Supporting Information

Thiamine hydrochloride as a recyclable organocatalyst for the synthesis of bis(indolyl)methanes, tris(indolyl)methanes, 3,3-di(indol-3-yl)indolin-2-ones and biscoumarins

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General Information

Reagents and all solvents were analytically pure grade and were used without further purification. All chemicals were purchased from Sigma-Aldrich, Alfa Aesar and Avra Synthesis, Pvt. Ltd. India and used as received. Melting points were recorded on a Fischer – John's apparatus and are uncorrected. ^{1}H NMR spectra was recorded on Bruker 300 MHz spectrometer. ^{13}C NMR spectra were recorded on Bruker 75 MHz spectrometer. ^{1}H NMR chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane (with the $CHCl_3$ peak around 7.26 ppm used as standard). ^{13}C NMR chemical shifts are expressed in parts per million (δ) downfield from tetramethylsilane (with the central peak of $CHCl_3$ around 77.2 ppm used as standard). All ^{13}C spectra were measured with complete proton decoupling. NMR coupling constants (*J*) are reported in Hertz (Hz), and splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. Elemental analysis was performed on a PerkinElmer 2400 elemental analyser. Melting points were recorded using apparatus manufactured by GUNA enterprises, India in the open capillary tube and are uncorrected.

General procedure for the synthesis of bis(indolyl)methanes:

Method A: A mixture of aldehyde (0.25 mmol), indole (0.5 mmol) and VB_1 (1 mg) in 1 mL water were taken in a 5 mL round-bottomed flask and the mixture was stirred for appropriate time at room temperature. After completion (monitored by TLC using a 3:7 mixture of EtOAc/n-hexane), 2 mL water was added and extracted with EtOAc (2 x 5 mL) and the combined organic layers were dried over anhyd. Na_2SO_4, and the solvent was evaporated under vacuum. The crude product was recrystallized from EtOH to get the pure product.

Method B: A mixture of aldehyde (0.25 mmol), indole (0.5 mmol), and VB_1 (1 mg) was stirred in a 5 mL round-bottomed flask at room temperature under solvent-free conditions for the appropriate time. After completion (monitored by TLC using a 3:7 mixture of EtOAc/n-hexane), EtOAc (2 x 3 mL) was added to the reaction mixture, triturated and filtered. The filtrate was concentrated to get the crude product which was recrystallized from EtOH to get the pure product. The catalyst was collected from the residue and washed with EtOAc (5 mL), dried and used for the next cycle.

Method C: A mixture of aldehyde (0.25 mmol), indole (0.5 mmol), and VB_1 (1 mg) in a agate mortar were grinded without solvent at room temperature for 20-30 min. After completion of the reaction (monitored by TLC using a 3:7 mixture of EtOAc/n-hexane), water was added and extracted with EtOAc (2 x 5 mL), dried over anhyd. Na_2SO_4, and the solvent was evaporated under vacuum. The crude product was recrystallized from EtOH to get the pure product.

Analytical Data for Products

Characterization data of bis(indolyl)methane Products

1. 3,3'-(Phenylmethylene)bis(1H-indole) (3a)[1] Yield 96 %, 77.5 mg; pale pink solid; mp 91-93 ^oC; ^1H NMR (300 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.40 – 7.33 (m, 6H), 7.30 – 7.14 (m, 5H), 7.00 (t, J = 7.5 Hz, 2H), 6.65 (d, J = 1.5 Hz, 2H), 5.88 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 136.7, 128.8, 128.4, 127.1, 126.3, 123.8, 122.0, 120.0, 119.6, 119.3, 111.3, 40.3.

2. *3,3'-(4-Nitrophenyl)methylene)bis(1H(indole) (3b)[1]* Yield 86 %, 79.2 mg; yellow solid; mp 220-222 ^oC; ^{1}HNMR (300 MHz, $CDCl_3$+DMSO-d_6) δ 10.23 (br s, 2H), 8.11 (d, J = 8.7 Hz, 2H), 7.53 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 7.9 Hz, 2H), 7.10 (t, J = 7.6 Hz, 2H), 6.93 (t, J = 7.5 Hz, 2H), 6.72 (d, J = 2.0 Hz, 2H), 5.97 (s, 1H). ^{13}C NMR (75 MHz,

DMSO-d_6) δ 153.6, 146.2, 137.1, 129.9, 126.8, 124.4, 123.9, 121.60, 119.4, 118.9, 117.2, 112.1, 40.0.

3. ***3,3'-(4-Chlorophenyl)methylene)bis(1H-indole) (3c)***[1] Yield 90 %, 80.5 mg; white solid; mp 78-80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (br s, 2H), 7.38 (d, *J* = 8.7 Hz, 4H), 7.29 – 7.23 (m, 4H), 7.21 – 7.15 (m, 2H), 7.02 (dd, *J* = 11.1, 4.3 Hz, 2H), 6.65 (d, *J* = 1.5 Hz, 2H), 5.86 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.6, 136.7, 131.8, 130.1, 128.4, 126.9, 123.6, 122.1, 119.8, 119.4, 119.2, 111.2, 39.6.

4. ***3,3'-(4-Bromophenyl)methylene)bis(1H-indole) (3d)***[1] Yield 84 %, 84.6 mg; pink solid; mp 112-114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 2.0 Hz, 2H), 7.37 (dd, *J* = 12.0, 5.3 Hz, 6H), 7.22 – 7.15 (m, 4H), 7.00 (dd, *J* = 11.3, 4.5 Hz, 2H), 6.62 (d, *J* = 1.5 Hz, 2H), 5.84 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1, 136.7, 131.4, 130.6, 126.9, 123.8, 122.2, 120.0, 119.9, 119.4, 119.0, 111.3, 111.2, 39.7.

5. ***3,3'-(4-Methoxyphenyl)methylene)bis(1H-indole) (3e)***[1] Yield 86 %, 76.1 mg; orange solid; mp 191-192 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.40 – 7.34 (dd, *J* = 10.7, 8.1 Hz, 4H), 7.26 – 7.24 (m, 1H), 7.19 – 7.13 (m, 2H), 7.02 – 6.97 (m, 3H), 6.83 – 6.80 (m, 2H), 6.65 (d, *J* = 1.4 Hz, 2H), 5.84 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.9, 136.7, 136.2, 129.6, 127.1, 123.5, 121.9, 120.0, 112.0, 119.2, 113.6, 111.0, 55.2, 39.3.

6. ***3,3'-(3,4,5-Trimethoxyphenyl)methylene)bis(1H-indole) (3f)***[2] Yield 89 %, 91.8 mg; pale pink solid; mp 202-204 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.39 (s, 2H), 7.41 – 7.37 (m, 4H), 7.12 (t, *J* = 7.6 Hz, 2H), 6.96 (t, *J* = 7.4 Hz, 2H), 6.72 (d, *J* = 1.7 Hz, 2H), 6.61 (s, 2H), 5.81 (s, 1H), 3.81 (s, 3H), 3.71 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.5, 140.7, 136.6, 135.7, 126.7, 123.5, 120.8, 119.1, 118,1 118.1, 111.4, 105.9, 60.0, 55.8, 40.0.

7. ***3,3'-(o-Tolylmethylene)bis(1H-indole) (3g)*** Yield 89 %, 75.1 mg; white colour solid; mp 161-163 °C ; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (d, *J* = 18.3 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 6.9 Hz, 1H), 7.13 – 7.08 (m, 4H), 7.05 – 6.97 (m, 1H), 6.93 (t, *J* = 7.4 Hz, 2H), 6.60 (d, *J* = 1.7 Hz, 2H), 6.00 (s, 1H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.0, 136.7, 136.0, 130.2, 127.20, 123.9, 121.9, 119.8, 119.2, 119.1, 111.0, 36.2, 19.5; Anal. Calcd for $C_{24}H_{20}N_2$: C, 85.68; H, 5.99; N, 8.33. Found: C, 85.65; H, 5.93; N, 8.29.

8. 2-(Di(1H-indol-3-yl)methyl)phenol (3h)[5] Yield 87 %, 73.7 mg; orange solid; mp > 300 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.41 – 7.35 (m, 4H), 7.19 (dt, *J* = 12.8, 6.4 Hz, 4H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.89 – 6,84 (m, 2H), 6.78 – 6.75 (m, 2H), 6.00 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.6, 136.0, 130.1, 128.8, 126.3, 125.9, 123.0, 120.0, 118.8, 117.7, 117.4, 114.5, 110.4, 31.6.

9. ***4-(di(1H-indol-3-yl)methyl)benzonitrile (3i)[4]*** Yield 85 %, 73.8 mg; pale pink solid; mp 201-203 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (br s, 2H), 7.97 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.35 (dd, *J* = 15.0, 8.1 Hz, 4H), 7.19 (t, *J* = 7.5 Hz, 2H), 7.02 (t, *J* = 7.5 Hz, 2H), 6.65 (d, *J* = 2.1 Hz, 2H), 5.93 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 136.7, 132.4, 129.4, 126.7, 123.7, 122.3, 119.9, 119.6, 119.2, 118.3, 111.3, 110.1, 40.4.

10. ***3,3'-(2-nitrophenyl)methylene)bis(1H-indole) (3j)[5]*** Yield 86 %, 79.2 mg; yellow colour solid; mp 136-138 °C; ^{1}H NMR (300 MHz, $CDCl_3$+ DMSO-d_6) δ 9.83 (s, 2H), 8.11 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 2H), 6.71 (d, *J* = 1.9 Hz, 2H), 5.98 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.8, 146.6, 136.7, 129.5, 126.7, 123.7, 122.4, 119.64, 119.58, 118.2, 111.3, 40.2.

11. ***3-(di(1H-indol-3-yl)methyl)-4-nitrophenol (3k)*** Yield 87 %, 83.4 mg; yellow solid; mp 110-112 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.89 (br s, 2H), 7.40 – 7.31 (m, 4H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.8 Hz, 2H), 6.83 (br s, 1H), 6.78 – 6.71 (m, 2H), 6.60 (d, J = 2.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.1, 145.5, 136.8, 133.9, 126.9, 123.8, 122.2, 119.8, 119.5, 118.8, 117.9, 117.8 115.2, 111.2, 39.8; Anal. Calcd for $C_{23}H_{17}N_3O_3$: C, 72.05; H, 4.47; N, 10.96. Found: C, 72.09; H, 4.52; N, 10.98.

12. ***3,3'-(pyridin-2-yl)methylene)bis(1H-indole) (3l)[2]*** Yield 84 %, 68.3 mg; brown solid; mp 185-187 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 5.5 Hz, 2H), 7.63 – 7.57 (m, 1H), 7.36 (dt, *J* = 6.7, 5.5 Hz, 5H), 7.19 – 7.12 (m, 4H), 7.00 (t, *J* = 7.5 Hz, 2H), 6.78 (d, *J* = 1.7 Hz, 2H), 6.07 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 148.7, 136.4, 126.7, 123.6, 122.5, 121.2, 120.9, 118.9, 118.2, 116.9, 111.4, 42.6.

13. ***3,3'-(thiophen-2-ylmethylene)bis(1H-indole) (3m)[3]*** Yield 84 %, 69.1 mg; brown solid; mp 187-189 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (br s, 2H), 7.47 (d, *J* = 7.9 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 7.20 – 7.13 (m, 3H), 7.03 (dd, *J* = 11.0, 4.0 Hz, 2H), 6.93 – 6.88 (m, 2H),

6.84 (d, J = 1.7 Hz, 2H), 6.16 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 136.9, 126.8, 125.1, 124.2, 123.7, 121.4, 119.6, 118.7, 118.6, 111.9, 35.3.

14. ***tri(1H-indol-3-yl)methane (3n)***[4] Yield 80 %, 72.4 mg; white solid; mp 163-165 °C; ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.43 (br s, 3H), 7.46 (d, J = 7.8 Hz, 3H), 7.35 (d, J = 8.1 Hz, 3H), 7.08 (app t, J = 7.5 Hz, 3H), 6.91 (app t, J = 7.5 Hz, 3H), 6.80 (d, J = 1.8 Hz, 3H), 6.12 (s, 1H). ^{13}C NMR (75 MHz DMSO-d_6) δ 137.0, 127.2, 123.7, 121.1, 119.7, 118.7, 118.4, 111.8.

15. ***3,3'-(phenylmethylene)bis(5-methoxy-1H-indole) (3o)***[4] Yield 89 %, 85.3 mg; pink solid; mp 220-222 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (br s, 2H), 7.36 – 7.28 (m, 2H), 7.25 – 7.18 (m, 5H), 6.84 – 6.78 (m, 4H), 6.66 (d, J = 1.9 Hz, 2H), 5.77 (s, 1H), 3.69 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 143.9, 131.9, 128.7, 128.2, 127.5, 126.1, 124.4, 119.3, 111.9, 111.7, 102.0, 55.9, 40.3.

16. ***3,3'-(phenylmethylene)bis(5-bromo-1H-indole) (3p)***[3] Yield 86 %, 103.4 mg; red solid; mp 243-245 °C ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (br s, 2H), 7.47 (s, 2H), 7.30 – 7.27 (m, 5H), 7.25 - 7.23 (m, 4H), 6.65 (d, J = 1.8 Hz, 2H), 5.76 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.8, 135.7, 128.8, 128.7, 126.5, 125.7, 123.9, 121.6, 118.1, 114.0, 111.4.

17. ***3,3'-(phenylmethylene)bis(2-methyl-1H-indole) (3q)***[8] Yield 82 %, 71.9 mg; pink solid; mp 252-254 °C; ^{1}H NMR (300 MHz, $CDCl_3$+DMSO-d_6) δ 9.07 (br s, 2H), 7.26 – 7.16 (m, 7H), 7.00 – 6.92 (m, 4H), 6.78 (dd, J = 11.0, 3.9 Hz, 2H), 5.98 (s, 1H), 2.07 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 135.0, 131.8, 129.1, 129.0, 128.1, 126.0, 120.6, 119.4, 119.1, 113.4, 110.0, 39.2, 12.5.

18. ***3,3'-(Phenylmethylene)bis(1-ethyl-1H-indole) (3r)***[4] Yield 90 %, 85.3 mg; white solid; mp 160-162 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 – 7.25 (m, 8H), 7.23 – 7.15 (m, 3H), 6.97 (t, J = 7.8 Hz, 2H), 6.58 (s, 2H), 5.87 (s, 1H), 4.06 (q, J = 7.2 Hz, 4H), 1.37 (t, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.4, 136.3, 128.7, 128.1, 127.6, 126.6, 125.9, 121.1, 120.2, 118.5, 118.2, 109.1, 40.8, 40.2, 15.5.

19. ***Di(1H-indol-3-yl)methane (3s)***[4] Yield 87%, 81 mg; white solid; mp 159-161 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ 8.79 (br s, 2H), 7.59 (d, J = 7.8 Hz, 2H), 7.36 – 7.30 (m, 2H), 7.13 (dd, J = 11.1, 4.0 Hz, 2H), 7.05 (dd, J = 10.9, 3.9 Hz, 2H), 6.91 (d, J = 2.0 Hz, 2H), 4.22 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ 135.9, 126.7, 121.8, 120.4, 118.1, 117.7, 114.1, 110.6, 20.5.

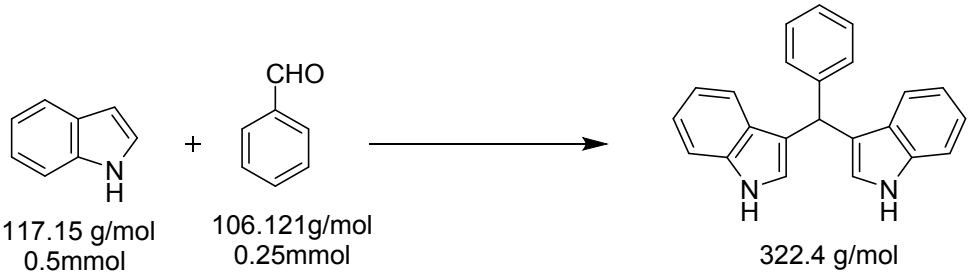
20. ***3,3'-(ethane-1,1-diyl)bis(1H-indole)(3t)***[4] Yield 78%, 101.4 mg; colourless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (br s, 2H), 7.57 (d, *J* = 7.9 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 7.5 Hz, 2H), 7.04 (t, *J* = 7.5 Hz, 2H), 6.92 (d, *J* = 1.8 Hz, 2H), 4.68 (q, *J* = 7.0 Hz, 1H), 1.81 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.6, 126.9, 121.7, 121.2, 119.7, 119.0, 111.0, 28.1, 21.7.

21. ***1,4-bis(di(1H-indol-3-yl)methyl)benzene(3u)***[6] Yield 87%, 81 mg; red solid; mp 192-193 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 4H), 7.24 – 7.20 (m, 4H), 7.19 (s, 4H), 7.13 (t, *J* = 7.2 Hz, 4H), 7.02 (dd, *J* = 10.9, 3.9 Hz, 4H), 6.13 (d, *J* = 1.5 Hz, 4H), 5.72 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.5, 136.5, 128.5, 126.9, 123.7, 121.7, 119.9, 119.3, 118.9, 111.2, 39.9.

Green chemistry matrices calculations: Green chemistry matrix has been calculated based on the following parameters.

1) E-factor or environmental factor
2) Atom economy (AE)
3) Product mass intensity (PMI)
4) Reaction mass efficiency (RME)

Green chemistry matrices calculations for the synthesis of bis(indolyl)methanes



E-factor or environmental factor: E-factor is defined as the ratio of the mass of waste per mass of the product.

E-factor = [mass of waste]/ mass of product

Where mass of waste = total mass of raw materials minus the total mass of product

$$E - factor = \frac{(117.15\ mg\ x\ 0.5) + (106.121\ mg\ x\ 0.25) - 77.5\ mg}{77.5\ mg}$$

= 0.098 (Ideal value of E-factor is considered zero)

Atom economy (AE): AE of a chemical reaction is a measure of the efficiency of that reaction with regard to how many atoms from the starting materials reside within the product. The ideal value of AE factor is 100% (i.e., all atoms from the starting materials reside in the product).

AE = MW of product ÷ Σ(MW of stoichiometric reactants) × 100

$$Atom\ economy = \frac{322.4}{117.15\ x\ 2 + 106.121}$$

= 0.947× 100

= 94.7 %

Product mass intensity (PMI): PMI is defined as the total mass used in a chemical process divided by the mass of product.

PMI = Σ(mass of stoichiometric reactants + solvent) / mass of product

$$PMI = \frac{(117.15\ mg\ x\ 0.5) + (106.121\ mg\ x\ 0.25)}{77.5\ mg}$$

= 1.098

(OR) ideal value for PMI = E-factor + 1

Hence PMI = 0.098 + 1 = 1.098

Reaction mass efficiency (RME): Reaction mass efficiency is defined as the mass of product divided by the sum of total mass of stoichiometric reactants. The value of RME varies from 0-100%. The larger number of RME is considered as better as it is the measure of "cleanness" of the reaction.

RME = mass of product /Σ(mass of stoichiometric reactants) × 100

$$RME = \frac{77.5\ mg}{(117.15\ mg\ x\ 0.5\ mg) + (106.121\ mg\ x\ 0.25)}$$

= 0.9106 × 100

= 91.0 %

General procedure for the synthesis of 3,3-di(indol-3-yl)indolin-2-one derivatives:

Method A: A mixture of isatin (0.25 mmol), indole (0.5 mmol), and VB_1 (1 mg) in 1 mL water were taken in a 5 mL round-bottomed flask and the mixture was stirred for the appropriate time at room temperature. After completion, the precipitated product was filtered, washed with water (1 mL) and dried to get the pure product. The obtained solid was found to be pure enough for further characterization.

Method B: A mixture of isatin (0.25 mmol), indole (0.5 mmol), and VB_1 (1 mg) was stirred in a 5 mL round-bottomed flask at room temperature under solvent-free conditions for the appropriate time. After completion, (monitored by TLC using a 3:7 mixture of EtOAc/n-hexane), EtOAc (2 x 3 mL) was added to the reaction mixture, triturated and filtered. The filtrate was concentrated to get the crude product. The catalyst was collected from the residue, and washed with EtOAc (5 mL), dried and used for the next cycle.

Characterization data of 3,3-di(indol-3-yl)indolin-2-one derivatives

1. ***3,3'-(cyclohexane-1,1-diyl)bis(1H-indole) (5a)***[4] Yield 75 %, 59.0 mg; white colour solid; mp 278-280 ^oC .^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (br s, 2H), 7.54 (d, J = 8.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.07 – 7.03 (m, 4H), 6.88 (app t, J = 7.4 Hz, 2H), 2.55 – 2.52 (m, 4H), 1.65 – 1.57 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 131.1, 126.5, 123.4, 121.3, 121.1, 120.9, 118.5, 110.1, 38.6, 29.6, 23.9.

2. ***1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one (5b)***[7] Yield 90 %, 81.7 mg; white colour solid; mp > 300 ^oC. ^1H NMR (300 MHz, DMSO-d_6) δ 10.97 (s, 2H), 10.61 (s, 1H), 7.34 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 7.5 Hz, 4H), 6.96-7.07 (m, 3H), 6.93 - 6.89 (m, 1H), 6.85 (d, J = 2.1 Hz, 2H), 6.80 (t, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.6, 141.3, 136.8, 134.5, 127.7, 125.6, 124.8, 124.2, 121.4, 120.8, 120.7, 118.1, 114.2, 111.5, 109.5, 52.5.

3. ***5,5''-dimethoxy-[3,3':3',3''-terindolin]-2'-one (5c)*** Yield 88 %, 93.3 mg; white colour solid; mp 280-282 ^oC. ^1H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) 9.99 (br s, 1H), 9.90 (br s, 2H), 7.29 (d, J = 7.2 Hz, 1H), 7.23 – 7.17 (m, 3H), 7.02 – 6.89 (m, 4H), 6.78 (d, J = 1.8 Hz, 2H), 6.72 – 6.68 (m, 2H), 3.59 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.0, 152.1, 140.5, 134.0, 131.6, 126.9, 125.6, 124.6, 124.4, 120.9, 113.2, 111.2, 110.2, 108.9, 102.6, 54.7, 54.3. Anal. Calcd for $C_{26}H_{21}N_3O_3$: C, 73.74; H, 5.00; N, 9.92. Found: C, 73.69; H, 4.95; N, 9.84.

4. ***5,5''-dibromo-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one (5d)***[7] Yield 85 %, 110.6 mg; pale brown colur solid; mp 285-287 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.29 (br s, 2H), 10.80 (s, 1H), 7.41 (dd, *J* = 5.1, 3.4 Hz, 4H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.05 (dd, *J* = 12.5, 7.5 Hz, 2H), 6.97 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.5, 142.2, 137.8, 136.6, 135, 128.9, 128.4, 126.7, 126.4, 125.8, 125.2, 124.4, 124.2, 122.5, 121.9, 121.1, 119.3, 115, 114.9, 114.6, 112.6, 111.8, 110.6, 53.3.

5. ***2,2''-dimethyl-[3,3':3',3''-terindolin]-2'-one (5e)***[7] Yield 82 %, 80.3 mg; white colour solid; mp >300 °C. ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ 10.25 (br s, 2H), 10.15 (s, 1H), 7.24 – 7.16 (m, 4H), 6.97 – 6.81 (m, 5H), 6.65 (q, J = 7.5 Hz, 2H), 6.96 (d, J = 8.1 Hz, 1H), 2.16 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 179.2, 140.2, 134.9, 134.3, 134.2, 133.6, 131.1, 126.7, 119.0, 118.8, 117.2, 109.9, 109.4, 108.7, 52.0, 12.6. 12.4.

6. ***1,1''-diethyl-1H,1''H-[3,3':3',3''-terindol]-2'(1'H)-one (5f)*** Yield 86 %, 90.4 mg; white colour solid; mp 273-275 °C; ^{1}H NMR (300 MHz, $CDCl_3$ + DMSO-d_6) δ 10.36 (br s, 1H), 7.81 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 4H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 7.7 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H), 6.88 (s, 2H), 6.84 (d, *J* = 7.7 Hz, 1H), 4.11 (q, *J* = 7.3 Hz, 4H), 1.39 (t, *J* = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 178.0, 140.1, 139.2, 135.3, 134.8, 133.4, 126.2, 125.5, 123.7, 120.6, 120.0, 117.3, 112.7, 108.3, 108.1, 51.6, 28.2, 14.2, 14.7; Anal. Calcd for $C_{28}H_{25}N_3O$: C, 80.16; H, 6.01; N, 10.02. Found: C, 80.21; H, 6.14; N, 10.11.

General procedure for the synthesis of biscoumarin derivatives:

Method A: A mixture of aldehyde (0.25 mmol), 4-hydroxy coumarin (0.5 mmol), and VB_1 (1 mg) in 1 mL water were taken in a 5 mL round-bottomed flask and the mixture was stirred for the appropriate time at room temperature. After completion, the precipitated product was filtered, washed with water (1 mL) and dried to get the pure product. The obtained solid was found to be pure enough for further characterization.

Method B: A mixture of aldehyde (0.25 mmol), 4-hydoxy coumarin (0.5 mmol), and VB_1 (1 mg) were stirred in 5 mL round-bottomed flask at room temperature under solvent-free conditions for the appropriate time. After completion, (monitored by TLC using a 3:7 mixture of EtOAc/n-hexane), EtOAc (2 x 3 mL) was added to the reaction mixture, triturated and

filtered. The filtrate was concentrated to get the pure product. The catalyst was collected from the residue and washed with EtOAc (5 mL), dried and used for the next cycle.

