# Electronic supporting information

for the paper

## Application of the intramolecular Diels–Alder vinylarene (IMDAV) reaction for the synthesis of benzo- and carbocyclofuroisoindolecarboxylic acids and its limitations

Elizaveta D. Yakovleva,[a] Evgeniya R. Shelukho,[a] Pavel P. Erokhin,[a] Valentina V. Ilyushenkova,[b] Aleksandra S. Guryeva,[a] Nikita A. Logvinenko,[a] Victor N. Khrustalev,[a,b] Mikhail S. Grigoriev,[c] Fedor I. Zubkov[a] and Vladimir P. Zaytsev[a]

[a] *RUDN University, 6 Miklukho-Maklaya St., 117198Moscow, Russian Federation. E-mail: zaytsev-vp@rudn.ru*

[b] *Zelinsky Institute of Organic Chemistry of RAS, 47 Leninsky Prospect, 119991Moscow, Russian Federation*

[c] *Frumkin Institute of Physical Chemistry and Electrochemistry, Russian Academy ofSciences, Leninsky pr. 31, bldg. 4, 119071 Moscow, Russian Federation*

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## 1. Synthetic procedures

### General Information.

All reagents and solvents were purchased from commercial suppliers (Acros Organics, Aldrich, Alfa Aesar, AstaTech and Reachim) and used without further purification. Solvents ($CH_2Cl_2$, DCE, PhH, PhMe, *o*-xylene, EtOAc, 1,4-dioxane, DMF) were dried and distilled before synthesis according to standard procedures. MaOH and EtOH (95%) were used without additional purification. Argon atmosphere was used during the synthesis of products **25**. Thin layer chromatography, when necessary, was carried out on aluminum backed silica plates Sorbfil. The plates were visualized under UV light (254 nm) or in $I_2$ vapor. Organic layers were dried over anhydrous $MgSO_4$ or $Na_2SO_4$ and concentrated *in vacuo*. In rare cases, when the precipitate of acids **10**, **12**, **19**, **20**, **23**, **28** was not formed after 12 h standing at room temperature, the solvent was removed *in vacuo* and the residue was solidified by addition of a mixture of hexane/diethyl ether.

Melting points for all crystalline compounds were measured on a capillary point apparatus Stuart SMP 10 equipped with a digital thermometer and were uncorrected.

IR spectra were obtained in KBr pellets using an Infralum FT-801 IR-Fourier spectrometer.

GC-MS mass spectra were taken on a Thermo Focus DSQ II GC-MS spectrometer (electron ionization, 70 eV, ion source temperature 200 °C, gas chromatographic inlet with a Varian Factor-Four VF-5ms column). LC-MS mass spectra were taken on Agilent 1100 series LC/MSD spectrometer with an API-ES/APCI ionization mode. The samples for the ESITOF-HRMS experiments were prepared in 1.8 mL glass vials with screw top caps fitted with Teflon-lined septa (Agilent Technologies). High-resolution mass spectra (HRMS) were recorded on a Bruker maXis q-TOF (tandem quadrupole/time-of-flight mass analyzer) mass spectrometer equipped with an electrospray ionization (ESI) source. The *m/z* scanning range was 50–3000. The measurements were carried out in positive ion mode (+) (grounded spray needle, –4500 V high-voltage capillary; 500 V HV End Plate) and in negative ion mode (–) (grounded spray needle, +4000 V high-voltage capillary; –500 V HV End Plate Offset). External calibration of the mass scale was carried out using a low-concentration calibration solution “Tuning mix” (Agilent Technologies). Samples were injected using a 500 μL Hamilton RN 1750 syringe (Switzerland). The flow rate during injection was controlled with a syringe pump (3 μL/min). Nitrogen was used as a nebulizer gas (1.0 bar) and dry gas (4.0 L/min, 200 °C).

NMR spectra were run in deuterated (>99.5%) solvents on Jeol JNM-ECA 600 (600.2 MHz for $^{1}$H, 150.9 MHz for $^{13}$C and 564.7 for $^{19}$F) or Bruker Avance NEO 700 (700.2 MHz for $^{1}$H, 176.1 MHz for $^{13}$C and 658.8 MHz for $^{19}$F) spectrometer for 2−8% solutions in $CDCl_3$ or DMSO-$d_6$ at 23−25 °C. Residual signals of deuterated solvents were used as internal standards ($CDCl_3$: 7.25 ppm for $^{1}$H nuclei, 77.2 ppm for $^{13}$C nuclei; DMSO-$d_6$: 2.50 ppm for $^{1}$H nuclei, 39.5 ppm for $^{13}$C nuclei). $^{19}$F NMR chemical shifts are reported relative to $CFCl_3$ (δ = 0.0 ppm), using $CF_3CO_2H$ as an internal standard. All chemical shifts in spectra are given in ppm.

Microanalyses were performed for C, H, N, and S with the elemental analysis system Eurovector EA 3000 (CHNS) and were within ±0.4 % of theoretical values.

Microwave-assisted reactions were carried out using a Monowave 400 reactor (Anton Paar GmbH), with temperature monitored by an IR sensor. Standard 10 mL G10 reaction vials sealed with silicone septa were used for microwave irradiation experiments.

**General Procedure for the Synthesis of Products 13, 14a-c and Characterization Data.** A mixture of the corresponding benzofuranocarbaldehyde (2.2 mmol) and (triphenylphosphoranylidine)acetaldehyde (1.00 g, 3.3 mmol) in dry chloroform was refluxed until the process was complete (TLC and GC/MS monitoring, ~ 24 h). The reaction mixture was cooled to 25 °C, concentrated, and then purified by column chromatography ($SiO_2$; 20 × 1.8 cm, eluent: EtOAc/heptane (1:100)).

**(*E*)-3-(Benzo[*b*]furan-2-yl)acrylaldehyde (13).** The physicochemical characteristics of the compound **13** have been published previously [1, 2]. Yield: 0.32 g (85%); yellow powder. M.p. 57–59 °C. $R_f$ 0.47 (EtOAc/ hexane, 1:10). $^{1}$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 9.72 (d, *J* = 7.5 Hz, 1H, CHO), 7.64 (d, *J* = 7.6 Hz, 1H, H Ar), 7.53 (d, *J* = 8.6 Hz, 1H, H Ar), 7.44-7.33 (m, 2H, H Ar, H-3), 7.31-7.29 (m, 1H, H Ar), 7.09 (s, 1H, H-3 Furyl), 6.83 (dd, *J* = 15.6, 8.1 Hz, 1H, H-2) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 192.9 (CHO), 156.0 (C Ar), 152.0 (C Ar), 138.0 (C-3), 128.4 (C Ar), 128.3 (C Ar), 127.3 (C Ar), 123.7 (C-2), 122.1 (C Ar), 113.1 (C Ar), 111.7 (C Ar) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1667 (C=O), 1615 (C=C). HRMS (ESI): calcd. for $C_{11}H_8O_2$, $[M+H]^+$, 173.0597; found, 173.0598, (Δ = 0.58 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 172 (100) [$M^+$], 171 (57), 144 (22), 143 (8), 142 (2), 131 (15), 118 (16), 116 (6), 115 (39), 90 (2), 88 (3), 64 (2), 63 (13), 62 (6), 58 (3), 57 (4), 51 (4), 39 (5), 38 (2).

**(*E*)-3-(Benzo[*b*]furan-3-yl)acrylaldehyde (14a)**. Yield: 0.19 g (49%); yellow powder. M.p. 119–123 °C. $R_f$0.58 (EtOAc/hexane, 1:10). $^{1}$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 9.70 (d, *J* = 7.9 Hz,

1H, CHO), 7.99 (s, 1H, H-2 Furyl), 7.85 (d, *J* = 7.6 Hz, 1H, H-3), 7.62-7.57 (m, 2H, H Ar, H-3), 7.43-7.38 (m, 2H, H Ar), 6.86 (dd, *J* = 16.0, 7.9 Hz, 1H, H-2) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 192.6 (CHO), 155.2 (C Ar), 147.6 (C-3), 141.1 (C Ar), 127.9 (C-2), 124.8 (C Ar), 123.3 (C Ar), 123.1 (C Ar), 119.9 (C Ar), 117.1 (C Ar), 111.1 (C Ar) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1669 (C=O), 1610 (C=C). HRMS (ESI): calcd. for $C_{11}H_8O_2$, $[M+H]^+$, 173.0597; found, 173.0597, (Δ = 0 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 172 (71) [$M^+$], 171 (33), 144 (27), 131 (6), 118 (31), 116 (37), 115 (100), 114 (19), 113 (11), 89 (19), 88 (8), 87 (6), 86 (7), 74 (6), 63 (21), 62 (12), 58 (15), 57 (9), 51 (6), 39 (11).

**(*E*)-3-(5-Fluoro-1-benzo[*b*]furan-3-yl)acrylaldehyde (14b).** Yield: 0.10 g (23%); yellow powder. M.p. 141–143 °C. $R_f$ 0.29 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 9.70 (d, *J* = 7.6 Hz, 1H, CHO), 8.02 (s, 1H, H-2 Furyl), 7.56 (d, *J* = 16.2 Hz, 1H, H-3), 7.51-7.48 (m, 2H, H Ar), 7.14 (dt, *J* = 8.9, 2.6 Hz, 1H, H Ar), 6.76 (dd, 16.2, 7.6 Hz, 1H, H-2) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 193.4 (CHO), 159.8 (d, *J* = 241.7 Hz, C-5 Ar), 152.4 (C Ar), 149.9 (C-3), 141.4 (C Ar), 128.9 (C-2), 125.1 (d, *J* = 9.5 Hz, C Ar), 118.3 (d, *J* = 2.7 Hz, C Ar), 113.6 (d, *J* = 27.0 Hz, C Ar), 112.9 (d, *J* = 9.5 Hz, C Ar), 106.9 (d, *J* = 25.7 Hz, C Ar) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C): *δ* (ppm) -118.2 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1665 (C=O), 1637 (C=C). HRMS (ESI): calcd. for $C_{11}H_7FO_2$, $[M+H]^+$, 191.0503; found, 191.0504, (Δ = 0.52 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 190 (83) [$M^+$], 162 (32), 149 (12), 136 (26), 134 (20), 133 (100), 131 (10), 108 (4), 107 (12), 106 (5), 87 (3), 86 (3), 83 (8), 81 (8), 67 (4), 66 (3), 63 (7), 62 (5), 57 (9).

**General Procedure for the Synthesis of Products 9, 15.** Corresponding benzofurylacrolein (0.7 mmol) was added at room temperature to a solution of the corresponding aniline (0.7 mmol) in $CH_2Cl_2$ (10 mL) in the presence of molecular sieves (MS 4Å). The mixture was stirred for 4 h at r.t, the molecular sieves were filtered off, washed with $CH_2Cl_2$ (2 × 5 mL), and the solution was concentrated under reduced pressure. $NaBH_4$ (29.3 mg, 0.77 mmol) was added to the residue diluted in 11 mL of a mixture of MeOH/THF (10/1 mL). The mixture was stirred vigorously at room temperature for 24 h (TLC or GC-MS control), then poured into $H_2O$ (20 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL), the combined organic layers were dried over anhydrous $MgSO_4$, concentrated, and purified by column chromatography ($SiO_2$, 20 × 1.8 cm, eluent: EtOAc/heptane (1:100)).

**(*E*)-*N*-(3-(Benzo[*b*]furan-2-yl)allyl)aniline (9a).** Yield: 0.09 g (51%); yellow oil. $R_f$ 0.48 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.56 (d, *J* = 7.6 Hz, 1H, H Ar), 7.49 (d, *J* = 8.3 Hz, 1H, H Ar), 7.33–7.24 (m, 4H, H Ar), 6.81 (t, *J* = 7.6 Hz, 1H, H Ar), 6.74 (d, *J* = 8.6 Hz, 2H, H Ar), 6.63-6.60 (m, 2H, H-3, H-2), 6.58 (s, 1H, H-3 Furyl), 4.04 (d, *J* = 3.1 Hz, 2H, H-1), 3.97 (br.s, 1H, NH) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.8 (C Ar), 154.4 (C Ar), 147.9 (C Ar), 129.5 (C Ar), 129.3 (2C, C Ar), 129.0 (C Ar), 124.5 (C Ar), 122.8 (C-2), 120.9 (C Ar), 119.6 (C Ar), 117.8 (C Ar), 113.0 (2C, C Ar), 110.9 (C-3), 104.3 (C Ar), 45.8 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3410 (NH), 1600 (C=C). HRMS (ESI): calcd. for $C_{17}H_{15}NO$, $[M-H]^+$, 248.1070; found, 248.1073, (Δ = 1.21 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 249 (57) $[M^+]$, 246 (4), 158 (8), 157 (100), 143 (13), 131 (8), 130 (7), 129 (31), 128 (35), 127 (22), 124 (3), 115 (13), 104 (4), 102 (4), 77 (20), 65 (4), 63 (4), 51 (7), 39 (5).

***(E)*-*N*-(3-(Benzo[*b*]furan-2-yl)allyl)-2-fluoroaniline (9b).** Yield: 0.09 g (47%); yellow oil. $R_f$ 0.67 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.51 (d, *J* = 7.6 Hz, 1H, H Ar), 7.44 (d, *J* = 8.3 Hz, 1H, H Ar), 7.26 (t, *J* = 7.6 Hz, 1H, H Ar), 7.20 (t, *J* = 7.6 Hz, 1H, H Ar), 7.03-7.00 (m, 2H, H Ar), 6.75 (t, *J* = 8.3 Hz, 1H, H Ar), 6.68-6.65 (m, 1H, H Ar), 6.58-6.57 (m, 2H, H-3, H-2), 6.55 (s, 1H, H-3 Furyl), 4.22 (br.s, 1H, NH), 4.05 (br.s, 2H, H-1) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 154.2 (C Ar), 151.6 (d, *J* = 237.7 Hz, 1C, C Ar), 136.3 (d, *J* = 10.8 Hz, 1C, C Ar), 128.9 (C Ar), 124.6 (d, *J* = 4.0 Hz, 1C, C Ar), 124.5 (C Ar), 122.8 (C-2), 120.9 (C Ar), 119.7 (C Ar), 117.0 (d, *J* = 6.8 Hz, 1C, C Ar), 114.5 (d, *J* = 18.9 Hz, 1C, C Ar), 112.4 (d, *J* = 2.7 Hz, 1C, C Ar), 110.9 (C-3), 104.4 (2C, C Ar), 45.3 ($CH_2N$) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C) δ -136.4 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3405 (NH), 1509 (C=C). HRMS (ESI): calcd. for $C_{17}H_{14}NOF$, $[M-H]^+$, 266.0976; found, 266.0979, (Δ = 1.38 ppm). MS (ESI): *m/z* = 268 $[M+H]^+$.

***(E)*-*N*-(3-(Benzo[*b*]furan-2-yl)-3-methylallylaniline (9c).** Yield: 0.15 g (74%); yellow oil. $R_f$ 0.77 (EtOAc/hexane, 1:10). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.1 Hz, 1H, H Ar), 7.43 (d, *J* = 7.6 Hz, 1H, H Ar), 7.28-7.26 (m, 1H, H Ar), 7.21 (t, *J* = 7.6 Hz, 1H, H Ar), 7.12 (t, *J* = 7.6 Hz, 1H, H Ar), 6.60-6.50 (m, 6H, H Ar, H-3 Furyl, H-2, H-3), 4.00 (d, *J* = 3.0 Hz, 2H, H-1), 3.88 (br.s, 1H, NH), 2.31 (s, 3H, $CH_3$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 154.8 (C Ar), 154.5 (C Ar), 148.0 (C Ar), 139.2 (C Ar), 129.7 (C Ar), 129.3 (C Ar), 129.0 (C Ar), 124.5 (C Ar), 122.9 (C-2), 120.9 (C Ar), 119.6 (C Ar), 118.8 (C Ar), 113.9 (C Ar), 111.0 (C-3), 110.2 (C Ar), 104.3 (C Ar), 45.9 ($CH_2N$), 21.7 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3411 (NH), 1604 (C=C). HRMS (ESI): calcd. for $C_{18}H_{17}NO$, $[M-H]^+$, 262.1226; found, 262.1228, (Δ = 0.74 ppm). GC-MS

(EI, 70 eV): *m/z*(%) = 263 (85) [$M^+$], 262 (100), 260 (14), 246 (10), 170 (37), 158 (31), 157 (67), 156 (92), 144 (11), 132 (12), 131 (28), 130 (16), 129 (77), 128 (77), 118 (9), 115 (19), 91 (27), 77 (11), 65 (14).

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-3-methoxyaniline (9d).** Yield: 0.18 g (91%); yellow oil. $R_f$ 0.77 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.51 (d, *J* = 7.6 Hz, 1H, H Ar), 7.43 (d, *J* = 8.1 Hz, 1H, H Ar), 7.26 (t, *J* = 8.1 Hz, 1H, H Ar), 7.19 (t, *J* = 7.6 Hz, 1H, H Ar), 7.11 (t, *J* = 8.1 Hz, 1H, H Ar), 6.57 (br.s, 2H, H-2, H-3), 6.54 (s, 1H, H-3 Furyl), 6.33-6.31 (m, 2H, H Ar), 6.25 (br.s, 1H, H Ar), 4.00 (d, *J* = 2.4 Hz, 2H, H-1), 3.78 (s, 3H, $CH_3$) ppm (*the signal of the NH-group was not detected*). $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 160.9 (C Ar), 154.7 (C Ar), 154.3 (C Ar), 130.1 (C Ar), 129.2 (C Ar), 128.9 (C Ar), 124.4 (C Ar), 122.8 (C-2), 120.9 (C Ar), 119.8 (2C, C Ar), 110.9 (C-3), 106.3 (C Ar), 104.3 (C Ar), 103.0 (C Ar), 99.2 (C Ar), 55.1 ($OCH_3$), 45.9 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3408 (NH), 1575 (C=C). GC-MS (EI, 70 eV): *m/z*(%) = 279 (29) [$M^+$], 278 (23), 277 (28), 276 (99), 262 (9), 261 (9), 233 (7), 158 (8), 157 (100), 155 (6), 131 (16), 129 (24), 128 (55), 127 (17), 115 (19), 102 (6), 92 (8), 77 (15), 64 (7), 63 (10). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.25; H, 6.37; N, 5.21.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-3-fluoroaniline (9e).** Yield: 0.13 g (71%); yellow oil. $R_f$ 0.60 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.44 (d, *J* = 8.3 Hz, 1H, H Ar), 7.27 (t, *J* = 8.3 Hz, 1H, H Ar), 7.20 (t, *J* = 7.4 Hz, 1H, H Ar), 7.14-7.11 (m, 1H, H Ar), 6.58-6.55 (m, 3H, H-3 Furyl, H-2, H-3), 6.44-6.42 (m, 2H, H Ar), 6.38-6.35 (m, 1H, H Ar), 4.07 (br.s, 1H, NH), 3.99 (br.d, *J* = 3.6 Hz, 2H, H-1) ppm (*the signal of the NH-group was not detected*). $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 164.2 (d, *J* = 243.1 Hz, 1C, C Ar), 154.8 (C Ar), 154.2 (C Ar), 149.6 (d, *J* = 10.8 Hz, 1C, C Ar), 130.4 (d, *J* = 9.5 Hz, 1C, C Ar), 128.9 (C Ar), 128.7 (C Ar), 124.5 (C Ar), 122.8 (C-2), 120.9 (C Ar), 119.9 (C Ar), 110.9 (C-3), 108.8 (C Ar), 104.5 (C Ar), 104.1 (d, *J* = 21.6 Hz, 1C, C Ar), 99.7 (d, *J* = 24.3 Hz, 1C, C Ar), 45.6 ($CH_2N$) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C) δ -112.7 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3488 (NH), 1501 (C=C). GC-MS (EI, 70 eV): *m/z*(%) = 267 (32) [$M^+$], 267 (55), 174 (12), 161 (12), 158 (10), 157 (100), 131 (11), 130 (6), 129 (41), 128 (48), 127 (8), 127 (21), 115 (11), 102 (5), 95 (11), 83 (6), 77 (6), 75 (7), 51 (5). Anal. Calcd for $C_{17}H_{14}FNO$: C, 76.39; H, 5.28; N, 5.24. Found: C, 76.11; H, 5.42; N, 5.37.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)-4-methylallylaniline (9f).** Yield: 0.13 g (74%); yellow oil. $R_f$ 0.7 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.44 (d, *J* = 8.3 Hz, 1H, H Ar), 7.26 (t, *J* = 7.6 Hz, 1H, H Ar), 7.20 (t, *J* = 7.6 Hz, 1H, H Ar), 7.04

(d, *J* = 8.3 Hz, 2H, H Ar), 6.62 (d, *J* = 8.3 Hz, 2H, H Ar), 6.59-6.56 (m, 2H, H-2, H-3), 6.54 (s, 1H, H-3 Furyl), 3.99 (d, *J* = 3.6 Hz, 2H, H-1), 2.27 (s, 3H, $CH_3$) ppm. $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 154.4 (C Ar). 145.6 (C Ar), 129.8 (2C, C Ar), 129.7 (C Ar), 129.0 (C Ar), 127.0 (C Ar), 124.4 (C Ar), 122.8 (C-2), 120.8 (C Ar), 119.5 (C Ar), 113.2 (2C, C Ar), 110.9 (C-3), 104.2 (C Ar), 46.1 ($CH_2N$), 20.4 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3414 (NH), 1499 (C=C). HRMS (ESI): calcd. for $C_{18}H_{17}NO$, $[M-H]^+$, 262.1226; found, 262.1230, (Δ = 1.2 ppm). MS (ESI): *m/z* = 264 $[M+H]^+$.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-ethylaniline (9g).** Yield: 0.14 g (72%); yellow oil. $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.44 (d, *J* = 8.1 Hz, 1H, H Ar), 7.26 (t, *J* = 7.4 Hz, 1H, H Ar), 7.20 (t, *J* = 7.4 Hz, 1H, H Ar), 7.07 (d, *J* = 8.1 Hz, 2H, H Ar), 6.65 (d, *J* = 8.1 Hz, 2H, H Ar), 6.60-6.57 (m, 2H, H-2, H-3), 6.54 (s, 1H, H-3 Furyl), 3.99 (d, *J* = 3.3 Hz, 2H, H-1), 2.58 (q, *J* = 7.6 Hz, 2H, $CH_2$), 1.22 (t, *J* = 7.6 Hz, 3H, $CH_3$) ppm (*the signal of the NH-group was not detected*). $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 154.4 (C Ar), 145.8 (C Ar), 133.6 (C Ar), 129.8 (C Ar), 129.0 (C Ar), 128.6 (2C, C Ar), 124.4 (C Ar), 122.8 (C-2), 120.8 (C Ar), 119.5 (C Ar), 113.2 (2C, C Ar), 110.9 (C-3), 104.2 (C Ar), 46.1 ($CH_2N$), 27.9 ($CH_2$), 16.0 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3398 (NH), 1507 (C=C). MS (ESI): *m/z* = 278 $[M+H]^+$. Anal. Calcd for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.02; H, 7.16; N, 4.78.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)-4-methoxyaniline (9h).** Yield: 0.12 g (62%); yellow oil. $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.54 (d, *J* = 7.6, 1H, H Ar), 7.45 (dd, *J* = 8.1, 3.3 Hz, 1H, H Ar), 7.29-7.27 (m, 1H, H Ar), 7.23-7.21 (m, 1H, H Ar), 6.84 (d, *J* = 9.1, 2H, H Ar), 6.67 (d, *J* = 9.1, 2H, H Ar), 6.62-6.57 (m, 2H, H-2, H-3), 6.58 (s, 1H, H-3 Furyl), 3.98 (d, *J* = 3.6 Hz, 2H, H-1), 3.79 (s, 3H, $CH_3$) ppm (*the NH-group signal was not detected*). $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 154.4 (C Ar), 152.4 (C Ar), 142.0 (C Ar), 129.8 (C Ar), 129.0 (C Ar), 124.4 (C Ar), 122.8 (C-2), 120.8 (C Ar), 119.6 (C Ar), 115.0 (2C, C Ar), 114.4 (2C, C Ar), 110.9 (C-3), 104.2 (C Ar), 55.8 ($OCH_3$), 46.7 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3388 (NH), 1501 (C=C). GC-MS (EI, 70 eV): *m/z* (%) = 279 (60) $[M^+]$, 277 (7), 276 (19), 261 (3), 158 (9), 157 (100), 134 (3), 131 (5), 130 (4), 129 (24), 128 (61), 122 (15), 115 (6), 102 (3), 95 (4), 77 (5), 65 (3), 64 (3), 63 (4). Anal. Calcd for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.15; H, 6.39; N, 5.32.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-(trifluoromethyl)aniline (9i).** Yield: 0.09 g (43%); yellow oil. $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.53 (d, *J* = 7.6 Hz, 1H, H Ar), 7.45-7.44 (m,

3H, H Ar), 7.29-7.27 (m, 1H, H Ar), 7.21 (t, *J* = 7.6 Hz, 1H, H Ar), 6.70 (d, *J* = 8.6 Hz, 2H, H Ar), 6.58-6.54 (m, 3H, H-3 Furyl, H-2, H-3), 4.38 (s, 1H, NH), 4.06 (d, *J* = 3.6 Hz, 2H, H-1) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.8 (C Ar), 154.0 (C Ar), 150.1 (C Ar), 128.8 (C Ar), 128.1 (C Ar), 126.7 (q, *J* = 2.7 Hz, 2C, C Ar), 124.9 (q, *J* = 270.1 Hz, 1C, C Ar), 124.6 (C Ar), 122.9 (C-2), 120.9 (C Ar), 120.1 (C Ar), 114.2 (C Ar), 112.2 (2C, C Ar), 110.9 (C-3), 104.7 (C Ar), 45.3 ($CH_2N$) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C) δ - 61.1 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3474 (NH), 1503 (C=C). GC-MS (EI, 70 eV): *m/z* (%) = 317 (39) [$M^+$], 316 (16), 224 (5), 223 (5), 211 (5), 210 (5), 172 (4), 158 (8), 157 (100), 145 (9), 140 (3), 131 (14), 129 (22), 128 (65), 115 (12), 102 (4), 89 (3), 77 (5), 63 (4). Anal. Calcd for $C_{18}H_{14}F_3NO$: C, 68.13; H, 4.45; N, 4.41. Found: C, 67.89; H, 4.17; N, 4.58.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-fluoroaniline (9j).** Yield: 0.14 g (78%); white oil. $R_f$ 0.47 (EtOAc/hexane, 1:10). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.45 (d, *J* = 8.6 Hz, 1H, H Ar), 7.28 (t, *J* = 7.6 Hz, 1H, H Ar), 7.21 (t, *J* = 7.6 Hz, 1H, H Ar), 6.93 (t, *J* = 8.8 Hz, 2H, H Ar), 6.62 (dd, *J* = 8.8, 4.5 Hz, 2H, H Ar), 6.57-6.54 (m, 3H, H-Furyl, H-2, H-3), 3.97 (d, *J* = 2.5 Hz, 2H, H-1) ppm (*the signal of the NH-group was not detected*). $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 156.1 (d, *J* = 234.1 Hz, 1C, C Ar), 154.8 (C Ar), 154.3 (C Ar), 144.2 (d, *J* = 2.9 Hz, 1C, C Ar), 129.3 (C Ar), 129.0 (C Ar), 124.6 (C Ar), 122.9 (C-2), 121.0 (C Ar), 119.8 (C Ar), 115.8 (d, *J* = 23.1 Hz, 2C, C Ar), 113.9 (d, *J* = 7.2 Hz, 2C, C Ar), 111.0 (C-3), 104.4 (C Ar), 46.4 ($CH_2N$) ppm. $^{19}$F NMR (564.7 MHz, $CDCl_3$, 25 °C) δ -127.6 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3350 (NH), 1501 (C=C). HRMS (ESI): calcd. for $C_{17}H_{14}NOF$, $[M-H]^+$, 266.0977; found, 266.0976, (Δ = 0.35 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 267 (100) [$M^+$], 174 (28), 161 (25), 158 (30), 157 (55), 157 (39), 156 (49), 133 (16), 131 (26), 130 (16), 129 (77), 128 (31), 128 (51), 127 (71), 122 (11), 115 (19), 95 (28), 83 (12), 77 (11).

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-chloroaniline (9k).** Yield: 0.07 g (38%); yellow powder. M.p. 76–78 °C. $R_f$ 0.62 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.44 (d, *J* = 8.1 Hz, 1H, H Ar), 7.27 (t, *J* = 7.6 Hz, 1H, H Ar), 7.20 (t, *J* = 7.6 Hz, 1H, H Ar), 7.16 (d, *J* = 8.6 Hz, 2H, H Ar), 6.59 (d, *J* = 8.6 Hz, 2H, H Ar), 6.55-6.54 (m, 3H, H-3 Furyl, H-2, H-3), 3.97 (d, *J* = 2.2 Hz, 2H), 3.95 (br.s, 1H, NH) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.8 (C Ar), 154.2 (C Ar), 146.4 (C Ar), 129.2 (2C, C Ar), 128.9 (C Ar), 128.8 (C Ar), 124.6 (C Ar), 122.9 (C-2), 122.3 (C Ar), 120.9 (C Ar), 119.8 (C Ar), 114.1 (2C, C Ar), 110.9 (C-3), 104.5 (C Ar), 45.8 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3358 (NH), 1498 (C=C).

Anal. Calcd for $C_{17}H_{14}ClNO$: C, 71.96; H, 4.97; N, 4.94. Found: C, 72.34; H, 4.73; N, 5.12. MS (ESI): *m/z* = 284 $[M+H, Cl^{35}]^+$, 286 $[M+H, Cl^{37}]^+$.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-bromoaniline (9l).** Yield: 0.16 g (70%); yellow oil. $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.9 Hz, 1H, H Ar), 7.43 (d, *J* = 8.1 Hz, 1H, H Ar), 7.28-7.25 (m, 3H, H Ar), 7.20 (t, *J* = 7.6 Hz, 1H, H Ar), 6.55-6.43 (m, 5H, H Ar, H-3 Furyl, H-2, H-3), 3.96 (br.s, 3H, H-1, NH) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.8 (C Ar), 154.1 (C Ar), 146.8 (C Ar), 132.0 (2C, C Ar), 128.9 (C Ar), 128.7 (C Ar), 124.6 (C Ar), 122.9 (C-2), 120.9 (C Ar), 119.8 (C Ar), 114.6 (2C, C Ar), 110.9 (C-3), 109.3 (C Ar), 104.5 (C Ar), 45.7 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3489 (NH), 1487 (C=C). MS (ESI): *m/z* = 328 $[M+H, Br^{79}]^+$, 330 $[M+H, Br^{81}]^+$. Anal. Calcd for $C_{17}H_{14}BrNO$: C, 62.21; H, 4.30; N, 4.27. Found: C, 62.03; H, 4.51; N, 4.39.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-3,5-dimethylaniline (9m).** Yield: 0.14 g (74%); yellow oil. $R_f$ 0.80 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.45 (*J* = 8.3 Hz, 1H, H Ar), 7.28 (t, *J* = 7.6 Hz, 1H, H Ar), 7.21 (t, *J* = 7.6 Hz, 1H, H Ar), 6.60-6.57 (m, 2H, H-2, H-3), 6.55 (s, 1H, H-3 Furyl), 6.45 (s, 1H, H Ar), 6.36 (s, 2H, H Ar), 4.00 (d, *J* = 3.6 Hz, 2H, H-1), 2.28 (s, 6H, 2 $CH_3$) ppm (*the signal of the NH-group was not detected*). $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 154.4 (C Ar), 147.6 (C Ar), 139.1 (2C, C Ar), 129.4 (C Ar), 129.0 (C Ar), 124.4 (C Ar), 122.8 (C-2), 120.9 (C Ar), 120.1 (C Ar), 119.6 (C Ar), 111.2 (2C, C Ar), 110.9 (C-3), 104.3 (C Ar), 46.0 ($CH_2N$), 21.5 (2C, 2 $CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3452 (NH), 1479 (C=C). HRMS (ESI): calcd. for $C_{19}H_{19}NO$, $[M-H]^+$, 276.1383; found, 276.1385, (Δ = 0.69 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 277 (100) $[M^+]$, 274 (10), 260 (30), 184 (26), 171 (33), 158 (28), 157 (70), 156 (74), 146 (12), 144 (9), 132 (7), 131 (19), 130 (12), 129 (62), 128 (66), 127 (41), 115 (14), 91 (9), 77 (13).

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-3,5-dimethoxylaniline (9n).** Yield: 0.16 g (72%); colorless oil. $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.9 Hz, 1H, H Ar), 7.43 (d, *J* = 8.3 Hz, 1H, H Ar), 7.26 (t, *J* = 8.1 Hz, 1H, H Ar), 7.20 (t, *J* = 7.4 Hz, 1H, H Ar), 6.59-6.54 (m, 3H, H-3 Furyl, H-2, H-3), 5.93 (t, *J* = 2.0 Hz, 1H, H Ar), 5.87 (d, *J* = 2.0 Hz, 2H, H Ar), 3.98 (br.s, 3H, H-1, NH), 3.77 (s, 6H, 2 $OCH_3$) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 161.8 (2C, C Ar), 154.7 (C Ar), 154.3 (C Ar), 149.8 (C Ar), 129.3 (C Ar), 128.9 (C Ar), 124.4 (C Ar), 122.8 (C-2), 120.9 (C Ar), 119.7 (C Ar), 110.9 (C-3), 104.3 (C Ar), 91.9 (2C, C Ar), 90.0 (C Ar), 55.2 (2C, 2 $OCH_3$), 45.7 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3441 (NH), 1501 (C=C). MS (ESI): *m/z* = 310

$[M+H]^+$. Anal. Calcd for $C_{19}H_{19}NO_3$: C, 73.77; H, 6.19; N, 4.53. Found: C, 73.69; H, 5.88; N, 4.61.

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-methoxy-3-(trifluoromethyl)aniline (9o).** Yield: 0.16 g (66%); black oil. $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.52 (d, *J* = 7.6 Hz, 1H, H Ar), 7.44 (d, *J* = 8.1 Hz, 1H, H Ar), 7.27 (t, *J* = 7.6 Hz, 1H, H Ar), 7.20 (t, *J* = 7.6 Hz, 1H, H Ar), 6.91-6.90 (m, 2H, H Ar), 6.79 (dd, *J* = 8.8, 2.4 Hz, 1H, H Ar), 6.58-6.53 (s, 3H, H-3 Furyl, H-2, H-3), 3.97 (d, *J* = 2.6 Hz, 2H, H-1), 3.84 (s, 3H, $OCH_3$), 3.81 (br.s, 1H, NH) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.8 (C Ar), 154.2 (C Ar), 149.8 (C Ar), 141.5 (C Ar), 128.9 (2C, C Ar), 124.6 (C Ar), 123.7 (q, *J* = 272.8 Hz, 1C, C Ar), 122.9 (C-2), 120.9 (C Ar), 119.9 (C Ar), 119.7 (q, *J* = 29.7 Hz, 1C, C Ar), 116.9 (C Ar), 114.3 (C Ar), 112.0 (q, *J* = 5.4 Hz, 1C, C Ar), 110.9 (C-3), 104.5 (C Ar), 56.8 ($OCH_3$), 46.3 ($CH_2N$) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C) δ -62.17 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3451 (NH), 1499 (C=C). MS (ESI): *m/z* = 348 $[M+H]^+$. Anal. Calcd for $C_{19}H_{16}F_3NO_2$: C, 65.70; H, 4.64; N, 4.03. Found: C, 65.48; H, 4.92; N, 4.15.

***(E)-N*-(3-(Benzo[*b*]furan-3-yl)allyl)aniline (15a).** Yield: 0.09 g (55%); colorless oil. $R_f$ 0.52 (EtOAc/hexane, 1:10). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.82 (d, *J* = 7.6 Hz, 1H, H Ar), 7.65 (s, 1H, H-2 Furyl), 7.50 (d, *J* = 8.1 Hz, 1H, H Ar), 7.34 (dt, *J* = 7.6, 1.5 Hz, 1H, H Ar), 7.30 (dt, *J* = 8.1, 1.5 Hz, 1H, H Ar), 7.34 (dd, *J* = 8.6, 7.6 Hz, 2H, H Ar), 6.77-6.71 (m, 4H, H Ar, H-3), 6.46 (dt, *J* = 16.1, 5.5 Hz, 1H, H-2), 3.90 (br.s, 1H, NH) 4.00 (dd. *J* = 5.5, 1.5 Hz, 2H, H-1) ppm.$^{13}$C NMR (150.1 MHz, $CDCl_3$, 25 °C) δ 155.9 (C Ar), 148.1 (C Ar), 143.3 (C Ar), 129.4 (2C, C Ar), 128.0 (C Ar), 125.9 (C Ar), 124.7 (C-2), 123.1 (C Ar), 121.2 (C-3), 120.9 (C Ar), 118.8 (C Ar), 117.8 (C Ar), 113.2 (2C, C Ar), 111.8 (C Ar), 46.7 ($CH_2N$) ppm. IR (KBr, $cm^{-1}$):$\nu_{max}$= 3410 (NH), 1501 (C=C). HRMS (ESI): calcd. for $C_{17}H_{15}NO$, $[M-H]^+$, 248.1070; found, 248.1076, (Δ = 2.31 ppm). MS (ESI): *m/z* = 250 $[M+H]^+$.

***(E)-N*-(3-(Benzo[*b*]furan-3-yl)allyl)-4-(trifluoromethyl)aniline (15b).** Yield: 0.12 g (54%); yellow oil. $R_f$0.55 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.81 (d, *J* = 7.9 Hz, 1H, H Ar), 7.67 (s, 1H, H-2 Furyl), 7.52 (d, *J* = 8.1 Hz, 1H, H Ar), 7.46 (d, *J* = 8.3 Hz, 2H, H Ar), 7.37 (t, *J* = 8.3 Hz, 1H, H Ar), 7.32 (t, *J* = 7.6 Hz, 1H, H Ar), 6.73-6.70 (m, 3H, H Ar, H-3), 6.43 (dt, *J* = 16.0, 5.5 Hz, 1H, H-2), 4.03 (dd, *J* = 5.5, 1.3 Hz, 2H, H-1) ppm (*the signal of the NH-group was not detected*). $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 155.8 (C Ar), 150.4 (C Ar), 143.4 (C Ar), 126.7 (q, *J* = 4.1 Hz, 2C, C Ar), 125.7 (C Ar), 125.0 (q, *J* = 270.1 Hz, 1C, C Ar), 124.8 (C-2), 124.2 (C Ar), 123.1 (C Ar), 121.6 (C-3), 120.7 (C Ar), 119.1 (q, *J* = 32.4 Hz,

1C, (C Ar)), 118.6 (C Ar), 112.1 (2C, C Ar), 111.8 (C Ar), 46.0 ($CH_2N$) ppm. $^{19}F$ NMR (658.8 MHz, $CDCl_3$, 25 °C) δ -61.0 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3418 (NH), 1487 (C=C). HRMS (ESI): calcd. for $C_{18}H_{14}F_3NO$, $[M-H]^+$, 316.0944; found, 316.0951, (Δ = 2.14 ppm). GC-MS (EI, 70 eV): *m/z* (%) = 317 (83) [$M^+$], 316 (100), 298 (6), 174 (7), 172 (12), 158 (29), 155 (10), 145 (26), 131 (18), 130 (18), 129 (32), 129 (39), 128 (71), 127 (73), 115 (15), 114 (7), 103 (6), 102 (9), 77 (10), 63 (7).

***(E)-N*-(3-(Benzo[*b*]furan-3-yl)allyl)-4-fluoroaniline (15c).** Yield: 0.10 g (56%); colorless oil. $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.80 (d, *J* = 7.6 Hz, 1H, H Ar), 7.65 (s, 1H, H-2 Furyl), 7.51 (d, *J* = 8.1 Hz, 1H, H Ar), 7.35 (t, *J* = 8.3 Hz, 1H, H Ar), 7.30 (t, *J* = 7.6 Hz, 1H, H Ar), 6.93 (t, *J* = 8.6 Hz, 2H, H Ar), 6.71 (d, *J* = 16.0 Hz, 1H, H-3), 6.64 (dd, *J* = 8.8, 4.3 Hz, 2H, H Ar), 6.44 (dt, *J* = 16.0, 5.7 Hz, 1H, H-2), 3.95 (dd, *J* = 5.7, 1.4 Hz, 2H, H-1), 3.76 (br.s, 1H, NH) ppm. $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 155.9 (d, *J* = 235.0 Hz, 1C, C Ar), 155.8 (C Ar), 144.3 (C Ar), 143.2 (C Ar), 127.6 (C Ar), 125.7 (C Ar), 124.7 (C-2), 123.0 (C Ar), 121.2 (C-3), 120.7 (C Ar), 118.7 (C Ar), 115.7 (d, *J* = 23.0 Hz, 2C, C Ar), 113.8 (d, *J* = 8.1 Hz, 2C, C Ar), 111.7 (C Ar), 47.2 ($CH_2N$)ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3290 (NH), 1485 (C=C). Anal. Calcd for $C_{17}H_{14}FNO$: C, 76.39; H, 5.28; N, 5.24. Found: C, 76.13; H, 5.44; N, 4.98. MS (ESI): *m/z* = 268 $[M+H]^+$.

***(E)-N*-(3-(Benzo[*b*]furan-3-yl)allyl)-4-chloroaniline (15d).** Yield: 0.11 g (58%); yellow oil. $R_f$ 0.62 (EtOAc/hexane, 1:10). $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.79 (d, *J* = 7.6 Hz, 1H, H Ar), 7.64 (s, 1H, H-2 Furyl), 7.50 (d, *J* = 8.1 Hz, 1H, H Ar), 7.34 (t, *J* = 7.6 Hz, 1H, H Ar), 7.30 (t, *J* = 7.6 Hz, 1H, H Ar), 7.15 (d, *J* = 8.8 Hz, 2H, H Ar), 6.70 (d, *J* = 16.0 Hz, 1H, H-3), 6.62 (d, *J* = 8.6 Hz, 2H, H Ar), 6.42 (dt, *J* = 16.0, 5.7 Hz, 1H, H-2), 3.96 (d, *J* = 5.7 Hz, 2H, H-1), 3.95 (br.s, 1H, NH) ppm. $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 155.8 (C Ar), 146.5 (C Ar), 143.3 (C Ar), 129.1 (2C, C Ar), 127.3 (C Ar), 125.7 (C Ar), 124.7 (C-2), 123.0 (C Ar), 122.2 (C Ar), 121.4 (C-3), 120.7 (C Ar), 118.6 (C Ar), 114.1 (2C, C Ar), 111.7 (C Ar), 46.6 ($CH_2N$)ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3286 (NH), 1493 (C=C). HRMS (ESI): calcd. for $C_{17}H_{14}ClNO$, $[M-H]^+$, 282.0680; found, 282.0685, (Δ = 1.79 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 285 (10) [$M^+$], 284 (14), 283 (38), 282 (38), 158 (10), 157 (100), 155 (4), 141 (3), 131 (5), 130 (7), 129 (54), 128 (48), 127 (36), 115 (10), 111 (6), 102 (4), 99 (4), 77 (7), 75 (5), 63 (5).

***(E)-N*-(3-(5-Fluorobenzo[*b*]furan-3-yl)allyl)aniline (15e).** Yield: 0.08 g (43%); yellow oil. $R_f$ 0.7 (EtOAc/hexane, 1:10). $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.66 (s, 1H, H-2 Furyl), 7.45

(dd, *J* = 8.8, 2.4 Hz, 1H, H Ar), 7.42 (dd, *J* = 9.1, 4.1 Hz, 1H, H Ar), 7.23 (t, *J* = 8.6 Hz, 2H, H Ar), 7.06 (dt, *J* = 9.1, 2.6 Hz, 1H, H Ar), 6.76 (t, *J* = 7.3 Hz, 1H, H Ar), 6.71 (d, *J* = 8.3 Hz, 2H, H Ar), 6.67 (d, *J* = 16.0 Hz, 1H, H-3), 6.37 (dt, *J* = 16.0, 5.5 Hz, 1H, H-2), 3.99 (d, *J* = 5.5 Hz, 2H, H-1), 3.90 (br.s, 1H, NH) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 159.3 (d, *J* = 237.7 Hz, 1C, C Ar), 152.0 (C Ar), 148.0 (C Ar), 144.8 (C Ar), 129.3 (2C, C Ar), 128.2 (C-2), 126.6 (d, *J* = 10.8 Hz, 1C, C Ar), 120.5 (C-3), 119.0 (d, *J* = 2.7 Hz, 1C, C Ar), 117.8 (C Ar), 113.0 (2C, C Ar), 112.4 (d, *J* = 18.9 Hz, C Ar), 112.3 (C Ar), 106.5 (d, *J* = 24.3 Hz, C Ar), 46.5 ($CH_2N$) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C) δ -120.4 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3414 (NH), 1484 (C=C). HRMS (ESI): calcd. for $C_{17}H_{14}NOF$, $[M-H]^+$, 266.0976; found, 266.0979, (Δ = 1.23 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 267 (53) $[M^+]$, 266 (100), 175 (93), 147 (59), 146 (78), 133 (16), 127 (44), 77 (14).

***(E)-N*-(3-(5-Fluorobenzo[*b*]furan-3-yl)allyl)-4-methoxyaniline (15g).** Yield: 0.15 g (74%); yellow oil. $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.66 (s, 1H, H-2 Furyl), 7.45 (dd, *J* = 8.8, 2.4 Hz, 1H, H Ar), 7.42 (dd, *J* = 8.8, 4.1 Hz, 1H, H Ar), 7.05 (dt, *J* = 8.8, 2.4 Hz, 1H, H Ar), 6.82 (d, *J* = 9.1 Hz, 2H, H Ar), 6.68-6.65 (m, 3H, H Ar, H-2), 6.37 (dt, *J* = 16.2, 5.7 Hz, 1H, H-3), 3.94 (d, *J* = 5.7 Hz, 2H, H-1), 3.77 (s, 3H, $OCH_3$), 3.62 (br.s, 1H, NH) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 159.3 (d, *J* = 239.0 Hz, 1C, C Ar), 152.3 (C Ar), 151.9 (C Ar), 144.7 (C Ar), 142.1 (C Ar), 128.5 (C-2), 126.6 (d, *J* = 10.8 Hz, 1C, C Ar), 120.4 (C-3), 119.0 (d, *J* = 4.0 Hz, 1C, C Ar), 114.9 (2C, C Ar), 114.4 (2C, C Ar), 112.3 (d, *J* = 17.6 Hz, 1C, C Ar), 112.2 (C Ar), 106.5 (d, *J* = 25.7 Hz, 1C, C Ar), 55.8 ($OCH_3$), 47.4 ($CH_2N$) ppm. $^{19}$F NMR (658.8 MHz, $CDCl_3$, 25 °C) δ -125.2 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3415 (NH), 1489 (C=C). MS (ESI): *m/z* = 298 $[M+H]^+$. Anal. Calcd for $C_{18}H_{16}FNO_2$: C, 72.71; H, 5.42; N, 4.71. Found: C, 72.48; H, 5.34; N, 4.85.

***(E)-N*-(3-(5-Fluorobenzo[*b*]furan-3-yl)allyl)-4-(trifluoromethyl)aniline (15h).** Yield: 0.17 g (71%); yellow oil. $R_f$ 0.48 (EtOAc/hexane, 1:10). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.67 (s, 1H, H-2 Furyl), 7.45-7.42 (m, 4H, H Ar), 7.06 (dt, *J* = 8.8, 2.4 Hz, 1H, H Ar), 6.69 (d, *J* = 8.6 Hz, 2H, H Ar), 6.66 (d, *J* = 16.0 Hz, 1H, H-3), 6.33 (dt, *J* = 16.0, 5.5 Hz, 1H, H-2), 4.26 (br.s, 1H, NH), 4.03 (br.s, 2H, H-1) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 159.4 (d, *J* = 239.0 Hz, 1C, C Ar), 152.0 (C Ar), 150.3 (C Ar), 145.0 (C Ar), 127.0 (C-2), 126.7 (q, *J* = 4.1 Hz, 2C, C Ar), 126.4 (d, *J* = 10.8 Hz, 1C, C Ar), 124.9 (q, *J* = 270.1 Hz, 1C, C Ar), 121.0 (C-3), 119.2 (q, *J* = 32.4 Hz, 2C, C Ar), 118.8 (d, *J* = 2.8 Hz, C Ar), 112.5 (d, *J* = 21.6 Hz, 1C, C Ar), 112.4

(d, *J* = 5.4 Hz, 1C, C Ar), 112.1 (C Ar), 106.5 (d, *J* = 25.7 Hz, 1C, C Ar), 45.9 ($CH_2N$) ppm. $^{19}F$ NMR (564.7 MHz, $CDCl_3$, 25 °C) δ -61.0, -120.3 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3417 (NH), 1483 (C=C). HRMS (ESI): calcd. for $C_{18}H_{13}F_4NO$, $[M-H]^+$, 334.0850; found, 334.0852, (Δ = 0.60 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 335 (42) [$M^+$], 334 (51), 316 (4), 198 (3), 176 (6), 175 (100), 172 (7), 149 (7), 148 (7), 147 (53), 146 (49), 145 (29), 133 (14), 128 (4), 127 (41), 125 (9), 120 (5), 101 (4), 95 (4), 75 (3).

**General Procedure for the Synthesis of Products 10, 19.** Maleic anhydride (0.5 mmol) was added to the corresponding allylamine **9a-d**,**f-k**,**n**, **15b-h** (0.5 mmol) diluted in PhH (5 mL). The resulting mixture was heated at reflux for 4 h and then cooled to room temperature. The resulting precipitate was filtered off, washed with PhH (5 mL), $Et_2O$ (2 × 5 mL), and air dried to give the title acids **10a-k**, **19a-g** as colorless or yellow powders.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-1-Oxo-2-phenyl-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10a).** Yield: 0.12 g (69 %); colorless powder. M.p. 248-250 °C. $^1H$ NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.88 (s, 1H, $CO_2H$), 7.62-7.60 (m, 1H, H Ar), 7.44-7.40 (m, 3H, H Ar), 7.29 (t, *J* = 7.6 Hz, 1H, H Ar), 7.10 (t, *J* = 7.6 Hz, 1H, H Ar), 7.06 (d, *J* = 7.6 Hz, 1H, H Ar), 6.98-6.95 (m, 1H, H Ar), 5.69 (t, *J* = 3.1 Hz, 1H, H-4), 4.21 (br.s, 1H, H-9b), 4.16 (t, *J* = 8.3 Hz, 1H, H-3A), 3.70 (dd, *J* = 11.0, 9.3 Hz, 1H, H-3B), 3.11-3.05 (m, 2H, H-3a, H-10), 2.61 (dd, *J* = 12.4, 8.6 Hz, 1H, H-10a) ppm. $^{13}C$ NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 172.7, 172.6 ($CO_2$, C-1), 155.3, 154.8 (C-4a, C Ar), 140.2 (C Ar), 129.2 (2C, C Ar), 127.6 (C Ar), 124.4 (C Ar), 124.2 (C Ar), 123.3 (C Ar), 120.4 (C Ar), 119.4 (2C, C Ar), 111.9, 111.5 (C-4, C Ar), 51.5, 47.8 (C-3, C-9b), 36.5, 32.4, 27.2 (C-3a, C-10, C-10a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 1697 ($CO_2H$), 1612 (N-C=O). MS (ESI): *m/z* = 348 $[M+H]^+$. Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03; Found: C, 72.87; H, 5.02; N, 4.27.

**Optimization of reaction conditions of *N*-phenyl-*N*-benzofurylallylamine 9a and maleic anhydride.** Maleic anhydride 40 mg (0.4 mmol) was added to the allylamine **9a** 100 mg (0.4 mmol) diluted in variouse solvents (5 mL). The resulting mixture was stirred or heated at reflux for 1-24 h and then the resulting precipitate was filtered off, washed with PhH (5 mL), $Et_2O$ (2 × 5 mL), and air dried to give the title acid **10a** or mixture **10a**/**23a** as colorless powder.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(2-Fluorophenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10b).** Yield: 0.06 g (34 %); colorless powder. M.p. > 250 °C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.83 (s, 1H, $CO_2H$), 7.47-7.23 (m, 6H, H Ar), 7.10 (t, *J* = 7.6 Hz, 1H, H Ar), 7.06 (d, *J* = 7.9 Hz, 1H, H Ar), 5.68 (br.s, 1H, H-4), 4.20 (br.s, 1H, H-9b), 3.96 (t, *J* = 7.4 Hz, 1H, H-3A), 3.75 (t, *J* = 9.8 Hz, 1H, H-3B), 3.19-3.14 (m, 1H, H-3a), 3.04 (t, *J* = 7.3 Hz, 1H, H-10), 2.53-2.51 (m, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.5, 171.7 ($CO_2$, C-1), 157.9, 157.2 (C-4a, C Ar), 156.7 (d, *J* = 249.8 Hz, 1C, C Ar), 129.2 (C Ar), 128.8 (C Ar), 128.5 (d, *J* = 6.8 Hz, 1C, C Ar), 127.9 (C Ar), 127.1 (d, *J* = 12.1 Hz, 1C, C Ar), 125.0 (d, *J* = 2.7 Hz, 1C, C Ar), 124.5 (C Ar), 123.1 (C Ar), 116.9 (d, *J* = 20.3 Hz, 1C, C Ar), 110.2 (C Ar), 99.4 (C-4), 52.3, 48.8 (C-3, C-9b), 43.9, 41.3, 36.2 (C-3a, C-10, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -119.7 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = br. 1699 (N-C=O, $CO_2$). HRMS (ESI): calcd. for $C_{21}H_{16}FNO_4$, $[M+H]^+$, 366.1133; found, 366.1136 (Δ = 0.82 ppm); calcd. for $C_{21}H_{16}FNO_4$, $[M+Na]^+$, 388.095; found, 388.0956 (Δ = 1.55 ppm). Anal. Calcd for $C_{21}H_{16}FNO_4$: C, 69.04; H, 4.41; N, 3.83; Found: C, 69.27; H, 4.31; N, 3.67.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3-Methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10c).** Yield: 0.09 g (53 %); colorless powder. M.p. 232-234 °C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.85 (br.s, 1H, $CO_2H$), 7.46 (s, 1H, H Ar), 7.43-7.40 (m, 2H, H Ar), 7.30-7.24 (m, 2H, H Ar), 7.10 (d, *J* = 7.6 Hz, 1H, H Ar), 7.05 (d, *J* = 8.1 Hz, 1H, H Ar), 6.94 (d, *J* = 7.6 Hz, 1H, H Ar), 5.69 (t, *J* = 3.1 Hz, 1H, H-4), 4.20-4.19 (m, 1H, H-9b), 4.07 (t, *J* = 8.3 Hz, 1H, H-3A), 3.70 (dd, *J* = 11.0, 9.1 Hz, 1H, H-3B), 3.09-3.03 (m, 2H, H-3a, H-10), 2.55 (dd, *J* = 12.4, 8.6 Hz, 1H, H-10a), 2.32 (s, 3H, $CH_3$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.7, 171.7 ($CO_2$, C-1), 157.9, 157.3 (C-4a, C Ar), 140.2 (C Ar), 138.3 (C Ar), 129.1 (C Ar), 128.9 (C Ar), 128.8 (C Ar), 124.9 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 120.1 (C Ar), 116.7 (C Ar), 110.2 (C Ar), 99.5 (C-4), 50.5, 50.1 (C-3, C-9b), 43.9, 41.4, 34.8 (C-3a, C-10, C-10a), 21.7 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1698 ($CO_2H$), 1606 (N-C=O). HRMS (ESI): calcd. for $C_{22}H_{19}NO_4$, $[M+H]^+$, 362.1397; found, 362.1387 (Δ = 2.76 ppm); calcd. for $C_{22}H_{19}NO_4$, $[M+Na]^+$, 384.1203; found, 384.1206 (Δ = 0.78 ppm). Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88; Found: C, 73.33; H, 5.41; N, 3.74.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10d).** Yield: 0.14 g (74 %); colorless

powder. M.p. 232-234 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.86 (s, 1H, $CO_2H$), 7.42 (d, $J$ = 7.2 Hz, 1H, H Ar), 7.31 (s, 1H, H Ar), 7.30-7.27 (m, 2H, H Ar), 7.15 (d, $J$ = 8.1 Hz, 1H, H Ar), 7.10 (t, $J$ = 7.4 Hz, 1H, H Ar), 7.05 (d, $J$ = 7.9 Hz, 1H, H Ar), 6.72 (d, $J$ = 8.1 Hz, 1H, H Ar), 5.69 (t, $J$ = 2.9 Hz, 1H, H-4), 4.20 (br.s, 1H, H-9b), 4.11 (t, $J$ = 8.1 Hz, 1H, H-3A), 3.76 (s, 3H, $CH_3$), 3.69 (t, $J$ = 9.9 Hz, 1H, H-3B), 3.09-3.04 (m, 2H, H-3a, H-10), 2.58 (dd, $J$ = 12.4, 8.6 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.7, 171.9 ($CO_2$, C-1), 159.9 (C Ar), 157.9, 157.3 (C-4a, C Ar), 141.4 (C Ar), 129.9 (C Ar), 129.2 (C Ar), 128.8 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 111.6 (C Ar), 110.2 (C Ar), 109.6 (C Ar), 105.5 (C Ar), 99.4 (C-4), 55.5, 50.5, 50.2 (C-3, C-9b, $OCH_3$), 43.8, 41.4, 34.7 (C-3a, C-10, C-10a) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1669 ($CO_2H$), 1603 (N-C=O). HRMS (ESI): calcd. for $C_{22}H_{19}NO_5$, $[M+H]^+$, 378.1344; found, 378.1336, (Δ = 2.12 ppm); calcd. for $C_{22}H_{19}NO_5$, $[M+Na]^+$, 400.1164; found, 400.1155, (Δ = 2.25 ppm). Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71; Found: C, 70.31; H, 5.31; N, 3.59.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10e).** Yield: 0.13 g (73%); colorless powder. M.p. 241-243 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.84 (s, 1H, $CO_2H$), 7.50 (d, $J$ = 8.3 Hz, 2H, H Ar), 7.42 (d, $J$ = 7.4 Hz, 1H, H Ar), 7.28 (t, $J$ = 7.6 Hz, 1H, H Ar), 7.18 (d, $J$ = 8.3 Hz, 2H, H Ar), 7.10 (t, $J$ = 7.6 Hz, 1H, H Ar), 7.06 (d, $J$ = 8.1 Hz, 1H, H Ar), 5.69 (t, $J$ = 3.3 Hz, 1H, H-4), 4.21-4.18 (m, 1H, H-9b), 4.06 (dd, $J$ = 8.6, 7.6 Hz, 1H, H-3A), 3.69 (dd, $J$ = 11.0, 9.1 Hz, 1H, H-3B), 3.09-3.03 (m, 2H, H-3a, H-10), 2.55 (dd, $J$ = 12.4, 8.6 Hz, 1H, H-10a), 2.28 (s, 3H, $CH_3$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.7, 171.6 ($CO_2$, C-1), 157.9, 157.3 (C-4a, C Ar), 137.9 (C Ar), 133.2 (C Ar), 129.5 (2C, C Ar), 129.1 (C Ar), 128.8 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 119.5 (2C, C Ar), 110.2 (C Ar), 99.5 (C 4), 50.4, 50.0 (C-3, C-9b), 43.9, 41.4, 34.8 (C-3a, C-10, C-10a), 20.9 ($CH_3$) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1697 ($CO_2H$), 1612 (N-C=O). MS (ESI): *m/z* = 362 $[M+H]^+$. Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88; Found: C, 73.50; H, 5.21; N, 3.92.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Ethylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10f).** Yield: 0.08 (44%); yellow powder. M.p. 238-240 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.85 (br.s, 1H, $CO_2H$), 7.52 (d, $J$ = 8.6 Hz, 2H, H Ar), 7.42 (d, $J$ = 7.1 Hz, 1H, H Ar), 7.28 (t, $J$ = 7.6 Hz, 1H, H Ar), 7.21 (d, $J$ = 8.3 Hz, 2H, H Ar), 7.10 (t, $J$ = 7.4 Hz, 1H, H Ar), 7.06 (d, $J$ = 7.9 Hz, 1H, H Ar), 5.69 (t, $J$ = 3.3 Hz, 1H,

H-4), 4.19 (br.s, 1H, H-9b), 4.06 (t, *J* = 8.1 Hz, 1H, H-3A), 3.69 (dd, *J* = 10.7, 9.3 Hz, 1H, H-3B), 3.09-3.03 (m, 2H, H-3a, H-10), 2.60-2.52 (m, 3H, H-10a, $CH_2$), 1.17 (t, *J* = 7.6 Hz, 3H, $CH_3$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.7, 171.6 ($CO_2$, C-1), 157.9, 157.3 (C-4a, C Ar), 139.6 (C Ar), 138.0 (C Ar), 129.1 (C Ar), 128.8 (C Ar), 128.3 (2C, C Ar), 124.5 (C Ar), 123.1 (C Ar), 119.6 (2C, C Ar), 110.2 (C Ar), 99.5 (C-4), 50.5, 50.0 (C-3, C-9b), 43.9, 41.4, 34.9 (C-3a, C-10, C-10a), 28.0 ($CH_2$), 16.2 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 1695 ($CO_2H$), 1607 (N-C=O). HRMS (ESI): calcd. for $C_{23}H_{21}NO_4$, $[M+H]^+$, 376.1561; found, 376.1543 (Δ = 4.79 ppm); calcd. for $C_{23}H_{21}NO_4$, $[M+Na]^+$, 398.1382; found, 398.1363 (Δ = 4.77 ppm). Calcd for $C_{23}H_{21}NO_4$: C, 73.58; H, 5.64; N, 3.73; Found: C, 73.41; H, 5.31; N, 3.91.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Methoxyphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10g).** Yield: 0.08 g (44%); colorless powder. M.p. 232-234 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.83 (s, 1H, $CO_2H$), 7.52 (d, *J* = 8.6 Hz, 2H, H Ar), 7.42 (d, *J* = 7.6 Hz, 1H, H Ar), 7.28 (t, *J* = 7.6 Hz, 1H, H Ar), 7.10 (t, *J* = 7.6 Hz, 1H, H Ar), 7.06 (d, *J* = 7.6 Hz, 1H, H Ar), 6.95 (d, *J* = 8.6 Hz, 2H, H Ar), 5.69 (br.s, 1H, H-4), 4.19 (br.s, 1H, H-9b), 4.04 (t, *J* = 8.1 Hz, 1H, H-3A), 3.75 (s, 3H, $CH_3$), 3.69 (t, *J* = 9.8 Hz, 1H, H-3B), 3.09-3.02 (m, 2H, H-3a, H-10), 2.59-2.48 (dd, *J* = 12.2, 8.8 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.7, 171.3 ($CO_2$, C-1), 157.9, 157.2 (C-4a, C Ar), 156.0 (C Ar), 133.5 (C Ar), 129.1 (C Ar), 128.8 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 121.2 (2C, C Ar), 114.3 (2C, C Ar), 110.2 (C Ar), 99.5 (C-4), 55.7, 50.7, 49.9 (C-3, C-9b, $OCH_3$), 43.9, 41.4, 35.0 (C-3a, C-10, C-10a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 1679 ($CO_2H$), 1608 (N-C=O). MS (ESI): *m/z* = 378 $[M+H]^+$. Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71; Found: C, 70.21; H, 5.38; N, 3.55.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-1-Oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10h).** Yield: 0.16 g (76%); colorless powder. M.p. 240-243 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C): δ 12.91 (br.s, 1H, $CO_2H$), 7.85 (d, *J* = 8.6 Hz, 2H, H Ar), 7.75 (d, *J* = 8.6 Hz, 2H, H Ar), 7.43 (d, *J* = 7.6 Hz, 1H, H Ar), 7.29 (t, *J* = 7.6 Hz, 1H, H Ar), 7.11 (t, *J* = 7.6 Hz, 1H, H Ar), 7.06 (d, *J* = 7.6 Hz, 1H, H Ar), 5.71 (br.s, 1H, H-4), 4.23-4.19 (m, 2H, H-9b, H-3A), 3.76 (t, *J* = 10.3 Hz, 1H, H-3B), 3.12-3.08 (m, 2H, H-3a, H-10), 2.65 (dd, *J* = 12.4, 8.3 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.5, 172.6 ($CO_2$, C-1), 157.8, 157.4 (C-4a, C Ar), 143.6 (C Ar), 129.2 (C Ar), 128.8 (C Ar), 126.4 (2C, C Ar), 124.8 (q, *J* = 271.4 Hz, 1C, $CF_3$), 124.6 (C Ar), 124.1 (C Ar), 123.1 (C Ar),

119.2 (2C, C Ar), 110.2 (C Ar), 99.4 (C-4), 50.3, 50.0 (C-3, C-9b), 43.8, 41.3, 34.6 (C-3a, C-10, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ - 60.34 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1703 ($CO_2H$), 1680 (N-C=O). MS (ESI): *m/z* = 416 $[M+H]^+$. Anal. Calcd for $C_{22}H_{16}F_3NO_4$: C, 63.62; H, 3.88; N, 3.37; Found: C, 63.24; H, 3.91; N, 3.70.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Fluorophenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10i).** Yield: 63%; colorless powder. M.p. > 250 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.86 (br.s, 1H, $CO_2H$), 7.65 (dd, *J* = 8.8, 4.8 Hz, 2H, H Ar), 7.42 (d, *J* = 7.6 Hz, 1H, H Ar), 7.28 (t, *J* = 7.6 Hz, 1H, H Ar), 7.23 (t, *J* = 8.8 Hz, 2H, H Ar), 7.10 (t, *J* = 7.6 Hz, 1H, H Ar), 7.06 (d, *J* = 7.6 Hz, 1H, H Ar), 5.69 (t, *J* = 3.1 Hz, 1H, H-4), 4.20 (br.s, 1H, H-9b), 4.09 (t, *J* = 8.1 Hz, 1H, H-3A), 3.72 (dd, *J* = 10.5, 9.3 Hz, 1H, H-3B), 3.10-3.04 (m, 2H, H-3a, H-10), 2.57 (dd, *J* = 12.4, 8.6 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.6, 171.7 ($CO_2$, C-1), 158.8 (d, *J* = 241.7 Hz, 1C, C Ar), 157.8, 157.3 (C-4a, C Ar), 136.7 (C Ar), 129.2 (C Ar), 128.8 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 121.4 (d, *J* = 8.1 Hz, 2C, C Ar), 115.8 (d, *J* = 21.6 Hz, 2C, C Ar), 110.2 (C Ar), 99.4 (C-4), 50.6, 49.9 (C-3, C-9b), 43.8, 41.3, 34.8 (C-3a, C-10, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -118.8 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1694 ($CO_2H$), 1612 (N-C=O). HRMS (ESI): calcd. for $C_{21}H_{16}FNO_4$, $[M+H]^+$, 366.1153; found, 366.1136 (Δ = 4.64 ppm); calcd. for $C_{21}H_{16}FNO_4$, $[M+Na]^+$, 388.0975; found, 388.0956 (Δ = 4.9 ppm). Anal. Calcd for $C_{21}H_{16}FNO_4$: C, 69.04; H, 4.41; N, 3.83; Found: C, 69.34; H, 4.01; N, 3.60.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Chlorophenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10j).** Yield: 0.10 g (54%); colorless powder. M.p. > 250 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.88 (br.s, 1H, $CO_2H$), 7.66 (d, *J* = 7.6 Hz, 2H, H Ar), 7.44-7.41 (m, 3H, H Ar), 7.28 (t, *J* = 7.6 Hz, 1H, H Ar), 7.10-7.05 (m, 2H, H Ar), 5.69 (br.s, 1H, H-4), 4.19 (br.s, 1H, H-9b), 4.10 (t, *J* = 8.8 Hz, 1H, H-3A), 3.70 (t, *J* = 9.8 Hz, 1H, H-3B), 3.09-3.04 (m, 2H, H-3a, H-10), 2.60-2.57 (m, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.6, 172.0 ($CO_2$, C-1), 157.8, 157.3 (C-4a, C Ar), 139.1 (C Ar), 129.2 (C Ar), 129.0 (2C, C Ar), 128.8 (C Ar), 127.9 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 121.0 (2C, C Ar), 110.2 (C Ar), 99.4 (C-4), 50.3, 50.0 (C-3, C-9b), 43.8, 41.3, 34.6 (C-3a, C-10, C-10a) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1703 ($CO_2H$), 1687 (N-C=O). HRMS (ESI): calcd. for $C_{21}H_{16}ClNO_4$, $[M+H, Cl^{35}]^+$, 382.0843; found, 382.0841 (Δ = 0.52 ppm); calcd. for

$C_{21}H_{16}ClNO_4$, [M+Na, $Cl^{35}$]$^+$, 404.0665; found, 404.066 (Δ = 1.24 ppm). Anal. Calcd for $C_{21}H_{16}ClNO_4$: C, 66.06; H, 4.22; N, 3.67; Found: C, 66.36; H, 4.33; N, 3.50.

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3,5-Dimethoxyphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10k).** Yield: 0.09 g (46%); colorless powder. M.p. 227-229 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.86 (br.s, 1H, $CO_2H$), 7.41 (d, *J* = 7.6 Hz, 1H, H Ar), 7.28 (t, *J* = 7.6 Hz, 1H, H Ar), 7.10 (t, *J* = 7.6 Hz, 1H, H Ar), 7.06 (d, *J* = 7.6 Hz, 1H, H Ar), 6.86 (d, *J* = 1.7 Hz, 2H, H Ar), 6.30 (s, 1H, H Ar), 5.68 (t, *J* = 3.1 Hz, 1H, H-4), 4.19 (br.s, 1H, H-9b), 4.11 (t, *J* = 8.1 Hz, 1H, H-3A), 3.74 (s, 6H, $2CH_3$), 3.66 (dd, *J* = 10.5, 9.5 Hz, 1H, H-3B), 3.07-3.02 (m, 2H, H-3a, H-10), 2.57 (dd, *J* = 12.4, 8.6 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 175.7, 172.0 ($CO_2$, C-1), 160.9 (2C, C Ar), 157.8, 157.3 (C-4a, C Ar), 141.9 (C Ar), 129.2 (C Ar), 128.8 (C Ar), 124.5 (C Ar), 123.1 (C Ar), 110.2 (C Ar), 99.4 (C-4), 98.0 (2C, C Ar), 96.1 (C Ar), 55.6 (2C, $2OCH_3$), 50.5, 50.3 (C-3, C-9b), 43.8, 41.3, 34.6 (C-3a, C-10, C-10a) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1742 ($CO_2H$), 1670 (N-C=O). HRMS (ESI): calcd. for$C_{23}H_{21}NO_6$, [M+H]$^+$, 408.1448; found, 408.1442 (Δ = 1.47 ppm); calcd. for$C_{23}H_{21}NO_6$, [M+Na]$^+$, 430.1270; found, 430.1261 (Δ = 2.09 ppm). Anal. Calcd for $C_{23}H_{21}NO_6$: C, 67.80; H, 5.20; N, 3.44; Found: C, 67.51; H, 5.28; N, 3.80.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-3-Oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19a).** Yield: 0.14 g (68%); colorless powder. M.p. 235-237 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.85 (br.s, 1H, $CO_2H$), 7.86 (d, *J* = 8.3 Hz, 2H, H Ar), 7.75 (d, *J* = 8.3 Hz, 2H, H Ar), 7.59 (d, *J* = 7.6 Hz, 1H, H Ar), 7.26 (t, *J* = 7.6 Hz, 1H, H Ar), 6.97-6.97 (m, 2H, H Ar), 6.61 (t, *J* = 3.1 Hz, 1H, H-10), 5.30 (br.s, 1H, H-4a), 4.22 (t, *J* = 8.0 Hz, 1H, H-1A), 3.83 (dd, *J* = 10.3, 9.5 Hz, 1H, H-1B), 3.09-3.05 (m, 2H, H-4, H-10a), 2.75 (dd, *J* = 12.6, 9.1 Hz, 1H, H-3a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 174.9, 172.2 ($CO_2$, C-3), 162.5 (C Ar), 143.5 (C Ar), 139.5 (C-10), 130.7 (C Ar), 126.4 (q, *J* = 4.1 Hz, 2C, C Ar), 124.8 (q, *J* = 271.4 Hz, 1C, $CF_3$), 124.1 (q, *J* = 32.4 Hz, 1C, C Ar), 123.9 (C Ar), 122.0 (C Ar), 121.8 (C Ar), 119.3 (2C, C Ar), 117.6 (C-9b), 111.0 (C Ar), 84.7 (C-4a), 49.9, 47.7, 42.6, 36.9 (C-1, C-3a, C-4, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ - 60.35 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1712 ($CO_2H$), 1683 (N-C=O). HRMS (ESI): calcd. for $C_{22}H_{16}F_3NO_4$, [M+H]$^+$, 416.1091; found, 416.1104 (Δ = 3.12 ppm); calcd. for $C_{22}H_{16}F_3NO_4$, [M+Na]$^+$, 438.0906; found, 438.0924 (Δ = 4.11 ppm). Anal. Calcd for $C_{22}H_{16}F_3NO_4$: C, 63.62; H, 3.88; N, 3.37; Found: C, 63.49; H, 3.67; N, 3.57.

**(3a*R*,4*R*,4a*S*,10a*S*)-2-(4-Fluorophenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19b).** Yield: 0.13 g (74%); colorless powder. M.p. 240-242 °C. $^{1}$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 12.81 (br.s, 1H, $CO_2H$), 7.65 (dd, *J* = 9.1, 5.0 Hz, 2H, H Ar), 7.58 (d, *J* = 7.6 Hz, 1H, H Ar), 7.26-7.21 (m, 3H, H Ar), 6.99-6.96 (m, 2H, H Ar), 6.59 (t, *J* = 3.5 Hz, 1H, H-10), 5.30-5.28 (m, 1H, H-4a), 4.12 (t, *J* = 8.1 Hz, 1H, H-1A), 3.79 (dd, *J* = 11.1, 9.1 Hz, 1H, H-1B), 3.07-3.02 (m, 2H, H-4, H-10a), 2.67 (dd, *J* = 12.6, 9.1 Hz, 1H, H-3a) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 175.0, 171.4 ($CO_2$, C-3), 162.6 (C Ar), 158.9 (d, *J* = 239.9 Hz, 1C, C Ar), 139.4 (C-10), 136.7 (C Ar), 130.7 (C Ar), 124.0 (C Ar), 122.1 (C Ar), 121.9 (C Ar), 121.6 (d, *J* = 7.2 Hz, 2C, C Ar), 117.8 (C-9b), 115.8 (d, *J* = 23.1 Hz, 2C, C Ar), 111.1 (C Ar), 84.9 (C-4a), 50.3, 47.7, 42.7, 36.2 (C-1, C-3a, C-4, C-10a) ppm. $^{19}$F NMR (564.7 MHz, DMSO-$d_6$, 25 °C) δ -118.6 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1751 ($CO_2H$), 1650 (N-C=O). MS (ESI): *m/z* = 366 $[M+H]^+$. Anal. Calcd for $C_{21}H_{16}FNO_4$: C, 69.04; H, 4.41; N, 3.83; Found: C, 69.12; H, 4.28; N, 3.57.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-2-(4-Chlorophenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19c) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-2-(4-chlorophenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17c).** Contains around 23% on an impurity of *endo*-isomer. NMR, IR, LCMS and elemental analysis data are presented for the mixture **19c** / *endo*-**17c**. Yield: 0.14 g (74%); colorless powder. M.p. 231-233 °C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.82 (br.s, 1H, $CO_2H$), 12.28 (br.s, 0.3H, $CO_2H$), 7.68-7.66 (m, 2.6H, H Ar), 7.59 (d, *J* = 7.2 Hz, 1H, H Ar), 7.51 (d, *J* = 7.4 Hz, 0.3H, H Ar), 7.45-7.43 (m, 2.6H, H Ar), 7.26 (d, *J* = 7.6 Hz, 1H, H Ar), 7.20 (d, *J* = 7.6 Hz, 0.3H, H Ar), 6.99-6.97 (m, 2H, H Ar), 6.93-6.89 (m, 0.6H, H Ar), 6.60 (t, *J* = 3.3 Hz, 1H, H-10), 6.09 (t, *J* = 2.8 Hz, 0.3H, H-10), 5.41-5.39 (m, 0.3H, H-4a), 5.30-5.28 (m, 1H, H-4a), 4.14 (t, *J* = 8.1 Hz, 1H, H-1A), 4.10 (t, *J* = 9.1 Hz, 0.3H, H-1A), 3.79 (dd, *J* = 10.7, 9.1 Hz, 1H, H-1B), 3.71 (t, *J* = 6.2 Hz, 0.3H, H-4), 3.67 (t, *J* = 8.8 Hz, 0.3H, H-1B), 3.39-3.34 (m, 0.3H, H-10a), 3.30 (dd, *J* = 10.7, 6.2 Hz, 0.3H, H-3a), 3.07-3.02 (m, 2H, H-4, H-10a), 2.70 (dd, *J* = 12.9, 9.1 Hz, 1H, H-3a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 174.9, 173.4, 171.7, 171.6 ($CO_2$, C-3), 162.5, 162.3 (C Ar), 139.4, 139.1 (C-10), 138.7, 135.4 (C Ar), 130.7, 130.5 (C Ar), 129.0 (2.6C, C Ar), 128.5, 128.0 (C Ar), 124.9, 123.9 (C Ar), 122.0, 121.9 (C Ar), 121.8, 121.5 (C Ar), 121.0 (2.6C, C Ar), 117.7, 116.2 (C-9b), 111.0, 110.7 (C Ar), 84.8, 82.2 (C-4a), 52.9, 49.9, 47.7, 42.9, 42.6, 41.9, 36.0, 30.0 (C-1, C-3a, C-4, C-10a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 1749 ($CO_2H$), 1661 (N-C=O). HRMS (ESI): calcd. for $C_{21}H_{16}O_4ClN$, [M+H,

$Cl^{35}]^+$, 382.085; found, 382.0841 (Δ = 4.19 ppm); calcd. for $C_{21}H_{16}O_4ClN$, $[M+Na, Cl^{35}]^+$, 404.0679; found, 404.066 (Δ = 4.7 ppm). Anal. Calcd for $C_{21}H_{16}ClNO_4$: C, 66.06; H, 4.22; N, 3.67; Found: C, 66.22; H, 4.28; N, 3.57.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19d) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-8-fluoro-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17d).** Contains around 17% on an impurity of *endo*-isomer. NMR, IR, LCMS and elemental analysis data are presented for the mixture **19d** / *endo*-**17d**. Yield: 70%; colorless powder. M.p. 234-235 °C. $^1$H NMR(700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.83 (br.s, 1H, $CO_2H$), 12.33 (br.s, 0.2H, $CO_2H$), 7.63 (d, *J* = 8.1 Hz, 2H, H Ar), 7.61 (d, *J* = 8.6 Hz, 0.4H, H Ar), 7.50 (dd, *J* = 8.1, 2.4 Hz, 1H, H Ar), 7.42-7.37 (m, 2.6H, H Ar), 7.15-7.07 (m, 2.2H, H Ar), 7.03-7.00 (m, 0.2H, H Ar), 6.98 (dd, *J* = 8.6, 3.8 Hz, 1H, H Ar), 6.89 (dd, *J* = 8.6, 3.8 Hz, 0.2H, H Ar), 6.68 (t, *J* = 3.3 Hz, 1H, H-10), 6.19 (br.s, 0.2H, H-10), 5.45 (br.s, 0.2H, H-4a), 5.34 (br.s, 1H, H-4a), 4.14 (t, *J* = 8.1 Hz, 1H, H-1A), 4.10 (t, *J* = 9.1 Hz, 0.2H, H-1A), 3.80 (dd, *J* = 10.7, 9.3 Hz, 1H, H-1B), 3.71-3.68 (m, 0.4H, H-1B, H-4), 3.40-3.37 (m, 0.2H, H-10a), 3.29 (dd, *J* = 10.7, 6,2 Hz, 0.2H, H-3a), 3.08-3.03 (m, 2H, H-4, H-10a), 2.69 (dd, *J* = 12.6, 9.1 Hz, 1H, H-3a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 174.9, 173.0, 171.5, 171.4 ($CO_2$, C-3), 158.6, 158.4 (C Ar), 157.8 (d, *J* = 236.3 Hz, 1C, C Ar), 157.6 (d, *J* = 236.3 Hz, 0.2C, C Ar), 140.2, 139.8 (C-10), 138.9 (d, *J* = 2.7 Hz, 1C, C Ar), 135.0 (d, *J* = 2.7 Hz, 0.2C, C Ar), 129.1 (2.4C, C Ar), 126.4 (d, *J* = 9.5 Hz, 0.2C, C Ar), 125.3 (d, *J* = 10.8 Hz, 1C, C Ar), 124.8, 124.3 (C Ar), 120.5, 119.7 (0.4C, C Ar), 119.5 (2C, C-9b, C Ar), 118.1 (C-9b), 117.0 (d, *J* = 24.3 Hz, 1C, C Ar), 116.7 (d, *J* = 24.3 Hz, 0.2C, C Ar), 111.7 (d, *J* = 8.1 Hz, 1C, C Ar), 111.3 (d, *J* = 8.1 Hz, 0.2C, C Ar), 108.6 (d, *J* = 25.7 Hz, 1C, C Ar), 108.5 (d, *J* = 25.7 Hz, 0.2C, C Ar), 85.6, 83.1 (C-4a), 52.8, 49.9, 47.6, 42.8, 42.6, 41.9, 36.2, 30.2 (C-1, C-3a, C-4, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -122.7, -123.2 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 1712 ($CO_2H$), 1649 (N-C=O). HRMS (ESI): calcd. for $C_{21}H_{16}FNO_4$, $[M+H]^+$, 366.1136; found, 366.1139, (Δ = 0.66 ppm). MS (ESI): *m/z* = 366 $[M+H]^+$. Anal. Calcd for $C_{21}H_{16}FNO_4$: C, 69.04; H, 4.41; N, 3.83; Found: C, 69.33; H, 4.58; N, 3.59.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-2-(4-methylphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19e) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-8-fluoro-2-(4-methylphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17e).** Contains around 20% on an impurity of *endo*-isomer.

Physicochemical data are presented for the major *exo*-isomer, obtained by crystallization from an ethanol - DMF mixture. Yield: 66%; colorless powder. M.p. 254-255 °C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.80 (br.s, 1H, $CO_2H$), 7.51-7.49 (m, 3H, H Ar), 7.19 (d, $J$ = 8.4 Hz, 2H, H Ar), 7.08 (dt, $J$ = 8.8, 2.1 Hz, 1H, H Ar), 6.98 (dd, $J$ = 8.8, 4.1 Hz, 1H, H Ar), 6.67 (t, $J$ = 3.3 Hz, 1H, H-10), 5.33 (br.s, 1H, H-4a), 4.10 (t, $J$ = 8.1 Hz, 1H, H-1A), 3.77 (dd, $J$ = 10.5, 9.3 Hz, 1H, H-1B), 3.06-3.01 (m, 2H, H-4, H-10a), 2.67 (dd, $J$ = 12.6, 9.1 Hz, 1H, H-3a), 2.28 (s, 3H, $CH_3$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 174.9, 171.1 ($CO_2$, C-3), 158.6 (C Ar), 157.8 (d, $J$ = 236.3 Hz, 1C, C Ar), 138.9 (C-10), 137.8 (C Ar), 133.3 (C Ar), 129.5 (2C, C Ar), 125.3 (d, $J$ = 9.5 Hz, 1C, C Ar), 119.7 (C-9b), 119.6 (2C, C Ar), 117.0 (d, $J$ = 24.3 Hz, 1C, C Ar), 111.7 (d, $J$ = 9.5 Hz, 1C, C Ar), 108.6 (d, $J$ = 25.7 Hz, 1C, C Ar), 85.6 (C-4a), 49.9, 47.5, 42.6, 36.2 (C-1, C-3a, C-4, C-10a), 20.9 ($CH_3$) ppm. $^{19}$F NMR (658 MHz, DMSO-$d_6$, 25 °C) δ -122.7 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$ = 1724 ($CO_2H$), 1640 (N-C=O). MS (ESI): $m/z$ = 380 $[M+H]^+$. Anal. Calcd for $C_{22}H_{18}FNO_4$: C, 69.65; H, 4.78; N, 3.69; Found: C, 69.37; H, 4.88; N, 3.39.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19f) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-8-fluoro-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17f).** Contains around 29% on an impurity of *endo*-isomer. NMR, IR, LCMS and elemental analysis data are presented for the mixture **19f** / *endo*-**17f**. Yield: 73%; colorless powder. M.p. 246-247 °C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.79 (br.s, 1H, $CO_2H$), 12.32 (br.s, 0.4H, $CO_2H$), 7.53 (d, $J$ = 9.3 Hz, 2H, H Ar), 7.49-7.48 (m, 1.8H, H Ar), 7.39 (dd, $J$ = 8.1, 2.6 Hz, 0.4H, H Ar), 7.08 (dt, $J$ = 8.8, 2.6 Hz, 1H, H Ar), 7.01 (dt, $J$ = 9.1, 2.9 Hz, 0.4H, H Ar), 6.97 (dd, $J$ = 8.8, 4.1 Hz, 1H, H Ar), 6.96-6.94 (m, 2.8H, H Ar), 6.90 (dd, $J$ = 8.8, 4.3 Hz, 0.4H, H Ar), 6.67 (t, $J$ = 3.6 Hz, 1H, H-10), 6.17 (t, $J$ = 3.1 Hz, 0.4H, H-10), 5.45-5.43 (m, 0.4H, H-4a), 5.34-5.33 (m, 1H, H-4a), 4.08-4.04 (m, 1.4H, H-1A), 3.77 (dd, $J$ = 11.0, 8.8 Hz, 1H, H-1B), 3.75 (s, 3H, $CH_3$), 3.75 (s, 1.2H, $CH_3$), 3.68 (t, $J$ = 6.2 Hz, 0.4H, H-4), 3.63 (t, $J$ = 8.8 Hz, 0.4H, H-1B), 3.37-3.34 (m, 0.4H, H-10a), 3.24 (dd, $J$ = 10.7, 6.2 Hz, 0.4H, H-3a), 3.06-3.01 (m, 2H, H-4, H-10a), 2.65 (dd, $J$ = 12.9, 9.1 Hz, 1H, H-3a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 174.9, 172.5, 171.5, 170.8 ($CO_2$, C-3), 158.6, 158.4, 157.8 (d, $J$ = 235.0 Hz, 1C, C Ar), 157.8 (d, $J$ = 236.3 Hz, 0.4C, C Ar), 157.6, 156.1 (C Ar), 138.9 (d, $J$ = 2.7 Hz, 1C, C Ar), 135.0 (d, $J$ = 2.7 Hz, 0.4C, C Ar), 133.4, 133.0 (C-10), 126.4 (d, $J$ = 9.5 Hz, 0.4C, C Ar), 125.3 (d, $J$ = 9.5 Hz, 1C, C Ar), 122.5 (0.8C, C Ar), 121.3 (2C, C Ar), 119.7, 118.2 (C-9b), 116.9 (d, $J$ = 24.3 Hz, 1C, C Ar), 116.6 (d, $J$ = 25.7 Hz, 0.4C, C Ar), 114.3 (2.8C, C Ar),

111.7 (d, *J* = 8.1 Hz, 1C, C Ar), 111.3 (d, *J* = 9.5 Hz, 0.4C, C Ar), 108.6 (d, *J* = 25.7 Hz, 1C, C Ar), 108.5 (d, *J* = 24.3 Hz, 0.4C, C Ar), 85.7, 83.1 (C-4a), 55.7 (1.4C, $OCH_3$), 53.3, 50.2, 47.4, 42.8, 42.6, 41.7, 36.3, 30.3 (C-1, C-3a, C-4, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -122.1, -123.2 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 1704 ($CO_2H$), 1612 (N-C=O). MS (ESI): *m/z* = 396 $[M+H]^+$. Anal. Calcd for $C_{22}H_{18}FNO_5$: C, 66.83; H, 4.59; N, 3.54; Found: C, 66.74; H, 4.48; 3.63.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-3-oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19g).** Yield: 0.16 g (75%); colorless powder. M.p. 247-248 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.88 (br.s, 1H, $CO_2H$), 7.87 (d, *J* = 8.6 Hz, 2H, H Ar), 7.76 (d, *J* = 8.6 Hz, 2H, H Ar), 7.52 (dd, *J* = 8.3, 2.9 Hz, 1H, H Ar), 7.09 (dt, *J* = 8.8, 2.6 Hz, 1H, H Ar), 6.99 (dd, *J* = 8.6, 4.1 Hz, 1H, H Ar), 6.70 (t, *J* = 3.6 Hz, 1H, H-10), 5.36-5.34 (m, 1H, H-4a), 4.24 (dd, *J* = 8.6, 7.6 Hz, 1H, H-1A), 3.85 (dd, *J* = 11.0, 8.8 Hz, 1H, H-1B), 3.11-3.02 (m, 2H, H-4, H-10a), 2.77 (dd, *J* = 12.9, 8.8 Hz, 1H, H-3a) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 174.7, 172.1 ($CO_2$, C-3), 158.6 (C Ar), 157.8 (d, *J* = 236.3 Hz, 1C, C Ar), 143.5 (C Ar), 139.1 (C-10), 126.4 (2C, C Ar), 125.3 (d, *J* = 9.5 Hz, 1C, C Ar), 124.8 (q, *J* = 271.4 Hz, 1C, $CF_3$), 124.1 (q, *J* = 32.4 Hz, 1C, C Ar), 119.5 (C-9b), 119.3 (2C, C Ar), 117.0 (d, *J* = 24.3 Hz, 1C, C Ar), 111.7 (d, *J* = 9.5 Hz, 1C, C Ar), 108.7 (d, *J* = 25.7 Hz, 1C, C Ar), 85.5 (C-4a), 49.8, 47.6, 42.6, 35.9 (C-1, C-3a, C-4, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -60.3, -122.7 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1702 ($CO_2H$), 1598 (N-C=O). MS (ESI): *m/z* = 434 $[M+H]^+$. Anal. Calcd for $C_{22}H_{15}F_4NO_4$: C, 60.97; H, 3.49; N, 3.23; Found: C, 60.87; H, 3.68; N, 3.47.

**General Procedure for the Synthesis of Products 20, 22.** Trifluoromethylmaleic or citraconic anhydride (0.5 mmol) was added at room temperature to the corresponding allylamine **9a**,**c-e**,**j**,**l**,**m**,**o**, **15a** (0.5 mmol) diluted in PhH (5 mL). The resulting mixture was stirred for 24 h. The resulting precipitate was filtered off, washed with PhH (5 mL), $Et_2O$ (2 × 5 mL), and air dried to give the title acids **20a-i**, **21e**,**f**,**h**,**i** as colorless or yellow solid powders.

**(3a*R*,9b*R*,10*S*,10a*S*)-1-Oxo-2-phenyl-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20a).** Yield: 0.15 g (71%); colorless powder. M.p. 244-246 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 14.15 (br.s, 1H, $CO_2H$), 7.61 (d, *J* = 7.6 Hz, 2H, H Ar), 7.39 (t, *J* = 7.6 Hz, 2H, H Ar), 7.32 (t, *J* = 7.6 Hz, 1H, H Ar), 7.26 (d, *J* = 7.6 Hz, 1H, H Ar), 7.15 (t, *J* = 7.6 Hz, 1H, H Ar), 7.11-7.06 (m, 2H, H Ar), 5.74 (t, *J* = 3.5 Hz, 1H, H-4), 4.73 (br.s, 1H, H-9b), 4.12 (t, *J* = 7.8 Hz, 1H, H-3A), 3.89 (dd, *J* = 11.1, 9.6 Hz, 1H,

H-3B), 3.04-2.98 (m, 1H, H-3a), 2.85 (d, *J* = 12.6 Hz, 1H, H-10a) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 169.7, 169.4 ($CO_2$, C-1), 158.5, 156.0 (C-4a, C Ar), 140.2 (C Ar), 129.9 (C Ar), 129.3 (2C, C Ar), 127.3 (C Ar), 125.8 (q, *J* = 283.2 Hz, 1C, $CF_3$), 124.6 (C Ar), 123.8 (C Ar), 122.6 (C Ar), 119.8 (2C, C Ar), 110.7 (C Ar), 97.4 (C-4), 53.9 (q, *J* = 23.1 Hz, 1C, C-10), 53.1, 49.6, 47.6, 36.4 (C-3, C-3a, C-9b, C-10a) ppm. $^{19}$F NMR (564.7 MHz, DMSO-$d_6$, 25 °C) δ -63.9, -66.0 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1715 ($CO_2H$), 1604 (N-C=O). MS (ESI): *m/z* = 416 $[M+H]^+$. Anal. Calcd for $C_{22}H_{16}F_3NO_4$: C, 63.62; H, 3.88; N, 3.37; Found: C, 66.57; H, 3.80; N, 3.53.

**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20b).** Yield: 0.14 g (62%); colorless powder. M.p. 252-254 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 14.14 (br.s, 1H, $CO_2H$), 7.32-7.26 (m, 4H, H Ar), 7.14-7.07 (m, 3H, H Ar), 6.75 (d, *J* = 7.6 Hz, 1H, H Ar), 5.74 (br.s, 1H, H-4), 4.73 (br.s, 1H, H-9b), 4.14 (t, *J* = 7.9 Hz, 1H, H-3A), 3.91 (t, *J* = 10.0 Hz, 1H, H-3B), 3.77 (s, 3H, $CH_3$), 3.03-2.98 (m, 1H, H-3a), 2.85 (d, *J* = 12.4 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 169.7, 169.5 ($CO_2$, C-1), 159.9 (C Ar), 158.4, 155.9 (C-4a, C Ar), 141.3 (C Ar), 130.0 (C Ar), 129.8 (C Ar), 127.2 (C Ar), 125.8 (q, *J* = 283.2 Hz, 1C, $CF_3$), 123.7 (C Ar), 122.5 (C Ar), 111.8 (C Ar), 110.6 (C Ar), 110.0 (C Ar), 105.6 (C Ar), 97.2 (C-4), 55.6 ($OCH_3$), 53.8 (q, *J* = 21.6 Hz, 1C, C-10), 53.1, 49.6, 47.6, 36.3 (C-3, C-3a, C-9b, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C): δ -66.0, -66.8 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1705 ($CO_2H$), 1600 (N-C=O). MS (ESI): *m/z* = 446 $[M+H]^+$. Anal. Calcd for $C_{23}H_{18}F_3NO_5$: C, 62.02; H, 4.07; N, 3.14; Found: C, 62.37; H, 3.98; N, 3.03.

**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-2-(3-Fluorophenyl)-1-oxo-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20c).** Yield: 0.12 g (55%); colorless powder. M.p. 240-243 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 14.17 (br.s, 1H, $CO_2H$), 7.64-7.55 (dt, *J* = 12.1, 2.0 Hz, 1H, H Ar), 7.46-7.39 (m, 2H, H Ar), 7.32 (t, *J* = 7.6 Hz, 1H, H Ar), 7.26 (d, *J* = 7.6 Hz, 1H, H Ar), 7.11 (d, *J* = 8.1 Hz, 1H, H Ar), 7.08 (t, *J* = 7.6 Hz, 1H, H Ar), 6.99(dt, *J* = 8.1, 2.0 Hz, 1H, H Ar), 5.74 (t, *J* = 3.5 Hz, 1H, H-4), 4.72 (br.s, 1H, H-9b), 4.18 (dd, *J* = 8.6, 7.1 Hz, 1H, H-3A), 3.90 (dd, *J* = 10.6, 8.6 Hz, 1H, H-3B), 3.03-2.98 (m, 1H, H-3a), 2.89 (d, *J* = 12.6 Hz, 1H, H-10a) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 169.9, 169.7 ($CO_2$, C-1), 162.6 (d, *J* = 241.3 Hz, 1C, C Ar), 158.5, 156.1 (C-4a, C Ar), 141.8 (d, *J* = 10.1 Hz, 1C, C Ar), 130.9 (d, *J* = 8.7 Hz, 1C, C Ar), 129.9 (C Ar), 127.3 (C Ar), 125.8 (q, *J* = 283.2 Hz, 1C, $CF_3$), 123.7 (C Ar), 122.6 (C Ar), 115.1 (C Ar), 111.0 (d, *J* = 20.2 Hz, 1C, C Ar),

110.7 (C Ar), 106.6 (d, *J* = 26.0 Hz, 1C, C Ar), 97.2 (C-4), 53.9 (q, *J* = 23.1 Hz, 1C, C-10), 53.1, 49.6, 47.6, 36.2 (C-3, C-3a, C-9b, C-10a) ppm. $^{19}$F NMR (564.7 MHz, DMSO-$d_6$, 25 °C): δ -63.9, -66.0, -111.8 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1710 ($CO_2H$), 1610 (N-C=O). MS (ESI): *m/z* = 434 $[M+H]^+$. Anal. Calcd for $C_{22}H_{15}F_4NO_4$: C, 60.98; H, 3.49; N, 3.23; Found: C, 61.07; H, 3.57; N, 3.43.

**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-2-[4-Methoxy-3-(trifluoromethyl)phenyl]-1-oxo-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20d).** Yield: 0.18 g (77%); colorless powder. M.p. 239-241 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C): δ 14.14 (br.s, 1H, $CO_2H$), 8.01 (br.s, 1H, H Ar), 7.69 (d, *J* = 8.3 Hz, 1H, H Ar), 7.32-7.31 (m, 2H, H Ar), 7.26 (d, *J* = 7.6 Hz, 1H, H Ar), 7.11-7.07 (m, 2H, H Ar), 5.74 (br.s, 1H, H-4), 4.72 (br.s, 1H, H-9b), 4.13 (t, *J* = 7.3 Hz, 1H, H-3A), 3.94 (t, *J* = 9.8 Hz, 1H, H-3B), 3.89 (s, 3H, $CH_3$), 3.04-2.99 (m, 1H, H-3a), 2.85 (d, *J* = 12.4 Hz, 1H, H-10a) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 169.6, 169.5 ($CO_2$, C-1), 158.4, 156.0 (C-4a, C Ar), 153.8 (C Ar), 132.8 (C Ar), 129.8 (C Ar), 127.2 (C Ar), 125.7 (q, *J* = 283.6 Hz, 1C, $CF_3$), 125.3 (C Ar), 124.0 (q, *J* = 271.4 Hz, 1C, $CF_3$), 123.6 (C Ar), 122.5 (C Ar), 118.8 (q, *J* = 5.4 Hz, 1C, C Ar), 117.0 (q, *J* = 29.7 Hz, 1C, C Ar), 113.8 (C Ar), 110.6 (C Ar), 97.2 (C-4), 56.8 ($OCH_3$), 53.9 (q, *J* = 21.6 Hz, 1C, C-10), 52.8, 49.7, 47.5, 36.4 (C-3, C-3a, C-9b, C-10a) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C): δ -61.0, -66.1 ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1701 ($CO_2H$), 1598 (N-C=O). MS (ESI): *m/z* = 514 $[M+H]^+$. Anal. Calcd for $C_{24}H_{17}F_6NO_5$: C, 56.15; H, 3.34; N, 2.73; Found: C, 56.37; H, 3.47; N, 2.48.

**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-10-Methyl-2-(3-methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20e) and (3a*RS*,9b*SR*,10*RS*,10a*SR*)-10a-Methyl-2-(3-methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (21e).** Contains around 9% of an impurity of the regioisomer **21e**. NMR data are presented for the major regioisomer **20e**, IR, HRMS and elemental analysis data – for a mixture **20e** / **21e**. Yield: 0.06 g (33%); colorless powder. M.p. 238-240 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.87 (br.s, 1H, $CO_2H$), 7.45 (s, 1H, H Ar), 7.40-7.24 (m, 4H, H Ar), 7.10-7.07 (m, 2H, H Ar), 6.95 (d, *J* = 7.6 Hz, 1H, H Ar), 5.71 (br.s, 1H, H-4), 4.32 (br.s, 1H, H-9b), 4.06 (t, *J* = 8.3 Hz, 1H, H-3A), 3.73 (t, *J* = 9.5 Hz, 1H, H-3B), 3.06-3.01 (m, 1H, H-3a) 2.31 (s, 3H, $CH_3$), 2.19 (d, *J* = 12.2 Hz, 1H, H-10a), 1.01 (s, 3H, $CH_3$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 177.2, 171.6 ($CO_2$, C-1), 158.7, 156.9 (C-4a, C Ar), 140.2 (C Ar), 138.3 (C Ar), 129.3 (C Ar), 129.0 (C Ar), 126.3 (C Ar),

125.3 (C Ar), 124.9 (C Ar), 122.7 (C Ar), 120.2 (C Ar), 116.8 (C Ar), 110.5 (C Ar), 98.8 (C-4), 58.8, 50.2, 49.6, 42.8, 35.8 (C-3, C-3a, C-9b, C-10, C-10a), 22.8 ($CH_3$), 21.7 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1694 ($CO_2H$), 1661 (N-C=O). HRMS (ESI): calcd. for $C_{23}H_{21}NO_4$, $[M+H]^+$, 376.1554; found, 376.1543 (Δ = 2.92 ppm); calcd. for $C_{23}H_{21}NO_4$, $[M+Na]^+$, 398.1374; found, 398.1363 (Δ = 2.77 ppm). Anal. Calcd for $C_{23}H_{21}NO_4$: C, 73.58; H, 5.64; N, 3.73; Found: C, 73.22; H, 5.21; N, 3.68.

**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-2-(4-Fluorophenyl)-10-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20f) and (3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-fluorophenyl)-10a-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (21f).** Contains around 17% on an impurity of regioisomer **21f**. NMR, IR, HRMS and elemental analysis data are presented for a mixture **20f** / **21f**. Yield: 0.11 g (57%); yellow powder. M.p. 243-245 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 7.65 (dd, *J* = 9.1, 4.5 Hz, 0.4H, H Ar), 7.62 (dd, *J* = 9.1, 5.1 Hz, 2H, H Ar), 7.38 (d, *J* = 7.6 Hz, 0.2H, H Ar), 7.30-7.20 (m, 4.6H, H Ar), 7.09 (t, *J* = 7.1 Hz, 0.4H, H Ar), 7.08 (t, *J* = 8.1 Hz, 2H, H Ar), 5.70 (t, *J* = 3.5 Hz, 1H, H-4), 5.51 (t, *J* = 3.5 Hz, 0.2H, H-4), 4.31 (br.s., 1H, H-9b), 4.17 (br.s., 0.2H, H-9b), 4.07 (t, *J* = 8.1 Hz, 1H, H-3A), 4.02 (dd, *J* = 9.1, 7.6 Hz, 0.2H, H-3A), 3.84 (t, *J* = 11.6, 9.1 Hz, 0.2H, H-3B), 3.73 (t, *J* = 10.6, 9.1 Hz, 1H, H-3B), 3.22-3.18 (m, 0.2H, H-3a), 3.06-3.01 (m, 1H, H-3a), 2.55 (d, *J* = 6.1 Hz, 0.2H, H-10), 2.19 (d, *J* = 12.1 Hz, 1H, H-10a), 1.00 (s, 3H, $CH_3$), 0.79 (s, 0.6H, $CH_3$) (the $CO_2H$-group signal was not detected) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 177.2, 175.6, 175.5, 171.7 ($CO_2$, C-1), 159.0 (d, *J* = 241.3 Hz, 0.2C, C Ar), 158.9 (d, *J* = 241.3 Hz, 1C, C Ar), 158.7, 157.9, 157.4, 156.9 (C-4a, C Ar), 136.7 (1.2C, C Ar), 129.4, 129.3 (C Ar), 129.1, 126.4 (C Ar), 125.4, 124.6 (C Ar), 123.2, 122.8 (C Ar), 121.9 (d, *J* = 8.7 Hz, 0.4C, C Ar), 121.6 (d, *J* = 8.7 Hz, 2C, C Ar), 115.8 (d, *J* = 23.1 Hz, 0.4C, C Ar), 115.7 (d, *J* = 21.7 Hz, 2C, C Ar), 110.6, 110.5 (C Ar), 98.8, 95.5 (C-4), 58.7 (1.2C), 50.9, 50.4, 49.7, 48.6, 44.0, 42.9, 37.9, 35.9 (C-3, C-3a, C-9b, C-10, C-10a), 22.8, 19.3 ($CH_3$) ppm. $^{19}$F NMR (564.7 MHz, DMSO-$d_6$, 25 °C) δ -118.4, -118.7 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1764 ($CO_2H$), 1685 (N-C=O). HRMS (ESI): calcd. for for $C_{22}H_{18}FNO_4$, $[M+H]^+$, 380.1307; found, 380.1293 (Δ = 3.68 ppm); calcd. for $C_{22}H_{18}FNO_4$, $[M+Na]^+$, 402.112; found, 402.1112 (Δ = 1.99 ppm). Anal. Calcd for $C_{22}H_{18}FNO_4$: C, 69.65; H, 4.78; N, 3.69; Found: C, 69.39; H, 4.57; N, 3.39.

**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-2-(4-Bromophenyl)-10-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20g).** Yield: 0.07 g (32%); yellow powder. M.p. 245-247 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) 7.59 (d, *J* = 8.6 Hz,

2H, H Ar), 7.56 (d, *J* = 8.6 Hz, 2H, H Ar), 7.30-7.25 (m, 2H, H Ar), 7.07-7.07 (m, 2H, H Ar), 5.70 (br.s., 1H, H-4), 4.31 (br.s., 1H, H-9b), 4.08 (t, *J* = 8.1 Hz, 1H, H-3A), 3.71 (dd, *J* =10.1, 9.6 Hz, 1H, H-3B), 3.06-3.00 (m, 1H, H-3a), 2.21 (d, *J* = 12.6 Hz, 1H, H-10a), 1.00 (s, 3H, $CH_3$) ppm (the $CO_2H$-group signal was not detected). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 177.2, 172.0 ($CO_2$, C-1), 158.7, 157.0 (C-4a, C Ar) , 139.6 (C Ar), 132.0 (2C, C Ar), 129.4 (C Ar), 126.4 (C Ar), 125.4 (C Ar), 122.8 (C Ar), 121.5 (2C, C Ar), 116.1 (C Ar), 110.6 (C Ar), 98.8 (C-4), 58.7, 50.1, 49.7, 42.9, 35.7 (C-3, C-3a, C-9b, C-10, C-10a), 22.8 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1740 ($CO_2H$), 1665 (N-C=O). MS (ESI): *m/z* = 440 [M+H, $Br^{79}$]$^+$, 442 [M+H, $Br^{81}$]$^+$. Anal. Calcd for $C_{22}H_{18}BrNO_4$: C, 60.02; H, 4.12; N, 3.18; Found: C, 60.12; H, 4.27; N, 3.29.

**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-2-(3,5-Dimethylphenyl)-10-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20h) and (3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3,5-dimethylphenyl)-10a-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (21h).** Contains around 8% of an impurity of the regioisomer **21h**. NMR data are presented for the major regioisomer **20h**, IR, LCMS and elemental analysis data for a mixture **20h** / **21h**. Yield: 0.07 g (35%); yellow powder. M.p. 247-249 °C. $^1H$ NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 7.30-7.22 (m, 4H, H Ar), 7.09-7.06 (m, 2H, H Ar), 6.76 (s, 1H, H Ar), 5.69 (t, *J* = 3.5 Hz, 1H, H-4), 4.31 (br.s, 1H, H-9b), 4.02 (dd, *J* = 8.6, 7.6 Hz, 1H, H-3A), 3.69 (dd, *J* = 10.1, 9.6 Hz, 1H, H-3B), 3.03-2.98 (m, 1H, H-3a), 2.26 (s, 6H, $CH_3$), 2.14 (d, *J* = 12.6 Hz, 1H, H-10a), 0.99 (s, 3H, $CH_3$) ppm (the $CO_2H$-group signal was not detected). $^{13}C$ NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 177.3, 171.6 ($CO_2$, C-1), 158.7, 156.9 (C-4a, C Ar), 140.2 (C Ar), 138.2 (2C, C Ar), 129.3 (C Ar), 126.4 (C Ar), 125.8 (C Ar), 125.4 (C Ar), 122.8 (C Ar), 117.6 (2C, C Ar), 110.6 (C Ar), 98.8 (C-4), 58.9, 50.3, 49.7, 42.9, 35.9 (C-3, C-3a, C-9b, C-10, C-10a), 22.8 ($CH_3$), 21.7 (2C, $CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1739 ($CO_2H$), 1667 (N-C=O). MS (ESI): *m/z* = 390 [M+H]$^+$. Anal. Calcd for $C_{24}H_{23}NO_4$: C, 74.02; H, 5.95; N, 3.60; Found: C, 74.22; H, 6.09; N, 3.88.

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-3a-Methyl-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (21i) and (3a*RS*,4*RS*,4a*RS*,10a*SR*)-4-methyl-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (20i).** Contains around 12% of an impurity of the regioisomer **20i**. NMR data are presented for the major regioisomer **21i**, IR, LCMS and elemental analysis data for a mixture **20i** / **21i**.Yield: 0.06 g (35%); yellow powder. M.p. 238-240 °C. $^1H$ NMR (600.2 MHz, DMSO-$d_6$, 25

°C) δ 7.61-7.58 (m, 3H, H Ar), 7.35 (t, *J* = 7.6 Hz, 2H, H Ar), 7.23 (t, *J* = 7.6 Hz, 1H, H Ar), 7.11 (t, *J* = 7.6 Hz, 1H, H Ar), 6.97-6.93 (m, 2H, H Ar), 6.41 (t, *J* = 3.5 Hz, 1H, H-10), 5.23 (t, *J* = 5.1 Hz, 1H, H-4a), 4.04 (dd, *J* = 9.1, 8.1 Hz, 1H, H-1A), 3.90 (dd, *J* = 11.1, 9.6 Hz, 1H, H-1B), 3.17-3.13 (m, 1H, H-10a), 2.54 (d, *J* = 5.1 Hz, 1H, H-4), 0.82 (s, 3H, $CH_3$) ppm (the $CO_2H$-group signal was not detected). $^{13}$C NMR (150.9 MHz, DMSO-*d*$_6$, 25 °C) δ 175.1, 174.9 ($CO_2$, C-3), 162.5 (C Ar), 140.3 (C Ar), 139.4 (C-10), 130.8 (C Ar), 129.2 (2C, C Ar), 124.6 (C Ar), 123.8 (C Ar), 122.1 (C Ar), 122.0 (C Ar), 120.0 (2C, C Ar), 114.6 (C-9b), 111.1 (C Ar), 85.1 (C-4a), 52.0, 48.4, 48.2, 44.5 (C-1, C-3a, C-4, C-10a), 19.9 ($CH_3$) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1755 ($CO_2H$), 1670 (N-C=O). MS (ESI): *m/z* = 362 $[M+H]^+$. Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88; Found: C, 73.33; H, 5.65; N, 3.97.

**General Procedure for the Synthesis of Products 23a-j and Characterization Data.** To a suspension of benzofuro[2,3-*f*]isoindolecarboxylic acids **10a**,**d**,**f**, **19a-c**, **20b**,**d** (0.250 mmol) in DCE (10 mL) was added an equimolar volume of HCl in dioxane (5.0 mol/L; 0.250 mmol, 0.0045 mL) and stirred for 30 min. The crystalline phase is filtered off, washed with pentane, and dried in vacuo.

**(3a*RS*,10*SR*,10a*SR*)-1-Oxo-2-phenyl-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23a).** Yield: 0.06 g (72%); colorless powder. M.p. > 250 °C. $^1$H NMR (700.2 MHz, DMSO-*d*$_6$, 25 °C) δ 12.79 (br.s, 1H, $CO_2H$), 7.72-7.68 (m, 3H, H Ar), 7.55-7.54 (m, 1H, H Ar), 7.41 (t, *J* = 7.6 Hz, 2H, H Ar), 7.30-7.27 (m, 2H, H Ar), 7.15 (t, *J* = 7.6 Hz, 1H, H Ar), 4.12 (d, *J* = 4.2 Hz, 1H, H-10), 4.06 (t, *J* = 7.9 Hz, 1H, H-3A), 3.78 (t, *J* = 9.8 Hz, 1H, H-3B), 3.34-3.26 (m, 1H, H-3a), 3.11 (dd, *J* = 16.0, 5.0 Hz, 1H, H-4A), 2.97 (dd, *J* = 13.1, 5.3 Hz, 1H, H-10a), 2.88 (dd, *J* = 15.3, 11.9 Hz, 1H, H-4B) ppm. $^{13}$C NMR (150.9 MHz, DMSO-*d*$_6$, 25 °C) δ 172.7, 172.6 ($CO_2$, C-1), 155.2 (C Ar), 154.8 (C Ar), 140.2 (C Ar), 129.2 (2C, C Ar), 127.6 (C Ar), 124.4 (C Ar), 124.2 (C Ar), 123.3 (C Ar), 120.4 (C Ar), 119.4 (2C, C Ar), 111.9 (C Ar), 111.5 (C Ar), 51.5, 47.8 (C-3, C-10a), 36.5, 32.4, 27.1 (C-3a, C-4, C-10) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1704 ($CO_2H$), 1612 (N-C=O). MS (ESI): *m/z* = 348 $[M+H]^+$. Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03; Found: C, 72.49; H, 4.81; N, 3.84.

**Attempts to "aromatize" acid 10a. Method A.** Trifluoroacetic acid (TFA) (10 mol%) was added to a stirred suspension of "non-aromatic" benzofuroisoindolecarboxylic acid **10a** (30.0 mg, 0.086 mmol) in dry DCE (5 mL). The mixture became homogeneous within 10 minutes at room temperature. The reaction was allowed to proceed for 24 hours. Subsequently, the volatiles were removed in vacuo, and the crude residue is diluted with ether (5 mL), filtered off, washed

with PhH (5 mL), and dried in vacuo. The crystalline phase 21 mg (70%) was directly analyzed by NMR spectroscopy to assess the conversion and the formation of the aromatized product - mixture of **10a**/**23a** (82/18) was observed.

**Method B.** Boron trifluoride diethyl etherate (0.086 mmol, 1.0 equiv.) was added to a stirred suspension of "non-aromatic" benzofuroisoindolecarboxylic acid **10a** (30.0 mg, 0.086 mmol, 1 equiv.) in dry DCE (5 mL). The heterogeneous mixture was stirred at room temperature for 24 hours. The solid was then collected by vacuum filtration, washed with a small portion of cold DCE (1 mL), and dried in vacuo to afford 22 mg (73%) of a **23a**.

**Method C.** *Conc*. sulfuric acid (1 drop, ~ 0.02 mL) was addes to a stirred suspension of "non-aromatic" benzofuroisoindolecarboxylic acid **10a** (30.0 mg, 0.086 mmol) in anhydrous benzene (5 mL). The reaction mixture was stirred at room temperature for 24 hours. . The solid was then collected by vacuum filtration, washed with a small portion of cold ether (5 mL), and dried in vacuo to afford 20 mg (67%) of a **23a** contained an impurity of **10a**.

**Method D.** Tetrafluoroboric acid diethyl ether complex (0.086 mmol, 1.0 equiv.) was added to a stirred suspension of "non-aromatic" benzofuroisoindolecarboxylic acid **10a** (30.0 mg, 0.086 mmol, 1 equiv.) in dry DCE (5 mL). The heterogeneous mixture was stirred at room temperature for 24 hours. The solid was then collected by vacuum filtration, washed with a small portion of cold DCE (1 mL), and dried in vacuo to afford 15 mg (50%) of a **23a**.

**(3a*RS*,10*SR*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23b).** Yield: 0.07 g (80%); colorless powder. M.p. > 250°C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 7.71 (d, $J$ = 7.6 Hz, 1H, H Ar), 7.53 (d, $J$ = 7.9 Hz, 1H, H Ar), 7.36 (br.s, 1H, H Ar), 7.31-7.25 (m, 3H, H Ar), 7.20 (d, $J$ = 7.9 Hz, 1H, H Ar), 6.73 (d, $J$ = 8.0 Hz, 1H, H Ar), 4.09 (d, $J$ = 4.5 Hz, 1H, H-10), 4.06 (t, $J$ = 8.1 Hz, 1H, H-3A), 3.76-3.73 (m, 4H, $OCH_3$, H-3B), 3.30-3.23 (m, 1H, H-3a), 3.09 (dd, $J$ = 16.1, 5.0 Hz, 1H, H-4A), 2.96 (dd, $J$ = 13.1, 5.0 Hz, 1H, H-10a), 2.85 (dd, $J$ = 15.1, 12.1 Hz, 1H, H-4B) ppm (the $CO_2H$-group signal was not detected). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 172.7 (2C, $CO_2$, C-1), 160.0 (C Ar), 155.2 (C Ar), 154.7 (C Ar), 141.4 (C Ar), 130.0 (C Ar), 127.6 (C Ar), 124.4 (C Ar), 123.3 (C Ar), 120.4 (C Ar), 111.9 (C Ar), 111.6 (C Ar), 111.5 (C Ar), 109.6 (C Ar), 105.4 (C Ar), 55.6 ($OCH_3$), 51.6, 47.9 (C-3, C-10a), 36.5, 32.2, 27.1 (C-3a, C-4, C-10) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1699 ($CO_2H$), 1600 (N-C=O). HRMS (ESI): calcd. for $C_{22}H_{19}NO_5$, $[M+H]^+$, 378.1338; found, 378.1336 (Δ = 0.53 ppm); calcd. for $C_{22}H_{19}NO_5$,

$[M+Na]^+$, 400.1155; found, 400.1155 (Δ = 0 ppm). Anal. Calcd for $C_{22}H_{19}NO_5$: C, 70.02; H, 5.07; N, 3.71; Found: C, 70.22; H, 5.15; N, 3.95.

**(3a*RS*,10*SR*,10a*SR*)-2-(4-Methylphenyl)-1-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23c).** Yield: 0.07 g (83%); colorless powder. M.p. > 250 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 7.70-7.69 (m, 1H, H Ar), 7.56-7.53 (m, 3H, H Ar), 7.29-7.26 (m, 2H, H Ar), 7.19 (d, *J* = 8.6 Hz, 2H, H Ar), 4.09 (br.d, *J* = 4.0 Hz, 1H, H-10), 4.01 (t, *J* = 8.6 Hz, 1H, H-3A), 3.75 (t, *J* = 10.1 Hz, 1H, H-3B), 3.30-3.22 (m, 1H, H-3a), 3.09 (dd, *J* = 16.1, 5.0 Hz, 1H, H-4A), 2.94 (dd, *J* = 13.1, 5.5 Hz, 1H, H-10a), 2.85 (dd, *J* = 15.1, 11.6 Hz, 1H, H-4B), 2.28 (s, 3H, $CH_3$) ppm (the $CO_2H$-group signal was not detected). $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 172.7, 172.4 ($CO_2$, C-1), 155.4 (C Ar), 154.8 (C Ar), 137.8 (C Ar), 133.3 (C Ar), 129.7 (2C, C Ar), 127.6 (C Ar), 124.4 (C Ar), 123.3 (C Ar), 120.4 (C Ar), 119.5 (2C, C Ar), 112.0 (C Ar), 111.5 (C Ar), 51.7, 47.8 (C-3, C-10a), 36.5, 32.5, 27.2 (C-3a, C-4, C-10), 20.9 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1660 ($CO_2H$), 1613 (N-C=O). HRMS (ESI): calcd. for $C_{22}H_{19}NO_4$, $[M+H]^+$, 362.1387; found, 362.1387 (Δ = 0 ppm); calcd. for $C_{22}H_{19}NO_4$, $[M+Na]^+$, 384.1214; found, 384.1206 (Δ = 2.08 ppm). Anal. Calcd for $C_{22}H_{19}NO_4$: C, 73.12; H, 5.30; N, 3.88; Found: C, 73.33; H, 5.45; N, 3.99.

**(3a*RS*,4*RS*,10a*SR*)-3-Oxo-2-phenyl-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (23d).** Maleic anhydride (49 mg, 0.5 mmol) was added to the allylamine **15a** (124.5 mg, 0.5 mmol) diluted in PhH (5 mL). The resulting mixture was heated at reflux for 4 h and then cooled to room temperature. The resulting precipitate was filtered off, washed with PhH (5 mL), $Et_2O$ (2 × 5 mL), and air dried to give the intermediate acid **22** as colorless solid. To a suspension of the obtained acid **22** in DCE (10 mL) was added an equimolar volume of HCl in dioxane (0.5 mmol) and stirred for 30 min. The crystalline phase was filtered off, washed with pentane, and dried in vacuo. Yield: 0.15 g (87%); colorless powder. M.p. 245-246 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.93 (br.s, 1H, $CO_2H$), 7.68 (d, *J* = 8.1 Hz, 2H, H Ar), 7.60-7.57 (m, 2H, H Ar), 7.40 (t, *J* = 7.9 Hz, 2H, H Ar), 7.32 (t, *J* = 7.6 Hz, 1H, H Ar), 7.27 (t, *J* = 7.6 Hz, 1H, H Ar), 7.14 (t, *J* = 7.6 Hz, 1H, H Ar), 4.17 (br.d, *J* = 4.8 Hz, 1H, H-4), 4.08 (t, *J* = 7.9 Hz, 1H, H-1A), 3.79 (t, *J* = 9.5 Hz, 1H, H-1B), 3.20-3.13 (m, 1H, H-10a), 3.11 (dd, *J* = 13.1, 5.3 Hz, 1H, H-3a), 3.02 (dd, *J* = 15.0, 4.5 Hz, 1H, H-10A), 2.61 (dd, *J* = 14.3, 11.4 Hz, 1H, H-10B) ppm. $^{13}$C NMR (176.0 MHz, DMSO-$d_6$, 25 °C) δ 171.8, 170.6 ($CO_2$, C-3), 154.4 (C Ar), 149.9 (C Ar), 139.7 (C Ar), 128.7 (2C, C Ar), 127.3 (C Ar), 124.5 (C Ar), 123.8 (C Ar), 122.8 (C Ar), 119.3 (C Ar), 119.0 (2C, C Ar), 115.7 (C Ar), 111.2 (C Ar), 51.2, 47.9, 45.1

(C-1, C-3a, C-4), 32.3, 22.9 (C-10, C-10a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1752 ($CO_2H$), 1649 (N-C=O). HRMS (ESI): calcd. for $C_{21}H_{17}NO_4$, $[M+H]^+$, 348.1227; found, 348.123 (Δ = 0.86 ppm); calcd. for $C_{21}H_{17}NO_4$, $[M+Na]^+$, 370.1049; found, 370.105 (Δ = 0.27 ppm). Anal. Calcd for $C_{21}H_{17}NO_4$: C, 72.61; H, 4.93; N, 4.03; Found: C, 72.83; H, 5.13; N, 4.33.

**(3a*RS*,4*RS*,10a*SR*)-3-Oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (23e).** Yield: 0.09 g (86%); colorless powder. M.p. > 250 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 13.01 (br.s, 1H, $CO_2H$), 7.93 (m, *J* = 8.6 Hz, 2H, H Ar), 7.78 (m, *J* = 8.6 Hz, 2H, H Ar), 7.61-7.58 (m, 2H, H Ar), 7.33 (t, *J* = 7.4 Hz, 1H, H Ar), 7.28 (t, *J* = 7.4 Hz, 1H, H Ar), 4.21 (br.s, 1H, H-4), 4.18-4.16 (m, 1H, H-1A), 3.85-3.82 (m, 1H, H-1B), 3.20-3.16 (m, 2H, H-3a, H-10a), 3.05 (dd, *J* = 16.0, 3.3 Hz, 1H, H-10A), 2.65-2.61 (m, 1H, H-10B) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 173.0, 171.0 ($CO_2$, C-3), 154.9 (C Ar), 150.2 (C Ar), 143.5 (C Ar), 127.8 (C Ar), 126.5 (2C, C Ar), 125.0 (C Ar), 124.8 (q, *J* = 271.4 Hz, 1C, $CF_3$), 124.1 (q, *J* = 32.4 Hz, 2C, C Ar), 123.3 (C Ar), 119.8 (C Ar), 119.3 (C Ar), 116.1 (C Ar), 111.7 (C Ar), 51.6, 48.3, 40.4 (C-1, C-3a, C-4), 32.6, 23.3 (C-10, C-10a) ppm. $^{19}$F NMR (564.7 MHz, DMSO-$d_6$, 25 °C) δ -60.34 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1750 ($CO_2H$), 1660 (N-C=O). HRMS (ESI): calcd. for $C_{22}H_{16}F_3NO_4$, $[M+H]^+$, 416.1074; found, 416.1104 (Δ = 2.73 ppm); calcd. for $C_{22}H_{16}F_3NO_4$, $[M+Na]^+$, 438.0928; found, 438.0924 (Δ = 2.58 ppm). Anal. Calcd for $C_{22}H_{16}F_3NO_4$: C, 63.62; H, 3.88; N, 3.37; Found: C, 63.84; H, 3.93; N, 3.63.

**(3a*RS*,4*RS*,10a*SR*)-2-(4-Fluorophenyl)-3-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (23f).** Yield: 0.08 g (86%); colorless powder. M.p. > 250 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 12.95 (br.s, 1H, $CO_2H$), 7.70 (dd, *J* = 9.1, 5.0 Hz, 2H, H Ar), 7.60-7.57 (m, 2H, H Ar), 7.32 (dt, *J* = 8.1, 1.5 Hz,1H, H Ar), 7.28-7.23 (m, 3H, H Ar), 4.17 (dd, *J* = 5.1, 1.5 Hz, 1H, H-4), 4.06 (dd, *J* = 8.6, 7.1 Hz, 1H, H-1A), 3.78 (t, *J* = 9.6 Hz, 1H, H-1B), 3.20-3.13 (m, 1H, H-10a), 3.09 (dd, *J* = 13.1, 5.5 Hz, H-3a), 3.01 (dd, *J* = 15.1, 4.5 Hz, 1H, H-10A), 2.60 (ddd, *J* = 15.1, 10.6, 1.5 Hz, 1H, H-10B) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 172.3, 171.1 ($CO_2$, C-3), 158.9 (d, *J* = 241.3 Hz, 1C, C Ar), 155.0 (C Ar), 150.4 (C Ar), 136.7 (C Ar), 127.9 (C Ar), 125.0 (C Ar), 123.4 (C Ar), 121.5 (d, *J* = 8.7 Hz, 2C, C Ar), 119.8 (C Ar), 116.2 (C Ar), 115.9 (d, *J* = 21.7 Hz, 2C, C Ar), 111.8 (C Ar), 52.0, 48.3, 45.6 (C-1, C-3a, C-4), 32.8, 23.4 (C-10, C-10a) ppm. $^{19}$F NMR (564.7 MHz, DMSO-$d_6$, 25 °C) δ -118.6 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1753 ($CO_2H$), 1660 (N-C=O). HRMS (ESI): calcd. for $C_{21}H_{16}FNO_4$, $[M+H]^+$, 366.1146; found, 366.1136 (Δ = 2.73 ppm); calcd. for $C_{21}H_{16}FNO_4$,

$[M+Na]^+$, 388.0966; found, 388.0956 (Δ = 2.58 ppm). Anal. Calcd for $C_{21}H_{16}FNO_4$: C, 69.04; H, 4.41; N, 3.83; Found: C, 69.24; H, 4.65; N, 3.93.

**(3a*RS*,10*RS*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-10-(trifluoromethyl)-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23g).** Yield: 0.10 g (89%); colorless powder. M.p. 250 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 13.97 (br.s, 1H, $CO_2H$), 7.60 (t, *J* = 8.1 Hz, 2H, H Ar), 7.37 (s, 1H, H Ar), 7.34-7.28 (m, 3H, H Ar), 7.16 (d, *J* = 8.1 Hz, 1H, H Ar), 6.74 (d, *J* = 8.1 Hz, 1H, H Ar), 3.98 (t, *J* = 8.1 Hz, 1H, H-3A), 3.87 (t, *J* = 9.6 Hz, 1H, H-3B), 3.76 (s, 3H, $CH_3$), 3.48 (d, *J* = 12.6 Hz, 1H, H-10a), 3.14-3.00 (m, 3H, H-3a, H-4) ppm. $^{13}$C NMR (176.10 MHz, DMSO-$d_6$, 25 °C) δ 170.2, 167.9 ($CO_2$, C-1), 160.0 (C Ar), 158.2 (C Ar), 154.6 (C Ar), 141.3 (C Ar), 130.1 (C Ar), 126.1 (q, *J* = 283.6 Hz, 1C, $CF_3$), 125.9 (C Ar), 124.8 (C Ar), 123.8 (C Ar), 121.1 (C Ar), 111.9 (C Ar), 111.5 (C Ar), 110.0 (C Ar), 109.2 (C Ar), 105.4 (C Ar), 55.6 ($OCH_3$), 52.3 (q, *J* = 27.0 Hz, 1C, C-10), 50.2, 48.9 (C-3, C-10a), 35.9, 26.7 (C-3a, C-4) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -66.8 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1756 ($CO_2H$), 1669 (N-C=O). HRMS (ESI): calcd. for $C_{23}H_{18}F_3NO_5$, $[M+H]^+$, 446.1217; found, 446.121 (Δ = 1.57 ppm); calcd. for $C_{23}H_{18}F_3NO_5$, $[M+Na]^+$, 468.1039; found, 468.1029 (Δ = 2.14 ppm). Anal. Calcd for $C_{23}H_{18}F_3NO_5$: C, 62.02; H, 4.07; N, 3.14; Found: C, 69.13; H, 4.35; N, 3.33.

**(3a*RS*,10*RS*,10a*SR*)-2-[4-Methoxy-3-(trifluoromethyl)phenyl]-1-oxo-10-(trifluoromethyl)-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23h).** Yield: 0.11 g (90%); colorless powder. M.p. 270 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 13.99 (br.s, 1H, $CO_2H$), 8.06 (d, *J* = 2.5 Hz, 1H, H Ar), 7.72 (dd, *J* = 9.1, 2.5 Hz, 1H, H Ar), 7.61-7.59 (m, 2H, H Ar), 7.34-7.28 (m, 3H, H Ar), 3.98 (dd, *J* = 8.6, 6.6 Hz, 1H, H-3A), 3.92-3.89 (m, 4H, H-3B, CH3), 3.48 (d, *J* = 12.6 Hz, 1H, H-10a), 3.15-3.11 (m, 2H, H-4A, H-3a), 3.02 (dd, *J* = 16.6, 12.6 Hz, 1H, H-4B) ppm. $^{13}$C NMR (176.0 MHz, DMSO-$d_6$, 25 °C) δ 170.2, 167.8 ($CO_2$, C-1), 158.2 (C Ar), 154.6 (C Ar), 153.8 (C Ar), 132.8 (C Ar), 126.0 (q, *J* = 283.6 Hz, 1C, $CF_3$), 125.8 (C Ar), 125.0 (C Ar), 124.8 (C Ar), 124.0 (q, *J* = 272.7 Hz, 1C, $CF_3$), 123.8 (C Ar), 121.1 (C Ar), 118.4 (q, *J* = 4.1 Hz, 1C, C Ar), 117.1 (q, *J* = 31.1 Hz, 1C, C Ar), 113.7 (C Ar), 111.9 (C Ar), 109.1 (C Ar), 56.8 ($OCH_3$), 52.3 (q, *J* = 27.0 Hz, 1C, C-10), 50.3, 48.6 (C-3, C-10a), 36.1, 26.7 (C-3a, C-4) ppm. $^{19}$F NMR (658.8 MHz, DMSO-$d_6$, 25 °C) δ -60.9, -66.8 ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1757 ($CO_2H$), 1673 (N-C=O). HRMS (ESI): calcd. for $C_{24}H_{17}F_6NO_5$, $[M+H]^+$, 514.1095; found, 514.1084 (Δ = 2.14 ppm); calcd. for $C_{24}H_{17}F_6NO_5$, $[M+Na]^+$, 536.0915; found,

536.0903 (Δ = 2.24 ppm). Anal. Calcd for $C_{24}H_{17}F_6NO_5$: C, 56.15; H, 3.34; N, 2.73; Found: C, 56.23; H, 3.55; N, 2.93.

**General Procedure for the Synthesis of 2-Bromocycloalk-1-ene-1-carbaldehydes 24a-e.** A solution of DMF (3.87 mL, 50 mmol) in anhydrous $CHCl_3$ (15 mL) was placed in a 100 mL three necked flask. The resulting reaction mixture was stirred while cooling to 0 °C. Then $PBr_3$ (1.9 mL, 20 mmol) was added dropwise over 10 min. The resulting white suspension was warmed to room temperature and stirred for 30 min. A solution of a carbonyl compound (10 mmol) dissolved in $CHCl_3$ (15 mL) was added dropwise and the resulting reaction mixture was stirred for 12 h at r.t. Then the reaction mixture was poured into ice water (50 mL) and neutralized with $NaHCO_3$. The mixture was extracted with DCM (3 × 15 mL). The organic layer was further dried over anhyd. $Na_2SO_4$. The solvent was evaporated under reduced pressure to constant weight of the residue. Compounds **24a-e** were used in the next step without further purification.

**2-Bromocyclopent-1-ene-1-carbaldehyde (24a):** Yield: 1.00 g (60 %); orange oil.

**2-Bromocyclohex-1-ene-1-carbaldehyde (24b):** Yield: 1.19 g (63 %); orange oil.

**2-Bromocyclohept-1-ene-1-carbaldehyde (24c)**: Yield: 1.09 g (54 %); orange oil.

**2-Bromocyclooct-1-ene-1-carbaldehyde (24d):** Yield: 1.67 g (77 %); orange oil.

**1-Bromo-3,4-dihydronaphthal-2-ene-2-carbaldehyde (24e):** Yield: 2.22 g (94 %); brown oil.

**General Procedure for Synthesis of Products 25a-h (Method A).** In a 50 mL Schlenk flask, bromaldehyde **24a-e** (9.8 mmol) was dissolved in a mixture of ethanol (30 mL) and toluene (30 mL). Then the corresponding boronic acid (19.6 mmol) and 2 M sodium carbonate aqua solution (5 mL) was degassed with constant stirring in an argon atmosphere for 10 min. Then 0.57 g (0.49 mmol) of tetrakis(triphenylphosphine)palladium was added, the mixture was heated at 110 °C for 6 h in an argon atmosphere. Once the reaction was complete (TLC control), water (50 mL) was added and the mixture was extracted with ethyl acetate (3 × 10 mL). The organic phase was dried over anhyd. $Na_2SO_4$, filtered off and evaporated under reduced pressure. After column chromatography ($SiO_2$, 20 × 1.5 cm), carbocycloacroleins **25a-h** were isolated as light-yellow oils in yields given below.

**General Procedure for the Synthesis of Products 25e,f in a Continuous Flow Reactor (Method B).** In a 50 mL round-bottomed flask, 2-bromocyclocarbaldehyde **24b**,**c** (1 mmol, 0.025mol/L) and 2-furanylboronic acid (1.2 mmol) were dissolved in the 1:1 *v*/*v* mixture of water (20 mL) and ethanol (20 mL), and $Na_2CO_3$ (1.2 eq.) was added. The resulting reaction mixture

was introduced in a flow reactor ThalesNano H-Cube® (without hydrogen) at 120 °C with a 1.0 mL/min flow rate pumping. A commercially available cartridge FibreCat 1001 was used as a catalyst, through which the reaction mixture flowed. The total reaction time was ~ 40 min at this flow rate. The resulting reaction mixture was controlled by GCMS to analyze the conversion of the starting 2-bromocyclocarbaldehyde **24b**,**c**. The resulting reaction mixture was evaporated at low pressure and the remaining water phase was extracted with ethyl acetate (3 × 20 mL), dried over anhyd. $Na_2SO_4$, filtered off and evaporated under reduced pressure. After column chromatography ($SiO_2$, 20 × 1.5 cm), carbocycloacroleins **25e**,**f** were isolated as light-yellow oils in the yields given below.

**2-(Furan-2-yl)cyclopent-1-ene-1-carbaldehyde (25a).** Eluent: EtOAc/heptane (1:100). Yield: 0.87 g (55%); yellow oil. $R_f$ 0.49 (EtOAc/hexane, 1:6). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 10.58 (s, 1H, CHO), 7.58 (br.d, *J* = 1.4 Hz, 1H, H-5 Fur), 6.61 (d, *J* = 3.3 Hz, 1H, H-3 Fur), 6.51 (dd, *J* = 3.3, 1.9 Hz, 1H, H-4 Fur), 2.94-2.91 (m, 2H, $CH_2$), 2.75 (br.t, *J* = 7.6 Hz, 2H, $CH_2$), 1.97 (pent, *J* = 7.6, 2H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 191.2 (CHO), 151.0 (C Ar), 145.3 (C Ar), 144.8 (C-2), 137.4 (C-1), 114.0 (C Ar), 111.8 (C Ar), 36.0 ($CH_2$), 31.1 ($CH_2$), 21.6 ($CH_2$) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1652 (CHO). HRMS (ESI): calcd. for $C_{10}H_{10}O_2$, $[M-H]^+$, 163.0754; found, 163.0755, (Δ = 0.78 ppm). MS (ESI): *m/z* = 163 $[M+H]^+$.

**2-(Furan-3-yl)cyclopent-1-ene-1-carbaldehyde (25b).** Eluent: EtOAc/heptane (1:100). Yield: 0.71 g (45%); yellow oil. $R_f$ 0.51 (EtOAc/hexane, 1:6). $^1$H NMR (600.2 MHz, $CDCl_3$, 37 °C) δ 10.16 (s, 1H, CHO), 7.65 (br.s, 1H, H-2 Fur), 7.50-7.49 (m, 1H, H-5 Fur), 6.60 (br.d, *J* = 1.0 Hz, 1H, H-4 Fur), 2.92-2.89 (m, 2H, $CH_2$), 2.74-2.71 (m, 2H, $CH_2$), 1.98 (pent, *J* = 7.6, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 189.0 (CHO), 151.8 (C-2), 144.1 (C Ar), 142.8 (C Ar), 138.9 (C-1), 120.6 (C Ar), 110.5(C Ar), 38.6 ($CH_2$), 31.1 ($CH_2$), 21.6 ($CH_2$) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1648 (CHO). MS (ESI): *m/z* = 163 $[M+H]^+$. Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.22. Found: C, 74.32; H, 6.07.

**2-(5-Methylfuran-2-yl)cyclopent-1-ene-1-carbaldehyde (25c).** Eluent: EtOAc/heptane (1:100). Yield: 1.29 g (75%); yellow oil. $R_f$ 0.41 (EtOAc/hexane, 1:33). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 10.59 (s, 1H, CHO), 6.51 and 6.11 (2d, *J* = 3.5 Hz, 2H, H-3 Fur and H-4 Fur), 2.89-2.86 (m, 2H, $CH_2$), 2.74-2.72 (m, 2H, $CH_2$), 2.37 (s, 3H, $CH_3$), 1.95 (pent, *J* = 7.6 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 191.4 (CHO), 156.1 (C Ar), 149.7 (C Ar), 145.2 (C-2), 136.2 (C-1), 115.6 (C Ar), 108.3 (C Ar), 35.8 ($CH_2$), 31.1 ($CH_2$), 21.8 ($CH_2$), 14.0 ($CH_3$) ppm.

IR (KBr, $cm^{-1}$): $\nu_{max}$= 1649 (CHO). MS (ESI): *m/z* = 177 $[M+H]^+$. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.56; H, 6.93.

**2-(Benzofuran-2-yl)cyclopent-1-ene-1-carbaldehydecarbaldehyde (25d).** Yield: 1.04 g (50%); yellow oil. $R_f$ 0.47 (EtOAc/hexane, 1:6). $^1H$ NMR (600.2 MHz, $CDCl_3$, 23 °C) δ 10.81 (s, 1H, CHO), 7.62 (d, *J* = 7.6 Hz, 1H, H Ar), 7.49 (d, *J* = 7.6 Hz, 1H, H Ar), 7.38 (dt, *J* = 8.1, 1.5 Hz, 1H, H Ar), 7.27 (dt, *J* = 7.6, 1.0 Hz, 1H, H Ar), 6.93 (s, 1H, H-3 Fur), 3.04-3.01 (m, 2H, $CH_2$), 2.83-2.80 (m, 2H, $CH_2$), 2.06-2.01 (pent, *J* = 7.6 Hz, 2H, $CH_2$) ppm. $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 191.5 (CHO), 155.9 (C Ar), 152.3 (C Ar), 144.4 (C-2), 140.3 (C-1), 127.7 (C Ar), 126.4 (C Ar), 123.5 (C Ar), 121.9 (C Ar), 111.5 (C Ar), 110.1 (C Ar), 36.0 ($CH_2$), 31.5 ($CH_2$), 21.7 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1651 (CHO). HRMS (ESI): calcd. for $C_{14}H_{12}O_2$, $[M-H]^+$, 211.0754; found, 211.0755, (Δ = 0.47 ppm). MS (ESI): *m/z* = 213 $[M+H]^+$.

**2-(Furan-2-yl)cyclohex-1-ene-1-carbaldehyde (25e).** Eluent: EtOAc/heptane (1:100). Yield: 0.86 g (50%), method A; 42.7 mg (24%), method B; yellow oil. $R_f$ 0.57 (EtOAc/hexane, 1:33). $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 10.11 (s, 1H, CHO), 7.53 (d, *J* = 1.4 Hz, 1H, H-5 Fur), 6.51 (d, *J* = 3.3 Hz, 1H, H-3 Fur), 6.48 (dd, *J* = 3.3, 1.4 Hz, 1H, H-4 Fur), 2.62-2.59 (m, 2H, $CH_2$), 2.39-2.37 (m, 2H, $CH_2$), 1.76-1.72 (m, 2H, $CH_2$), 1.68-1.65 (m, 2H, $CH_2$) ppm. $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 193.5 (CHO), 151.9 (C Ar), 144.1 (C Ar), 143.8 (C-2), 135.8 (C-1), 113.1 (C Ar), 111.5 (C Ar), 29.2 ($CH_2$), 23.0 ($CH_2$), 22.0 ($CH_2$), 21.4 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1658 (CHO). HRMS (ESI): calcd. for $C_{11}H_{12}O_2$, $[M+H]^+$, 177.0910; found, 177.0911, (Δ = 0.56 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 176 (85) $[M]^+$, 148 (49), 147 (56), 133 (17), 120 (100), 119 (32), 117 (13), 115 (21), 107 (20), 105 (14), 92 (20), 91 (78), 81 (19), 79 (20), 78 (12), 77 (27), 65 (18), 51 (14), 41 (13), 39 (22).

**2-(Furan-2-yl)cyclohept-1-ene-1-carbaldehyde (25f).** Eluent: heptane. Yield: 0.91 g (49%), method A; 49.6 mg (22%), method B; yellow oil. $R_f$ 0.53 (EtOAc/hexane, 1:33). $^1H$ NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 9.95 (s, 1H, CHO), 7.55 (d, *J* = 1.4 Hz, 1H, H-5 Fur), 6.52 (d, *J* = 3.3 Hz, 1H, H-3 Fur), 6.49 (dd, *J* = 3.3, 1.4 Hz, 1H, H-4 Fur), 2.79-2.78 (m, 2H, $CH_2$), 2.64-2.63 (m, 2H, $CH_2$), 1.85-1.81 (m, 2H, $CH_2$), 1.70-1.65 (m, 2H, $CH_2$), 1.52-1.49 (m, 2H, $CH_2$) ppm. $^{13}C$ NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 192.6 (CHO), 151.9 (C Ar), 150.4 (C-2), 144.7 (C Ar), 141.8 (C-1), 114.8 (C Ar), 111.7 (C Ar), 33.9 ($CH_2$), 32.1 ($CH_2$), 26.0, 25.9 ($CH_2$), 25.2 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1653 (CHO). HRMS (ESI): calcd. for $C_{12}H_{14}O_2$, $[M+H]^+$, 191.1067; found, 191.1067, (Δ = 0 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 190 (100) $[M]^+$, 162 (33), 161 (48), 147 (45), 134

(31), 133 (80), 131 (14), 121 (18), 120 (30), 119 (25), 115 (14), 107 (21), 105 (29), 92 (14), 91 (70), 79 (18), 77 (29), 65 (21), 39 (17).

**2-(Furan-2-yl)cyclooct-1-ene-1-carbaldehyde (25g).** Eluent: EtOAc/heptane (1:50). Yield: 0.66 g (33%); yellow oil. $R_f$ 0.39 (EtOAc/hexane, 1:33). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 10.00 (s, 1H, CHO), 7.53 (d, *J* = 1.5 Hz, 1H, H-5 Fur), 6.51 (d, *J* = 3.5 Hz, 1H, H-3 Fur), 6.48 (dd, *J* = 3.5, 1.5 Hz, 1H, H-4 Fur), 2.78-276 (m, 2H, $CH_2$), 2.58-2.56 (m, 2H, $CH_2$), 1.76-1.70 (m, 2H, $CH_2$), 1.63-1.59 (m, 2H, $CH_2$), 1.50-1.46 (m, 4H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 193.0 (CHO), 151.7 (C Ar), 147.4 (C-2), 144.5 (C Ar), 139.5 (C-1), 114.7 (C Ar), 111.6 (C Ar), 31.4 ($CH_2$), 30.1 ($CH_2$), 29.8 ($CH_2$), 26.8 ($CH_2$), 26.2 ($CH_2$), 25.0 ($CH_2$) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1659 (CHO). MS (ESI): *m/z* = 205 $[M+H]^+$. Anal. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.90. Found: C, 76.68; H, 7.72.

**1-(Furan-2-yl)-3,4-dihydronaphthalene-2-carbaldehyde (25h).** Eluent: EtOAc/heptane (1:50). Yield: 1.56 g (71%); yellow oil. $R_f$ 0.51 (EtOAc/hexane, 1:6). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 9.89 (s, 1H, CHO), 7.63 (dd, *J* = 2.0, 1.0 Hz, 1H, H-5 Fur), 7.33 (dt, *J* = 7.6, 1.5 Hz, 1H, H Ar), 7.26-7.21 (m, 2H, H Ar), 7.14 (dd, *J* = 8.1, 1.0 Hz, 1H, H Ar), 6.62 (d, *J* = 3.5 Hz, 1H, H-3 Fur), 6.59 (dd, *J* = 3.5, 2.0 Hz, 1H, H-4 Fur), 2.87 (dd, *J* = 8.6, 7.1 Hz, 2H, $CH_2$), 2.69 (dd, *J* = 8.6, 7.1 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 193.0 (CHO), 147.8 (C Ar), 144.1 (C Ar), 142.7 (C-2), 138.9 (C Ar), 137.0 (C Ar), 133.3 (C Ar), 130.5 (C Ar), 128.2 (C-1), 128.0 (C Ar), 126.8 (C Ar), 115.4 (C Ar), 111.2 (C Ar), 27.5 ($CH_2$), 21.0 ($CH_2$) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= 1650 (CHO). MS (ESI): *m/z* = 225 $[M+H]^+$. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.22; H, 5.57.

**General Procedure for the Synthesis of Products 11.** Corresponding furylacrolein **25** (0.7 mmol) was added at room temperature to a solution of aniline (0.7 mmol) in anhydrous $CH_2Cl_2$ (10 mL) in the presence of a molecular sieves (MS 4Å) (1 g). The mixture was stirred for 4 h. The molecular sieves were filtered off, washed with $CH_2Cl_2$ (2 × 5 mL), after that, the solution was concentrated. $NaBH_4$ (53.2 mg, 1.4 mmol) was added at r.t. to the residue diluted in MeOH (10 mL). The mixture was stirred vigorously at r.t. for 24 h (TLC or GC-MS control), then poured into $H_2O$ (10 mL) and extracted with $CH_2Cl_2$ (3 × 10 mL), the combined organic layers were dried over anhydrous $Na_2SO_4$, concentrated, and purified by column chromatography ($SiO_2$, 20 × 1.5 cm).

***N*-((2-(Furan-2-yl)cyclopent-1-enyl)methyl)aniline (11a).** Eluent: heptane. Yield: 118.8 mg (71%); yellow oil. $R_f$ 0.47 (EtOAc/hexane, 1:33). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.44 (d,

*J* = 1.5 Hz, 1H, H-5 Fur), 7.18 (dd, *J* = 8.6, 7.6 Hz, 2H, H-3,5 Ph), 6.72 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.67 (dd, *J* = 8.6, 1.0 Hz, 2H, H-2,6 Ph), 6.43 (dd, *J* = 3.5, 1.5 Hz, 1H, H-4 Fur), 6.26 (d, *J* = 3.5 Hz, 1H, H-3 Fur), 4.26 (br.s, 2H, $CH_2N$), 3.88 (br.s, 1H, NH), 2.76-2.73 (m, 2H, $CH_2$), 2.62 (t, *J* = 7.6 Hz, 2H, $CH_2$), 1.93 (pent, *J* = 7.6 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 152.6 (C Ar), 148.7 (C Ar), 141.8, 137.0 (C-2), 129.3 (2C), 127.1 (C-1), 117.4 (C Ar), 113.0 (2C, C Ar), 111.0 (C Ar), 107.9 (C Ar), 43.0 ($NCH_2$), 36.5 ($CH_2$), 34.9 ($CH_2$), 22.0 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3411 (NH), 1601, 1504 (C=C). HRMS (ESI): calcd. for $C_{16}H_{17}NO$, $[M-H]^+$, 238.1226; found, 238.1228, (Δ = 0.57 ppm). MS (ESI): *m/z* = 240 $[M+H]^+$.

***N*-((2-(Furan-3-yl)cyclopent-1-enyl)methyl)aniline (11b).** Eluent: heptane. Yield: 65.2 mg (39%); yellow oil. $R_f$ 0.51 (EtOAc/hexane, 1:33). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.45 (br.s, 1H, H-5 Fur), 7.41 (t, *J* = 2.0 Hz, 1H, H-2 Fur), 7.19 (dd, *J* = 8.6, 7.6 Hz, 2H, H-3,5 Ph), 6.72 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.62 (dd, *J* = 8.6, 1.0 Hz, 2H, H-2,6 Ph), 6.52 (dd, *J* = 2.0, 1.0 Hz, 1H, H-4 Fur), 3.97 (br.s, 2H, $CH_2N$), 3.73 (br.s, 1H, NH), 2.69 (t, *J* = 7.6 Hz, 2H, $CH_2$), 2.60 (t, *J* = 7.6 Hz, 2H, $CH_2$), 1.94 (pent, *J* = 7.6 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 148.5 (C Ar), 143.2 (C Ar), 140.1 (C Ar), 135.6 (C Ar), 129.7 (C-2), 129.3 (2C, C Ar), 121.9 (C-1), 117.5 (C Ar), 112.8 (2C, C Ar), 109.7 (C Ar), 43.0 ($NCH_2$), 36.6 ($CH_2$), 36.5 ($CH_2$), 21.9 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3415 (NH), 1609, 1507 (C=C). HRMS (ESI): calcd. for $C_{16}H_{17}NO$, $[M-H]^+$, 238.1226; found, 238.1228, (Δ = 0.57 ppm). MS (ESI): *m/z* = 240 $[M+H]^+$.

