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Synthesis of Asymmetric Indolonaphthyridines with Enhanced Excited State Charge-Transfer Character

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Synthesis

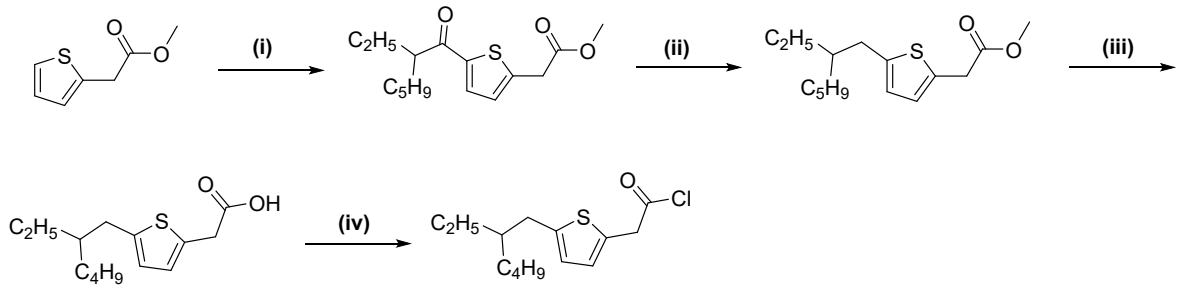
General

^{1}H NMR spectra were recorded on a 400 MHz Avance III HD Spectrometer in the stated solvent using residual protic solvent as the internal standard. ^{1}H NMR chemical shifts are reported to the nearest 0.01 ppm. The coupling constants (*J*) are measured in Hertz. ^{13}C NMR spectra were recorded on the 500 MHz DCH Cryoprobe Spectrometer in the stated solvent using the residual protic solvent as the internal standard. ^{13}C NMR chemical shifts are reported to the nearest 0.1 ppm. Mass spectra were obtained using a Waters LCT, Finnigan MAT 900XP or Waters MALDI micro MX spectrometer at the Department of Chemistry, University of Cambridge. Reactions requiring an inert atmosphere were carried out under argon. Thin layer chromatography (TLC) was carried out on silica gel and visualized using UV light (254, 365 nm). Flash chromatography was carried out on a Biotage® Isolera automated flash chromatography machine on 60 micron silica gel cartridges purchased from Biotage®.

Chemicals

All commercial chemicals were of ≥95% purity and were used as received without further purification. Anhydrous solvents were purchased from Sigma Aldrich or Acros Organics and used as received.

2-(5-(2-Ethylhexyl)thiophen-2-yl)acetyl chloride synthesis

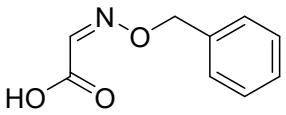


Scheme S1. *Synthesis of 2-(5-(2-ethylhexyl)thiophen-2-yl)acetyl chloride*. Reagents and conditions: (i) 2-ethylhexanoyl chloride (1.5 equiv), aluminium trichloride (1.5 equiv), DCM, 0 ° C → r.t., 2 h, (45 %) (ii) Triethylsilane (4 equiv), trifluoroacetic acid, r.t., 12 h (81 %). (iii) 10 % Sodium hydroxide solution (10 equiv), hydrochloric acid, tetrahydrofuran, r.t., (57 %). (iv) Thionyl chloride (3 equiv), DMF (1 drop), DCM, reflux, 3 h (R_1 = 82 %, R_2= 82 %).

Procedures

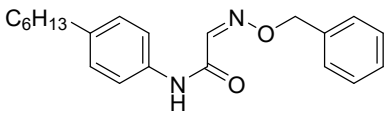
*Preparation of **5** was based on literature route and NMR data obtained in this work was in full accordance with what had been reported.*[1] *Clear ^{13}C spectra of **11** and **8** could not be obtained due to aggregation at required concentration for analysis.*

(*Z*)-2-((Benzyloxy)imino)acetic acid (2)



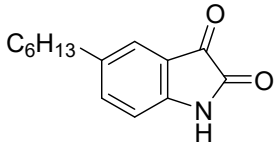
Under normal atmospheric conditions, glyoxylic acid (13.80 g, 0.19 mol) was added to a solution of O-benzylhydroxylamine hydrochloride (15 g, 0.12 mol) in distilled water (200 mL). After stirring at RT for 2 h, the solution was extracted with DCM (×2100 mL), and the combined organic extracts washed with brine (×2 50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was taken up in cold hexane and the title compound was collected by vacuum filtration as a white solid (11.98 g, 36%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.04 (s br, 1H), 7.55 (s, 1H), 7.44 – 7.31 (m, 5H), 5.32 (s, 2H)

(*Z*)-2-((Benzyloxy)imino)-*N*-(4-hexylphenyl)acetamide (3)



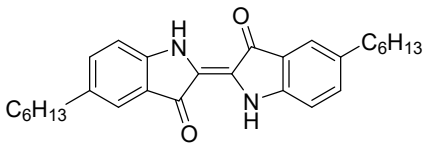
Thionyl chloride (14.53 mL, 0.2 mol) was added to a solution of iminoacetic acid **5** (11.98 g, 66.92 mmol), in anhydrous DCM (25 mL) and anhydrous DMF (1 drop, cat.) and the reaction was heated at reflux under argon for 2 h. The corresponding acetyl chloride was isolated *in vacuo* as a dark yellow oil which was used immediately without further purification. To a solution of 4-hexylaniline (11.86 g, 66.92 mmol) in anhydrous DCM (40 mL) was added DIPEA (12.7 mL, 73.08 mmol). The solution was cooled using an ice bath whilst a solution of the prepared acetyl chloride in anhydrous DCM (40 mL) was added dropwise. The reaction was allowed to warm to RT naturally and stirred overnight. The reaction was quenched carefully with methanol (15 mL), diluted with DCM (100 mL) and extracted with water (×3 100 mL). The organic layer was washed with brine (×2 50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was recrystallised from hexane to give the title compound as a white solid (14.98 g, 66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s br, 1H), 7.55 (s, 1H), 7.48 – 7.46 (d, *J* = 8.4 Hz , 2H), 7.42 – 7.35 (m, 5H), 7.15 (d, *J* = 8.4 Hz, 2H), 5.26 (s, 2H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.63 – 1.55 (m, 4H), 1.37 – 1.24 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) 159.4, 144.0, 139.6, 136.3, 134.7, 129.1, 128.8, 128.7,128.5, 120.0, 77.8, 35.6, 31.9, 31.6, 29.1, 22.8, 14.3. **HRMS** Found (TOF MS+): $[M+H]^+$ 339.2069, $C_{21}H_{27}N_2O_2$ requires 339.2073.

5-Hexylindoline-2,3-dione (4)



Under normal atmospheric conditions, acetamide **6** (14.98 g, 44.24 mmol) was added portionwise to conc. H_2SO_4 (44.94 mL, 3 mL/g) and heated to 50 °C over 1 h. The reaction temperature was increased to 80 °C for 10 min, then cooled to RT. The viscous purple mixture was added portionwise to 300 g of ice with vigorous stirring, precipitating a bright orange solid. The suspension was extracted with EtOAc (×3 100 mL). The combined organic extracts were washed with brine (50 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The residue was recrystallised from hexane to give the title compound as an orange solid (6.17 g, 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (s br, 1H), 7.44 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.62 – 1.54 (m, 2H), 1.37 – 1.19 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (150 MHz, CDCl3) 183.5, 160.0, 147.4, 139.2, 139.0, 125.6, 112.4, 35.3, 31.8, 31.4, 28.9, 22.7, 14.2. **HRMS** Found (TOF MS+): $[M+H]^+$ 232.1342, $C_{14}H_{18}NO_2$ requires 232.1338.

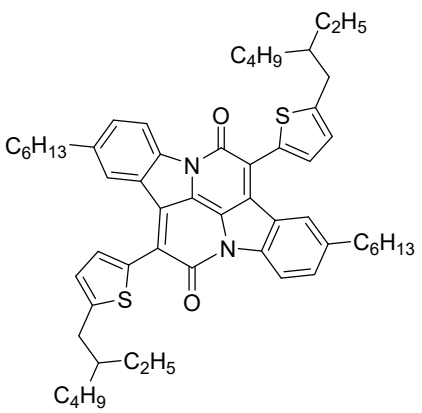
(*E*)-5,5'-Dihexyl-[2,2'-biindolinylidene]-3,3'-dione (5)



To a solution of isatin **7** (6.17 g, 26.7 mmol) in anhydrous toluene (260mL) under argon was added phosphorus pentachloride (6.17 g, 11.3 mmol) in one portion. The reaction was heated to 100 °C for

3.5 h, then cooled to 50 °C. To the dark red solution was added thiophenol (2.5 mL, 23.8 mmol) in one portion, turning the reaction green. The reaction was heated at 50 °C for 16 h then cooled. Methanol (150 mL) was then added to precipitate the title compound as a blue solid which was collected by vacuum filtration (826 mg, 18 %). ^{1}H NMR (400 MHz, CDCl3) δ 8.82 (s, 2H), 7.53 (s, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 8.3 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 4H), 1.37 – 1.64 (m, 4H), 1.28 – 1.35 (m, 12H), 0.88 (t, *J* = 6.7 Hz, 6H). **HRMS** Found (TOF MS+): $[M+H]^+$ 431.2703, $C_{28}H_{35}N_2O_2$ requires 431.2699.

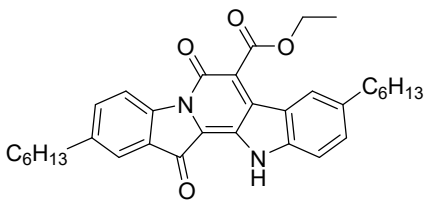
7,14-Bis(5-(2-ethylhexyl)thiophen-2-yl)-2,9-dihexyldiindolo[3,2,1-*de*:3',2',1'-*ij*][1,5]naphthyridine-6,13-dione (6)



S-INDT

Under normal atmospheric conditions, a solution of acid chloride **4** (2.17 g, 8 mmol) in xylenes (5 mL) was added dropwise to a refluxing solution of Hexyl-Indigo **8** (317 mg, 0.74 mmol) in xylenes (15 mL). The reaction was heated under reflux overnight and then allowed to cool to room temperature. The xylenes were removed *in vacuo* and the residue passed through a silica plug eluting with chloroform. The fractions containing a purple solution were collected and the solvent removed *in vacuo*. The crude residue was dry loaded onto a silica column and eluted with 0 → 20 % Chloroform:Hexane over five column lengths. The fractions containing a dark purple solution were collected and the solvent removed *in vacuo*. The residue was columned a second time using 0 → 10 % EtOAc:Hexane and again the purple fractions were collected and the solvent removed *in vacuo*. The residue was precipitated from MeOH and the dark solid collected by vacuum filtration. The crude solid was recrystallised from EtOH to give the product as a dark purple crystalline solid (20 mg, 0.02 mmol, 4 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.3 Hz, 2H), 8.03 (s, 2H), 7.60 (d, *J* = 3.5 Hz, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 3.5 Hz, 2H), 2.90 (d, *J* = 6.6 Hz, 4H), 2.65 (t, *J* = 6.7 Hz, 4H), 1.72-1.79 (m, 2H), 1.61 – 1.64 (m, 4H), 1.25-1.48 (m, 28H), 0.87-0.96 (m, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.0, 150.2, 142.3, 141.3, 132.7, 132.3, 130.3, 129.7, 126.3, 125.0, 124.9, 124.8, 122.1, 117.6, 41.7, 36.0, 34.6, 32.7, 31.8, 31.5, 31.1, 29.1, 29.0, 25.9, 23.2, 22.8, 14.4, 14.3, 11.1. **HRMS** Found (TOF MS+): $[M+H]^+$ 867.4946, $C_{56}H_{71}N_2O_2S_2$ requires 867.4957.

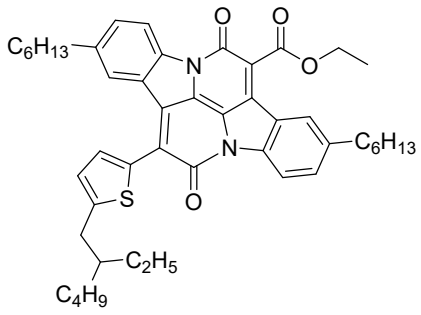
Ethyl 2,9-dihexyl-6,13-dioxo-12,13-dihydro-6*H*-pyrido[1,2-*a*:3,4-*b*']diindole-7-carboxylate (7)



NaH 60 % dispersion in mineral oil (174 mg, 7.3 mmol) was added to a stirred solution of hexyl-indigo **8** (500 mg, 1.2 mmol) in dry DMF (24 mL). Once effervescence ceased, diethyl malonate (742 mg, 4.8 mmol) was added dropwise and the reaction mixture heated to reflux. After 30 min the reaction was cooled and then diluted with water (50 mL) and acidified with hydrochloric acid. The suspension was

filtered leaving a purple residue which was washed with small amounts of MeOH leaving **9** as a dark purple solid (255 mg, 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s 1H), 8.54 (d, *J* = 8.3 Hz, 1H), 7.60 (s, 1H), 7.57 (s, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 1H), 4.62 (q, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 6.7 Hz, 2H), 2.61 (t, *J* = 6.7 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.25-1.41 (m, 16H), 0.88 (t, *J* = 6.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 207.3, 182.5, 165.3, 155.1, 145.2, 142.0, 139.3, 137.0, 136.7, 133.9, 129.1, 124.9, 124.8, 124.5, 123.8, 118.8, 118.5, 116.4, 111.6, 62.6, 35.8, 35.6, 31.9, 31.8, 31.4, 31.1, 29.0 (2C), 22.8 (2C), 14.5, 14.3. **HRMS** Found (TOF MS+): $[M+H]^+$ 527.2891, $C_{33}H_{39}N_2O_4$ requires 527.2910.

Ethyl 14-(5-(2-ethylhexyl)thiophen-2-yl)-2,9-dihexyl-6,13-dioxo-6,13-dihydrodiindolo[3,2,1-*de*:3',2',1'-*ij*][1,5]naphthyridine-7-carboxylate (8)

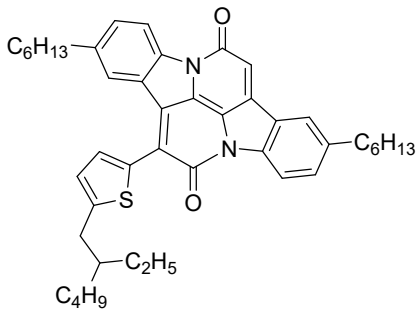


AE-INDT

Under normal atmospheric conditions, a solution of acid chloride **4** (660 mg, 2.5 mmol) in xylene (3 mL) was added dropwise to a refluxing solution of half-annulated indigo **9** (255 mg, 0.5 mmol) in xylenes (15 mL). The reaction was heated under reflux overnight and then allowed to cool to room temperature. The xylenes were removed *in vacuo* and the residue passed through a silica plug eluting with 50 % chloroform in hexane. The fractions containing a bright purple solution were collected and the solvent removed *in vacuo*. The crude residue was dry loaded onto a silica column and eluted with 0 → 20 % EtOAc in Hexane over five column lengths. The fractions containing a bright purple solution were collected and the solvent removed *in vacuo*. The product was precipitated from MeOH, air dried and collected as a dark purple solid (125 mg, 0.17 mmol, 35 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.3 Hz, 1H), 8.36 (d, *J* = 8.3 Hz, 1H), 8.10 (s 1H), 8.04 (s 1H), 7.68 (d, *J* = 3.5 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 6.96 (d, *J* = 3.5 Hz, 1H), 4.60 (q, *J* = 7.1 Hz, 2H), 2.91 (d, *J* = 6.7 Hz, 2H),

2.72 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 6.7 Hz, 3H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.46-1.72 (m, 15H), 1.16-1.41 (m, 17 H), 0.83-0.96 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.6, 158.4, 157.7, 152.1, 142.9, 142.4, 142.0, 141.6, 136.5, 133.7, 132.7, 132.2, 131.2, 129.3, 129.0, 128.3, 125.7, 125.6, 125.1, 124.7, 120.3, 118.1, 117.8, 117.3, 62.1, 41.7, 36.2, 36.0, 34.7, 32.7, 32.1, 31.9, 31.8, 31.7, 31.5, 31.1, 29.9, 29.9, 29.6, 29.1 (2C), 29.0, 25.9, 23.2, 22.9, 22.8, 14.6, 14.3 (3C),11.1. **HRMS** Found (TOF MS+): $[M+H]^+$ 745.4036, $C_{47}H_{57}N_2O_4S$ requires 745.4039.