Characteristic data of biscoumarin Products

1. ***3,3'-(Phenylmethylene)bis(4-hydroxy-2H-chromen-2-one) (7a)***[8] Yield 95 %, 98.1 mg; white colour solid; mp 230-232 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.53 (s, 1H), 11.31 (br s, 1H), 8.04 (dd, *J* = 12.9, 7.5 Hz, 2H), 7.63 (td, *J* = 8.7, 1.5 Hz, 2H), 7.43 – 7.40 (m, 4H), 7.35 – 7.21 (m, 5H), 6.11 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.70, 136.96, 132.83, 128.60, 127.99, 127.66, 127.55, 127.24, 124.88, 124.39, 116.63, 114.95, 109.10, 70.08, 35.54.

2. ***3,3'-((4-Nitrophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7b)***[8] Yield 94 %, 107.5 mg; white colour solid; mp 229-231 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.57 (s, 1H), 11.38 (br s, 1H), 8.20 (d, *J* = 8.9 Hz, 2H), 8.10 (d, *J* = 7.0 Hz, 1H), 8.01 (d, *J* = 7.9 Hz, 1H), 7.68 (app t, *J* = 7.6 Hz, 2H), 7.46 – 7.40 (m, 6H), 6.13 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 167.0, 166.4, 164.8, 152.6, 152.3, 146.9, 143.3, 133.8, 127.5, 125.1, 123.9, 116.8, 116. 6, 104.7, 104.2, 36.5.

3. ***3,3'-((4-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7c)***[3] Yield 90 %, 105.3 mg; pale pink solid; mp 250-252 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.55 (s, 1H), 11.32 (br s, 1H), 8.04 (dd, *J* = 22.3, 7.6 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 4H), 7.31 – 7.26 (m, 2H), 7.18 – 7.15 (m, 2H), 6.05 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.18, 154.35, 142.86, 132.08, 130.99, 130.05, 127.15, 126.79, 126.45, 125.34, 125.76, 112.01, 110.24, 100.60, 100.60, 88.42, 18.32.

4. ***3,3'-((4-Bromophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7d)***[8] Yield 90 %, 110.7 mg; white solid; mp 262-264 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.55 (br s, 1H), 11.36 (br, 1H), 8.03 (dd, *J* = 7.8, 8.1 Hz, 2H), 7.62 (app t, *J* = 8.4 Hz, 2H), 7.45 – 7.40 (m, 6H), 7.10 (d, *J* = 7.8 Hz, 2H), 6.02 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 166.8, 166.0, 164.4, 152.5, 152.3, 134.4, 133.0, 131.7, 128.3, 125.0, 124.4, 120.8, 116.7, 105.2, 103.6, 35.8.

5. ***3,3'-((3-Fluorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7e)*** Yield 82 %, 88.4 mg; pale pink solid; mp 184-186 ^{o}C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.60 (s, 1H), 11.31 (br s,

1H), 8.02 (dd, *J* = 11.4, 8.1 Hz, 2H), 7.44 (m, 2H), 7.44 – 7.37 (m, 4H), 7.33 – 7.28 (m, 1H), 7.03 - 6.92 (m, 3H), 6.07 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.2, 166.8, 166.0, 164.7, 161.5, 152.5, 152.2, 138.1, 133.0, 130.1, 125.00, 124.4, 122.1, 116.7, 116.3, 113.8, 105.2, 103.5, 36.1; Anal. Calcd for $C_{25}H_{15}FO_6$: C, 69.77; H, 3.51. Found: C, 69.84; H, 3.58.

6. ***3,3'-((4-Methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7f)***[8] Yield 89 %, 98.4 mg; white solid; mp 243-245 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.51 (s, 1H), 11.31 (br, 1H), 8.05 – 8.00 (br m, 2H), 7.66 – 7.60 (m, 2H), 7.41 (d, *J* = 8.1 Hz, 4H), 7.13 (d, *J* = 8.1 Hz, 1H), 6.88 – 6.83 (m, 2H), 6.05 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 166.8, 165.7, 164.5, 158.4, 132.8, 127.6, 126.9, 124.8, 124.3, 116.6, 114.0, 105.7, 104.2, 55.2, 35.5.

7. ***3,3'-(o-Tolylmethylene)bis(4-hydroxy-2H-chromen-2-one) (7g)***[8] Yield 85 %, 90.7 mg; white solid; mp 217-219 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.45 (s, 2H), 8.04 – 7.97 (m, 2H), 7.62 (t, *J* = 8.1 Hz, 2H), 7.41 - 7.32 (m, 5H), 7.22 – 7.15 (m, 3H), 6.07 (s, 1H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 166.6, 164.7, 152.3, 136.1, 133.8, 132.8, 131.8, 127.4, 127.2, 126.0, 124.8, 124.4, 116.5, 106.3, 104.8, 35.6, 21.0.

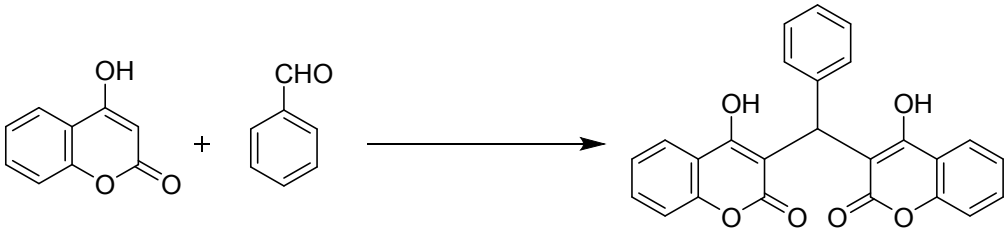
8. ***3,3'-((3,4,5-Trimethoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (7h)*** Yield 88 %, 110.6 mg; white solid; mp 219-220 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.56 (br s, 1H), 11.30 (br s, 1H), 8.07 (br m, 2H), 7.67 – 7.62 (m, 2H), 7.42 (d, *J* = 8.3 Hz, 4H), 6.42 (d, *J* = 0.8 Hz, 2H), 6.08 (s, 1H), 3.85 (s, 3H), 3.72 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 166.8, 165.6, 164.2, 153.3, 137.2, 132.9, 130.9, 124.9, 124.3, 116.7, 104.2, 60.9, 56.3, 36.2; Anal. Calcd for $C_{28}H_{22}O_9$: C, 66.93; H, 4.41. Found: C, 66.99; H, 4.52.

9. ***4-(bis(4-hydroxy-2-oxo-2H-chromen-3-yl)methyl)benzonitrile (7i)***[10] Yield 88 %, 96.2 mg; white solid; mp 239-240 °C; ^{1}H NMR (300 MHz, $CDCl_3$+ DMSO-d_6) δ 11.66 (br s, 2H), 8.07 (app d, *J* = 8.4 Hz, 2H), 7.68 – 7.61 (m, 4H), 7.43 – 7.37 (m, 6H), 6.32 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$ + DMSO-d_6) δ 169.0, 167.3, 164.7, 152.6, 148.4, 132.3, 131.9, 128.3, 124.5, 123.7, 119.6, 119.3, 116.4, 108.3, 103.4, 37.5.

10. ***3,3'-(Pyridine-2-ylmethylene)bis(4-hydroxy-2H-chromen-2-one) (7j)*** Yield 84 %, 86.8 mg; white solid; mp 209-211 °C ; ^{1}H NMR (300 MHz, $CDCl_3$+ DMSO-d_6) δ 8.43 (d, *J* = 5.3 Hz, 1H), 8.28 (br m, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.68 (br m, 1H), 7.55 – 7.49 (m, 6H), 7.38 – 7.22 (s, 3H), 6.74 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.8,

164.4, 153.2, 132.1, 124.7, 123.7, 119.8, 116.2, 101.3, 37.4. Anal. Calcd for $C_{24}H_{15}NO_6$: C, 69.73; H, 3.66; N, 3.39. Found: C, 69.76; H, 3.73; N, 3.46.

Green chemistry matrices calculations for the synthesis of biscoumarins



162.144 g/mol
0.5mmol

106.121g/mol
0.25mmol

412.4 g/mol

E-factor or environmental factor

E-factor = [mass of waste]/ mass of product

Where mass of waste = total mass of raw materials minus the total mass of product

$$E-factor = \frac{(162.144\ mg\ x\ 0.5) + (106.121\ mg\ x\ 0.25) - 98.1\ mg}{98.1\ mg}$$

= 0.0968

Atom economy (AE)

AE = MW of product ÷ Σ(MW of stoichiometric reactants) × 100

$$Atom\ economy = \frac{412.4}{162.144\ x\ 2 + 106.121}$$

= 0.958 × 100

= 95.8 %

Product mass intensity (PMI)

PMI = Σ(mass of stoichiometric reactants + solvent) / mass of product

$$PMI = \frac{(162.144\ mg\ x\ 0.5) + (106.121\ mg\ x\ 0.25)}{98.1\ mg}$$

= 1.096

Reaction mass efficiency (RME)

