Electrochemical NaI/NaCl-mediated one-pot synthesis of 2-aminobenzoxazoles and 2-aminobenzothiazoles in aqueous media via tandem addition-cyclization

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Electronic Supplementary Information

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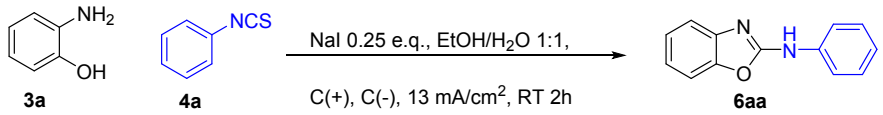
Table S1. Additional optimization experiments



3a 4a 6aa

Entry	Deviation from initial condition	Yield(%)[b]
1	0.25 eq. NH_4I instead of 0.25 eq. NaI	95
2	0.25 eq. KI instead of 0.25 eq. NaI	90
3	0.25 eq. TBAI instead of 0.25 eq. NaI	81
4	Acetonitrile:water 1:1 instead of EtOH:water 1:1	90
5	4 mA/cm^2 instead of 13 mA/cm^2	62
6	0.25 eq. NH_4I and 4 mA/cm^2 instead of 0.25 eq. NaI and 13 mA/cm^2	48

Reaction conditions: graphite rod (ϕ 5 mm, 5 mm immersion depth, immersed surface area of 2.3 cm^2) as both cathode and anode, current density = 13 mA/cm^2, **3a** (0.6 mmol), **4a** (0.5 mmol), NaI (0.05 mmol), NaCl (0.075 mmol) EtOH 1 mL, water 1 mL, room temperature, 2 hrs., undivided cell.

Faradaic efficiency calculation:

$$Faradaic\ efficiency = \frac{Q_{experimental}}{Q_{theoretical}} \times 100$$

$$Faradaic\ efficiency = \frac{z\ \times n\ \times F}{Q_{theoretical}} \times 100$$

With z = number of electron that the reaction used = 2

n = mol of product that obtained = 0.5 x 95% = 0.475 mmol

F = Faradaic constant (96485 C/mol)

$Q_{theoretical}$ can be calculated from I (current, Ampere) x t (reaction time, second)

$$Faradaic\ efficiency = \frac{2\ \times\ 0.475 \times 10^{-3} \times 96485}{0.03\ \times 7200} \times 100$$

$$Faradaic\ efficiency = \ 42\ \%$$

Experimental Section

Materials and methods

All chemicals and solvents were obtained from commercially available suppliers such as Sigma-Aldrich and TCI (Japan) and were used without further purification, unless otherwise stated. Pyrex reactor (ϕ = 2.0 cm, Height = 6.2 cm) was used for electrochemical reaction. Power supply (KORAD, KA3005D) was purchased from Shenzhen Korad Technology CO., LTD. All electrodes such as graphite rod (ϕ = 5 mm) and platinum plate (5x5x0.1 mm) were purchased from Minihua Store, China. Electrochemical reaction setup was depicted in Figure S1 and S2. Analytical thin layer chromatography (TLC) was performed with precoated Merck silica gel 60 F254 plates (0.25 mm for thick layer) and visualized at 254 nm using an ultraviolet lamp. Column chromatography was performed with Silicycle silica gel 60-200 μm (70-230 mesh). ^{1}H-NMR, ^{13}C-NMR spectra were obtained with JEOL JNM-ECZ500R/S1 NMR spectrometers operating at 500 MHz for ^{1}H or 125 MHz for ^{13}C nuclei. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) with a MicroTOF Bruker mass spectrometer. Fourier transform infrared spectra were acquired on Nicolet 6700 FTIR spectrometer equipped with a mercury-cadmium telluride (MCT) detector (Nicolet, USA).

General procedure for synthesis of 2-aminobenzoxazoles (General Procedure A)

A mixture of 2-aminophenol (1.2 equiv., 0.600 mmol), isothiocyanate (1.0 equiv., 0.500 mmol), sodium iodide (0.1 equiv., 0.050 mmol) and sodium chloride (0.15 equiv., 0.075 mmol) was dissolved in mixed 1 mL of water with 1 mL of ethanol in a tube. The reaction mixture was electrolysed at a constant current of 30 mA (13 mA/cm^2, graphite rods as both cathode and anode) at room temperature for 2 hours. The reaction was extracted with water and ethyl acetate. The organic layer was evaporated under reduced pressure to give the

crude product, which was further purified by column chromatography (eluted with ethyl acetate/hexane) to afford the desired compound.

General procedure for synthesis of 2-aminobenzothiazoles (General Procedure B)

A mixture of 2-aminobenzenethiol (1.2 equiv., 0.600 mmol), isothiocyanate (1.0 equiv., 0.500 mmol), sodium iodide (0.1 equiv., 0.050 mmol) and sodium chloride (0.15 equiv., 0.075 mmol) was dissolved in mixed 1 mL of water with 1 mL of ethanol in a tube. The reaction mixture was electrolysed at a constant current of 30 mA (13 mA/cm^2, graphite rods as both cathode and anode) at room temperature for 2 hours. The reaction was extracted with water and ethyl acetate. The organic layer was evaporated under reduced pressure to give the crude product, which was further purified by column chromatography (eluted with ethyl acetate/hexane) to afford the desired compound.

***N*-phenylbenzo[d]oxazol-2-amine** (**6aa**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6aa** (99.8 mg, 0.475 mmol, 95%) as a white solid: ^{1}H NMR (500 MHz, DMSO) δ ppm 10.62 (s, 1H), 7.78 (d, J = 7.7 Hz, 2H), 7.47 (dd, J = 7.2, 5.7 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.22 (td, J = 7.6, 1 Hz, 1H), 7.12 (td, J = 7.8, 1 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.0, 147.1, 142.5, 138.8, 129.2, 124.0, 122.2, 121.7, 117.6, 116.7, 109.0. IR (ATR, cm^{-1}): 3385, 3167, 3039, 2920, 2853, 1635, 1571, 1455, 1240, 736. ESI-MS: m/z: 211.1167 $[M+H]^+$ (calcd for $[C_{13}H_{11}N_2O]^+$ 211.0871).[1]

For gram-scale synthesis: A mixture of 2-aminophenol (1.2 equiv., 9.60 mmol), isothiocyanate (1.0 equiv., 8.00 mmol), sodium iodide (0.1 equiv., 0.80 mmol), and sodium

chloride (0.15 equiv., 1.20 mmol) was dissolved in mixed 16 mL of water with 16 mL of ethanol in a 50 mL three-necked round bottom flask. The reaction mixture was elecrtolysed at a constant current of 30 mA (13 mA/cm^2, graphite rods as both cathode and anode) at room temperature for 24 hours. The reaction was extracted with water and ethyl acetate. The organic layer was evaporated under reduced pressure to give the crude product, which was further washed carefully with ethanol and filtered to afford the desired compound (1.179 g, 5.614 mmol, 70%). The ^{1}H and ^{13}C NMR data are identical to above procedure and were shown in figures S64-S65.

6-methyl-*N*-phenylbenzo[d]oxazol-2-amine (**6ba**) Synthesized according to the General procedure A using 2-amino-5-methylphenol (73.8mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ba** (103.3 mg, 0.461 mmol, 92%) as a white solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.55 (s, 1H), 7.81 (d, J = 7.7 Hz, 2H), 7.37 (t, J = 8 Hz, 2H), 7.33 (d, J = 7.9 Hz, 1H), 7.27 (s, 1H), 7.02 (t, J = 7.3 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ ppm 157.7, 147.3, 140.2, 138.9, 131.2, 129.0, 124.7, 122.0, 117.5, 116.1, 109.3, 21.1. IR (ATR, cm^{-1}): 3160, 3038, 2920, 2853, 1666, 1597, 1577, 1487, 1431, 1372, 1274, 751. ESI-MS: m/z: 225.1014 $[M+H]^+$ (calcd for $[C_{14}H_{13}N_2O]^+$ 225.1028).[1]

5-(tert-butyl)-*N*-phenylbenzo[d]oxazol-2-amine (**6ca**) Synthesized according to the General procedure A using 2-amino-4-tert-butylphenol (99.1 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ca** (129 mg, 0.485 mmol, 97%) as a white solid: : ^{1}H NMR (500 MHz, DMSO): δ ppm 10.56 (s, 1H), 7.8 (d, J = 8 Hz, 2H), 7.48 (d, J = 1.9 Hz, 1H), 7.36 (m, 3H), 7.12 (dd, J = 8.4, 1.9 Hz, 1H),

7.02 (t, J = 7.4 Hz, 1H), 1.3 (s, 9H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.2, 146.9, 145.0, 142.4, 139.0, 129.0, 122.0, 118.6, 117.5, 113.6, 108.0, 34.5, 31.6. IR (ATR, cm^{-1}):3042, 2950, 1672, 1603, 1581, 1495, 1425, 1371, 1264, 1226, 977, 736. ESI-MS: m/z: 267.1492 $[M+H]^+$ (calcd for $[C_{17}H_{19}N_2O]^+$ 267.1497).[2]

5-bromo-*N*-phenylbenzo[d]oxazol-2-amine (**6da**) Synthesized according to the General procedure A using 2-amino-4-bromophenol (112.8 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h.) to afford **6da** (121.3 mg, 0.420 mmol, 84%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.78 (s, 1H), 7.76 (d, J = 8 Hz, 2H), 7.62 (d, J = 2 Hz, 1H), 7.41 (d, J = 8.5 Hz, 1H), 7.37 (t, J = 7.9 Hz, 2H), 7.24 (dd, J = 8.3, 2.0 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 159.0, 146.3, 144.6, 138.4, 129.0, 124.1, 122.5, 119.2, 117.9, 116.0, 110.6. IR (ATR, cm^{-1}): 3036, 2853, 1674, 1591, 1570, 1495, 1457, 1441, 1420, 1366, 1247, 1228, 971, 795, 733. ESI-MS: m/z: 288.9963 $[M+H]^+$ (calcd for $[C_{13}H_{10}N_2OBr]^+$ 288.9977).[1]

5-chloro-*N*-phenylbenzo[d]oxazol-2-amine (**6ea**) Synthesized according to the General procedure A using 2-amino-4-chlorophenol (86.1 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h.) to afford **6ea** (111.8 mg, 0.457 mmol, 91%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.78 (s, 1H), 7.76 (d, J = 7.7 Hz, 2H), 7.49 (d, J = 2.2 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.37 (dt, J = 8.3, 7.9 Hz, 2H), 7.11 (dd, J = 8.5, 2.2 Hz, 1H), 7.04 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 159.2, 145.9, 144.1, 138.4, 129.0, 128.2, 122.5,

121.3, 117.9, 116.3, 110.0. IR (ATR, cm^{-1}): 3034, 2921, 1675, 1598, 1574, 1489, 1466, 1447, 1425, 1367, 1233, 974, 788, 747, 690. ESI-MS: m/z: 245.0470 $[M+H]^+$ (calcd for $[C_{13}H_{10}N_2OCl]^+$ 245.0482).[3]

5-methoxy-*N*-phenylbenzo[d]oxazol-2-amine (**6fa**) Synthesized according to the General procedure A using 2-amino-4-methoxyphenol (83.0 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6fa** (98.0 mg, 0.408 mmol, 82%) as a light pink solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.59 (s, 1H), 7.77 (dd, J = 8.5, 0.8 Hz, 2H), 7.36 (m, 3H), 7.07 (d, J = 2.5 Hz, 1H), 7.02 (t, J = 7.4 Hz, 1H), 6.67 (dd, J = 8.8, 2.6 Hz, 1H), 3.76 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.8, 156.7, 143.5, 141.5, 138.8, 129.0, 122.1, 117.6, 108.9, 108.0, 101.9, 55.6. IR (ATR, cm^{-1}): 3047, 2924, 1656, 1600, 1572, 1499, 1458, 1446, 1249, 1246, 736. ESI-MS: m/z: 241.1071 $[M+H]^+$ (calcd for $[C_{14}H_{13}N_2O_2]$+ 241.1077).[1]

5-nitro-*N*-phenylbenzo[d]oxazol-2-amine (**6ga**) Synthesized according to the General procedure A using 2-amino-4-nitrophenol (92.5 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h.) to afford **6ga** (53.4 mg, 0.209 mmol, 42%) as a yellow solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 11.01 (s, 1H), 8.21 (dd, J = 2.2, 1.2 Hz, 1H), 8.06 (ddd, J = 8.8, 2.2, 1.2 Hz, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.70 (dd, J = 8.8, 0.9 Hz, 1H), 7.4 (t, J = 7.5 Hz, 2H), 7.08 (t, J = 7.4 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 160.1, 151.4, 144.6, 143.5, 138.0, 129.1, 122.9, 118.2, 118.1, 111.5, 109.3. IR (ATR, cm^{-1}): 3035, 2921, 1688, 1584, 1528, 1495, 1465, 1440, 1341, 1263, 1234, 976, 735, 685. ESI-MS: m/z: 256.0723 $[M+H]^+$ (calcd for $[C_{13}H_{10}N_3O_3]^+$ 256.0722).[1]

***N*-(m-tolyl)benzo[d]oxazol-2-amine** (**6ab**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), m-tolyl isothiocyanate (74.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ab** (104.3 mg, 0.466 mmol, 93%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO) δ ppm 10.56 (s, 1H), 7.62 (d, *J* = 6 Hz, 2H), 7.47 (dd, *J* = 10.6, 7.8 Hz, 2H), 7.23 (m, 2H), 7.11 (td, *J* = 7.8, 1 Hz, 1H), 6.84 (d, *J* = 7.5 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (125 MHz, DMSO): *δ* ppm 158.1, 147.1, 142.6, 138.8, 138.3, 128.9, 124.0, 123.0, 121.6, 118.1, 116.7, 114.9, 108.9, 21.3. IR (ATR, cm^{-1}): 3046, 2920, 1641, 1606, 1574, 1499, 1487, 1460, 1242, 736. ESI-MS: m/z: 225.1017 $[M+H]^+$ (calcd for $[C_{14}H_{13}N_2O]^+$ 225.1028).[4]

***N*-(4-ethylphenyl)benzo[d]oxazol-2-amine** (**6ac**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-ethylphenyl isothiocyanate (81.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ac** (105.4 mg, 0.443 mmol, 89%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): *δ* ppm 10.52 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.46 (dd, *J* = 8.8 Hz, 2H), 7.2 (m, 3H), 7.10 (td, *J* = 8.8, 1 Hz, 1H), 2.55 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (125 MHz, DMSO): *δ* ppm 158.2, 147.1, 142.7, 137.6, 136.5, 128.2, 124.0, 121.5, 117.8, 116.5, 108.9, 27.6, 15.8. IR (ATR, cm^{-1}): 3390, 2965, 1652, 1615, 1574, 1511, 1439, 1339, 1270, 1229, 822, 734. ESI-MS: m/z: 239.1178 $[M+H]^+$ (calcd for $[C_{15}H_{15}N_2O]^+$ 239.1184).[3]

***N*-(4-methoxyphenyl)benzo[d]oxazol-2-amine** (**6ad**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-methoxyphenyl

isothiocyanate (82.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ad** (86.4 mg, 0.360 mmol, 72%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.42 (s, 1H), 7.69 (dd, J = 6.9, 2 Hz, 2H), 7.43 (dd, J = 7.6, 4.7 Hz, 2H), 7.19 (t, J = 7.7 Hz, 1H), 7.09 (t, J = 7.8 Hz, 1H), 6.96 (dd, J = 7, 2 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.5, 154.7, 147.2, 142.7, 132.0, 123.9, 121.3, 119.3, 116.4, 114.3, 108.8, 55.2. IR (ATR, cm^{-1}): 2837, 2359, 2341, 1672, 1580, 1510, 1459, 1283, 1267, 1230, 1163, 1030, 965, 820, 752, 738, 700. ESI-MS: m/z: 241.0971 $[M+H]^+$ (calcd for $[C_{14}H_{13}N_2O_2]^+$ 241.0999).[1]

***N*-(3-iodophenyl)benzo[d]oxazol-2-amine** (**6ae**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 3-iodophenyl isothiocyanate (130.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ae** (105.6 mg, 0.314 mmol, 63%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.75 (s, 1H), 8.25 (s, 1H), 7.73 (dd, J = 8.2, 1.8 Hz, 1H), 7.49 (dd, J = 10.2, 8 Hz, 2H), 7.37 (d, J = 7.8 Hz, 1H), 7.22 (t, J = 7.7 Hz, 1H), 7.15 (t, J = 8.3 Hz, 2H). ^{13}C NMR (125 MHz, DMSO): δ ppm 157.4, 147.0, 142.2, 140.2, 131.0, 130.6, 125.5, 124.1, 122.0, 117.0, 109.1, 94.9. IR (ATR, cm^{-1}): 3038, 2926, 1673, 1586, 1568, 1488, 1458, 1240, 1224, 735. ESI-MS: m/z: 336.9816 $[M+H]^+$ (calcd for $[C_{13}H_{10}IN_2O]^+$ 336.9838).

***N*-(4-bromophenyl)benzo[d]oxazol-2-amine** (**6af**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-bromophenyl isothiocyanate (107.0 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6af** (91.7 mg, 0.317 mmol, 64%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.79 (s,

1H), 7.74 (dd, *J* = 6.8, 2.1 Hz, 2H), 7.52 (dd, *J* = 6.9, 1.9 Hz, 2H), 7.46 (dd, *J* = 7.8, 0.8 Hz, 2H), 7.21 (td, *J* = 7.6, 0.7 Hz, 1H), 7.12 (td, *J* = 8.3, 0.8 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 157.7, 147.1, 142.3, 138.2, 131.8, 124.2, 122.0, 119.6, 116.8, 113.7, 109.1. IR (ATR, cm^{-1}): 3160, 3029, 2920, 1675, 1592, 1573, 1487, 1458, 1364, 1352, 1248, 1232, 733. ESI-MS: m/z: 288.9960 $[M+H]^+$ (calcd for $[C_{13}H_{10}BrN_2O]^+$ 288.9977).[1]

***N*-(2-fluorophenyl)benzo[d]oxazol-2-amine** (**6ag**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 2-fluorophenyl isothiocyanate (76.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ag** (102.9 mg, 0.45 mmol, 90%) as a white solid: ^{1}H NMR (400 MHz, DMSO): *δ* ppm 10.42 (s, 1H), 8.27 (t, *J* = 7.9 Hz, 1H), 7.46 (t, *J* = 9.0 Hz, 2H), 7.24 (m, 3H), 7.12 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO): *δ* ppm 158.5, 154.0, 152.1, 147.5, 142.2, 126.6 (d, *J* = 11.3 Hz), 124.7 (d, *J* = 2.5 Hz), 124.1 (d, *J* = 6.3 Hz). 121.9 (d, *J* = 16.3 Hz), 116.8, 115.6 (d, *J* = 17.5 Hz), 109.1. IR (ATR, cm^{-1}): 3141, 3002, 1644, 1573, 1504, 1459, 1366, 1282, 1243, 1197, 1100, 737. ESI-MS: m/z: 229.0764 $[M+H]^+$ (calcd for $[C_{13}H_{10}FN_2O]^+$ 229.0777).

***N*-(4-chlorophenyl)benzo[d]oxazol-2-amine** (**6ah**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-chlorophenyl isothiocyanate (84.8 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ah** (88.7 mg, 0.363 mmol, 73%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): *δ* ppm 10.78 (s, 1H), 7.8 (d, *J* = 7.3 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.42 (d, *J* = 7 Hz, 2H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): *δ* ppm 157.7, 147.0, 142.2, 137.8, 128.9, 125.7, 124.1, 121.9, 119.1, 116.8, 109.1. IR (ATR, cm^{-1}): 3378, 2924, 1653, 1598,

1569, 1489, 1458, 1228, 736. ESI-MS: m/z: 245.0471 $[M+H]^+$ (calcd for $[C_{13}H_{10}ClN_2O]^+$ 245.0482).[4]

***N*-(4-hydroxyphenyl)benzo[d]oxazol-2-amine** (**6ai**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-hydroxyphenyl isothiocyanate (75.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ai** (82.4 mg, 0.365 mmol, 73%) as a light orange solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.25 (s, 1H), 9.21 (s, 1H), 7.55 (dd, J = 6.7, 2.2 Hz, 2H), 7.42 (d, J = 7.8 Hz, 1H), 7.39 (d, J = 7.7 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 7.07 (t, J = 7.7 Hz, 1H), 6.80 (dd, J = 6.7, 2.2 Hz, 2H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.7, 152.9, 147.2, 142.8, 130.5, 123.9, 121.2, 119.6, 116.3, 115.5, 108.8. IR (ATR, cm^{-1}): 3261, 3176, 3069, 1632, 1571, 1540, 1505, 1457, 1235, 1219, 1007, 817, 745. ESI-MS: m/z: 227.08188 $[M+H]^+$ (calcd for $[C_{13}H_{11}N_2O_2]^+$ 227.08205).[5]

***N*-(3-hydroxyphenyl)benzo[d]oxazol-2-amine** (**6aj**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 3-hydroxyphenyl isothiocyanate (75.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6aj** (76.8 mg, 0.340 mmol, 68%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.50 (s, 1H), 9.50 (s, 1H), 7.47 (d, J = 7.6 Hz, 1H), 7.44 (dd, J = 7.8, 0.7 Hz, 1H), 7.36 (t, J = 1.9 Hz, 1H), 7.21 (td, J = 7.6, 1.2 Hz, 1H), 7.12 (m, 3H), 6.44 (dt, J= 7.2, 2.1 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.0, 147.0, 142.6, 139.8, 129.7, 124.1, 121.7, 116.6, 109.5, 109.0, 108.6, 104.8. IR (ATR, cm^{-1}): 3321, 2919, 1651, 1615, 1504, 1461, 1352, 1249, 1157, 944, 764, 737. ESI-MS: m/z: 227.08213 $[M+H]^+$ (calcd for $[C_{13}H_{11}N_2O_2]^+$ 227.08205).

***N*-(4-(trifluoromethyl)phenyl)benzo[d]oxazol-2-amine (6ak)** Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-(trifluoromethyl)phenyl isothiocyanate (101.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h) to afford **6ak** (107.5 mg, 0.387 mmol, 77%) as a white solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 11.07 (s, 1H), 7.97 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.7 Hz, 2H), 7.50 (dd, J = 7.8, 2.3 Hz, 2H), 7.24 (t, J = 7.7 Hz, 1H), 7.16 (t, J = 7.7 Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ ppm 157.4, 147.0, 142.4, 142.1, 126.3, 125.7, 124.2, 123.5, 122.2, 122.0, 117.4, 117.0, 109.2. IR (ATR, cm^{-1}): 2359, 1615, 1574, 1486, 1459, 1325, 1282, 1235, 1160, 1106, 1069, 1014, 978, 829, 737. ESI-MS: m/z: 279.0750 $[M+H]^+$ (calcd for $[C_{14}H_{10}F_3N_2O]^+$ 279.0745).[1]

***N*-(naphthalen-1-yl)benzo[d]oxazol-2-amine (6al)** Synthesized according to the General procedure A using 2-aminophenol (65.0 mg, 0.600 mmol), 1-naphthyl isothiocyanate (92.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h) to afford **6al** (56.6 mg, 0.218 mmol, 44%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.49 (s, 1H), 8.31 (d, J = 7.3 Hz, 1H), 8.16 (d, J = 7.5 Hz, 1H), 7.95 (dd, J = 6.7, 2.7 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.57 (m, 3H), 7.49 (d, J = 7.9 Hz, 1H), 7.42 (d, J = 7.7 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.12 (t, J = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 159.8, 147.6, 142.5, 133.9, 128.3, 126.7, 126.2, 126.0, 125.9, 124.3, 124.0, 122.4, 121.5, 118.6, 116.5, 109.0. IR (ATR, cm^{-1}): 2900, 2359, 1627, 1580, 1515, 1462, 1401, 1353, 1274, 1241, 956, 774, 731. ESI-MS: m/z: 261.1025 $[M+H]^+$ (calcd for $[C_{17}H_{13}N_2O]^+$ 261.1020).[1]

***N*-(pyridin-3-yl)benzo[d]oxazol-2-amine** (**6am**) Synthesized according to the General procedure A using 2-aminophenol (65.0 mg, 0.600 mmol), 3-pyridyl isothiocyanate (68.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h) to afford **6am** (69.0 mg, 0.327 mmol, 65%) as a yellow solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.89 (s, 1H), 8.88 (d, J = 2.6 Hz, 1H), 8.28 (dd, J = 8.4, 2.4 Hz, 1H), 8.25 (dd, J = 4.6, 1.2 Hz, 1H), 7.49 (dd, J = 11.7, 7.9 Hz, 2H), 7.41 (d, J = 8.3, 4.7 Hz, 1H), 7.23 (t, J = 7.4 Hz, 1H), 7.14 (t, J = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 157.8, 147.2, 143.1, 142.2, 139.6, 135.7, 124.3, 124.2, 123.9, 122.1, 116.9, 109.2. IR (ATR, cm^{-1}): 3380, 2359, 1640, 1594, 1568, 1460, 1430, 1332, 1300, 1235, 1168, 981, 824, 735. ESI-MS: m/z: 212.0828 $[M+H]^+$ (calcd for $[C_{12}H_{10}N_3O]^+$ 212.0824).

***N*-(4-nitrophenyl)benzo[d]oxazol-2-amine** (**6an**) Synthesized according to the General procedure A using 2-aminophenol (**3a**) (65.4 mg, 0.600 mmol), 4-nitrophenyl isothiocyanate (**4i**) (90.1 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol) and sodium chloride (4.4 mg,).075 mmol in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 8h) to afford **6an** (16.0 mg, 0.065 mmol, 13%) as a yellow solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 11.44 (s, 1H), 8.29 (dd, J = 11.9, 2.8 Hz, 2H), 7.97 (dd, J = 12, 2.9 Hz, 2H), 7.55 (dd, J = 7.7, 5.3 Hz, 2H), 7.28 (t, J = 7.7 Hz, 1H), 7.21 (t, J = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 156.9, 147.1, 145.0, 141.7, 141.3, 125.4, 124.4, 122.7, 117.4, 117.2, 109.5. IR (ATR, cm^{-1}): 2922, 2359, 1671, 1585, 1518, 1457, 1328, 1307, 1239, 1183, 1109, 731. ESI-MS: m/z: 256.0710 $[M+H]^+$ (calcd for $[C_{13}H_{10}N_3O_3]^+$ 256.0722).[1]

***N*-(3-nitrophenyl)benzo[d]oxazol-2-amine** (**6ao**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 3-nitrophenyl

isothiocyanate (90.1 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ao** (38.8 mg, 0.152 mmol, 30%) as a light yellow solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 11.17 (s, 1H), 8.77 (t, J = 2.2 Hz, 1H), 8.08 (ddd, J = 8.2, 2.1, 0.7 Hz, 1H), 7.87 (ddd, J = 8.2, 2.2, 0.7 Hz, 1H), 7.65 (t, J = 8.2 Hz, 1H), 7.53 (m, 1H), 7.26 (td, J = 7.7, 1.1 Hz, 1H), 7.18 (td, J = 7.8, 1.2 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 157.4, 148.4, 147.0, 141.9, 140.0, 130.4, 124.3, 123.6, 122.4, 117.1, 116.6, 111.5, 109.3. IR (ATR, cm^{-1}): 3156, 3100, 3075, 2915, 1674, 1530, 1490, 1457, 1348, 1235, 984, 817, 727. ESI-MS: m/z: 256.07176 $[M+H]^+$ (calcd for $[C_{13}H_{10}N_3O_3]^+$ 256.07222).[6]

***N*-cyclohexylbenzo[d]oxazol-2-amine** (**6ap**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), cyclohexyl isothiocyanate (70.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ap** (27.2 mg, 0.126 mmol, 25%) as a white solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 7.85 (d, J = 7.8 Hz, 1H), 7.3 (dd, J = 7.8, 2.6 Hz, 1H), 7.22 (dd, J = 7.6, 2.5 Hz, 1H), 7.08 (td, J = 7.6, 2.8 Hz, 1H), 6.94 (td, J = 7.7, 2.6 Hz, 1H), 3.54 (m, 1H), 1.96 (s, 2H), 1.71 (s, 2H), 1.32-1.13 (m, 6H). ^{13}C NMR (125 MHz, DMSO): δ ppm 161.7, 147.9, 143.4, 123.5, 119.9, 115.3, 108.4, 51.6, 32.4, 25.2, 24.6. IR (ATR, cm^{-1}): 3372, 3021, 2915, 2873, 1662, 1581, 1499, 1455, 1336, 1245. ESI-MS: m/z: 217.1012 $[M+H]^+$ (calcd for $[C_{13}H_{17}N_2O]^+$ 217.1340).[7]

Ethyl 4-(benzo[d]oxazol-2-ylamino)benzoate (**6aq**) Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), 4-ethylbenzoate isothiocyanate (103.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) (reaction time is 4h)

to afford **6aq** (76.5 mg, 0.271 mmol, 54%) as a white solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 11.07 (s, 1H), 7.97 (d, J = 8.7 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.25 (t, J = 7.8 Hz, 1H), 7.17 (dd, J = 8.3, 7.5 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.31 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO): δ ppm 165.5, 157.3, 147.0, 143.1, 142.1, 130.6, 124.2, 123.1, 122.3, 117.1, 116.9, 109.2, 60.4, 14.3. IR (ATR, cm^{-1}): 3279, 3137, 2954, 2923, 1692, 1645, 1600, 1565, 1440, 1425, 1367, 1280, 848, 727. ESI-MS: m/z: 305.0903 $[M+Na]^+$ (calcd for $[C_{16}H_{14}N_2O_3Na]^+$ 305.0902).[8]

***N*-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)benzo[d]oxazol-2-amine (6ar)**

Synthesized according to the General procedure A using 2-aminophenol (65.4 mg, 0.600 mmol), tert-butyl(4-isothiocyanatophenoxy)dimethylsilane (132.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **6ar** (80 mg, 0.235 mmol, 47%) as a white-orange solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.44 (s, 1H), 7.64 (dd, J = 6.7, 2.2 Hz, 2H), 7.44 (d, J = 7.7 Hz, 1H), 7.41 (dd, J = 7.7, 0.5 Hz, 1H), 7.19 (td, J = 7.7, 1.1 Hz, 1H), 7.09 (td, J = 7.8, 1.2 Hz, 1H), 6.86 (dd, J = 6.7, 2.2 Hz, 2H), 0.93 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (125 MHz, DMSO): δ ppm 158.3, 150.1, 147.1, 142.7, 132.7, 123.9, 121.4, 120.1, 119.1, 116.4, 108.8, 25.6, 17.9, -4.6. IR (ATR, cm^{-1}): 3044, 2954, 2929, 2890, 2857, 1686, 1577, 1507, 1457, 1353, 1250, 1229, 1007, 972, 914, 824, 778, 737. ESI-MS: m/z: 341.16960 $[M+H]^+$ (calcd for $[C_{19}H_{25}N_2O_2Si]^+$ 341.16853).

***N*-phenylbenzo[d]thiazol-2-amine** (**8aa**) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), phenyl isothiocyanate (67.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **8aa** (77.2 mg, 0.342 mmol, 68%)

as a light brown solid: ^{1}H NMR (500 MHz, DMSO) δ ppm 10.51 (s, 1H), 7.82 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.37 (t, J = 7.9 Hz, 2H), 7.33 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.4 Hz, 1H), 7.02 (t, J = 7.3 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 161.6, 152.2, 140.7, 130.1, 129.0, 125.9, 122.3, 122.1, 121.1, 119.3, 117.8. IR (ATR, cm^{-1}): 3234, 3189, 3125, 3057, 2931, 1620, 1597, 1562, 1499, 1443, 1225, 1019, 922, 741, 686, 667. ESI-MS: m/z: 227.06358 $[M+H]^+$ (calcd for $[C_{13}H_{11}N_2S]^+$ 227.06429).[9]

***N*-(m-tolyl)benzo[d]thiazol-2-amine** (**8ab**) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), m-tolyl isothiocyanate (74.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **8ab** (67.6 mg, 0.282 mmol, 56%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO) δ ppm 10.42 (s, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.65 (d, J = 8.1 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.58 (s, 1H), 7.32 (t, J = 7.7 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.6 Hz, 1H), 6.84 (d, J = 7.5 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (125 MHz, DMSO): δ ppm 161.7, 152.2, 140.6, 138.2, 130.0, 128.9, 125.9, 122.9, 122.2, 121.0, 119.2, 118.3, 115.1, 21.4. IR (ATR, cm^{-1}): 3234, 3195, 3137, 3055, 2919, 2851 1620, 1591, 1571, 1488, 1445, 1274, 1245, 879, 743, 719, 671. ESI-MS: m/z: 241.07868 $[M+H]^+$ (calcd for $[C_{14}H_{13}N_2S]^+$ 241.07994).[9]

***N*-(3-iodophenyl)benzo[d]thiazol-2-amine** (**8ae**) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), 3-iodophenyl isothiocyanate (130.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **8ae** (83.5 mg, 0.237 mmol, 47%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.60 (s, 1H), 8.29 (t, J = 1.8 Hz, 1H), 7.82 (dd, J = 7.9, 0.8 Hz, 1H), 7.75 (ddd, J = 8.2, 2.0, 0.7 Hz,

1H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.35 (m, *2*H), 7.16 (m, 2H). ^{13}C NMR (125 MHz, DMSO): δ ppm 161.2, 151.9, 142.0, 131.1, 130.5, 130.1, 126.1 125.7, 122.7, 121.2, 119.6, 117.0, 95.0. IR (ATR, cm^{-1}): 3226, 3160, 3096, 2997, 2919, 2845, 1616, 1581, 1552, 1445, 1328, 1241, 988, 926, 745, 714. ESI-MS: m/z: 352.9609 $[M+H]^+$ (calcd for $[C_{13}H_{10}IN_2S]^+$ 352.9618).

***N*-(2-fluorophenyl)benzo[d]thiazol-2-amine** (**8ag**) Synthesized according to the General procedure B using 2-aminophenol (75.0 mg, 0.600 mmol), 2-fluorophenyl isothiocyanate (76.6 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **8ag** (89.6 mg, 0.367 mmol, 73%) as a white solid: ^{1}H NMR (400 MHz, DMSO): δ ppm 10.34 (s, 1H), 8.56 (t, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.34-7.22 (m, 3H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.07 (dd, J = 7.8, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO): δ ppm 162.2, 153.3, 151.6, 151.4, 130.6, 128.5 (d, *J* = 10.0 Hz), 125.9, 124.7 (d, *J* = 3.8 Hz), 123.4 (d, *J* = 7.5 Hz). 122.5, 121.4, 121.1 119.4, 115.4 (d, *J* = 18.8 Hz). ESI-MS: m/z: 229.0764 $[M+H]^+$ (calcd for $[C_{13}H_{10}FN_2O]^+$ 229.0777).[10]

***N*-(4-chlorophenyl)benzo[d]thiazol-2-amine** (**8ah**) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), 4-chlorophenyl isothiocyanate (84.8 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **8ah** (56.4 mg, 0.217 mmol, 43%) as a light brown solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.64 (s, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.63 (d, *J* = 8 Hz, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H). ^{13}C NMR (125 MHz, DMSO): δ ppm 161.3, 152.0, 139.6, 130.0, 128.9, 126.0, 125.4, 122.5, 121.1, 119.4, 119.2. IR (ATR, cm^{-1}): 3239, 3174, 3116, 3066, 2961, 2850, 1619, 1565, 1492, 1442, 1272, 1245, 1224, 822, 747, 724. ESI-MS: m/z: 261.02457 $[M+H]^+$ (calcd for $[C_{13}H_{10}ClN_2S]^+$ 261.02432).[9]

Ethyl 4-(benzo[d]thiazol-2-ylamino)benzoate (**8aq**) Synthesized according to the General procedure B using 2-aminobenzenethiol (75.0 mg, 0.600 mmol), 4-ethylbenzoate isothiocyanate (103.5 mg, 0.500 mmol), sodium iodide (7.5 mg, 0.050 mmol), and sodium chloride (4.4 mg, 0.075 mmol) in ethanol (1.00 mL) and water (1.00 mL) to afford **8aq** (76.5 mg, 0.271 mmol, 54%) as a white solid: ^{1}H NMR (500 MHz, DMSO): δ ppm 10.91 (s, 1H), 7.97 (dd, J = 6.9, 2.0 Hz, 2H), 7.93 (dd, J = 7.0, 2.0 Hz, 2H), 7.84 (dd, J = 7.9, 0.7 Hz, 1H), 7.68 (d, J = 7.8 Hz, 1H), 7.36 (td, J = 7.7, 1.2 Hz, 1H), 7.2 (td, J = 7.6, 1.1 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 1.3 (t, J = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, DMSO): δ ppm 165.5, 161.0, 151.8, 144.8, 130.6, 130.3, 126.1, 122.9, 122.8, 121.3, 119.8, 117.0, 60.4, 14.3. IR (ATR, cm^{-1}): 3283, 3192, 3126, 3090, 2952, 1677, 1594, 1531, 1438, 1416, 1361, 1332, 1283, 1257, 1243, 1166, 1103, 1012, 921, 846. ESI-MS: m/z: 299.08674 $[M+H]^+$ (calcd for $[C_{16}H_{15}N_2O_2S]^+$ 305.08542).

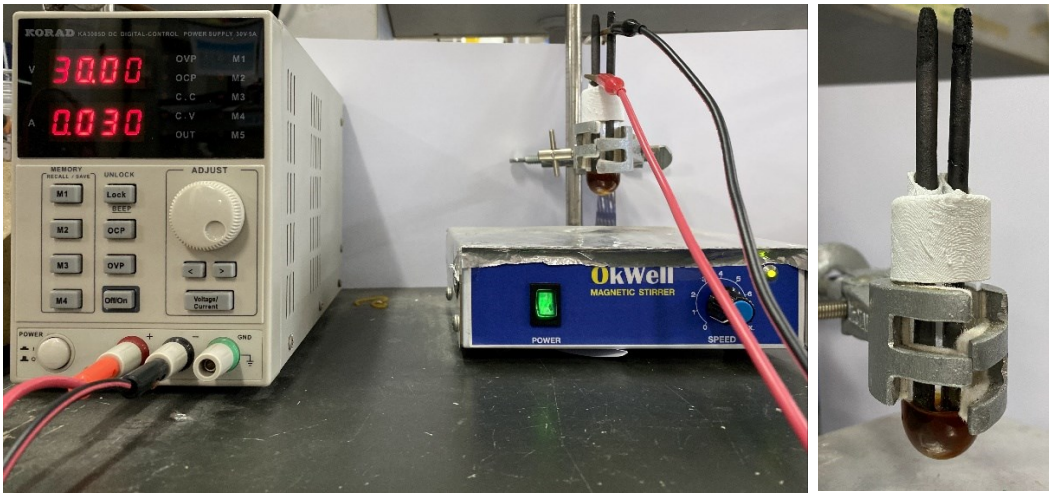
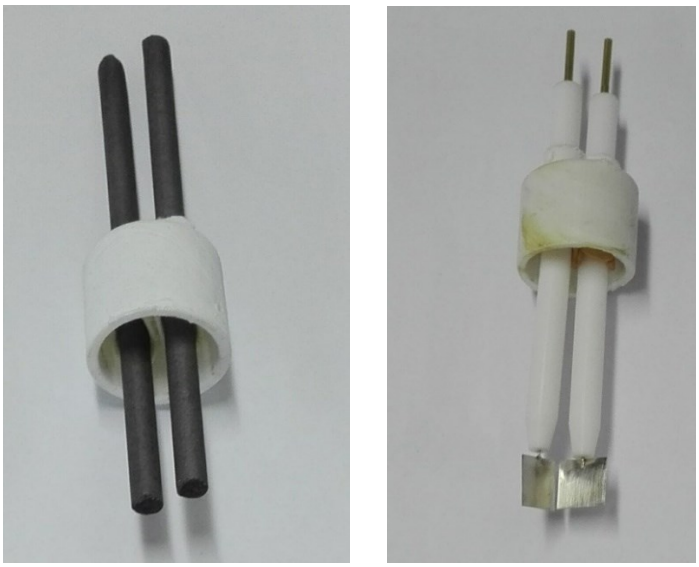


Figure S1. Reactors set up



a) b)

Figure S2. Electrodes a) Carbon and b) Platinum

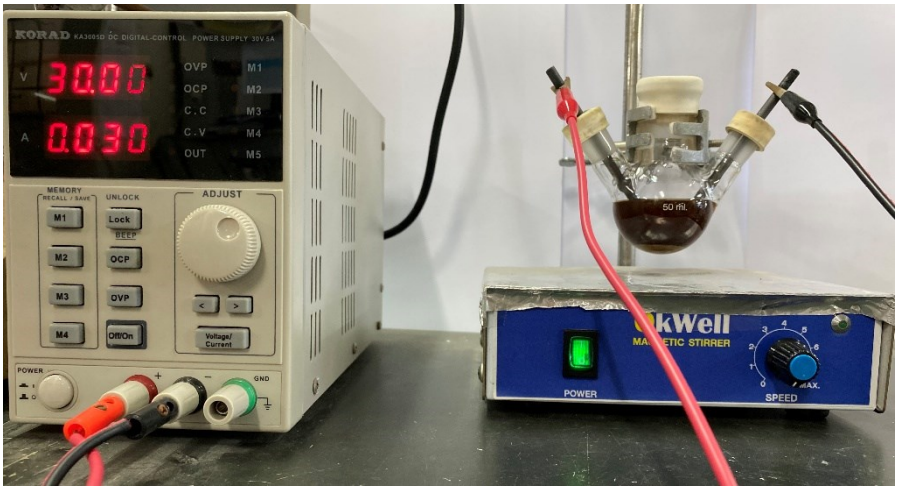


Figure S3. Gram scale set up

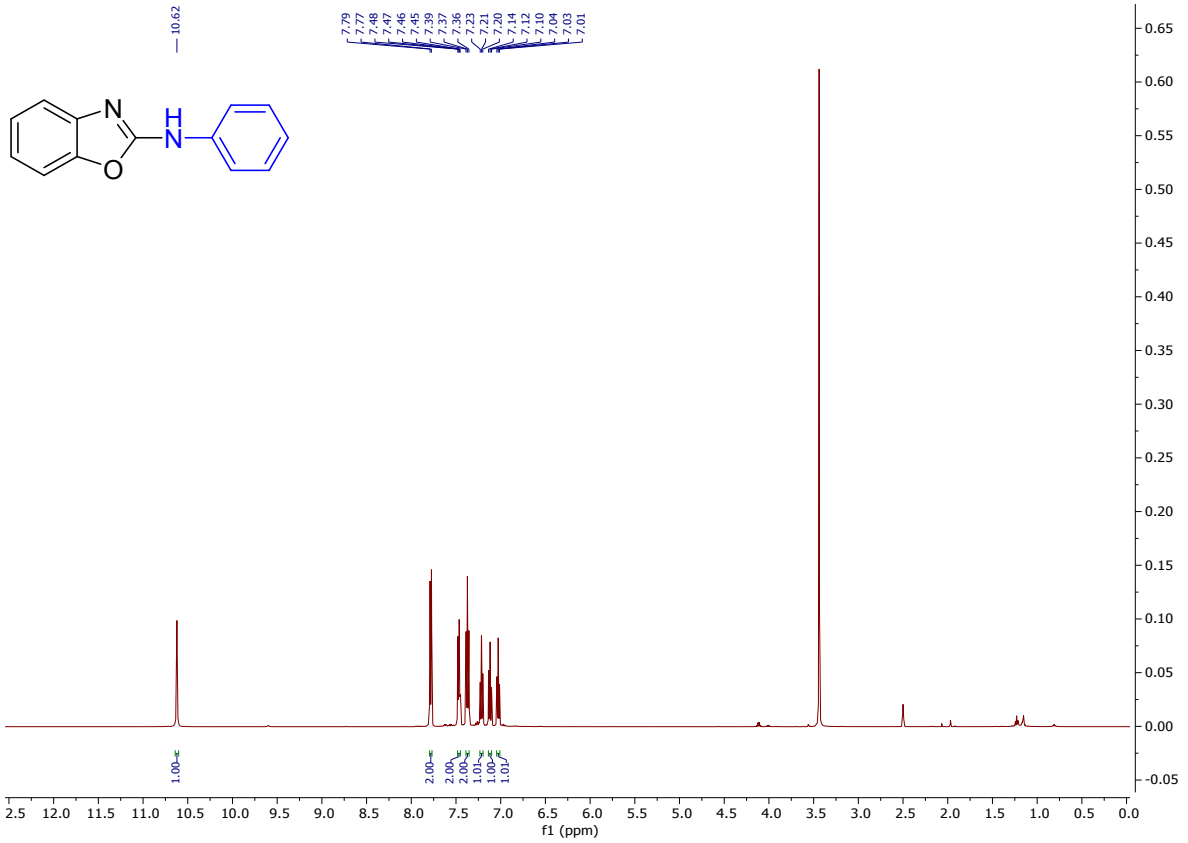


Figure S4 ^{1}H NMR spectra of **6aa** ($(CD_3)_2SO$)