***N*-((2-(5-Methylfuran-2-yl)cyclopent-1-enyl)methyl)aniline (11c).** Eluent: EtOAc/heptane (1:100). Yield: 30.1 mg (17%); yellow oil. $R_f$ 0.38 (EtOAc/hexane, 1:33). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.17 (t, *J* = 7.6 Hz, 2H, H-3,5 Ph), 6.70 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.66 (d, *J* = 7.6 Hz, 2H, H-2,6 Ph), 6.12 and 6.00 (2d, *J* = 2.4 Hz, 2H, H-3 and H-4 Fur), 4.24 (s, 2H, $NCH_2$), 3.90 (br.s, 1H, NH), 2.70 (br.t, *J* = 6.9 Hz, 2H, $CH_2$), 2.59 (br.t, *J* = 6.9 Hz, 2H, $CH_2$), 2.31 (s, 3H, $CH_3$), 1.90 (pent, *J* = 6.9 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 151.5 (C Ar), 151.0 (C Ar), 148.8 (C Ar), 135.4 (C-2), 129.2 (2C, C Ar), 127.1 (C-1), 117.2 (C Ar), 112.9 (2C, C Ar), 108.8 (C Ar), 106.9 (C Ar), 43.0 ($NCH_2$), 36.3 ($CH_2$), 34.7 ($CH_2$), 22.0 ($CH_2$), 13.8 ($CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3416 (NH), 1602, 1505 (C=C). HRMS (ESI): calcd. for $C_{17}H_{19}NO$**,** $[M-H]^+$, 252.1383; found, 252.1384, (Δ = 0.40 ppm). MS (ESI): *m/z* = 254 $[M+H]^+$.

***N*-((2-(Benzofuran-2-yl)cyclopent-1-enyl)methyl)aniline (11d).** Eluent: heptane. Yield: 115.3 mg (57 %); yellow oil. $R_f$ 0.54 (EtOAc/hexane, 1:20). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.56 (d, *J* = 7.6 Hz, 1H, H Ar), 7.45 (d, *J* = 8.1 Hz, 1H, H Ar), 7.28-7.16 (m, 4H, H Ar), 6.73-6.68

(m, 3H, H Ar), 6.59 (s, 1H, H-3 Fur), 4.42 (s, 2H, $NCH_2$), 3.99 (br.s, 1H, NH), 2.84 (t, *J* = 7.6 Hz, 2H, $CH_2$), 2.67 (t, *J* = 7.6 Hz, 2H, $CH_2$), 1.97 (pent, *J* = 7.6 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 154.4 (C Ar), 148.6 (C Ar), 141.5 (C Ar), 129.3 (2C, C Ar), 128.6 (C-2), 126.9 (C-1), 124.2 (C Ar), 122.9 (C Ar), 120.8 (C Ar), 117.5 (C Ar), 113.0 (2C, C Ar), 111.0 (C Ar), 104.3 (C Ar), 43.2 ($NCH_2$), 36.8 ($CH_2$), 35.0 ($CH_2$), 22.0 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3408 (NH), 1604, 1503 (C=C). HRMS (ESI): calcd. for $C_{20}H_{19}NO$, $[M-H]^+$, 288.1383; found, 288.1385, (Δ = 0.67 ppm). MS (ESI): *m/z* = 290 $[M+H]^+$.

***N*-((2-(Furan-2-yl)cyclohex-1-enyl)methyl)aniline (11e).** Eluent: EtOAc/heptane (1:100). Yield: 42.5 mg (24 %); yellow oil. $R_f$ 0.48 (EtOAc/hexane, 1:33). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.39 (br.d, *J* = 1.2 Hz, 1H, H-5 Fur), 7.19 (dd, *J* = 8.3, 7.4 Hz, 2H, H-3,5 Ph), 6.72 (t, *J* = 7.4 Hz, 1H, H-4 Ph), 6.63 (dd, *J* = 8.4, 1.0 Hz, 2H, H-2,6 Ph), 6.39 (dd, *J* = 3.3, 1.9 Hz, 1H, H-4 Fur), 6.30 (d, *J* = 3.3 Hz, 1H, H-3 Fur), 3.94 (s, 2H, $NCH_2$), 3.82 (br.s, 1H, NH), 2.43-2.41 (m, 2H, $CH_2$), 2.31-2.29 (m, 2H, $CH_2$), 1.74-1.66 (m, 4H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.6 (C Ar), 148.8 (C Ar), 141.2 (C Ar), 133.5 (C-2), 129.2 (2C, C Ar), 125.2 (C-1), 117.2 (C Ar), 112.9 (2C, C Ar), 110.8 (C Ar), 107.5 (C Ar), 47.7 ($NCH_2$), 29.5 ($CH_2$), 28.1 ($CH_2$), 22.6 (2C, 2 $CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3417 (NH), 1610, 1508 (C=C). HRMS (ESI): calcd. for $C_{17}H_{19}NO$**,** $[M+H]^+$, 254.1539; found, 254.1540, (Δ = 0.39 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 253 (100) $[M]^+$, 210 (14), 162 (11), 161 (56), 160 (54), 143 (12), 133 (13), 131 (12), 128 (13), 117 (12), 115 (10), 106 (10), 105 (12), 104 (9), 93 (17), 91 (53), 81 (16), 77 (23), 65 (10).

***N*-((2-(Furan-2-yl)cyclohept-1-enyl)methyl)aniline (11f).** Eluent: heptane. Yield: 20.5 mg (11%); yellow oil. $R_f$ 0.42 (EtOAc/hexane, 1:33). $^1$H NMR (700.2 MHz, $CDCl_3$, 25 °C) δ 7.38 (br.s, 1H, H-5 Fur), 7.17 (t, *J* = 7.6 Hz, 2H, H-3,5 Ph), 6.70 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.60 (d, *J* = 7.6 Hz, 2H, H-2,6 Ph), 6.37 (dd, *J* = 3.3, 1.9 Hz, 1H, H-4 Fur), 6.25 (d, *J* = 3.3 Hz, 1H, H-3 Fur), 3.91 (s, 2H, $NCH_2$), 3.76 (br.s, 1H, NH), 2.59-2.58 (m, 2H, $CH_2$), 2.44-2.43 (m, 2H, $CH_2$), 1.82-1.79 (m, 2H, $CH_2$), 1.62-1.59 (m, 2H, $CH_2$), 1.54-1.51 (m, 2H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, $CDCl_3$, 25 °C) δ 154.9 (C Ar), 148.7 (C Ar), 141.2 (C Ar), 139.4 (C-2), 132.1 (C-1), 129.2 (2C, C Ar), 117.2 (C Ar), 112.9 (2C, C Ar), 110.8 (C Ar), 107.9 (C Ar), 48.8 ($NCH_2$), 33.3 ($CH_2$), 32.6 ($CH_2$), 32.5 ($CH_2$), 26.6 ($CH_2$), 26.4 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3401 (NH), 1605, 1503 (C=C). HRMS (ESI): calcd. for $C_{18}H_{21}NO$, $[M-H]^+$, 266.1539; found, 266.1540, (Δ = 0.38 ppm). GC-MS (EI, 70 eV): *m/z*(%) = 267 (100) $[M]^+$, 238 (11), 244 (31), 210 (13), 175 (35), 174 (58), 157 (16), 145 (12), 133 (10), 131 (10), 129 (17), 119 (13), 119 (13), 117 (13), 106 (16), 105 (15), 93 (17), 91 (34), 81 (20), 79 (12), 77 (24).

***N*-((2-(Furan-2-yl)cyclooct-1-enyl)methyl)aniline (11g).** Eluent: heptane. Yield: 88.5 mg (45%); yellow oil. $R_f$ 0.50 (EtOAc/hexane, 1:33). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.38 (dd, *J* = 2.0, 1.0 Hz, 1H, H-5 Fur), 7.19 (dd, *J* = 8.6, 7.6 Hz, 2H, H-3,5 Ph), 6.71 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.62 (d, *J* = 8.6 Hz, 2H, H-2,6 Ph), 6.37 (dd, *J* = 3.0, 1.5 Hz, 1H, H-4 Fur), 6.31 (d, *J* = 3.0 Hz, 1H, H-3 Fur), 3.93 (s, 2H, $NCH_2$), 3.77 (br.s, 1H, NH), 2.61-2.59 (m, 2H, $CH_2$), 2.46-2.44 (m, 2H, $CH_2$), 1.72-1.64 (m, 4H, $CH_2$), 1.58-1.52 (m, 4H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 154.7 (C Ar), 148.8 (C Ar), 141.2 (C Ar), 136.3 (C-2), 129.3 (2C), 128.7 (C-1), 117.3 (C Ar), 112.9 (2C, C Ar), 110.9 (C Ar), 108.1 (C Ar), 47.1 ($NCH_2$), 31.3 ($CH_2$), 30.1 ($CH_2$), 29.7 ($CH_2$), 29.7 ($CH_2$), 27.0 ($CH_2$), 26.4 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$ = 3397 (NH), 1601, 1504 (C=C). HRMS (ESI): calcd. for $C_{19}H_{23}NO$, $[M-H]^+$, 280.1696; found, 280.1697, (Δ = 0.36 ppm). MS (ESI): *m/z* = 282 $[M+H]^+$.

***N*-((1-(Furan-2-yl)-3,4-dihydronaphthalen-2-yl)methyl)aniline (11h).** Eluent: EtOAc/heptane (1:50). Yield: 162.2 mg (77%); yellow oil. $R_f$ 0.67 (EtOAc/hexane, 1:33). $^1$H NMR (600.2 MHz, $CDCl_3$, 25 °C) δ 7.53 (dd, *J* = 2.0, 1.0 Hz, 1H, H-5 Fur), 7.17-7.11 (m, 5H, H Ar), 6.88 (d, *J* = 7.1 Hz, 1H, H Ar), 6.70 (t, *J* = 7.6 Hz, 1H, H Ar), 6.60 (dd, *J* = 8.6, 1.0 Hz, 2H, H Ar), 6.50 (dd, *J* = 3.5, 2.0 Hz, 1H, H-Fur), 6.39 (dd, *J* = 3.5, 1.0 Hz, 1H, H-Fur), 3.94 (s, 2H, $NCH_2$), 3.83 (br.s, 1H, NH), 2.82 (t, *J* = 7.6 Hz, 2H, $CH_2$), 2.52 (t, *J* = 7.6 Hz, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, $CDCl_3$, 25 °C) δ 150.5 (C Ar), 148.3 (C Ar), 142.1 (C Ar), 140.8 (C Ar), 135.6 (C-1), 134.9 (C Ar), 129.3 (2C, C Ar), 127.3 (C-2), 127.2 (C Ar), 126.9 (C Ar), 126.5 (C Ar), 125.5 (C Ar), 117.6 (C Ar), 113.1 (2C, C Ar), 110.7 (C Ar), 100.0 (C Ar), 47.2 ($NCH_2$), 28.1 ($CH_2$), 26.3 ($CH_2$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 3416 (NH), 1601, 1503 (C=C). MS (ESI): *m/z* = 302 $[M+H]^+$. Anal. Calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.54; H, 6.43; N, 4.37.

**General Procedure for the Synthesis of Products 12**. Maleic anhydride (0.5 mmol) was added to the corresponding allylamine **11a-h** (0.5 mmol) diluted in PhH (5 mL). The resulting mixture was heated at reflux (**12c-h**) and at 50 °C (**12a**) for 5 h and then cooled to room temperature. The resulting precipitate was filtered off, washed with PhH (5 mL), $Et_2O$ (2 × 5 mL), and air dried to give the title acids **12a**,**c-h**, **28** as colorless solid powders.

**(3a*RS*,6a*RS*,7*RS*,7a*RS*)-6-Oxo-5-phenyl-2,3,4,5,6,6a,7,7a-octahydro-1H-cyclopenta[*d*]furo[2,3-*f*]isoindole-7-carboxylic acid (12a).** Reflux for 5 h. Contains around 7% of impurity of the "aromatic" isomer. Yield: 134.8 mg (80 %). At 50 °C for 5 h. Yield: 107.8 mg (64 %); colorless powder. M.p. 201-202 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ

12.26 (s, 1H, $CO_2H$), 7.62 (d, *J* = 7.6 Hz, 2H, H-2,6 Ph), 7.36 (t, *J* = 7.6 Hz, 2H, H-3,5 Ph), 7.14 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.77 (t, *J* = 2.6 Hz, 1H, H-9), 5.48 (t, *J* = 2.6 Hz, 1H, H-8), 3.84 (d, *J* = 9.5 Hz, 1H, H-4A), 3.72 (d, *J* = 9.5 Hz, 1H, H-4B), 3.47-3.44 (m, 1H, H-7a), 3.43 (d, *J* = 4.3 Hz, 1H, H-6a), 2.42-2.32 (m, 2H, $CH_2$), 2.28 (dd, *J* = 11.2, 4.3 Hz, 1H, H-7), 2.01-1.98 (m, 1H, $CH_2$), 1.83-1.77 (m, 2H, $CH_2$), 1.67-1.63 (m, 1H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 173.7, 172.6 ($CO_2$, C-6), 149.2, 146.5 (C-9, C-10a), 139.6 (C Ar), 129.1 (2C, C Ar), 124.7 (C Ar), 120.2 (2C, C Ar), 114.2, 106.6 (C-8, C-10b), 58.0, 46.9 (2C), 45.1, 40.5, 36.8, 23.2, 21.2 (C-1, C-2, C-3, C-3a, C-4, C-6a, C-7, C-7a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1731 ($CO_2$), 1656 (N-C=O). HRMS (ESI): calcd. for $C_{20}H_{19}NO_4$, $[M+H]^+$, 338.1387; found, 338.1403, (Δ = 4.73 ppm); calcd. for $C_{20}H_{19}NO_4$, $[M+Na]^+$, 360.1206; found, 360.1227, (Δ = 5.83 ppm). Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15.Found: C, 70.93; H, 5.97; N, 4.23.

**(3a*RS*,6a*RS*,7*SR*,7a*RS*)-6-Oxo-5-phenyl-2,3,4,5,6,6a,7,7a-octahydro-1H-cyclopenta[*d*]furo[3,2-*f*]isoindole-7-carboxylic acid (28).** Yield: 80.9 mg (48 %); beige powder. M.p. 169-170 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 12.43 (br.s, 1H, $CO_2H$), 7.59-7.57 (m, 3H, H-9, H-2,6 Ph), 7.36 (t, *J* = 8.6 Hz, 2H, H-3,5 Ph), 7.13 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.34 (d, *J* = 1.5 Hz, 1H, H-10), 4.06 (d, *J* = 6.6 Hz, 1H, H-7a), 3.80 (d, *J* = 9.1 Hz, 1H, H-4A), 3.72 (d, *J* = 9.1 Hz, 1H, H-4B), 3.31 (d, *J* = 7.6 Hz, 1H, H-6a), 2.85-2.83 (m, 1H, H-7), 2.18-2.13 (m, 1H, $CH_2$), 1.83-1.79 (m, 1H, $CH_2$), 1.70-1.46 (m, 4H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 172.9, 171.4 ($CO_2$, C-6), 145.2 (C-9), 143.4 (C Ar), 140.1 (C-10b), 129.2 (2C, C Ar), 124.5 (C Ar), 122.7 (C-10a), 120.1 (2C, C Ar), 110.0 (C-10), 59.9, 50.5, 47.5, 40.6, 38.5, 36.8, 32.9, 24.3 (C-1, C-2, C-3, C-3a, C-4, C-6a, C-7, C-7a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1731 ($CO_2$), 1664 (N-C=O). HRMS (ESI): calcd. for $C_{20}H_{19}NO_4$, $[M+H]^+$, 338.1387; found, 338.1403, (Δ = 3.55 ppm); calcd. for $C_{20}H_{19}NO_4$, $[M+Na]^+$, 360.1206; found, 360.1227, (Δ = 1.11 ppm). Anal. Calcd for $C_{20}H_{19}NO_4$: C, 71.20; H, 5.68; N, 4.15. Found: C, 71.11; H, 5.73; N, 4.18.

**(3a*RS*,4*RS*,5*RS*,6a*SR*,9a*SR*)-3,6-Dioxo-5-(2-oxopropyl)-2-phenyldecahydro-1*H*-cyclopenta[*d*]isoindole-4-carboxylic acid (12c).** Yield: 86.7 mg (47 %); colorless powder. M.p. > 250 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.49 (s, 1H, $CO_2H$), 7.66 (d, *J* = 8.1 Hz, 2H, H-2,6 Ph), 7.38 (t, *J* = 7.6 Hz, 2H, H-3,5 Ph), 7.15 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 3.74 (d, *J* = 9.5 Hz, 1H, H-1A), 3.64 (d, *J* = 9.5 Hz, 1H, H-1B), 3.49 (d, *J* = 4.8 Hz, 1H, H-3a), 3.03-2.93 (m, 3H, $COCH_2$, H-4), 2.83 (dd, *J* = 17.4, 8.3 Hz, 1H, H-5), 2.65 (d, *J* = 7.6 Hz, 1H, H-6a), 2.27-2.23 (m, 1H, $CH_2$), 2.12 (s, 3H, $CH_3$), 1.76-1.71 (m, 2H, $CH_2$), 1.65-1.51 (m, 3H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 209.6, 207.7 (2CO), 173.0, 172.2 ($CO_2$, C-3), 139.9 (C Ar),

129.1 (2C, C Ar), 124.6 (C Ar), 120.1 (2C, C Ar), 58.0, 53.5, 51.7, 47.7, 44.0, 42.4, 41.5, 32.4, 30.5, 22.5, 21.5 (C-1, C-3a, C-4, C-5, C-6a, C-7, C-8, C-9, C-9a, $CH_2$, $CH_3$) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= br. 1705 (N-C=O, $CO_2$). MS (ESI): *m/z* = 370 $[M+H]^+$. Anal. Calcd for $C_{21}H_{23}NO_5$: C, 68.28; H, 6.28; N, 3.79. Found: C, 68.32; H, 6.21; N, 3.62.

**(3a*RS*,6a*RS*,7*RS*,7a*SR*)-6-Oxo-5-phenyl-2,3,4,5,6,6a,7,7a-octahydro-1*H*-[1]benzofuro[2,3-*f*]cyclopenta[*d*]isoindole-7-carboxylic acid (12d).** Yield: 187.7 mg (97 %); colorless powder. M.p. 225-226 °C. $^1$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 12.68 (s, 1H, $CO_2H$), 7.72 (d, *J* = 7.6 Hz, 1H, H Ar), 7.64 (d, *J* = 8.1 Hz, 2H, H Ar), 7.39-7.35 (m, 2H, H Ar), 7.21 (t, *J* = 7.6 Hz, 1H, H Ar), 7.14 (t, *J* = 7.6 Hz, 1H, H Ar), 6.98-6.95 (m, 2H, H Ar), 4.03 (d, *J* = 11.1 Hz, 1H, H-7a), 3.86 (d, *J* = 9.6 Hz, 1H, H-4A), 3.75 (d, *J* = 9.6 Hz, 1H, H-4B), 3.53 (d, *J* = 4.0 Hz, 1H, H-6a), 2.71 (dd, *J* = 11.1, 4.5 Hz, 1H, H-7), 2.52-2.41 (m, 2H, $CH_2$), 1.99-1.96 (m, 1H, $CH_2$), 1.86-1.79 (m, 2H, $CH_2$), 1.70-1.66 (m, 1H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 173.7, 172.5 ($CO_2$, C-6), 158.4 (C Ar), 148.3 (C-12a), 139.6 (C Ar), 129.2 (2C, C Ar), 128.1 (2C, C Ar), 127.7 (C Ar), 124.8 (C Ar), 122.5 (C Ar), 120.4 (2C, C Ar), 115.5 (C Ar), 109.8 (C-12b), 57.7, 47.7, 46.8, 45.4, 39.3, 36.7, 23.5, 21.2 (C-1, C-2, C-3, C-3a, C-4, C-6a, C-7, C-7a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= 1743 ($CO_2$), 1659 (N-C=O). HRMS (ESI): calcd. for $C_{24}H_{21}NO_4$, $[M+H]^+$, 388.1543; found, 388.1559, (Δ = 4.12 ppm); calcd. for $C_{24}H_{21}NO_4$, $[M+Na]^+$, 410.1363; found, 410.1381, (Δ = 4.39 ppm). Anal. Calcd for $C_{24}H_{21}NO_4$: C, 74.40; H, 5.46; N, 3.62. Found: C, 74.51; H, 5.42; N, 3.74.

**(4a*RS*,7a*RS*,8*RS*,8a*RS*)-7-Oxo-6-phenyl-1,2,3,4,5,6,7,7a,8,8a-decahydrobenzo[*d*]furo[2,3-*f*]isoindole-8-carboxylic acid (12e).** Yield: 26.3 mg (73 %); colorless powder. M.p. 233-234 °C. $^1$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.47 (s, 1H, $CO_2H$), 7.65 (d, *J* = 7.6 Hz, 2H, H-2,6 Ph), 7.35 (t, *J* = 7.6 Hz, 2H, H-3,5 Ph), 7.13 (t, *J* = 7.6 Hz, 1H, H-4 Ph), 6.77 (t, *J* = 2.6 Hz, 1H, H-10), 5.48 (t, *J* = 2.6 Hz, 1H, H-9), 3.96 (d, *J* = 9.8 Hz, 1H, H-5A), 3.85 (d, *J* = 9.8 Hz, 1H, H-5B), 3.53-3.50 (m, 1H, $CH_2$), 3.19 (d, *J* = 3.6 Hz, 1H, H-7a), 2.60 (br.d, *J* = 11.4 Hz, 1H, H-8a), 2.49 (dd, *J* = 11.4, 3.6 Hz, 1H, H-8), 1.99-1.94 (m, 2H, $CH_2$), 1.71-1.62 (m, 3H, $CH_2$), 1.58-1.51 (m, 1H, $CH_2$), 1.18-1.12 (m, 1H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 173.8, 172.8 ($CO_2$, C-7), 150.2, 146.5 (C-10, C-11a), 139.7 (C Ar), 129.1 (2C, C Ar), 124.6 (C Ar), 120.1 (2C, C Ar), 111.0, 106.7 (C-9, C-11b), 62.5, 56.7, 51.9, 42.3, 41.2, 38.7, 26.3, 22.9, 22.5 (C-1, C-2, C-3, C-4, C-4a, C-5, C-7a, C-8, C-8a) ppm. IR (KBr, $cm^{-1}$): $\nu_{max}$= br. 1706 ($CO_2$, N-C=O). HRMS (ESI): calcd. for $C_{21}H_{21}NO_4$, $[M+H]^+$, 352.1543; found, 352.1550, (Δ = 1.99 ppm); calcd. for $C_{21}H_{21}NO_4$, $[M+Na]^+$, 374.1363; found, 374.1372, (Δ = 4.39 ppm). Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.83; H, 5.97; N, 4.03.

**(5a*RS*,8a*RS*,9*RS*,9a*RS*)-8-Oxo-7-phenyl-2,3,4,5,6,7,8,8a,9,9a-decahydro-1*H*-cyclohepta[*d*]furo[2,3-*f*]isoindole-9-carboxylic acid (12f).** Yield: 85.8 mg (47 %); colorless powder. M.p. 244-245 °C. $^{1}$H NMR (700.2 MHz, DMSO-$d_6$, 25 °C) δ 12.47 (s, 1H, $CO_2H$), 7.59 (d, $J$ = 7.6 Hz, 2H, H-2,6 Ph), 7.35 (t, $J$ = 7.6 Hz, 2H, H-3,5 Ph), 7.13 (t, $J$ = 7.6 Hz, 1H, H-4 Ph), 6.82 (br.s, 1H, H-11), 5.50 (br.s, 1H, H-10), 3.74 (d, $J$ = 9.8 Hz, 1H, H-6A), 3.68 (d, $J$ = 9.8 Hz, 1H, H-8B), 3.51 (d, $J$ = 11.3 Hz, 1H, H-9a), 3.30 (d, $J$ = 3.6 Hz, 1H, H-8a), 2.52-2.50 (m, 1H, $CH_2$), 2.46 (dd, $J$ = 11.3, 3.6 Hz, 1H, H-9), 2.18-2.15 (m, 1H, $CH_2$), 1.82-1.67 (m, 5H, $CH_2$), 1.32-1.23 (m, 3H, $CH_2$) ppm. $^{13}$C NMR (176.1 MHz, DMSO-$d_6$, 25 °C) δ 173.6, 172.9 ($CO_2$, C-8), 153.1, 146.5 (C-11, C-12a), 139.5 (C Ar), 129.1 (2C, C Ar), 124.6 (C Ar), 120.1 (2C, C Ar), 113.6, 107.1 (C-10, C-12b), 58.5, 53.2, 44.0, 43.5, 40.7, 30.9, 28.0, 24.6 (2C), 21.5 (C-1, C-2, C-3, C-4, C-5, C-5a, C-6, C-8a, C-9, C-9a) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= br. 1699 ($CO_2$, N-C=O). HRMS (ESI): calcd. for $C_{22}H_{23}NO_4$, $[M+H]^+$, 366.1700; found, 366.1716, (Δ = 4.37 ppm); calcd. for $C_{22}H_{23}NO_4$, $[M+Na]^+$, 388.1519; found, 388.1535, (Δ = 4.12 ppm). Anal. Calcd for $C_{22}H_{23}NO_4$:C, 72.31; H, 6.34; N, 3.83. Found: C, 72.28; H, 6.41; N, 3.80.

**(6a*RS*,9a*RS*,10*RS*,10a*RS*)-9-Oxo-8-phenyl-5,6,7,8,9,9a,10,10a-octahydrofuro[2,3-*f*]naphtho[2,1-*d*]isoindole-10-carboxylic acid (12h).** Yield: 130.3 mg (65 %); colorless powder. M.p. > 250 °C. $^{1}$H NMR (600.2 MHz, DMSO-$d_6$, 25 °C) δ 12.62 (br.s, 1H, $CO_2H$), 7.70-7.68 (m, 1H, H Ar), 7.58 (d, $J$ = 7.6 Hz, 2H, H Ar), 7.30 (t, $J$ = 7.6 Hz, 2H, H Ar), 7.17-7.08 (m, 4H, H Ar), 6.88 (t, $J$ = 2.5 Hz, 1H, H-12), 5.66 (t, $J$ = 2.5 Hz, 1H, H-11), 4.07 (d, $J$ = 10.1 Hz, 1H, H-7A), 3.82 (br.d, $J$ = 11.6 Hz, 1H, H-10a), 3.47 (d, $J$ = 3.5 Hz, 1H, H-9a), 3.44 (d, $J$ = 10.1 Hz, 1H, H-7A), 3.15-3.09 (m, 1H, $CH_2$), 2.96-2.93 (m, 1H, $CH_2$), 2.69 (dd, $J$ = 11.6, 3.5 Hz, 1H, H-10), 2.20-2.17 (m, 2H, $CH_2$) ppm. $^{13}$C NMR (150.9 MHz, DMSO-$d_6$, 25 °C) δ 173.6, 172.7 ($CO_2$, C-9), 152.5, 146.4 (C-12, C-13a), 139.6 (C Ar), 134.4 (C Ar), 130.7 (C Ar), 129.2 (2C, C Ar), 129.1 (C Ar), 126.8 (C Ar), 126.2 (C Ar), 126.0 (C Ar), 124.7 (C Ar), 120.0 (2C, C Ar), 111.0, 107.2 (C-11, C-13b), 56.8, 52.0, 42.0, 41.8, 40.6, 34.2, 26.3 (C-5, C-6, C-6a, C-7, C-9a, C-10, C-10a) ppm. IR (KBr, cm$^{-1}$): $\nu_{max}$= br. 1704 (N-C=O, $CO_2$). HRMS (ESI): calcd. for $C_{25}H_{21}NO_4$, $[M+H]^+$, 400.1543; found, 400.1544, (Δ = 0.25 ppm); calcd. for $C_{25}H_{21}NO_4$, $[M+Na]^+$, 422.1363; found, 422.1366, (Δ = 0.71 ppm). Anal. Calcd for $C_{25}H_{21}NO_4$: C, 75.17; H, 5.30; N, 3.51. Found: C, 75.02; H, 5.41; N, 3.36.

**2. X-ray diffraction analysis**

X-ray diffraction experiments of **10g**, **20a**, **20d** and **23a** were carried out on an automatic four-circle area-detector diffractometer Bruker KAPPA APEX II (MoKα radiation). The unit cell constants were refined over the whole data set together with data reduction [3]. The experimental intensities were corrected for absorption using the SADABS program [4] or TWINABS one [5] for the twinned crystal **20a**. The structures were solved by the intrinsic phasing method (SHELXT [6]) and refined by the full-matrix least-squares method (SHELXL-2018/3 [7]) on $F^2$ for all data in the anisotropic approximation for all non-hydrogen atoms. The H atoms of CH, $CH_2$ and $CH_3$ groups were placed in geometrically calculated positions with $U_{iso}(H) = 1.2U_{equ}(C)$ for CH and $CH_2$ groups and $U_{iso}(H) = 1.5U_{equ}(C)$ for $CH_3$ ones. The orientation of $CH_3$ groups was refined. The H atoms of OH-groups were located from difference Fourier maps and refined with individual temperature parameters, except for the structure **20a**, where the H atoms of OH-groups with $U_{iso}(H) = 1.2U_{equ}(O)$ were oriented to obtain the best H-bonding.

Crystal data and structure refinement details are given in Tables S1-S48. The atomic coordinates were deposited at Cambridge Crystallographic Data Centre, depositions CCDC 2495035 (**10g**), 2495036 (**20a**), 2495037 (**20d**), and 2495038 (**23a**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

The structure **10g** contains an intramolecular H-bond of C-H···O type and an H-bond between OH-group and O atom of DMSO solvate (Fig. S1, S2, Tables S1-S8).

The structure **20a** contains two crystallographically independent units **20a**·DMSO (Fig. S4, S5 shows one of them with the H-bond between OH-group and O atom of DMSO solvate). The second unit contains a similar H-bond with disordered DMSO solvate. Both **20a** molecules have the same conformation, the mean deviation of atoms at superposition is 0.041 Å (Tables S1, S21-28). Intramolecular H-bonds similar to that found in **10g** are absent due to an essential rotation (about 30°) of the $C_6$ rings around the C-N bond (Tables S2-S8). The structure **20d** contains an H-bond between OH-group and O atom of DMSO solvate (Fig. S6, S7, Tables S1, S29-S35). In the structure **23a** (Fig. S8, S9, Tables S1, S36-S42) solvate molecules are absent. The crystal package of **23a** (Fig. S9) contains layers of molecules parallel to (120) plane. The molecules are connected by H-bonds of O-H···O and C-H···O types into a 3D network.

The single-crystal X-ray diffraction studies of **12a**, **12c**, and **23e** were carried out on a four-circle Rigaku Synergy-S diffractometer equipped with a HyPix6000HE area-detector ($T$ = 100 K,

$\lambda$(Cu$K\alpha$)-radiation, graphite monochromator, shutterless $\omega$-scanning mode). The data were integrated and corrected for absorption by the *CrysAlisPro* program [8]. For details, see Table S1.

The structures were solved by intrinsic phasing modification of direct methods [9] and refined by a full-matrix least-squares technique on $F^2$ with anisotropic displacement parameters for all non-hydrogen atoms. The absolute structure of **12c** was objectively determined by the refinement of Flack parameter which has become equal to 0.18(4)). The hydrogen atom of the OH-group in **23e** was objectively localized in the difference-Fourier maps and refined freely. The hydrogen atoms of the OH-groups in **12a** were objectively localized in the difference-Fourier maps and refined freely with fixed isotropic displacement parameters [$U_{iso}$(H) = 1.5$U_{eq}$(O)]. The hydrogen atoms of the OH-groups in **12c** were objectively localized in the difference-Fourier maps and refined within the riding model with fixed isotropic displacement parameters [$U_{iso}$(H) = 1.5$U_{eq}$(O)]. The other hydrogen atoms in all compounds were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [$U_{iso}$(H) = 1.5$U_{eq}$(C) for the $CH_3$-groups and 1.2$U_{eq}$(C) for the other groups]. All calculations were carried out using the *SHELXTL* program [7].

Crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2513916 (**12a**), CCDC 2513917 (**12c**), and CCDC 2513919 (**23e**). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

The molecular structure of compound **23e** is shown in Figure S10 along with the atomic numbering schemes. Compound **23e** include a fused tetracyclic core containing the two six-membered (benzene and cyclohexene) and two five-membered (furan and 2-pyrrolidinone) rings. The cyclohexene and 2-pyrrolidinone rings adopt the typical *half-chair* and *envelope* conformations, respectively. Compound **23e** possess three asymmetric centers at the C3A, C4 and C10A carbon atoms, respectively, and can have potentially eight diastereomers. The crystals of **23e** are racemic and consist of enantiomeric pairs with the following relative configuration of the centers: 3A***RS***,4***RS***,10A***SR***. In the crystal, the molecule of **23e** form the hydrogen-bonded associates with the solvate dimethylsulfoxide molecules by the strong O─H···O(═S) hydrogen bonds (see Tables S43-S48). The associates are packed in stacks along the crystallographic *b* axes.

The molecular structures of compounds **12a** and **12c** are shown in Figure S3 along with the atomic numbering schemes. Compound **12c** crystallizes in the chiral space group *P*1, with the four crystallographically independent molecules within the unit cell. These four crystallographically independent molecules are represented different conformers distinguished by the conformation of the carboxylic group. Compounds **12a** and **12c** include the fused tetracyclic and tricyclic cores, respectively. The tetracyclic core of **12a** contains one six-membered (cyclohexene) and three five-membered (cyclopentane, 2-pyrrolidinone and dihydrofuran) rings, and the tricyclic core of **12c** contains one six-membered (cyclohexanone) and two five-membered (cyclopentane and 2-pyrrolidinone) rings. The cyclohexene, cycloxehanone, cyclopentane and 2-pyrrolidinone rings adopt the typical *half-chair*, *chair*, slightly distorted *envelope* and *envelope* conformations, respectively. Compounds **12a** and **12c** possess four and five asymmetric centers at the C3A, C6A, C7, C7A and C3A, C6A, C7, C8 and C9A carbon atoms, respectively, and can have potentially numerous diastereomers. The crystal of **12a** is racemic and consists of enantiomeric pairs with the following relative configuration of the centers: 3A***RS***,6A***RS***,7***RS***,7A***RS***. The crystal of **12c** is a racemic twin and consists of enantiomeric pairs with the following relative configuration of the centers: 3A***SR***,6A***RS***,7***RS***,8***RS***,9A***SR***. In the crystal of **12a**, the molecules form the centrosymmetric hydrogen-bonded dimers by the strong O─H···O(═C) hydrogen bonds (see Tables S1, S9-S14). The dimers are packed in stacks along the crystallographic *b* axis. In the crystal of **12c**, the molecules form the hydrogen-bonded associates with the solvate dimethylsulfoxide molecules by the strong O─H···O(═S) hydrogen bonds (see Tables S1, S15-S20). The associates are packed in stacks along the crystallographic *a* axis.

**Table S1.** Crystal data and structure refinement for **10g**, **12a**, **12c**, **20a**, **20d**, **23a** and **23e**.

| Identification code | **10g** • DMSO | **12a** | **12c** • DMSO |
|---|---|---|---|
| CCDC number | 2495035 | 2513916 | 2513917 |
| Empirical formula | $C_{24}H_{19}D_6NO_6S$ | $C_{20}H_{19}NO_4$ | $C_{23}H_{29}NO_6S$ |
| Formula weight | 461.55 | 337.36 | 447.53 |
| Temperature, K | 100(2) | 100(2) | 100(2) |
| Crystal size, mm | 0.46 × 0.4 × 0.32 | 0.03 × 0.20 × 0.25 | 0.03 × 0.03 × 0.33 |
| Radiation | MoKα (λ = 0.71073) | Cu*K*α (λ = 1.5418) | Cu*K*α (λ = 1.5418) |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | *P*-1 | *C*2/c | *P*1 |
| *a*, Å | 6.5687(2) | 25.1111(6) | 9.14531(17) |
| *b*, Å | 13.3383(4) | 8.92502(12) | 11.43369(19) |
| *c*, Å | 13.7786(4) | 18.2650(5) | 21.5910(4) |
| *α*, deg. | 61.374(1) | 90 | 100.0863(15) |

| | | | |
|---|---|---|---|
| $\beta$, deg. | 86.879(2) | 127.400(4) | 90.7070(14) |
| $\gamma$, deg. | 86.332(1) | 90 | 90.2151(13) |
| $V$, Å$^3$ | 1057.09(6) | 3251.93(19) | 2222.55(7) |
| $Z$ | 2 | 8 | 4 |
| Density (calc.), Mg/m$^3$ | 1.450 | 1.378 | 1.337 |
| $\mu$, mm$^{-1}$ | 0.196 | 0.787 | 1.629 |
| $F$(000) | 480.0 | 1424 | 952 |
| Theta range, deg. | 8.35 – 60 | 4.433 – 79.768 | 3.927 – 83.712 |
| Index ranges | -9 ≤ h ≤ 9,<br>-18 ≤ k ≤ 18,<br>-19 ≤ l ≤ 19 | -31 ≤ $h$ ≤ 31,<br>-11 ≤ $k$ ≤ 10,<br>-23 ≤ $l$ ≤ 21 | -11 ≤ $h$ ≤ 11,<br>-12 ≤ $k$ ≤ 14,<br>-27 ≤ $l$ ≤ 27 |
| Reflections collected | 18048 | 24152 | 30564 |
| Independent reflections, $R_{int}$ | 6156, 0.0241 | 3513, 0.0564 | 11897, 0.0542 |
| Reflections observed | 5256 | 3223 | 11411 |
| $R_1$ / w$R_2$ ($I > 2\sigma(I)$) | 0.0365 / 0.0968 | 0.0525 / 0.1268 | 0.0914 / 0.2050 |
| $R_1$ / w$R_2$ (all data) | 0.0439 / 0.1021 | 0.0593 / 0.1300 | 0.0941 / 0.2067 |
| Goodness-of-fit on $F^2$ | 1.037 | 1.041 | 1.011 |
| $T_{min}$ / $T_{max}$ | 0.874 / 0.940 | 0.596 / 1.000 | 0.541 / 1.000 |
| $\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å$^{-3}$ | 0.48 / -0.43 | 0.62 / -0.34 | 0.79 / -0.69 |
| Flack parameter | — | — | 0.18(4) |

**Table S1 (continuation).** Crystal data and structure refinement for **10g**, **12a**, **12c**, **20a**, **20d**, **23a** and **23e**.

| Identification code | **20a** • DMSO | **20d** • DMSO | **23a** | **23e** • DMSO |
|---|---|---|---|---|
| CCDC number | 2495036 | 2495037 | 2495038 | 2513919 |
| Empirical formula | $C_{24}H_{16}D_6NO_5F_3S$ | $C_{13}H_{8.5}D_3N_{0.5}O_3F_3S_{0.5}$ | $C_{21}H_{17}NO_4$ | $C_{24}H_{22}F_3NO_5S$ |
| Formula weight | 499.52 | 298.77 | 347.36 | 493.49 |
| Temperature, K | 100(2) | 100(2) | 100(2) | 100(2) |
| Crystal size, mm | 0.3 × 0.16 × 0.08 | 0.44 × 0.36 × 0.18 | 0.4 × 0.2 × 0.12 | 0.06 × 0.06 × 0.24 |
| Radiation, Å | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | MoKα (λ = 0.71073) | Cu$K\alpha$ (λ = 1.5418) |
| Crystal system | Monoclinic | Orthorhombic | Monoclinic | Triclinic |
| Space group | $P2_1$ | $P2_12_12_1$ | $P2_1$/c | $P$-1 |
| $a$, Å | 8.1549(7) | 8.9019(6) | 12.3473(8) | 6.69436(16) |
| $b$, Å | 16.3136(13) | 13.4092(9) | 8.0310(5) | 7.4987(2) |
| $c$, Å | 16.7975(14) | 21.1363(14) | 16.2960(11) | 23.1930(6) |
| $\alpha$, deg. | 90 | 90 | 90 | 80.904(2) |
| $\beta$, deg. | 92.219(5) | 90 | 96.882(2) | 85.135(2) |
| $\gamma$, deg. | 90 | 90 | 90 | 72.729(2) |
| $V$, Å$^3$ | 2233.0(3) | 2523.0(3) | 1604.29(18) | 1096.90(5) |
| $Z$ | 4 | 8 | 4 | 2 |
| Density (calc.), Mg/m$^3$ | 1.486 | 1.573 | 1.438 | 1.494 |
| $\mu$, mm$^{-1}$ | 0.207 | 0.217 | 0.100 | 1.883 |
| $F$(000) | 1024.0 | 1216.0 | 728.0 | 512 |

| Theta range, deg. | 8.468 – 54.998 | 7.198 – 60 | 8.366 – 60 | 3.863 – 79.938 |
|---|---|---|---|---|
| Index ranges | -10 ≤ h ≤ 10,<br>-19 ≤ k ≤ 21,<br>-21 ≤ l ≤ 21 | -12 ≤ h ≤ 12,<br>-18 ≤ k ≤ 18,<br>-29 ≤ l ≤ 29 | -17 ≤ h ≤ 17,<br>-11 ≤ k ≤ 11,<br>-22 ≤ l ≤ 22 | -8 ≤ *h* ≤ 6,<br>-9 ≤ *k* ≤ 9<br>-29 ≤ *l* ≤ 29 |
| Reflections collected | 38520 | 48308 | 26484 | 26336 |
| Independent reflections, $R_{int}$ | 14240, 0.0571 | 7330, 0.0396 | 4675, 0.0511 | 4689, 0.0831 |
| Reflections observed | 11435 | 6555 | 3448 | 4317 |
| $R_1$ / w$R_2$ ($I > 2\sigma(I)$) | 0.0548 / 0.1191 | 0.0315 / 0.0730 | 0.0441 / 0.1015 | 0.0618 / 0.1477 |
| $R_1$ / w$R_2$ (all data) | 0.0742 / 0.1277 | 0.0386 / 0.0767 | 0.0681 / 0.1124 | 0.0659 / 0.1504 |
| Goodness-of-fit on $F^2$ | 1.029 | 1.022 | 1.028 | 1.037 |
| $T_{min}$ / $T_{max}$ | 0.809 / 0.984 | 0.885 / 0.962 | 0.929 / 1.000 | 0.651 / 1.000 |
| $\Delta\rho_{max}$ / $\Delta\rho_{min}$, e·Å$^{-3}$ | 0.73 / -0.50 | 0.34 / -0.26 | 0.42 / -0.23 | 0.54 / -0.56 |
| Flack parameter | 0.12(4) | 0.46(7) | — | — |

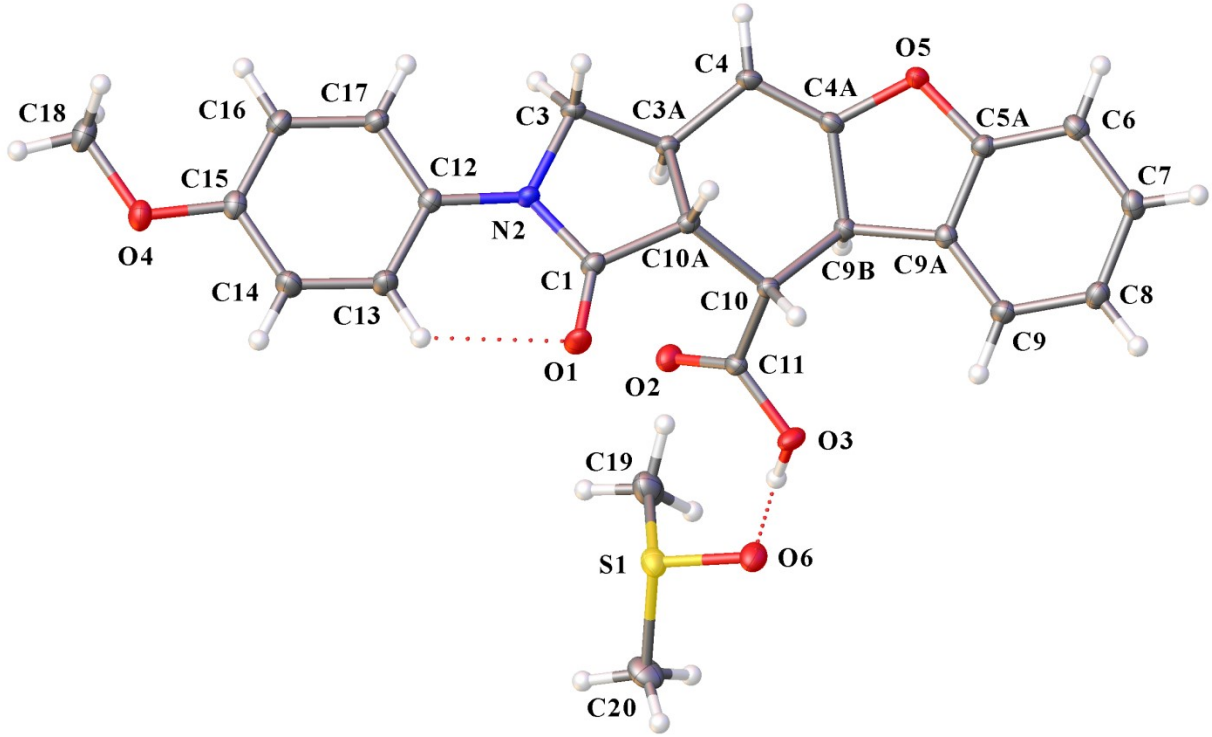


**Figure S1**. Molecular structure of **10g**. Dotted lines show H-bonding interactions.

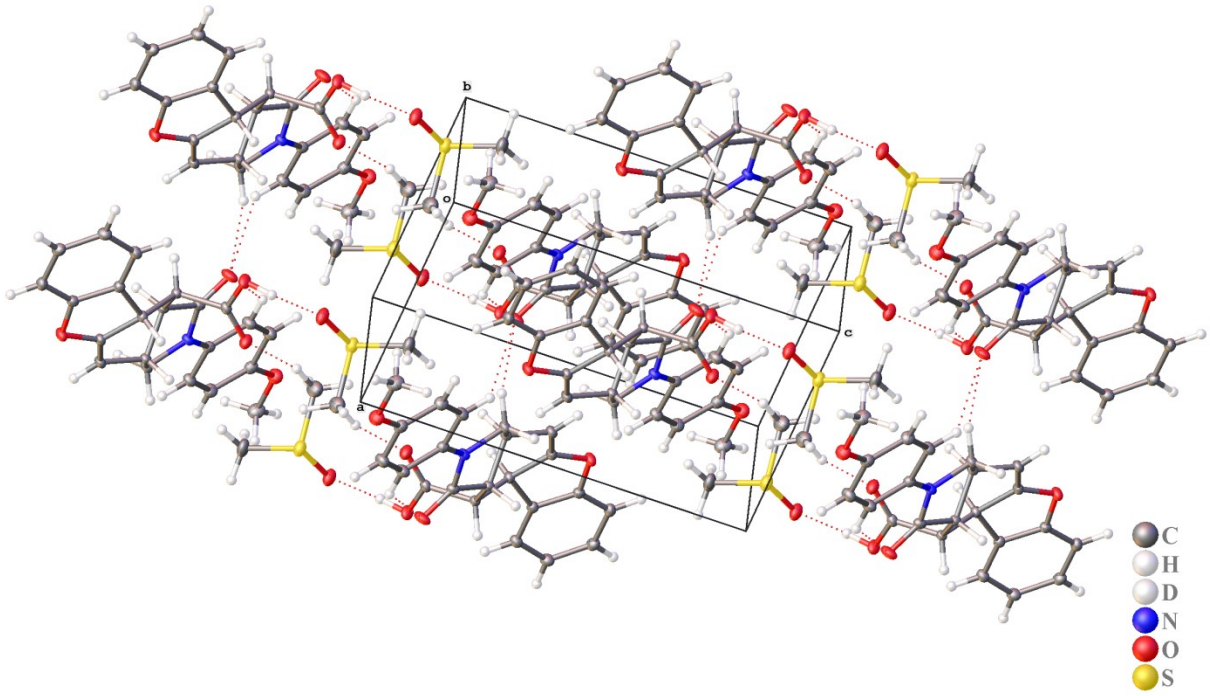


**Figure S2.** Crystal structure of **10g**.

**Table S2.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **10g**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| S1 | 8019.5(5) | 10869.1(2) | 25.5(2) | 18.40(8) |
| O1 | 7092.7(12) | 6270.0(8) | 3122.6(8) | 19.40(18) |
| O2 | 5694.5(13) | 8855.3(8) | 2282.1(7) | 18.36(17) |
| O3 | 8441.9(13) | 9185.5(8) | 2965.4(7) | 17.78(17) |
| O4 | 2260.5(14) | 3845.2(8) | 848.4(7) | 19.50(18) |
| O5 | 2898.4(12) | 7956.1(7) | 6413.9(7) | 15.83(16) |
| O6 | 8873.2(14) | 10926.3(8) | 997.2(7) | 20.60(18) |
| N2 | 3594.2(14) | 6002.8(8) | 3364.4(8) | 12.55(18) |
| C1 | 5418.2(16) | 6360.8(9) | 3515.1(9) | 13.0(2) |
| C3 | 1906.8(16) | 6194.6(10) | 4024.7(9) | 13.6(2) |
| C3A | 2693.2(16) | 7141.7(9) | 4204.4(9) | 12.19(19) |
| C4 | 1937.5(17) | 7250.8(10) | 5198.7(9) | 14.6(2) |
| C4A | 3172.4(17) | 7818.3(10) | 5477.4(9) | 13.6(2) |
| C5A | 4705.3(17) | 8359.6(9) | 6542.6(9) | 13.3(2) |
| C6 | 5078.0(18) | 8523.0(10) | 7431.0(9) | 15.7(2) |
| C7 | 6989.9(18) | 8916.8(10) | 7441.0(10) | 16.6(2) |
| C8 | 8438.2(18) | 9128.0(10) | 6596.0(10) | 16.5(2) |
| C9 | 8000.3(17) | 8971.6(10) | 5693.9(9) | 14.8(2) |
| C9A | 6105.9(17) | 8586.7(9) | 5673.5(9) | 12.7(2) |
| C9B | 5070.0(16) | 8403.8(9) | 4823.2(9) | 12.16(19) |
| C10 | 6280.3(16) | 7766.7(9) | 4245.6(9) | 11.29(19) |
| C10A | 4981.9(16) | 6825.2(9) | 4318.1(9) | 11.73(19) |

| | | | | |
|---|---|---|---|---|
| C11 | 6761.8(17) | 8645.4(9) | 3055.7(9) | 12.8(2) |
| C12 | 3297.5(16) | 5401.5(9) | 2768.8(9) | 12.9(2) |
| C13 | 4846.8(18) | 5246.7(11) | 2103.0(10) | 17.4(2) |
| C14 | 4441.8(18) | 4709.9(11) | 1492.4(10) | 18.7(2) |
| C15 | 2507.8(18) | 4317.2(10) | 1520.6(9) | 15.7(2) |
| C16 | 984.0(18) | 4443.6(10) | 2195.9(10) | 16.6(2) |
| C17 | 1386.5(17) | 4981.1(10) | 2815.4(10) | 15.3(2) |
| C18 | 289(2) | 3431.8(11) | 871.7(11) | 22.0(2) |
| C19 | 5561(2) | 11573.4(14) | -200.6(12) | 27.6(3) |
| D19A | 4943.02 | 11558.79 | -824.96 | 41 |
| D19B | 4694.92 | 11181.21 | 465.12 | 41 |
| D19C | 5692.04 | 12368.08 | -366.63 | 41 |
| C20 | 9322(2) | 11919.1(12) | -1164.7(10) | 25.5(3) |
| D20A | 8839.89 | 11928.7 | -1829.85 | 38 |
| D20B | 9049.25 | 12672.98 | -1214.21 | 38 |
| D20C | 10792.89 | 11732.41 | -1103.73 | 38 |

**Table S3.** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **10g**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| S1 | 25.14(16) | 16.65(14) | 13.58(14) | -7.14(11) | 0.59(10) | -3.53(11) |
| O1 | 9.4(4) | 27.1(4) | 29.4(5) | -19.9(4) | 1.8(3) | -1.4(3) |
| O2 | 19.4(4) | 21.6(4) | 13.1(4) | -6.9(3) | -1.4(3) | -5.6(3) |
| O3 | 16.2(4) | 20.5(4) | 14.5(4) | -5.8(3) | 1.2(3) | -8.7(3) |
| O4 | 20.4(4) | 22.7(4) | 21.0(4) | -14.6(4) | -1.6(3) | -2.4(3) |
| O5 | 12.1(4) | 24.0(4) | 15.3(4) | -12.5(3) | 2.7(3) | -3.9(3) |
| O6 | 25.8(5) | 20.8(4) | 13.4(4) | -5.9(3) | -0.3(3) | -7.9(3) |
| N2 | 9.3(4) | 14.6(4) | 15.5(4) | -8.7(4) | 1.3(3) | -1.6(3) |
| C1 | 10.5(5) | 12.6(5) | 15.9(5) | -6.8(4) | -1.2(4) | -0.2(4) |
| C3 | 9.5(5) | 16.7(5) | 15.7(5) | -8.7(4) | 2.6(4) | -2.6(4) |
| C3A | 9.0(4) | 14.6(5) | 13.1(5) | -6.6(4) | 0.7(4) | -1.2(4) |
| C4 | 10.2(5) | 19.3(5) | 15.0(5) | -8.9(4) | 2.5(4) | -1.7(4) |
| C4A | 11.6(5) | 17.0(5) | 12.6(5) | -7.7(4) | 1.4(4) | 0.3(4) |
| C5A | 11.4(5) | 14.2(5) | 13.8(5) | -6.4(4) | -0.8(4) | -0.3(4) |
| C6 | 16.4(5) | 17.9(5) | 13.2(5) | -7.9(4) | 0.7(4) | 0.4(4) |
| C7 | 17.4(5) | 18.9(5) | 15.6(5) | -10.1(4) | -3.1(4) | 1.7(4) |
| C8 | 14.0(5) | 18.9(5) | 19.4(5) | -11.3(4) | -1.9(4) | -0.9(4) |
| C9 | 13.1(5) | 16.5(5) | 16.9(5) | -9.7(4) | 1.6(4) | -1.6(4) |
| C9A | 13.1(5) | 12.9(5) | 13.0(5) | -6.9(4) | -0.6(4) | 0.1(4) |
| C9B | 11.5(5) | 14.1(5) | 11.6(5) | -6.7(4) | 0.8(4) | -1.1(4) |
| C10 | 9.4(4) | 13.3(5) | 11.3(5) | -6.0(4) | 0.3(3) | -1.0(4) |
| C10A | 9.6(4) | 12.8(5) | 12.5(5) | -5.7(4) | -0.4(4) | -0.9(4) |
| C11 | 12.4(5) | 13.9(5) | 13.6(5) | -8.0(4) | 2.3(4) | -1.9(4) |
| C12 | 12.5(5) | 12.2(5) | 13.9(5) | -6.1(4) | -1.5(4) | -0.1(4) |
| C13 | 12.3(5) | 22.5(6) | 21.1(6) | -13.4(5) | 0.5(4) | -1.2(4) |
| C14 | 15.0(5) | 24.3(6) | 21.2(6) | -14.7(5) | 1.7(4) | -0.6(4) |
| C15 | 18.1(5) | 13.9(5) | 15.6(5) | -7.4(4) | -2.7(4) | -0.3(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C16 | 15.6(5) | 17.0(5) | 18.6(5) | -9.2(4) | -0.4(4) | -4.0(4) |
| C17 | 13.0(5) | 16.5(5) | 18.2(5) | -9.6(4) | 1.7(4) | -3.0(4) |
| C18 | 23.5(6) | 21.1(6) | 24.8(6) | -13.0(5) | -5.7(5) | -3.1(5) |
| C19 | 24.7(6) | 39.4(8) | 23.0(6) | -18.2(6) | -2.7(5) | 0.5(6) |
| C20 | 33.5(7) | 22.9(6) | 13.4(5) | -3.6(5) | 2.9(5) | -1.3(5) |

**Table S4.** Bond Lengths for **10g**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S1 | O6 | 1.5159(9) | C6 | C7 | 1.3952(16) |
| S1 | C19 | 1.7797(15) | C7 | C8 | 1.3926(16) |
| S1 | C20 | 1.7841(13) | C8 | C9 | 1.4022(15) |
| O1 | C1 | 1.2239(13) | C9 | C9A | 1.3828(15) |
| O2 | C11 | 1.2151(14) | C9A | C9B | 1.5090(15) |
| O3 | C11 | 1.3241(13) | C9B | C10 | 1.5748(14) |
| O4 | C15 | 1.3670(13) | C10 | C10A | 1.5238(15) |
| O4 | C18 | 1.4326(15) | C10 | C11 | 1.5203(15) |
| O5 | C4A | 1.3889(13) | C12 | C13 | 1.4046(15) |
| O5 | C5A | 1.3877(13) | C12 | C17 | 1.3933(15) |
| N2 | C1 | 1.3791(14) | C13 | C14 | 1.3845(16) |
| N2 | C3 | 1.4828(14) | C14 | C15 | 1.3964(16) |
| N2 | C12 | 1.4223(14) | C15 | C16 | 1.3868(16) |
| C1 | C10A | 1.5131(15) | C16 | C17 | 1.3956(15) |
| C3 | C3A | 1.5235(15) | C19 | D19A | 0.9800 |
| C3A | C4 | 1.5008(15) | C19 | D19B | 0.9800 |
| C3A | C10A | 1.5310(14) | C19 | D19C | 0.9800 |
| C4 | C4A | 1.3301(16) | C20 | D20A | 0.9800 |
| C4A | C9B | 1.5178(15) | C20 | D20B | 0.9800 |
| C5A | C6 | 1.3787(15) | C20 | D20C | 0.9800 |
| C5A | C9A | 1.3929(15) | | | |

**Table S5.** Bond Angles for **10g**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O6 | S1 | C19 | 106.39(6) | C10A | C10 | C9B | 108.75(8) |
| O6 | S1 | C20 | 105.08(6) | C11 | C10 | C9B | 107.97(8) |
| C19 | S1 | C20 | 98.44(7) | C11 | C10 | C10A | 112.17(9) |
| C15 | O4 | C18 | 116.89(9) | C1 | C10A | C3A | 103.50(8) |
| C5A | O5 | C4A | 106.64(8) | C1 | C10A | C10 | 119.14(9) |
| C1 | N2 | C3 | 111.54(9) | C10 | C10A | C3A | 113.97(9) |
| C1 | N2 | C12 | 126.89(9) | O2 | C11 | O3 | 123.84(10) |
| C12 | N2 | C3 | 121.20(9) | O2 | C11 | C10 | 124.00(10) |
| O1 | C1 | N2 | 126.90(10) | O3 | C11 | C10 | 112.13(9) |
| O1 | C1 | C10A | 126.17(10) | C13 | C12 | N2 | 122.34(10) |
| N2 | C1 | C10A | 106.84(9) | C17 | C12 | N2 | 119.12(10) |
| N2 | C3 | C3A | 102.43(8) | C17 | C12 | C13 | 118.51(10) |
| C3 | C3A | C10A | 101.35(8) | C14 | C13 | C12 | 119.93(11) |
| C4 | C3A | C3 | 119.03(9) | C13 | C14 | C15 | 121.24(11) |
| C4 | C3A | C10A | 108.36(9) | O4 | C15 | C14 | 116.14(10) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4A | C4 | C3A | 113.34(10) | O4 | C15 | C16 | 124.72(10) |
| O5 | C4A | C9B | 110.50(9) | C16 | C15 | C14 | 119.12(10) |
| C4 | C4A | O5 | 124.43(10) | C15 | C16 | C17 | 119.83(11) |
| C4 | C4A | C9B | 125.07(10) | C12 | C17 | C16 | 121.32(10) |
| O5 | C5A | C9A | 112.69(9) | S1 | C19 | D19A | 109.5 |
| C6 | C5A | O5 | 123.84(10) | S1 | C19 | D19B | 109.5 |
| C6 | C5A | C9A | 123.47(10) | S1 | C19 | D19C | 109.5 |
| C5A | C6 | C7 | 116.49(10) | D19A | C19 | D19B | 109.5 |
| C8 | C7 | C6 | 121.36(10) | D19A | C19 | D19C | 109.5 |
| C7 | C8 | C9 | 120.78(11) | D19B | C19 | D19C | 109.5 |
| C9A | C9 | C8 | 118.30(10) | S1 | C20 | D20A | 109.5 |
| C5A | C9A | C9B | 107.47(9) | S1 | C20 | D20B | 109.5 |
| C9 | C9A | C5A | 119.58(10) | S1 | C20 | D20C | 109.5 |
| C9 | C9A | C9B | 132.83(10) | D20A | C20 | D20B | 109.5 |
| C4A | C9B | C10 | 114.54(9) | D20A | C20 | D20C | 109.5 |
| C9A | C9B | C4A | 100.44(8) | D20B | C20 | D20C | 109.5 |
| C9A | C9B | C10 | 119.55(9) | | | | |

**Table S6.** Hydrogen Bonds for **10g**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O3 | H3 | O6 | 0.91(2) | 1.70(2) | 2.6063(12) | 176(2) |
| C3 | H3B | O1[1] | 0.99 | 2.50 | 3.4384(14) | 157.1 |
| C13 | H13A | O1 | 0.95 | 2.25 | 2.8868(14) | 123.5 |
| C17 | H17A | O1[1] | 0.95 | 2.54 | 3.3221(14) | 139.5 |
| C19 | D19A | O2[2] | 0.98 | 2.39 | 3.3349(16) | 162.7 |

[1]-1+X,+Y,+Z; [2]1-X,2-Y,-Z

**Table S7.** Torsion Angles for **10g**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C10A | C3A | 160.42(11) | C5A | C6 | C7 | C8 | -0.18(17) |
| O1 | C1 | C10A | C10 | 32.67(16) | C5A | C9A | C9B | C4A | -11.61(11) |
| O4 | C15 | C16 | C17 | -177.39(11) | C5A | C9A | C9B | C10 | -137.77(10) |
| O5 | C4A | C9B | C9A | 15.22(11) | C6 | C5A | C9A | C9 | 1.60(17) |
| O5 | C4A | C9B | C10 | 144.68(9) | C6 | C5A | C9A | C9B | -174.95(10) |
| O5 | C5A | C6 | C7 | 178.98(10) | C6 | C7 | C8 | C9 | 1.27(18) |
| O5 | C5A | C9A | C9 | -178.61(10) | C7 | C8 | C9 | C9A | -0.92(17) |
| O5 | C5A | C9A | C9B | 4.84(13) | C8 | C9 | C9A | C5A | -0.45(16) |
| N2 | C1 | C10A | C3A | -22.93(11) | C8 | C9 | C9A | C9B | 175.06(11) |
| N2 | C1 | C10A | C10 | -150.68(9) | C9 | C9A | C9B | C4A | 172.48(12) |
| N2 | C3 | C3A | C4 | -153.95(9) | C9 | C9A | C9B | C10 | 46.32(17) |
| N2 | C3 | C3A | C10A | -35.33(10) | C9A | C5A | C6 | C7 | -1.25(17) |
| N2 | C12 | C13 | C14 | -176.40(11) | C9A | C9B | C10 | C10A | 129.98(10) |
| N2 | C12 | C17 | C16 | 176.26(10) | C9A | C9B | C10 | C11 | -108.07(11) |
| C1 | N2 | C3 | C3A | 23.03(11) | C9B | C10 | C10A | C1 | 159.08(9) |
| C1 | N2 | C12 | C13 | -10.08(17) | C9B | C10 | C10A | C3A | 36.37(12) |
| C1 | N2 | C12 | C17 | 172.05(10) | C9B | C10 | C11 | O2 | -93.30(12) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C3 | N2 | C1 | O1 | 176.57(11) | C9B | C10 | C11 | O3 | 84.42(11) |
| C3 | N2 | C1 | C10A | -0.05(12) | C10A | C3A | C4 | C4A | 43.72(13) |
| C3 | N2 | C12 | C13 | 177.47(10) | C10A | C10 | C11 | O2 | 26.51(15) |
| C3 | N2 | C12 | C17 | -0.40(15) | C10A | C10 | C11 | O3 | -155.77(9) |
| C3 | C3A | C4 | C4A | 158.64(10) | C11 | C10 | C10A | C1 | 39.73(13) |
| C3 | C3A | C10A | C1 | 35.82(10) | C11 | C10 | C10A | C3A | -82.98(11) |
| C3 | C3A | C10A | C10 | 166.72(9) | C12 | N2 | C1 | O1 | 3.51(19) |
| C3A | C4 | C4A | O5 | -174.71(10) | C12 | N2 | C1 | C10A | -173.10(10) |
| C3A | C4 | C4A | C9B | 5.27(16) | C12 | N2 | C3 | C3A | -163.47(9) |
| C4 | C3A | C10A | C1 | 161.84(9) | C12 | C13 | C14 | C15 | 0.17(19) |
| C4 | C3A | C10A | C10 | -67.25(11) | C13 | C12 | C17 | C16 | -1.70(17) |
| C4 | C4A | C9B | C9A | -164.76(11) | C13 | C14 | C15 | O4 | 177.27(11) |
| C4 | C4A | C9B | C10 | -35.30(16) | C13 | C14 | C15 | C16 | -1.65(18) |
| C4A | O5 | C5A | C6 | -175.09(11) | C14 | C15 | C16 | C17 | 1.43(17) |
| C4A | O5 | C5A | C9A | 5.13(12) | C15 | C16 | C17 | C12 | 0.24(18) |
| C4A | C9B | C10 | C10A | 10.77(12) | C17 | C12 | C13 | C14 | 1.48(17) |
| C4A | C9B | C10 | C11 | 132.72(10) | C18 | O4 | C15 | C14 | 179.65(11) |
| C5A | O5 | C4A | C4 | 166.87(11) | C18 | O4 | C15 | C16 | -1.50(17) |
| C5A | O5 | C4A | C9B | -13.11(12) | | | | | |

**Table S8.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for **10g**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H3 | 8530(30) | 9791(19) | 2269(19) | 48(6) |
| H3A | 1676.26 | 5495.64 | 4736.77 | 16 |
| H3B | 622.55 | 6442.67 | 3612.55 | 16 |
| H3AA | 2469.62 | 7892.33 | 3523.76 | 15 |
| H4A | 699.74 | 6944.78 | 5590.41 | 18 |
| H6A | 4085.14 | 8375.31 | 8005.98 | 19 |
| H7A | 7310.43 | 9043.43 | 8036.64 | 20 |
| H8A | 9738.22 | 9381.07 | 6631.13 | 20 |
| H9A | 8979.97 | 9126.05 | 5111.74 | 18 |
| H9BA | 4617.12 | 9174.42 | 4225.21 | 15 |
| H10A | 7584.48 | 7418.27 | 4637.04 | 14 |
| H10B | 5161.19 | 6163.81 | 5076 | 14 |
| H13A | 6171.21 | 5509.98 | 2071.6 | 21 |
| H14A | 5499.53 | 4606.78 | 1045.9 | 22 |
| H16A | -330.5 | 4165.07 | 2236.62 | 20 |
| H17A | 336.36 | 5061.93 | 3278.14 | 18 |
| H18A | 296.76 | 3115.06 | 359.96 | 33 |
| H18B | -41.01 | 2834.3 | 1622.73 | 33 |
| H18C | -737.88 | 4063.17 | 648.32 | 33 |

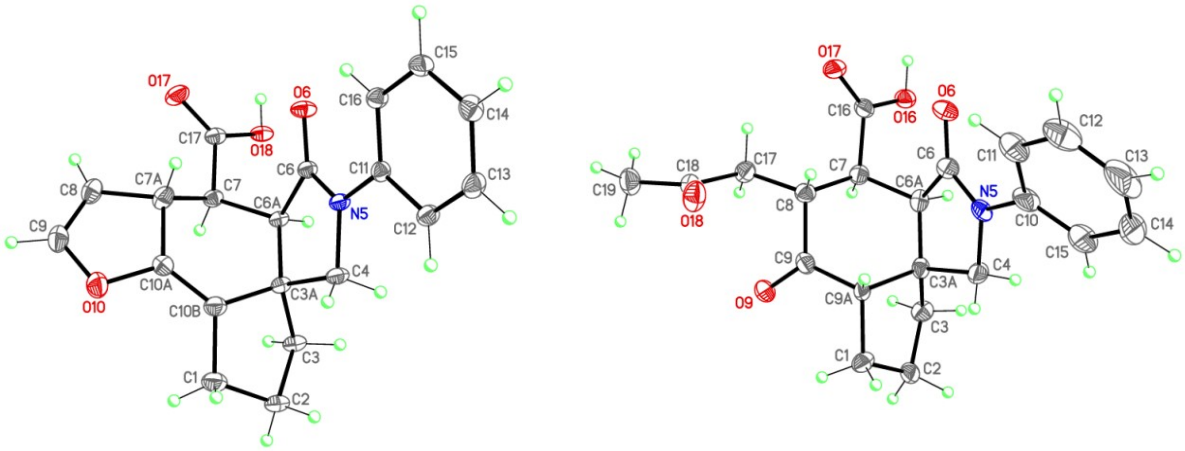


**Figure S3.** Molecular structure of **12a** (left) and **12c** (right) (40%-ellipsoids; only one of the four crystallographically independent molecules is presented for **12c**; the solvate dimethylsulfoxide molecules of **12c** are not shown).

**Table S9.** Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **12a**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| C(1) | 5033(1) | 7795(2) | 4200(1) | 32(1) |
| C(2) | 5618(1) | 8609(2) | 5075(1) | 26(1) |
| C(3) | 6213(1) | 7517(2) | 5512(1) | 23(1) |
| C(3A) | 6124(1) | 6826(2) | 4673(1) | 18(1) |
| C(4) | 6342(1) | 7944(2) | 4256(1) | 23(1) |
| N(5) | 6575(1) | 7001(1) | 3843(1) | 19(1) |
| C(6) | 6707(1) | 5580(2) | 4171(1) | 19(1) |
| O(6) | 6929(1) | 4570(1) | 3969(1) | 24(1) |
| C(6A) | 6541(1) | 5422(2) | 4844(1) | 18(1) |
| C(7) | 6195(1) | 3916(2) | 4715(1) | 21(1) |
| C(7A) | 5514(1) | 3886(2) | 3748(1) | 28(1) |
| C(8) | 5012(1) | 2665(2) | 3502(1) | 29(1) |
| C(9) | 4432(1) | 3310(2) | 3159(1) | 32(1) |
| O(10) | 4452(1) | 4862(2) | 3185(1) | 33(1) |
| C(10A) | 5124(1) | 5236(2) | 3656(1) | 22(1) |
| C(10B) | 5373(1) | 6571(2) | 4047(1) | 26(1) |
| C(11) | 6703(1) | 7629(2) | 3246(1) | 19(1) |
| C(12) | 6681(1) | 9186(2) | 3146(1) | 22(1) |
| C(13) | 6792(1) | 9823(2) | 2555(1) | 26(1) |
| C(14) | 6927(1) | 8936(2) | 2065(1) | 26(1) |
| C(15) | 6953(1) | 7391(2) | 2171(1) | 23(1) |
| C(16) | 6839(1) | 6728(2) | 2753(1) | 21(1) |
| C(17) | 6623(1) | 2580(2) | 4863(1) | 21(1) |
| O(17) | 6414(1) | 1494(1) | 4366(1) | 32(1) |
| O(18) | 7251(1) | 2710(1) | 5625(1) | 23(1) |

**Table S10.** Bond lengths [Å] and angles [°] for **12a**.

| | | | |
|---|---|---|---|
| C(1)-C(10B) | 1.514(2) | C(1)-H(1B) | 0.9900 |
| C(1)-C(2) | 1.547(2) | C(2)-C(3) | 1.539(2) |
| C(1)-H(1A) | 0.9900 | C(2)-H(2A) | 0.9900 |

| | | | |
|---|---|---|---|
| C(2)-H(2B) | 0.9900 | H(2A)-C(2)-H(2B) | 108.9 |
| C(3)-C(3A) | 1.537(2) | C(3A)-C(3)-C(2) | 103.28(12) |
| C(3)-H(3A) | 0.9900 | C(3A)-C(3)-H(3A) | 111.1 |
| C(3)-H(3B) | 0.9900 | C(2)-C(3)-H(3A) | 111.1 |
| C(3A)-C(10B) | 1.514(2) | C(3A)-C(3)-H(3B) | 111.1 |
| C(3A)-C(6A) | 1.5392(19) | C(2)-C(3)-H(3B) | 111.1 |
| C(3A)-C(4) | 1.543(2) | H(3A)-C(3)-H(3B) | 109.1 |
| C(4)-N(5) | 1.4680(18) | C(10B)-C(3A)-C(3) | 99.98(12) |
| C(4)-H(4A) | 0.9900 | C(10B)-C(3A)-C(6A) | 114.39(12) |
| C(4)-H(4B) | 0.9900 | C(3)-C(3A)-C(6A) | 117.09(12) |
| N(5)-C(6) | 1.3549(19) | C(10B)-C(3A)-C(4) | 112.13(13) |
| N(5)-C(11) | 1.4255(18) | C(3)-C(3A)-C(4) | 110.63(12) |
| C(6)-O(6) | 1.2304(18) | C(6A)-C(3A)-C(4) | 102.98(11) |
| C(6)-C(6A) | 1.5235(19) | N(5)-C(4)-C(3A) | 104.76(12) |
| C(6A)-C(7) | 1.539(2) | N(5)-C(4)-H(4A) | 110.8 |
| C(6A)-H(6A) | 1.0000 | C(3A)-C(4)-H(4A) | 110.8 |
| C(7)-C(17) | 1.515(2) | N(5)-C(4)-H(4B) | 110.8 |
| C(7)-C(7A) | 1.542(2) | C(3A)-C(4)-H(4B) | 110.8 |
| C(7)-H(7) | 1.0000 | H(4A)-C(4)-H(4B) | 108.9 |
| C(7A)-C(10A) | 1.497(2) | C(6)-N(5)-C(11) | 126.78(12) |
| C(7A)-C(8) | 1.513(2) | C(6)-N(5)-C(4) | 112.04(12) |
| C(7A)-H(7A) | 1.0000 | C(11)-N(5)-C(4) | 120.87(12) |
| C(8)-C(9) | 1.317(3) | O(6)-C(6)-N(5) | 125.85(14) |
| C(8)-H(8) | 0.9500 | O(6)-C(6)-C(6A) | 124.82(13) |
| C(9)-O(10) | 1.386(2) | N(5)-C(6)-C(6A) | 109.33(12) |
| C(9)-H(9) | 0.9500 | C(6)-C(6A)-C(7) | 111.28(12) |
| O(10)-C(10A) | 1.3906(19) | C(6)-C(6A)-C(3A) | 104.25(11) |
| C(10A)-C(10B) | 1.334(2) | C(7)-C(6A)-C(3A) | 115.37(12) |
| C(11)-C(16) | 1.397(2) | C(6)-C(6A)-H(6A) | 108.6 |
| C(11)-C(12) | 1.399(2) | C(7)-C(6A)-H(6A) | 108.6 |
| C(12)-C(13) | 1.392(2) | C(3A)-C(6A)-H(6A) | 108.6 |
| C(12)-H(12) | 0.9500 | C(17)-C(7)-C(6A) | 112.76(12) |
| C(13)-C(14) | 1.383(2) | C(17)-C(7)-C(7A) | 111.28(13) |
| C(13)-H(13) | 0.9500 | C(6A)-C(7)-C(7A) | 108.72(12) |
| C(14)-C(15) | 1.388(2) | C(17)-C(7)-H(7) | 108.0 |
| C(14)-H(14) | 0.9500 | C(6A)-C(7)-H(7) | 108.0 |
| C(15)-C(16) | 1.390(2) | C(7A)-C(7)-H(7) | 108.0 |
| C(15)-H(15) | 0.9500 | C(10A)-C(7A)-C(8) | 100.06(14) |
| C(16)-H(16) | 0.9500 | C(10A)-C(7A)-C(7) | 108.05(13) |
| C(17)-O(17) | 1.207(2) | C(8)-C(7A)-C(7) | 119.82(14) |
| C(17)-O(18) | 1.331(2) | C(10A)-C(7A)-H(7A) | 109.4 |
| O(18)-H(18) | 0.89(2) | C(8)-C(7A)-H(7A) | 109.4 |
| C(10B)-C(1)-C(2) | 103.92(13) | C(7)-C(7A)-H(7A) | 109.4 |
| C(10B)-C(1)-H(1A) | 111.0 | C(9)-C(8)-C(7A) | 107.93(16) |
| C(2)-C(1)-H(1A) | 111.0 | C(9)-C(8)-H(8) | 126.0 |
| C(10B)-C(1)-H(1B) | 111.0 | C(7A)-C(8)-H(8) | 126.0 |
| C(2)-C(1)-H(1B) | 111.0 | C(8)-C(9)-O(10) | 114.48(15) |
| H(1A)-C(1)-H(1B) | 109.0 | C(8)-C(9)-H(9) | 122.8 |
| C(3)-C(2)-C(1) | 104.61(13) | O(10)-C(9)-H(9) | 122.8 |
| C(3)-C(2)-H(2A) | 110.8 | C(9)-O(10)-C(10A) | 105.37(13) |
| C(1)-C(2)-H(2A) | 110.8 | C(10B)-C(10A)-O(10) | 122.98(15) |
| C(3)-C(2)-H(2B) | 110.8 | C(10B)-C(10A)-C(7A) | 126.59(14) |
| C(1)-C(2)-H(2B) | 110.8 | O(10)-C(10A)-C(7A) | 110.02(13) |

| | |
|---|---|
| C(10A)-C(10B)-C(1) | 127.51(15) |
| C(10A)-C(10B)-C(3A) | 120.19(14) |
| C(1)-C(10B)-C(3A) | 109.64(13) |
| C(16)-C(11)-C(12) | 119.62(14) |
| C(16)-C(11)-N(5) | 121.68(13) |
| C(12)-C(11)-N(5) | 118.70(13) |
| C(13)-C(12)-C(11) | 119.72(14) |
| C(13)-C(12)-H(12) | 120.1 |
| C(11)-C(12)-H(12) | 120.1 |
| C(14)-C(13)-C(12) | 120.90(15) |
| C(14)-C(13)-H(13) | 119.5 |
| C(12)-C(13)-H(13) | 119.5 |
| C(13)-C(14)-C(15) | 119.12(15) |
| C(13)-C(14)-H(14) | 120.4 |
| C(15)-C(14)-H(14) | 120.4 |
| C(14)-C(15)-C(16) | 121.08(15) |
| C(14)-C(15)-H(15) | 119.5 |
| C(16)-C(15)-H(15) | 119.5 |
| C(15)-C(16)-C(11) | 119.57(14) |
| C(15)-C(16)-H(16) | 120.2 |
| C(11)-C(16)-H(16) | 120.2 |
| O(17)-C(17)-O(18) | 123.66(15) |
| O(17)-C(17)-C(7) | 124.05(15) |
| O(18)-C(17)-C(7) | 112.24(13) |
| C(17)-O(18)-H(18) | 110.0(14) |

**Table S11.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **12a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12} ]$.

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 27(1) | 29(1) | 36(1) | -4(1) | 18(1) | 6(1) |
| C(2) | 34(1) | 22(1) | 28(1) | -1(1) | 22(1) | 6(1) |
| C(3) | 30(1) | 20(1) | 22(1) | -1(1) | 17(1) | 5(1) |
| C(3A) | 23(1) | 16(1) | 19(1) | -1(1) | 14(1) | 2(1) |
| C(4) | 34(1) | 16(1) | 30(1) | 0(1) | 25(1) | 3(1) |
| N(5) | 26(1) | 14(1) | 23(1) | 0(1) | 18(1) | 1(1) |
| C(6) | 22(1) | 16(1) | 21(1) | 0(1) | 14(1) | 1(1) |
| O(6) | 37(1) | 18(1) | 29(1) | 5(1) | 25(1) | 9(1) |
| C(6A) | 22(1) | 15(1) | 18(1) | 0(1) | 13(1) | 3(1) |
| C(7) | 27(1) | 16(1) | 22(1) | 1(1) | 17(1) | 1(1) |
| C(7A) | 30(1) | 20(1) | 29(1) | -1(1) | 16(1) | -2(1) |
| C(8) | 34(1) | 23(1) | 29(1) | -1(1) | 18(1) | -6(1) |
| C(9) | 31(1) | 32(1) | 32(1) | -4(1) | 19(1) | -10(1) |
| O(10) | 23(1) | 31(1) | 37(1) | -3(1) | 14(1) | -2(1) |
| C(10A) | 22(1) | 25(1) | 19(1) | 1(1) | 12(1) | 1(1) |
| C(10B) | 25(1) | 24(1) | 28(1) | -2(1) | 16(1) | 3(1) |
| C(11) | 21(1) | 17(1) | 20(1) | 1(1) | 13(1) | -1(1) |
| C(12) | 28(1) | 18(1) | 25(1) | -1(1) | 18(1) | 0(1) |
| C(13) | 32(1) | 18(1) | 30(1) | 3(1) | 20(1) | -1(1) |
| C(14) | 30(1) | 26(1) | 25(1) | 5(1) | 19(1) | -1(1) |
| C(15) | 27(1) | 24(1) | 22(1) | -1(1) | 16(1) | 1(1) |
| C(16) | 24(1) | 18(1) | 23(1) | 1(1) | 15(1) | 1(1) |
| C(17) | 32(1) | 17(1) | 24(1) | 3(1) | 22(1) | 3(1) |
| O(17) | 39(1) | 19(1) | 38(1) | -5(1) | 23(1) | 1(1) |
| O(18) | 30(1) | 20(1) | 23(1) | 3(1) | 18(1) | 9(1) |

**Table S12.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **12a**.

| Atom | *x* | *y* | *z* | U(iso) |
|---|---|---|---|---|
| H(1A) | 4717 | 7365 | 4298 | 38 |
| H(1B) | 4785 | 8488 | 3667 | 38 |
| H(2A) | 5721 | 9569 | 4914 | 31 |
| H(2B) | 5508 | 8812 | 5502 | 31 |
| H(3A) | 6645 | 8054 | 5912 | 28 |
| H(3B) | 6191 | 6739 | 5879 | 28 |
| H(4A) | 5960 | 8577 | 3782 | 28 |
| H(4B) | 6707 | 8599 | 4740 | 28 |
| H(6A) | 6968 | 5467 | 5486 | 21 |
| H(7) | 6107 | 3861 | 5180 | 25 |
| H(7A) | 5590 | 3925 | 3271 | 33 |
| H(8) | 5099 | 1619 | 3582 | 35 |
| H(9) | 4033 | 2757 | 2913 | 38 |
| H(12) | 6590 | 9807 | 3482 | 27 |
| H(13) | 6775 | 10881 | 2487 | 31 |
| H(14) | 7002 | 9378 | 1661 | 31 |
| H(15) | 7050 | 6778 | 1840 | 28 |
| H(16) | 6855 | 5669 | 2815 | 25 |
| H(18) | 7486(11) | 1900(30) | 5698(15) | 34 |

**Table S13.** Torsion angles [°] for **12a**.

| | |
|---|---|
| C(10B)-C(1)-C(2)-C(3) | -16.40(18) |
| C(1)-C(2)-C(3)-C(3A) | 37.36(16) |
| C(2)-C(3)-C(3A)-C(10B) | -42.51(15) |
| C(2)-C(3)-C(3A)-C(6A) | -166.63(13) |
| C(2)-C(3)-C(3A)-C(4) | 75.85(15) |
| C(10B)-C(3A)-C(4)-N(5) | -98.50(14) |
| C(3)-C(3A)-C(4)-N(5) | 150.83(12) |
| C(6A)-C(3A)-C(4)-N(5) | 24.96(15) |
| C(3A)-C(4)-N(5)-C(6) | -17.55(17) |
| C(3A)-C(4)-N(5)-C(11) | 168.46(13) |
| C(11)-N(5)-C(6)-O(6) | -3.9(3) |
| C(4)-N(5)-C(6)-O(6) | -177.44(15) |
| C(11)-N(5)-C(6)-C(6A) | 175.62(13) |
| C(4)-N(5)-C(6)-C(6A) | 2.07(17) |
| O(6)-C(6)-C(6A)-C(7) | -41.2(2) |
| N(5)-C(6)-C(6A)-C(7) | 139.27(13) |
| O(6)-C(6)-C(6A)-C(3A) | -166.20(14) |
| N(5)-C(6)-C(6A)-C(3A) | 14.29(16) |
| C(10B)-C(3A)-C(6A)-C(6) | 98.32(14) |
| C(3)-C(3A)-C(6A)-C(6) | -145.22(13) |
| C(4)-C(3A)-C(6A)-C(6) | -23.62(14) |
| C(10B)-C(3A)-C(6A)-C(7) | -24.01(18) |
| C(3)-C(3A)-C(6A)-C(7) | 92.45(16) |
| C(4)-C(3A)-C(6A)-C(7) | -145.95(13) |
| C(6)-C(6A)-C(7)-C(17) | 59.59(16) |
| C(3A)-C(6A)-C(7)-C(17) | 178.08(12) |
| C(6)-C(6A)-C(7)-C(7A) | -64.31(16) |
| C(3A)-C(6A)-C(7)-C(7A) | 54.18(16) |
| C(17)-C(7)-C(7A)-C(10A) | -179.92(13) |
| C(6A)-C(7)-C(7A)-C(10A) | -55.14(16) |
| C(17)-C(7)-C(7A)-C(8) | 66.59(19) |
| C(6A)-C(7)-C(7A)-C(8) | -168.63(14) |
| C(10A)-C(7A)-C(8)-C(9) | 11.50(18) |
| C(7)-C(7A)-C(8)-C(9) | 129.18(17) |
| C(7A)-C(8)-C(9)-O(10) | -4.9(2) |
| C(8)-C(9)-O(10)-C(10A) | -4.8(2) |
| C(9)-O(10)-C(10A)-C(10B) | -160.47(16) |
| C(9)-O(10)-C(10A)-C(7A) | 12.59(18) |
| C(8)-C(7A)-C(10A)-C(10B) | 158.07(17) |
| C(7)-C(7A)-C(10A)-C(10B) | 32.0(2) |
| C(8)-C(7A)-C(10A)-O(10) | -14.68(17) |
| C(7)-C(7A)-C(10A)-O(10) | -140.77(13) |
| O(10)-C(10A)-C(10B)-C(1) | 11.0(3) |
| C(7A)-C(10A)-C(10B)-C(1) | -160.89(17) |
| O(10)-C(10A)-C(10B)-C(3A) | 170.52(14) |
| C(7A)-C(10A)-C(10B)-C(3A) | -1.4(3) |
| C(2)-C(1)-C(10B)-C(10A) | 150.40(17) |
| C(2)-C(1)-C(10B)-C(3A) | -10.88(19) |
| C(3)-C(3A)-C(10B)-C(10A) | -129.52(16) |
| C(6A)-C(3A)-C(10B)-C(10A) | -3.5(2) |
| C(4)-C(3A)-C(10B)-C(10A) | 113.24(17) |
| C(3)-C(3A)-C(10B)-C(1) | 33.35(17) |

| | |
|---|---|
| C(6A)-C(3A)-C(10B)-C(1) | 159.32(14) |
| C(4)-C(3A)-C(10B)-C(1) | -83.90(16) |
| C(6)-N(5)-C(11)-C(16) | 15.5(2) |
| C(4)-N(5)-C(11)-C(16) | -171.50(14) |
| C(6)-N(5)-C(11)-C(12) | -165.37(15) |
| C(4)-N(5)-C(11)-C(12) | 7.7(2) |
| C(16)-C(11)-C(12)-C(13) | 0.3(2) |
| N(5)-C(11)-C(12)-C(13) | -178.88(14) |
| C(11)-C(12)-C(13)-C(14) | -0.3(2) |
| C(12)-C(13)-C(14)-C(15) | -0.2(3) |
| C(13)-C(14)-C(15)-C(16) | 0.6(2) |
| C(14)-C(15)-C(16)-C(11) | -0.6(2) |
| C(12)-C(11)-C(16)-C(15) | 0.1(2) |
| N(5)-C(11)-C(16)-C(15) | 179.28(14) |
| C(6A)-C(7)-C(17)-O(17) | -135.72(16) |
| C(7A)-C(7)-C(17)-O(17) | -13.2(2) |
| C(6A)-C(7)-C(17)-O(18) | 46.93(16) |
| C(7A)-C(7)-C(17)-O(18) | 169.41(13) |

**Table S14.** Hydrogen bonds for **12a** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| C(12)-H(12)...O(17)#1 | 0.95 | 2.44 | 3.387(2) | 177 |
| C(16)-H(16)...O(6) | 0.95 | 2.23 | 2.8431(19) | 122 |
| O(18)-H(18)...O(6)#2 | 0.89(2) | 1.78(2) | 2.6599(15) | 170(2) |

Symmetry transformations used to generate equivalent atoms: #1 x, y+1, z; #2 -x+3/2, -y+1/2, -z+1

**Table S15**. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **12c**. U(eq) is defined as one third of the trace of the orthogonalized $U^{ij}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| C(1) | -2046(10) | 1764(9) | 2093(4) | 38(2) |
| C(2) | -1303(11) | 1819(8) | 2754(4) | 40(2) |
| C(3) | 278(10) | 2204(8) | 2672(4) | 38(2) |
| C(3A) | 148(10) | 3047(7) | 2204(4) | 33(2) |
| C(4) | -511(12) | 4247(8) | 2489(4) | 42(2) |
| N(5) | -23(9) | 5069(6) | 2068(4) | 40(2) |
| C(6) | 1172(10) | 4617(8) | 1740(4) | 39(2) |
| O(6) | 1883(8) | 5143(6) | 1386(3) | 49(2) |
| C(6A) | 1557(10) | 3419(8) | 1914(4) | 36(2) |
| C(7) | 2219(10) | 2527(8) | 1371(4) | 34(2) |
| C(8) | 1058(9) | 1996(8) | 881(4) | 34(2) |
| C(9) | -178(10) | 1469(8) | 1227(4) | 36(2) |
| O(9) | -447(8) | 440(6) | 1114(3) | 46(2) |
| C(9A) | -959(10) | 2368(7) | 1706(4) | 31(2) |
| C(10) | -654(12) | 6212(9) | 2113(5) | 50(2) |
| C(11) | -669(13) | 6796(10) | 1588(6) | 57(3) |
| C(12) | -1310(16) | 7917(12) | 1638(7) | 73(4) |
| C(13) | -1993(19) | 8441(12) | 2198(10) | 97(6) |
| C(14) | -1910(20) | 7885(11) | 2716(7) | 88(5) |
| C(15) | -1286(16) | 6760(10) | 2667(7) | 69(3) |
| C(16) | 3516(10) | 3083(8) | 1091(4) | 36(2) |

| | | | | |
|---|---|---|---|---|
| O(16) | 4555(7) | 3405(6) | 1533(3) | 40(1) |
| O(17) | 3618(8) | 3217(7) | 553(3) | 48(2) |
| C(17) | 1637(10) | 1044(9) | 360(4) | 40(2) |
| C(18) | 491(10) | 642(9) | -151(4) | 40(2) |
| O(18) | -563(8) | 1199(8) | -210(3) | 55(2) |
| C(19) | 830(12) | -504(10) | -577(5) | 52(2) |
| S(1) | 7406(3) | 4750(3) | 619(1) | 42(1) |
| O(1) | 6925(7) | 4331(7) | 1217(3) | 44(2) |
| C(20) | 6051(15) | 5729(11) | 437(6) | 65(3) |
| C(21) | 6993(14) | 3558(12) | -4(5) | 63(3) |
| C(22) | 2896(10) | 8073(8) | 7883(4) | 37(2) |
| C(23) | 3671(11) | 8015(9) | 7245(4) | 42(2) |
| C(24) | 5214(10) | 7583(8) | 7341(4) | 36(2) |
| C(24A) | 5048(9) | 6774(7) | 7842(3) | 28(2) |
| C(25) | 4345(11) | 5606(8) | 7567(4) | 40(2) |
| N(26) | 4832(9) | 4823(7) | 8002(4) | 43(2) |
| C(27) | 6045(10) | 5257(8) | 8339(4) | 39(2) |
| O(27) | 6712(8) | 4763(6) | 8706(3) | 47(2) |
| C(27A) | 6463(9) | 6425(7) | 8139(4) | 32(2) |
| C(28) | 7156(9) | 7346(8) | 8664(3) | 31(2) |
| C(29) | 6023(9) | 7921(8) | 9154(4) | 35(2) |
| C(30) | 4808(9) | 8440(8) | 8789(4) | 31(2) |
| O(30) | 4552(8) | 9472(6) | 8873(3) | 44(2) |
| C(30A) | 3972(9) | 7520(8) | 8305(4) | 33(2) |
| C(31) | 4176(14) | 3704(11) | 7992(8) | 75(2) |
| C(32) | 4178(14) | 3157(11) | 8524(8) | 75(2) |
| C(33) | 3444(14) | 2065(11) | 8498(8) | 75(2) |
| C(34) | 2694(14) | 1522(11) | 7944(8) | 75(2) |
| C(35) | 2694(14) | 2055(11) | 7423(8) | 75(2) |
| C(36) | 3415(14) | 3146(11) | 7436(8) | 75(2) |
| C(37) | 8462(10) | 6823(8) | 8963(4) | 36(2) |
| O(37) | 9497(7) | 6507(6) | 8545(3) | 40(1) |
| O(38) | 8563(7) | 6721(6) | 9509(3) | 42(2) |
| C(38) | 6607(10) | 8873(8) | 9665(4) | 37(2) |
| C(39) | 5513(10) | 9278(10) | 10162(4) | 41(2) |
| O(39) | 4436(8) | 8753(7) | 10234(3) | 47(2) |
| C(40) | 5817(13) | 10494(12) | 10576(5) | 59(3) |
| S(2) | 2353(3) | 5262(3) | 9499(2) | 55(1) |
| O(2) | 1926(7) | 5676(7) | 8894(3) | 50(2) |
| C(41) | 949(14) | 4266(14) | 9636(7) | 75(4) |
| C(42) | 1943(12) | 6457(12) | 10124(5) | 57(3) |
| C(43) | 8909(12) | 4356(9) | 4590(5) | 49(2) |
| C(44) | 10003(11) | 5010(10) | 4232(4) | 49(2) |
| C(45) | 10457(10) | 6149(10) | 4689(5) | 46(2) |
| C(45A) | 9079(9) | 6436(8) | 5076(4) | 34(2) |
| C(46) | 7887(9) | 6978(9) | 4695(4) | 39(2) |
| N(47) | 6904(8) | 7573(7) | 5187(3) | 32(1) |
| C(48) | 7641(9) | 7879(7) | 5759(4) | 31(2) |
| O(48) | 7161(6) | 8441(5) | 6243(3) | 32(1) |
| C(48A) | 9193(9) | 7427(8) | 5666(4) | 34(2) |
| C(49) | 9875(9) | 7041(7) | 6249(4) | 32(2) |
| C(50) | 9220(9) | 5858(8) | 6377(4) | 35(2) |
| C(51) | 9418(9) | 4951(8) | 5770(4) | 36(2) |

| | | | | |
|---|---|---|---|---|
| O(51) | 10217(8) | 4122(6) | 5756(3) | 46(2) |
| C(51A) | 8573(9) | 5232(7) | 5208(4) | 34(2) |
| C(52) | 5489(9) | 7963(7) | 5059(4) | 34(2) |
| C(53) | 4442(10) | 8253(8) | 5519(4) | 36(2) |
| C(54) | 3078(10) | 8649(9) | 5376(5) | 42(2) |
| C(55) | 2717(10) | 8735(8) | 4765(5) | 42(2) |
| C(56) | 3758(11) | 8446(8) | 4302(4) | 43(2) |
| C(57) | 5107(10) | 8063(9) | 4428(4) | 40(2) |
| C(58) | 9775(10) | 8068(8) | 6799(4) | 38(2) |
| O(58) | 10358(7) | 9057(6) | 6751(3) | 38(1) |
| O(59) | 9091(7) | 7907(6) | 7293(3) | 38(1) |
| C(59) | 9926(10) | 5392(8) | 6924(4) | 38(2) |
| C(60) | 8999(11) | 4425(9) | 7153(5) | 46(2) |
| O(60) | 7798(8) | 4161(7) | 6925(4) | 57(2) |
| C(61) | 9662(13) | 3908(9) | 7696(5) | 54(3) |
| S(3) | 8260(5) | 907(4) | 7891(2) | 49(1) |
| O(3) | 8388(11) | -310(5) | 8059(4) | 49(1) |
| C(62) | 6670(10) | 889(10) | 7413(5) | 49(1) |
| C(63) | 7543(15) | 1839(8) | 8558(4) | 49(1) |
| S(3') | 7735(9) | 456(7) | 7861(4) | 59(2) |
| O(3') | 9177(15) | 702(13) | 7580(9) | 59(2) |
| C(62') | 8050(30) | -703(15) | 8294(10) | 59(2) |
| C(63') | 7500(30) | 1587(14) | 8525(9) | 59(2) |
| C(64) | 3958(12) | 4754(10) | 5544(5) | 51(2) |
| C(65) | 5103(11) | 4024(11) | 5868(5) | 52(3) |
| C(66) | 5513(10) | 2962(10) | 5398(4) | 42(2) |
| C(66A) | 4091(9) | 2659(8) | 4984(4) | 34(2) |
| C(67) | 2888(10) | 2091(8) | 5321(4) | 38(2) |
| N(68) | 1907(8) | 1577(7) | 4804(3) | 35(2) |
| C(69) | 2612(9) | 1398(8) | 4251(4) | 34(2) |
| O(69) | 2108(7) | 925(6) | 3734(3) | 36(1) |
| C(69A) | 4189(10) | 1801(8) | 4371(4) | 35(2) |
| C(70) | 4888(9) | 2269(8) | 3810(4) | 36(2) |
| C(71) | 4251(9) | 3494(8) | 3730(4) | 34(2) |
| C(72) | 4404(9) | 4314(8) | 4367(4) | 38(2) |
| O(72) | 5195(8) | 5160(7) | 4423(3) | 50(2) |
| C(72A) | 3600(9) | 3945(8) | 4902(4) | 35(2) |
| C(73) | 485(10) | 1200(8) | 4928(4) | 38(2) |
| C(74) | -565(10) | 912(8) | 4426(4) | 38(2) |
| C(75) | -1947(10) | 519(9) | 4560(5) | 45(2) |
| C(76) | -2305(10) | 389(8) | 5163(5) | 41(2) |
| C(77) | -1278(10) | 682(9) | 5644(4) | 42(2) |
| C(78) | 97(10) | 1054(9) | 5520(4) | 41(2) |
| C(79) | 4794(10) | 1303(9) | 3236(4) | 39(2) |
| O(79) | 5357(7) | 333(6) | 3244(3) | 42(1) |
| O(80) | 4102(8) | 1588(6) | 2745(3) | 43(1) |
| C(80) | 4940(11) | 4043(9) | 3222(4) | 42(2) |
| C(81) | 4128(12) | 5137(9) | 3105(5) | 48(2) |
| O(81) | 2866(9) | 5313(7) | 3259(4) | 59(2) |
| C(82) | 4879(19) | 5919(13) | 2719(8) | 90(5) |
| S(4) | 2645(5) | 8889(4) | 1729(2) | 52(1) |
| O(4) | 3389(11) | 10079(5) | 1806(4) | 52(1) |
| C(83) | 2149(14) | 8678(10) | 2492(4) | 52(1) |

| | | | | |
|---|---|---|---|---|
| C(84) | 4029(11) | 7804(8) | 1620(6) | 52(1) |
| S(4') | 3085(16) | 9127(13) | 2112(6) | 46(2) |
| O(4') | 4390(30) | 8740(30) | 2450(13) | 46(2) |
| C(83') | 2700(50) | 7970(20) | 1471(13) | 46(2) |
| C(84') | 3720(50) | 10150(30) | 1650(15) | 46(2) |
| S(4") | 3283(13) | 8179(10) | 2014(4) | 46(2) |
| O(4") | 4726(16) | 8700(30) | 2262(10) | 46(2) |
| C(83") | 2030(20) | 8500(30) | 2637(9) | 46(2) |
| C(84") | 2520(30) | 9170(30) | 1553(14) | 46(2) |

**Table S16.** Bond lengths [Å] and angles [°] for **12c**.

| | | | |
|---|---|---|---|
| C(1)-C(9A) | 1.543(11) | C(16)-O(17) | 1.202(10) |
| C(1)-C(2) | 1.564(12) | C(16)-O(16) | 1.343(10) |
| C(1)-H(1A) | 0.9900 | O(16)-H(16) | 0.8998 |
| C(1)-H(1B) | 0.9900 | C(17)-C(18) | 1.523(13) |
| C(2)-C(3) | 1.531(13) | C(17)-H(17A) | 0.9900 |
| C(2)-H(2A) | 0.9900 | C(17)-H(17B) | 0.9900 |
| C(2)-H(2B) | 0.9900 | C(18)-O(18) | 1.176(12) |
| C(3)-C(3A) | 1.516(10) | C(18)-C(19) | 1.499(13) |
| C(3)-H(3A) | 0.9900 | C(19)-H(19A) | 0.9800 |
| C(3)-H(3B) | 0.9900 | C(19)-H(19B) | 0.9800 |
| C(3A)-C(4) | 1.531(12) | C(19)-H(19C) | 0.9800 |
| C(3A)-C(6A) | 1.531(12) | S(1)-O(1) | 1.522(6) |
| C(3A)-C(9A) | 1.568(11) | S(1)-C(20) | 1.759(11) |
| C(4)-N(5) | 1.488(10) | S(1)-C(21) | 1.775(13) |
| C(4)-H(4A) | 0.9900 | C(20)-H(20A) | 0.9800 |
| C(4)-H(4B) | 0.9900 | C(20)-H(20B) | 0.9800 |
| N(5)-C(6) | 1.363(12) | C(20)-H(20C) | 0.9800 |
| N(5)-C(10) | 1.419(12) | C(21)-H(21A) | 0.9800 |
| C(6)-O(6) | 1.241(11) | C(21)-H(21B) | 0.9800 |
| C(6)-C(6A) | 1.523(12) | C(21)-H(21C) | 0.9800 |
| C(6A)-C(7) | 1.544(11) | C(22)-C(30A) | 1.543(11) |
| C(6A)-H(6A) | 1.0000 | C(22)-C(23) | 1.548(12) |
| C(7)-C(16) | 1.524(11) | C(22)-H(22A) | 0.9900 |
| C(7)-C(8) | 1.536(12) | C(22)-H(22B) | 0.9900 |
| C(7)-H(7) | 1.0000 | C(23)-C(24) | 1.521(13) |
| C(8)-C(17) | 1.522(12) | C(23)-H(23A) | 0.9900 |
| C(8)-C(9) | 1.541(11) | C(23)-H(23B) | 0.9900 |
| C(8)-H(8) | 1.0000 | C(24)-C(24A) | 1.549(11) |
| C(9)-O(9) | 1.182(10) | C(24)-H(24A) | 0.9900 |
| C(9)-C(9A) | 1.512(12) | C(24)-H(24B) | 0.9900 |
| C(9A)-H(9A) | 1.0000 | C(24A)-C(25) | 1.503(12) |
| C(10)-C(15) | 1.383(16) | C(24A)-C(27A) | 1.522(11) |
| C(10)-C(11) | 1.413(14) | C(24A)-C(30A) | 1.557(11) |
| C(11)-C(12) | 1.399(16) | C(25)-N(26) | 1.473(12) |
| C(11)-H(11) | 0.9500 | C(25)-H(25A) | 0.9900 |
| C(12)-C(13) | 1.41(2) | C(25)-H(25B) | 0.9900 |
| C(12)-H(12) | 0.9500 | N(26)-C(27) | 1.361(12) |
| C(13)-C(14) | 1.38(2) | N(26)-C(31) | 1.408(14) |
| C(13)-H(13) | 0.9500 | C(27)-O(27) | 1.212(11) |
| C(14)-C(15) | 1.398(17) | C(27)-C(27A) | 1.523(11) |
| C(14)-H(14) | 0.9500 | C(27A)-C(28) | 1.534(12) |
| C(15)-H(15) | 0.9500 | C(27A)-H(27A) | 1.0000 |

| | | | |
|---|---|---|---|
| C(28)-C(37) | 1.524(11) | C(46)-N(47) | 1.474(11) |
| C(28)-C(29) | 1.554(11) | C(46)-H(46A) | 0.9900 |
| C(28)-H(28) | 1.0000 | C(46)-H(46B) | 0.9900 |
| C(29)-C(38) | 1.498(13) | N(47)-C(48) | 1.388(10) |
| C(29)-C(30) | 1.534(11) | N(47)-C(52) | 1.410(11) |
| C(29)-H(29) | 1.0000 | C(48)-O(48) | 1.216(10) |
| C(30)-O(30) | 1.187(10) | C(48)-C(48A) | 1.515(12) |
| C(30)-C(30A) | 1.541(12) | C(48A)-C(49) | 1.532(11) |
| C(30A)-H(30A) | 1.0000 | C(48A)-H(48A) | 1.0000 |
| C(31)-C(32) | 1.40(2) | C(49)-C(58) | 1.521(11) |
| C(31)-C(36) | 1.43(2) | C(49)-C(50) | 1.547(11) |
| C(32)-C(33) | 1.407(16) | C(49)-H(49) | 1.0000 |
| C(32)-H(32) | 0.9500 | C(50)-C(59) | 1.516(12) |
| C(33)-C(34) | 1.42(2) | C(50)-C(51) | 1.535(12) |
| C(33)-H(33) | 0.9500 | C(50)-H(50) | 1.0000 |
| C(34)-C(35) | 1.37(2) | C(51)-O(51) | 1.196(11) |
| C(34)-H(34) | 0.9500 | C(51)-C(51A) | 1.513(12) |
| C(35)-C(36) | 1.405(16) | C(51A)-H(51A) | 1.0000 |
| C(35)-H(35) | 0.9500 | C(52)-C(53) | 1.387(12) |
| C(36)-H(36) | 0.9500 | C(52)-C(57) | 1.426(11) |
| C(37)-O(38) | 1.207(10) | C(53)-C(54) | 1.378(13) |
| C(37)-O(37) | 1.324(10) | C(53)-H(53) | 0.9500 |
| O(37)-H(37) | 0.9000 | C(54)-C(55) | 1.375(14) |
| C(38)-C(39) | 1.491(12) | C(54)-H(54) | 0.9500 |
| C(38)-H(38A) | 0.9900 | C(55)-C(56) | 1.387(14) |
| C(38)-H(38B) | 0.9900 | C(55)-H(55) | 0.9500 |
| C(39)-O(39) | 1.177(12) | C(56)-C(57) | 1.351(13) |
| C(39)-C(40) | 1.538(15) | C(56)-H(56) | 0.9500 |
| C(40)-H(40A) | 0.9800 | C(57)-H(57) | 0.9500 |
| C(40)-H(40B) | 0.9800 | C(58)-O(58) | 1.269(11) |
| C(40)-H(40C) | 0.9800 | C(58)-O(59) | 1.283(11) |
| S(2)-O(2) | 1.512(6) | O(58)-H(58) | 0.9000 |
| S(2)-C(41) | 1.775(12) | O(59)-H(59) | 0.9001 |
| S(2)-C(42) | 1.789(13) | C(59)-C(60) | 1.543(12) |
| C(41)-H(41A) | 0.9800 | C(59)-H(59A) | 0.9900 |
| C(41)-H(41B) | 0.9800 | C(59)-H(59B) | 0.9900 |
| C(41)-H(41C) | 0.9800 | C(60)-O(60) | 1.213(13) |
| C(42)-H(42A) | 0.9800 | C(60)-C(61) | 1.525(14) |
| C(42)-H(42B) | 0.9800 | C(61)-H(61A) | 0.9800 |
| C(42)-H(42C) | 0.9800 | C(61)-H(61B) | 0.9800 |
| C(43)-C(44) | 1.540(15) | C(61)-H(61C) | 0.9800 |
| C(43)-C(51A) | 1.556(12) | S(3)-O(3) | 1.503(3) |
| C(43)-H(43A) | 0.9900 | S(3)-C(63) | 1.769(3) |
| C(43)-H(43B) | 0.9900 | S(3)-C(62) | 1.770(4) |
| C(44)-C(45) | 1.543(14) | C(62)-H(62A) | 0.9800 |
| C(44)-H(44A) | 0.9900 | C(62)-H(62B) | 0.9800 |
| C(44)-H(44B) | 0.9900 | C(62)-H(62C) | 0.9800 |
| C(45)-C(45A) | 1.525(12) | C(63)-H(63A) | 0.9800 |
| C(45)-H(45A) | 0.9900 | C(63)-H(63B) | 0.9800 |
| C(45)-H(45B) | 0.9900 | C(63)-H(63C) | 0.9800 |
| C(45A)-C(51A) | 1.525(12) | S(3')-O(3') | 1.504(4) |
| C(45A)-C(48A) | 1.552(11) | S(3')-C(63') | 1.771(4) |
| C(45A)-C(46) | 1.553(12) | S(3')-C(62') | 1.771(4) |

| | | | |
|---|---|---|---|
| C(62')-H(62D) | 0.9800 | C(80)-H(80A) | 0.9900 |
| C(62')-H(62E) | 0.9800 | C(80)-H(80B) | 0.9900 |
| C(62')-H(62F) | 0.9800 | C(81)-O(81) | 1.213(13) |
| C(63')-H(63D) | 0.9800 | C(81)-C(82) | 1.496(16) |
| C(63')-H(63E) | 0.9800 | C(82)-H(82A) | 0.9800 |
| C(63')-H(63F) | 0.9800 | C(82)-H(82B) | 0.9800 |
| C(64)-C(72A) | 1.556(12) | C(82)-H(82C) | 0.9800 |
| C(64)-C(65) | 1.574(16) | S(4)-O(4) | 1.501(3) |
| C(64)-H(64A) | 0.9900 | S(4)-C(84) | 1.765(3) |
| C(64)-H(64B) | 0.9900 | S(4)-C(83) | 1.771(3) |
| C(65)-C(66) | 1.491(14) | C(83)-H(83A) | 0.9800 |
| C(65)-H(65A) | 0.9900 | C(83)-H(83B) | 0.9800 |
| C(65)-H(65B) | 0.9900 | C(83)-H(83C) | 0.9800 |
| C(66)-C(66A) | 1.572(12) | C(84)-H(84A) | 0.9800 |
| C(66)-H(66A) | 0.9900 | C(84)-H(84B) | 0.9800 |
| C(66)-H(66B) | 0.9900 | C(84)-H(84C) | 0.9800 |
| C(66A)-C(69A) | 1.506(12) | S(4')-O(4') | 1.501(4) |
| C(66A)-C(67) | 1.530(11) | S(4')-C(84') | 1.771(4) |
| C(66A)-C(72A) | 1.578(12) | S(4')-C(83') | 1.771(4) |
| C(67)-N(68) | 1.462(11) | C(83')-H(83D) | 0.9800 |
| C(67)-H(67A) | 0.9900 | C(83')-H(83E) | 0.9800 |
| C(67)-H(67B) | 0.9900 | C(83')-H(83F) | 0.9800 |
| N(68)-C(69) | 1.349(10) | C(84')-H(84D) | 0.9800 |
| N(68)-C(73) | 1.412(11) | C(84')-H(84E) | 0.9800 |
| C(69)-O(69) | 1.234(10) | C(84')-H(84F) | 0.9800 |
| C(69)-C(69A) | 1.518(12) | S(4")-O(4") | 1.500(4) |
| C(69A)-C(70) | 1.552(11) | S(4")-C(84") | 1.770(4) |
| C(69A)-H(69A) | 1.0000 | S(4")-C(83") | 1.771(4) |
| C(70)-C(79) | 1.510(12) | C(83")-H(83G) | 0.9800 |
| C(70)-C(71) | 1.555(12) | C(83")-H(83H) | 0.9800 |
| C(70)-H(70) | 1.0000 | C(83")-H(83I) | 0.9800 |
| C(71)-C(80) | 1.501(12) | C(84")-H(84G) | 0.9800 |
| C(71)-C(72) | 1.527(12) | C(84")-H(84H) | 0.9800 |
| C(71)-H(71) | 1.0000 | C(84")-H(84I) | 0.9800 |
| C(72)-O(72) | 1.194(11) | C(9A)-C(1)-C(2) | 105.6(7) |
| C(72)-C(72A) | 1.497(12) | C(9A)-C(1)-H(1A) | 110.6 |
| C(72A)-H(72A) | 1.0000 | C(2)-C(1)-H(1A) | 110.6 |
| C(73)-C(78) | 1.370(12) | C(9A)-C(1)-H(1B) | 110.6 |
| C(73)-C(74) | 1.432(12) | C(2)-C(1)-H(1B) | 110.6 |
| C(74)-C(75) | 1.391(13) | H(1A)-C(1)-H(1B) | 108.8 |
| C(74)-H(74) | 0.9500 | C(3)-C(2)-C(1) | 105.1(7) |
| C(75)-C(76) | 1.379(14) | C(3)-C(2)-H(2A) | 110.7 |
| C(75)-H(75) | 0.9500 | C(1)-C(2)-H(2A) | 110.7 |
| C(76)-C(77) | 1.388(14) | C(3)-C(2)-H(2B) | 110.7 |
| C(76)-H(76) | 0.9500 | C(1)-C(2)-H(2B) | 110.7 |
| C(77)-C(78) | 1.370(13) | H(2A)-C(2)-H(2B) | 108.8 |
| C(77)-H(77) | 0.9500 | C(3A)-C(3)-C(2) | 103.8(7) |
| C(78)-H(78) | 0.9500 | C(3A)-C(3)-H(3A) | 111.0 |
| C(79)-O(79) | 1.226(12) | C(2)-C(3)-H(3A) | 111.0 |
| C(79)-O(80) | 1.318(11) | C(3A)-C(3)-H(3B) | 111.0 |
| O(79)-H(79) | 0.9000 | C(2)-C(3)-H(3B) | 111.0 |
| O(80)-H(80) | 0.9000 | H(3A)-C(3)-H(3B) | 109.0 |
| C(80)-C(81) | 1.514(14) | C(3)-C(3A)-C(4) | 113.0(7) |

| | | | |
|---|---|---|---|
| C(3)-C(3A)-C(6A) | 117.8(7) | C(14)-C(13)-C(12) | 119.2(12) |
| C(4)-C(3A)-C(6A) | 102.2(7) | C(14)-C(13)-H(13) | 120.4 |
| C(3)-C(3A)-C(9A) | 101.9(7) | C(12)-C(13)-H(13) | 120.4 |
| C(4)-C(3A)-C(9A) | 108.8(7) | C(13)-C(14)-C(15) | 120.3(13) |
| C(6A)-C(3A)-C(9A) | 113.3(6) | C(13)-C(14)-H(14) | 119.8 |
| N(5)-C(4)-C(3A) | 104.5(7) | C(15)-C(14)-H(14) | 119.8 |
| N(5)-C(4)-H(4A) | 110.9 | C(10)-C(15)-C(14) | 121.0(11) |
| C(3A)-C(4)-H(4A) | 110.9 | C(10)-C(15)-H(15) | 119.5 |
| N(5)-C(4)-H(4B) | 110.9 | C(14)-C(15)-H(15) | 119.5 |
| C(3A)-C(4)-H(4B) | 110.9 | O(17)-C(16)-O(16) | 124.0(8) |
| H(4A)-C(4)-H(4B) | 108.9 | O(17)-C(16)-C(7) | 125.8(7) |
| C(6)-N(5)-C(10) | 129.0(8) | O(16)-C(16)-C(7) | 110.2(6) |
| C(6)-N(5)-C(4) | 110.0(7) | C(16)-O(16)-H(16) | 109.4 |
| C(10)-N(5)-C(4) | 120.4(8) | C(18)-C(17)-C(8) | 112.1(8) |
| O(6)-C(6)-N(5) | 124.6(9) | C(18)-C(17)-H(17A) | 109.2 |
| O(6)-C(6)-C(6A) | 125.7(8) | C(8)-C(17)-H(17A) | 109.2 |
| N(5)-C(6)-C(6A) | 109.6(7) | C(18)-C(17)-H(17B) | 109.2 |
| C(6)-C(6A)-C(3A) | 103.4(7) | C(8)-C(17)-H(17B) | 109.2 |
| C(6)-C(6A)-C(7) | 114.2(7) | H(17A)-C(17)-H(17B) | 107.9 |
| C(3A)-C(6A)-C(7) | 117.3(7) | O(18)-C(18)-C(19) | 122.9(9) |
| C(6)-C(6A)-H(6A) | 107.1 | O(18)-C(18)-C(17) | 122.4(8) |
| C(3A)-C(6A)-H(6A) | 107.1 | C(19)-C(18)-C(17) | 114.7(8) |
| C(7)-C(6A)-H(6A) | 107.1 | C(18)-C(19)-H(19A) | 109.5 |
| C(16)-C(7)-C(8) | 113.7(6) | C(18)-C(19)-H(19B) | 109.5 |
| C(16)-C(7)-C(6A) | 110.5(7) | H(19A)-C(19)-H(19B) | 109.5 |
| C(8)-C(7)-C(6A) | 112.1(7) | C(18)-C(19)-H(19C) | 109.5 |
| C(16)-C(7)-H(7) | 106.7 | H(19A)-C(19)-H(19C) | 109.5 |
| C(8)-C(7)-H(7) | 106.7 | H(19B)-C(19)-H(19C) | 109.5 |
| C(6A)-C(7)-H(7) | 106.7 | O(1)-S(1)-C(20) | 106.7(5) |
| C(17)-C(8)-C(7) | 114.1(7) | O(1)-S(1)-C(21) | 105.6(5) |
| C(17)-C(8)-C(9) | 109.5(7) | C(20)-S(1)-C(21) | 97.1(6) |
| C(7)-C(8)-C(9) | 108.0(6) | S(1)-C(20)-H(20A) | 109.5 |
| C(17)-C(8)-H(8) | 108.3 | S(1)-C(20)-H(20B) | 109.5 |
| C(7)-C(8)-H(8) | 108.3 | H(20A)-C(20)-H(20B) | 109.5 |
| C(9)-C(8)-H(8) | 108.3 | S(1)-C(20)-H(20C) | 109.5 |
| O(9)-C(9)-C(9A) | 125.2(8) | H(20A)-C(20)-H(20C) | 109.5 |
| O(9)-C(9)-C(8) | 120.5(8) | H(20B)-C(20)-H(20C) | 109.5 |
| C(9A)-C(9)-C(8) | 114.3(7) | S(1)-C(21)-H(21A) | 109.5 |
| C(9)-C(9A)-C(1) | 111.6(7) | S(1)-C(21)-H(21B) | 109.5 |
| C(9)-C(9A)-C(3A) | 110.9(7) | H(21A)-C(21)-H(21B) | 109.5 |
| C(1)-C(9A)-C(3A) | 104.8(6) | S(1)-C(21)-H(21C) | 109.5 |
| C(9)-C(9A)-H(9A) | 109.8 | H(21A)-C(21)-H(21C) | 109.5 |
| C(1)-C(9A)-H(9A) | 109.8 | H(21B)-C(21)-H(21C) | 109.5 |
| C(3A)-C(9A)-H(9A) | 109.8 | C(30A)-C(22)-C(23) | 105.7(7) |
| C(15)-C(10)-C(11) | 119.1(10) | C(30A)-C(22)-H(22A) | 110.6 |
| C(15)-C(10)-N(5) | 120.5(9) | C(23)-C(22)-H(22A) | 110.6 |
| C(11)-C(10)-N(5) | 120.4(10) | C(30A)-C(22)-H(22B) | 110.6 |
| C(12)-C(11)-C(10) | 119.6(12) | C(23)-C(22)-H(22B) | 110.6 |
| C(12)-C(11)-H(11) | 120.2 | H(22A)-C(22)-H(22B) | 108.7 |
| C(10)-C(11)-H(11) | 120.2 | C(24)-C(23)-C(22) | 106.1(7) |
| C(11)-C(12)-C(13) | 120.4(12) | C(24)-C(23)-H(23A) | 110.5 |
| C(11)-C(12)-H(12) | 119.8 | C(22)-C(23)-H(23A) | 110.5 |
| C(13)-C(12)-H(12) | 119.8 | C(24)-C(23)-H(23B) | 110.5 |

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| C(22)-C(23)-H(23B) | 110.5 | C(32)-C(31)-N(26) | 121.7(13) |
| H(23A)-C(23)-H(23B) | 108.7 | C(32)-C(31)-C(36) | 119.2(12) |
| C(23)-C(24)-C(24A) | 104.3(7) | N(26)-C(31)-C(36) | 119.0(12) |
| C(23)-C(24)-H(24A) | 110.9 | C(31)-C(32)-C(33) | 119.5(15) |
| C(24A)-C(24)-H(24A) | 110.9 | C(31)-C(32)-H(32) | 120.3 |
| C(23)-C(24)-H(24B) | 110.9 | C(33)-C(32)-H(32) | 120.3 |
| C(24A)-C(24)-H(24B) | 110.9 | C(32)-C(33)-C(34) | 120.8(14) |
| H(24A)-C(24)-H(24B) | 108.9 | C(32)-C(33)-H(33) | 119.6 |
| C(25)-C(24A)-C(27A) | 103.9(7) | C(34)-C(33)-H(33) | 119.6 |
| C(25)-C(24A)-C(24) | 111.4(6) | C(35)-C(34)-C(33) | 119.8(12) |
| C(27A)-C(24A)-C(24) | 116.0(7) | C(35)-C(34)-H(34) | 120.1 |
| C(25)-C(24A)-C(30A) | 109.5(7) | C(33)-C(34)-H(34) | 120.1 |
| C(27A)-C(24A)-C(30A) | 115.3(6) | C(34)-C(35)-C(36) | 120.6(15) |
| C(24)-C(24A)-C(30A) | 100.8(6) | C(34)-C(35)-H(35) | 119.7 |
| N(26)-C(25)-C(24A) | 102.7(7) | C(36)-C(35)-H(35) | 119.7 |
| N(26)-C(25)-H(25A) | 111.2 | C(35)-C(36)-C(31) | 120.2(14) |
| C(24A)-C(25)-H(25A) | 111.2 | C(35)-C(36)-H(36) | 119.9 |
| N(26)-C(25)-H(25B) | 111.2 | C(31)-C(36)-H(36) | 119.9 |
| C(24A)-C(25)-H(25B) | 111.2 | O(38)-C(37)-O(37) | 123.9(8) |
| H(25A)-C(25)-H(25B) | 109.1 | O(38)-C(37)-C(28) | 125.2(7) |
| C(27)-N(26)-C(31) | 126.4(9) | O(37)-C(37)-C(28) | 110.9(7) |
| C(27)-N(26)-C(25) | 112.0(7) | C(37)-O(37)-H(37) | 110.1 |
| C(31)-N(26)-C(25) | 121.1(9) | C(39)-C(38)-C(29) | 112.9(7) |
| O(27)-C(27)-N(26) | 125.7(8) | C(39)-C(38)-H(38A) | 109.0 |
| O(27)-C(27)-C(27A) | 126.4(8) | C(29)-C(38)-H(38A) | 109.0 |
| N(26)-C(27)-C(27A) | 107.8(7) | C(39)-C(38)-H(38B) | 109.0 |
| C(24A)-C(27A)-C(27) | 102.4(7) | C(29)-C(38)-H(38B) | 109.0 |
| C(24A)-C(27A)-C(28) | 117.0(6) | H(38A)-C(38)-H(38B) | 107.8 |
| C(27)-C(27A)-C(28) | 114.4(6) | O(39)-C(39)-C(38) | 124.3(9) |
| C(24A)-C(27A)-H(27A) | 107.5 | O(39)-C(39)-C(40) | 119.7(8) |
| C(27)-C(27A)-H(27A) | 107.5 | C(38)-C(39)-C(40) | 115.9(8) |
| C(28)-C(27A)-H(27A) | 107.5 | C(39)-C(40)-H(40A) | 109.5 |
| C(37)-C(28)-C(27A) | 110.9(7) | C(39)-C(40)-H(40B) | 109.5 |
| C(37)-C(28)-C(29) | 112.9(6) | H(40A)-C(40)-H(40B) | 109.5 |
| C(27A)-C(28)-C(29) | 112.7(7) | C(39)-C(40)-H(40C) | 109.5 |
| C(37)-C(28)-H(28) | 106.6 | H(40A)-C(40)-H(40C) | 109.5 |
| C(27A)-C(28)-H(28) | 106.6 | H(40B)-C(40)-H(40C) | 109.5 |
| C(29)-C(28)-H(28) | 106.6 | O(2)-S(2)-C(41) | 105.8(5) |
| C(38)-C(29)-C(30) | 109.3(7) | O(2)-S(2)-C(42) | 106.4(5) |
| C(38)-C(29)-C(28) | 115.8(7) | C(41)-S(2)-C(42) | 98.1(7) |
| C(30)-C(29)-C(28) | 107.0(6) | S(2)-C(41)-H(41A) | 109.5 |
| C(38)-C(29)-H(29) | 108.2 | S(2)-C(41)-H(41B) | 109.5 |
| C(30)-C(29)-H(29) | 108.2 | H(41A)-C(41)-H(41B) | 109.5 |
| C(28)-C(29)-H(29) | 108.2 | S(2)-C(41)-H(41C) | 109.5 |
| O(30)-C(30)-C(29) | 122.1(8) | H(41A)-C(41)-H(41C) | 109.5 |
| O(30)-C(30)-C(30A) | 123.2(7) | H(41B)-C(41)-H(41C) | 109.5 |
| C(29)-C(30)-C(30A) | 114.8(7) | S(2)-C(42)-H(42A) | 109.5 |
| C(30)-C(30A)-C(22) | 114.0(7) | S(2)-C(42)-H(42B) | 109.5 |
| C(30)-C(30A)-C(24A) | 110.8(7) | H(42A)-C(42)-H(42B) | 109.5 |
| C(22)-C(30A)-C(24A) | 105.2(6) | S(2)-C(42)-H(42C) | 109.5 |
| C(30)-C(30A)-H(30A) | 108.9 | H(42A)-C(42)-H(42C) | 109.5 |
| C(22)-C(30A)-H(30A) | 108.9 | H(42B)-C(42)-H(42C) | 109.5 |
| C(24A)-C(30A)-H(30A) | 108.9 | C(44)-C(43)-C(51A) | 105.7(8) |

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| C(44)-C(43)-H(43A) | 110.6 | O(51)-C(51)-C(51A) | 124.6(8) |
| C(51A)-C(43)-H(43A) | 110.6 | O(51)-C(51)-C(50) | 121.0(8) |
| C(44)-C(43)-H(43B) | 110.6 | C(51A)-C(51)-C(50) | 114.4(7) |
| C(51A)-C(43)-H(43B) | 110.6 | C(51)-C(51A)-C(45A) | 108.8(7) |
| H(43A)-C(43)-H(43B) | 108.7 | C(51)-C(51A)-C(43) | 112.8(7) |
| C(43)-C(44)-C(45) | 106.1(7) | C(45A)-C(51A)-C(43) | 104.0(7) |
| C(43)-C(44)-H(44A) | 110.5 | C(51)-C(51A)-H(51A) | 110.3 |
| C(45)-C(44)-H(44A) | 110.5 | C(45A)-C(51A)-H(51A) | 110.3 |
| C(43)-C(44)-H(44B) | 110.5 | C(43)-C(51A)-H(51A) | 110.3 |
| C(45)-C(44)-H(44B) | 110.5 | C(53)-C(52)-N(47) | 123.1(7) |
| H(44A)-C(44)-H(44B) | 108.7 | C(53)-C(52)-C(57) | 118.1(8) |
| C(45A)-C(45)-C(44) | 102.2(8) | N(47)-C(52)-C(57) | 118.8(7) |
| C(45A)-C(45)-H(45A) | 111.3 | C(54)-C(53)-C(52) | 121.2(8) |
| C(44)-C(45)-H(45A) | 111.3 | C(54)-C(53)-H(53) | 119.4 |
| C(45A)-C(45)-H(45B) | 111.3 | C(52)-C(53)-H(53) | 119.4 |
| C(44)-C(45)-H(45B) | 111.3 | C(55)-C(54)-C(53) | 120.2(8) |
| H(45A)-C(45)-H(45B) | 109.2 | C(55)-C(54)-H(54) | 119.9 |
| C(51A)-C(45A)-C(45) | 103.9(7) | C(53)-C(54)-H(54) | 119.9 |
| C(51A)-C(45A)-C(48A) | 114.6(7) | C(54)-C(55)-C(56) | 118.9(8) |
| C(45)-C(45A)-C(48A) | 117.4(7) | C(54)-C(55)-H(55) | 120.5 |
| C(51A)-C(45A)-C(46) | 110.2(7) | C(56)-C(55)-H(55) | 120.5 |
| C(45)-C(45A)-C(46) | 111.0(7) | C(57)-C(56)-C(55) | 122.3(8) |
| C(48A)-C(45A)-C(46) | 99.8(7) | C(57)-C(56)-H(56) | 118.9 |
| N(47)-C(46)-C(45A) | 103.2(6) | C(55)-C(56)-H(56) | 118.9 |
| N(47)-C(46)-H(46A) | 111.1 | C(56)-C(57)-C(52) | 119.2(8) |
| C(45A)-C(46)-H(46A) | 111.1 | C(56)-C(57)-H(57) | 120.4 |
| N(47)-C(46)-H(46B) | 111.1 | C(52)-C(57)-H(57) | 120.4 |
| C(45A)-C(46)-H(46B) | 111.1 | O(58)-C(58)-O(59) | 122.4(7) |
| H(46A)-C(46)-H(46B) | 109.1 | O(58)-C(58)-C(49) | 118.9(8) |
| C(48)-N(47)-C(52) | 124.6(7) | O(59)-C(58)-C(49) | 118.8(8) |
| C(48)-N(47)-C(46) | 111.0(7) | C(58)-O(58)-H(58) | 109.6 |
| C(52)-N(47)-C(46) | 123.4(6) | C(58)-O(59)-H(59) | 109.4 |
| O(48)-C(48)-N(47) | 126.9(8) | C(50)-C(59)-C(60) | 112.9(8) |
| O(48)-C(48)-C(48A) | 125.5(7) | C(50)-C(59)-H(59A) | 109.0 |
| N(47)-C(48)-C(48A) | 107.5(7) | C(60)-C(59)-H(59A) | 109.0 |
| C(48)-C(48A)-C(49) | 114.0(6) | C(50)-C(59)-H(59B) | 109.0 |
| C(48)-C(48A)-C(45A) | 103.9(6) | C(60)-C(59)-H(59B) | 109.0 |
| C(49)-C(48A)-C(45A) | 115.0(7) | H(59A)-C(59)-H(59B) | 107.8 |
| C(48)-C(48A)-H(48A) | 107.9 | O(60)-C(60)-C(61) | 124.0(9) |
| C(49)-C(48A)-H(48A) | 107.9 | O(60)-C(60)-C(59) | 120.5(9) |
| C(45A)-C(48A)-H(48A) | 107.9 | C(61)-C(60)-C(59) | 115.4(8) |
| C(58)-C(49)-C(48A) | 108.5(7) | C(60)-C(61)-H(61A) | 109.5 |
| C(58)-C(49)-C(50) | 114.4(7) | C(60)-C(61)-H(61B) | 109.5 |
| C(48A)-C(49)-C(50) | 112.3(7) | H(61A)-C(61)-H(61B) | 109.5 |
| C(58)-C(49)-H(49) | 107.1 | C(60)-C(61)-H(61C) | 109.5 |
| C(48A)-C(49)-H(49) | 107.1 | H(61A)-C(61)-H(61C) | 109.5 |
| C(50)-C(49)-H(49) | 107.1 | H(61B)-C(61)-H(61C) | 109.5 |
| C(59)-C(50)-C(51) | 109.5(7) | O(3)-S(3)-C(63) | 106.5(3) |
| C(59)-C(50)-C(49) | 114.5(7) | O(3)-S(3)-C(62) | 106.8(3) |
| C(51)-C(50)-C(49) | 106.1(7) | C(63)-S(3)-C(62) | 96.1(2) |
| C(59)-C(50)-H(50) | 108.9 | S(3)-C(62)-H(62A) | 109.5 |
| C(51)-C(50)-H(50) | 108.9 | S(3)-C(62)-H(62B) | 109.5 |
| C(49)-C(50)-H(50) | 108.9 | H(62A)-C(62)-H(62B) | 109.5 |

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| S(3)-C(62)-H(62C) | 109.5 | H(67A)-C(67)-H(67B) | 109.1 |
| H(62A)-C(62)-H(62C) | 109.5 | C(69)-N(68)-C(73) | 127.9(7) |
| H(62B)-C(62)-H(62C) | 109.5 | C(69)-N(68)-C(67) | 111.0(7) |
| S(3)-C(63)-H(63A) | 109.5 | C(73)-N(68)-C(67) | 120.5(7) |
| S(3)-C(63)-H(63B) | 109.5 | O(69)-C(69)-N(68) | 126.7(8) |
| H(63A)-C(63)-H(63B) | 109.5 | O(69)-C(69)-C(69A) | 124.6(7) |
| S(3)-C(63)-H(63C) | 109.5 | N(68)-C(69)-C(69A) | 108.5(7) |
| H(63A)-C(63)-H(63C) | 109.5 | C(66A)-C(69A)-C(69) | 102.3(7) |
| H(63B)-C(63)-H(63C) | 109.5 | C(66A)-C(69A)-C(70) | 117.1(7) |
| O(3')-S(3')-C(63') | 106.5(3) | C(69)-C(69A)-C(70) | 113.6(7) |
| O(3')-S(3')-C(62') | 106.5(3) | C(66A)-C(69A)-H(69A) | 107.8 |
| C(63')-S(3')-C(62') | 95.9(3) | C(69)-C(69A)-H(69A) | 107.8 |
| S(3')-C(62')-H(62D) | 109.5 | C(70)-C(69A)-H(69A) | 107.8 |
| S(3')-C(62')-H(62E) | 109.5 | C(79)-C(70)-C(69A) | 108.6(7) |
| H(62D)-C(62')-H(62E) | 109.5 | C(79)-C(70)-C(71) | 115.9(7) |
| S(3')-C(62')-H(62F) | 109.5 | C(69A)-C(70)-C(71) | 111.6(7) |
| H(62D)-C(62')-H(62F) | 109.5 | C(79)-C(70)-H(70) | 106.7 |
| H(62E)-C(62')-H(62F) | 109.5 | C(69A)-C(70)-H(70) | 106.7 |
| S(3')-C(63')-H(63D) | 109.5 | C(71)-C(70)-H(70) | 106.7 |
| S(3')-C(63')-H(63E) | 109.5 | C(80)-C(71)-C(72) | 110.9(7) |
| H(63D)-C(63')-H(63E) | 109.5 | C(80)-C(71)-C(70) | 114.8(7) |
| S(3')-C(63')-H(63F) | 109.5 | C(72)-C(71)-C(70) | 107.1(7) |
| H(63D)-C(63')-H(63F) | 109.5 | C(80)-C(71)-H(71) | 108.0 |
| H(63E)-C(63')-H(63F) | 109.5 | C(72)-C(71)-H(71) | 108.0 |
| C(72A)-C(64)-C(65) | 104.3(8) | C(70)-C(71)-H(71) | 108.0 |
| C(72A)-C(64)-H(64A) | 110.9 | O(72)-C(72)-C(72A) | 123.8(8) |
| C(65)-C(64)-H(64A) | 110.9 | O(72)-C(72)-C(71) | 119.8(8) |
| C(72A)-C(64)-H(64B) | 110.9 | C(72A)-C(72)-C(71) | 116.4(7) |
| C(65)-C(64)-H(64B) | 110.9 | C(72)-C(72A)-C(64) | 112.6(7) |
| H(64A)-C(64)-H(64B) | 108.9 | C(72)-C(72A)-C(66A) | 109.7(7) |
| C(66)-C(65)-C(64) | 107.7(8) | C(64)-C(72A)-C(66A) | 105.3(7) |
| C(66)-C(65)-H(65A) | 110.2 | C(72)-C(72A)-H(72A) | 109.7 |
| C(64)-C(65)-H(65A) | 110.2 | C(64)-C(72A)-H(72A) | 109.7 |
| C(66)-C(65)-H(65B) | 110.2 | C(66A)-C(72A)-H(72A) | 109.7 |
| C(64)-C(65)-H(65B) | 110.2 | C(78)-C(73)-N(68) | 121.1(8) |
| H(65A)-C(65)-H(65B) | 108.5 | C(78)-C(73)-C(74) | 118.6(8) |
| C(65)-C(66)-C(66A) | 104.1(7) | N(68)-C(73)-C(74) | 120.2(7) |
| C(65)-C(66)-H(66A) | 110.9 | C(75)-C(74)-C(73) | 118.9(8) |
| C(66A)-C(66)-H(66A) | 110.9 | C(75)-C(74)-H(74) | 120.5 |
| C(65)-C(66)-H(66B) | 110.9 | C(73)-C(74)-H(74) | 120.5 |
| C(66A)-C(66)-H(66B) | 110.9 | C(76)-C(75)-C(74) | 121.0(9) |
| H(66A)-C(66)-H(66B) | 108.9 | C(76)-C(75)-H(75) | 119.5 |
| C(69A)-C(66A)-C(67) | 101.9(7) | C(74)-C(75)-H(75) | 119.5 |
| C(69A)-C(66A)-C(66) | 119.0(7) | C(75)-C(76)-C(77) | 119.2(8) |
| C(67)-C(66A)-C(66) | 113.0(7) | C(75)-C(76)-H(76) | 120.4 |
| C(69A)-C(66A)-C(72A) | 113.5(7) | C(77)-C(76)-H(76) | 120.4 |
| C(67)-C(66A)-C(72A) | 109.1(7) | C(78)-C(77)-C(76) | 120.7(8) |
| C(66)-C(66A)-C(72A) | 100.4(7) | C(78)-C(77)-H(77) | 119.7 |
| N(68)-C(67)-C(66A) | 102.7(7) | C(76)-C(77)-H(77) | 119.7 |
| N(68)-C(67)-H(67A) | 111.2 | C(77)-C(78)-C(73) | 121.5(9) |
| C(66A)-C(67)-H(67A) | 111.2 | C(77)-C(78)-H(78) | 119.2 |
| N(68)-C(67)-H(67B) | 111.2 | C(73)-C(78)-H(78) | 119.2 |
| C(66A)-C(67)-H(67B) | 111.2 | O(79)-C(79)-O(80) | 124.2(8) |

| | | | |
|---|---|---|---|
| O(79)-C(79)-C(70) | 120.2(8) | H(84A)-C(84)-H(84C) | 109.5 |
| O(80)-C(79)-C(70) | 115.6(8) | H(84B)-C(84)-H(84C) | 109.5 |
| C(79)-O(79)-H(79) | 109.5 | O(4')-S(4')-C(84') | 106.7(3) |
| C(79)-O(80)-H(80) | 109.0 | O(4')-S(4')-C(83') | 106.7(3) |
| C(71)-C(80)-C(81) | 112.0(8) | C(84')-S(4')-C(83') | 95.9(3) |
| C(71)-C(80)-H(80A) | 109.2 | S(4')-C(83')-H(83D) | 109.5 |
| C(81)-C(80)-H(80A) | 109.2 | S(4')-C(83')-H(83E) | 109.5 |
| C(71)-C(80)-H(80B) | 109.2 | H(83D)-C(83')-H(83E) | 109.5 |
| C(81)-C(80)-H(80B) | 109.2 | S(4')-C(83')-H(83F) | 109.5 |
| H(80A)-C(80)-H(80B) | 107.9 | H(83D)-C(83')-H(83F) | 109.5 |
| O(81)-C(81)-C(82) | 120.6(11) | H(83E)-C(83')-H(83F) | 109.5 |
| O(81)-C(81)-C(80) | 121.8(9) | S(4')-C(84')-H(84D) | 109.5 |
| C(82)-C(81)-C(80) | 117.2(10) | S(4')-C(84')-H(84E) | 109.5 |
| C(81)-C(82)-H(82A) | 109.5 | H(84D)-C(84')-H(84E) | 109.5 |
| C(81)-C(82)-H(82B) | 109.5 | S(4')-C(84')-H(84F) | 109.5 |
| H(82A)-C(82)-H(82B) | 109.5 | H(84D)-C(84')-H(84F) | 109.5 |
| C(81)-C(82)-H(82C) | 109.5 | H(84E)-C(84')-H(84F) | 109.5 |
| H(82A)-C(82)-H(82C) | 109.5 | O(4")-S(4")-C(84") | 106.8(3) |
| H(82B)-C(82)-H(82C) | 109.5 | O(4")-S(4")-C(83") | 106.7(3) |
| O(4)-S(4)-C(84) | 107.1(3) | C(84")-S(4")-C(83") | 95.9(3) |
| O(4)-S(4)-C(83) | 106.6(3) | S(4")-C(83")-H(83G) | 109.5 |
| C(84)-S(4)-C(83) | 96.3(2) | S(4")-C(83")-H(83H) | 109.5 |
| S(4)-C(83)-H(83A) | 109.5 | H(83G)-C(83")-H(83H) | 109.5 |
| S(4)-C(83)-H(83B) | 109.5 | S(4")-C(83")-H(83I) | 109.5 |
| H(83A)-C(83)-H(83B) | 109.5 | H(83G)-C(83")-H(83I) | 109.5 |
| S(4)-C(83)-H(83C) | 109.5 | H(83H)-C(83")-H(83I) | 109.5 |
| H(83A)-C(83)-H(83C) | 109.5 | S(4")-C(84")-H(84G) | 109.5 |
| H(83B)-C(83)-H(83C) | 109.5 | S(4")-C(84")-H(84H) | 109.5 |
| S(4)-C(84)-H(84A) | 109.5 | H(84G)-C(84")-H(84H) | 109.5 |
| S(4)-C(84)-H(84B) | 109.5 | S(4")-C(84")-H(84I) | 109.5 |
| H(84A)-C(84)-H(84B) | 109.5 | H(84G)-C(84")-H(84I) | 109.5 |
| S(4)-C(84)-H(84C) | 109.5 | H(84H)-C(84")-H(84I) | 109.5 |

**Table S17.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **12c**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\, h^2\, a^{*2} U^{11} + ... + 2\, h\, k\, a^*\, b^*\, U^{12}\, ]$.

| **Atom** | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| C(1) | 45(5) | 38(5) | 33(4) | 10(3) | 10(3) | 4(4) |
| C(2) | 56(5) | 30(4) | 34(4) | 6(3) | 3(4) | -9(4) |
| C(3) | 46(5) | 35(5) | 36(4) | 15(4) | 3(3) | 6(4) |
| C(3A) | 51(5) | 21(4) | 27(3) | 5(3) | 1(3) | 1(3) |
| C(4) | 64(6) | 29(4) | 35(4) | 7(3) | 15(4) | 1(4) |
| N(5) | 60(5) | 17(3) | 45(4) | 8(3) | 6(3) | -5(3) |
| C(6) | 45(5) | 34(5) | 41(4) | 9(4) | 3(4) | -2(4) |
| O(6) | 64(4) | 32(3) | 53(4) | 18(3) | 8(3) | -10(3) |
| C(6A) | 41(5) | 33(5) | 31(4) | 1(3) | -2(3) | 4(4) |
| C(7) | 44(5) | 29(4) | 30(4) | 8(3) | 1(3) | 1(4) |
| C(8) | 38(4) | 30(4) | 36(4) | 10(3) | 4(3) | 0(3) |
| C(9) | 44(5) | 30(4) | 33(4) | 6(3) | -6(3) | -6(4) |
| O(9) | 64(4) | 23(3) | 51(4) | 1(3) | 12(3) | -8(3) |
| C(9A) | 45(4) | 22(4) | 26(3) | 1(3) | 4(3) | -4(3) |
| C(10) | 58(6) | 26(5) | 69(6) | 18(4) | 8(5) | -1(4) |
| C(11) | 64(7) | 39(6) | 70(7) | 19(5) | -8(5) | -2(5) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C(12) | 78(9) | 46(7) | 106(10) | 40(7) | -4(7) | 0(6) |
| C(13) | 91(11) | 29(6) | 171(17) | 18(9) | 18(11) | 5(7) |
| C(14) | 140(14) | 30(6) | 92(10) | 5(6) | 47(10) | -2(7) |
| C(15) | 96(9) | 29(5) | 85(8) | 20(5) | 18(7) | -1(6) |
| C(16) | 40(5) | 34(5) | 33(4) | 9(3) | -4(3) | -8(4) |
| O(16) | 44(3) | 42(4) | 34(3) | 12(3) | -1(2) | -9(3) |
| O(17) | 56(4) | 58(4) | 32(3) | 13(3) | 1(3) | -19(3) |
| C(17) | 46(5) | 40(5) | 34(4) | 6(4) | 3(3) | 0(4) |
| C(18) | 43(5) | 36(5) | 36(4) | -2(4) | 6(4) | -5(4) |
| O(18) | 49(4) | 65(5) | 45(4) | -6(3) | -8(3) | 5(4) |
| C(19) | 52(6) | 44(6) | 53(5) | -8(4) | 1(4) | 0(5) |
| S(1) | 38(1) | 43(1) | 51(1) | 23(1) | 1(1) | -1(1) |
| O(1) | 41(3) | 51(4) | 45(3) | 20(3) | -3(3) | -3(3) |
| C(20) | 81(8) | 43(6) | 79(8) | 33(6) | -5(6) | 11(6) |
| C(21) | 58(7) | 79(9) | 55(6) | 17(6) | 11(5) | -13(6) |
| C(22) | 37(4) | 34(5) | 39(4) | 5(4) | -5(3) | 0(4) |
| C(23) | 56(6) | 37(5) | 33(4) | 7(4) | -1(4) | -7(4) |
| C(24) | 42(5) | 39(5) | 26(3) | 3(3) | 6(3) | -7(4) |
| C(24A) | 36(4) | 24(4) | 24(3) | 1(3) | 3(3) | 1(3) |
| C(25) | 44(5) | 35(5) | 37(4) | 1(4) | 1(3) | -5(4) |
| N(26) | 45(4) | 28(4) | 56(4) | 9(3) | 10(3) | -6(3) |
| C(27) | 42(5) | 34(5) | 45(4) | 16(4) | 5(4) | -5(4) |
| O(27) | 50(4) | 41(4) | 59(4) | 29(3) | 5(3) | 0(3) |
| C(27A) | 42(4) | 26(4) | 31(4) | 12(3) | 11(3) | 11(3) |
| C(28) | 37(4) | 31(4) | 28(3) | 13(3) | -3(3) | -3(3) |
| C(29) | 34(4) | 37(5) | 40(4) | 19(4) | 3(3) | 4(3) |
| C(30) | 37(4) | 30(4) | 29(3) | 11(3) | 3(3) | 0(3) |
| O(30) | 54(4) | 31(4) | 49(3) | 7(3) | -7(3) | 1(3) |
| C(30A) | 38(4) | 34(4) | 29(4) | 11(3) | 3(3) | -1(3) |
| C(31) | 55(3) | 37(3) | 135(5) | 23(3) | 13(3) | -4(2) |
| C(32) | 55(3) | 37(3) | 135(5) | 23(3) | 13(3) | -4(2) |
| C(33) | 55(3) | 37(3) | 135(5) | 23(3) | 13(3) | -4(2) |
| C(34) | 55(3) | 37(3) | 135(5) | 23(3) | 13(3) | -4(2) |
| C(35) | 55(3) | 37(3) | 135(5) | 23(3) | 13(3) | -4(2) |
| C(36) | 55(3) | 37(3) | 135(5) | 23(3) | 13(3) | -4(2) |
| C(37) | 34(4) | 36(5) | 41(4) | 11(4) | 5(3) | 2(4) |
| O(37) | 38(3) | 53(4) | 32(3) | 16(3) | 4(2) | 9(3) |
| O(38) | 45(3) | 54(4) | 31(3) | 20(3) | 3(2) | 6(3) |
| C(38) | 40(4) | 38(5) | 34(4) | 9(3) | -2(3) | -1(4) |
| C(39) | 36(4) | 58(6) | 28(4) | 2(4) | -7(3) | 2(4) |
| O(39) | 53(4) | 46(4) | 38(3) | 0(3) | 8(3) | -12(3) |
| C(40) | 56(6) | 69(8) | 43(5) | -15(5) | 5(4) | -13(5) |
| S(2) | 32(1) | 79(2) | 65(2) | 47(1) | 2(1) | 2(1) |
| O(2) | 35(3) | 69(5) | 54(4) | 36(4) | 0(3) | -3(3) |
| C(41) | 52(7) | 99(11) | 88(9) | 56(8) | 5(6) | -8(7) |
| C(42) | 53(6) | 81(8) | 48(5) | 36(6) | 0(4) | 0(6) |
| C(43) | 54(6) | 39(5) | 47(5) | -8(4) | -3(4) | -3(4) |
| C(44) | 43(5) | 59(7) | 40(5) | -10(4) | 1(4) | 11(5) |
| C(45) | 37(5) | 52(6) | 47(5) | 4(4) | 1(4) | 2(4) |
| C(45A) | 31(4) | 35(5) | 36(4) | 5(3) | -1(3) | 0(3) |
| C(46) | 34(4) | 43(5) | 38(4) | 4(4) | -1(3) | 3(4) |
| N(47) | 33(3) | 34(4) | 29(3) | 5(3) | 1(3) | -6(3) |
| C(48) | 37(4) | 26(4) | 32(4) | 12(3) | -1(3) | -8(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O(48) | 36(3) | 31(3) | 31(3) | 8(2) | 4(2) | 2(2) |
| C(48A) | 36(4) | 35(5) | 29(4) | 5(3) | -2(3) | -8(3) |
| C(49) | 30(4) | 20(4) | 42(4) | -2(3) | 1(3) | 2(3) |
| C(50) | 30(4) | 28(4) | 47(4) | 5(4) | 0(3) | 4(3) |
| C(51) | 32(4) | 27(4) | 46(4) | 0(4) | -2(3) | -5(3) |
| O(51) | 50(4) | 28(3) | 58(4) | -1(3) | 3(3) | 14(3) |
| C(51A) | 35(4) | 24(4) | 42(4) | -1(3) | 0(3) | 2(3) |
| C(52) | 37(4) | 23(4) | 41(4) | 9(3) | 0(3) | -1(3) |
| C(53) | 38(4) | 30(4) | 43(4) | 10(4) | -2(3) | -1(4) |
| C(54) | 32(4) | 34(5) | 57(5) | 0(4) | 8(4) | -1(4) |
| C(55) | 38(5) | 26(4) | 65(6) | 14(4) | -10(4) | 4(4) |
| C(56) | 55(6) | 28(5) | 47(5) | 9(4) | -8(4) | 2(4) |
| C(57) | 42(5) | 37(5) | 42(4) | 11(4) | 0(4) | -4(4) |
| C(58) | 41(5) | 22(4) | 47(5) | -7(3) | -15(4) | 9(3) |
| O(58) | 44(3) | 26(3) | 44(3) | 4(2) | -4(3) | -2(3) |
| O(59) | 50(4) | 29(3) | 35(3) | 5(2) | -2(2) | 4(3) |
| C(59) | 36(4) | 24(4) | 54(5) | 9(4) | 0(4) | 1(3) |
| C(60) | 41(5) | 32(5) | 69(6) | 15(4) | 9(4) | -2(4) |
| O(60) | 41(4) | 54(5) | 78(5) | 23(4) | -7(3) | -6(3) |
| C(61) | 63(7) | 29(5) | 74(7) | 22(5) | 2(5) | 4(5) |
| S(3) | 65(2) | 29(2) | 52(2) | 7(2) | 13(2) | 6(2) |
| O(3) | 65(2) | 29(2) | 52(2) | 7(2) | 13(2) | 6(2) |
| C(62) | 65(2) | 29(2) | 52(2) | 7(2) | 13(2) | 6(2) |
| C(63) | 65(2) | 29(2) | 52(2) | 7(2) | 13(2) | 6(2) |
| S(3') | 56(4) | 20(3) | 99(6) | -1(3) | 21(4) | -7(3) |
| O(3') | 56(4) | 20(3) | 99(6) | -1(3) | 21(4) | -7(3) |
| C(62') | 56(4) | 20(3) | 99(6) | -1(3) | 21(4) | -7(3) |
| C(63') | 56(4) | 20(3) | 99(6) | -1(3) | 21(4) | -7(3) |
| C(64) | 52(6) | 45(6) | 50(5) | -13(4) | 1(4) | -14(5) |
| C(65) | 43(5) | 62(7) | 46(5) | -7(5) | -4(4) | -10(5) |
| C(66) | 34(4) | 50(6) | 40(4) | -2(4) | -2(3) | -1(4) |
| C(66A) | 32(4) | 31(4) | 38(4) | -2(3) | -2(3) | -7(3) |
| C(67) | 37(4) | 35(5) | 40(4) | 4(4) | -1(3) | -8(4) |
| N(68) | 33(3) | 38(4) | 33(3) | 7(3) | -4(3) | 2(3) |
| C(69) | 36(4) | 31(4) | 35(4) | 9(3) | 2(3) | 6(3) |
| O(69) | 44(3) | 30(3) | 36(3) | 11(2) | 2(2) | -5(3) |
| C(69A) | 37(4) | 24(4) | 44(4) | 8(3) | 6(3) | 6(3) |
| C(70) | 30(4) | 42(5) | 35(4) | 6(4) | 5(3) | 0(4) |
| C(71) | 32(4) | 28(4) | 38(4) | -5(3) | -2(3) | -7(3) |
| C(72) | 29(4) | 26(4) | 56(5) | 2(4) | -1(3) | -1(3) |
| O(72) | 51(4) | 39(4) | 59(4) | 4(3) | 3(3) | -11(3) |
| C(72A) | 35(4) | 27(4) | 40(4) | -2(3) | 4(3) | -4(3) |
| C(73) | 34(4) | 36(5) | 44(4) | 13(4) | -2(3) | 0(4) |
| C(74) | 37(4) | 32(5) | 46(4) | 8(4) | 1(4) | -2(4) |
| C(75) | 38(5) | 34(5) | 65(6) | 9(4) | -1(4) | 5(4) |
| C(76) | 30(4) | 26(4) | 67(6) | 7(4) | 4(4) | -2(3) |
| C(77) | 42(5) | 38(5) | 48(5) | 11(4) | 5(4) | -3(4) |
| C(78) | 36(4) | 45(5) | 42(4) | 9(4) | -3(3) | 5(4) |
| C(79) | 37(4) | 44(5) | 34(4) | -2(4) | 11(3) | -11(4) |
| O(79) | 42(3) | 35(4) | 52(4) | 11(3) | 5(3) | 8(3) |
| O(80) | 54(4) | 42(4) | 35(3) | 11(3) | 4(3) | 3(3) |
| C(80) | 45(5) | 35(5) | 43(4) | 0(4) | -2(4) | -7(4) |
| C(81) | 58(6) | 29(5) | 56(5) | 6(4) | -2(4) | -5(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| O(81) | 57(5) | 43(4) | 79(5) | 14(4) | -8(4) | 5(3) |
| C(82) | 106(12) | 47(7) | 127(13) | 43(8) | 32(10) | 2(7) |
| S(4) | 71(2) | 40(2) | 46(2) | 13(1) | 2(2) | 0(2) |
| O(4) | 71(2) | 40(2) | 46(2) | 13(1) | 2(2) | 0(2) |
| C(83) | 71(2) | 40(2) | 46(2) | 13(1) | 2(2) | 0(2) |
| C(84) | 71(2) | 40(2) | 46(2) | 13(1) | 2(2) | 0(2) |
| S(4') | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| O(4') | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| C(83') | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| C(84') | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| S(4") | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| O(4") | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| C(83") | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |
| C(84") | 66(5) | 43(4) | 25(3) | -2(3) | -6(3) | -9(4) |

