

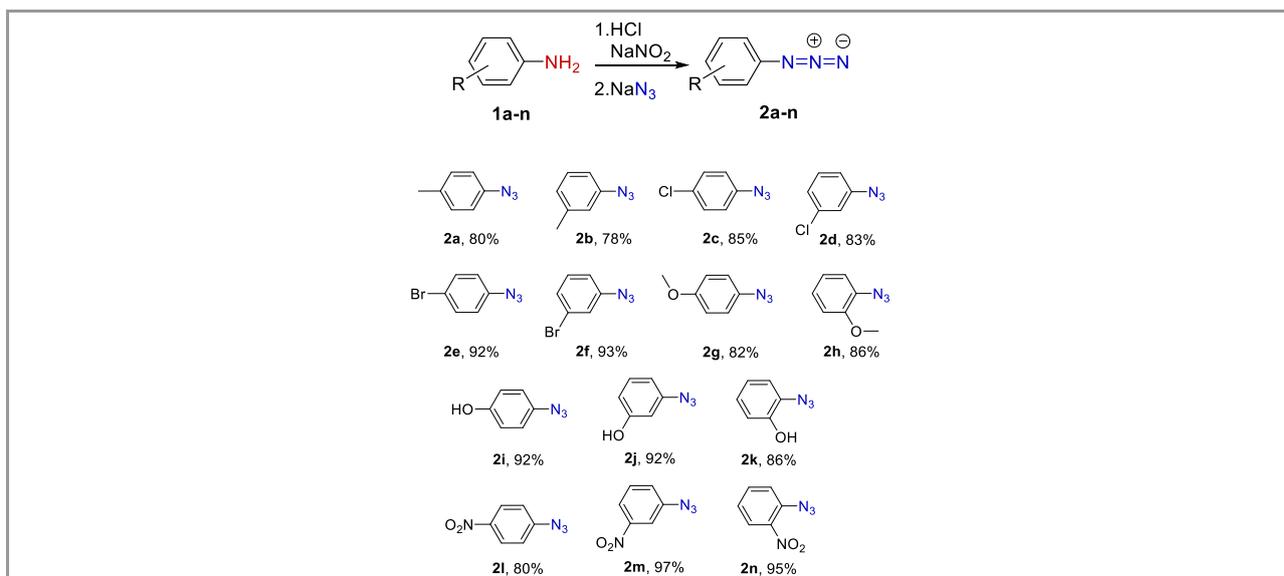
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**A convenient *E*-diastereoselective synthesis of *NH*-isatin *N'*-arylimines
via the aza-Wittig reaction**

Vadim E. Filatov, Dmitrii A. Iuzabchuk, Boris N. Tarasevich,
Nikolai V. Zyk and Elena K. Beloglazkina

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Scheme S1 Synthesis of aryl azides

General Information

All starting materials were obtained through commercial source. All solvents used were purified and dehydrated using the methods described in ¹. The reactions were analyzed by TLC analysis using silica plates with a fluorescent indicator (254 nm) and visualized with a UV lamp. ¹H and ¹³C NMR spectra were recorded using a Bruker Avance spectrometer (400 MHz for ¹H, 100 MHz for ¹³C) in DMSO-*d*₆. Chemical shifts are reported in parts per million relative to TMS. Electrospray ionization high-resolution mass spectra were recorded in positive ion mode using a TripleTOF 5600+ quadrupole time-of-flight mass spectrometer (ABSciex, Concord, Canada) equipped with a DuoSpray ion source. The following MS parameters were applied: capillary voltage 5.5 kV; nebulizing and curtain gas pressure 15 and 25 psi, respectively; ion source temperature - ambient; declustering potential 20 V; *m/z* range 100–1200. Elemental compositions of the detected ions were determined based on accurate masses and isotopic distributions using Formula Finder software (ABSciex, Concord, Canada). The maximum allowed deviation of the experimental molecular mass from the calculated one was 5 ppm. IR spectra were recorded using a Fourier transform spectrometer Nicolet iS5 (Thermo Scientific) using an internal reflectance attachment with diamond optical element – attenuated total reflection (ATR, iD7) with 45° angle of incidence. Resolution 4 cm⁻¹, the number of scans is 20.

General procedure for synthesis of aryl azides.^{2,3}

Aniline (930 mg, 10 mmol), water (15 mL), and concentrated HCl (37% w/w, 4 mL) were added to a round-bottom flask that was cooled at 0 °C in an ice bath. A solution of NaNO₂ (690 mg, 10 mmol) in water (2.5 mL) was added dropwise, and this was stirred for 10 min. Solid NaN₃ (780 mg, 12 mmol) was then added in portions and stirred for 1 h, while the reaction mixture was allowed to warm to room temperature. The solution was extracted with ethyl acetate (40 mL × 3). The organic layers were combined and washed with H₂O and saturated brine sequentially before being dried over Na₂SO₄.

1-Azido-4-methylbenzene (2a).³ A reaction of *p*-toluidine (2143 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-4-methylbenzene as orange oil (2137 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.17 (2 H, d, *J*=8.07 Hz) 6.94 (2 H, d, *J*=8.44 Hz) 2.34 (3 H, s).

1-Azido-3-methylbenzene (2b).⁴ A reaction of *m*-toluidine (2143 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-3-methylbenzene as colorless oil darkening at storage (2069 mg, 78%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.21 - 7.29 (1 H, m) 6.97 (1 H, d, *J*=7.51 Hz) 6.81 - 6.90 (2 H, m) 2.37 (3 H, s).

1-Azido-4-chlorobenzene (2c).⁵ A reaction of 4-chloroaniline (2551 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-4-chlorobenzene as yellow oil darkening at storage (2605 mg, 85%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.29 - 7.35 (2 H, m) 6.93 - 7.00 (2 H, m).

1-Azido-3-chlorobenzene (2d).⁶ A reaction of 3-chloroaniline (2551 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-3-chlorobenzene as brown oil (2548 mg, 83%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.29 (1 H, t, J=8.06 Hz) 7.13 (1 H, ddd, J=8.03, 1.89, 0.87 Hz) 7.04 (1 H, t, J=2.05 Hz) 6.93 (1 H, ddd, J=8.06, 2.18, 0.85 Hz).

1-Azido-4-bromobenzene (2e).⁷ A reaction of 4-bromoaniline (3441 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-4-bromobenzene yellow oil darkening at storage (3634 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.43 - 7.50 (2 H, m) 6.87 - 6.95 (2 H, m).

1-Azido-3-bromobenzene (2f).⁸ A reaction of 3-bromoaniline (3441 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-3-bromobenzene as orange oil darkening at storage (3689 mg, 93%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.21 - 7.30 (2 H, m) 7.17 - 7.21 (1 H, m) 6.97 (1 H, ddd, J=7.87, 2.09, 1.04 Hz).

1-Azido-4-methoxybenzene (2g).³ A reaction of 4-methoxyaniline (2463 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-4-methoxybenzene as brown oil (2454 mg, 82%).

¹H NMR (400 MHz, CDCl₃) δ ppm 6.94 - 7.00 (2 H, m) 6.86 - 6.93 (2 H, m).

1-Azido-2-methoxybenzene (2h).⁸ A reaction of 2-methoxyaniline (2463 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-2-methoxybenzene as yellow oil darkening at storage (2578 mg, 86%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.09 - 7.14 (1 H, m) 7.03 (1 H, dd, J=7.84, 1.64 Hz) 6.95 (1 H, td, J=7.56, 1.26 Hz) 6.91 (1 H, dd, J=8.17, 1.15 Hz).

4-Azidophenol (2i).⁷ A reaction of 4-aminophenol (2183 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 4-azidophenol as brown oil (2494 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ ppm 6.89 - 6.95 (2 H, m) 6.80 - 6.86 (2 H, m).

3-Azidophenol (2j).⁷ A reaction of 3-aminophenol (2183 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 3-azidophenol as orange oil darkening at storage (2382 mg, 92%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.22 (1 H, t, J=8.07 Hz) 6.59 - 6.69 (2 H, m) 6.52 (1 H, t, J=2.20 Hz) 5.19 (1 H, br. s.).

2-Azidophenol (2k).⁷ A reaction of 2-aminophenol (2183 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 2-azidophenol as colorless oil darkening at storage (2324 mg, 86%).

¹H NMR (400 MHz, CDCl₃) δ ppm 7.02 - 7.13 (2 H, m) 6.90 - 7.00 (2 H, m) 5.34 (1 H, br. s.).

1-Azido-4-nitrobenzene (2l).⁸ A reaction of 4-nitroaniline (2763 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-4-nitrobenzene as red solid (3108 mg, 95%).

¹H NMR (400 MHz, CDCl₃) δ ppm 8.22 - 8.29 (2 H, m) 7.11 - 7.19 (2 H, m).

1-Azido-3-nitrobenzene (2m).⁶ A reaction of 3-nitroaniline (2763 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-3-nitrobenzene as yellow oil (2640 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ ppm 8.01 (1 H, ddd, J=8.22, 2.08, 0.77 Hz) 7.90 (1 H, t, J=2.16 Hz) 7.55 (1 H, t, J=8.14 Hz) 7.36 (1 H, ddd, J=8.06, 2.22, 0.79 Hz).

1-Azido-2-nitrobenzene (2n).⁹ A reaction of 2-nitroaniline (2763 mg, 20 mmol), sodium nitrite (1725 mg, 25 mmol) and sodium azide (1625 mg, 25 mmol) yields a 1-azido-2-nitrobenzene as brown oil (3197 mg, 97%).

^1H NMR (400 MHz, CDCl_3) δ ppm 7.95 (1 H, dd, $J=8.19, 1.45$ Hz) 7.60 - 7.67 (1 H, m) 7.35 (1 H, dd, $J=8.17, 1.10$ Hz) 7.23 - 7.30 (1 H, m).

General procedure for synthesis of isatinimines 3a-m.

To triphenylphosphine (2623 mg, 10 mmol) dissolved in dry dichloromethane (10 ml), aryl azide (10 mmol) solution in dichloromethane (10 ml) was slowly added. After the end of gas evolution, isatin (1471 mg, 10 mmol) was added in a single portion. The reaction then was stirred until a precipitate was formed (TLC control). The precipitate was separated by suction filtration washed by two portions of methanol (5 ml) and one portion of diethyl ether (5ml) to afford final product. An additional portion of product can be obtained by precipitating washings.

3-(p-Tolylimino)indolin-2-one (3a). A reaction of 1-azido-4-methylbenzene (1331 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-(p-tolylimino)indolin-2-one as an orange solid (1839 mg, 78%, E/Z=6.7/1).

IR (cm^{-1}): 3255, 1741, 1723, 1611, 1463 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO-d_6) δ ppm 10.98 (s, 1 H) 7.33 (td, $J=7.73, 1.09$ Hz, 1 H) 7.26 (d, $J=8.19$ Hz, 2 H) 6.88 (d, $J=8.24$ Hz, 3 H) 6.72 (t, $J=7.66$ Hz, 1 H) 6.48 (d, $J=7.51$ Hz, 1 H) 2.35 (s, 3 H)

(Z) ^1H NMR (400 MHz, DMSO-d_6) δ ppm 10.86 (s, 1 H) 7.57 (d, $J=7.04$ Hz, 1 H) 7.43 (td, $J=7.72, 1.15$ Hz, 1 H) 7.11 (d, $J=8.24$ Hz, 2 H) 7.04 (t, $J=7.55$ Hz, 1 H) 6.94 (d, $J=8.24$ Hz, 2 H) 6.85 (d, $J=7.81$ Hz, 1 H) 2.29 (s, 3 H)

(E) ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 163.57, 154.79, 147.87, 146.90, 134.19, 130.03, 125.26, 121.72, 117.47, 115.75, 111.51, 20.61.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}^+$: 237,1022; found: 237,1021.

3-(m-Tolylimino)indolin-2-one (3b). A reaction of 1-azido-3-methylbenzene (1332 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-(m-tolylimino)indolin-2-one as orange solid (1878 mg, 80%, E/Z=7.3/1).

IR (cm^{-1}): 3186, 1745, 1725, 1615, 1462 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO-d_6) δ ppm 10.98 (s, 1 H) 7.33 (td, $J=7.70, 3.78$ Hz, 2 H) 7.03 - 7.09 (m, 1 H) 6.89 (d, $J=7.84$ Hz, 1 H) 6.68 - 6.81 (m, 3 H) 6.38 (d, $J=7.67$ Hz, 1 H) 2.33 (s, 3 H)

(Z) ^1H NMR (400 MHz, DMSO-d_6) δ ppm 10.86 (s, 1 H) 7.57 (d, $J=7.45$ Hz, 1 H) 7.44 (td, $J=7.73, 1.10$ Hz, 1 H) 7.18 (t, $J=7.62$ Hz, 1 H) 7.02 - 7.09 (m, 1 H) 6.83 - 6.94 (m, 2 H) 6.67 - 6.81 (m, 2 H) 2.28 (s, 1 H)

(E) ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 163.53, 154.83, 150.59, 146.93, 139.12, 134.40, 129.46, 125.58, 125.43, 121.75, 117.61, 115.70, 114.19, 111.52, 21.06.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}^+$: 237,1022; found: 237,1020.

3-((4-Chlorophenyl)imino)indolin-2-one (3c). A reaction of 1-azido-4-chlorobenzene (1536 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((4-chlorophenyl)imino)indolin-2-one as orange solid (2045 mg, 76%, E/Z=4/1).

IR (cm^{-1}): 3261, 1739, 1722, 1611, 1481, 1463, 1334 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO-d_6) δ ppm 11.00 (s, 1 H) 7.51 (d, $J=8.55$ Hz, 2 H) 7.31 - 7.38 (m, 1 H) 7.04 (d, $J=8.61$ Hz, 2 H) 6.89 (d, $J=7.84$ Hz, 1 H) 6.76 (t, $J=7.65$ Hz, 1 H) 6.43 (d, $J=7.67$ Hz, 1 H)

(Z) ^1H NMR (400 MHz, DMSO-d_6) δ ppm 10.90 (s, 1 H) 7.58 (d, $J=7.56$ Hz, 1 H) 7.45 (t, $J=7.73$ Hz, 1 H) 7.31 - 7.38 (m, 2 H) 7.00 - 7.09 (m, 2 H) 6.86 (d, $J=7.89$ Hz, 1 H)

(E) ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 163.37, 155.44, 149.21, 147.15, 134.67, 129.59, 129.09, 125.45, 121.85, 119.42, 115.60, 111.63.

(Z) ^{13}C NMR (101 MHz, DMSO-d_6) δ ppm 158.54, 153.61, 147.99, 145.87, 134.41, 128.55, 128.26, 122.95, 122.34, 121.24, 120.94, 110.85.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{10}\text{ClN}_2\text{O}^+$: 257,0476; found: 257,0476.

3-((3-Chlorophenyl)imino)indolin-2-one (3d). A reaction of 1-azido-3-chlorobenzene (1536 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((3-chlorophenyl)imino)indolin-2-one as orange solid (1944 mg, 80%, E/Z=3.5/1).

IR (cm⁻¹): 3199, 1744, 1723, 1615, 1586, 1461, 1337 cm⁻¹.

(E) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 11.01 (br. s., 1 H) 7.49 (t, J=8.03 Hz, 1 H) 7.36 (t, J=7.65 Hz, 1 H) 7.27 - 7.33 (m, 1 H) 7.12 (s, 1 H) 6.97 (d, J=7.84 Hz, 1 H) 6.90 (d, J=7.84 Hz, 1 H) 6.77 (t, J=7.62 Hz, 1 H) 6.35 (d, J=7.67 Hz, 1 H)

(Z) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 10.90 (br. s., 1 H) 7.59 (d, J=7.34 Hz, 1 H) 7.43 - 7.52 (m, 1 H) 7.27 - 7.35 (m, 1 H) 7.04 - 7.16 (m, 3 H) 6.84 - 6.99 (m, 2 H)

(E) ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 163.32, 155.68, 152.02, 147.20, 134.81, 134.04, 131.44, 125.48, 124.61, 121.90, 117.20, 116.13, 115.59, 111.68.

HRMS (ESI): calcd for C₁₄H₁₀ClN₂O⁺: 257,0476; found: 257,0475.

3-((4-Bromophenyl)imino)indolin-2-one (3e). A reaction of 1-azido-4-bromobenzene (1980 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((4-bromophenyl)imino)indolin-2-one as orange solid (2752 mg, 91%, E/Z=3.5/1).

IR (cm⁻¹): 3267, 3196, 1739, 1721, 1611, 1461, 1334 cm⁻¹.

(E) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 11.01 (s, 1 H) 7.64 (d, J=8.60 Hz, 2 H) 7.36 (t, J=7.76 Hz, 1 H) 6.98 (d, J=8.60 Hz, 2 H) 6.90 (d, J=7.84 Hz, 1 H) 6.77 (t, J=7.65 Hz, 1 H) 6.43 (d, J=7.67 Hz, 1 H)

(Z) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 10.90 (s, 1 H) 7.61 - 7.67 (m, 1 H) 7.43 - 7.49 (m, 3 H) 7.06 (t, J=7.56 Hz, 1 H) 6.94 - 7.00 (m, 2 H) 6.86 (d, J=7.84 Hz, 1 H)

(E) ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 163.33, 155.31, 149.61, 147.13, 134.71, 132.49, 125.45, 121.89, 119.77, 117.16, 115.60, 111.62.

HRMS (ESI): calcd for C₁₄H₁₀BrN₂O⁺: 300,9971; found: 300,9969.

3-((3-Bromophenyl)imino)indolin-2-one (3f). A reaction of 1-azido-3-bromobenzene (1980 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((3-bromophenyl)imino)indolin-2-one as orange solid (2024 mg, 67%, E/Z=3/1).

IR (cm⁻¹): 3196, 1745, 1723, 1657, 1615, 1585, 1462, 1337 cm⁻¹.

(E) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 10.99 (br. s., 1 H) 7.44 (s, 2 H) 7.37 (td, J=7.73, 0.77 Hz, 1 H) 7.25 (s, 1 H) 7.01 (dt, J=6.47, 2.11 Hz, 1 H) 6.90 (d, J=7.84 Hz, 1 H) 6.77 (t, J=7.59 Hz, 1 H) 6.36 (d, J=7.62 Hz, 1 H)

(Z) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 10.99 (br. s., 1 H) 7.60 (s, 1 H) 7.45 - 7.49 (m, 1 H) 7.41 - 7.43 (m, 1 H) 7.26 - 7.29 (m, 1 H) 7.19 - 7.23 (m, 1 H) 7.07 (t, J=7.51 Hz, 1 H) 6.96 - 6.99 (m, 1 H) 6.87 (d, J=7.84 Hz, 1 H)

(E) ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 163.32, 155.69, 152.15, 147.22, 134.83, 131.69, 127.53, 125.48, 122.43, 121.91, 119.94, 116.54, 115.62, 111.70.

HRMS (ESI): calcd for C₁₄H₁₀BrN₂O⁺: 300,9971; found: 300,9971.

3-((4-Methoxyphenyl)imino)indolin-2-one (3g). A reaction of 1-azido-4-methoxybenzene (1492 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((4-methoxyphenyl)imino)indolin-2-one as orange solid (2215 mg, 88%, E/Z=5/1).

IR (cm⁻¹): 3229, 3116, 1738, 1722, 1611, 1499, 1461, 1245 cm⁻¹.

(E) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 10.96 (s, 1 H) 7.33 (t, J=7.70 Hz, 1 H) 7.03 (d, J=8.71 Hz, 2 H) 6.98 (d, J=8.93 Hz, 2 H) 6.89 (d, J=7.67 Hz, 1 H) 6.75 (t, J=7.65 Hz, 1 H) 6.65 (d, J=7.67 Hz, 1 H) 3.79 (s, 3 H).

(Z) ¹H NMR (400 MHz, DMSO-d₆) δ ppm 10.85 (s, 1 H) 7.55 (d, J=7.23 Hz, 2 H) 7.40 (t, J=7.70 Hz, 1 H) 7.18 (d, J=8.77 Hz, 2 H) 6.86 - 6.92 (m, 2 H) 6.84 (d, J=7.78 Hz, 1 H) 3.77 (s, 3 H).

(E) ¹³C NMR (101 MHz, DMSO-d₆) δ ppm 163.70, 157.11, 154.56, 146.82, 143.10, 134.22, 124.98, 121.72, 119.51, 115.82, 114.73, 111.48, 55.31.

HRMS (ESI): calcd for C₁₅H₁₃N₂O₂⁺: 253,0972; found: 253,0973.

3-((2-Methoxyphenyl)imino)indolin-2-one (3h). A reaction of 1-azido-2-methoxybenzene (1492 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((2-methoxyphenyl)imino)indolin-2-one as orange solid (1536 mg, 61%, E/Z=5.4/1).

IR (cm⁻¹): 3154, 3092, 1747, 1727, 1608, 1489, 1459, 1245 cm⁻¹.

(E) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.97 (s, 1 H) 7.34 (t, $J=7.72$ Hz, 1 H) 7.23 (t, $J=7.74$ Hz, 1 H) 7.15 (d, $J=8.15$ Hz, 1 H) 7.03 (t, $J=7.62$ Hz, 1 H) 6.89 (dd, $J=7.85, 3.54$ Hz, 2 H) 6.74 (t, $J=7.64$ Hz, 1 H) 6.44 (d, $J=7.68$ Hz, 1 H) 3.70 (s, 3 H).

(Z) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.80 (s, 1 H) 7.61 (d, $J=7.64$ Hz, 1 H) 7.45 (t, $J=7.70$ Hz, 1 H) 6.96 - 7.10 (m, 3 H) 6.84 - 6.93 (m, 3 H) 3.70 (s, 3 H).

^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 163.55, 155.64, 147.57, 146.52, 139.00, 134.43, 126.14, 124.97, 121.97, 121.10, 118.45, 116.35, 112.21, 111.44, 55.48.

HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{O}_2^+$: 253,0972; found: 253,0973.

3-((4-Hydroxyphenyl)imino)indolin-2-one (3i). A reaction of 4-azidophenol (1351 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((4-hydroxyphenyl)imino)indolin-2-one as red solid (2382 mg, 80%, E/Z=5/1).

IR (cm^{-1}): 3265, 1714, 1611, 1599, 1503, 1462, 1346 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.92 (s, 1 H) 9.57 (br. s., 1 H) 6.82 - 6.91 (m, 5 H) 6.70 - 6.79 (m, 3 H).

(Z) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.82 (br. s., 1H), 9.55 (br. s., 1H), 7.53 (d, $J = 7.34$ Hz, 1H), 7.39 (t, $J = 7.70$ Hz, 1H), 7.17 (d, $J = 8.68$ Hz, 2H), 7.03 (t, $J = 7.52$ Hz, 1H), 6.82-6.91 (m, 1H), 6.70-6.79 (m, 2H).

(E) ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 163.80, 155.48, 154.03, 146.67, 141.60, 134.02, 124.85, 123.89, 121.66, 119.85, 115.96, 115.88, 114.76, 111.41.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2^+$: 239,0815; found: 239,0811.

3-((3-Hydroxyphenyl)imino)indolin-2-one (3j). A reaction of 3-azidophenol (1351 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((3-hydroxyphenyl)imino)indolin-2-one as yellow solid (1578 mg, 53%, E/Z=11/1).

IR (cm^{-1}): 3404, 3334, 3210, 1721, 1704, 1615, 1592, 1463, 1452, 1336 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.97 (s, 1 H) 9.65 (s, 1 H) 7.33 (t, $J=7.62$ Hz, 1 H) 7.24 (t, $J=7.84$ Hz, 1 H) 6.89 (d, $J=7.78$ Hz, 1 H) 6.75 (t, $J=7.56$ Hz, 1 H) 6.64 (d, $J=7.67$ Hz, 1 H) 6.48 (d, $J=7.62$ Hz, 1 H) 6.31 - 6.39 (m, 2 H).

(E) ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 163.60, 158.51, 154.79, 151.87, 146.89, 134.42, 130.62, 125.66, 121.78, 115.63, 111.88, 111.51, 107.52, 103.95.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2^+$: 239,0815; found: 239,0813.

3-((2-Hydroxyphenyl)imino)indolin-2-one (3k). A reaction of 2-azidophenol (1351 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((2-hydroxyphenyl)imino)indolin-2-one as orange solid (mg, 45%, E/Z=7.8/1).

IR (cm^{-1}): 3244, 3130, 1722, 1615, 1590, 1463, 1451, 1343 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.94 (s, 1 H) 9.36 (br. s., 1 H) 7.34 (td, $J=7.73, 1.15$ Hz, 1 H) 7.03 - 7.10 (m, 1 H) 6.94 (d, $J=8.06$ Hz, 1 H) 6.82 - 6.92 (m, 3 H) 6.76 (td, $J=7.63, 0.79$ Hz, 1 H) 6.56 (d, $J=7.62$ Hz, 1 H).

(Z) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.79 (s, 1 H) 9.16 (s, 1 H) 7.62 (d, $J=7.23$ Hz, 1 H) 7.44 (td, $J=7.76, 0.99$ Hz, 1 H) 7.03 - 7.10 (m, 1 H) 6.70 - 6.92 (m, 5 H).

(E) ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 163.78, 155.62, 146.43, 145.45, 137.78, 134.25, 126.09, 125.28, 121.95, 119.70, 119.14, 116.73, 116.45, 111.28.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2^+$: 239,0815; found: 239,0810.

3-((4-Nitrophenyl)imino)indolin-2-one (3l). A reaction of 1-azido-4-nitrobenzene (1641 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((4-nitrophenyl)imino)indolin-2-one as orange solid (2467 mg, 95%, E/Z=2/1).

IR (cm^{-1}): 3271, 1739, 1722, 1617, 1585, 1513, 1340 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 11.06 (br. s., 1 H) 8.34 (d, $J=8.66$ Hz, 2 H) 7.37 (t, $J=7.70$ Hz, 1 H) 7.24 (d, $J=8.60$ Hz, 2 H) 6.90 (d, $J=7.78$ Hz, 1 H) 6.74 (t, $J=7.56$ Hz, 1 H) 6.36 (d, $J=7.62$ Hz, 1 H).

(Z) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.98 (br. s., 1 H) 8.19 (d, $J=8.44$ Hz, 2 H) 7.63 (d, $J=6.80$ Hz, 1 H) 7.46 - 7.53 (m, 1 H) 7.16 (d, $J=8.55$ Hz, 2 H) 7.09 (t, $J=6.99$ Hz, 1 H) 6.90 (d, $J=7.78$ Hz, 1 H).

(E) ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 163.06, 156.58, 155.43, 147.47, 144.31, 135.18, 125.98, 125.69, 122.07, 118.27, 115.48, 111.75.

HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}_3^+$: 268,0717; found: 268,0717.

3-((3-Nitrophenyl)imino)indolin-2-one (3m). A reaction of 1-azido-3-nitrobenzene (1641 mg, 10 mmol), triphenylphosphine (2623 mg, 10 mmol) and isatin (1471 mg, 10 mmol) in DCM (10 ml) yields 3-((3-nitrophenyl)imino)indolin-2-one as orange solid (2273 mg, 82%, E/Z=2/1).

IR (cm^{-1}): 3204, 1745, 1616, 1524, 1350, 1339 cm^{-1} .

(E) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 11.04 (s, 1 H) 8.10 (ddd, $J=8.22, 2.25, 0.82$ Hz, 1 H) 7.84 - 7.87 (m, 1 H) 7.76 (t, $J=8.08$ Hz, 1 H) 7.47 - 7.51 (m, 1 H) 7.36 (td, $J=7.74, 1.12$ Hz, 1 H) 6.89 (t, $J=8.22$ Hz, 1 H) 6.72 (td, $J=7.66, 0.85$ Hz, 1 H) 6.35 (d, $J=7.62$ Hz, 1 H).

(Z) ^1H NMR (400 MHz, DMSO- d_6) δ ppm 10.93 (s, 1 H) 7.96 (ddd, $J=8.18, 2.23, 0.88$ Hz, 1 H) 7.86 (t, $J=1.62$ Hz, 1 H) 7.57 - 7.64 (m, 2 H) 7.43 - 7.51 (m, 2 H) 7.05 - 7.11 (m, 1 H) 6.89 (t, $J=8.22$ Hz, 1 H).