7-(5-(2-Ethylhexyl)thiophen-2-yl)-2,9-dihexyldiindolo[3,2,1-*de*:3',2',1'-*ij*][1,5]naphthyridine-6,13-dione (9)

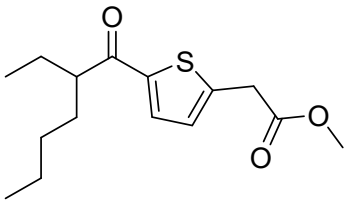


AH-INDT

10 (80 mg, 0.1 mmol) was coated on the surface of a 25 mL RBF and 47 % HBr was added. The mixture was heated to reflux for 2 h under normal atmospheric conditions and then allowed to cool to room temperature leaving a black solid suspension. 15 mL of H_2O was added to the suspension and then transferred into a separating funnel followed by DCM (100 mL). The organic layer was removed, washed with H_2O (100 mL) followed by brine (100 mL) and dried over $MgSO_4$. The solvent was removed

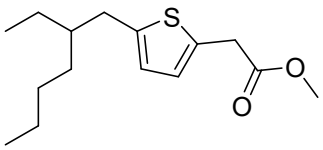
in vacuo and the solid precipitated from MeOH and air dried to give the product as a dark purple solid (20 mg, 0.03 mmol, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 14.76 (s 1H), 9.17 (s 1H), 8.43 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.3 Hz, 1H), 8.12 (s, 2H), 7.78 (d, *J* = 3.7 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.44 (d, *J* = 8.3 Hz, 1H), 7.00 (d, *J* = 3.7 Hz, 1H), 2.93 (d, *J* = 6.7 Hz, 2H), 2.75 (t, *J* = 6.7 Hz, 3H), 2.69 (t, *J* = 6.7 Hz, 3H), 1.60 -.179 (m, 6H), 1.27 – 1.45 (m, 20 H), 0.84 – 0.97 (m, 12H). Unable to obtain carbon as signal to noise ratio too high. **HRMS** Found (TOF MS+): $[M+H]^+$ 673.3828, $C_{44}H_{53}N_2O_2S$ requires 673.3828.

Methyl 2-(5-(2-ethylhexanoyl)thiophen-2-yl)acetate (10)



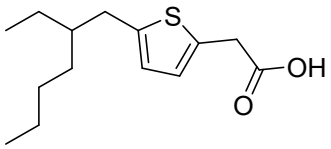
To a solution of methyl-2(thiophen-2-yl)acetate (12.4 g, 80 mmol) in DCM (100 mL) was added 2-ethylhexanoyl chloride (19.4 g, 120 mmol) in one portion followed by $AlCl_3$ (16.0 g, 120 mmol) in three portions at 0 °C under inert atmosphere. The reaction was warmed to room temperature and stirred for 2 hr. The reaction was quenched carefully using water (100 mL) and extracted three times using CH_2Cl_2 (100 mL). The organic phase was washed with brine (100 mL) and then dried over anhydrous $MgSO_4$ and purified by column chromatography eluting with 50 % chloroform in hexane to give the product as an orange oil (9.6 g, 35.8 mmol, 45 %). ^{1}H NMR (400 MHz, CDCl3) δ 7.59 (d, *J* = 3.7, 1H), 6.99 (d, *J* = 3.7, 1H), 3.86 (s, 2H), 3.75 (s, 3H), 3.08 (m, 1H), 1.54-1.79 (m, 8H), 0.87-0.94 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 207.3, 197.5, 181.6, 170.2, 145.2, 144.1, 131.7, 128.3, 52.7, 49.9, 47.1, 36.0, 31.7, 29.7, 25.4. **HRMS** Found (TOF MS+): $[M+H]^+$ 283.1380, $C_{15}H_{23}O_3S$ requires 283.1368.

Methyl 2-(5-(2-ethylhexyl)thiophen-2-yl)acetate (11)



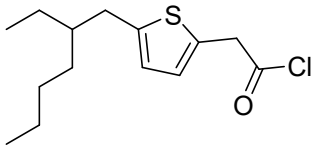
1 (7.4 g, 27.6 mmol) was dissolved in trifluoroacetic acid (TFA) (54 mL) and Et_3SiH (12.3 g, 105 mmol) was added dropwise under inert atmosphere. The mixture was stirred at room temperature overnight and then the TFA was removed under reduced pressure followed by an extraction using diethyl ether (×2 200 mL). The organic phase was washed three times with saturated $NaHCO_3$ solution (100 mL), followed by water (200 mL), brine (×2 100 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the crude purified by column chromatography eluting with 25 % chloroform in hexane yielding the product as a colourless oil (6 g, 24.6 mmol, 81 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 3.7 Hz, 1H), 6.59 (d, *J* = 3.7 Hz, 1H), 3.77 (s, 2H), 3.72 (s, 3H), 2.70 (d, *J* = 6.6 Hz, 2H), 2.31 (m, 1H), 1.48-1.69 (m, 8H), 0.87-0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.0, 171.4, 144.5, 132.6, 126.5, 124.9, 52.4, 47.0, 41.5, 35.7, 34.2, 32.5, 31.7, 29.7, 29.0, 25.7, 23.2. **HRMS** Found (TOF MS+): $[M+H]^+$ 269.1577, $C_{15}H_{25}O_2S$ requires 269.1575.

2-(5-(2-Ethylhexyl)thiophen-2-yl)acetic acid (12)

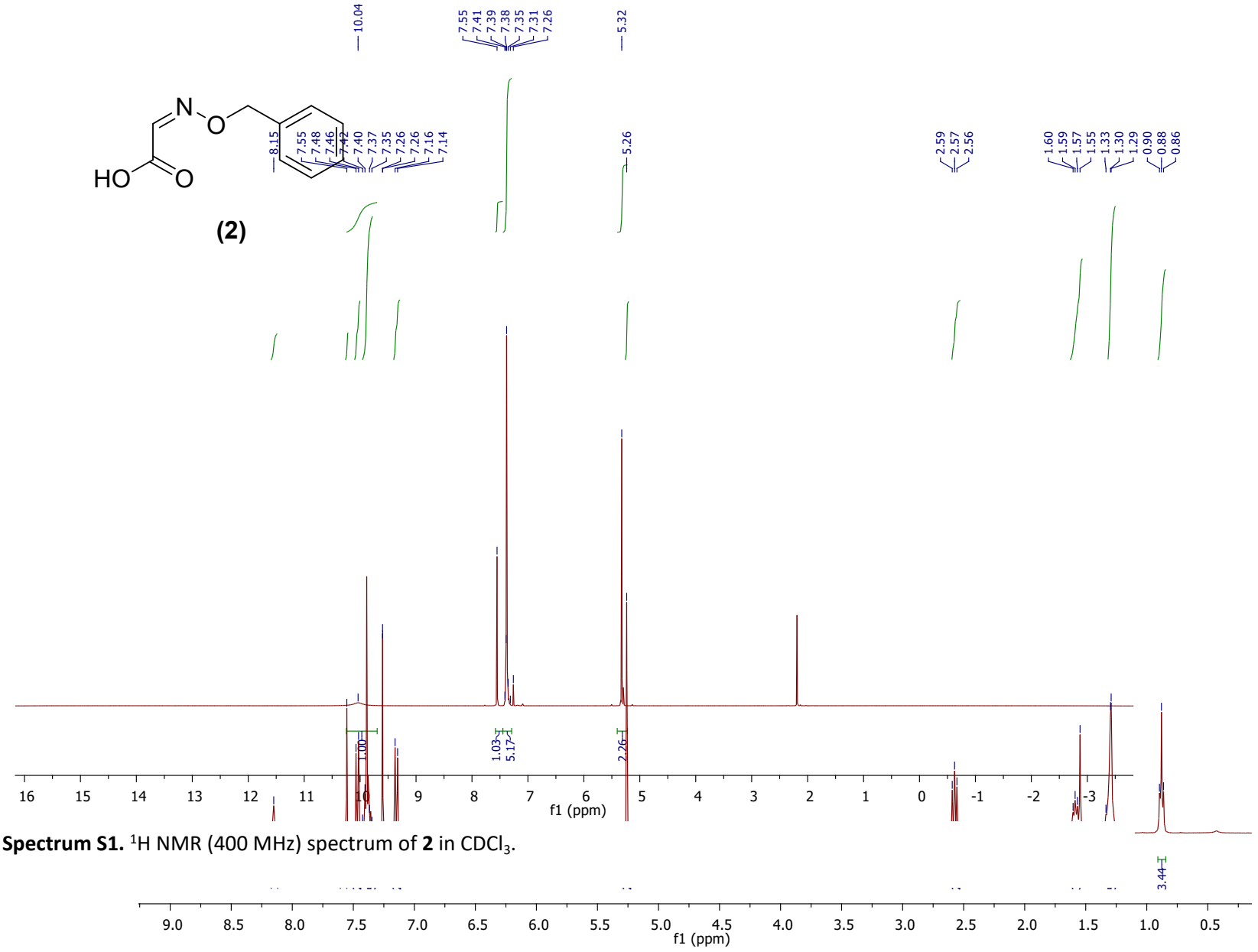


To a solution of **2** (6.0 g, 22.4 mmol) in THF (50 mL) was added 2.8 M NaOH (50 mL) and the reaction stirred overnight under normal atmospheric conditions. The solvent was removed under reduced pressure and then 1 M HCl was added until a pH of 1 was achieved. The crude was extracted three times using CH_2Cl_2 (100 mL) and the organic phase washed with brine (×2 100 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure yielding 23 as a pale yellow oil (3.27 g, 12.8 mmol, 57 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (d, *J* = 3.7 Hz, 1H), 6.61 (d, *J* = 3.7 Hz, 1H), 3.81 (s, 2H), 2.70 (d, *J* = 6.6 Hz, 2H), 2.27-2.23 (m, 1H), 1.29-1.35 (m, 8H), 0.87-0.94 (m, 6H). 13C NMR (150 MHz, CDCl3) ^{13}C NMR (101 MHz, $CDCl_3$) δ 182.2, 176.2, 144.8, 131.8, 126.9, 125.0, 47.1, 41.5, 35.4, 34.2, 32.5, 29.0, 25.7, 23.2. **HRMS** Found (TOF MS+): $[M+H]^+$ 255.1423, $C_{14}H_{23}O_2S$ requires 255.1419.

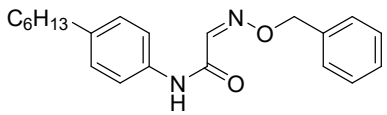
2-(5-(2-Ethylhexyl)thiophen-2-yl)acetyl chloride (13)



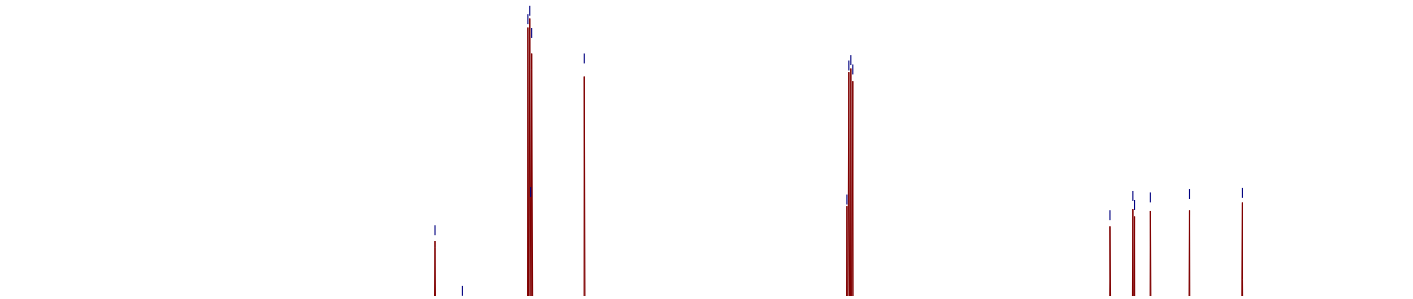
Thionyl chloride (4.51 g, 37.83 mmol) was added to a solution of **3** (2 g, 7.9 mmol), in anhydrous DCM (20 mL) and anhydrous DMF (1 drop, cat.) and the reaction was heated at reflux under argon for 2 h. The corresponding acetyl chloride was isolated *in vacuo* as a dark yellow oil (2 g, 7.4 mmol, 93 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (d, *J* = 3.7 Hz, 1H), 6.64 (d, *J* = 3.7 Hz, 1H), 4.27 (s, 2H), 2. (d, *J* = 6.6 Hz, 2H), 1.71-1.81 (m, 1H), 1.28-1.43 (m, 8H), 0.87-0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 146.0, 129.5, 128.1, 125.3, 125.2, 58.9, 47.4, 41.5, 34.3, 32.5, 29.0, 25.7, 23.2. **HRMS** Found (TOF MS+): $[M+H]^+$ 273.1075, $C_{14}H_{22}OSCl$ requires 273.1080.



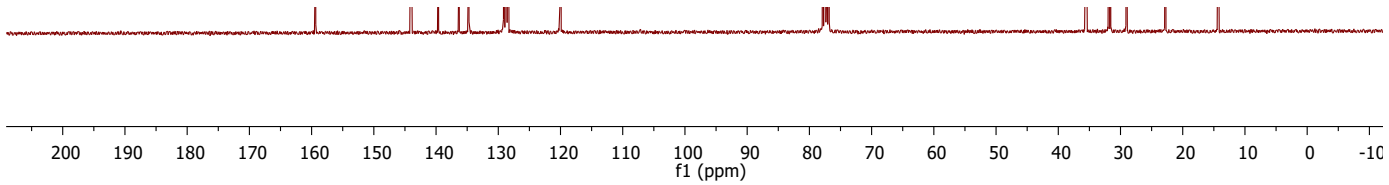
Spectrum S1. ^{1}H NMR (400 MHz) spectrum of **2** in $CDCl_3$.



(3)



Spectrum S2. ^{1}H NMR (400 MHz) spectrum of **3** in $CDCl_3$.