**Table S18.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **12c**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(iso)** |
|---|---|---|---|---|
| H(1A) | -2228 | 929 | 1890 | 46 |
| H(1B) | -2989 | 2191 | 2132 | 46 |
| H(2A) | -1801 | 2401 | 3075 | 48 |
| H(2B) | -1333 | 1031 | 2884 | 48 |
| H(3A) | 704 | 2612 | 3076 | 45 |
| H(3B) | 893 | 1513 | 2504 | 45 |
| H(4A) | -1591 | 4197 | 2495 | 51 |
| H(4B) | -143 | 4515 | 2924 | 51 |
| H(6A) | 2311 | 3570 | 2258 | 43 |
| H(7) | 2614 | 1854 | 1561 | 41 |
| H(8) | 642 | 2652 | 684 | 41 |
| H(9A) | -1488 | 2947 | 1488 | 38 |
| H(11) | -246 | 6430 | 1203 | 68 |
| H(12) | -1285 | 8327 | 1291 | 88 |
| H(13) | -2503 | 9169 | 2220 | 116 |
| H(14) | -2286 | 8269 | 3108 | 105 |
| H(15) | -1293 | 6365 | 3019 | 82 |
| H(16) | 5315 | 3731 | 1362 | 59 |
| H(17A) | 2501 | 1360 | 170 | 48 |
| H(17B) | 1956 | 351 | 544 | 48 |
| H(19A) | 1892 | -605 | -604 | 78 |
| H(19B) | 420 | -490 | -997 | 78 |
| H(19C) | 398 | -1166 | -408 | 78 |
| H(20A) | 5124 | 5298 | 346 | 97 |
| H(20B) | 6346 | 6060 | 68 | 97 |
| H(20C) | 5929 | 6375 | 796 | 97 |
| H(21A) | 7755 | 2952 | -24 | 95 |
| H(21B) | 6950 | 3855 | -403 | 95 |
| H(21C) | 6046 | 3208 | 71 | 95 |
| H(22A) | 2681 | 8906 | 8072 | 44 |
| H(22B) | 1967 | 7617 | 7827 | 44 |
| H(23A) | 3152 | 7458 | 6911 | 51 |
| H(23B) | 3696 | 8810 | 7123 | 51 |
| H(24A) | 5880 | 8258 | 7494 | 43 |
| H(24B) | 5599 | 7129 | 6944 | 43 |

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|---|---|---|---|---|
| H(25A) | 3266 | 5669 | 7559 | 47 |
| H(25B) | 4691 | 5315 | 7135 | 47 |
| H(27A) | 7196 | 6242 | 7796 | 39 |
| H(28) | 7547 | 7999 | 8458 | 37 |
| H(29) | 5586 | 7280 | 9355 | 42 |
| H(30A) | 3419 | 6974 | 8533 | 39 |
| H(32) | 4670 | 3520 | 8899 | 90 |
| H(33) | 3453 | 1688 | 8857 | 90 |
| H(34) | 2191 | 790 | 7934 | 90 |
| H(35) | 2203 | 1683 | 7049 | 90 |
| H(36) | 3396 | 3514 | 7075 | 90 |
| H(37) | 10260 | 6195 | 8726 | 60 |
| H(38A) | 7477 | 8568 | 9861 | 45 |
| H(38B) | 6922 | 9561 | 9477 | 45 |
| H(40A) | 6875 | 10611 | 10635 | 88 |
| H(40B) | 5356 | 10523 | 10985 | 88 |
| H(40C) | 5414 | 11123 | 10370 | 88 |
| H(41A) | 11 | 4682 | 9676 | 113 |
| H(41B) | 1167 | 3967 | 10026 | 113 |
| H(41C) | 894 | 3598 | 9284 | 113 |
| H(42A) | 2685 | 7084 | 10142 | 86 |
| H(42B) | 1943 | 6164 | 10524 | 86 |
| H(42C) | 978 | 6779 | 10049 | 86 |
| H(43A) | 9341 | 3614 | 4685 | 58 |
| H(43B) | 8004 | 4154 | 4337 | 58 |
| H(44A) | 9538 | 5211 | 3848 | 59 |
| H(44B) | 10866 | 4507 | 4109 | 59 |
| H(45A) | 11298 | 6003 | 4958 | 55 |
| H(45B) | 10710 | 6798 | 4460 | 55 |
| H(46A) | 8319 | 7555 | 4456 | 46 |
| H(46B) | 7362 | 6352 | 4400 | 46 |
| H(48A) | 9808 | 8084 | 5556 | 40 |
| H(49) | 10938 | 6901 | 6162 | 38 |
| H(50) | 8151 | 5967 | 6458 | 42 |
| H(51A) | 7499 | 5243 | 5291 | 41 |
| H(53) | 4668 | 8177 | 5941 | 44 |
| H(54) | 2386 | 8864 | 5700 | 50 |
| H(55) | 1770 | 8987 | 4662 | 51 |
| H(56) | 3513 | 8521 | 3882 | 52 |
| H(57) | 5793 | 7863 | 4100 | 48 |
| H(58) | 9955 | 9640 | 7030 | 57 |
| H(59) | 8894 | 8616 | 7530 | 57 |
| H(59A) | 10081 | 6062 | 7277 | 45 |
| H(59B) | 10896 | 5061 | 6795 | 45 |
| H(61A) | 10658 | 4217 | 7784 | 81 |
| H(61B) | 9689 | 3040 | 7583 | 81 |
| H(61C) | 9065 | 4134 | 8072 | 81 |
| H(62A) | 6844 | 402 | 7001 | 73 |
| H(62B) | 6436 | 1702 | 7361 | 73 |
| H(62C) | 5851 | 554 | 7614 | 73 |
| H(63A) | 8282 | 1963 | 8896 | 73 |
| H(63B) | 6673 | 1465 | 8701 | 73 |
| H(63C) | 7277 | 2606 | 8447 | 73 |

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|---|---|---|---|---|
| H(62D) | 8224 | -1446 | 8002 | 89 |
| H(62E) | 7188 | -797 | 8548 | 89 |
| H(62F) | 8903 | -506 | 8571 | 89 |
| H(63D) | 7289 | 2340 | 8385 | 89 |
| H(63E) | 8394 | 1670 | 8783 | 89 |
| H(63F) | 6681 | 1376 | 8774 | 89 |
| H(64A) | 3069 | 4910 | 5801 | 62 |
| H(64B) | 4382 | 5522 | 5480 | 62 |
| H(65A) | 5980 | 4517 | 6005 | 63 |
| H(65B) | 4671 | 3773 | 6243 | 63 |
| H(66A) | 5789 | 2292 | 5609 | 51 |
| H(66B) | 6340 | 3148 | 5139 | 51 |
| H(67A) | 3290 | 1471 | 5541 | 45 |
| H(67B) | 2381 | 2694 | 5628 | 45 |
| H(69A) | 4770 | 1102 | 4450 | 42 |
| H(70) | 5951 | 2401 | 3915 | 43 |
| H(71) | 3184 | 3383 | 3629 | 41 |
| H(72A) | 2523 | 3949 | 4817 | 42 |
| H(74) | -321 | 989 | 4008 | 46 |
| H(75) | -2655 | 336 | 4231 | 54 |
| H(76) | -3245 | 102 | 5248 | 50 |
| H(77) | -1530 | 624 | 6063 | 50 |
| H(78) | 797 | 1214 | 5853 | 49 |
| H(79) | 5019 | -197 | 2915 | 64 |
| H(80) | 3943 | 926 | 2459 | 65 |
| H(80A) | 4952 | 3451 | 2828 | 50 |
| H(80B) | 5966 | 4262 | 3343 | 50 |
| H(82A) | 5893 | 5660 | 2648 | 135 |
| H(82B) | 4868 | 6743 | 2942 | 135 |
| H(82C) | 4367 | 5866 | 2313 | 135 |
| H(83A) | 1353 | 9220 | 2645 | 78 |
| H(83B) | 2996 | 8842 | 2777 | 78 |
| H(83C) | 1823 | 7855 | 2476 | 78 |
| H(84A) | 4464 | 7775 | 1205 | 78 |
| H(84B) | 3606 | 7026 | 1647 | 78 |
| H(84C) | 4785 | 8007 | 1946 | 78 |
| H(83D) | 2277 | 7288 | 1629 | 68 |
| H(83E) | 3601 | 7727 | 1247 | 68 |
| H(83F) | 1995 | 8249 | 1184 | 68 |
| H(84D) | 4045 | 10886 | 1926 | 68 |
| H(84E) | 2934 | 10337 | 1372 | 68 |
| H(84F) | 4548 | 9809 | 1396 | 68 |
| H(83G) | 2255 | 8017 | 2958 | 68 |
| H(83H) | 1031 | 8317 | 2475 | 68 |
| H(83I) | 2097 | 9344 | 2824 | 68 |
| H(84G) | 3087 | 9135 | 1168 | 68 |
| H(84H) | 2544 | 9976 | 1794 | 68 |
| H(84I) | 1504 | 8933 | 1441 | 68 |

**Table S19.** Torsion angles [°] for **12c**.

| | | | |
|---|---|---|---|
| C(9A)-C(1)-C(2)-C(3) | -11.5(9) | C(2)-C(3)-C(3A)-C(6A) | -168.3(7) |
| C(1)-C(2)-C(3)-C(3A) | 34.7(9) | C(2)-C(3)-C(3A)-C(9A) | -43.7(8) |
| C(2)-C(3)-C(3A)-C(4) | 72.9(9) | C(3)-C(3A)-C(4)-N(5) | 158.6(8) |

| | | | |
|---|---|---|---|
| C(6A)-C(3A)-C(4)-N(5) | 31.0(9) | C(13)-C(14)-C(15)-C(10) | 4(3) |
| C(9A)-C(3A)-C(4)-N(5) | -89.0(8) | C(8)-C(7)-C(16)-O(17) | 6.6(13) |
| C(3A)-C(4)-N(5)-C(6) | -20.8(10) | C(6A)-C(7)-C(16)-O(17) | -120.5(10) |
| C(3A)-C(4)-N(5)-C(10) | 167.7(8) | C(8)-C(7)-C(16)-O(16) | -173.0(7) |
| C(10)-N(5)-C(6)-O(6) | -4.1(16) | C(6A)-C(7)-C(16)-O(16) | 59.9(9) |
| C(4)-N(5)-C(6)-O(6) | -174.7(9) | C(7)-C(8)-C(17)-C(18) | -173.7(7) |
| C(10)-N(5)-C(6)-C(6A) | 171.7(9) | C(9)-C(8)-C(17)-C(18) | 65.1(9) |
| C(4)-N(5)-C(6)-C(6A) | 1.2(10) | C(8)-C(17)-C(18)-O(18) | 17.2(13) |
| O(6)-C(6)-C(6A)-C(3A) | -165.4(9) | C(8)-C(17)-C(18)-C(19) | -163.9(8) |
| N(5)-C(6)-C(6A)-C(3A) | 18.8(9) | C(30A)-C(22)-C(23)-C(24) | -6.8(9) |
| O(6)-C(6)-C(6A)-C(7) | -36.8(13) | C(22)-C(23)-C(24)-C(24A) | 30.7(9) |
| N(5)-C(6)-C(6A)-C(7) | 147.4(8) | C(23)-C(24)-C(24A)-C(25) | 74.2(8) |
| C(3)-C(3A)-C(6A)-C(6) | -154.4(7) | C(23)-C(24)-C(24A)-C(27A) | -167.2(7) |
| C(4)-C(3A)-C(6A)-C(6) | -29.9(8) | C(23)-C(24)-C(24A)-C(30A) | -41.9(8) |
| C(9A)-C(3A)-C(6A)-C(6) | 86.9(8) | C(27A)-C(24A)-C(25)-N(26) | 31.6(8) |
| C(3)-C(3A)-C(6A)-C(7) | 79.0(9) | C(24)-C(24A)-C(25)-N(26) | 157.3(7) |
| C(4)-C(3A)-C(6A)-C(7) | -156.6(7) | C(30A)-C(24A)-C(25)-N(26) | -92.1(7) |
| C(9A)-C(3A)-C(6A)-C(7) | -39.8(10) | C(24A)-C(25)-N(26)-C(27) | -20.4(10) |
| C(6)-C(6A)-C(7)-C(16) | 52.8(9) | C(24A)-C(25)-N(26)-C(31) | 166.6(9) |
| C(3A)-C(6A)-C(7)-C(16) | 174.0(7) | C(31)-N(26)-C(27)-O(27) | -3.6(16) |
| C(6)-C(6A)-C(7)-C(8) | -75.1(9) | C(25)-N(26)-C(27)-O(27) | -176.2(9) |
| C(3A)-C(6A)-C(7)-C(8) | 46.0(9) | C(31)-N(26)-C(27)-C(27A) | 172.8(10) |
| C(16)-C(7)-C(8)-C(17) | 57.9(10) | C(25)-N(26)-C(27)-C(27A) | 0.2(10) |
| C(6A)-C(7)-C(8)-C(17) | -175.8(7) | C(25)-C(24A)-C(27A)-C(27) | -31.5(8) |
| C(16)-C(7)-C(8)-C(9) | 180.0(7) | C(24)-C(24A)-C(27A)-C(27) | -154.2(7) |
| C(6A)-C(7)-C(8)-C(9) | -53.7(9) | C(30A)-C(24A)-C(27A)-C(27) | 88.3(8) |
| C(17)-C(8)-C(9)-O(9) | 7.0(11) | C(25)-C(24A)-C(27A)-C(28) | -157.5(6) |
| C(7)-C(8)-C(9)-O(9) | -117.8(9) | C(24)-C(24A)-C(27A)-C(28) | 79.8(8) |
| C(17)-C(8)-C(9)-C(9A) | -173.3(7) | C(30A)-C(24A)-C(27A)-C(28) | -37.6(9) |
| C(7)-C(8)-C(9)-C(9A) | 61.9(9) | O(27)-C(27)-C(27A)-C(24A) | -163.9(9) |
| O(9)-C(9)-C(9A)-C(1) | 6.9(12) | N(26)-C(27)-C(27A)-C(24A) | 19.8(9) |
| C(8)-C(9)-C(9A)-C(1) | -172.9(7) | O(27)-C(27)-C(27A)-C(28) | -36.3(13) |
| O(9)-C(9)-C(9A)-C(3A) | 123.3(9) | N(26)-C(27)-C(27A)-C(28) | 147.4(7) |
| C(8)-C(9)-C(9A)-C(3A) | -56.4(9) | C(24A)-C(27A)-C(28)-C(37) | 173.7(6) |
| C(2)-C(1)-C(9A)-C(9) | 105.1(8) | C(27)-C(27A)-C(28)-C(37) | 53.9(9) |
| C(2)-C(1)-C(9A)-C(3A) | -15.0(9) | C(24A)-C(27A)-C(28)-C(29) | 46.0(9) |
| C(3)-C(3A)-C(9A)-C(9) | -84.4(8) | C(27)-C(27A)-C(28)-C(29) | -73.8(9) |
| C(4)-C(3A)-C(9A)-C(9) | 156.0(6) | C(37)-C(28)-C(29)-C(38) | 56.2(9) |
| C(6A)-C(3A)-C(9A)-C(9) | 43.2(9) | C(27A)-C(28)-C(29)-C(38) | -177.2(7) |
| C(3)-C(3A)-C(9A)-C(1) | 36.2(8) | C(37)-C(28)-C(29)-C(30) | 178.2(7) |
| C(4)-C(3A)-C(9A)-C(1) | -83.4(8) | C(27A)-C(28)-C(29)-C(30) | -55.2(8) |
| C(6A)-C(3A)-C(9A)-C(1) | 163.8(7) | C(38)-C(29)-C(30)-O(30) | 8.2(11) |
| C(6)-N(5)-C(10)-C(15) | -145.4(11) | C(28)-C(29)-C(30)-O(30) | -117.8(9) |
| C(4)-N(5)-C(10)-C(15) | 24.4(16) | C(38)-C(29)-C(30)-C(30A) | -172.4(6) |
| C(6)-N(5)-C(10)-C(11) | 35.8(16) | C(28)-C(29)-C(30)-C(30A) | 61.6(8) |
| C(4)-N(5)-C(10)-C(11) | -154.5(10) | O(30)-C(30)-C(30A)-C(22) | 6.9(11) |
| C(15)-C(10)-C(11)-C(12) | 0.4(18) | C(29)-C(30)-C(30A)-C(22) | -172.5(7) |
| N(5)-C(10)-C(11)-C(12) | 179.3(11) | O(30)-C(30)-C(30A)-C(24A) | 125.3(8) |
| C(10)-C(11)-C(12)-C(13) | -3(2) | C(29)-C(30)-C(30A)-C(24A) | -54.0(8) |
| C(11)-C(12)-C(13)-C(14) | 6(2) | C(23)-C(22)-C(30A)-C(30) | 102.1(8) |
| C(12)-C(13)-C(14)-C(15) | -6(3) | C(23)-C(22)-C(30A)-C(24A) | -19.5(9) |
| C(11)-C(10)-C(15)-C(14) | -1(2) | C(25)-C(24A)-C(30A)-C(30) | 156.4(6) |
| N(5)-C(10)-C(15)-C(14) | -179.9(13) | C(27A)-C(24A)-C(30A)-C(30) | 39.7(9) |

| | | | |
|---|---|---|---|
| C(24)-C(24A)-C(30A)-C(30) | -86.0(7) | C(48A)-C(49)-C(50)-C(59) | 176.2(7) |
| C(25)-C(24A)-C(30A)-C(22) | -80.0(8) | C(58)-C(49)-C(50)-C(51) | 179.5(7) |
| C(27A)-C(24A)-C(30A)-C(22) | 163.3(7) | C(48A)-C(49)-C(50)-C(51) | 55.3(9) |
| C(24)-C(24A)-C(30A)-C(22) | 37.6(8) | C(59)-C(50)-C(51)-O(51) | -10.5(11) |
| C(27)-N(26)-C(31)-C(32) | 33.5(17) | C(49)-C(50)-C(51)-O(51) | 113.6(9) |
| C(25)-N(26)-C(31)-C(32) | -154.6(10) | C(59)-C(50)-C(51)-C(51A) | 171.6(7) |
| C(27)-N(26)-C(31)-C(36) | -150.3(11) | C(49)-C(50)-C(51)-C(51A) | -64.4(9) |
| C(25)-N(26)-C(31)-C(36) | 21.6(16) | O(51)-C(51)-C(51A)-C(45A) | -117.8(9) |
| N(26)-C(31)-C(32)-C(33) | 176.9(11) | C(50)-C(51)-C(51A)-C(45A) | 60.0(9) |
| C(36)-C(31)-C(32)-C(33) | 0.7(19) | O(51)-C(51)-C(51A)-C(43) | -2.9(12) |
| C(31)-C(32)-C(33)-C(34) | -0.7(19) | C(50)-C(51)-C(51A)-C(43) | 174.9(7) |
| C(32)-C(33)-C(34)-C(35) | 0.8(19) | C(45)-C(45A)-C(51A)-C(51) | 83.0(8) |
| C(33)-C(34)-C(35)-C(36) | -1.0(19) | C(48A)-C(45A)-C(51A)-C(51) | -46.4(10) |
| C(34)-C(35)-C(36)-C(31) | 1.0(19) | C(46)-C(45A)-C(51A)-C(51) | -158.0(7) |
| C(32)-C(31)-C(36)-C(35) | -0.8(19) | C(45)-C(45A)-C(51A)-C(43) | -37.5(9) |
| N(26)-C(31)-C(36)-C(35) | -177.1(11) | C(48A)-C(45A)-C(51A)-C(43) | -166.9(7) |
| C(27A)-C(28)-C(37)-O(38) | -119.1(9) | C(46)-C(45A)-C(51A)-C(43) | 81.5(8) |
| C(29)-C(28)-C(37)-O(38) | 8.5(13) | C(44)-C(43)-C(51A)-C(51) | -100.3(9) |
| C(27A)-C(28)-C(37)-O(37) | 62.0(9) | C(44)-C(43)-C(51A)-C(45A) | 17.5(9) |
| C(29)-C(28)-C(37)-O(37) | -170.5(7) | C(48)-N(47)-C(52)-C(53) | -28.2(12) |
| C(30)-C(29)-C(38)-C(39) | 66.4(9) | C(46)-N(47)-C(52)-C(53) | 163.8(8) |
| C(28)-C(29)-C(38)-C(39) | -172.8(7) | C(48)-N(47)-C(52)-C(57) | 152.0(8) |
| C(29)-C(38)-C(39)-O(39) | 16.2(13) | C(46)-N(47)-C(52)-C(57) | -16.0(12) |
| C(29)-C(38)-C(39)-C(40) | -160.7(8) | N(47)-C(52)-C(53)-C(54) | 178.9(8) |
| C(51A)-C(43)-C(44)-C(45) | 8.7(10) | C(57)-C(52)-C(53)-C(54) | -1.3(13) |
| C(43)-C(44)-C(45)-C(45A) | -31.4(10) | C(52)-C(53)-C(54)-C(55) | 1.8(14) |
| C(44)-C(45)-C(45A)-C(51A) | 42.6(9) | C(53)-C(54)-C(55)-C(56) | -1.7(14) |
| C(44)-C(45)-C(45A)-C(48A) | 170.3(8) | C(54)-C(55)-C(56)-C(57) | 1.2(14) |
| C(44)-C(45)-C(45A)-C(46) | -75.8(9) | C(55)-C(56)-C(57)-C(52) | -0.8(14) |
| C(51A)-C(45A)-C(46)-N(47) | 84.8(8) | C(53)-C(52)-C(57)-C(56) | 0.8(13) |
| C(45)-C(45A)-C(46)-N(47) | -160.7(7) | N(47)-C(52)-C(57)-C(56) | -179.4(8) |
| C(48A)-C(45A)-C(46)-N(47) | -36.2(8) | C(48A)-C(49)-C(58)-O(58) | -57.7(10) |
| C(45A)-C(46)-N(47)-C(48) | 25.4(9) | C(50)-C(49)-C(58)-O(58) | 176.0(7) |
| C(45A)-C(46)-N(47)-C(52) | -165.2(7) | C(48A)-C(49)-C(58)-O(59) | 121.6(8) |
| C(52)-N(47)-C(48)-O(48) | 5.9(12) | C(50)-C(49)-C(58)-O(59) | -4.6(11) |
| C(46)-N(47)-C(48)-O(48) | 175.2(8) | C(51)-C(50)-C(59)-C(60) | -76.8(9) |
| C(52)-N(47)-C(48)-C(48A) | -171.8(7) | C(49)-C(50)-C(59)-C(60) | 164.2(7) |
| C(46)-N(47)-C(48)-C(48A) | -2.5(9) | C(50)-C(59)-C(60)-O(60) | -4.4(14) |
| O(48)-C(48)-C(48A)-C(49) | 34.9(11) | C(50)-C(59)-C(60)-C(61) | 179.1(8) |
| N(47)-C(48)-C(48A)-C(49) | -147.3(7) | C(72A)-C(64)-C(65)-C(66) | 7.6(11) |
| O(48)-C(48)-C(48A)-C(45A) | 160.8(7) | C(64)-C(65)-C(66)-C(66A) | -31.5(10) |
| N(47)-C(48)-C(48A)-C(45A) | -21.4(8) | C(65)-C(66)-C(66A)-C(69A) | 166.6(8) |
| C(51A)-C(45A)-C(48A)-C(48) | -82.8(8) | C(65)-C(66)-C(66A)-C(67) | -73.9(10) |
| C(45)-C(45A)-C(48A)-C(48) | 154.9(7) | C(65)-C(66)-C(66A)-C(72A) | 42.1(9) |
| C(46)-C(45A)-C(48A)-C(48) | 34.9(8) | C(69A)-C(66A)-C(67)-N(68) | -34.7(8) |
| C(51A)-C(45A)-C(48A)-C(49) | 42.5(10) | C(66)-C(66A)-C(67)-N(68) | -163.6(7) |
| C(45)-C(45A)-C(48A)-C(49) | -79.9(9) | C(72A)-C(66A)-C(67)-N(68) | 85.5(8) |
| C(46)-C(45A)-C(48A)-C(49) | 160.2(7) | C(66A)-C(67)-N(68)-C(69) | 22.1(9) |
| C(48)-C(48A)-C(49)-C(58) | -54.8(9) | C(66A)-C(67)-N(68)-C(73) | -165.6(7) |
| C(45A)-C(48A)-C(49)-C(58) | -174.6(7) | C(73)-N(68)-C(69)-O(69) | 4.6(14) |
| C(48)-C(48A)-C(49)-C(50) | 72.7(9) | C(67)-N(68)-C(69)-O(69) | 176.2(8) |
| C(45A)-C(48A)-C(49)-C(50) | -47.2(9) | C(73)-N(68)-C(69)-C(69A) | -171.5(8) |
| C(58)-C(49)-C(50)-C(59) | -59.5(10) | C(67)-N(68)-C(69)-C(69A) | 0.1(10) |

| | | | |
|---|---|---|---|
| C(67)-C(66A)-C(69A)-C(69) | 34.4(8) | C(71)-C(80)-C(81)-C(82) | 166.6(11) |
| C(66)-C(66A)-C(69A)-C(69) | 159.5(8) | | |
| C(72A)-C(66A)-C(69A)-C(69) | -82.7(8) | | |
| C(67)-C(66A)-C(69A)-C(70) | 159.3(7) | | |
| C(66)-C(66A)-C(69A)-C(70) | -75.6(10) | | |
| C(72A)-C(66A)-C(69A)-C(70) | 42.2(10) | | |
| O(69)-C(69)-C(69A)-C(66A) | 161.2(8) | | |
| N(68)-C(69)-C(69A)-C(66A) | -22.6(9) | | |
| O(69)-C(69)-C(69A)-C(70) | 34.0(12) | | |
| N(68)-C(69)-C(69A)-C(70) | -149.8(7) | | |
| C(66A)-C(69A)-C(70)-C(79) | -176.5(7) | | |
| C(69)-C(69A)-C(70)-C(79) | -57.5(9) | | |
| C(66A)-C(69A)-C(70)-C(71) | -47.5(10) | | |
| C(69)-C(69A)-C(70)-C(71) | 71.5(9) | | |
| C(79)-C(70)-C(71)-C(80) | -58.7(10) | | |
| C(69A)-C(70)-C(71)-C(80) | 176.3(7) | | |
| C(79)-C(70)-C(71)-C(72) | 177.8(7) | | |
| C(69A)-C(70)-C(71)-C(72) | 52.8(9) | | |
| C(80)-C(71)-C(72)-O(72) | -11.3(12) | | |
| C(70)-C(71)-C(72)-O(72) | 114.6(9) | | |
| C(80)-C(71)-C(72)-C(72A) | 172.5(8) | | |
| C(70)-C(71)-C(72)-C(72A) | -61.6(9) | | |
| O(72)-C(72)-C(72A)-C(64) | -2.4(13) | | |
| C(71)-C(72)-C(72A)-C(64) | 173.6(8) | | |
| O(72)-C(72)-C(72A)-C(66A) | -119.4(9) | | |
| C(71)-C(72)-C(72A)-C(66A) | 56.7(9) | | |
| C(65)-C(64)-C(72A)-C(72) | -100.3(9) | | |
| C(65)-C(64)-C(72A)-C(66A) | 19.2(9) | | |
| C(69A)-C(66A)-C(72A)-C(72) | -44.1(9) | | |
| C(67)-C(66A)-C(72A)-C(72) | -156.9(7) | | |
| C(66)-C(66A)-C(72A)-C(72) | 84.1(8) | | |
| C(69A)-C(66A)-C(72A)-C(64) | -165.5(7) | | |
| C(67)-C(66A)-C(72A)-C(64) | 81.7(8) | | |
| C(66)-C(66A)-C(72A)-C(64) | -37.3(8) | | |
| C(69)-N(68)-C(73)-C(78) | 156.1(9) | | |
| C(67)-N(68)-C(73)-C(78) | -14.8(13) | | |
| C(69)-N(68)-C(73)-C(74) | -21.1(13) | | |
| C(67)-N(68)-C(73)-C(74) | 168.0(8) | | |
| C(78)-C(73)-C(74)-C(75) | 1.3(13) | | |
| N(68)-C(73)-C(74)-C(75) | 178.6(8) | | |
| C(73)-C(74)-C(75)-C(76) | -0.9(14) | | |
| C(74)-C(75)-C(76)-C(77) | 1.5(14) | | |
| C(75)-C(76)-C(77)-C(78) | -2.4(14) | | |
| C(76)-C(77)-C(78)-C(73) | 2.9(15) | | |
| N(68)-C(73)-C(78)-C(77) | -179.6(9) | | |
| C(74)-C(73)-C(78)-C(77) | -2.3(14) | | |
| C(69A)-C(70)-C(79)-O(79) | -58.3(10) | | |
| C(71)-C(70)-C(79)-O(79) | 175.1(7) | | |
| C(69A)-C(70)-C(79)-O(80) | 122.6(8) | | |
| C(71)-C(70)-C(79)-O(80) | -3.9(10) | | |
| C(72)-C(71)-C(80)-C(81) | -66.9(10) | | |
| C(70)-C(71)-C(80)-C(81) | 171.6(7) | | |
| C(71)-C(80)-C(81)-O(81) | -21.1(13) | | |

**Table S20.** Hydrogen bonds for **12c** [Å and °].

| D-H...A | d(D-H) | d(H...A) | d(D...A) | <(DHA) |
|---|---|---|---|---|
| O(16)-H(16)...O(1) | 0.90 | 1.68 | 2.561(9) | 165.9 |
| O(37)-H(37)...O(2)#1 | 0.90 | 1.70 | 2.575(9) | 164.8 |
| O(58)-H(58)...O(3')#2 | 0.90 | 1.71 | 2.606(16) | 177.6 |
| O(59)-H(59)...O(3)#2 | 0.90 | 1.60 | 2.483(10) | 166.8 |
| O(79)-H(79)...O(4')#3 | 0.90 | 1.53 | 2.42(3) | 168.8 |
| O(80)-H(80)...O(4)#3 | 0.90 | 1.64 | 2.500(10) | 159.3 |

Symmetry transformations used to generate equivalent atoms: #1 x+1, y, zl #2 x, y+1, z; #3 x, y-1, z

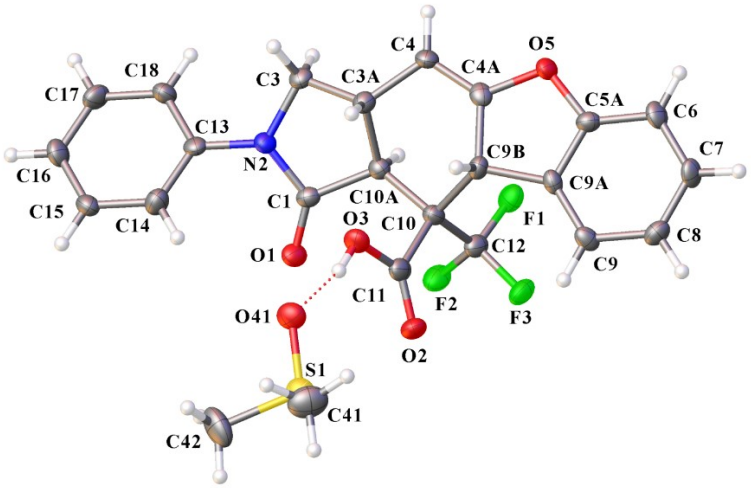



**Figure S4**. Molecular structure of **20a**. Dotted lines show H-bonding interactions.

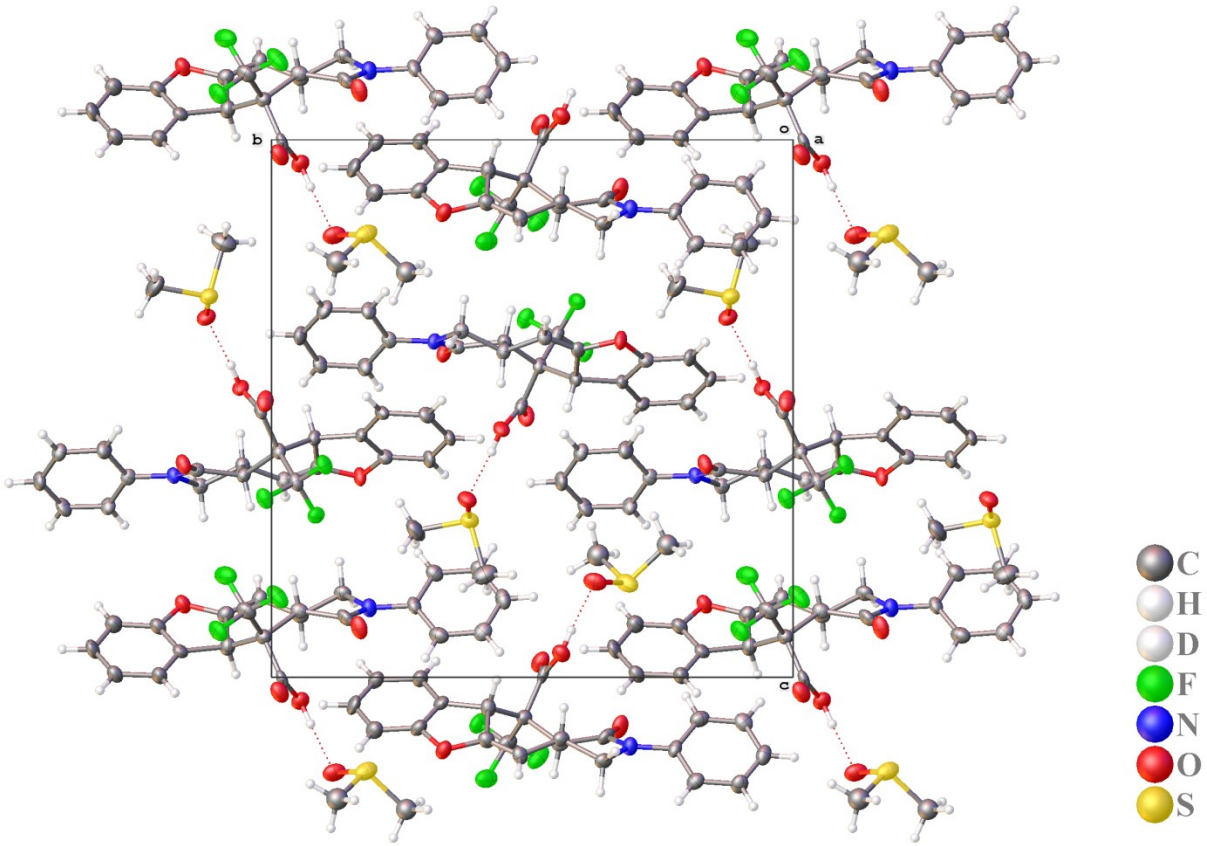



**Figure S5.** Crystal packing of the structure **20a**.

**Table S21.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **20a**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| F1 | 6488(4) | 4143(2) | 3012(2) | 30.4(9) |
| F2 | 4865(4) | 5129(2) | 3324(2) | 32.9(8) |
| F3 | 4805(4) | 3986(2) | 3953(2) | 31.1(8) |
| O1 | 6264(5) | 6691(3) | 3962(3) | 29.1(10) |
| O2 | 5028(5) | 5119(3) | 5136(3) | 34.0(11) |
| O3 | 7576(5) | 5592(3) | 5385(3) | 29.0(10) |
| O5 | 10242(5) | 3305(2) | 3730(3) | 26.3(10) |
| N2 | 9019(6) | 6877(3) | 3752(3) | 22.4(11) |
| C1 | 7623(7) | 6432(4) | 3857(3) | 21.7(13) |
| C3 | 10431(7) | 6362(4) | 3554(4) | 22.9(13) |
| C3A | 9967(7) | 5551(4) | 3939(4) | 23.9(13) |
| C4 | 10715(7) | 4763(4) | 3664(4) | 23.9(13) |
| C4A | 9874(7) | 4118(4) | 3907(3) | 23.0(13) |
| C5A | 9085(7) | 2818(4) | 4098(4) | 23.4(13) |
| C6 | 9072(8) | 1980(4) | 4055(4) | 27.1(14) |
| C7 | 7824(8) | 1583(4) | 4453(4) | 27.5(15) |
| C8 | 6704(8) | 2023(4) | 4877(4) | 27.8(15) |

| | | | | |
|---|---|---|---|---|
| C9 | 6750(7) | 2880(4) | 4920(4) | 24.6(14) |
| C9A | 7950(7) | 3278(4) | 4505(4) | 21.6(13) |
| C9B | 8442(7) | 4171(4) | 4452(4) | 23.1(13) |
| C10 | 7156(7) | 4859(4) | 4205(4) | 23.1(13) |
| C10A | 8110(7) | 5532(4) | 3756(4) | 21.5(13) |
| C11 | 6423(7) | 5211(4) | 4962(4) | 25.6(14) |
| C12 | 5832(7) | 4524(4) | 3632(4) | 27.1(14) |
| C13 | 9071(7) | 7744(4) | 3723(4) | 22.4(13) |
| C14 | 8134(8) | 8208(4) | 4228(4) | 31.5(15) |
| C15 | 8167(7) | 9067(4) | 4181(4) | 26.5(14) |
| C16 | 9157(8) | 9446(4) | 3646(4) | 30.9(15) |
| C17 | 10115(8) | 8982(4) | 3162(4) | 31.5(15) |
| C18 | 10070(7) | 8134(4) | 3181(4) | 26.8(14) |
| F21 | 6575(5) | 5880(3) | 1890(2) | 45.5(11) |
| F22 | 4974(4) | 4884(3) | 1495(2) | 45.4(11) |
| F23 | 4943(4) | 6020(2) | 859(2) | 39.8(10) |
| O21 | 6377(5) | 3318(3) | 921(3) | 36.5(12) |
| O22 | 5208(6) | 4844(3) | -281(3) | 38.7(12) |
| O23 | 7814(5) | 4447(3) | -442(3) | 33.5(11) |
| O25 | 10419(6) | 6697(3) | 1357(3) | 32.5(11) |
| N22 | 9123(6) | 3125(3) | 1289(3) | 29.7(13) |
| C21 | 7725(9) | 3584(4) | 1106(4) | 30.7(16) |
| C23 | 10510(8) | 3635(4) | 1560(4) | 27.7(14) |
| C23A | 10102(7) | 4446(4) | 1150(4) | 27.6(15) |
| C24 | 10826(7) | 5232(4) | 1457(4) | 27.8(14) |
| C24A | 10035(8) | 5879(4) | 1167(4) | 29.3(15) |
| C25A | 9266(8) | 7176(4) | 944(4) | 32.0(16) |
| C26 | 9269(9) | 8025(4) | 986(4) | 36.7(17) |
| C27 | 8093(9) | 8424(4) | 520(4) | 38.3(18) |
| C28 | 6942(8) | 7997(4) | 56(4) | 32.0(16) |
| C29 | 6968(8) | 7148(4) | 29(4) | 33.4(16) |
| C29A | 8153(8) | 6746(4) | 482(4) | 27.3(14) |
| C29B | 8604(8) | 5842(4) | 569(4) | 31.1(16) |
| C30 | 7315(7) | 5153(4) | 751(4) | 25.9(14) |
| C30A | 8229(7) | 4466(4) | 1235(4) | 25.0(14) |
| C31 | 6617(8) | 4794(4) | -44(4) | 25.9(14) |
| C32 | 5916(8) | 5479(5) | 1233(4) | 36.2(17) |
| C33 | 9113(7) | 2263(4) | 1333(4) | 25.5(14) |
| C34 | 8212(8) | 1790(5) | 779(4) | 34.0(16) |
| C35 | 8212(7) | 947(4) | 842(4) | 30.7(15) |
| C36 | 9122(8) | 562(4) | 1451(4) | 33.7(16) |
| C37 | 10025(8) | 1024(4) | 1991(4) | 32.2(16) |
| C38 | 10046(8) | 1871(4) | 1937(4) | 29.6(15) |

| | | | | |
|---|---|---|---|---|
| S1 | 5166(2) | 6199.8(11) | 7084.3(9) | 33.0(4) |
| O41 | 6821(5) | 6250(3) | 6696(2) | 33.8(11) |
| C41 | 5671(9) | 5911(6) | 8092(5) | 52(2) |
| D41A | 4662.36 | 5864.79 | 8388.12 | 77 |
| D41B | 6240.76 | 5382.37 | 8098.66 | 77 |
| D41C | 6385.12 | 6328.78 | 8342.09 | 77 |
| C42 | 4605(10) | 7235(5) | 7269(5) | 52(2) |
| D42A | 3541.58 | 7247.41 | 7521.5 | 78 |
| D42B | 5439.14 | 7490.66 | 7624.02 | 78 |
| D42C | 4525.7 | 7535.92 | 6764.6 | 78 |
| S2A | 5556(3) | 3186(2) | -1750.0(18) | 41.3(12) |
| O42 | 6994(5) | 3796(3) | -1776(3) | 39.7(12) |
| C43 | 3958(17) | 3740(8) | -2270(8) | 50(3) |
| D43A | 2954.83 | 3408.99 | -2294.03 | 76 |
| D43B | 3752.11 | 4254.45 | -1989.42 | 76 |
| D43C | 4290.58 | 3861.08 | -2812.06 | 76 |
| C44 | 5947(15) | 2414(7) | -2463(7) | 46(3) |
| D44A | 5059.1 | 2009.01 | -2468.97 | 68 |
| D44B | 6006.04 | 2663.61 | -2991.98 | 68 |
| D44C | 6991.06 | 2143.53 | -2322.15 | 68 |
| S2B | 5253(11) | 3724(4) | -2152(4) | 67(3) |
| C45 | 5460(30) | 3877(19) | -3157(17) | 72(8) |
| D45A | 4381.82 | 3838.64 | -3432.69 | 108 |
| D45B | 5927.47 | 4421.55 | -3245.64 | 108 |
| D45C | 6190.49 | 3457.93 | -3365.51 | 108 |
| C46 | 4920(40) | 2660(20) | -2110(20) | 98(11) |
| D46A | 3821.13 | 2536.21 | -2334.71 | 147 |
| D46B | 5745.45 | 2378.13 | -2410.95 | 147 |
| D46C | 4994.74 | 2482.45 | -1550.54 | 147 |

**Table S22.** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **20a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | $\mathbf{U_{11}}$ | $\mathbf{U_{22}}$ | $\mathbf{U_{33}}$ | $\mathbf{U_{23}}$ | $\mathbf{U_{13}}$ | $\mathbf{U_{12}}$ |
|---|---|---|---|---|---|---|
| F1 | 31(2) | 31(2) | 29(2) | -2.9(17) | -1.4(15) | -7.4(15) |
| F2 | 22.8(19) | 31(2) | 44(2) | 9.0(18) | -4.6(16) | 0.0(17) |
| F3 | 25(2) | 27(2) | 41(2) | 7.7(16) | 1.7(16) | -6.7(16) |
| O1 | 24(2) | 23(2) | 41(3) | 7(2) | 4.4(19) | 4.4(19) |
| O2 | 25(2) | 29(3) | 48(3) | -2(2) | 15(2) | -5(2) |
| O3 | 33(3) | 29(3) | 26(2) | -4(2) | 11.3(19) | 0(2) |
| O5 | 24(2) | 17(2) | 38(3) | 2.4(19) | 7.7(19) | 4.0(18) |
| N2 | 19(3) | 20(3) | 28(3) | 2(2) | 2(2) | 3(2) |
| C1 | 18(3) | 25(4) | 21(3) | 0(3) | 2(2) | -1(3) |
| C3 | 16(3) | 24(3) | 28(3) | -1(3) | -1(2) | -2(3) |
| C3A | 20(3) | 22(3) | 30(3) | 2(3) | 2(3) | -1(3) |
| C4 | 16(3) | 24(3) | 32(3) | -1(3) | 5(2) | 3(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4A | 21(3) | 22(3) | 26(3) | 0(3) | -5(3) | 3(3) |
| C5A | 19(3) | 26(4) | 25(3) | 1(3) | 4(2) | 0(2) |
| C6 | 32(4) | 17(3) | 32(4) | 3(3) | -1(3) | 7(3) |
| C7 | 40(4) | 15(3) | 27(3) | 6(3) | 4(3) | 1(3) |
| C8 | 27(3) | 28(4) | 29(4) | 5(3) | 4(3) | -7(3) |
| C9 | 30(4) | 23(3) | 21(3) | 4(3) | 5(3) | 8(3) |
| C9A | 28(3) | 16(3) | 21(3) | -1(3) | 2(2) | 3(3) |
| C9B | 24(3) | 18(3) | 27(3) | -1(3) | 3(2) | -4(2) |
| C10 | 21(3) | 20(3) | 29(3) | 0(3) | 7(2) | 2(2) |
| C10A | 21(3) | 21(3) | 23(3) | -2(3) | 2(2) | 0(2) |
| C11 | 25(3) | 18(3) | 34(4) | 7(3) | 7(3) | 3(3) |
| C12 | 23(3) | 22(3) | 37(4) | 7(3) | 4(3) | 1(3) |
| C13 | 13(3) | 24(3) | 30(3) | -2(3) | 0(2) | -1(2) |
| C14 | 34(4) | 25(4) | 36(4) | 0(3) | 9(3) | -6(3) |
| C15 | 21(3) | 24(4) | 35(4) | -4(3) | 5(3) | 3(3) |
| C16 | 35(4) | 19(3) | 39(4) | 2(3) | 3(3) | 6(3) |
| C17 | 29(4) | 27(4) | 39(4) | 10(3) | 8(3) | -3(3) |
| C18 | 25(3) | 24(3) | 32(3) | -1(3) | 10(3) | 4(3) |
| F21 | 48(3) | 53(3) | 36(2) | 3(2) | 1.6(19) | 21(2) |
| F22 | 33(2) | 49(3) | 55(3) | 24(2) | 11.6(19) | 10.0(19) |
| F23 | 37(2) | 38(2) | 44(2) | 12.3(18) | -0.8(17) | 13.4(17) |
| O21 | 23(2) | 29(3) | 56(3) | 9(2) | -8(2) | 4(2) |
| O22 | 35(3) | 35(3) | 46(3) | 11(2) | -7(2) | -5(2) |
| O23 | 34(3) | 34(3) | 32(3) | -5(2) | -8(2) | -1(2) |
| O25 | 34(3) | 27(2) | 36(3) | 7(2) | -7(2) | -2(2) |
| N22 | 27(3) | 25(3) | 37(3) | 2(2) | -2(2) | -1(2) |
| C21 | 33(4) | 30(4) | 29(3) | 12(3) | 0(3) | 9(3) |
| C23 | 25(3) | 33(4) | 25(3) | 2(3) | -5(3) | 4(3) |
| C23A | 27(4) | 30(4) | 26(3) | 1(3) | -1(3) | 5(3) |
| C24 | 23(3) | 26(4) | 34(4) | -4(3) | -1(3) | 3(3) |
| C24A | 28(4) | 30(4) | 29(4) | -2(3) | -3(3) | 2(3) |
| C25A | 38(4) | 29(4) | 28(4) | 8(3) | -5(3) | -2(3) |
| C26 | 44(5) | 32(4) | 34(4) | 2(3) | -5(3) | -5(3) |
| C27 | 54(5) | 21(4) | 39(4) | 10(3) | -4(3) | -9(3) |
| C28 | 36(4) | 28(4) | 31(4) | 8(3) | -5(3) | -3(3) |
| C29 | 43(4) | 26(4) | 30(4) | 3(3) | -6(3) | -1(3) |
| C29A | 36(4) | 25(3) | 21(3) | 5(3) | 3(3) | -3(3) |
| C29B | 32(4) | 25(4) | 36(4) | -1(3) | -2(3) | 1(3) |
| C30 | 27(3) | 26(3) | 24(3) | 1(3) | 0(3) | 4(3) |
| C30A | 16(3) | 33(4) | 26(4) | 3(3) | 1(2) | 2(3) |
| C31 | 24(3) | 16(3) | 38(4) | 11(3) | -2(3) | -1(3) |
| C32 | 35(4) | 41(4) | 32(4) | 10(3) | -4(3) | 5(3) |
| C33 | 24(3) | 21(3) | 32(3) | 6(3) | 8(3) | 1(3) |
| C34 | 32(4) | 41(4) | 29(4) | 5(3) | 1(3) | 7(3) |
| C35 | 20(3) | 36(4) | 37(4) | -6(3) | 4(3) | 1(3) |
| C36 | 31(4) | 26(4) | 45(4) | 6(3) | 10(3) | 5(3) |
| C37 | 27(4) | 31(4) | 37(4) | 4(3) | -7(3) | 3(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C38 | 25(4) | 33(4) | 31(4) | 6(3) | 1(3) | -2(3) |
| S1 | 35.3(9) | 35.6(9) | 28.0(8) | -2.0(8) | 0.3(7) | 1.5(8) |
| O41 | 35(3) | 38(3) | 29(2) | -6(2) | 5.9(19) | -2(2) |
| C41 | 47(5) | 67(6) | 42(5) | 14(4) | 7(3) | -1(4) |
| C42 | 68(6) | 38(4) | 50(5) | -19(4) | -6(4) | 12(4) |
| S2A | 34.4(17) | 54(2) | 36.3(18) | -10.4(15) | 6.1(12) | -12.3(14) |
| O42 | 29(3) | 56(3) | 33(3) | -7(2) | -6(2) | -5(2) |
| S2B | 82(6) | 54(4) | 62(4) | 35(4) | -37(4) | -32(4) |

**Table S23.** Bond Lengths for **20a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| F1 | C12 | 1.341(7) | C23A | C30A | 1.541(8) |
| F2 | C12 | 1.354(7) | C24 | C24A | 1.321(9) |
| F3 | C12 | 1.340(7) | C24A | C29B | 1.511(9) |
| O1 | C1 | 1.206(6) | C25A | C26 | 1.386(9) |
| O2 | C11 | 1.195(6) | C25A | C29A | 1.365(9) |
| O3 | C11 | 1.313(8) | C26 | C27 | 1.378(10) |
| O5 | C4A | 1.395(7) | C27 | C28 | 1.384(9) |
| O5 | C5A | 1.396(7) | C28 | C29 | 1.387(9) |
| N2 | C1 | 1.367(7) | C29 | C29A | 1.374(9) |
| N2 | C3 | 1.474(7) | C29A | C29B | 1.525(9) |
| N2 | C13 | 1.416(8) | C29B | C30 | 1.578(9) |
| C1 | C10A | 1.532(8) | C30 | C30A | 1.557(9) |
| C3 | C3A | 1.527(8) | C30 | C31 | 1.547(9) |
| C3A | C4 | 1.503(8) | C30 | C32 | 1.520(9) |
| C3A | C10A | 1.534(8) | C33 | C34 | 1.395(9) |
| C4 | C4A | 1.329(8) | C33 | C38 | 1.400(9) |
| C4A | C9B | 1.513(8) | C34 | C35 | 1.379(10) |
| C5A | C6 | 1.370(9) | C35 | C36 | 1.390(9) |
| C5A | C9A | 1.391(8) | C36 | C37 | 1.372(9) |
| C6 | C7 | 1.398(9) | C37 | C38 | 1.385(9) |
| C7 | C8 | 1.381(9) | S1 | O41 | 1.524(4) |
| C8 | C9 | 1.400(9) | S1 | C41 | 1.790(8) |
| C9 | C9A | 1.384(9) | S1 | C42 | 1.780(7) |
| C9A | C9B | 1.515(8) | C41 | D41A | 0.9800 |
| C9B | C10 | 1.581(8) | C41 | D41B | 0.9800 |
| C10 | C10A | 1.557(8) | C41 | D41C | 0.9800 |
| C10 | C11 | 1.537(9) | C42 | D42A | 0.9800 |
| C10 | C12 | 1.520(9) | C42 | D42B | 0.9800 |
| C13 | C14 | 1.387(9) | C42 | D42C | 0.9800 |
| C13 | C18 | 1.398(8) | S2A | O42 | 1.540(6) |
| C14 | C15 | 1.404(9) | S2A | C43 | 1.786(14) |
| C15 | C16 | 1.378(9) | S2A | C44 | 1.776(12) |
| C16 | C17 | 1.377(9) | O42 | S2B | 1.536(8) |
| C17 | C18 | 1.384(9) | C43 | D43A | 0.9800 |
| F21 | C32 | 1.374(8) | C43 | D43B | 0.9800 |
| F22 | C32 | 1.324(8) | C43 | D43C | 0.9800 |

| | | | | | |
|---|---|---|---|---|---|
| F23 | C32 | 1.328(7) | C44 | D44A | 0.9800 |
| O21 | C21 | 1.211(7) | C44 | D44B | 0.9800 |
| O22 | C31 | 1.204(7) | C44 | D44C | 0.9800 |
| O23 | C31 | 1.330(7) | S2B | C45 | 1.72(3) |
| O25 | C24A | 1.405(8) | S2B | C46 | 1.76(4) |
| O25 | C25A | 1.387(8) | C45 | D45A | 0.9800 |
| N22 | C21 | 1.388(8) | C45 | D45B | 0.9800 |
| N22 | C23 | 1.462(8) | C45 | D45C | 0.9800 |
| N22 | C33 | 1.408(8) | C46 | D46A | 0.9800 |
| C21 | C30A | 1.510(9) | C46 | D46B | 0.9800 |
| C23 | C23A | 1.523(9) | C46 | D46C | 0.9800 |
| C23A | C24 | 1.495(9) | | | |

**Table S24.** Bond Angles for **20a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C4A | O5 | C5A | 107.0(4) | C25A | C29A | C29B | 106.9(6) |
| C1 | N2 | C3 | 112.8(5) | C29 | C29A | C29B | 132.6(6) |
| C1 | N2 | C13 | 124.1(5) | C24A | C29B | C29A | 101.7(5) |
| C13 | N2 | C3 | 122.5(5) | C24A | C29B | C30 | 113.8(5) |
| O1 | C1 | N2 | 127.4(6) | C29A | C29B | C30 | 123.2(6) |
| O1 | C1 | C10A | 126.6(5) | C30A | C30 | C29B | 107.8(5) |
| N2 | C1 | C10A | 105.9(5) | C31 | C30 | C29B | 109.1(5) |
| N2 | C3 | C3A | 101.0(4) | C31 | C30 | C30A | 109.3(5) |
| C3 | C3A | C10A | 101.0(5) | C32 | C30 | C29B | 111.9(6) |
| C4 | C3A | C3 | 120.0(5) | C32 | C30 | C30A | 109.1(5) |
| C4 | C3A | C10A | 109.3(5) | C32 | C30 | C31 | 109.5(5) |
| C4A | C4 | C3A | 111.2(5) | C21 | C30A | C23A | 103.4(5) |
| O5 | C4A | C9B | 111.1(5) | C21 | C30A | C30 | 119.2(5) |
| C4 | C4A | O5 | 124.7(5) | C23A | C30A | C30 | 115.0(5) |
| C4 | C4A | C9B | 124.1(5) | O22 | C31 | O23 | 124.9(6) |
| C6 | C5A | O5 | 123.2(5) | O22 | C31 | C30 | 125.0(6) |
| C6 | C5A | C9A | 124.1(6) | O23 | C31 | C30 | 110.0(5) |
| C9A | C5A | O5 | 112.7(5) | F21 | C32 | C30 | 108.4(5) |
| C5A | C6 | C7 | 116.1(6) | F22 | C32 | F21 | 107.2(6) |
| C8 | C7 | C6 | 121.0(6) | F22 | C32 | F23 | 107.5(5) |
| C7 | C8 | C9 | 121.9(6) | F22 | C32 | C30 | 112.2(6) |
| C9A | C9 | C8 | 117.4(6) | F23 | C32 | F21 | 105.8(6) |
| C5A | C9A | C9B | 107.8(5) | F23 | C32 | C30 | 115.3(6) |
| C9 | C9A | C5A | 119.4(6) | C34 | C33 | N22 | 121.5(6) |
| C9 | C9A | C9B | 132.5(5) | C34 | C33 | C38 | 119.2(6) |
| C4A | C9B | C9A | 101.2(5) | C38 | C33 | N22 | 119.3(6) |
| C4A | C9B | C10 | 113.7(5) | C35 | C34 | C33 | 120.1(6) |
| C9A | C9B | C10 | 121.6(5) | C34 | C35 | C36 | 120.3(6) |
| C10A | C10 | C9B | 106.8(4) | C37 | C36 | C35 | 119.8(6) |
| C11 | C10 | C9B | 108.9(5) | C36 | C37 | C38 | 120.8(6) |
| C11 | C10 | C10A | 110.8(5) | C37 | C38 | C33 | 119.7(6) |
| C12 | C10 | C9B | 111.0(5) | O41 | S1 | C41 | 104.2(3) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C12 | C10 | C10A | 107.7(5) | O41 | S1 | C42 | 105.2(3) |
| C12 | C10 | C11 | 111.6(5) | C42 | S1 | C41 | 97.8(4) |
| C1 | C10A | C3A | 102.5(5) | S1 | C41 | D41A | 109.5 |
| C1 | C10A | C10 | 119.0(5) | S1 | C41 | D41B | 109.5 |
| C3A | C10A | C10 | 115.2(5) | S1 | C41 | D41C | 109.5 |
| O2 | C11 | O3 | 126.5(6) | D41A | C41 | D41B | 109.5 |
| O2 | C11 | C10 | 124.1(6) | D41A | C41 | D41C | 109.5 |
| O3 | C11 | C10 | 109.3(5) | D41B | C41 | D41C | 109.5 |
| F1 | C12 | F2 | 106.5(5) | S1 | C42 | D42A | 109.5 |
| F1 | C12 | C10 | 111.3(5) | S1 | C42 | D42B | 109.5 |
| F2 | C12 | C10 | 111.6(5) | S1 | C42 | D42C | 109.5 |
| F3 | C12 | F1 | 106.4(5) | D42A | C42 | D42B | 109.5 |
| F3 | C12 | F2 | 105.5(5) | D42A | C42 | D42C | 109.5 |
| F3 | C12 | C10 | 114.9(5) | D42B | C42 | D42C | 109.5 |
| C14 | C13 | N2 | 120.4(5) | O42 | S2A | C43 | 101.6(5) |
| C14 | C13 | C18 | 119.9(6) | O42 | S2A | C44 | 106.4(5) |
| C18 | C13 | N2 | 119.7(5) | C44 | S2A | C43 | 100.1(6) |
| C13 | C14 | C15 | 119.9(6) | S2A | C43 | D43A | 109.5 |
| C16 | C15 | C14 | 119.8(6) | S2A | C43 | D43B | 109.5 |
| C17 | C16 | C15 | 119.9(6) | S2A | C43 | D43C | 109.5 |
| C16 | C17 | C18 | 121.3(6) | D43A | C43 | D43B | 109.5 |
| C17 | C18 | C13 | 119.1(6) | D43A | C43 | D43C | 109.5 |
| C25A | O25 | C24A | 106.3(5) | D43B | C43 | D43C | 109.5 |
| C21 | N22 | C23 | 112.4(6) | S2A | C44 | D44A | 109.5 |
| C21 | N22 | C33 | 123.0(6) | S2A | C44 | D44B | 109.5 |
| C33 | N22 | C23 | 123.9(5) | S2A | C44 | D44C | 109.5 |
| O21 | C21 | N22 | 126.4(7) | D44A | C44 | D44B | 109.5 |
| O21 | C21 | C30A | 128.1(6) | D44A | C44 | D44C | 109.5 |
| N22 | C21 | C30A | 105.4(6) | D44B | C44 | D44C | 109.5 |
| N22 | C23 | C23A | 101.6(5) | O42 | S2B | C45 | 105.6(10) |
| C23 | C23A | C30A | 100.2(5) | O42 | S2B | C46 | 101.6(12) |
| C24 | C23A | C23 | 120.9(5) | C45 | S2B | C46 | 101.9(17) |
| C24 | C23A | C30A | 109.2(5) | S2B | C45 | D45A | 109.5 |
| C24A | C24 | C23A | 112.2(6) | S2B | C45 | D45B | 109.5 |
| O25 | C24A | C29B | 110.4(5) | S2B | C45 | D45C | 109.5 |
| C24 | C24A | O25 | 125.1(6) | D45A | C45 | D45B | 109.5 |
| C24 | C24A | C29B | 124.6(6) | D45A | C45 | D45C | 109.5 |
| C26 | C25A | O25 | 122.5(6) | D45B | C45 | D45C | 109.5 |
| C29A | C25A | O25 | 114.6(6) | S2B | C46 | D46A | 109.5 |
| C29A | C25A | C26 | 122.9(6) | S2B | C46 | D46B | 109.5 |
| C27 | C26 | C25A | 116.3(6) | S2B | C46 | D46C | 109.5 |
| C26 | C27 | C28 | 121.5(6) | D46A | C46 | D46B | 109.5 |
| C27 | C28 | C29 | 120.7(6) | D46A | C46 | D46C | 109.5 |
| C29A | C29 | C28 | 118.1(6) | D46B | C46 | D46C | 109.5 |
| C25A | C29A | C29 | 120.5(6) | | | | |

**Table S25.** Hydrogen Bonds for **20a**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O3 | H3 | O41 | 0.84 | 1.72 | 2.546(6) | 166.7 |
| O23 | H23 | O42 | 0.84 | 1.71 | 2.545(6) | 169.4 |

**Table S26.** Torsion Angles for **20a**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C10A | C3A | -160.9(6) | O21 | C21 | C30A | C23A | -160.1(7) |
| O1 | C1 | C10A | C10 | -32.5(9) | O21 | C21 | C30A | C30 | -31.0(10) |
| O5 | C4A | C9B | C9A | -4.7(6) | O25 | C24A | C29B | C29A | -3.4(7) |
| O5 | C4A | C9B | C10 | -136.7(5) | O25 | C24A | C29B | C30 | -138.0(6) |
| O5 | C5A | C6 | C7 | -179.7(5) | O25 | C25A | C26 | C27 | 177.5(6) |
| O5 | C5A | C9A | C9 | -178.2(5) | O25 | C25A | C29A | C29 | -178.6(6) |
| O5 | C5A | C9A | C9B | -3.8(7) | O25 | C25A | C29A | C29B | -1.3(8) |
| N2 | C1 | C10A | C3A | 22.9(6) | N22 | C21 | C30A | C23A | 23.4(6) |
| N2 | C1 | C10A | C10 | 151.4(5) | N22 | C21 | C30A | C30 | 152.5(5) |
| N2 | C3 | C3A | C4 | 158.7(5) | N22 | C23 | C23A | C24 | 158.5(6) |
| N2 | C3 | C3A | C10A | 38.5(6) | N22 | C23 | C23A | C30A | 38.7(6) |
| N2 | C13 | C14 | C15 | -178.5(5) | N22 | C33 | C34 | C35 | -179.3(6) |
| N2 | C13 | C18 | C17 | -179.7(5) | N22 | C33 | C38 | C37 | 179.0(6) |
| C1 | N2 | C3 | C3A | -26.5(6) | C21 | N22 | C23 | C23A | -26.7(7) |
| C1 | N2 | C13 | C14 | 39.1(9) | C21 | N22 | C33 | C34 | 41.0(9) |
| C1 | N2 | C13 | C18 | -140.7(6) | C21 | N22 | C33 | C38 | -139.9(6) |
| C3 | N2 | C1 | O1 | -173.9(6) | C23 | N22 | C21 | O21 | -174.6(6) |
| C3 | N2 | C1 | C10A | 2.3(6) | C23 | N22 | C21 | C30A | 2.0(7) |
| C3 | N2 | C13 | C14 | -150.1(6) | C23 | N22 | C33 | C34 | -149.8(6) |
| C3 | N2 | C13 | C18 | 30.2(8) | C23 | N22 | C33 | C38 | 29.3(9) |
| C3 | C3A | C4 | C4A | -163.7(6) | C23 | C23A | C24 | C24A | -163.8(6) |
| C3 | C3A | C10A | C1 | -37.9(6) | C23 | C23A | C30A | C21 | -38.4(6) |
| C3 | C3A | C10A | C10 | -168.8(5) | C23 | C23A | C30A | C30 | -170.1(5) |
| C3A | C4 | C4A | O5 | 178.4(5) | C23A | C24 | C24A | O25 | 179.0(6) |
| C3A | C4 | C4A | C9B | -5.1(8) | C23A | C24 | C24A | C29B | -2.1(9) |
| C4 | C3A | C10A | C1 | -165.4(5) | C24 | C23A | C30A | C21 | -166.3(5) |
| C4 | C3A | C10A | C10 | 63.7(7) | C24 | C23A | C30A | C30 | 62.0(7) |
| C4 | C4A | C9B | C9A | 178.5(6) | C24 | C24A | C29B | C29A | 177.6(6) |
| C4 | C4A | C9B | C10 | 46.5(8) | C24 | C24A | C29B | C30 | 43.0(9) |
| C4A | O5 | C5A | C6 | -179.8(6) | C24A | O25 | C25A | C26 | -179.7(6) |
| C4A | O5 | C5A | C9A | 0.7(7) | C24A | O25 | C25A | C29A | -0.9(8) |
| C4A | C9B | C10 | C10A | -27.1(7) | C24A | C29B | C30 | C30A | -26.0(7) |
| C4A | C9B | C10 | C11 | -146.8(5) | C24A | C29B | C30 | C31 | -144.7(5) |
| C4A | C9B | C10 | C12 | 89.9(6) | C24A | C29B | C30 | C32 | 94.0(6) |
| C5A | O5 | C4A | C4 | 179.6(6) | C25A | O25 | C24A | C24 | -178.2(6) |
| C5A | O5 | C4A | C9B | 2.7(6) | C25A | O25 | C24A | C29B | 2.8(7) |
| C5A | C6 | C7 | C8 | -1.3(9) | C25A | C26 | C27 | C28 | 2.0(11) |
| C5A | C9A | C9B | C4A | 4.9(6) | C25A | C29A | C29B | C24A | 2.7(7) |
| C5A | C9A | C9B | C10 | 131.9(6) | C25A | C29A | C29B | C30 | 131.5(6) |
| C6 | C5A | C9A | C9 | 2.3(10) | C26 | C25A | C29A | C29 | 0.2(11) |
| C6 | C5A | C9A | C9B | 176.7(6) | C26 | C25A | C29A | C29B | 177.5(6) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C6 | C7 | C8 | C9 | 0.8(10) | C26 | C27 | C28 | C29 | -1.8(12) |
| C7 | C8 | C9 | C9A | 1.3(10) | C27 | C28 | C29 | C29A | 0.8(11) |
| C8 | C9 | C9A | C5A | -2.7(9) | C28 | C29 | C29A | C25A | 0.0(10) |
| C8 | C9 | C9A | C9B | -175.5(6) | C28 | C29 | C29A | C29B | -176.5(7) |
| C9 | C9A | C9B | C4A | 178.3(7) | C29 | C29A | C29B | C24A | 179.5(7) |
| C9 | C9A | C9B | C10 | -54.7(10) | C29 | C29A | C29B | C30 | -51.6(11) |
| C9A | C5A | C6 | C7 | -0.2(10) | C29A | C25A | C26 | C27 | -1.2(11) |
| C9A | C9B | C10 | C10A | -148.3(5) | C29A | C29B | C30 | C30A | -149.6(6) |
| C9A | C9B | C10 | C11 | 92.0(7) | C29A | C29B | C30 | C31 | 91.8(7) |
| C9A | C9B | C10 | C12 | -31.3(7) | C29A | C29B | C30 | C32 | -29.6(8) |
| C9B | C10 | C10A | C1 | -144.8(5) | C29B | C30 | C30A | C21 | -145.1(6) |
| C9B | C10 | C10A | C3A | -22.4(7) | C29B | C30 | C30A | C23A | -21.5(7) |
| C9B | C10 | C11 | O2 | -112.0(6) | C29B | C30 | C31 | O22 | -115.6(7) |
| C9B | C10 | C11 | O3 | 65.7(6) | C29B | C30 | C31 | O23 | 62.2(6) |
| C9B | C10 | C12 | F1 | -52.0(6) | C29B | C30 | C32 | F21 | -51.8(7) |
| C9B | C10 | C12 | F2 | -170.8(5) | C29B | C30 | C32 | F22 | -170.0(5) |
| C9B | C10 | C12 | F3 | 69.1(6) | C29B | C30 | C32 | F23 | 66.5(8) |
| C10A | C3A | C4 | C4A | -47.8(7) | C30A | C23A | C24 | C24A | -48.6(7) |
| C10A | C10 | C11 | O2 | 130.9(6) | C30A | C30 | C31 | O22 | 126.8(6) |
| C10A | C10 | C11 | O3 | -51.4(6) | C30A | C30 | C31 | O23 | -55.4(6) |
| C10A | C10 | C12 | F1 | 64.5(6) | C30A | C30 | C32 | F21 | 67.4(7) |
| C10A | C10 | C12 | F2 | -54.3(6) | C30A | C30 | C32 | F22 | -50.8(7) |
| C10A | C10 | C12 | F3 | -174.4(5) | C30A | C30 | C32 | F23 | -174.3(5) |
| C11 | C10 | C10A | C1 | -26.3(7) | C31 | C30 | C30A | C21 | -26.6(8) |
| C11 | C10 | C10A | C3A | 96.0(6) | C31 | C30 | C30A | C23A | 97.0(6) |
| C11 | C10 | C12 | F1 | -173.7(5) | C31 | C30 | C32 | F21 | -173.0(5) |
| C11 | C10 | C12 | F2 | 67.5(6) | C31 | C30 | C32 | F22 | 68.8(7) |
| C11 | C10 | C12 | F3 | -52.6(7) | C31 | C30 | C32 | F23 | -54.7(8) |
| C12 | C10 | C10A | C1 | 96.0(6) | C32 | C30 | C30A | C21 | 93.1(7) |
| C12 | C10 | C10A | C3A | -141.7(5) | C32 | C30 | C30A | C23A | -143.2(6) |
| C12 | C10 | C11 | O2 | 10.9(8) | C32 | C30 | C31 | O22 | 7.2(9) |
| C12 | C10 | C11 | O3 | -171.4(5) | C32 | C30 | C31 | O23 | -175.0(5) |
| C13 | N2 | C1 | O1 | -2.2(9) | C33 | N22 | C21 | O21 | -4.2(11) |
| C13 | N2 | C1 | C10A | 173.9(5) | C33 | N22 | C21 | C30A | 172.3(6) |
| C13 | N2 | C3 | C3A | 161.7(5) | C33 | N22 | C23 | C23A | 163.0(6) |
| C13 | C14 | C15 | C16 | -1.3(10) | C33 | C34 | C35 | C36 | -0.7(10) |
| C14 | C13 | C18 | C17 | 0.5(9) | C34 | C33 | C38 | C37 | -1.9(10) |
| C14 | C15 | C16 | C17 | -0.3(10) | C34 | C35 | C36 | C37 | -0.1(10) |
| C15 | C16 | C17 | C18 | 2.1(10) | C35 | C36 | C37 | C38 | -0.1(10) |
| C16 | C17 | C18 | C13 | -2.2(10) | C36 | C37 | C38 | C33 | 1.1(10) |
| C18 | C13 | C14 | C15 | 1.2(10) | C38 | C33 | C34 | C35 | 1.6(10) |

**Table S27.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for **20a**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H3 | 7182.03 | 5777.04 | 5803.09 | 35 |
| H3A | 11471.82 | 6581.78 | 3789.5 | 27 |

| | | | | |
|---|---|---|---|---|
| H3B | 10525.12 | 6304.61 | 2970.53 | 27 |
| H3AA | 10164.02 | 5598.02 | 4528.24 | 29 |
| H4A | 11666.15 | 4730.11 | 3355.63 | 29 |
| H6A | 9865.49 | 1684.62 | 3770.12 | 33 |
| H7A | 7745.62 | 1002.47 | 4432.23 | 33 |
| H8A | 5877.99 | 1735.97 | 5147.45 | 33 |
| H9A | 5988.04 | 3176.57 | 5221.5 | 29 |
| H9BA | 8911.51 | 4326.37 | 4989.51 | 28 |
| H10A | 7959.45 | 5405.73 | 3175.15 | 26 |
| H14A | 7470.73 | 7944.22 | 4603.72 | 38 |
| H15A | 7509.31 | 9385.84 | 4518.31 | 32 |
| H16A | 9177.53 | 10027.55 | 3611.34 | 37 |
| H17A | 10821.66 | 9249.34 | 2807.25 | 38 |
| H18A | 10708.38 | 7821.45 | 2830.24 | 32 |
| H23 | 7425.64 | 4253.05 | -872.55 | 40 |
| H23A | 11563.58 | 3408.65 | 1383.98 | 33 |
| H23B | 10559.97 | 3693.31 | 2146.66 | 33 |
| H23C | 10336.18 | 4394.7 | 571.97 | 33 |
| H24A | 11747.44 | 5262.21 | 1819.78 | 33 |
| H26A | 10039.99 | 8314.7 | 1317.33 | 44 |
| H27A | 8070.97 | 9006.54 | 516.96 | 46 |
| H28A | 6126.01 | 8289.49 | -246.72 | 38 |
| H29A | 6189.07 | 6852.94 | -293.73 | 40 |
| H29B | 9083.48 | 5683.16 | 52.44 | 37 |
| H30A | 8048.94 | 4586.51 | 1809.3 | 30 |
| H34A | 7597.57 | 2049.07 | 358.16 | 41 |
| H35A | 7587.2 | 627.81 | 467.11 | 37 |
| H36A | 9117.33 | -18.51 | 1493.31 | 40 |
| H37A | 10643.77 | 759.51 | 2407.88 | 39 |
| H38A | 10691.24 | 2184.79 | 2308.33 | 36 |

**Table S28.** Atomic Occupancy for **20a**.

| **Atom** | ***Occupancy*** | **Atom** | ***Occupancy*** | **Atom** | ***Occupancy*** |
|---|---|---|---|---|---|
| S2A | 0.651(7) | C43 | 0.651(7) | D43A | 0.651(7) |
| D43B | 0.651(7) | D43C | 0.651(7) | C44 | 0.651(7) |
| D44A | 0.651(7) | D44B | 0.651(7) | D44C | 0.651(7) |
| S2B | 0.349(7) | C45 | 0.349(7) | D45A | 0.349(7) |
| D45B | 0.349(7) | D45C | 0.349(7) | C46 | 0.349(7) |
| D46A | 0.349(7) | D46B | 0.349(7) | D46C | 0.349(7) |

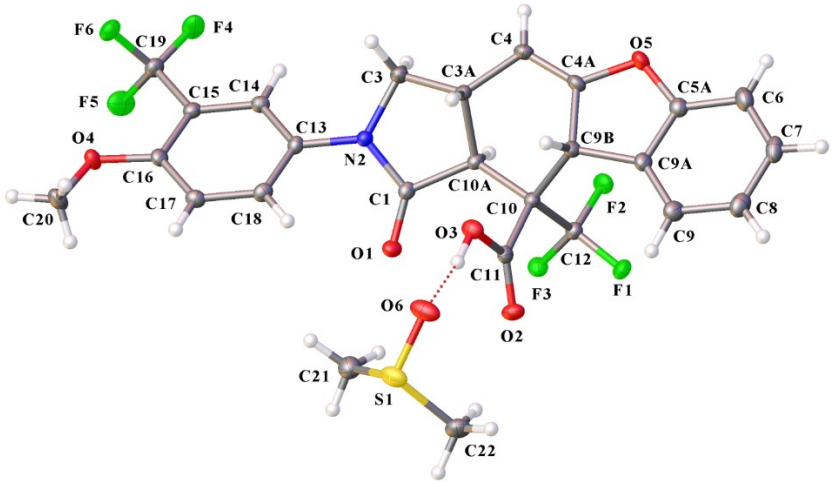



**Figure S6**. Molecular structure of **20d**. Dotted lines show H-bonding interactions.

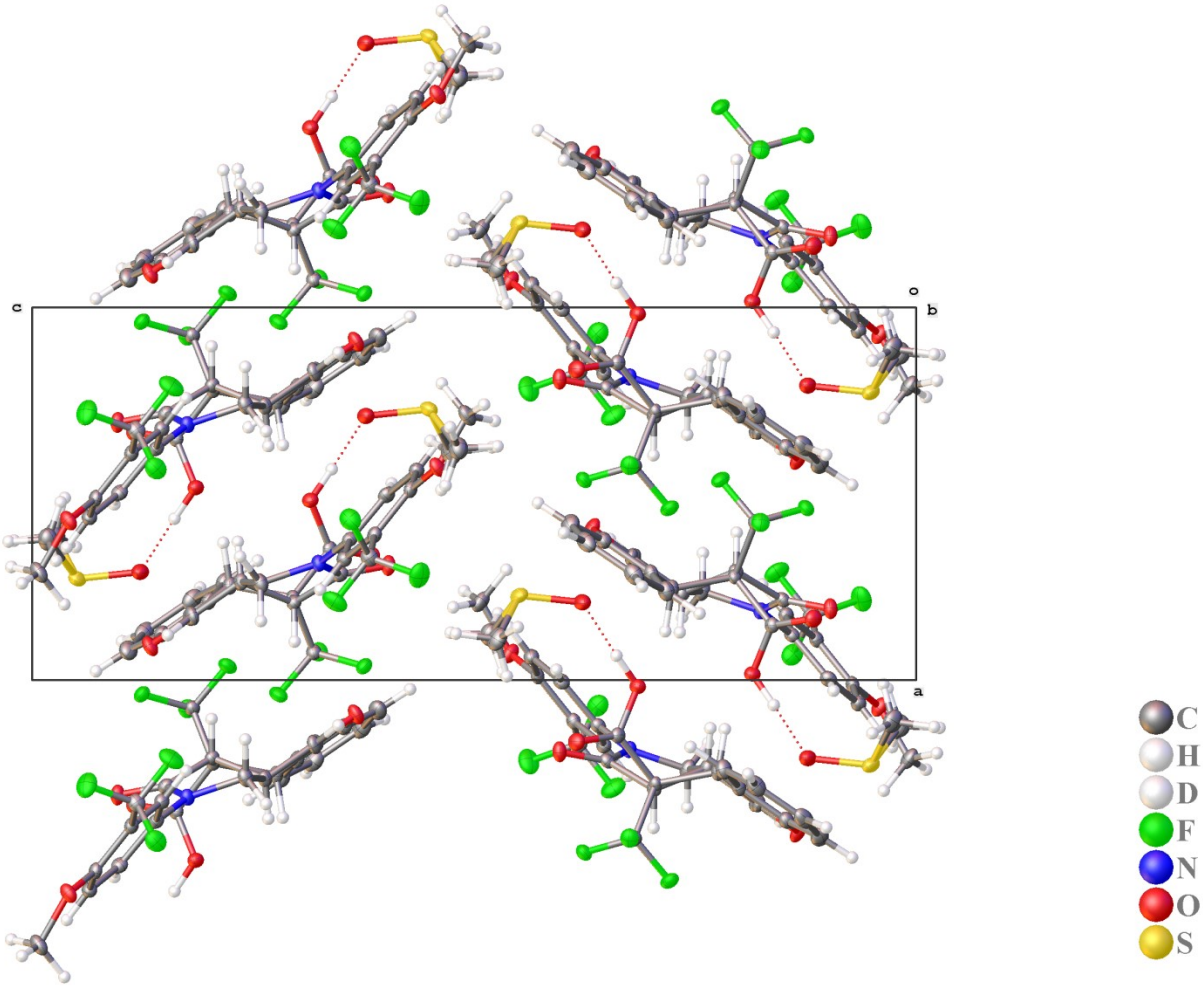



**Figure S7**. Crystal package of the structure **20d**.

**Table S29.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters

($Å^2×10^3$) for **20d**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor**.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| S1 | 7275.8(6) | 7662.3(5) | 4488.7(2) | 24.22(12) |
| F1 | 763.0(14) | 8462.7(8) | 3240.3(6) | 19.1(2) |
| F2 | -383.4(12) | 7244.7(9) | 2787.2(5) | 19.8(2) |
| F3 | 376.5(12) | 7101.7(9) | 3756.9(5) | 17.3(2) |
| F4 | 2109.2(15) | 734.6(9) | 3424.2(6) | 26.8(3) |
| F5 | 2817.6(16) | 427.0(10) | 4381.0(6) | 29.1(3) |
| F6 | 4315.0(14) | 130.6(9) | 3600.6(6) | 24.0(3) |
| O1 | 3080.2(16) | 5554.2(10) | 4032.0(6) | 18.2(3) |
| O2 | 3346.0(15) | 7875.3(11) | 3840.3(6) | 19.1(3) |
| O3 | 4831.9(15) | 7071.9(11) | 3148.1(7) | 18.4(3) |
| O4 | 5717.4(17) | 1212.4(10) | 4588.1(7) | 18.5(3) |
| O5 | 916.0(16) | 7239.9(11) | 1335.2(7) | 20.1(3) |
| O6 | 7092.2(16) | 7584.0(13) | 3775.9(7) | 27.0(3) |
| N2 | 3139.7(18) | 4358.8(12) | 3242.1(7) | 14.2(3) |
| C1 | 2836(2) | 5281.3(14) | 3490.7(8) | 13.7(3) |
| C3 | 2610(2) | 4251.8(15) | 2583.1(9) | 18.0(4) |
| C3A | 2645(2) | 5334.8(14) | 2363.7(9) | 14.5(3) |
| C4 | 1726(2) | 5676.3(15) | 1807.9(9) | 18.0(4) |
| C4A | 1681(2) | 6668.2(15) | 1779.6(9) | 16.1(4) |
| C5A | 1244(2) | 8231.2(15) | 1467.8(9) | 17.2(4) |
| C6 | 803(2) | 9017.9(17) | 1089.5(11) | 23.6(4) |
| C7 | 1291(2) | 9964.2(17) | 1270.7(11) | 24.0(4) |
| C8 | 2166(3) | 10108.1(16) | 1809.9(10) | 23.4(4) |
| C9 | 2610(2) | 9294.0(16) | 2175.6(10) | 20.5(4) |
| C9A | 2128(2) | 8350.8(14) | 2002.4(9) | 16.1(4) |
| C9B | 2540(2) | 7320.8(15) | 2238.9(8) | 15.3(3) |
| C10A | 2079(2) | 5867.9(13) | 2963.8(8) | 12.8(3) |
| C10 | 2225(2) | 7023.5(13) | 2946.5(8) | 12.4(3) |
| C11 | 3522(2) | 7383.1(14) | 3370.8(8) | 13.8(3) |
| C12 | 753(2) | 7470.6(14) | 3187.0(9) | 14.8(3) |
| C13 | 3783(2) | 3565.2(14) | 3595.9(9) | 13.8(3) |
| C14 | 3248(2) | 2596.3(14) | 3530.8(9) | 14.8(3) |
| C15 | 3903(2) | 1820.4(14) | 3874.1(9) | 14.5(3) |
| C16 | 5118(2) | 2013.2(14) | 4281.9(9) | 14.8(4) |
| C17 | 5627(2) | 2985.7(15) | 4350.8(9) | 16.0(4) |
| C18 | 4967(2) | 3754.4(15) | 4010.5(9) | 15.7(4) |
| C19 | 3293(2) | 782.1(15) | 3817.7(10) | 18.1(4) |
| C20 | 7107(3) | 1369.9(17) | 4922.2(10) | 22.6(4) |
| C21 | 6221(3) | 6657.8(19) | 4821.1(12) | 27.1(5) |
| D21A | 6790(40) | 6040(20) | 4729(13) | 37(8) |
| D21B | 6280(30) | 6730(20) | 5265(14) | 32(7) |
| D21C | 5220(40) | 6700(20) | 4678(13) | 32(7) |
| C22 | 6105(3) | 8668.6(18) | 4737.3(12) | 27.0(5) |
| D22A | 6420(40) | 9250(30) | 4505(17) | 52(9) |
| D22B | 5110(40) | 8520(20) | 4630(13) | 34(8) |

| | | | | |
|---|---|---|---|---|
| D22C | 6250(30) | 8750(20) | 5204(14) | 34(7) |

**Table S30.** Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for **20d**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | **$U_{11}$** | **$U_{22}$** | **$U_{33}$** | **$U_{23}$** | **$U_{13}$** | **$U_{12}$** |
|---|---|---|---|---|---|---|
| S1 | 14.3(2) | 38.7(3) | 19.7(2) | -4.8(2) | -3.09(18) | -0.4(2) |
| F1 | 22.2(6) | 14.1(6) | 20.9(6) | -1.6(4) | 0.4(4) | 4.5(4) |
| F2 | 15.0(5) | 23.6(6) | 20.9(6) | -2.5(5) | -4.9(4) | 3.8(5) |
| F3 | 16.2(5) | 20.1(6) | 15.6(5) | 0.7(4) | 3.8(4) | 1.4(4) |
| F4 | 25.9(6) | 17.5(6) | 37.1(7) | -3.6(5) | -12.1(5) | -4.1(5) |
| F5 | 39.2(7) | 21.8(6) | 26.4(6) | 4.3(5) | 5.5(6) | -12.5(6) |
| F6 | 28.9(6) | 14.8(6) | 28.2(7) | -4.2(5) | -3.4(5) | 3.0(5) |
| O1 | 26.2(7) | 16.2(7) | 12.2(6) | -0.2(5) | 0.7(5) | 1.1(6) |
| O2 | 19.2(6) | 20.3(7) | 17.7(7) | -6.5(6) | -0.5(5) | -0.4(5) |
| O3 | 13.8(6) | 25.0(8) | 16.5(7) | -2.1(6) | 0.5(5) | 1.1(5) |
| O4 | 22.6(7) | 15.7(7) | 17.2(7) | 3.8(5) | -6.6(5) | -1.2(5) |
| O5 | 24.3(7) | 20.2(7) | 15.9(6) | 1.0(6) | -7.9(5) | 2.8(6) |
| O6 | 15.8(7) | 46.7(10) | 18.4(7) | -5.6(7) | 0.2(5) | -2.1(6) |
| N2 | 17.3(7) | 12.4(8) | 12.7(7) | -0.6(6) | -1.1(6) | 1.4(6) |
| C1 | 14.2(8) | 12.5(8) | 14.4(8) | 1.2(6) | 2.8(7) | -0.3(7) |
| C3 | 23.5(10) | 14.8(9) | 15.8(8) | -2.0(7) | -4.0(7) | 1.5(8) |
| C3A | 17.8(9) | 12.8(8) | 12.8(8) | -1.8(6) | -0.8(7) | 1.7(7) |
| C4 | 22.6(9) | 18.3(10) | 13.1(8) | -3.3(7) | -3.9(7) | 0.7(8) |
| C4A | 17.7(8) | 19.9(10) | 10.7(8) | 0.0(7) | -2.8(7) | 0.5(7) |
| C5A | 17.8(8) | 18.2(10) | 15.6(9) | 1.0(7) | 1.7(7) | 1.4(7) |
| C6 | 23.6(10) | 26.5(11) | 20.8(10) | 4.3(8) | -1.6(8) | 7.0(8) |
| C7 | 25.8(10) | 22.0(11) | 24.0(10) | 9.0(9) | 6.7(8) | 7.8(8) |
| C8 | 28.0(10) | 17.3(10) | 24.9(10) | 3.5(8) | 7.4(9) | 1.3(9) |
| C9 | 25.1(10) | 18.8(10) | 17.8(9) | 1.5(7) | 2.3(8) | -1.1(8) |
| C9A | 19.4(9) | 15.4(9) | 13.5(8) | 1.8(7) | 2.0(7) | 1.0(7) |
| C9B | 19.7(9) | 14.3(8) | 12.0(8) | 0.1(7) | 0.0(6) | 1.2(7) |
| C10A | 13.5(8) | 11.7(8) | 13.3(8) | -0.9(6) | 1.3(6) | 0.3(6) |
| C10 | 13.7(7) | 12.1(8) | 11.5(7) | -0.3(6) | 0.9(6) | 1.1(7) |
| C11 | 15.4(8) | 12.5(9) | 13.4(8) | 2.3(7) | 0.2(6) | -0.2(6) |
| C12 | 15.5(8) | 14.6(9) | 14.5(8) | -0.5(7) | 0.0(6) | 2.2(7) |
| C13 | 13.9(8) | 12.6(9) | 14.9(8) | 1.1(7) | 1.7(6) | 1.5(6) |
| C14 | 14.8(8) | 15.4(9) | 14.3(8) | -1.4(7) | -0.1(7) | -0.8(7) |
| C15 | 17.0(8) | 13.5(9) | 13.1(8) | -1.5(7) | 1.5(7) | -0.3(6) |
| C16 | 17.8(8) | 15.1(9) | 11.6(8) | 1.8(7) | 1.5(6) | 0.3(7) |
| C17 | 15.1(8) | 18.0(9) | 14.9(9) | -0.4(7) | 0.0(7) | -2.0(7) |
| C18 | 16.0(9) | 13.6(9) | 17.6(9) | -0.1(7) | 2.3(7) | -2.7(7) |
| C19 | 21.0(9) | 13.4(9) | 19.9(9) | -0.4(7) | -1.8(8) | -1.5(7) |
| C20 | 26.2(10) | 22.3(11) | 19.2(10) | 3.7(8) | -9.5(8) | -2.6(9) |
| C21 | 31.5(12) | 26.3(12) | 23.5(11) | -1.3(9) | -0.7(9) | 5.0(9) |
| C22 | 33.1(12) | 23.5(12) | 24.5(11) | -6.9(9) | -5.6(9) | -2.4(9) |

**Table S31.** Bond Lengths for **20d**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S1 | O6 | 1.5192(15) | C5A | C6 | 1.381(3) |
| S1 | C21 | 1.786(3) | C5A | C9A | 1.386(3) |
| S1 | C22 | 1.784(3) | C6 | C7 | 1.395(3) |
| F1 | C12 | 1.335(2) | C7 | C8 | 1.394(3) |
| F2 | C12 | 1.353(2) | C8 | C9 | 1.395(3) |
| F3 | C12 | 1.345(2) | C9 | C9A | 1.385(3) |
| F4 | C19 | 1.344(2) | C9A | C9B | 1.514(3) |
| F5 | C19 | 1.350(2) | C9B | C10 | 1.573(2) |
| F6 | C19 | 1.342(2) | C10A | C10 | 1.555(3) |
| O1 | C1 | 1.221(2) | C10 | C11 | 1.540(3) |
| O2 | C11 | 1.202(2) | C10 | C12 | 1.527(3) |
| O3 | C11 | 1.325(2) | C13 | C14 | 1.391(3) |
| O4 | C16 | 1.363(2) | C13 | C18 | 1.394(3) |
| O4 | C20 | 1.440(2) | C14 | C15 | 1.396(3) |
| O5 | C4A | 1.390(2) | C15 | C16 | 1.407(3) |
| O5 | C5A | 1.389(3) | C15 | C19 | 1.499(3) |
| N2 | C1 | 1.371(2) | C16 | C17 | 1.388(3) |
| N2 | C3 | 1.478(2) | C17 | C18 | 1.387(3) |
| N2 | C13 | 1.421(2) | C21 | D21A | 0.99(3) |
| C1 | C10A | 1.521(3) | C21 | D21B | 0.95(3) |
| C3 | C3A | 1.525(3) | C21 | D21C | 0.94(3) |
| C3A | C4 | 1.503(3) | C22 | D22A | 0.96(4) |
| C3A | C10A | 1.541(2) | C22 | D22B | 0.94(3) |
| C4 | C4A | 1.332(3) | C22 | D22C | 1.00(3) |
| C4A | C9B | 1.514(3) | | | |

**Table S32.** Bond Angles for **20d**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| O6 | S1 | C21 | 106.34(10) | C12 | C10 | C11 | 109.05(14) |
| O6 | S1 | C22 | 106.35(11) | O2 | C11 | O3 | 125.53(17) |
| C22 | S1 | C21 | 98.49(12) | O2 | C11 | C10 | 123.70(16) |
| C16 | O4 | C20 | 117.00(16) | O3 | C11 | C10 | 110.77(15) |
| C5A | O5 | C4A | 106.76(14) | F1 | C12 | F2 | 106.30(15) |
| C1 | N2 | C3 | 112.70(15) | F1 | C12 | F3 | 107.01(15) |
| C1 | N2 | C13 | 123.61(16) | F1 | C12 | C10 | 114.44(16) |
| C13 | N2 | C3 | 123.50(15) | F2 | C12 | C10 | 110.22(15) |
| O1 | C1 | N2 | 126.49(17) | F3 | C12 | F2 | 106.89(15) |
| O1 | C1 | C10A | 127.59(17) | F3 | C12 | C10 | 111.57(15) |
| N2 | C1 | C10A | 105.86(15) | C14 | C13 | N2 | 120.64(17) |
| N2 | C3 | C3A | 100.82(15) | C14 | C13 | C18 | 119.42(17) |
| C3 | C3A | C10A | 100.64(15) | C18 | C13 | N2 | 119.94(17) |
| C4 | C3A | C3 | 121.10(17) | C13 | C14 | C15 | 120.11(17) |
| C4 | C3A | C10A | 108.90(15) | C14 | C15 | C16 | 120.17(17) |
| C4A | C4 | C3A | 110.83(17) | C14 | C15 | C19 | 119.96(17) |
| O5 | C4A | C9B | 111.20(16) | C16 | C15 | C19 | 119.85(17) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C4 | C4A | O5 | 126.55(18) | O4 | C16 | C15 | 116.57(17) |
| C4 | C4A | C9B | 122.22(17) | O4 | C16 | C17 | 124.23(17) |
| C6 | C5A | O5 | 123.68(18) | C17 | C16 | C15 | 119.20(17) |
| C6 | C5A | C9A | 123.0(2) | C18 | C17 | C16 | 120.35(18) |
| C9A | C5A | O5 | 113.22(17) | C17 | C18 | C13 | 120.73(18) |
| C5A | C6 | C7 | 116.6(2) | F4 | C19 | F5 | 106.48(16) |
| C8 | C7 | C6 | 121.6(2) | F4 | C19 | C15 | 112.16(16) |
| C7 | C8 | C9 | 120.2(2) | F5 | C19 | C15 | 111.77(16) |
| C9A | C9 | C8 | 118.7(2) | F6 | C19 | F4 | 106.80(16) |
| C5A | C9A | C9B | 107.53(17) | F6 | C19 | F5 | 106.52(16) |
| C9 | C9A | C5A | 119.81(18) | F6 | C19 | C15 | 112.69(16) |
| C9 | C9A | C9B | 132.12(18) | S1 | C21 | D21A | 106.5(18) |
| C4A | C9B | C10 | 111.91(16) | S1 | C21 | D21B | 106.3(18) |
| C9A | C9B | C4A | 101.14(15) | S1 | C21 | D21C | 109.0(18) |
| C9A | C9B | C10 | 120.14(15) | D21A | C21 | D21B | 105(2) |
| C1 | C10A | C3A | 102.58(14) | D21A | C21 | D21C | 118(2) |
| C1 | C10A | C10 | 119.70(15) | D21B | C21 | D21C | 111(3) |
| C3A | C10A | C10 | 114.55(15) | S1 | C22 | D22A | 107(2) |
| C10A | C10 | C9B | 106.85(14) | S1 | C22 | D22B | 108.6(18) |
| C11 | C10 | C9B | 109.92(15) | S1 | C22 | D22C | 107.0(17) |
| C11 | C10 | C10A | 111.15(15) | D22A | C22 | D22B | 109(3) |
| C12 | C10 | C9B | 111.70(15) | D22A | C22 | D22C | 112(3) |
| C12 | C10 | C10A | 108.16(15) | D22B | C22 | D22C | 113(2) |

**Table S33.** Hydrogen Bonds for **20d**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O3 | H3A | O6 | 0.96(4) | 1.55(4) | 2.506(2) | 173(4) |

**Table S34.** Torsion Angles for **20d**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C10A | C3A | 158.51(19) | C6 | C7 | C8 | C9 | 1.7(3) |
| O1 | C1 | C10A | C10 | 30.4(3) | C7 | C8 | C9 | C9A | -1.9(3) |
| O4 | C16 | C17 | C18 | 178.75(18) | C8 | C9 | C9A | C5A | 1.2(3) |
| O5 | C4A | C9B | C9A | 1.2(2) | C8 | C9 | C9A | C9B | 171.6(2) |
| O5 | C4A | C9B | C10 | 130.33(16) | C9 | C9A | C9B | C4A | -174.4(2) |
| O5 | C5A | C6 | C7 | -176.66(19) | C9 | C9A | C9B | C10 | 62.0(3) |
| O5 | C5A | C9A | C9 | 176.71(18) | C9A | C5A | C6 | C7 | -0.1(3) |
| O5 | C5A | C9A | C9B | 4.2(2) | C9A | C9B | C10 | C10A | 155.12(16) |
| N2 | C1 | C10A | C3A | -23.92(18) | C9A | C9B | C10 | C11 | -84.2(2) |
| N2 | C1 | C10A | C10 | -152.04(16) | C9A | C9B | C10 | C12 | 37.0(2) |
| N2 | C3 | C3A | C4 | -158.79(16) | C9B | C10 | C11 | O2 | 127.85(19) |
| N2 | C3 | C3A | C10A | -38.91(17) | C9B | C10 | C11 | O3 | -52.5(2) |
| N2 | C13 | C14 | C15 | 179.07(17) | C9B | C10 | C12 | F1 | -67.3(2) |
| N2 | C13 | C18 | C17 | -178.79(17) | C9B | C10 | C12 | F2 | 52.4(2) |
| C1 | N2 | C3 | C3A | 26.5(2) | C9B | C10 | C12 | F3 | 171.02(14) |
| C1 | N2 | C13 | C14 | 137.86(19) | C10A | C3A | C4 | C4A | 51.4(2) |
| C1 | N2 | C13 | C18 | -42.5(3) | C10A | C10 | C11 | O2 | -114.1(2) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C1 | C10A | C10 | C9B | 136.66(16) | C10A | C10 | C11 | O3 | 65.62(19) |
| C1 | C10A | C10 | C11 | 16.7(2) | C10A | C10 | C12 | F1 | 175.39(15) |
| C1 | C10A | C10 | C12 | -102.95(18) | C10A | C10 | C12 | F2 | -64.88(18) |
| C3 | N2 | C1 | O1 | 176.06(19) | C10A | C10 | C12 | F3 | 53.71(19) |
| C3 | N2 | C1 | C10A | -1.5(2) | C11 | C10 | C12 | F1 | 54.4(2) |
| C3 | N2 | C13 | C14 | -36.8(3) | C11 | C10 | C12 | F2 | 174.13(15) |
| C3 | N2 | C13 | C18 | 142.88(19) | C11 | C10 | C12 | F3 | -67.29(19) |
| C3 | C3A | C4 | C4A | 167.19(18) | C12 | C10 | C11 | O2 | 5.1(2) |
| C3 | C3A | C10A | C1 | 38.92(17) | C12 | C10 | C11 | O3 | -175.23(16) |
| C3 | C3A | C10A | C10 | 170.22(15) | C13 | N2 | C1 | O1 | 0.9(3) |
| C3A | C4 | C4A | O5 | -178.86(17) | C13 | N2 | C1 | C10A | -176.70(16) |
| C3A | C4 | C4A | C9B | 3.2(3) | C13 | N2 | C3 | C3A | -158.37(17) |
| C3A | C10A | C10 | C9B | 14.2(2) | C13 | C14 | C15 | C16 | -0.7(3) |
| C3A | C10A | C10 | C11 | -105.69(17) | C13 | C14 | C15 | C19 | 178.13(18) |
| C3A | C10A | C10 | C12 | 134.63(16) | C14 | C13 | C18 | C17 | 0.9(3) |
| C4 | C3A | C10A | C1 | 167.23(16) | C14 | C15 | C16 | O4 | -178.46(17) |
| C4 | C3A | C10A | C10 | -61.5(2) | C14 | C15 | C16 | C17 | 1.7(3) |
| C4 | C4A | C9B | C9A | 179.47(18) | C14 | C15 | C19 | F4 | -0.7(3) |
| C4 | C4A | C9B | C10 | -51.4(2) | C14 | C15 | C19 | F5 | -120.22(19) |
| C4A | O5 | C5A | C6 | 173.51(19) | C14 | C15 | C19 | F6 | 119.85(19) |
| C4A | O5 | C5A | C9A | -3.3(2) | C15 | C16 | C17 | C18 | -1.4(3) |
| C4A | C9B | C10 | C10A | 36.8(2) | C16 | C15 | C19 | F4 | 178.12(16) |
| C4A | C9B | C10 | C11 | 157.52(15) | C16 | C15 | C19 | F5 | 58.6(2) |
| C4A | C9B | C10 | C12 | -81.29(19) | C16 | C15 | C19 | F6 | -61.3(2) |
| C5A | O5 | C4A | C4 | -177.1(2) | C16 | C17 | C18 | C13 | 0.2(3) |
| C5A | O5 | C4A | C9B | 1.1(2) | C18 | C13 | C14 | C15 | -0.6(3) |
| C5A | C6 | C7 | C8 | -0.7(3) | C19 | C15 | C16 | O4 | 2.7(3) |
| C5A | C9A | C9B | C4A | -3.1(2) | C19 | C15 | C16 | C17 | -177.12(18) |
| C5A | C9A | C9B | C10 | -126.74(18) | C20 | O4 | C16 | C15 | 169.95(17) |
| C6 | C5A | C9A | C9 | -0.2(3) | C20 | O4 | C16 | C17 | -10.2(3) |
| C6 | C5A | C9A | C9B | -172.71(19) | | | | | |

**Table S35.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for **20d**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H3A | 5660(50) | 7320(30) | 3389(17) | 69(11) |
| H3B | 1590(30) | 3993(18) | 2588(11) | 18(6) |
| H3C | 3320(30) | 3790(20) | 2353(12) | 30(7) |
| H3AA | 3710(30) | 5509(18) | 2327(11) | 15(6) |
| H4A | 1210(30) | 5240(20) | 1536(12) | 25(7) |
| H6A | 240(30) | 8910(20) | 724(14) | 33(8) |
| H7A | 1050(30) | 10570(20) | 1017(12) | 24(6) |
| H8A | 2490(30) | 10760(20) | 1901(12) | 28(7) |
| H9A | 3210(30) | 9420(20) | 2551(14) | 37(8) |
| H9BA | 3690(30) | 7210(20) | 2163(13) | 29(7) |
| H10A | 1040(20) | 5724(16) | 2970(10) | 8(5) |
| H14A | 2430(30) | 2414(19) | 3259(12) | 27(7) |

| | | | | |
|---|---|---|---|---|
| H17A | 6430(30) | 3138(18) | 4608(11) | 14(6) |
| H18A | 5280(30) | 4408(18) | 4068(10) | 11(5) |
| H20A | 7400(30) | 760(20) | 5113(12) | 27(7) |
| H20B | 7960(30) | 1600(20) | 4635(13) | 32(7) |
| H20C | 6960(30) | 1820(20) | 5235(12) | 22(6) |

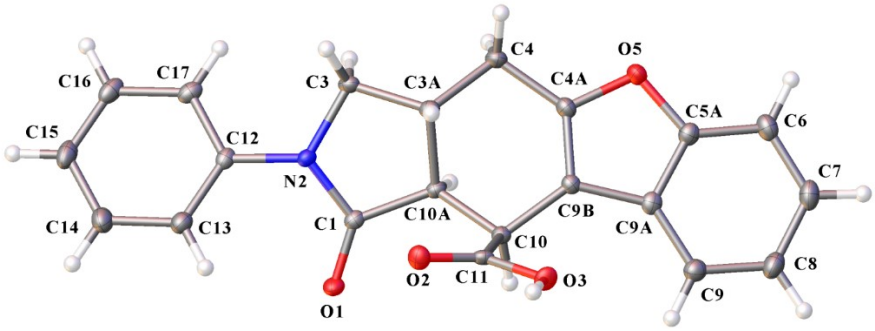



**Figure S8**. Molecular structure of **23a**.

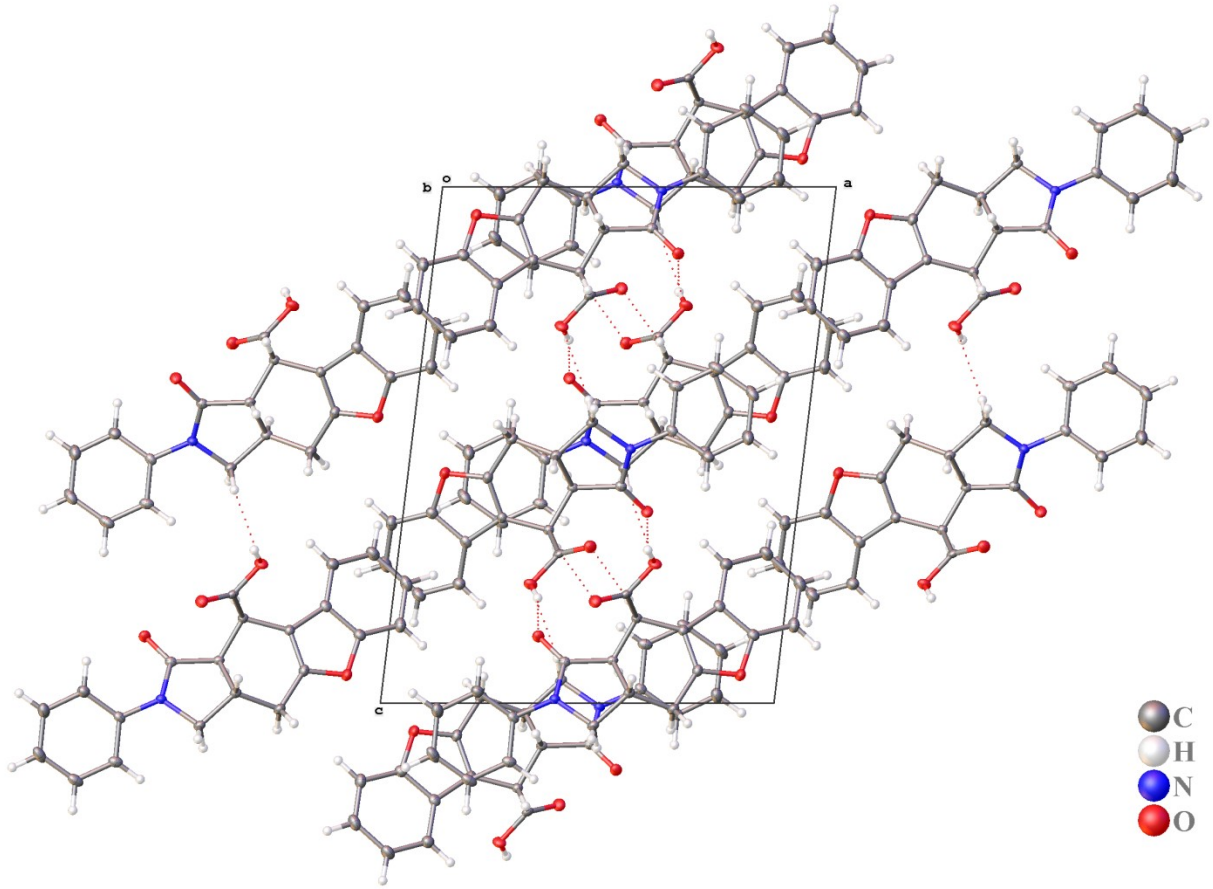



**Figure S9.** Crystal structure of **23a**. Dotted lines show H-bonding interactions.

**Table S36.** Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **23a**. $U_{eq}$ is defined as 1/3 of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| O1 | 3809.5(7) | 3768.8(11) | 3706.6(6) | 15.9(2) |
| O2 | 5149.0(8) | 856.2(12) | 3029.3(6) | 17.7(2) |

| | | | | |
|---|---|---|---|---|
| O3 | 6549.2(8) | 1372.4(12) | 2302.0(6) | 16.5(2) |
| O5 | 9060.3(7) | 3568.8(12) | 4453.7(6) | 16.8(2) |
| N2 | 4422.9(9) | 2412.5(13) | 4925.2(6) | 11.9(2) |
| C1 | 4553.7(10) | 3201.5(15) | 4199.4(8) | 11.8(2) |
| C3 | 5476.2(10) | 2079.2(16) | 5434.7(8) | 13.5(2) |
| C3A | 6292.2(10) | 2157.7(15) | 4804.8(8) | 12.2(2) |
| C4 | 7458.5(11) | 2680.9(17) | 5116.0(8) | 15.7(3) |
| C4A | 7960.2(10) | 3206.9(16) | 4370.4(8) | 14.2(3) |
| C5A | 9267.7(11) | 4108.3(16) | 3681.1(8) | 15.4(3) |
| C6 | 10265.1(11) | 4688.9(17) | 3489.6(9) | 19.4(3) |
| C7 | 10289.6(12) | 5244.8(18) | 2685.1(9) | 22.0(3) |
| C8 | 9354.0(12) | 5205.2(18) | 2107.2(9) | 21.5(3) |
| C9 | 8364.9(11) | 4606.6(17) | 2311.7(9) | 17.7(3) |
| C9A | 8321.2(11) | 4053.2(15) | 3120.7(8) | 13.9(3) |
| C9B | 7473.8(10) | 3462.3(15) | 3588.9(8) | 11.9(2) |
| C10 | 6255.5(10) | 3304.8(15) | 3356.1(8) | 11.7(2) |
| C10A | 5765.3(10) | 3413.3(15) | 4171.0(7) | 11.1(2) |
| C11 | 5918.5(10) | 1706.7(15) | 2891.4(8) | 12.6(2) |
| C12 | 3420.6(10) | 2243.8(15) | 5274.9(8) | 12.8(2) |
| C13 | 2428.0(11) | 2082.2(16) | 4776.3(8) | 17.2(3) |
| C14 | 1473.7(12) | 1900.1(18) | 5147.1(9) | 22.4(3) |
| C15 | 1501.4(12) | 1867.8(18) | 6001.7(9) | 22.7(3) |
| C16 | 2489.7(12) | 2018.1(17) | 6492.9(9) | 19.7(3) |
| C17 | 3451.6(12) | 2211.0(15) | 6136.7(8) | 16.0(3) |

**Table S37.** Anisotropic Displacement Parameters ($Å^2×10^3$) for **23a**. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

| **Atom** | $\mathbf{U_{11}}$ | $\mathbf{U_{22}}$ | $\mathbf{U_{33}}$ | $\mathbf{U_{23}}$ | $\mathbf{U_{13}}$ | $\mathbf{U_{12}}$ |
|---|---|---|---|---|---|---|
| O1 | 15.2(5) | 17.7(5) | 14.9(5) | 5.3(4) | 1.6(4) | 2.4(3) |
| O2 | 17.3(5) | 18.5(5) | 17.1(5) | -3.8(4) | 1.8(4) | -3.9(4) |
| O3 | 20.5(5) | 16.9(5) | 12.5(4) | -4.8(4) | 3.9(4) | -1.8(4) |
| O5 | 12.5(5) | 22.4(5) | 15.0(5) | 0.1(4) | 0.1(4) | -2.5(4) |
| N2 | 13.1(5) | 12.4(5) | 10.1(5) | 1.0(4) | 1.7(4) | 0.5(4) |
| C1 | 15.2(6) | 8.7(5) | 11.5(6) | -0.5(4) | 2.1(5) | 0.2(4) |
| C3 | 14.6(6) | 14.0(6) | 11.2(6) | 1.1(4) | -1.1(5) | -1.0(5) |
| C3A | 14.3(6) | 10.9(5) | 11.2(6) | 0.9(4) | -0.1(5) | -0.3(4) |
| C4 | 14.5(6) | 19.3(6) | 12.5(6) | 1.4(5) | -1.4(5) | -0.6(5) |
| C4A | 12.0(6) | 14.3(6) | 15.9(6) | -1.0(5) | 0.4(5) | -0.7(4) |
| C5A | 16.8(7) | 14.6(6) | 15.2(6) | -1.3(5) | 3.7(5) | -0.3(5) |
| C6 | 14.6(7) | 19.1(6) | 24.4(7) | -2.0(5) | 2.5(5) | -1.9(5) |
| C7 | 18.7(7) | 21.0(7) | 27.8(8) | -0.9(6) | 9.8(6) | -1.9(5) |
| C8 | 22.1(7) | 22.5(7) | 21.5(7) | 3.7(5) | 8.7(6) | 0.5(5) |
| C9 | 18.0(7) | 18.9(6) | 16.5(6) | 0.3(5) | 2.7(5) | 1.7(5) |
| C9A | 15.8(6) | 10.8(5) | 15.7(6) | -2.3(5) | 4.3(5) | 0.8(4) |
| C9B | 11.9(6) | 11.4(5) | 12.5(6) | -1.4(4) | 1.5(5) | 0.4(4) |
| C10 | 12.6(6) | 11.8(5) | 10.7(6) | -0.3(4) | 0.7(5) | 0.7(4) |
| C10A | 14.0(6) | 9.6(5) | 9.4(5) | 0.0(4) | 0.7(5) | -0.1(4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C11 | 14.3(6) | 14.0(6) | 8.7(5) | 0.2(4) | -2.0(5) | 1.8(5) |
| C12 | 15.8(6) | 9.1(5) | 14.4(6) | 0.5(4) | 5.1(5) | 1.4(4) |
| C13 | 18.1(7) | 18.1(6) | 15.8(6) | 2.1(5) | 3.7(5) | 1.1(5) |
| C14 | 16.1(7) | 26.6(7) | 25.1(8) | 5.1(6) | 5.1(6) | 2.7(5) |
| C15 | 22.2(7) | 21.9(7) | 26.6(8) | 6.4(6) | 13.2(6) | 5.1(5) |
| C16 | 28.1(8) | 15.6(6) | 17.3(7) | 2.1(5) | 10.3(6) | 4.8(5) |
| C17 | 23.4(7) | 11.9(6) | 13.1(6) | 0.3(5) | 3.6(5) | 1.3(5) |

**Table S38.** Bond Lengths for **23a**.

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| O1 | C1 | 1.2329(15) | C5A | C9A | 1.3950(19) |
| O2 | C11 | 1.2128(15) | C6 | C7 | 1.389(2) |
| O3 | C11 | 1.3342(15) | C7 | C8 | 1.401(2) |
| O5 | C4A | 1.3797(15) | C8 | C9 | 1.3897(19) |
| O5 | C5A | 1.3841(16) | C9 | C9A | 1.3984(18) |
| N2 | C1 | 1.3684(16) | C9A | C9B | 1.4468(17) |
| N2 | C3 | 1.4811(16) | C9B | C10 | 1.5119(18) |
| N2 | C12 | 1.4295(16) | C10 | C10A | 1.5265(17) |
| C1 | C10A | 1.5118(17) | C10 | C11 | 1.5226(17) |
| C3 | C3A | 1.5233(18) | C12 | C13 | 1.3930(19) |
| C3A | C4 | 1.5272(18) | C12 | C17 | 1.4005(17) |
| C3A | C10A | 1.5316(17) | C13 | C14 | 1.3949(19) |
| C4 | C4A | 1.4895(18) | C14 | C15 | 1.389(2) |
| C4A | C9B | 1.3571(18) | C15 | C16 | 1.382(2) |
| C5A | C6 | 1.3870(18) | C16 | C17 | 1.3916(19) |

**Table S39.** Bond Angles for **23a**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C4A | O5 | C5A | 105.30(10) | C5A | C9A | C9B | 105.50(11) |
| C1 | N2 | C3 | 112.42(10) | C9 | C9A | C9B | 135.51(13) |
| C1 | N2 | C12 | 125.87(11) | C4A | C9B | C9A | 106.13(11) |
| C12 | N2 | C3 | 120.23(10) | C4A | C9B | C10 | 122.54(11) |
| O1 | C1 | N2 | 125.32(12) | C9A | C9B | C10 | 130.98(11) |
| O1 | C1 | C10A | 126.98(11) | C9B | C10 | C10A | 105.27(10) |
| N2 | C1 | C10A | 107.36(10) | C9B | C10 | C11 | 113.56(10) |
| N2 | C3 | C3A | 102.83(10) | C11 | C10 | C10A | 111.57(10) |
| C3 | C3A | C4 | 117.46(11) | C1 | C10A | C3A | 104.31(10) |
| C3 | C3A | C10A | 102.70(10) | C1 | C10A | C10 | 121.14(10) |
| C4 | C3A | C10A | 110.50(10) | C10 | C10A | C3A | 111.61(10) |
| C4A | C4 | C3A | 105.96(10) | O2 | C11 | O3 | 123.90(12) |
| O5 | C4A | C4 | 118.71(11) | O2 | C11 | C10 | 123.78(11) |
| C9B | C4A | O5 | 112.35(11) | O3 | C11 | C10 | 112.30(11) |
| C9B | C4A | C4 | 128.89(12) | C13 | C12 | N2 | 121.30(11) |
| O5 | C5A | C6 | 125.17(12) | C13 | C12 | C17 | 119.97(12) |
| O5 | C5A | C9A | 110.71(11) | C17 | C12 | N2 | 118.72(12) |
| C6 | C5A | C9A | 124.07(13) | C12 | C13 | C14 | 119.14(13) |
| C5A | C6 | C7 | 116.16(13) | C15 | C14 | C13 | 121.04(14) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C6 | C7 | C8 | 121.20(13) | C16 | C15 | C14 | 119.53(13) |
| C9 | C8 | C7 | 121.62(13) | C15 | C16 | C17 | 120.44(13) |
| C8 | C9 | C9A | 118.06(13) | C16 | C17 | C12 | 119.88(13) |
| C5A | C9A | C9 | 118.89(12) | | | | |

**Table S40.** Hydrogen Bonds for **23a**.

| D | H | A | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|---|---|---|---|---|---|---|
| O3 | H3 | O1[1] | 0.90(2) | 1.79(2) | 2.6637(13) | 161(2) |
| C3 | H3B | O3[2] | 0.99 | 2.53 | 3.4052(16) | 147.3 |
| C10 | H10B | O2[3] | 1.00 | 2.42 | 3.3711(15) | 158.4 |
| C13 | H13A | O1 | 0.95 | 2.40 | 2.9147(16) | 113.4 |

[1]1-X,-1/2+Y,1/2-Z; [2]+X,1/2-Y,1/2+Z; [3]1-X,1/2+Y,1/2-Z

**Table S41.** Torsion Angles for **23a**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| O1 | C1 | C10A | C3A | -167.97(12) | C5A | O5 | C4A | C9B | 1.03(14) |
| O1 | C1 | C10A | C10 | -41.22(18) | C5A | C6 | C7 | C8 | -0.3(2) |
| O5 | C4A | C9B | C9A | -0.48(14) | C5A | C9A | C9B | C4A | -0.27(13) |
| O5 | C4A | C9B | C10 | -174.37(11) | C5A | C9A | C9B | C10 | 172.90(12) |
| O5 | C5A | C6 | C7 | -177.09(12) | C6 | C5A | C9A | C9 | 0.2(2) |
| O5 | C5A | C9A | C9 | 177.92(11) | C6 | C5A | C9A | C9B | -176.76(12) |
| O5 | C5A | C9A | C9B | 0.92(14) | C6 | C7 | C8 | C9 | -0.2(2) |
| N2 | C1 | C10A | C3A | 18.53(13) | C7 | C8 | C9 | C9A | 0.7(2) |
| N2 | C1 | C10A | C10 | 145.28(11) | C8 | C9 | C9A | C5A | -0.68(19) |
| N2 | C3 | C3A | C4 | 151.97(10) | C8 | C9 | C9A | C9B | 175.19(13) |
| N2 | C3 | C3A | C10A | 30.53(12) | C9 | C9A | C9B | C4A | -176.52(14) |
| N2 | C12 | C13 | C14 | 179.20(12) | C9 | C9A | C9B | C10 | -3.3(2) |
| N2 | C12 | C17 | C16 | -178.86(11) | C9A | C5A | C6 | C7 | 0.3(2) |
| C1 | N2 | C3 | C3A | -20.81(13) | C9A | C9B | C10 | C10A | -153.99(12) |
| C1 | N2 | C12 | C13 | 33.30(18) | C9A | C9B | C10 | C11 | 83.69(16) |
| C1 | N2 | C12 | C17 | -147.90(12) | C9B | C10 | C10A | C1 | -176.31(10) |
| C3 | N2 | C1 | O1 | -172.19(12) | C9B | C10 | C10A | C3A | -52.94(12) |
| C3 | N2 | C1 | C10A | 1.45(13) | C9B | C10 | C11 | O2 | 136.90(13) |
| C3 | N2 | C12 | C13 | -161.64(11) | C9B | C10 | C11 | O3 | -44.67(14) |
| C3 | N2 | C12 | C17 | 17.16(16) | C10A | C3A | C4 | C4A | -43.94(13) |
| C3 | C3A | C4 | C4A | -161.25(11) | C10A | C10 | C11 | O2 | 18.14(17) |
| C3 | C3A | C10A | C1 | -30.27(12) | C10A | C10 | C11 | O3 | -163.43(10) |
| C3 | C3A | C10A | C10 | -162.74(10) | C11 | C10 | C10A | C1 | -52.71(14) |
| C3A | C4 | C4A | O5 | -172.73(10) | C11 | C10 | C10A | C3A | 70.66(13) |
| C3A | C4 | C4A | C9B | 10.28(18) | C12 | N2 | C1 | O1 | -6.1(2) |
| C4 | C3A | C10A | C1 | -156.35(10) | C12 | N2 | C1 | C10A | 167.50(11) |
| C4 | C3A | C10A | C10 | 71.18(13) | C12 | N2 | C3 | C3A | 172.25(10) |
| C4 | C4A | C9B | C9A | 176.67(12) | C12 | C13 | C14 | C15 | -0.4(2) |
| C4 | C4A | C9B | C10 | 2.8(2) | C13 | C12 | C17 | C16 | -0.05(18) |
| C4A | O5 | C5A | C6 | 176.46(13) | C13 | C14 | C15 | C16 | 0.0(2) |
| C4A | O5 | C5A | C9A | -1.19(13) | C14 | C15 | C16 | C17 | 0.4(2) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| C4A | C9B | C10 | C10A | 18.22(15) | C15 | C16 | C17 | C12 | -0.36(19) |
| C4A | C9B | C10 | C11 | -104.10(14) | C17 | C12 | C13 | C14 | 0.42(19) |
| C5A | O5 | C4A | C4 | -176.44(11) | | | | | |

**Table S42.** Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$×10$^3$) for **23a**.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H3 | 6326(18) | 420(30) | 2036(14) | 57(7) |
| H3A | 5477.89 | 967.67 | 5697.49 | 16 |
| H3B | 5636.15 | 2936.16 | 5868.99 | 16 |
| H3C | 6314.05 | 1045.86 | 4531.01 | 15 |
| H4A | 7458.05 | 3614.22 | 5512.8 | 19 |
| H4B | 7867.93 | 1737.49 | 5394.03 | 19 |
| H6A | 10895.39 | 4705.26 | 3885.95 | 23 |
| H7A | 10952.95 | 5659.43 | 2523.81 | 26 |
| H8A | 9396.57 | 5597.23 | 1561.93 | 26 |
| H9A | 7736.81 | 4574.24 | 1913.58 | 21 |
| H10B | 5994.24 | 4276.81 | 3003.04 | 14 |
| H10A | 5956.59 | 4542.78 | 4402.93 | 13 |
| H13A | 2401.45 | 2095.94 | 4191.32 | 21 |
| H14A | 794.09 | 1796.45 | 4809.88 | 27 |
| H15A | 845.68 | 1743.24 | 6246.82 | 27 |
| H16A | 2512.57 | 1989.67 | 7077.49 | 24 |
| H17A | 4127.99 | 2320.13 | 6477.44 | 19 |

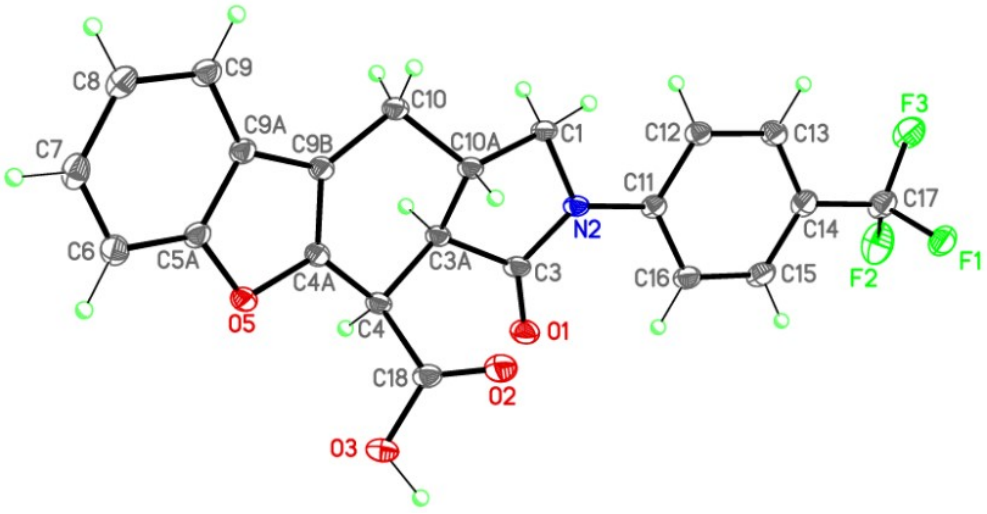



**Figure S10.** Molecular structure of **23e** (40%-ellipsoids; the solvate dimethylsulfoxide molecules are not shown).

**Table S43.** Atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) for **23e**. U(eq) is defined as one third of the trace of the orthogonalized U$^{ij}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| F(1) | 1483(2) | 5780(2) | -344(1) | 35(1) |
| F(2) | 2167(3) | 8423(3) | -435(1) | 48(1) |

| | | | | |
|---|---|---|---|---|
| F(3) | -950(3) | 8263(3) | -169(1) | 48(1) |
| O(1) | 6887(2) | 5547(2) | 2208(1) | 27(1) |
| O(2) | 7322(3) | 1513(2) | 2877(1) | 32(1) |
| O(3) | 10106(3) | 1580(2) | 3336(1) | 29(1) |
| C(1) | 1761(3) | 5610(3) | 2758(1) | 19(1) |
| N(2) | 3356(3) | 5695(2) | 2282(1) | 18(1) |
| C(3) | 5279(3) | 5476(3) | 2497(1) | 20(1) |
| C(3A) | 5041(3) | 5188(3) | 3154(1) | 18(1) |
| C(4) | 6944(3) | 3942(3) | 3489(1) | 19(1) |
| C(4A) | 6105(3) | 3399(3) | 4089(1) | 19(1) |
| O(5) | 7500(2) | 2447(2) | 4518(1) | 22(1) |
| C(5A) | 6252(3) | 2125(3) | 5008(1) | 20(1) |
| C(6) | 6964(4) | 1140(3) | 5543(1) | 24(1) |
| C(7) | 5431(4) | 958(3) | 5972(1) | 26(1) |
| C(8) | 3296(4) | 1720(3) | 5865(1) | 25(1) |
| C(9) | 2619(4) | 2688(3) | 5325(1) | 23(1) |
| C(9A) | 4135(3) | 2897(3) | 4886(1) | 20(1) |
| C(9B) | 4084(3) | 3710(3) | 4279(1) | 19(1) |
| C(10) | 2256(3) | 4615(3) | 3893(1) | 21(1) |
| C(10A) | 3107(3) | 4475(3) | 3266(1) | 18(1) |
| C(11) | 2832(3) | 6153(3) | 1692(1) | 19(1) |
| C(12) | 717(3) | 6753(3) | 1557(1) | 21(1) |
| C(13) | 138(4) | 7157(3) | 978(1) | 24(1) |
| C(14) | 1654(4) | 6991(3) | 529(1) | 25(1) |
| C(15) | 3761(4) | 6414(3) | 660(1) | 27(1) |
| C(16) | 4357(4) | 5980(3) | 1236(1) | 24(1) |
| C(17) | 1080(4) | 7365(3) | -96(1) | 31(1) |
| C(18) | 8114(3) | 2214(3) | 3199(1) | 22(1) |
| S(1) | 2986(1) | 1336(1) | 2139(1) | 28(1) |
| O(4) | 2590(3) | -279(2) | 2565(1) | 31(1) |
| C(19) | 1295(5) | 1683(4) | 1552(1) | 44(1) |
| C(20) | 5437(5) | 375(4) | 1779(1) | 40(1) |

**Table S44.** Bond lengths [Å] and angles [°] for **23e**.

| | | | |
|---|---|---|---|
| F(1)-C(17) | 1.348(3) | C(4)-H(4) | 1.0000 |
| F(2)-C(17) | 1.351(3) | C(4A)-C(9B) | 1.350(3) |
| F(3)-C(17) | 1.337(3) | C(4A)-O(5) | 1.383(2) |
| O(1)-C(3) | 1.229(3) | O(5)-C(5A) | 1.384(3) |
| O(2)-C(18) | 1.213(3) | C(5A)-C(6) | 1.383(3) |
| O(3)-C(18) | 1.324(3) | C(5A)-C(9A) | 1.397(3) |
| O(3)-H(3) | 0.96(5) | C(6)-C(7) | 1.389(3) |
| C(1)-N(2) | 1.477(2) | C(6)-H(6) | 0.9500 |
| C(1)-C(10A) | 1.527(3) | C(7)-C(8) | 1.400(3) |
| C(1)-H(1A) | 0.9900 | C(7)-H(7) | 0.9500 |
| C(1)-H(1B) | 0.9900 | C(8)-C(9) | 1.385(3) |
| N(2)-C(3) | 1.374(3) | C(8)-H(8) | 0.9500 |
| N(2)-C(11) | 1.406(3) | C(9)-C(9A) | 1.400(3) |
| C(3)-C(3A) | 1.507(3) | C(9)-H(9) | 0.9500 |
| C(3A)-C(4) | 1.527(3) | C(9A)-C(9B) | 1.442(3) |
| C(3A)-C(10A) | 1.530(3) | C(9B)-C(10) | 1.503(3) |
| C(3A)-H(3A) | 1.0000 | C(10)-C(10A) | 1.523(3) |
| C(4)-C(4A) | 1.497(3) | C(10)-H(10A) | 0.9900 |
| C(4)-C(18) | 1.526(3) | C(10)-H(10B) | 0.9900 |

| | | | |
|---|---|---|---|
| C(10A)-H(10C) | 1.0000 | C(5A)-C(6)-C(7) | 116.0(2) |
| C(11)-C(12) | 1.400(3) | C(5A)-C(6)-H(6) | 122.0 |
| C(11)-C(16) | 1.400(3) | C(7)-C(6)-H(6) | 122.0 |
| C(12)-C(13) | 1.390(3) | C(6)-C(7)-C(8) | 121.8(2) |
| C(12)-H(12) | 0.9500 | C(6)-C(7)-H(7) | 119.1 |
| C(13)-C(14) | 1.385(3) | C(8)-C(7)-H(7) | 119.1 |
| C(13)-H(13) | 0.9500 | C(9)-C(8)-C(7) | 121.3(2) |
| C(14)-C(15) | 1.392(3) | C(9)-C(8)-H(8) | 119.4 |
| C(14)-C(17) | 1.493(3) | C(7)-C(8)-H(8) | 119.4 |
| C(15)-C(16) | 1.388(3) | C(8)-C(9)-C(9A) | 118.0(2) |
| C(15)-H(15) | 0.9500 | C(8)-C(9)-H(9) | 121.0 |
| C(16)-H(16) | 0.9500 | C(9A)-C(9)-H(9) | 121.0 |
| S(1)-O(4) | 1.5103(17) | C(5A)-C(9A)-C(9) | 119.21(19) |
| S(1)-C(20) | 1.779(3) | C(5A)-C(9A)-C(9B) | 105.85(18) |
| S(1)-C(19) | 1.784(3) | C(9)-C(9A)-C(9B) | 134.9(2) |
| C(19)-H(19A) | 0.9800 | C(4A)-C(9B)-C(9A) | 105.76(18) |
| C(19)-H(19B) | 0.9800 | C(4A)-C(9B)-C(10) | 123.94(19) |
| C(19)-H(19C) | 0.9800 | C(9A)-C(9B)-C(10) | 130.17(19) |
| C(20)-H(20A) | 0.9800 | C(9B)-C(10)-C(10A) | 106.53(17) |
| C(20)-H(20B) | 0.9800 | C(9B)-C(10)-H(10A) | 110.4 |
| C(20)-H(20C) | 0.9800 | C(10A)-C(10)-H(10A) | 110.4 |
| C(18)-O(3)-H(3) | 108(3) | C(9B)-C(10)-H(10B) | 110.4 |
| N(2)-C(1)-C(10A) | 101.83(15) | C(10A)-C(10)-H(10B) | 110.4 |
| N(2)-C(1)-H(1A) | 111.4 | H(10A)-C(10)-H(10B) | 108.6 |
| C(10A)-C(1)-H(1A) | 111.4 | C(10)-C(10A)-C(1) | 119.91(17) |
| N(2)-C(1)-H(1B) | 111.4 | C(10)-C(10A)-C(3A) | 110.61(17) |
| C(10A)-C(1)-H(1B) | 111.4 | C(1)-C(10A)-C(3A) | 101.46(16) |
| H(1A)-C(1)-H(1B) | 109.3 | C(10)-C(10A)-H(10C) | 108.1 |
| C(3)-N(2)-C(11) | 126.23(18) | C(1)-C(10A)-H(10C) | 108.1 |
| C(3)-N(2)-C(1) | 111.57(16) | C(3A)-C(10A)-H(10C) | 108.1 |
| C(11)-N(2)-C(1) | 121.85(17) | C(12)-C(11)-C(16) | 118.99(19) |
| O(1)-C(3)-N(2) | 126.51(19) | C(12)-C(11)-N(2) | 118.86(19) |
| O(1)-C(3)-C(3A) | 126.15(19) | C(16)-C(11)-N(2) | 122.13(19) |
| N(2)-C(3)-C(3A) | 107.31(17) | C(13)-C(12)-C(11) | 120.6(2) |
| C(3)-C(3A)-C(4) | 117.11(17) | C(13)-C(12)-H(12) | 119.7 |
| C(3)-C(3A)-C(10A) | 103.03(16) | C(11)-C(12)-H(12) | 119.7 |
| C(4)-C(3A)-C(10A) | 114.06(16) | C(14)-C(13)-C(12) | 120.2(2) |
| C(3)-C(3A)-H(3A) | 107.4 | C(14)-C(13)-H(13) | 119.9 |
| C(4)-C(3A)-H(3A) | 107.4 | C(12)-C(13)-H(13) | 119.9 |
| C(10A)-C(3A)-H(3A) | 107.4 | C(13)-C(14)-C(15) | 119.6(2) |
| C(4A)-C(4)-C(18) | 111.66(17) | C(13)-C(14)-C(17) | 121.3(2) |
| C(4A)-C(4)-C(3A) | 105.37(16) | C(15)-C(14)-C(17) | 119.0(2) |
| C(18)-C(4)-C(3A) | 112.63(17) | C(16)-C(15)-C(14) | 120.7(2) |
| C(4A)-C(4)-H(4) | 109.0 | C(16)-C(15)-H(15) | 119.7 |
| C(18)-C(4)-H(4) | 109.0 | C(14)-C(15)-H(15) | 119.7 |
| C(3A)-C(4)-H(4) | 109.0 | C(15)-C(16)-C(11) | 120.0(2) |
| C(9B)-C(4A)-O(5) | 113.07(18) | C(15)-C(16)-H(16) | 120.0 |
| C(9B)-C(4A)-C(4) | 128.03(19) | C(11)-C(16)-H(16) | 120.0 |
| O(5)-C(4A)-C(4) | 118.90(18) | F(3)-C(17)-F(1) | 106.2(2) |
| C(4A)-O(5)-C(5A) | 104.72(16) | F(3)-C(17)-F(2) | 106.7(2) |
| C(6)-C(5A)-O(5) | 125.6(2) | F(1)-C(17)-F(2) | 104.84(19) |
| C(6)-C(5A)-C(9A) | 123.8(2) | F(3)-C(17)-C(14) | 113.0(2) |
| O(5)-C(5A)-C(9A) | 110.58(18) | F(1)-C(17)-C(14) | 113.06(19) |

| | |
|---|---|
| F(2)-C(17)-C(14) | 112.5(2) |
| O(2)-C(18)-O(3) | 123.9(2) |
| O(2)-C(18)-C(4) | 124.2(2) |
| O(3)-C(18)-C(4) | 111.92(19) |
| O(4)-S(1)-C(20) | 105.48(12) |
| O(4)-S(1)-C(19) | 105.89(13) |
| C(20)-S(1)-C(19) | 99.52(15) |
| S(1)-C(19)-H(19A) | 109.5 |
| S(1)-C(19)-H(19B) | 109.5 |
| H(19A)-C(19)-H(19B) | 109.5 |
| S(1)-C(19)-H(19C) | 109.5 |
| H(19A)-C(19)-H(19C) | 109.5 |
| H(19B)-C(19)-H(19C) | 109.5 |
| S(1)-C(20)-H(20A) | 109.5 |
| S(1)-C(20)-H(20B) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 |
| S(1)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 |

**Table S45.** Anisotropic displacement parameters ($Å^2 \times 10^3$) for **23e**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[ h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12} ]$

| Atom | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{23}$ | $U^{13}$ | $U^{12}$ |
|---|---|---|---|---|---|---|
| F(1) | 36(1) | 38(1) | 27(1) | -11(1) | -3(1) | 0(1) |
| F(2) | 73(1) | 46(1) | 23(1) | 6(1) | -4(1) | -20(1) |
| F(3) | 41(1) | 56(1) | 26(1) | -9(1) | -14(1) | 20(1) |
| O(1) | 19(1) | 36(1) | 23(1) | 0(1) | 2(1) | -6(1) |
| O(2) | 25(1) | 31(1) | 38(1) | -13(1) | -2(1) | 0(1) |
| O(3) | 18(1) | 29(1) | 34(1) | -7(1) | -2(1) | 3(1) |
| C(1) | 14(1) | 22(1) | 18(1) | -1(1) | 1(1) | 0(1) |
| N(2) | 15(1) | 18(1) | 17(1) | 1(1) | 0(1) | 0(1) |
| C(3) | 16(1) | 18(1) | 22(1) | -1(1) | 0(1) | 1(1) |
| C(3A) | 14(1) | 17(1) | 19(1) | -1(1) | -1(1) | 0(1) |
| C(4) | 14(1) | 20(1) | 19(1) | -1(1) | -1(1) | 0(1) |
| C(4A) | 17(1) | 19(1) | 18(1) | -1(1) | -3(1) | 1(1) |
| O(5) | 18(1) | 22(1) | 19(1) | 0(1) | -3(1) | 2(1) |
| C(5A) | 22(1) | 18(1) | 18(1) | -4(1) | 0(1) | 0(1) |
| C(6) | 26(1) | 19(1) | 22(1) | -3(1) | -4(1) | 1(1) |
| C(7) | 36(1) | 18(1) | 18(1) | 0(1) | -4(1) | 0(1) |
| C(8) | 31(1) | 22(1) | 21(1) | -4(1) | 3(1) | -4(1) |
| C(9) | 22(1) | 21(1) | 22(1) | -4(1) | 2(1) | -2(1) |
| C(9A) | 20(1) | 18(1) | 18(1) | -3(1) | 0(1) | -1(1) |
| C(9B) | 17(1) | 19(1) | 18(1) | -1(1) | -1(1) | -1(1) |
| C(10) | 15(1) | 25(1) | 19(1) | -2(1) | -1(1) | 0(1) |
| C(10A) | 15(1) | 19(1) | 18(1) | 0(1) | 0(1) | 0(1) |
| C(11) | 20(1) | 15(1) | 18(1) | 0(1) | -1(1) | -1(1) |
| C(12) | 20(1) | 20(1) | 20(1) | 0(1) | -1(1) | -1(1) |
| C(13) | 22(1) | 23(1) | 24(1) | 0(1) | -4(1) | -1(1) |
| C(14) | 28(1) | 21(1) | 20(1) | -1(1) | -4(1) | 2(1) |
| C(15) | 27(1) | 27(1) | 21(1) | -3(1) | 3(1) | 1(1) |
| C(16) | 20(1) | 25(1) | 22(1) | -2(1) | 1(1) | 1(1) |
| C(17) | 34(1) | 28(1) | 22(1) | -4(1) | -2(1) | 3(1) |
| C(18) | 19(1) | 20(1) | 21(1) | 0(1) | 1(1) | 1(1) |
| S(1) | 32(1) | 21(1) | 28(1) | -4(1) | -1(1) | -1(1) |
| O(4) | 32(1) | 21(1) | 31(1) | -1(1) | 2(1) | 2(1) |
| C(19) | 52(2) | 36(1) | 41(2) | 2(1) | -20(1) | -6(1) |
| C(20) | 44(2) | 36(1) | 38(1) | -8(1) | 8(1) | -9(1) |

**Table S46.** Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **23e**.

| Atom | *x* | *y* | *z* | U(iso) |
|---|---|---|---|---|
| H(3) | 10830(70) | 680(60) | 3081(19) | 68(12) |
| H(1A) | 772 | 4958 | 2662 | 23 |
| H(1B) | 967 | 6887 | 2846 | 23 |
| H(3A) | 4665 | 6459 | 3285 | 22 |
| H(4) | 7922 | 4703 | 3517 | 23 |
| H(6) | 8415 | 619 | 5612 | 29 |
| H(7) | 5842 | 300 | 6347 | 31 |
| H(8) | 2292 | 1570 | 6170 | 30 |
| H(9) | 1168 | 3195 | 5254 | 27 |
| H(10A) | 1627 | 5951 | 3949 | 25 |
| H(10B) | 1170 | 3948 | 3986 | 25 |
| H(10C) | 3535 | 3116 | 3210 | 22 |
| H(12) | -332 | 6886 | 1863 | 26 |
| H(13) | -1301 | 7547 | 891 | 29 |
| H(15) | 4802 | 6317 | 352 | 33 |
| H(16) | 5800 | 5564 | 1321 | 29 |

| | | | | |
|---|---|---|---|---|
| H(19A) | 1513 | 485 | 1402 | 66 |
| H(19B) | 1607 | 2614 | 1238 | 66 |
| H(19C) | -165 | 2141 | 1692 | 66 |
| H(20A) | 6555 | 46 | 2058 | 60 |
| H(20B) | 5693 | 1309 | 1458 | 60 |
| H(20C) | 5412 | -759 | 1624 | 60 |

**Table S47.** Torsion angles [°] for **23e**.

| | |
|---|---|
| C(10A)-C(1)-N(2)-C(3) | -24.1(2) |
| C(10A)-C(1)-N(2)-C(11) | 162.26(17) |
| C(11)-N(2)-C(3)-O(1) | -4.1(3) |
| C(1)-N(2)-C(3)-O(1) | -177.3(2) |
| C(11)-N(2)-C(3)-C(3A) | 174.35(17) |
| C(1)-N(2)-C(3)-C(3A) | 1.1(2) |
| O(1)-C(3)-C(3A)-C(4) | -33.0(3) |
| N(2)-C(3)-C(3A)-C(4) | 148.55(18) |
| O(1)-C(3)-C(3A)-C(10A) | -159.1(2) |
| N(2)-C(3)-C(3A)-C(10A) | 22.5(2) |
| C(3)-C(3A)-C(4)-C(4A) | -162.25(17) |
| C(10A)-C(3A)-C(4)-C(4A) | -41.9(2) |
| C(3)-C(3A)-C(4)-C(18) | -40.3(2) |
| C(10A)-C(3A)-C(4)-C(18) | 80.1(2) |
| C(18)-C(4)-C(4A)-C(9B) | -114.5(2) |
| C(3A)-C(4)-C(4A)-C(9B) | 8.1(3) |
| C(18)-C(4)-C(4A)-O(5) | 65.1(2) |
| C(3A)-C(4)-C(4A)-O(5) | -172.27(17) |
| C(9B)-C(4A)-O(5)-C(5A) | 0.8(2) |
| C(4)-C(4A)-O(5)-C(5A) | -178.86(18) |
| C(4A)-O(5)-C(5A)-C(6) | 177.2(2) |
| C(4A)-O(5)-C(5A)-C(9A) | -1.3(2) |
| O(5)-C(5A)-C(6)-C(7) | -178.90(19) |
| C(9A)-C(5A)-C(6)-C(7) | -0.6(3) |
| C(5A)-C(6)-C(7)-C(8) | 0.3(3) |
| C(6)-C(7)-C(8)-C(9) | 0.2(3) |
| C(7)-C(8)-C(9)-C(9A) | -0.5(3) |
| C(6)-C(5A)-C(9A)-C(9) | 0.3(3) |
| O(5)-C(5A)-C(9A)-C(9) | 178.85(18) |
| C(6)-C(5A)-C(9A)-C(9B) | -177.3(2) |
| O(5)-C(5A)-C(9A)-C(9B) | 1.2(2) |
| C(8)-C(9)-C(9A)-C(5A) | 0.2(3) |
| C(8)-C(9)-C(9A)-C(9B) | 177.0(2) |
| O(5)-C(4A)-C(9B)-C(9A) | 0.0(2) |
| C(4)-C(4A)-C(9B)-C(9A) | 179.6(2) |
| O(5)-C(4A)-C(9B)-C(10) | -176.32(18) |
| C(4)-C(4A)-C(9B)-C(10) | 3.3(4) |
| C(5A)-C(9A)-C(9B)-C(4A) | -0.7(2) |
| C(9)-C(9A)-C(9B)-C(4A) | -177.8(2) |
| C(5A)-C(9A)-C(9B)-C(10) | 175.2(2) |
| C(9)-C(9A)-C(9B)-C(10) | -1.8(4) |
| C(4A)-C(9B)-C(10)-C(10A) | 18.1(3) |
| C(9A)-C(9B)-C(10)-C(10A) | -157.2(2) |
| C(9B)-C(10)-C(10A)-C(1) | -167.41(18) |
| C(9B)-C(10)-C(10A)-C(3A) | -50.0(2) |
| N(2)-C(1)-C(10A)-C(10) | 158.21(18) |
| N(2)-C(1)-C(10A)-C(3A) | 36.15(19) |
| C(3)-C(3A)-C(10A)-C(10) | -164.33(16) |
| C(4)-C(3A)-C(10A)-C(10) | 67.7(2) |

| | |
|---|---|
| C(3)-C(3A)-C(10A)-C(1) | -36.04(18) |
| C(4)-C(3A)-C(10A)-C(1) | -164.03(16) |
| C(3)-N(2)-C(11)-C(12) | -165.22(19) |
| C(1)-N(2)-C(11)-C(12) | 7.4(3) |
| C(3)-N(2)-C(11)-C(16) | 16.6(3) |
| C(1)-N(2)-C(11)-C(16) | -170.80(19) |
| C(16)-C(11)-C(12)-C(13) | 0.5(3) |
| N(2)-C(11)-C(12)-C(13) | -177.78(19) |
| C(11)-C(12)-C(13)-C(14) | -0.8(3) |
| C(12)-C(13)-C(14)-C(15) | 0.2(3) |
| C(12)-C(13)-C(14)-C(17) | 178.3(2) |
| C(13)-C(14)-C(15)-C(16) | 0.8(3) |
| C(17)-C(14)-C(15)-C(16) | -177.4(2) |
| C(14)-C(15)-C(16)-C(11) | -1.2(3) |
| C(12)-C(11)-C(16)-C(15) | 0.5(3) |
| N(2)-C(11)-C(16)-C(15) | 178.7(2) |
| C(13)-C(14)-C(17)-F(3) | 14.5(3) |
| C(15)-C(14)-C(17)-F(3) | -167.3(2) |
| C(13)-C(14)-C(17)-F(1) | -106.1(3) |
| C(15)-C(14)-C(17)-F(1) | 72.1(3) |
| C(13)-C(14)-C(17)-F(2) | 135.4(2) |
| C(15)-C(14)-C(17)-F(2) | -46.4(3) |
| C(4A)-C(4)-C(18)-O(2) | 93.8(3) |
| C(3A)-C(4)-C(18)-O(2) | -24.6(3) |
| C(4A)-C(4)-C(18)-O(3) | -86.8(2) |
| C(3A)-C(4)-C(18)-O(3) | 154.82(18) |

**Table S48.** Hydrogen bonds for **23e** [Å and °].

| **D-H...A** | **d(D-H)** | **d(H...A)** | **d(D...A)** | **<(DHA)** |
|---|---|---|---|---|
| O(3)-H(3)...O(4)#1 | 0.96(5) | 1.69(5) | 2.609(2) | 158(4) |

Symmetry transformations used to generate equivalent atoms: #1 x+1, y, z

## 3. DFT Calculations

All calculations were performed using ORCA 6.0 [9]. To optimize the geometry of all stationary points (e.g., reactants and intermediates), we used the B3LYP/cc-pvdz model with a D3 correction. To accurately calculate the energies of the products, we used the B3LYP/aug-cc-pvtz model with a D3 correction. The CPCM model was chosen to model the solvent effect. The nature of the optimized structure was confirmed using frequency analysis at the same computational level as for the reactants. Products and intermediates do not have an imaginary frequency, while transition states do.

