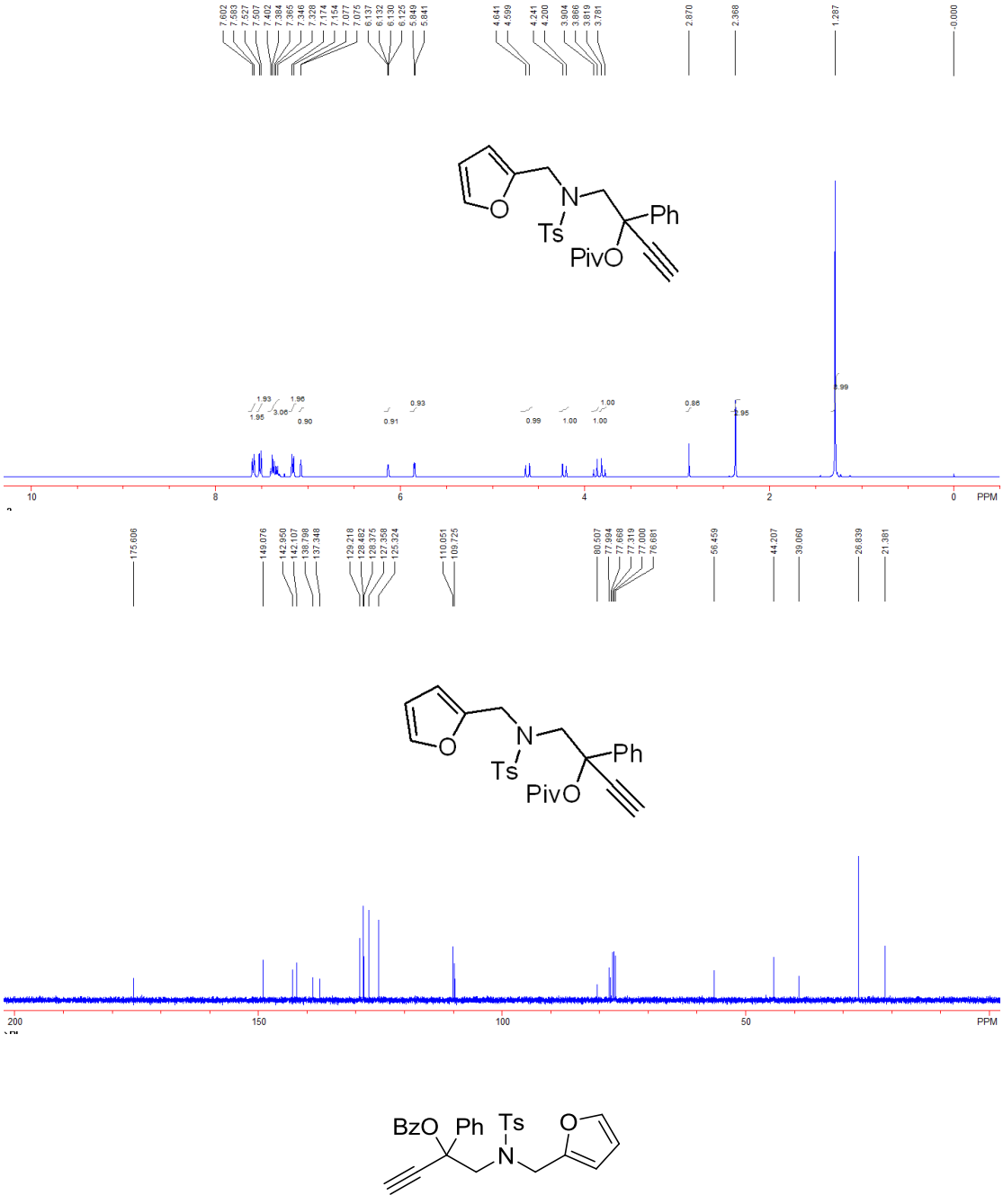
1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 1, entry 1a): a white solid (787 mg, 90% yield), mp: 138-140 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58-7.56 (m, 4H, ArH), 7.40-7.33 (m, 3H, ArH), 7.20 (d, 2H, J = 8.0 Hz, ArH), 7.13-7.12 (m, 1H, ArH), 6.18 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 5.95 (d, 1H, J = 3.2 Hz, ArH), 4.57 (d, 1H, J = 16.4 Hz, CH_2), 4.09 (d, 1H, J = 16.4 Hz, CH_2), 3.96 (d, 1H, J = 15.2 Hz, CH_2), 3.65 (d, 1H, J = 15.2 Hz, CH_2), 2.88 (s, 1H, CH), 2.39 (s, 3H, CH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.8, 148.9, 142.7, 141.9, 137.9, 137.0, 129.0, 128.2, 128.1,

127.0, 125.2, 109.9, 109.6, 79.9, 78.1, 77.8, 55.9, 44.6, 21.2, 21.0; IR (DCM) ν 3267, 2927, 2117, 1750, 1344, 1221, 1157, 995, 734, 699 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 455.1635, found 455.1641.



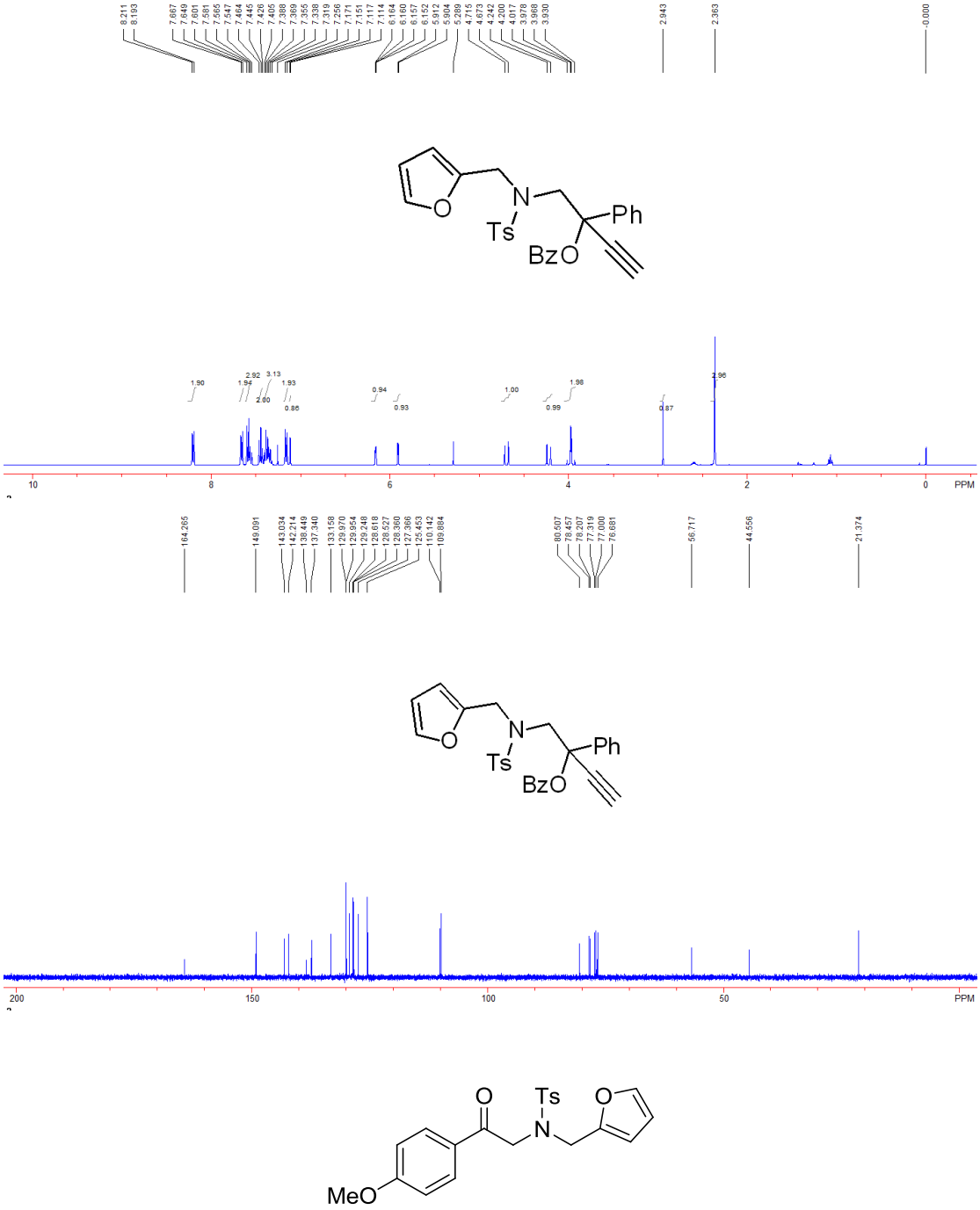
1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl pivalate (Table 2, entry 1b): a white solid (756 mg, 86% yield), mp: 144-146 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.0 Hz, ArH), 7.52 (d, 2H, *J* = 8.0 Hz, ArH), 7.40-7.33 (m, 3H, ArH), 7.16 (d, 2H, *J* = 8.0 Hz, ArH), 7.08 (d, 1H, *J* = 0.8 Hz, ArH), 6.13 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.84 (d, 1H, *J* = 3.2 Hz, ArH), 4.62 (d, 1H, *J* = 16.8 Hz, CH_2), 4.22 (d, 1H, *J* =

16.8 Hz, CH_2), 3.88 (d, 1H, *J* = 15.2 Hz, CH_2), 3.80 (d, 1H, *J* = 15.2 Hz, CH_2), 2.87 (s, 1H, CH), 2.37 (s, 3H, CH_3), 1.29 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 175.6, 149.1, 142.9, 142.1, 138.8, 137.3, 129.2, 128.5, 128.4, 127.3, 125.3, 110.0, 109.7, 80.5, 78.0, 77.7, 56.4, 44.2, 39.1, 26.8, 21.4; IR (DCM) ν 3265, 2972, 2109, 1743, 1598, 1350, 1160, 1133, 735, 699 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{33}N_2O_5S$ $[M + NH_4]^+$ m/z 497.2105, found 497.2104.



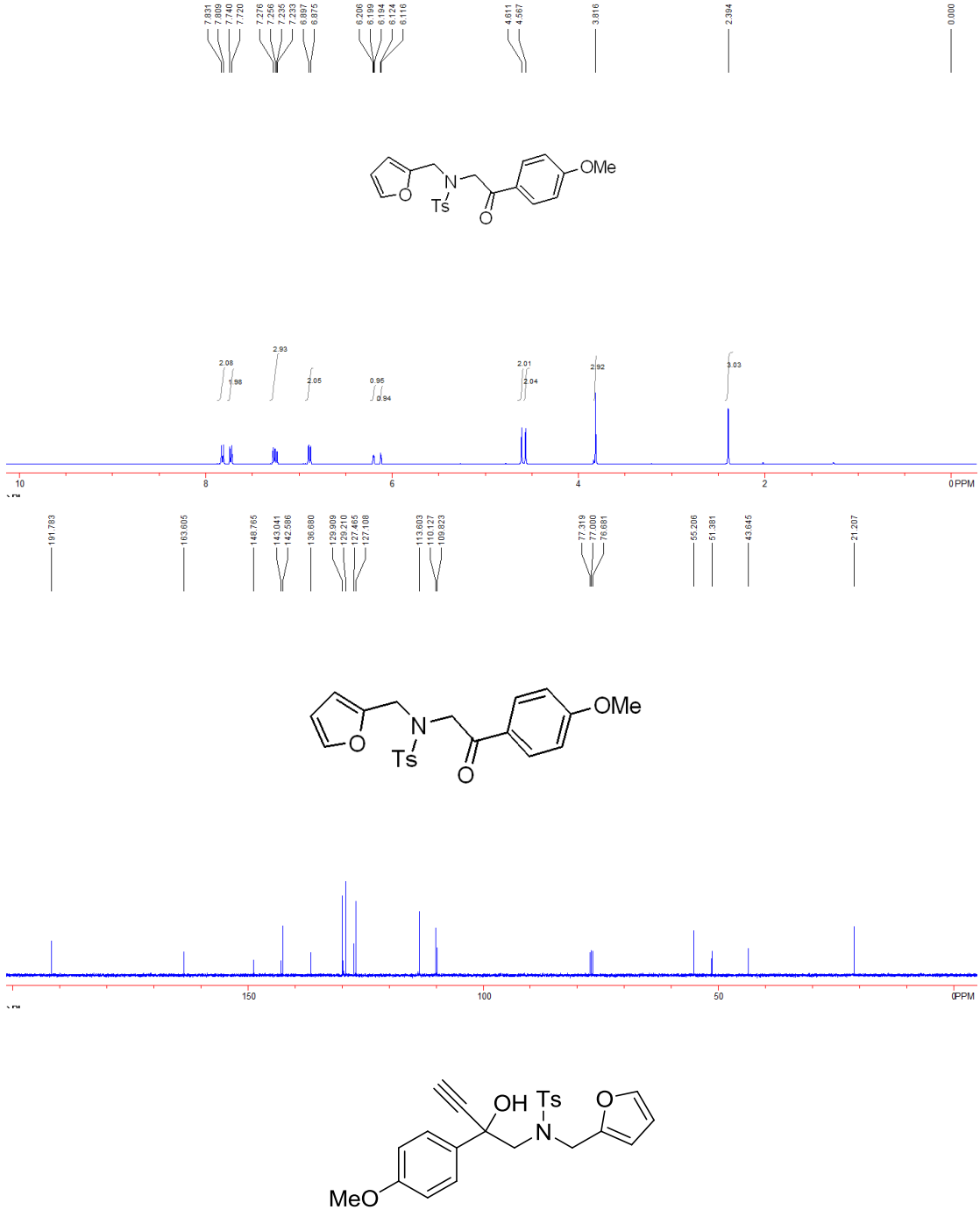
1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl benzoate (Table 2, entry 1c): a white solid (1.0 g, 89% yield), mp: 145-147 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.20 (d, 2H, *J* = 7.2 Hz, ArH), 7.66 (d, 2H, *J* = 7.2 Hz, ArH), 7.60-7.55 (m, 3H, ArH), 7.44 (t, 2H, *J* = 7.6 Hz, ArH), 7.40-7.32 (m, 3H, ArH), 7.16 (d, 2H, *J* = 8.0 Hz, ArH), 7.11

(d, 1H, J = 1.2 Hz, ArH), 6.16 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 5.91 (d, 1H, J = 3.2 Hz, ArH), 4.69 (d, 1H, J = 16.8 Hz, CH_2), 4.22 (d, 1H, J = 16.8 Hz, CH_2), 4.02-3.93 (m, 2H, CH_2), 2.94 (s, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 164.3, 149.1, 143.0, 142.2, 138.4, 137.3, 133.1, 130.0, 129.9, 129.2, 128.6, 128.5, 128.4, 127.4, 125.4, 110.1, 109.9, 80.5, 78.4, 78.2, 56.7, 44.5. 21.4; IR (DCM) ν 3267, 2117, 1730, 1333, 1266, 1157, 1090, 732, 711, 699 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NNaO_5S$ $[M + Na]^+$ m/z 522.1346, found 522.1351.



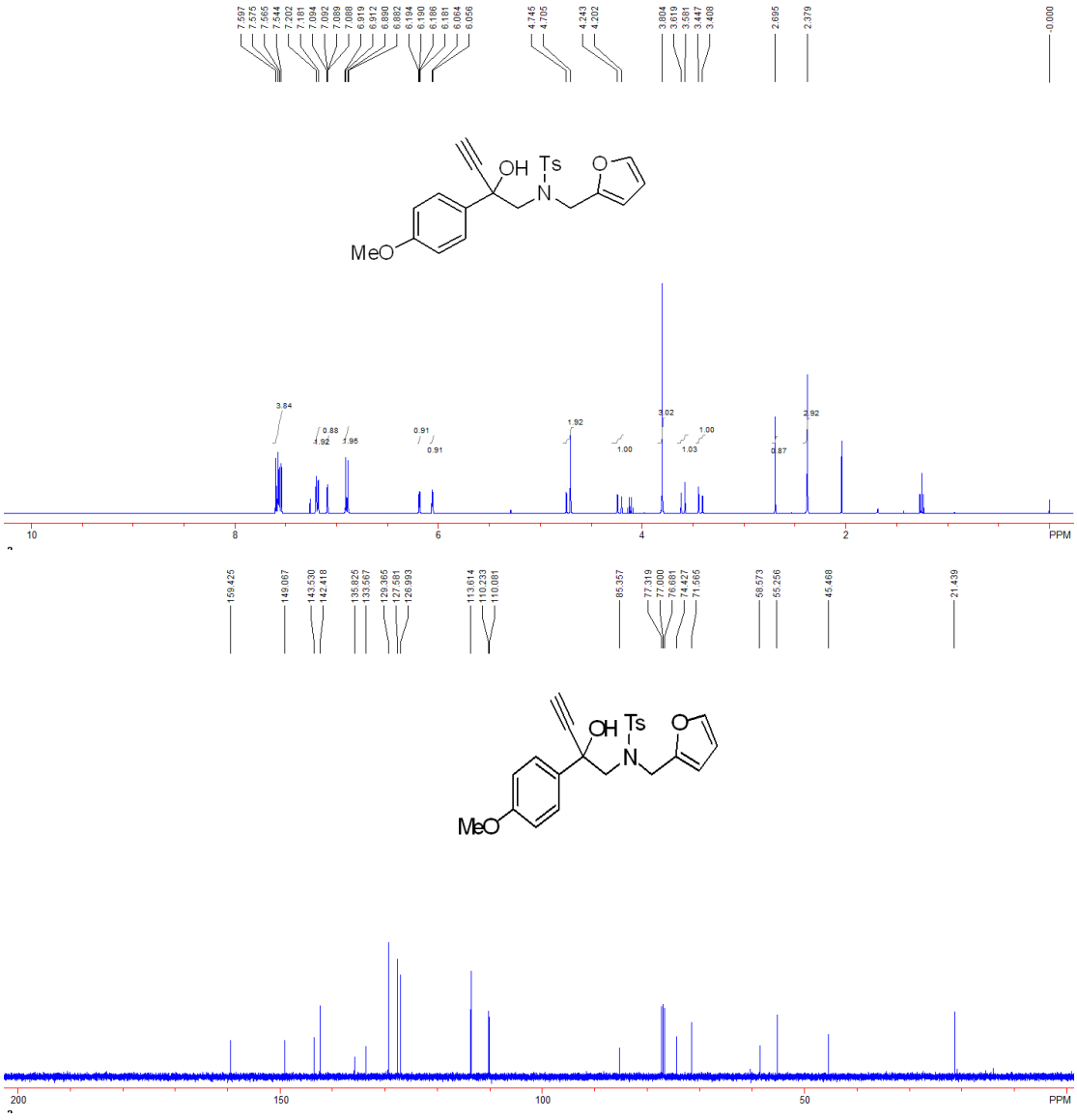
N-(furan-2-ylmethyl)-N-(2-(4-methoxyphenyl)-2-oxoethyl)-4-methylbenzenesulfonamide (S-3d): a colorless oil (1.9 g, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.82 (d, 2H, J =

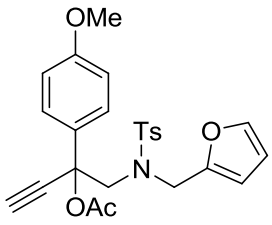
8.8 Hz, ArH), 7.73 (d, 2H, *J* = 8.0 Hz, ArH), 7.28-7.23 (m, 3H, ArH), 6.89 (d, 2H, *J* = 8.8 Hz, ArH), 6.21-6.19 (m, 1H, ArH), 6.12 (d, 1H, *J* = 3.2 Hz, ArH), 4.61 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 3.82 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 191.8, 163.6, 148.8, 143.0, 142.6, 136.7, 129.9, 129.2, 127.5, 127.1, 113.6, 110.1, 109.8, 55.2, 51.4, 43.6, 21.2; IR (DCM) ν 2923, 1688, 1598, 1335, 1235, 1155, 1011, 813, 730, 655 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_5S$ $[M + NH_4]^+$ m/z 417.1479, found 417.1490.



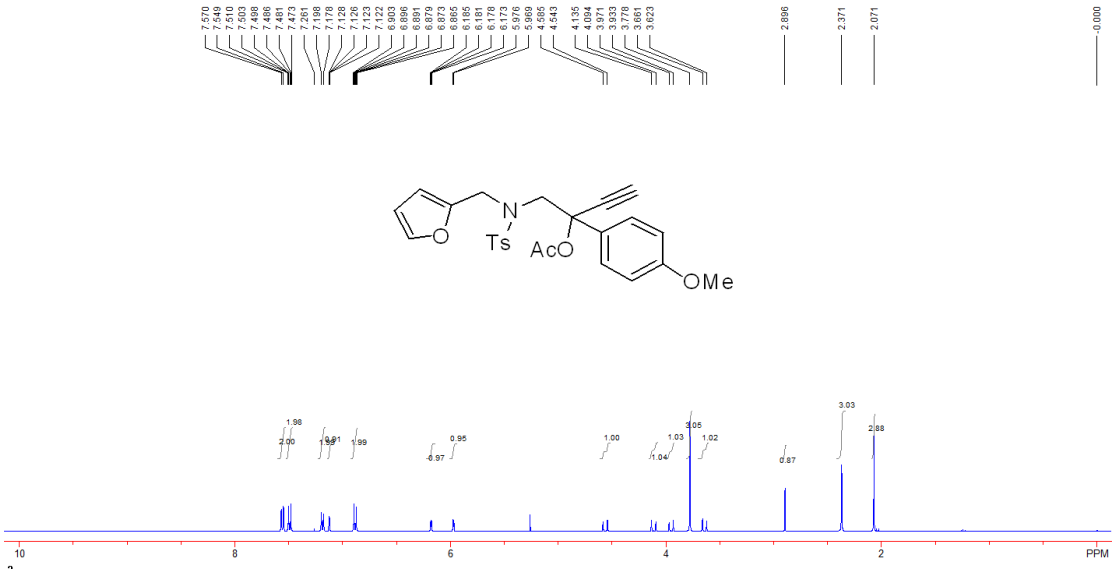
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-(4-methoxyphenyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S-4d): a colorless oil (878 mg, 57% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ

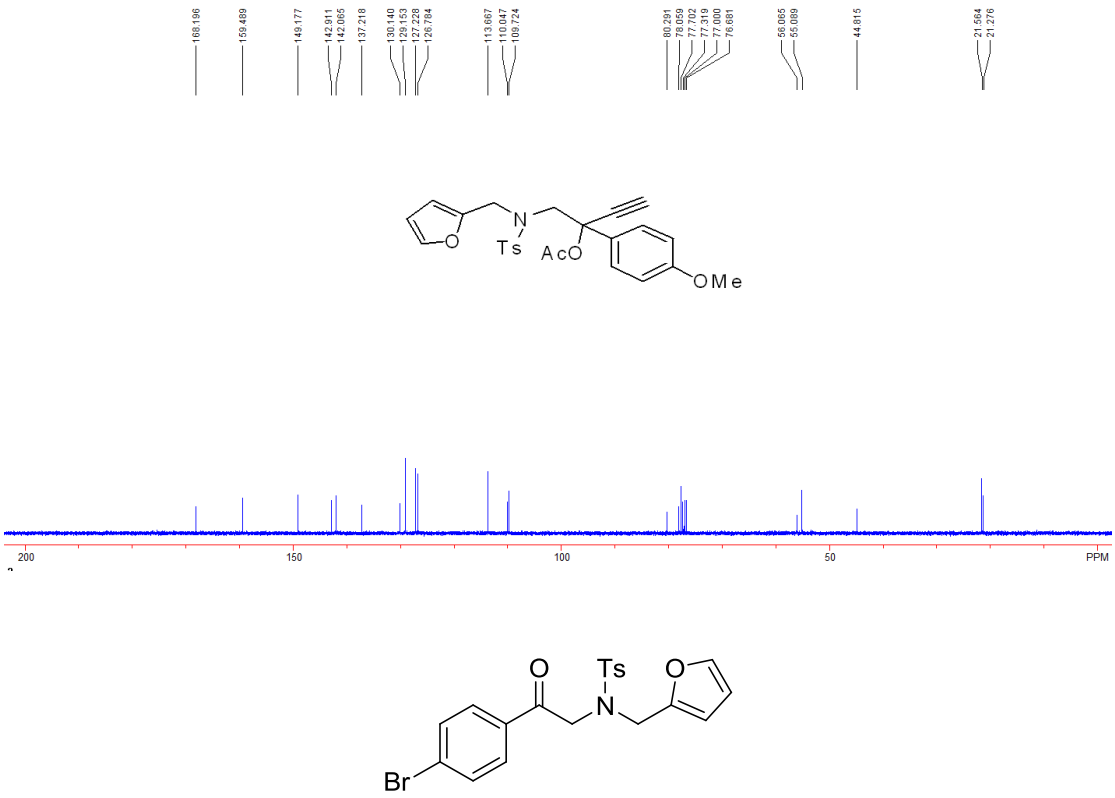
7.60-7.54 (m, 4H, ArH), 7.19 (d, 2H, J = 8.4 Hz, ArH), 7.09 (dd, 1H, J_1 = 2.0 Hz, J_2 = 0.8 Hz, ArH), 6.92-6.88 (m, 2H, ArH), 6.19 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 6.06 (d, 1H, J = 3.2 Hz, ArH), 4.72 (d, 2H, J = 16.4 Hz, OH and CH_2), 4.22 (d, 1H, J = 16.4 Hz, CH_2), 3.80 (s, 3H, CH_3), 3.60 (d, 1H, J = 15.2 Hz, CH_2), 3.43 (d, 1H, J = 15.2 Hz, CH_2), 2.70 (s, 1H, CH), 2.38 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 159.4, 149.1, 143.5, 142.4, 135.8, 133.6, 129.4, 127.6, 127.0, 113.6, 110.2, 110.1, 85.3, 74.4, 71.6, 58.6, 55.2, 45.5, 21.4; IR (DCM) ν 3461, 3287, 2923, 1608, 1508, 1329, 1151, 832, 734, 653 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}NNaO_5S$ [M + Na]$^+$ m/z 448.1189, found 448.1193.



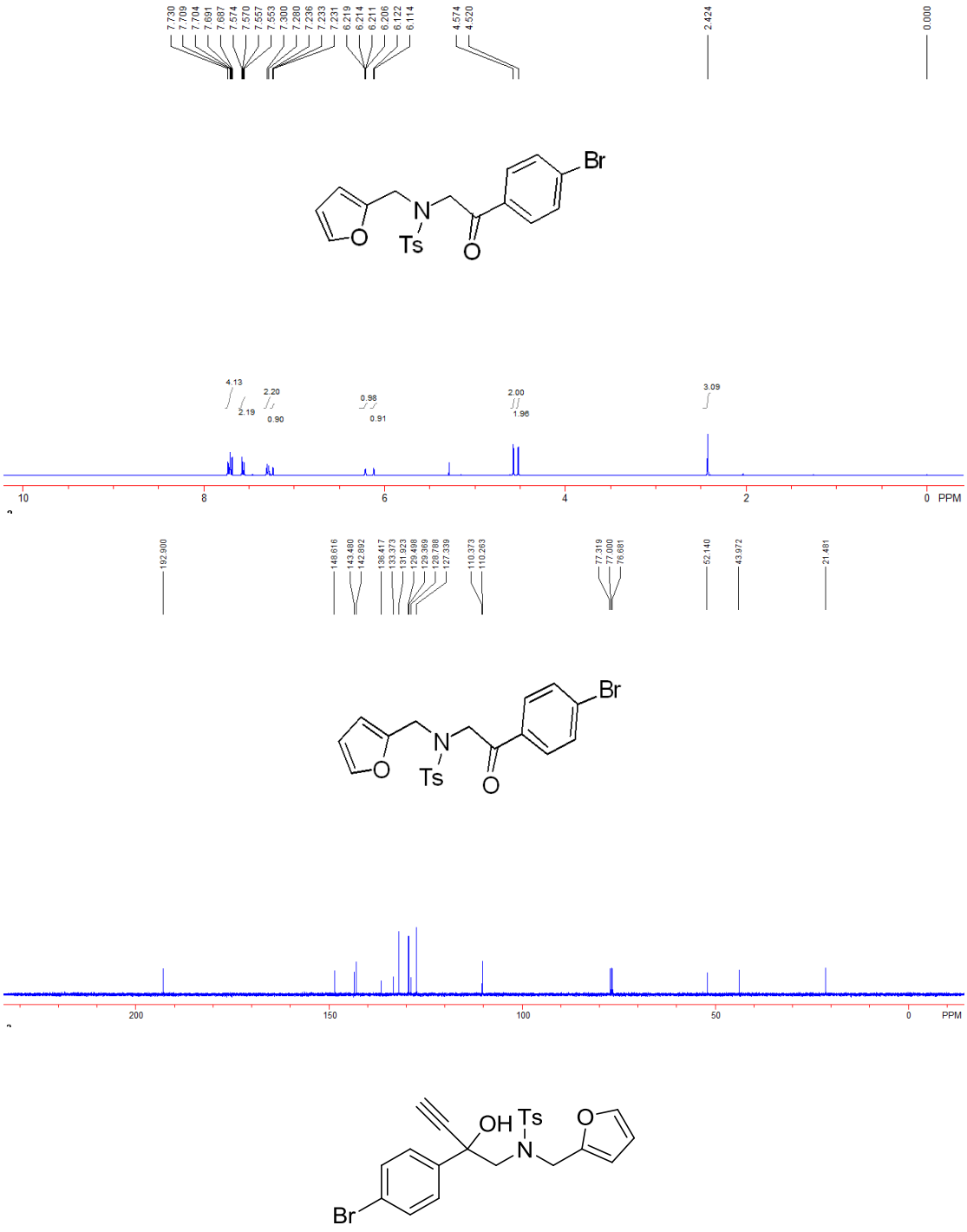


1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-(4-methoxyphenyl)but-3-yn-2-yl acetate (Table 2, entry 1d): a colorless oil (408 mg, 50% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.56 (d, 2H, *J* = 8.4 Hz, ArH), 7.51-7.47 (m, 2H, ArH), 7.19 (d, 2H, *J* = 8.0 Hz, ArH), 7.13-7.12 (m, 1H, ArH), 6.90-6.86 (m, 2H, ArH), 6.18-6.17 (m, 1H, ArH), 5.97 (d, 1H, *J* = 2.8 Hz, ArH), 4.56 (d, 1H, *J* = 16.8 Hz, CH_2), 4.11 (d, 1H, *J* = 16.8 Hz, CH_2), 3.95 (d, 1H, *J* = 15.2 Hz, CH_2), 3.78 (s, 3H, CH_3), 3.64 (d, 1H, *J* = 15.2 Hz, CH_2), 2.90 (s, 1H, CH), 2.37 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.2, 159.5, 149.2, 142.9, 142.1, 137.2, 130.1, 129.1, 127.2, 126.8, 113.7, 110.0, 109.7, 80.3, 78.0, 77.7, 56.1, 55.1, 44.8, 21.6, 21.3; IR (DCM) ν 3291, 2931, 1751, 1511, 1345, 1224, 1159, 1101, 831, 732 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_6S$ $[M + NH_4]^+$ m/z 485.1741, found 485.1730.



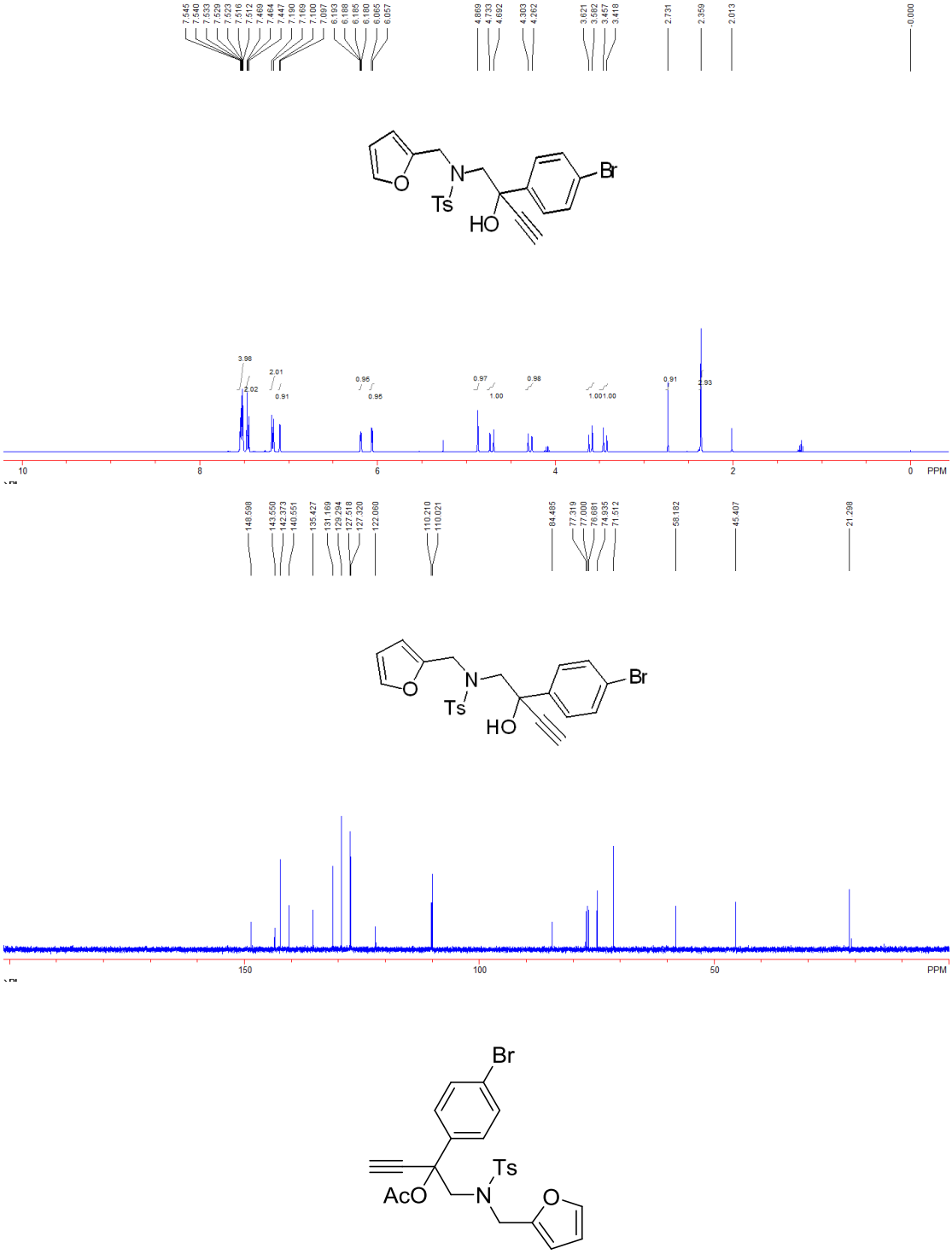


N-(2-(4-bromophenyl)-2-oxoethyl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-3e): a colorless oil (1.7 g, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.73-7.69 (m, 4H, ArH), 7.57-7.55 (m, 2H, ArH), 7.29 (d, 2H, *J* = 8.0 Hz, ArH), 7.24-7.23 (m, 1H, ArH), 6.21 (dd, 1H, J_1 = 3.6 Hz, J_2 = 2.0 Hz, ArH), 6.12 (d, 1H, *J* = 3.2 Hz, ArH), 4.57 (s, 2H, CH_2), 4.52 (s, 2H, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 192.9, 148.6, 143.5, 142.9, 136.4, 133.4, 131.9, 129.5, 129.4, 128.8, 127.3, 110.4, 110.3, 52.1, 44.0, 21.5; IR (DCM) ν 2923, 1807, 1699, 1585, 1336, 1157, 1092, 989, 813, 744 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{19}BrNO_4S$ $[M + H]^+$ m/z 448.0213, found 448.0202.



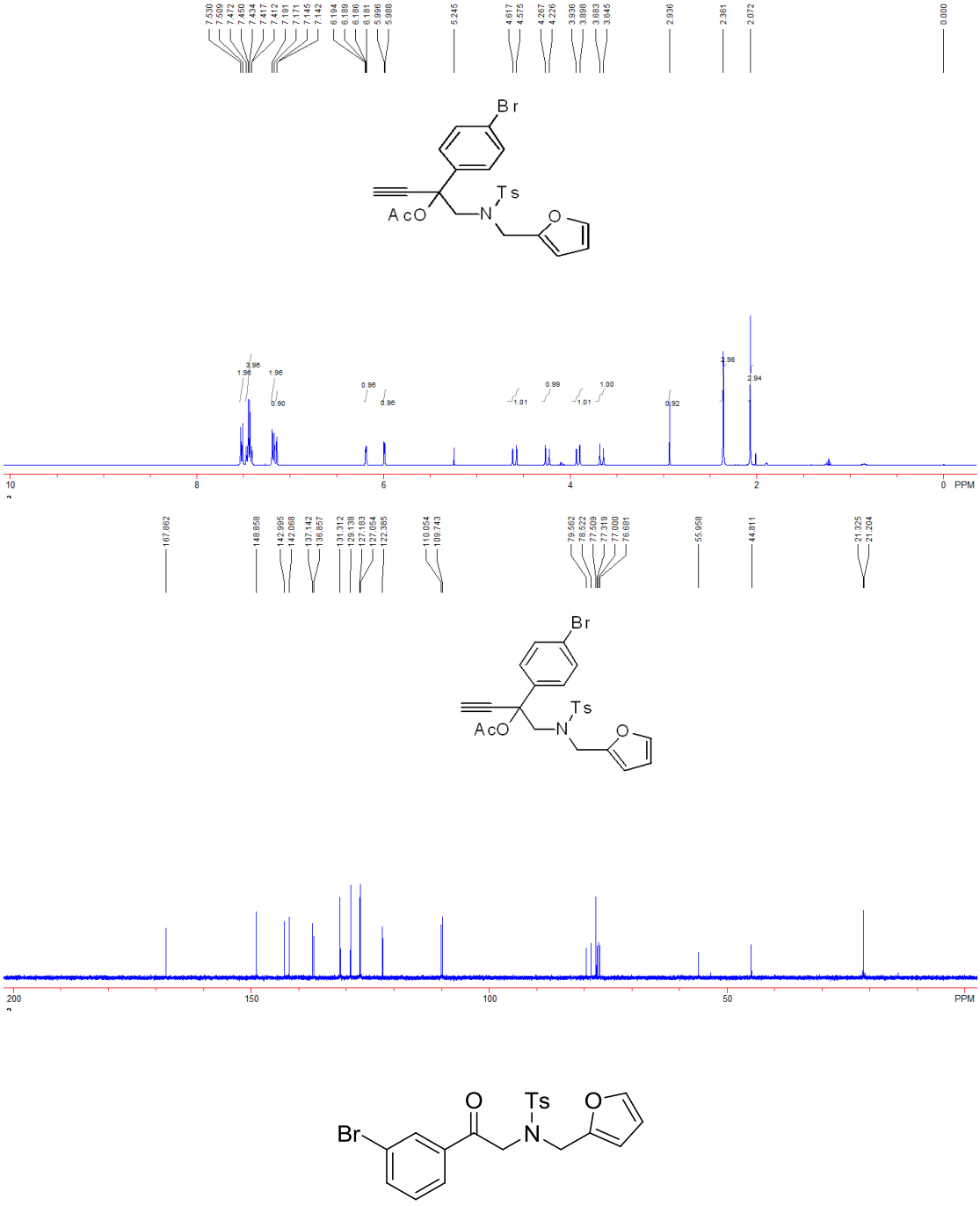
N-(2-(4-bromophenyl)-2-hydroxybut-3-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-4e): a colorless oil (917 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.54-7.51 (m, 4H, ArH), 7.46 (d, 2H, *J* = 8.4 Hz, ArH), 7.18 (d, 2H, *J* = 8.4 Hz, ArH), 7.10 (d, 1H, *J* = 1.2 Hz, ArH), 6.19 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.06 (d, 1H, *J* = 3.2 Hz, ArH), 4.87 (s, 1H, OH), 4.71 (d, 1H, *J* = 16.4 Hz, CH_2), 4.28 (d, 1H, *J* = 16.4 Hz, CH_2), 3.60 (d, 1H, *J* = 15.6 Hz, CH_2), 3.44 (d, 1H, *J* = 15.6 Hz, CH_2), 2.73 (s, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.6, 143.5, 142.4, 140.5, 135.4, 131.2, 129.3, 127.5, 127.3, 122.1,

110.2, 110.0, 84.5, 74.9, 71.5, 58.2, 45.4, 21.3; IR (DCM) ν 3450, 3294, 1597, 1485, 1330, 1151, 1009, 929, 814, 734 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}BrN_2O_4S$ $[M + NH_4]^+$ m/z 491.0635, found 491.0636.



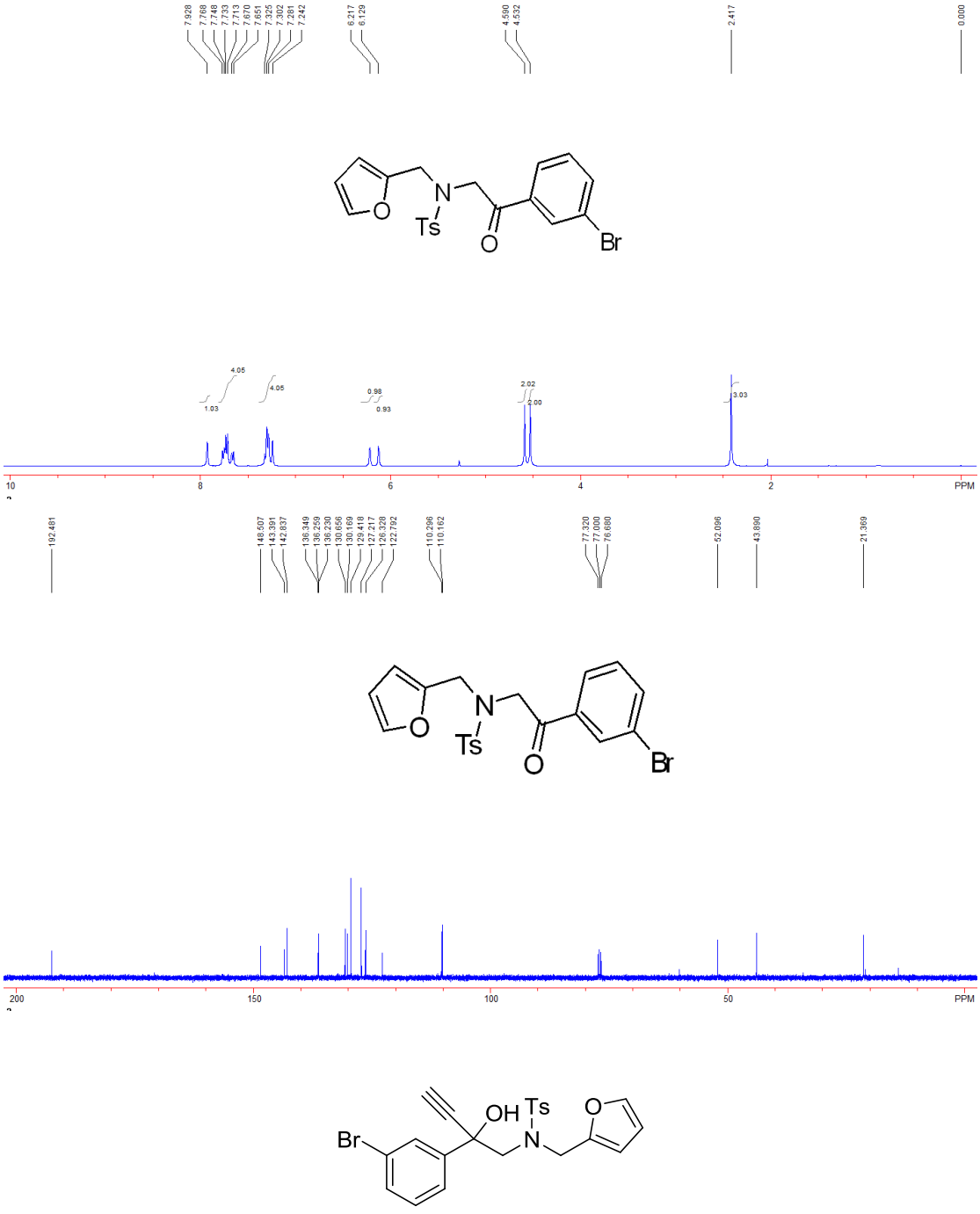
2-(4-bromophenyl)-1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)but-3-yn-2-yl acetate (Table 2, entry 1e): a colorless oil (855 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.52 (d, 2H, *J* = 8.4 Hz, ArH), 7.47-7.41 (m, 4H, ArH), 7.18 (d, 2H, *J* = 8.0 Hz, ArH), 7.14 (d, 1H, *J* = 1.2 Hz, ArH), 6.19 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.99 (d, 1H, *J* = 3.2

Hz, ArH), 4.60 (d, 1H, J = 16.4 Hz, CH_2), 4.25 (d, 1H, J = 16.4 Hz, CH_2), 3.93 (d, 1H, J = 15.2 Hz, CH_2), 3.66 (d, 1H, J = 15.2 Hz, CH_2), 2.94 (s, 1H, CH), 2.36 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.9, 148.8, 143.0, 142.1, 137.1, 136.8, 131.3, 129.1, 127.2, 127.0, 122.4, 110.0, 109.7, 79.6, 78.5, 77.5, 55.9, 44.8, 21.3, 21.2; IR (DCM) ν 3295, 2919, 2121, 1751, 1346, 1220, 1158, 1009, 815, 732 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}BrN_2O_5S$ [M + NH_4]$^+$ m/z 533.0740, found 533.0744.



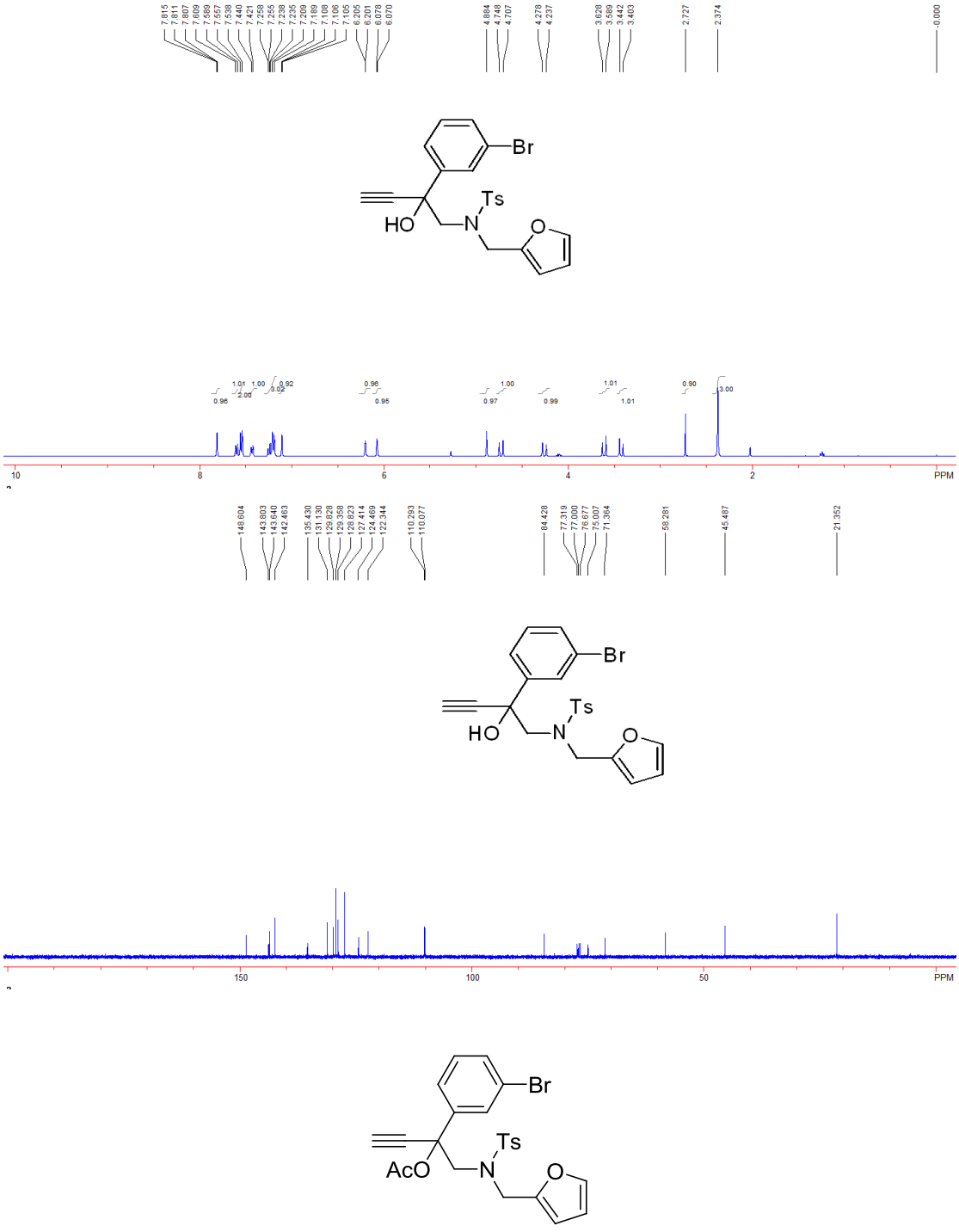
N-(2-(3-bromophenyl)-2-oxoethyl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-3f): a colorless oil (1.9 g, 99% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.93 (s, 1H, ArH),

7.77-7.65 (m, 4H, ArH), 7.32-7.24 (m, 4H, ArH), 6.22 (s, 1H, ArH), 6.13 (s, 1H, ArH), 4.59 (s, 2H. CH_2), 4.53 (s, 2H, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 192.5, 148.5, 143.4, 142.8, 136.3, 136.26, 136.23, 130.6, 130.2, 129.4, 127.2, 126.3, 122.8, 110.3, 110.2, 52.1, 43.9, 21.4; IR (DCM) ν 3069, 2927, 1703, 1567, 1337, 1216, 1145, 1092, 767, 658 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_4S$ $[M + NH_4]^+$ m/z 465.0478, found 465.0465.

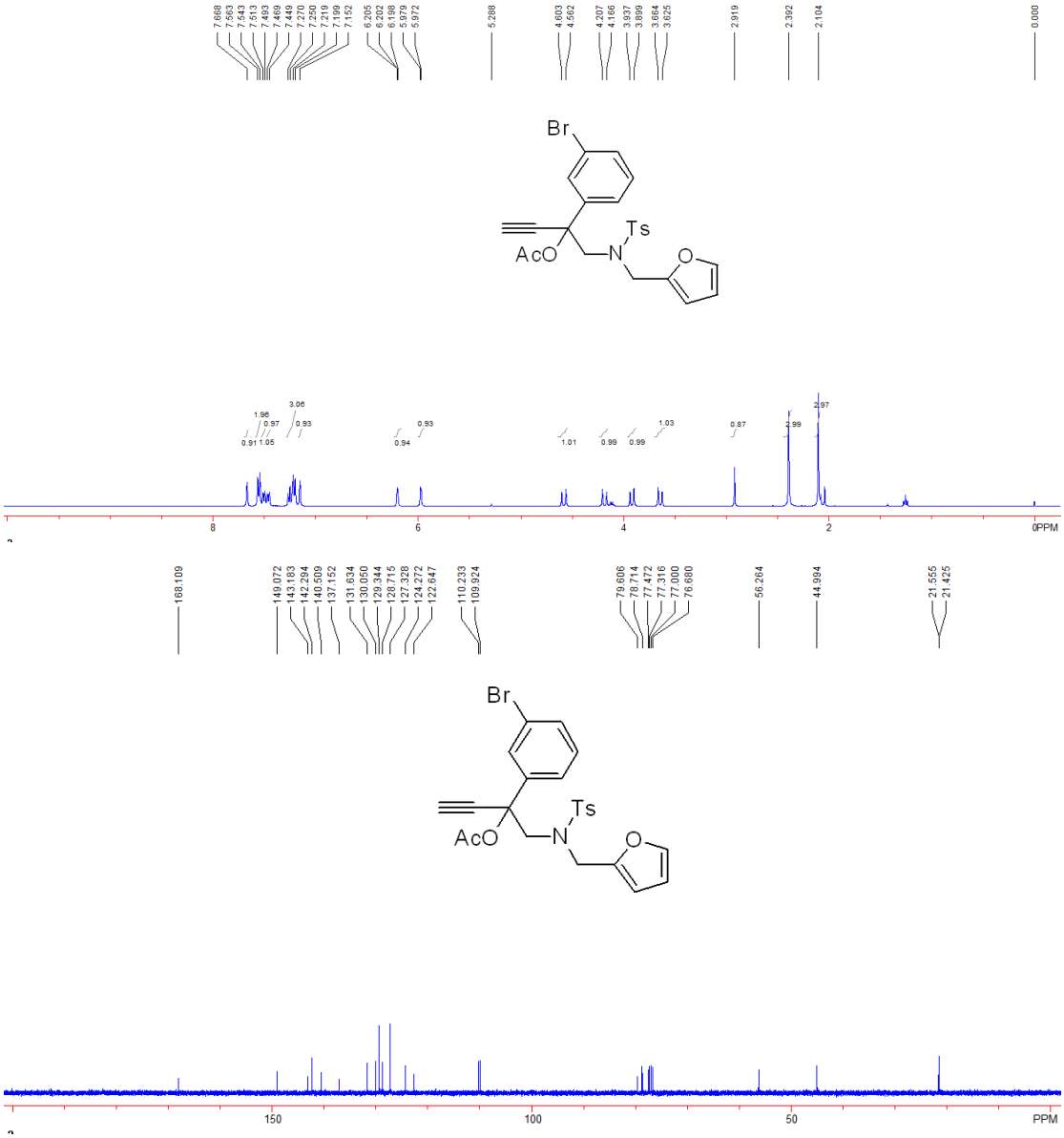


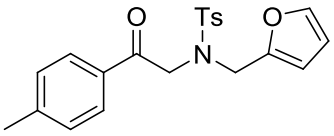
N-(2-(3-bromophenyl)-2-hydroxybut-3-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-4f): a colorless oil (921 mg, 76% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.81 (t, 1H, *J* = 1.6 Hz, ArH), 7.60 (d, 1H, *J* = 8.0 Hz, ArH), 7.55 (d, 2H, *J* = 7.6 Hz, ArH), 7.43 (d, 1H, *J*

= 7.6 Hz, ArH), 7.26-7.19 (m, 3H, ArH), 7.11-7.10 (m, 1H, ArH), 6.20 (d, 1H, *J* = 1.6 Hz, ArH), 6.07 (d, 1H, *J* = 3.2 Hz, ArH), 4.88 (s, 1H, OH), 4.73 (d, 1H, *J* = 16.4 Hz, CH_2), 4.26 (d, 1H, *J* = 16.4 Hz, CH_2), 3.61 (d, 1H, *J* = 15.6 Hz, CH_2), 3.42 (d, 1H, *J* = 15.6 Hz, CH_2), 2.73 (s, 1H, CH), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.6, 143.8, 143.6, 142.5, 135.4, 131.1, 129.8, 129.3, 128.8, 127.4, 124.5, 122.3, 110.3, 110.1, 84.4, 75.0, 71.4, 58.3, 45.5, 21.3; IR (DCM) ν 3449, 3289, 1596, 1329, 1150, 1007, 934, 814, 729, 698 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}BrN_2O_4S$ $[M + NH_4]^+$ m/z 491.0635, found 491.0633.

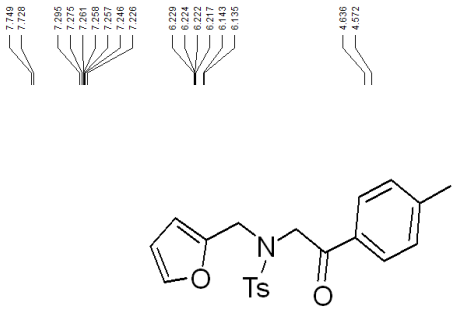


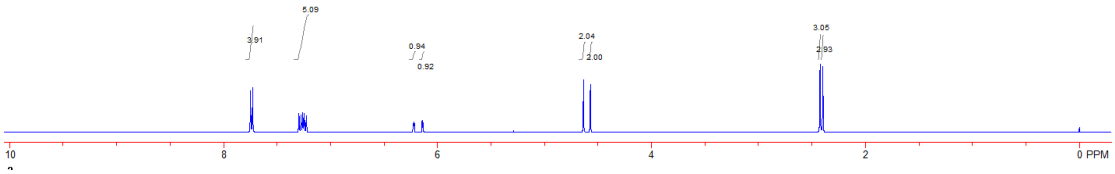
2-(3-bromophenyl)-1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)but-3-yn-2-yl acetate (Table 2, entry 1f): a colorless oil (854 mg, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.67 (s, 1H, ArH), 7.55 (d, 2H, *J* = 8.0 Hz, ArH), 7.50 (d, 2H, *J* = 8.0 Hz, ArH), 7.46 (d, 1H, *J* = 8.0 Hz, ArH), 7.27-7.20 (m, 3H, ArH), 7.15 (s, 1H, ArH), 6.20 (s, 1H, ArH), 5.97 (d, 1H, *J* = 2.8 Hz, ArH), 4.58 (d, 1H, *J* = 16.4 Hz, CH_2), 4.19 (d, 1H, *J* = 16.4 Hz, CH_2), 3.92 (d, 1H, *J* = 15.2 Hz, CH_2), 3.64 (d, 1H, *J* = 15.2 Hz, CH_2), 2.92 (s, 1H, CH), 2.39 (s, 3H, CH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.1, 149.1, 143.2, 142.3, 140.5, 137.1, 131.6, 130.0, 129.3, 128.7, 127.3, 124.3, 122.6, 110.2, 109.9, 79.6, 78.7, 77.5, 56.3, 45.0, 21.5, 21.4; IR (DCM) ν 3267, 2931, 2121, 1752, 1345, 1217, 1158, 1000, 940, 730 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}BrN_2O_5S$ $[M + NH_4]^+$ m/z 533.0740, found 533.0741.

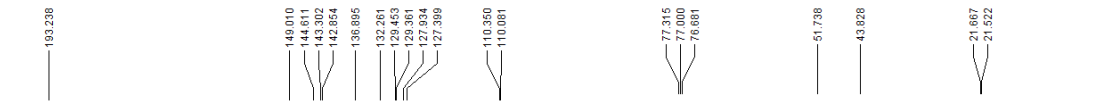


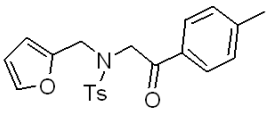


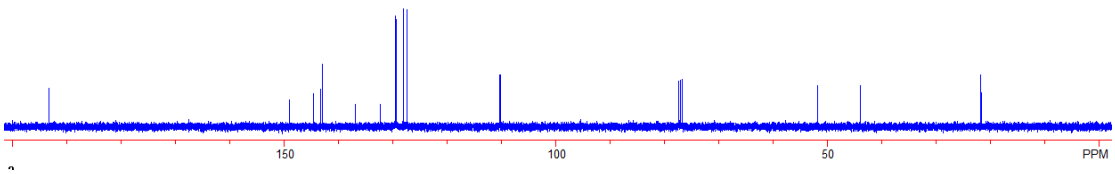
N-(furan-2-ylmethyl)-4-methyl-N-(2-oxo-2-(p-tolyl)ethyl)benzenesulfonamide (S-3g): a white solid (1.6 g, 99% yield), mp: 99-101 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.74 (d, 4H, J = 8.4 Hz, ArH), 7.29-7.23 (m, 5H, ArH), 6.22 (dd, 1H, J_1 = 2.8 Hz, J_2 = 2.0 Hz, ArH), 6.14 (d, 1H, J = 3.2 Hz, ArH), 4.64 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.2, 149.0, 144.6, 143.3, 142.8, 136.9, 132.3, 129.45, 129.36, 127.9, 127.4, 110.3, 110.1, 51.7, 43.8, 21.7, 21.5; IR (DCM) ν 2919, 1694, 1606, 1335, 1228, 1155, 1092, 917, 808, 727 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}NO_4S$ $[M + H]^+$ m/z 384.1264, found 384.1268.

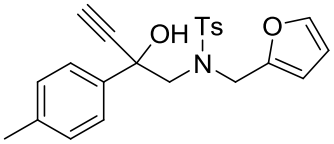




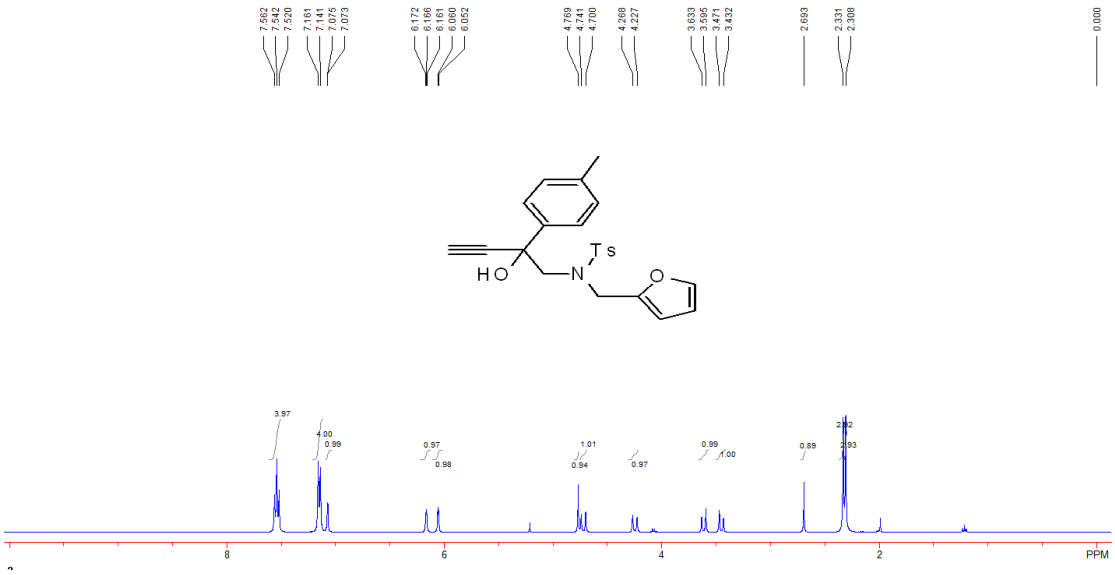


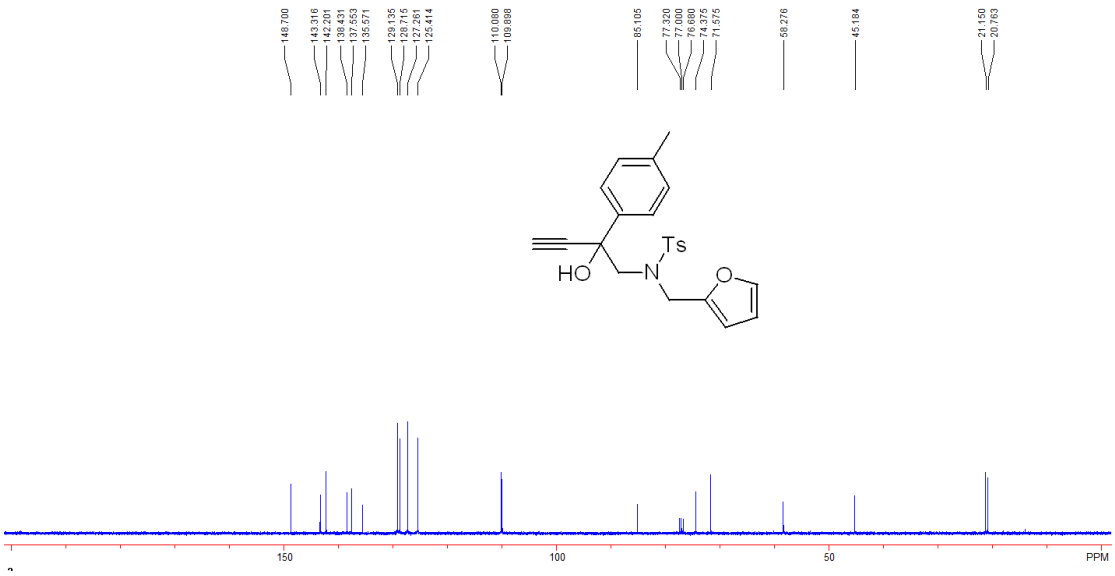


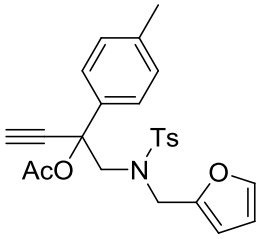




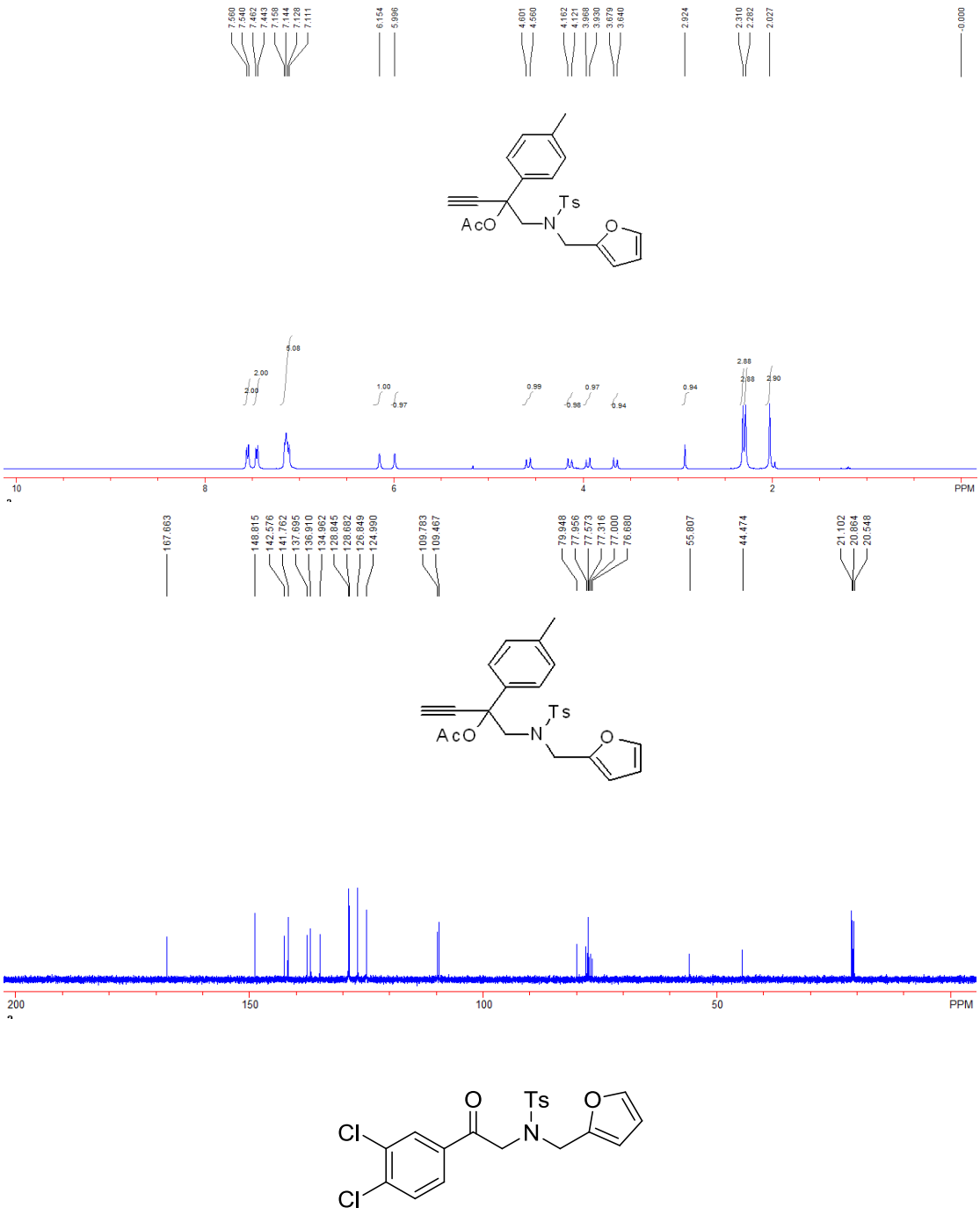
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-(p-tolyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S-4g): a colorless oil (854 mg, 89% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.56-7.52 (m, 4H, ArH), 7.15 (d, 4H, *J* = 8.0 Hz, ArH), 7.07 (d, 1H, *J* = 0.8 Hz, ArH), 6.17-6.16 (m, 1H, ArH), 6.06 (d, 1H, *J* = 3.2 Hz, ArH), 4.77 (s, 1H, OH), 4.72 (d, 1H, *J* = 16.4 Hz, CH_2), 4.25 (d, 1H, *J* = 16.4 Hz, CH_2), 3.61 (d, 1H, *J* = 15.2 Hz, CH_2), 3.45 (d, 1H, *J* = 15.2 Hz, CH_2), 2.69 (s, 1H, CH), 2.33 (s, 3H, CH_3), 2.31 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.7, 143.3, 142.2, 138.4, 137.5, 135.6, 129.1, 128.7, 127.3, 125.4, 110.1, 109.9, 85.1, 74.4, 71.6, 58.3, 45.2, 21.1, 20.8; IR (DCM) ν 3459, 3288, 2924, 2598, 1329, 1151, 1007, 930, 815, 732 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}NNaO_4S$ $[M + Na]^+$ m/z 432.1240, found 432.1241.





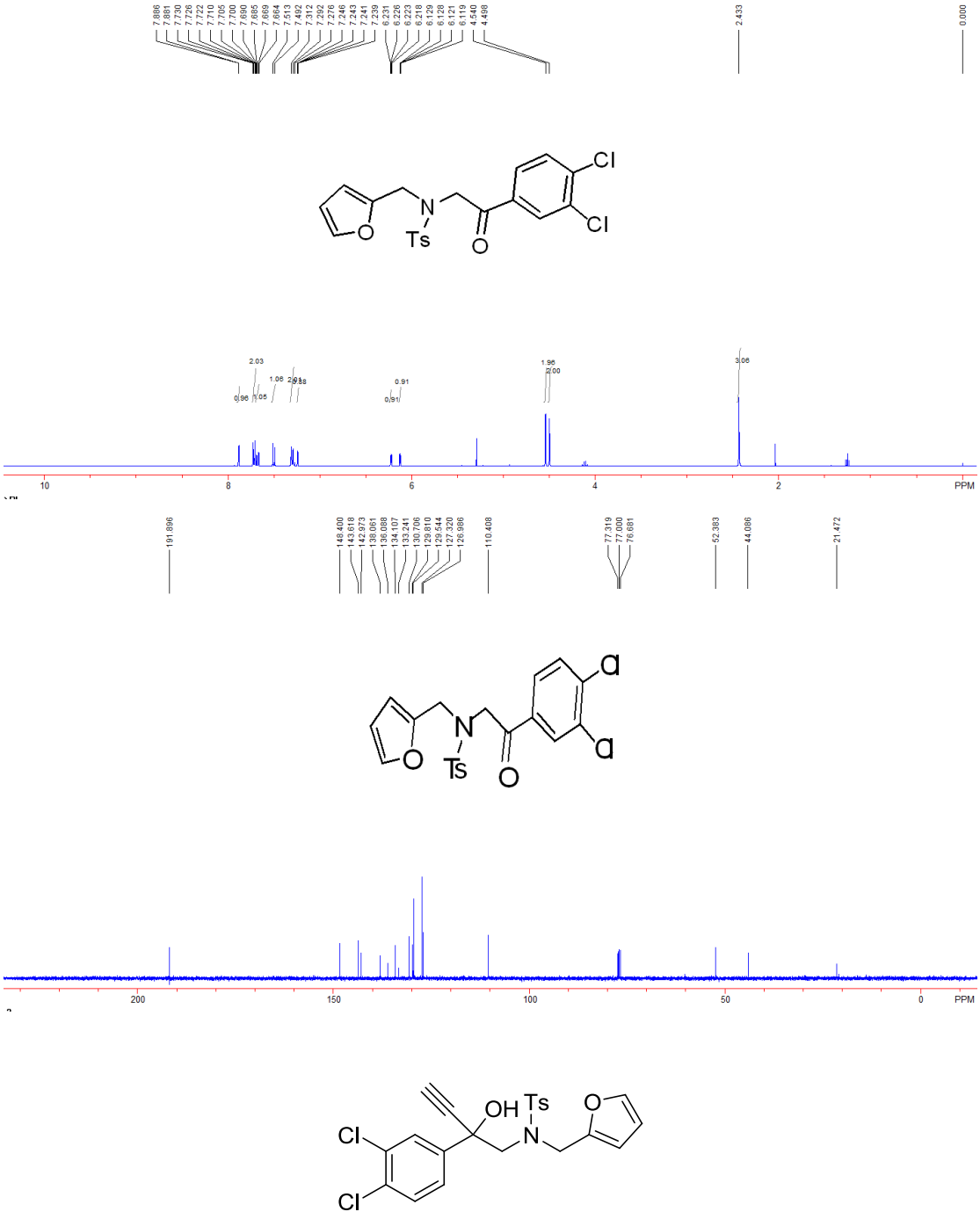


1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-(p-tolyl)but-3-yn-2-yl acetate (Table 2, entry 1g): a colorless oil (828 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.55 (d, 2H, *J* = 8.0 Hz, ArH), 7.45 (d, 2H, *J* = 7.6 Hz, ArH), 7.16-7.11 (m, 5H, ArH), 6.15 (s, 1H, ArH), 6.00 (s, 1H, ArH), 4.58 (d, 1H, *J* = 16.4 Hz, CH_2), 4.14 (d, 1H, *J* = 16.4 Hz, CH_2), 3.95 (d, 1H, *J* = 15.2 Hz, CH_2), 3.66 (d, 1H, *J* = 15.2 Hz, CH_2), 2.92 (s, 1H, CH), 2.31 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.03 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.7, 148.8, 142.6, 141.8, 137.7, 136.9, 135.0, 128.8, 128.7, 126.8, 125.0, 109.8, 109.5, 79.9, 77.9, 77.6, 55.8, 44.5, 21.1, 20.9, 20.5; IR (DCM) ν 3268, 2923, 1751, 1439, 1344, 1223, 1158, 1011, 815, 736 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1779.



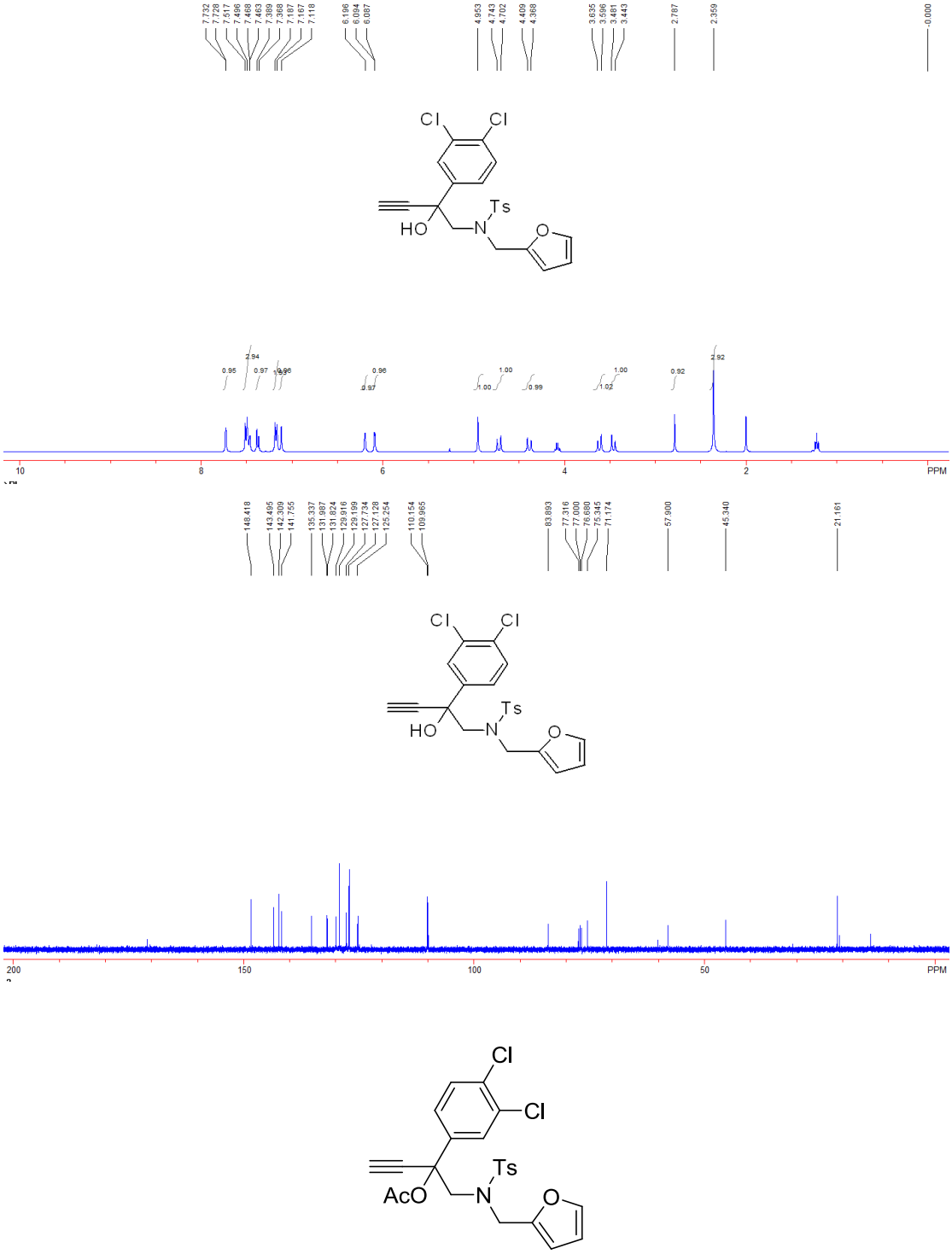
N-(2-(3,4-dichlorophenyl)-2-oxoethyl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-3h): a white solid (2.0 mg, 99% yield), mp: 182-184 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.88 (d, 1H, *J* = 2.0 Hz, ArH), 7.73-7.68 (m, 2H, ArH), 7.67 (d, 1H, *J* = 2.0 Hz, ArH), 7.50 (d, 1H, *J* = 8.0 Hz, ArH), 7.31-7.28 (m, 2H, ArH), 7.25-7.24 (m, 1H, ArH), 6.23-6.22 (m, 1H, ArH), 6.13-6.12 (m, 1H, ArH), 4.54 (s, 2H, CH_2), 4.50 (s, 2H, CH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 191.9, 148.4, 143.6, 143.0, 138.1, 136.1, 134.1, 133.2, 130.7, 129.8, 129.5, 127.3, 127.0, 110.4, 52.3, 44.1, 21.5; IR (DCM) ν 3057, 2923, 1704, 1336, 1212, 1157, 1092, 1031, 815, 721 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}Cl_2N_2O_4S$ $[M + NH_4]^+$ m/z 455.0594,

found 455.0595.



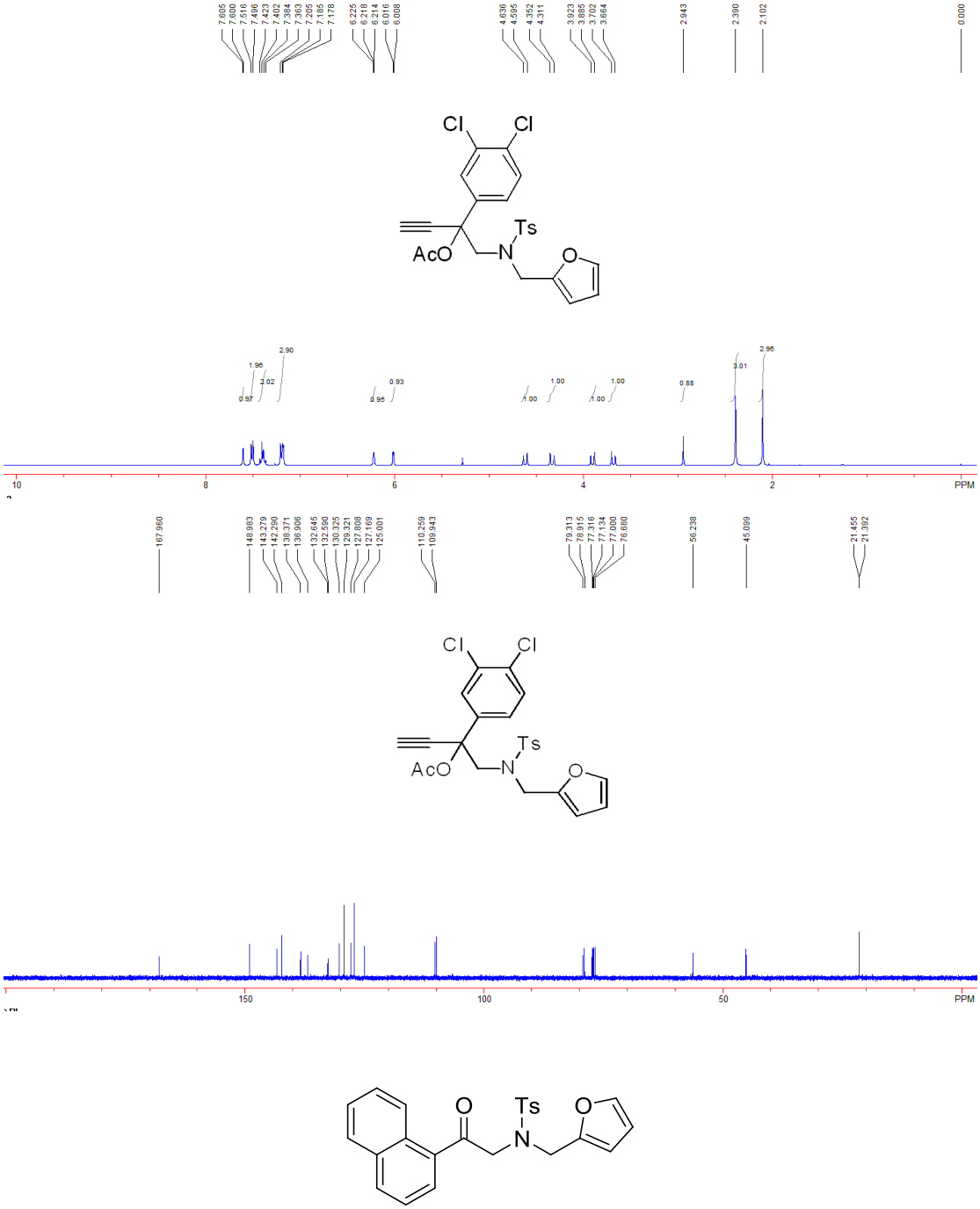
N-(2-(3,4-dichlorophenyl)-2-hydroxybut-3-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenes ulfonamide (S-4h): a colorless oil (956 mg, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.73 (d,1H, *J* = 1.6 Hz, ArH), 7.52-7.46 (m, 3H, ArH), 7.38 (d, 1H, *J* = 8.4 Hz, ArH), 7.18 (d, 2H, *J* = 8.0 Hz, ArH), 7.12 (s, 1H, ArH), 6.20 (s, 1H, ArH), 6.09 (d, 1H, *J* = 2.8 Hz, ArH), 4.95 (s, 1H, OH), 4.72 (d, 1H, *J* = 16.4 Hz, CH_2), 4.39 (d, 1H, *J* = 16.4 Hz, CH_2), 3.62 (d, 1H, *J* = 15.6 Hz, CH_2), 3.46 (d, 1H, *J* = 15.6 Hz, CH_2), 2.79 (s, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.4, 143.5, 142.3, 141.7, 135.3, 132.0, 131.8, 129.9, 129.2, 127.7, 127.1, 125.2,

110.1, 110.0, 83.9, 75.3, 71.2, 57.9, 45.3, 21.2; IR (DCM) ν 3447, 3293, 1597, 1467, 1330, 1152, 1008, 935, 814, 737 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}Cl_2N_2O_4S$ $[M + NH_4]^+$ m/z 481.0750, found 481.0754.



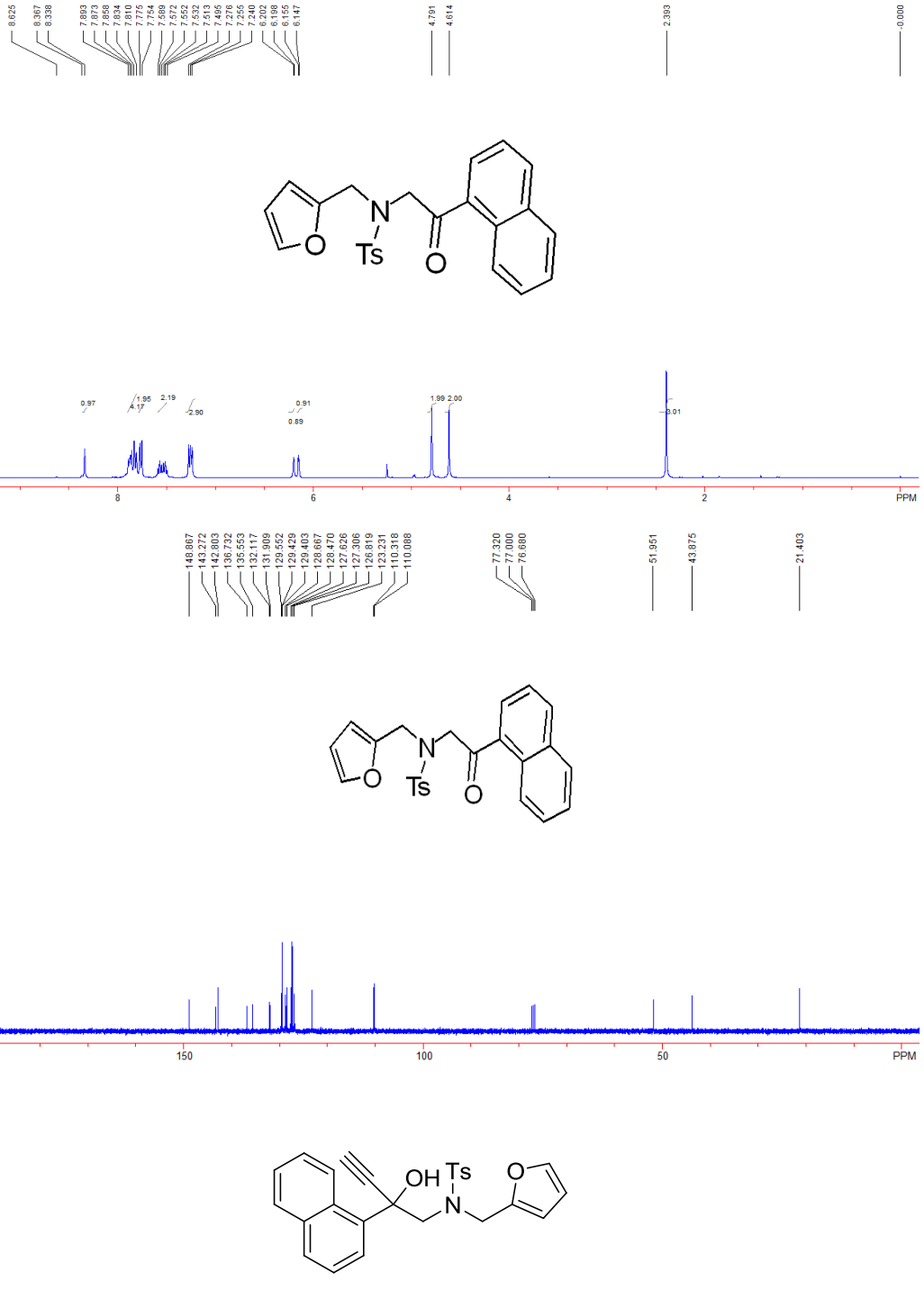
2-(3,4-dichlorophenyl)-1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)but-3-yn-2-yl acetate (Table 2, entry 1h): a colorless oil (902 mg, 87% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.60 (d, 1H, *J* = 2.0 Hz, ArH), 7.51 (d, 2H, *J* = 8.0 Hz, ArH), 7.42-7.36 (m, 2H, ArH), 7.20-7.18 (m, 3H, ArH), 6.22-6.21 (m, 1H, ArH), 6.01 (d, 1H, *J* = 3.2 Hz, ArH), 4.62 (d, 1H, *J* =

16.4 Hz, CH_2), 4.33 (d, 1H, *J* = 16.4 Hz, CH_2), 3.90 (d, 1H, *J* = 15.2 Hz, CH_2), 3.68 (d, 1H, *J* = 15.2 Hz, CH_2), 2.94 (s, 1H, CH), 2.39 (s, 3H, CH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.0, 149.0, 143.3, 142.3, 138.4, 136.9, 132.64, 132.59, 130.3, 129.3, 127.8, 127.2, 125.0, 110.2, 109.9, 79.3, 78.9, 77.1, 56.2, 45.1, 21.45, 21.39; IR (DCM) ν 3295, 2923, 1754, 1467, 1332, 1215, 1158, 1010, 814, 734 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}Cl_2N_2O_5S$ [M + NH_4]$^+$ m/z 523.0856, found 523.0855.

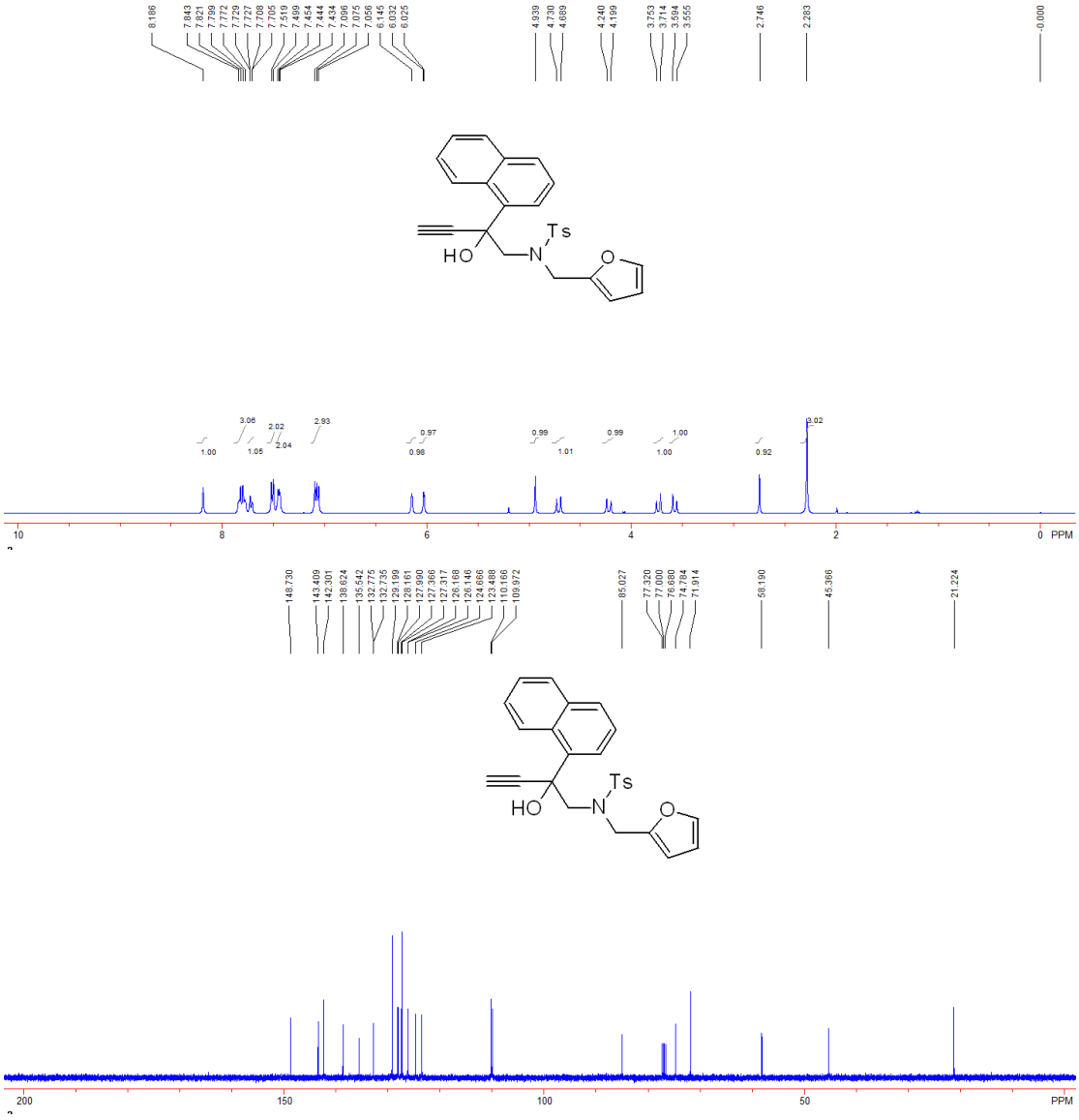


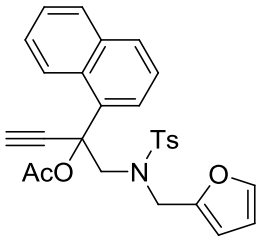
N-(furan-2-ylmethyl)-4-methyl-N-(2-(naphthalen-1-yl)-2-oxoethyl)benzenesulfonamide (S-3i): a white solid (1.9 g, 99% yield), mp: 125-127 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ

8.62 (s, 1H, ArH), 7.89-7.81 (m, 4H, ArH), 7.76 (d, 2H, *J* = 8.4 Hz, ArH), 7.59-7.49 (m, 2H, ArH), 7.27 (d, 2H, *J* = 8.4 Hz, ArH), 7.24 (s, 1H, ArH), 6.20 (d, 1H, *J* = 1.6 Hz, ArH), 6.15 (d, 1H, *J* = 3.2 Hz, ArH), 4.79 (s, 2H, CH_2), 4.61 (s, 2H, CH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.5, 148.9, 143.3, 142.8, 136.7, 135.5, 132.1, 131.9, 129.5, 129.43, 129.40, 128.7, 128.5, 127.6, 127.3, 126.8, 123.2, 110.3, 110.1, 51.9, 43.9, 21.4; IR (DCM) ν 3059, 2923, 1921, 1692, 1469, 1333, 1155, 1091, 812, 726 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{22}NO_4S$ [M + H]$^+$ m/z 420.1264, found 420.1269.

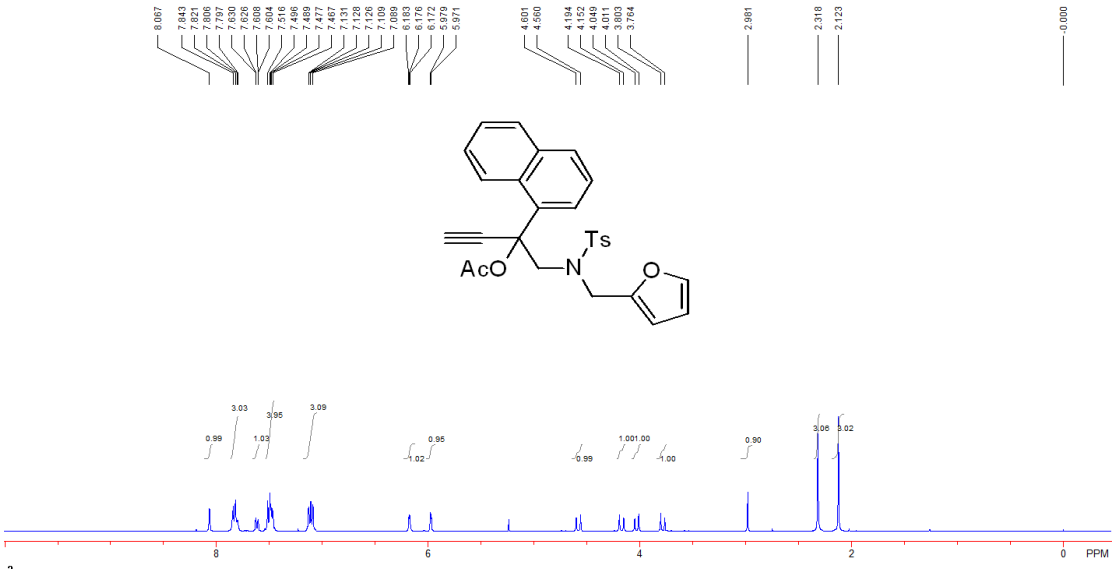


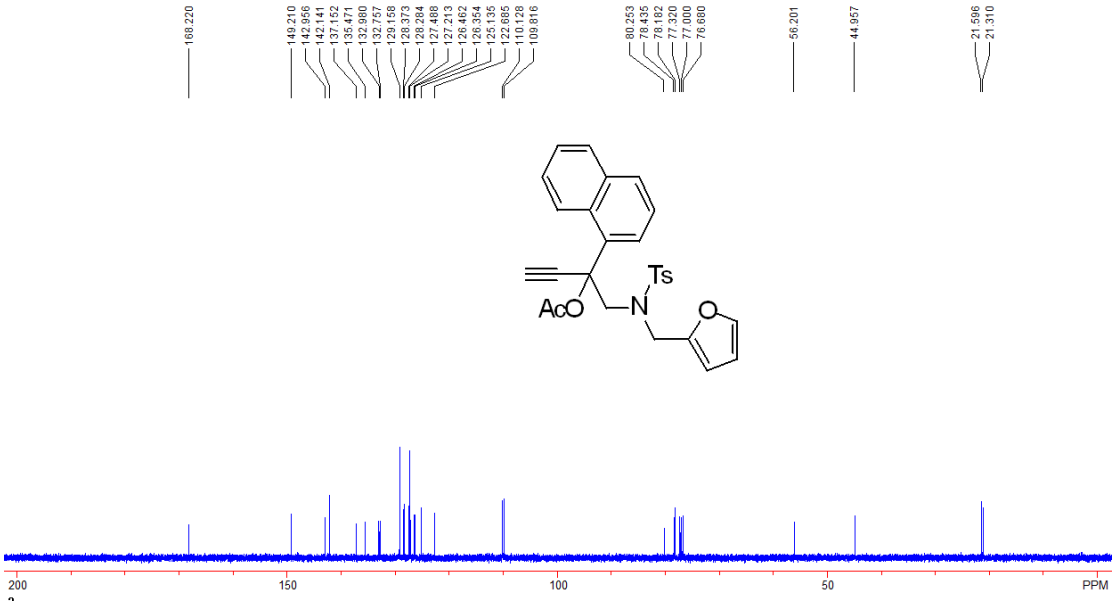
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-(naphthalen-1-yl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S-4i): a colorless oil (857 mg, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.19 (s, 1H, ArH), 7.84-7.77 (m, 3H, ArH), 7.72 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.8 Hz, ArH), 7.51 (d, 2H, J = 8.0 Hz, ArH), 7.45-7.43 (m, 2H, ArH), 7.09 (d, 2H, J = 8.4 Hz, ArH), 7.06 (s, 1H, ArH), 6.14 (s, 1H, ArH), 6.03 (d, 1H, J = 2.8 Hz, ArH), 4.94 (s, 1H, OH), 4.71 (d, 1H, J = 16.4 Hz, CH_2), 4.22 (d, 1H, J = 16.4 Hz, CH_2), 3.73 (d, 1H, J = 15.6 Hz, CH_2), 3.57 (d, 1H, J = 15.6 Hz, CH_2), 2.75 (s, 1H, CH), 2.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.7, 143.4, 142.3, 138.6, 135.5, 132.8, 129.2, 128.2, 128.0, 127.4, 127.3, 126.2, 126.1, 124.7, 123.5, 110.2, 110.0, 85.0, 74.8, 71.9, 58.2, 45.4, 21.2; IR (DCM) ν 3451, 3289, 3047, 1597, 1328, 1151, 1088, 1007, 815, 734 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{27}N_2O_4S$ $[M + NH_4]^+$ m/z 463.1686, found 463.1681.

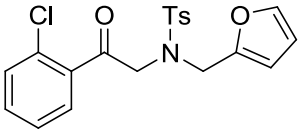




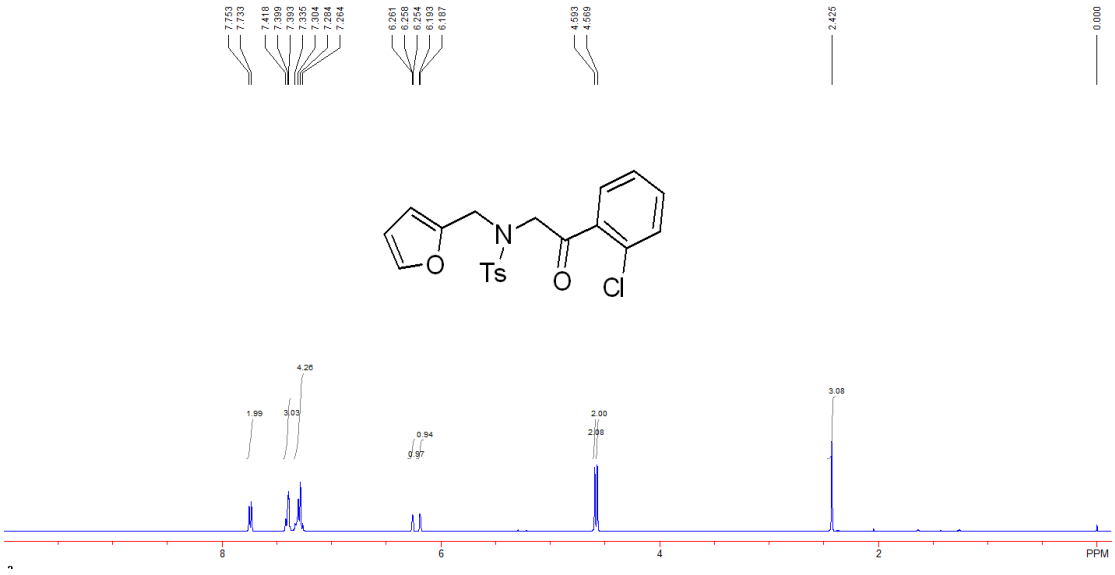
1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-(naphthalen-1-yl)but-3-yn-2-yl acetate (Table 2, entry 1i): a colorless oil (856mg, 91% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.07 (s, 1H, ArH), 7.84-7.80 (m, 3H, ArH), 7.62 (dd, 1H, J_1 = 8.8 Hz, J_2 = 1.6 Hz, ArH), 7.52-7.47 (m, 4H, ArH), 7.13-7.09 (m, 3H, ArH), 6.18-6.17 (m, 1H, ArH), 5.97 (d, 1H, J = 3.2 Hz, ArH), 4.58 (d, 1H, J = 16.4 Hz, CH_2), 4.17 (d, 1H, J = 16.4 Hz, CH_2), 4.03 (d, 1H, J = 15.2 Hz, CH_2), 3.78 (d, 1H, J = 15.2 Hz, CH_2), 2.98 (s, 1H, CH), 2.32 (s, 3H, CH_3), 2.12 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.2, 149.2, 142.9, 142.1, 137.1, 135.5, 133.0, 132.7, 129.1, 128.4, 128.3, 127.5, 127.2, 126.5, 126.3, 125.1, 122.7, 110.1, 109.8, 80.2, 78.4, 78.2, 56.2, 44.9, 21.6, 21.3; IR (DCM) ν 3285, 3057, 2117, 1751, 1332, 1224, 1157, 1011, 815, 735 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 505.1792, found 505.1789.