RME = mass of product /Σ(mass of stoichiometric reactants) × 100

$$RME = \frac{98.1\ mg}{(162.144\ mg\ x\ 0.5) + (106.121\ mg\ x\ 0.25)}$$

= 0.911 × 100

= 91.1 %

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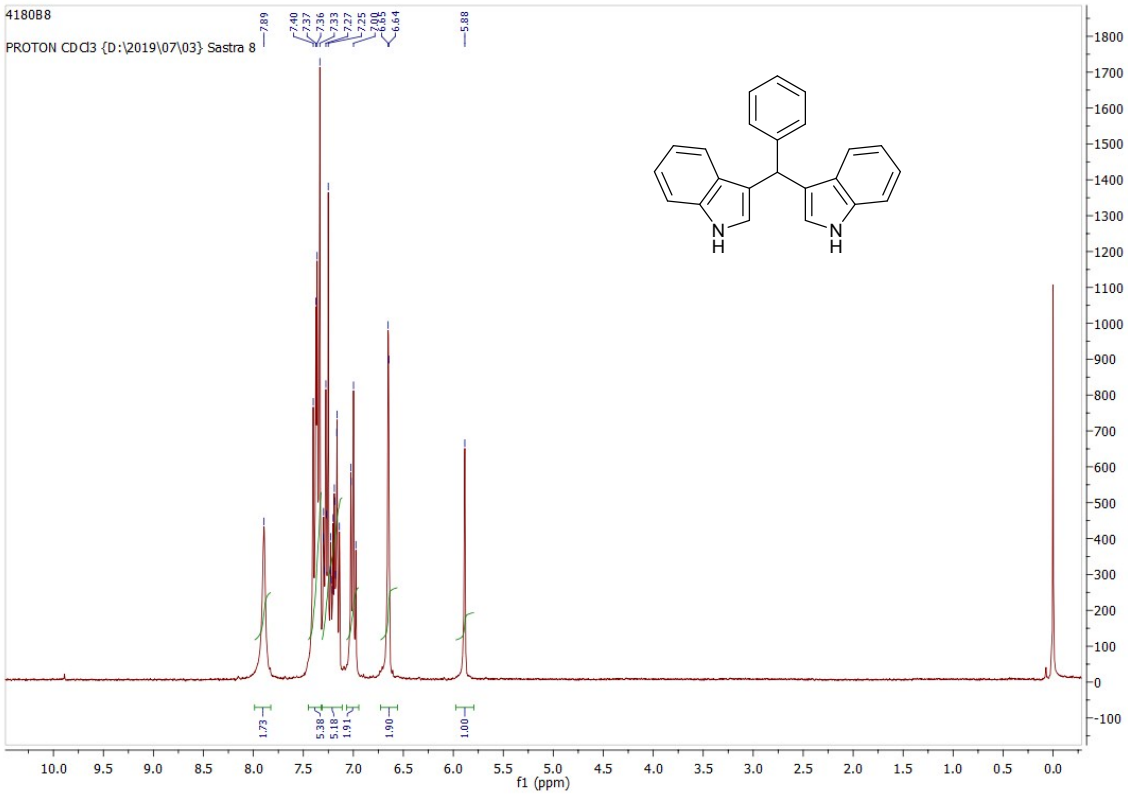
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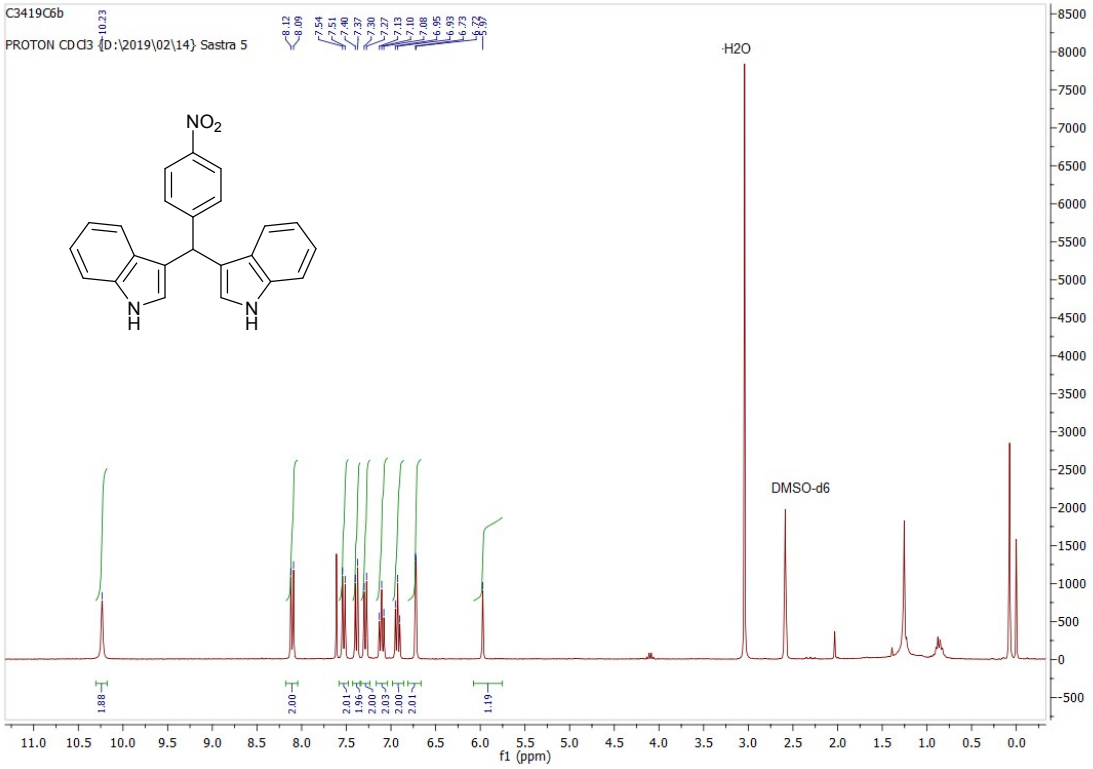
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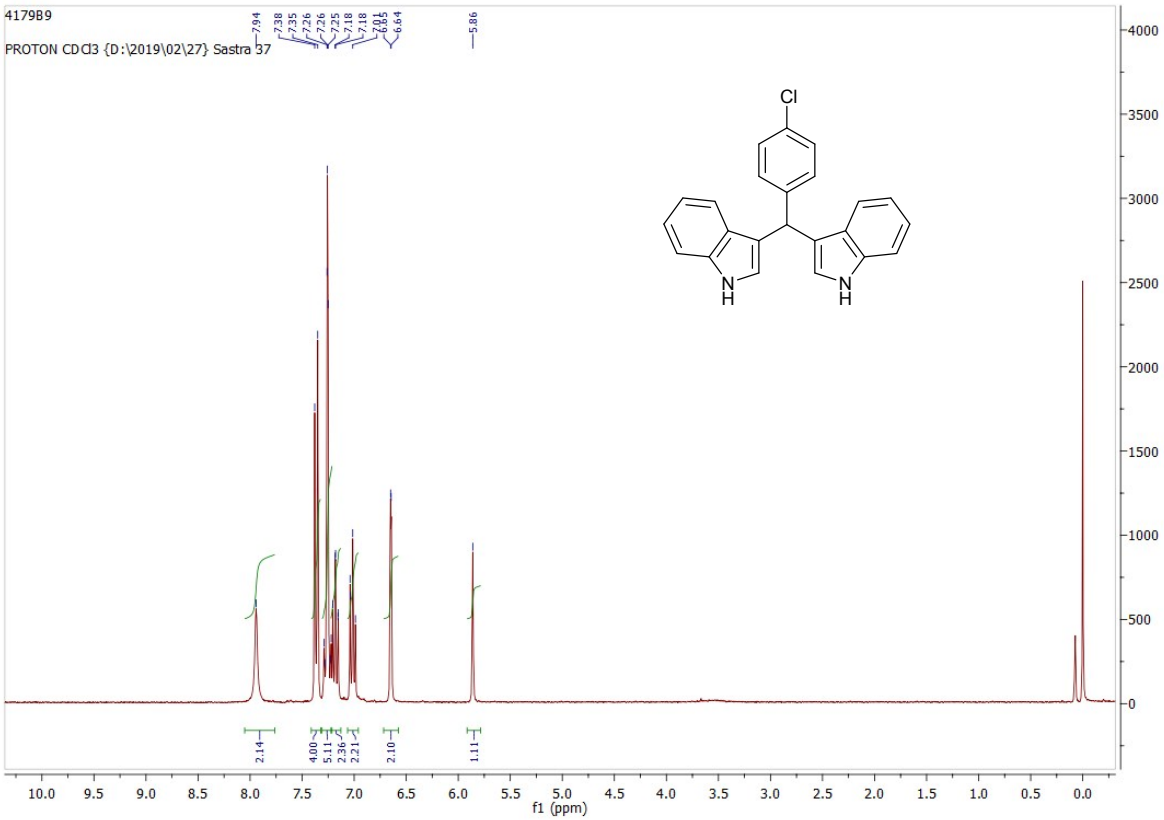
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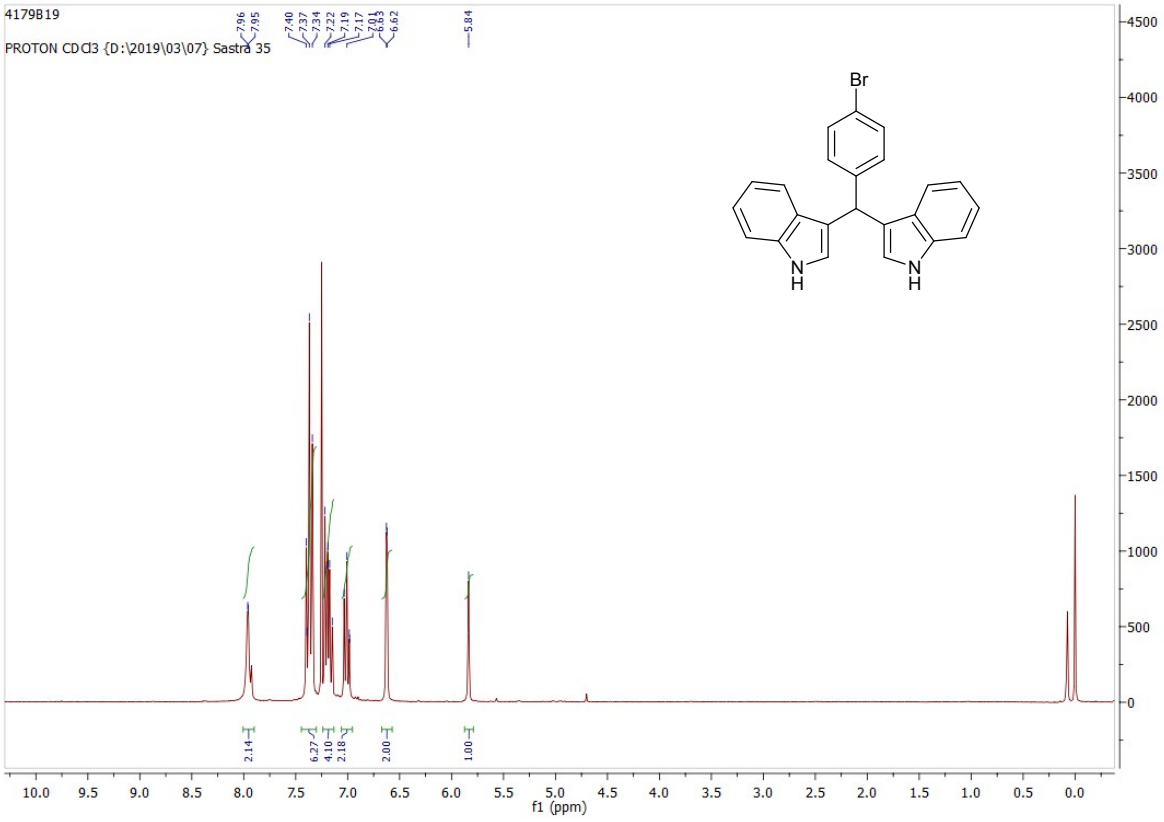
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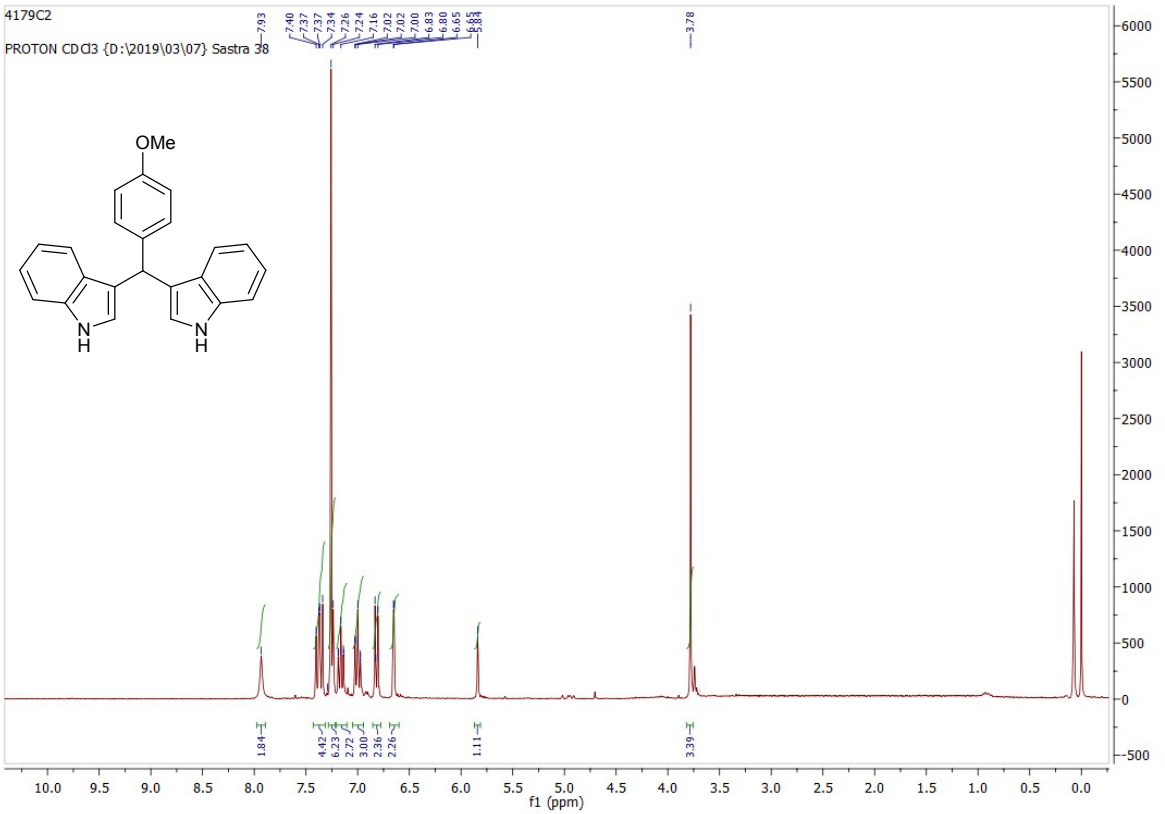
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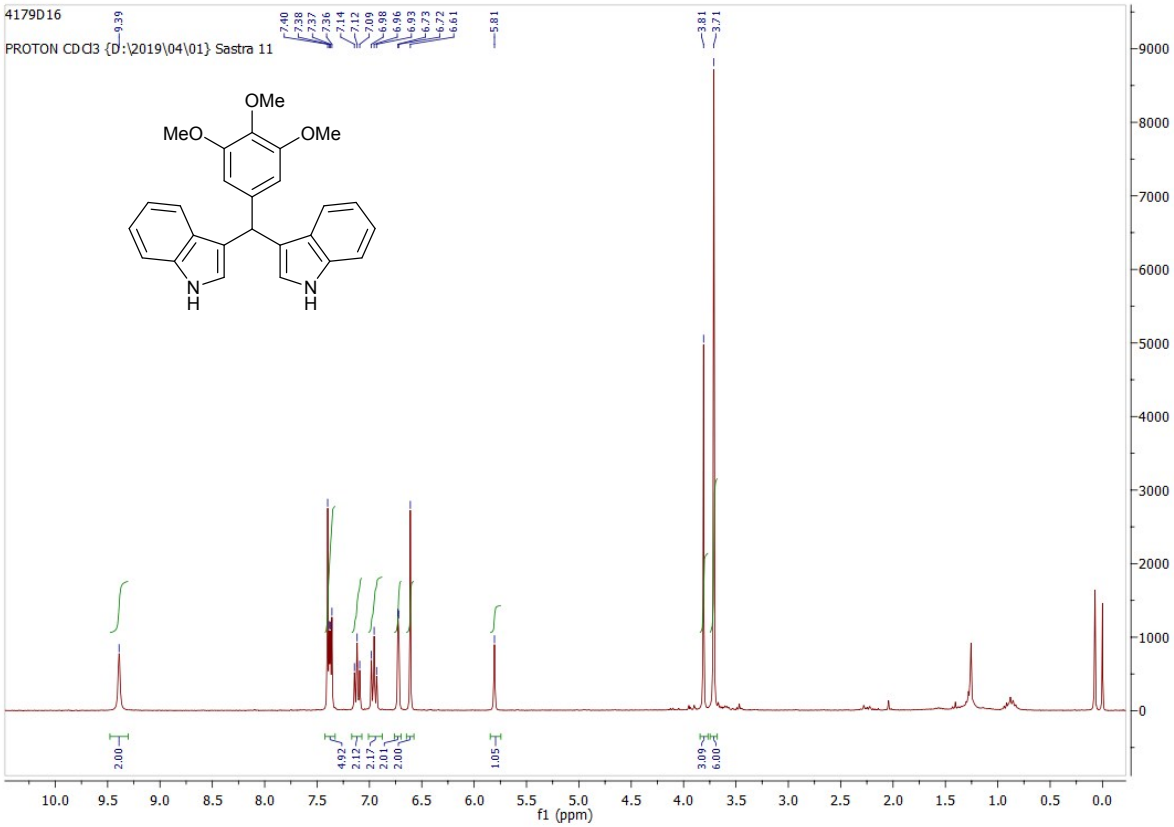
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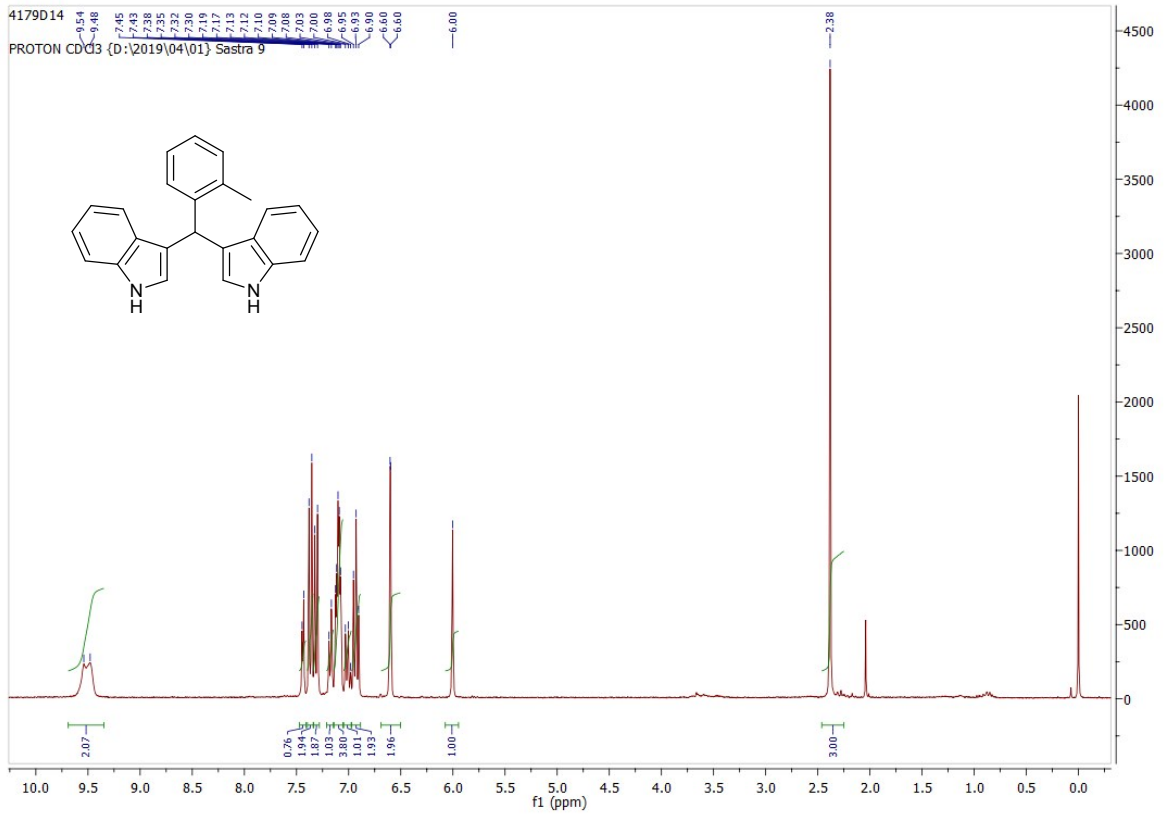
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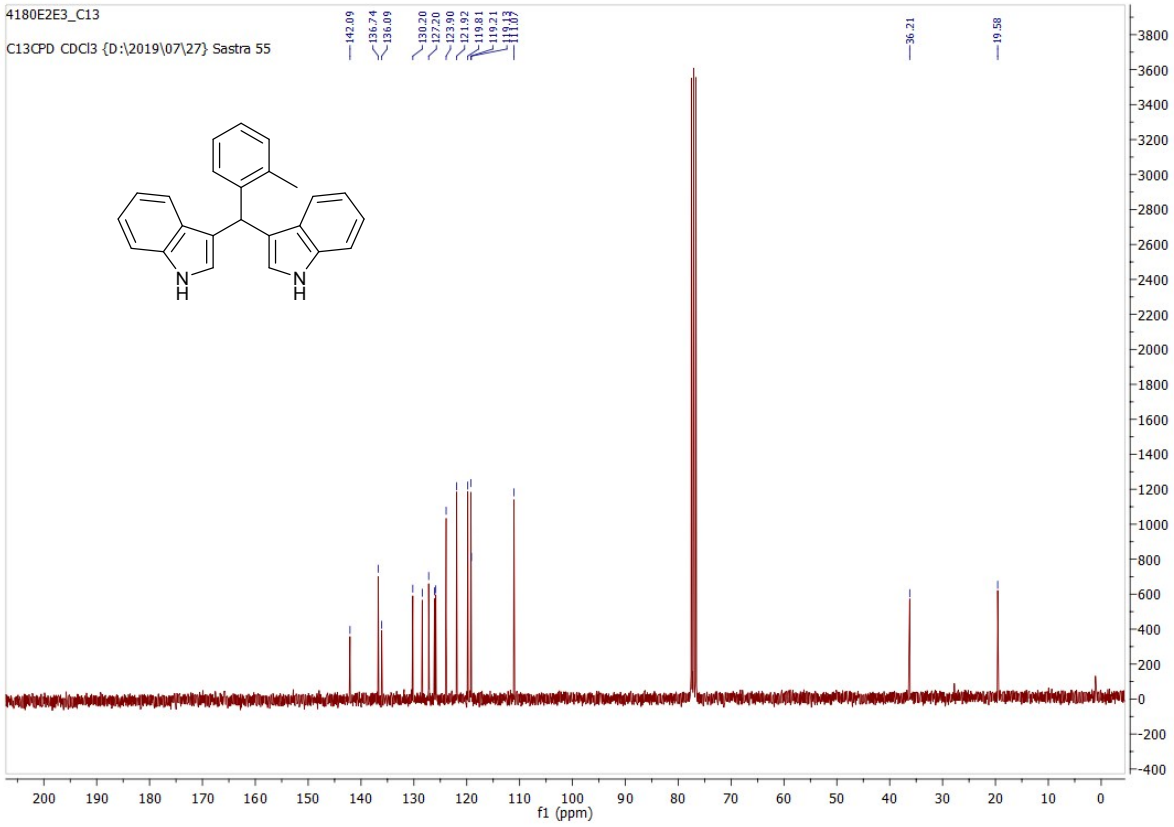
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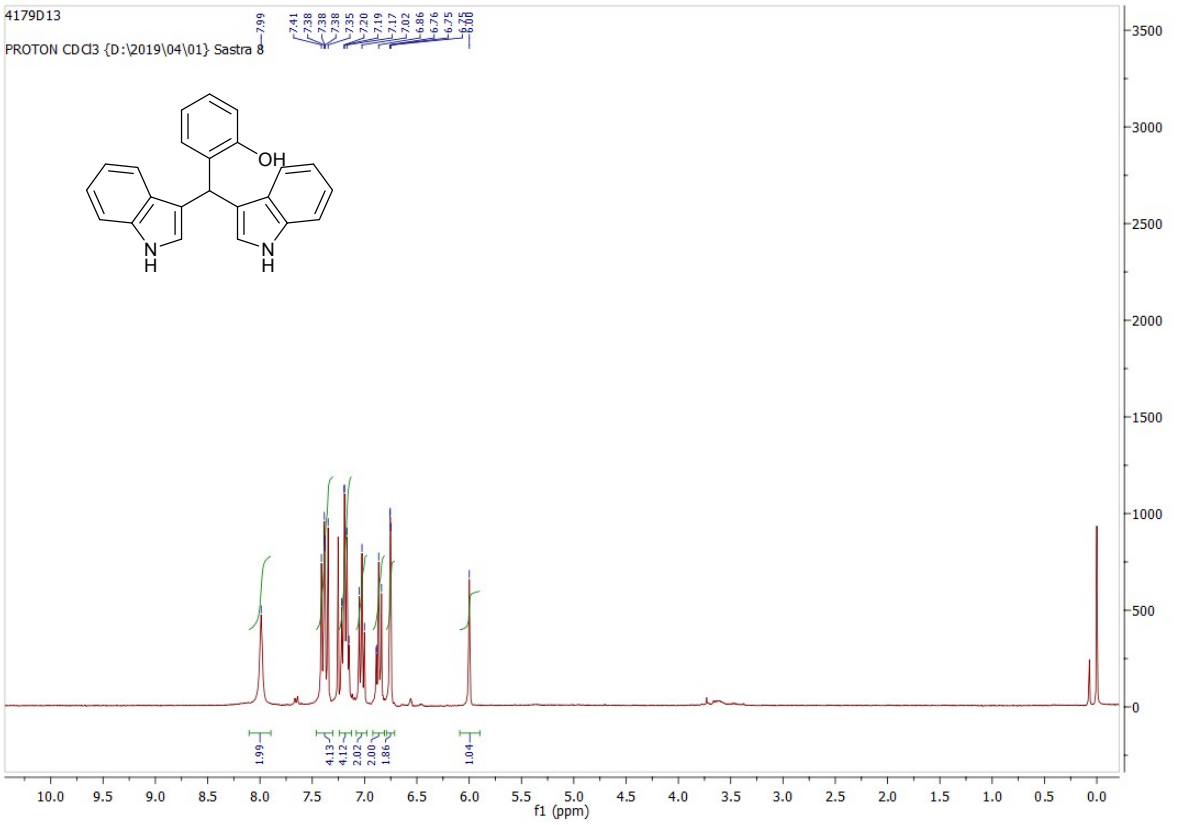
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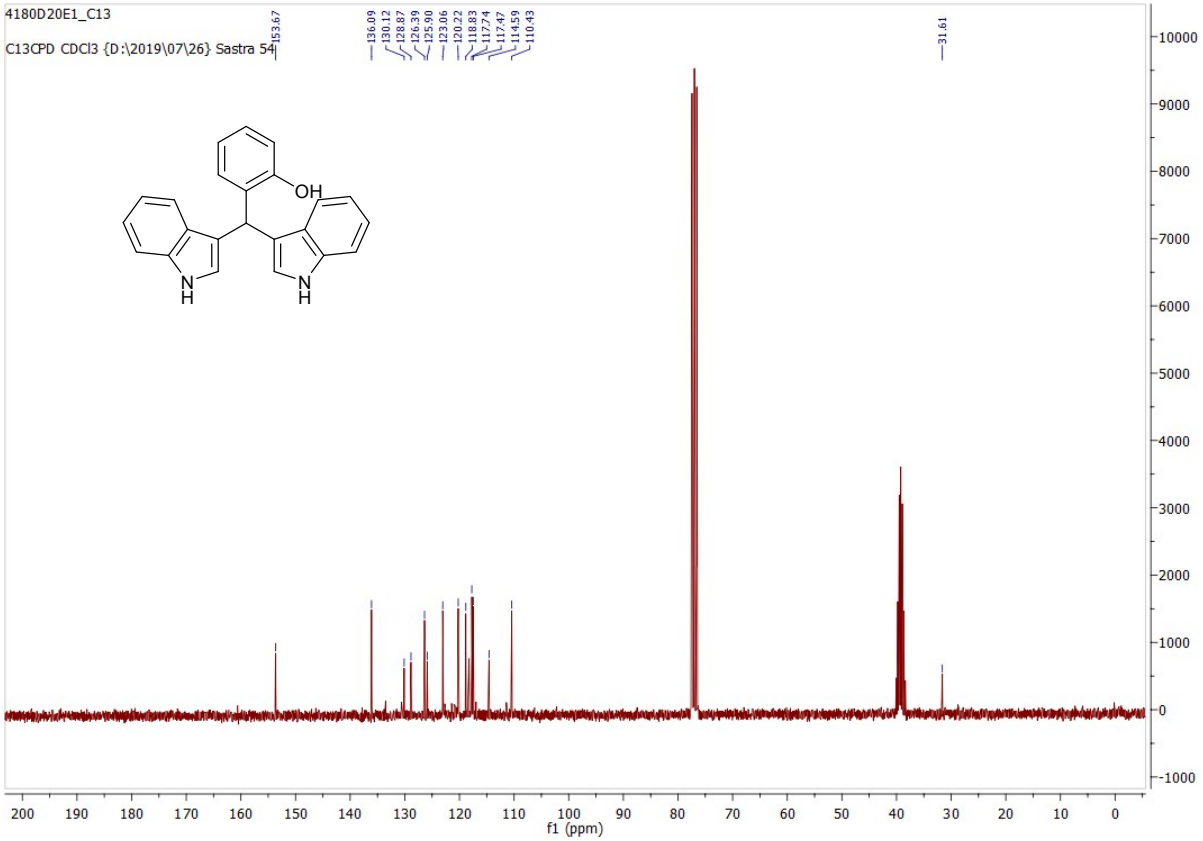
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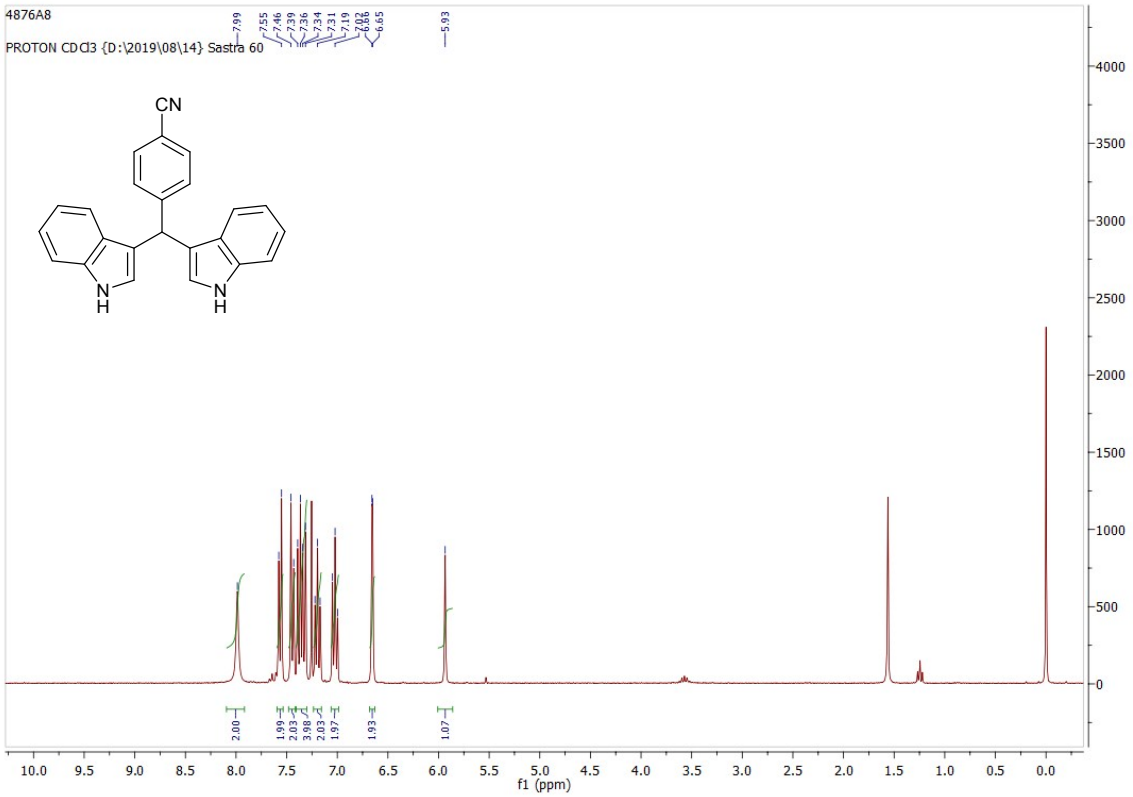
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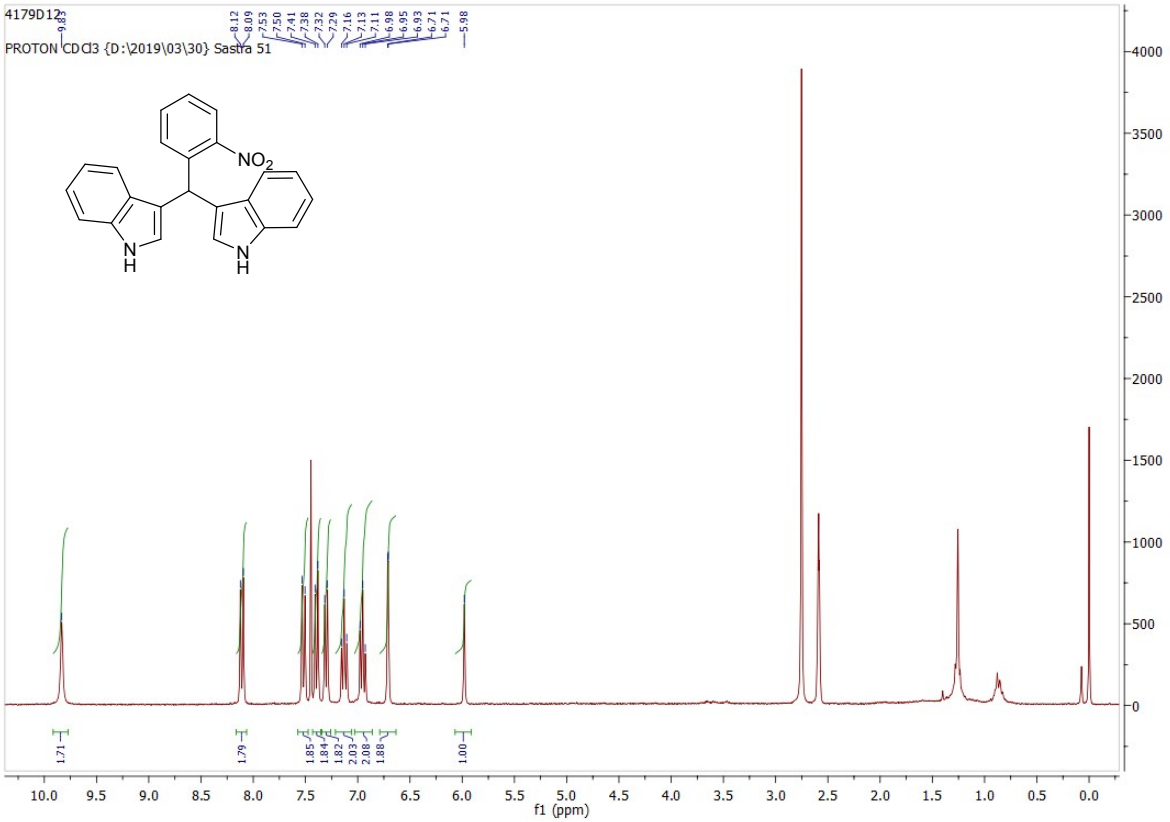
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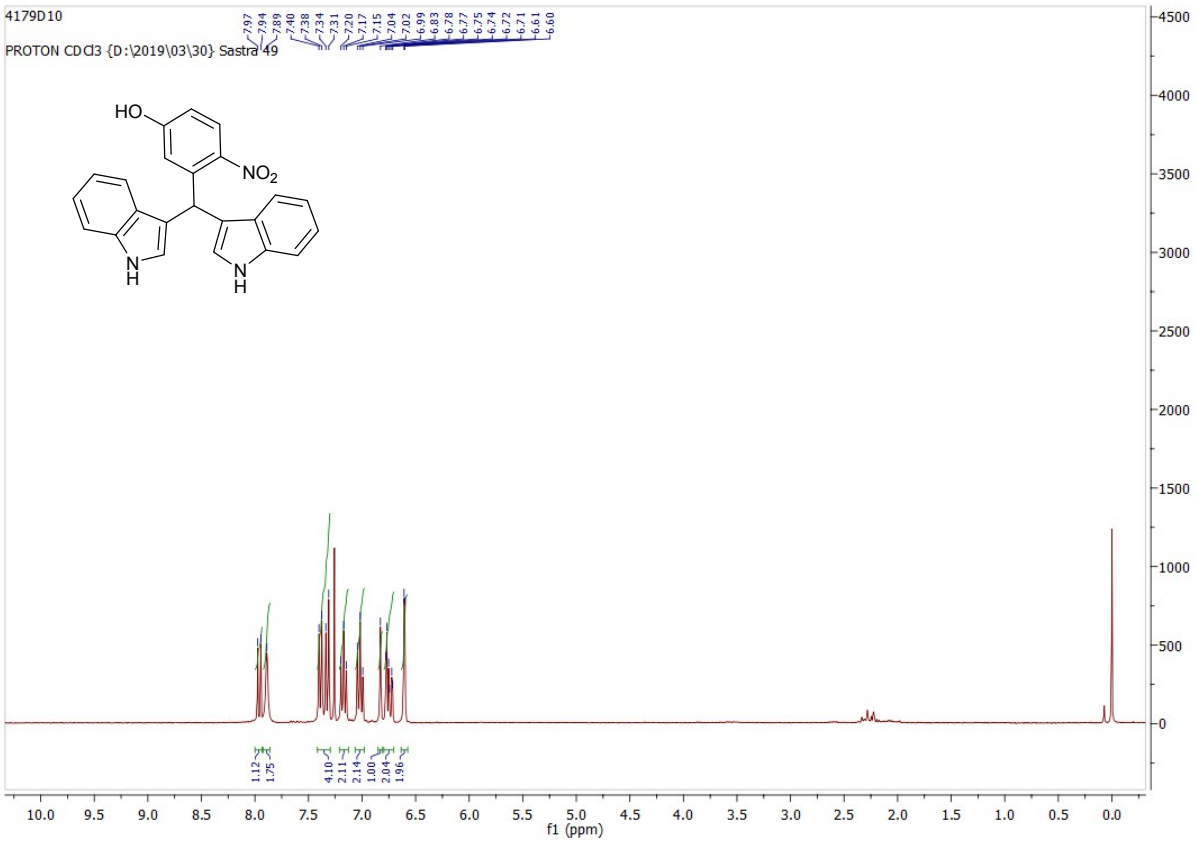
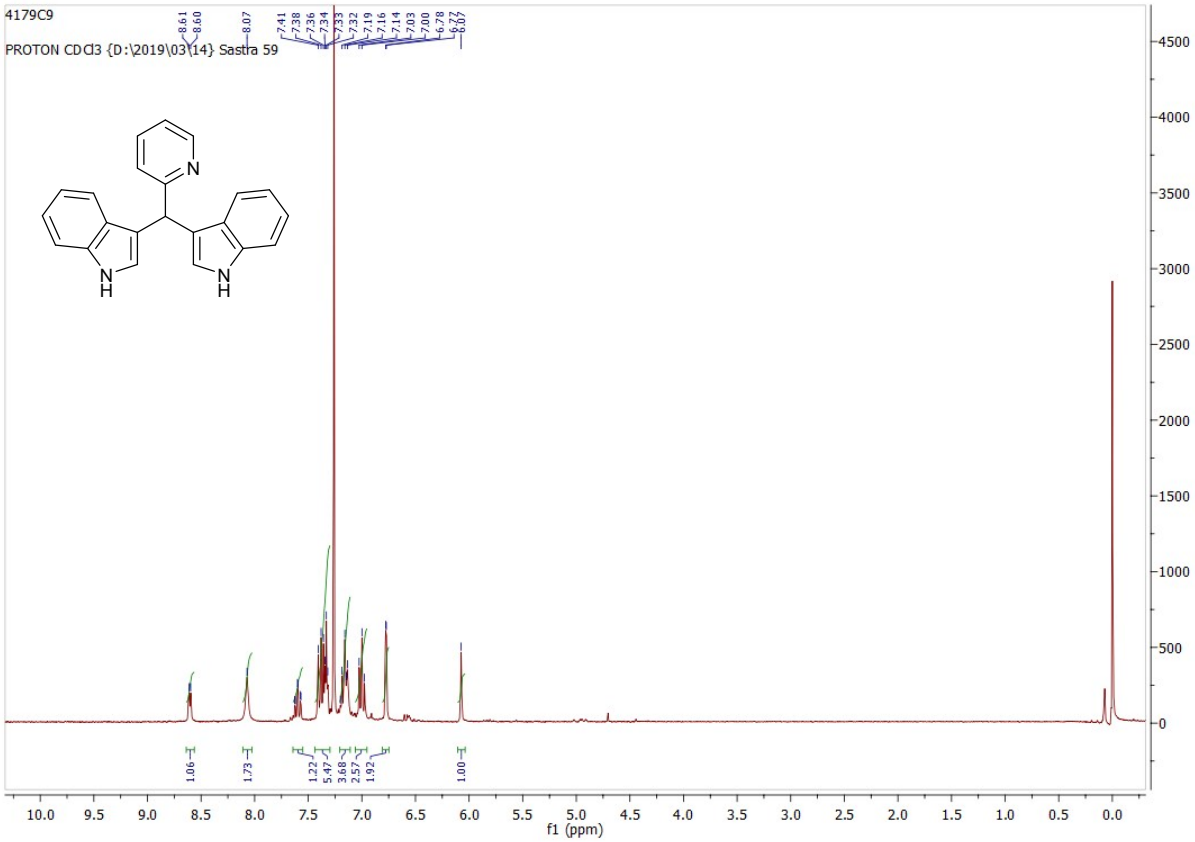
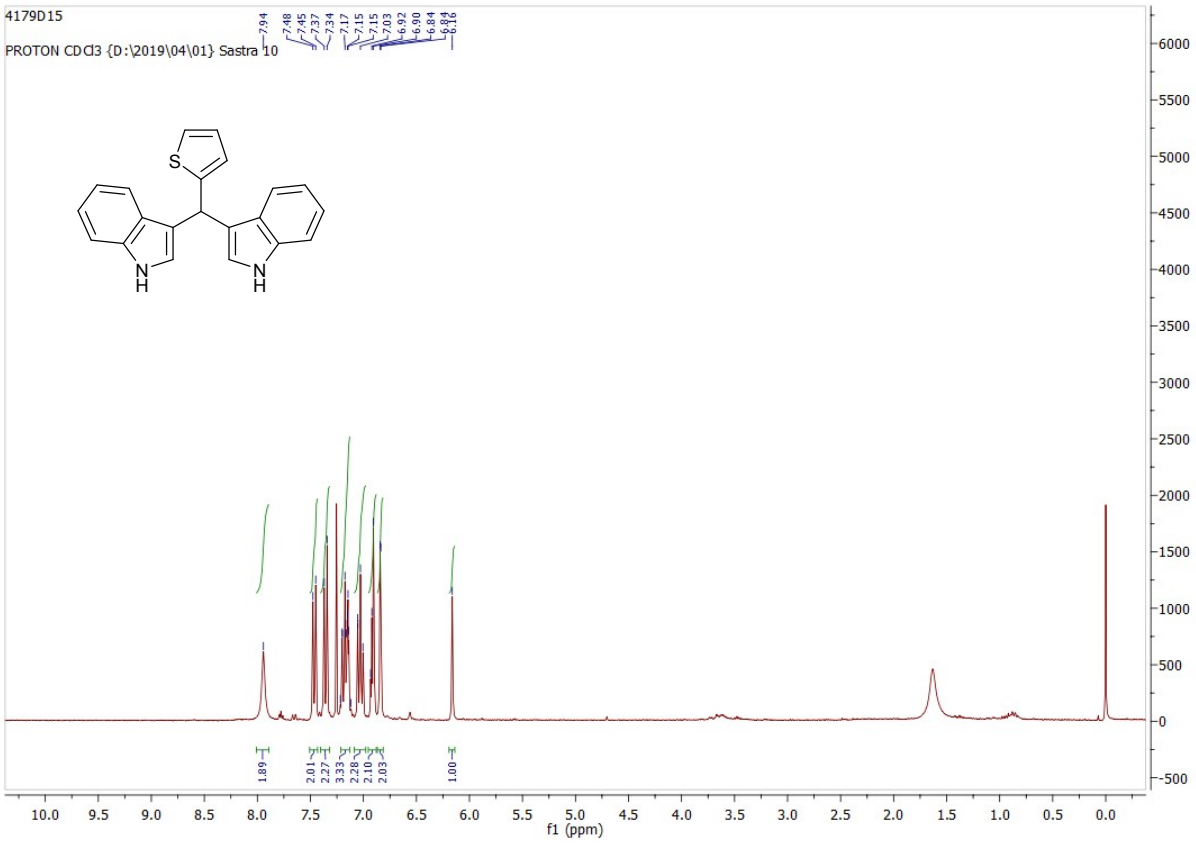
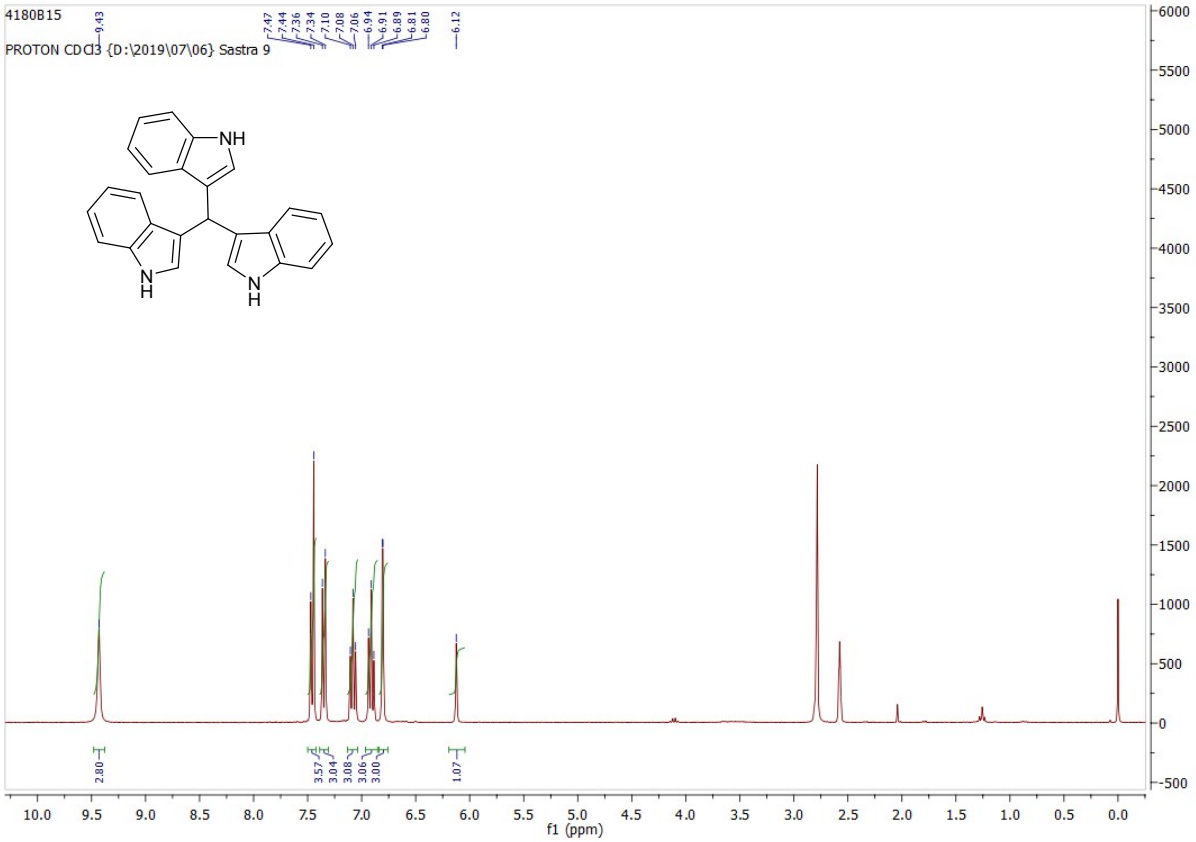
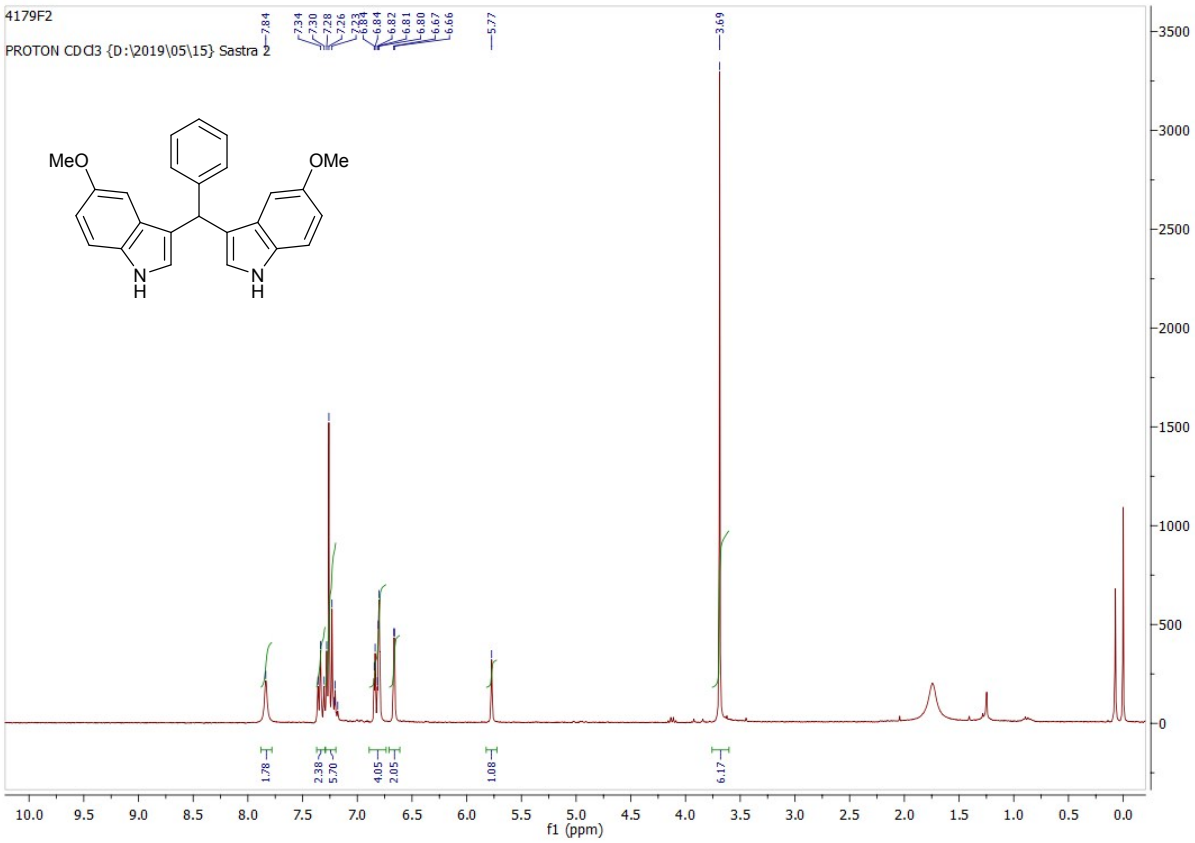
H
f1 (ppm)