**Table S49.** Calculated energies of structures, pre-reaction complexes and transition states.

| **Structures** | **kcal/mol** | **Structures** | **kcal/mol** |
|---|---|---|---|
| 3a*S*,9b*R*-**10a** | -9.4 | 4a*R*,10a*S*-**22** | -14.4 |
| 3a*R*,9b*S*-**10a** | -9.2 | 4a*S*,10a*R*-**22** | -13.5 |
| *endo*-**17a** | -13.6 | *endo*-**17b** | -18.2 |
| *exo*-**10a** | -10.8 | *exo*-**22** | -15.7 |
| TS-*endo*$_{\mathbf{IMDAV16a\rightarrow17a}}$ | 18.8 | TS-*endo*$_{\mathbf{IMDAV18a\rightarrow17b}}$ | 19.2 |
| TS-*exo*$_{\mathbf{IMDAV16a\rightarrow10a}}$ | 18.1 | TS-*exo*$_{\mathbf{IMDAV18a\rightarrow22}}$ | 18.5 |
| IRC-*endo*$_{\mathbf{IMDAV16a\rightarrow17a}}$ | 8.5 | IRC-*endo*$_{\mathbf{IMDAV18a\rightarrow17b}}$ | 10.8 |
| IRC-*exo*$_{\mathbf{IMDAV16a\rightarrow10a}}$ | 8.0 | IRC-*exo*$_{\mathbf{IMDAV18a\rightarrow22}}$ | 9.2 |

**Table S50.** xyz-Coordinates and DFT-calculated energies

3a*R*,9b*S*-**10a**

E = -1165.988749925493 Eh

Δ(G-E(el)) = 0.28151963 Eh

ΔG = -1165.70723029549 Eh

ΔH = -1165.27514280 Eh

TΔS = 0.08641925 Eh

| | | | |
|---|---|---|---|
| C | -2.11343331710784 | 0.10339556454282 | 2.98300622744410 |
| C | -3.01233345272960 | 0.37390083652889 | 1.94497985066562 |
| C | -2.55856538404912 | 0.70060345319763 | 0.65637963511280 |
| C | -1.18553004203999 | 0.74279975248227 | 0.46759394312175 |
| C | -0.26859517282958 | 0.47237026609640 | 1.48840563513645 |
| C | -0.72725616649769 | 0.14335582635046 | 2.75733666919685 |
| O | -0.56627872319355 | 1.06550820371793 | -0.73321025100450 |
| C | 0.79361028693557 | 1.16738171325128 | -0.47704034738096 |
| C | 1.10544431638032 | 0.50838232667677 | 0.86357431515061 |
| H | -2.49250395872407 | -0.14103258247526 | 3.97724586579339 |
| H | -0.02571821130604 | -0.07132079156154 | 3.56644384673574 |

| | | | |
|---|---|---|---|
| H | -4.08693442834640 | 0.33744008607581 | 2.13658309411585 |
| H | -3.24688852270195 | 0.92217198611640 | -0.16017487917679 |
| H | 1.38743773982114 | -0.54199043008181 | 0.65303918659891 |
| C | 1.64800678081285 | 1.81967380912457 | -1.27507918390558 |
| C | 3.00606759236318 | 2.13031092012295 | -0.71341523797085 |
| H | 1.29375225872888 | 2.30908068276336 | -2.18470374043971 |
| C | 4.30068224204769 | 2.05360544281558 | -1.53312232110757 |
| H | 2.97027214403952 | 3.16900935483469 | -0.32641554881382 |
| N | 5.32634027064478 | 2.07135009360768 | -0.45863634564258 |
| H | 4.44805922943103 | 2.91270839136011 | -2.19977544553895 |
| H | 4.36311972574822 | 1.12232167747303 | -2.12219394712851 |
| C | 4.79343293662956 | 1.67188045070624 | 0.74396297932371 |
| O | 5.33281444738802 | 1.67755114529576 | 1.85310301487624 |
| C | 3.38255109015791 | 1.21138104566428 | 0.44845283954574 |
| C | 2.32875428213967 | 1.12814183524385 | 1.55939682684347 |
| H | 3.49195393850343 | 0.18779574645622 | 0.04036965360228 |
| C | 2.06891776251733 | 2.49153556748840 | 2.19127866296641 |
| H | 2.69272875295620 | 0.45498542617724 | 2.35218739158478 |
| O | 1.03117837601357 | 3.10328763107302 | 2.08684075738333 |
| O | 3.10327834224934 | 2.99694147100560 | 2.89093305831917 |
| H | 3.90366812026691 | 2.42793552807533 | 2.79479735743809 |
| C | 6.67495295315336 | 2.42380738022170 | -0.71361282846943 |
| C | 7.14138151206231 | 2.42234813132239 | -2.03986120515733 |
| C | 8.46290964407337 | 2.77666187730500 | -2.32005510367669 |
| C | 9.33676676377682 | 3.13096976512009 | -1.28945025482133 |
| C | 8.87175931406556 | 3.12655026879751 | 0.02938067316547 |
| C | 7.55312248337545 | 2.77901467682839 | 0.32706265118439 |
| H | 7.19838676945190 | 2.77514338455794 | 1.35386417131197 |
| H | 6.48135185330771 | 2.13421286276456 | -2.85783285155386 |
| H | 8.80769137839754 | 2.76927442783840 | -3.35640741287977 |
| H | 10.36960028715302 | 3.40707797259589 | -1.51109634498476 |
| H | 9.54206378493358 | 3.40257682244212 | 0.84655494303585 |

3a*S*,9b*R*-**10a**

E = -1165.989079105615 Eh

Δ(G-E(el)) = 0.28155943 Eh

ΔG = -1165.70751967561 Eh

ΔH = -1165.27760393 Eh

TΔS = 0.08636487 Eh

| | | | |
|---|---|---|---|
| C | -1.85048223262589 | 1.80735889521969 | 3.00201550057906 |
| C | -2.77675960623189 | 1.42151535065386 | 2.02633612752021 |
| C | -2.35332732342910 | 1.03138568816761 | 0.74773657699312 |
| C | -0.98639144980988 | 1.04397293763689 | 0.50868092196709 |
| C | -0.03536632321786 | 1.42277455181983 | 1.46367508314015 |
| C | -0.47387684483046 | 1.81863379983793 | 2.72671370869655 |
| O | -0.41468466588320 | 0.67970937878807 | -0.69848033718515 |
| C | 0.95562739410467 | 0.71335573281945 | -0.52564663090092 |
| C | 1.33224042932121 | 1.35064985783468 | 0.79798017585258 |
| H | -2.20119839599764 | 2.11027611550473 | 3.99071237482275 |
| H | 0.24421034908426 | 2.13745368703046 | 3.47943637888058 |
| H | -3.84412580378355 | 1.42251958210672 | 2.25828839376072 |
| H | -3.05530383972987 | 0.72583024780192 | -0.02917060956242 |
| H | 1.71384116159566 | 2.37467750418670 | 0.63585997617953 |
| C | 1.82303452561707 | 0.17333807226519 | -1.38235196936303 |
| C | 3.27350955028000 | 0.21208179110609 | -1.00892980164505 |
| H | 1.49397618819824 | -0.30833389842739 | -2.30358357921326 |
| C | 4.00466834441892 | 1.53002451423376 | -1.33846846269826 |
| H | 3.80684608165677 | -0.59155177345304 | -1.53880986362444 |
| N | 5.13993945483031 | 1.53552834869965 | -0.40428632695241 |
| H | 3.36077101018193 | 2.40904395963388 | -1.17138041158495 |
| H | 4.36518870677448 | 1.55665442058222 | -2.37564191256996 |
| C | 4.92904748973478 | 0.69092792525948 | 0.64806915149443 |
| O | 5.70915422874746 | 0.47156812609514 | 1.58143692708353 |
| C | 3.56628184856741 | 0.02085775056846 | 0.50552477037221 |
| C | 2.45282145799639 | 0.53979935320992 | 1.49817826430950 |
| H | 3.72026416310134 | -1.04310212736981 | 0.72675942935413 |
| C | 2.95930406323545 | 1.29804802025715 | 2.73754541890939 |
| H | 1.98059941709411 | -0.36667221998537 | 1.91140824644897 |
| O | 2.44399077725352 | 2.32911215132447 | 3.11560614370219 |
| O | 3.92558357542991 | 0.72136153486995 | 3.46720413854261 |
| H | 4.58341941625853 | 0.26458505643355 | 2.88195833103794 |
| C | 6.24252959916219 | 2.41278366990516 | -0.57520041494862 |
| C | 6.11946856709671 | 3.48925005407180 | -1.47144237048148 |
| C | 7.18844238982406 | 4.36617517050525 | -1.66725142284430 |
| C | 8.38960956652384 | 4.18640991739525 | -0.97743694850787 |
| C | 8.50952759119395 | 3.11550768446661 | -0.08652747873160 |
| C | 7.45177454567105 | 2.22853142445946 | 0.12029524786600 |

| | | | |
|---|---|---|---|
| H | 7.55097222563453 | 1.40257640312549 | 0.81816745521401 |
| H | 5.18834082567502 | 3.65706816668267 | -2.01160134370827 |
| H | 7.07308166063598 | 5.19837257134108 | -2.36511480858937 |
| H | 9.22378786887558 | 4.87370522384626 | -1.13191605362981 |
| H | 9.44269201176389 | 2.95996537948908 | 0.45952200401394 |

**16a**

E = -1165.96297016015 Eh

Δ(G-E(el)) = 0.27041040 Eh

ΔG = -1165.69255976015 Eh

ΔH = -1165.24265265 Eh

TΔS = 0.09509176 Eh

| | | | |
|---|---|---|---|
| C | -2.55233245216317 | -1.28300221480319 | 0.42557834164720 |
| C | -2.30087111839726 | -1.39123606732234 | -0.95905734053567 |
| C | -1.25905087324538 | -0.68488347250486 | -1.56543512733386 |
| C | -0.49119516308391 | 0.12387813530129 | -0.73301289148058 |
| C | -0.71728443376742 | 0.25393151693149 | 0.65578029181296 |
| C | -1.77269313704667 | -0.46782895048910 | 1.24383230813665 |
| O | 0.57039028046000 | 0.89702921950905 | -1.11289143155711 |
| C | 1.03426434357531 | 1.53015662286000 | 0.03103168344097 |
| C | 0.28690609271042 | 1.17212055539933 | 1.12441721991790 |
| H | -3.37651226720629 | -1.85198548379533 | 0.86122746266083 |
| H | -1.97382598304116 | -0.38966726462904 | 2.31415160777603 |
| H | -2.93249929229746 | -2.03981856000685 | -1.56956506391786 |
| H | -1.05147982423157 | -0.75758988486573 | -2.63384605471693 |
| H | 0.43620967774552 | 1.52195840534921 | 2.14272731184060 |
| C | 2.17414654003093 | 2.39840036408305 | -0.17003461172712 |
| C | 2.78603054849315 | 3.11646321928973 | 0.78843434277524 |
| H | 2.54110941817653 | 2.44403520167958 | -1.20035470920420 |
| C | 3.99121152500963 | 3.97115858417115 | 0.52696445031670 |
| H | 2.43886355855014 | 3.06376373076899 | 1.82611212782087 |
| N | 5.20344641976242 | 3.42064633358717 | 1.17338722798923 |
| H | 3.84296440867996 | 5.00407592510281 | 0.86838476863177 |
| H | 4.20083007253683 | 4.01658787881601 | -0.55036410579656 |
| C | 5.65559546219089 | 3.72837485529403 | 2.42170814493912 |
| O | 6.69414799380915 | 3.18710004318907 | 2.84941414577790 |
| C | 4.86147218901792 | 4.69396941119230 | 3.22603631849745 |
| C | 5.19082594900751 | 5.25259744687180 | 4.40860496078187 |
| H | 3.88489319295878 | 4.97458302381081 | 2.83203964202171 |

| | | | |
|---|---|---|---|
| C | 6.40859054331601 | 5.17272615729061 | 5.29155037347143 |
| H | 4.45898988603670 | 5.93674623787378 | 4.84636512834604 |
| O | 6.46269895250877 | 5.91605501315480 | 6.25678316466981 |
| O | 7.37498330323350 | 4.31089024556673 | 5.01501907518697 |
| H | 7.15291017434970 | 3.79380038222278 | 4.17337417534915 |
| C | 5.87996823145027 | 2.38084410095164 | 0.44002798011698 |
| C | 5.58079194356485 | 1.04002178199427 | 0.69627211653853 |
| C | 6.20743871561876 | 0.03945481016095 | -0.05115949409221 |
| C | 7.12525600748975 | 0.37973635836545 | -1.05037587167529 |
| C | 7.41927473933383 | 1.72400762357245 | -1.30159774708091 |
| C | 6.79649243105006 | 2.72839219354189 | -0.55572866479317 |
| H | 7.01972339903934 | 3.78173827890597 | -0.73594178238153 |
| H | 4.86171696725910 | 0.79030258641891 | 1.47745156968402 |
| H | 5.97556177113519 | -1.00901223749567 | 0.14722427412731 |
| H | 7.61279986364589 | -0.40411924941032 | -1.63397197252749 |
| H | 8.13868994273323 | 1.99307714209522 | -2.07781334545481 |

*endo*-**17a**

E = -1165.995673590290 Eh

Δ(G-E(el)) = 0.28145523 Eh

ΔG = -1165.71421836029 Eh

ΔH = -1165.28188288 Eh

TΔS = 0.08675662 Eh

| | | | |
|---|---|---|---|
| C | -1.93923329450002 | 0.86187341672300 | 2.97652256420384 |
| C | -2.78123261753876 | 1.26455899335985 | 1.93363170296180 |
| C | -2.33871346425204 | 1.26964668102270 | 0.60059535798186 |
| C | -1.03327467317269 | 0.86153871552613 | 0.37117022315247 |
| C | -0.17490533984221 | 0.45257353520780 | 1.39677888477212 |
| C | -0.62391926563176 | 0.44473166625459 | 2.71122097718390 |
| O | -0.43247007579712 | 0.81524383541003 | -0.87650369161045 |
| C | 0.89583317248137 | 0.47008060569934 | -0.68006002790673 |
| C | 1.11936023962081 | 0.01956686942390 | 0.75083024147636 |
| H | -2.30743128754468 | 0.87118127293860 | 4.00424694365114 |
| H | 0.03330260230178 | 0.12710103346107 | 3.52397624964268 |
| H | -3.80158643628913 | 1.58477135933930 | 2.15562925302299 |
| H | -2.98224861298660 | 1.58767718511218 | -0.22053244756378 |
| H | 1.18203018032250 | -1.08431802765384 | 0.78188917332900 |
| C | 1.84948735370952 | 0.60421134276057 | -1.60139097237744 |
| C | 3.28488861153437 | 0.32695495093294 | -1.24099207627485 |

| | | | |
|---|---|---|---|
| H | 1.61546612912558 | 0.98324579618375 | -2.59868741621105 |
| C | 4.21544034306936 | 1.51925098811159 | -1.55565892595024 |
| H | 3.66181375124662 | -0.54078391693267 | -1.80927889802907 |
| N | 5.27033855660631 | 1.44450436755319 | -0.53379204679427 |
| H | 3.67746387835724 | 2.47755785870870 | -1.46758603900964 |
| H | 4.65386547320681 | 1.45565829581138 | -2.56104883262478 |
| C | 4.89764722201540 | 0.68101427975168 | 0.53925207465744 |
| O | 5.48875035218420 | 0.57574391212447 | 1.61619317251221 |
| C | 3.54978592967411 | 0.03697252862833 | 0.25493642305696 |
| C | 2.46667728067535 | 0.54485558444729 | 1.25694261462656 |
| H | 3.64610704179979 | -1.04310879462944 | 0.43582449459445 |
| C | 2.46331730525479 | 2.06497280604828 | 1.44149819035267 |
| H | 2.70472893322977 | 0.09927839537015 | 2.23565295078700 |
| O | 1.61006293434113 | 2.80265084246446 | 1.00698850202317 |
| O | 3.49113434368981 | 2.57038115553959 | 2.15706817501742 |
| H | 4.14539393369536 | 1.87463722893623 | 2.37672286242820 |
| C | 6.41309292358718 | 2.28396222843349 | -0.59558220695555 |
| C | 6.44230523904538 | 3.33455033003984 | -1.52922491587900 |
| C | 7.56355200474394 | 4.16241043144441 | -1.62069465316038 |
| C | 8.66751415295004 | 3.95762868261279 | -0.79038135174313 |
| C | 8.63739684076508 | 2.91062939182150 | 0.13620468442634 |
| C | 7.52525206217205 | 2.07433346410893 | 0.24101832119701 |
| H | 7.50680579203265 | 1.26921728806772 | 0.96969081026823 |
| H | 5.59061144232907 | 3.52151803633061 | -2.18173096562081 |
| H | 7.56582997035750 | 4.97555625331088 | -2.34983959696936 |
| H | 9.54269133574759 | 4.60630099663620 | -0.86419012954625 |
| H | 9.49364773568245 | 2.73534813355844 | 0.79149034690095 |

*exo*-**10a**

E = -1165.99109784066 Eh

Δ(G-E(el)) = 0.28135157 Eh

ΔG = -1165.70974627066

ΔH = -1165.27919993 Eh

TΔS = 0.08633448 Eh

| | | | |
|---|---|---|---|
| C | -2.14662172907369 | -0.00712170968054 | 2.90075773338483 |
| C | -2.83485350716073 | -0.47337059820788 | 1.77363628791645 |
| C | -2.35252466388094 | -0.23677403220771 | 0.47641325865582 |
| C | -1.16503994931625 | 0.47341790959649 | 0.37071031633662 |
| C | -0.45828227042402 | 0.94566455360147 | 1.48128948794341 |

| | | | |
|---|---|---|---|
| C | -0.95085523166108 | 0.71582201464275 | 2.76158702569371 |
| O | -0.54284675563682 | 0.79160603351605 | -0.82875487984639 |
| C | 0.65332981321484 | 1.41325610116285 | -0.51790192531027 |
| C | 0.74327240119438 | 1.69899722374050 | 0.97117504072198 |
| H | -2.54765416922601 | -0.20160482662980 | 3.89745670856365 |
| H | -0.41911112620075 | 1.10166483176937 | 3.63282406170620 |
| H | -3.76533426171119 | -1.03110902390207 | 1.90044724471500 |
| H | -2.87813008458481 | -0.59344702140113 | -0.41030157514140 |
| H | 0.57697738211128 | 2.77957356157687 | 1.12600789147450 |
| C | 1.61815285910394 | 1.72864242076766 | -1.38830753118956 |
| C | 2.86573135243503 | 2.25543336007985 | -0.72887200586938 |
| H | 1.54459209562683 | 1.54638480317937 | -2.46113281850159 |
| C | 4.17725781162065 | 2.20168606134741 | -1.51221456420156 |
| H | 2.72425858985381 | 3.29343531408408 | -0.37047866870846 |
| N | 5.19558736310110 | 2.11713469043888 | -0.44596151342013 |
| H | 4.35497084227590 | 3.09141455987746 | -2.12986748712488 |
| H | 4.22049945695866 | 1.30645142354831 | -2.15681908386665 |
| C | 4.66655114662958 | 1.66003788068185 | 0.73066328631077 |
| O | 5.29289908574465 | 1.44832551539397 | 1.77635297652947 |
| C | 3.19724390705092 | 1.37187454712065 | 0.48875523124668 |
| C | 2.13369935784439 | 1.40343472252786 | 1.61210936213216 |
| H | 3.20285559544359 | 0.33273117051865 | 0.10845645164709 |
| C | 2.33873885078636 | 2.35269446641169 | 2.80866715145461 |
| H | 2.10687896015039 | 0.39968474521362 | 2.06773162323013 |
| O | 1.44491245785077 | 3.06721270298947 | 3.21900183201130 |
| O | 3.50394418309228 | 2.29320447299073 | 3.45015137462214 |
| H | 4.19274791585832 | 1.78929895557691 | 2.92940856248977 |
| C | 6.57066943044993 | 2.34930214087201 | -0.71287022526194 |
| C | 7.02128098470979 | 2.31569384325115 | -2.04354626644593 |
| C | 8.36453276133291 | 2.56251373578956 | -2.33649044902059 |
| C | 9.27360768539163 | 2.84247183325022 | -1.31381626881236 |
| C | 8.82249804995656 | 2.87519834686950 | 0.00948276234456 |
| C | 7.48321945530888 | 2.63373884668010 | 0.31905459189635 |
| H | 7.14280869998846 | 2.65829719529222 | 1.35027086859333 |
| H | 6.33197182696535 | 2.08790376174243 | -2.85617551308371 |
| H | 8.69746754800165 | 2.53079020987050 | -3.37618916765417 |
| H | 10.32323479448083 | 3.03463779800278 | -1.54500197230169 |
| H | 9.52020108434255 | 3.09687545805380 | 0.82015078414015 |

TS-*endo*

| | | | |
|---|---|---|---|
| C | -5.84459421606813 | 0.32084001056462 | 0.81287130700407 |
| C | -5.79396368143176 | 0.89597321199081 | -0.47334414323590 |
| C | -4.67787420906911 | 0.74299881835396 | -1.30208744256483 |
| C | -3.62737621872089 | -0.00985221733815 | -0.79111761789598 |
| C | -3.65301305876755 | -0.60646498618009 | 0.48856889386309 |
| C | -4.77910095437835 | -0.42657982382259 | 1.30904375641139 |
| O | -2.44674926465772 | -0.27794537210708 | -1.43395965942181 |
| C | -1.68846062098949 | -1.05285760358997 | -0.56660695380485 |
| C | -2.38693782973773 | -1.26868123737354 | 0.63987584565511 |
| H | -6.73034692649570 | 0.47703950785557 | 1.43158358267360 |
| H | -4.80556412746031 | -0.85132676548017 | 2.31310841556804 |
| H | -6.64332053451972 | 1.48229927326494 | -0.83046961332142 |
| H | -4.62443253841465 | 1.19172629380271 | -2.29445974643495 |
| H | -2.13896558348267 | -2.01937492010562 | 1.38058528799611 |
| C | -0.35931173352309 | -1.30466565303827 | -0.85276341767893 |
| C | 0.47846552651585 | -1.83332254080033 | 0.15489990974643 |
| H | 0.07345034650742 | -0.81291210561853 | -1.72822820261309 |
| C | 1.97813714236696 | -1.80149775355097 | -0.06909488049589 |
| H | 0.09179182074366 | -2.65116204214685 | 0.76602451893867 |
| N | 2.36386888217823 | -0.38396561713121 | 0.05358952031260 |
| H | 2.25473083728294 | -2.17302517898989 | -1.06331997322688 |
| H | 2.50808018792022 | -2.41135916144964 | 0.68135389799800 |
| C | 1.51651055075683 | 0.37593675909051 | 0.81525765239112 |
| O | 1.56796788523672 | 1.60976526808557 | 0.86789984360441 |
| C | 0.53075160270473 | -0.47988053272859 | 1.57575409076680 |
| C | -0.72034533356917 | -0.05968650799262 | 2.08447096643497 |
| H | 1.06330211337088 | -1.15271355105044 | 2.26045812562141 |
| C | -1.48537086395266 | 1.18665739207578 | 1.87881925386219 |
| H | -1.10381356307573 | -0.62288847703583 | 2.93535989403925 |
| O | -2.53070526367008 | 1.38651672171115 | 2.47927123201761 |
| O | -1.03357747683474 | 2.09364997524393 | 0.98997633207857 |
| H | -0.05334675150366 | 1.99158179309975 | 0.87470497414755 |
| C | 3.49535113044669 | 0.15480978473643 | -0.62505882476547 |
| C | 4.34815516471422 | 1.05313008881431 | 0.03311133290645 |
| C | 5.45534604728979 | 1.57779746616500 | -0.63522138439294 |
| C | 5.73031789215537 | 1.20621044062619 | -1.95543697252947 |
| C | 4.88108845969120 | 0.30843121809768 | -2.60832343212437 |

| | | | |
|---|---|---|---|
| C | 3.76404430253113 | -0.21273159960214 | -1.95098711314211 |
| H | 3.09627439238031 | -0.89468053179985 | -2.47917743917922 |
| H | 4.13654631873024 | 1.34370388605244 | 1.06146286711002 |
| H | 6.11168564228267 | 2.27866758530945 | -0.11480470161202 |
| H | 6.60099817709134 | 1.61484682222739 | -2.47235088727381 |
| H | 5.08030632742555 | 0.01499186176416 | -3.64123909543354 |

TS-*exo*

| | | | |
|---|---|---|---|
| C | -5.86415303969604 | -0.31658120184178 | 1.91575386799617 |
| C | -6.29851369472859 | -1.29309721813849 | 0.99565797002027 |
| C | -5.51170702477050 | -1.67289178391773 | -0.09723238501912 |
| C | -4.28322635415869 | -1.03506661430775 | -0.22494923795399 |
| C | -3.82587976078261 | -0.04877751368242 | 0.67705605225638 |
| C | -4.63020042775606 | 0.31491088717933 | 1.77062018675286 |
| O | -3.35996565858041 | -1.26154170472373 | -1.21474014569598 |
| C | -2.29032939169758 | -0.41135463367824 | -0.96067906519455 |
| C | -2.53059365094077 | 0.35204006430617 | 0.19844051580666 |
| H | -6.50771416983059 | -0.05675676606330 | 2.75859030631714 |
| H | -4.27474004022218 | 1.05126369890458 | 2.49077515106875 |
| H | -7.27141240656632 | -1.76818956822551 | 1.13913509682989 |
| H | -5.83644571128914 | -2.42944447581974 | -0.81247512270562 |
| H | -1.99079827679209 | 1.24592301414972 | 0.48565955748280 |
| C | -1.09565964228089 | -0.57168435876174 | -1.64622865205501 |
| C | 0.04300113637638 | 0.07998149151910 | -1.13459805290572 |
| H | -1.00475105113525 | -1.39643962051087 | -2.35737867036966 |
| C | 1.41679182901075 | -0.10885428355112 | -1.72231867709237 |
| H | -0.11164198649283 | 1.09000100471114 | -0.74099070824209 |
| N | 2.35309835018541 | 0.11506729927853 | -0.60801501844772 |
| H | 1.63420990163715 | 0.62659399621434 | -2.51093002266328 |
| H | 1.52903872607497 | -1.11986791837101 | -2.14981206535998 |
| C | 1.81010341821034 | -0.06786742612131 | 0.63591128758528 |
| O | 2.37530177215779 | 0.23328475520849 | 1.69306045078084 |
| C | 0.44673597338517 | -0.72956977805535 | 0.56898416292989 |
| C | -0.58259219404365 | -0.61054245614784 | 1.53426333807404 |
| H | 0.56107438748512 | -1.75138532452084 | 0.18674411528499 |
| C | -0.76883859214502 | 0.40037211852895 | 2.59876015462119 |
| H | -1.26273567913355 | -1.45393291271673 | 1.64075329770673 |
| O | -1.79672972423012 | 0.45917620331340 | 3.25655186117554 |
| O | 0.22035627427691 | 1.28878976005786 | 2.82748953009881 |

| | | | |
|---|---|---|---|
| H | 1.08062244186191 | 0.93303119160960 | 2.48839634218713 |
| C | 3.70155601260342 | 0.48518912650959 | -0.87525125637912 |
| C | 4.27018979253587 | 0.10122676969515 | -2.10229487110181 |
| C | 5.58263704032103 | 0.46203554700486 | -2.41390533194280 |
| C | 6.34654521887848 | 1.20410173225534 | -1.50988043926171 |
| C | 5.78013211827773 | 1.58315658613228 | -0.28937221257687 |
| C | 4.46772028340253 | 1.23390240159727 | 0.03541559932144 |
| H | 4.03750327409470 | 1.53256006004189 | 0.98635381177372 |
| H | 3.69839213263866 | -0.49384373528215 | -2.81439181390210 |
| H | 6.00790025605018 | 0.15249465482132 | -3.37108014919186 |
| H | 7.37291108143166 | 1.48515151729664 | -1.75420924741809 |
| H | 6.36280705637672 | 2.16743541410211 | 0.42636048940897 |

4a*R*,10a*S*-**22**

E = -1165.991498272532 Eh

ΔG = -1165.71040754253 Eh

ΔH = -1165.27827679 Eh

TΔS = 0.08686889 Eh

| | | | |
|---|---|---|---|
| C | -1.62783631622042 | -2.46315990413617 | 0.46612180089343 |
| C | -0.73145472579292 | -3.46163990168711 | 0.88177488633455 |
| C | 0.43546693229070 | -3.14914554602165 | 1.59110708200089 |
| C | 0.67144762196513 | -1.80524781763993 | 1.87148974693753 |
| C | -0.21412633054658 | -0.79154671981181 | 1.46362861450369 |
| C | -1.37188073622350 | -1.11781797139969 | 0.75112210845494 |
| O | 1.76137430201410 | -1.33528487051233 | 2.54206117182296 |
| C | 1.58241283735214 | 0.09558159751926 | 2.73482304769125 |
| C | 0.38815425077406 | 0.46939747215413 | 1.87902068930578 |
| H | -2.52977491661678 | -2.74097131905490 | -0.08247696137635 |
| H | -2.06352013648057 | -0.33646175559300 | 0.42845721572670 |
| H | -0.94756108466425 | -4.50726831094428 | 0.65082459417627 |
| H | 1.13702712178301 | -3.91818215629209 | 1.91668699716012 |
| H | 1.38193159117517 | 0.24382562299890 | 3.80991755227015 |
| C | 0.13751878403979 | 1.74676350317374 | 1.55404771564172 |
| C | 1.06499275189420 | 2.81275551446224 | 2.05348155548552 |
| H | -0.70456178556534 | 2.02111704354648 | 0.91549558159705 |
| C | 0.77194009318337 | 3.29214255791520 | 3.49244844853844 |
| H | 1.00289311280001 | 3.69561746456604 | 1.39996144755762 |
| N | 2.06726278968398 | 3.80262224372771 | 3.96095891646453 |

| | | | |
|---|---|---|---|
| H | 0.42445754174923 | 2.46718606679158 | 4.13613153924544 |
| H | 0.01749829480201 | 4.08993365544157 | 3.51657714171515 |
| C | 3.10212612649616 | 3.31480593036795 | 3.21541136129451 |
| O | 4.30121998023143 | 3.56977430923651 | 3.36822477981535 |
| C | 2.56420837368658 | 2.40004713279195 | 2.12026521368610 |
| C | 2.84656282346371 | 0.86669141419959 | 2.33361052907678 |
| H | 3.07615326935220 | 2.69349391270847 | 1.19477733651161 |
| C | 4.02154238731445 | 0.48775206619713 | 3.25576317271198 |
| H | 3.13973370474407 | 0.47238857085646 | 1.34625393921467 |
| O | 3.93963788365590 | -0.42087435025980 | 4.04994147093006 |
| O | 5.18937111287570 | 1.12412799761098 | 3.05864842250707 |
| H | 5.03117225737442 | 2.08151396742395 | 2.85668454940827 |
| C | 2.17157370626422 | 4.61502538424871 | 5.12044083934522 |
| C | 1.07350290988835 | 4.69267337289809 | 5.99516190577426 |
| C | 1.14128940077321 | 5.49181966989734 | 7.13838205879261 |
| C | 2.29695706983580 | 6.22112943442366 | 7.42717472038520 |
| C | 3.38791716777537 | 6.14147019339521 | 6.55630039850411 |
| C | 3.33704569134647 | 5.34887640532797 | 5.40852762793852 |
| H | 4.19119794686794 | 5.28708486595563 | 4.74087336313738 |
| H | 0.16577366696151 | 4.12352084493713 | 5.79778267612425 |
| H | 0.27934462208626 | 5.53754276331660 | 7.80757016937482 |
| H | 2.34759634978414 | 6.84495469408908 | 8.32179690483018 |
| H | 4.29872155582552 | 6.70635495117342 | 6.76716766848954 |

4a*S*,10a*R*-**22**

E = -1165.990759455858 Eh

Δ(G-E(el)) = 0.28164987 Eh

ΔG = -1165.70910958585 Eh

ΔH = -1165.27673340 Eh

TΔS = 0.08650644 Eh

| | | | |
|---|---|---|---|
| C | -1.65424778117902 | -2.79226755753372 | 0.55943685160561 |
| C | -0.58854335974098 | -3.47991827010762 | -0.04233611688363 |
| C | 0.71303968557141 | -2.96093671279963 | -0.03573777945190 |
| C | 0.90916105379484 | -1.73372533654834 | 0.59054832473708 |
| C | -0.14714607368064 | -1.02656617131858 | 1.19844262526401 |
| C | -1.43773886563020 | -1.56265542058896 | 1.19101025232504 |
| O | 2.11803372725928 | -1.10294655587660 | 0.69357328697787 |
| C | 1.85575056176295 | 0.21102332257608 | 1.23565276962674 |
| C | 0.44534941004250 | 0.15501821593814 | 1.82142586059008 |

| | | | |
|---|---|---|---|
| H | -2.65745845466437 | -3.22200174621494 | 0.53516465461170 |
| H | -2.26188009888139 | -1.02681073283578 | 1.66711425678892 |
| H | -0.77428772137493 | -4.44031142427075 | -0.52853328593415 |
| H | 1.54742739222573 | -3.49117381692015 | -0.49656145564514 |
| H | 1.84025333280673 | 0.89913294934201 | 0.36935230061243 |
| C | -0.00145142780878 | 0.98589763176434 | 2.78210520231337 |
| C | 1.00090026012441 | 1.82951965181883 | 3.51549292641556 |
| H | -1.01452044054847 | 0.88594051087048 | 3.18117540533645 |
| C | 0.74391048762449 | 3.27151185649774 | 3.96901193817076 |
| H | 1.25743755688724 | 1.27626361351022 | 4.44251336950019 |
| N | 2.12282182759553 | 3.72758447799881 | 4.28087594077597 |
| H | 0.11805066932697 | 3.34266398074789 | 4.86756745684733 |
| H | 0.29844601873230 | 3.88539731488214 | 3.16714870750164 |
| C | 3.06234516844479 | 2.95631767090824 | 3.63629782449605 |
| O | 4.28776815228323 | 2.98958464155470 | 3.76118571983578 |
| C | 2.28979851689218 | 2.03210452991553 | 2.71960018601312 |
| C | 2.92097456532829 | 0.73490544058946 | 2.19917511006016 |
| H | 2.04131994465336 | 2.64767754155496 | 1.83310302242382 |
| C | 3.26455644060952 | -0.21338636469946 | 3.34330069072564 |
| H | 3.84923306451982 | 0.96814269662008 | 1.65382405735463 |
| O | 2.68611478460293 | -1.24907557415018 | 3.57226199488316 |
| O | 4.27996994966708 | 0.20134354720606 | 4.12751698452777 |
| H | 4.56348251031250 | 1.11229954037408 | 3.88109960646533 |
| C | 2.37047830196346 | 4.85421970599879 | 5.10402177004288 |
| C | 1.32072718476835 | 5.75234834474479 | 5.36497107367004 |
| C | 1.53484512894971 | 6.86480040601597 | 6.18175130773300 |
| C | 2.79158198133078 | 7.10189958269888 | 6.74353101490903 |
| C | 3.83542203583877 | 6.21010079783970 | 6.47787555758628 |
| C | 3.63812315273579 | 5.09085411169079 | 5.66759445401114 |
| H | 4.45342636045215 | 4.40260801916313 | 5.46343804559235 |
| H | 0.33631241984777 | 5.59590644781094 | 4.92441437493334 |
| H | 0.70744115649414 | 7.55159644278002 | 6.37325047790027 |
| H | 2.95646159354683 | 7.97255550200612 | 7.38135934872935 |
| H | 4.82378982651290 | 6.38057718844574 | 6.91069388602081 |

**18a**

E = -1165.958835982159 Eh

Δ(G-E(el)) = 0.27131123 Eh

ΔG = -1165.68752475215 Eh

ΔH = -1165.23829594 Eh

TΔS = 0.09450579 Eh

| | | | |
|---|---|---|---|
| C | -2.45169247202838 | 0.48314908825141 | 1.21740111793762 |
| C | -2.41293268900754 | -0.25692992778162 | 0.01748983530828 |
| C | -1.20431116126655 | -0.71129629689069 | -0.51696686636227 |
| C | -0.05407641381238 | -0.39636795169123 | 0.20002516537501 |
| C | -0.06104361508372 | 0.33688794575840 | 1.40201256139635 |
| C | -1.28554538315092 | 0.79058576967364 | 1.91867423402082 |
| O | 1.23265507899530 | -0.73543445841700 | -0.13869846241075 |
| C | 2.04095716254049 | -0.21637575028463 | 0.84102008624878 |
| C | 1.33284596582452 | 0.45028773478492 | 1.80512031711349 |
| H | -3.41576057176308 | 0.82392620815238 | 1.60100146360251 |
| H | -1.32392254431075 | 1.37344291063234 | 2.84120349185264 |
| H | -3.34498505657022 | -0.47824128978610 | -0.50652032954571 |
| H | -1.15656585621324 | -1.28127229250814 | -1.44570738312426 |
| H | 3.10096242438368 | -0.42544452815473 | 0.72866326216950 |
| C | 1.82803958265459 | 1.13602866472959 | 2.99291427195950 |
| C | 3.05890757064195 | 1.64839214467564 | 3.15727684740051 |
| H | 1.10278940826271 | 1.25186731531490 | 3.80660051840878 |
| C | 3.47452277436515 | 2.38369279823511 | 4.39827717876943 |
| H | 3.78870800426494 | 1.60984338081851 | 2.34067243689489 |
| N | 3.54253210991389 | 3.84585978003288 | 4.16438474980645 |
| H | 4.44177896091175 | 2.03717396340013 | 4.78337727463489 |
| H | 2.73766635131039 | 2.23030428814299 | 5.19845688879149 |
| C | 4.64132535169282 | 4.54767125091710 | 3.76935161085563 |
| O | 4.55117006208234 | 5.77810030934577 | 3.58634158556307 |
| C | 5.90519334735552 | 3.79355367109760 | 3.55917315455714 |
| C | 7.13205916819010 | 4.29048831172844 | 3.30036161178865 |
| H | 5.83893381744049 | 2.70650902126147 | 3.59515409673454 |
| C | 7.68287172657859 | 5.68672353299386 | 3.17464816935142 |
| H | 7.93581133386452 | 3.56144204960474 | 3.16667183876016 |
| O | 8.88886302847284 | 5.81463620332020 | 3.04578777759382 |
| O | 6.86583894938585 | 6.72815828742005 | 3.19921916287734 |
| H | 5.90876745022455 | 6.41931568785931 | 3.32056088963806 |
| C | 2.27755047884661 | 4.53339350829610 | 4.22321905336246 |
| C | 1.54201247775956 | 4.74178544369925 | 3.05290477580418 |
| C | 0.28983860980080 | 5.35750216773345 | 3.12641424540299 |
| C | -0.22392780754277 | 5.75945483993139 | 4.36395750557115 |

| | | | |
|---|---|---|---|
| C | 0.51787093391762 | 5.54828663080511 | 5.53087617201767 |
| C | 1.77134969471115 | 4.93391715664743 | 5.46245315272428 |
| H | 2.36407384085641 | 4.76580775377884 | 6.36370767430561 |
| H | 1.95362482234605 | 4.41969600823402 | 2.09589698289251 |
| H | -0.28649129064524 | 5.52080184409031 | 2.21337190085103 |
| H | -1.20335830748912 | 6.23950630020343 | 4.41883683020910 |
| H | 0.12243268128864 | 5.86569052394327 | 6.49804314889110 |

*endo*-**17b**

E = -1165.998184730573 Eh

Δ(G-E(el)) = 0.28164818 Eh

ΔG = -1165.71653655057 Eh

ΔH = -1165.28387782 Eh

TΔS = 0.08675718 Eh

| | | | |
|---|---|---|---|
| C | -2.00749729956813 | -2.58127110103914 | 1.13943627145689 |
| C | -0.93553569926520 | -3.47767417353920 | 1.00957274004631 |
| C | 0.39273073069028 | -3.03011529099260 | 0.98362234497235 |
| C | 0.60724628094431 | -1.65979087553905 | 1.09104782427526 |
| C | -0.45407521953071 | -0.74439249852956 | 1.22104840236611 |
| C | -1.77189685236350 | -1.20603319010467 | 1.25137509613136 |
| O | 1.84059345776211 | -1.06715249255654 | 1.08965699118638 |
| C | 1.62545665731874 | 0.36458547736821 | 1.08248316585572 |
| C | 0.15101497279027 | 0.57559853215329 | 1.37244276873664 |
| H | -3.03102749826758 | -2.96058766398841 | 1.15438385108553 |
| H | -2.60186455461049 | -0.50397315590936 | 1.35765087012834 |
| H | -1.13642150203669 | -4.54809655867083 | 0.92508652153366 |
| H | 1.23159794959099 | -3.72059317684899 | 0.88719392576488 |
| H | 1.86880091940905 | 0.71617554970463 | 0.06340972848220 |
| C | -0.32934231178688 | 1.75543833529455 | 1.78904057590673 |
| C | 0.58473350564800 | 2.92124351984841 | 2.05516983658922 |
| H | -1.39226237103845 | 1.88034146840494 | 2.01499640514099 |
| C | 0.43264544382497 | 3.47981254100748 | 3.48815793140619 |
| H | 0.35885989433474 | 3.74478802901421 | 1.35578862200661 |
| N | 1.77338133193437 | 3.97222378457852 | 3.83738969265973 |
| H | 0.12951838014675 | 2.68878588123780 | 4.19391021714520 |
| H | -0.29993509528250 | 4.29668888967801 | 3.54348977788723 |
| C | 2.74660696289769 | 3.45186348681337 | 3.02689883644445 |
| O | 3.96592551667105 | 3.54822024280892 | 3.17459256956427 |
| C | 2.09581010034690 | 2.61964086943336 | 1.93241260255513 |

| | | | |
|---|---|---|---|
| C | 2.50973504262381 | 1.12115295379985 | 2.06310340112634 |
| H | 2.49015983660487 | 2.96434085680269 | 0.96573973647025 |
| C | 2.40330196842979 | 0.57506770026157 | 3.49042251092029 |
| H | 3.56594048391588 | 1.04885364606969 | 1.76083586883805 |
| O | 1.53437813819165 | -0.16842075829194 | 3.87899783232686 |
| O | 3.37784251005060 | 0.97666856106787 | 4.33546928324149 |
| H | 3.95362324121130 | 1.64737958625981 | 3.91401018507337 |
| C | 1.99549806007979 | 4.70902435992510 | 5.03024882252576 |
| C | 0.96210730555494 | 4.80538545991685 | 5.97859729328420 |
| C | 1.15095089644417 | 5.53901272049759 | 7.15205395598584 |
| C | 2.36359236248135 | 6.18639958911949 | 7.39785984983109 |
| C | 3.38951692533340 | 6.09124226349553 | 6.45236439504411 |
| C | 3.21798056553809 | 5.36225382376948 | 5.27489241580860 |
| H | 4.02333259129786 | 5.28625193091267 | 4.55041433614045 |
| H | 0.01000808940109 | 4.30253200875537 | 5.81571520581265 |
| H | 0.33730672250586 | 5.59880913561835 | 7.87818899380343 |
| H | 2.50846963477521 | 6.75917678135616 | 8.31603449945116 |
| H | 4.34367192500021 | 6.59318295103649 | 6.62813384498858 |

*exo*-**22**

E = -1165.993877178734 Eh

Δ(G-E(el)) = 0.28131919 Eh

ΔG = -1165.71255798873 Eh

ΔH = -1165.28054987 Eh

TΔS = 0.08657536 Eh

| | | | |
|---|---|---|---|
| C | -1.82311022512163 | -1.98983068131155 | -0.02179628174604 |
| C | -0.77232933262873 | -2.51971908377412 | -0.78786130392912 |
| C | 0.56765960321843 | -2.28120025892219 | -0.45532575593214 |
| C | 0.81868727126536 | -1.49798029851555 | 0.66846625966006 |
| C | -0.22190334862394 | -0.95835182810297 | 1.45061365895191 |
| C | -1.55366913034655 | -1.19918599568192 | 1.10045433532631 |
| O | 2.06395889328152 | -1.15802116632089 | 1.11392868766865 |
| C | 1.88890443213436 | -0.50232856509954 | 2.40252048051017 |
| C | 0.41362044458412 | -0.14164831389687 | 2.47978750928847 |
| H | -2.85671993474776 | -2.19825827836519 | -0.30455534972455 |
| H | -2.36702065613780 | -0.78159309844349 | 1.69803177557258 |
| H | -1.00089285699039 | -3.13543670299196 | -1.66073849332003 |
| H | 1.38930419581273 | -2.68891660834064 | -1.04568147515203 |
| H | 2.10608880230415 | -1.26391632955895 | 3.17003295976704 |

| | | | |
|---|---|---|---|
| C | -0.04595565053663 | 0.79542286478064 | 3.32859374779137 |
| C | 0.99972209113701 | 1.60458838804391 | 4.04468684653047 |
| H | -1.10991572338833 | 1.02209305601531 | 3.43050437635696 |
| C | 0.64196511384221 | 3.01516101162615 | 4.51861933832367 |
| H | 1.41821997009806 | 1.05116129743402 | 4.90764651325053 |
| N | 1.94613185334177 | 3.71112690047816 | 4.49893168715391 |
| H | 0.21971142818429 | 3.04163847751127 | 5.53140032188947 |
| H | -0.06460162031410 | 3.50409175858778 | 3.82556246710175 |
| C | 2.85047690443477 | 3.07878360044183 | 3.68715811968574 |
| O | 4.01061109620735 | 3.43651475805644 | 3.45569601746139 |
| C | 2.14363880910839 | 1.89391432502056 | 3.06013494327693 |
| C | 2.91066535675910 | 0.63851594317519 | 2.60975418906367 |
| H | 1.67336145123323 | 2.31351507014380 | 2.15037740426829 |
| C | 4.03581363674540 | 0.17729845986249 | 3.55923859126123 |
| H | 3.39120903738002 | 0.84667712221721 | 1.64119256569141 |
| O | 4.05206036803707 | -0.91446924782172 | 4.08752826690585 |
| O | 5.04550238164689 | 1.03283075469380 | 3.73890269377736 |
| H | 4.81606123173959 | 1.94077726099898 | 3.40446019092228 |
| C | 2.13402592287318 | 4.95450955376112 | 5.15740936004820 |
| C | 1.00611767006931 | 5.69752441729349 | 5.54619023052353 |
| C | 1.16276860808688 | 6.91399302611628 | 6.21450630312899 |
| C | 2.43775710964999 | 7.40689266634444 | 6.50103428230215 |
| C | 3.55832118887493 | 6.66622968381299 | 6.11185381592059 |
| C | 3.41960636780339 | 5.44753527656842 | 5.44607134368051 |
| H | 4.29540882157541 | 4.88029459455149 | 5.14447613999754 |
| H | 0.00197407910275 | 5.33822430979014 | 5.32264098859964 |
| H | 0.27508734132247 | 7.47850113706495 | 6.50807856296677 |
| H | 2.55780801968971 | 8.35824781167629 | 7.02310221486332 |
| H | 4.56218897729196 | 7.03658293108033 | 6.33146147031505 |

TS-*endo*

| | | | |
|---|---|---|---|
| C | -2.89156192631883 | -3.80641754542009 | -1.18404906600287 |
| C | -2.11559807865534 | -4.87827397727493 | -1.66594466807057 |
| C | -0.83981374244491 | -4.67106829603988 | -2.19975558468649 |
| C | -0.39288498395048 | -3.35702060583554 | -2.23416974715767 |
| C | -1.14134463182677 | -2.26726038395672 | -1.75934614950872 |
| C | -2.41445372445447 | -2.49483056488294 | -1.22040350454118 |
| O | 0.82789128758606 | -2.93357736759916 | -2.72531403978541 |
| C | 0.91250782871683 | -1.59744678441060 | -2.48129384519452 |

| | | | |
|---|---|---|---|
| C | -0.29897543786755 | -1.09019242610506 | -1.94724400849146 |
| H | -3.88140914415260 | -4.00820753323804 | -0.76977094691233 |
| H | -3.01707176761722 | -1.66828864179672 | -0.83872888166343 |
| H | -2.51397720726633 | -5.89368266028431 | -1.61666977606112 |
| H | -0.21792437056378 | -5.48979493046250 | -2.56186818506698 |
| H | 1.69378764800588 | -1.08690011972594 | -3.03295176173206 |
| C | -0.45065172389053 | 0.21084290612445 | -1.47405364611357 |
| C | 0.64137179808417 | 1.09528365686228 | -1.50647179997943 |
| H | -1.31164369106145 | 0.43891533613923 | -0.83872471226387 |
| C | 0.60940022291584 | 2.37356655232172 | -0.70030354971792 |
| H | 1.28583207371102 | 1.09314560608831 | -2.38755153175070 |
| N | 0.70336160708191 | 1.96900044898171 | 0.71606920748689 |
| H | -0.32987740327809 | 2.93068193063869 | -0.83198410877897 |
| H | 1.44351196566258 | 3.03583580775646 | -0.98355152414803 |
| C | 1.31900930098707 | 0.76532580470611 | 0.94189826523231 |
| O | 1.33532247994264 | 0.20468900654778 | 2.04557069848621 |
| C | 2.00422649936874 | 0.21641018611727 | -0.28543397484590 |
| C | 2.25878157903598 | -1.14485842512518 | -0.57300583211712 |
| H | 2.80081863320270 | 0.89250702841547 | -0.61932121851447 |
| C | 1.79817867679224 | -2.37706734424421 | 0.11841354168501 |
| H | 3.12677795368009 | -1.34753986534910 | -1.20062716979773 |
| O | 2.11690030501374 | -3.48053841853091 | -0.29330956897325 |
| O | 0.99558549460553 | -2.26472078244591 | 1.19259147438743 |
| H | 1.09264895946851 | -1.36389676874546 | 1.59661197876039 |
| C | 0.16705750948480 | 2.81059964426756 | 1.73054061686121 |
| C | -0.42609148149899 | 2.28910778598651 | 2.89271031875704 |
| C | -0.96360267322990 | 3.15926304148402 | 3.84342815334402 |
| C | -0.92762389291648 | 4.54415166603483 | 3.65318861331562 |
| C | -0.34198506461605 | 5.05972190198235 | 2.49417085506435 |
| C | 0.20595304933299 | 4.20168021022338 | 1.53808080195532 |
| H | 0.67632941821641 | 4.61969301632331 | 0.64735960024458 |
| H | -0.45965457849753 | 1.21444208432994 | 3.04741783240051 |
| H | -1.42343731173949 | 2.74240840219375 | 4.74231849027389 |
| H | -1.35332177238015 | 5.21554722374309 | 4.40167299296169 |
| H | -0.30234968266881 | 6.13876419420494 | 2.32980536065928 |
| TS-*exo* | | | |
| C | -2.34448364881461 | -4.28472736367079 | -3.44830772878130 |
| C | -1.18263893421860 | -4.76379958834074 | -4.08370081418174 |

| | | | |
|---|---|---|---|
| C | 0.09312250430199 | -4.41532873936369 | -3.62751197754900 |
| C | 0.14667585981289 | -3.58305785407393 | -2.51564878175966 |
| C | -0.99512188134717 | -3.08975417043165 | -1.86029118057270 |
| C | -2.26507759550679 | -3.44336526364646 | -2.33656554358795 |
| O | 1.29633467015692 | -3.12968654684396 | -1.90527136051675 |
| C | 0.91270695878203 | -2.27506175406511 | -0.90745995752462 |
| C | -0.50060504398727 | -2.24845327897804 | -0.77612879517573 |
| H | -3.32325087247392 | -4.57652883889864 | -3.83457095844619 |
| H | -3.16937528720985 | -3.07434852847327 | -1.84816729841953 |
| H | -1.27748277381799 | -5.41916828040010 | -4.95195075115117 |
| H | 1.00268457999253 | -4.77354384106465 | -4.11067911972900 |
| H | 1.67760171050479 | -2.09012304105225 | -0.16049216993699 |
| C | -1.18635312286636 | -1.33943313405171 | 0.03043294590164 |
| C | -0.44418429937268 | -0.39547705880203 | 0.74853908595835 |
| H | -2.25937463595453 | -1.19592745864697 | -0.12582187827377 |
| C | -1.02268973559892 | 0.79314853594558 | 1.46435353002878 |
| H | 0.50772681466289 | -0.73004850923055 | 1.17352965819197 |
| N | 0.01315794874596 | 1.84187374259157 | 1.38607560472094 |
| H | -1.21899342173127 | 0.59161092755551 | 2.52835345849256 |
| H | -1.96772587667506 | 1.11558830629465 | 0.99466730886016 |
| C | 0.89623564484179 | 1.72135883222469 | 0.34279283104668 |
| O | 1.93653858119373 | 2.38523077923908 | 0.24666199223914 |
| C | 0.43397597818992 | 0.72610049324640 | -0.69275231697400 |
| C | 1.22972107723789 | -0.03982457075827 | -1.57771016880913 |
| H | -0.52454552673742 | 1.04355118096349 | -1.11698429452491 |
| C | 2.71177434743054 | -0.17390973322831 | -1.65168096423616 |
| H | 0.76304271487150 | -0.31902439697411 | -2.52262639744152 |
| O | 3.23496902369741 | -0.90450144609710 | -2.47430081249606 |
| O | 3.47219664407845 | 0.50884980949918 | -0.77589979154232 |
| H | 2.96269860363669 | 1.26938159816456 | -0.38978775215235 |
| C | 0.05037375385965 | 2.86941767330302 | 2.37165292017299 |
| C | -1.16368184640546 | 3.29802223533161 | 2.93432582510206 |
| C | -1.17162268654580 | 4.28350574808054 | 3.92349300571479 |
| C | 0.02582017975674 | 4.85662131039683 | 4.35929720123200 |
| C | 1.23247744435664 | 4.43000124063126 | 3.79667228469619 |
| C | 1.25634199268290 | 3.44107422137883 | 2.81081501510510 |
| H | 2.19816010777360 | 3.11444310197246 | 2.37977279864340 |
| H | -2.10816482308800 | 2.87446248383293 | 2.59126309559187 |

| | | | |
|---|---|---|---|
| H | -2.12441049268326 | 4.60696764027388 | 4.34826272736851 |
| H | 0.01892420618303 | 5.62856551891198 | 5.13145575589979 |
| H | 2.17652115828448 | 4.86531801725428 | 4.13189376881563 |

**Table S51.** Some bond lengths of key carbon atoms in transition complexes [Å].

| | | C9B-C10 | C3A-C10A | C4A-C4 |
|---|---|---|---|---|
| **16a→17a** | Pre-TS-*endo* | 2.922 | 2.554 | 1.434 |
| | TS-*endo* | 2.515 | 1.963 | 1.383 |
| **16a→10a** | Pre-TS-*exo* | 2.923 | 2.530 | 1.438 |
| | TS-*exo* | 2.550 | 1.929 | 1.387 |
| | | C4A-C4 | C3A-C10A | C10-C10A |
| **18a→17b** | Pre-TS-*endo* | 2.856 | 2.540 | 1.444 |
| | TS-*endo* | 2.379 | 2.030 | 1.392 |
| **18a→22** | Pre-TS-*exo* | 2.852 | 2.540 | 1.449 |
| | TS-*exo* | 2.355 | 2.026 | 1.395 |

**Table S52.** Visualization of calculated structures of pre-reaction complexes and transition states.

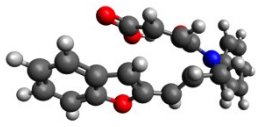
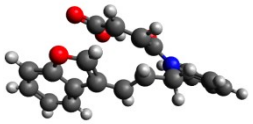
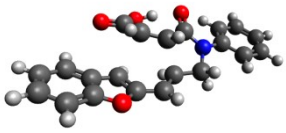
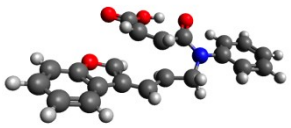
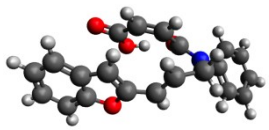
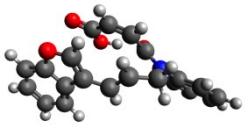
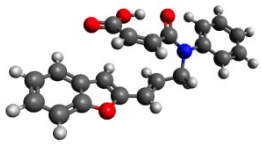
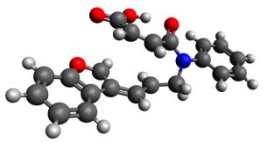
| | **Structures** | | **Structures** |
|---|---|---|---|
| TS-*endo*$_{\mathbf{IMDAV16a→17a}}$ |  | TS-*endo*$_{\mathbf{IMDAV18a→17b}}$ |  |
| TS-*exo*$_{\mathbf{IMDAV16a→10a}}$ |  | TS-*exo*$_{\mathbf{IMDAV18a→22}}$ |  |
| IRC-*endo*$_{\mathbf{IMDAV16a→17a}}$ |  | IRC-*endo*$_{\mathbf{IMDAV18a→17b}}$ |  |
| IRC-*exo*$_{\mathbf{IMDAV16a→10a}}$ |  | IRC-*exo*$_{\mathbf{IMDAV18a→22}}$ |  |

**Table S53.** Bond advancement indices

| 1 | | C9B-C10 | C3A-C10A |
|---|---|---|---|
| **16a→17a** | Pre-TS-*endo* | 0.838 | 0.699 |
| | TS-*endo* | 0.358 | 0.731 |
| **16a→10a** | Pre-TS-*exo* | 0.854 | 0.688 |

| | | | |
|---|---|---|---|
| | TS-*exo* | 0.364 | 0.748 |
| | | C4A-C4 | C3A-C10A |
| **18a→17b** | Pre-TS-*endo* | 0.799 | 0.749 |
| | TS-*endo* | 0.465 | 0.689 |
| **18a→22** | Pre-TS-*exo* | 0.789 | 0.746 |
| | TS-*exo* | 0.496 | 0.678 |

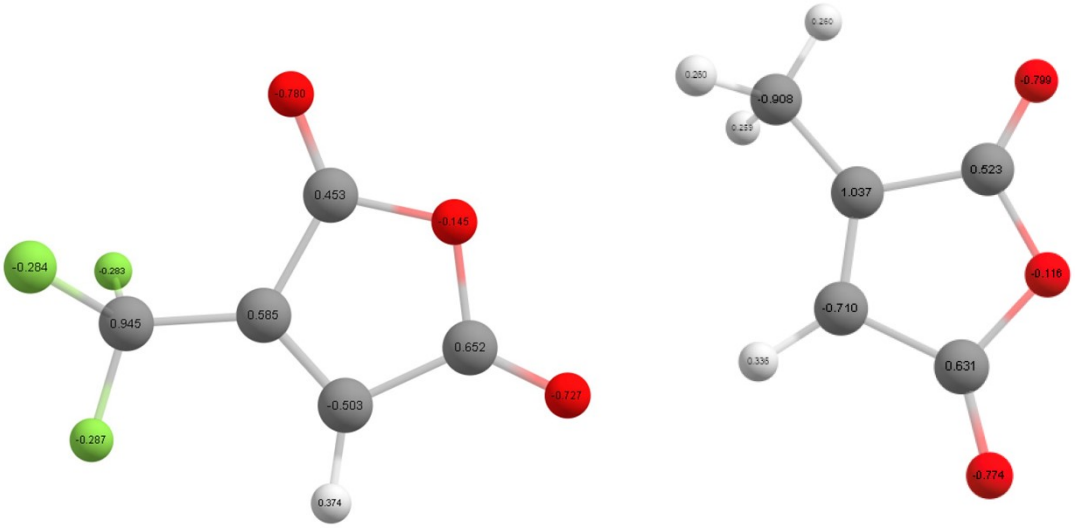



**Figure S11.** The Mulliken charge distribution calculation (M062X/aug-cc-pVTZ) [10-13] of methyl- and trifluoromethyl-substituted maleic anhydrides.

## 4. References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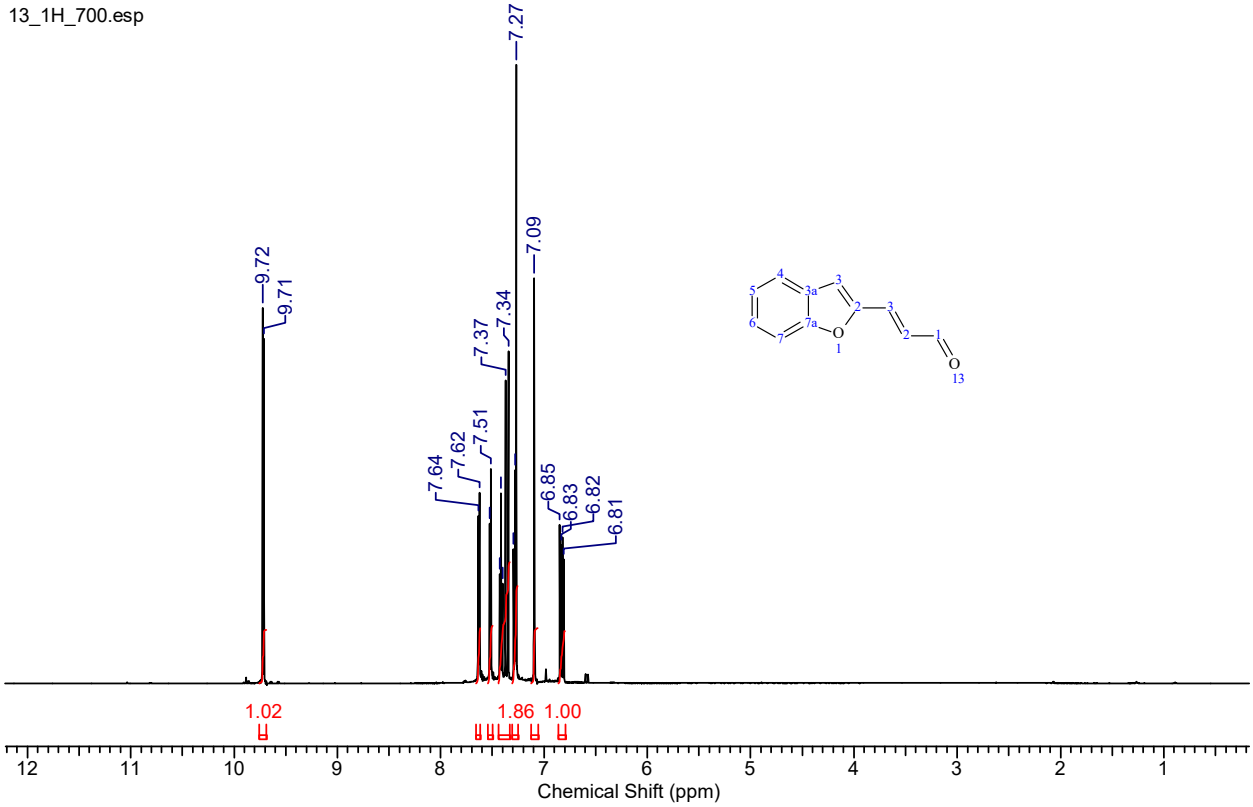
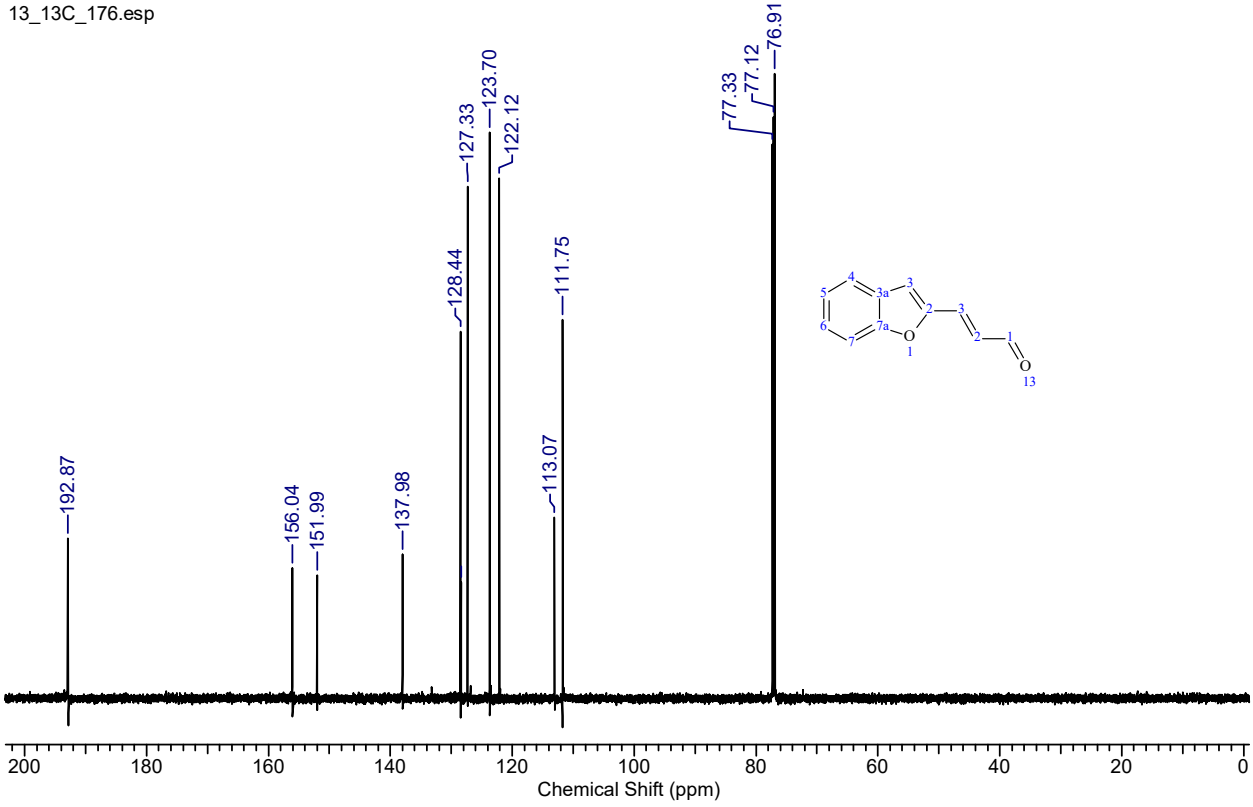
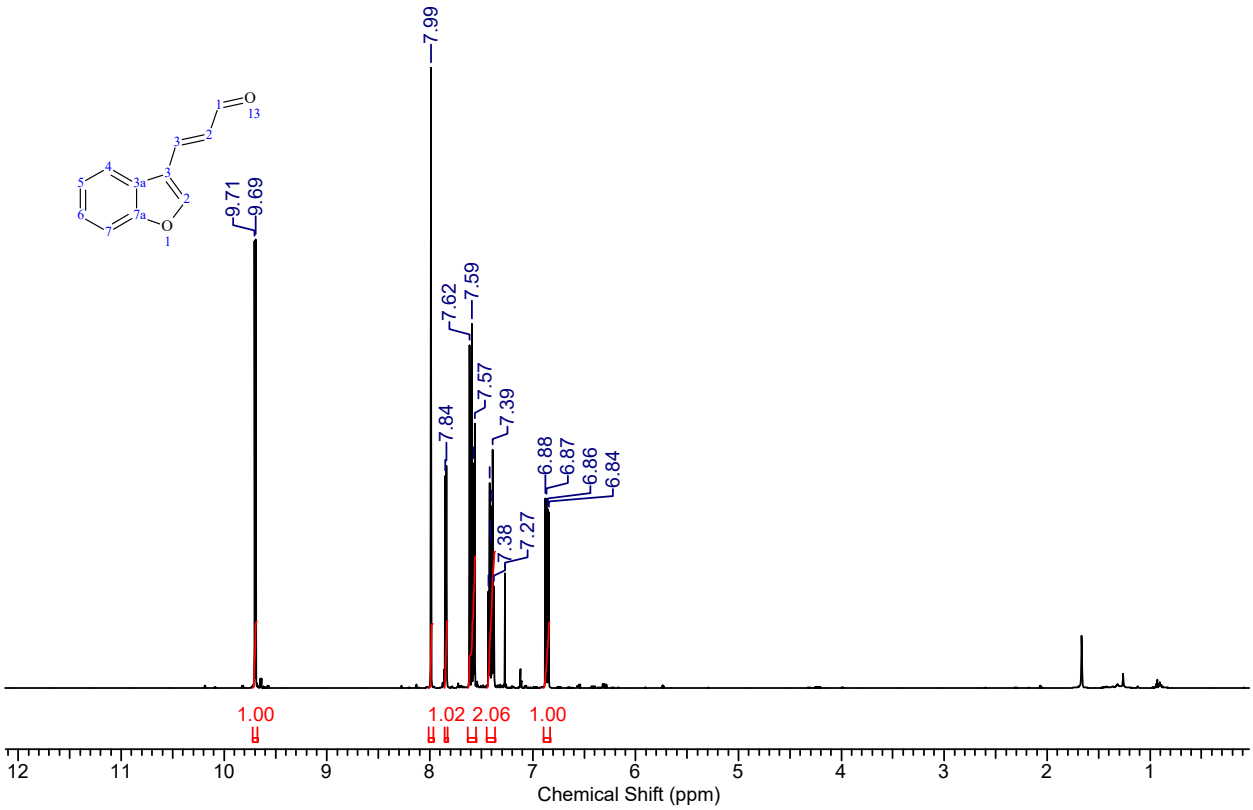
## 5. Copies of NMR spectra

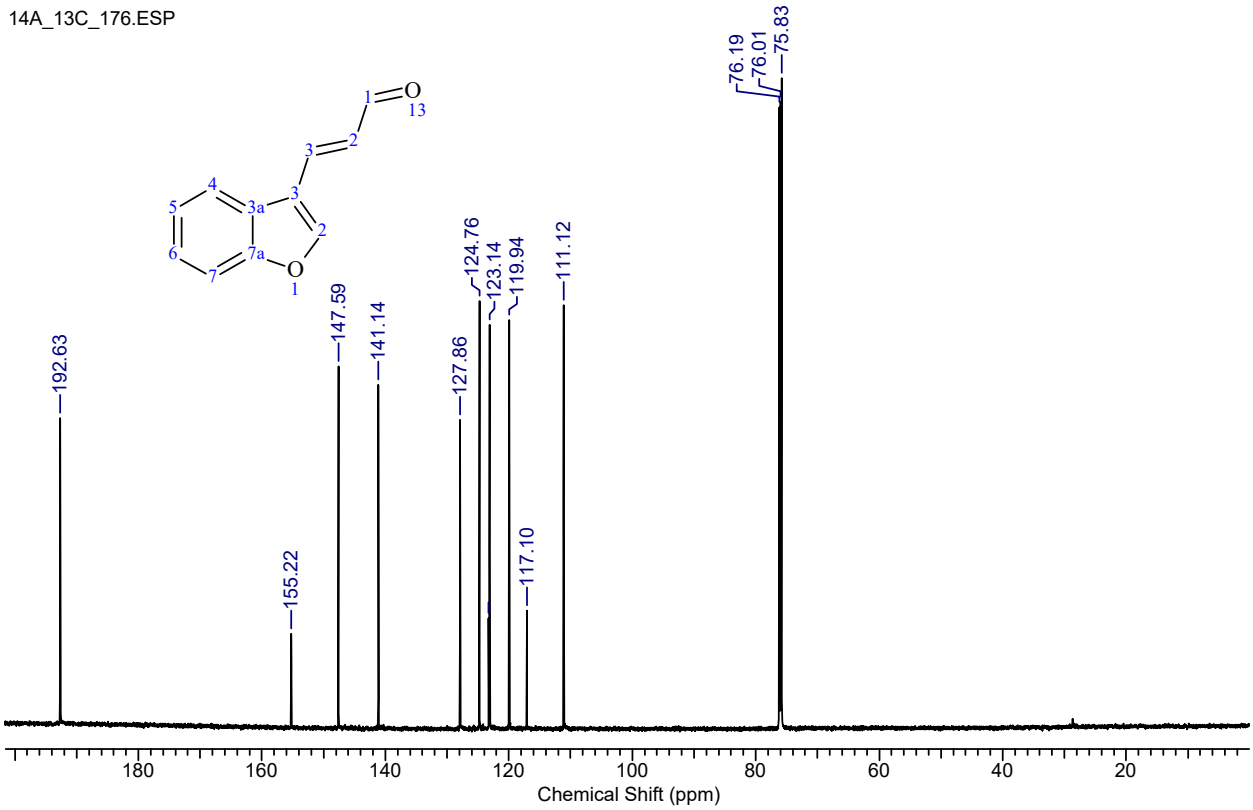
### (*E*)-3-(Benzo[*b*]furan-2-yl)acrylaldehyde (13).



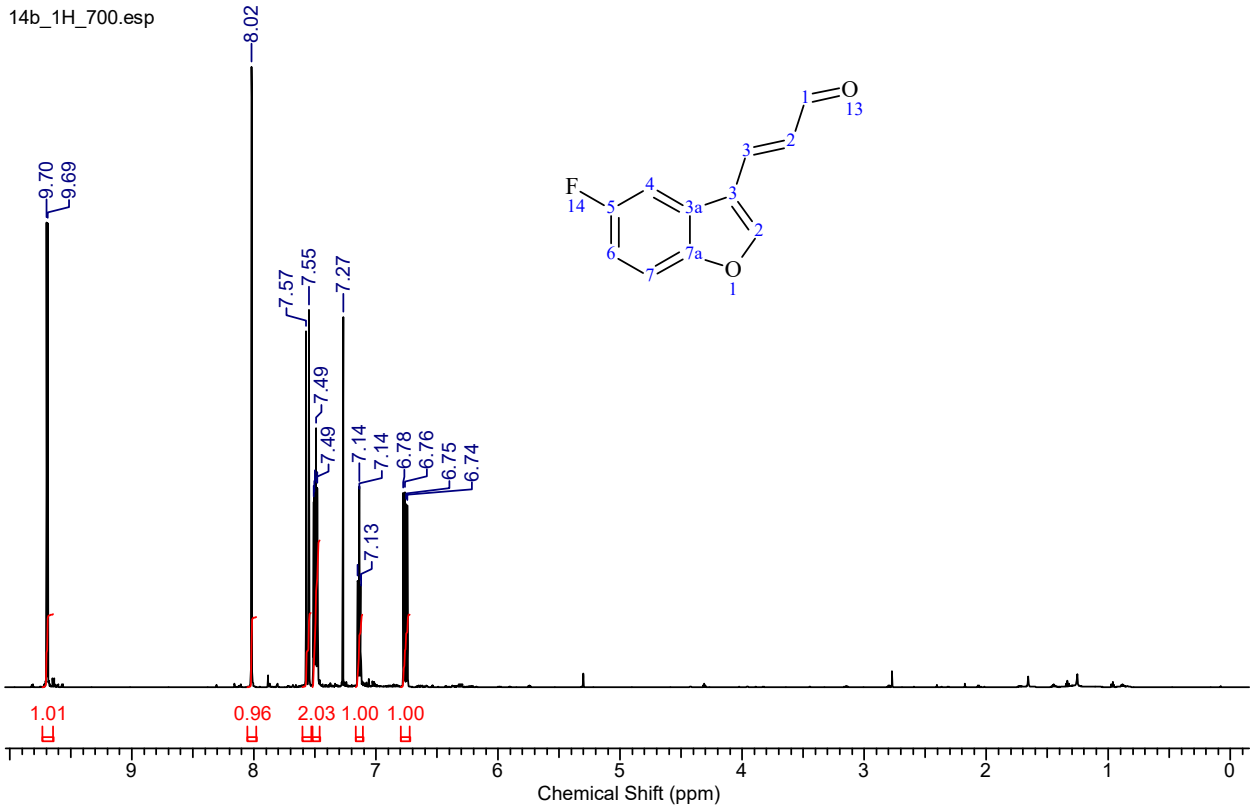



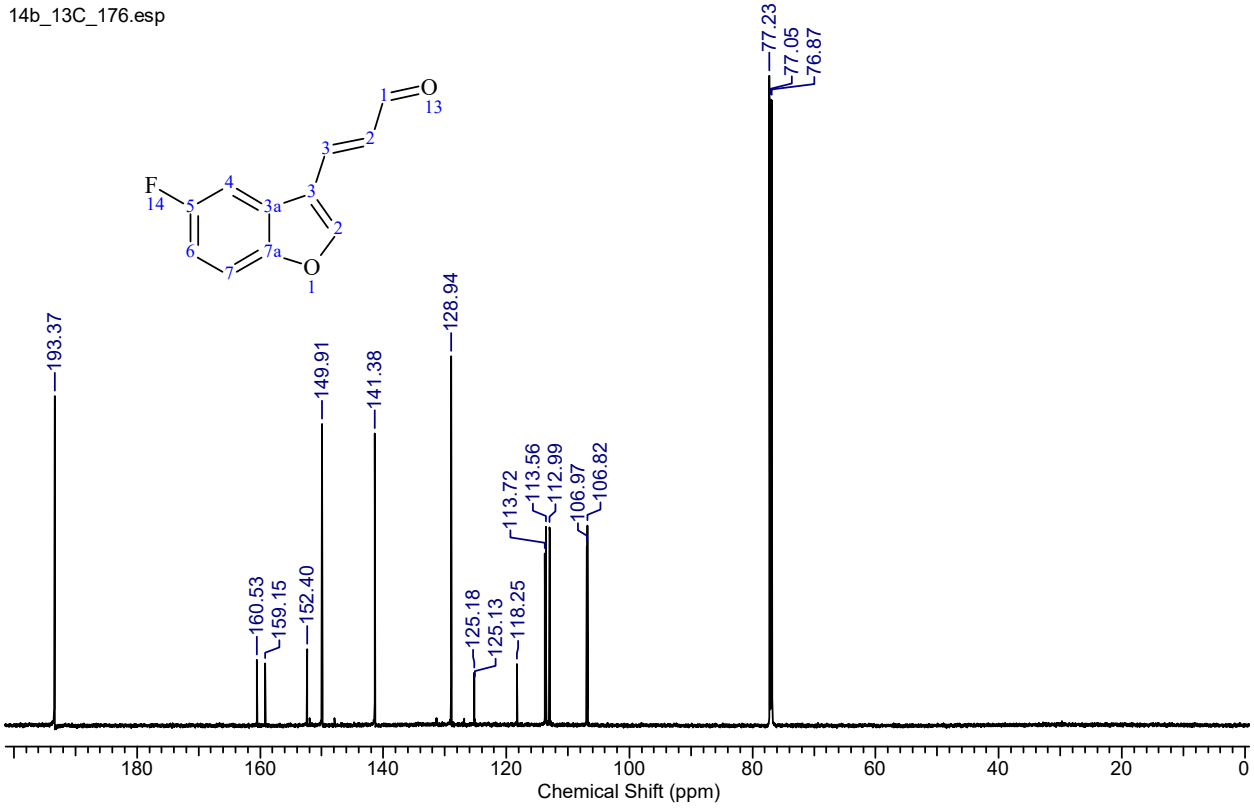
**(*E*)-3-(Benzo[*b*]furan-3-yl)acrylaldehyde (14a).**

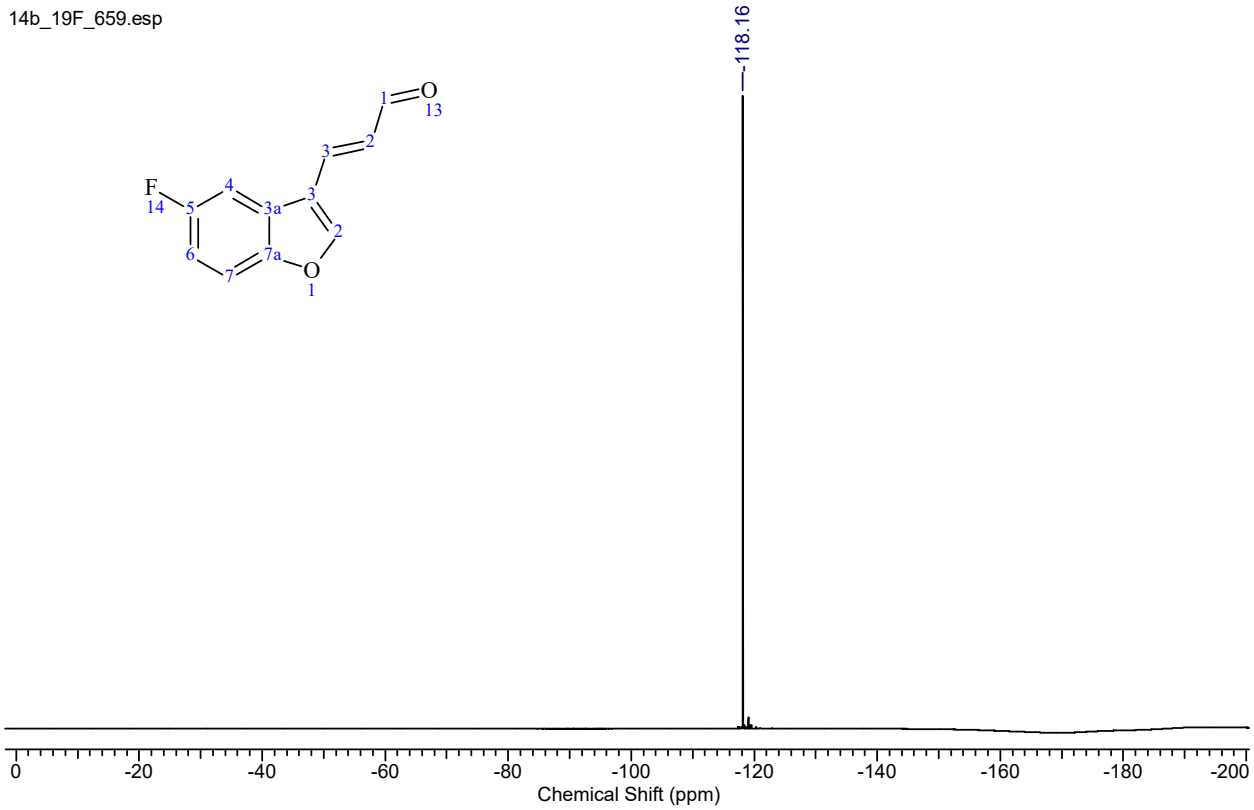


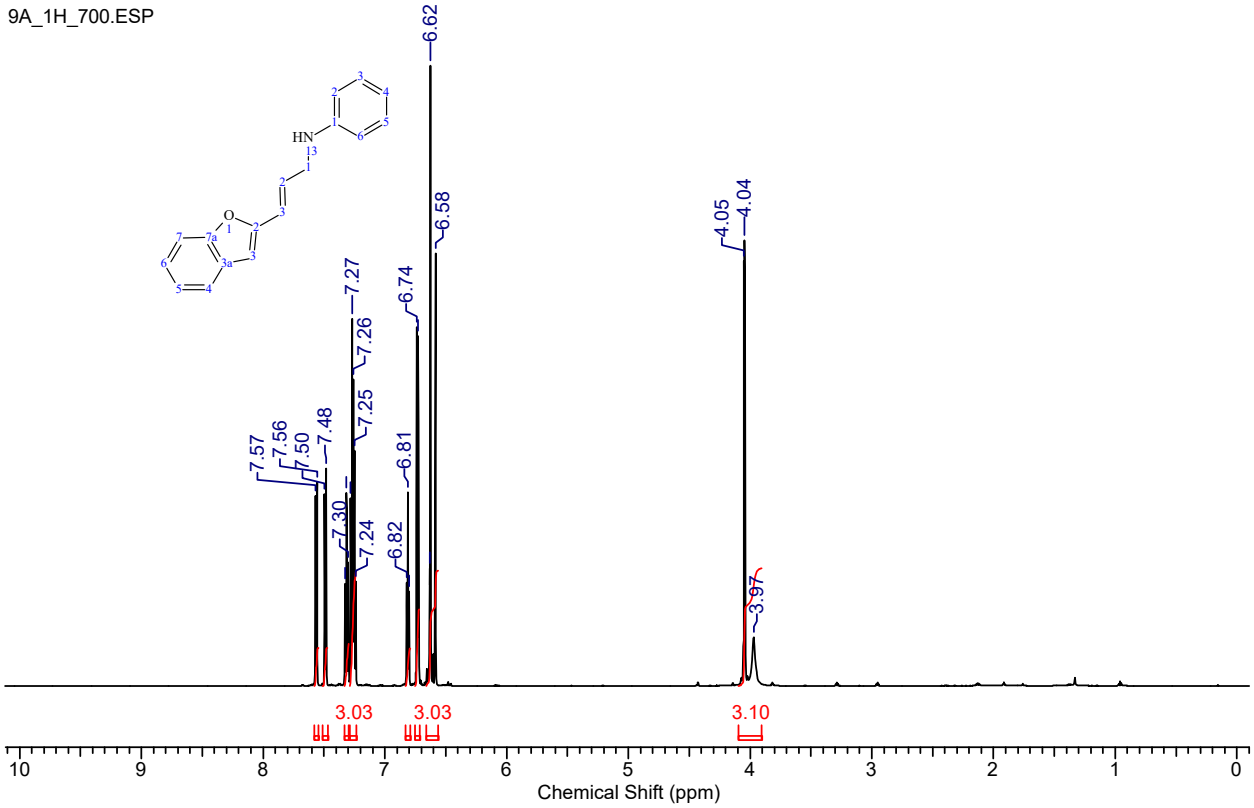
**(*E*)-3-(5-Fluoro-1-benzo[*b*]furan-3-yl)acrylaldehyde (14b).**

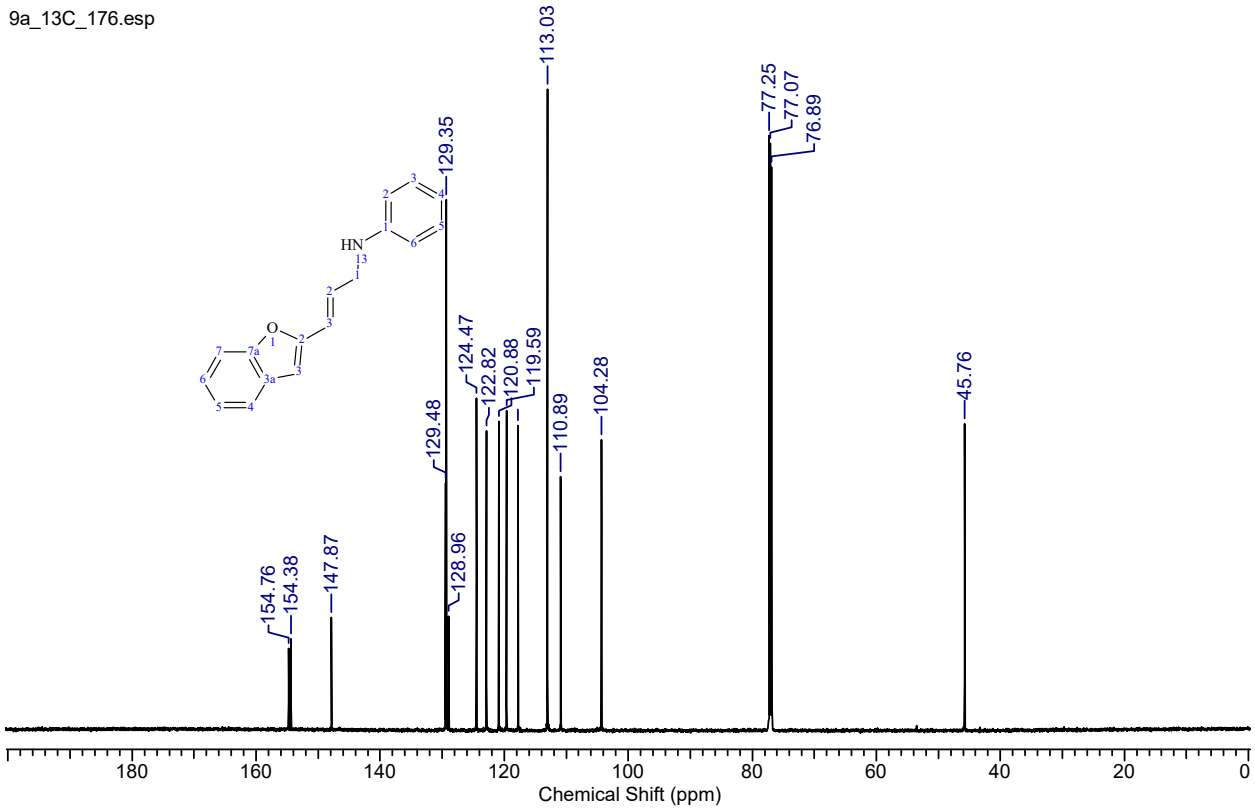





***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)aniline (9a).**



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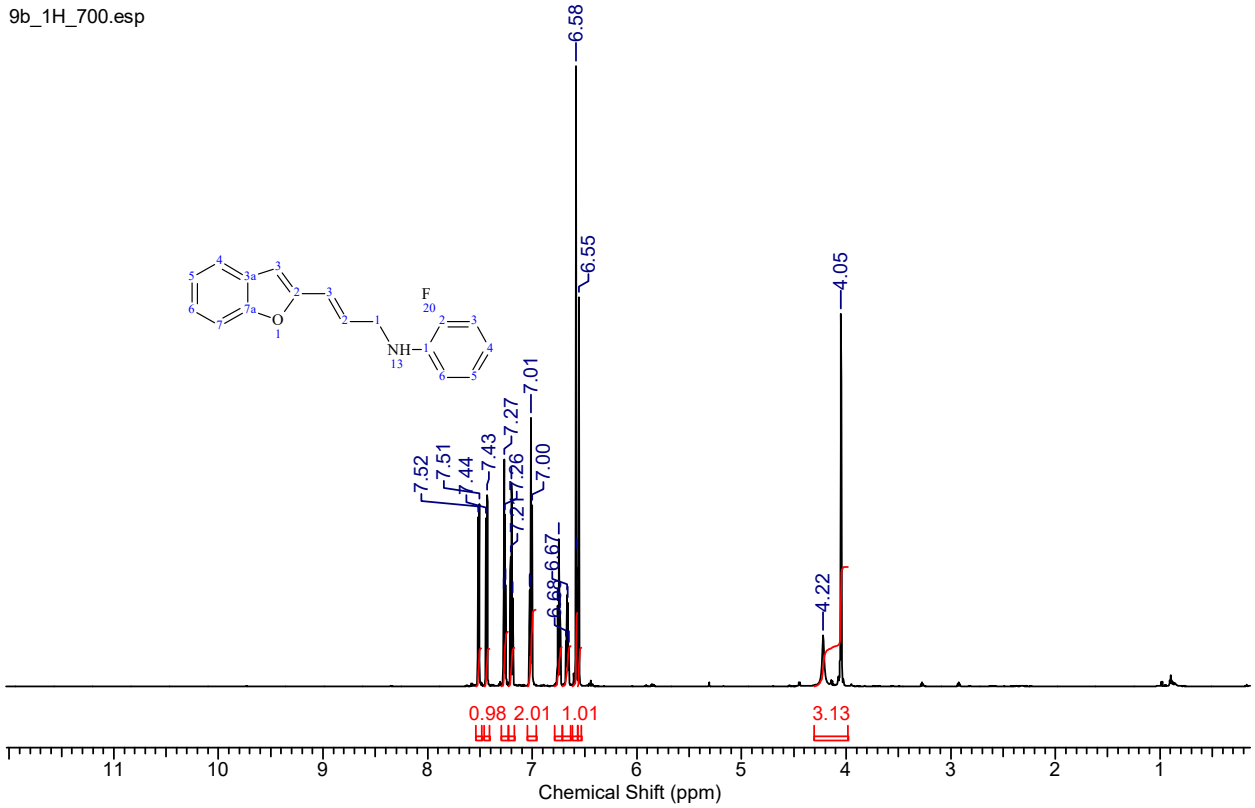
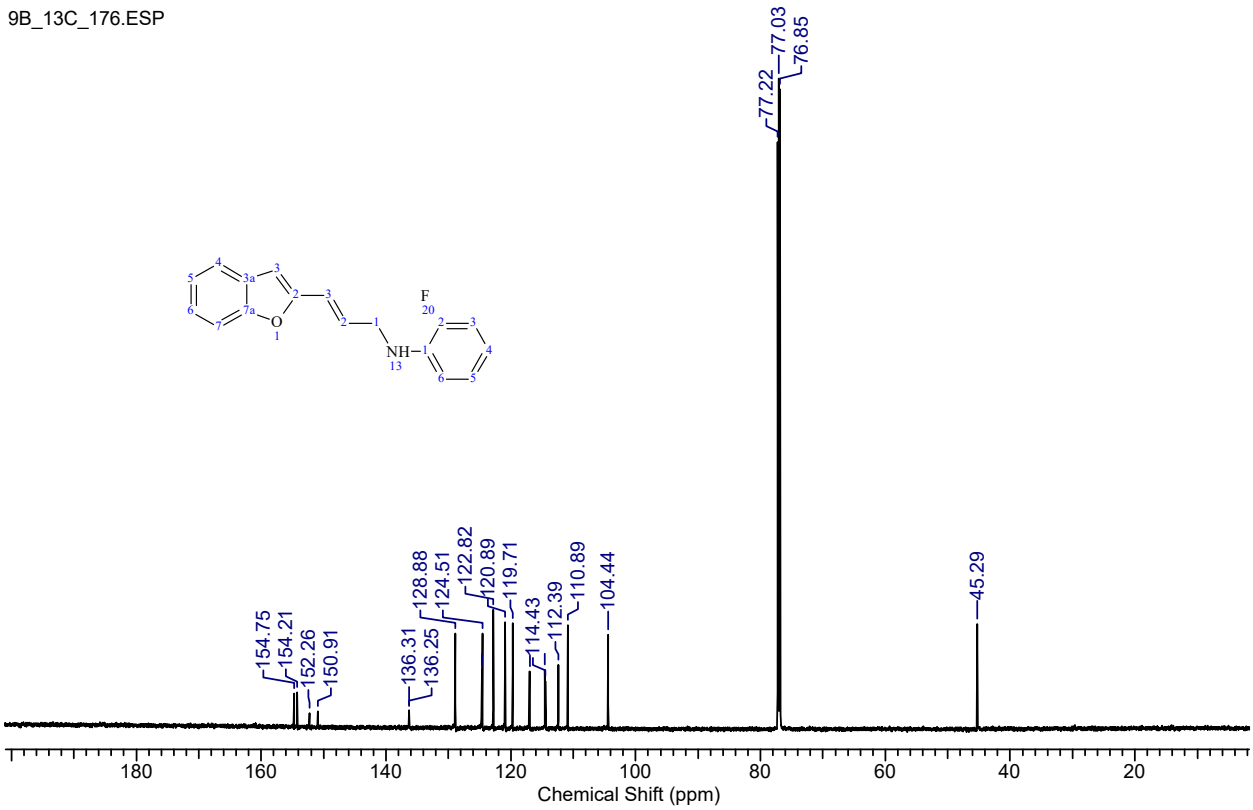
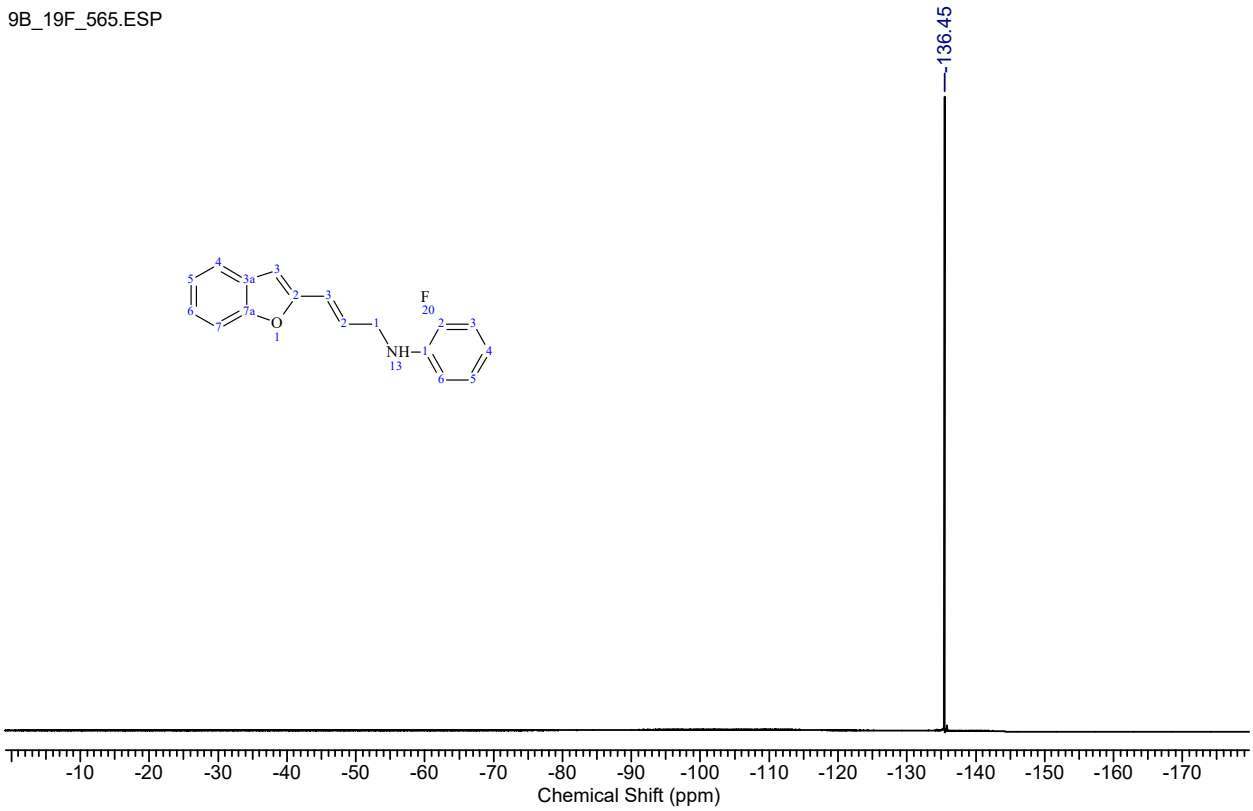
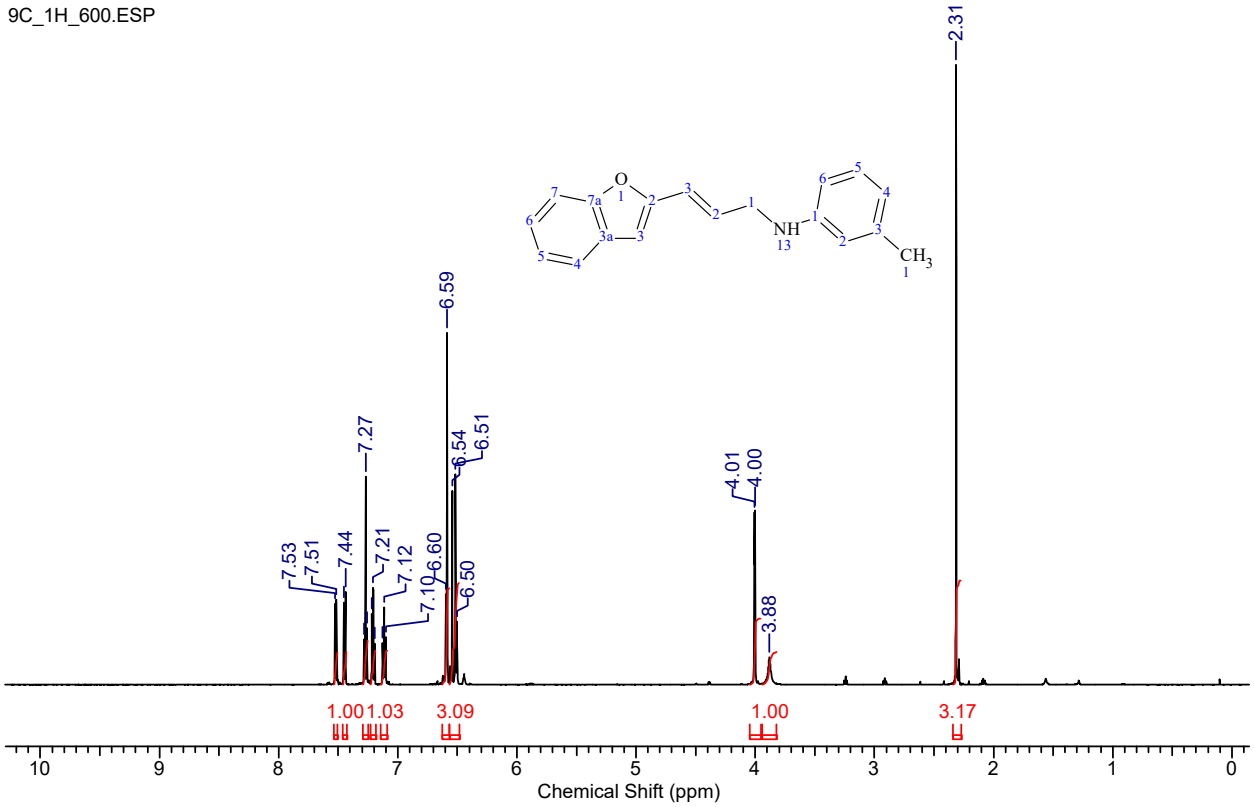
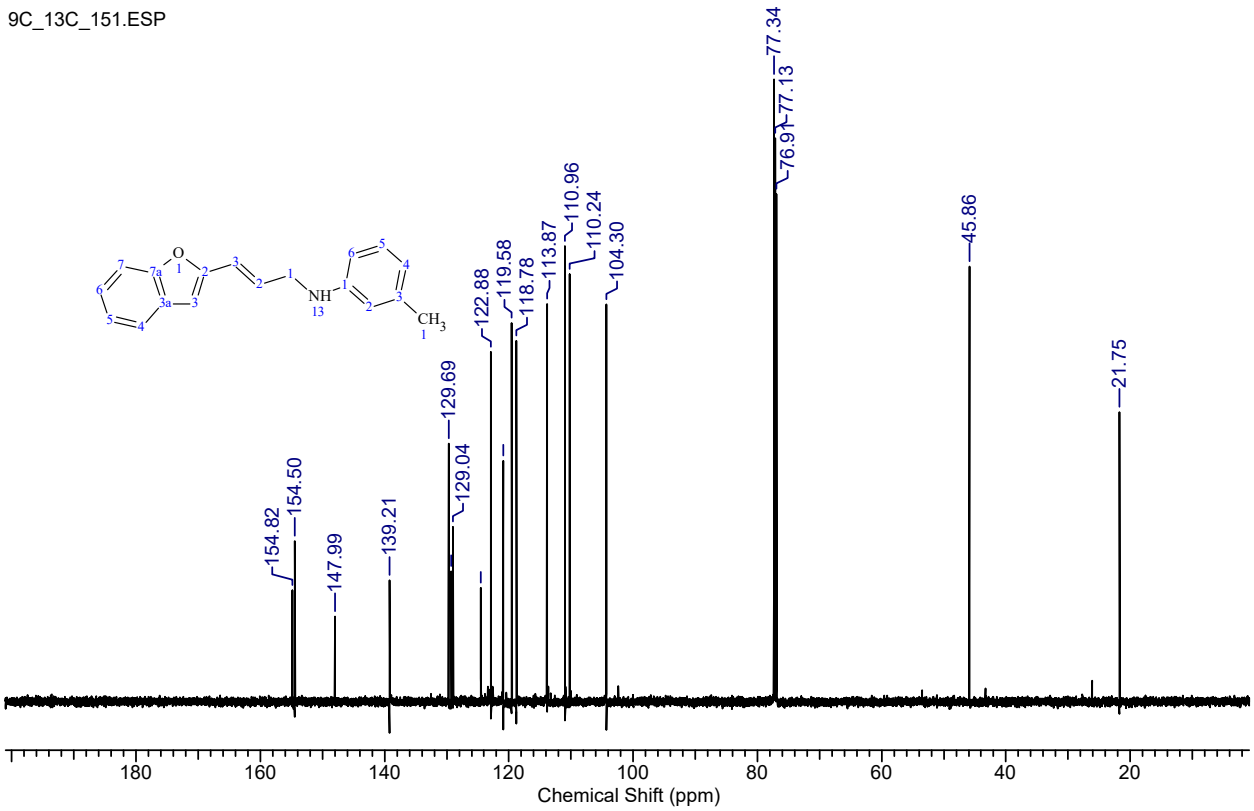





***(E)-N*-(3-(Benzo[*b*]furan-2-yl)-3-methylallylaniline (9c).**

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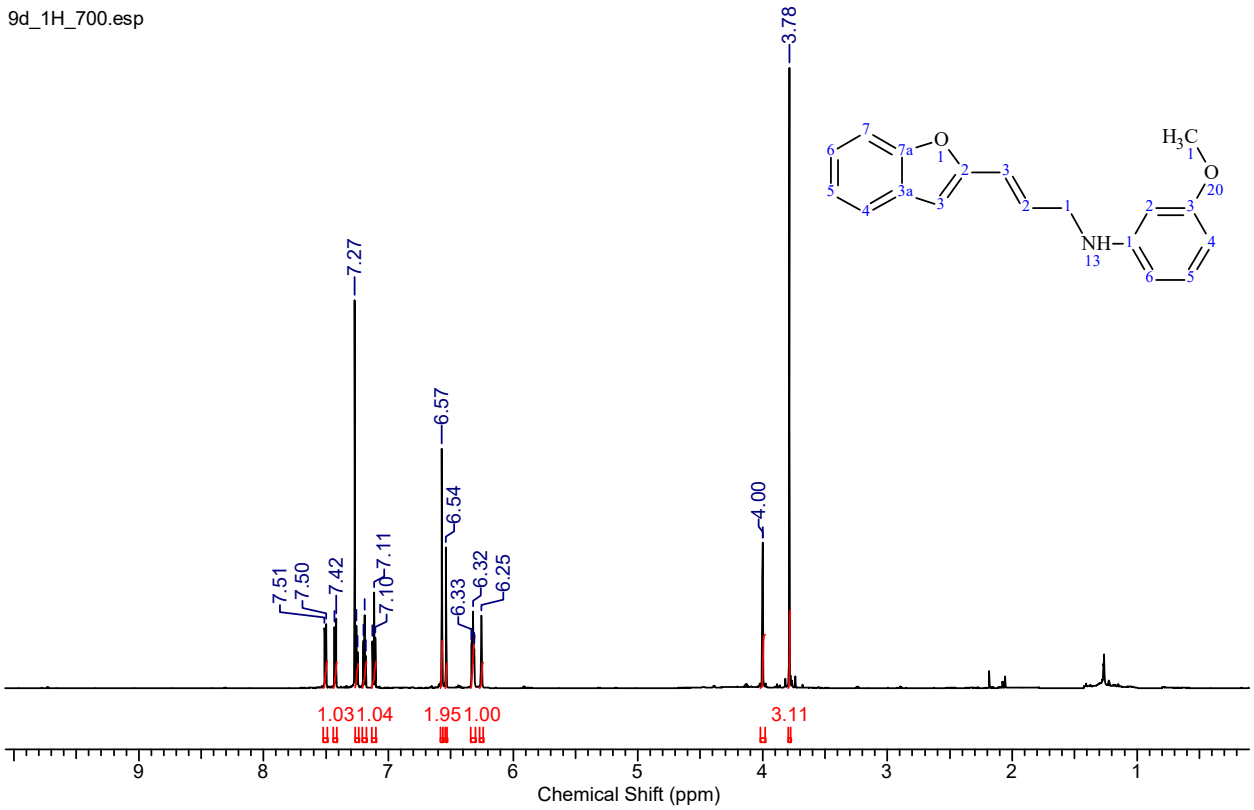


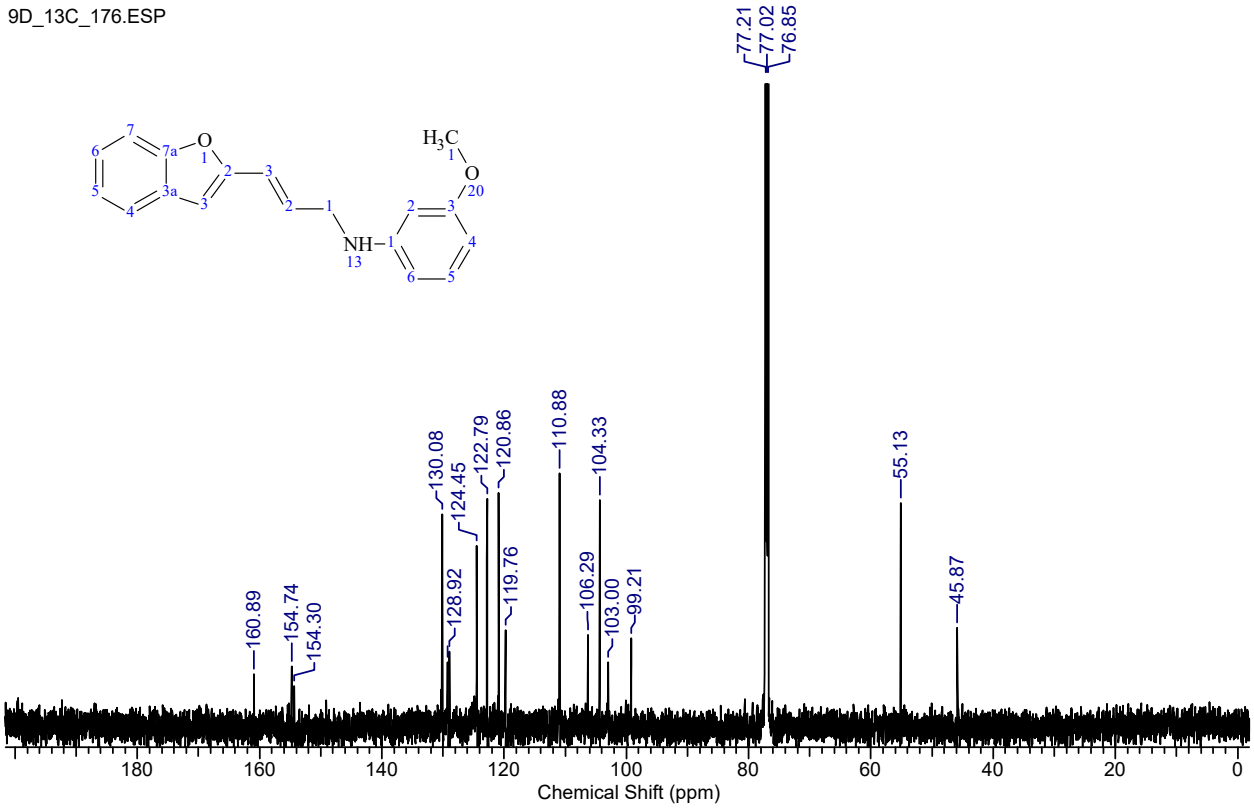


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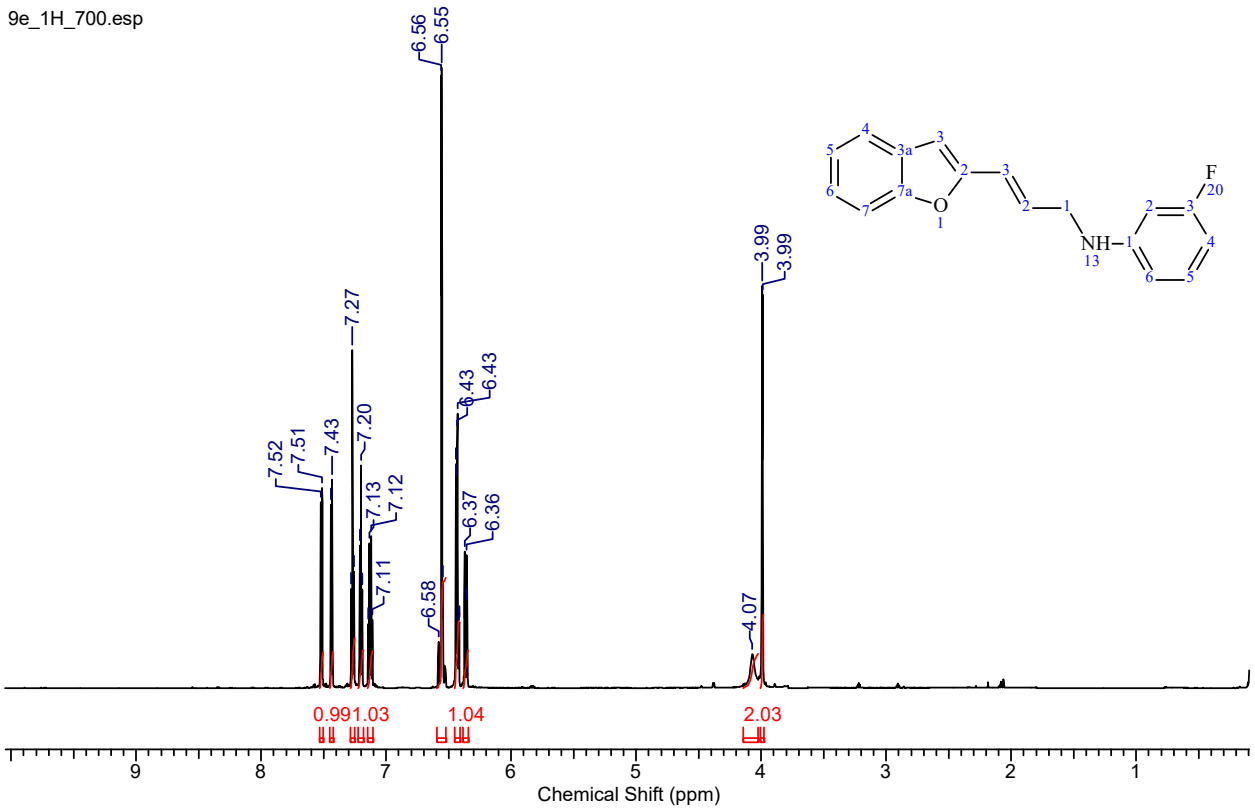
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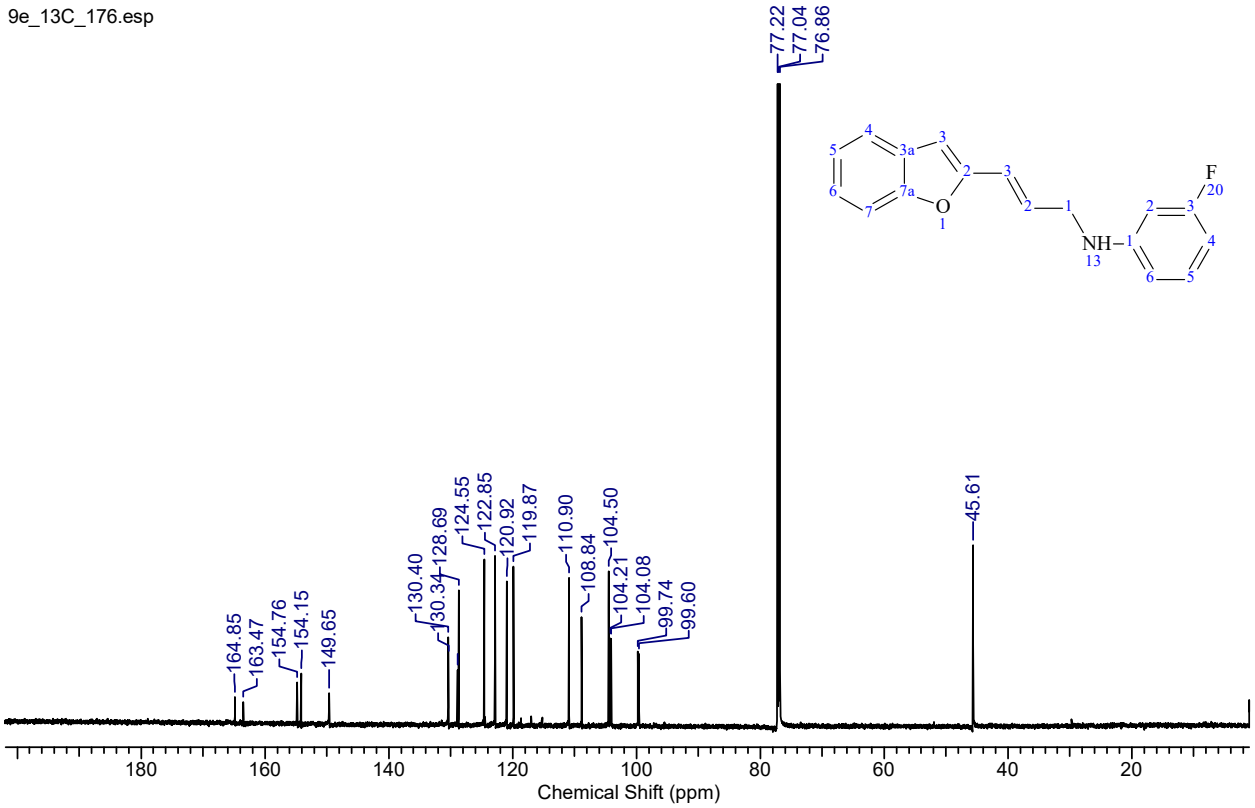
2.03
Chemical Shift (ppm)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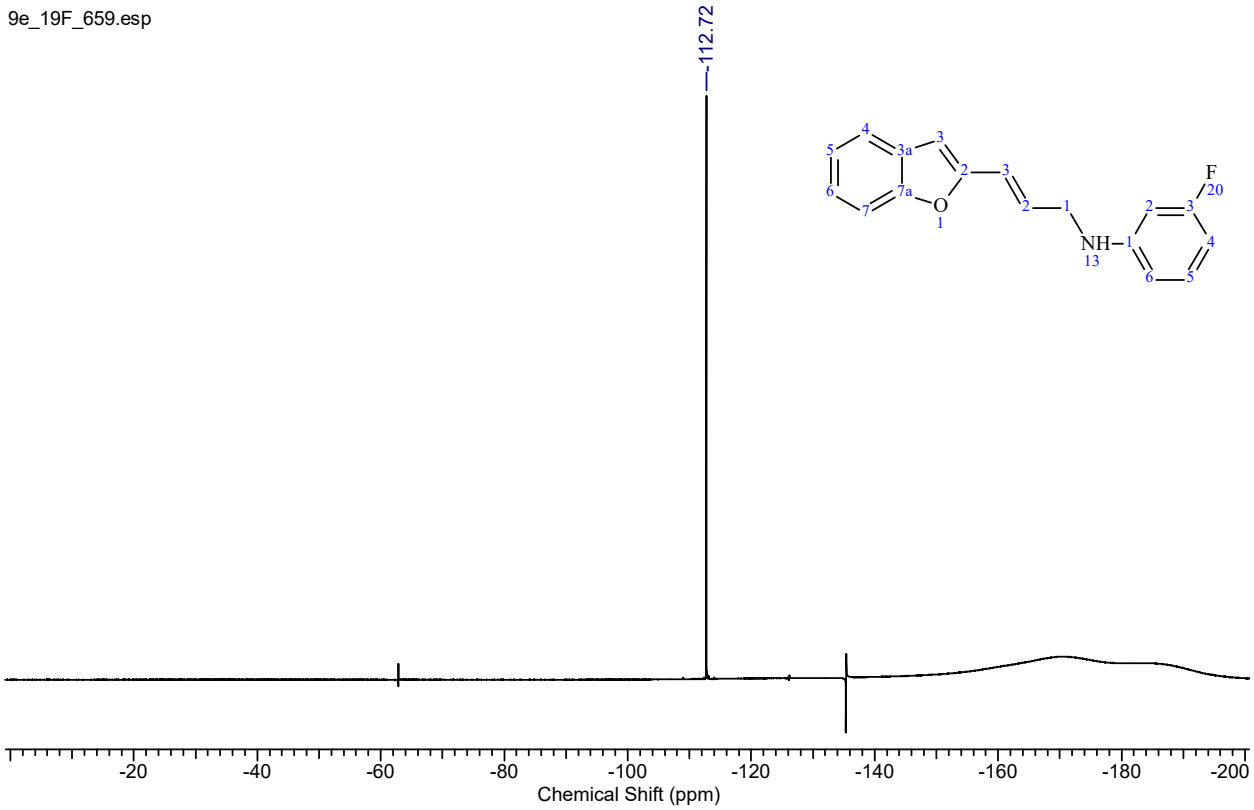
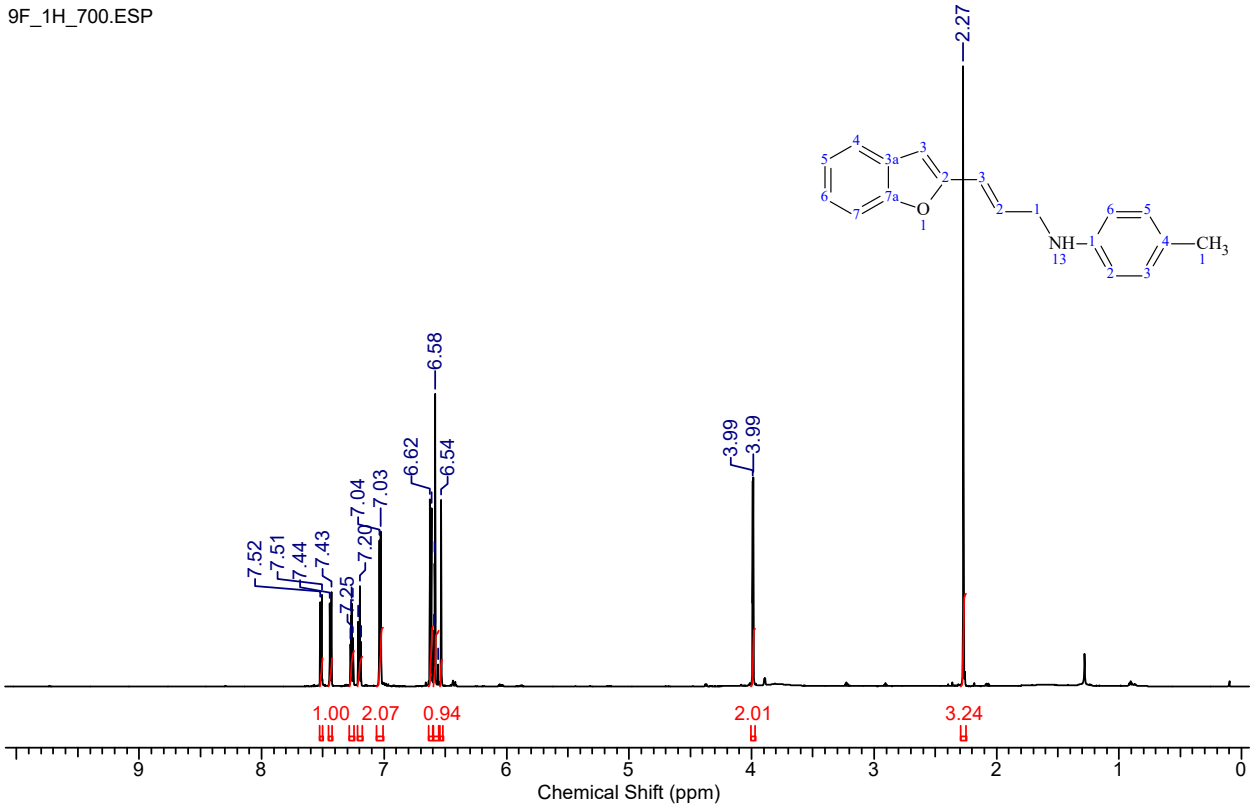
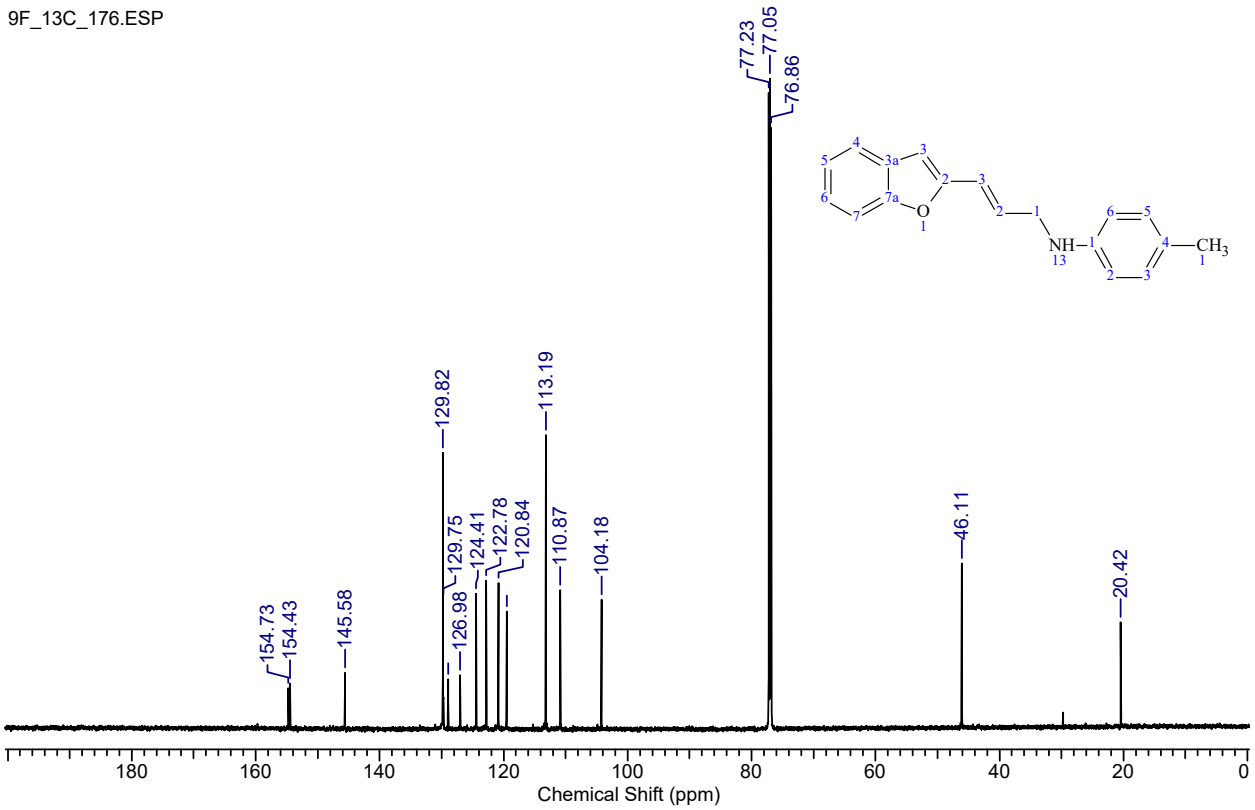
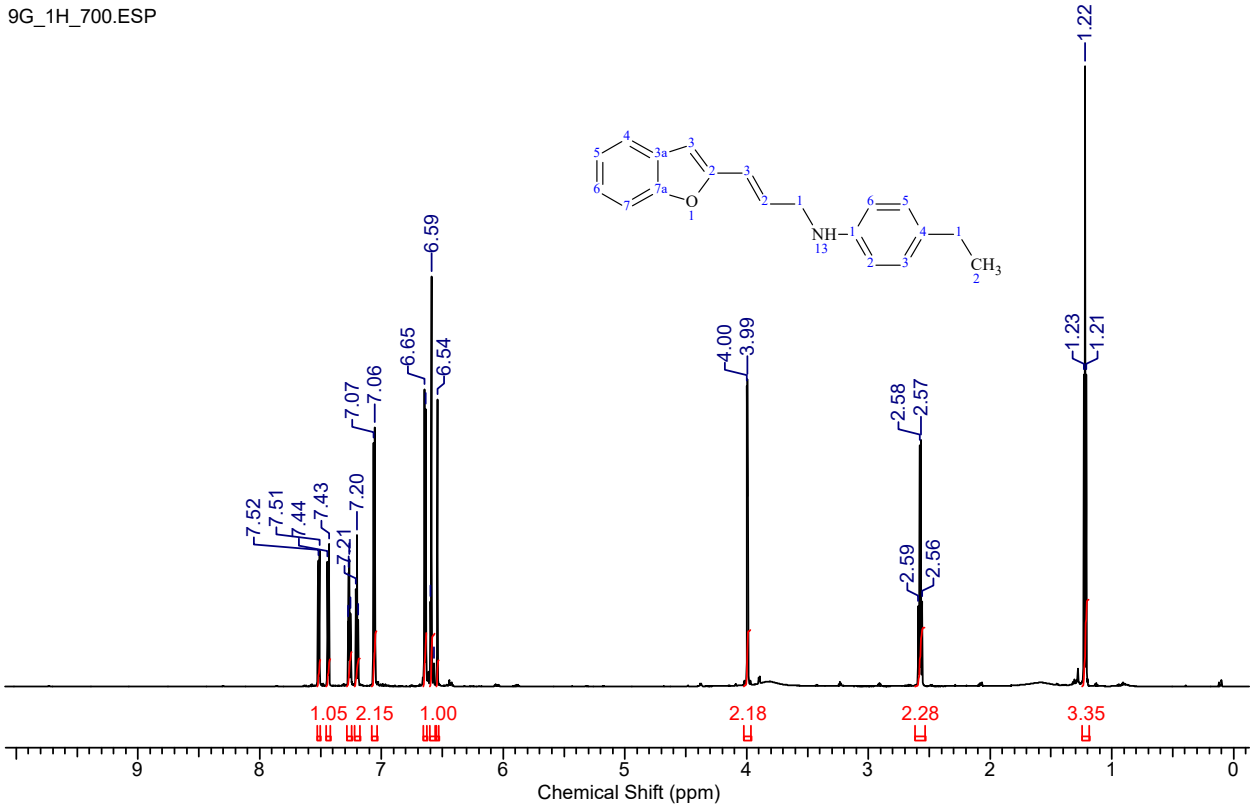


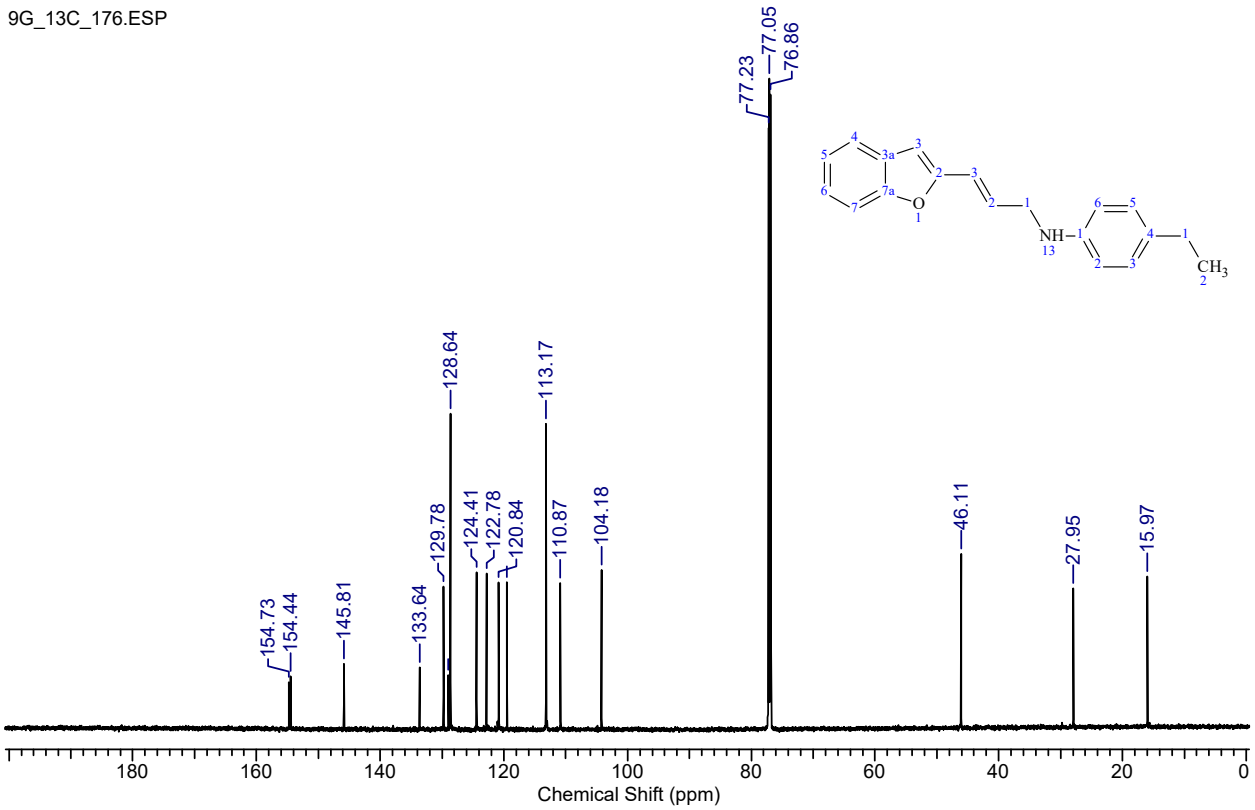

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)-4-methylallylaniline (9f).**






***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-ethylaniline (9g).**



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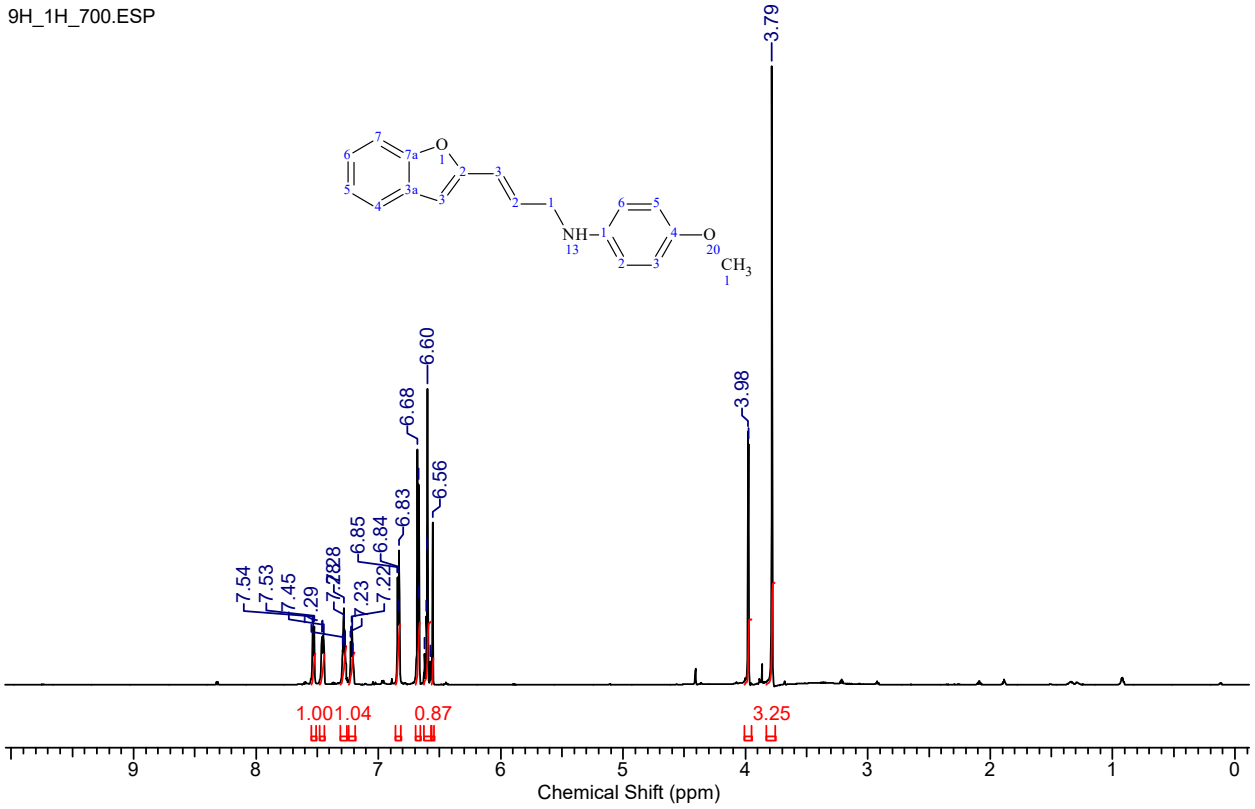

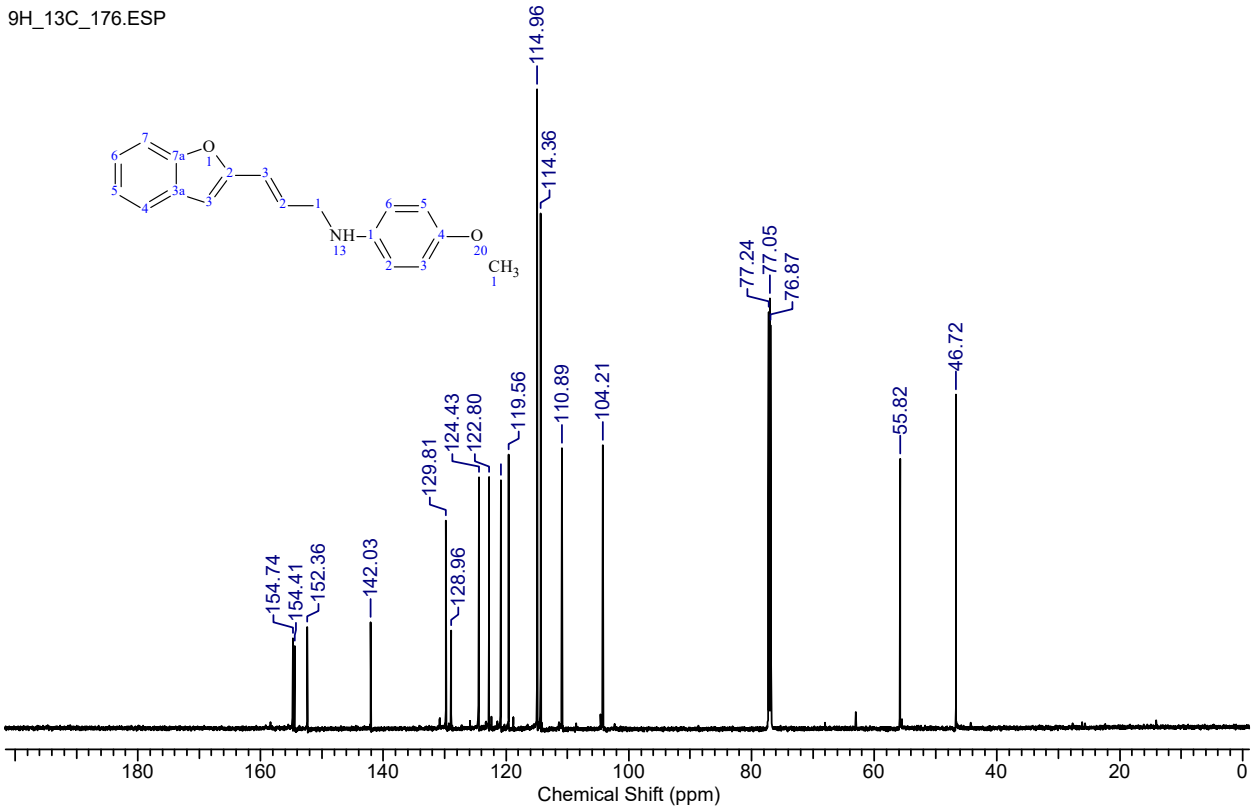


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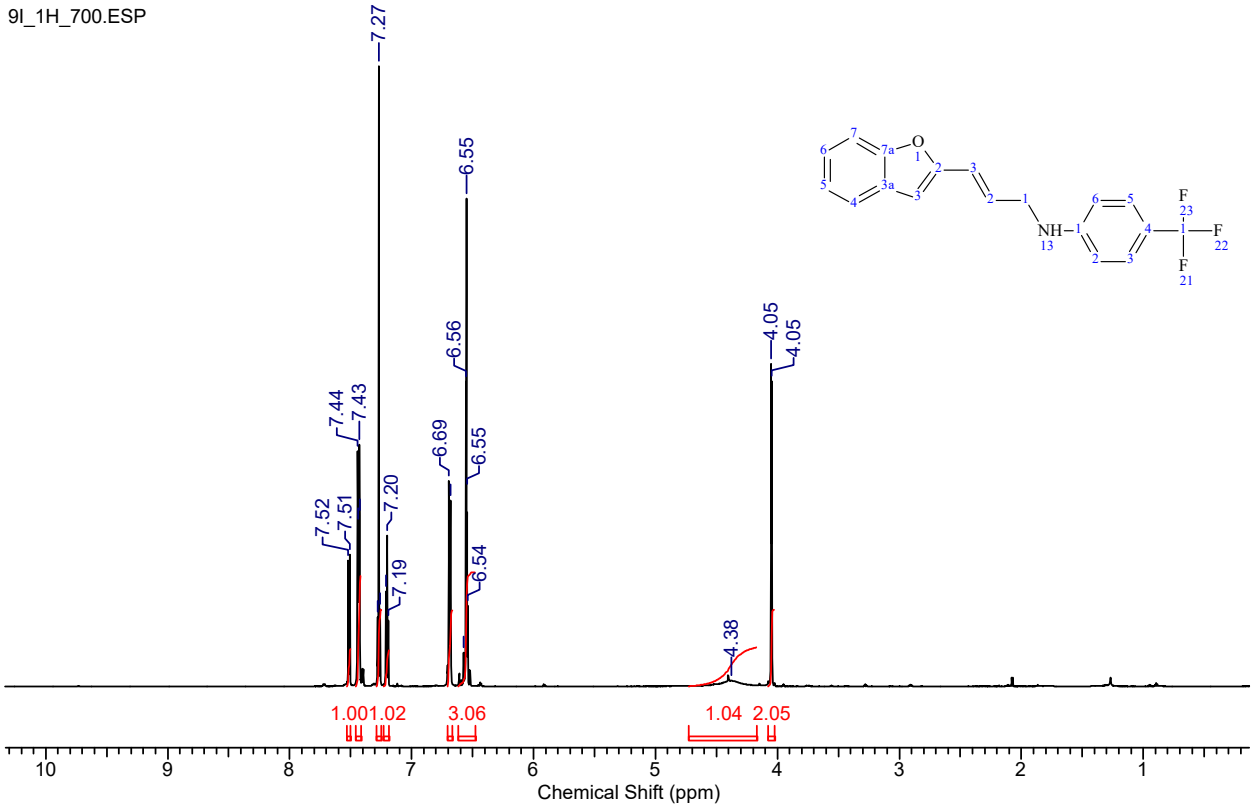

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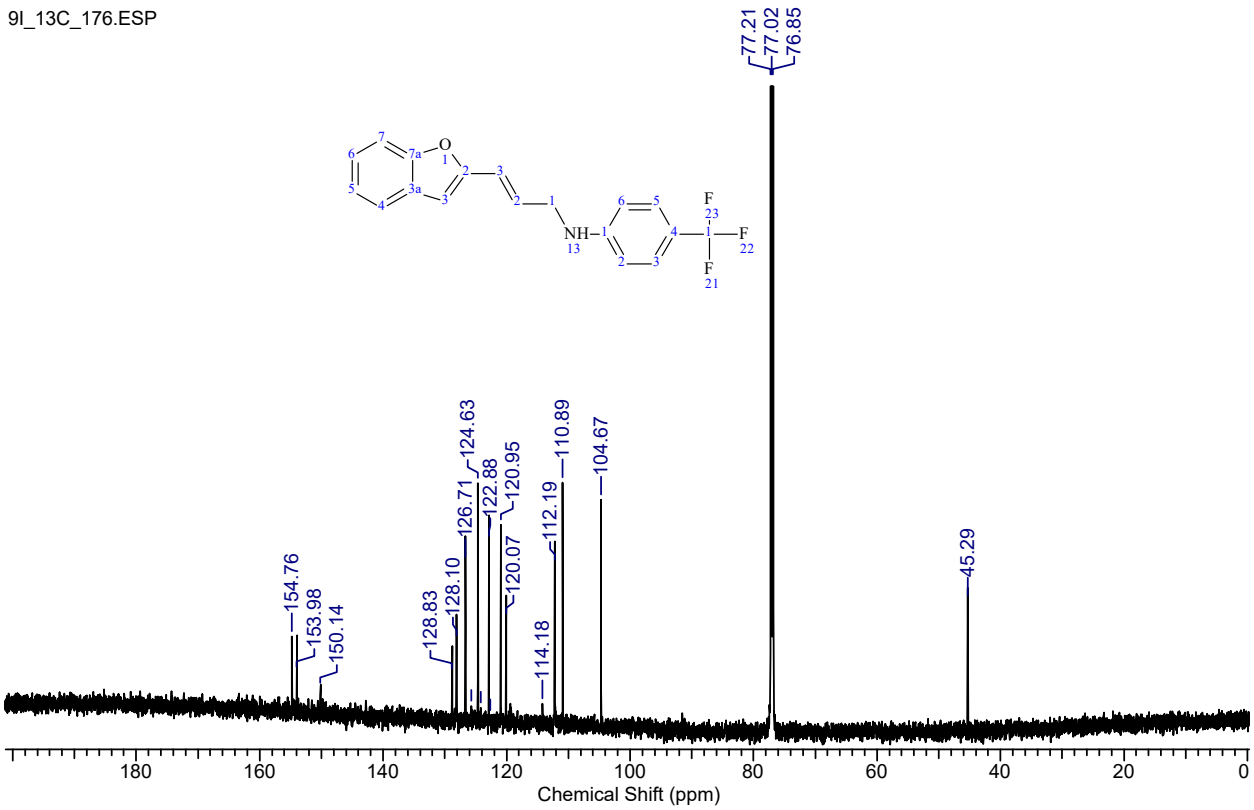