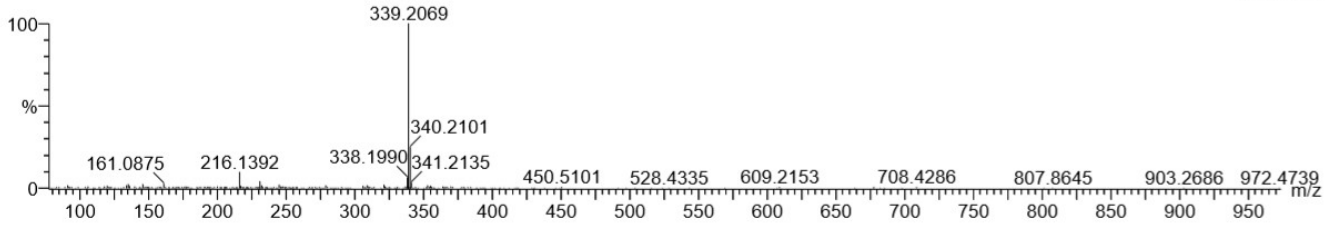
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
46 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-21 H: 0-27 N: 0-2 O: 0-2 P: 0-1 Cl: 0-1

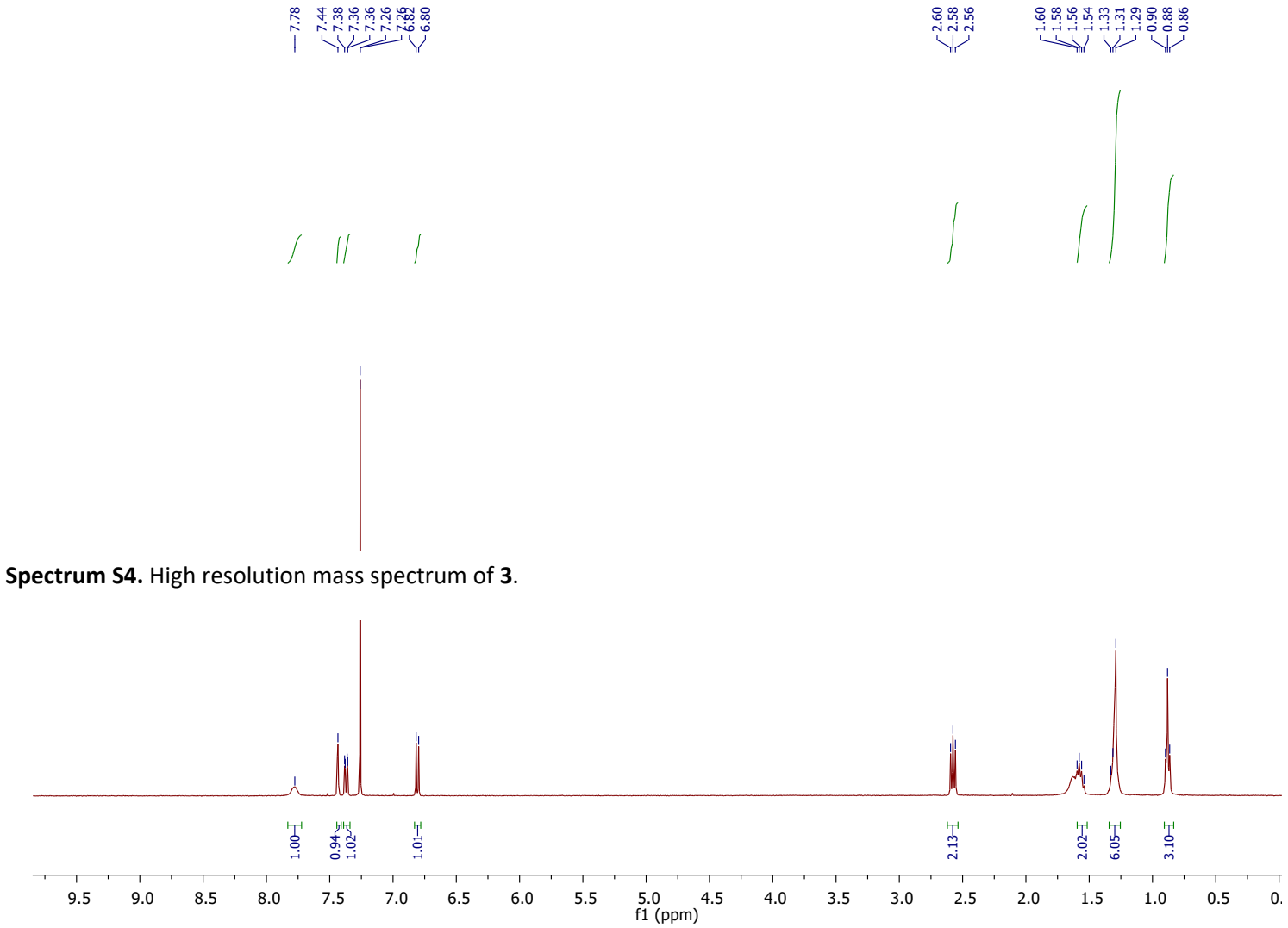
HAB_46707 M Purdy mp9-IAA
HAB_46707 M Purdy mp9-IAA 775 (1.690) Cm (731:836)

1: TOF MS ASAP+
3.46e+004

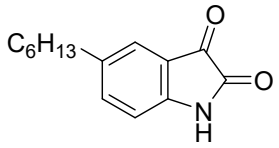


Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
339.2069	339.2073	-0.4	-1.2	9.5	111.1	n/a	n/a	C21 H27 N2 O2

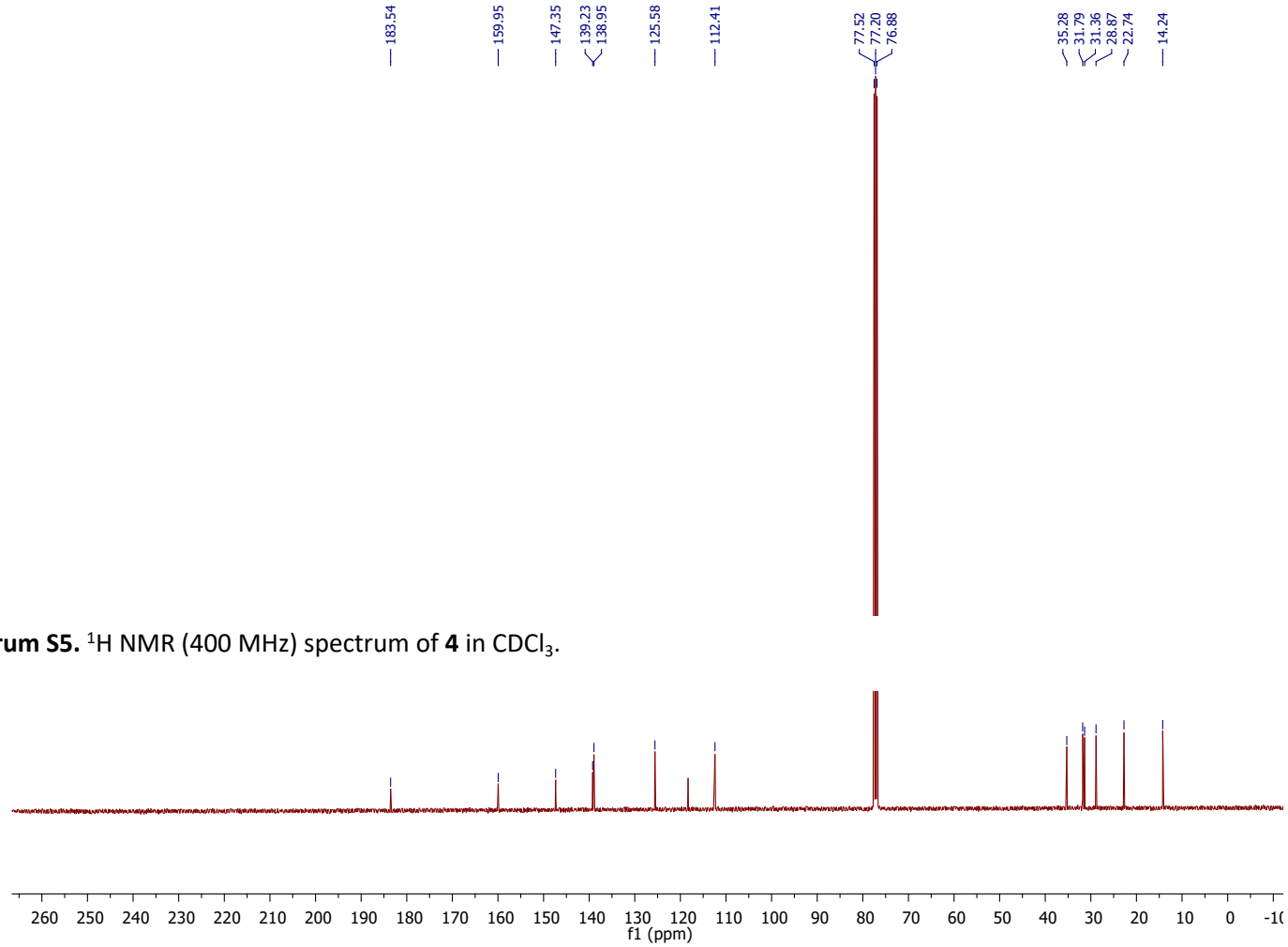
Spectrum S3. ^{13}C NMR



Spectrum S4. High resolution mass spectrum of **3**.



(4)



Spectrum S5. ^{1}H NMR (400 MHz) spectrum of **4** in $CDCl_3$.

Elemental Composition Report **Page 1**

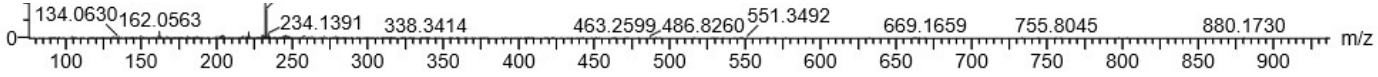
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
86 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-21 H: 0-27 N: 0-2 O: 0-2 P: 0-1 Cl: 0-1

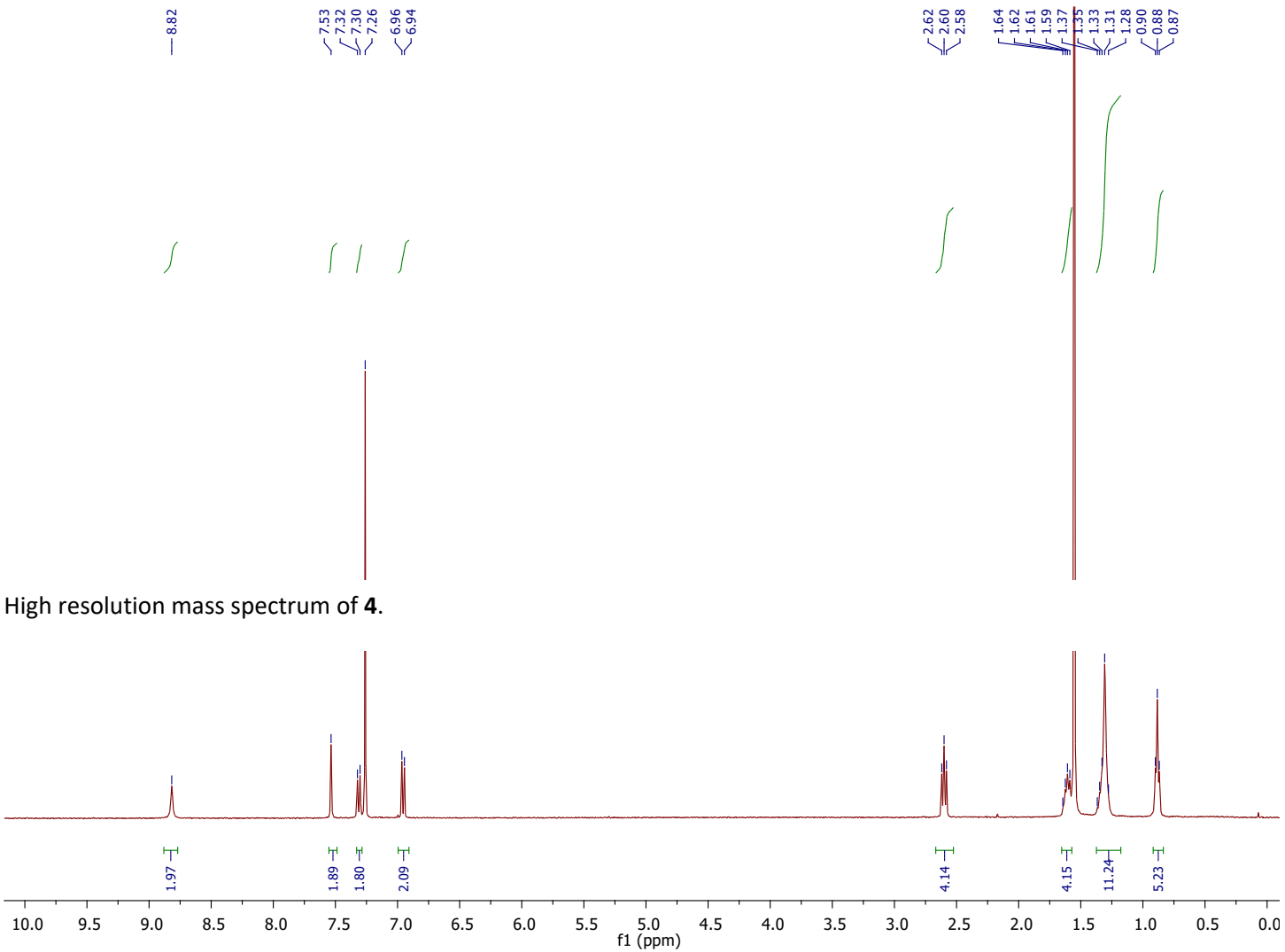
HAB_46706 M Purdy mp-Isa
HAB_46706 M Purdy mp-Isa 610 (1.337) Cm (603:688)

1: TOF MS ASAP+
2.27e+005

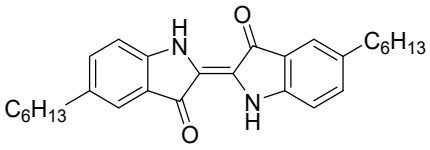
Spectrum S6. ^{13}C NMR (400 MHz) spectrum of **4** in $CDCl_3$.



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
232.1342	232.1338	0.4	1.7	6.5	277.7	n/a	n/a	C14 H18 N O2



Spectrum S7. High resolution mass spectrum of **4**.



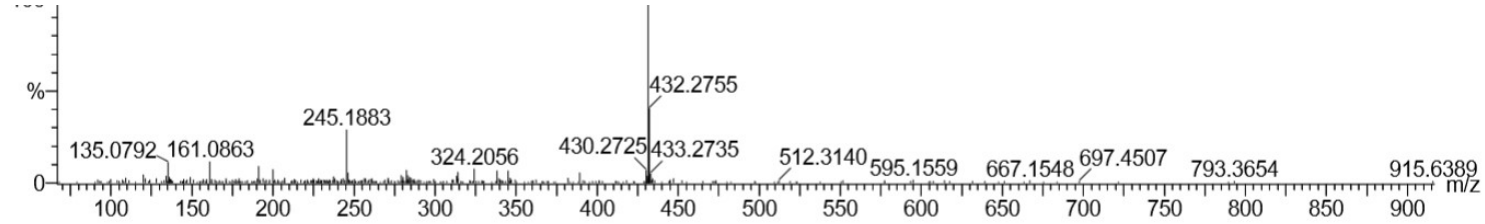
(5)