(E+Z) ^{13}C NMR (101 MHz, DMSO- d_6) δ ppm 163.24, 158.70, 156.39, 154.82, 151.44, 150.61, 148.72, 147.97, 147.40, 146.34, 135.03, 134.89, 131.29, 129.85, 125.80, 125.72, 124.50, 123.33, 122.46, 122.01, 120.95, 119.57, 118.69, 115.59, 113.60, 112.38, 111.71, 111.01.

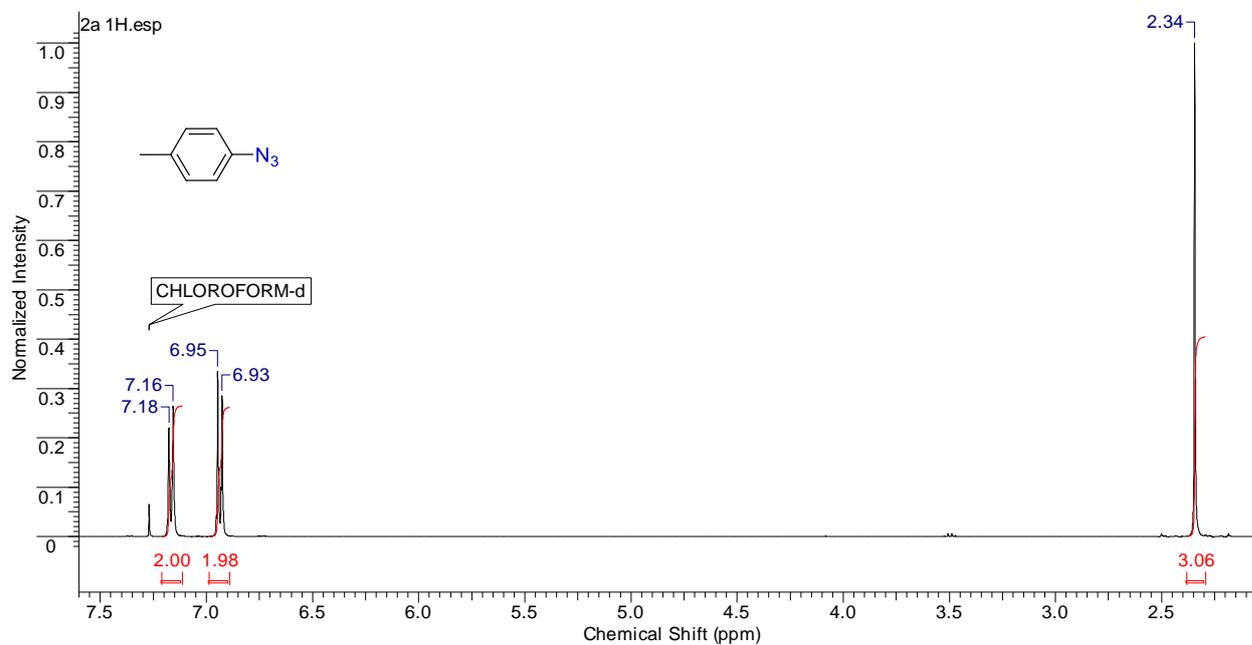
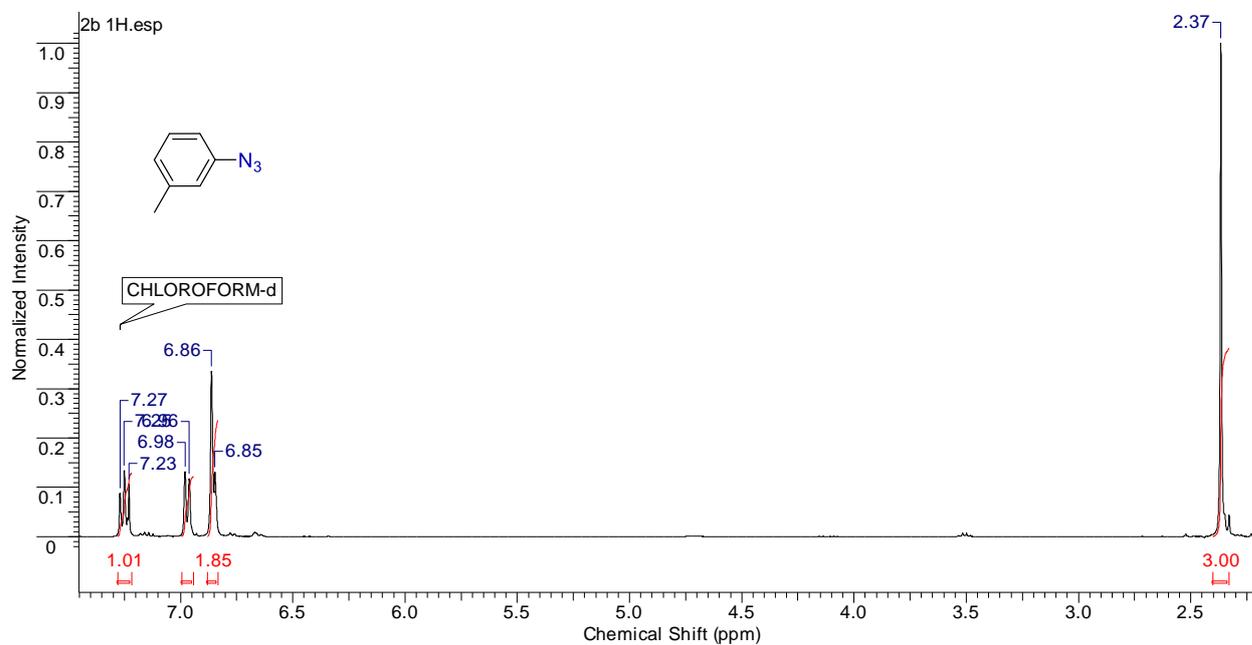
HRMS (ESI): calcd for $\text{C}_{14}\text{H}_{10}\text{N}_3\text{O}_3^+$: 268,0717; found: 268,0718.

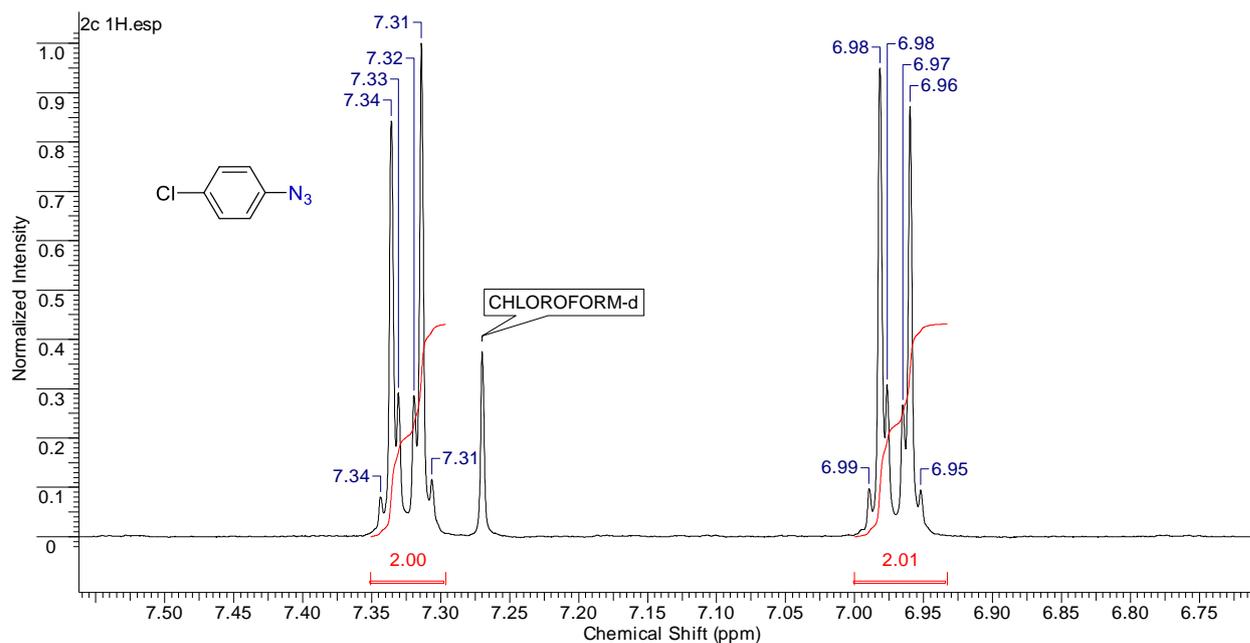
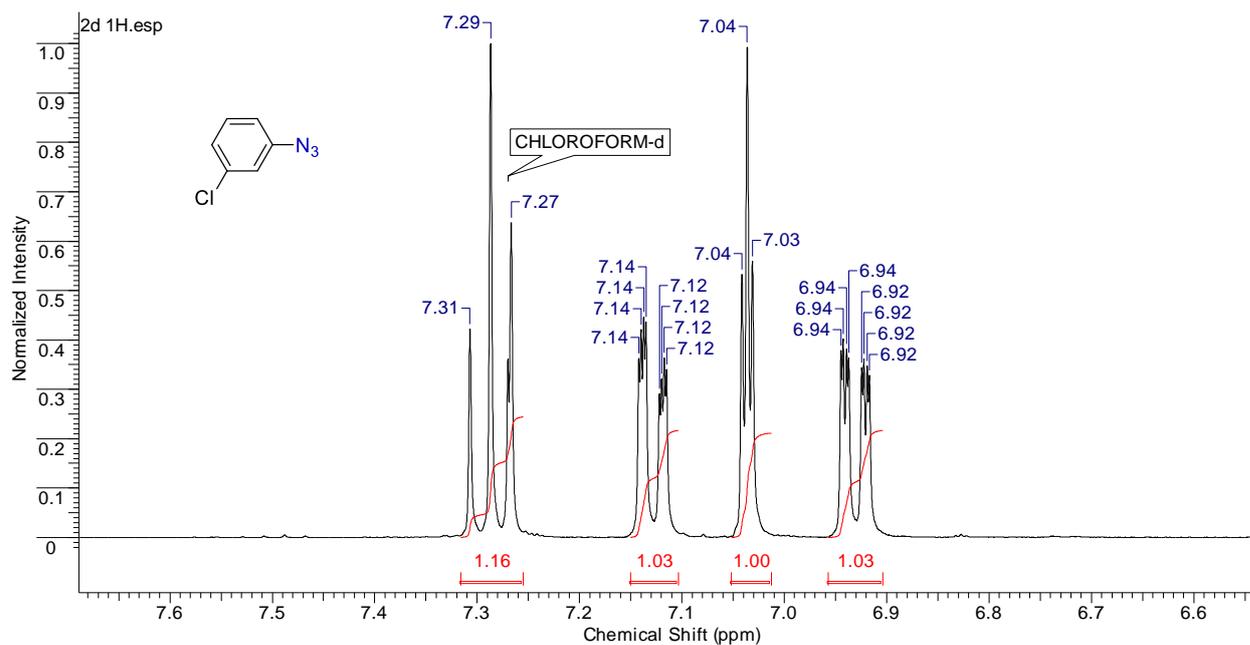
References

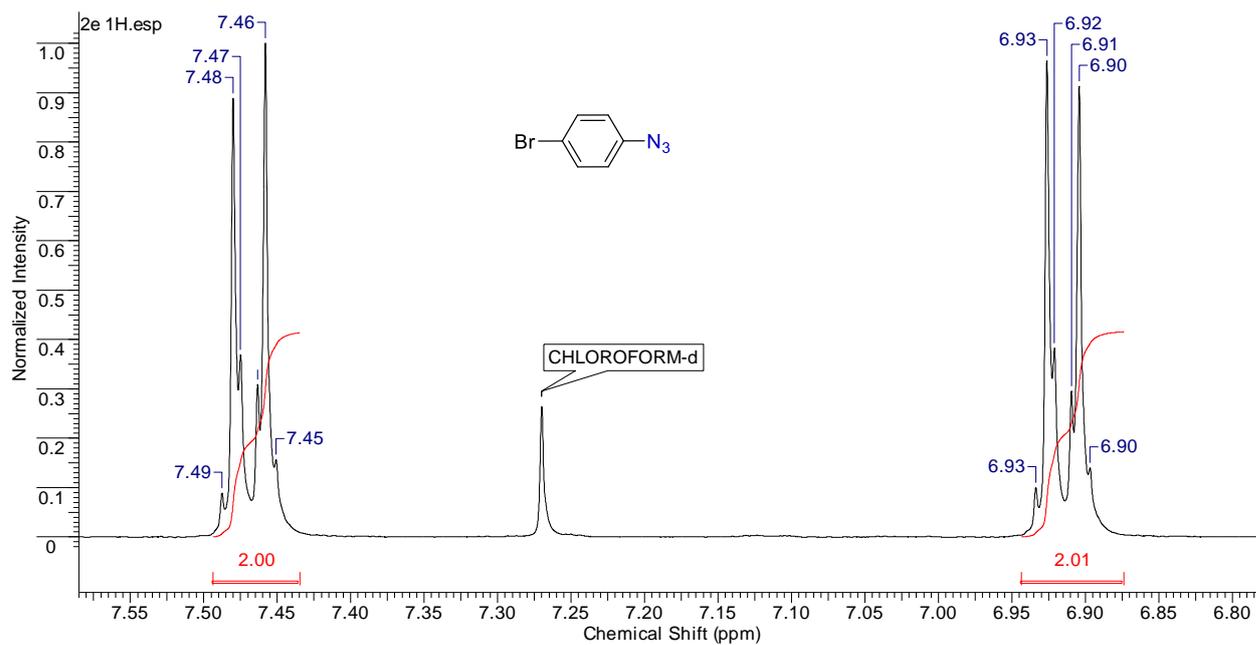
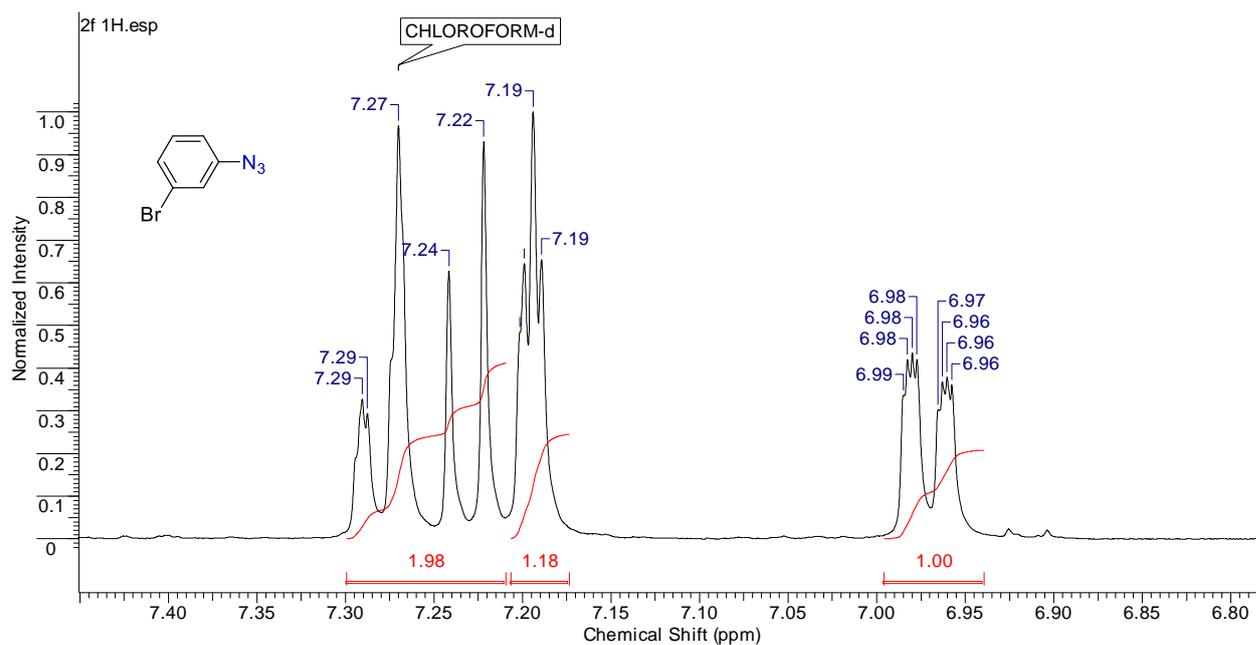
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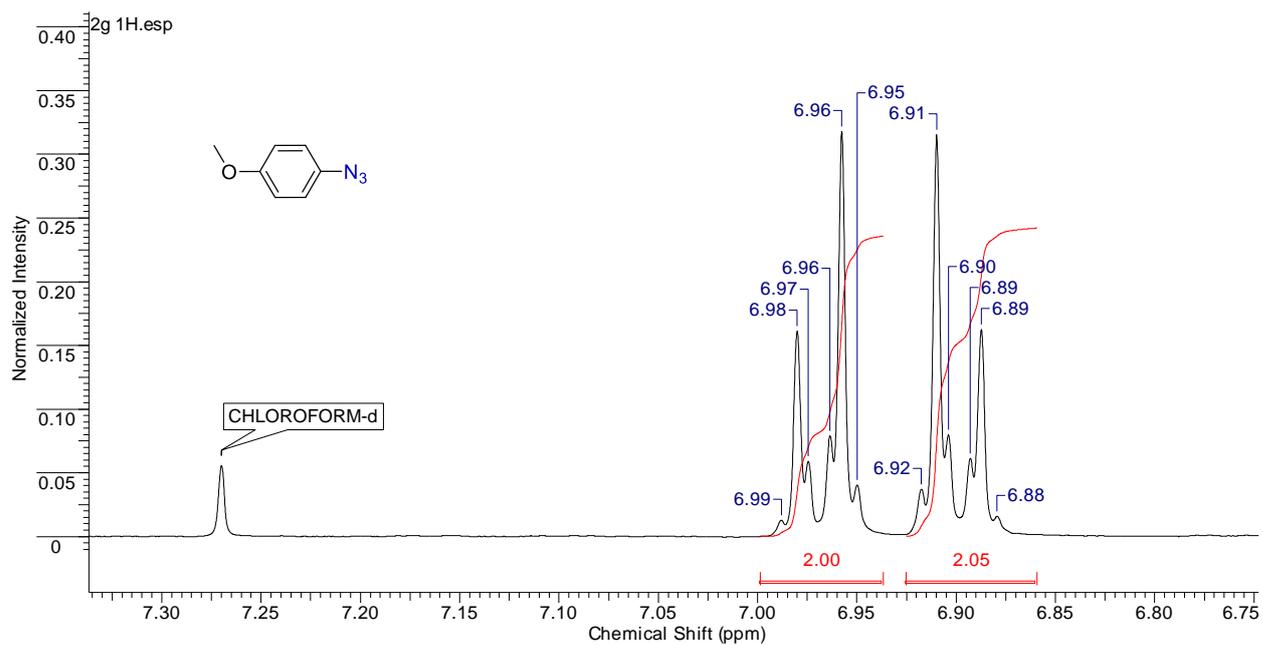
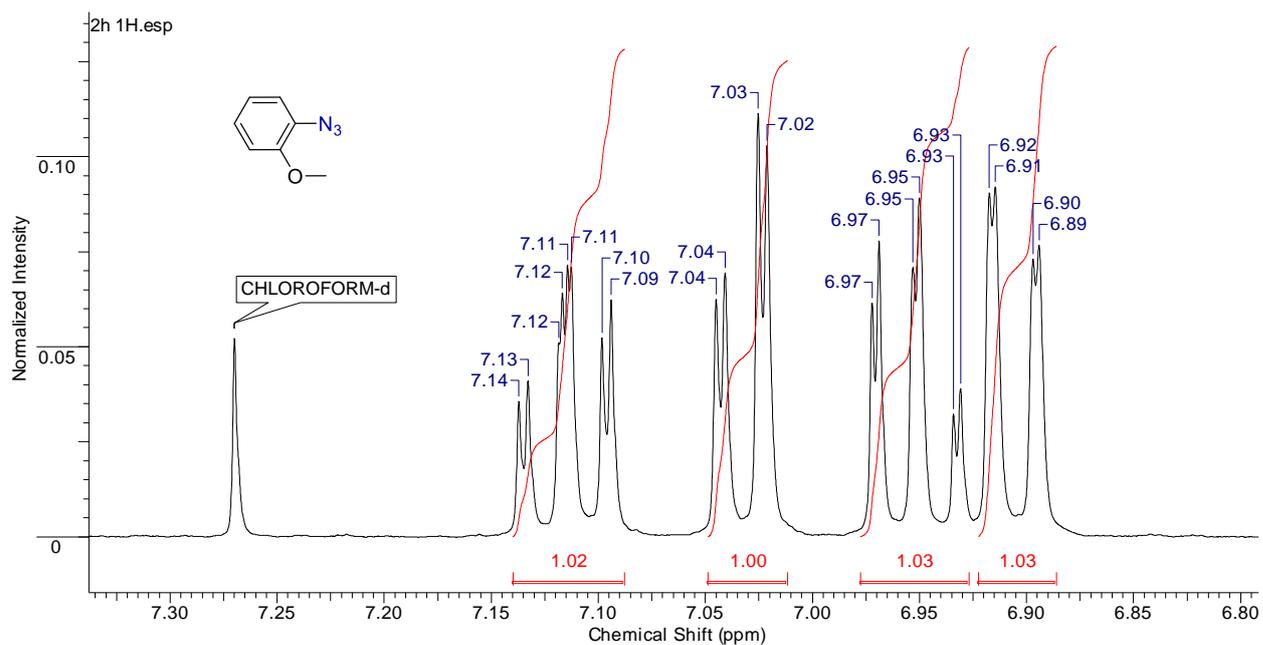
Spectral data

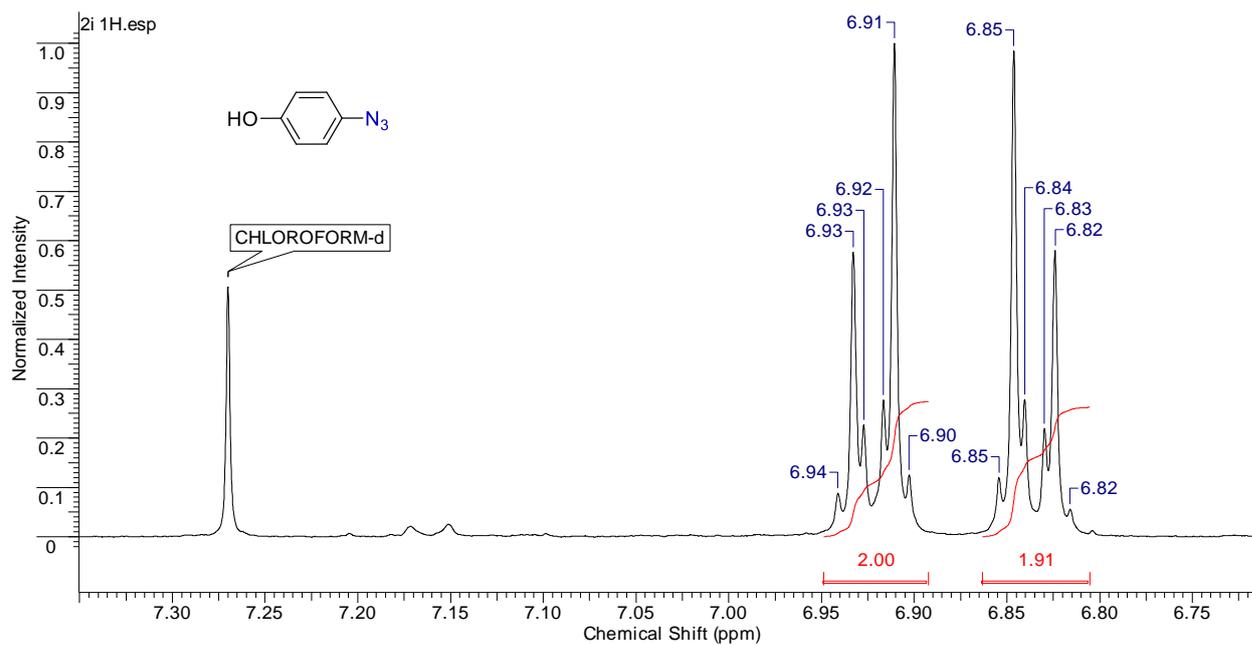
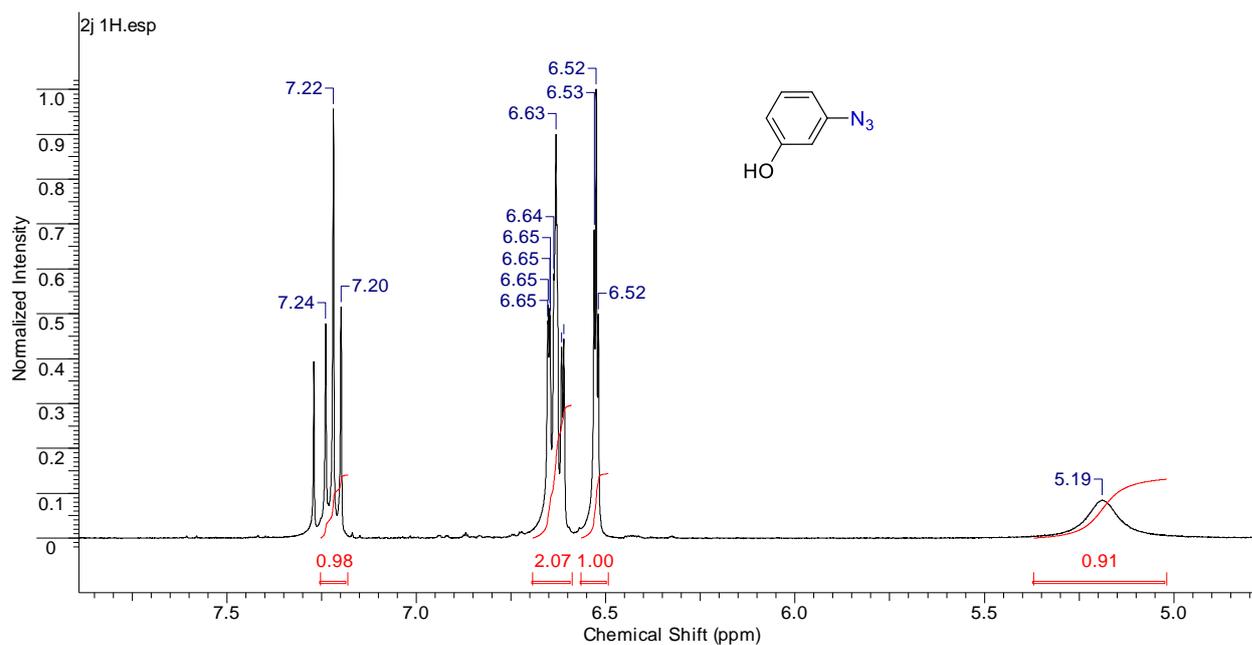
Azides