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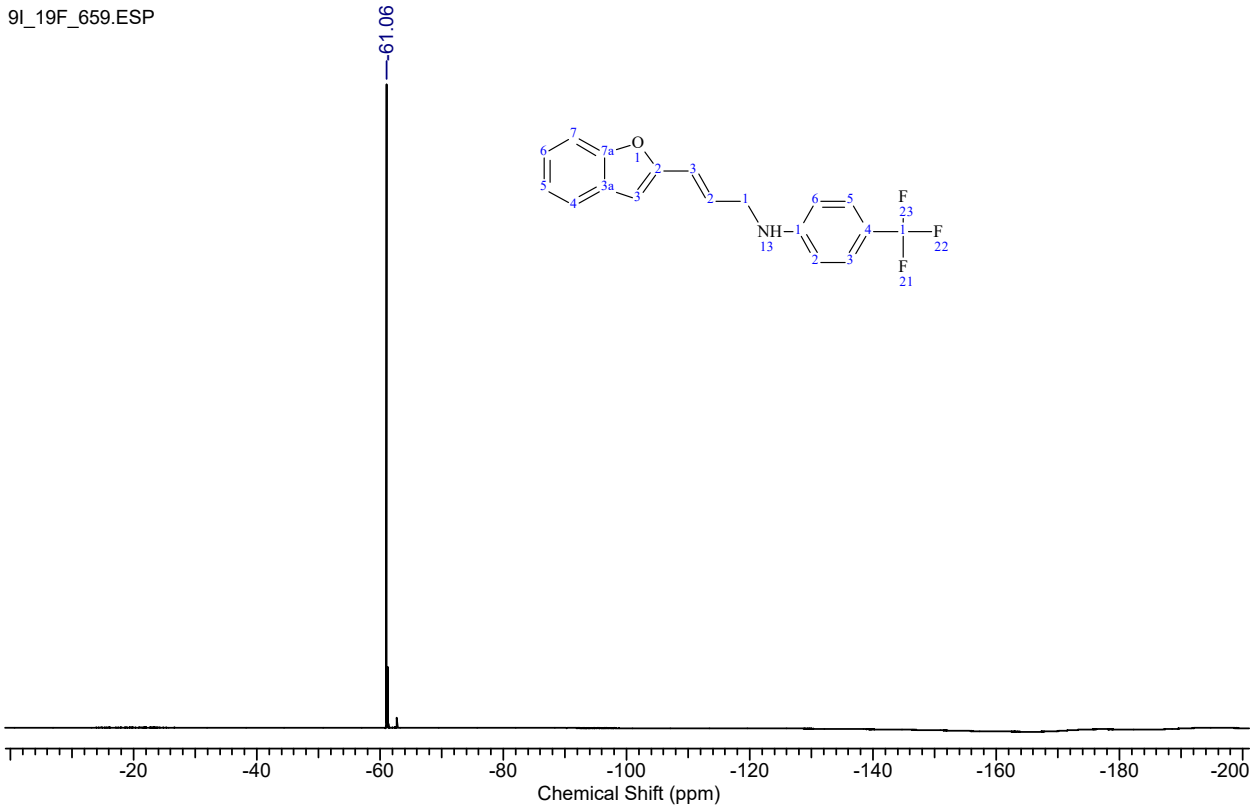
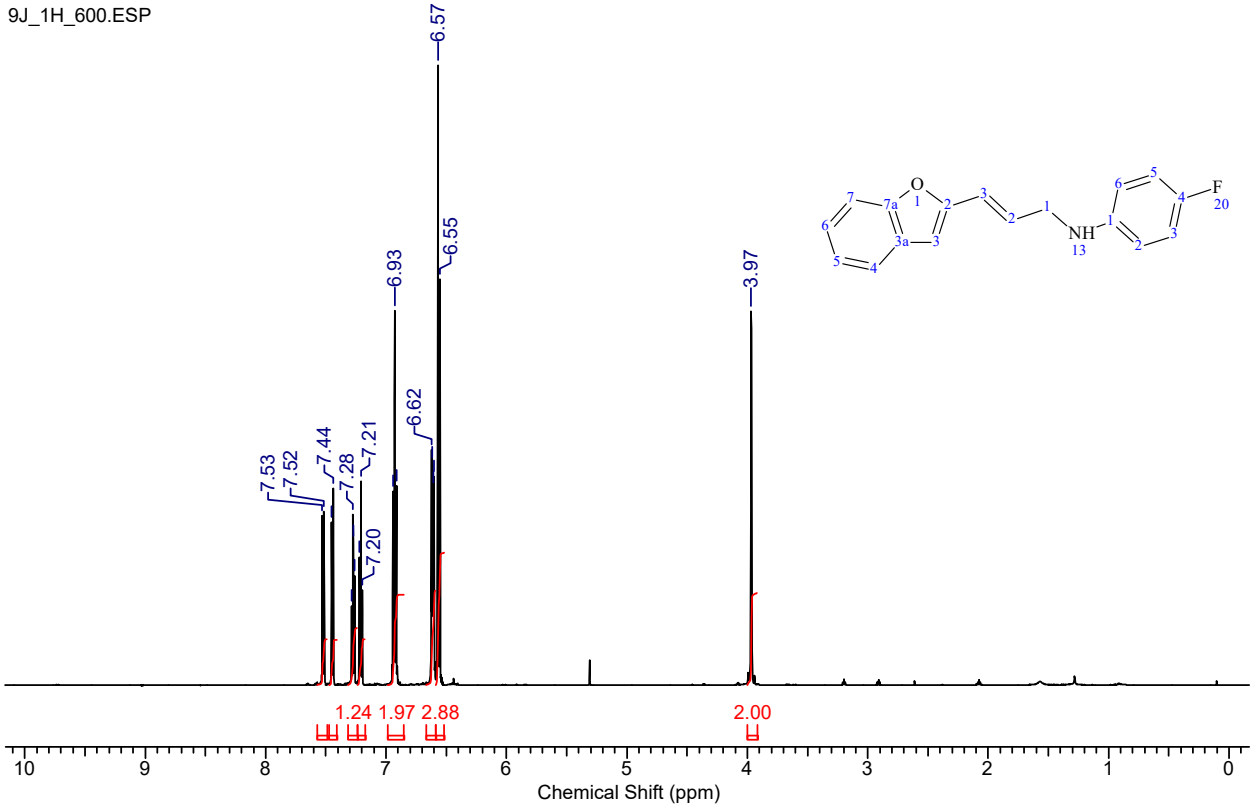
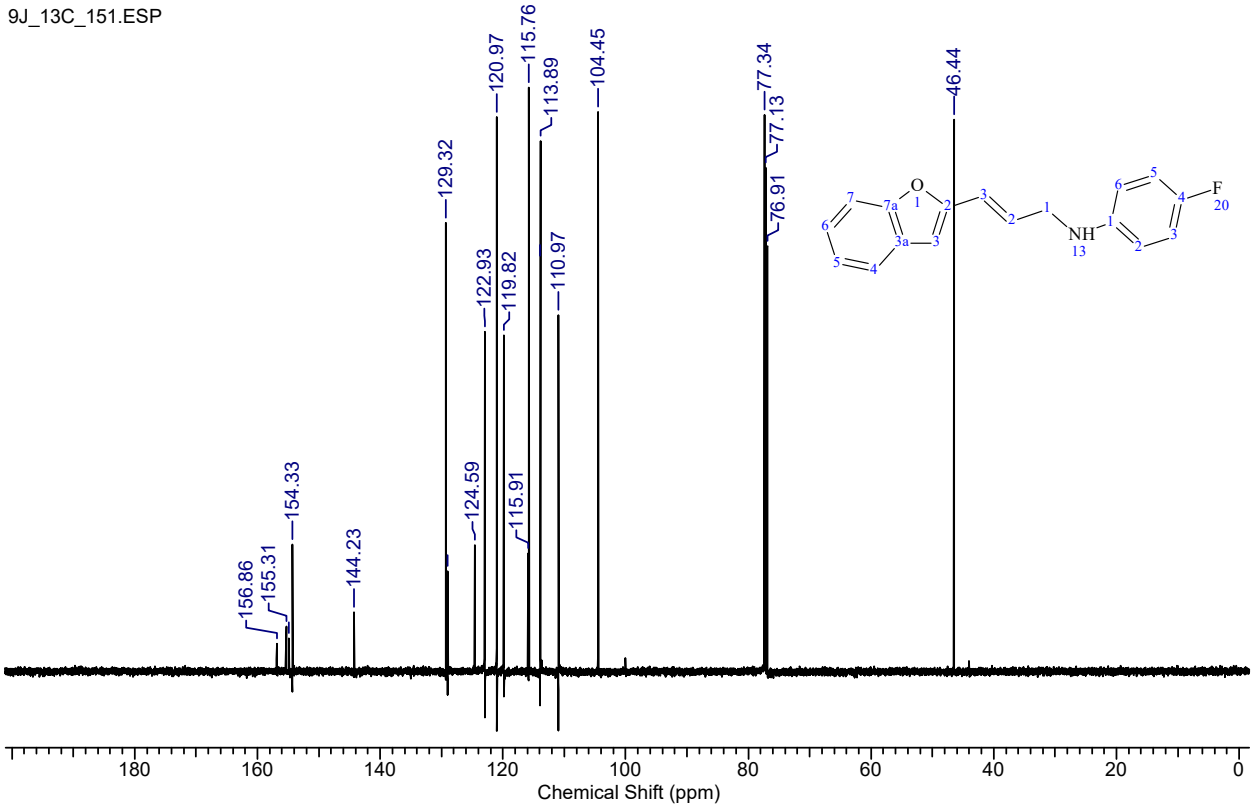
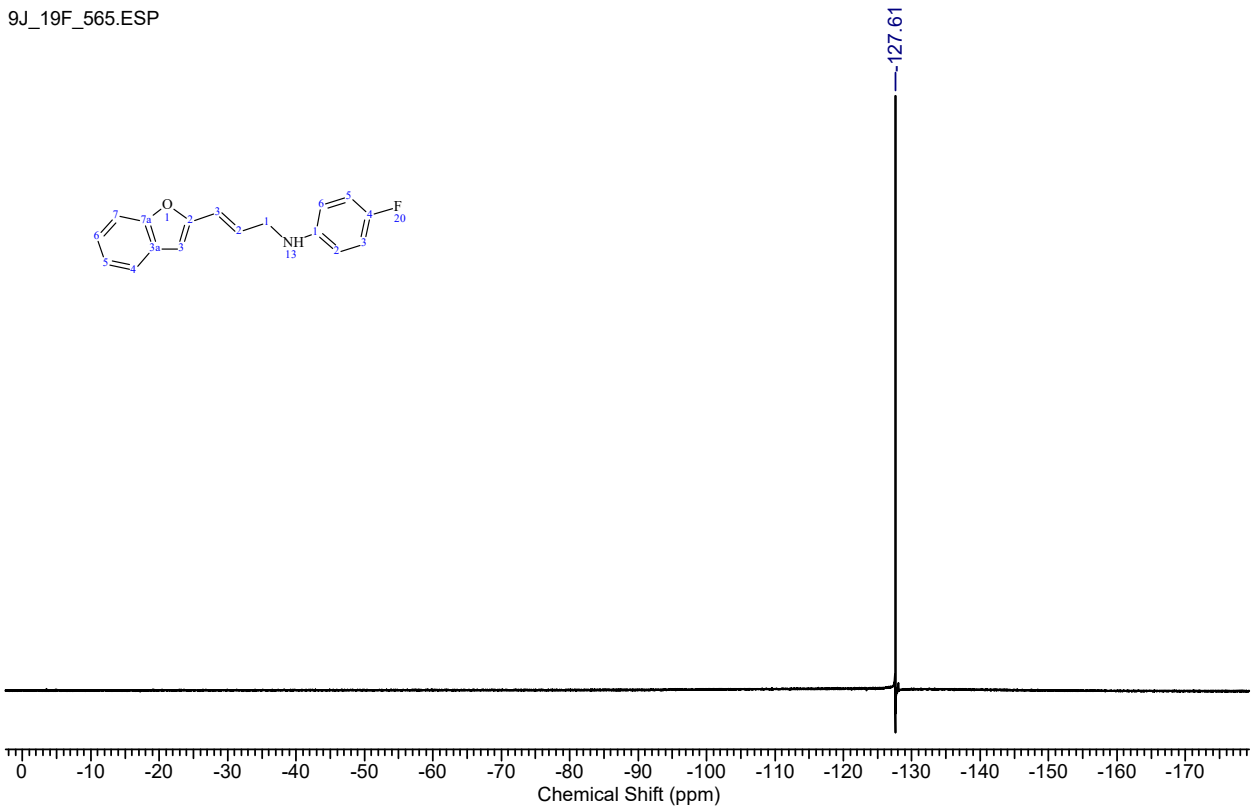


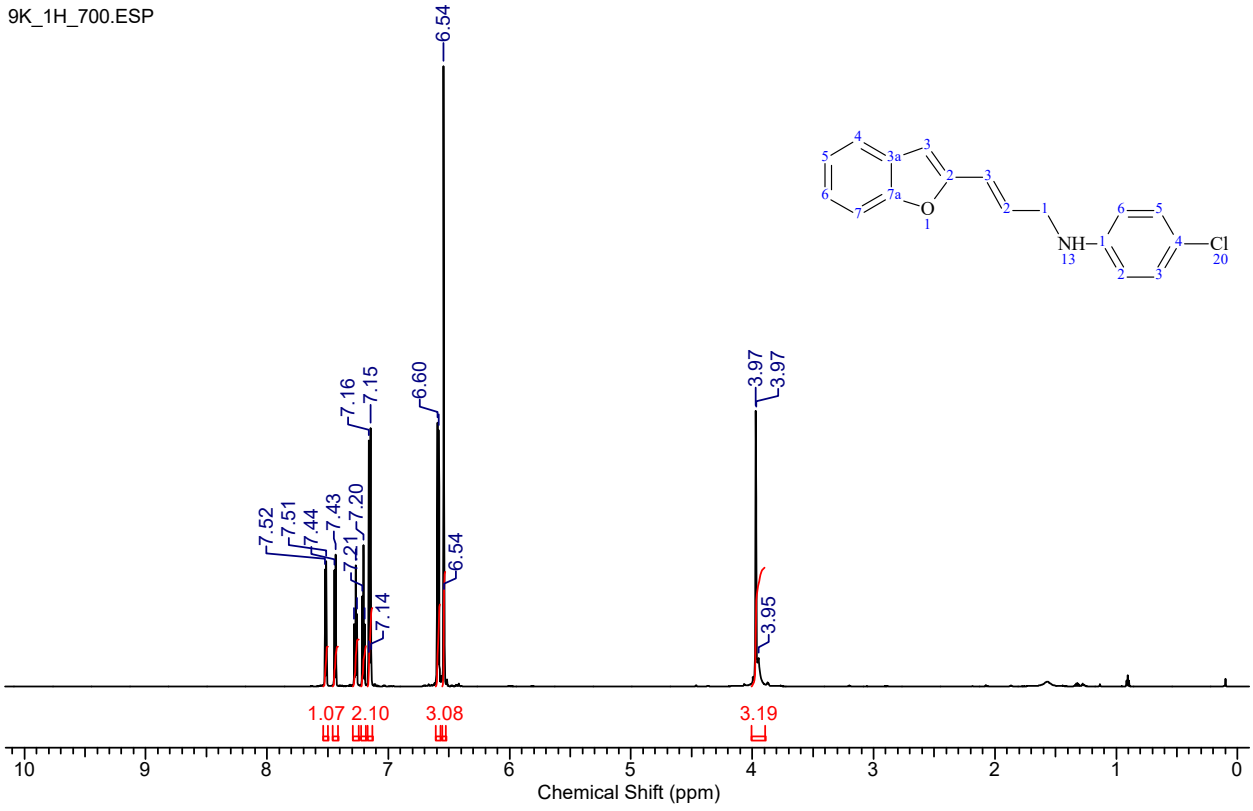
***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-fluoroaniline (9j).**

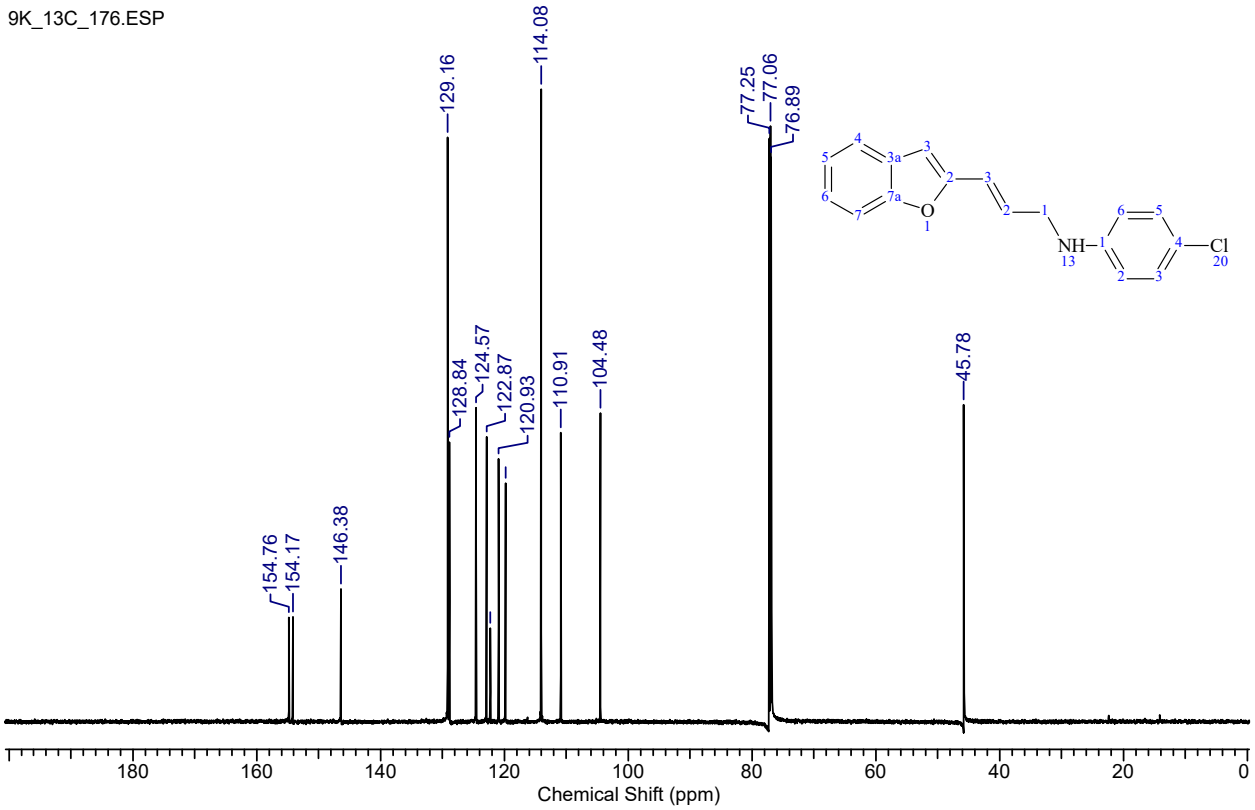





***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-chloroaniline (9k).**



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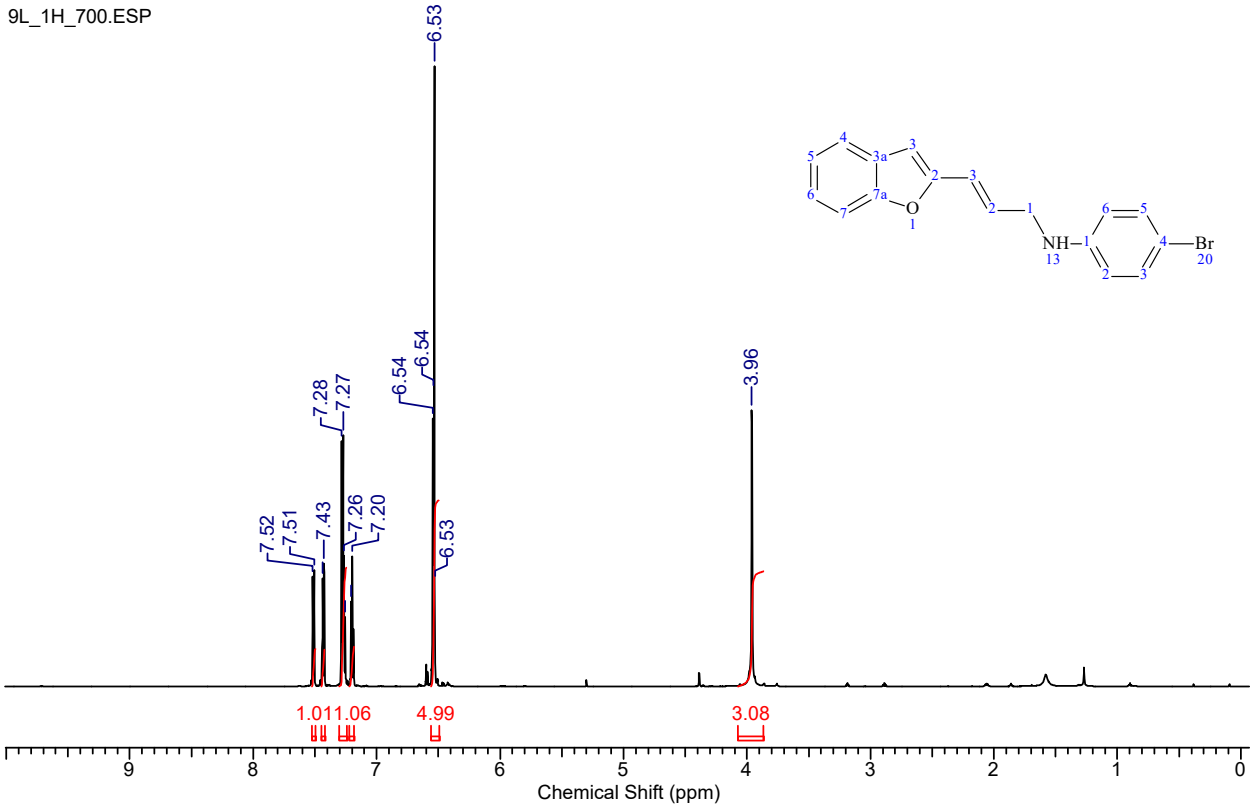

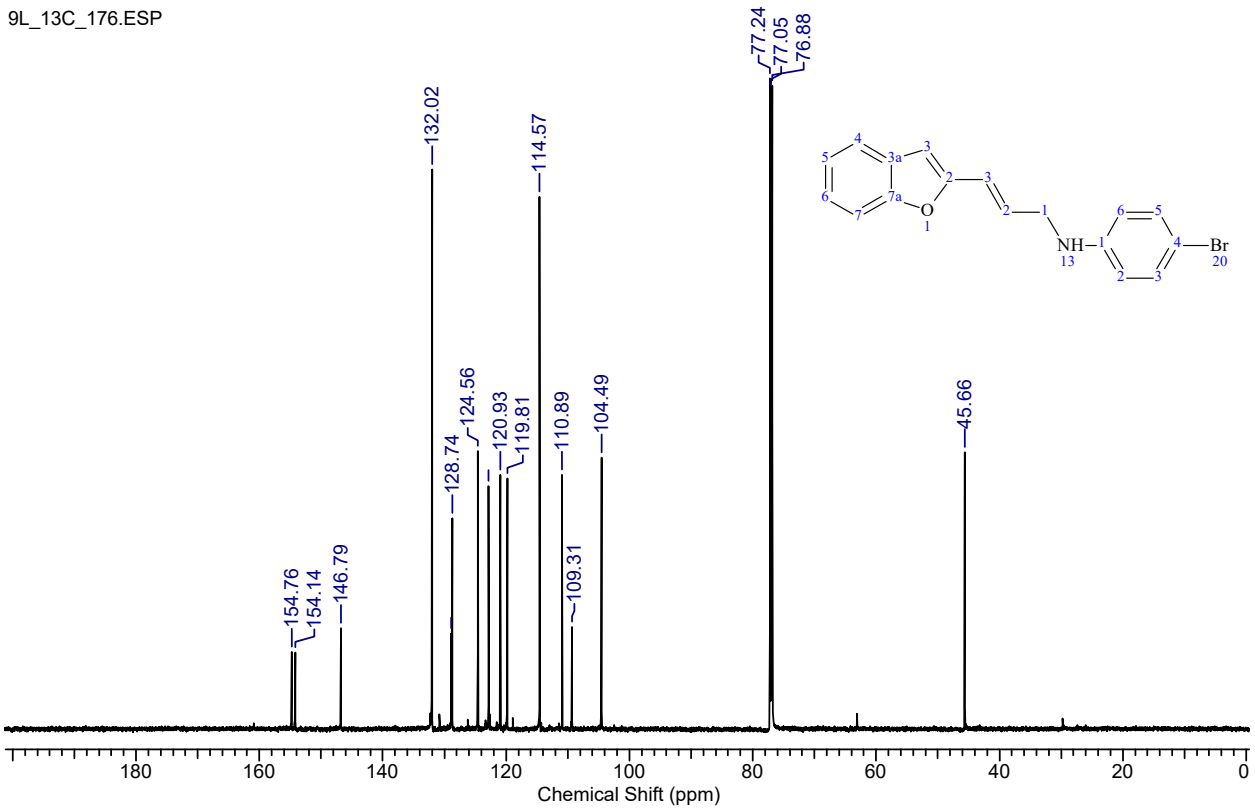


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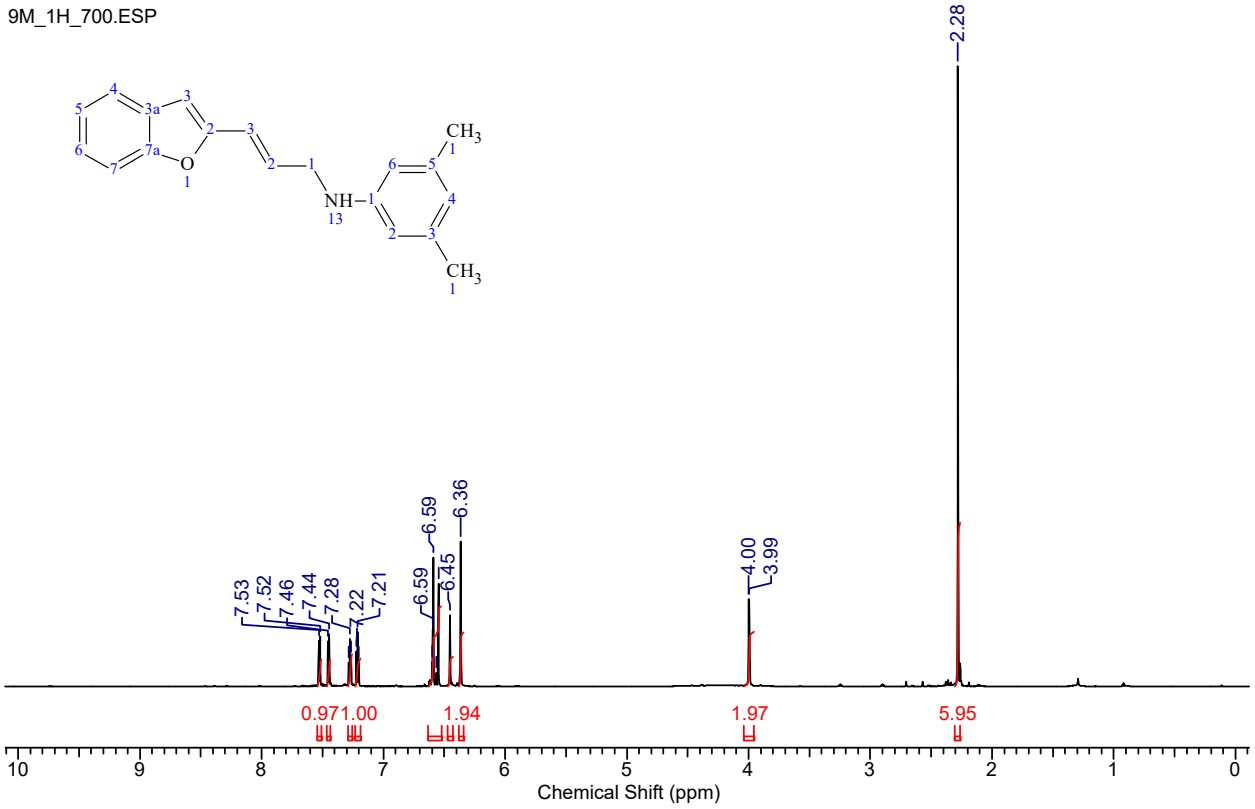

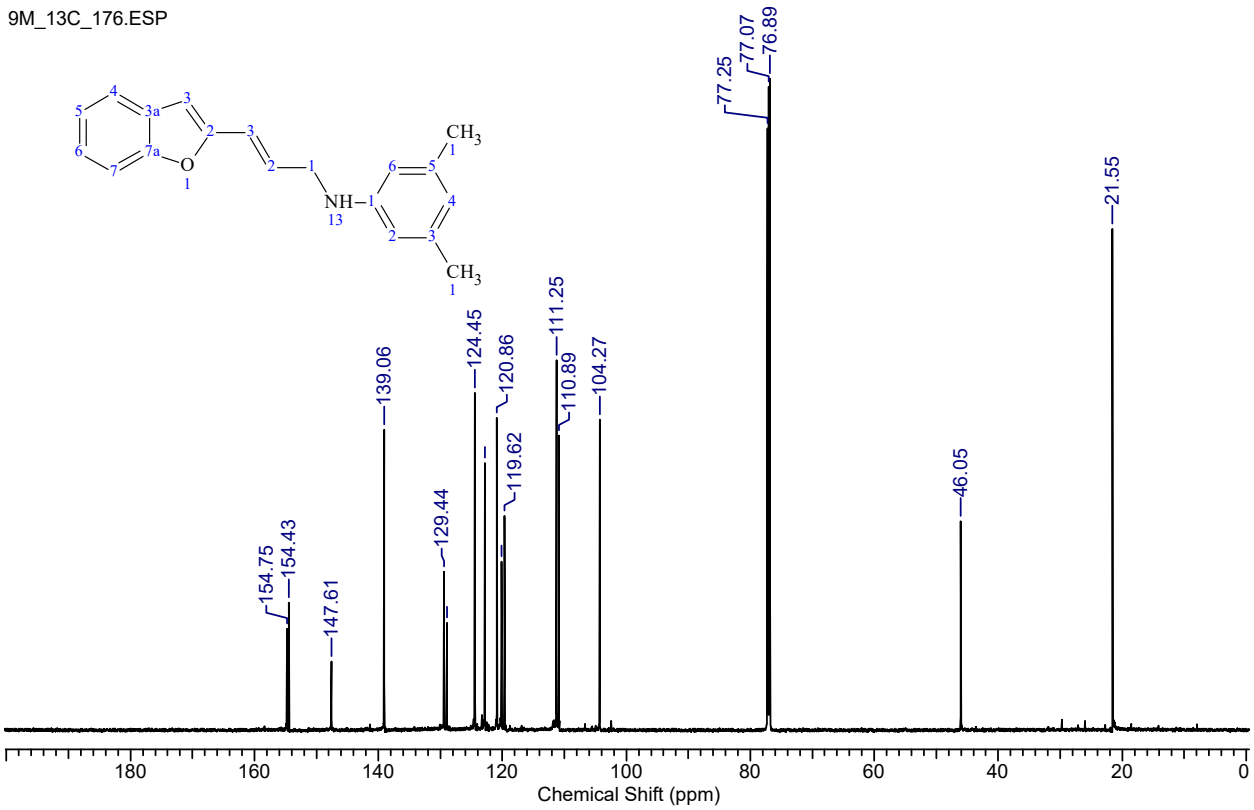


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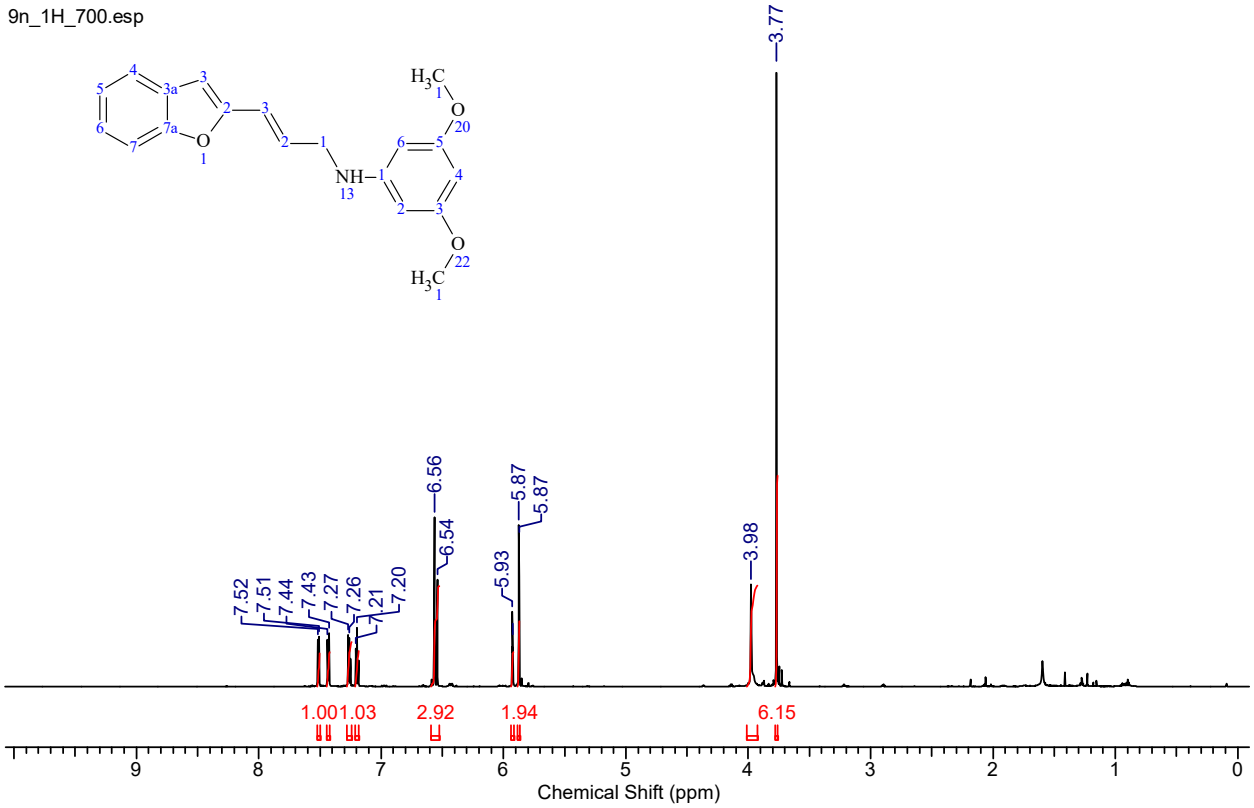
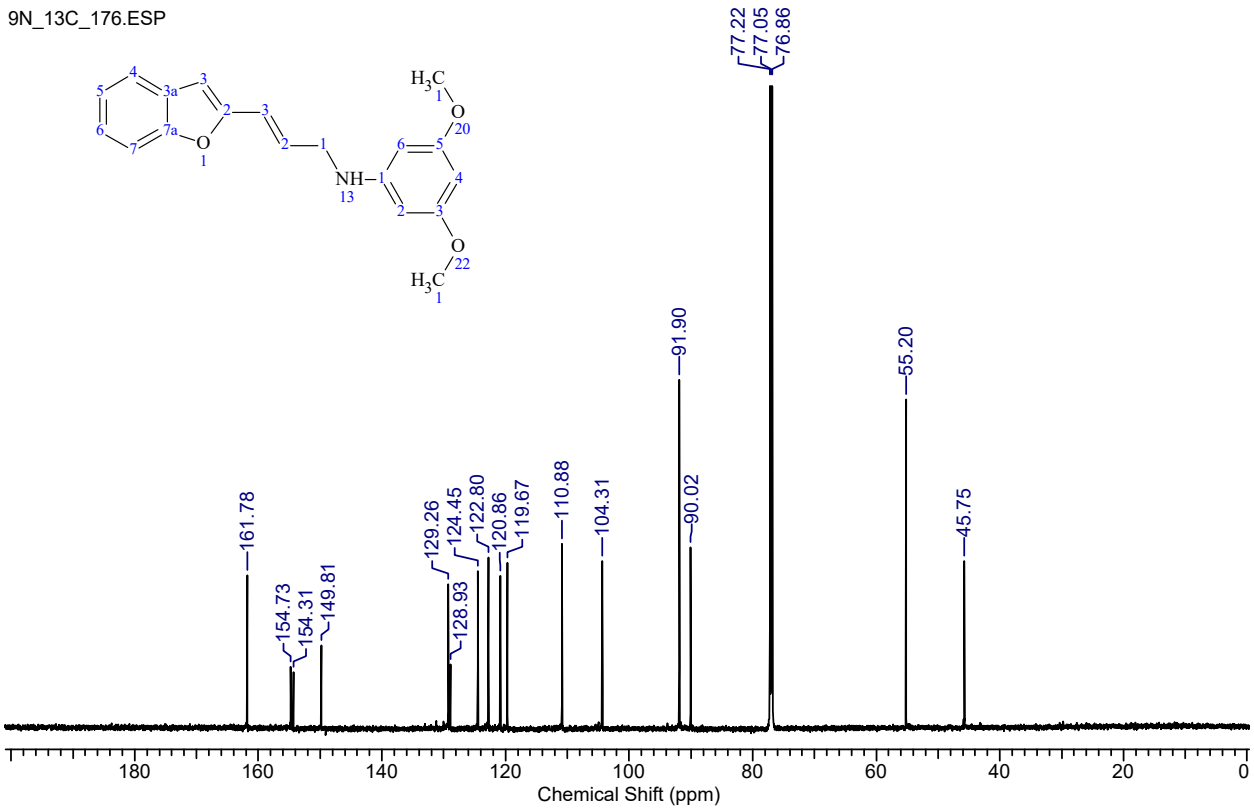
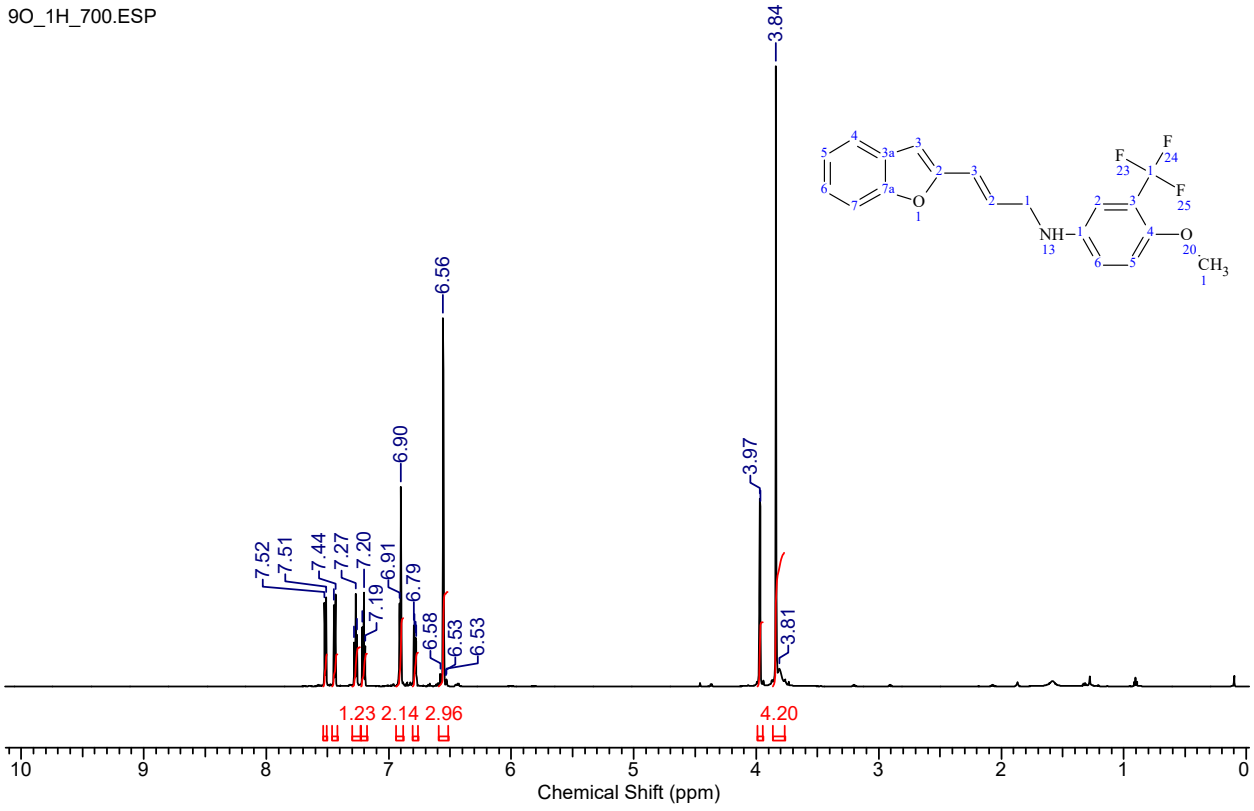
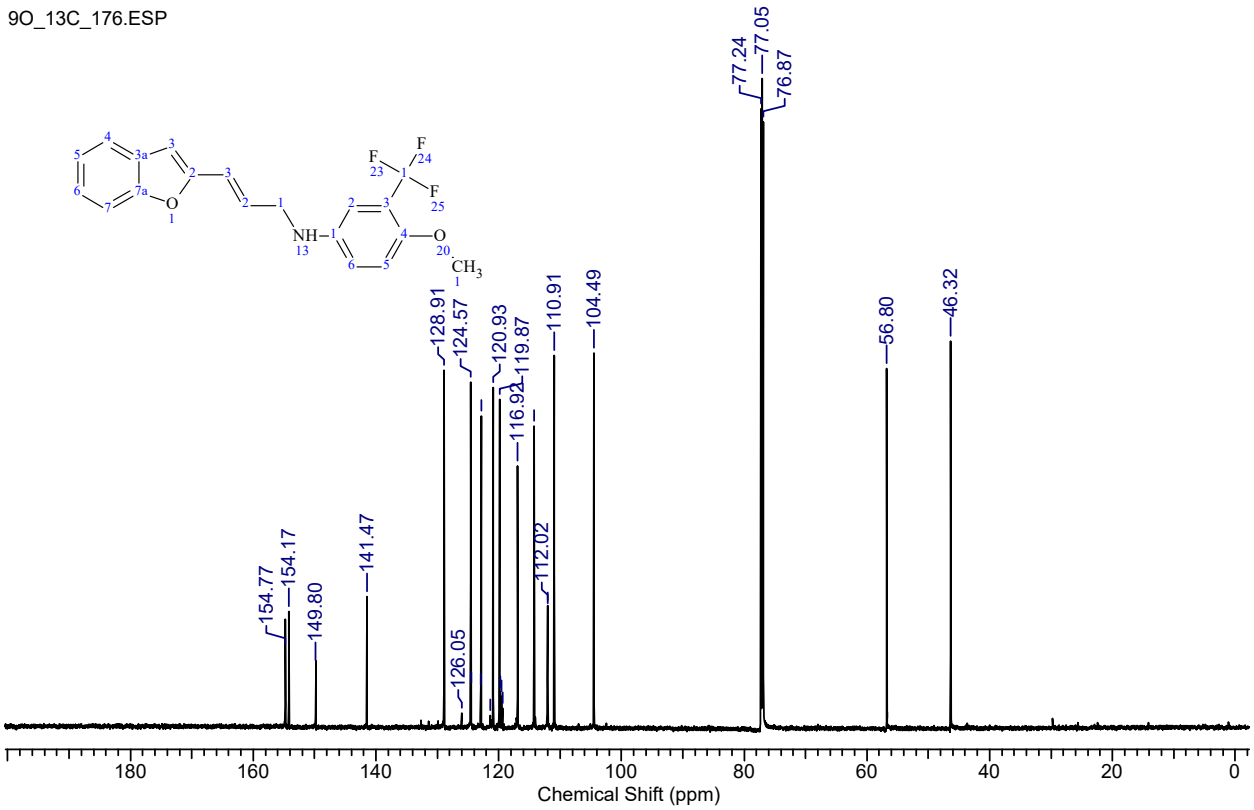




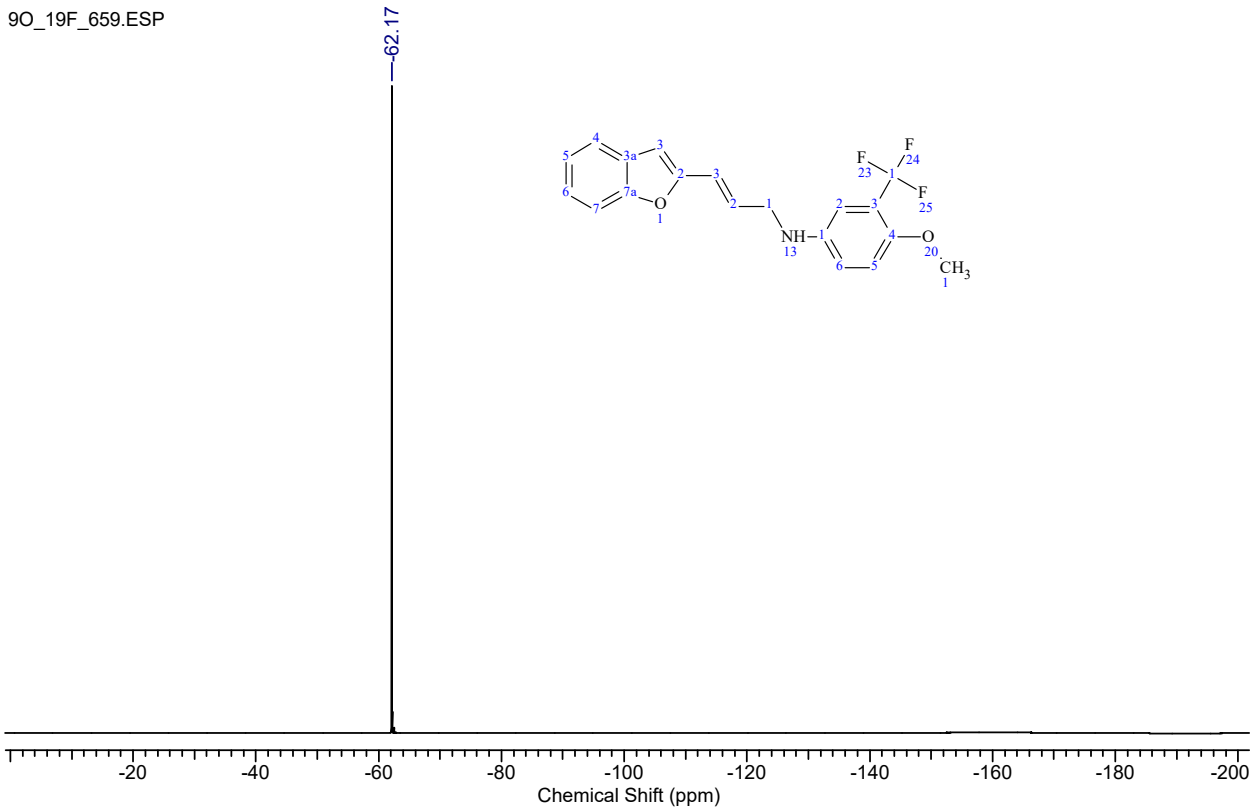

***(E)-N*-(3-(Benzo[*b*]furan-2-yl)allyl)-4-methoxy-3-(trifluoromethyl)aniline (9o).**



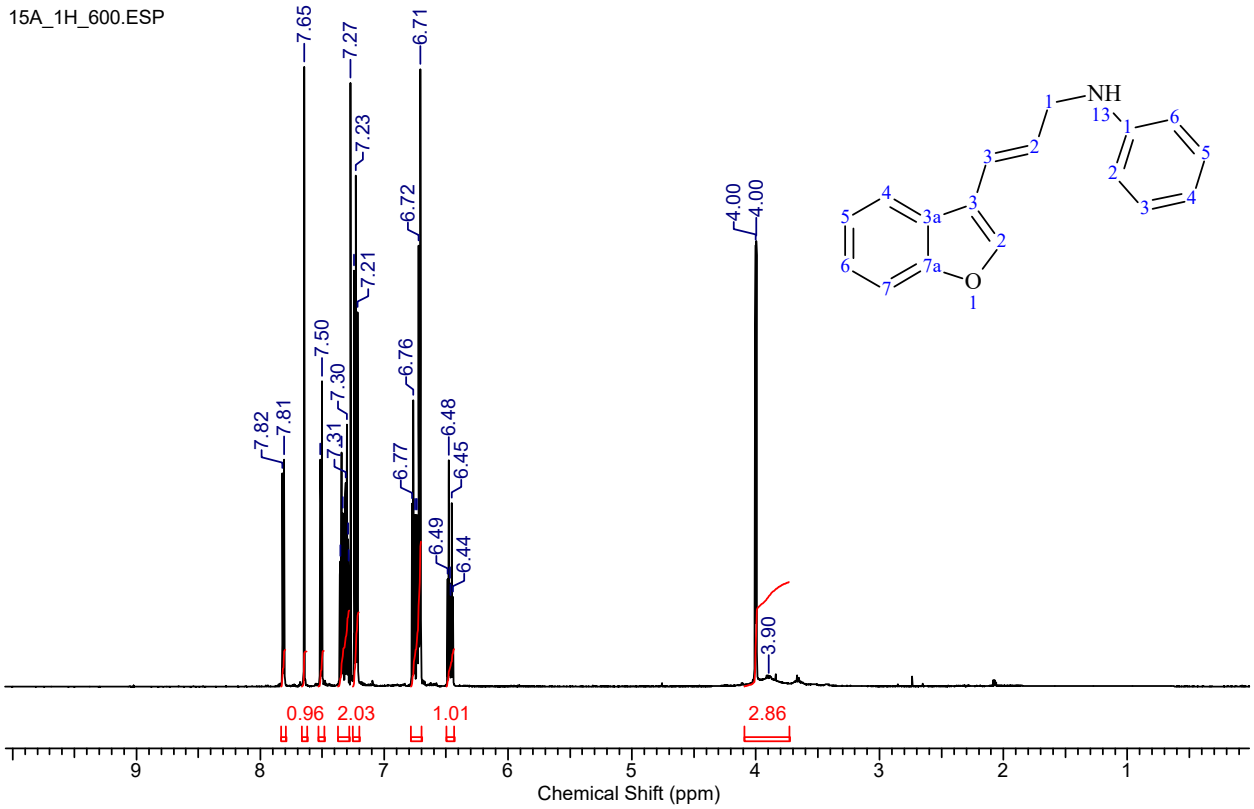
9O_13C_176.ESP

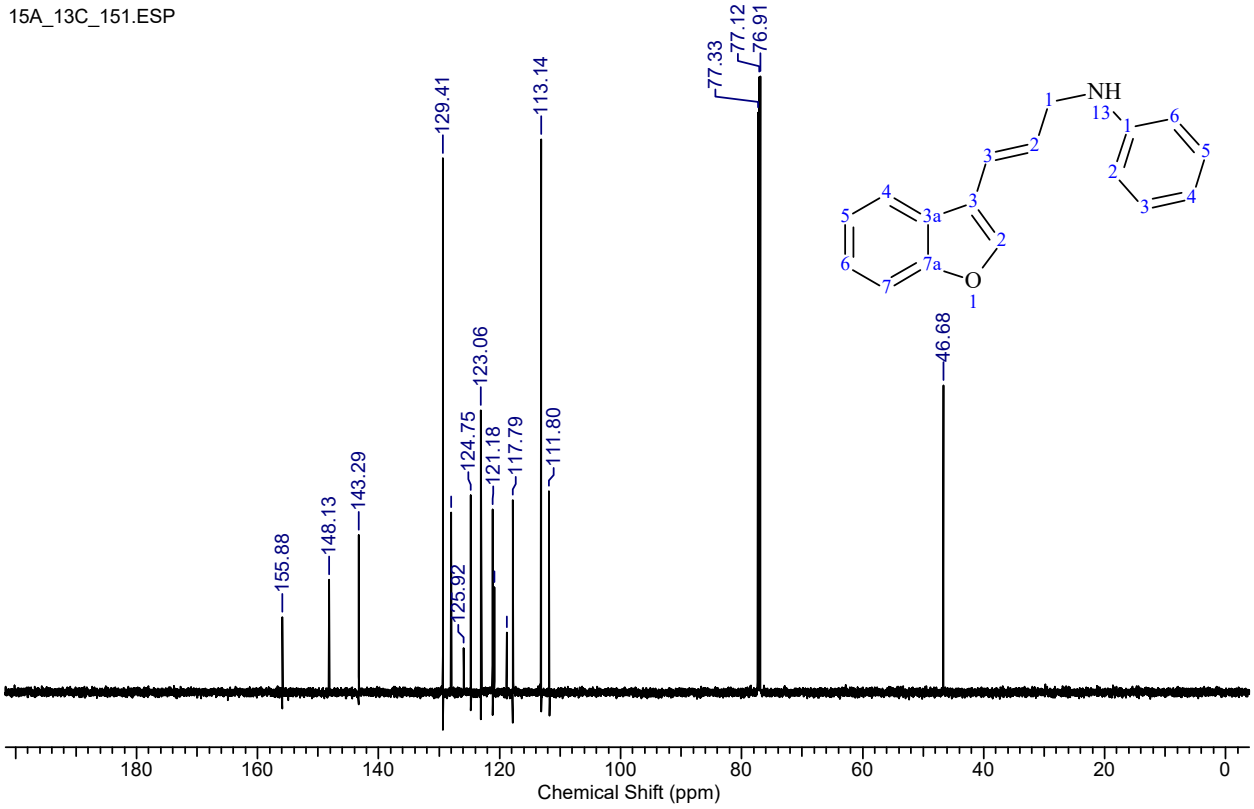



9O_19F_659.ESP

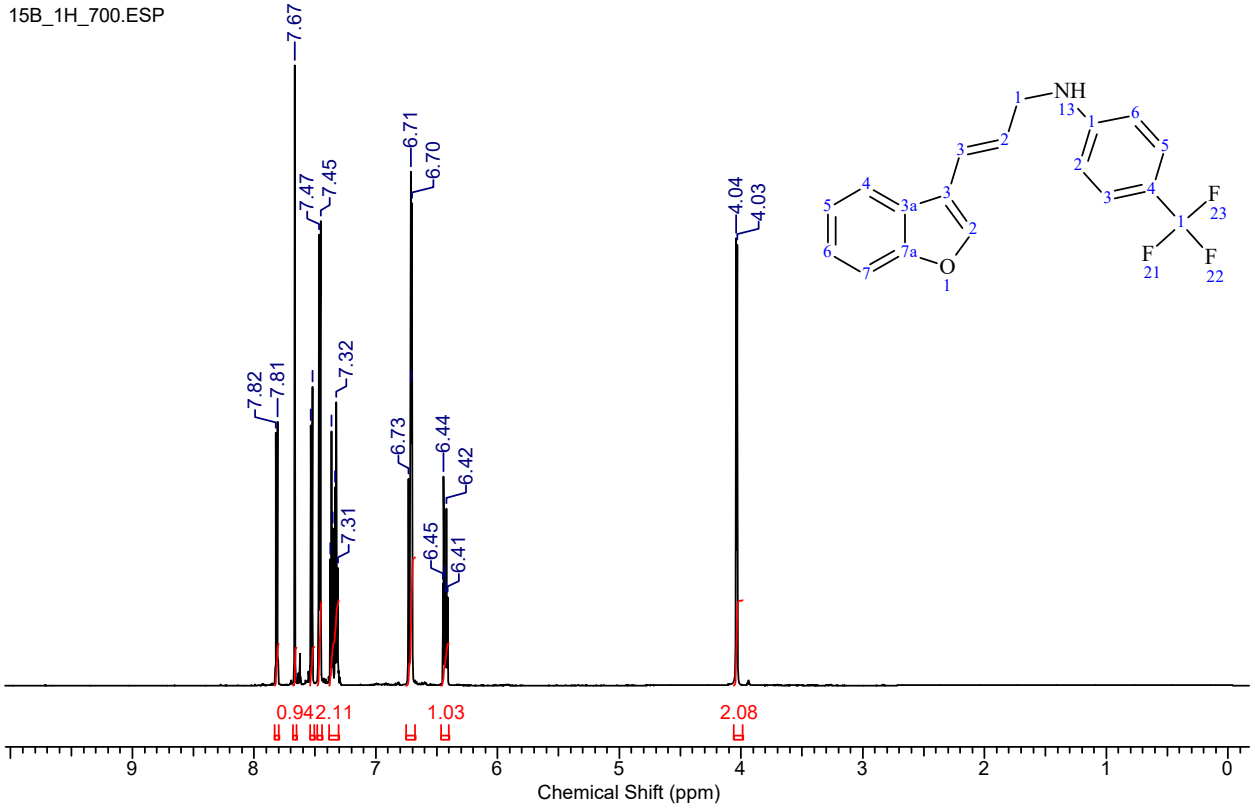


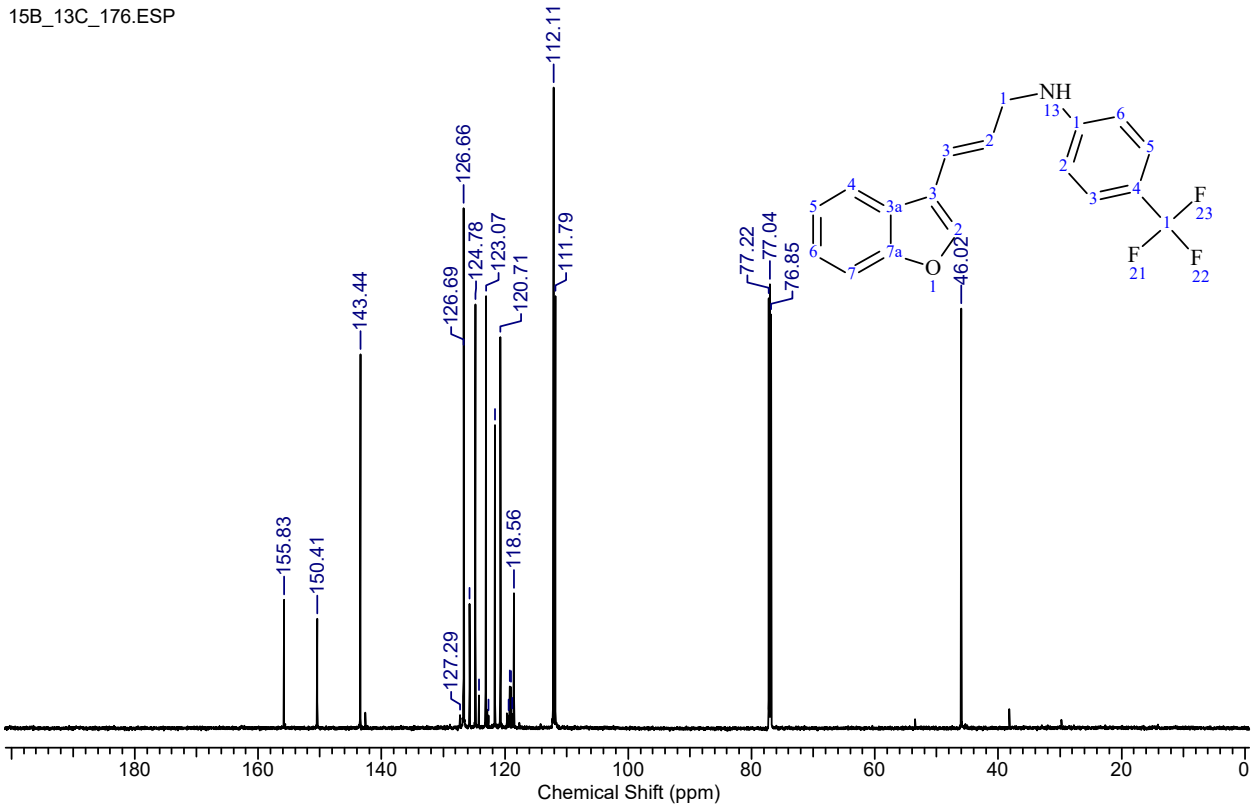
***(E)-N*-(3-(Benzo[b]furan-3-)allyl)aniline (15a).**

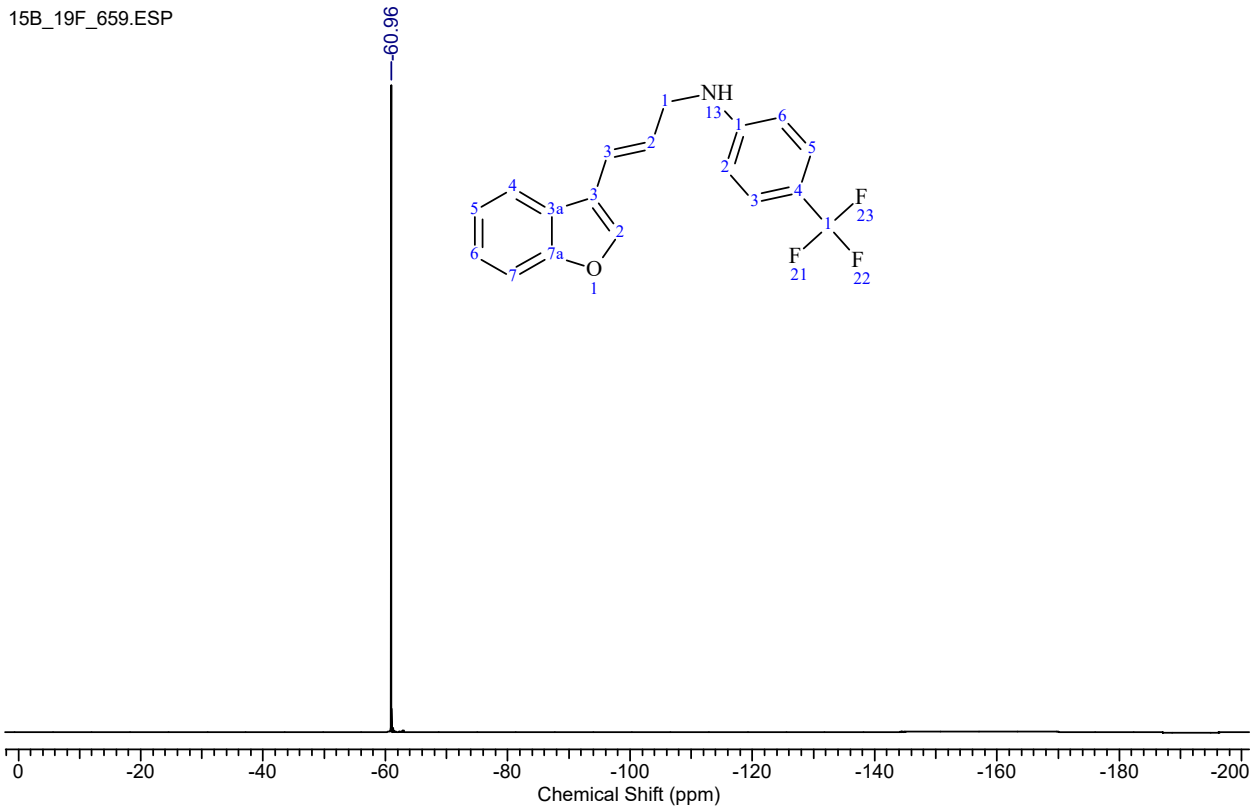


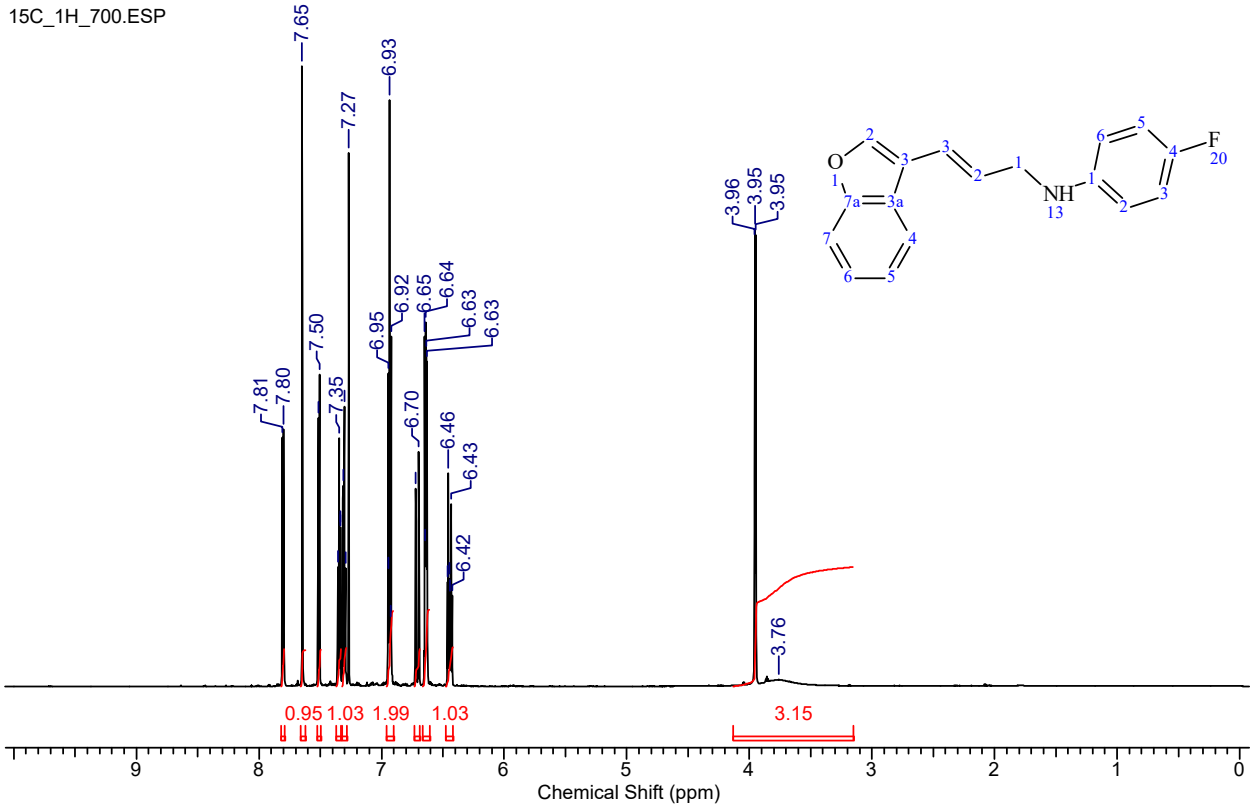
**(*E*)-*N*-(3-(Benzo[b]furan-3-)allyl)-4-(trifluoromethyl)aniline (15b).**

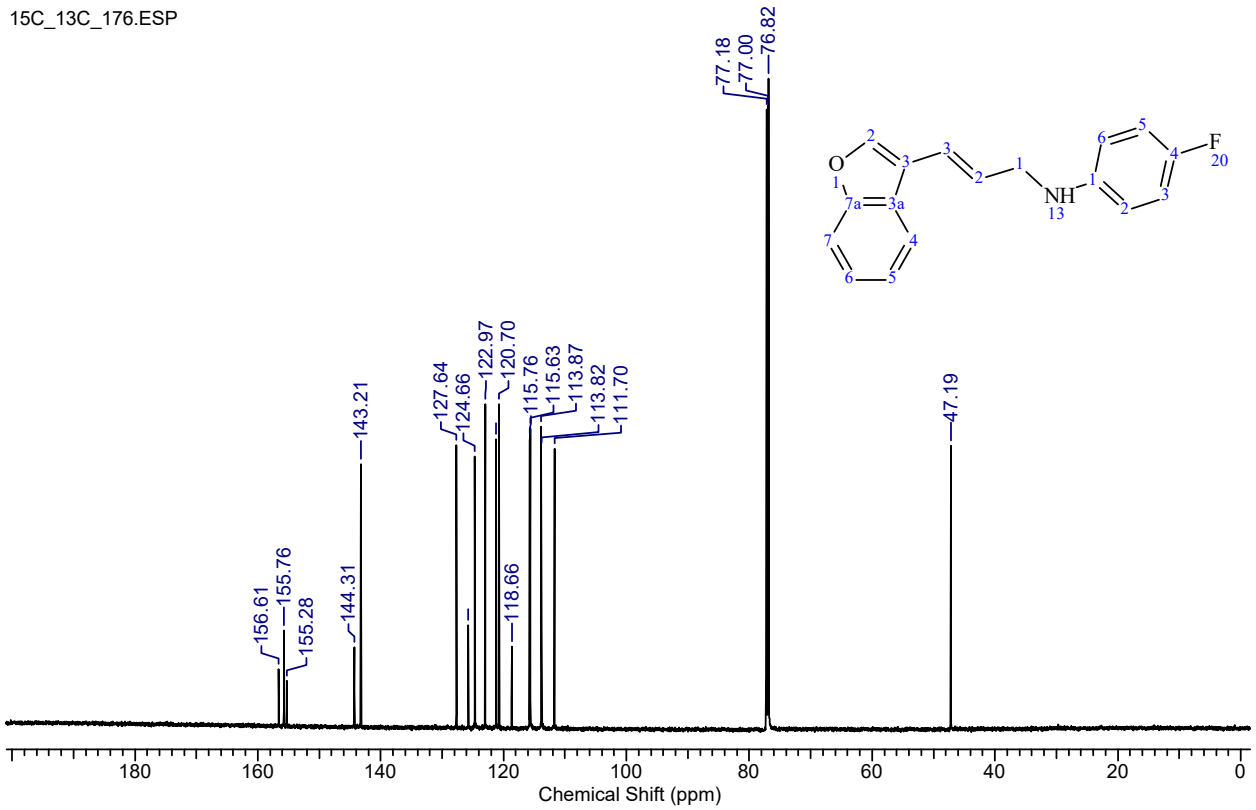


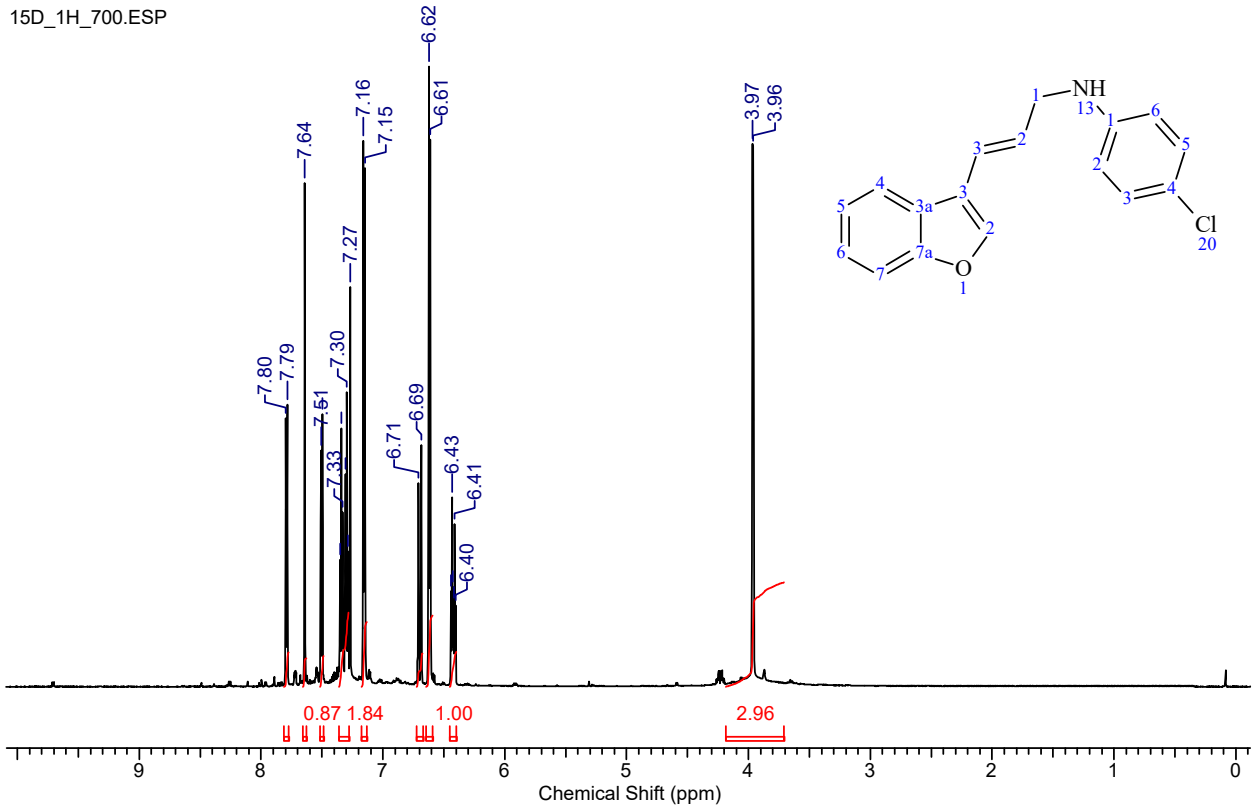


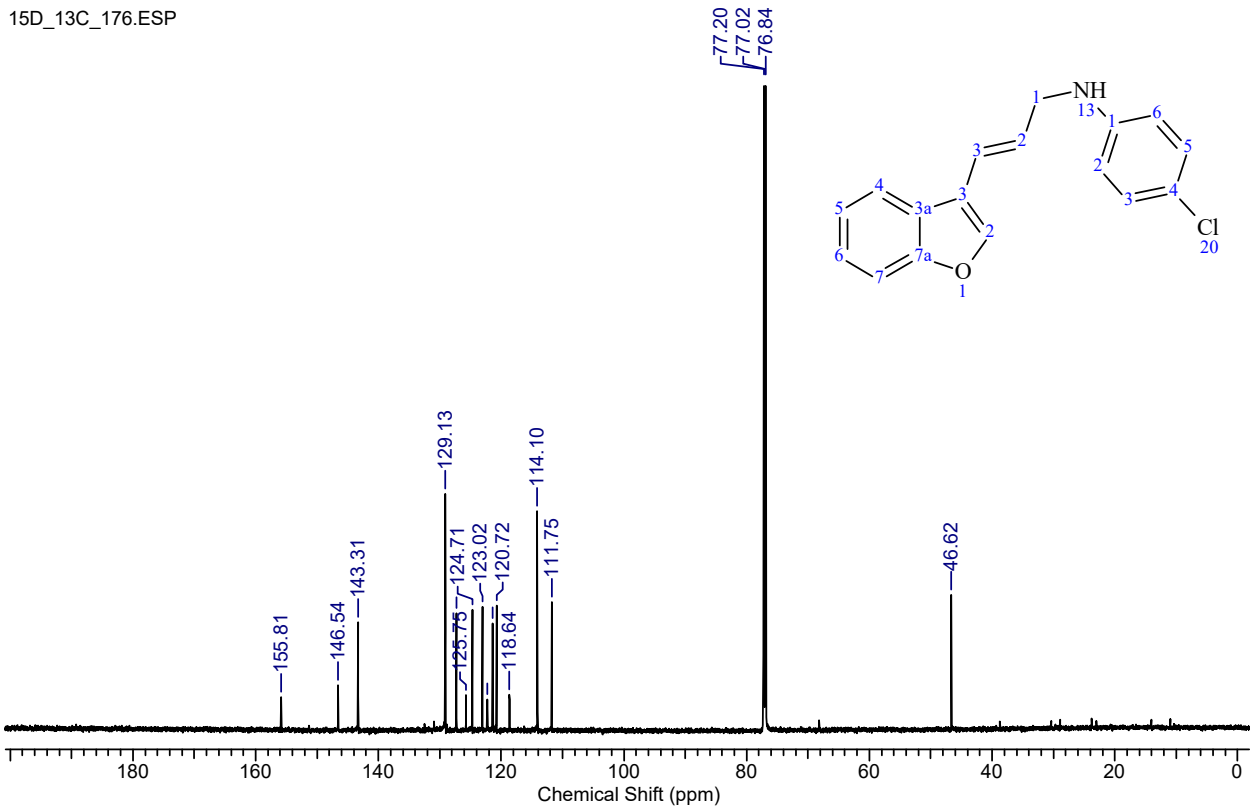

***(E)-N*-(3-(Benzo[b]furan-3-)allyl)-4-fluoro-aniline (15c).**



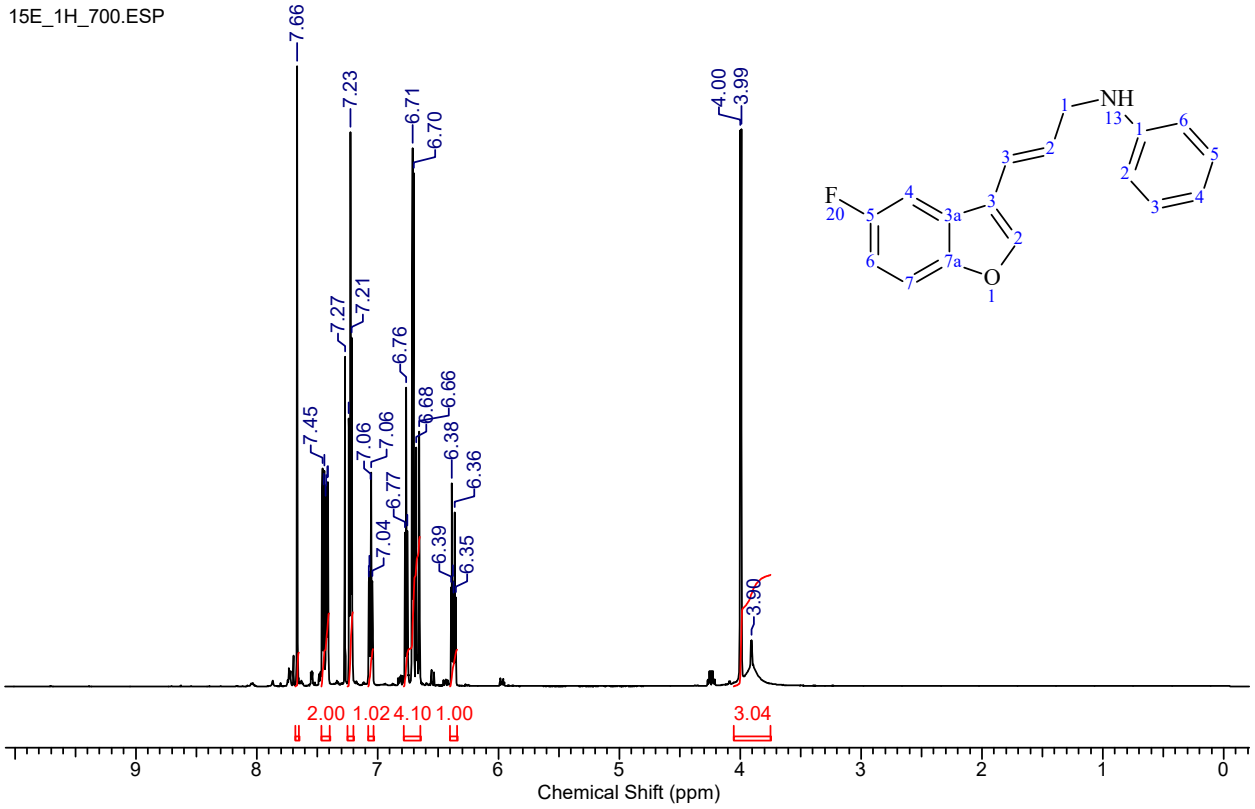


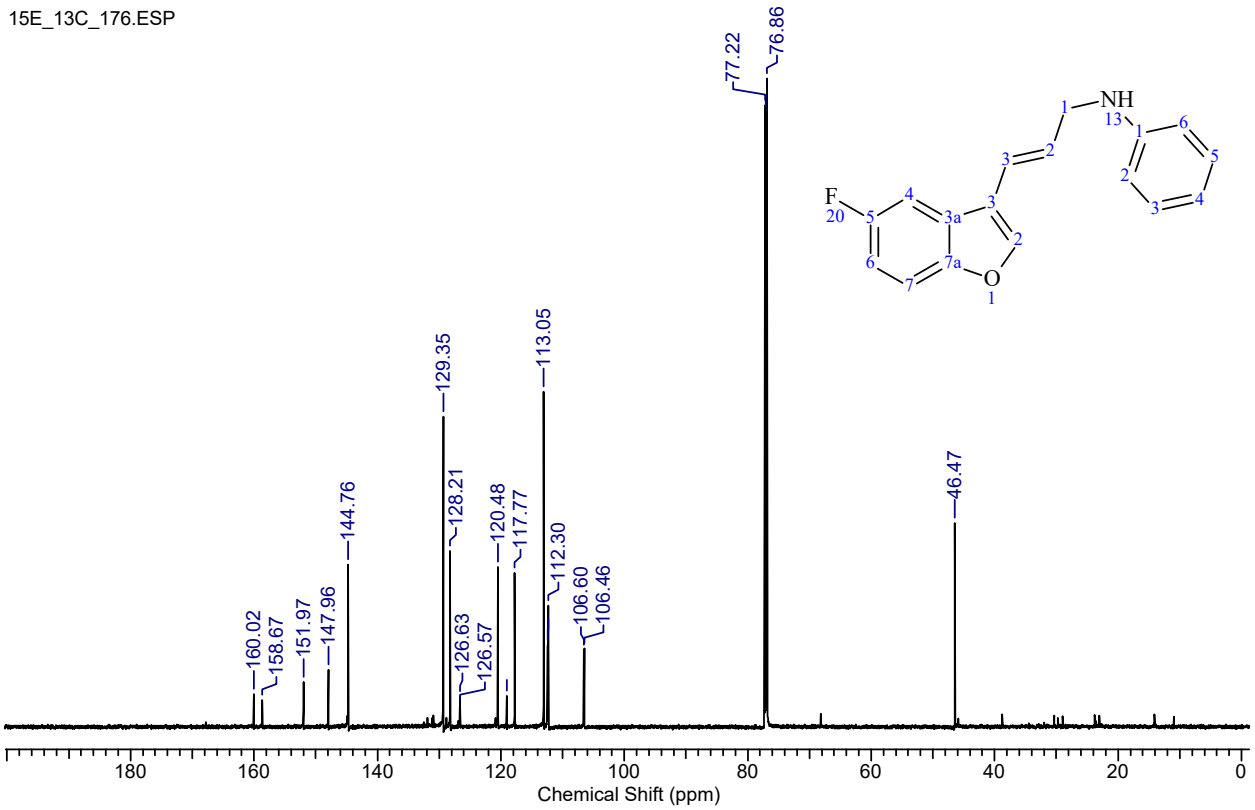

***(E)-N*-(3-(Benzo[b]furan-3-)allyl)-4-chloro-aniline (15d).**

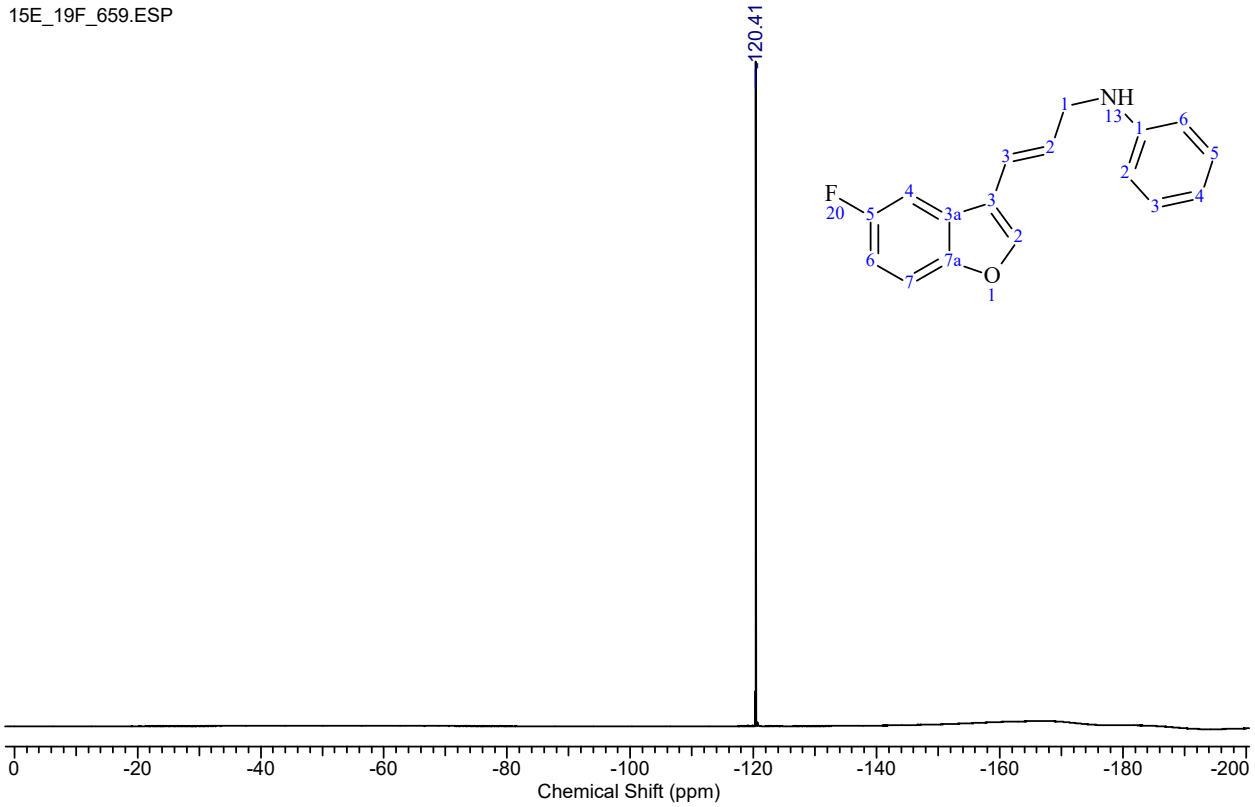





***(E)-N*-(3-(5-Fluoro-benzo[b]furan-3-)allyl)aniline (15e).**

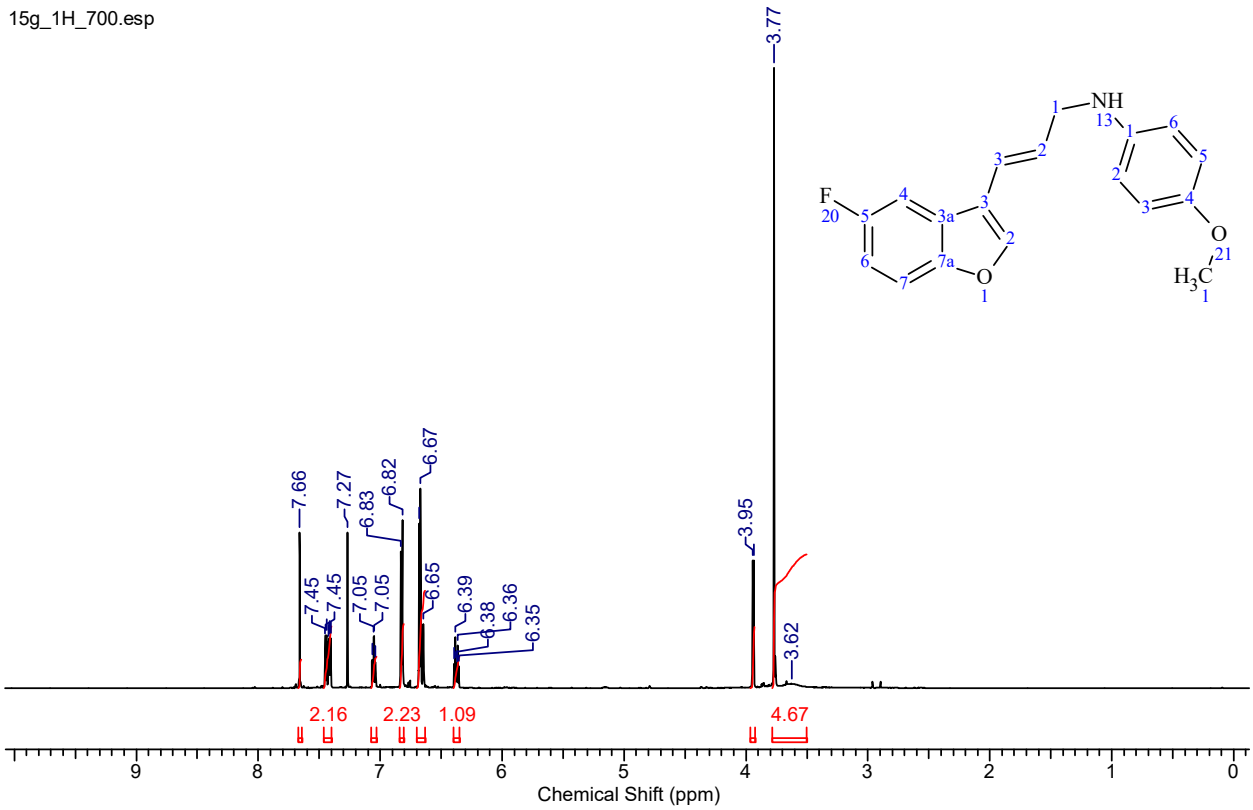




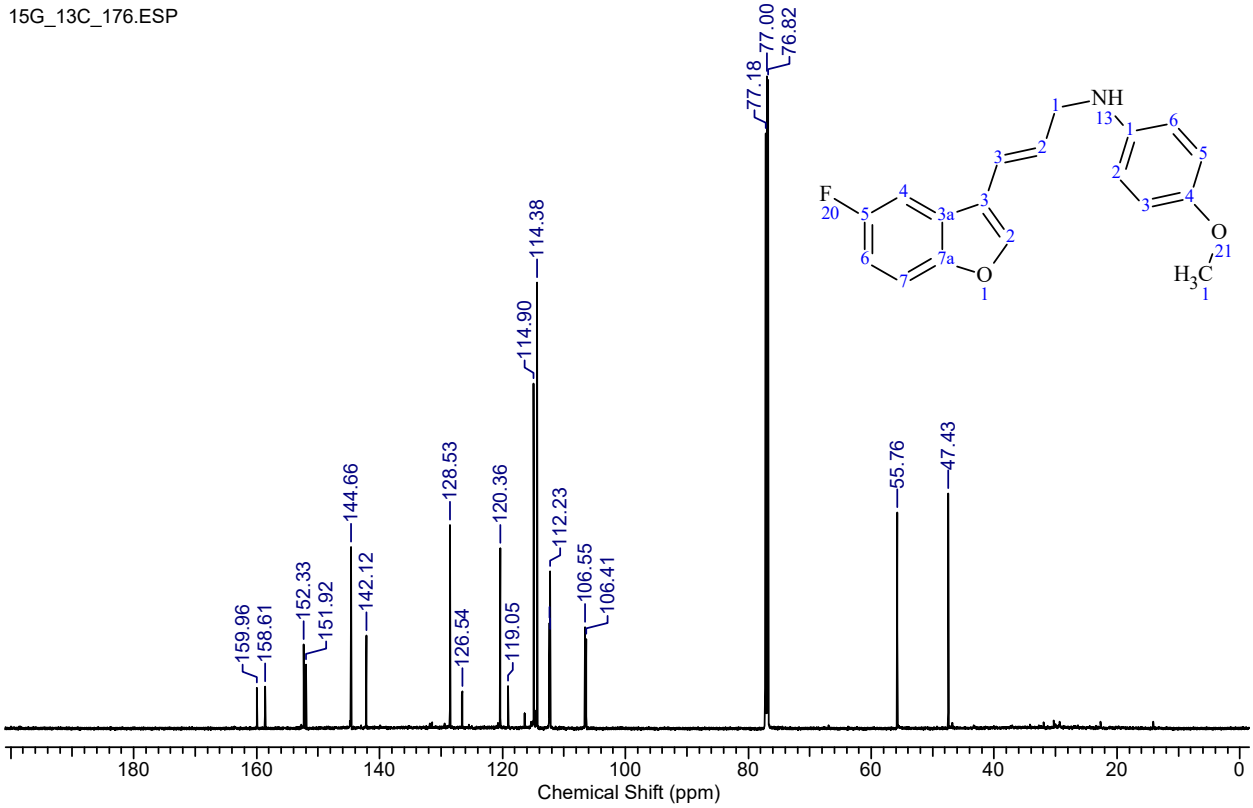



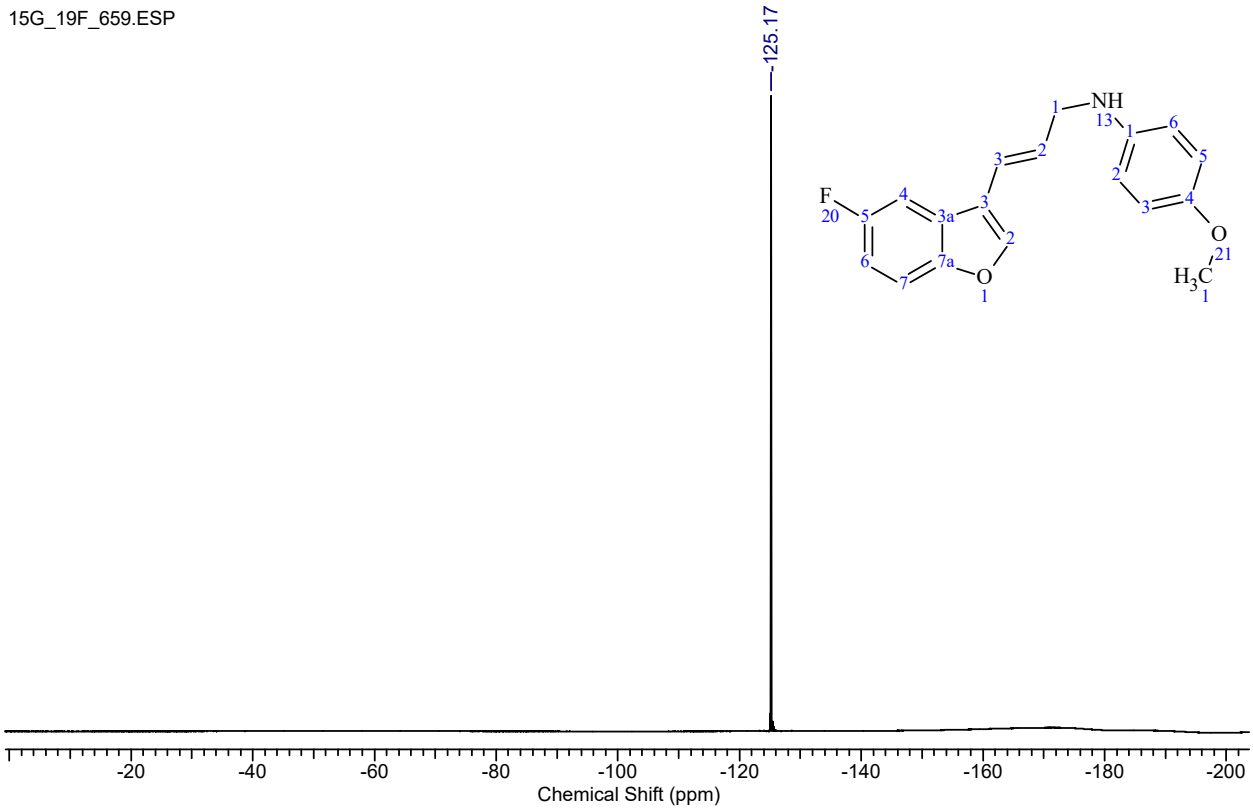

***(E)-N*-(3-(5-Fluoro-benzo[b]furan-3-)allyl)-4-methoxyaniline (15g).**

15g_1H_700.esp

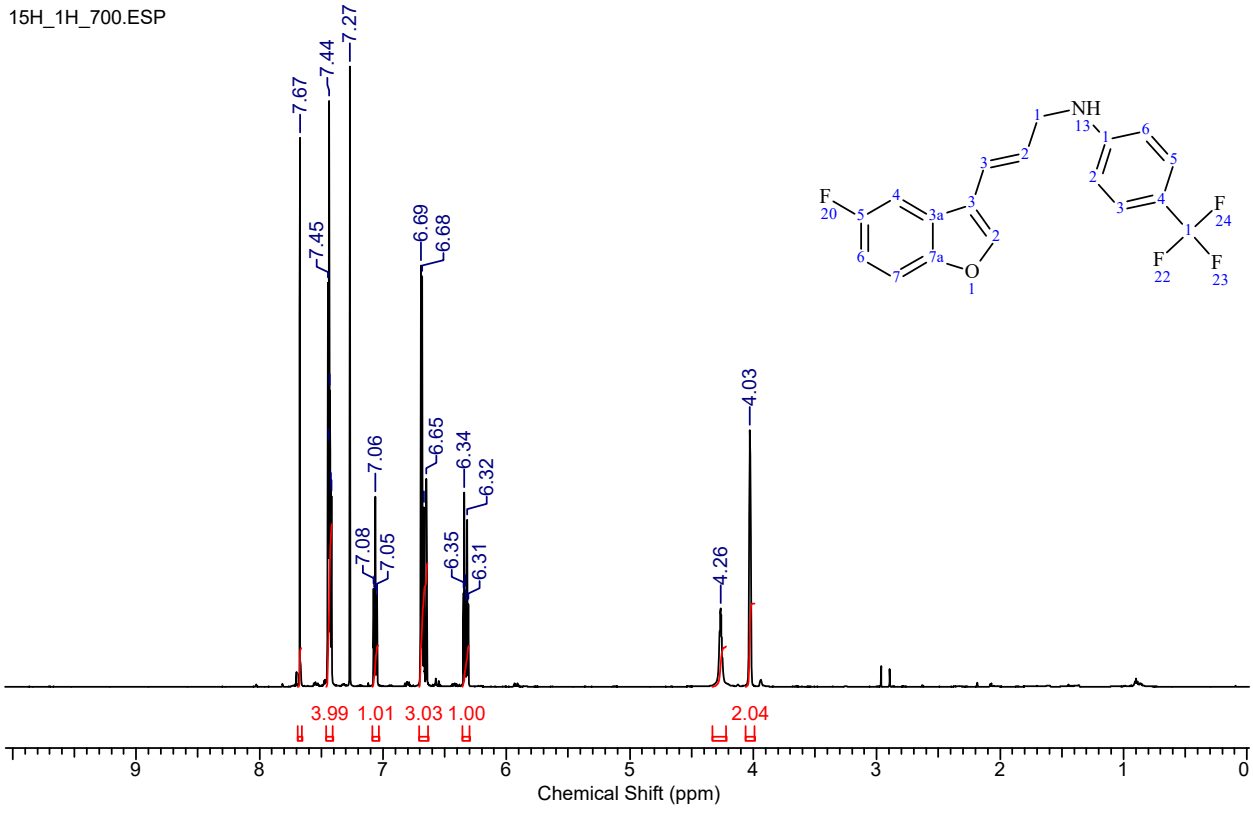



15G_13C_176.ESP

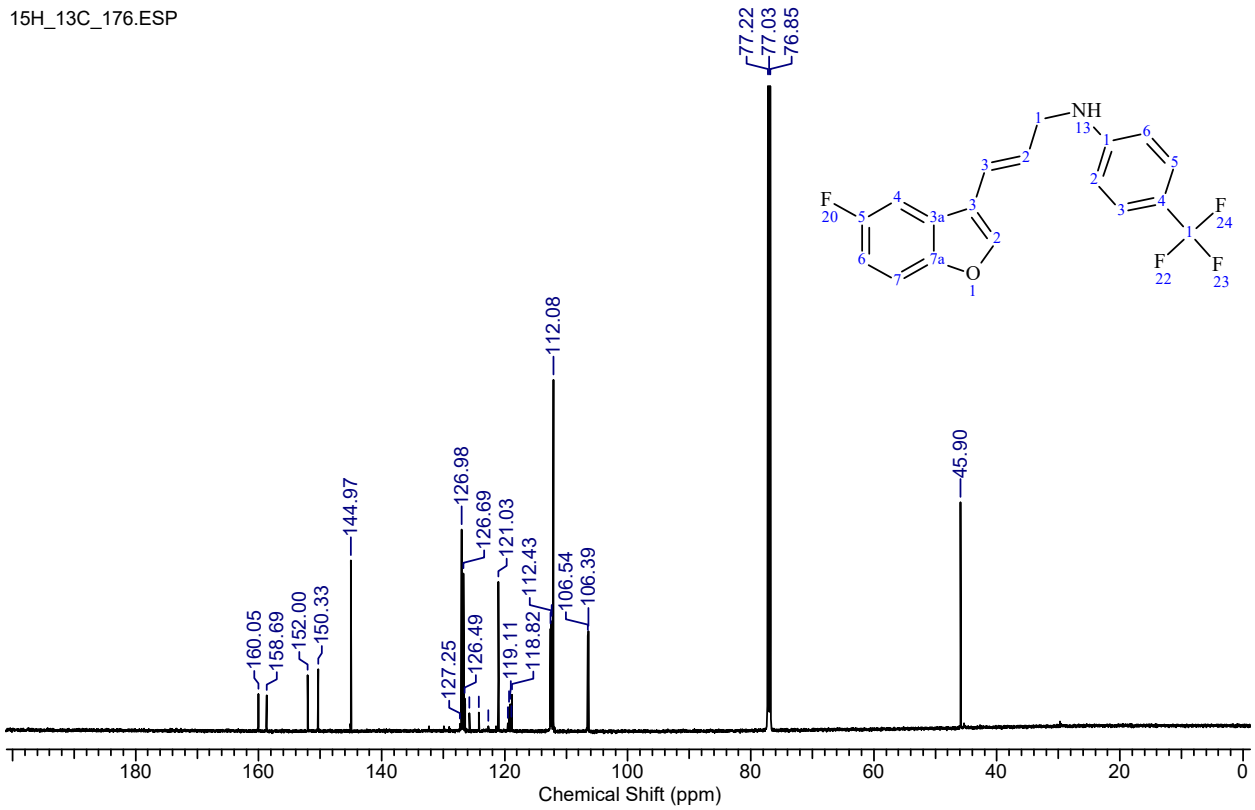




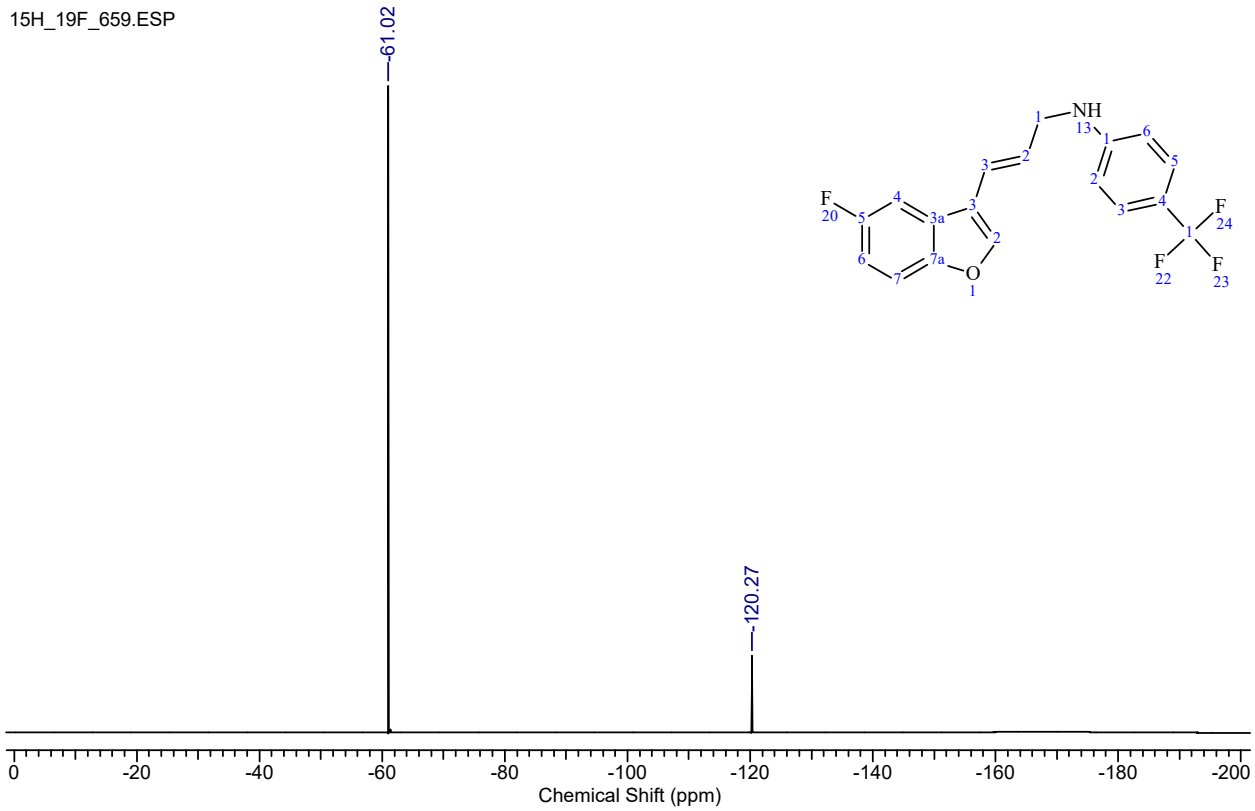

***(E)-N*-(3-(5-Fluoro-benzo[b]furan-3-)allyl)-4-(trifluoromethyl)aniline (15h).**



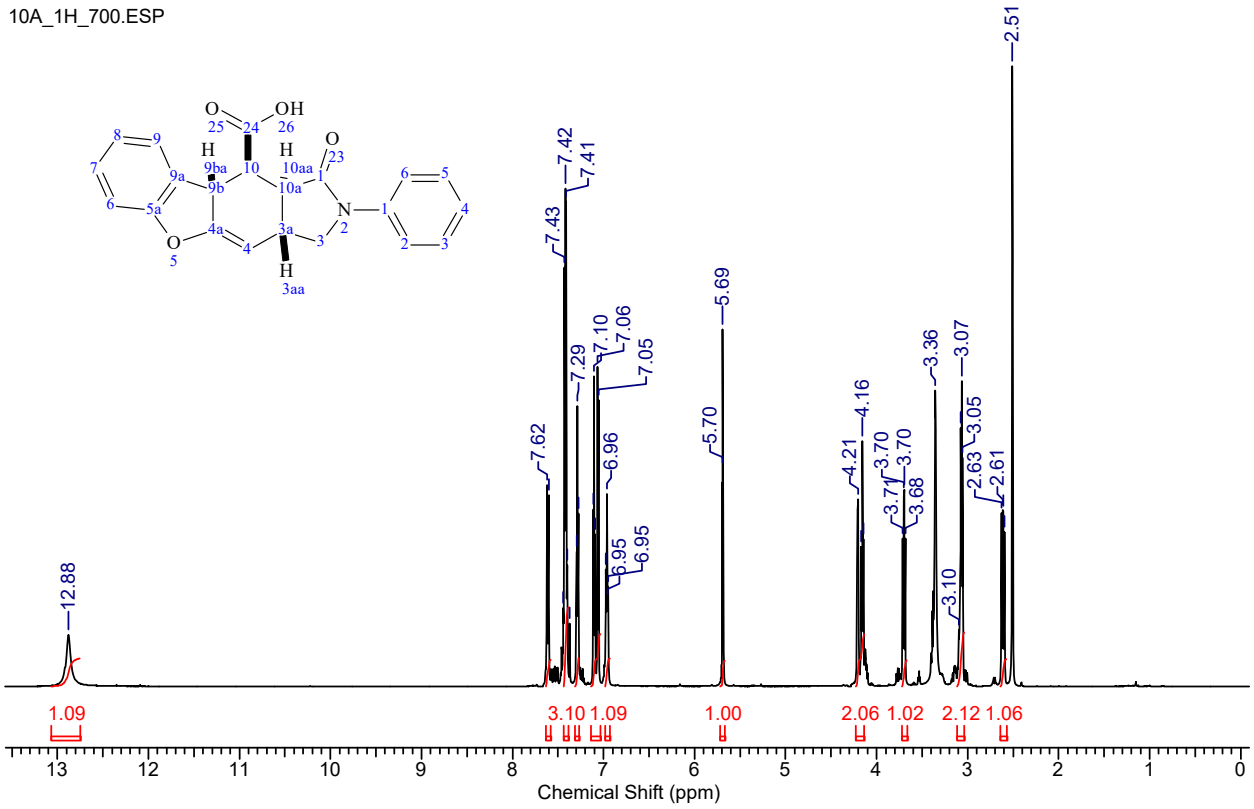
15H_13C_176.ESP

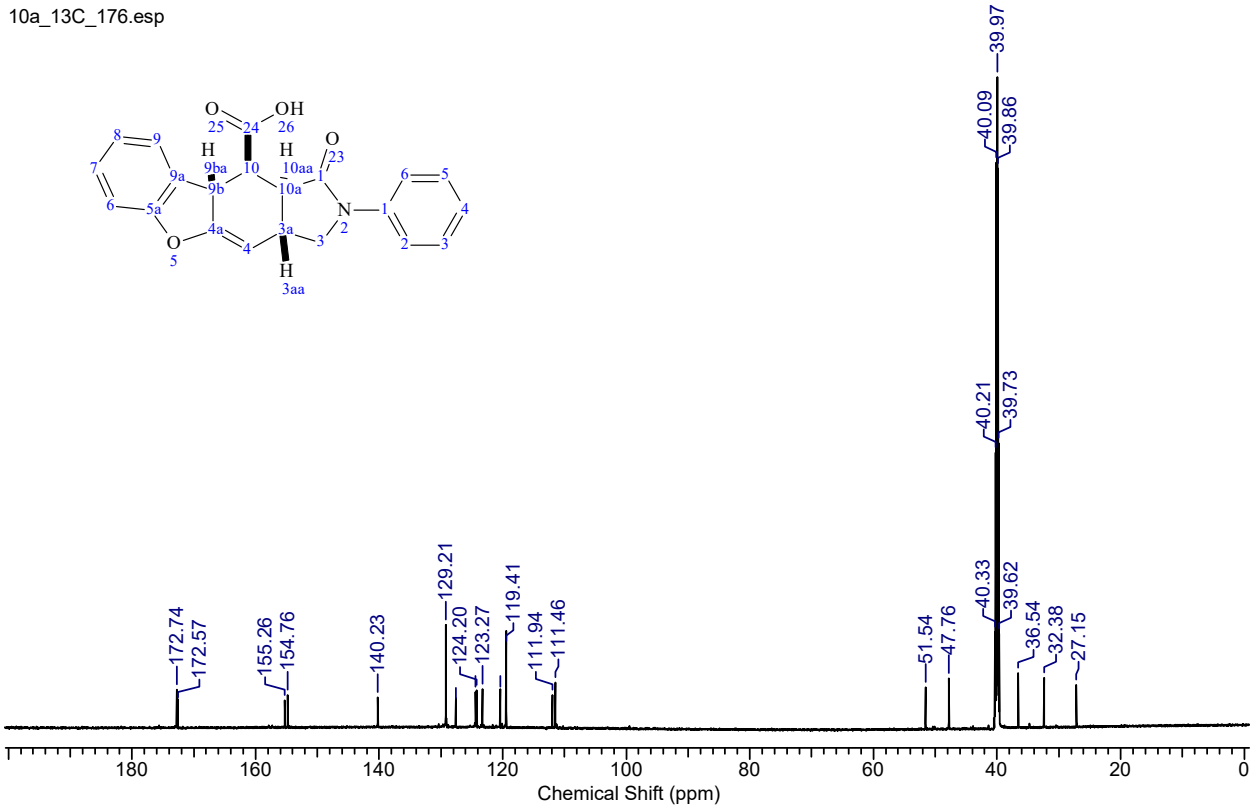



15H_19F_659.ESP



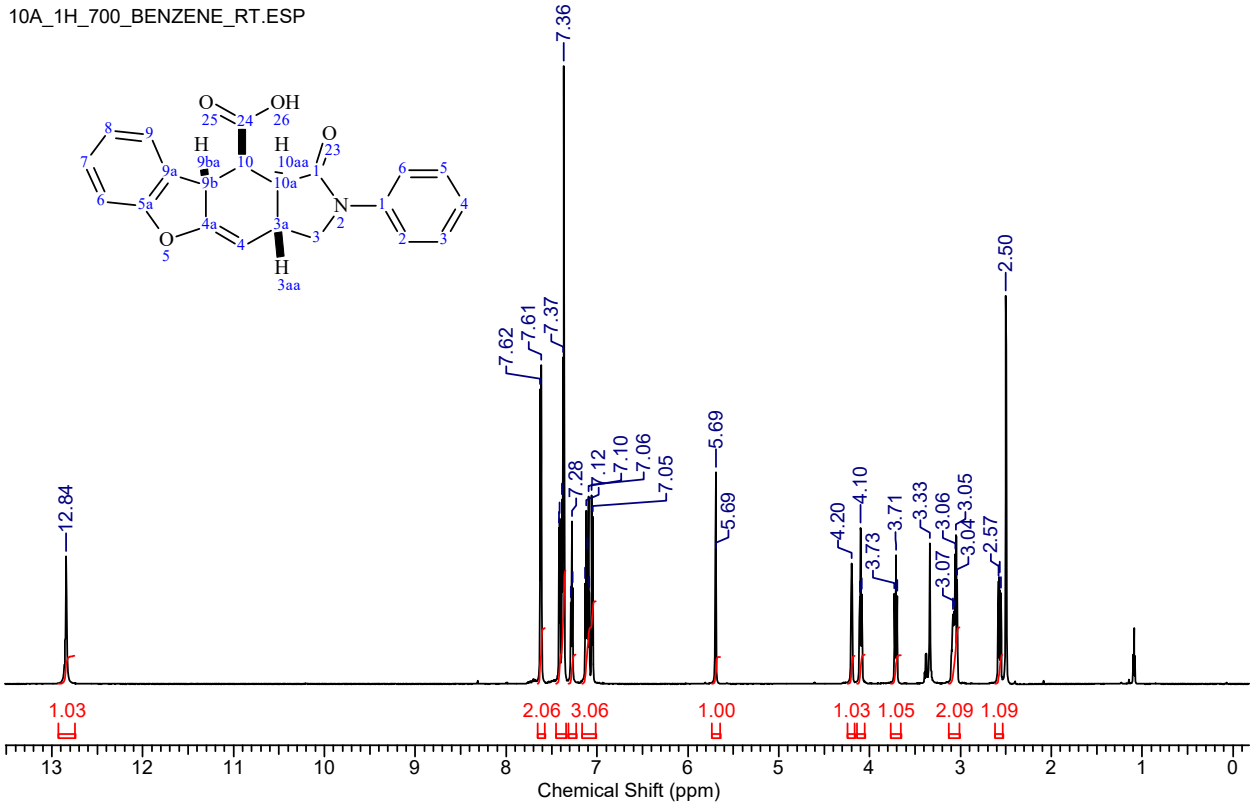
**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-1-Oxo-2-phenyl-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10a).**



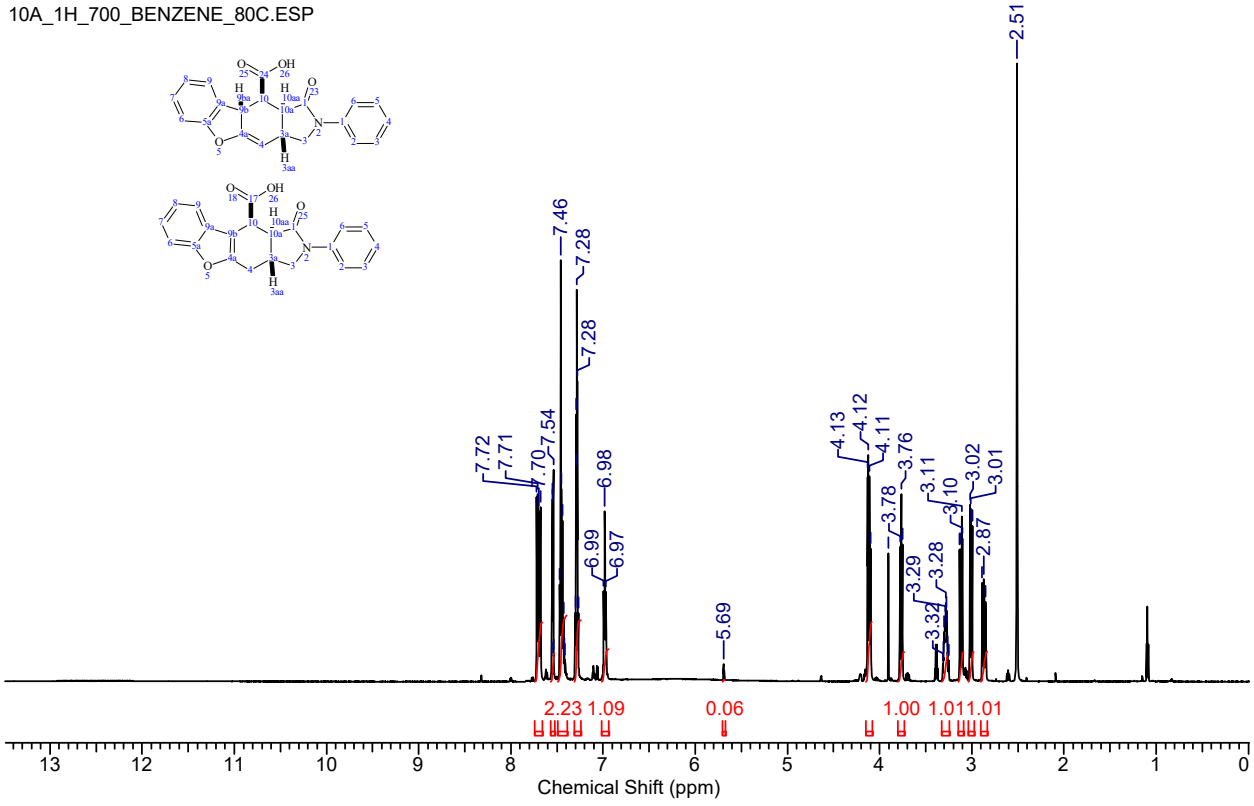



**Optimization of IMDAV reaction conditions of *N*-phenyl-*N*-benzofurylallylamine 9a and maleic anhydride**

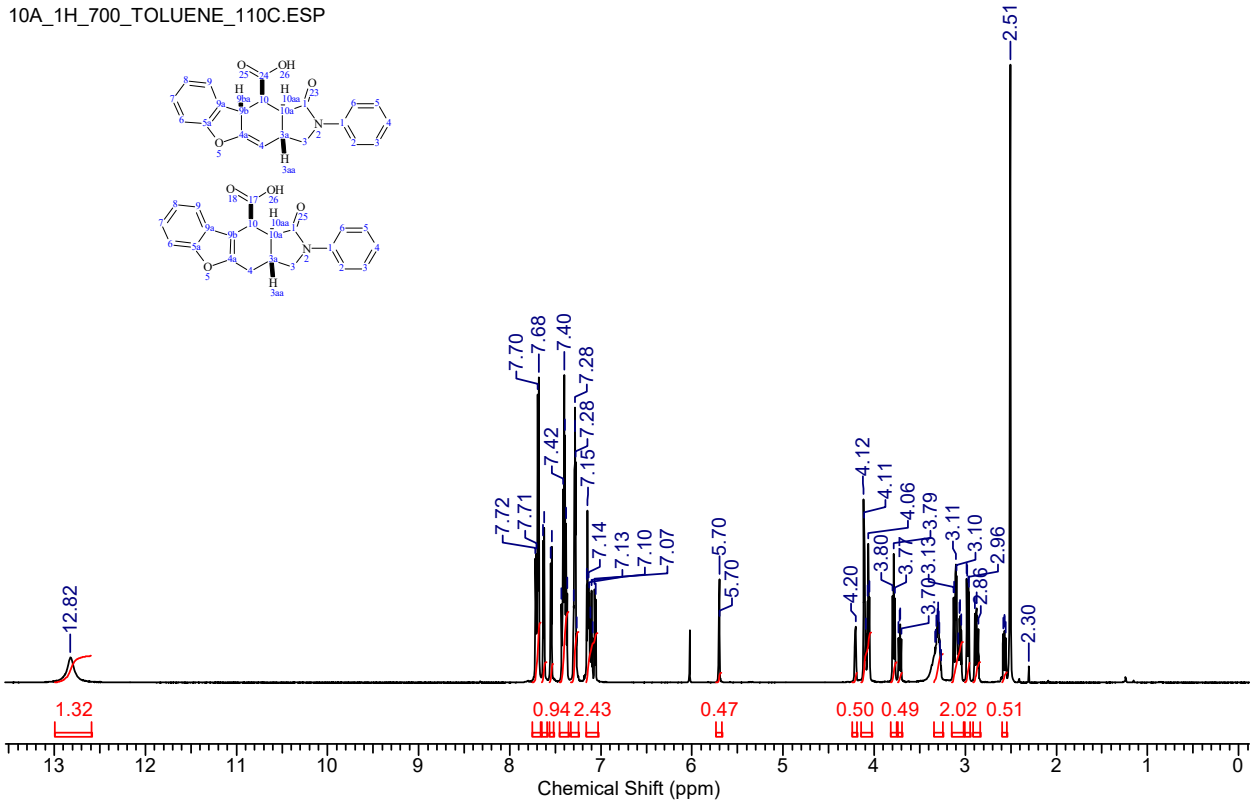
**PhH, r.t., 24**



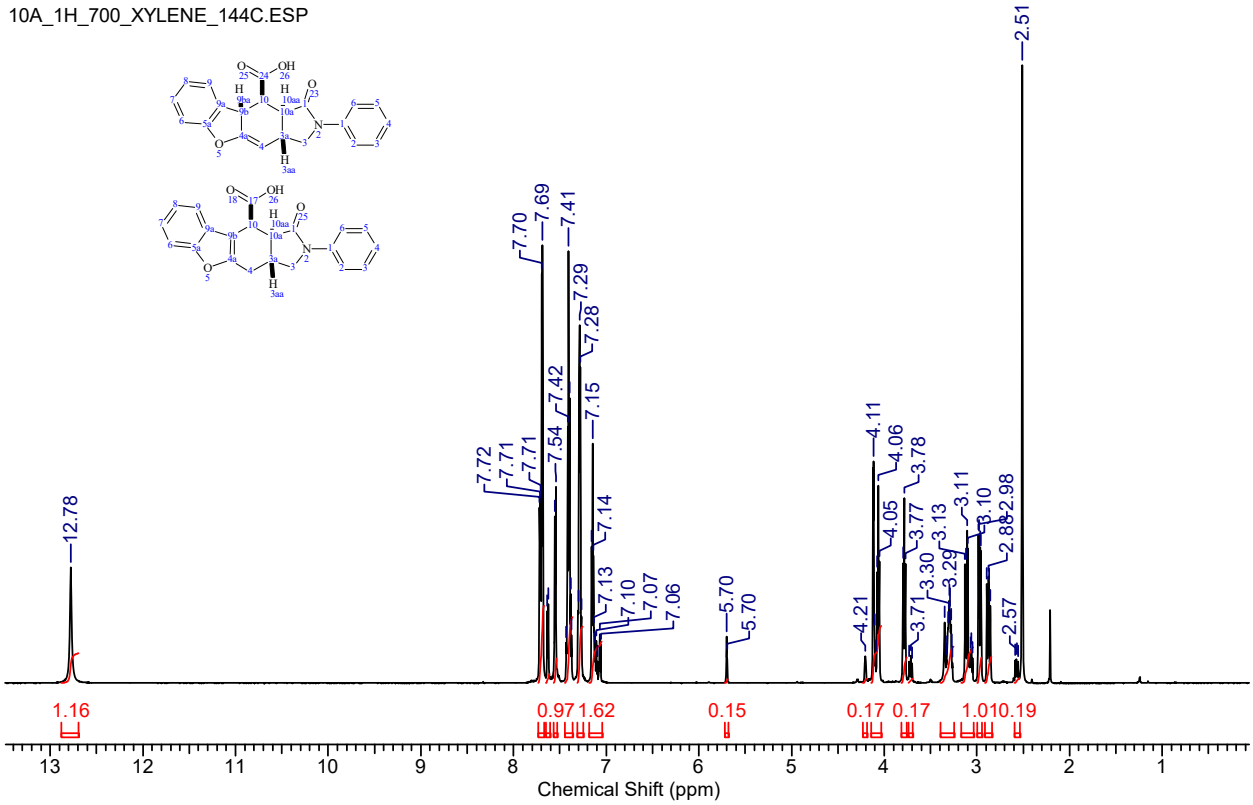

**PhH, reflux, 12 h**



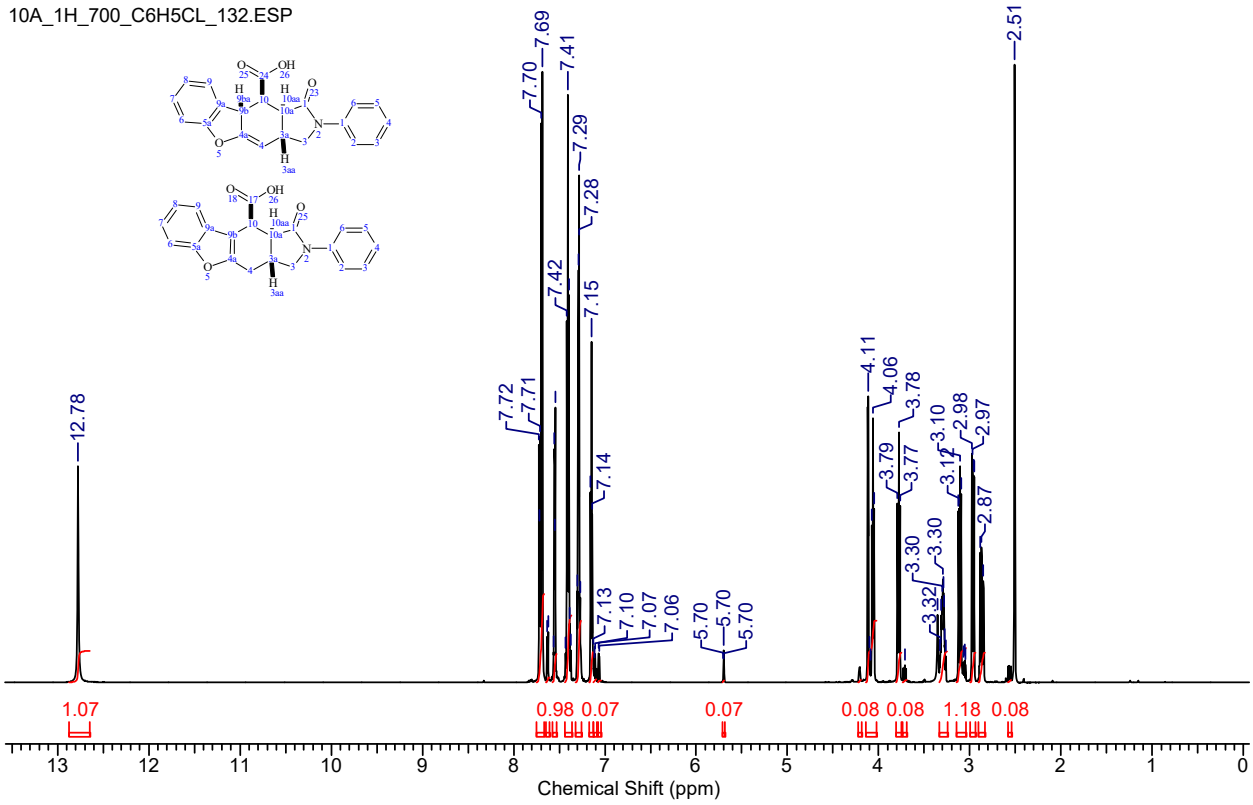
## PhMe, reflux , 12 h



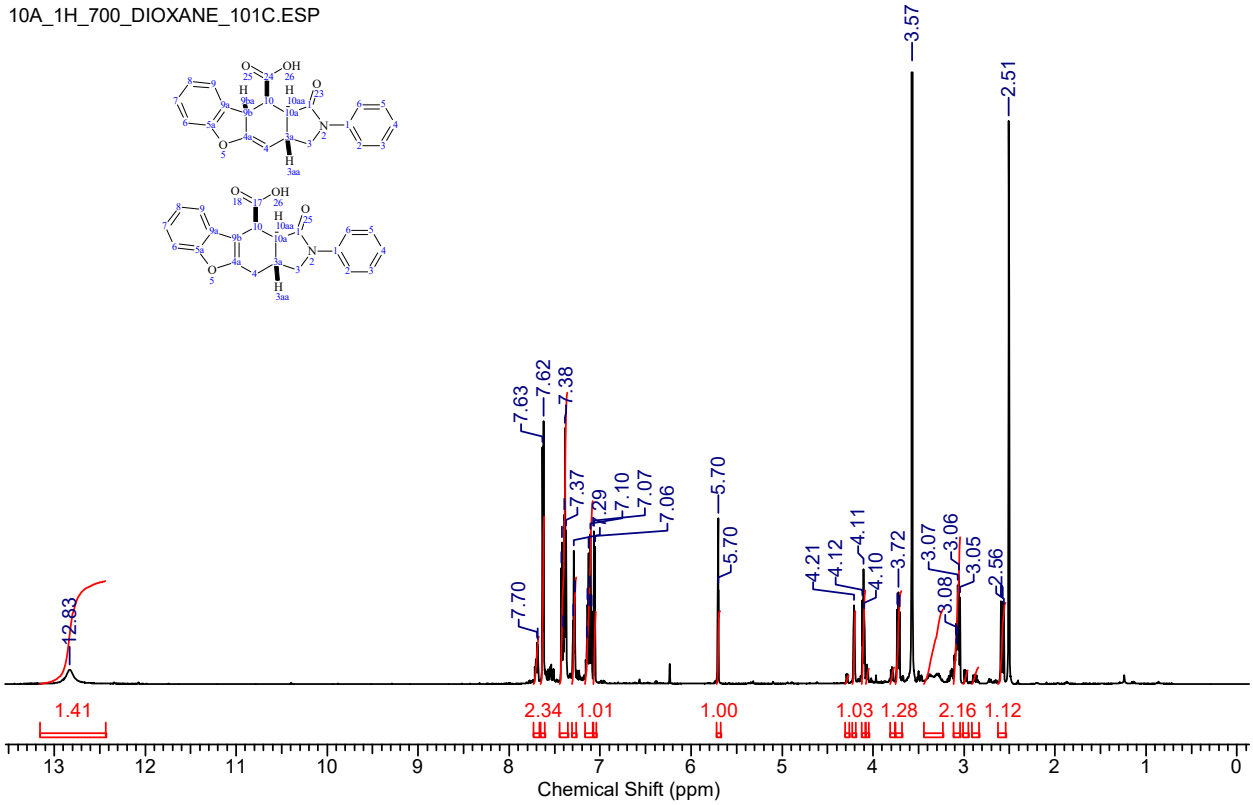

## o-xylene, reflux, 12h



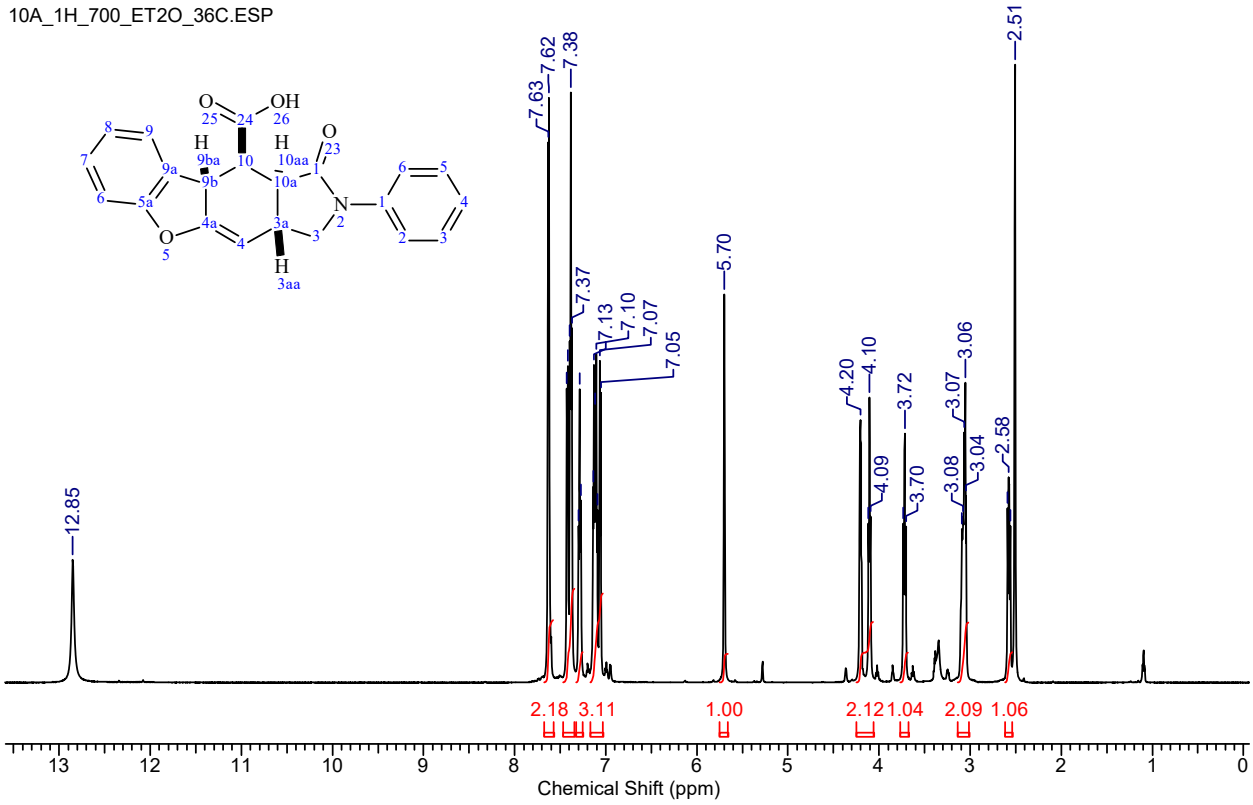
## PhCl, reflux, 12h



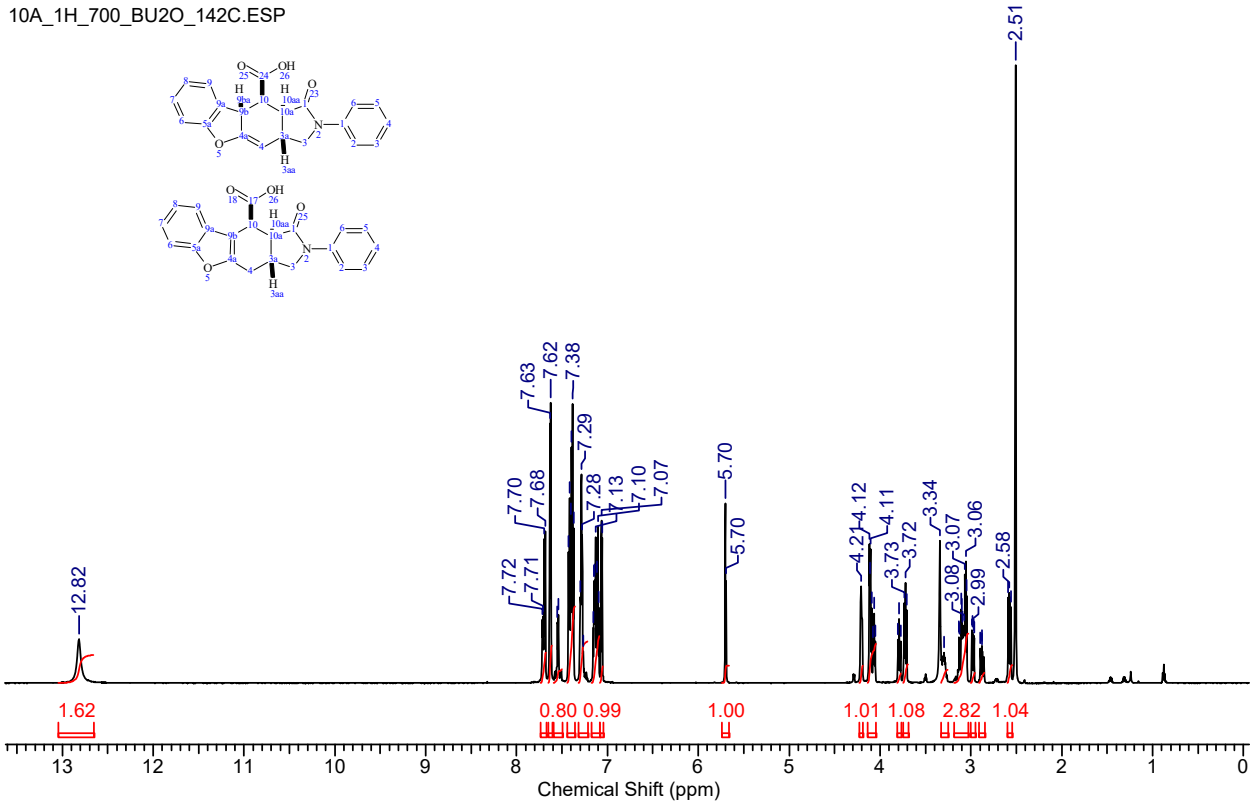

## 1,4-dioxane, reflux, 12h



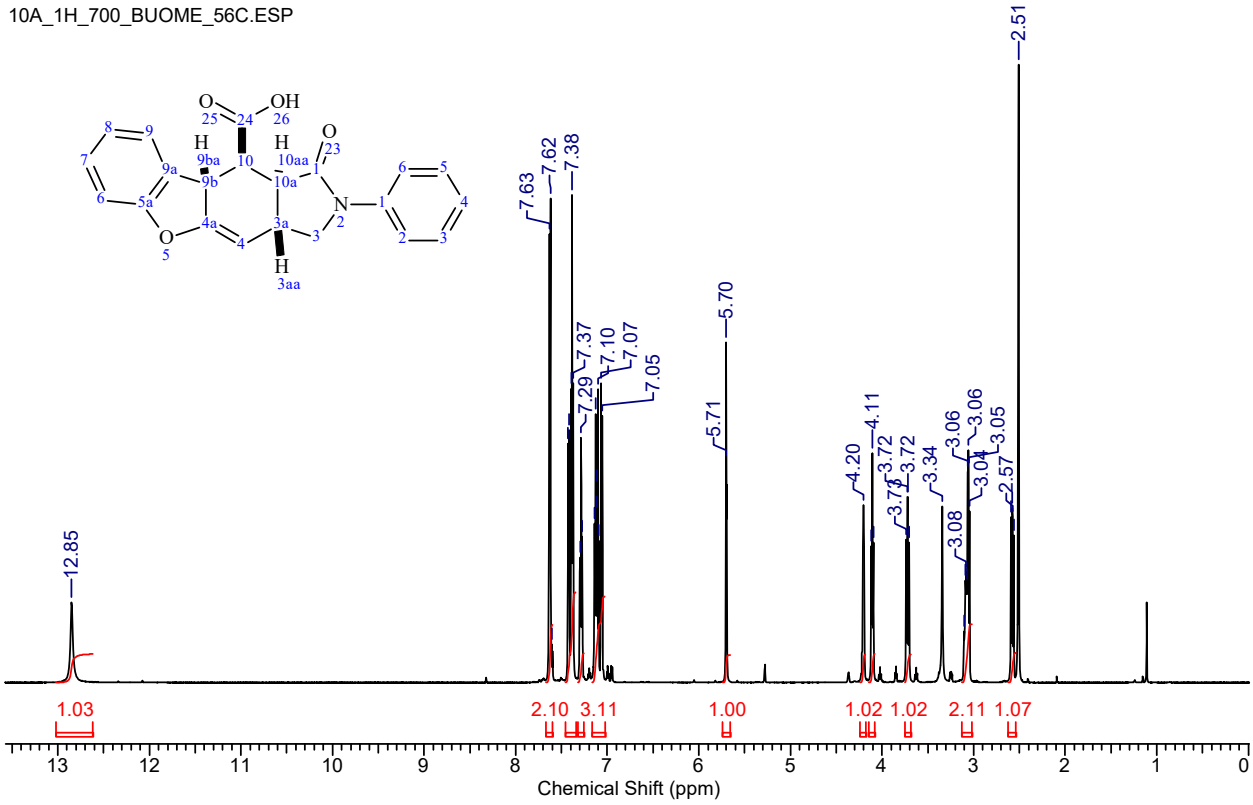
## $Et_2O$, reflux, 12h



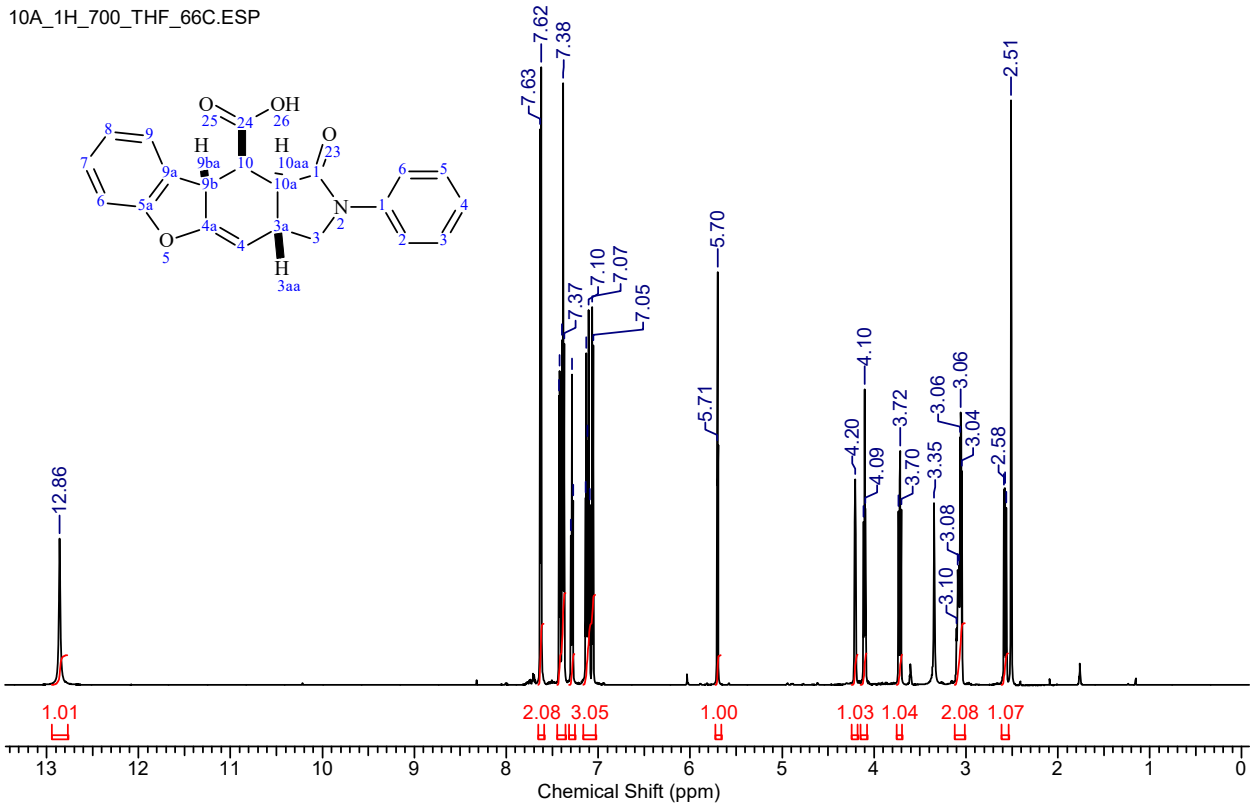

## $n$-$Bu_2O$, reflux, 12h



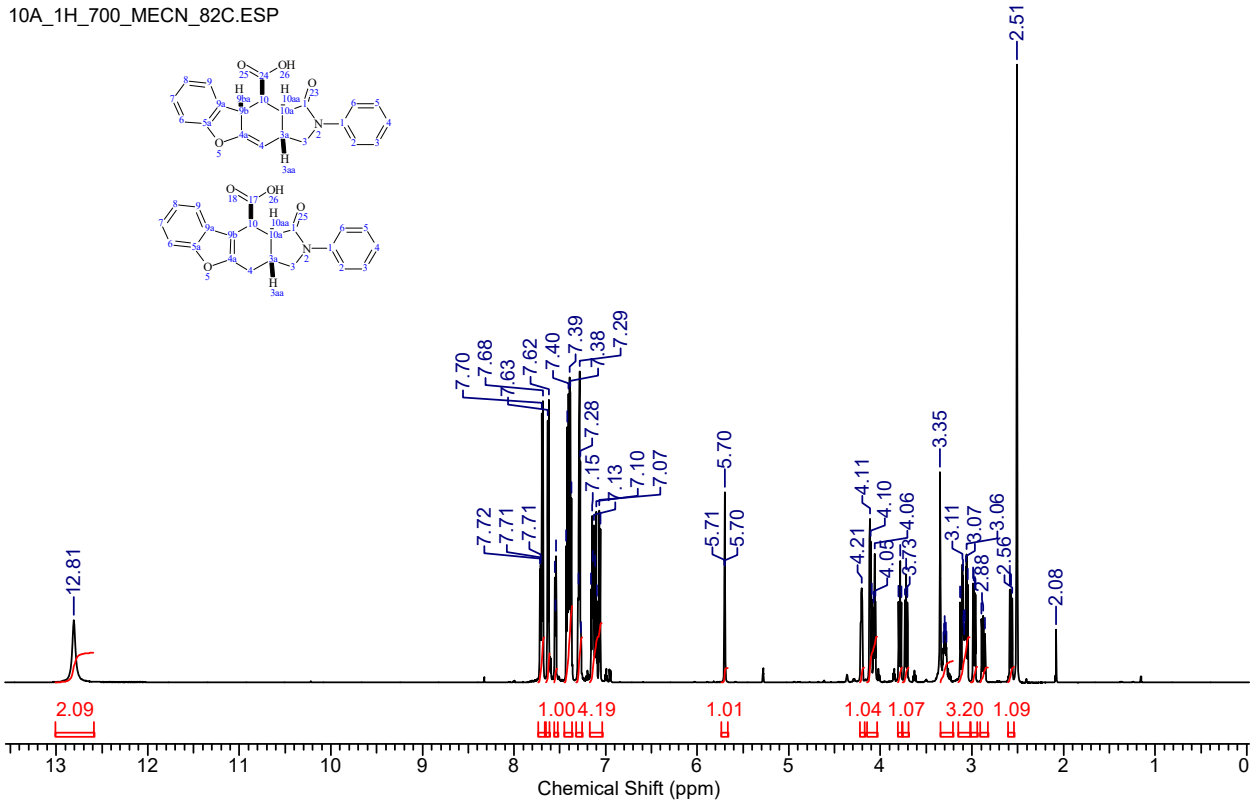
## *t*-BuOMe, reflux, 12h



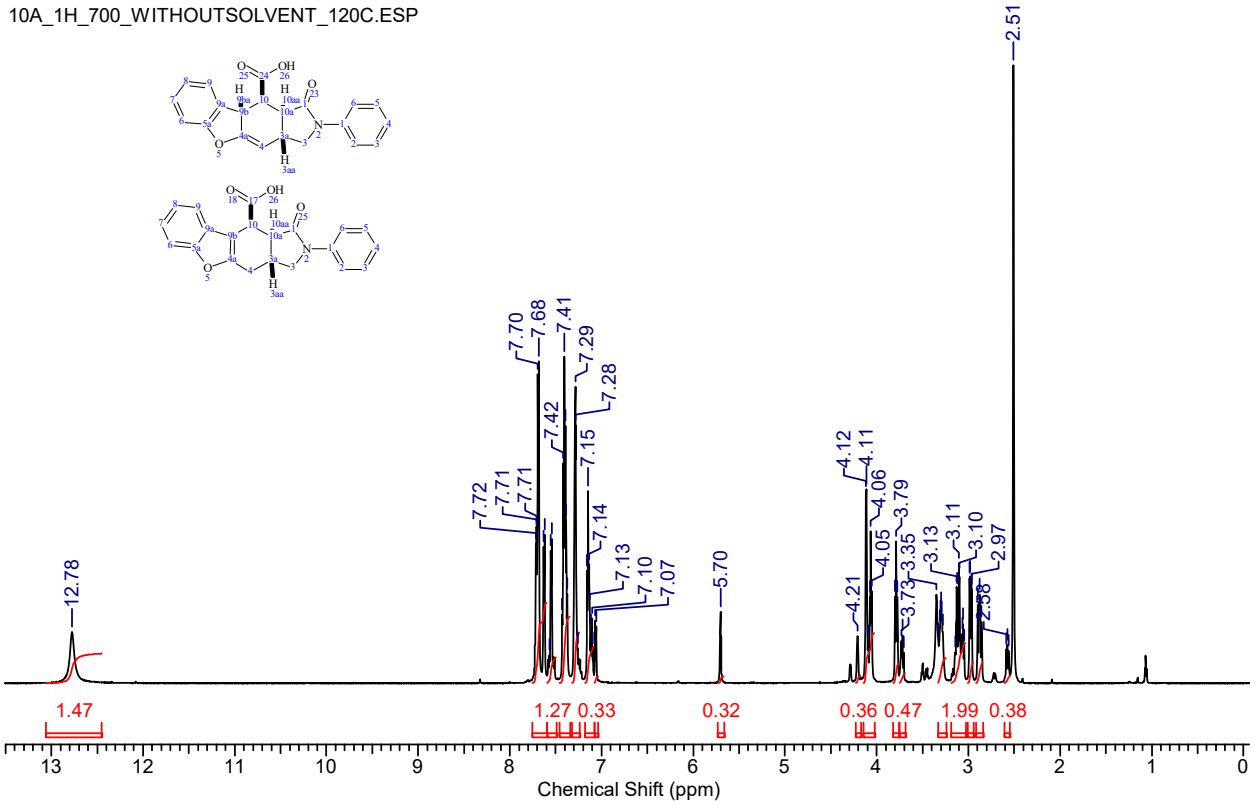

## THF, reflux, 12h



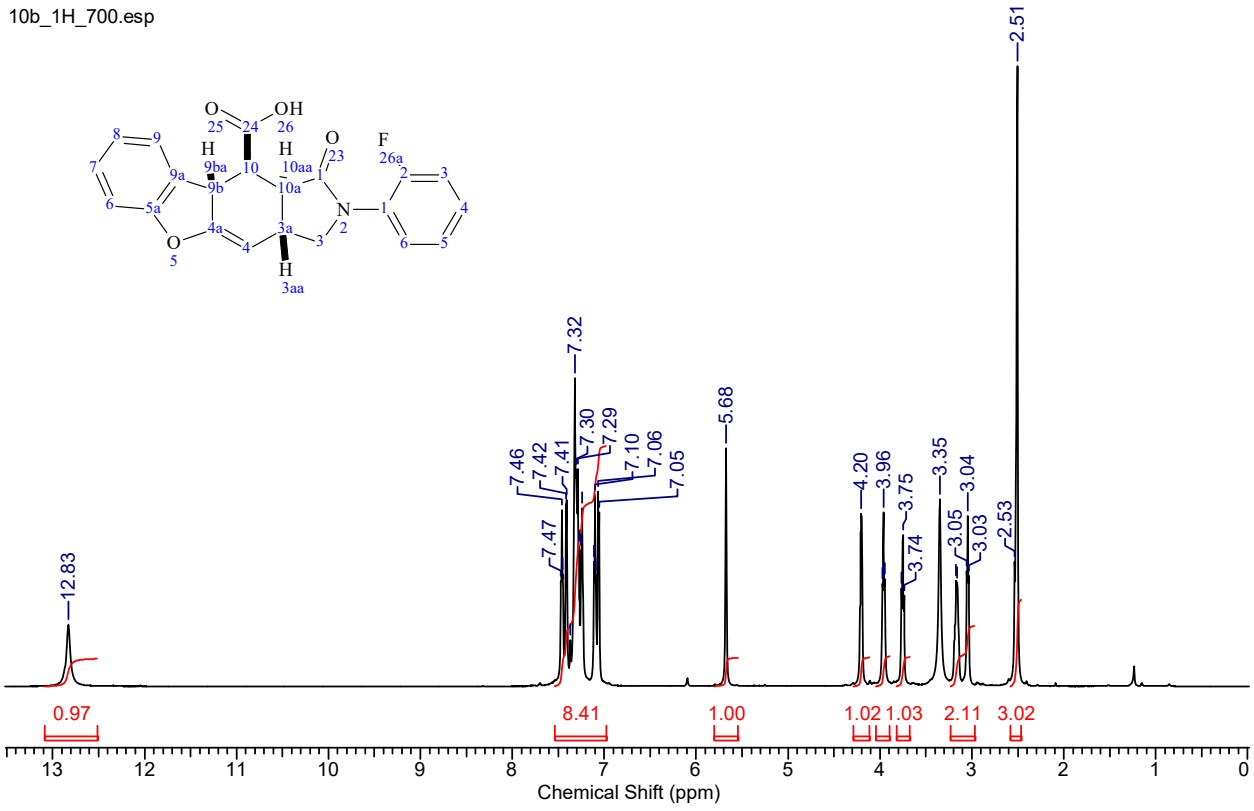
## MeCN, reflux, 12h

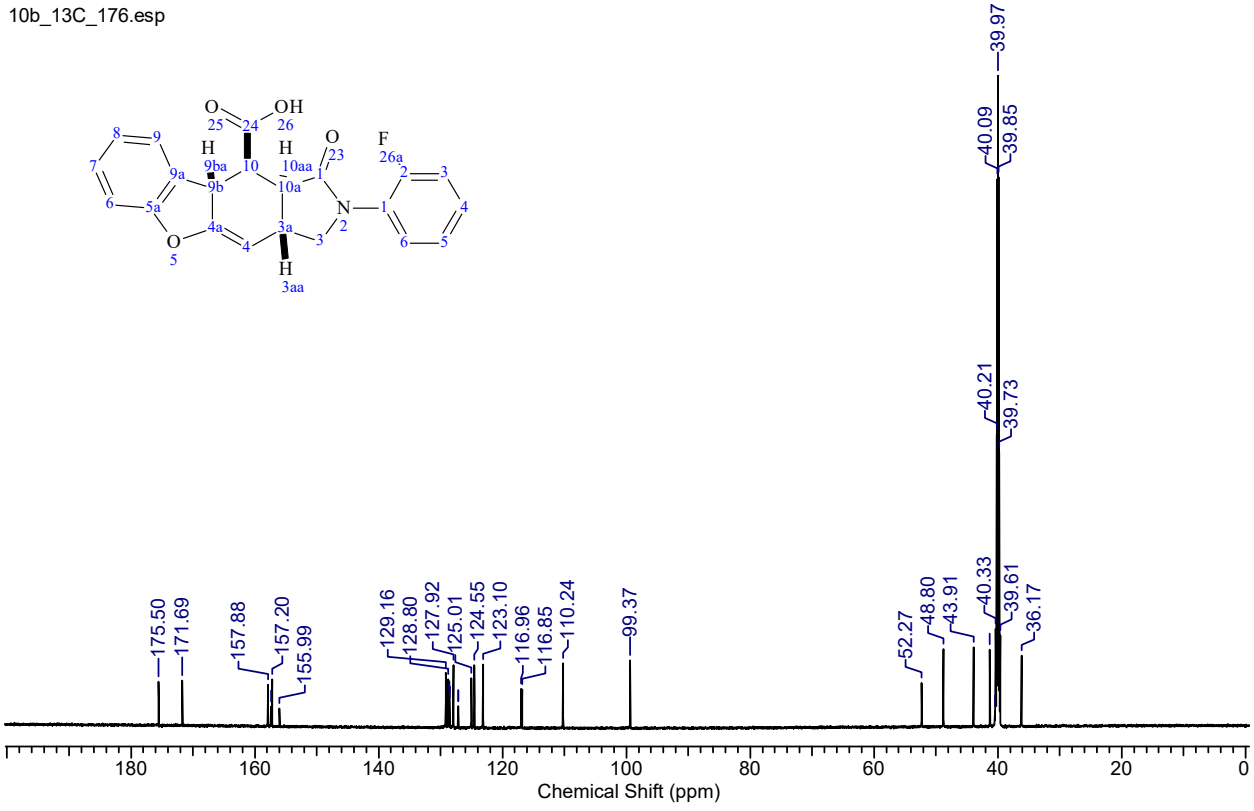


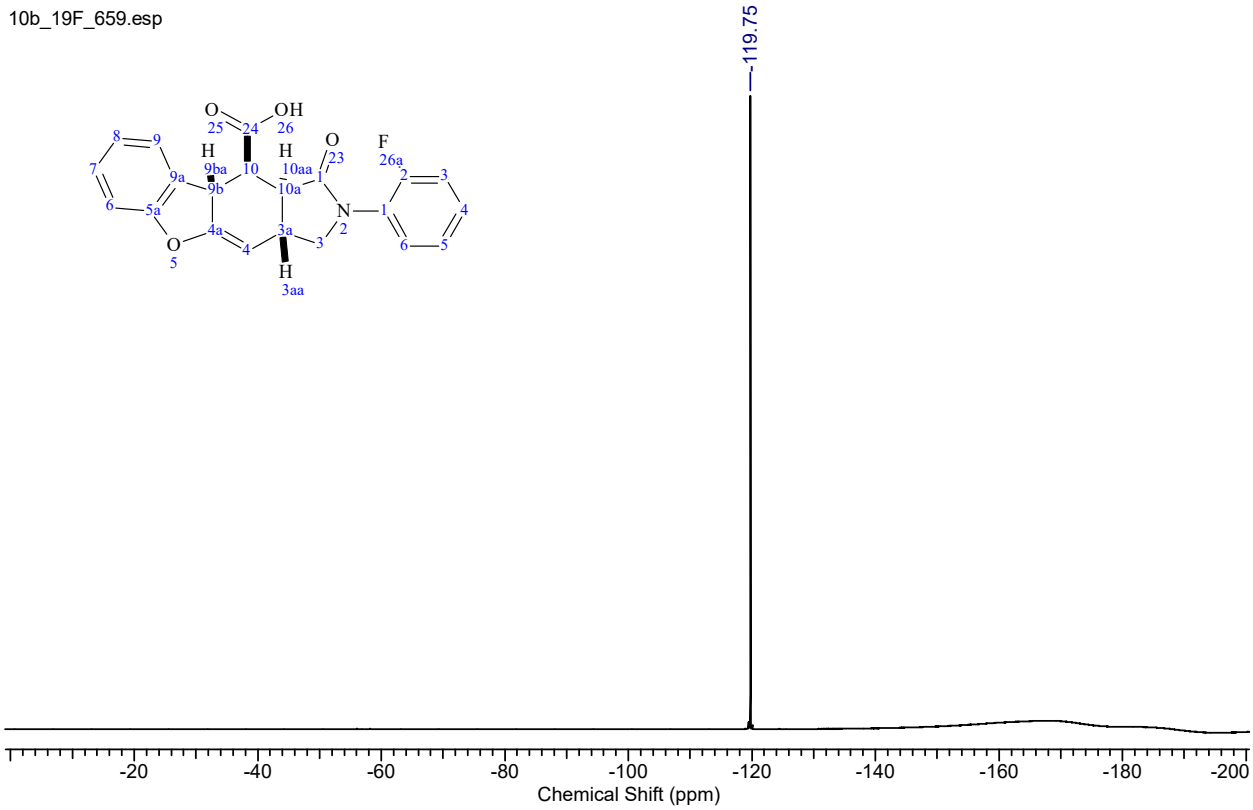

## without solvent, 120° C, 2h



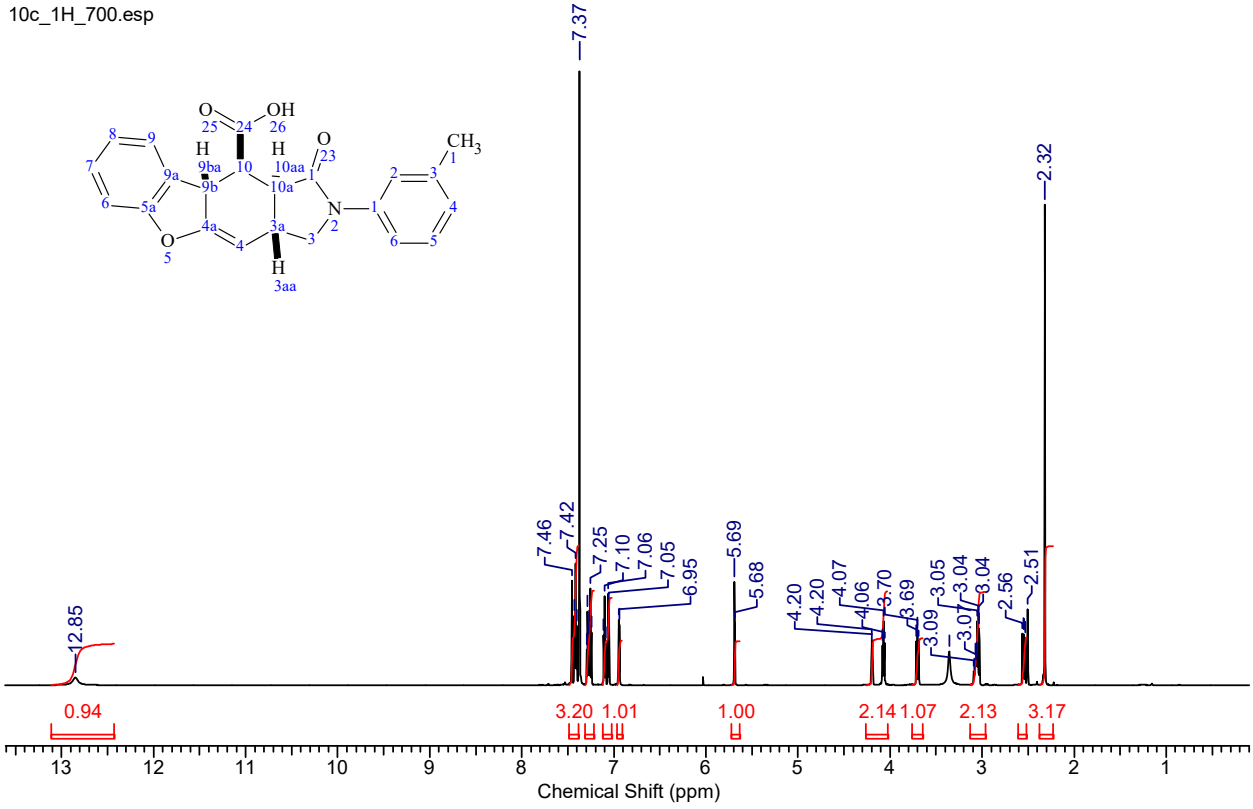
**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(2-Fluorophenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10b).**