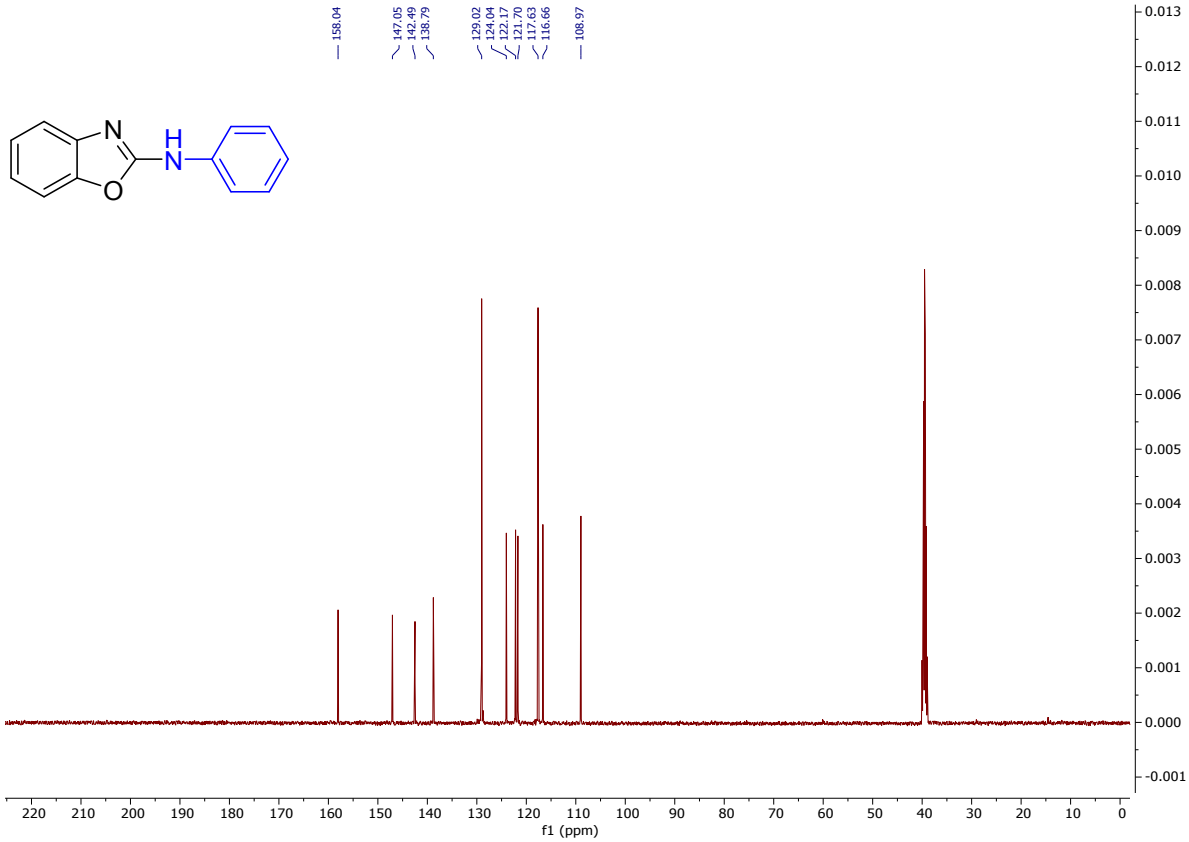


Figure S5 ^{13}C NMR spectra of **6aa** ($(CD_3)_2SO$)

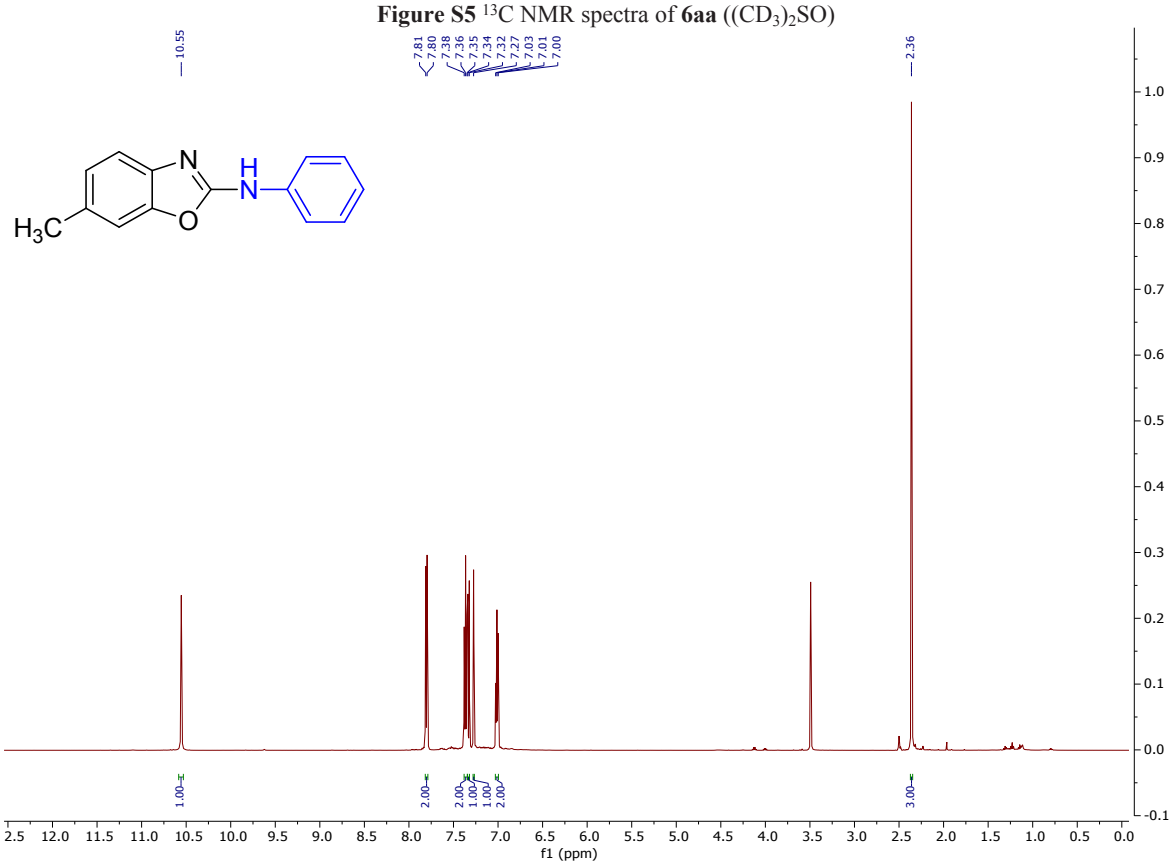


Figure S6 ^{1}H NMR spectra of **6ba** ($(CD_3)_2SO$)

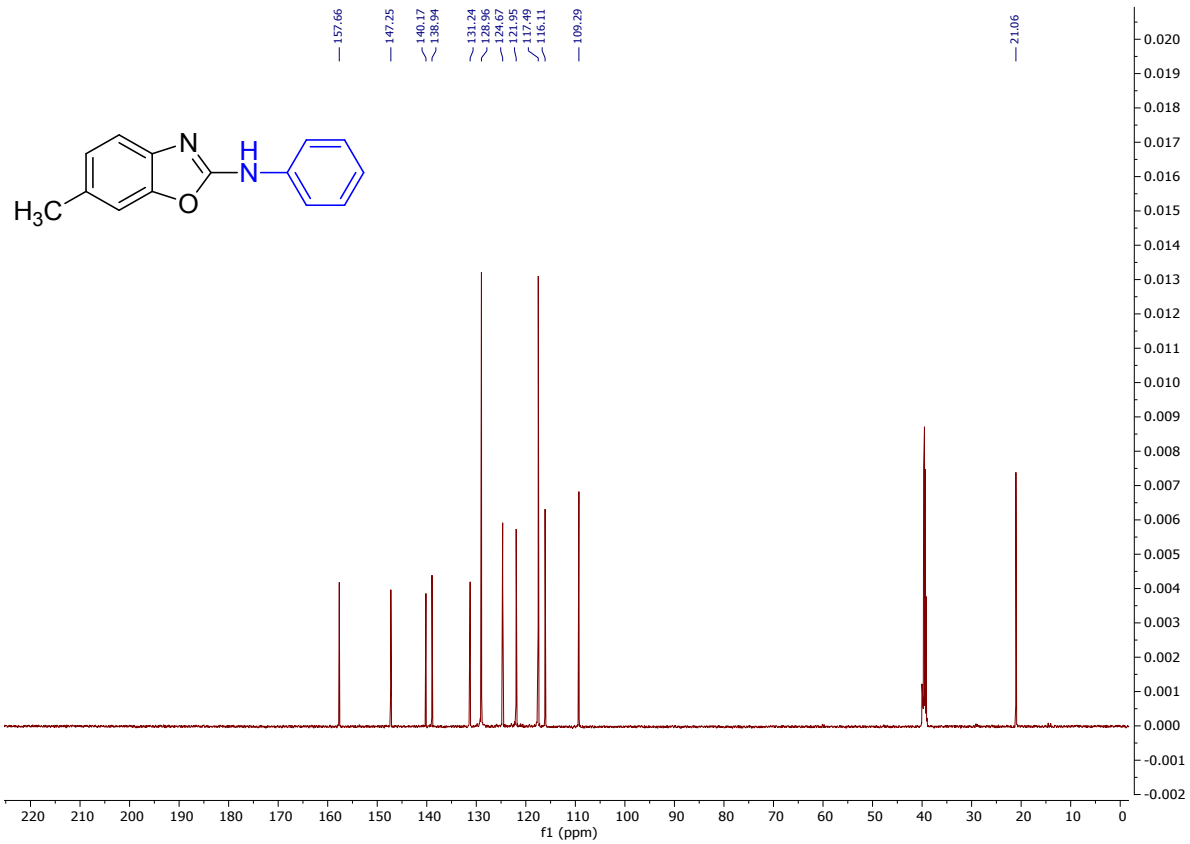


Figure S7 ^{13}C NMR spectra of **6ba** ($(CD_3)_2SO$)

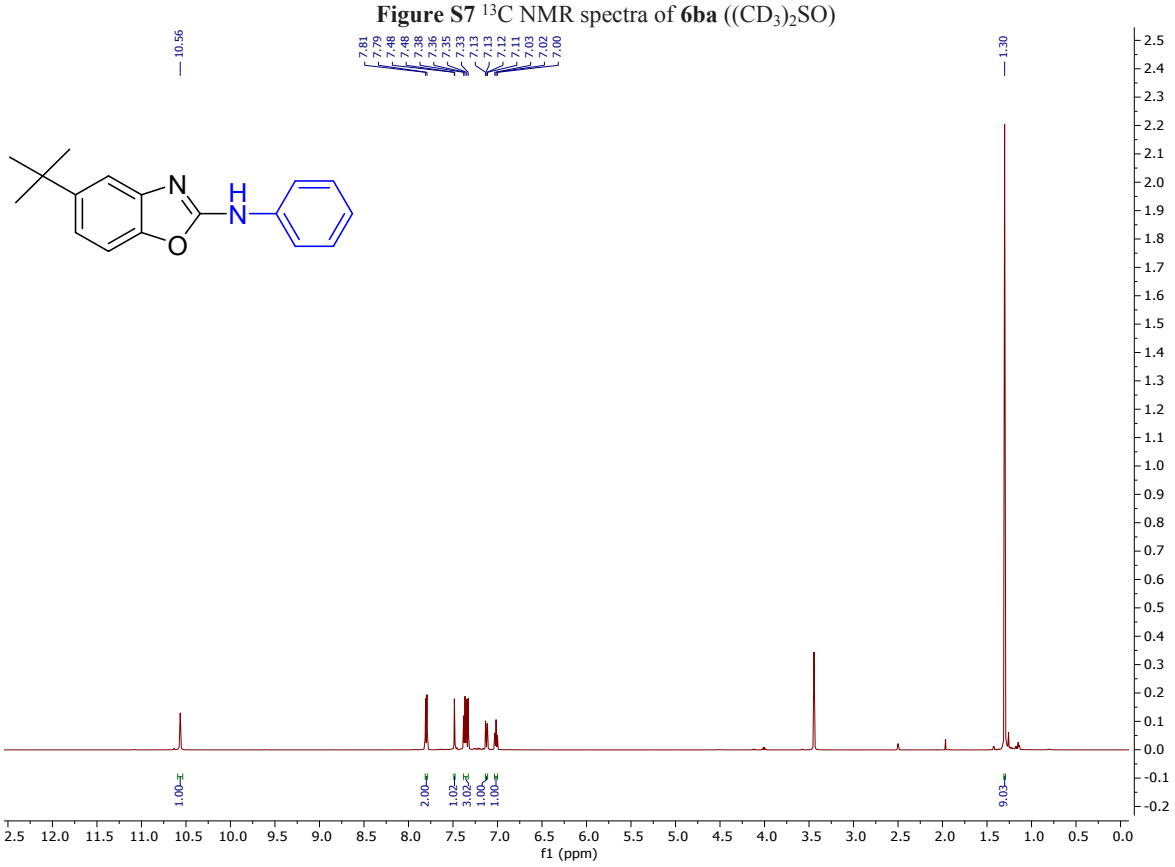


Figure S8 ^{1}H NMR spectra of **6ca** ($(CD_3)_2SO$)

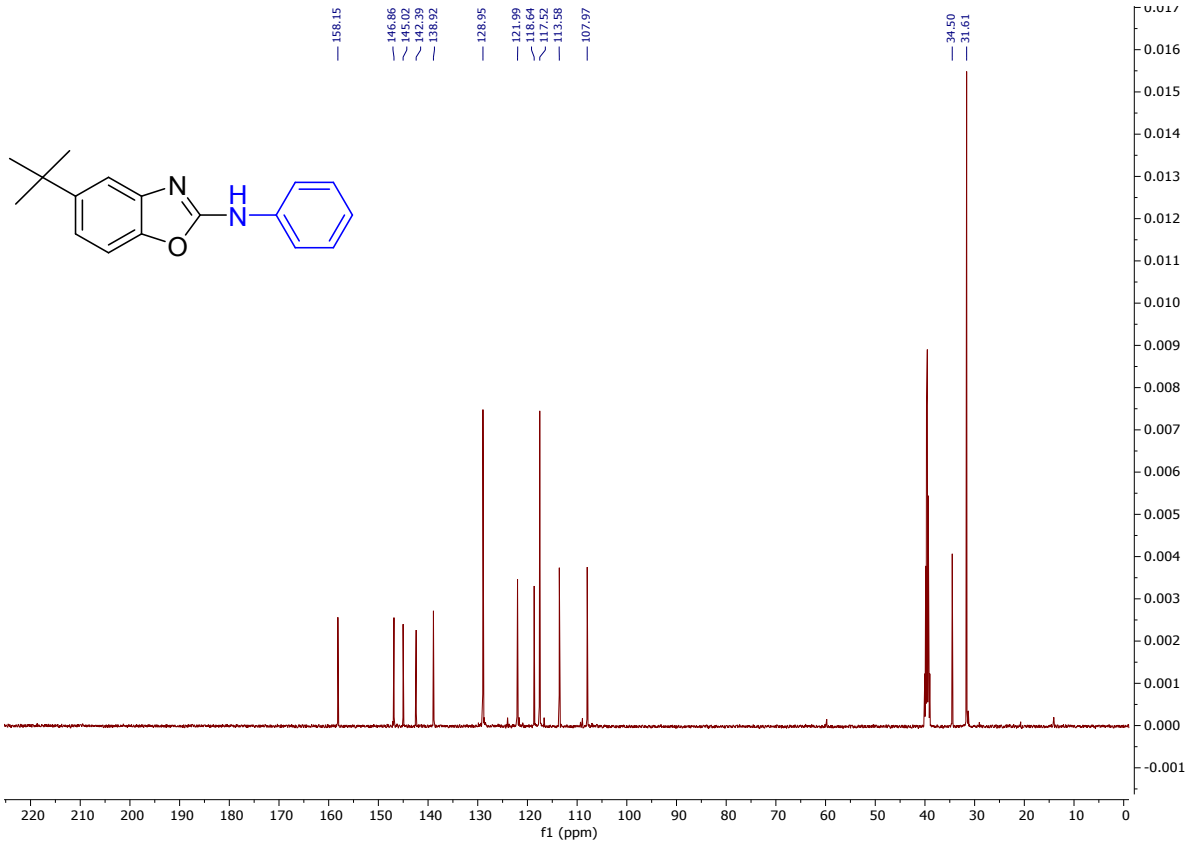


Figure S9 ^{13}C NMR spectra of **6ca** ($(CD_3)_2SO$)

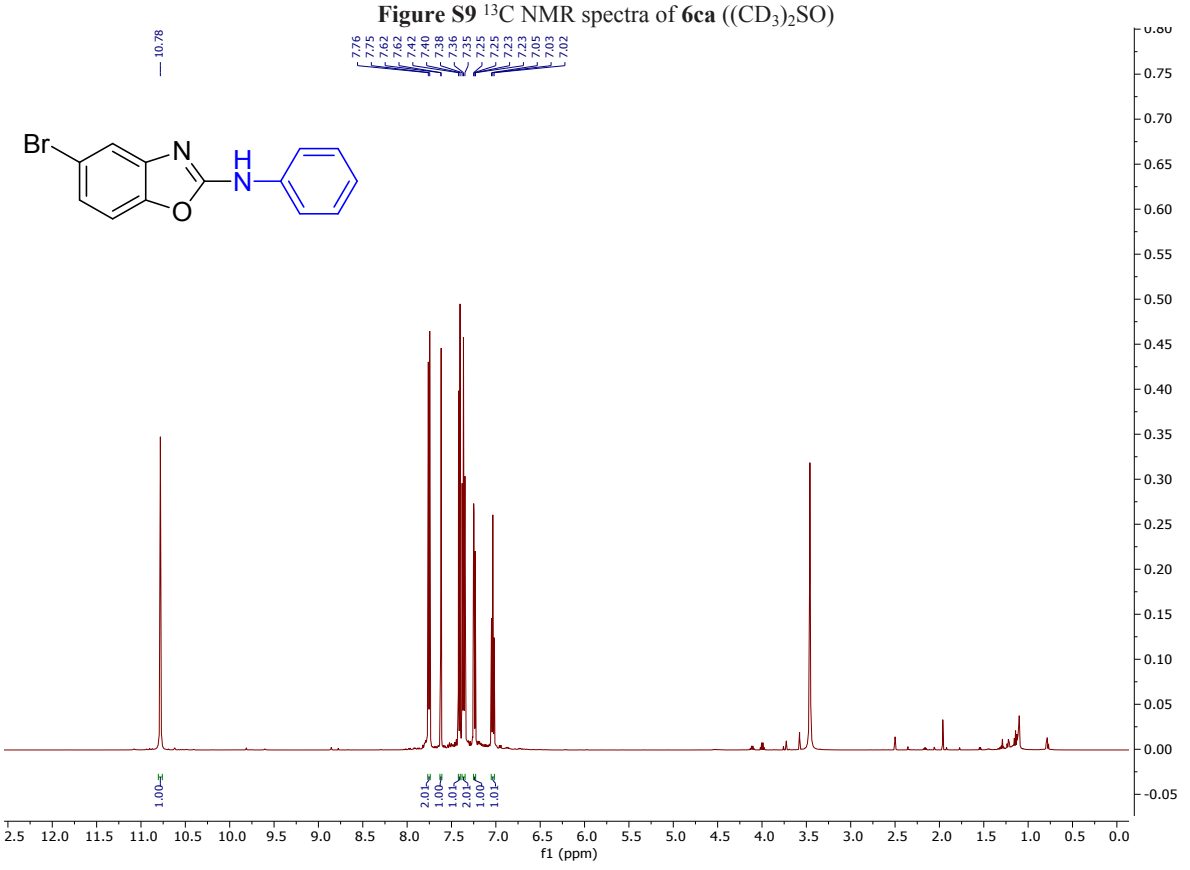


Figure S10 ^{1}H NMR spectra of **6da** ($(CD_3)_2SO$)

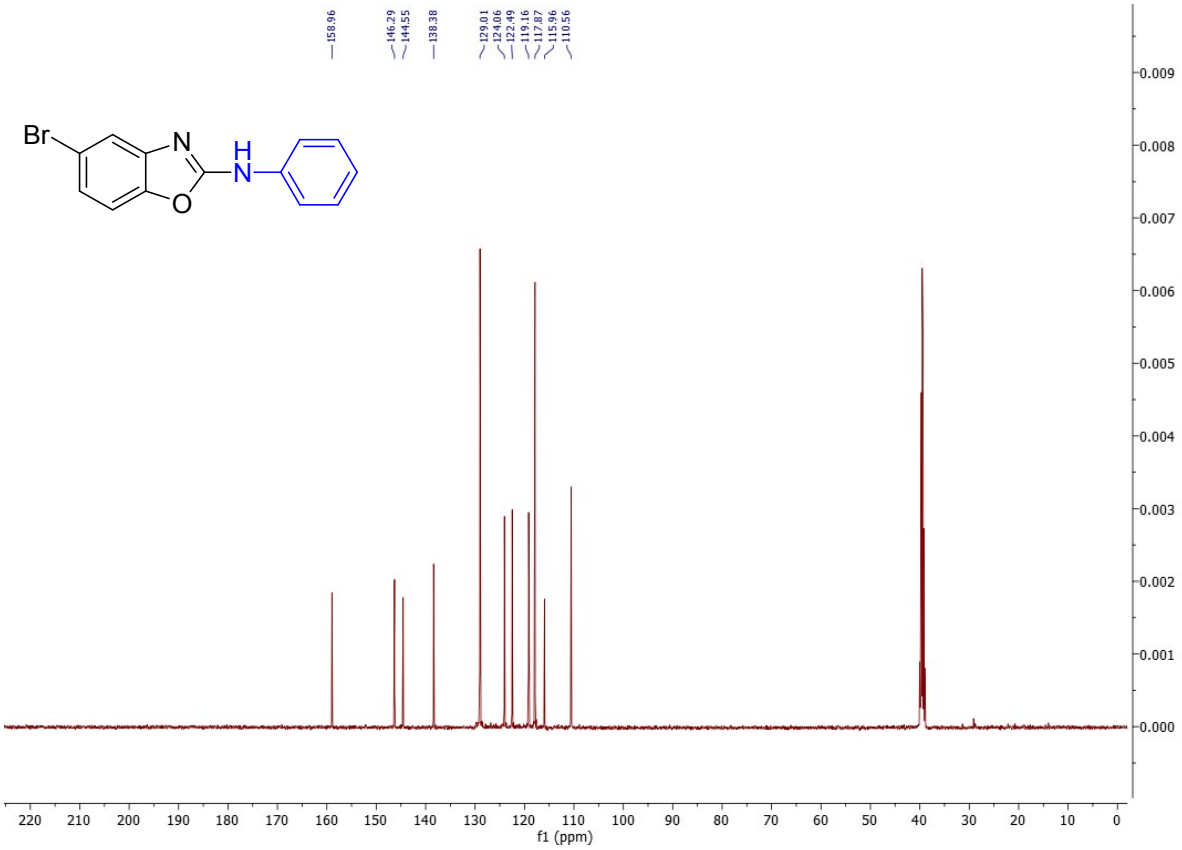


Figure S11 ^{13}C NMR spectra of **6da** ($(CD_3)_2SO$)

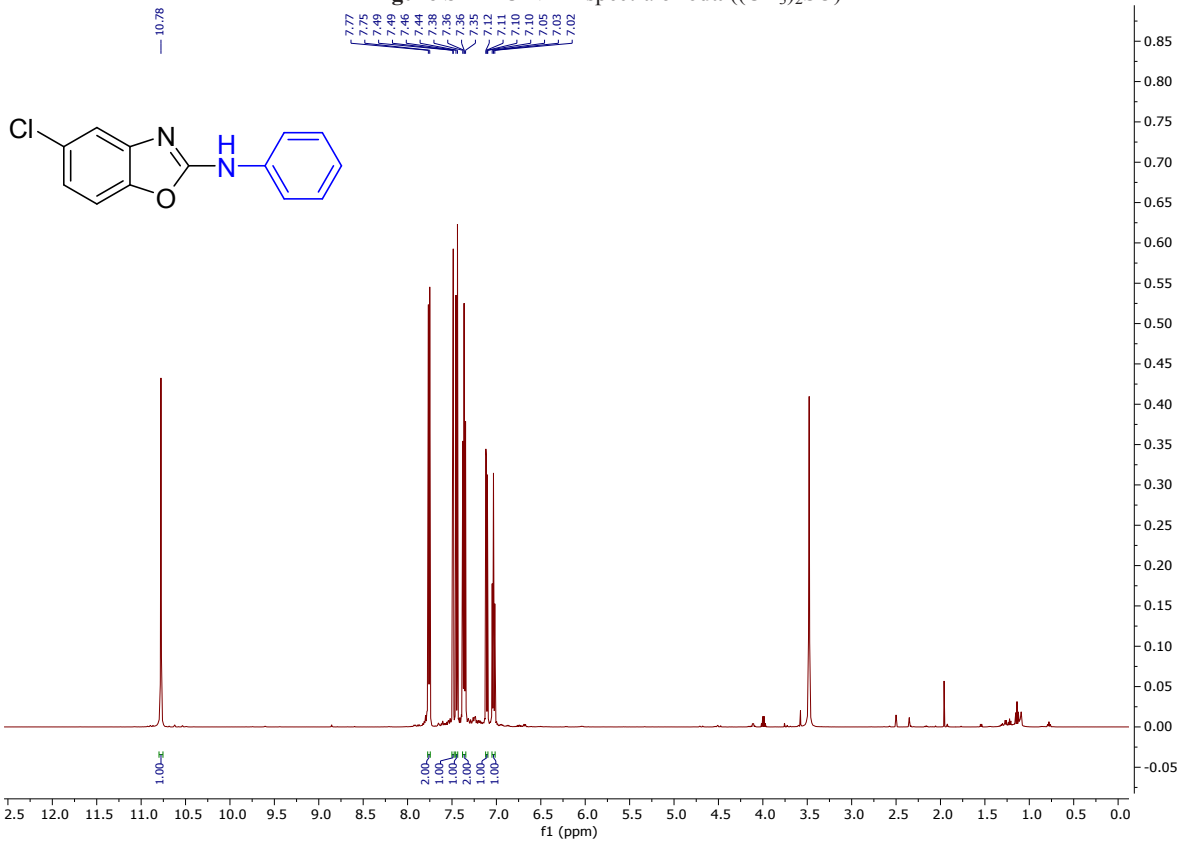


Figure S12 ^{1}H NMR spectra of **6ea** ($(CD_3)_2SO$)

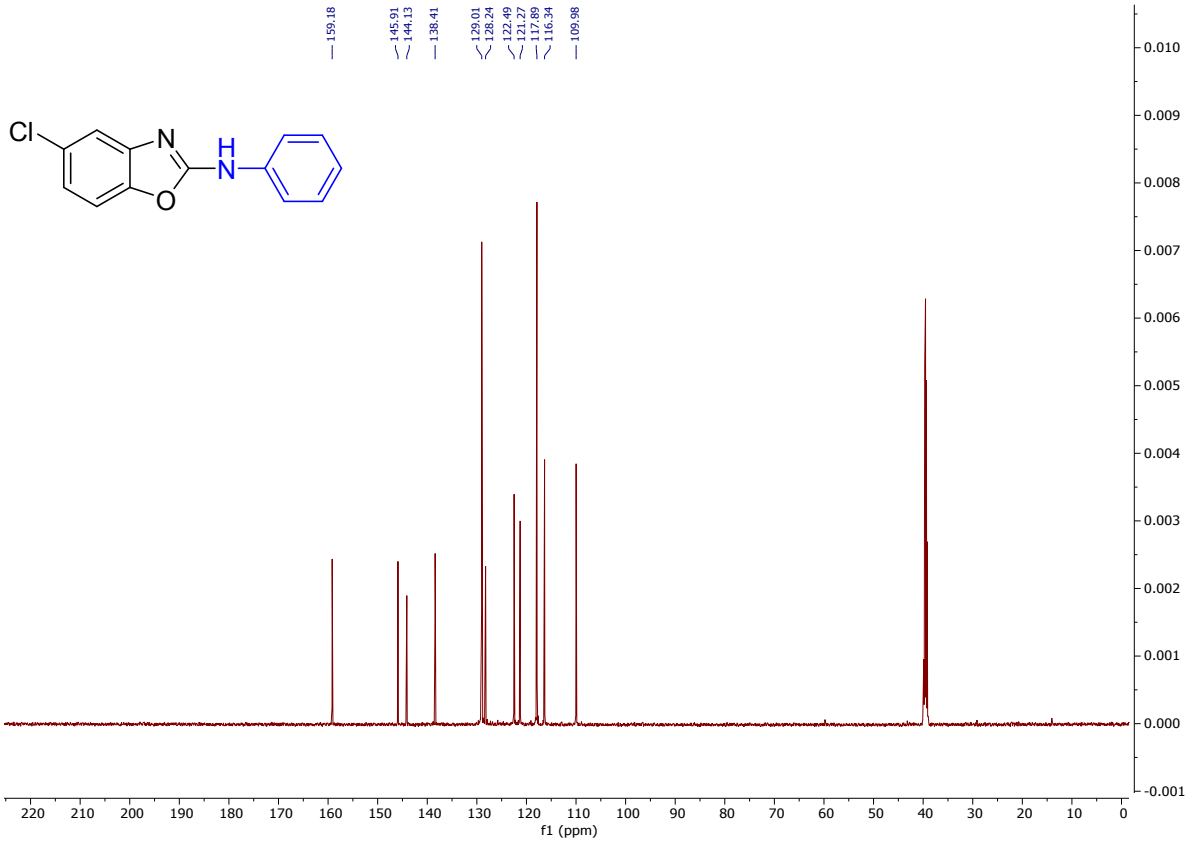


Figure S13 ^{13}C NMR spectra of **6ea** ($(CD_3)_2SO$)

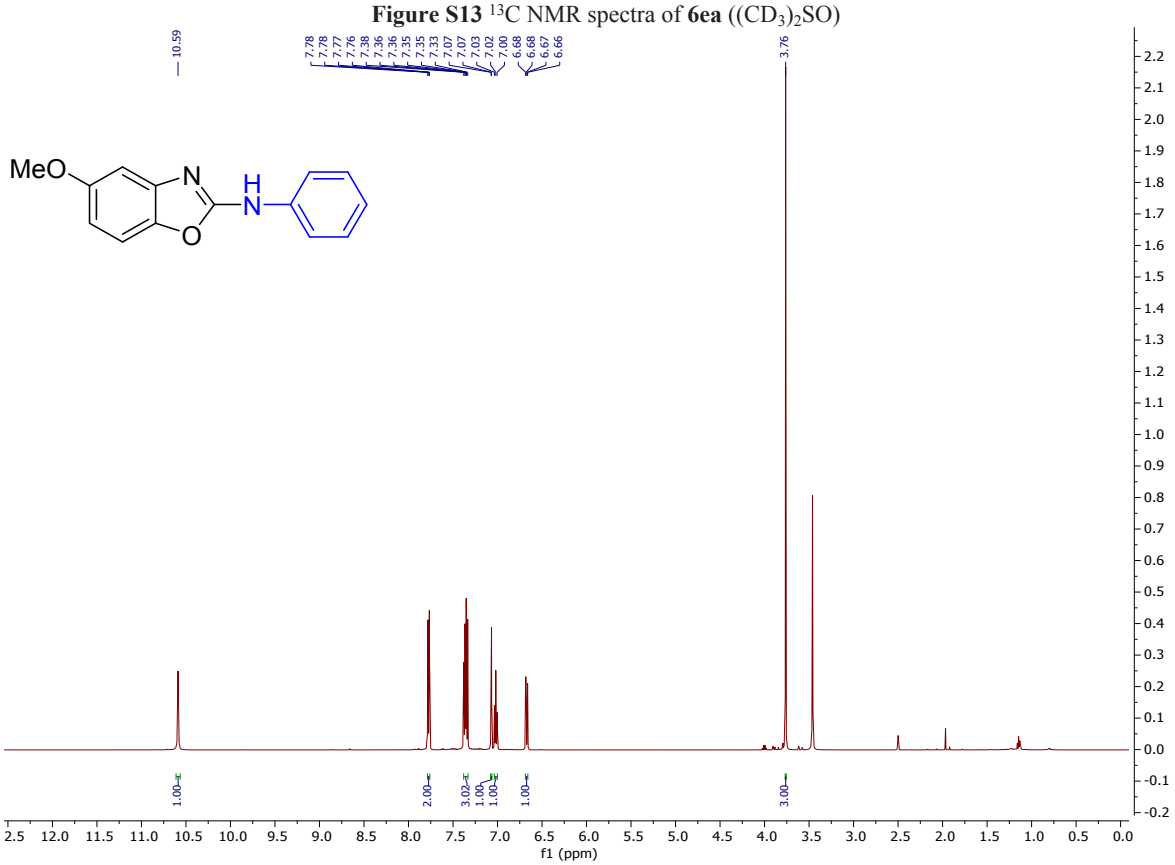


Figure S14 ^{1}H NMR spectra of **6fa** ($(CD_3)_2SO$)

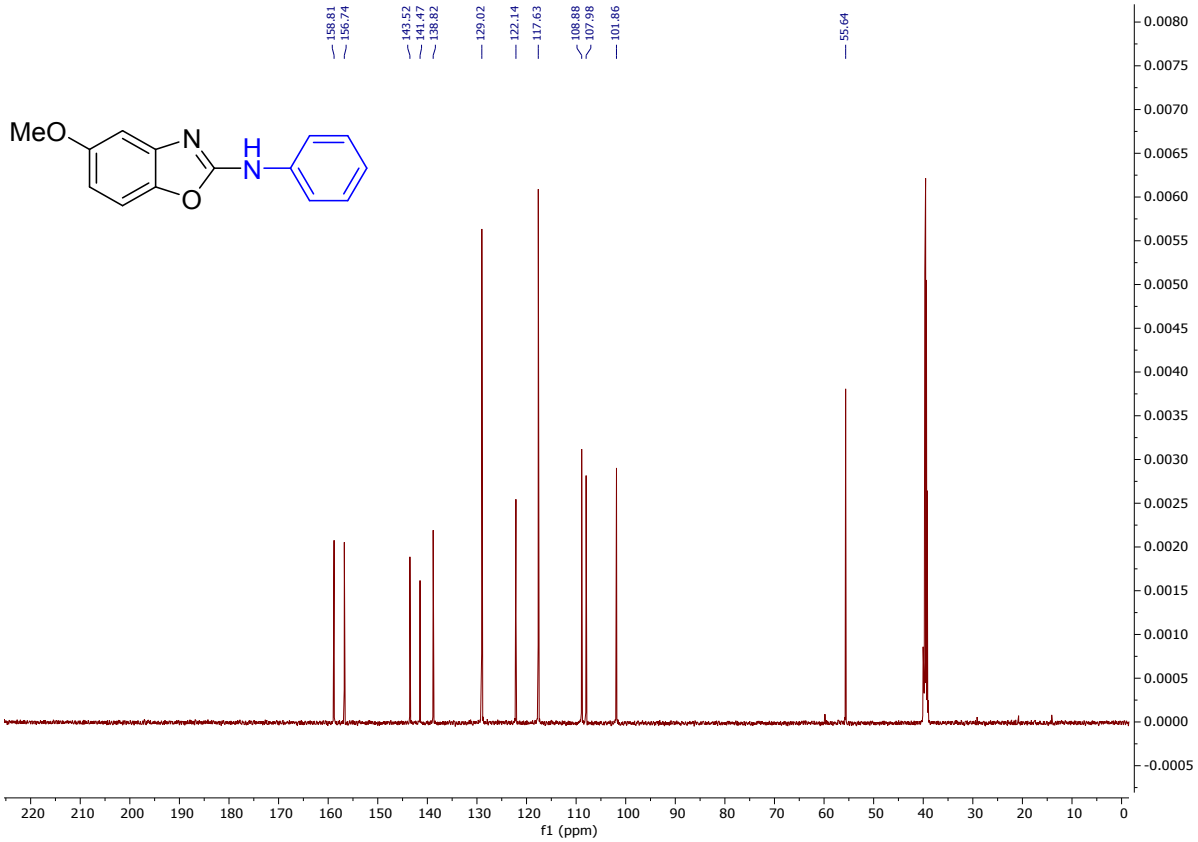


Figure S15 ^{13}C NMR spectra of **6fa** ($(CD_3)_2SO$)

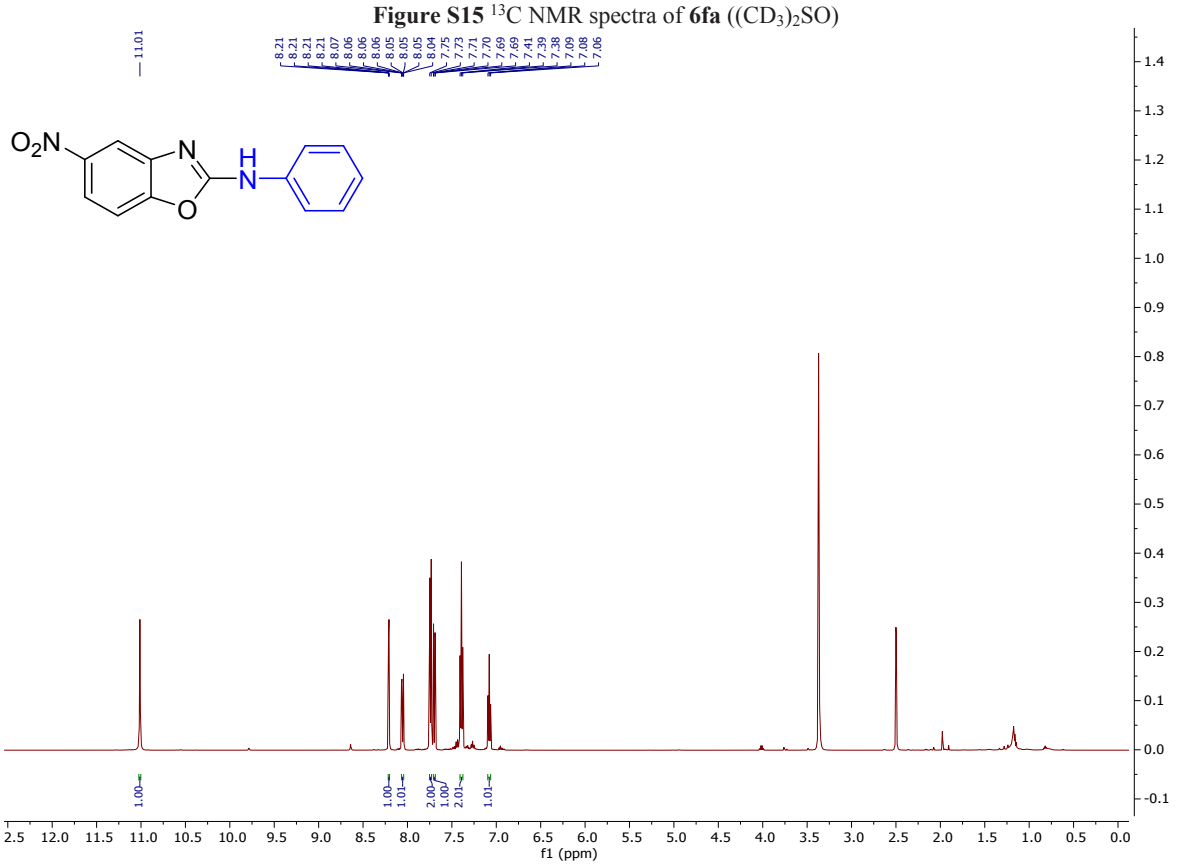


Figure S16 ^{1}H NMR spectra of **6ga** ($(CD_3)_2SO$)

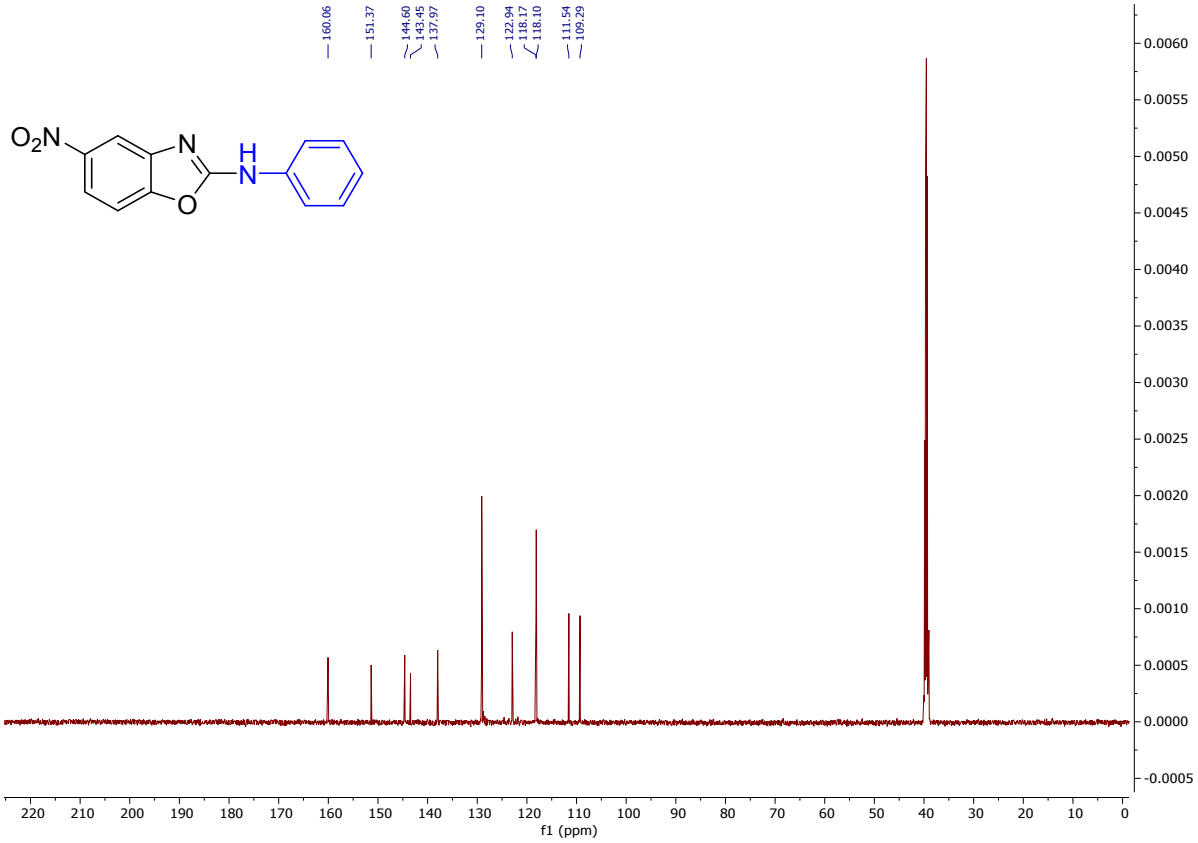


Figure S17 ^{13}C NMR spectra of **6ga** ($(CD_3)_2SO$)

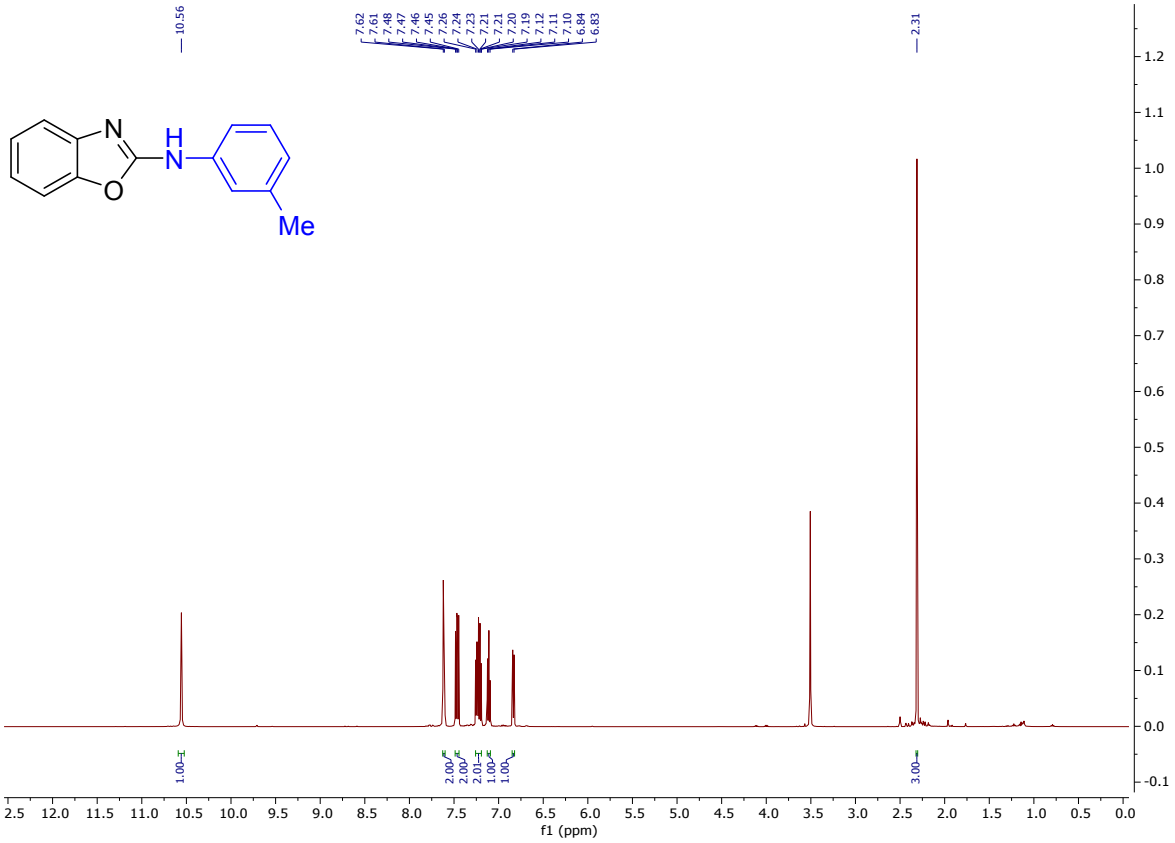


Figure S18 ^{1}H NMR spectra of **6ab** ($(CD_3)_2SO$)

