Supplementary Information

Efficient synthesis of isoindolones by intramolecular cyclisation of pyridinylbenzoic acids

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Contents

Experimental section

General Information. Reagent grade chemicals were purchased from Sigma Aldrich and Acros Organics and used without further purification. Yields reported are for isolated, spectroscopically pure compounds. (-)-Pinocarvone,[1] (1-(2-(2-bromophenyl)-2-oxoethyl)pyridin-1-ium iodide) and **1** (5S,7S)-2-(2-bromophenyl)-6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinoline) were obtained as described in the literature.[2] When inert conditions were required, the reactions were performed under Ar atmosphere using glassware dried overnight at 120°C. Analytical thin layer chromatography (TLC) was performed on SiO_2 plates GF254 (0.25 mm layer thickness). Flash chromatography purifications were performed on a CombiFlash EZ Prep from Teledyne®. Optical rotations were measured on an Anton Paar Modular Circular Polarimeter MCP 100. The measurements were carried out in a quartz vessel (λ = 100 mm) with the sodium D line of a sodium lamp (589 nm) using spectroscopic-grade solvents. $[\alpha]_D^{20}$values are given in 10^{-1} deg cm^2 g^{-1}. IR spectra were recorded as solids between 4000 – 400 cm^{-1} on a Bruker ALPHA FTIR. UV-Vis spectra were recorded at 20°C on an Evolution 220 spectrometer equipped with a thermostat. Fluorescence spectra were recorded at 20°C on a Fluoromax 4 spectrometer from HORIBA equipped with a thermostat. NMR spectra were recorded on a Bruker Advance DPX 300 spectrometer using TMS or the residual solvent proton as internal standard. HRMS spectra were recorded on FTMS 4.7T BioAPEX II and Waters SynaptG2-Si or at the Spectrometry Service of University of Bern. Crystallographic data were collected on a STOE IPDS-II diffractometer.

*Synthesis of 2-((5S,7S)-6,6-dimethyl-5,6,7,8-tetrahydro-5,7-methanoquinolin-2-yl)benzoic acid (**2**).* Under inert atmosphere, a solution of **1** (4.07 g, 12.4 mmol, 1 eq) in anhydrous THF (40 mL) was cooled at -78°C. n-BuLi (5.7 mL, 12.4 mmol, 2.2M in hexane, 1 eq) was added dropwise. The solution turned dark red. The reaction mixture was stirred at -78°C for 2h. Then, gaseous CO_2 was bubbled into the solution until complete discoloration. The reaction mixture was left to warm to RT and quenched with H_2O (0.9 mL). The solvents were removed under reduced pressure, and 20 mL of HCl 1M were added. Afterwards the solution was extracted with CH_2Cl_2 (3x 40 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Trituration of the crude compound with pentane gave the desired

compound **2** as a white solid (2.37 g, yield: 65%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 8.34 – 8.21 (m, 1H, H3), 7.70 – 7.39 (m, 5H, H4, H5, H6, H9, H10), 3.23 (d, J = 2.9 Hz, 2H, H15), 2.91 (t, J = 5.6 Hz, 1H, H12), 2.79 (dt, J = 9.8, 5.8 Hz, 1H, H13a), 2.46 (tt, J = 5.9, 2.9 Hz, 1H, H14), 1.47 (s, 3H, H18), 1.35 (d, J = 9.9 Hz, 1H, H13b), 0.71 (s, 3H, H19). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 170.2 (C1), 154.3 (C16), 154.1 (C11), 142.8 (C2), 136.4 (C_{arom}), 136.2 (C_{arom}), 136.2 (C_{arom}), 134.3 (C3), 133.3 (C_{arom}), 131.7 (C_{arom}), 130.8 (C_{arom}), 129.3 (C_{arom}), 121.8 (C_{arom}), 46.3 (C17) 46.2 (C12), 39.9 (C14), 34.9 (C15), 32.0 (C13), 26.0 (C18), 21.5 (C19). HRMS (ESI) *m/z* calcd. for $C_{19}H_{20}NO_2^+$ $[M+H]^+$ 294.1489, found 294.1478. $[\alpha]_D^{20}$ -90° (c 1 in CH_2Cl_2).

*Synthesis of (2S,4S)-3,3-dimethyl-3,4-dihydro-2,4-methanoisoindolo[2,1-a]quinolin-11(2H)-one (**3**).* Under inert atmosphere, **2** (50 mg, 0.186 mmol, 1 eq.) was added into a 3-neck 10 mL flask. K_2CO_3 (327 mg, 2.366 mmol, 12.8 eq) and anhydrous MeCN (5 mL) were added successively. The suspension was stirred for 5 minutes at RT. Afterwards, p-TsCl (36 mg, 0.186 mmol, 1 eq.) was added in one portion. The suspension turned orange. The reaction mixture was stirred for 2h at RT. Then, the solvent was removed under high vacuum. CH_2Cl_2 was added and the suspension was filtered under Ar. The filtrate was concentrated under vacuum. After drying the solid under high vacuum, the desired isoindolone **3** was obtained as an orange solid (51 mg, yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.93 (dt, J = 7.5, 1.0 Hz, 1H, H3), 7.69 (dt, J = 7.7, 1.0 Hz, 1H, H6), 7.58 (td, J = 7.5, 1.2 Hz, 1H, H5), 7.49 (td, J = 7.4, 1.1 Hz, 1H, H4), 7.41 (dd, J = 6.9, 1.7 Hz, 1H, H15), 6.37 (d, J = 6.4 Hz, 1H, H9), 5.99 (dd, J = 6.5, 1.7 Hz, 1H, H10), 2.84 (t, J = 5.9 Hz, 1H, H12), 2.68 – 2.61 (m, 1H, H13b), 2.58 (dd, J = 6.7, 5.5 Hz, 1H, H14), 1.69 (d, J = 8.3 Hz, 1H, H13a), 1.42 (s, 3H, H18), 0.93 (s, 3H, H19). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.5 (C1), 145.1 (C16), 134.6 (C11), 132.7 (C8), 131.5 (C5), 131.4 (C2), 128.9 (C4), 128.1 (C7), 123.4 (C3), 119.6 (C6), 116.5 (C15), 113.8 (C10), 104.5 (C9), 50.8 (C12), 44.4 (C17), 42.8 (C14), 35.3 (C13), 26.4 (C18), 22.6 (C19). HRMS (ESI) *m/z* calcd. for $C_{19}H_{18}NO^+$ $[M+H]^+$ 276.1383, found 276.1383. $[\alpha]_D^{20}$ -359 (c 0.276 in CH_2Cl_2). IR (neat, cm^{-1}): 2924 (C-H), 1661 (C=O), 1429, 1203, 1126, 800, 758, 722, 696. UV-Vis (THF): $\lambda_{max}(\varepsilon)$: 288 nm (7200 $M^{-1}cm^{-1}$), 470 nm (2600 $M^{-1}cm^{-1}$).

*Synthesis of ethyl 2-(5,6,7,8-tetrahydroquinolin-2-yl)benzoate (**P4**).* Under inert atmosphere, a solution of 2-ethoxycarbonylphenyl boronic acid (1.44 g, 7.44 mmol, 1.05 eq) was mixed with degassed toluene (50 mL) and EtOH (15 mL) at RT. A solution of K_2CO_3 (6.60 g, 47.73 mmol, 6.74 eq) in water (22 mL), a degassed solution of $Pd(PPh_3)_4$ (0.21 g, 0.177 mmol, 0.025 eq) in EtOH (1 mL) and 2-bromo-5,6,7,8-tetrahydroquinoline (1.50 g, 7.08 mmol, 1 eq) were added successively. The reaction mixture was refluxed under inert atmosphere for 16h and then cooled to RT and extracted with CH_2Cl_2 (3x 50 mL). The organic phase was dried over $MgSO_4$. The purification of the crude compound by column chromatography on SiO_2 (eluent: heptane/EtOAc = 4/1 (Rf = 0.3)) gave the compound **P4** as a translucent oil (0.14 g, yield: 21%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.82 – 7.73 (m, 1H, H5), 7.57 – 7.46 (m, 2H, H1, H8), 7.45 – 7.37 (m, 2H, H6, H9), 7.20 (dt, J = 7.9, 0.8 Hz, 1H, H2), 4.16 (q, J = 7.1 Hz, 2H, H20), 2.93 (t, J = 6.3 Hz, 2H, H16), 2.81 (t, J = 6.3 Hz, 2H, H13), 1.98 – 1.76 (m, 4H, H14, H15), 1.10 (t, J = 7.1 Hz, 3H, H21). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 169.2 (C17), 156.7 (C7), 155.7 (C10), 141.3 (C4), 137.1 (C6), 132.1 (C3), 131.0 (C1), 130.7 (C11), 129.8 (C5), 129.7 (C8), 128.0 (C9), 120.0 (C2), 60.9 (C20), 32.8 (C16), 28.7 (C13), 23.3 (C15), 22.9 (C14), 14.1 (C21). HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}NO_2^+$ $[M+H]^+$, 282.1494, found 282.1504.

*Synthesis of 2-(5,6,7,8-tetrahydroquinolin-2-yl)benzoic acid (**4**).* A solution of **P4** (100 mg, 0.355 mmol, 1 eq) in MeOH (10 mL) was mixed with a solution of NaOH (250 mg, 6.25 mmol, 17.6 eq) in H_2O (5 mL). The reaction mixture was stirred at RT for 16h. The MeOH was removed under reduced pressure. After pH adjustment to 2 with HCl 10%, water was removed under reduced pressure. The purification of the residue by column chromatography (eluent: EtOAc) gave the desired acid **4** as a white solid (48 mg, yield: 53%). ^{1}H NMR (300 MHz, DMSO-d_6) δ_H 7.65 (d, J = 7.4 Hz, 1H, H5), 7.59 – 7.53 (m, 2H, H1, H2), 7.53 – 7.42 (m,

2H, H6, H8), 7.29 (d, J = 7.9 Hz, 1H, H9), 2.79 (q, J = 6.6 Hz, 4H, H13, H16), 1.89 – 1.70 (m, 4H, H14, H15). ^{13}C NMR (75 MHz, DMSO-d6) δ_C 170.0 (C17), 155.7 (C4), 154.6 (C_{arom}), 139.8 (C3), 137.0 (C6), 133.1 (C_{arom}), 130.4 (C_{arom}), 130.3 (C2), 129.6 (C1), 128.8 (C5), 127.9 (C8), 112.0 (C9), 31.9 (C16), 27.8 (C13), 22.6 (C15), 22.3 (C14). HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}NO_2^+$ $[M+H]^+$, 254.1181, found 254.1195.

*Synthesis of 3,4-dihydroisoindolo[2,1-a]quinolin-11(2H)-one (**5**).* Under inert atmosphere, 4 (9 mg, 0.0335 mmol, 1 eq.) was added into a 3-neck 10 mL flask. K_2CO_3 (59 mg, 0.4288 mmol, 12.8 eq), anhydrous MeCN (3 mL) and anhydrous acetone (3 mL) were added successively. The suspension was stirred for 5 minutes at RT. Then, p-TsCl (7 mg, 0.0335 mmol, 1 eq.) was added in one portion. The reaction mixture was stirred for 2h at RT, and the solvent was removed under high vacuum. After the addition of CH_2Cl_2 the suspension was filtered under Ar. The filtrate was concentrated under vacuum. Drying the resulting solid under high vacuum gave the desired isoindolone **5** as an orange solid (10 mg, yield: 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.94 – 7.88 (m, 1H, H5), 7.67 (dt, J = 7.7, 1.0 Hz, 1H, H2), 7.57 (td, J = 7.5, 1.3 Hz, 1H, H1), 7.49 (td, J = 7.4, 1.2 Hz, 1H, H6), 7.40 (td, J = 5.2, 1.8 Hz, 1H, H16), 6.33 (d, J = 6.4 Hz, 1H, H7), 5.98 (dtt, J = 7.3, 1.7, 0.9 Hz, 1H, H8), 2.60 (ddd, J = 12.7, 6.2, 1.7 Hz, 3H, H13), 2.50 – 2.42 (m, 2H, H15), 1.84 – 1.74 (m, 2H, H14). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 165.6 (C17), 136.9 (C9), 134.8 (C4), 133.5 (C10), 132.1 (C12), 131.3 (C1), 128.8 (C6), 128.00 (C3), 123.2 (C5), 119.3 (C2), 116.4 (C8), 110.5 (C16), 104.3 (C7), 31.17 (C13), 25.4 (C15), 21.6 (C14). HRMS (ESI) *m/z* calcd. for $C_{16}H_{14}NO^+$ $[M+H]^+$ 236.1075, found 236.1077. IR (neat) ν_{max} (cm^{-1}) 2933 (C-H), 1681 (C=O), 1457, 1334, 1125, 754, 542. UV-Vis (THF): $\lambda_{max}(\varepsilon)$: 284 nm (9700 $M^{-1}cm^{-1}$) 322 nm (3500 $M^{-1}cm^{-1}$), 470 nm (2500 $M^{-1}cm^{-1}$).

*Synthesis of 2-(2-bromophenyl)-6-methylpyridine (**P6**).* Under inert atmosphere, a solution of 2-bromo-6-methyl pyridine (0.53 mL, 4.7 mmol) in anhydrous THF (20 mL) was cooled to -78°C. A 2.2M n-BuLi solution in hexane (2.4 mL, 5.7 mmol) was added. The solution became red. The reaction mixture was stirred at -78°C for 30 minutes and afterwards a cold solution (0°C) of $ZnCl_2$ (0.769 g, 5.64 mmol) in anhydrous THF (6.5 mL) was added dropwise. The reaction mixture was brought to RT and stirred for 30 minutes. Separately, in a 100 mL 3-necked flask equipped with a condenser and a dropping funnel, under inert atmosphere, $Pd(PPh_3)_4$ (90 mg, 0.078 mmol), 2-bromo-iodobenzene (0.5 mL, 3.9 mmol) and anhydrous THF (20 mL) were mixed. To this, the aryl-zinc compound was added dropwise at RT with the dropping funnel. The reaction mixture was then refluxed under inert atmosphere overnight. After cooling to RT, 20 mL NH_4Cl sat. was added. The mixture was extracted with CH_2Cl_2 (3x50 mL) and washed twice with 15 mL of NH_4Cl (saturated aqueous solution) and 15 mL H_2O. The combined organic phases were dried over anhydrous $MgSO_4$ and the solvent was eliminated under reduced pressure. Hexane was added over the crude solid and the precipitate (NH_4Cl) was filtered off. The solvent was removed under reduced pressure. After purification by column chromatography on SiO_2 (eluent: hexane/EtOAc=4/0.5. Rf=0.5), the compound **P6** was obtained as a yellow oil (0.37 g, yield: 38%). ^{1}H NMR (300 MHz, CDCl3) δ_H 7.69 – 7.61 (m, 2H, H3, H10), 7.51 (dd, J = 7.6, 1.8 Hz, 1H, H7), 7.43 – 7.34 (m, 2H, H4, H9), 7.22 (dd, J = 7.6, 1.8 Hz, 1H, H8), 7.16 (d, J = 7.8 Hz, 1H, H2), 2.63 (s, 3H, H12). ^{13}C NMR (75 MHz, CDCl3) δ_C 158.3 (C11), 157.9 (C1), 141.7 (C6), 136.2 (C10), 133.4 (C3), 131.5 (C7), 129.7 (C8), 127.7 (C9), 122.1 (C2), 122.0 (C5), 121.8 (C4), 24.8 (C12). HRMS (ESI) *m/z* calcd. for $C_{12}H_{11}NBr+$ $[M+H]+$ 248.0075 , found 248.0082.

*Synthesis of 2-(6-methylpyridin-2-yl)benzoic acid (**6**).* Under inert atmosphere, a 2.2M BuLi solution (3.6 mL, 7.98 mmol) in hexane was added dropwise to a solution of P6 (1.80 g, 7.25 mmol) in anhydrous THF (30mL) at-78°C. The solution turned dark red, and was stirred for 2h at -78°C. Into this was bubbled gaseous CO_2until the colour changed from dark red to yellow. The mixture was warmed up to RT and stirred for 1h. H_2O (0.3 mL) was added for quenching. The solvent was removed under reduced pressure

and the light brown solid was dissolved in CH_2Cl_2. The solution was treated with HCl 1M until pH 4. After the evaporation of the solvent under reduced pressure and purification by column chromatography on SiO_2 (eluent: EtOAc/MeOH=9/1) the acid **6** was obtained (0.71 g, yield: 45%) ^{1}H NMR (300 MHz, CD_3OD) δ_H 7.92 (dd, J = 7.6, 1.5 Hz, 1H, H10), 7.80 (t, J = 7.8 Hz, 1H, H3), 7.66 – 7.47 (m, 3H, H7, H8, H9), 7.36 (d, J = 7.8 Hz, 1H, H4), 7.29 (d, J = 7.8 Hz, 1H, H2), 2.57 (s, 3H, H12). ^{13}C NMR (75 MHz, CD_3OD) δ_C 170.2 (C13), 158.0 (C11), 156.8 (C1), 140.0 (C5), 137.8 (C3), 132.34 (C6), 130.8 (C_{arom}), 129.9 (C_{arom}), 129.7 (C10), 128.3 (C_{arom}), 122.1 (C2), 120.8 (C4), 21.9 (C12). HRMS (ESI) *m/z* calcd. for $C_{13}H_{11}NO_2Na^+$ $[M+Na]^+$, 236.0687, found 236.0695.

General procedure for **P7** and **P8**

Under inert atmosphere, a solution of 2-ethoxycarbonylphenyl boronic acid (548 mg, 2.82 mmol, 1.05 eq) was mixed with degassed toluene (25 mL), H_2O (10 mL) and EtOH (7 mL) at RT. K_2CO_3 (2.506 g, 18.13 mmol, 6.74 eq) is afterwards added, followed by 6-bromo-2,3-dimethylpyridine (for **P7**) or 2-bromo-6-ethylpyridine (for **P8**) (2.69 mmol, 1 eq) and $[Pd(PPh_3)_4]$ (78 mg, 0.067 mmol, 0.025 eq). The reaction mixture was refluxed under inert atmosphere for 16h and then cooled to RT. The two phases were separated and the aqeous phase was extracted with EtOAc (3x25 mL). The combined organic phases were dried over $MgSO_4$. The purification of the crude compound by column chromatography on SiO_2 (eluent: heptane/EtOAc = 4/1-> EtOAc 100% (Rf = 0.1)) gave the compound **P7** as a yellow oil (100 mg, yield: 15%), respectively **P8** as a light yellow oil (100 mg, yield: 15%). **P7:** ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.77 (d, *J* = 7.6 Hz, 1H, H5), 7.57 – 7.50 (m, 2H, H1, H2), 7.50 – 7.38 (m, 2H, H6, H8), 7.23 (d, *J* = 7.7 Hz, 1H, H9), 4.16 (q, *J* = 7.2 Hz, 2H, H18), 2.52 (s, 3H, H13), 2.32 (s, 3H, H14), 1.10 (t, *J* = 7.1 Hz, 3H, H19). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 169.19, 156.27, 155.32, 140.98, 137.34, 132.06, 130.82, 129.73, 129.58, 129.48, 127.84, 119.99, 60.80, 22.62, 18.92, 13.90. HRMS (ESI) calcd. for $C_{16}H_{18}NO_2^+$ $[M+H]^+$, 256.1338, found 256.1357. **P8:** ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.83 – 7.77 (m, 1H, H5), 7.66 (t, *J* = 7.7 Hz, 1H, H9), 7.57 – 7.51 (m, 2H, H1, H2), 7.44 (ddd, *J* = 7.6, 5.7, 3.2 Hz, 1H, H6), 7.28 (d, *J* = 7.9 Hz, 1H, H8), 7.13 (d, *J* = 7.7 Hz, 1H, H10), 4.12 (q, *J* = 7.2 Hz, 2H, H18), 2.85 (q, *J* = 7.6 Hz, 2H, H13), 1.36 – 1.28 (m, 3H, H14), 1.04 (t, *J* = 7.1 Hz, 3H, H19). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 162.82, 141.28, 136.51, 132.08, 130.90, 129.69, 129.66, 128.05, 120.20, 119.83, 60.80, 31.41, 29.70, 13.89, 13.81. HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}NO_2^+$ $[M+Na]^+$, 278.0865, found 278.1012.

General procedure for **7** and **8**

A solution of **P7** or **P8** (0.355 mmol, 1 eq) in MeOH (10 mL) was mixed with a solution of NaOH (220 mg, 6.25 mmol, 17.6 eq) in H_2O (10 mL). The reaction mixture was refluxed for 16h. The MeOH was removed under reduced pressure. After pH adjustment to 2 with HCl 1 M, the water was removed under reduced pressure. 20 mL were added over the crude product and the suspension was filtered, The filtrate was concentrated under reduced pressure and the obtained solid was further dried under high vacuum to give **7** as an off-white solid (70 mg,yield: 88%), respectively **8** and a white solid (49 mg,yield: 61%). **7**: ^{1}H NMR (300 MHz, CD_3OD) δ_H 7.98 – 7.93 (m, 1H, H5), 7.78 (d, *J* = 7.9 Hz, 1H, H8), 7.69 – 7.53 (m, 3H, H1, H2, H6), 7.42 (d, *J* = 7.9 Hz, 1H, H9), 2.59 (s, 3H, H13), 2.43 (s, 3H, H14). ^{13}C NMR (75 MHz, CD_3OD) δ_C 154.79, 139.42, 138.53, 133.36, 131.38, 130.58, 129.85, 129.80, 128.41, 121.50, 19.49, 17.16. HRMS (ESI) calcd. for $C_{14}H_{14}NO_2^+$ $[M+H]^+$, 228.1015, found 228.1019. **8:** ^{1}H NMR (300 MHz, CD_3OD) δ_H 7.90 – 7.80 (m, 2H, H5, H9), 7.65 – 7.48 (m, 3H, H1, H2, H6), 7.40 (dd, *J* = 7.8, 1.0 Hz, 1H, H8), 7.31 (dd, *J* = 7.8, 0.9 Hz, 1H, H10), 2.85 (q, *J* = 7.6 Hz, 2H, H13), 1.36 – 1.27 (m, 3H, H14). ^{13}C NMR (75 MHz, CD_3OD) δ_C 162.05, 157.38,

139.58, 138.02, 130.39, 129.78, 129.41, 128.24, 121.01, 120.77, 29.98, 13.11. HRMS (ESI) *m/z* calcd. for $C_{14}H_{14}NO_2^+$ $[M+H]^+$, 228.1015, found 228.1019.

Synthesis of *4-methylpyrido[2,1-a]isoindol-6(2H)-one* **14**

Compound **14** was synthesised by following a reported procedure.[3] Under inert atmosphere, 2-bromo-6-methylpyridine (860 mg, 5 mmol, 1 eq) and $Pd(PPh_3)_4$ (787 mg, 5.25 mmol, 1.05 eq) were disolved in degassed toluene (20 mL). Over this, a solution of (2-formylphenyl)boronic acid (787 mg, 5.25 mmol, 1.05 eq) in degassed EtOH (10 mL) was added over, followed by a degassed Na_2CO_3 (1.060 g, 5 mmol, 1 eq) aqeous solution (5 mL. The reaction mixture was refluxed under inert atmosphere for 16h and then cooled to RT. 10 mL H_2O were added. The two phases were separated and the aqeous phase was extracted with EtOAc (3x25 mL). The combined organic phases were dried over Na_2SO_4. The purification of the crude compound by column chromatography on SiO_2 (eluent: heptane/EtOAc = 95/5 (Rf = 0.3) gave **14** as an orange solid (337 mg, yield: 34%). ^{1}H NMR (300 MHz, $CDCl_3$) δ_H 7.81 (dt, *J* = 7.5, 1.1 Hz, 1H, H5), 7.62 (dt, *J* = 7.6, 1.1 Hz, 1H, H2), 7.55 (td, *J* = 7.4, 1.2 Hz, 1H, H1), 7.46 (td, *J* = 7.3, 1.3 Hz, 1H, H6), 5.89 (td, *J* = 4.1, 1.7 Hz, 1H, H8), 4.76 (tp, *J* = 3.0, 1.5 Hz, 1H, H10), 3.05 (tq, *J* = 3.8, 1.9 Hz, 2H, H9), 2.45 (q, *J* = 1.8 Hz, 3H, H13). ^{13}C NMR (75 MHz, $CDCl_3$) δ_C 164.37 (C14), 134.67 (C7), 133.47 (C3), 133.27 (C4), 131.83 (C1), 130.06 (C11), 129.09 (C6), 123.25 (C5), 119.19 (C2), 104.94 (C8), 104.63 (C10), 24.99 (C9), 20.03 (C13). HRMS (ESI) *m/z* calcd. for $C_{13}H_{10}NO^+$ $[M+H]^+$, 196.0753, found 196.0757.

*Procedures for the titrations of **6**-**8** with TsCl*

0.025 mmol (1eq.) of the corresponding substrate was dissolved in anhydrous acetone-*d6* and treated with anhydrous Et_3N (8 uL, 0.055 mmol, 2.2 eq). Additions of 1.2 mg solid TsCl were made, corresponding to 0.25 eq.

Structures, Emission, and UV-VIS spectra and ^{1}H-NMR spectra of compounds 2, 3 and 5

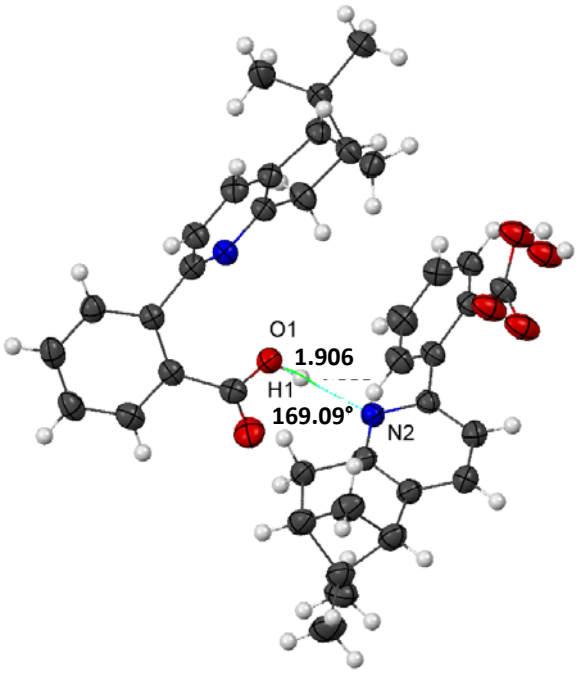


*Figure S1. Asymmetric unit of the structure of **2**, with depiction of the intermolecular H bonding and O1-H1-N2 angle with ellipsoids at 30% probability*

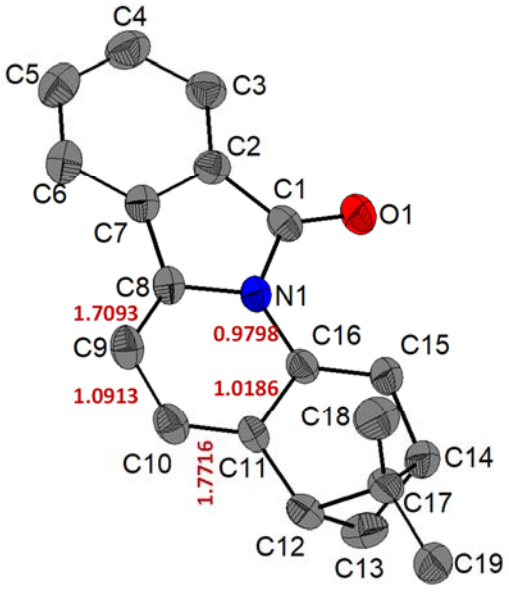


Figure S2. Molecular structure of 2 determined by single-crystal X-Ray diffraction with ellipsoids at 30% probability with atom numbering scheme and bond order values in red. The H atoms were omitted for clarity.

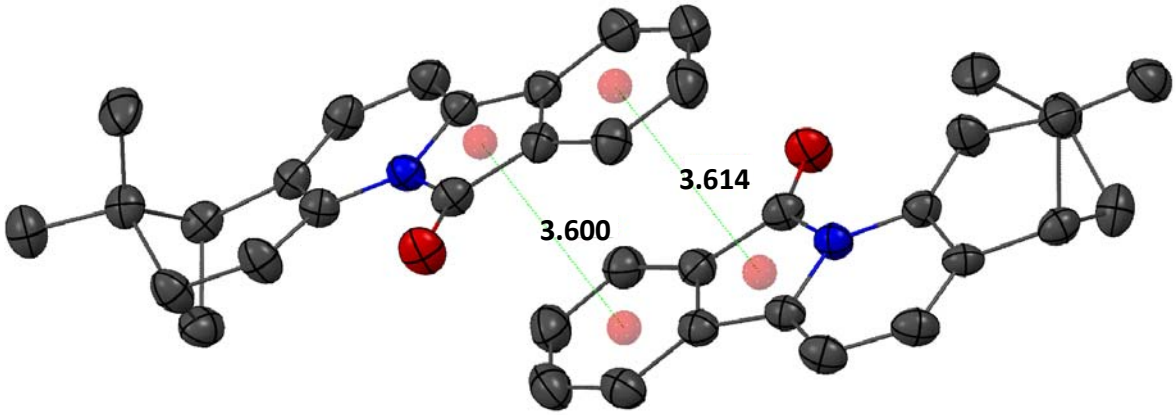


*Figure S3. Depiction of the π-π stacking interactions (with the centrodi-centroid distances in black) in the crystal of **3**, with ellipsoids at 30% probability. The H atoms were omitted for clarity.*