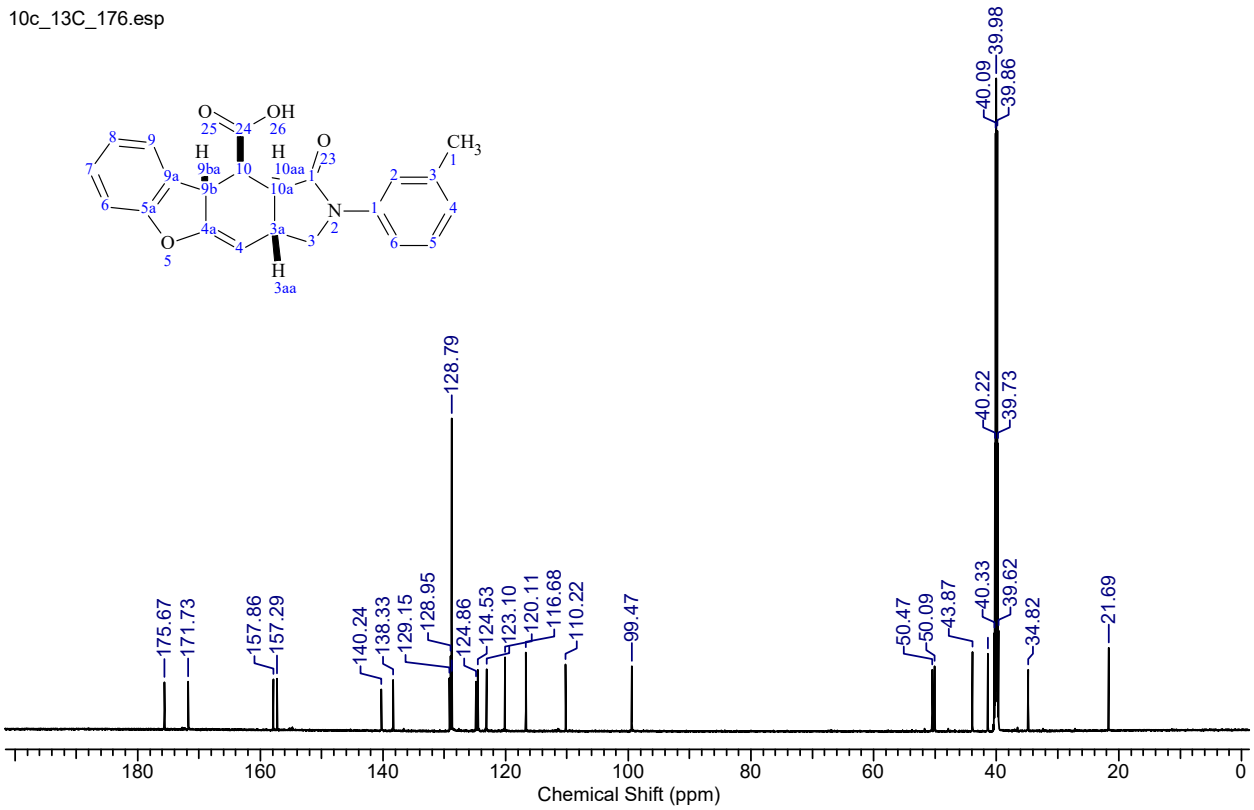


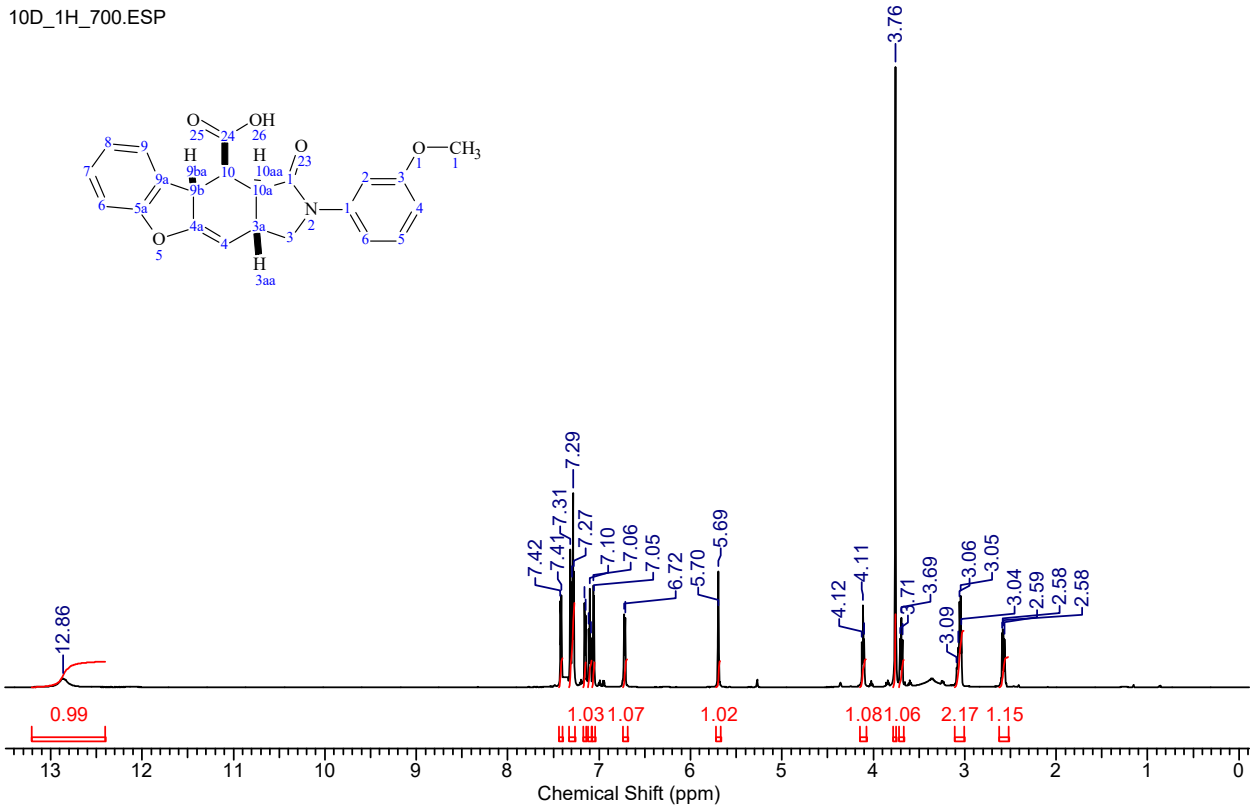


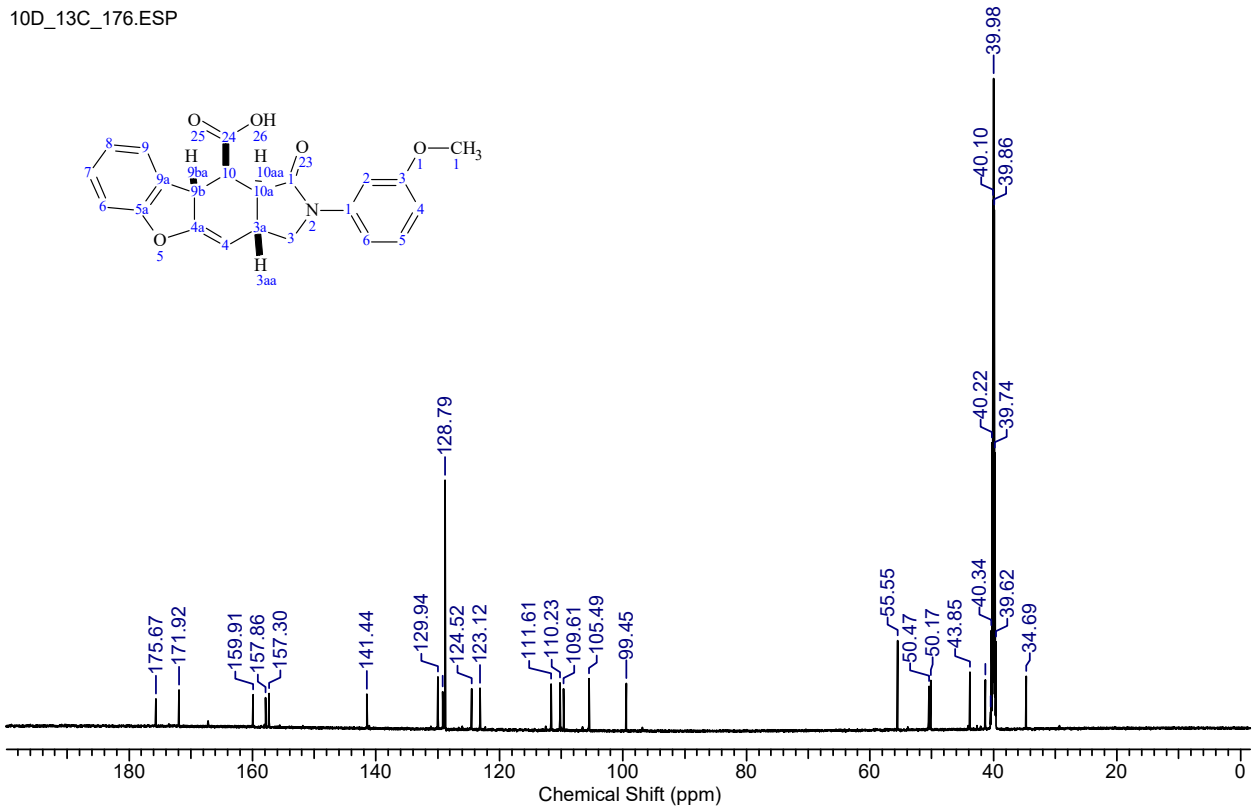

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3-Methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10c).**



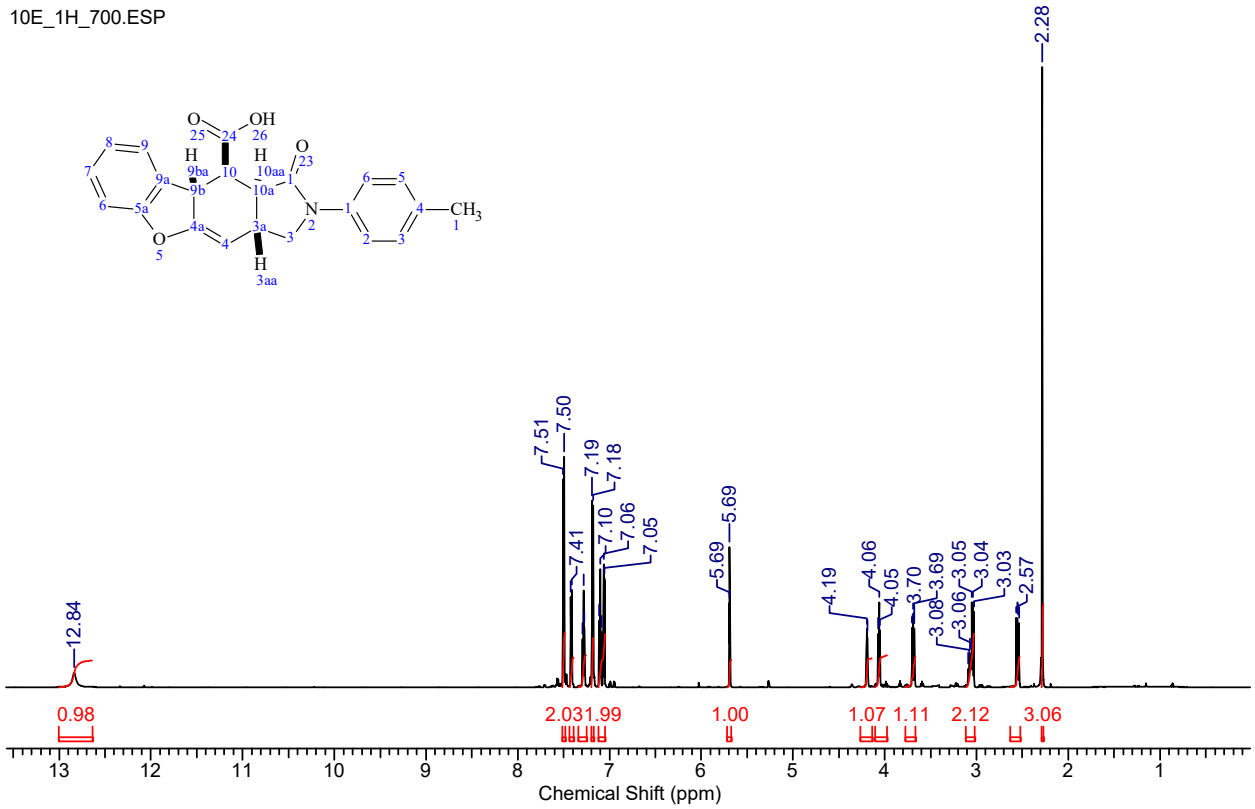


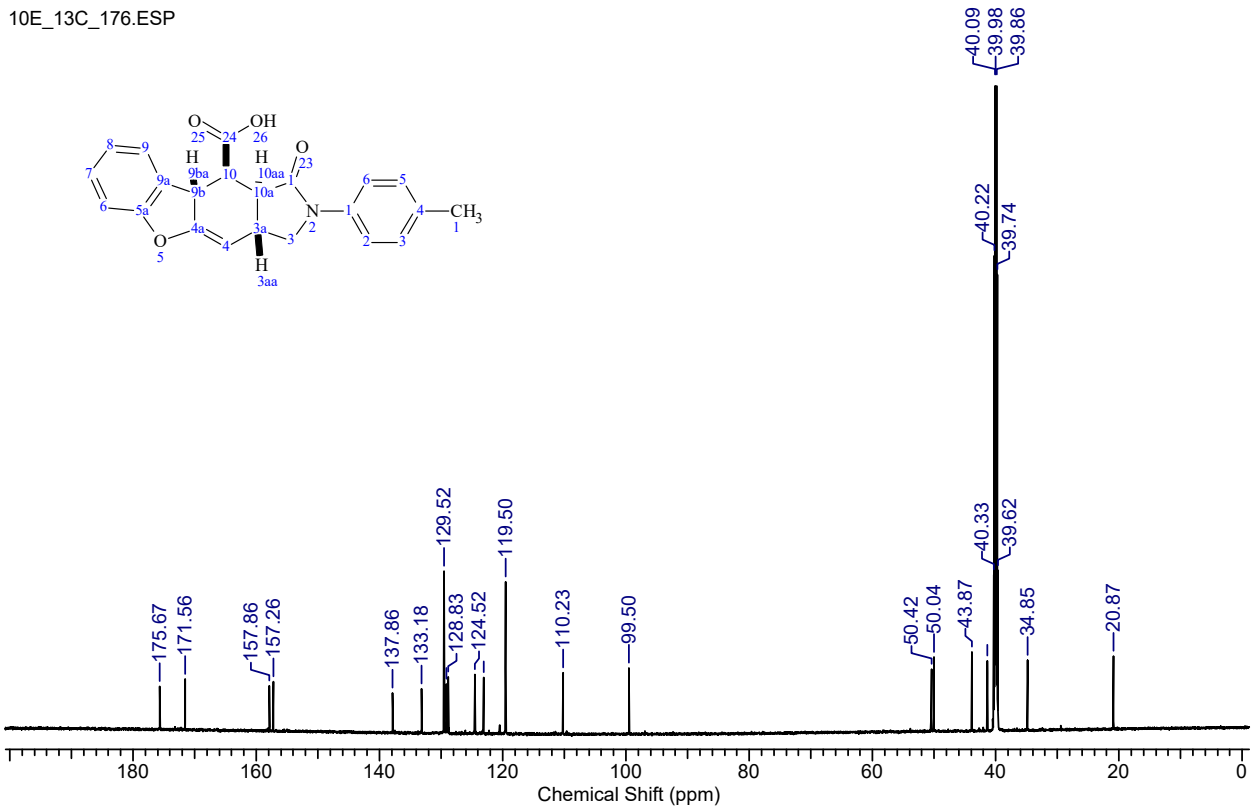

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10d).**



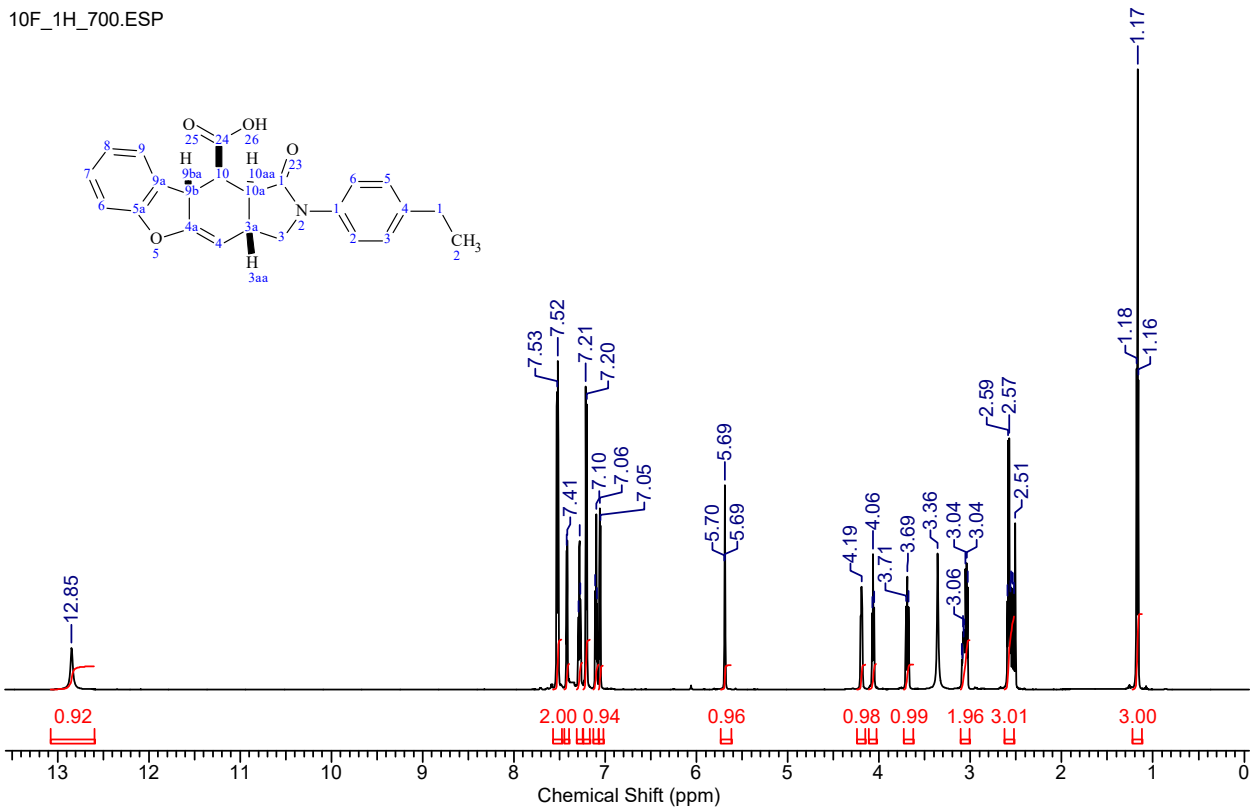


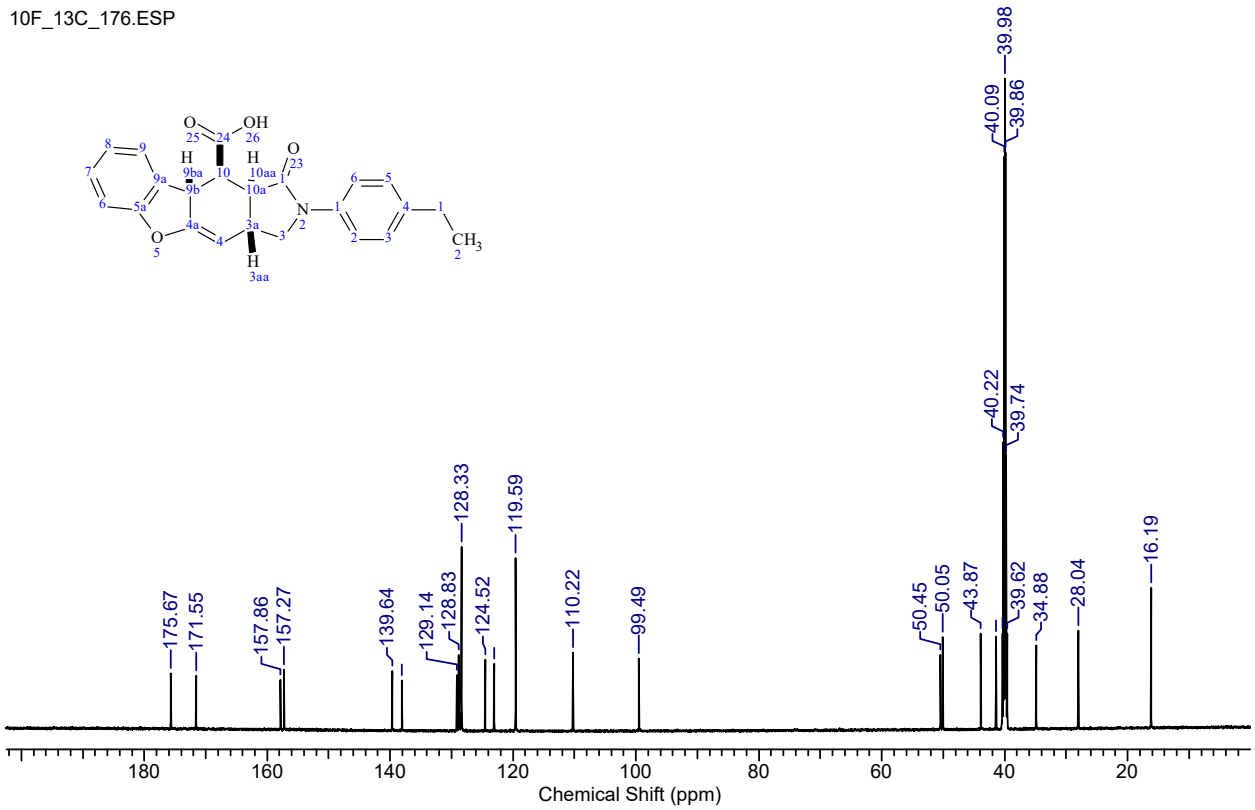

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10e).**



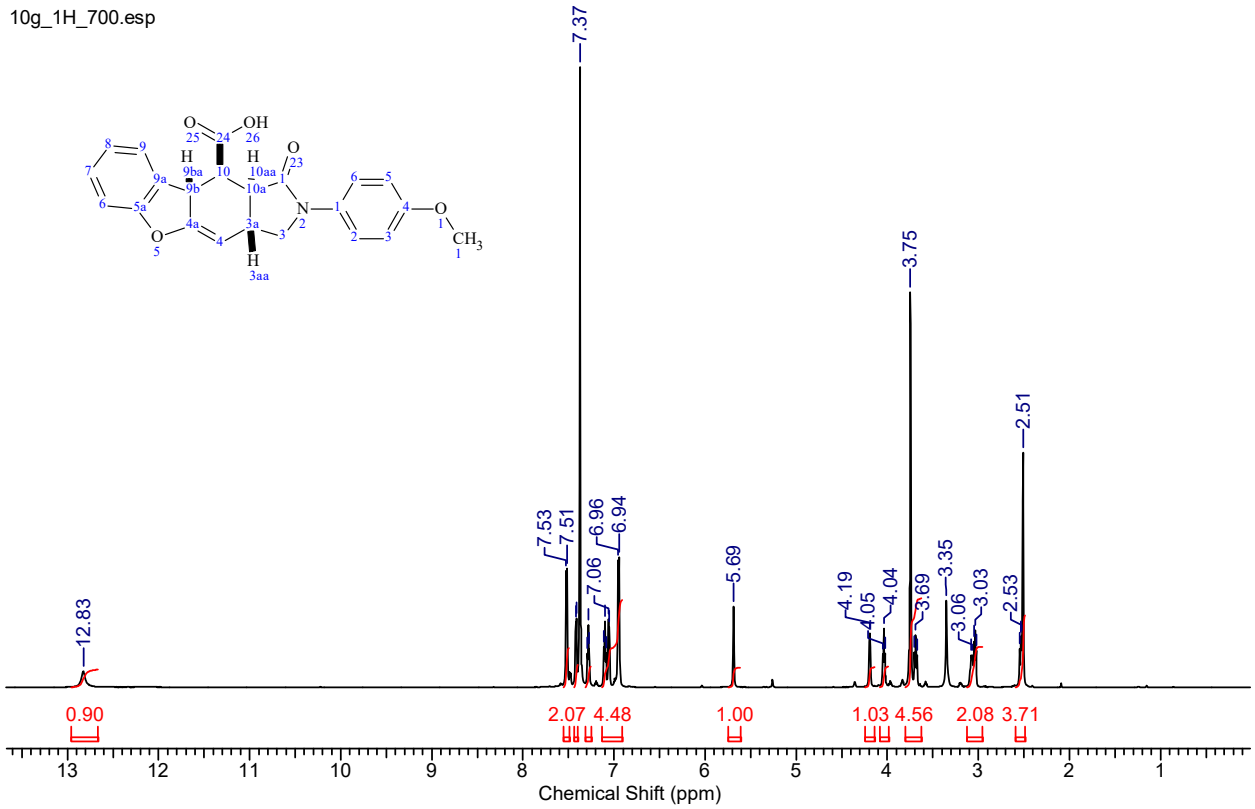


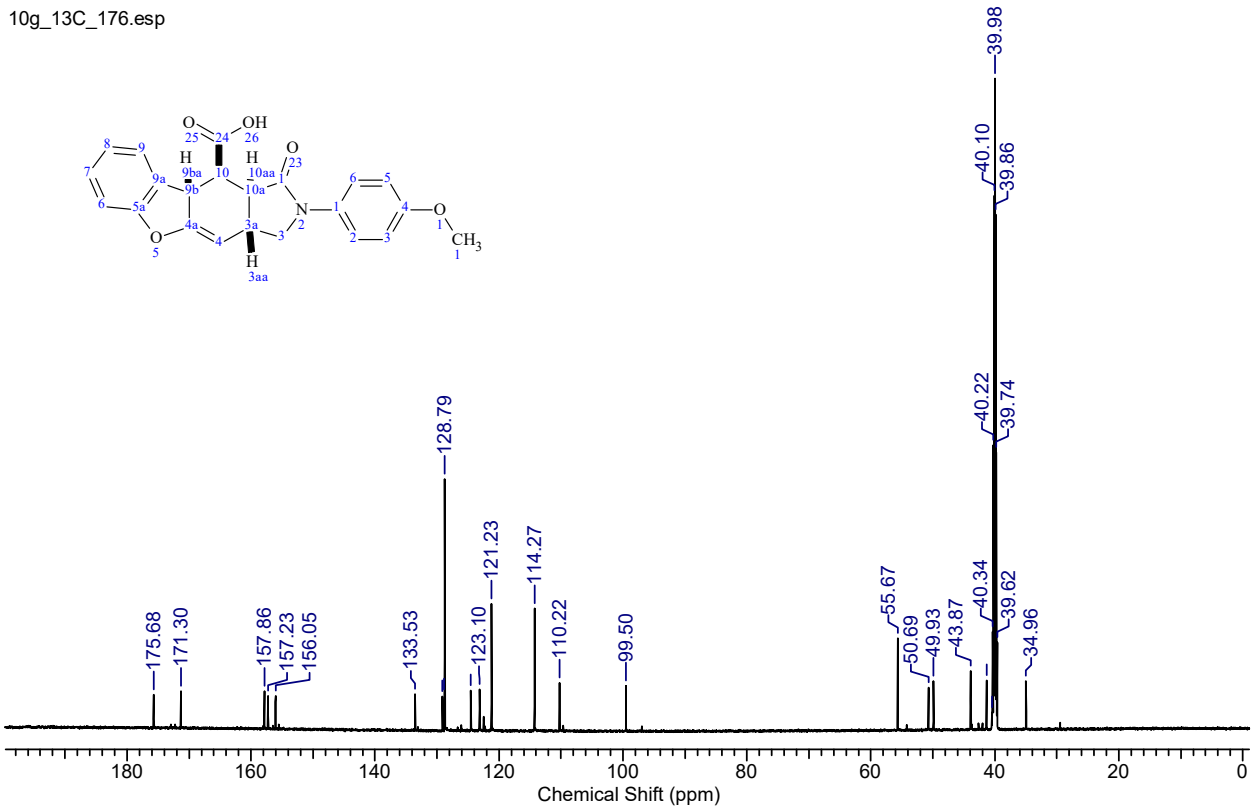

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Ethylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10f).**



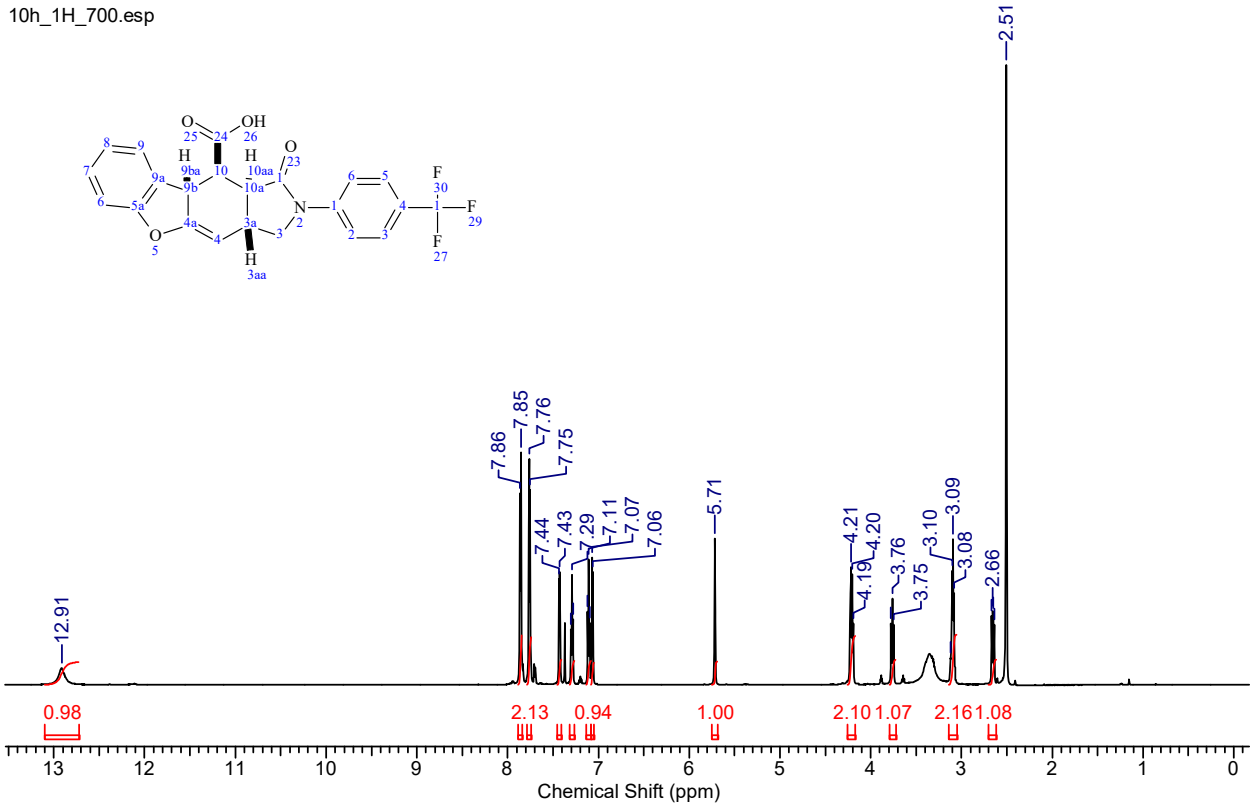



**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Methoxyphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10g).** *Contains an impurity of benzene.*

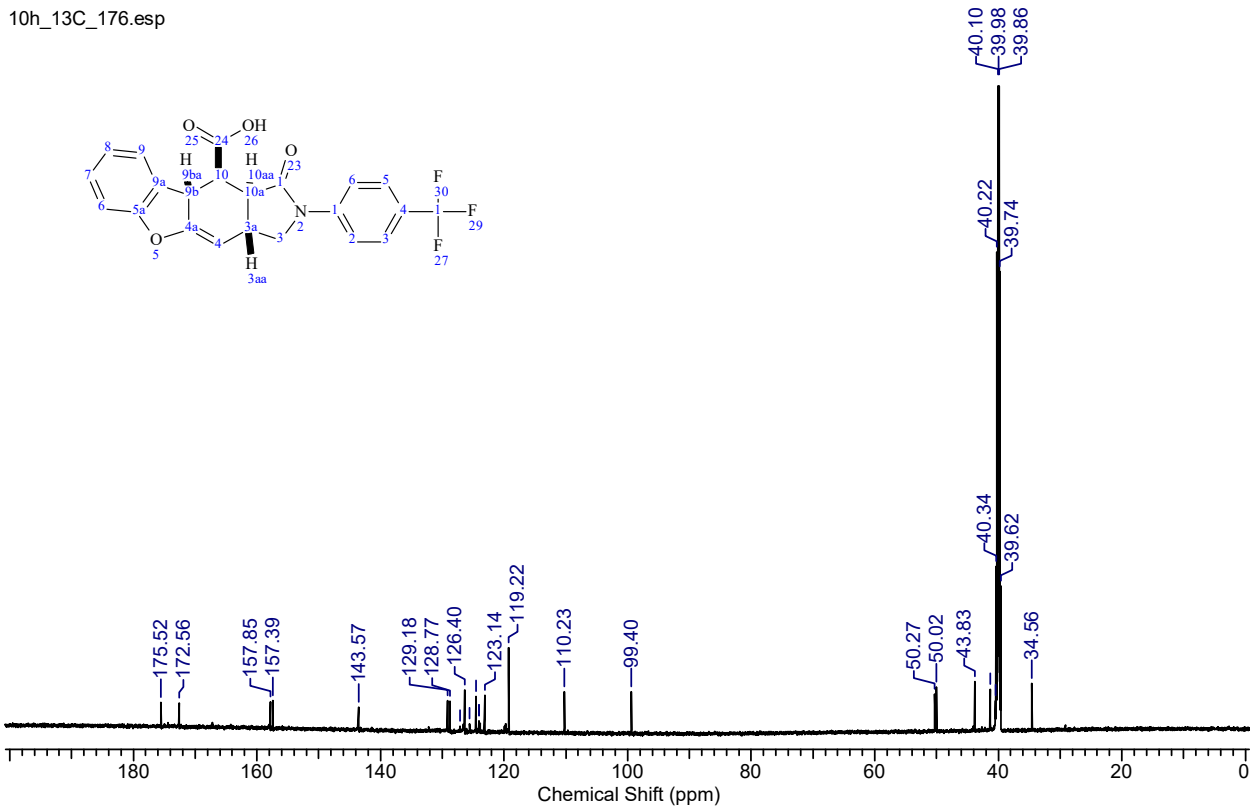





**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-1-Oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10h).**



10h_13C_176.esp

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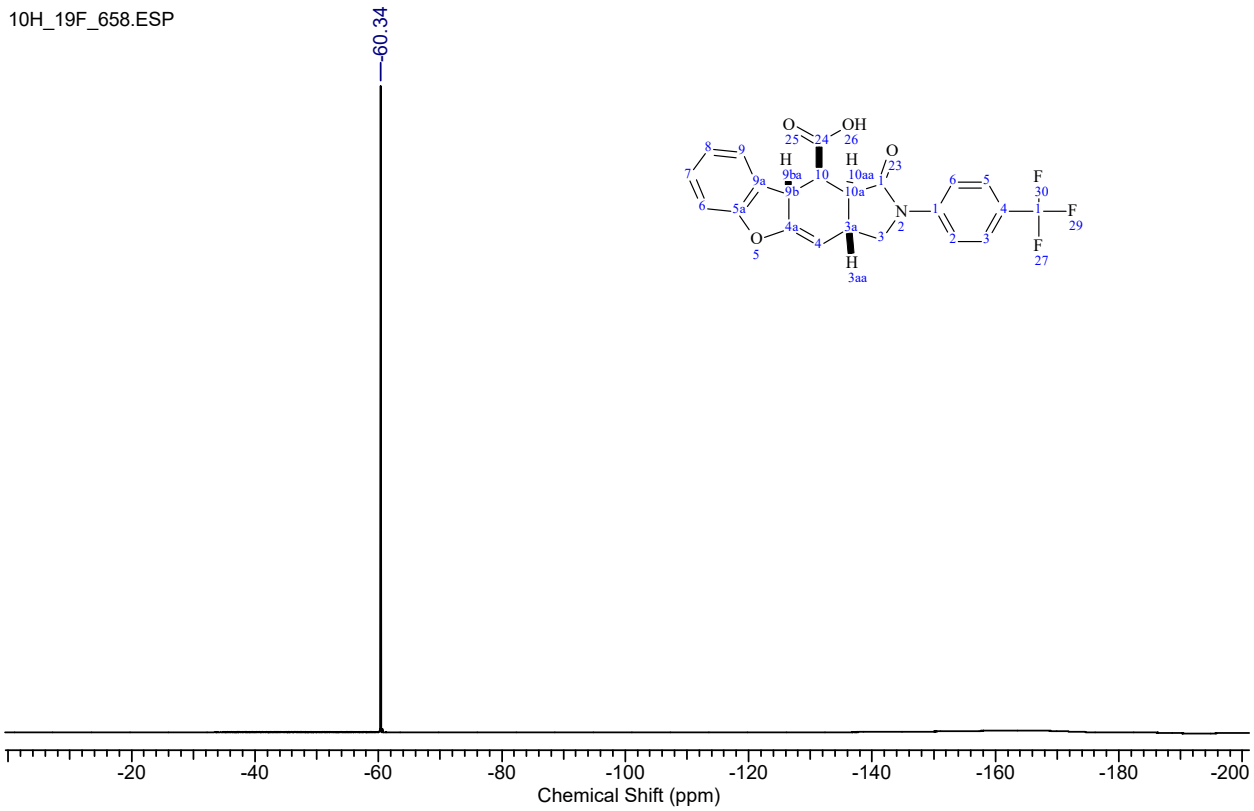
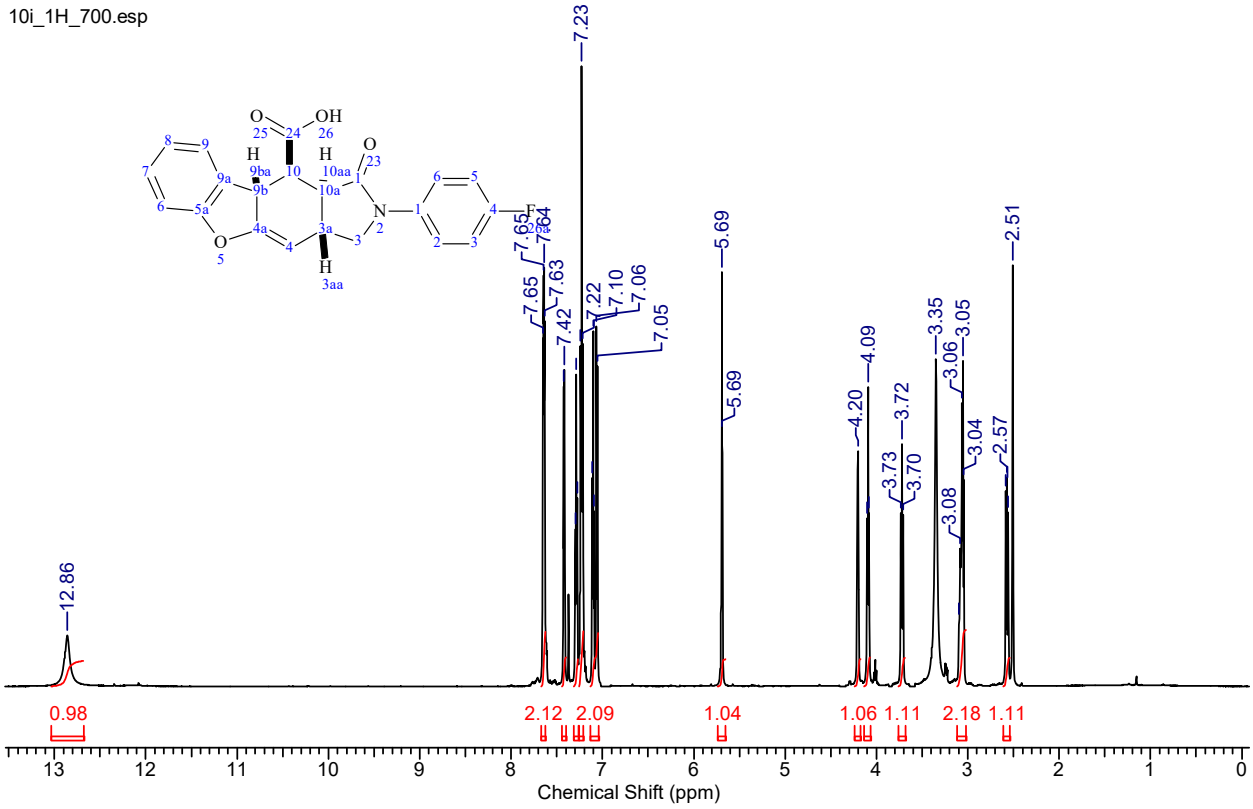
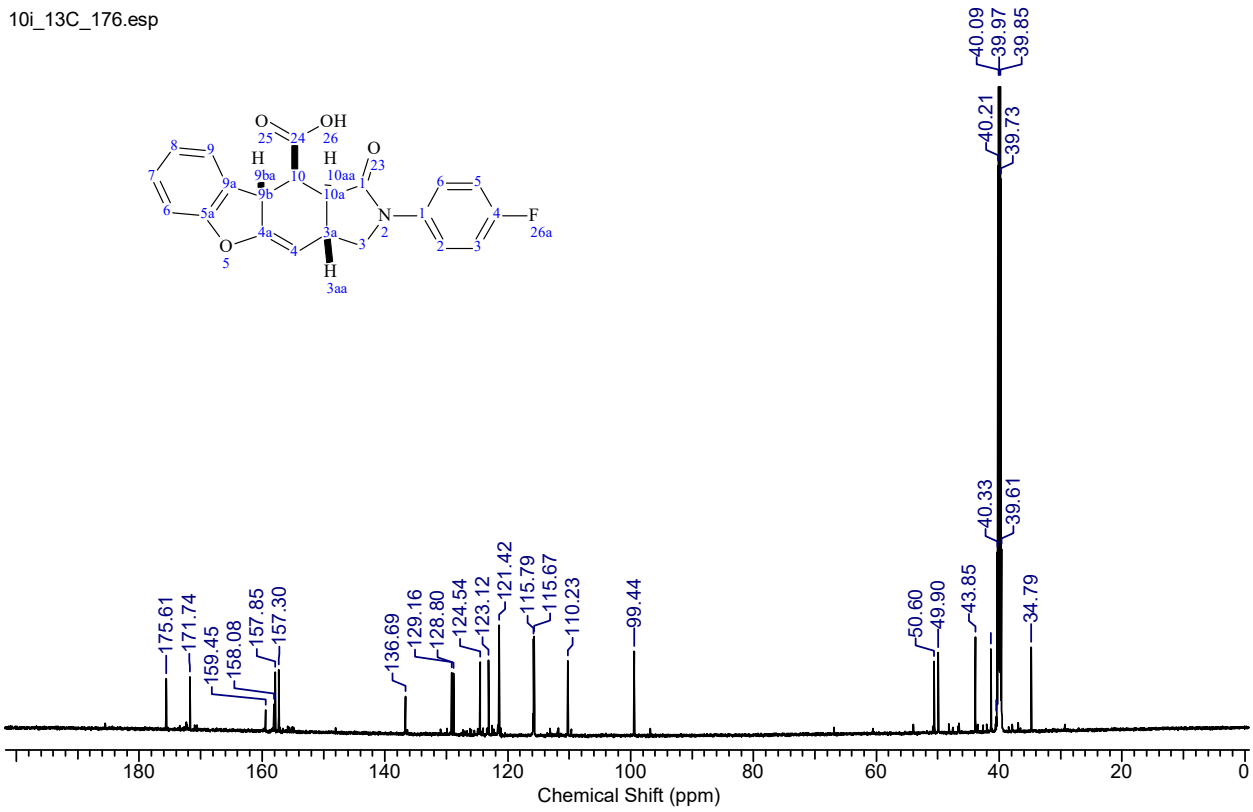
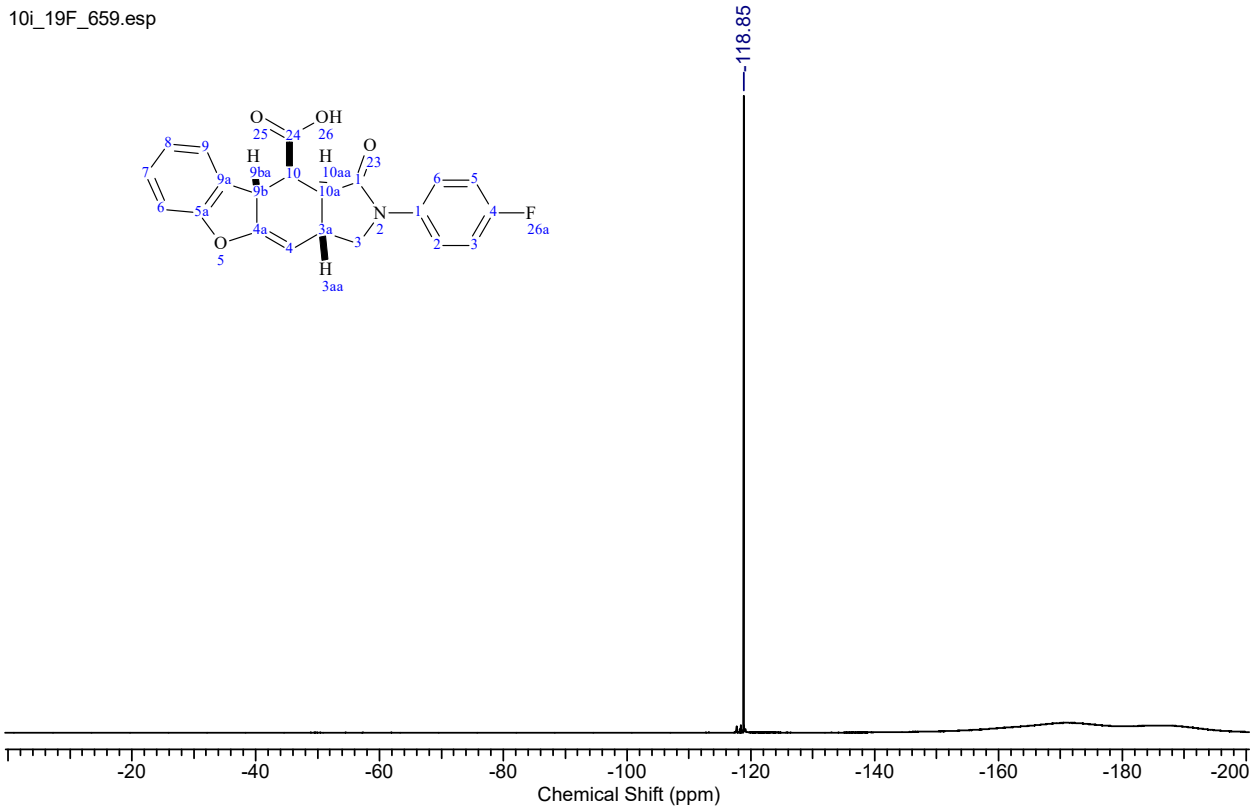


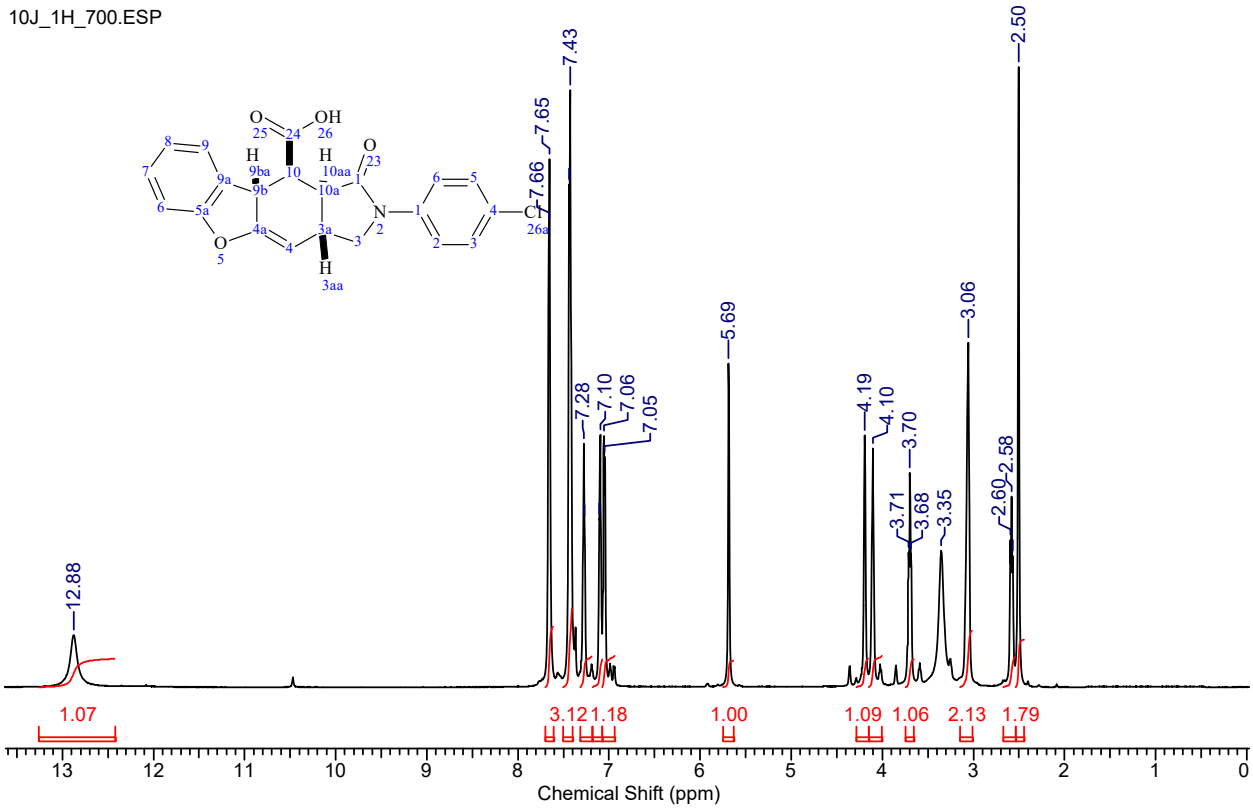
**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Fluorophenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10i).**

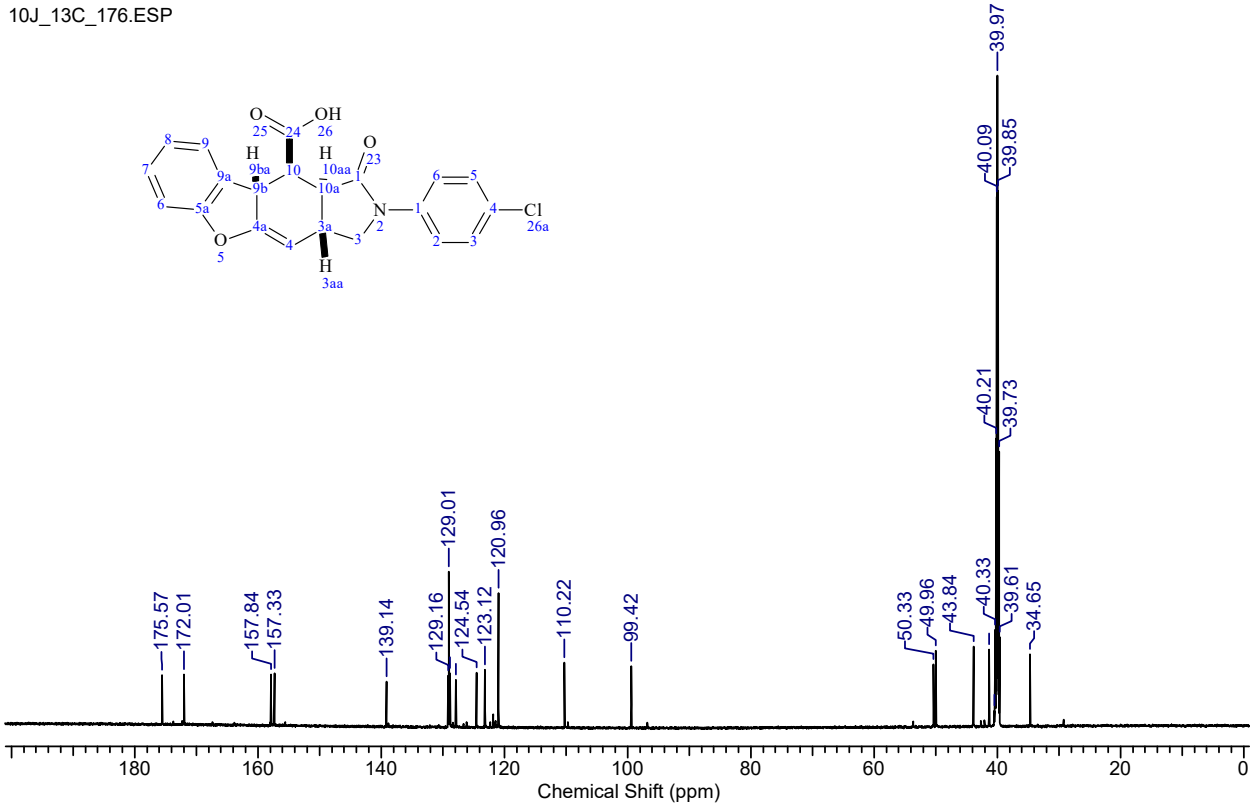


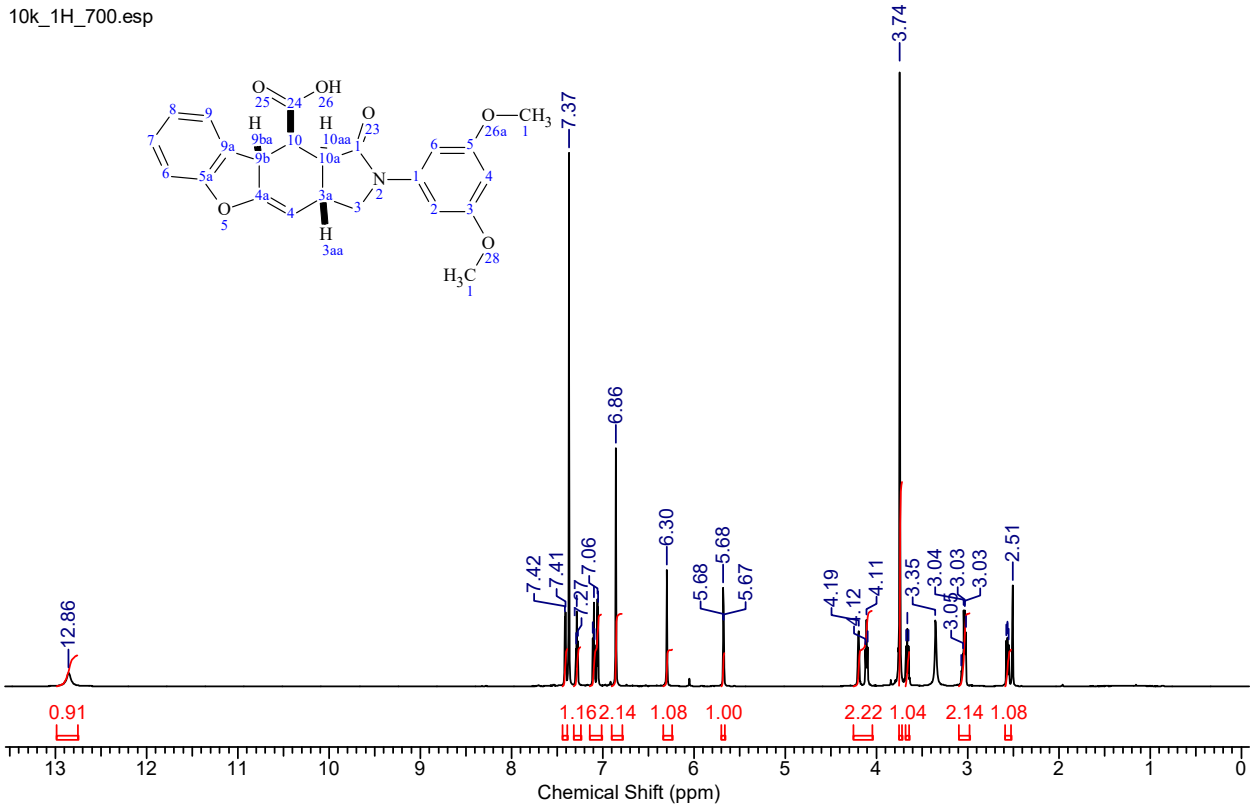


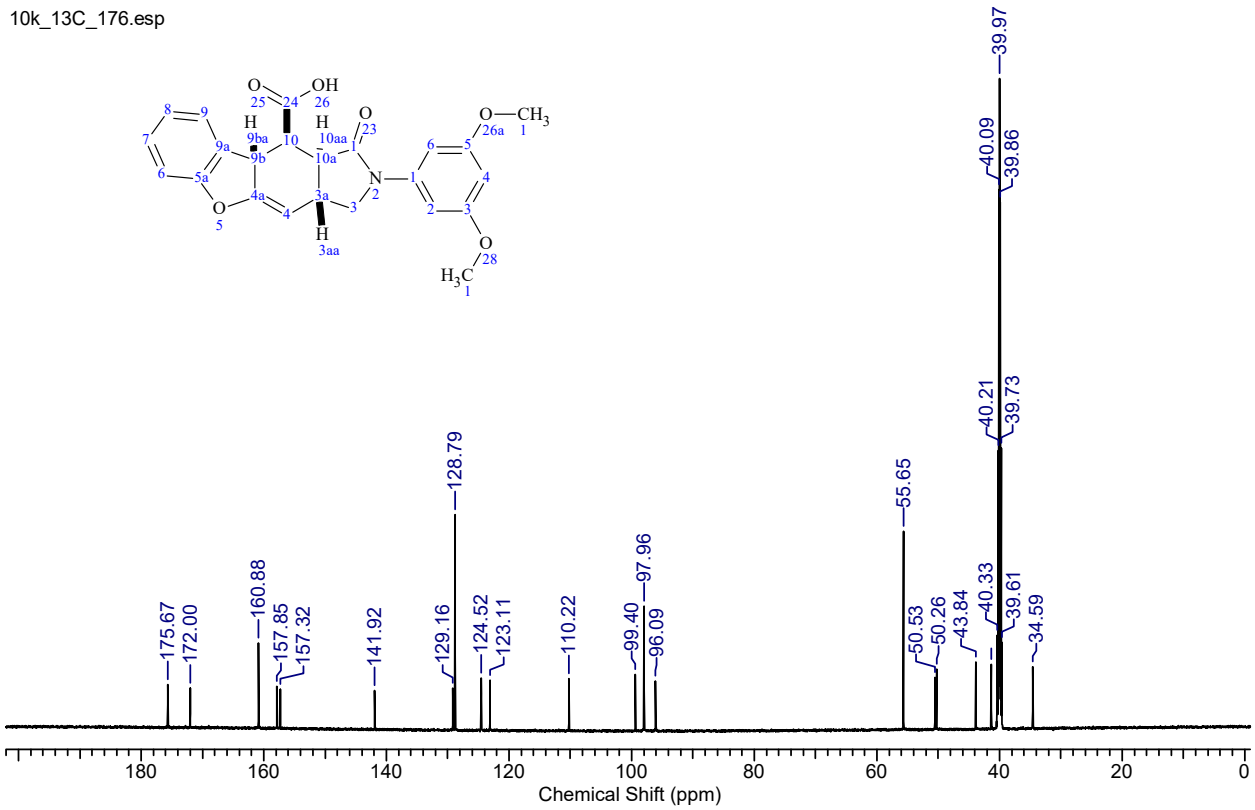

**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-Chlorophenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10j).**



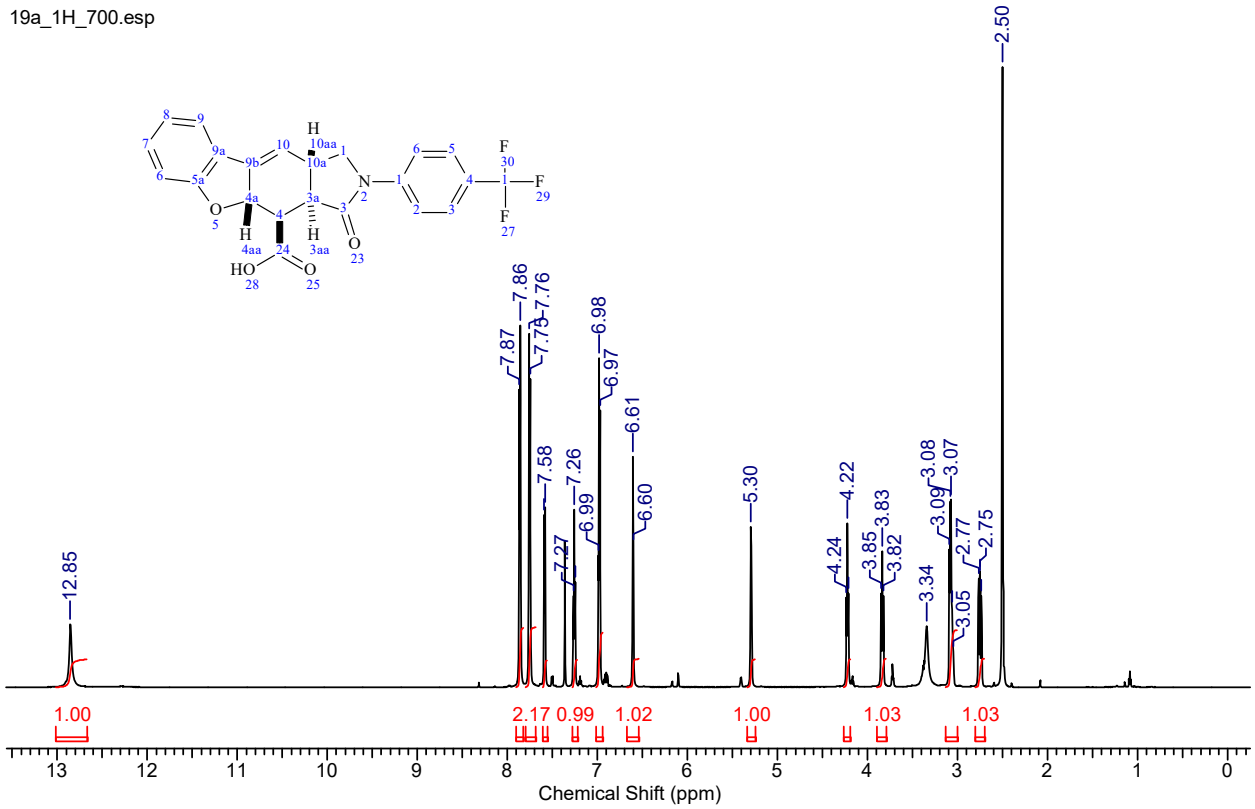



**(3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3,5-Dimethoxyphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (10k).** *Contains an impurity of benzene.*






**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-3-Oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19a).**



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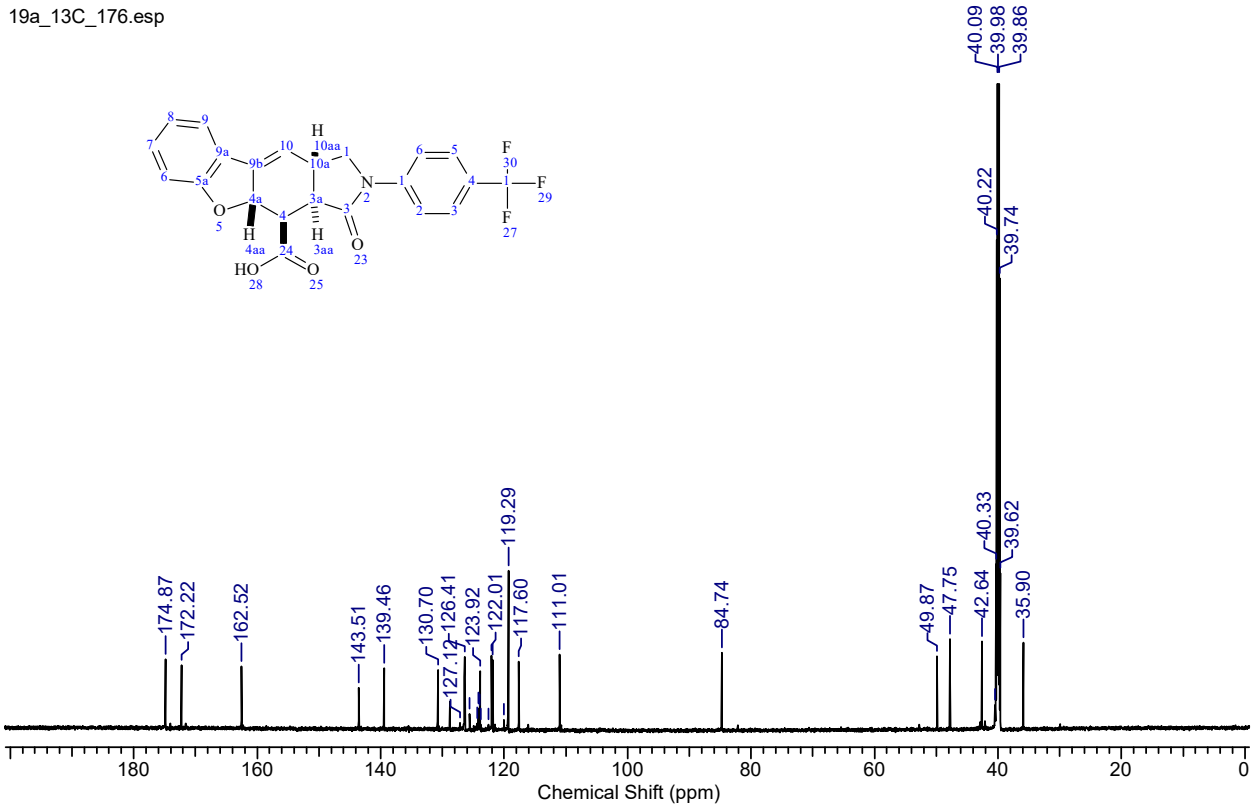


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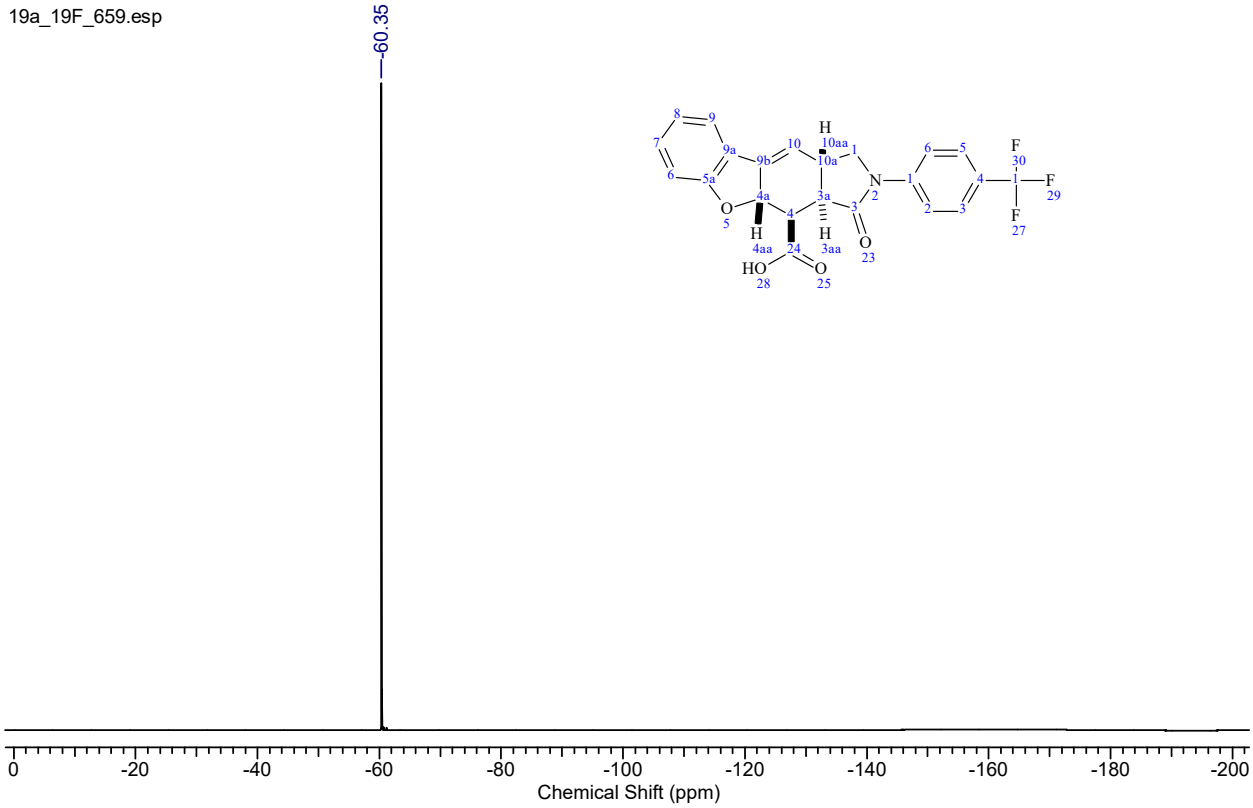
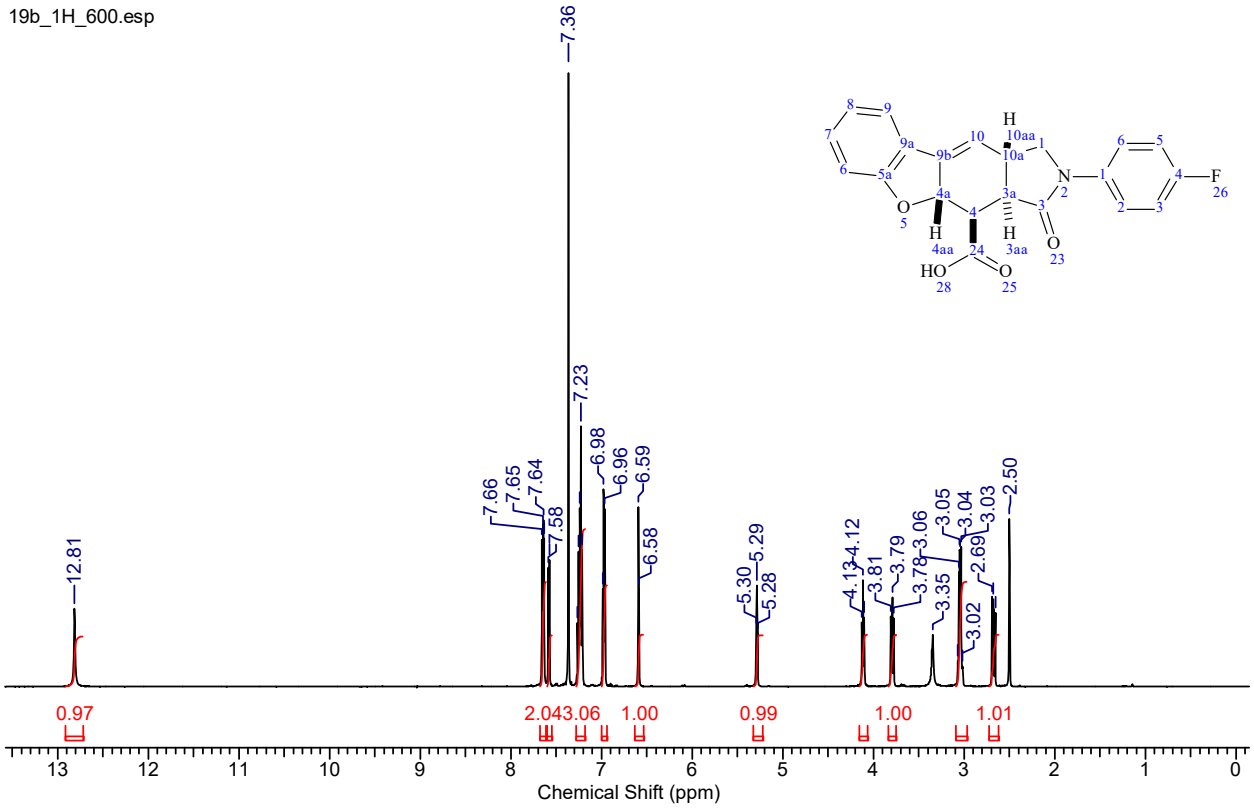
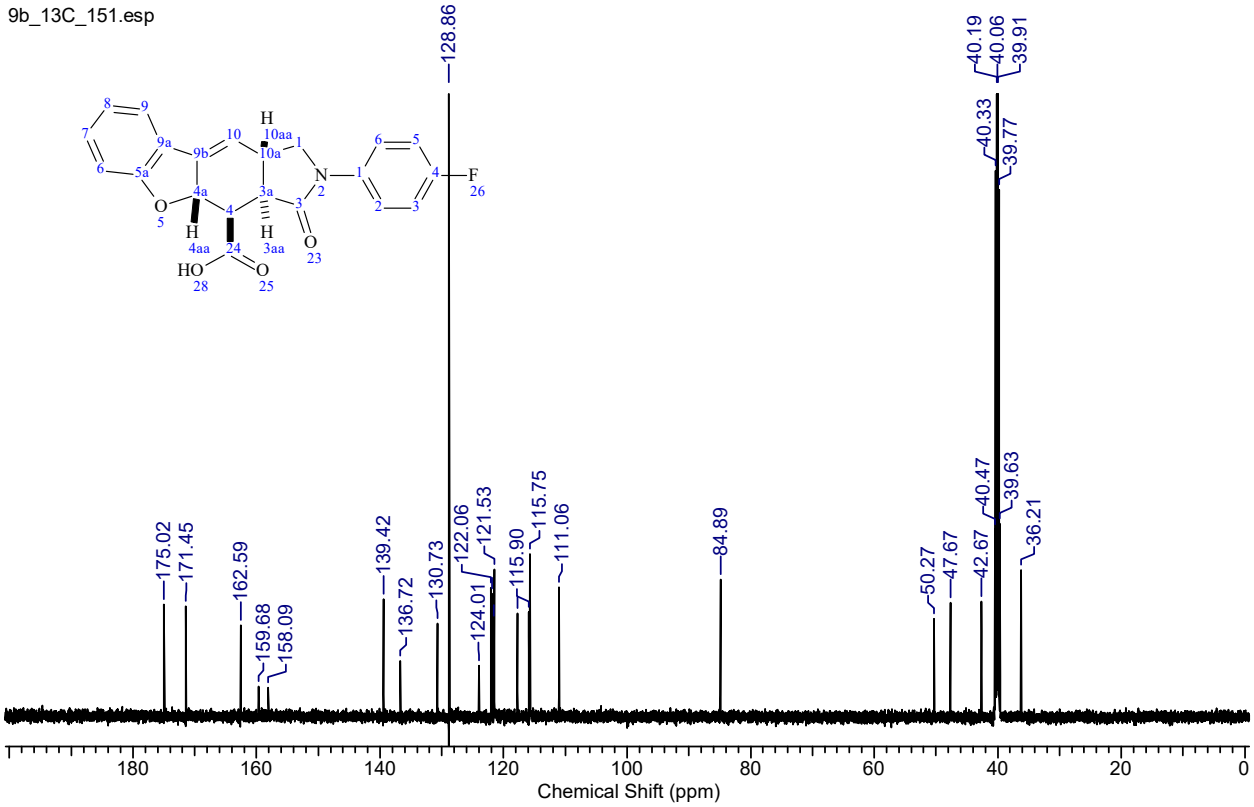
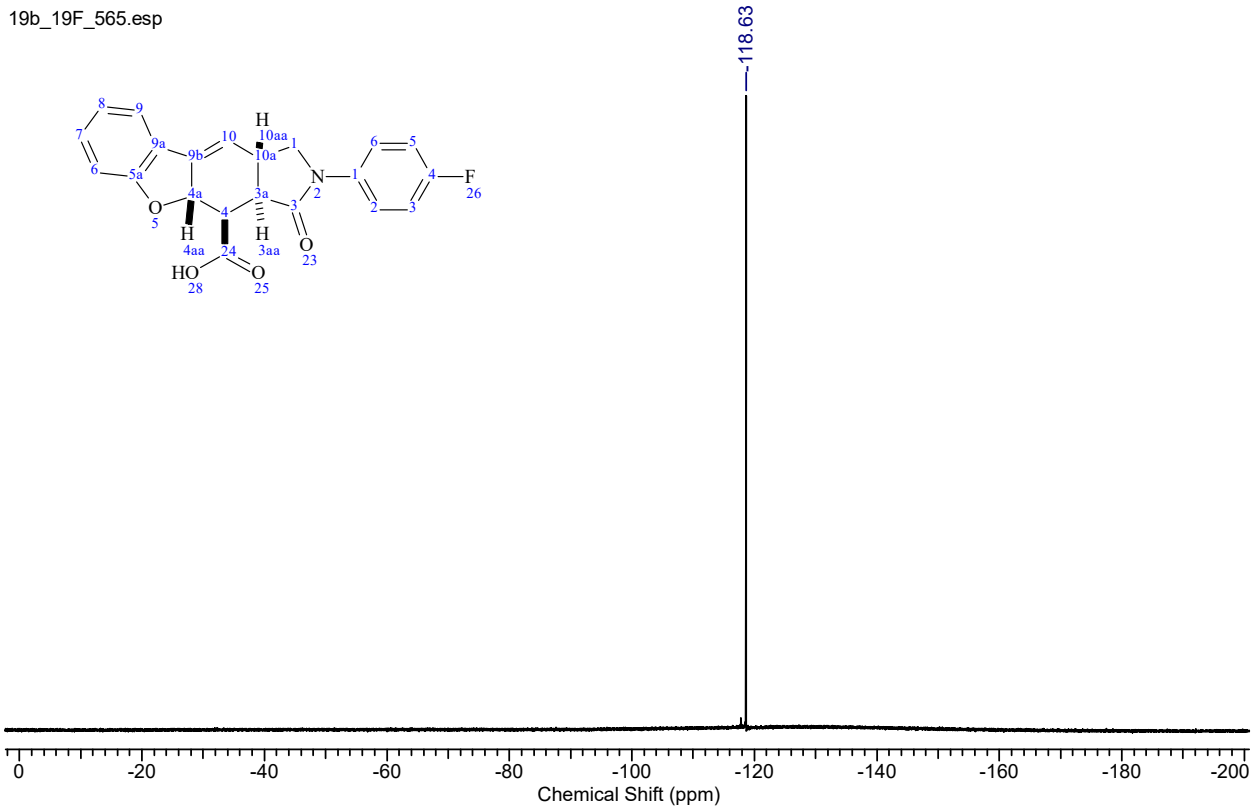


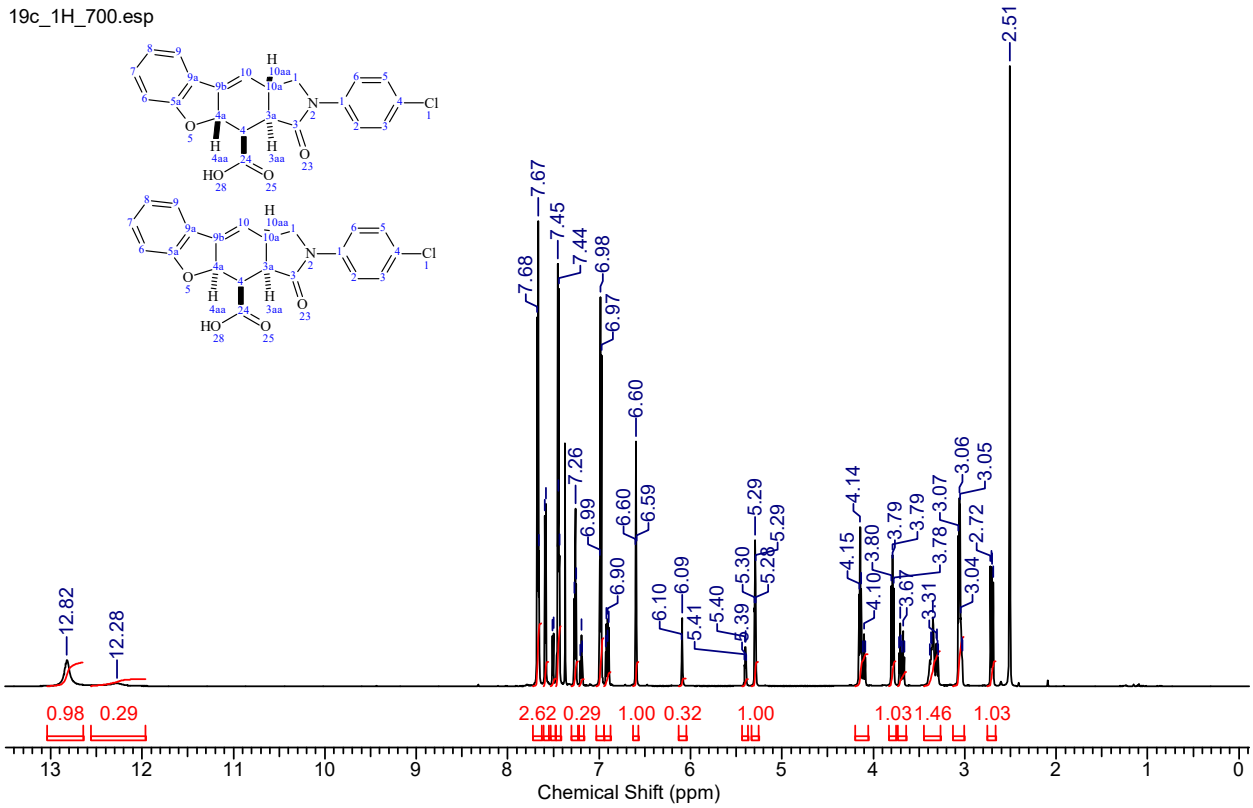
**(3a*R*,4*R*,4a*S*,10a*S*)-2-(4-Fluorophenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19b).** *Contains an impurity of benzene.*

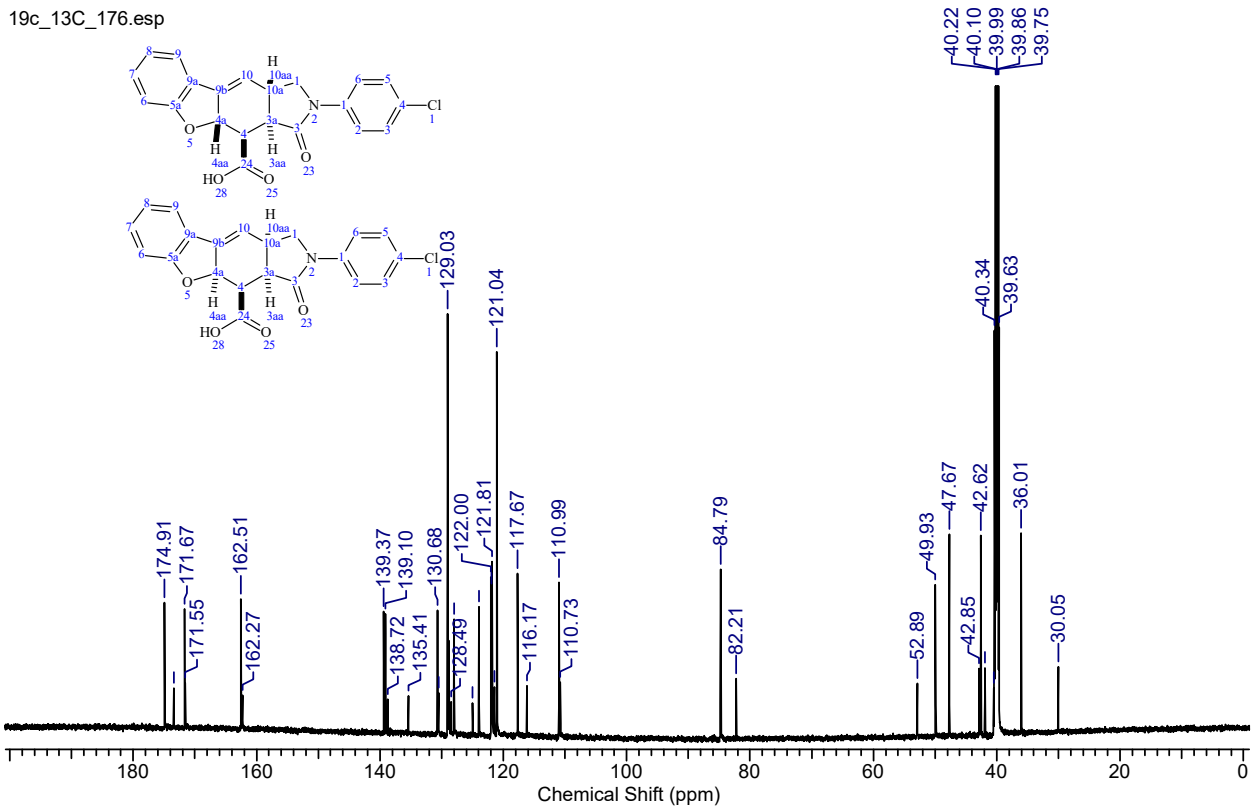


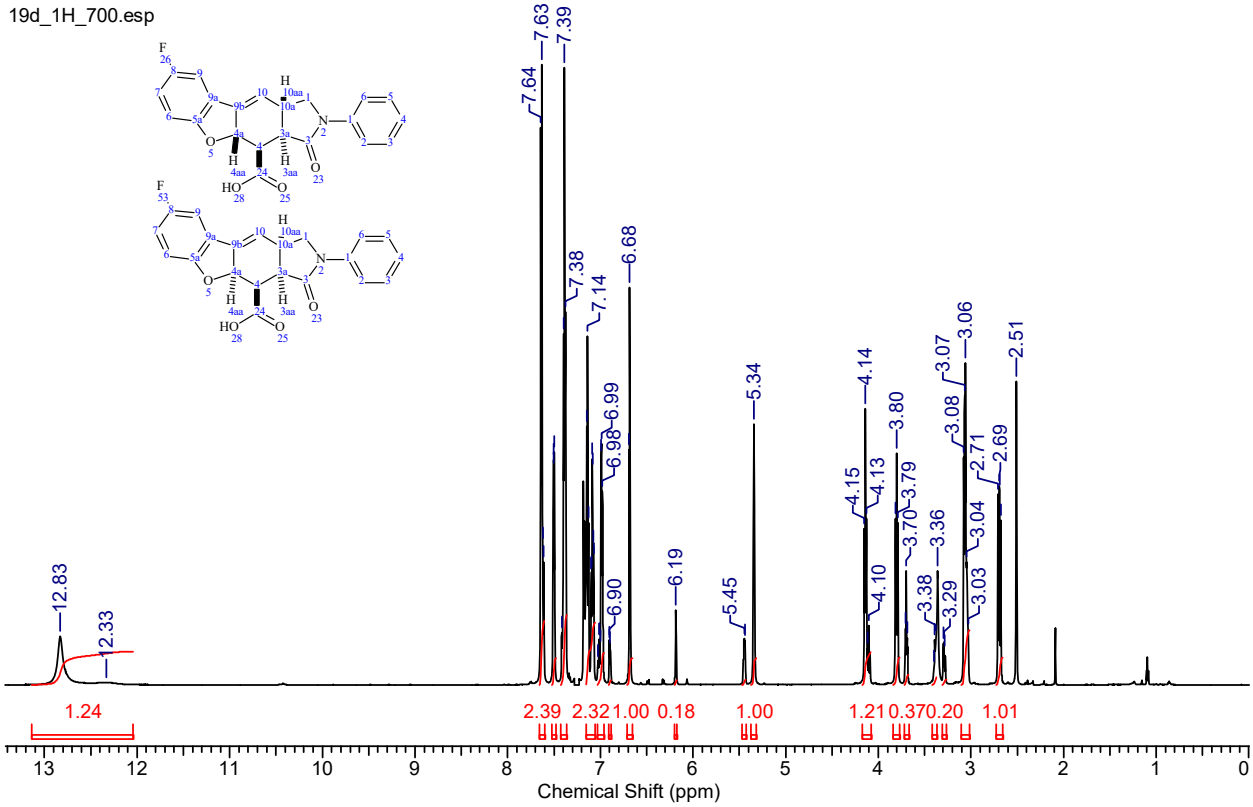



**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-2-(4-Chlorophenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19c) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-2-(4-chlorophenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17c).** *Contains around 23% on an impurity of endo-isomer.*






**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19d) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-8-fluoro-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17d).** *Contains around 17% on an impurity of endo-isomer.*



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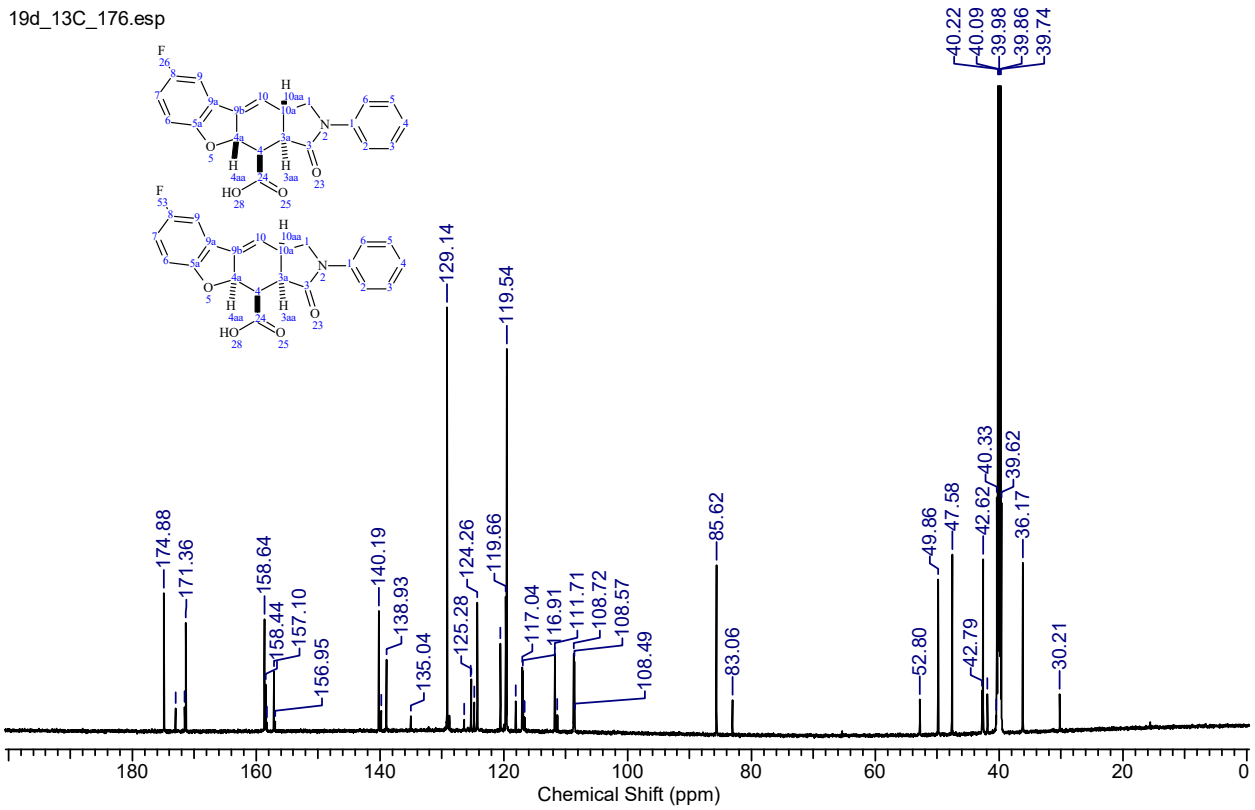


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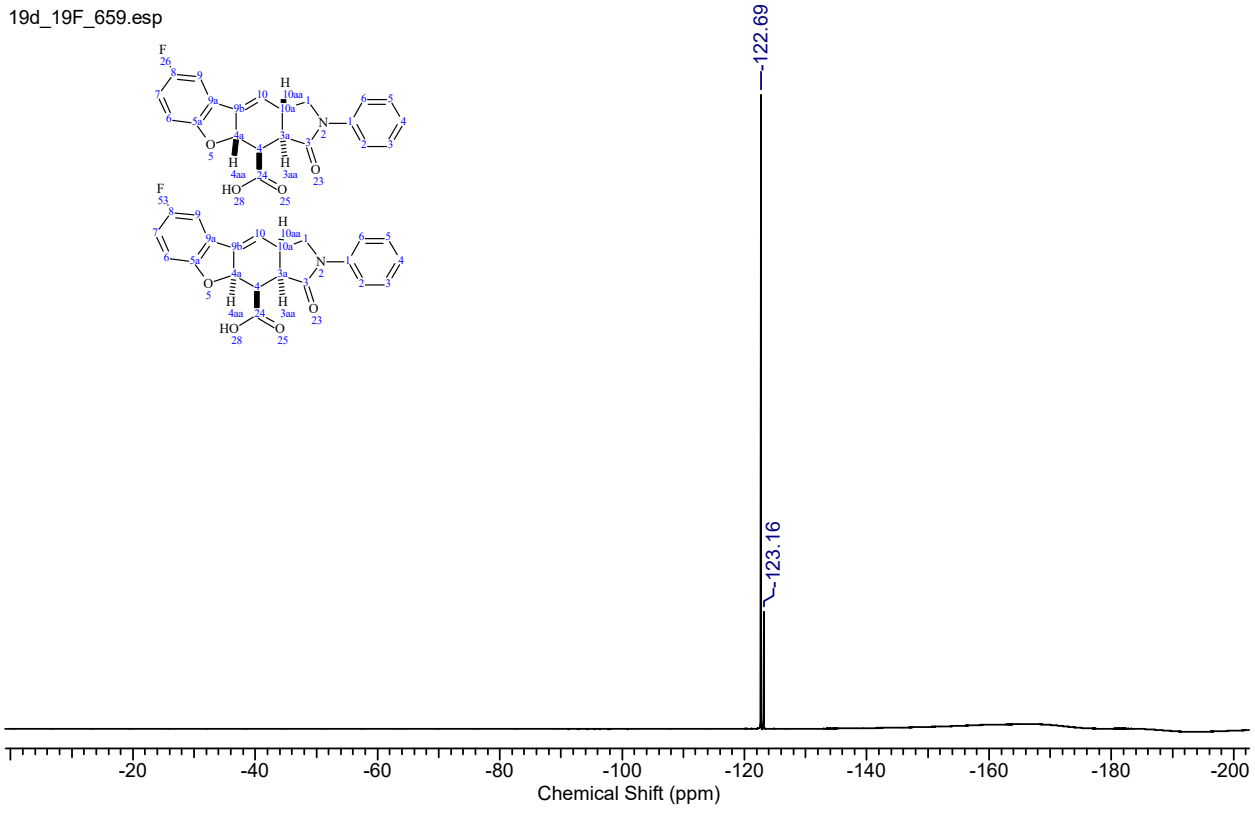
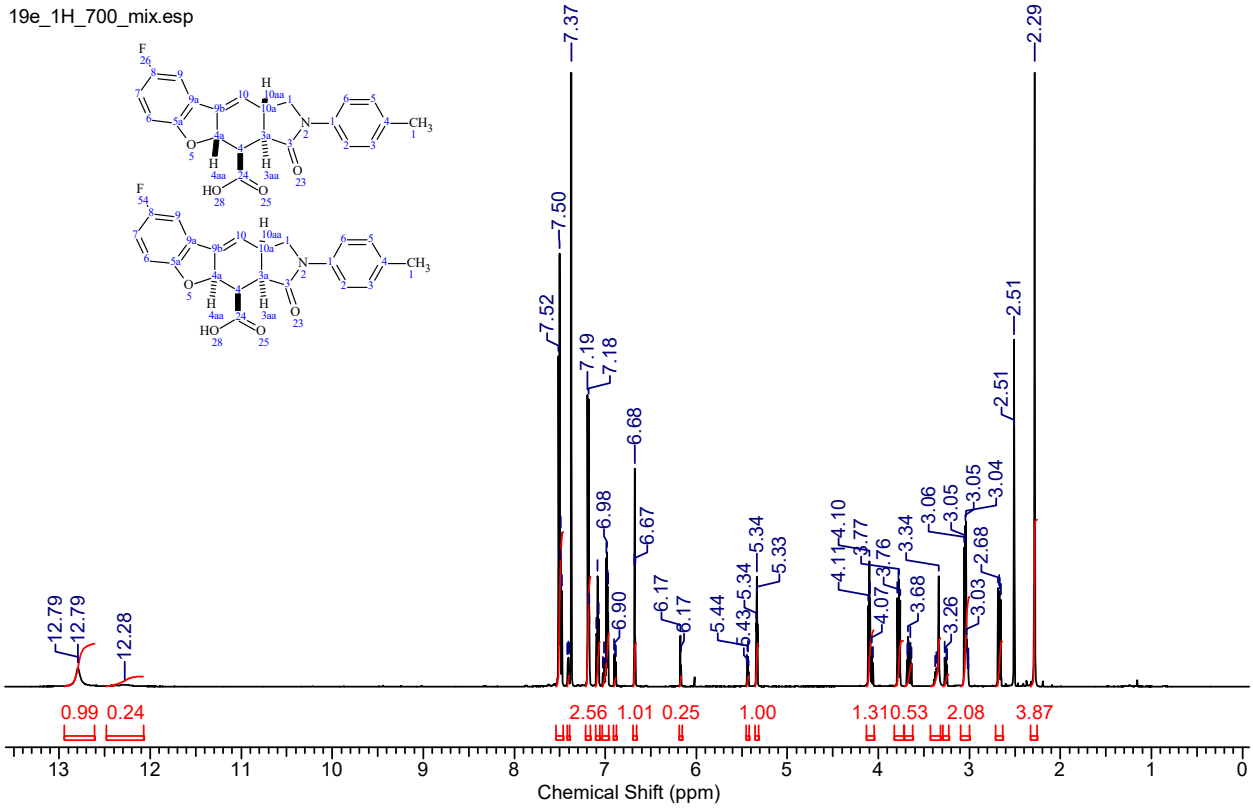
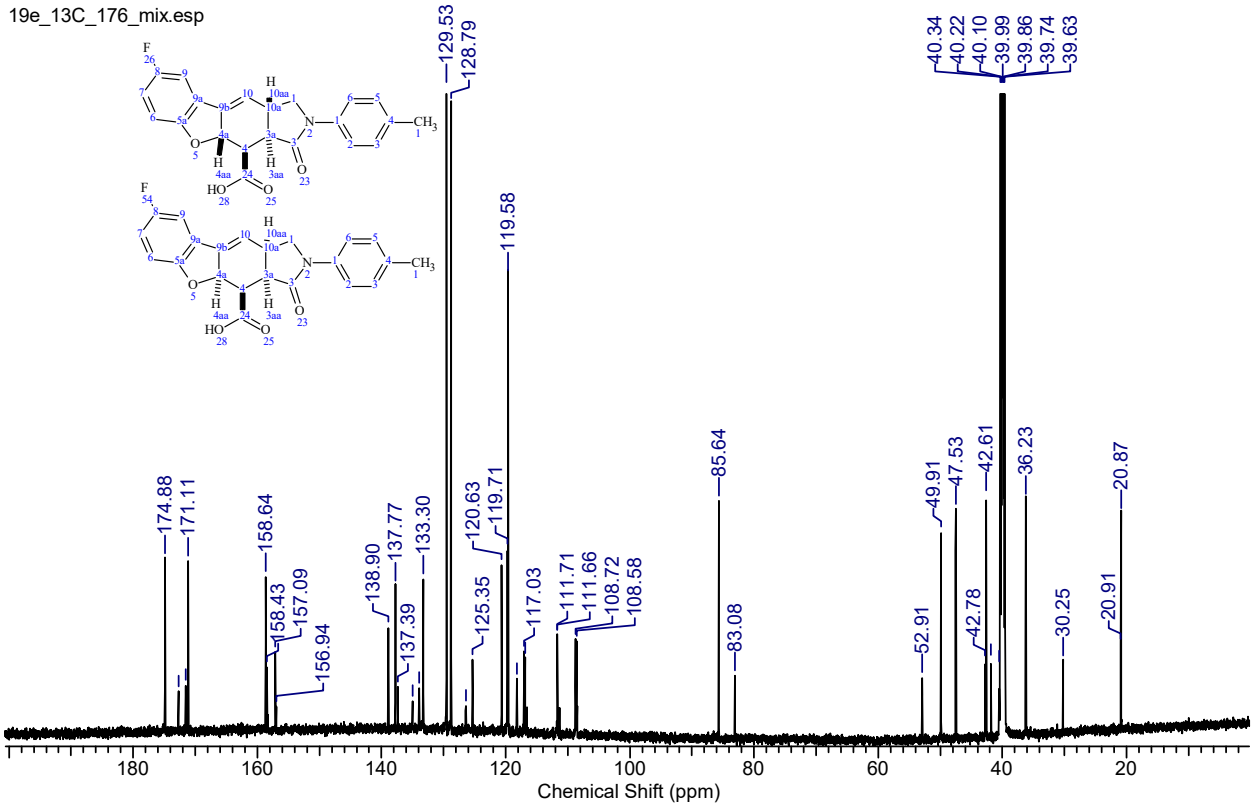
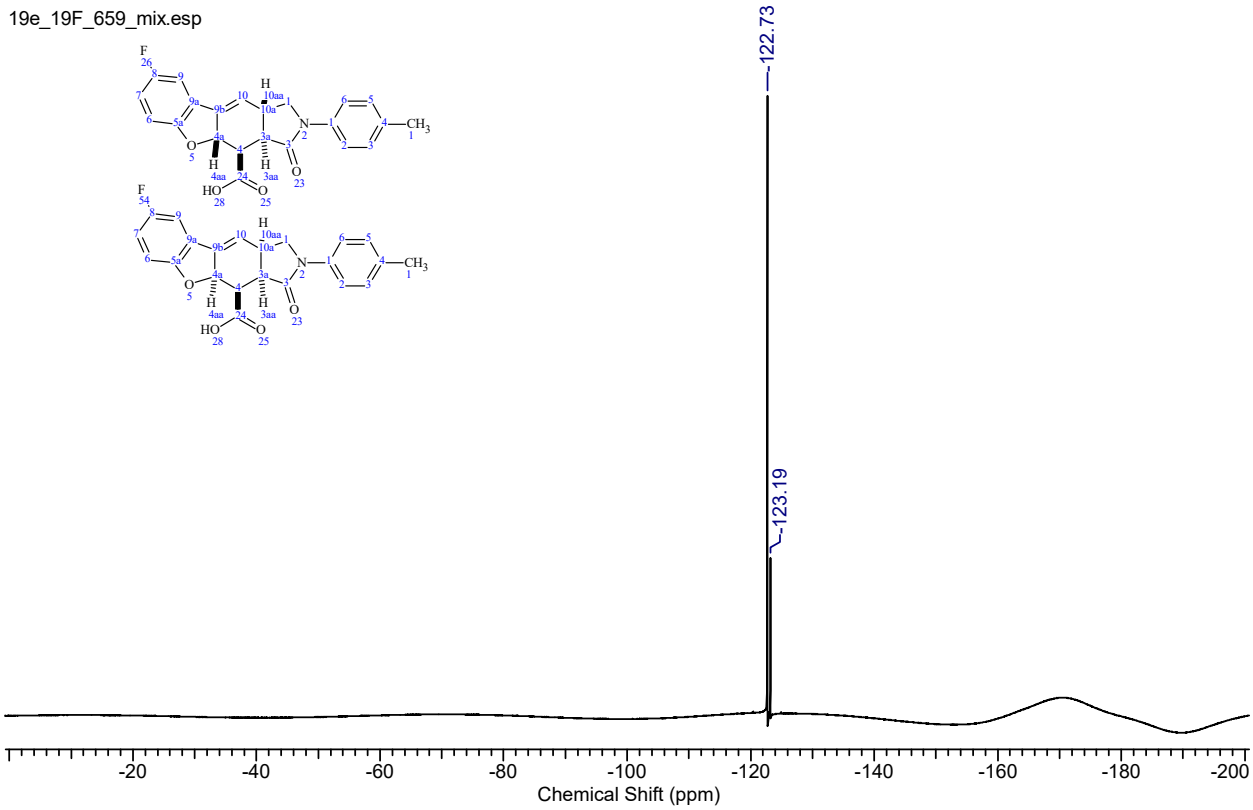


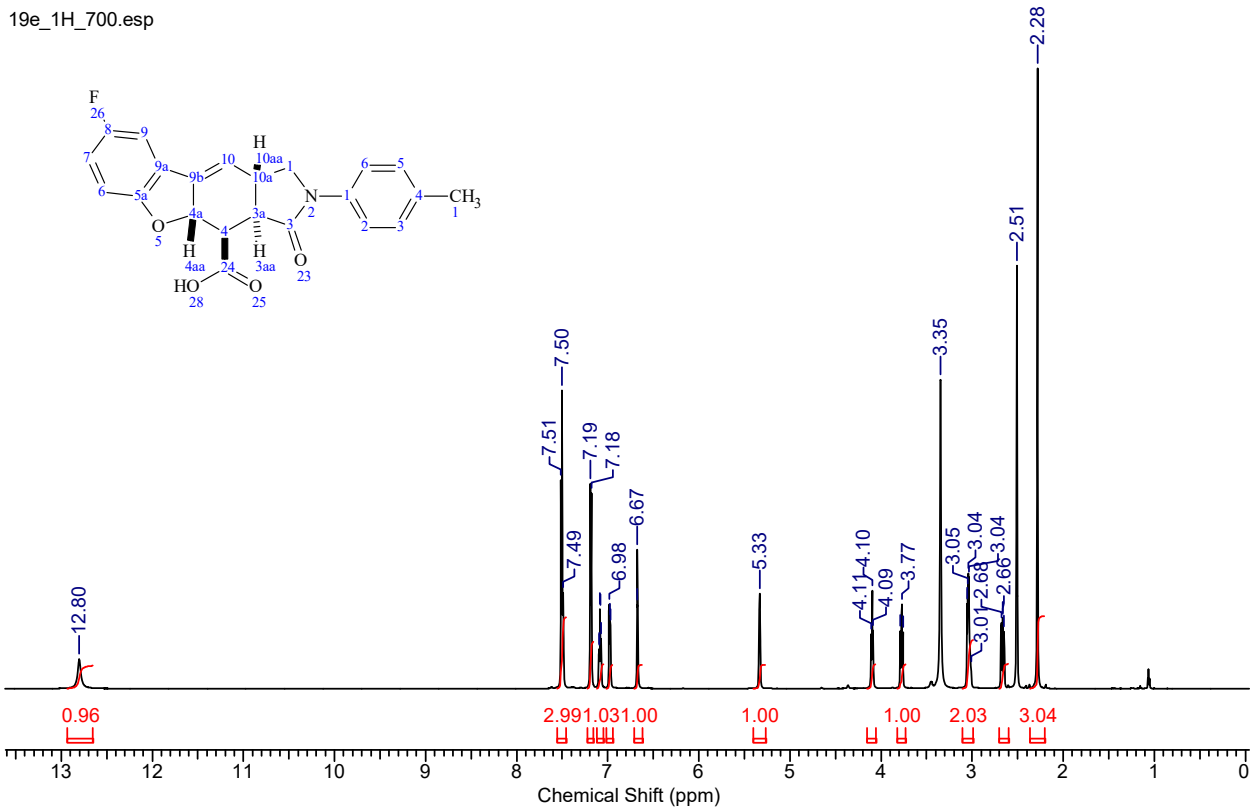
**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-2-(4-methylphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19e) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-8-fluoro-2-(4-methylphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (*endo*-17e).** *Contains around 20% on an impurity of endo-isomer.*






**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-2-(4-methylphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19e)**



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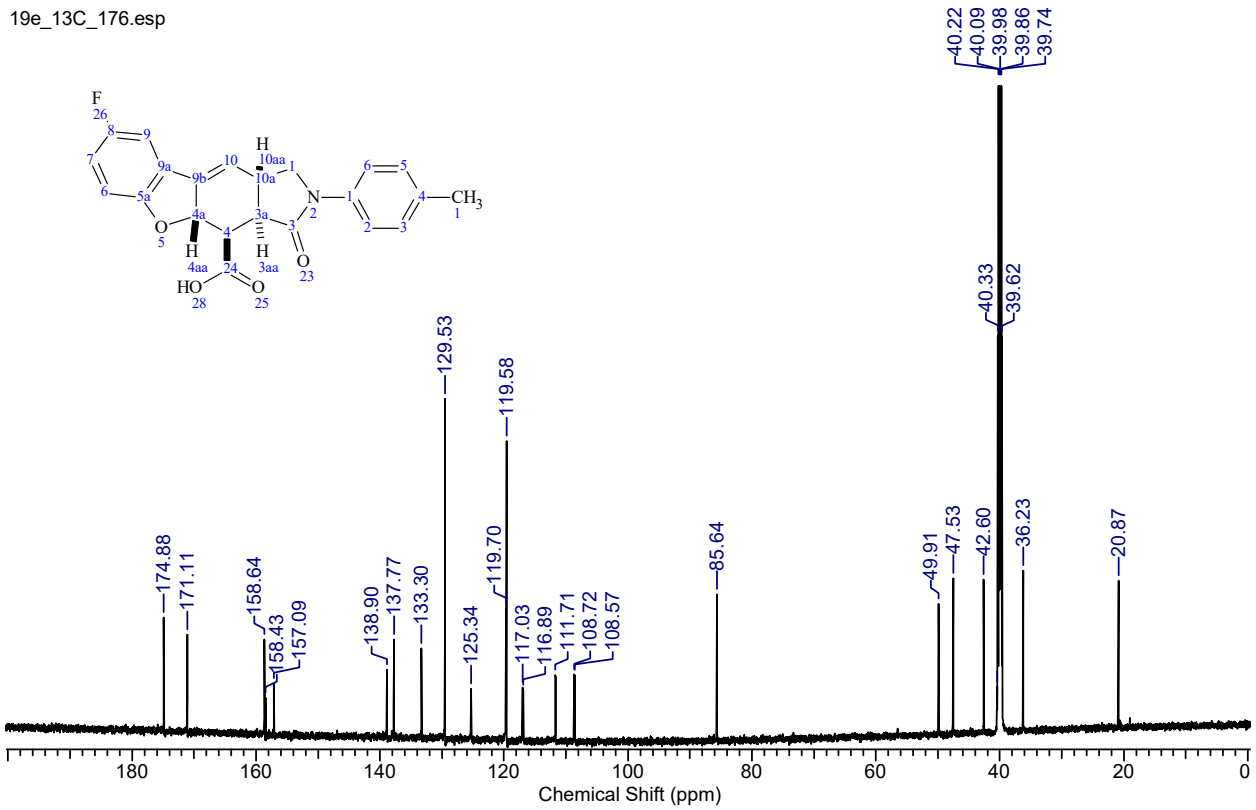


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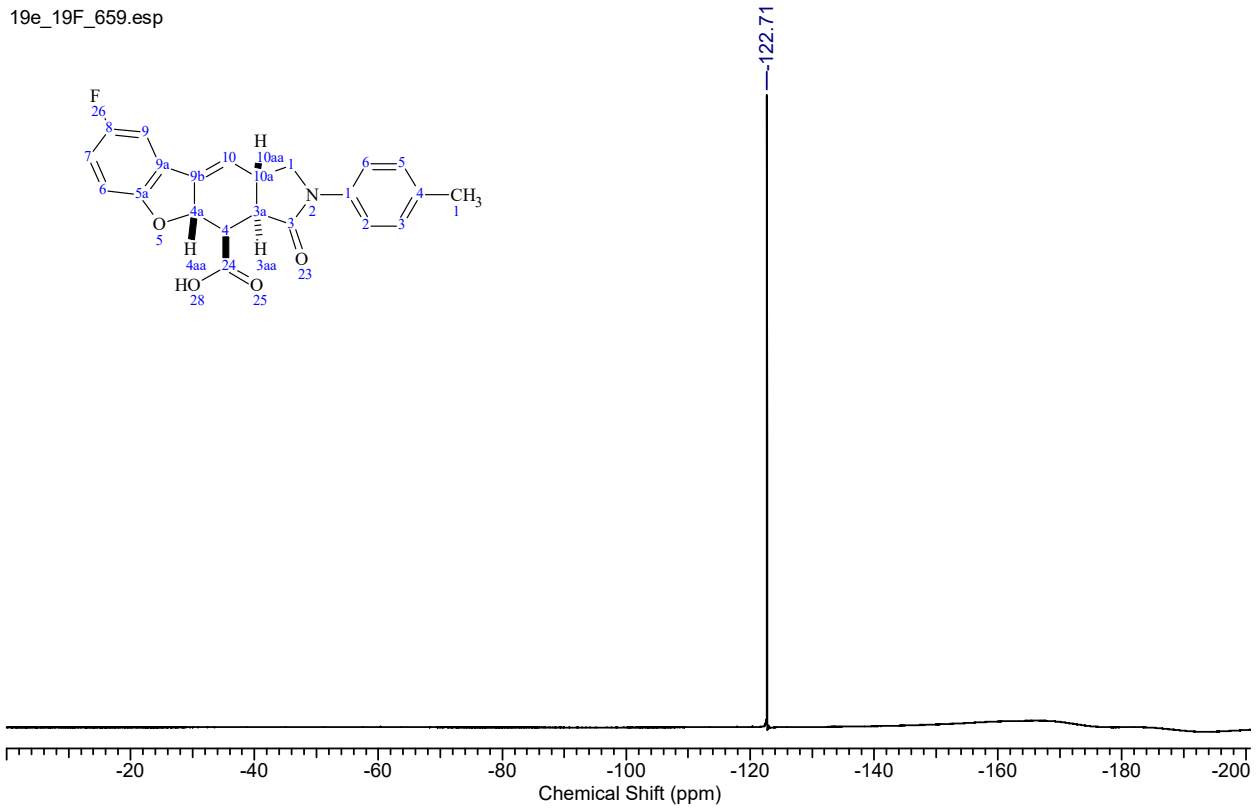
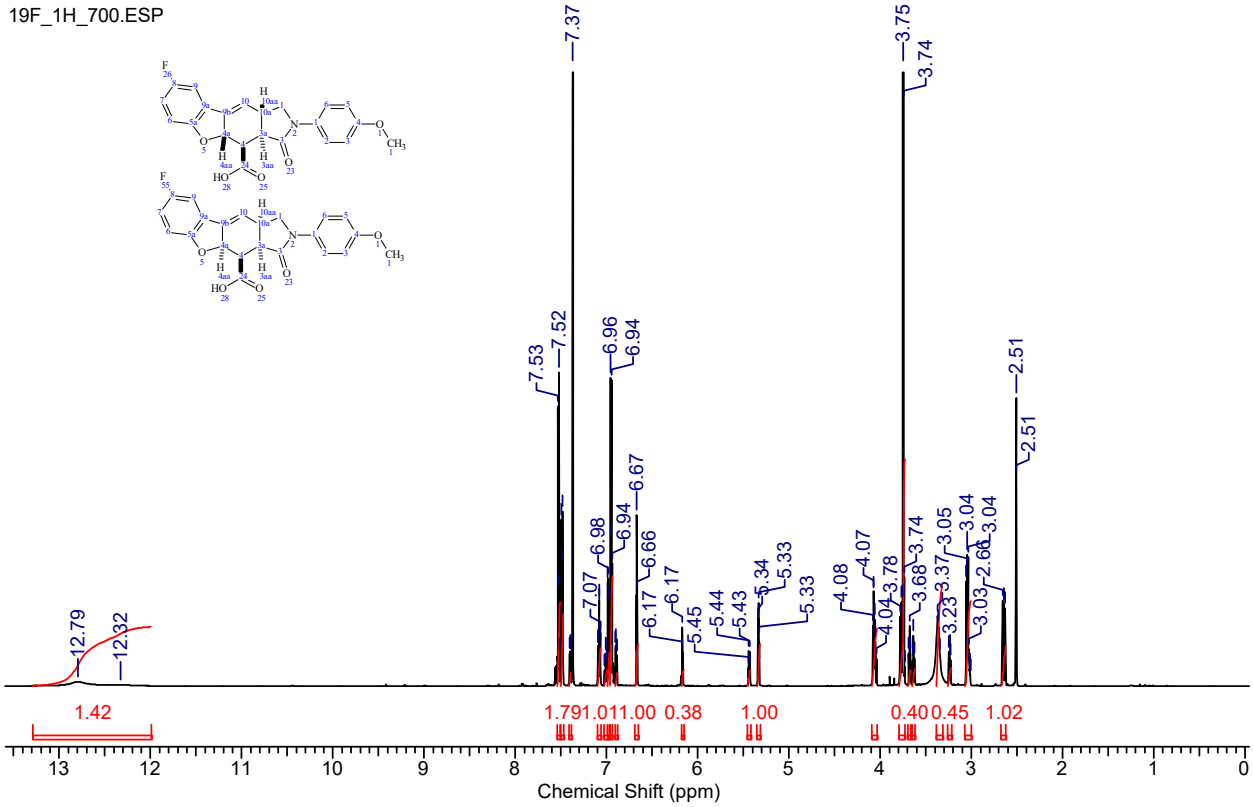
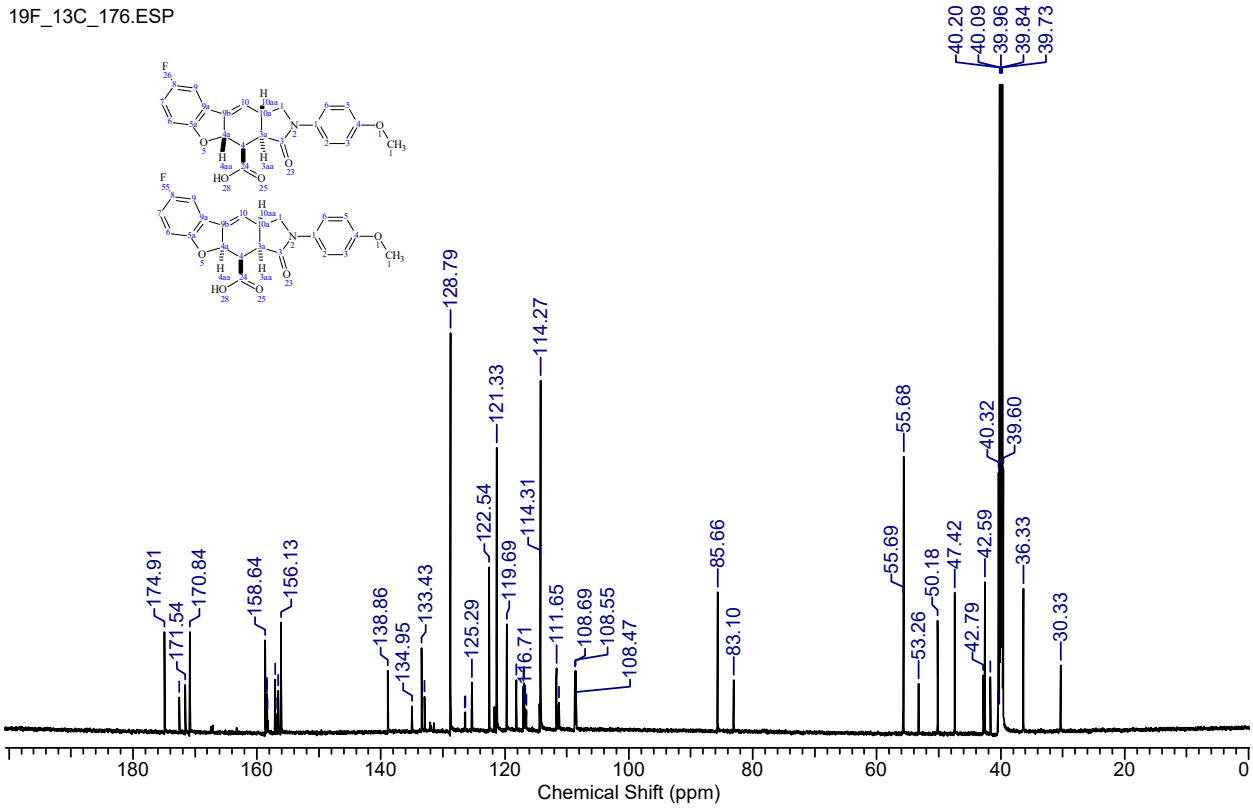
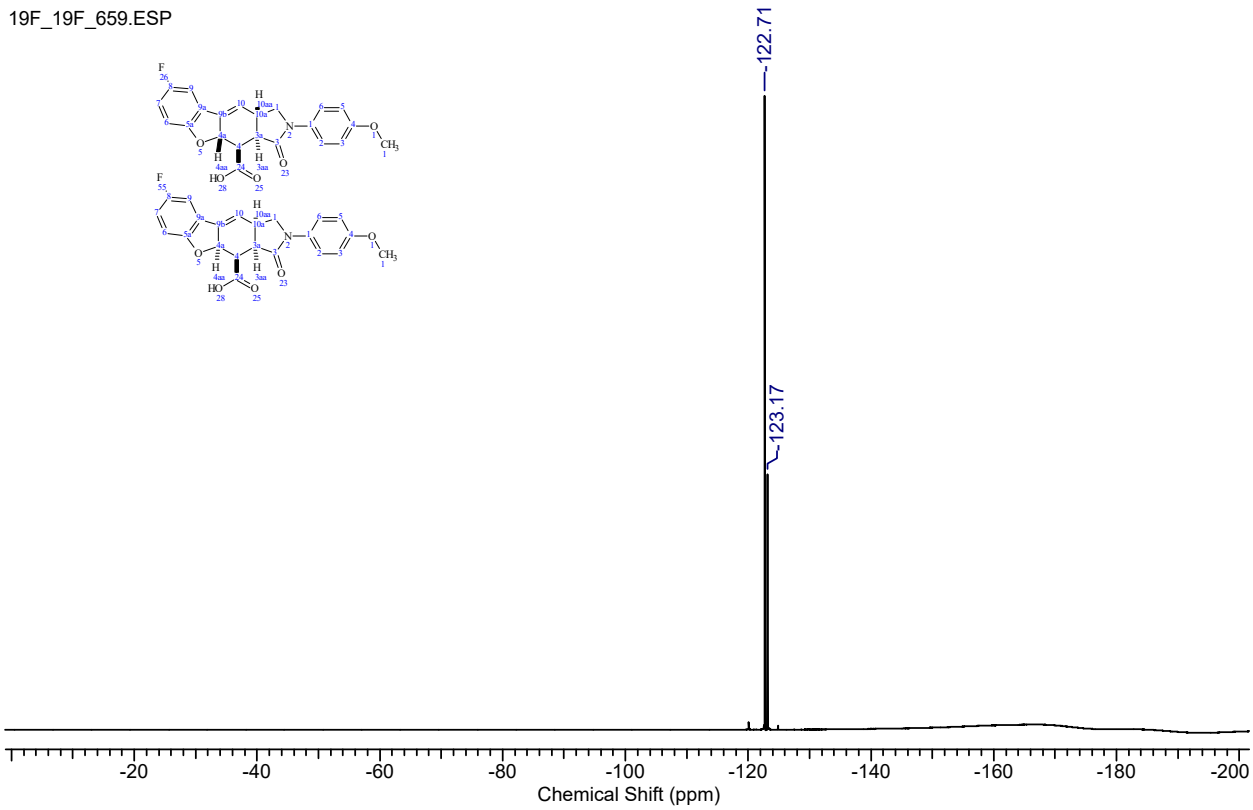


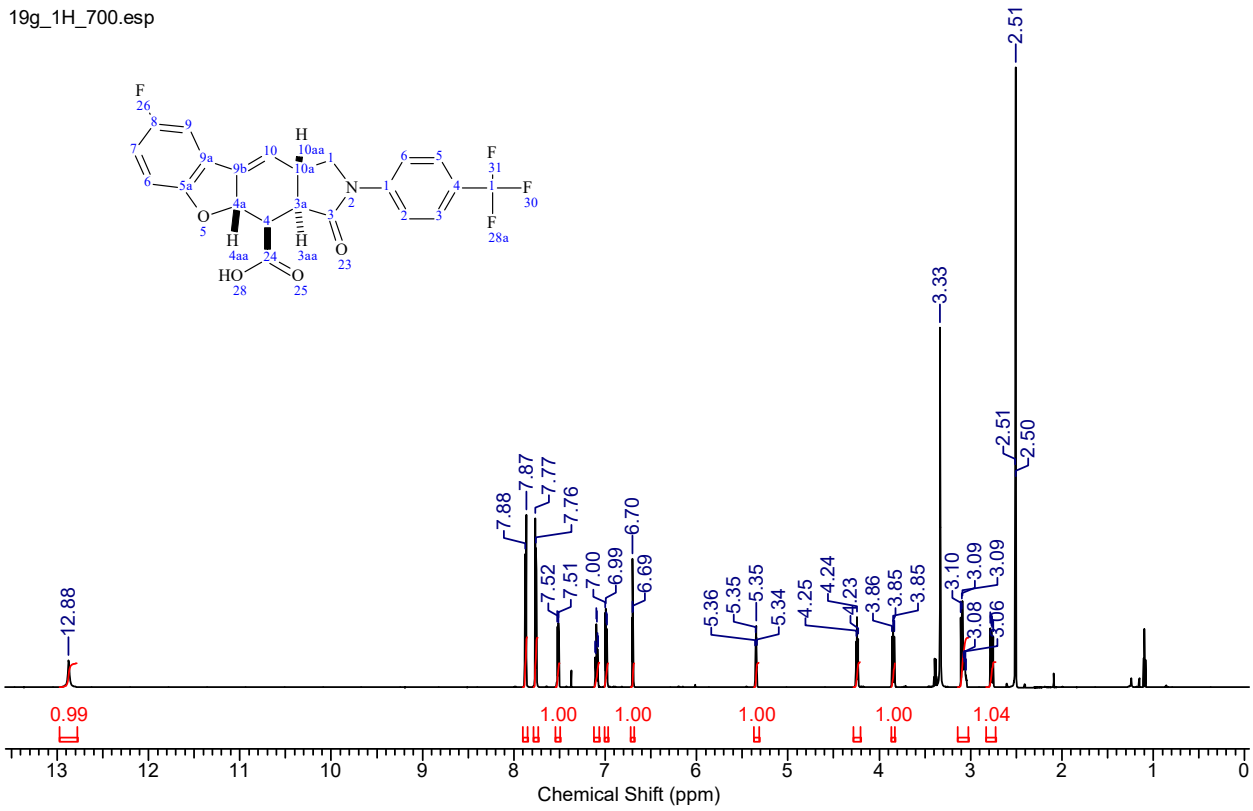
**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19f) and (3a*RS*,4*RS*,4a*RS*,10a*RS*)-8-fluoro-2-(4-methoxyphenyl)-3-oxo-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (17f).** *Contains around 29% on an impurity of endo-isomer and benzene.*






**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-8-Fluoro-3-oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (19g).**



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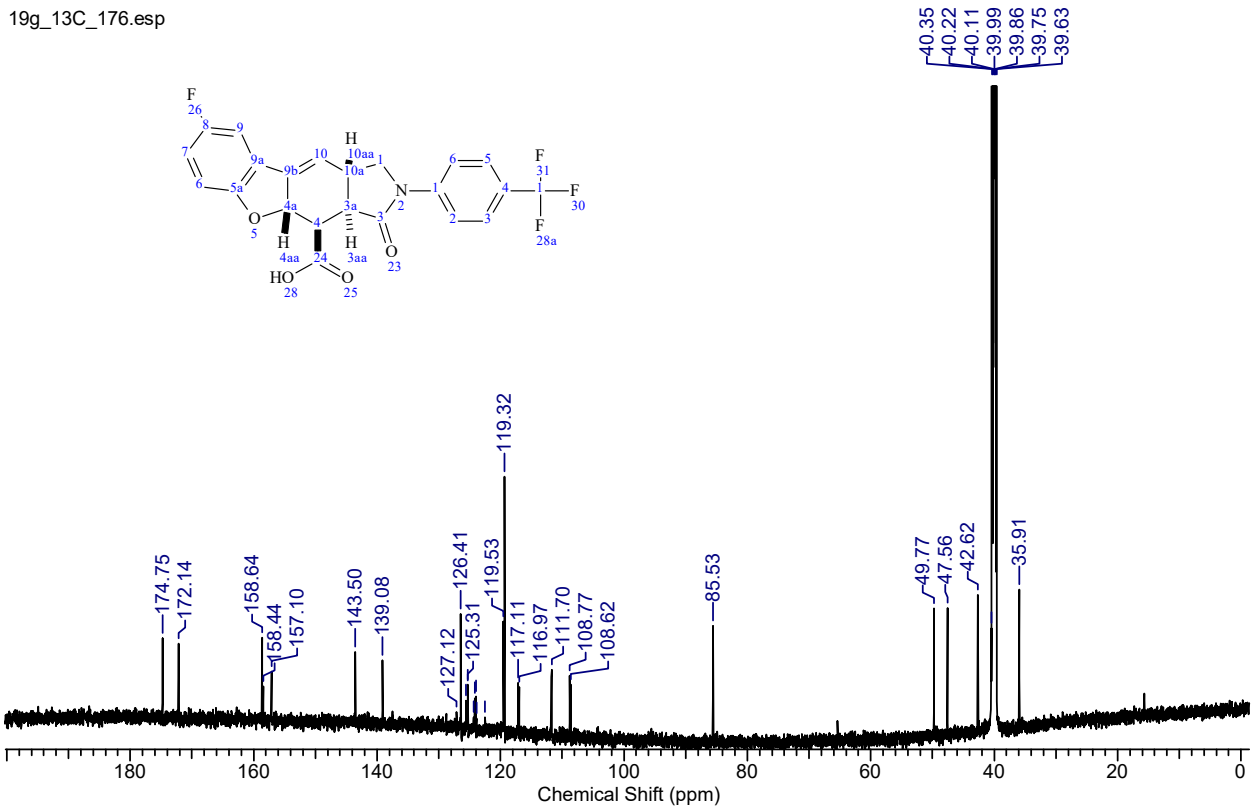


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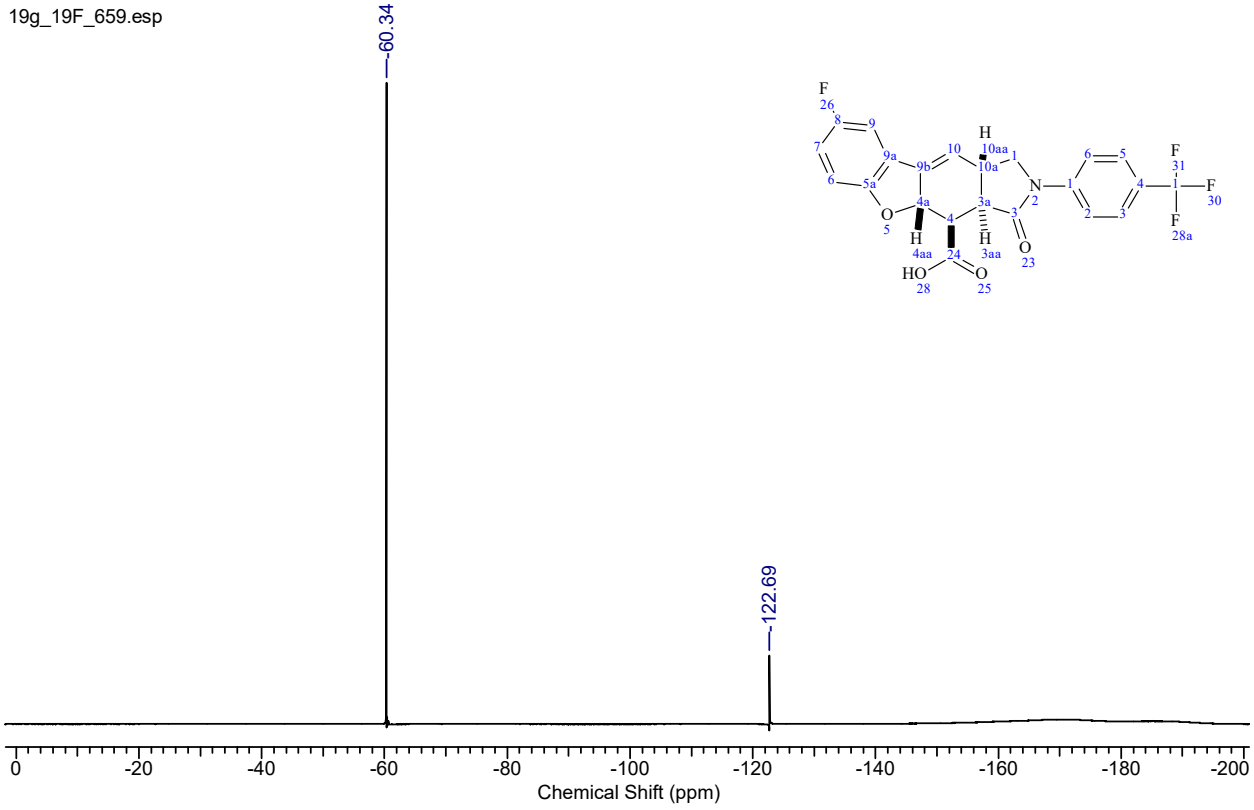
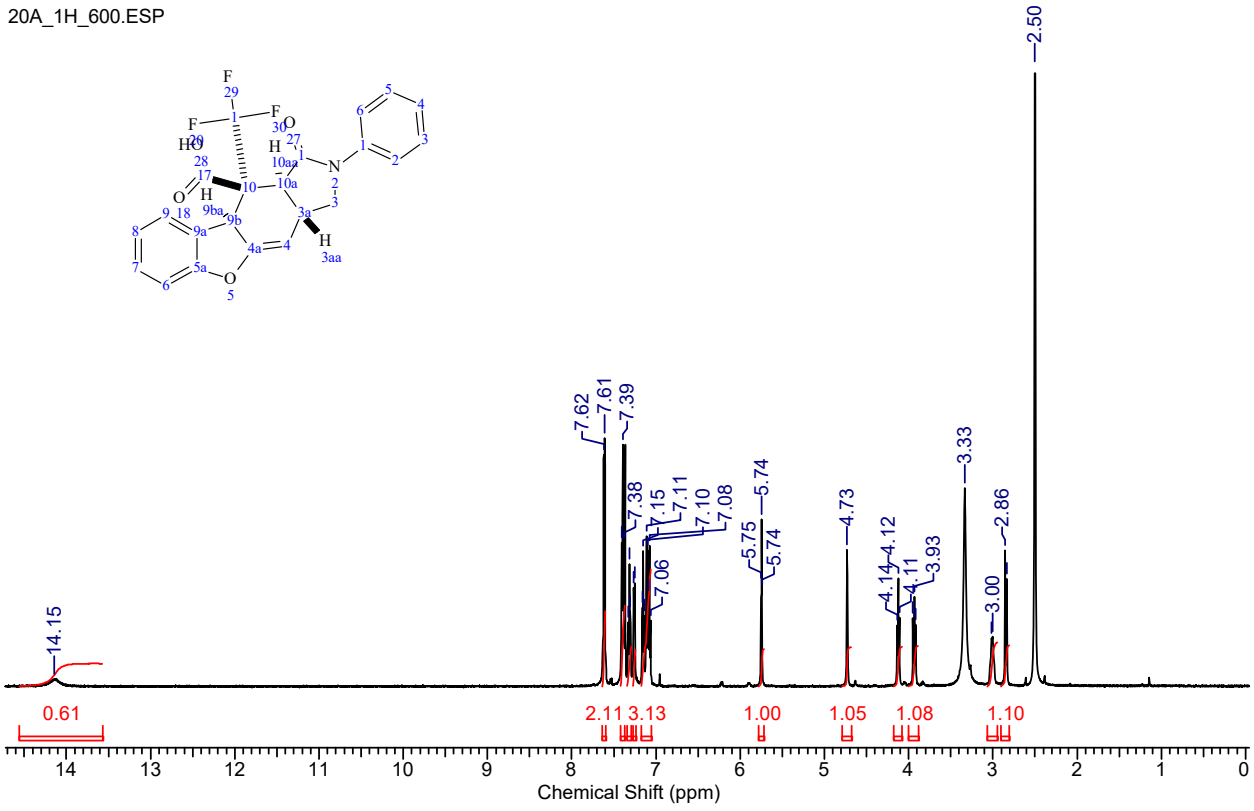
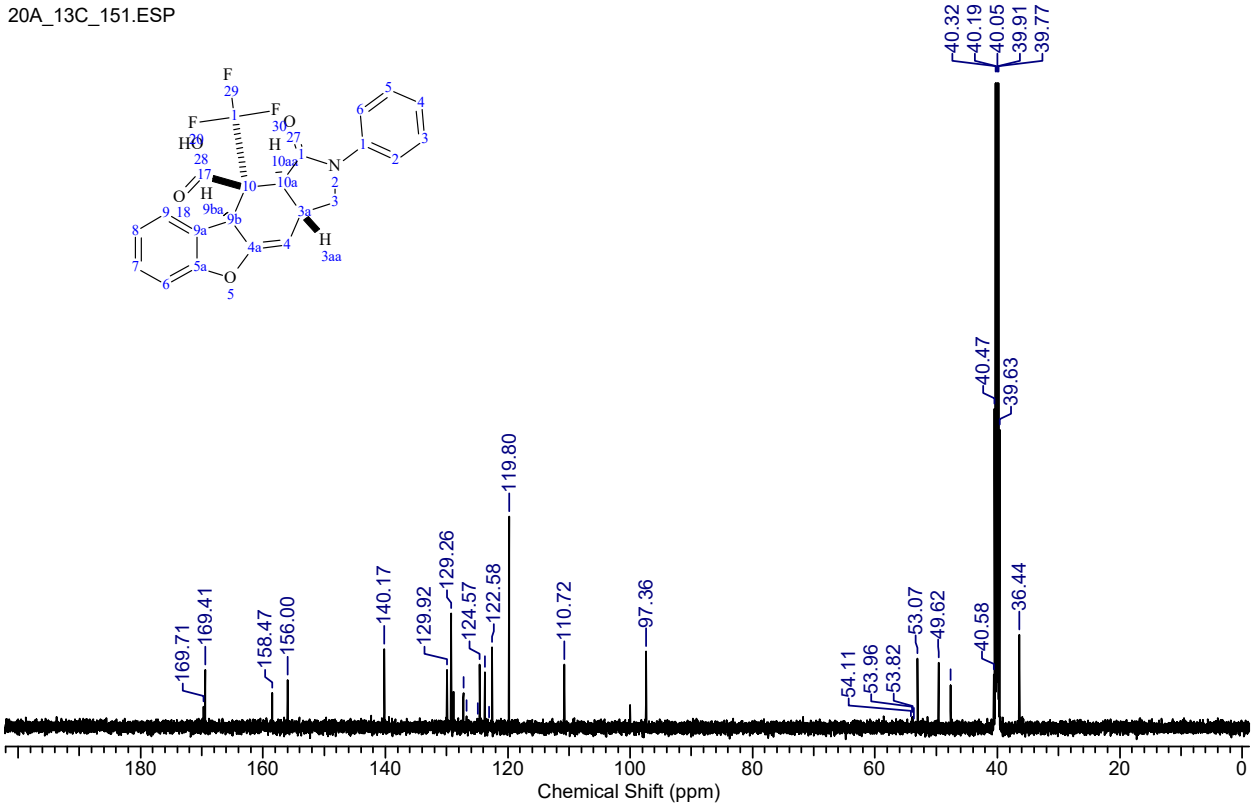
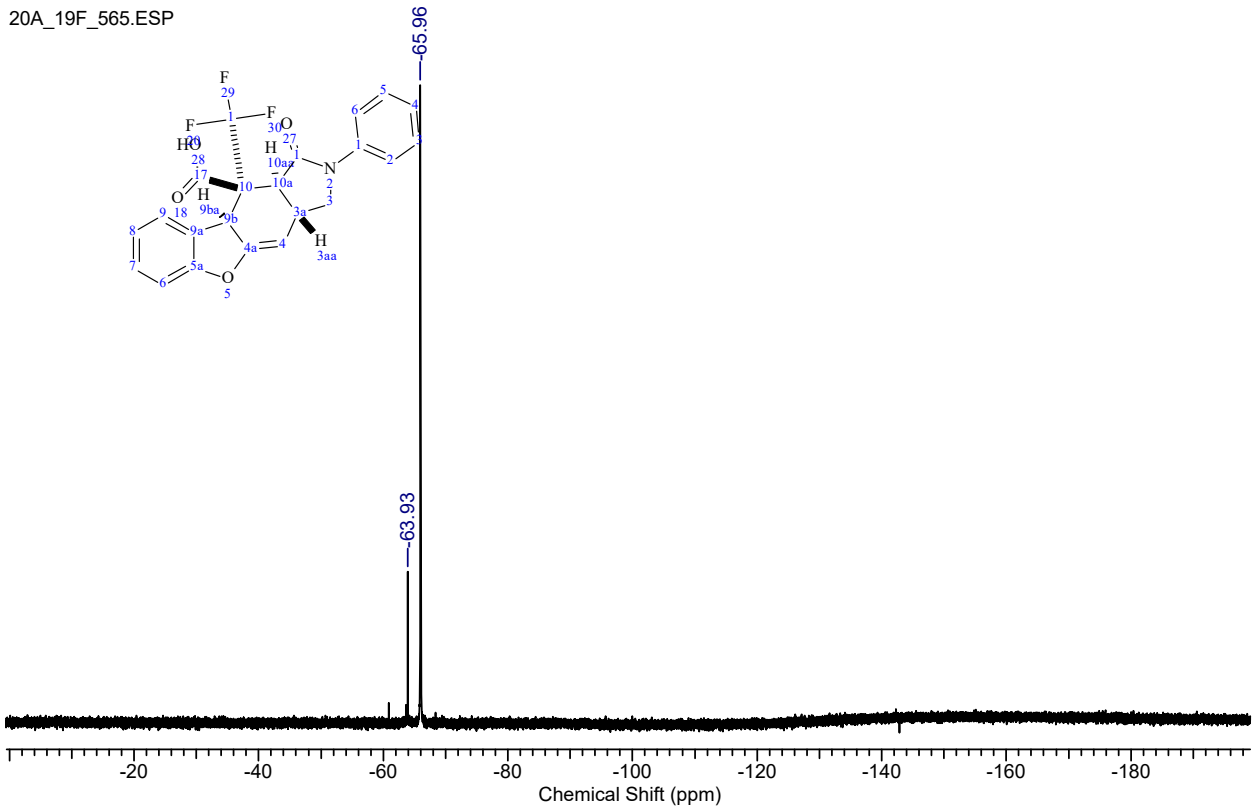