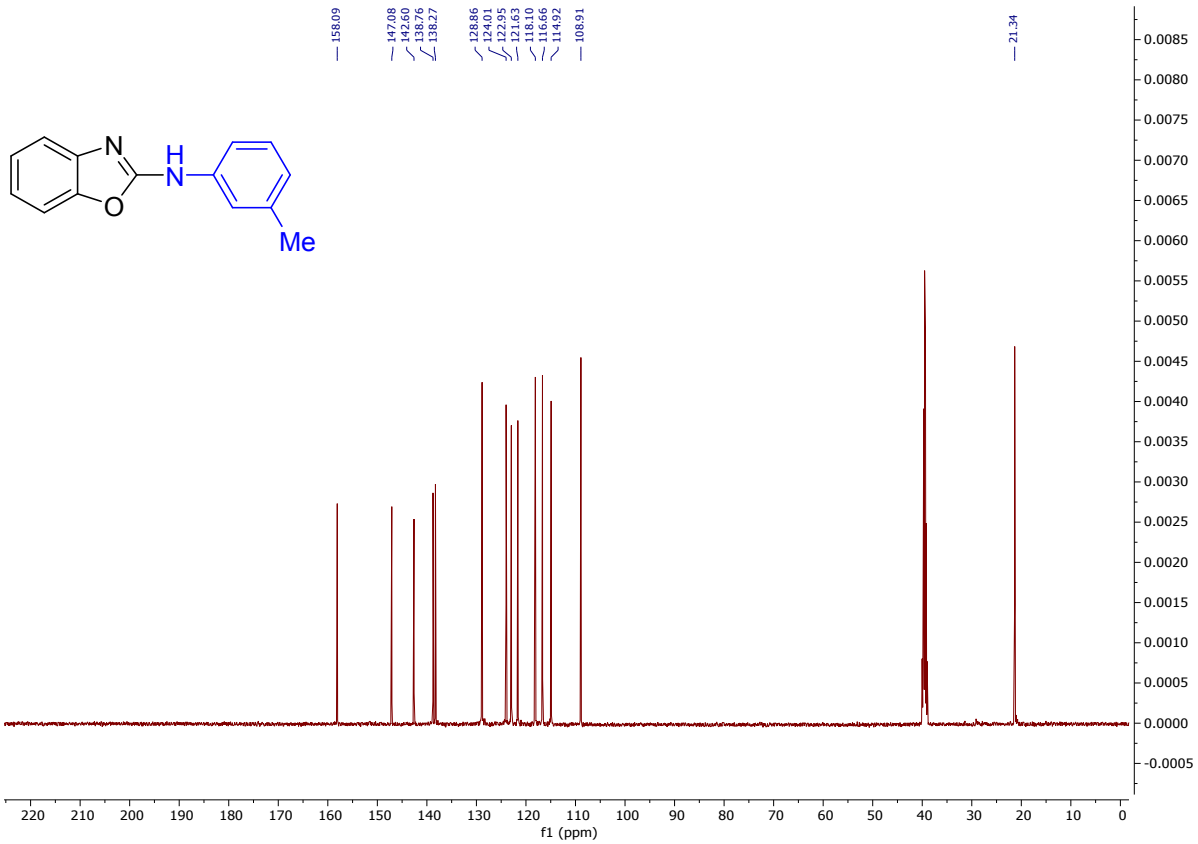


Figure S19 ^{13}C NMR spectra of **6ab** ($(CD_3)_2SO$)

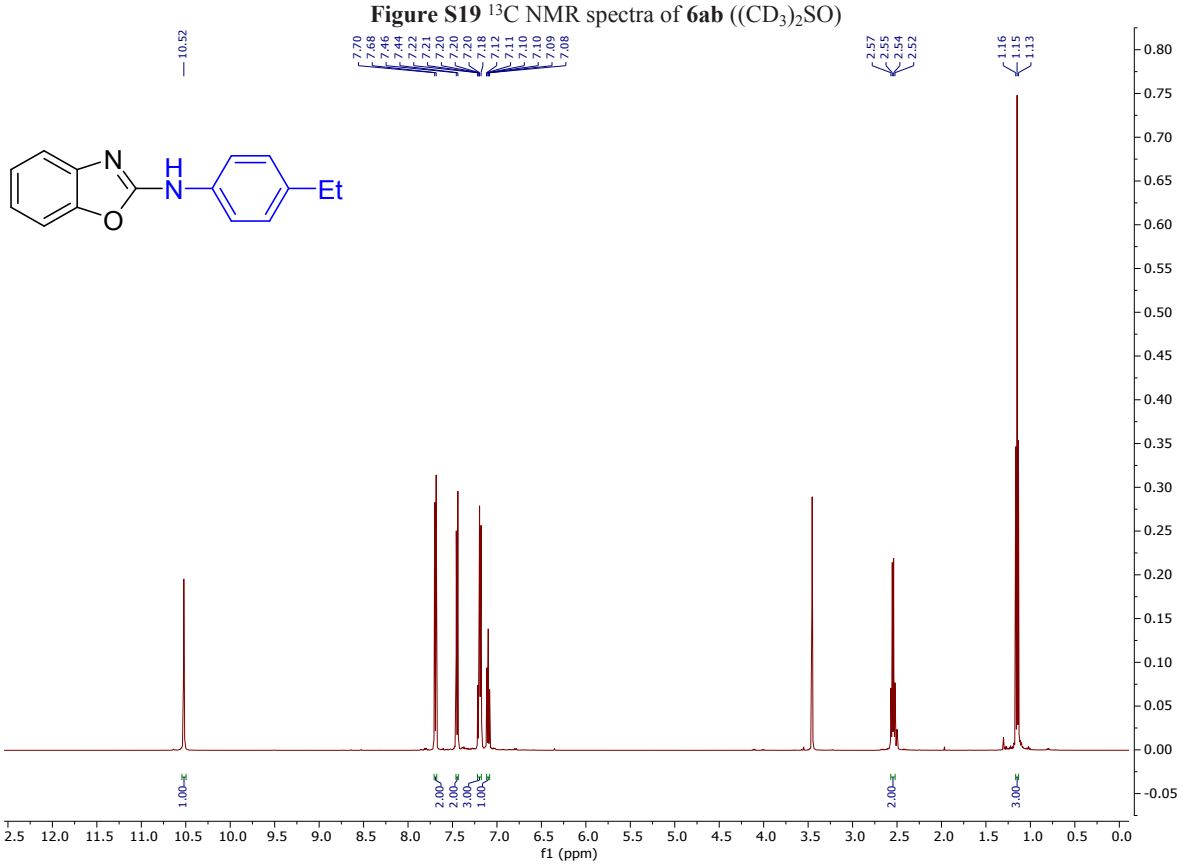


Figure S20 ^{1}H NMR spectra of **6ac** ($(CD_3)_2SO$)

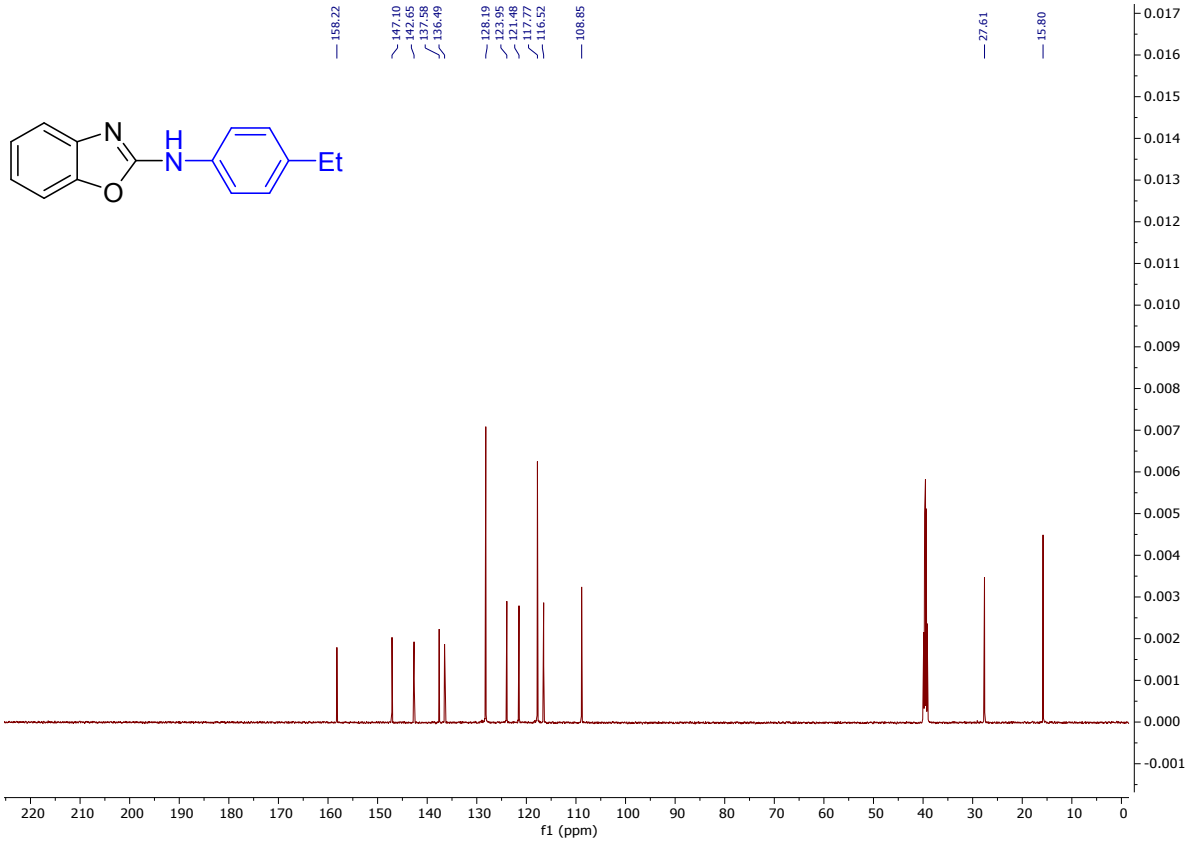


Figure S21 ^{13}C NMR spectra of **6ac** ($(CD_3)_2SO$)

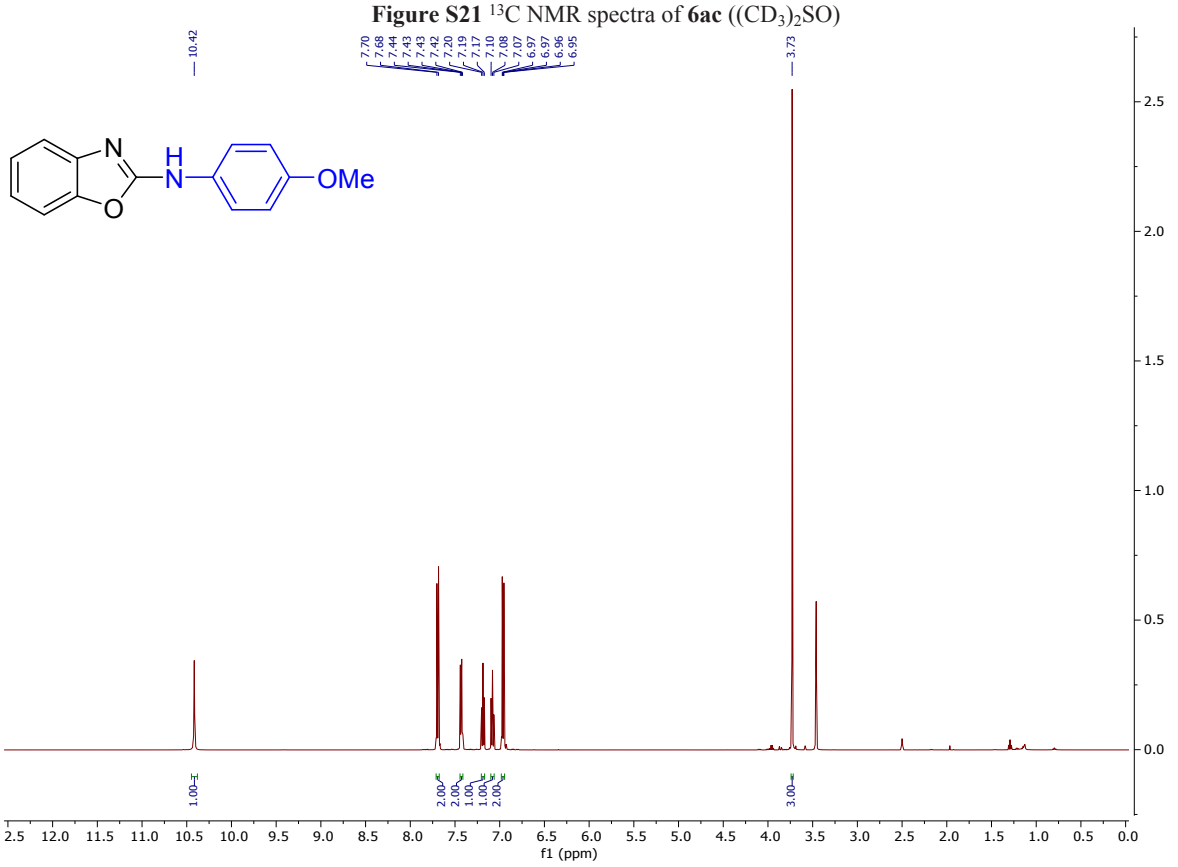


Figure S22 ^{1}H NMR spectra of **6ad** ($(CD_3)_2SO$)

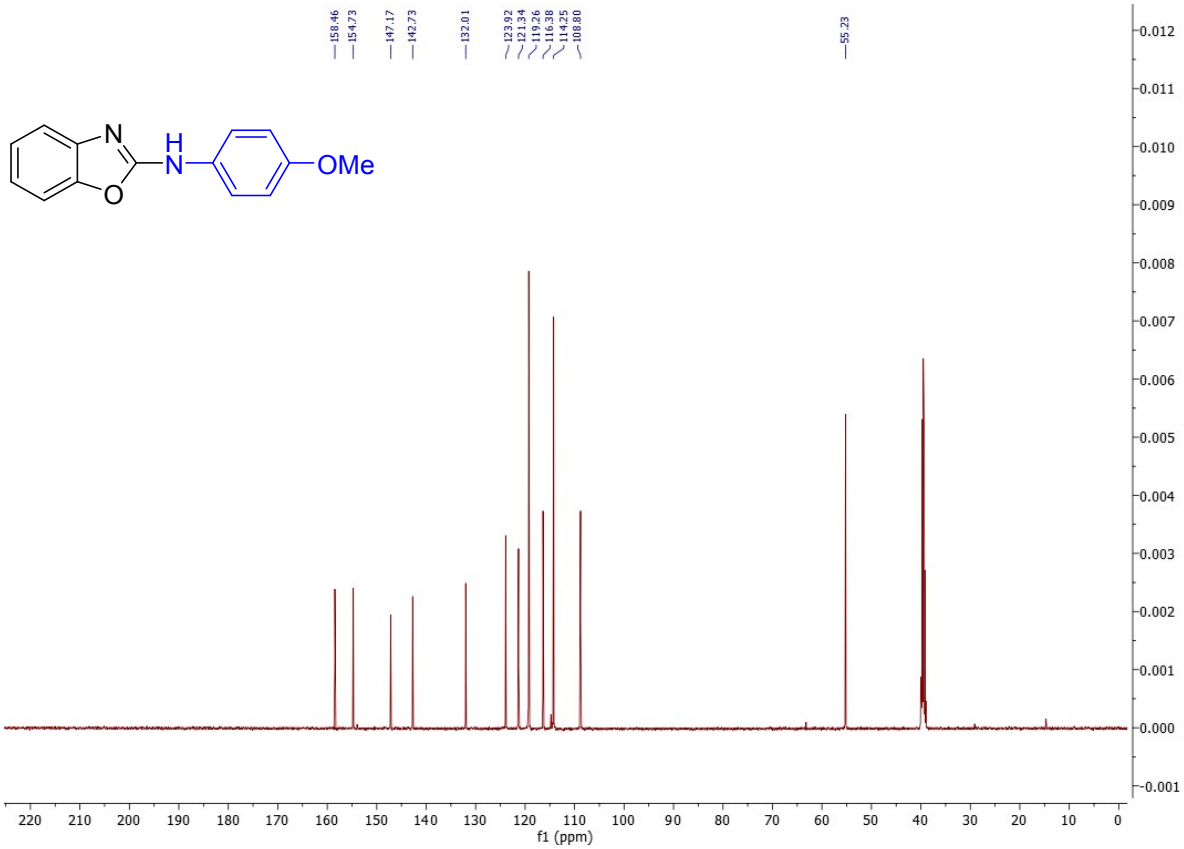


Figure S23 ^{13}C NMR spectra of **6ad** ($(CD_3)_2SO$)

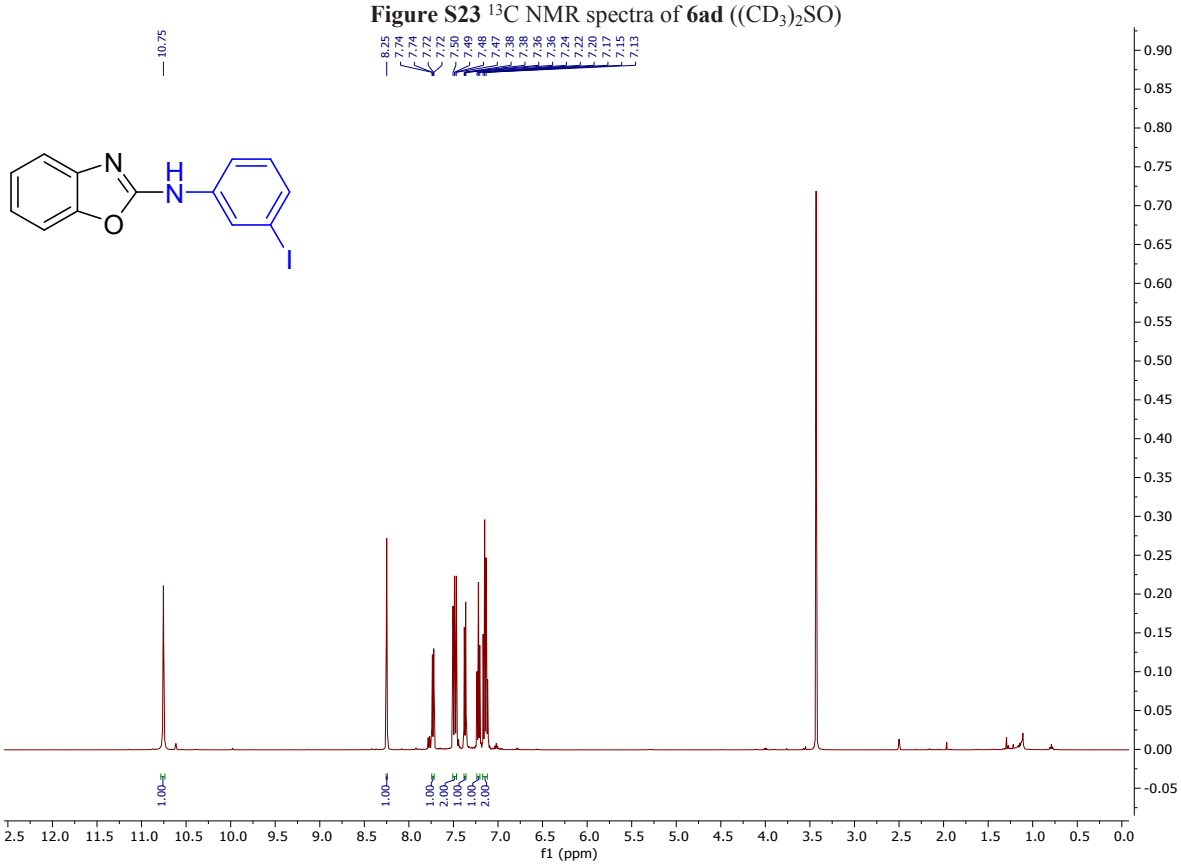


Figure S24 ^{1}H NMR spectra of **6ae** ($(CD_3)_2SO$)

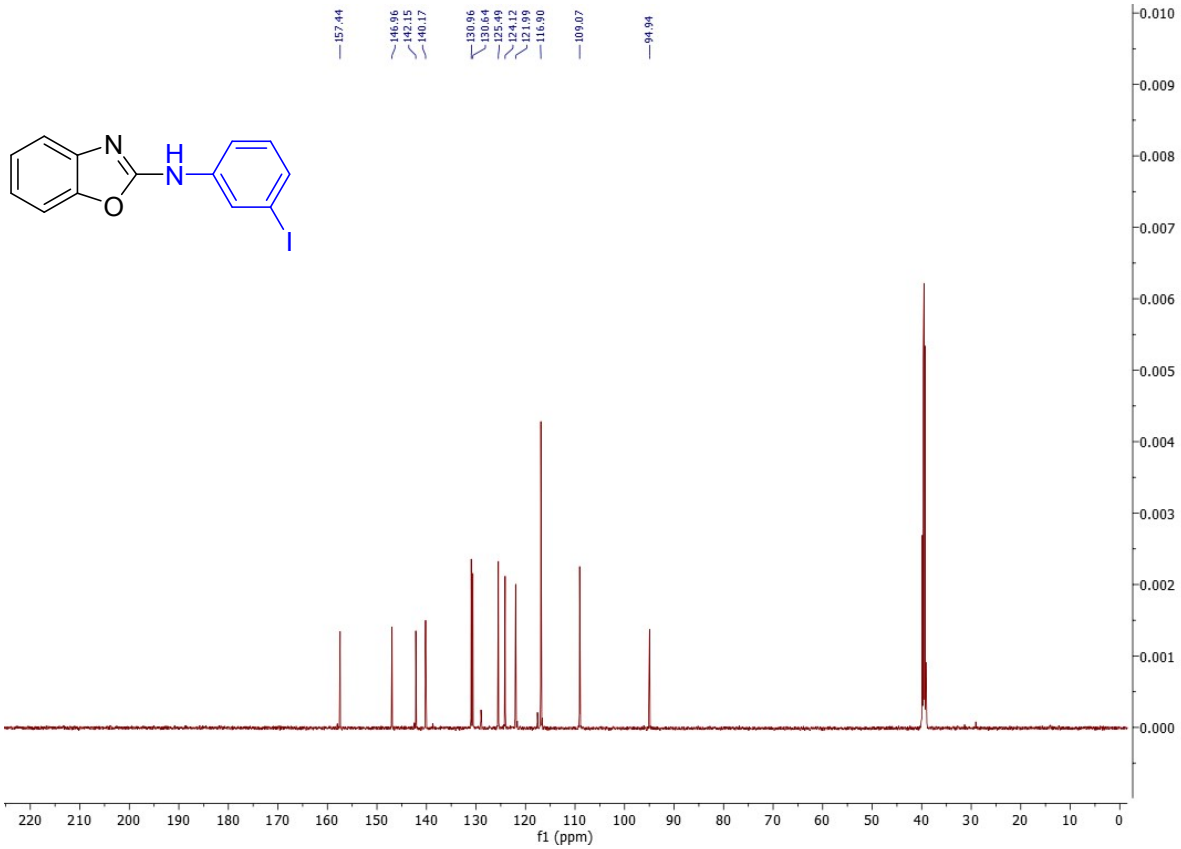


Figure S25 ^{13}C NMR spectra of **6ae** ($(CD_3)_2SO$)

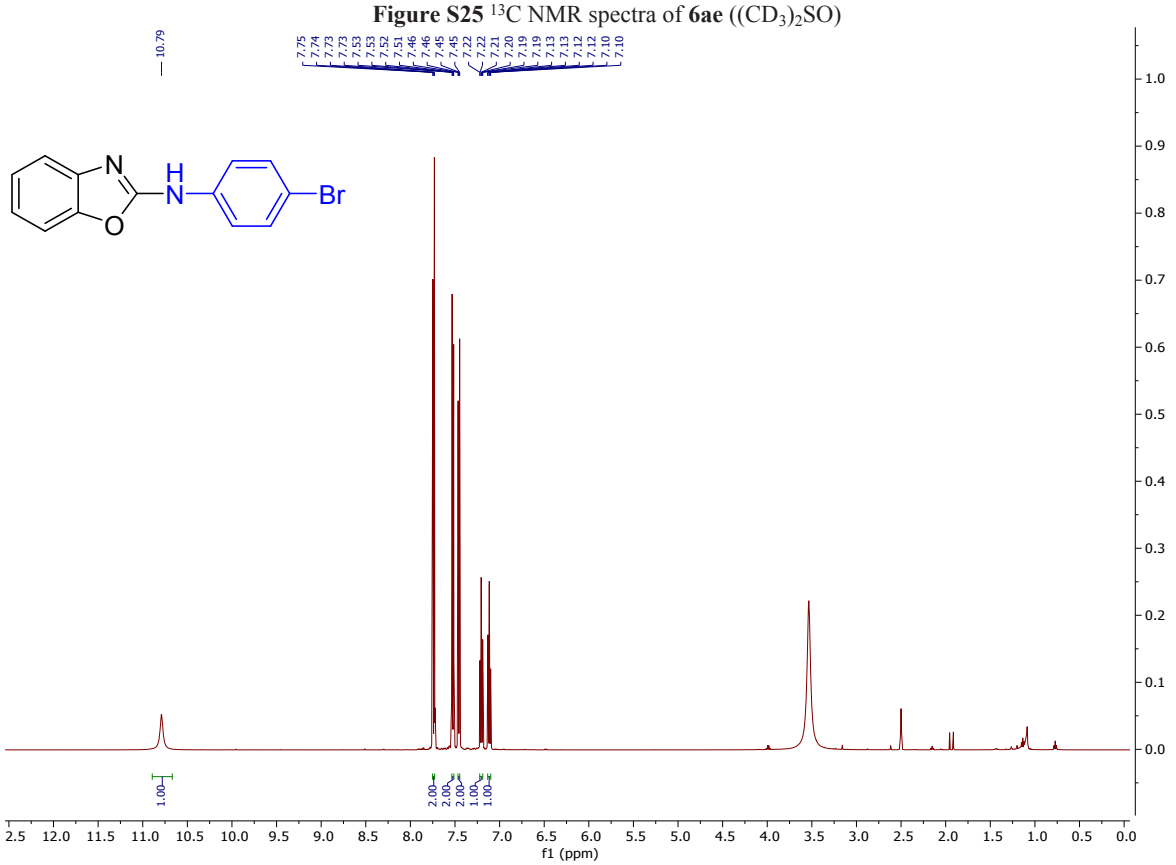


Figure S26 ^{1}H NMR spectra of **6af** ($(CD_3)_2SO$)

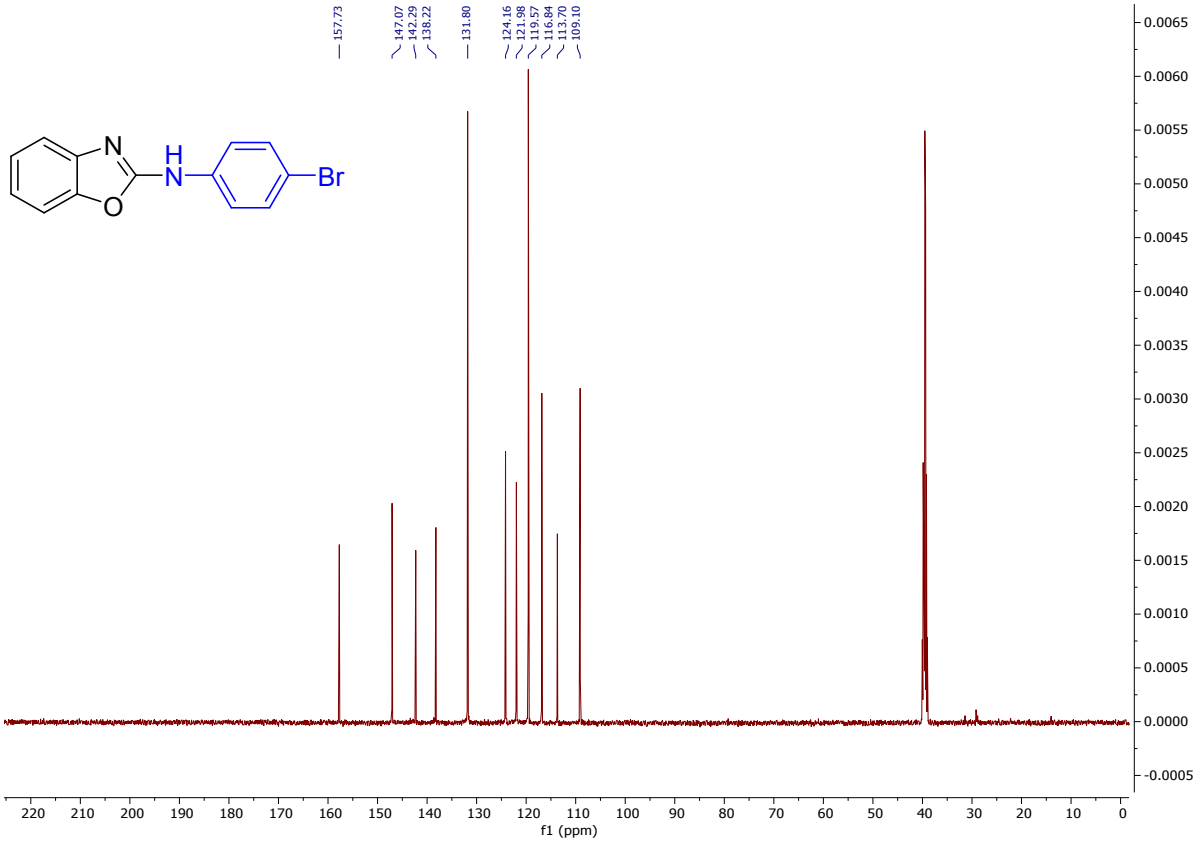


Figure S27 ^{13}C NMR spectra of **6af** ($(CD_3)_2SO$)

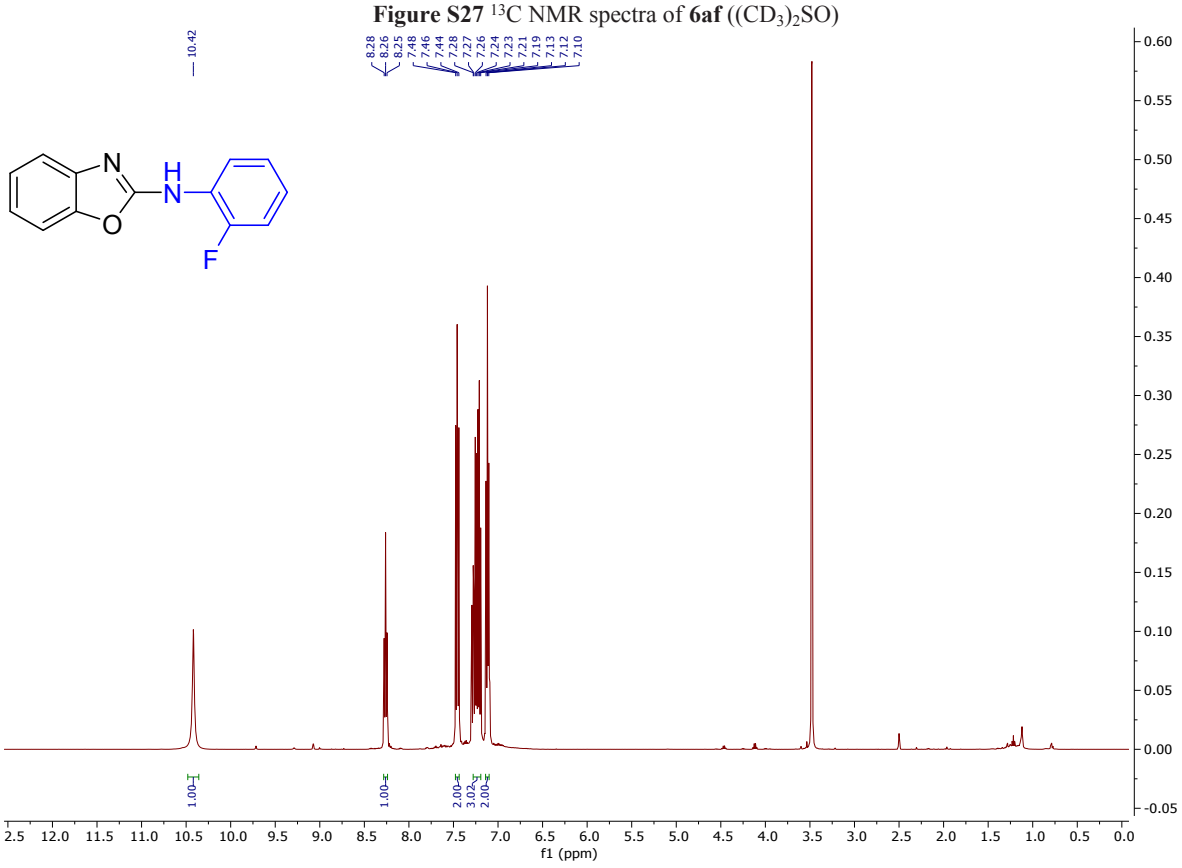


Figure S28 ^{1}H NMR spectra of **6ag** ($(CD_3)_2SO$)

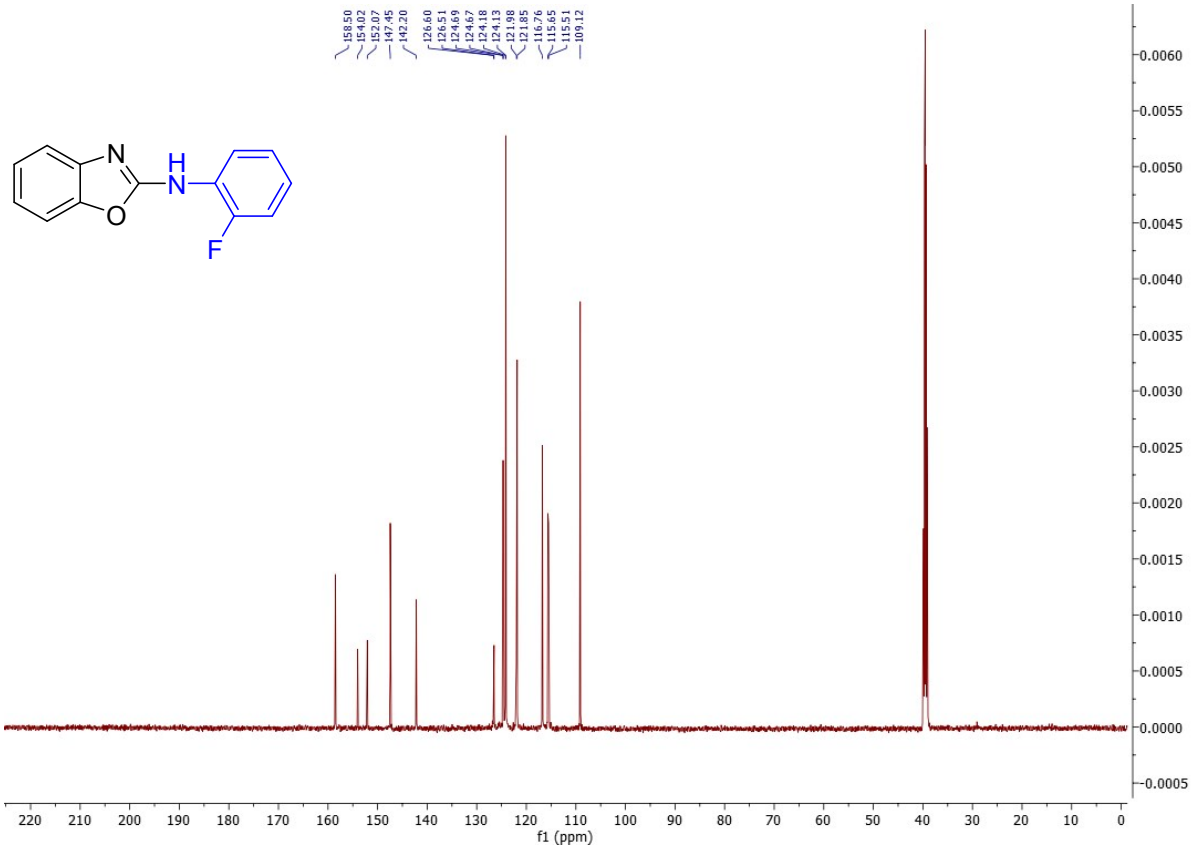


Figure S29 ^{13}C NMR spectra of **6ag** ($(CD_3)_2SO$)

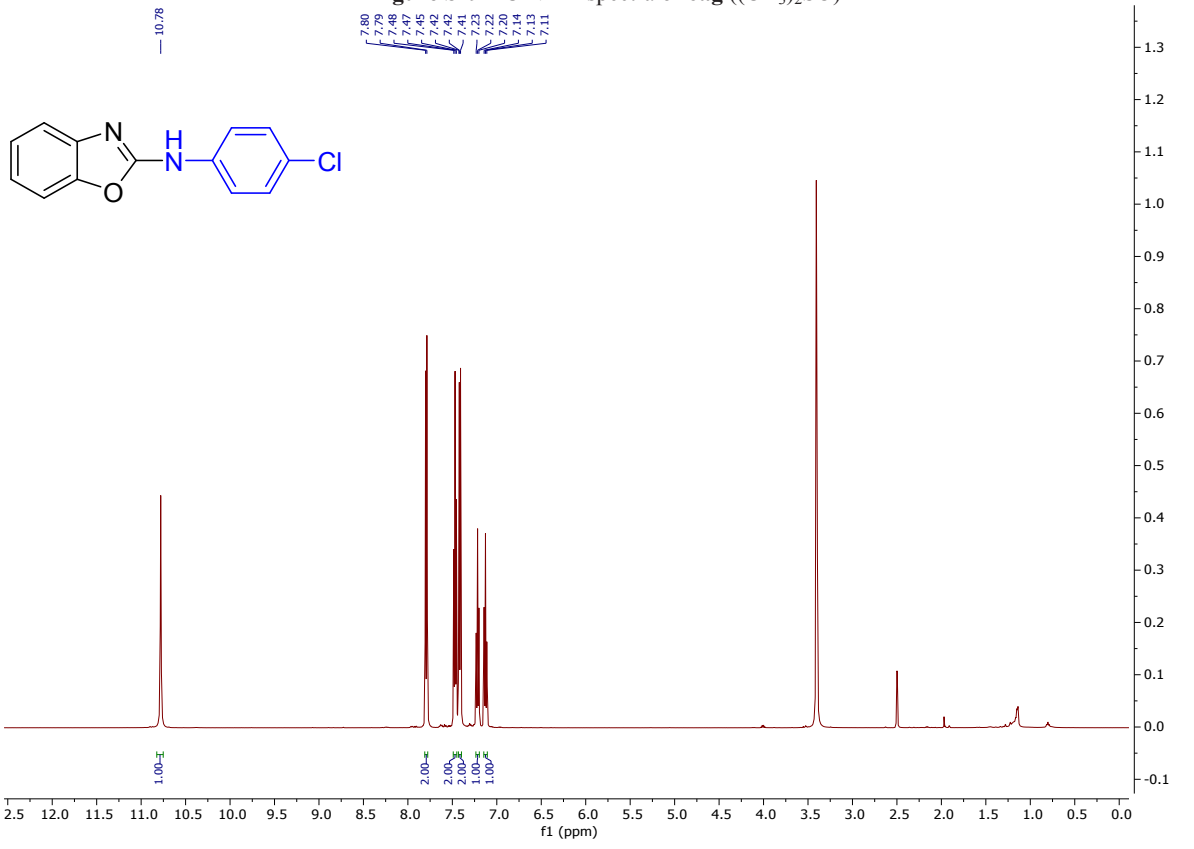


Figure S30 ^{1}H NMR spectra of **6ah** ($(CD_3)_2SO$)

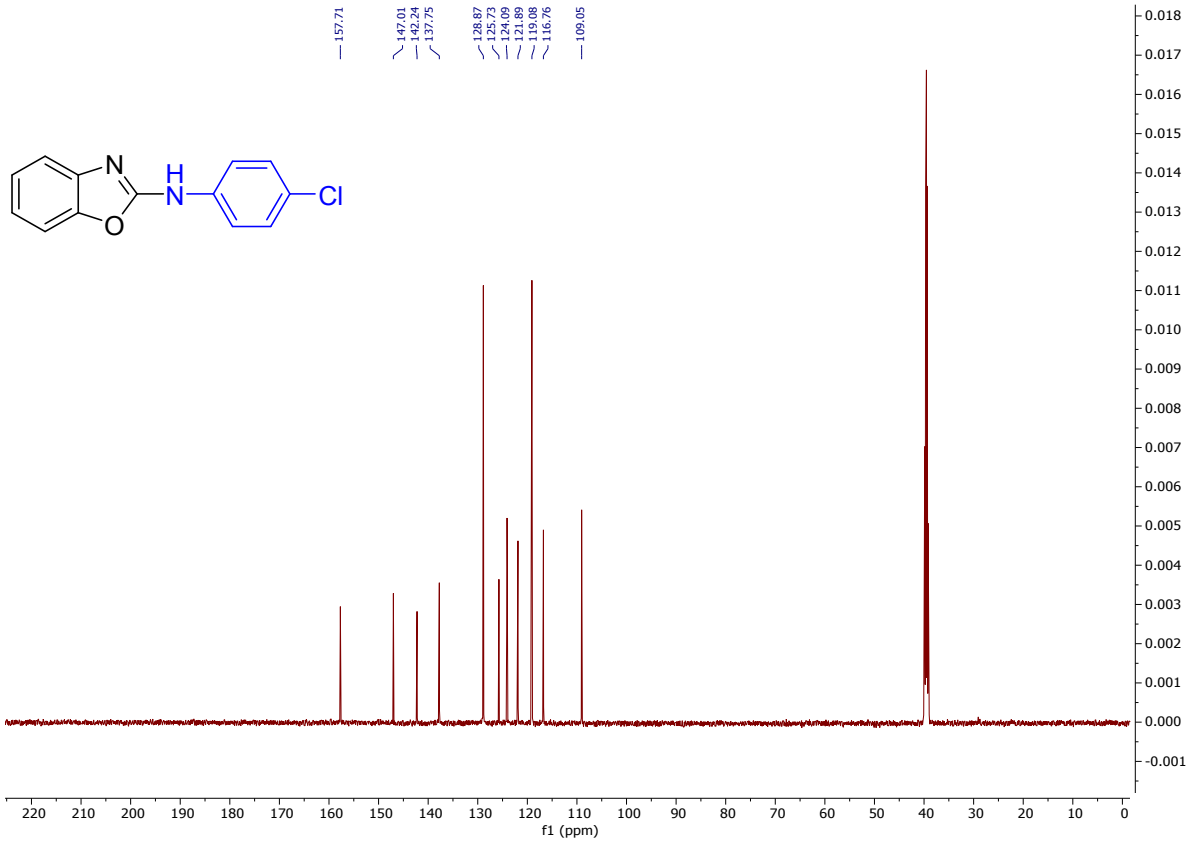


Figure S31 ^{13}C NMR spectra of **6ah** ($(CD_3)_2SO$)

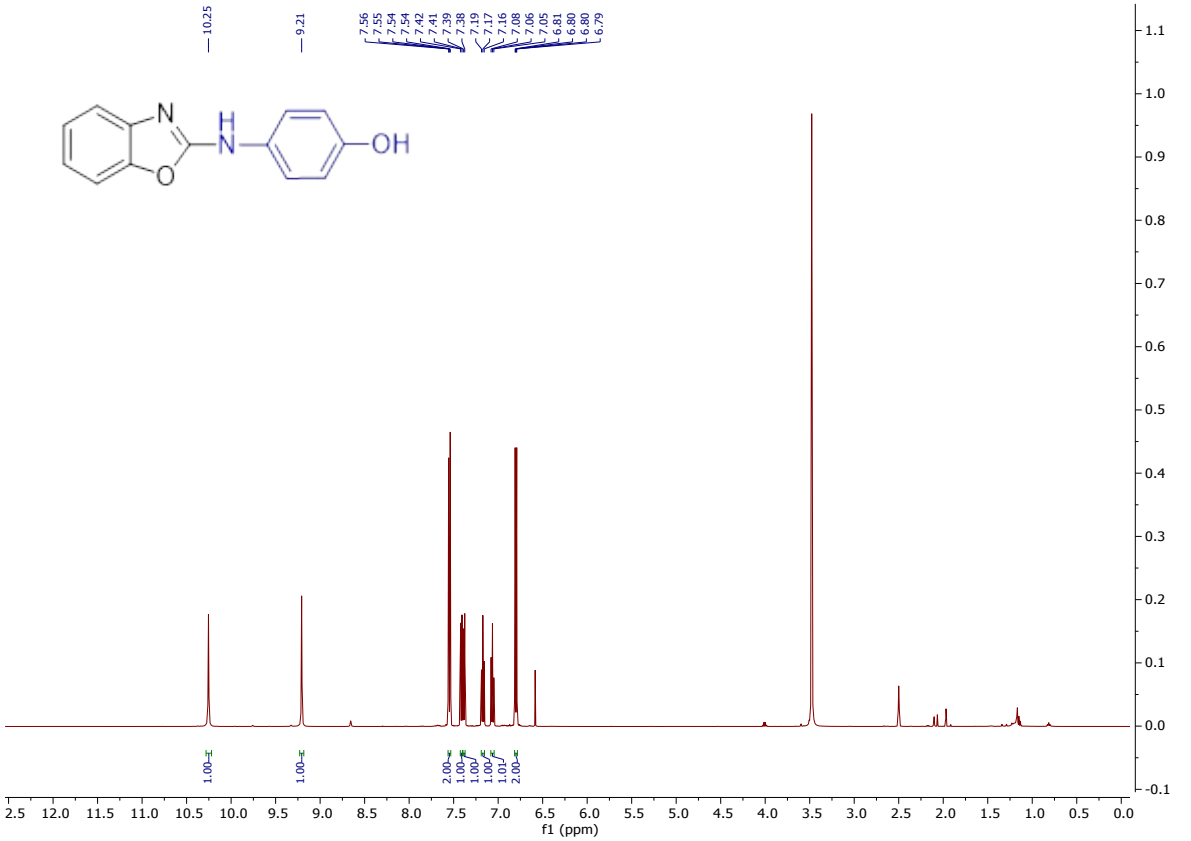


Figure S32 ^{1}H NMR spectra of **6ai** ($(CD_3)_2SO$)