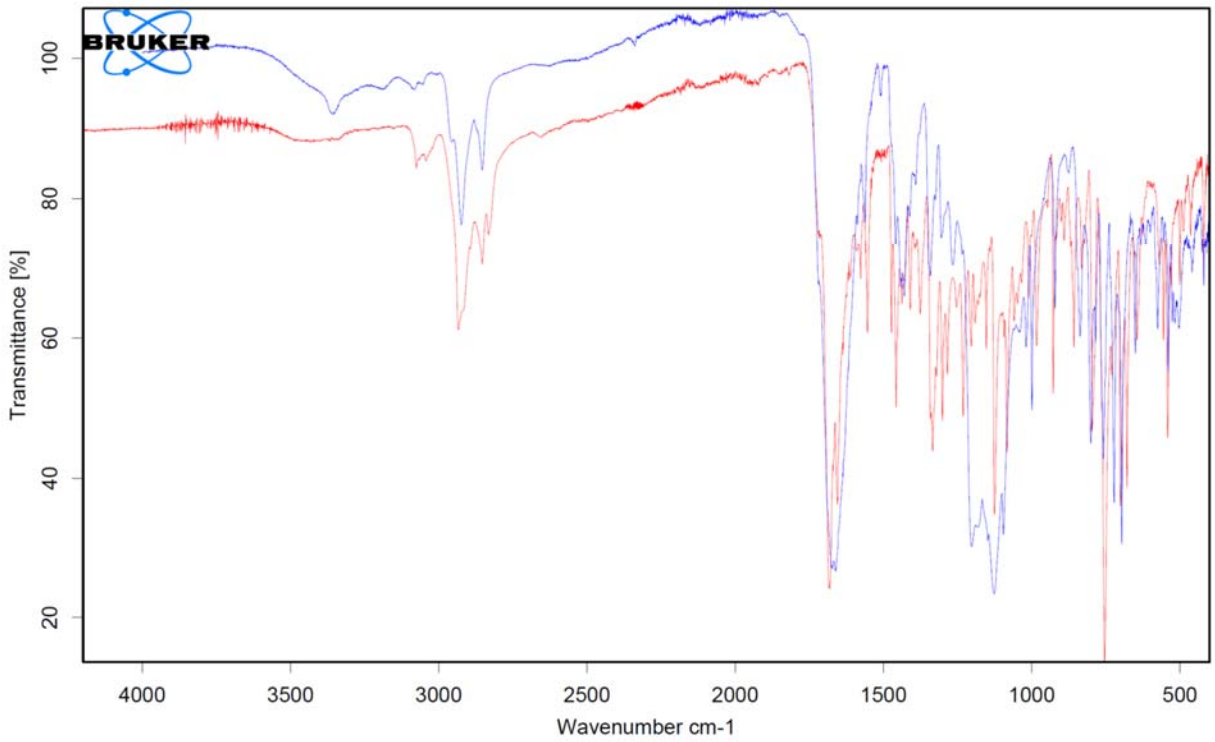


*Figure S4. IR spectra of **3** (blue) and **5** (red)*

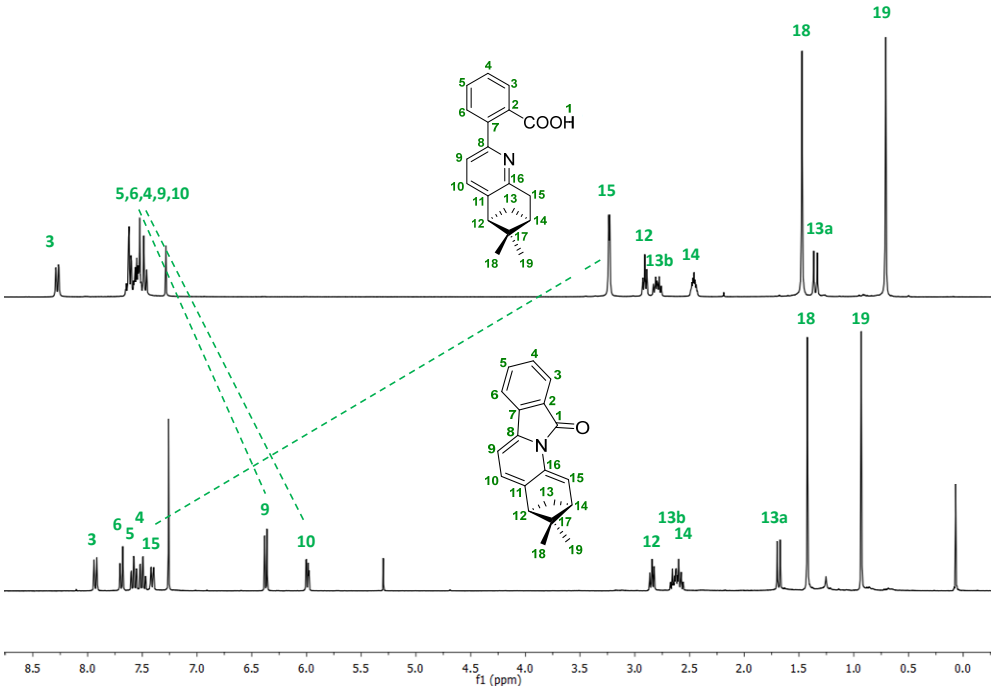


*Figure S5. Stacked ^{1}H-NMR spectra of **2** (top) and **3** (bottom)*

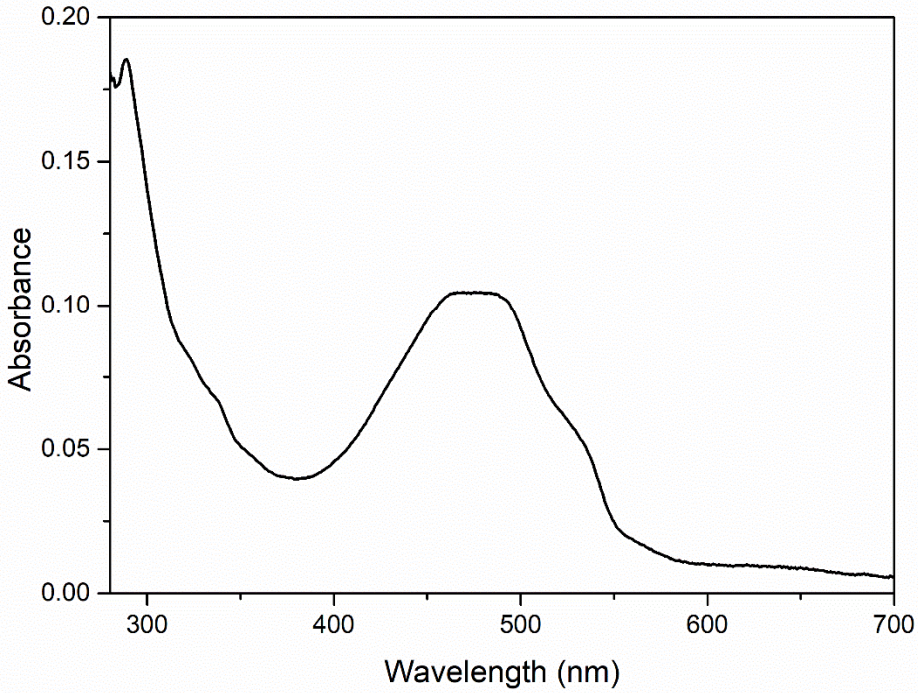


*Figure S6. UV-Vis spectrum of **3** in THF (0.04 mM in THF)*

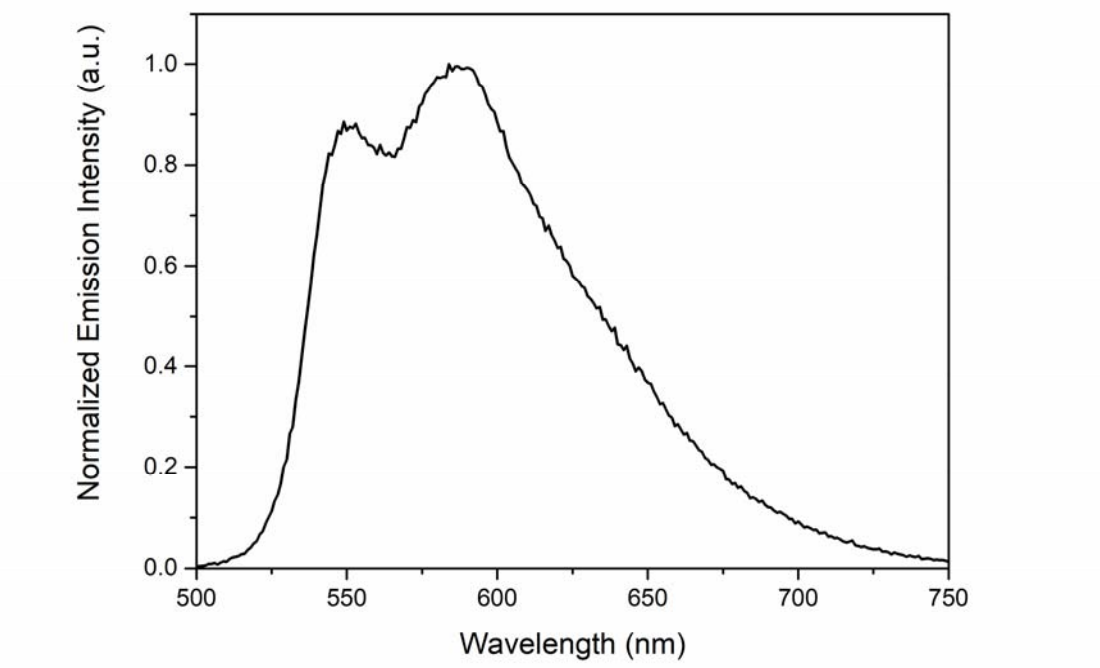


*Figure S7. Emission spectrum of **3** in THF (0.04 mM, λ_{ex} =470 nm)*

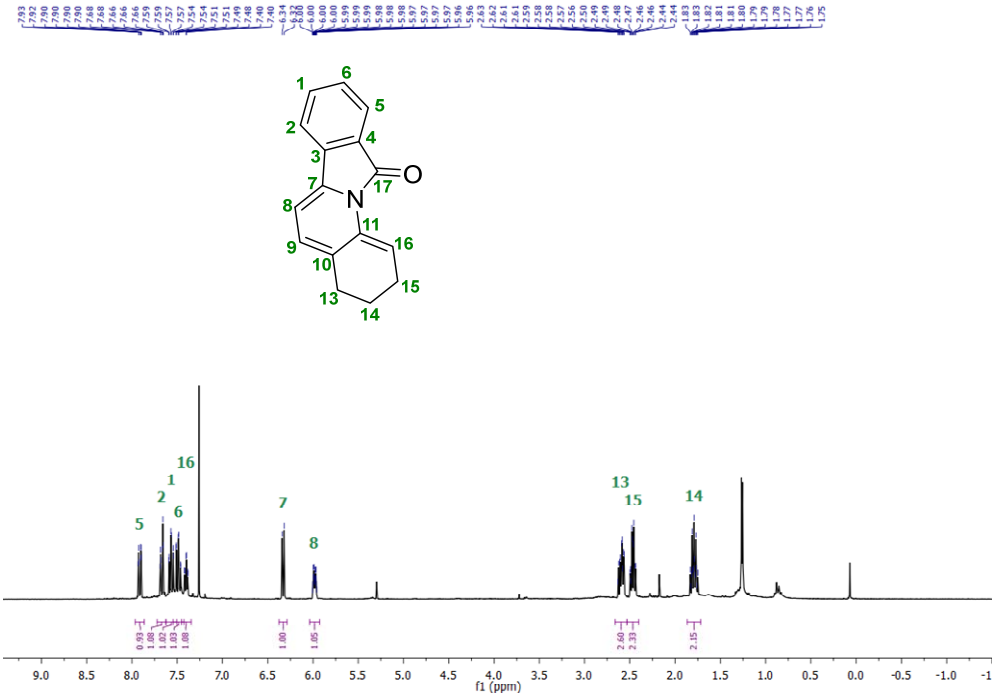


*Figure S8. ^{1}H-NMR spectrum of **5** in $CDCl_3$*

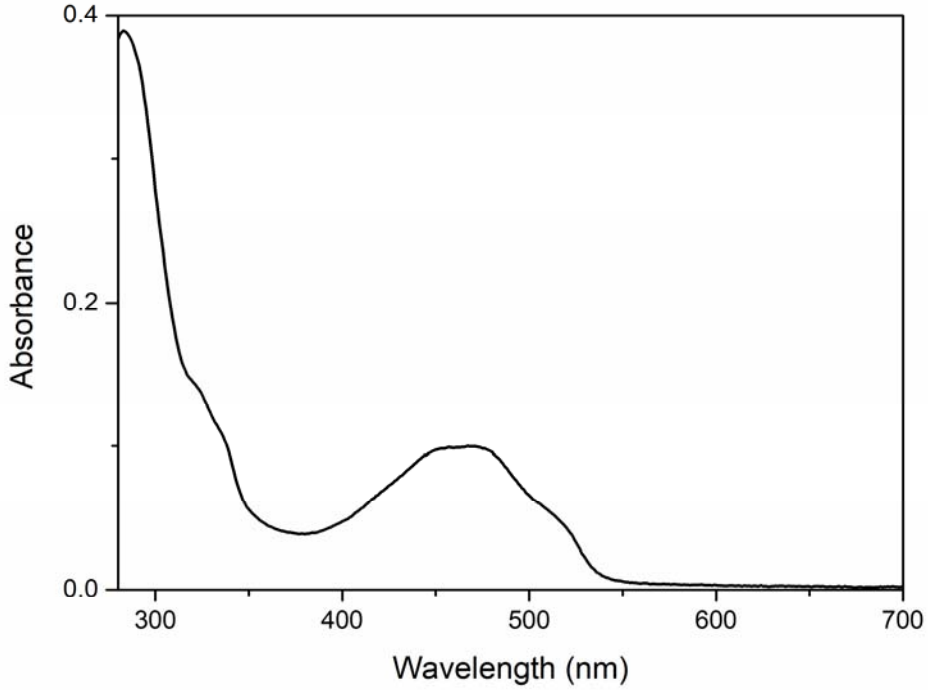


*Figure S9. UV-Vis spectrum of **5** in THF (0.04 mM in THF)*

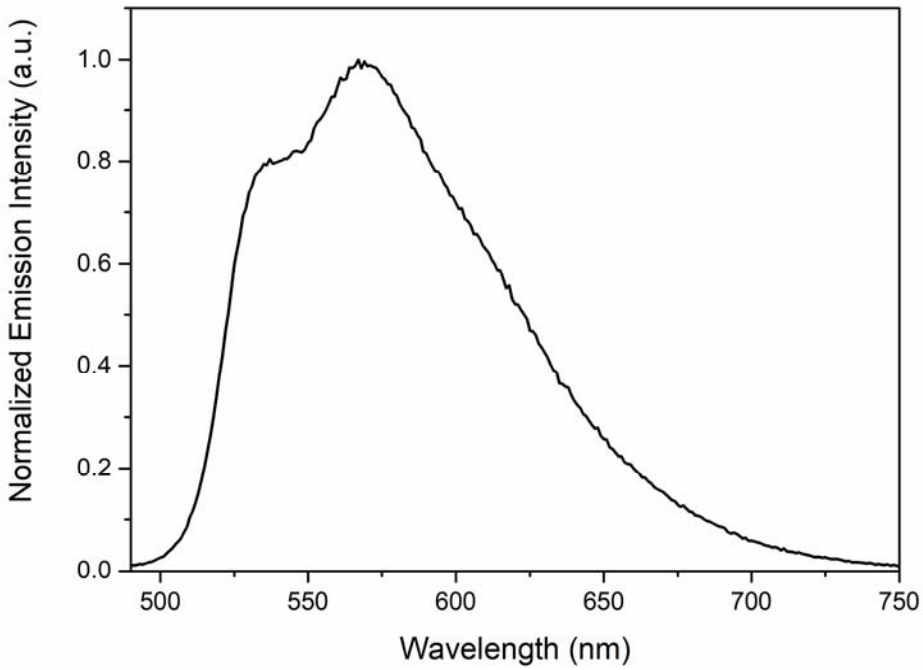


*Figure S10. Emission spectrum of **5** in THF (0.04 mM, λ_{ex} =470 nm)*

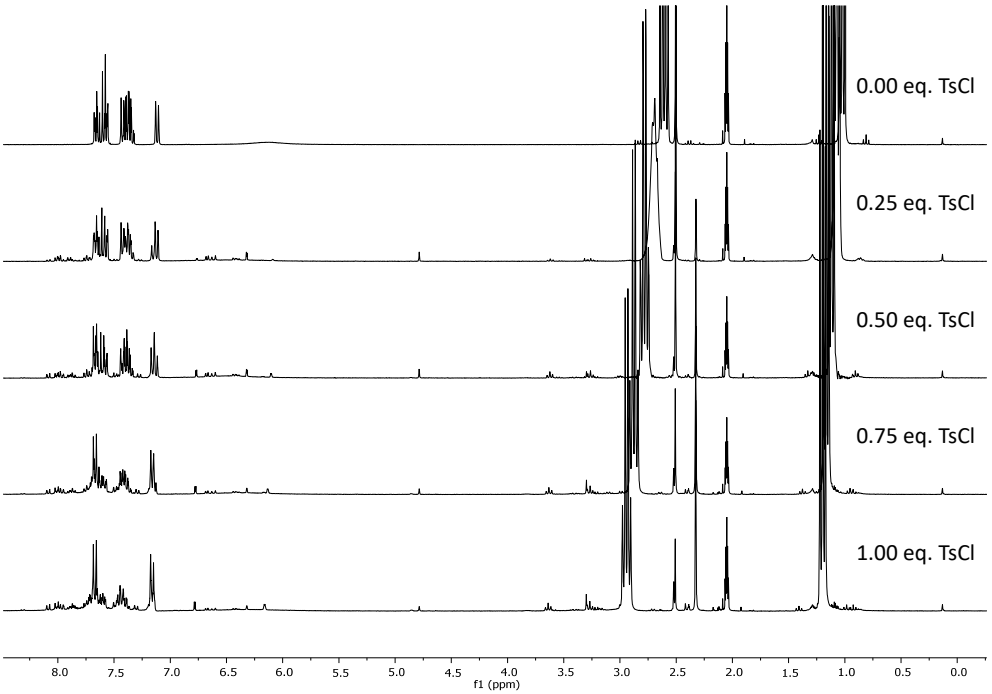


*Figure S11. ^{1}H-NMR spectrum of the titration of **6** with TsCl in the presence of 2.2 eq. Et_3N, in acetone-d6*

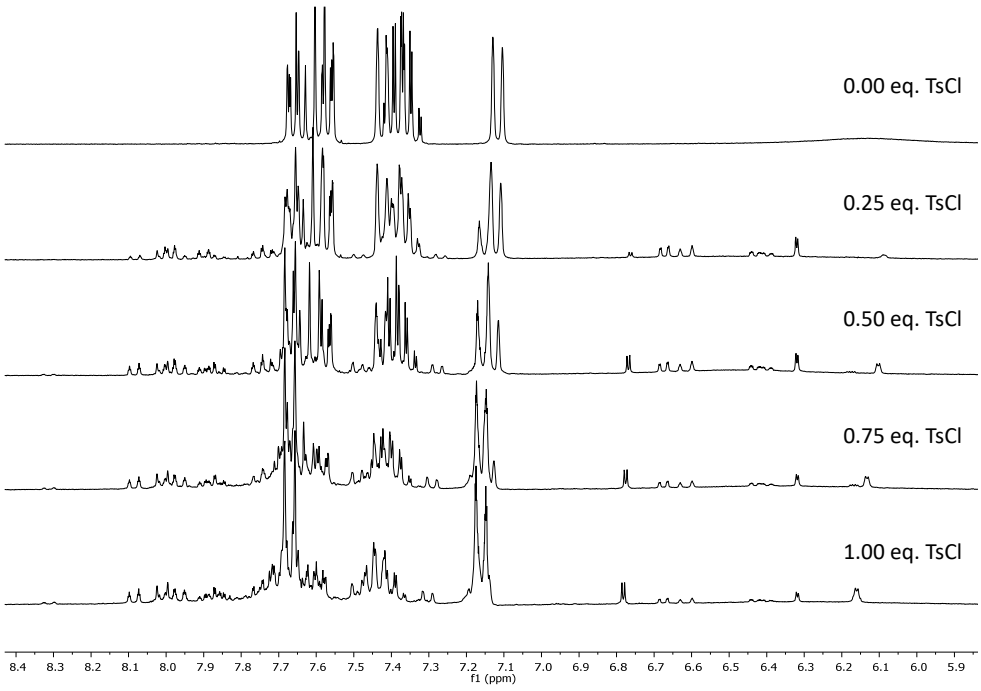


*Figure S12. Aromatic region of the ^{1}H-NMR spectrum of the titration of **6** with TsCl in the presence of 2.2 eq. Et_3N, in acetone-d6*

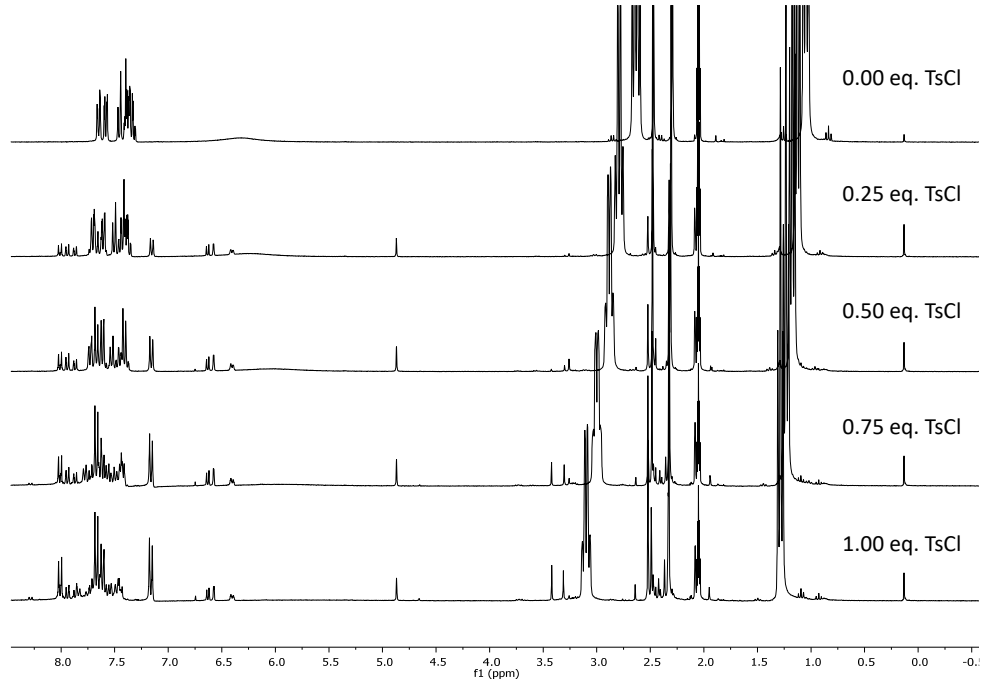


*Figure S13. ^{1}H-NMR spectrum of the titration of **7** with TsCl in the presence of 2.2 eq. Et_3N, in acetone-d6*

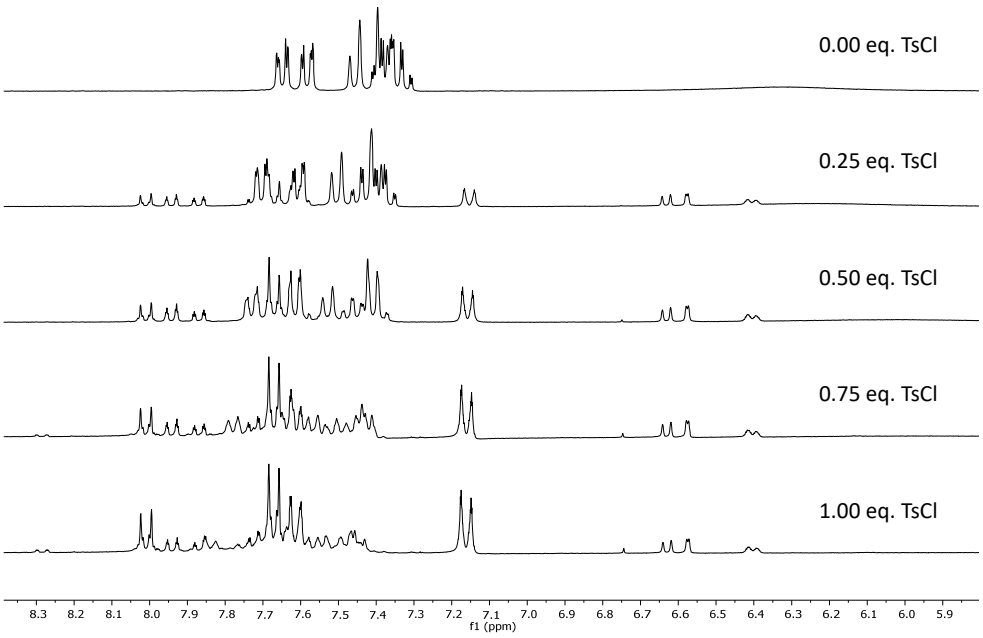


*Figure S14. Aromatic region of the ^{1}H-NMR spectrum of the titration of **7** with TsCl in the presence of 2.2 eq. Et_3N, in acetone-d6*

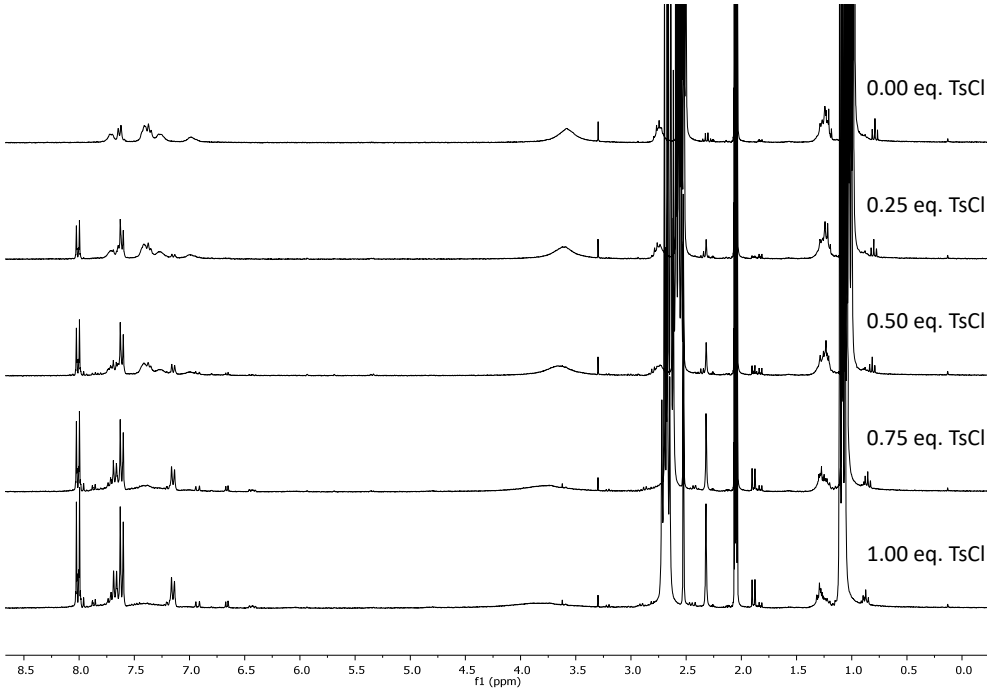


*Figure S15. ^{1}H-NMR spectrum of the titration of **8** with TsCl in the presence of 2.2 eq. Et_3N, in acetone-d6*

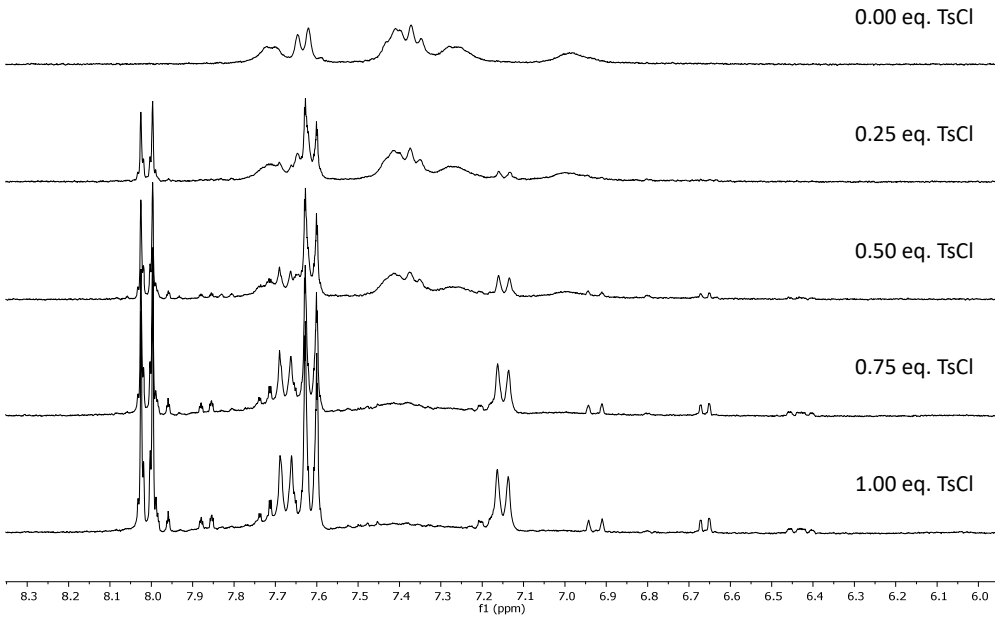


*Figure S16. Aromatic region of the ^{1}H-NMR spectrum of the titration of **8** with TsCl in the presence of 2.2 eq. Et_3N, in acetone-d6*

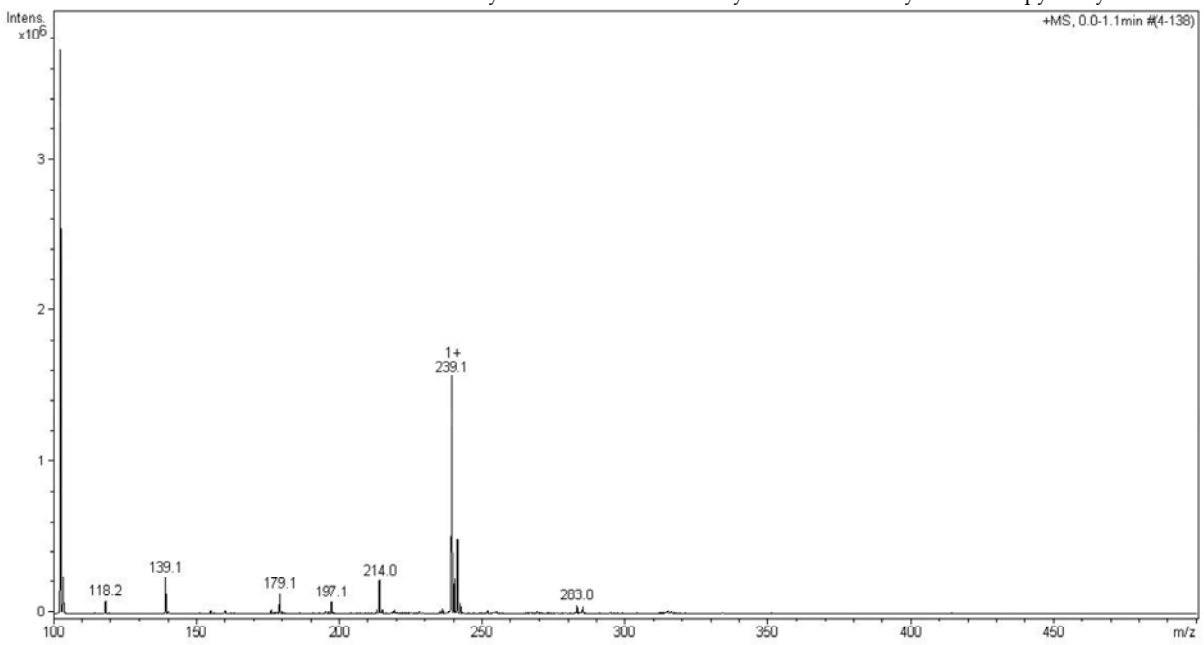


*Figure S17. (+)-ESI-MS spectrum of **9** ([M+H]⁺ at 196.1)*

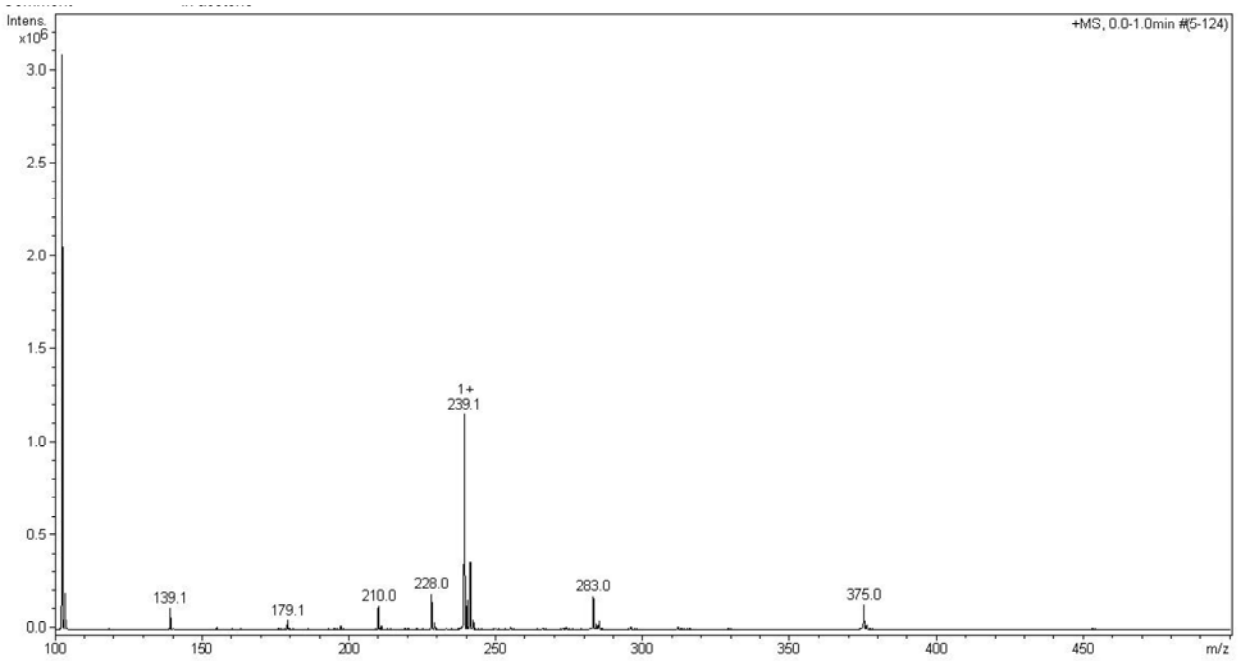


*Figure S18. (+)-ESI-MS spectrum of **10** ([M+H]⁺ at 210.0)*

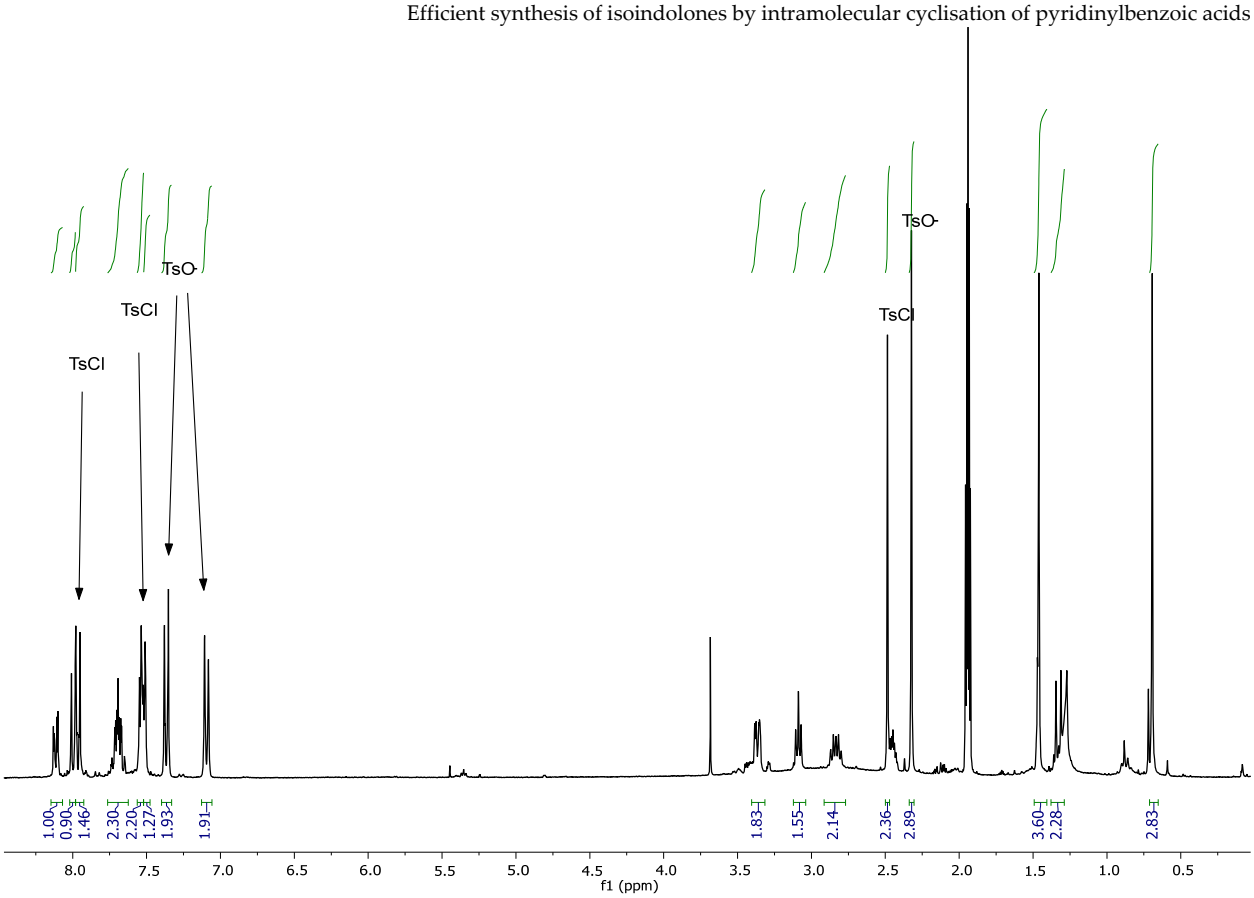


*Figure S19. ^{1}H-NMR spectrum of **Complex-1** in CD_3CN*

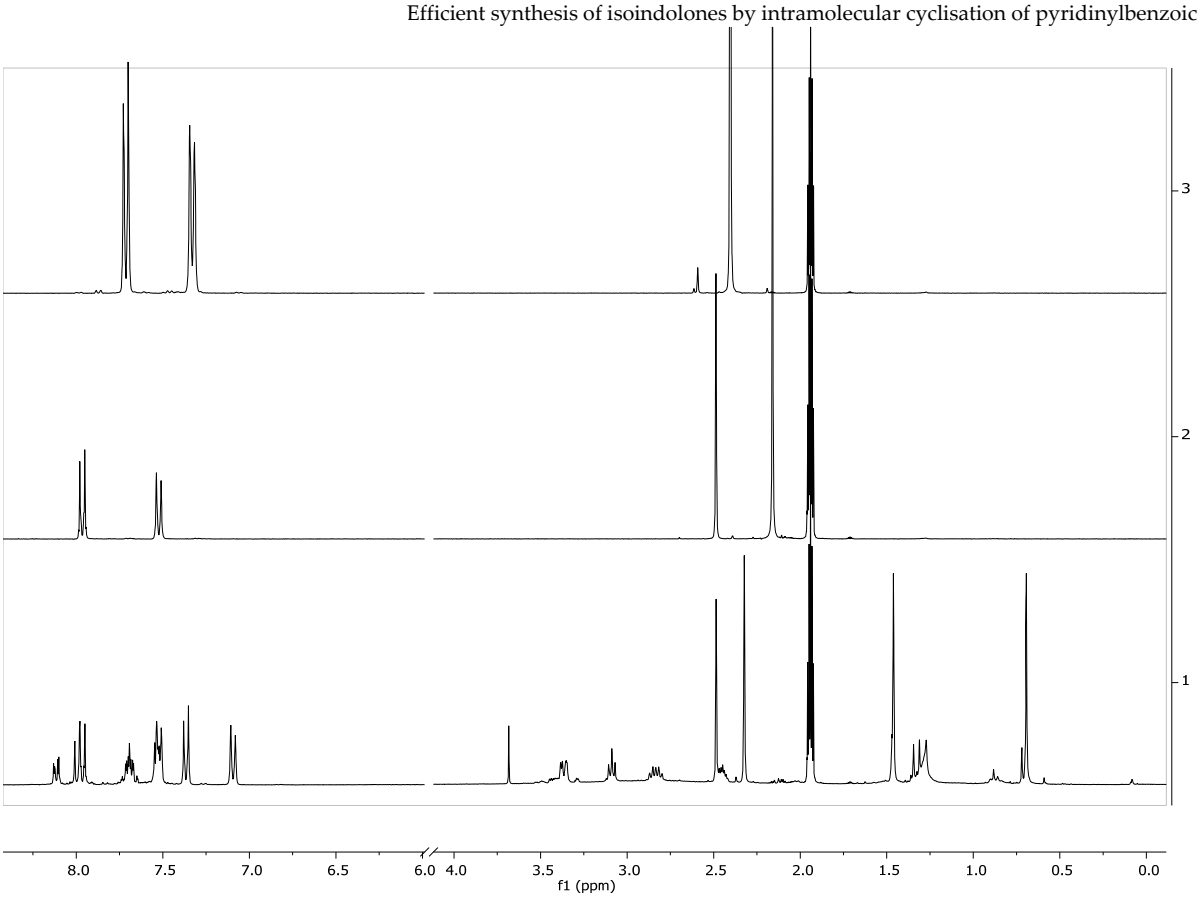


*Figure S20. Stacked ^{1}H-NMR spectra of TsOK (top), TsCl (middle) and **Complex-1** in CD_3CN*

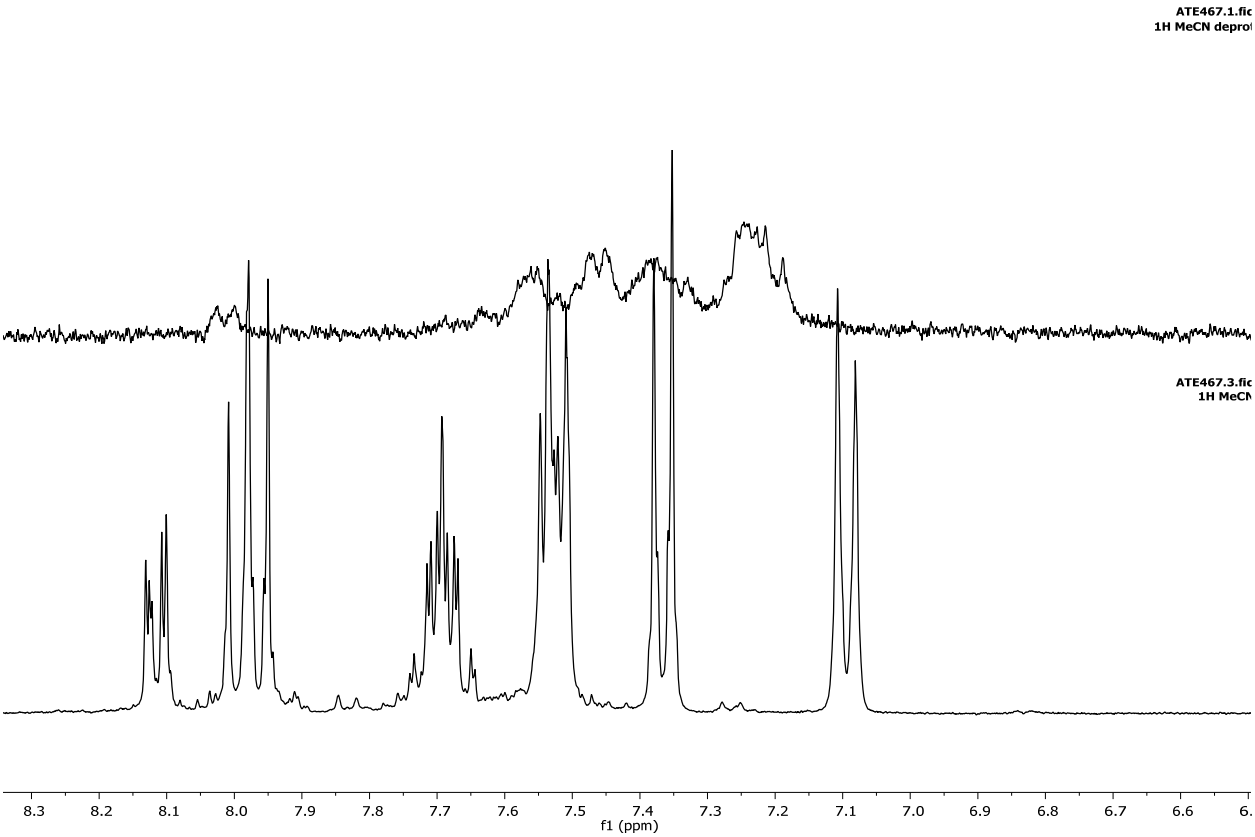


*Figure 21. Aromatic region of the ^{1}H-NMR spectra of R-COOK (top) and **Complex-1** in CD_3CN*