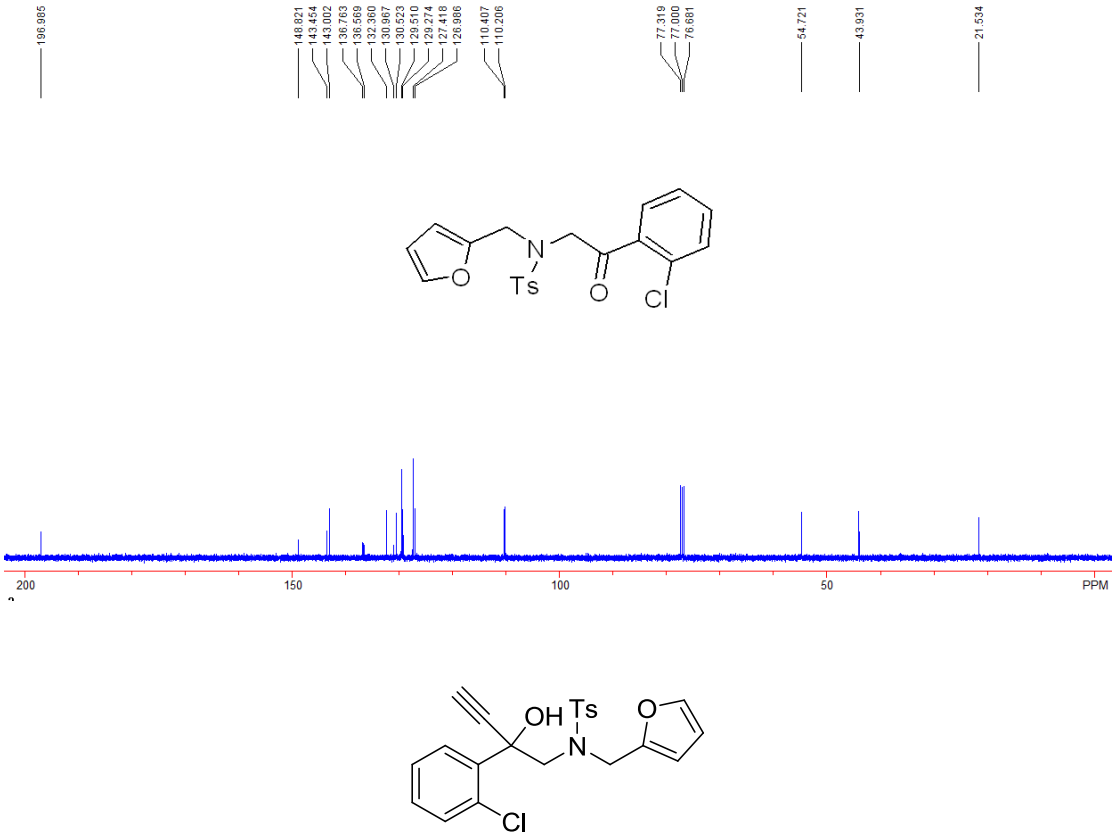




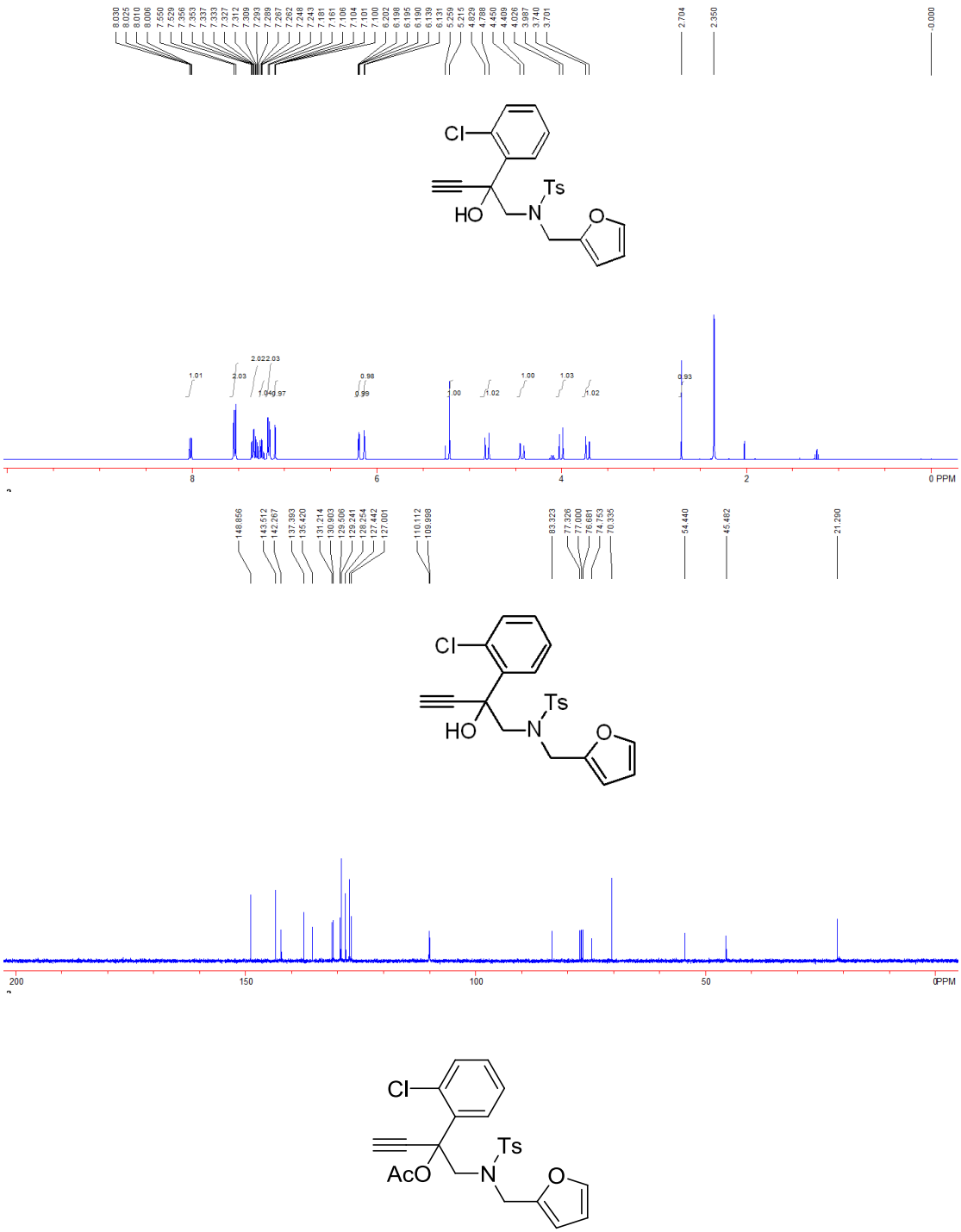


N-(2-(2-chlorophenyl)-2-oxoethyl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-3j): a colorless oil (1.9 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.74 (d, 2H, *J* = 8.0 Hz, ArH), 7.42-7.39 (m, 3H, ArH), 7.33-7.26 (m, 4H, ArH), 6.26-6.25 (m, 1H, ArH), 6.19 (d, 1H, *J* = 2.0 Hz, ArH), 4.59 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 197.0, 148.8, 143.4, 143.0, 136.8, 136.6, 132.4, 131.0, 130.5, 129.5, 129.3, 127.4, 127.0, 110.4, 110.2, 54.7, 43.9, 21.5; IR (DCM) ν 2923, 1712, 1590, 1335, 1156, 1092, 814, 754 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{19}NO_4S$ $[M + H]^+$ m/z 404.0718, found 404.0718.



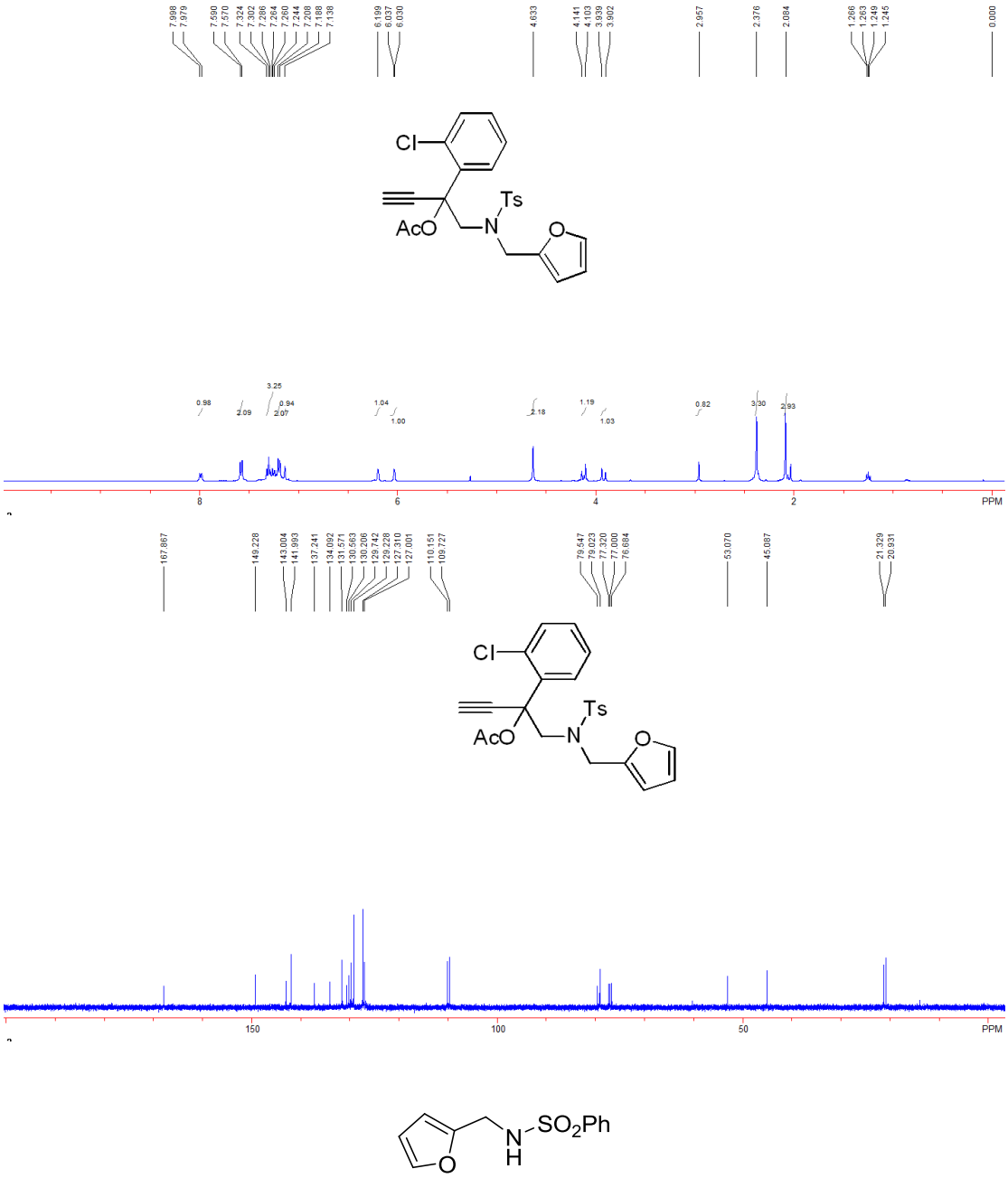


N-(2-(2-chlorophenyl)-2-hydroxybut-3-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-4j): a colorless oil (265 mg, 23% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.02 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz, ArH), 7.54 (d, 2H, J = 8.4 Hz, ArH), 7.36-7.29 (m, 2H, ArH), 7.25 (dd, 1H, J_1 = 8.0 Hz, J_2 = 2.0 Hz, ArH), 7.17 (d, 2H, J = 8.4 Hz, ArH), 7.11-7.10 (m, 1H, ArH), 6.20 (dd, 1H, J_1 = 2.8 Hz, J_2 = 2.0 Hz, ArH), 6.13 (d, 1H, J = 2.8 Hz, ArH), 5.21 (s, 1H, OH), 4.81 (d, 1H, J = 16.4 Hz, CH_2), 4.43 (d, 1H, J = 16.4 Hz, CH_2), 4.01 (d, 1H, J = 15.6 Hz, CH_2), 3.72 (d, 1H, J = 15.6 Hz, CH_2), 2.70 (s, 1H, CH), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.8, 143.5, 142.3, 137.4, 135.4, 131.2, 130.9, 129.5, 129.2, 128.2, 127.4, 127.0, 110.1, 110.0, 83.3, 74.7, 70.3, 54.4, 45.5, 21.3; IR (DCM) ν 3437, 3293, 1603, 1330, 1151, 1007, 930, 734 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}ClN_2O_4S$ $[M + NH_4]^+$ m/z 447.1140, found 447.1160.

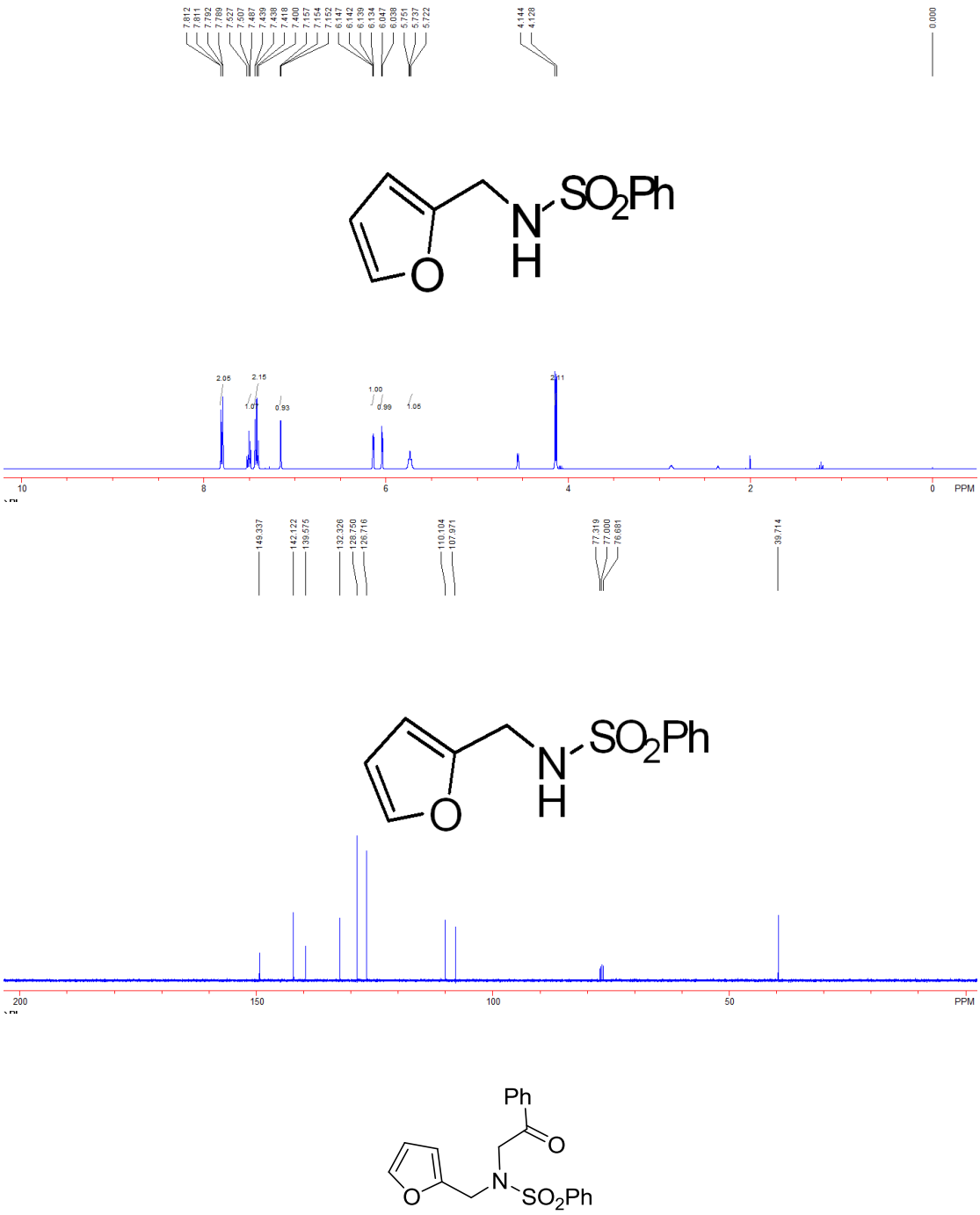


2-(2-chlorophenyl)-1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)but-3-yn-2-yl acetate (Table 2, entry 1j): a colorless oil (287 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.99 (d, 1H, *J* = 8.0 Hz, ArH), 7.58 (d, 2H, *J* = 8.0 Hz, ArH), 7.32-7.24 (m, 3H, ArH), 7.20 (d, 2H, *J* = 8.0 Hz, ArH), 7.14 (s, 1H, ArH), 6.20 (s, 1H, ArH), 6.03 (d, 1H, *J* = 2.8 Hz, ArH), 4.63 (s, 2H, CH_2), 4.12 (d, 1H, *J* = 15.2 Hz, CH_2), 3.92 (d, 1H, *J* = 15.2 Hz, CH_2), 2.96 (s, 1H, CH), 2.38 (s, 3H, CH_3), 2.09 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.9, 149.2, 143.0, 142.0, 137.2, 134.0, 131.6, 130.6, 130.2, 129.7, 129.2, 127.3, 127.0, 110.1, 109.7, 79.5,

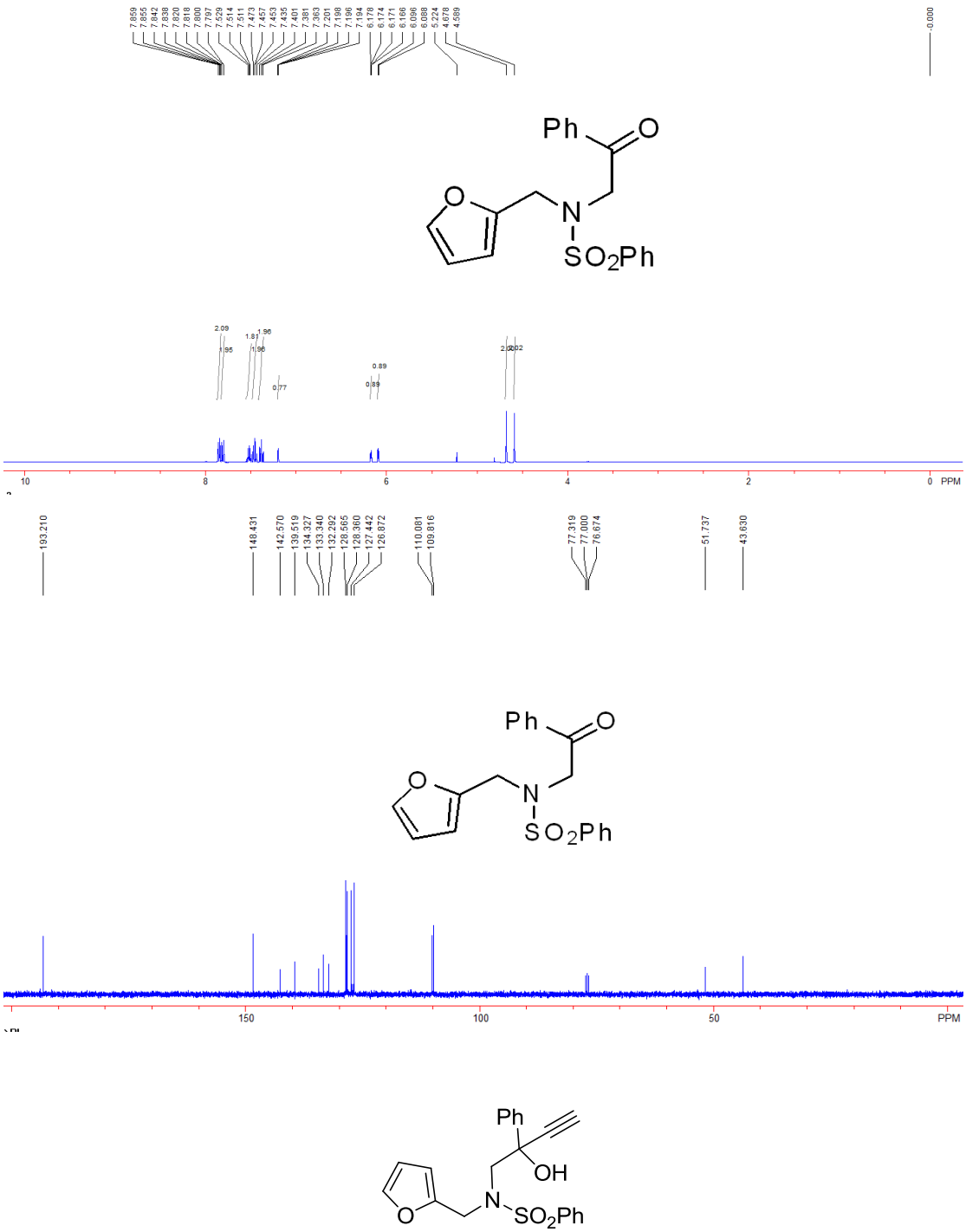
79.0, 53.1, 45.1, 21.3, 20.9; IR (DCM) ν 3285, 2925, 1754, 1596, 1370, 1173, 1161, 1062, 757 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}ClN_2O_5S$ $[M + NH_4]^+$ m/z 489.1245, found 489.1237.



N-(furan-2-ylmethyl)benzenesulfonamide (S-2k): a white solid (2.6 g, 75% yield), mp: 149-151 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.81-7.79 (m, 2H, ArH), 7.51 (t, 1H, *J* = 8.0 Hz, ArH), 7.44-7.40 (m, 2H, ArH), 7.16-7.15 (m, 1H, ArH), 6.15-6.13 (m, 1H, ArH), 6.04 (d, 1H, *J* = 3.6 Hz, ArH), 5.74 (t, 1H, *J* = 6.4 Hz, NH), 4.14 (d, 2H, *J* = 6.4 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.3, 142.1, 139.6, 132.3, 128.7, 126.7, 110.1, 108.0, 39.7; IR (DCM) ν 3278, 1447, 1321, 1154, 1092, 1054, 1013, 922, 827, 733 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{15}N_2O_3S$ $[M + NH_4]^+$ m/z 255.0798, found 255.0802.

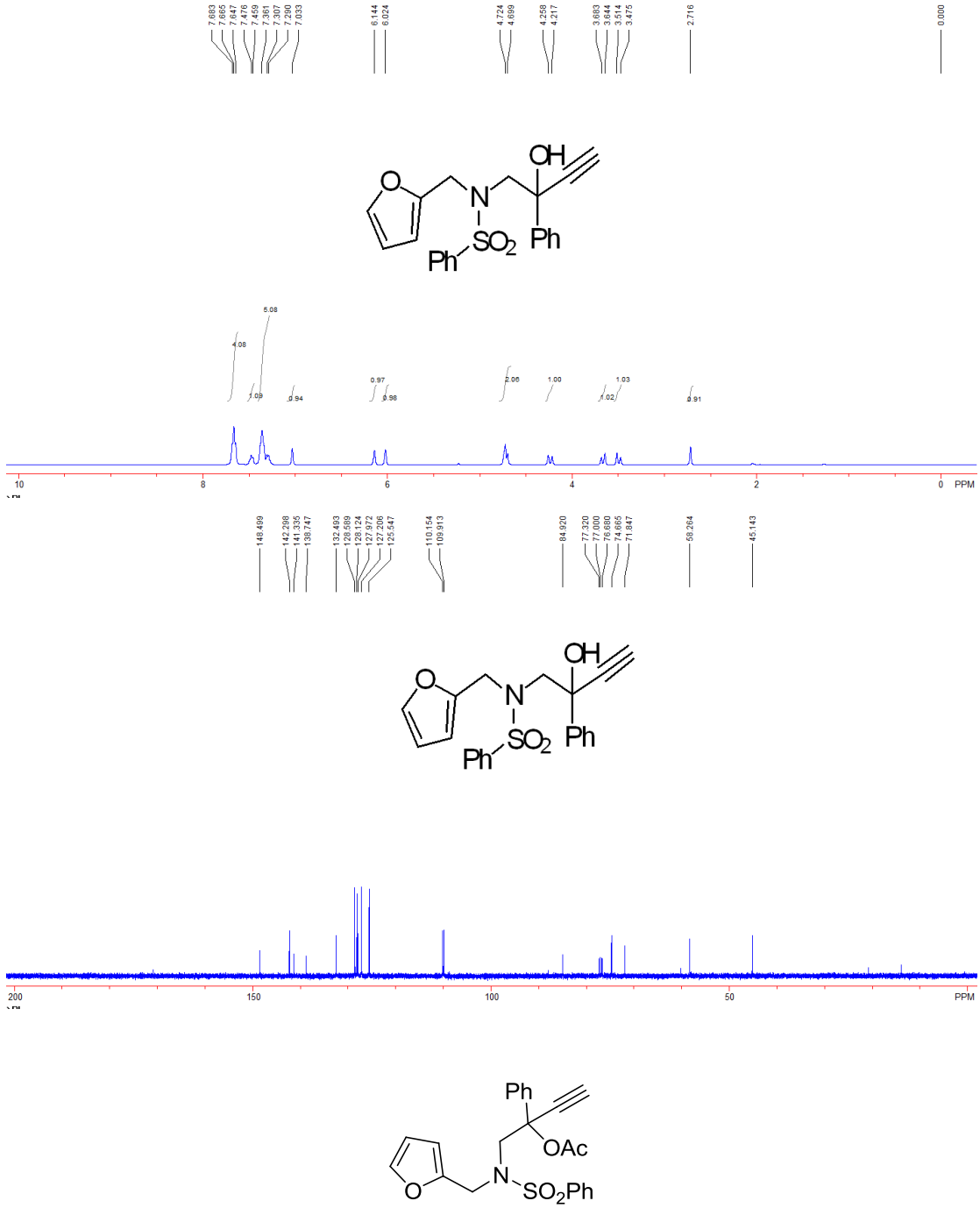


N-(furan-2-ylmethyl)-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3k): a colorless oil (2.9 mg, 86% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.85 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.6 Hz, ArH), 7.81 (dd, 2H, J_1 = 8.0 Hz, J_2 = 0.8 Hz, ArH), 7.53-7.51 (m, 2H, ArH), 7.47-7.43 (m, 2H, ArH), 7.38 (t, 2H, J = 8.0 Hz, ArH), 7.20-7.19 (m, 1H, ArH), 6.17 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 6.09 (d, 1H, J = 3.2 Hz, ArH), 4.68 (s, 2H, CH_2), 4.59 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.2, 148.4, 142.6, 139.5, 134.3, 133.3, 132.3, 128.6, 128.4, 127.4, 126.9, 110.1, 109.8, 51.7, 43.6; IR (DCM) ν 3061, 1698, 1447, 1332, 1156, 1092, 732 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{21}N_2O_4S$ $[M + NH_4]^+$ m/z 373.1217, found 373.1220.



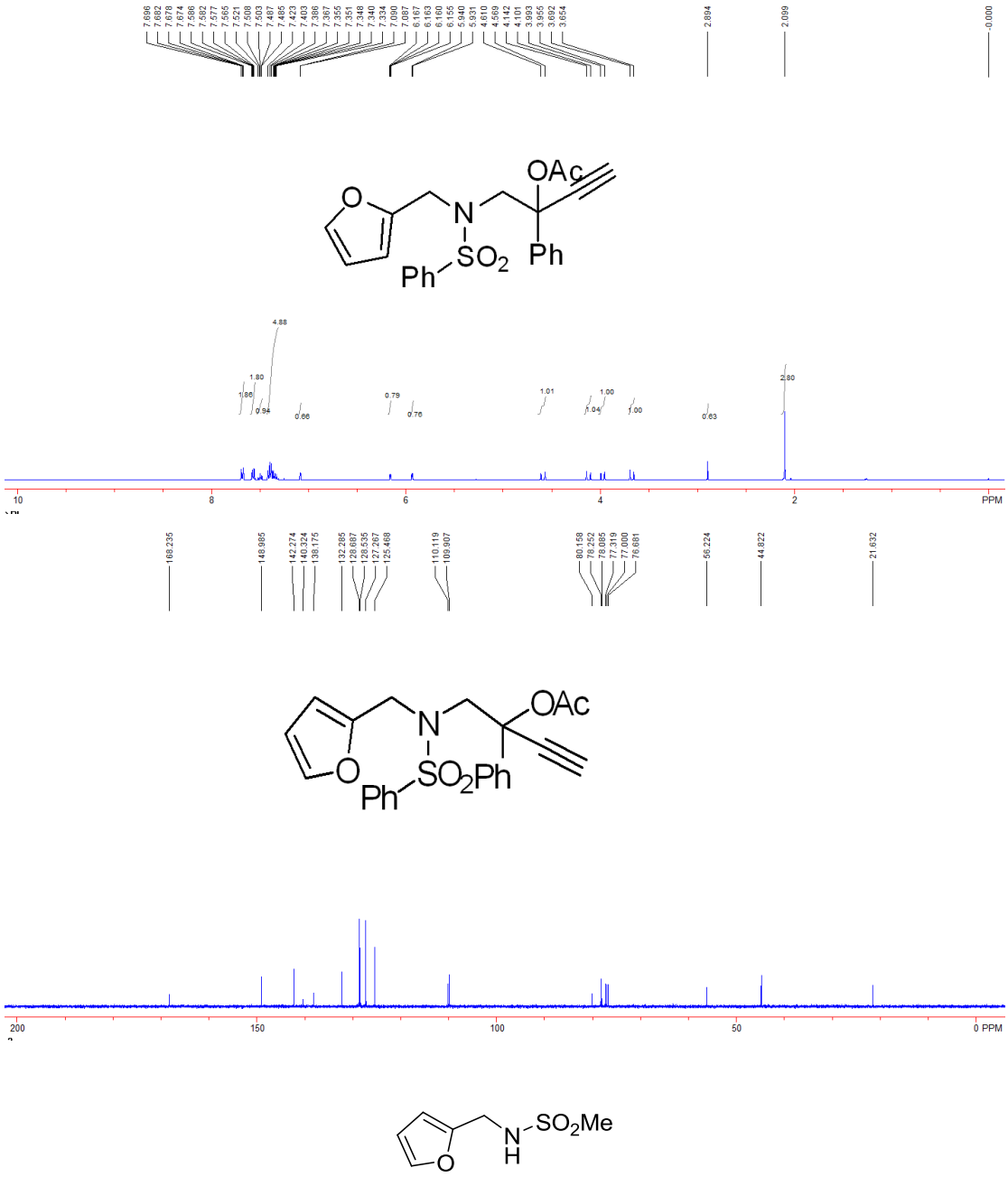
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)benzenesulfonamide (S-4k): a colorless oil (541 mg, 45% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.68-7.65 (m, 4H, ArH), 7.48-7.46 (m, 1H, ArH), 7.36-7.29 (m, 5H, ArH), 7.03 (s, 1H, ArH), 6.14 (s, 1H, ArH), 6.02 (s, 1H, ArH), 4.72-4.70 (m, 2H, OH and CH_2), 4.24 (d, 1H, *J* = 16.4 Hz, CH_2), 3.66 (d, 1H, *J* = 15.6 Hz, CH_2), 3.49 (d, 1H, *J* = 15.6 Hz, CH_2), 2.72 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.5, 142.3, 141.3, 138.7, 132.5, 128.6, 128.1, 128.0, 127.2, 125.5, 110.1, 109.9, 84.9, 74.7, 71.8, 58.3, 45.1; IR (DCM) ν 3458, 3288, 1447, 1327, 1151, 1007, 932, 734 cm^{-1}; HRMS (ESI)

calcd for $C_{21}H_{23}N_2O_4S$ $[M + NH_4]^+$ m/z 399.1373, found 399.1362.

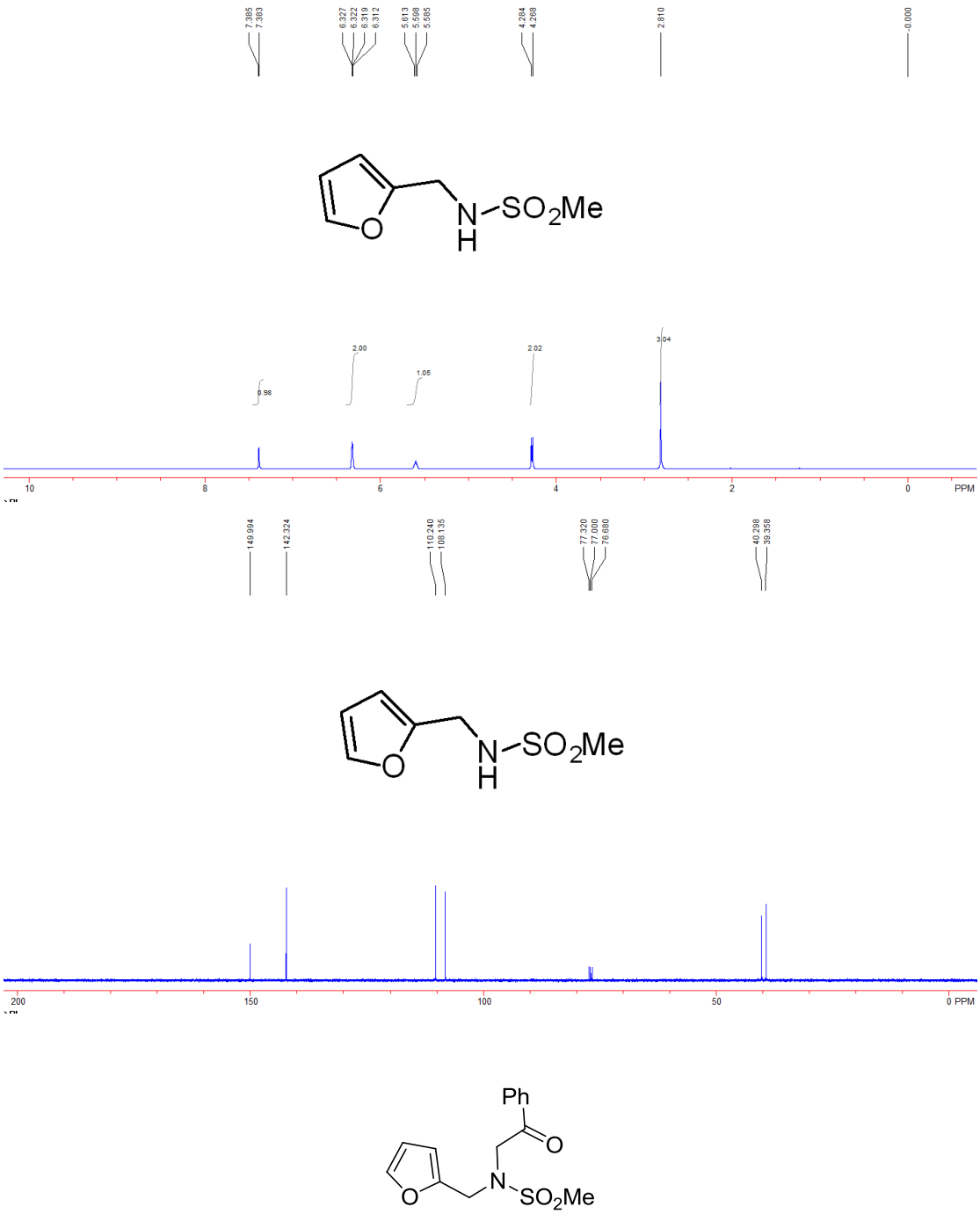


1-(N-(furan-2-ylmethyl)phenylsulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 1k): a colorless oil (549 mg, 65% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.68 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.6 Hz, ArH), 7.59-7.56 (m, 2H, ArH), 7.52-7.50 (m, 1H, ArH), 7.49-7.33 (m, 5H, ArH), 7.09 (d, 1H, J = 1.2 Hz, ArH), 6.16 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.93 (d, 1H, J = 3.6 Hz, ArH), 4.59 (d, 1H, J = 16.4 Hz, CH_2), 4.12 (d, 1H, J = 16.4 Hz, CH_2), 3.97 (d, 1H, J = 15.2 Hz, CH_2), 3.67 (d, 1H, J = 15.2 Hz, CH_2), 2.89 (s, 1H, CH), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.2, 149.0, 142.3, 140.3, 138.2, 132.3, 128.7, 128.5, 127.3, 125.5,

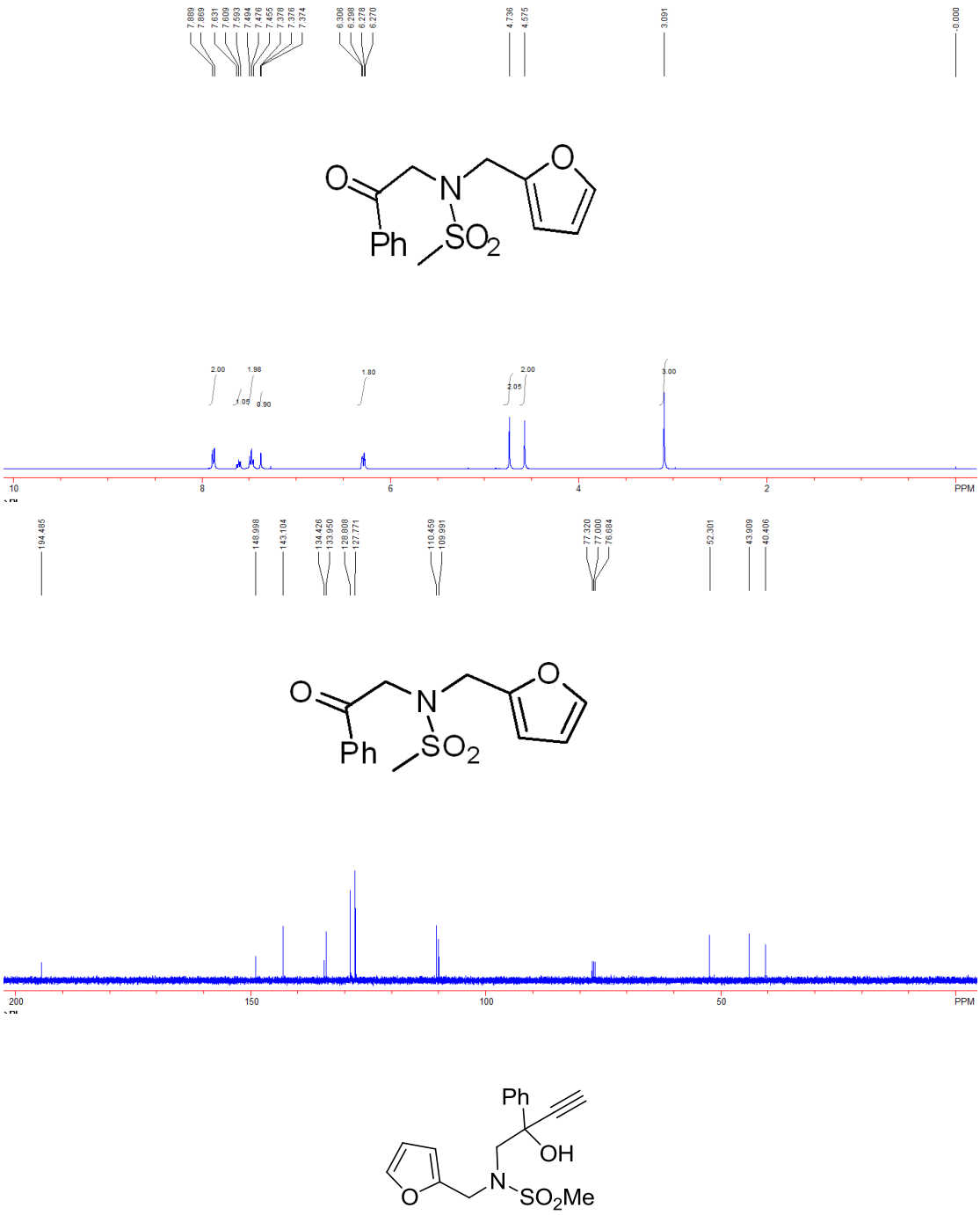
110.1, 109.9, 80.1, 78.2, 78.1, 56.2, 44.8, 21.6; IR (DCM) ν 3273, 1751, 1448, 1331, 1223, 1157, 1011, 735, 698 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_5S$ $[M + NH_4]^+$ m/z 441.1479, found 441.1470.



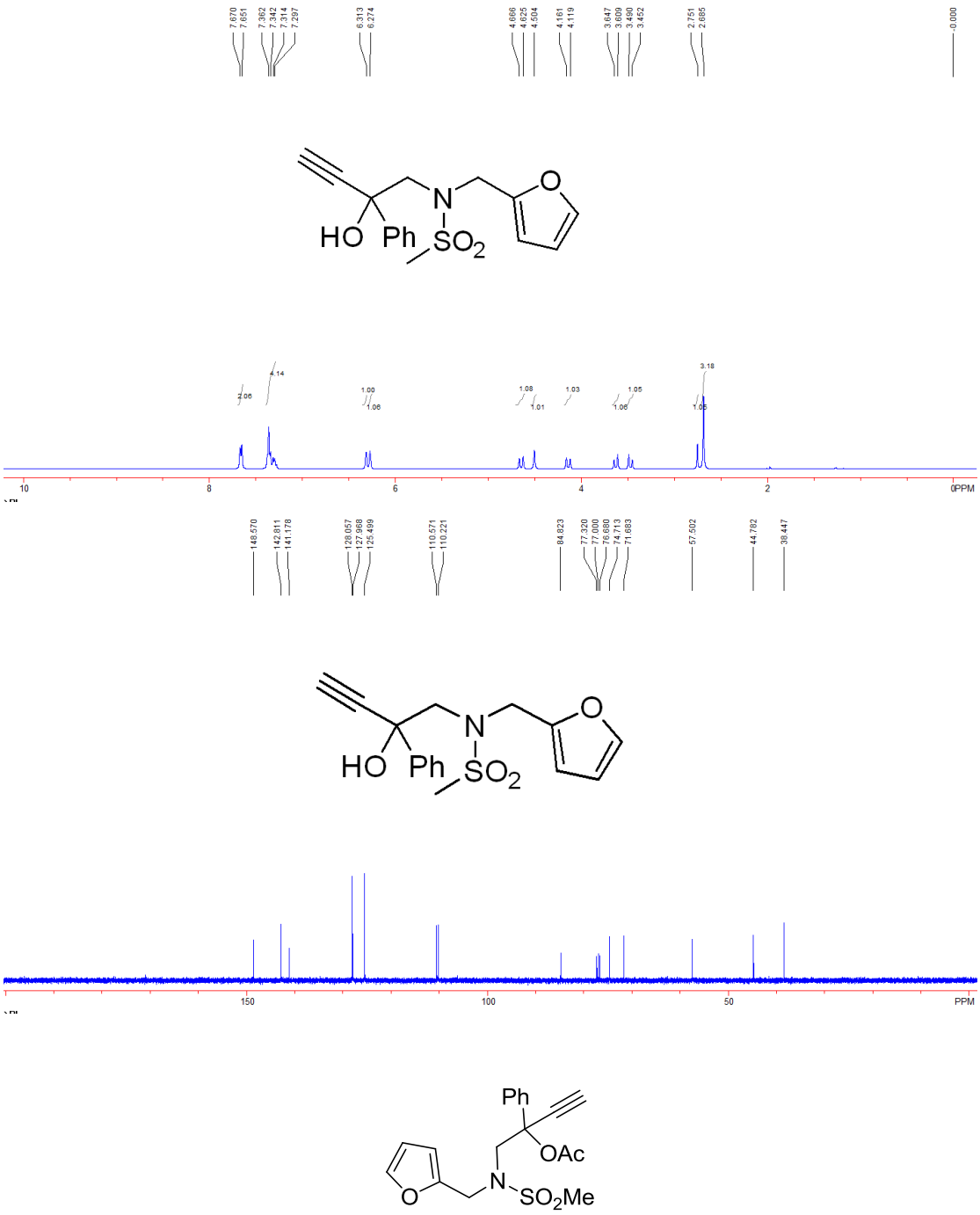
N-(furan-2-ylmethyl)methanesulfonamide (S-2l): known compound,[3] a white solid (4.8 g, 75% yield), mp: 84-86 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.38 (d, 1H, *J* = 0.8 Hz, ArH), 6.33-6.31 (m, 2H, ArH), 5.60 (t, 1H, *J* = 6.4 Hz, NH), 4.27 (d, 2H, *J* = 6.4 Hz, CH_2), 2.81 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 150.0, 142.3, 110.2, 108.1, 40.3, 39.3.



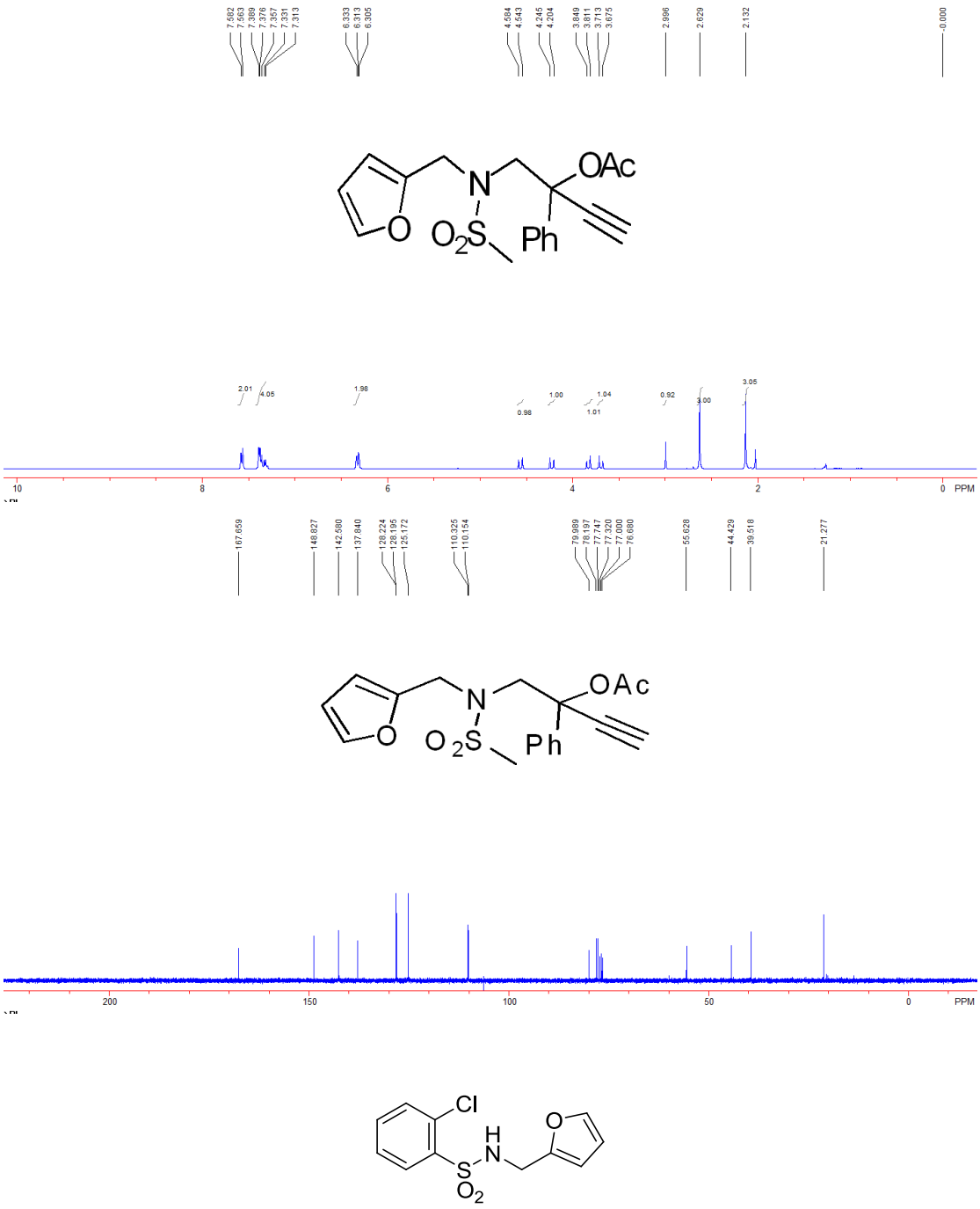
N-(furan-2-ylmethyl)-N-(2-oxo-2-phenylethyl)methanesulfonamide (S-3l): a white solid (3.4 g, 99% yield), mp: 113-115 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.88 (d, 2H, *J* = 8.0 Hz, ArH), 7.63-7.59 (m, 1H, ArH), 7.49-7.45 (m, 2H, ArH), 7.38 (t, 1H, *J* = 0.8 Hz, ArH), 6.31-6.27 (m, 2H, ArH), 4.74 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 3.09 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 194.5, 149.0, 143.1, 134.4, 133.9, 128.8, 127.7, 110.4, 110.0, 52.3, 43.9, 40.4; IR (DCM) ν 3364, 1697, 1325, 1224, 1144, 754, 734, 688 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_4S$ $[M + NH_4]^+$ m/z 311.1060, found 311.1060.



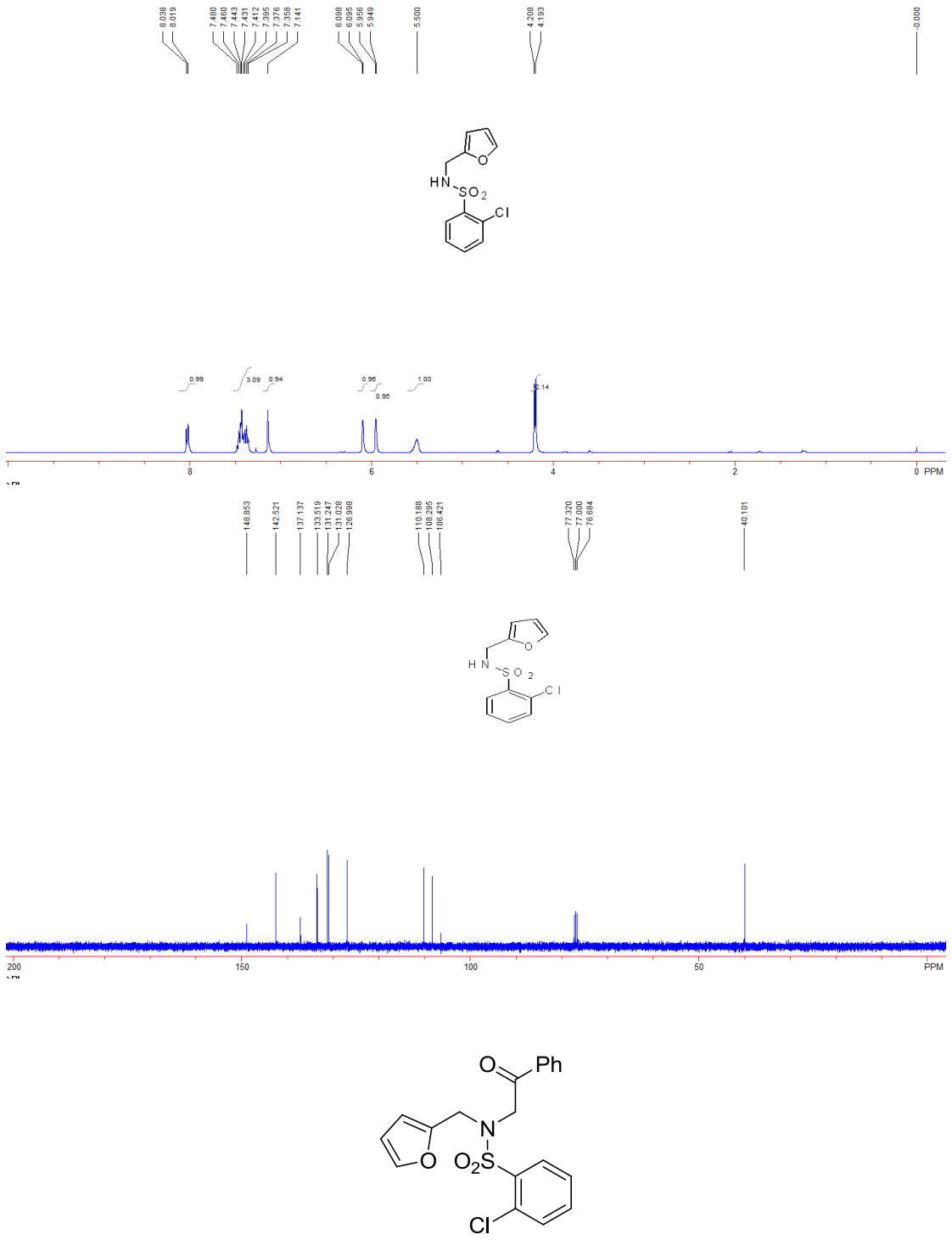
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)methanesulfonamide (S-4l): a colorless oil (286 mg, 42% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 2H, *J* = 7.6 Hz, ArH), 7.36-7.30 (m, 4H, ArH), 6.31 (s, 1H, ArH), 6.27 (s, 1H, ArH), 4.64 (d, 1H, *J* = 16.4 Hz, CH_2), 4.50 (s, 1H, OH), 4.14 (d, 1H, *J* = 16.4 Hz, CH_2), 3.63 (d, 1H, *J* = 15.2 Hz, CH_2), 3.47 (d, 1H, *J* = 15.2 Hz, CH_2), 2.75 (s, 1H, CH), 2.68 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.6, 142.8, 141.2, 128.06, 127.97, 125.5, 110.6, 110.2, 84.8, 74.7, 71.7, 57.5, 44.8, 38.4; IR (DCM) ν 3454, 3284, 1448, 1321, 1142, 1008, 966, 932, 750 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{21}N_2O_4S$ $[M + NH_4]^+$ m/z 337.1217, found 337.1219.



1-(N-(furan-2-ylmethyl)methylsulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 1l): a colorless oil (237 mg, 84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 7.6 Hz, ArH), 7.39-7.31 (m, 4H, ArH), 6.33-6.30 (m, 2H, ArH), 4.56 (d, 1H, *J* = 16.4 Hz, CH_2), 4.22 (d, 1H, *J* = 16.4 Hz, CH_2), 3.83 (d, 1H, *J* = 15.2 Hz, CH_2), 3.69 (d, 1H, *J* = 15.2 Hz, CH_2), 3.00 (s, 1H, CH), 2.63 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.6, 148.8, 142.6, 137.8, 128.22, 128.19, 125.2, 110.3, 110.1, 80.0, 78.2, 77.7, 55.6, 44.4, 39.5, 21.3; IR (DCM) ν 3270, 2931, 1751, 1326, 1220, 1145, 1005, 734, 698 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_5S$ $[M + NH_4]^+$ m/z 379.1322, found 379.1324.

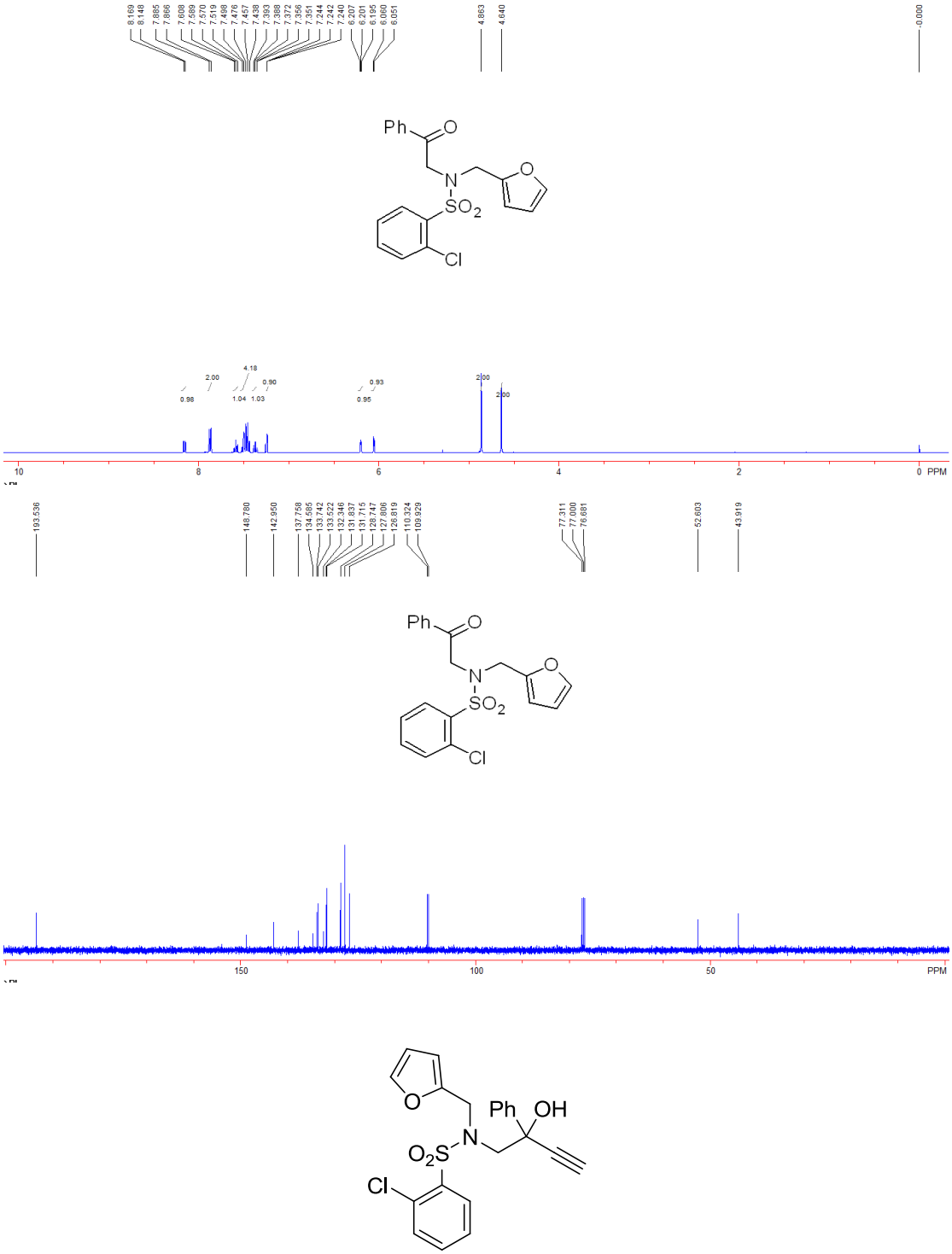


2-chloro-N-(furan-2-ylmethyl)benzenesulfonamide (S-2m): a white solid (7.1 g, 76% yield), mp: 184-186 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.03 (d, 2H, *J* = 7.6 Hz, ArH), 7.48-7.36 (m, 3H, ArH), 7.14 (s, 1H, ArH), 6.10 (d, 1H, *J* = 1.2 Hz, ArH), 5.95 (d, 1H, *J* = 2.8 Hz, ArH), 5.50 (s, 1H, NH), 4.20 (d, 2H, *J* = 6.0 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.8, 142.5, 137.1, 133.5, 131.2, 131.0, 127.0, 110.2, 108.3, 106.4, 40.1; IR (DCM) ν 3317, 1579, 1429, 1330, 1159, 1042, 744 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{14}ClN_2O_3S$ $[M + NH_4]^+$ m/z 289.0408, found 289.0413.



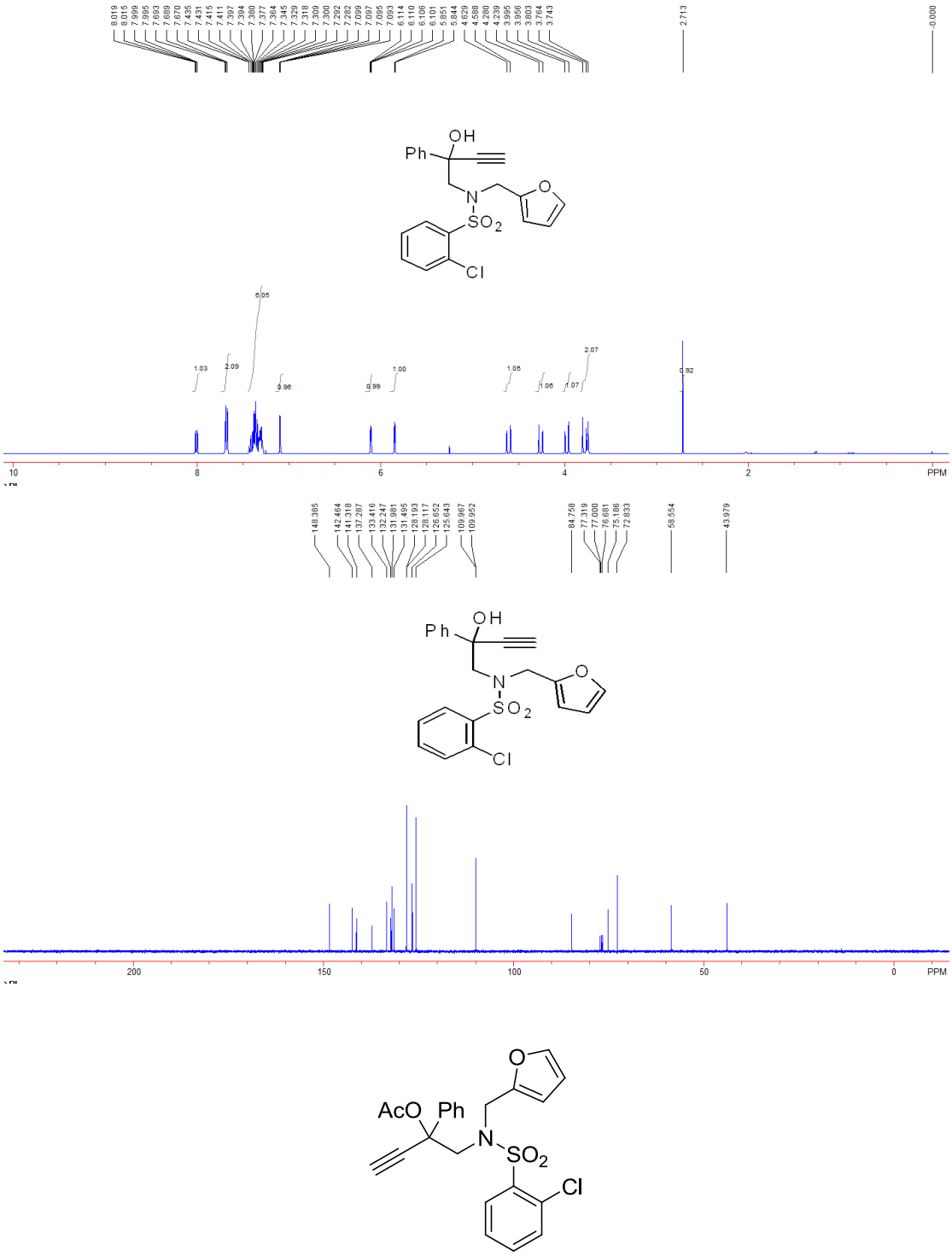
2-chloro-N-(furan-2-ylmethyl)-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3m): a colorless oil (3.2 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.12 (d, 1H, *J* = 4.8 Hz, ArH), 7.87 (d, 2H, *J* = 7.6 Hz, ArH), 7.59 (t, 1H, *J* = 7.6 Hz, ArH), 7.52-7.44 (m, 4H, ArH), 7.39-7.35 (m, 1H, ArH), 7.24 (t, 1H, *J* = 0.8 Hz, ArH), 6.20 (t, 1H, *J* = 2.4 Hz, ArH), 6.05 (d, 1H, *J* = 3.6 Hz, ArH), 4.86 (s, 2H, CH_2), 4.64 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.5, 148.8, 142.9, 137.7, 134.6, 133.7, 133.5, 132.3, 131.8, 131.7, 128.7, 127.8, 126.8, 110.3, 109.9, 52.6, 49.9; IR (DCM) ν 2927, 1698, 1450, 1338, 1156, 1059, 911, 752, 688 cm^{-1}; HRMS

(ESI) calcd for $C_{19}H_{20}ClN_2O_4S$ $[M + NH_4]^+$ m/z 407.0827, found 407.0830.



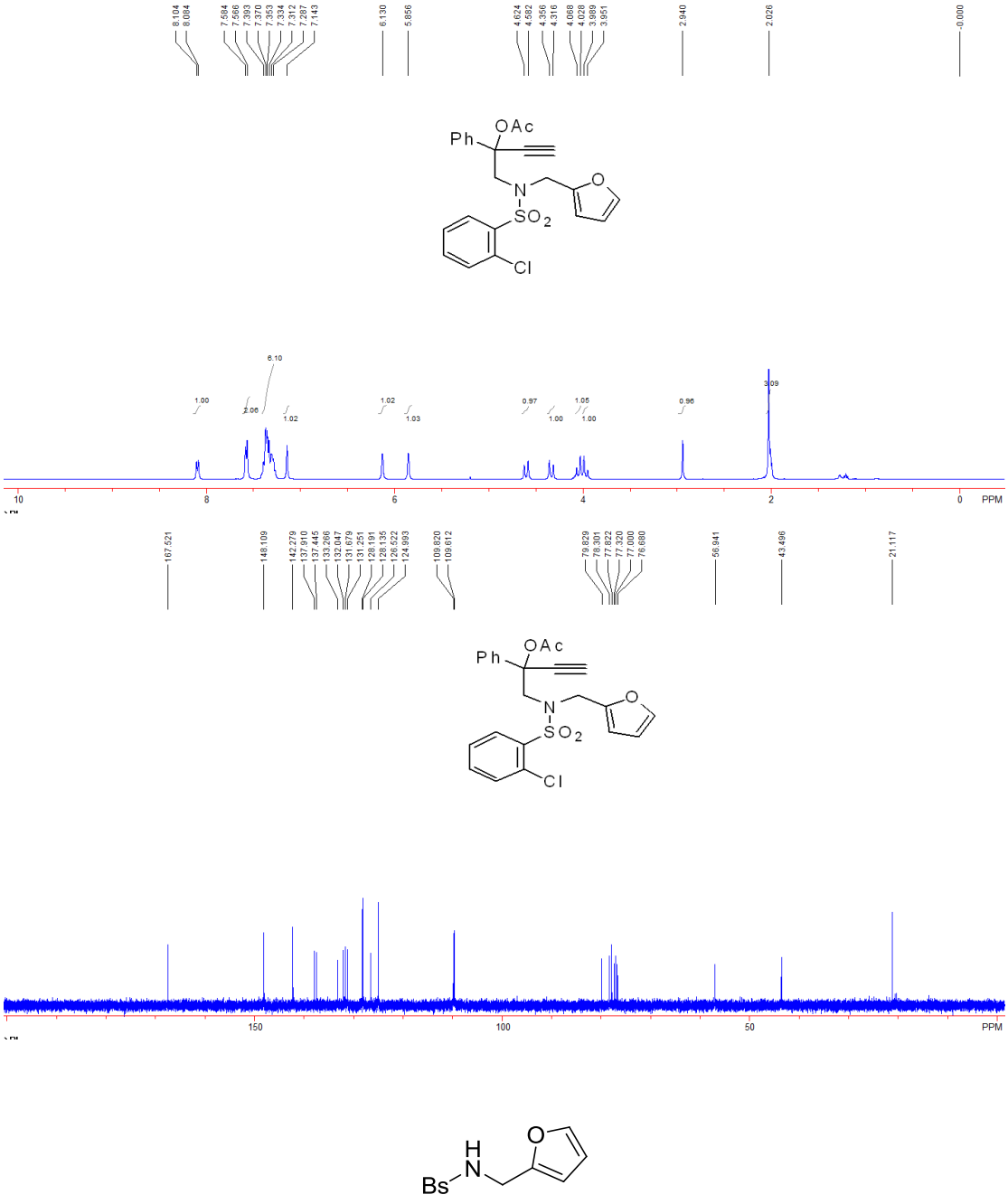
2-chloro-N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)benzenesulfonamide (S-4m): a white solid (1.1 g, 64% yield), mp: 131-133 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.01 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.6 Hz, ArH), 7.69-7.67 (m, 2H, ArH), 7.43-7.28 (m, 6H, ArH), 7.10-7.09 (m, 1H, ArH), 6.11 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 5.85 (d, 1H, J = 2.8 Hz, ArH), 4.61 (d, 1H, J = 16.4 Hz, CH_2), 4.26 (d, 1H, J = 16.4 Hz, CH_2), 3.97 (d, 1H, J = 15.6 Hz, CH_2), 3.80-3.74 (m, 2H, OH and CH_2), 2.71 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ

148.4, 142.5, 141.3, 137.3, 133.4, 132.2, 132.0, 131.5, 128.2, 128.1, 126.6, 125.6, 109.97, 109.95, 84.7, 75.2, 72.8, 58.5, 44.0; IR (DCM) ν 3483, 3290, 1453, 1330, 1155, 1041, 1007, 934, 754 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}ClN_2O_4S$ $[M + NH_4]^+$ m/z 433.0983, found 433.0985.



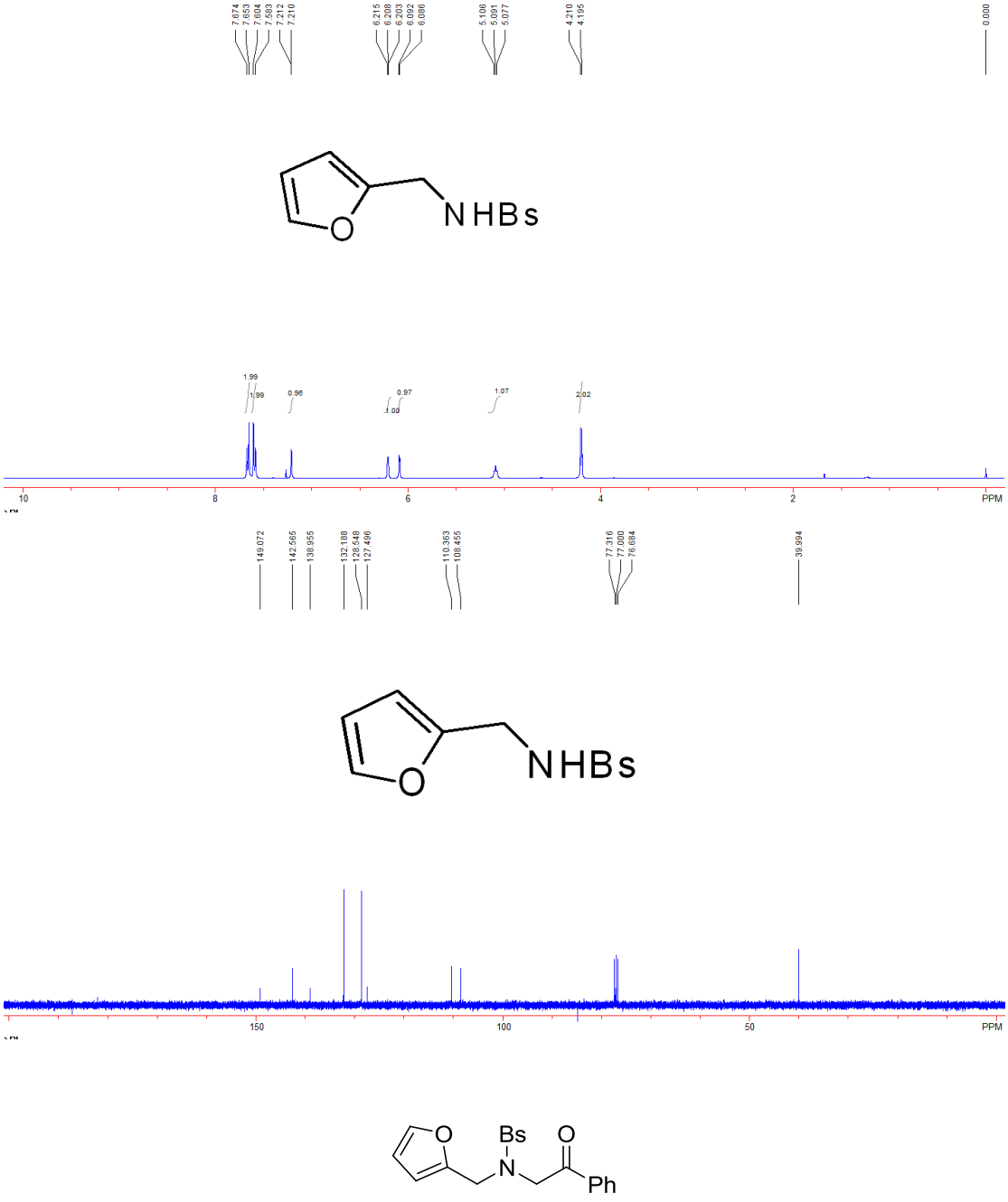
1-((2-chloro-N-(furan-2-ylmethyl)phenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 1m): a white solid (846 mg, 74% yield), mp: 149-151 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.09 (d, 1H, *J* = 8.0 Hz, ArH), 7.57 (d, 2H, *J* = 7.2 Hz, ArH), 7.39-7.29 (m, 6H, ArH), 7.14 (s, 1H, ArH), 6.13 (s, 1H, ArH), 5.86 (s, 1H, ArH), 4.60 (d, 1H, *J* = 16.8 Hz, CH_2), 4.34 (d,

1H, J = 16.8 Hz, CH_2), 4.05 (d, 1H, J = 15.2 Hz, CH_2), 3.97 (d, 1H, J = 15.2 Hz, CH_2), 2.94 (s, 1H, CH), 2.03 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.5, 148.1, 142.3, 137.9, 137.4, 133.3, 132.0, 131.7, 131.2, 128.2, 128.1, 126.5, 125.0, 109.8, 109.6, 79.8, 78.3, 77.8, 56.9, 43.5, 21.1; IR (DCM) ν 3268, 1752, 1332, 1222, 1158, 997, 756, 735 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}ClN_2O_5S$ $[M + NH_4]^+$ m/z 475.1089, found 475.1086.



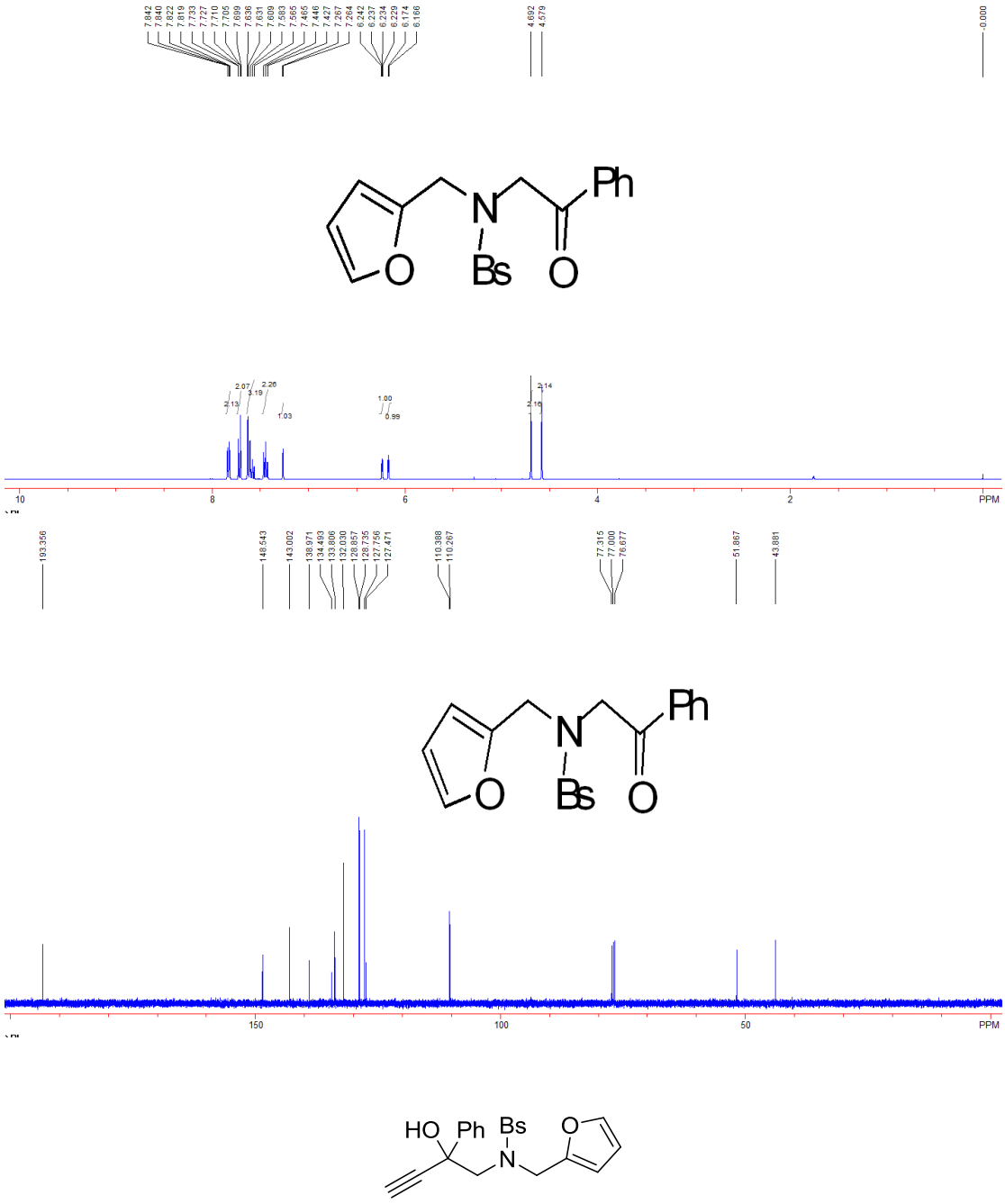
4-bromo-N-(furan-2-ylmethyl)benzenesulfonamide (S-2n): a white solid (5.1 g, 77% yield), mp: 113-115 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 2H, J = 8.4 Hz, ArH), 7.59 (d, 2H, J = 8.4 Hz, ArH), 7.21 (d, 1H, J = 0.8 Hz, ArH), 6.21 (t, 1H, J = 2.4 Hz, ArH), 6.09 (d, 1H, J = 2.4 Hz, ArH), 5.09 (t, 1H, J = 6.0 Hz, NH), 4.20 (d, 2H, J = 6.0 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 100

MHz, TMS) δ 149.1, 142.6, 138.9, 132.2, 128.5, 127.5, 110.4, 108.4, 40.0; IR (DCM) ν 3257, 1575, 1321, 1158, 1067, 1009, 922, 745, 726 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{14}BrN_2O_3S$ [M + NH_4]$^+$ m/z 332.9903, found 332.9906.



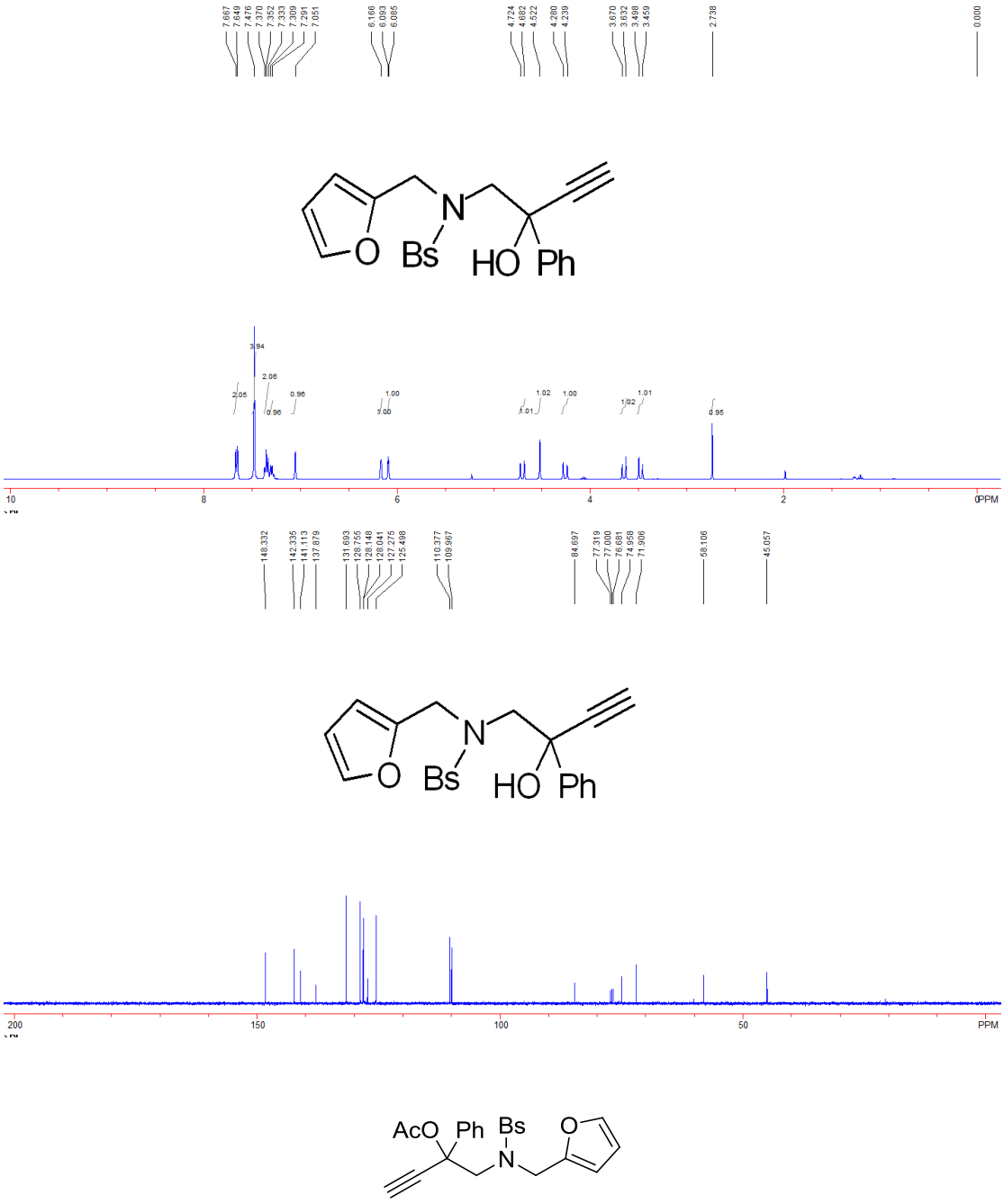
4-bromo-N-(furan-2-ylmethyl)-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3n): a colorless oil (4.4 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.83 (dd, 2H, J_1 = 8.0 Hz, J_2 = 0.8 Hz, ArH), 7.73-7.70 (m, 2H, ArH), 7.64-7.56 (m, 3H, ArH), 7.45 (t, 2H, J = 7.6 Hz, ArH), 7.27 (d, 1H, J = 1.2 Hz, ArH), 6.23 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.17 (d, 1H, J = 3.2 Hz, ArH), 4.69 (s, 2H, CH_2), 4.58 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.3, 148.5, 143.0, 139.0, 134.5, 133.8, 132.0, 128.8, 128.7, 127.7, 127.5, 110.4, 110.3, 51.9, 43.9; IR

(DCM) ν 2935, 1698, 1574, 1338, 1156, 1090, 1009, 910, 750, 688 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}BrN_2O_4S$ $[M + NH_4]^+$ m/z 451.0322, found 451.0318.



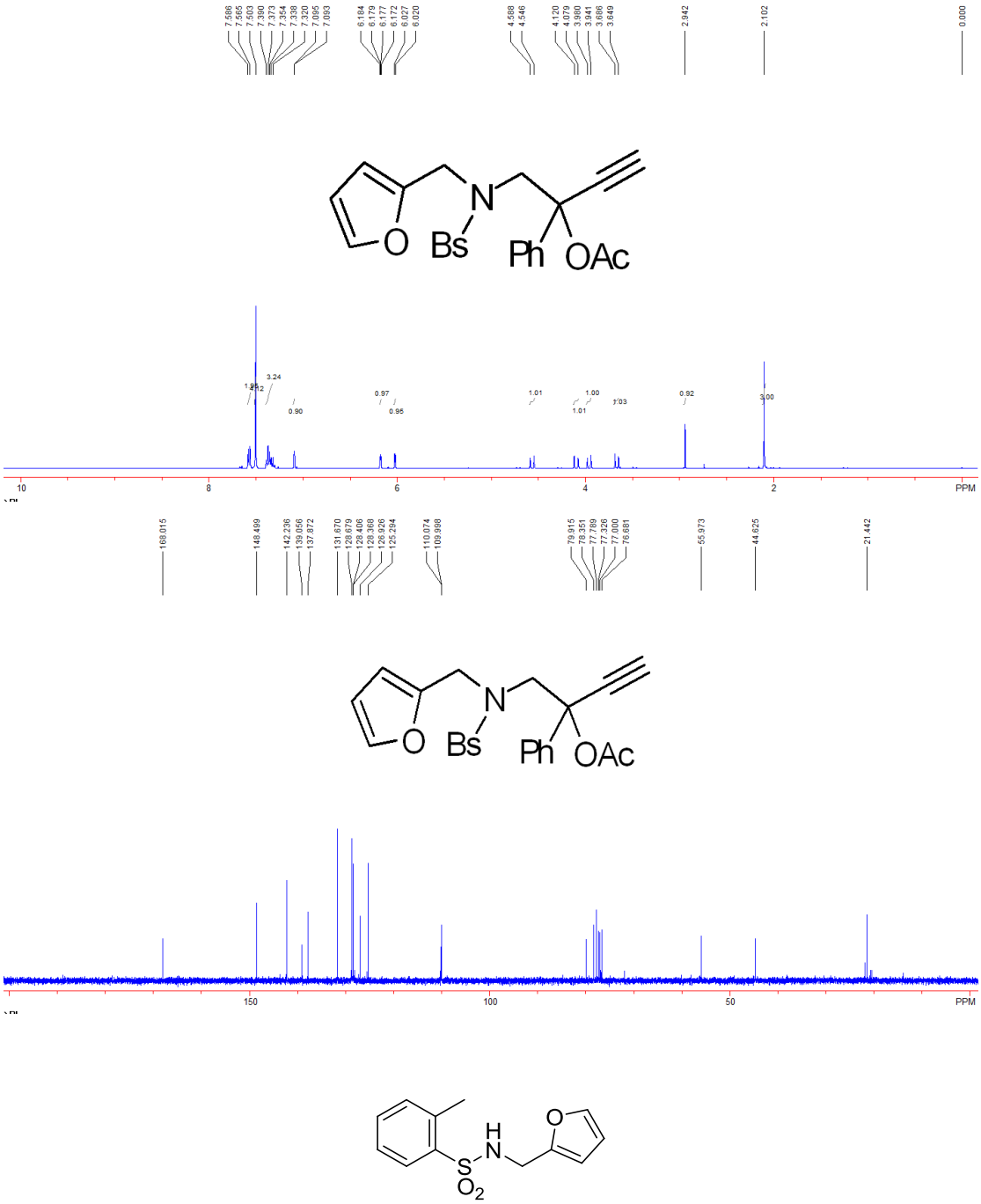
4-bromo-N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)benzenesulfonamide (S-4n): a colorless oil (940 g, 63% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 2H, *J* = 7.2 Hz, ArH), 7.48 (s, 4H, ArH), 7.37-7.33 (m, 2H, ArH), 7.31-7.29 (m, 1H, ArH), 7.05 (s, 1H, ArH), 6.17 (s, 1H, ArH), 6.09 (d, 1H, *J* = 3.2 Hz, ArH), 4.70 (d, 1H, *J* = 16.8 Hz, CH_2), 4.52 (s, 1H, OH), 4.26 (d, 1H, *J* = 16.8 Hz, CH_2), 3.65 (d, 1H, *J* = 15.2 Hz, CH_2), 3.48 (d, 1H, *J* = 15.2 Hz, CH_2), 2.74 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.3, 142.3, 141.1, 137.9, 131.7, 128.7, 128.1, 128.0, 127.3, 125.5, 110.4, 110.0, 84.7, 74.9, 71.9, 58.1, 45.0; IR (DCM) ν

3472, 3293, 1574, 1333, 1153, 1068, 1005, 932, 773, 737 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}BrN_2O_4S$ $[M + NH_4]^+$ m/z 477.0478, found 477.0478.

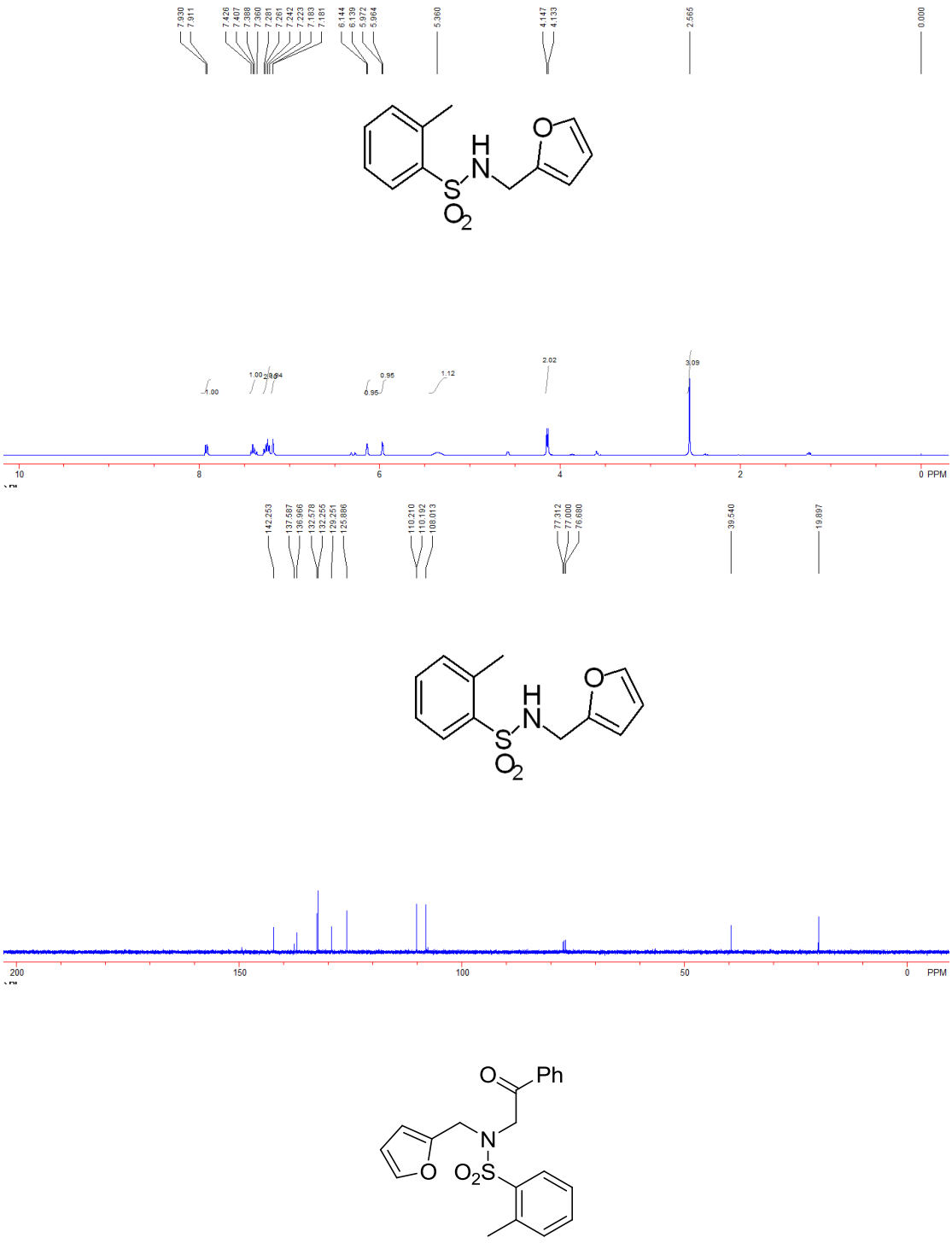


1-((4-bromo-N-(furan-2-ylmethyl)phenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 1n): a white solid (969 mg, 89% yield), mp: 138-140 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 7.50 (s, 4H, ArH), 7.39-7.32 (m, 3H, ArH), 7.09 (d, 1H, *J* = 0.8 Hz, ArH), 6.18 (dd, 1H, J_1 = 2.8 Hz, J_2 = 2.0 Hz, ArH), 6.02 (d, 1H, *J* = 2.8 Hz, ArH), 4.57 (d, 1H, *J* = 16.8 Hz, CH_2), 4.10 (d, 1H, *J* = 16.8 Hz, CH_2), 3.96 (d, 1H, *J* = 15.6 Hz, CH_2), 3.67 (d, 1H, *J* = 15.6 Hz, CH_2), 2.94 (s, 1H, CH), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.0, 148.5, 142.2, 139.0, 137.9, 131.7, 128.7, 128.41, 128.37, 126.9, 125.3, 110.1, 110.0, 79.9,

78.3, 77.8, 56.0, 44.6, 21.4; IR (DCM) ν 3283, 1751, 1574, 1350, 1221, 1159, 1009, 734, 698 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}BrN_2O_5S$ $[M + NH_4]^+$ m/z 519.0584, found 519.0582.

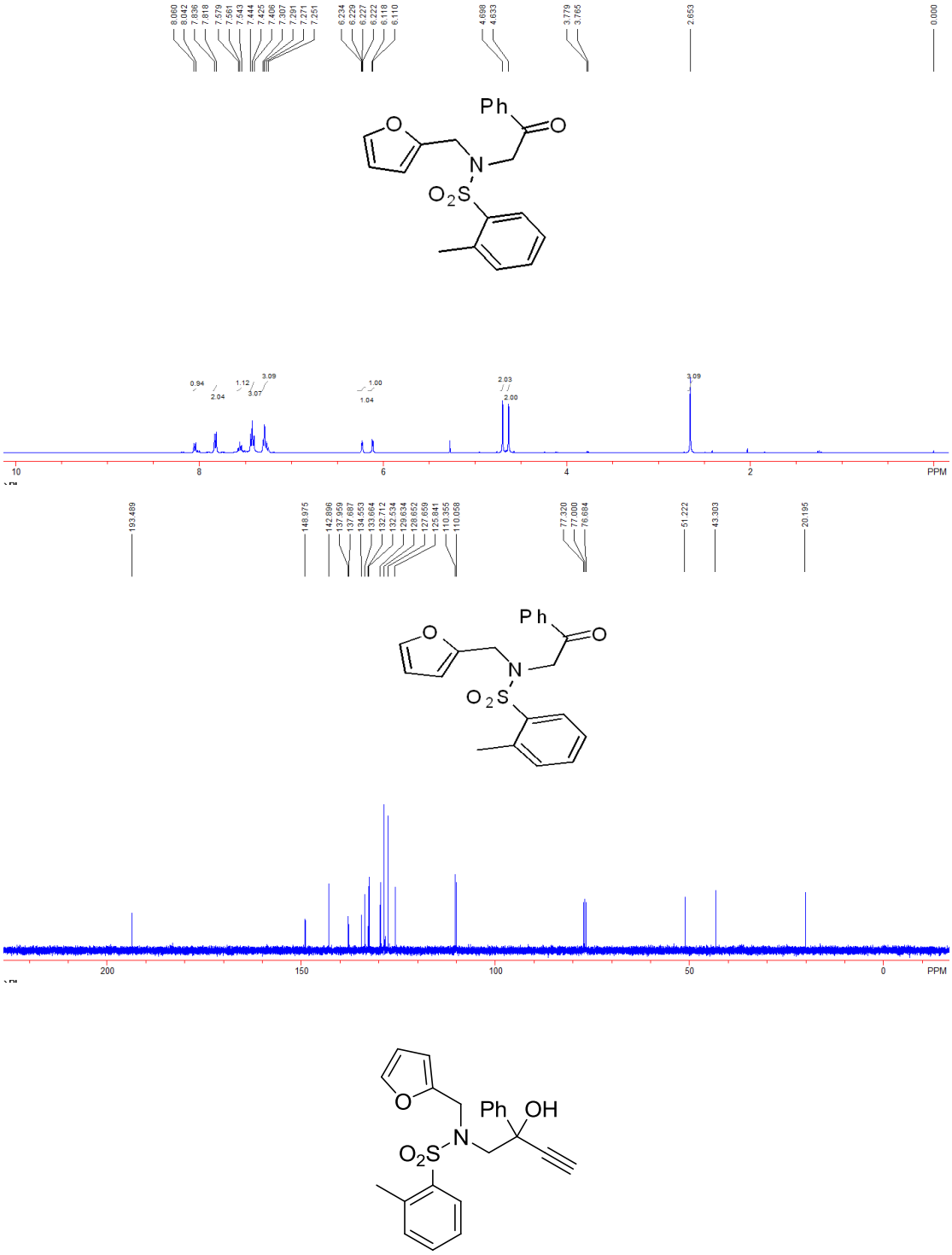


N-(furan-2-ylmethyl)-2-methylbenzenesulfonamide (S-2o): a white solid (8.0 g, 76% yield), mp: 194-196 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.92 (d, 1H, *J* = 7.6 Hz, ArH), 7.43-7.36 (m, 1H, ArH), 7.28-7.22 (m, 2H, ArH), 7.18 (d, 1H, *J* = 0.8 Hz, ArH), 6.14 (d, 1H, *J* = 2.0 Hz, ArH), 5.97 (d, 1H, *J* = 3.2 Hz, ArH), 5.36 (br, 1H, NH), 4.14 (d, 2H, *J* = 5.6 Hz, CH_2), 2.56 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 142.2, 137.6, 137.0, 132.6, 132.2, 129.2, 125.9, 110.21, 110.19, 108.0, 39.5, 19.9.



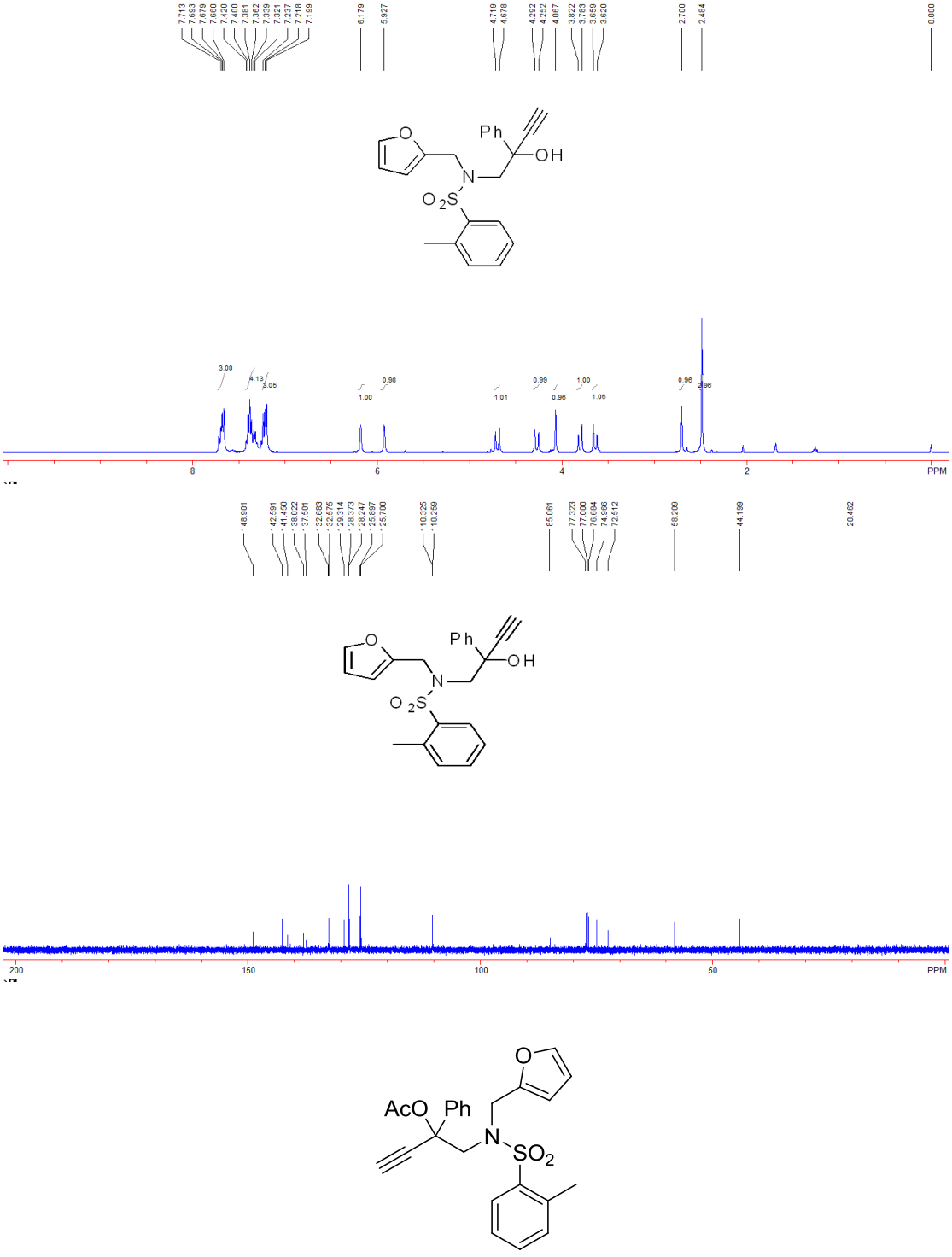
N-(furan-2-ylmethyl)-2-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3o): a colorless oil (4.5 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.05 (d, 1H, *J* = 7.2 Hz, ArH), 7.83 (d, 2H, *J* = 7.2 Hz, ArH), 7.56 (t, 1H, *J* = 7.2 Hz, ArH), 7.42 (t, 3H, *J* = 7.2 Hz, ArH), 7.31-7.25 (m, 3H, ArH), 6.23 (dd, 1H, J_1 = 2.8 Hz, J_2 = 2.0 Hz, ArH), 6.11 (d, 1H, *J* = 3.2 Hz, ArH), 4.70 (s, 2H, CH_2), 4.63 (s, 2H, CH_2), 2.65 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.5, 149.0, 142.9, 137.9, 137.7, 134.5, 133.7, 132.7, 132.5, 129.6, 128.6, 127.6, 125.8, 110.3, 110.0, 51.2, 43.3, 20.2; IR (DCM) ν 3061, 1698, 1323, 1224, 1155, 933, 909, 747, 687 cm^{-1};

HRMS (ESI) calcd for $C_{20}H_{20}NO_4S$ $[M + H]^+$ m/z 370.1108, found 370.1111.