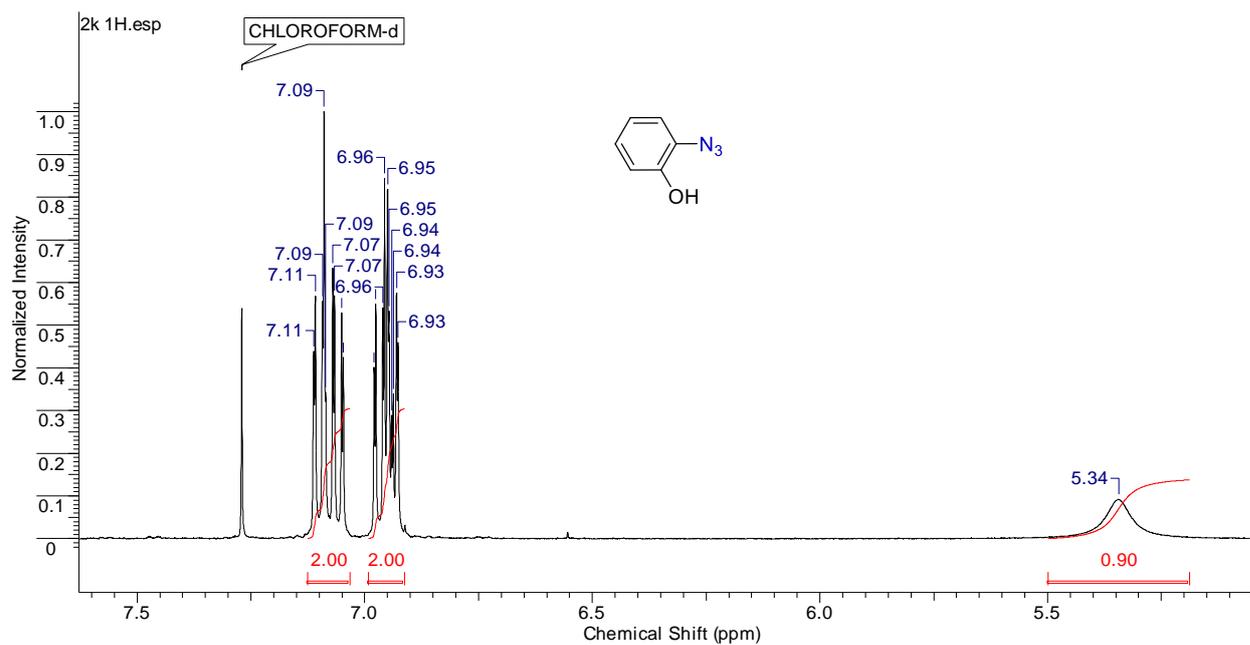
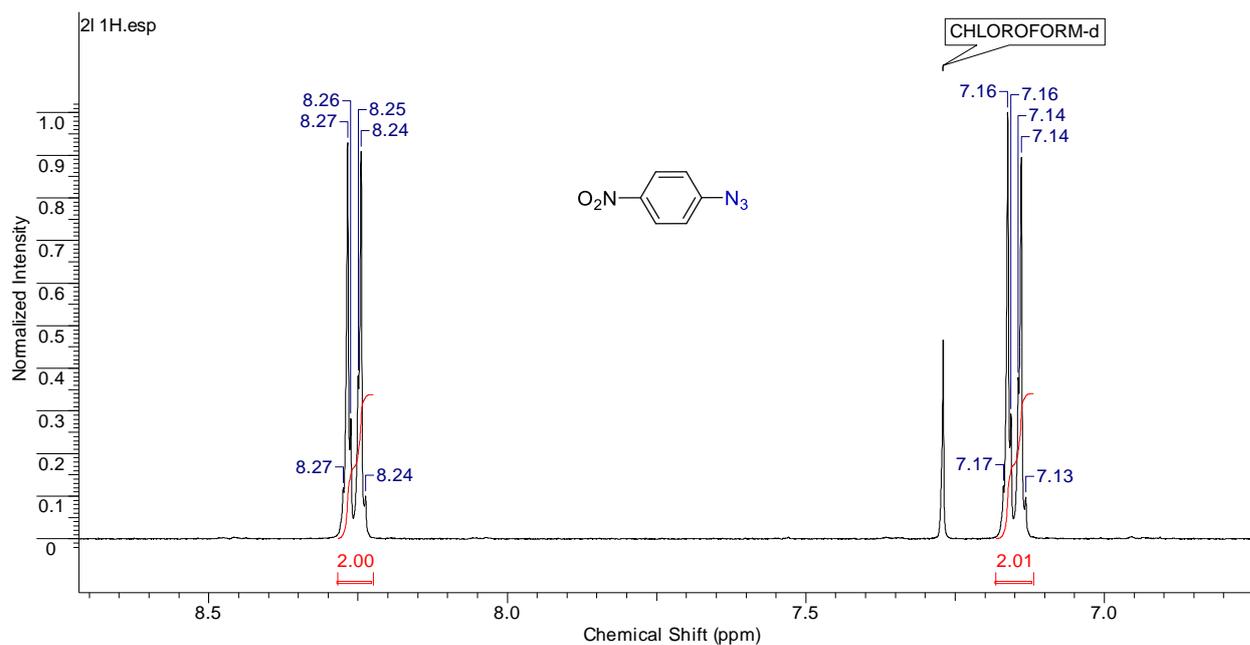
(2a) 1-azido-4-methylbenzene*(2b)* 1-azido-3-methylbenzene

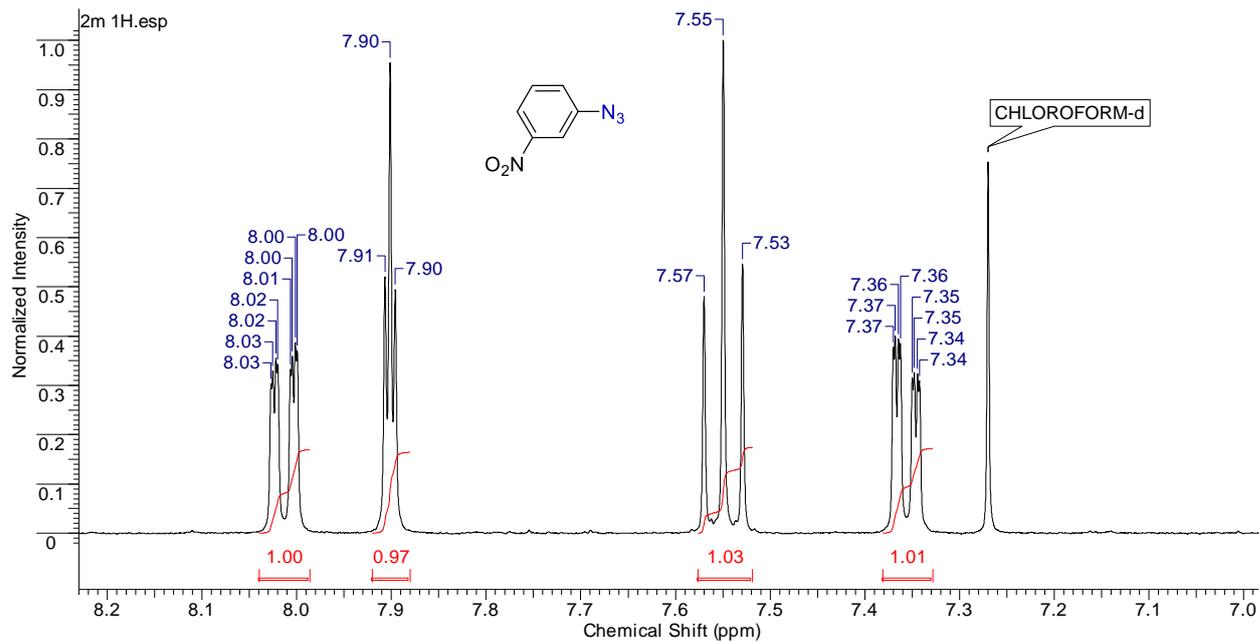
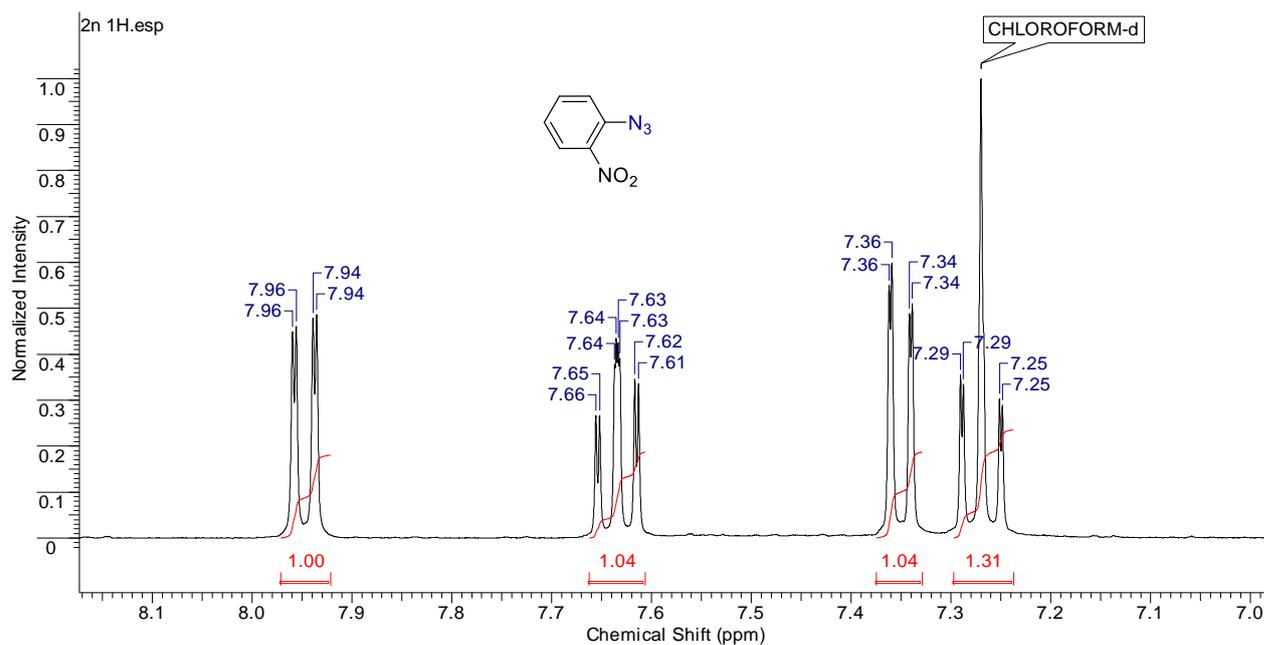
(2c) 1-azido-4-chlorobenzene**(2d) 1-azido-3-chlorobenzene**

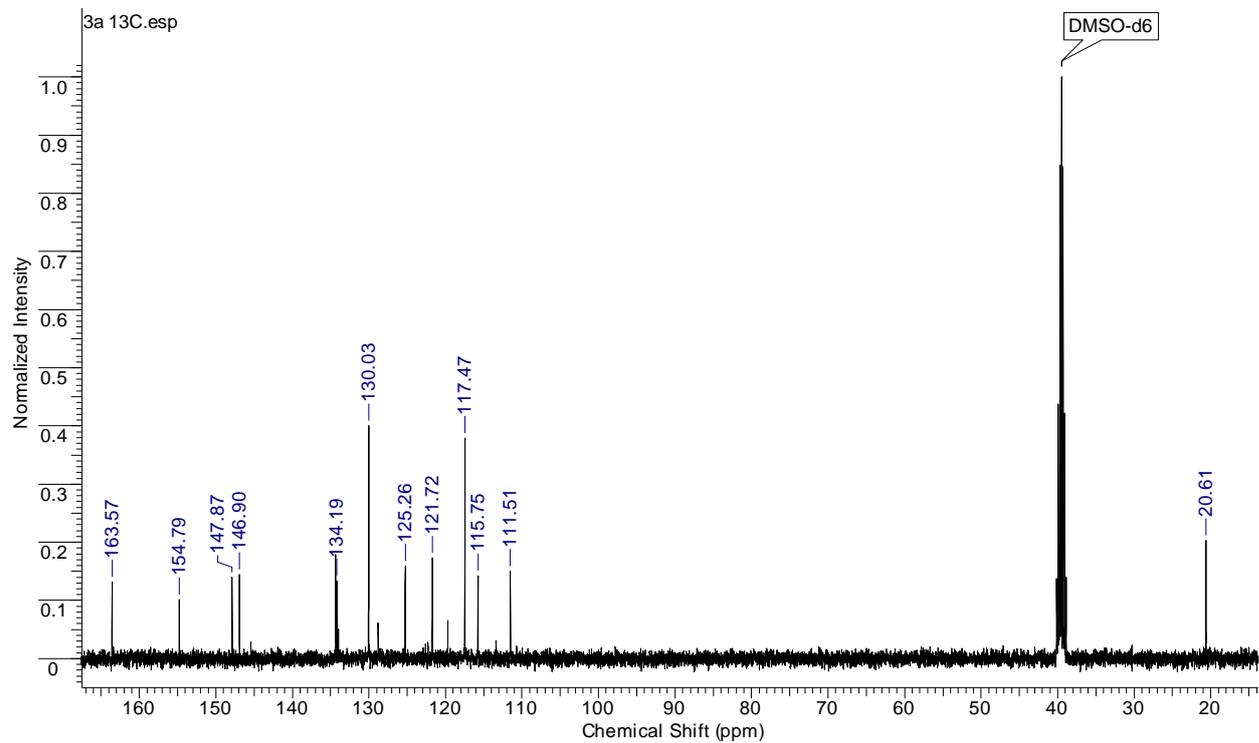
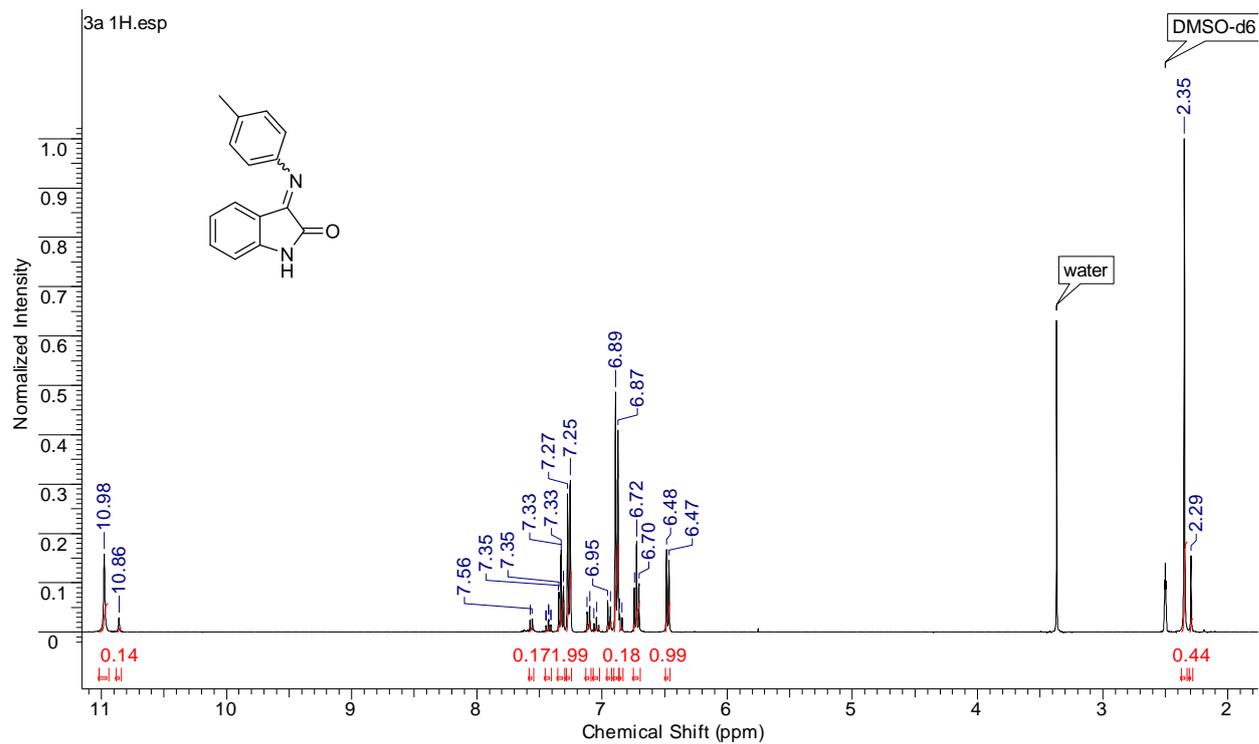
(2e) 1-azido-4-bromobenzene**(2f)** 1-azido-3-bromobenzene

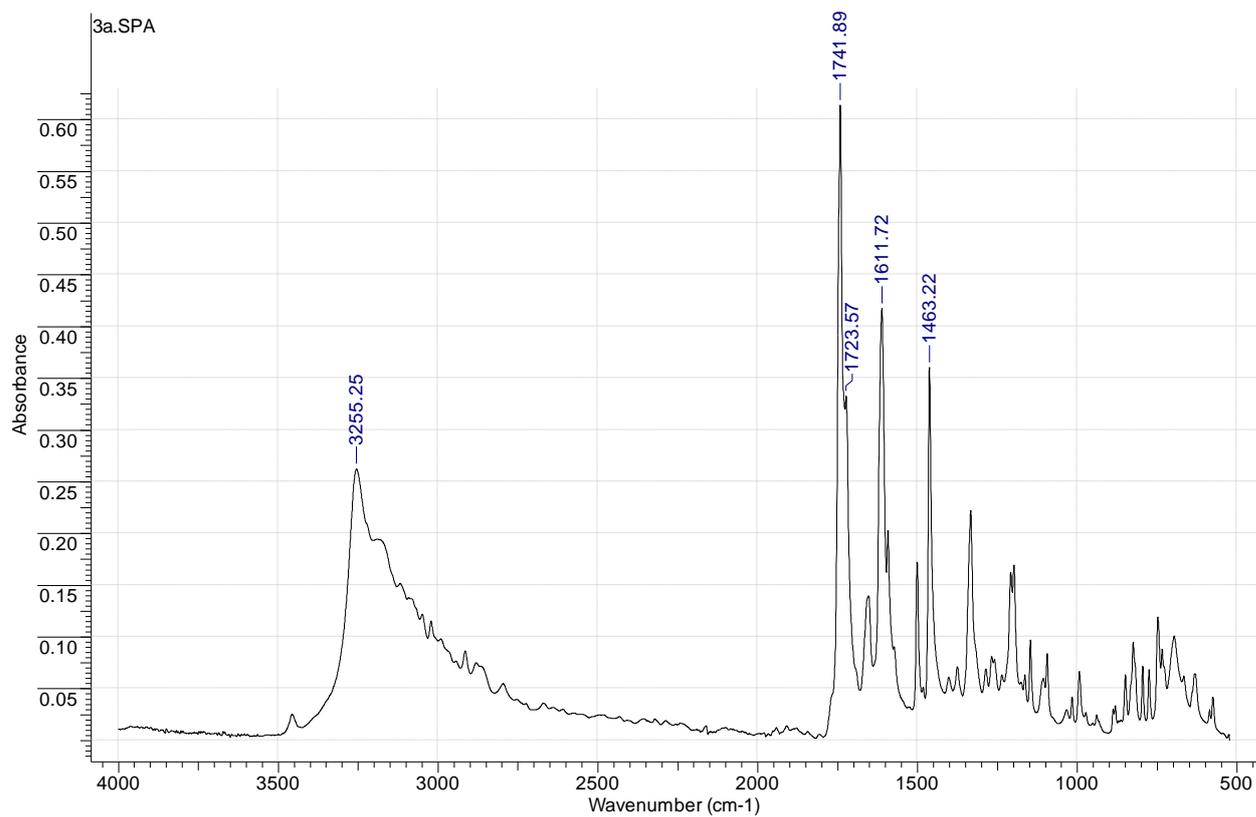
(2g) 1-azido-4-methoxybenzene**(2h) 1-azido-2-methoxybenzene**

(2i) 4-azidophenol**(2j) 3-azidophenol**

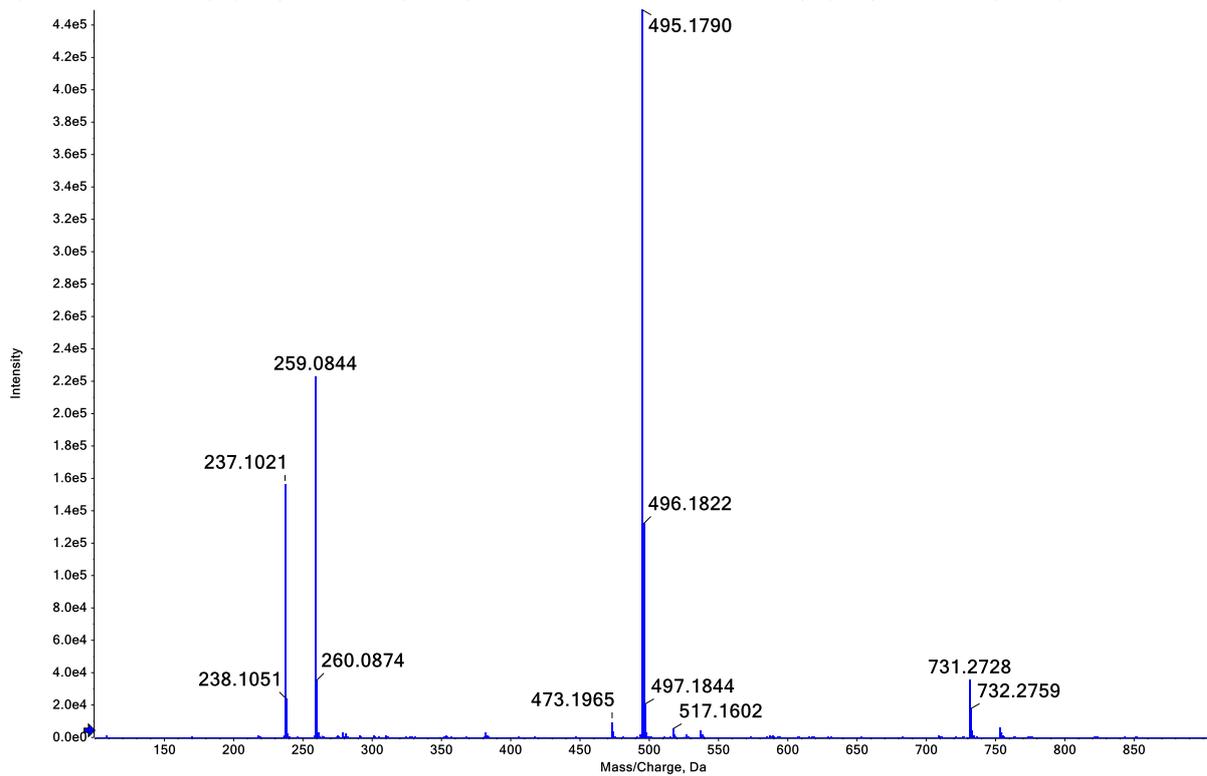
(2k) 2-azidophenol**(2l) 1-azido-4-nitrobenzene**

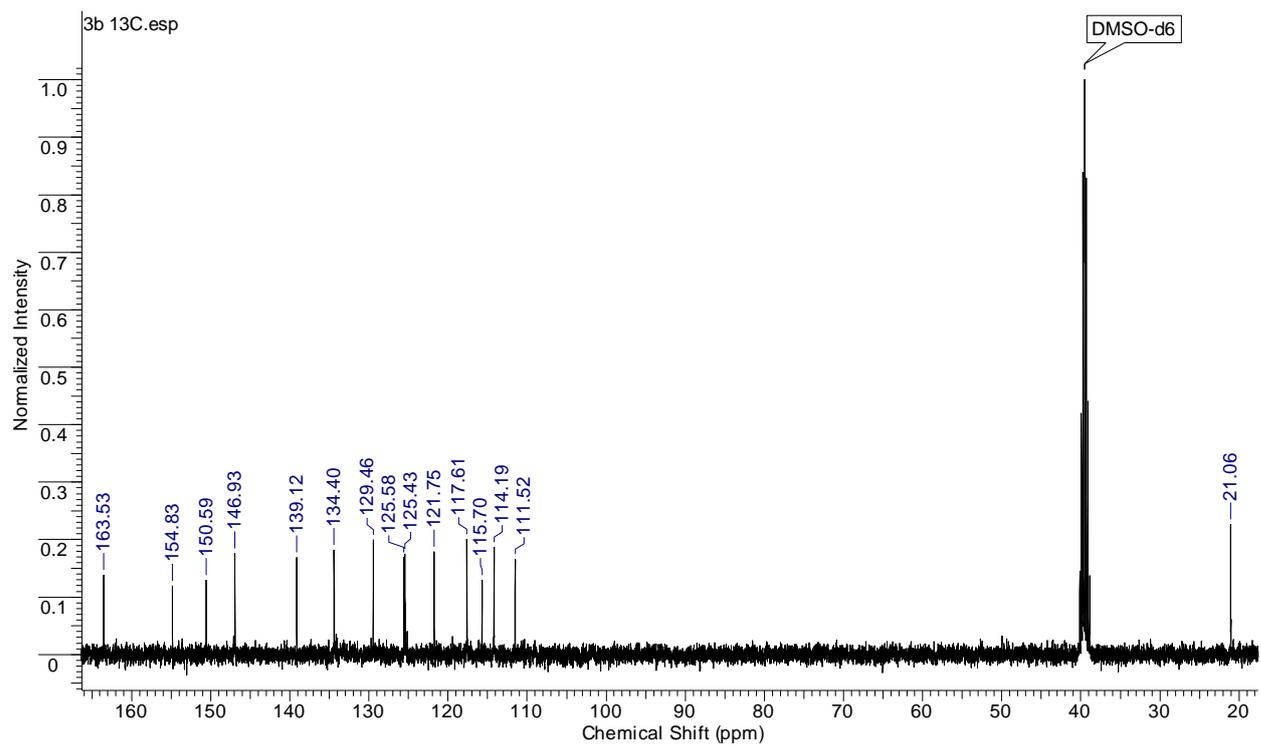
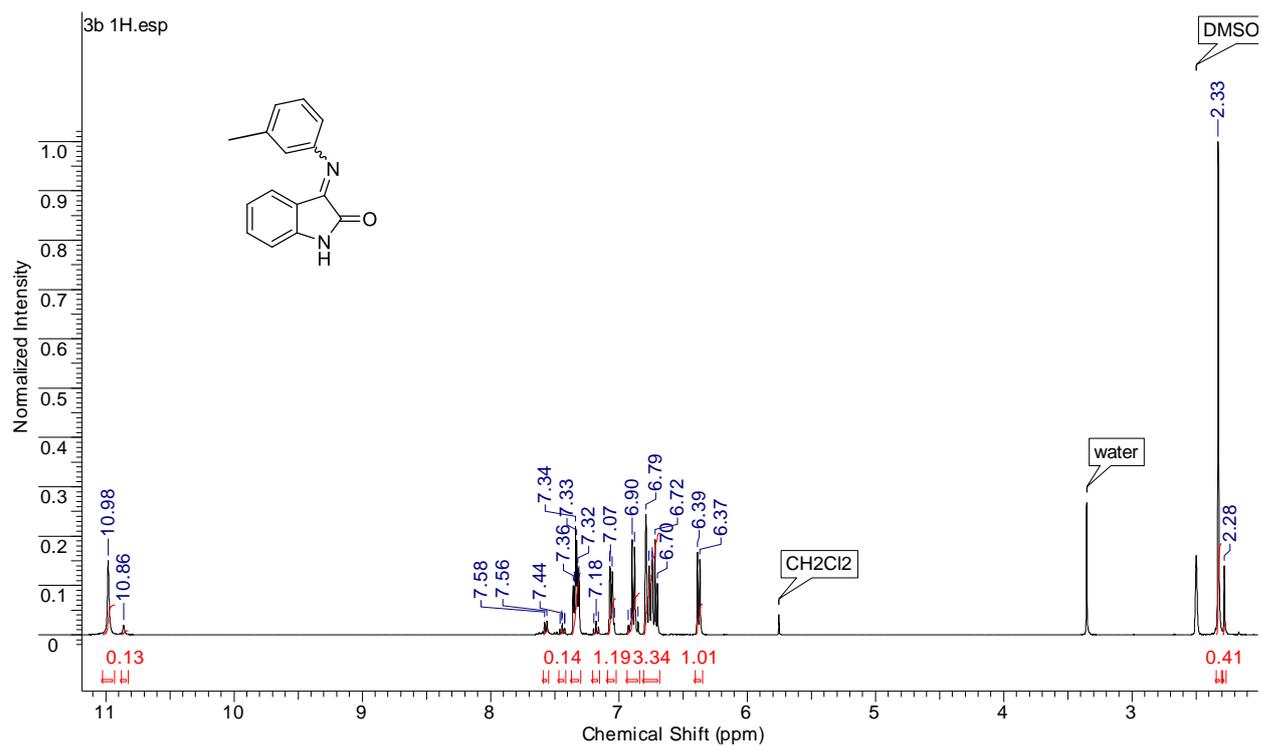
(2m) 1-azido-3-nitrobenzene**(2n) 1-azido-2-nitrobenzene**