NMR spectra

NMR spectra of 2

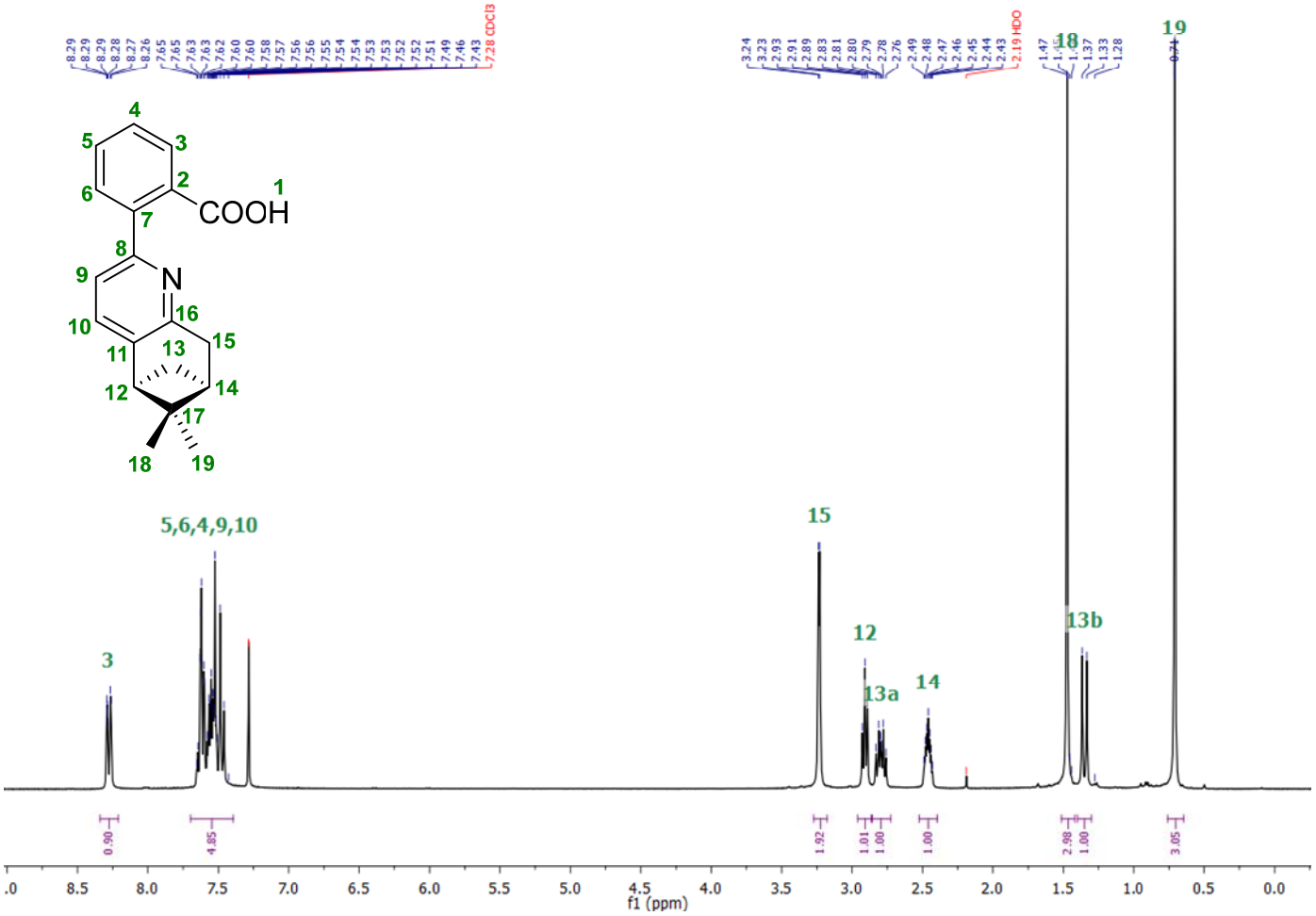


*Figure S22. ^{1}H-NMR spectrum of **2** in $CDCl_3$*

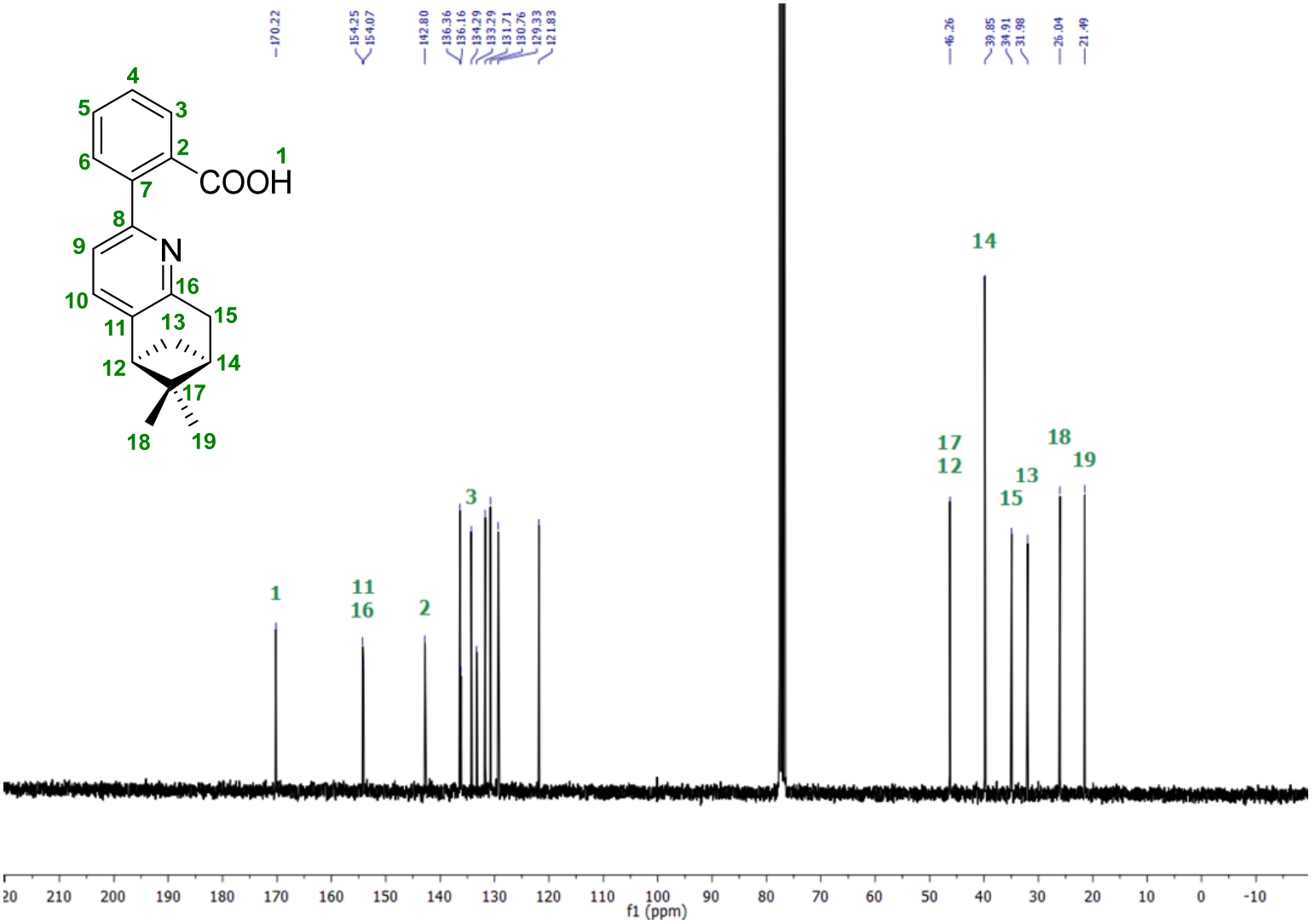


*Figure S23. ^{13}C-NMR spectrum of **2** in $CDCl_3$*

NMR spectra of 3

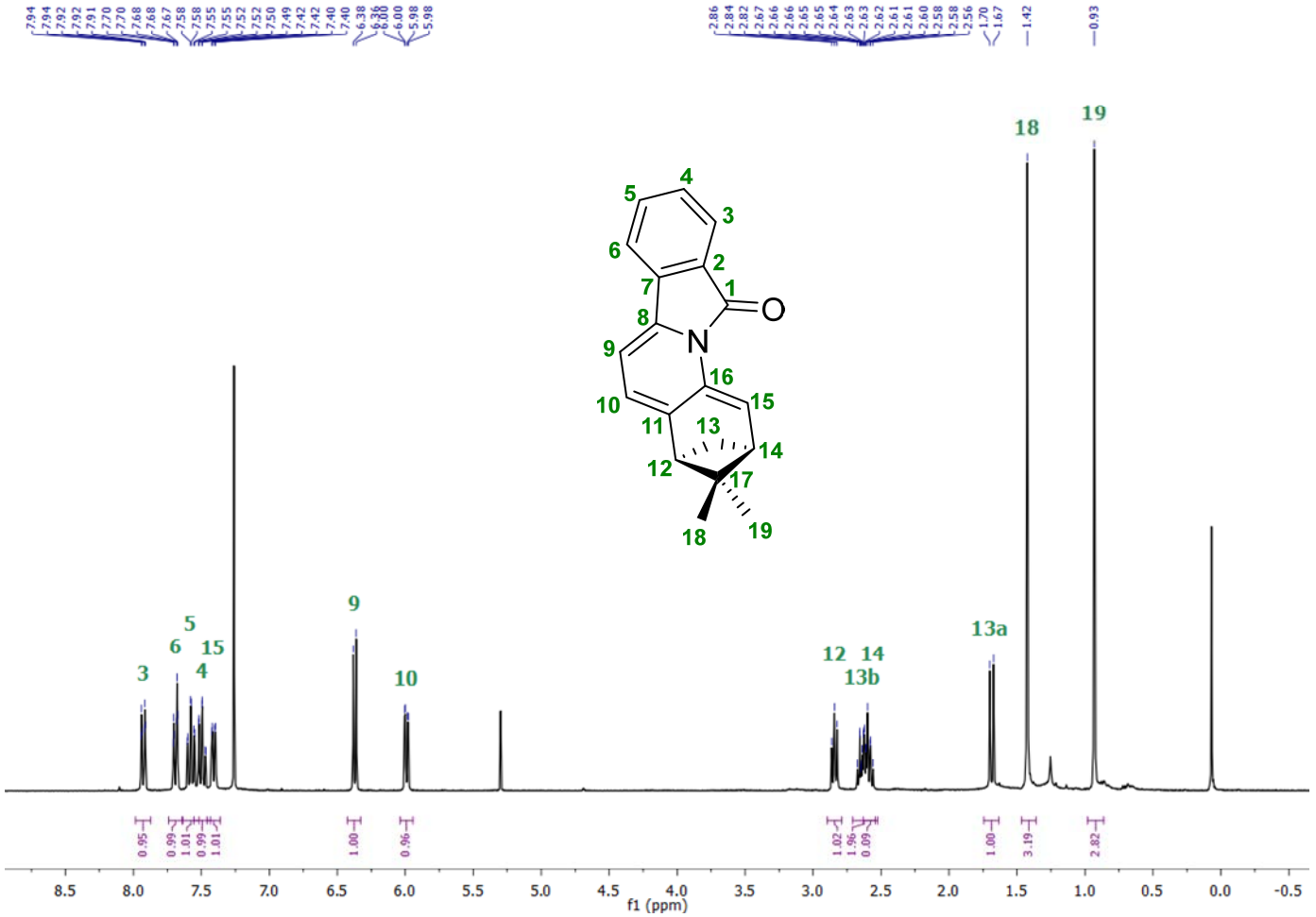


*Figure S24. ^{1}H-NMR spectrum of **3** in $CDCl_3$*

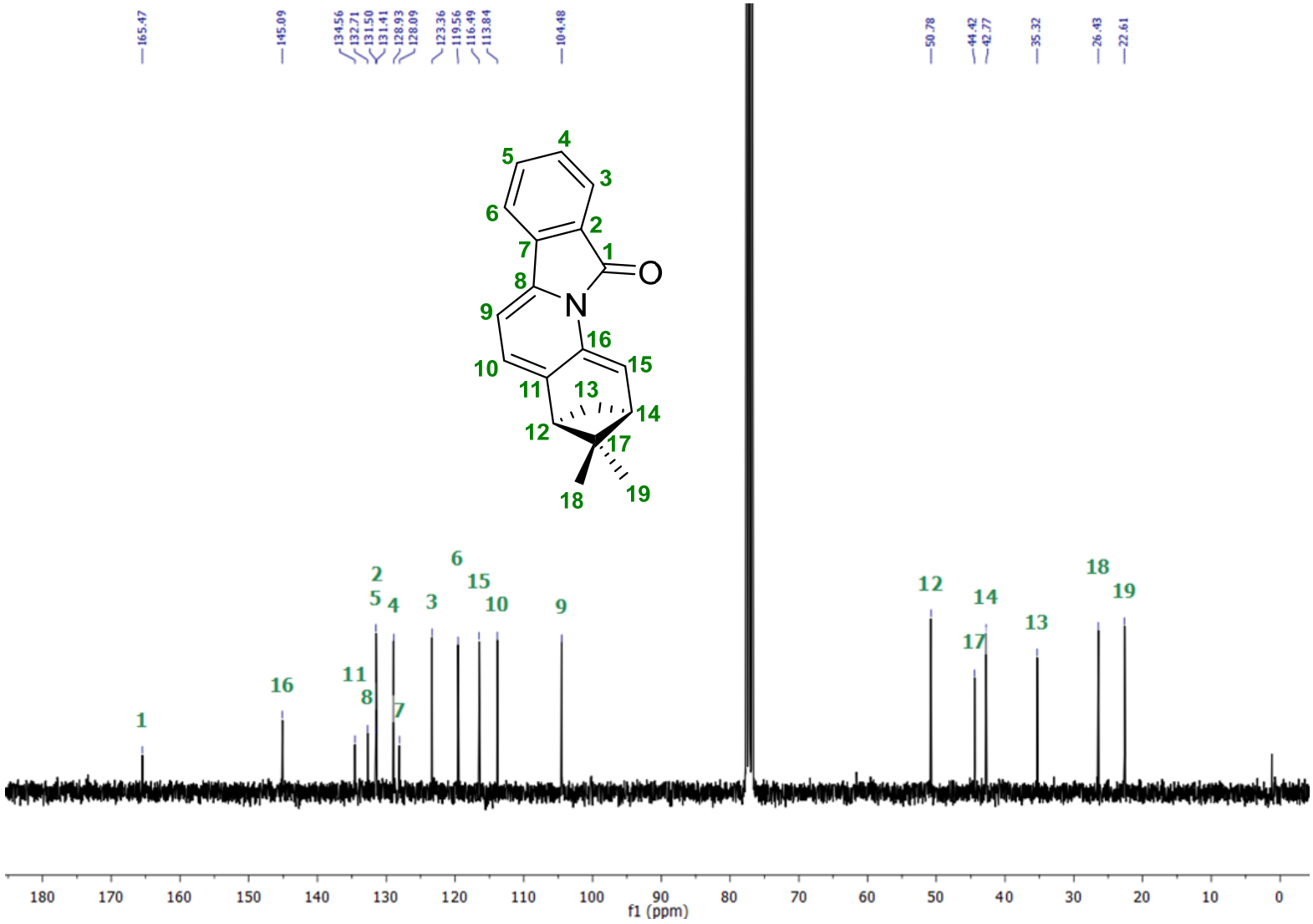


*Figure S25. ^{13}C-NMR spectrum of **3** in $CDCl_3$*

NMR spectra of P4

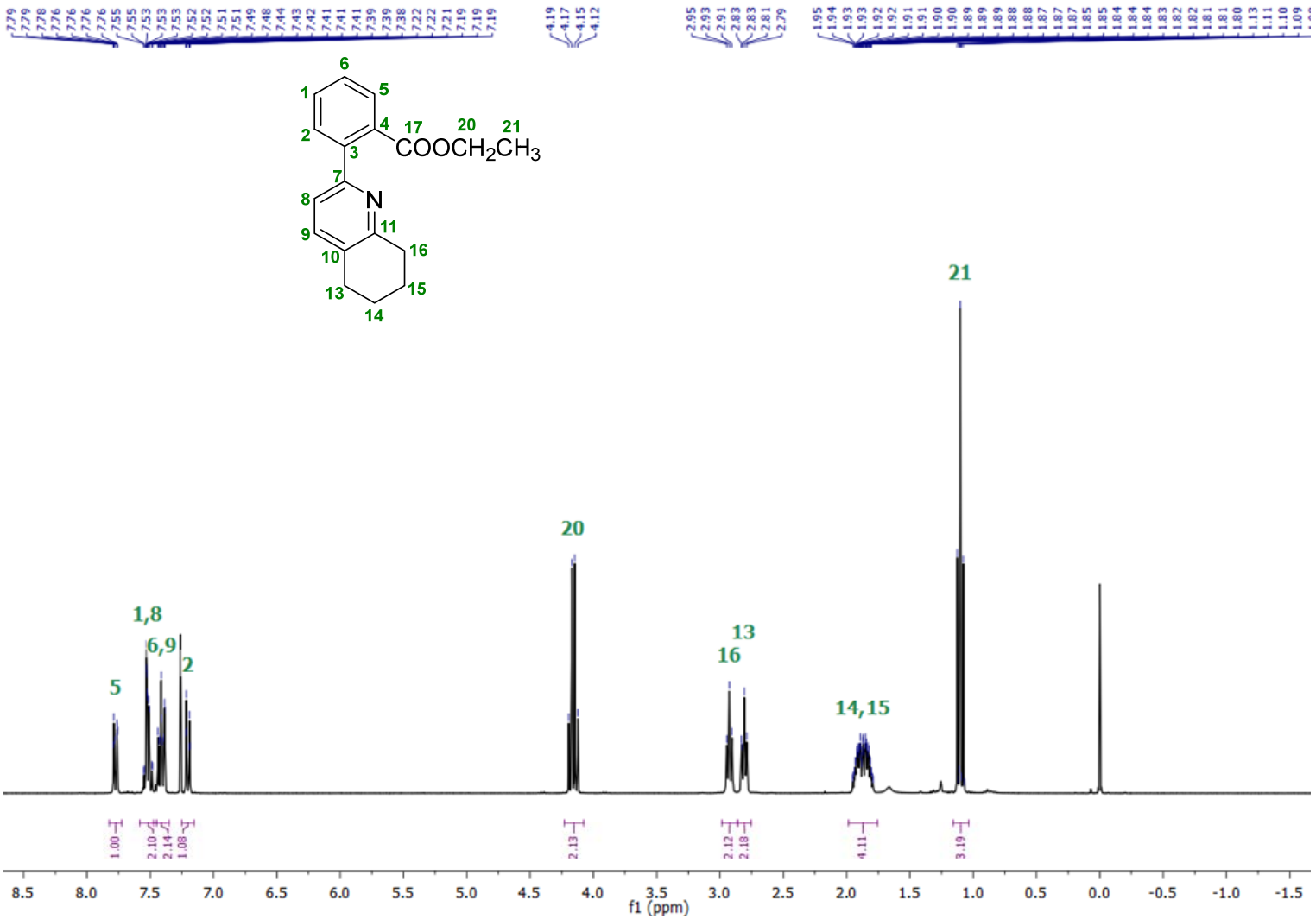


*Figure S26. ^{1}H-NMR spectrum of **P4** in $CDCl_3$*

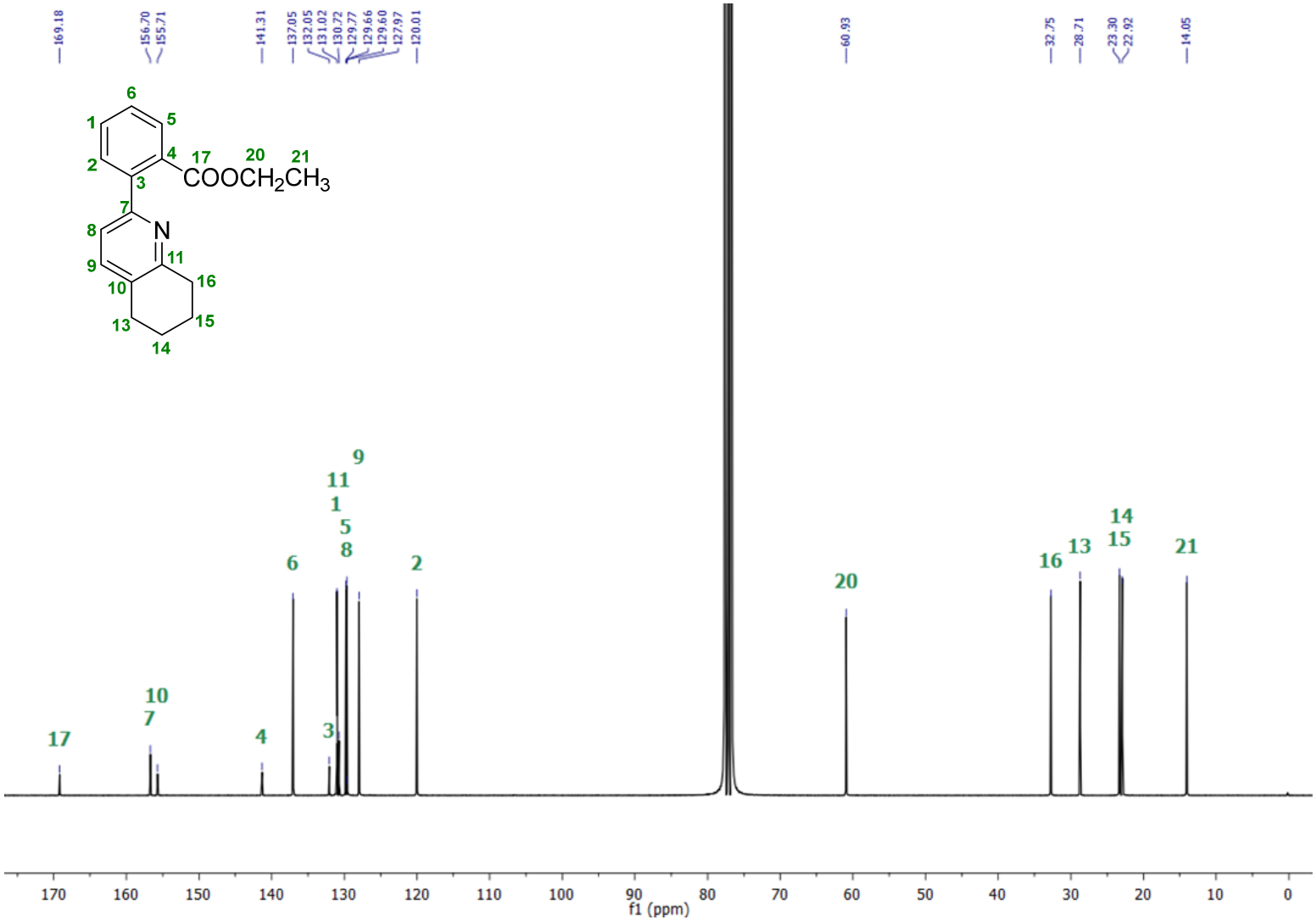


*Figure S27. ^{13}C-NMR spectrum of **P4** in $CDCl_3$*

NMR spectra of 4

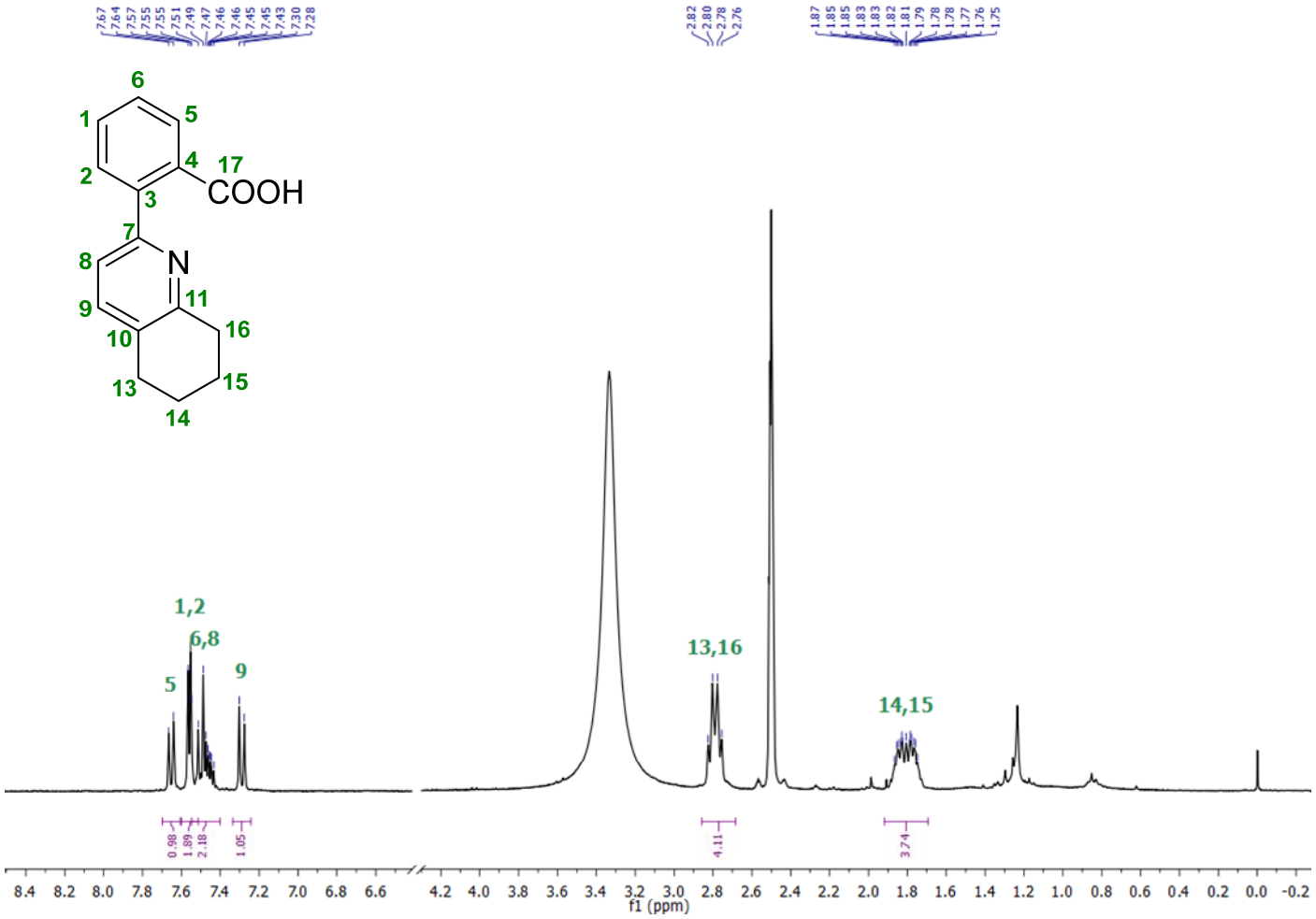


*Figure S28. ^{1}H-NMR spectrum of **4** in DMSO-d6*

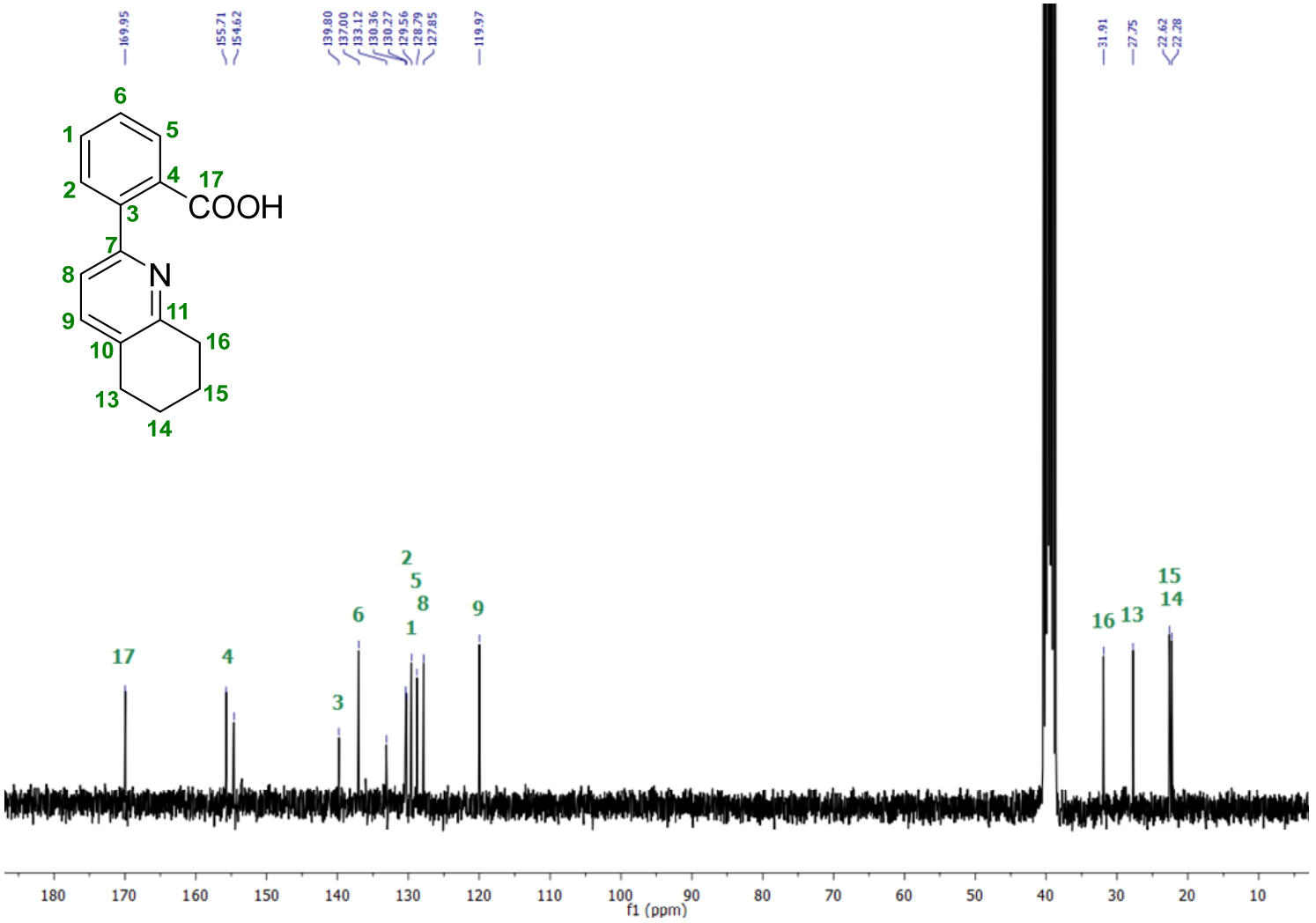


*Figure S29. ^{13}C-NMR spectrum of **4** in DMSO-d6*

NMR spectra of 5

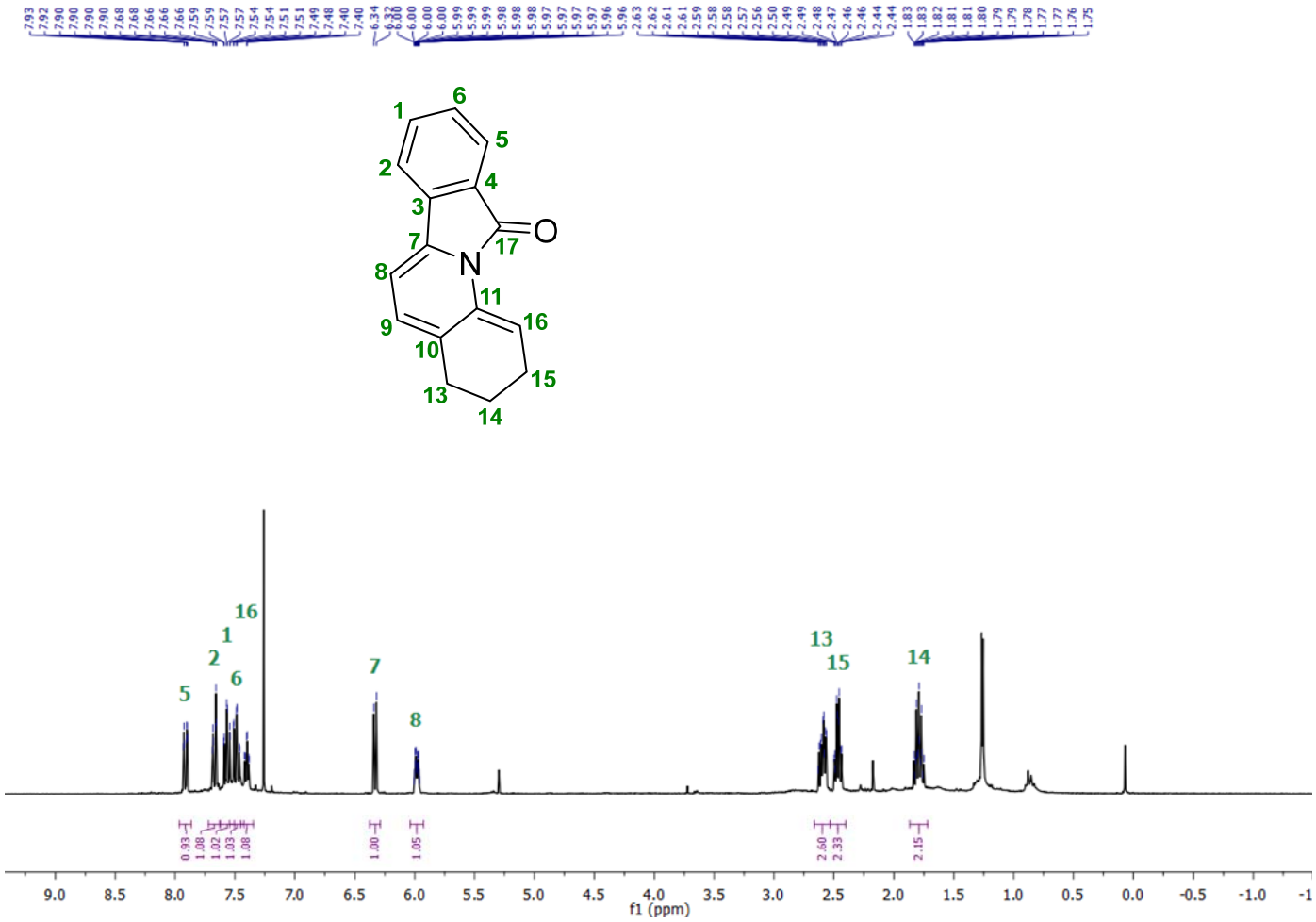


*Figure S30. ^{1}H-NMR spectrum of **5** in $CDCl_3$*

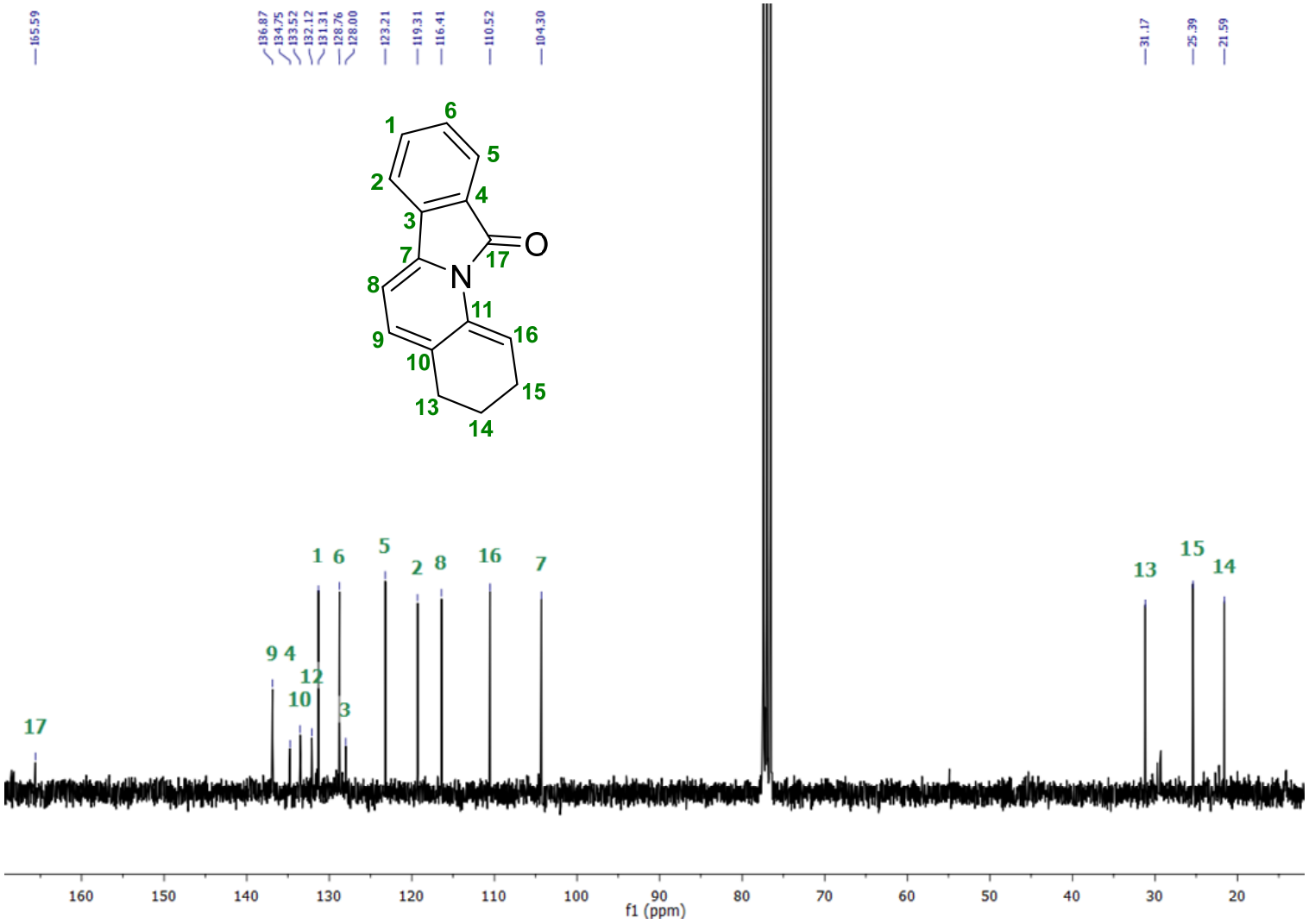


*Figure S31. ^{13}C-NMR spectrum of **5** in $CDCl_3$*

NMR spectra of P6

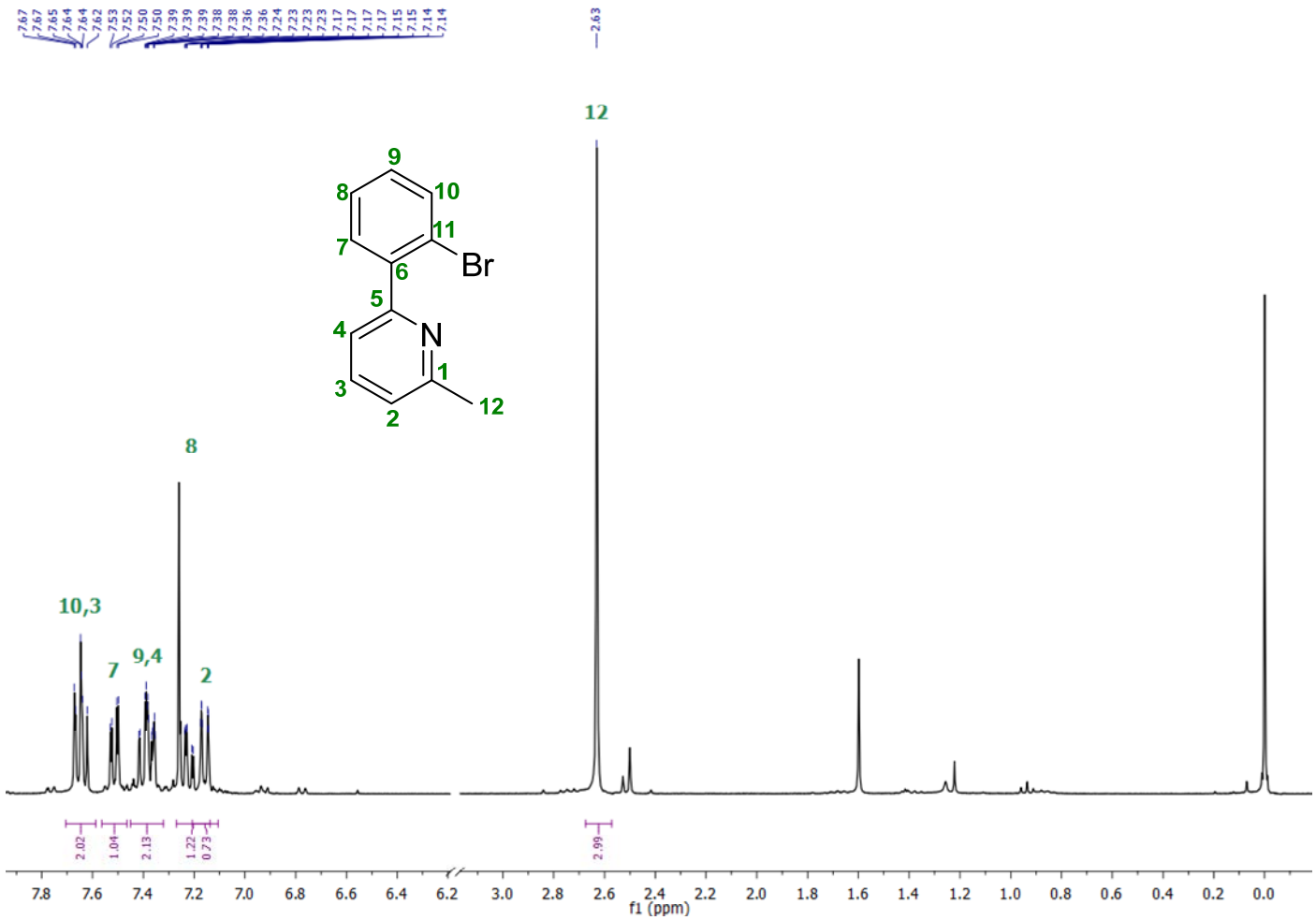


*Figure S32. ^{1}H-NMR spectrum of **P6** in $CDCl_3$*

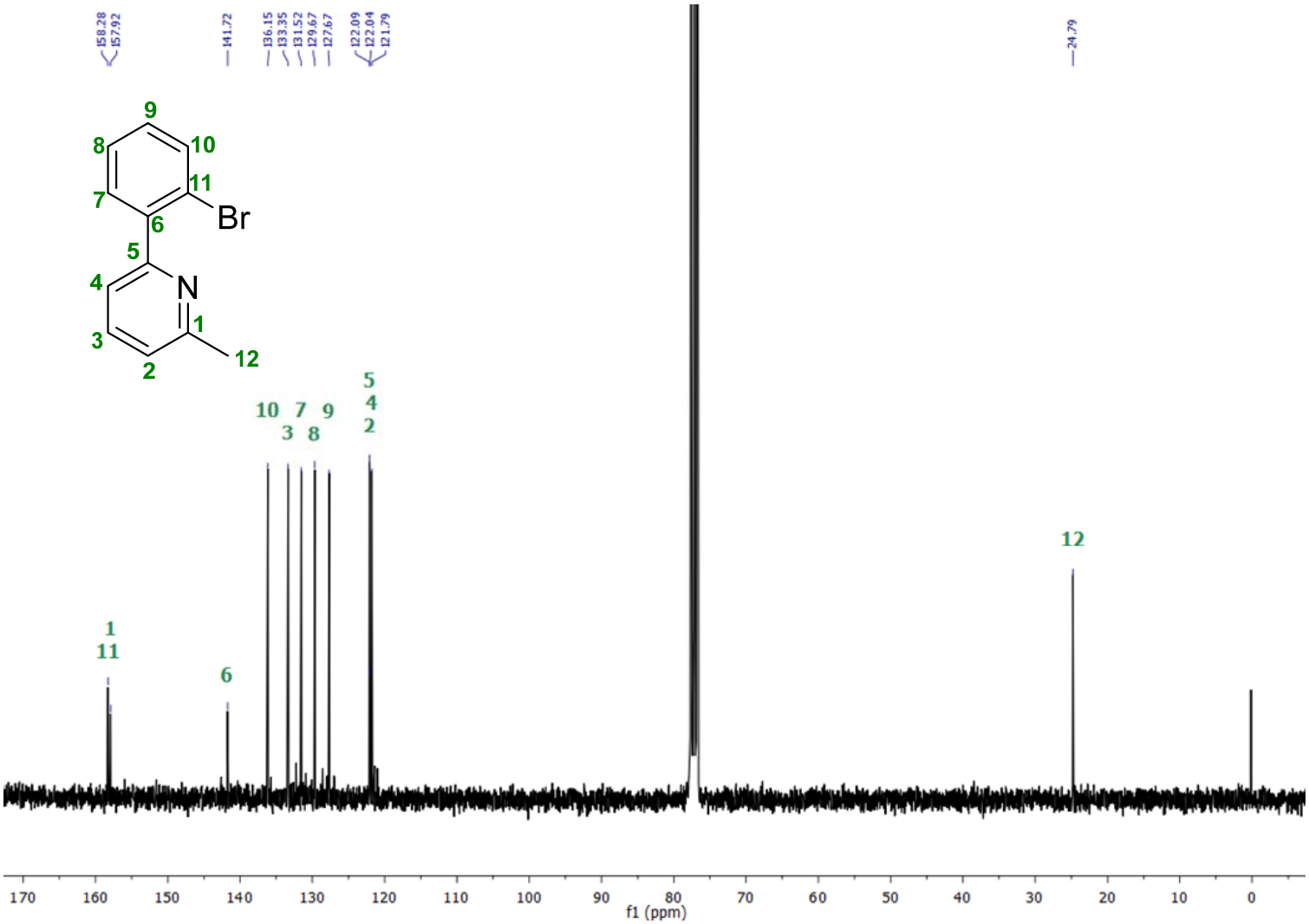


*Figure S33. ^{13}C-NMR spectrum of **P6** in $CDCl_3$*

NMR spectra of 6

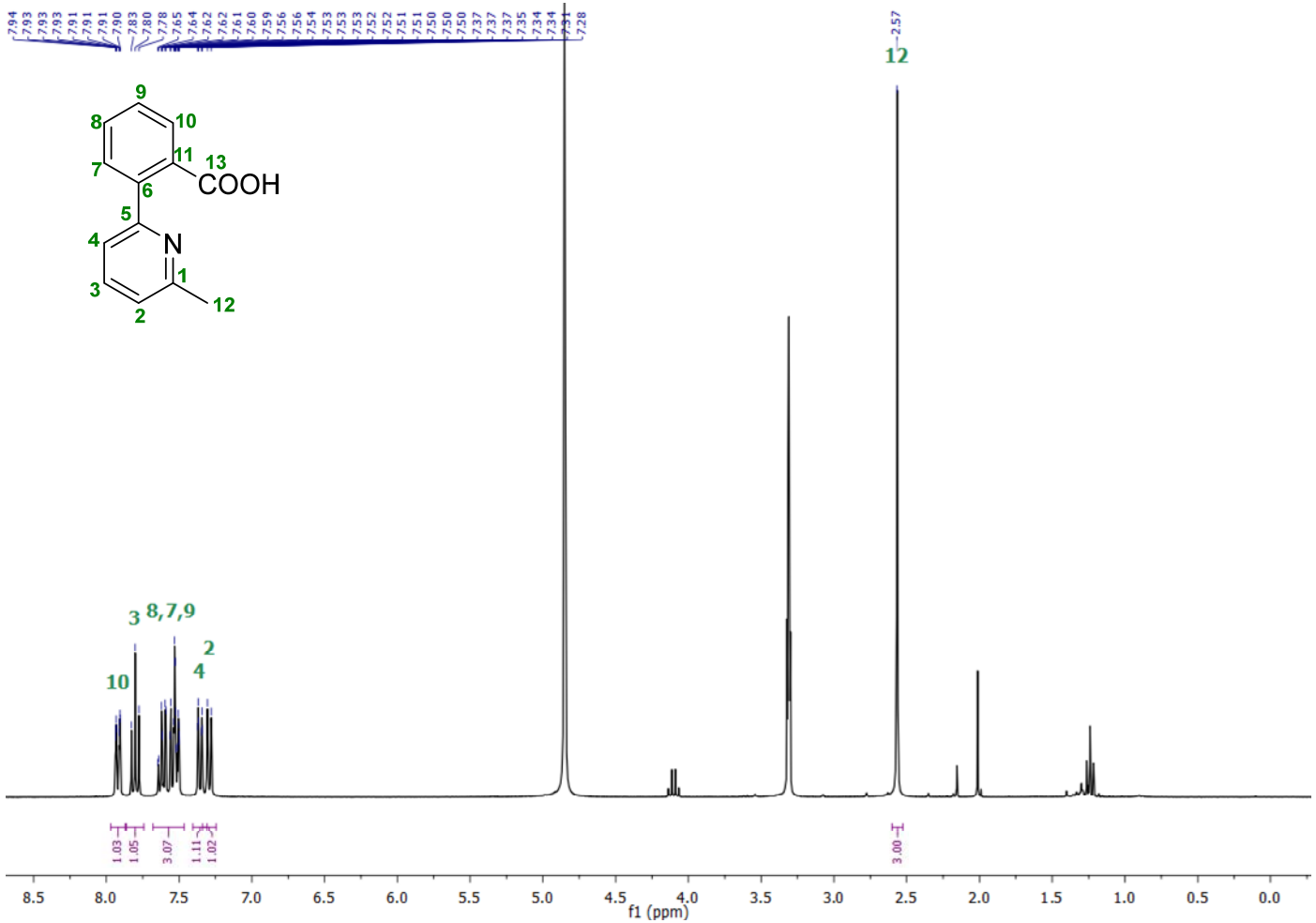


