Supporting Information

Auto-Tandem PET and EnT Photocatalysis by Crude Chlorophyll under Visible Light towards Oxidative Functionalization of Indoles

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1.1 General Information

Commercial reagents and solvents were purchased from Merck, Thermo fischer, TCI, Spectrochem, Avra chemicals, and they were directly used without any further purification. Organic solutions were concentrated under reduced pressure using Buchi rotary evaporator and chiller. Flash column chromatography was performed using silica gel (230-400 mesh). Thin layer chromatography (TLC) was performed on Merck (Darmstadt, Germany) TLC Aluminium plates precoated with silica gel 60 F_{254} of size (20 x 20 cm). ^{1}H , ^{13}C and ^{19}F NMR were recorded on Bruker 300 MHz (75 MHz) and 400 MHz (100 MHz) instruments, ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to residual chloroform (7.26 ppm) and dimethyl sulfoxide (2.5 ppm) in deuterated solvents respectively. ^{13}C NMR chemical shifts are reported in ppm relative to chloroform (77.16 ppm) and dimethyl sulfoxide (39.52 ppm) in deuterated solvents (chemical shifts were internally referenced to TMS). Coupling constants are reported in Hz. Data for ^{1}H NMR is written following the pattern: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, dt = doublet of triplets, br = broad signal), coupling constants (*J* Hz). Data for ^{13}C NMR are reported in terms of chemical shifts only. Melting points were recorded on DBK- Programmable Melting point Apparatus. ESMS were recorded on LC/triple quadrupole mass spectrometer by electrospray ionisation. High resolution mass spectra (HRMS) were acquired on LC/QTOF (quadrupole time of flight) mass spectrometer with electrospray ionisation source.

2. Experimental Procedures

2.1. Extraction method of Chlorophylls, and estimation of Chl a concentration

The shade dried leaves of spinach (10kg), purchased from local market, were soaked in acetone (10L) and the cold percolation was done. The percolate was concentrated under reduced pressure to obtain 100g of crude chlorophyll extract (c-Chl) which was used directly in the reaction, without further purification. The concentration of chlorophyll a in the crude extract was determined by UV-Vis spectroscopy based on Wellburn equation.[1] The spinach leaves extract thus obtained was found to contain 12.30 μg/mL of chlorophyll a.

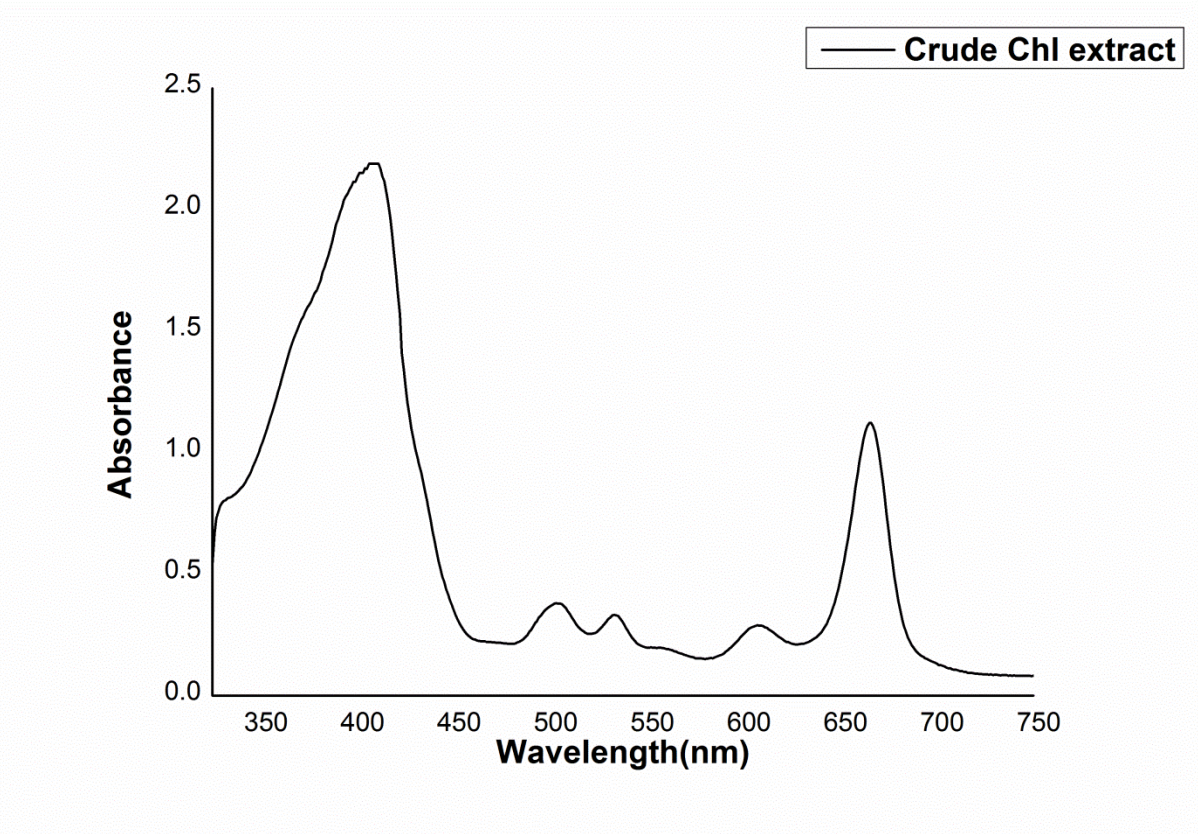
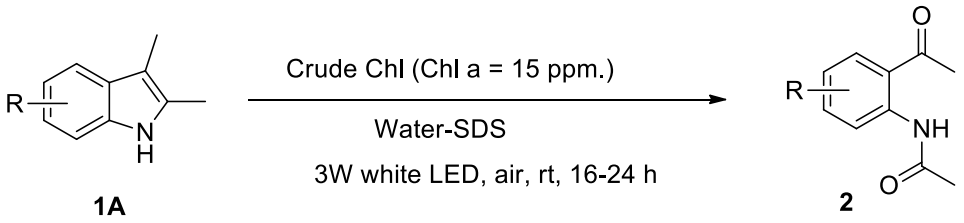
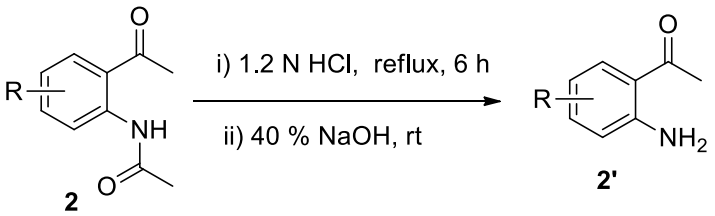


Figure FS1: UV-Vis Spectroscopy of crude chlorophyll extract dissolved in 90% Acetone/Water (triple distilled water)

2.2. General procedures for synthesis of compounds 2, 3, 4, 5, 7



2,3-Dimethylindoles (either commercially available or synthesized as per literatures)[2] **(1A)** (0.2 mmol, 1equiv.), crude chlorophyll [containing Chl a = 15 ppm) were added to a glass vial (30 mL) with water (10 mL)- SDS (1 equiv.) [K_3PO_4 was used for the synthesis of compounds 3, 4, 5 whereas same reaction method was followed for the synthesis of compound 7] and the mixture was then irradiated with a 3W white LED (approximately 2 cm away from the light source) under air atmosphere. Progress of the reaction was monitored by TLC. After completion, the reaction mixture was diluted with 5 mL of 5% aqueous sodium thiosulfate pentahydrate ($Na_2S_2O_3{\cdot}5H_2O$) solution and extracted with EtOAc (3 x 50 mL). The organic layer was washed with brine and dried over anhydrous Na_2SO_4, filtered and concentrated by rotary evaporator. The residue was purified by flash chromatography to give desired product **2** using hexane/ EtOAc as the eluent.

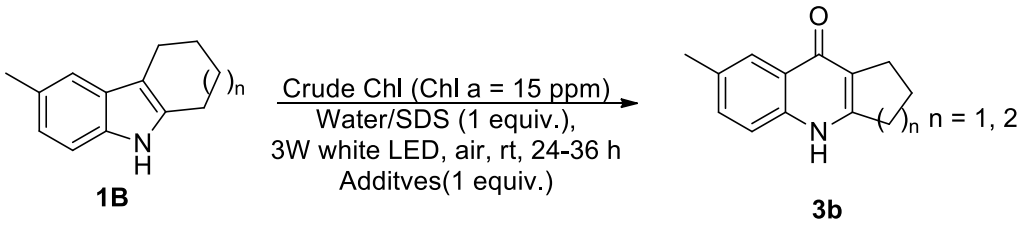


To synthesize unsubstituted or substituted 2'-aminoacetophenones (**2'**) from corresponding N-acetylaminoacetophenones,[3] removal of N-acetyl group was carried out by refluxing 0.2 mmol of the substrate (**2**) in 1.2 N hydrochloric acid for 6 hours. Thereafter cooled to room temperature, and pH is set to 10 by

adding 40% (w/v) sodium hydroxide, and the reaction mixture was extracted with MTBE (methyl tert-butyl ether, 2 x 50 mL) and dried over Na_2SO_4 and evaporated on rotary evaporator to give the desired product **2'** as brown coloured oil.

2.2A. General procedure for synthesis of compounds **3**,**4**,**5**

Table TS1. Optimisation of acid/Base added in reaction of 1B



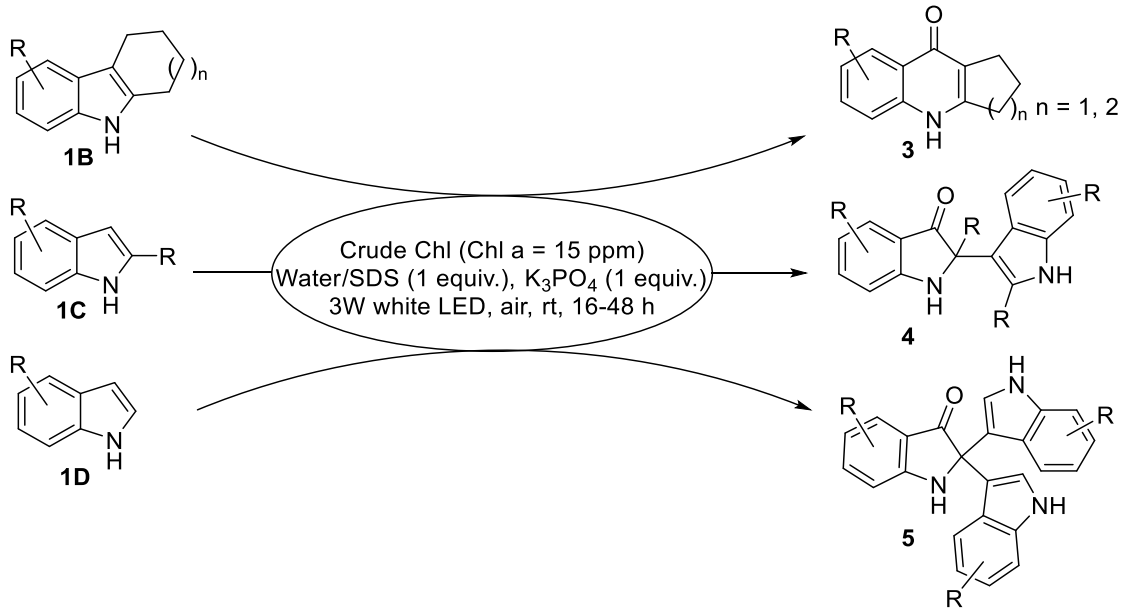
Entry	Additive	Time (h)	Yield (%)[a]
1	-	48	10
2	HCl	24	14
3	p-TSA	36	15
4	NaOH	36	19
5	$NaHCO_3$	48	23
6	K_2CO_3	36	33
7	K_3PO_4	24	45
8	Pyridine	36	21

[a]Isolated yields

For the synthesis of compound **3**, (0.2 mmol, 1 equiv.) base K_3PO_4 was added to the reaction mixture of 1B (0.2 mmol, 1 equiv.) in addition to the aforementioned optimized reaction condition (for 1A).