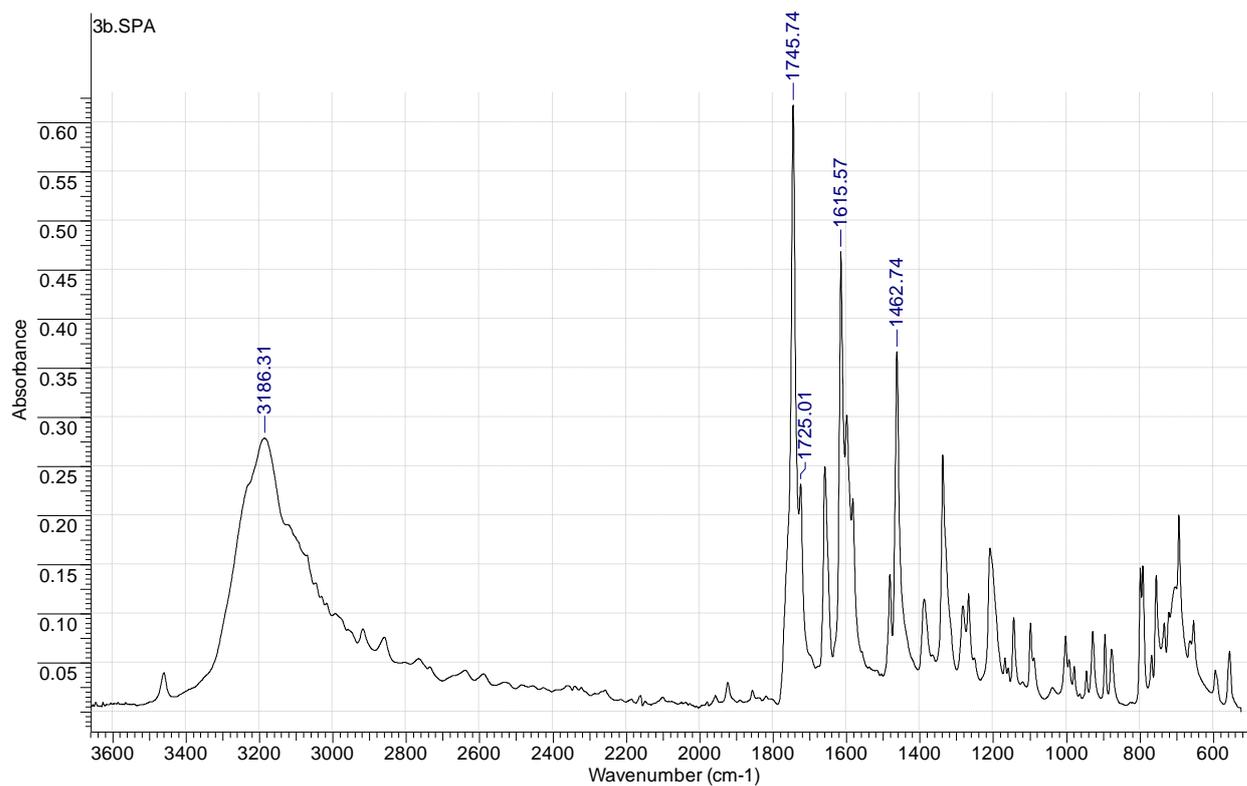
Isatinimines**(3a) 3-(p-tolylimino)indolin-2-one**



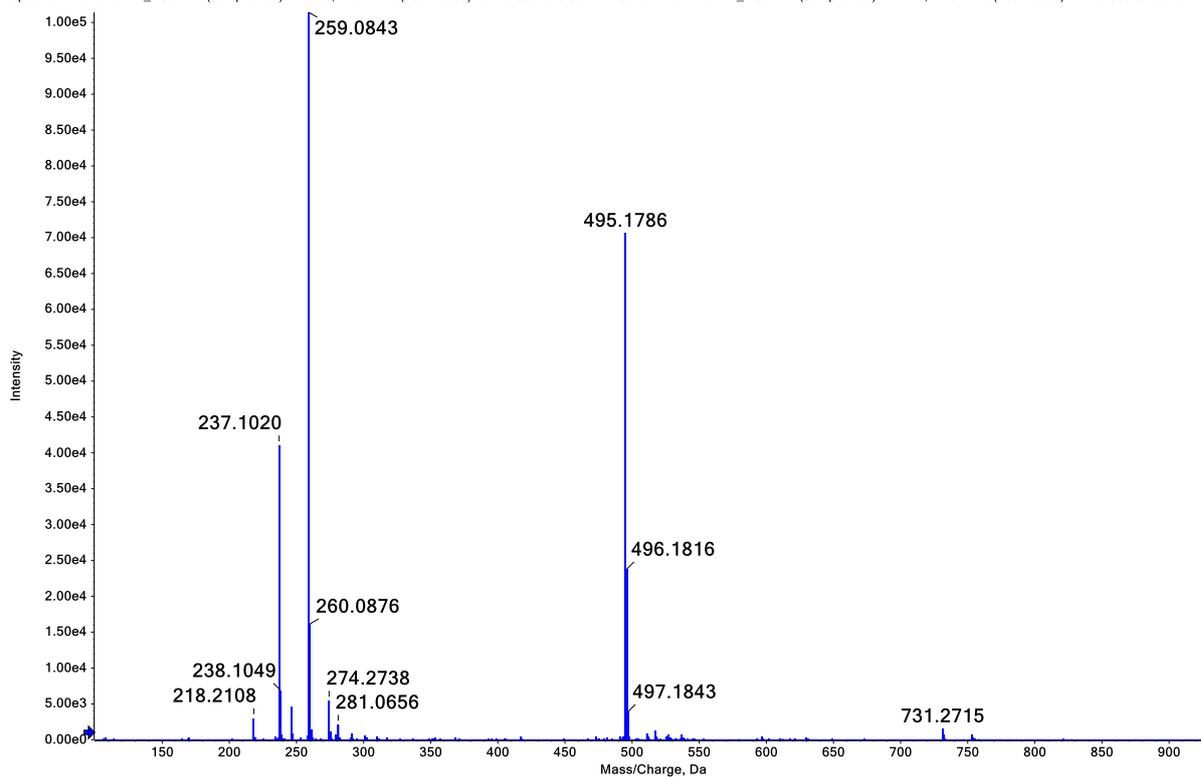
Spectrum from 010122_POS.wiff (sample 151) - DY 52, +TOF MS (100 - 3000) from 0.804 to 0.832 min...ectrum from 010122_POS.wiff (sample 151) - DY 52, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

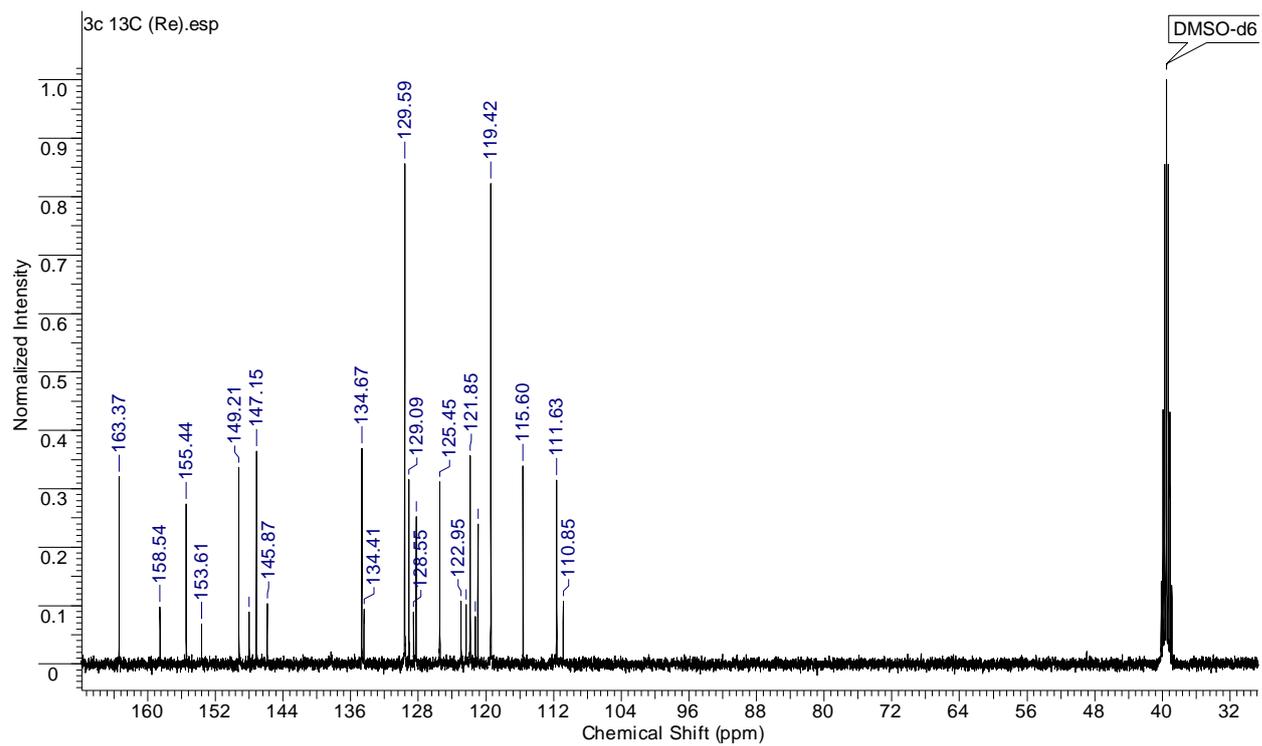
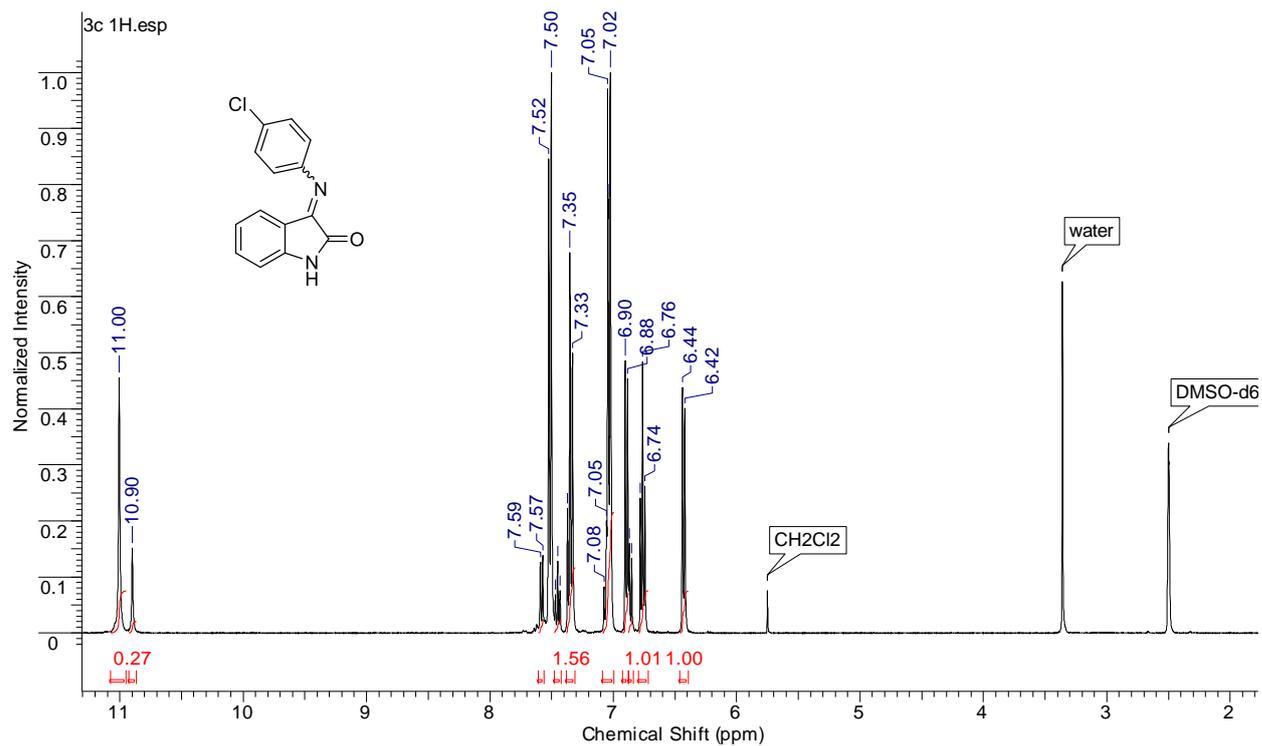


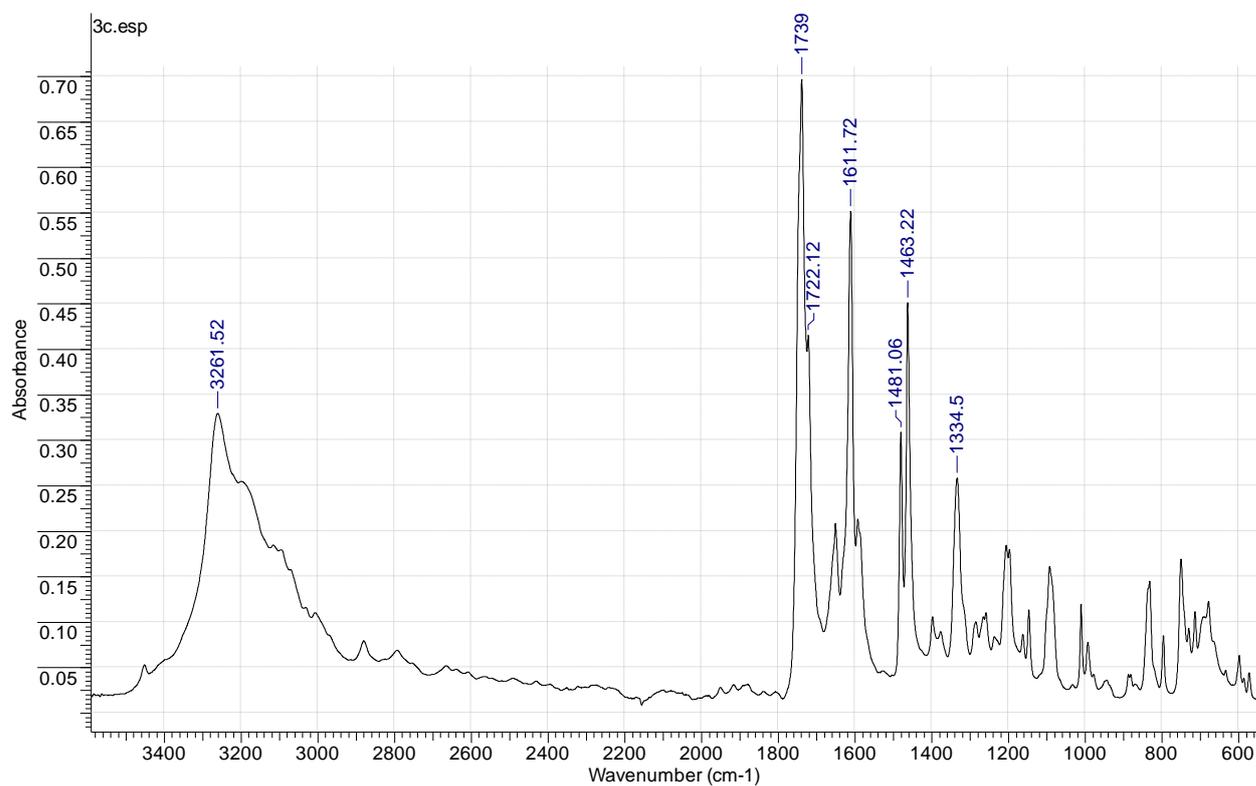
(3b) 3-(*m*-tolylimino)indolin-2-one



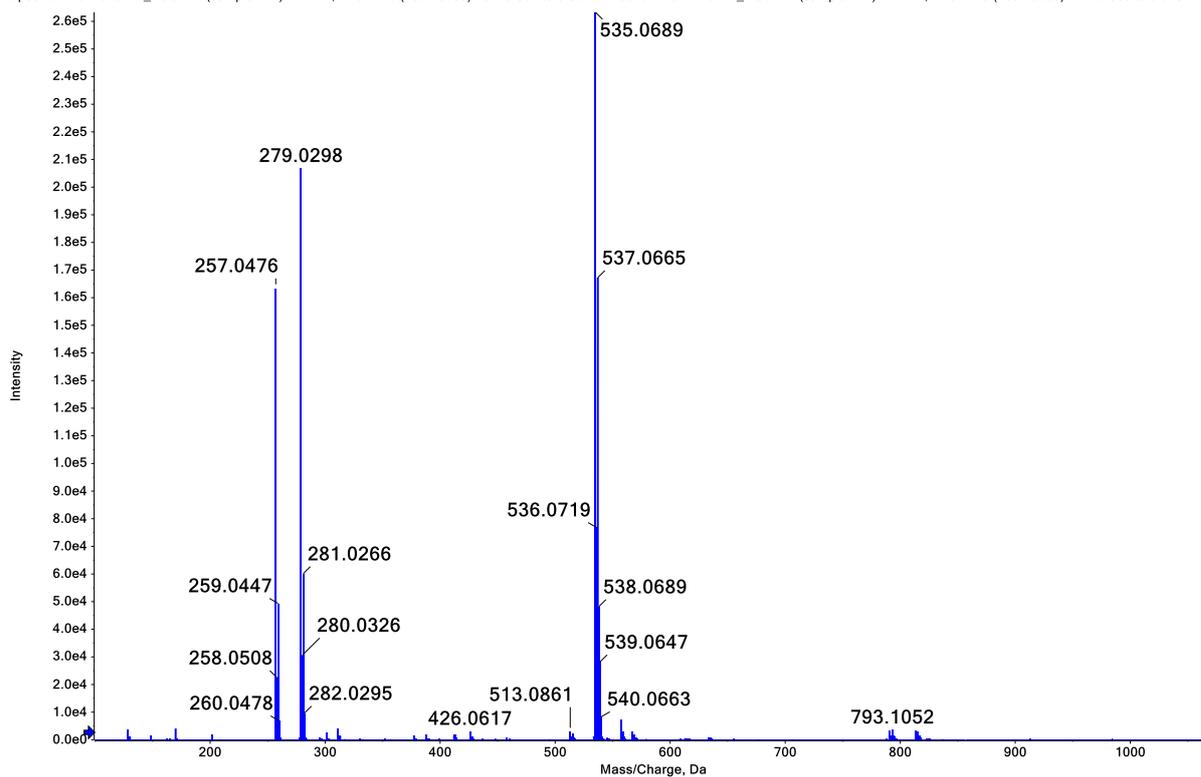
Spectrum from 010122_POS.wiff (sample 156) - DY 46, +TOF MS (100 - 3000) from 0.856 to 0.884 mi...ectrum from 010122_POS.wiff (sample 156) - DY 46, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

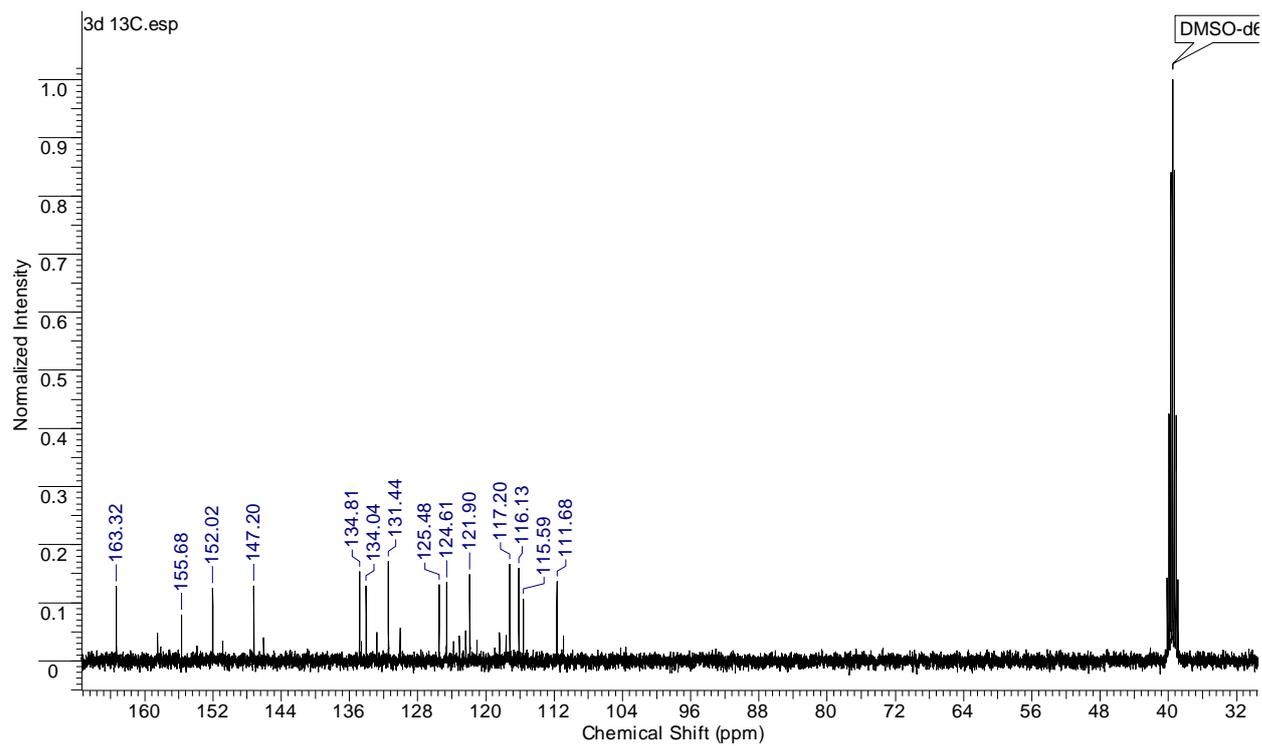
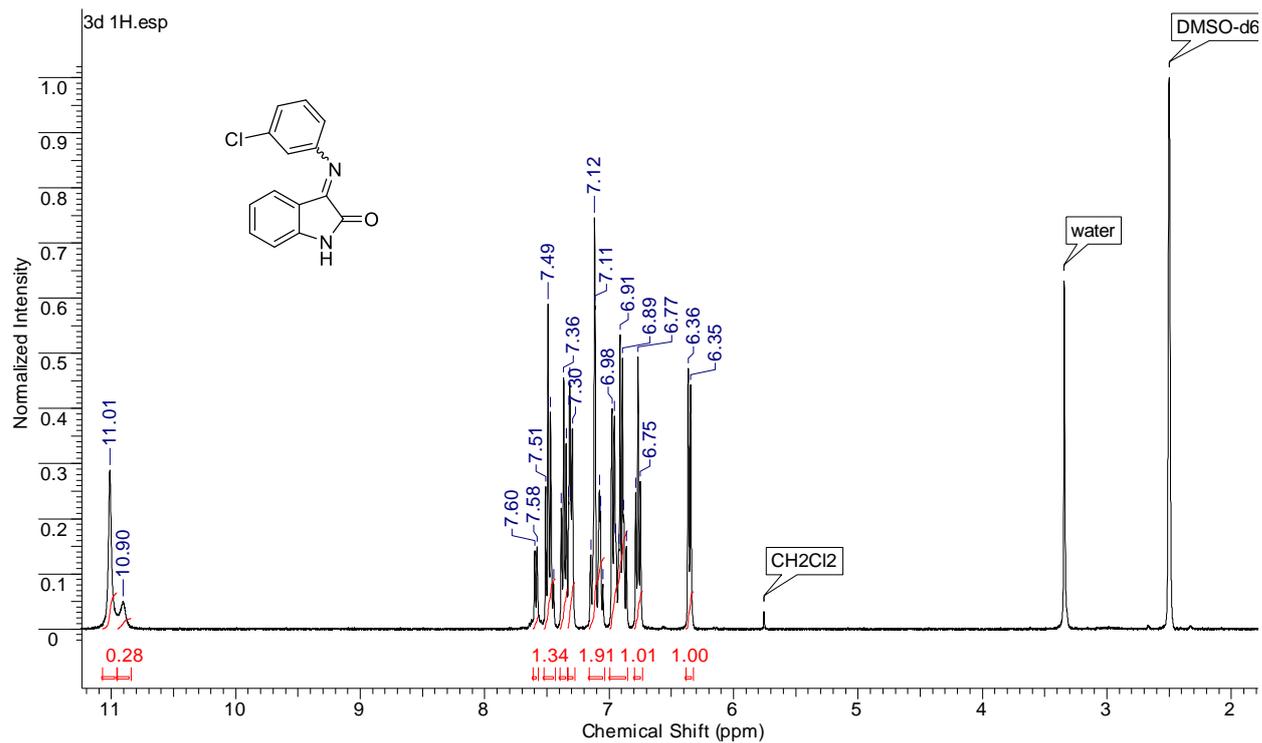


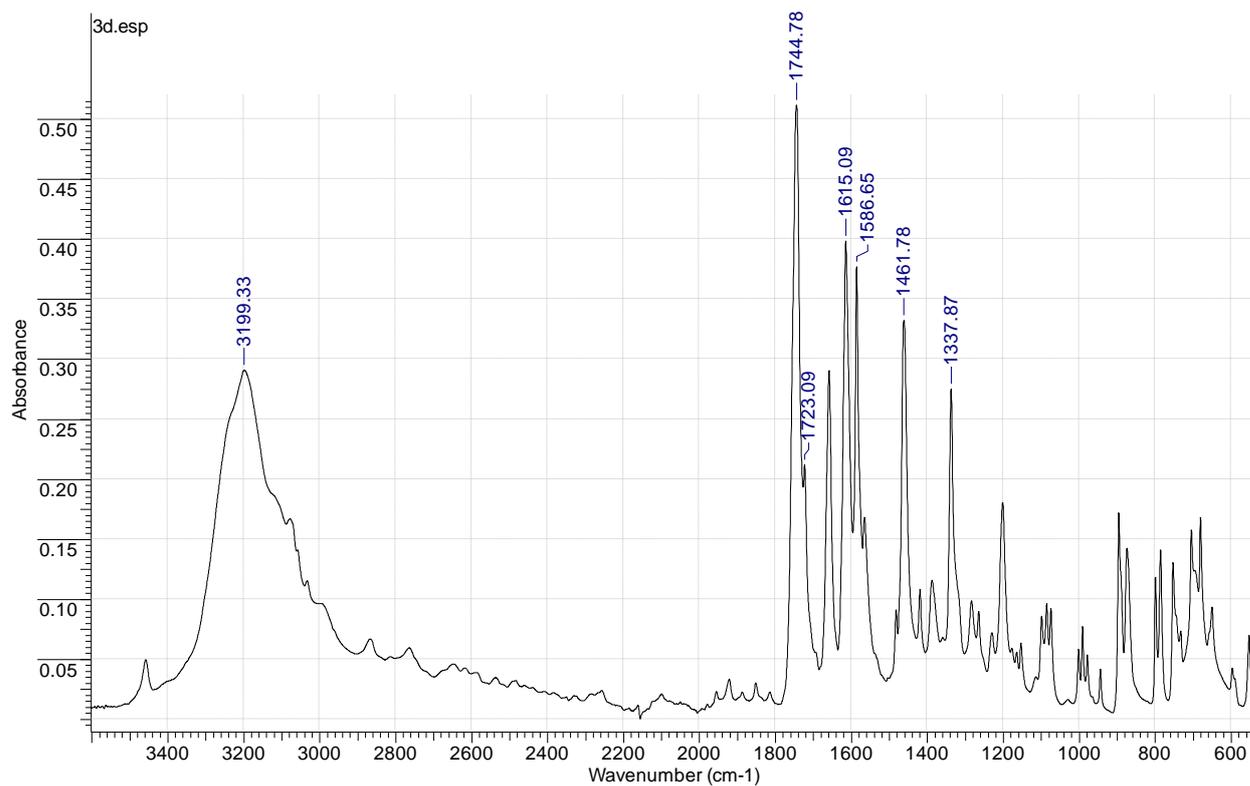
(3c) 3-((4-chlorophenyl)imino)indolin-2-one