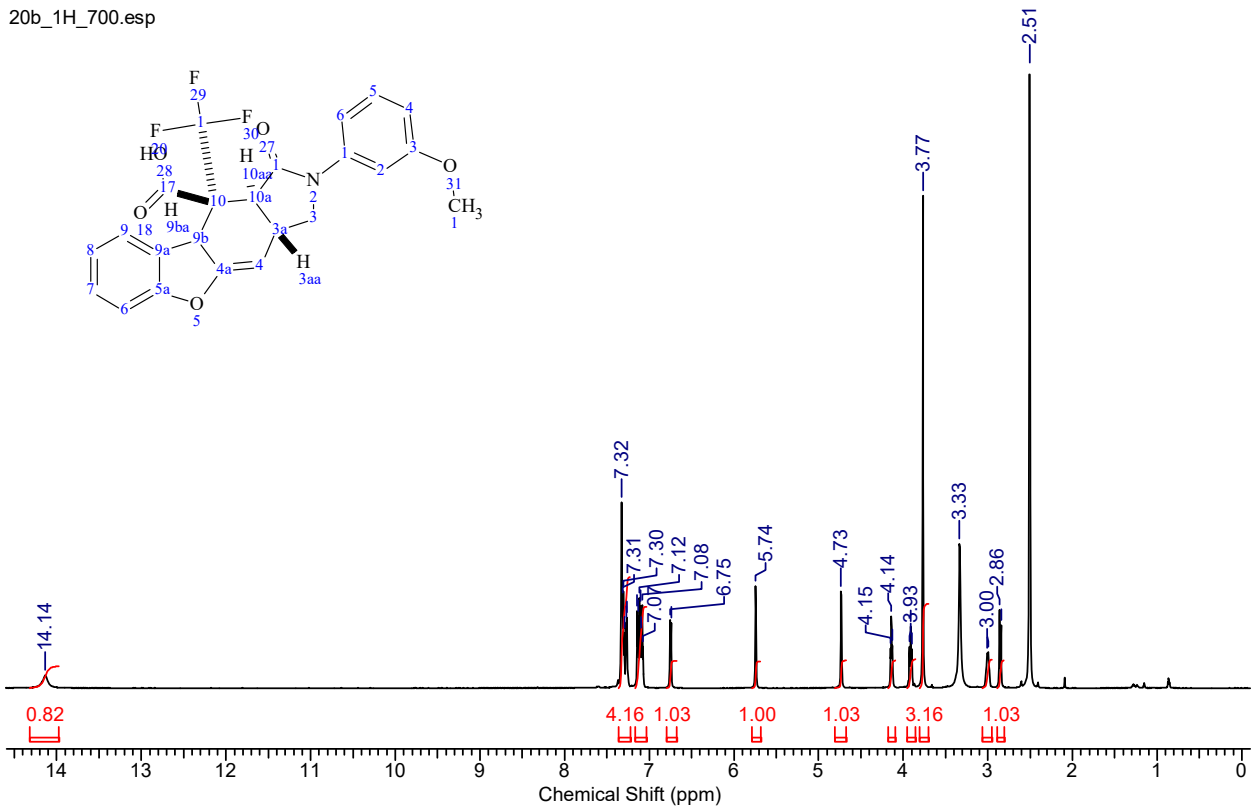
**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-1-Oxo-2-phenyl-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20a).**






**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20b).**



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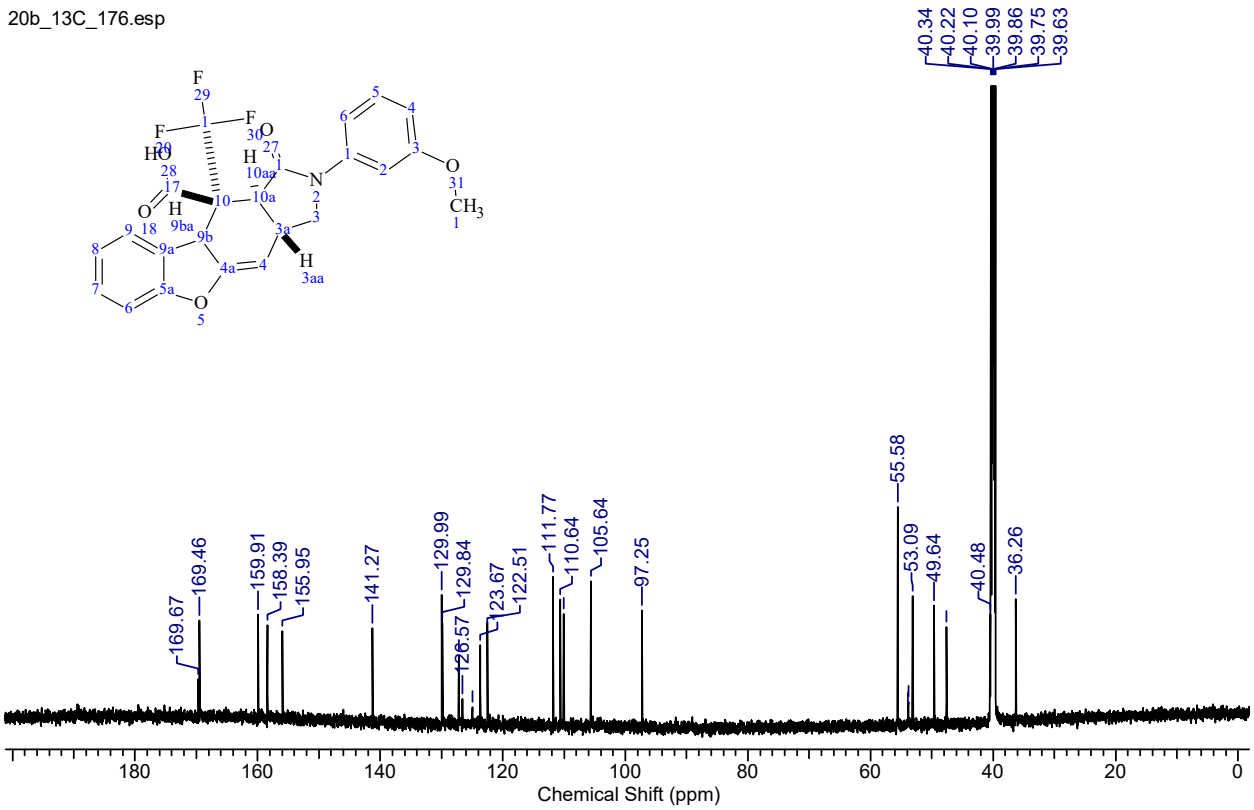


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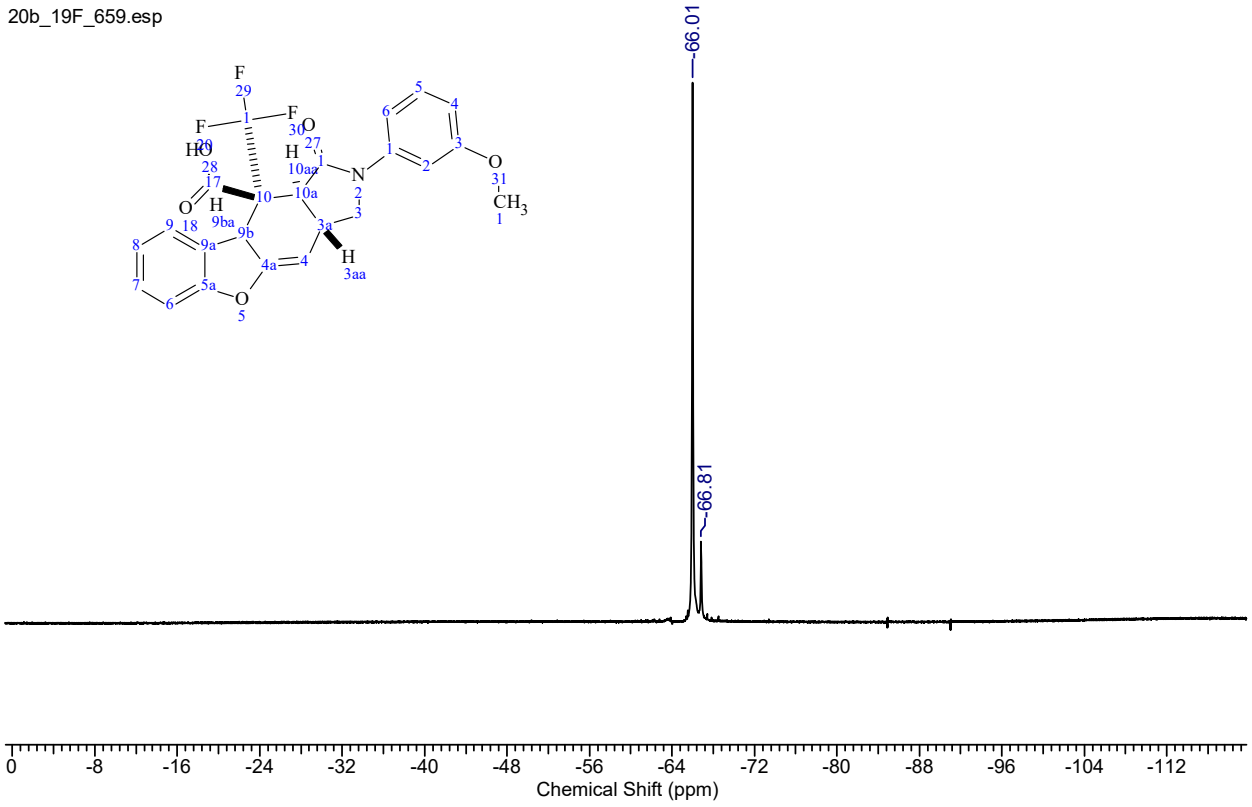
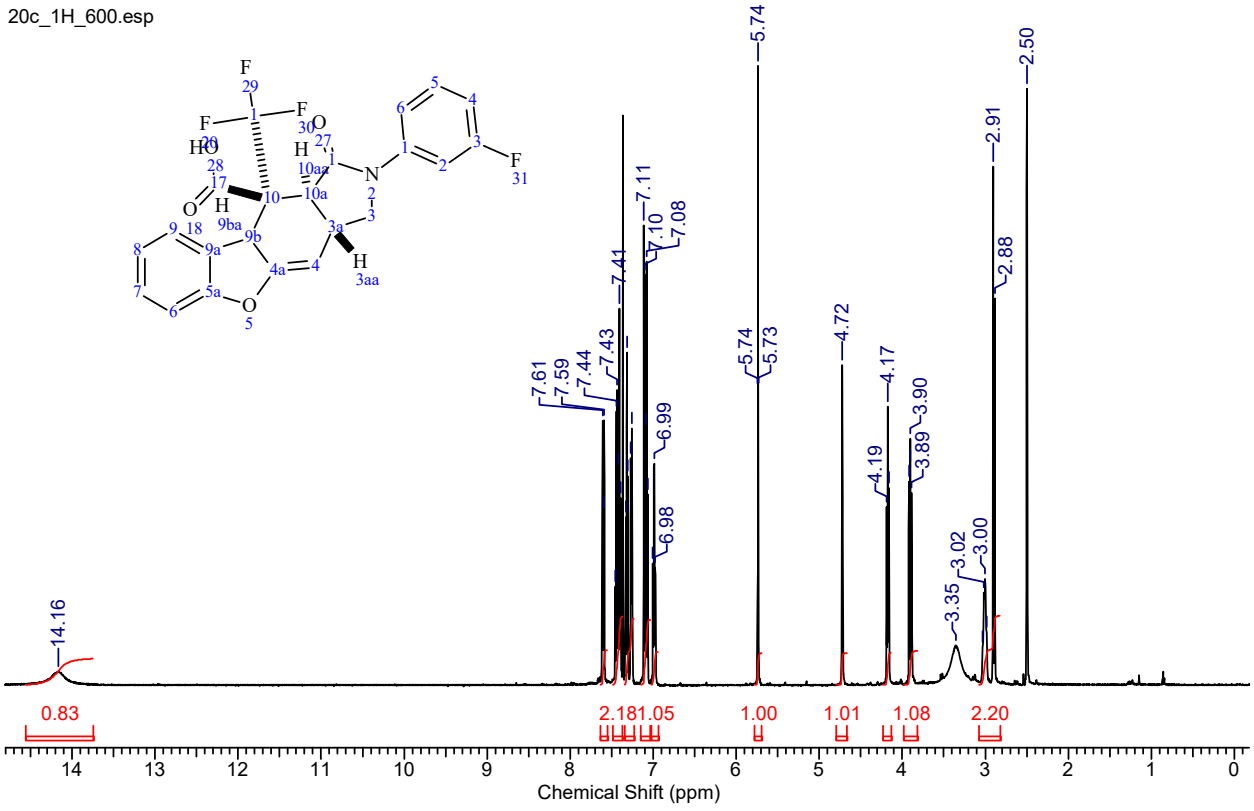
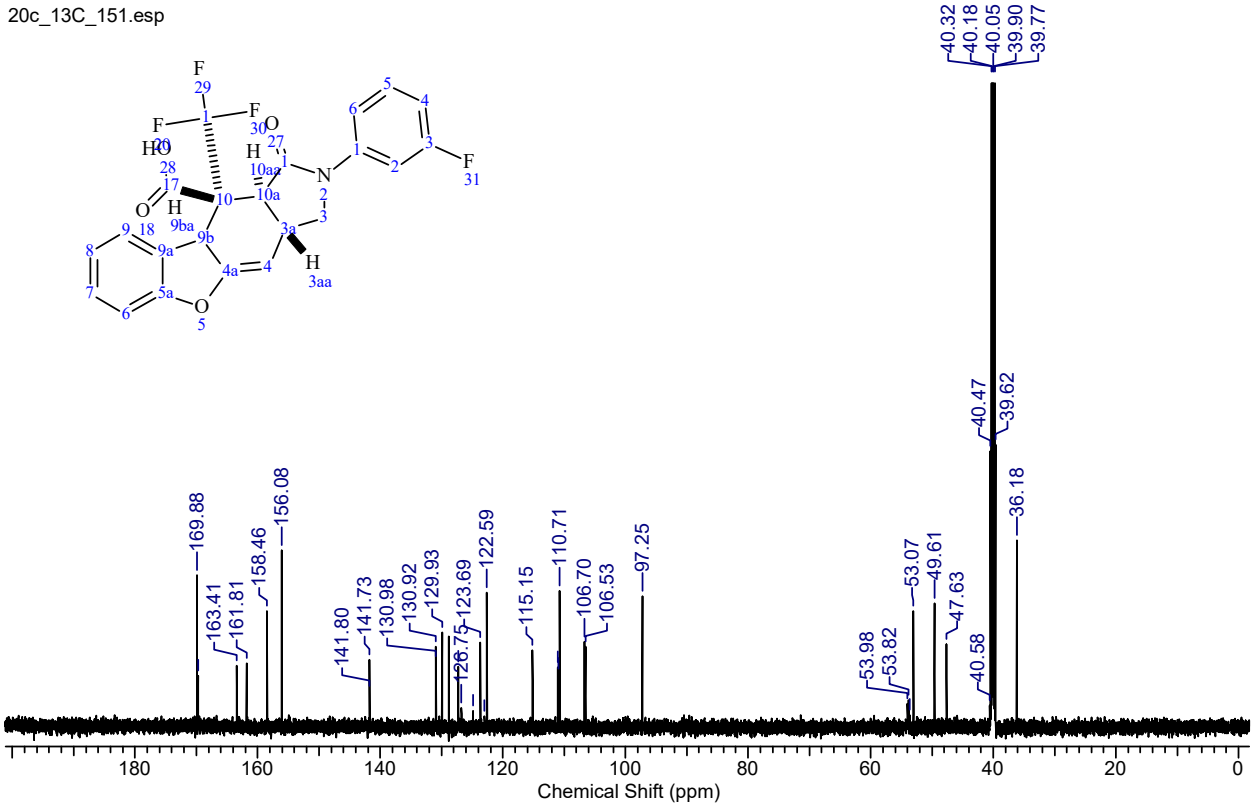
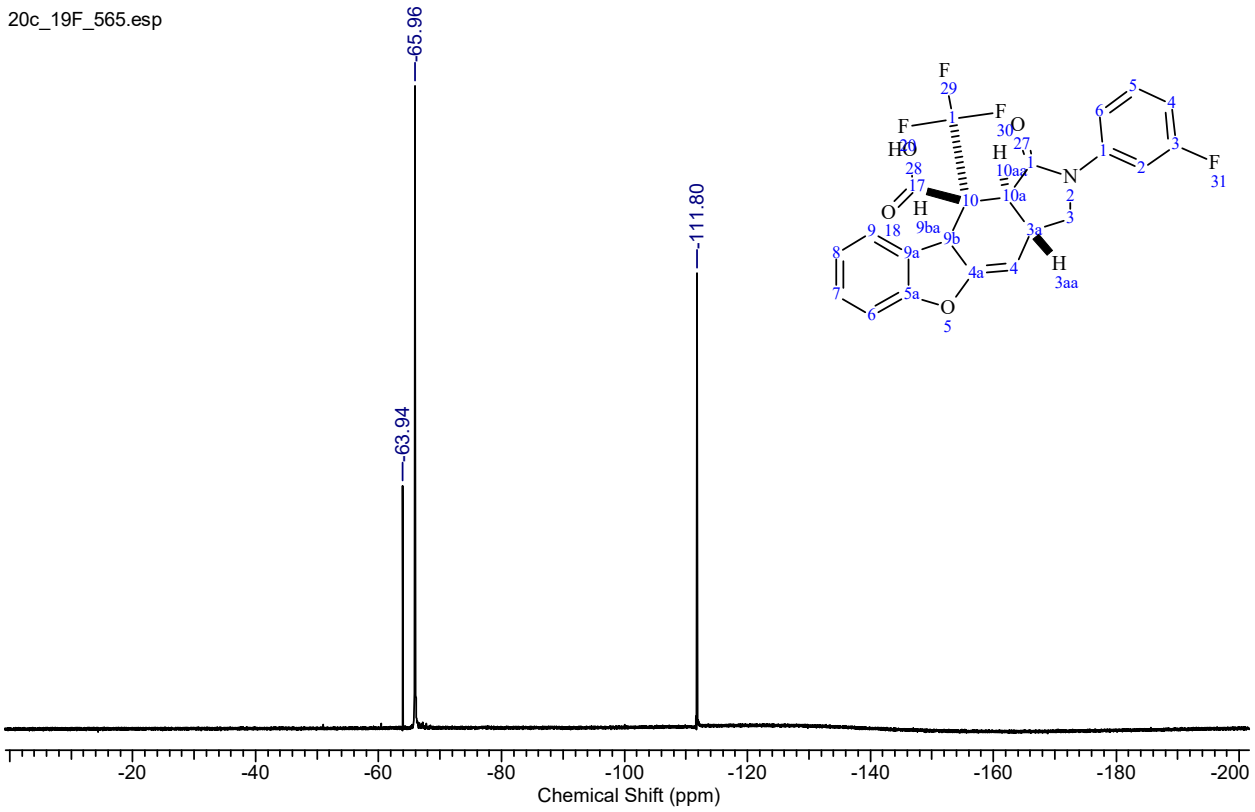


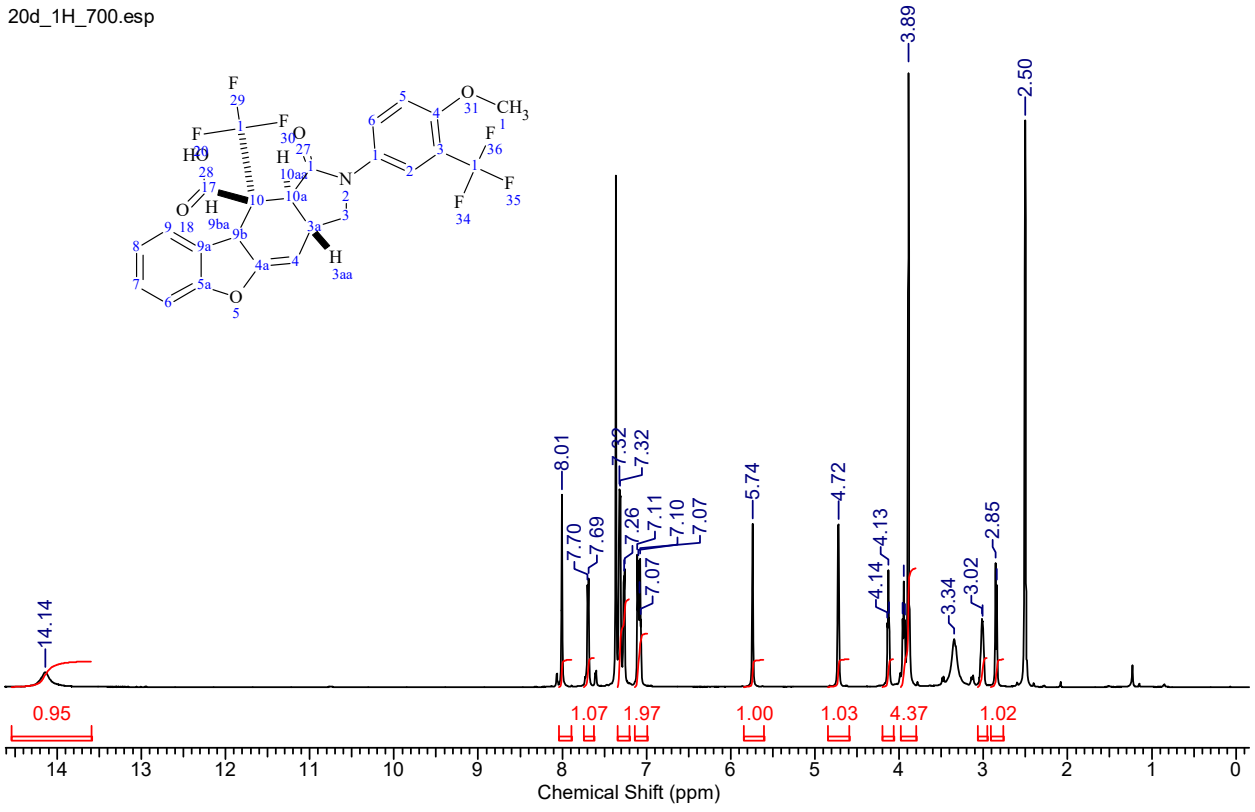
**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-2-(3-Fluorophenyl)-1-oxo-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20c).**






**(3a*RS*,9b*RS*,10*SR*,10a*SR*)-2-[4-Methoxy-3-(trifluoromethyl)phenyl]-1-oxo-10-(trifluoromethyl)-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20d).** *Contains an impurity of benzene.*



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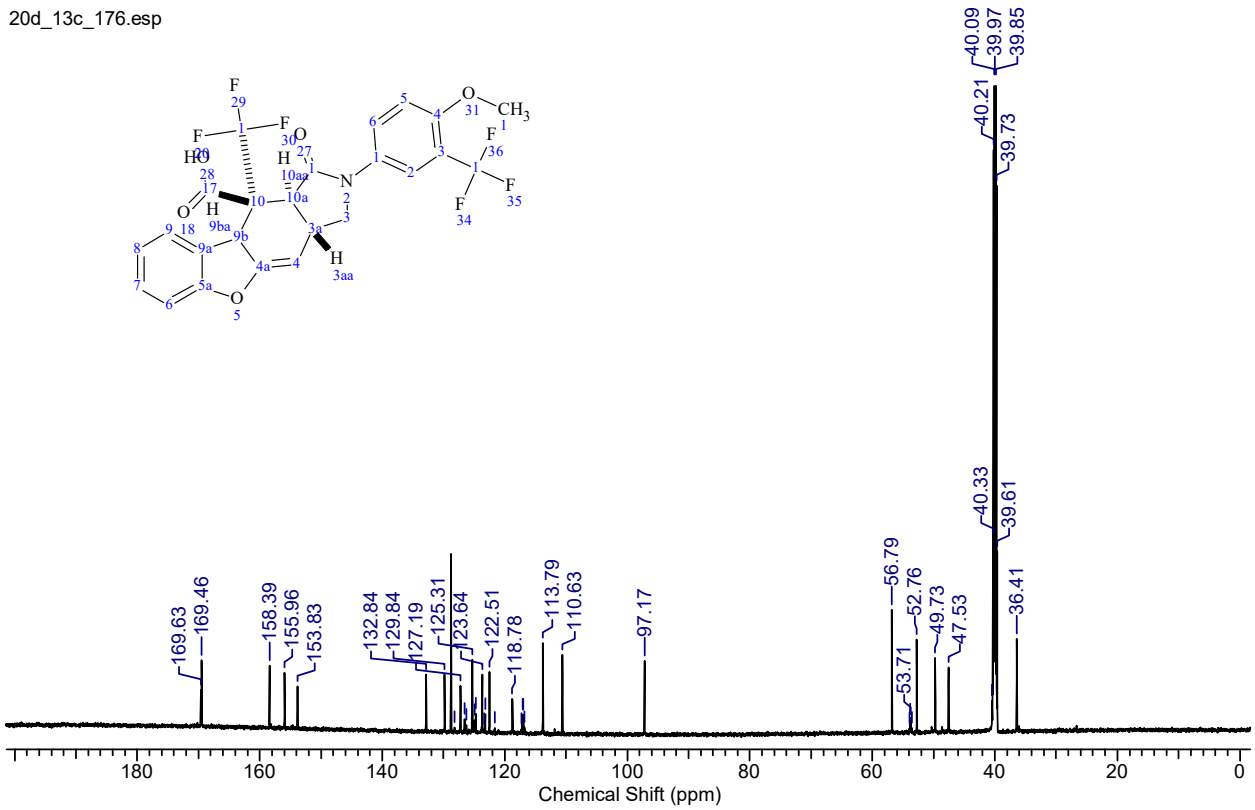


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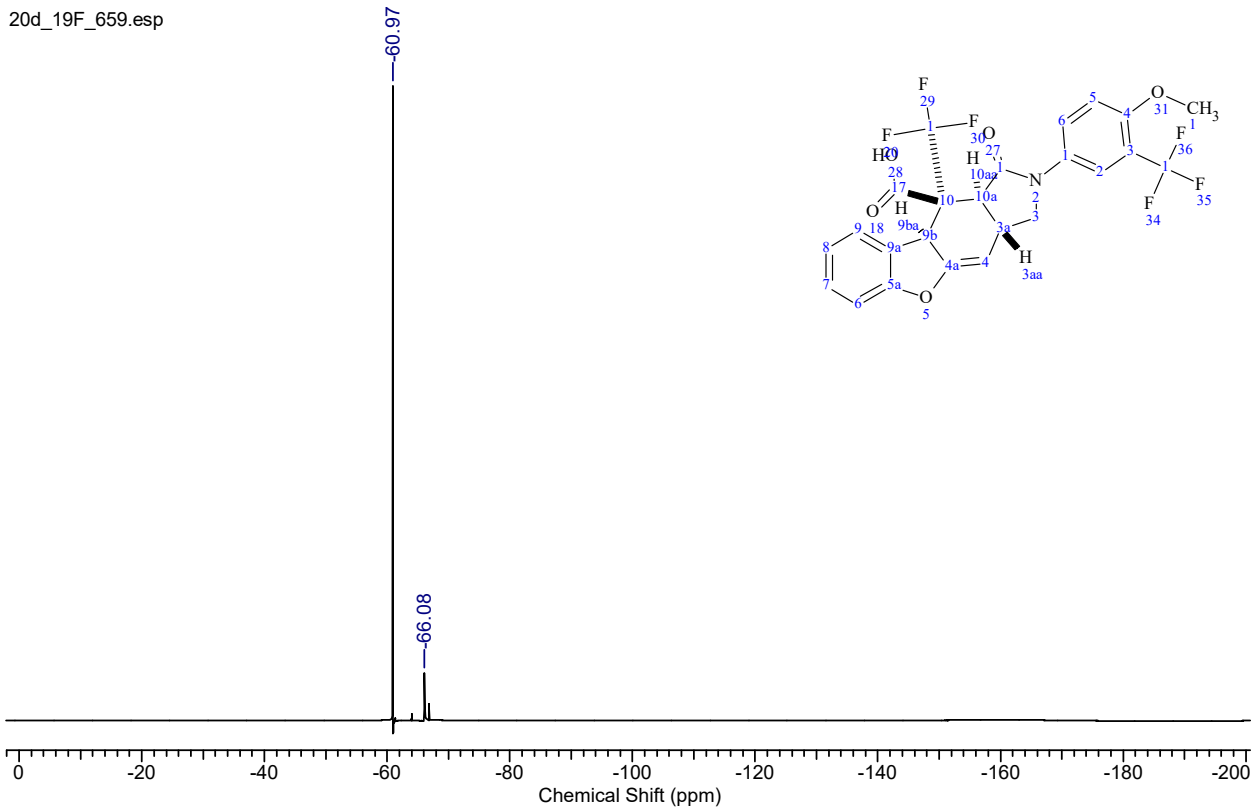
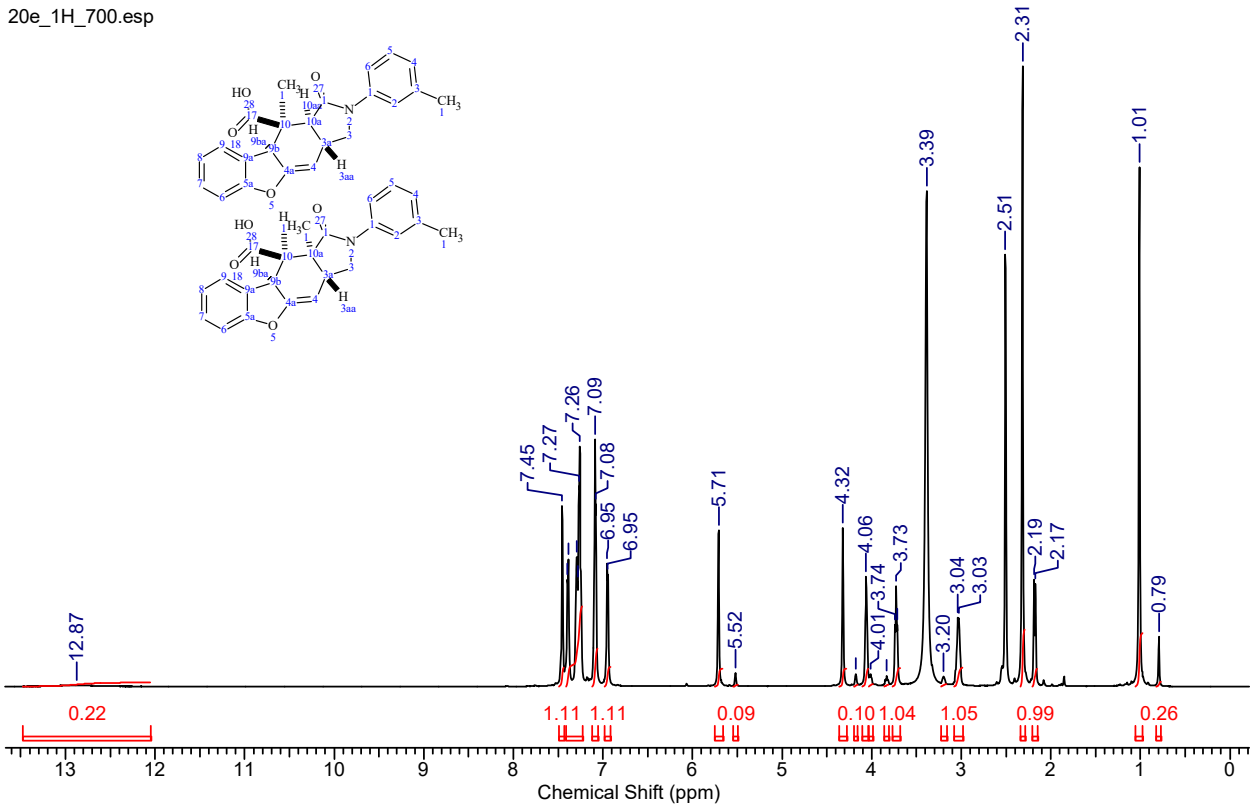
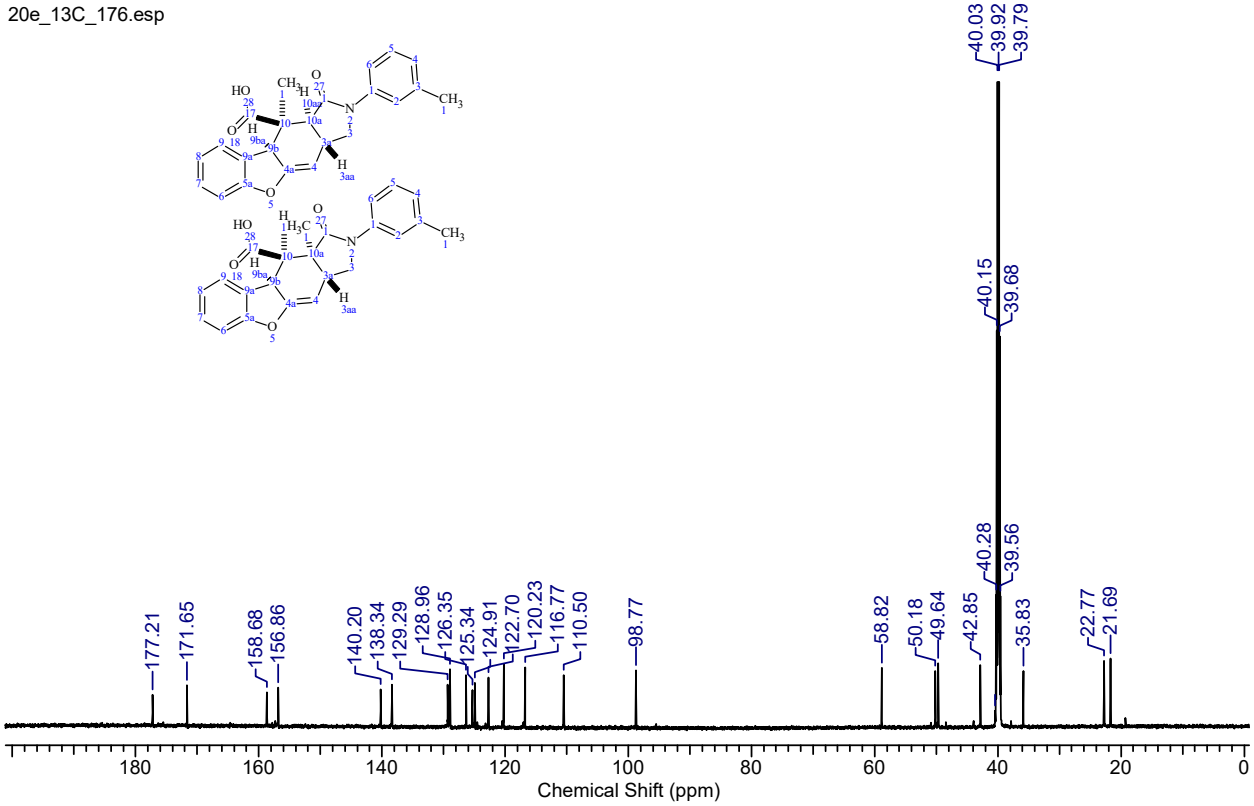
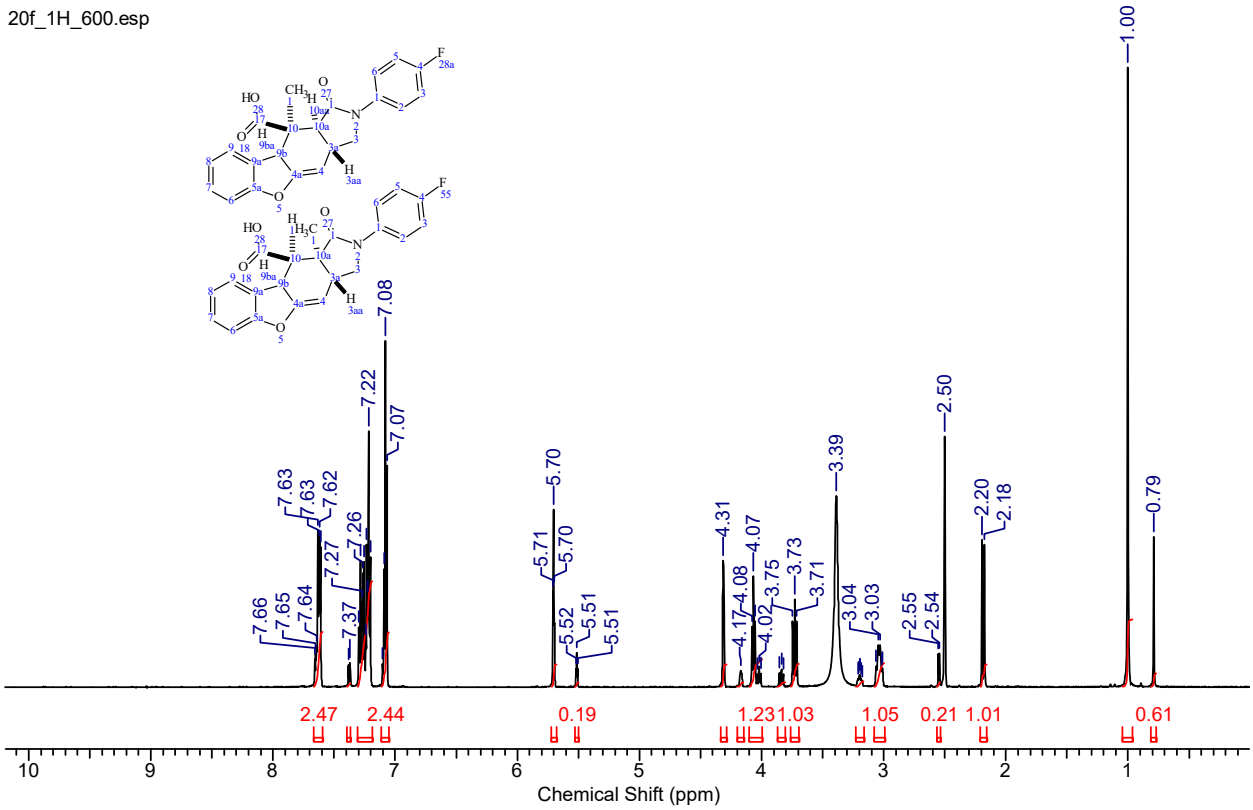


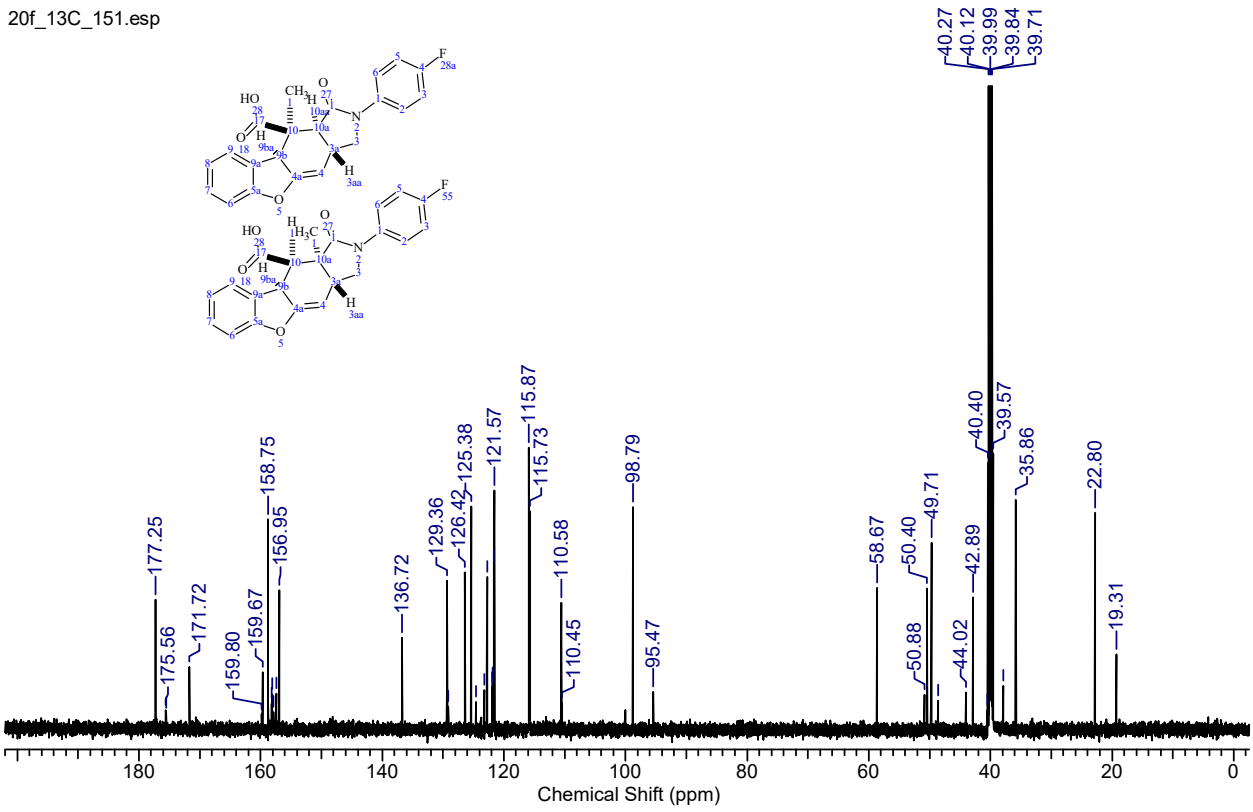
**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-10-Methyl-2-(3-methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20e) and (3a*RS*,9b*SR*,10*RS*,10a*SR*)-10a-methyl-2-(3-methylphenyl)-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (21e).** *Contains around 9% on an impurity of regioisomer* **21e**.

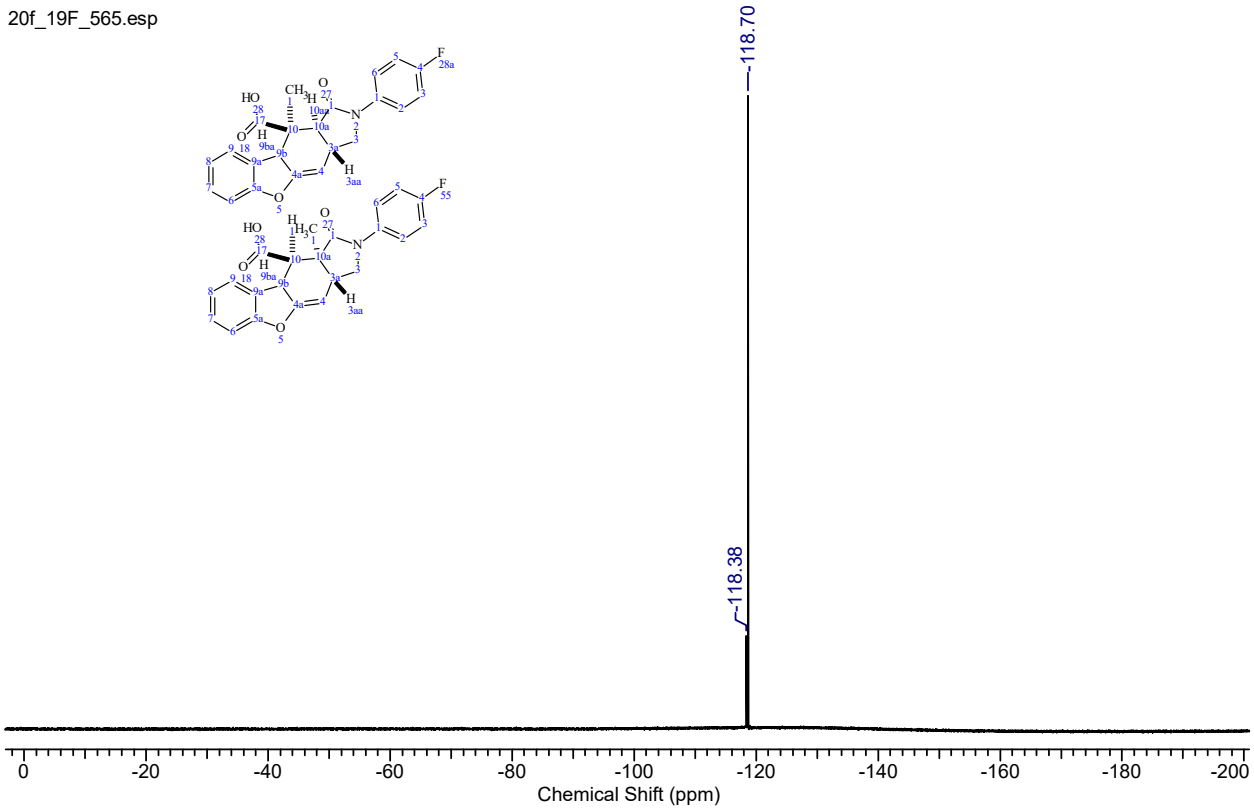


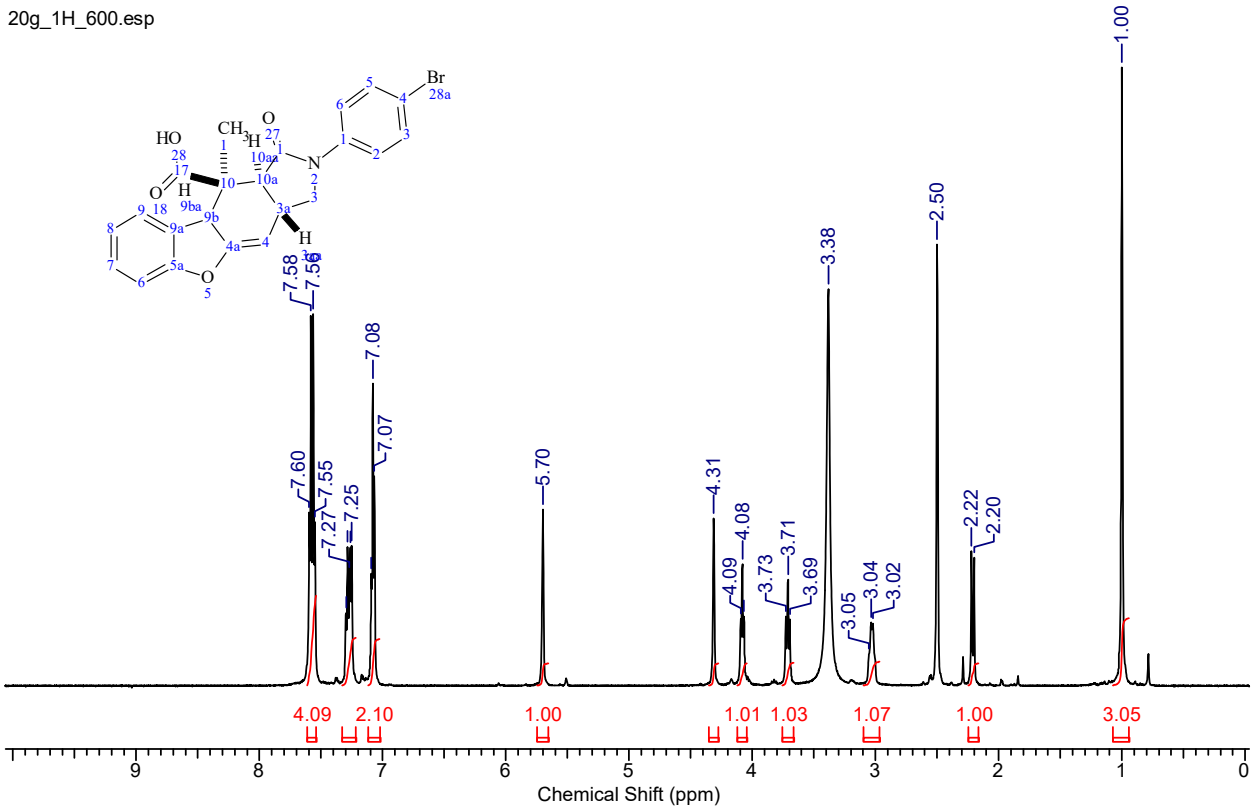
**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-2-(4-Fluorophenyl)-10-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20f) and (3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(4-fluorophenyl)-10a-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (21f).** *Contains around 17% on an impurity of regioisomer* **21f**.

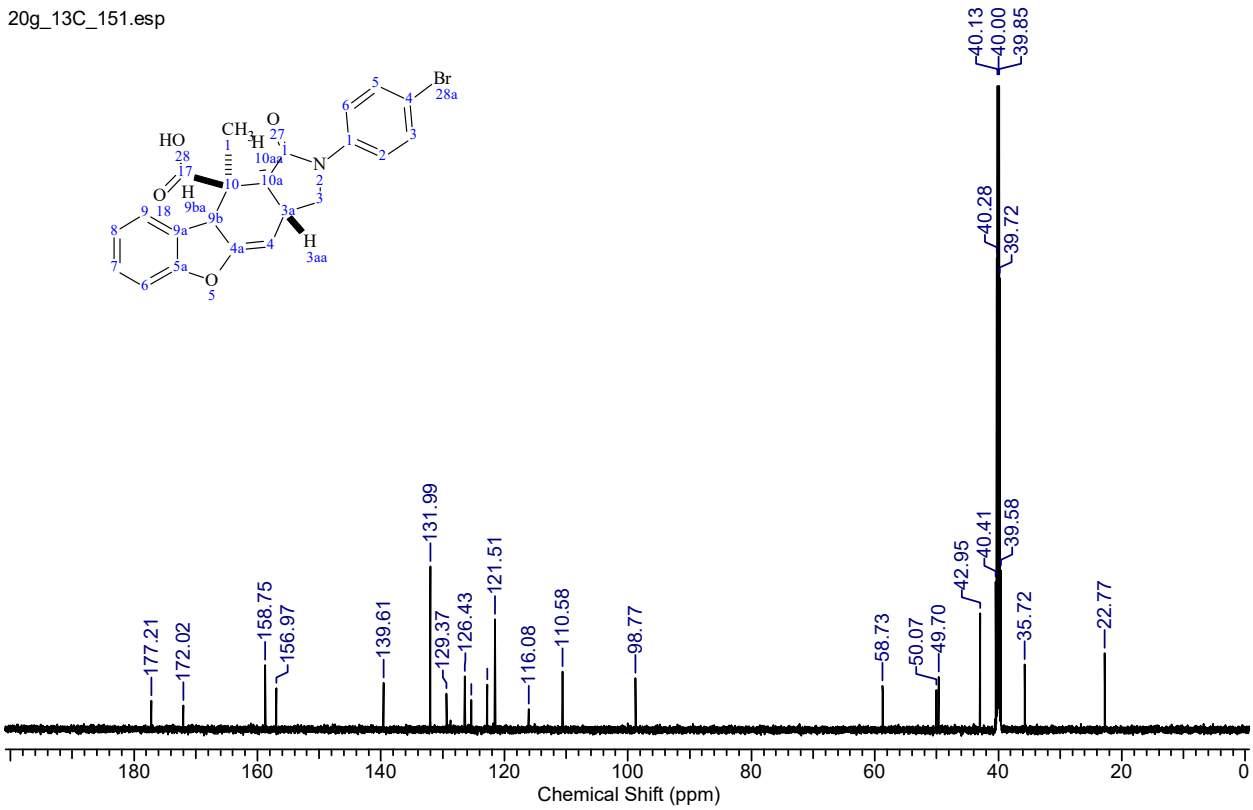


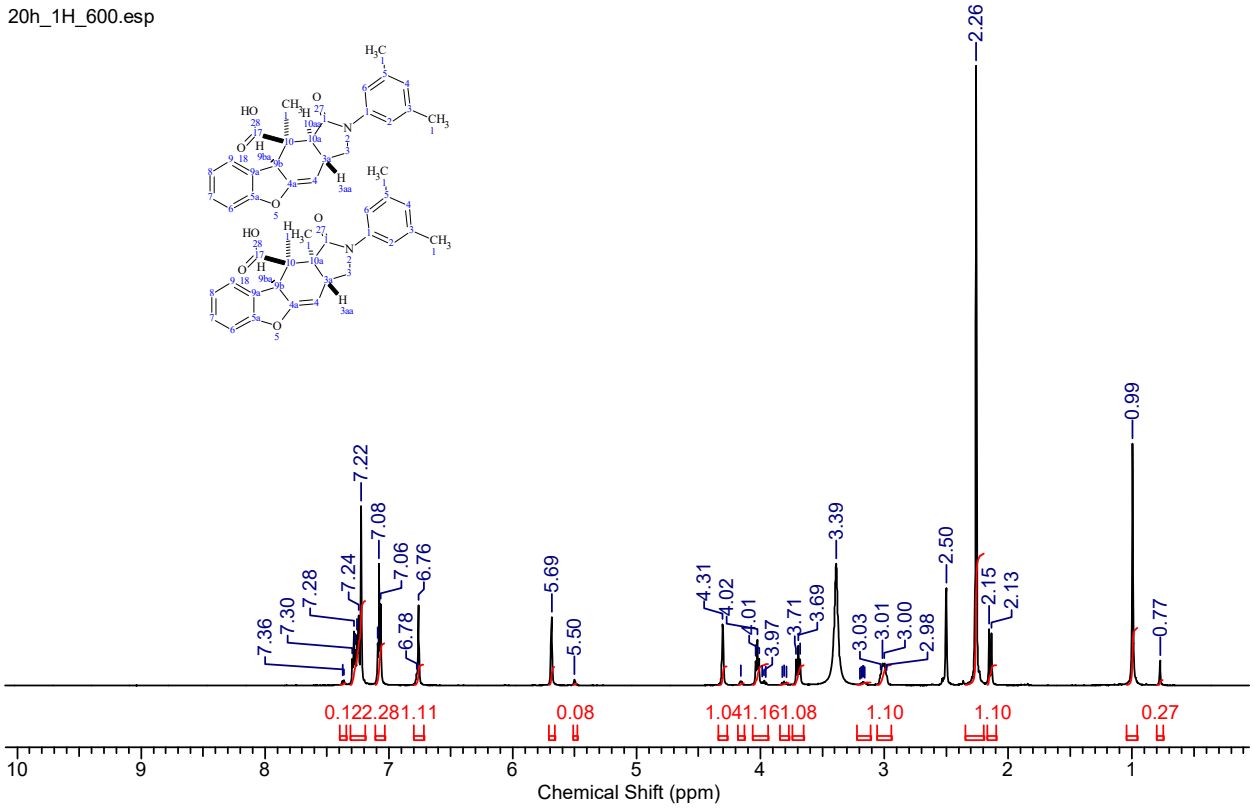


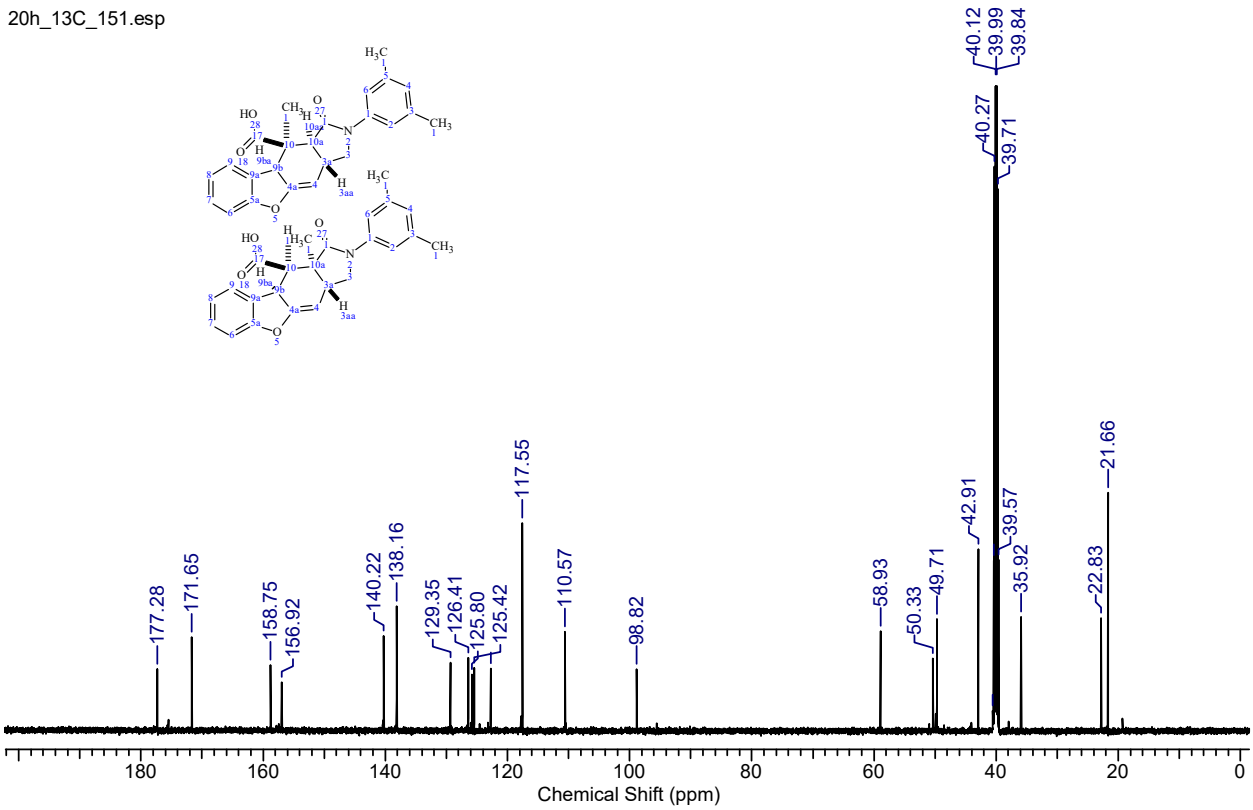

**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-2-(4-Bromophenyl)-10-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20g).**



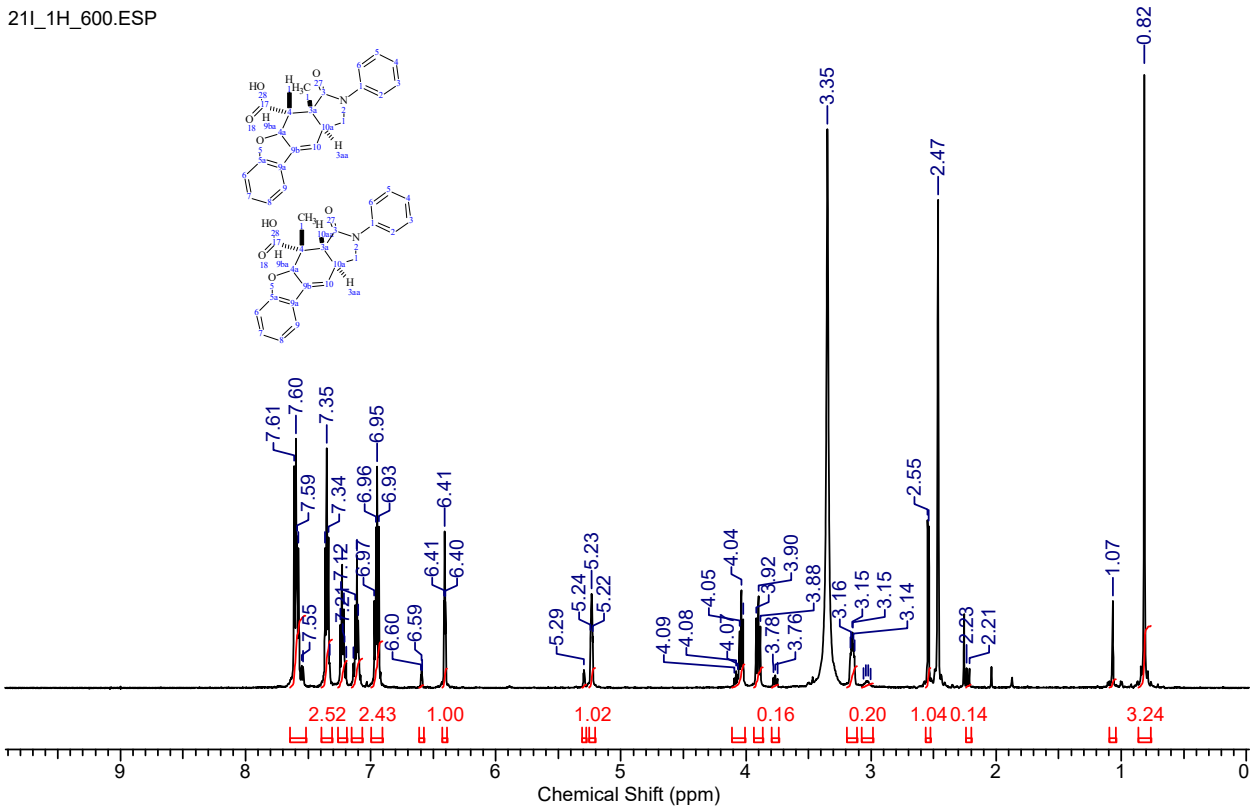


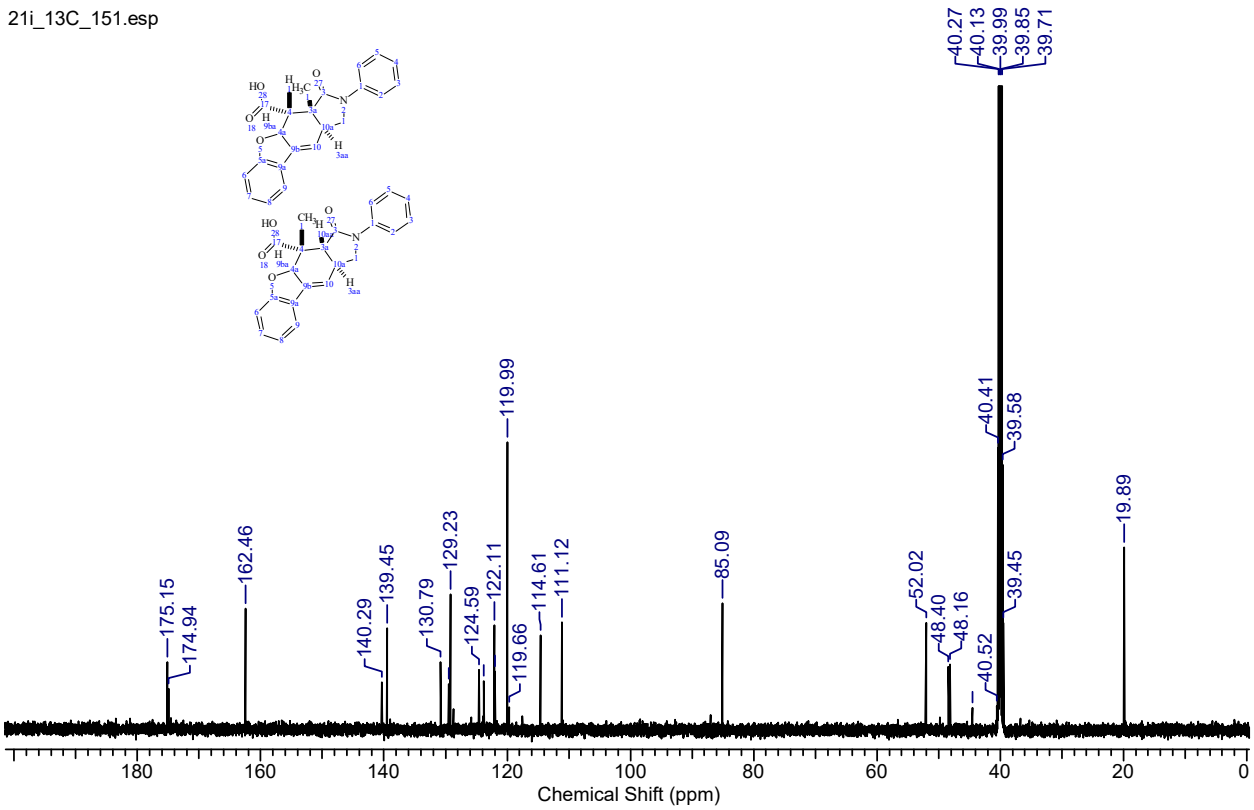

**(3a*RS*,9b*RS*,10*RS*,10a*SR*)-2-(3,5-Dimethylphenyl)-10-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (20h) and (3a*RS*,9b*SR*,10*RS*,10a*SR*)-2-(3,5-dimethylphenyl)-10a-methyl-1-oxo-2,3,3a,9b,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (21h).** *Contains around 8% on an impurity of regioisomer* **21h**.



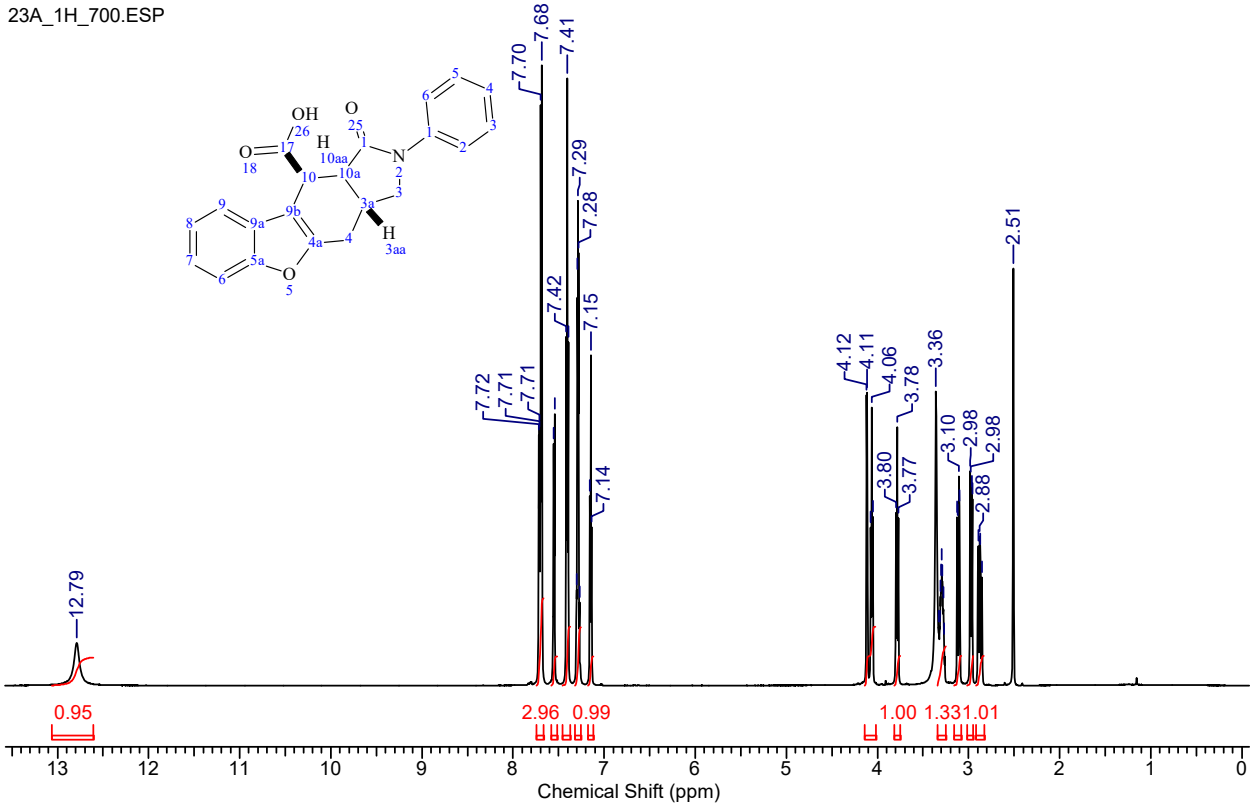


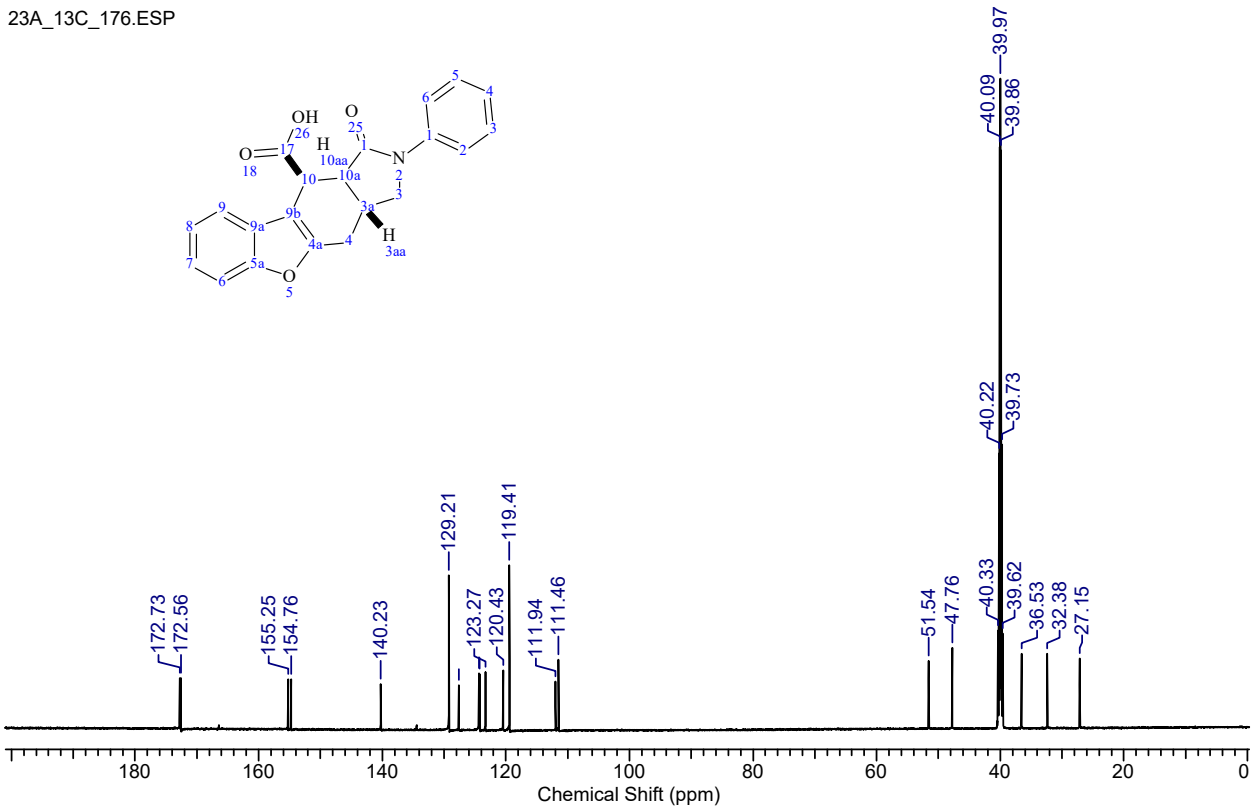

**(3a*RS*,4*RS*,4a*SR*,10a*SR*)-3a-Methyl-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (21i) and (3a*RS*,4*RS*,4a*RS*,10a*SR*)-4-methyl-3-oxo-2-phenyl-2,3,3a,4,4a,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (20i).** Contains around 12% on an impurity of regioisomer **20i**.





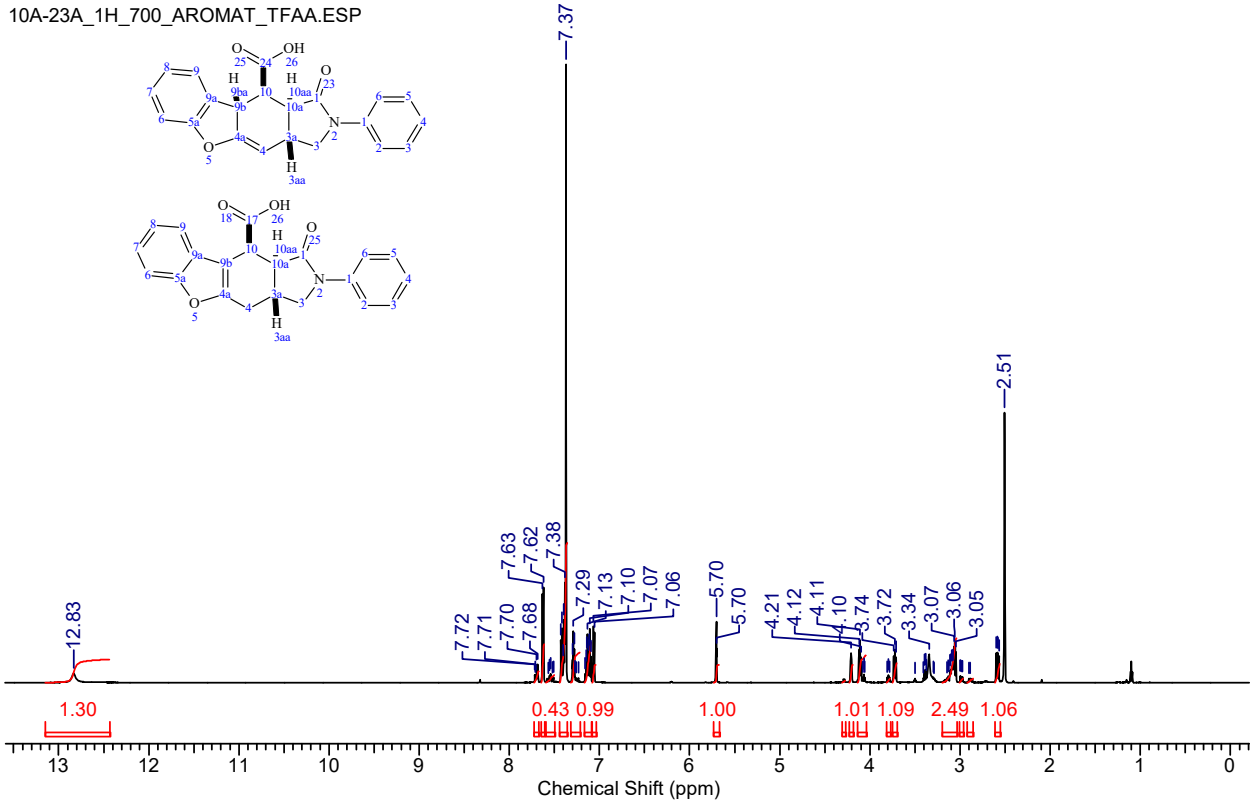

**(3a*RS*,10*SR*,10a*SR*)-1-Oxo-2-phenyl-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23a).**



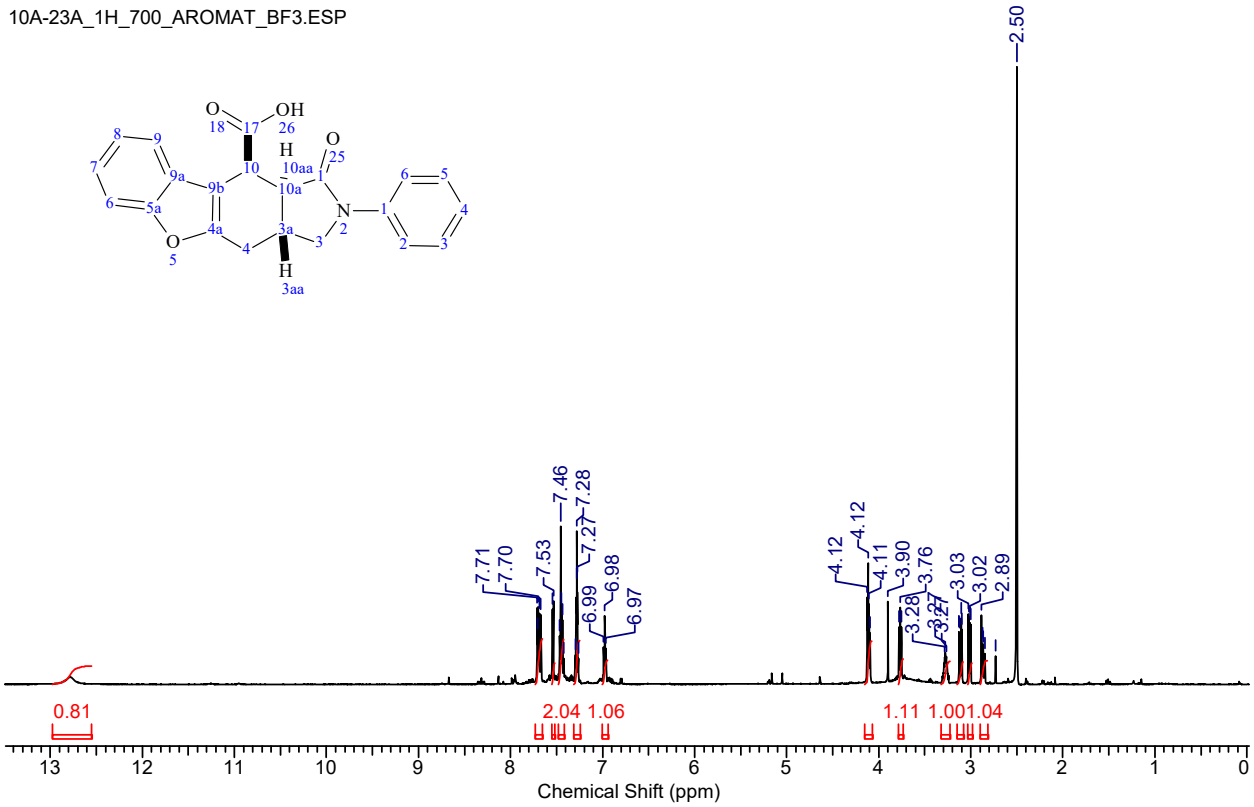



## Attempts to “aromatize” acid 10a.

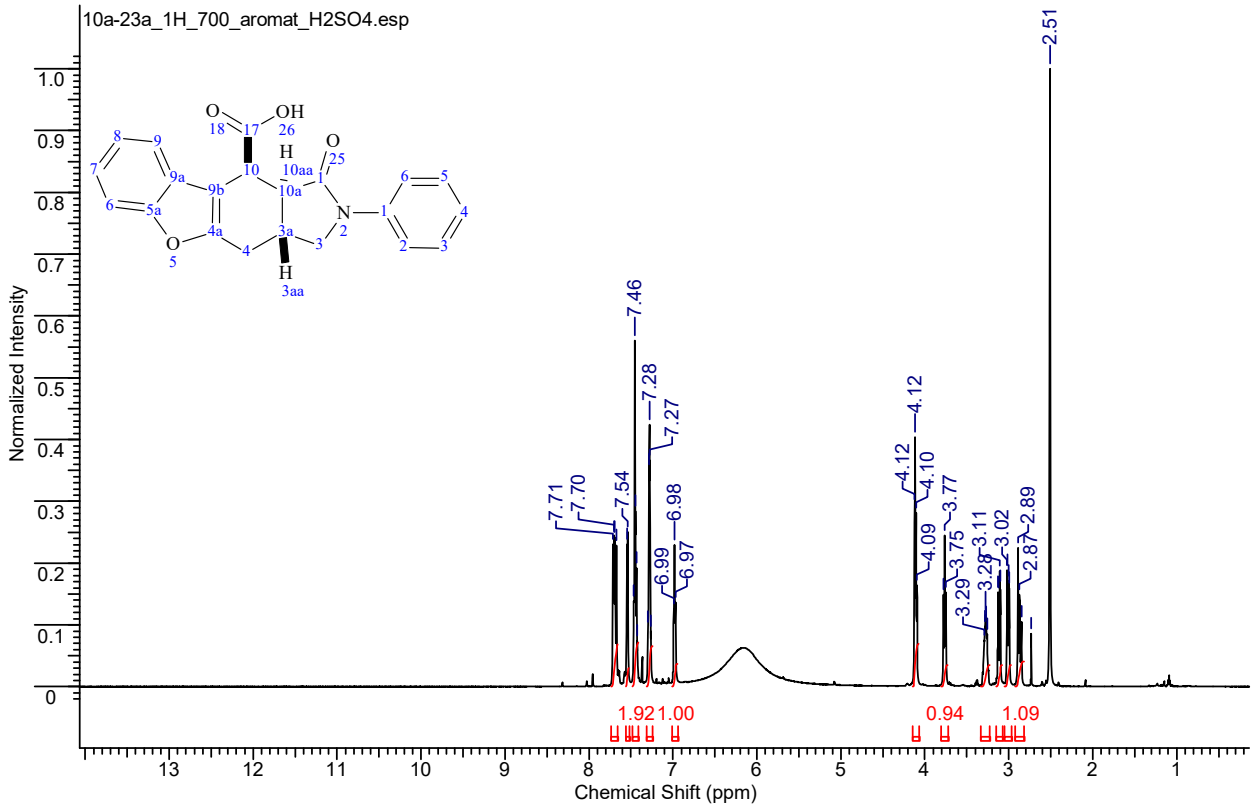
## Trifluoroacetic acid (TFA) (10 mol%), DCE



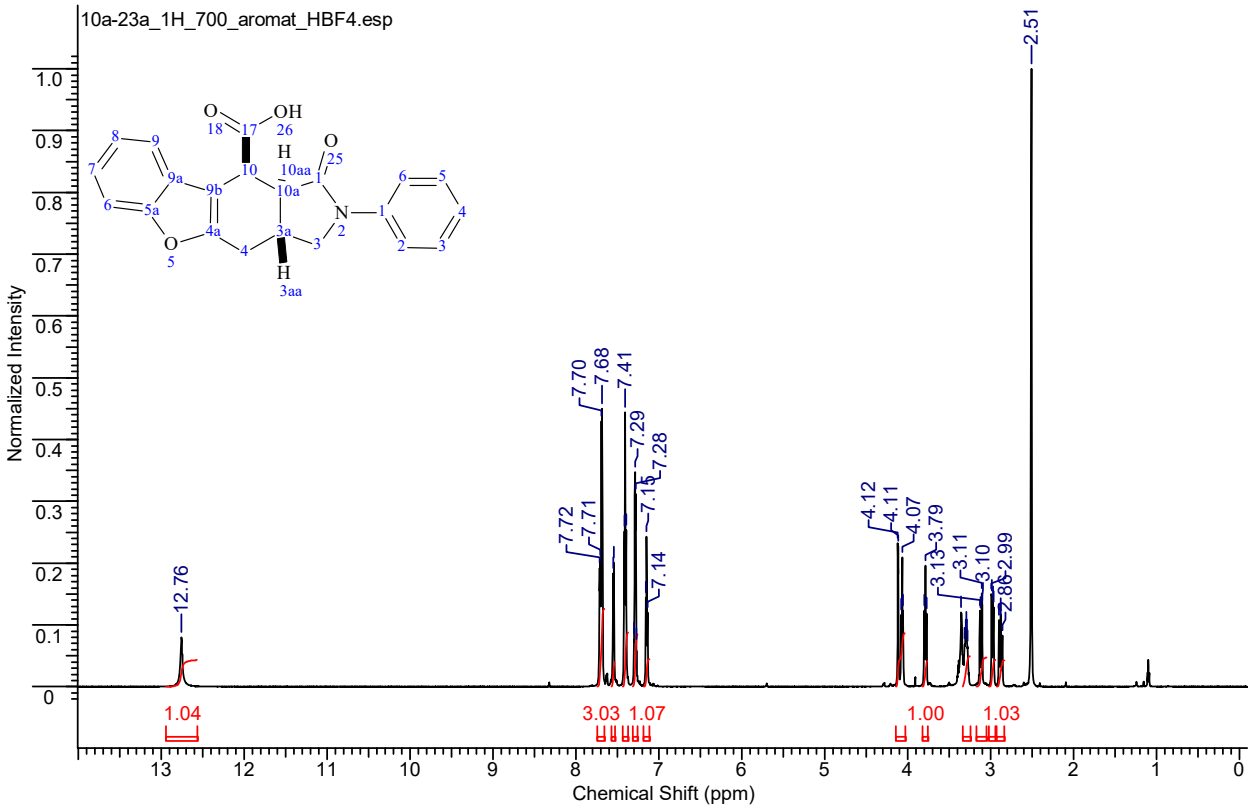
**Boron trifluoride diethyl etherate (1.0 equiv.), DCE**



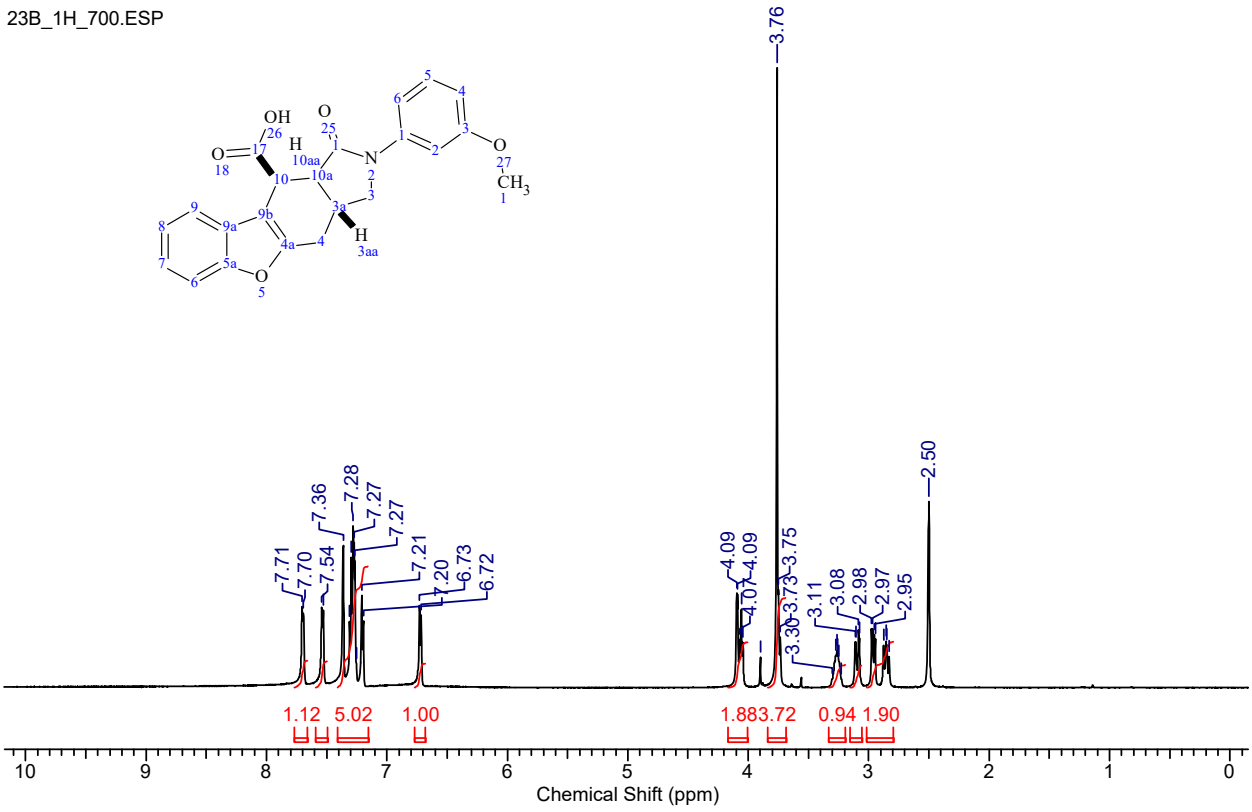

***Conc*. sulfuric acid (1 drop), PhH**

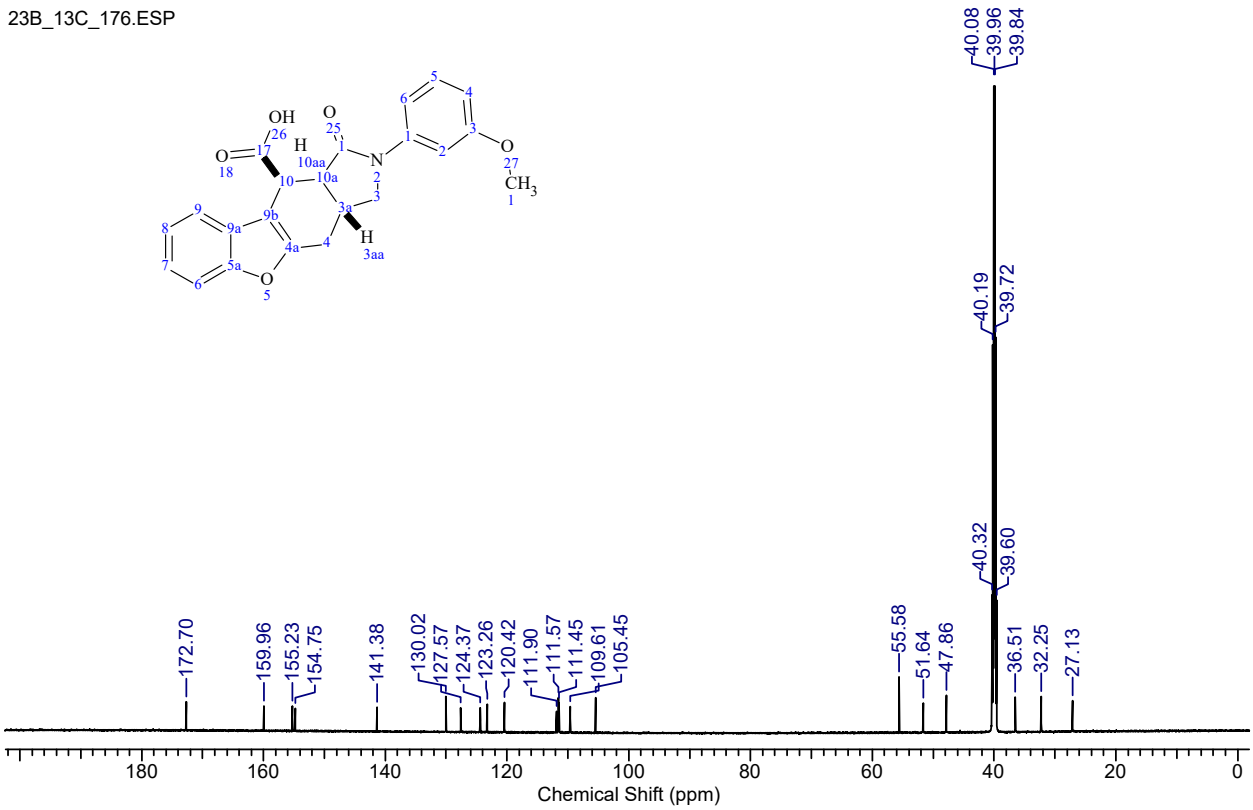


**Tetrafluoroboric acid diethyl ether complex (1.0 equiv.), DCE**

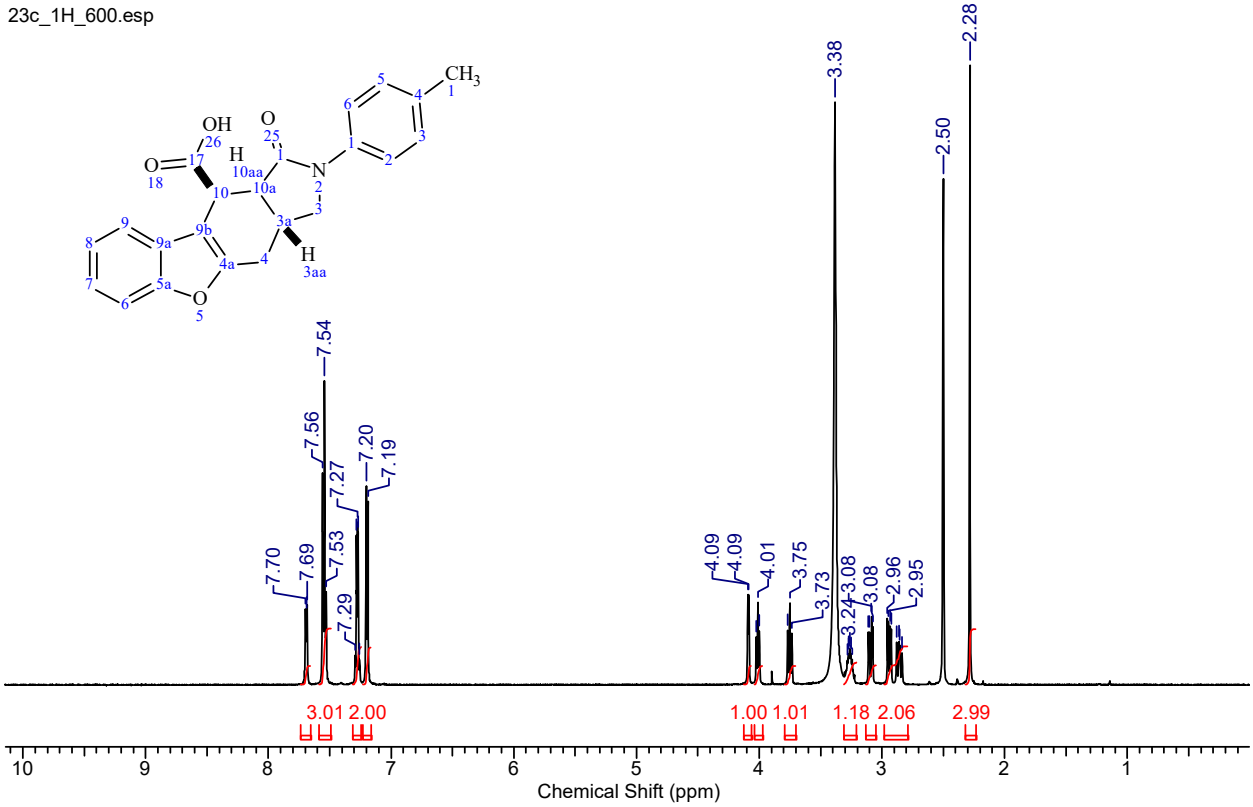


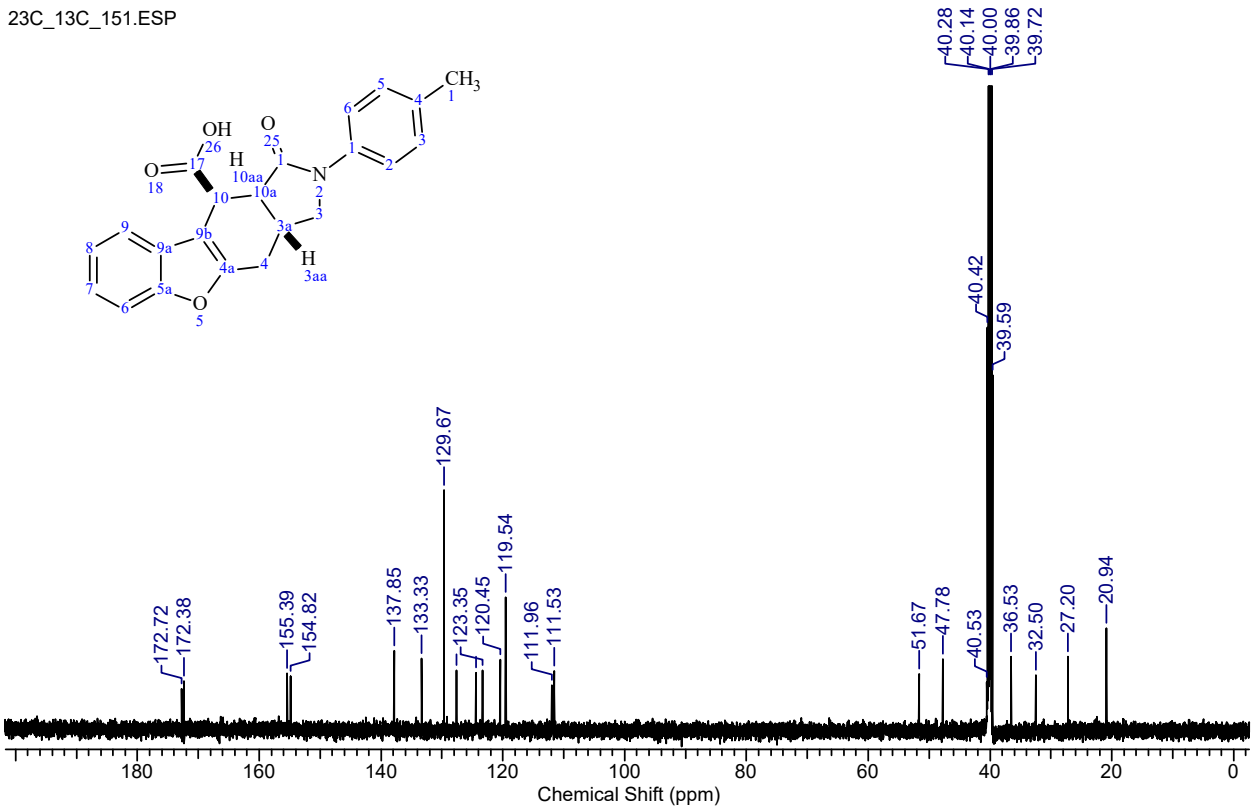

**(3a*RS*,10*SR*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23b).**



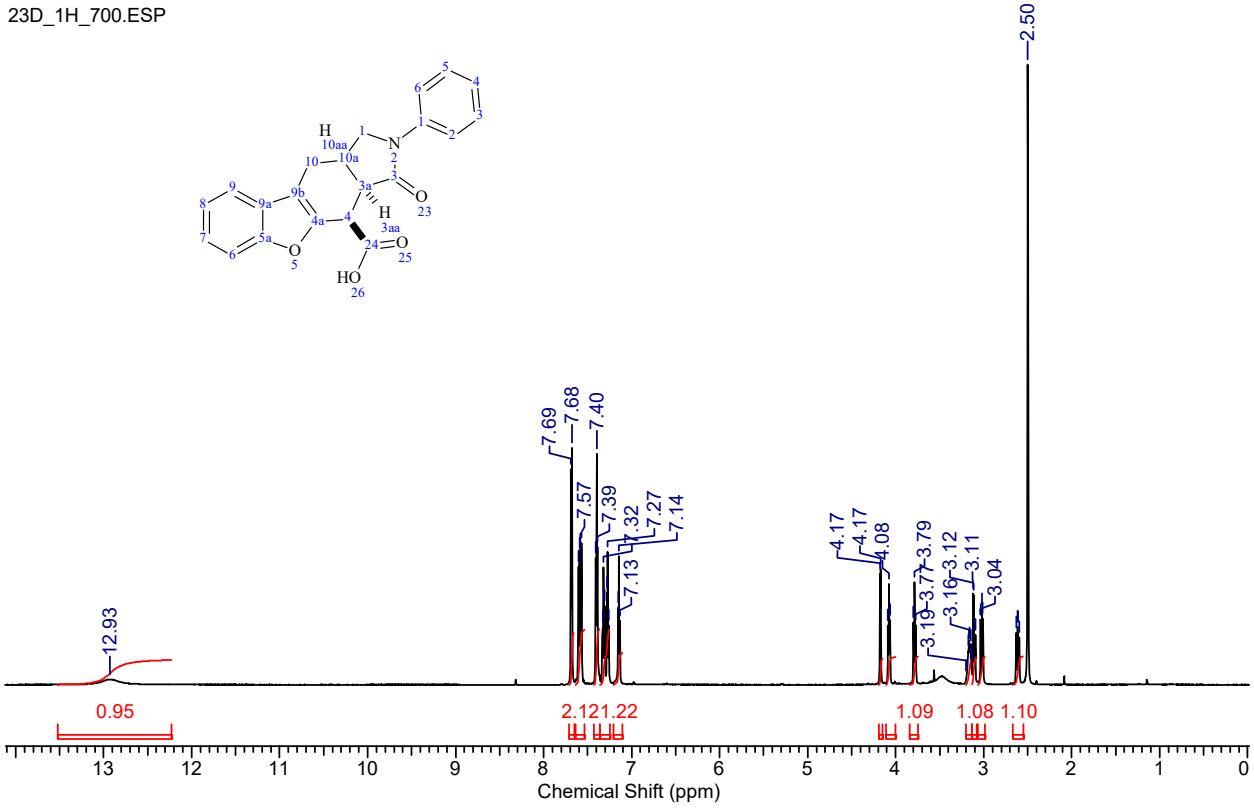


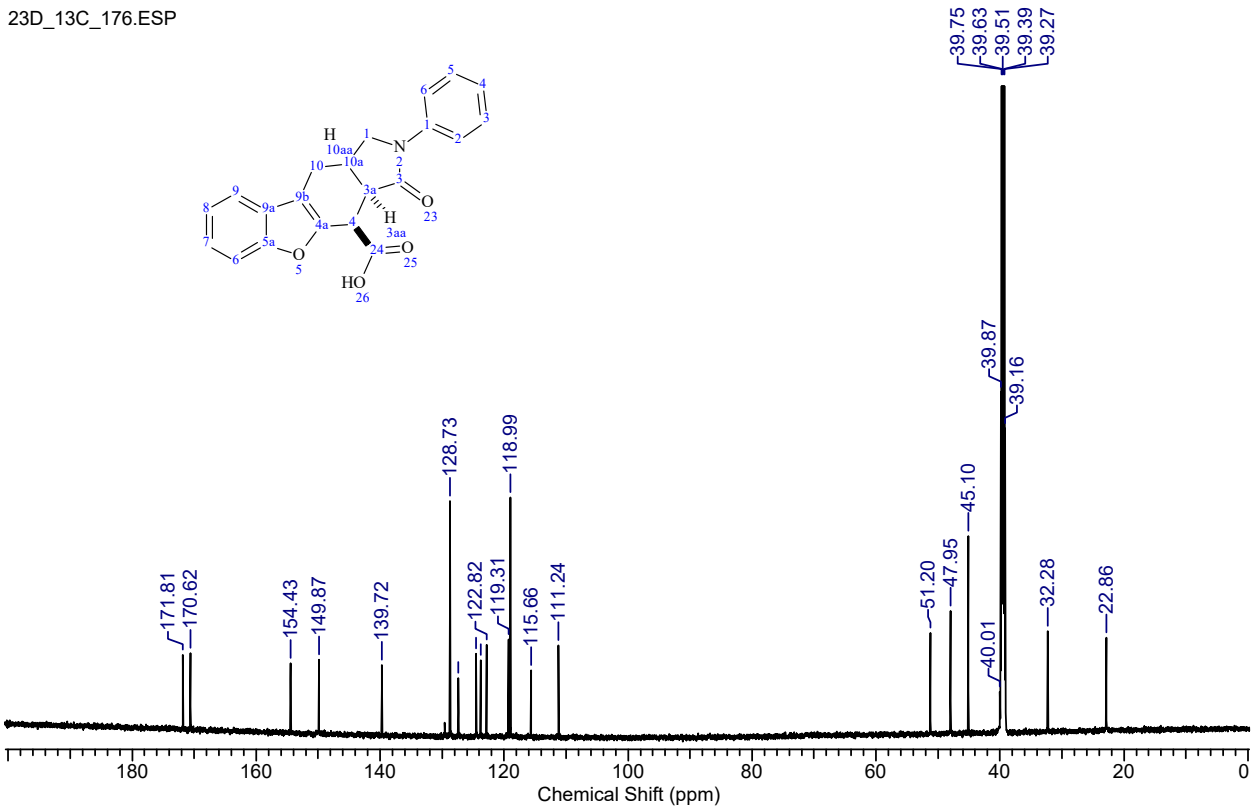

**(3a*RS*,10*RS*,10a*RS*)-2-(4-Methylphenyl)-1-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23c).**



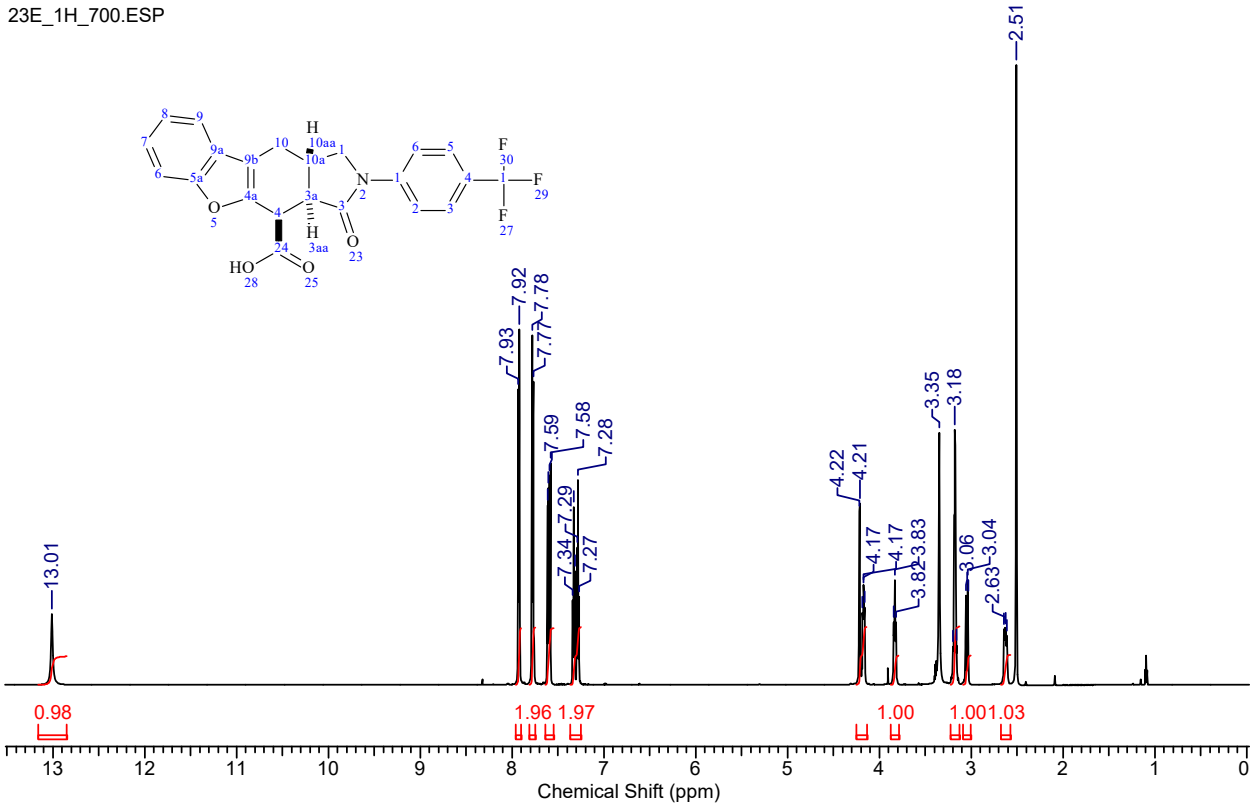



**(3a*RS*,4*RS*,10a*SR*)-3-Oxo-2-phenyl-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (23d).**

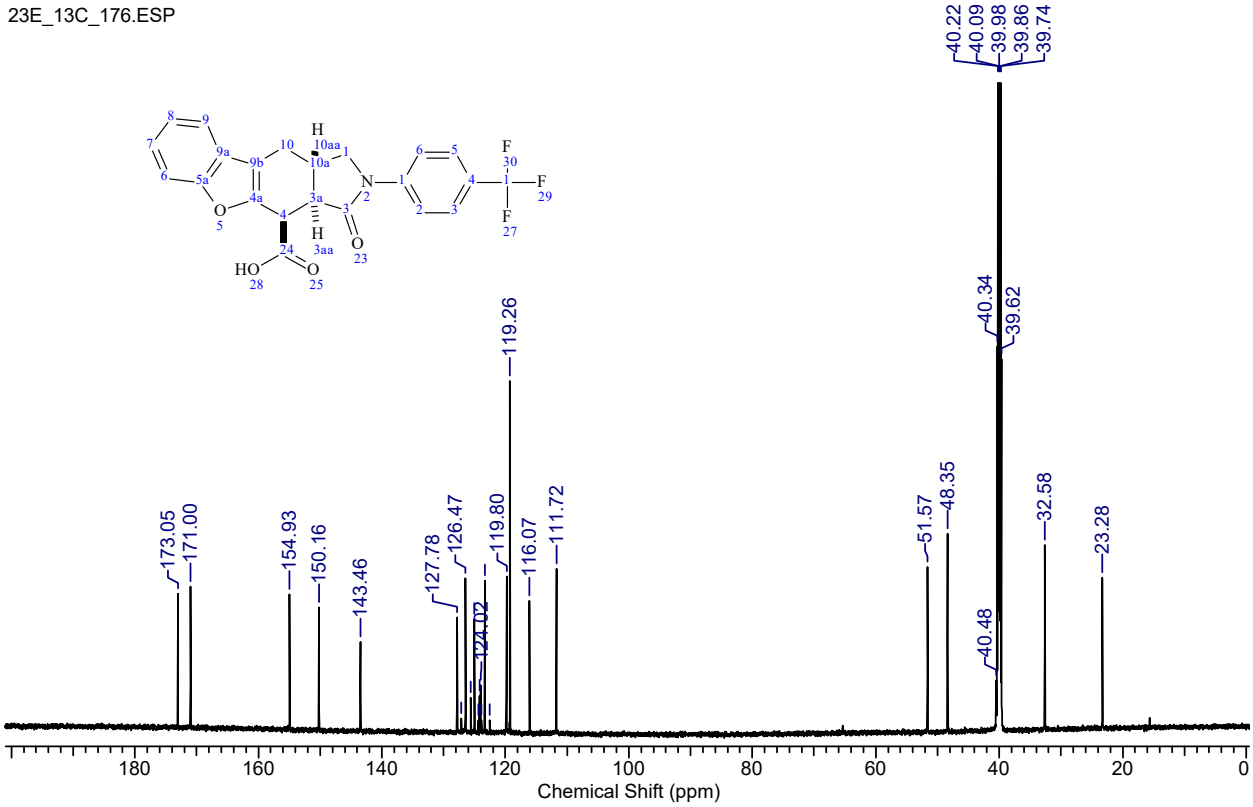




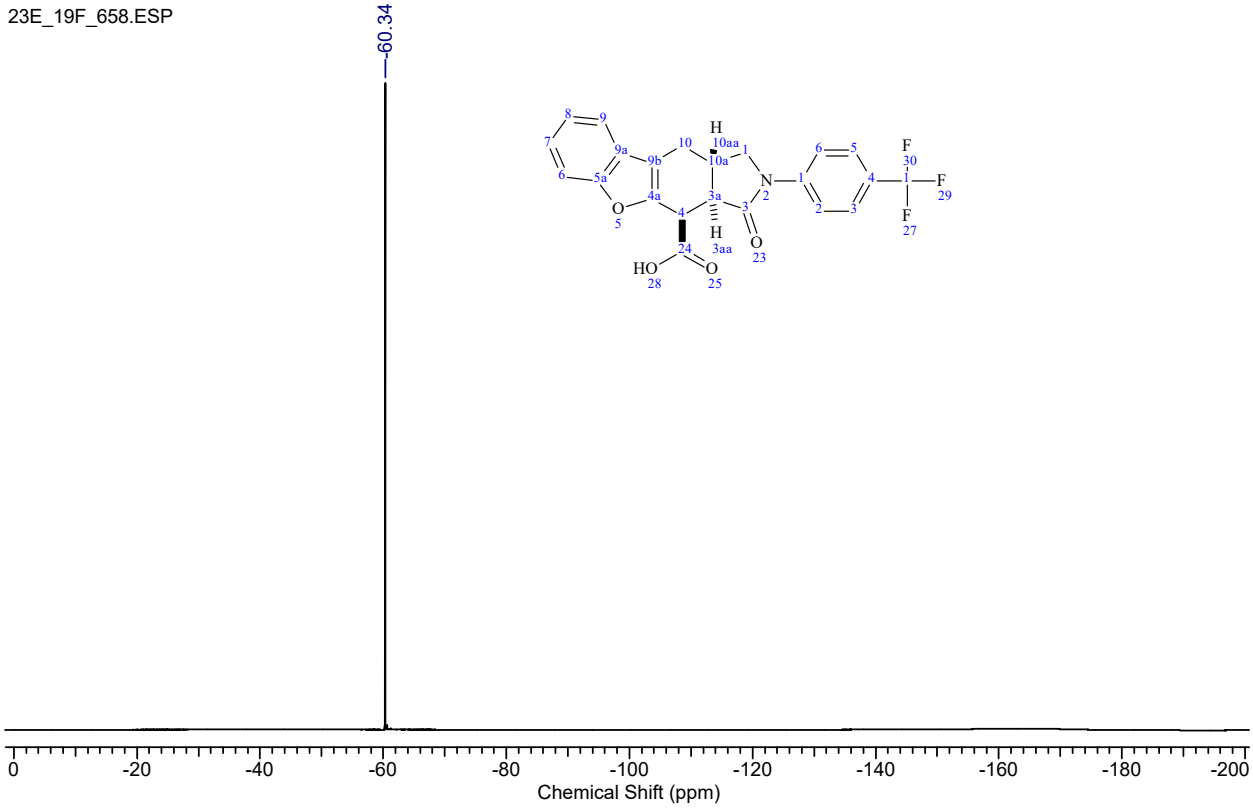

**(3a*RS*,4*RS*,10a*SR*)-3-Oxo-2-[4-(trifluoromethyl)phenyl]-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (23e).**



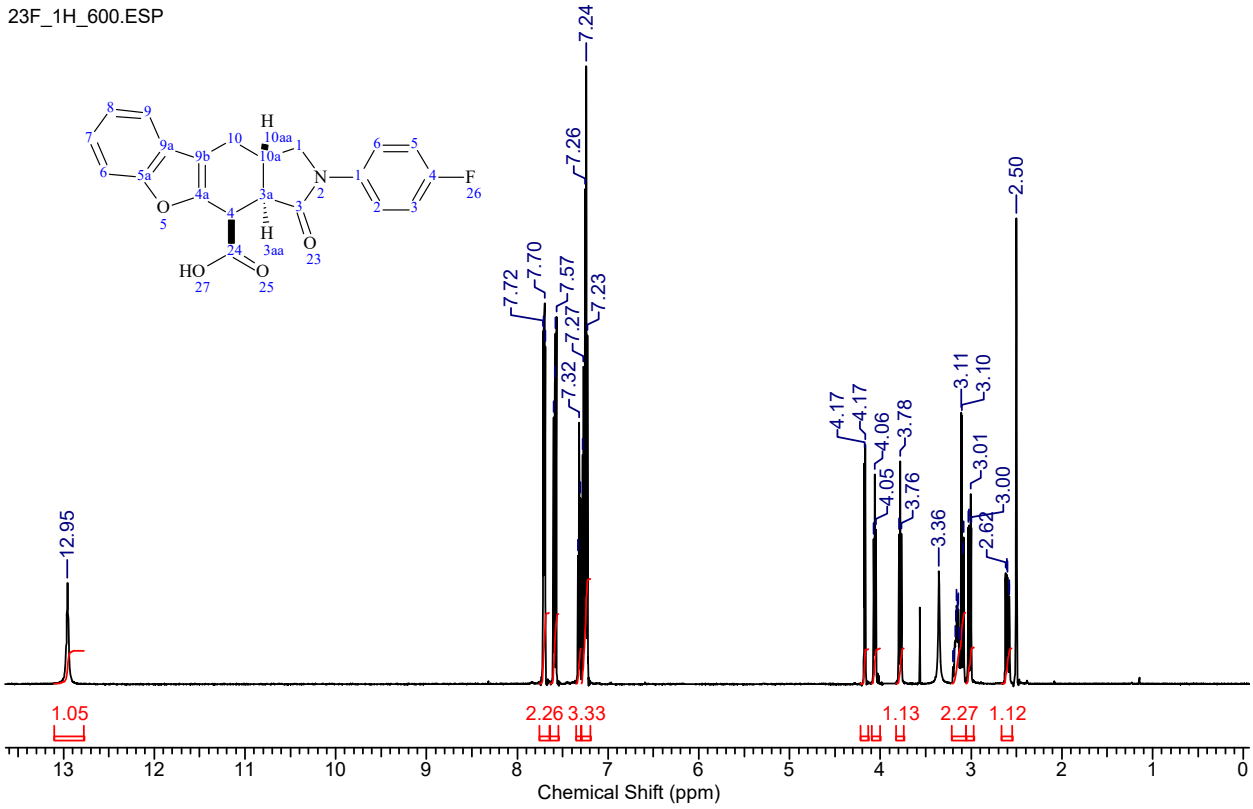
23E_13C_176.ESP

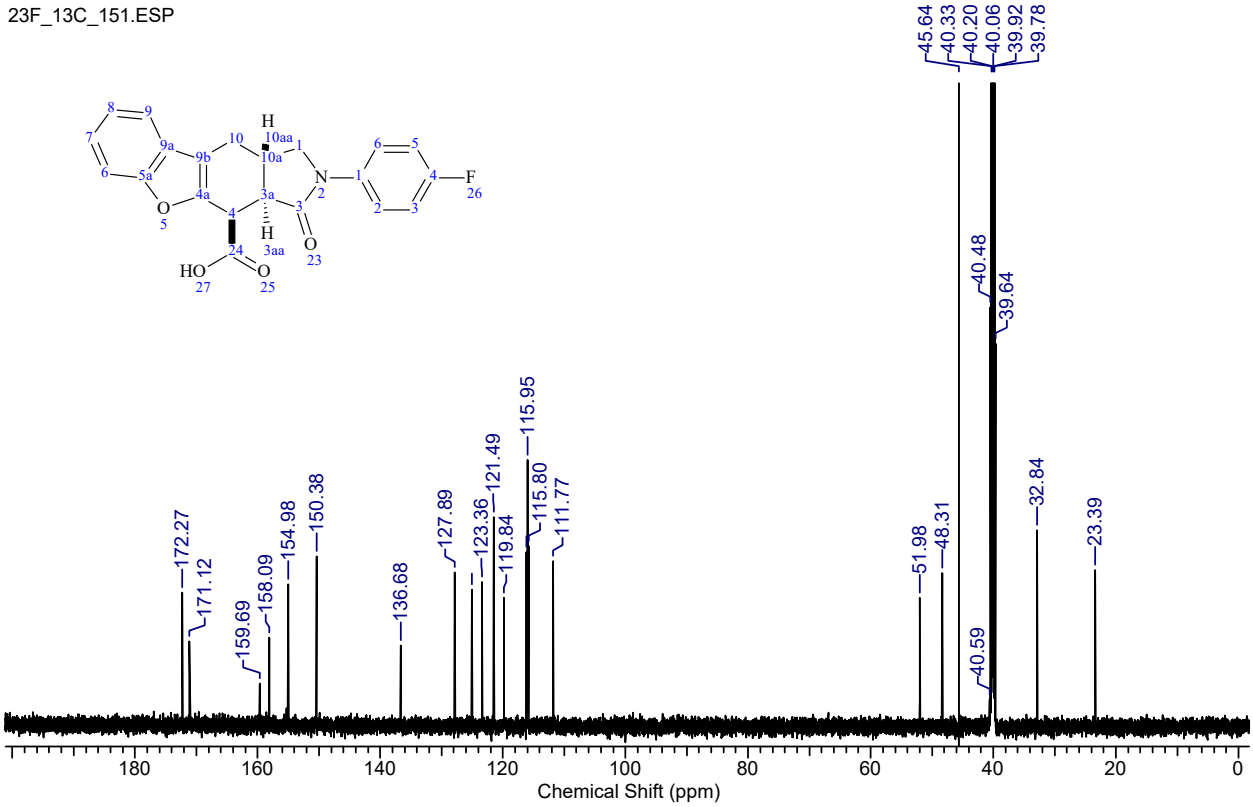


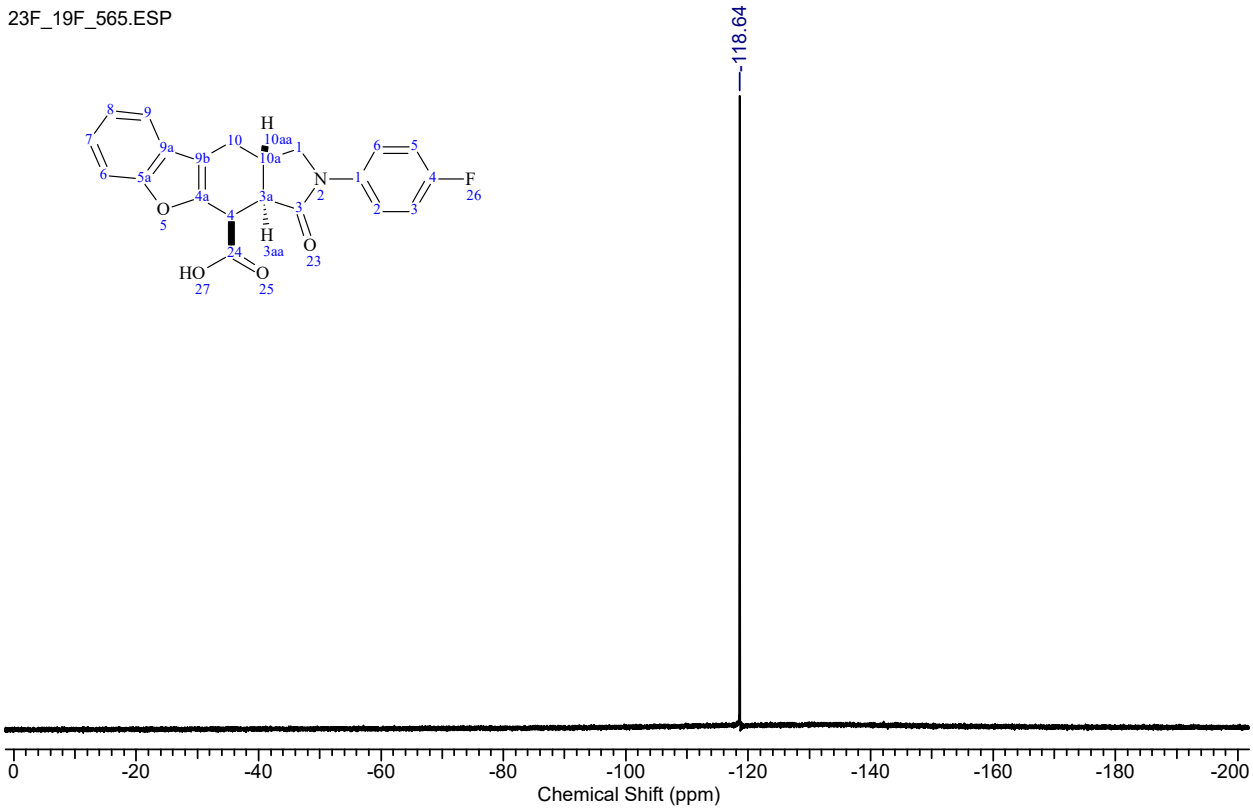

23E_19F_658.ESP



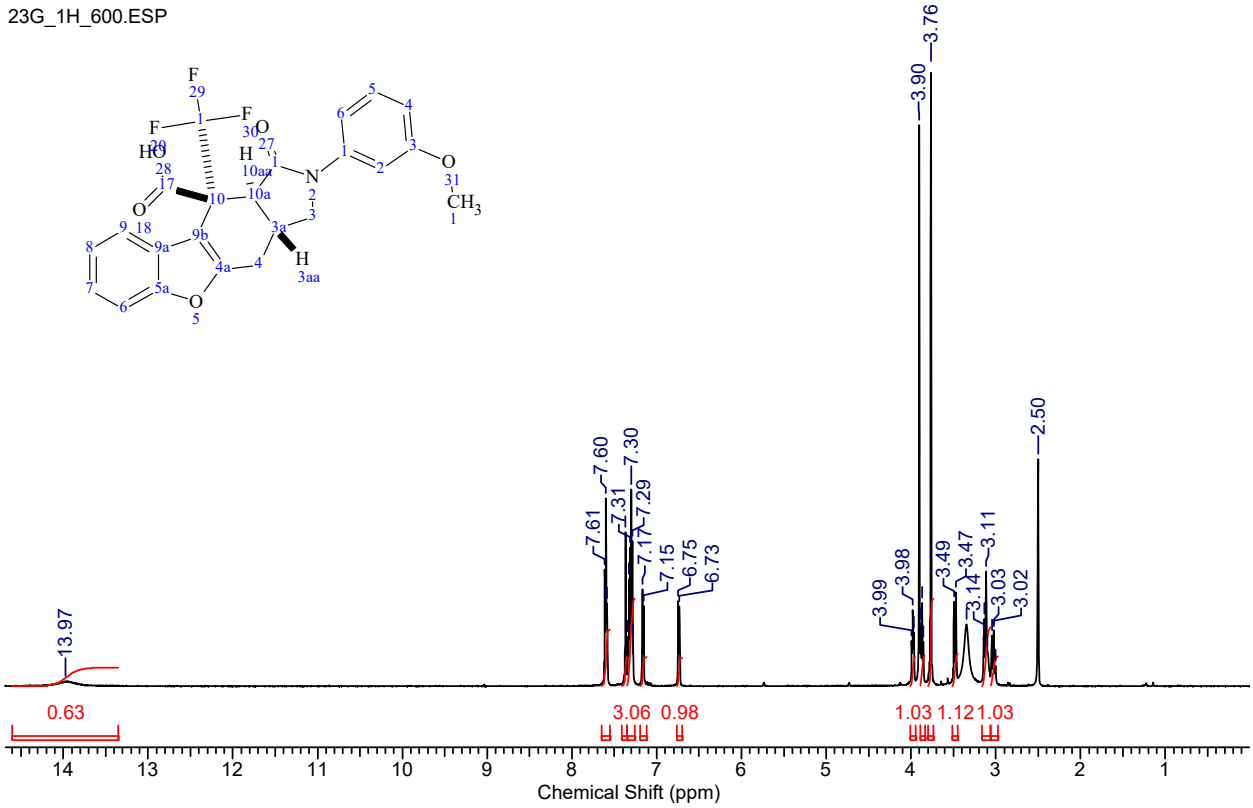
**(3a*RS*,4*RS*,10a*SR*)-2-(4-Fluorophenyl)-3-oxo-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-4-carboxylic acid (23f).**



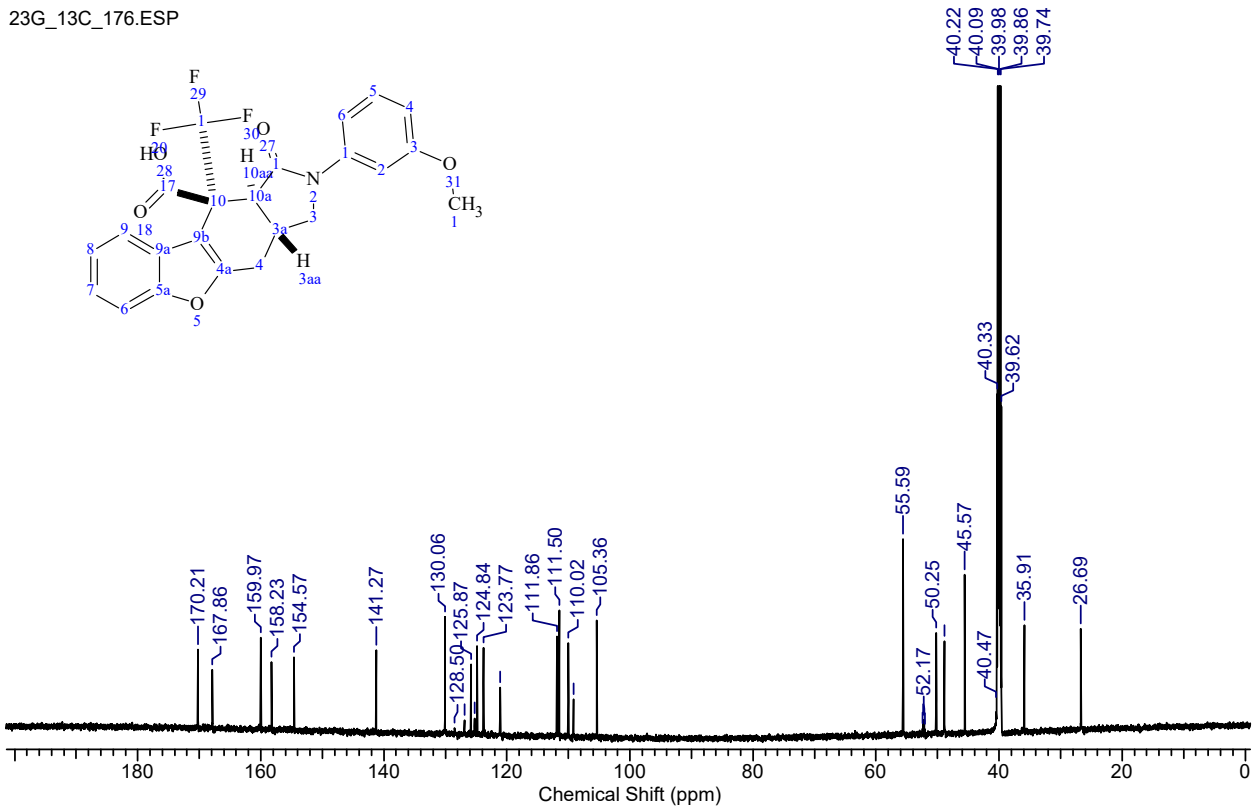






**(3a*RS*,10*RS*,10a*SR*)-2-(3-Methoxyphenyl)-1-oxo-10-(trifluoromethyl)-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23g).** *Contains an impurity of 1,2-dichloroethane.*



23G_13C_176.ESP

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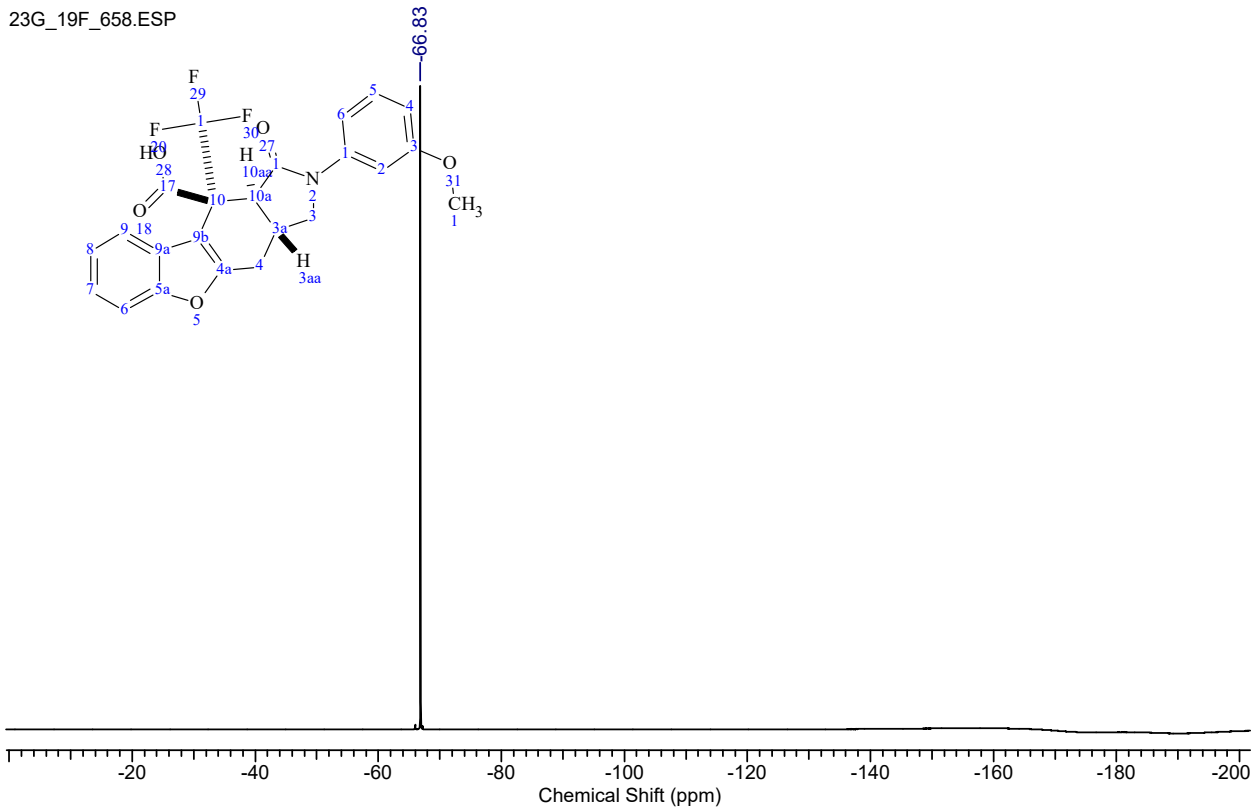
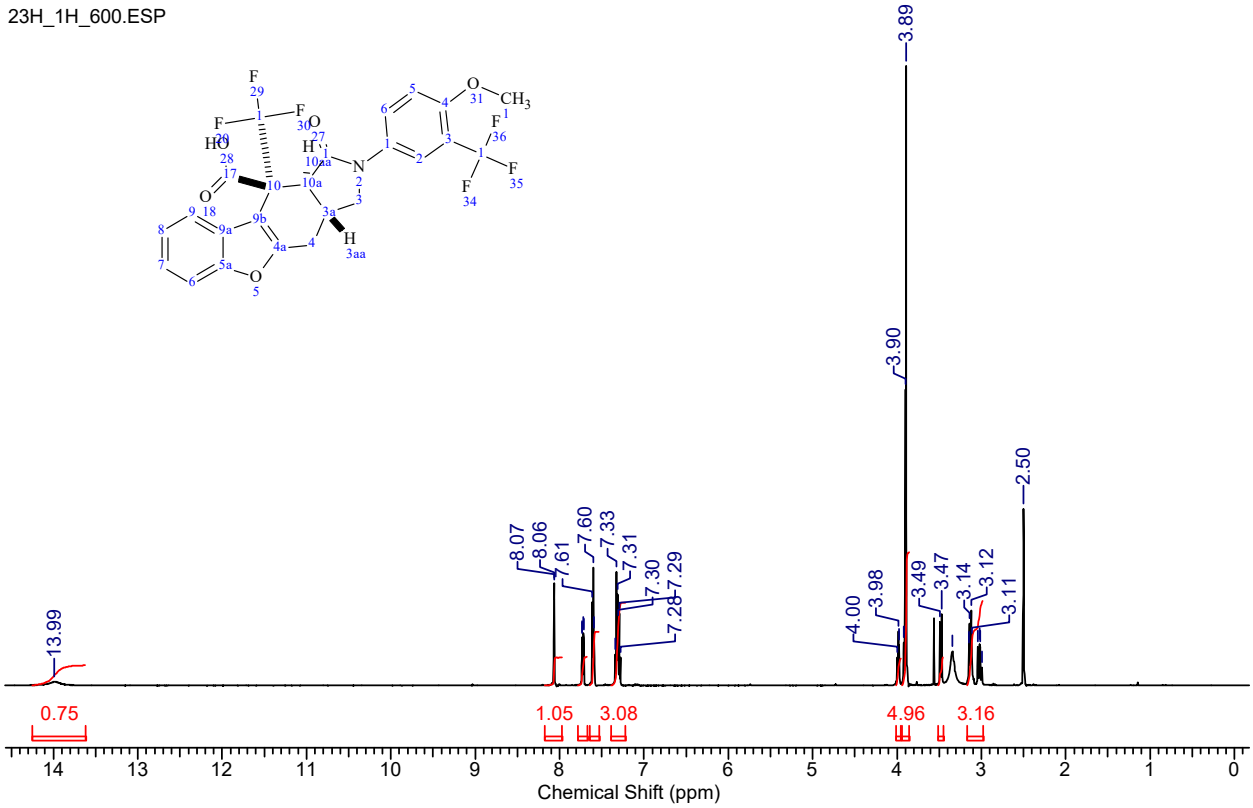
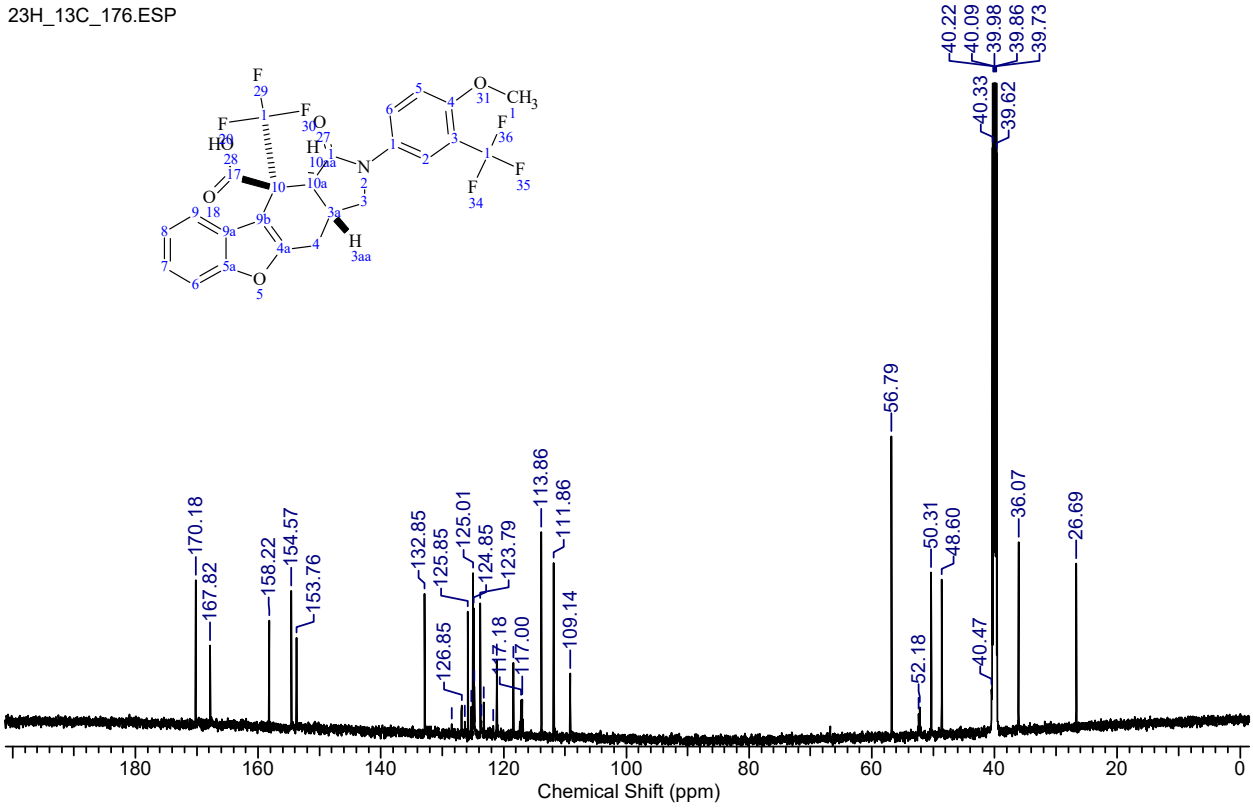
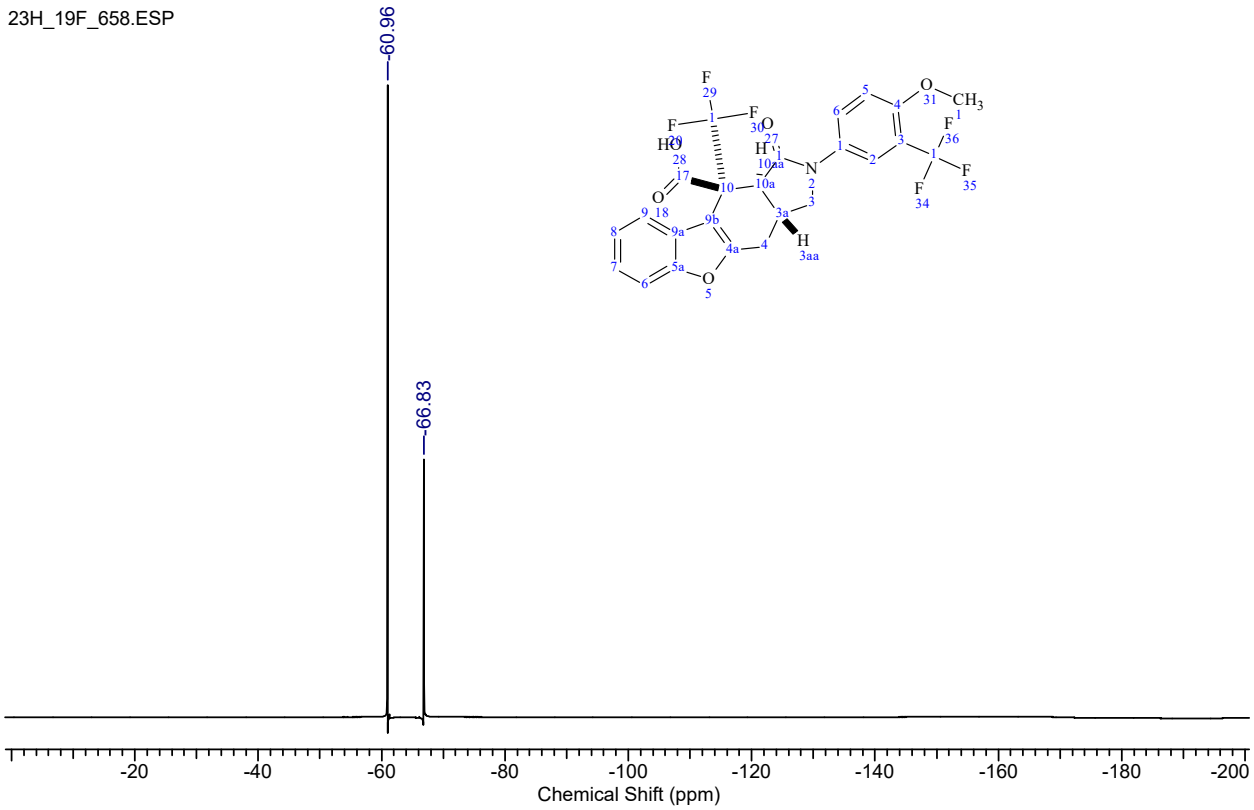


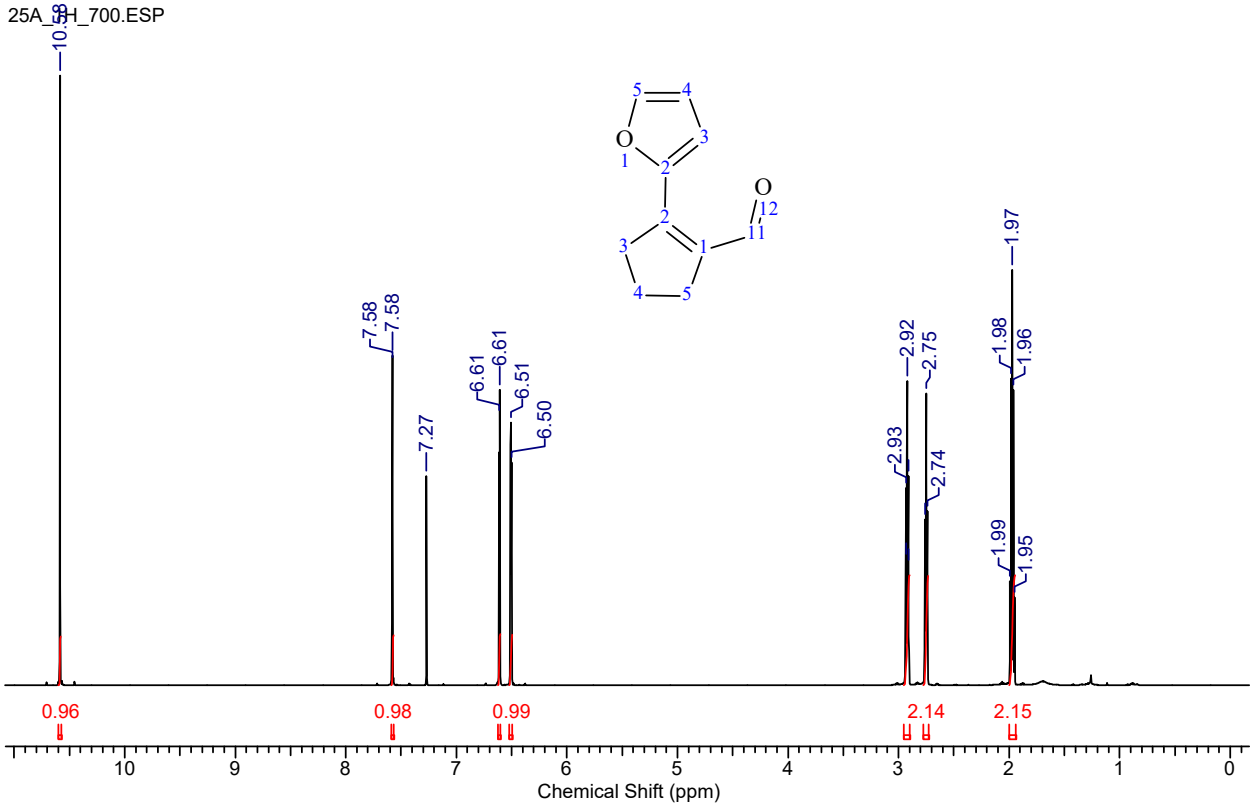
**(3a*RS*,10*RS*,10a*SR*)-2-[4-Methoxy-3-(trifluoromethyl)phenyl]-1-oxo-10-(trifluoromethyl)-2,3,3a,4,10,10a-hexahydro-1*H*-[1]benzofuro[2,3-*f*]isoindole-10-carboxylic acid (23h).**