*Figure S34. ^{1}H-NMR spectrum of **6** in CD_3OD*

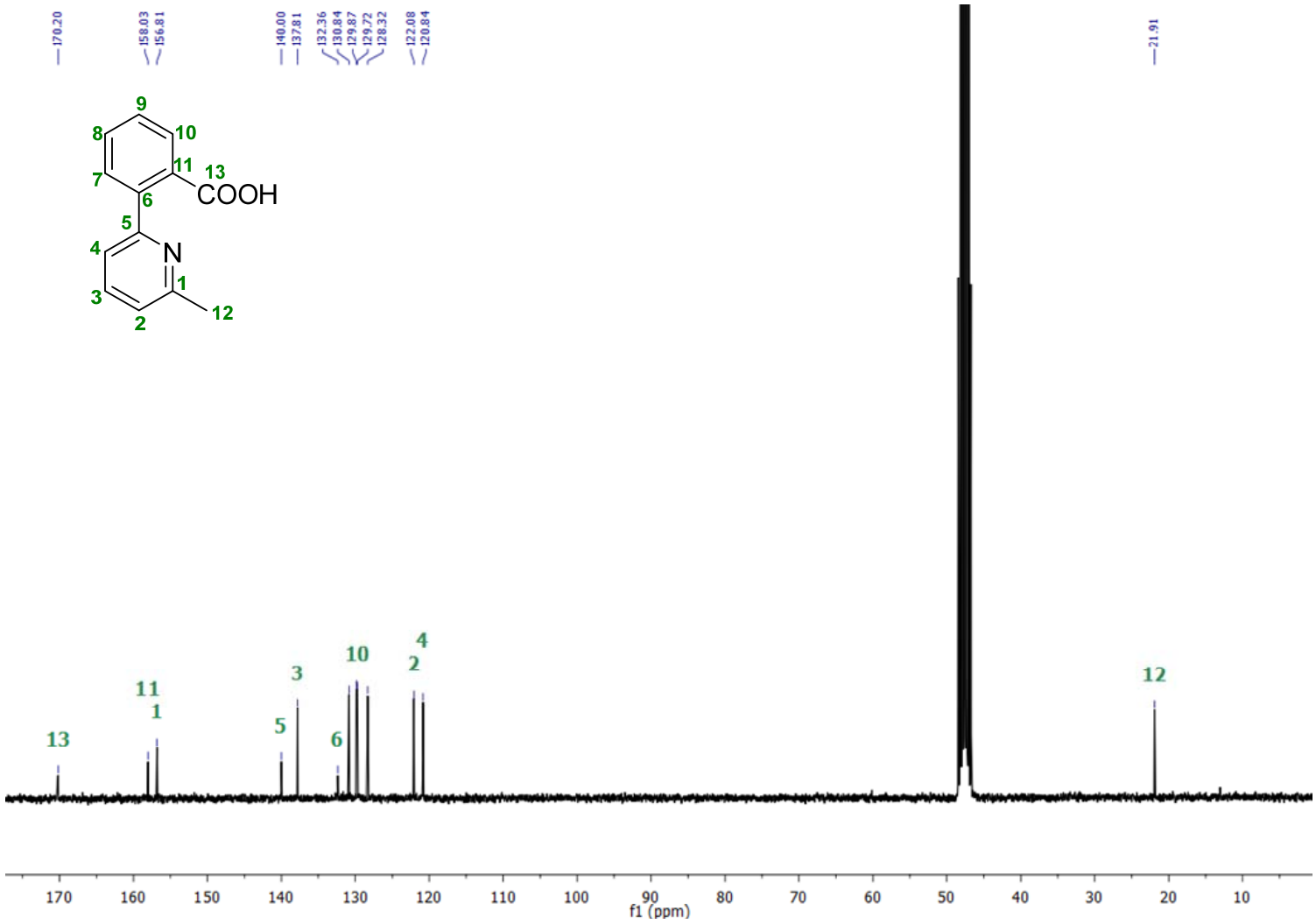


*Figure S35. ^{13}C-NMR spectrum of **6** in CD_3OD*

NMR spectra of P7

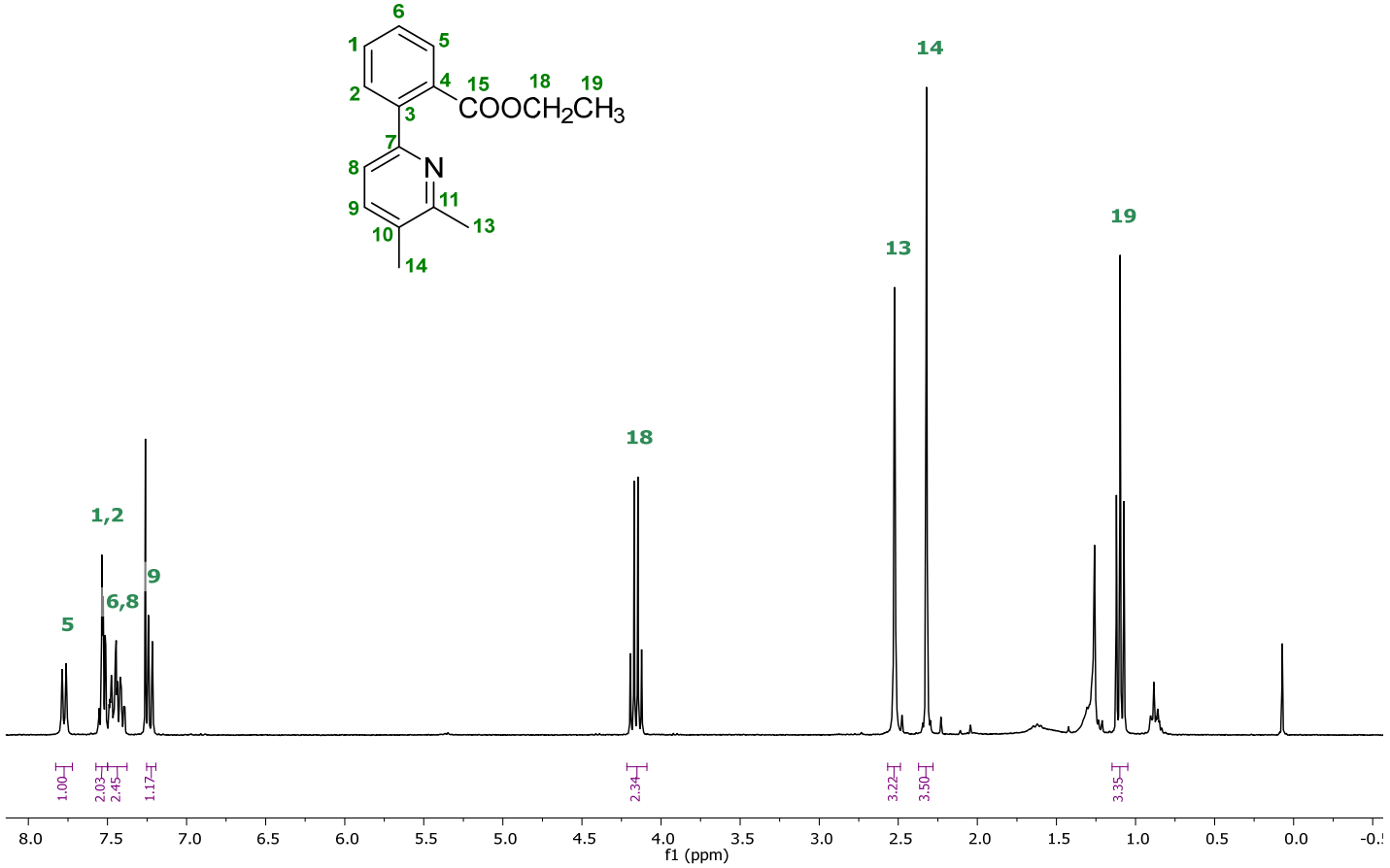


*Figure S36. ^{1}H-NMR spectrum of **P7** in $CDCl_3$*

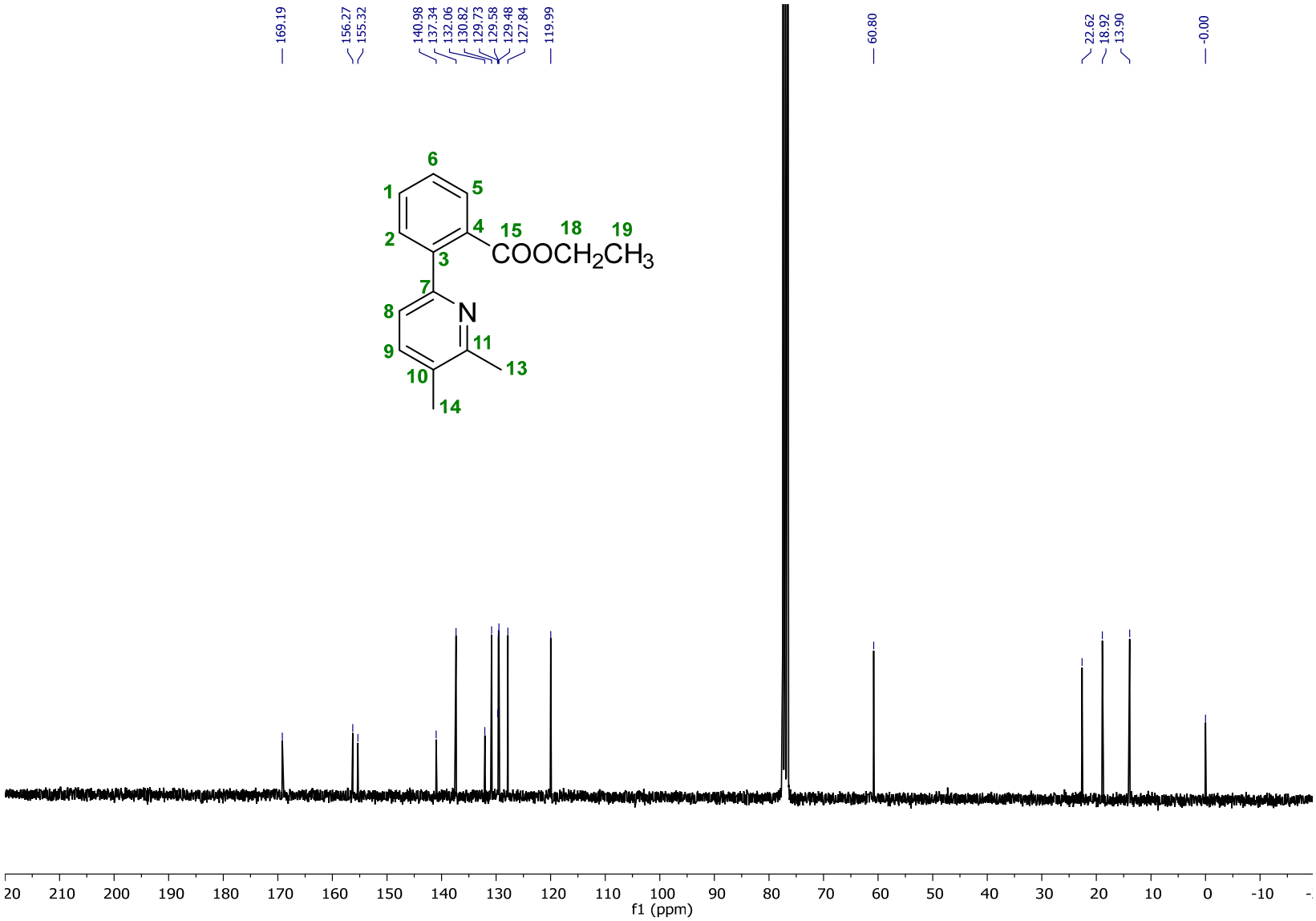


*Figure S37. ^{13}C-NMR spectrum of **P7** in $CDCl_3$*

NMR spectra of 7

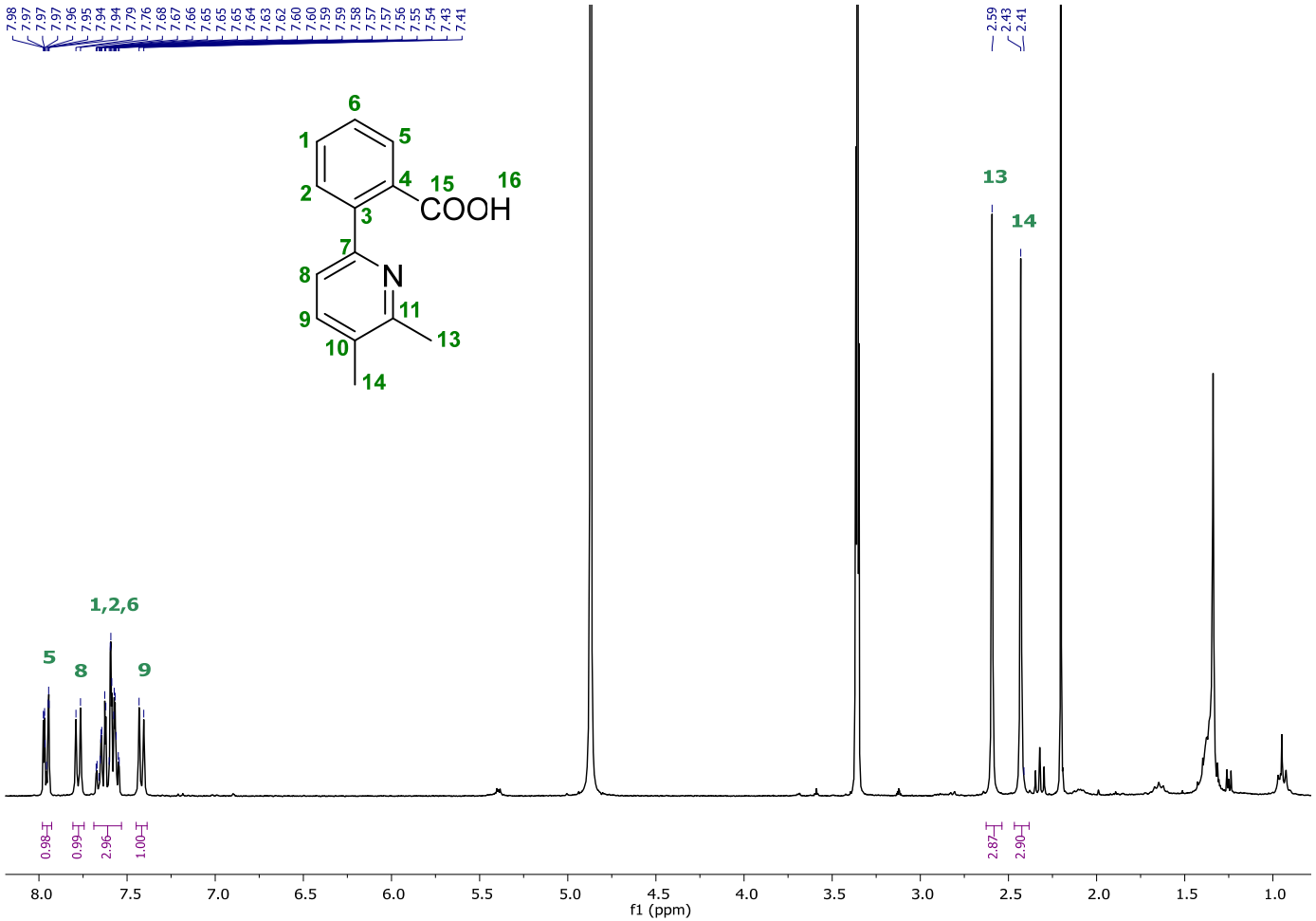


*Figure S38. ^{1}H-NMR spectrum of **7** in CD_3OD*

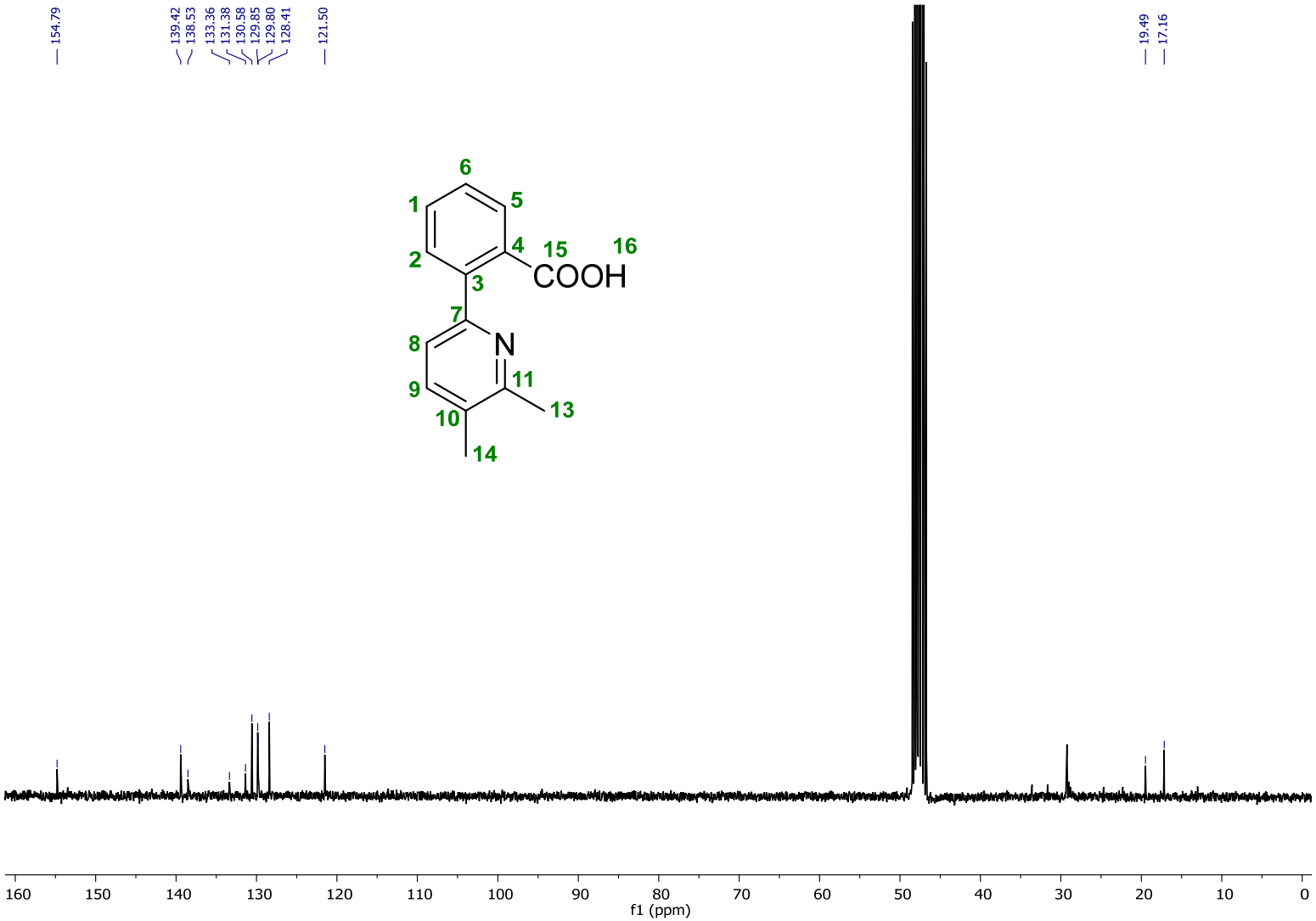


*Figure S39. ^{13}C-NMR spectrum of **7** in CD_3OD*

NMR spectra of P8

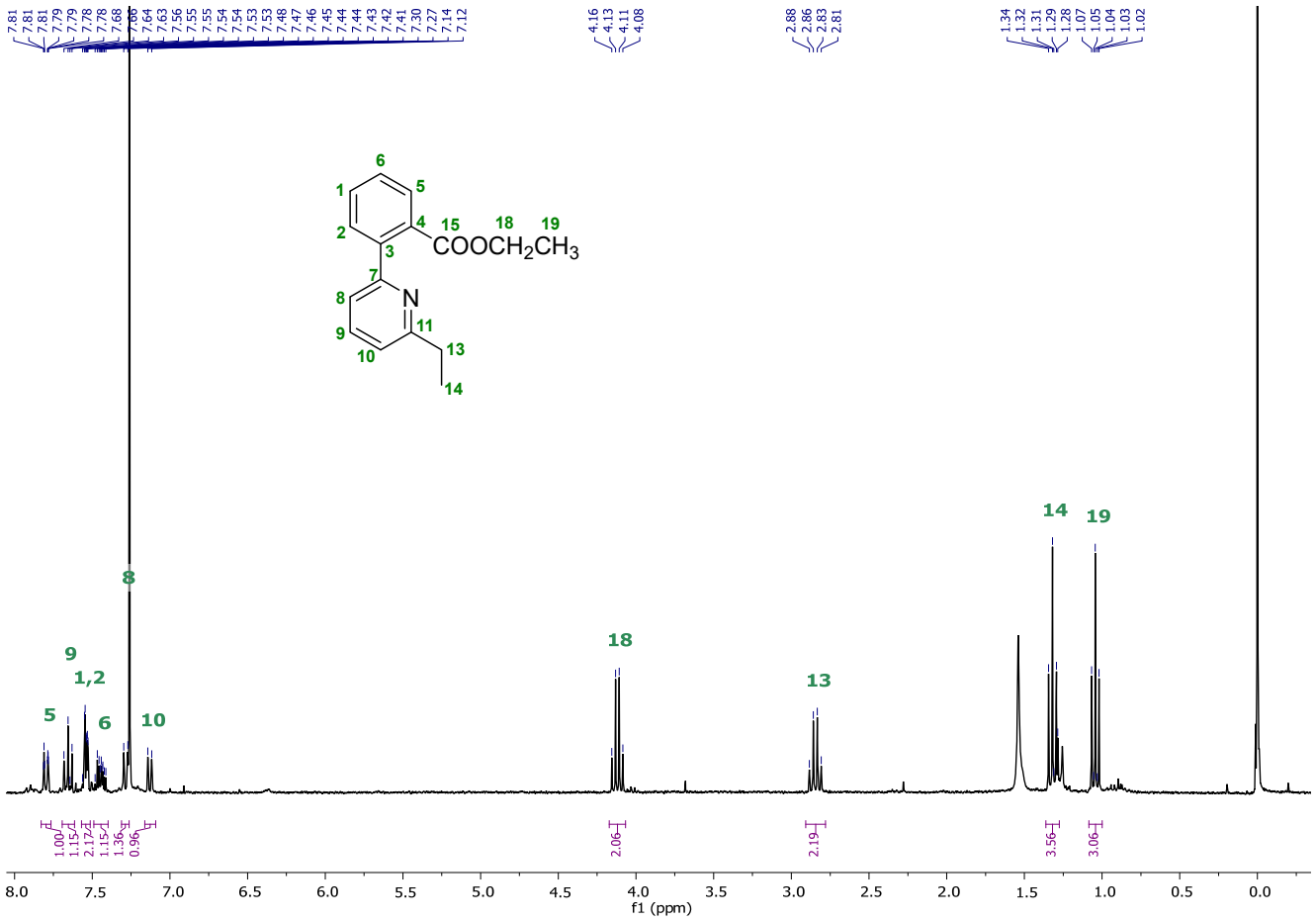


*Figure S40. ^{1}H-NMR spectrum of **P8** in $CDCl_3$*

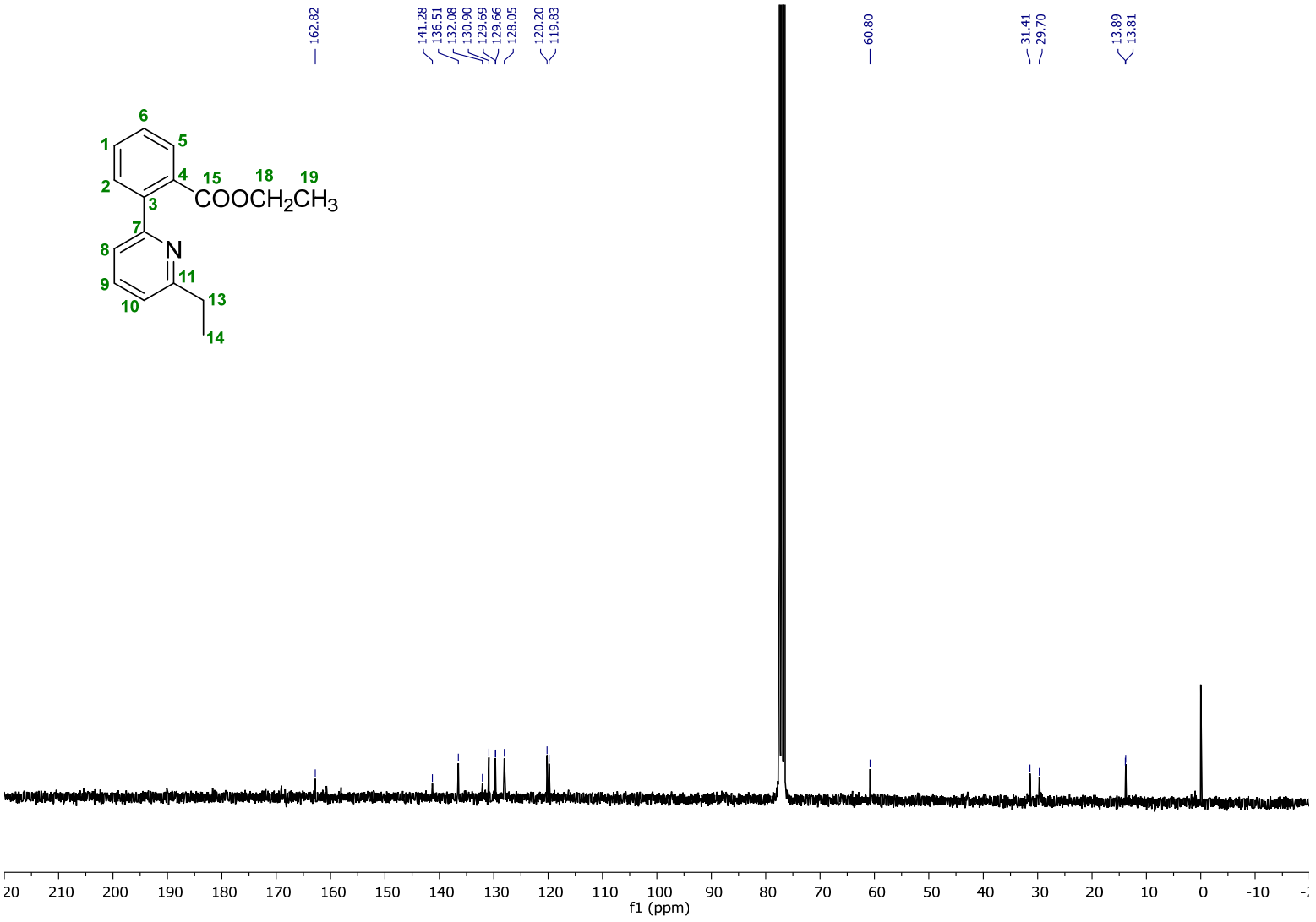


*Figure S41. ^{13}C-NMR spectrum of **P8** in $CDCl_3$*

NMR spectra of 8

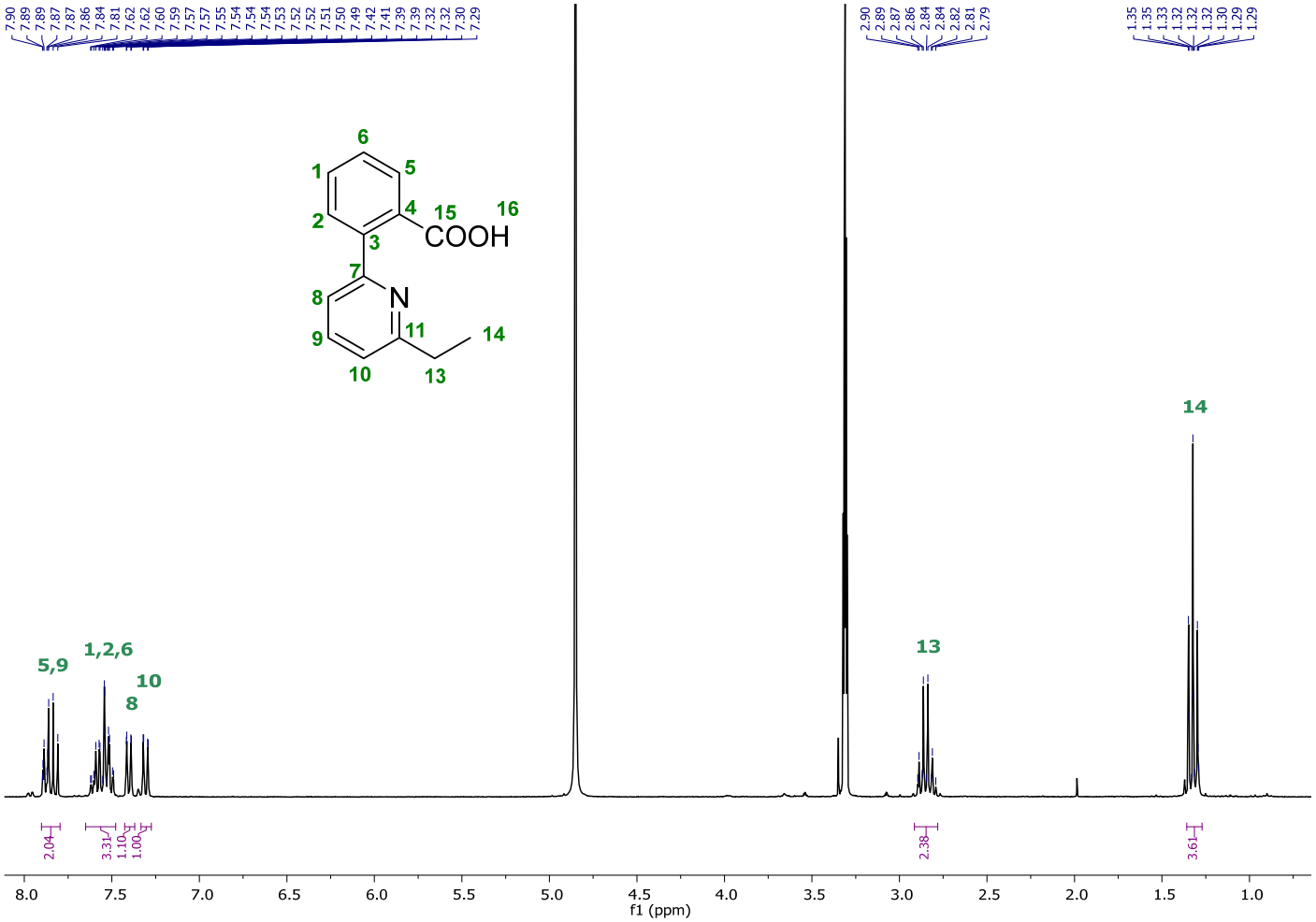


*Figure S42. ^{1}H-NMR spectrum of **8** in CD_3OD*

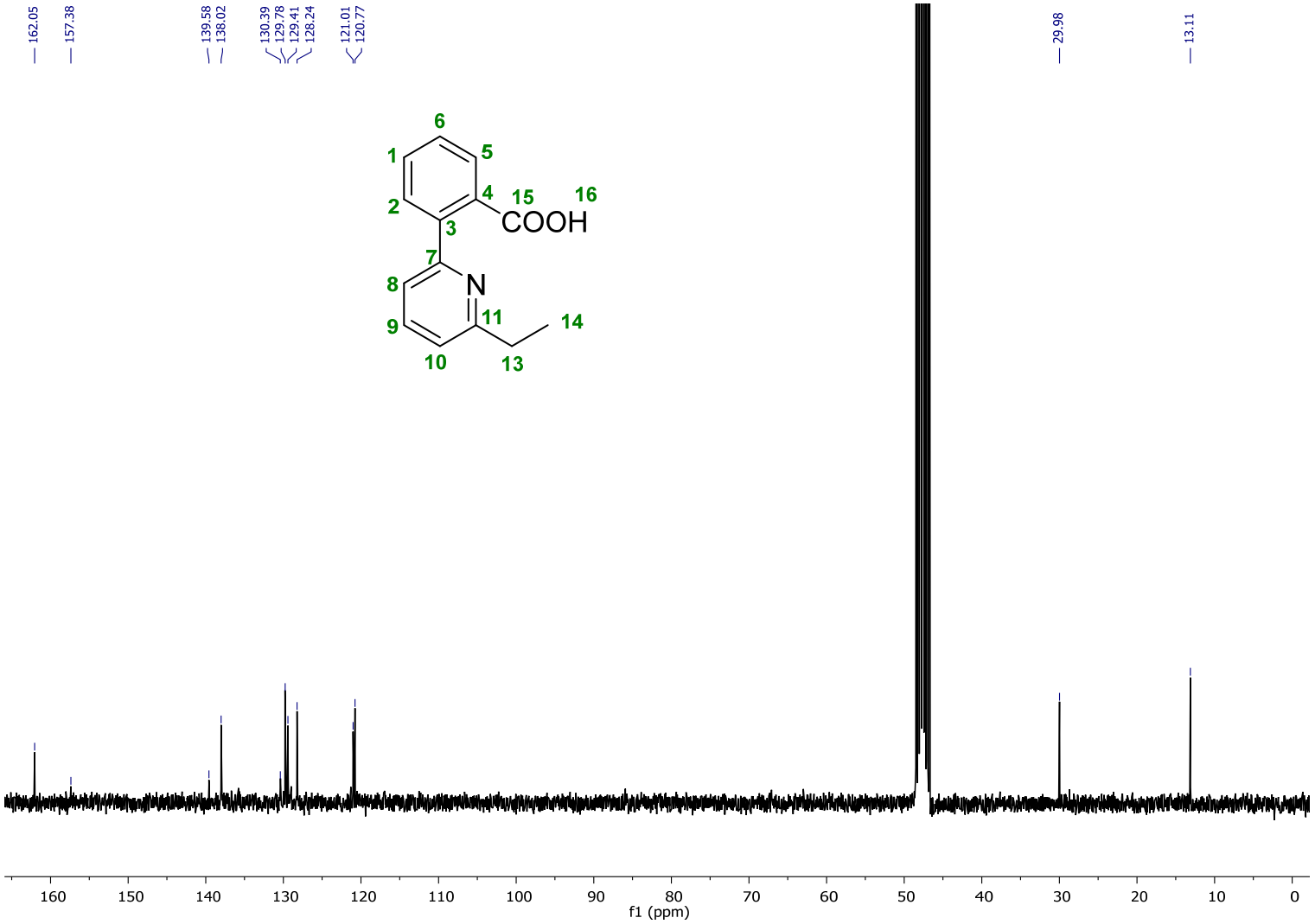


*Figure S43. ^{13}C-NMR spectrum of **8** in CD_3OD*

NMR spectra of 14

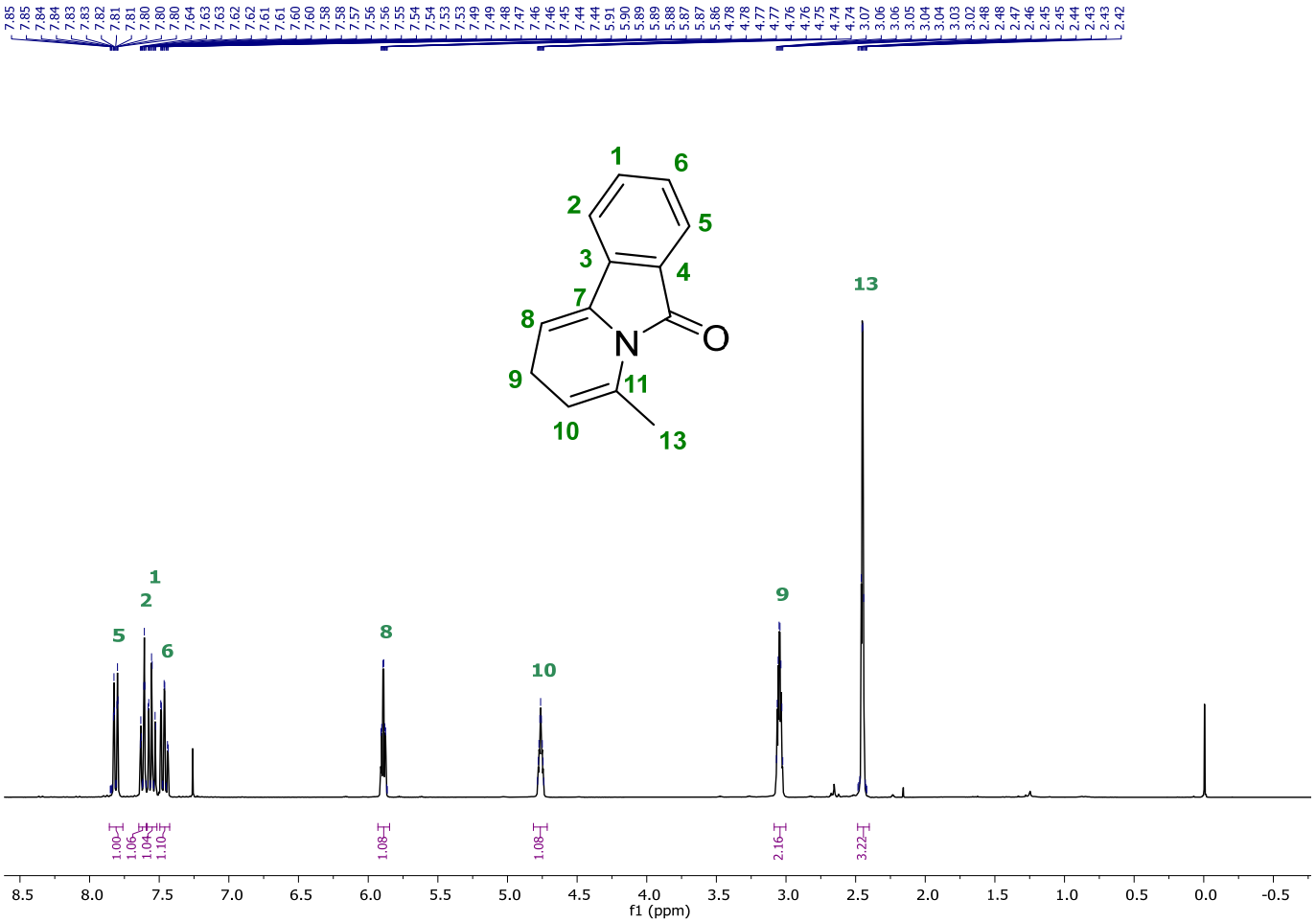


*Figure S44. ^{1}H-NMR spectrum of **14** in $CDCl_3$*

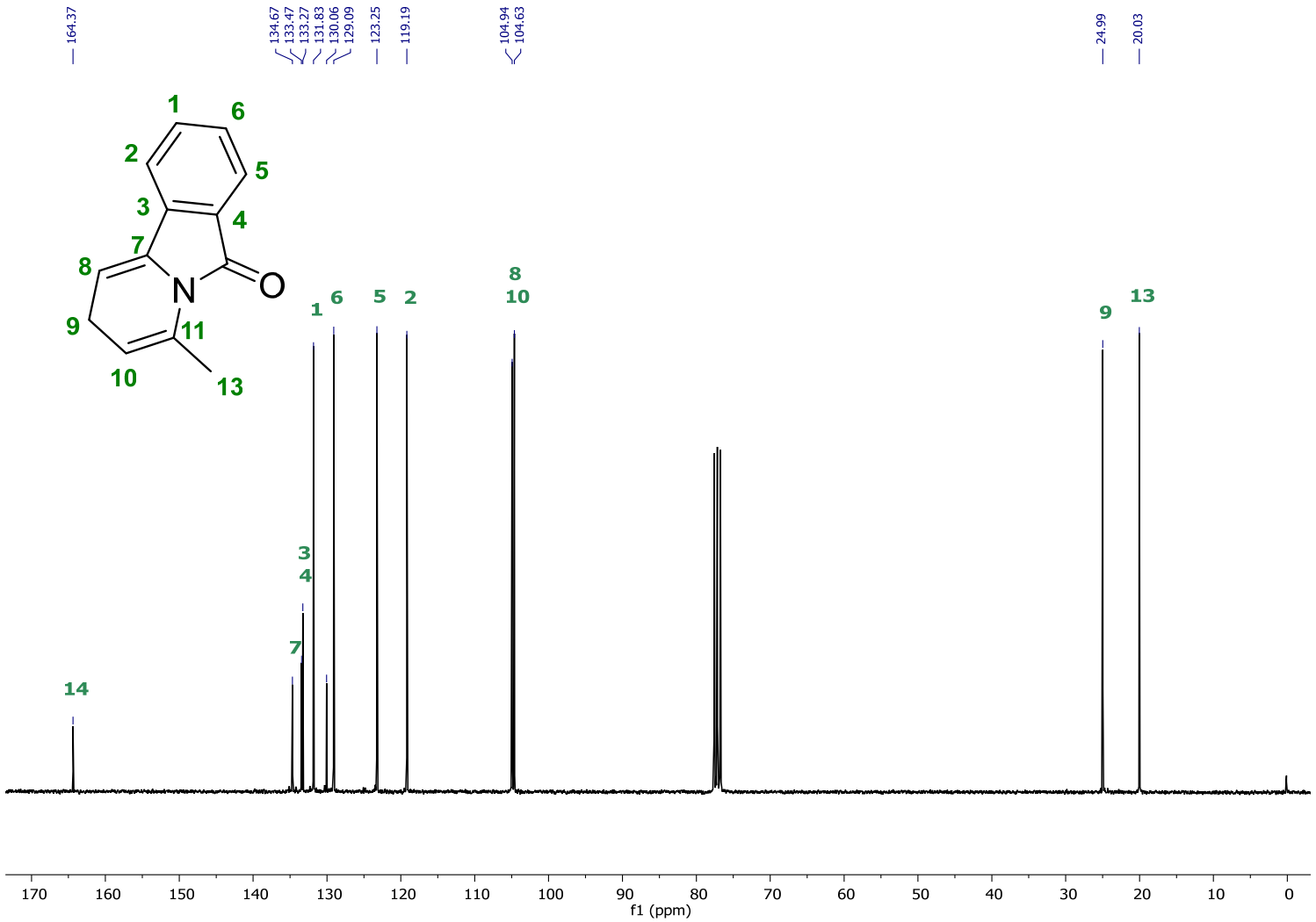


*Figure S45. ^{13}C-NMR spectrum of **14** in $CDCl_3$*

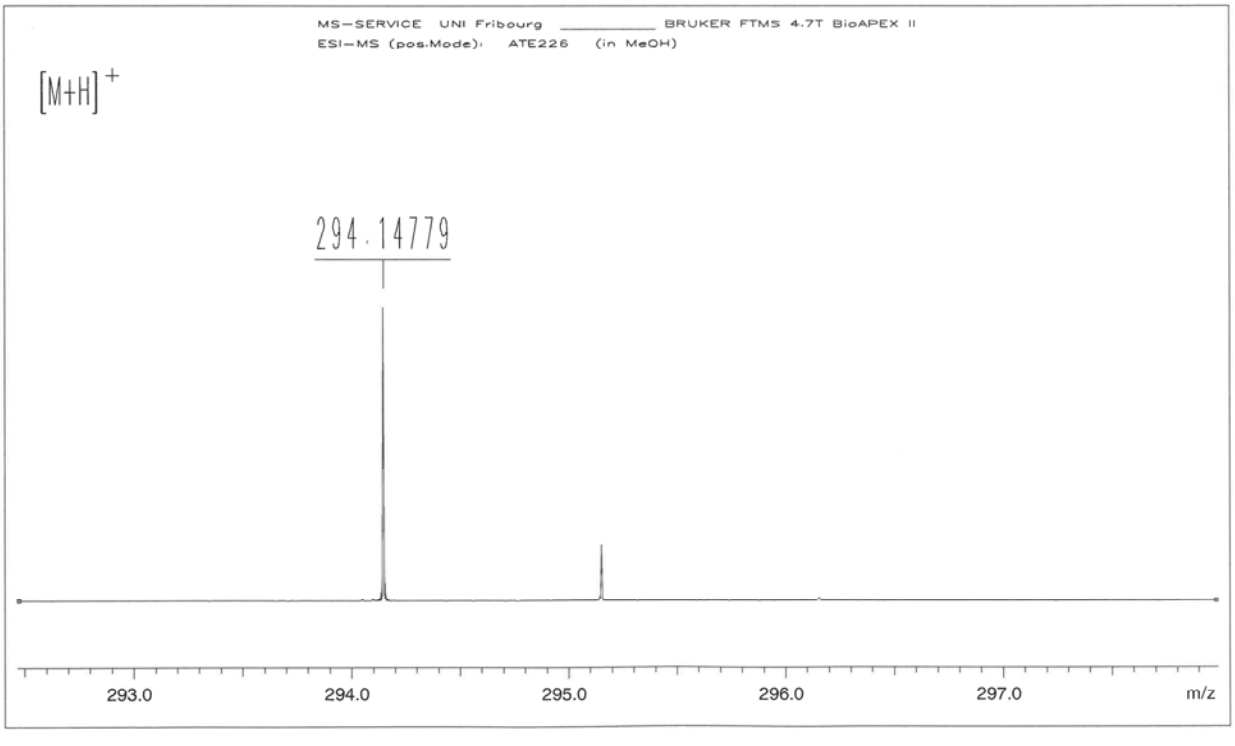
HRMS spectra

HRMS spectrum of 2

Ion mass = 294.1477860

Charge = +1