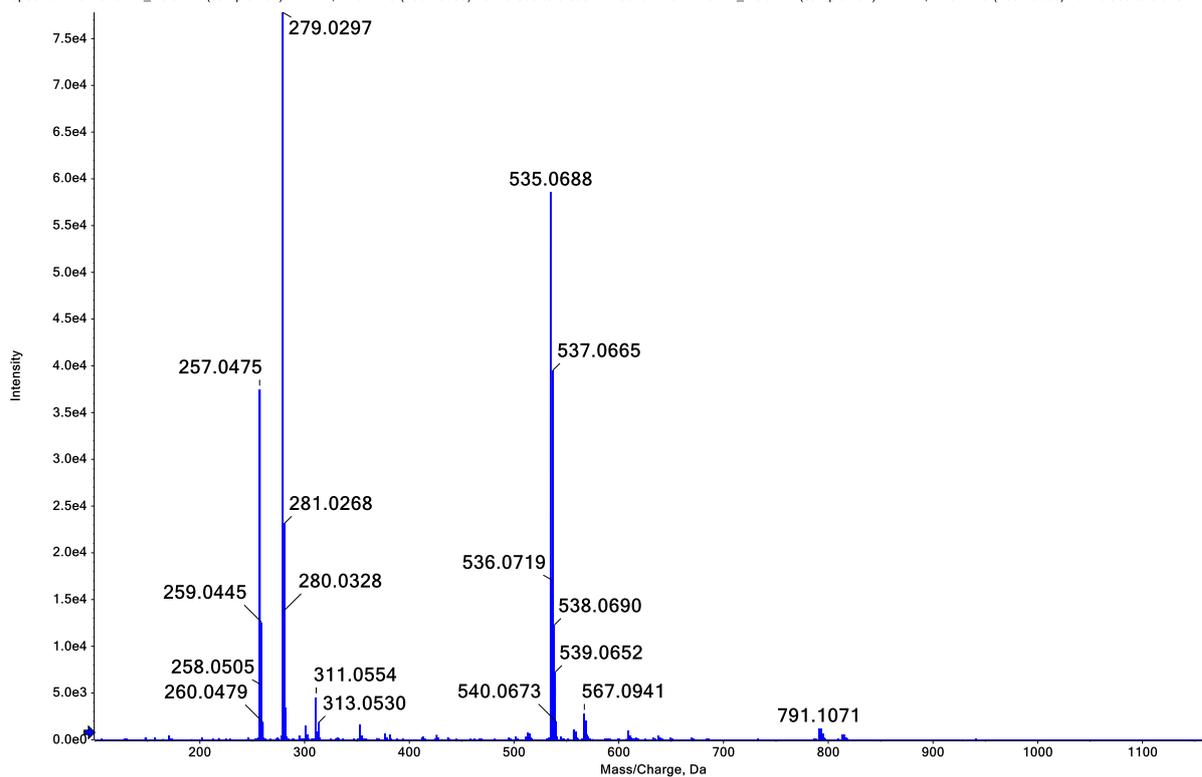
Spectrum from 010122_POS.wiff (sample 147) - DY 47, +TOF MS (100 - 3000) from 0.804 to 0.832 mi...ectrum from 010122_POS.wiff (sample 147) - DY 47, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

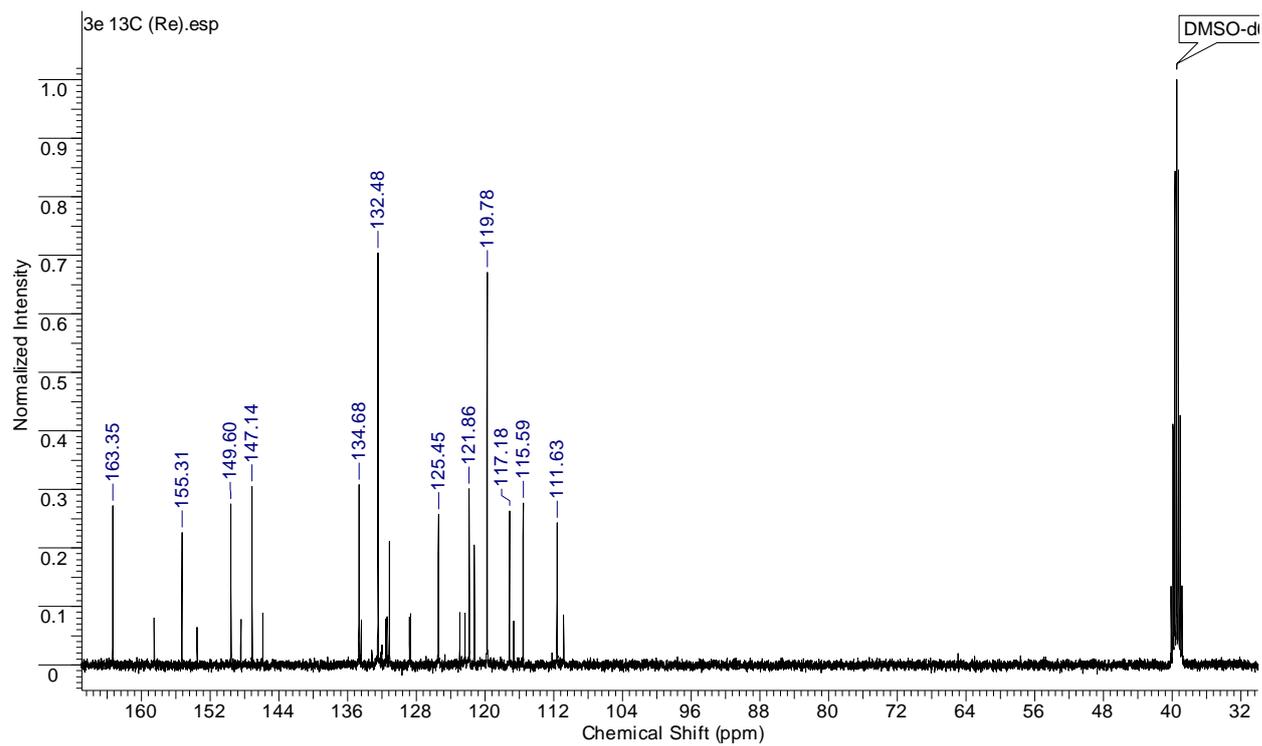
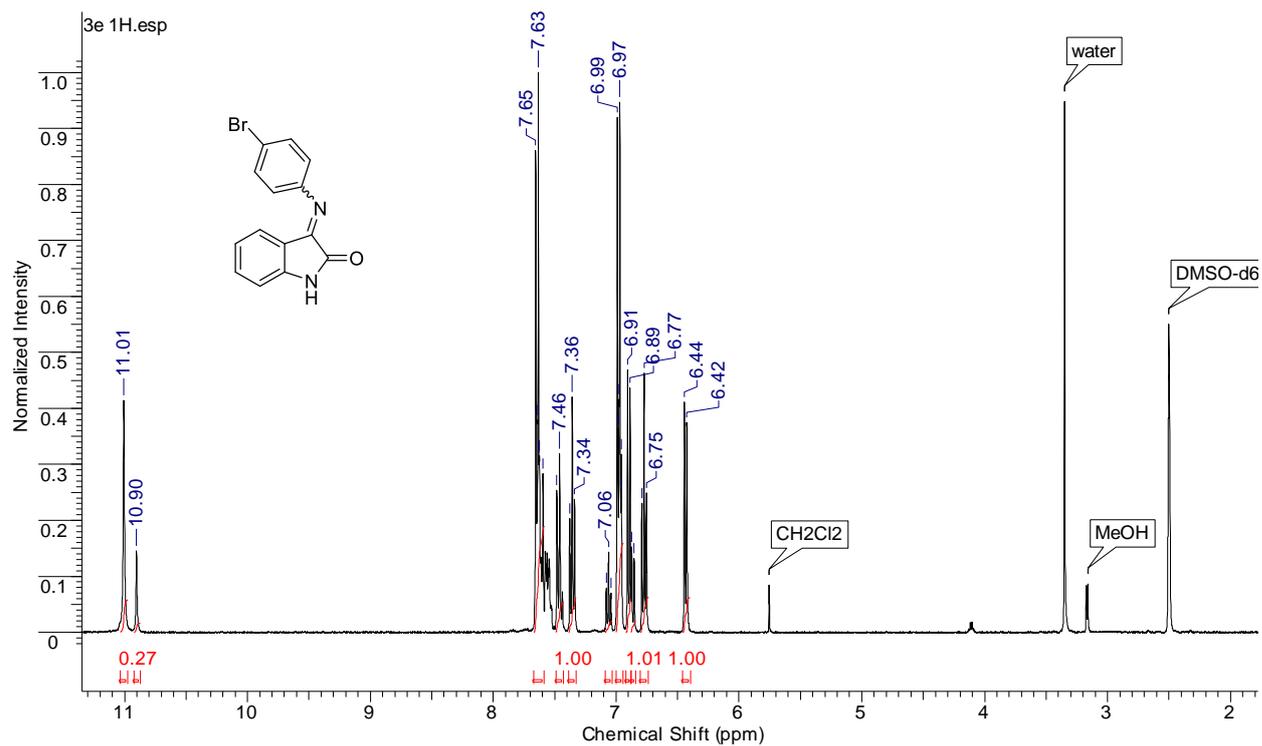


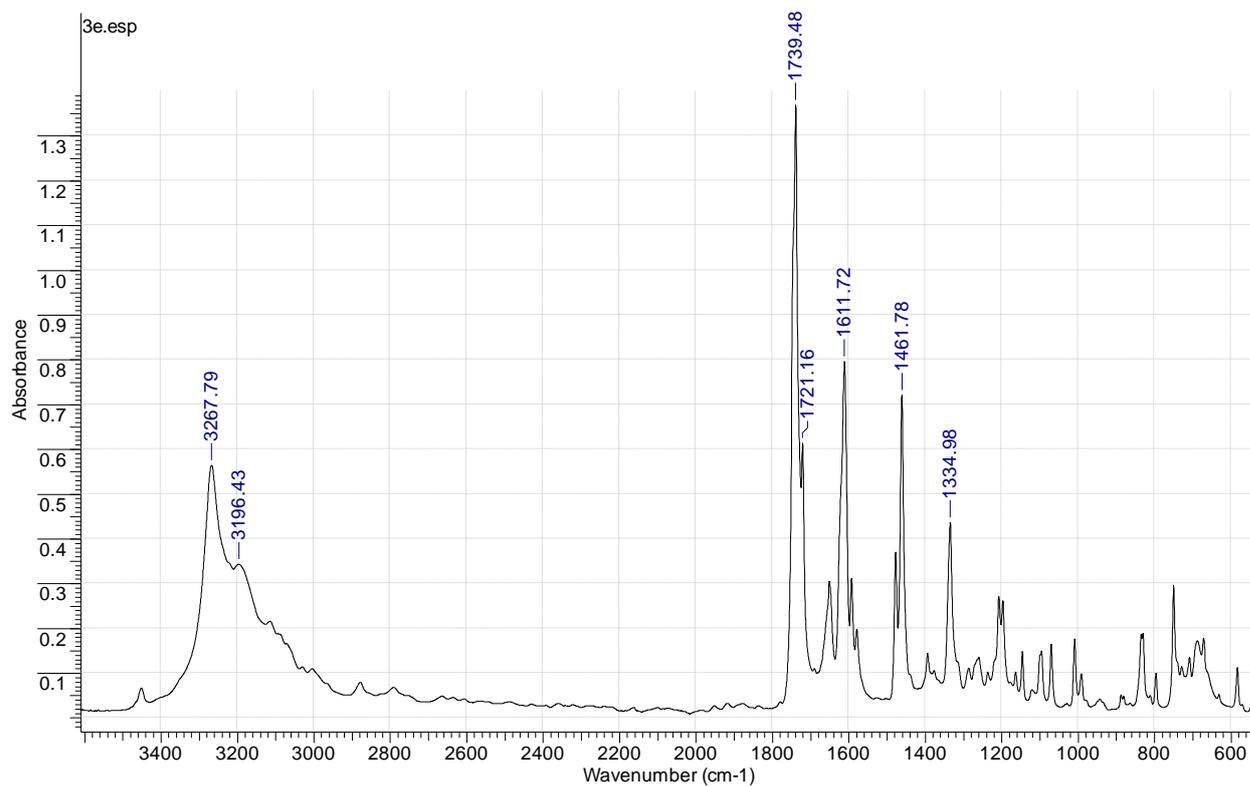
(3d) 3-((3-chlorophenyl)imino)indolin-2-one



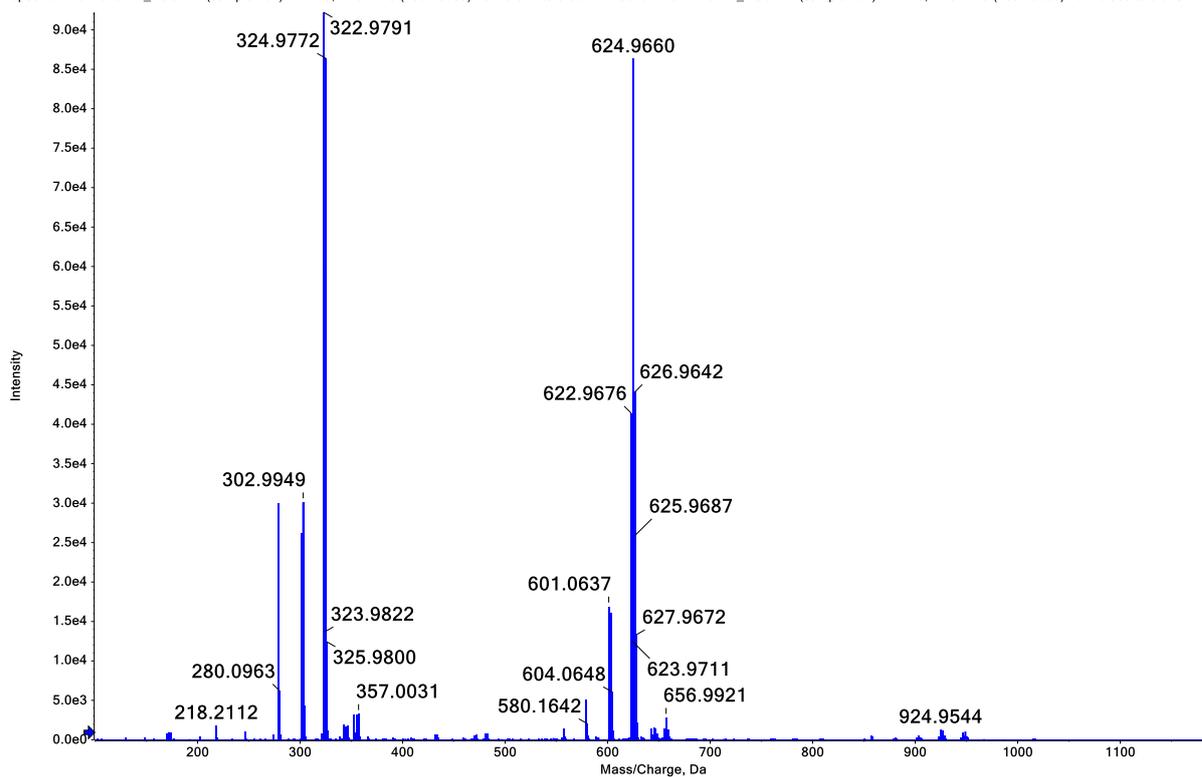
Spectrum from 010122_POS.wiff (sample 157) - DY 42, +TOF MS (100 - 3000) from 0.856 to 0.883 mi...ectrum from 010122_POS.wiff (sample 157) - DY 42, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

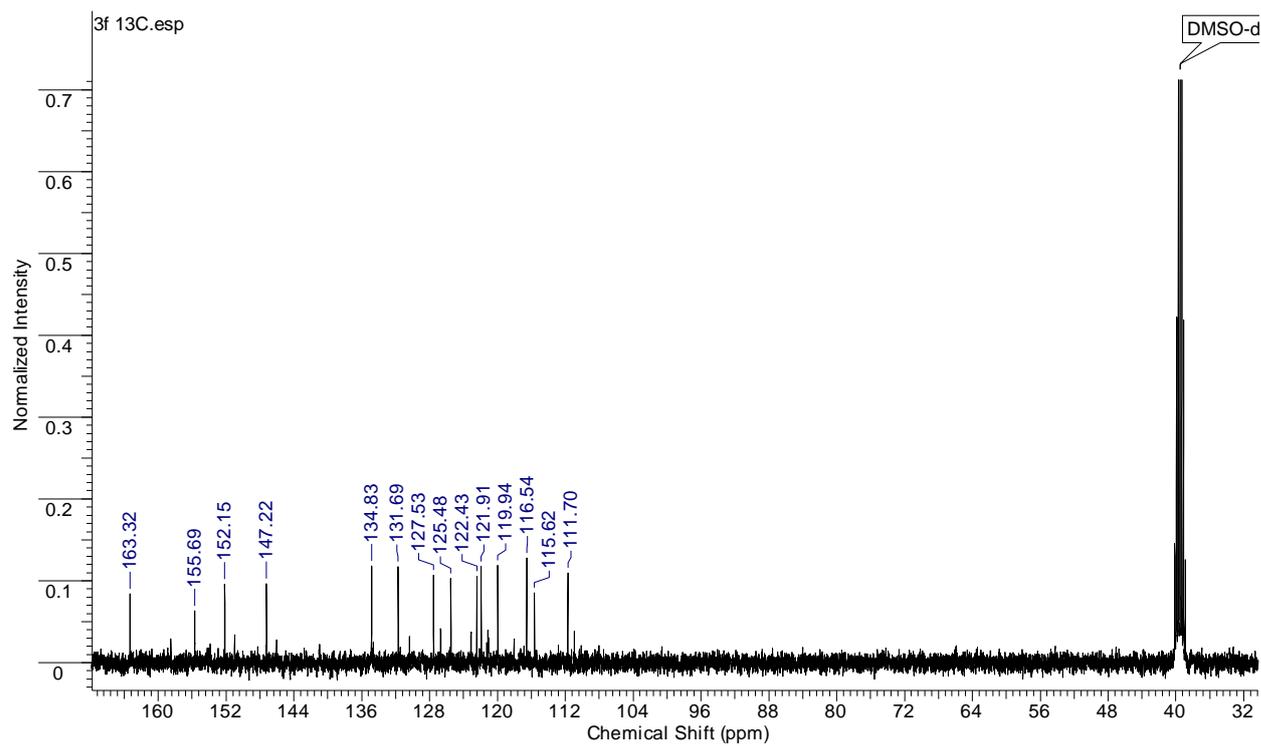
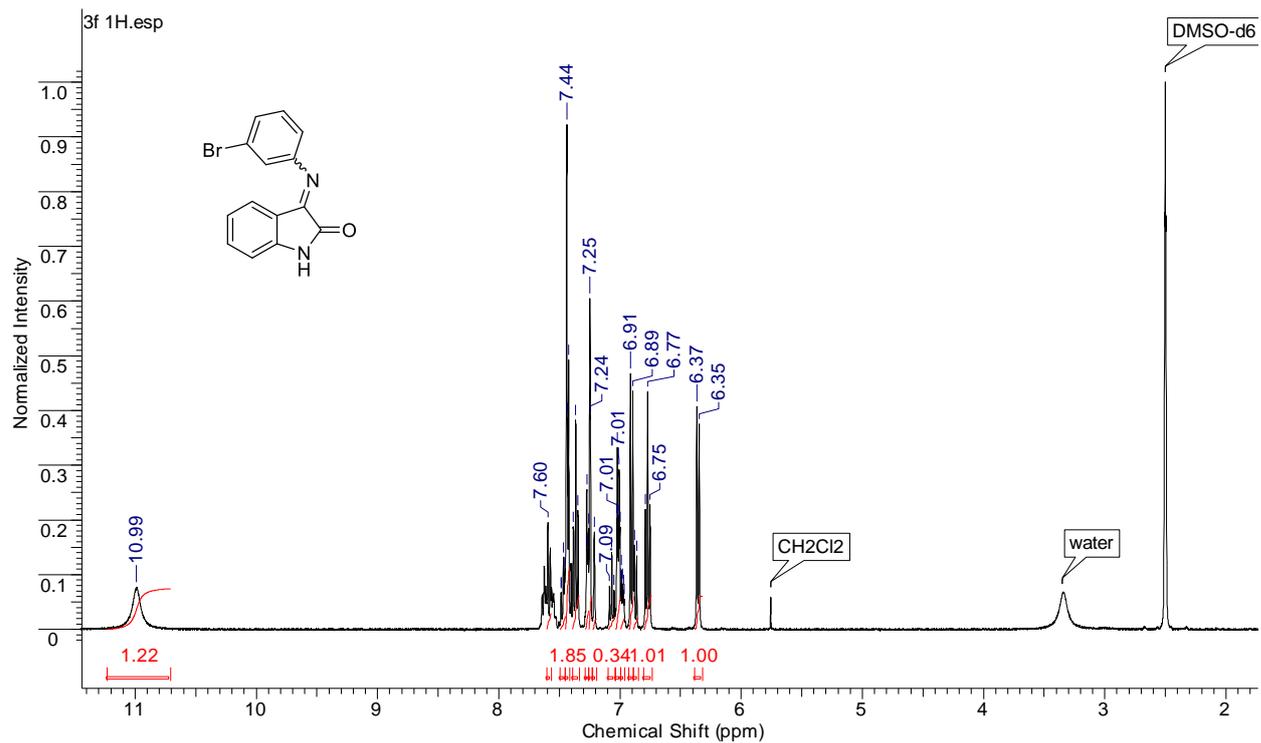


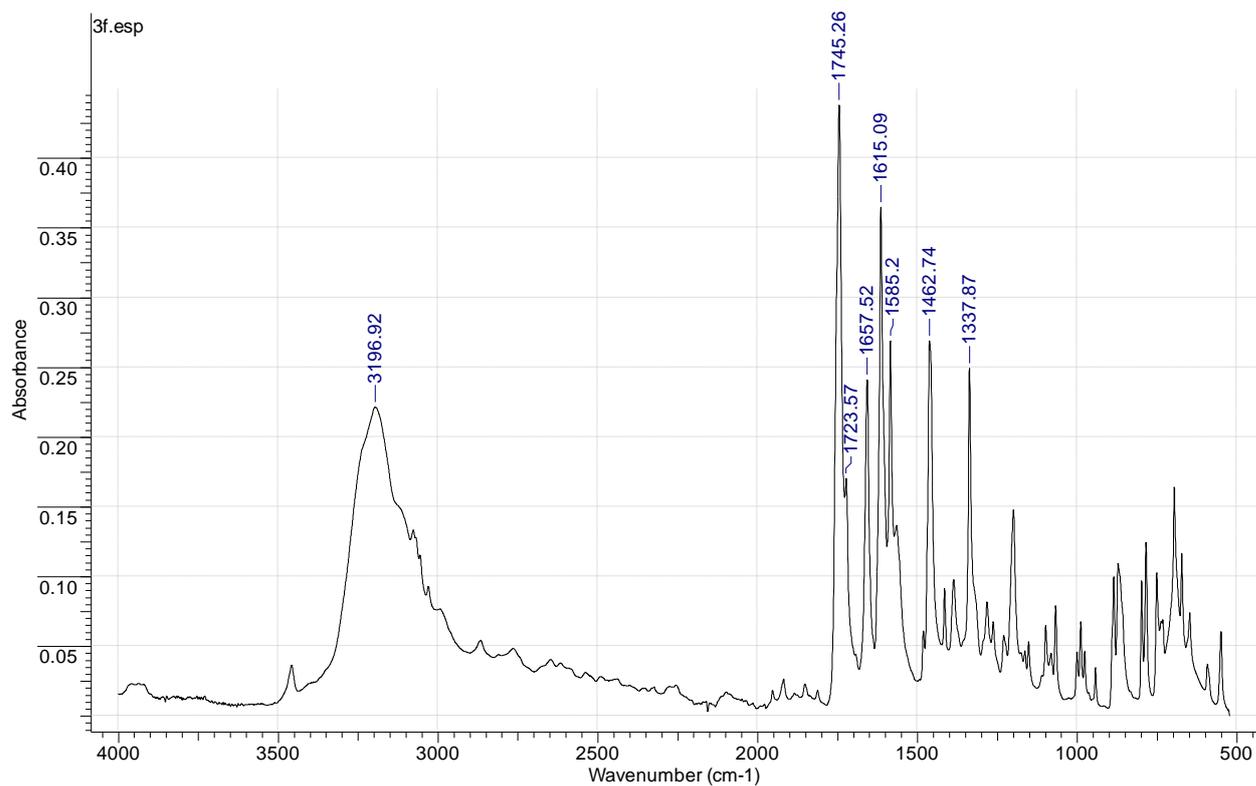
(3e) 3-((4-bromophenyl)imino)indolin-2-one



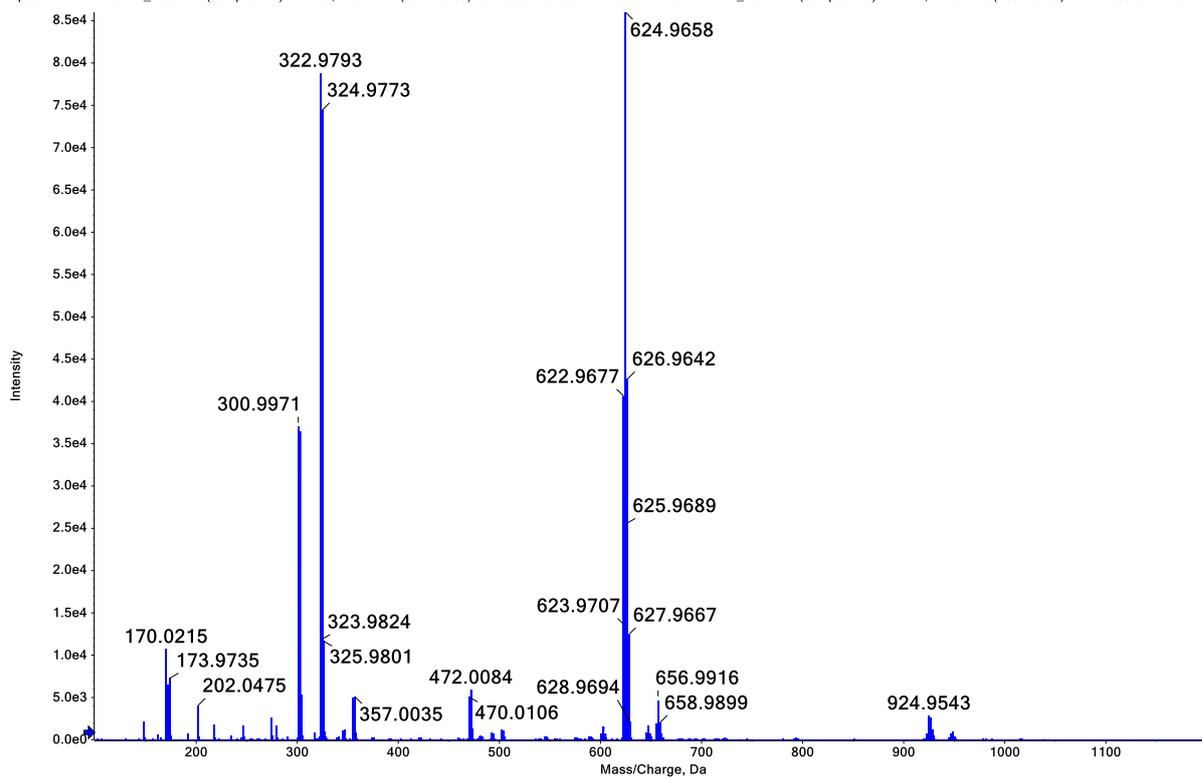
Spectrum from 010122_POS.wiff (sample 164) - DY 48, +TOF MS (100 - 3000) from 0.874 to 0.902 mi...ectrum from 010122_POS.wiff (sample 164) - DY 48, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