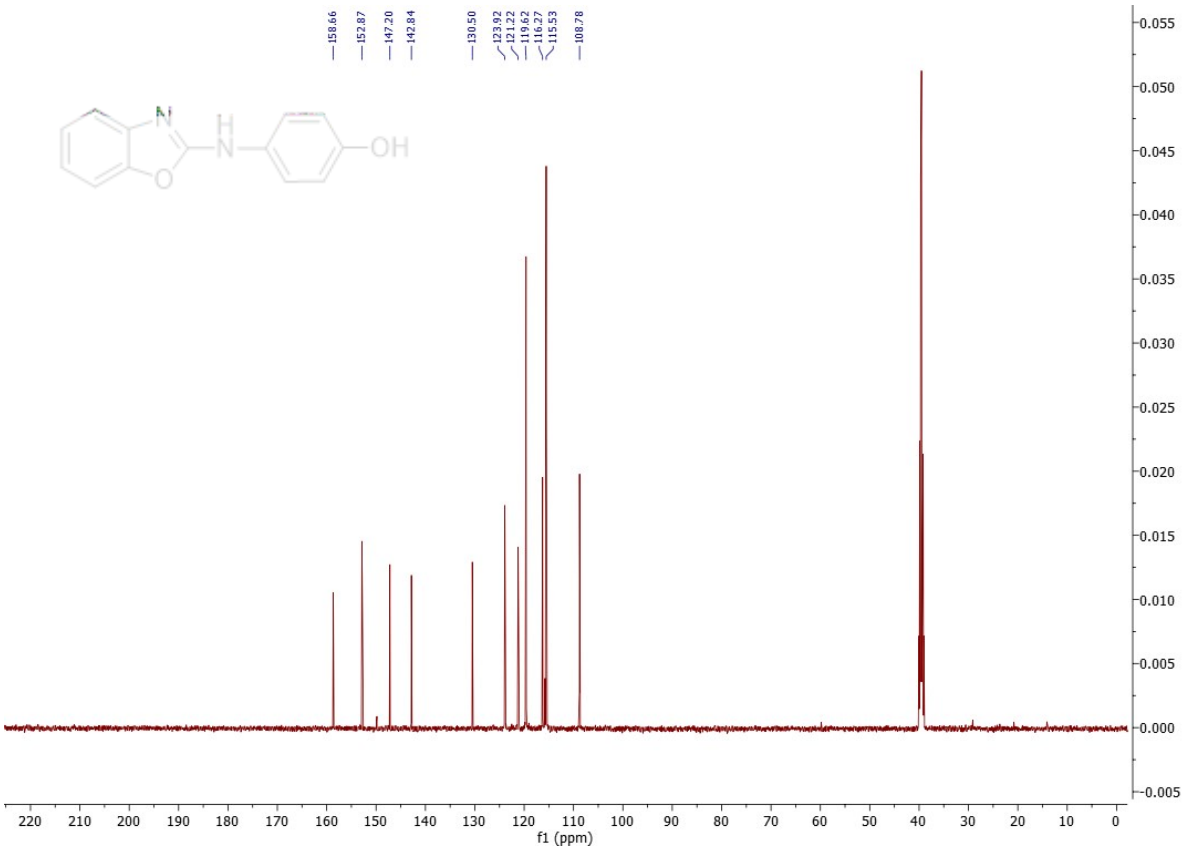


Figure S33 ^{13}C NMR spectra of **6ai** ($(CD_3)_2SO$)

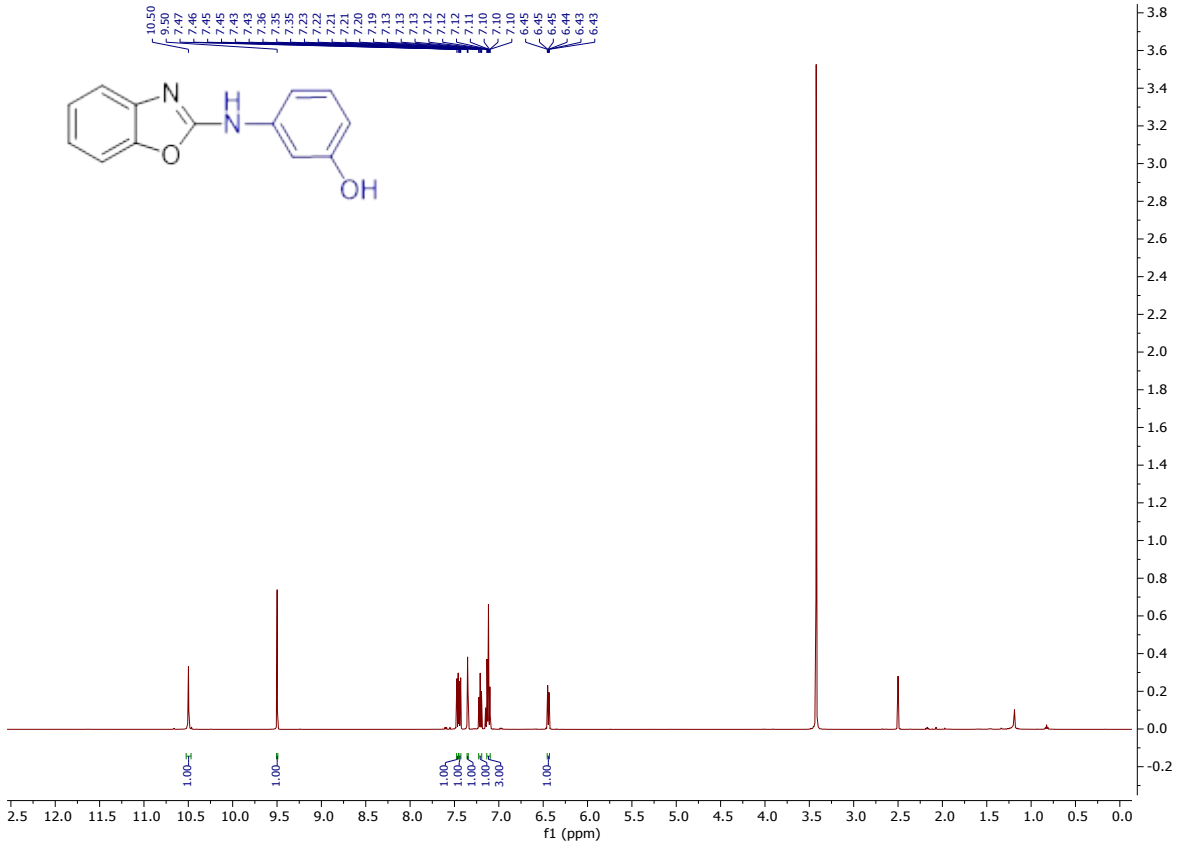


Figure S34 ^{1}H NMR spectra of **6aj** ($(CD_3)_2SO$)

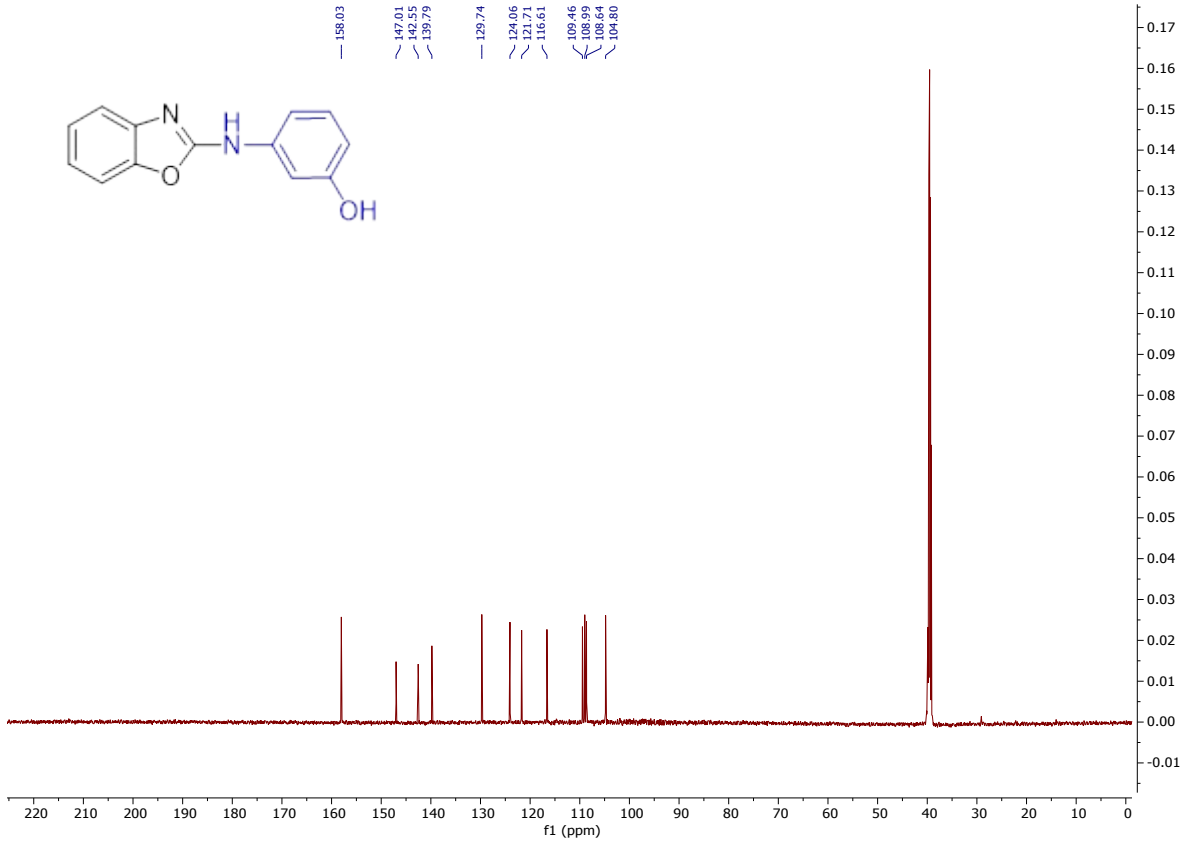


Figure S35 ^{13}C NMR spectra of **6aj** ($(CD_3)_2SO$)

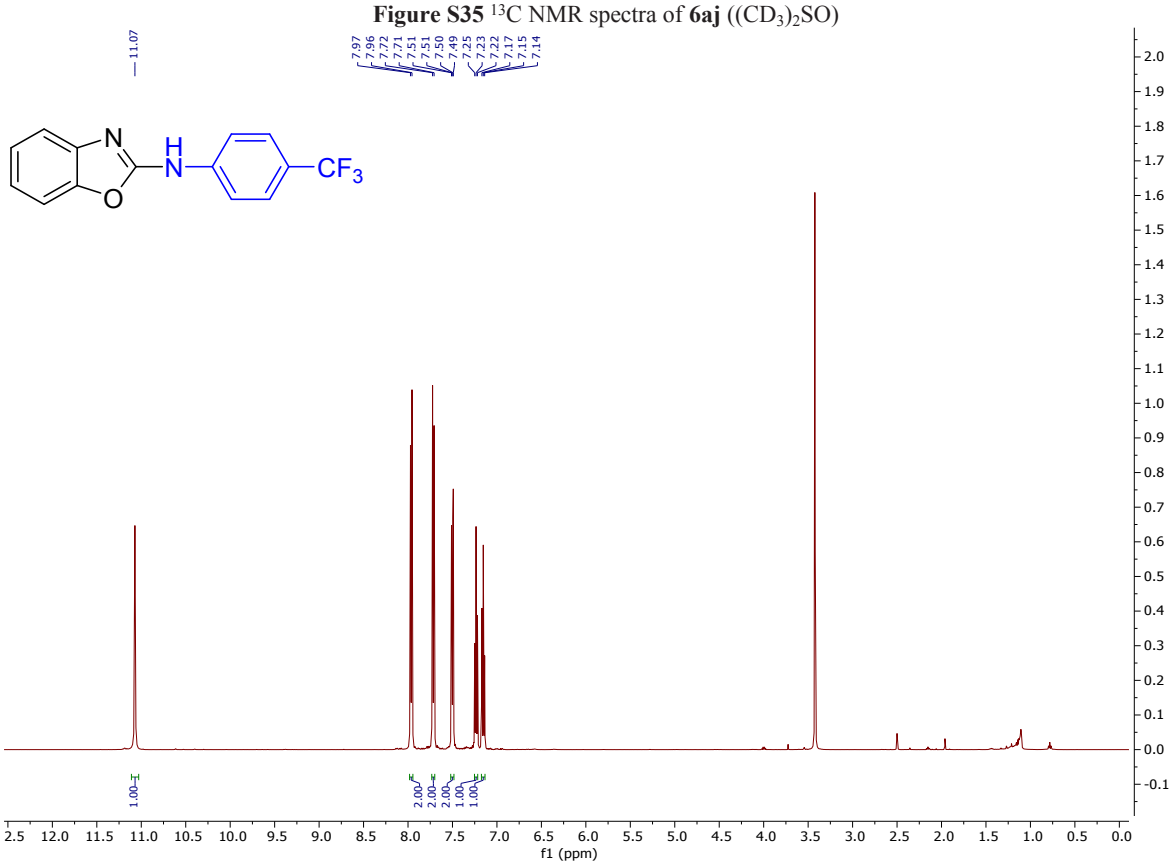


Figure S36 ^{1}H NMR spectra of **6ak** ($(CD_3)_2SO$)

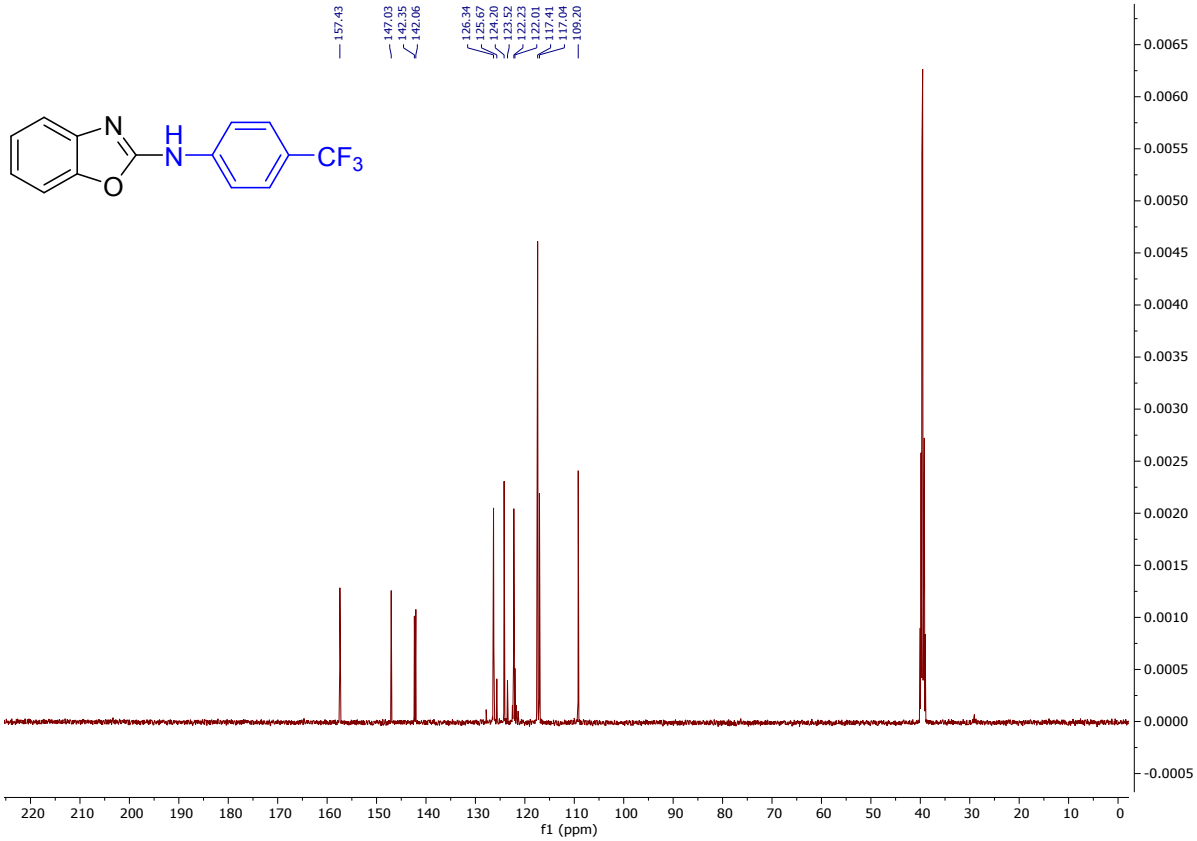


Figure S37 ^{13}C NMR spectra of **6ak** ($(CD_3)_2SO$)

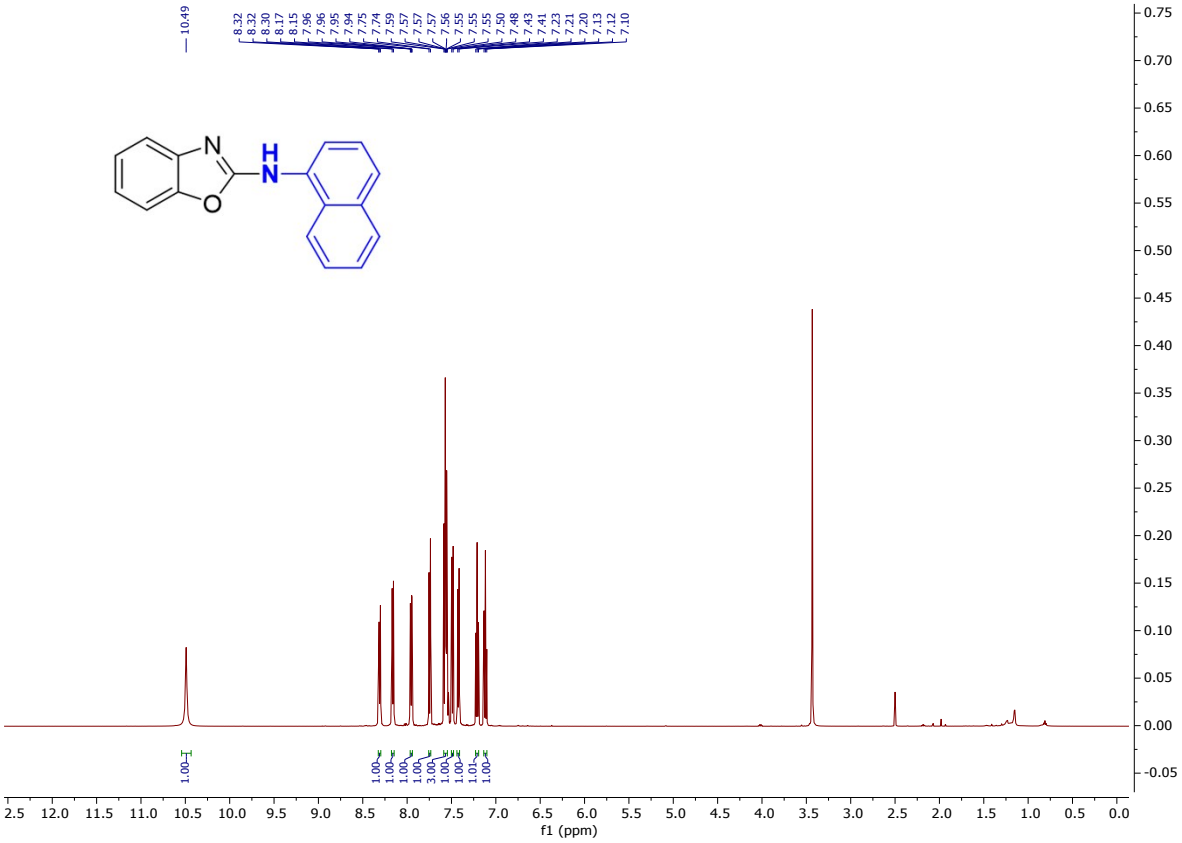


Figure S38 ^{1}H NMR spectra of **6al** ($(CD_3)_2SO$)

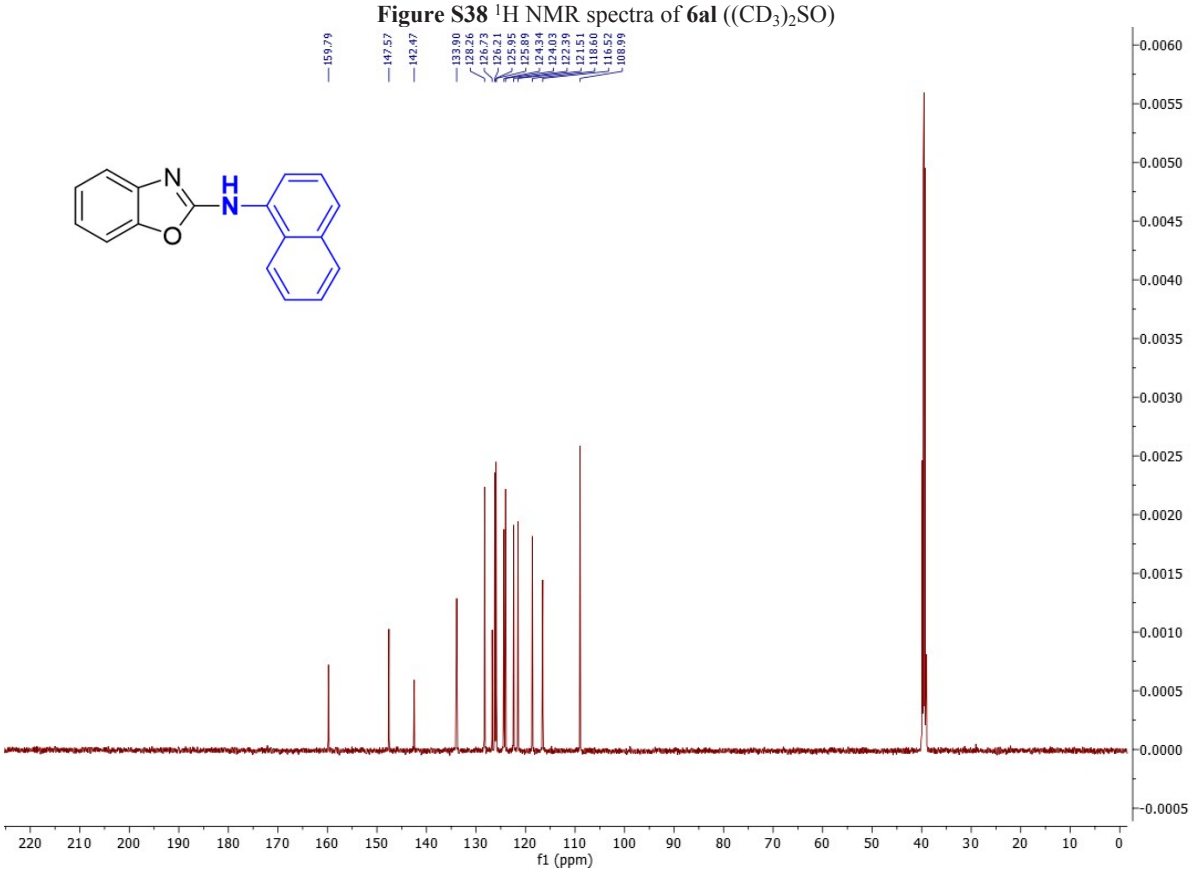


Figure S39 ^{13}C NMR spectra of **6al** ($(CD_3)_2SO$)

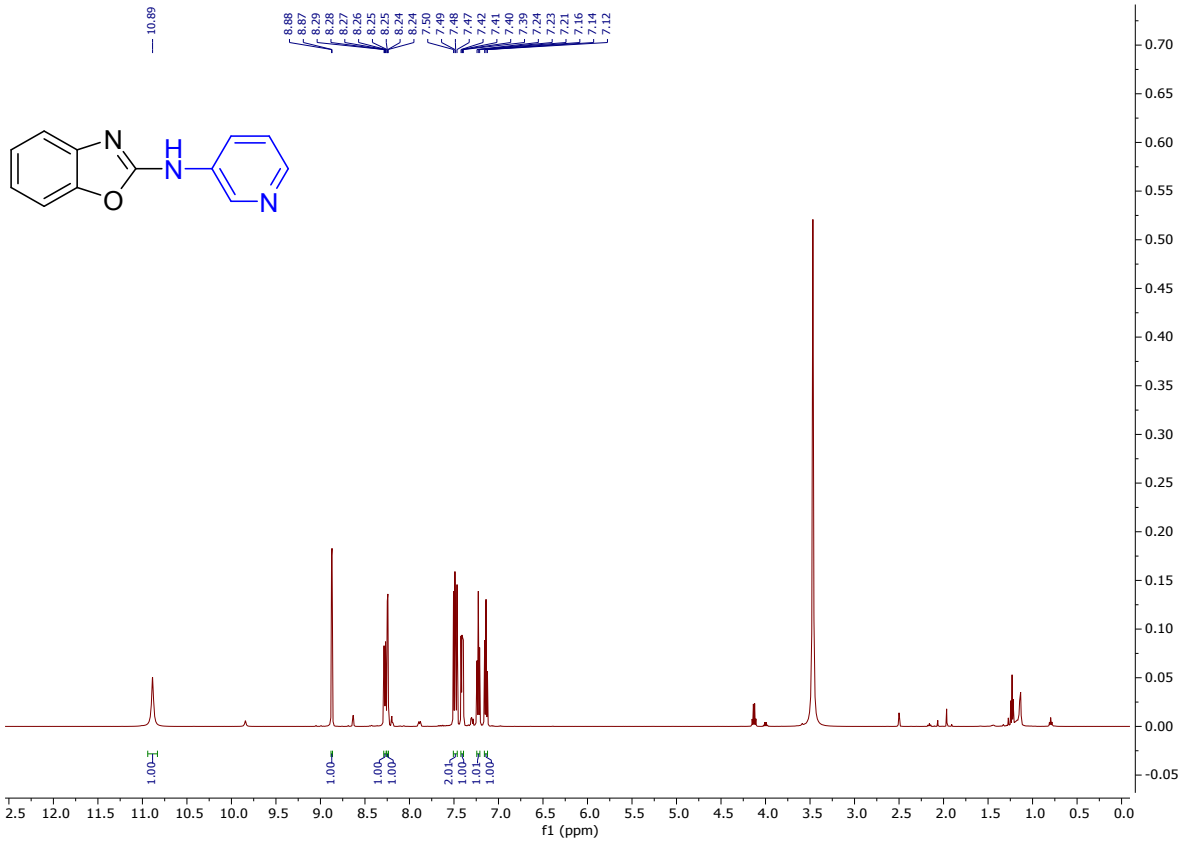


Figure S40 ^{1}H NMR spectra of **6am** ($(CD_3)_2SO$)

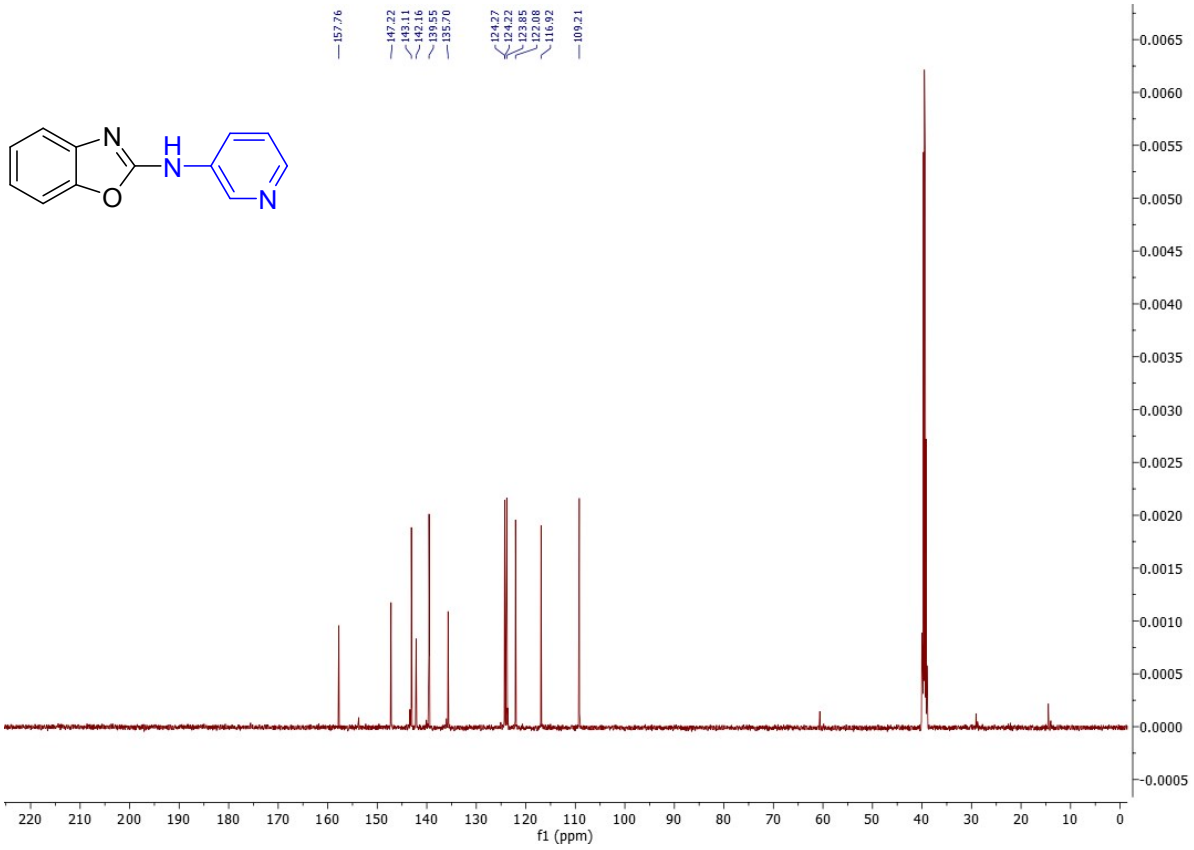


Figure S41 ^{13}C NMR spectra of **6am** ($(CD_3)_2SO$)

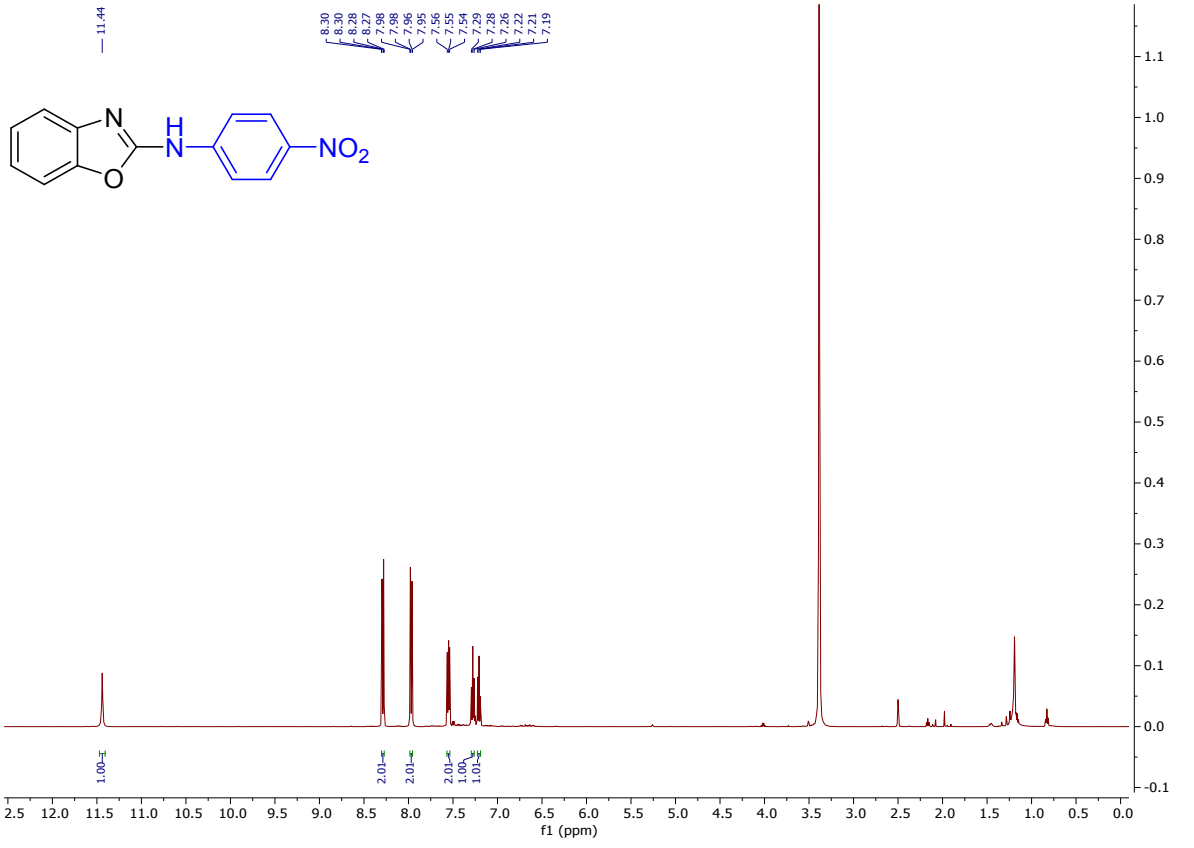


Figure S42 ^{1}H NMR spectra of **6an** ($(CD_3)_2SO$)

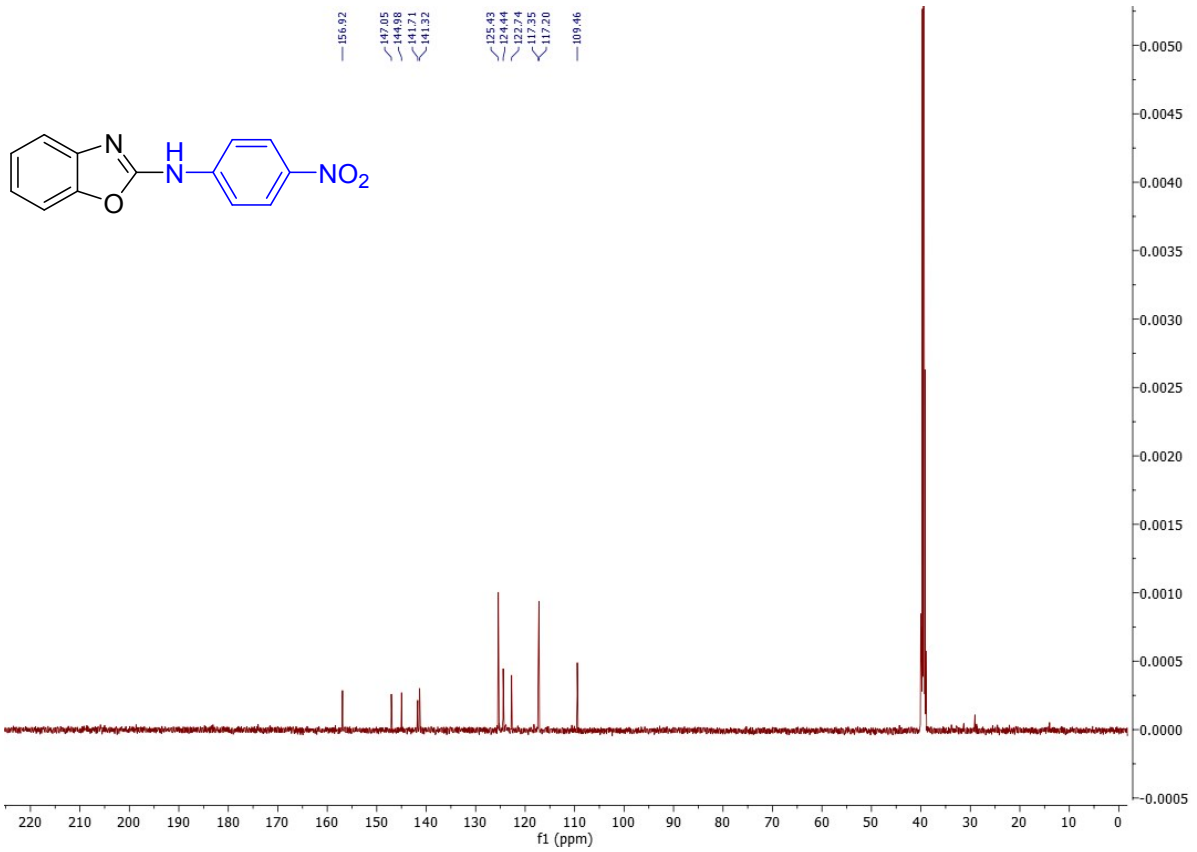


Figure S43 ^{13}C NMR spectra of **6an** ($(CD_3)_2SO$)

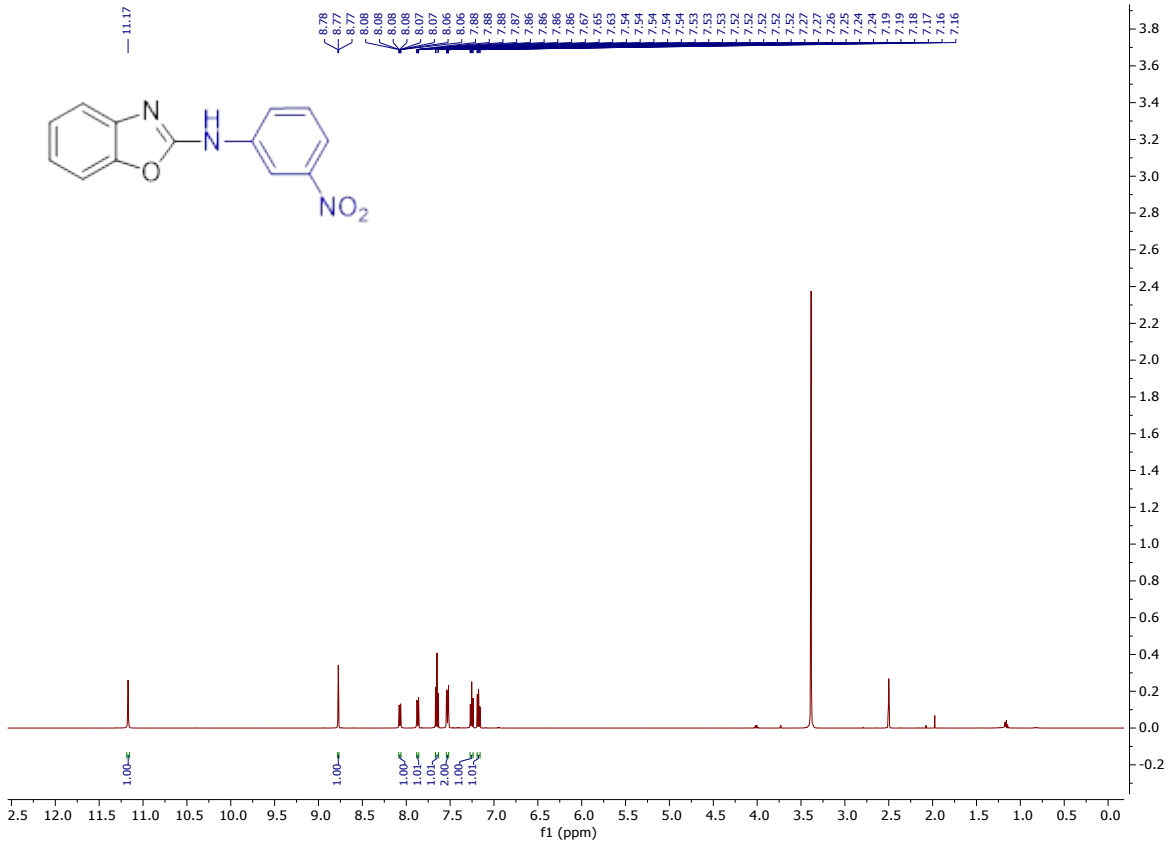


Figure S44 ^{1}H NMR spectra of **6ao** ($(CD_3)_2SO$)

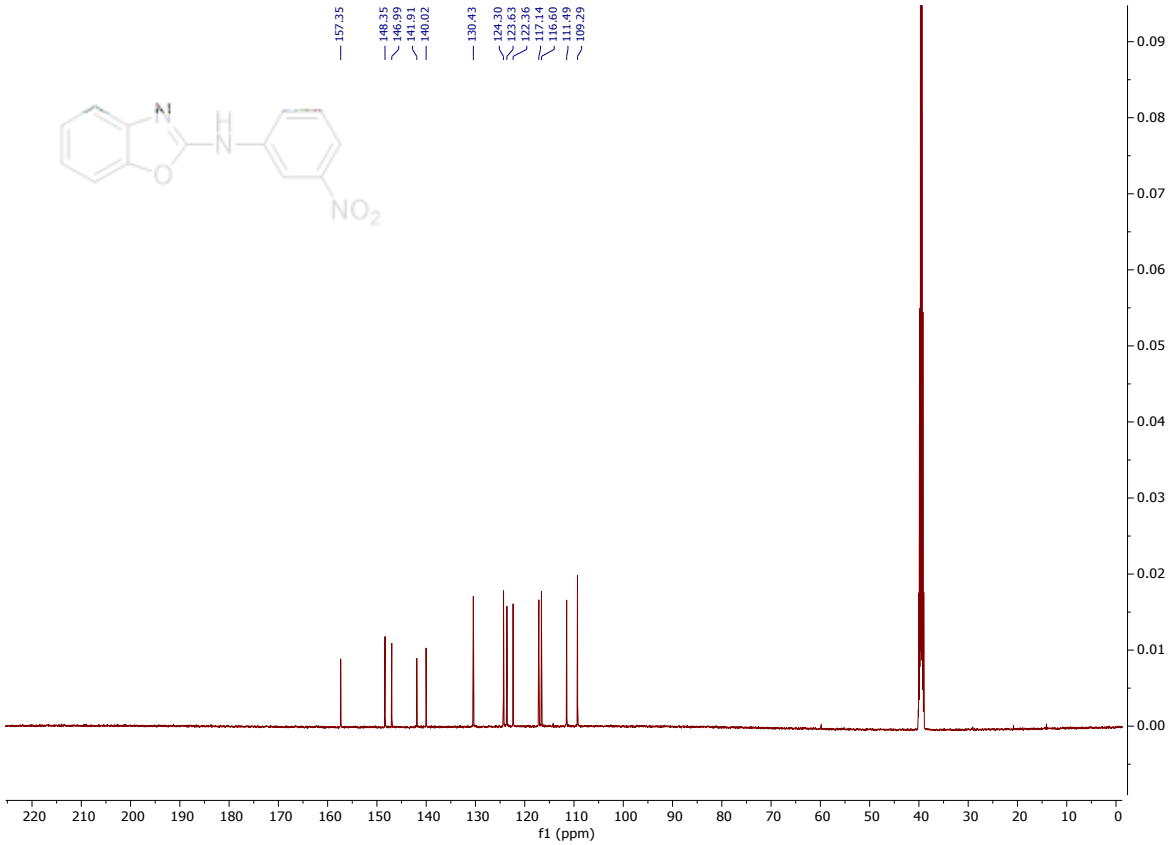


Figure S45 ^{13}C NMR spectra of **6ao** ($(CD_3)_2SO$)

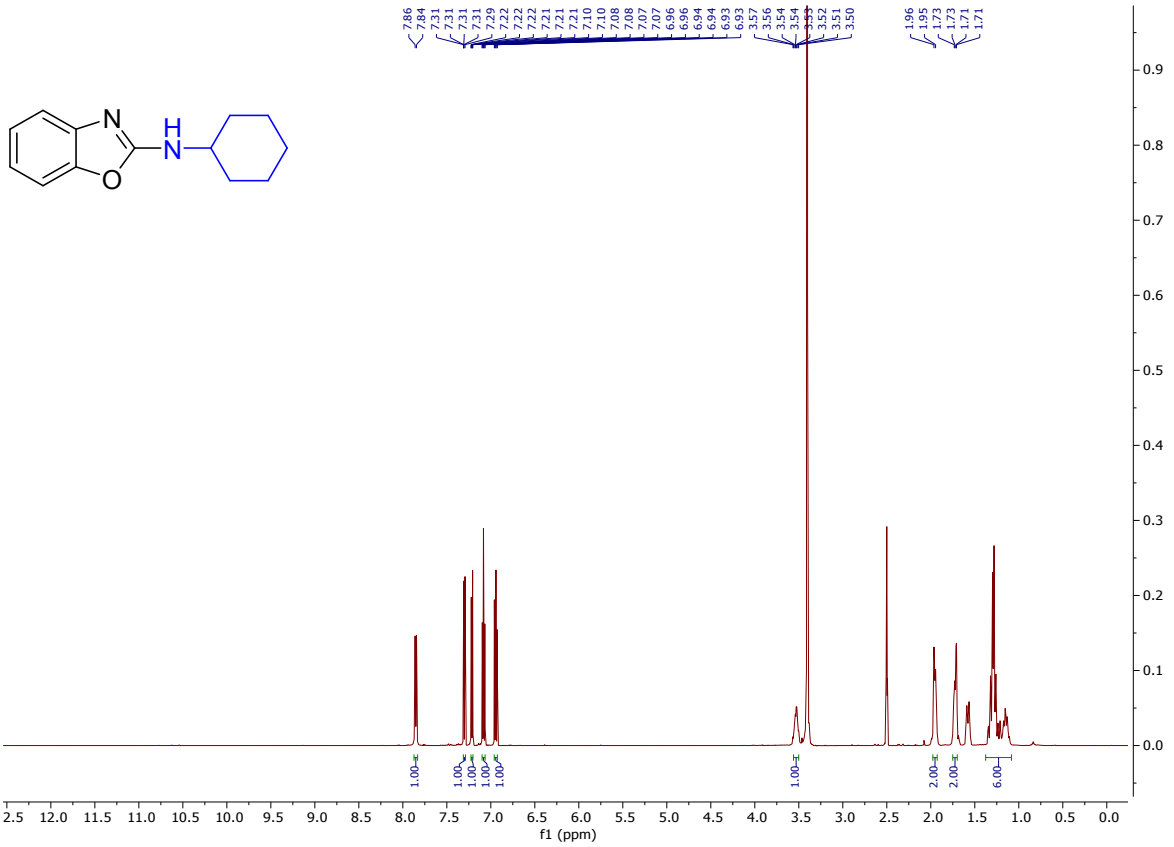


Figure S46 ^{1}H NMR spectra of **6ap** (DMSO)