#	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 294.1477860							
1	**19**	**20**	**1**	**2**	**294.1488553**	10.5	1.069e-03
2	7	24	3	9	294.1507058	-2.5	2.920e-03
3	14	20	3	4	294.1448326	6.5	2.953e-03
4	11	22	2	7	294.1421525	2.0	5.634e-03
5	12	24	1	7	294.1547286	1.5	6.943e-03
6	8	24	1	10	294.1394724	-2.5	8.314e-03
7	15	22	2	4	294.1574086	6.0	9.623e-03
8	18	18	2	2	294.1362793	11.0	1.151e-02
9	18	20	3	1	294.1600887	10.5	1.230e-02
10	15	20	1	5	294.1335992	6.5	1.419e-02

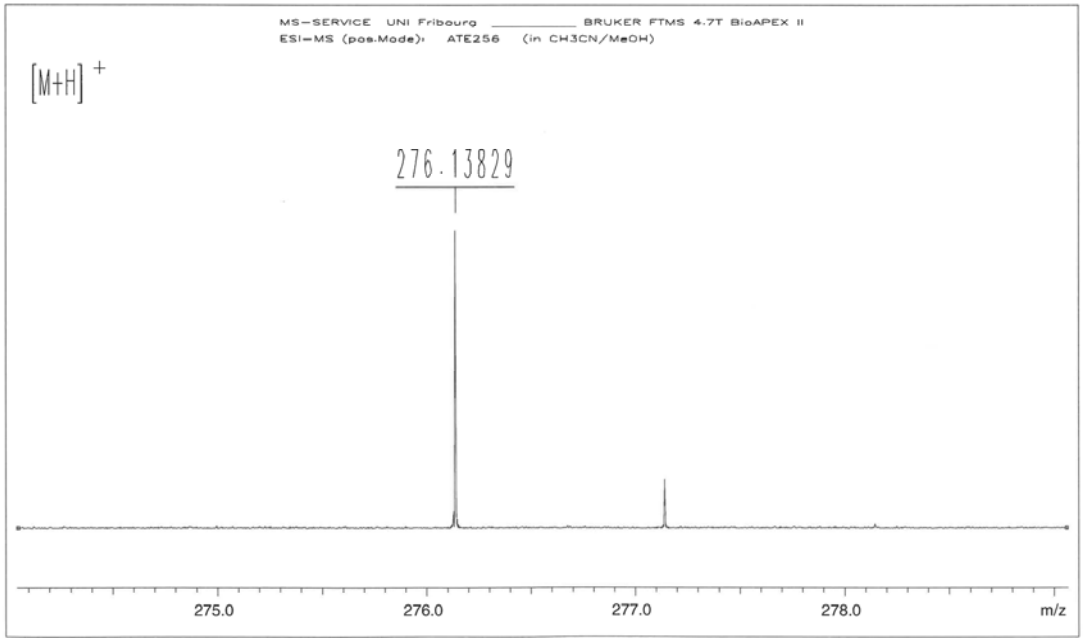


HRMS spectrum of 3

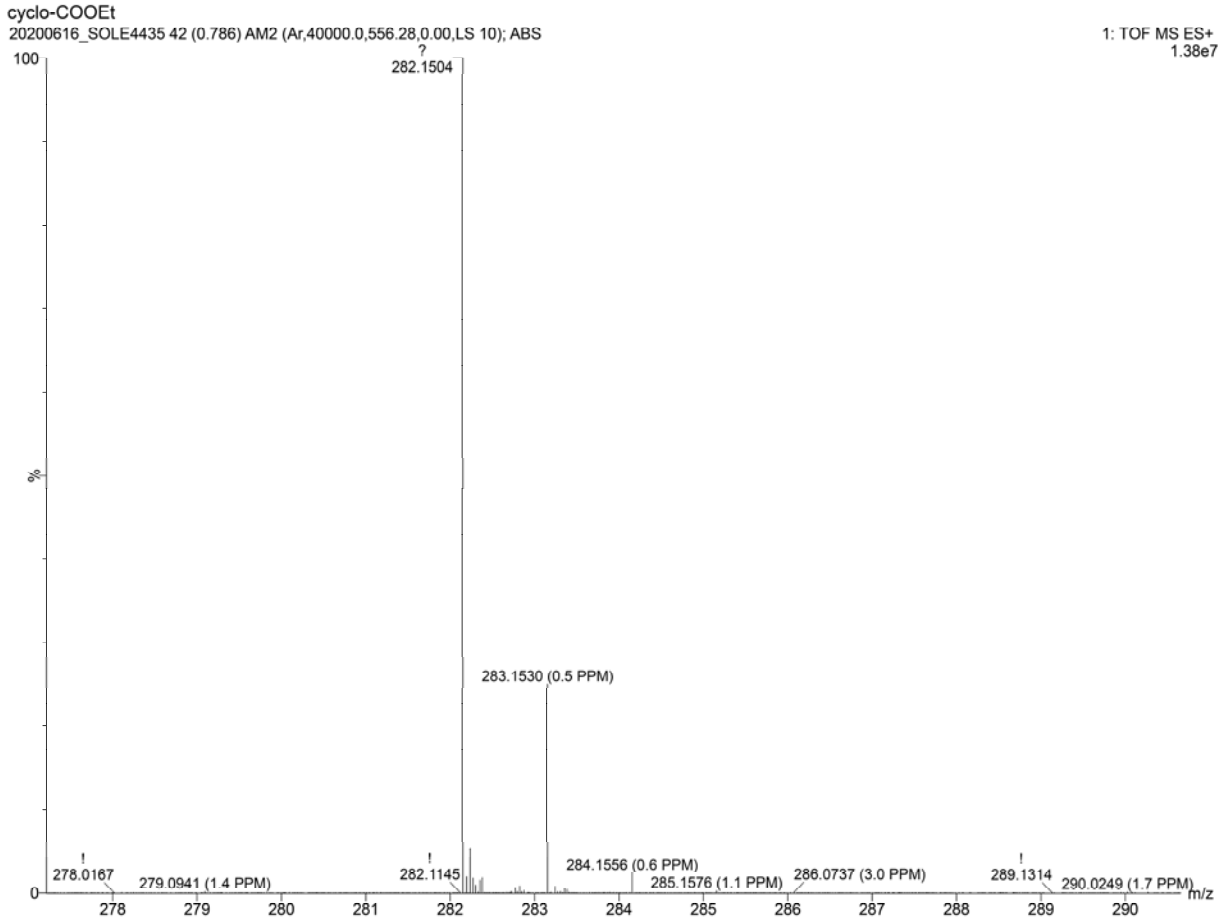
Ion mass = 276.1382870

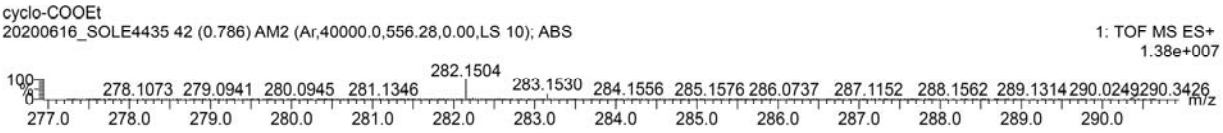
Charge = +1

#	C	H	N	O	mass	DBE	error
*** Mass Analysis for mass 276.1382870							
1	**19**	**18**	**1**	**1**	**276.1382906**	11.5	3.625e-06
2	7	22	3	8	276.1401411	-1.5	1.854e-03
3	14	18	3	3	276.1342679	7.5	4.019e-03
4	12	22	1	6	276.1441639	2.5	5.877e-03
5	11	20	2	6	276.1315878	3.0	6.699e-03
6	15	20	2	3	276.1468439	7.0	8.557e-03
7	8	22	1	9	276.1289077	-1.5	9.379e-03
8	18	16	2	1	276.1257146	12.0	1.257e-02
9	8	24	2	8	276.1527172	-2.0	1.443e-02
10	15	18	1	4	276.1230345	7.5	1.525e-02



HRMS spectrum of P4



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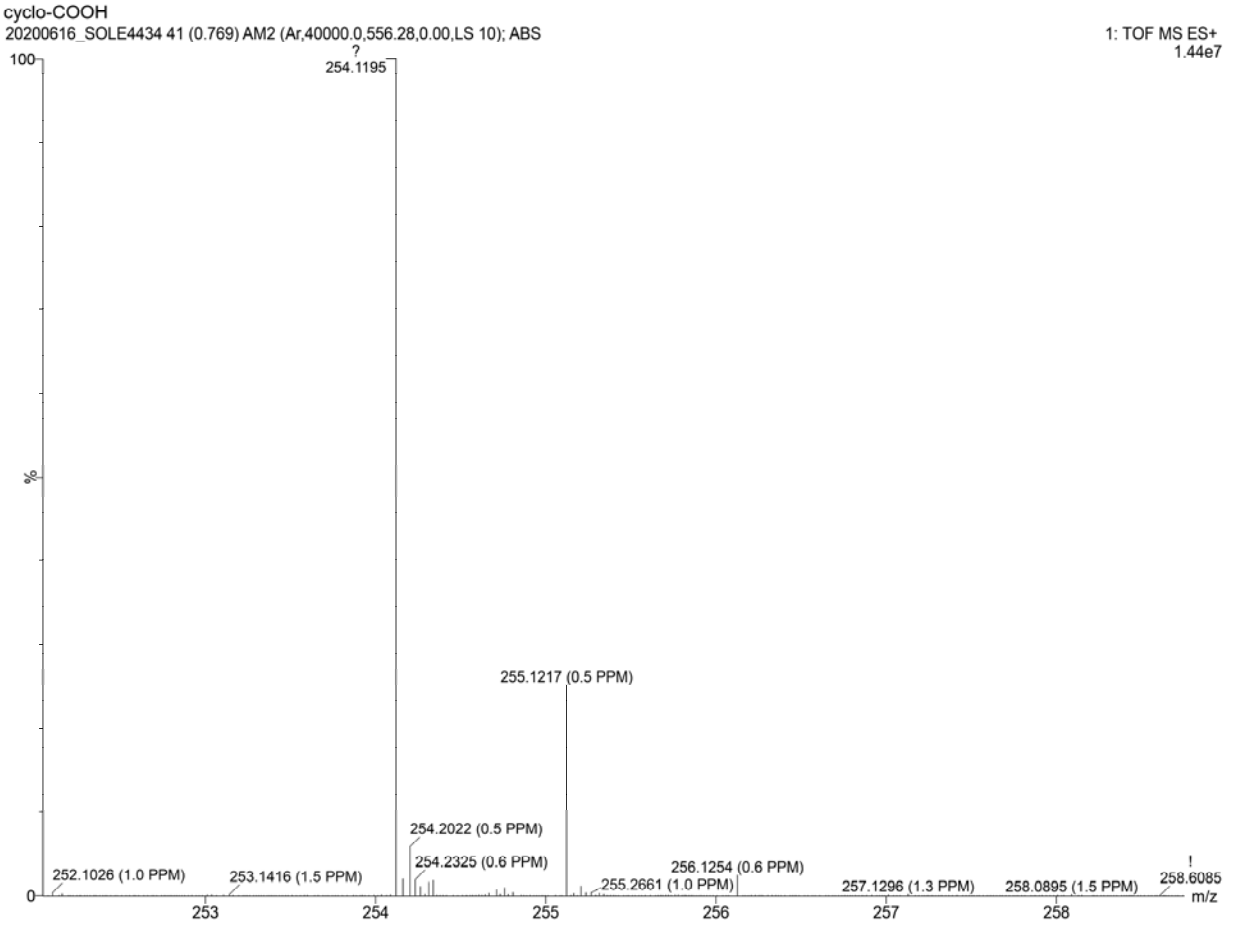
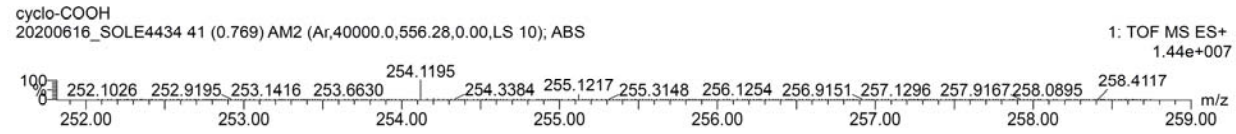
Minimum:                        -1.5
Maximum:              100.0  1000.0 50.0