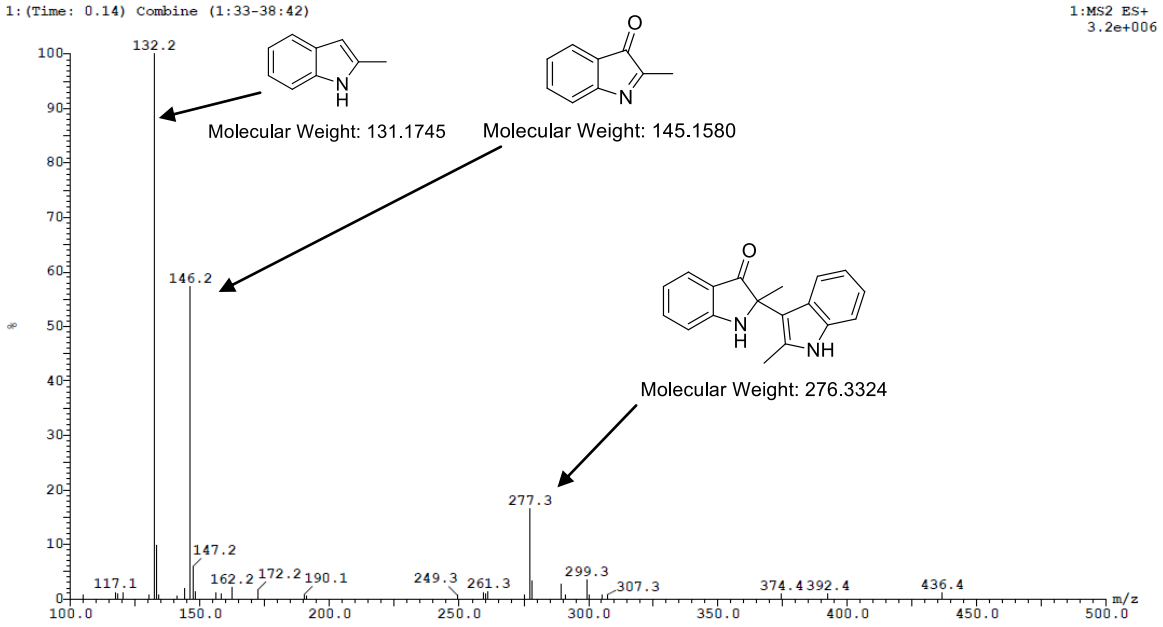
Similar reaction method was followed for the synthesis of compounds **4** and **5** (0.1 mmol, 0.5 equiv. of K_3PO_4 was used) as in the case of compound 3. In case of substituted 2-phenylindoles (i.e., for the synthesis of products, 4c-e),

Cs_2CO_3 (0.2 mmol, 1equiv.) and acetonitrile were used as base and reaction solvent respectively instead of K_3PO_4 and water-SDS solvent system.

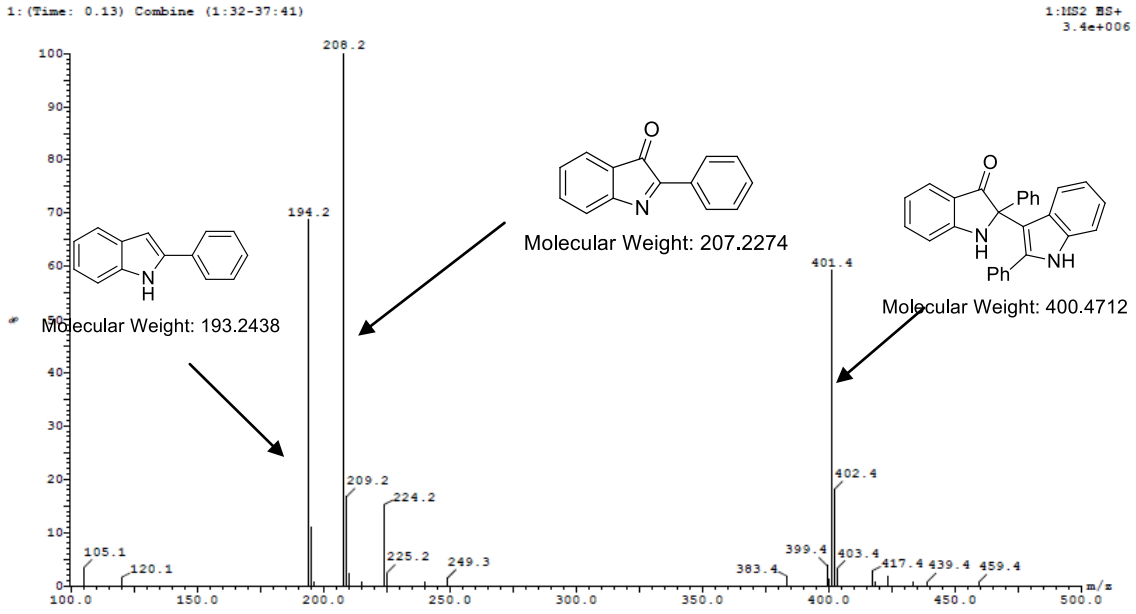


2.2B. ESMS Spectrum of Reaction Mixture of substrate 1C (for identification of possible intermediate)

For a reaction of 2-methylindole



For a reaction of 2-phenylindole



3. Mechanistic Investigation

3.1. Control Experiments

Some control experiments were performed to investigate the mechanism of the photooxidative cleavage of 2,3-dimethylindoles **(1a)**. At first 2,2,6,6-tetramethylpiperidinooxy (TEMPO) or 2,6-di-tert-butyl-4-methylphenol (BHT) (radical scavengers) (0.6 mmol, 3 equiv.) was added to the reaction system, and the yield of **2a** decreased, which suggested the involvement of radicals in reaction method. Then the singlet oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO), or sodium azide (NaN_3) (0.6 mmol, 3 equiv.) was added, in these cases also decreased yield of **2a** was observed.

Therefore, the role of singlet oxygen was also found to be significant for the reaction to proceed.

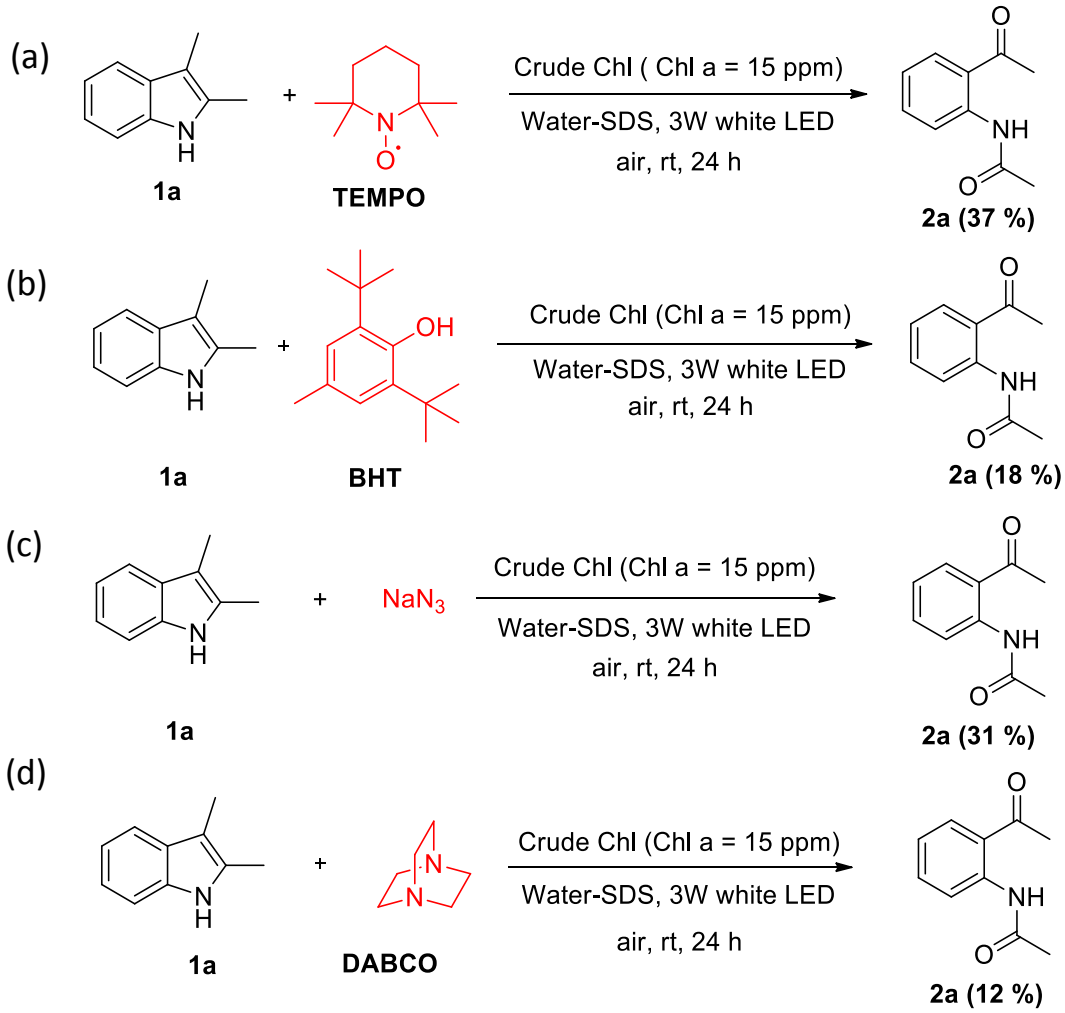


Figure FS2. Control experiments under different conditions. Reaction conditions: air atmosphere and irradiation with 3W white LED, **(1a)** (0.2 mmol), SDS (0.2 mmol) crude Chl a (PC) (15 ppm), temperature (rt, 25 °C) in a 30 mL glass vial (H_2O,10 mL) with: (a) 2,2,6,6-tetramethylpiperidinooxy (TEMPO) (0.6 mmol,3 equiv.) was added; (b) 2,6-di-tert-butyl-4-methylphenol (BHT) (0.6 mmol) was added; (c) Sodium azide (NaN_3) (0.6 mmol) was added; (d) 1,4-diazabicyclo[2.2.] (0.6 mmol) was added. Yields were determined by ^{1}H NMR using dibromomethane as the internal standard.

3.2. Stern-Volmer fluorescence quenching experiments

At first we investigated the excitation and emission spectra of the photocatalyst crude chlorophyll. A solution of crude chlorophyll (**PC**) (with chlorophyll a concentration 1.0 μM) in DMSO was chosen as the model. The fluorescence maximum was obtained at 671 nm when exited at 433 nm (excitation maximum of chlorophyll a) [Fig. FS3a and FS3b]

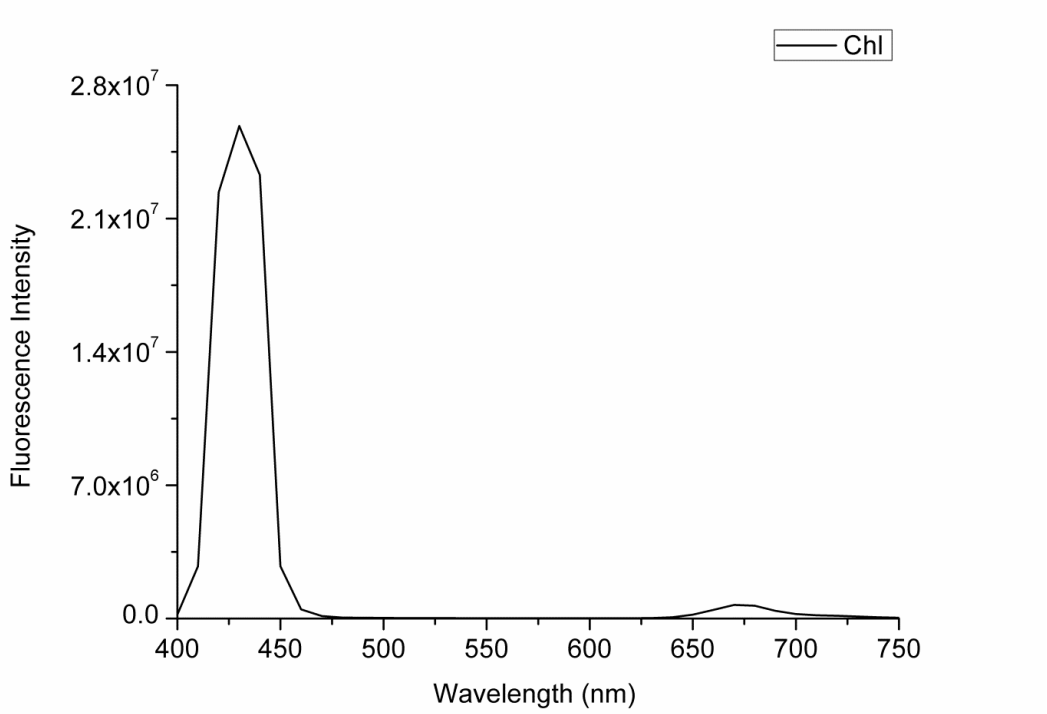


Figure FS3a. The fluorescence excitation spectrum of crude chl a with the detection wavelength of 670 nm.