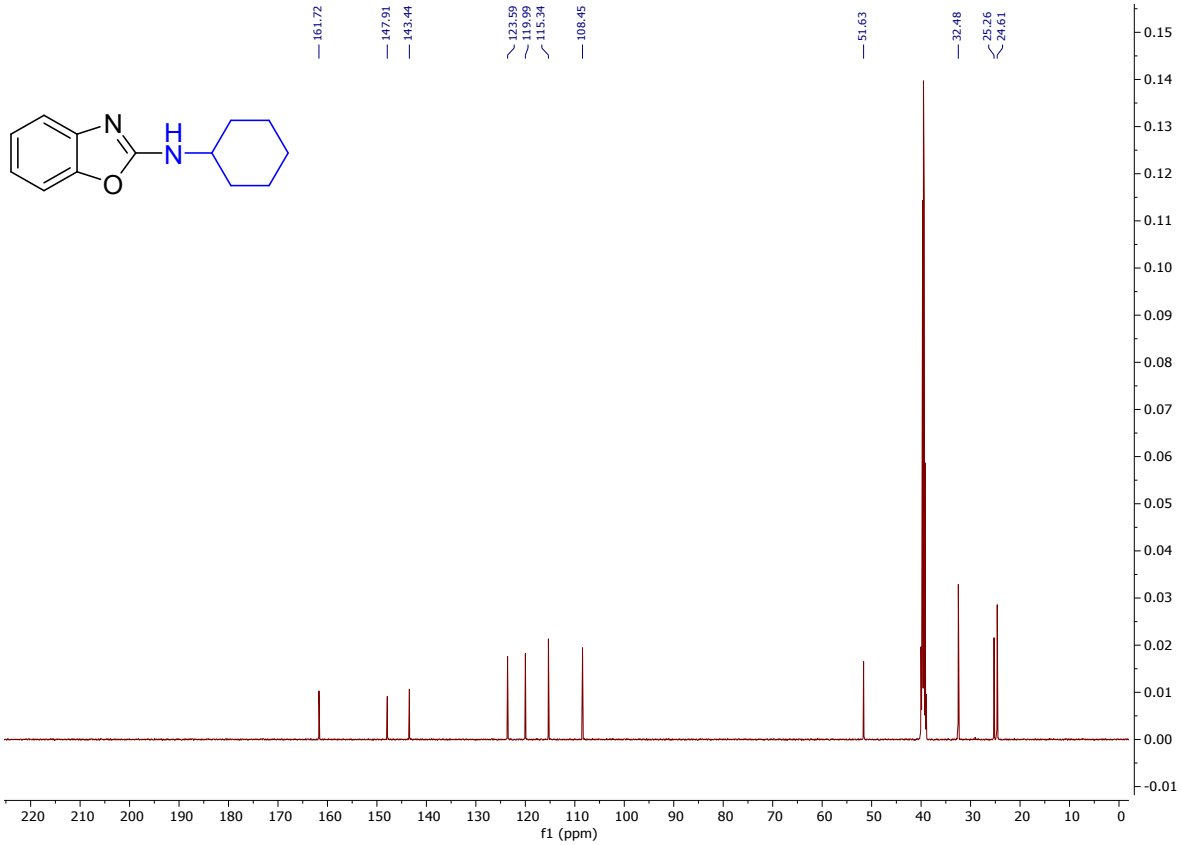


Figure S47 ^{13}C NMR spectra of **6ap** (DMSO)

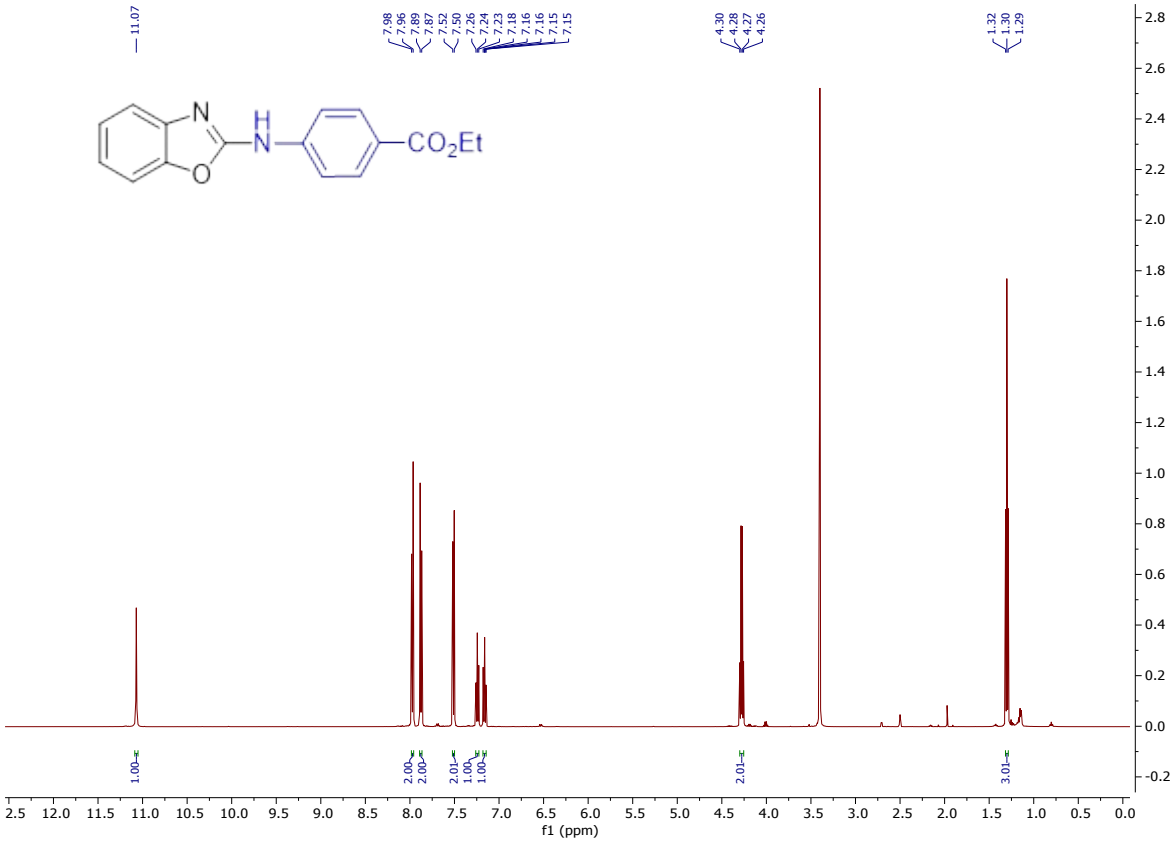


Figure S48 ^{1}H NMR spectra of **6aq** ($(CD_3)_2SO$)

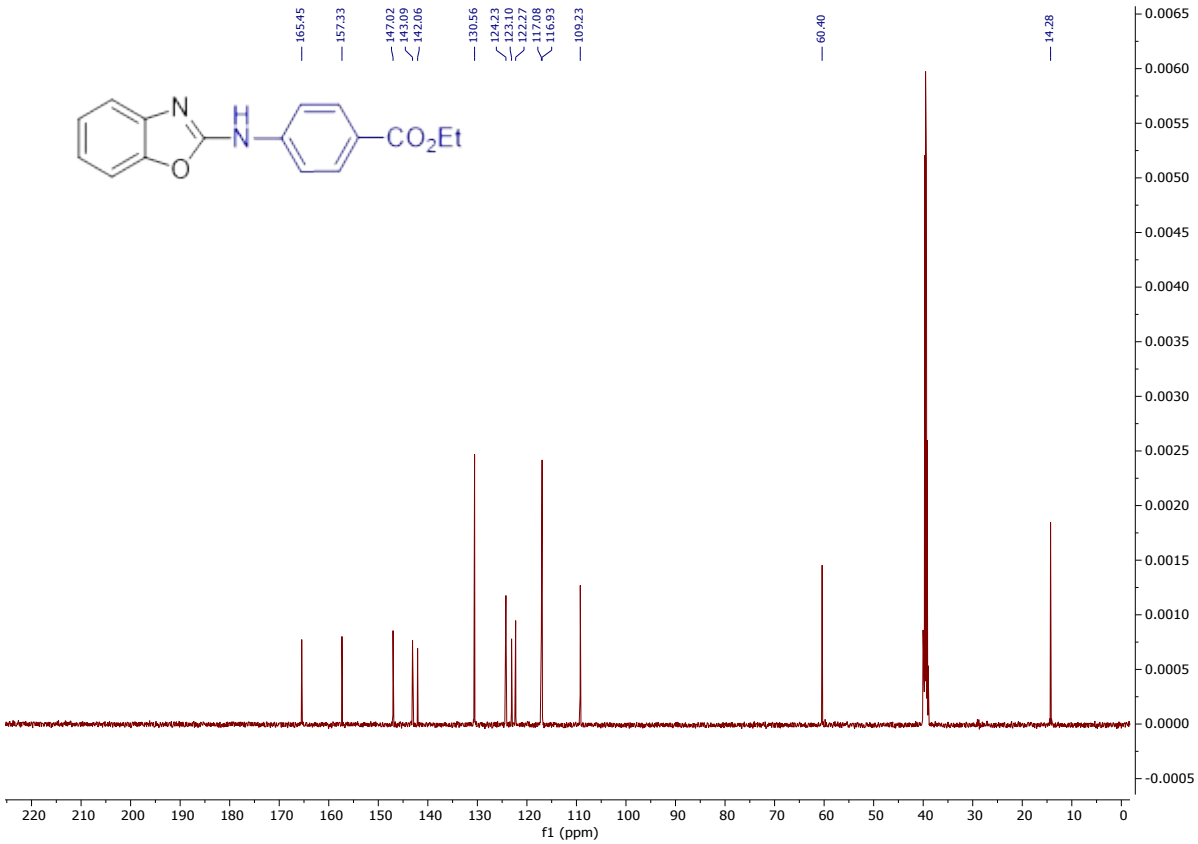


Figure S49 ^{13}C NMR spectra of **6aq** ($(CD_3)_2SO$)

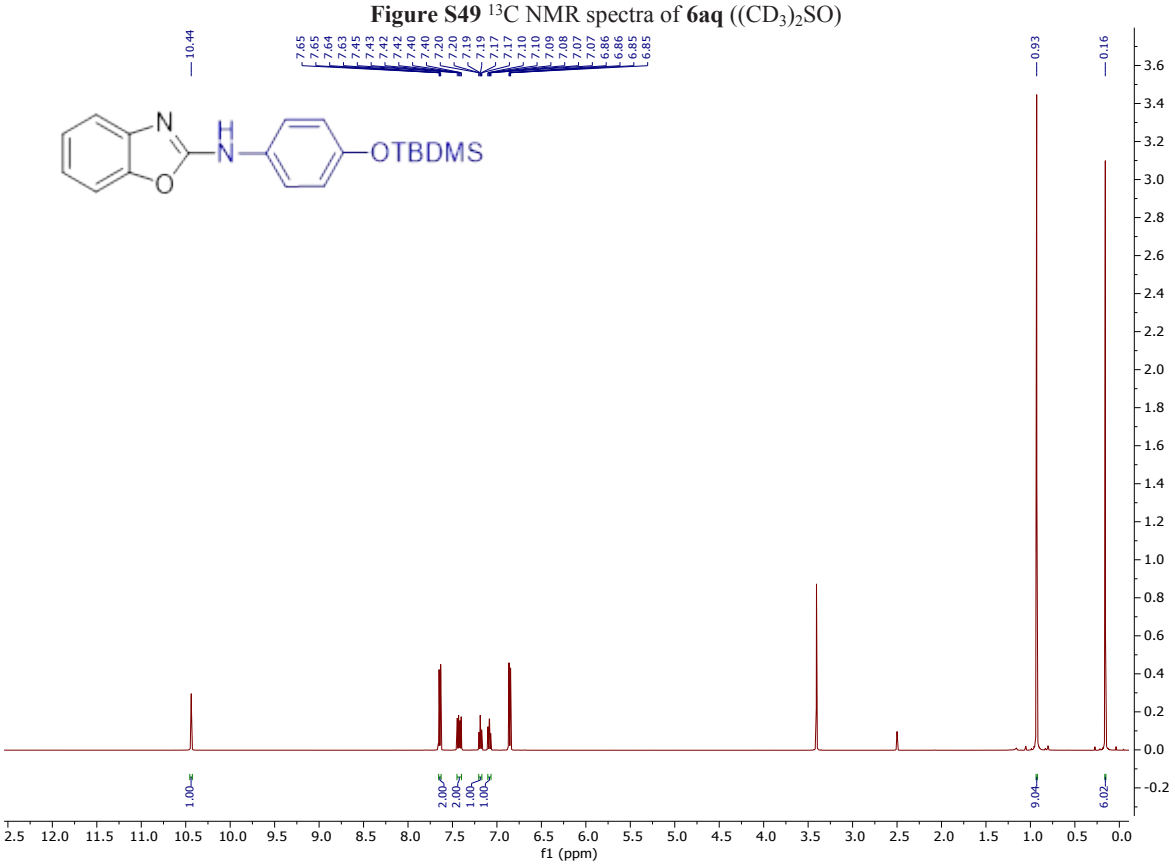


Figure S50 ^{1}H NMR spectra of **6ar** ($(CD_3)_2SO$)

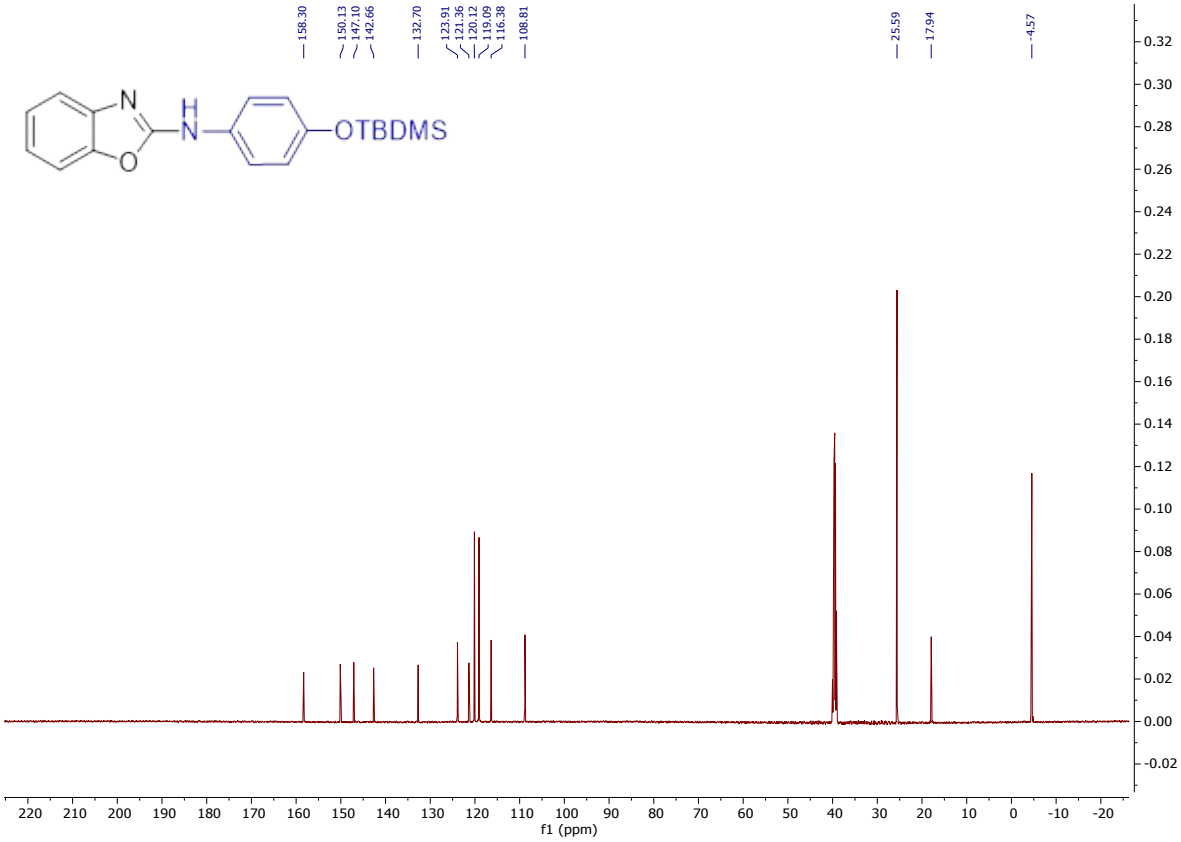


Figure S51 ^{13}C NMR spectra of **6ar** ($(CD_3)_2SO$)

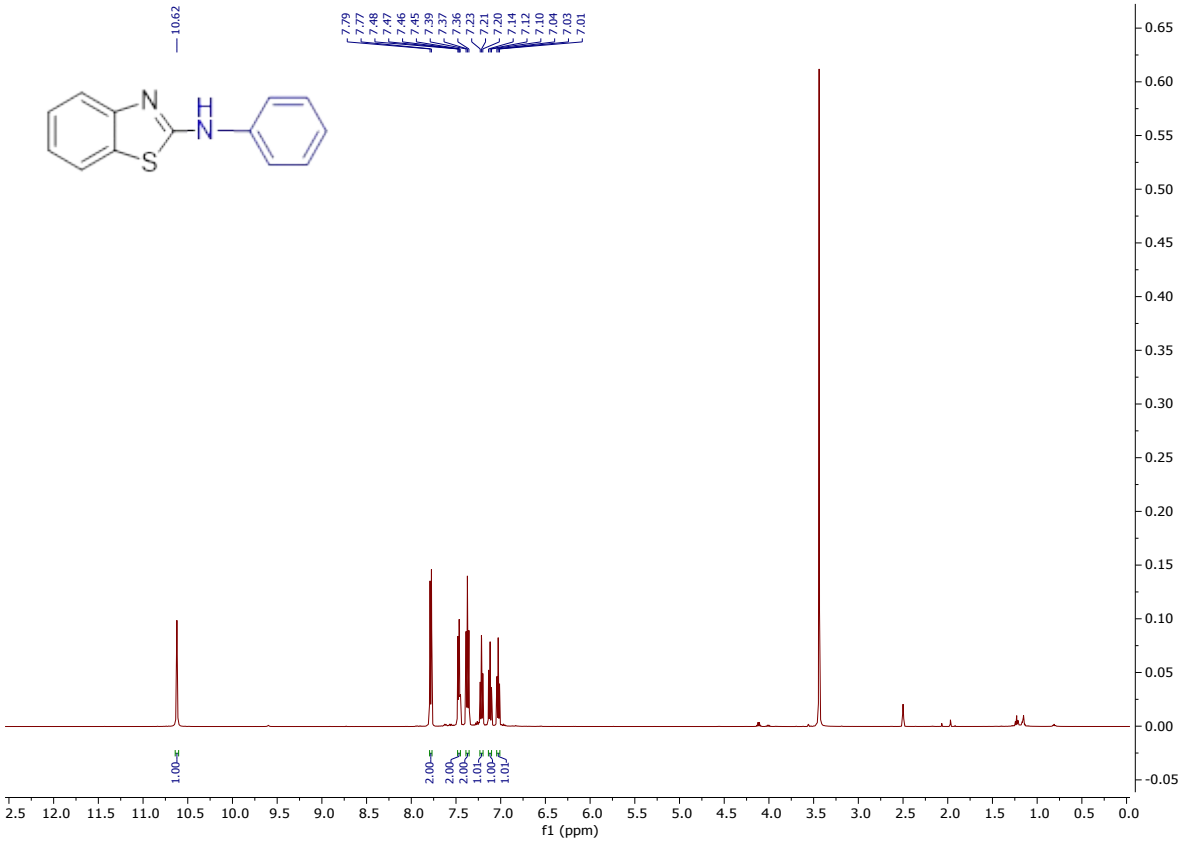


Figure S52 ^{1}H NMR spectra of **8aa** ($(CD_3)_2SO$)

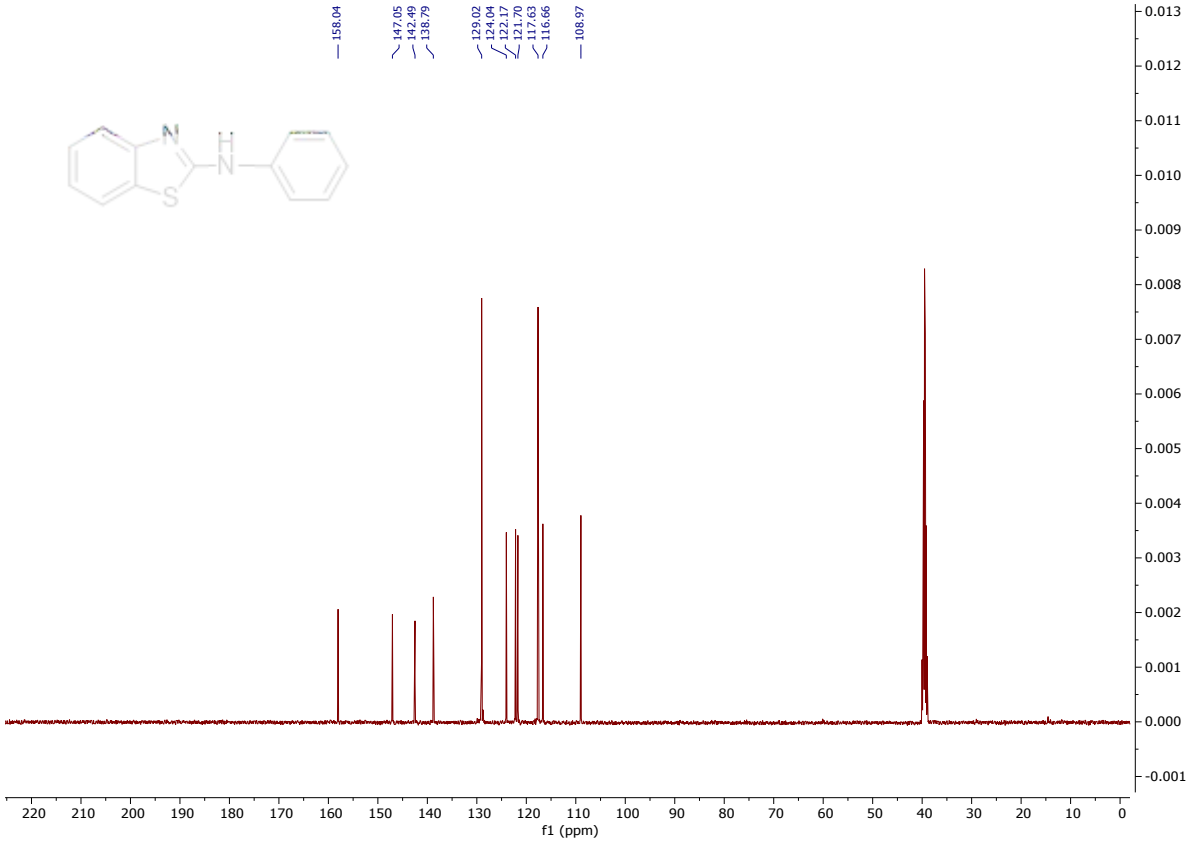


Figure S53 ^{13}C NMR spectra of **8aa** ($(CD_3)_2SO$)

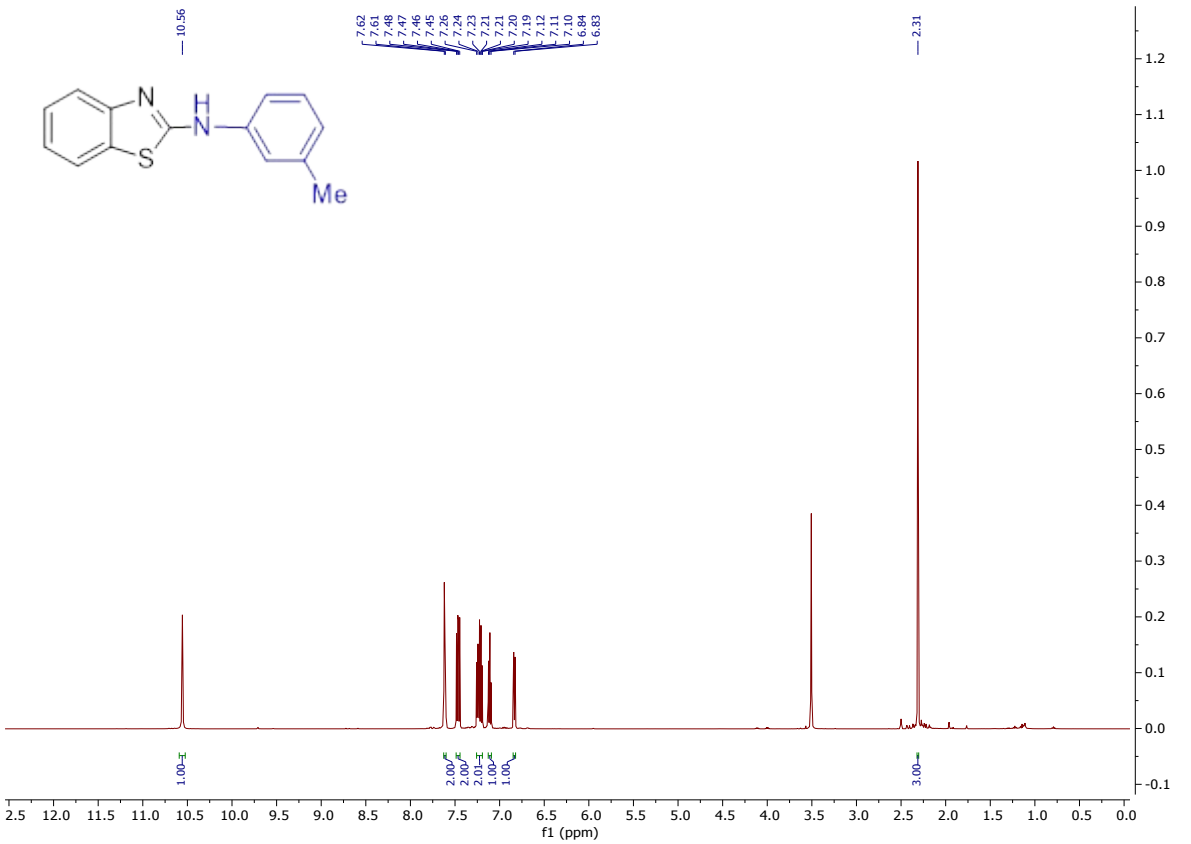


Figure S54 ^{1}H NMR spectra of **8ab** ($(CD_3)_2SO$)

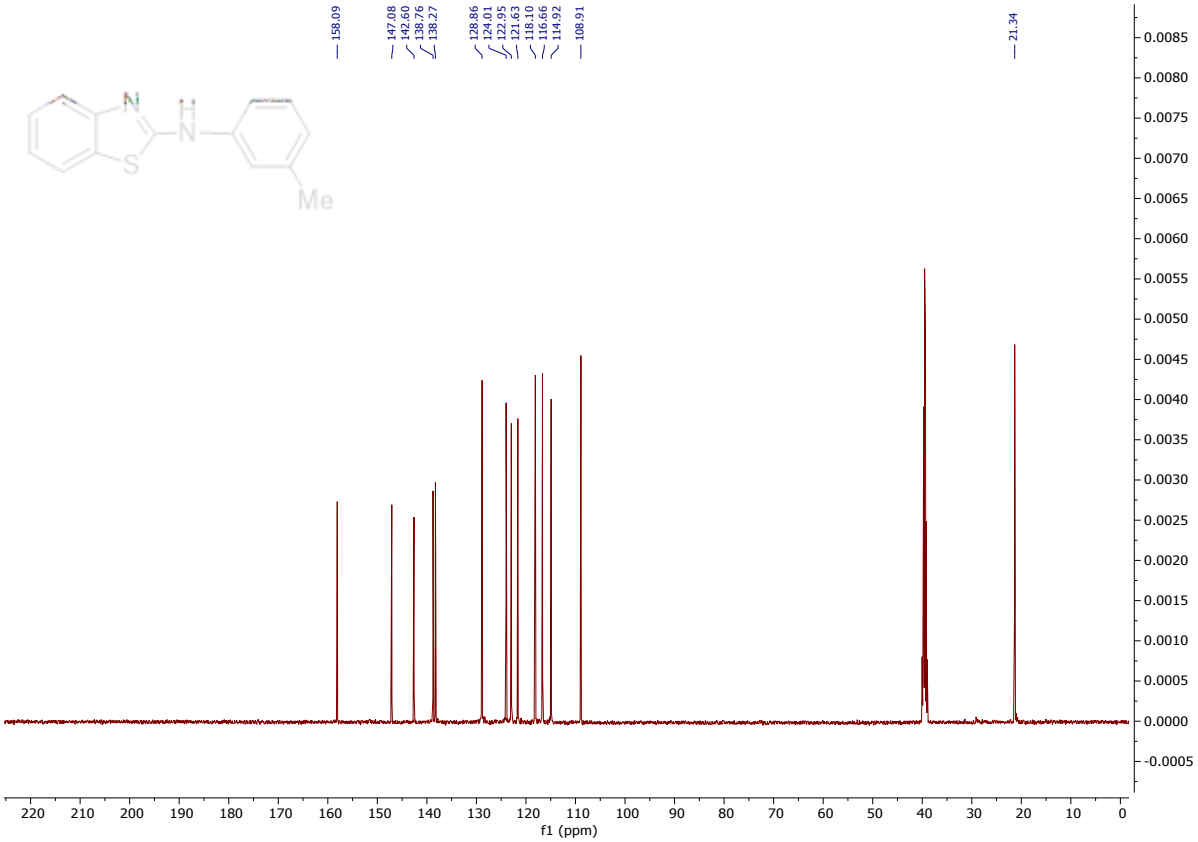


Figure S55 ^{13}C NMR spectra of **8ab** ($(CD_3)_2SO$)

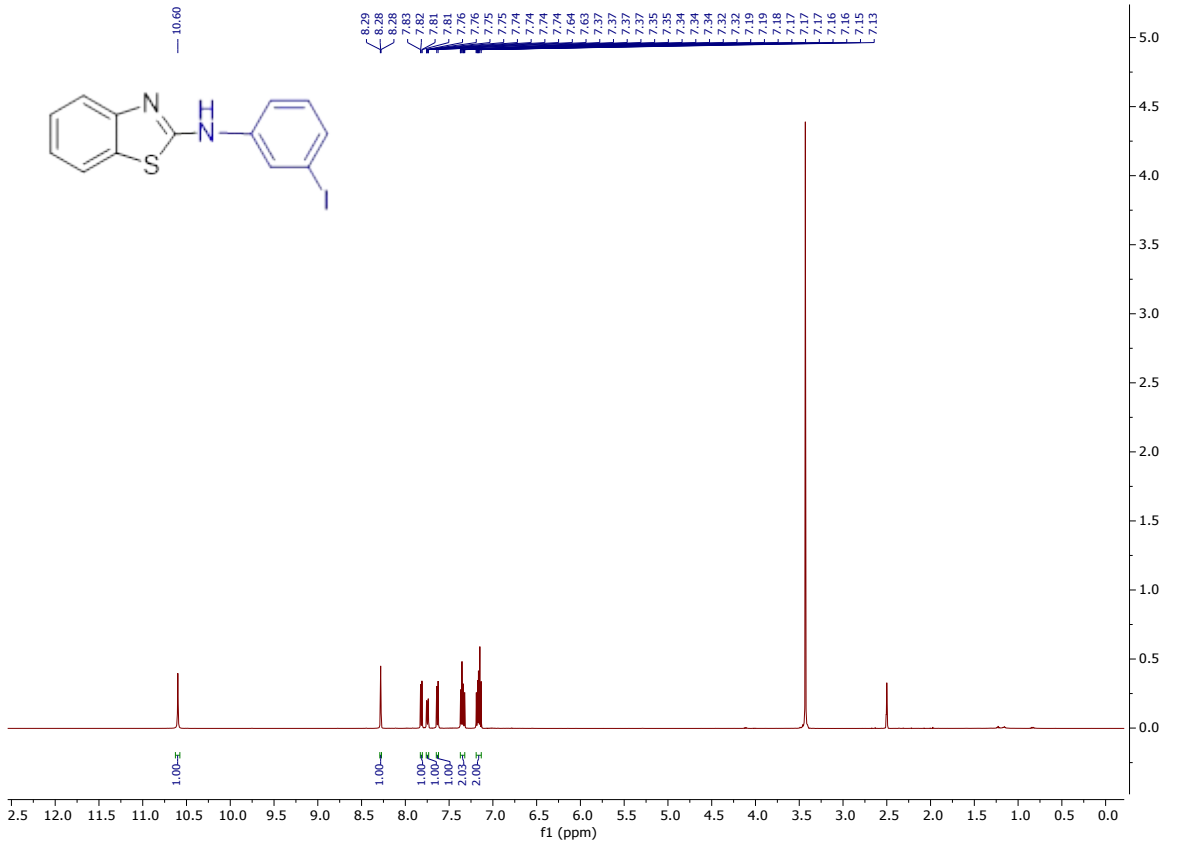


Figure S56 ^{1}H NMR spectra of **8ae** ($(CD_3)_2SO$)

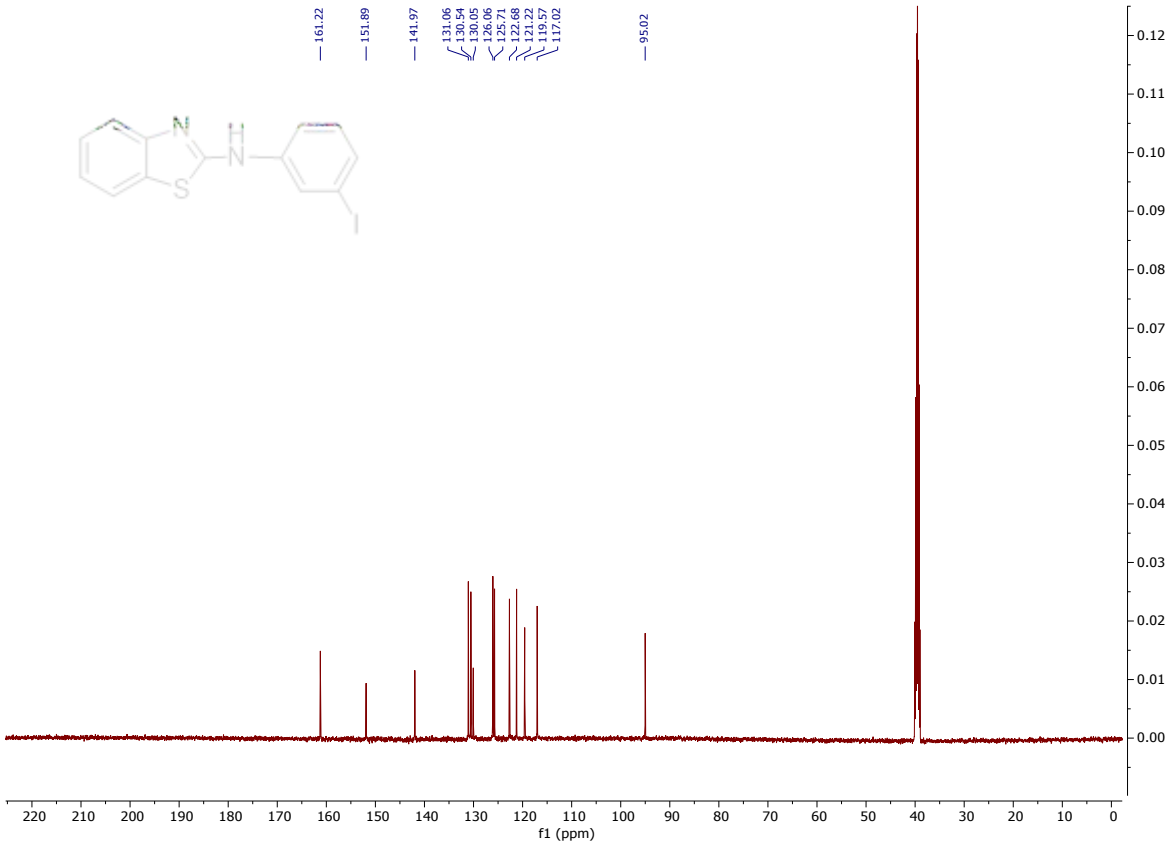


Figure S57 ^{13}C NMR spectra of **8ae** ($(CD_3)_2SO$)

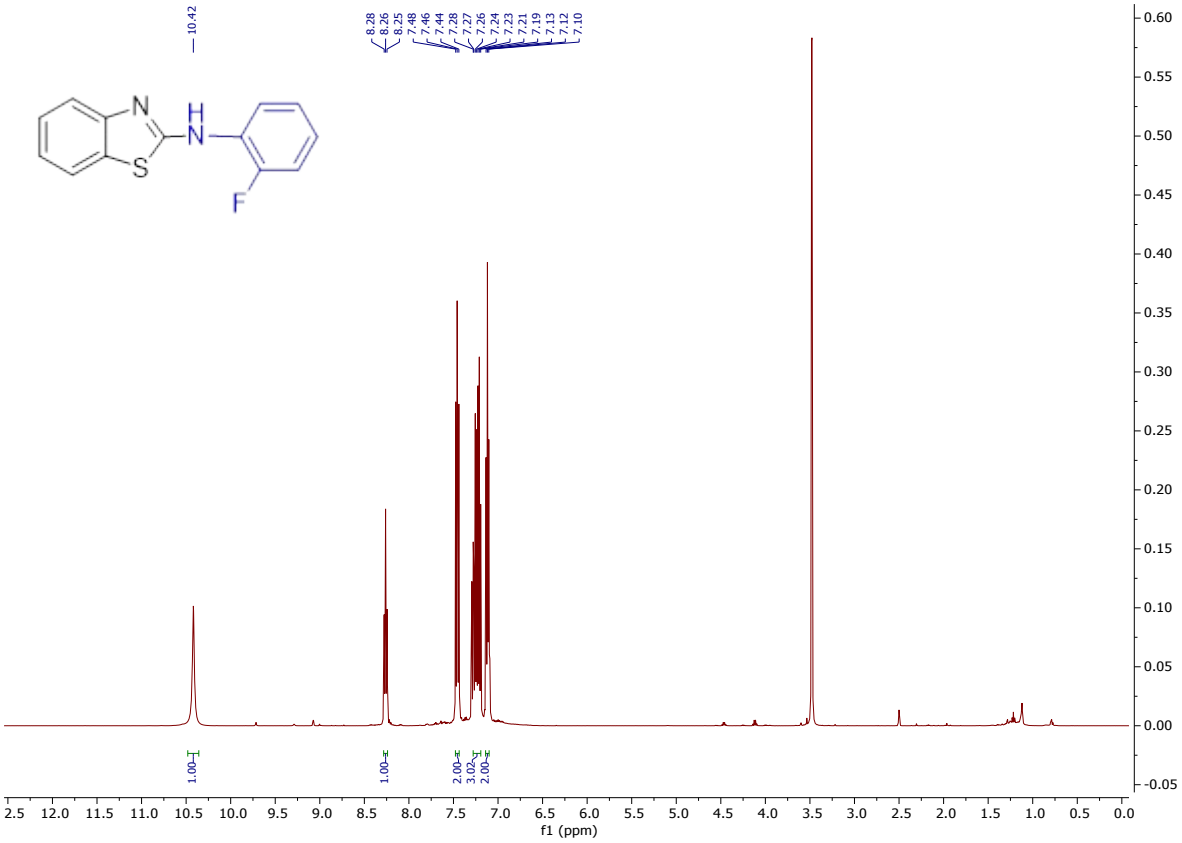


Figure S58 ^{1}H NMR spectra of **8ag** ($(CD_3)_2SO$)

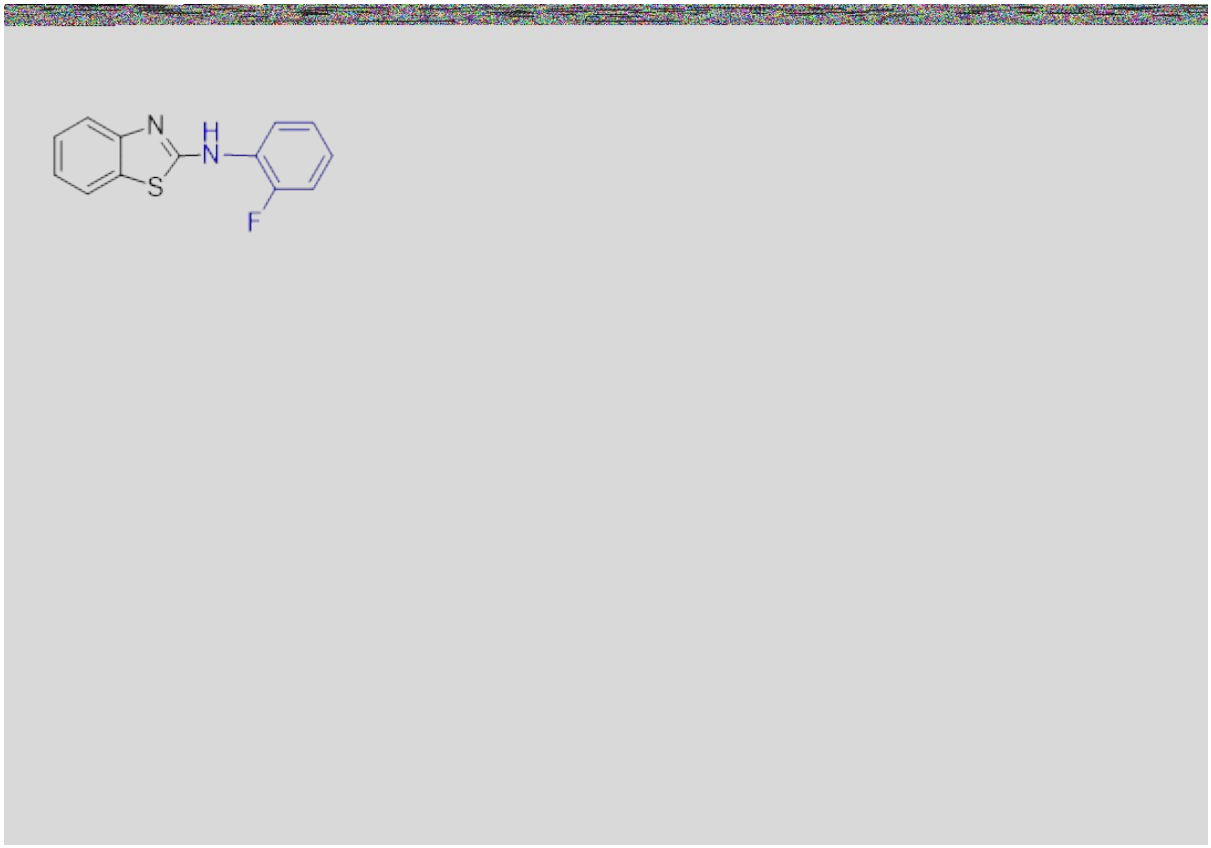


Figure S59 ^{13}C NMR spectra of **8ag** ($(CD_3)_2SO$)