Elemental Composition Report **Page 1**

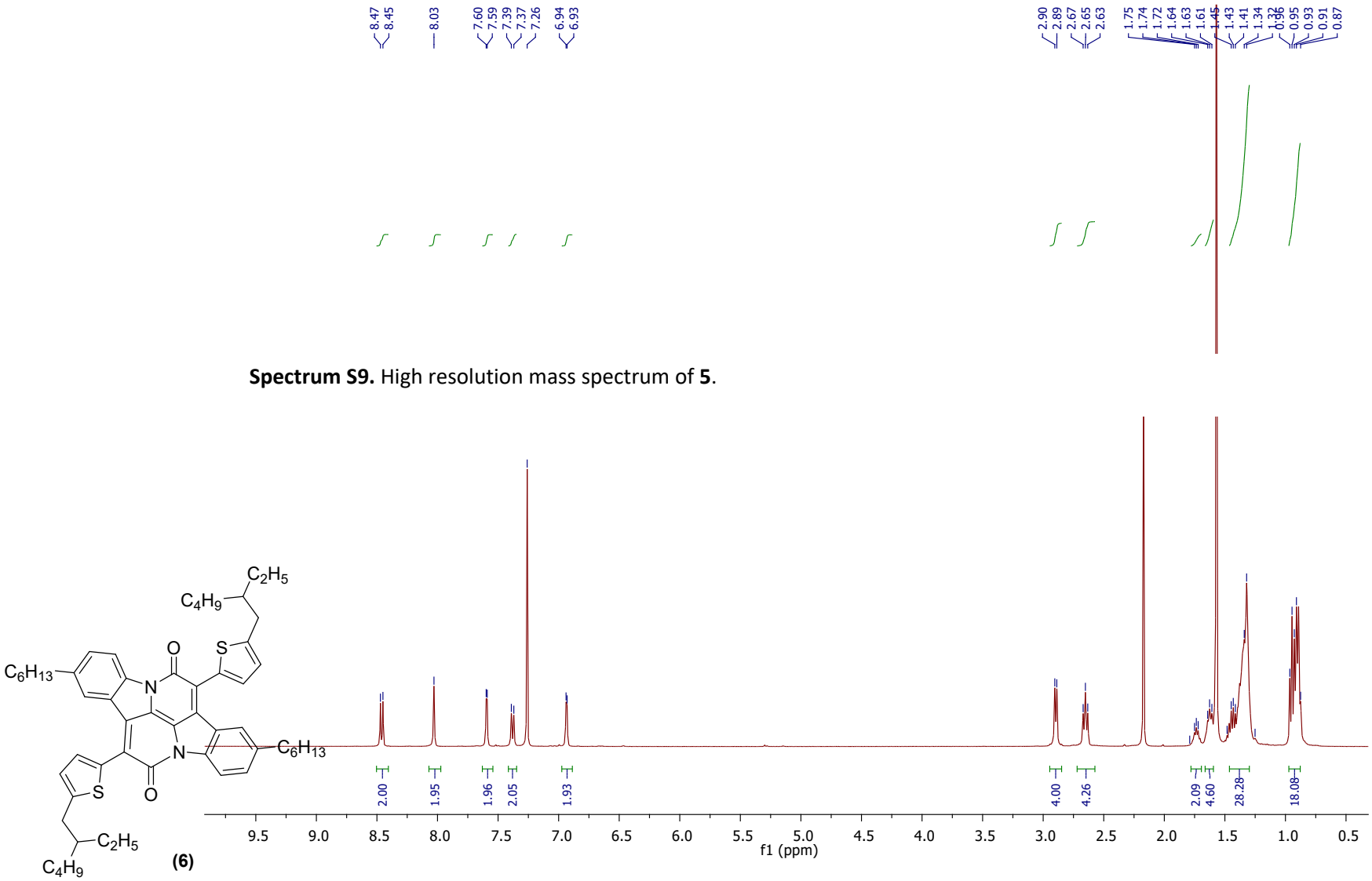
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
47 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-28 H: 0-35 N: 0-2 O: 0-2 P: 0-1 Cl: 0-1
HAB_46705 M Purdy mp-Ind

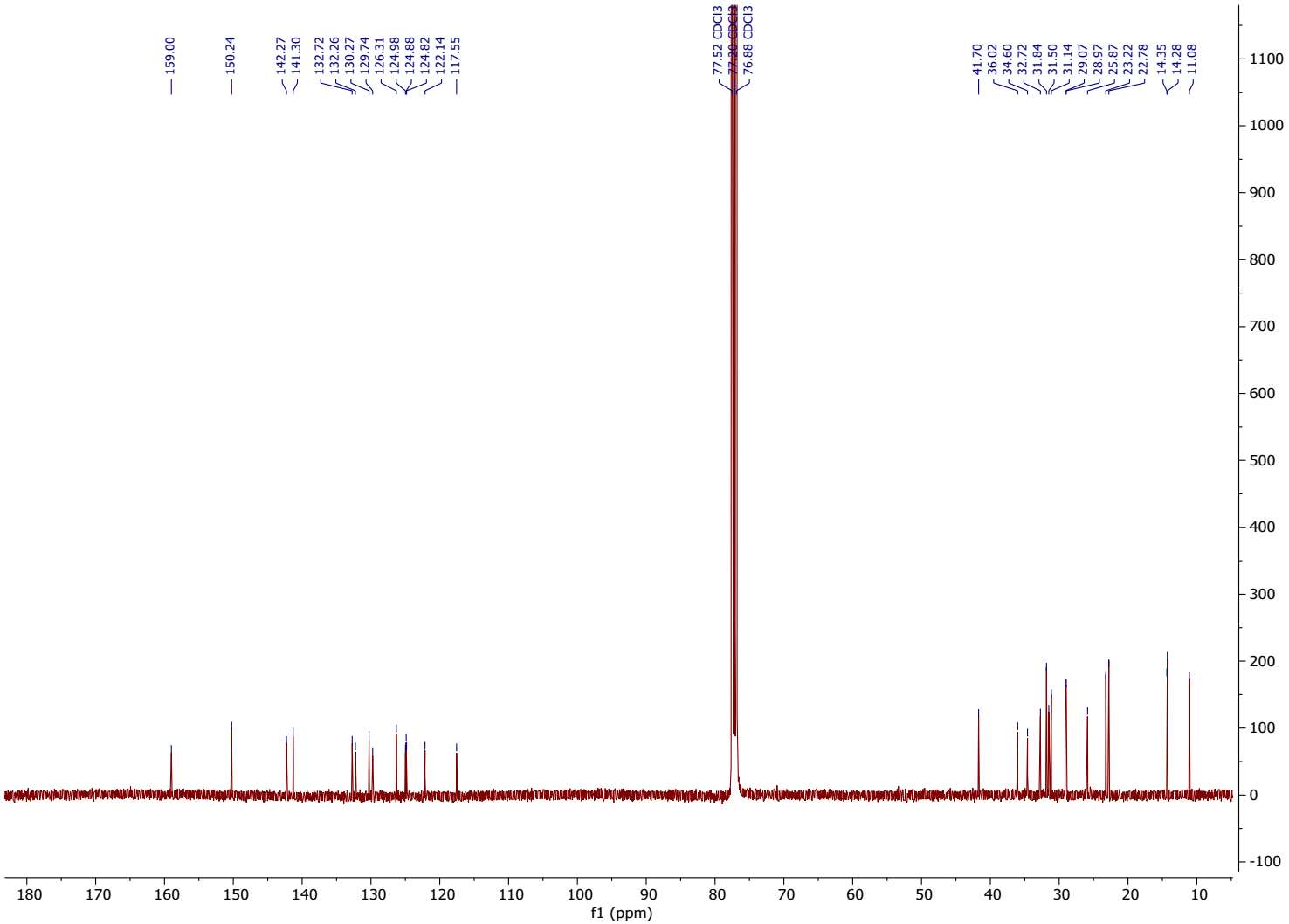
Spectrum S8. ^{1}H NMR (400 MHz) spectrum of **5** in $CDCl_3$.



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
431.2703	431.2699	0.4	0.9	12.5	71.5	n/a	n/a	C28 H35 N2 O2



Spectrum S9. High resolution mass spectrum of **5**.


159.00
150.24
142.27
141.30
132.72
132.26
130.27
129.74
126.31
124.98
124.88
124.82
122.14
117.55
77.52 CDCl3
77.20 CDCl3
76.88 CDCl3
41.70
36.02
34.60
32.72
31.84
31.50
31.14
29.07
28.97
25.87
23.22
22.78
14.35
14.28
11.08
f1 (ppm)

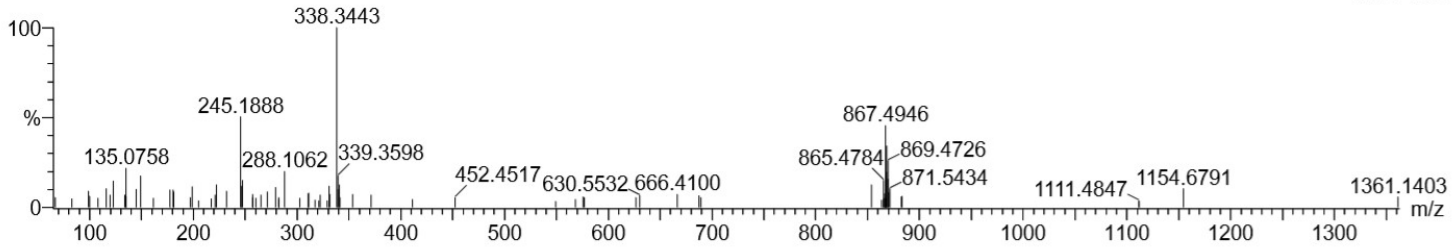
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-56 H: 0-71 N: 0-2 O: 0-2 S: 1-2

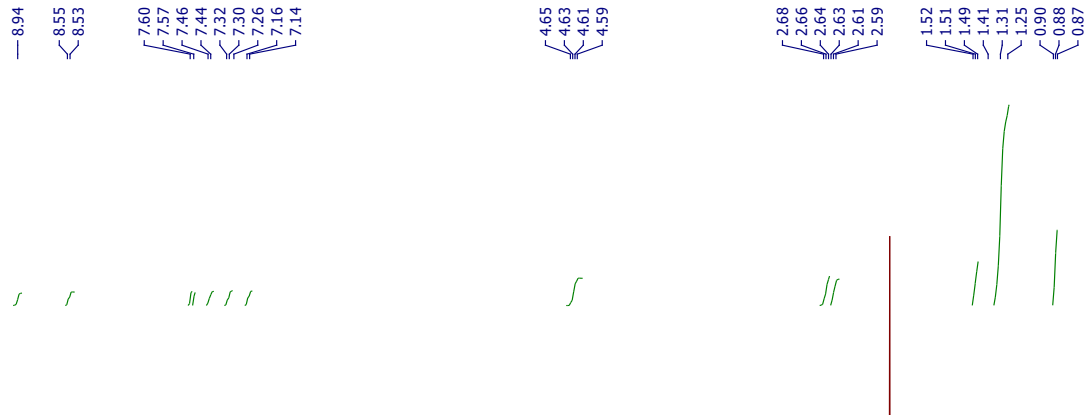
HAB_46671 M Purdy ALK-INDT
HAB_46671 M Purdy ALK-INDT 1979 (4.260) Cm (1976:1983)

1: TOF MS ASAP+
5.17e+002

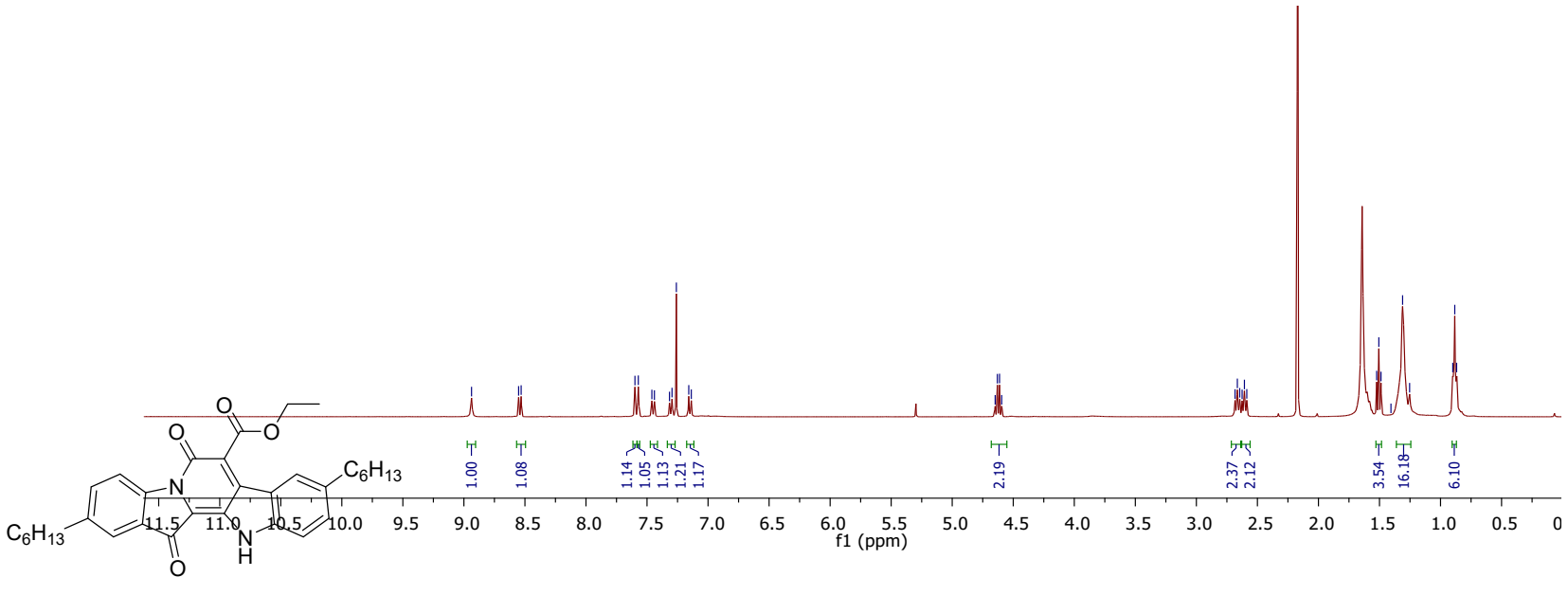


Minimum:				-1.5				
Maximum:		5.0	500.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
867.4946	867.4957	-1.1	-1.3	22.5	40.7	n/a	n/a	C56 H71 N2 O2 S2

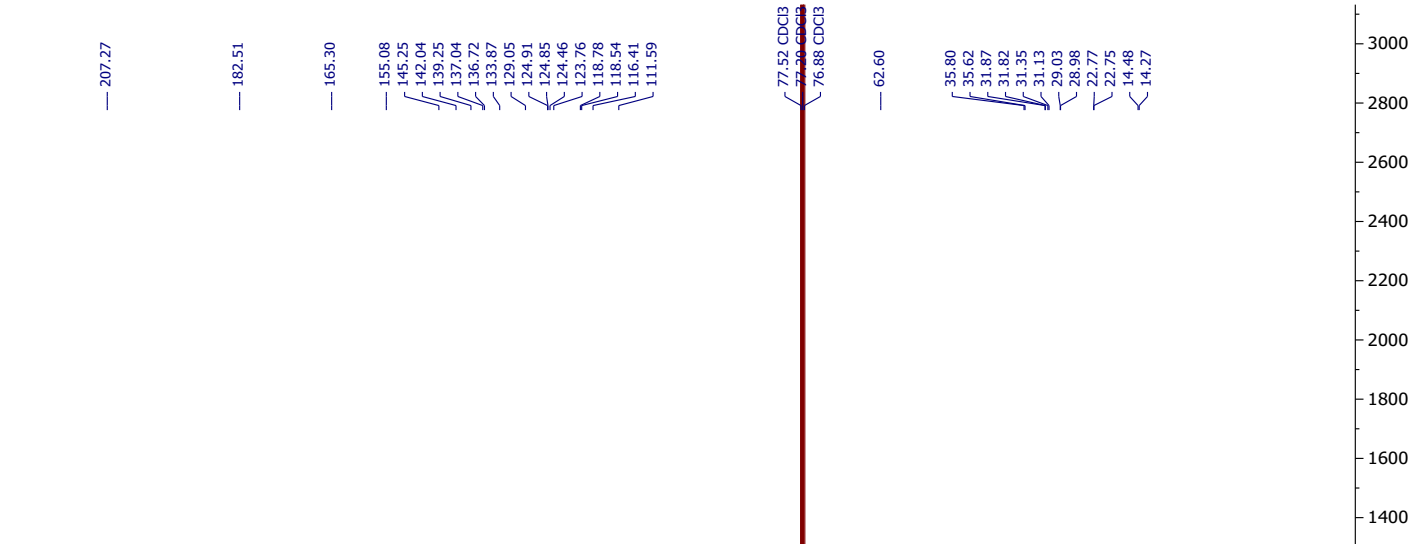
Spectrum S11. ^{13}C NMR (400



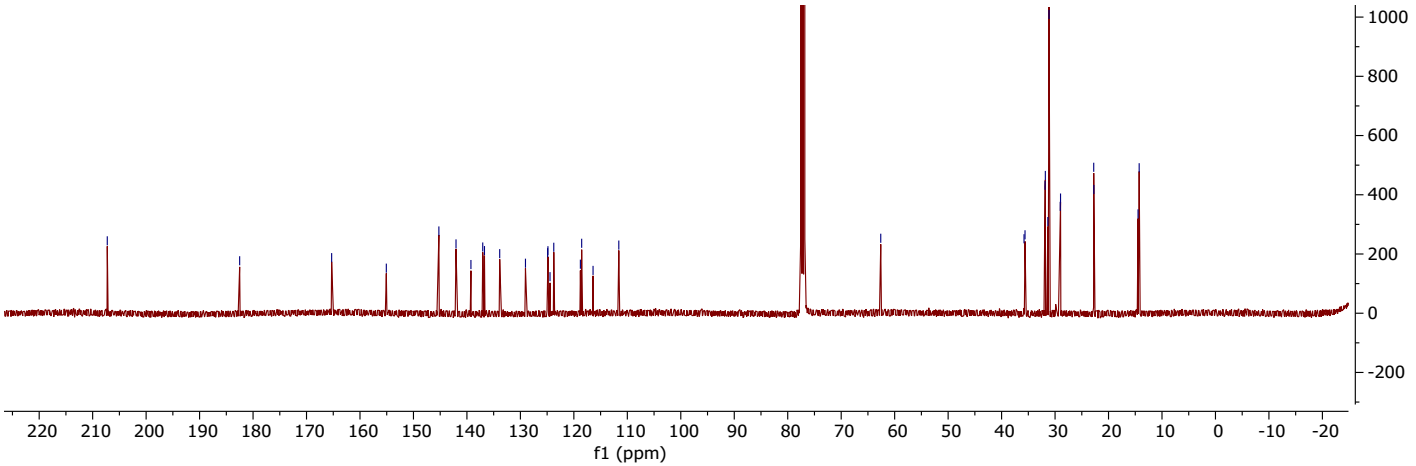
Spectrum S12. High resolution mass spectrum of **6.**



(7)



Spectrum S13. ^{1}H NMR (400 MHz) spectrum of **7** in $CDCl_3$.