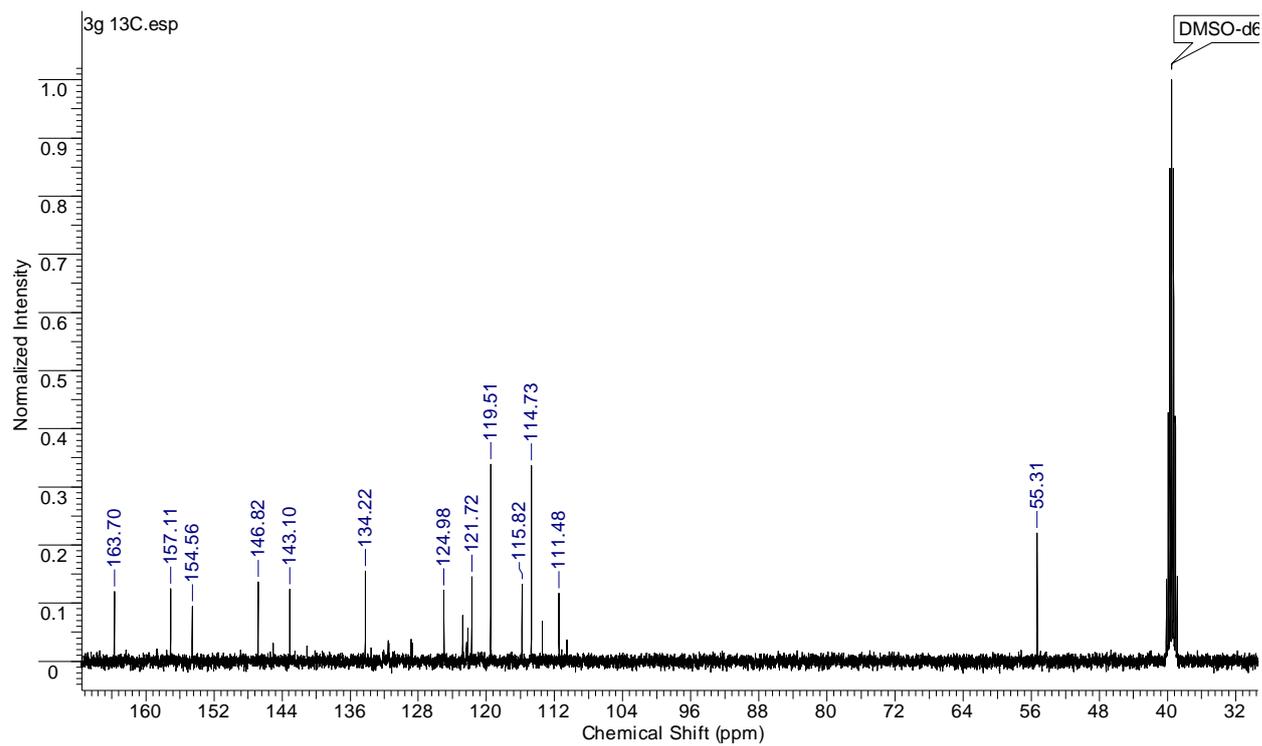
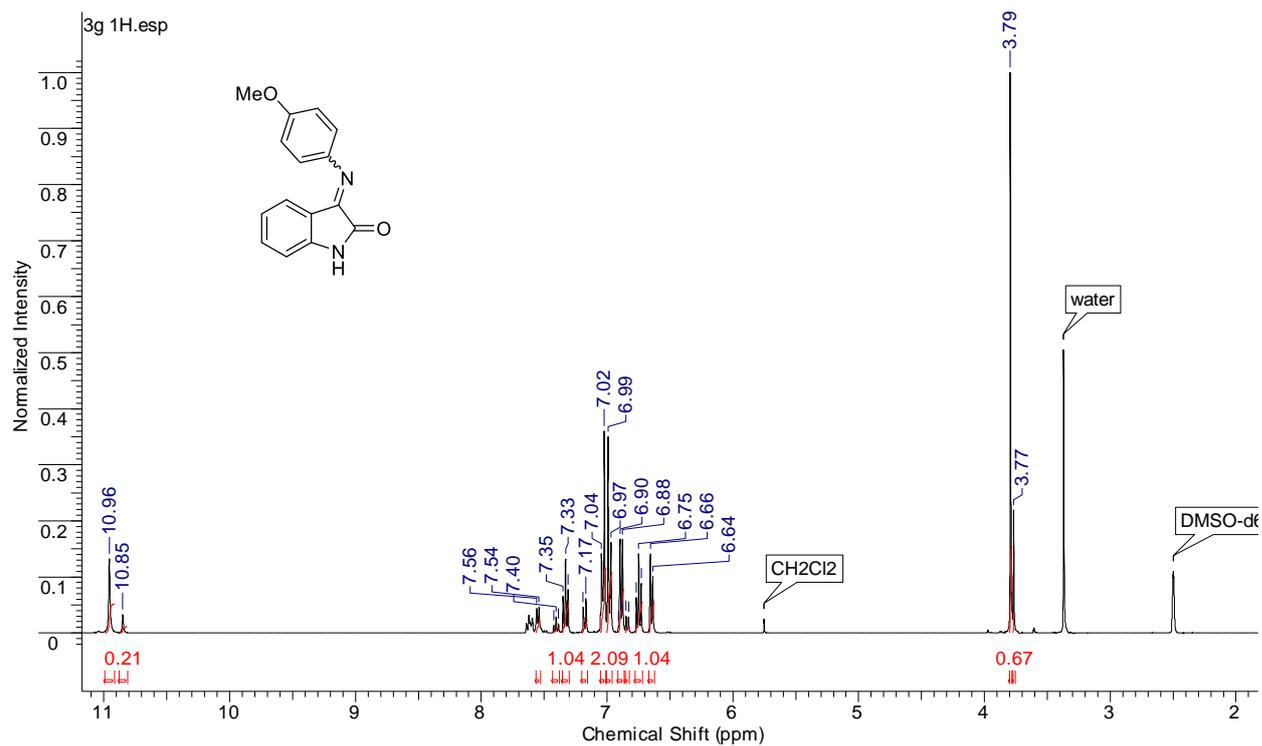


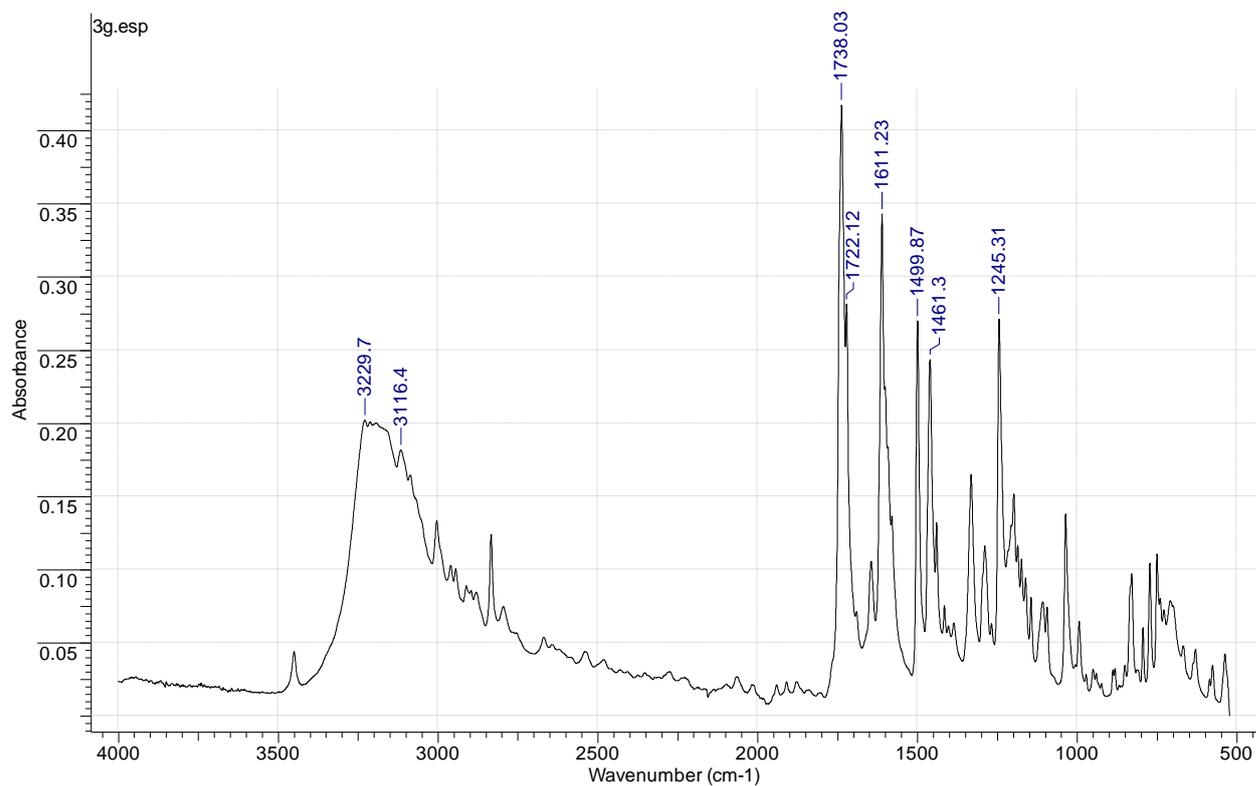
(3f) 3-((3-bromophenyl)imino)indolin-2-one



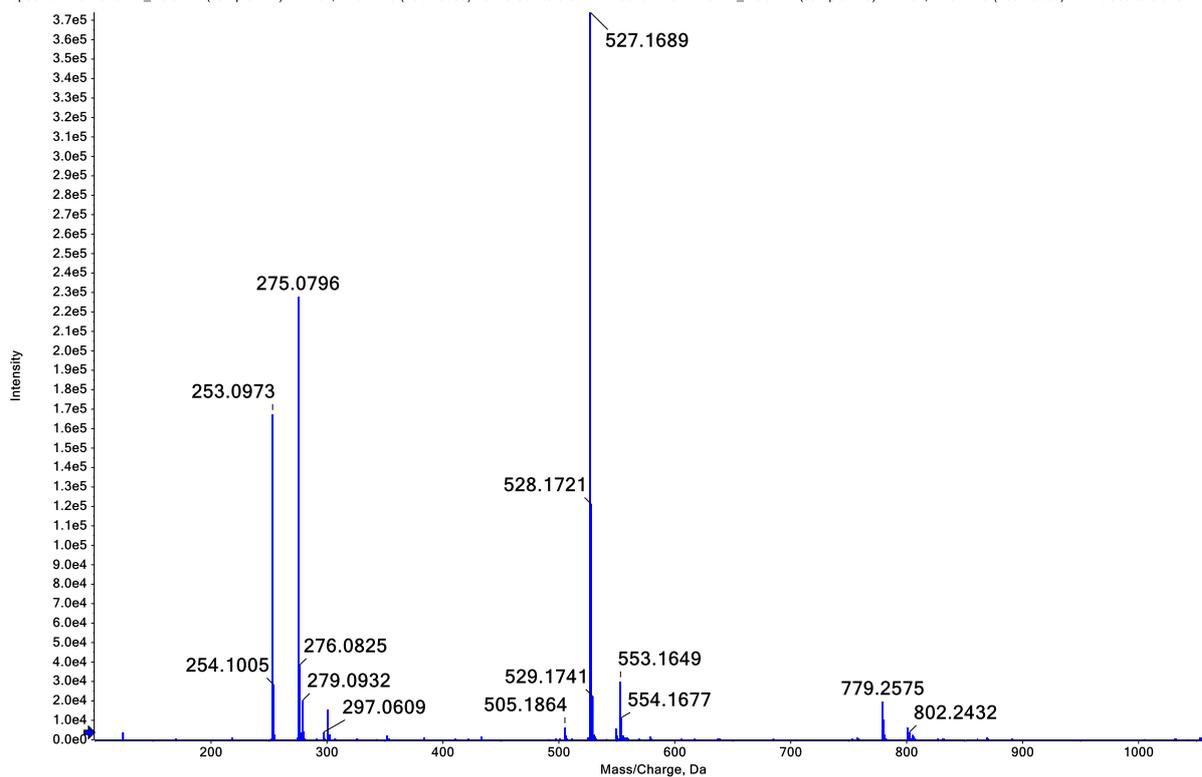
Spectrum from 010122_POS.wiff (sample 145) - DY 43, +TOF MS (100 - 3000) from 0.804 to 0.832 mi...ectrum from 010122_POS.wiff (sample 145) - DY 43, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

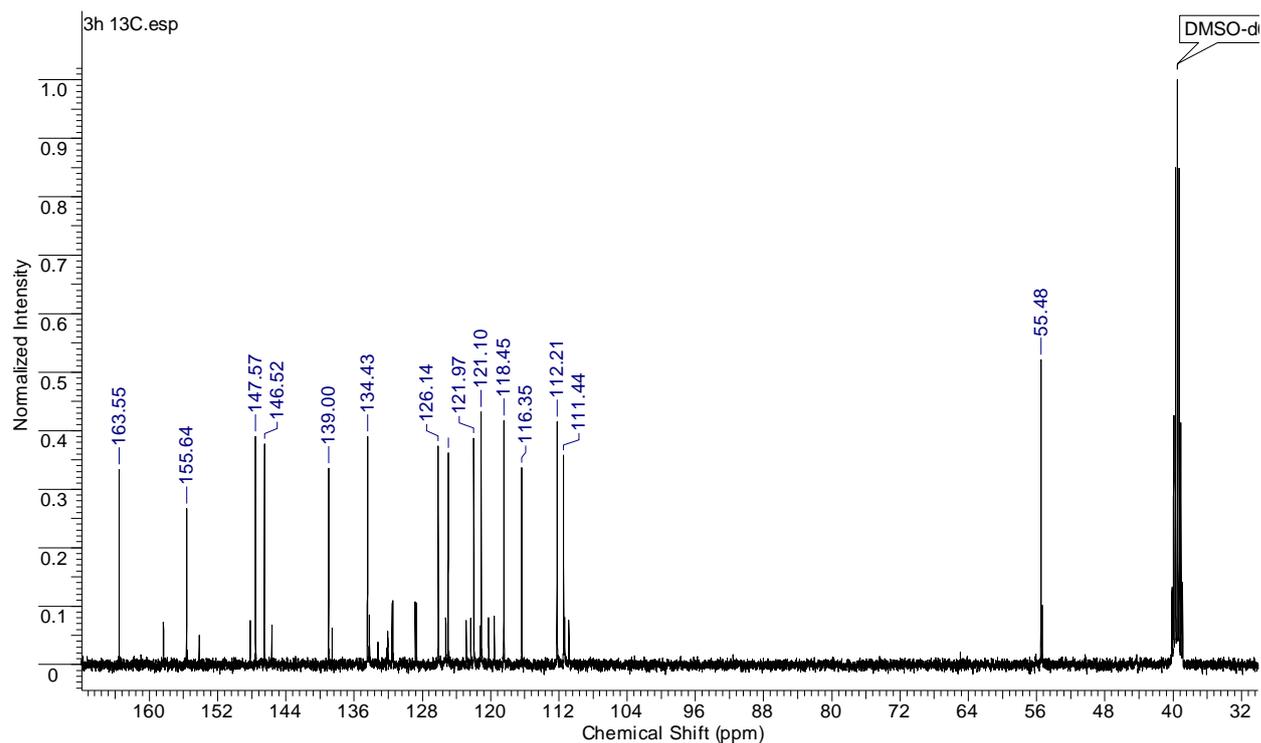
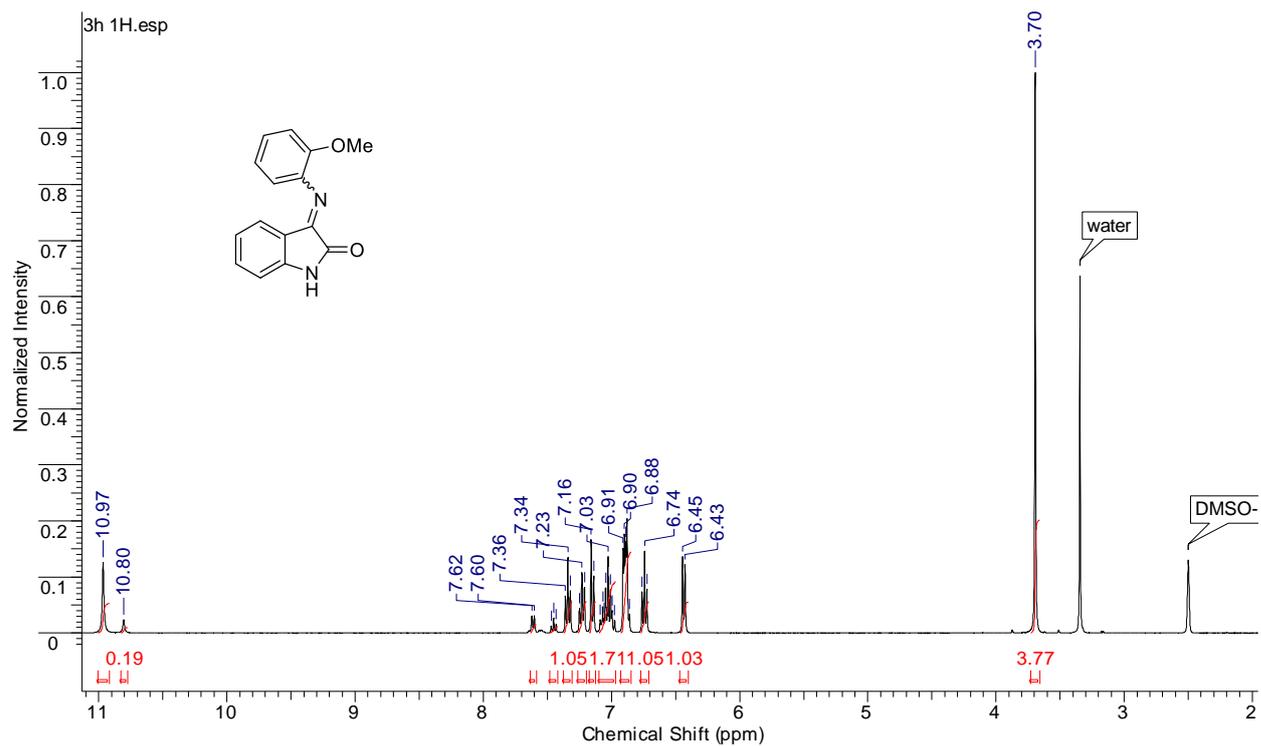


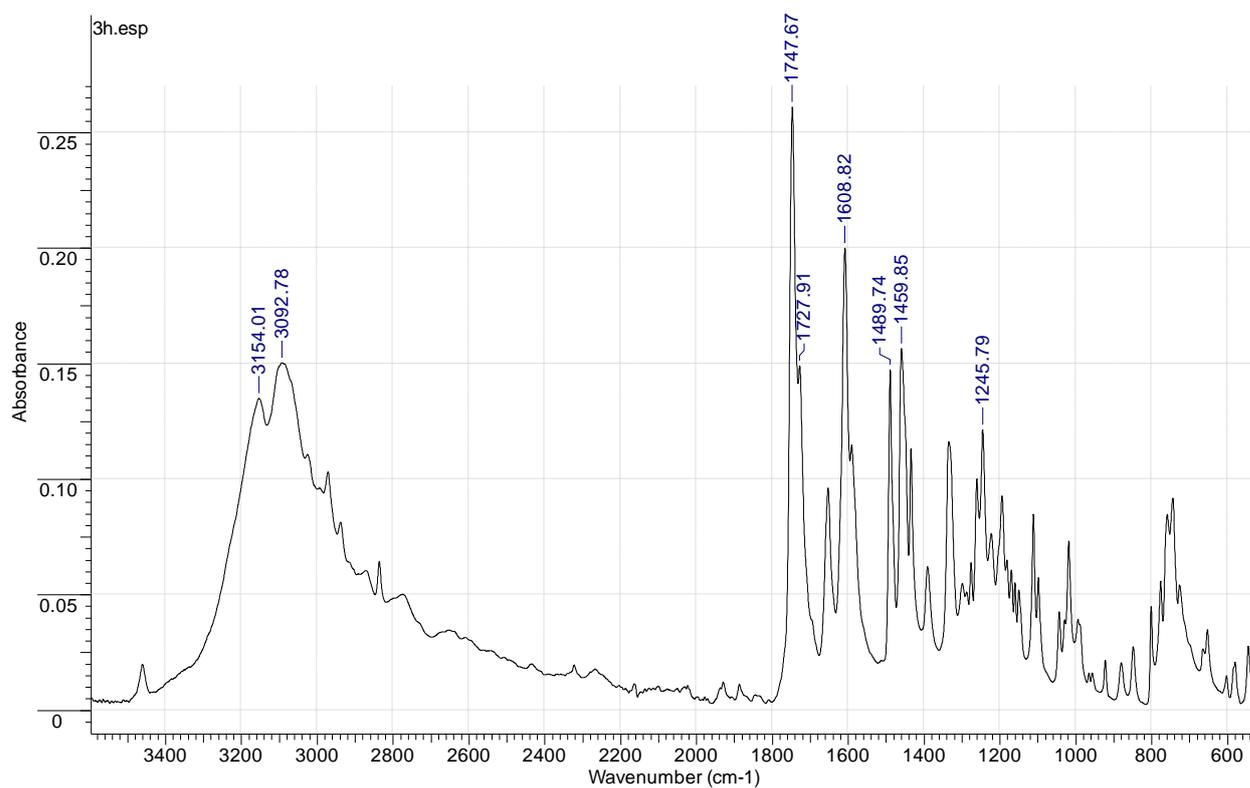
(3g) 3-((4-methoxyphenyl)imino)indolin-2-one



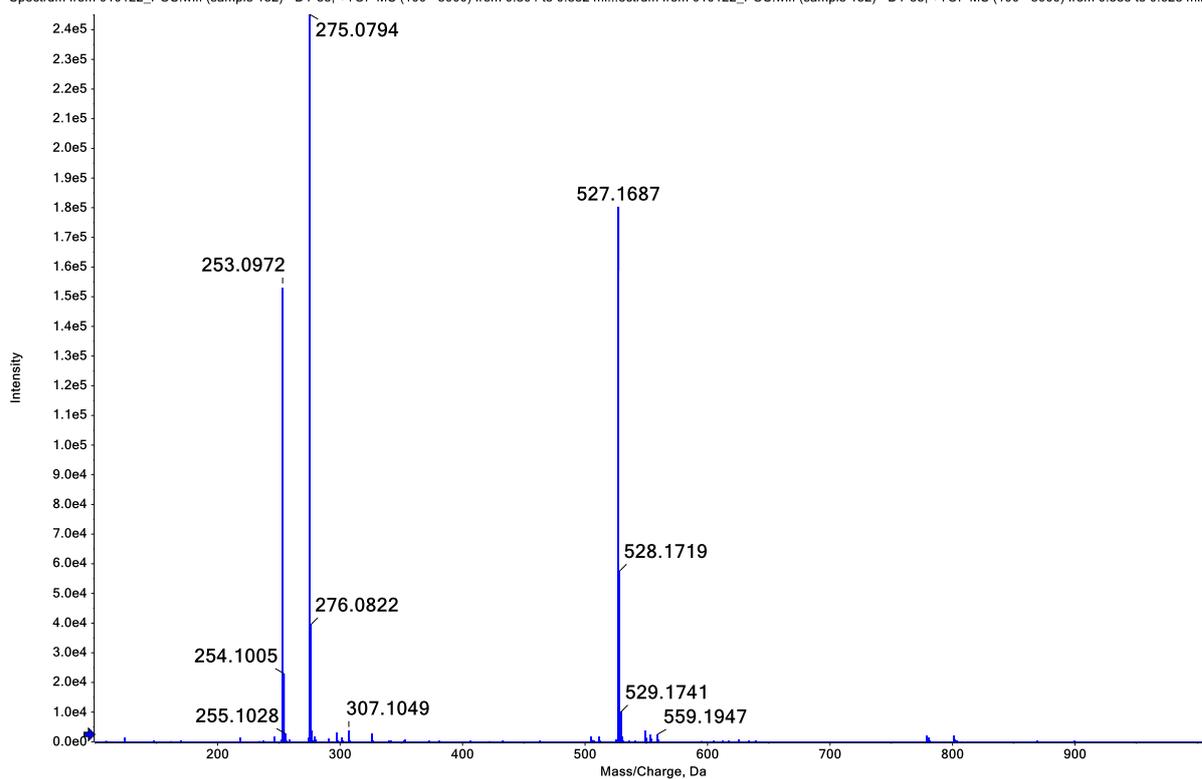
Spectrum from 010122_POS.wiff (sample 143) - DY 54, +TOF MS (100 - 3000) from 0.804 to 0.832 mi...ectrum from 010122_POS.wiff (sample 143) - DY 54, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

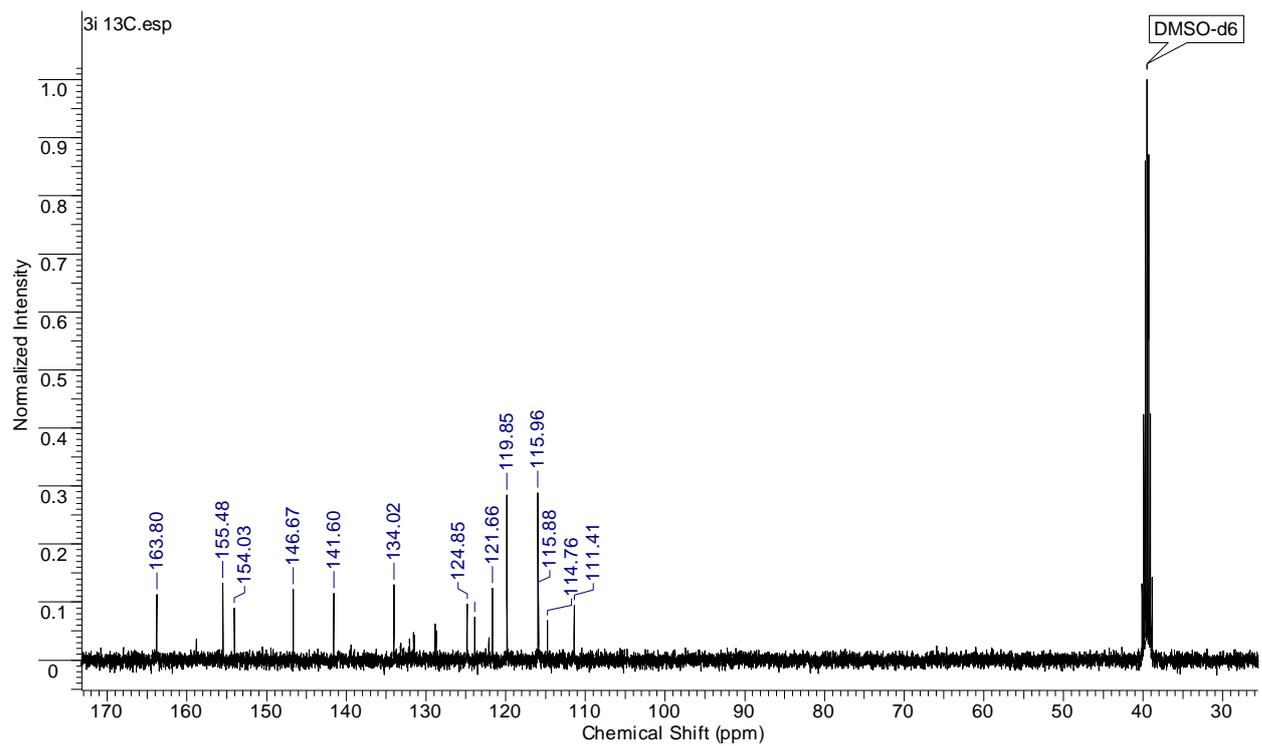
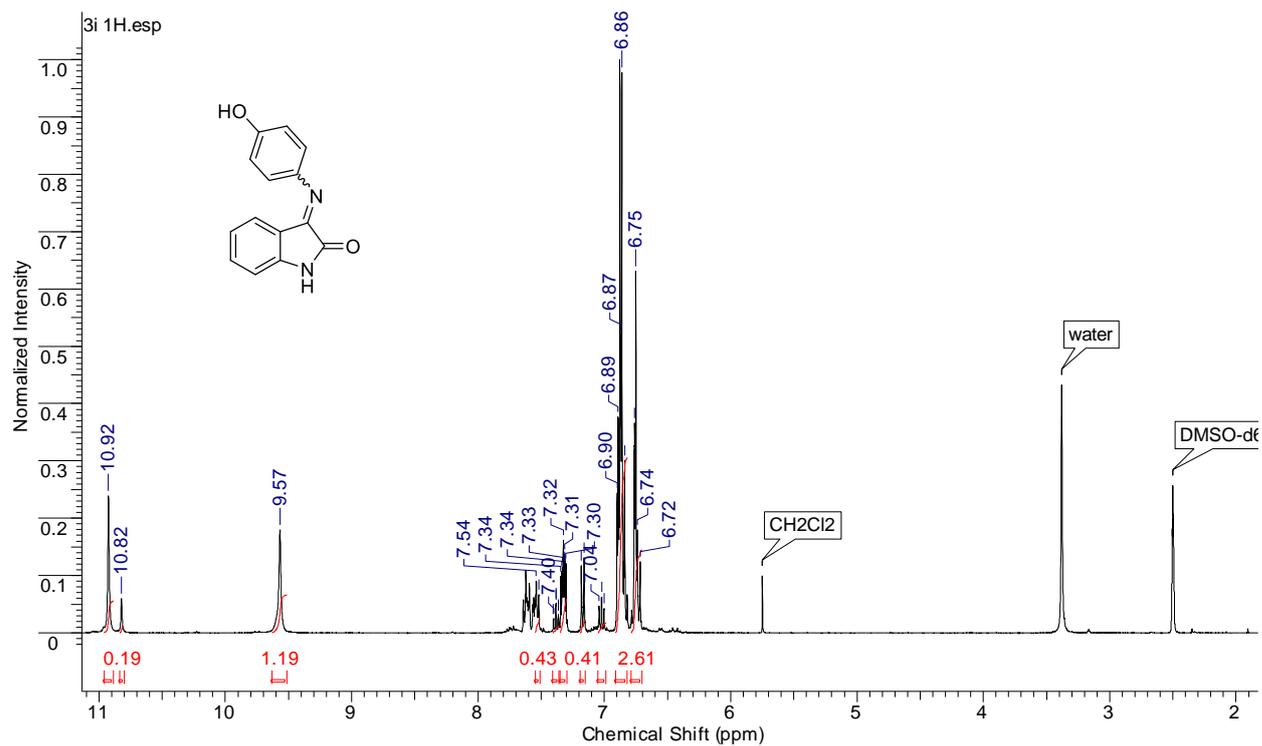