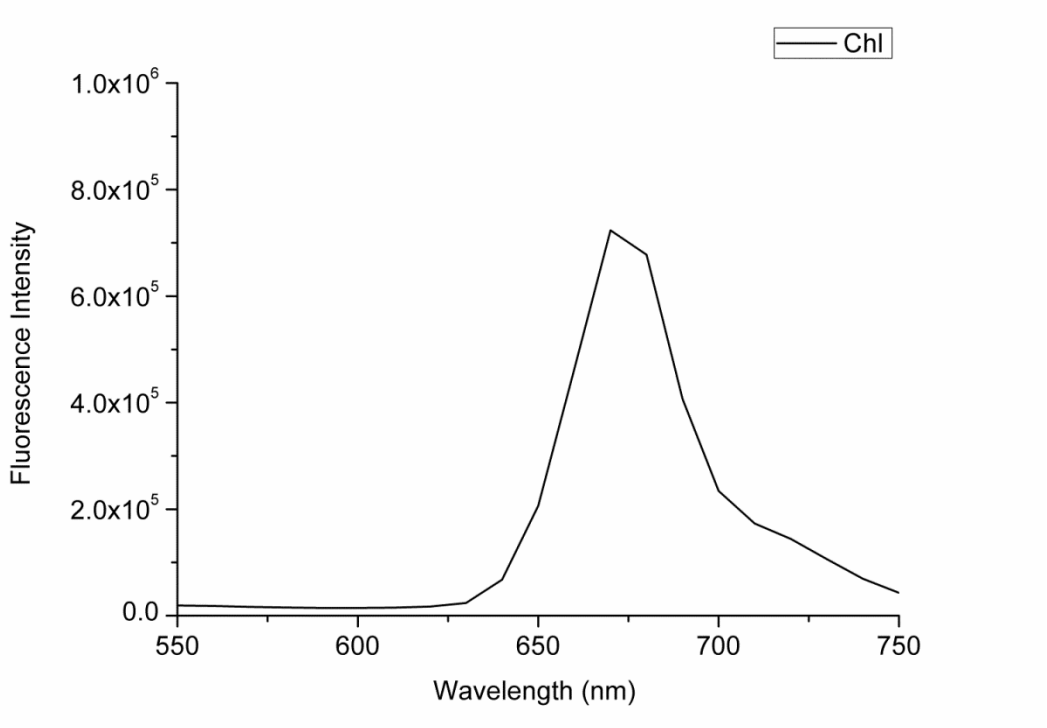


Figure FS3b. The fluorescence emission spectrum of crude chl a excited at 433 nm.

Next we performed the Stern-Volmer fluorescence quenching experiment on the FlexStation 3 Multi-Mode Microplate Reader. The experiments were conducted by adding 300 μL solution of crude chlorophyll (Chl a conc. = 1μM) in DMSO,

to individual well of Corning 96 well cell plate, then 1mM solution of quencher in DMSO **(1a)** was added into the well by 5µL successively, and the emission spectrum of the sample was recorded (Fig. FS4). The solution was excited at λ = 433 nm (excitation maxima of Chl a) and the emission intensity at λ = 672 nm (670 nm) (emission maxima of Chl a) was observed (Fig. FS5), significant decrease in emission intensity occurred on subsequent addition of quencher. Thereafter we conducted another Stern-Volmer fluorescence quenching experiment to investigate the effect of oxygen. 300 µL solution of crude chlorophyll (1µM of Chl a) in DMSO was bubbled with oxygen stream for several seconds. The solution was excited at λ = 431 nm and emission intensity at λ = 672 nm was recorded (Fig.FS6) and there was no significant decrease in emission intensity of chlorophyll. As per the observations, probability of an electron transfer between chlorophyll and quencher **1a** could be envisioned.

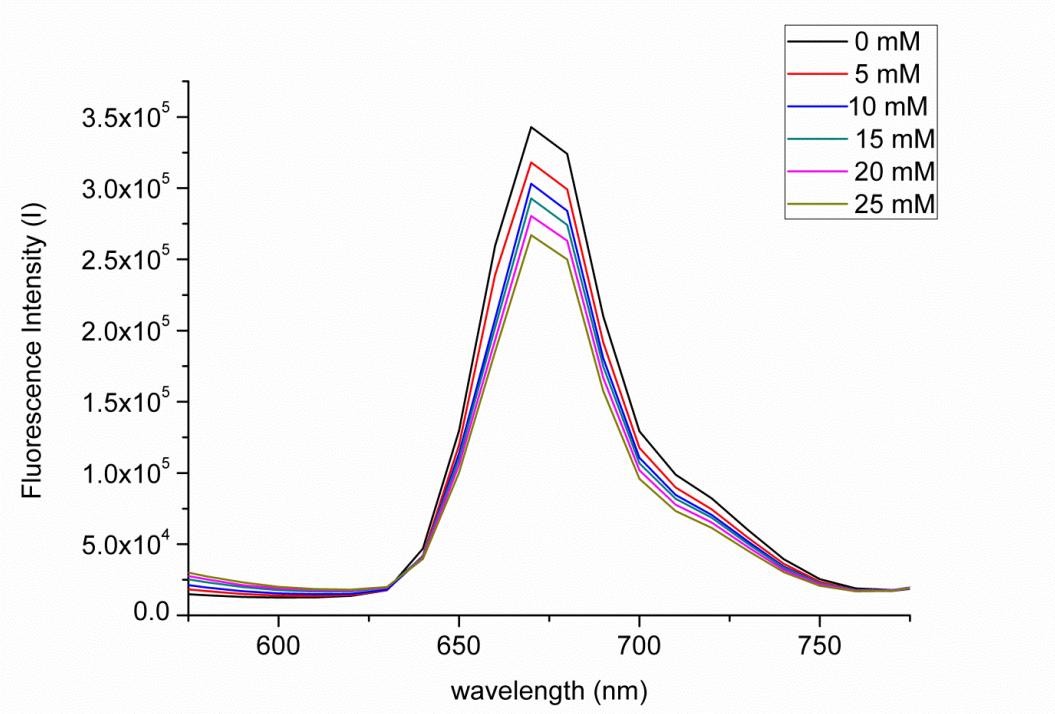


Figure FS4. The fluorescence emission spectra of crude chlorophyll a with different concentration of added quencher excited at 433 nm.

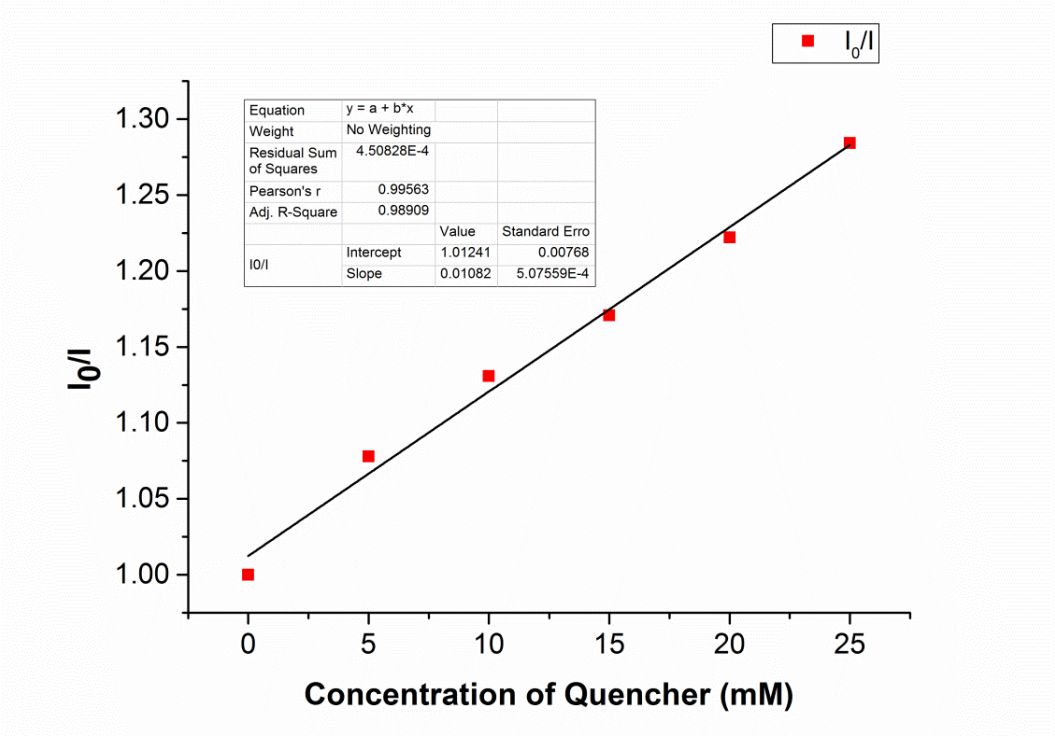


Figure FS5. Crude Chl a (**PC**) emission quenching by **1a**. Linear quenching was observed.

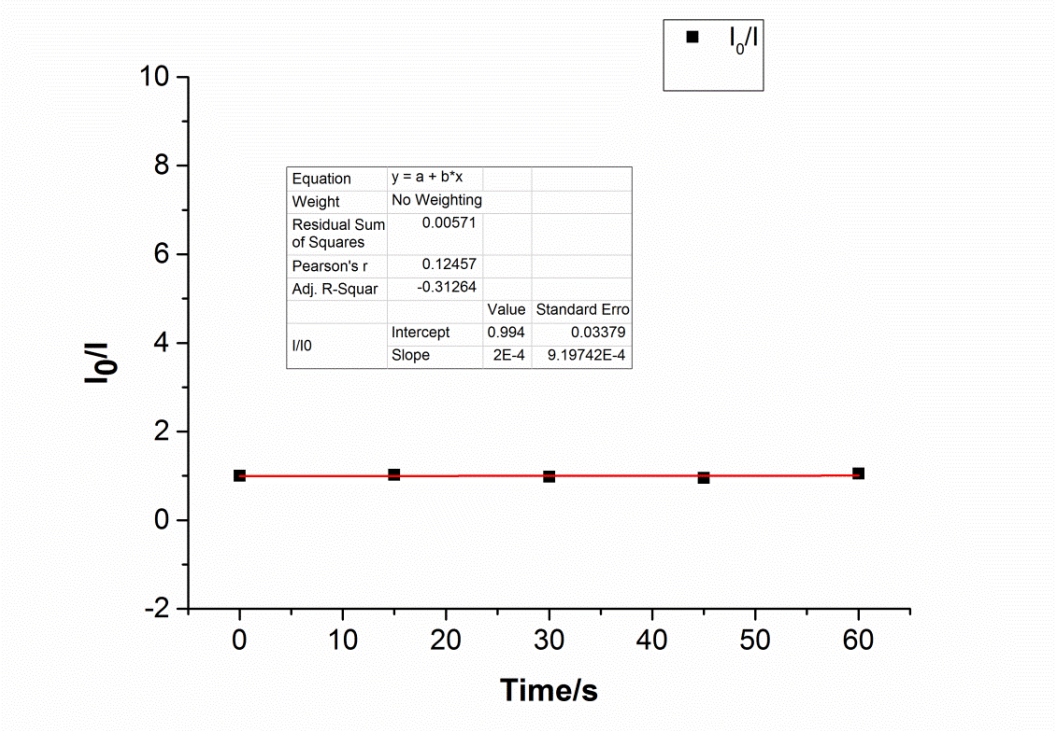


Figure FS6. Crude Chl a (**PC**) emission quenching by oxygen. There was no significant quenching

3.3. Redox potential estimation of Photocatalyst and Substrates

3.3A. Estimation of excited state redox potentials of Chl a as per Nicewicz *et al*.[4]

$E^*_{red}(cat^*/cat^{\bullet-}) = E_{red}(cat/cat^{\bullet-}) + E_{0,0}$
$E^*_{oxd}(cat^{\bullet+}/cat^*) = E_{oxd}(cat^{\bullet+}/cat) - E_{0,0}$

E* refers to either S_1 or T_1 excited state, with the corresponding $E_{0,0}$ value ($E_{0,0}{}^{S1}$ or $E_{0,0}{}^{T1}$)
For Chl a ground state reduction potential, $E_{red}(cat/cat^{\bullet-})$ = –1.12 V vs SHE and ground state oxidation potential $E_{oxd}(cat^{\bullet+}/cat)$ = 0.81 V vs SHE.[5]
$E_{0,0}(S_1)$ = 1.85 eV, $E_{0,0}(T_1)$ = 1.34 eV.[6] S_1= singlet state, T_1= triplet state
Hence, $E^*_{red}{}^{S1}$(chl a*/chla$^{\bullet-}$) = E_{red}(chl a/chl a$^{\bullet-}$) + $E_{0,0}{}^{S1}$ = -1.12+ 1.84 V= 0.73 V vs SHE. Similarly for $E^*_{red}{}^{T1}$(chl a*/chla$^{\bullet-}$) is found to be 0.22 V vs SHE.

And $E^*_{oxd}{}^{S1}$(chl a$^{\bullet+}$/ chl a*) = E_{oxd}(chl a$^{\bullet+}$/ chl a) – $E_{0,0}{}^{S1}$ = 0.81-1.85 V= –1.04 V vs SHE. Similarly for $E^*_{oxd}{}^{T1}$(chl a$^{\bullet+}$/ chl a*) is found to be –0.53 V vs SHE.

Thus, it is found that Chl a possess E^*_{oxd}(chl $^{\bullet+}$/ chl *) < 0; E^*_{red}(chl */ chl $^{\bullet-}$) > 0 (criteria; prerequisite for an efficient photoredox catalyst)[4] both in singlet excited state as well as in triplet excited state.