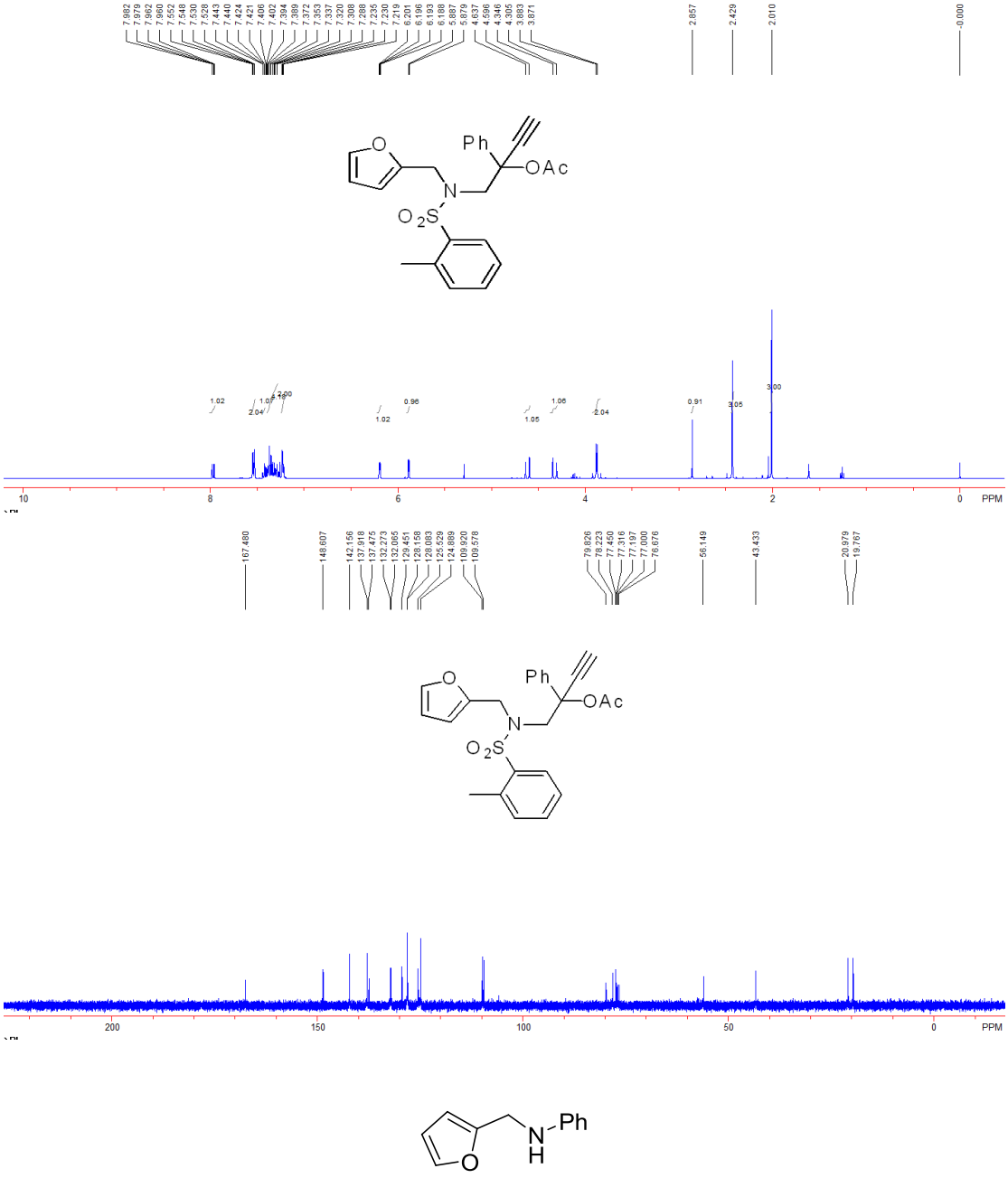
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-2-methylbenzenesulfonamide (S-4o): a white solid (1.2 g, 63% yield), mp: 124-126 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.71-7.66 (m, 3H, ArH), 7.42-7.32 (m, 4H, ArH), 7.24-7.20 (m, 3H, ArH), 6.18 (s, 1H, ArH), 5.93 (s, 1H, ArH), 4.70 (d, 1H, *J* = 16.4 Hz, CH_2), 4.27 (d, 1H, *J* = 16.4 Hz, CH_2), 4.07 (s, 1H, OH), 3.80 (d, 1H, *J* = 15.6 Hz, CH_2), 3.64 (d, 1H, *J* = 15.6 Hz, CH_2), 2.70 (s, 1H, CH), 2.48 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.9, 142.6, 141.4, 138.0, 137.5, 132.7, 132.6,

129.3, 128.4, 128.2, 125.9, 125.7, 110.3, 110.2, 85.1, 75.0, 72.5, 58.2, 44.2, 20.5; IR (DCM) ν 3465, 3295, 1449, 1319, 1154, 1006, 933, 733, 699 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}NNaO_4S$ $[M + Na]^+$ m/z 418.1083, found 418.1085.



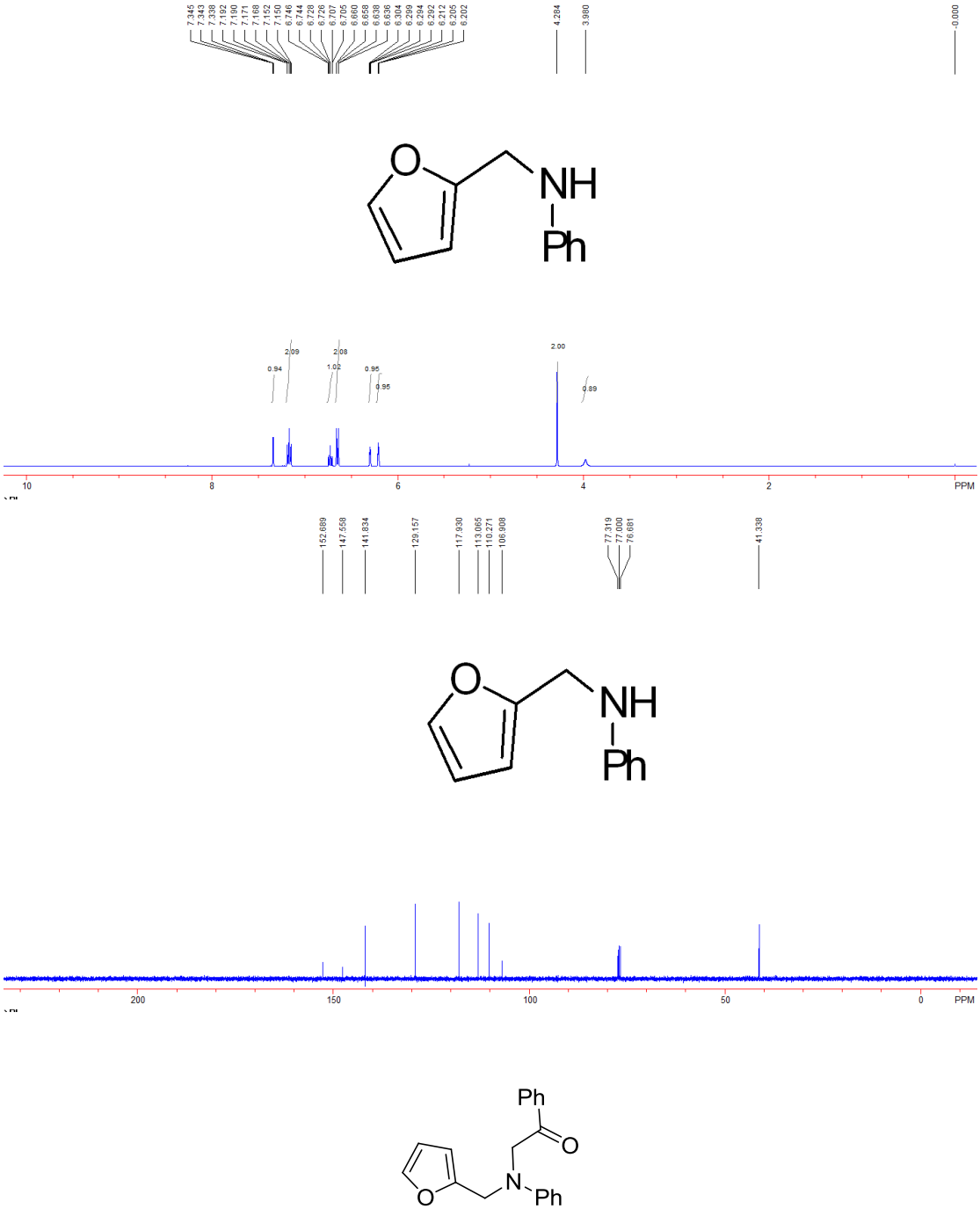
1-((N-(furan-2-ylmethyl)-2-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 2o): a white solid (1.2 g, 94% yield), mp: 134-136 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.97 (dd, 1H, J_1 = 8.0 Hz, J_2 = 0.8 Hz, ArH), 7.54 (dd, 2H, J_1 = 8.0 Hz, J_2 = 0.8 Hz, ArH), 7.44-7.42 (m, 1H, ArH), 7.41-7.29 (m, 4H, ArH), 7.23-7.22 (m, 2H, ArH), 6.19 (dd, 1H, J_1

= 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.88 (d, 1H, J = 3.2 Hz, ArH), 4.62 (d, 1H, J = 16.4 Hz, CH_2), 4.32 (d, 1H, J = 16.4 Hz, CH_2), 3.88 (d, 2H, J = 4.8 Hz, CH_2), 2.86 (s, 1H, CH), 2.43 (s, 3H, CH_3), 2.01 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.5, 148.6, 142.1, 137.9, 137.5, 132.3, 132.1, 129.4, 128.15, 128.08, 125.5, 124.9, 109.9, 109.6, 79.8, 78.2, 77.4, 56.1, 43.4, 21.0, 19.8; IR (DCM) ν 3271, 1752, 1449, 1324, 1222, 1157, 1011, 733, 699 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 455.1635, found 455.1636.



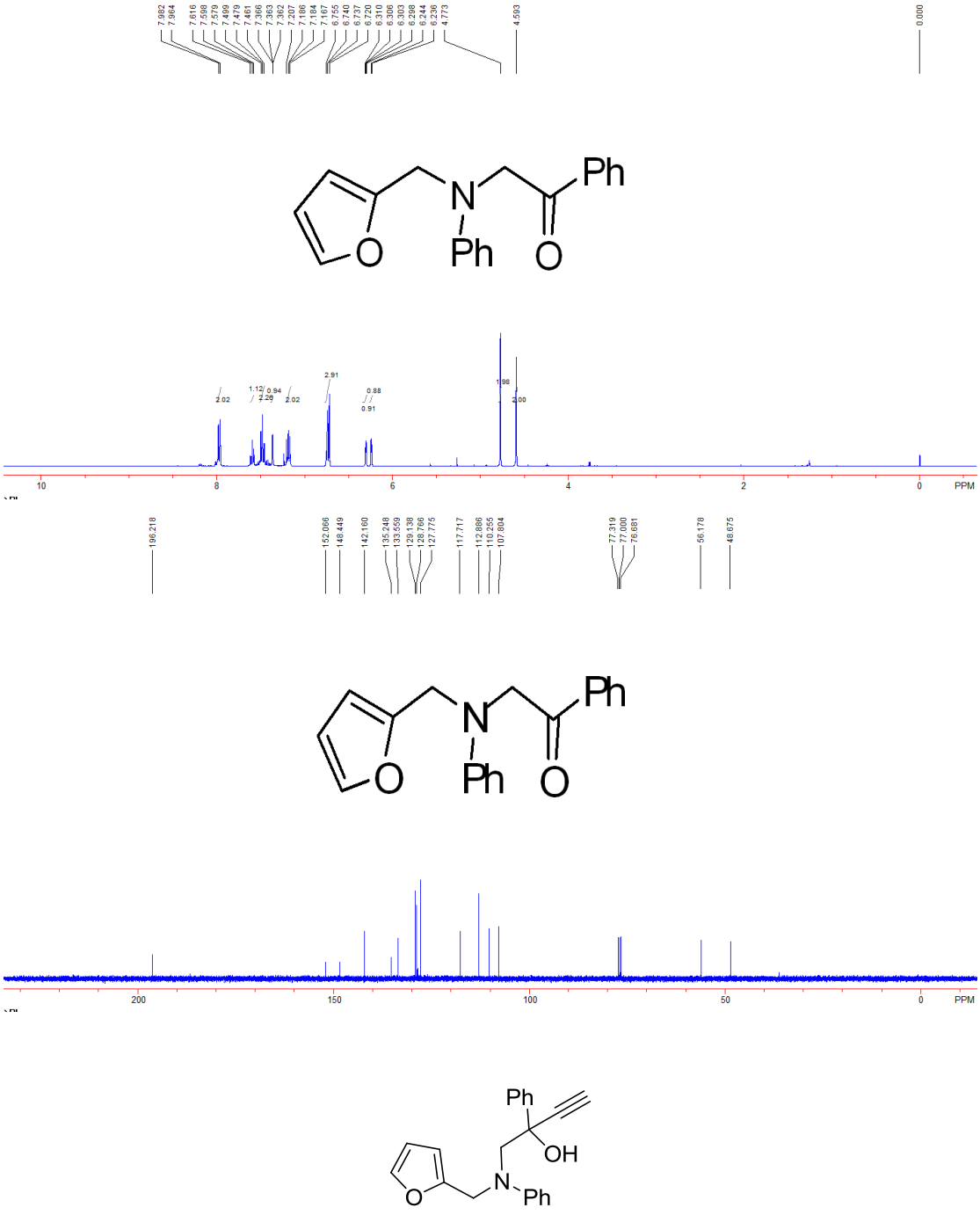
N-(furan-2-ylmethyl)aniline (S-2p): a white solid (2.6 g, 66% yield), mp: 101-103 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.34 (d, 1H, J = 2.8 Hz, ArH), 7.19-7.15 (m, 2H, ArH), 6.73 (td, 1H, J_1 = 7.2 Hz, J_2 = 0.8 Hz, ArH), 6.65 (dd, 1H, J_1 = 7.2 Hz, J_2 = 0.8 Hz, ArH), 6.30-6.30 (m, 1H,

ArH), 6.21-6.20 (m, 1H, ArH), 4.28 (s, 2H, CH_2), 3.98 (br, 1H, NH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 152.7, 147.5, 141.8, 129.1, 117.9, 113.0, 110.3, 106.9, 41.3; IR (DCM) ν 3412, 1601, 1503, 1316, 1180, 1145, 1011, 731, 690 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_{12}NO$ $[M + H]^+$ m/z 174.0913, found 174.0917.



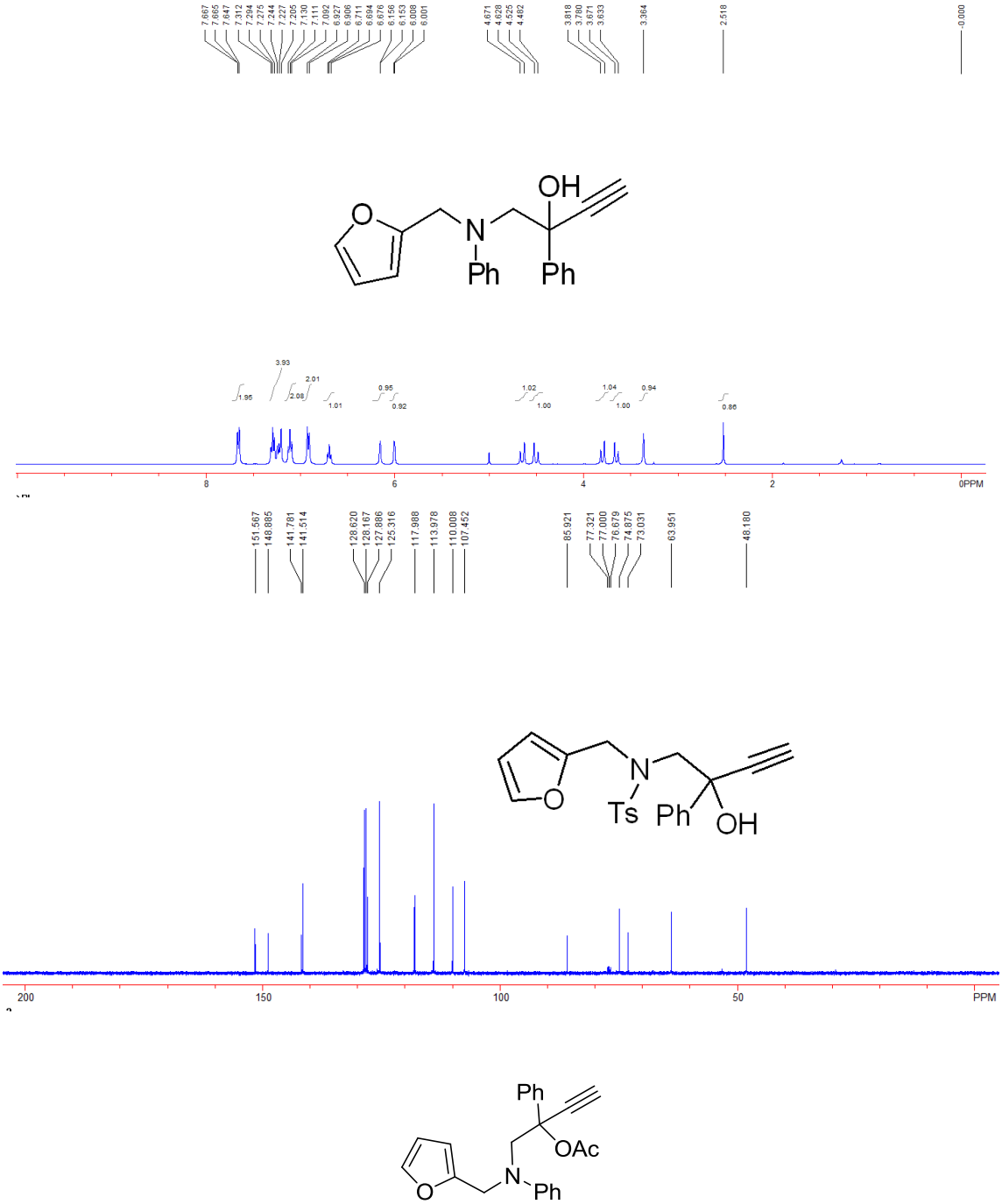
2-((furan-2-ylmethyl)(phenyl)amino)-1-phenylethan-1-one (S-3p): a colorless oil (3.4 g, 99% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.97 (d, 2H, *J* = 7.2 Hz, ArH), 7.60 (t, 1H, *J* = 7.2 Hz, ArH), 7.48 (t, 2H, *J* = 7.2 Hz, ArH), 7.37-7.36 (m, 1H, ArH), 7.21-7.17 (m, 2H, ArH), 6.75-6.72 (m, 3H, ArH), 6.31-6.30 (m, 1H, ArH), 6.24 (d, 1H, *J* = 3.2 Hz, ArH), 4.77 (s, 2H, CH_2), 4.59 (s,

2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 196.2, 152.1, 148.4, 142.2, 135.2, 133.5, 129.1, 128.8, 127.8, 117.7, 112.9, 110.2, 107.8, 56.2, 48.7; IR (DCM) ν 3061, 2921, 1694, 1597, 1504, 1218, 936, 745, 687 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{18}NO_2$ $[M + H]^+$ m/z 292.1332, found 292.1333.



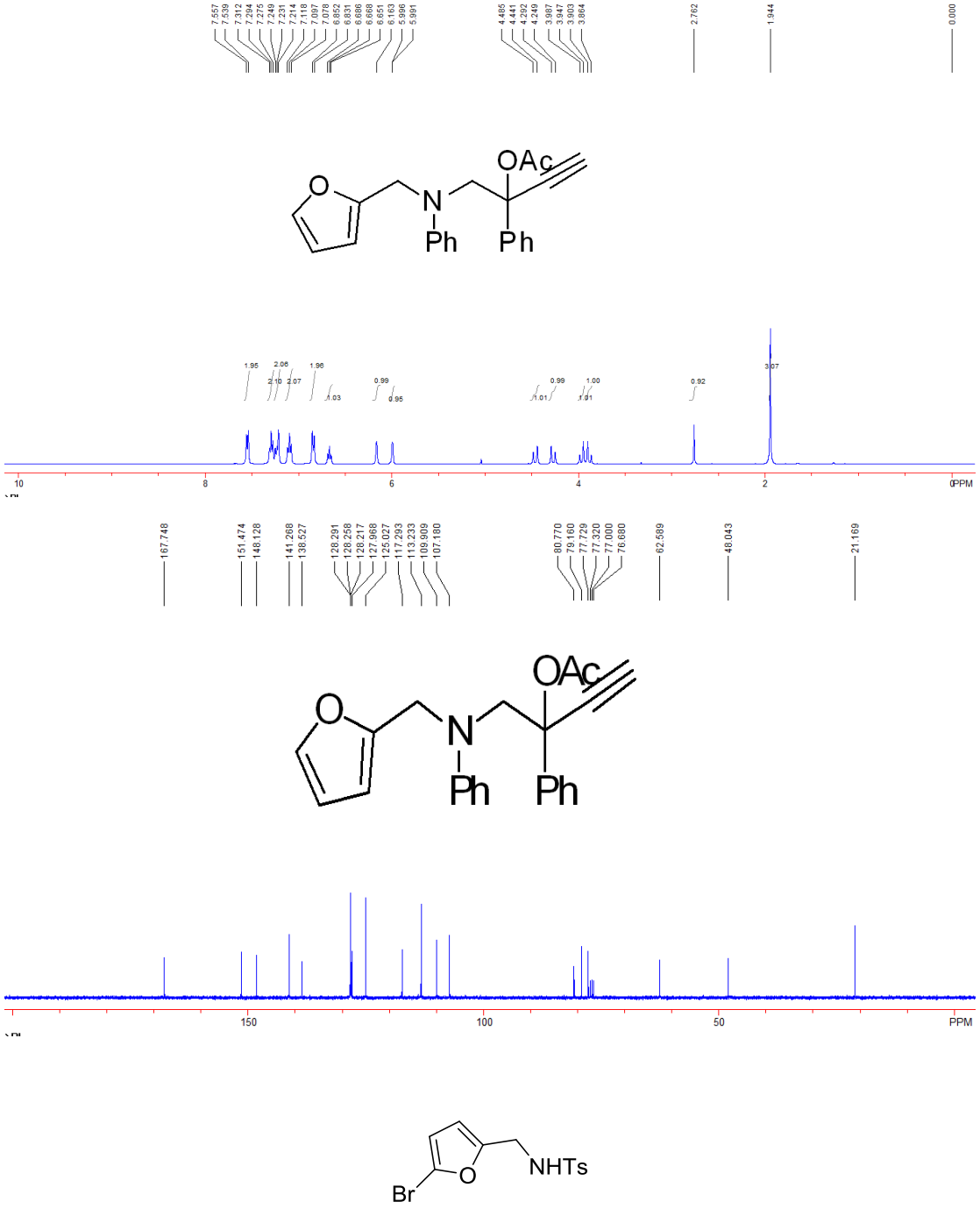
1-((furan-2-ylmethyl)(phenyl)amino)-2-phenylbut-3-yn-2-ol (S-4p): a colorless oil (641 mg, 57% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.67-7.65 (m, 2H, ArH), 7.31-7.20 (m, 4H, ArH), 7.11 (t, 2H, *J* = 7.6 Hz, ArH), 6.92 (d, 2H, *J* = 8.4 Hz, ArH), 6.69 (t, 1H, *J* = 3.2 Hz, ArH), 6.15 (d, 1H, *J* = 1.2 Hz, ArH), 6.00 (d, 1H, *J* = 2.8 Hz, ArH), 4.65 (d, 1H, *J* = 17.2 Hz, CH_2), 4.50

(d, 1H, J = 17.2 Hz, CH_2), 3.80 (d, 1H, J = 15.2 Hz, CH_2), 3.65 (d, 1H, J = 15.2 Hz, CH_2), 3.36 (s, 1H, OH), 2.51 (s, 1H, CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 151.6, 148.9, 141.8, 141.5, 128.6, 128.2, 127.9, 125.3, 118.0, 114.0, 110.0, 107.4, 85.9, 74.9, 73.0, 63.9, 48.2; IR (DCM) ν 3520, 3285, 1597, 1503, 1347, 1174, 1002, 747 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}NO_2$ [M + H]$^+$ m/z 318.1489, found 318.1488.



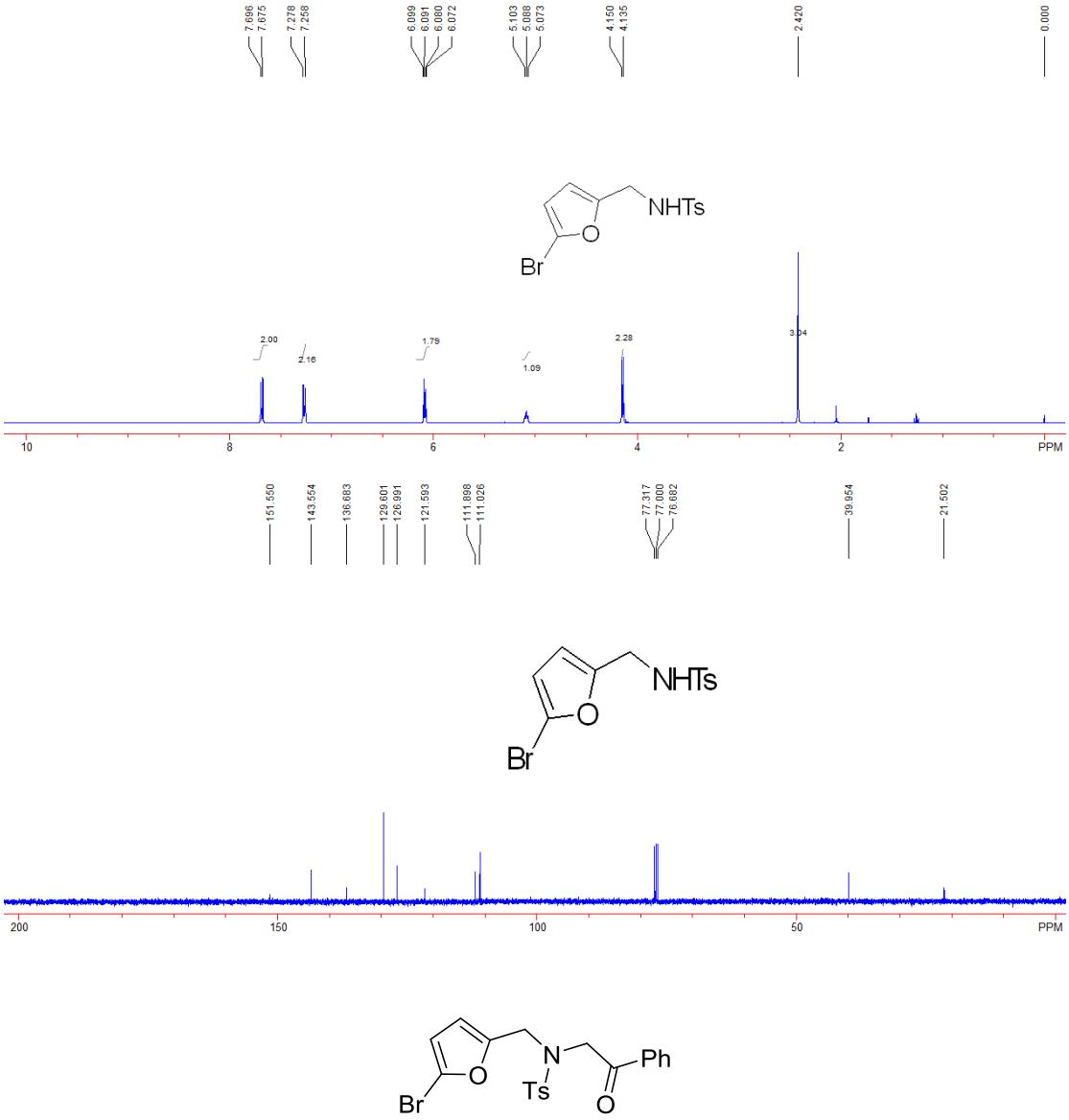
1-((furan-2-ylmethyl)(phenyl)amino)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 1p): a colorless oil (653 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.55 (d, 2H, J = 7.2 Hz, ArH), 7.31-7.27 (m, 2H, ArH), 7.25-7.21 (m, 2H, ArH), 7.10 (t, 2H, J = 8.4 Hz, ArH), 6.84 (d, 2H,

J = 8.4 Hz, ArH), 6.67 (t, 1H, *J* = 7.2 Hz, ArH), 6.16 (s, 1H, ArH), 5.99 (d, 1H, *J* = 2.0 Hz, ArH), 4.46 (d, 1H, *J* = 17.6 Hz, CH_2), 4.27 (d, 1H, *J* = 17.6 Hz, CH_2), 3.97 (d, 1H, *J* = 16.0 Hz, CH_2), 3.85 (d, 1H, *J* = 16.0 Hz, CH_2), 2.76 (s, 1H, CH), 1.94 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.7, 151.5, 148.1, 141.3, 138.5, 128.3, 128.0, 125.0, 117.3, 113.2, 109.9, 107.2, 80.8, 79.2, 77.7, 62.6, 48.0, 21.2; IR (DCM) ν 3278, 2113, 1751, 1598, 1504, 1367, 1223, 1011, 747, 697 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}NO_3$ $[M + H]^+$ m/z 360.1594, found 360.1595.

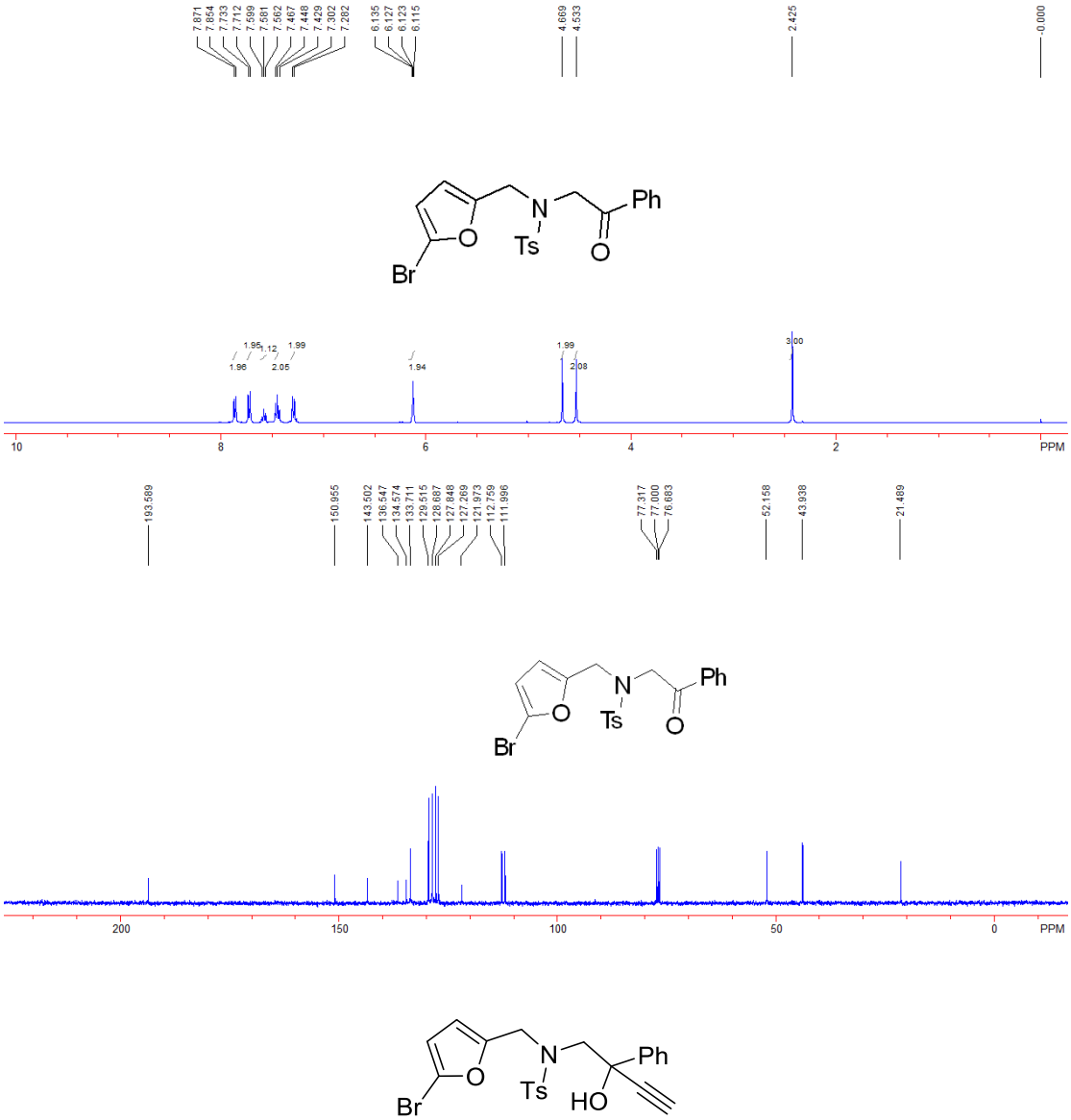


N-((5-bromofuran-2-yl)methyl)-4-methylbenzenesulfonamide (S-2z): known compound,[4] a white solid (6.9 g, 73% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.68 (d, 2H, *J* = 8.4 Hz, ArH),

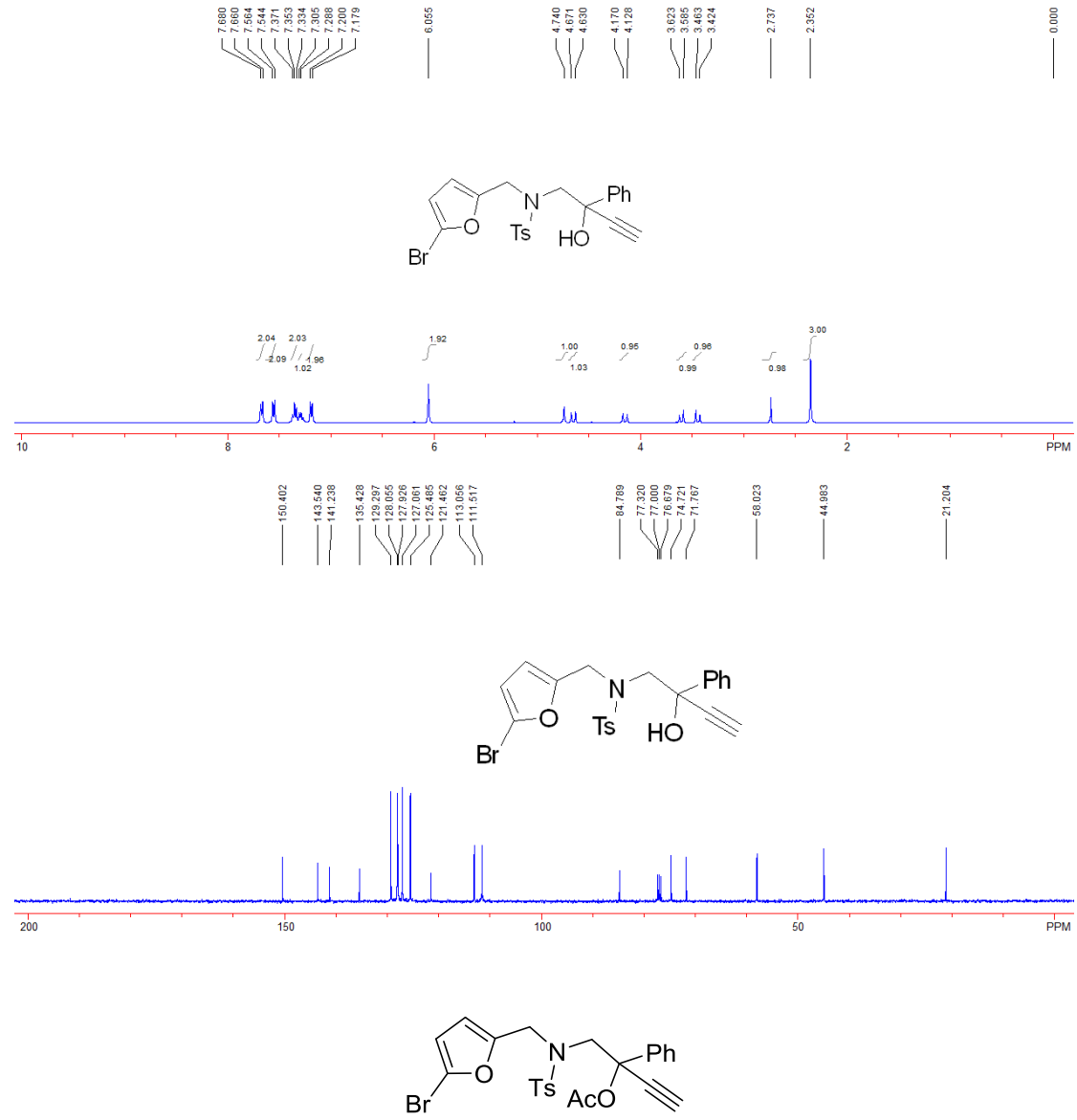
7.27 (d, 2H, *J* = 8.4 Hz, ArH), 6.10-6.07 (m, 2H, ArH), 5.09 (t, 1H, *J* = 6.0 Hz, NH), 4.14 (d, 2H, *J* = 6.0 Hz, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 151.5, 143.5, 136.7, 129.6, 127.0, 121.6, 111.9, 111.0, 39.9, 21.5.



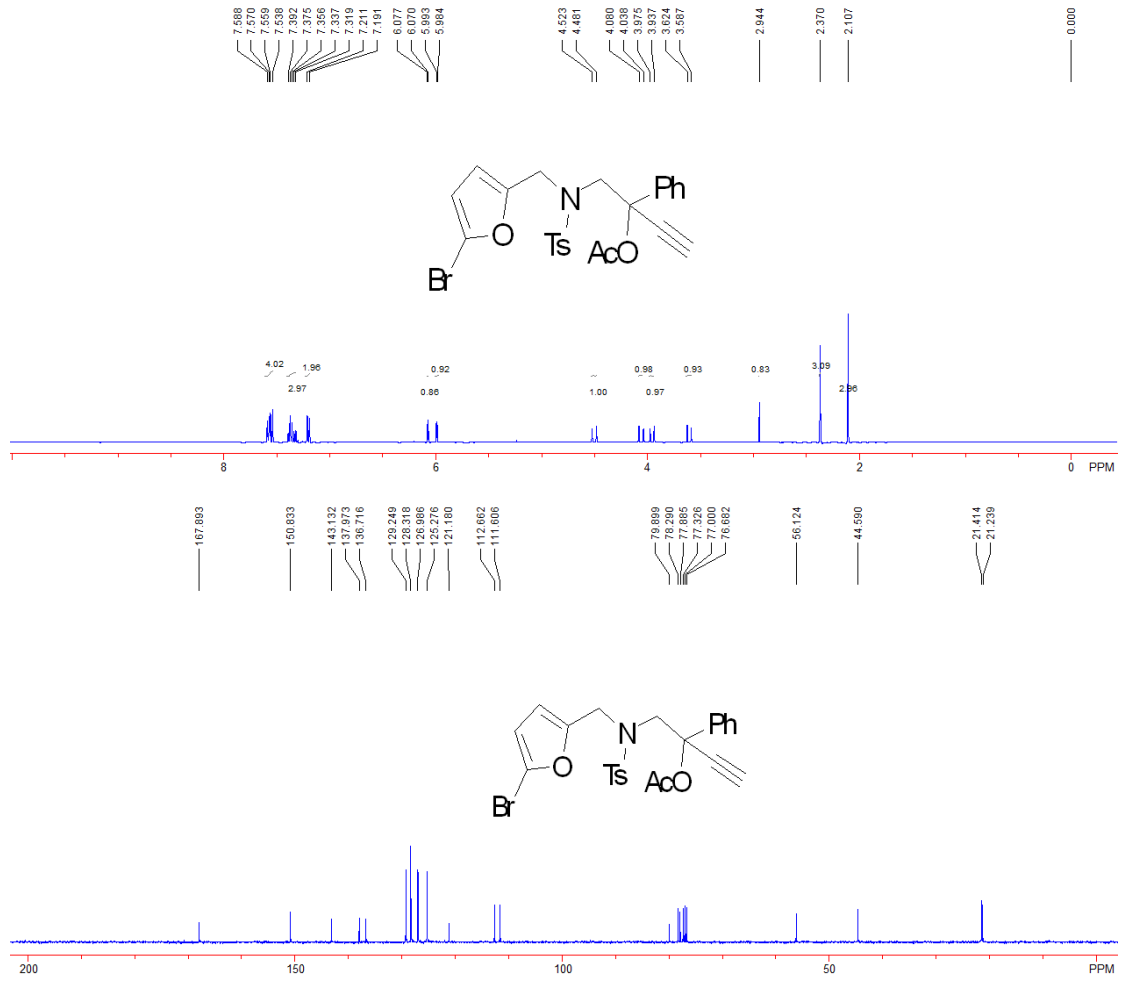
N-((5-bromofuran-2-yl)methyl)-4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3z): a white solid (4.2 g, 90% yield), mp: 129-131 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.86 (d, 2H, *J* = 6.8 Hz, ArH), 7.72 (d, 2H, *J* = 8.4 Hz, ArH), 7.58 (t, 1H, *J* = 7.6 Hz, ArH), 7.45 (t, 2H, *J* = 7.6 Hz, ArH), 7.29 (d, 2H, *J* = 8.4 Hz, ArH), 6.13-6.11 (m, 2H, ArH), 4.67 (s, 2H, CH_2), 4.53 (s, 2H, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.6, 150.9, 143.5, 136.5, 134.6, 133.7, 129.5, 128.7, 127.8, 127.3, 122.0, 112.7, 112.0, 52.1, 43.9, 21.5; IR (DCM) ν 3065, 2927, 1698, 1335, 1155, 1090, 911, 749 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{22}BrN_2O_4S$ $[M + NH_4]^+$ m/z 465.0478, found 465.0470.

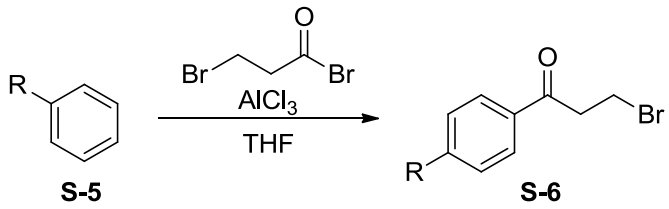


N-((5-bromofuran-2-yl)methyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-4z): a white solid (1.71 g, 70% yield), mp: 97-99 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.67 (d, 2H, *J* = 8.0 Hz, ArH), 7.55 (d, 2H, *J* = 8.0 Hz, ArH), 7.37-7.33 (m, 2H, ArH), 7.30-7.29 (m, 1H, ArH), 7.19 (d, 2H, *J* = 8.4 Hz, ArH), 6.05 (s, 2H, ArH), 4.74 (s, 1H, OH), 4.65 (d, 1H, *J* = 16.4 Hz, CH_2), 4.15 (d, 1H, *J* = 16.4 Hz, CH_2), 3.61 (d, 1H, *J* = 15.2 Hz, CH_2), 3.44 (d, 1H, *J* = 15.2 Hz, CH_2), 2.74 (s, 1H, CH), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 150.4, 143.5, 141.2, 135.4, 129.3, 128.0, 127.9, 127.1, 125.5, 121.5, 113.0, 111.5, 84.8, 74.7, 71.8, 58.0, 45.0, 21.2; IR (DCM) ν 3460, 3296, 1494, 1332, 1153, 1007, 730 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}BrNNaO_4S$ $[M + Na]^+$ m/z 496.0189, found 496.0190.



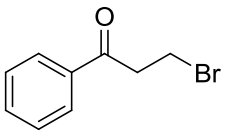
1-((N-((5-bromofuran-2-yl)methyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Scheme 3, compound 1z): a coulourless oil (1.19 g, 64% yield) . ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59-7.54 (m, 4H, ArH), 7.39-7.32 (m, 3H, ArH), 7.20 (d, 2H, *J* = 8.0 Hz, ArH), 6.07 (d, 1H, *J* = 2.8 Hz, ArH), 5.99 (d, 1H, *J* = 2.8 Hz, ArH), 4.50 (d, 1H, *J* = 16.8 Hz, CH_2), 4.06 (d, 1H, *J* = 16.8 Hz, CH_2), 3.96 (d, 1H, *J* = 15.2 Hz, CH_2), 3.60 (d, 1H, *J* = 15.2 Hz, CH_2), 2.94 (s, 1H, CH), 2.37 (s, 3H, CH_3), 2.11 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.9, 150.8, 143.1, 138.0, 136.7, 129.2, 128.3, 127.0, 125.3, 121.2, 112.7, 111.6, 79.9, 78.3, 77.9, 56.1, 44.6, 21.4, 21.2; IR (DCM) ν 3271, 1751, 1340, 1223, 995, 732 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}BrN_2O_5S$ $[M + NH_4]^+$ m/z 533.0740, found 533.0731.



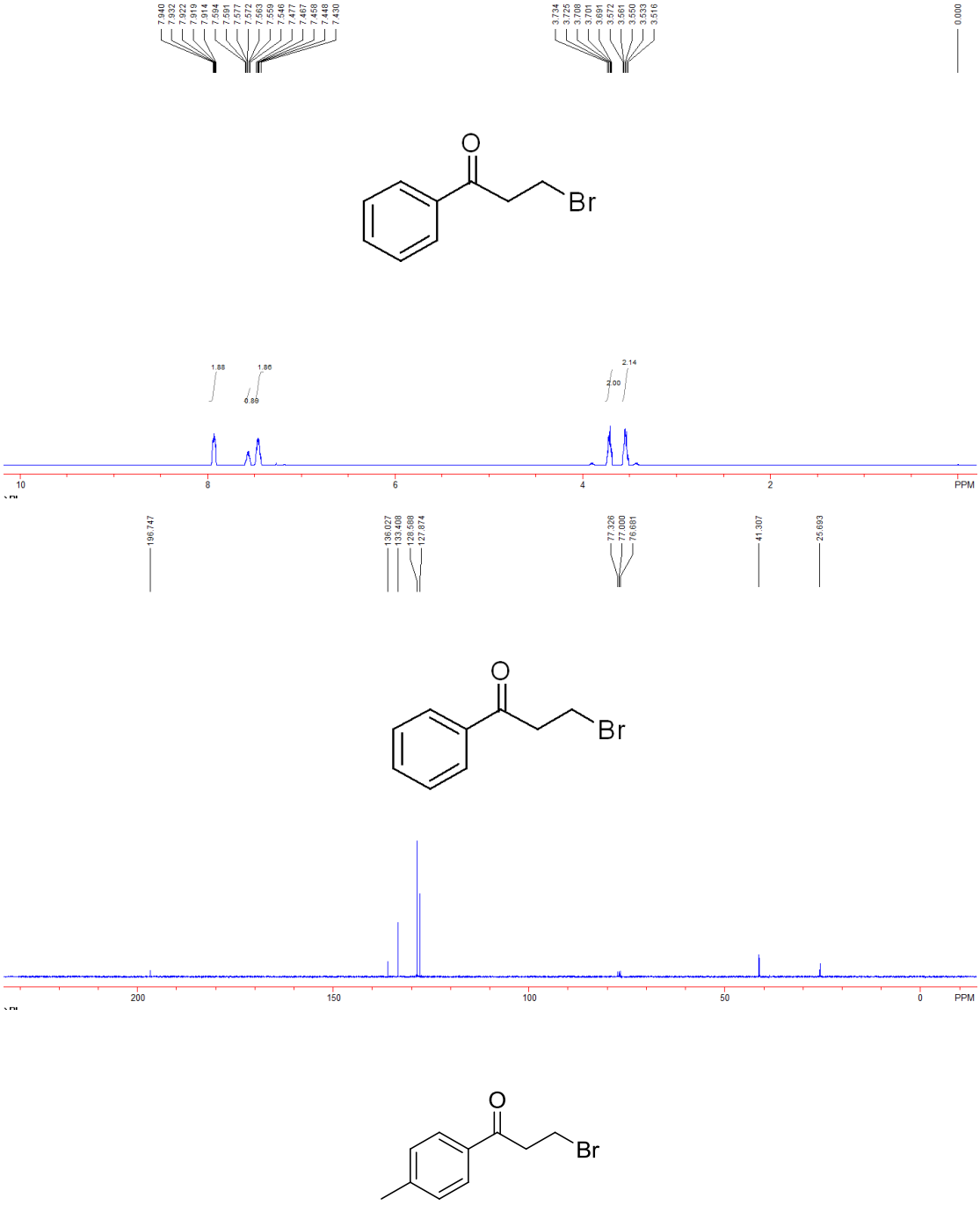


S-5 **S-6**

Procedure for the preparation of **S-6r**: A flame-dried, Ar-purged 50-mL round bottomed flask was charged with 3-bromopropanoyl chloride (2.1 g, 12 mmol), benzene (5.4 mL, 61 mmol) and dry DCM (20 mL). The solution was cooled to 0 ^{o}C and aluminum chloride (1.8 g, 14 mmol) was added in one portion. The resulting suspension was stirred for 3 h at rt. The reaction was quenched by pouring the orange-colored solution into an ice/water mixture. The combined organic layers were washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 20/1) to provide product **S-6s** (2.39 g) in 94% yield.[5]

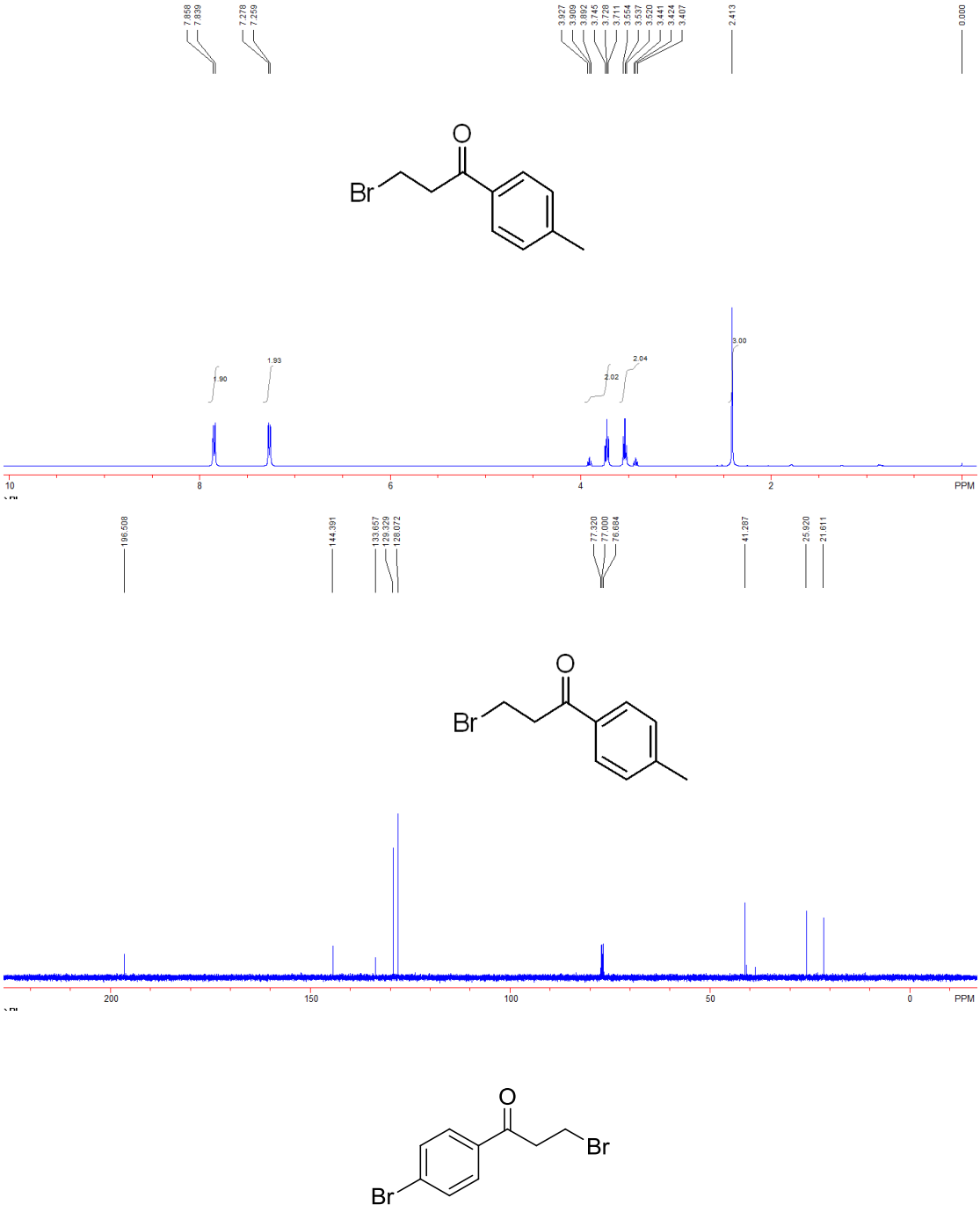


3-bromo-1-phenylpropan-1-one (S-6s): known compound,[5] a white solid (2.4 g, 94% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.94-7.91 (m, 2H, ArH), 7.59-7.55 (m, 1H, ArH), 7.48-7.43 (m, 2H, ArH), 3.73-3.69 (m, 2H, CH_2), 3.57-3.52 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 196.7, 136.0, 133.4, 128.6, 127.9, 41.3, 25.7.



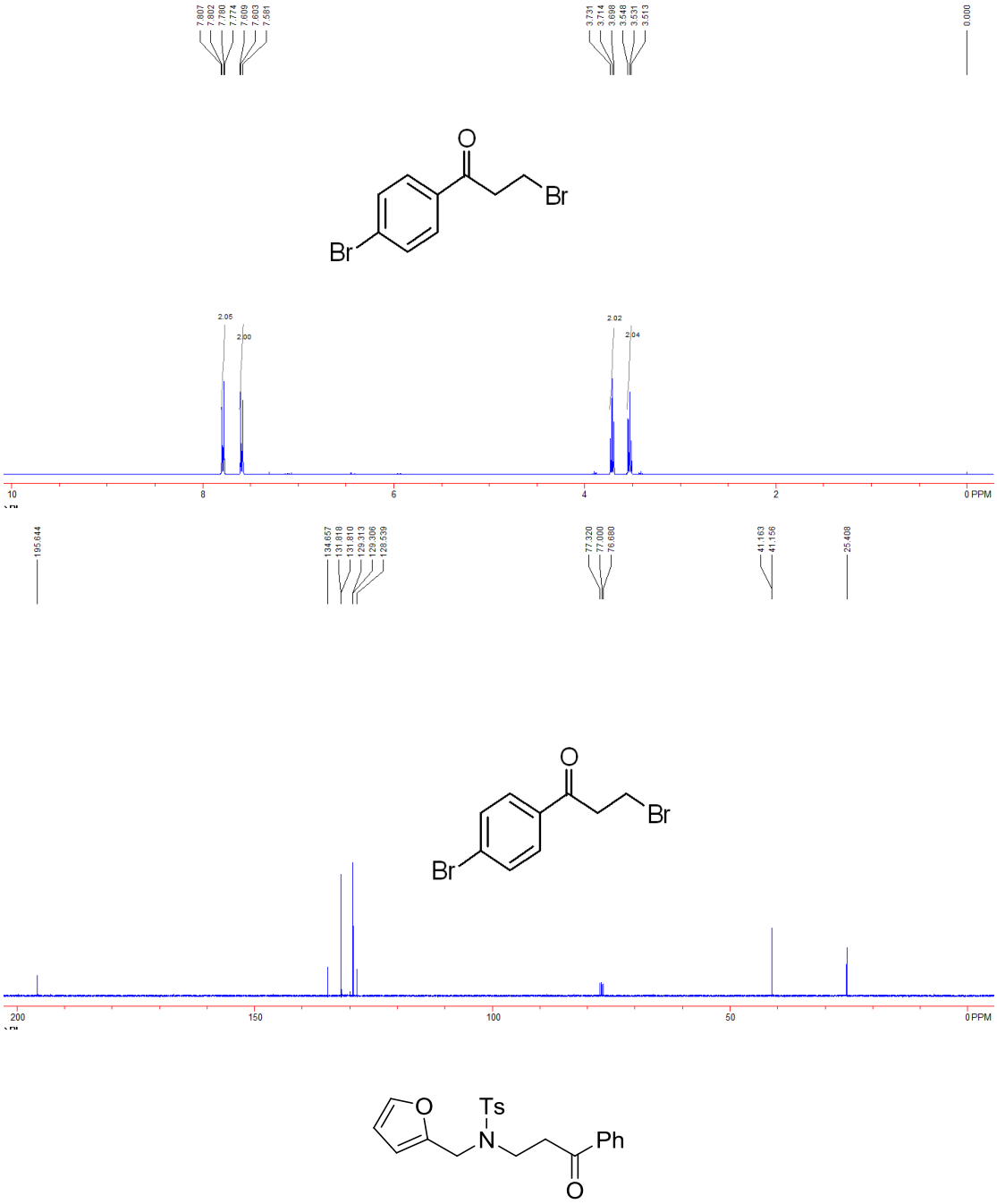
3-bromo-1-(p-tolyl)propan-1-one (S-6t): a white solid (3.4 g, 99% yield), mp: 113-115 ^{o}C. ^{1}H

NMR ($CDCl_3$, 400 MHz, TMS) δ 7.88 (d, 2H, *J* = 8.0 Hz, ArH), 7.63-7.59 (m, 1H, ArH), 7.48 (m, 2H, ArH), 7.38 (t, 1H, *J* = 0.8 Hz, ArH), 6.31-6.27 (m, 2H, ArH), 4.74 (s, 2H, CH_2), 4.57 (s, 2H, CH_2), 3.09 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 194.5, 149.0, 143.1, 134.4, 133.9, 128.8, 127.7, 110.4, 110.0, 52.3, 43.9, 40.4; IR (DCM) ν 3364, 1697, 1325, 1224, 1144, 754, 734, 688 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{19}N_2O_4S$ $[M + NH_4]^+$ m/z 311.1060, found 311.1060.

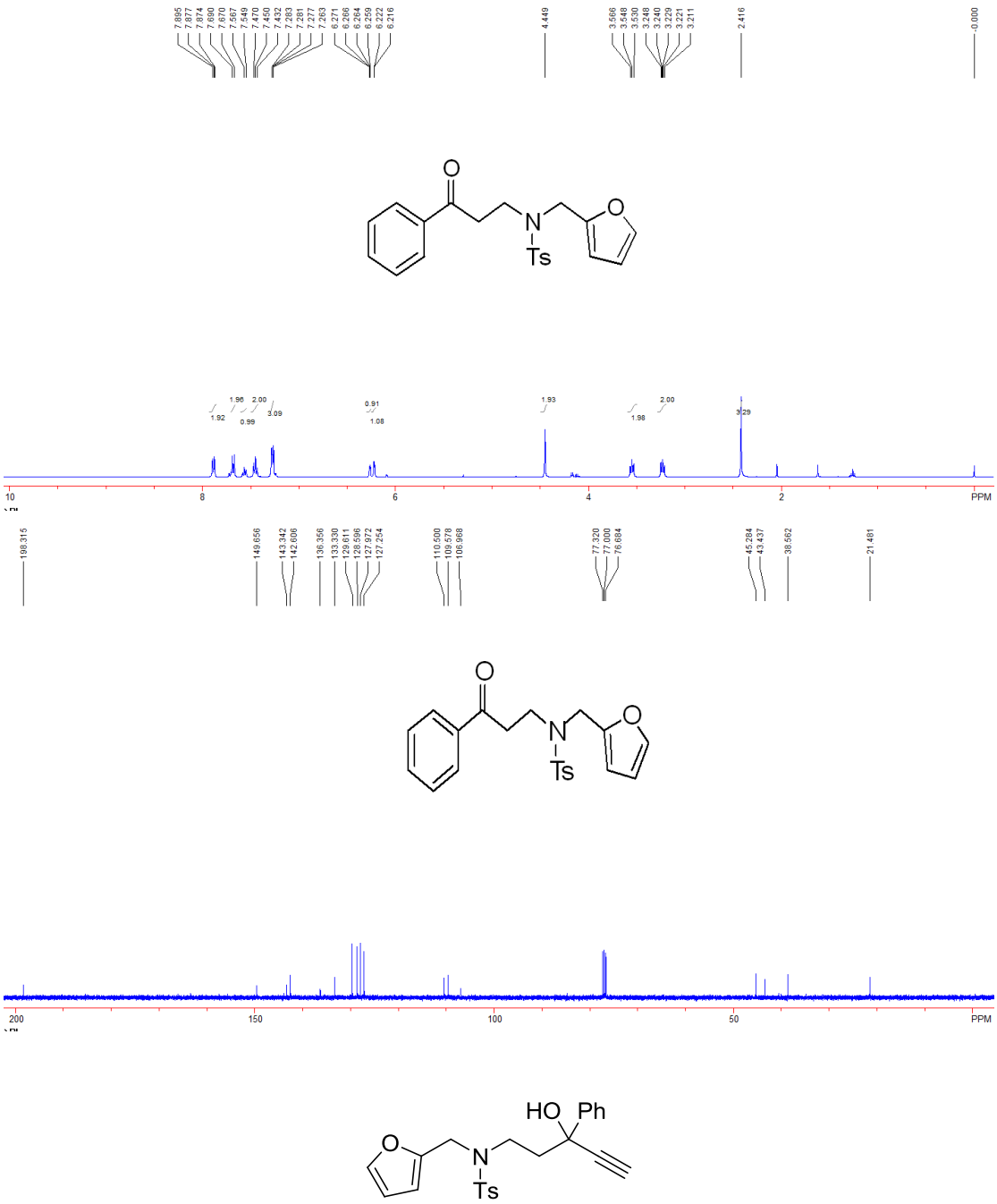


3-bromo-1-(4-bromophenyl)propan-1-one (S-6u): known compound,[6] a white solid (12.0 g, 83% yield), mp: 99-101 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.81-7.77 (m, 2H, ArH), 7.61-7.58 (m, 2H, ArH), 3.71 (t, 2H, *J* = 6.8 Hz, CH_2), 3.53 (t, 2H, *J* = 6.8 Hz, CH_2); ^{13}C NMR

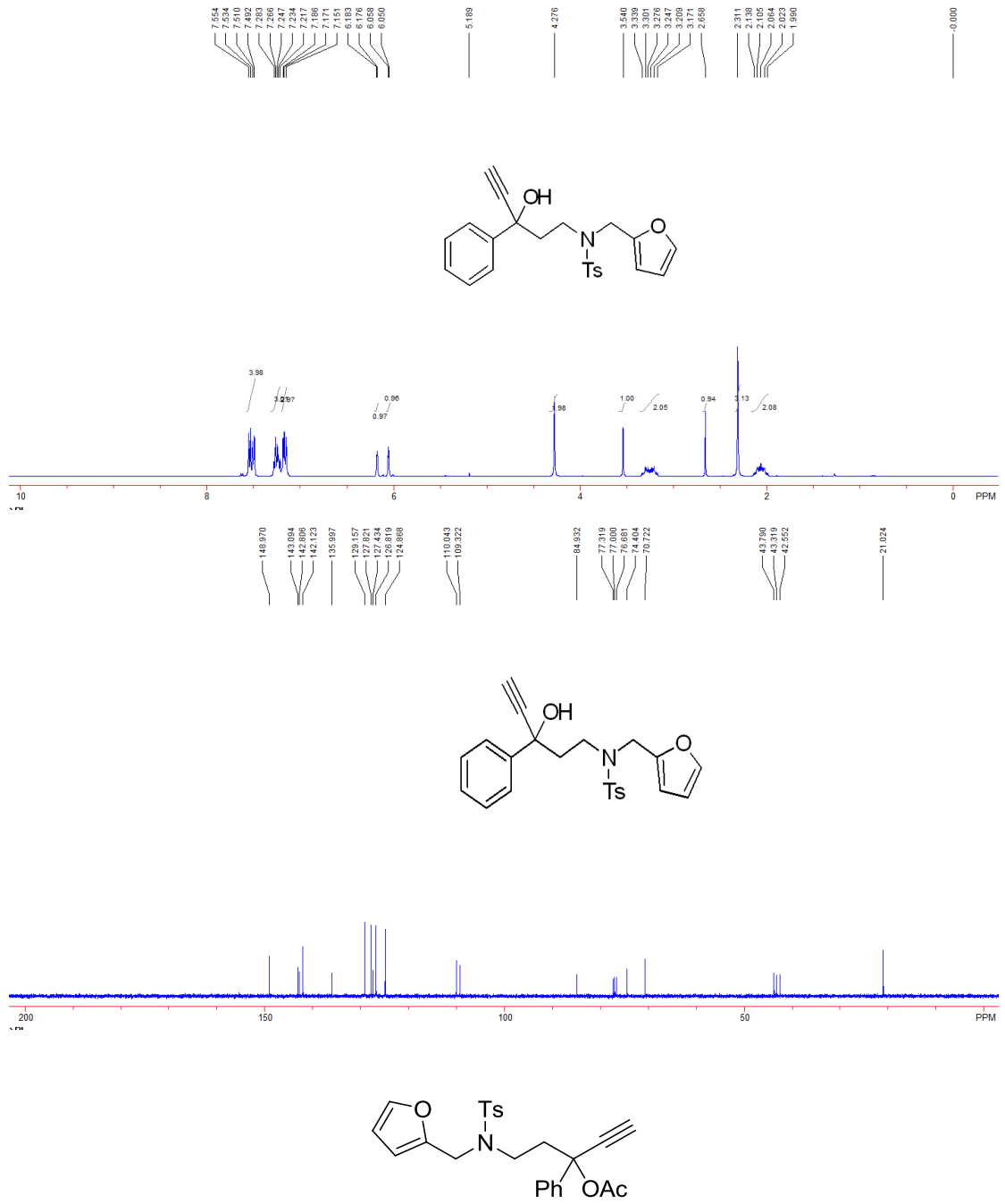
($CDCl_3$, 100 MHz, TMS) δ 195.6, 134.6, 131.8, 129.3, 128.5, 41.2, 25.4.



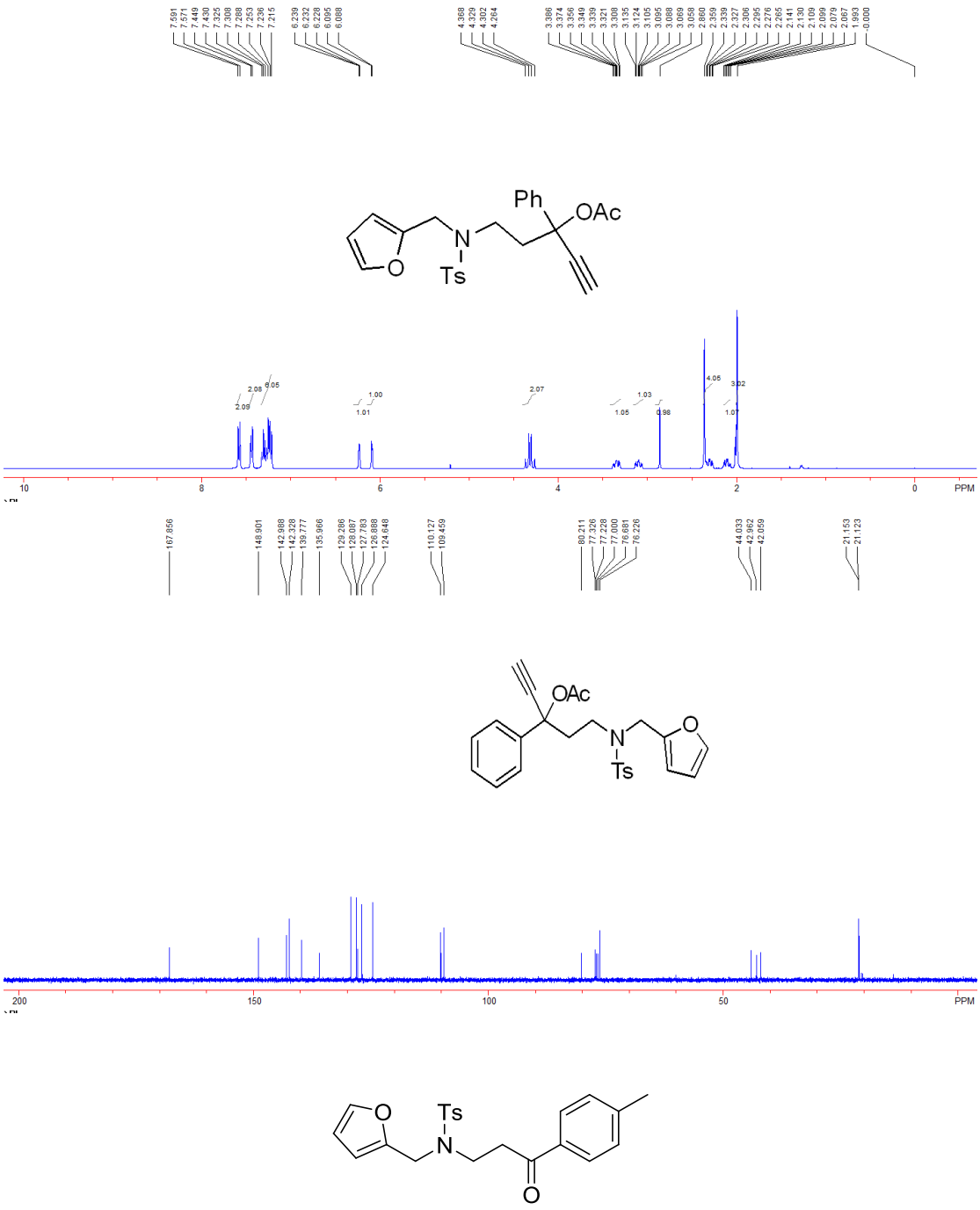
N-(furan-2-ylmethyl)-4-methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (S-3s): a colorless oil (4.5 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.89-7.87 (m, 2H, ArH), 7.68 (d, 2H, *J* = 8.0 Hz, ArH), 7.56 (d, 1H, *J* = 7.2 Hz, ArH), 7.45 (t, 2H, *J* = 8.0 Hz, ArH), 7.28-7.26 (m, 3H, ArH), 6.27-6.26 (m, 1H, ArH), 6.22 (d, 1H, *J* = 2.4 Hz, ArH), 4.45 (s, 2H, CH_2), 3.55 (t, 2H, *J* = 7.2 Hz, CH_2), 3.25-3.21 (m, 2H, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 198.3, 149.6, 143.3, 142.6, 136.3, 133.3, 129.6, 128.6, 128.0, 127.2, 110.5, 109.6, 107.0, 45.3, 43.4, 38.6, 21.5; IR (DCM) ν 2927, 1681, 1323, 1154, 1092, 814, 738, 725 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{22}NO_4S$ $[M + H]^+$ m/z 384.1264, found 384.1264.



N-(furan-2-ylmethyl)-N-(3-hydroxy-3-phenylpent-4-yn-1-yl)-4-methylbenzenesulfonamide (S-4s): a colorless oil (1.0 g, 56% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.55-7.49 (m, 4H, ArH), 7.28-7.22 (m, 3H, ArH), 7.19-7.15 (m, 3H, ArH), 6.18 (d, 1H, *J* = 2.8 Hz, ArH), 6.05 (d, 1H, *J* = 3.2 Hz, ArH), 4.28 (s, 2H, CH_2), 3.54 (s, 1H, OH), 3.34-3.17 (m, 2H, CH_2), 2.66 (s, 1H, CH), 2.31 (s, 3H, CH_3), 2.14-1.99 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.0, 143.1, 142.8, 142.1, 136.0, 129.1, 127.8, 127.4, 126.8, 124.9, 110.0, 109.3, 84.9, 74.4, 70.7, 43.8, 43.3, 42.5, 21.0; IR (DCM) ν 3473, 3289, 1598, 1448, 1331, 1153 cm^{-1}; HRMS (MALDI) calcd for $C_{23}H_{24}O_4$ NS $[M + H]^+$ m/z 410.1421, found 410.1477.

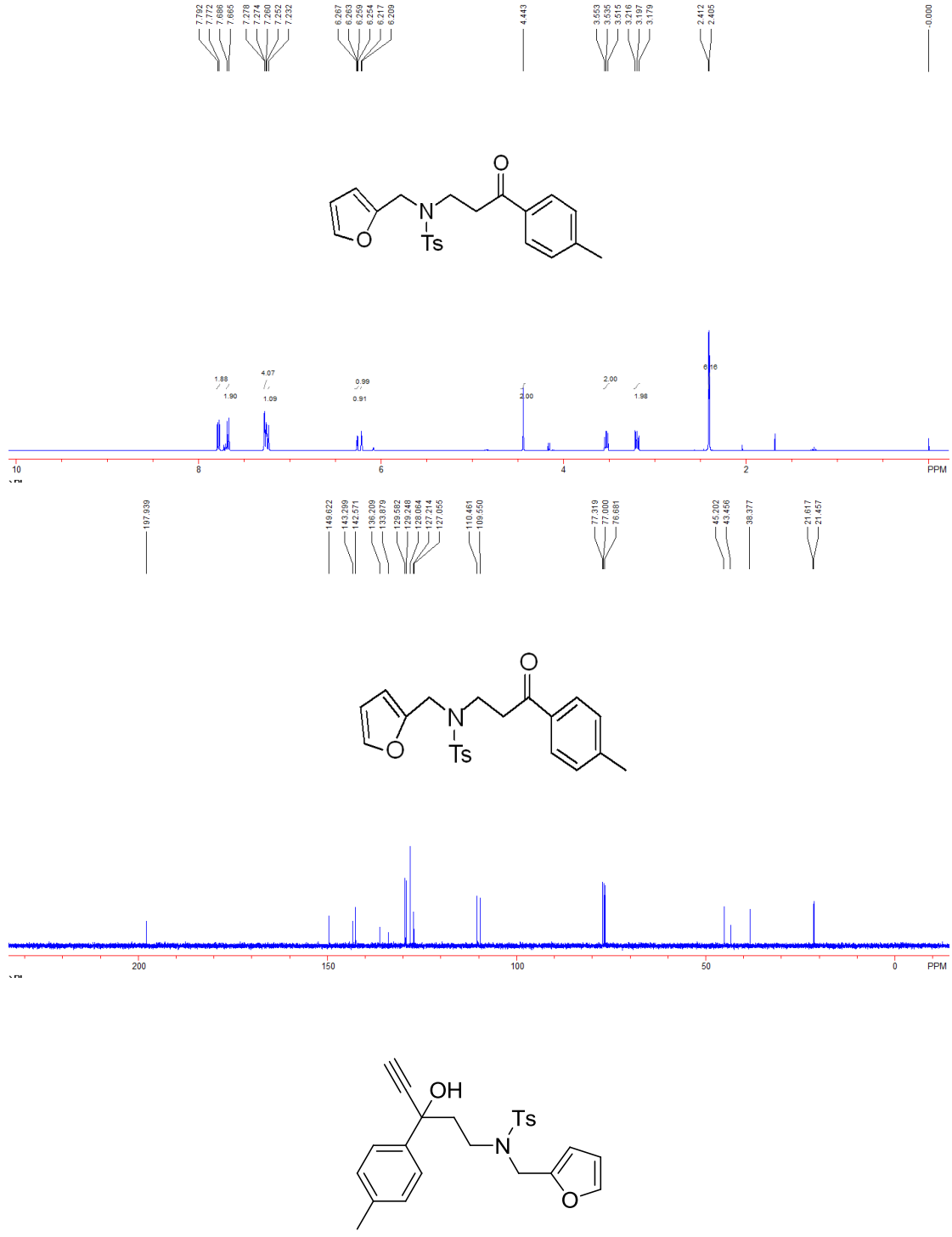


5-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-3-phenylpent-1-yn-3-yl acetate (Table 3, entry 1s): a colorless oil (1.0 g, 89% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 8.0 Hz, ArH), 7.44 (d, 2H, *J* = 8.0 Hz, ArH), 7.32-7.21 (m, 6H, ArH), 6.24-6.23 (m, 1H, ArH), 6.09 (d, 1H, J = 2.8 Hz, ArH), 4.31 (q, 2H, *J* = 15.6 Hz, CH_2), 3.39-3.31 (m, 1H, CH_2), 3.13-3.06 (m, 1H, CH_2), 2.86 (s, 1H, CH), 2.36-2.26 (m, 4H, CH_3 and CH_2), 2.14-2.07 (m, 1H, CH_2), 1.99 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.8, 148.9, 143.0, 142.3, 139.8, 136.0, 129.3, 128.1, 127.8, 126.9, 124.6, 110.1, 109.4, 80.2, 77.2, 76.2, 44.0, 43.0, 42.0, 21.15, 21.12; IR (DCM) ν 3294, 1750, 1338, 1224, 1156, 1011, 730, 700 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1792.



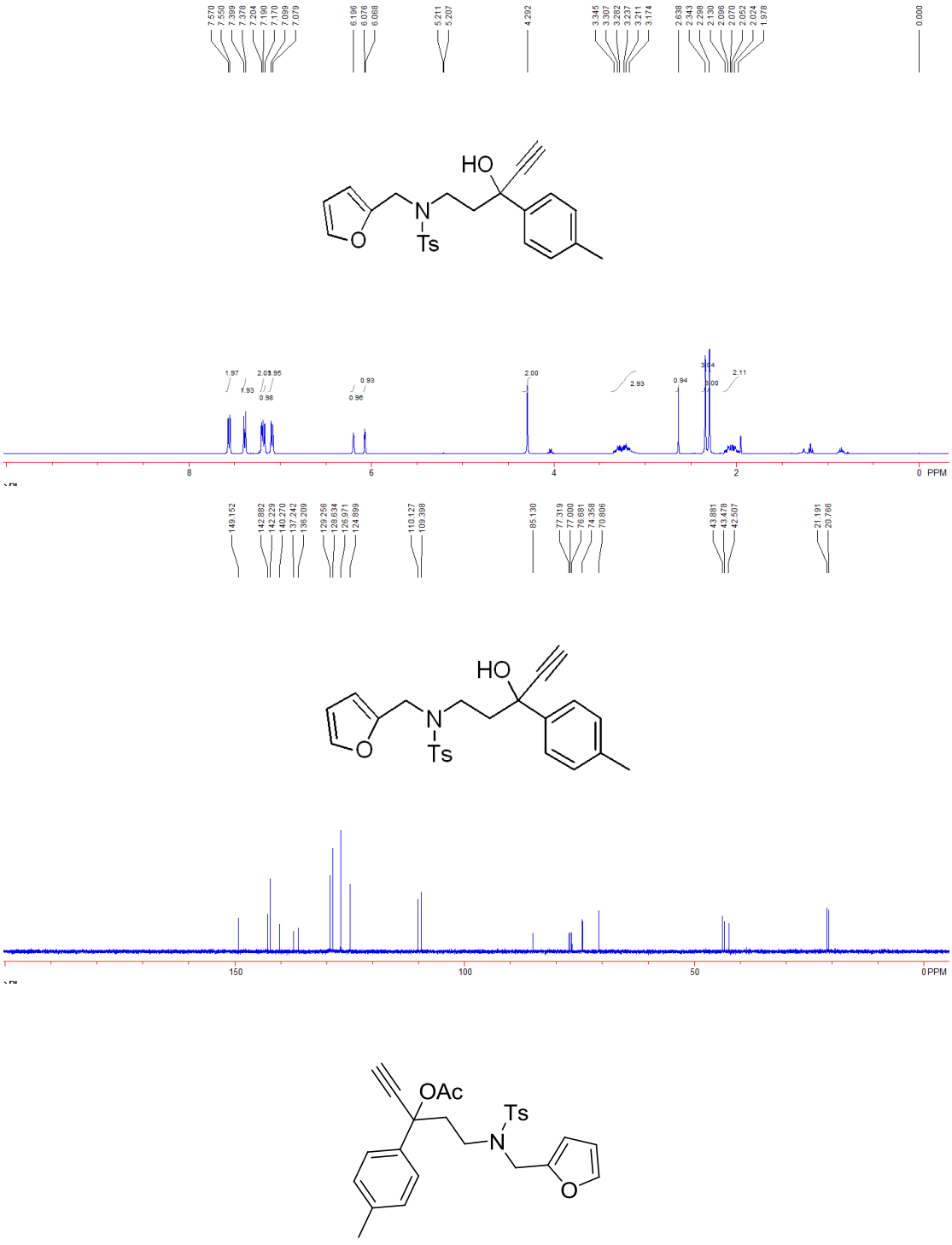
N-(furan-2-ylmethyl)-4-methyl-N-(3-oxo-3-(p-tolyl)propyl)benzenesulfonamide (S-3t): a white solid (1.8 g, 99% yield), mp: 82-84 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.78 (d, 2H, *J* = 8.0 Hz, ArH), 7.67 (d, 2H, *J* = 8.0 Hz, ArH), 7.28-7.25 (m, 4H, ArH), 7.23 (s, 1H, ArH), 6.26 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.21 (d, 1H, *J* = 3.2 Hz, ArH), 4.44 (s, 2H, CH_2), 3.53 (t, 2H, *J* = 7.2 Hz, CH_2), 3.20 (t, 2H, *J* = 7.2 Hz, CH_2), 2.41 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 197.9, 149.6, 143.3, 142.6, 136.2, 133.9, 129.6, 129.2, 128.1, 127.2, 127.0, 110.5, 109.5, 45.2, 43.4, 38.4, 21.6, 21.4; IR (DCM) ν 3279, 2921, 1676, 1605, 1321, 1154, 813, 721 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{24}NO_4S$ $[M + H]^+$ m/z 398.1421, found

398.1424.



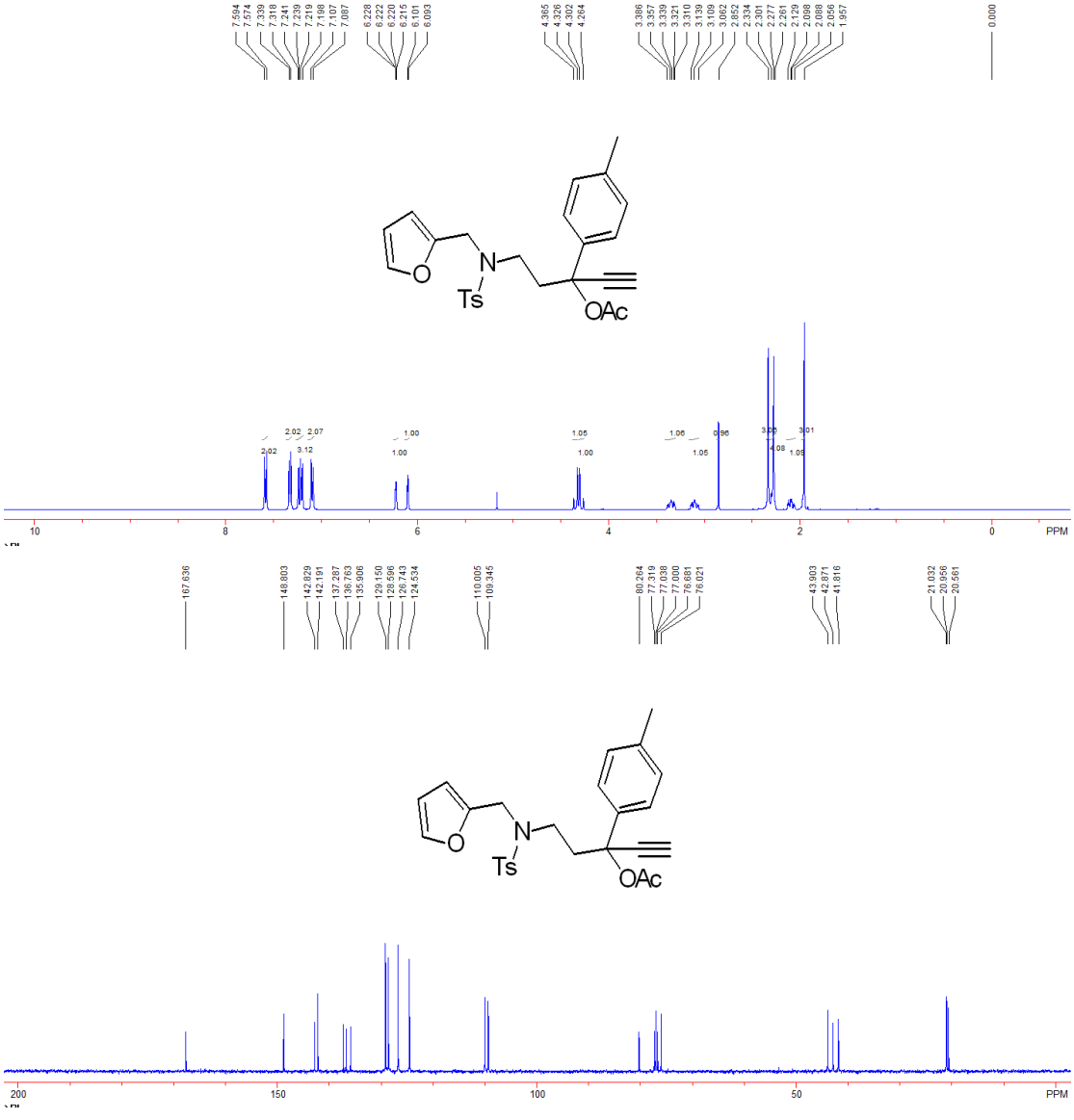
N-(furan-2-ylmethyl)-N-(3-hydroxy-3-(p-tolyl)pent-4-yn-1-yl)-4-methylbenzenesulfonamide (S-4t): a white solid (1.1 g, 47% yield), mp: 130-132 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.56 (d, 2H, *J* = 8.0 Hz, ArH), 7.38 (d, 2H, *J* = 8.0 Hz, ArH), 7.19 (d, 2H, *J* = 5.6 Hz, ArH), 7.17 (s, 1H, ArH), 7.09 (d, 2H, *J* = 8.0 Hz, ArH), 6.20 (s, 1H, ArH), 6.07 (d, 1H, *J* = 3.2 Hz, ArH), 4.29 (s, 2H, CH_2), 3.34-3.17 (m, 3H, OH and CH_2), 2.64 (s, 1H, CH), 2.34 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.13-1.98 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.1, 142.9, 142.2,

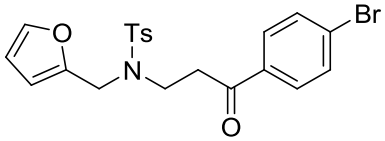
140.3, 137.2, 136.2, 129.2, 128.6, 127.0, 124.9, 110.1, 109.4, 85.1, 74.3, 70.8, 43.9, 43.5, 42.5, 21.2, 20.8; IR (DCM) ν 3481, 3289, 1509, 1332, 1155, 815, 731 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}NO_3S$ $[M + NH_4]^+$ m/z 406.1471, found 406.1477.



5-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-3-(p-tolyl)pent-1-yn-3-yl acetate (Table 3, entry 2t): a colorless oil (967 mg, 77% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 8.0 Hz, ArH), 7.33 (d, 2H, *J* = 8.0 Hz, ArH), 7.24-7.20 (m, 3H, ArH), 7.10 (d, 2H, *J* = 8.0 Hz, ArH), 6.22 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.10 (d, 1H, *J* = 3.2 Hz, ArH),

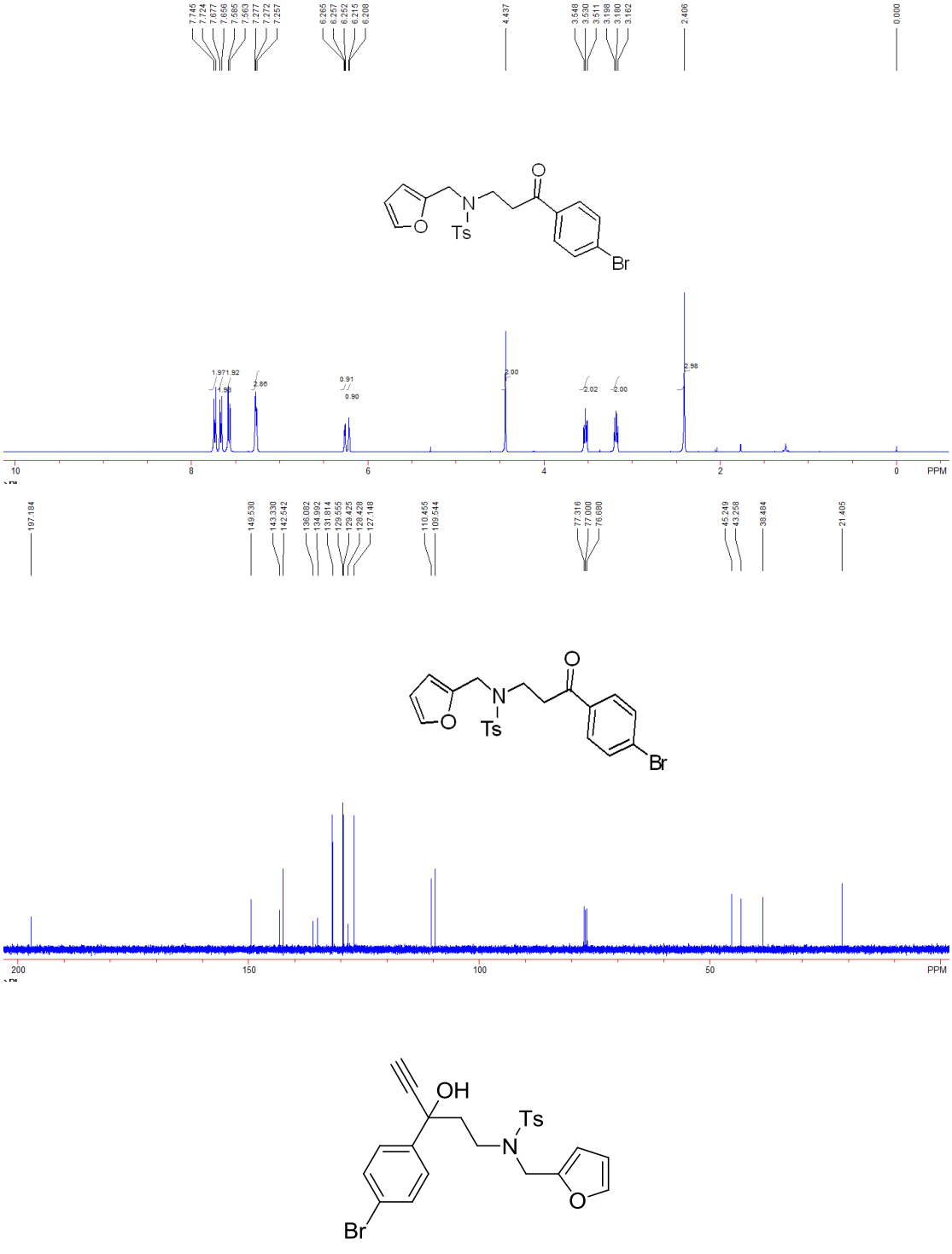
4.34 (d, 1H, *J* = 15.6 Hz, CH_2), 4.28 (d, 1H, *J* = 15.6 Hz, CH_2), 3.39-3.31 (m, 1H, CH_2), 3.14-3.06 (m, 1H, CH_2), 2.85 (s, 1H, CH), 2.33 (s, 3H, CH_3), 2.30-2.26 (m, 4H, CH_3 and CH_2), 2.13-2.06 (m, 1H, CH_2), 1.96 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.6, 148.8, 142.8, 142.2, 137.3, 136.8, 135.9, 129.1, 128.6, 126.7, 124.5, 110.0, 109.3, 80.3, 77.0, 76.0, 43.9, 42.9, 41.8, 21.0, 20.9, 20.6; IR (DCM) ν 3271, 1750, 1340, 1225, 1158, 1011, 816 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_5S$ $[M + NH_4]^+$ m/z 483.1948, found 483.1948.





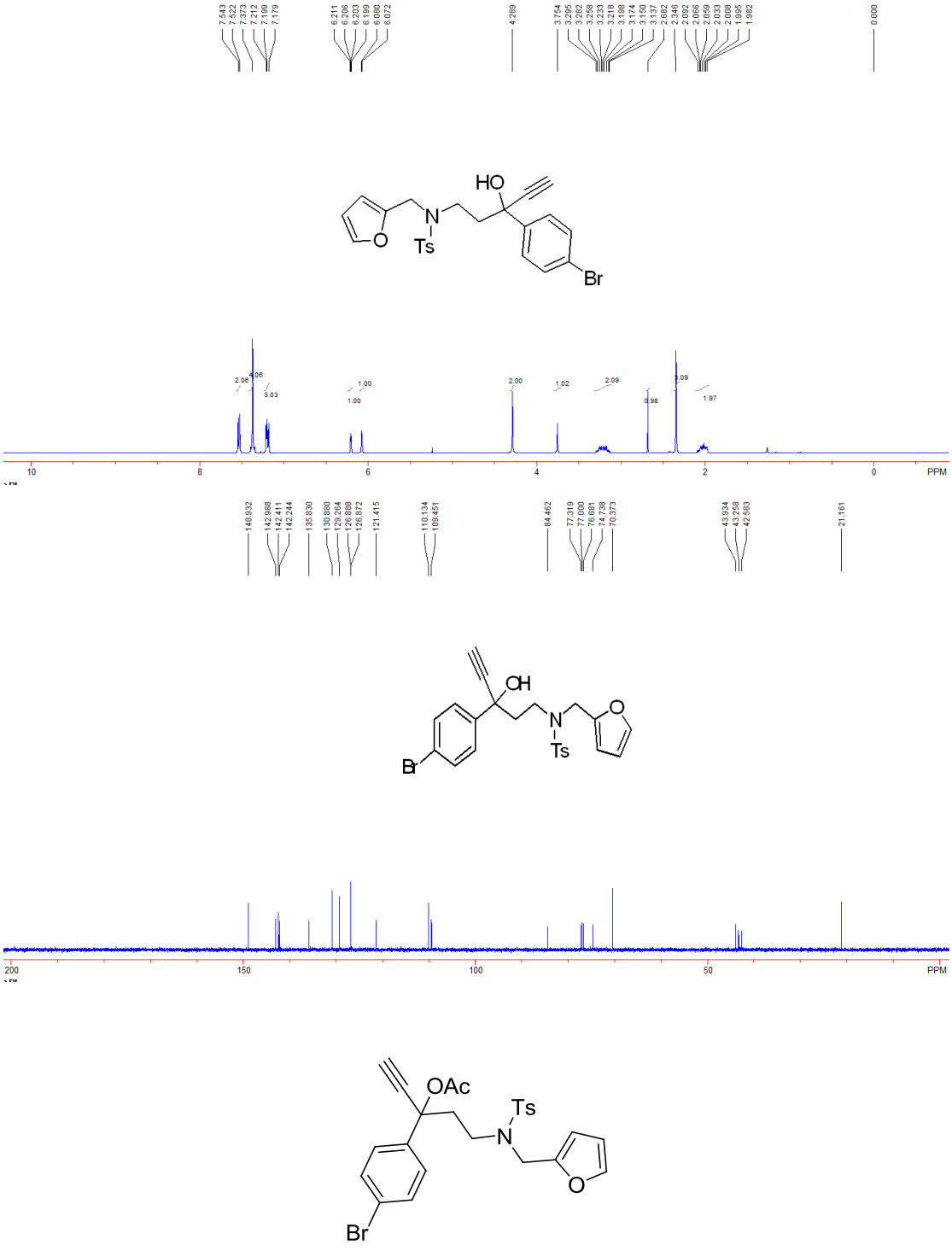
N-(3-(4-bromophenyl)-3-oxopropyl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-3u): a white solid (1.4 g, 99% yield), mp: 98-100 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ

7.73 (d, 2H, *J* = 8.4 Hz, ArH), 7.67 (d, 2H, *J* = 8.4 Hz, ArH), 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 7.28-7.16 (m, 3H, ArH), 6.26-6.25 (m, 1H, ArH), 6.21 (d, 1H, *J* = 2.8 Hz, ArH), 4.44 (s, 2H, CH_2), 3.53 (t, 2H, *J* = 7.2 Hz, CH_2), 3.18 (t, 2H, *J* = 7.2 Hz, CH_2), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 197.2, 149.5, 143.3, 142.5, 136.1, 135.0, 131.8, 129.5, 129.4, 128.4, 127.1, 110.4, 109.5, 45.2, 43.2, 38.5, 21.4; IR (DCM) ν 2927, 1683, 1584, 1320, 1154, 1069, 733 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{24}BrN_2O_4S$ $[M + NH_4]^+$ m/z 479.0635, found 479.0635.

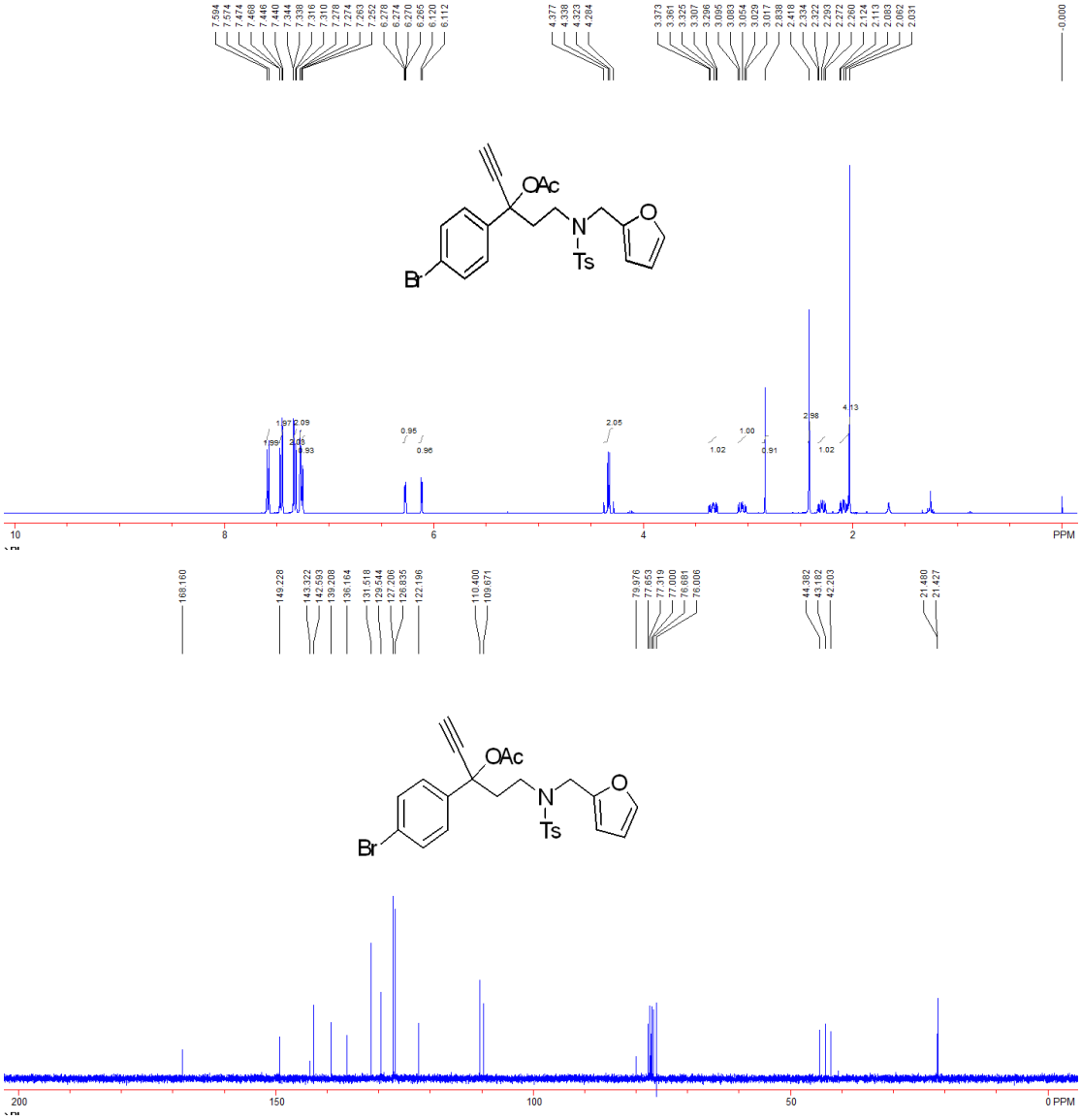


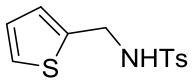
N-(3-(4-bromophenyl)-3-hydroxypent-4-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulf

onamide (S-4u): a white solid (994 mg, 54% yield), mp: 84-86 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.53 (d, 2H, *J* = 8.4 Hz, ArH), 7.37 (s, 4H, ArH), 7.21-7.18 (m, 3H, ArH), 6.20 (dd, 1H, J_1 = 2.8 Hz, J_2 = 1.6 Hz, ArH), 6.08 (d, 1H, *J* = 3.2 Hz, ArH), 4.29 (s, 2H, CH_2), 3.75 (s, 1H, OH), 3.29-3.14 (m, 2H, CH_2), 2.68 (s, 1H, CH), 2.35 (s, 3H, CH_3), 2.09-1.97 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.9, 143.0, 142.4, 142.2, 135.8, 130.9, 129.3, 126.89, 126.87, 121.4, 110.1, 109.4, 84.5, 74.7, 70.4, 43.9, 43.2, 42.6, 21.2; IR (DCM) ν 3469, 3290, 1486, 1331, 1154, 1009 cm^{-1}; HRMS (MALDI) calcd for $C_{23}H_{23}O_4NBrS$ $[M + H]^+$ m/z 488.0526, found 488.0521.