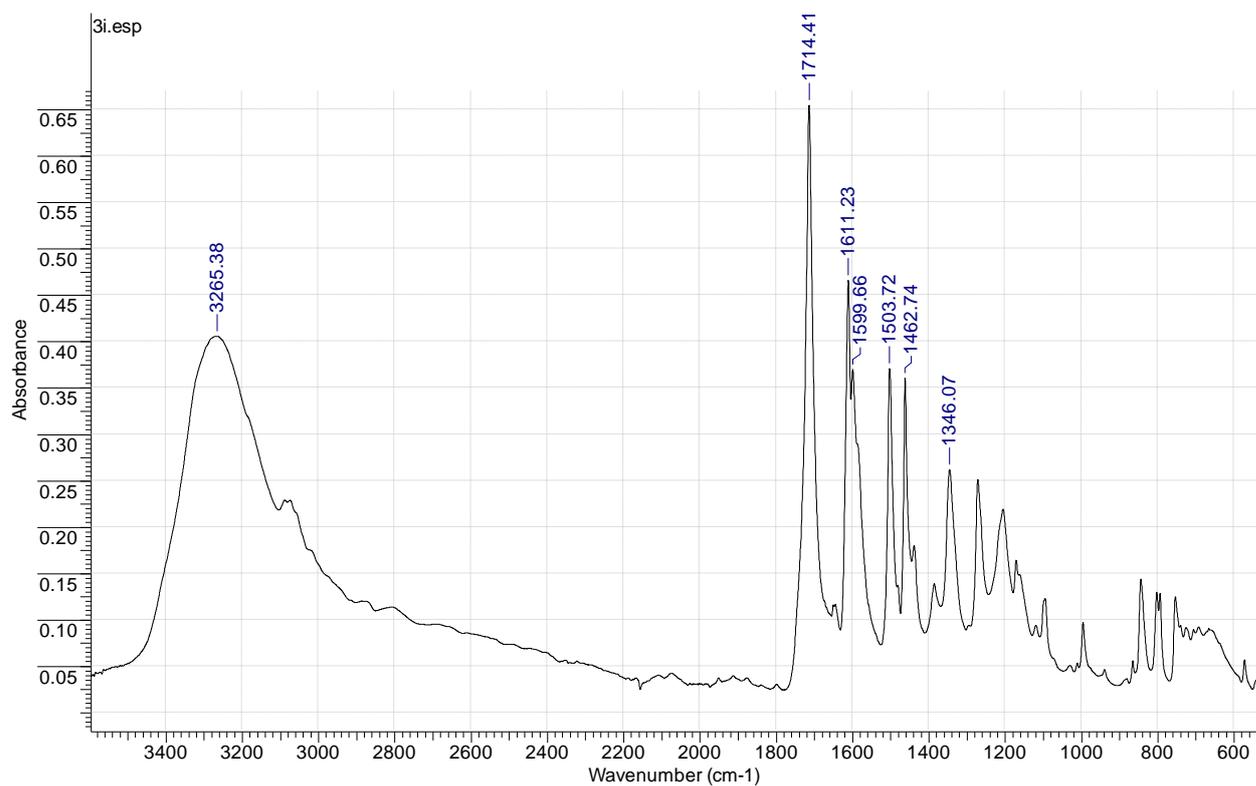
(3h) 3-((2-methoxyphenyl)imino)indolin-2-one



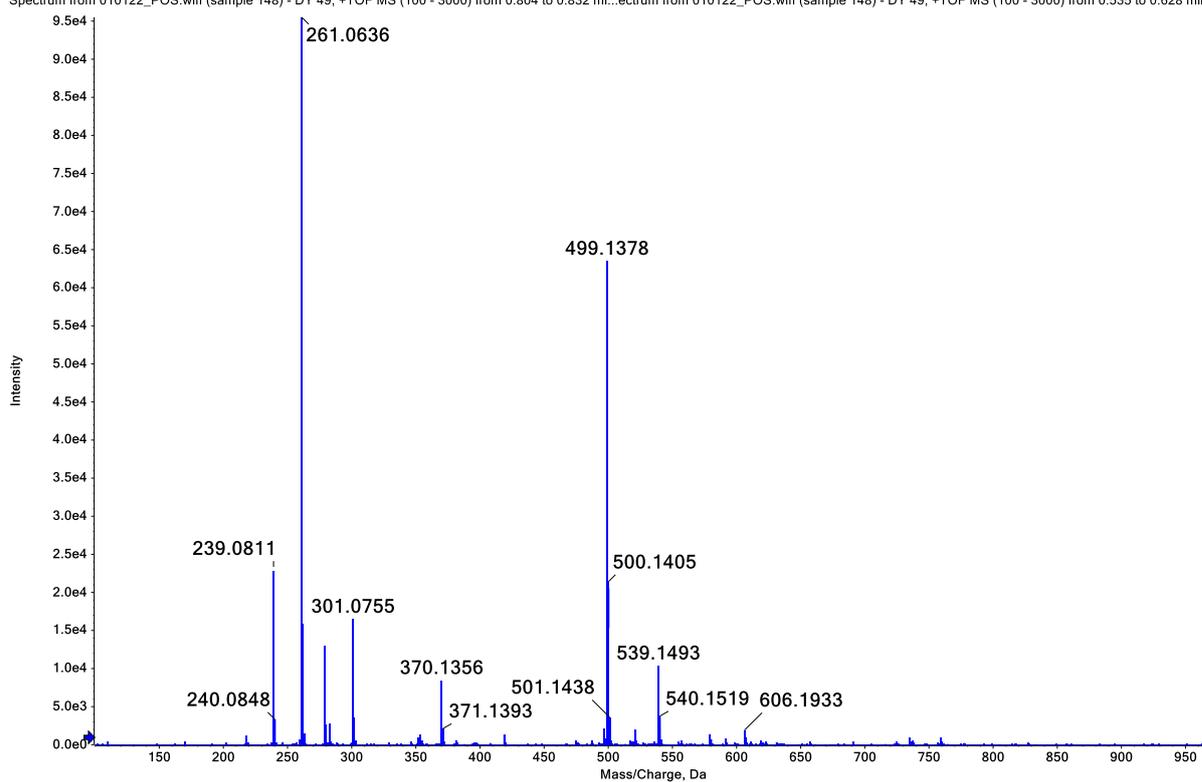
Spectrum from 010122_POS.wiff (sample 152) - DY 55, +TOF MS (100 - 3000) from 0.804 to 0.832 mi...ectrum from 010122_POS.wiff (sample 152) - DY 55, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

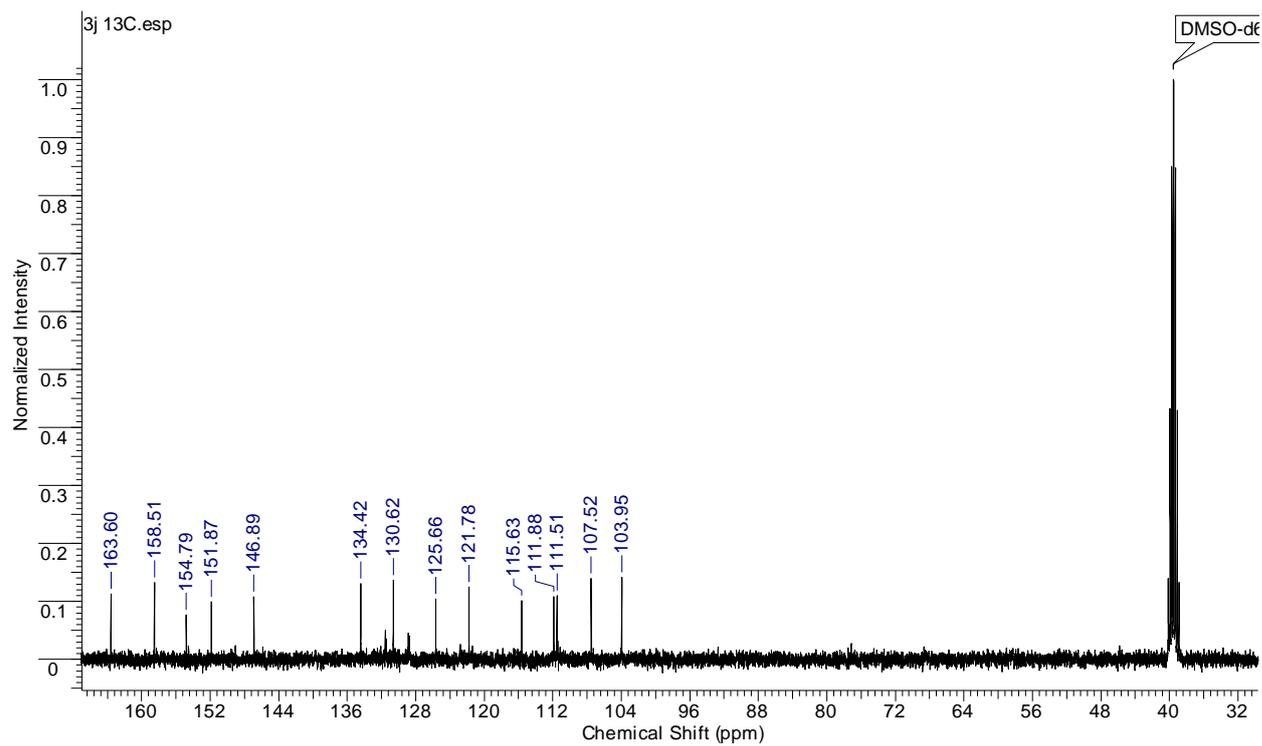
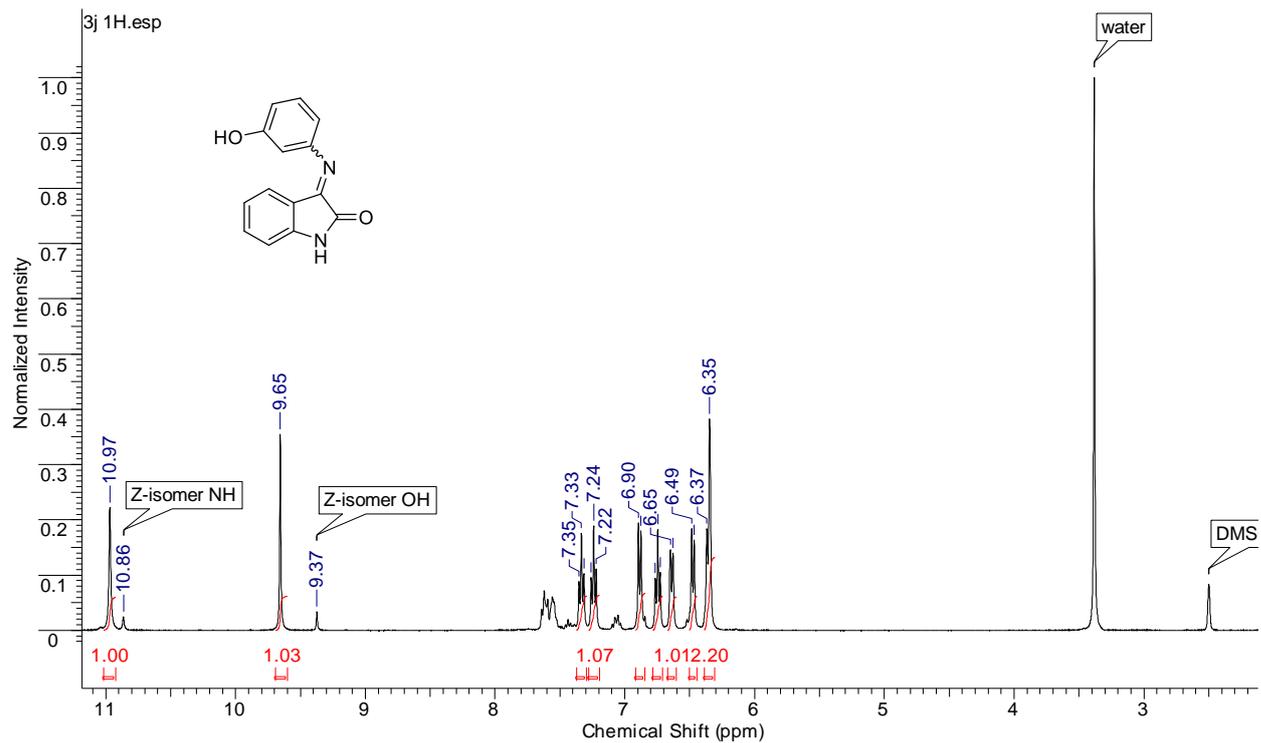


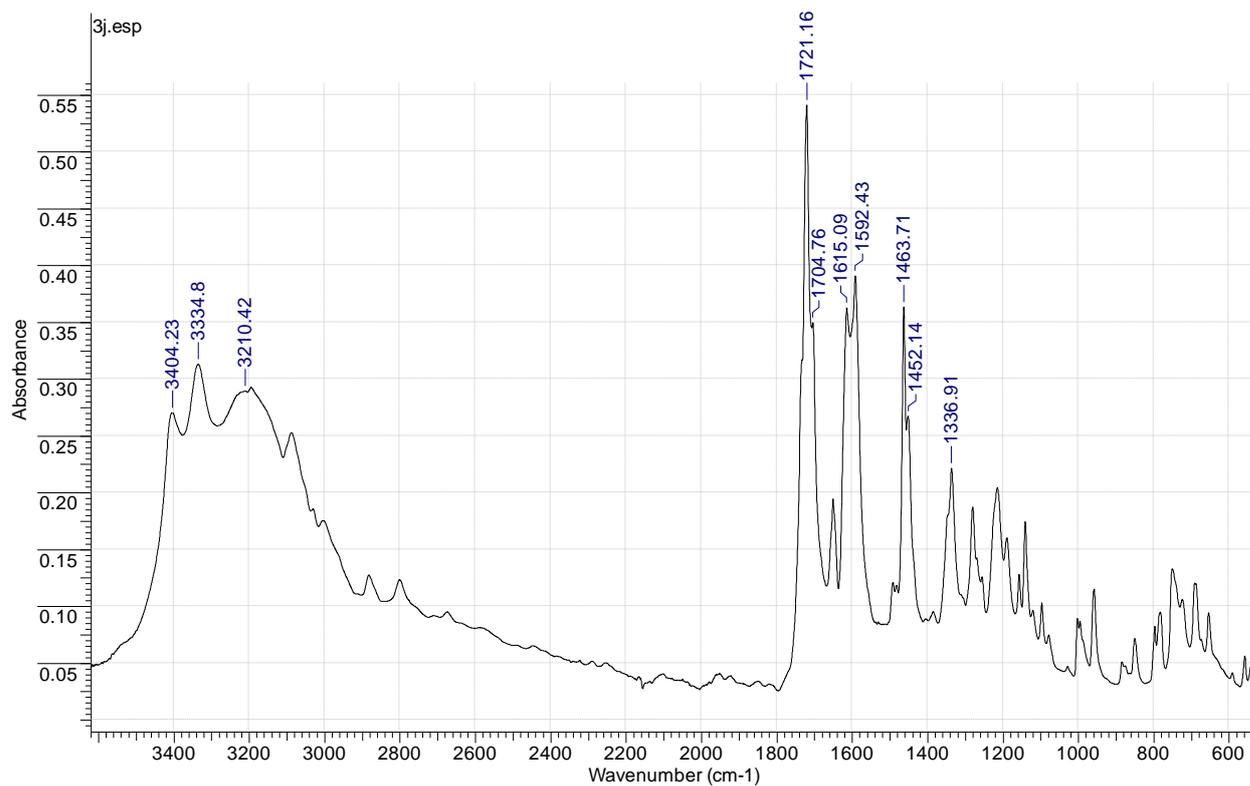
(3i) 3-((4-hydroxyphenyl)imino)indolin-2-one



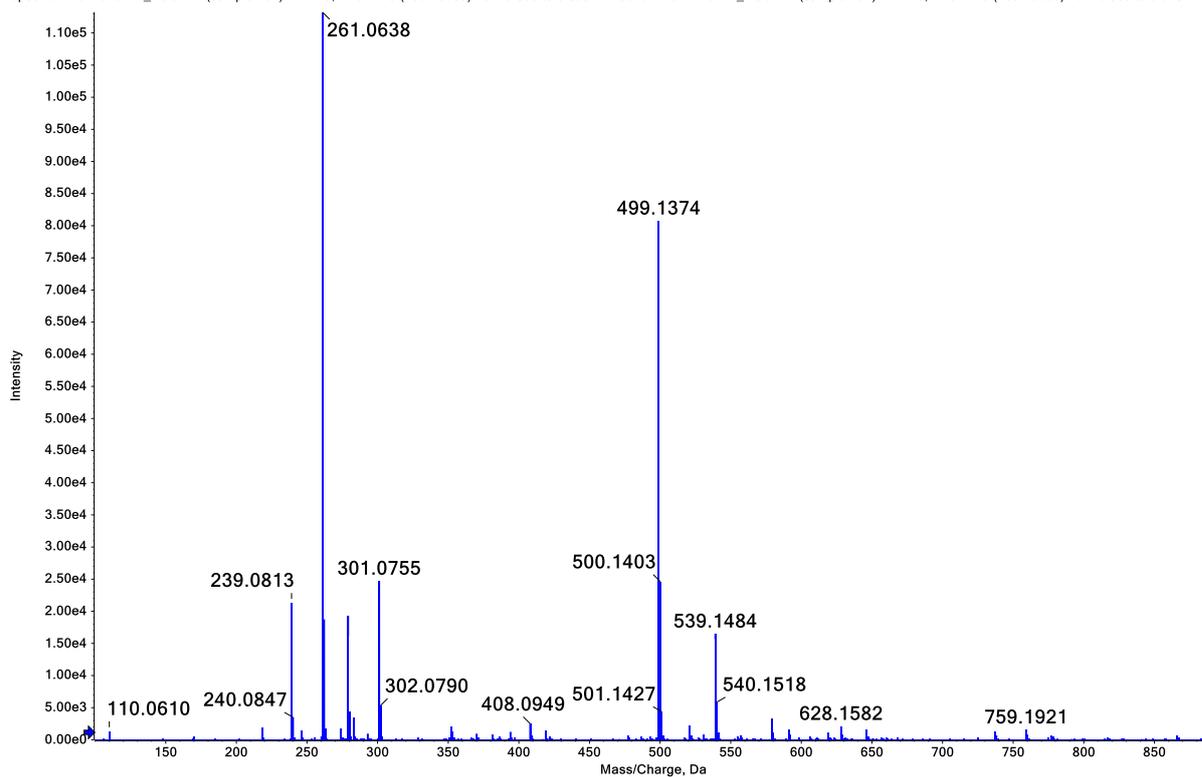
Spectrum from 010122_POS.wiff (sample 148) - DY 49, +TOF MS (100 - 3000) from 0.804 to 0.832 mi...ectrum from 010122_POS.wiff (sample 148) - DY 49, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

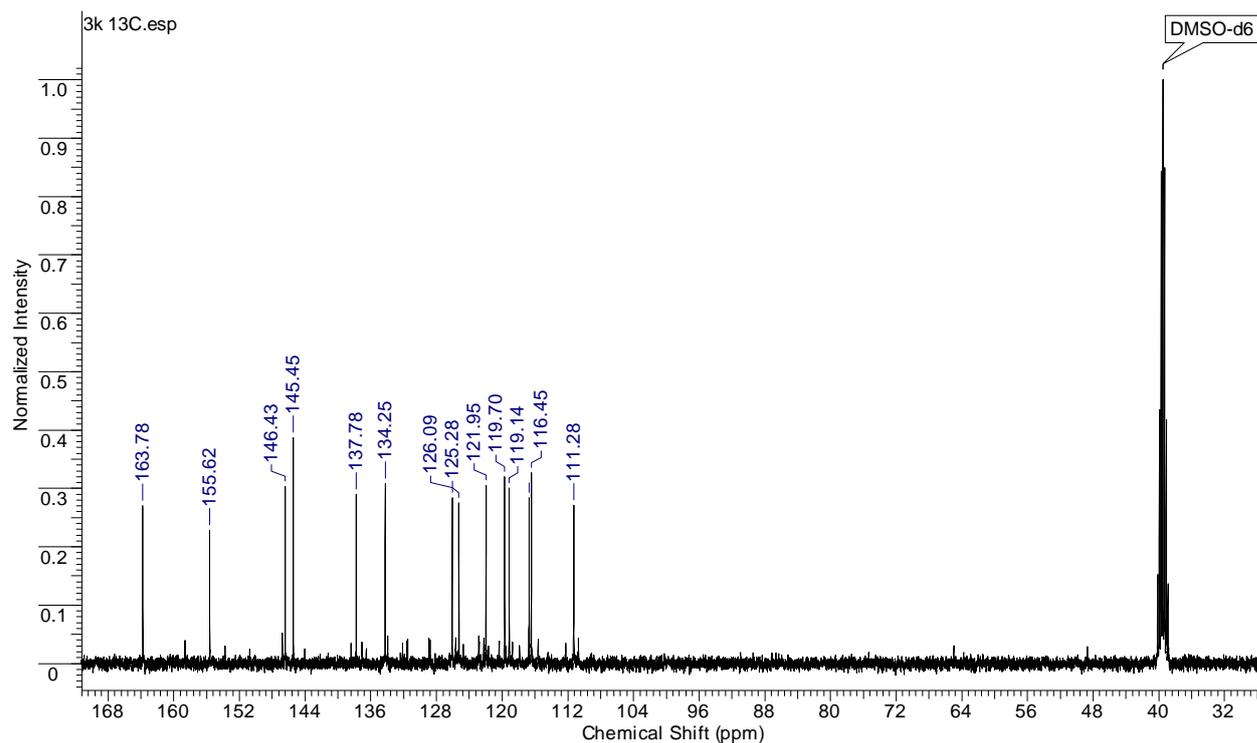
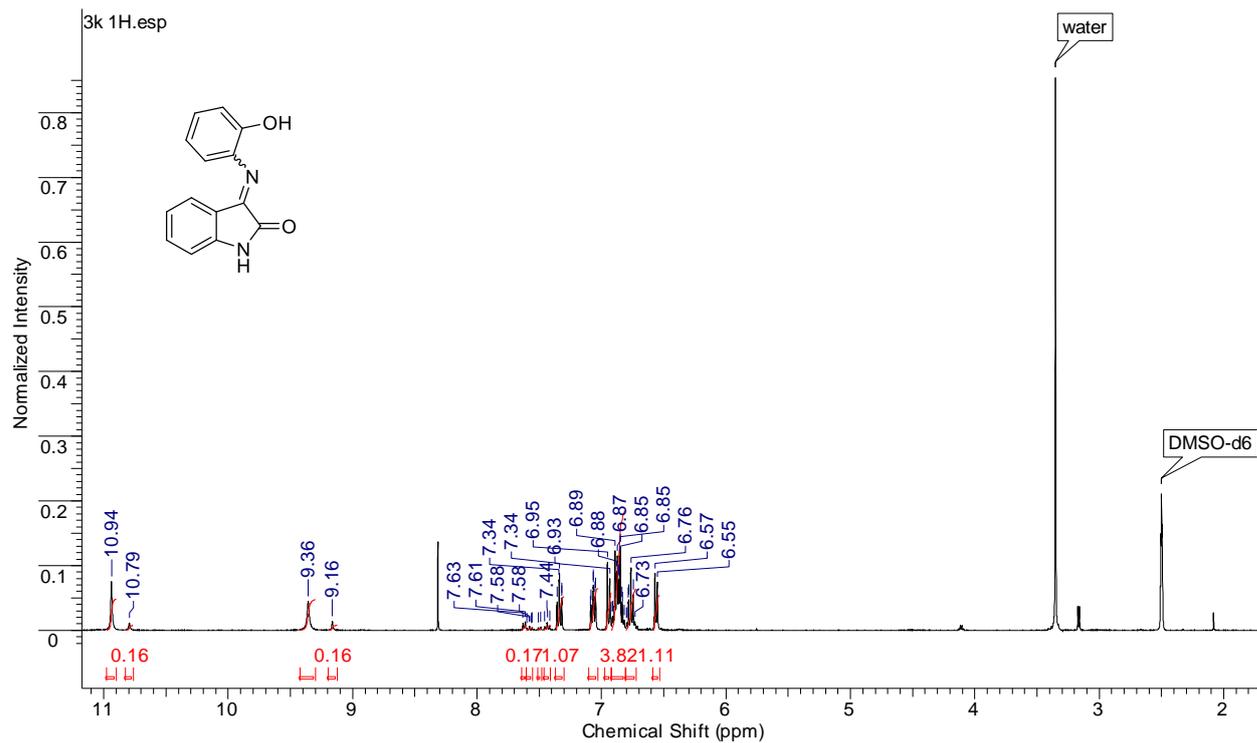