3.3B. CV experiments performed for estimation of redox potentials of Substrates

Cyclic voltammetry (CV) was performed on an EG&G PAR 273 potentiostat/ galvanostat with an IBM PS2computer with EG&G M270 software for data acquisition. The three-electrode cell configuration comprised a platinum sphere, a platinum plate and Ag(s)/$AgNO_3$ (0.01 M) as the working, auxiliary and reference electrodes respectively. The supporting electrolyte used was tetraethylammonium hexafluorophosphate $(C_2H_5)_4N(PF_6)$. Samples were prepared with a substrate concentration of 0.01 M in a 0.1 M TEAHFP in acetonitrile electrolyte solution. From the result it was found that, E_{red} (**1a**) = +0.087 V vs SHE[7] (Fig. FS8) is higher than $E^*_{Oxd}{}^{T1}$(Chl a) = -0.53 V vs SHE, $E^*_{Oxd}{}^{S1}$(Chl a) = -1.04 V vs SHE so the excited state of the photocatalyst chlorophyll a could undergo oxidative quenching readily by donating electron to the substrate (**1a**).

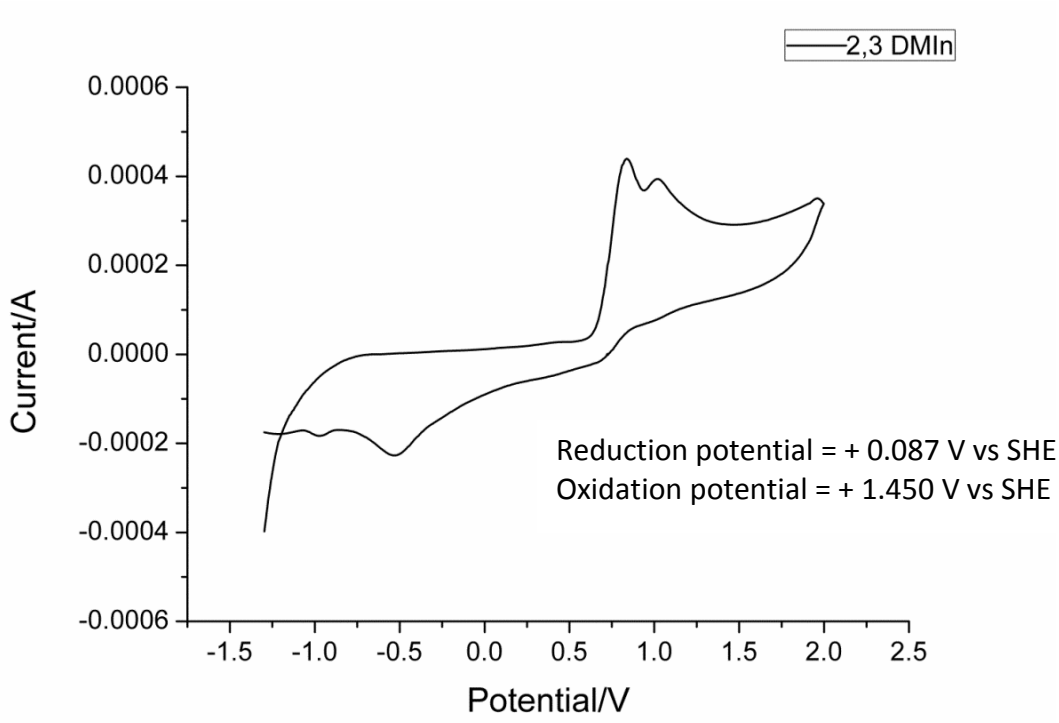
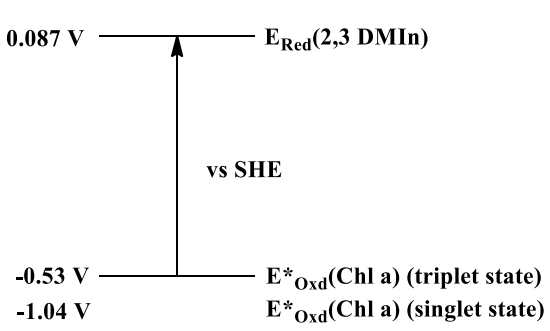
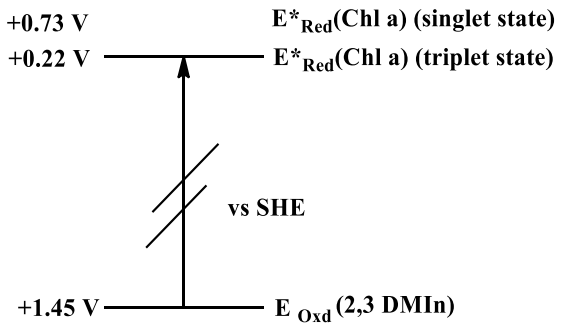


Figure FS7. Cyclic voltammetry experiment of **1a**. Experiment conditions: Init E = 2.0 V, High E = 2.0 V, Low E = -2.0 V, Init P/N = N, Scan Rate = 0.1 V/s, Sample Interval = 0.001 V, Quiet Time = 2s, Sensitivity = $2e^{-4}$ A/V.



Reductive electron transfer (Oxidative quenching of PC)



Oxidative electron transfer (Reductive quenching of PC)

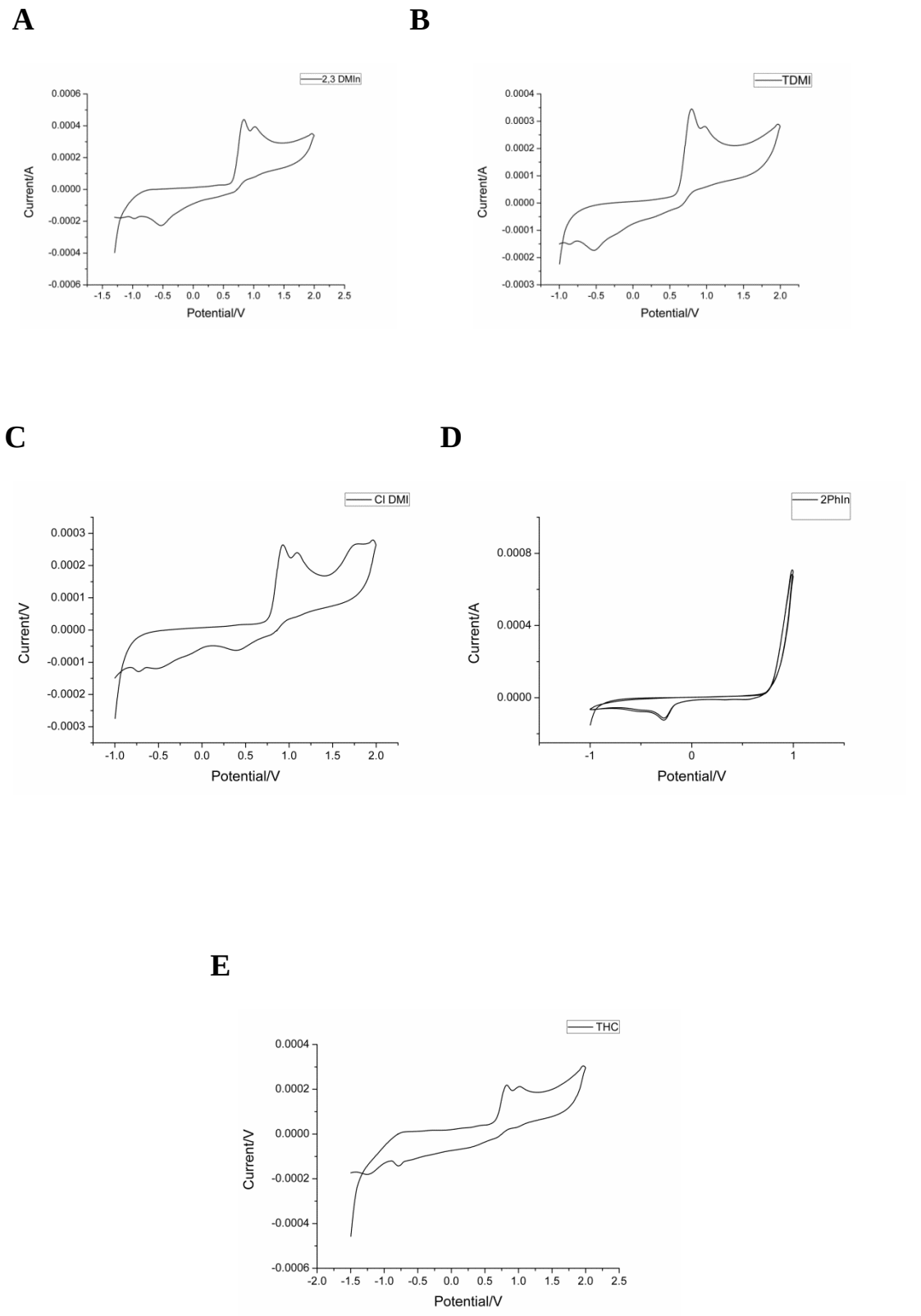
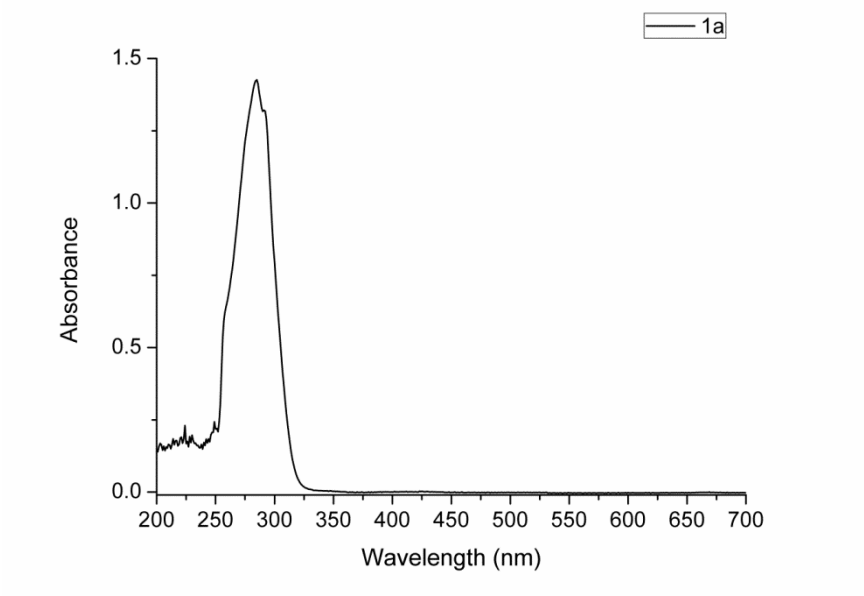


Figure FS8. CV curve of different substrates (0.01M), tetraethylammonium hexafluorophosphate (0.1 M) in CH_3CN. A = 2,3-Dimethylindole, B = 5-Methyl-2,3-dimethylindole, C = 5-Chloro-2,3-dimethylindole **,** D = 2-Phenylindole, E = Tetrahydrocarbazole

3.4. Investigation for EDA complexes

To find out whether chlorophyll could combine with 2,3-dimethylindoles to form the electron donor-acceptor (EDA) complexes, UV-visible experiments were performed on LABINDIA UV 3092 Spectrophotometer with a quartz cuvette of 1.0 cm path length. UV-Vis spectra of **1a** and crude chlorophyll (PC) in DMSO are shown in Fig. FS10 and FS11 respectively. After different concentration of 1a was added to 10^{-6} M (Chl a= 10^{-6} M in DMSO) solution of PC the UV-Vis spectra were recorded.



FigureFS9. UV-visible spectrum of 1a (10^{-2} M in DMSO)

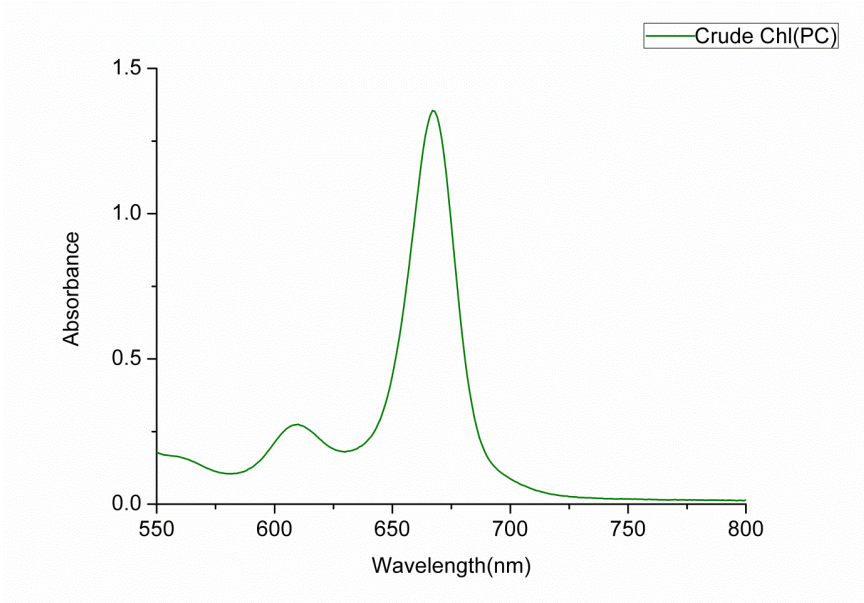


Figure FS10. UV-visible spectrum of PC (10^{-6} M in DMSO)

As it could be observed from the Fig. FS12a, there was no red shift band, which ruled out formation of any EDA complex formation in between PC and substrate. Furthermore we recorded the UV-Vis spectra of the reaction mixture after running the reaction under optimized condition for 5 hours, and compared with that of the crude chlorophyll. In that case also as shown in Fig. FS12b, no red-shift band was observed.