Mass       Calc. Mass  mDa    PPM    DBE    i-FIT   Norm   Conf(%) Formula

282.1504   282.1494    1.0    3.5    9.5    1793.1  1.972  13.92   C18 H20 N O2
           282.1858    -35.4  -125.5 8.5    1791.9  0.839  43.22   C19 H24 N O
           282.1130    37.4   132.6  10.5   1794.3  3.240  3.92    C17 H16 N O3
           282.2069    -56.5  -200.2 3.5    1792.6  1.549  21.24   C16 H28 N O3
           282.0919    58.5   207.3  15.5   1793.0  1.948  14.26   C20 H12 N O
           282.0555    94.9   336.3  16.5   1794.5  3.372  3.43    C19 H8 N O2
           282.0191    131.3  465.4  17.5   1848.8  57.735 0.00    C18 H4 N O3
```

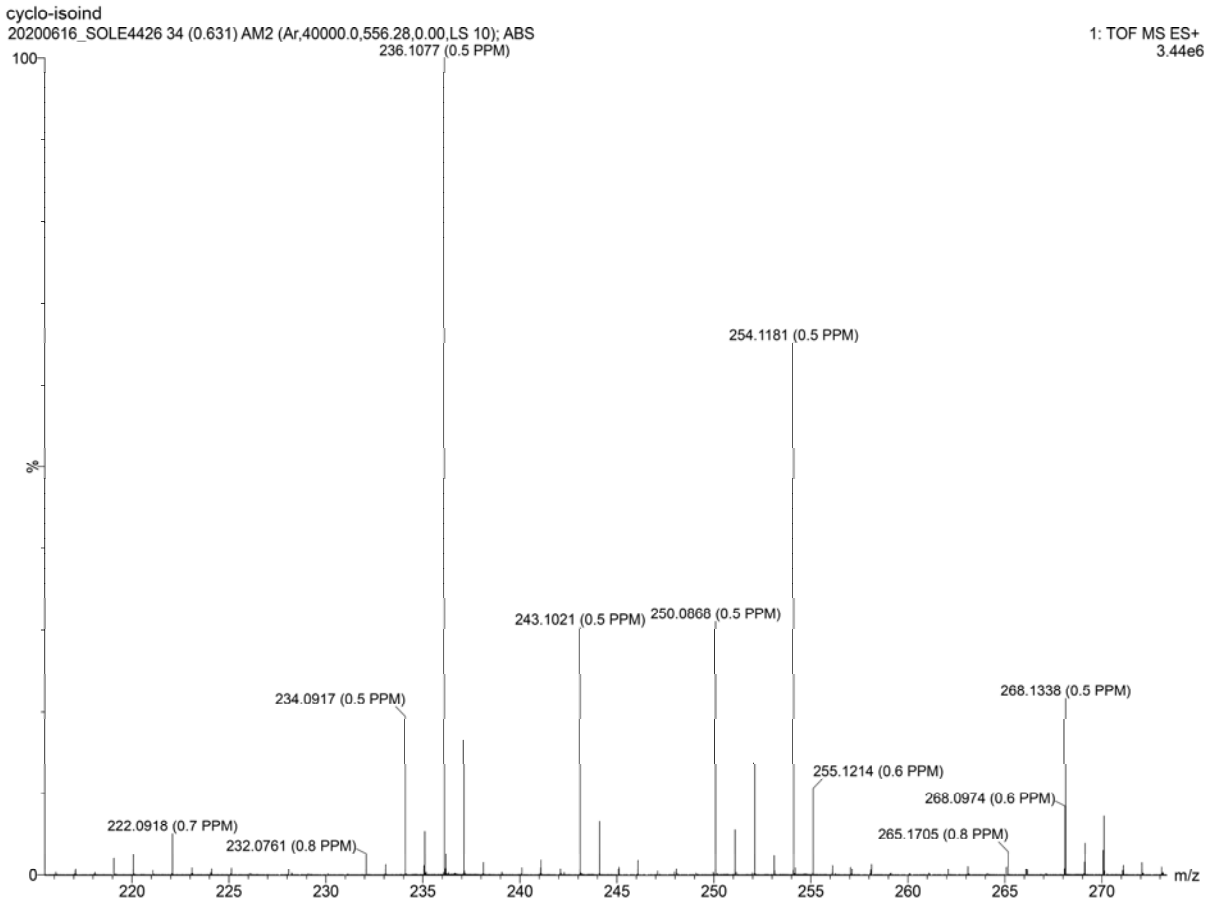
HRMS spectrum of 4





Minimum:				-1.5				
Maximum:		100.0	1000.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
254.1195	254.1181	1.4	5.5	9.5	1887.7	2.064	12.70	C16 H16 N O2
	254.1545	-35.0	-137.7	8.5	1886.6	0.946	38.82	C17 H20 N O
	254.0817	37.8	148.7	10.5	1888.7	3.089	4.56	C15 H12 N O3
	254.1756	-56.1	-220.8	3.5	1889.7	4.000	1.83	C14 H24 N O3
	254.0606	58.9	231.8	15.5	1886.9	1.215	29.68	C18 H8 N O
	254.2120	-92.5	-364.0	2.5	1888.9	3.284	3.75	C15 H28 N O2
	254.0242	95.3	375.0	16.5	1888.1	2.445	8.67	C17 H4 N O2
	253.9878	131.7	518.3	17.5	1936.6	50.957	0.00	C16 N O3

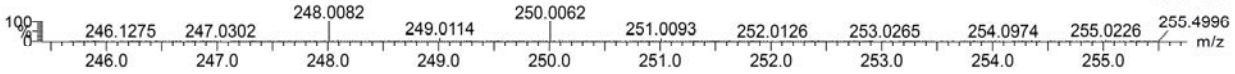
HRMS spectrum of 5



HRMS spectrum of P6

Me-Br
20200616_SOLE4433 46 (0.854) AM2 (Ar,40000.0,556.28,0.00,LS 10); ABS

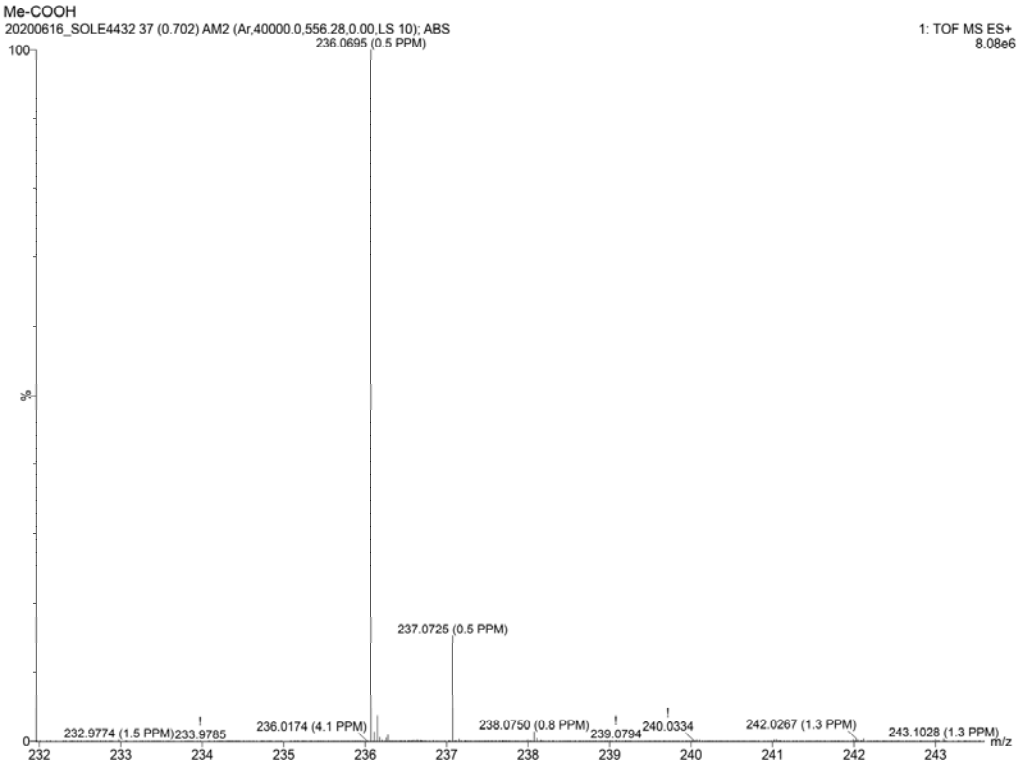
1: TOF MS ES+
1.02e+007

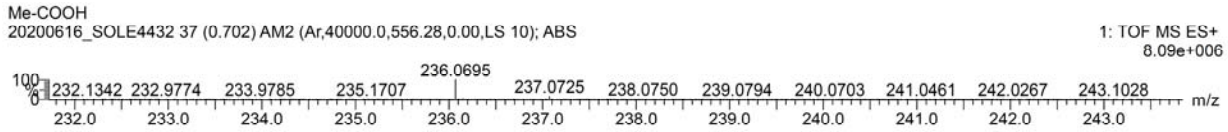


Minimum:	80.00			-1.5	
Maximum:	100.00		100.0	1000.0	50.0

Mass	RA	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
248.0082	100.00	248.0075	0.7	2.8	7.5	2065.4	1.684	18.57	C12 H11 N 79Br
		247.9898	18.4	74.2	8.5	2065.4	1.727	17.77	C12 H9 N 81Br
		248.0500	-41.8	-168.5	17.5	2065.3	1.619	19.80	C19 H6 N
		247.9473	60.9	245.6	-1.5	2065.6	1.849	15.73	C5 H14 N 79Br 81Br
		248.0837	-75.5	-304.4	1.5	2065.2	1.481	22.73	C11 H21 N 81Br
		248.1014	-93.2	-375.8	0.5	2066.6	2.921	5.39	C11 H23 N 79Br
		248.1439	-135.7	-547.2	10.5	2076.4	12.708	0.00	C18 H18 N
		247.8534	154.8	624.2	5.5	2099.9	36.225	0.00	C6 H2 N 79Br 81Br
		248.2378	-229.6	-925.8	3.5	2082.0	18.262	0.00	C17 H30 N
250.0062	99.02	250.0054	0.8	3.2	7.5	1839.2	1.284	27.69	C12 H11 N 81Br
		250.0231	-16.9	-67.6	6.5	1839.4	1.471	22.97	C12 H13 N 79Br
		250.0657	-59.5	-238.0	16.5	1848.3	10.385	0.00	C19 H8 N
		249.9292	77.0	308.0	13.5	1843.7	5.786	0.31	C13 H N 79Br
		250.0993	-93.1	-372.4	0.5	1838.7	0.713	49.03	C11 H23 N 81Br
		250.1170	-110.8	-443.2	-0.5	1867.5	29.557	0.00	C11 H25 N 79Br
		249.8690	137.2	548.8	4.5	1893.8	55.884	0.00	C6 H4 N 79Br 81Br
		250.1596	-153.4	-613.6	9.5	1865.1	27.147	0.00	C18 H20 N

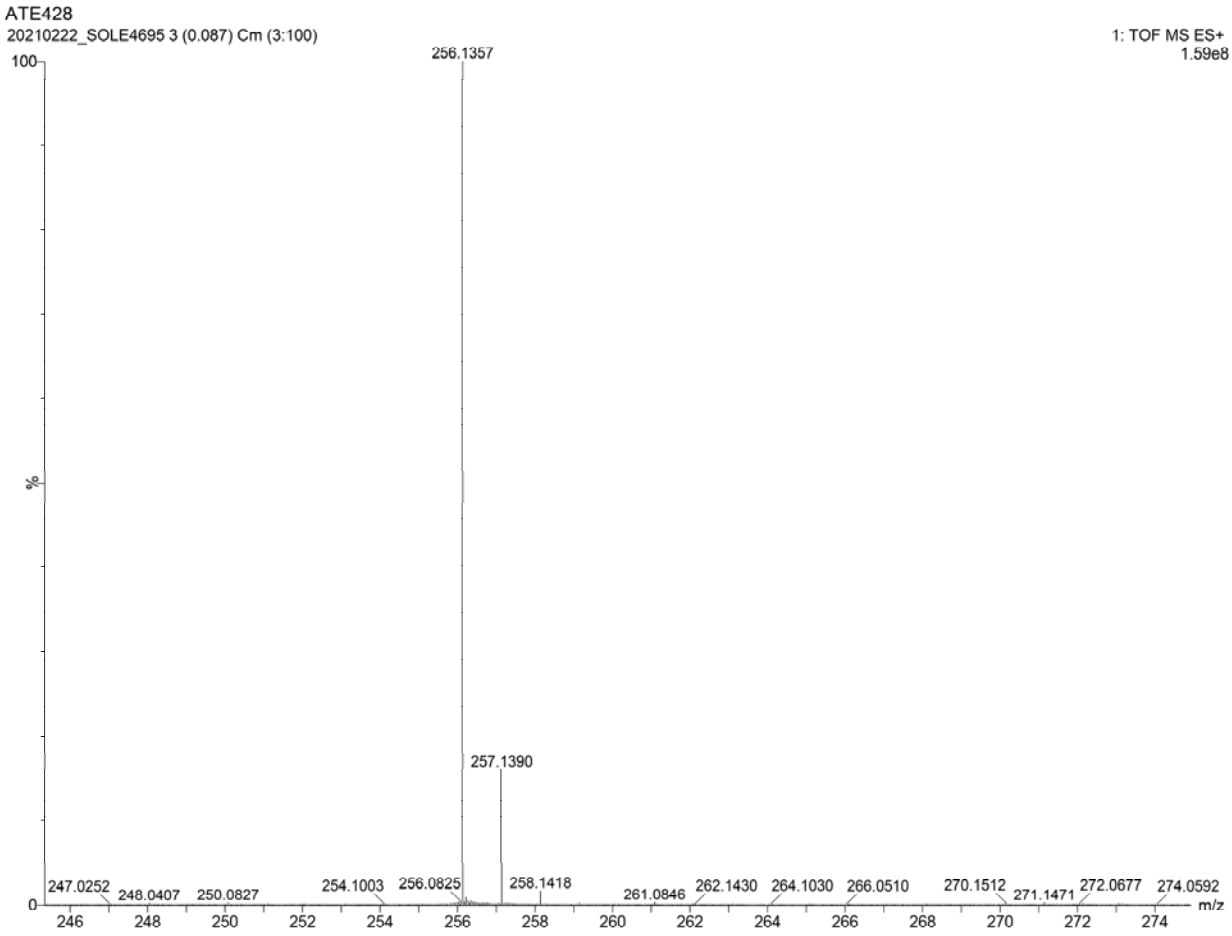
HRMS spectrum of 6

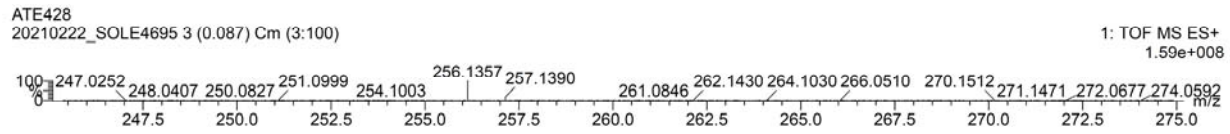




Minimum:				-1.5				
Maximum:		100.0	1000.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
236.0695	236.0687	0.8	3.4	8.5	1822.0	1.029	35.73	C13 H11 N O2 Na
	236.1051	-35.6	-150.8	7.5	1821.4	0.452	63.65	C14 H15 N O Na
	236.0324	37.1	157.2	9.5	1826.5	5.516	0.40	C12 H7 N O3 Na
	236.1263	-56.8	-240.6	2.5	1829.5	8.500	0.02	C11 H19 N O3 Na
	236.0112	58.3	247.0	14.5	1829.1	8.101	0.03	C15 H3 N O Na
	236.1626	-93.1	-394.4	1.5	1827.4	6.404	0.17	C12 H23 N O2 Na
	236.1990	-129.5	-548.6	0.5	1851.3	30.307	0.00	C13 H27 N O Na

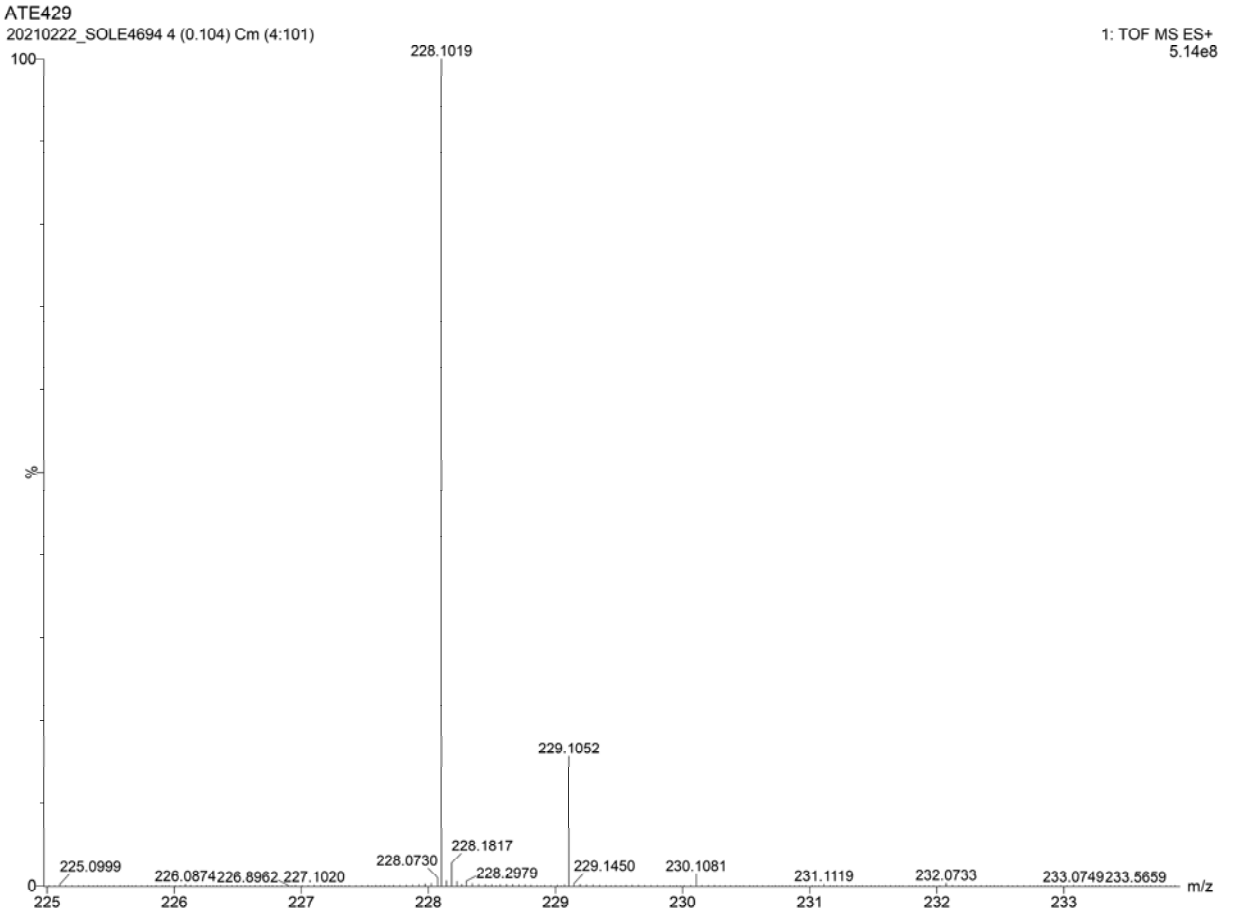
HRMS spectrum of P7

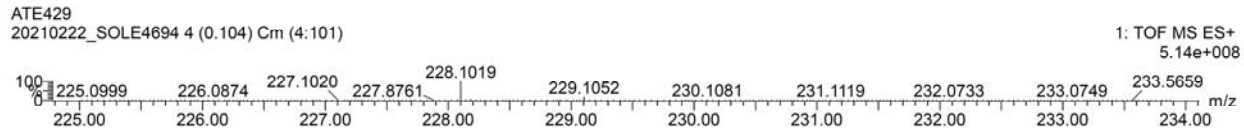




Minimum:				-1.5				
Maximum:		100.0	1000.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
256.1357	256.1338	1.9	7.4	8.5	1507.3	1.502	22.27	C16 H18 N O2
	256.1396	-3.9	-15.2	-0.5	1516.6	10.711	0.00	C9 H22 N O7
	256.1410	-5.3	-20.7	4.5	1514.3	8.457	0.02	C10 H18 N5 O3
	256.1297	6.0	23.4	4.5	1512.2	6.392	0.17	C11 H18 N3 O4
	256.1450	-9.3	-36.3	8.5	1507.3	1.493	22.48	C15 H18 N3 O
	256.1257	10.0	39.0	0.5	1518.6	12.740	0.00	C6 H18 N5 O6
	256.1509	-15.2	-59.3	-0.5	1517.2	11.340	0.00	C8 H22 N3 O6
	256.1198	15.9	62.1	9.5	1506.6	0.754	47.05	C13 H14 N5 O
	256.1185	17.2	67.2	4.5	1510.8	4.922	0.73	C12 H18 N O5
	256.1549	-19.2	-75.0	3.5	1508.5	2.620	7.28	C13 H22 N O4

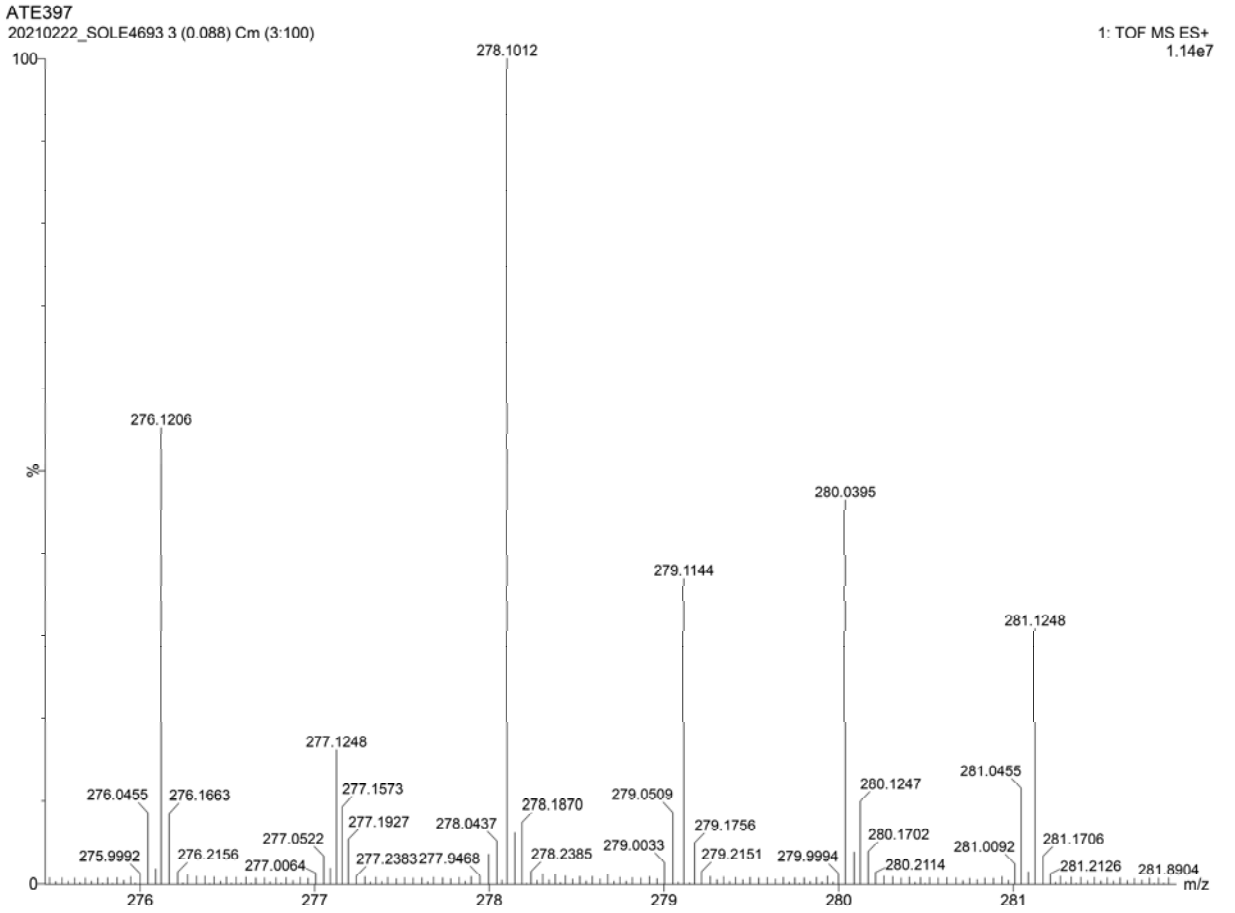
HRMS spectrum of 7

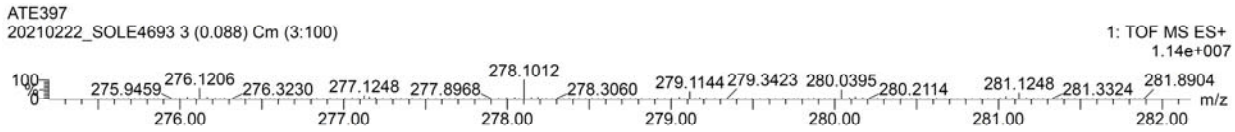




Minimum:				-1.5				
Maximum:		100.0	1000.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
228.1019	228.1025	-0.6	-2.6	8.5	1481.9	1.277	27.89	C14 H14 N O2
	228.0984	3.5	15.3	4.5	1494.1	13.531	0.00	C9 H14 N3 O4
	228.1083	-6.4	-28.1	-0.5	1497.2	16.558	0.00	C7 H18 N O7
	228.0944	7.5	32.9	0.5	1498.7	18.093	0.00	C4 H14 N5 O6
	228.1097	-7.8	-34.2	4.5	1495.6	15.007	0.00	C8 H14 N5 O3
	228.1137	-11.8	-51.7	8.5	1480.9	0.327	72.10	C13 H14 N3 O
	228.0885	13.4	58.7	9.5	1490.1	9.461	0.01	C11 H10 N5 O
	228.0872	14.7	64.4	4.5	1493.1	12.522	0.00	C10 H14 N O5
	228.1196	-17.7	-77.6	-0.5	1497.7	17.049	0.00	C6 H18 N3 O6
	228.0832	18.7	82.0	0.5	1497.7	17.085	0.00	C5 H14 N3 O7

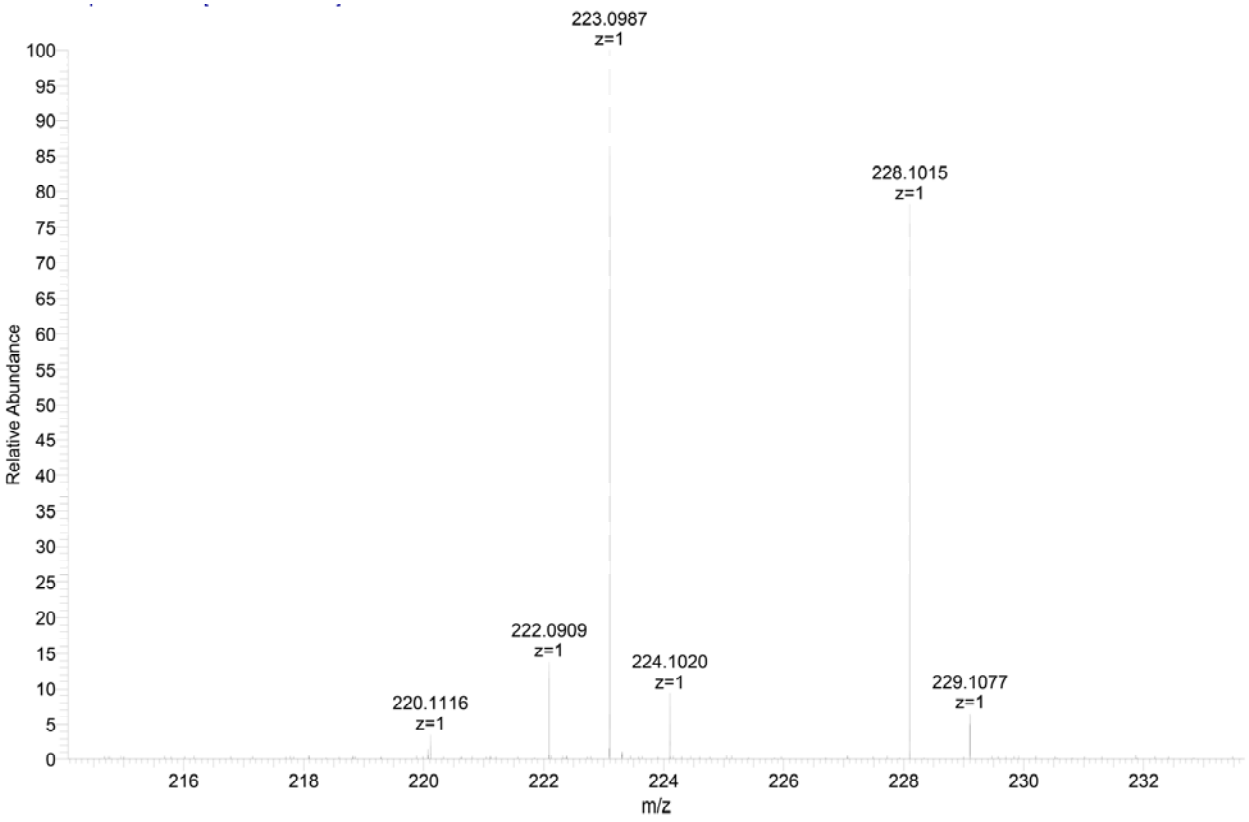
HRMS of P8





Minimum:				-1.5				
Maximum:		100.0	1000.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
278.1012	278.1018	-0.6	-2.2	9.5	1459.0	2.039	13.01	C13 H13 N5 O Na
	278.1004	0.8	2.9	4.5	1459.1	2.213	10.93	C12 H17 N O5 Na
	278.0964	4.8	17.3	0.5	1459.9	2.991	5.03	C7 H17 N3 O7 Na
	278.1077	-6.5	-23.4	0.5	1460.1	3.153	4.27	C6 H17 N5 O6 Na
	278.1117	-10.5	-37.8	4.5	1459.3	2.391	9.16	C11 H17 N3 O4 Na
	278.0905	10.7	38.5	9.5	1458.8	1.831	16.03	C14 H13 N3 O2 Na
	278.1157	-14.5	-52.1	8.5	1458.4	1.490	22.54	C16 H17 N O2 Na
	278.0865	14.7	52.9	5.5	1459.6	2.687	6.81	C9 H13 N5 O4 Na
	278.0852	16.0	57.5	0.5	1459.8	2.848	5.80	C8 H17 N O8 Na
	278.1216	-20.4	-73.4	-0.5	1459.7	2.747	6.41	C9 H21 N O7 Na

HRMS of 8

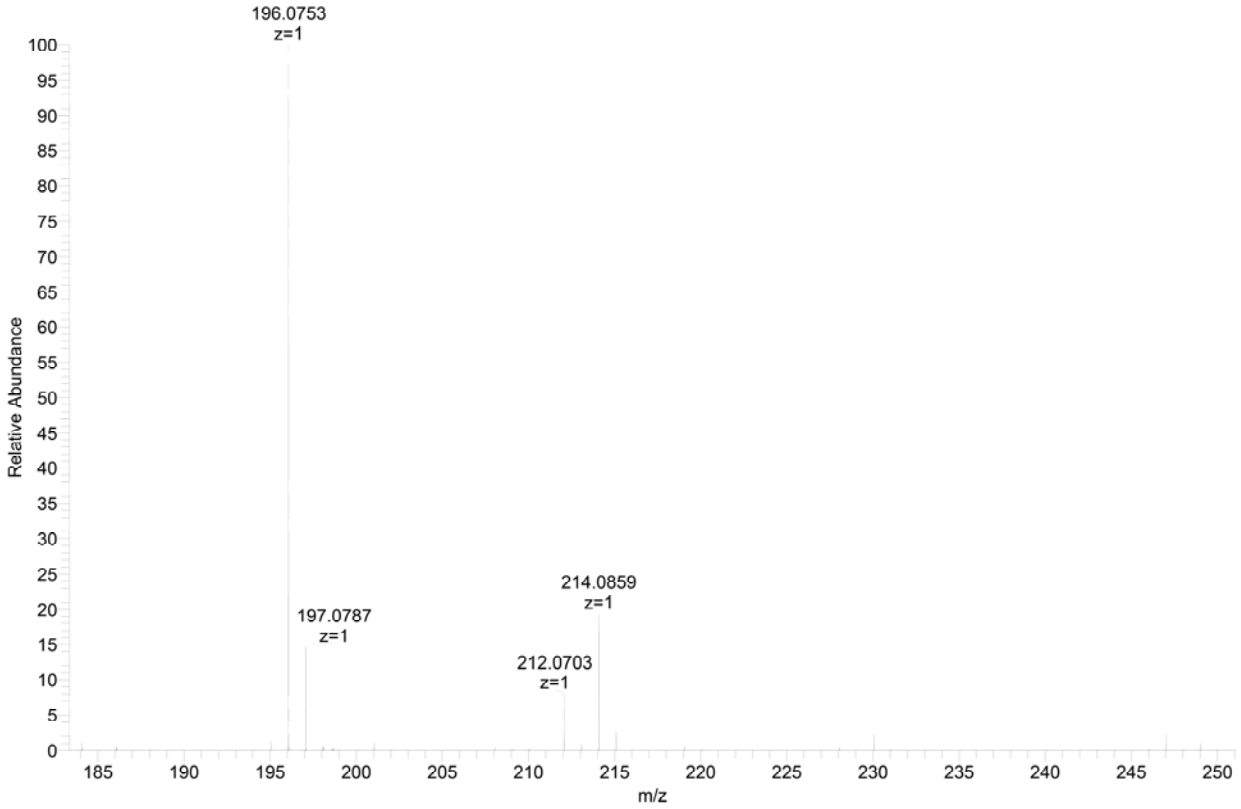


Elemental composition search on mass 228.1015

m/z= 223.1015-233.1015

m/z	Theo. Mass	Delta (ppm)	Composition
228.1015	228.1019	-1.86	$C_{14}H_{14}O_2N$
	228.0995	8.68	$C_{12}H_{15}O_2NNa$
	228.0992	9.89	$C_{11}H_{16}O_5$

HRMS of 14



Elemental composition search on mass 196.0753

m/z= 191.0753-201.0753

m/z	Theo. Mass	Delta (ppm)	Composition
196.0753	196.0757	-1.84	$C_{13}H_{10}ON$
	196.0733	10.43	$C_{11}H_{11}ONNa$
	196.0730	11.83	$C_{10}H_{12}O_4$

IR spectra

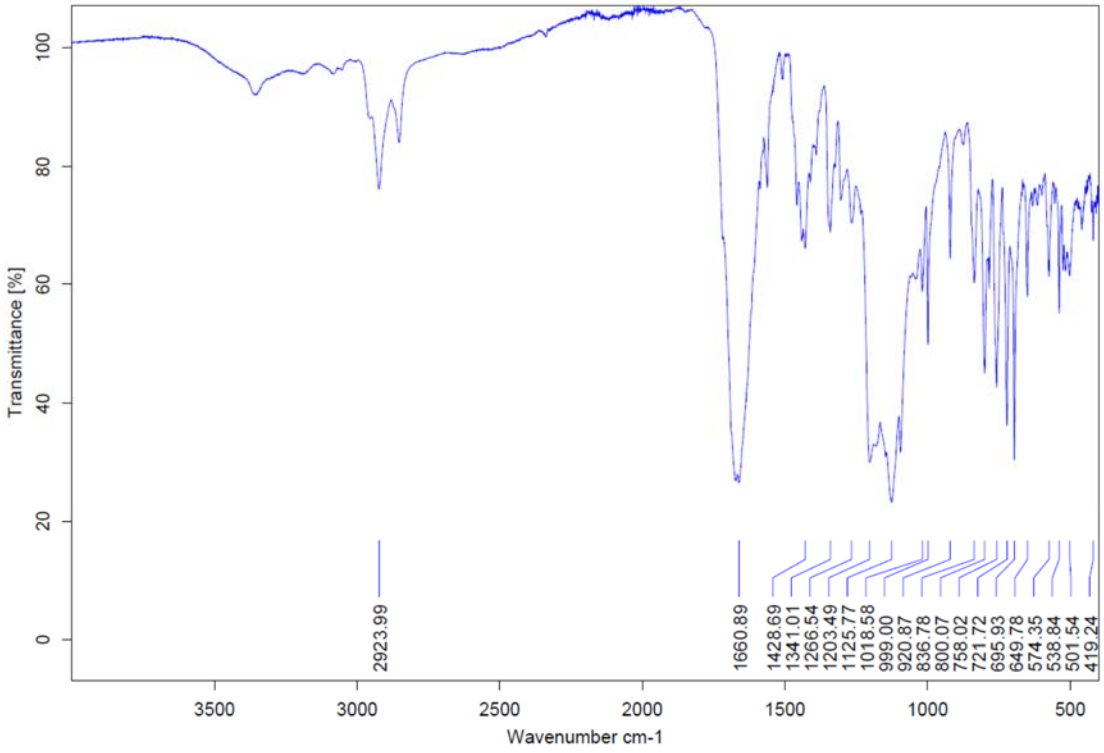


*Figure S46. IR spectrum of **3***

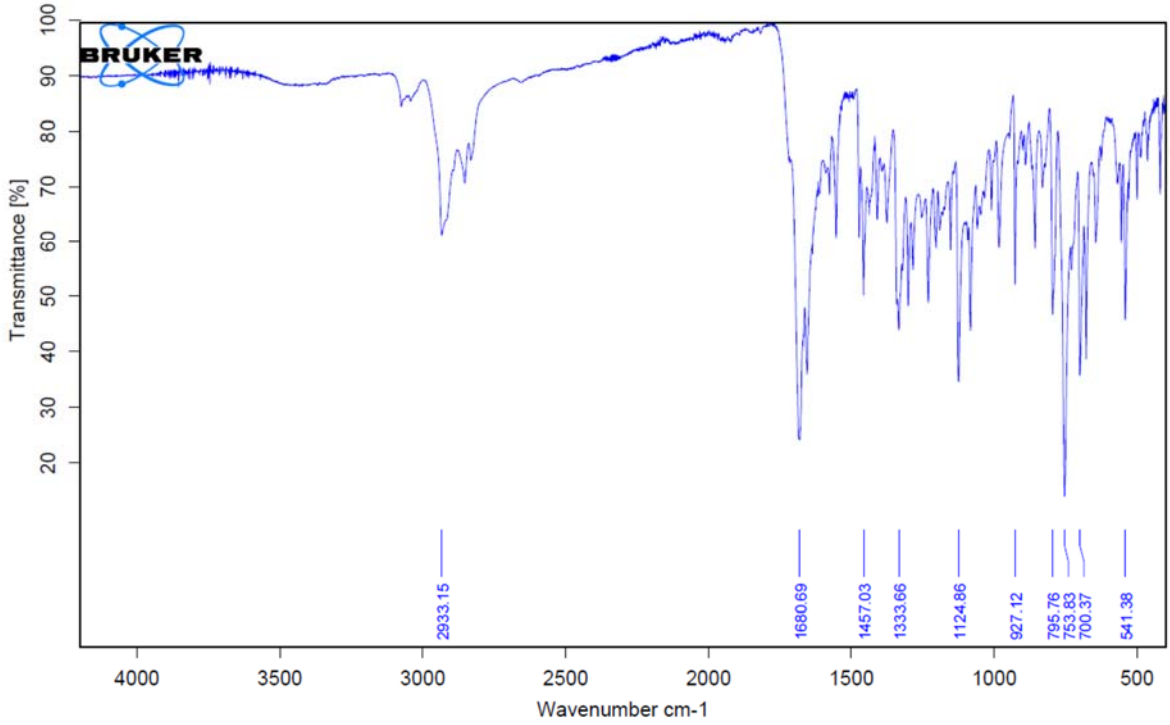


*Figure S47. IR spectrum of **5***

Computational study

Computational methodologies

The bond orders for component **3** have been calculated with MOPAC2016[4] with the AM1 Hamiltonian and a Molecular Mechanics correction. The interface Mercury[5] has been used. Calculations have been performed on the x-ray crystal structure without structure optimization. All density functional theory (DFT) calculations were performed using Gaussian 16, Revision C.01.[6] Geometry optimizations, as well as frequency and single-point energy calculations, were performed using the B3LYP[7] functional augmented with Grimme's D3[8] empirical dispersion term and the 6-31G(d) basis set. Solvation effects were included in the optimization and single-point calculations using the SMD[9] solvation model with acetonitrile as the solvent. Gibbs free energies were obtained by summing the thermal correction and single point energies obtained from DFT. No scaling was applied for the ΔG values. Normal vibrational mode analysis was used to verify the structures of minima (zero imaginary frequencies) and transition states (single imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were also used to verify transition state structures, and that they indeed connected the reactants and products. Mixed torsional/Low-Mode conformational sampling in gas phase was performed for the reactant, key intermediates, and transition states, where applicable, using the Merck molecular force field (MMFF94) implemented in MacroModel,[10] followed by DFT optimization. Conformers obtained from each run that fell within 10 kcal/mol of the lowest energy conformer were selected and reoptimized using DFT. GaussView 6.0.16 was used to render optimized structures as well as construct the initial structures used in our calculations.[11] Conformational search calculations were set up and rendered in the Maestro GUI.[12] 3D renderings of minima and transition state structures were generated with CYLview 1.0.[13]

Supplemental Figures

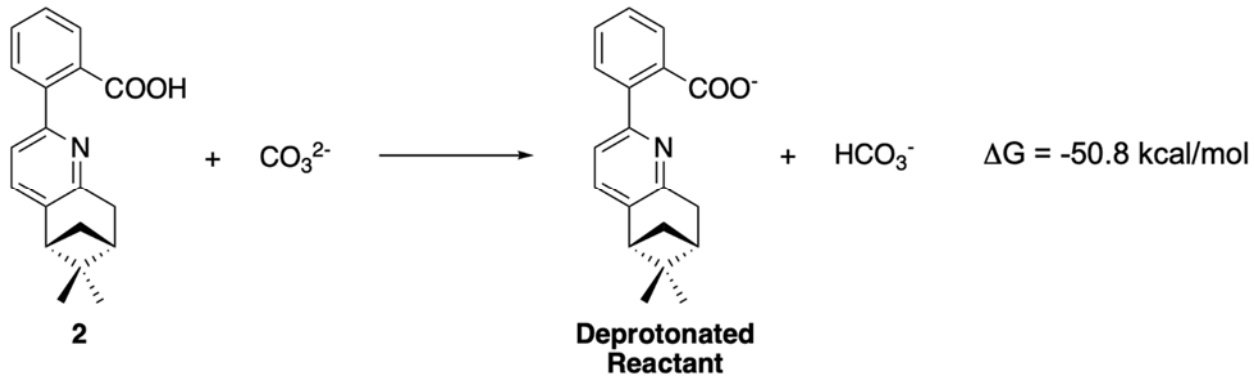


*Figure S48. Schematic and energetics of the deprotonation of **2**.*

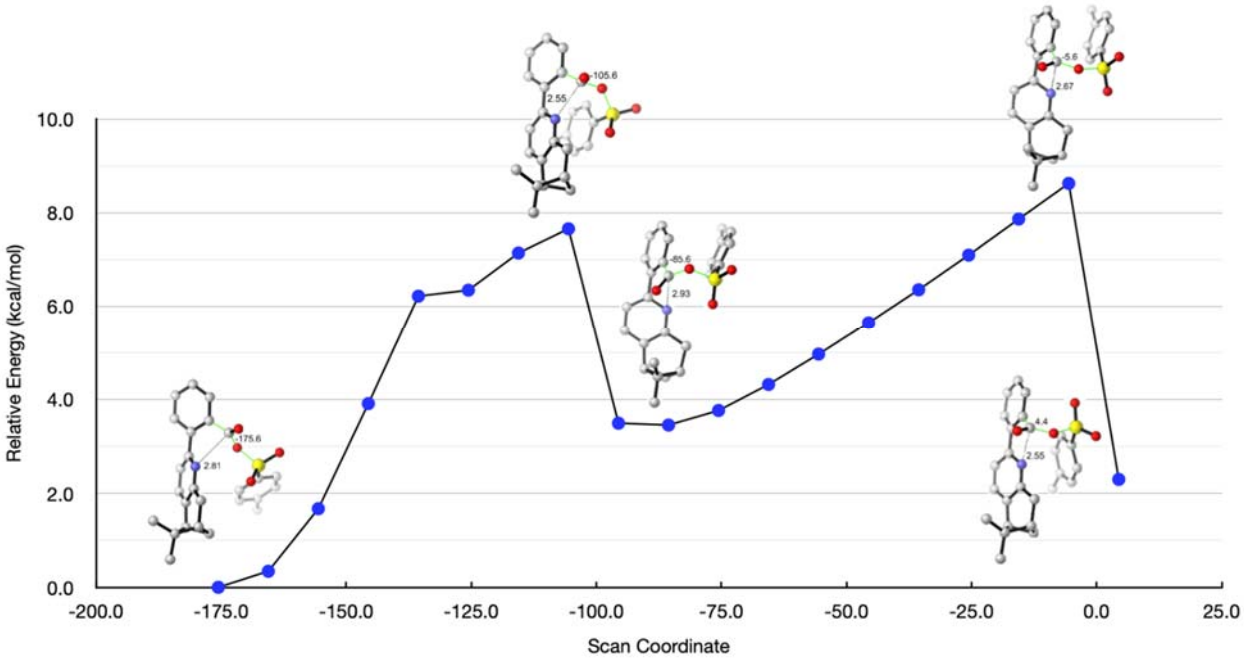
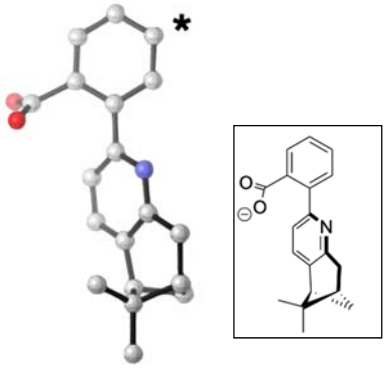


Figure S49. Scan of rotation about the tosyl ester bond in int-1a. Energies shown are single point energies; scan coordinate refers to dihedral angles.

B3LYP-D3/6-31G(d), SMD(CH3CN) Calculated Cartesian Coordinates and Thermal Corrections

Reactant (deprotonated)



** For all 3D renderings, hydrogens are omitted for clarity.*

C	4.69131300	-0.08823100	0.24013900
C	3.36663400	0.35636400	0.11599700
C	2.34401200	-0.60398700	-0.06415300
C	2.68028300	-1.96996400	-0.07632700
C	3.99868100	-2.39515300	0.07974000
C	5.01350400	-1.44579700	0.23578200
C	3.09893200	1.86509700	0.24756000
O	3.57749800	2.58411200	-0.66867800
O	2.44916000	2.20842100	1.26457500
C	0.92066800	-0.22278300	-0.28560700
C	0.56895400	0.91304900	-1.03113600
N	-0.01793000	-1.05684400	0.21513400
C	-0.77843900	1.19150900	-1.25481400
C	-1.30698600	-0.78306300	-0.00429900
C	-1.74865500	0.33503400	-0.74076300
C	-2.35912800	-1.70491000	0.59360500
C	-3.23783100	0.48705000	-0.91827700
C	-3.77489300	-1.23864500	0.20814900
C	-3.96731700	0.29967300	0.47092800
C	-3.35039700	0.92610100	1.72273000
C	-5.44322900	0.71713800	0.40255700
C	-3.79644000	-0.91650200	-1.31247100
H	5.47823700	0.65381000	0.35717500
H	1.88856900	-2.69994300	-0.22018300
H	4.23313700	-3.45668700	0.06665500
H	6.04799100	-1.76194000	0.35008900
H	1.34288700	1.55844400	-1.43185600
H	-1.07150200	2.06427100	-1.83440200
H	-2.23689500	-1.73319900	1.68456900
H	-2.19065200	-2.72955600	0.23556600
H	-3.50209600	1.35994700	-1.52416300
H	-4.53989300	-1.91261200	0.60952100
H	-3.87276000	0.57107600	2.62058000

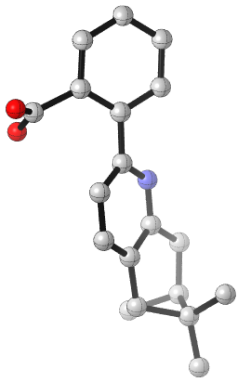
H	-2.28794900	0.70117300	1.84547500
H	-3.45289800	2.01868600	1.69035500
H	-5.52852100	1.81061500	0.36216400
H	-5.96990600	0.31206100	-0.46663600
H	-5.97427400	0.37433700	1.30004400
H	-3.16508900	-1.53077300	-1.96394600
H	-4.80413100	-0.87395000	-1.73016400

Zero-point correction= 0.326923 (Hartree/Particle)
Thermal correction to Energy= 0.345038
Thermal correction to Enthalpy= 0.345982
Thermal correction to Gibbs Free Energy= 0.280336
Sum of electronic and zero-point Energies= -939.915887
Sum of electronic and thermal Energies= -939.897772
Sum of electronic and thermal Enthalpies= -939.896828
Sum of electronic and thermal Free Energies= -939.962475

Single point energy: -940.242810398
Total free energy: -939.962474398

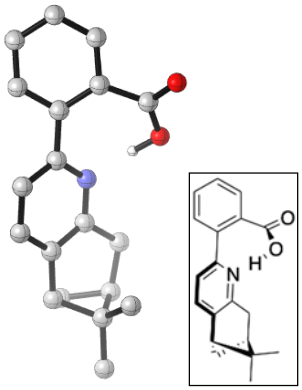
Number of imaginary frequencies: 0

<u>Reactant (deprotonated) alternative conformations</u>



Thermal correction to Gibbs Free Energy= 0.281174 (Hartree/Particle)
Single point energy: -940.242823439
Total free energy: -939.961649439
ΔG (relative to lowest energy conformer): 0.5 kcal/mol

Reactant (protonated)



C	4.54987400	0.52007200	0.07190900
C	3.14793800	0.56197100	-0.01966100
C	2.42422200	-0.66236100	-0.00470000
C	3.15369500	-1.86103300	0.11637700
C	4.54089800	-1.87777900	0.22799500
C	5.24753800	-0.67566700	0.20658300
H	5.08987600	1.45960500	0.03267800
H	2.61239300	-2.80131800	0.14550000
H	5.06181900	-2.82498300	0.33598100
H	6.33036100	-0.66672600	0.29211500
C	2.60291000	1.97048000	-0.18131400
O	1.42668600	2.28547400	0.35362600
O	3.26874100	2.82792700	-0.74183600
C	0.94382800	-0.80452900	-0.12561700
C	0.37111500	-1.82343700	-0.89608800
N	0.16467900	0.05359200	0.56811300
C	-1.01788400	-1.95836400	-0.92749900
H	0.99961600	-2.48946800	-1.47661700
C	-1.16489800	-0.06809300	0.53793600
C	-1.81258600	-1.08289200	-0.19403300
H	-1.47788300	-2.73874100	-1.52840200
C	-2.01176700	0.94464200	1.28466100
H	-1.73531500	0.93618500	2.34701700
H	-1.78168700	1.95033400	0.90861200
C	-3.31655600	-1.10267500	-0.12567400
H	-3.75128400	-1.93108500	-0.69305200
C	-3.50675700	0.61499900	1.12285100
H	-4.13075000	1.32377500	1.67716700
C	-3.87948700	0.35332000	-0.38197500
C	-3.23802600	1.21604400	-1.47057100
H	-3.62923400	2.24012700	-1.41885000
H	-2.14859400	1.27471000	-1.40089300
H	-3.48223500	0.81688600	-2.46346200
C	-5.39759600	0.34318700	-0.60872300
H	-5.79187900	1.36612200	-0.55713900
H	-5.63060700	-0.05480200	-1.60445300

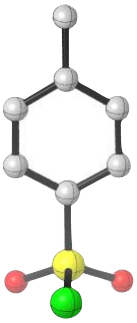
H	-5.94325500	-0.25826600	0.12426200
C	-3.70884200	-0.90571900	1.37252800
H	-4.74631400	-1.17437000	1.57771900
H	-3.06157200	-1.38197200	2.11706300
H	0.93466800	1.45863300	0.68372700

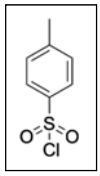
Zero-point correction= 0.340325 (Hartree/Particle)
Thermal correction to Energy= 0.358049
Thermal correction to Enthalpy= 0.358994
Thermal correction to Gibbs Free Energy= 0.294897
Sum of electronic and zero-point Energies= -940.398315
Sum of electronic and thermal Energies= -940.380590
Sum of electronic and thermal Enthalpies= -940.379646
Sum of electronic and thermal Free Energies= -940.443742

Single point energy: -940.738639147
Total free energy: -940.443842147

Number of imaginary frequencies: 0

TsCl





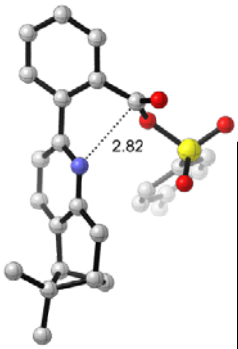
C	2.16224000	-1.21115300	0.01675500
C	2.87086600	-0.00220100	0.10628700
C	2.16273700	1.20763500	0.00703900
C	0.78482700	1.22326900	-0.17967500
C	0.11915800	-0.00229100	-0.27450400
C	0.78320500	-1.22681900	-0.17015900
H	2.69675700	-2.15359000	0.09473100
H	2.69868800	2.15003100	0.07737000
H	0.24344900	2.16001800	-0.25481400
H	0.24129300	-2.16382300	-0.23790300
S	-1.63608200	-0.00234300	-0.51096800
O	-2.07741500	1.26842300	-1.08069500
O	-2.07940700	-1.27823800	-1.06748000
Cl	-2.36580000	0.00871300	1.52935200
C	4.36629400	0.00316600	0.28273600
H	4.86377300	0.13765200	-0.68716900
H	4.68740900	0.82700700	0.92897800
H	4.72315200	-0.93905000	0.70983900

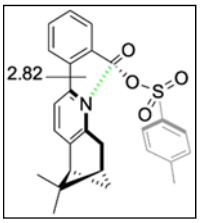
Zero-point correction= 0.129064 (Hartree/Particle)
Thermal correction to Energy= 0.139872
Thermal correction to Enthalpy= 0.140816
Thermal correction to Gibbs Free Energy= 0.090888
Sum of electronic and zero-point Energies= -1279.638496
Sum of electronic and thermal Energies= -1279.627689
Sum of electronic and thermal Enthalpies= -1279.626745
Sum of electronic and thermal Free Energies= -1279.676672

Single point energy: -1279.76756048
Total free energy: -1279.67667248

Number of imaginary frequencies: 0

Int-1a





C	-0.32001500	3.11661100	1.39070000
C	0.38675600	4.32115600	1.55606600
C	1.46648800	4.59087900	0.70342300
C	1.84187800	3.69162500	-0.29505800
C	1.11251700	2.51179600	-0.43418600
C	0.03066600	2.20951100	0.39862500
S	1.54814500	1.36343900	-1.71455300
O	0.35768800	0.92600700	-2.44103500
O	2.72814800	1.82972100	-2.43914800
C	-0.02752500	5.30334000	2.62113800
O	2.01454900	0.11571500	-0.66958200
C	2.33175300	-1.14034200	-1.17641900
O	2.48960500	-1.36092200	-2.35077900
C	2.60218700	-2.07763800	-0.05077900
C	3.83093800	-2.74705200	-0.08757500
C	1.71681200	-2.25517200	1.03587300
C	4.21771200	-3.56695000	0.97178700
C	2.12499500	-3.08519000	2.08946000
C	3.36498500	-3.72533300	2.06598700
C	0.34943600	-1.67532500	1.01864000
C	-0.27712700	-1.21010000	2.17997700
N	-0.26167400	-1.64998200	-0.18557300
C	-1.57961700	-0.71387300	2.09107300
C	-1.50534700	-1.17514900	-0.26559600
C	-2.21761300	-0.68814600	0.85461200
C	-2.20176000	-1.17314600	-1.61499700
C	-3.60357900	-0.15834500	0.59433200
C	-3.60948000	-0.56136900	-1.49806300
C	-4.41178700	-1.18324100	-0.29754900
C	-4.28240900	-2.67999600	-0.00885300
C	-5.90534200	-0.83300200	-0.35572200
C	-3.51450500	0.75164900	-0.67191600
H	-1.15357900	2.88665300	2.04912300
H	2.02526900	5.51501200	0.82215000
H	2.68245700	3.90191500	-0.94740500
H	-0.51631400	1.28213000	0.28324200
H	0.74639400	6.05644100	2.79768200

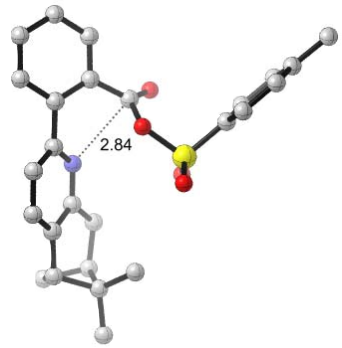
H	-0.94519800	5.82792800	2.32392800
H	-0.24079600	4.79302200	3.56723300
H	4.48941400	-2.59887600	-0.93820500
H	5.17697200	-4.07508000	0.94234000
H	1.44729900	-3.25954200	2.91984800
H	3.65387100	-4.36555800	2.89478000
H	0.24768100	-1.21947700	3.12961900
H	-2.08736000	-0.33883800	2.97636200
H	-2.24756300	-2.20117200	-1.99772100
H	-1.59340100	-0.59770800	-2.32244100
H	-4.08236200	0.22629900	1.50043100
H	-4.11177800	-0.52984800	-2.47102100
H	-4.76408300	-3.26108500	-0.80575100
H	-3.24779000	-3.02339100	0.07191700
H	-4.78594300	-2.92968500	0.93412400
H	-6.39712400	-1.41371700	-1.14672000
H	-6.39309300	-1.08414100	0.59478200
H	-6.09673700	0.22529400	-0.55635700
H	-2.60583800	1.35170500	-0.78577200
H	-4.38501600	1.39921900	-0.78984400

Zero-point correction= 0.457872 (Hartree/Particle)
Thermal correction to Energy= 0.485954
Thermal correction to Enthalpy= 0.486898
Thermal correction to Gibbs Free Energy= 0.397716
Sum of electronic and zero-point Energies= -1759.245146
Sum of electronic and thermal Energies= -1759.217064
Sum of electronic and thermal Enthalpies= -1759.216119
Sum of electronic and thermal Free Energies= -1759.305301

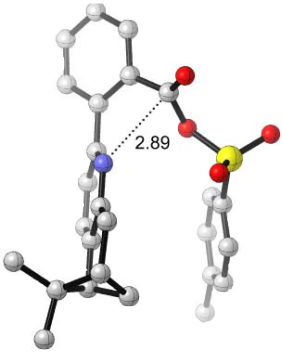
Single point energy: -1759.70301746
Total free energy: -1759.30530146

Number of imaginary frequencies: 0

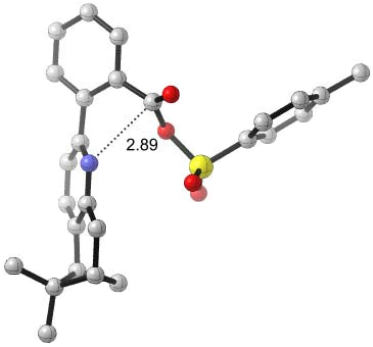
Int-1a alternative conformations



Thermal correction to Gibbs Free Energy= 0.397753 (Hartree/Particle)
Single point energy: -1759.70214757
Total free energy: -1759.30439457
ΔG (relative to lowest energy conformer): 0.6 kcal/mol



Thermal correction to Gibbs Free Energy= 0.397522 (Hartree/Particle)
Single point energy: -1759.70156833
Total free energy: -1759.30404633
ΔG: 0.8 kcal/mol



Thermal correction to Gibbs Free Energy= 0.397442 (Hartree/Particle)
Single point energy: -1759.70136351
Total free energy: -1759.30392151
ΔG: 0.9 kcal/mol

Cl^-

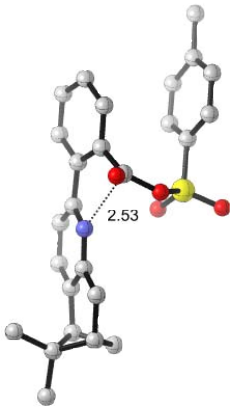
Cl	0.00000000	0.00000000	0.00000000

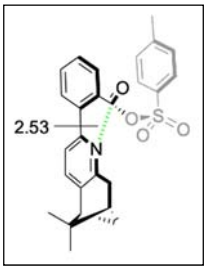