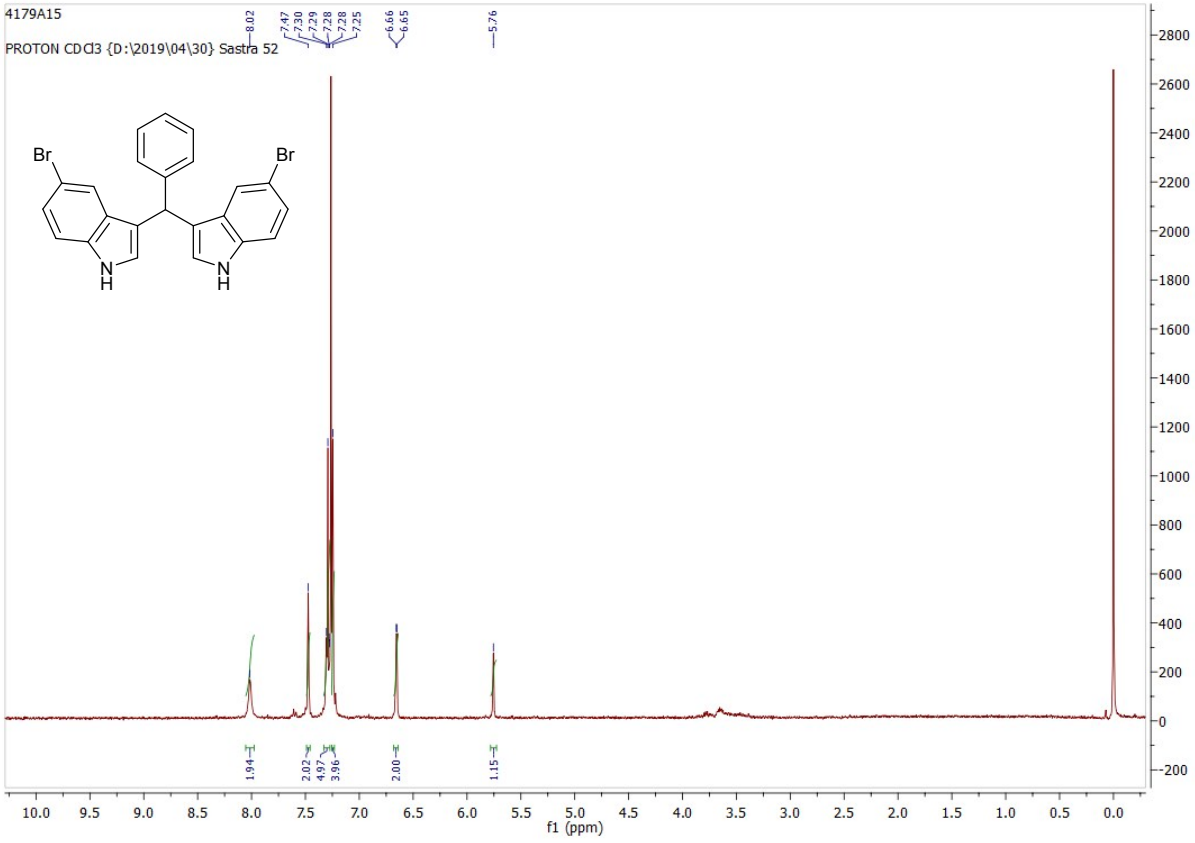

4179D10
PROTON CDCl3 {D:\2019\03\30} Sastra 49
HO
NO2
N
H
N
H
f1 (ppm)

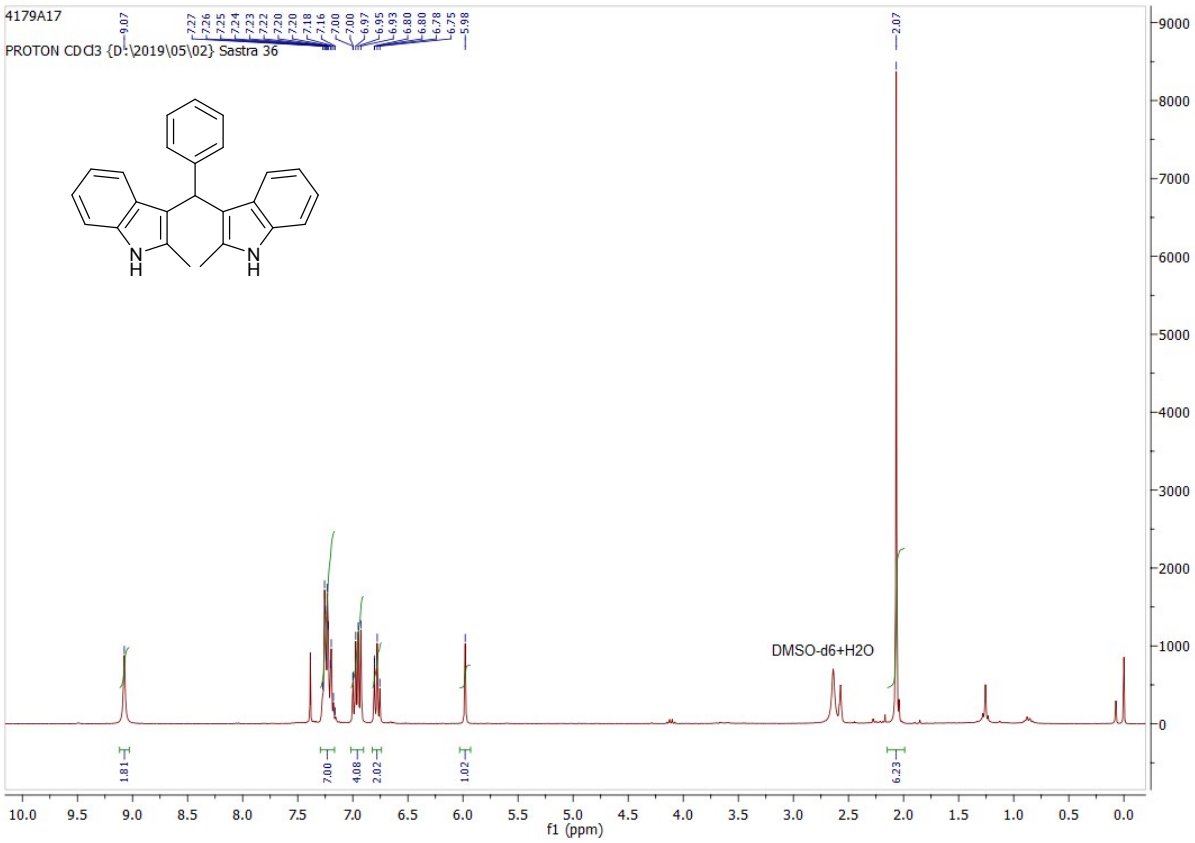

4179C9
PROTON CDCl3 {D:\2019\03\14} Sastra 59
N
N
H
N
H
f1 (ppm)

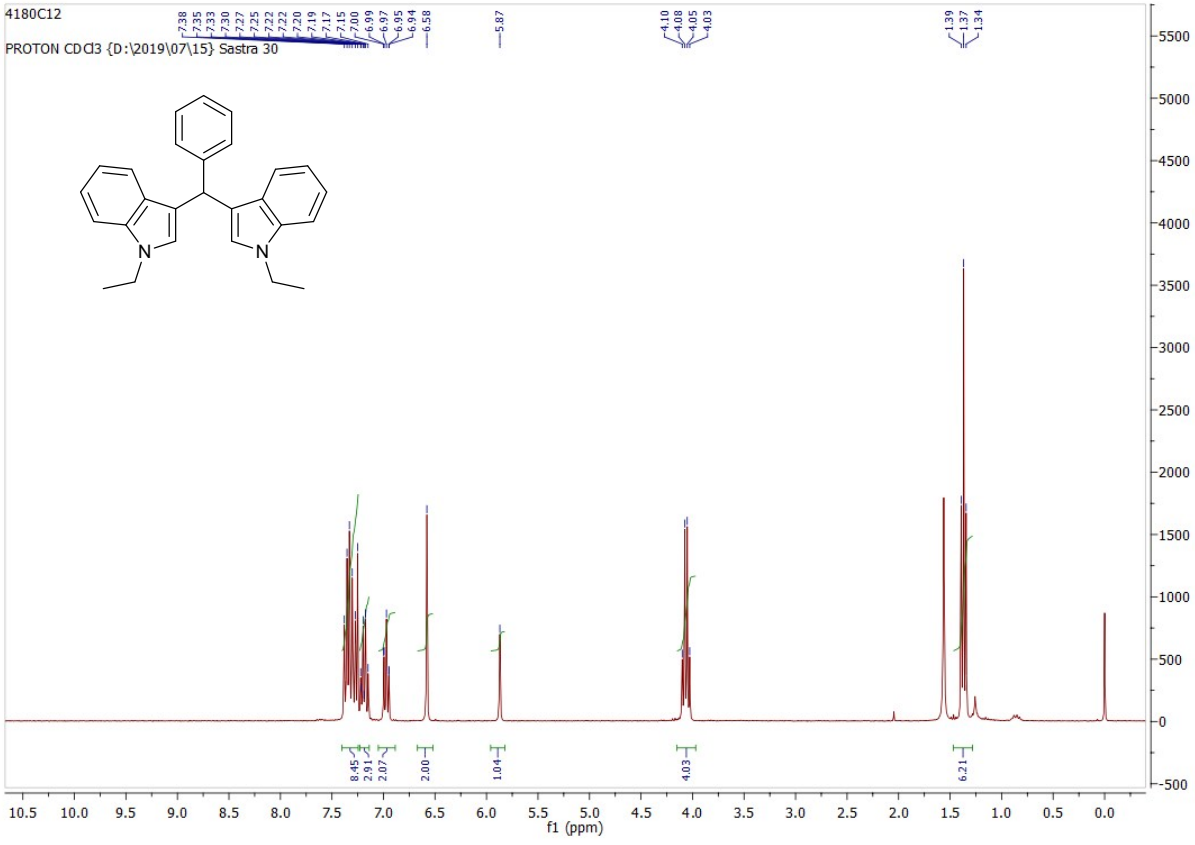

4179D15
PROTON CDCl3 {D:\2019\04\01} Sastra 10
S
N
H
N
H
f1 (ppm)

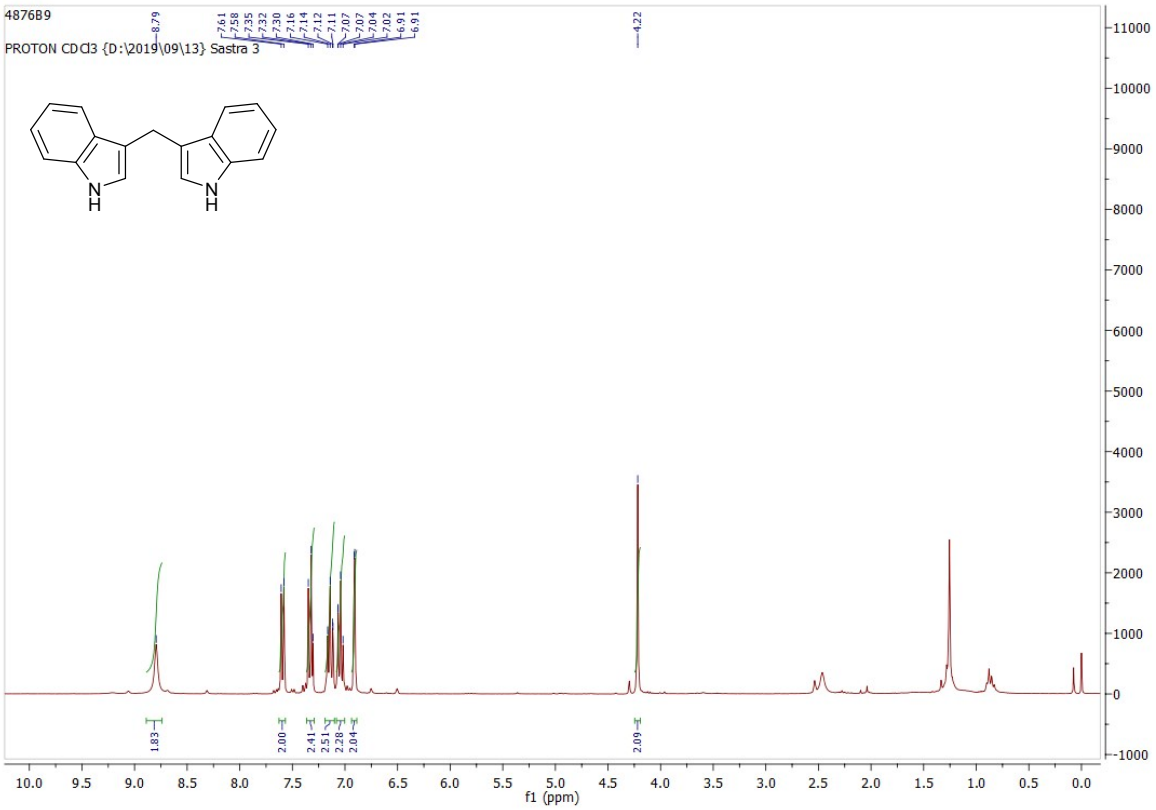

4180B15
PROTON CDCl3 {D:\2019\07\06} Sastra 9
NH
N
H
N
H
f1 (ppm)

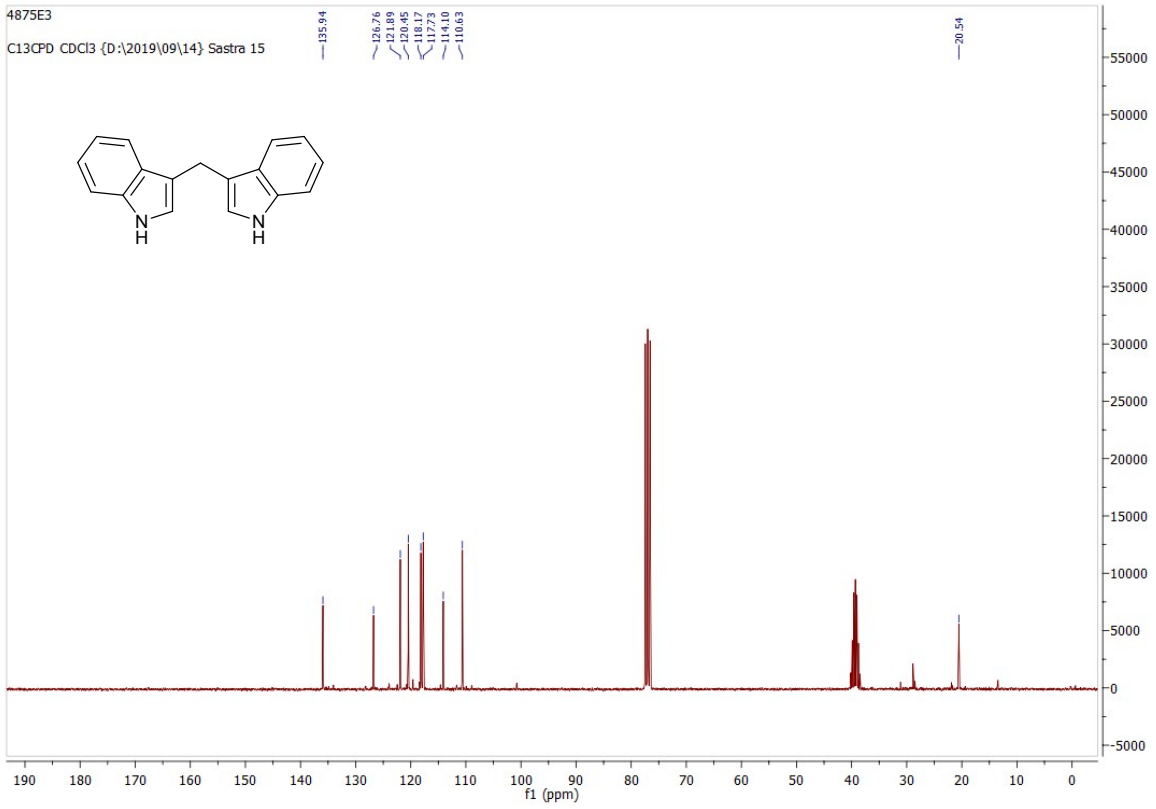

4179F2
PROTON CDCl3 {D:\2019\05\15} Sastra 2
MeO
OMe
N
H
N
H
7.84
7.34
7.30
7.28
7.26
7.23
6.84
6.82
6.81
6.80
6.67
6.66
5.77
3.69
1.78
2.38
5.70
4.05
2.05
1.08
6.17
f1 (ppm)