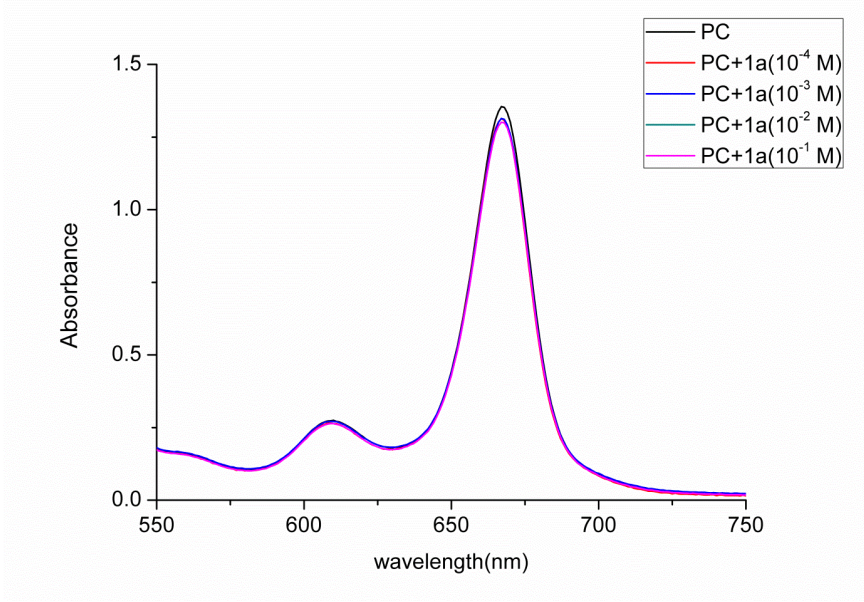


Figure FS11a. UV-visible spectra of PC (10^{-6} M in DMSO) with different concentration of 1a. No red-shift band was observed

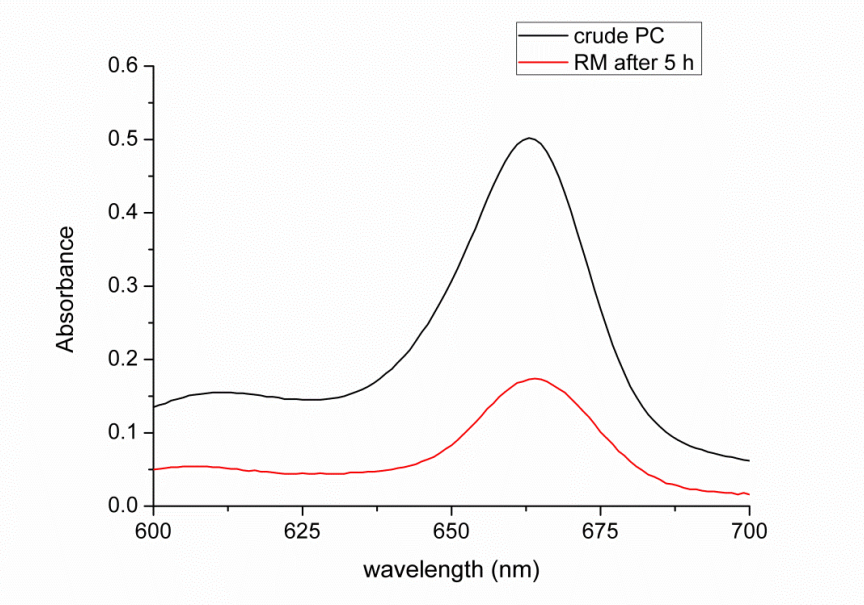
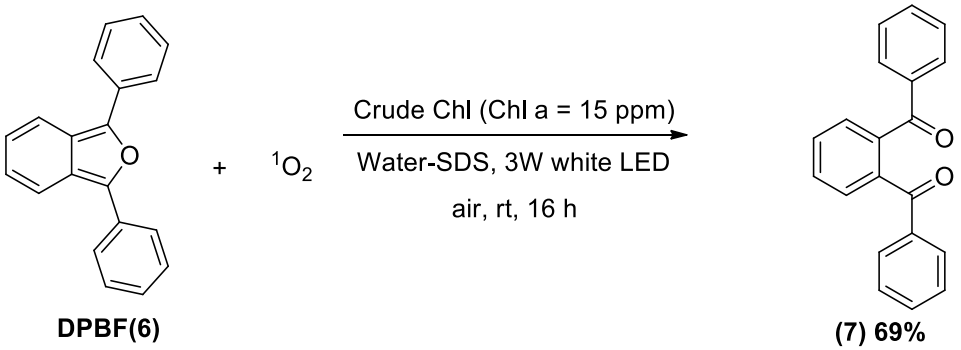
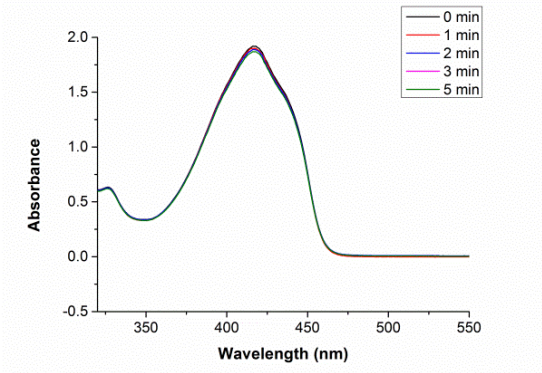


Figure FS11b. UV-Vis spectra RM, PC and 1a, under 3W LED for 5 h

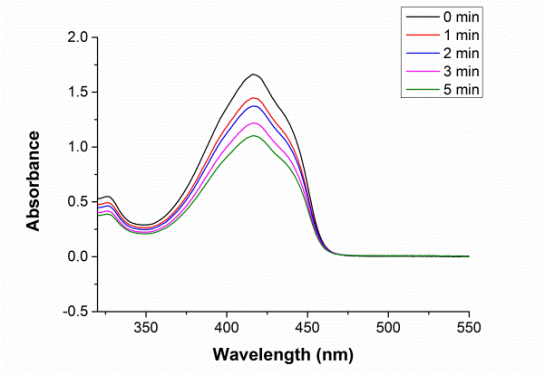
3.5. Investigation of generation of singlet oxygen



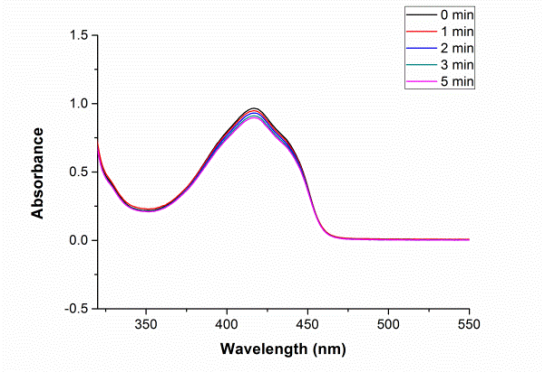
(a) DPBF + [c-Chl] without light



(b) DPBF + [c-Chl] with light



(c) DPBF+[c-Chl]+ SM(200 equiv.)with light



(d) DPBF+[c-Chl]+ SM(500 equiv.) with light

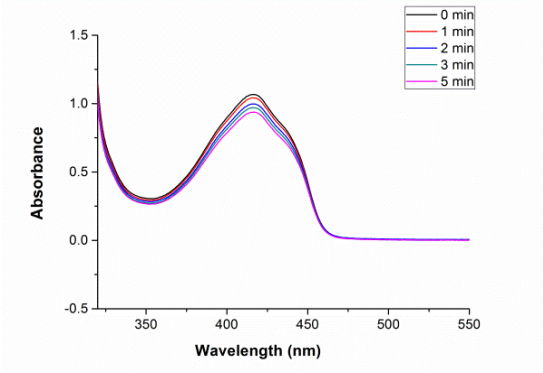


Figure FS12. Time dependent changes in UV spectra of the product formed during oxidation of DPBF (1,3 diphenylbenzo[*c*]furan) by singlet oxygen. **Figure FS13a** and **Figure FS13b** indicated that light did significantly enhance the production of singlet oxygen, which can be determined by DPBF. When **1a** (SM) was added, **Figure FS13c** and **Figure FS13d** indicated that its oxidation is dependent on singlet oxygen. All Reactions were performed by using DPBF (1.5 μM), crude chlorophyll (c-Chl) (Chl a =1.5 μM) without or with **1a** (200 equi. and 500 equi.) in DMSO (2 mL), 3W white LED as light source.

3.6. Electron Spin-Resonance (ESR) spectroscopy experiments

Electron spin-resonance (ESR) spectra were recorded on a JEOL JES FA200 (X-band). The reactions were performed in glass vial (30 mL) under different conditions, then smaller fractions of the samples were transferred to the capillaries, and ESR spectra were recorded.

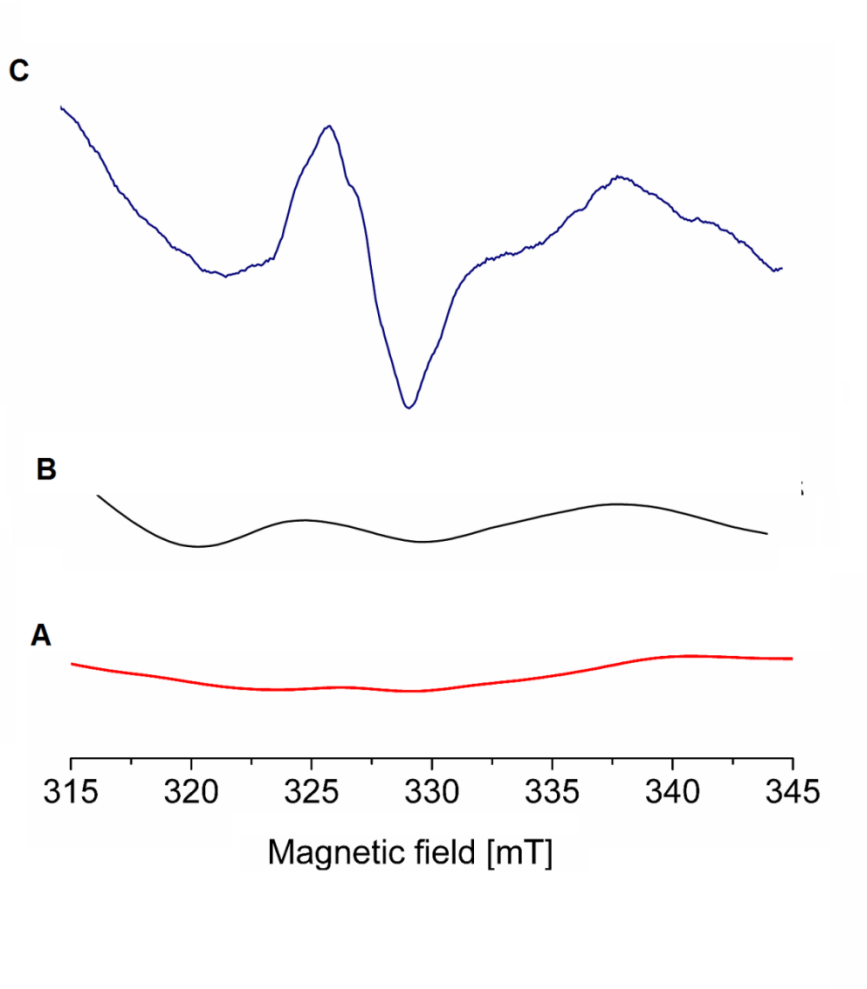


Figure FS13. (A) ESR spectrum of mixture of crude Chlorophyll (PC), DMPO in DMSO under irradiation of 3W white LED for 10 min. **(B)** ESR spectrum of mixture of PC, 1a, DMPO in DMSO under dark condition for 10 min. **(C)** ESR spectrum of mixture of PC,1a, DMPO in DMSO under irradiation of 3W white LED for 10 min. **ESR conditions**: Frequency = 9.17 GHz, Power = 0.998 mW, Modulation width = 2.0 mT, Centre field = 390.317 mT, Amplitude = 2.000 x 1 (modulation frequency 100 kHz), Sweep width = 4 x 100 mT, Sweep time = 30 sec, Time constant = 0.03, Temperature = -35 ^{o}C

At first, mixture of crude chlorophyll (containing Chl a; 15ppm), DMPO (0.7 mM) in DMSO was irradiated with 3W white LED for 10 minutes, then ESR spectrum was recorded (Fig. FS14A). From the spectrum we could ascertain that only chlorophyll could not produce radical under irradiation of visible light. When mixture of 1a(0.7mM), crude chlorophyll (Chl a; 15ppm), DMPO (0.7 mM) in DMSO was treated under dark condition for 10 minutes, and ESR spectrum was recorded, no signal was observed then also(Fig. FS14B). Next, mixture of 1a(0.7mM), crude chlorophyll (Chl a; 15ppm), DMPO (0.7 mM) in DMSO was irradiated with 3W white LED for 10 minutes, and ESR spectrum showed a new broad signal (Fig. FS14C) without any detectable hyperfine splitting (g = 2.0024, with epr line width = 9 gauss). From the observation it was envisaged that the signal corresponds to pi-radical cation of Chl a, which was formed upon reduction of the substrate indole (1a). Similar set of experiments were performed with tetrahydrocarbazole (1B) and 2-phenylindole (1C) and similar results obtained (Fig. FS15) as in case of 2,3-dimethyl indole(1a).