Zero-point correction= 0.000000 (Hartree/Particle)
Thermal correction to Energy= 0.001416
Thermal correction to Enthalpy= 0.002360
Thermal correction to Gibbs Free Energy= -0.015023
Sum of electronic and zero-point Energies= -460.360860
Sum of electronic and thermal Energies= -460.359444
Sum of electronic and thermal Enthalpies= -460.358500
Sum of electronic and thermal Free Energies= -460.375883

Single point energy: -460.360860002
Total free energy: -460.375883002

Number of imaginary frequencies: 0

Int-1b





C	0.66742100	-0.18468200	1.80184600
O	0.39614900	-0.24089700	2.97190100
C	1.28431000	1.00270700	1.13095600
C	2.55599400	1.35657400	1.59865100
C	0.64853900	1.76417500	0.12721300
C	3.23760700	2.43564700	1.04089100
C	1.34889400	2.85543000	-0.41174400
C	2.62997000	3.18182600	0.02829300
C	-0.72910500	1.42115000	-0.29428900
C	-1.31928600	1.87953200	-1.47738800
N	-1.37898600	0.58687900	0.53888500
C	-2.60394800	1.44027000	-1.80143400
C	-2.59667700	0.15546300	0.22412400
C	-3.26359900	0.55430600	-0.95435900
C	-3.30878900	-0.79214500	1.17312500
C	-4.62355000	-0.04692800	-1.19341100
C	-4.67795500	-1.19926100	0.59962600
C	-5.49736700	0.05405600	0.12001000
C	-5.44607500	1.34016700	0.94663900
C	-6.96991500	-0.28678300	-0.14855100
C	-4.49770000	-1.57573400	-0.89783400
H	3.02034200	0.76139600	2.37879200
H	4.23248600	2.69003800	1.39395900
H	0.87815600	3.47439900	-1.16830800
H	3.14756200	4.02997700	-0.41076600
H	-0.78482200	2.53795200	-2.15312500
H	-3.08097000	1.77291800	-2.72014900
H	-3.41501800	-0.31106800	2.15415600
H	-2.68281100	-1.68097800	1.32768400
H	-5.07021000	0.28416000	-2.13623300
H	-5.19066000	-1.90875000	1.25802400
H	-5.96802500	1.19691500	1.90152200
H	-4.43035500	1.67587300	1.17127600
H	-5.95074200	2.15528100	0.41186300
H	-7.50260800	-0.42721100	0.80081000

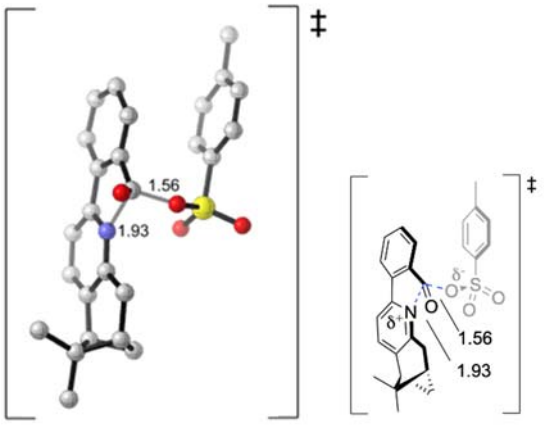
H	-7.45898300	0.53478700	-0.68728300
H	-7.10472400	-1.19718400	-0.74011000
H	-3.55457100	-2.05434500	-1.18400600
H	-5.32955400	-2.15686900	-1.29961800
C	4.50330300	0.14353600	-1.44119300
C	5.44817600	-0.36178800	-0.53555400
C	5.04174400	-1.33780700	0.38961700
C	3.72730000	-1.79291000	0.42475900
C	2.80912100	-1.25282100	-0.48010900
C	3.18069800	-0.29149300	-1.42067500
S	1.12373800	-1.80563400	-0.43063400
O	1.06519400	-3.26548900	-0.39767900
O	0.62474200	-1.42688100	1.12333900
C	6.86081300	0.16234200	-0.53001600
O	0.33168300	-1.06660900	-1.40987600
H	4.80328300	0.89627400	-2.16495100
H	5.76445500	-1.74427100	1.09175600
H	3.42270200	-2.54420000	1.14640100
H	2.44837600	0.11869300	-2.10641500
H	7.18245700	0.45617800	-1.53459100
H	6.93199800	1.05242700	0.10982500
H	7.56365200	-0.58038400	-0.13918500

Zero-point correction= 0.457440 (Hartree/Particle)
Thermal correction to Energy= 0.485454
Thermal correction to Enthalpy= 0.486399
Thermal correction to Gibbs Free Energy= 0.397883
Sum of electronic and zero-point Energies= -1759.238527
Sum of electronic and thermal Energies= -1759.210513
Sum of electronic and thermal Enthalpies= -1759.209568
Sum of electronic and thermal Free Energies= -1759.298084

Single point energy: -1759.69596697
Total free energy: -1759.29808397

Number of imaginary frequencies: 0

TS1



C	0.16842500	0.13962600	1.63006300
O	-0.26534700	0.10227800	2.75710500
C	1.16953500	1.13113800	1.10372200
C	2.42613000	1.28380900	1.68277800
C	0.76832800	1.93558300	0.02792700
C	3.30359400	2.23568100	1.15673300
C	1.64605400	2.88999200	-0.49356800
C	2.91448100	3.03083200	0.07210900
C	-0.60104900	1.65085700	-0.42439400
C	-1.31393600	2.22487400	-1.47177400
N	-1.15055800	0.67489300	0.32051500
C	-2.60128600	1.74454000	-1.73674500
C	-2.36435200	0.19425500	0.08948500
C	-3.14193100	0.71694400	-0.96688200
C	-2.92808500	-0.91380400	0.95271400
C	-4.48528900	0.06928000	-1.17479200
C	-4.31919600	-1.32025600	0.43562400
C	-5.24040500	-0.06687400	0.20751800
C	-5.18112400	1.09410200	1.20194600
C	-6.71121400	-0.46050300	0.01358700
C	-4.25117700	-1.47458500	-1.10966800
H	2.72143400	0.65670900	2.51822400
H	4.29284700	2.35406300	1.58907700
H	1.34438000	3.51541500	-1.32843700
H	3.60380700	3.76606500	-0.33304400
H	-0.87476500	3.01382700	-2.07260000
H	-3.18012500	2.16619100	-2.55413200
H	-2.96455000	-0.57721100	1.99534600
H	-2.24192900	-1.76868600	0.92716500
H	-5.02965700	0.49757800	-2.02151400
H	-4.73263900	-2.14441900	1.02585700
H	-5.61035200	0.78817900	2.16452000
H	-4.16825100	1.45856600	1.39316900
H	-5.76999500	1.94225400	0.82971900

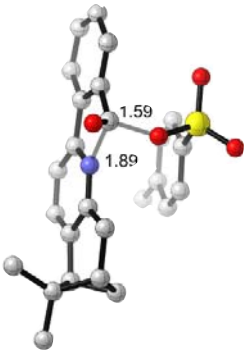
H	-7.28745400	0.39411800	-0.36278400
H	-6.85087300	-1.28908200	-0.68693000
H	-7.14848500	-0.76183200	0.97400700
H	-3.31219200	-1.84653800	-1.53426400
H	-5.08277600	-2.04695200	-1.52360800
C	4.40880000	-0.05064400	-1.41600800
C	5.31868900	-0.54652300	-0.47193400
C	4.85524900	-1.45222400	0.49695100
C	3.52048800	-1.84424500	0.53475900
C	2.63490000	-1.31843400	-0.41032000
C	3.06696700	-0.42841800	-1.39244500
S	0.91906500	-1.80066400	-0.35359100
O	0.83809800	-3.26419800	-0.27492200
O	0.41144900	-1.30607700	1.09856800
C	6.75476900	-0.08805000	-0.47004600
O	0.20514200	-1.11212700	-1.43557600
H	4.75114800	0.64797100	-2.17481400
H	5.54972100	-1.85219000	1.23115300
H	3.17293100	-2.54102800	1.29100600
H	2.36375900	-0.02892600	-2.11415900
H	7.42582600	-0.87228500	-0.10403400
H	7.08134000	0.21262300	-1.47092700
H	6.87679500	0.78125900	0.19043600

Zero-point correction= 0.456855 (Hartree/Particle)
Thermal correction to Energy= 0.484192
Thermal correction to Enthalpy= 0.485137
Thermal correction to Gibbs Free Energy= 0.397928
Sum of electronic and zero-point Energies= -1759.234696
Sum of electronic and thermal Energies= -1759.207359
Sum of electronic and thermal Enthalpies= -1759.206414
Sum of electronic and thermal Free Energies= -1759.293623

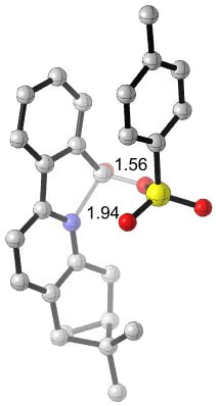
Single point energy: -1759.69155109
Total free energy: -1759.29362309

Number of imaginary frequencies: 1
Frequencies -- -169.8427
Red. masses -- 10.5269
Frc consts -- 0.1789
IR Inten -- 289.0098

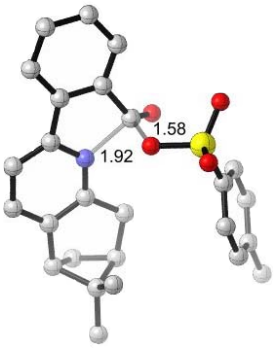
TS1 alternative conformations



Thermal correction to Gibbs Free Energy= 0.399527 (Hartree/Particle)
Single point energy: -1759.69309030
Total free energy: -1759.2935633
ΔG (relative to lowest energy conformer): 0.04 kcal/mol

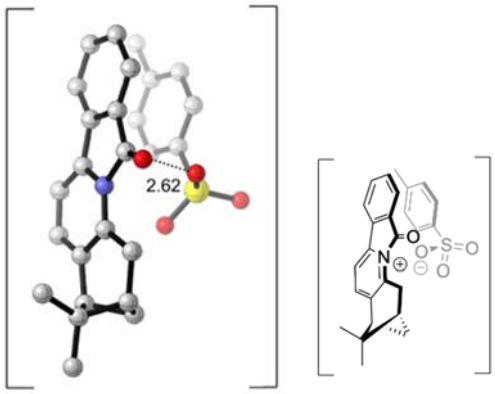


Thermal correction to Gibbs Free Energy= 0.400004 (Hartree/Particle)
Single point energy: -1759.69313692
Total free energy: -1759.29313292
ΔG: 0.3 kcal/mol



Thermal correction to Gibbs Free Energy= 0.399603 (Hartree/Particle)
Single point energy: -1759.69271515
Total free energy: -1759.29311215
ΔG: 0.3 kcal/mol

Complex-1



C	0.20748800	-1.73477700	1.23474000
O	0.81515100	-2.02125700	2.22924600
C	-1.15107000	-2.06225400	0.78435700
C	-2.17488400	-2.68285300	1.48878700
C	-1.29957100	-1.68206800	-0.55741200
C	-3.37811500	-2.91282100	0.81230700
C	-2.48944700	-1.91598500	-1.23541800
C	-3.52898400	-2.53501900	-0.52899500
C	-0.05522200	-1.05664900	-1.00238600
C	0.32626500	-0.52557800	-2.21306300
N	0.82568300	-1.05055800	0.05336200
C	1.61105100	0.02363400	-2.32653000
C	2.04471300	-0.48314800	-0.00410600
C	2.46719000	0.06499500	-1.23235700
C	2.94595900	-0.40166500	1.19861600
C	3.82416000	0.71686800	-1.22298400
C	4.23440700	0.35504500	0.83261500
C	4.87192400	-0.20845800	-0.48828200
C	4.84524400	-1.71563800	-0.75069600
C	6.30826600	0.29037400	-0.69524600
C	3.86044700	1.63757800	0.03991400
H	-2.04321900	-2.97140500	2.52678300
H	-4.20471200	-3.38781500	1.33144900
H	-2.61488300	-1.62157100	-2.27184100
H	-4.47270900	-2.72284200	-1.03236400
H	-0.36489500	-0.53640900	-3.04777200
H	1.93497900	0.44291400	-3.27443200
H	3.16090000	-1.40856100	1.57057700
H	2.39232400	0.11149500	1.99402500
H	4.08749200	1.12625700	-2.20201300
H	4.88481900	0.44647400	1.70794300
H	5.51546600	-2.23094500	-0.05127700
H	3.85443000	-2.16740100	-0.64875000
H	5.19709900	-1.92829100	-1.76812500
H	6.98662600	-0.22776800	-0.00575700

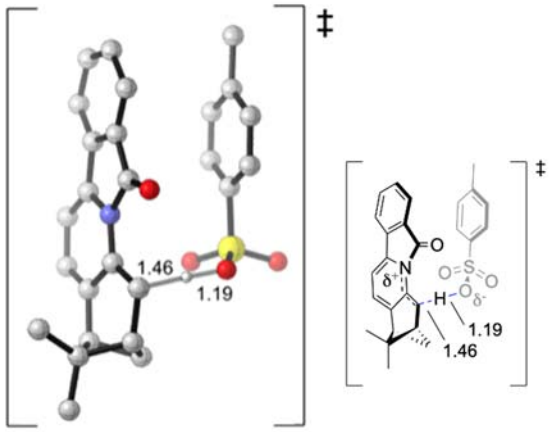
H	6.64152400	0.07488100	-1.71812500
H	6.42357600	1.36502900	-0.52743700
H	2.92239100	2.13395000	0.30212100
H	4.66957200	2.36808400	-0.00014700
C	-3.43555600	1.58621400	-1.66369600
C	-4.52134600	1.04202600	-0.96496400
C	-4.36061900	0.76378700	0.40245500
C	-3.15245700	1.01095600	1.04924700
C	-2.07922200	1.55216000	0.33400000
C	-2.22136400	1.84342900	-1.02276200
S	-0.52861100	1.90172000	1.18815000
O	-0.75426000	3.14682200	1.97126600
O	-0.29893500	0.70042300	2.05470700
C	-5.81656800	0.71330600	-1.66541300
O	0.49036900	2.04312300	0.10644500
H	-3.53815600	1.80603500	-2.72401800
H	-5.18924600	0.33327600	0.96004500
H	-3.03270700	0.76609500	2.10017100
H	-1.37864100	2.25055400	-1.57166000
H	-5.90803300	1.24834800	-2.61639100
H	-5.87735100	-0.36187900	-1.88329300
H	-6.68337900	0.96424700	-1.04333200

Zero-point correction= 0.458872 (Hartree/Particle)
Thermal correction to Energy= 0.486720
Thermal correction to Enthalpy= 0.487664
Thermal correction to Gibbs Free Energy= 0.400634
Sum of electronic and zero-point Energies= -1759.261117
Sum of electronic and thermal Energies= -1759.233269
Sum of electronic and thermal Enthalpies= -1759.232325
Sum of electronic and thermal Free Energies= -1759.319355

Single point energy: -1759.7199889
Total free energy: -1759.3193549

Number of imaginary frequencies: 0

TS2a



C	-0.55741800	1.01665700	-1.26998900
O	-0.35546700	0.48412100	-2.34272200
C	-1.75350400	1.70013700	-0.75942000
C	-2.97840300	1.90358800	-1.38652400
C	-1.50444000	2.14546100	0.54833100
C	-3.97156400	2.57160500	-0.66631100
C	-2.49605800	2.80636300	1.27056900
C	-3.73073800	3.01099000	0.64585100
C	-0.13633700	1.78273400	0.89816900
C	0.62185600	2.02420500	2.00032800
N	0.40575600	1.09347600	-0.19701100
C	1.98053200	1.58796900	2.01131800
C	1.68889600	0.58772800	-0.20060700
C	2.50675700	0.89009200	0.95935700
C	2.22905400	-0.22263600	-1.21505000
C	3.92937500	0.40292200	0.86813800
C	3.70667900	-0.55661300	-1.01583600
C	4.52390800	0.71879200	-0.56524600
C	4.22253700	2.07201000	-1.20944700
C	6.04136300	0.49492700	-0.61233500
C	3.88711300	-1.09528100	0.43329100
H	-3.15147900	1.54660900	-2.39674100
H	-4.94209400	2.74653900	-1.12012000
H	-2.31934900	3.14918100	2.28531300
H	-4.52136300	3.52159000	1.18808600
H	0.19846500	2.56445600	2.83934200
H	2.60639500	1.82537000	2.86671500
H	1.84811000	-0.09853500	-2.22441400
H	1.46860200	-1.43689000	-0.93457400
H	4.51476000	0.69423100	1.74535100
H	4.10010000	-1.14578900	-1.84938100
H	4.60122400	2.09305600	-2.23928700
H	3.15714100	2.31398900	-1.24594600
H	4.72436800	2.87468600	-0.65380500

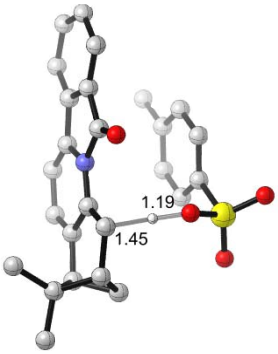
H	6.38738900	0.49956800	-1.65384800
H	6.56187500	1.30484500	-0.08532800
H	6.35988200	-0.44999900	-0.16369900
H	3.07508800	-1.69971700	0.84188100
H	4.83889500	-1.60212800	0.59684200
C	-3.51099400	-0.88609600	1.02956500
C	-4.13616000	-1.07428200	-0.21087800
C	-3.41101700	-1.69992100	-1.23766800
C	-2.10636400	-2.14323100	-1.03333500
C	-1.50958700	-1.94914900	0.21503800
C	-2.20367800	-1.31757900	1.24920100
S	0.12200700	-2.60492900	0.55339600
O	-0.00786800	-4.03821300	0.86905900
O	0.88537400	-2.46785100	-0.80738200
C	-5.55550400	-0.61977800	-0.44036800
O	0.73081000	-1.73807000	1.58216400
H	-4.04702500	-0.38125600	1.82870400
H	-3.87310300	-1.83430600	-2.21252000
H	-1.54991300	-2.61264500	-1.83757200
H	-1.72015900	-1.15008200	2.20596400
H	-6.25738800	-1.45190700	-0.29374300
H	-5.83747900	0.17721500	0.25452700
H	-5.69595400	-0.25312200	-1.46281200

Zero-point correction= 0.452782 (Hartree/Particle)
Thermal correction to Energy= 0.480177
Thermal correction to Enthalpy= 0.481121
Thermal correction to Gibbs Free Energy= 0.395635
Sum of electronic and zero-point Energies= -1759.231733
Sum of electronic and thermal Energies= -1759.204338
Sum of electronic and thermal Enthalpies= -1759.203394
Sum of electronic and thermal Free Energies= -1759.288879

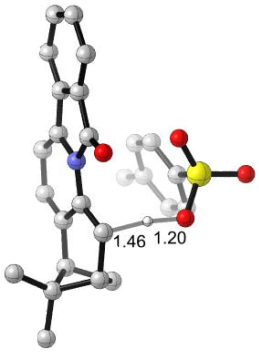
Single point energy: -1759.68451445
Total free energy: -1759.28887945

Number of imaginary frequencies: 1
Frequencies -- -1428.0717
Red. masses -- 1.2064
Frc consts -- 1.4496
IR Inten -- 10320.3909

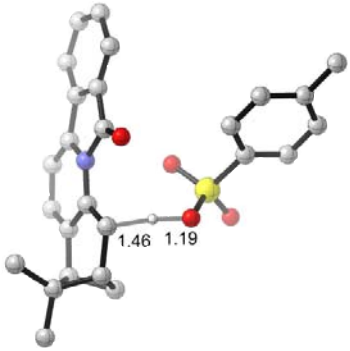
TS2a alternative conformations



Thermal correction to Gibbs Free Energy= 0.394365 (Hartree/Particle)
Single point energy: -1759.6829728
Total free energy: -1759.2886078
ΔG (relative to lowest energy conformer): 0.2 kcal/mol

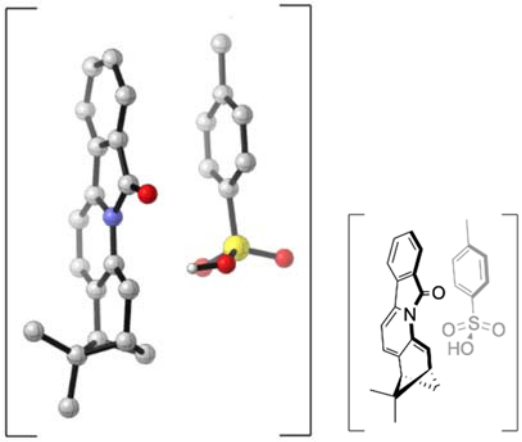


Thermal correction to Gibbs Free Energy= 0.393034 (Hartree/Particle)
Single point energy: -1759.68058554
Total free energy: -1759.28755154
ΔG: 0.8 kcal/mol



Thermal correction to Gibbs Free Energy= 0.391846 (Hartree/Particle)
Single point energy: -1759.67888435
Total free energy: -1759.28703835
ΔG: 1.2 kcal/mol

Complex-2a



C	0.49346000	-1.02897700	-1.34253200
O	0.26929900	-0.50470000	-2.42694000
C	1.70770400	-1.70579600	-0.85633800
C	2.90862700	-1.94508000	-1.51888200
C	1.50202400	-2.11171300	0.47341600
C	3.91582400	-2.61197600	-0.81957600
C	2.51310900	-2.76899000	1.17670100
C	3.71775800	-3.01396000	0.51348000
C	0.15646700	-1.71491300	0.85820700
C	-0.54583600	-1.85332000	2.00866900
N	-0.42034800	-1.08428600	-0.26722000
C	-1.89742200	-1.36637700	2.07387600
C	-1.74095200	-0.60342300	-0.26048200
C	-2.47618000	-0.76328400	1.00077000
C	-2.39952300	-0.04740600	-1.32247100
C	-3.89204900	-0.25132000	0.95800000
C	-3.83398500	0.37093000	-1.07580100
C	-4.62503500	-0.78903900	-0.34002200
C	-4.40085700	-2.24075800	-0.76224800
C	-6.13710500	-0.53346200	-0.29385400
C	-3.88306000	1.15089100	0.27342500
H	3.05040100	-1.61778600	-2.54434900
H	4.86573700	-2.81676300	-1.30415900
H	2.36901900	-3.08096600	2.20676700
H	4.51969100	-3.52523900	1.03853200
H	-0.08696000	-2.33884100	2.86284000
H	-2.46214800	-1.49509600	2.99266800
H	-1.96917600	-0.02282800	-2.31452700
H	-1.18159300	1.54798500	-1.04025100
H	-4.39765200	-0.37539200	1.92055000
H	-4.29154200	0.81659600	-1.96325500
H	-4.86474900	-2.42687100	-1.73935200
H	-3.34598900	-2.51448700	-0.83810500
H	-4.86994000	-2.91866400	-0.03758600

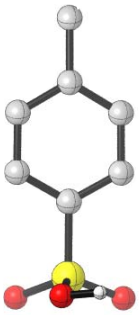
H	-6.57687000	-0.71380700	-1.28309400
H	-6.61564800	-1.22307300	0.41330200
H	-6.40376300	0.48399500	0.00471900
H	-3.03942700	1.80565000	0.49973100
H	-4.81602000	1.69335800	0.42990900
C	3.40060200	0.78727900	1.24903700
C	4.15707500	0.89586800	0.07445900
C	3.57992400	1.52536600	-1.04127400
C	2.29552100	2.05693600	-0.98523700
C	1.57077100	1.94210000	0.20527800
C	2.10915300	1.30687100	1.32545800
S	-0.01168500	2.74340700	0.36322000
O	0.16809700	4.19636100	0.38275600
O	-0.73675900	2.44207200	-1.05403100
C	5.56481600	0.36194000	0.00882200
O	-0.76047900	2.09216300	1.44398000
H	3.82225300	0.28278700	2.11370500
H	4.14528600	1.59618100	-1.96664000
H	1.85752400	2.53510100	-1.85493300
H	1.52589900	1.20981800	2.23462900
H	6.28779600	1.16149300	0.22006300
H	5.72568200	-0.43339100	0.74275900
H	5.79535000	-0.03175400	-0.98631700

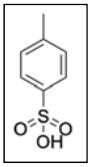
Zero-point correction= 0.456821 (Hartree/Particle)
Thermal correction to Energy= 0.485038
Thermal correction to Enthalpy= 0.485982
Thermal correction to Gibbs Free Energy= 0.397438
Sum of electronic and zero-point Energies= -1759.234295
Sum of electronic and thermal Energies= -1759.206078
Sum of electronic and thermal Enthalpies= -1759.205134
Sum of electronic and thermal Free Energies= -1759.293678

Single point energy: -1759.6911159
Total energy: -1759.2936779

Number of imaginary frequencies: 0

TsOH





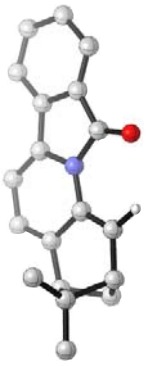
C	-1.94852400	1.20745700	0.00835600
C	-2.66550800	0.00040300	-0.02081300
C	-1.95198900	-1.20817500	-0.00219400
C	-0.56008600	-1.22227100	0.04643500
C	0.12135800	-0.00357000	0.07333400
C	-0.55726400	1.21756300	0.05699000
H	-2.48780700	2.15075600	-0.00585300
H	-2.49340700	-2.15002300	-0.02469100
H	-0.01408000	-2.15946300	0.06557300
H	-0.00902900	2.15331400	0.08450300
S	1.89474700	-0.00492000	0.12296000
O	2.38582300	-1.27914000	0.65570600
O	2.17879300	0.03023800	-1.49620400
C	-4.17255800	0.00485400	-0.03995000
H	-4.56822300	0.05136300	0.98361000
H	-4.56221700	0.87436000	-0.57966300
H	-4.57007800	-0.90317900	-0.50463800
O	2.39114700	1.24612900	0.70469800
H	3.15020700	0.10620400	-1.63275000

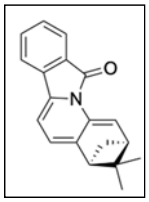
Zero-point correction= 0.141777 (Hartree/Particle)
Thermal correction to Energy= 0.152755
Thermal correction to Enthalpy= 0.153699
Thermal correction to Gibbs Free Energy= 0.102371
Sum of electronic and zero-point Energies= -895.250978
Sum of electronic and thermal Energies= -895.240001
Sum of electronic and thermal Enthalpies= -895.239057
Sum of electronic and thermal Free Energies= -895.290385

Single point energy: -895.392755863
Total free energy: -895.290384863

Number of imaginary frequencies: 0

Product





C	1.46781800	-1.33075700	-0.10098800
O	1.14001300	-2.51351700	-0.13736600
C	2.81499000	-0.74096800	0.02075500
C	4.05144700	-1.37532000	0.11786900
C	2.70162500	0.66047000	0.02625200
C	5.18902400	-0.57334400	0.22340000
H	4.11999900	-2.45927600	0.11087200
C	3.83995500	1.46311200	0.13223000
C	5.08032400	0.82939700	0.23064600
H	6.16982800	-1.03367900	0.30105200
H	3.76466600	2.54658300	0.13837600
H	5.98087100	1.43149300	0.31446600
C	1.29085300	0.98968800	-0.09488500
C	0.63337100	2.17323200	-0.14137300
N	0.58857100	-0.23741300	-0.16984000
C	-0.80019200	2.18453000	-0.27613600
H	1.19373000	3.09991400	-0.08026900
C	-0.81971000	-0.28272400	-0.29049400
C	-1.49837300	1.02005000	-0.35533200
H	-1.32213600	3.13620000	-0.31764200
C	-1.58781500	-1.40338300	-0.31547600
H	-1.16136400	-2.39303900	-0.24034900
C	-2.99365800	0.92607600	-0.50919200
H	-3.45726100	1.91450700	-0.58857100
C	-3.07835500	-1.19842500	-0.46061100
H	-3.62761400	-2.14366100	-0.49576500
C	-3.59024000	-0.08954500	0.54877400
C	-3.30056600	-0.15138100	-1.59735900
H	-2.62013200	-0.20552100	-2.45234000
H	-4.32948000	-0.09930300	-1.95642700
C	-3.04897500	-0.06124800	1.97793300
H	-3.35922400	0.86500100	2.47850400
H	-3.45673700	-0.90157500	2.55442600
H	-1.95958000	-0.12046800	2.02982600
C	-5.12152200	-0.01753500	0.61824600