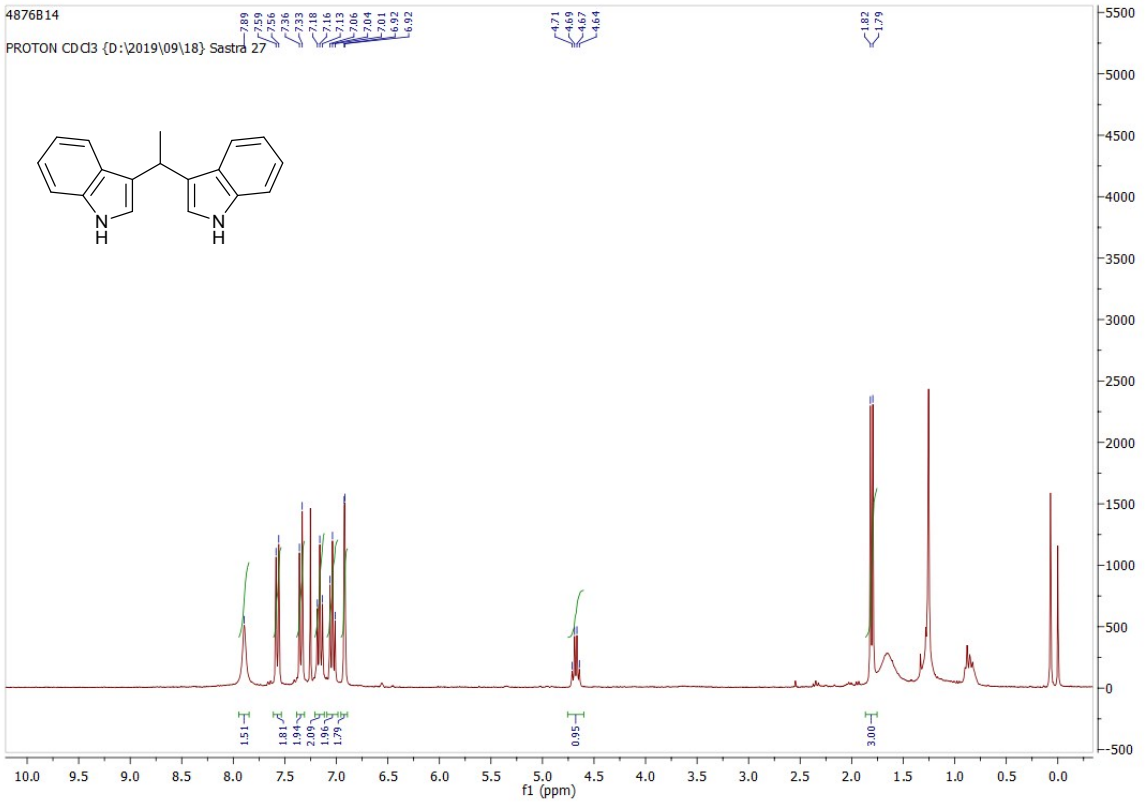

4179A15
PROTON CDCl3 {D:\2019\04\30} Sastra 52
Br
Br
N
H
N
H
8.02
7.47
7.30
7.29
7.28
7.28
7.25
6.66
6.65
5.76
1.94
2.02
4.97
3.96
2.00
1.15
f1 (ppm)

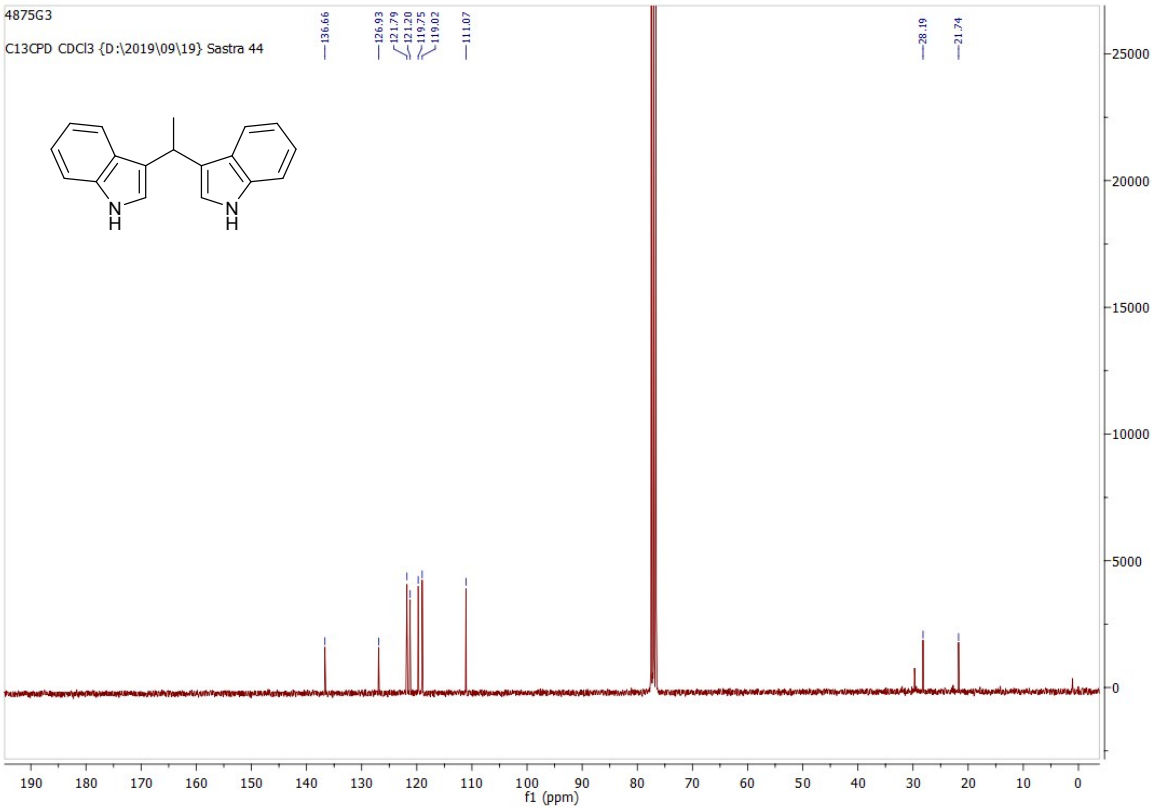

4179A17
PROTON CDCl3 {D:\2019\05\02} Sastra 36
DMSO-d6+H2O
f1 (ppm)

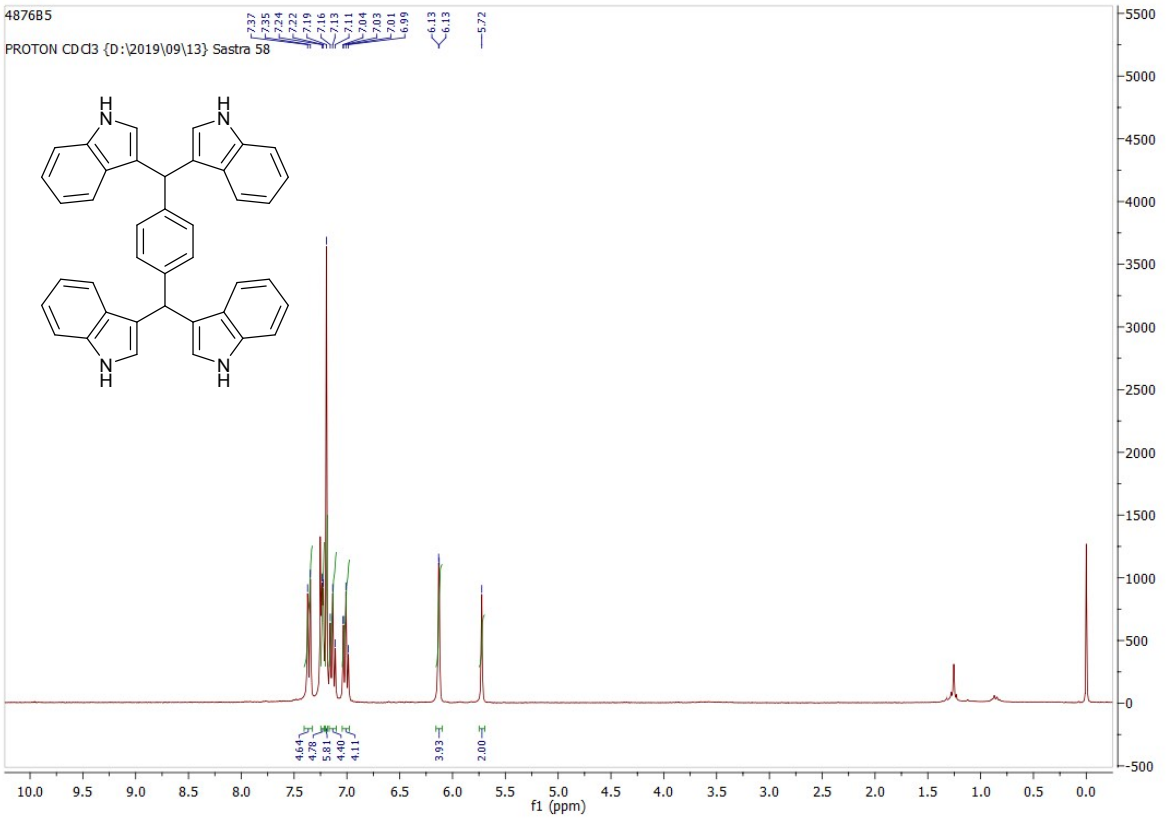

4180C12
PROTON CDCl3 {D:\2019\07\15} Sastra 30
f1 (ppm)

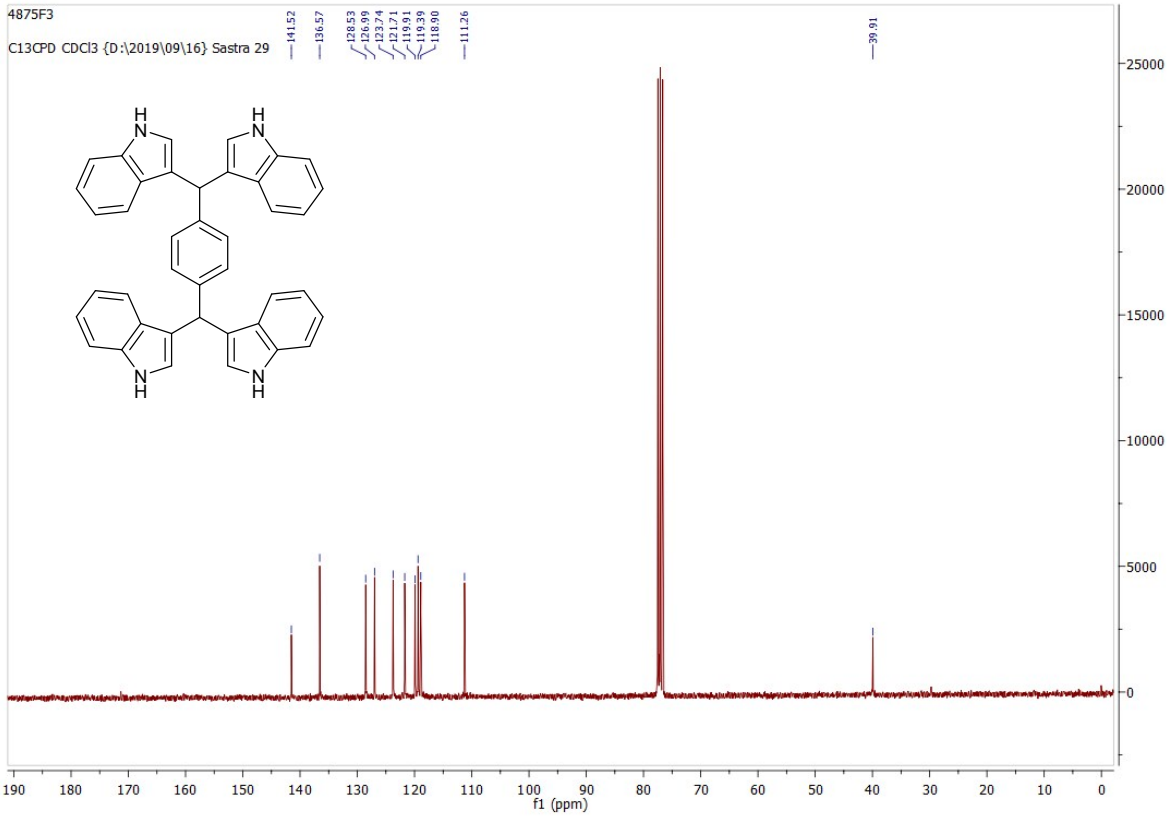

4876B9
PROTON CDCl3 {D:\2019\09\13} Sastra 3
8.79
7.61
7.58
7.35
7.32
7.30
7.16
7.14
7.12
7.11
7.07
7.07
7.04
7.02
6.91
6.91
4.22
1.83
2.00
2.41
2.51
2.28
2.04
2.09
f1 (ppm)

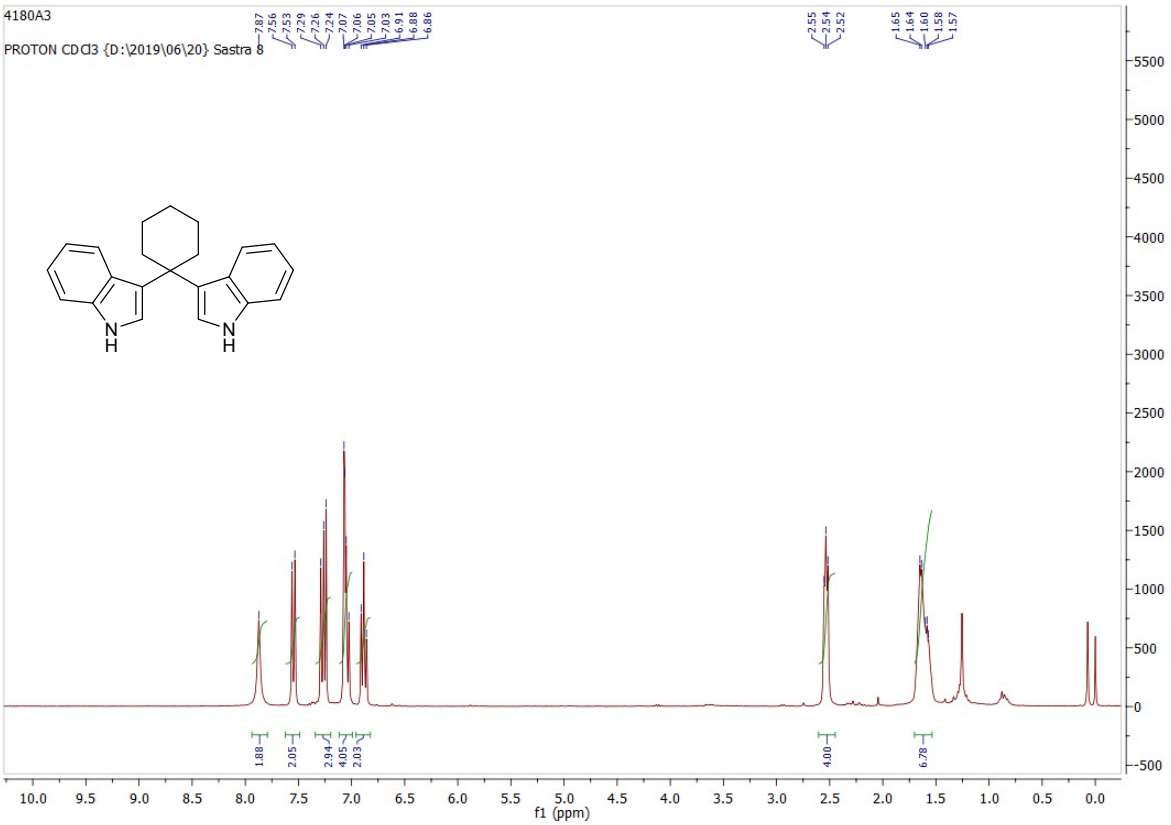

4875E3
C13CPD CDCl3 {D:\2019\09\14} Sastra 15
135.94
126.76
121.89
120.45
118.17
117.73
114.10
110.63
20.54
f1 (ppm)

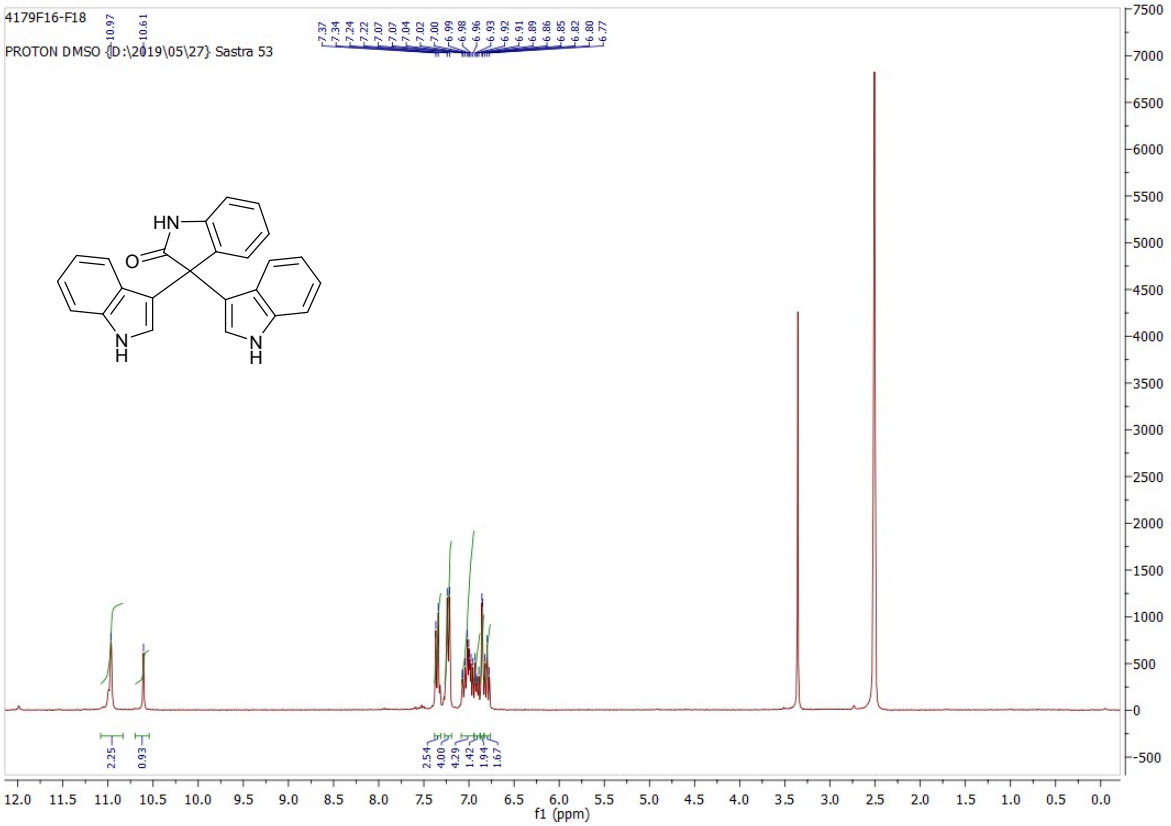

4876B14
PROTON CDCl3 {D:\2019\09\18} Sastra 27
7.89
7.59
7.56
7.36
7.33
7.18
7.16
7.13
7.06
7.04
7.01
6.92
6.92
4.71
4.69
4.67
4.64
1.82
1.79
1.51
1.81
1.94
2.09
1.96
1.79
0.95
3.00
f1 (ppm)

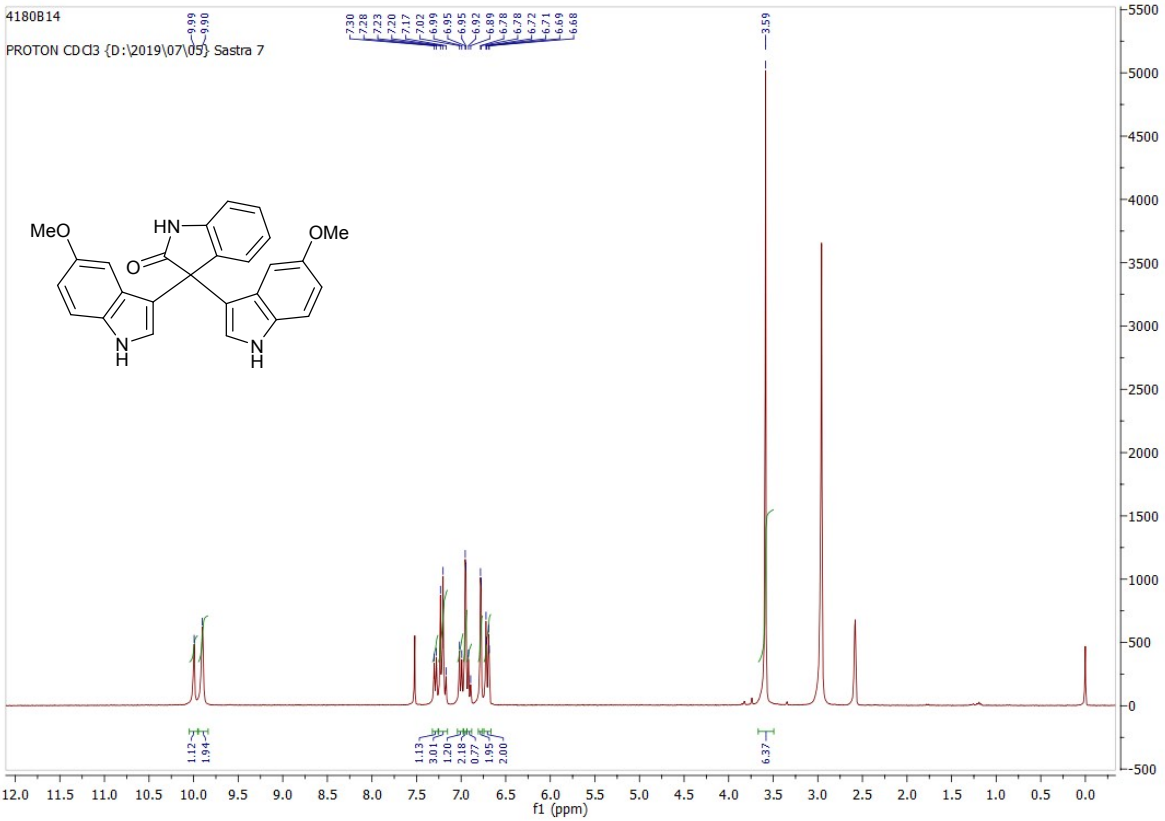

4875G3
C13CPD CDCl3 {D:\2019\09\19} Sastra 44
136.66
126.93
121.79
121.20
119.75
119.02
111.07
28.19
21.74
f1 (ppm)