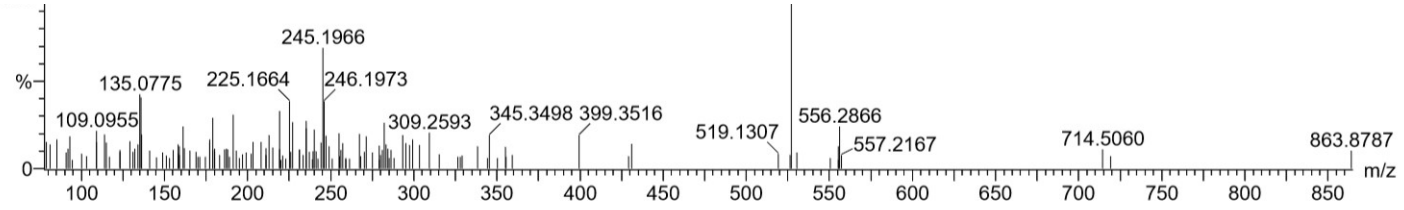


Elemental Composition Report **Page 1**

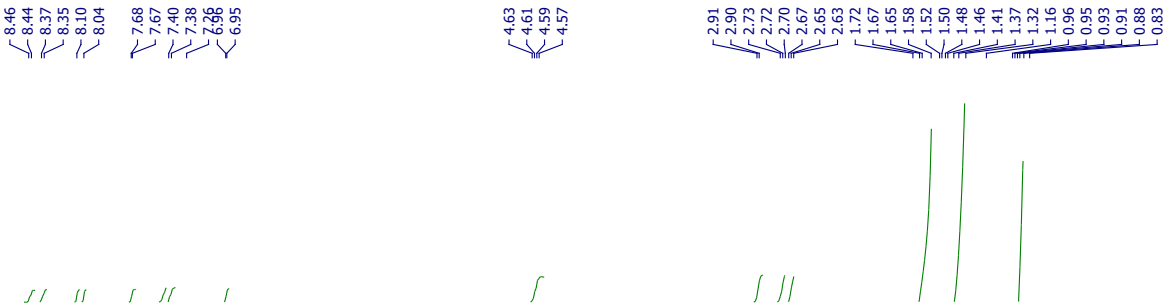
Single Mass Analysis
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
10 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-33 H: 0-39 N: 0-2 O: 0-4
HAB_46656 M Purdy Mp918-ASES

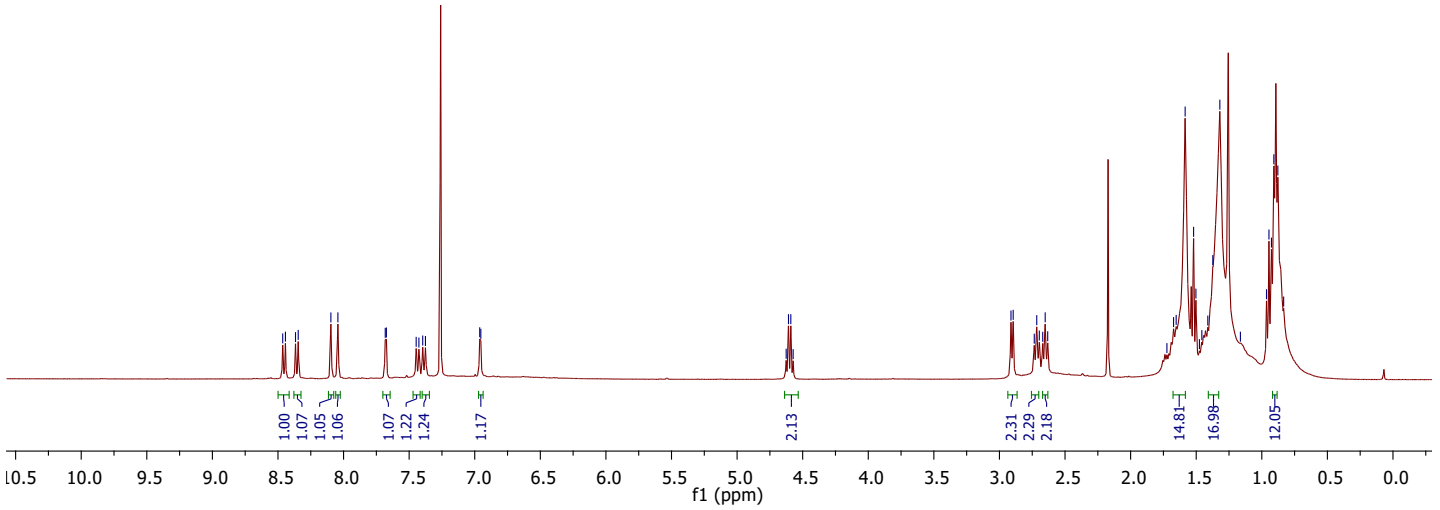
Spectrum S14. ^{13}C NMR (400 MHz) spectrum of **7** in $CDCl_3$.

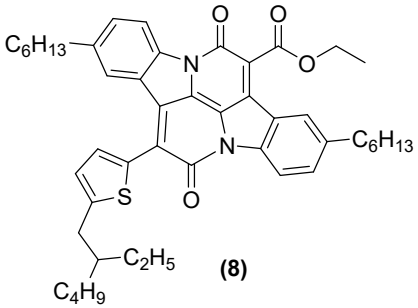


Minimum:				-1.5				
Maximum:		5.0	500.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
527.2891	527.2910	-1.9	-3.6	15.5	22.0	n/a	n/a	C33 H39 N2 O4



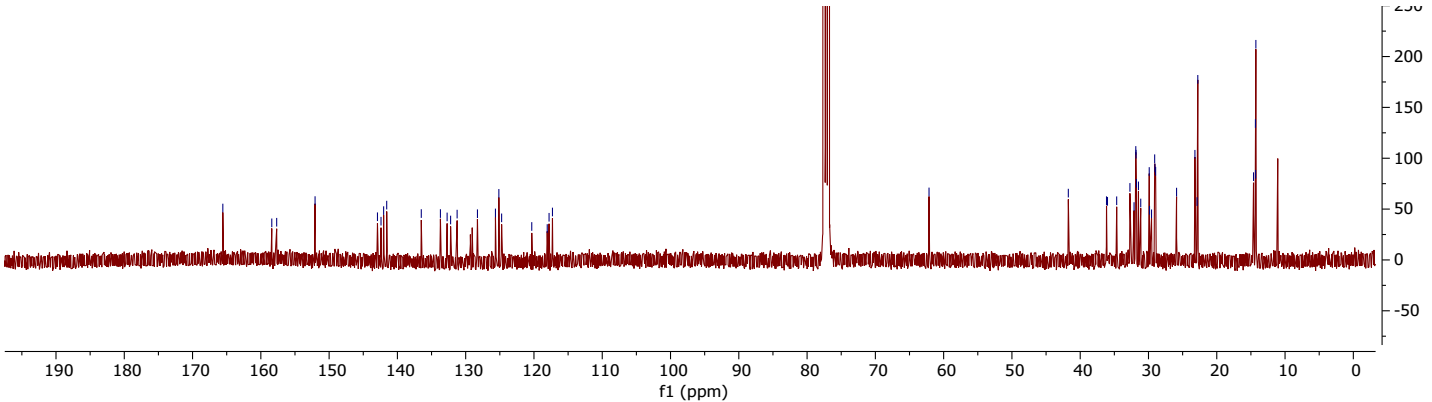
Spectrum S15. High resolution mass spectrum of **7.**





(8)

Spectrum S16. ^{1}H NMR (400 MHz) spectrum of **8** in $CDCl_3$.

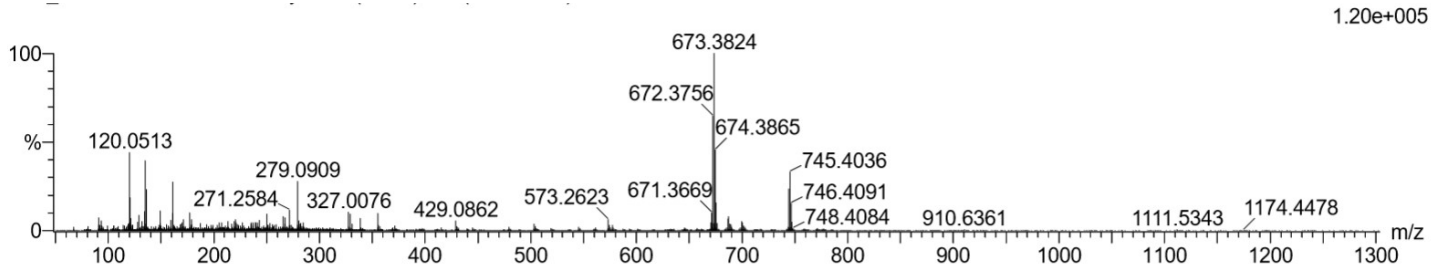


Elemental Composition Report **Page 1**

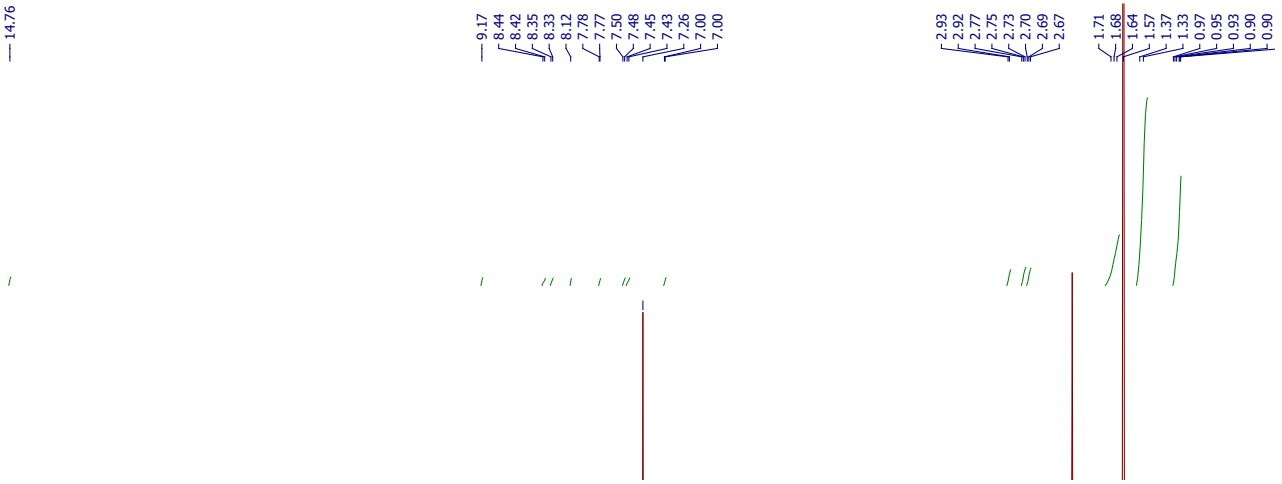
Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
19 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

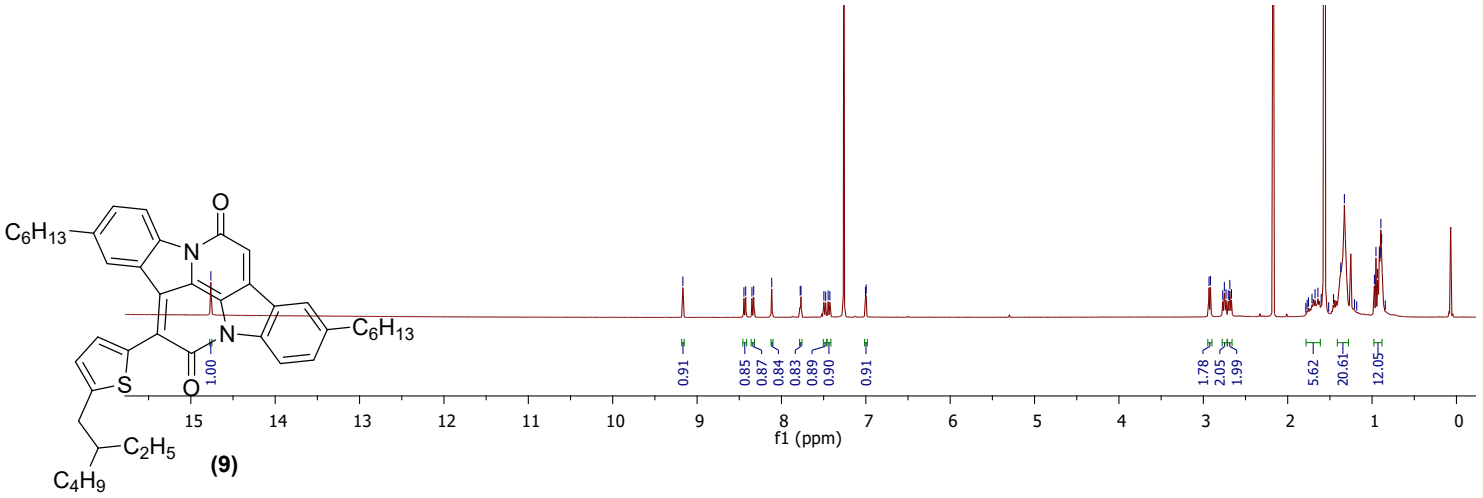
Spectrum S17. ^{13}C NMR (400 MHz) spectrum of **8** in $CDCl_3$.