H	-5.61048800	-0.03061100	-0.35968900

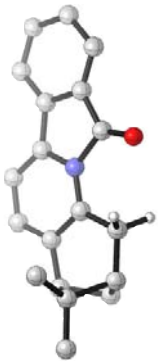
H	-5.51065500	-0.86802400	1.19261400
H	-5.43452400	0.89991900	1.13316700

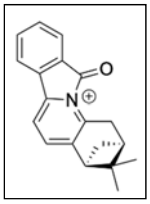
Zero-point correction= 0.313078 (Hartree/Particle)
Thermal correction to Energy= 0.329128
Thermal correction to Enthalpy= 0.330072
Thermal correction to Gibbs Free Energy= 0.270566
Sum of electronic and zero-point Energies= -863.958802
Sum of electronic and thermal Energies= -863.942751
Sum of electronic and thermal Enthalpies= -863.941807
Sum of electronic and thermal Free Energies= -864.001313

Single point energy: -864.27187935
Total free energy: -864.00131335

Number of imaginary frequencies: 0

Int-2





C	1.47317700	-1.33764200	-0.09716600
O	1.08596600	-2.47391500	-0.14301300
C	2.80912300	-0.75179700	0.02128200
C	4.03679200	-1.39847800	0.11020400
C	2.70266500	0.64778500	0.03097500
C	5.17966400	-0.59773500	0.21166900
H	4.10087900	-2.48177600	0.10036800
C	3.83470600	1.44553400	0.13066000
C	5.07652400	0.79988800	0.22139200
H	6.15732400	-1.06358000	0.28315000
H	3.76432200	2.52819800	0.13876800
H	5.97897800	1.39845300	0.30063300
C	1.28917300	1.00567600	-0.08092600
C	0.64699900	2.22205500	-0.11245800
N	0.55352100	-0.15629300	-0.16036700
C	-0.75022800	2.23626900	-0.22902600
H	1.22209300	3.13822600	-0.04770300
C	-0.79319600	-0.18166900	-0.27962400
C	-1.47573800	1.05095000	-0.31703300
H	-1.27739200	3.18511600	-0.25304100
C	-1.57706000	-1.46766800	-0.35363500
H	-1.21870800	-2.06003000	-1.20338600
H	-1.37489800	-2.06617200	0.54190600
C	-2.97019000	0.96866800	-0.47039900
H	-3.43035600	1.95885800	-0.51323900
C	-3.07689000	-1.15624600	-0.50712800
H	-3.64965200	-2.08466500	-0.58709800
C	-3.55650100	-0.09345100	0.54440400
C	-3.00128600	-0.15002700	1.96846800
H	-3.32039000	0.73326400	2.53545300
H	-3.38793600	-1.03730600	2.48483500
H	-1.90947300	-0.19123500	2.01965900
C	-5.08669100	-0.00844800	0.62676000
H	-5.48029100	-0.88285800	1.15969000
H	-5.38672100	0.88675600	1.18524000
H	-5.57597200	0.03073200	-0.35061000

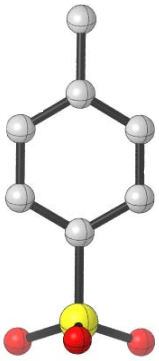
C	-3.25263300	-0.06977100	-1.60167900
H	-2.55310800	-0.08584800	-2.44402000
H	-4.27151800	-0.00412900	-1.98436000

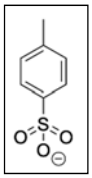
Zero-point correction= 0.326595 (Hartree/Particle)
Thermal correction to Energy= 0.342659
Thermal correction to Enthalpy= 0.343603
Thermal correction to Gibbs Free Energy= 0.284170
Sum of electronic and zero-point Energies= -864.423613
Sum of electronic and thermal Energies= -864.407549
Sum of electronic and thermal Enthalpies= -864.406605
Sum of electronic and thermal Free Energies= -864.466039

Single point energy: -864.750208299
Total free energy: -864.466038299

Number of imaginary frequencies: 0

$^{-}$OTs





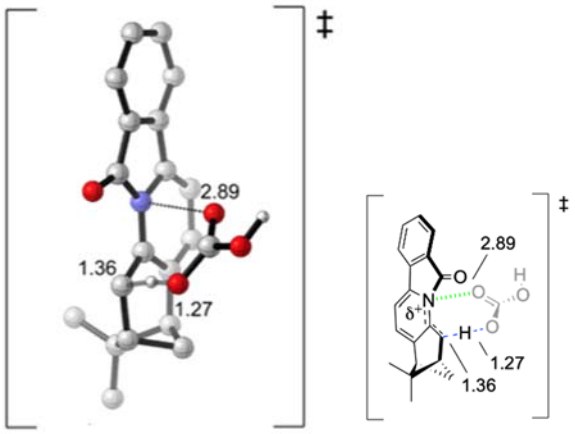
C	1.93358500	-1.20057900	-0.00250900
C	2.65441400	0.00442200	0.01233000
C	1.93333700	1.20632400	-0.00290700
C	0.53699600	1.20978100	-0.03021800
C	-0.16443700	0.00266700	-0.04203800
C	0.53974800	-1.20566100	-0.03008500
H	2.47373100	-2.14524100	0.00383600
H	2.47158100	2.15177300	0.00328800
H	-0.01166900	2.14646200	-0.05485300
H	-0.00752600	-2.14326900	-0.05537400
S	-1.97373000	-0.00084900	0.00579600
O	-2.32350500	-0.04771200	1.45653000
O	-2.37890800	1.27061200	-0.66092500
C	4.16401700	-0.00324000	0.01722200
H	4.56040300	-0.28798800	-0.96674500
H	4.56982200	0.98334100	0.26432600
H	4.55812800	-0.72622200	0.74139900
O	-2.37518100	-1.22884400	-0.74052600

Zero-point correction= 0.131292 (Hartree/Particle)
Thermal correction to Energy= 0.141209
Thermal correction to Enthalpy= 0.142154
Thermal correction to Gibbs Free Energy= 0.094920
Sum of electronic and zero-point Energies= -894.808888
Sum of electronic and thermal Energies= -894.798970
Sum of electronic and thermal Enthalpies= -894.798026
Sum of electronic and thermal Free Energies= -894.845259

Single point energy: -894.940179852
Total free energy: -894.845259852

Number of imaginary frequencies: 0

TS2b



C	-1.44187800	0.20405900	1.14797900
O	-1.07564000	0.93581100	2.04119300
C	-2.79640300	-0.21616900	0.75823700
C	-4.01949300	0.14191200	1.31601000
C	-2.70550800	-1.10877800	-0.32035500
C	-5.17313000	-0.41629200	0.75886900
C	-3.85370200	-1.66779100	-0.87651800
C	-5.08691700	-1.30829000	-0.32231900
C	-1.29599000	-1.26409900	-0.66223300
C	-0.66901500	-1.96840900	-1.64458500
N	-0.55660800	-0.48670100	0.23171100
C	0.74726700	-1.88058400	-1.74672400
C	0.80171100	-0.32353500	0.13642400
C	1.46879300	-1.07545600	-0.90245200
C	1.56867400	0.54760000	0.95582000
C	2.96609900	-0.92107500	-0.93225400
C	3.07317200	0.45305500	0.68479400
C	3.55338600	-1.04122900	0.53331000
C	3.28069700	0.60463900	-0.84932200
H	-4.06878100	0.83276200	2.15215400
H	-6.14707500	-0.15890700	1.16412700
H	-3.79595000	-2.35858500	-1.71198400
H	-5.99799200	-1.72921500	-0.73777300
H	-1.24787300	-2.57697500	-2.32966200
H	1.26328800	-2.46144900	-2.50579800
H	1.24405500	0.64790800	1.98914500
H	1.21952100	1.79429100	0.52620200
H	3.42203300	-1.52548900	-1.72195900
H	3.63914100	1.10433100	1.35779500
O	1.03739000	3.00105200	0.17049500
C	0.02212300	3.04926200	-0.62517500
O	-0.69594100	2.12263300	-1.00990400
O	-0.21616500	4.33013900	-1.05214800
H	-0.99143900	4.27012800	-1.64037700

H	2.59718300	1.28198500	-1.37053100
H	4.30681600	0.83727000	-1.13694900
C	2.98755400	-2.10740000	1.47080600
H	3.25328000	-3.10963000	1.11034100
H	1.89939200	-2.07031400	1.56910200
H	3.41358500	-1.99123600	2.47553500
C	5.08215200	-1.17414800	0.52026900
H	5.37418700	-2.18139900	0.19640100
H	5.47953400	-1.02164800	1.53190600
H	5.57863800	-0.45761700	-0.14021800

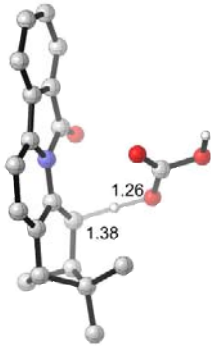
Zero-point correction= 0.348519 (Hartree/Particle)
Thermal correction to Energy= 0.369391
Thermal correction to Enthalpy= 0.370335
Thermal correction to Gibbs Free Energy= 0.298212
Sum of electronic and zero-point Energies= -1128.928226
Sum of electronic and thermal Energies= -1128.907354
Sum of electronic and thermal Enthalpies= -1128.906410
Sum of electronic and thermal Free Energies= -1128.978533

Single point energy: -1129.2767451
Total free energy: -1128.9785331

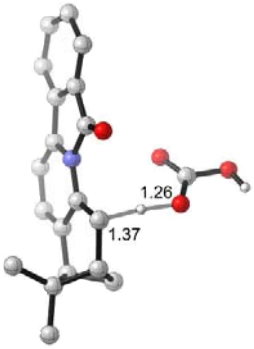
Number of imaginary frequencies: 1
Frequencies -- -1454.8392
Red. masses -- 1.1677
Frc consts -- 1.4562
IR Inten -- 11090.9759

TS2b alternative conformations

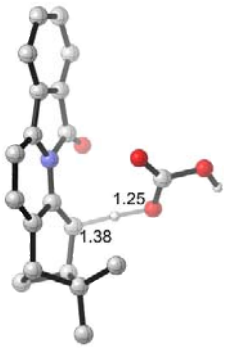
Thermal correction to Gibbs Free Energy= 0.299894 (Hartree/Particle)



Single point energy: -1129.27787337
Total free energy: -1128.97797938
ΔG (relative to lowest energy conformer): 0.3 kcal/mol

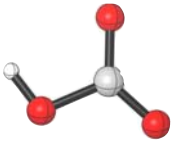


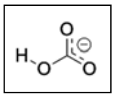
Thermal correction to Gibbs Free Energy= 0.298347 (Hartree/Particle)
Single point energy: -1129.2760669
Total free energy: -1128.9777199
ΔG: 0.5 kcal/mol



Thermal correction to Gibbs Free Energy= 0.299873 (Hartree/Particle)
Single point energy: -1129.27721464
Total free energy: -1128.97734164
ΔG: 0.7 kcal/mol

HCO_3^-



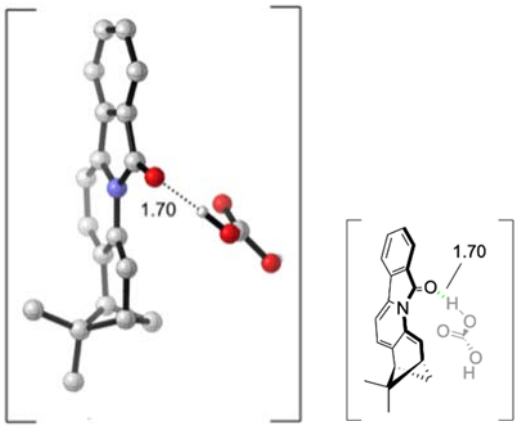


C	0.14740900	0.06222800	0.00004700
O	1.19921300	-0.60448400	-0.00004500
O	-0.04828700	1.30083300	0.00001100
O	-1.04176800	-0.73354300	0.00006700
H	-1.75771700	-0.07581600	-0.00054000

Zero-point correction= 0.026197 (Hartree/Particle)
Thermal correction to Energy= 0.029718
Thermal correction to Enthalpy= 0.030662
Thermal correction to Gibbs Free Energy= 0.000425
Sum of electronic and zero-point Energies= -264.494550
Sum of electronic and thermal Energies= -264.491029
Sum of electronic and thermal Enthalpies= -264.490085
Sum of electronic and thermal Free Energies= -264.520322
Single point energy: -264.520746874
Total free energy: -264.520321874

Number of imaginary frequencies: 0

Complex-2b



C	-1.53407300	0.42830700	0.95883300
O	-1.19012200	1.35643800	1.71111000
C	-2.89212000	-0.02641800	0.64241500
C	-4.11757000	0.44270600	1.11340000
C	-2.80997300	-1.07594400	-0.29199300
C	-5.27538100	-0.16842500	0.63196500
C	-3.97061100	-1.68396800	-0.77617600
C	-5.19845700	-1.21965600	-0.30114900
C	-1.40448700	-1.29172800	-0.58244700
C	-0.76683100	-2.09301900	-1.46923900
N	-0.67567000	-0.38935900	0.23524700
C	0.66433400	-2.02110900	-1.59939300
C	0.73739300	-0.34383400	0.20458600
C	1.38685100	-1.17437100	-0.81751700
C	1.53444400	0.35131600	1.05635900
C	2.88480700	-1.03129700	-0.86240300
C	3.02100100	0.28921100	0.79928200
C	3.48794700	-1.21082800	0.59212400
C	3.23400700	0.48462600	-0.73498000
H	-4.16074200	1.25724000	1.83041400
H	-6.24835200	0.16821100	0.97802100
H	-3.92081400	-2.49341700	-1.49850300
H	-6.11546400	-1.67852100	-0.66023100
H	-1.34730900	-2.76708600	-2.09004500
H	1.16347900	-2.64868000	-2.33169100
H	1.13965500	0.92628500	1.88070600
H	-0.23990800	2.57617300	1.00375800
H	3.32583000	-1.61772200	-1.67432200
H	3.59019900	0.90778500	1.49842400
O	0.35334000	3.26607200	0.59480300
C	0.37526200	3.06033600	-0.71551600
O	-0.31293400	2.27360700	-1.33971600
O	1.29018900	3.87680200	-1.27406100
H	1.26476100	3.70790700	-2.23535000

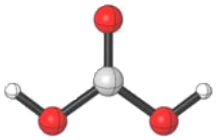
H	2.56948400	1.19496200	-1.23514800
H	4.26716700	0.69920600	-1.01089000
C	2.91749600	-2.30643700	1.49151800
H	3.18720300	-3.29439400	1.09674300
H	1.82968800	-2.26809000	1.58233300
H	3.34052000	-2.22575700	2.50101900
C	5.01475000	-1.35597900	0.56931000
H	5.29359600	-2.35067600	0.19854900
H	5.41491400	-1.25623400	1.58634900
H	5.51928100	-0.61597700	-0.05782600

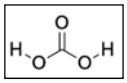
Zero-point correction= 0.354004 (Hartree/Particle)
Thermal correction to Energy= 0.375203
Thermal correction to Enthalpy= 0.376148
Thermal correction to Gibbs Free Energy= 0.303617
Sum of electronic and zero-point Energies= -1128.944450
Sum of electronic and thermal Energies= -1128.923251
Sum of electronic and thermal Enthalpies= -1128.922307
Sum of electronic and thermal Free Energies= -1128.994837

Single point energy: -1129.29845416
Total free energy: -1128.99483716

Number of imaginary frequencies: 0

H_2CO_3





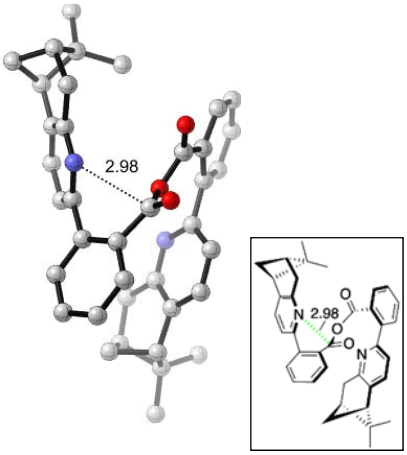
O	1.08628900	-0.68312400	-0.00002900
H	1.86609700	-0.09493400	-0.00002900
C	0.00000000	0.10107500	-0.00009000
O	-1.08628800	-0.68312600	0.00006900
H	-1.86609500	-0.09493500	0.00015700
O	-0.00000100	1.31417700	0.00001200

Zero-point correction= 0.039122 (Hartree/Particle)
Thermal correction to Energy= 0.042862
Thermal correction to Enthalpy= 0.043806
Thermal correction to Gibbs Free Energy= 0.013206
Sum of electronic and zero-point Energies= -264.966649
Sum of electronic and thermal Energies= -264.962909
Sum of electronic and thermal Enthalpies= -264.961965
Sum of electronic and thermal Free Energies= -264.992565

Single point energy: -265.005771132
Total free energy: -264.992565132

Number of imaginary frequencies: 0

Anhydride intermediate



C	-0.13606400	-1.17922700	2.49518200
O	-0.33962700	-1.26989800	3.68138000
C	0.70670900	-2.11347600	1.69950800
C	1.79954800	-2.66740000	2.38115900
C	0.50495600	-2.39756800	0.32973000
C	2.71634800	-3.47856500	1.71672500
C	1.43602200	-3.22034000	-0.31965000
C	2.53361100	-3.75101200	0.35978700
C	-0.68918900	-1.91769000	-0.41290500
C	-0.57658500	-1.39691900	-1.70615200
N	-1.87524000	-2.01851000	0.22482800
C	-1.73473700	-0.98720100	-2.37035600
C	-2.97507500	-1.61493500	-0.41191200
C	-2.96373900	-1.10243600	-1.72913900
C	-4.30508100	-1.67958500	0.32004200
C	-4.29975800	-0.73875100	-2.32378100
C	-5.45311100	-1.22253800	-0.59839200
C	-5.12136500	0.14361300	-1.30255600
C	-4.38742900	1.22661000	-0.51385600
C	-6.35847900	0.77417300	-1.95642300
C	-5.28165500	-1.90487400	-1.98457400
O	-0.51577400	-0.08561700	1.73853100
C	-1.46277600	0.82494800	2.15617900
O	-2.36342400	0.53574900	2.90978900
C	-1.30439300	2.14523800	1.48415400
C	-2.41917000	2.99662700	1.59529600
C	-0.19485900	2.54398600	0.69727600
C	-2.47246600	4.20986800	0.92083100
C	-0.28412200	3.76043100	0.00144500
C	1.09733300	1.80358600	0.57043000
C	-1.40215800	4.58507400	0.10462600
C	1.86278400	1.46224700	1.69114000
N	1.52205100	1.57600400	-0.68779700
C	3.09327800	0.83468700	1.50238300

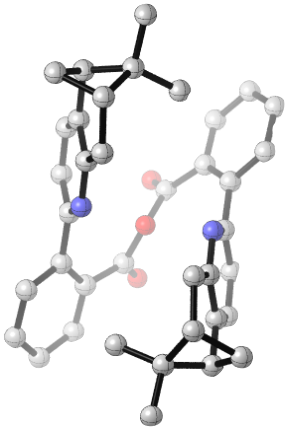
C	2.70600300	0.97871700	-0.86161200
C	3.53366400	0.57606600	0.20627900
C	3.20483600	0.75592100	-2.28003700
C	4.83505400	-0.08821400	-0.16117700
C	4.58191200	0.06718200	-2.27122800
C	5.57310600	0.76490400	-1.27019000
C	4.52359500	-1.12874000	-1.28221400
C	5.57099700	2.29061200	-1.15785800
C	7.02199200	0.30071900	-1.47509100
H	1.93447900	-2.43073800	3.43174100
H	3.56628800	-3.89072300	2.25239400
H	1.28092200	-3.46691200	-1.36587400
H	3.23899000	-4.38408000	-0.17098000
H	0.39737100	-1.30106100	-2.17523400
H	-1.67800200	-0.57786400	-3.37608800
H	-4.24171600	-1.05659900	1.22230000
H	-4.48225100	-2.70766700	0.66232300
H	-4.21734100	-0.38784700	-3.35738000
H	-6.42229500	-1.30148100	-0.09398600
H	-5.03874500	1.63665400	0.26839400
H	-3.47719300	0.86852300	-0.03058700
H	-4.10067200	2.05493000	-1.17430000
H	-7.01952200	1.19128100	-1.18574500
H	-6.06084400	1.59568000	-2.62052500
H	-6.94712000	0.06669000	-2.54799000
H	-4.86516700	-2.91815400	-1.99703800
H	-6.18961300	-1.88557700	-2.59004200
H	-3.25779600	2.66943700	2.19969900
H	-3.34559100	4.84831100	1.01677900
H	0.55588400	4.06363700	-0.61577500
H	-1.43270300	5.52255800	-0.44370800
H	1.49354500	1.67714700	2.68903200
H	3.70590600	0.55309800	2.35535900
H	3.24599400	1.72122800	-2.80173000
H	2.47988800	0.13721800	-2.82659300
H	5.41015300	-0.39964300	0.71657600
H	4.94432100	-0.11220300	-3.28938200
H	3.57267600	-1.66234800	-1.20272300
H	5.32785100	-1.85256500	-1.42635100
H	5.98212500	2.73729400	-2.07234500
H	4.57700100	2.71662300	-0.99911300
H	6.20345000	2.61057900	-0.31948600
H	7.43571700	0.74864900	-2.38781100
H	7.64769800	0.62205700	-0.63264500
H	7.12202100	-0.78488000	-1.56640700

Zero-point correction= 0.654790 (Hartree/Particle)
Thermal correction to Energy= 0.690528

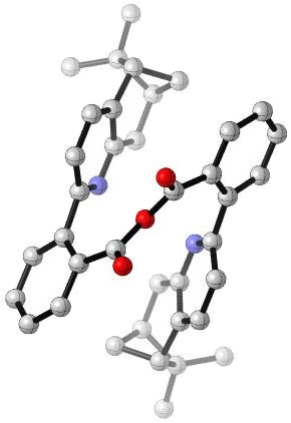
Thermal correction to Enthalpy= 0.691472
Thermal correction to Gibbs Free Energy= 0.585613
Sum of electronic and zero-point Energies= -1804.386831
Sum of electronic and thermal Energies= -1804.351093
Sum of electronic and thermal Enthalpies= -1804.350149
Sum of electronic and thermal Free Energies= -1804.456008

Single point energy: -1805.04162086
Total free energy: -1804.45600786
Number of imaginary frequencies: 0

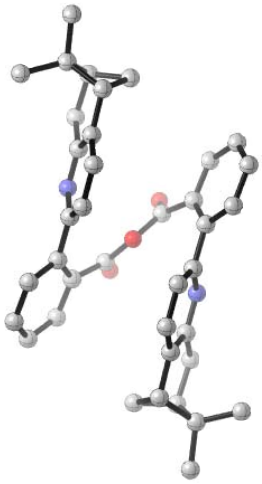
Anhydride intermediate alternative conformations



Thermal correction to Gibbs Free Energy= 0.588524 (Hartree/Particle)
Single point energy: -1805.04376414
Total free energy: -1804.45524014
ΔG (relative to lowest energy conformer): 0.5 kcal/mol



Thermal correction to Gibbs Free Energy= 0.587995 (Hartree/Particle)
Single point energy: -1805.04268603
Total free energy: -1804.45469103
ΔG: 0.8 kcal/mol



Thermal correction to Gibbs Free Energy= 0.587094 (Hartree/Particle)
Single point energy: -1805.04170734
Total free energy: -1804.45461334
ΔG: 0.9 kcal/mol

X-Ray data

Table 1 Crystal data and structure refinement for 2 (CCDC n° 2036677).

Empirical formula	$C_{19}H_{19}NO_2$
Formula weight	293.35
Temperature/K	250(2)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	25.3513(5)
b/Å	13.4380(7)
c/Å	9.4134(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3206.9(4)
Z	8
ρ_{calc}g/cm^3	1.215
μ/mm^{-1}	0.079
F(000)	1248.0
Crystal size/mm^3	0.35 × 0.35 × 0.13
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.214 to 53.74
Index ranges	$-32 \leq h \leq 32$, $-17 \leq k \leq 16$, $-11 \leq l \leq 11$
Reflections collected	48181
Independent reflections	6844 [R_{int} = 0.1844, R_{sigma} = 0.0780]
Data/restraints/parameters	6844/0/405
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0720, wR_2 = 0.1638
Final R indexes [all data]	R_1 = 0.1163, wR_2 = 0.2001
Largest diff. peak/hole / e Å^{-3}	0.29/-0.33
Flack parameter	2.2(10)

Table 2. Crystal data and structure refinement for 3 (CCDC n° 2036678).

Empirical formula	$C_{19}H_{17}NO$
Formula weight	275.33
Temperature/K	250(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.0872(8)
b/Å	12.3506(16)
c/Å	16.599(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1452.9(3)
Z	4
ρ_{calc}g/cm^3	1.259
μ/mm^{-1}	0.077
F(000)	584.0
Crystal size/mm^3	0.21 × 0.1 × 0.034
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.11 to 53.89
Index ranges	$-9 \leq h \leq 8$, $-15 \leq k \leq 15$, $-21 \leq l \leq 20$
Reflections collected	20659
Independent reflections	3105 [R_{int} = 0.1351, R_{sigma} = 0.0797]
Data/restraints/parameters	3105/0/193
Goodness-of-fit on F^2	0.964
Final R indexes [I>=2σ (I)]	R_1 = 0.0471, wR_2 = 0.0857
Final R indexes [all data]	R_1 = 0.1384, wR_2 = 0.1140
Largest diff. peak/hole / e Å^{-3}	0.15/-0.14
Flack parameter	-0.2(10)

Table 3. Crystal data and structure refinement for 6 (CCDC n° 2036679).

Empirical formula	$C_{13}H_{11}NO_2$
Formula weight	213.23
Temperature/K	250(2)
Crystal system	orthorhombic
Space group	$Pna2_1$
a/Å	13.0488(6)
b/Å	7.7427(5)
c/Å	10.6551(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1076.52(10)
Z	4
ρ_{calc}g/cm^3	1.316
μ/mm^{-1}	0.090
F(000)	448.0
Crystal size/mm^3	0.37 × 0.29 × 0.21
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.118 to 52.758
Index ranges	$-15 \leq h \leq 16$, $-9 \leq k \leq 9$, $-13 \leq l \leq 13$
Reflections collected	12251
Independent reflections	2163 [R_{int} = 0.0297, R_{sigma} = 0.0198]
Data/restraints/parameters	2163/1/150
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0685
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.0732
Largest diff. peak/hole / e Å^{-3}	0.10/-0.11
Flack parameter	0.4(3)

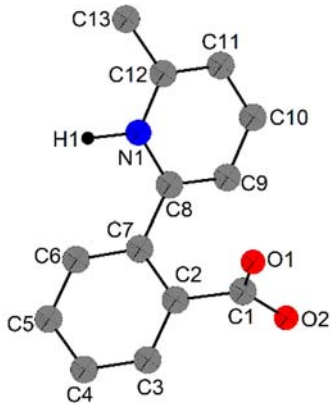


*Figure S50. Molecular structure of **6** determined by single-crystal X-Ray diffraction with ellipsoids at 50% probability. The H atoms attached to C atoms were omitted for clarity.*

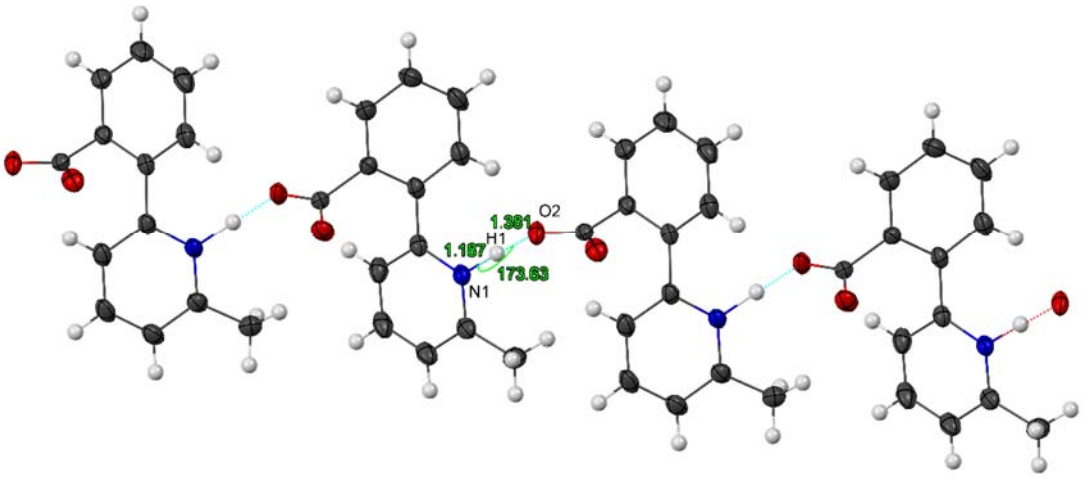


*Figure S51. Depiction of the H-bond motif in the crystal of **6** with N1-H1-O1 angle, H1···O1 and N1-H1 distances shown in green.*

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