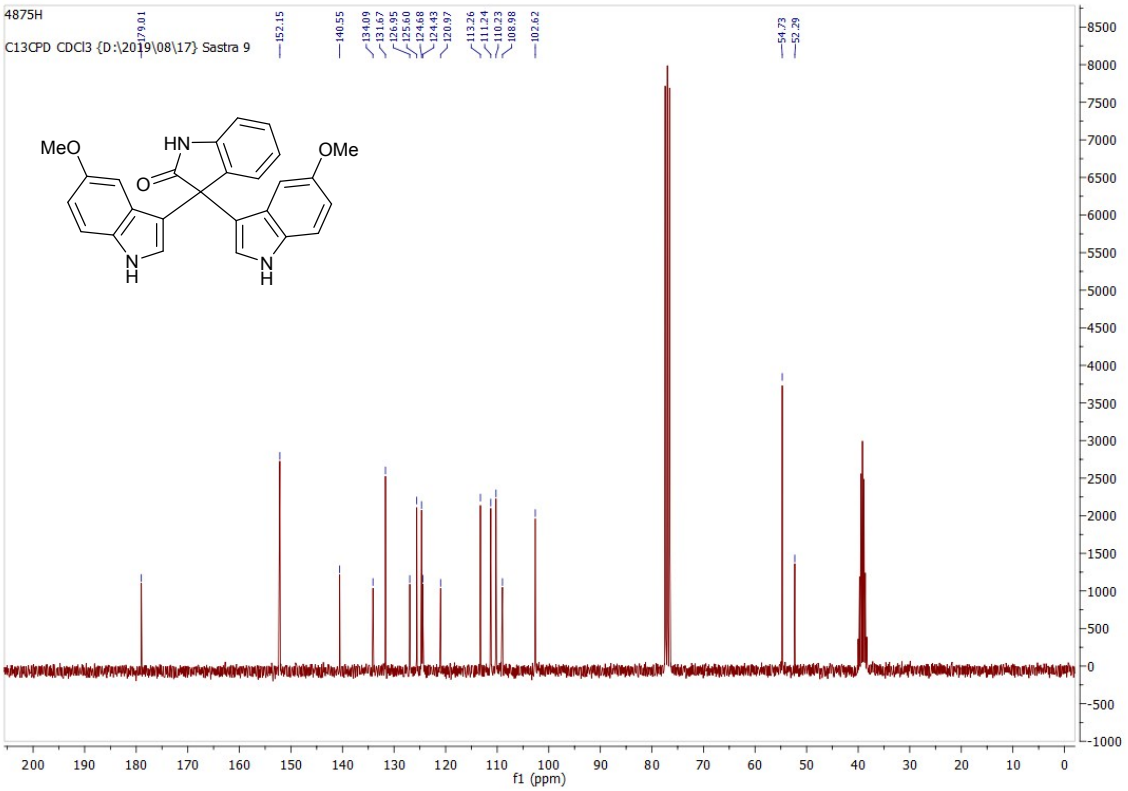

4876B5
PROTON CDCl3 {D:\2019\09\13} Sastra 58
7.37
7.35
7.24
7.22
7.19
7.16
7.13
7.11
7.04
7.03
7.01
6.99
6.13
6.13
5.72
4.64
4.78
5.81
4.40
4.11
3.93
2.00
f1 (ppm)

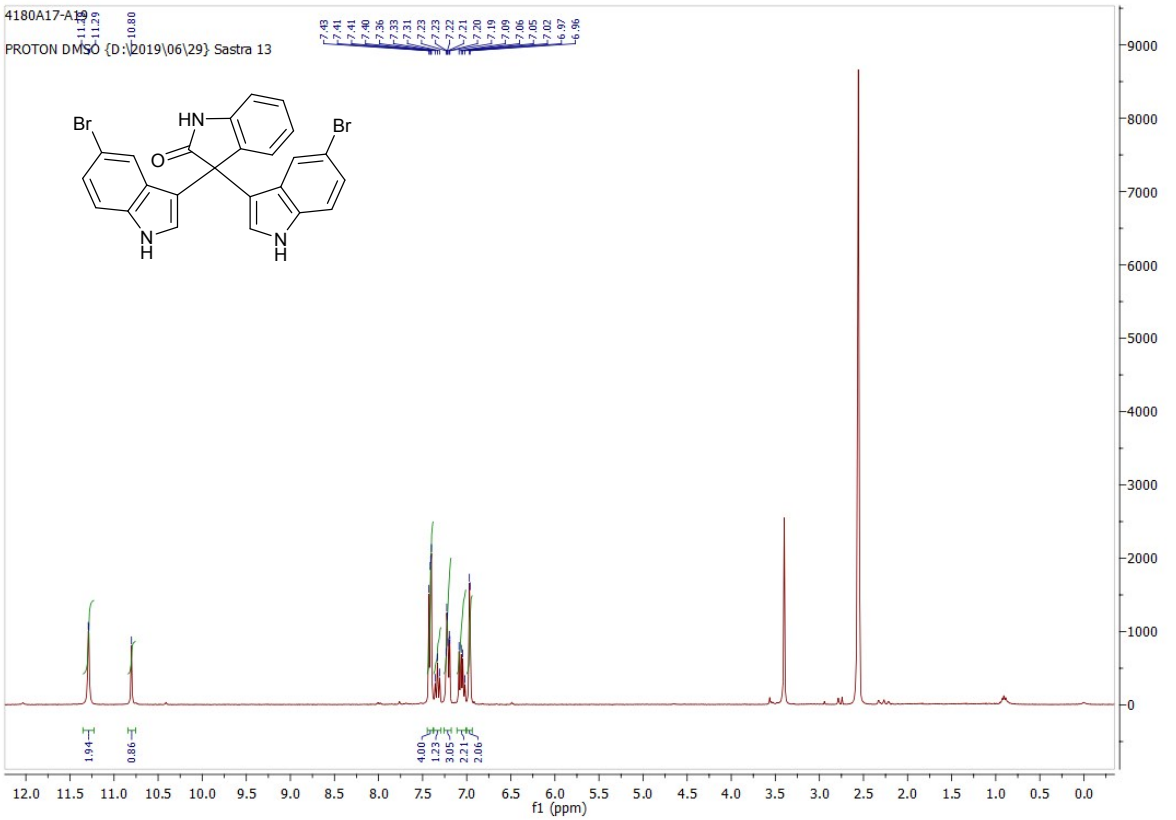

4875F3
C13CPD CDCl3 {D:\2019\09\16} Sastra 29
141.52
136.57
128.53
126.99
123.74
121.71
119.91
119.39
118.90
111.26
39.91
f1 (ppm)

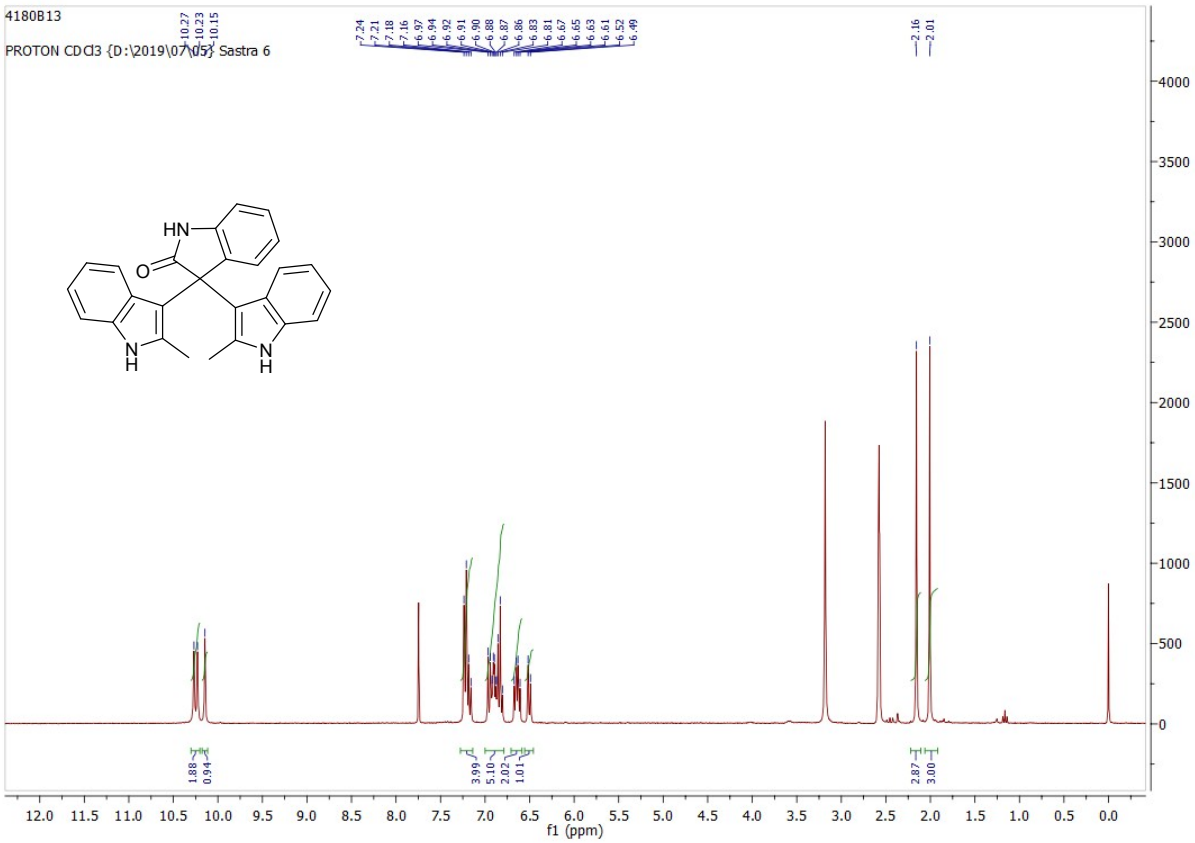

4180A3
PROTON CDCl3 {D:\2019\06\20} Sastra 8
7.87
7.56
7.53
7.29
7.26
7.24
7.07
7.06
7.05
7.03
6.91
6.88
6.86
2.55
2.54
2.52
1.65
1.64
1.60
1.58
1.57
N
H
N
H
1.88
2.05
2.94
4.05
2.03
4.00
6.78
f1 (ppm)

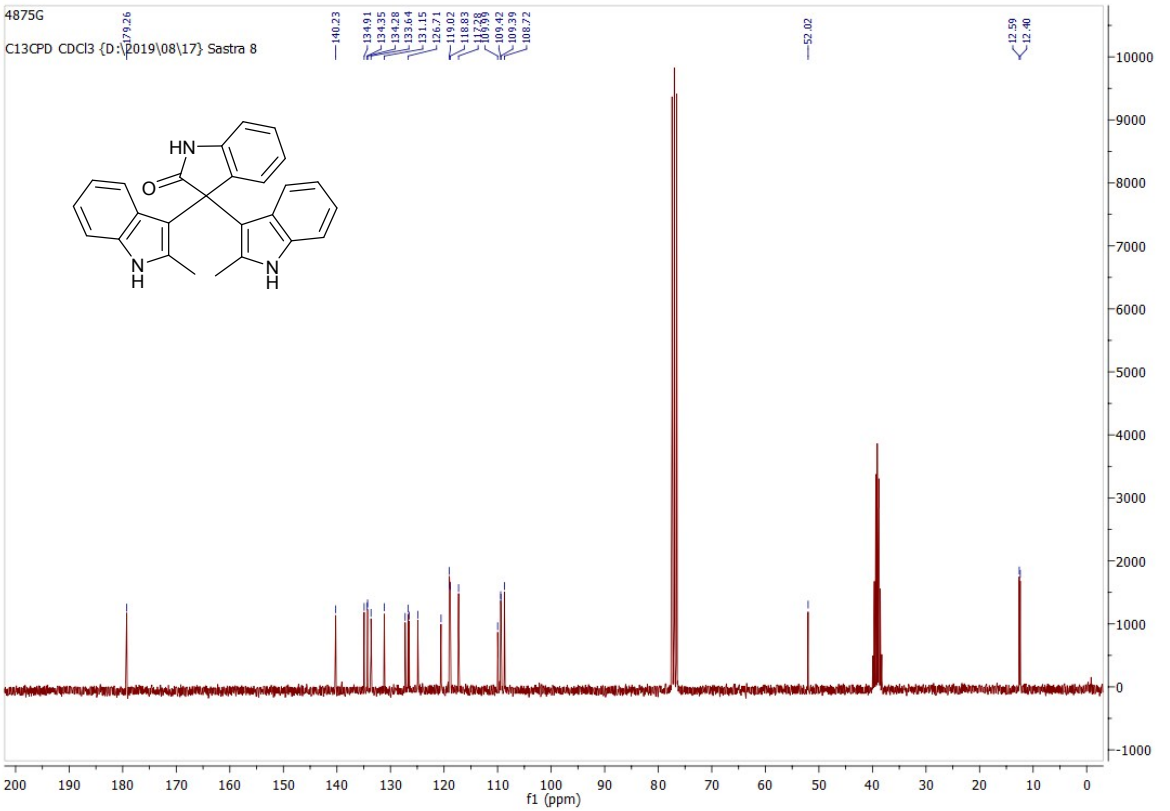

4179F16-F18
PROTON DMSO {D:\2019\05\27} Sastra 53
10.97
10.61
7.37
7.34
7.24
7.22
7.07
7.07
7.04
7.02
7.00
6.99
6.98
6.96
6.93
6.92
6.91
6.89
6.86
6.85
6.82
6.80
6.77
HN
O
N
H
N
H
2.25
0.93
2.54
4.00
4.29
1.42
1.94
1.67
f1 (ppm)

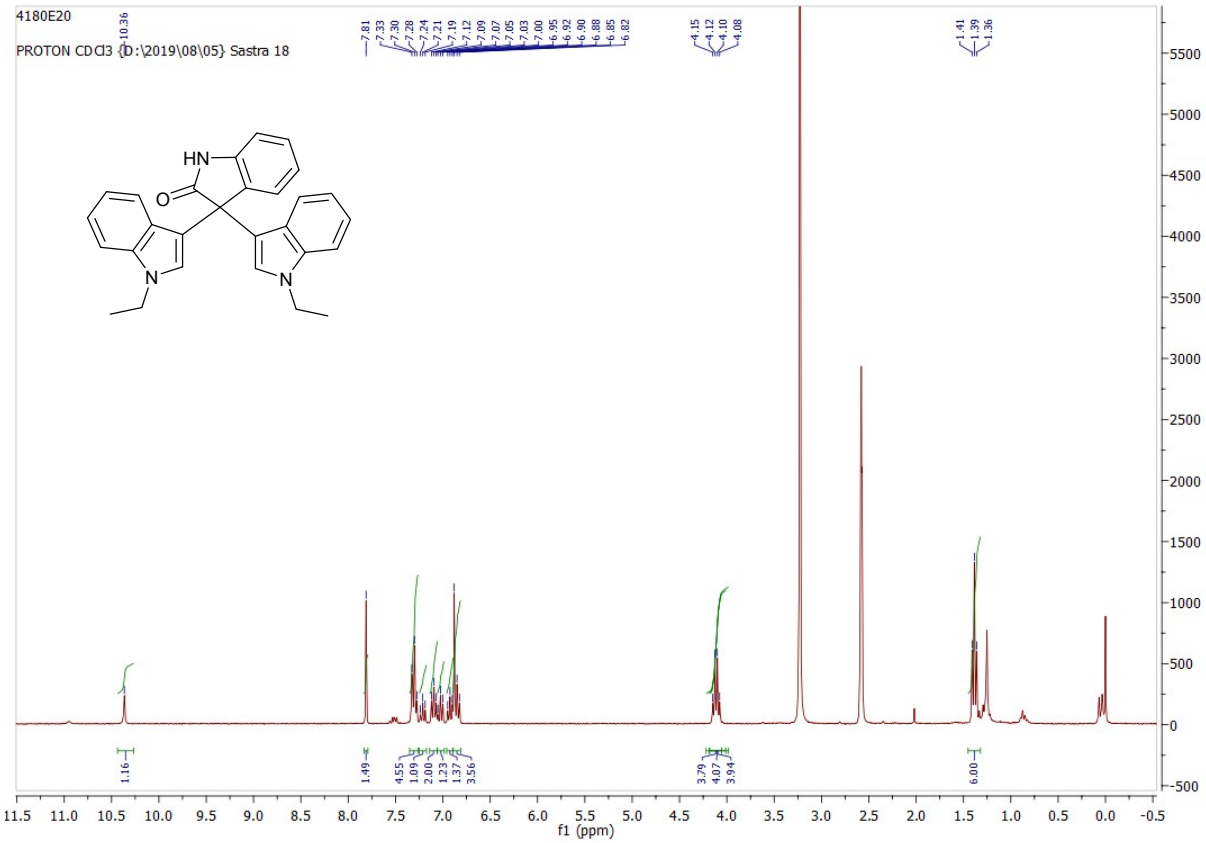

4180B14
PROTON CDCl3 {D:\2019\07\05} Sastra 7
MeO
HN
O
OMe
N
H
N
H
f1 (ppm)

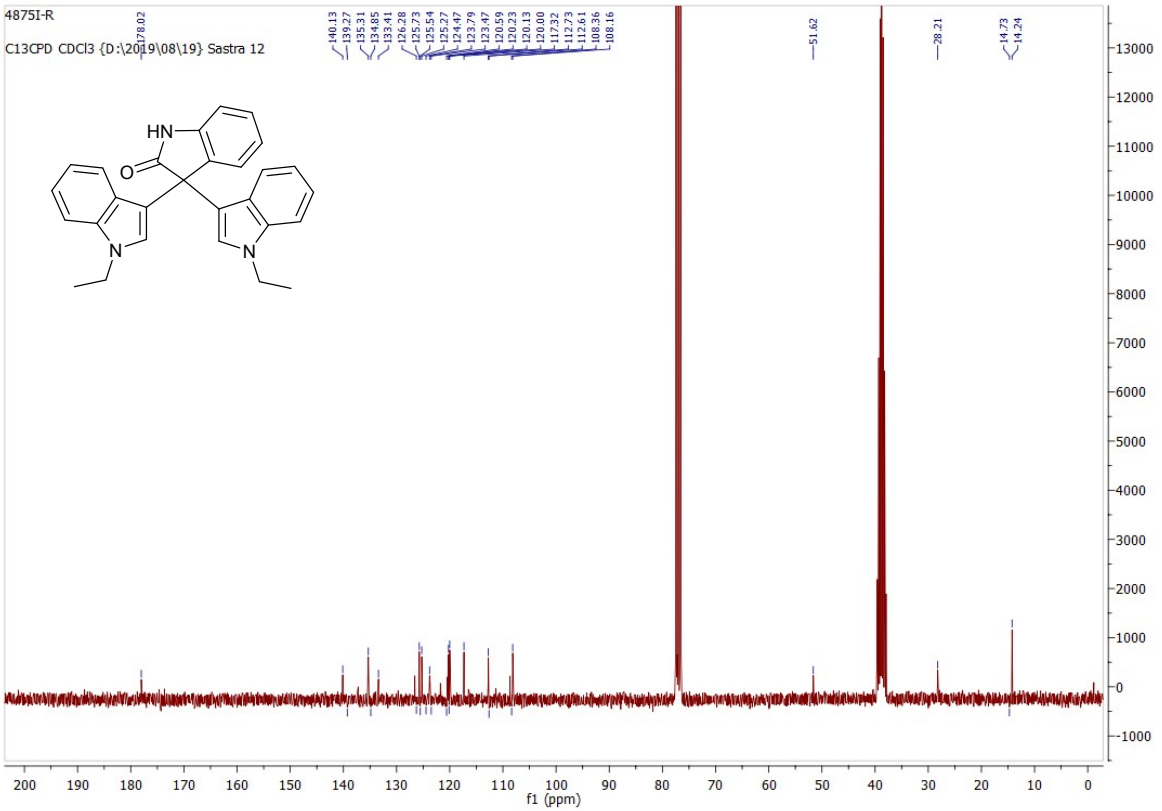

4875H
C13CPD CDCl3 {D:\2019\08\17} Sastra 9
MeO
HN
O
OMe
N
H
N
H
f1 (ppm)

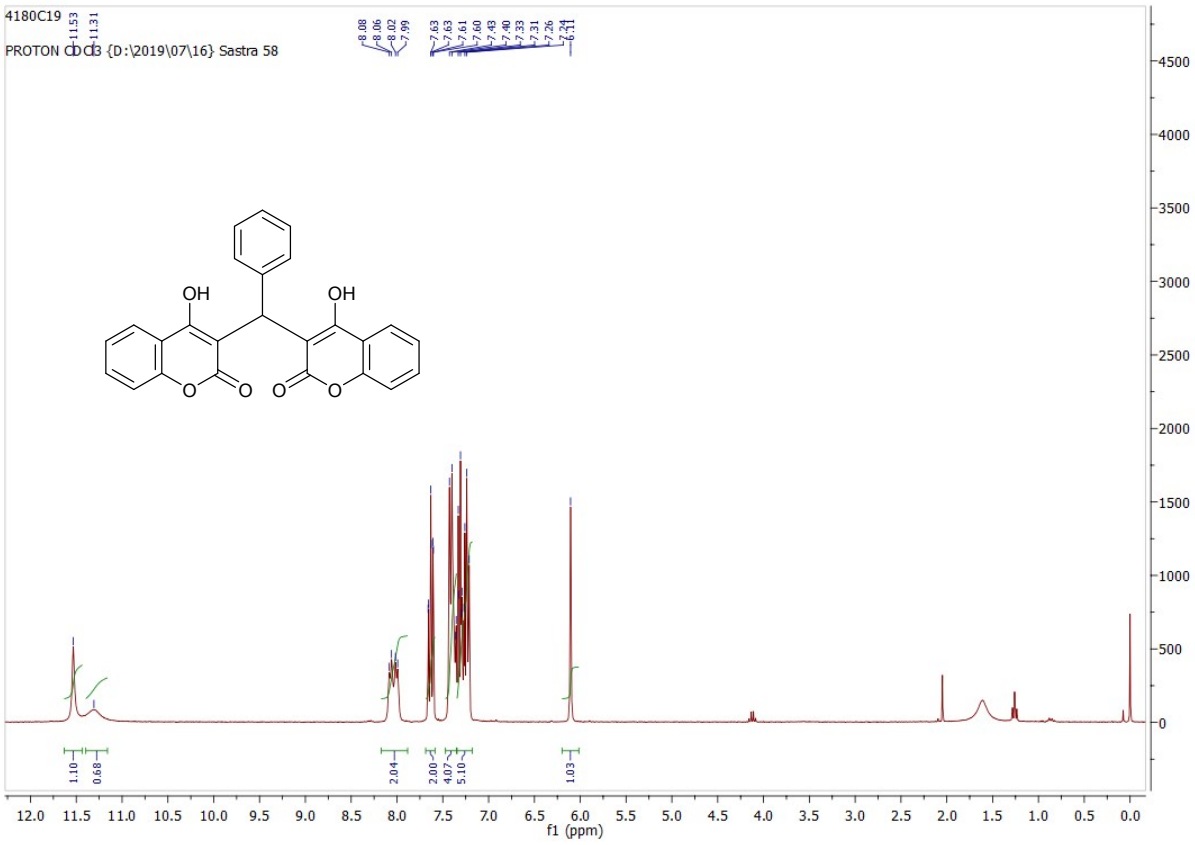

4180A17-A19
PROTON DMSO {D:\2019\06\29} Sastra 13
Br
HN
O
Br
N
H
N
H
f1 (ppm)

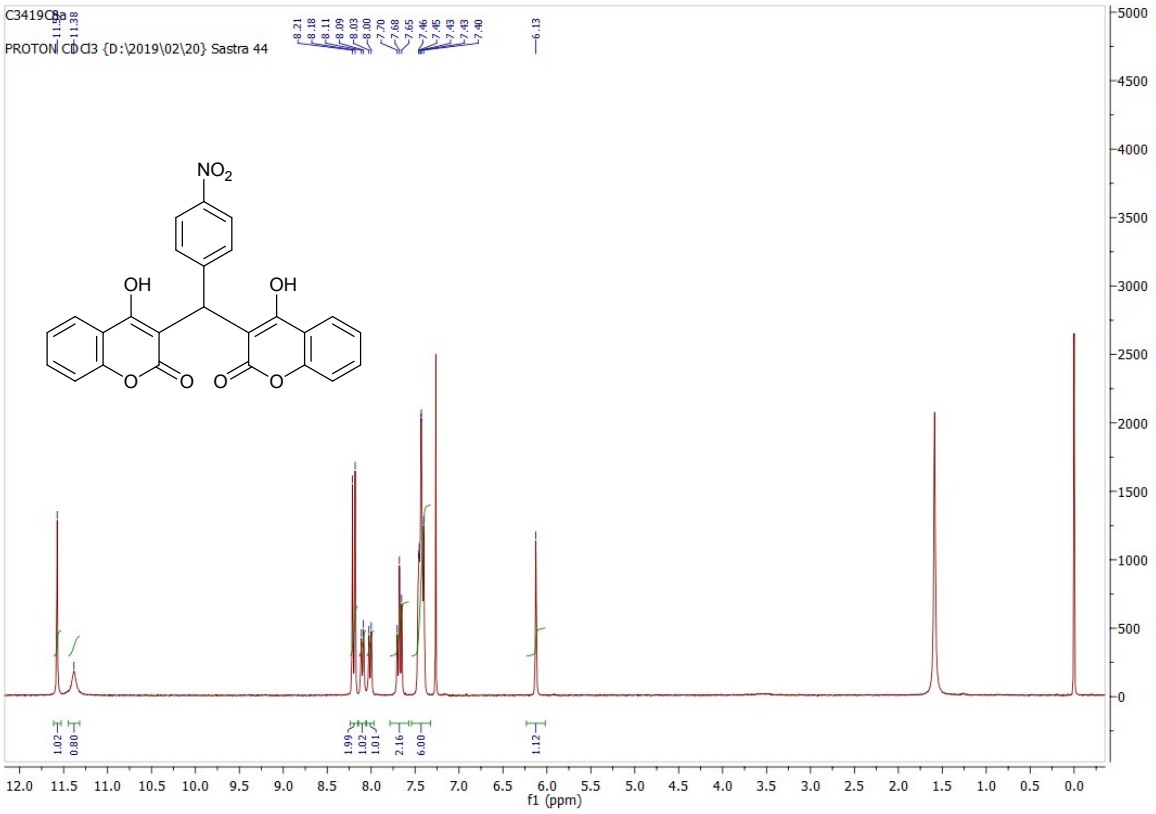

4180B13
PROTON CDCl3 {D:\2019\07\05} Sastra 6
HN
O
N
H
N
H
f1 (ppm)