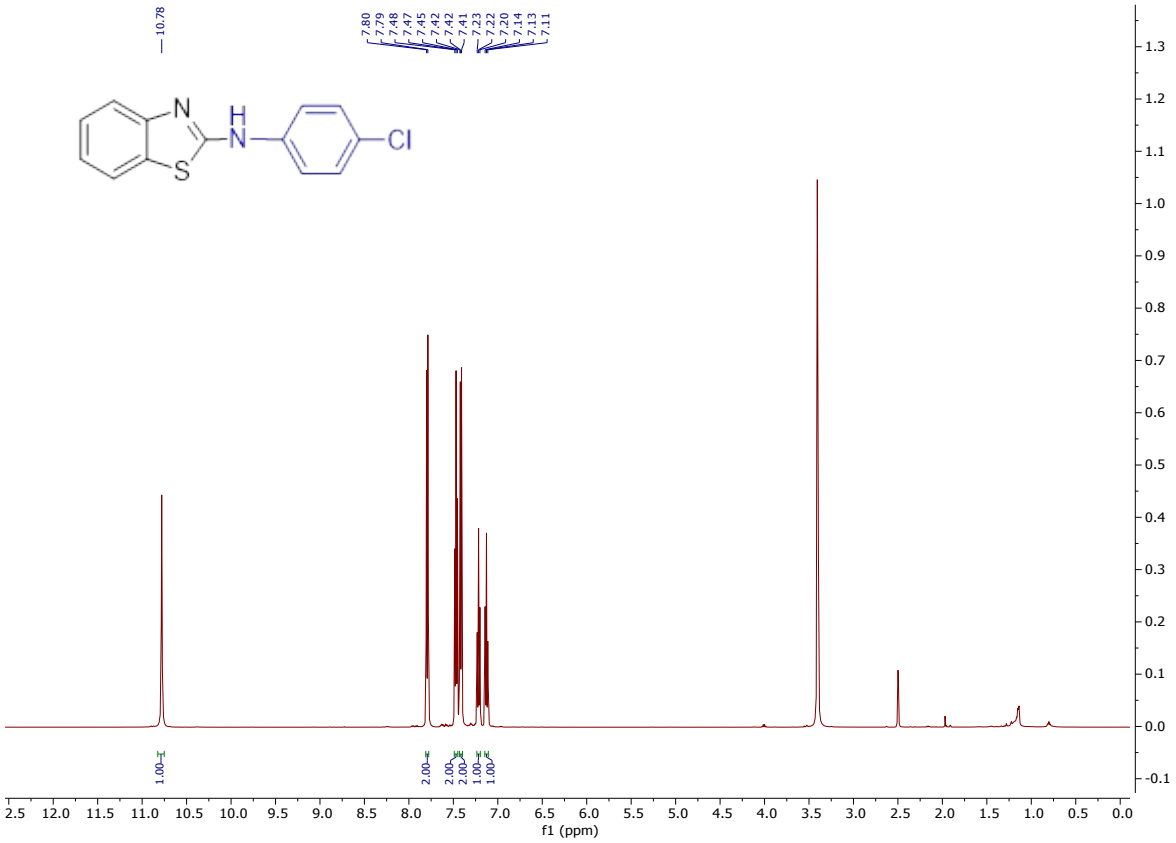


Figure S60 ^{1}H NMR spectra of **8ah** ($(CD_3)_2SO$)

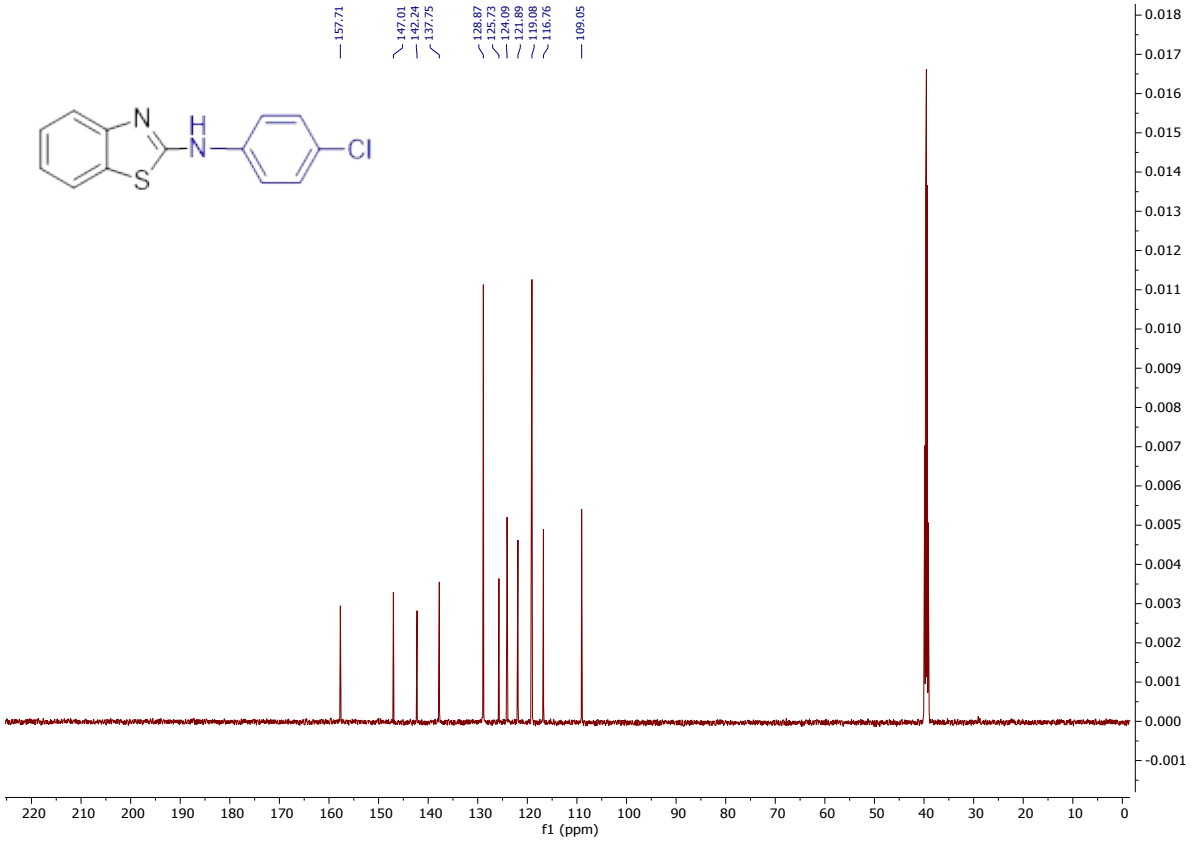


Figure S61 ^{13}C NMR spectra of **8ah** ($(CD_3)_2SO$)

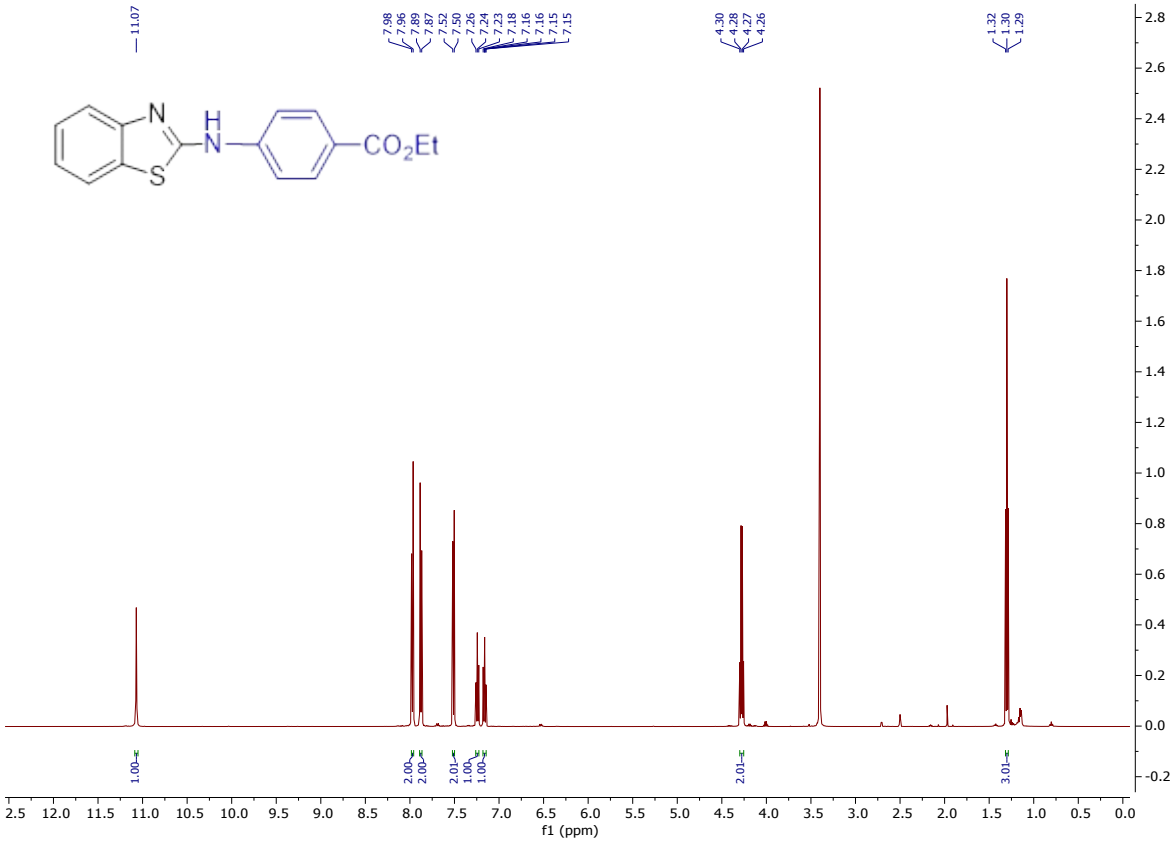


Figure S62 ^{1}H NMR spectra of **8aq** ($(CD_3)_2SO$)

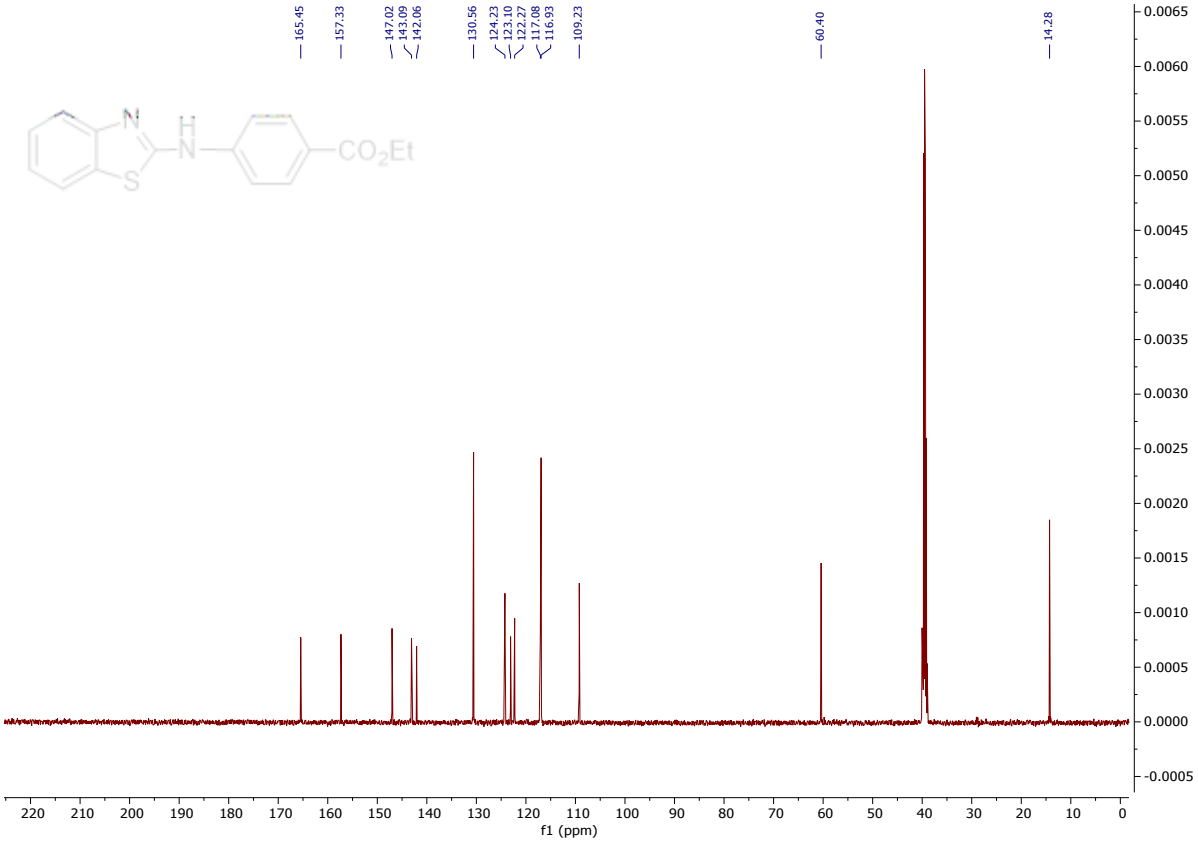


Figure S63 ^{13}C NMR spectra of **8aq** ($(CD_3)_2SO$)

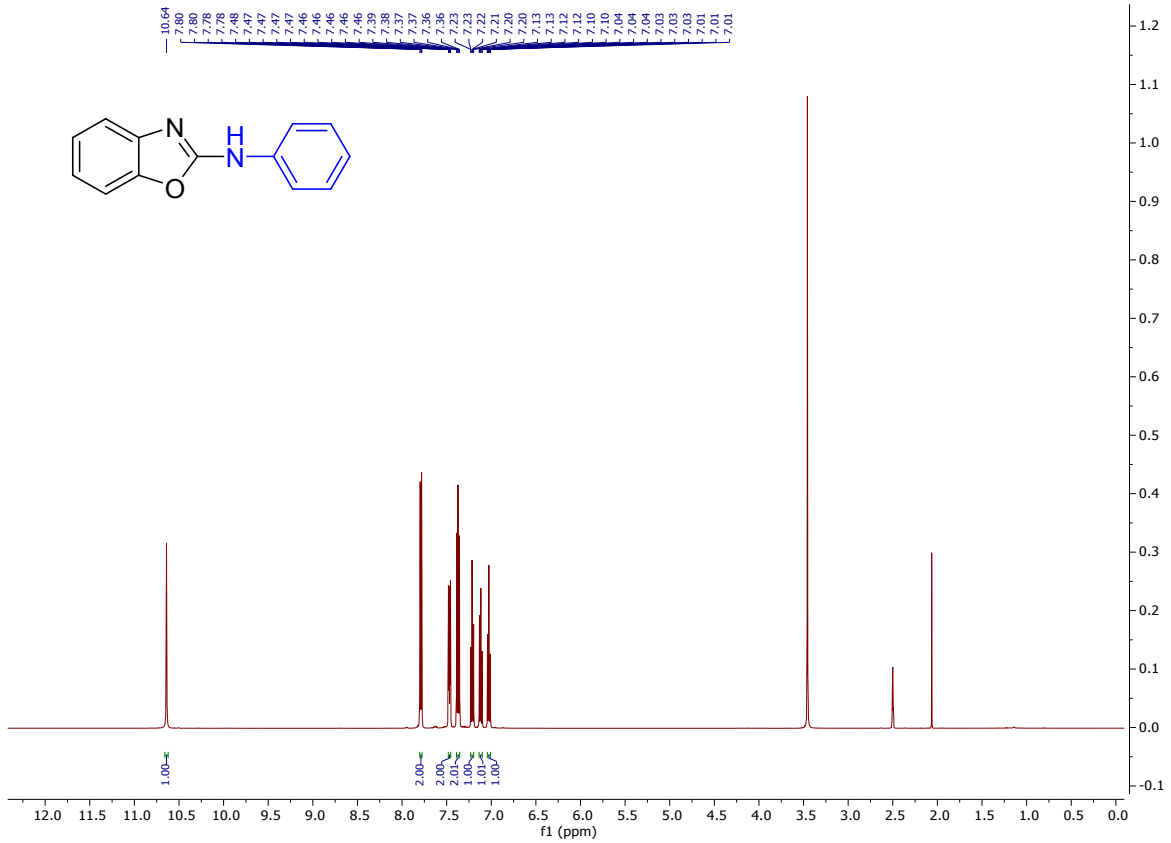


Figure S64 ^{1}H NMR spectra of **6aa** (gram-scale) ($(CD_3)_2SO$)

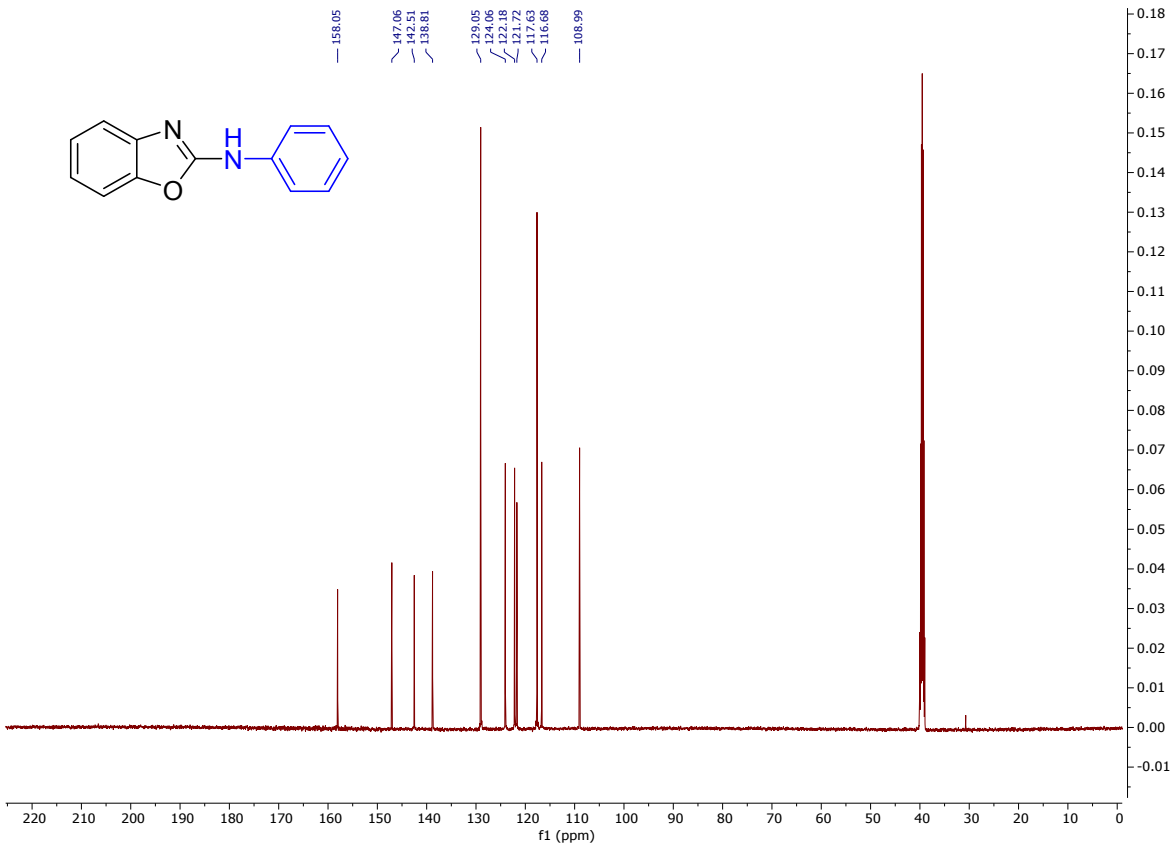


Figure S65 ^{13}C NMR spectra of **6aa** (gram-scale) ($(CD_3)_2SO$)