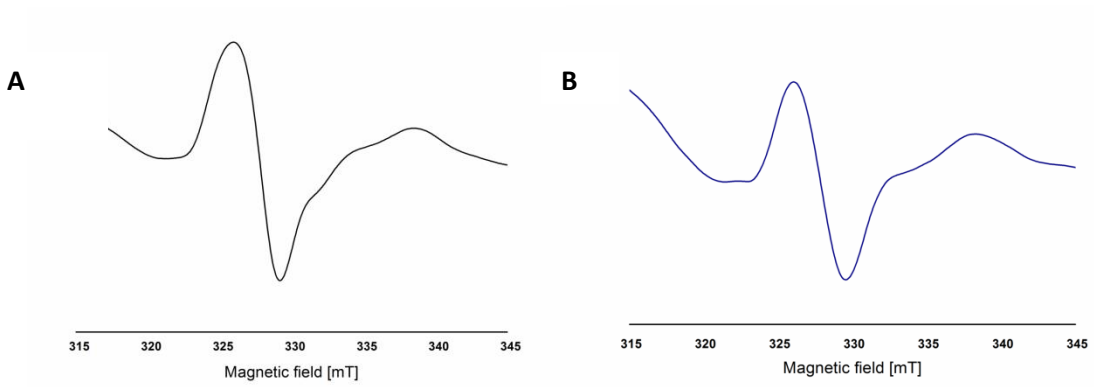


Figure FS14. (A) ESR spectrum of mixture of PC, 1B(Tetrahydrocarbazole), DMPO in DMSO under irradiation of 3W white LED for 10 min. **(B)** ESR spectrum of mixture of PC, 1C (2-Phenylindole),DMPO in DMSO under irradiation of 3W white LED for 10 min. **ESR conditions:** Same as in Fig. FS13

3.7. De-metalation of Crude Chlorophylls and subsequent studies performed

Pheophytins (Phes) was prepared from Chls by a short treatment with a small volume of fresh glacial acetic acid at room temperature, following previously

described methods with some modifications.[8] The acid was removed in a stream of nitrogen, the solid residue was dried thoroughly under vacuum and then the product was quickly passed through a short column packed with Sephadex LH-20 equilibrated in acetone. Next, UV-Vis spectroscopy of crude pheophytin was performed (Fig. FS16a) a prominent Soret peak at 410 nm[9] (characteristic peak for Pheo a) appeared. Thereafter, reaction was installed with 1a using the obtained crude pheophytin as photocatalyst (Fig. FS16b) under the optimized reaction condition, which resulted in 15% yield of 2a. Henceforth, Mg ion is found to be crucial for the photocatalytic activity of chlorophyll in the present reaction protocol.

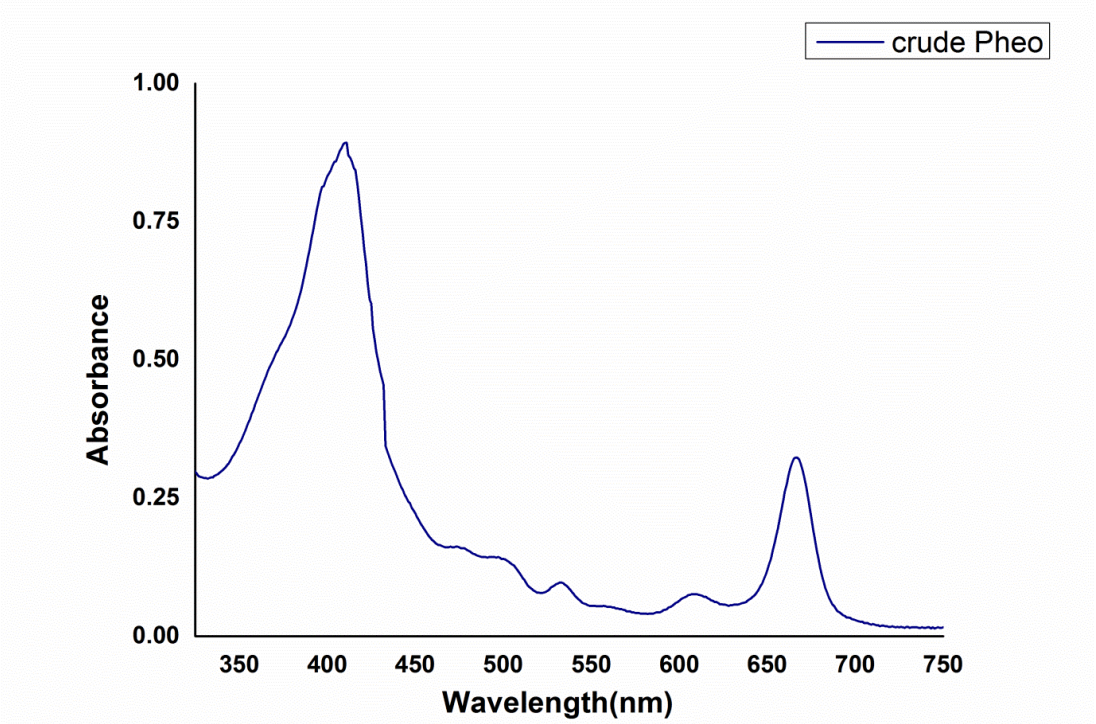


Figure FS15a. UV-Vis Spectroscopy of crude pheophytins dissolved in 3:1 Acetone/Water (triple distilled water). A Soret band of 410 nm appears (significant peak for Pheophytin a)[9].

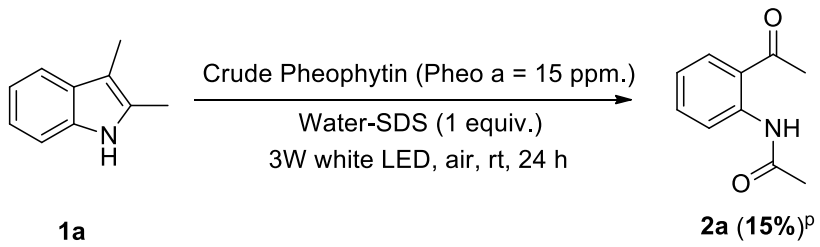
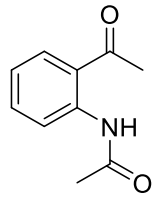


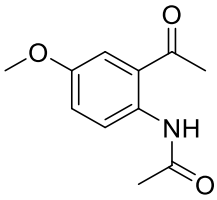
Figure FS15b. Reaction conditions: air atmosphere and irradiation with 3W white LED, **(1a)** (0.2 mmol), SDS (0.2 mmol) crude Pheo a (PC) (15 ppm), temperature (rt, 25 °C) in a 30 mL glass vial (H_2O,10 mL). [P]Yield determined by ^1H NMR using dibromomethane as the internal standard.

4. Characterisation of the products:



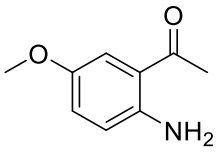
2a

N-(2-acetylphenyl)acetamide (2a).[10] Eluent Hexane/EtOAc (2.5:1) Yield 28.5 mg (79%). Off-white solid, mp 75 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.68 (br s, 1H), 8.73 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.57-7.51 (m, 1H), 7.11 (ddd, *J* = 8.0, 7.3, 1.2 Hz, 1H), 2.66 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 169.6, 141.1, 135.2, 131.7, 122.4, 121.8, 120.8, 28.7, 25.6. HRMS (ESI^+): Calcd for $C_{10}H_{12}NO_2$, $[M+H]^+$ m/z 178.0863. Found 178.0860.



2b

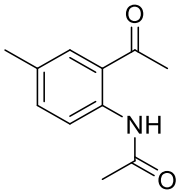
N-(2-acetyl-4-methoxyphenyl)acetamide (2b).[11] Eluent Hexane/EtOAc (3:1) Yield 31 mg (75%). Off-white solid, mp 91-93 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.32 (br s, 1H), 8.65 (d, *J* = 9.3 Hz, 1H), 7.36 (d, *J* = 3.0 Hz, 1H), 7.12 (dd, *J* = 9.3, 3.0 Hz, 1H), 3.84 (s, 3H), 2.64 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 169.2, 154.4, 134.6, 123.1, 122.4, 120.2, 116.8, 55.8, 28.7, 25.5. HRMS (ESI^+): Calcd for $C_{11}H_{14}NO_3$, $[M+H]^+$ m/z 208.0968. Found 208.0965.



2b'

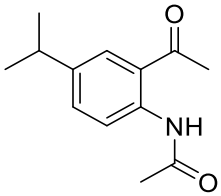
1-(2-amino-5-methoxyphenyl)ethanone (2b′). Eluent Hexane/EtOAc (9:1) Yield 23.4 mg (68%). Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 2.9 Hz, 1H), 6.97 (dd, *J* = 8.9, 2.9 Hz, 1H), 6.62 (d, *J* = 8.9 Hz, 1H), 5.95 (b s, 2H), 3.78 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3, 150.1, 145.1,

123.2, 118.7, 118.3, 114.9, 56.2, 28.0. HRMS (ESI^+): Calcd for $C_9H_{12}NO_2$, $[M+H]^+$ m/z 166.0863. Found 166.0861.



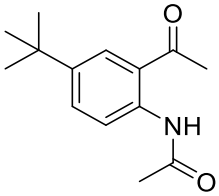
2c

N-(2-acetyl-4-methylphenyl)acetamide (2c).[12] Eluent Hexane/EtOAc (5:1) Yield 30.9 mg (81%). Light brown solid, mp 125-127 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 11.56 (br s, 1H), 8.61 (d, *J* = 8.5 Hz, 1H), 7.67 (s, 1H), 7.36 (dd, *J* = 8.5, 1.6 Hz, 1H), 2.65 (s, 3H), 2.36 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 169.4, 138.7, 136.0, 131.8, 121.9, 120.8, 28.7, 25.6, 20.9. HRMS (ESI^+): Calcd for $C_{11}H_{14}NO_2$, $[M+H]^+$ m/z 192.1019. Found 192.1020.



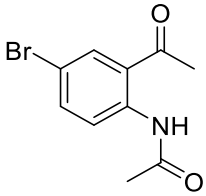
2d

N-(2-acetyl-4-isopropylphenyl)acetamide (2d). Eluent Hexane/EtOAc (6:1) Yield 33.4 mg (75%). White solid, mp 75 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 11.55 (br s, 1H), 8.63 (d, *J* = 8.7 Hz, 1H), 7.69 (d, *J* = 2.1 Hz, 1H), 7.43 (dd, *J* = 8.7, 2.1 Hz, 1H), 2.92 (dt, *J* = 13.8, 6.9 Hz, 1H), 2.67 (s, 3H), 2.21 (s, 3H), 1.26 (d, *J* = 6.9 Hz, 6H). HRMS (ESI^+): Calcd for $C_{13}H_{18}NO_2$, $[M+H]^+$ m/z 220.1332. Found 220.1329.



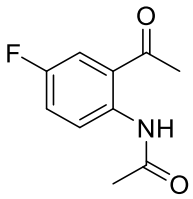
2e

N-(2-acetyl-4-(tert-butyl)phenyl)acetamide (2e). Eluent Hexane/EtOAc (2:1) Yield 31.5 mg (68%). Brown coloured semi solid compound. ^1H NMR (300 MHz, $CDCl_3$) δ 11.54 (br s, 1H), 8.63 (d, *J* = 8.6 Hz, 1H), 7.86 (d, *J* = 2.3 Hz, 1H), 7.59 (dd, *J* = 8.6, 2.3 Hz, 1H), 2.68 (s, 3H), 2.21 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.1, 169.5, 145.2, 138.6, 132.6, 127.9, 121.7, 120.7, 34.4, 31.3, 28.7, 25.6.HRMS (ESI^+): Calcd for $C_{14}H_{20}NO_2$, $[M+H]^+$ m/z 234.1489. Found 234.1484.



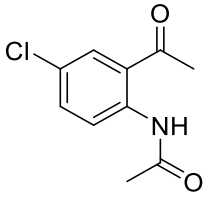
2f

N-(2-acetyl-4-bromophenyl)acetamide (2f).[12] Eluent Hexane/EtOAc (5:1) Yield 32.4 mg (63%). Brown solid, mp 149-151 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.57 (br s, 1H), 8.68 (d, *J* = 9.1 Hz, 1H), 7.98 (d, *J* = 2.3 Hz, 1H), 7.64 (dd, *J* = 9.1, 2.3 Hz, 1H), 2.66 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.8, 169.6, 140.1, 137.9, 134.1, 123.3, 122.6, 114.6, 28.7, 25.6. HRMS (ESI^+): Calcd for $C_{10}H_{11}BrNO_2$, $[M+H]^+$ m/z 255.9968. Found 255.9966.