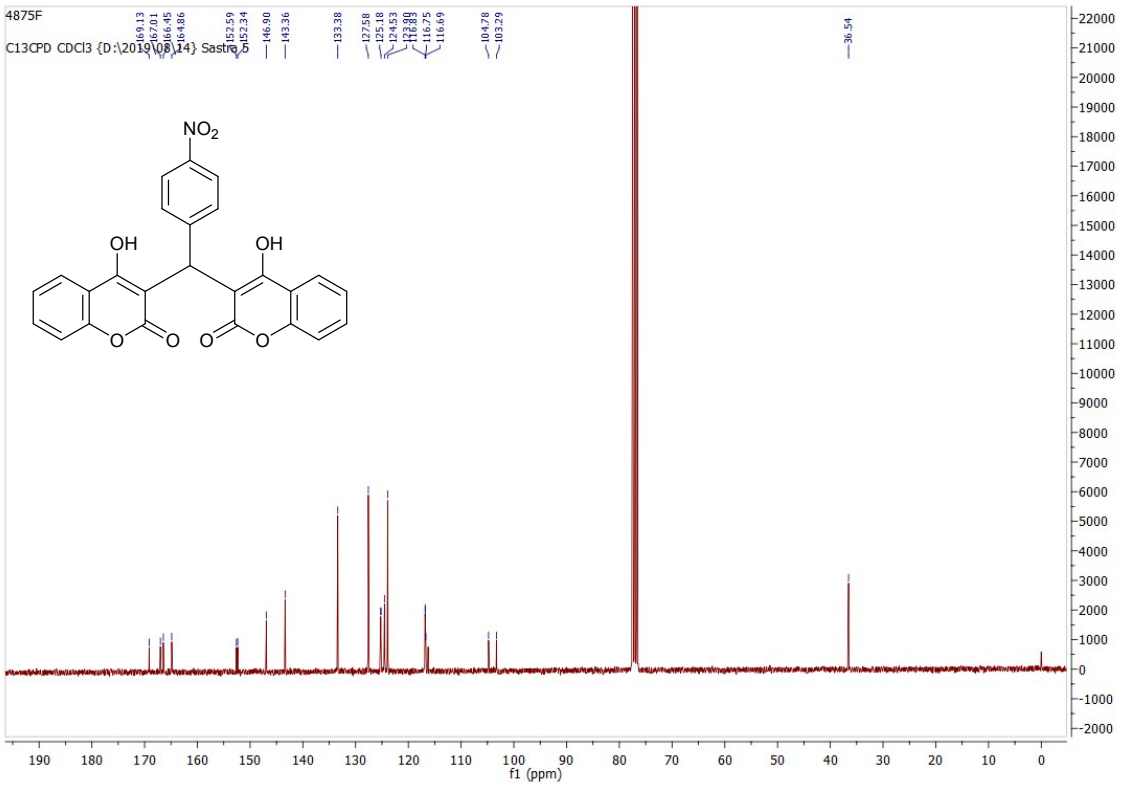

4875G
C13CPD CDCl3 {D:\2019\08\17} Sastra 8
179.26
140.23
134.91
134.35
134.28
133.64
131.15
126.71
119.02
118.83
117.28
109.59
109.42
109.39
108.72
52.02
12.59
12.40
HN
O
N
H
N
H
f1 (ppm)

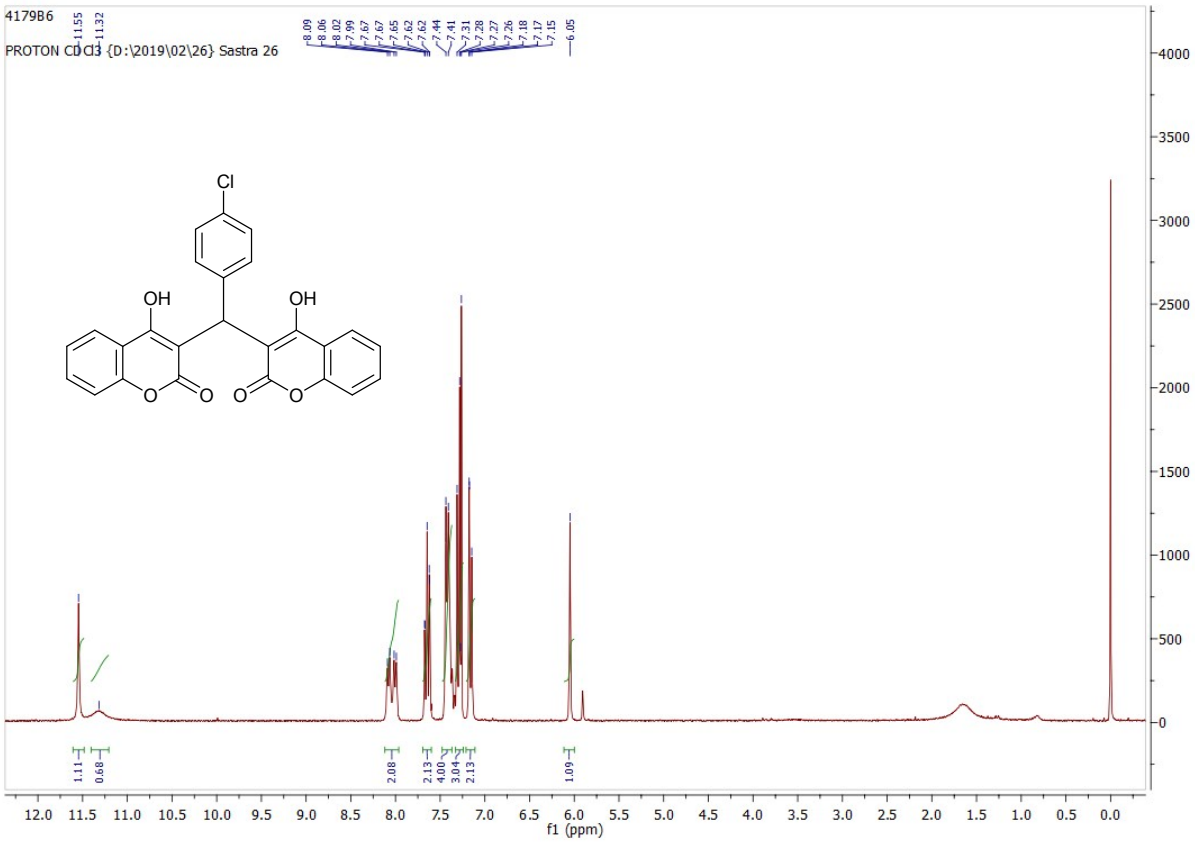

4180E20
PROTON CDCl3 {D:\2019\08\05} Sastra 18
10.36
7.81
7.33
7.30
7.28
7.24
7.21
7.19
7.12
7.09
7.07
7.05
7.03
7.00
6.95
6.92
6.90
6.88
6.85
6.82
4.15
4.12
4.10
4.08
1.41
1.39
1.36
HN
O
N
N
1.16
1.49
4.55
1.09
2.00
1.23
1.37
3.56
3.79
4.07
3.94
6.00
f1 (ppm)

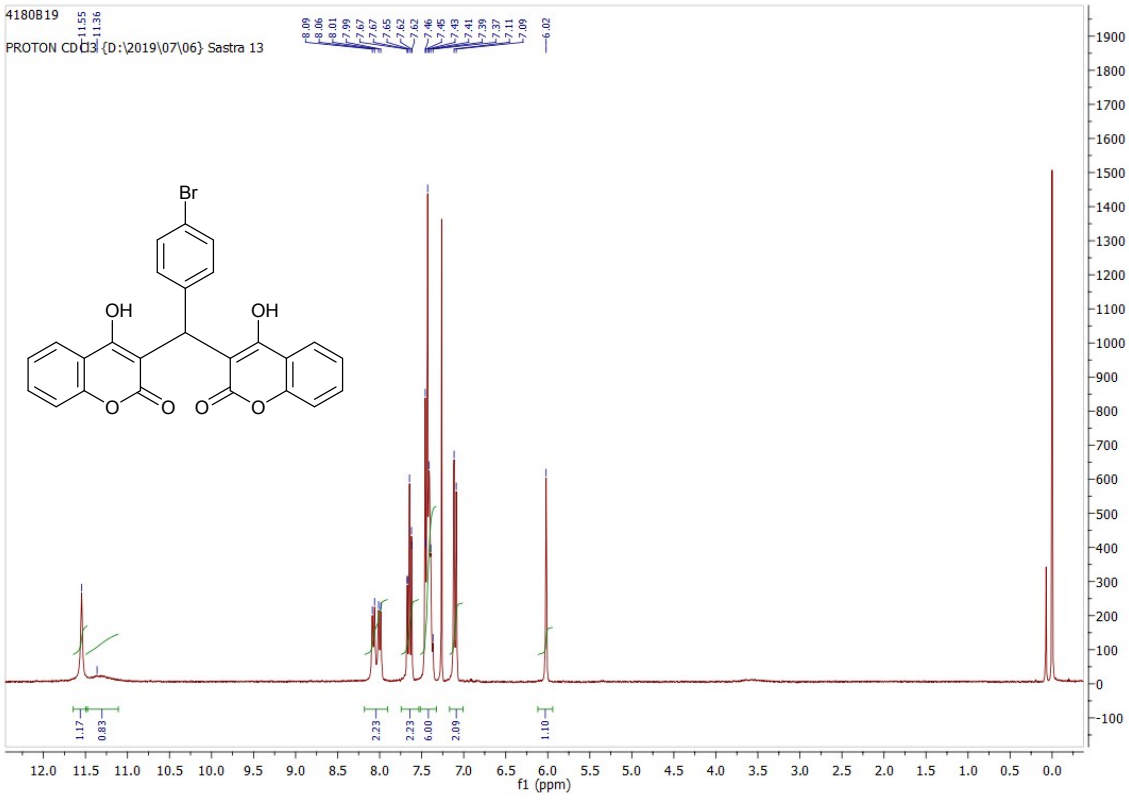

4875I-R
C13CPD CDCl3 {D:\2019\08\19} Sastra 12
178.02
140.13
139.27
135.31
134.85
133.41
126.28
125.73
125.54
125.27
124.47
123.79
123.47
120.59
120.23
120.13
120.00
117.32
112.73
112.61
108.36
108.16
51.62
28.21
14.73
14.24
HN
O
N
N
f1 (ppm)

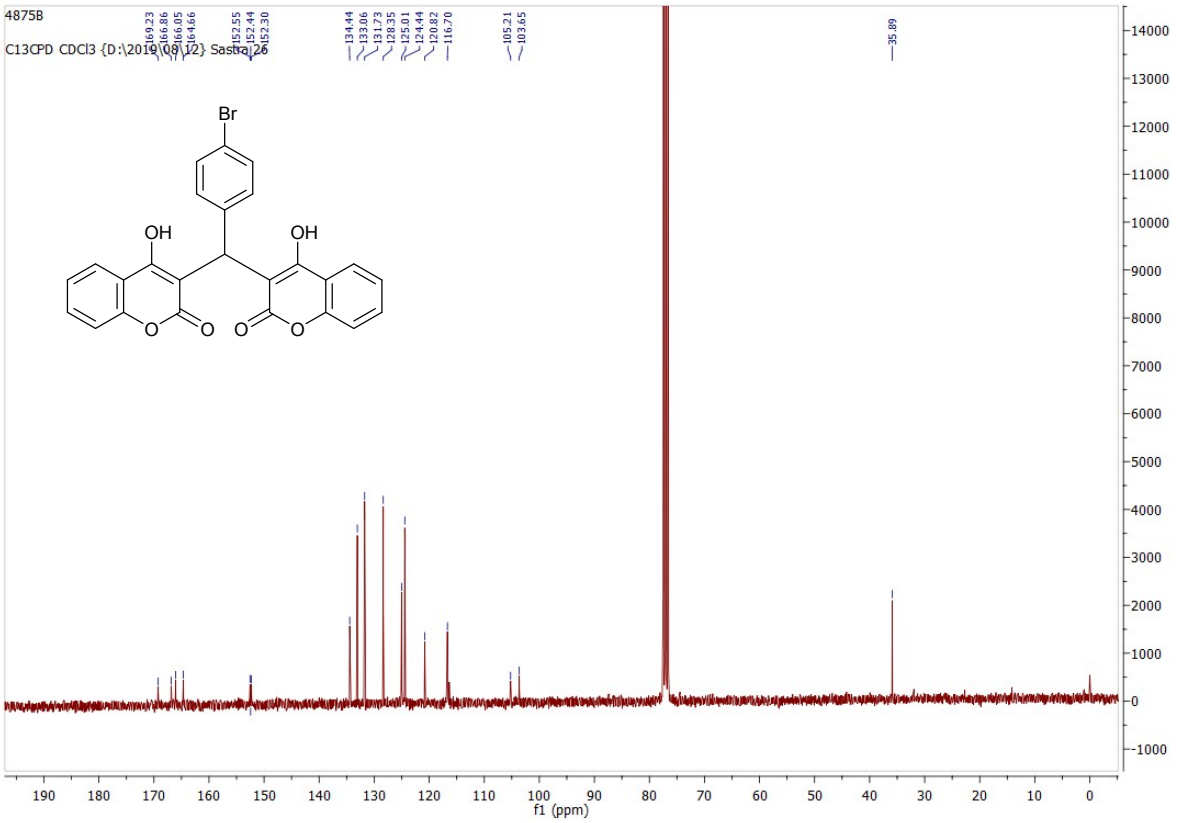

4180C19
PROTON CDCl3 {D:\2019\07\16} Sastra 58
11.53
11.31
8.08
8.06
8.02
7.99
7.63
7.63
7.61
7.60
7.43
7.40
7.33
7.31
7.26
7.24
6.11
OH
OH
O
O
O
O
1.10
0.68
2.04
2.00
4.07
5.10
1.03
f1 (ppm)

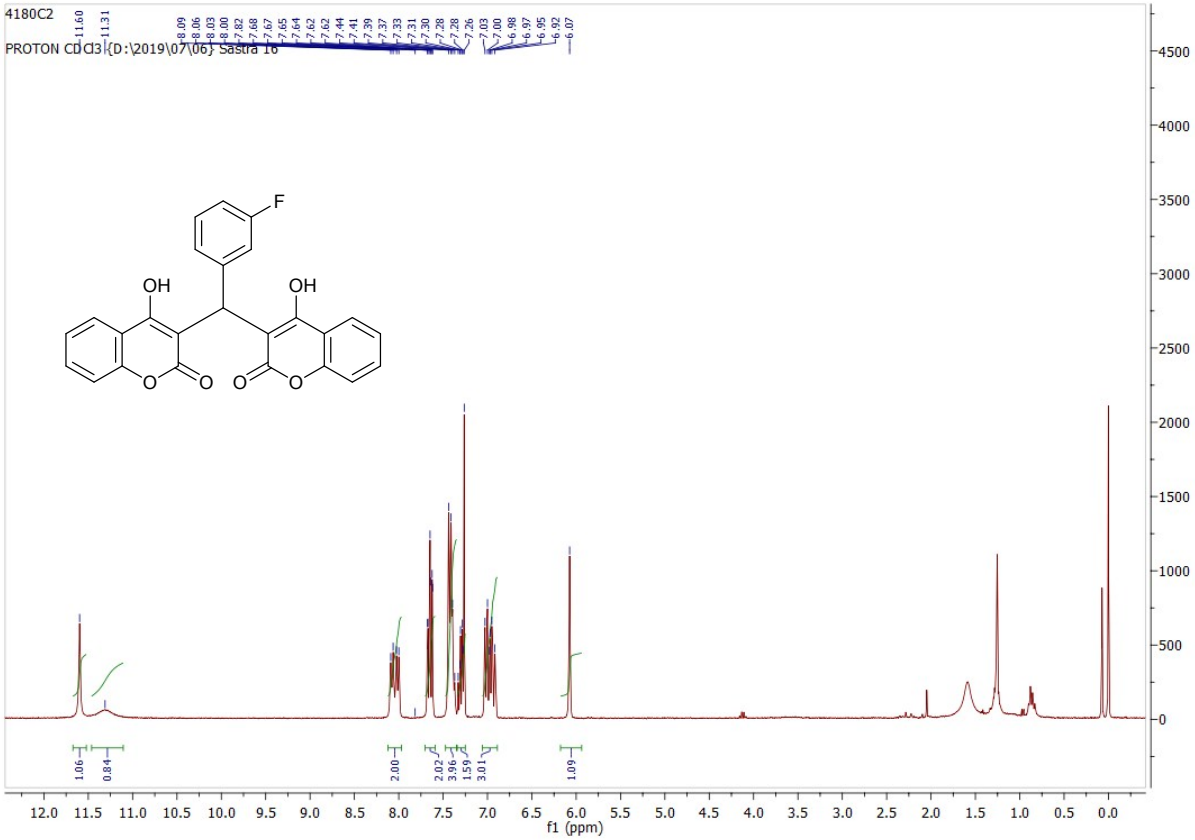

C3419CBa
PROTON CDCl3 {D:\2019\02\20} Sastra 44
NO2
OH
OH
O
O
O
O
f1 (ppm)

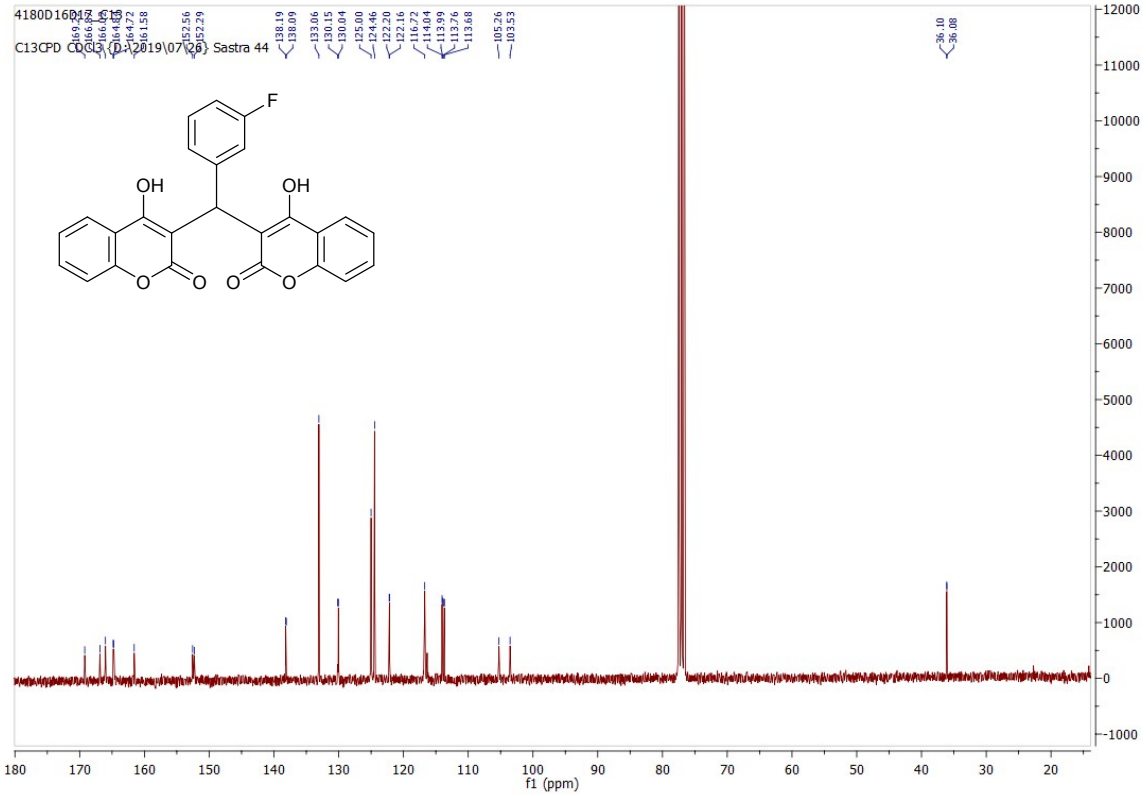

4875F
C13CPD CDCl3 {D:\2019\08\14} Sastra 5
NO2
OH
OH
O
O
O
O
f1 (ppm)

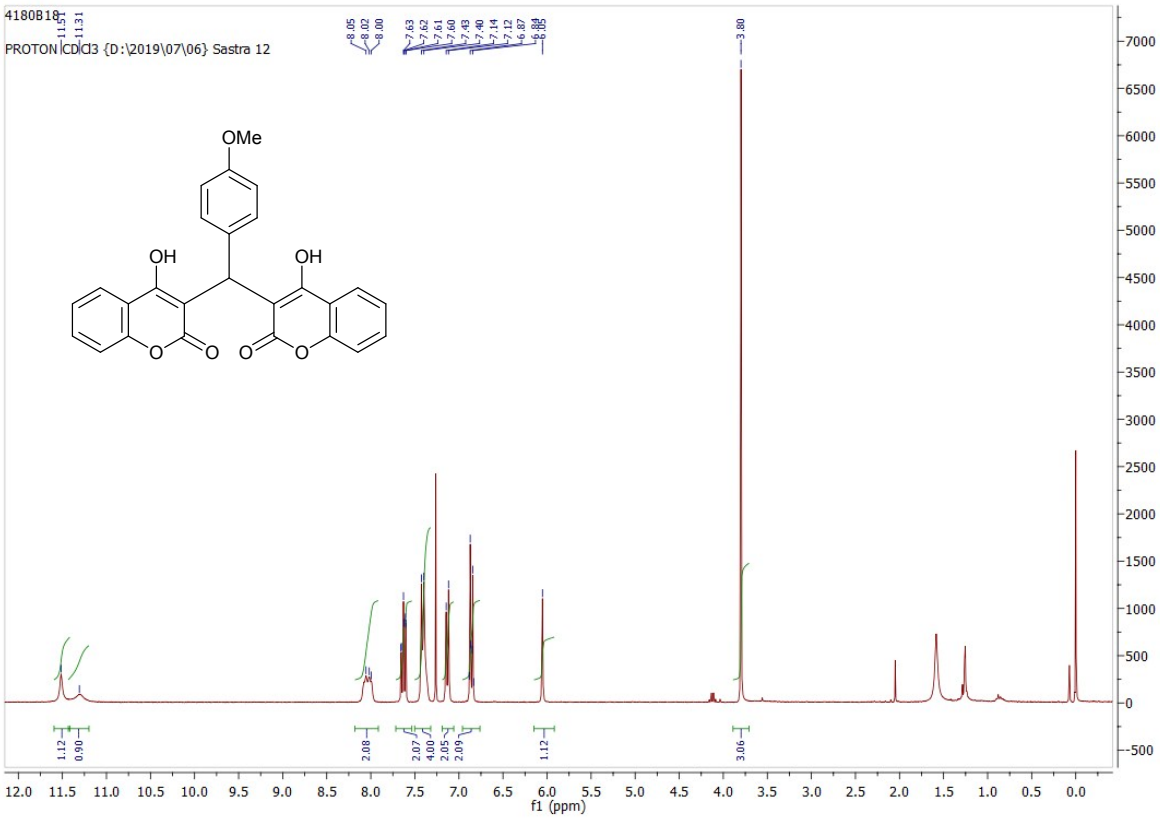

4179B6
PROTON CDCl3 {D:\2019\02\26} Sastra 26
Cl
OH
OH
O
O
O
O
f1 (ppm)

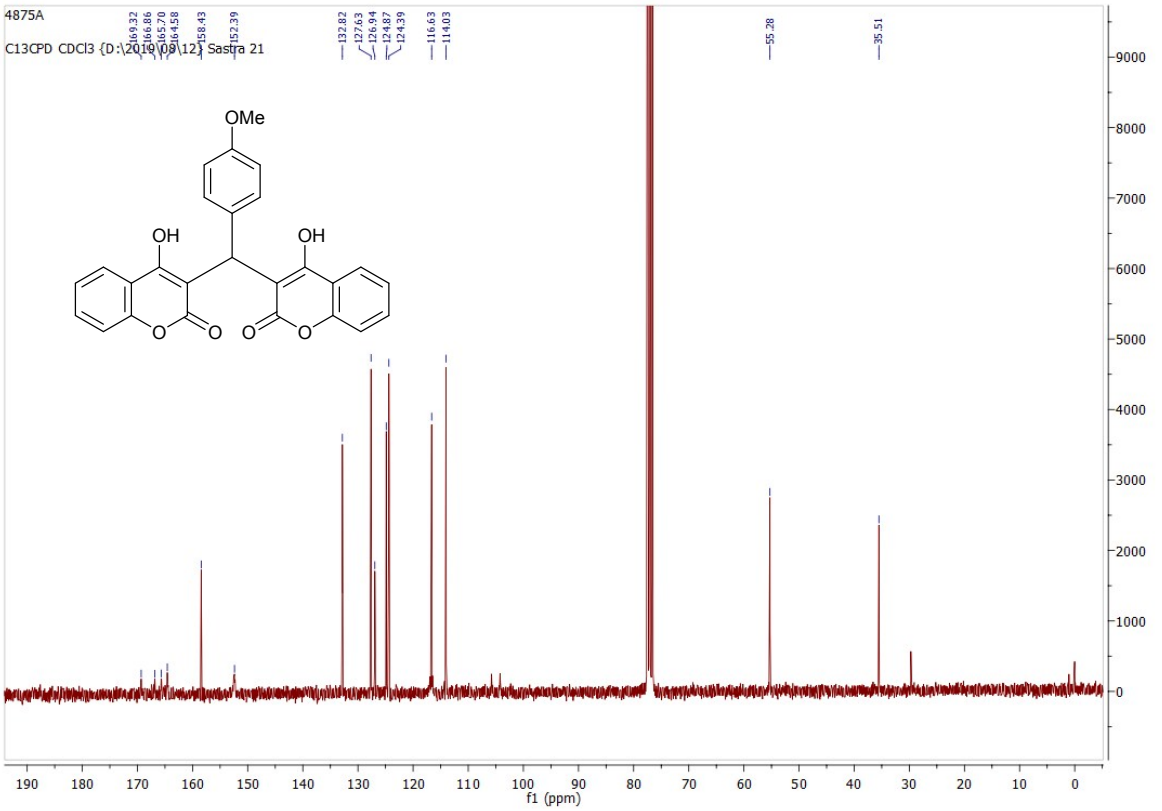

4180B19
PROTON CDCl3 {D:\2019\07\06} Sastra 13
Br
OH
OH
O
O
O
O
f1 (ppm)