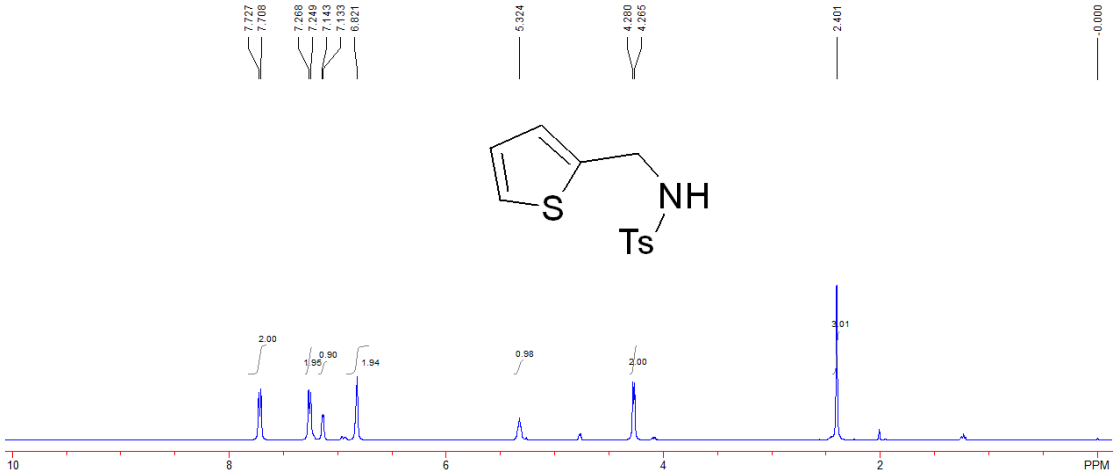


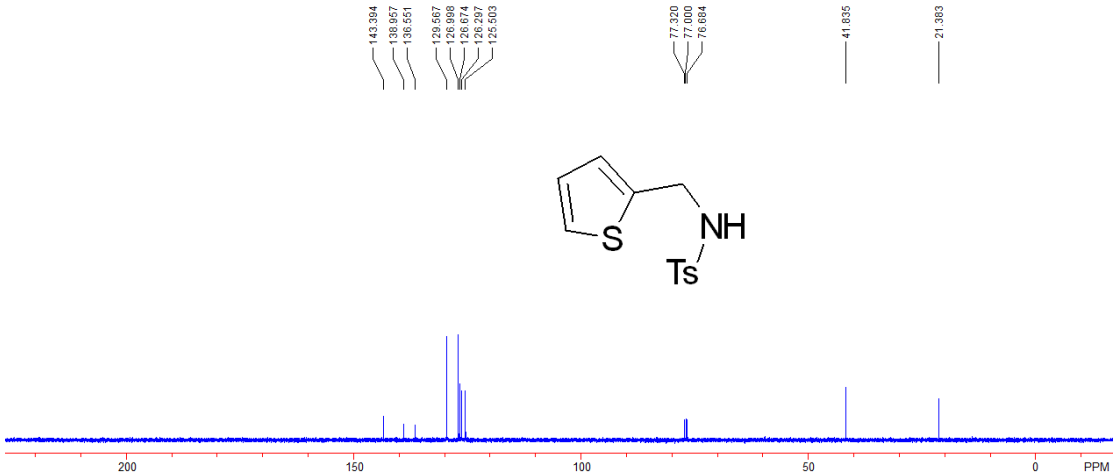
3-(4-bromophenyl)-5-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)pent-1-yn-3-yl acetate (Table 3, entry 2u): a white solid (874 g, 84% yield), mp: 149-151 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, J = 8.0 Hz, ArH), 7.45 (dd, 2H, J_1 = 11.2 Hz, J_2 = 2.4 Hz, ArH), 7.33 (dd, 2H, J_1 = 11.2 Hz, J_2 = 2.4 Hz, ArH), 7.28-7.26 (m, 2H, ArH), 7.25 (s, 1H, ArH), 6.27 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.12 (d, 1H, J = 3.2 Hz, ArH), 4.36 (d, 1H, J = 15.6 Hz, CH_2), 4.30 (d, 1H, J = 15.6 Hz, CH_2), 3.37-3.30 (m, 1H, CH_2), 3.09-3.02 (m, 1H, CH_2), 2.84 (s, 1H, CH), 2.42 (s, 3H, CH_3), 2.33-2.26 (m, 1H, CH_2), 2.14-2.03 (m, 4H, CH_3 and CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.2, 149.2, 143.3, 142.6, 139.2, 136.2, 131.5, 129.5, 127.2, 126.8, 122.2, 110.4, 109.7, 80.0, 77.6, 76.0, 44.4, 43.2, 42.2, 21.5, 21.4; IR (DCM) ν 3300, 1750, 1338, 1222, 1157, 1009, 815, 732 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}BrN_2O_5S$ $[M + NH_4]^+$ m/z 547.0897, found 547.0900.

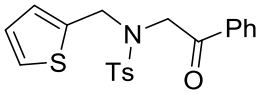




4-methyl-N-(thiophen-2-ylmethyl)benzenesulfonamide (S-2-10): a white solid (9.1 g, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.72 (d, 2H, *J* = 7.6 Hz, ArH), 7.26 (d, 2H, *J* = 7.6 Hz, ArH), 7.14 (d, 1H, *J* = 4.0 Hz, ArH), 6.82 (s, 2H, ArH), 5.32 (br, 1H, NH), 4.27 (d, 2H, *J* = 6.0 Hz, CH_2), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 143.4, 138.9, 136.5, 129.6, 127.0, 126.7, 126.3, 125.5, 41.8, 21.4; IR (DCM) ν 3287, 1264, 1157, 1036, 813, 735 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{17}N_2O_2S_2$ $[M + NH_4]^+$ m/z 285.0726, found 285.0730.

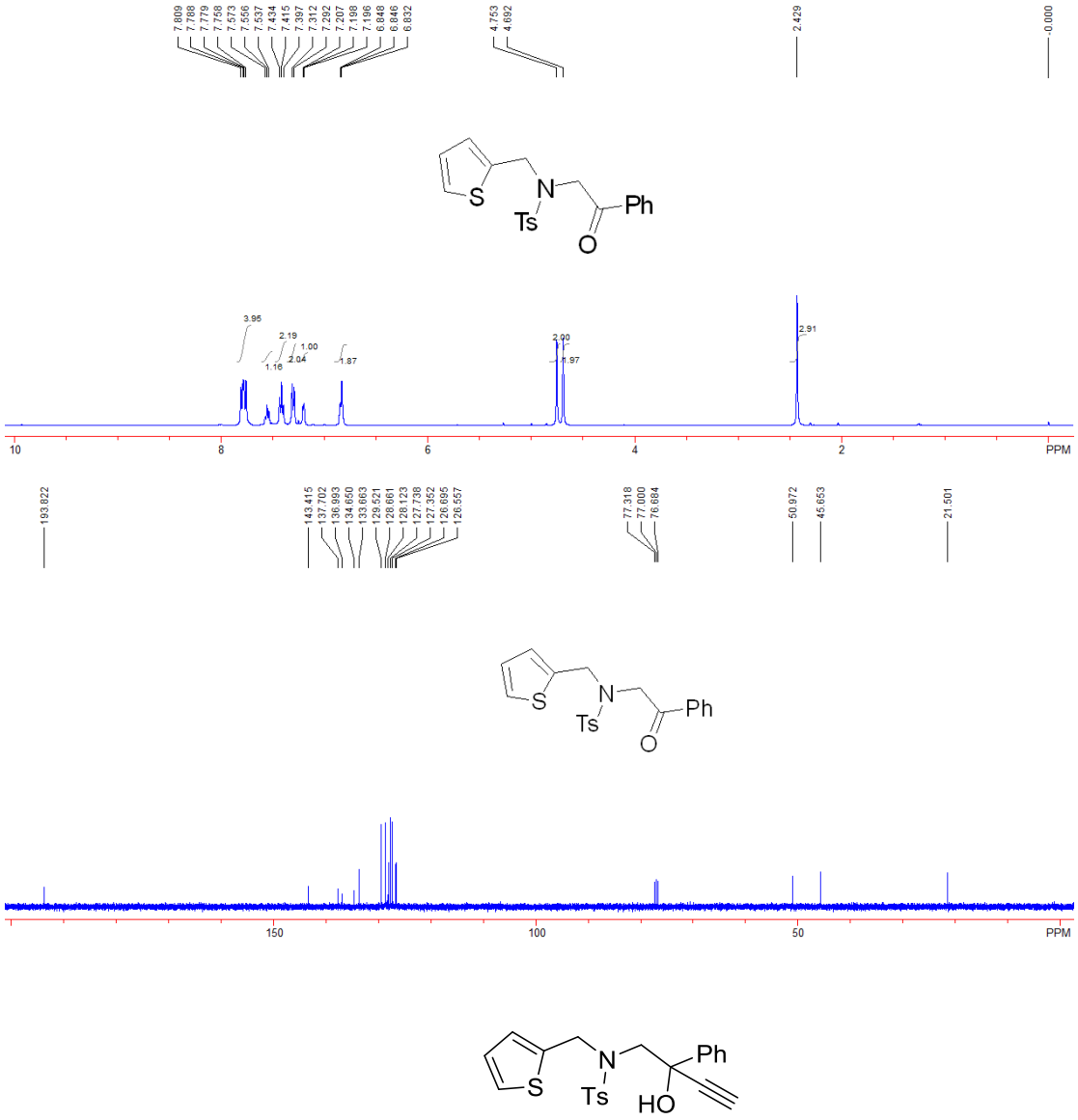






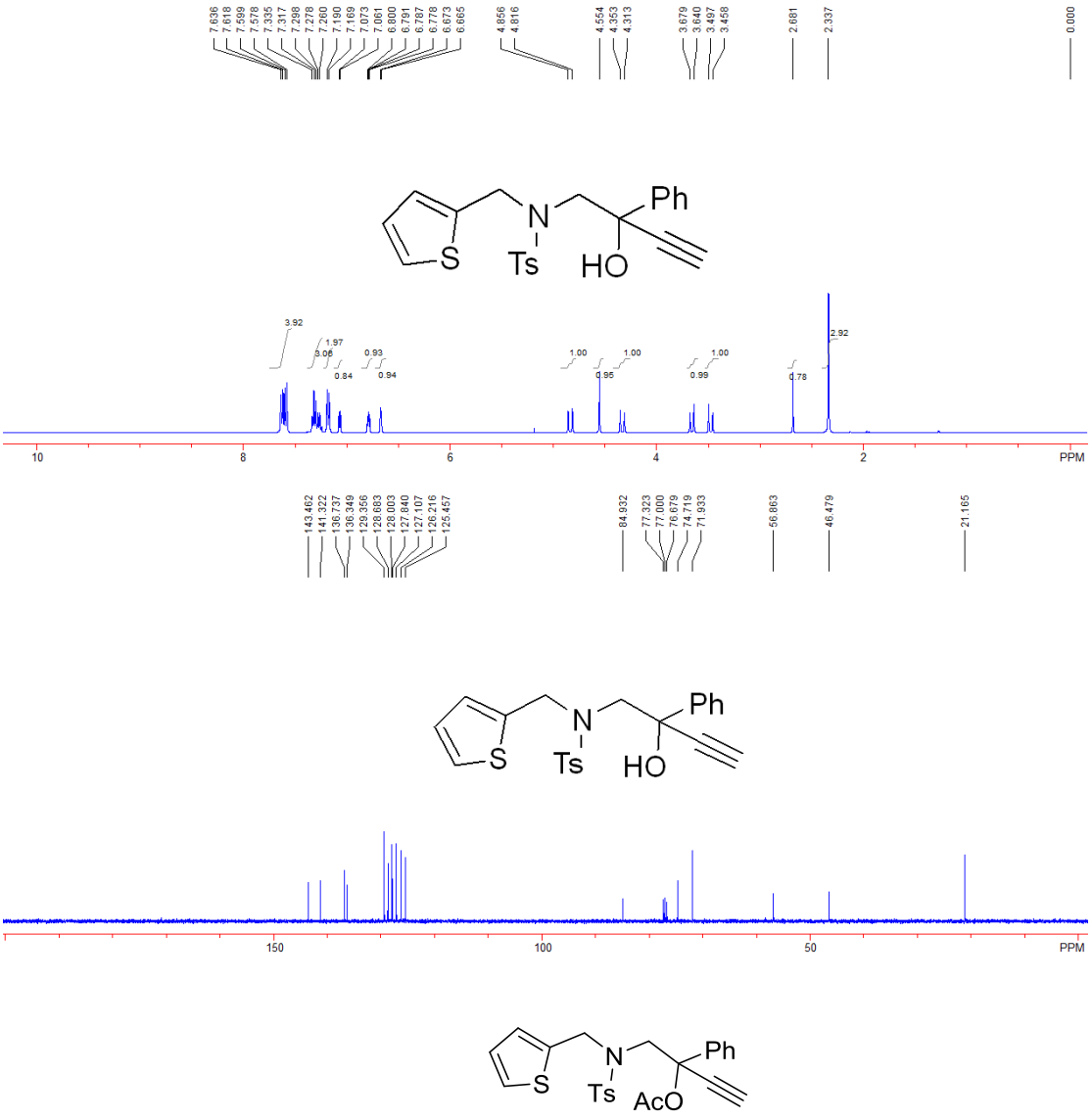
4-methyl-N-(2-oxo-2-phenylethyl)-N-(thiophen-2-ylmethyl)benzenesulfonamide (S-3-10): a white solid (2.8 g, 72% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.81-7.76 (m, 4H, ArH), 7.57-7.54 (m, 1H, ArH), 7.43-7.40 (m, 2H, ArH), 7.30 (d, 2H, *J* = 8.0 Hz, ArH), 7.21-7.20 (m, 1H, ArH), 6.85-6.83 (m, 2H, ArH), 4.75 (s, 2H, CH_2), 4.69 (s, 2H, CH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR

($CDCl_3$, 100 MHz, TMS) δ 193.8, 143.4, 137.7, 137.0, 134.6, 133.7, 129.5, 128.7, 128.1, 127.7, 127.3, 126.7, 126.5, 51.0, 45.6, 21.5; IR (DCM) ν 3061, 1698, 1334.5, 1154, 1091, 908, 746 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{20}NO_3S_2$ $[M + H]^+$ m/z 386.0879, found 386.0882.

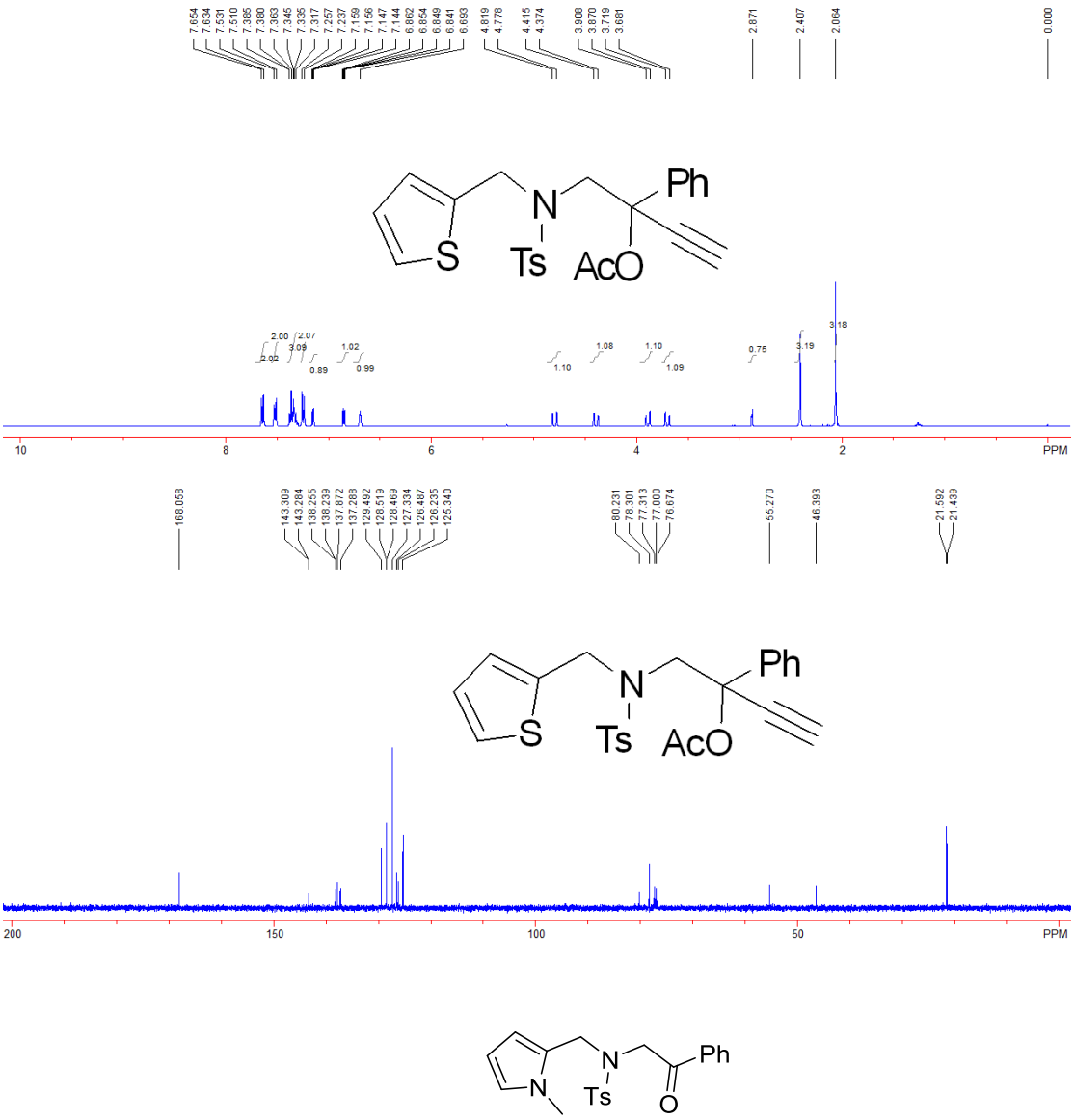


N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methyl-N-(thiophen-2-ylmethyl)benzenesulfonamide (S-4-10): a white solid (1.04 g, 63% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64-7.58 (m, 4H, ArH), 7.33-7.26 (m, 3H, ArH), 7.18 (d, 2H, *J* = 7.6 Hz, ArH), 7.07 (d, 1H, *J* = 4.8 Hz, ArH), 6.80-6.78 (m, 1H, ArH), 6.67 (d, 1H, *J* = 3.2 Hz, ArH), 4.84 (d, 1H, *J* = 16.0 Hz, CH_2), 4.55 (s, 1H, OH), 4.33 (d, 1H, *J* = 16.0 Hz, CH_2), 3.66 (d, 1H, *J* = 15.6 Hz, CH_2), 3.48 (d, 1H, *J* = 15.6 Hz, CH_2), 2.68 (s, 1H, CH), 2.34 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 143.5, 141.3, 136.7, 136.3, 129.3, 128.7, 128.0, 127.8, 127.1, 126.2, 125.4, 84.9, 74.7, 71.9, 56.9, 46.5, 21.2; IR (DCM) ν 3464, 3286, 1448, 1328, 1151, 1088, 698 cm^{-1}; HRMS (ESI) calcd for

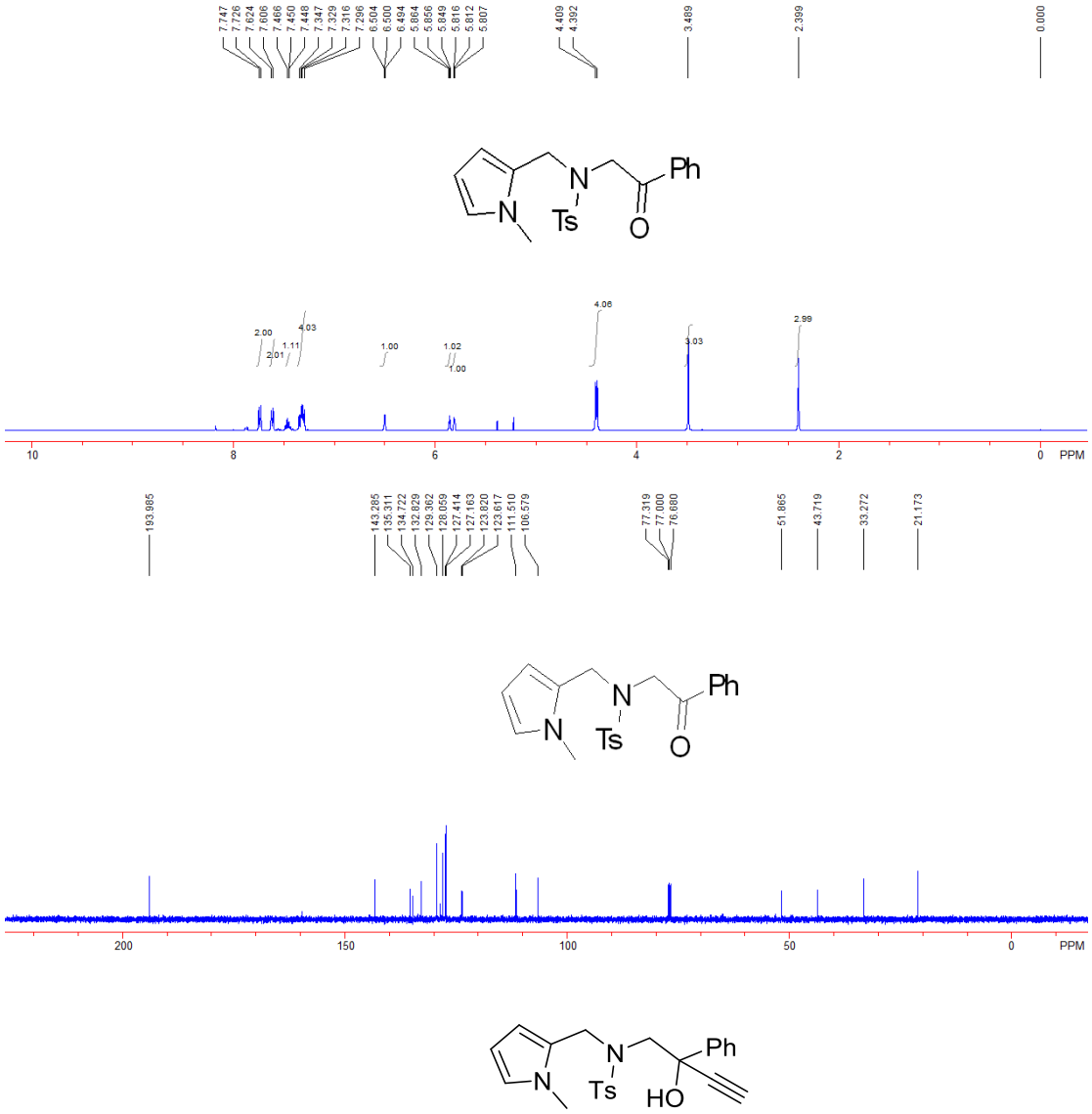
$C_{22}H_{21}NNaO_3S_2$ $[M + Na]^+$ m/z 434.0855, found 434.0856.



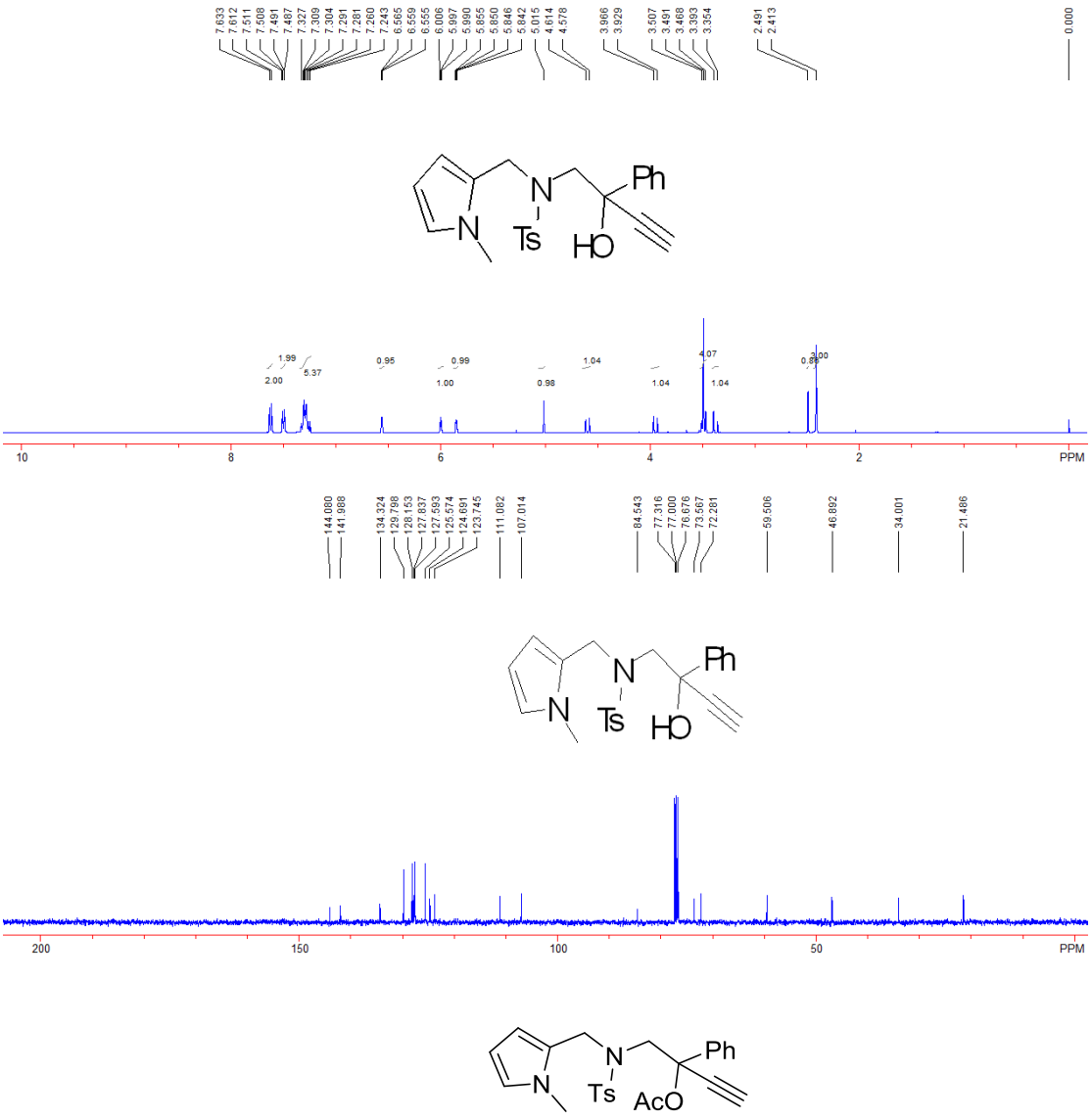
1-((4-methyl-N-(thiophen-2-ylmethyl)phenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (10): a white solid (1.00 g, 87% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64 (d, 2H, *J* = 8.0 Hz, ArH), 7.52 (d, 2H, *J* = 8.4 Hz, ArH), 7.38-7.32 (m, 3H, ArH), 7.25 (d, 2H, *J* = 8.0 Hz, Ar), 7.16-7.14 (m, 1H, ArH), 6.86-6.84 (m, 1H, ArH), 6.69 (s, 1H, ArH), 4.80 (d, 1H, *J* = 16.4 Hz, CH_2), 4.39 (d, 1H, *J* = 16.4 Hz, CH_2), 3.89 (d, 1H, *J* = 15.2 Hz, CH_2), 3.70 (d, 1H, *J* = 15.2 Hz, CH_2), 2.87 (s, 1H, CH), 2.41 (s, 3H, CH_3), 2.06 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.0, 143.31, 143.28, 138.25, 138.24, 137.9, 137.3, 129.5, 128.52, 128.47, 127.3, 126.5, 126.2, 125.3, 80.2, 78.3, 55.3, 46.4, 21.6, 21.4; IR (DCM) ν 3268, 1751, 1327, 1220, 1155, 995, 734, 698 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_4S_2$ $[M + NH_4]^+$ m/z 471.1407, found 471.1407.



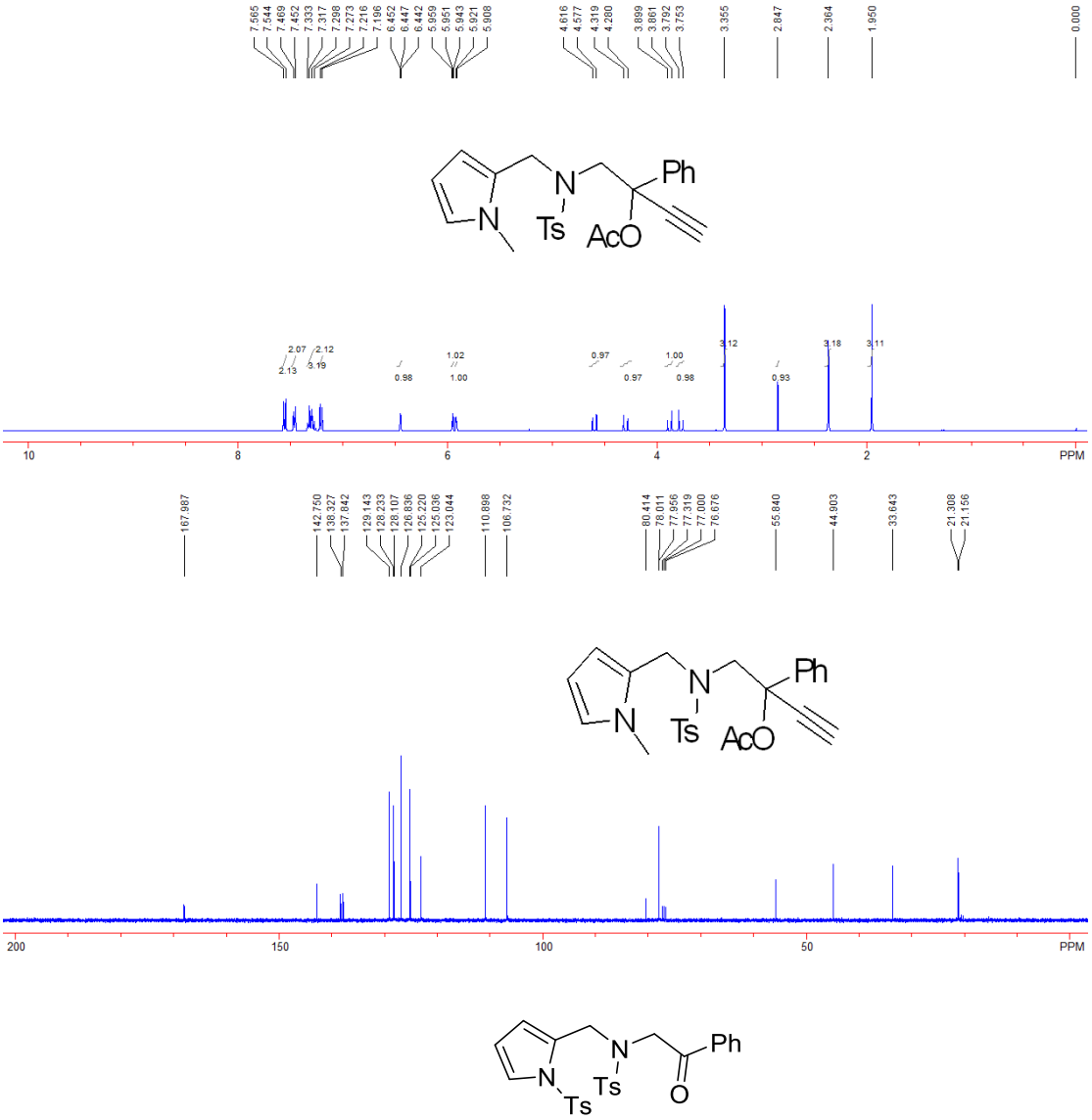
4-methyl-N-((1-methyl-1H-pyrrol-2-yl)methyl)-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-3-11a): a white solid (4.6 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.74 (d, 2H, *J* = 8.4 Hz, ArH), 7.61 (d, 2H, *J* = 7.2 Hz, ArH), 7.47-7.45 (m, 1H, ArH), 7.35-7.30 (m, 4H, ArH), 6.50-6.49 (m, 1H, ArH), 5.86-5.85 (m, 1H, ArH), 5.82-5.81 (m, 1H, ArH), 4.41 (s, 2H, CH_2), 4.39 (s, 2H, CH_2), 3.49 (s, 3H, CH_3), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 194.0, 143.3, 135.3, 134.7, 132.8, 129.4, 128.0, 127.4, 127.2, 123.8, 123.6, 111.5, 106.6, 51.9, 43.7, 33.3, 21.2; IR (DCM) ν 1699, 1336, 1156, 1091, 904, 727 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{26}N_3O_3S$ $[M + NH_4]^+$ m/z 400.1689, found 400.1694.



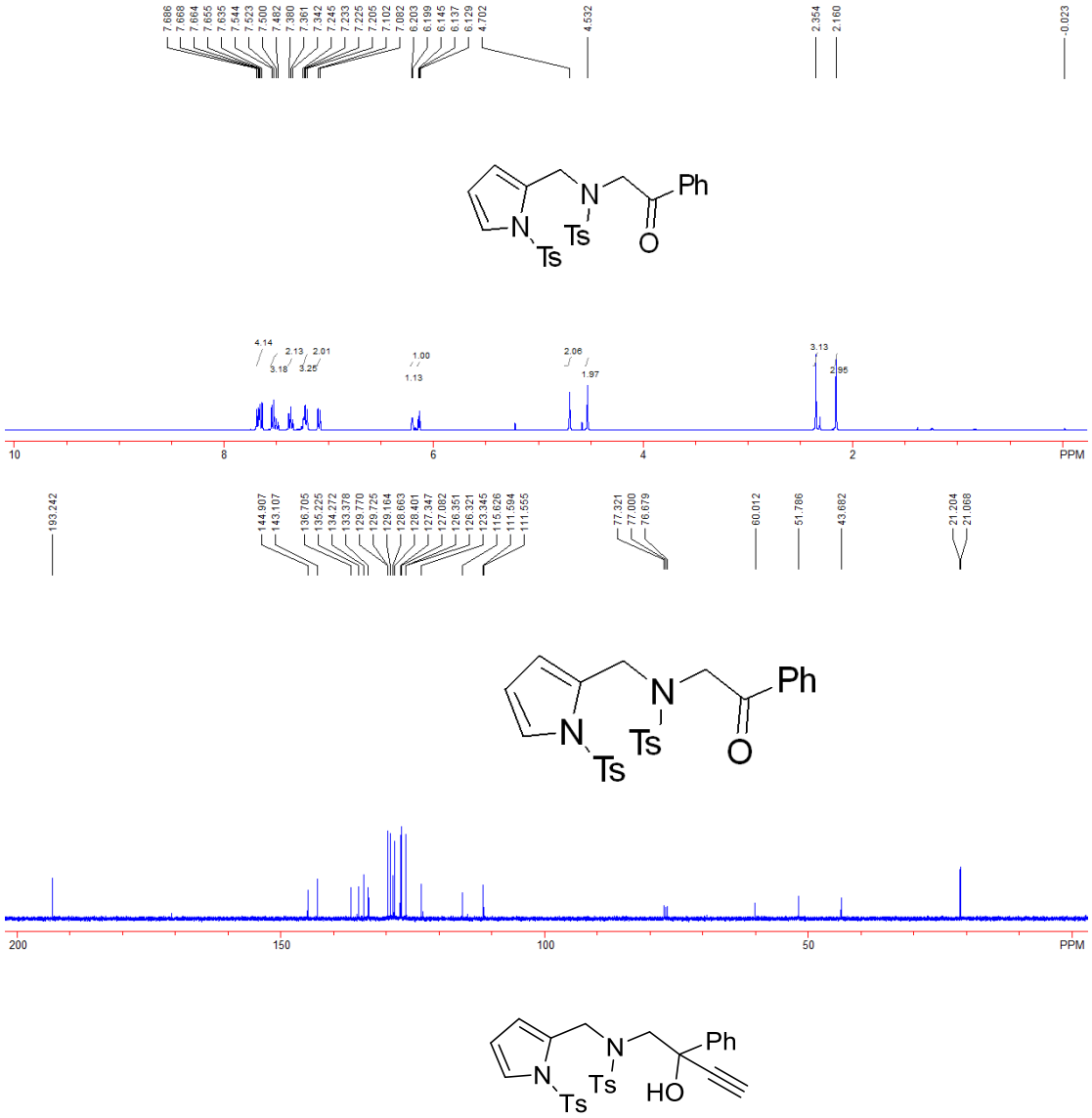
N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methyl-N-((1-methyl-1H-pyrrol-2-yl)methyl)benzenesulfonamide (S-4-11a): a white solid (2.86 g, 58% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.62 (d, 2H, *J* = 8.4 Hz, ArH), 7.51-7.49 (m, 2H, ArH), 7.33-7.24 (m, 5H, ArH), 6.56-6.55 (m, 1H, ArH), 6.00 (t, 1H, *J* = 2.8 Hz, ArH), 5.85-5.84 (m, 1H, ArH), 5.01 (s, 1H, OH), 4.60 (d, 1H, *J* = 14.4 Hz, CH_2), 3.95 (d, 1H, *J* = 14.4 Hz, CH_2), 3.51-3.47 (m, 4H, CH_2 and CH_3), 3.37 (d, 1H, *J* = 15.6 Hz, CH_2), 2.49 (s, 1H, CH), 2.41 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.1, 142.0, 134.3, 129.8, 128.1, 127.8, 127.6, 125.6, 124.7, 123.7, 111.1, 107.0, 84.5, 73.6, 72.3, 59.5, 46.9, 34.0, 21.5; IR (DCM) ν 3439, 3289, 1328, 1153, 1088, 905, 699 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_3S$ $[M + NH_4]^+$ m/z 409.1580, found 409.1580.



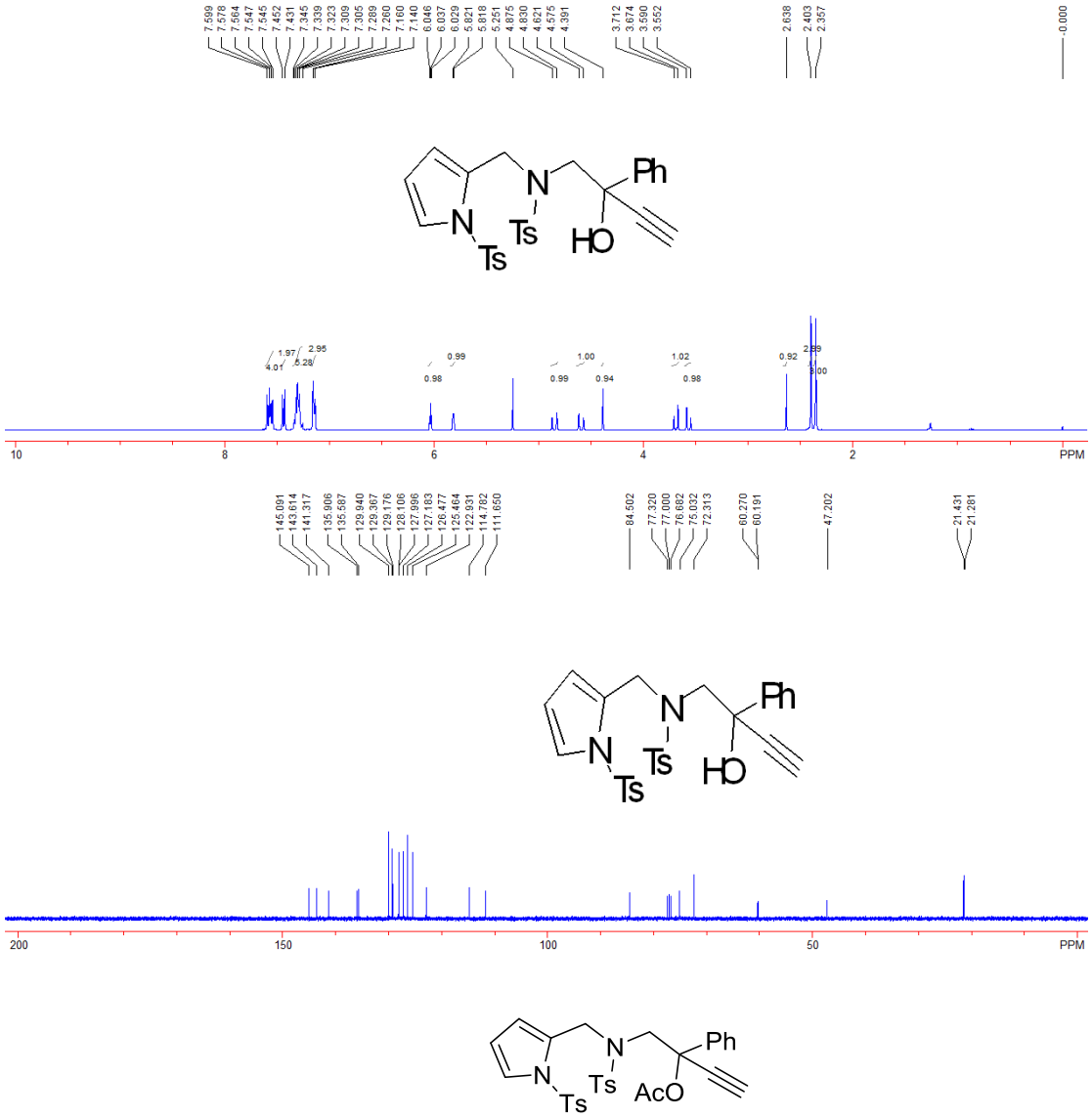
1-((4-methyl-N-((1-methyl-1H-pyrrol-2-yl)methyl)phenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (11a): a white solid (1.84 g, 82% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.55 (d, 2H, *J* = 8.4 Hz, ArH), 7.46 (d, 2H, *J* = 6.8 Hz, ArH), 7.33-7.27 (m, 3H, ArH), 7.21 (d, 2H, *J* = 8.4 Hz, Ar), 6.45-6.44 (m, 1H, ArH), 5.96-5.94 (m, 1H, ArH), 5.92-5.91 (m, 1H, ArH), 4.60 (d, 1H, *J* = 15.6 Hz, CH_2), 4.30 (d, 1H, *J* = 15.6 Hz, CH_2), 3.88 (d, 1H, *J* = 15.2 Hz, CH_2), 3.77 (d, 1H, *J* = 15.2 Hz, CH_2), 3.35 (s, 3H, CH_3), 2.85 (s, 1H, CH), 2.36 (s, 3H, CH_3), 1.95 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.0, 142.7, 138.3, 137.8, 129.1, 128.2, 128.1, 126.8, 125.2, 125.0, 123.0, 110.9, 106.7, 80.4, 78.0, 77.9, 55.8, 44.9, 33.6, 21.3, 21.1; IR (DCM) ν 3267, 1750, 1222, 1155, 995, 732, 699 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}N_3O_4S$ $[M + NH_4]^+$ m/z 468.1952, found 468.1955.



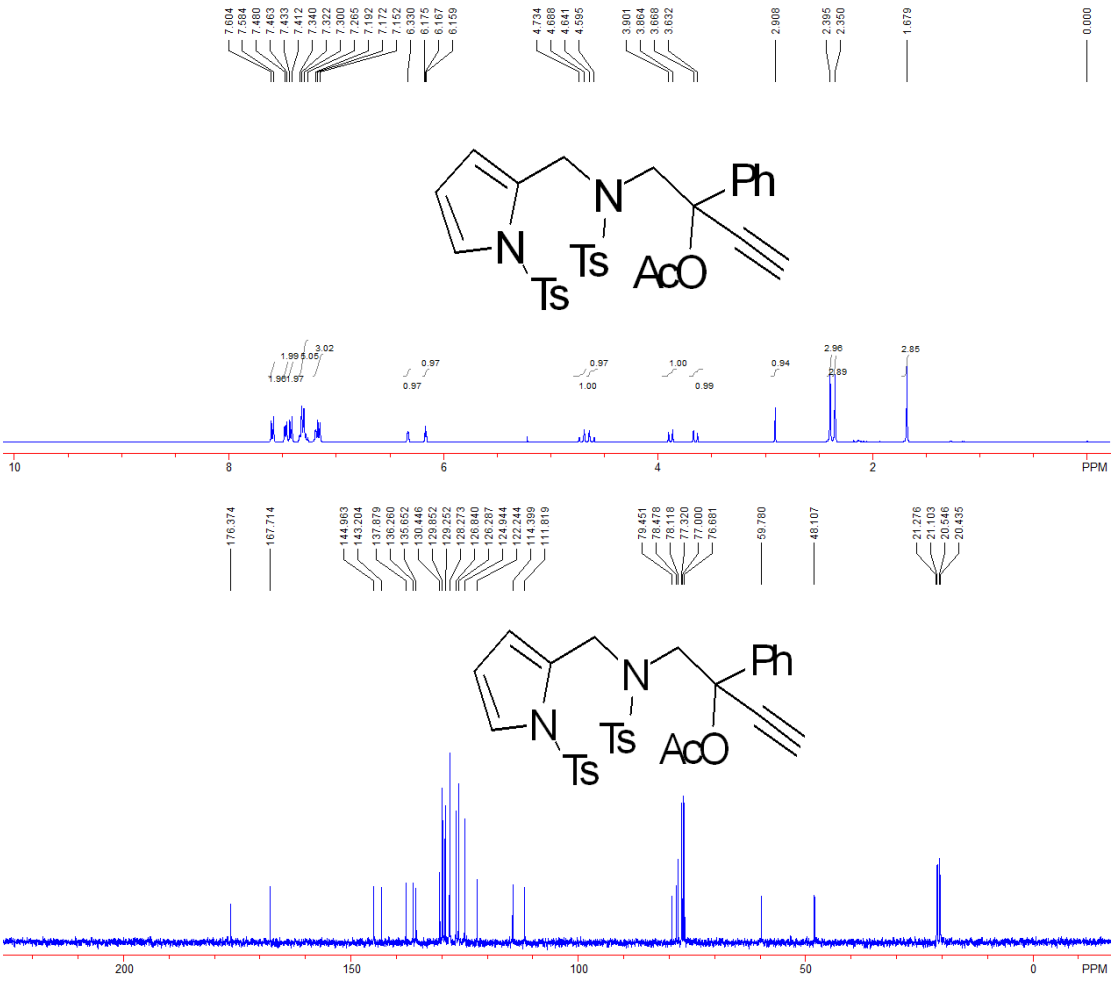
4-methyl-N-(2-oxo-2-phenylethyl)-N-((1-tosyl-1H-pyrrol-2-yl)methyl)benzenesulfonamide (S-3-11b): a white solid (3.1 g, 85% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.67-7.63 (m, 4H, ArH), 7.54-7.48 (m, 3H, ArH), 7.36 (t, 2H, *J* = 7.6 Hz, ArH), 7.24-7.20 (m, 3H, ArH), 7.09 (d, 2H, *J* = 8.0 Hz, ArH), 6.203-6.199 (m, 1H, ArH), 6.14-6.13 (m, 1H, ArH), 4.70 (s, 2H, CH_2), 4.53 (s, 2H, CH_2), 2.35 (s, 3H, CH_3), 2.16 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.2, 144.9, 143.1, 136.7, 135.2, 134.3, 133.4, 129.8, 129.7, 129.2, 128.7, 128.4, 127.3, 127.1, 126.35, 126.32, 123.3, 115.6, 111.6, 111.5, 60.0, 51.8, 43.7, 21.2, 21.1; IR (DCM) ν 1700, 1367, 1174, 1156, 907, 726 cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{30}N_3O_5S_2$ $[M + NH_4]^+$ m/z 540.1621, found 540.1626.



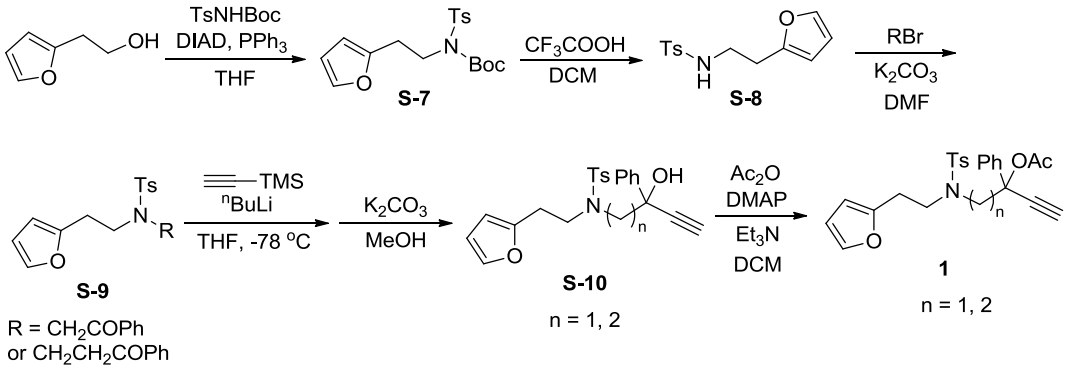
N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methyl-N-((1-tosyl-1H-pyrrol-2-yl)methyl)benzenesulfonamide (S-4-11b): a white solid (2.16 g, 65% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.60-7.54 (m, 4H, ArH), 7.44 (d, 2H, *J* = 8.4 Hz, ArH), 7.34-7.26 (m, 5H, ArH), 7.16-7.14 (m, 3H, ArH), 6.05-6.03 (m, 1H, ArH), 5.821-5.818 (m, 1H, ArH), 4.85 (d, 1H, *J* = 18.0 Hz, CH_2), 4.60 (d, 1H, *J* = 18.0 Hz, CH_2), 4.39 (s, 1H, OH), 3.69 (d, 1H, J = 15.2 Hz, CH_2), 3.57 (d, 1H, *J* = 15.2 Hz, CH_2), 2.64 (s, 1H, CH), 2.40 (s, 3H, CH_3), 2.36 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 145.1, 143.6, 141.3, 135.9, 135.6, 129.9, 129.4, 129.2, 128.1, 128.0, 127.2, 126.5, 125.5, 122.9, 114.8, 111.6, 84.5, 75.0, 72.3, 60.3, 60.1, 47.2, 21.4, 21.3; IR (DCM) ν 3451, 3284, 1333, 1173, 1151, 725, 668 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{32}N_3O_5S_2$ $[M + NH_4]^+$ m/z 566.1778, found 566.1781.



1-((4-methyl-N-((1-tosyl-1H-pyrrol-2-yl)methyl)phenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (11b): a colourless oil (968 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.0 Hz, ArH), 7.47 (d, 2H, *J* = 6.8 Hz, ArH), 7.42 (d, 2H, *J* = 8.0 Hz, ArH), 7.34-7.26 (m, 5H, ArH), 7.19-7.15 (m, 3H, Ar), 6.33 (s, 1H, ArH), 6.17-6.16 (m, 1H, ArH), 4.71 (d, 1H, *J* = 18.4 Hz, CH_2), 4.62 (d, 1H, *J* = 18.4 Hz, CH_2), 3.88 (d, 1H, *J* = 14.8 Hz, CH_2), 3.65 (d, 1H, *J* = 14.8 Hz, CH_2), 2.91 (s, 1H, CH), 2.39 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 1.68 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 176.4, 167.7, 145.0, 143.2, 137.9, 136.3, 135.6, 130.4, 129.8, 129.2, 128.3, 126.8, 126.3, 124.9, 122.2, 114.4, 111.8, 79.4, 78.5, 78.1, 59.8, 48.1, 21.3, 21.1, 20.5, 20.4; IR (DCM) ν 1752, 1366, 1224, 1153, 731 cm^{-1}; HRMS (ESI) calcd for $C_{31}H_{34}N_3O_6S_2$ $[M + NH_4]^+$ m/z 608.1884, found 608.1885.



The Syntheses and the Spectroscopic Data of Substrates 1v and 1x

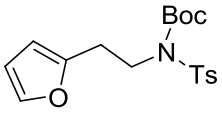


Procedure for the preparation of **1v**: A flame-dried 100-mL round bottomed flask was charged with 2-(furan-2-yl)ethanol[7] (2.24 g, 20 mmol), PPh_3 (5.76 g, 22 mmol), TsNHBoc (5.96 g, 22 mmol) and dry THF (50 mL). The solution was cooled to 0 ^oC and DIAD (4.44 g, 22 mmol) was added in dropwise. The reaction was stirred for overnight. The reaction mixture was washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced

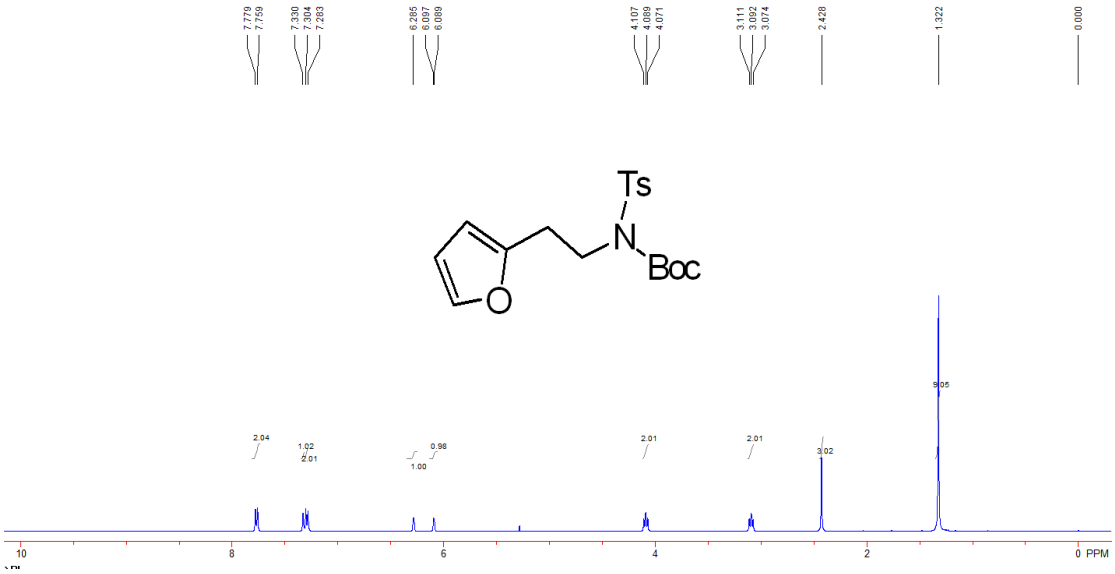
pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 4/1) to provide product **S-7** (6.64 g) in 91% yield.

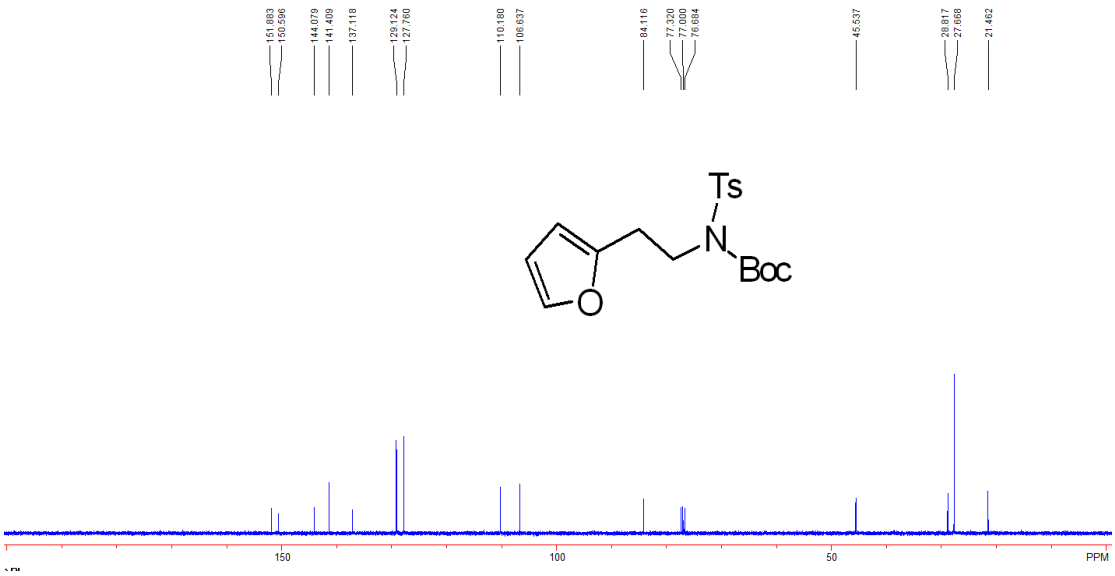
To a solution of **S-7** (3.65 g, 10 mmol) in DCM (50 mL) was added CF_3COOH (1.14 g, 10 mmol), the reaction mixture was stirred for 3 h. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 3/1) to provide product **S-8** (1.43 g) in 54% yield.

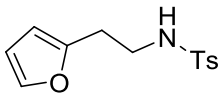
The next experiments were performed in the same procedure as that in the synthesis of compound **1a**.



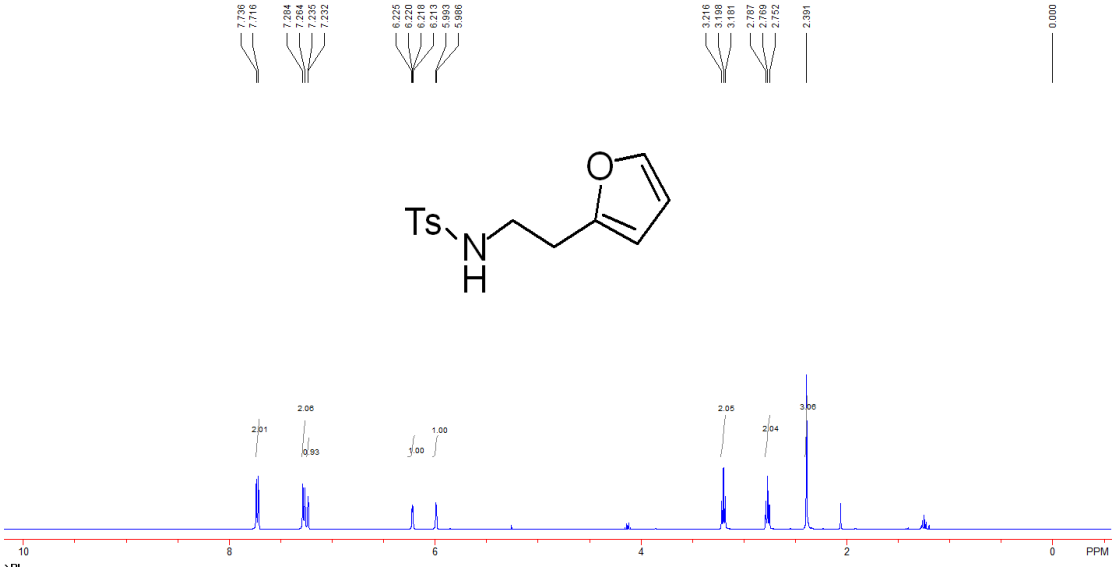
tert-butyl (2-(furan-2-yl)ethyl)(tosyl)carbamate (S-7): a white solid (6.64 g, 91% yield), mp: 81-83 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.77 (d, 2H, *J* = 8.0 Hz, ArH), 7.33 (s, 1H, ArH), 7.29 (d, 2H, *J* = 8.0 Hz, ArH), 6.28 (s, 1H, ArH), 6.08 (d, *J* = 3.2 Hz, ArH), 4.09 (t, 2H, *J* = 7.2 Hz, CH_2), 3.09 (t, 2H, *J* = 7.2 Hz, CH_2), 2.43 (s, 3H, CH_3), 1.32 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 151.9, 150.6, 144.1, 141.4, 137.1, 129.1, 127.8, 110.2, 106.6, 84.1, 45.5, 28.8, 27.7, 21.5; IR (DCM) ν 2980, 1726, 1351, 1285, 1153, 1087, 718 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 383.1635, found 383.1645.

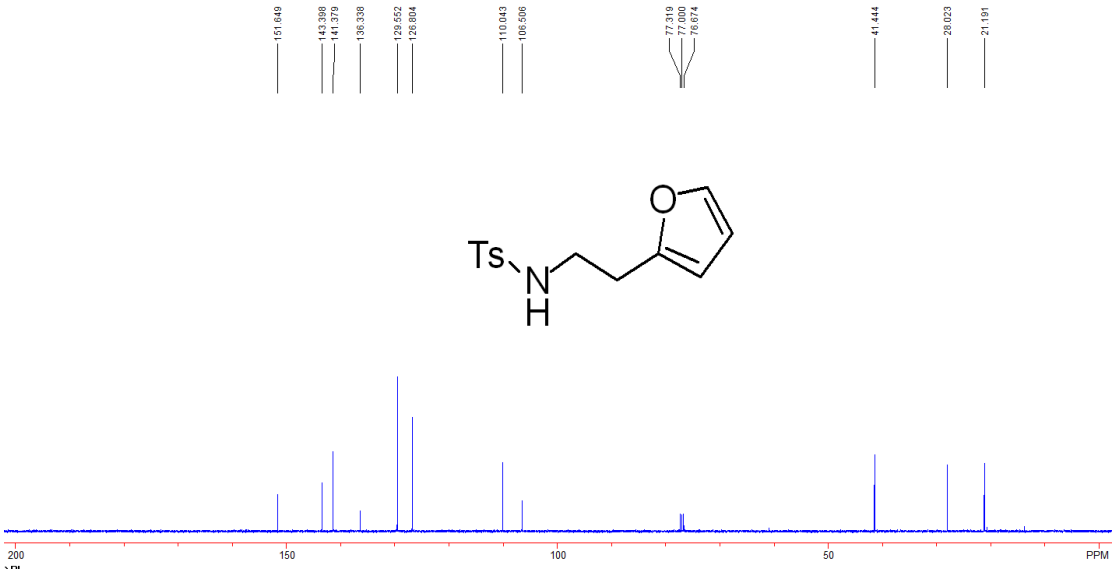


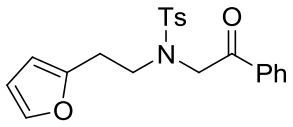




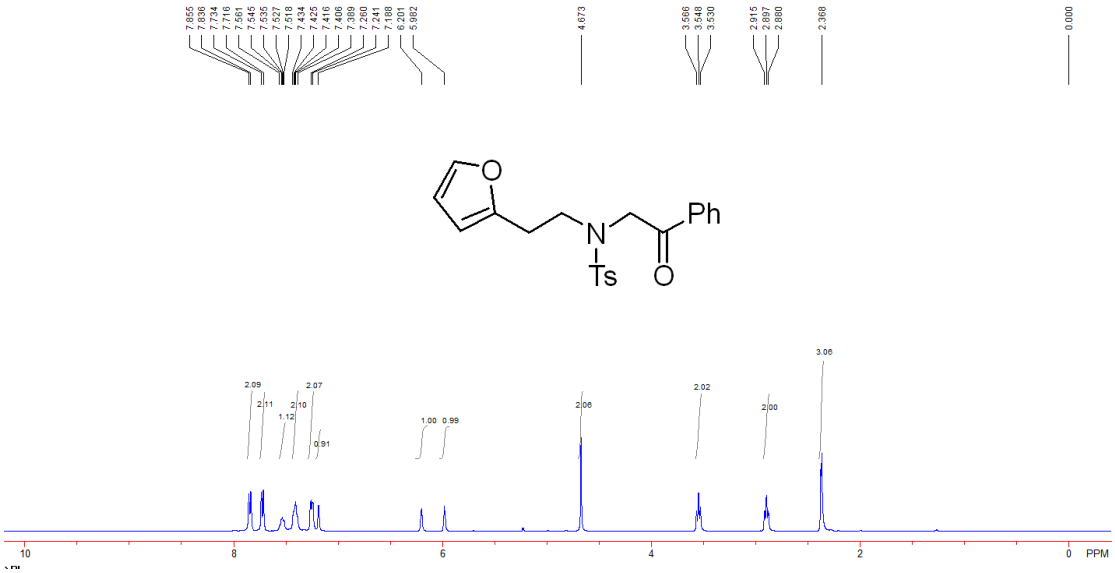
N-(2-(furan-2-yl)ethyl)-4-methylbenzenesulfonamide (S-8): a colorless oil (1.4 g, 54% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.73 (d, 2H, *J* = 8.0 Hz, ArH), 7.27 (d, 2H, *J* = 8.0 Hz, ArH), 7.23 (d, 1H, *J* = 1.2 Hz, ArH), 6.22 (dd, 1H, J_1 = 2.8 Hz, J_2 = 2.0 Hz, ArH), 5.99 (d, 1H, *J* = 2.8 Hz, ArH), 3.20 (t, 2H, *J* = 7.2 Hz, CH_2), 2.77 (t, 2H, *J* = 7.2 Hz, CH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 151.6, 143.4, 141.4, 136.3, 129.5, 126.8, 110.0, 106.5, 41.4, 28.0, 21.2; IR (DCM) ν 3282, 2931, 1713, 1418, 1323, 1153, 1092, 733 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{16}NO_3S$ $[M + H]^+$ m/z 266.0845, found 266.0851.

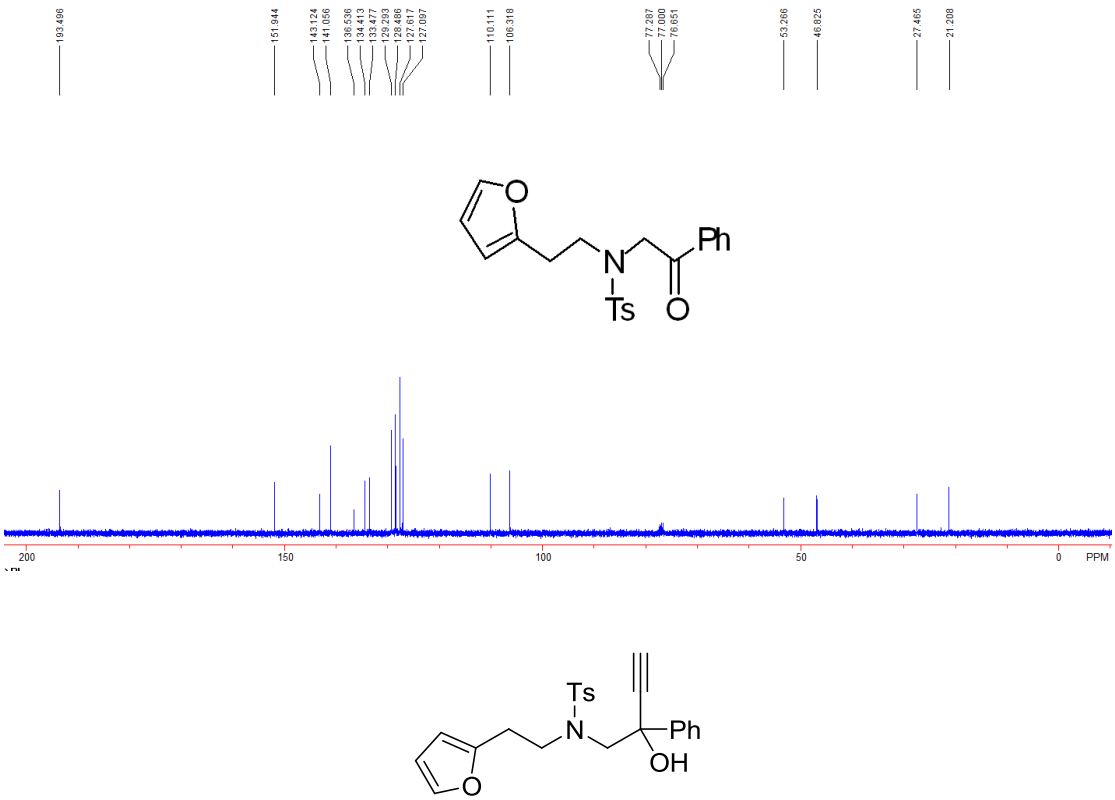




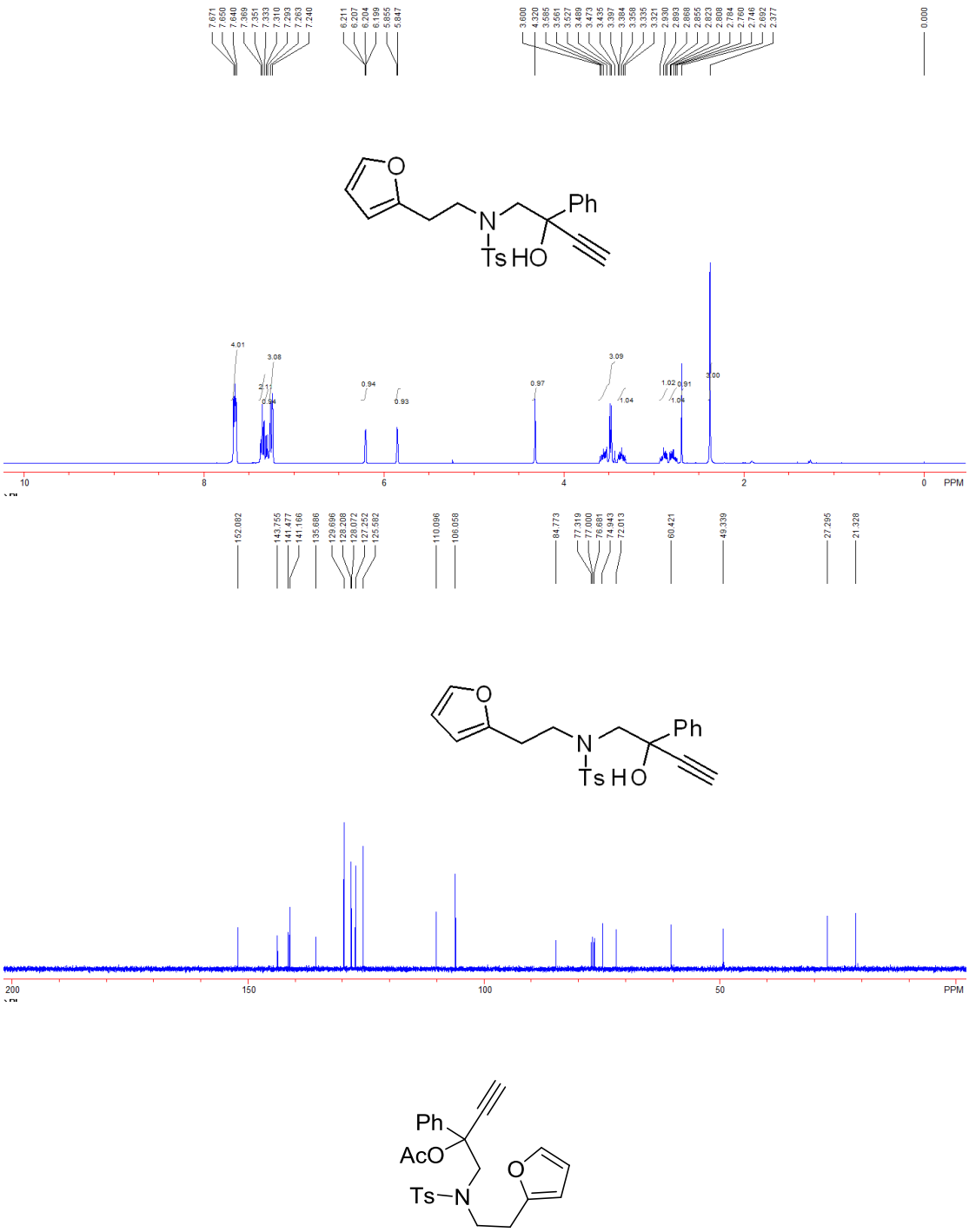


N-(2-(furan-2-yl)ethyl)-4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-9v): a white solid (1.4 g, 99% yield), mp: 99-101 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.84 (d, 2H, *J* = 7.6 Hz, ArH), 7.72 (d, 2H, *J* = 7.6 Hz, ArH), 7.56-7.52 (m, 1H, ArH), 7.43-7.39 (m, 2H, ArH), 7.25 (d, 2H, *J* = 7.6 Hz, ArH), 7.19 (s, 1H, ArH), 6.20 (s, 1H, ArH), 5.98 (s, 1H, ArH), 4.67 (s, 2H, CH_2), 3.55 (t, 2H, *J* = 7.2 Hz, CH_2), 2.90 (t, 2H, *J* = 7.2 Hz, CH_2), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.5, 151.9, 143.1, 141.0, 136.5, 134.4, 133.5, 129.3, 128.5, 127.6, 127.1, 110.1, 106.3, 53.3, 46.8, 27.5, 21.2; IR (DCM) ν 3061, 2919, 1701, 1597, 1335, 1154, 731 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4S$ $[M + NH_4]^+$ m/z 401.1530, found 401.1535.



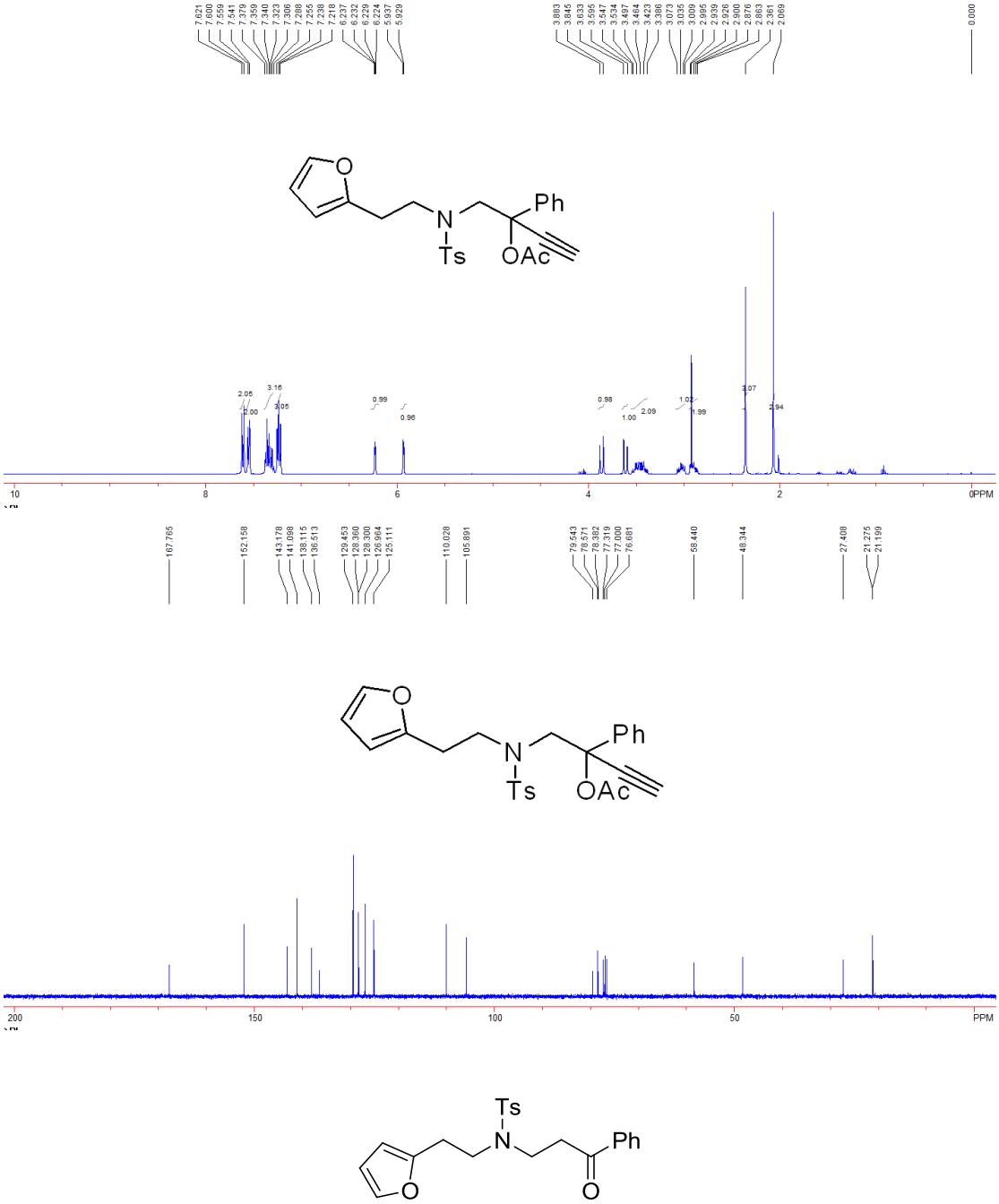


N-(2-(furan-2-yl)ethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-10v): a colorless oil (451 mg, 48% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.67-7.64 (m, 4H, ArH), 7.35 (t, 2H, *J* = 7.2 Hz, ArH), 7.30 (d, H, *J* = 6.8 Hz, ArH), 7.26-7.24 (m, 3H, ArH), 6.20 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.85 (d, 1H, *J* = 3.2 Hz, ArH), 4.32 (s, 1H, OH), 3.60-3.43 (m, 3H, CH_2), 3.40-3.32 (m, 1H, CH_2), 2.93-2.85 (m, 1H, CH_2), 2.82-2.75 (m, 1H, CH_2), 2.69 (s, 1H, CH), 2.38 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 152.1, 143.7, 141.5, 141.2, 135.7, 129.7, 128.2, 128.1, 127.2, 125.6, 110.1, 106.0, 84.8, 74.9, 72.0, 60.4, 49.3, 27.3, 21.3; IR (DCM) ν 3461, 3292, 1449, 1333, 1152, 733 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{23}NNaO_4S$ $[M + Na]^+$ m/z 432.1240, found 432.1241.



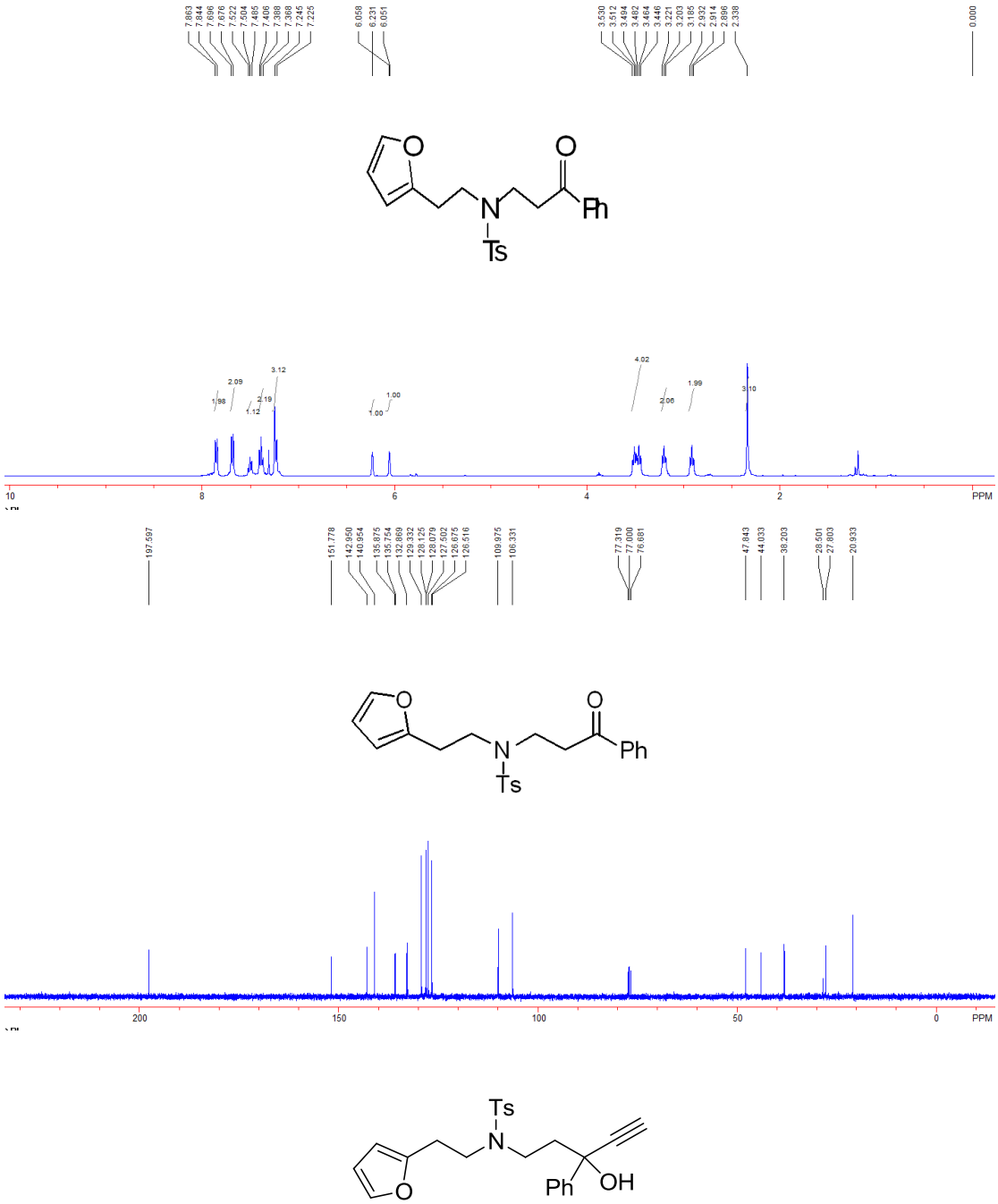
1-((N-(2-(furan-2-yl)ethyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 3, entry 1v): a colorless oil (443 mg, 89% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.61 (d, 2H, *J* = 8.4 Hz, ArH), 7.55 (d, 2H, *J* = 7.2 Hz, ArH), 7.38-7.29 (m, 3H, ArH), 7.25-7.22 (m, 3H, ArH), 6.23 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.93 (d, 1H, *J* = 3.2 Hz, ArH), 3.86 (d, 1H, *J* = 15.2 Hz, CH_2), 3.62 (d, 1H, *J* = 15.2 Hz, CH_2), 3.55-3.38 (m, 2H, CH_2), 3.07-2.99 (m, 1H, CH_2), 2.93-2.86 (m, 2H, CH and CH_2), 2.36 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.8, 152.1, 143.2, 141.1, 138.1, 136.5, 129.4, 128.4, 128.3, 127.0, 125.1,

110.0, 105.9, 79.5, 78.6, 78.4, 58.4, 48.3, 27.4, 21.3, 21.2; IR (DCM) ν 3275, 1752, 1340, 1221, 1155, 959, 732 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1804.



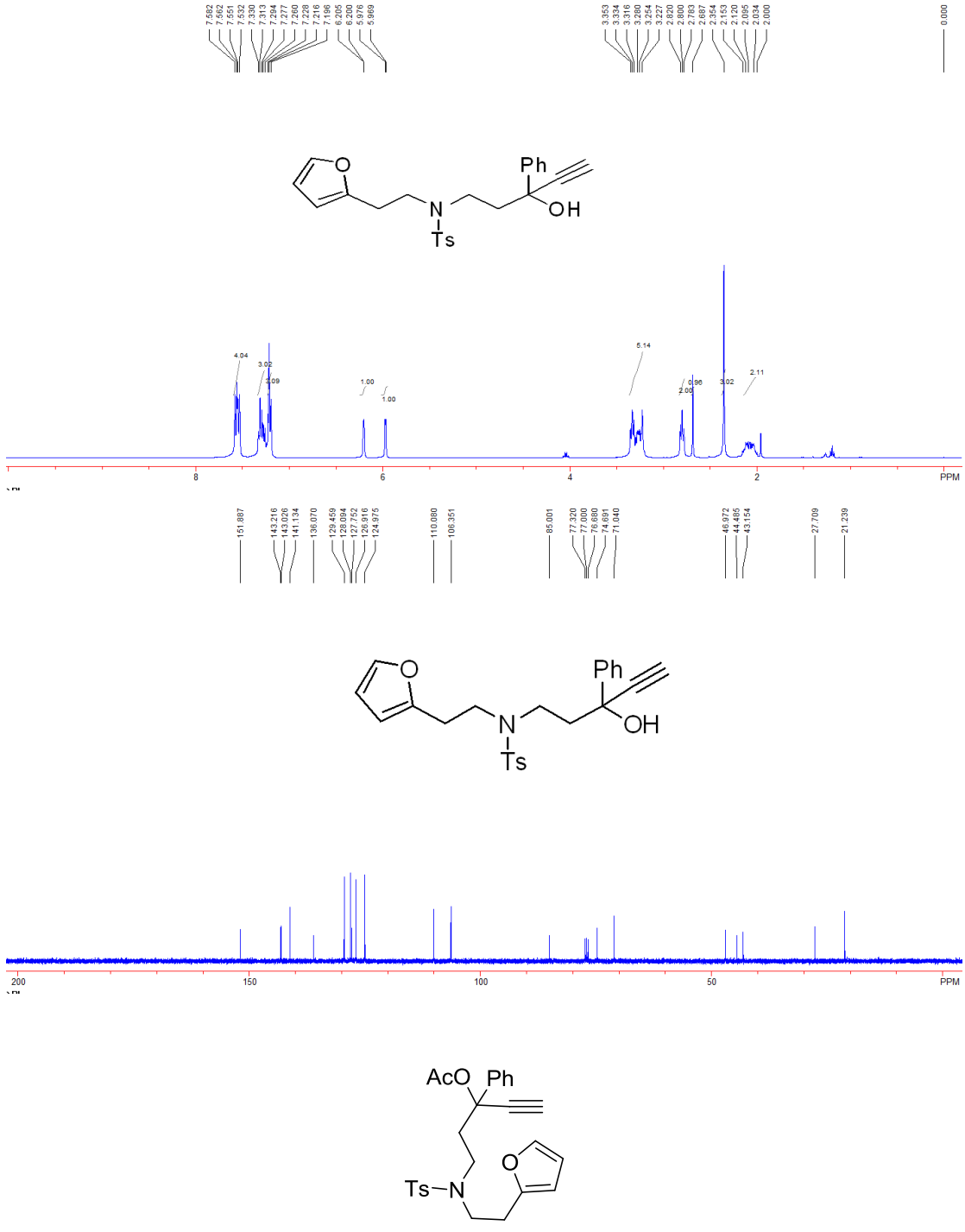
N-(2-(furan-2-yl)ethyl)-4-methyl-N-(3-oxo-3-phenylpropyl)benzenesulfonamide (S-9x): a colorless oil (3.8 g, 99% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.85 (d, 2H, *J* = 7.6 Hz, ArH), 7.69 (d, 2H, *J* = 8.0 Hz, ArH), 7.50 (t, 1H, *J* = 7.6 Hz, ArH), 7.39 (t, 2H, *J* = 8.0 Hz, ArH), 7.24-7.22 (m, 3H, ArH), 6.23 (s, 1H, ArH), 6.05 (d, 1H, *J* = 2.8 Hz, ArH), 3.53-3.45 (m, 4H, CH_2), 3.20 (t, 2H, *J* = 7.2 Hz, CH_2), 2.91 (t, 2H, *J* = 7.2 Hz, CH_2), 2.34 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 197.6, 151.8, 142.9, 140.9, 135.9, 135.7, 132.8, 129.3, 128.1, 127.5,

126.7, 110.0, 106.3, 47.8, 44.0, 38.2, 28.5, 27.8, 20.9; IR (DCM) ν 2923, 1681, 1325, 1154, 1092, 732, 689 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_4S$ $[M + NH_4]^+$ m/z 415.1686, found 415.1694.



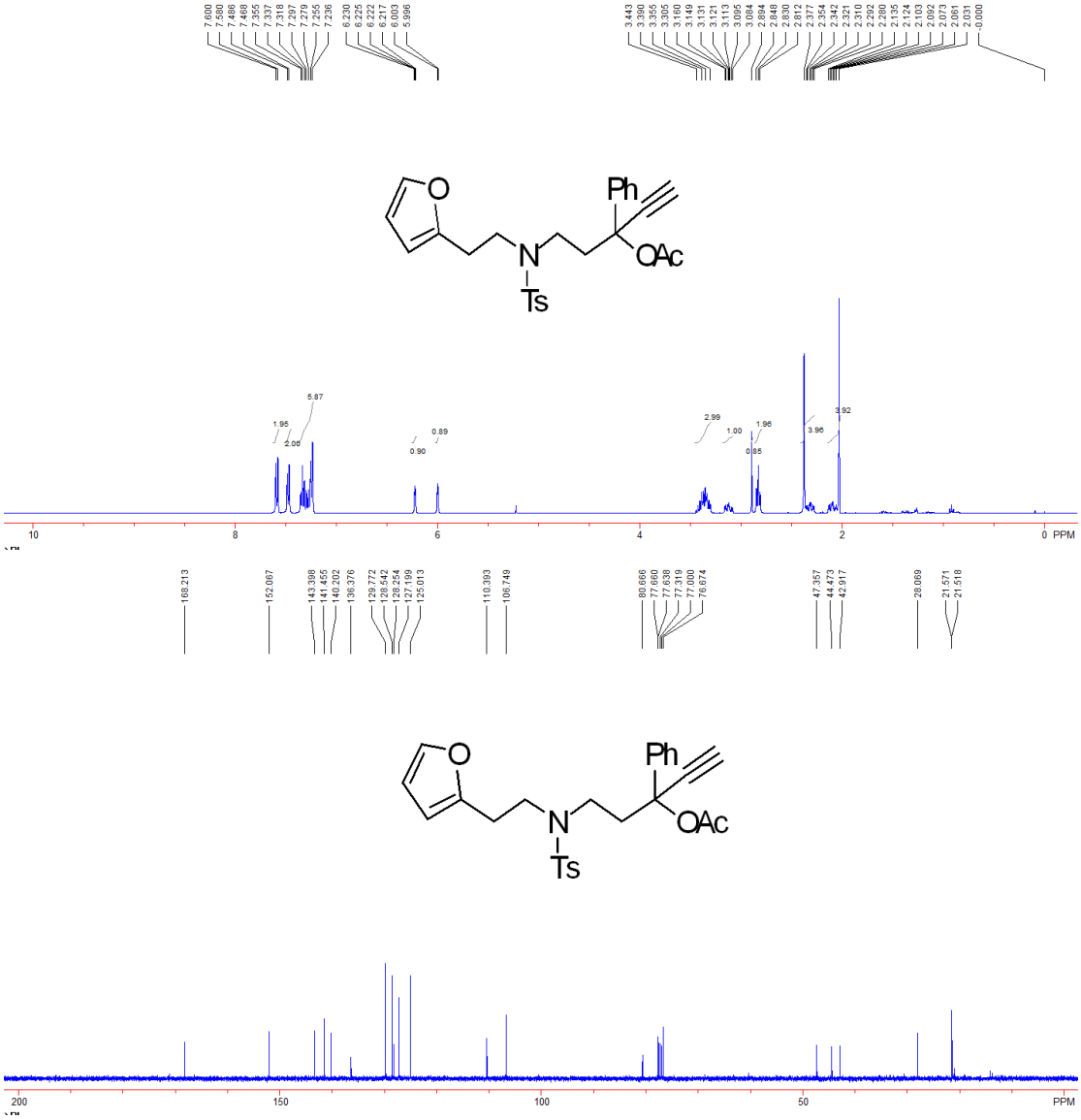
N-(2-(furan-2-yl)ethyl)-N-(3-hydroxy-3-phenylpent-4-yn-1-yl)-4-methylbenzenesulfonamide (S-10x): a colorless oil (868 mg, 49% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58-7.53 (m, 4H, ArH), 7.33-7.26 (m, 3H, ArH), 7.23-7.20 (m, 3H, ArH), 6.20 (d, 1H, *J* = 2.0 Hz, ArH), 5.97 (d, 1H, *J* = 2.8 Hz, ArH), 3.35-3.23 (m, 5H, OH and CH_2), 2.80 (t, 2H, *J* = 6.8 Hz, CH_2), 2.69 (s, 1H, CH), 2.35 (s, 3H, CH_3), 2.15-2.00 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 151.9, 143.2, 143.0, 141.1, 136.1, 129.4, 128.1, 127.7, 126.9, 125.0, 110.1, 106.3, 85.0, 74.7, 71.0, 47.0, 44.5, 43.1, 27.7, 21.2; IR (DCM) ν 3462, 3285, 1714, 1448, 1335, 1154, 699 cm^{-1}; HRMS (ESI)

calcd for $C_{24}H_{24}NO_3S$ $[M\text{-}H_2O + H]^+$ m/z 406.1471, found 406.1475.

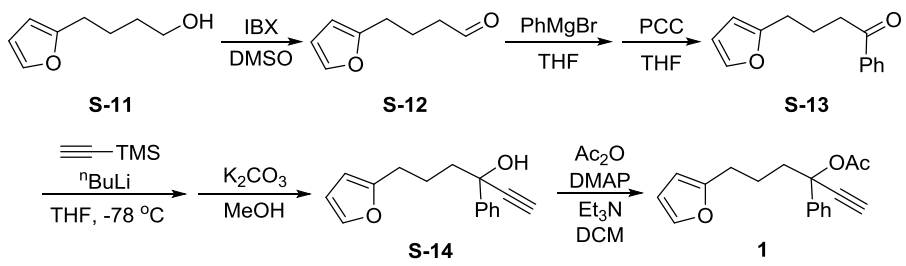


5-((N-(2-(furan-2-yl)ethyl)-4-methylphenyl)sulfonamido)-3-phenylpent-1-yn-3-yl acetate (Table 3, entry 1x): a colorless oil (663 mg, 34% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.0 Hz, ArH), 7.48 (d, 2H, *J* = 7.2 Hz, ArH), 7.35-7.24 (m, 6H, ArH), 6.22 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.00 (d, 1H, *J* = 2.8 Hz, ArH), 3.44-3.30 (m, 3H, CH_2), 3.16-3.08 (m, 1H, CH_2), 2.89 (s, 1H, CH), 2.83 (t, 2H, *J* = 7.2 Hz, CH_2), 2.38 (s, 3H, CH_3), 2.37-2.28 (m, 1H, CH_2), 2.13-2.06 (m, 1H, CH_2), 2.03 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz,

TMS) δ 168.2, 152.1, 143.4, 141.4, 140.2, 136.4, 129.8, 128.5, 128.2, 127.2, 125.0, 110.3, 106.7, 80.6, 77.7, 76.7, 47.3, 44.4, 42.9, 28.1, 21.6, 21.5; IR (DCM) ν 3267, 1750, 1339, 1224, 1154, 1012, 733 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_5S$ $[M + NH_4]^+$ m/z 483.1948, found 483.1858.



The Syntheses and the Spectroscopic Data of Substrate 1r

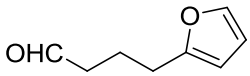


A solution of **S-11**[8] (0.91 g, 6.5 mmol) and IBX (1.82 g, 6.5 mmol) in DMSO (30 mL) was

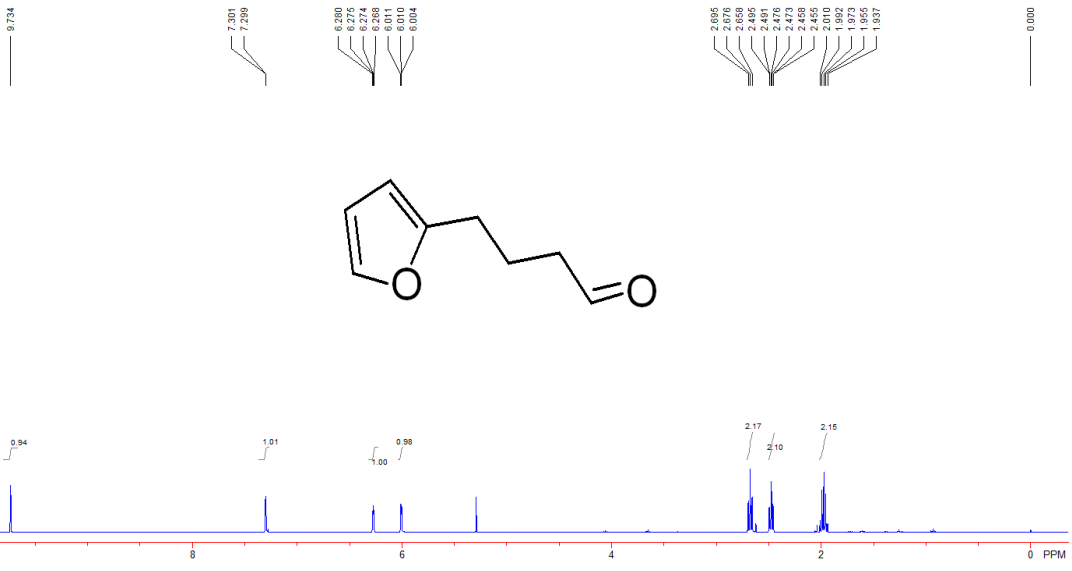
stirred overnight. EA was added to the reaction solution. The reaction mixture was washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 10/1) to provide product **S-12** (0.90 g) in 99% yield.

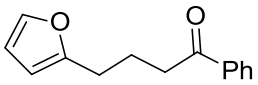
To a solution of **S-12** (0.66 g, 4.7 mmol) in THF (20 mL) was added PhMgBr (4.7 mL, 4.7 mmol, 1.0 mol/L in THF) under Ar atmosphere, the reaction mixture was stirred for 3 h. The reaction was quenched with water. The combined organic layers were washed with brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and PCC (1.01 g, 4.7 mmol), DCM (20 mL) was added. The reaction mixture was stirred for overnight. The reaction mixture was washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 10/1) to provide product **S-13** (0.91 g) in 90% yield for two steps.

The next experiments were performed in the same procedure as that in the synthesis of compound **1a**.

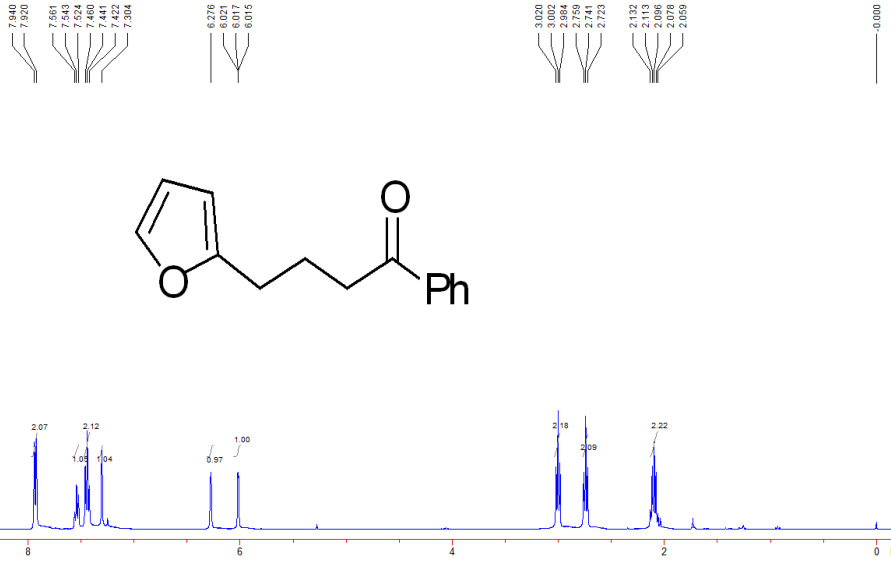


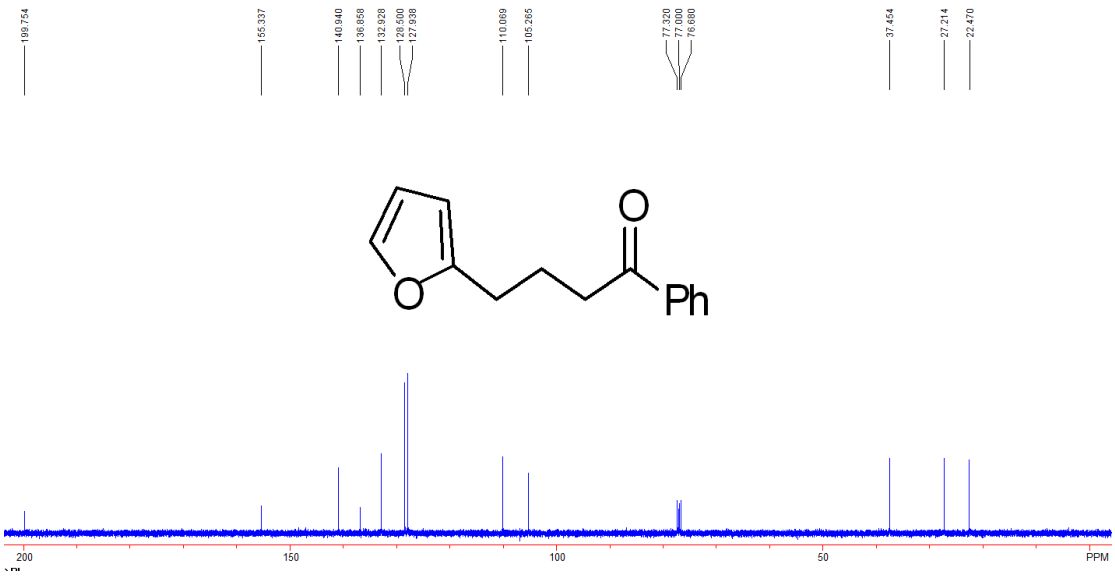
4-(furan-2-yl)butanal (S-12): known compound,[9] a colorless oil (900 mg, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 9.73 (s, 1H, CH), 7.30 (d, 1H, J = 0.8 Hz, ArH), 6.27 (dd, 1H, J_1 = 2.4 Hz, J_2 = 2.0 Hz, ArH), 6.01-6.00 (m, 1H, ArH), 2.68 (t, 2H, J = 7.6 Hz, CH_2), 2.49-2.45 (m, 2H, CH_2), 2.01-1.94 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 202.0, 154.7, 141.0, 110.0, 105.4, 42.8, 27.0, 20.4.

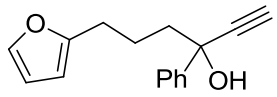




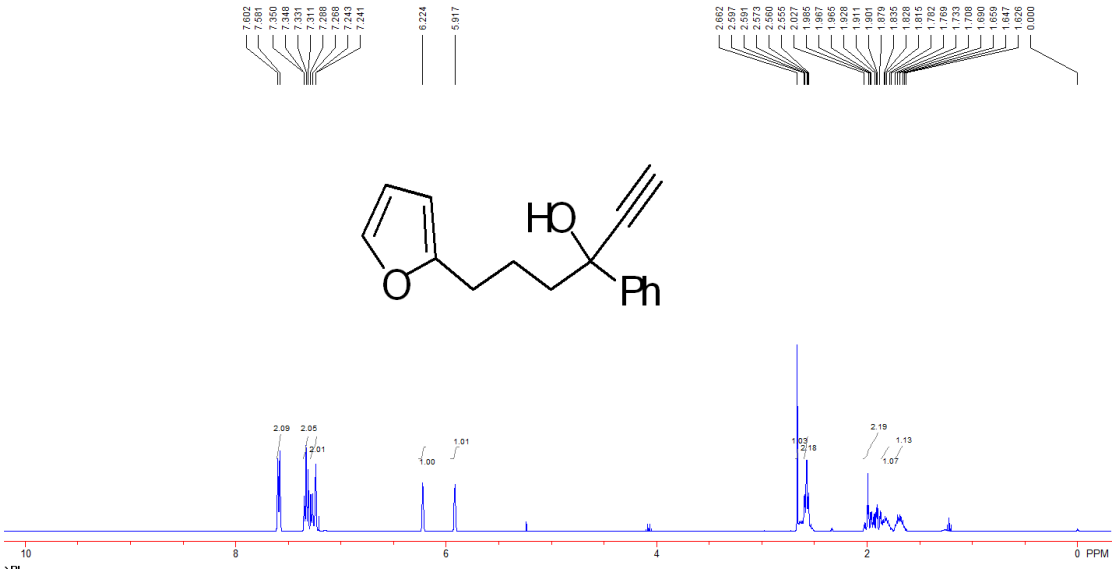
4-(furan-2-yl)-1-phenylbutan-1-one (S-13): a colorless oil (909 mg, 90% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.93 (d, 2H, *J* = 8.0 Hz, ArH), 7.54 (t, 1H, *J* = 7.6 Hz, ArH), 7.44 (t, 2H, *J*= 7.6 Hz, ArH), 7.30 (s, 1H, ArH), 6.28 (s, 1H, ArH), 6.02-6.01 (m, 1H, ArH), 3.00 (t, 2H, *J* = 7.2 Hz, CH_2), 2.74 (t, 2H, *J* = 7.2 Hz, CH_2), 2.13-2.06 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.7, 155.3, 140.9, 136.8, 132.9, 128.5, 127.9, 110.1, 105.3, 37.4, 27.2, 22.5; IR (DCM) ν 2936, 1683, 1448, 1220, 1002, 730, 689 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{15}O_2$ [M + H]$^{+}$ m/z 215.1067, found 215.1071.