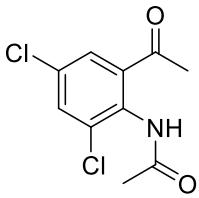
2g

N-(2-acetyl-4-fluorophenyl)acetamide (2g). Eluent Hexane/EtOAc (4:1) Yield 25.6 mg (65%). White powder, mp 142-144 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 11.46 (br s, 1H), 8.74 (dd, *J* = 9.3, 5.2 Hz, 1H), 7.54 (dd, *J* = 9.3, 3.0 Hz, 1H), 7.27 (m, 1H), 2.64 (s, 3H), 2.22 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 201.8, 169.4, 157.2 (d, J_{C-F} = 244.1 Hz), 137.4, 122.9-122.8 (m, 2C), 122.2 (d, J_{C-F} = 21.7 Hz), 117.4 (d, J_{C-F} = 23.1 Hz), 28.7, 25.5. **^{19}F NMR (282 MHz ,$CDCl_3$)** δ -118.8. HRMS (ESI^+): Calcd for $C_{10}H_{11}FNO_2$, $[M+H]^+$ m/z 196.0768. Found 196.0764.



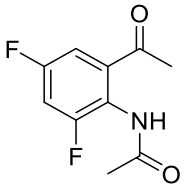
2h

N-(2-acetyl-4-chlorophenyl)acetamide (2h).[13] Eluent Hexane/EtOAc (9:1) Yield 29.1 mg (69%). White solid, mp 133-135 °C. **^{1}H NMR (300 MHz, $CDCl_3$)** δ 11.56 (br s, 1H), 8.73 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 2.5 Hz, 1H), 7.50 (dd, *J* = 9.1, 2.5 Hz, 1H), 2.66 (s, 3H), 2.22 (s, 3H). **^{13}C NMR (75 MHz, $CDCl_3$)** δ 201.8, 169.6, 139.6, 134.9, 131.1, 127.3, 122.9, 122.4, 28.7, 25.6. HRMS (ESI^+): Calcd for $C_{10}H_{11}ClNO_2$, $[M+H]^+$ m/z 212.0473. Found 212.0470.



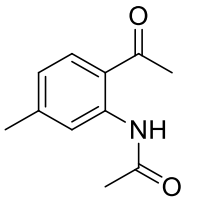
2i

N-(2-acetyl-4,6-dichlorophenyl)acetamide (2i). Eluent Hexane/EtOAc (5:1) Yield 30.1 mg (61%). White solid, mp 154-155°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (br s, 1H), 7.54 (d, *J* = 2.3 Hz, 1H), 7.50 (d, *J* = 2.3 Hz, 1H), 2.58 (s, 3H), 2.18 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.1, 168.6, 136.3, 132.4, 131.5, 130.8, 127.0, 28.6, 23.9. HRMS (ESI^+): Calcd for $C_{10}H_{10}Cl_2NO_2$, $[M+H]^+$ m/z 246.0083. Found 246.0081.



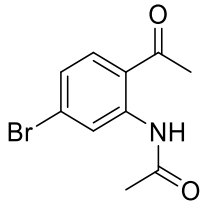
2j

N-(2-acetyl-4,6-difluorophenyl)acetamide (2j). Eluent Hexane/EtOAc (5:1) Yield 25 mg (59%). White solid, mp 154-155 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.77 (br s, 1H), 7.28-7.24 (m, 1H), 7.12-7.05 (m, 1H), 2.59 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.6, 168.6, 160.5-158.5 (m), 158.2-156.2 (m), 132.9, 121.7-121.6 (m), 112.0-111.8 (m), 109.0 (t, $J_{2C\text{-}F\text{-}F}$ = 25.1 Hz), 28.8, 23.7. **^{19}F NMR (282 MHz ,$CDCl_3$)** δ -109.7(d, *J*=7.2 Hz), -112.3(d, *J*=7.2 Hz). HRMS (ESI^+): Calcd for $C_{10}H_{10}F_2NO_2$, $[M+H]^+$ m/z 214.0674. Found 214.0670.



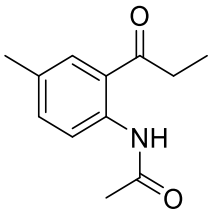
2k

N-(2-acetyl-5-methylphenyl)acetamide (2k).[14] Eluent Hexane/EtOAc (9:1) Yield 22.2 mg (58%). Colourless solid, mp 76 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.74 (s, 1H), 8.57 (d, *J* = 0.7 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 6.89-6.92 (m, 1H), 2.62 (s, 3H), 2.40 (s, 3H), 2.21 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.5, 169.6, 146.7, 141.3, 131.8, 123.3, 121.0, 119.6, 28.6, 25.7, 22.3. HRMS (ESI^+): Calcd for $C_{11}H_{14}NO_2$, $[M+H]^+$ m/z 192.1019. Found 192.1014.



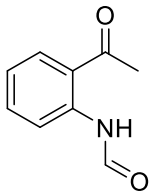
2l

N-(2-acetyl-5-bromophenyl)acetamide (2l). Eluent Hexane/EtOAc (9:1) Yield 27.1 mg (53%). Colourless solid, mp 165 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.72 (s, 1H), 9.00 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 1H), 7.24 (dd, *J* = 8.7, 2.0 Hz, 1H), 2.63 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 169.6, 142.0, 132.7, 130.4, 125.6, 123.7, 120.3, 28.7, 25.7. HRMS (ESI^+): Calcd for $C_{10}H_{11}BrNO_2$, $[M+H]^+$ m/z 255.9968. Found 255.9968.



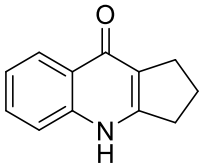
2m

N-(4-methyl-2-propionylphenyl)acetamide (2l). Eluent Hexane/EtOAc (4:1) Yield 28.6 mg (69%). White solid, mp 120^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.60 (br s, 1H), 8.61 (d, *J* = 8.6 Hz, 1H), 7.70 (d, *J* = 1.5 Hz, 1H), 7.35 (dd, *J* = 8.6, 1.8 Hz, 1H), 3.06 (q, *J* = 7.2 Hz, 2H), 2.35 (s, 3H), 2.21 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 169.4, 138.6, 135.6, 131.8, 130.8, 121.6, 120.9, 33.2, 25.6, 20.9, 8.5. HRMS (ESI^+): Calcd for $C_9H_{10}NO_2$, $[M+H]^+$ m/z 164.0706. Found 164.0702.



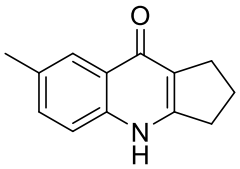
2n

N-(2-acetylphenyl)formamide (2m).[15] Eluent Hexane/EtOAc (6:1) Yield 18.1 mg (56%). Brown solid, mp 75-78 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.60 (br s, 1H), 8.74 (d, *J* = 8.4 Hz, 1H), 8.49 (s, 1H), 7.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.8 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.9, 160.0, 139.9, 135.3, 131.7, 123.2, 122.1, 121.7, 28.6. HRMS (ESI^+): Calcd for $C_9H_{10}NO_2$, $[M+H]^+$ m/z 164.0706. Found 164.0702.



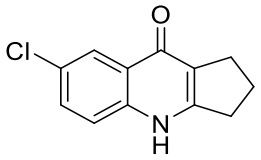
3a

2,3-dihydro-1H-cyclopenta[b]quinolin-9(4H)-one (3a).[16] Eluent DCM/MeOH (32:1) Yield 5.9 mg (16%). White powder, get decomposed at > 290 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.86 (s, 1H), 8.09 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.57(m, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 2.98 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.08-1.98 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 174.1, 153.8, 140.1, 130.7, 125.0, 124.8, 122.3, 119.4, 117.8, 31.8, 27.6, 21.3. HRMS (ESI$^+$): Calcd for $C_{12}H_{12}NO$, $[M+H]^+$ m/z 186.0913. Found 186.0911.



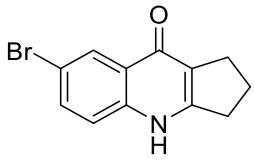
3b

7-methyl-2,3-dihydro-1H-cyclopenta[b]quinolin-9(4H)-one (3b). Eluent DCM/MeOH (32:1) 18 mg (45%). White powder, get decomposed at > 308°C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.83 (s, 1H), 7.88 (s, 1H), 7.40 (d, *J* = 1.9 Hz, 2H), 2.96 (t, *J* = 7.6 Hz, 2H), 2.69 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 2.02 (quint, *J* = 7.6 Hz, 7.2 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.8, 153.6, 138.2, 132.1, 131.5, 124.8, 124.1, 119.1, 117.8, 31.7, 27.6, 21.4, 20.7. HRMS (ESI$^+$): Calcd for $C_{13}H_{14}NO$, $[M+H]^+$ m/z 200.1070. Found 200.1065.



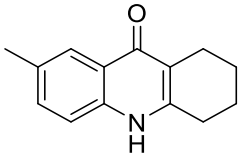
3c

7-chloro-2,3-dihydro-1H-cyclopenta[b]quinolin-9(4H)-one (3c). Eluent DCM/MeOH (32:1) 18.8 mg (43%). White powder, mp 312-315 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.07 (s, 1H), 8.02 (d, *J* = 2.5 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 2.99 (t, *J* = 7.7 Hz, 2H), 2.73-2.66 (m, 2H), 2.09-1.99 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.8, 154.4, 138.7, 130.8, 127.0, 126.0, 123.8, 120.2, 119.9, 31.8, 27.5, 21.3. HRMS (ESI$^+$): Calcd for $C_{12}H_{11}ClNO$, $[M+H]^+$ m/z 220.0524. Found 220.0521.



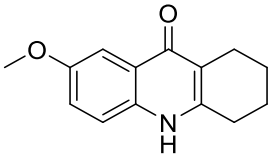
3d

7-bromo-2,3-dihydro-1H-cyclopenta[b]quinolin-9(4H)-one (3d). Eluent DCM/MeOH (32:1) 27.8 mg (53%). Brown powder, mp 230-232 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.16 (d, J = 2.3 Hz, 1H), 7.69 (dd, J = 8.6, 2.4 Hz, 1H), 7.54 (d, J = 8.6 Hz, 1H), 2.99 (t, J = 7.6 Hz, 2H), 2.69 (t, J = 7.3 Hz, 2H), 2.07-1.97 (m, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 172.5, 155.1, 139.6, 133.1, 126.9, 126.6, 121.1, 119.8, 114.8, 32.0, 27.6, 21.3. HRMS (ESI^{+}): Calcd for $C_{12}H_{11}BrNO$, $[M+H]^{+}$ m/z 264.0019. Found 264.0015.



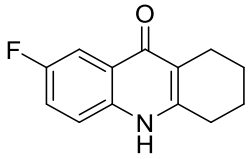
3e

7-methyl-1,2,3,4-tetrahydroacridin-9(10H)-one (3e).[17] Eluent DCM/MeOH (32:1) 18.3 mg (43%). Off-white powder, mp >350 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.21 (s, 1H), 7.83 (s, 1H), 7.40 – 7.33 (m, 2H), 2.68 (t, J = 6.0 Hz, 2H), 2.42 (t, J = 6.0 Hz, 2H), 2.37 (s, 3H), 1.76-1.68 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.7, 146.3, 137.3, 132.3, 130.9, 124.0, 123.1, 117.2, 115.1, 27.0, 21.9, 21.7, 21.5, 20.7. HRMS (ESI^{+}): Calcd for $C_{14}H_{16}NO$, $[M+H]^{+}$ m/z 214.1226. Found 214.1226.



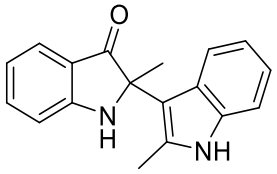
3f

7-methoxy-1,2,3,4-tetrahydroacridin-9(10H)-one (3f).[17] Eluent DCM/MeOH (32:1) Yield 17.8 mg (39%). Brown solid, mp 298-302 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.27 (s, 1H), 7.45 (d, J = 2.9 Hz, 1H), 7.42 (d, J = 9.0 Hz, 1H), 7.21 (dd, J = 9.0, 3.0 Hz, 3H), 3.81 (s, 9H), 2.68 (t, J = 6.0 Hz,2H), 2.44 (t, J = 6.0 Hz, 2H), 1.76-1.68 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.2, 154.7, 145.8, 133.9, 124.0, 121.4, 119.0, 114.4, 104.0, 55.2, 27.0, 21.9, 21.7, 21.5. HRMS (ESI^{+}): Calcd for $C_{14}H_{16}NO_2$, $[M+H]^{+}$ m/z 230.1176. Found 230.1172.