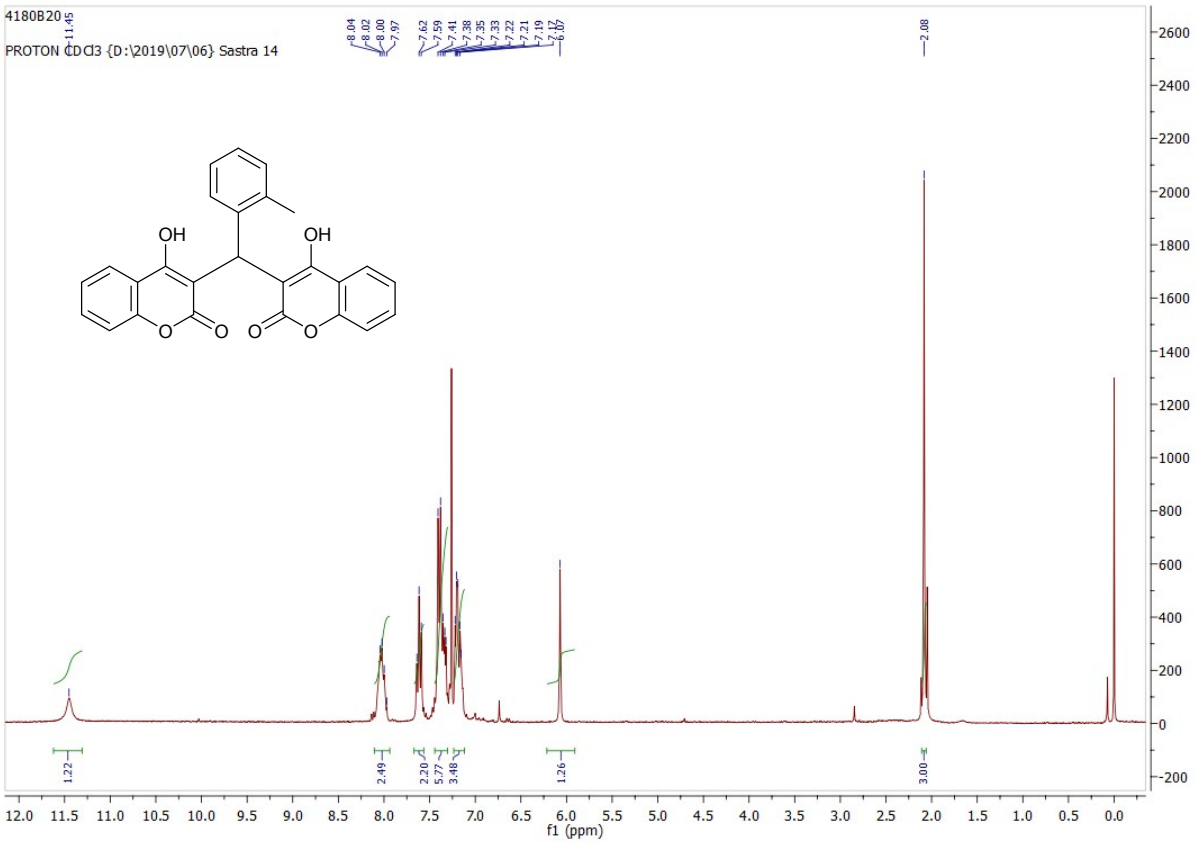

4875B
C13CPD CDCl3 {D:\2019\08\12} Sastra 26
169.23
166.86
166.05
164.66
152.55
152.44
152.30
134.44
133.06
131.73
128.35
125.01
124.44
120.82
116.70
105.21
103.65
35.89
Br
OH
OH
O
O
O
O
f1 (ppm)

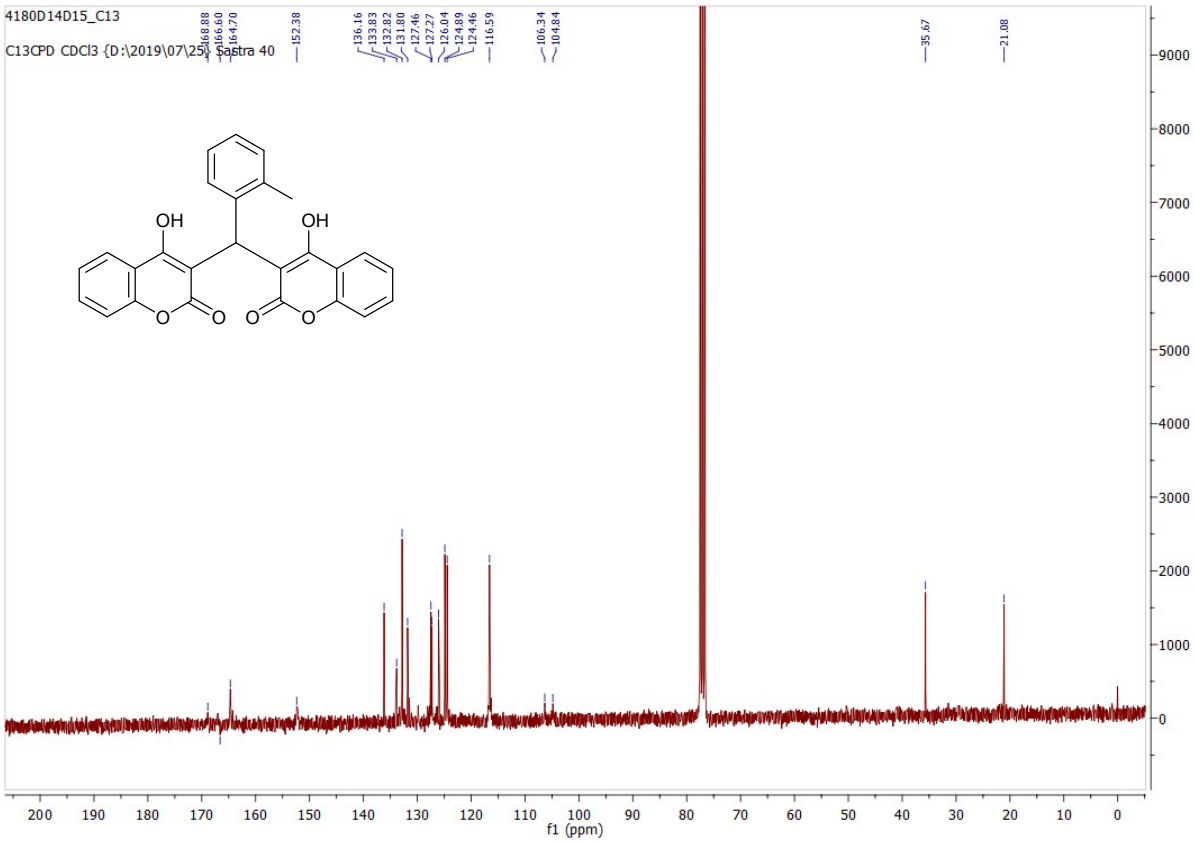

4180C2
PROTON CDCl3 {D:\2019\07\06} Sastra 16
11.60
11.31
8.09
8.06
8.03
8.00
7.82
7.68
7.67
7.65
7.64
7.62
7.62
7.44
7.41
7.39
7.37
7.33
7.31
7.30
7.28
7.28
7.26
7.03
7.00
6.98
6.97
6.95
6.92
6.07
F
OH
OH
O
O
O
O
1.06
0.84
2.00
2.02
3.96
1.59
3.01
1.09
f1 (ppm)

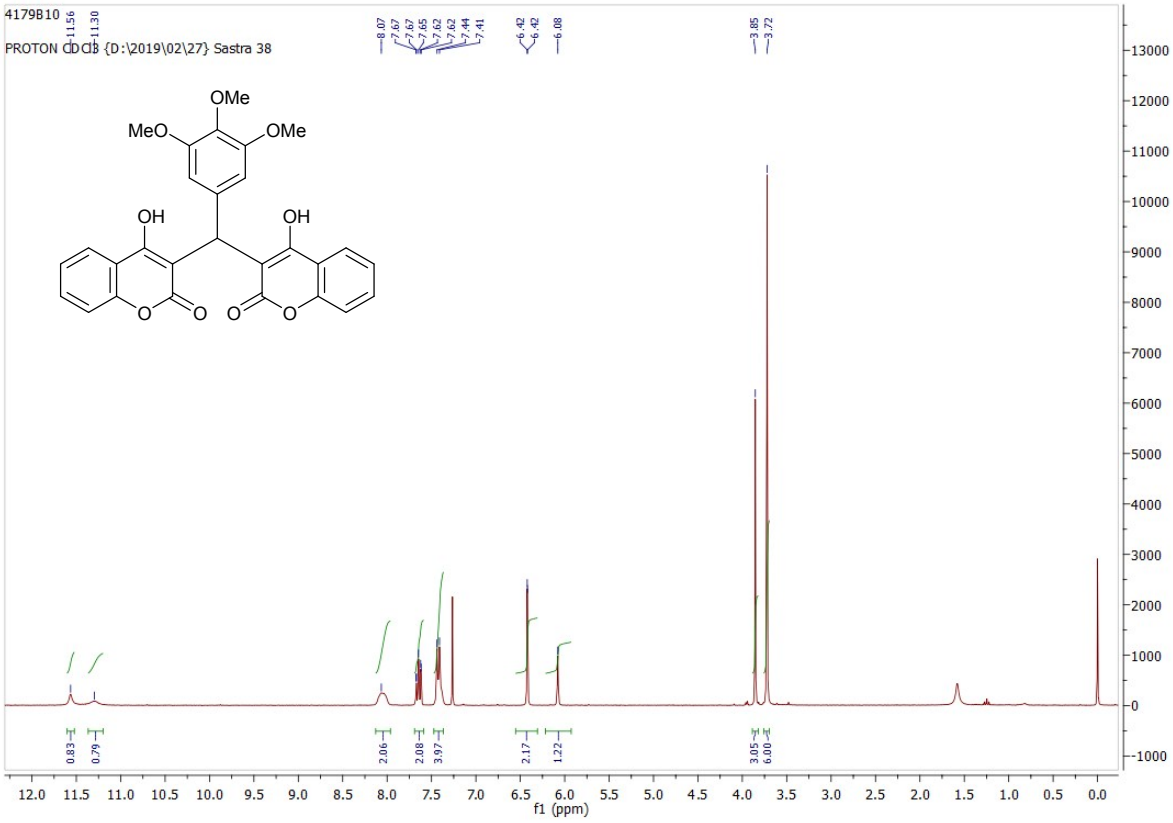

4180D16D13_C13
C13CPD CDCl3 {D:\2019\07\26} Sastra 44
F
OH
OH
O
O
O
O
f1 (ppm)

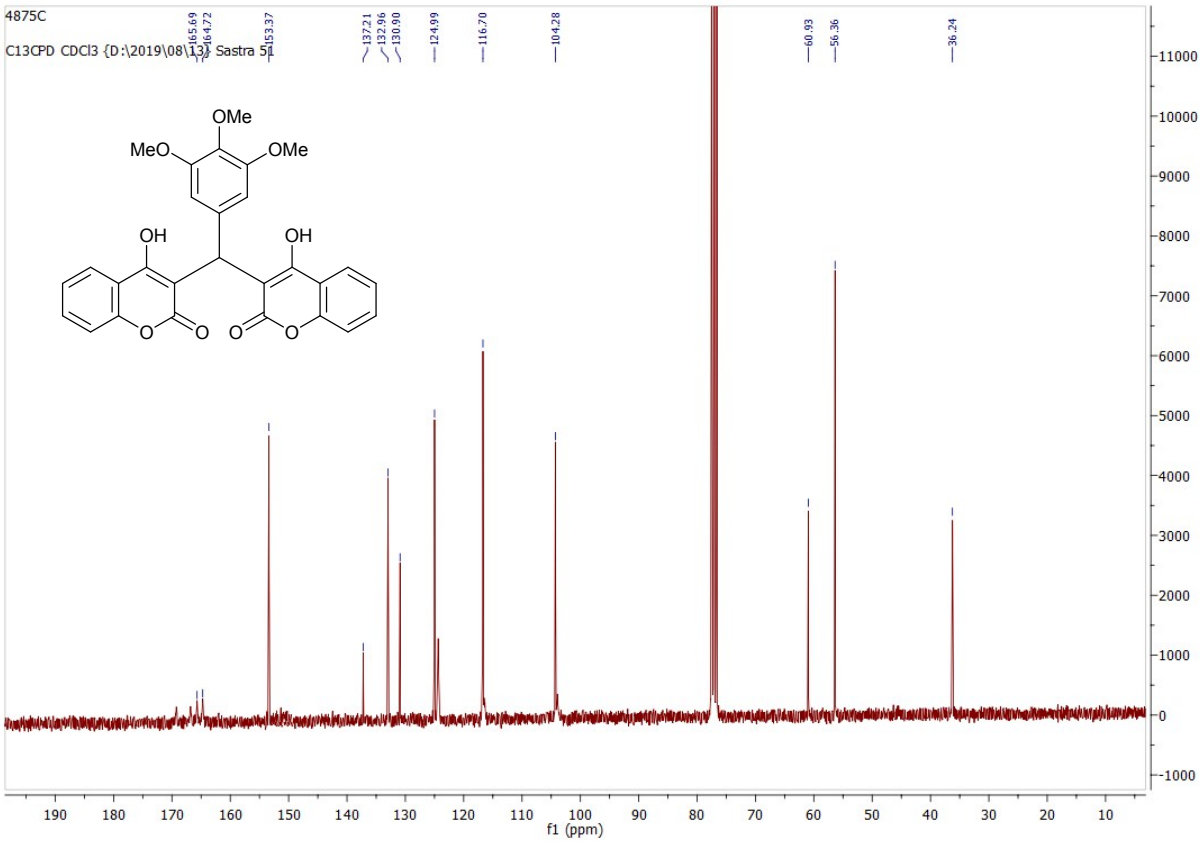

4180B18
PROTON CDCl3 {D:\2019\07\06} Sastra 12
OMe
OH
OH
O
O
O
O
f1 (ppm)

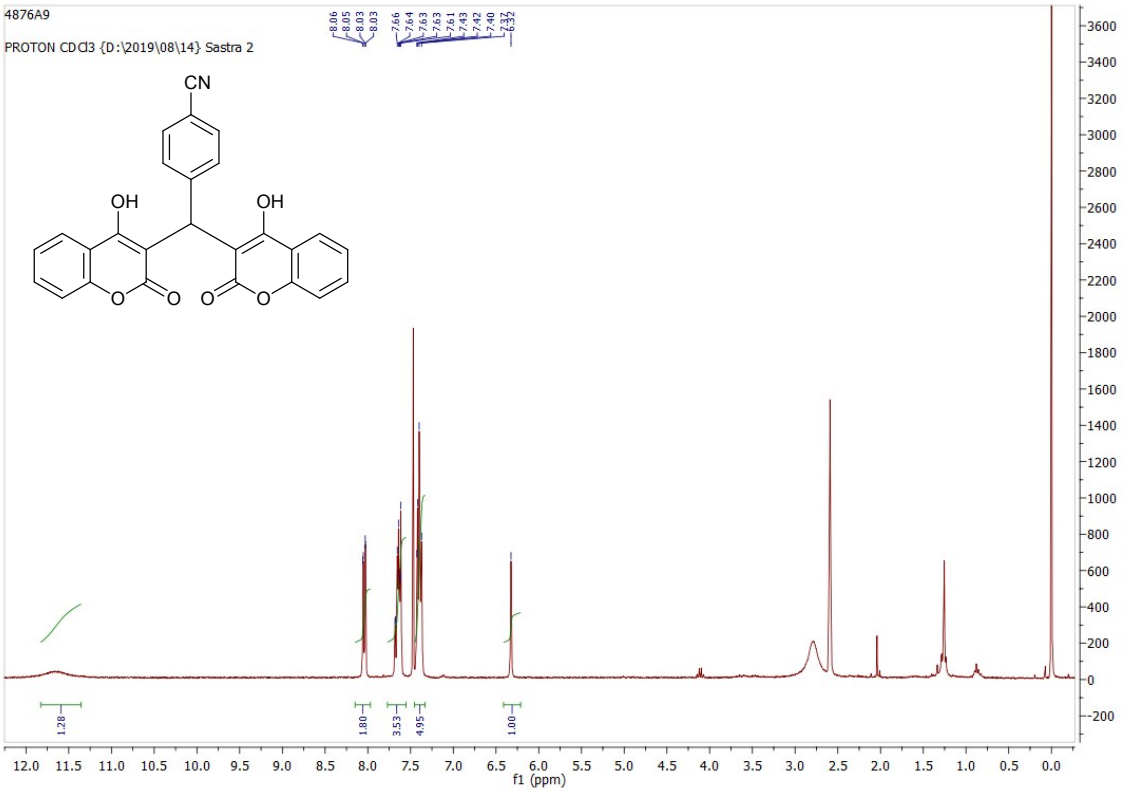

4875A
C13CPD CDCl3 {D:\2019\09\12} Sastra 21
OMe
OH
OH
O
O
O
O
f1 (ppm)

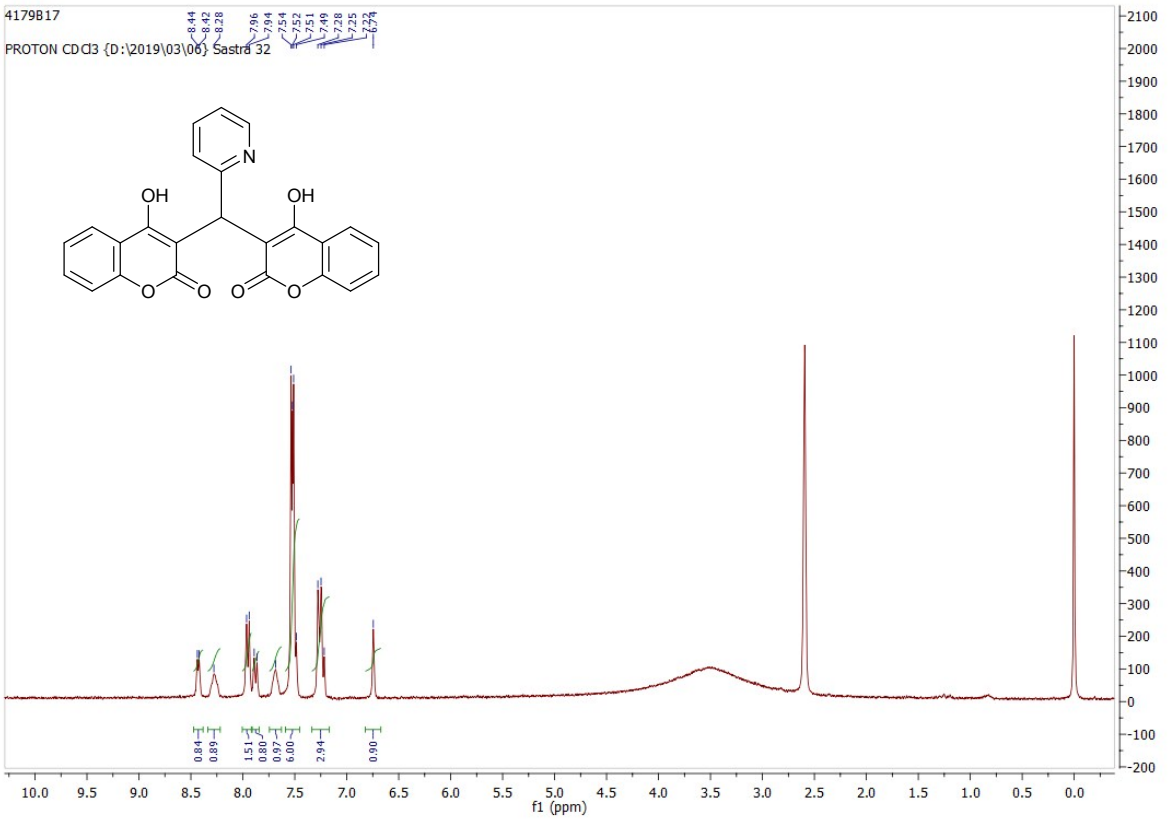

4180B20
PROTON CDCl3 {D:\2019\07\06} Sastra 14
OH
OH
O
O
O
O
f1 (ppm)

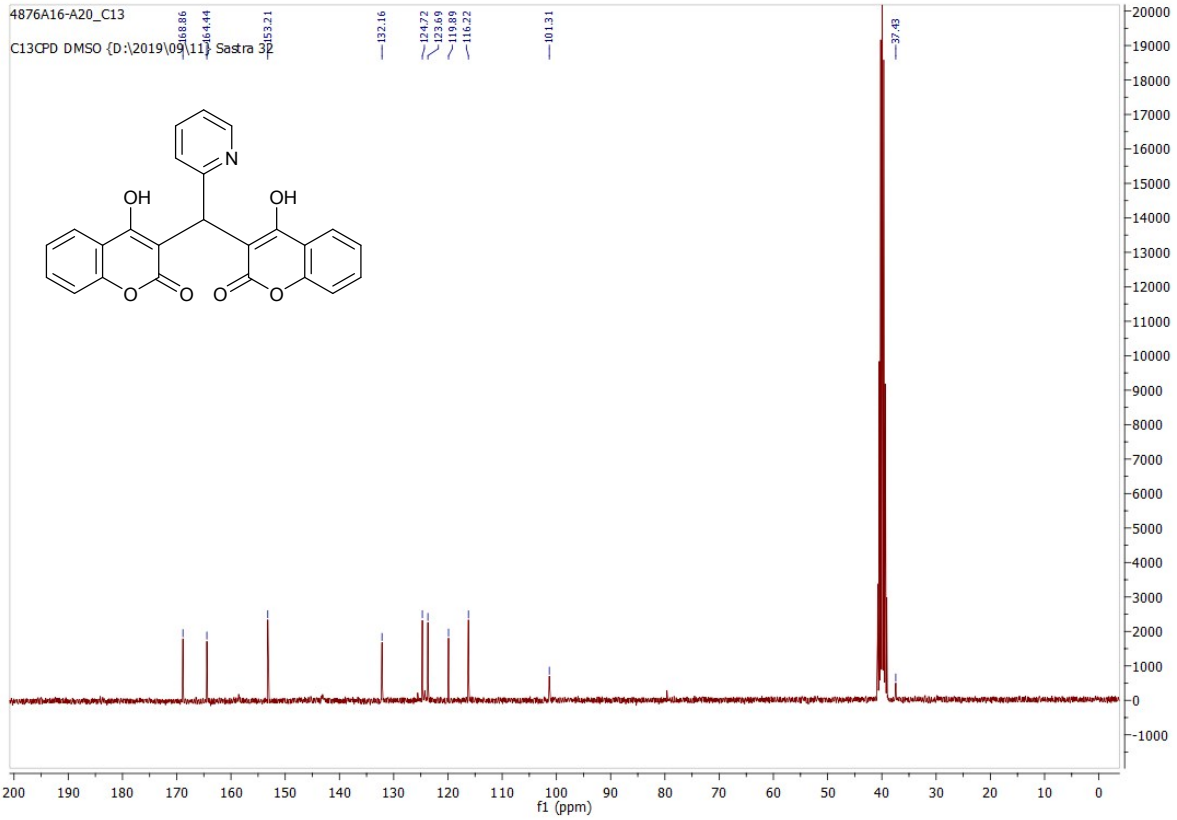

4180D14D15_C13
C13CPD CDCl3 {D:\2019\07\25} Sastra 40
168.88
166.60
164.70
152.38
136.16
133.83
132.82
131.80
127.46
127.27
126.04
124.89
124.46
116.59
106.34
104.84
35.67
21.08
OH
OH
O
O
O
O
f1 (ppm)


4179B10
PROTON CDCl3 {D:\2019\02\27} Sastra 38
11.56
11.30
8.07
7.67
7.67
7.65
7.62
7.62
7.44
7.41
6.42
6.42
6.08
3.85
3.72
OMe
MeO
OMe
OH
OH
O
O
O
O
0.83
0.79
2.06
2.08
3.97
2.17
1.22
3.05
6.00
f1 (ppm)


4875C
C13CPD CDCl3 {D:\2019\08\13} Sastra 5
OMe
MeO
OMe
OH
OH
O
O
O
O
f1 (ppm)


4876A9
PROTON CDCl3 {D:\2019\08\14} Sastra 2
CN
OH
OH
O
O
O
O
f1 (ppm)


4179B17
PROTON CDCl3 {D:\2019\03\06} Sastra 32
8.44
8.42
8.28
7.96
7.94
7.54
7.52
7.51
7.49
7.28
7.25
7.22
6.94
OH
OH
N
O
O
O
O
0.84
0.89
1.51
0.80
0.97
6.00
2.94
0.90
f1 (ppm)


4876A16-A20_C13
C13CPD DMSO {D:\2019\09\11} Sastra 32
168.86
164.44
153.21
132.16
124.72
123.69
119.89
116.22
101.31
37.48
OH
OH
N
O
O
O
O
f1 (ppm)