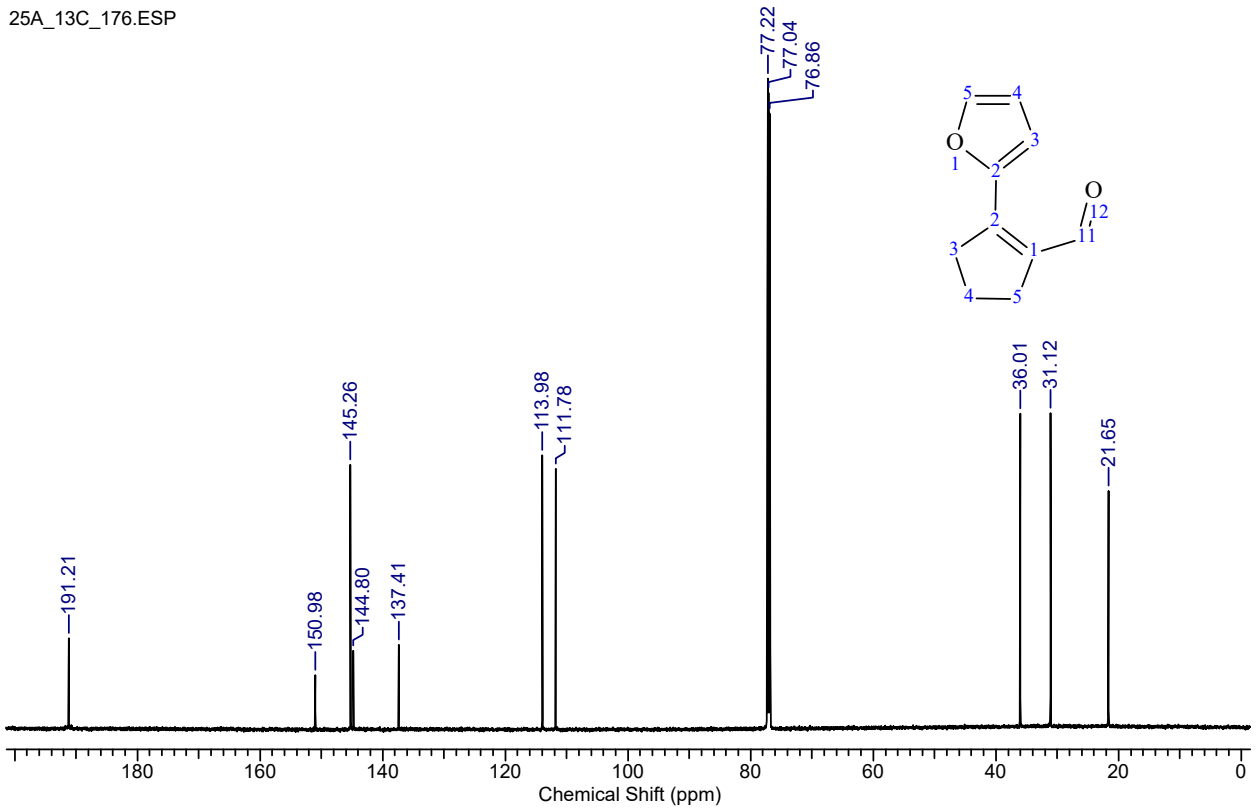


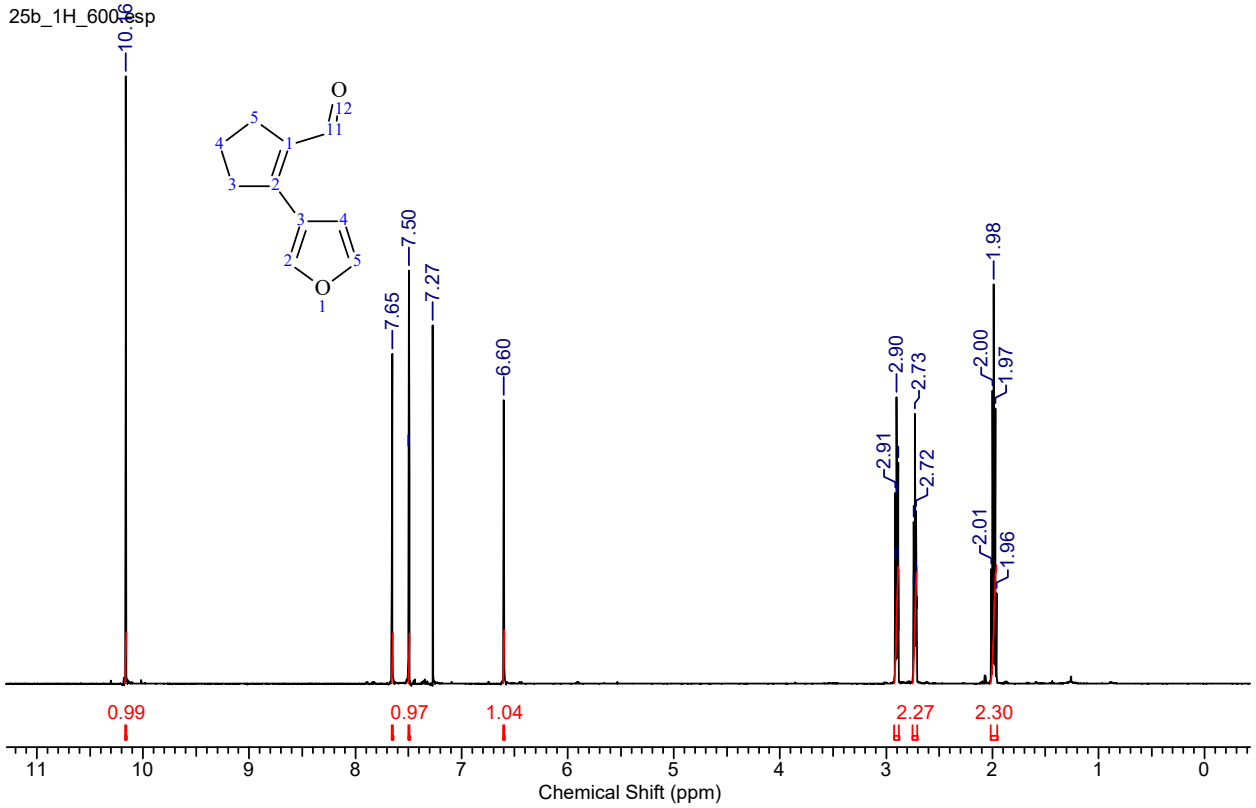


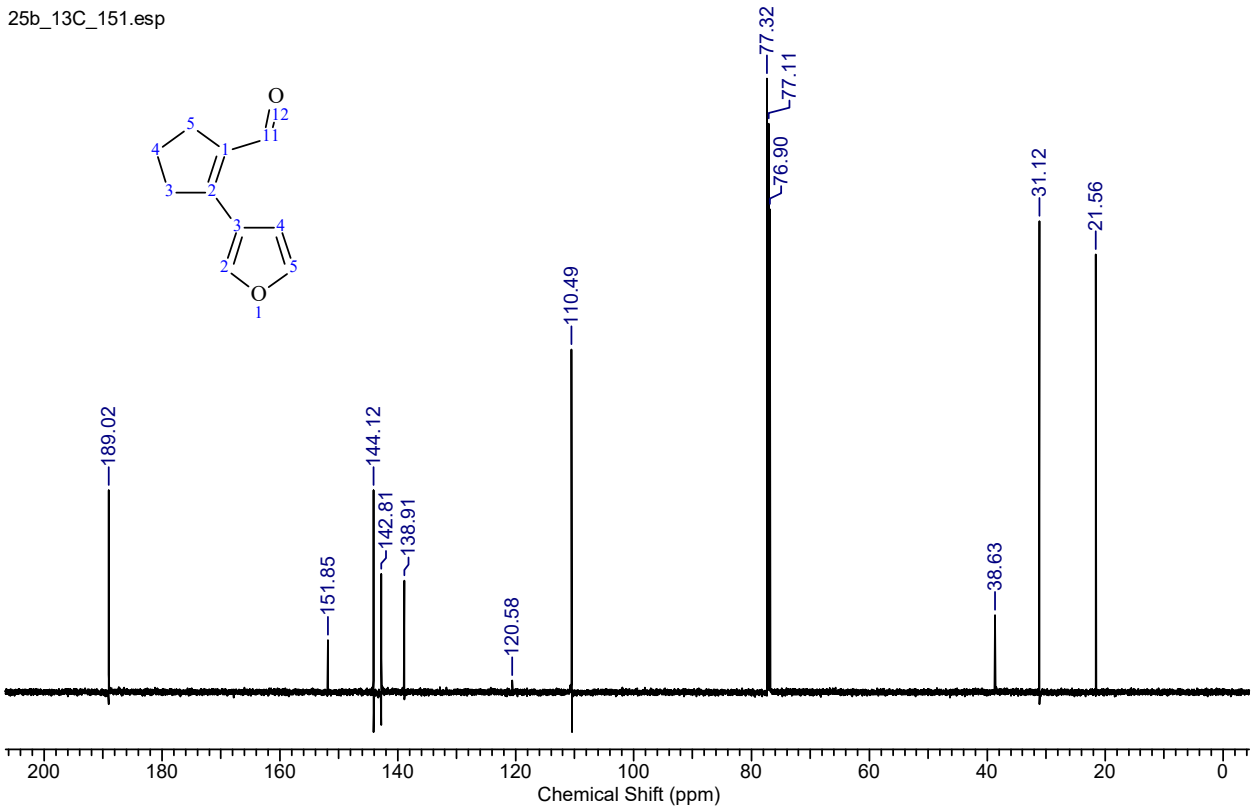

**2-(Furan-2-yl)cyclopent-1-ene-1-carbaldehyde(25a).**



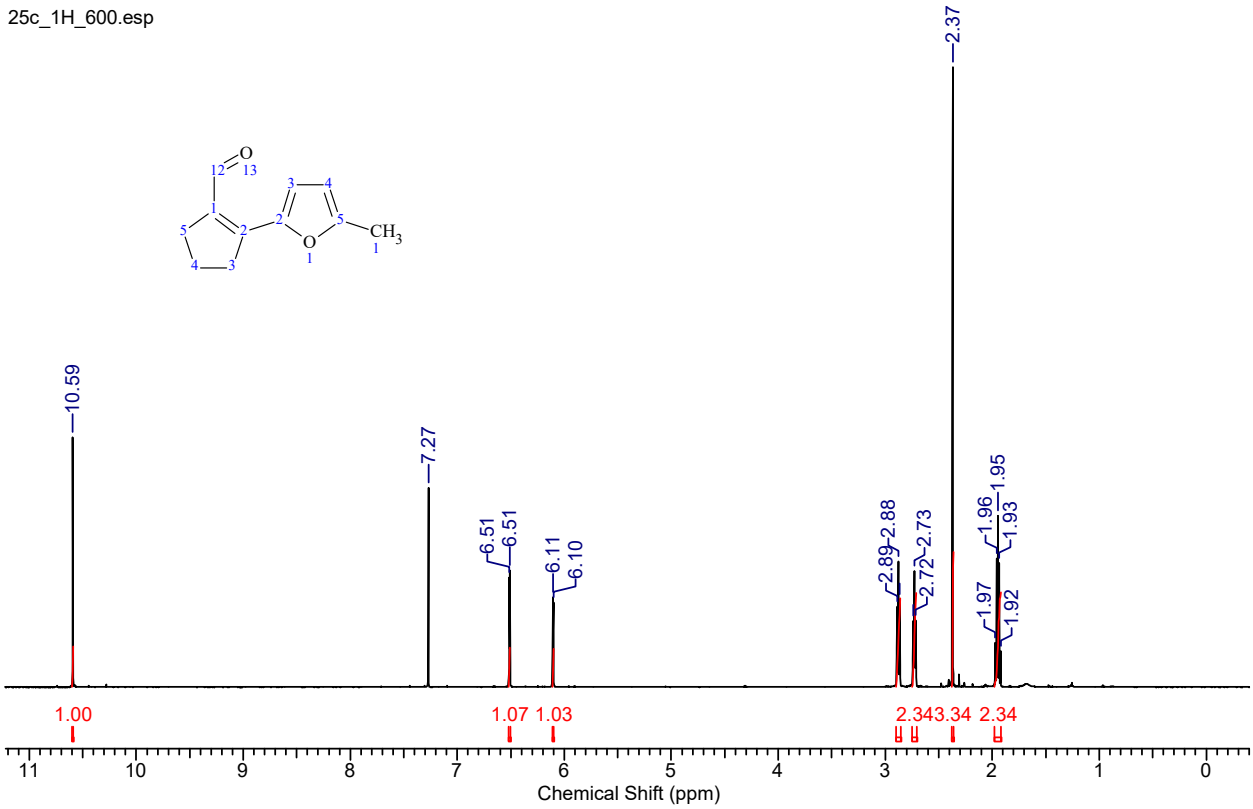


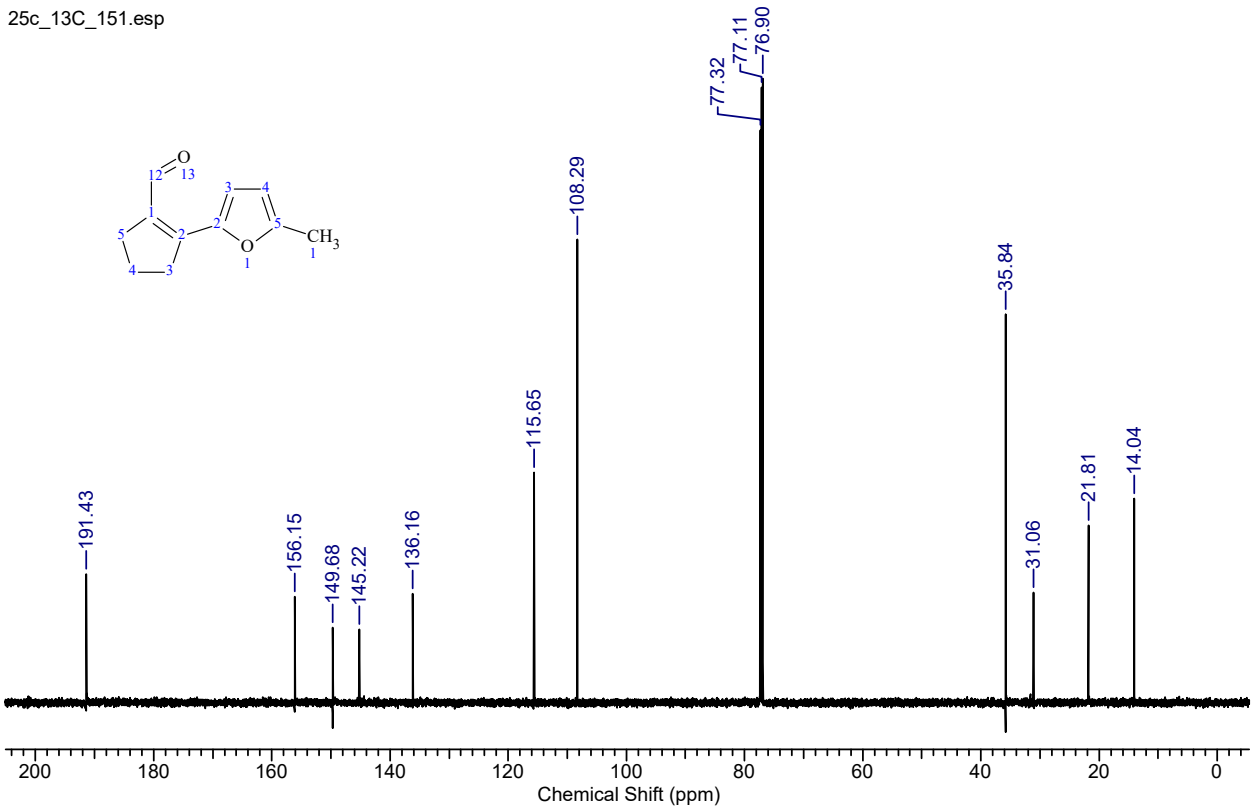

**2-(Furan-3-yl)cyclopent-1-ene-1-carbaldehyde (25b).**



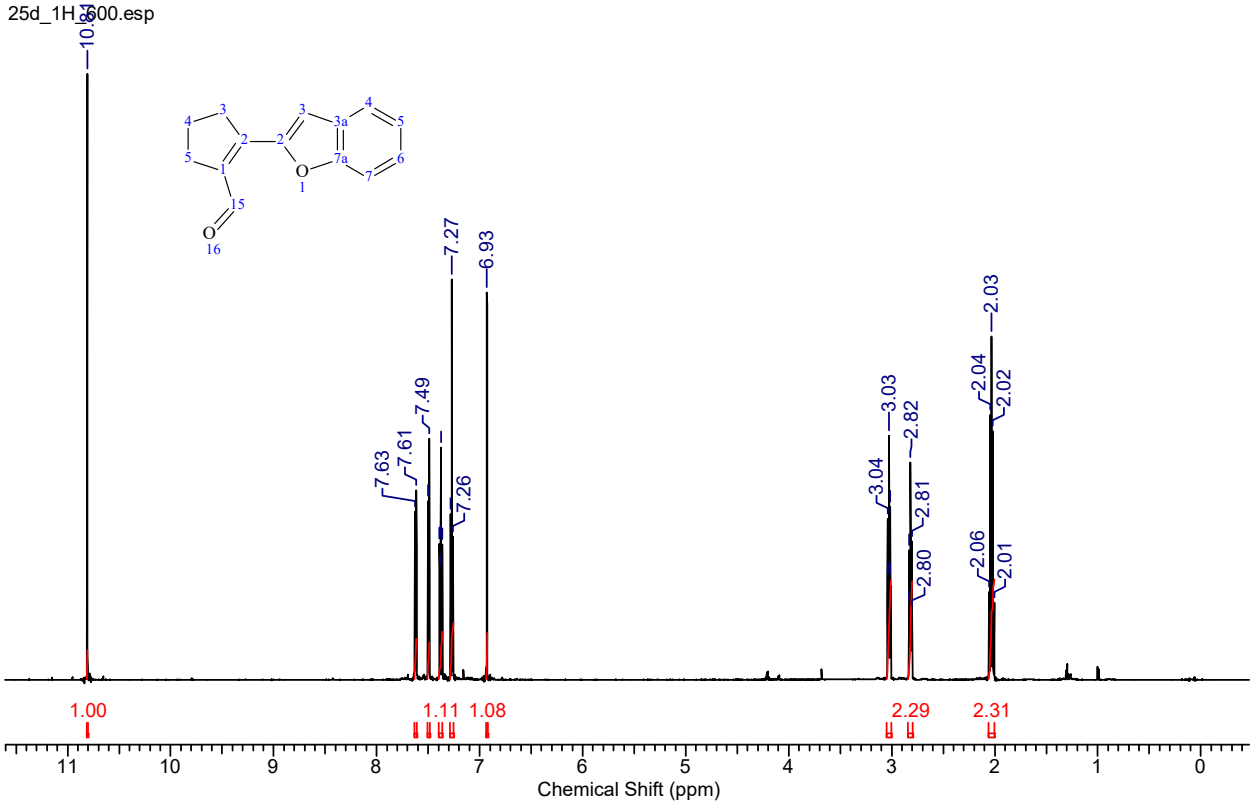


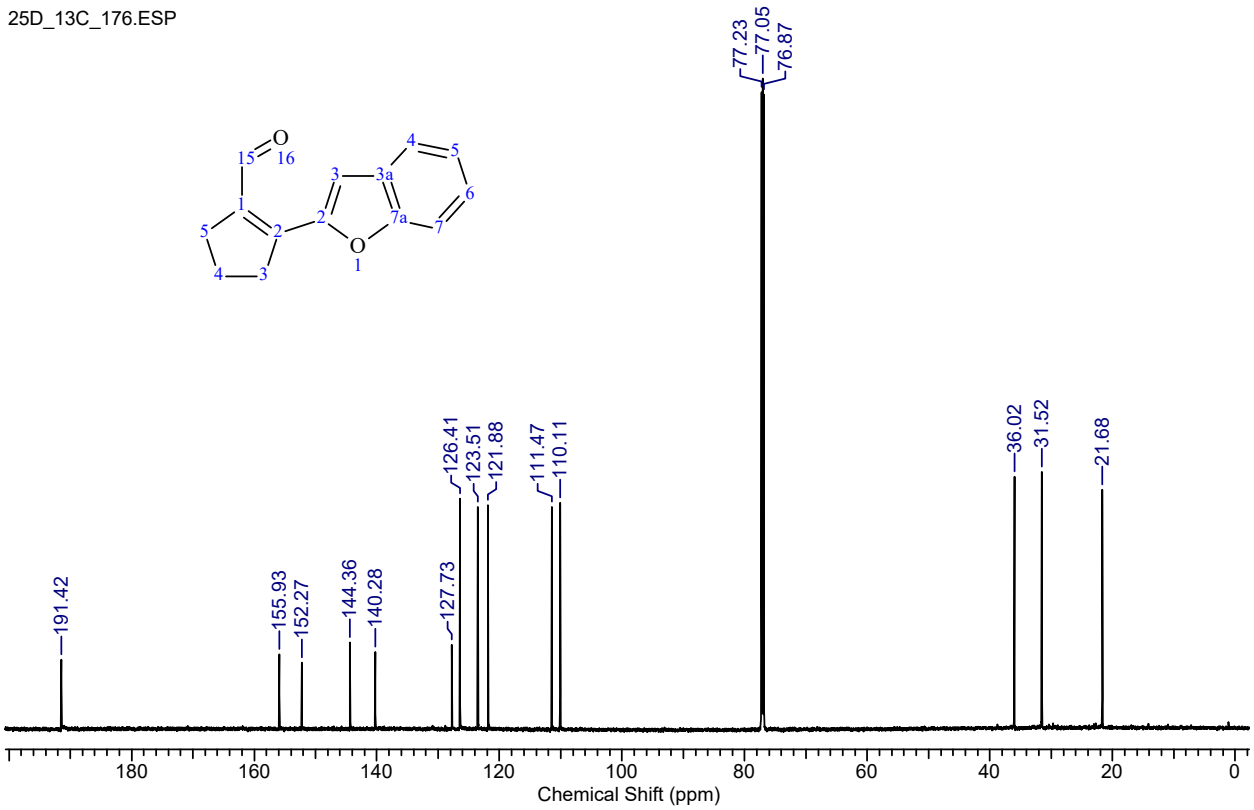

**2-(5-Methylfuran-2-yl)cyclopent-1-ene-1-carbaldehyde (25c).**



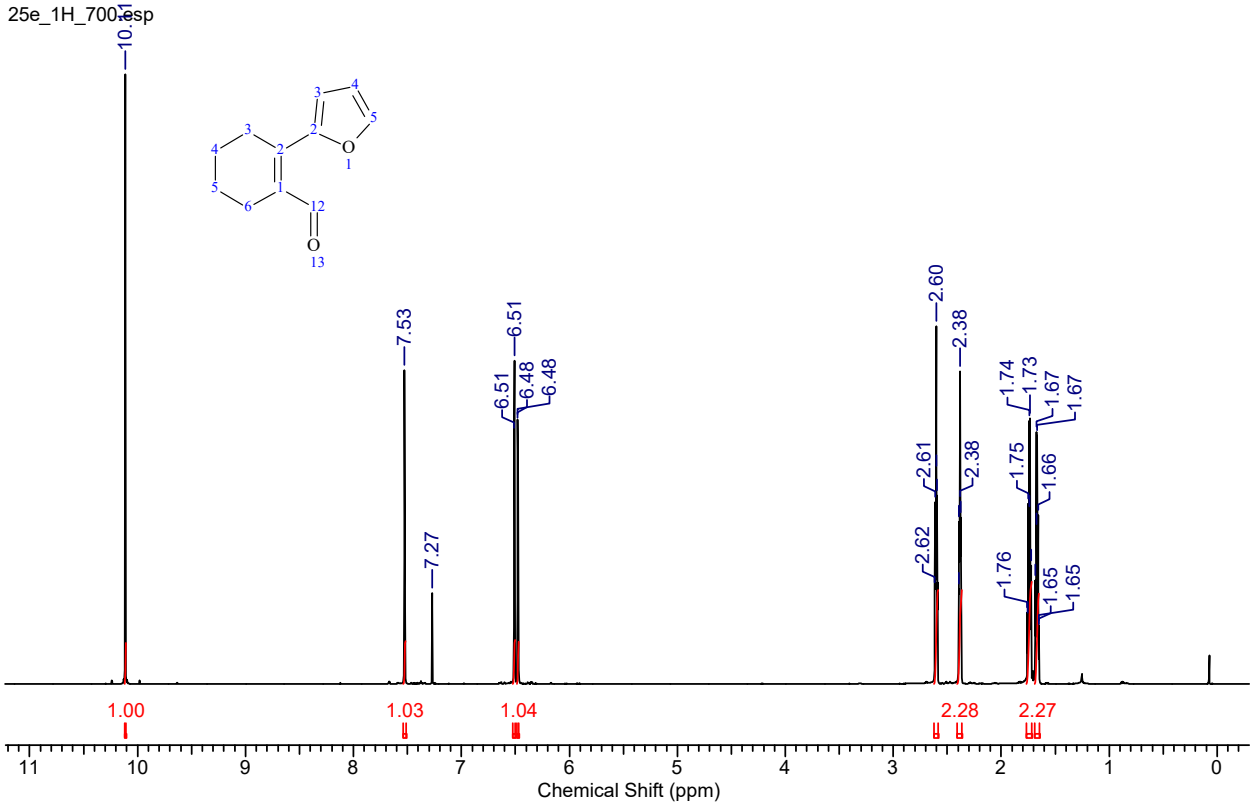


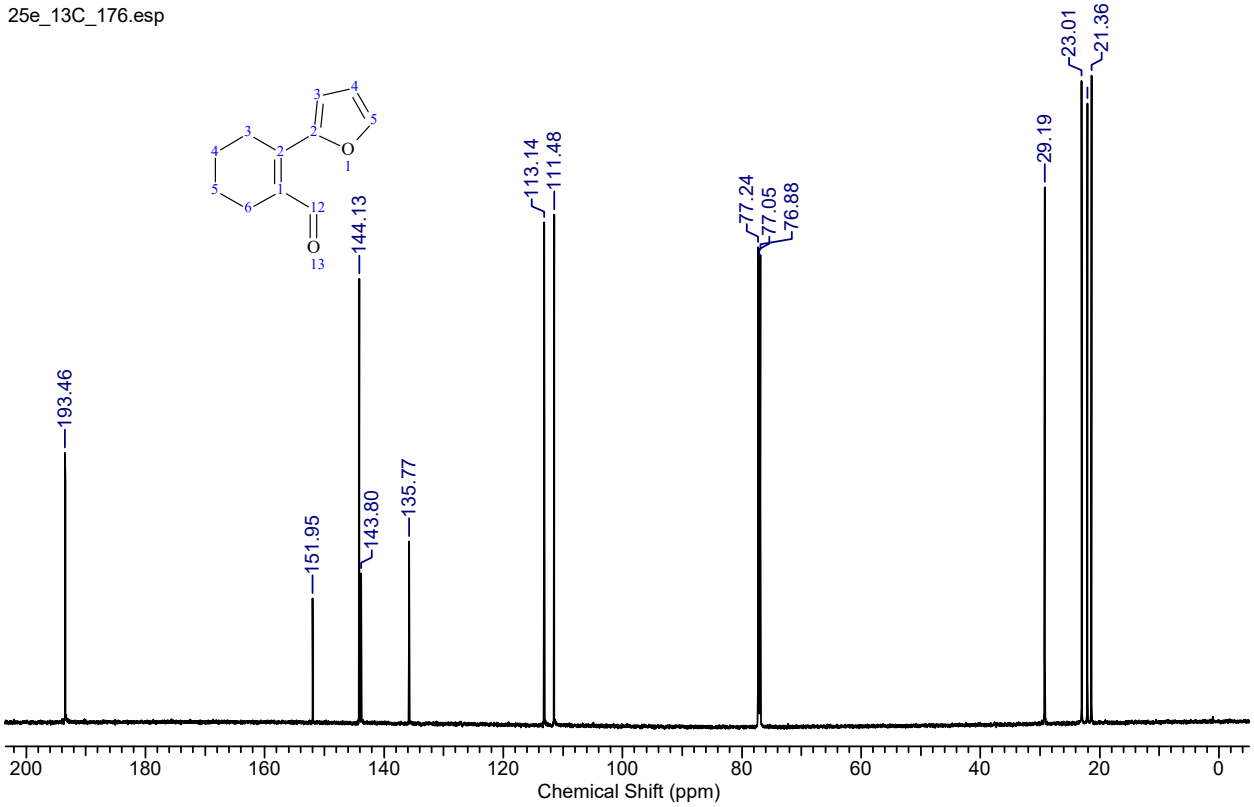

**2-(Benzofuran-2-yl)cyclopent-1-ene-1-carbaldehydecarbaldehyde (25d).**



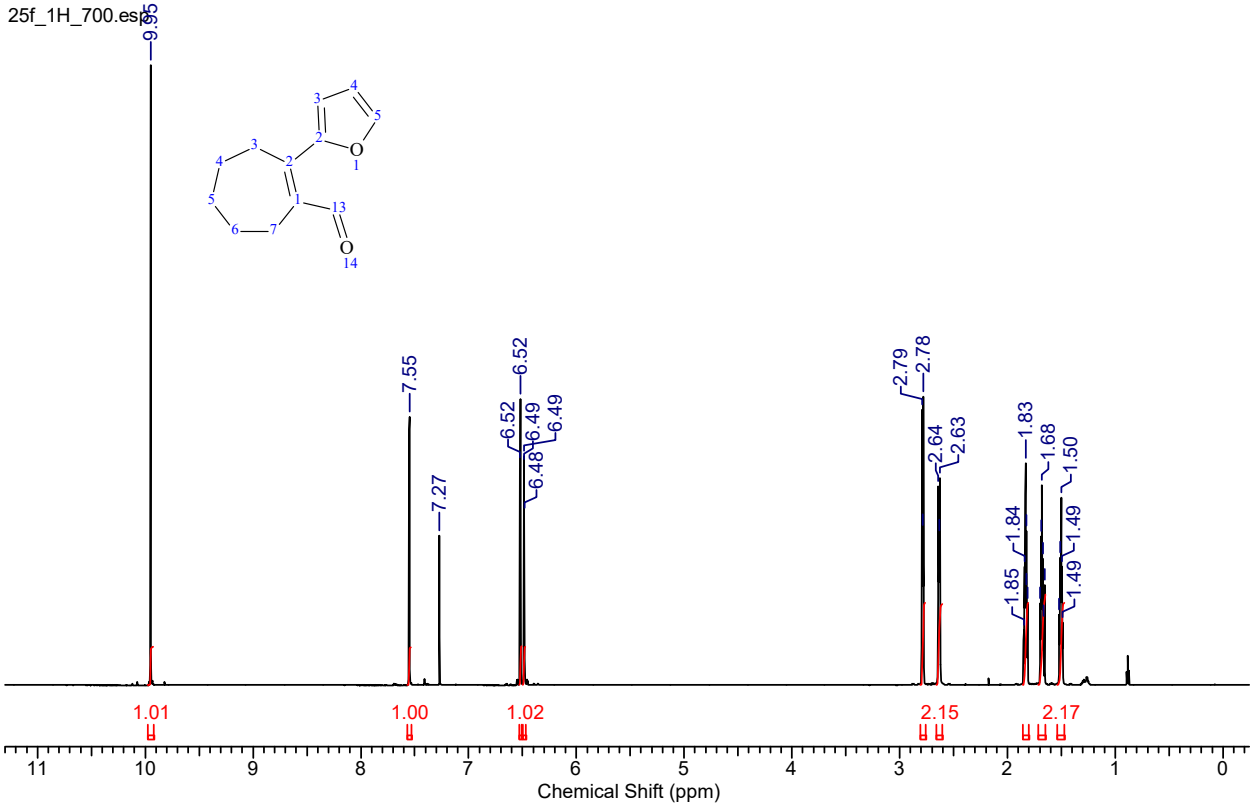


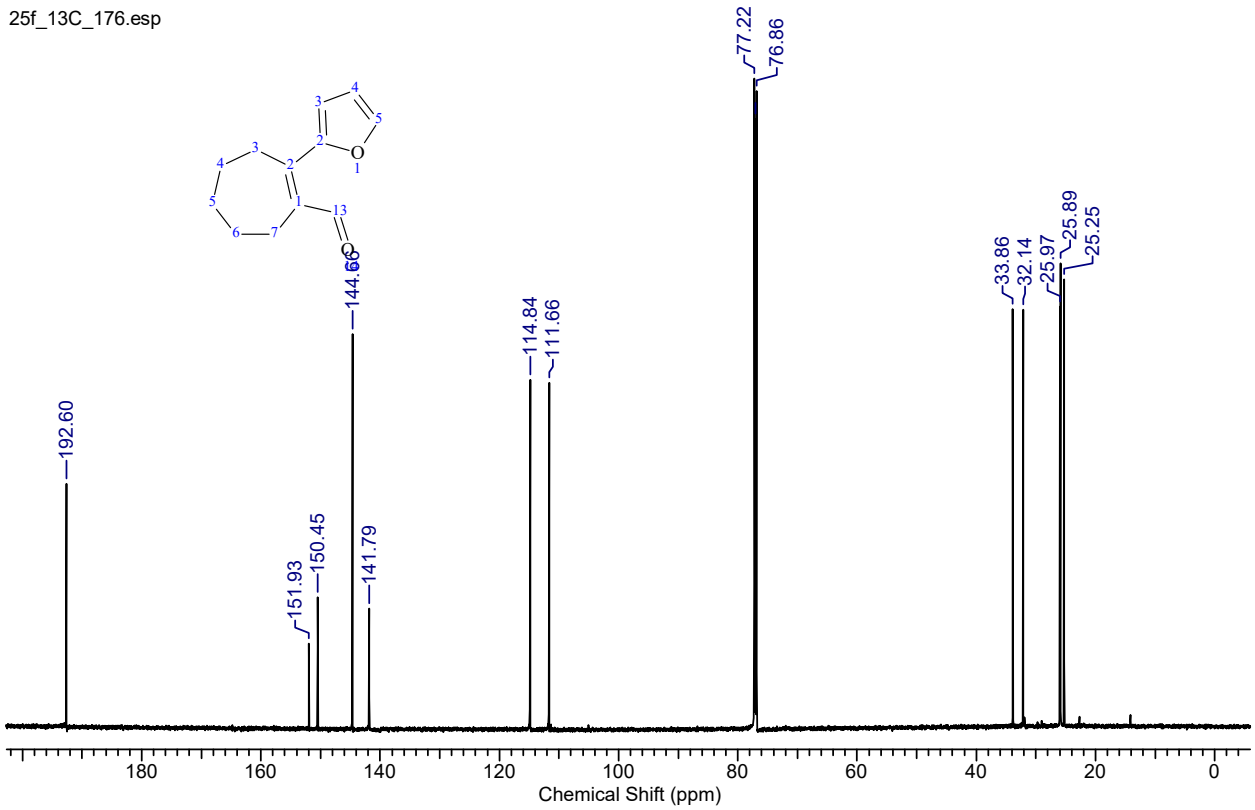

**2-(Furan-2-yl)cyclohex-1-ene-1-carbaldehyde (25e).**



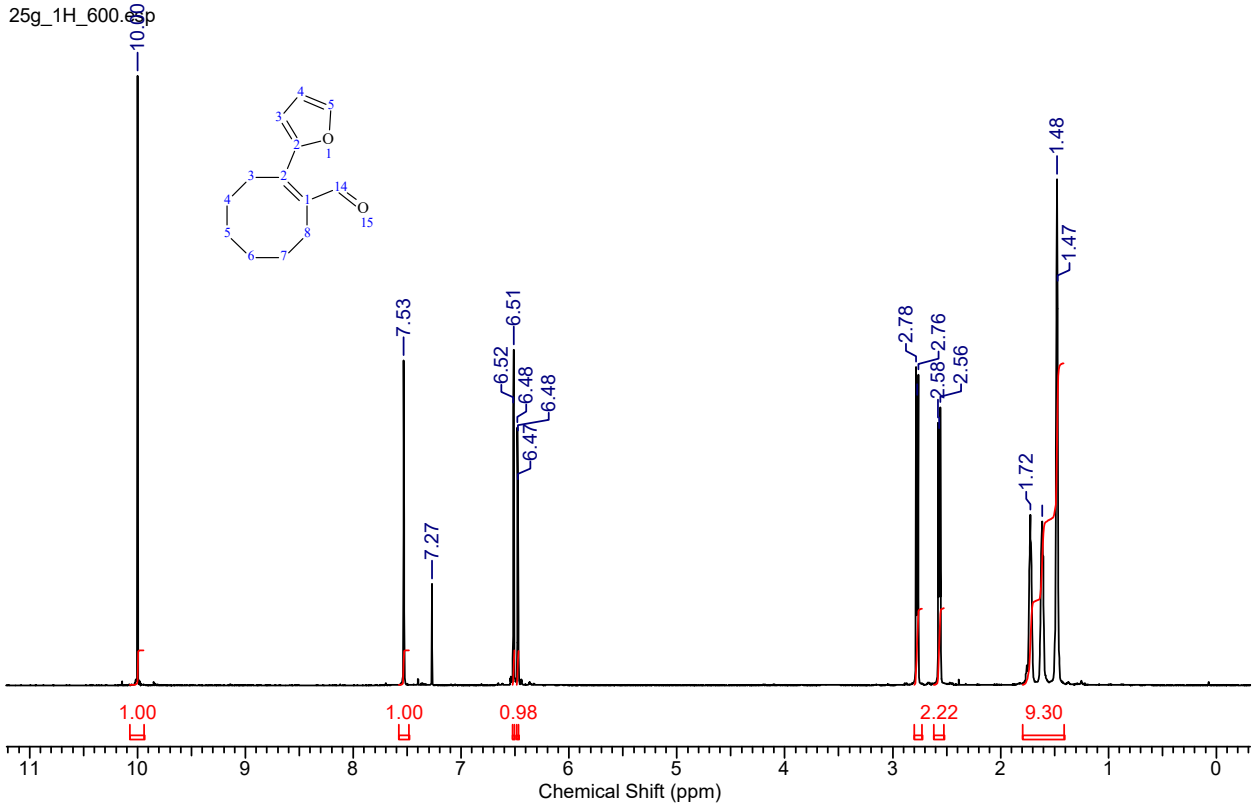


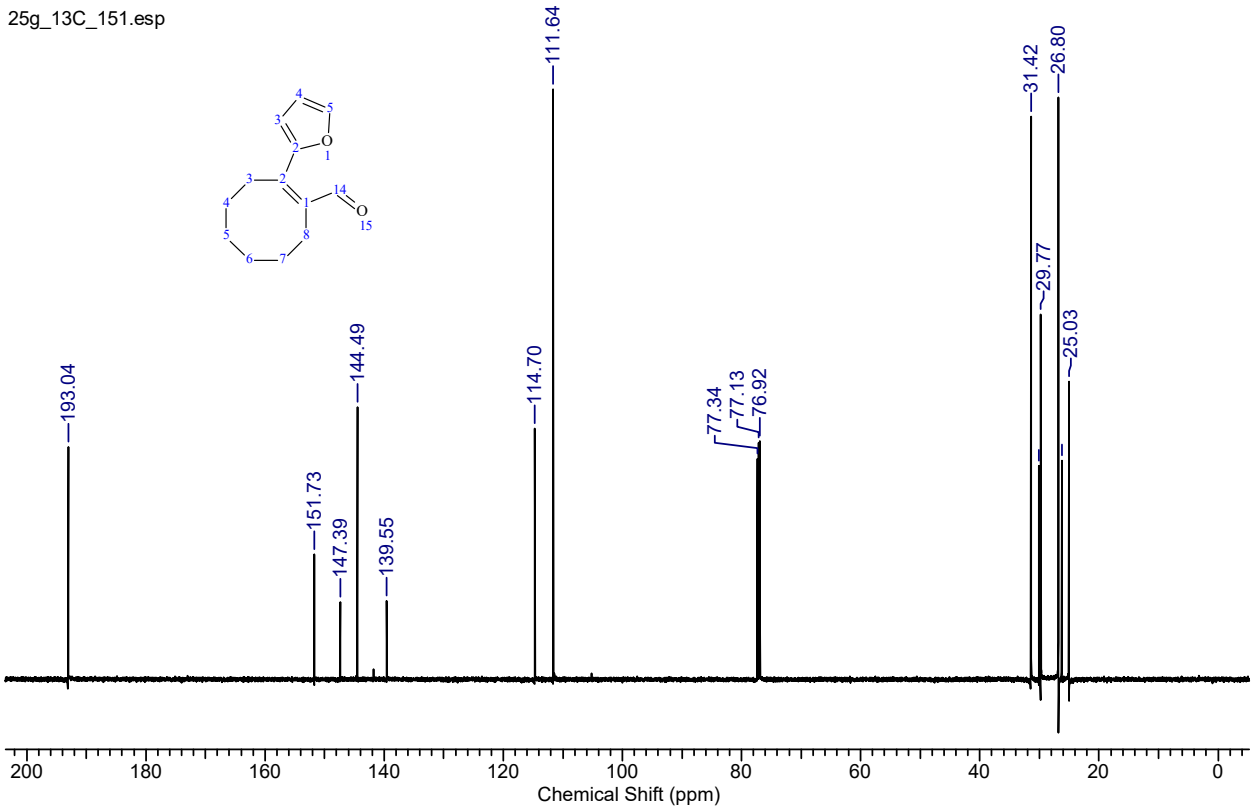

**2-(Furan-2-yl)cyclohept-1-ene-1-carbaldehyde (25f).**



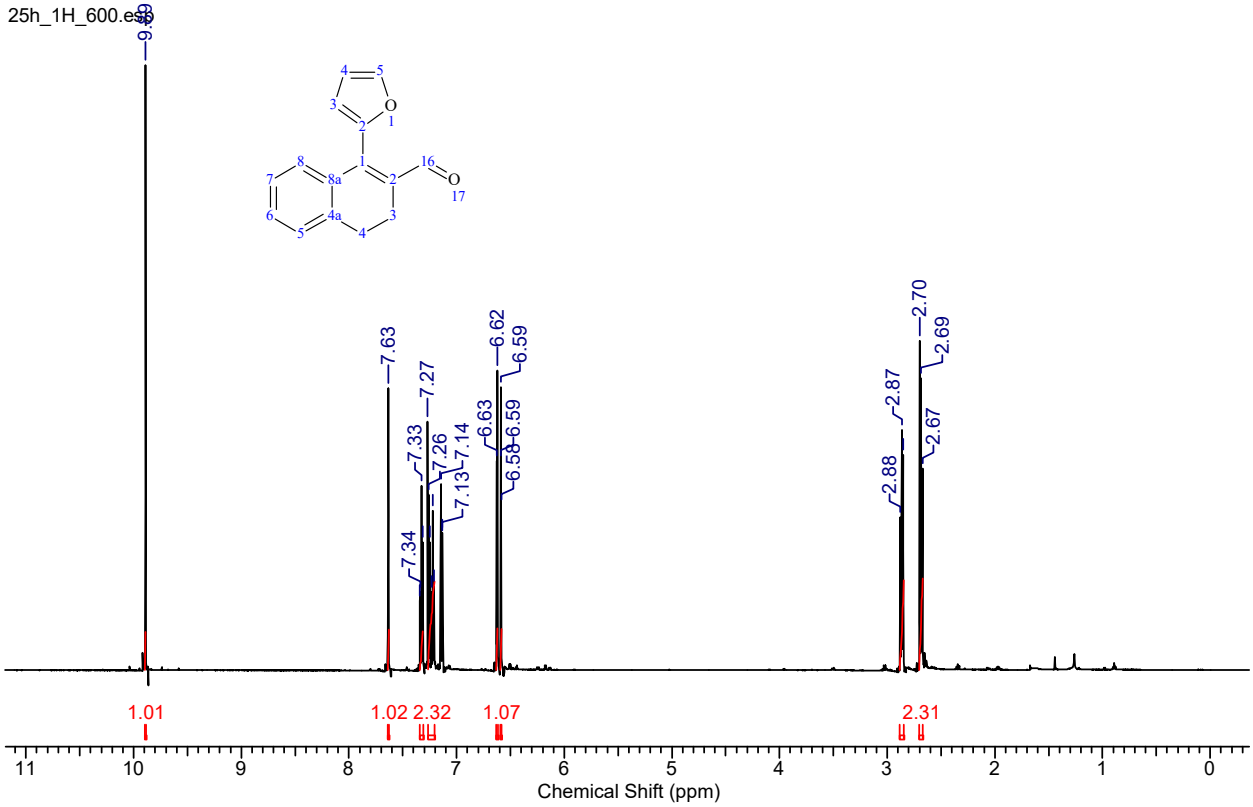


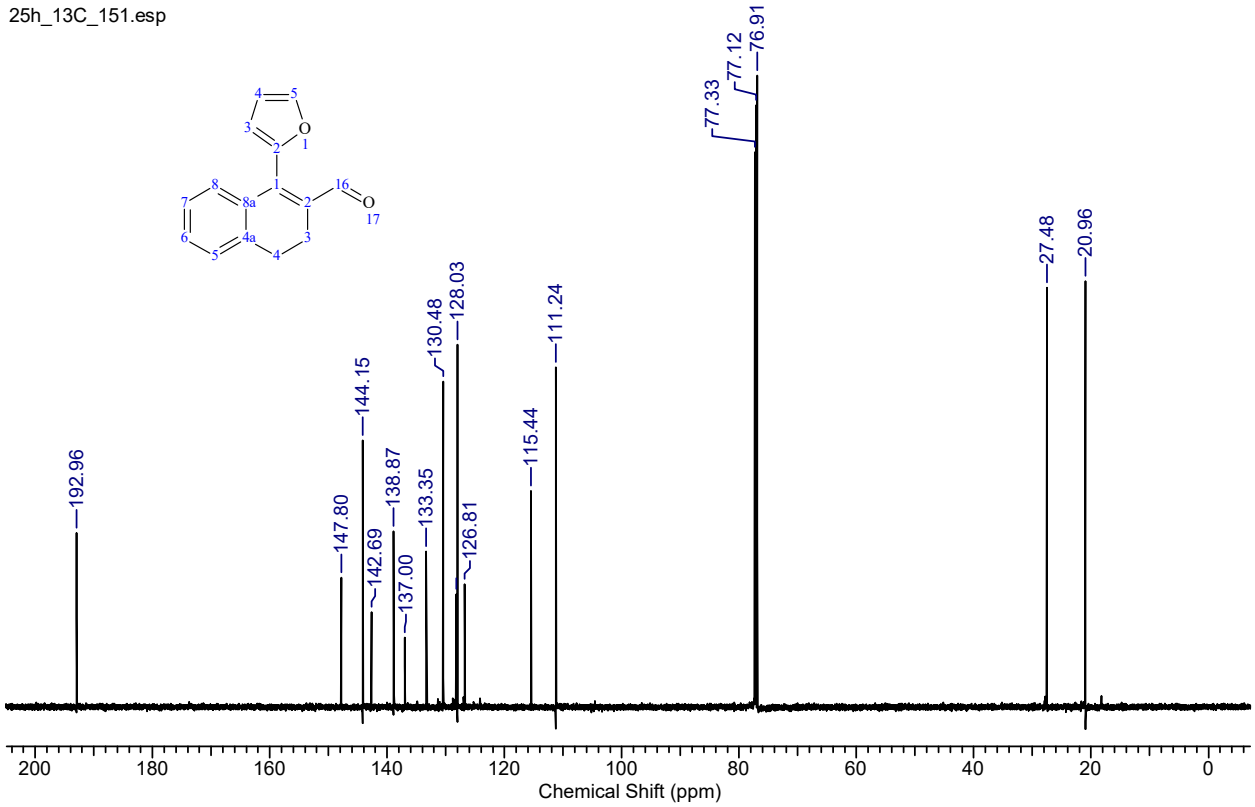

**2-(Furan-2-yl)cyclooct-1-ene-1-carbaldehyde (25g).**



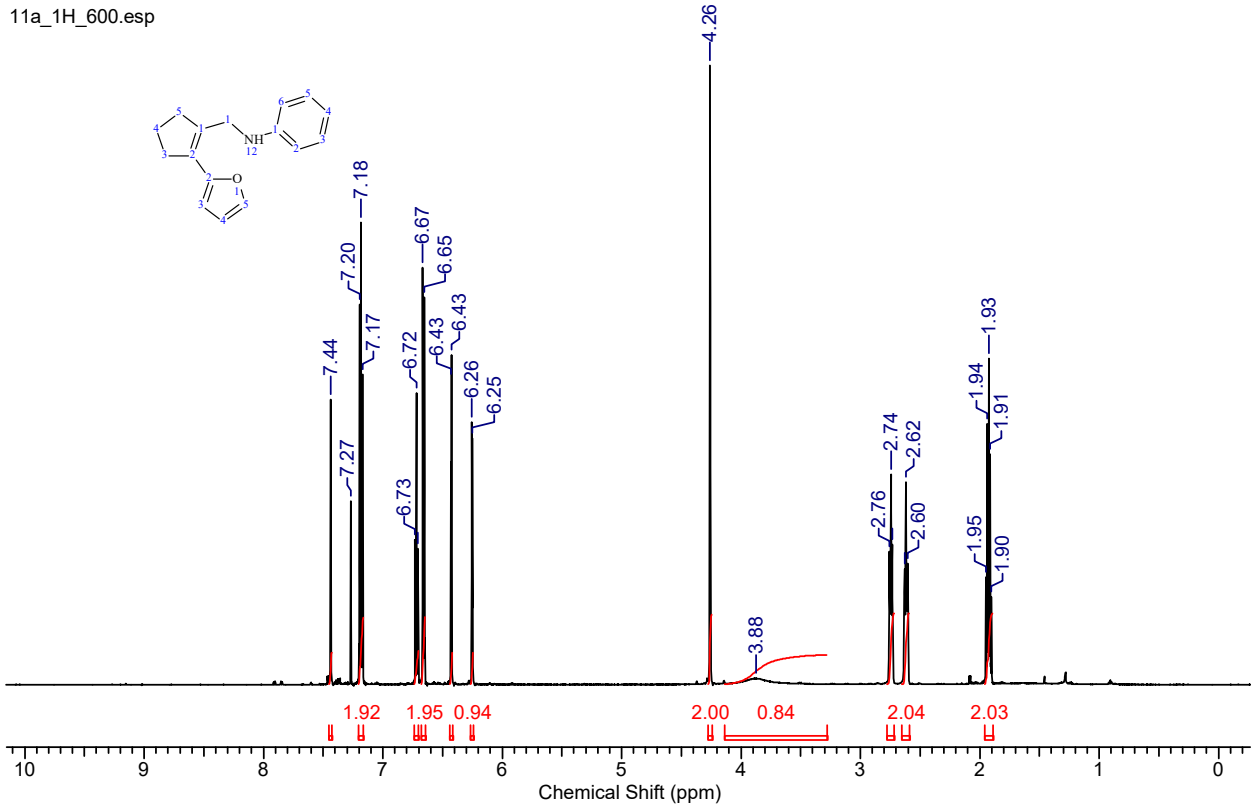


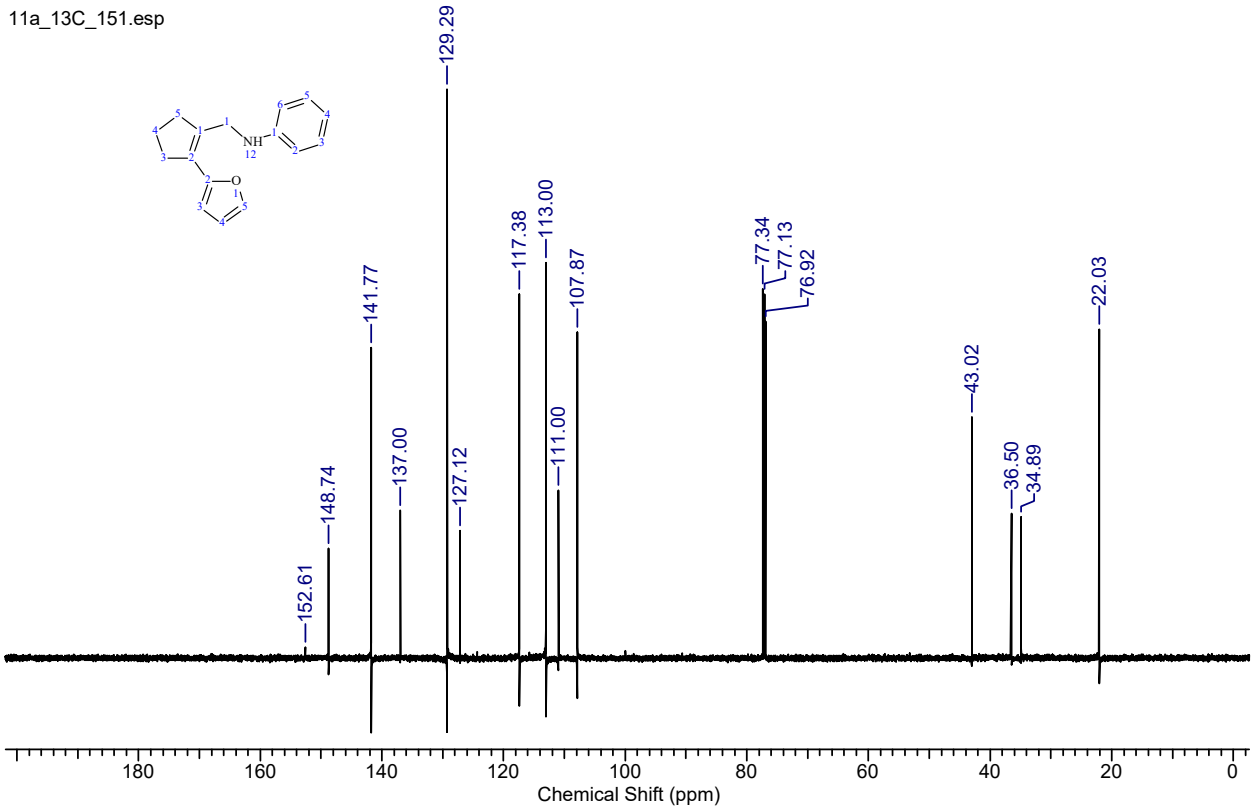

**1-(Furan-2-yl)-3,4-dihydronaphthalene-2-carbaldehyde (25h).**



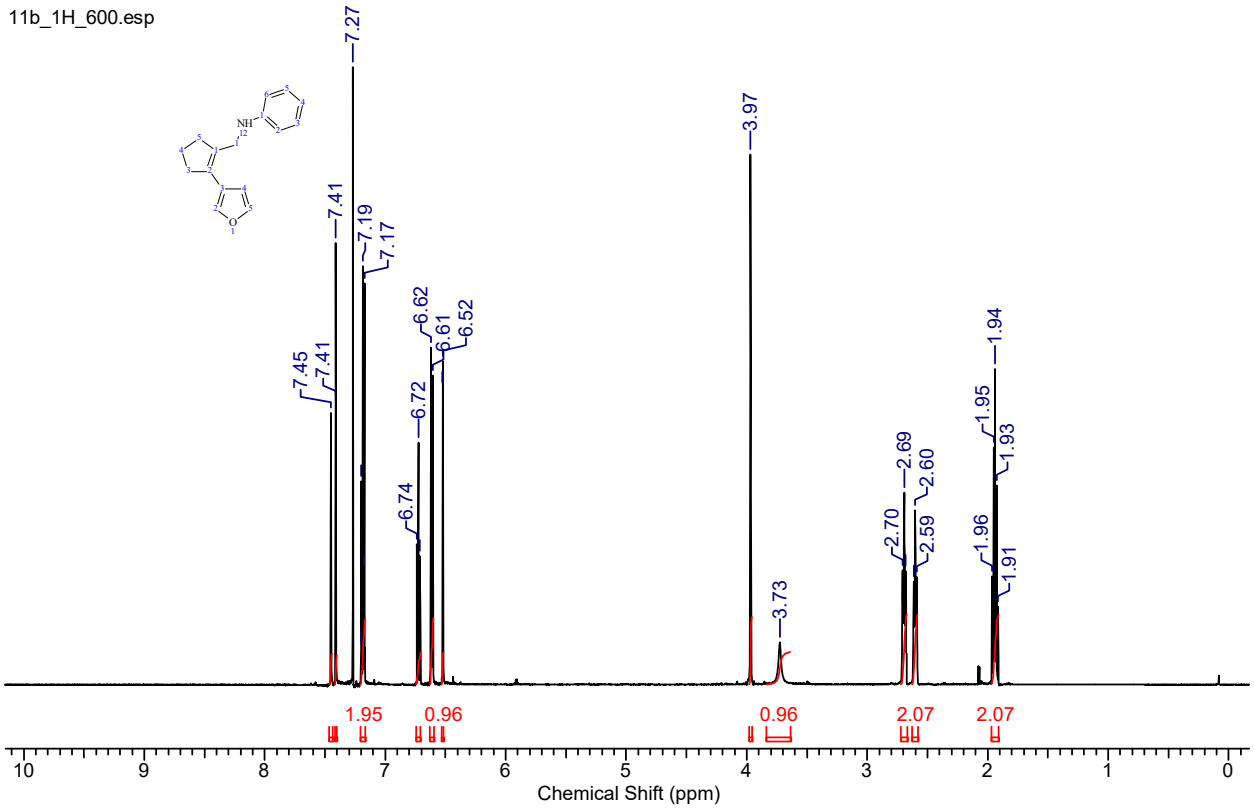


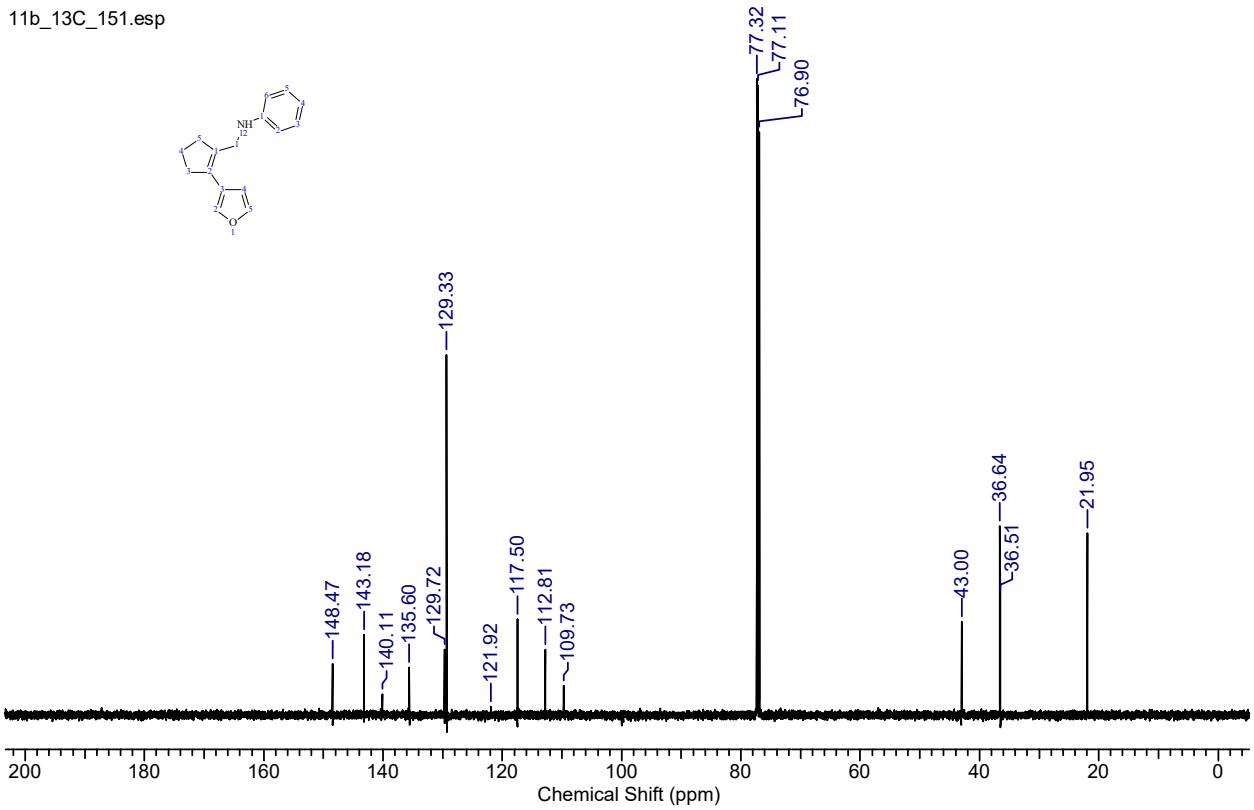

**_N_-((2-(Furan-2-yl)cyclopent-1-enyl)methyl)aniline (11a).**



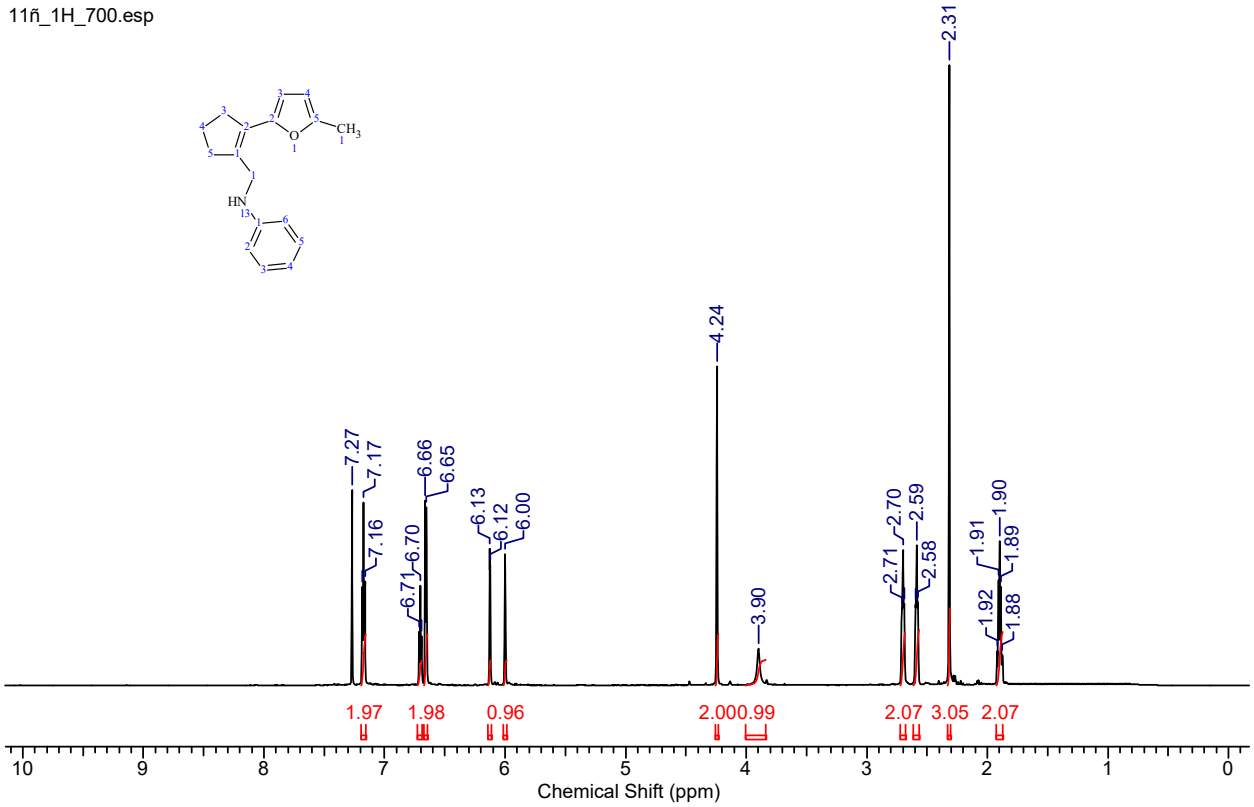


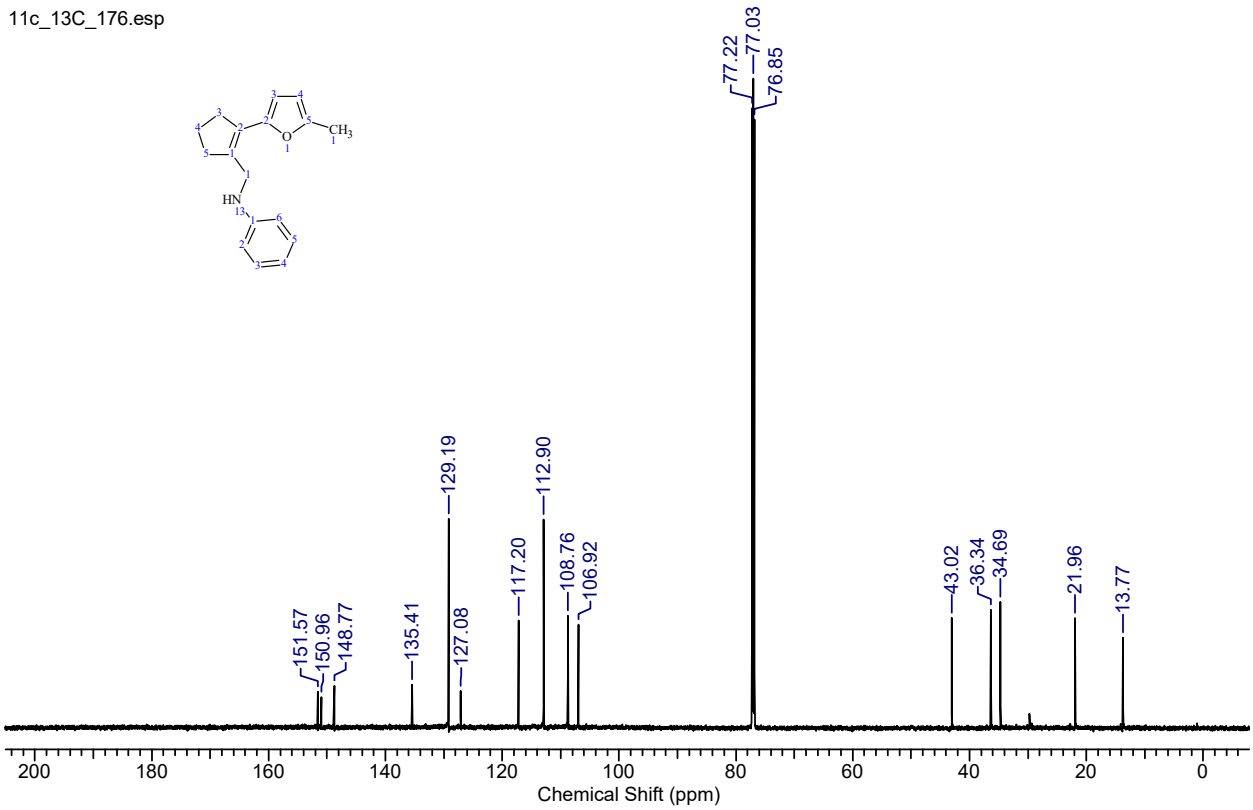

**_N_-((2-(Furan-3-yl)cyclopent-1-enyl)methyl)aniline (11b).**



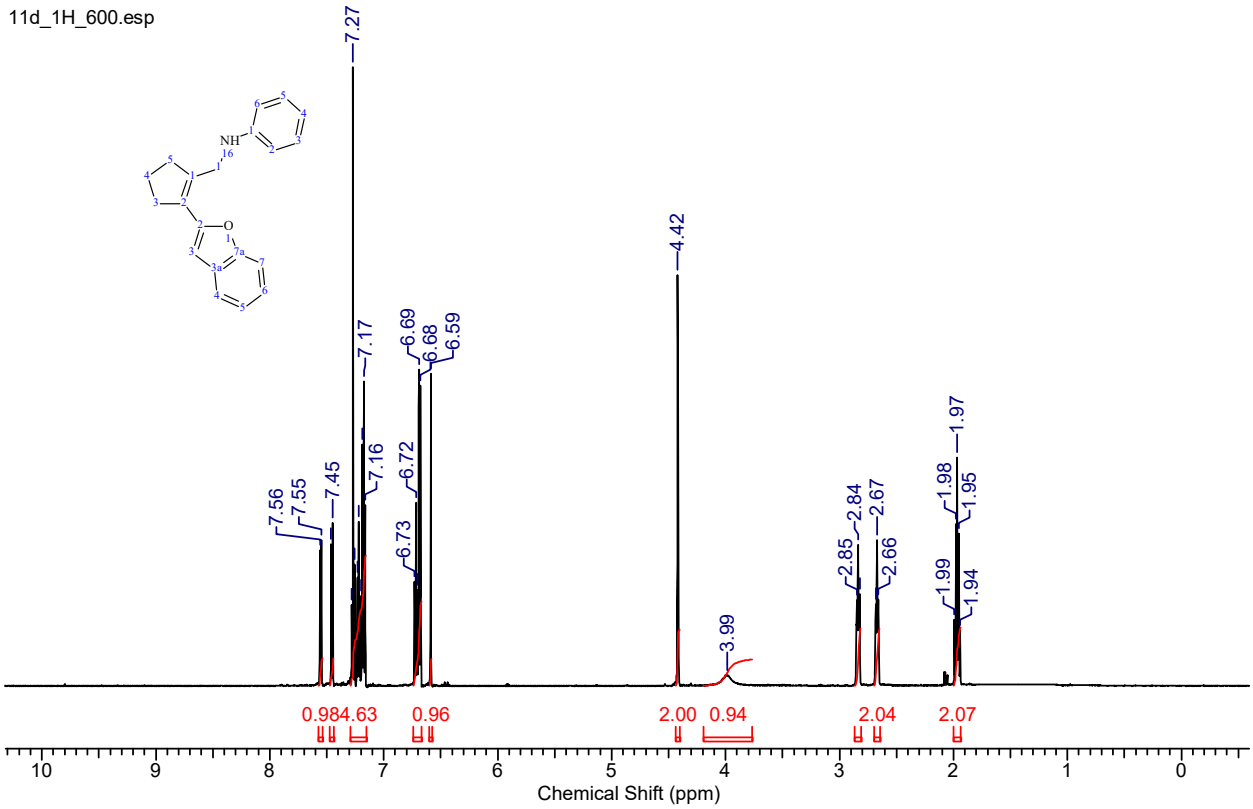


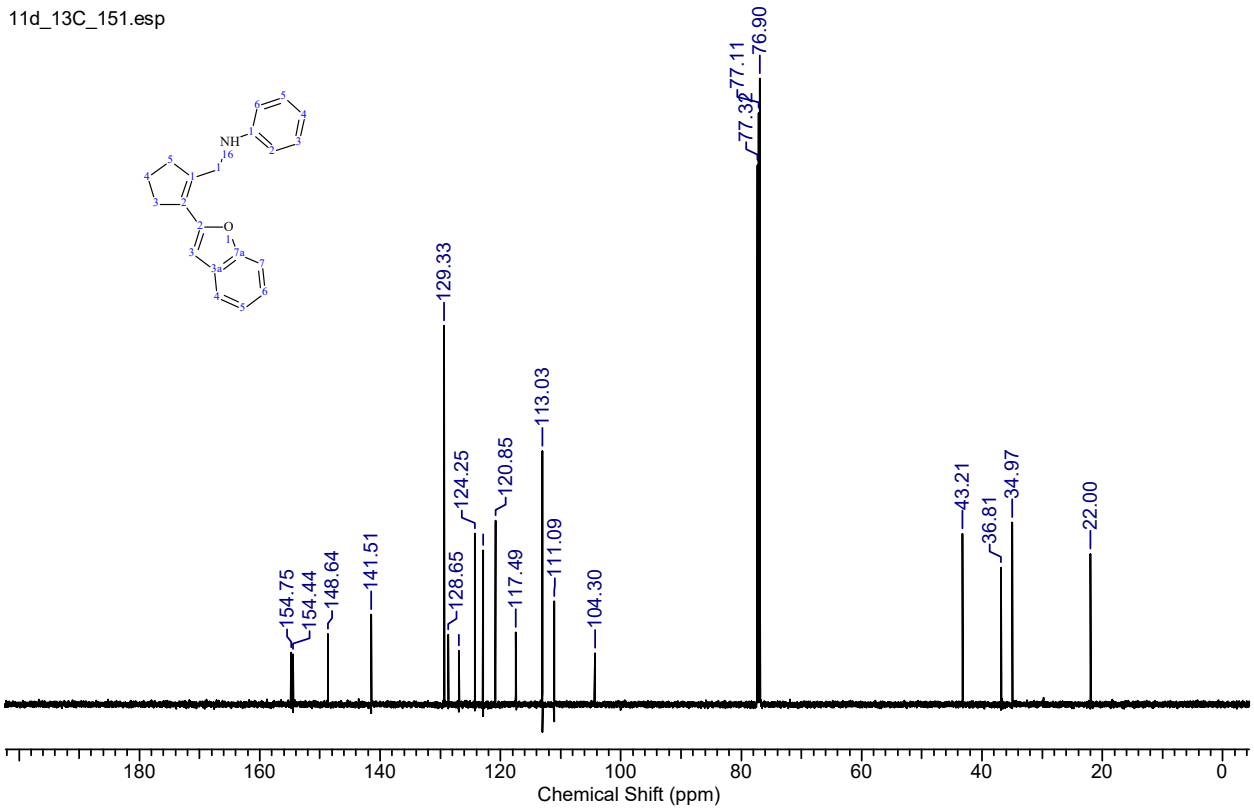

**_N_-((2-(5-Methylfuran-2-yl)cyclopent-1-enyl)methyl)aniline (11c).**



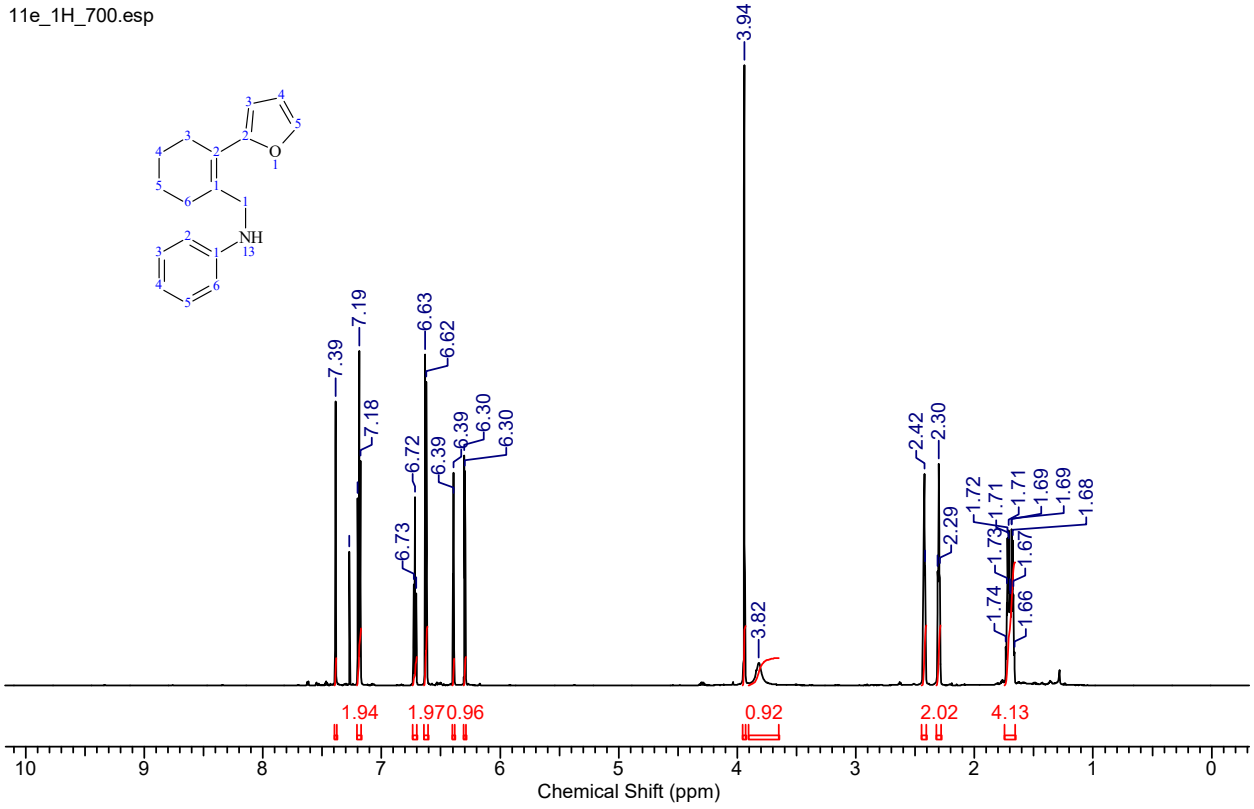


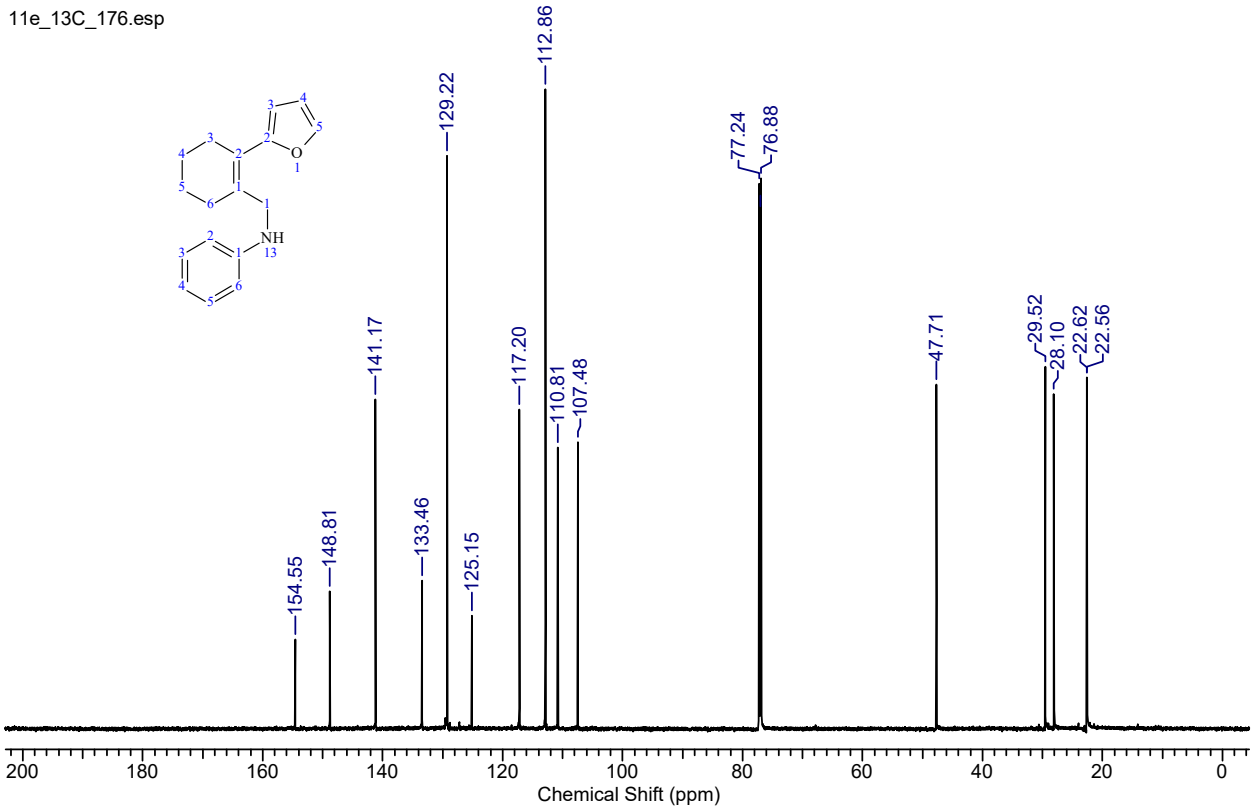

**_N_-((2-(Benzofuran-2-yl)cyclopent-1-enyl)methyl)aniline (11d).**



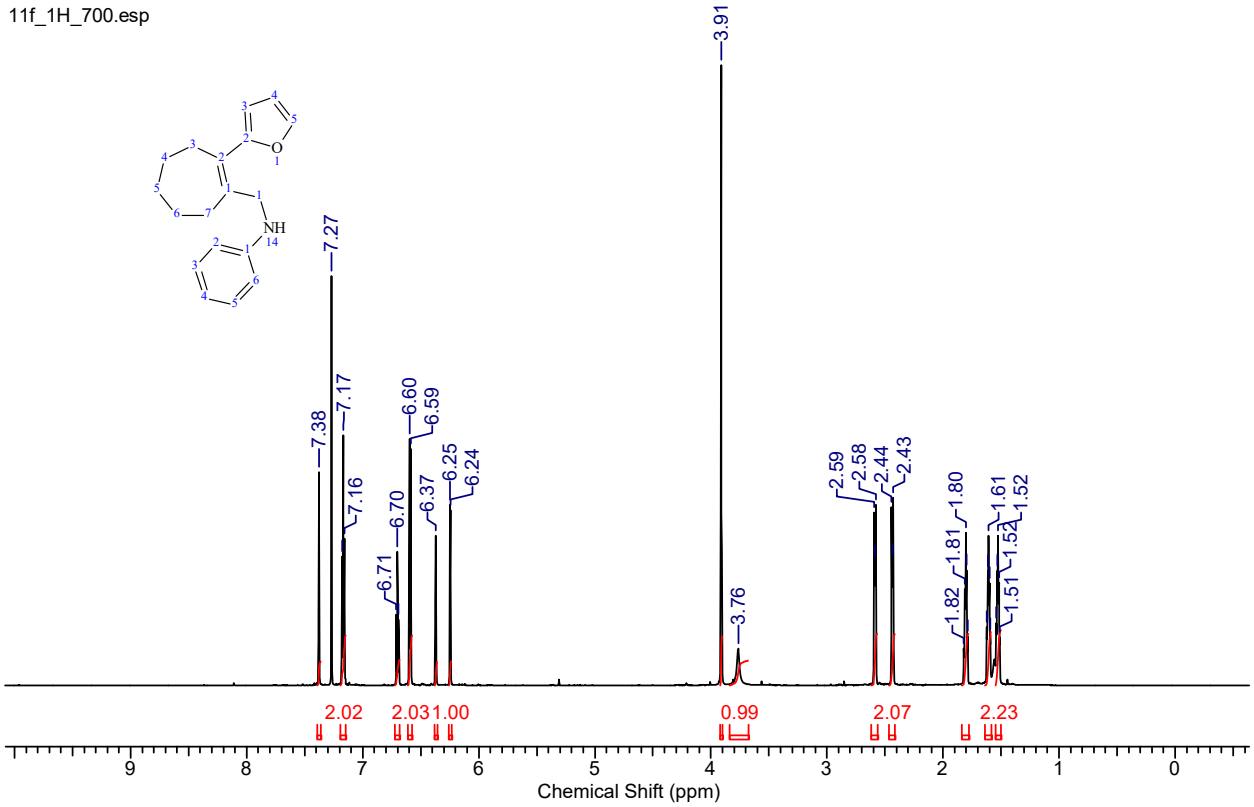


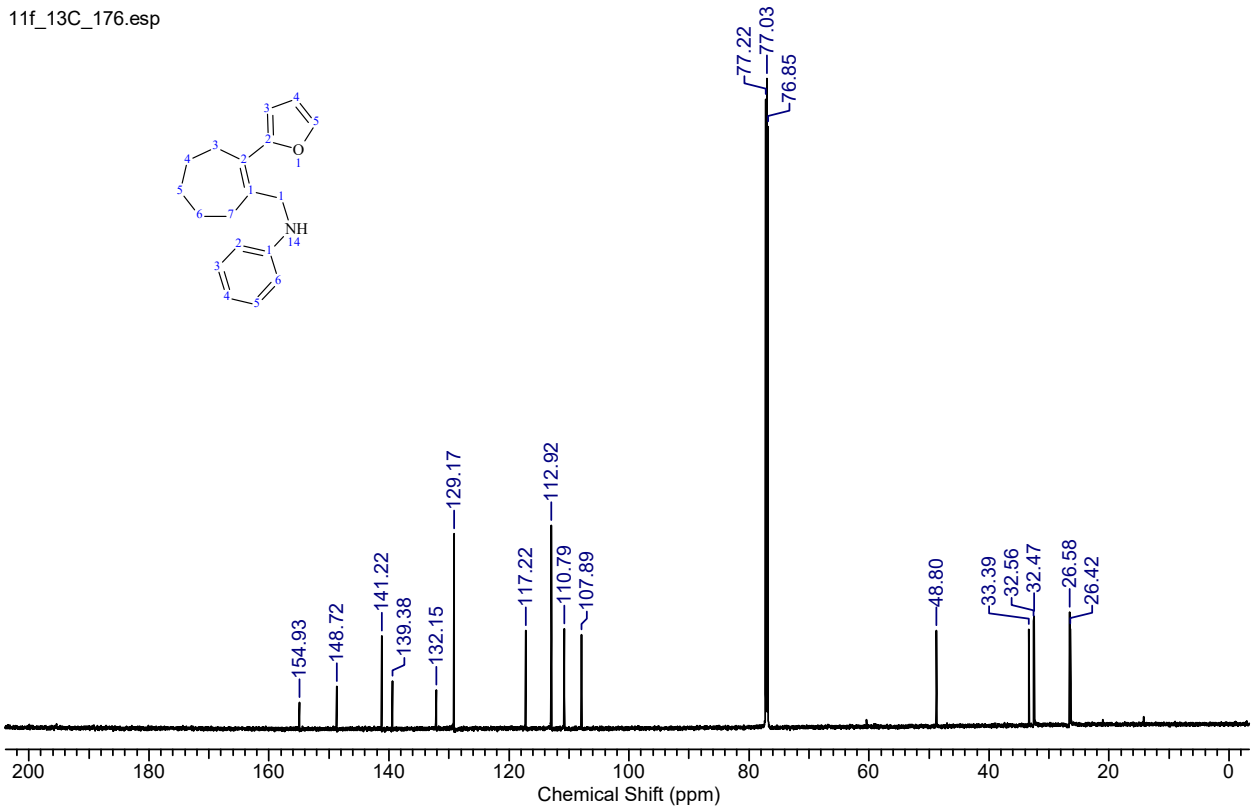

**_N_-((2-(Furan-2-yl)cyclohex-1-enyl)methyl)aniline (11e).**



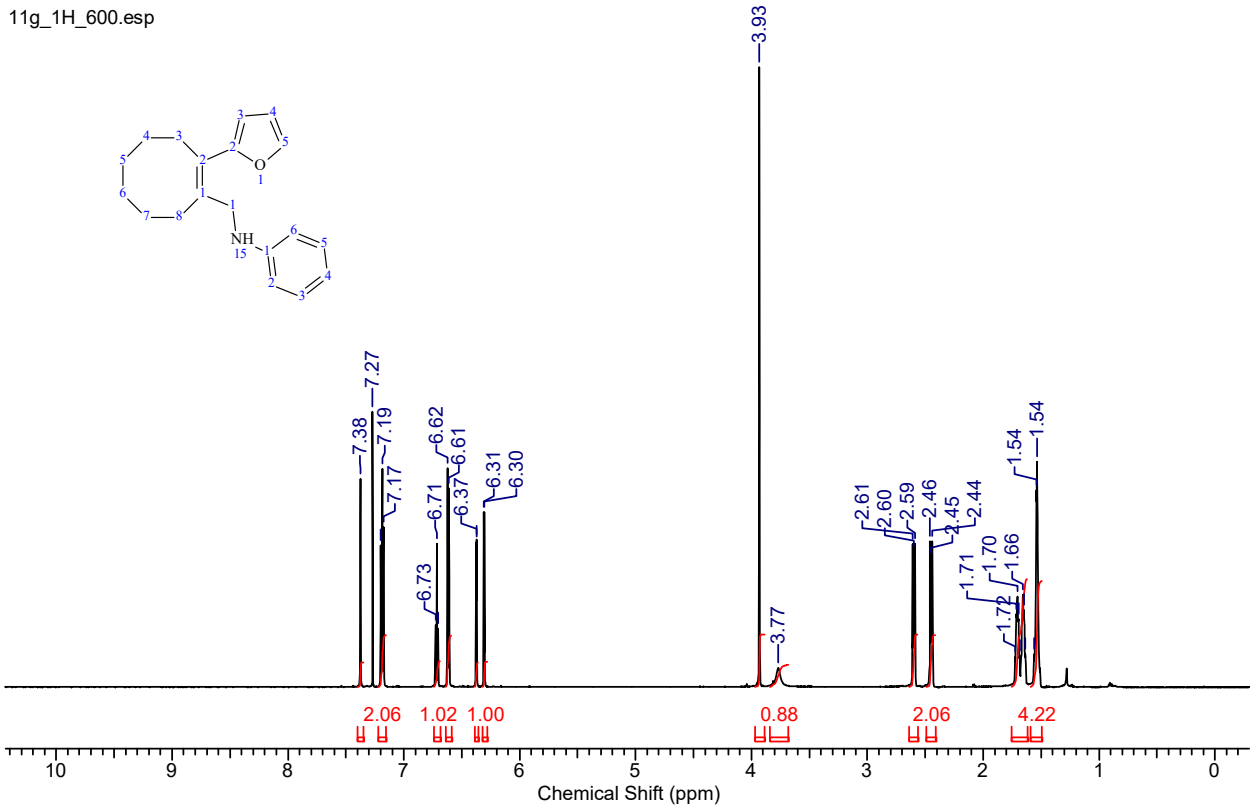


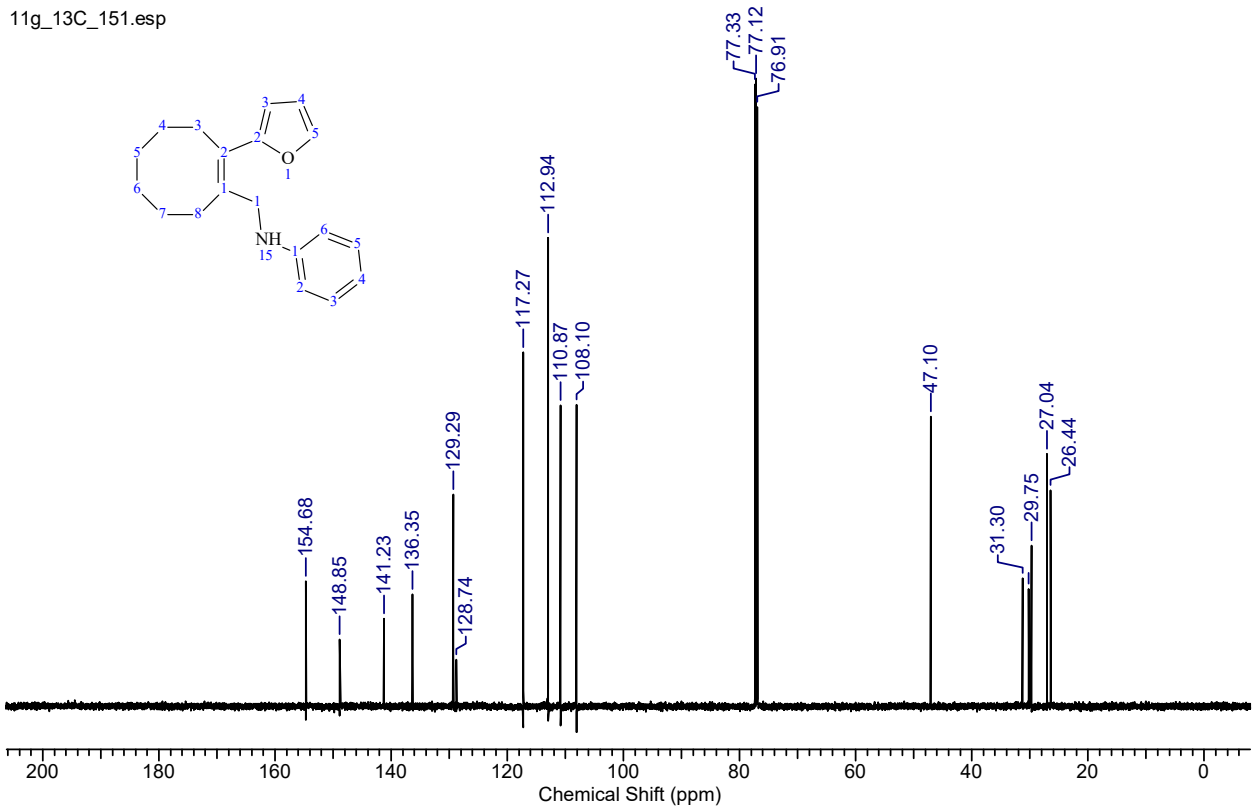

**_N_-((2-(Furan-2-yl)cyclohept-1-enyl)methyl)aniline(11f).**



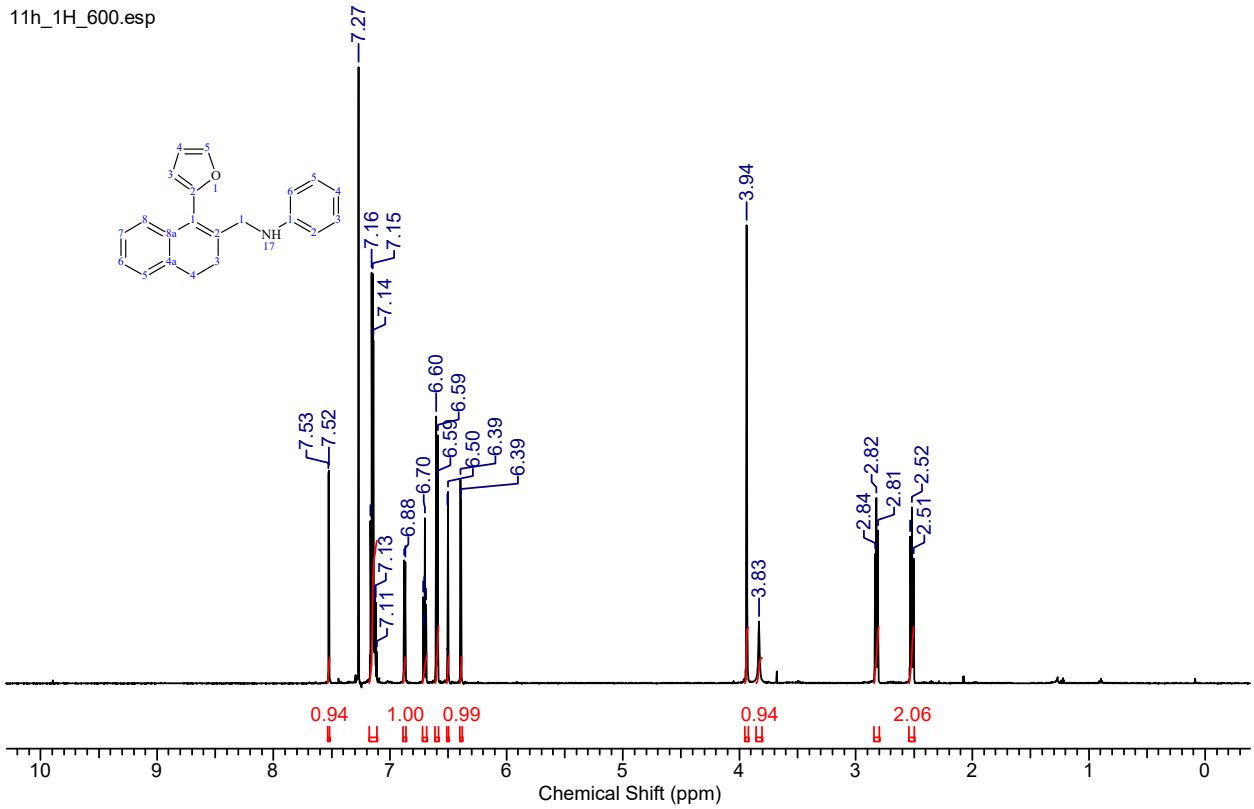


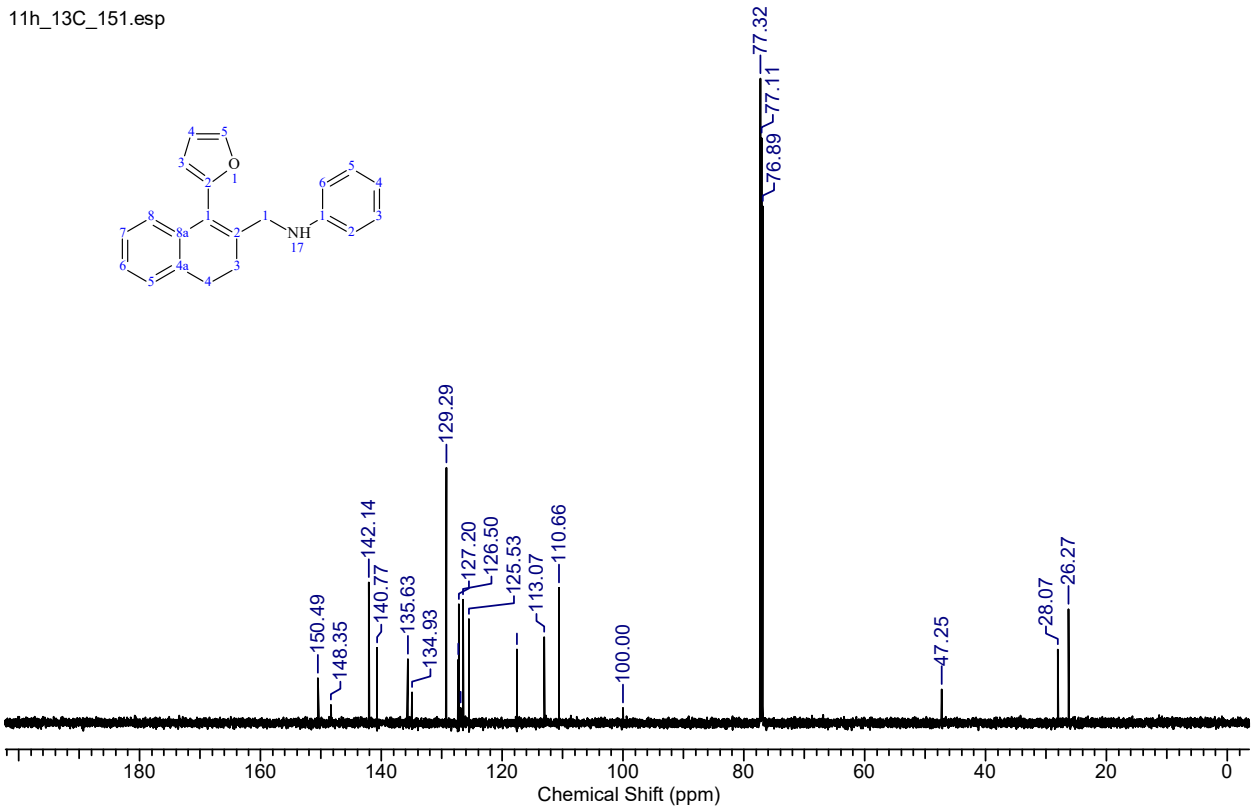

**_N_-((2-(Furan-2-yl)cyclooct-1-enyl)methyl)aniline(11g).**





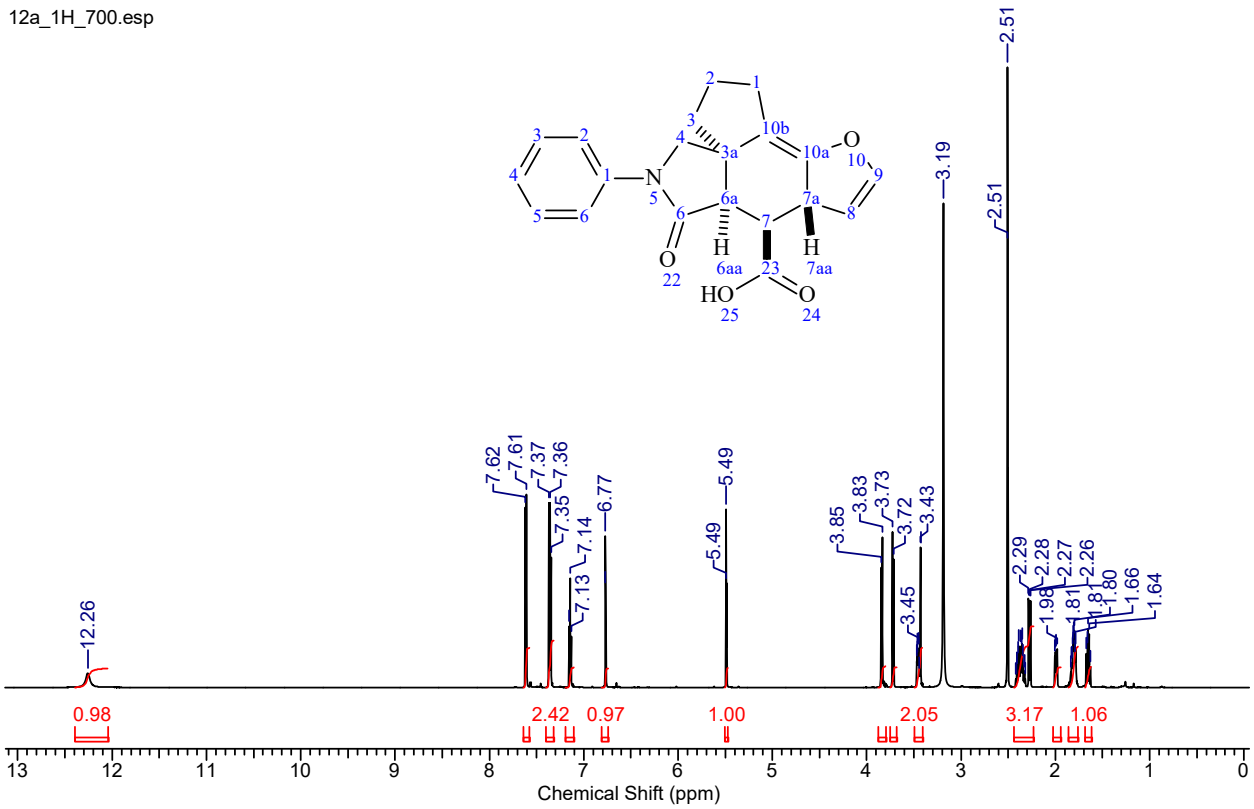

**_N_-((1-(Furan-2-yl)-3,4-dihydronaphthalen-2-yl)methyl)aniline (11h).**

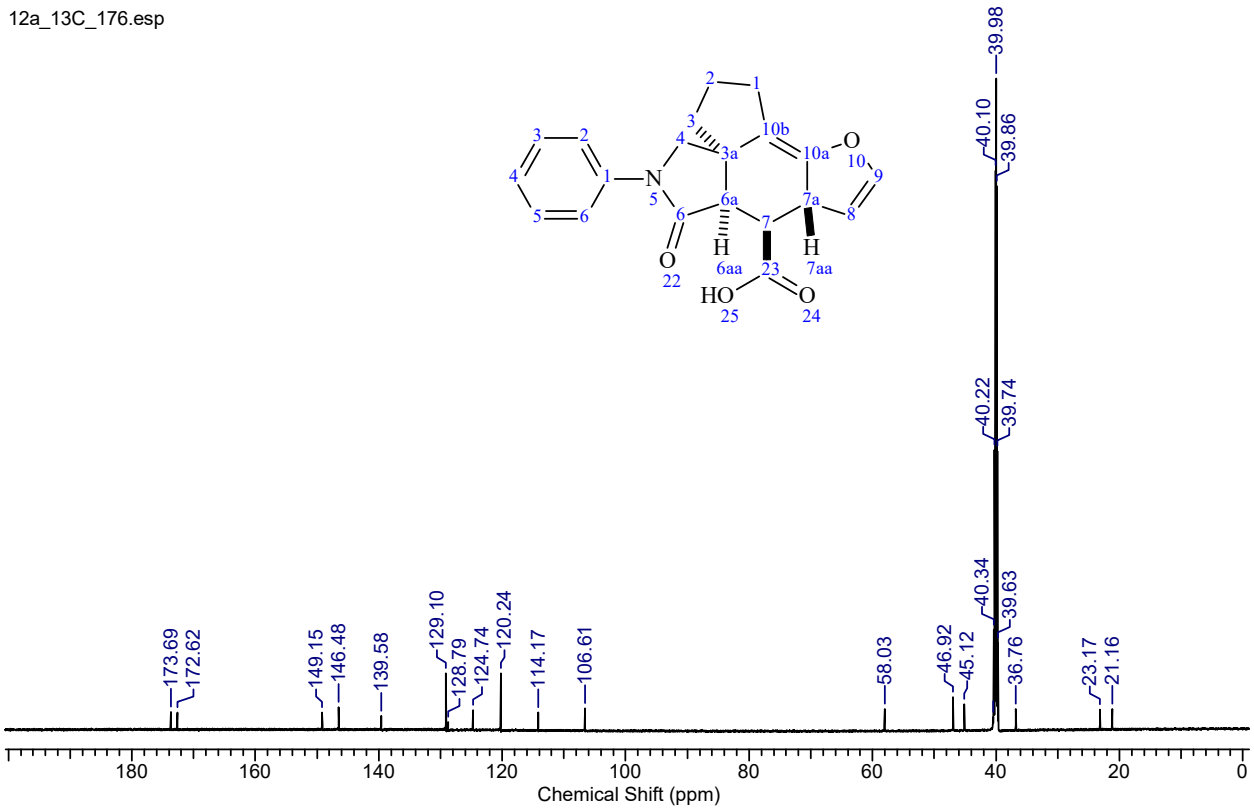




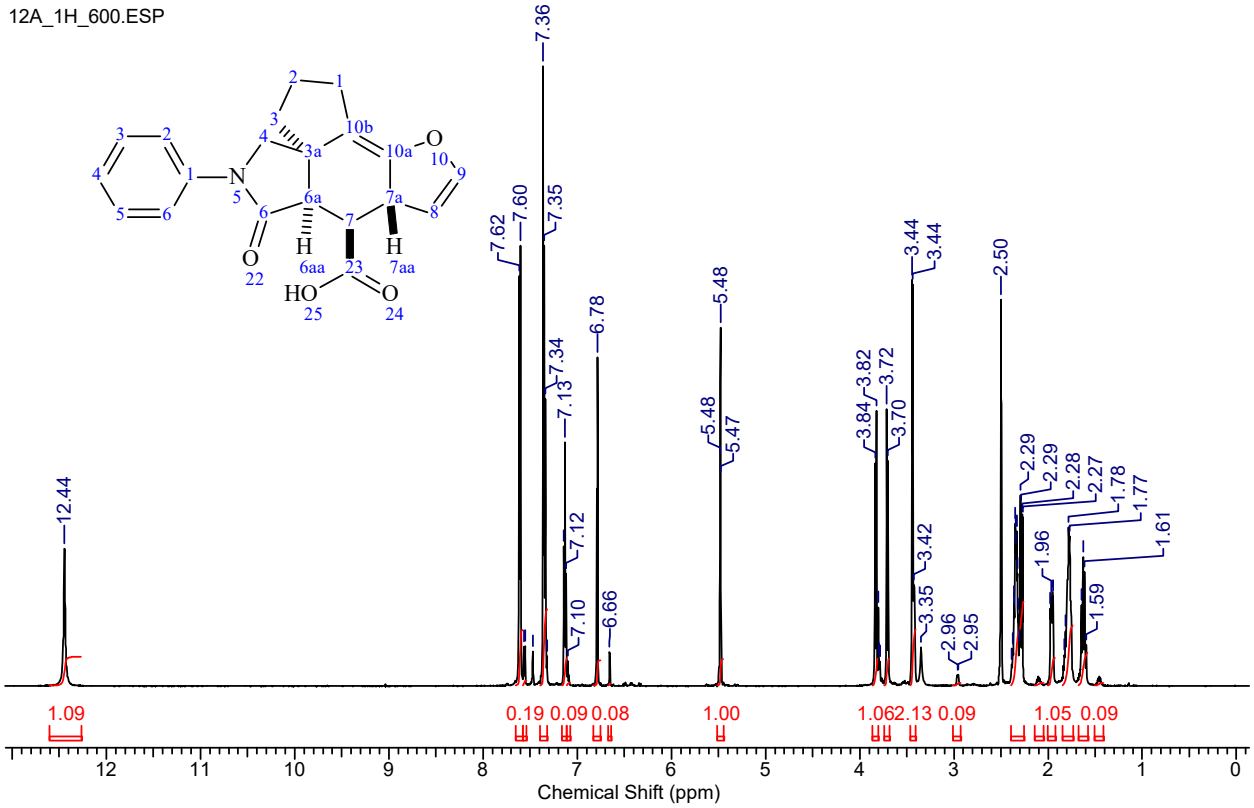

**(3a*RS*,6a*RS*,7*RS*,7a*RS*)-6-Oxo-5-phenyl-2,3,4,5,6,6a,7,7a-octahydro-1H-cyclopenta[*d*]furo[2,3-*f*]isoindole-7-carboxylic acid (12a).**

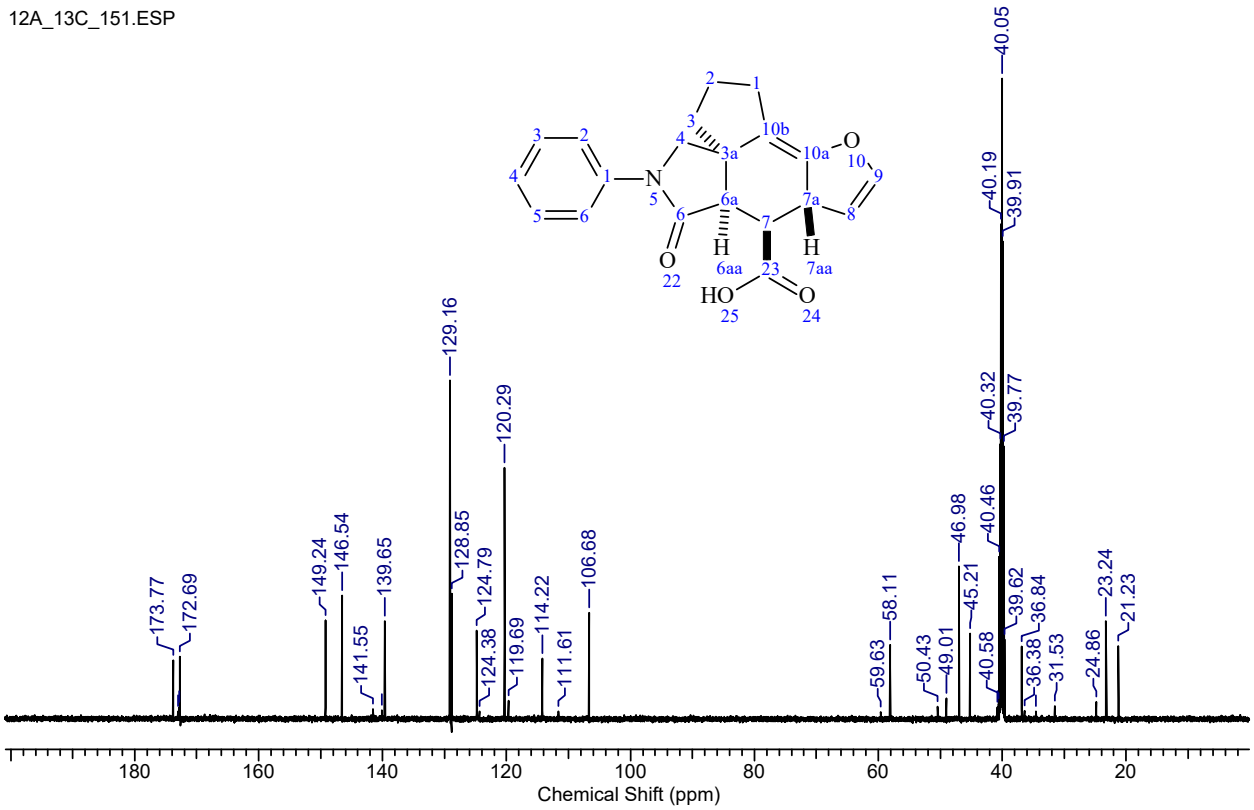
*At 50 °C for 5 hours.*



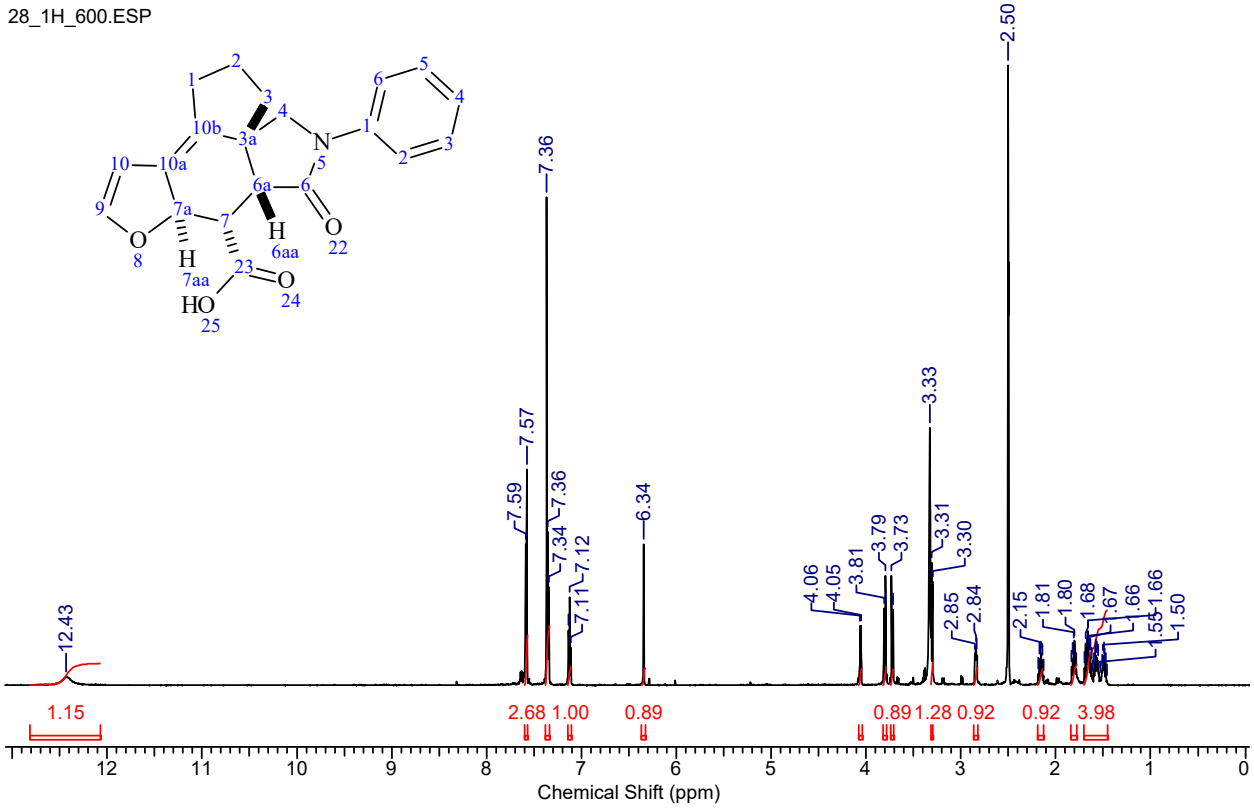


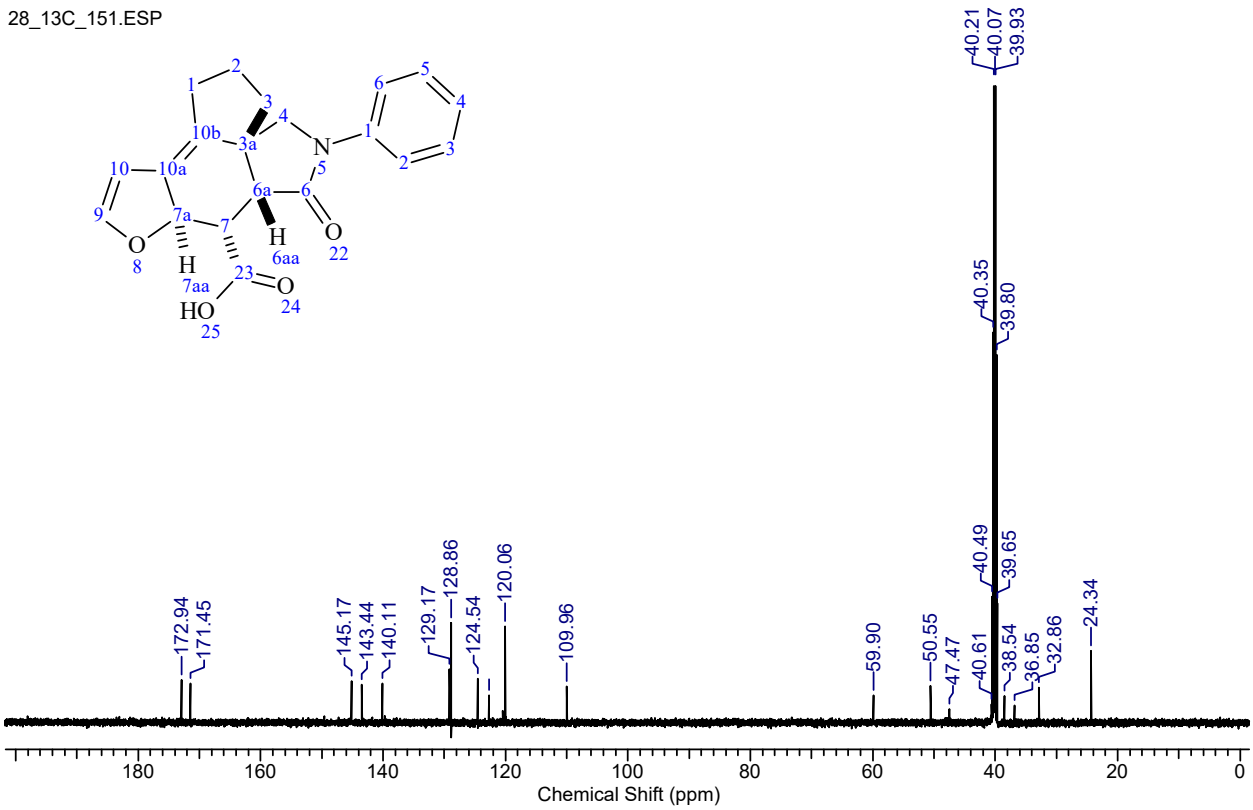

*Reflux for 5 hours. Contains around 7% on an impurity of "aromatic" isomer.*



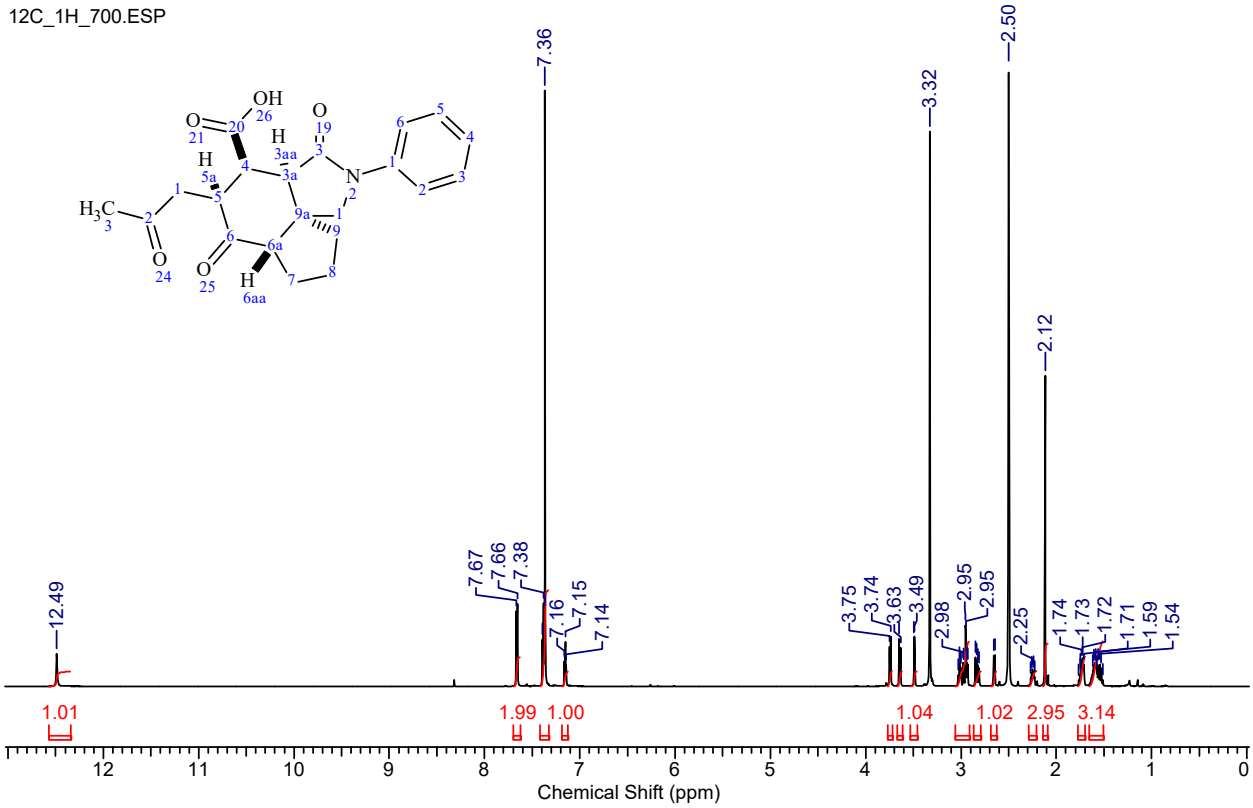


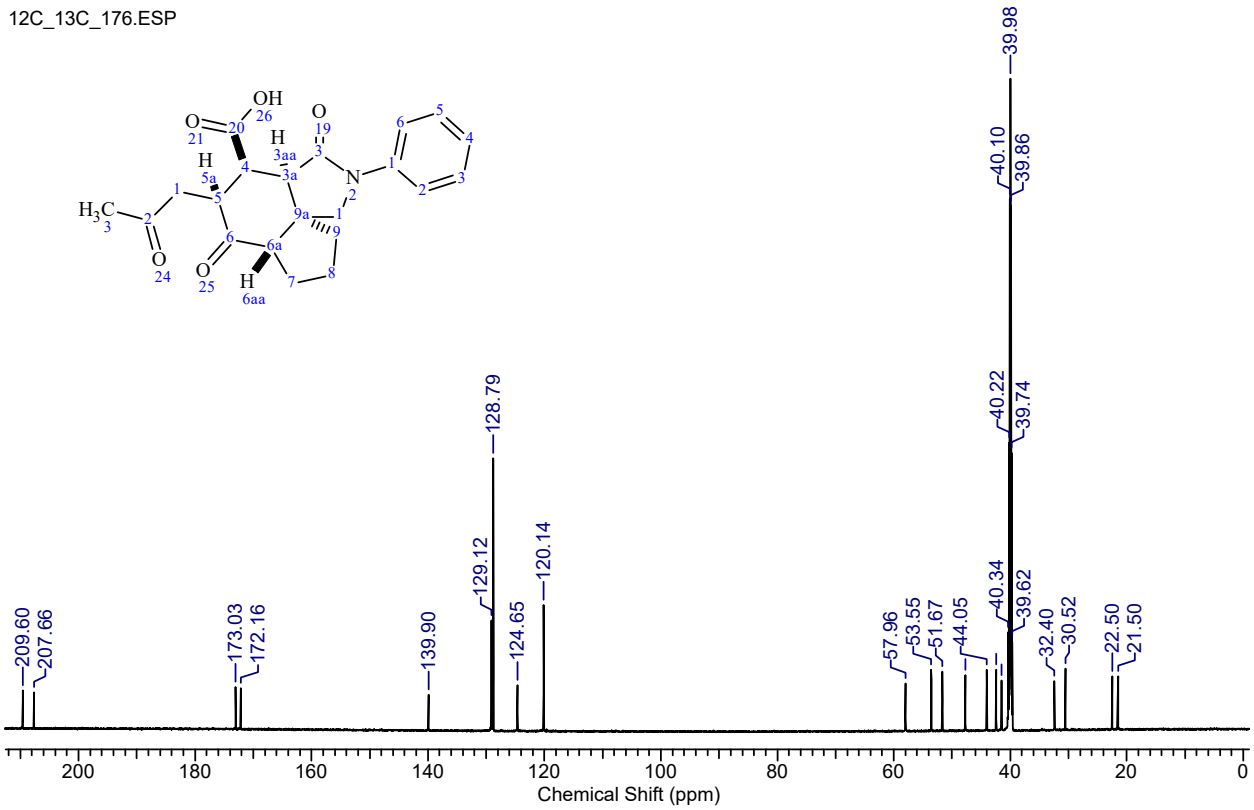

**(3a*RS*,6a*RS*,7*SR*,7a*RS*)-6-Oxo-5-phenyl-2,3,4,5,6,6a,7,7a-octahydro-1H-cyclopenta[*d*]furo[3,2-*f*]isoindole-7-carboxylic acid (28).** *Contains an impurity of benzene.*



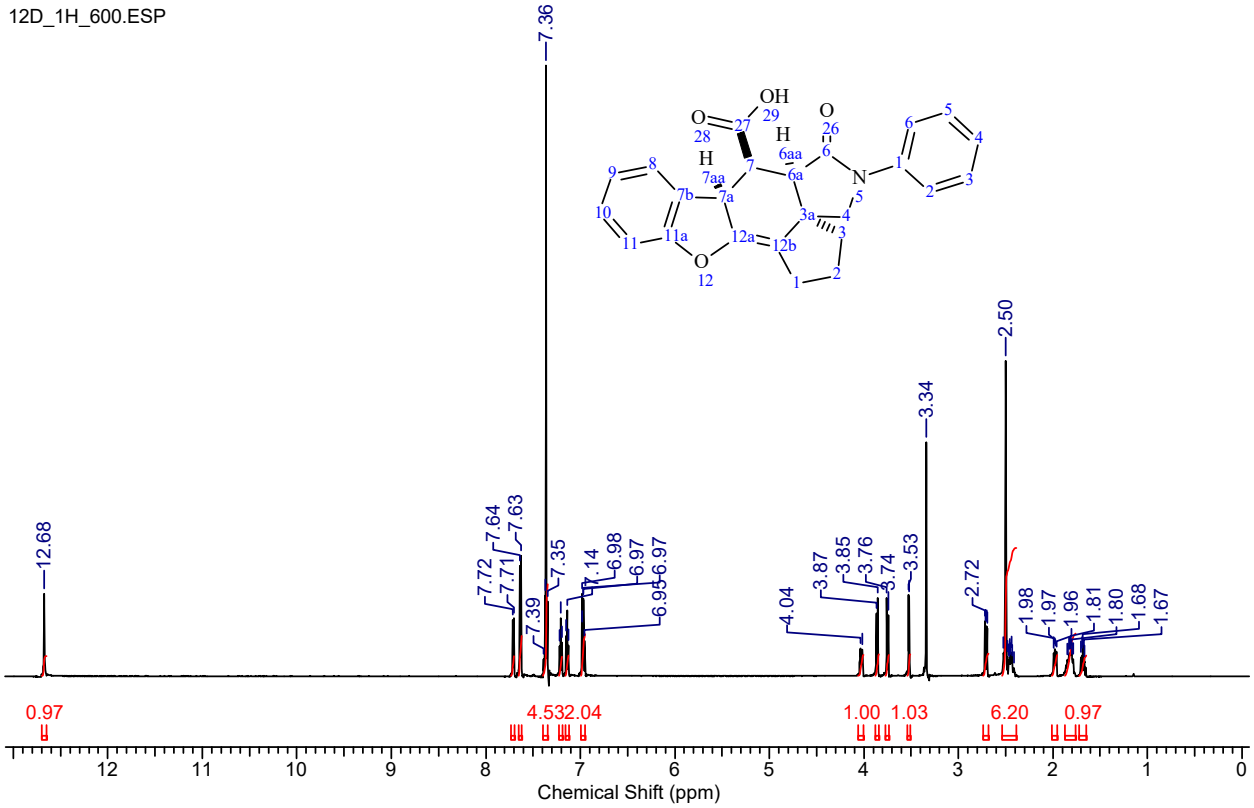


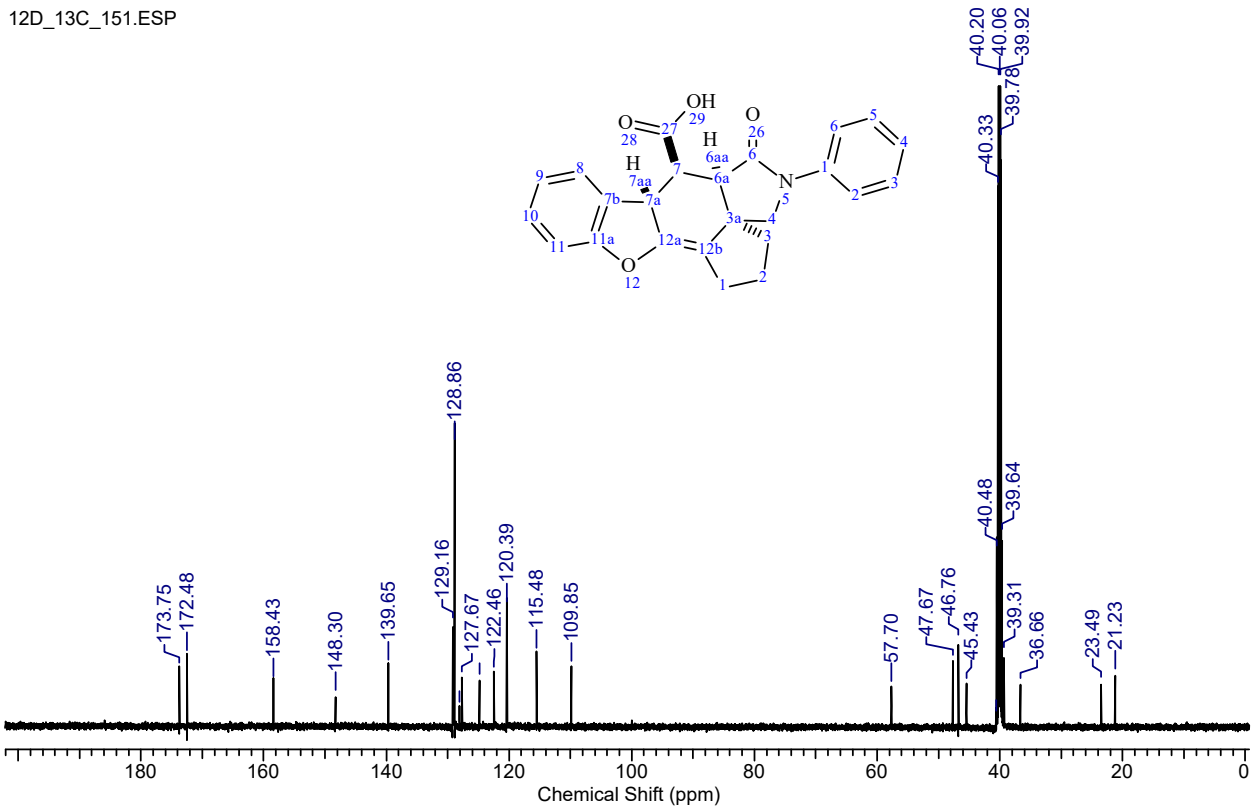

**(3a*RS*,4*RS*,5*RS*,6a*SR*,9a*SR*)-3,6-Dioxo-5-(2-oxopropyl)-2-phenyldecahydro-1*H*-cyclopenta[*d*]isoindole-4-carboxylic acid (12c).** *Contains an impurity of benzene.*



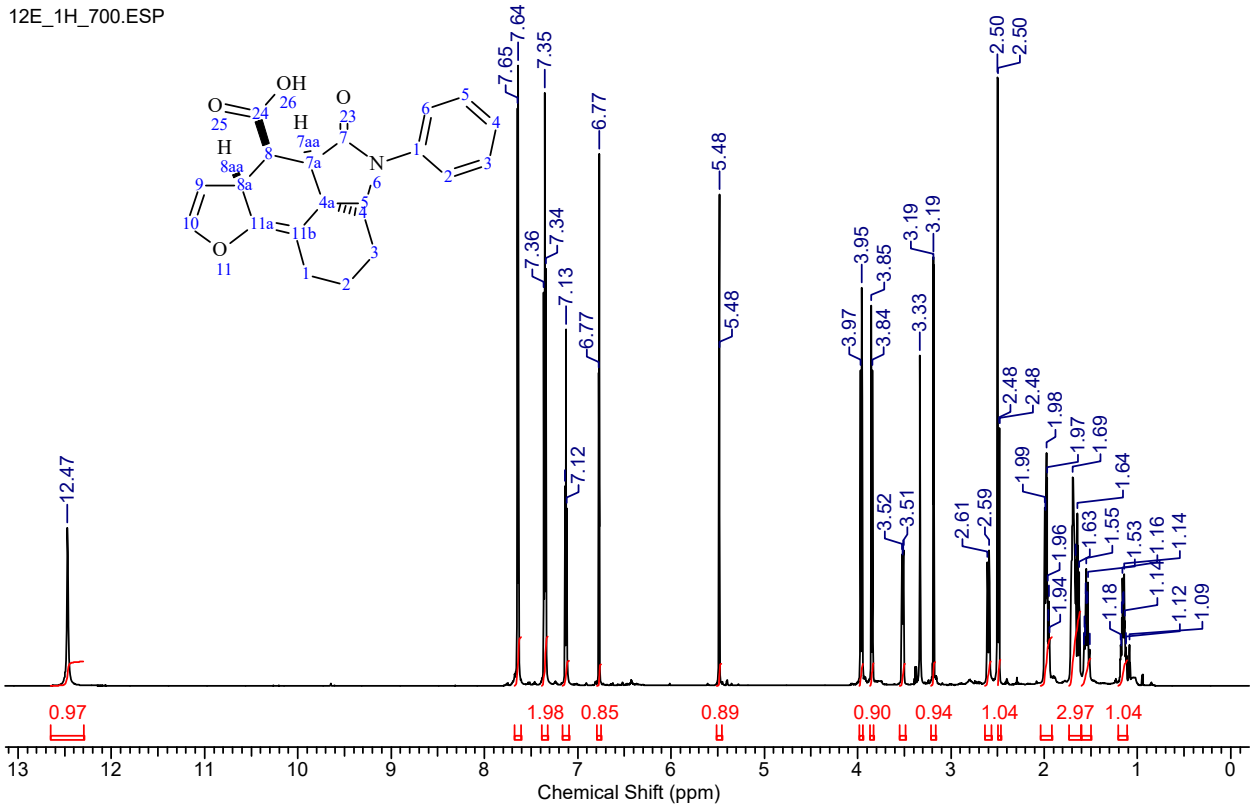


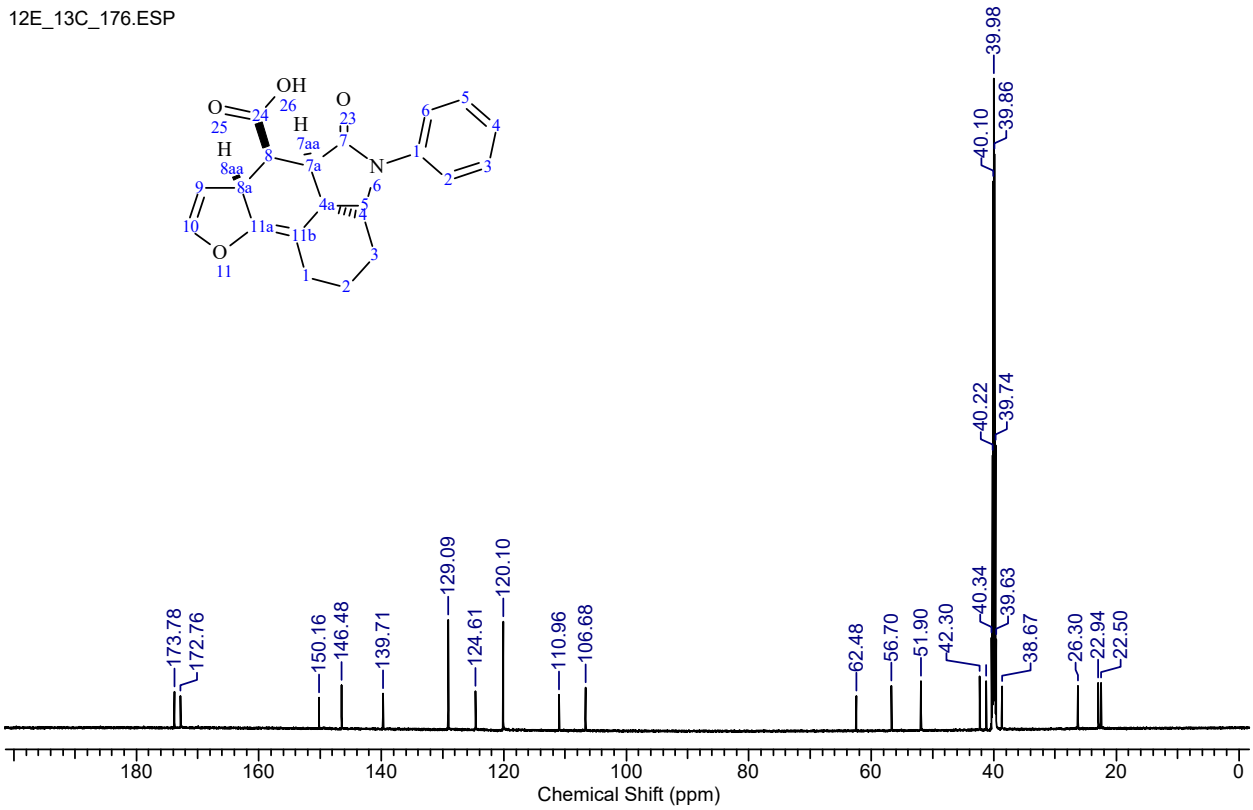

**(3a*RS*,6a*RS*,7*RS*,7a*SR*)-6-Oxo-5-phenyl-2,3,4,5,6,6a,7,7a-octahydro-1H-[1]benzofuro[2,3-*f*]cyclopenta[*d*]isoindole-7-carboxylic acid (12d).** *Contains an impurity of benzene.*



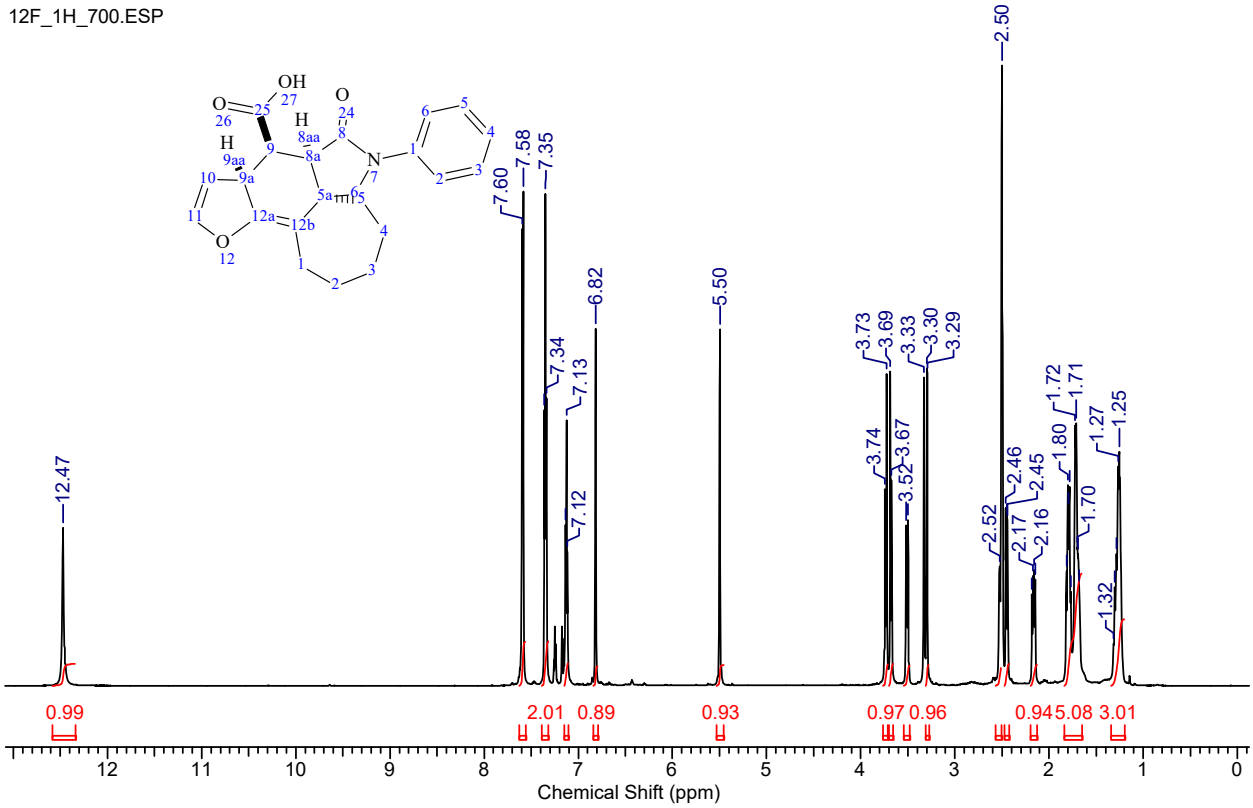


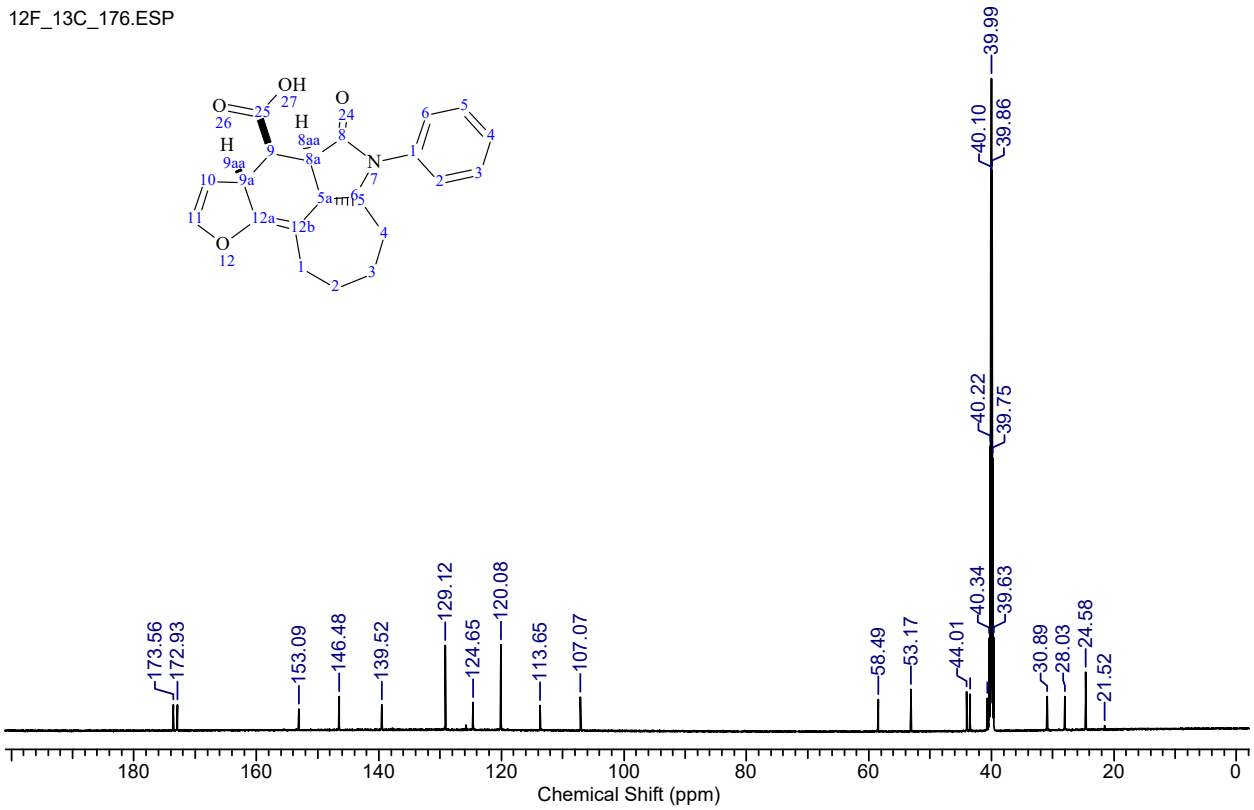

**(4a*RS*,7a*RS*,8*RS*,8a*RS*)-7-Oxo-6-phenyl-1,2,3,4,5,6,7,7a,8,8a-decahydrobenzo[*d*]furo[2,3-*f*]isoindole-8-carboxylic acid (12e).**



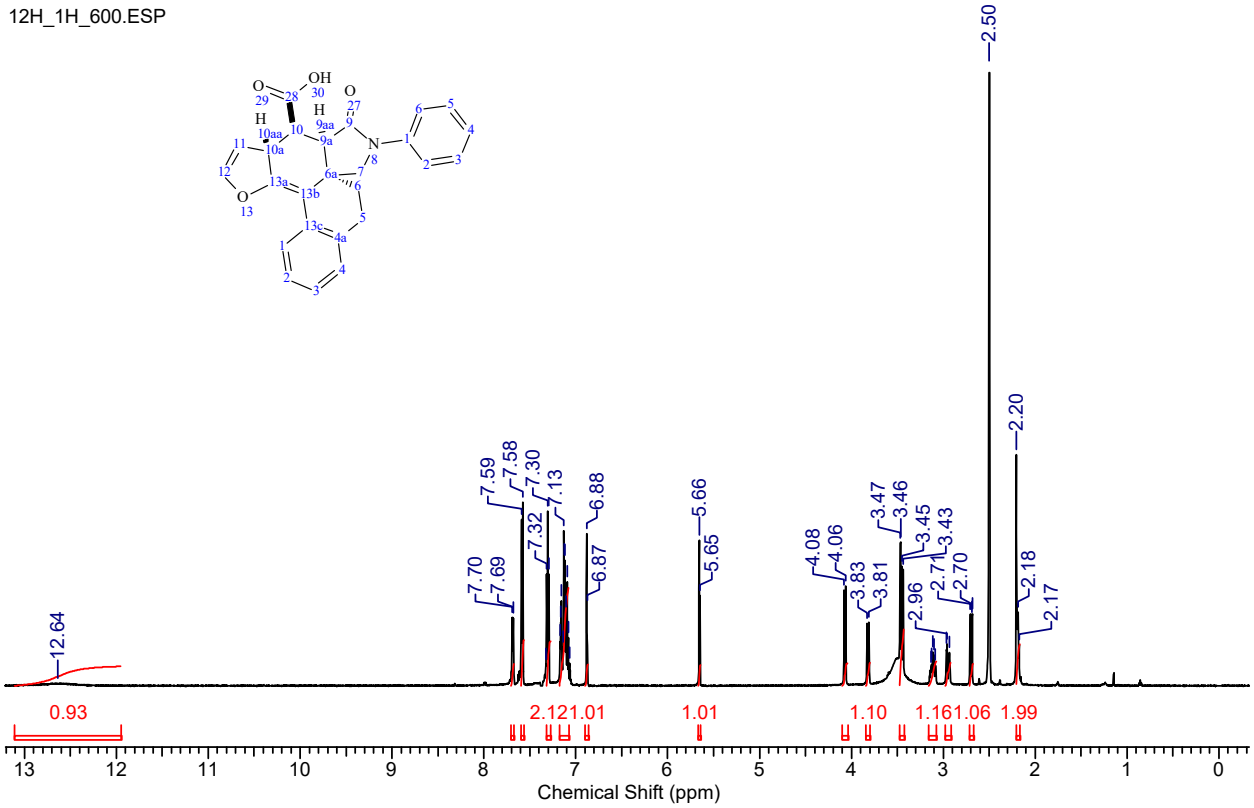


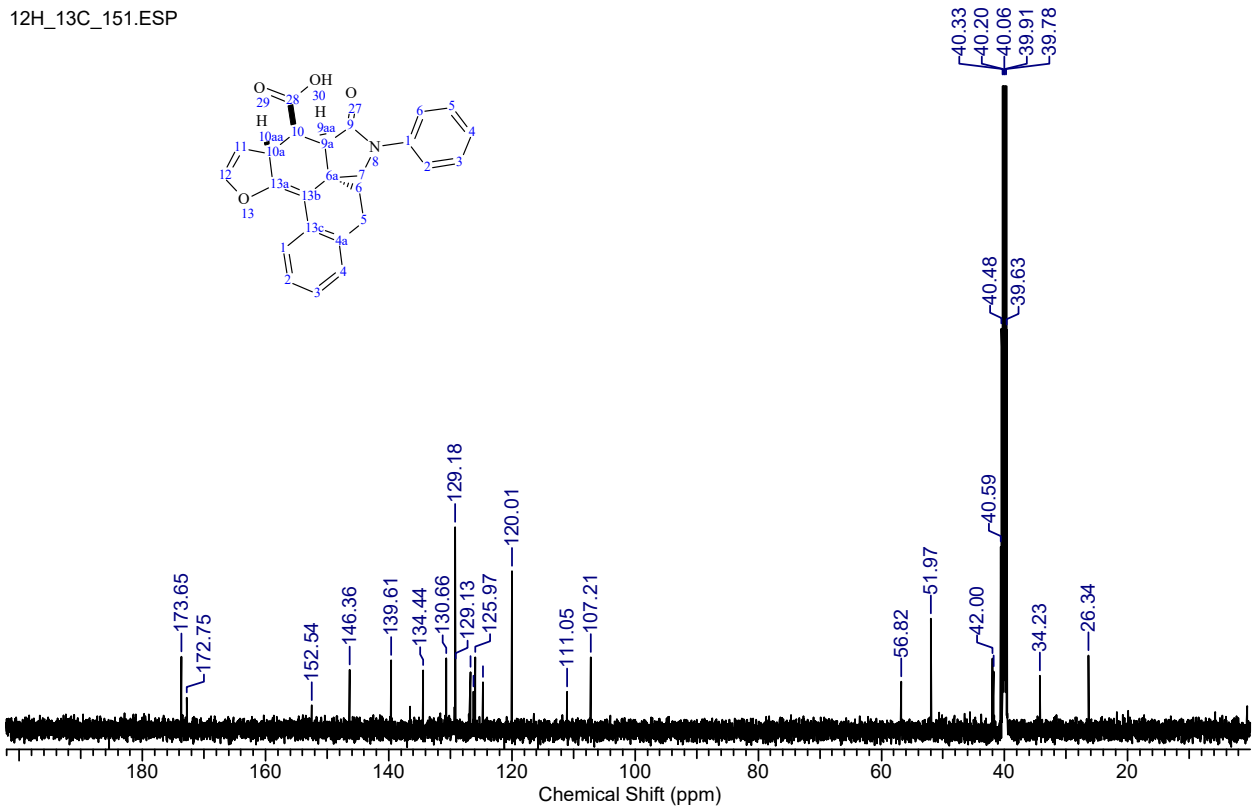

**(5a*RS*,8a*RS*,9*RS*,9a*RS*)-8-Oxo-7-phenyl-2,3,4,5,6,7,8,8a,9,9a-decahydro-1H-cyclohepta[*d*]furo[2,3-*f*]isoindole-9-carboxylic acid (12f).**






**(6a*RS*,9a*RS*,10*RS*,10a*RS*)-9-Oxo-8-phenyl-5,6,7,8,9,9a,10,10a-octahydrofuro[2,3-*f*]naphtho[2,1-*d*]isoindole-10-carboxylic acid (12h).**

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40.20
40.06
39.91
39.78
40.48
39.63
40.59
129.18
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173.65
172.75
152.54
146.36
139.61
134.44
130.66
129.13
125.97
111.05
107.21
56.82
51.97
42.00
34.23
26.34
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)