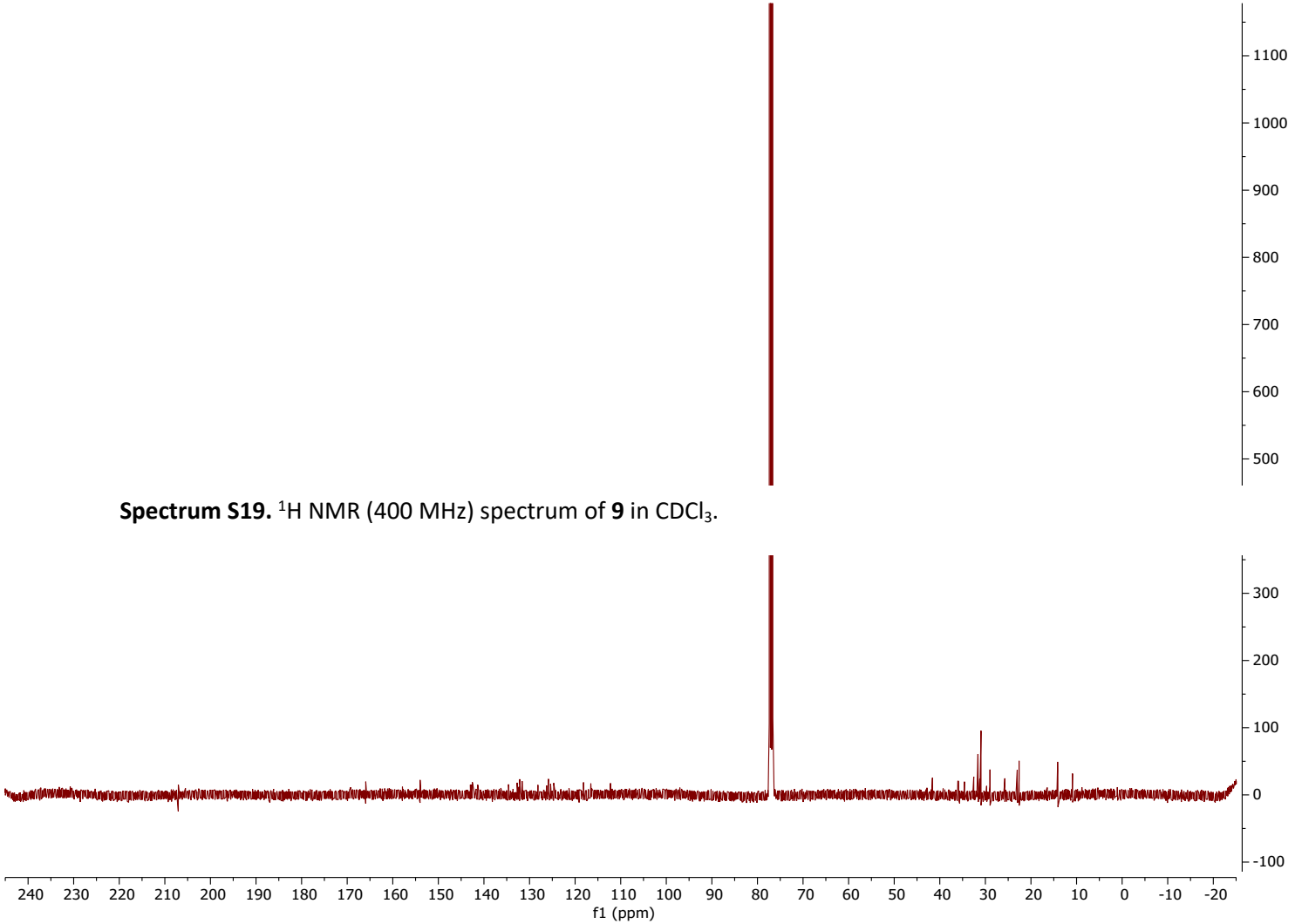


Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
745.4036	745.4039	-0.3	-0.4	20.5	252.6	n/a	n/a	C47 H57 N2 O4 S



Spectrum S18. High resolution mass spectrum of **8.**





Spectrum S19. ^{1}H NMR (400 MHz) spectrum of **9** in $CDCl_3$.

Elemental Composition Report **Page 1**

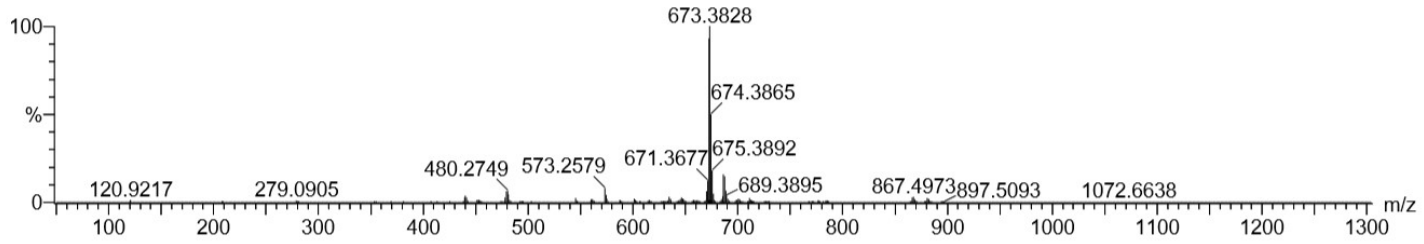
Single Mass Analysis

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
8 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-44 H: 0-53 N: 0-2 O: 0-2 S: 0-1

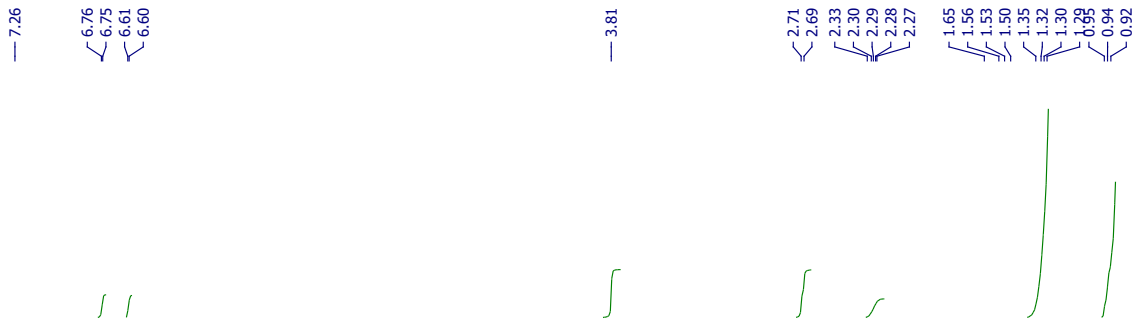
HAB_46053 As-H M Purdy
HAB_46053 As-H M Purdy 2255 (4.845) Cm (2234:2298)

1: TOF MS ASAP+
2.00e+007



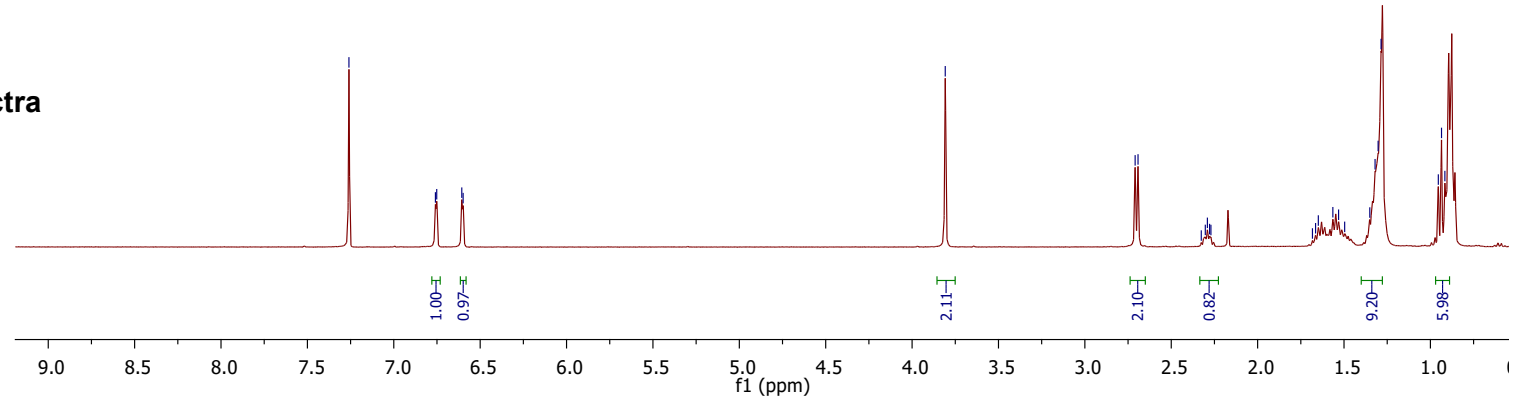
Minimum:				-1.5				
Maximum:		5.0	100.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
673.3828	673.3828	0.0	0.0	19.5	945.0	n/a	n/a	C44 H53 N2 O2 S

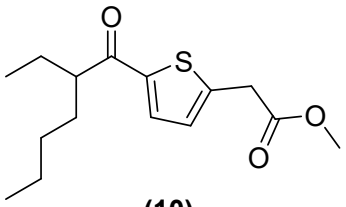
Spectrum S20. ^{13}C NMR (400 MHz



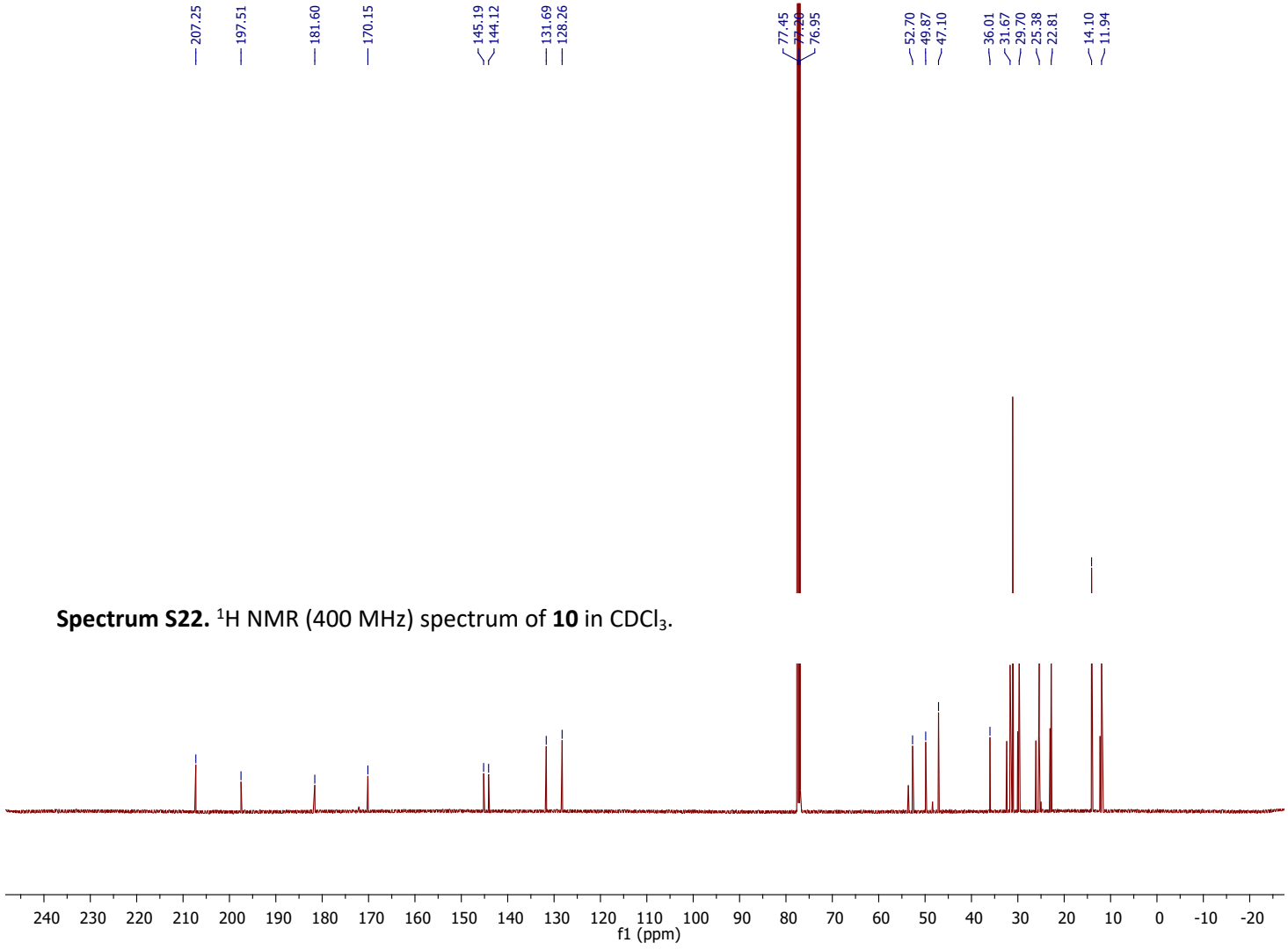
Spectrum S21. High resolution mass spectrum of **9.**

NMR spectra





(10)



Spectrum S22. ^{1}H NMR (400 MHz) spectrum of **10** in $CDCl_3$.

Elemental Composition Report

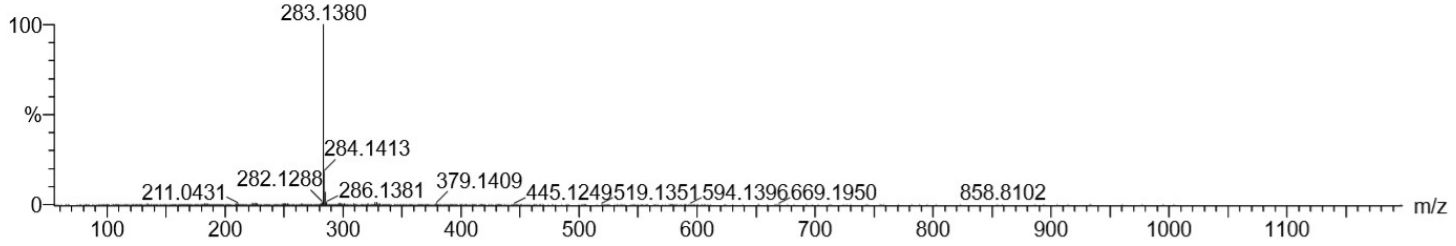
Single Mass Analysis

Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

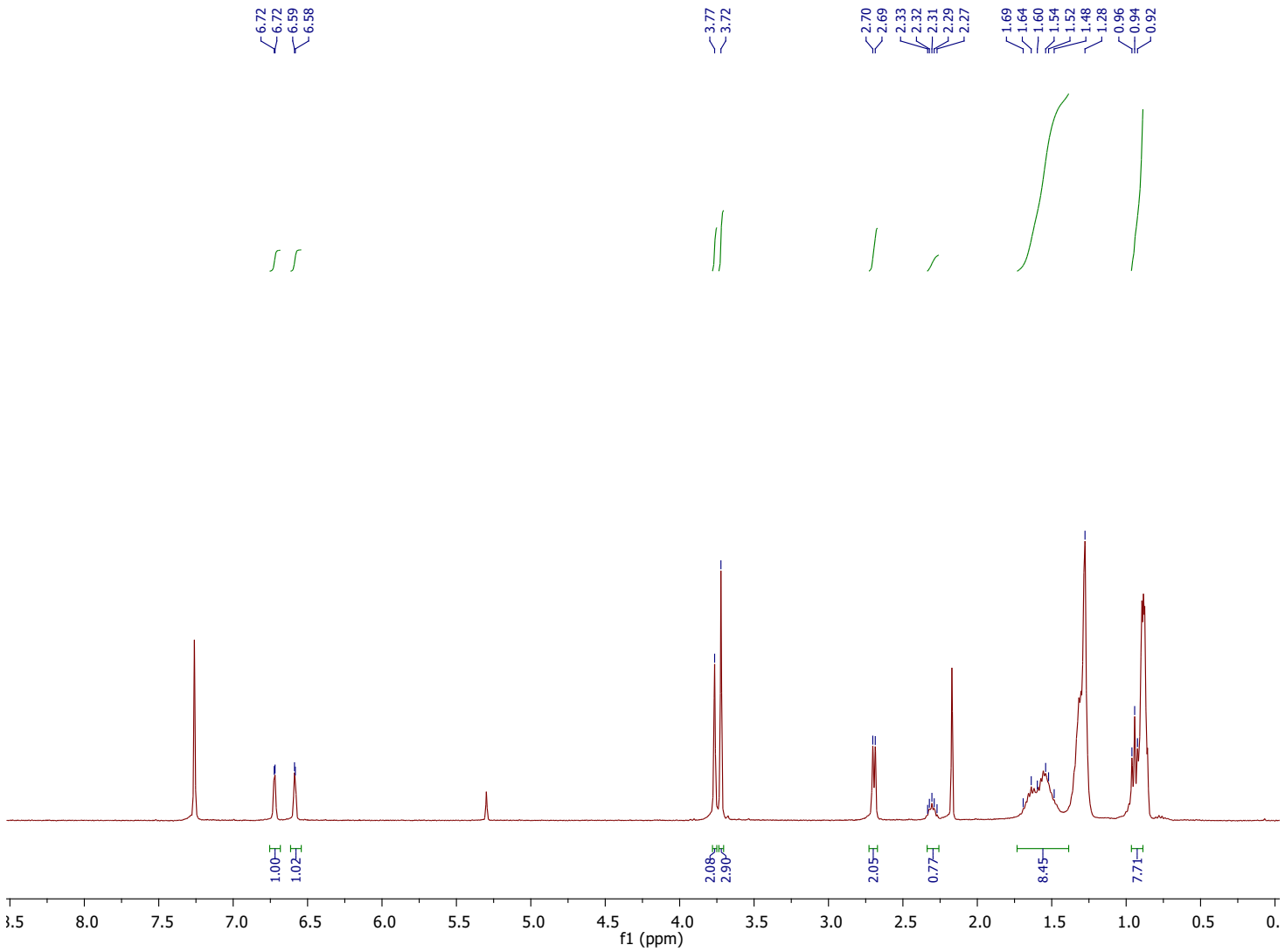
Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 15-15 H: 0-23 O: 0-3 S: 1-1