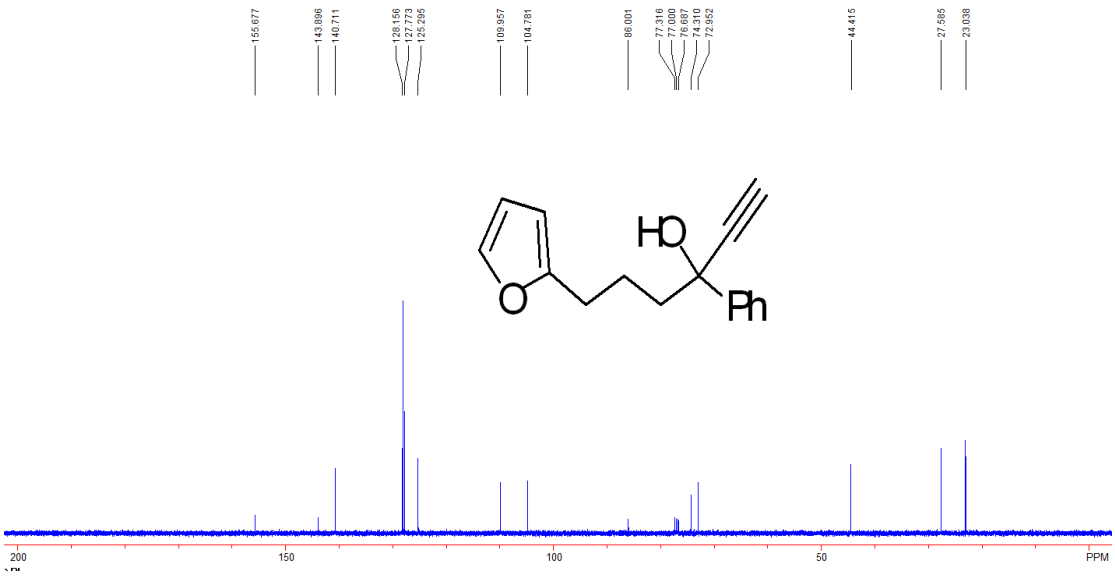


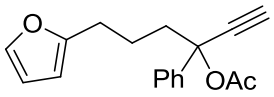




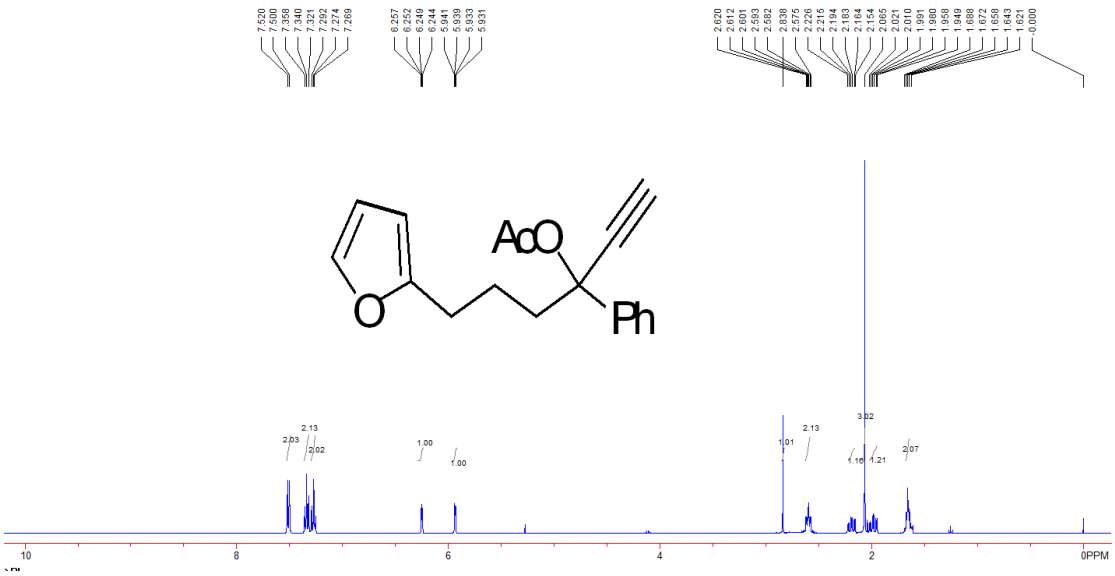
6-(furan-2-yl)-3-phenylhex-1-yn-3-ol (S-14): a colorless oil (525 mg, 47% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.4 Hz, ArH), 7.35-7.31 (m, 2H, ArH), 7.29-7.24 (m, 2H, ArH), 6.22 (s, 1H, ArH), 5.92 (s, 1H, ArH), 2.66 (s, 1H, CH), 2.60-2.55 (m, 2H, CH_2), 2.03-1.88 (m, 2H, CH_2), 1.83-1.73 (m, 1H, CH_2), 1.71-1.63 (m, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 155.7, 143.9, 140.7, 128.1, 127.8, 125.3, 109.9, 104.8, 86.0, 74.3, 72.9, 44.4, 27.6, 23.0; IR (DCM) ν 3291, 2953, 1597, 1448, 1005, 919, 698 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}O_2$ $[M + H]^+$ m/z 241.1223, found 241.1230.

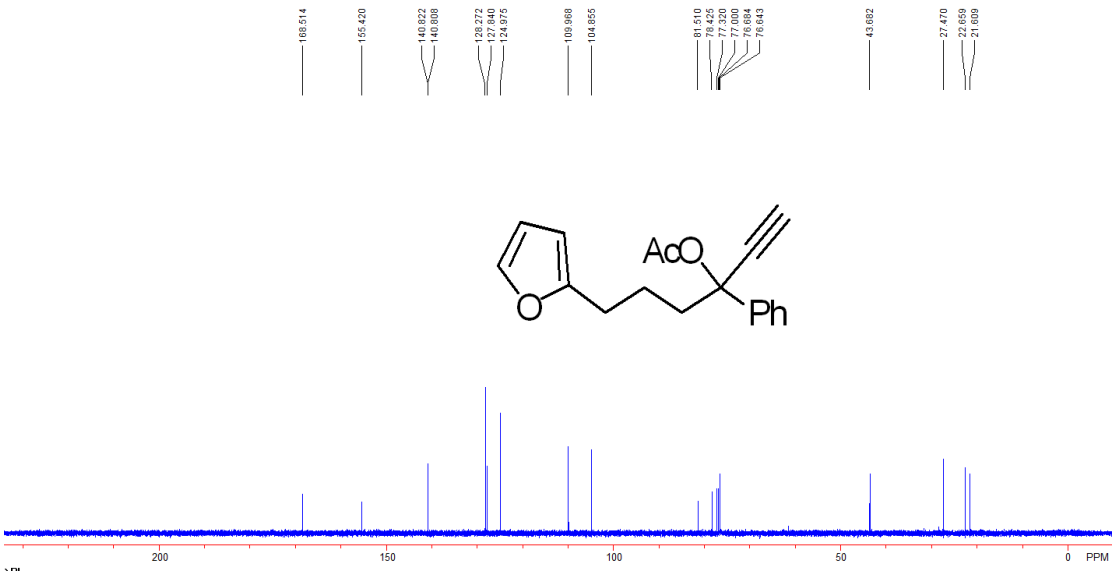




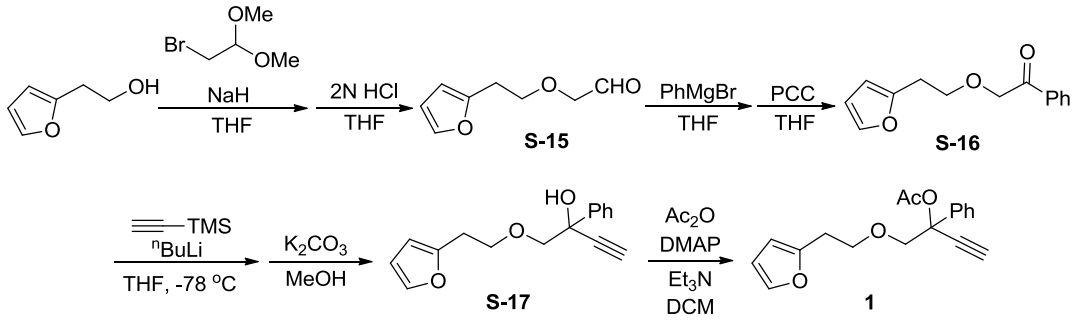


6-(furan-2-yl)-3-phenylhex-1-yn-3-yl acetate (Table 2, entry 1r): a colorless oil (802 mg, 78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.51 (d, 2H, J = 8.0 Hz, ArH), 7.34 (t, 2H, J = 7.2 Hz, ArH), 7.29-7.27 (m, 2H, ArH), 6.25 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 5.93 (dd, 1H, J_1 = 3.2 Hz, J_2 = 0.8 Hz, ArH), 2.84 (s, 1H, CH), 2.62-2.57 (m, 2H, CH_2), 2.23-2.15 (m, 1H, CH_2), 2.06 (s, 3H, CH_3), 2.02-1.95 (m, 1H, CH_2), 1.69-1.62 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.5, 155.4, 140.82, 140.81, 128.3, 127.8, 125.0, 110.0, 104.8, 81.5, 78.4, 76.6, 43.7, 27.5, 22.6, 21.6; IR (DCM) ν 3288, 2957, 1749, 1223, 1008, 698 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}NO_3$ $[M + NH_4]^+$ m/z 300.1594, found 300.1594.



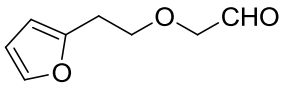


The Syntheses and the Spectroscopic Data of Substrate 1w

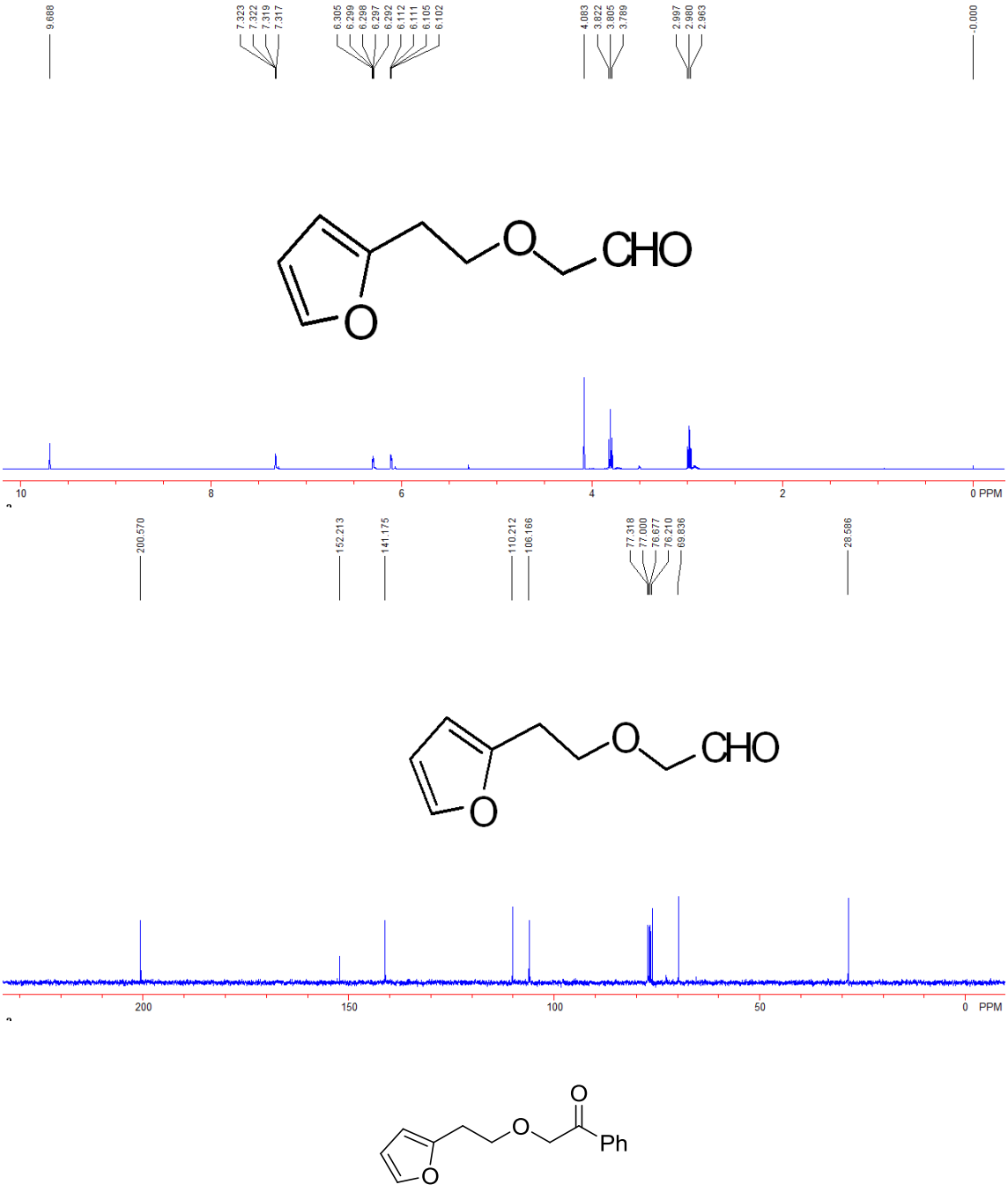


To a solution of NaH (0.41 g, 17 mmol) in THF (20 mL) was added 2-(furan-2-yl)ethanol (1.90 g, 17 mmol) under Ar atmosphere at 0 ^{o}C, the reaction mixture was stirred for 0.5 h. A solution of 2-bromo-1,1-dimethoxyethane (3.19 g, 19 mmol) in THF (10 mL) was added in dropwise. The reaction mixture was stirred for overnight. The reaction was quenched with water. The combined organic layers were washed with brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and THF (20 mL) was added. 2.0 N hydrochloric acid (9 mL) was added in dropwise. The reaction mixture was stirred overnight. The reaction mixture was washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 10/1) to provide product **S-15** (1.41 g) in 54% yield for two steps.

The next experiments were performed in the same procedure as that in the synthesis of compound **1r**.

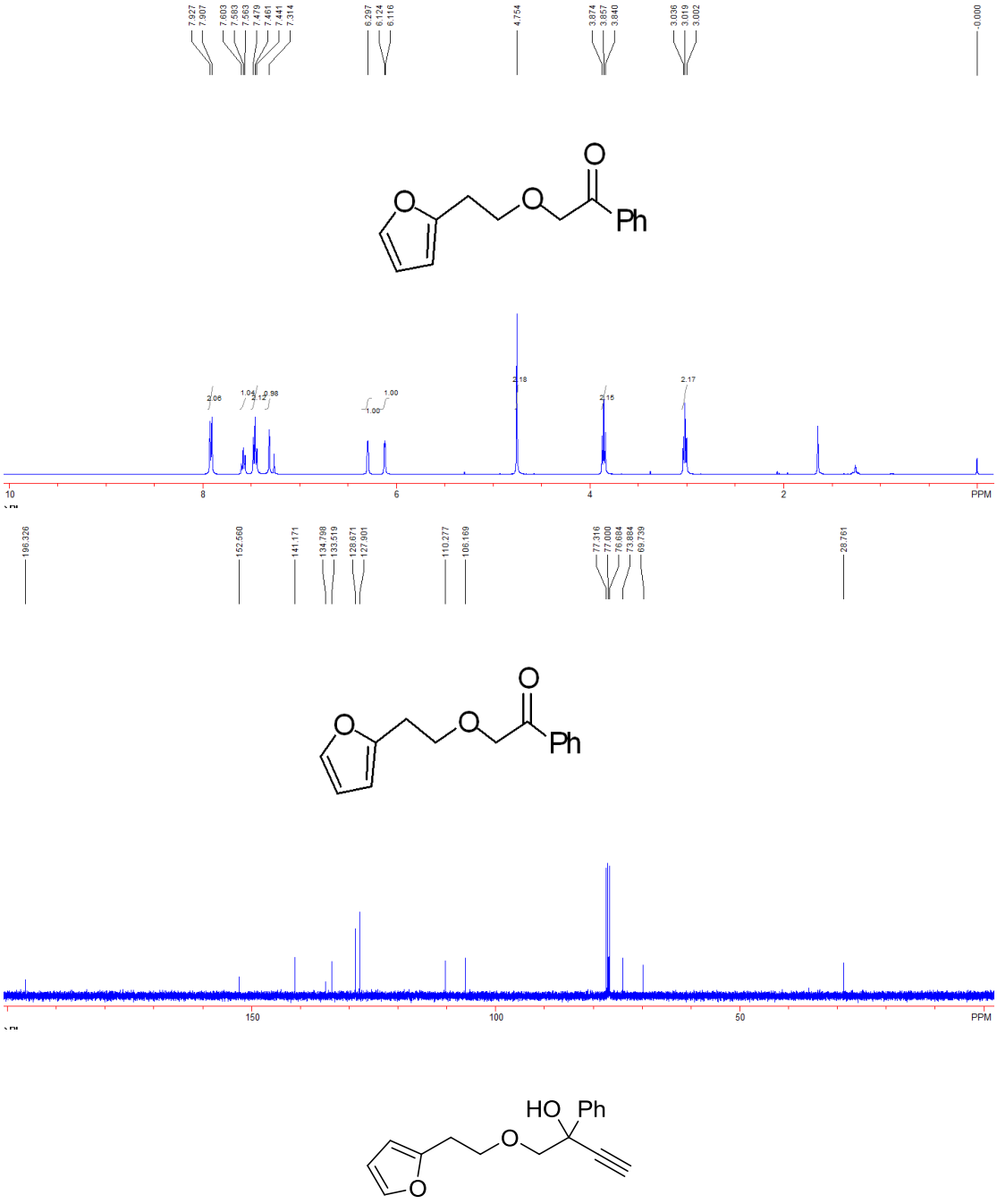


2-(2-(furan-2-yl)ethoxy)acetaldehyde (S-15): a colorless oil (1.4 g, 54% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 9.69 (s, 1H, CH), 7.32-7.32 (m, 1H, ArH), 6.30-6.29 (m, 1H, ArH), 6.11-6.10 (m, 1H, ArH), 4.08 (s, 2H, CH_2), 3.80 (t, 2H, *J* = 6.8 Hz, CH_2), 2.90 (t, 2H, J = 6.8 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 200.6, 152.2, 141.2, 110.2, 106.2, 76.2, 69.8, 28.6.



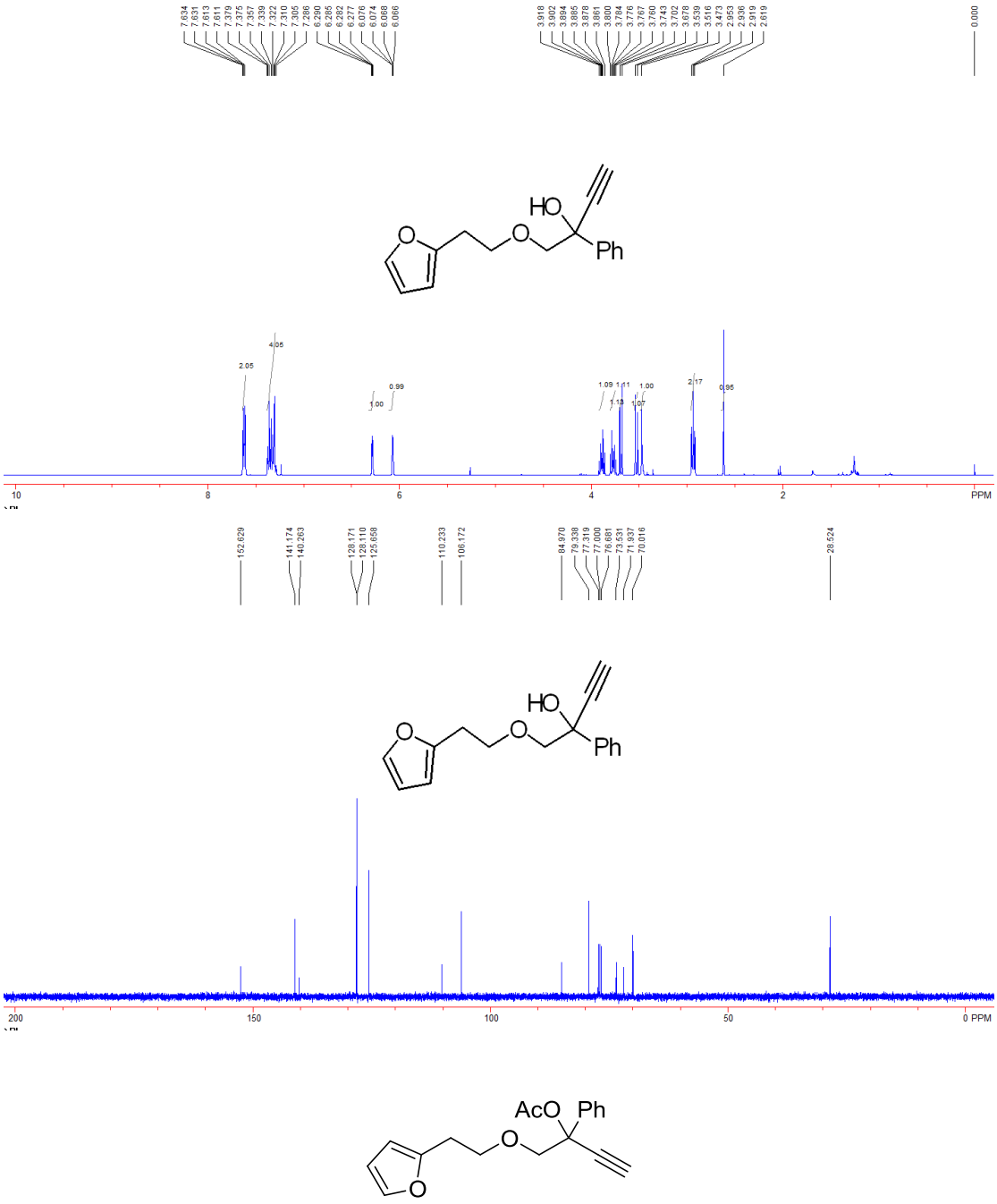
2-(2-(furan-2-yl)ethoxy)-1-phenylethan-1-one (S-16): a colorless oil (487 mg, 37% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.92 (d, 2H, *J* = 8.0 Hz, ArH), 7.58 (t, 1H, *J* = 8.0 Hz, ArH), 7.48-7.44 (m, 2H, ArH), 7.31 (s, 1H, ArH), 6.30 (s, 1H, ArH), 6.12 (d, 1H, *J* =3.2 Hz, ArH), 4.75

(s, 2H, CH_2), 3.86 (t, 2H, J = 6.8 Hz, CH_2), 3.02 (t, 2H, J = 6.8 Hz, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 196.3, 152.6, 141.2, 134.8, 133.5, 128.7, 127.9, 110.3, 106.2, 73.9, 69.7, 28.8; IR (DCM) ν 3445, 2870, 1698, 1226, 1136, 970, 754, 689 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{18}NO_3$ $[M + NH_4]^+$ m/z 248.1281, found 248.1281.



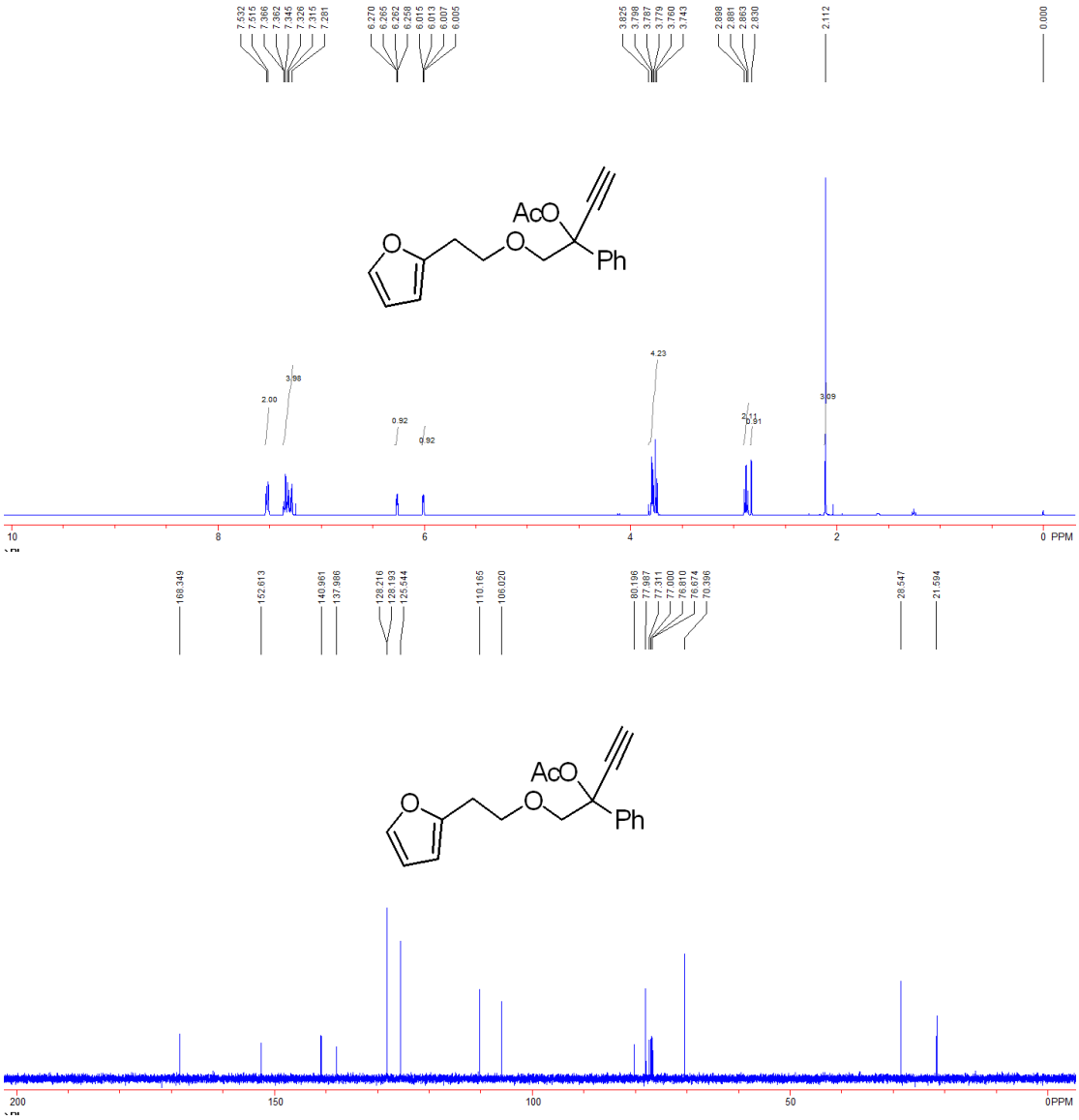
1-(2-(furan-2-yl)ethoxy)-2-phenylbut-3-yn-2-ol (S-17): a colorless oil (487 mg, 56% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.62 (dd, 2H, J_1 = 8.4 Hz, J_2 = 0.8 Hz, ArH), 7.38-7.29 (m, 4H, ArH), 6.28 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.07 (dd, 1H, J_1 = 3.2 Hz, J_2 = 0.8 Hz, ArH), 3.92-3.86 (m, 1H, CH_2), 3.80-3.74 (m, 1H, CH_2), 3.69 (d, 1H, J = 9.6 Hz, CH_2), 3.53 (d, 1H, J = 9.6 Hz, CH_2), 3.47 (s, 1H, OH), 2.94 (t, 2H, J = 6.8 Hz, CH_2), 2.62 (s, 1H, CH); ^{13}C NMR

($CDCl_3$, 100 MHz, TMS) δ 152.6, 141.2, 140.3, 128.2, 128.1, 125.6, 110.2, 106.2, 85.0, 79.3, 73.5, 71.9, 70.0, 28.5; IR (DCM) ν 3478, 2958, 2166, 1486, 1335, 1155, 842, 736 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{20}NO_3$ $[M + NH_4]^+$ m/z 274.1438, found 274.1442.

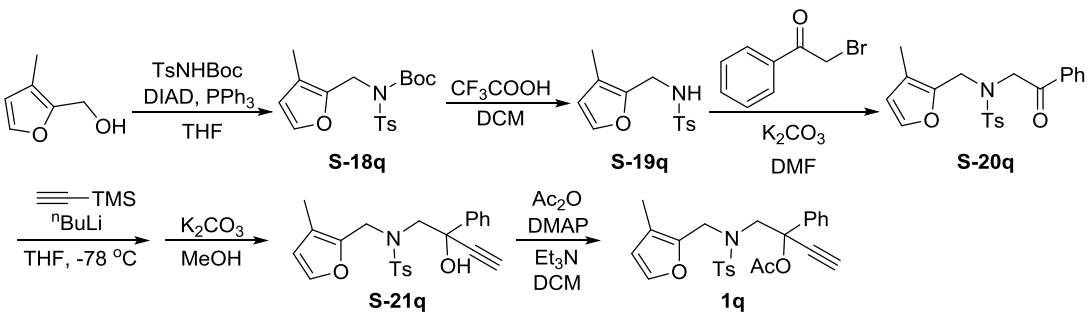


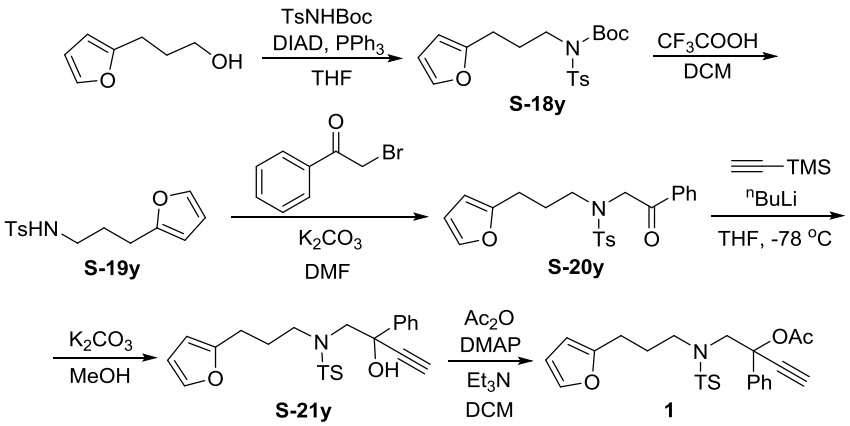
1-(2-(furan-2-yl)ethoxy)-2-phenylbut-3-yn-2-yl acetate (Table 3, entry 1w): a colorless oil (376 mg, 87% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.52 (d, 2H, J = 6.8 Hz, ArH), 7.37-7.28 (m, 4H, ArH), 6.26 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.01 (dd, 1H, J_1 = 3.2 Hz, J_2 = 0.8 Hz, ArH), 3.82-3.74 (m, 4H, CH_2), 2.88 (t, 2H, J = 6.8 Hz, CH_2), 2.83 (s, 1H, CH), 2.11 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.3, 152.6, 141.0, 138.0, 128.22, 128.19, 125.5, 110.2, 106.0, 80.2, 78.0, 76.8, 70.4, 28.5, 21.6; IR (DCM) ν 3279, 2919, 1749, 1367, 1224,

1118, 1010, 699 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}NO_4$ $[M + NH_4]^+$ m/z 316.1543, found 316.1548.

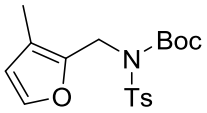


The Syntheses and the Spectroscopic Data of Substrate 1q and 1y

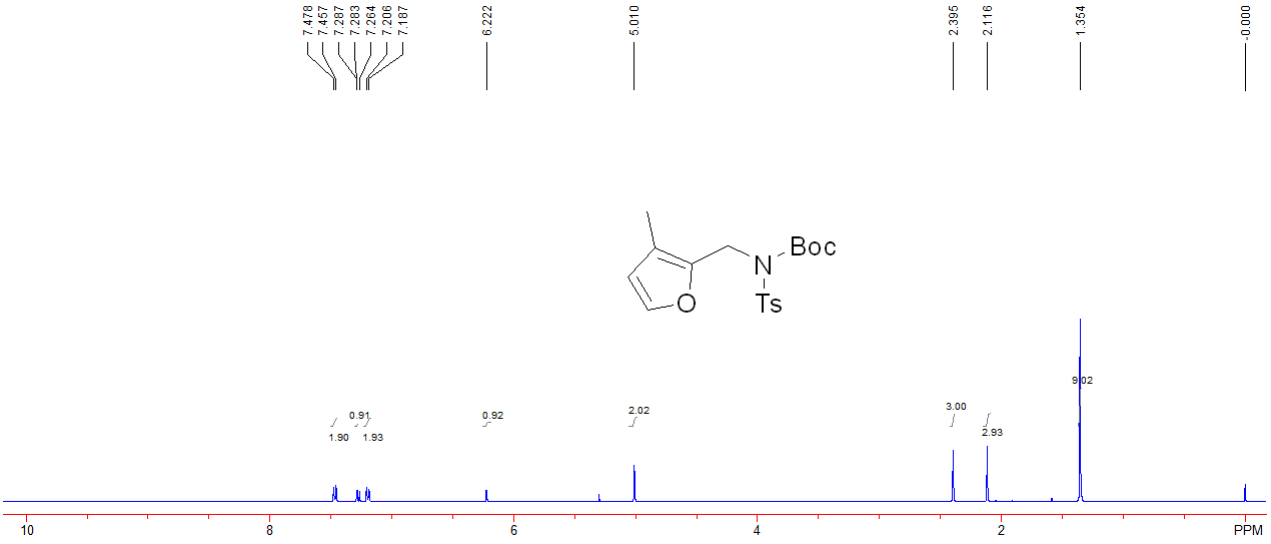


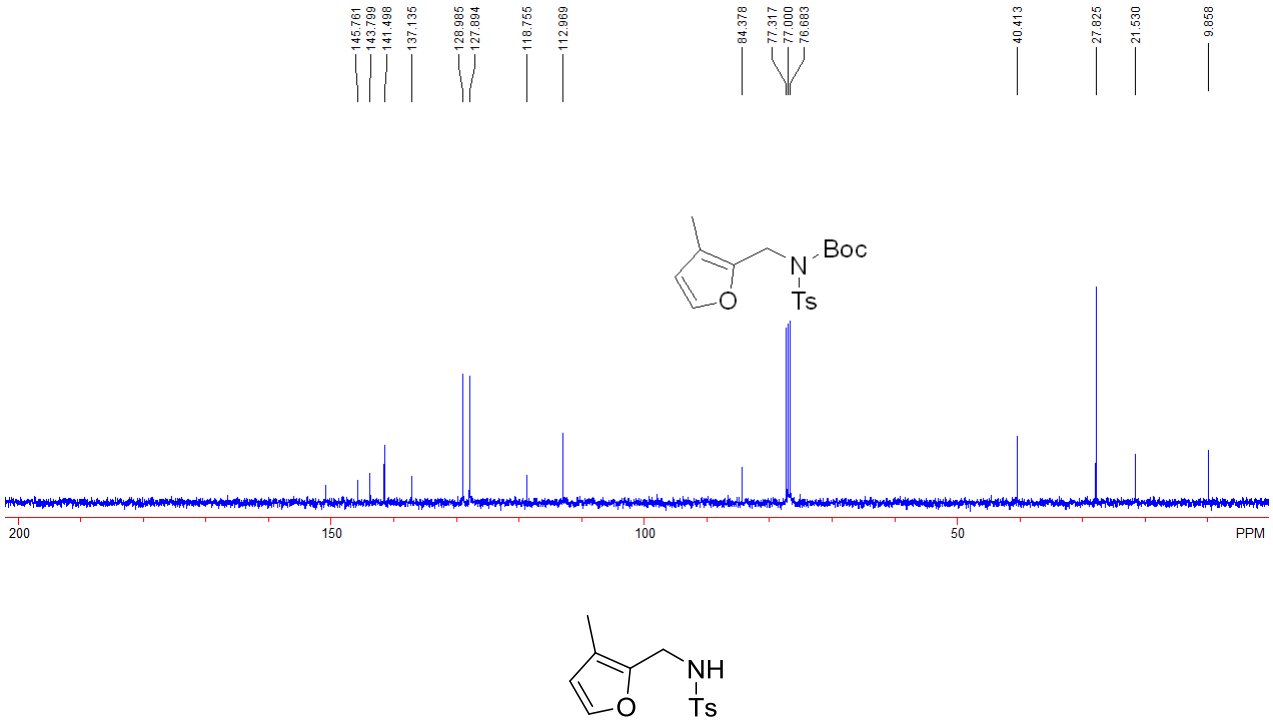


The experiments were performed in the same procedure as that in the synthesis of compound **1v**.

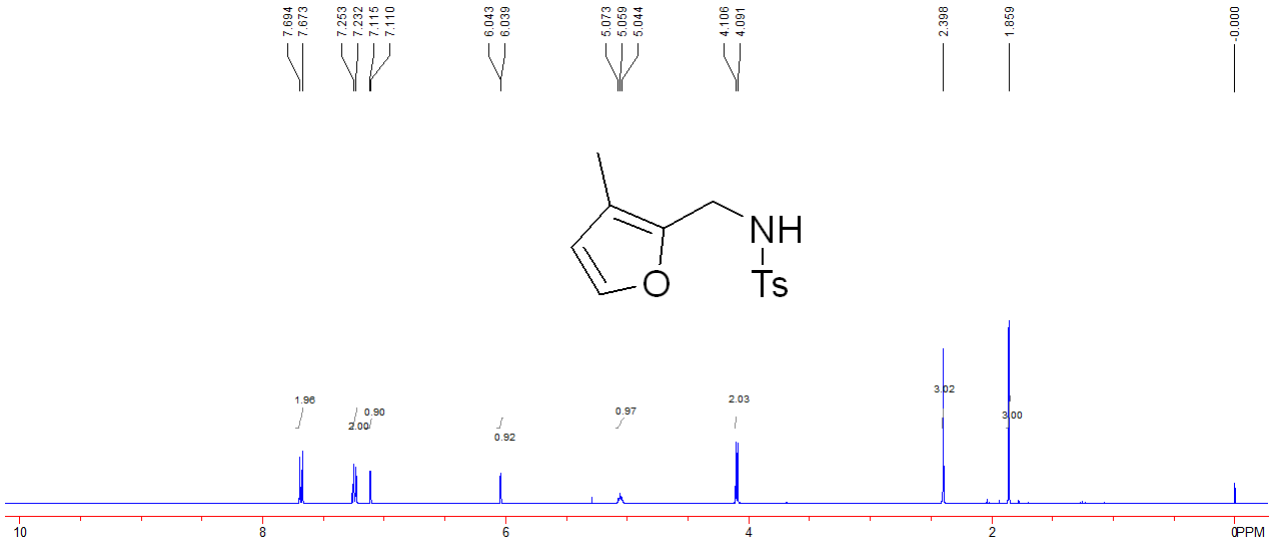


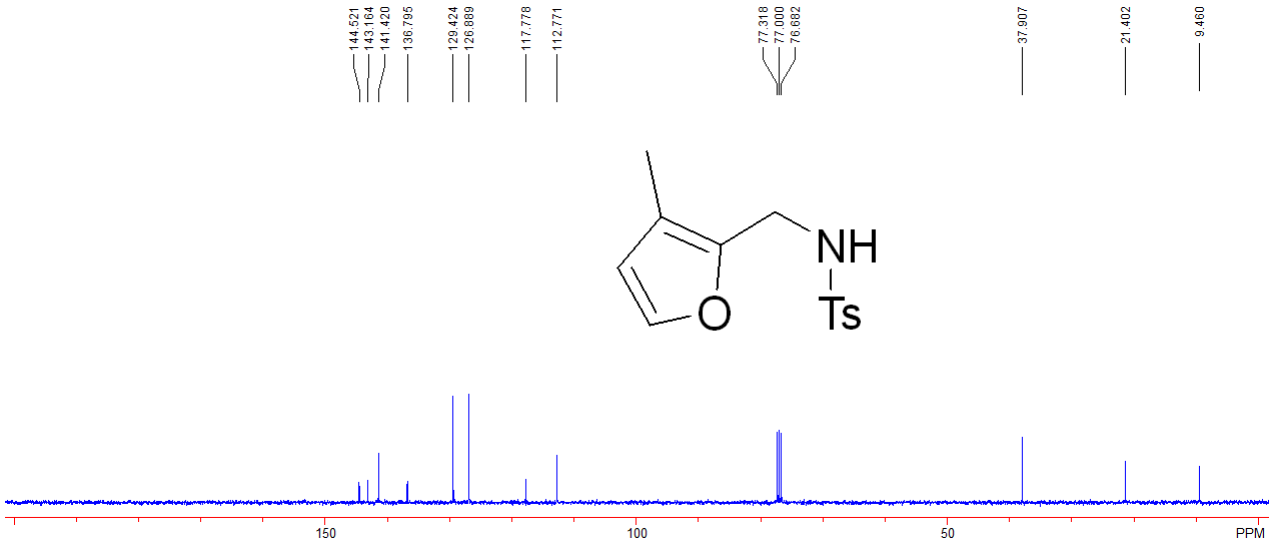
tert-butyl ((3-methylfuran-2-yl)methyl)(tosyl)carbamate (S-18q): a white solid (5.68 g, 54% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.47 (d, 2H, *J* = 8.4 Hz, ArH), 7.29-7.28 (m, 1H, ArH), 7.20 (d, 2H, *J* = 8.4 Hz, ArH), 6.22 (s, 1H, ArH), 5.01 (d, 2H, *J* = 7.6 Hz, CH_2), 2.39 (s, 3H, CH_3), 2.12 (m, 3H, CH_3), 1.35 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 145.8, 143.8, 141.5, 137.1, 128.0, 127.9, 118.7, 113.0, 84.4, 40.4, 27.8, 21.5, 9.8; IR (DCM) ν 2988, 1727, 1354, 1150, 1087, 675 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 383.1635, found 383.1638.

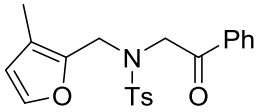




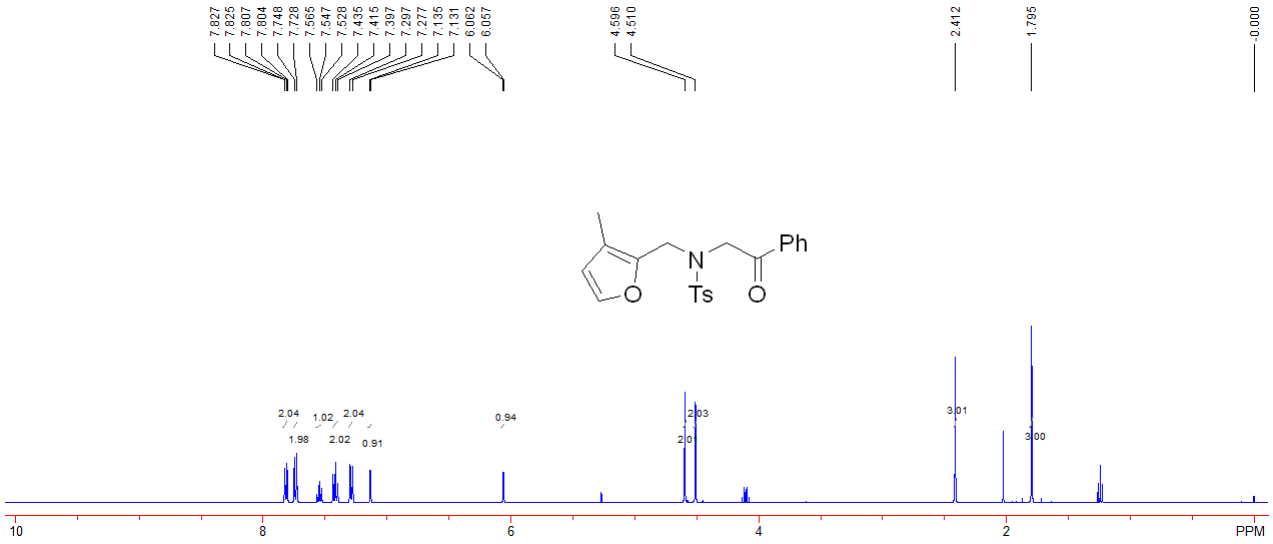
4-methyl-N-((3-methylfuran-2-yl)methyl)benzenesulfonamide (S-19q): a colorless oil (3.4 g, 83% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.68 (d, 2H, *J* = 8.4 Hz, ArH), 7.24 (d, 2H, *J* = 8.4 Hz, ArH), 7.11 (d, 1H, *J* = 2.0 Hz, ArH), 6.04 (d, 1H, *J* = 2.0 Hz, ArH), 5.06 (t, 1H, *J* = 5.6 Hz, NH), 4.10 (d, 2H, *J* = 5.6 Hz, CH_2), 2.40 (s, 3H, CH_3), 1.86 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.5, 143.2, 141.4, 136.8, 129.4, 126.9, 117.8, 112.8, 37.9, 21.4, 9.5; IR (DCM) ν 3280, 1321, 1153, 1092, 1047, 663 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{19}N_2O_3S$ [M + NH_4]$^{+}$ m/z 283.1111, found 283.1114.

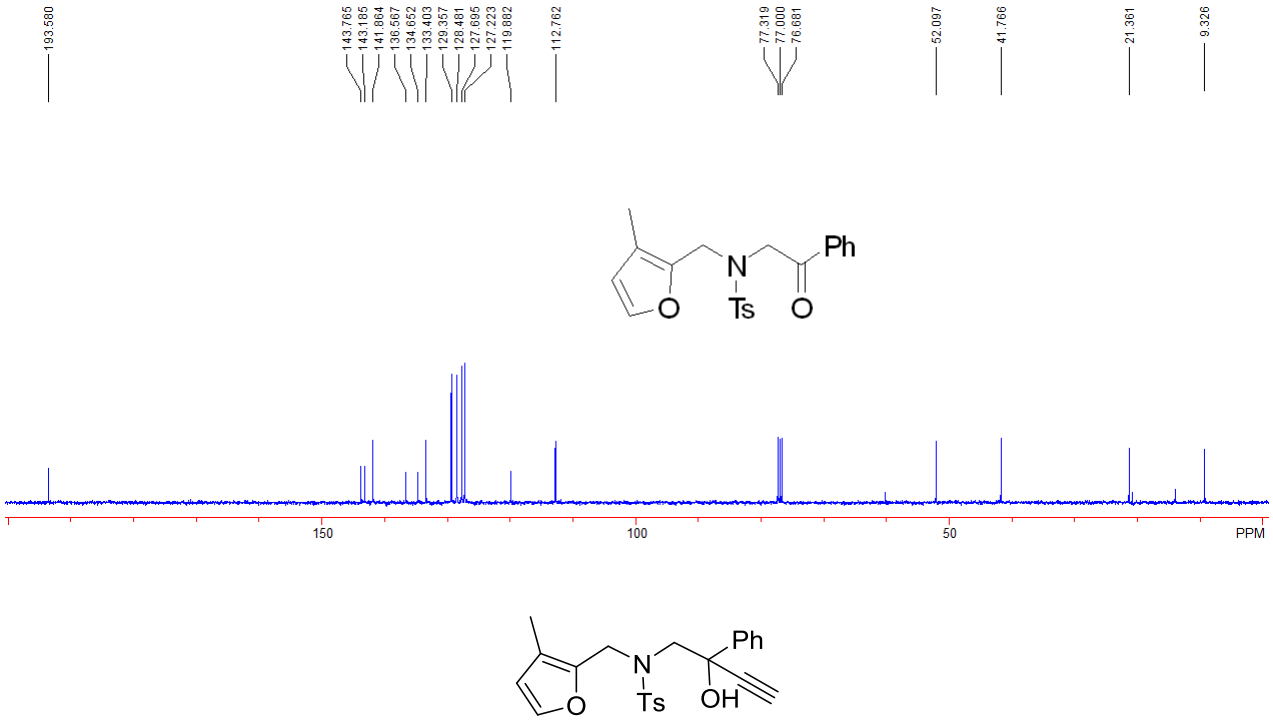




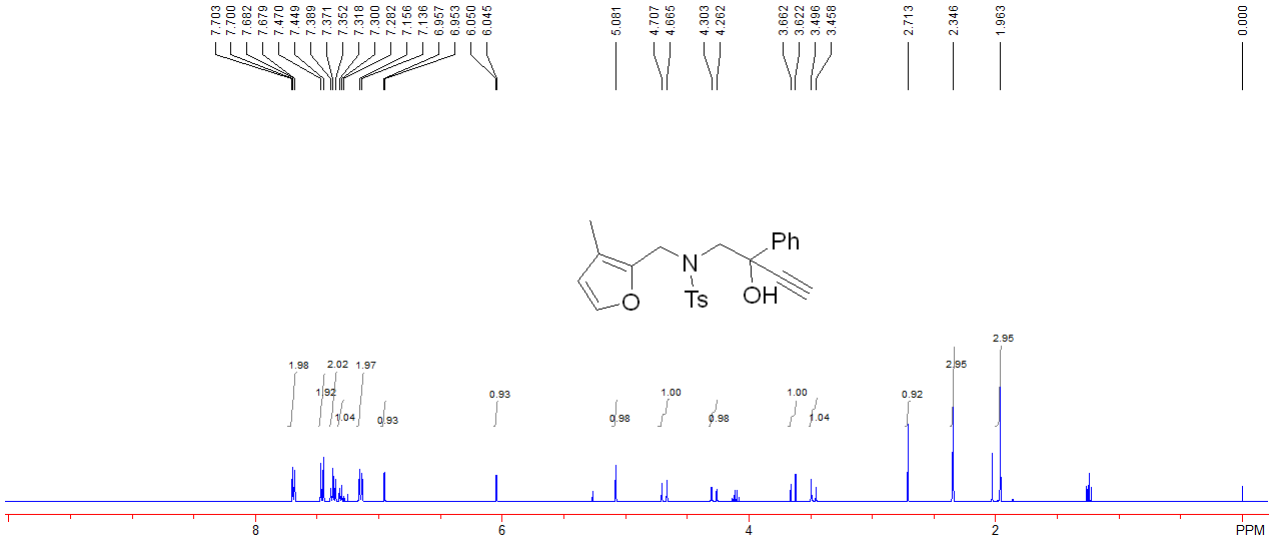


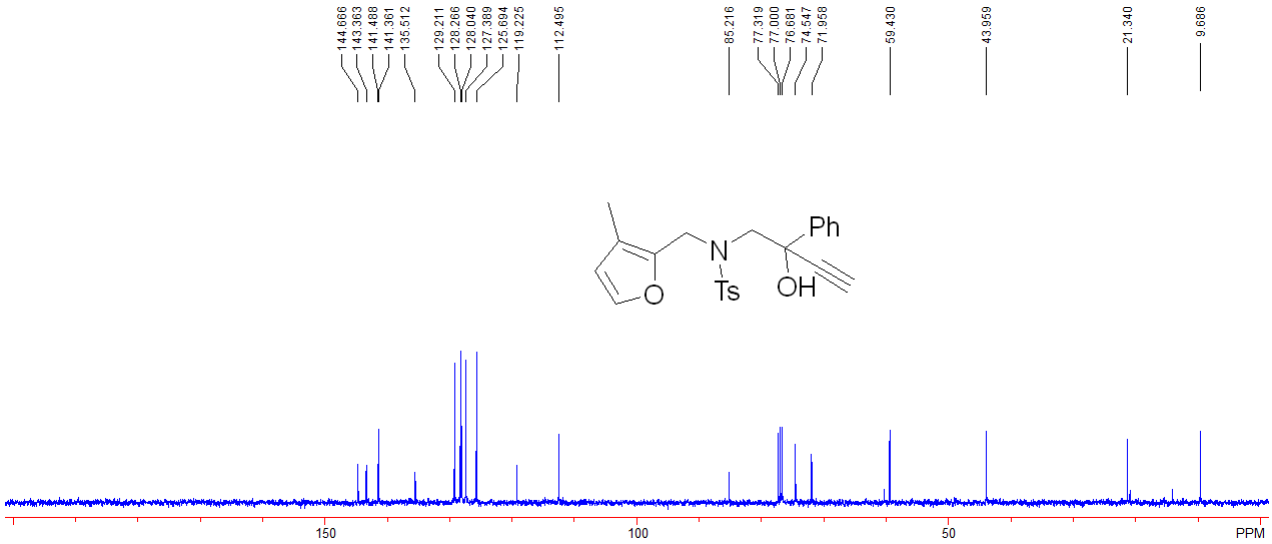
4-methyl-N-((3-methylfuran-2-yl)methyl)-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-20q): a colorless oil (5.1 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.83-7.80 (m, 2H, ArH), 7.74 (d, 2H, *J* = 8.0 Hz, ArH), 7.56-7.53 (m, 1H, ArH), 7.43-7.40 (m, 2H, ArH), 7.29 (d, 2H, *J* = 8.0 Hz, ArH), 7.13 (d, 1H, *J* = 1.6 Hz, ArH), 6.06 (d, 1H, *J* = 1.6 Hz, ArH), 4.60 (s, 2H, CH_2), 4.51 (s, 2H, CH_2), 2.41 (s, 3H, CH_3), 1.79 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.6, 143.8, 143.2, 141.9, 136.6, 134.6, 133.4, 129.3, 128.5, 127.7, 127.2, 119.9, 112.8, 52.1, 41.8, 21.4, 9.3; IR (DCM) ν 2923, 1698, 1335, 1154, 1089, 742 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{25}N_2O_4S$ $[M + NH_4]^+$ m/z 401.130, found 401.1534.

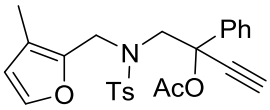




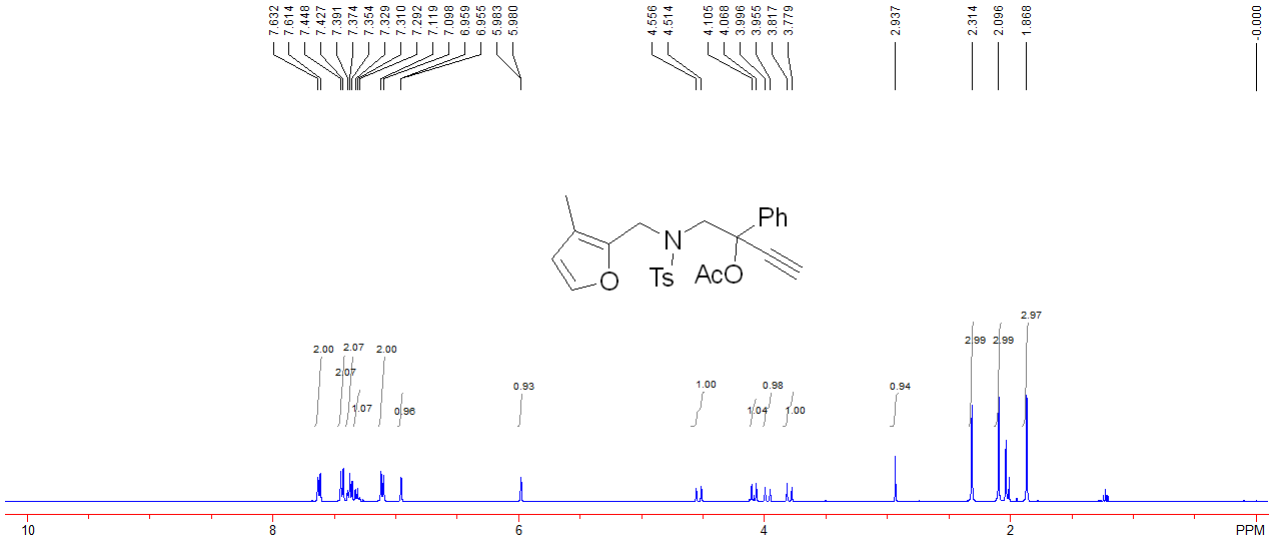
N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methyl-N-((3-methylfuran-2-yl)methyl)benzenesulfonamide (S-21q): a colorless oil (1.1 g, 35% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.70-7.68 (m, 2H, ArH), 7.46 (d, 2H, *J* = 8.4 Hz, ArH), 7.39-7.35 (m, 2H, ArH), 7.32-7.28 (m, 1H, ArH), 7.15 (d, 2H, *J* = 8.4 Hz, ArH), 6.95 (d, 1H, *J* = 1.6 Hz, ArH), 6.05 (d, 1H, *J* = 1.6 Hz, ArH), 5.08 (s, 1H, OH), 4.69 (d, 1H, *J* = 16.8 Hz, CH_2), 4.28 (d, 1H, *J* = 16.8 Hz, CH_2), 3.64 (d, 1H, *J* = 16.0 Hz, CH_2), 3.48 (d, 1H, J = 16.0, CH_2), 2.71 (s, 1H, CH), 2.35 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.7, 143.4, 141.5, 141.4, 135.5, 129.2, 128.3, 128.0, 127.4, 125.7, 119.2, 112.5, 85.2, 74.5, 71.9, 59.4, 43.9, 21.3, 9.7; IR (DCM) ν 3453, 3287, 1328, 1150, 1087, 698 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{27}N_2O_4S$ $[M + NH_4]^+$ m/z 427.1686, found 427.1689.

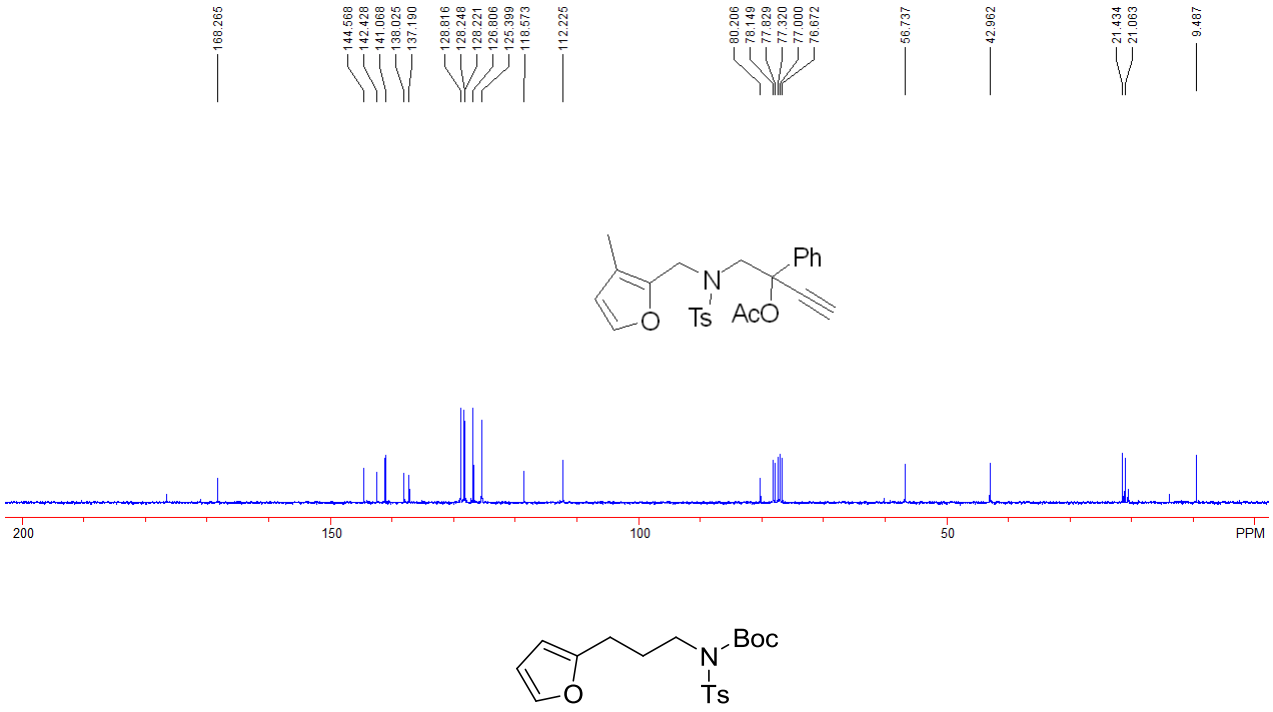




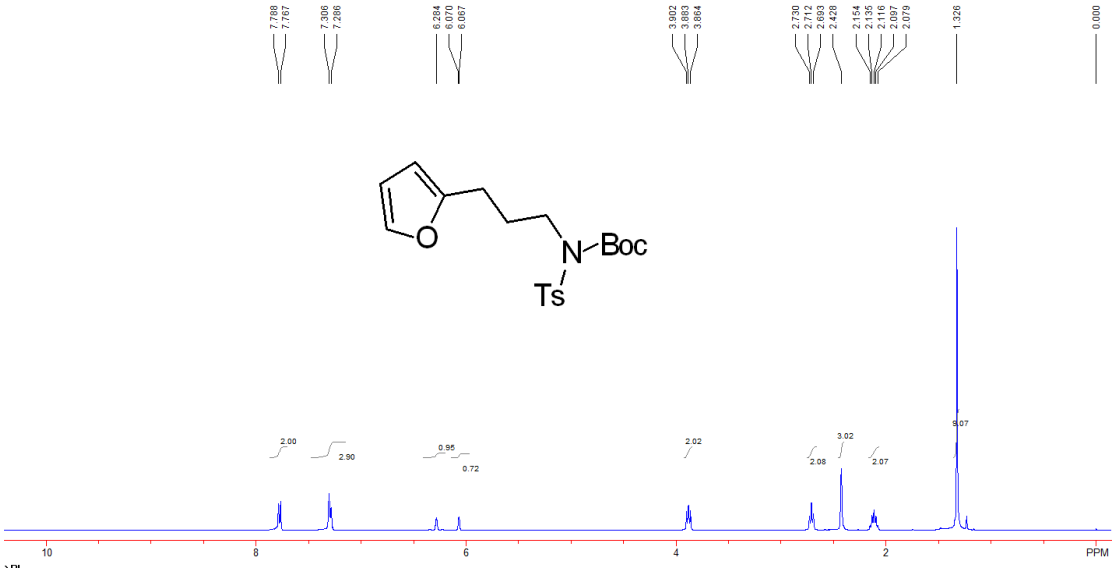


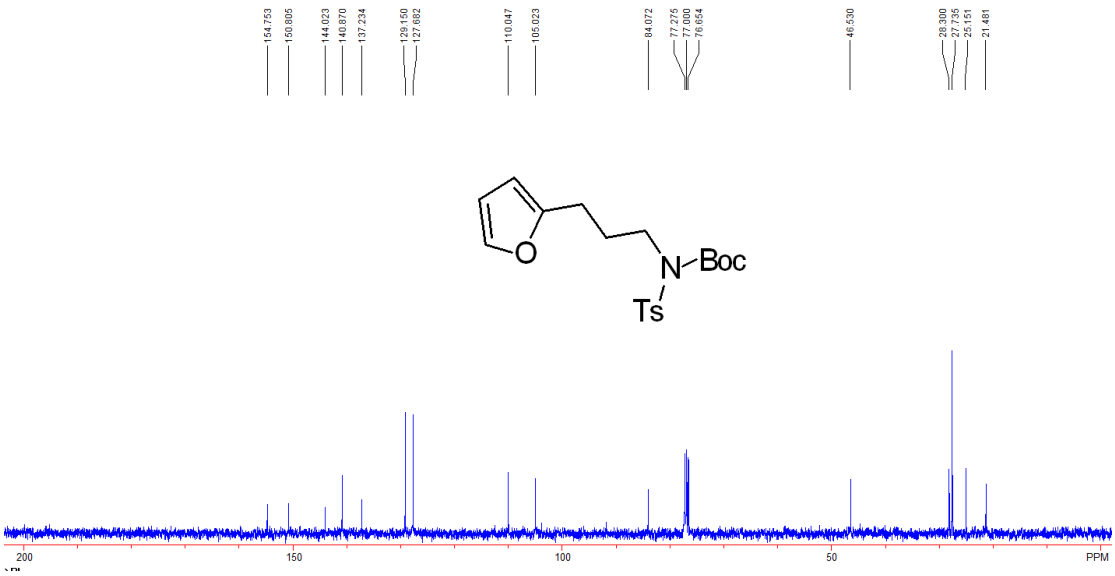
1-((4-methyl-N-((3-methylfuran-2-yl)methyl)phenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 2, entry 1q): a colorless oil (1.0 g, 80% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.62 (d, 2H, *J* = 7.2 Hz, ArH), 7.44 (d, 2H, *J* = 8.4 Hz, ArH), 7.39-7.35 (m, 2H, ArH), 7.33-9.29 (m, 1H, ArH), 7.11 (d, 2H, *J* = 8.4 Hz, ArH), 6.96 (d, 1H, *J* = 2.0 Hz, ArH), 5.98 (d, 1H, *J* = 2.0 Hz, ArH), 4.53 (d, 1H, *J* = 16.8 Hz, CH_2), 4.09 (d, 1H, *J* = 14.8 Hz, CH_2), 3.97 (d, 1H, *J* = 16.4 Hz, CH_2), 3.80 (d, 1H, *J* = 14.8 Hz, CH_2), 2.94 (s, 1H, CH), 2.31 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 1.87 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.3, 144.6, 142.4, 141.1, 138.0, 137.2, 128.8, 128.24, 128.22, 126.8, 125.4, 118.6, 112.2, 80.2, 78.1, 77.8, 56.7, 43.0, 21.4, 21.1, 9.5; IR (DCM) ν 3279, 1751, 1346, 1221, 1157, 730 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1794.

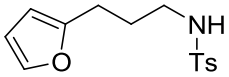




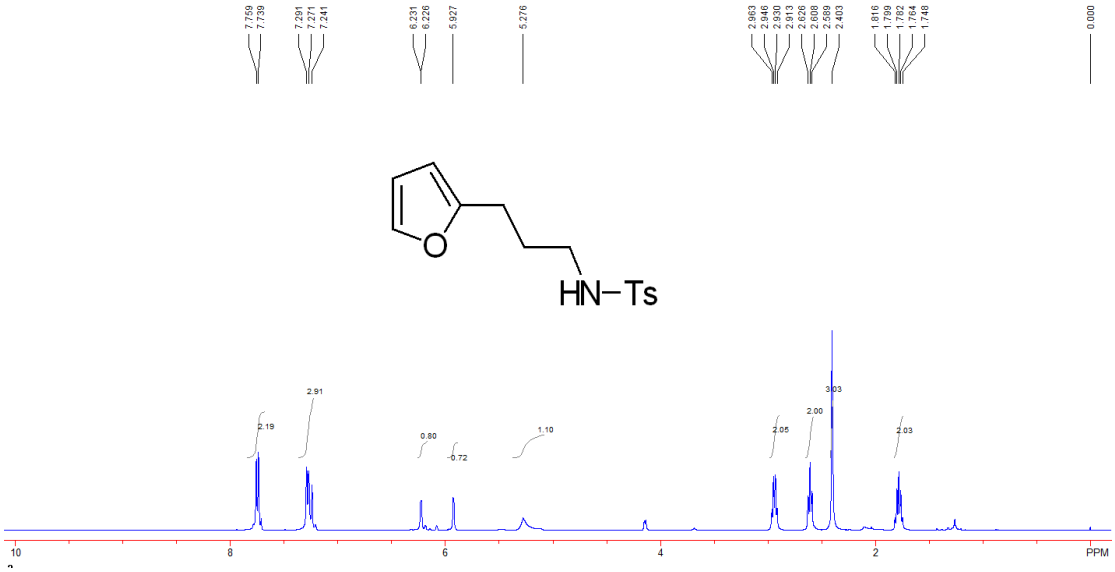
tert-butyl (3-(furan-2-yl)propyl)(tosyl)carbamate (S-18y): a colorless oil (1.6 g, 84% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.78 (d, 2H, *J* = 8.4 Hz, ArH), 7.31-7.29 (m, 3H, ArH), 6.28 (s, 1H, ArH), 6.07 (d, 1H, *J* = 1.2 Hz, ArH), 3.88 (d, 2H, *J* = 7.6 Hz, CH_2), 2.71 (d, 2H, *J* = 7.6 Hz, CH_2), 2.43 (s, 3H, CH_3), 2.15-2.08 (m, 2H, CH_2), 1.33 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 154.7, 150.8, 144.0, 140.9, 137.2, 129.1, 127.7, 110.0, 105.0, 84.1, 46.5, 28.3, 27.7, 25.1, 21.5; IR (DCM) ν 2979, 1724, 1351, 1285, 1151, 1087 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 397.1792, found 397.1789.

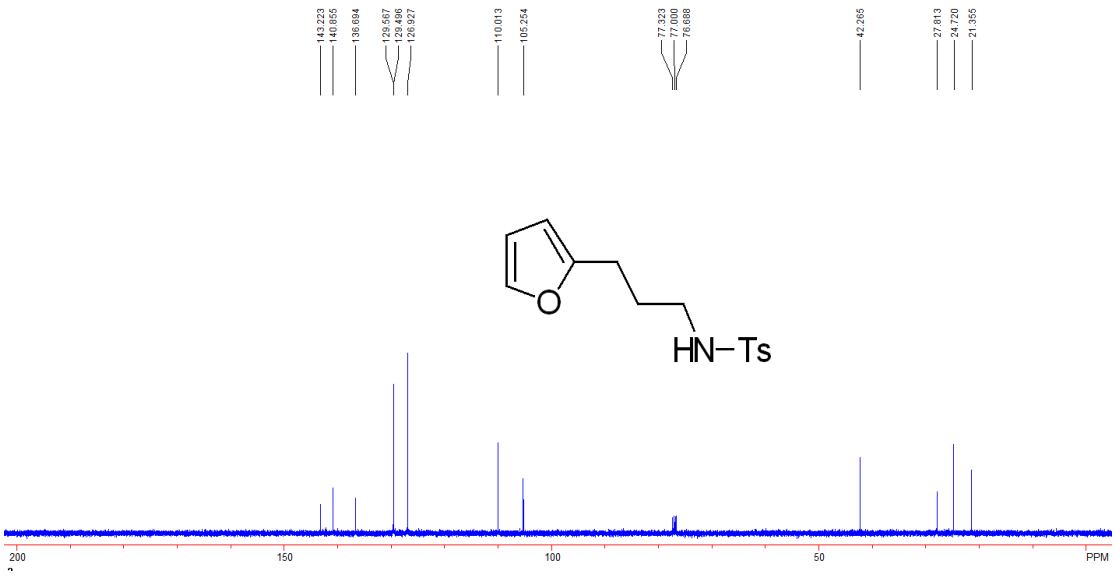


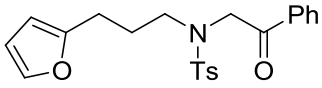




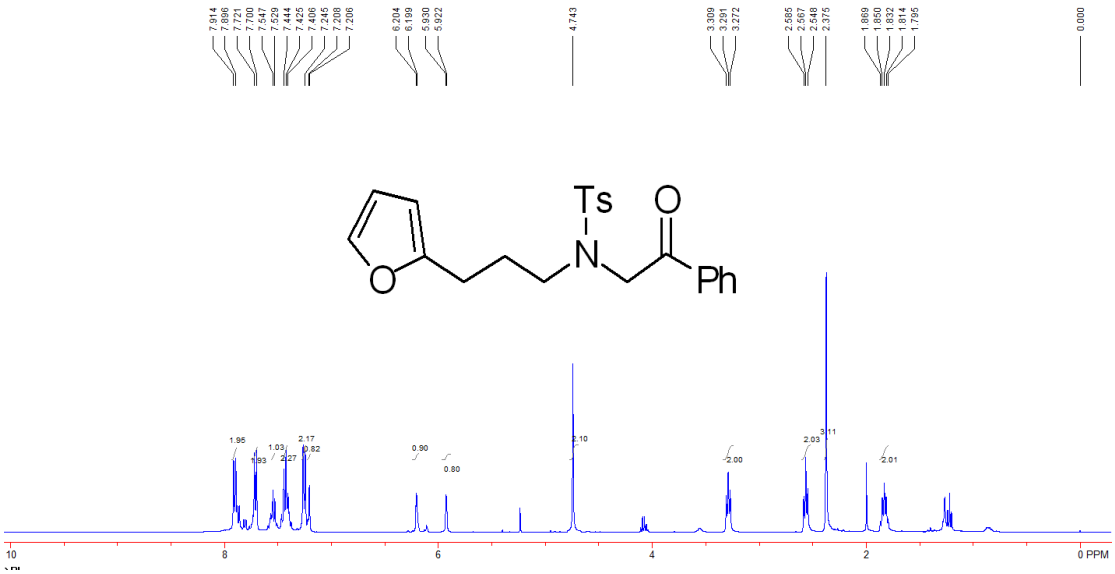
N-(3-(furan-2-yl)propyl)-4-methylbenzenesulfonamide (S-19y): a colorless oil (1.1 g, 45% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.75 (d, 2H, *J* = 8.0 Hz, ArH), 7.29-7.24 (m, 3H, ArH), 6.23-6.22 (m, 1H, ArH), 5.92 (d, 1H, *J* = 2.0 Hz, ArH), 5.28 (br, 1H, NH), 2.96-2.91 (m, 2H, CH_2), 2.61 (t, 2H, *J* = 7.2 Hz, CH_2), 2.40 (s, 3H, CH_3), 1.82-1.75 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 143.2, 140.8, 136.7, 129.6, 129.5, 126.9, 110.0, 105.2, 42.3, 27.8, 24.7, 21.3; IR (DCM) ν 3281, 2926, 1597, 1322, 1154, 1092, 813, 659 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{18}NO_3$ $[M + H]^+$ m/z 280.1002, found 280.1000.

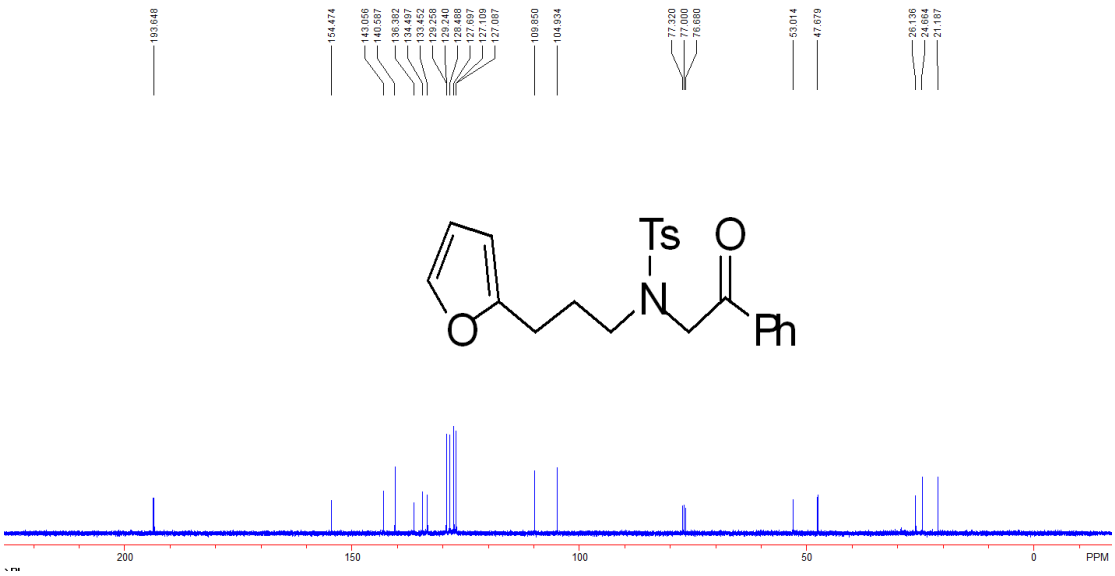


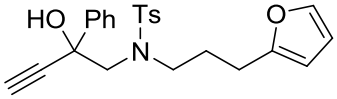




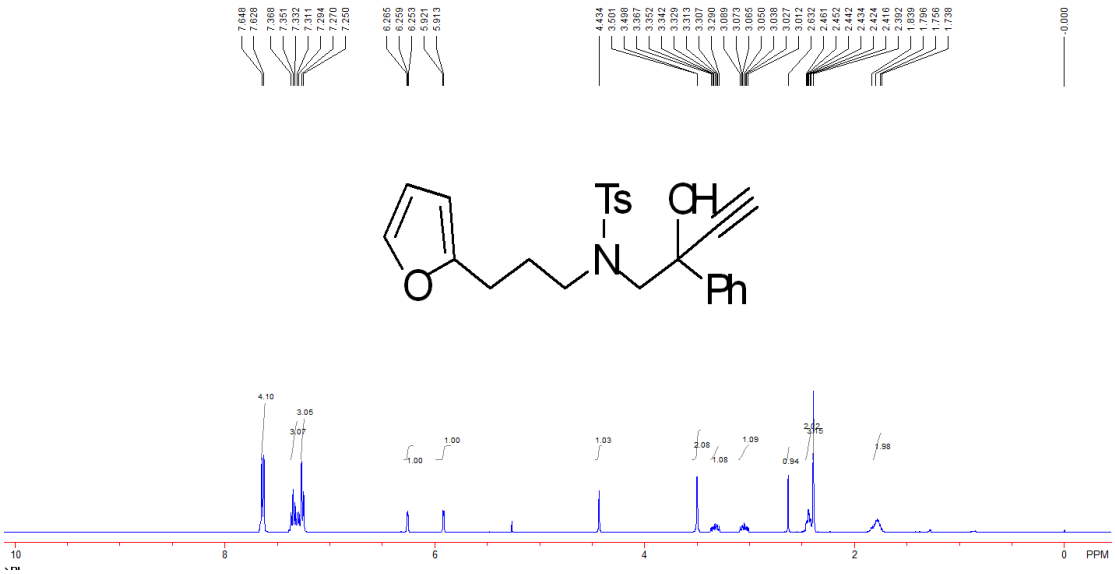
N-(3-(furan-2-yl)propyl)-4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-20y): a colorless oil (1.6 g, 99% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.90 (d, 2H, *J* = 7.2 Hz, ArH), 7.71 (d, 2H, *J* = 8.4 Hz, ArH), 7.55-7.53 (m, 1H, ArH), 7.44-7.41 (m, 2H, ArH), 7.24-7.21 (m, 3H, ArH), 6.20 (d, 1H, *J* = 2.0 Hz, ArH), 5.93 (d, 1H, *J* = 3.2 Hz, ArH), 4.74 (s, 2H, CH_2), 3.29 (t, 2H, *J* = 7.2 Hz, CH_2), 2.57 (t, 2H, *J* = 7.2 Hz, CH_2), 2.37 (s, 3H, CH_3), 1.87-1.79 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.6, 154.5, 143.0, 140.6, 136.4, 134.5, 133.4, 129.2, 128.5, 127.7, 127.1, 109.8, 104.9, 53.0, 47.7, 26.1, 24.7, 21.2; IR (DCM) ν 2923, 1698, 1597, 1333, 1153, 749 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{27}N_2O_4S$ $[M + NH_4]^+$ m/z 415.1686, found 415.1686.

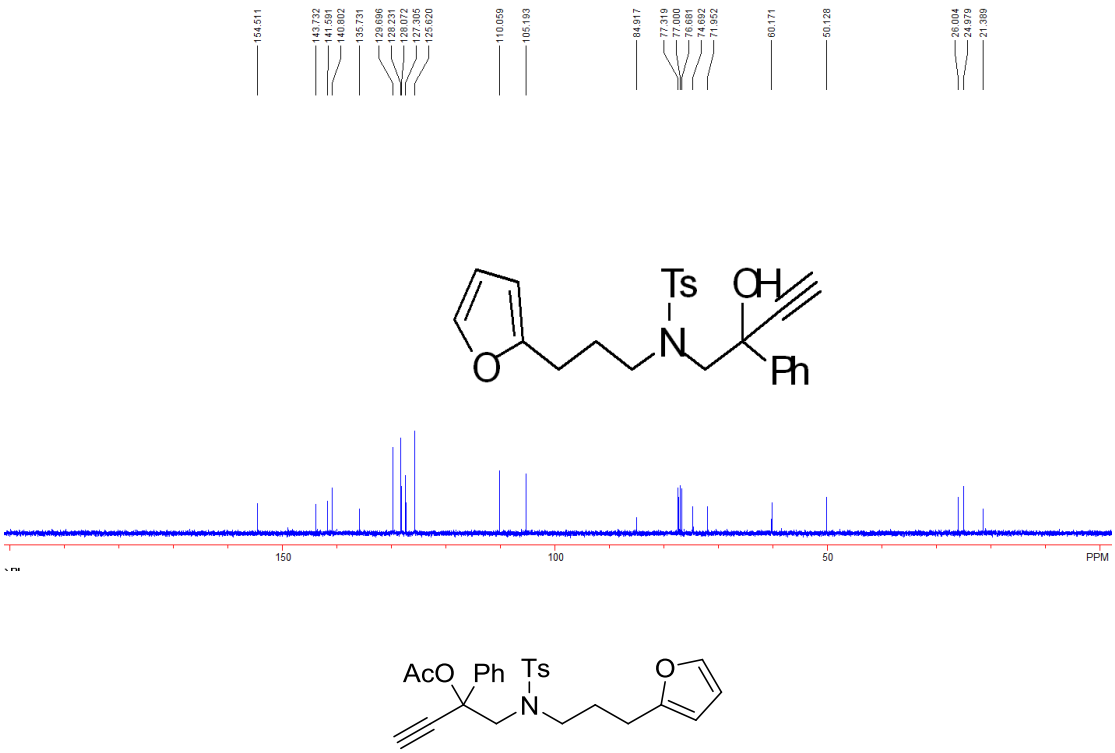




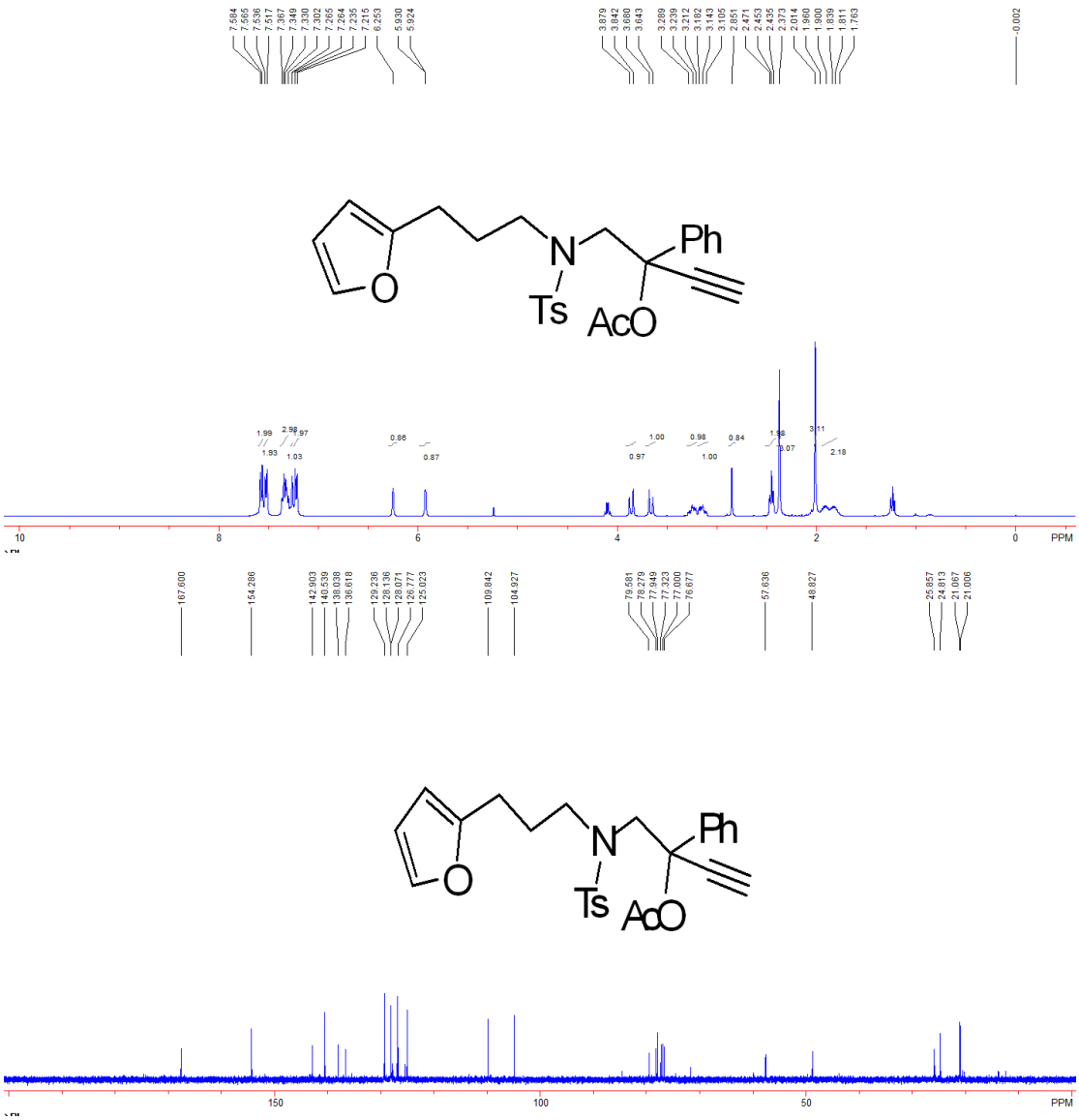


N-(3-(furan-2-yl)propyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-21y): a colorless oil (963 mg, 49% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64 (d, 4H, *J* = 8.0 Hz, ArH), 7.37-7.29 (m, 3H, ArH), 7.27-7.25 (m, 3H, ArH), 6.26-6.25 (m, 1H, ArH), 5.92 (d, 1H, *J* = 3.2 Hz, ArH), 4.43 (s, 1H, OH), 3.50 (d, 2H, *J* = 1.2 Hz, CH_2), 3.37-3.29 (m, 1H, CH_2), 3.09-3.01 (m, 1H, CH_2), 2.63 (s, 1H, CH), 2.46-2.42 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 1.84-1.74 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 154.5, 143.7, 141.6, 140.8, 135.7, 129.7, 128.2, 128.1, 127.3, 125.6, 110.0, 105.2, 84.9, 74.7, 71.9, 60.2, 50.1, 26.0, 25.0, 21.4; IR (DCM) ν 3478, 3286, 1598, 1332, 1154, 815, 730 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{24}NO_3S$ [M + H]$^{+}$ m/z 406.1471, found 406.1490.

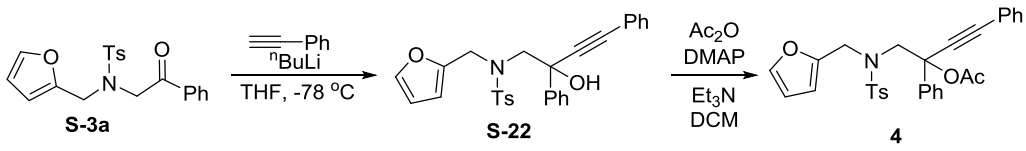




1-((N-(3-(furan-2-yl)propyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (Table 3, entry 1y): a colorless oil (483 mg, 59% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.57 (d, 2H, *J* = 7.6 Hz, ArH), 7.53 (d, 2H, *J* = 7.6 Hz, ArH), 7.37-7.30 (m, 3H, ArH), 7.26 (s, 1H, ArH), 7.22 (d, 2H, *J* = 8.0 Hz, ArH), 6.25 (s, 1H, ArH), 5.93 (d, 1H, *J* = 2.4 Hz, ArH), 3.86 (d, 1H, *J* = 14.8 Hz, CH_2), 3.66 (d, 1H, *J* = 14.8 Hz, CH_2), 3.29-3.21 (m, 1H, CH_2), 3.18-3.10 (m, 1H, CH_2), 2.85 (s, 1H, CH), 2.45 (t, 2H, *J* = 7.2 Hz, CH_2), 2.37 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.96-1.76 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 167.6, 154.3, 142.9, 140.5, 138.0, 136.6, 129.2, 128.14, 128.07, 126.8, 125.0, 109.8, 104.9, 79.6, 78.3, 77.9, 57.6, 48.8, 25.8, 24.8, 21.1, 21.0; IR (DCM) ν 3273, 2926, 1751, 1336, 1222, 1154, 1007, 732 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_5S$ $[M + NH_4]^+$ m/z 483.1948, found 483.1954.



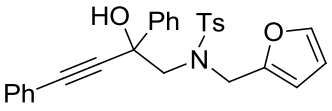
The Syntheses and the Spectroscopic Data of Substrate 4



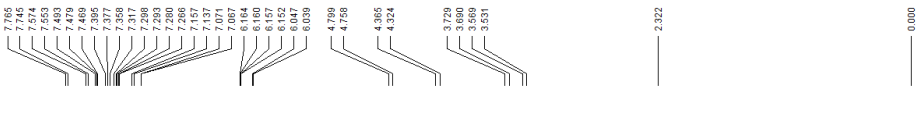
To a stirred solution of ethynylbenzene (1.02 g, 10 mmol) in THF (10 mL) was added ^{n}BuLi (4 mL, 10 mmol, 2.5 M in hexane) at -78 ^{o}C under Ar atmosphere, the reaction mixture stirred for 30 min. A solution of **S-3a** (2.95 g, 8 mmol) in THF (10 mL) was then added at -78 ^{o}C. The reaction was quenched with saturated ammonium chloride and extracted with EA after 2 h. The combined organic layers were washed with brine and dried over anhydrous $NaSO_4$. The solvent

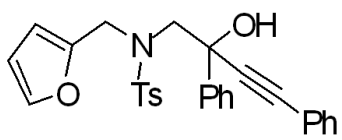
was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 5/1) to provide product **S-22** (3.16 g) in 84% yield.

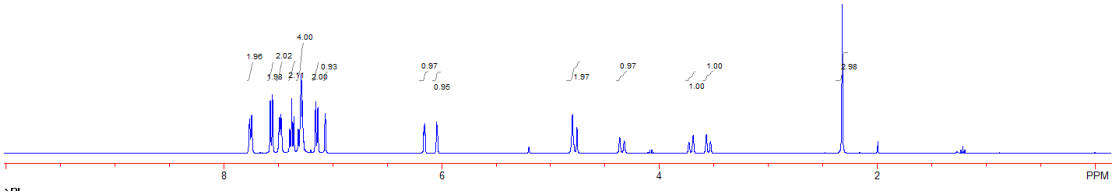
To a solution of **S-22** (2.83 g, 6 mmol) and DMAP (146 mg, 1.2 mmol) in DCM (30 mL) was added Et_3N (1.7 mL, 12 mmol) at 0 ^oC, then a solution of Ac_2O (0.9 mL, 9 mmol) in DCM (20 mL) was added in dropwise. The reaction mixture was stirred overnight. The reaction mixture was washed with water, brine and dried over anhydrous $NaSO_4$. The solvent was evaporated under reduced pressure and the residue was purified by flash column chromatography (silica gel, PE/EA = 5/1) to provide product **4** (2.37 g) in 77% yield.

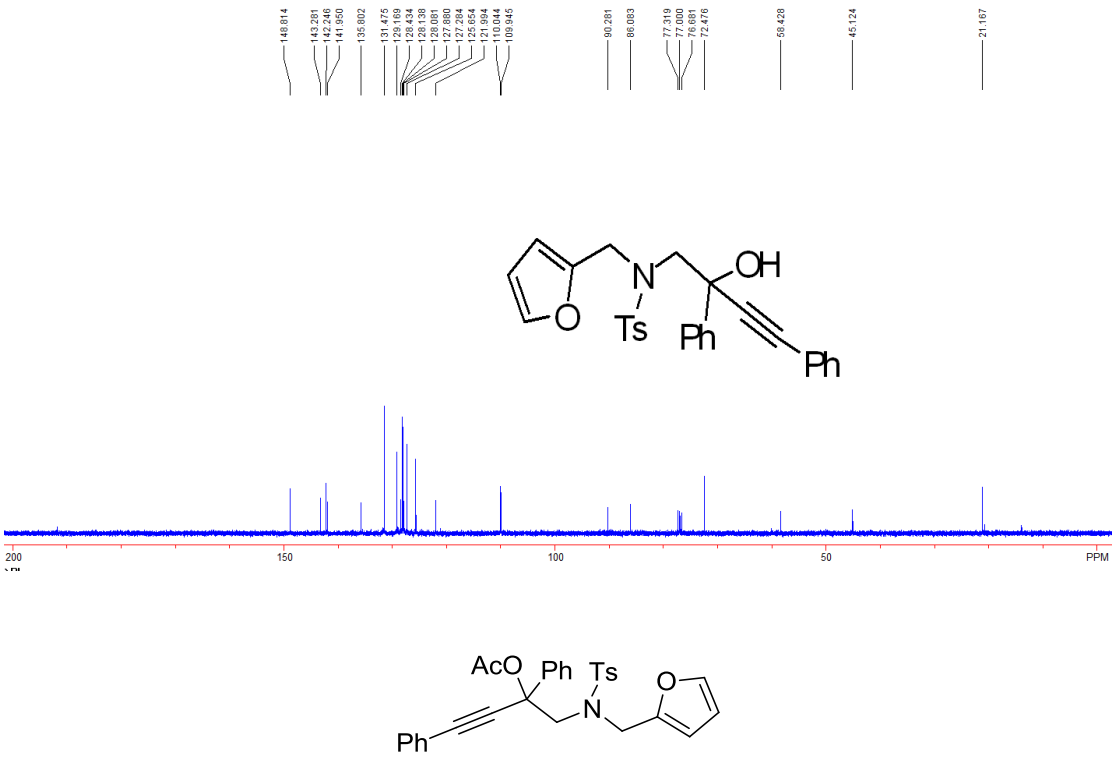


N-(furan-2-ylmethyl)-N-(2-hydroxy-2,4-diphenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-22): a colorless oil (3.2 g, 84% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.75 (d, 2H, *J* = 8.0 Hz, ArH), 7.56 (d, 2H, *J* = 8.4 Hz, ArH), 7.49-7.47 (m, 2H, ArH), 7.38 (t, 2H, *J* = 7.6 Hz, ArH), 7.32-7.27 (m, 4H, ArH), 7.15 (d, 2H, *J* = 8.0 Hz, ArH), 7.07 (d, 1H, *J* = 1.6 Hz, ArH), 6.16 (dd, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.04 (d, *J* = 3.2 Hz, ArH), 4.80-4.76 (m, 2H, OH and CH_2), 4.34 (d, 1H, *J* = 16.4 Hz, CH_2), 3.71 (d, 1H, *J* = 15.6 Hz, CH_2), 3.55 (d, 1H, *J* = 15.6 Hz, CH_2), 2.32 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 148.8, 143.3, 142.2, 141.9, 135.8, 131.5, 129.2, 128.4, 128.14, 128.08, 127.9, 127.3, 125.6, 122.0, 110.0, 109.9, 90.3, 86.1, 72.5, 58.4, 45.1, 21.2; IR (DCM) ν 3458, 1598, 1490, 1330, 1151, 1007, 756 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_4S$ $[M + NH_4]^+$ m/z 489.1843, found 489.1843.

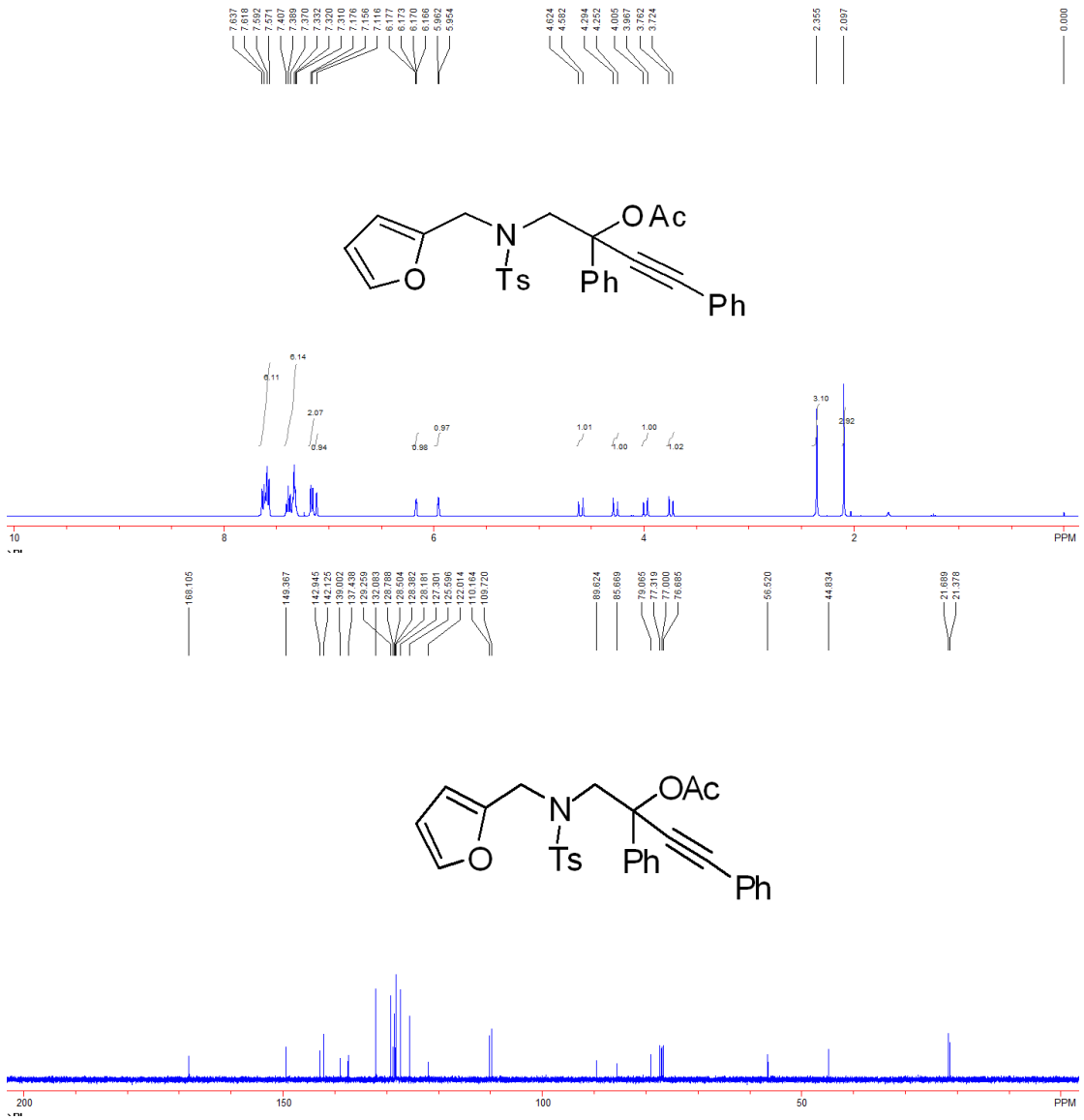




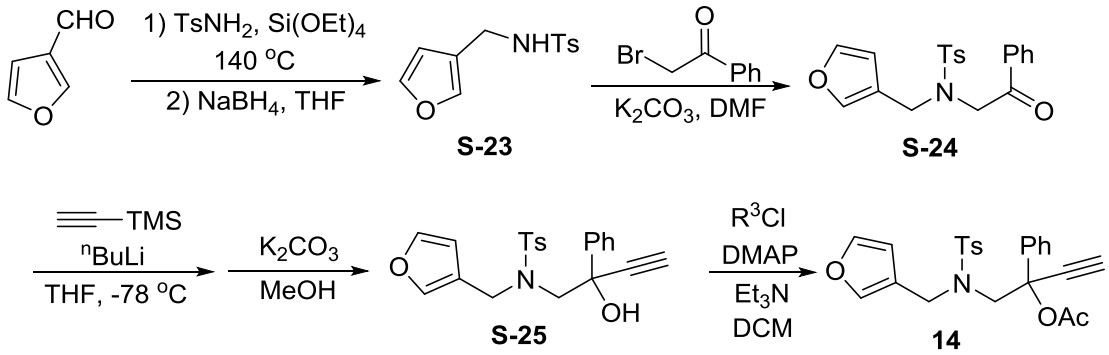




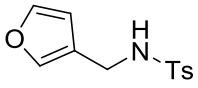
1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2,4-diphenylbut-3-yn-2-yl acetate (Scheme 3, compound 4): a white solid (2.4 g, 77% yield), mp: 144-146 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64-7.57 (m, 6H, ArH), 7.41-7.31 (m, 6H, ArH), 7.17 (d, 2H, *J* = 8.0 Hz, ArH), 7.12 (s, 1H, ArH), 6.17 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 5.96 (d, 1H, *J* = 3.2 Hz, ArH), 4.60 (d, 1H, *J* = 16.8 Hz, CH_2), 4.27 (d, 1H, *J* = 16.8 Hz, CH_2), 3.99 (d, 1H, *J* = 15.2 Hz, CH_2), 3.74 (d, 1H, *J* = 15.2 Hz, CH_2), 2.35 (s, 3H, CH_3), 2.10 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.1, 149.4, 142.9, 142.1, 139.0, 137.4, 132.1, 129.2, 128.8, 128.5, 128.4, 128.2, 127.3, 125.6, 122.0, 110.2, 109.7, 89.6, 85.7, 79.1, 56.5, 44.8, 21.7, 21.4; IR (DCM) ν 3061, 2233, 1756, 1347, 1223, 1158, 993, 731 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{31}N_2O_5S$ [M + NH_4]$^{+}$ m/z 531.1948, found 531.1941.



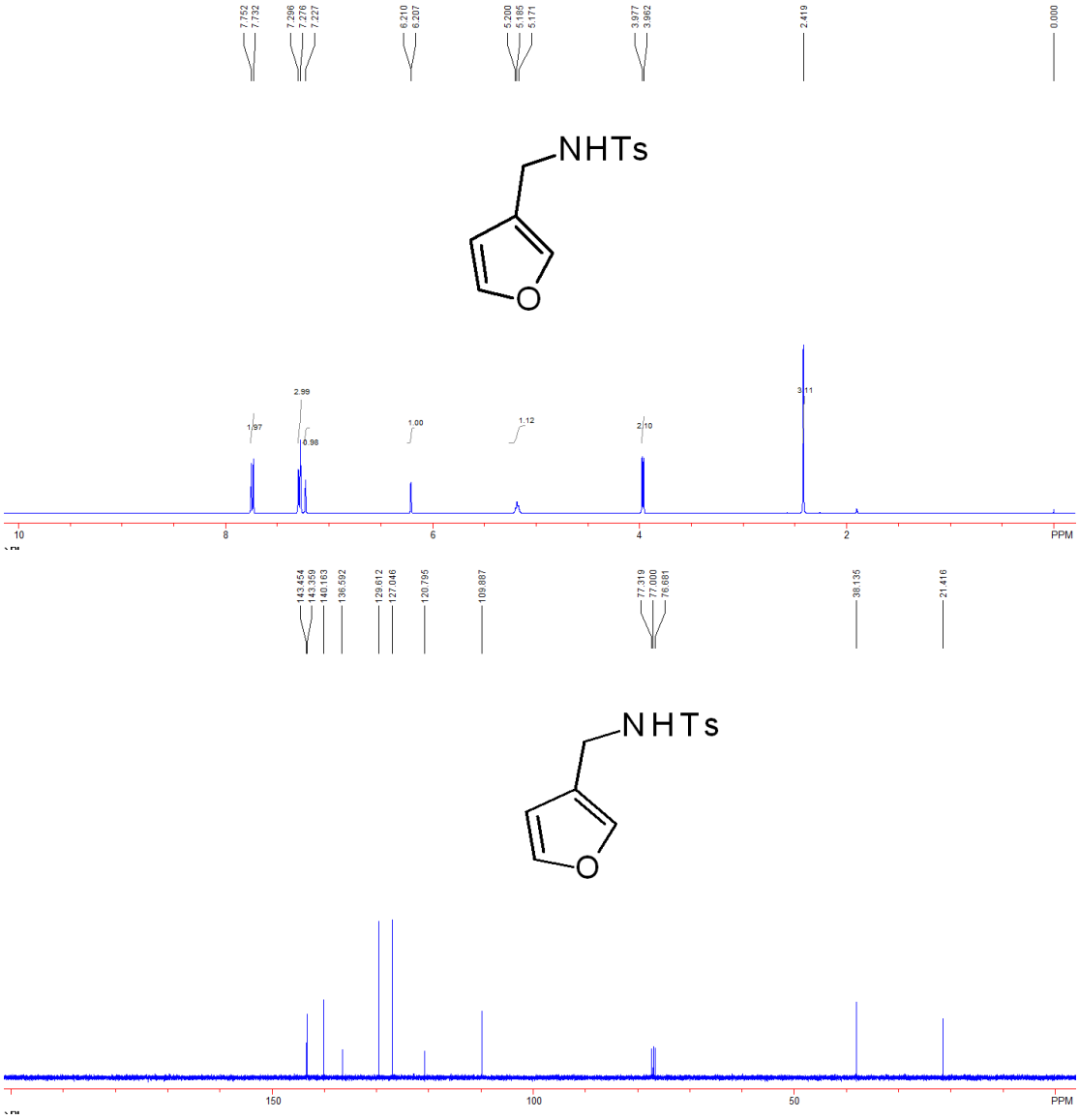
The Syntheses and the Spectroscopic Data of Substrate 14

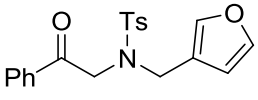


The experiments were performed in the same procedure as that in the synthesis of compound **1a**.