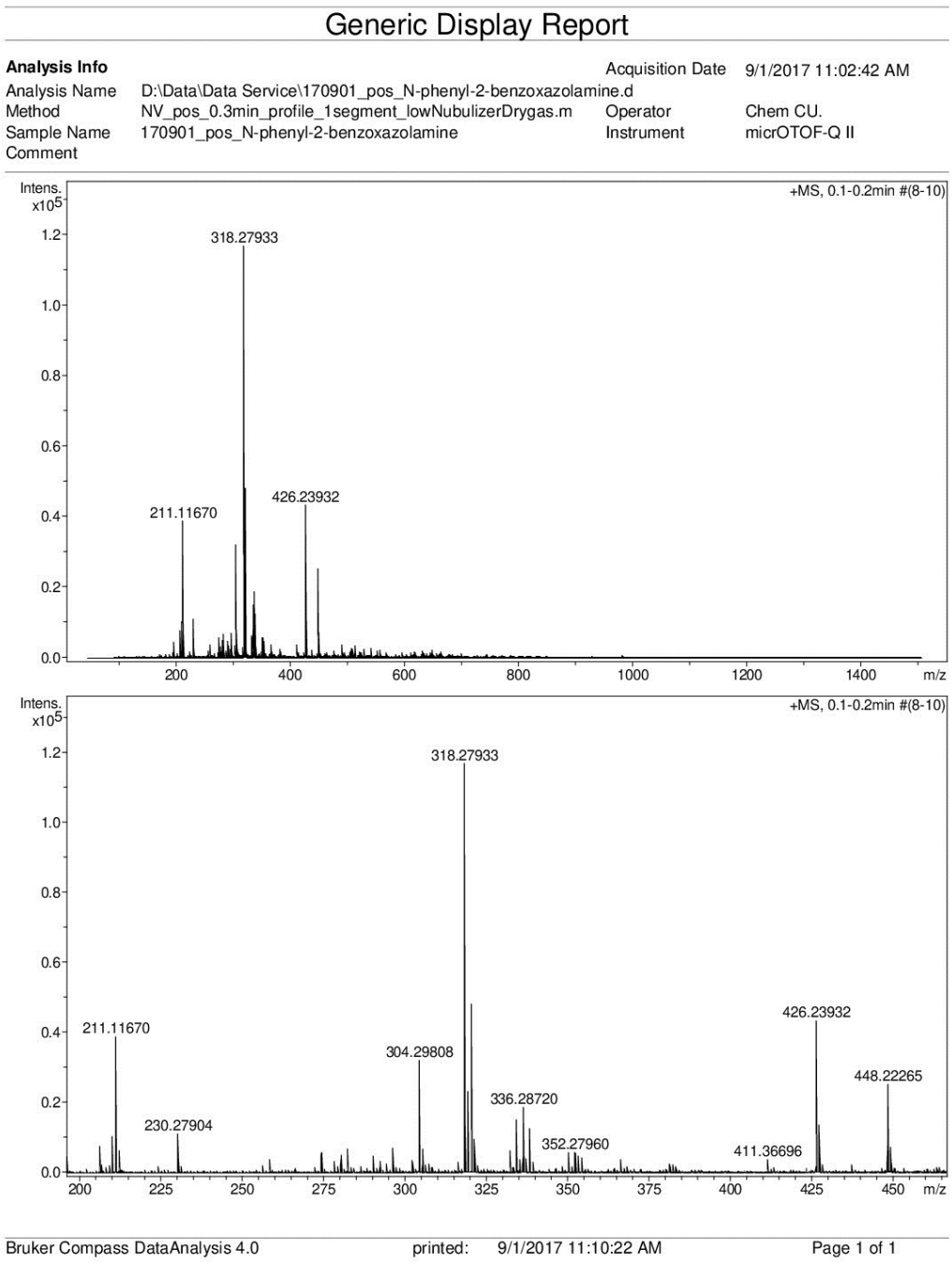


Figure S66 Mass spectrum of **6aa**

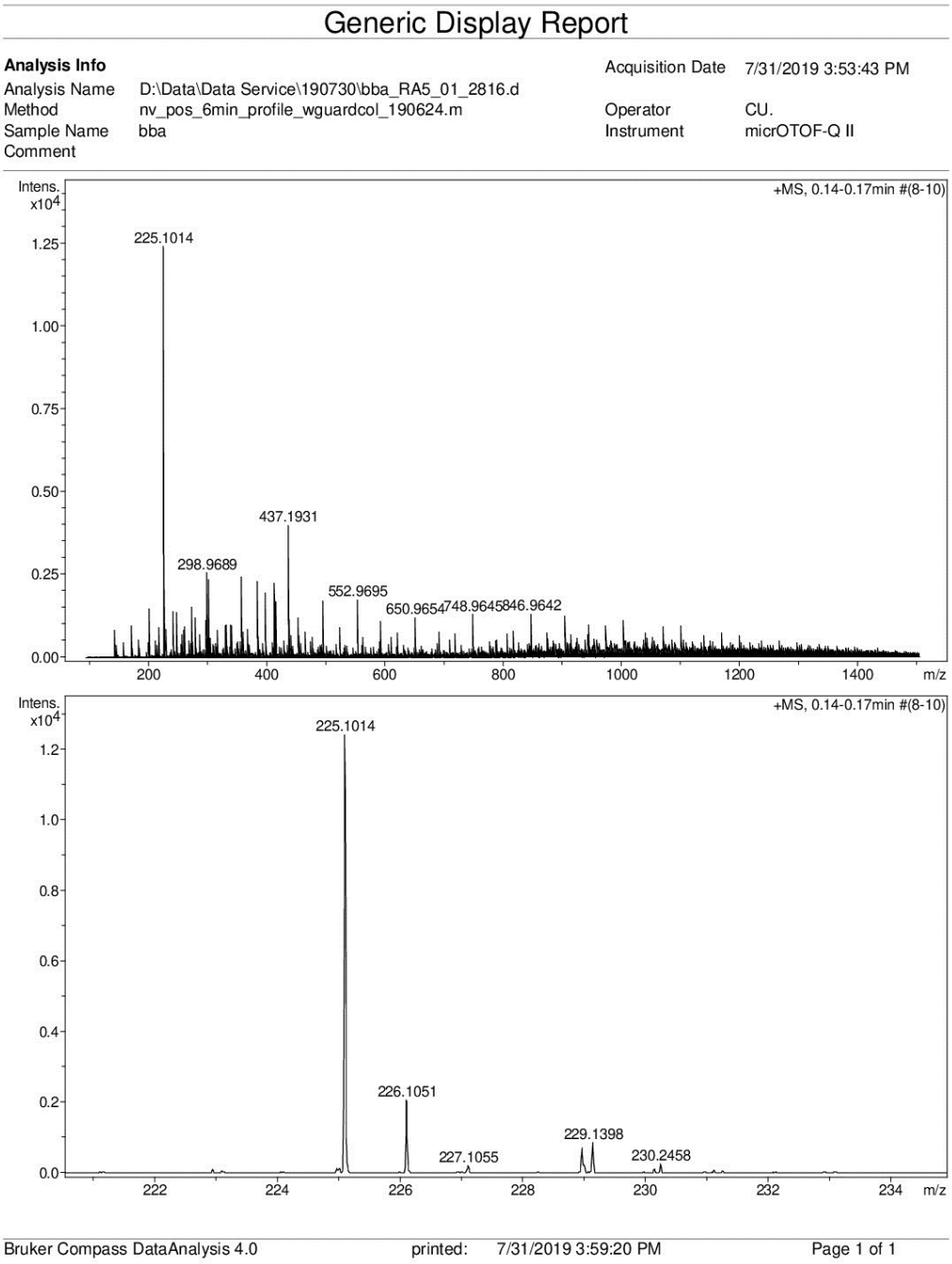


Figure S67 Mass spectrum of **6ba**

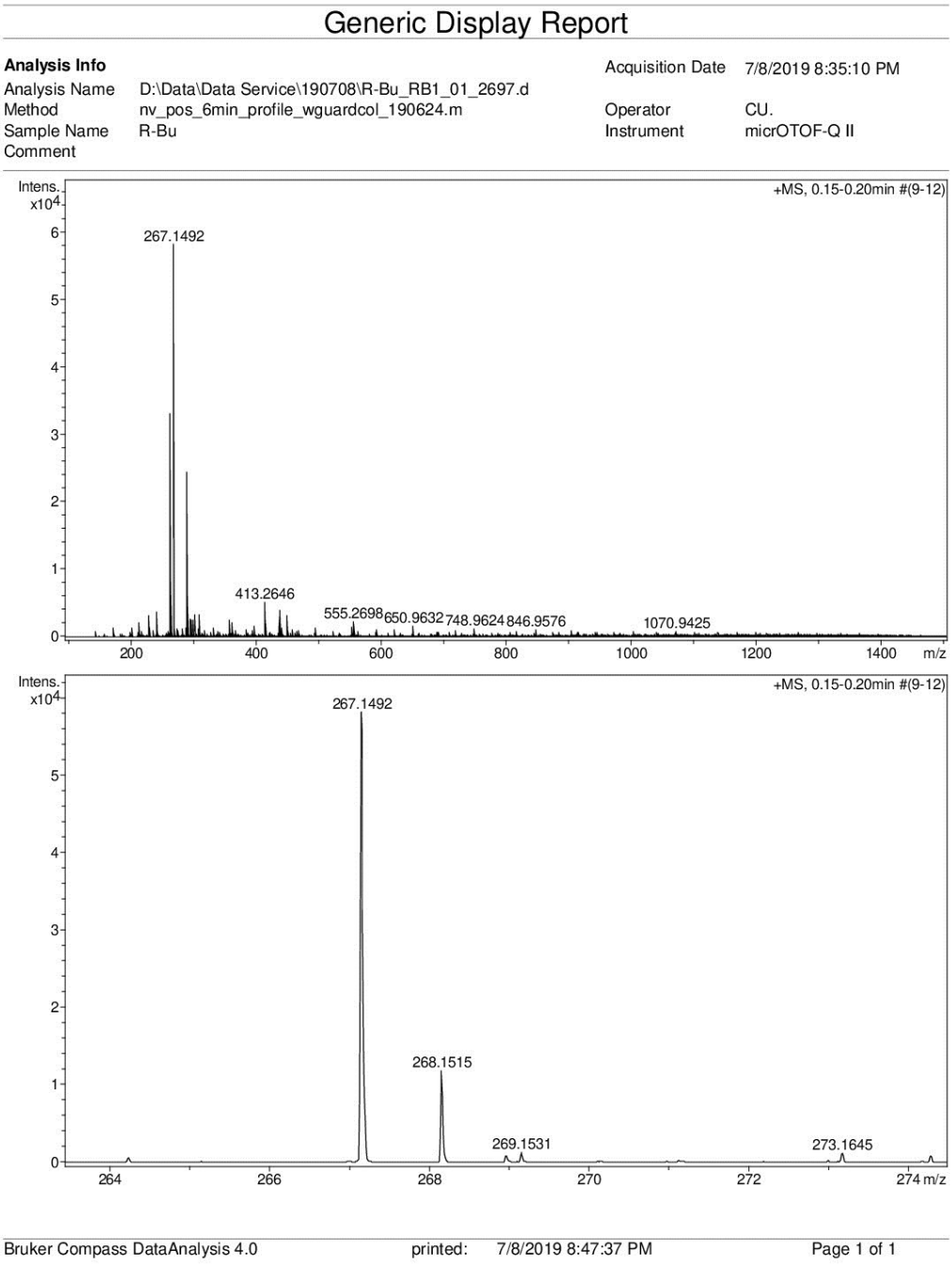


Figure S68 Mass spectrum of **6ca**

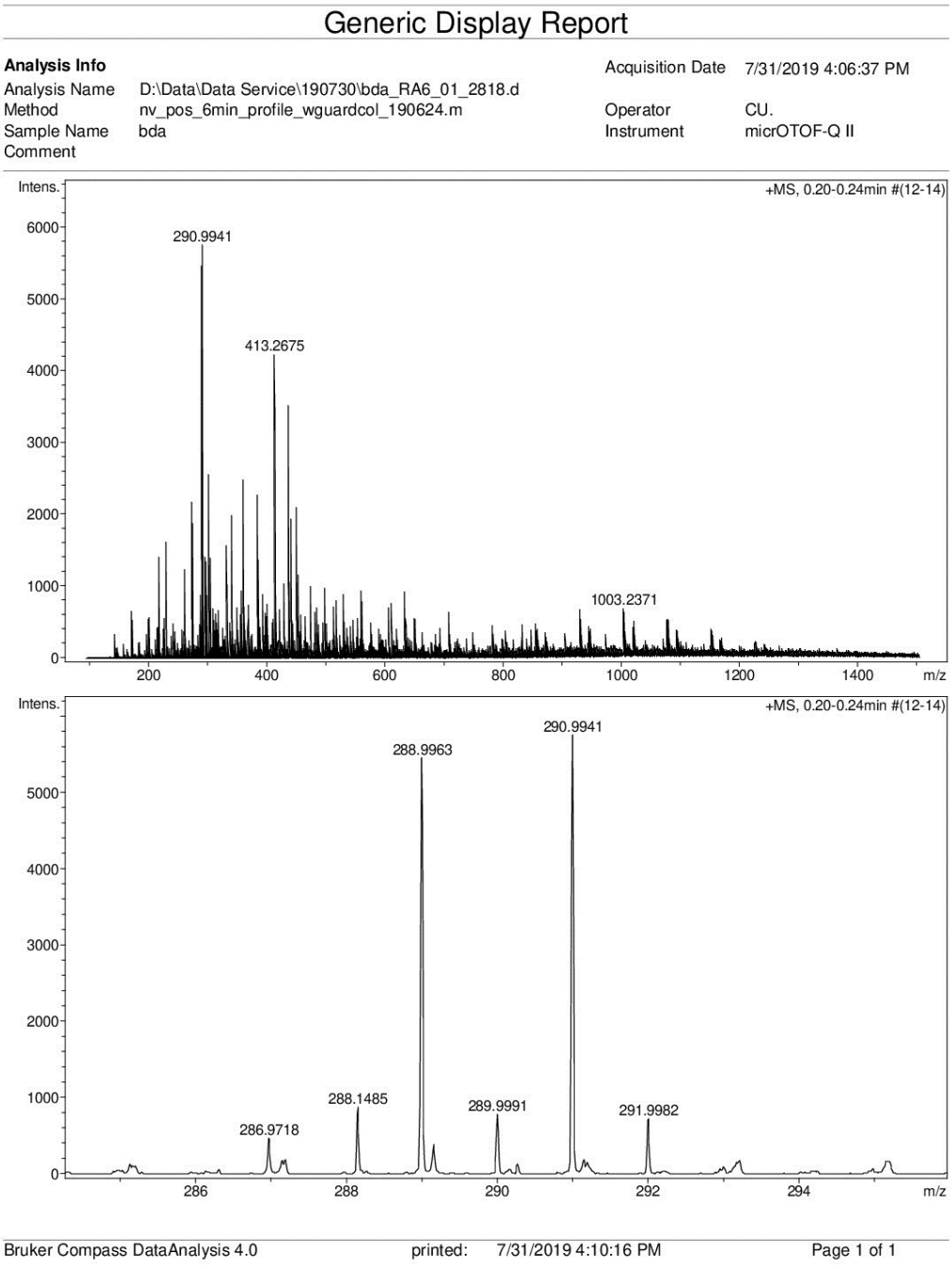


Figure S69 Mass spectrum of **6da**

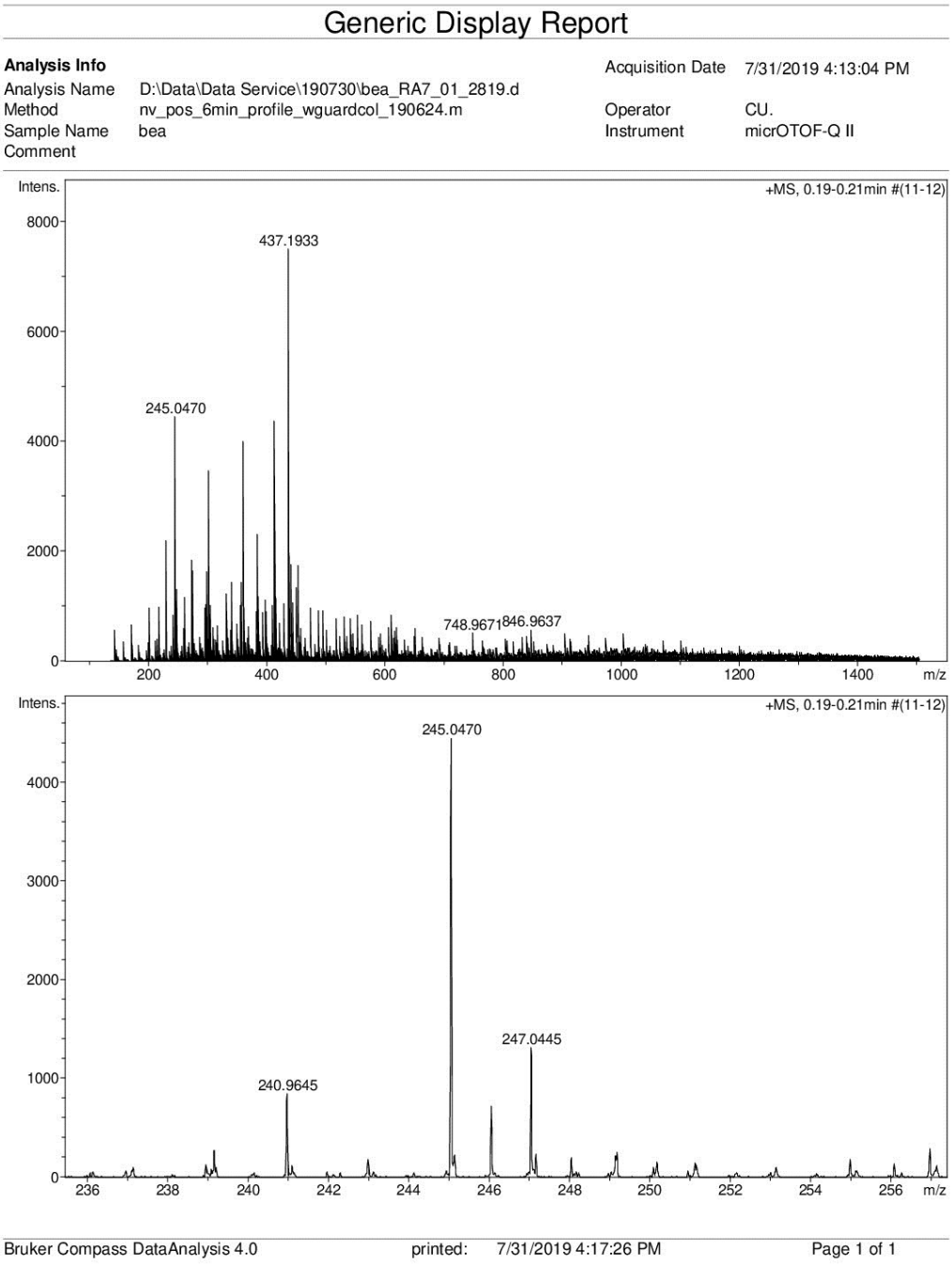


Figure S70 Mass spectrum of **6ea**

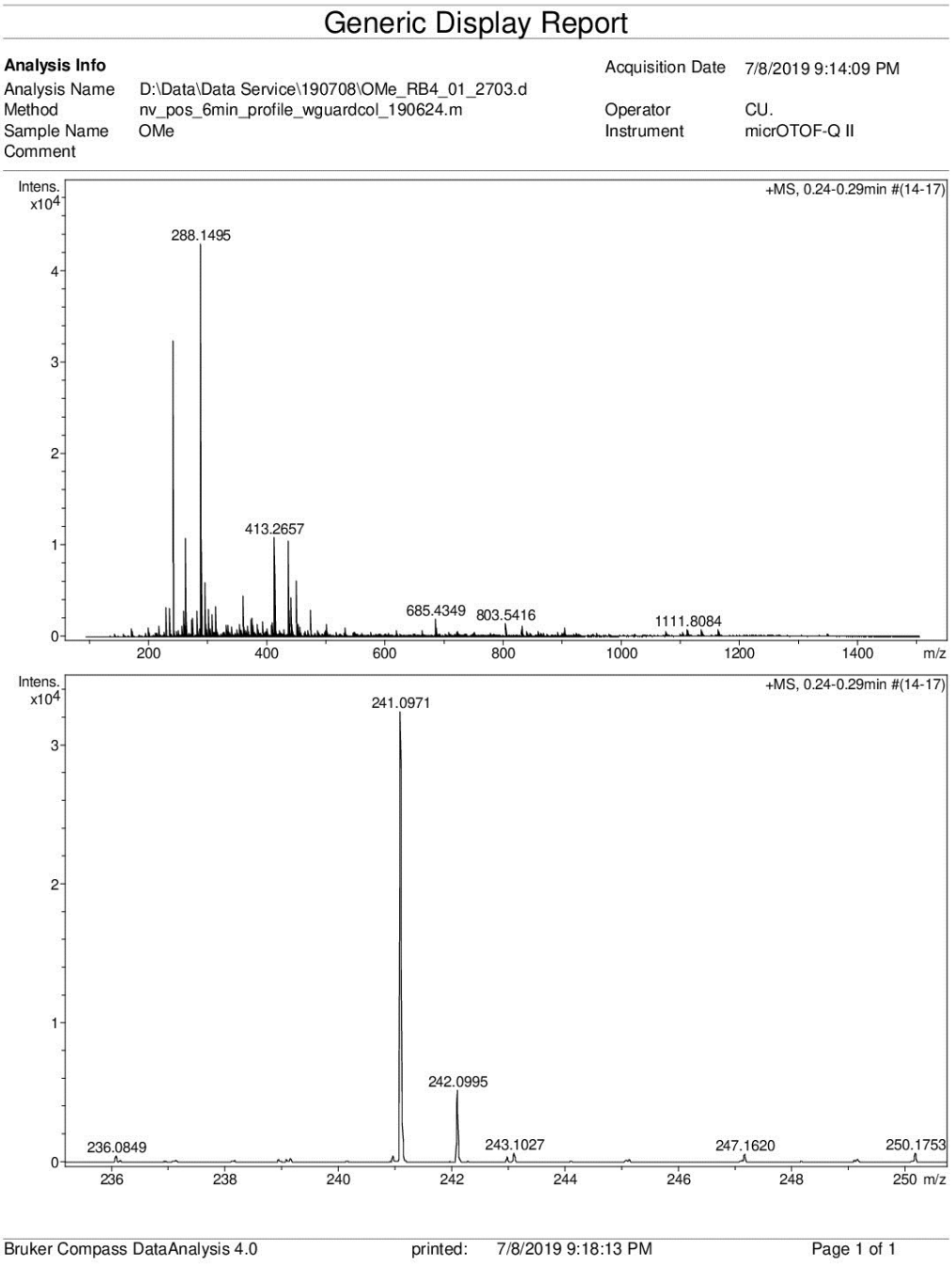


Figure S71 Mass spectrum of **6fa**

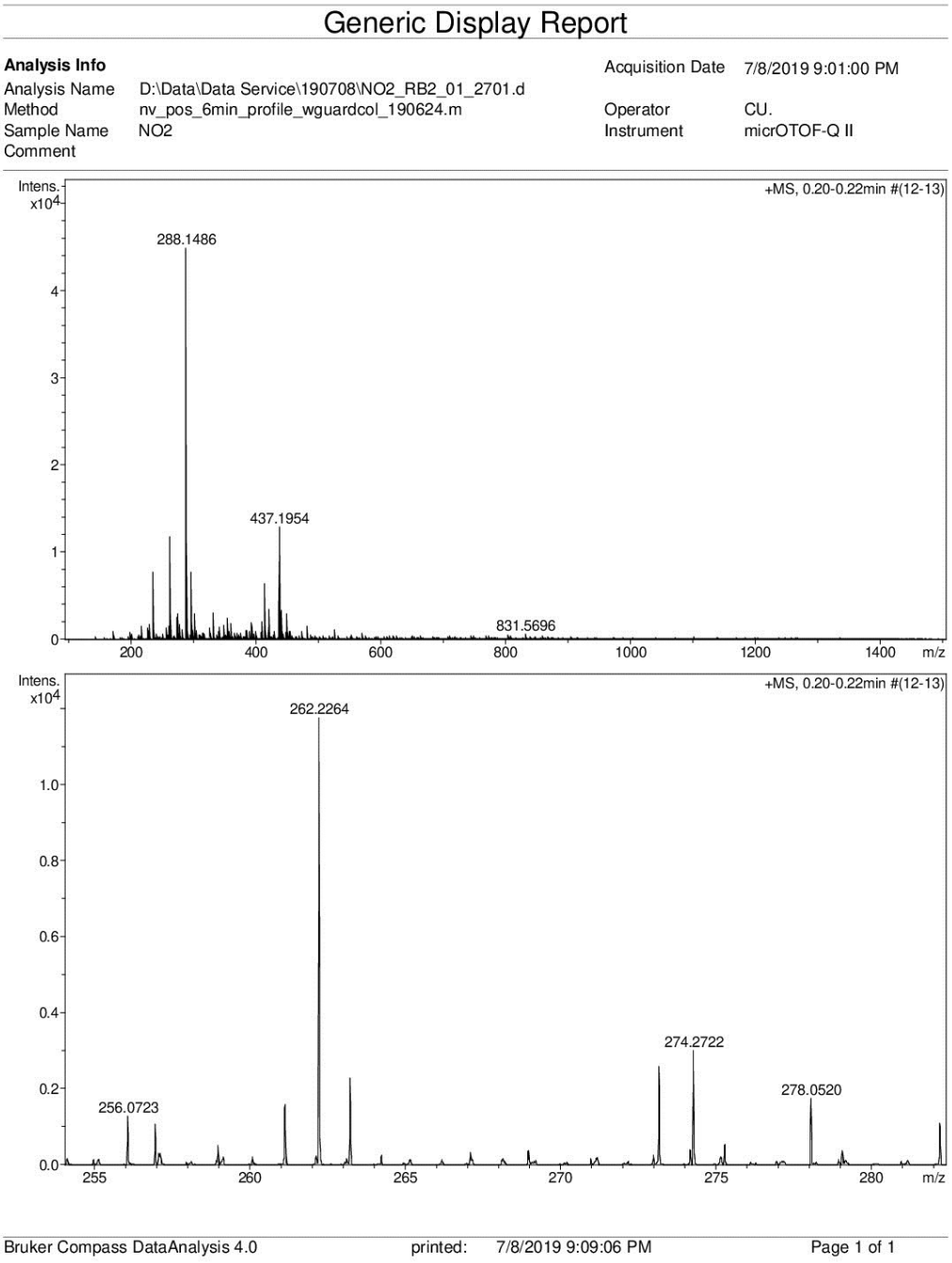


Figure S72 Mass spectrum of **6ga**

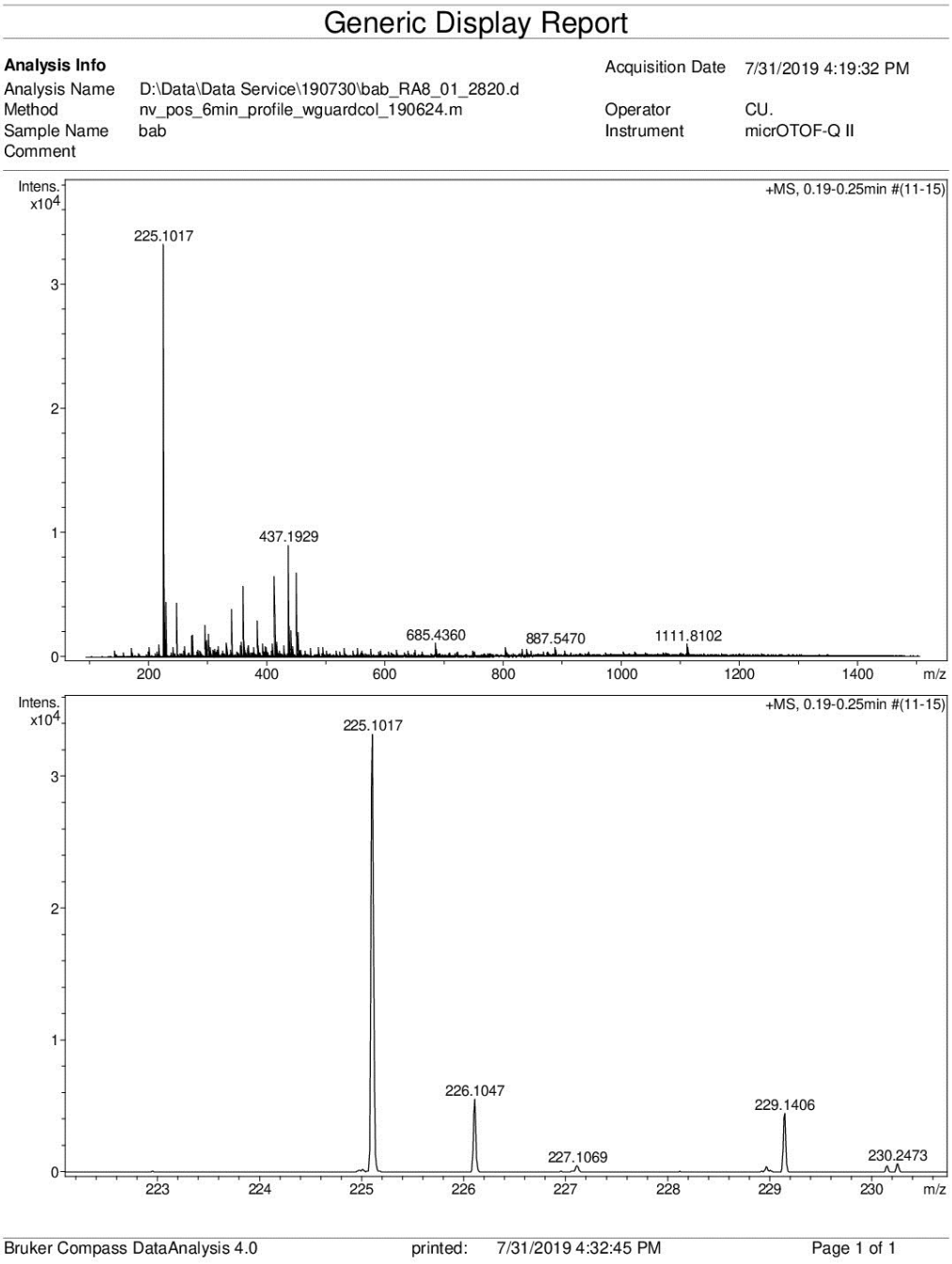


Figure S73 Mass spectrum of **6ab**

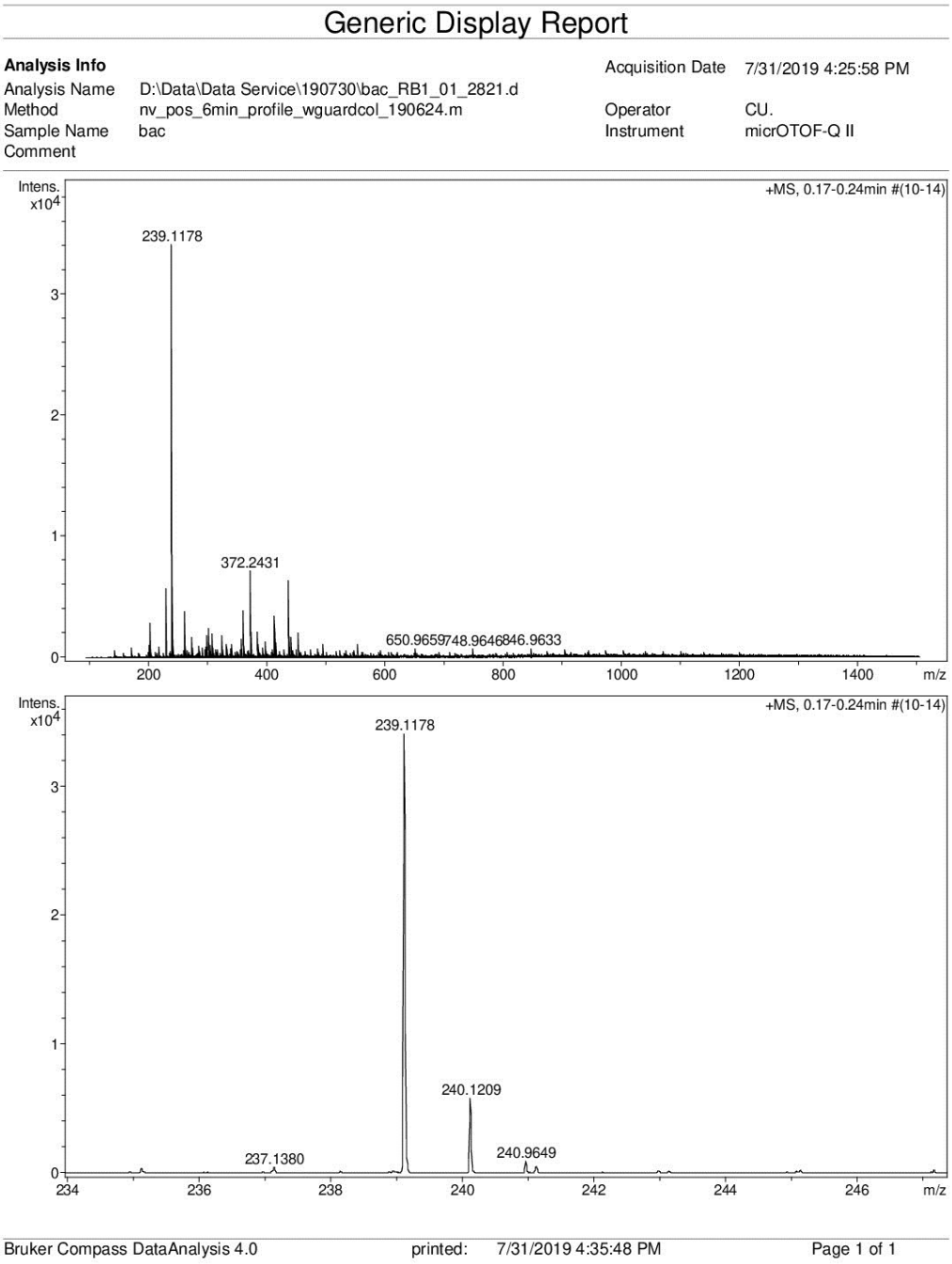


Figure S74 Mass spectrum of **6ac**

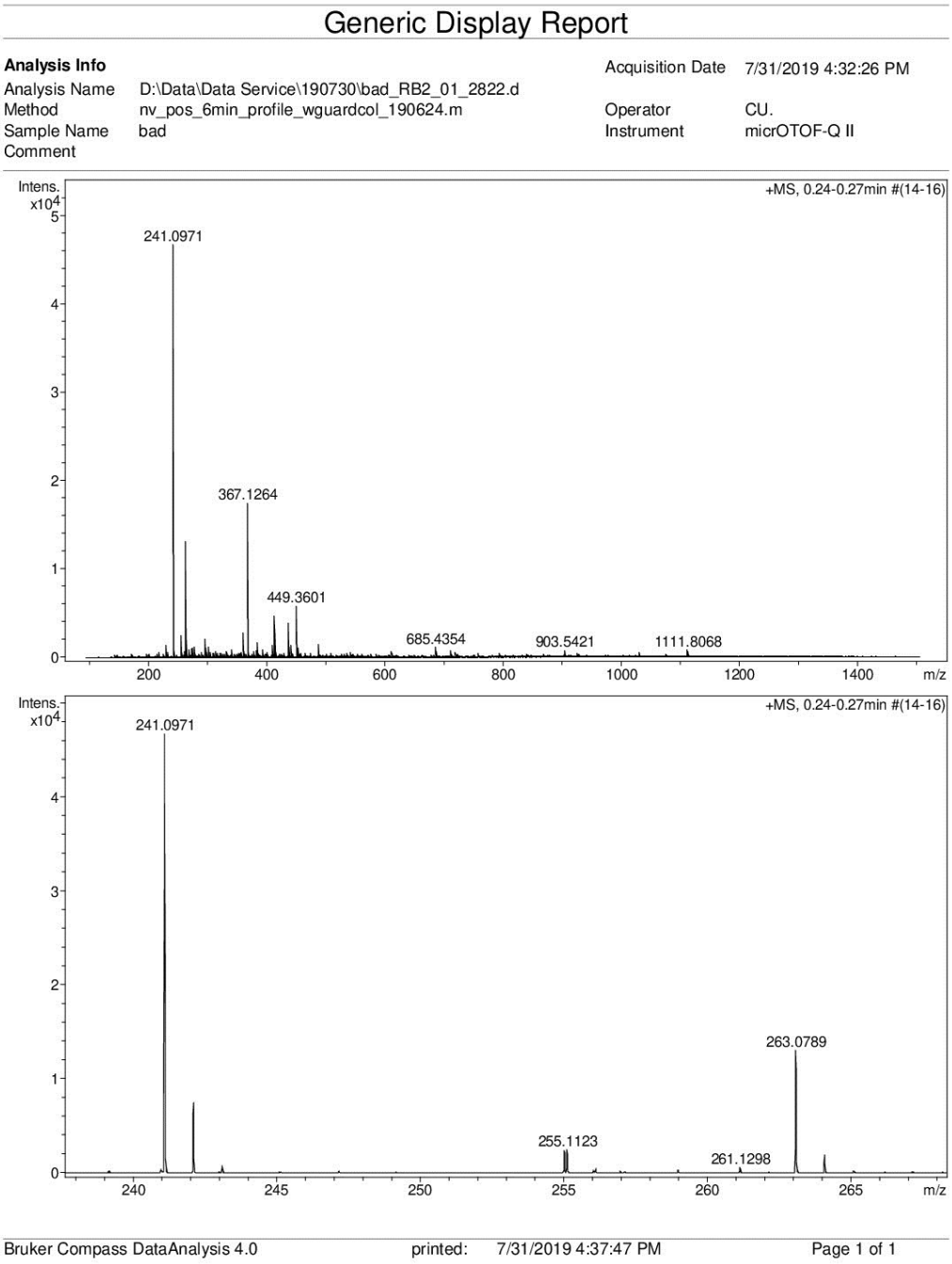


Figure S75 Mass spectrum of **6ad**

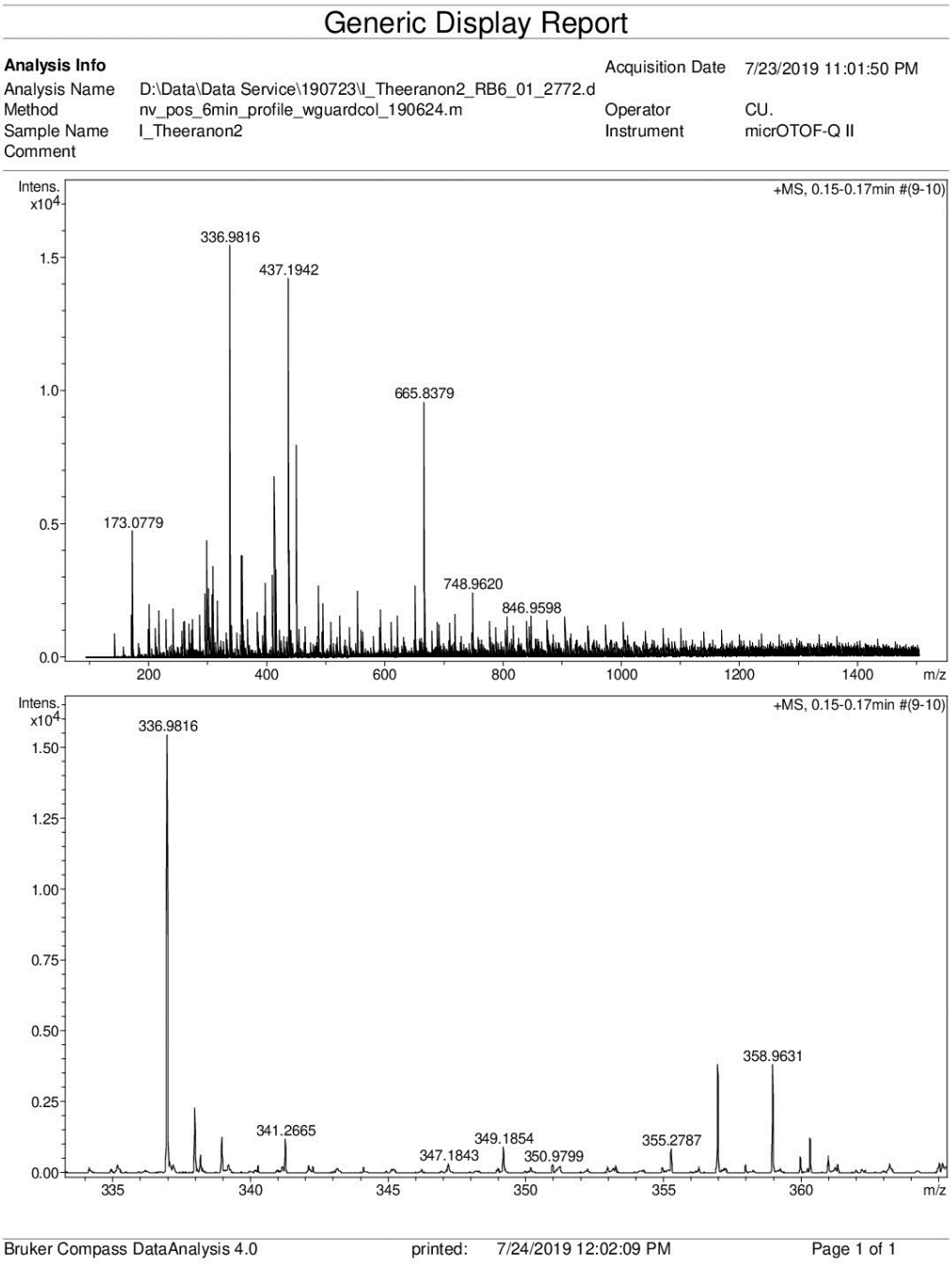


Figure S76 Mass spectrum of **6ae**

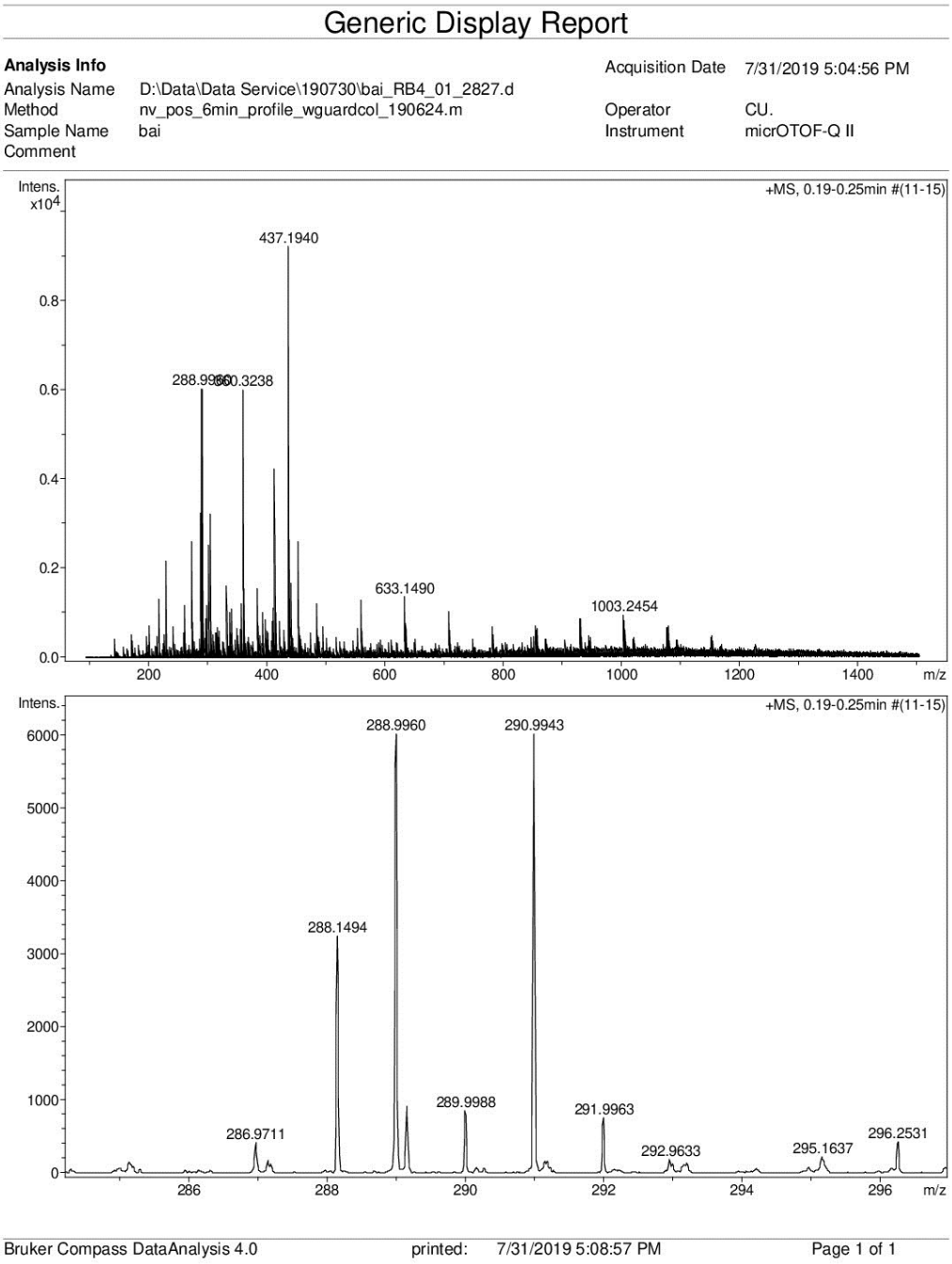


Figure S77 Mass spectrum of **6af**

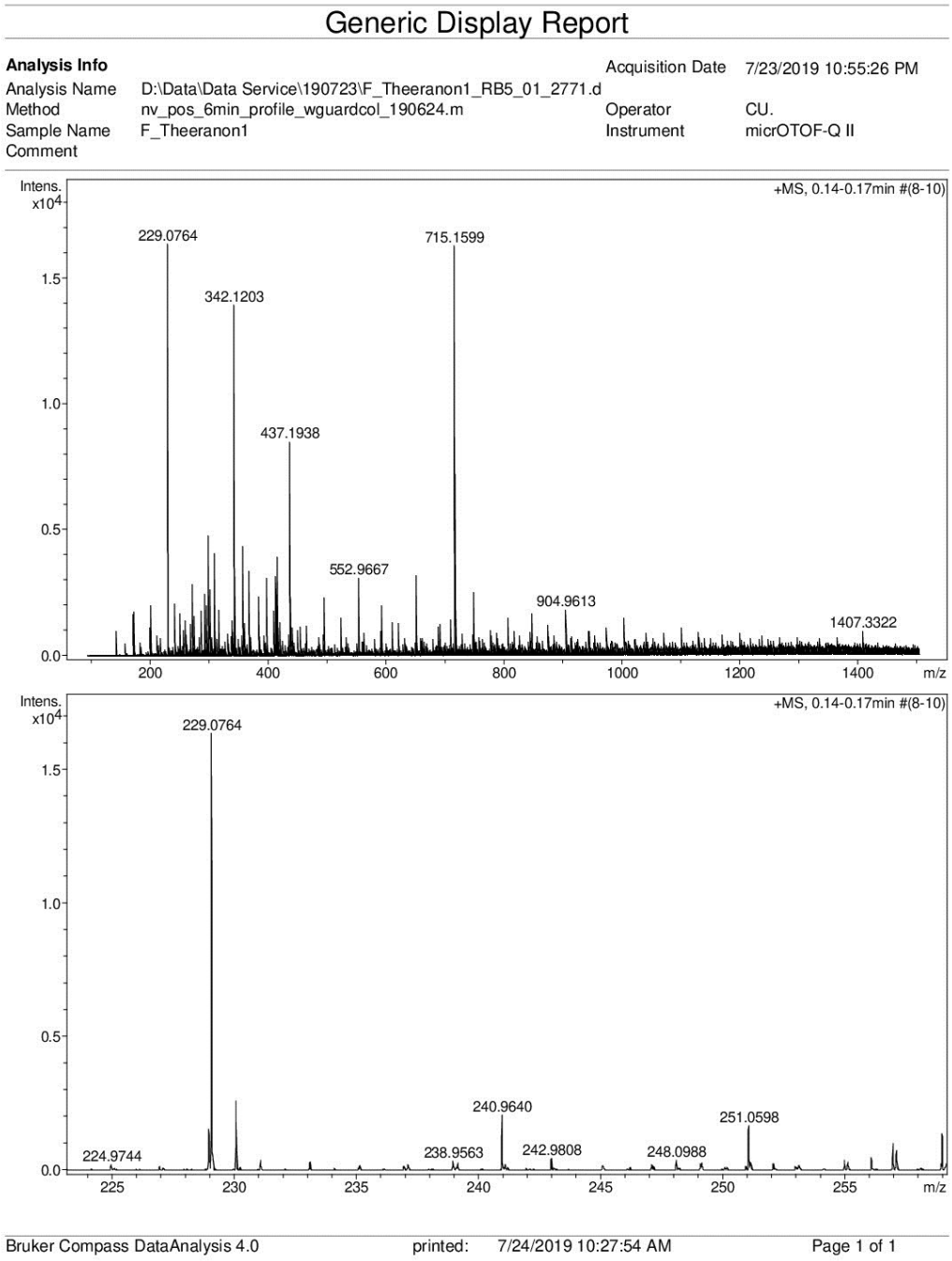


Figure S78 Mass spectrum of **6ag**

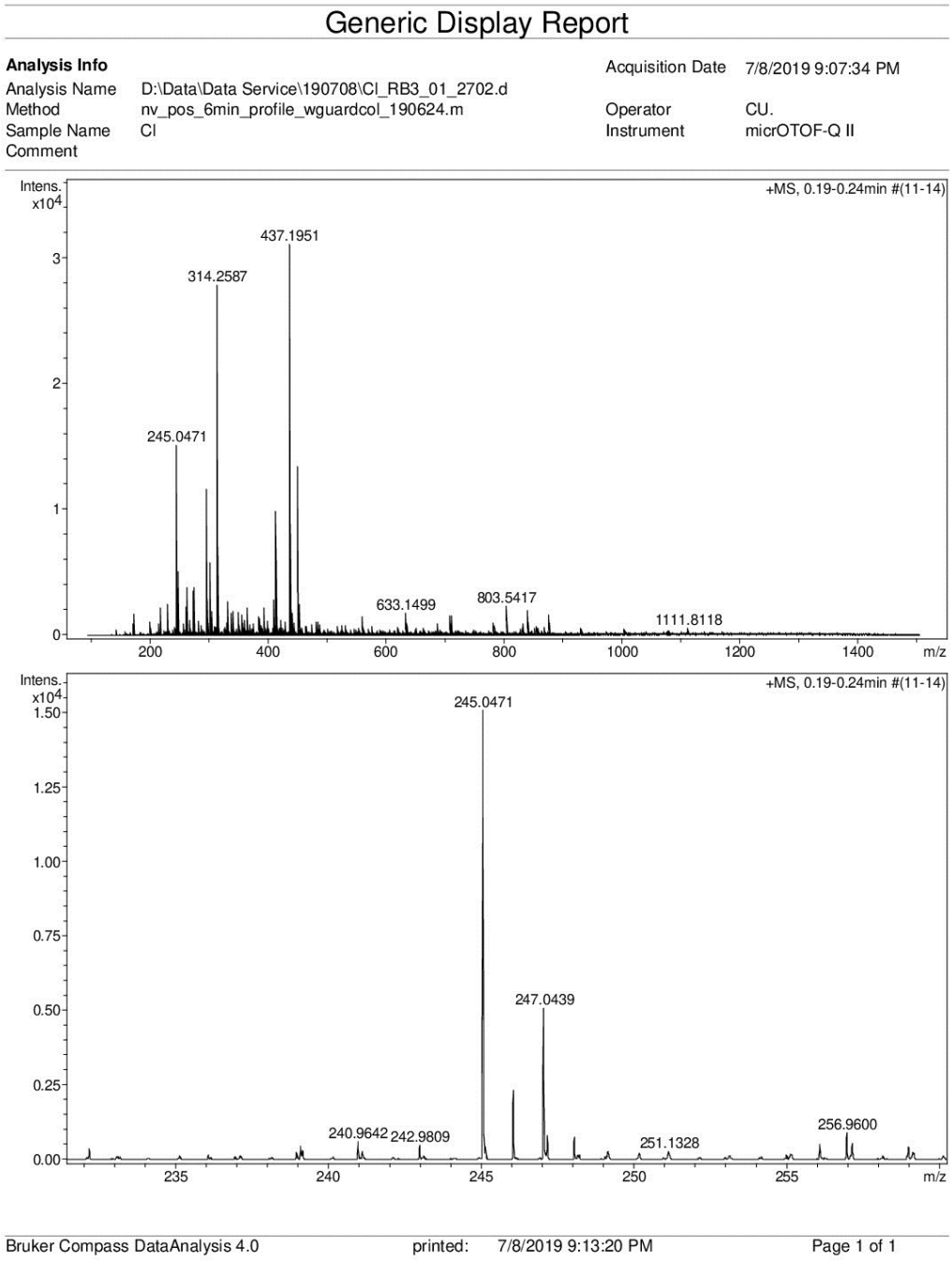


Figure S79 Mass spectrum of **6ah**

Generic Display Report

Analysis Info

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Sample Name	TM_4-OH NCS	Instrument	micrOTOF-Q II
Comment			

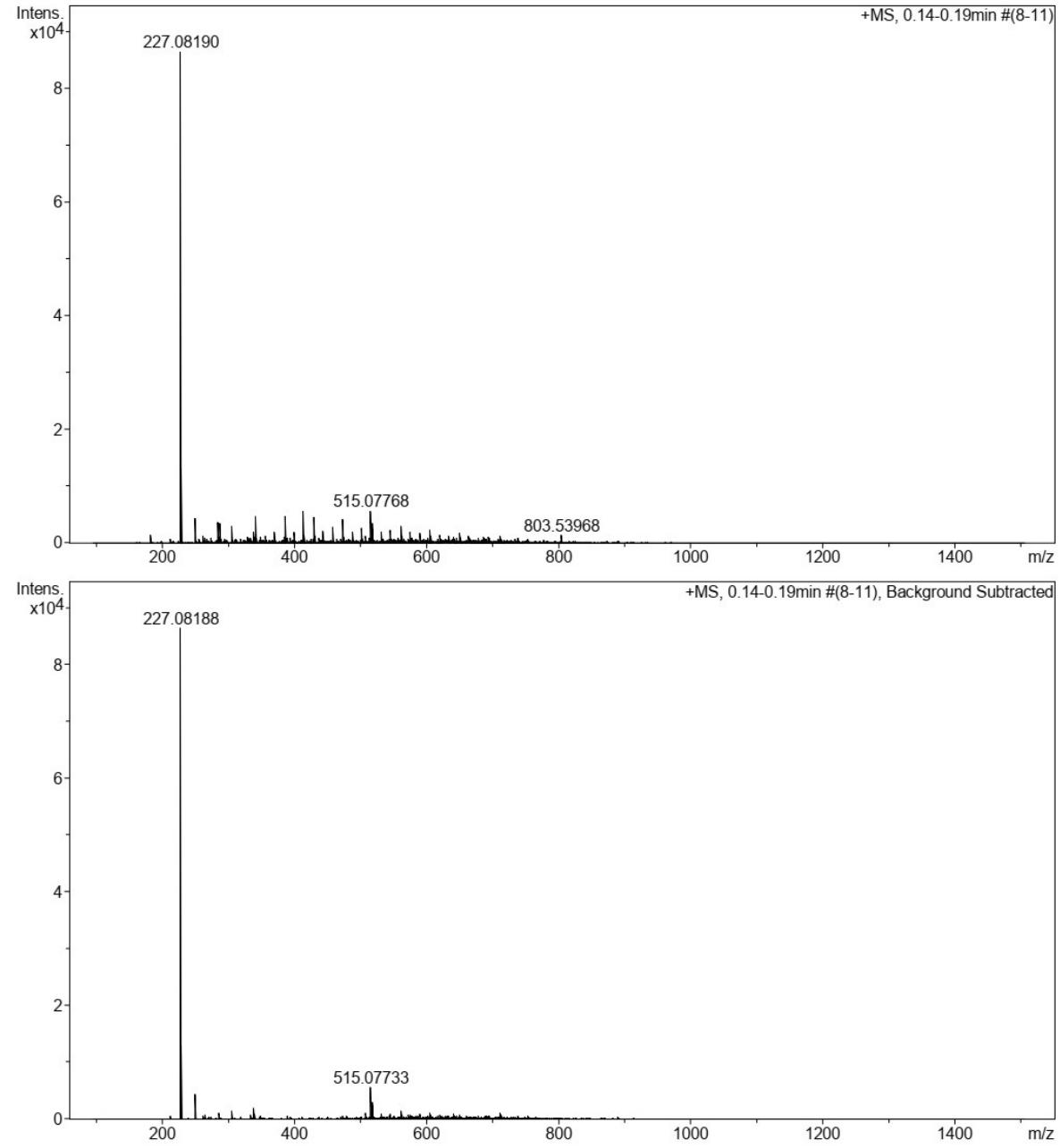

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Figure S80 Mass spectrum of **6ai**

Generic Display Report

Analysis Info

Analysis Name	D:\Data\Data Service\210301\TM_3-OH NCS_RA8_01_5355.d	Acquisition Date	3/1/2021 4:23:59 PM
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Sample Name	TM_3-OH NCS	Instrument	micrOTOF-Q II
Comment			

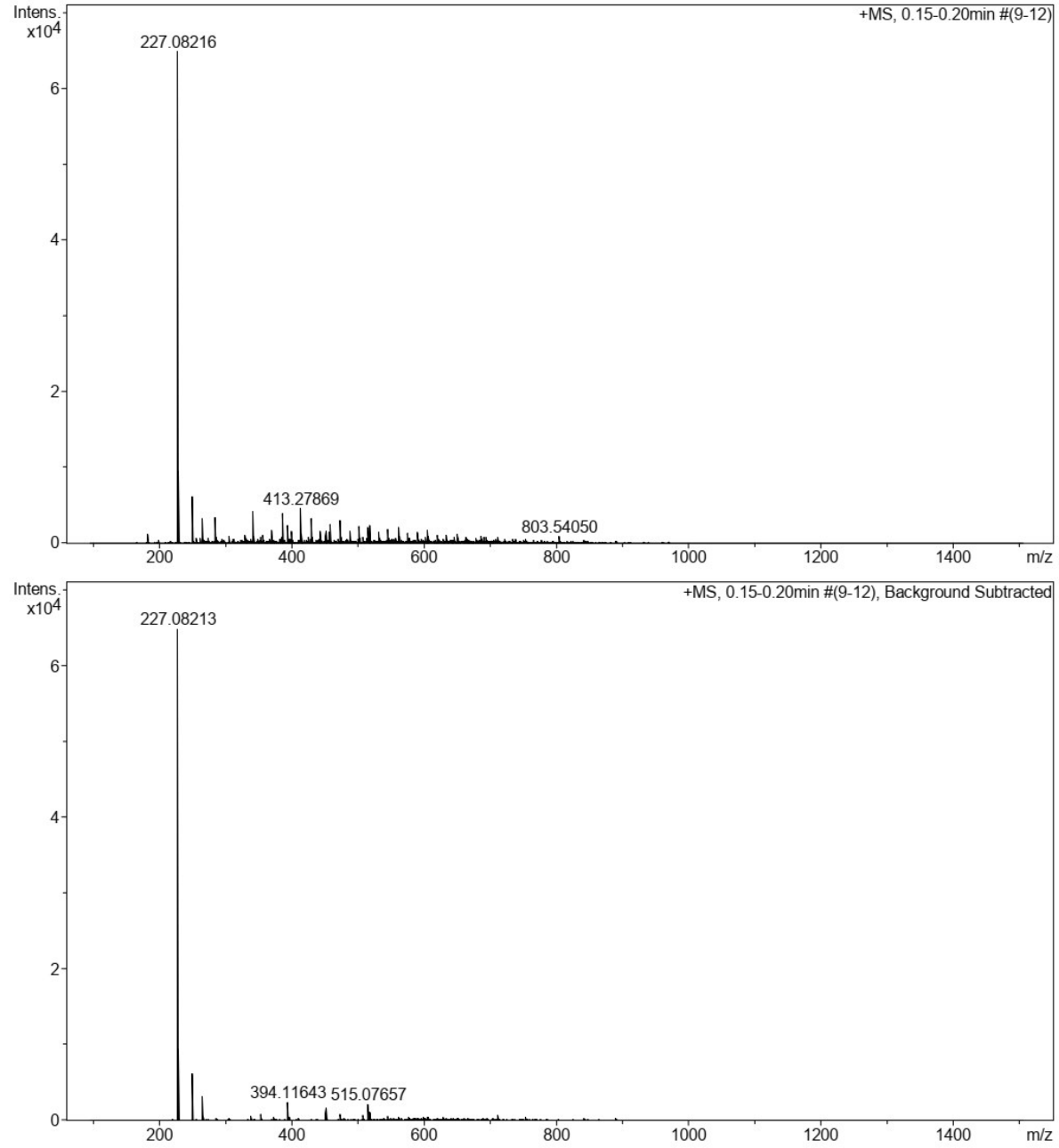

Figure S81 Mass spectrum of **6aj**

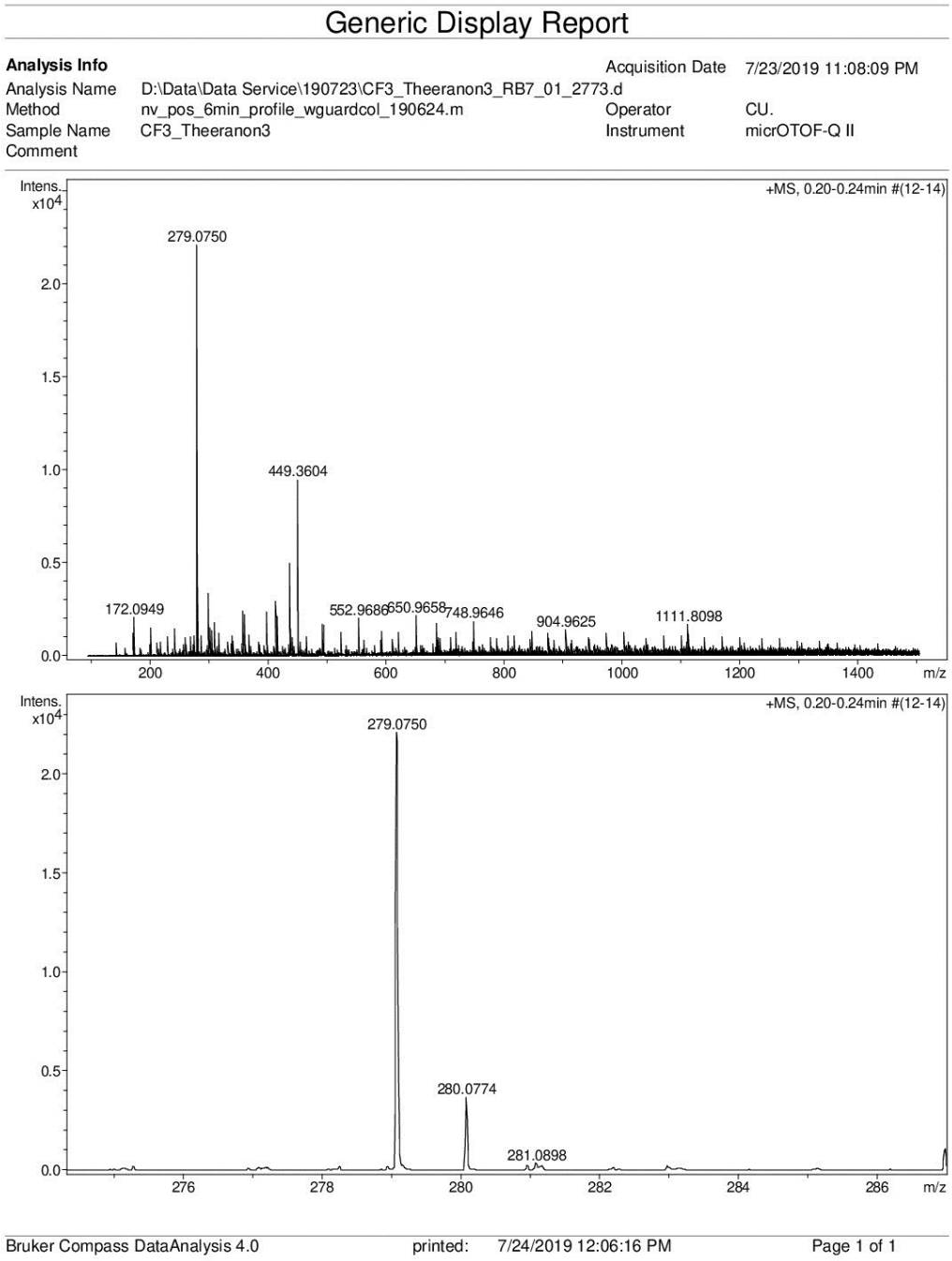

Figure S82 Mass spectrum of **6ak**

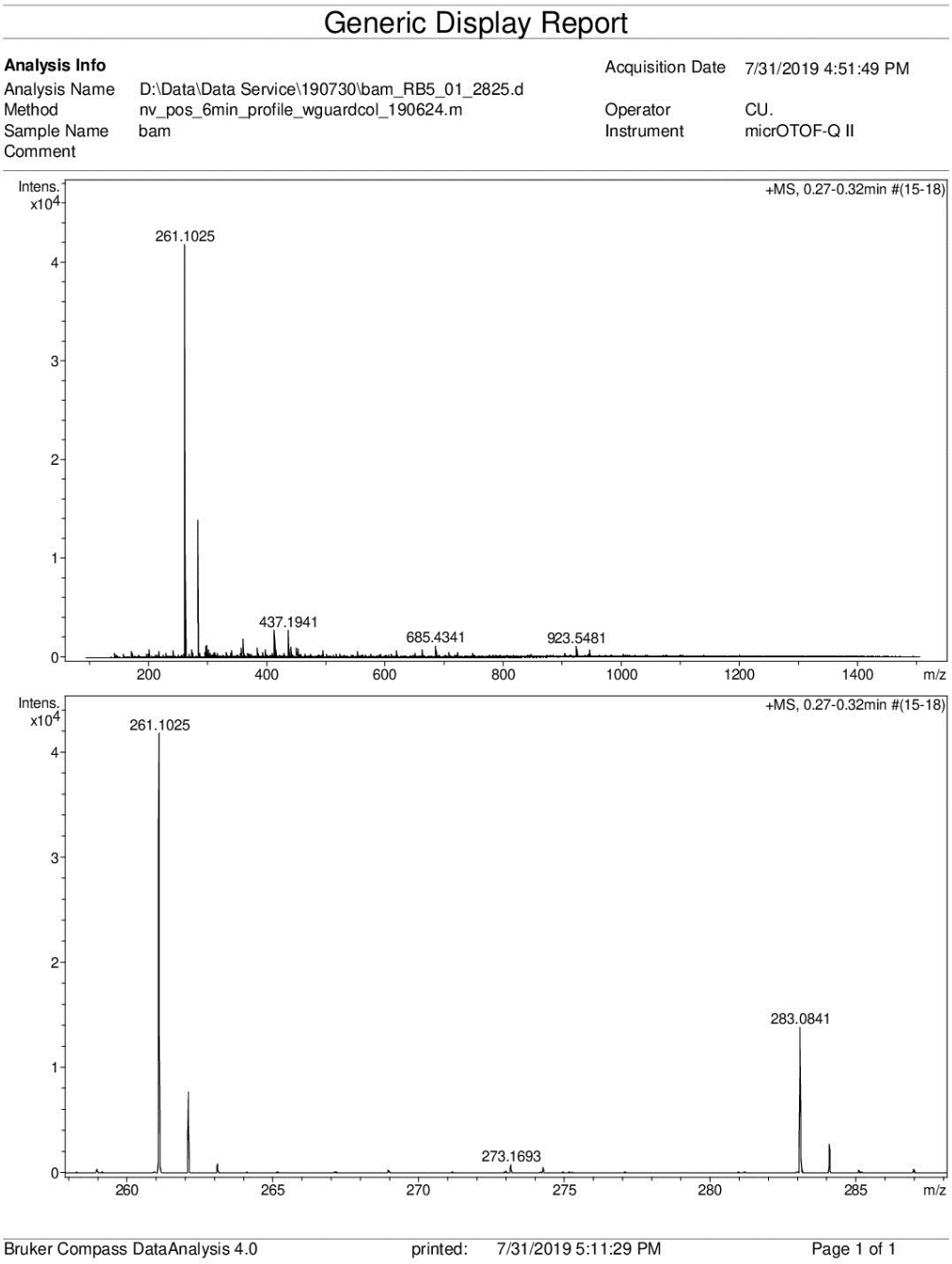

Figure S83 Mass spectrum of **6al**

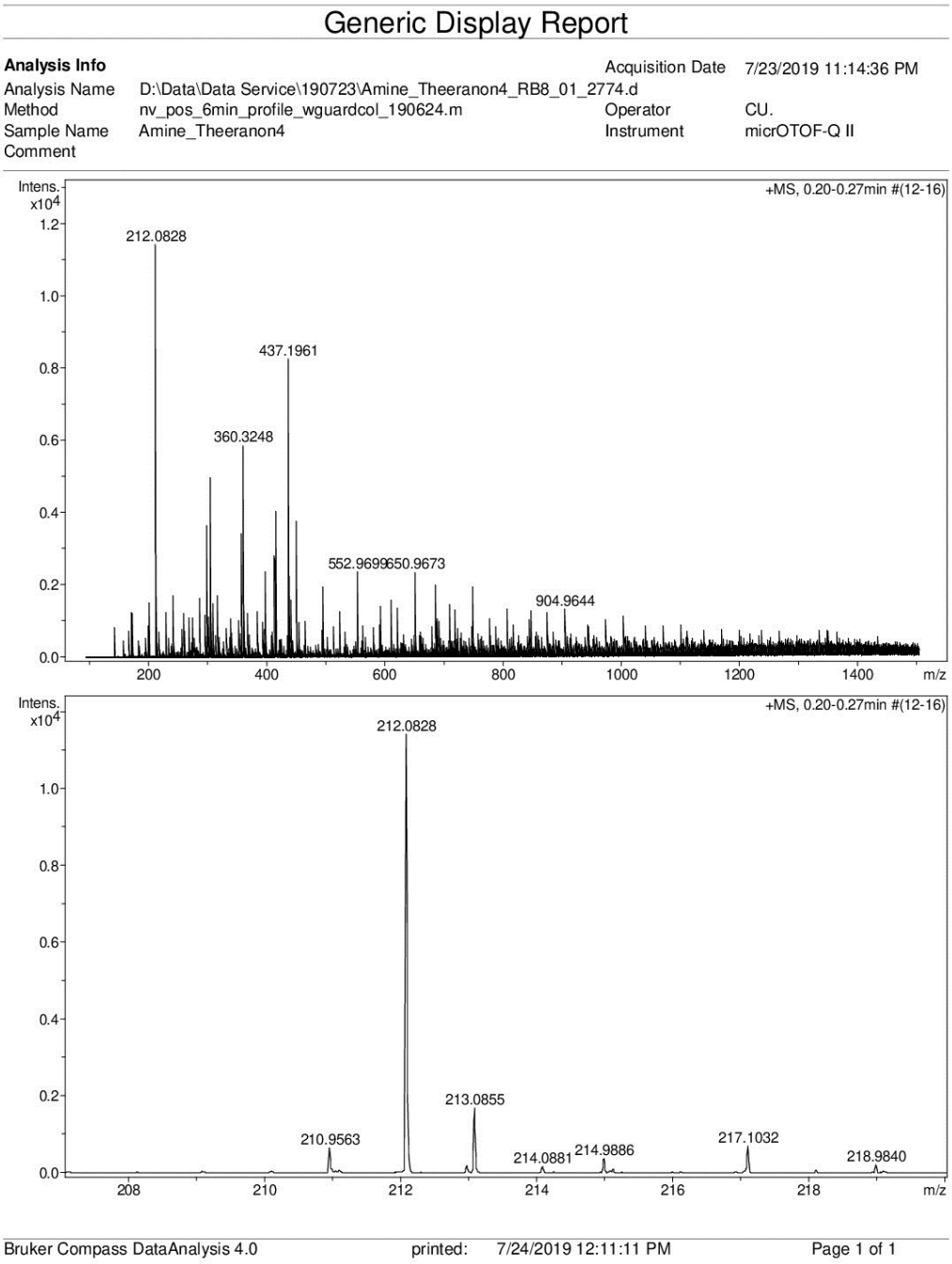

Figure S84 Mass spectrum of **6am**

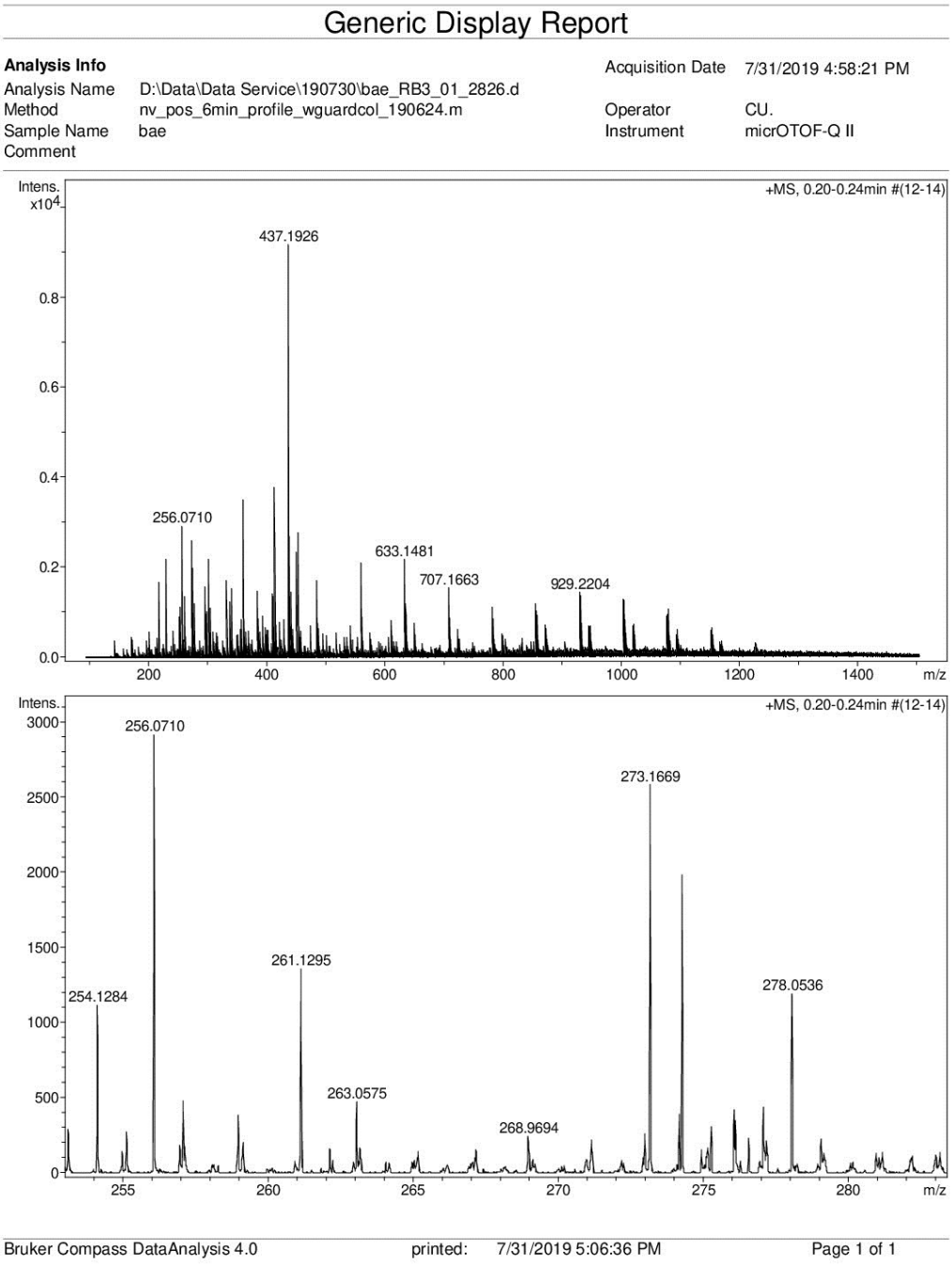

Figure S85 Mass spectrum of **6an**

Generic Display Report

Analysis Info

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Sample Name	TM_3-NO2 NCS	Instrument	micrOTOF-Q II
Comment			