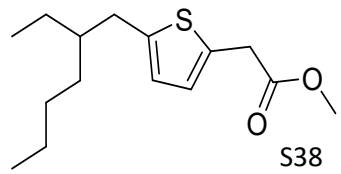
HAB_46642 M Purdy Mp918-FC
HAB_46642 M Purdy Mp918-FC 613 (1.342) Cm (555:733)

1: TOF MS ASAP+
1.19e+006



Minimum:				-1.5				
Maximum:		5.0	500.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
283.1380	283.1368	1.2	4.2	4.5	572.7	n/a	n/a	C15 H23 O3 S


6.72
6.72
6.59
6.58
3.77
3.72
2.70
2.69
2.33
2.32
2.31
2.29
2.27
1.69
1.64
1.60
1.54
1.52
1.48
1.28
0.96
0.94
0.92
1.00
1.02
2.08
2.90
2.05
0.77
8.45
7.71
f1 (ppm)


S
O
O

S38

(11)

180.97
171.38
144.49
132.61
126.52
124.87
77.52 CDCl3
77.40
77.20 CDCl3
76.88 CDCl3
52.42
46.99
41.46
35.69
34.21
32.52
31.69
29.71
29.03
25.65
23.18
1300
1200
1100
1000
900

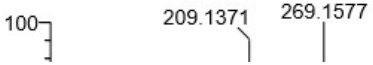
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

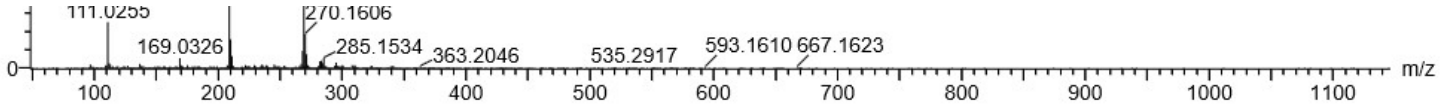
Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-15 H: 0-25 O: 0-2 S: 1-1

HAB_46654 M Purdy Mp918-RED
HAB_46654 M Purdy Mp918-RED 125 (0.295) Cm (95:236)

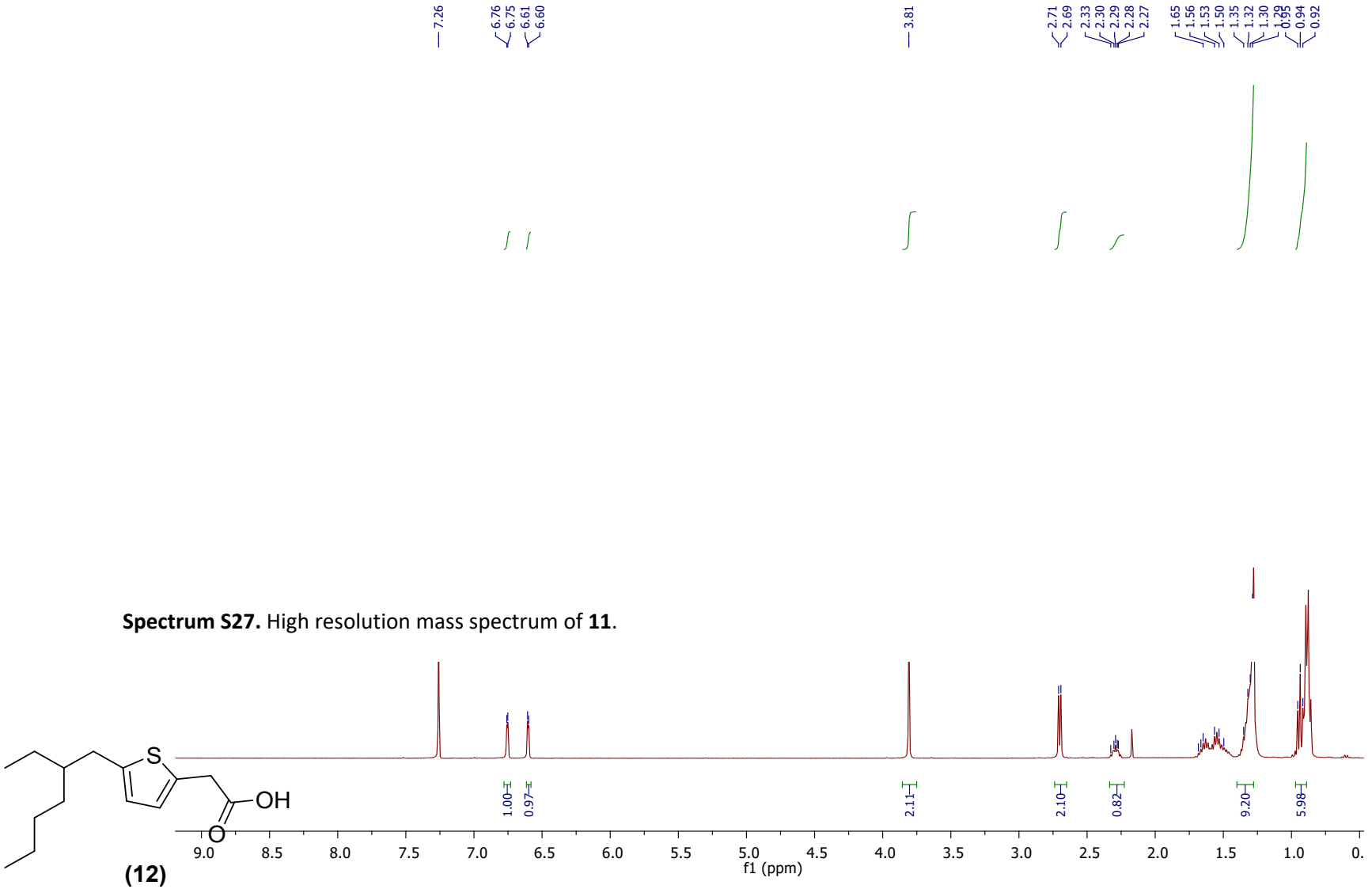
1: TOF MS ASAP+
5.05e+005



Spectrum S26. ^{13}C NMR (400 MHz) spectrum of **11** in $CDCl_3$.

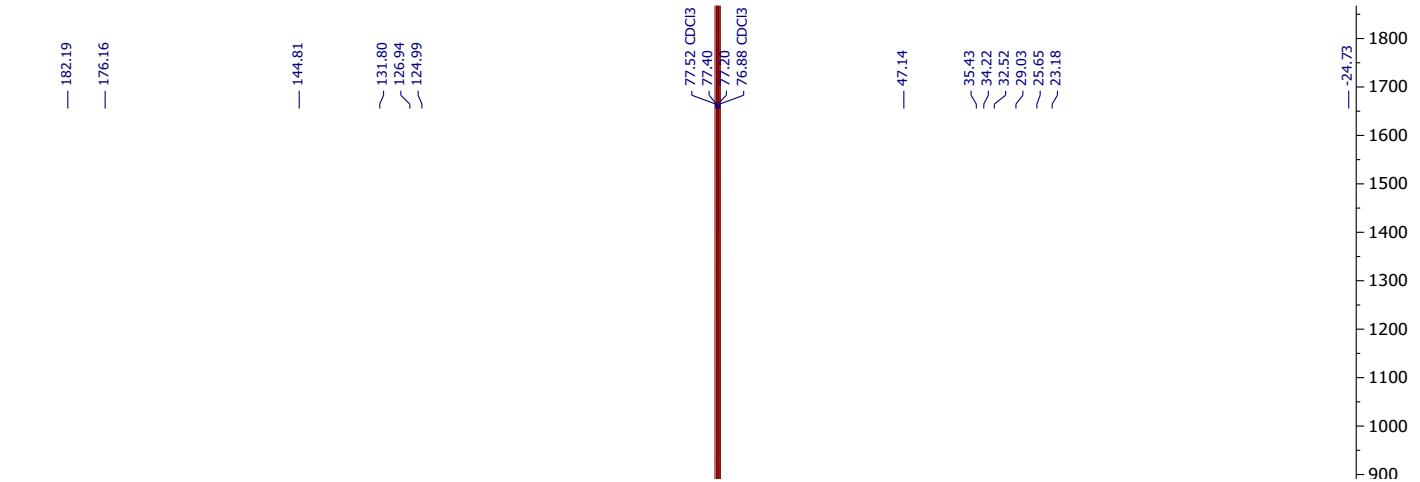


Minimum:				-1.5				
Maximum:		5.0	500.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
269.1577	269.1575	0.2	0.7	3.5	442.0	n/a	n/a	C15 H25 O2 S

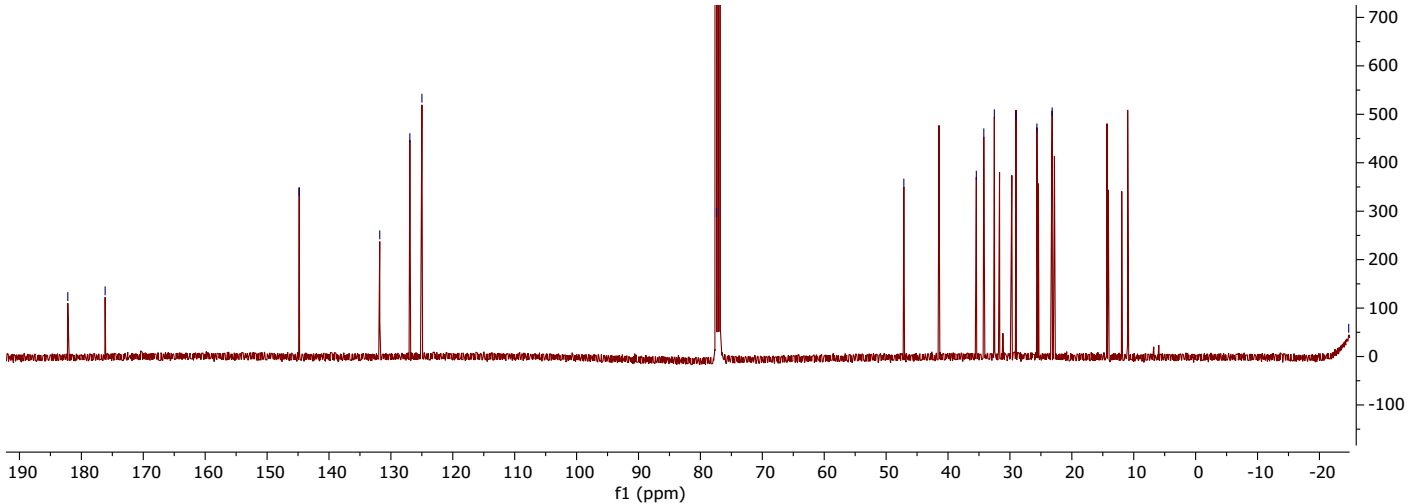


(12)

Spectrum S27. High resolution mass spectrum of **11**.



Spectrum S28. ^{1}H NMR (400 MHz) spectrum of **12** in $CDCl_3$.

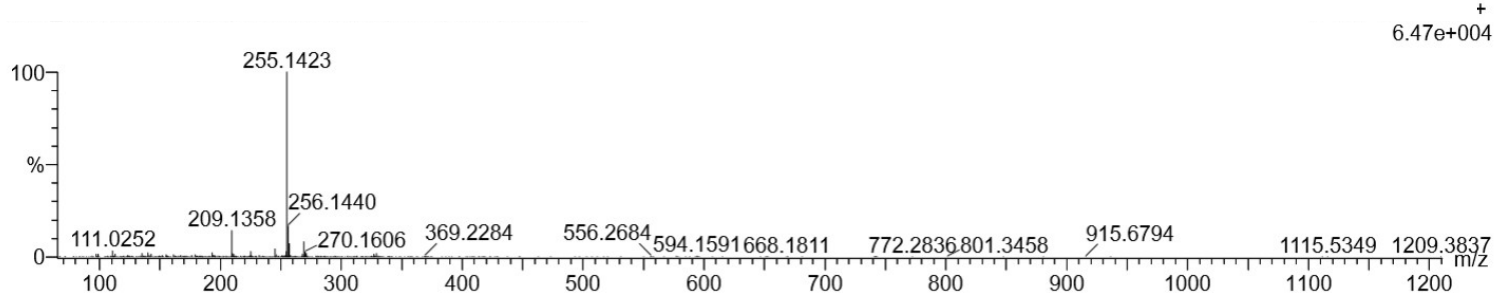


Elemental Composition Report **Page 1**

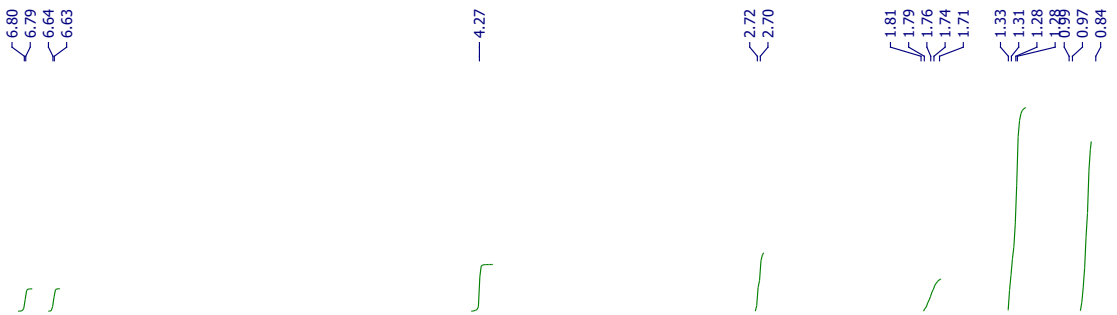
Single Mass Analysis
Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
2 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:

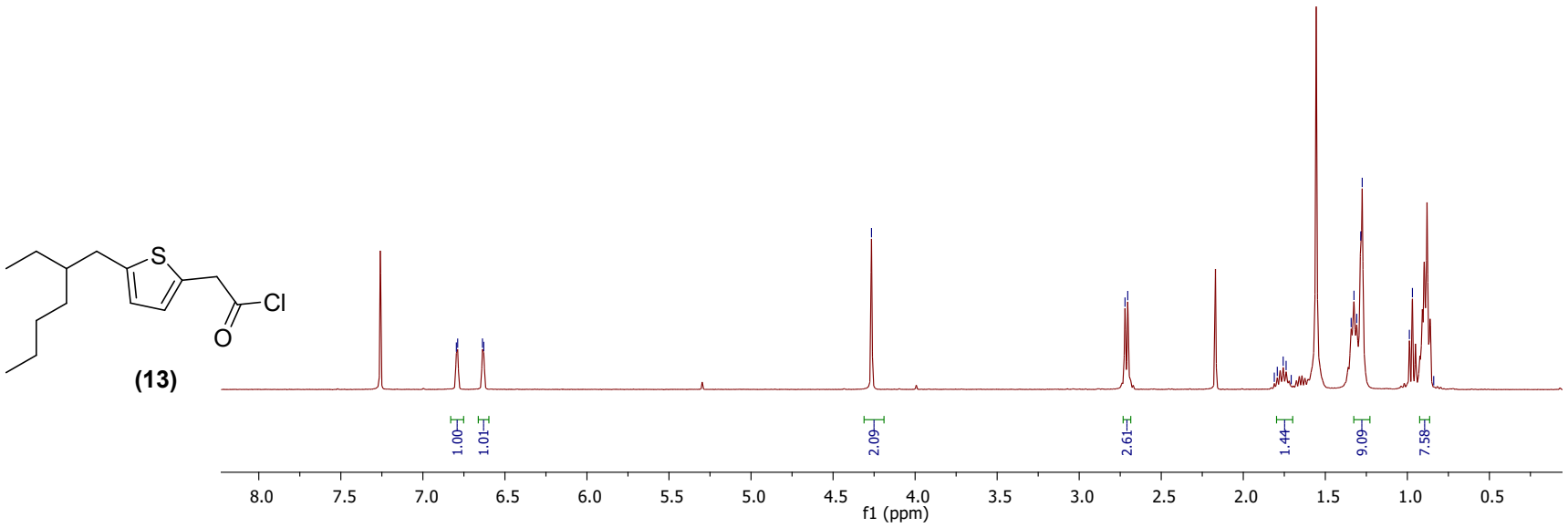
Spectrum S29. ^{13}C NMR (400 MHz) spectrum of **12** in $CDCl_3$.