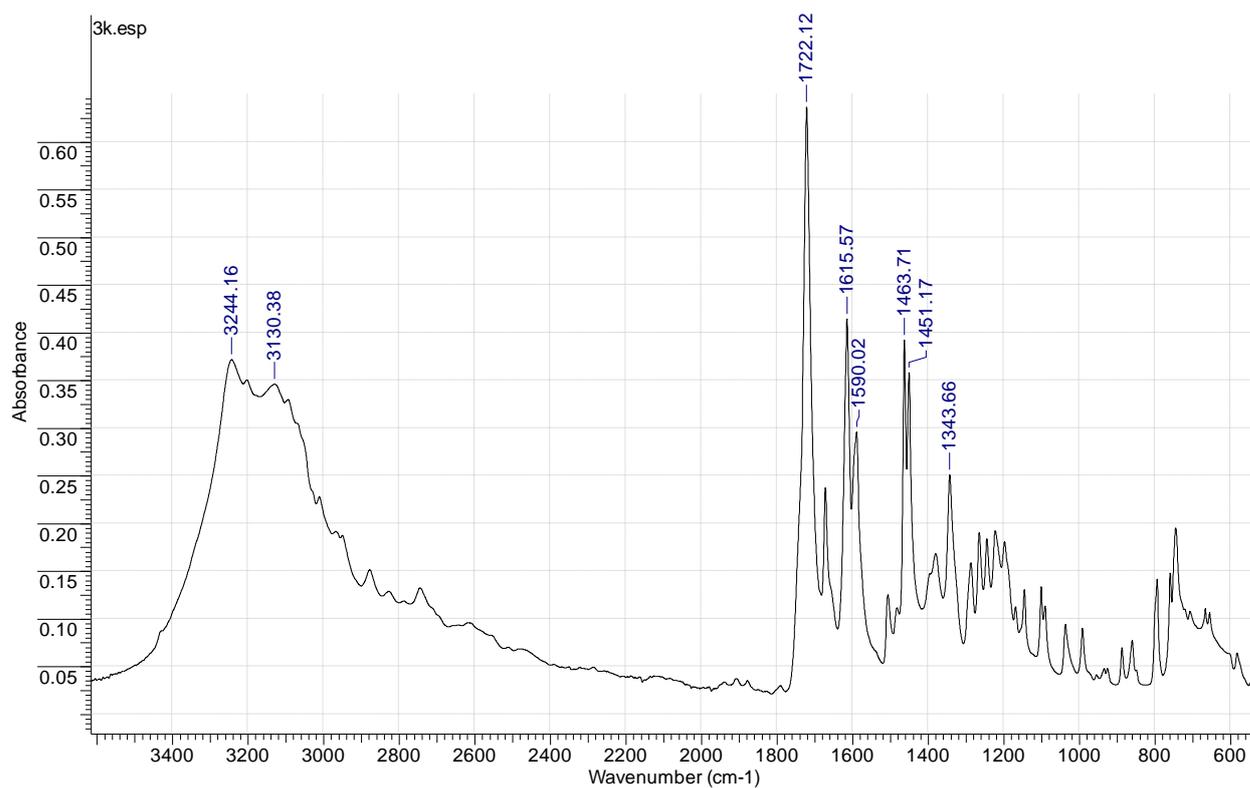
(3j) 3-((3-hydroxyphenyl)imino)indolin-2-one



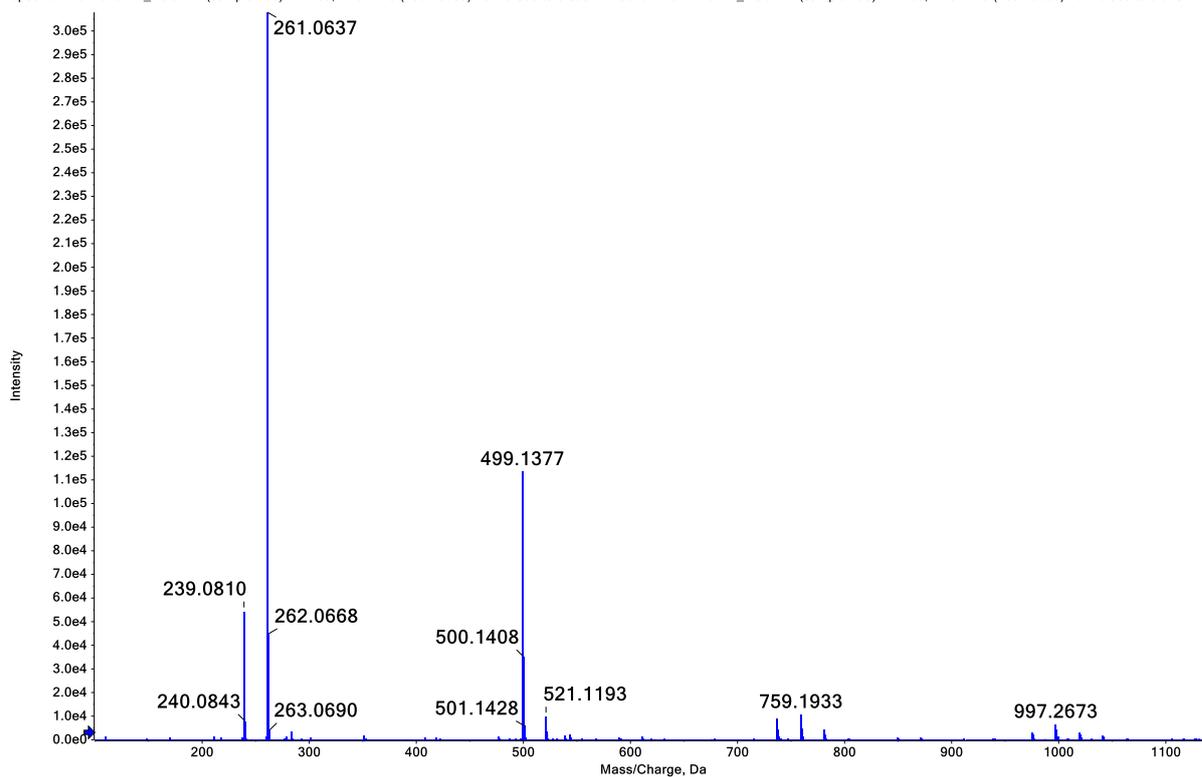
Spectrum from 010122_POS.wiff (sample 154) - DY 13, +TOF MS (100 - 3000) from 0.856 to 0.883 mi...ectrum from 010122_POS.wiff (sample 154) - DY 13, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

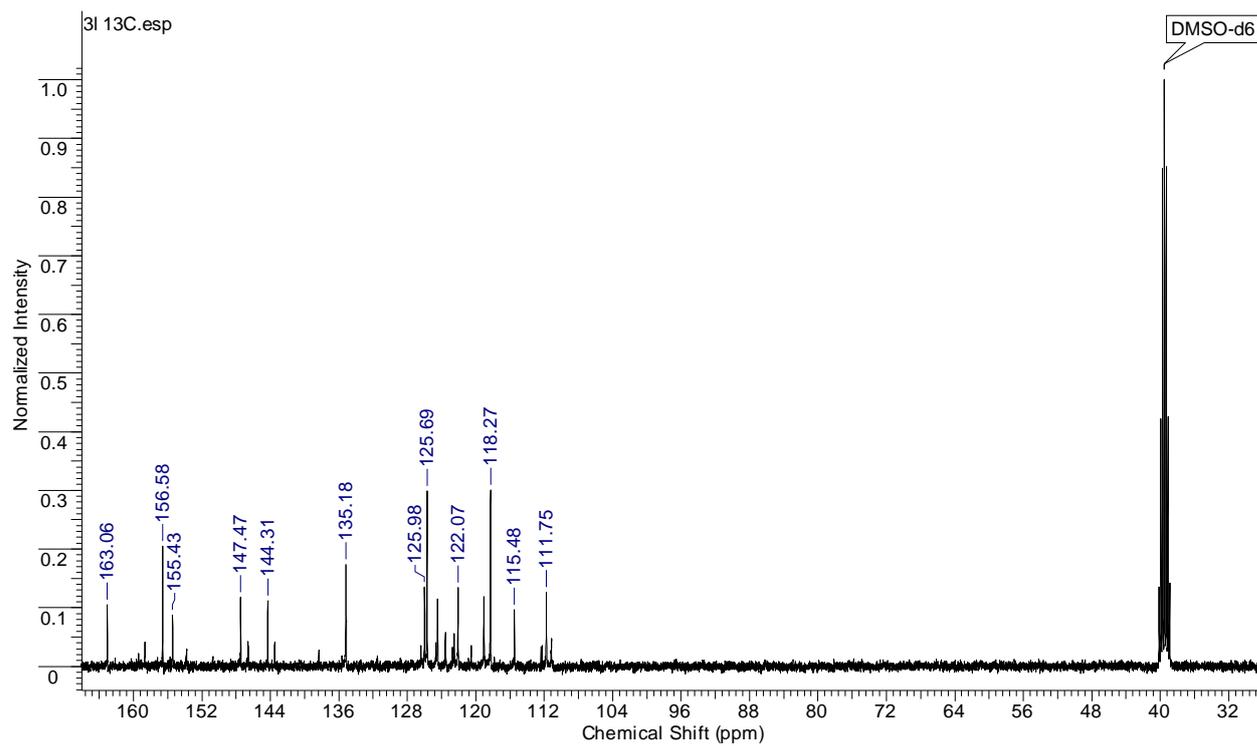
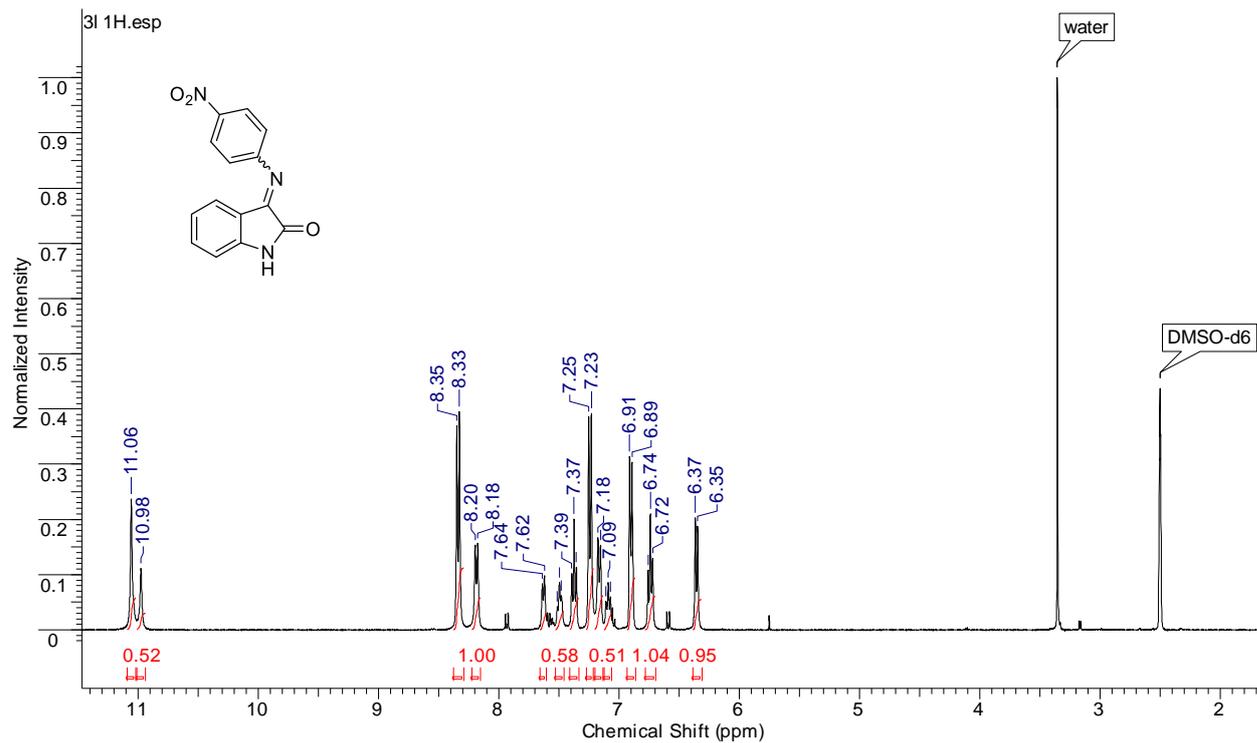


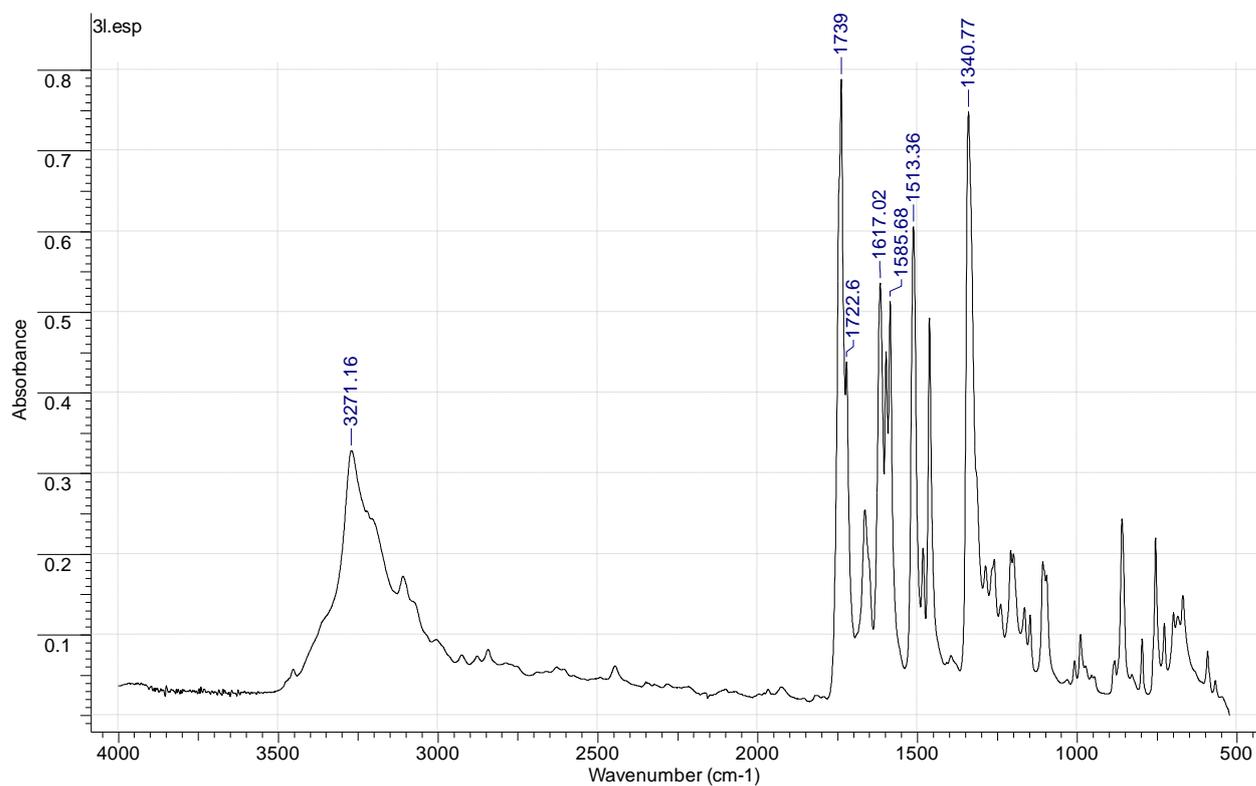
(3k) 3-((2-hydroxyphenyl)imino)indolin-2-one



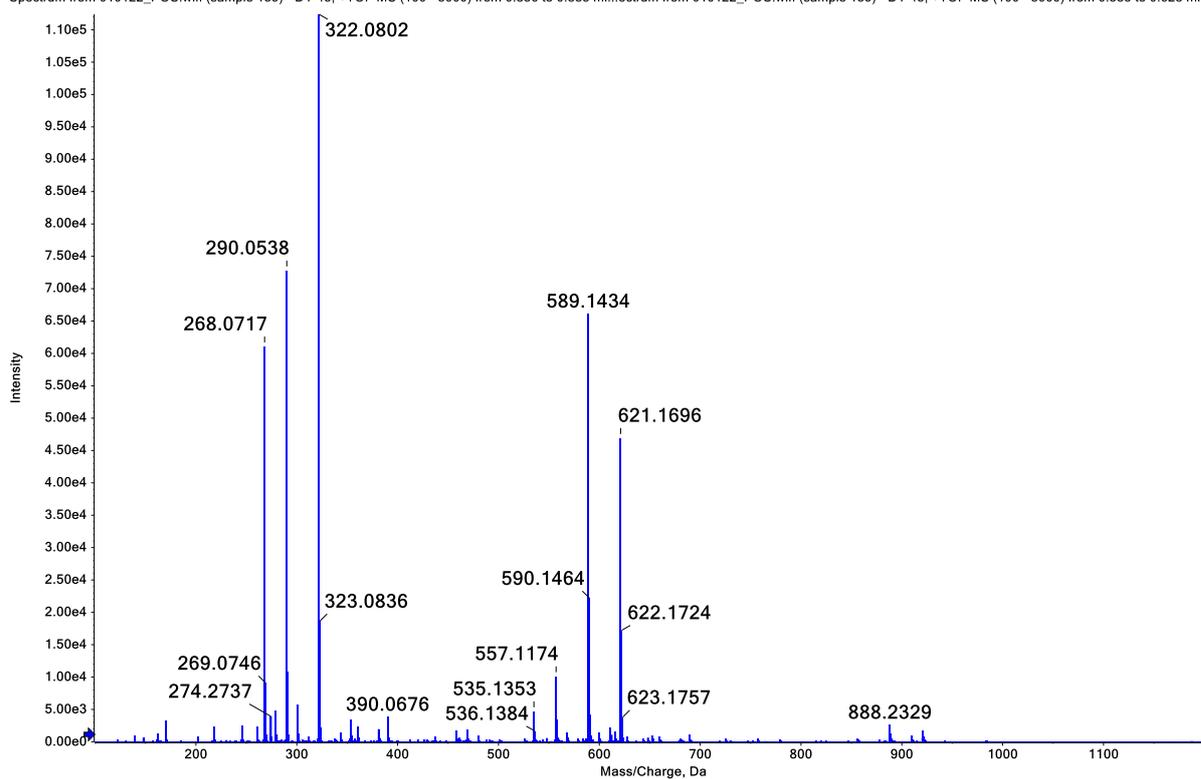
Spectrum from 010122_POS.wiff (sample 158) - DY 50, +TOF MS (100 - 3000) from 0.856 to 0.883 mi...ectrum from 010122_POS.wiff (sample 158) - DY 50, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

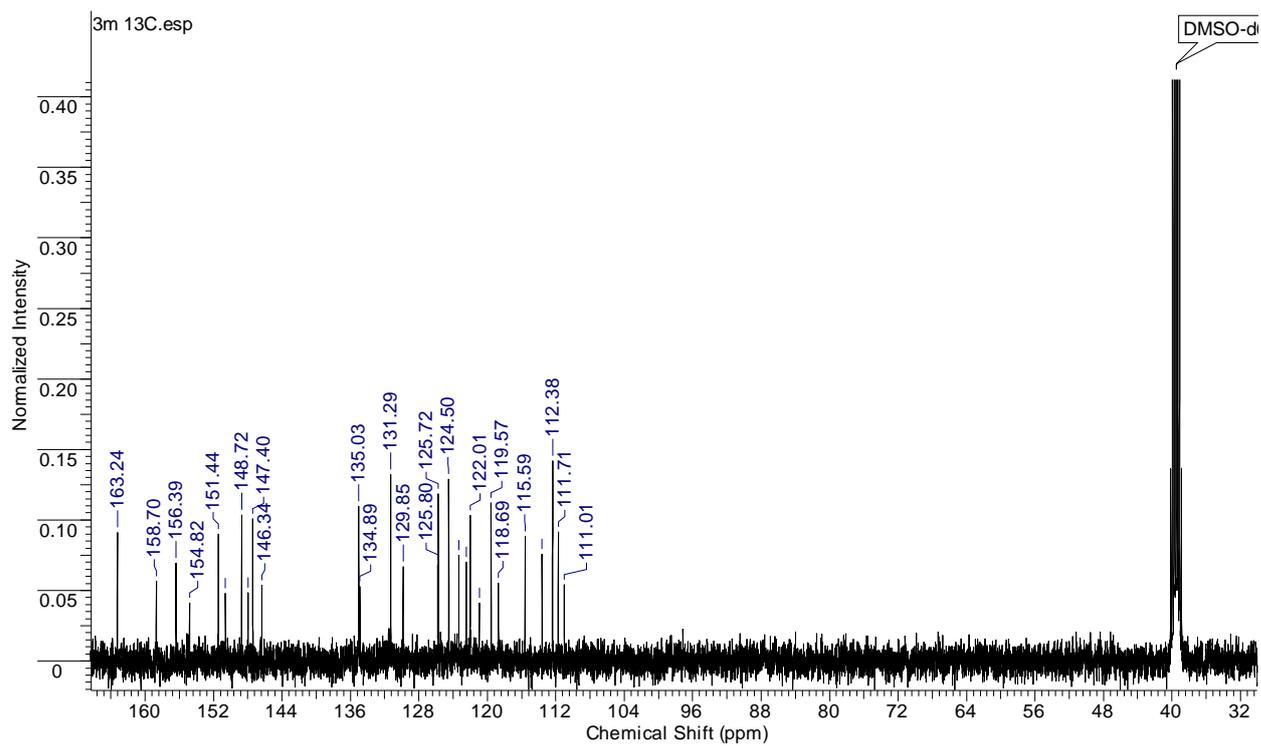
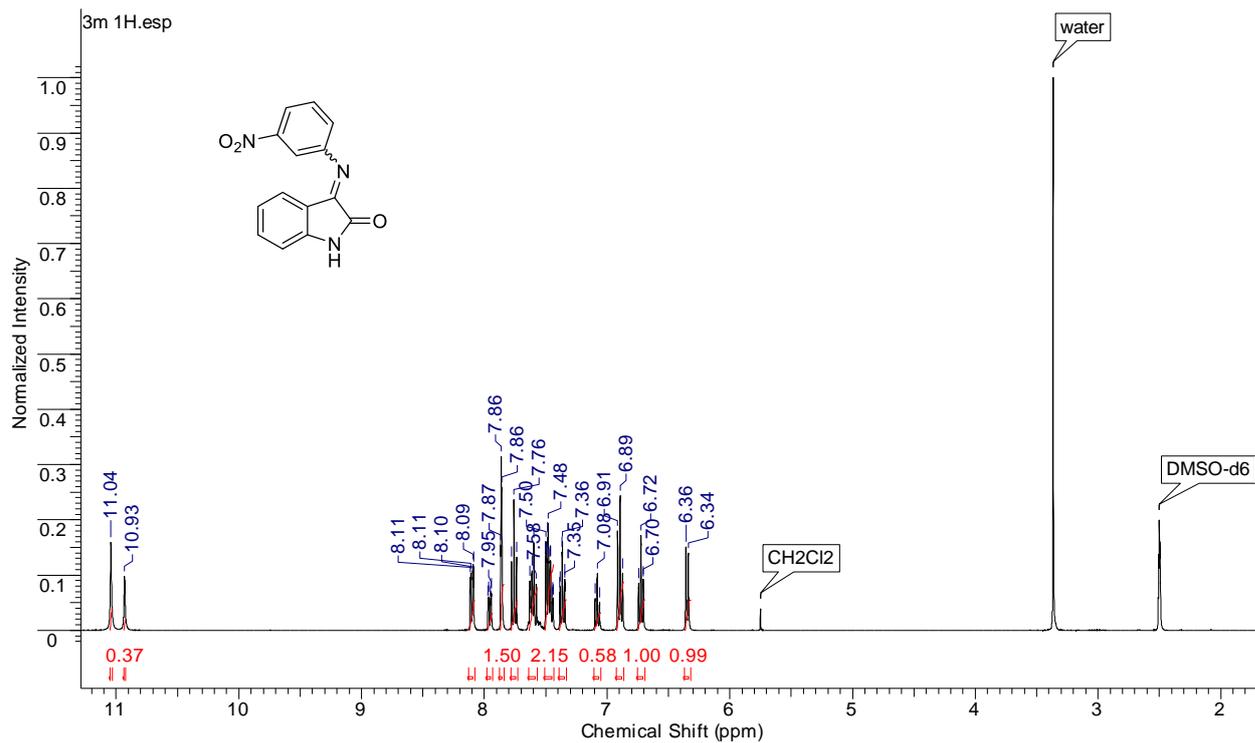


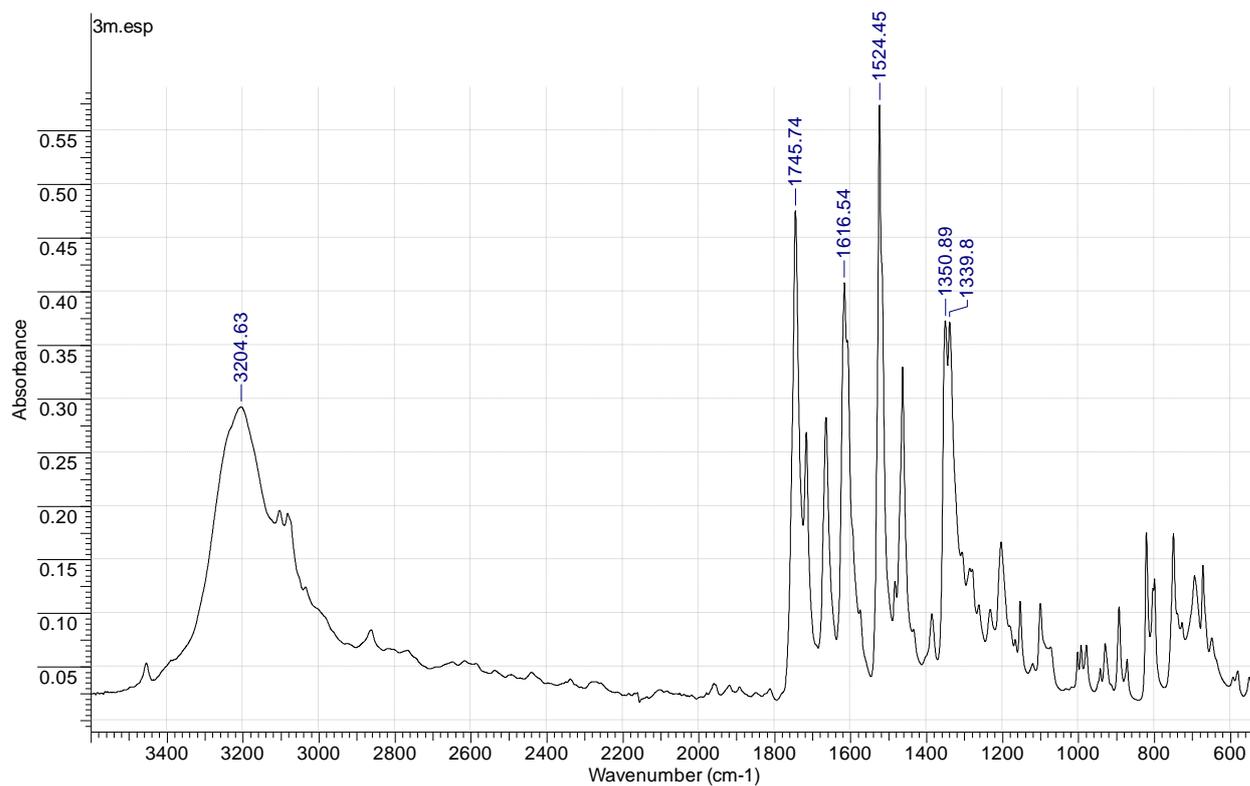
(3I) 3-((4-nitrophenyl)imino)indolin-2-one



Spectrum from 010122_POS.wiff (sample 159) - DY 45, +TOF MS (100 - 3000) from 0.856 to 0.883 mi...ectrum from 010122_POS.wiff (sample 159) - DY 45, +TOF MS (100 - 3000) from 0.535 to 0.628 min)



(3m) 3-((3-nitrophenyl)imino)indolin-2-one



Spectrum from 010122_POS.wiff (sample 144) - DY 51, +TOF MS (100 - 3000) from 0.804 to 0.832 mi...ectrum from 010122_POS.wiff (sample 144) - DY 51, +TOF MS (100 - 3000) from 0.535 to 0.628 min)