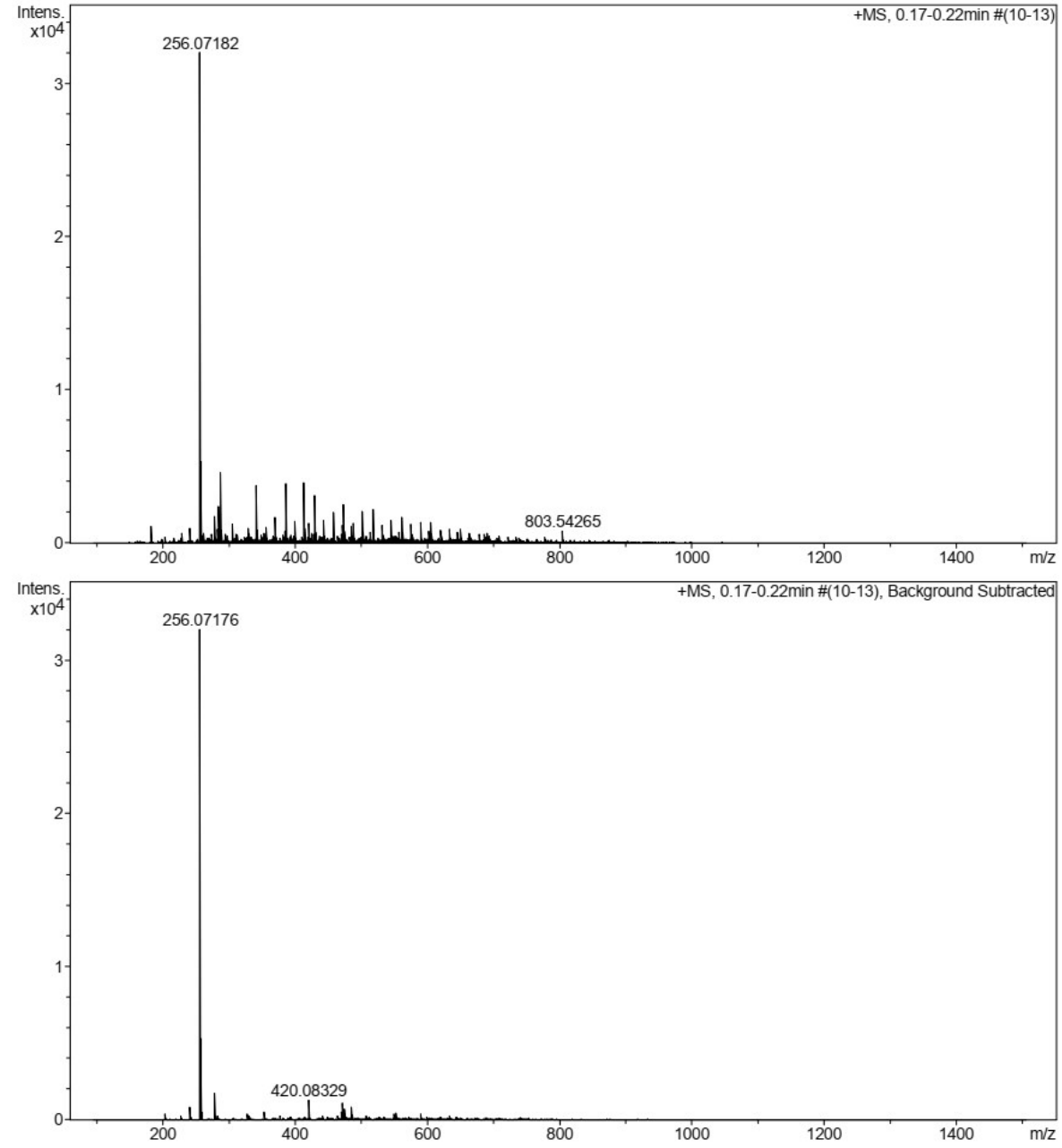

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Figure S86 Mass spectrum of **6ao**

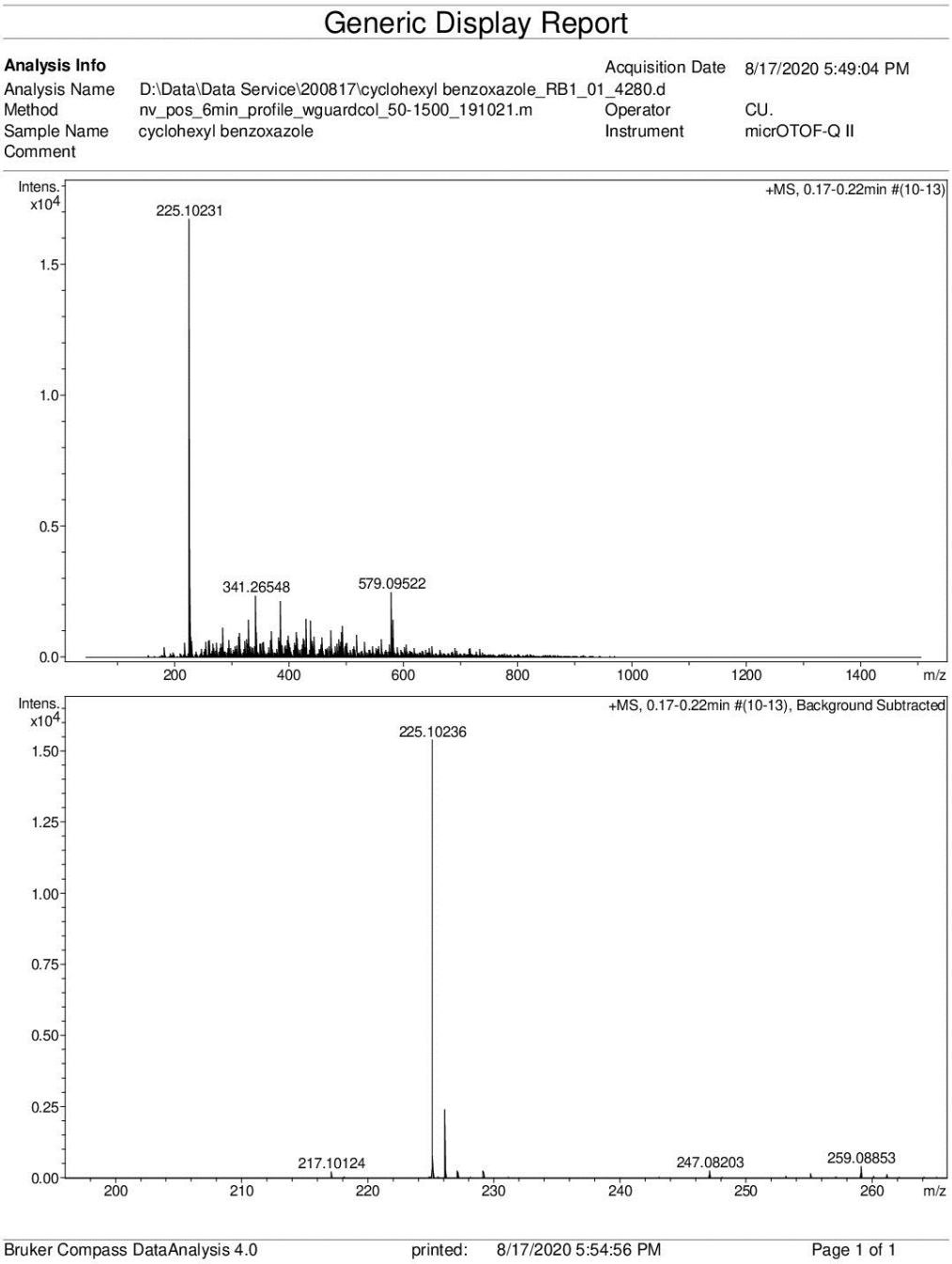

Figure S87 Mass spectrum of **6ap**

Generic Display Report

Analysis Info

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Sample Name	TM_Ester NCS	Instrument	micrOTOF-Q II
Comment			

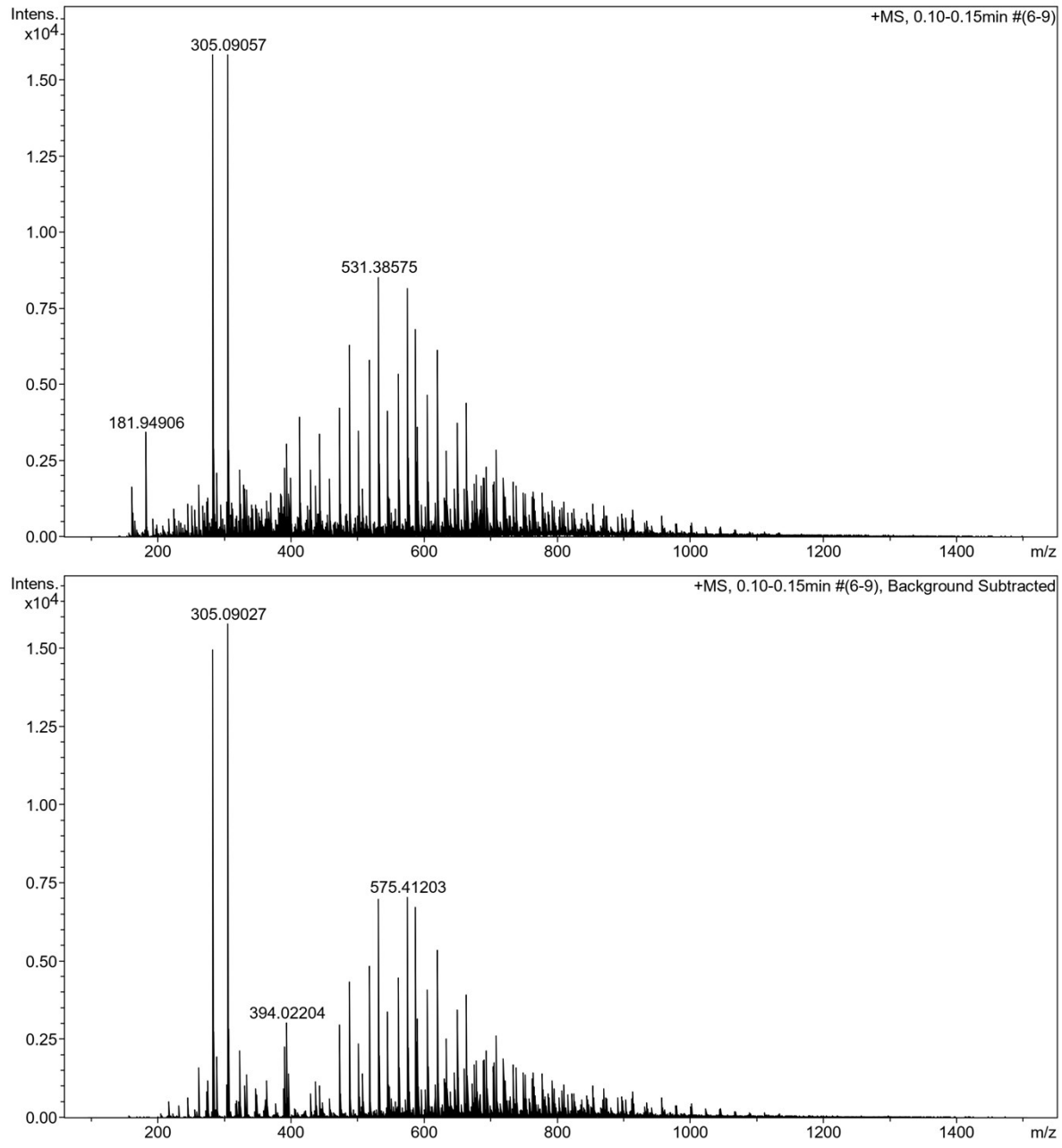

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Figure S88 Mass spectrum of **6aq**

Generic Display Report

Analysis Info

Acquisition Date	3/1/2021 4:29:10 PM		
Analysis Name	D:\Data\Data Service\210301\TM_4-OTBDMS NCS_RB1_01_5356.d		
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Sample Name	TM_4-OTBDMS NCS	Instrument	micrOTOF-Q II
Comment			

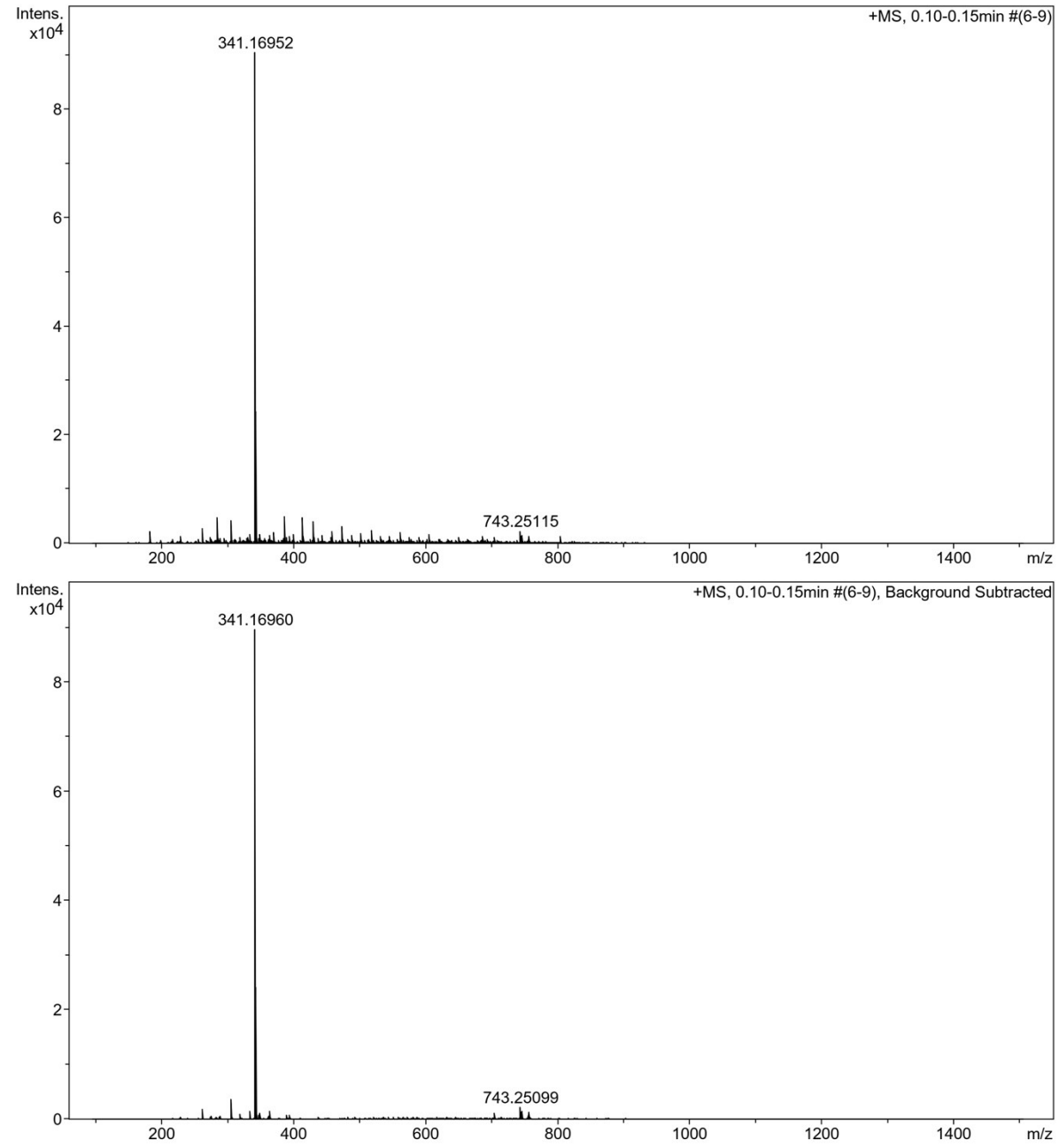

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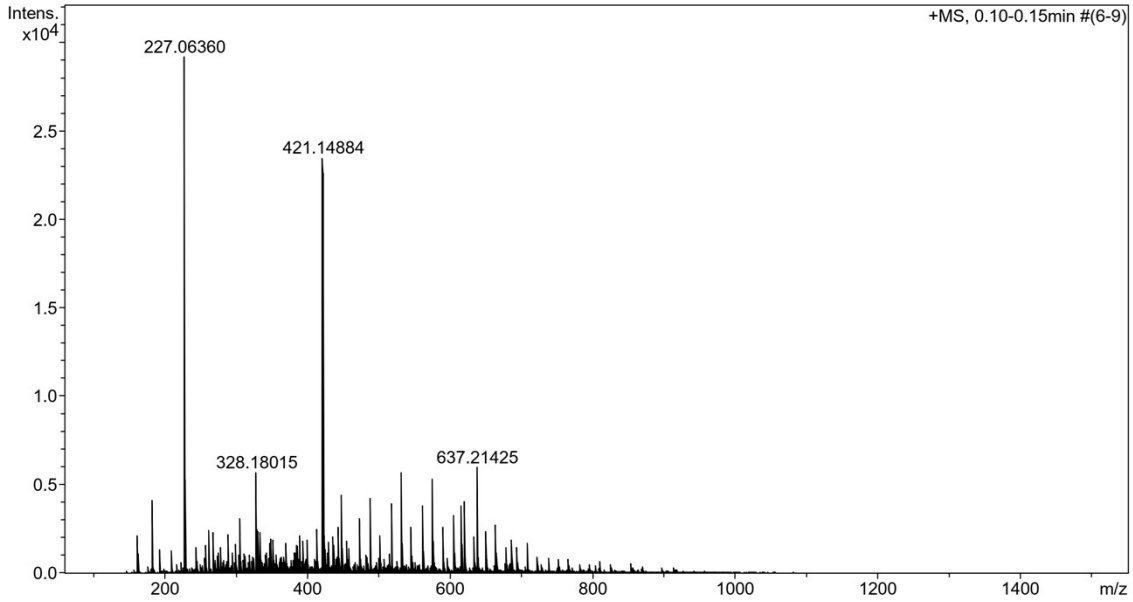
Figure S89 Mass spectrum of **6ar**

Generic Display Report

Analysis Info

Acquisition Date	1/11/2021 3:53:41 PM		
Analysis Name	D:\Data\Data Service\210111\TM_Benzothiazole_RA3_01_5132.d		
Method	nv_pos_5min_profile_190214.m	Operator	CU.
Sample Name	TM_Benzothiazole	Instrument	micrOTOF-Q II
Comment			



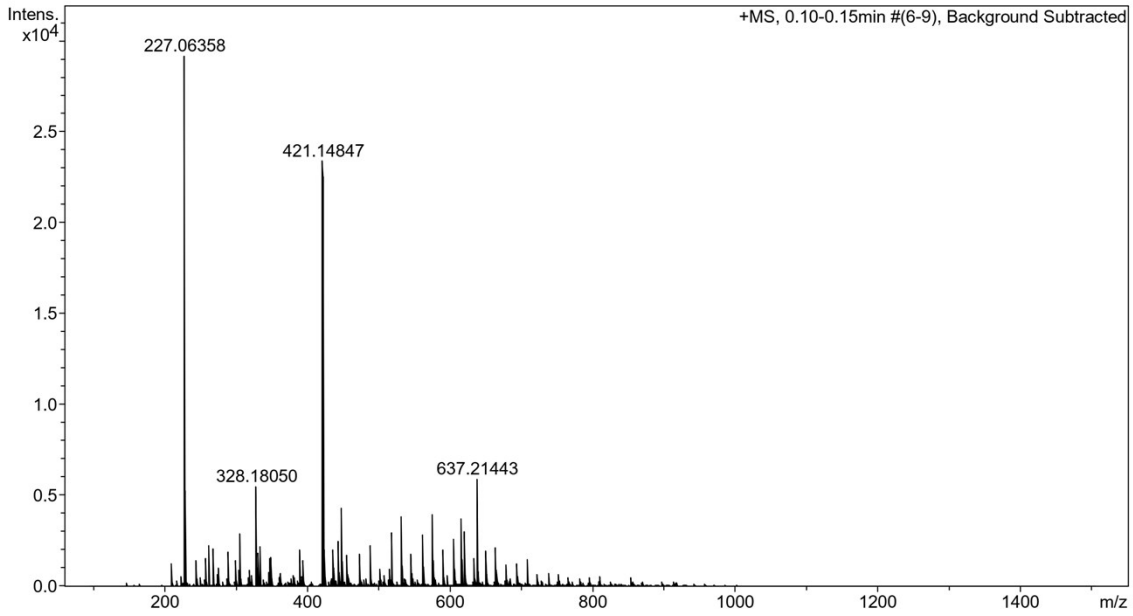


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Figure S90 Mass spectrum of **8aa**

Generic Display Report

Analysis Info

Acquisition Date	1/11/2021 4:06:30 PM		
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Sample Name	TM_3-CH3_NCS_thiazole	Instrument	micrOTOF-Q II
Comment			

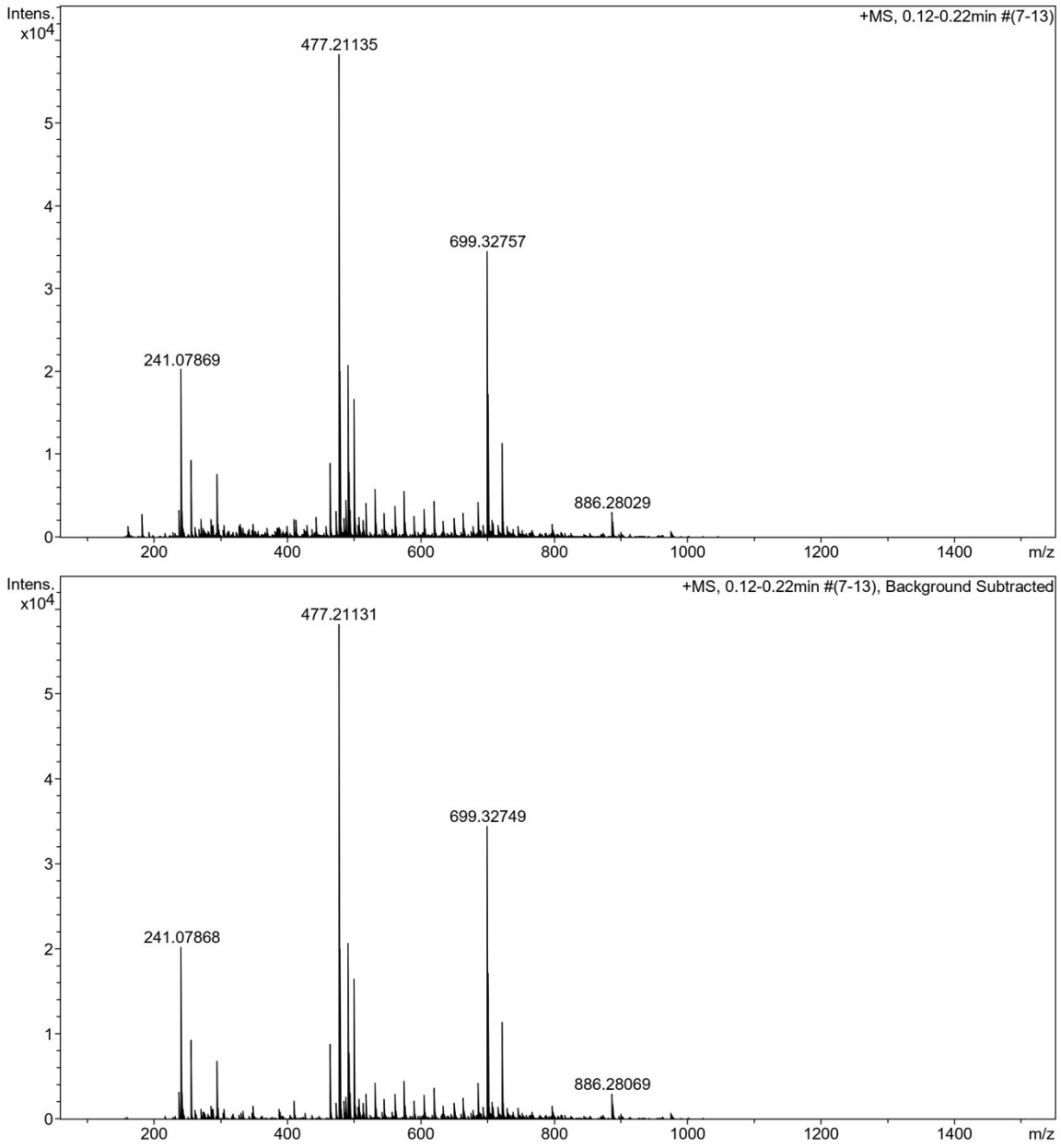

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Figure S91 Mass spectrum of **8ab**

Generic Display Report

Analysis Info

Acquisition Date	4/5/2021 3:10:20 PM		
Analysis Name	D:\Data\Data Service\210405\TM_3-I_NCS_thiazole_RB3_01_5702.d		
Method	nv_pos_5min_profile_190214.m	Operator	CU.
Sample Name	TM_3-I_NCS_thiazole	Instrument	micrOTOF-Q II
Comment			

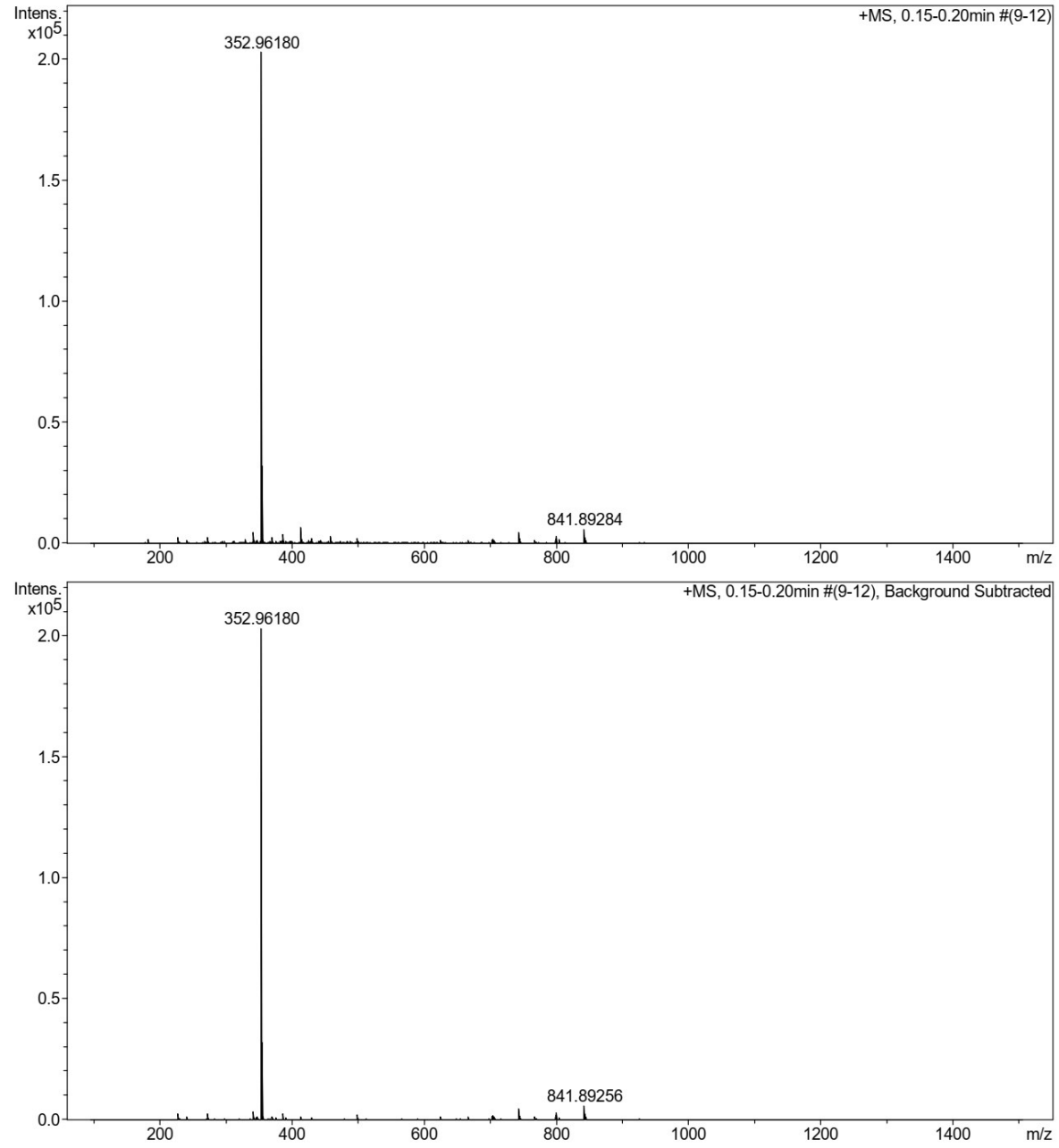

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Figure S92 Mass spectrum of **8ae**

Generic Display Report

Analysis Info

		Acquisition Date	1/11/2021 4:12:54 PM
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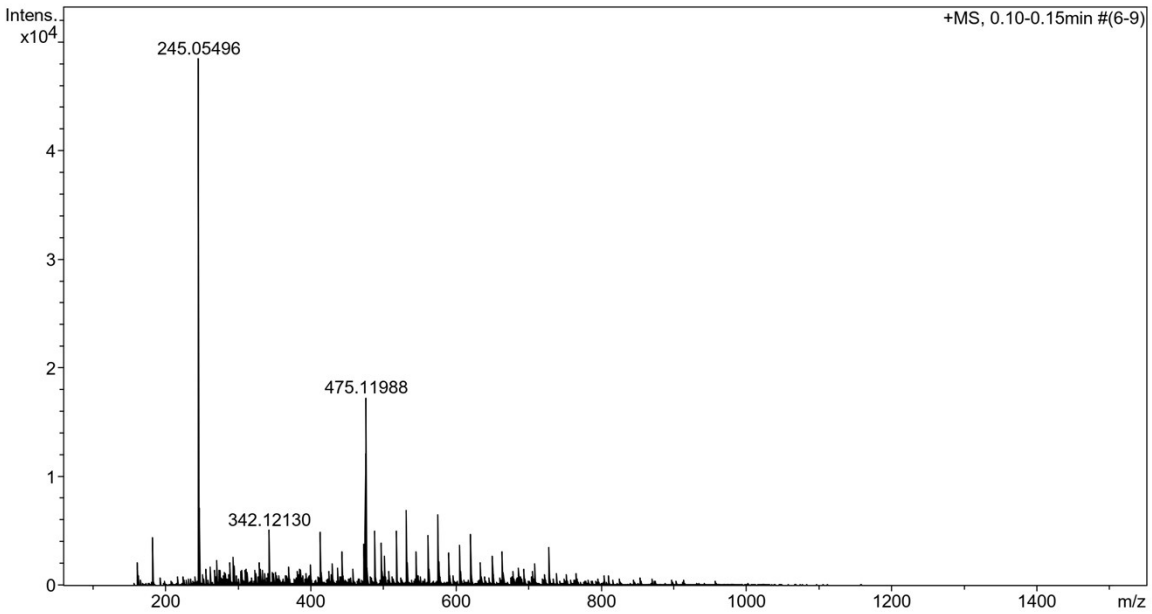
Sample Name	TM_2-F_NCS_thiazole	Instrument	micrOTOF-Q II
Comment			



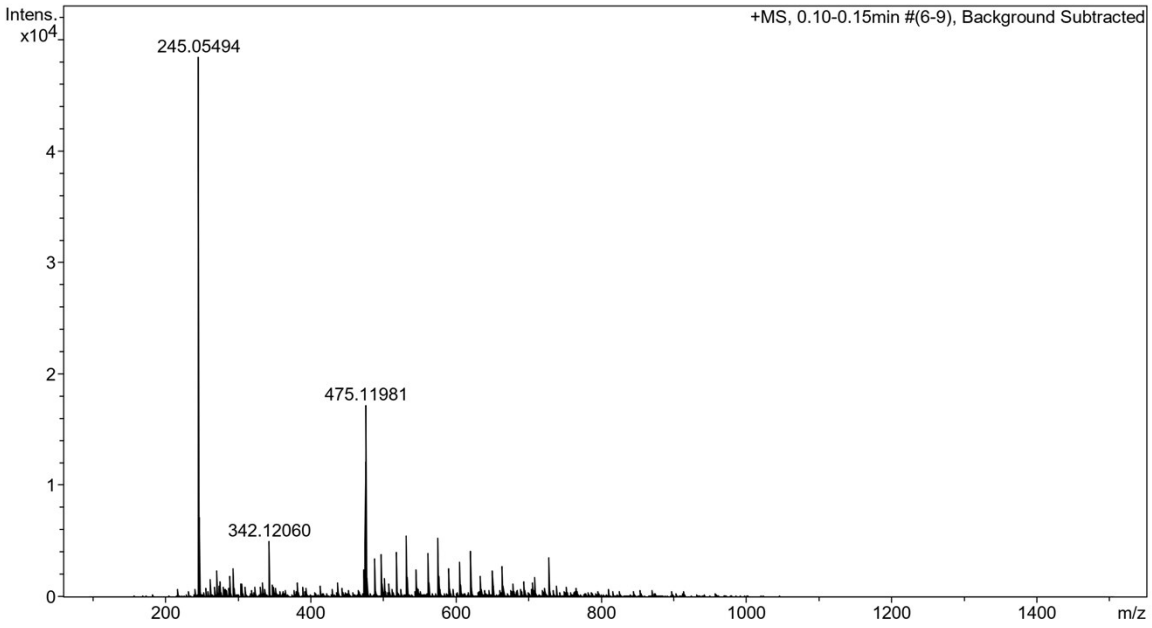


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Figure S93 Mass spectrum of **8ag**

Generic Display Report

Analysis Info

Analysis Name	D:\Data\Data Service\210111\TM_4-Cl_NCS_thiazole_RA4_01_5133.d	Acquisition Date	1/11/2021 4:00:05 PM
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Sample Name	TM_4-Cl_NCS_thiazole	Instrument	micrOTOF-Q II
Comment			

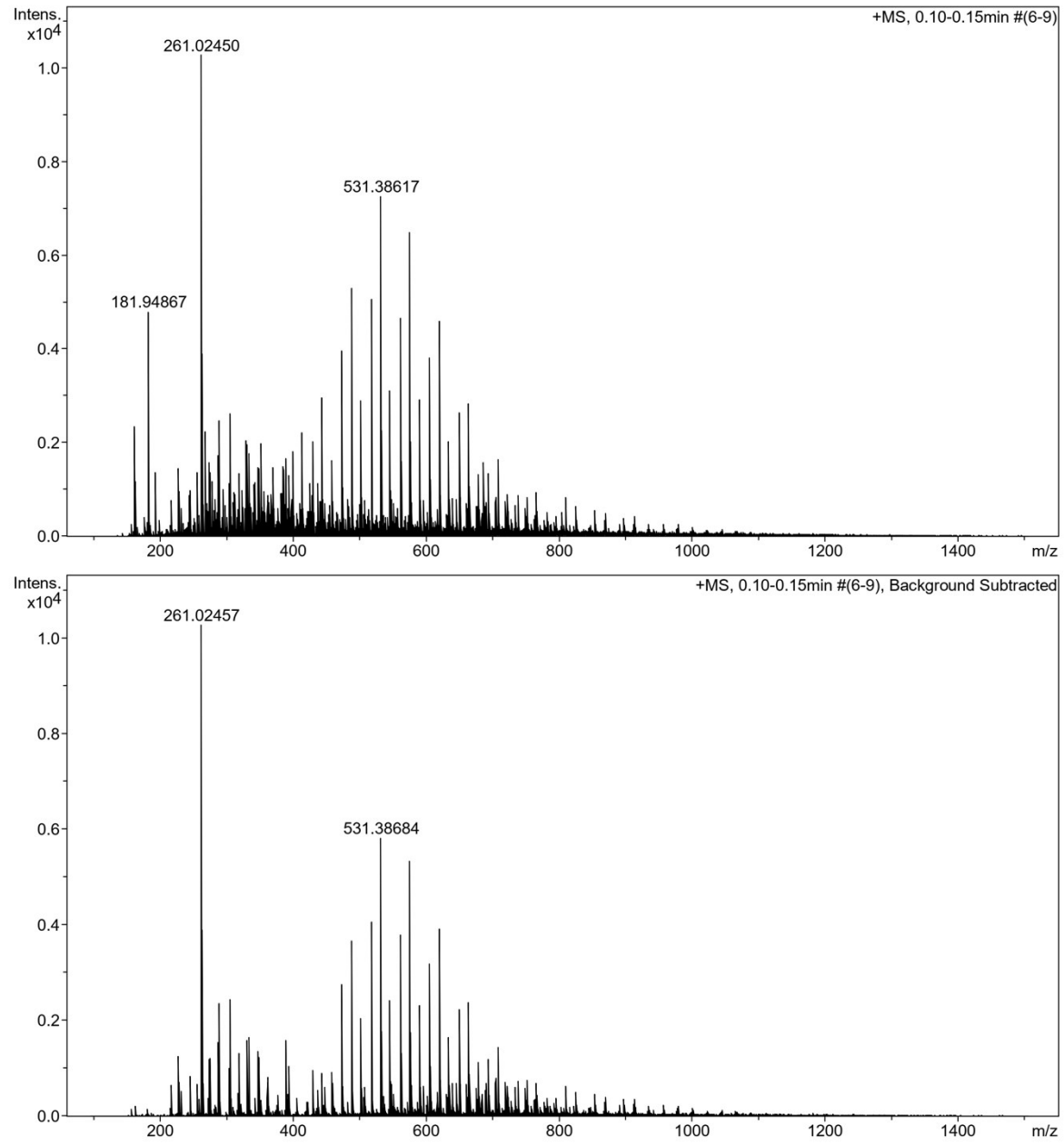

Figure S94 Mass spectrum of **8ah**

Generic Display Report

Analysis Info

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Analysis Name	D:\Data\Data Service\210315\TM_Ester NCS_benzothiazole_RC3_01_5490.d		
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Sample Name	TM_Ester NCS_benzothiazole	Instrument	micrOTOF-Q II
Comment			

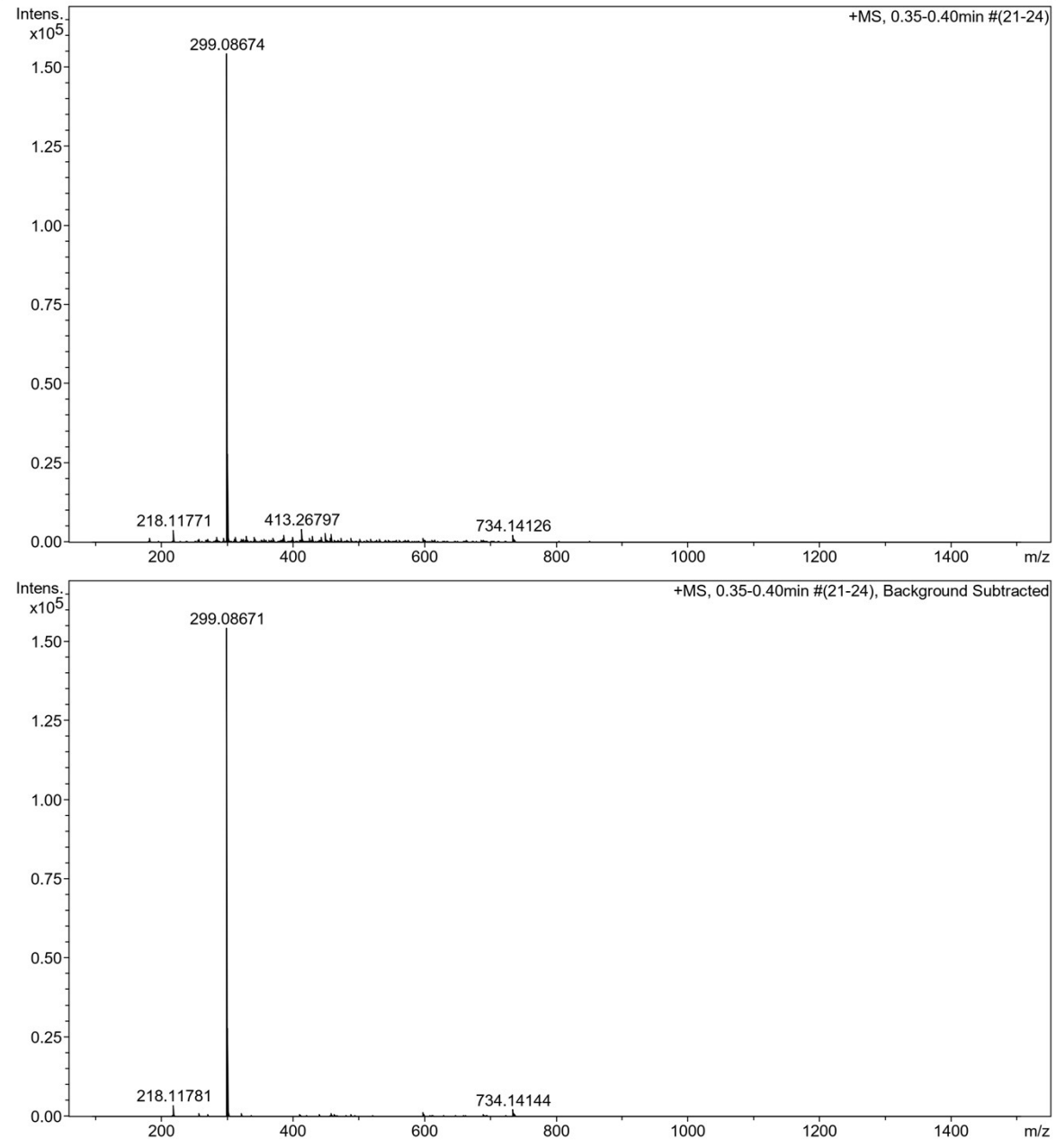

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Figure S95 Mass spectrum of **8aq**

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