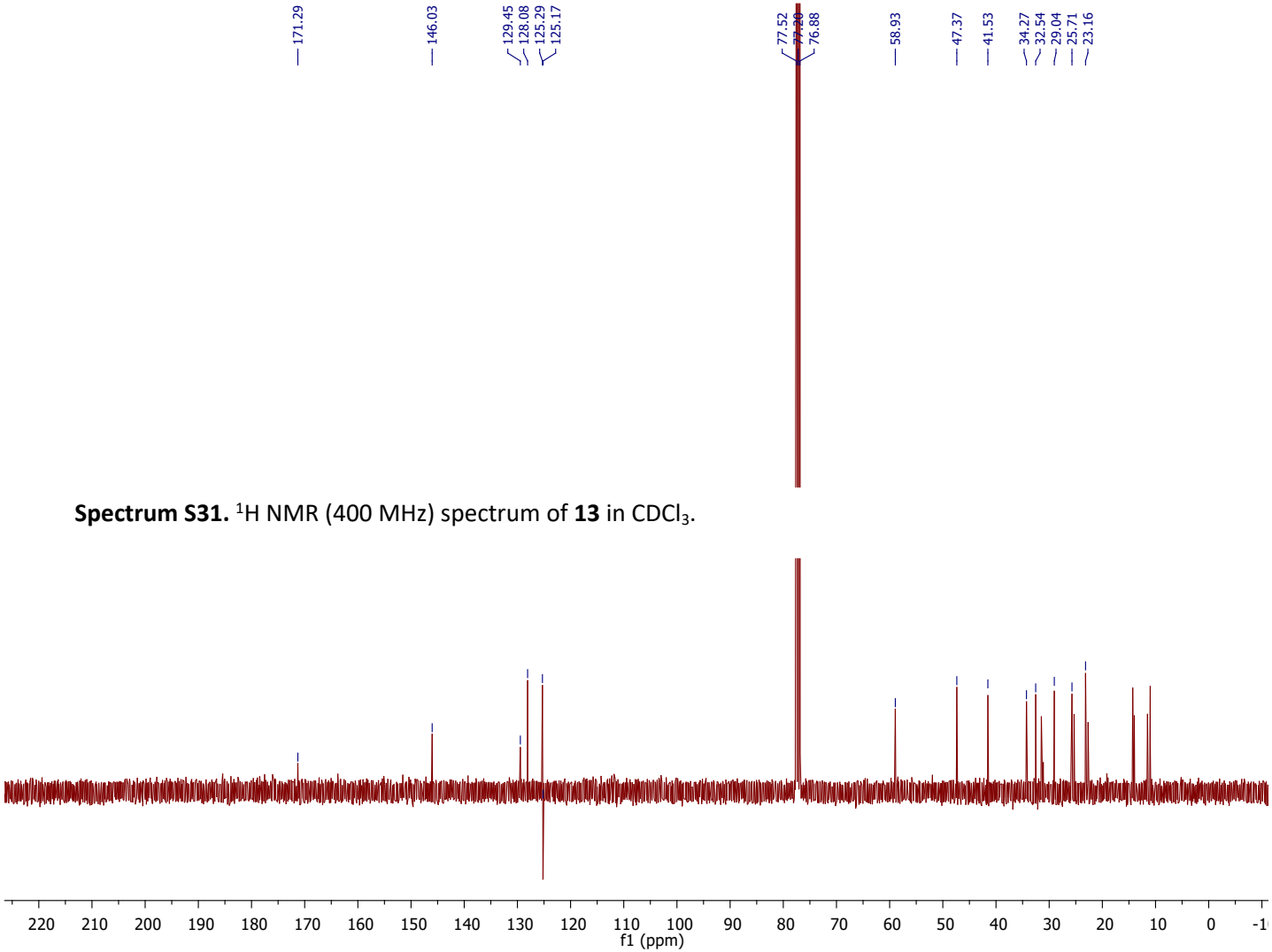


Minimum:				-1.5				
Maximum:		5.0	500.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
255.1423	255.1419	0.4	1.6	3.5	146.5	n/a	n/a	C14 H23 O2 S



Spectrum S30. High resolution mass spectrum of **12**.





Spectrum S31. ^{1}H NMR (400 MHz) spectrum of **13** in $CDCl_3$.

Elemental Composition Report

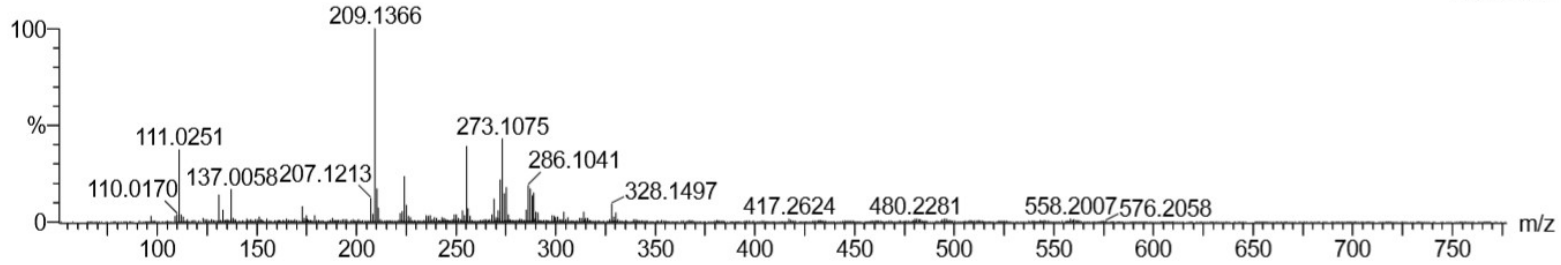
Single Mass Analysis

Tolerance = 500.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
3 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 0-14 H: 0-22 O: 0-1 S: 1-1 Cl: 0-1

HAB_46670 M Purdy ACID-CHL repeat
HAB_46670 M Purdy ACID-CHL repeat 421 (0.917) Cm (358:516)

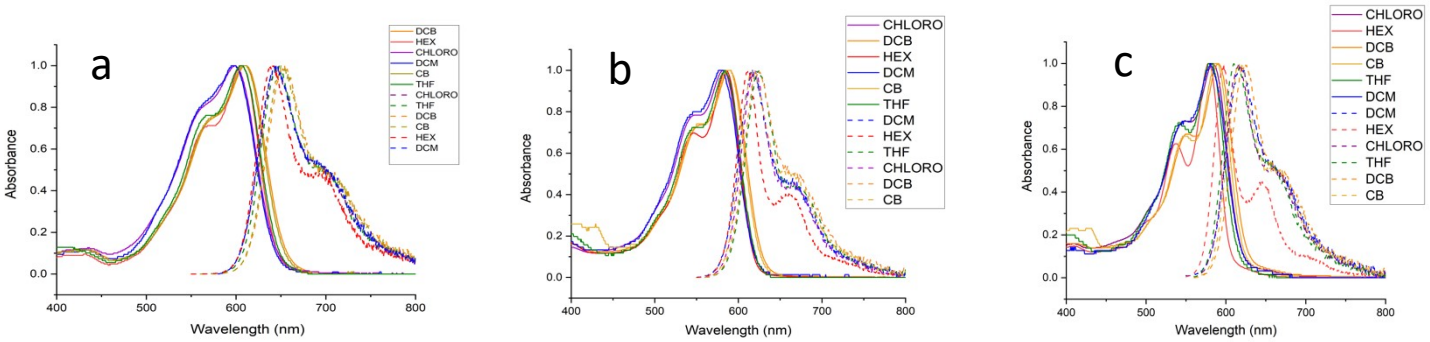
1: TOF MS ASAP+
3.01e+005



Minimum:				-1.5				
Maximum:		5.0	500.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
273.1075	273.1080	-0.5	-1.8	3.5	380.3	n/a	n/a	C14 H22 O S Cl

Spectrum S33. High resolution mass spectrum of **13**.

Absorption and emission spectroscopy



SI Figure 1. UV-Vis and Photoluminescence spectra of **S-INDT**[a], **AE-INDT**[b] and **AH-INDT**[c] in solvents of different polarity.

Lippert-Mataga equation

$$v_{ss} = \frac{2\Delta\mu_{ge}}{hca^3}\Delta f + v_{ss'} \qquad (1)$$

$$\Delta f = \left[\frac{(\varepsilon - 1)}{(2\varepsilon - 1)}\right] - \left[\frac{(n^2 - 1)}{(2n^2 + 1)}\right] \qquad (2)$$

- The difference between the excited and ground state dipole moments ($^{\Delta\mu_{ge}}$)
- $\boldsymbol{v_{ss}}$ is the Stokes shift and the superscript " ' " denotes the absence of solvent
- $\boldsymbol{h}$ is Planck's constant
- $\boldsymbol{c}$ is the speed of light
- $\boldsymbol{a}$ is the Onsager cavity radius and was calculated using B3LYP/6-31G*, with the volume keyword, as 6.08 Å for AE-INDT and AH-INDT and 5.97 for S-INDT
- $\Delta\boldsymbol{f}$ is the orientation polarizability
- $\boldsymbol{\varepsilon}$ and $\boldsymbol{n}$ are the dielectric constants and refractive indices of the solvents, respectively.

Solvent	ε	n	Δf	Molecule	λ_{abs} (nm)	λ_{em} (nm)	v_{ss} (cm^{-1})
Hexane	1.89	1.38	0.003	S-INDT	608	641	901
				AE-INDT	585	612	754
				AH-INDT	578	597	551
Chloroform	4.81	1.45	0.15	S-INDT	601	642	1061
				AE-INDT	583	619	998
				AH-INDT	584	618	942
Chlorobenzene	5.62	1.52	0.14	S-INDT	610	650	1039
				A-INDT	588	624	981
				AH-INDT	586	619	884
Dichlorobenzene	9.93	1.55	0.19	S-INDT	610	654	1145
				AE-INDT	589	627	1029
				AH-INDT	590	626	975
Tetrahydrofuran	7.58	1.41	0.21	S-INDT	606	650	1094
				AE-INDT	585	624	1067
				AH-INDT	578	614	1014
				S-INDT	599	642	1270

SI Table 1. Data used for Lippert-Mataga plot. λ_{abs} and λ_{em} are the absorption and emission maximum respectively taken from the spectra in **SI figure 1**.

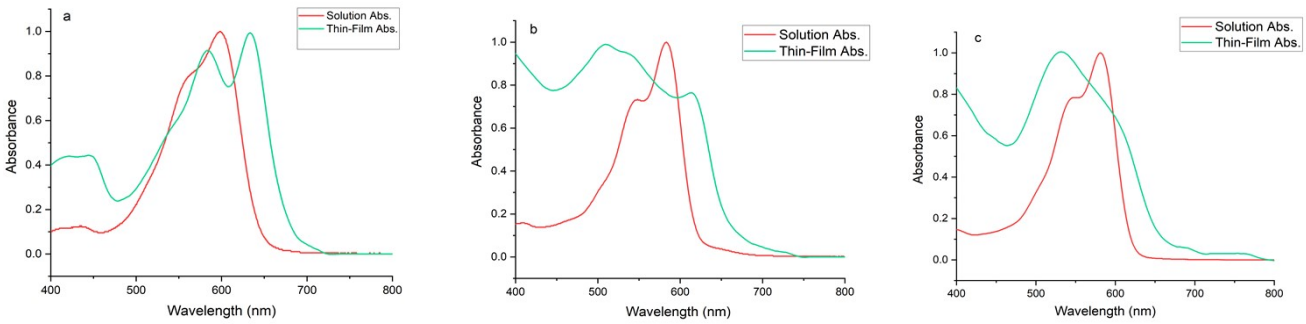
Solvent	ε	Molecule	PLQY (%)
Hexane	1.89	S-INDT	53
		AE-INDT	41
		AH-INDT	24
Chloroform	4.81	S-INDT	50
		AE-INDT	31
		AH-INDT	30
Tetrahydrofuran	7.58	S-INDT	62
		AE-INDT	23
		AH-INDT	22
Dichloromethane	8.93	S-INDT	53
		AE-INDT	35
		AH-INDT	32

SI Table 2. PLQY measurements performed in solvents of different polarity

Thin-film Preparation

Thin films, for absorption measurements, were prepared by spin coating on glass substrate using 5 mg/mL chloroform solution. The same method but using silicon substrates was used for GIWAXS measurements.

Thin-Film UV-Vis



SI Figure 2. UV-Vis absorption **S-INDT**[a], **AH-INDT**[b] and **AE-INDT**[c].

Grazing incidence X-ray scattering studies

Grazing incidence wide-angle X-ray scattering (GIWAXS) was performed on the Xuess instrument equipped with an Excillum MetalJet liquid gallium X-ray source. Alignment was performed on silicon substrates via three iterative height (z) and rocking curve (Ω) scans, with the final grazing incidence angle set to Ω = 0.2º. Scattering patterns were recorded on a vertically-offset Pilatus 1M detector with a sample to detector distance of 323 mm, calibrated using a silver behenate standard to achieve a q-range of 0.045 – 1.85 Å-1. Two-dimensional images were recorded with exposure times of 900 s. The images were masked to remove the sample horizon, detector module gaps and beamstop. Data correction and reduction was performed using the GIXSGUI MATLAB toolbox.[2]

References

1. Staas, D. D. *et al.* Discovery of potent, selective 4-fluoroproline-based thrombin inhibitors with improved metabolic stability. *Bioorganic Med. Chem.* **14**, 6900–6916 (2006).

2. Jiang, Z. GIXSGUI: A MATLAB toolbox for grazing-incidence X-ray scattering data visualization and reduction, and indexing of buried three-dimensional periodic nanostructured films. *J. Appl. Crystallogr.* **48**, 917–926 (2015).