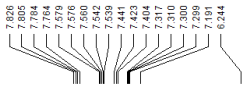


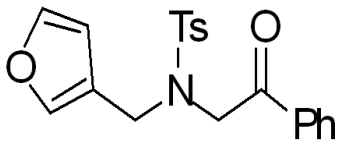
N-(furan-3-ylmethyl)-4-methylbenzenesulfonamide (S-23): a white solid (4.4 g, 76% yield), mp: 97-99 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.74 (d, 2H, *J* = 8.0 Hz, ArH), 7.29 (d, 2H, *J* = 8.0 Hz, ArH), 7.23 (s, 1H, ArH), 6.21 (d, 1H, *J* = 1.2 Hz, ArH), 5.18 (t, 1H, *J* = 6.0 Hz, NH), 3.97 (d, 2H, *J* = 6.0 Hz, CH_2), 2.42 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 143.4, 143.3, 140.2, 136.6, 129.6, 127.0, 120.8, 109.9, 38.1, 21.4; IR (DCM) ν 3257, 1430, 1317, 1154, 1038, 810 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}NO_3$ $[M + NH_4]^+$ m/z 252.0689, found 252.0697.

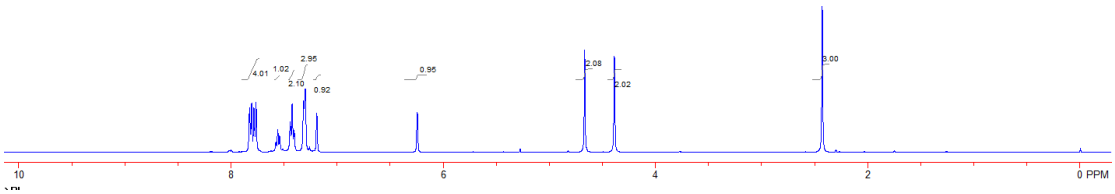


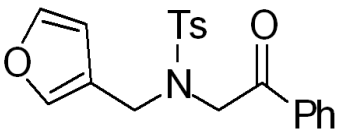


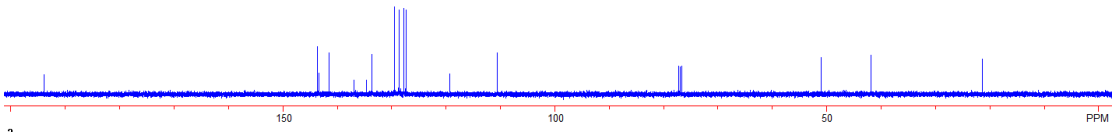
N-(furan-3-ylmethyl)-4-methyl-N-(2-oxo-2-phenylethyl)benzenesulfonamide (S-24): a white solid (3.1 g, 77% yield), mp: 107-109 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.83-7.76 (m, 4H, ArH), 7.58-7.54 (m, 1H, ArH), 7.44-7.41 (m, 2H, ArH), 7.32-7.30 (m, 3H, ArH), 7.19 (s, 1H, ArH), 6.24 (s, 1H, ArH), 4.67 (s, 2H, CH_2), 4.39 (s, 2H, CH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 193.9, 143.6, 143.4, 141.5, 136.9, 134.7, 133.6, 129.5, 128.7, 127.7, 127.3, 119.3, 110.6, 51.1, 41.9, 21.5; IR (DCM) ν 2915, 1698, 1334, 1153, 1092, 908, 749 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{20}NO_4S$ $[M + H]^+$ m/z 370.1108, found 370.1113.

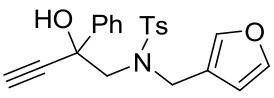






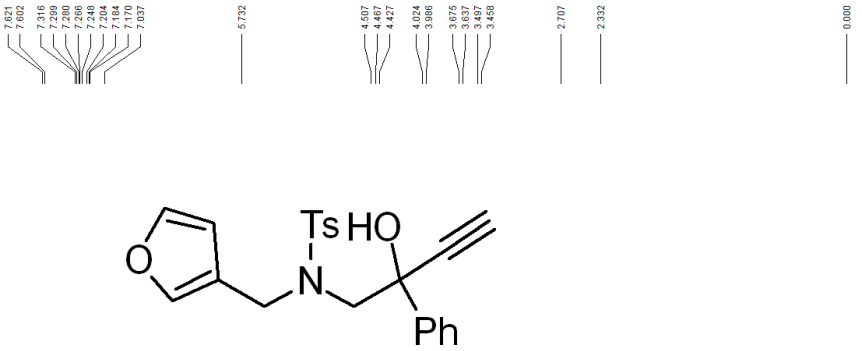


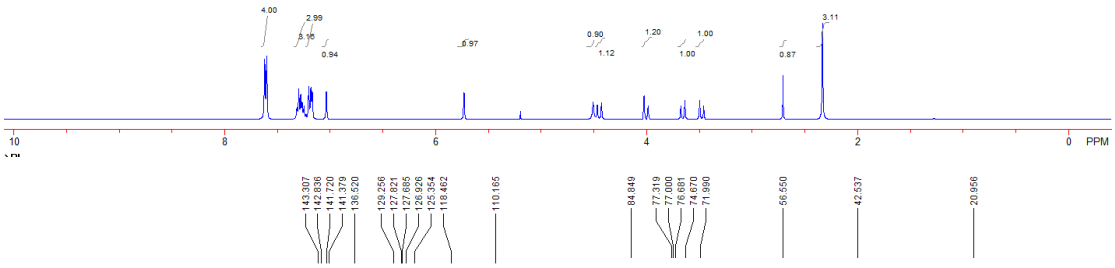


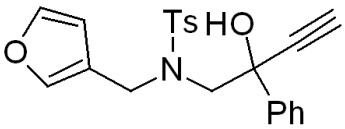


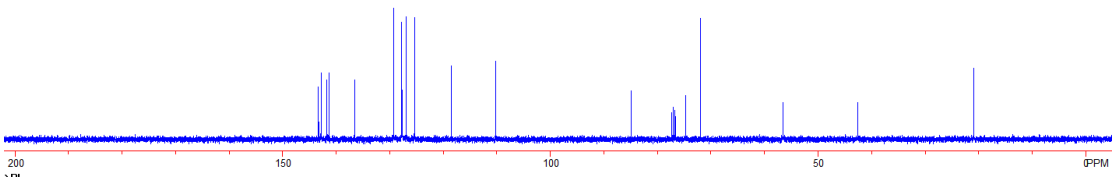
N-(furan-3-ylmethyl)-N-(2-hydroxy-2-phenylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-25): a white solid (1.1 g, 44% yield), mp: 121-123 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ

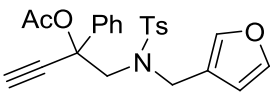
7.61 (d, 4H, *J* = 7.6 Hz, ArH), 7.32-7.25 (m, 3H, ArH), 7.20-7.17 (m, 3H, ArH), 7.04 (s, 1H, ArH), 5.73 (s, 1H, ArH), 4.51 (s, 1H, OH), 4.45 (d, 1H, *J* = 15.2 Hz, CH_2), 4.00 (d, 1H, *J* = 15.2 Hz, CH_2), 3.66 (d, 1H, *J* = 15.2 Hz, CH_2), 3.48 (d, 1H, *J* = 15.2 Hz, CH_2), 2.71 (s, 1H, CH), 2.33 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 143.3, 142.8, 141.7, 141.4, 136.5, 129.2, 127.8, 127.7, 126.9, 125.3, 118.5, 110.2, 84.8, 74.7, 72.0, 56.5, 42.5, 20.9; IR (DCM) ν 3465, 3288, 1597, 1328, 1152, 1022, 699 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}NNaO_4S$ $[M + Na]^+$ m/z 418.1083, found 418.1095.





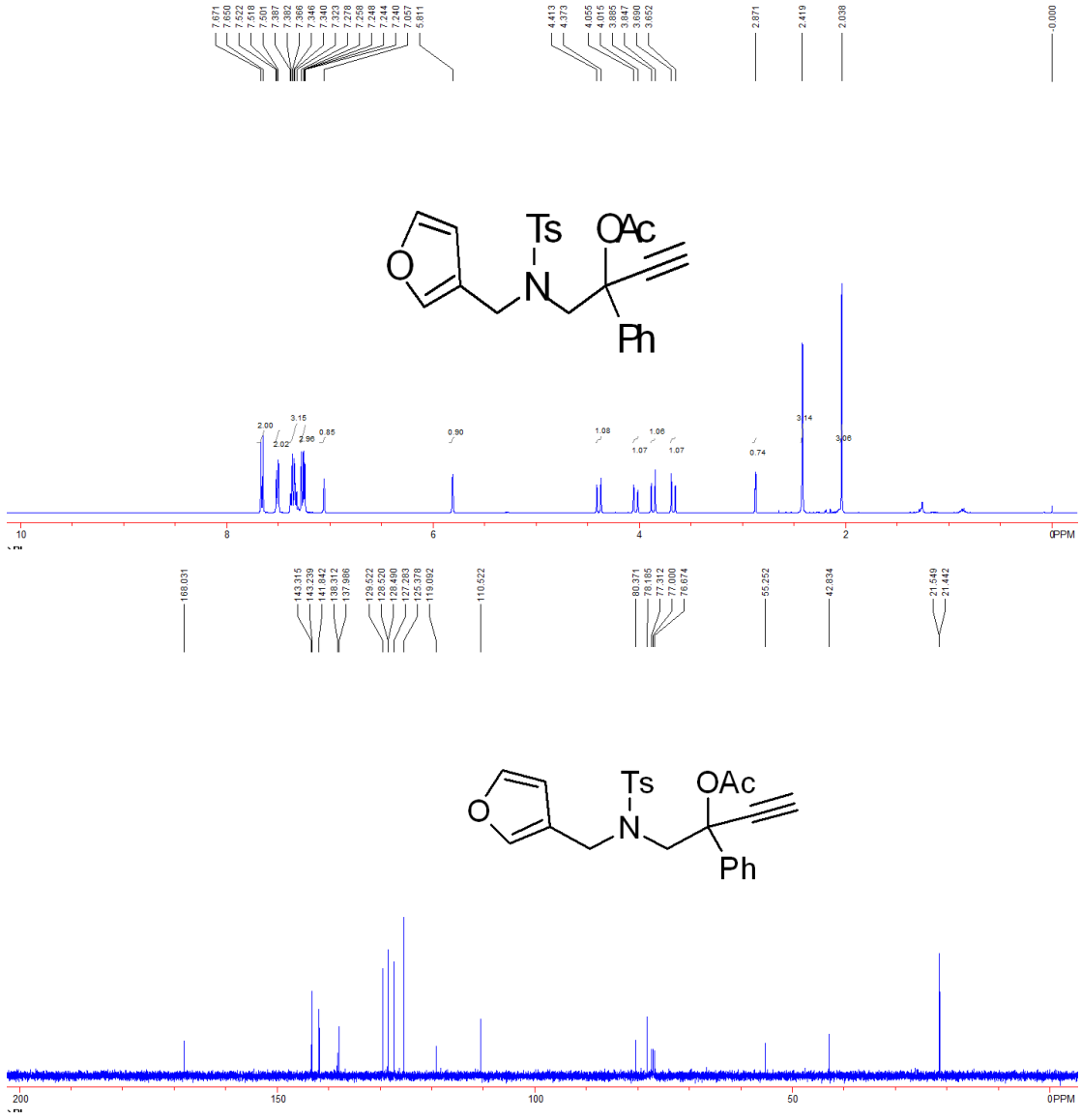




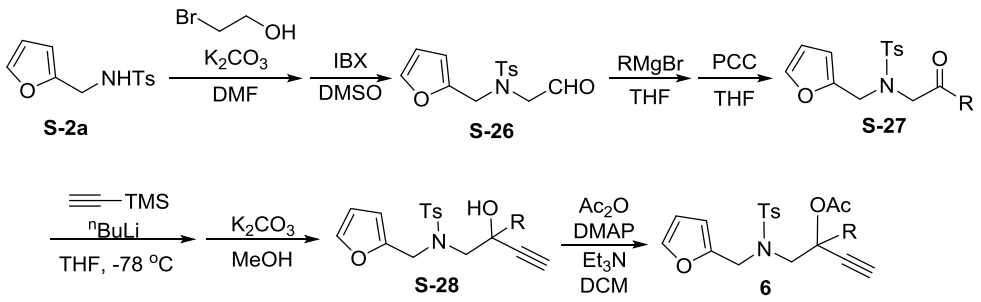


1-((N-(furan-3-ylmethyl)-4-methylphenyl)sulfonamido)-2-phenylbut-3-yn-2-yl acetate (compound 14): a white solid (1.0 g, 91% yield), mp: 152-154 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz,

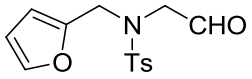
TMS) δ 7.66 (d, 2H, *J* = 8.4 Hz, ArH), 7.52-7.50 (m, 2H, ArH), 7.39-7.32 (m, 3H, ArH), 7.28-7.24 (m, 3H, ArH), 7.06 (s, 1H, ArH), 5.81 (s, 1H, ArH), 4.39 (d, 1H, *J* = 16.0 Hz, CH_2), 4.03 (d, 1H, *J* = 16.0 Hz, CH_2), 3.86 (d, 1H, *J* = 15.2 Hz, CH_2), 3.67 (d, 1H, *J* = 15.2 Hz, CH_2), 2.87 (s, 1H, CH), 2.42 (s, 3H, CH_3), 2.04 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.0, 143.3, 143.2, 141.8, 138.3, 138.0, 129.5, 128.52, 128.49, 127.3, 125.4, 119.1, 110.5, 80.4, 78.2, 55.2, 42.8, 21.5, 21.4; IR (DCM) ν 3271, 1752, 1329, 1221, 1155, 1019, 734 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 455.1635, found 455.1636.



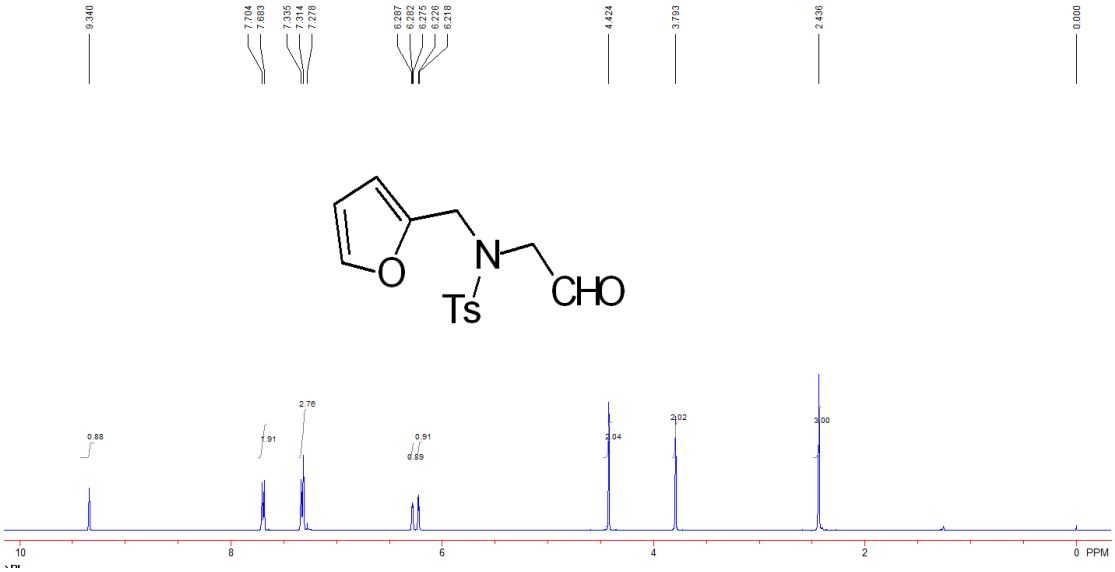
The Syntheses and the Spectroscopic Data of Substrate 6

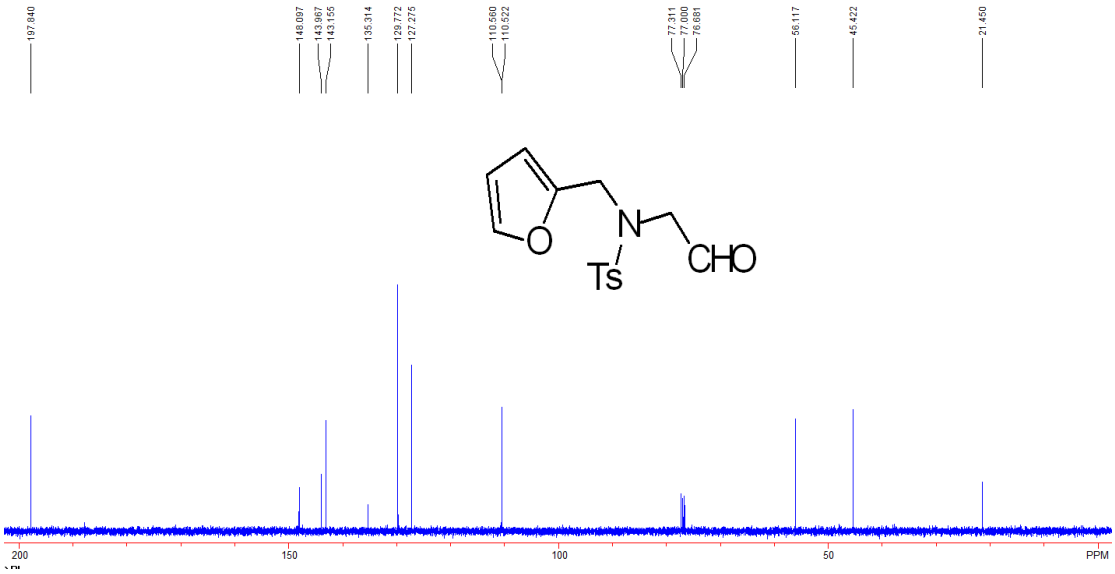


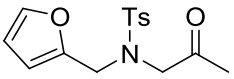
The experiments were performed in the same procedure as that in the synthesis of compound **1w**.



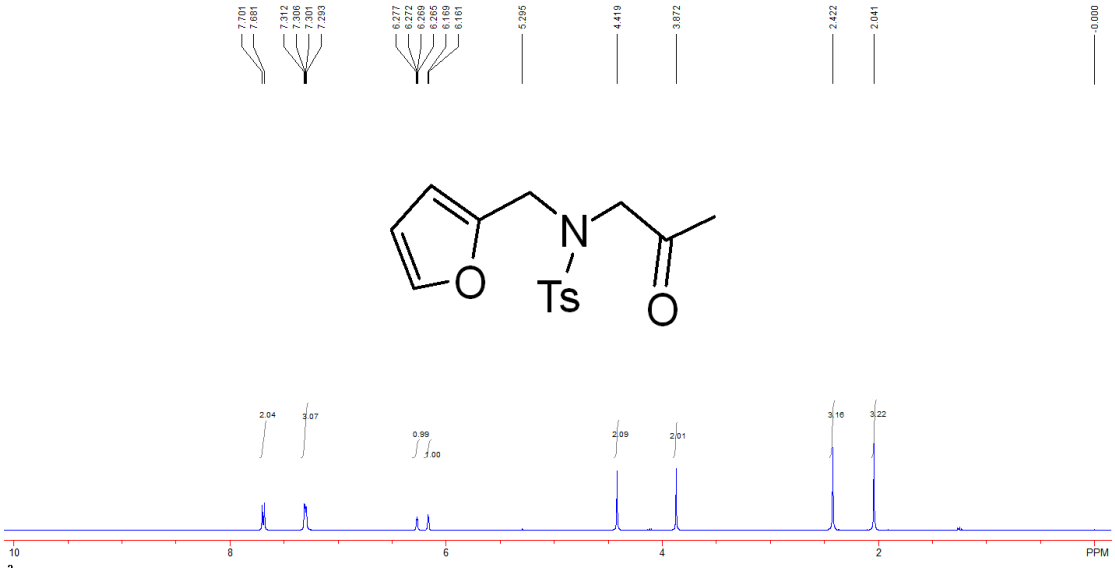
N-(furan-2-ylmethyl)-4-methyl-N-(2-oxoethyl)benzenesulfonamide (S-26): a colorless oil (1.4 g, 51% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 9.34 (s, 1H, CH), 7.69 (d, 2H, *J* = 8.4 Hz, ArH), 7.33-7.28 (m, 3H, ArH), 6.29-6.27 (m, 1H, ArH), 6.22 (d, 1H, *J* = 3.2 Hz, ArH), 4.42 (s, 2H, CH_2), 3.79 (s, 2H, CH_2), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 197.8, 148.1, 144.0, 143.1, 135.3, 129.8, 127.3, 110.6, 110.5, 56.1, 45.4, 21.4; IR (DCM) ν 3466, 2927, 1732, 1341, 1155 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{16}NO_4S$ $[M + H]^+$ m/z 294.0795, found 294.0797.

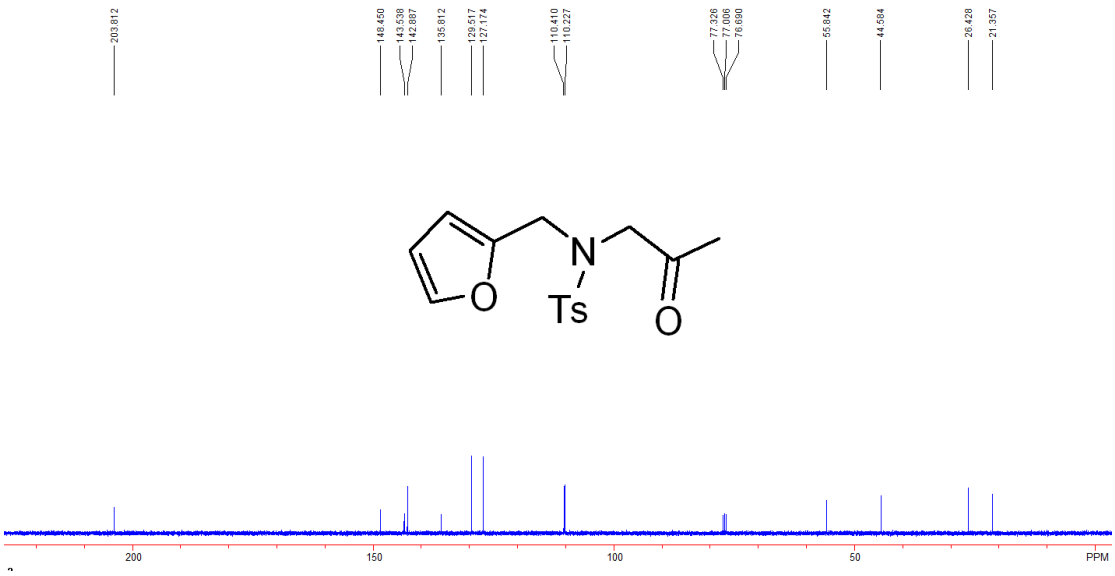


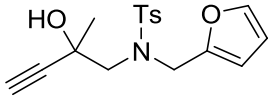




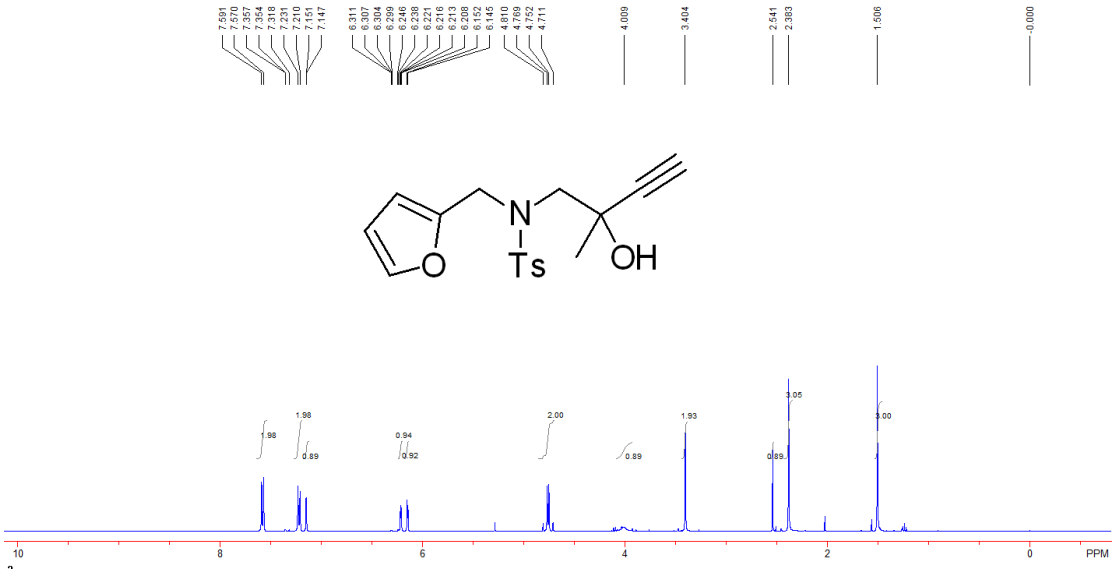
N-(furan-2-ylmethyl)-4-methyl-N-(2-oxopropyl)benzenesulfonamide (S-27a): a colorless oil (1.1 g, 74% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.69 (d, 2H, *J* = 8.0 Hz, ArH), 7.31-7.29 (m, 3H, ArH), 6.27 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.16 (d, 1H, *J* = 3.2 Hz, ArH), 4.42 (s, 2H, CH_2), 3.87 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.04 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 203.8, 148.4, 143.5, 142.9, 135.8, 129.5, 127.2, 110.4, 110.2, 55.8, 44.6, 26.4, 21.3; IR (DCM) ν 2923, 1732, 1335, 1155, 1096, 1000, 938, 815, 745 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{21}N_2O_4S$ $[M + NH_4]^+$ m/z 325.1217, found 325.1212.

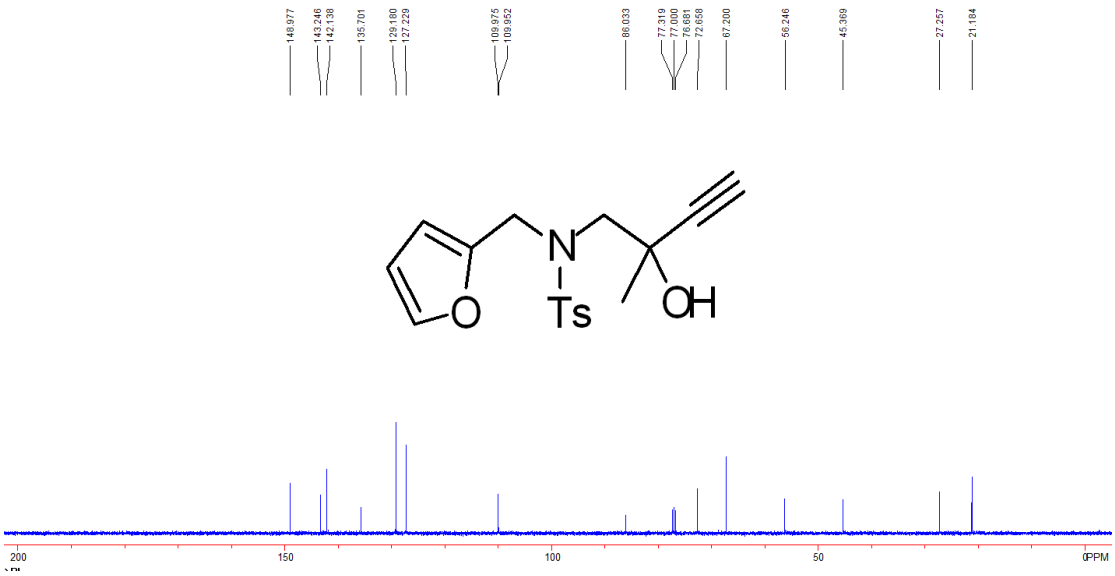


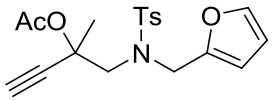




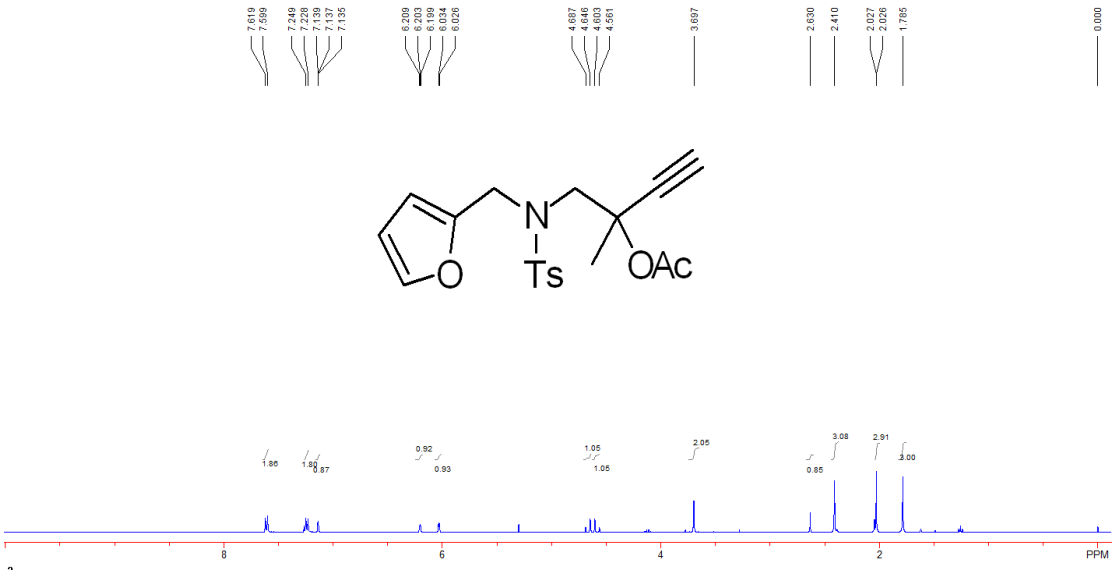
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-methylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-28a): a colorless oil (440 mg, 51% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 7.22 (d, 2H, *J* = 8.4 Hz, ArH), 7.15 (d, 1H, *J* = 1.6 Hz, ArH), 6.21 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.14 (d, 1H, *J* = 3.2 Hz, ArH), 4.81-4.71 (m, 2H, CH_2), 4.01 (br, 1H, OH), 3.40 (s, 2H, CH_2), 2.54 (s, 1H, CH), 2.38 (s, 3H, CH_3), 1.51 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.0, 143.2, 142.1, 135.7, 129.2, 127.2, 110.0, 109.9, 86.0, 72.6, 67.2, 56.2, 45.4, 27.2, 21.2; IR (DCM) ν 3486, 3285, 1498, 1328, 1151, 1088, 1009, 729 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{20}NO_4S$ $[M + H]^+$ m/z 334.1108, found 334.1099.

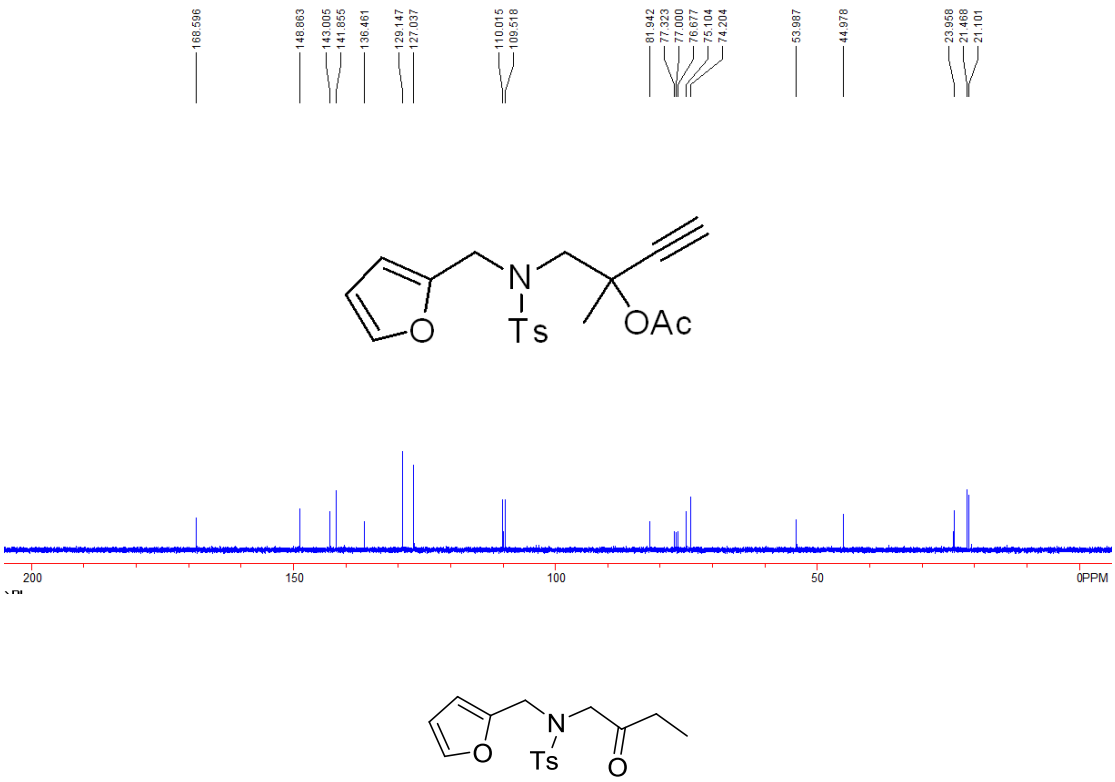




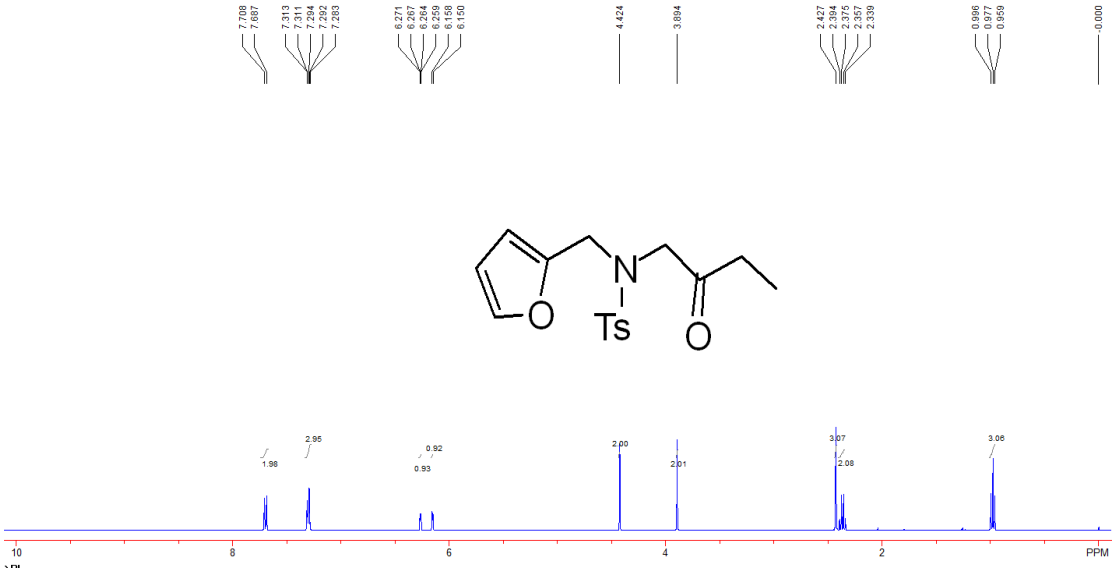


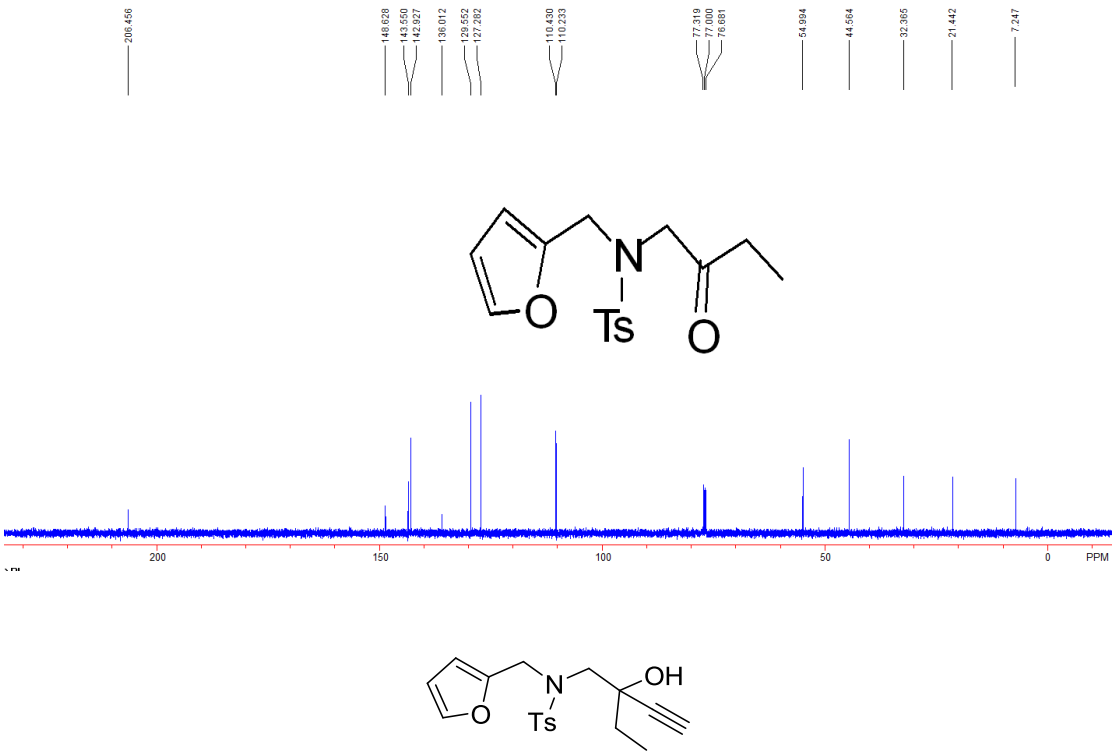
1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)-2-methylbut-3-yn-2-yl acetate (Table SI-2, entry 6a): a colorless oil (437 mg, 93% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.61 (d, 2H, *J* = 8.0 Hz, ArH), 7.24 (d, 2H, *J* = 8.0 Hz, ArH), 7.14 (t, 1H, *J* = 0.8 Hz, ArH), 6.21-6.20 (m, 1H, ArH), 6.03 (d, 1H, *J* = 3.2 Hz, ArH), 4.67 (d, 1H, *J* = 16.4 Hz, CH_2), 4.58 (d, 1H, *J* = 16.4 Hz, CH_2), 3.70 (s, 2H, CH_2), 2.63 (s, 1H, CH), 2.41 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.78 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.6, 148.9, 143.0, 141.8, 136.5, 129.1, 127.0, 110.0, 109.5, 81.9, 75.1, 74.2, 54.0, 45.0, 23.9, 21.5, 21.1; IR (DCM) ν 3278, 1744, 1343, 1237, 1158, 1010, 728 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{25}N_2O_5S$ $[M + NH_4]^+$ m/z 393.1479, found 393.1471.



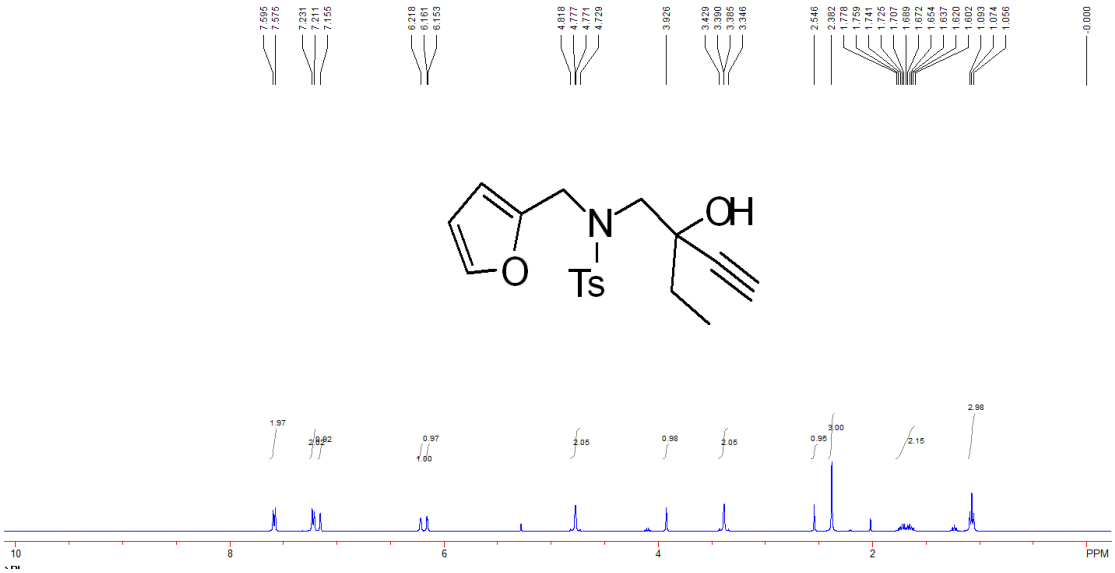


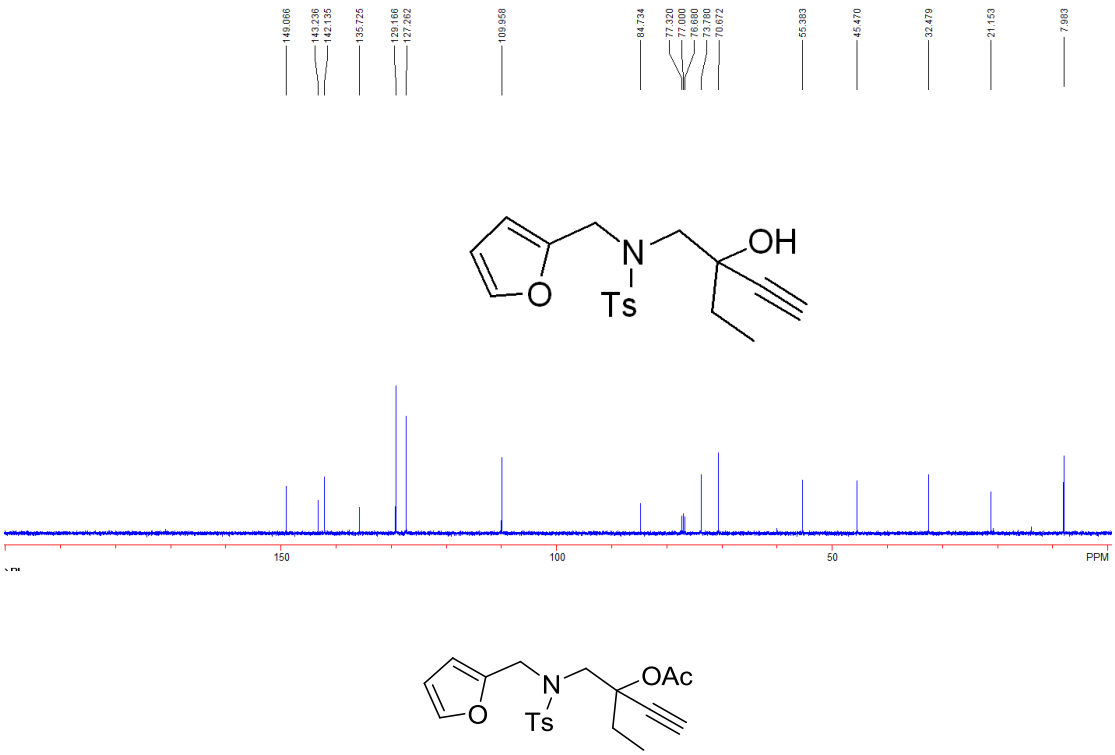
N-(furan-2-ylmethyl)-4-methyl-N-(2-oxobutyl)benzenesulfonamide (S-27b): a colorless oil (635 mg, 57% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.70 (d, 2H, *J* = 8.4 Hz, ArH), 7.31-7.28 (m, 3H, ArH), 6.27-6.26 (m, 1H, ArH), 6.15 (d, 1H, *J* = 3.2 Hz, ArH), 4.42 (s, 2H, CH_2), 3.89 (s, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.37 (q, 2H, *J* = 7.6 Hz, CH_2), 0.98 (t, 3H, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 206.4, 148.6, 143.5, 142.9, 136.0, 129.5, 127.3, 110.4, 110.2, 55.0, 44.6, 32.4, 21.4, 7.2; IR (DCM) ν 2976, 1728, 1338, 1156, 1101, 1009, 658 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{23}N_2O_4S$ $[M + NH_4]^+$ m/z 339.1373, found 339.1381.



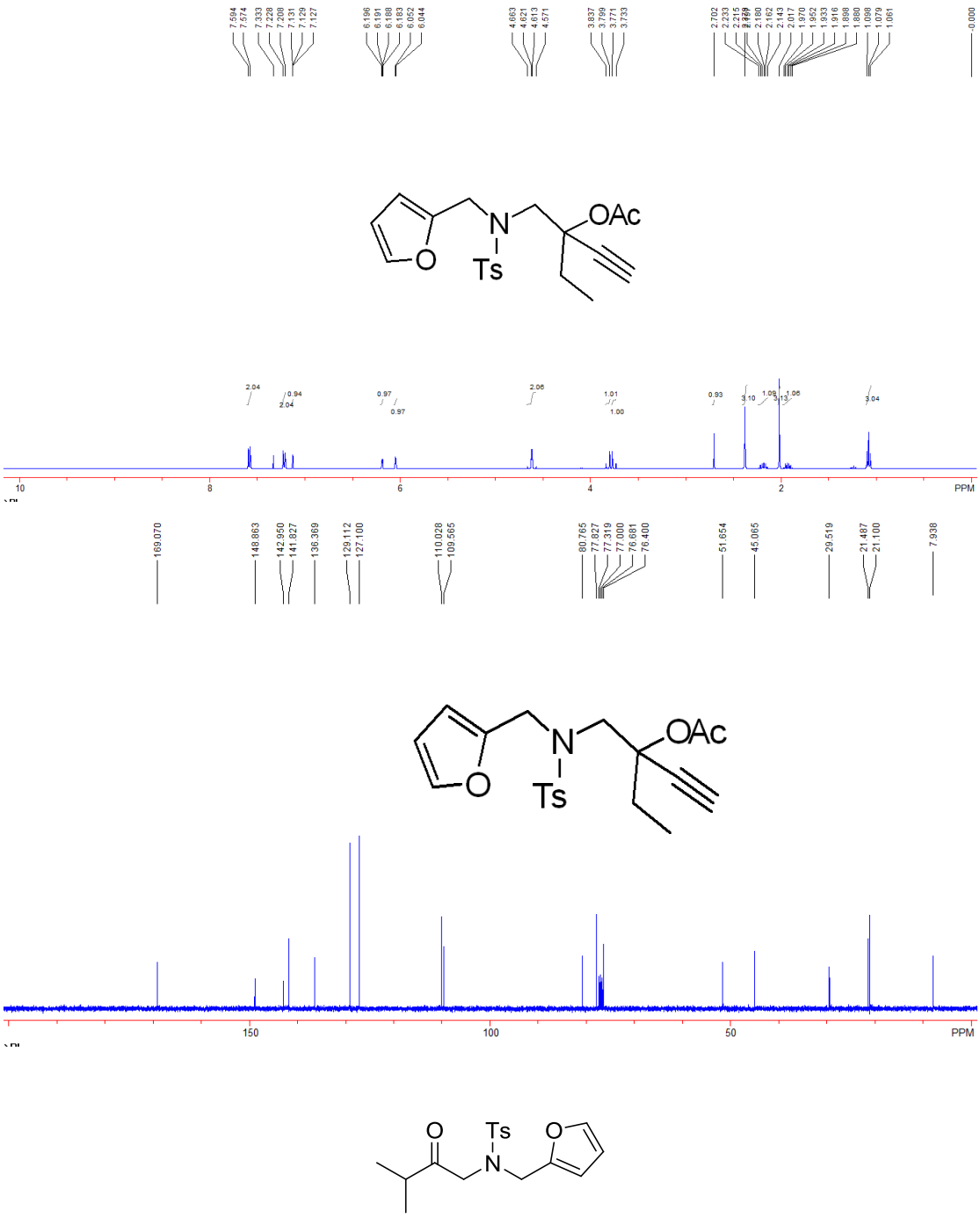


N-(2-ethyl-2-hydroxybut-3-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-28b): a colorless oil (567 mg, 92% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.0 Hz, ArH), 7.22 (d, 2H, *J* = 8.0 Hz, ArH), 7.15 (s, 1H, ArH), 6.22 (s, 1H, ArH), 6.16-6.15 (m, 1H, ArH), 4.82-4.73 (m, 2H, CH_2), 3.93 (s, 1H, OH), 3.43-3.35 (m, 2H, CH_2), 2.55 (s, 1H, CH), 2.38 (s, 3H, CH_3), 1.78-1.60 (m, 2H, CH_2), 1.07 (t, 3H, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.1, 143.2, 142.1, 135.7, 129.2, 127.3, 109.9, 84.7, 73.8, 70.7, 55.4, 45.5, 32.5, 21.1, 8.0; IR (DCM) ν 3482, 3293, 2973, 1329, 1151, 933, 730, 654 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{25}O_5N_2S$ $[M + NH_4]^+$ m/z 365.1530, found 365.1538.

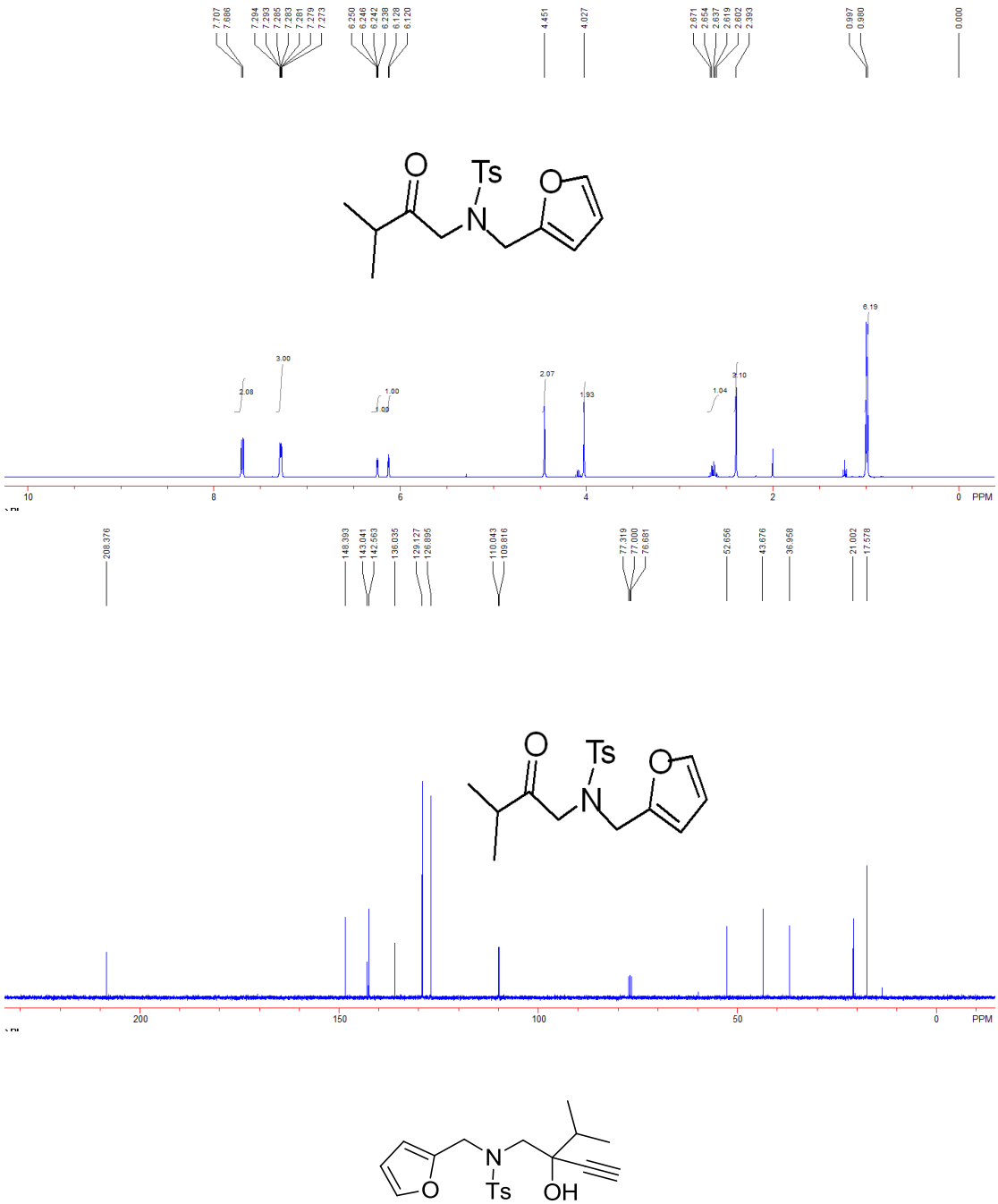




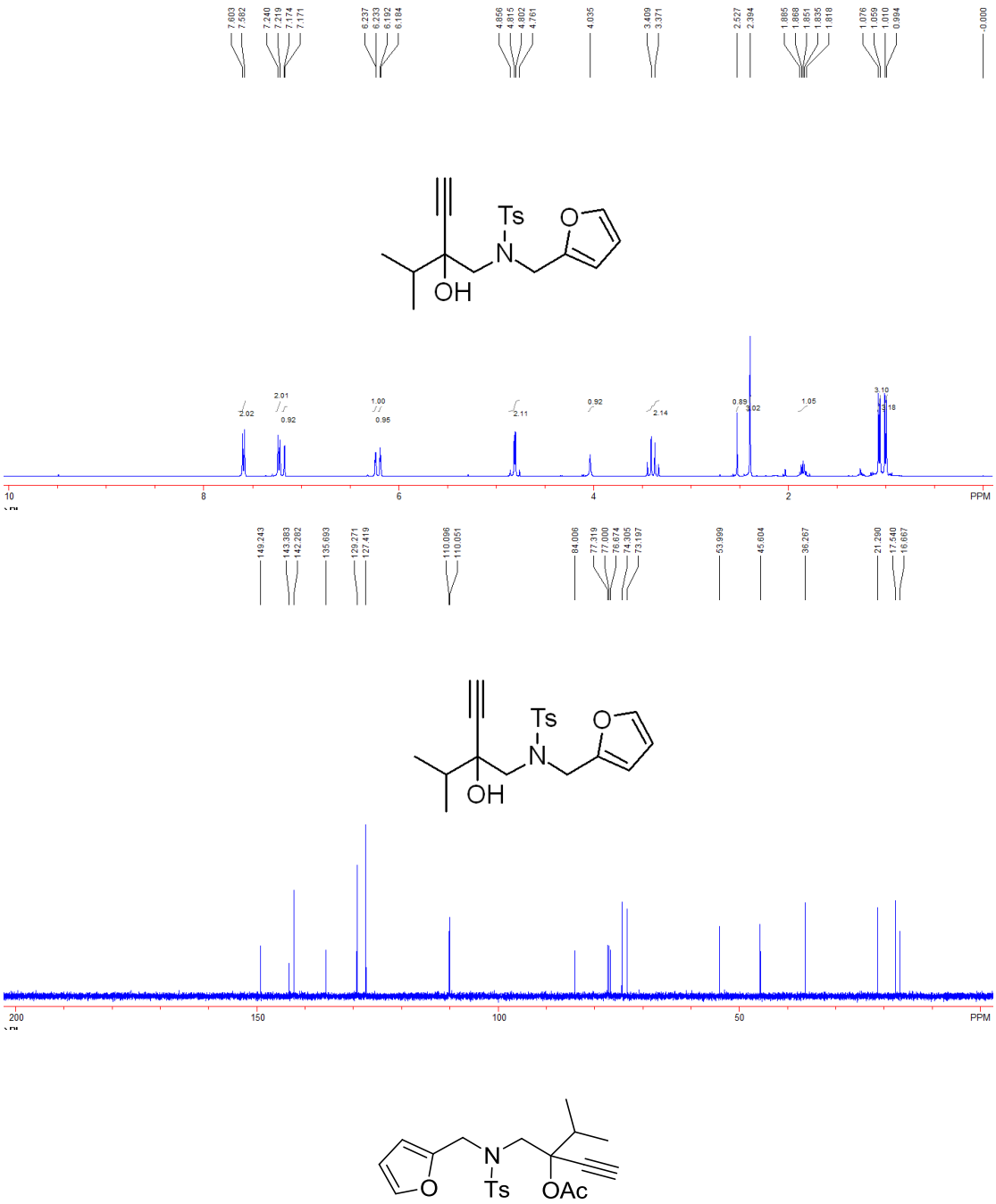
3-(((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)methyl)pent-1-yn-3-yl acetate (Table SI-2, entry 6b): a colorless oil (516 mg, 80% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 8.0 Hz, ArH), 7.22 (d, 2H, *J* = 8.0 Hz, ArH), 7.13-7.12 (m, 1H, ArH), 6.19 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.05 (d, 1H, *J* = 3.2 Hz, ArH), 4.66-4.57 (m, 2H, CH_2), 3.82 (d, 1H, *J* = 15.2 Hz, CH_2), 3.75 (d, 1H, *J* = 15.2 Hz, CH_2), 2.70 (s, 1H, CH), 2.38 (s, 3H, CH_3), 2.23-2.14 (m, 1H, CH_2), 2.02 (s, 3H, CH_3), 1.97-1.88 (m, 1H, CH_2), 1.08 (t, 3H, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 169.1, 148.9, 142.9, 141.8, 136.4, 129.1, 127.1, 110.0, 109.6, 80.8, 77.8, 76.4, 51.6, 45.1, 29.5, 21.5, 21.1, 7.9; IR (DCM) ν 3270, 2940, 1742, 1335, 1231, 1158, 1011, 975, 727 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 407.1635, found 407.1645.



N-(furan-2-ylmethyl)-4-methyl-N-(3-methyl-2-oxobutyl)benzenesulfonamide (S-27c): a colorless oil (1.4 g, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.70 (d, 2H, J = 8.4 Hz, ArH), 7.29-7.27 (m, 3H, ArH), 6.24 (dd, 1H, J_1 = 3.2 Hz, J_2 = 1.6 Hz, ArH), 6.12 (d, 1H, J = 3.2 Hz, ArH), 4.45 (s, 2H, CH_2), 4.03 (s, 2H, CH_2), 2.67-2.60 (m, 1H, CH), 2.39 (s, 3H, CH_3), 0.99 (d, 6H, J = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 208.4, 148.4, 143.0, 142.6, 136.0, 129.1, 126.9, 110.0, 109.8, 52.6, 43.7, 36.9, 21.0, 17.6; IR (DCM) ν 2972, 1727, 1339, 1156, 1010, 730 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{25}N_2O_4S$ $[M + NH_4]^+$ m/z 353.1530, found 353.1532.

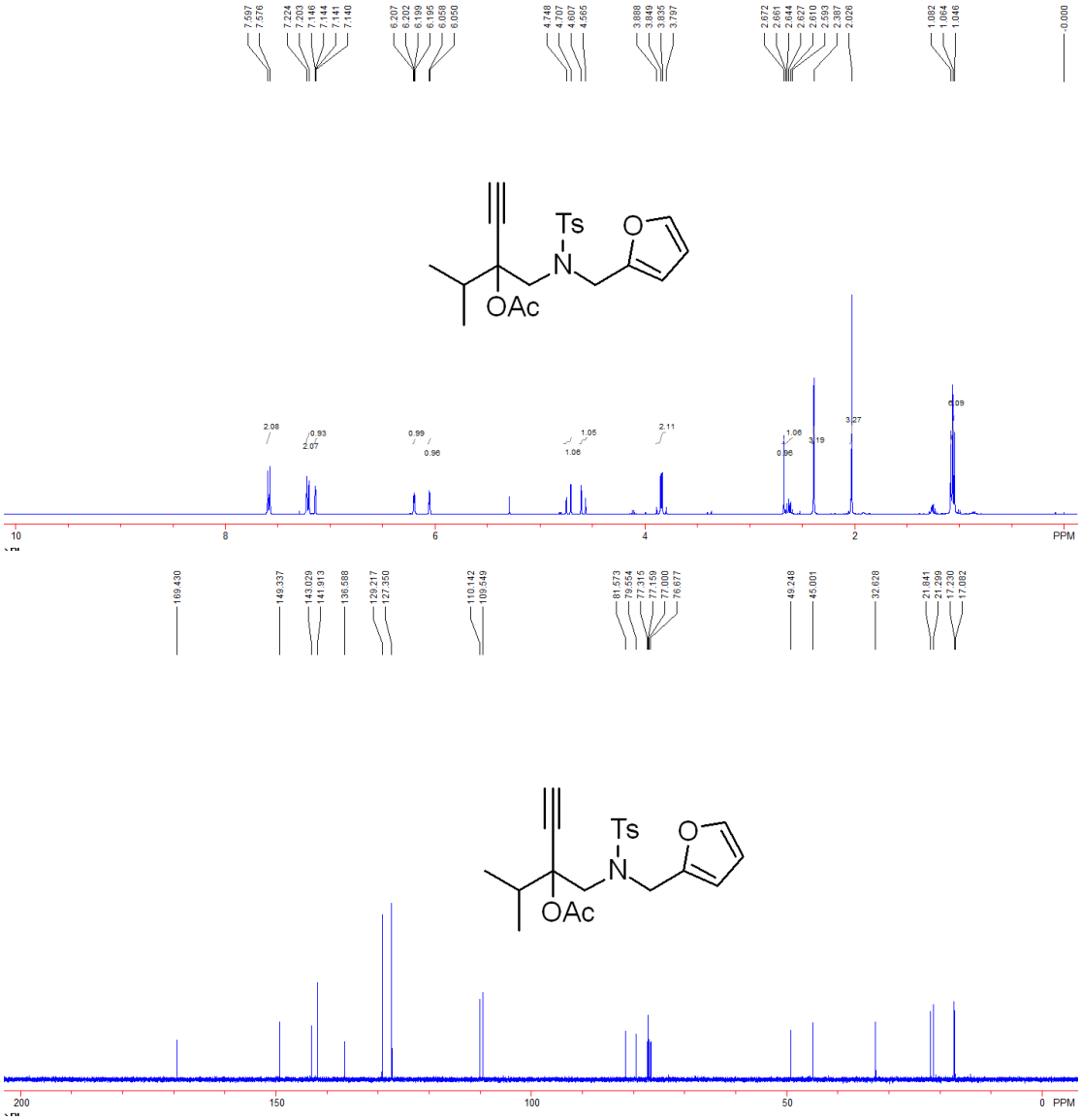


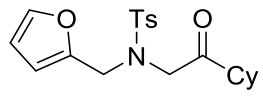
N-(furan-2-ylmethyl)-N-(2-hydroxy-2-isopropylbut-3-yn-1-yl)-4-methylbenzenesulfonamide (S-28c): a colorless oil (732 mg, 45% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.4 Hz, ArH), 7.23 (d, 2H, *J* = 8.4 Hz, ArH), 7.17 (d, 1H, *J* = 1.2 Hz, ArH), 6.23 (d, 1H, *J* = 1.6 Hz, ArH), 6.19 (d, 1H, *J* = 3.2 Hz, ArH), 4.86-4.76 (m, 2H, CH_2), 4.03 (br, 1H, OH), 3.41-3.37 (m, 2H, CH_2), 2.53 (s, 1H, CH), 2.39 (s, 3H, CH_3), 1.88-1.82 (m, 1H, CH), 1.07 (d, 3H, *J* = 6.8 Hz, CH_3), 1.00 (d, 3H, *J* = 6.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.2, 143.4, 142.3, 135.7, 129.3, 127.4, 110.1, 110.0, 84.0, 74.3, 73.2, 54.0, 45.6, 36.3, 21.3, 17.5, 16.7; IR (DCM) ν 3526, 3290, 1598, 1447, 1051, 1006, 698 cm^{-1}; HRMS (MADLI) calcd for $C_{19}H_{24}O_4NS$ $[M + H]^+$ m/z 362.1421, found 362.1418.



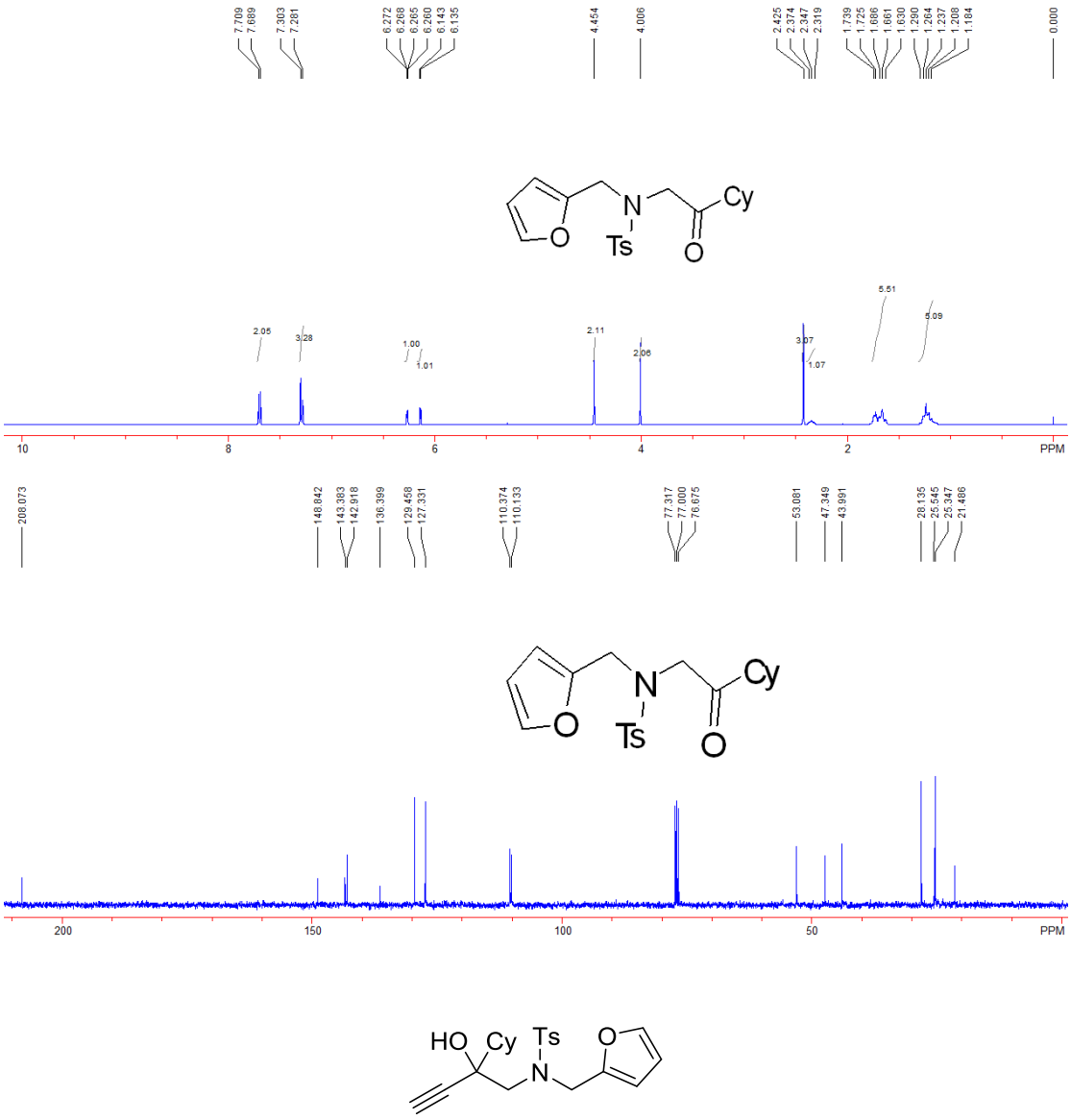
3-(((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)methyl)-4-methylpent-1-yn-3-yl acetate (Table SI-2, entry 6c): a colorless oil (334 mg, 59% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.4 Hz, ArH), 7.21 (d, 2H, *J* = 8.4 Hz, ArH), 7.15-7.14 (m, 1H, ArH), 6.20 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.05 (d, 1H, *J* = 3.2 Hz, ArH), 4.73 (d, 1H, *J* = 16.4 Hz, CH_2), 4.59 (d, 1H, *J* = 16.4 Hz, CH_2), 3.89-3.80 (m, 2H, CH_2), 2.67 (s, 1H, CH), 2.66-2.59 (m, 1H, CH), 2.39 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.06 (t, 6H, *J* = 7.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 169.4, 149.3, 143.0, 141.9, 136.6, 129.2, 127.3, 110.1, 109.5, 81.6, 79.5, 77.1, 49.2, 45.0, 32.6, 21.8, 21.3, 17.2, 17.1; IR (DCM) ν 3287, 2972, 1742, 1336, 1232, 1158, 1001, 734 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 421.1792, found

421.1796.

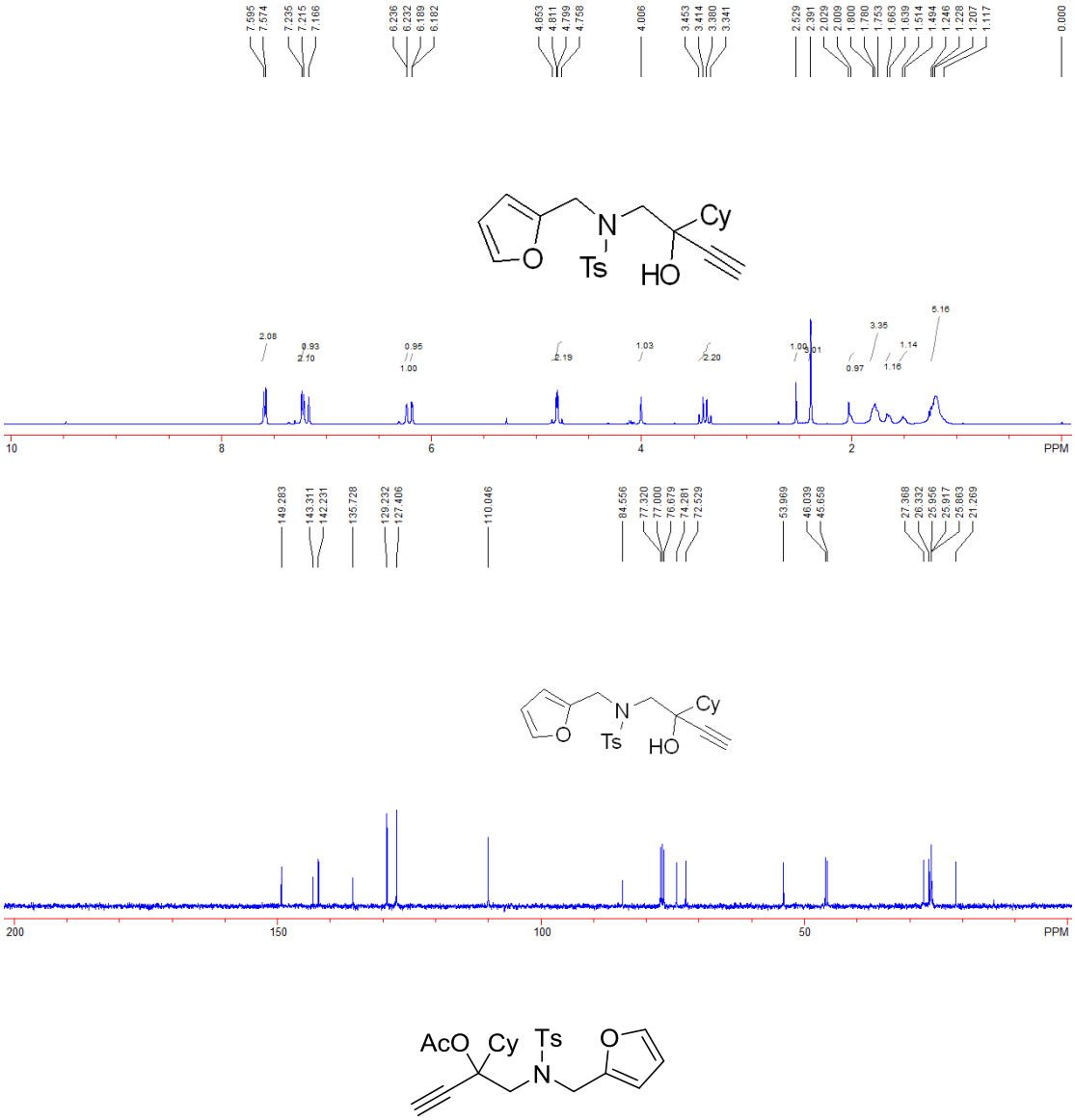




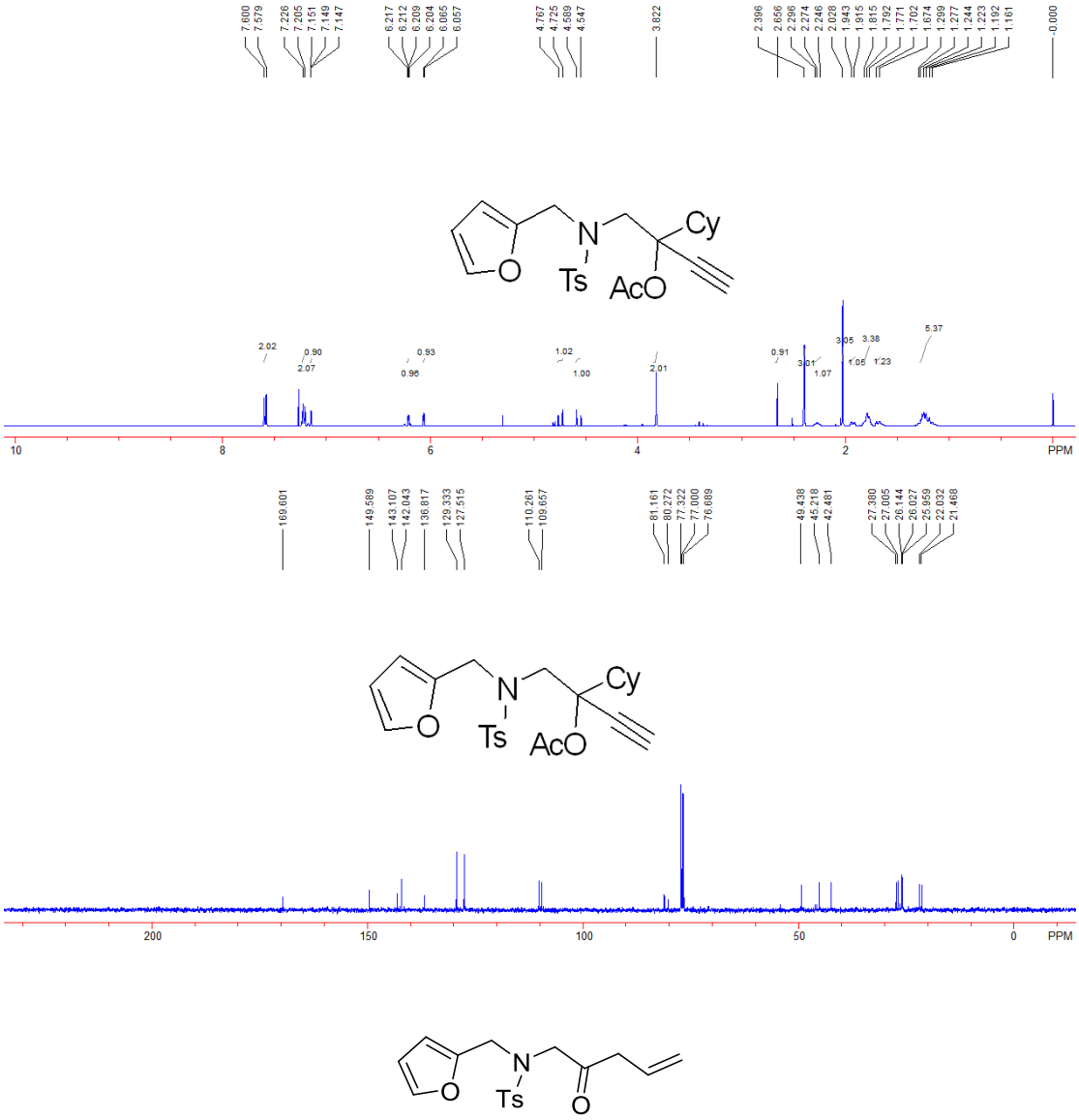
N-(2-cyclohexyl-2-oxoethyl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-27d): a white solid (777 mg, 41% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.70 (d, 2H, J = 8.0 Hz, ArH), 7.30-7.28 (m, 3H, ArH), 6.27 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.14 (d, 1H, J = 3.2 Hz, ArH), 4.45 (s, 2H, CH_2), 4.01 (s, 2H, CH_2), 2.42 (s, 3H, CH_3), 2.37-2.32 (m, 1H, CH), 1.74-1.63 (m, 5H, CH_2), 1.29-1.18 (m, 5H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 208.1, 148.8, 143.4, 142.9, 136.4, 129.4, 127.3, 110.4, 110.1, 53.1, 47.3, 44.0, 28.1, 25.5, 25.3, 21.5; IR (DCM) ν 2928, 2854, 1723, 1336, 1157, 1092, 1011, 731 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{29}N_2O_4S$ $[M + NH_4]^+$ m/z 393.1843, found 393.1842.



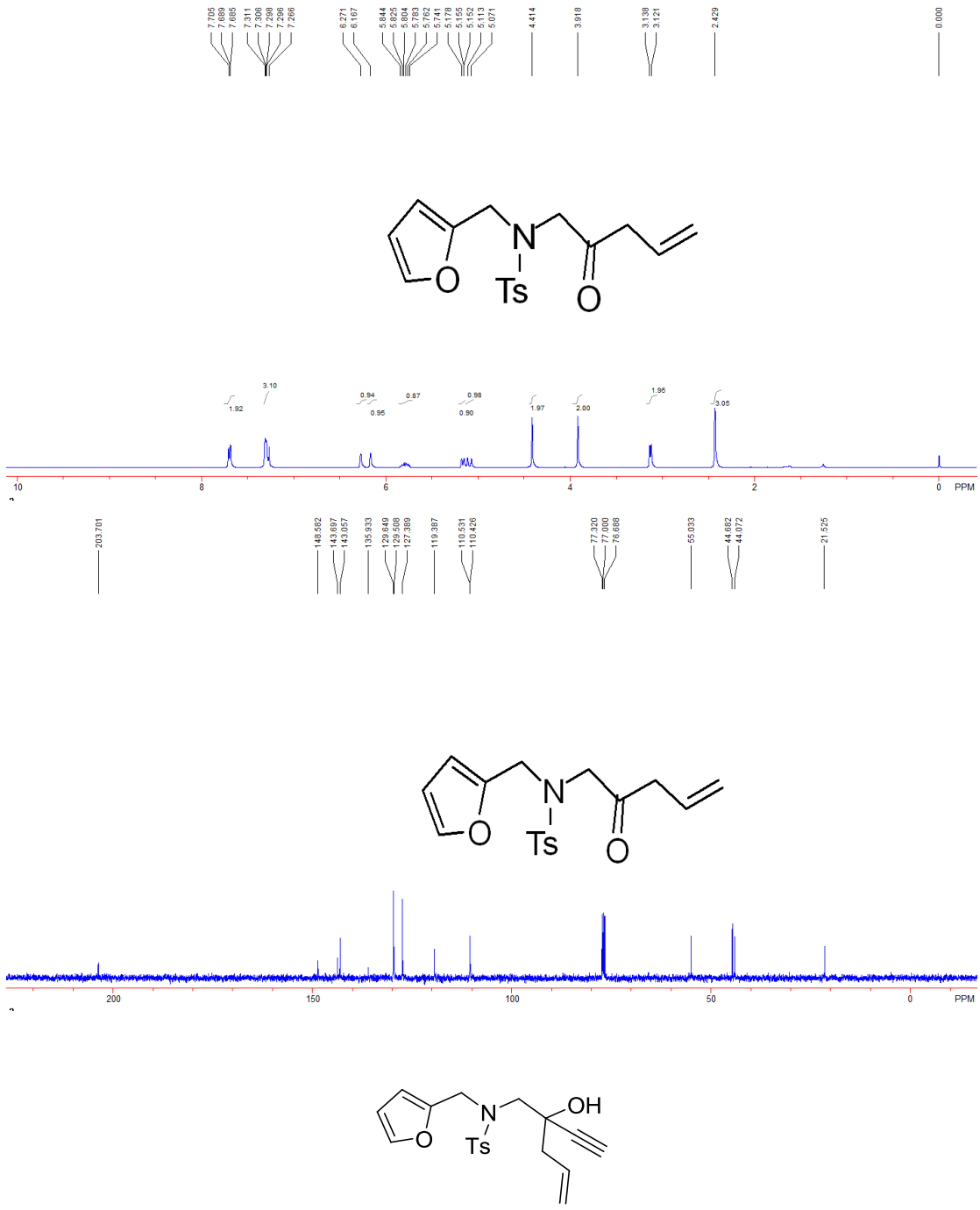
N-(2-cyclohexyl-2-hydroxybut-3-yn-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-28d): a colorless oil (608 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.58 (d, 2H, *J* = 8.4 Hz, ArH), 7.22 (d, 2H, *J* = 8.4 Hz, ArH), 7.17 (s, 1H, ArH), 6.23 (d, 1H, *J* = 1.6 Hz, ArH), 6.18 (d, 1H, *J* = 2.8 Hz, ArH), 4.85-4.76 (m, 2H, CH_2), 4.01 (br, 1H, OH), 3.45-3.34 (m, 2H, CH_2), 2.53 (s, 1H, CH), 2.39 (s, 3H, CH_3), 2.03-2.01 (m, 1H, CH), 1.80-1.75 (m, 3H, CH_2), 1.66-1.64 (m, 1H, CH_2), 1.51-1.49 (m, 1H, CH_2), 1.25-1.12 (m, 5H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.3, 143.3, 142.2, 135.7, 129.2, 127.4, 110.0, 84.5, 74.3, 72.5, 54.0, 46.0, 45.6, 27.4, 26.3, 25.96, 25.92, 25.86, 21.3; IR (DCM) ν 3474, 3287, 2928, 2853, 1330, 1151, 999, 732 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{31}N_2O_4S$ $[M + NH_4]^+$ m/z 419.1999, found 419.1998.



2-cyclohexyl-1-((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)but-3-yn-2-yl acetate (Table SI-2, entry 6d): a colorless oil (372 mg, 55% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.4 Hz, ArH), 7.22 (d, 2H, *J* = 8.4 Hz, ArH), 7.15-7.15 (m, 1H, ArH), 6.21 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.06 (d, 1H, *J* = 3.2 Hz, ArH), 4.75 (d, 1H, *J* = 16.8 Hz, CH_2), 4.57 (d, 1H, *J* = 16.8 Hz, CH_2), 3.82 (s, 2H, CH_2), 2.66 (s, 1H, CH), 2.40 (s, 3H, CH_3), 2.30-2.27 (m, 1H, CH), 2.03 (s, 3H, CH_3), 1.94-1.91 (m, 1H, CH_2), 1.81-1.77 (m, 3H, CH_2), 1.70-1.67 (m, 1H, CH_2), 1.30-1.16 (m, 5H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 169.6, 149.6, 143.1, 142.0, 136.8, 129.3, 127.5, 110.3, 109.6, 81.2, 80.3, 49.4, 45.2, 42.5, 27.4, 27.0, 26.1, 26.0, 25.9, 22.0, 21.5; IR (DCM) ν 3271, 2930, 2855, 1741, 1336, 1230, 1158, 1012, 730 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{33}N_2O_5S$ $[M + NH_4]^+$ m/z 461.2105, found 461.2104.

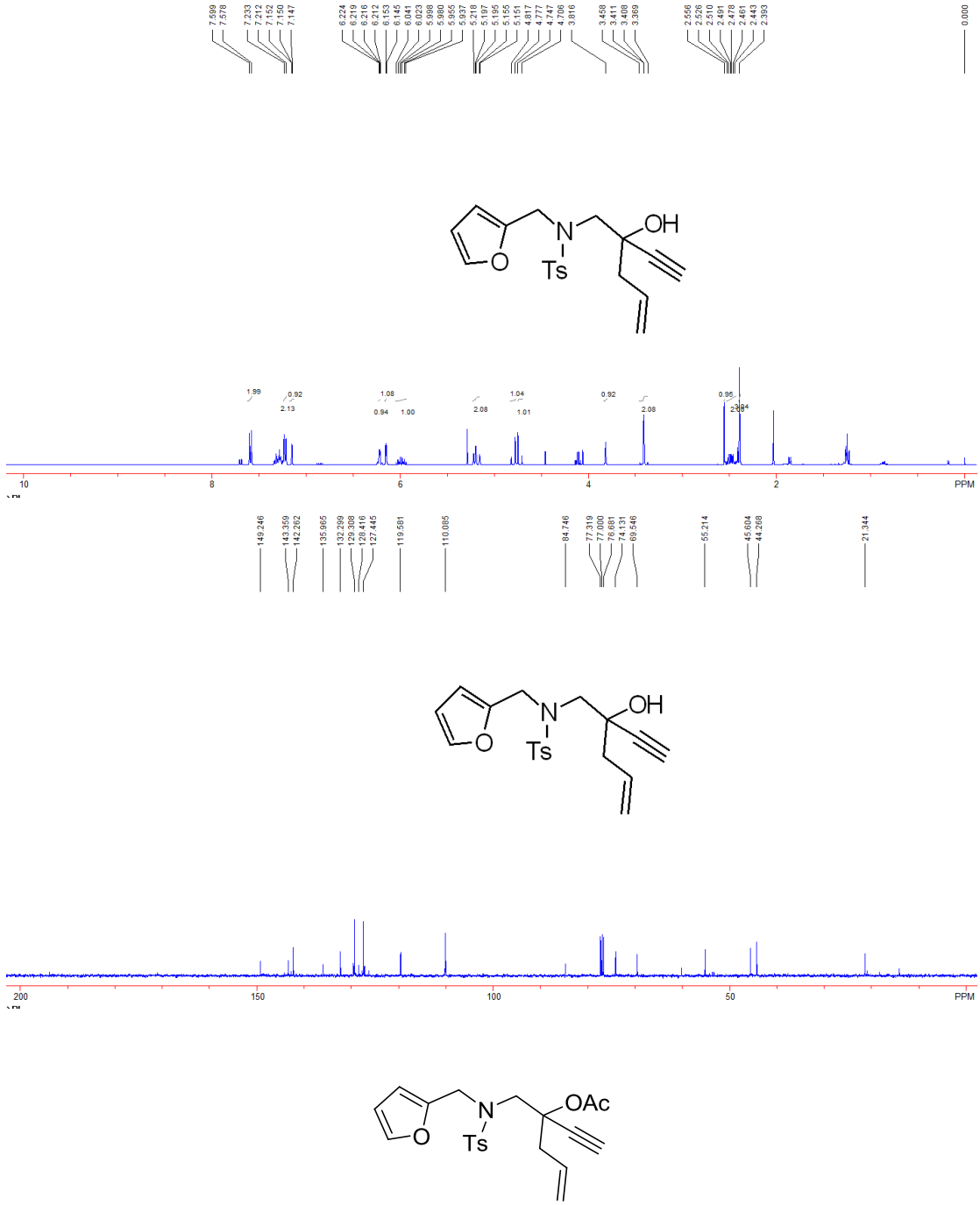


N-(furan-2-ylmethyl)-4-methyl-N-(2-oxopent-4-en-1-yl)benzenesulfonamide (S-27e): a colorless oil (725 mg, 67% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.70-7.68 (m, 2H, ArH), 7.31-7.27 (m, 3H, ArH), 6.27 (s, 1H, ArH), 6.17 (s, 1H, ArH), 5.84-5.74 (m, 1H, =CH), 5.18-5.15 (m, 1H, =CH), 5.09 (d, 1H, *J* = 16.8 Hz, =CH), 4.41 (s, 2H, CH_2), 3.92 (s, 2H, CH_2), 3.13 (d, 2H, *J* = 6.8 Hz, CH_2), 2.43 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 203.7, 148.6, 143.7, 143.0, 135.9, 129.6, 129.5, 127.4, 119.4, 110.5, 110.4, 55.0, 44.7, 44.1, 21.5; IR (DCM) ν 2919, 1729, 1335, 1156, 923, 656 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{23}N_2O_4S$ $[M + NH_4]^+$ m/z 351.1373, found 351.1381.



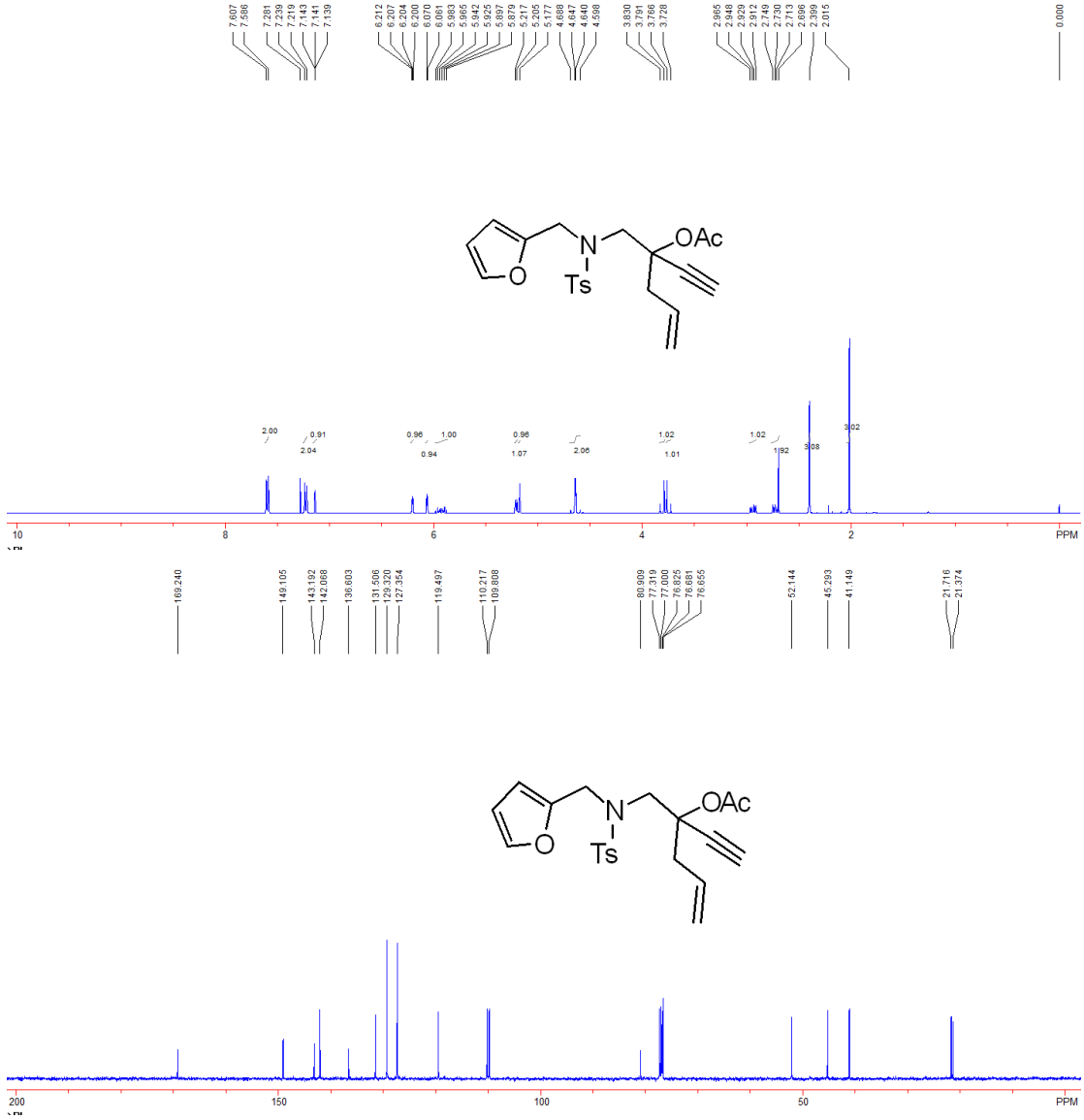
N-(2-ethynyl-2-hydroxypent-4-en-1-yl)-N-(furan-2-ylmethyl)-4-methylbenzenesulfonamide (S-28e): a colorless oil (636 mg, 87% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.59 (d, 2H, *J* = 8.4 Hz, ArH), 7.22 (d, 2H, *J* = 8.4 Hz, ArH), 7.15-7.15 (m, 1H, ArH), 6.22-6.21 (m, 1H, ArH), 6.15 (d, 1H, *J* = 3.2 Hz, ArH), 6.04-5.94 (m, 1H, =CH), 5.22-5.15 (m, 2H, =CH), 4.80 (d, 1H, *J* = 16.0 Hz, CH_2), 4.73 (d, 1H, *J* = 16.0 Hz, CH_2), 3.82 (s, 1H, OH), 3.46-3.37 (m, 2H, CH_2), 2.56 (s, 1H, CH), 2.51-2.41 (m, 2H, CH_2), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 149.2, 143.3, 142.3, 136.0, 132.3, 129.3, 128.4, 127.4, 119.6, 110.1, 84.7, 74.1, 69.5, 55.2, 45.6, 44.3, 21.3; IR (DCM) ν 3473, 3286, 1331, 1153, 1088, 1004, 730 cm^{-1}; HRMS (ESI) calcd for

$C_{19}H_{25}N_2O_4S$ $[M + NH_4]^+$ m/z 377.1530, found 377.1536.



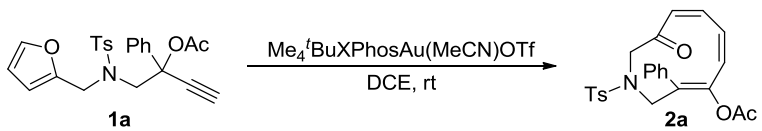
3-(((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)methyl)hex-5-en-1-yn-3-yl acetate (Scheme 5, compound 8): a colorless oil (559 mg, 76% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.60 (d, 2H, *J* = 8.4 Hz, ArH), 7.23 (d, 2H, *J* = 8.4 Hz, ArH), 7.14-7.13 (m, 1H, ArH), 6.21 (dd, 1H, J_1 = 3.2 Hz, J_2 = 2.0 Hz, ArH), 6.06 (d, 1H, *J* = 3.2 Hz, ArH), 5.98-5.88 (m, 1H, =CH), 5.21 (d, 1H, *J* = 4.8 Hz, =CH), 5.18 (s, 1H, =CH), 4.69-4.60 (m, 2H, CH_2), 3.81 (d, 1H, *J* = 15.6 Hz, CH_2), 3.75 (d, 1H, *J* = 15.6 Hz, CH_2), 2.96-2.91 (m, 1H, CH_2), 2.75-2.70 (m, 2H, CH_2 and CH), 2.40 (s, 3H, CH_3), 2.01 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 169.2,

149.1, 143.2, 142.1, 136.6, 131.5, 129.3, 127.3, 119.5, 110.2, 109.8, 80.9, 76.7, 76.6, 52.1, 45.3, 41.1, 21.7, 21.4; IR (DCM) ν 3271, 1743, 1346, 1226, 1158, 1011, 926, 727 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 419.1635, found 419.1643.



General Procedure for the Reaction and the Spectroscopic Data of Products.

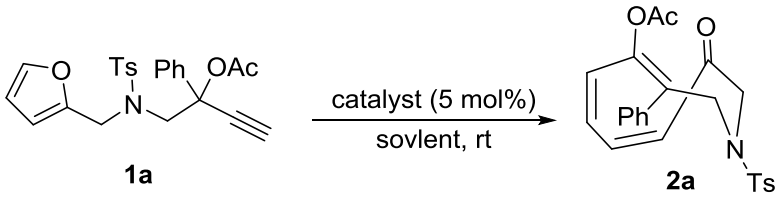
General Procedure for the Gold-Catalyzed 1,2-Acyloxy Migration/Intramolecular Cyclopropanation/Ring Enlargement Cascade Reaction and the Spectroscopic Data.



Into an oven-dried reaction flask under Ar gas protection were added substrates **1** (0.2 mmol) and DCE (1.5 mL), then a solution of Au-catalyst (0.005 mol/0.5 mL) was added. The reaction mixture was stirred at room temperature for several minutes, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

The ester **1a** was selected as substrate to investigate this reaction (Table SI-1). The reaction was run first used 5 mol% PPh_3AuCl as the catalyst, 5 mol% $AgSbF_6$ as an additive and DCE as a solvent. But the reaction became complex and no product has been isolated (Table SI-1, entry 1). Replacing $AgNTf_2$ with $AgSbF_6$， the reaction also became complex (Table SI-1, entry 2). Using already prepared electrophilic cationic phosphinogold(I) complexes dppm[$Au(MeCN)SbF_6)_2$ with bis-phosphine ligand and $^{n}BuPAd_2Au(MeCN)SbF_6$ with stericphosphine ligand as the gold catalysts, the reaction also became complex (Table SI-1, entry 3 and 4). Then we tried using gold complexes with dialkylbiarylphosphane ligands as catalysts. When using $SPhosAu(MeCN)SbF_6$ as catalysts, **2a** was obtained in 32% yield (Table SI-1, entry 5). $JohnPhosAu(MeCN)SbF_6$ gave product in 11% yield (Table SI-1, entry 6). During gold catalysts with various coordination anions, $Me_4{}^{t}BuXphosAu(MeCN)NTf_2$ and $Me_4{}^{t}BuXphosAu(MeCN)BF_4$ gave product in 64% and 80% isolated yield (Table SI-1, entries 7 and 8). Other solvents such as THF, CH_3CN, DCM and Toluene were less effective solvents (Table SI-1, entries 9-12). When the amount of catalyst was declined to 2.5 mol%, **2a** was isolated in 95% yield (Table SI-1, entry 13). But when 0.1 mol% catalyst was used, the yield of **2a** was sudden drop (Table SI-1, entry 14).

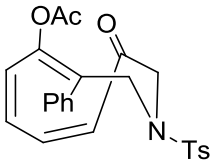
Table SI-1. Additional Information on Screening of the Reaction Conditions for this Reaction.



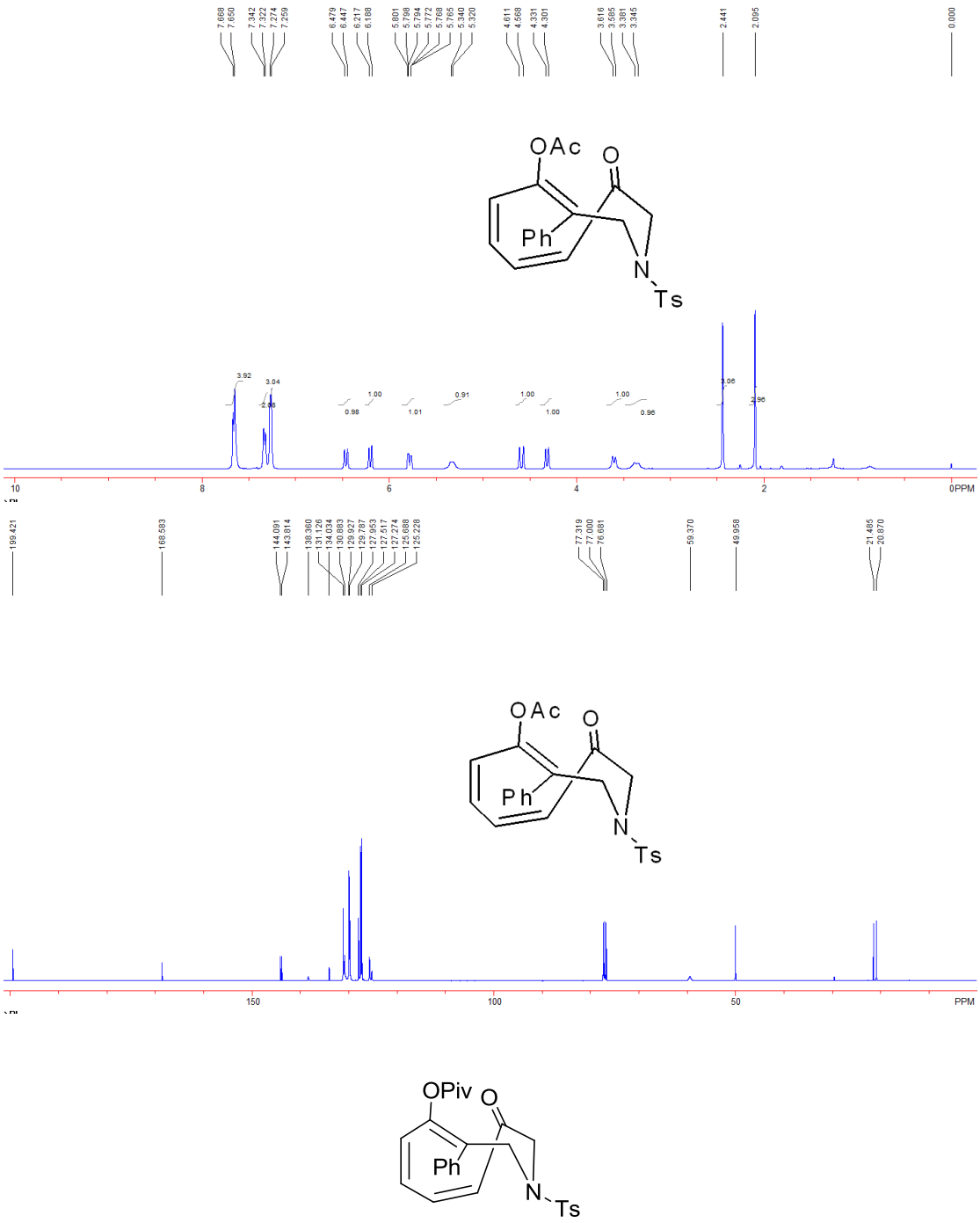
1a **2a**

entry[a]	catalyst	sovlent	yield(%)[b]
1	$Ph_3PAuCl/AgSbF_6$	DCE	complex
2	$Ph_3PAuCl/AgNTf_2$	DCE	complex
3	$dppm[Au(MeCN)SbF_6]_2$	DCE	complex
4	$^nBuPAd_2Au(MeCN)SbF_6$	DCE	complex
5	$SPhosAu(MeCN)SbF_6$	DCE	32
6	$JoPhosAu(MeCN)SbF_6$	DCE	11
7	$Me_4{}^tBuXPhosAuNTf$	DCE	64
8	$Me_4{}^tBuXPhosAu(MeCN)BF_4$	DCE	80
9	$Me_4{}^tBuXPhosAu(MeCN)OTf$	THF	68
10	$Me_4{}^tBuXPhosAu(MeCN)OTf$	CH_3CN	55
11	$Me_4{}^tBuXPhosAu(MeCN)OTf$	DCM	64
12	$Me_4{}^tBuXPhosAu(MeCN)OTf$	Toluene	N.R.
13[c]	$Me_4{}^tBuXPhosAu(MeCN)OTf$	DCE	95
14[d]	$Me_4{}^tBuXPhosAu(MeCN)OTf$	DCE	trace

[a] The reaction was carried out on a 0.1 mmol scale in solvents (1.0 mL). [b] Isolated yield. [c] 2.5 mol% Au catalysts and Ag salts were added. [d] 0.1 mol% Au catalysts and Ag salts were added.

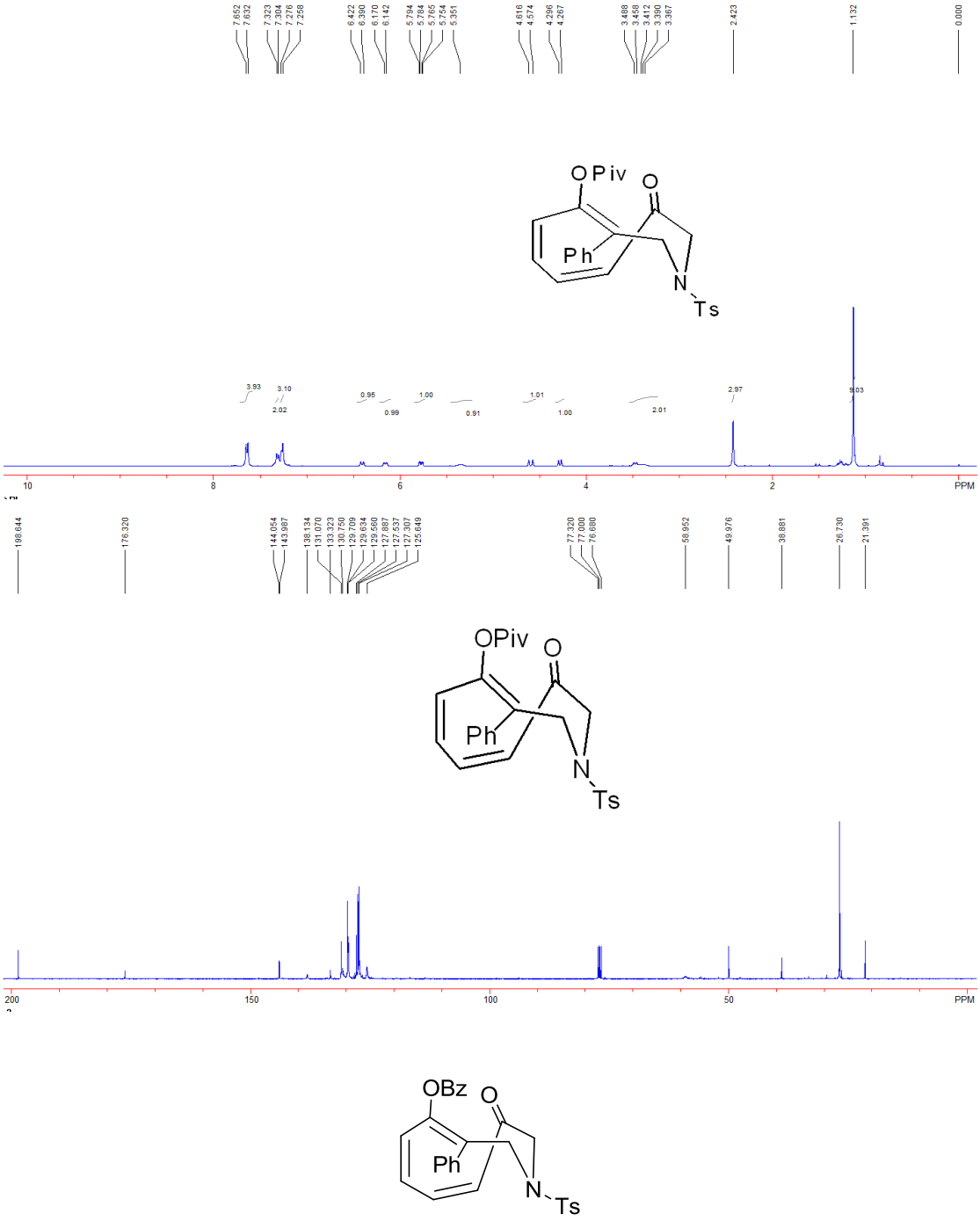


(3Z,5Z,7Z)-9-oxo-3-phenyl-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 1, entry 2a): a white solid (88 mg, 96% yield), mp: 100-102 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 4H, *J* = 8.0 Hz, ArH), 7.33 (d, 2H, *J* = 8.0 Hz, ArH), 7.27-7.26 (m, 3H, ArH), 6.46 (d, 1H, *J* = 12.8 Hz, =CH), 6.20 (d, 1H, *J* = 11.6 Hz, =CH), 5.80-5.76 (m, 1H, =CH), 5.34-5.32 (m, 1H, =CH), 4.59 (d, 1H, *J* = 17.2 Hz, CH_2), 4.32 (d, 1H, *J* = 12.0 Hz, CH_2), 3.60 (d, 1H, *J* = 12.0 Hz, CH_2), 3.38-3.34 (m, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.09 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.4, 168.6, 144.1, 143.8, 138.4, 134.0, 131.1, 130.9, 129.9, 129.8, 127.9, 127.5, 127.3, 125.7, 125.2, 59.4, 49.9, 21.5, 20.9; IR (DCM) ν 3051, 2927, 1757, 1698, 1347, 1204, 1162, 814 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{23}NNaO_5S$ $[M + Na]^+$ m/z 460.1189, found 460.1200.



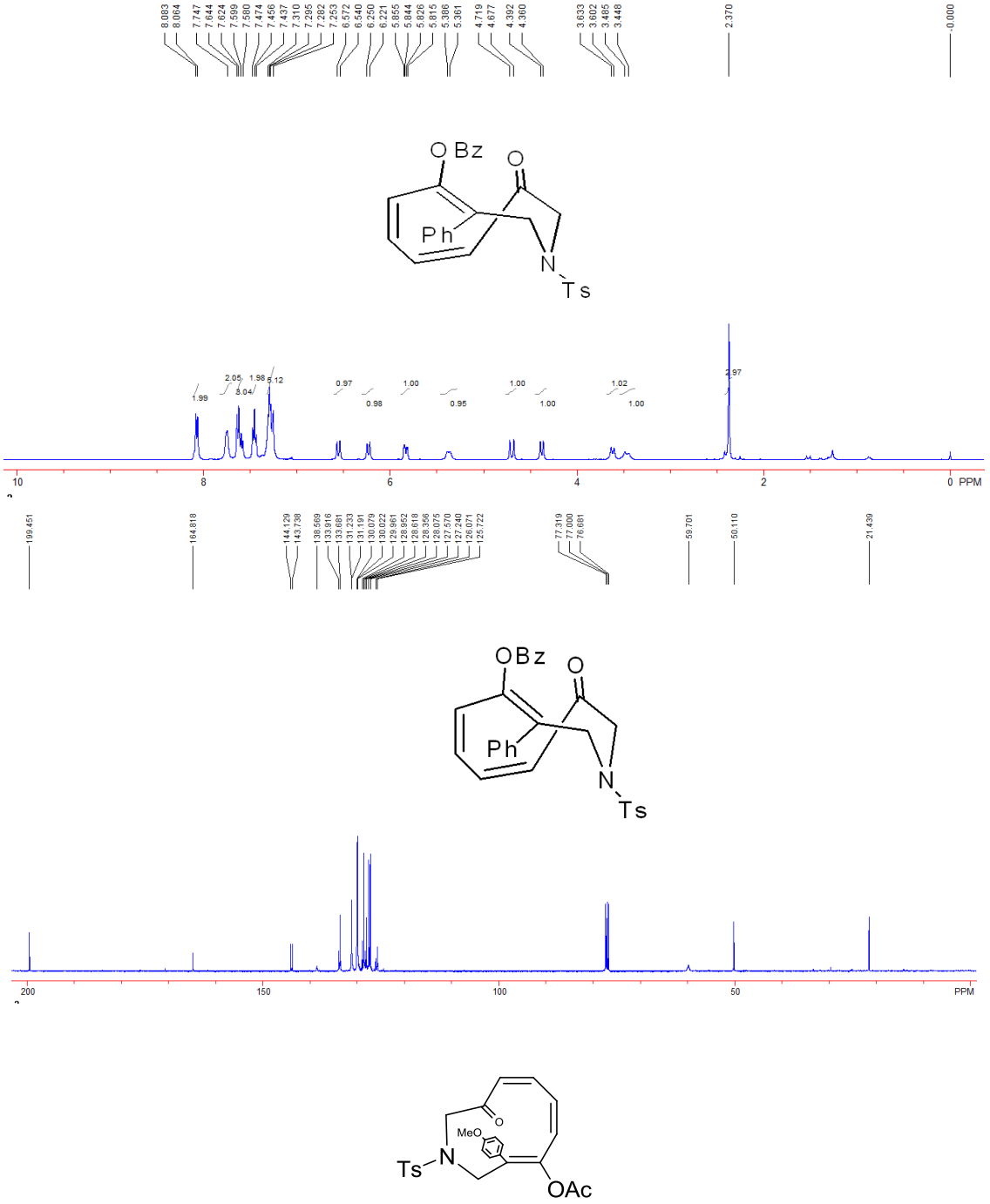
(3Z,5Z,7Z)-9-oxo-3-phenyl-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl pivalate (Table 2, entry 2b): a white solid (69 mg, 72% yield), mp: 133-135 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64 (d, 4H, *J* = 8.0 Hz, ArH), 7.31 (d, 2H, *J* = 8.0 Hz, ArH), 7.28-7.26 (m, 3H, ArH), 6.41 (d, 1H, *J* = 12.8 Hz, =CH), 6.16 (d, 1H, *J* = 11.2 Hz, =CH), 5.77 (dd, 1H, J_1 = 11.6 Hz, J_2 = 4.0 Hz, =CH), 5.35 (br, 1H, =CH), 4.59 (d, 1H, *J* = 16.8 Hz, CH_2), 4.28 (d, 1H, *J* = 11.6 Hz, CH_2), 3.49-3.37 (m, 2H, CH_2), 2.42 (s, 3H, CH_3), 1.13 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 198.6, 176.3, 144.05, 143.99, 138.1, 133.3, 131.1, 130.7, 129.7, 129.63, 129.56, 127.9, 127.5, 127.3, 125.6, 58.9, 50.0, 38.9, 26.7, 21.4; IR (DCM) ν 2974, 1743, 1696, 1350, 1165, 1104, 817, 716

cm^{-1}; HRMS (ESI) calcd for $C_{27}H_{33}N_2O_5S$ $[M + NH_4]^+$ m/z 497.2105, found 497.2110.



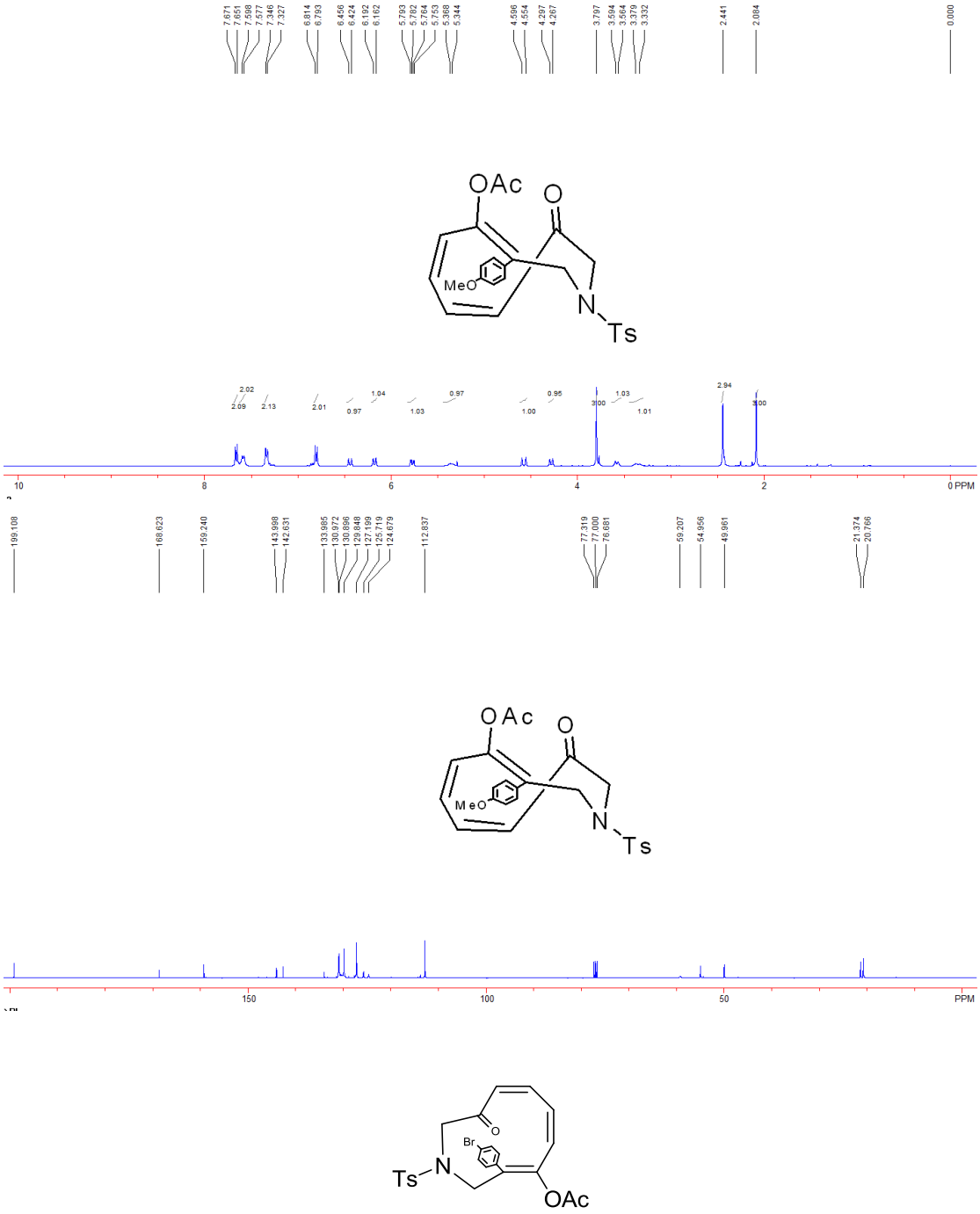
(3Z,5Z,7Z)-9-oxo-3-phenyl-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl benzoate (Table 2, entry 2c): a white solid (81 mg, 81% yield), mp: 111-113 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.07 (d, 2H, *J* = 7.6 Hz, ArH), 7.75 (s, 2H, ArH), 7.64-7.58 (m, 3H, ArH), 7.47-7.44 (m, 2H, ArH), 7.31-7.25 (m, 5H, ArH), 6.55 (d, 1H, *J* = 12.8 Hz, =CH), 6.23 (d, 1H, *J* = 11.6 Hz, =CH), 5.83 (dd, 1H, J_1 = 11.6 Hz, J_2 = 4.4 Hz, =CH), 5.37 (d, 1H, *J* = 10.0 Hz, =CH), 4.70 (d, 1H, *J* = 16.8 Hz, CH_2), 4.38 (d, 1H, *J* = 12.8 Hz, CH_2), 3.62 (d, 1H, *J* = 12.4 Hz, CH_2), 3.48-3.45 (m, 1H, CH_2), 2.37 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.4, 164.8, 144.1, 143.7, 138.6,

133.9, 133.7, 131.23, 131.19, 130.1, 130.02, 129.96, 128.9, 128.6, 128.3, 128.1, 127.6, 127.2, 126.1, 125.7, 59.7, 50.1, 21.4; IR (DCM) ν 3057, 2923, 1730, 1695, 1347, 1261, 1164, 1082, 1063, 704 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 517.1792, found 517.1792.



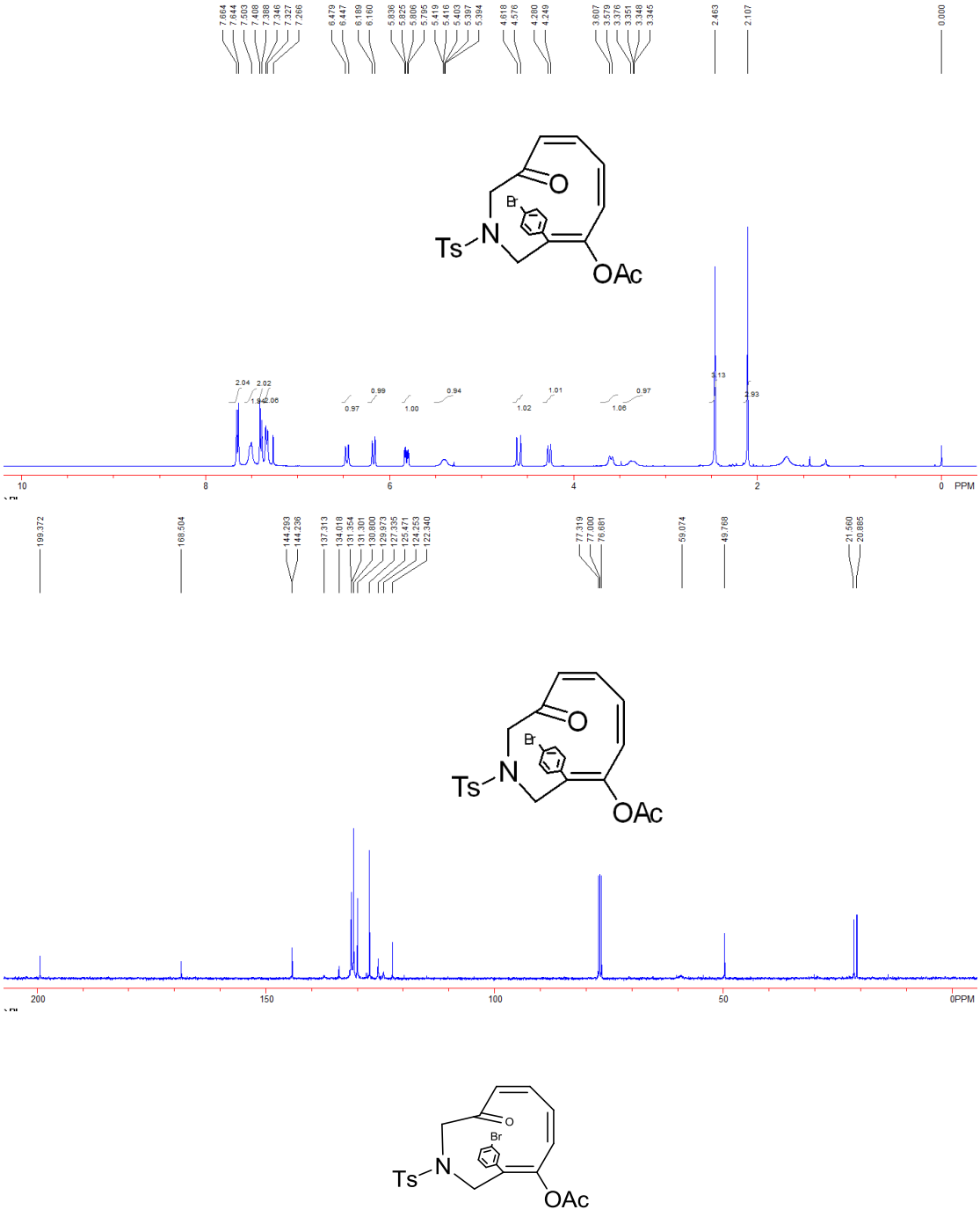
(3Z,5Z,7Z)-3-(4-methoxyphenyl)-9-oxo-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2d): a white solid (53 mg, 56% yield), mp: 105-107 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 2H, *J* = 8.0 Hz, ArH), 7.59 (d, 2H, *J* = 8.4 Hz, ArH), 7.34 (d, 2H, *J* = 8.0 Hz, ArH), 6.80 (d, 2H, *J* = 8.4 Hz, ArH), 6.44 (d, 1H, *J* = 12.8 Hz, =CH), 6.18 (d, 1H, *J* = 12.0 Hz, =CH), 5.77 (dd, 1H, J_1 = 12.0 Hz, J_2 = 4.4 Hz, =CH), 5.36-5.34 (m, 1H, =CH), 4.57 (d, 1H, *J* =

16.8 Hz, CH_2), 4.28 (d, 1H, *J* = 12.0 Hz, CH_2), 3.80 (s, 3H, CH_3), 3.58 (d, 1H, *J* = 12.0 Hz, CH_2), 3.38-3.33 (m, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.08 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.1, 168.6, 159.2, 144.0, 142.6, 134.0, 131.0, 130.9, 129.8, 127.2, 125.7, 124.7, 112.8, 59.2, 54.9, 50.0, 21.4, 20.8; IR (DCM) ν 2930, 1755, 1698, 1607, 1511, 1249, 1163, 834 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_6S$ $[M + NH_4]^+$ m/z 485.1741, found 485.1739.



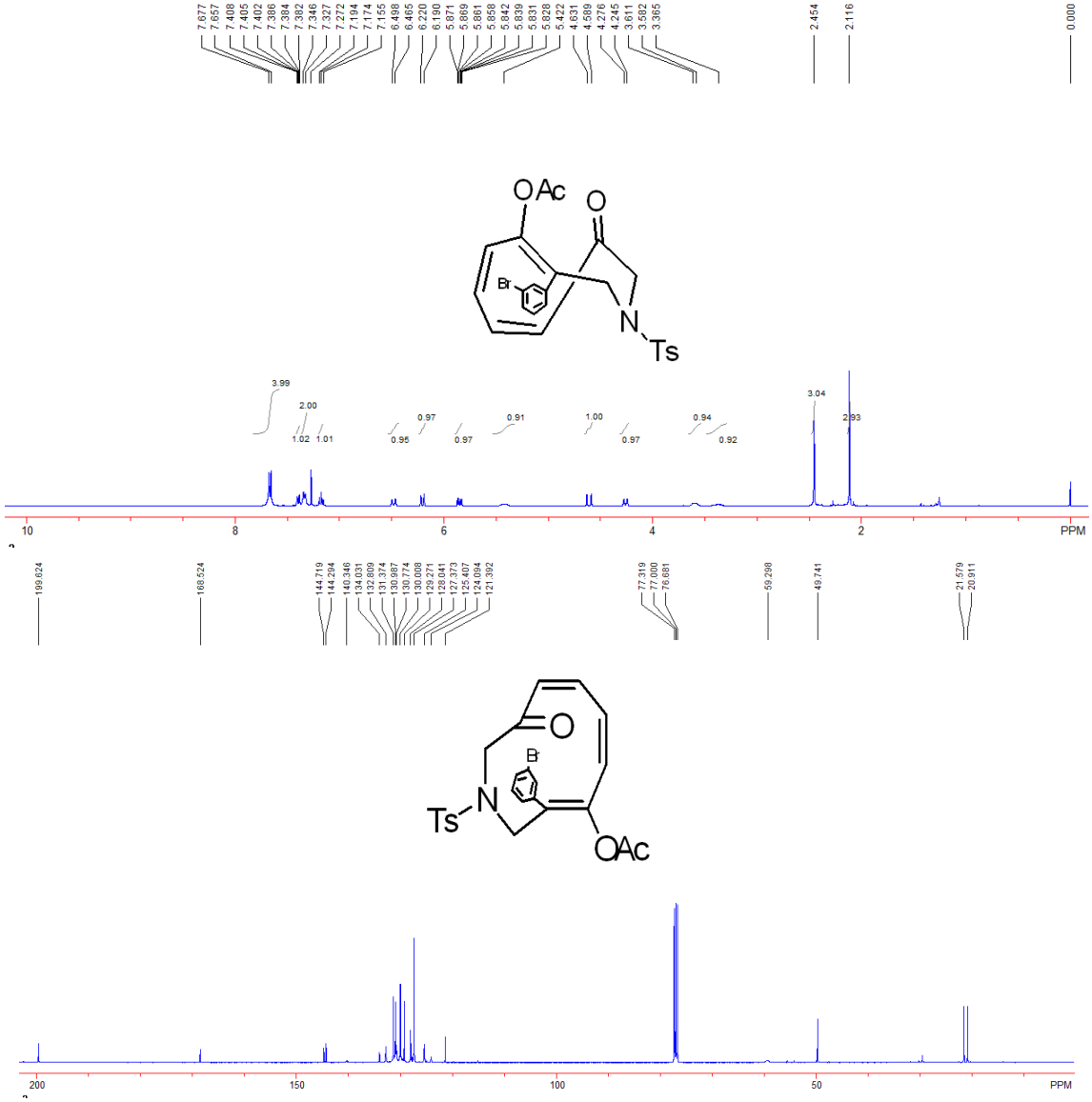
(3Z,5Z,7Z)-3-(4-bromophenyl)-9-oxo-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2e): a white solid (91 mg, 88% yield), mp: 110-112 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.65 (d, 2H, *J* = 8.0 Hz, ArH), 7.50 (s, 2H, ArH), 7.40 (d, 2H, *J* = 8.0 Hz, ArH), 7.34 (d, 2H, *J* =

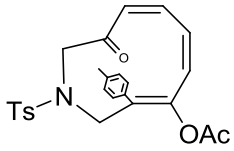
7.6 Hz, ArH), 6.46 (d, 1H, J = 12.8 Hz, =CH), 6.17 (d, 1H, J = 11.6 Hz, =CH), 5.81 (dd, 1H, J_1 = 9.0 Hz, J_2 = 4.4 Hz, =CH), 5.42-5.39 (m, 1H, =CH), 4.60 (d, 1H, J = 16.8 Hz, CH_2), 4.26 (d, 1H, J = 12.4 Hz, CH_2), 3.59 (d, 1H, J = 11.2 Hz, CH_2), 3.38-3.34 (m, 1H, CH_2), 2.46 (s, 3H, CH_3), 2.11 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.4, 168.5, 144.3, 144.2, 137.3, 134.0, 131.35, 131.30, 130.8, 130.0, 127.3, 125.5, 124.2, 122.3, 59.1, 49.8, 21.6, 20.9; IR (DCM) ν 2927, 1759, 1699, 1347, 1202, 1164, 830 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}BrN_2O_5S$ [M + NH_4]$^+$ m/z 533.0740, found 533.0741.



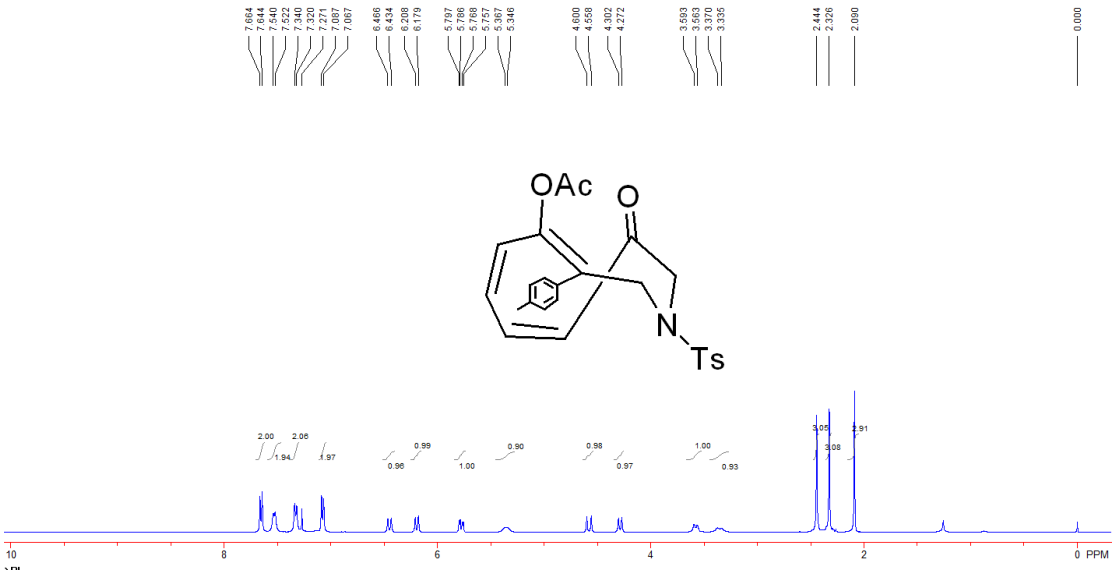
(3Z,5Z,7Z)-3-(3-bromophenyl)-9-oxo-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2,

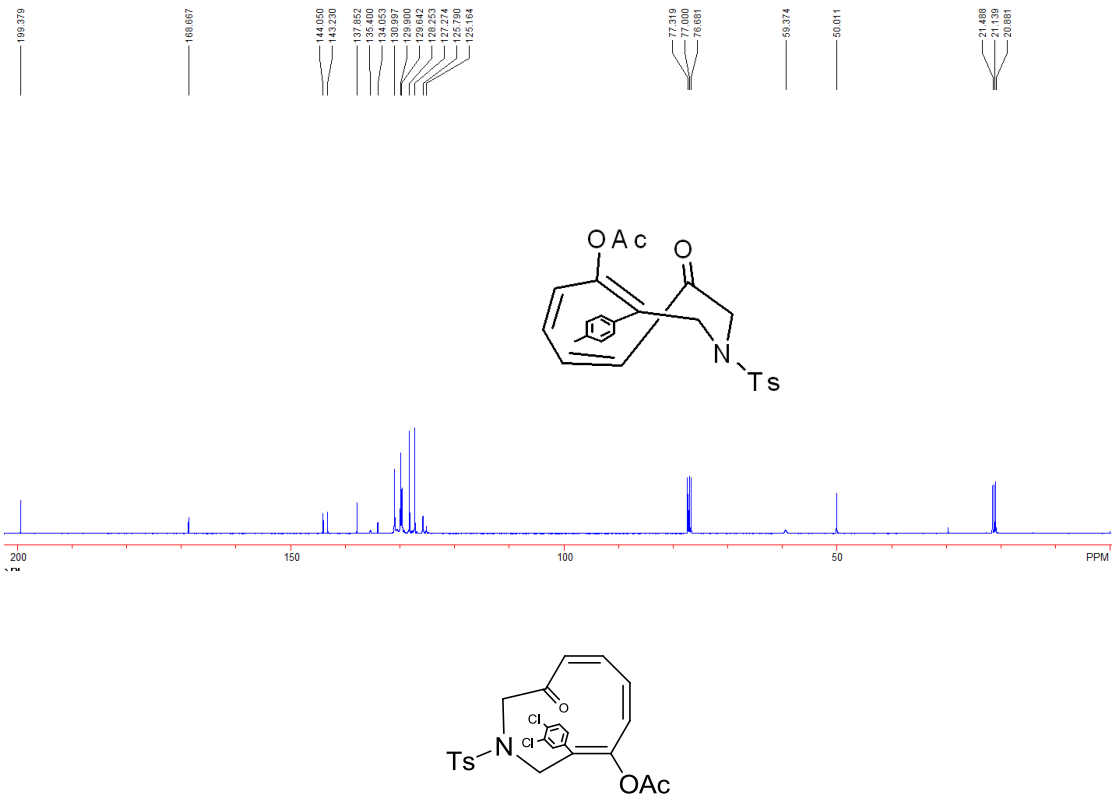
entry 2f): a white solid (94 mg, 91% yield), mp: 107-109 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 4H, *J* = 7.6 Hz, ArH), 7.41-7.38 (m, 1H, ArH), 7.34 (d, 2H, *J* = 7.6 Hz, ArH), 7.17 (t, 1H, *J* = 7.6 Hz, ArH), 6.48 (d, 1H, *J* = 13.2 Hz, =CH), 6.20 (d, 1H, *J* = 12.0 Hz, =CH), 5.87-5.83 (m, 1H, =CH), 5.42 (br, 1H, =CH), 4.61 (d, 1H, *J* = 16.8 Hz, CH_2), 4.28 (d, 1H, *J* = 12.4 Hz, CH_2), 3.60 (d, 1H, *J* = 11.6 Hz, CH_2), 3.36 (br, 1H, CH_2), 2.45 (s, 3H, CH_3), 2.12 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.6, 168.5, 144.7, 144.3, 140.3, 134.0, 132.8, 131.4, 131.0, 130.8, 130.0, 129.3, 128.0, 127.4, 125.4, 124.1, 121.4, 59.5, 49.7, 21.6, 20.9; IR (DCM) ν 3370, 1759, 1699, 1347, 1197, 1158, 1140 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}BrN_2O_5S$ [M + NH_4]$^{+}$ m/z 533.0740, found 533.0726.



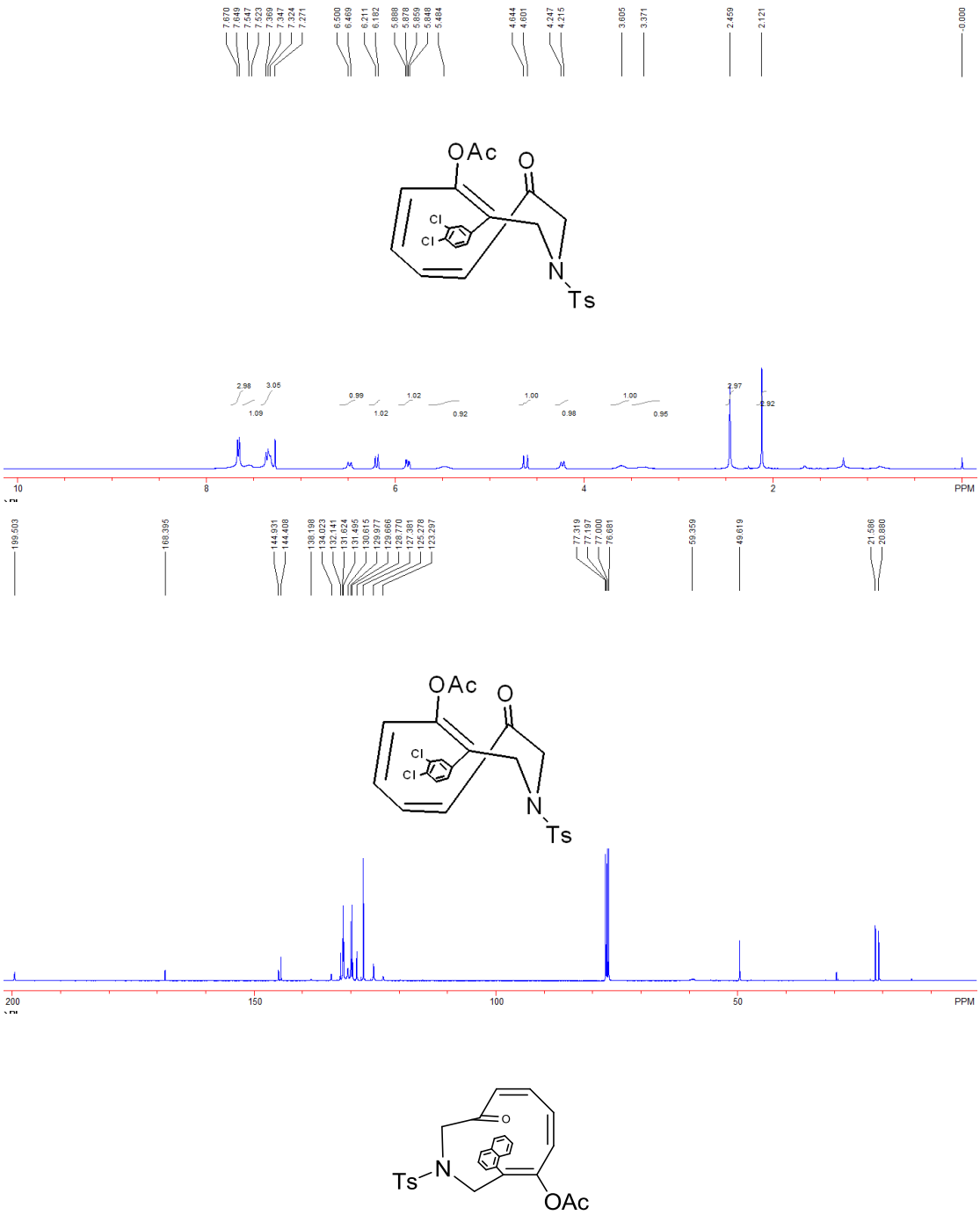


(3Z,5Z,7Z)-9-oxo-3-(p-tolyl)-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2g): a white solid (75 mg, 83% yield), mp: 98-100 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.65 (d, 2H, *J* = 8.0 Hz, ArH), 7.53 (d, 2H, *J* = 8.0 Hz, ArH), 7.33 (d, 2H, *J* = 8.0 Hz, ArH), 7.07 (d, 2H, *J* = 8.0 Hz, ArH), 6.45 (d, 1H, *J* = 12.8 Hz, =CH), 6.19 (d, 1H, *J* = 11.6 Hz, =CH), 5.78 (dd, 1H, J_1 = 11.6 Hz, J_2 = 4.4 Hz, =CH), 5.37-5.35 (m, 1H, =CH), 4.58 (d, 1H, *J* = 16.8 Hz, CH_2), 4.29 (d, 1H, *J* = 12.0 Hz, CH_2), 3.58 (d, 1H, *J* = 12.0 Hz, CH_2), 3.37-3.33 (m, 1H, CH_2), 2.44 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 2.09 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.4, 168.7, 144.0, 143.2, 137.8, 135.4, 134.0, 131.0, 129.9, 129.6, 128.2, 127.3, 125.8, 125.2, 59.4, 50.0, 21.5, 21.1, 20.9; IR (DCM) ν 2923, 1753, 1698, 1347, 1204, 1164, 823, 732 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1806.



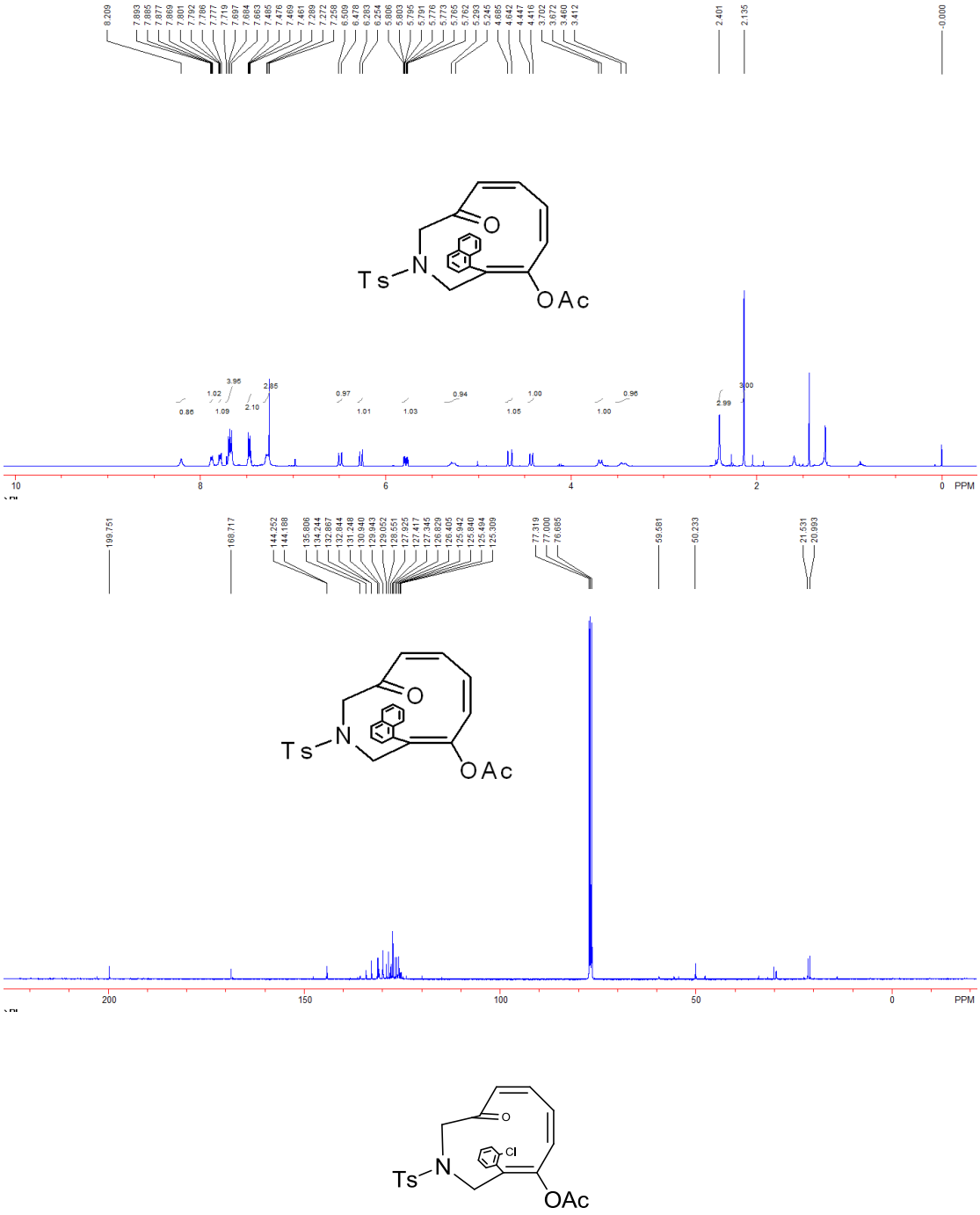


(3Z,5Z,7Z)-3-(3,4-dichlorophenyl)-9-oxo-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2h): a white solid (82 mg, 81% yield), mp: 105-107 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.66 (d, 3H, *J* = 8.4 Hz, ArH), 7.55-7.52 (m, 1H, ArH), 7.37-7.32 (m, 3H, ArH), 6.48 (d, 1H, *J* = 12.4 Hz, =CH), 6.20 (d, 1H, *J* = 11.6 Hz, =CH), 5.87 (dd, 1H, J_1 = 11.6 Hz, J_2 = 4.4 Hz, =CH), 5.48 (br, 1H, =CH), 4.62 (dd, 1H, *J* = 17.2 Hz, CH_2), 4.23 (d, 1H, *J* = 12.8 Hz, CH_2), 3.60 (br, 1H, CH_2), 3.37 (br, 1H, CH_2), 2.46 (s, 3H, CH_3), 2.12 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.5, 168.4, 144.9, 144.4, 138.2, 134.0, 132.1, 131.6, 131.5, 130.6, 130.0, 129.7, 128.8, 127.4, 125.3, 123.3, 59.3, 49.6, 21.6, 20.9; IR (DCM) ν 2923, 1760, 1699, 1347, 1156, 1141, 729 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{25}Cl_2N_2O_5S$ $[M + NH_4]^+$ m/z 523.0856, found 523.0856.



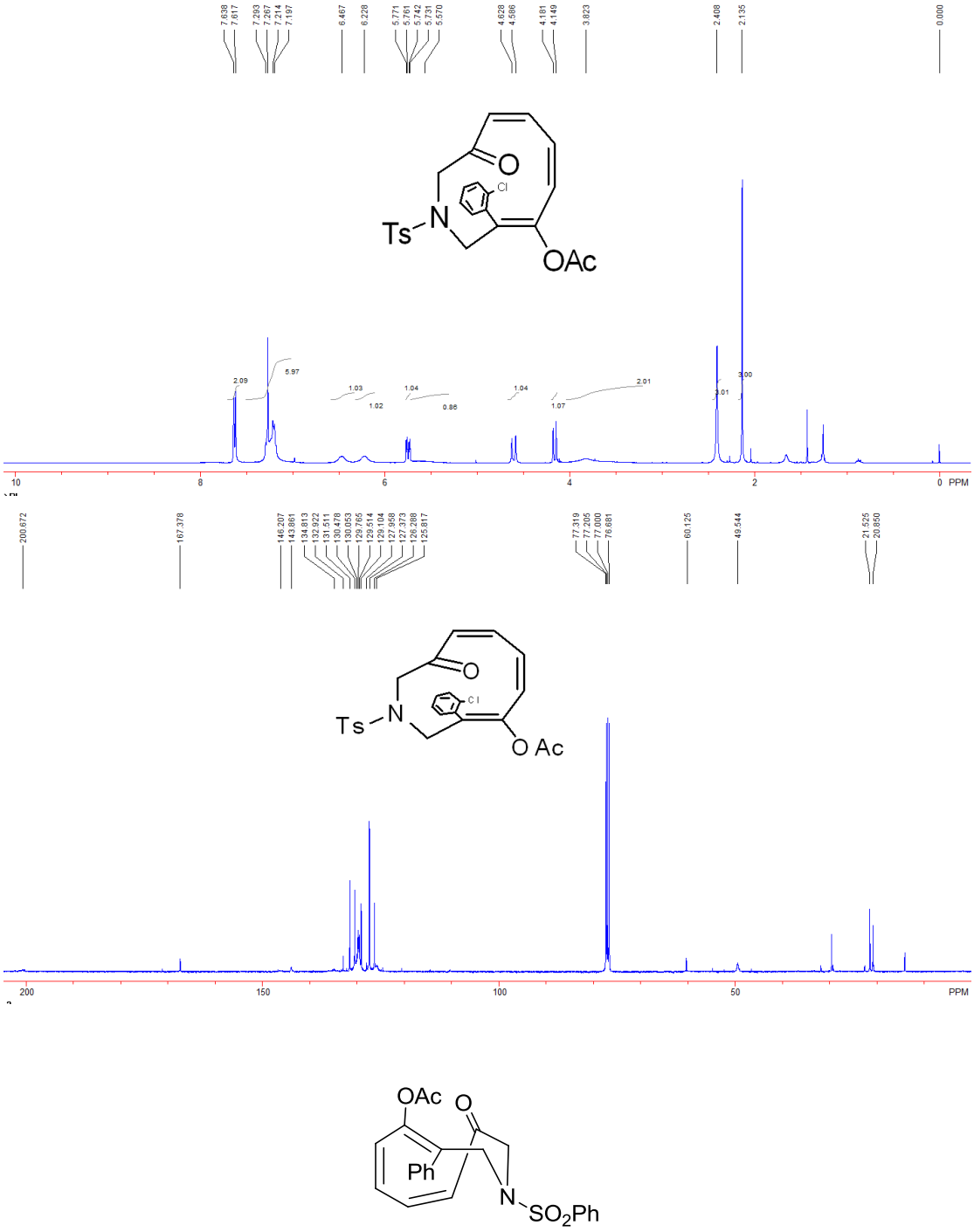
(3Z,5Z,7Z)-3-(naphthalen-1-yl)-9-oxo-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Talbe 2, entry 2i): a white solid (20 mg, 20% yield), few unknown compound which can not be separated from the product by SiO_2 chromatography was included. mp: 147-149 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.21 (br, 1H, ArH), 7.89-7.87 (m, 1H, ArH), 7.80-7.78 (m, 1H, ArH), 7.72-7.67 (m, 4H, ArH), 7.48-7.46 (m, 2H, ArH), 7.29-7.26 (m, 2H, ArH), 6.49 (d, 1H, *J* = 12.4 Hz, =CH), 6.27 (d, 1H, *J* = 11.6 Hz, =CH), 5.81-5.76 (m, 1H, =CH), 5.29-5.24 (m, 1H, =CH), 4.66 (d, 1H, *J* = 17.2 Hz, CH_2), 4.43 (d, 1H, *J* = 12.4 Hz, CH_2), 3.69 (d, 1H, *J* = 12.0 Hz, CH_2), 3.46-3.41 (m, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.7, 168.7,

144.25, 144.19, 135.8, 134.2, 132.9, 132.8, 131.2, 130.9, 129.9, 129.0, 128.5, 127.9, 127.4, 127.3, 126.8, 126.4, 125.9, 125.8, 125.5, 125.3, 59.6, 50.2, 21.5, 21.0; IR (DCM) ν 2924, 1754, 1698, 1347, 1196, 1165, 732 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 505.1792, found 505.1790.



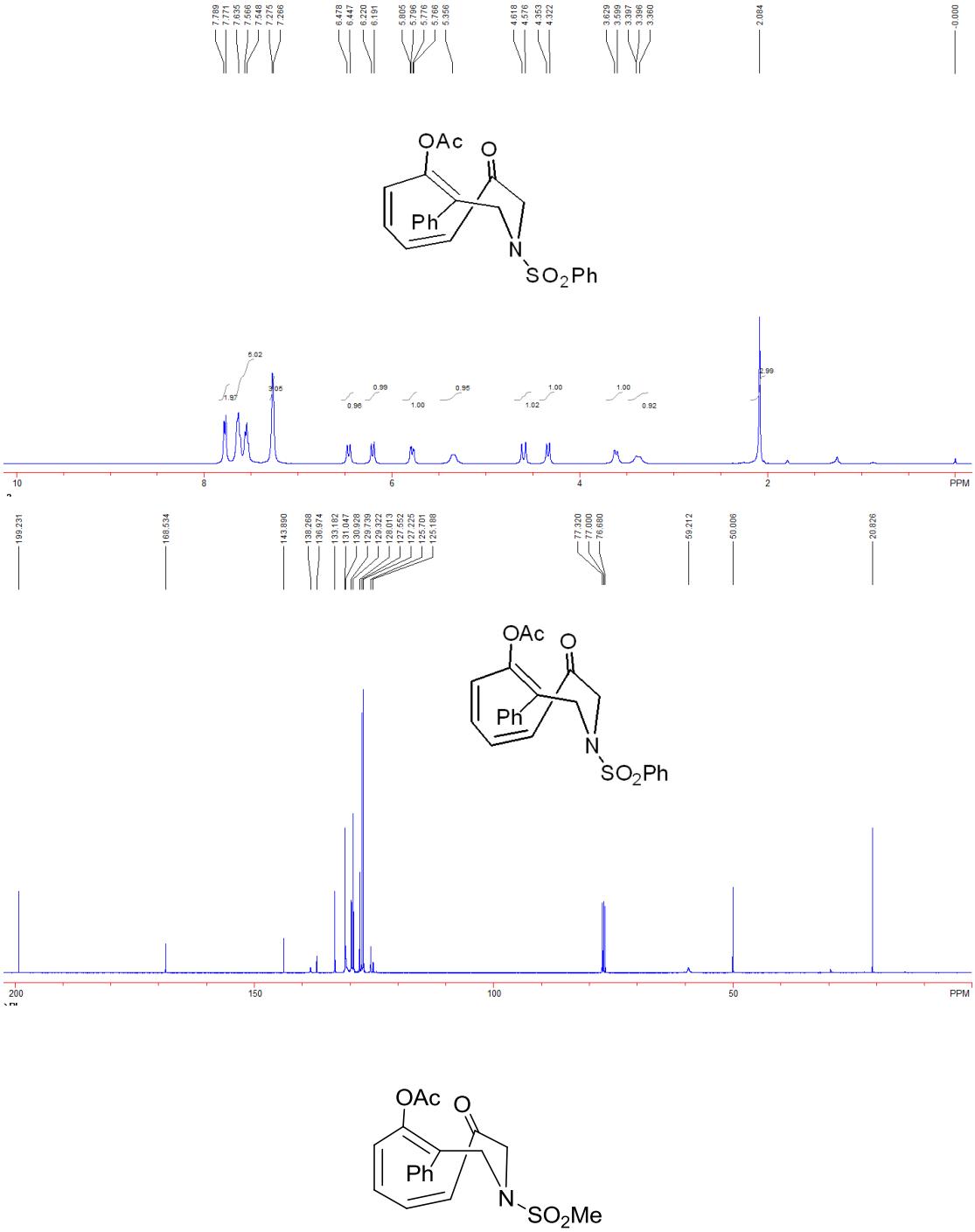
(3Z,5Z,7Z)-3-(2-chlorophenyl)-9-oxo-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2j): a white solid (43 mg, 45% yield), mp: 99-101 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.63 (d, 2H, *J* = 8.4 Hz, ArH), 7.29-7.20 (m, 6H, ArH), 6.47 (br, 1H, =CH), 6.23 (br, 1H, =CH), 5.75 (dd, 1H, J_1 = 12.0 Hz, J_2 = 4.4 Hz, =CH), 5.57 (br, 1H, =CH), 4.61 (d, 1H, *J* = 16.8 Hz,

CH_2), 4.16 (d, 1H, J = 12.8 Hz, CH_2), 3.82 (br, 2H, CH_2), 2.41 (s, 3H, CH_3), 2.13 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 200.7, 167.4, 146.2, 143.9, 134.8, 132.9, 131.5, 130.5, 130.0, 129.8, 129.5, 129.1, 127.9, 127.4, 126.3, 125.8, 60.1, 49.6, 21.5, 20.8; IR (DCM) ν 2924, 1761, 1703, 1339, 1195, 1156, 757, 733 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{26}ClN_2O_5S$ $[M + NH_4]^+$ m/z 489.1245, found 489.1244.

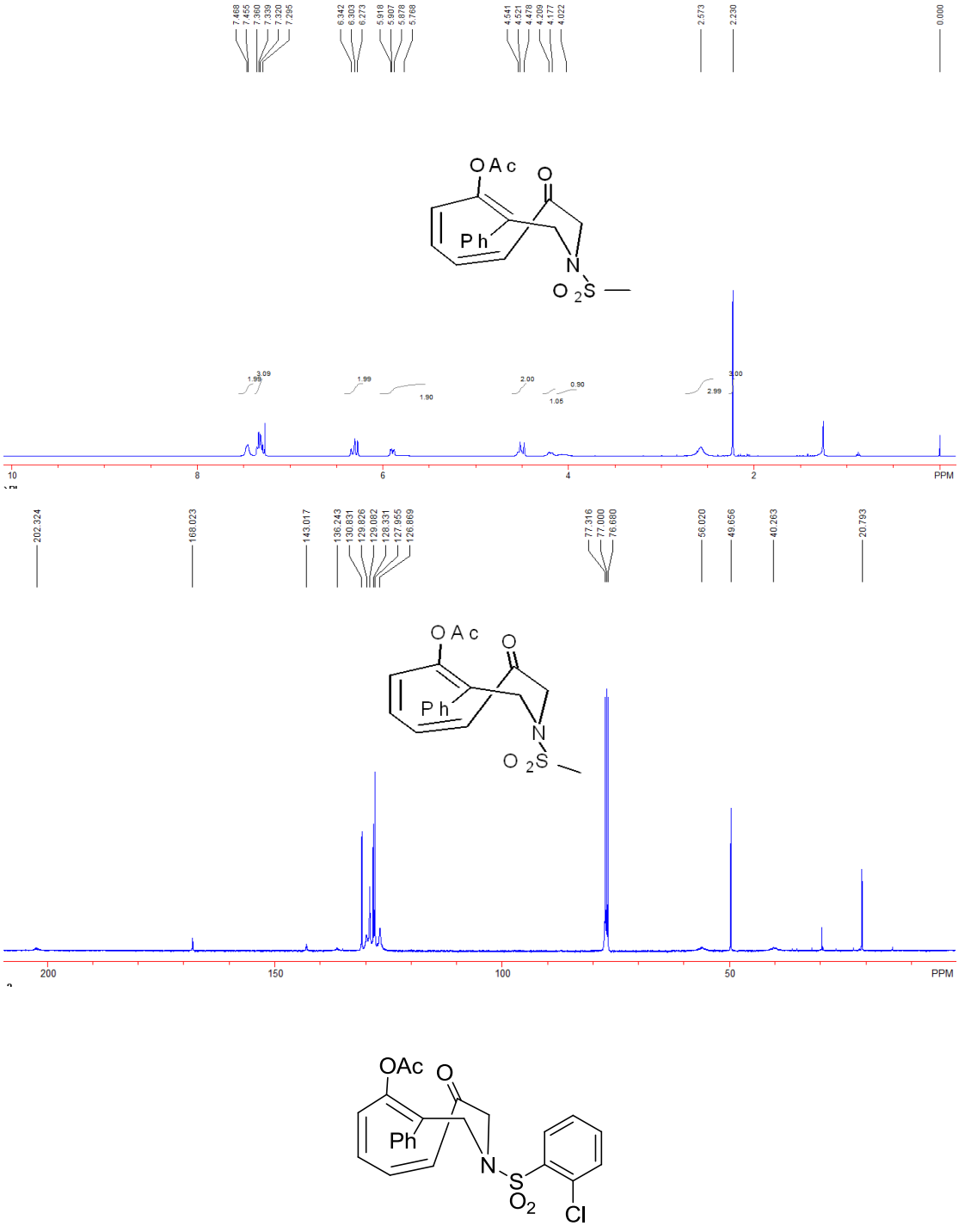


(3Z,5Z,7Z)-9-oxo-3-phenyl-1-(phenylsulfonyl)-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2k): a white solid (77 mg, 91% yield), mp: 123-125 ^oC. ^1H NMR ($CDCl_3$, 400 MHz,

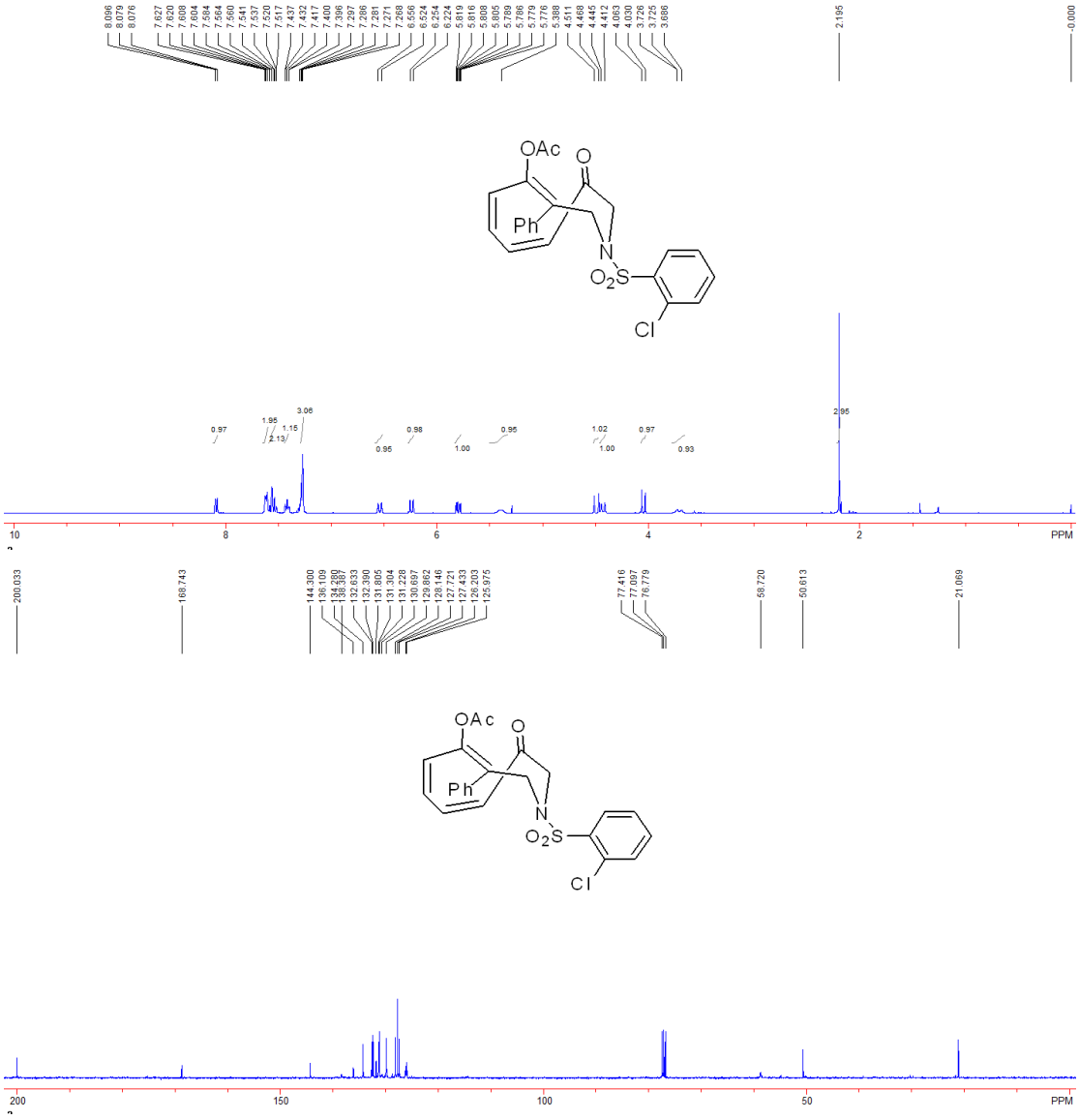
TMS) δ 7.78 (d, 2H, *J* = 7.2 Hz, ArH), 7.63-7.55 (m, 5H, ArH), 7.27-7.26 (m, 3H, ArH), 6.46 (d, 1H, *J* = 12.4 Hz, =CH), 6.20 (d, 1H, *J* =11.6 Hz, =CH), 5.79 (dd, 1H, J_1 = 11.6 Hz, J_2 = 4.0 Hz, =CH), 5.36 (br, 1H, =CH), 4.60 (d, 1H, *J* = 16.8 Hz, CH_2), 4.34 (d, 1H, *J* = 12.4 Hz, CH_2), 3.61 (d, 1H, *J* = 12.4 Hz, CH_2), 3.40-3.36 (m, 1H, CH_2), 2.08 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.2, 168.5, 143.9, 138.3, 137.0, 133.2, 131.0, 130.9, 129.7, 129.3, 128.0, 127.5, 127.2, 125.7, 125.2, 59.2, 50.0, 20.8; IR (DCM) ν 3061, 1757, 1699, 1347, 1205, 1164, 756 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_5S$ $[M + NH_4]^+$ m/z 441.1479, found 441.1479.

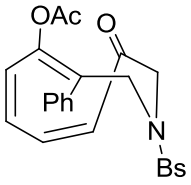


(3Z,5Z,7Z)-1-(methylsulfonyl)-9-oxo-3-phenyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2l): a white solid (59 mg, 81% yield), mp: 104-106 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.47-7.45 (m, 2H, ArH), 7.36-7.29 (m, 3H, ArH), 6.34-6.27 (m, 2H, =CH), 5.92-5.77 (m, 2H, =CH), 4.54-4.48 (m, 2H, CH_2), 4.19 (d, 1H, *J* = 12.8 Hz, CH_2), 4.02 (br, 1H, CH_2), 2.57 (s, 3H, CH_3), 2.23 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 202.3, 168.0, 143.0, 136.2, 130.8, 129.8, 129.1, 128.3, 127.9, 126.9, 56.0, 49.6, 40.3, 20.8; IR (DCM) ν 3263, 1770, 1345, 1164, 814 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{23}N_2O_5S$ $[M + NH_4]^+$ m/z 379.1322, found 379.1333.

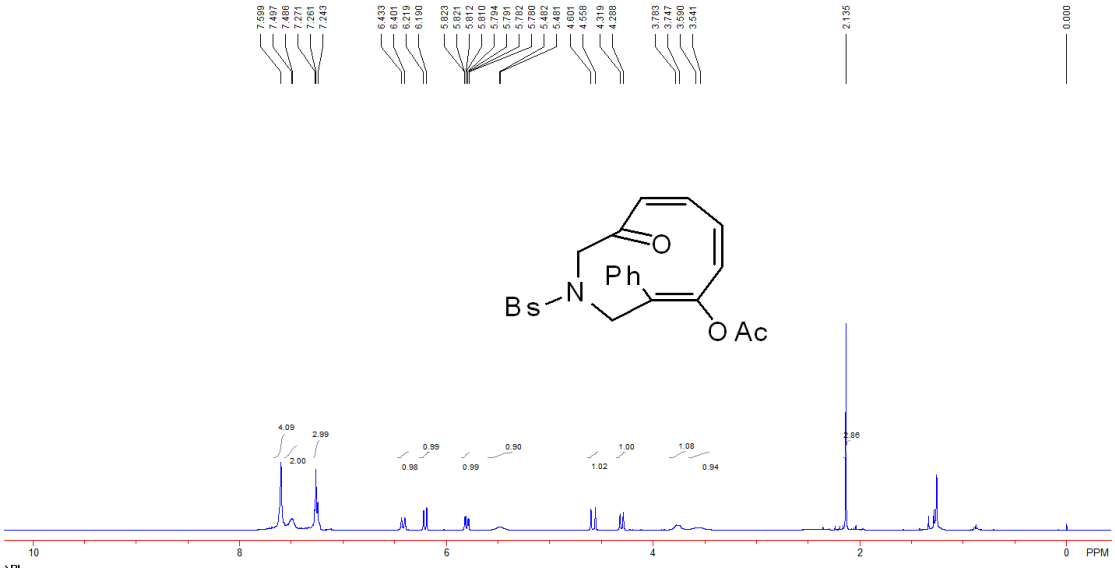


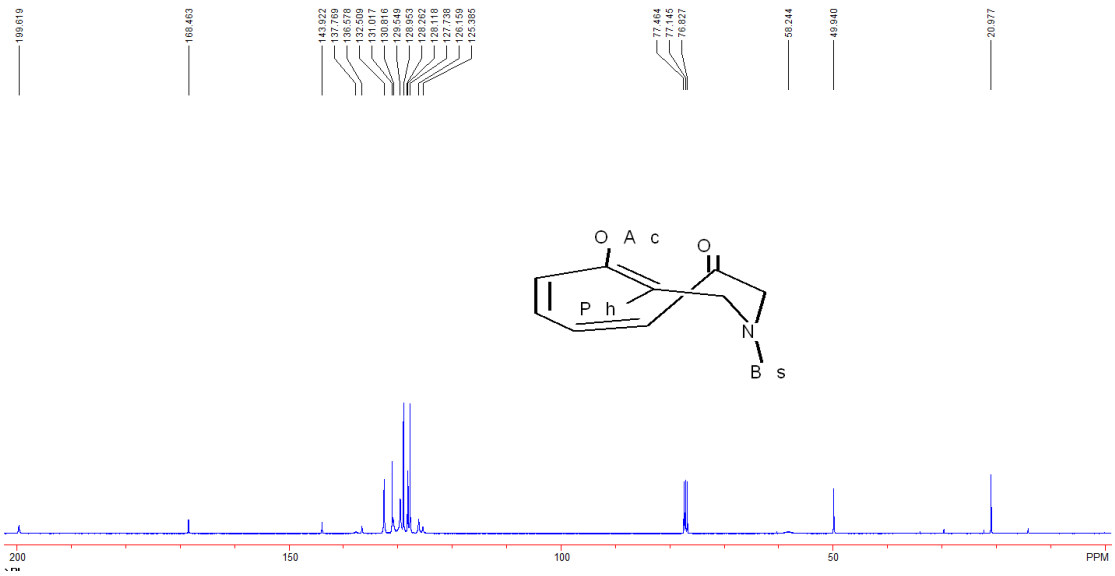
(3Z,5Z,7Z)-1-((2-chlorophenyl)sulfonyl)-9-oxo-3-phenyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2m): a white solid (82 mg, 89% yield), mp: 112-114 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 8.10-8.08 (m, 1H, ArH), 7.63-7.60 (m, 2H, ArH), 7.58-7.52 (m, 2H, ArH), 7.44-7.40 (m, 1H, ArH), 7.30-7.27 (m, 3H, ArH), 6.54 (d, 1H, *J* = 12.8 Hz, =CH), 6.24 (d, 1H, *J* =12.0 Hz, =CH), 5.82-5.78 (m, 1H, =CH), 5.39 (br, 1H, =CH), 4.49 (d, 1H, *J* = 17.2 Hz, CH_2), 4.43 (d, 1H, *J* = 13.2 Hz, CH_2), 4.05 (d, 1H, *J* = 13.2 Hz, CH_2), 3.73-3.69 (m, 1H, CH_2), 2.19 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.9, 168.6, 144.2, 138.3, 136.0, 134.2, 132.5, 132.3, 131.7, 131.2, 131.1, 130.6, 129.8, 128.0, 127.6, 127.3, 126.1, 125.9, 58.6, 50.5, 20.9; IR (DCM) ν 3057, 2927, 1757, 1698, 1341, 1201, 1163, 1139, 761 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}ClN_2O_5S$ $[M + NH_4]^+$ m/z 475.1089, found 475.1093.

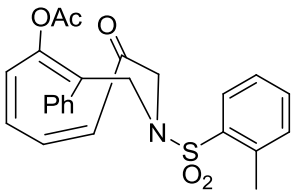




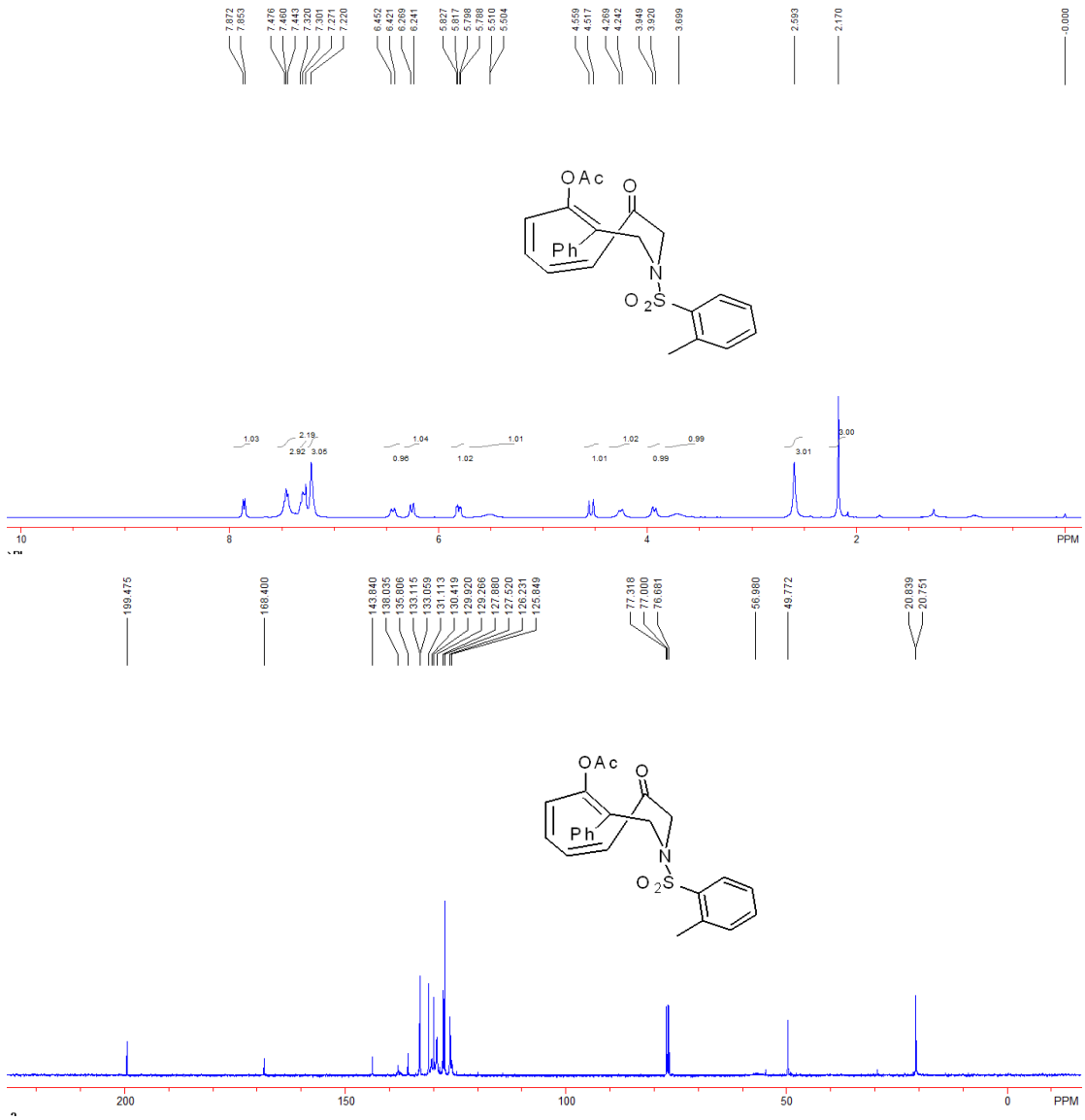
(3Z,5Z,7Z)-1-((4-bromophenyl)sulfonyl)-9-oxo-3-phenyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2n): a white solid (93 mg, 93% yield), mp: 117-119 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.60 (s, 4H, ArH), 7.50-7.49 (m, 2H, ArH), 7.27-7.24 (m, 3H, ArH), 6.42 (d, 1H, *J* = 12.8 Hz, =CH), 6.20 (d, 1H, *J* =11.6 Hz, =CH), 5.82-5.78 (m, 1H, =CH), 5.48 (br, 1H, =CH), 4.58 (d, 1H, *J* = 17.2 Hz, CH_2), 4.30 (d, 1H, *J* = 12.4 Hz, CH_2), 3.78-3.75 (m, 1H, CH_2), 3.59-3.54 (m, 1H, CH_2), 2.13 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.6, 168.5, 143.9, 137.8, 136.6, 132.5, 131.0, 130.8, 129.5, 128.9, 128.3, 128.1, 127.7, 126.1, 125.4, 58.2, 49.9, 21.0; IR (DCM) ν 2923, 1756, 1698, 1349, 1198, 1158, 1010, 733 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{24}BrN_2O_5S$ $[M + NH_4]^+$ m/z 519.0584, found 519.0587.

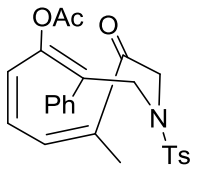






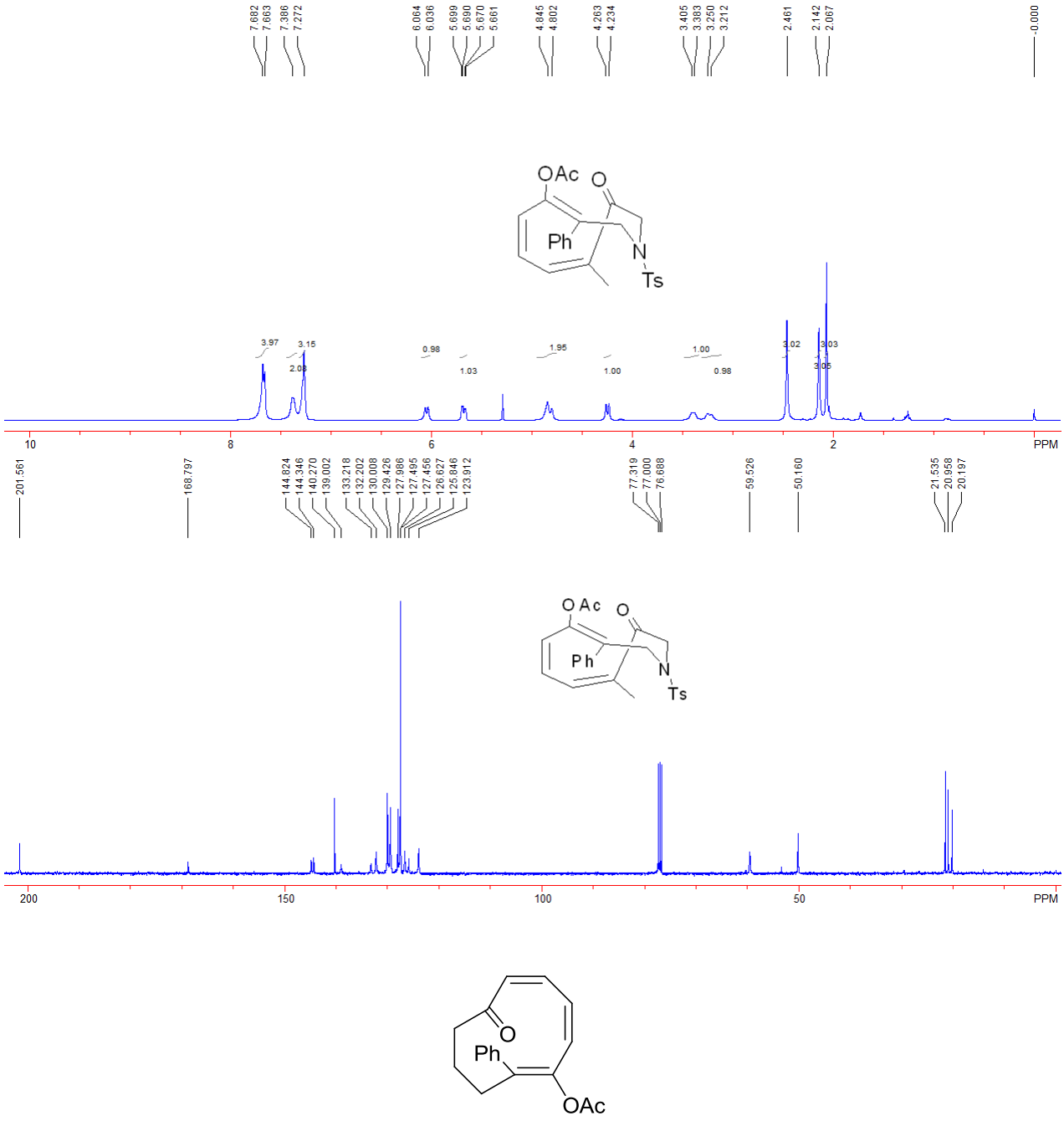
(3Z,5Z,7Z)-9-oxo-3-phenyl-1-(o-tolylsulfonyl)-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2o): a white solid (82 mg, 94% yield), mp: 110-112 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.86 (d, 1H, *J* = 7.6 Hz, ArH), 7.48-7.44 (m, 3H, ArH), 7.32-7.27 (m, 2H, ArH), 7.20 (s, 3H, ArH), 6.44 (d, 1H, *J* = 12.4 Hz, =CH), 6.25 (d, 1H, *J* =11.2 Hz, =CH), 5.81 (dd, 1H, J_1 = 11.2 Hz, J_2 = 4.0 Hz, =CH), 5.51-5.50 (m, 1H, =CH), 4.54 (d, 1H, *J* = 16.8 Hz, CH_2), 4.25 (d, 1H, *J* = 10.8 Hz, CH_2), 3.93 (d, 1H, *J* = 11.6 Hz, CH_2), 3.70 (br, 1H, CH_2), 2.59 (s, 3H, CH_3), 2.17 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.5, 168.4, 143.8, 138.0, 135.8, 133.11, 133.06, 131.1, 130.4, 129.9, 129.3, 127.9, 127.5, 126.2, 125.8, 57.0, 49.8, 20.8, 20.7; IR (DCM) ν 2919, 1756, 1698, 1331, 1197, 1155, 730 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 455.1635, found 455.1642.





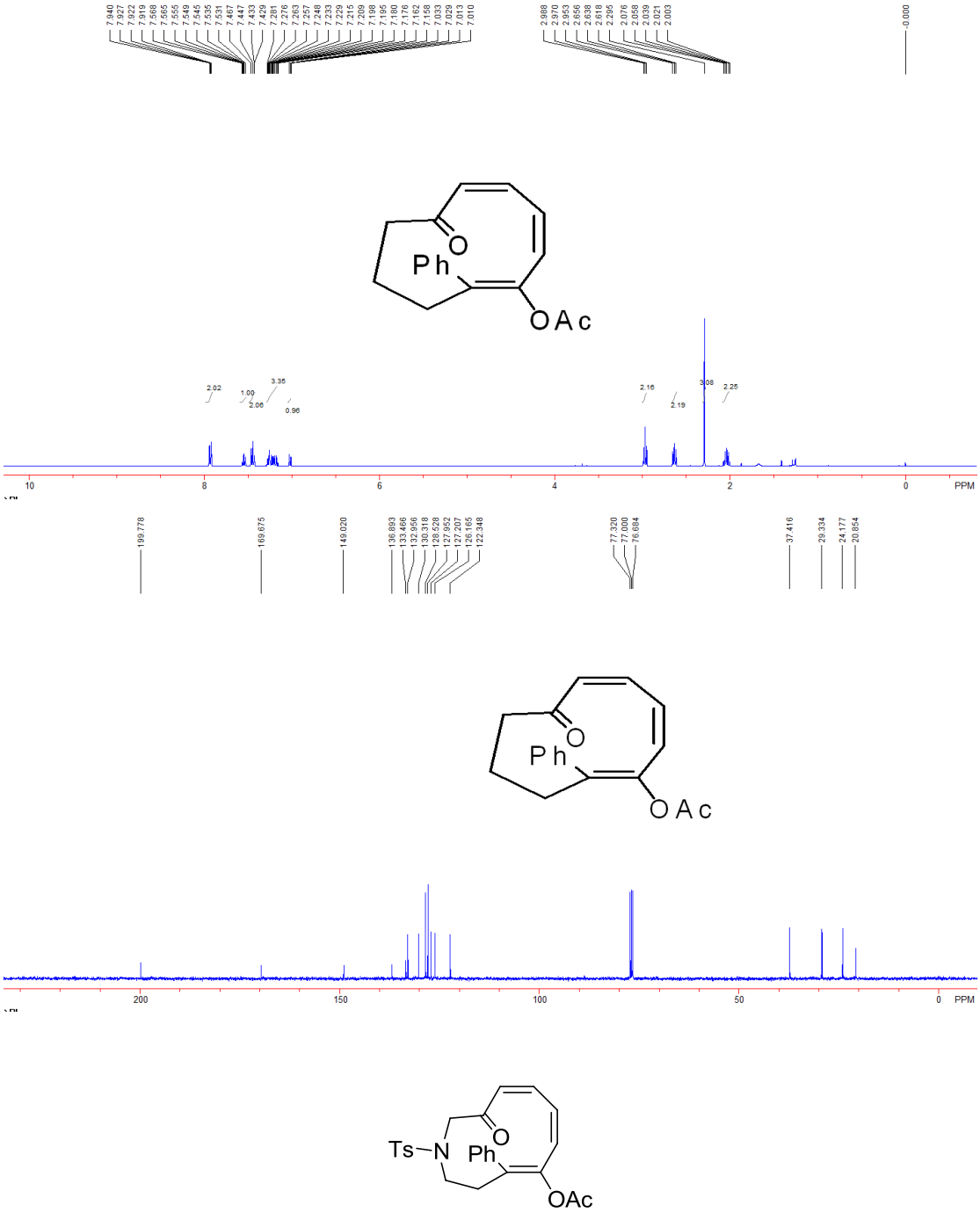
(3Z,5Z,7Z)-8-methyl-9-oxo-3-phenyl-1-tosyl-1,2,9,10-tetrahydroazecin-4-yl acetate (Table 2, entry 2q): a colorless oil (97 mg, 96% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.68-7.66 (m, 2H, ArH), 7.39 (br, 2H, ArH), 7.27 (br, 3H, ArH), 6.05 (d, 1H, J = 11.2 Hz, =CH), 5.68 (dd, 1H, J_1 = 11.6 Hz, J_2 = 3.6 Hz, =CH), 4.84-4.80 (m, 2H, =CH and CH_2), 4.25 (d, 1H, J = 11.6 Hz, CH_2), 3.40-3.38 (m, 1H, CH_2), 3.25-3.21 (m, 1H, CH_2), 2.46 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.07 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 201.6, 168.8, 144.8, 144.3, 140.3, 139.0, 133.2, 132.2, 130.0, 129.4, 128.0, 127.5, 127.4, 126.6, 125.8, 123.9, 59.5, 50.2, 21.5, 20.9, 20.2;

IR (DCM) ν 2923, 1757, 1693, 1347, 1206, 1163, 1089, 811 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1793.



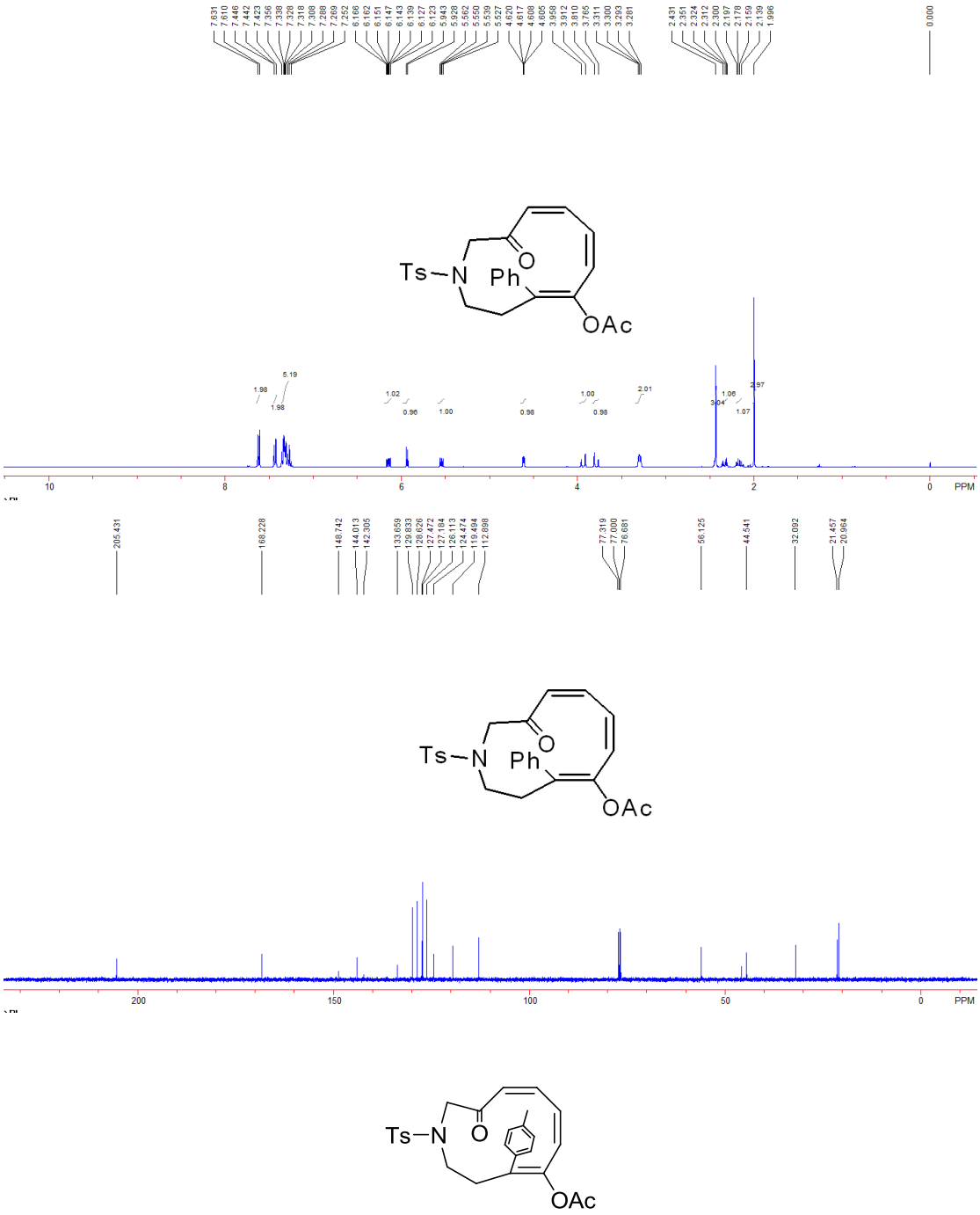
(1E,7Z,9Z)-6-oxo-2-phenylcyclodeca-1,7,9-trien-1-yl acetate (Table 2, entry 2r): a colorless oil (46 mg, 82% yield). ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.93 (dd, 2H, J_1 = 7.2 Hz, J_2 = 1.2 Hz, ArH), 7.57-7.53 (m, 1H, ArH), 7.47-7.43 (m, 2H, ArH), 7.28-7.16 (m, 3H, =CH), 7.02 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz, =CH), 2.97 (t, 2H, J = 7.2 Hz, CH_2), 2.64 (t, 2H, J = 7.2 Hz, CH_2), 2.29 (s, 3H, CH_3), 2.08-2.00 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 199.8, 169.7, 149.0, 136.9, 133.5, 132.9, 130.3, 128.5, 127.9, 127.2, 126.2, 122.3, 37.4, 29.3, 24.2, 20.8; IR (DCM) ν 2932, 1755, 1683, 1368, 1205, 1171 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}NO_3$ [M +

$NH_4]^+$ m/z 300.1594, found 300.1599.



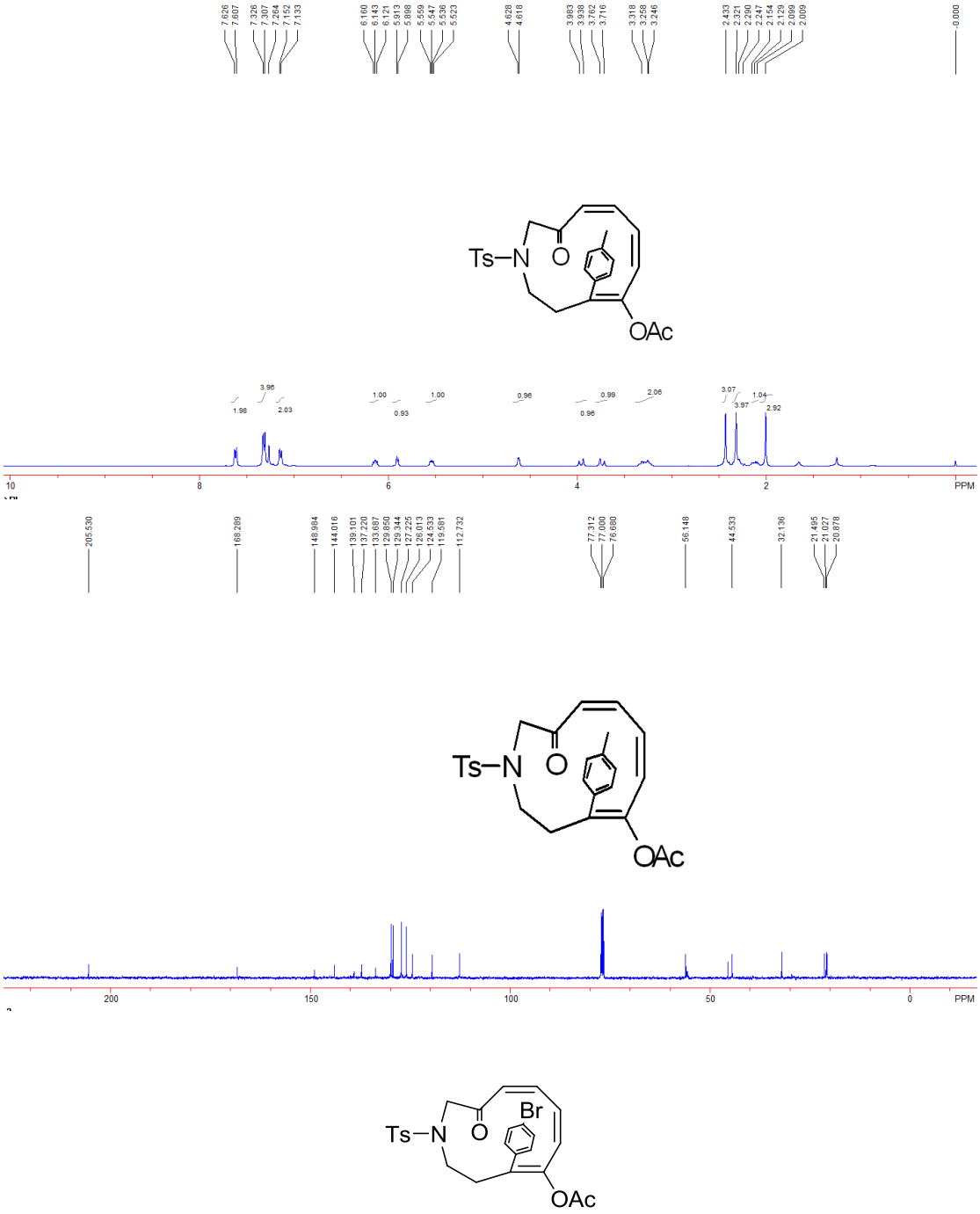
(4E,6Z,8Z)-10-oxo-4-phenyl-1-tosylazacycloundeca-4,6,8-trien-5-yl acetate (Table 3, entry 2s): a white solid (88 mg, 98% yield), mp: 105-107 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.62 (d, 2H, *J* = 8.4 Hz, ArH), 7.45-7.42 (m, 2H, ArH), 7.36-7.25 (m, 5H, ArH), 6.17-6.12 (m, 1H, =CH), 5.93 (d, 1H, *J* =6.0 Hz, =CH), 5.54 (dd, 1H, J_1 = 9.2 Hz, J_2 = 0.8 Hz, =CH), 4.62-4.60 (m, 1H, =CH), 3.93 (d, 1H, *J* = 18.4 Hz, CH_2), 3.79 (d, 1H, *J* = 18.4 Hz, CH_2), 3.31-3.28 (m, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.35-2.30 (m, 1H, CH_2), 2.20-2.14 (m, 1H, CH_2), 2.00 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 205.4, 168.2, 148.7, 144.0, 142.3, 133.6, 129.8, 128.6, 127.5,

127.2, 126.1, 124.5, 119.5, 112.9, 56.1, 44.5, 32.1, 21.4, 21.0; IR (DCM) ν 2925, 1760, 1722, 1347, 1185, 1159, 1135 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ $[M + NH_4]^+$ m/z 469.1792, found 469.1799.



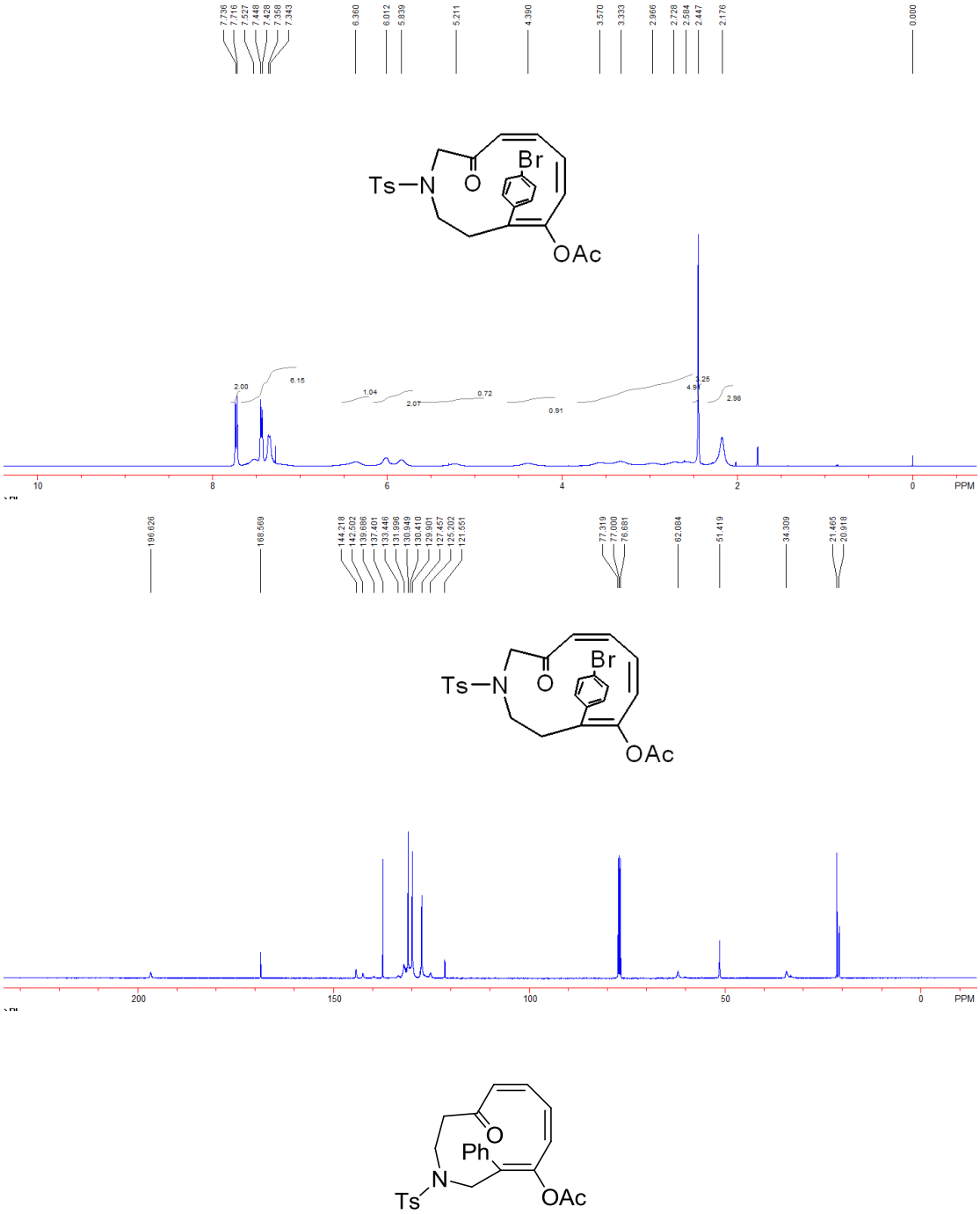
(4E,6Z,8Z)-10-oxo-4-(p-tolyl)-1-tosylazacycloundeca-4,6,8-trien-5-yl acetate (Table 3, entry 2t): a yellow solid (88 mg, 98% yield), mp: 113-115 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.62 (d, 2H, *J* = 7.6 Hz, ArH), 7.32 (d, 4H, *J* = 7.6 Hz, ArH), 7.14 (d, 2H, *J* = 7.6 Hz, ArH), 6.16-6.12 (m, 1H, =CH), 5.90 (d, 1H, *J* =6.0 Hz, =CH), 5.54 (dd, 1H, J_1 = 9.2 Hz, J_2 = 0.8 Hz, =CH), 4.63-4.62 (m, 1H, =CH), 3.96 (d, 1H, *J* = 18.0 Hz, CH_2), 3.74 (d, 1H, *J* = 18.0 Hz, CH_2),

3.32-3.25 (m, 2H, CH_2), 2.43 (s, 3H, CH_3), 2.32-2.25 (m, 4H, CH_3 and CH_2), 2.15-2.10 (m, 1H, CH_2), 2.01 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 205.5, 168.3, 149.0, 144.0, 139.1, 137.2, 133.7, 129.8, 129.3, 127.2, 126.0, 124.5, 119.6, 112.7, 56.1, 44.5, 32.1, 21.5, 21.0, 20.9; IR (DCM) ν 2924, 1763, 1723, 1348, 1188, 1162, 661 cm^{-1}; HRMS (ESI) calcd for $C_{26}H_{31}N_2O_5S$ $[M + NH_4]^+$ m/z 483.1948, found 483.1953.



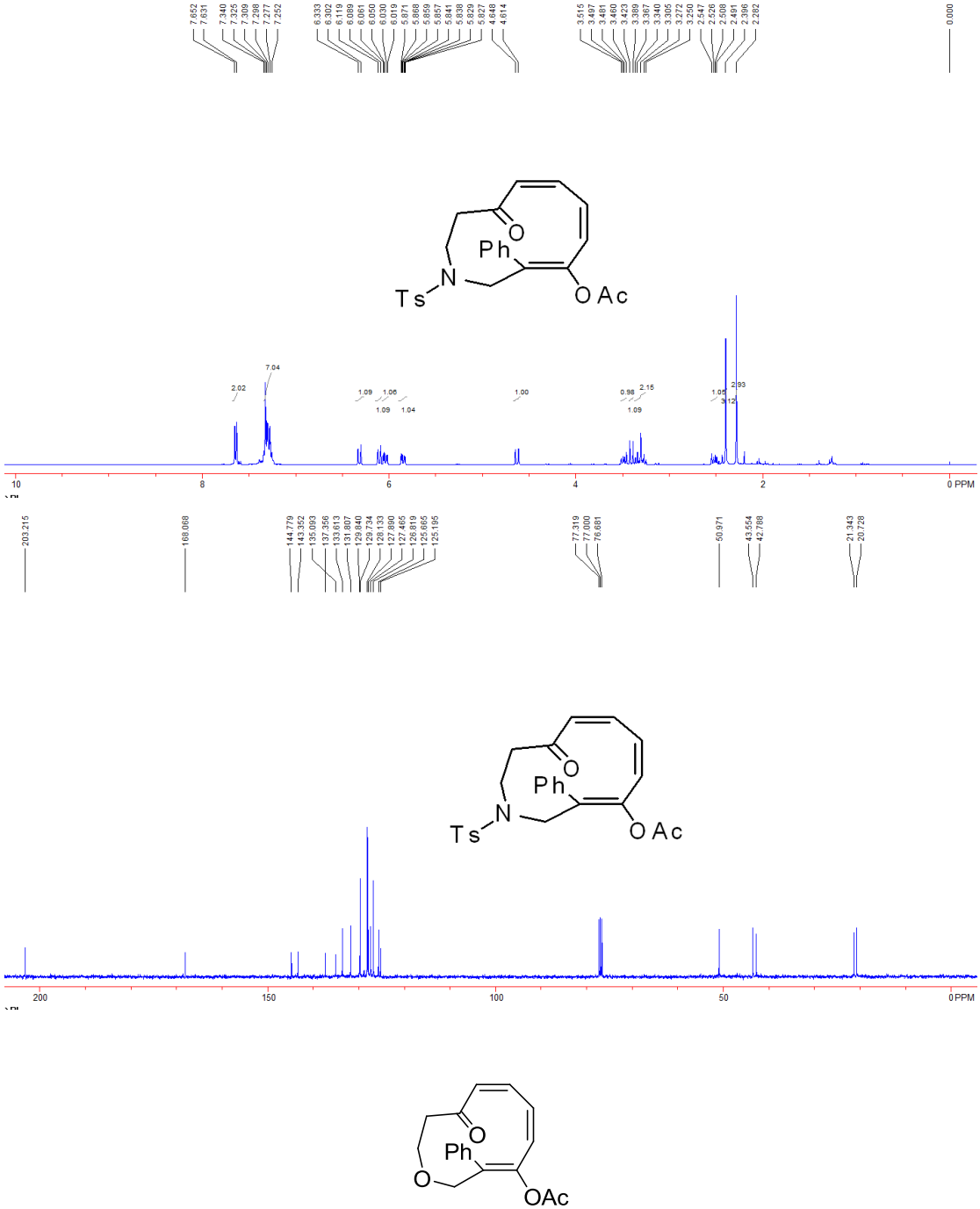
(4E,6Z,8Z)-4-(4-bromophenyl)-10-oxo-1-tosylazacycloundeca-4,6,8-trien-5-yl acetate (Table 3, entry 2u): a white solid (85 mg, 80% yield), mp: 118-120 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.73 (d, 2H, *J* = 8.0 Hz, ArH), 7.53-7.34 (m, 6H, ArH), 6.36 (br, 1H, =CH), 6.01-5.84 (m,

2H, =CH), 5.21 (br, 1H, =CH), 4.39 (br, 1H, CH_2), 3.57-2.58 (m, 5H), 2.45 (s, 3H, CH_3), 2.18 (br, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 196.6, 168.6, 144.2, 142.5, 139.7, 137.4, 133.4, 132.0, 130.9, 130.4, 129.9, 127.4, 125.2, 121.5, 62.1, 51.4, 34.3, 21.5, 20.9; IR (DCM) ν 2923, 1753, 1698, 1345, 1204, 1159, 716 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{28}BrN_2O_5S$ $[M + NH_4]^+$ m/z 547.0897, found 547.0901.



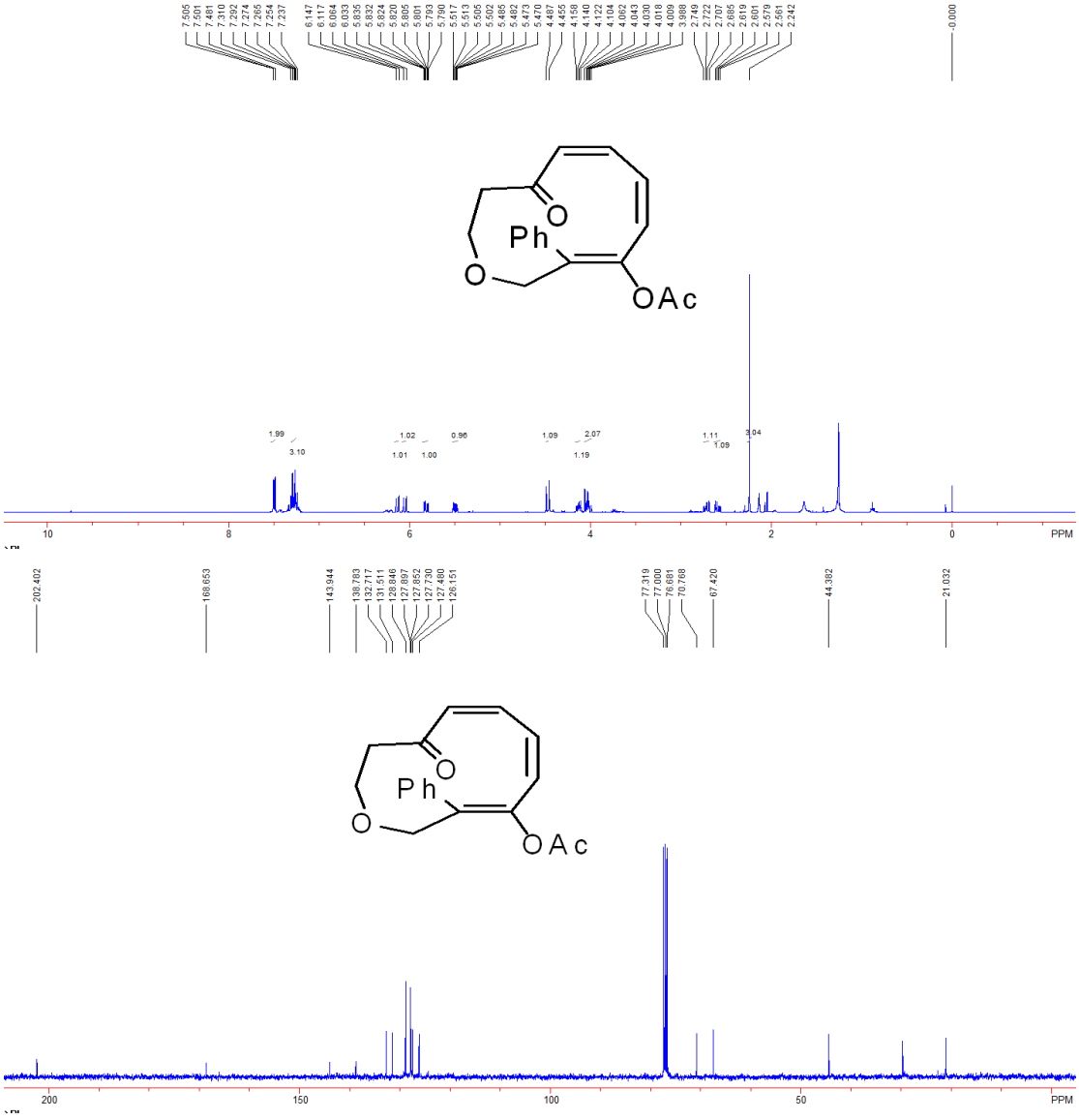
(3Z,5Z,7Z)-9-oxo-3-phenyl-1-tosylazacycloundeca-3,5,7-trien-4-yl acetate (Table 3, entry 2v): a white solid (87 mg, 97% yield), mp: 107-109 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64 (d, 2H, *J* = 8.4 Hz, ArH), 7.34-7.25 (m, 7H, ArH), 6.32 (d, 1H, *J* = 12.4 Hz, =CH), 6.10 (d, 1H, *J* =

12.0 Hz, =CH), 6.04 (dd, 1H, J_1 = 12.4 Hz, J_2 = 4.4 Hz, =CH), 5.87-5.83 (m, 1H, =CH), 4.63 (d, 1H, J = 13.6 Hz, CH_2), 3.51-3.46 (m, 1H, CH_2), 3.41 (d, 1H, J = 13.6 Hz, CH_2), 3.37-3.25 (m, 2H, CH_2), 2.55-2.49 (m, 1H, CH_2), 2.40 (s, 3H, CH_3), 2.28 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 203.2, 168.1, 144.8, 143.3, 137.3, 135.1, 133.6, 131.8, 129.8, 129.7, 128.1, 127.9, 127.5, 126.8, 125.7, 125.2, 51.0, 43.5, 42.8, 21.3, 20.7; IR (DCM) ν 2919, 1755, 1688, 1338, 1202, 1160, 732, 700 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{29}N_2O_5S$ [M + NH_4]$^+$ m/z 469.1792, found 469.1793.

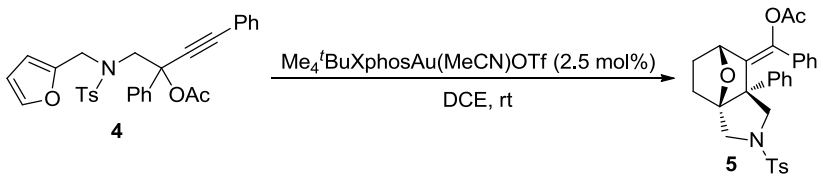


(3Z,5Z,7Z)-9-oxo-3-phenyloxacycloundeca-3,5,7-trien-4-yl acetate (Table 3, entry 2w): a colorless oil (46 mg, 78% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.50-7.48 (m, 2H, ArH),

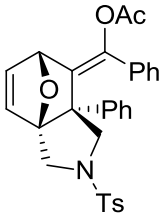
7.31-7.24 (m, 3H, ArH), 6.13 (d, 1H, *J* = 12.0 Hz, =CH), 6.05 (d, 1H, *J* = 12.4 Hz, =CH), 5.83-5.79 (m, 1H, =CH), 5.52-5.47 (m, 1H, =CH), 4.47 (d, 1H, *J* = 12.8 Hz, CH_2), 4.16-4.10 (m, 1H, CH_2), 4.06-3.99 (m, 2H, CH_2), 2.75-2.68 (m, 1H, CH_2), 2.62-2.56 (m, 1H, CH_2), 2.24 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 202.4, 168.6, 143.9, 138.8, 132.7, 131.5, 128.8, 127.9, 127.8, 127.7, 127.5, 126.1, 70.8, 67.4, 44.4, 21.0; IR (DCM) ν 2924, 1753, 1689, 1207, 1089, 1049 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{22}NO_4$ $[M + NH_4]^+$ m/z 316.1543, found 316.1545.



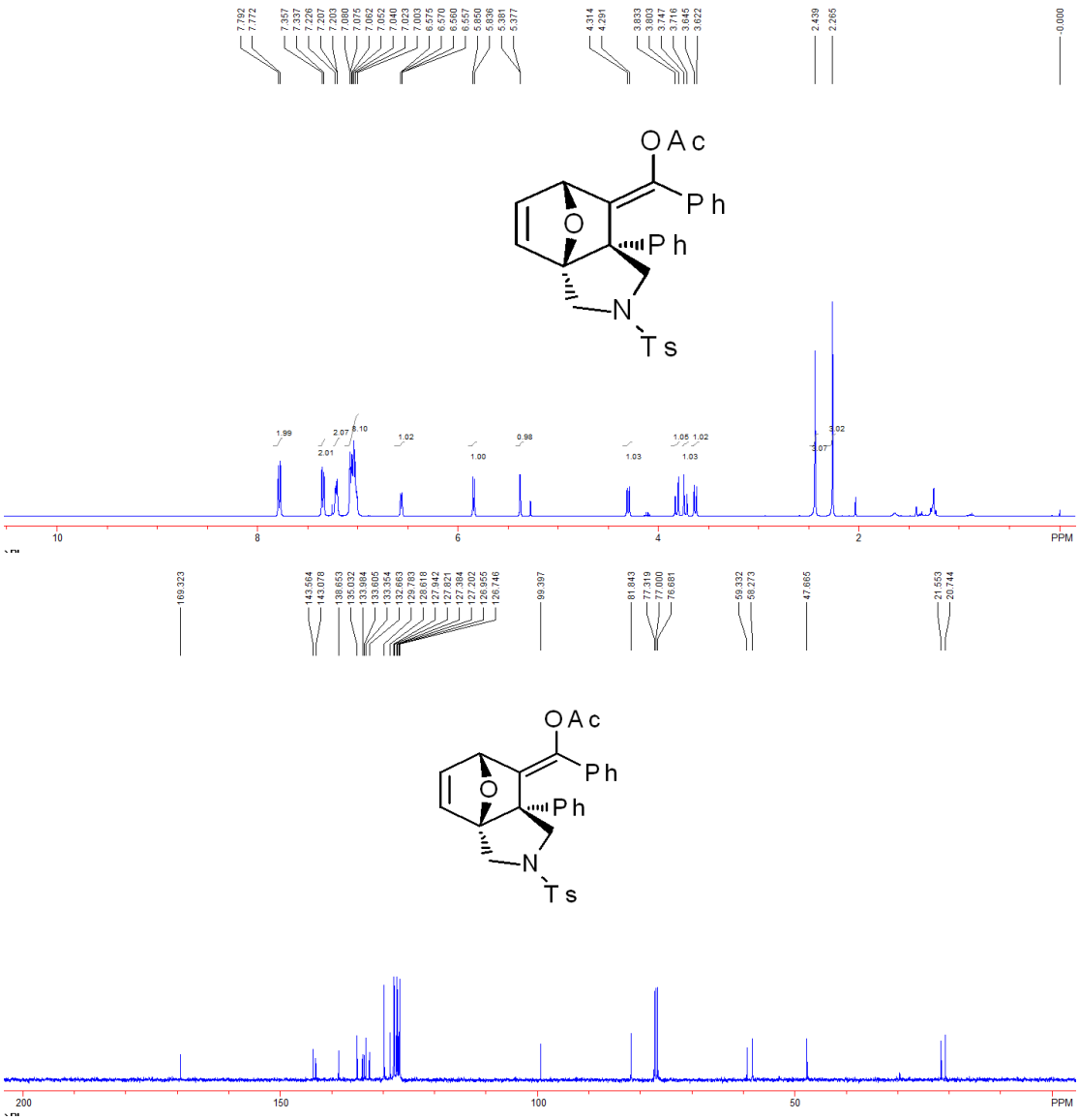
General Procedure for the Diels-Alder Reaction and the Spectroscopic Data of the Products.



Into an oven-dried reaction flask under Ar gas protection were added substrates **4** (0.2 mmol) and DCE (1.5 mL), then a solution of Au-catalysts (0.005 mol/0.5 mL) was added. The reaction mixture was stirred at room temperature for several minutes, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

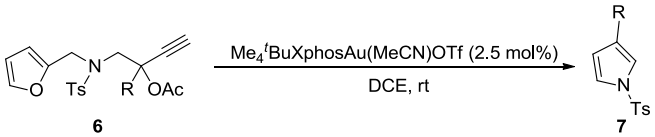


(Z)-phenyl(7a-phenyl-2-tosyl-1,2,3,7a-tetrahydro-3a,6-epoxyisoindol-7(6H)-ylidene)methyl acetate (Scheme 3, compound 5): a white solid (103 mg, 99% yield), mp: 142-144 ^{o}C. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.79 (d, 2H, *J* = 8.0 Hz, ArH), 7.35 (d, 2H, *J* = 8.0 Hz, ArH), 7.23-7.20 (m, 2H, ArH), 7.08-7.00 (m, 8H, ArH), 6.57-6.56 (m, 1H, =CH), 5.84 (d, 1H, *J* = 5.6 Hz, =CH), 5.38 (d, 1H, *J* = 1.6 Hz, CH), 4.30 (d, 1H, *J* = 9.2 Hz, CH_2), 3.82 (d, 1H, *J* = 12.0 Hz, CH_2), 3.73 (d, 1H, *J* = 12.0 Hz, CH_2), 3.63 (d, 1H, *J* = 9.2 Hz, CH_2), 2.44 (s, 3H, CH_3), 2.26 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 169.3, 143.6, 143.1, 138.6, 135.0, 134.0, 133.6, 133.3, 132.7, 129.8, 128.6, 127.9, 127.8, 127.4, 127.2, 126.9, 126.7, 99.4, 81.8, 59.3, 58.3, 47.7, 21.5, 20.7; IR (DCM) ν 2939, 1755, 1345, 1199, 1164, 1092, 701 cm^{-1}; HRMS (ESI) calcd for $C_{30}H_{27}NNaO_5S$ $[M + Na]^+$ m/z 536.1502, found 536.1513.



General Procedure for the Decomposition Reaction and the Spectroscopic Data of the Products

Table SI-2. Gold-catalyzed Decomposition Reaction of Alkyl Substrates

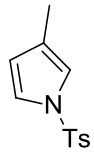


6 **7**

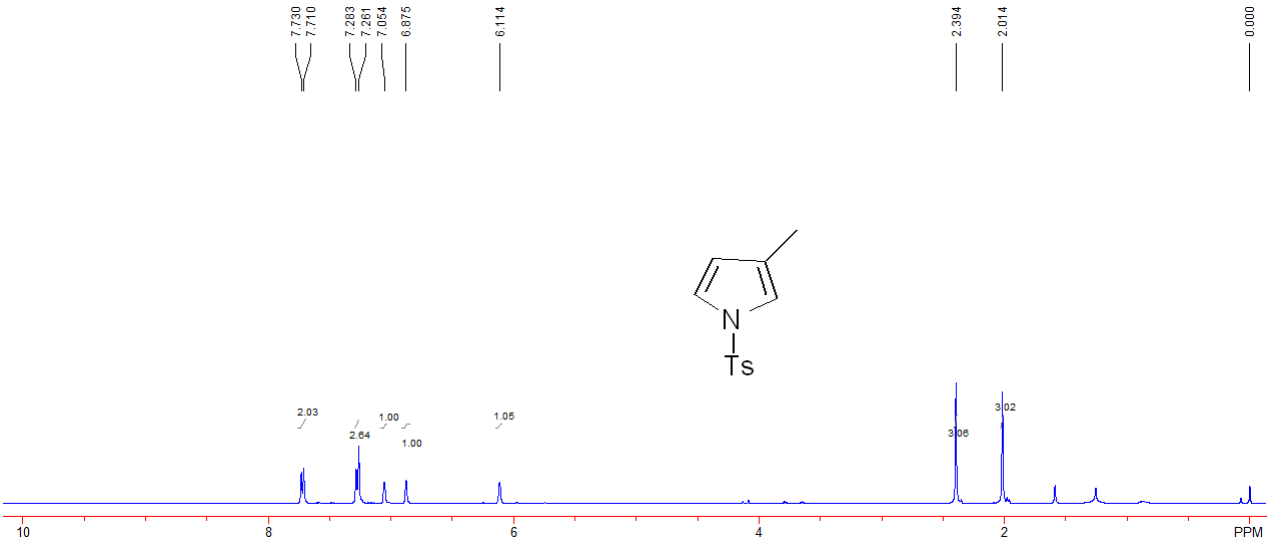
entry[a]	R	yield (%)[b]
1	**6a**: Me	**7a**: 76
2	**6b**: Et	**7b**: 64
3	**6c**: ^{i}Pr	**7c**: 64
4	**6d**: Cy	**7d**: 46

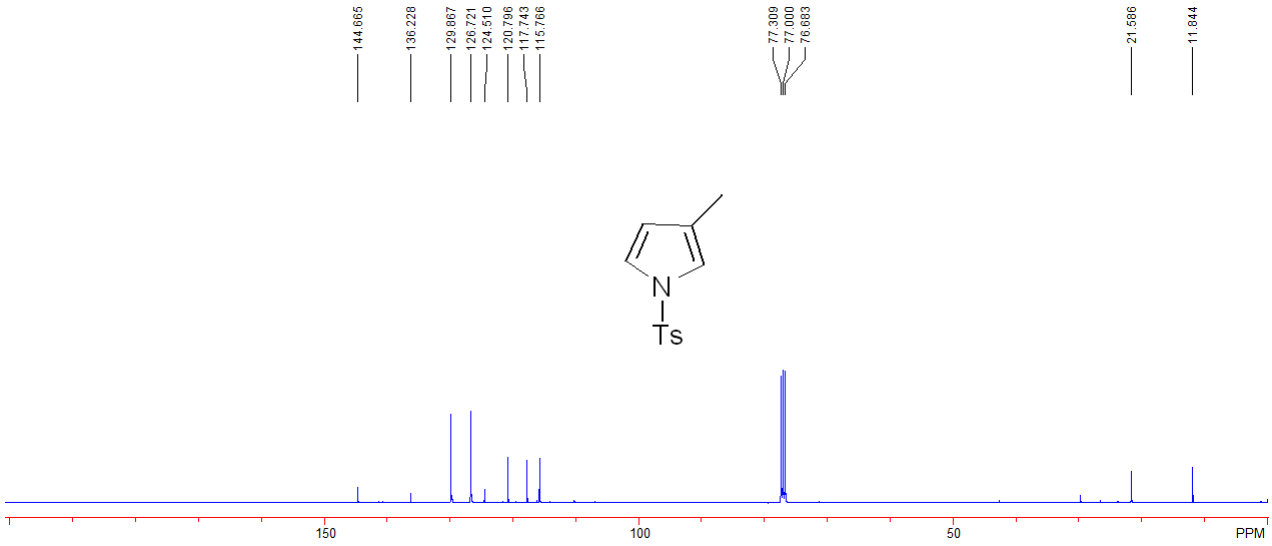
[a] The reaction was carried out on a 0.2 mmol scale with 2.5 mol% catalyst in solvent (2.0 mL). [b] Isolated yield.

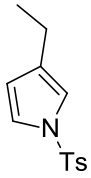
Into an oven-dried reaction flask under Ar gas protection were added substrates **6** (0.2 mmol) and DCE (1.5 mL), then a solution of Au-catalysts (0.005 mol/0.5 mL) was added. The reaction mixture was stirred at room temperature for several minutes, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.



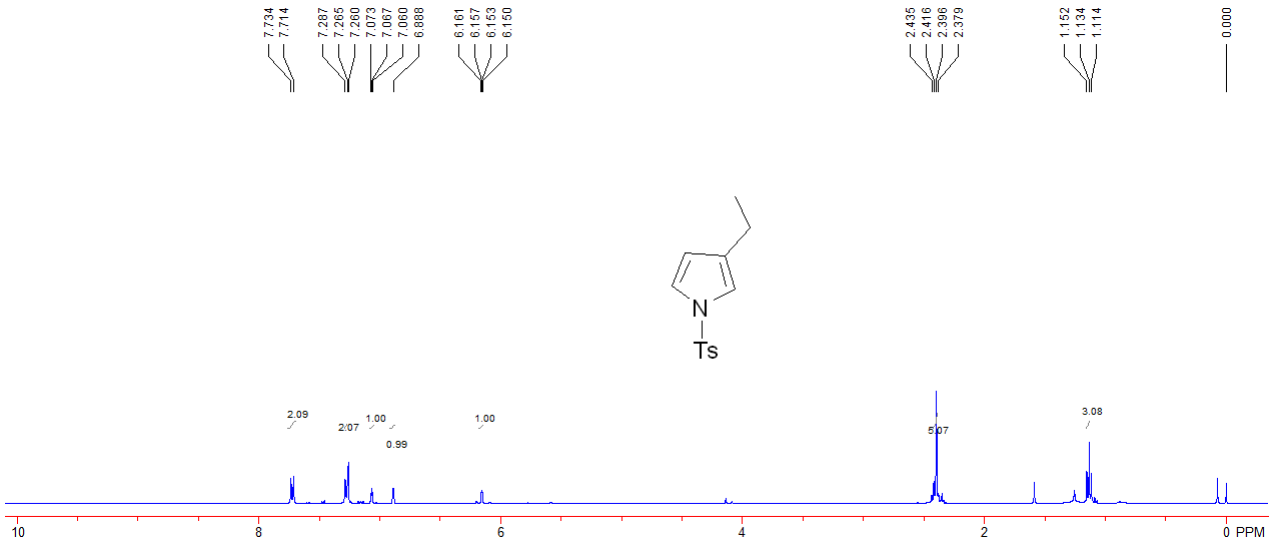
3-methyl-1-tosyl-1H-pyrrole (Table SI-2, entry 7a): known compound,[10] a colorless oil (40 mg, 76% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.72 (d, 2H, *J* = 8.0 Hz, ArH), 7.27 (d, 2H, *J* = 8.0 Hz, ArH), 7.05 (s, 1H, ArH), 6.88 (s, 1H, ArH), 6.11 (s, 1H, ArH), 2.39 (s, 3H, CH_3), 2.01 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.7, 136.2, 129.9, 126.7, 124.5, 120.8, 117.7, 115.8, 21.6, 11.8; IR (DCM) ν 2924, 1366, 1261, 1170, 1099, 1059, 678 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{14}NO_2S$ $[M + H]^+$ m/z 236.0740, found 236.0746.

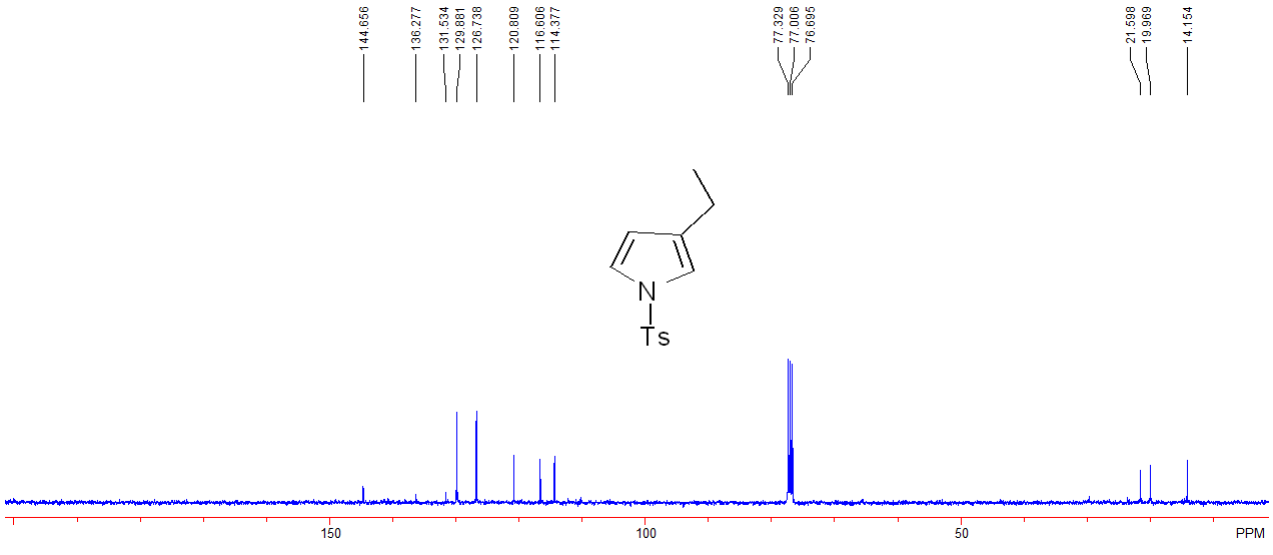


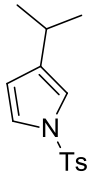




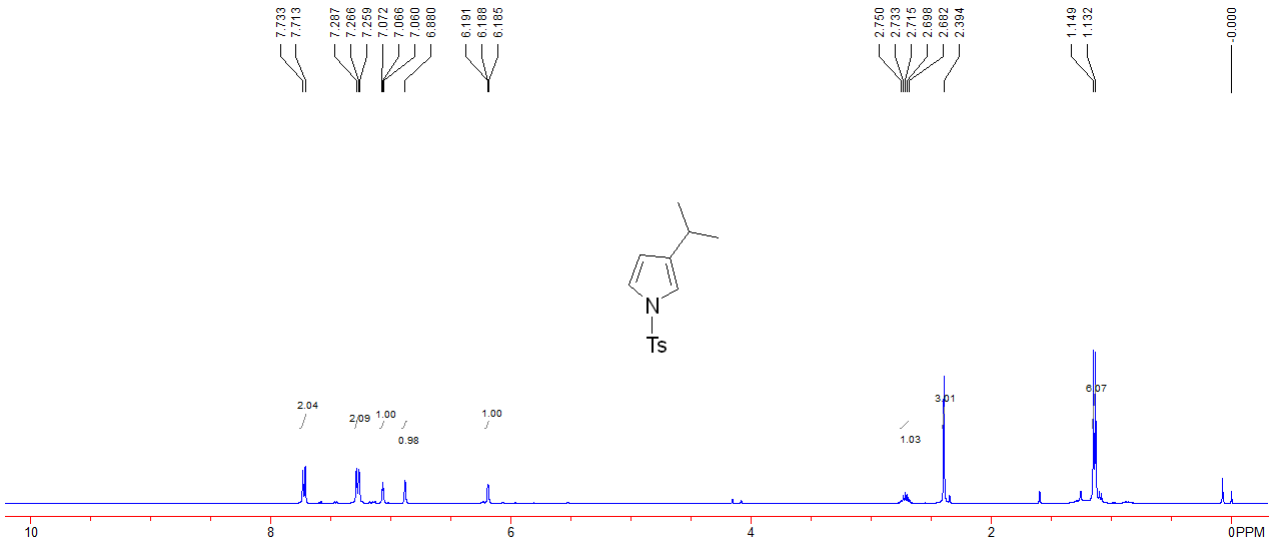
3-ethyl-1-tosyl-1H-pyrrole (Table SI-2, entry 7b): known compound,[11] a colorless oil (31 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.72 (d, 2H, *J* = 8.0 Hz, ArH), 7.28 (d, 2H, *J* = 8.0 Hz, ArH), 7.07-7.06 (m, 1H, ArH), 6.89 (s, 1H, ArH), 6.16-6.15 (m, 1H, ArH), 2.43-2.38 (m, 5H, CH_2 and CH_3), 1.13 (t, 3H, *J* = 7.6 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.6, 136.3, 131.5, 129.9, 126.7, 120.8, 116.6, 114.4, 21.6, 20.0, 14.1; IR (DCM) ν 2964, 2924, 1366, 1170, 1100, 1062, 676 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{16}NO_2S$ $[M + H]^+$ m/z 250.0896, found 250.0902.

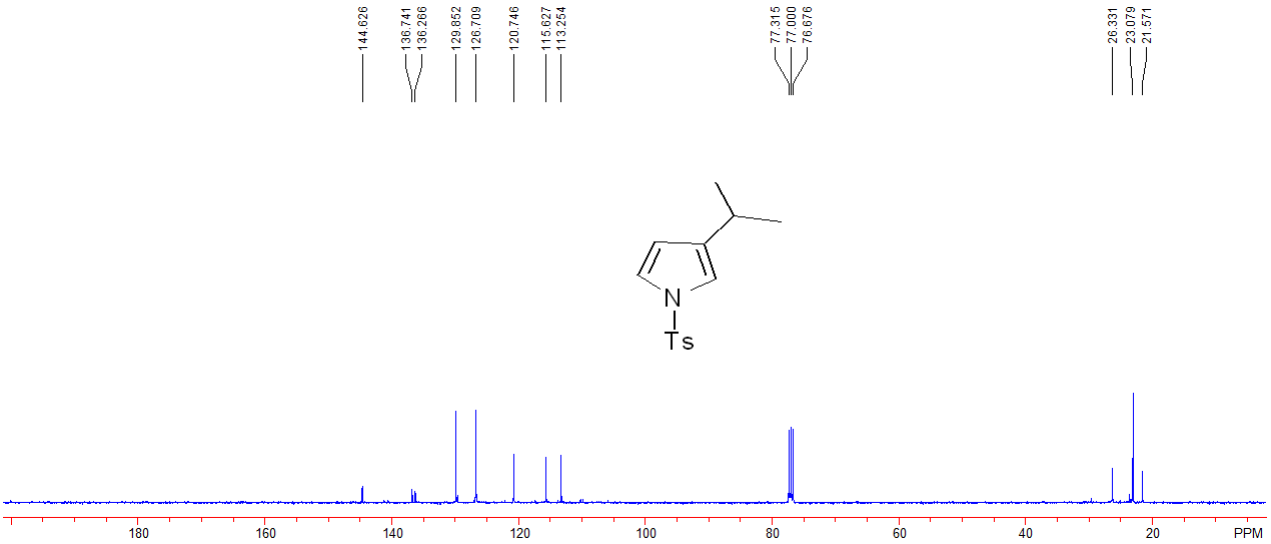


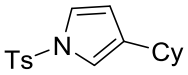




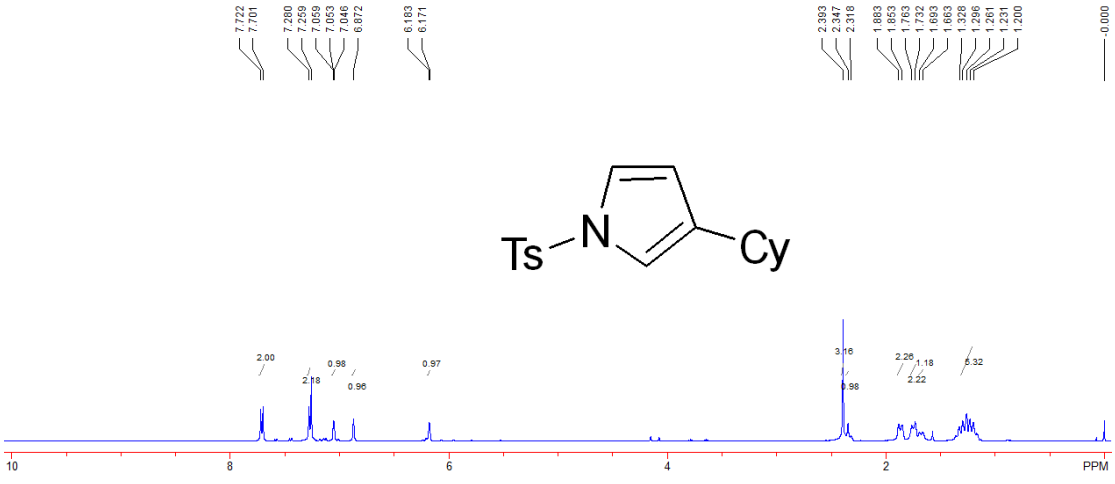
3-isopropyl-1-tosyl-1H-pyrrole (Table SI-2, entry 7c): known compound,[11] a colorless oil (35 mg, 64% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.72 (d, 2H, *J* = 8.0 Hz, ArH), 7.28 (d, 2H, *J* = 8.0 Hz, ArH), 7.07-7.06 (m, 1H, ArH), 6.88 (s, 1H, ArH), 6.19-6.18 (m, 1H, ArH), 2.75-2.68 (m, 1H, CH), 2.39 (s, 3H, CH_3), 1.14 (d, 6H, *J* = 6.8 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.6, 136.7, 136.3, 129.8, 126.7, 120.7, 115.6, 113.2, 26.3, 23.1, 21.6; IR (DCM) ν 2961, 1365, 1170, 1100, 1058, 778, 673 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{18}NO_2S$ $[M + H]^+$ m/z 264.1053, found 264.1059.

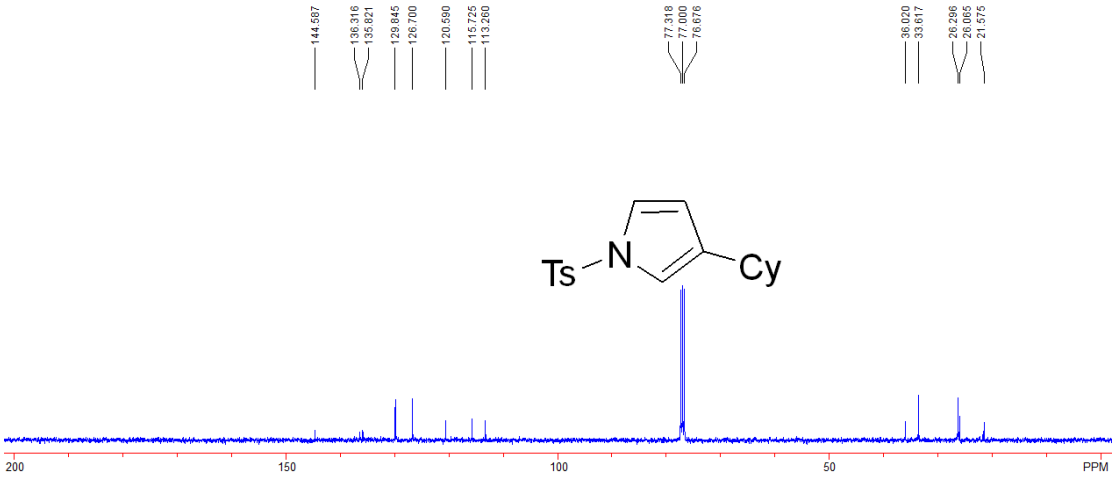


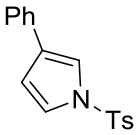




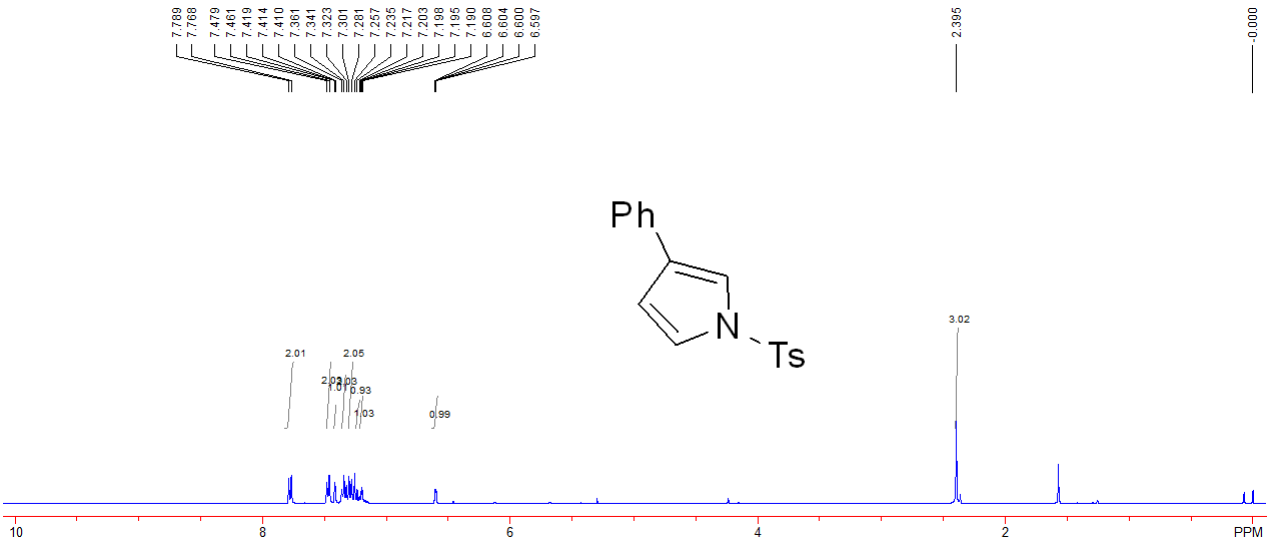
3-cyclohexyl-1-tosyl-1H-pyrrole (Table SI-2, entry 7d): a colorless oil (28 mg, 46% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.71 (d, 2H, *J* = 8.4 Hz, ArH), 7.27 (d, 2H, *J* = 8.4 Hz, ArH), 7.06-7.05 (m, 1H, ArH), 6.87 (s, 1H, ArH), 6.18 (d, 1H, *J* = 4.8 Hz, ArH), 2.39 (s, 3H, CH_3), 2.35-2.32 (m, 1H, CH), 1.88-1.85 (m, 2H, CH_2), 1.76-1.73 (m, 2H, CH_2), 1.69-1.66 (m, 1H, CH_2), 1.33-1.20 (m, 5H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 144.6, 136.3, 135.8, 129.8, 126.7, 120.6, 115.7, 113.3, 36.0, 33.6, 26.3, 26.1, 21.6; IR (DCM) ν 2923, 2851, 1367, 1170, 1101, 1059 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{22}NO_2S$ $[M + H]^+$ m/z 304.1366, found 304.1365.

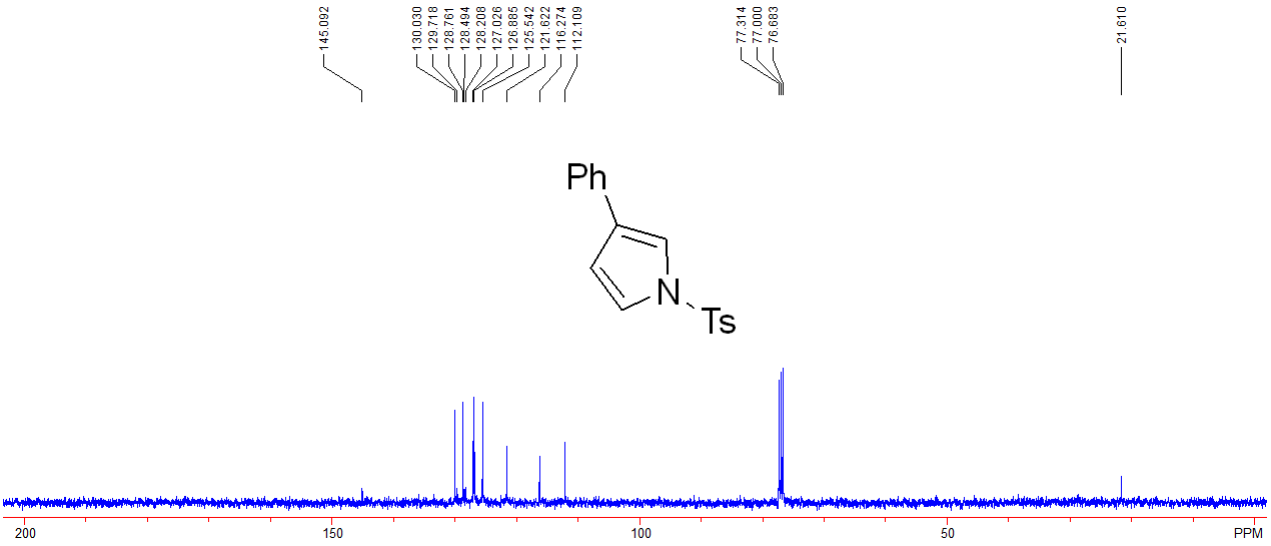




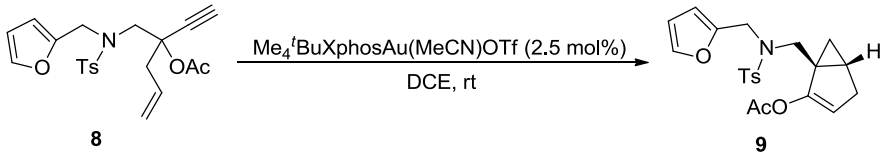


3-phenyl-1-tosyl-1H-pyrrole (Table 1, compound 3): known compound,[12] a white solid (18 mg, 31% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.78 (d, 2H, *J* = 8.4 Hz, ArH), 7.47 (d, 2H, *J* = 7.2 Hz, ArH), 7.41-7.41 (m, 1H, ArH), 7.36-7.32 (m, 2H, ArH), 7.29 (d, 2H, *J* = 8.4 Hz, ArH), 7.23-7.22 (m, 1H, ArH), 7.20-7.19 (m, 1H, ArH), 2.39 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 145.1, 130.0, 129.7, 128.8, 128.5, 128.2, 127.0, 126.9, 125.5, 121.6, 116.3, 112.1, 21.6.



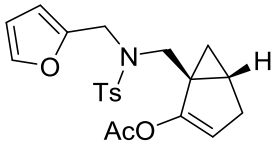


General Procedure for the Enyne Cyclization Reaction and the Spectroscopic Data of the Products.



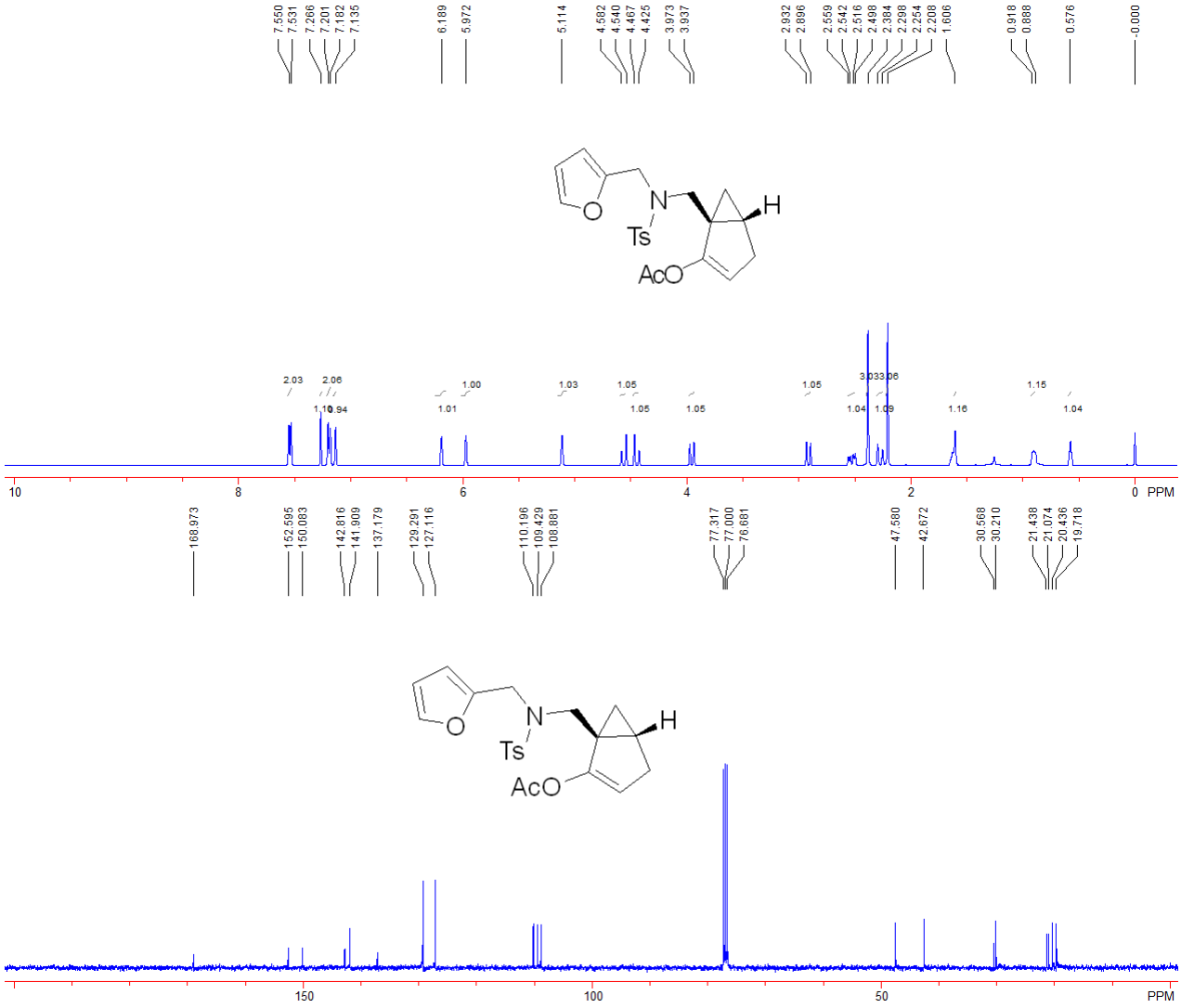
8 **9**

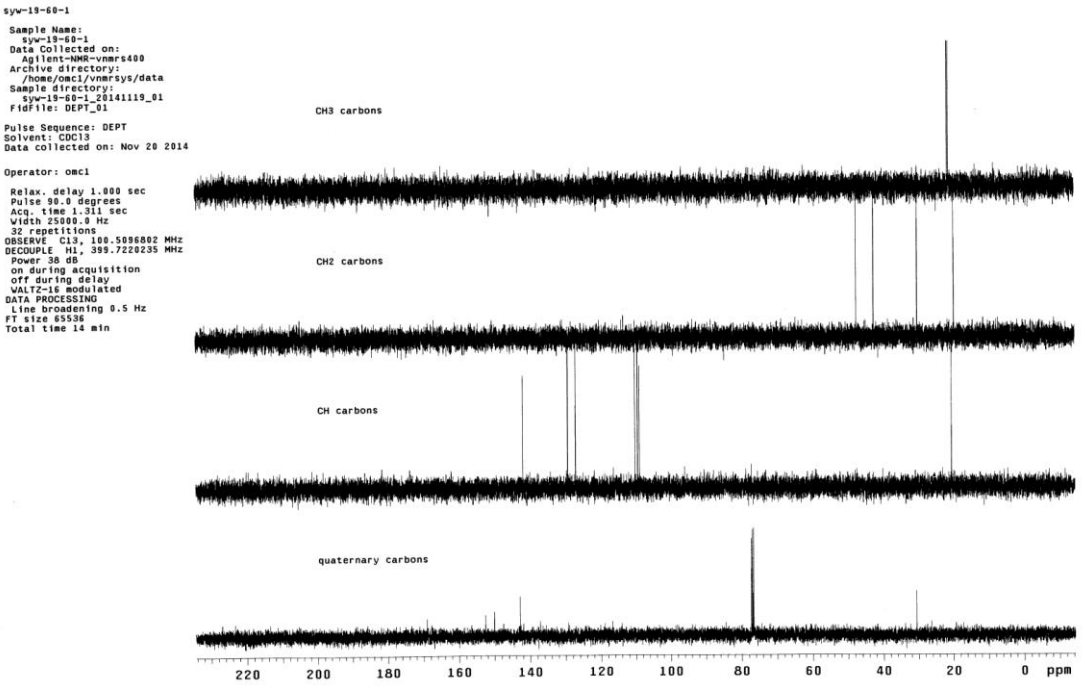
Into an oven-dried reaction flask under Ar gas protection were added substrates **8** (0.2 mmol) and DCE (1.5 mL), then a solution of Au-catalyst (0.005 mol/0.5 mL) was added. The reaction mixture was stirred at room temperature for several minutes, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.



1-(((N-(furan-2-ylmethyl)-4-methylphenyl)sulfonamido)methyl)bicyclo[3.1.0]hex-2-en-2-yl acetate (Scheme 5, compound 9): a colorless oil (41 mg, 50% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.54 (d, 2H, *J* = 7.6 Hz, ArH), 7.19 (d, 2H, *J* = 7.6 Hz, ArH), 7.13 (s, 1H, ArH), 6.19 (s, 1H, ArH), 5.97 (s, 1H, ArH), 5.11 (s, 1H, =CH), 4.56 (d, 1H, *J* = 16.8 Hz, CH_2), 4.45 (d, 1H, *J* = 16.8 Hz, CH_2), 3.95 (d, 1H, *J* = 14.4 Hz, CH_2), 2.91 (d, 1H, *J* = 14.4 Hz, CH_2), 2.53 (dd, 1H, J_1 = 17.6 Hz, J_2 = 3.2 Hz, CH_2), 2.38 (s, 3H, CH_3), 2.28 (d, 1H, *J* = 17.6 Hz, CH_2), 2.21 (s,

3H, CH_3), 1.63-1.60 (m, 1H, CH_2), 0.92-0.89 (m, 1H, CH), 0.58 (s, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 169.0, 152.6, 150.1, 142.8, 141.9, 137.2, 129.3, 127.1, 110.2, 109.4, 108.9, 47.6, 42.7, 30.6, 30.2, 21.4, 21.1, 20.4, 19.7; IR (DCM) ν 2921, 1752, 1347, 1333, 1205, 1157, 738, 656 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 419.1635, found 419.1640.

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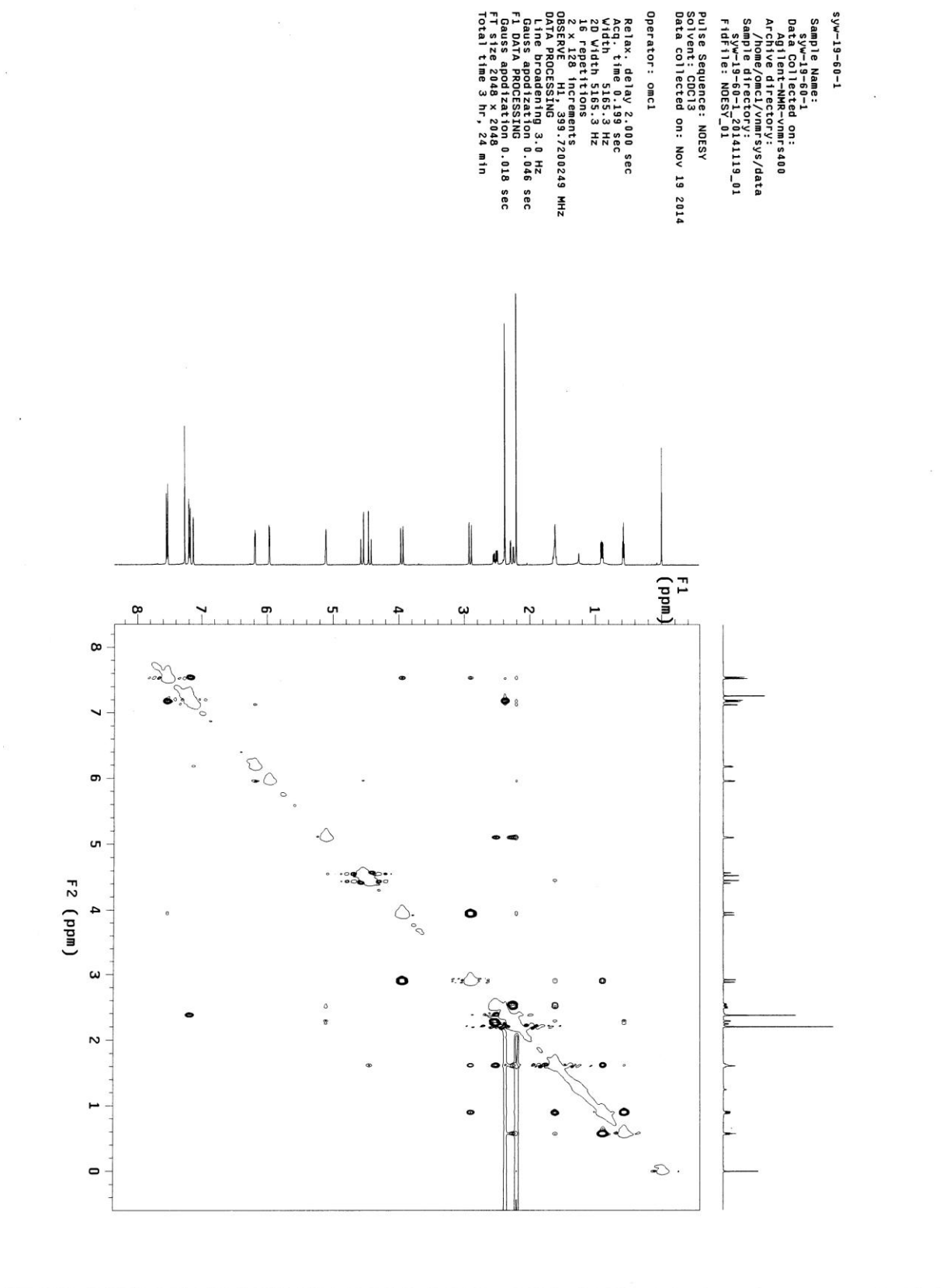
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/omc1/vnmrsys/data
Sample directory:
syw-19-60-1_20141119_01
FidFile: DEPT_01
Pulse Sequence: DEPT
Solvent: CDCl3
Data collected on: Nov 20 2014
Operator: omc1
Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.311 sec
Width 25000.0 Hz
32 repetitions
OBSERVE C13, 100.5096802 MHz
DECOUPLE H1, 399.7220235 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 14 min
CH3 carbons
CH2 carbons
CH carbons
quaternary carbons
220
200
180
160
140
120
100
80
60
40
20
0
ppm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Pulse Sequence: NOESY
Solvent: CDCl3
Data collected on: Nov 19 2014
Operator: omcl
Relax. delay 2.000 sec
Acq. time 0.199 sec
Width 5165.3 Hz
2D Width 5165.3 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 399.7200249 MHz
DATA PROCESSING
Line broadening 3.0 Hz
Gauss apodization 0.046 sec
F1 DATA PROCESSING
Gauss apodization 0.018 sec
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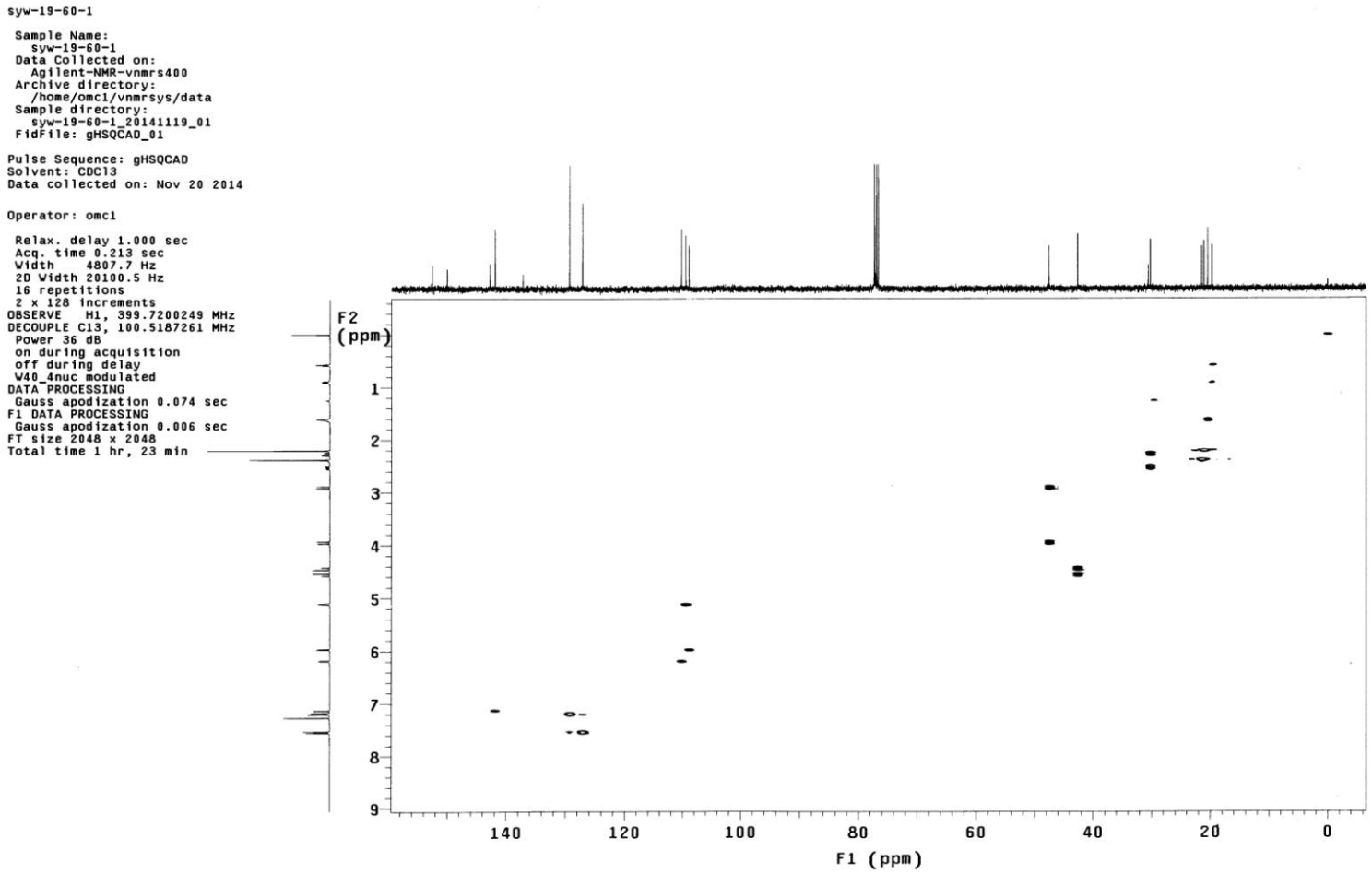
Total time 3 hr, 24 min
F1 (ppm)
F2 (ppm)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Archive directory:
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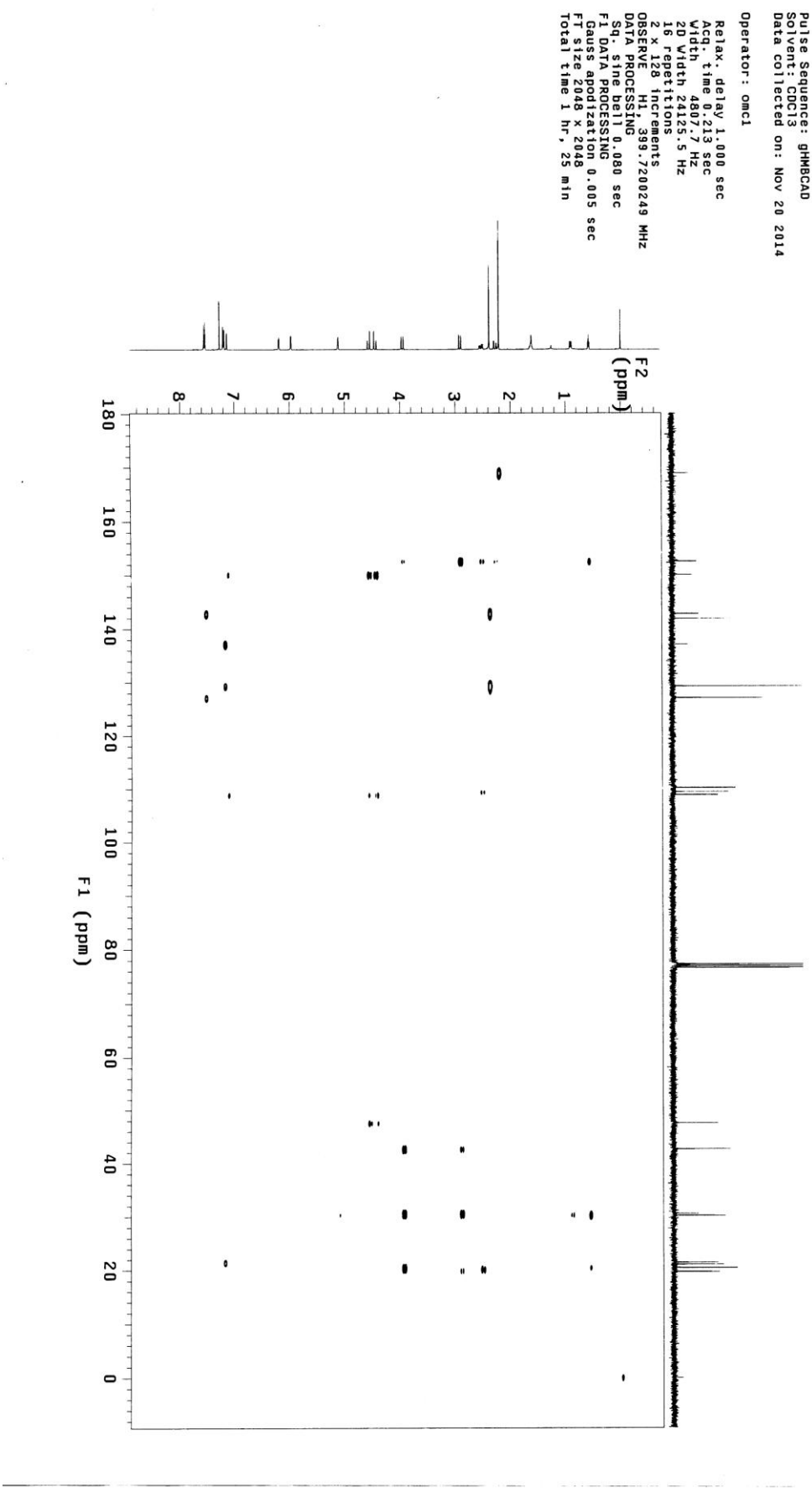
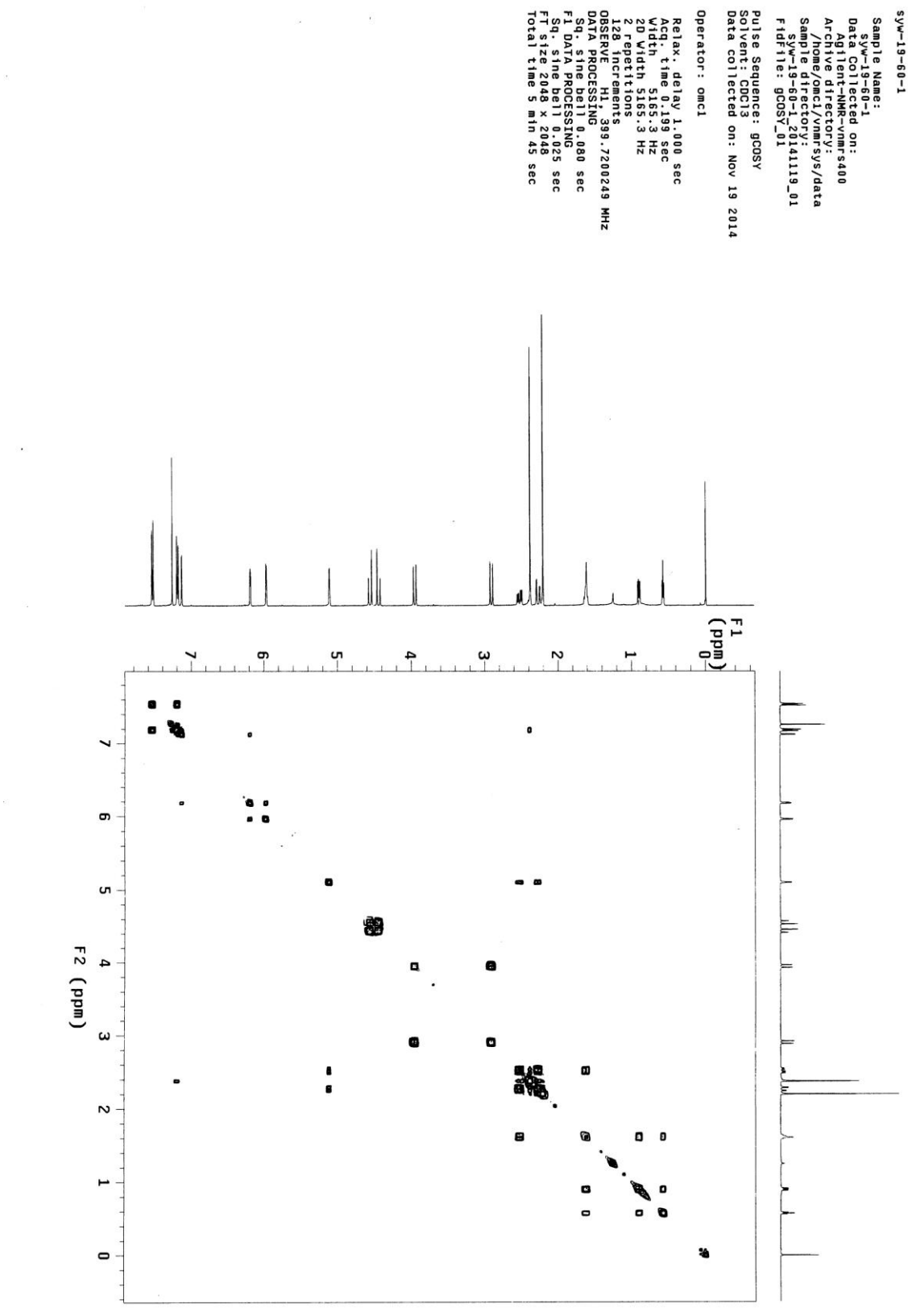
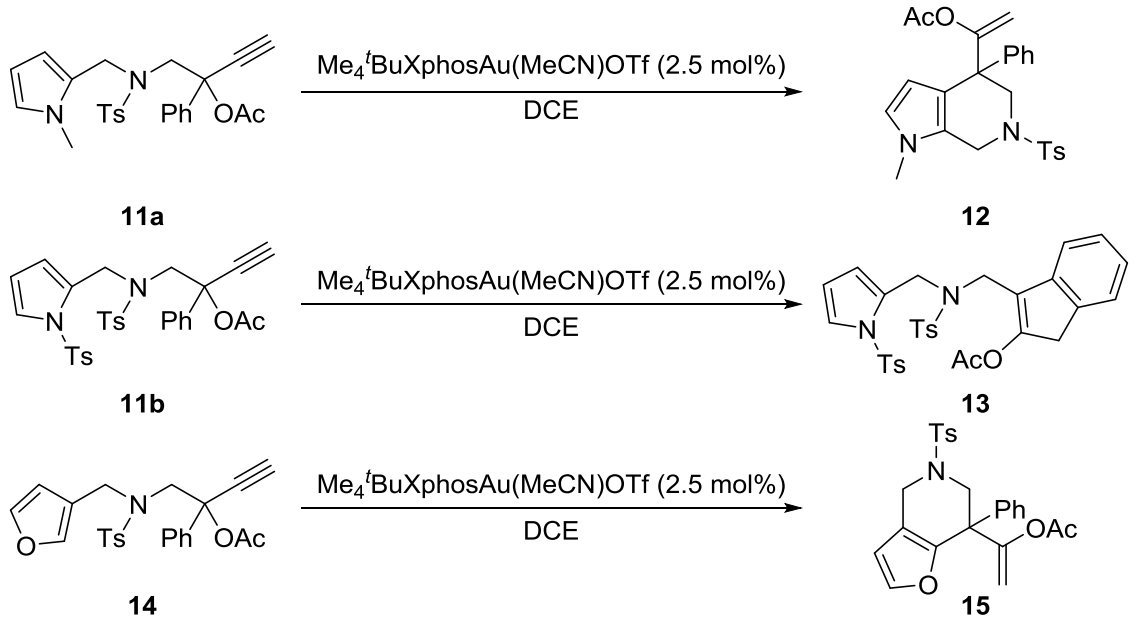
Sample directory:
syw-19-60-1_20141119_01
FidFile: gHSQCAD_01
Pulse Sequence: gHSQCAD
Solvent: CDCl3
Data collected on: Nov 20 2014
Operator: omc1
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 20100.5 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 399.7200249 MHz
DECOUPLE C13, 100.5187261 MHz
Power 36 dB
on during acquisition
off during delay
W40_4nuc modulated
DATA PROCESSING
Gauss apodization 0.074 sec
F1 DATA PROCESSING
Gauss apodization 0.006 sec
FT size 2048 x 2048
Total time 1 hr, 23 min
F2 (ppm)
F1 (ppm)

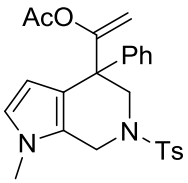

syw-19-60-1
Sample Name:
syw-19-60-1
Data Collected on:
Agilent-NMR-vnmrs400
Archive directory:
/home/omcl/vnmrsys/data
Sample directory:
syw-19-60-1_20141119_01
FidFile: gHMBCAD_01
Pulse Sequence: gHMBCAD
Solvent: CDCl3
Data collected on: Nov 20 2014
Operator: omcl
Relax. delay 1.000 sec
Acq. time 0.213 sec
Width 4807.7 Hz
2D Width 24125.5 Hz
16 repetitions
2 x 128 increments
OBSERVE H1, 399.7200249 MHz
DATA PROCESSING
Sq. sine bell 0.080 sec
F1 DATA PROCESSING
Gauss apodization 0.005 sec
FT size 2048 x 2048
Total time 1 hr, 25 min
F2 (ppm)
F1 (ppm)



General Procedure for the Friedel-Crafts Reaction and Spectroscopic Data of the Products.

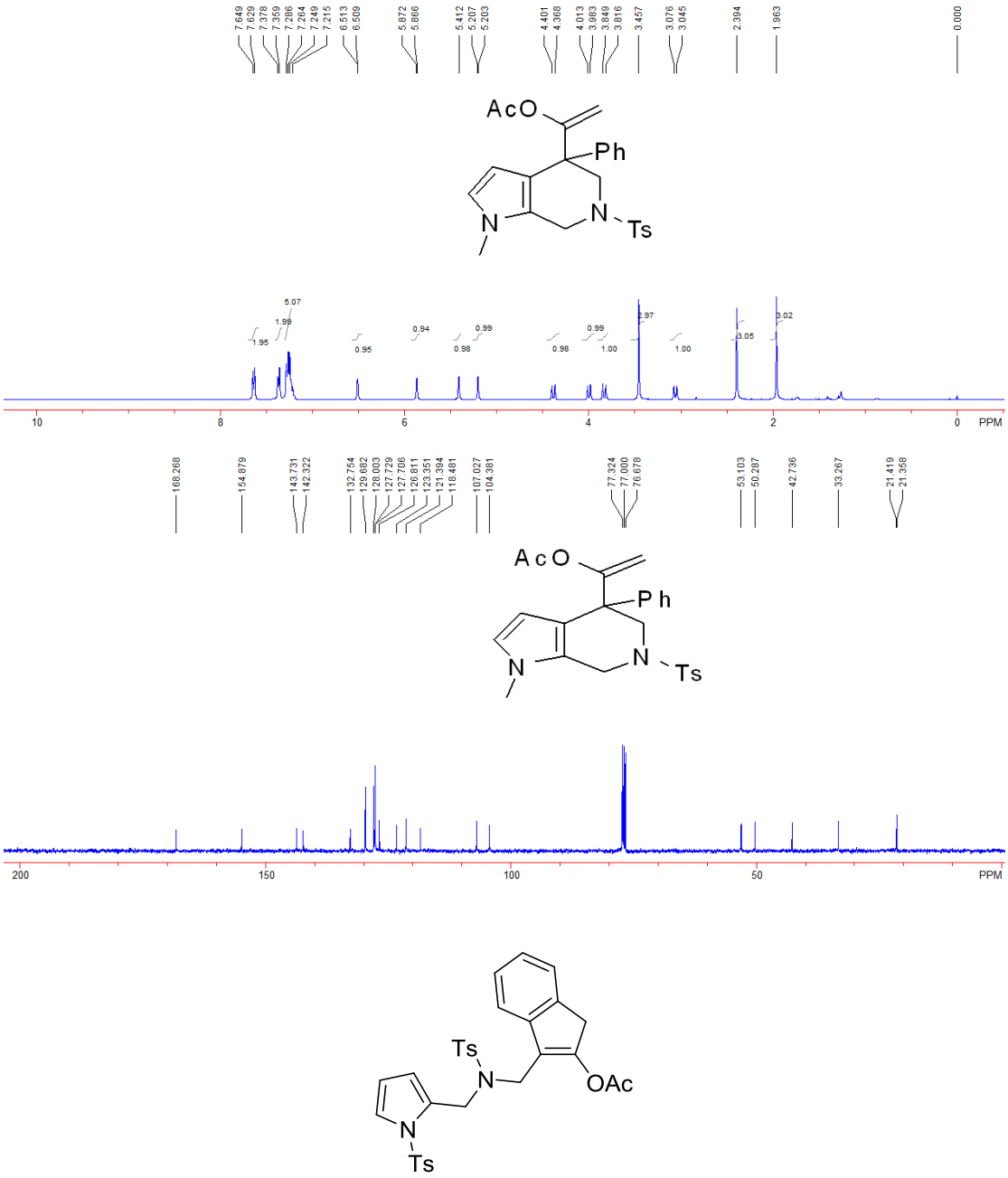


Into an oven-dried reaction flask under Ar protection were added substrates **11a**, **11b** or **14** (0.2 mmol) and DCE (1.5 mL), then a solution of Au-catalyst (0.005 mol/0.5 mL) was added. The reaction mixture was stirred at room temperature for several minutes, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.



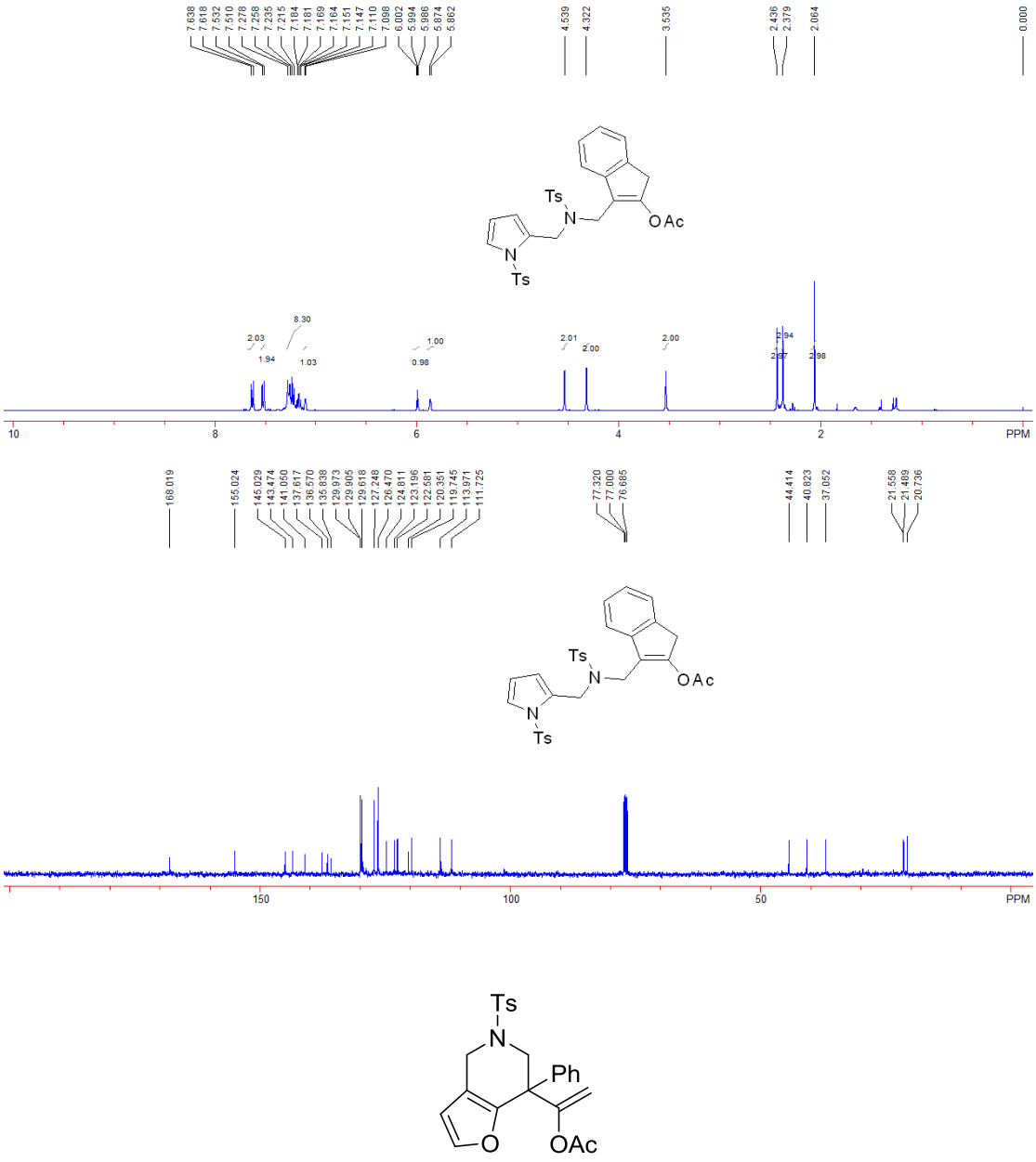
1-(1-methyl-4-phenyl-6-tosyl-4,5,6,7-tetrahydro-1H-pyrrolo[2,3-c]pyridin-4-yl)vinyl acetate (compound 12): a white solid (88 mg, 97% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.64 (d, 2H, *J* = 8.0 Hz, ArH), 7.37 (d, 2H, *J* = 7.6 Hz, ArH), 7.29-7.21 (m, 5H, ArH), 6.51 (d, 1H, *J* = 1.6 Hz, ArH), 5.87 (d, 1H, *J* = 2.4 Hz, ArH), 5.41 (s, 1H, ArH), 5.20 (d, 1H, *J* = 1.6 Hz, ArH), 4.38 (d, 1H, *J* = 13.2 Hz, CH_2), 4.00 (d, 1H, *J* = 12.0 Hz, CH_2), 3.83 (d, 1H, *J* = 13.2 Hz, CH_2), 3.46 (s, 3H, CH_3), 3.06 (d, 1H, *J* = 12.0 Hz, CH_2), 2.39 (s, 3H, CH_3), 1.96 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.3, 154.9, 143.7, 142.3, 132.7, 129.7, 128.0, 127.73, 127.71, 126.8, 123.3, 121.4, 118.5, 107.0, 104.4, 53.1, 50.3, 42.7, 33.3, 21.4, 21.3; IR (DCM) ν 2923, 1759, 1346, 1180, 1163, 969, 700 cm^{-1}; HRMS (ESI) calcd for $C_{25}H_{30}N_3O_4S$ $[M + NH_4]^+$ m/z 468.1952, found

468.1950.

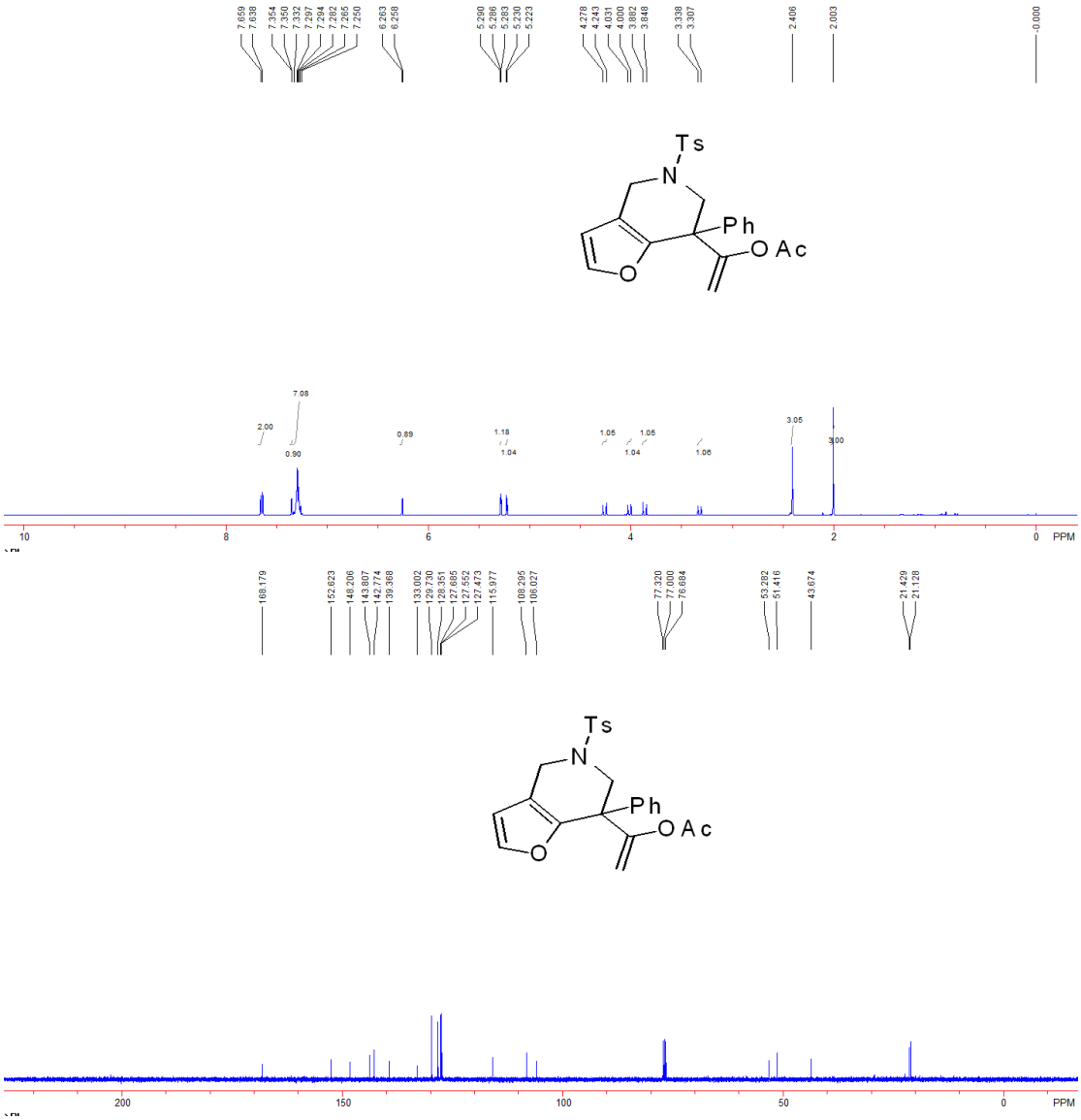


3-(((4-methyl-N-((1-tosyl-1H-pyrrol-2-yl)methyl)phenyl)sulfonamido)methyl)-1H-inden-2-yl acetate (compound 13): a white solid (77 mg, 65% yield). ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.63 (d, 2H, *J* = 8.0 Hz, ArH), 7.52 (d, 2H, *J* = 8.4 Hz, ArH), 7.28-7.15 (m, 8H, ArH), 7.11-7.10 (m, 1H, ArH), 5.99 (t, 1H, *J* = 3.2 Hz, ArH), 5.87-5.86 (m, 1H, ArH), 4.54 (s, 2H, CH_2), 4.32 (s, 2H, CH_2), 3.53 (s, 2H, CH_2), 2.44 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.06 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.0, 155.0, 145.0, 143.5, 141.0, 137.6, 136.6, 129.97, 129.90, 129.6, 127.2, 126.5, 124.8, 123.2, 122.6, 120.3, 119.7, 114.0, 111.7, 44.4, 40.8, 37.0, 21.56, 21.49, 20.7; IR (DCM) ν 2919, 1765, 1367, 1190, 1173, 1156, 669 cm^{-1}; HRMS (ESI) calcd for

$C_{31}H_{34}N_3O_6S_2$ $[M + NH_4]^+$ m/z 608.1884, found 608.1884.



1-(7-phenyl-5-tosyl-4,5,6,7-tetrahydrofuro[3,2-c]pyridin-7-yl)vinyl acetate (compound 15): a white solid (76 mg, 85% yield), mp: 142-144 ^oC. ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 7.65 (d, 2H, *J* = 8.4 Hz, ArH), 7.35-7.33 (m, 1H, ArH), 7.30-7.25 (m, 7H, ArH), 6.26 (d, 1H, *J* = 2.0 Hz, ArH), 5.29-5.28 (m, 1H, =CH), 5.23 (d, 1H, *J* = 2.8 Hz, =CH), 4.26 (d, 1H, *J* = 14.0 Hz, CH_2), 4.01 (d, 1H, *J* = 12.4 Hz, CH_2), 3.86 (d, 1H, *J* = 14.0 Hz, CH_2), 3.32 (d, 1H, *J* = 12.4 Hz, CH_2), 2.41 (s, 3H, CH_3), 2.00 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 168.2, 152.6, 148.2, 143.8, 142.8, 139.4, 133.0, 129.7, 128.3, 127.7, 127.55, 127.47, 116.0, 108.3, 106.0, 53.3, 51.4, 43.7, 21.4, 21.1; IR (DCM) ν 2923, 1764, 1335, 1191, 1155, 1018, 754 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}N_2O_5S$ $[M + NH_4]^+$ m/z 455.1635, found 455.1639.


7.659
7.638
7.354
7.350
7.332
7.297
7.294
7.282
7.265
7.250
6.263
6.258
5.290
5.286
5.283
5.230
5.223
4.278
4.243
4.031
4.000
3.882
3.848
3.338
3.307
2.406
2.003
0.000
Ts
N
Ph
O Ac
O
7.08
2.00
0.90
0.89
1.18
1.04
1.05
1.04
1.05
1.06
3.05
3.00
10
8
6
4
2
0
PPM

168.179
152.623
148.206
143.807
142.774
139.368
133.002
129.730
128.351
127.685
127.552
127.473
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108.295
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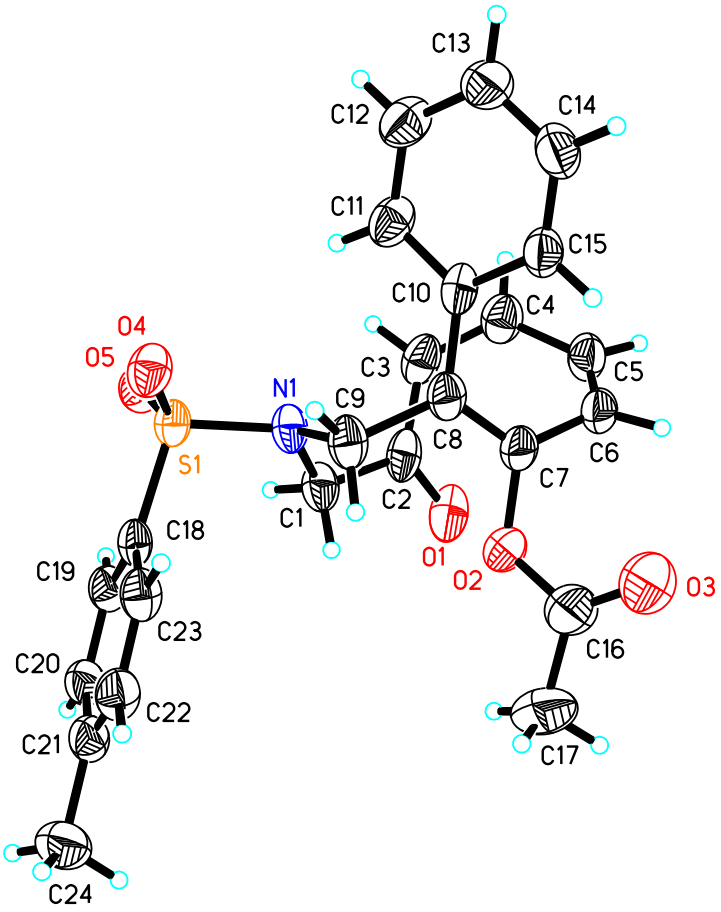
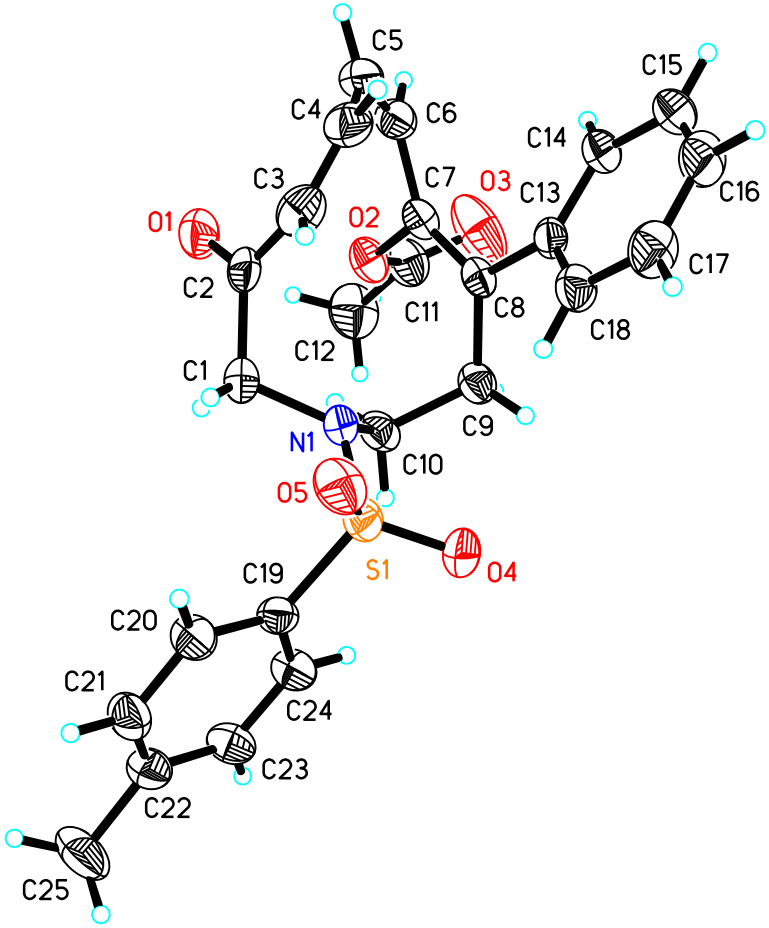
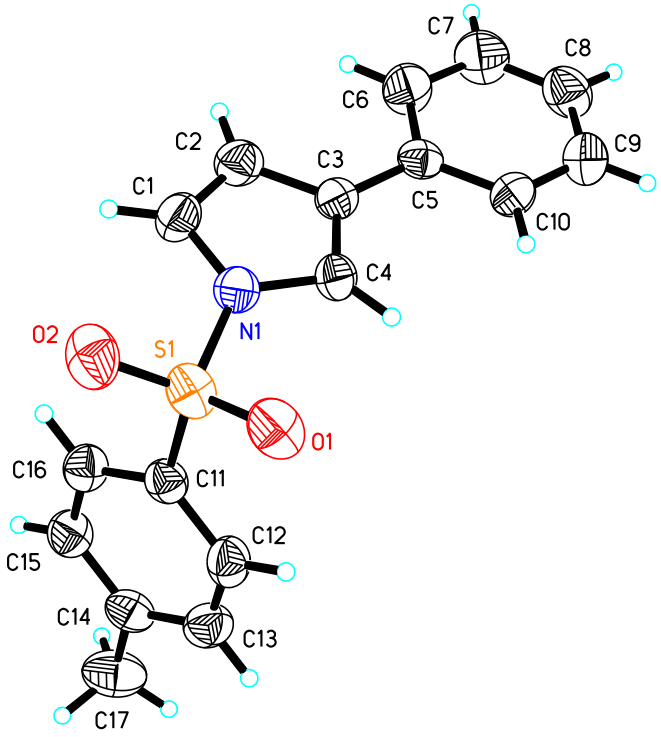


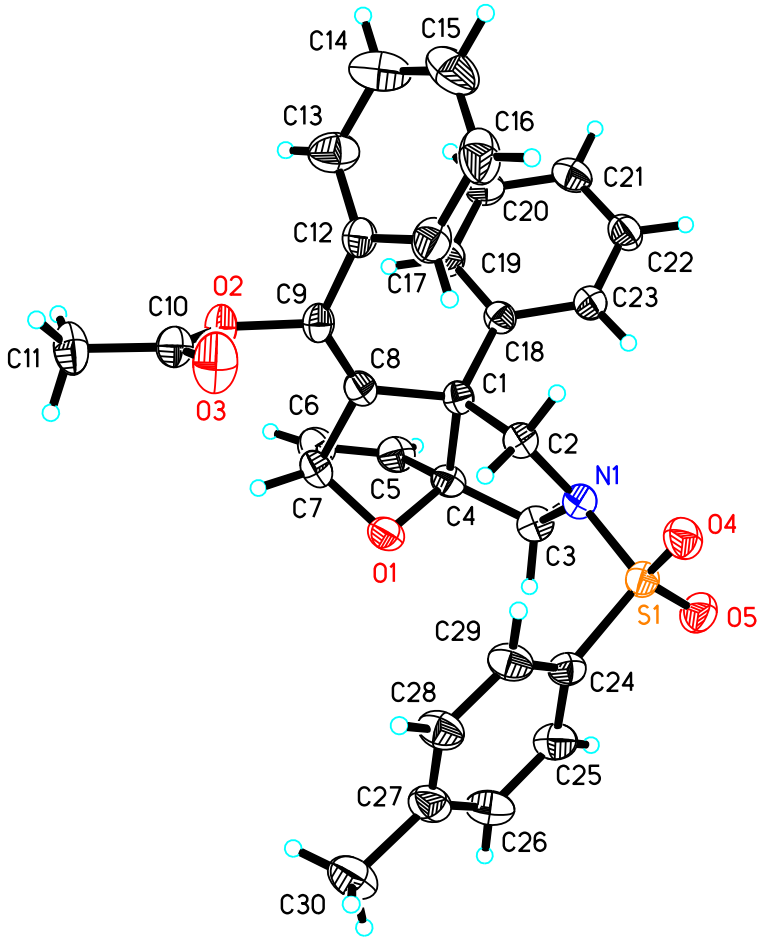
The crystal data of **2a** have been deposited in CCDC with number 973301. Empirical Formula: $C_{24}H_{23}NO_5S$; Formula Weight: 437.49; Crystal Color, Habit: colorless, Crystal Dimensions: 0.211 x 0.165 x 0.112 mm; Crystal System: Triclinic; Lattice Parameters: a = 11.0389(9)Å, b = 13.5784(11)Å, c = 24.5769(19)Å, α = 87.240(2)°, β = 84.094(2)°, γ = 69.682(2)°, V = 3436.0(5)Å^3; Space group: P-1; Z = 6; D_{calc}= 1.269 g/cm^3; F_{000} = 1380; Final R indices [I>2sigma(I)] R1 = 0.0622, wR2 = 0.1475.



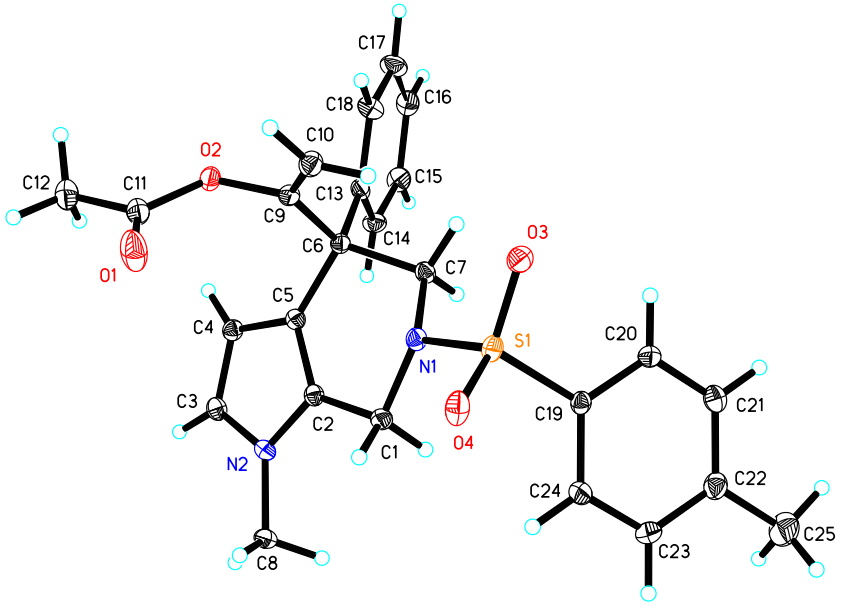
The crystal data of **2s** have been deposited in CCDC with number 996019. Empirical Formula: $C_{25}H_{25}NO_5S$; Formula Weight: 451.52; Crystal Color, Habit: colorless, Crystal Dimensions: 0.211 x 0.156 x 0.121 mm; Crystal System: Monoclinic; Lattice Parameters: a = 8.4273(17)Å, b = 18.696(5)Å, c = 14.628(3)Å, α = 90°, β = 96.208(5)°, γ = 90°, V = 2291.2(9)Å^3; Space group: Cc; Z = 4; D_{calc}= 1.309 g/cm^3; F_{000} = 952; Final R indices [I>2sigma(I)] R1 = 0.0527, wR2 = 0.1089.



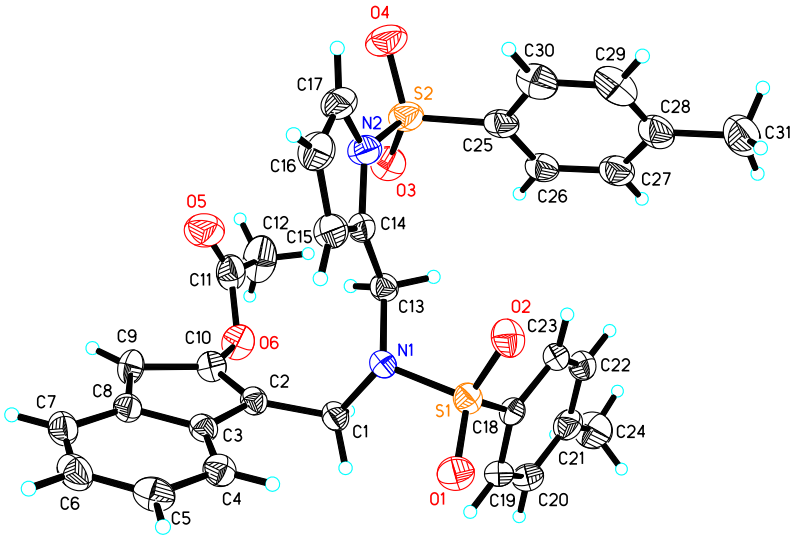
The crystal data of **3** have been deposited in CCDC with number 966978. Empirical Formula: C17H15NO2S; Formula weight: 297.36; Temperature: 293(2) K; Crystal system, space group: Orthorhombic, P2(1)2(1)2(1); Unit cell dimensions: a = 6.2454(10)Å, alpha = 90 deg. b = 7.9709(13)Å, beta = 90 deg. c = 30.185(5)Å, gamma = 90 deg. Volume 1502.7(4)A3; Z, Calculated density: 4, 1.314 Mg/m3; F(000): 624; Crystal size: 0.175 x 0.112 x 0.078 mm; Final R indices [I>2sigma(I)], R1 = 0.0513, wR2 = 0.1068.



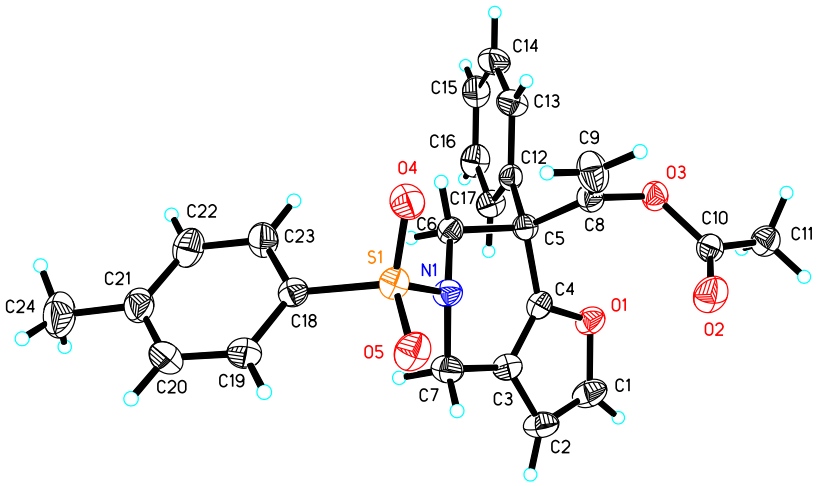
The crystal data of **5** have been deposited in CCDC with number 972417. Empirical Formula: $C_{60}H_{55}N_2O_{10.5}S_2$; Formula Weight: 1036.18; Crystal Color, Habit: colorless, Crystal Dimensions: 0.212 x 0.175 x 0.123 mm; Crystal System: Monoclinic; Lattice Parameters: a = 41.536(6)Å, b = 9.8916(15)Å, c = 25.763(4)Å, α = 90.00°, β = 93.590(3)°, γ = 90°, V = 10564(3)Å^3; Space group: C2/c; Z = 8; D_{calc}= 1.303 g/cm^3; F_{000} = 4360; Final R indices [I>2sigma(I)] R1 = 0.0643, wR2 = 0.1543.



The crystal data of **12** have been deposited in CCDC with number 1401380. Empirical Formula: $C_{25}H_{26}N_2O_4S$; Formula Weight: 450.54; Crystal Color, Habit: colorless, Crystal Dimensions: 0.25 x 0.2 x 0.15 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 12.5847(12)Å, b = 17.5982(16)Å, c = 20.1268(18)Å, $\alpha = 90^o$, $\beta = 92.772(2)^o$, $\gamma = 90^o$, V = 4452.2(7)$Å^3$; Space group: P bca; Z = 8; D_{calc}= 1.344 g/cm^3; F_{000} = 1904; Final R indices [I>2sigma(I)] R1 = 0.0565, wR2 = 0.1210.



The crystal data of **13** have been deposited in CCDC with number 1406576. Empirical Formula: $C_{62}H_{58}N_4O_{12}S_4$; Formula Weight: 1179.36; Crystal Color, Habit: colorless, Crystal Dimensions: 0.2 x 0.15 x 0.12 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 18.1593(16)Å, b = 10.1358(9)Å, c = 15.6691(13)Å, $\alpha = 90^o$, $\beta = 91.647(2)^o$, $\gamma = 90^o$, V = 2882.8(4)$Å^3$; Space group: P 1 21/c 1; Z = 2; D_{calc}= 1.359 g/cm^3; F_{000} = 1236; Final R indices [I>2sigma(I)] R1 = 0.0529, wR2 = 0.1261.



The crystal data of **15** have been deposited in CCDC with number 997457. Empirical Formula: $C_{24}H_{23}NO_5S$; Formula Weight: 437.49; Crystal Color, Habit: colorless, Crystal Dimensions: 0.211 x 0.175 x 0.123 mm; Crystal System: Orthorhombic; Lattice Parameters: a = 12.5654(9)Å, b = 18.5476(13)Å, c = 18.7414(13)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 4367.8(5)Å^3; Space group: P bca; Z = 8; D_{calc}= 1.331 g/cm^3; F_{000} = 1840; Final R indices [I>2sigma(I)] R1 = 0.0489, wR2 = 0.1210.

References

[1] Hopman, J. C. P.; Berg, E. V. D.; Ollero, L. O.; Hiemstra, H.; Speckamp, W. N. *Tetrahedron Lett.* **1995**, *36*, 4315-4318.

[2] Shu, X.-Z.; Li, X.; Shu, D.; Huang, S.; Schienebeck, C. M.; Zhou, X.; Robichaux, P. J.; Tang, W. *J. Am. Chem. Soc.* **2012**, *134*, 5211-5221.

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[4] Zou, G.-F.; Pan, F.; Liao, W.-W. *Org. Biomol. Chem.* **2013**, *11*, 7080-7083.

[5] Greszler, S. T.; Johnson, J. S. *Angew. Chem. Int. Ed.* **2009**, *48*, 3689-3691.

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