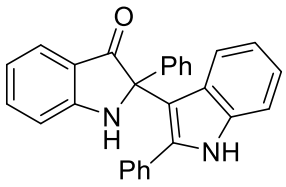
3g

7-fluoro-1,2,3,4-tetrahydroacridin-9(10H)-one (3g). Eluent DCM/MeOH (32:1)17.8 mg (41%). Off-white powder, mp >350 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.46 (s, 1H), 7.67 (dd, J = 9.5, 2.9 Hz, 1H), 7.56-7.44 (m, 2H), 2.70 (t, J = 5.9 Hz, 2H), 2.43 (t, J = 6.0 Hz, 2H), 1.80-1.66 (m, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 175.1, 157.6 (d, J_{C-F} = 236.9 Hz), 147.0, 135.9, 124.0 (d, J_{C-F} = 6.4 Hz), 119.8 (d, J_{C-F} = 34.4 Hz), 119.9, 114.9, 108.5 (d, J_{C-F} = 21.9 Hz), 27.0, 21.7, 21.6, 21.4. **^{19}F NMR (282 MHz, DMSO-d_6)** δ -119.5. HRMS (ESI^{+}): Calcd for $C_{13}H_{13}FNO$, $[M+H]^{+}$ m/z 218.0976. Found 218.0974.



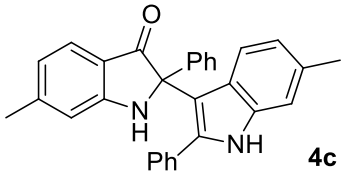
4a

2-methyl-2-(2-methyl-1H-indol-3-yl)indolin-3-one (4a).[18] Eluent Hexane/EtOAc (6:1) Yield 16.3 mg (59%). Yellow solid, mp 205-207 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.87 (br s, 1H), 7.70 (br s, 1H), 7.51-7.43 (m, 2H), 7.26-7.20 (m, 2H), 6.96-6.86 (m, 2H), 6.81-6.68 (m, 2H), 2.39 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 203.8, 159.9, 137.4, 134.7, 132.9, 127.1, 124.3, 119.9, 119.3, 118.3, 117.6, 116.9, 111.7, 110.4, 108.4, 66.2, 24.3, 13.9. HRMS (ESI^{+}): Calcd for $C_{18}H_{17}N_2O$, $[M+H]^{+}$ m/z 277.1335. Found 277.1331.



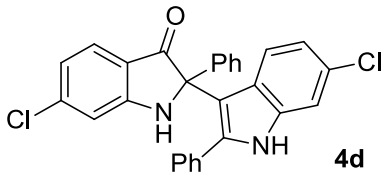
4b

2-phenyl-2-(2-phenyl-1H-indol-3-yl)indolin-3-one (4b).[18] Eluent Hexane/ EtOAc (6:1) Yield 26.8 mg (67%). Yellow solid, mp 230-232 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.33 (br s, 1H), 8.32 (br s, 1H), 7.52 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 7.40-7.33 (m, 3H), 7.26 (d, J = 7.4 Hz, 1H), 7.17-7.12 (m, 3H), 7.08-7.03 (m, 6H), 7.00 (dd, J = 8.3, 4.6 Hz, 1H), 6.74 (dt, J = 13.0, 7.6 Hz, 2H), 6.62 (d, J = 8.1 Hz, 1H).^{13}C NMR (75 MHz, DMSO-d_6) δ 200.4, 160.0, 139.7, 137.9, 137.4, 135.7, 133.1, 129.5, 127.5, 127.3, 127.2, 127.1, 127.0, 126.9, 124.3, 121.0, 120.2, 118.6, 118.4, 117.4, 111.8, 111.1, 110.9, 71.1. HRMS (ESI^{+}): Calcd for $C_{28}H_{21}N_2O$, $[M+H]^{+}$ m/z 401.1648. Found 401.1643.



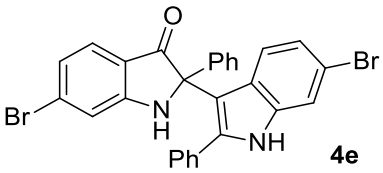
4c

6-methyl-2-(6-methyl-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (4c).[18] Eluent Hexane/EtOAc (8:1) Yield 49.7 mg (58%). Yellow solid, mp 258-260 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.14 (br s, 1H), 8.21 (br s, 1H), 7.36-7.33 (m, 2H), 7.15-7.09 (m, 5H), 7.06-7.01 (m, 5H), 6.77 (s, 1H), 6.59-6.47 (m, 3H), 2.35 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 199.5, 160.4, 148.2, 140.0, 137.1, 136.1, 133.3, 130.1, 129.4, 127.4, 127.07, 127.0, 126.9, 126.7, 125.3, 124.1, 120.3, 120.1, 119.2, 116.3, 111.5, 110.9, 110.8, 71.3, 22.0, 21.2. HRMS (ESI$^+$): Calcd for $C_{30}H_{25}N_2O$, $[M+H]^+$ m/z 429.1961. Found 429.1958.



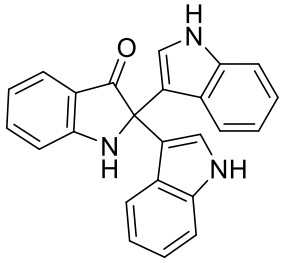
4d

6-chloro-2-(6-chloro-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (4d). Eluent Hexane/EtOAc (8:1) Yield 63.8 mg (68%). Yellow solid, mp 260-262 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.58 (br s, 1H), 8.63 (br s, 1H), 7.38-7.35 (m, 3H), 7.23-7.07 (m, 9H), 6.95 (d, J = 1.6 Hz, 1H), 6.82 (dd, J = 8.7, 2.0 Hz, 1H), 6.71 (dd, J = 8.2, 1.8 Hz, 1H), 6.49 (d, J = 8.7 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 198.7, 160.0, 142.3, 139.1, 138.9, 136.1, 132.5, 129.4, 127.8, 127.7, 127.3, 127.2, 126.8, 126.09, 126.03, 125.8, 121.4, 119.1, 117.8, 117.1, 111.0, 110.8, 110.7, 71.3. HRMS (ESI$^+$): Calcd for $C_{28}H_{19}C_{l2}N_2O$, $[M+H]^+$ m/z 469.0869. Found 469.0864.



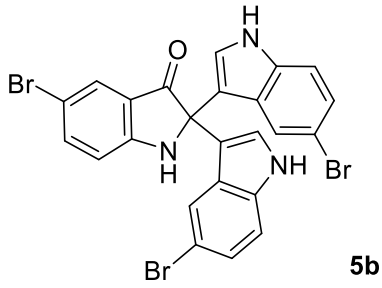
4e

6-bromo-2-(6-bromo-2-phenyl-1H-indol-3-yl)-2-phenylindolin-3-one (4e). Eluent Hexane/EtOAc (8:1) Yield 70.3 mg (63%). Yellow solid, mp 262-264 ^{o}C. ^{1}H NMR (300 MHz, DMSO-d_6) δ 11.58 (br s, 1H), 8.60 (br s, 1H), 7.49 (d, J = 1.7 Hz, 1H), 7.37-7.34 (m, 2H), 7.19-7.07 (m, 10H), 6.93 (dd, J = 8.7, 1.8 Hz, 1H), 6.85 (dd, J = 8.2, 1.6 Hz, 1H), 6.44 (d, J = 8.7 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 198.9, 160.0, 139.0, 138.8, 136.6, 132.5, 131.7, 129.4, 127.8, 127.3, 127.2, 126.8, 126.2, 126.1, 121.8, 121.6, 120.6, 117.4, 114.1, 113.8, 113.7, 110.7, 71.2.HRMS (ESI$^+$): Calcd for $C_{28}H_{19}Br_2N_2O$, $[M+H]^+$ m/z 558.9839. Found 558.9838.



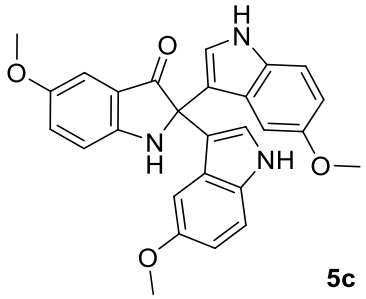
5a

1H,1''H-[3,2':2',3''-terbenzo[b]pyrrol]-3'(1'H)-one (5a).[18] Eluent Hexane/EtOAc (4:1) Yield 21.4 mg (87%). Pale yellow solid, mp 230-232 ^{o}C**.** ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.98 (br s, 2H), 8.15 (s, 1H), 7.49 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 8.2 Hz, 4H), 7.11 (s, 2H), 7.06 – 6.70 (m, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 200.8, 160.5, 137.4, 136.9, 125.6, 124.4, 124.0, 121.0, 120.5, 118.3, 117.7, 117.0, 113.9, 111.7, 111.5, 67.6. HRMS (ESI^{+}): Calcd for $C_{24}H_{18}N_3O$, $[M+H]^{+}$ m/z 364.1444. Found 364.1437.



5b

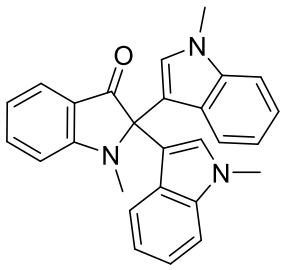
5,5',5''-tribromo-1H,1''H-[3,2':2',3''-terbenzo[b]pyrrol]-3'(1'H)-one (5b).[19] Eluent Hexane/EtOAc (4:1) Yield 37 mg (93%). Pale yellow solid, mp 251-253 ^{o}C**.** ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.29 (d, J = 2.2 Hz, 2H), 8.53 (s, 1H), 7.66-7.61 (m, 2H), 7.39-7.34 (m, 4H), 7.22 (d, J = 2.6 Hz, 2H), 7.16 (dd, J = 8.6, 1.9 Hz, 2H), 6.95 (dd, J = 8.7, 0.5 Hz, 1H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 198.9, 159.1, 140.0, 135.6, 127.1, 126.6, 125.4, 123.7, 122.2, 118.9, 114.1, 113.8, 112.8, 111.3, 108.3, 67.7. HRMS (ESI^{+}): Calcd for $C_{24}H_{15}Br_3N_3O$, $[M+H]^{+}$ m/z 599.8740. Found 599.8731.



5c

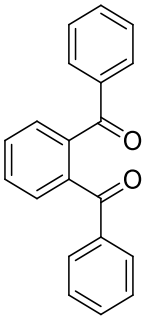
5,5',5''-trimethoxy-1H,1''H-[3,2':2',3''-terbenzo[b]pyrrol]-3'(1'H)-one (5c).[18] Eluent Hexane/EtOAc (4:1) Yield 23.5 mg (78%). Pale yellow solid, mp 228-230 ^{o}C**.** ^{1}H NMR (300 MHz, DMSO-d_6) δ 10.78 (d, J = 1.9 Hz, 2H), 7.78

(s, 1H), 7.26-7.20 (m, 3H), 7.04 (d, *J* = 2.5 Hz, 2H), 6.98-6.93 (m, 2H), 6.81 (d, *J* = 2.3 Hz, 2H), 6.70 (dd, *J* = 8.8, 2.4 Hz, 2H), 3.73 (s, 3H), 3.54 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 201.1, 156.8, 152.5, 151.7, 132.1, 127.6, 126.0, 124.6, 118.0, 113.6, 113.4, 112.0, 110.5, 104.5, 103.1, 68.4, 55.5, 55.0. HRMS (ESI$^+$): Calcd for $C_{27}H_{24}N_3O_4$, $[M+H]^+$ m/z 454.1761 . Found 454.1753.



5d

1,1',1''-trimethyl-1H,1''H-[3,2':2',3''-terbenzo[b]pyrrol]-3'(1'H)-one (5d).[19] Eluent Hexane/EtOAc (4:1) Yield 23.5 mg (69%). Pale yellow solid, mp 296-298 ^{o}C**.** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.55 (ddd, *J* = 8.4, 7.1, 1.4 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.21-7.16 (m, 2H), 7.01 (s, 2H), 6.97 (ddd, *J* = 8.1, 7.0, 1.0 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.77-6.72 (m, 1H), 3.73 (s, 6H), 2.97 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.8, 159.9, 137.9, 137.8, 130.0, 126.3, 125.8, 121.8, 121.7, 119.5, 118.7, 116.9, 111.4, 109.4, 108.0, 72.9, 33.0, 29.6. HRMS (ESI$^+$): Calcd for $C_{27}H_{24}N_3O$, $[M+H]^+$ m/z 406.1914. Found 406.1908.



7

1,2-phenylenebis(phenylmethanone) (7). Eluent Hexane/EtOAc (4:1) Yield 38.9 mg (68%). Pale yellow solid, mp 144-146 ^{o}C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.68 (m, 3H), 7.62 (s, 3H), 7.54 – 7.48 (m, 2H), 7.39-7.34 (m, 3H), 7.31 – 7.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 140.1, 137.3, 133.1, 130.5, 129.9, 129.8, 128.4. HRMS (ESI$^+$): Calcd for $C_{20}H_{15}O_2$, $[M+H]^+$ m/z 287.1067. Found 287.1057.

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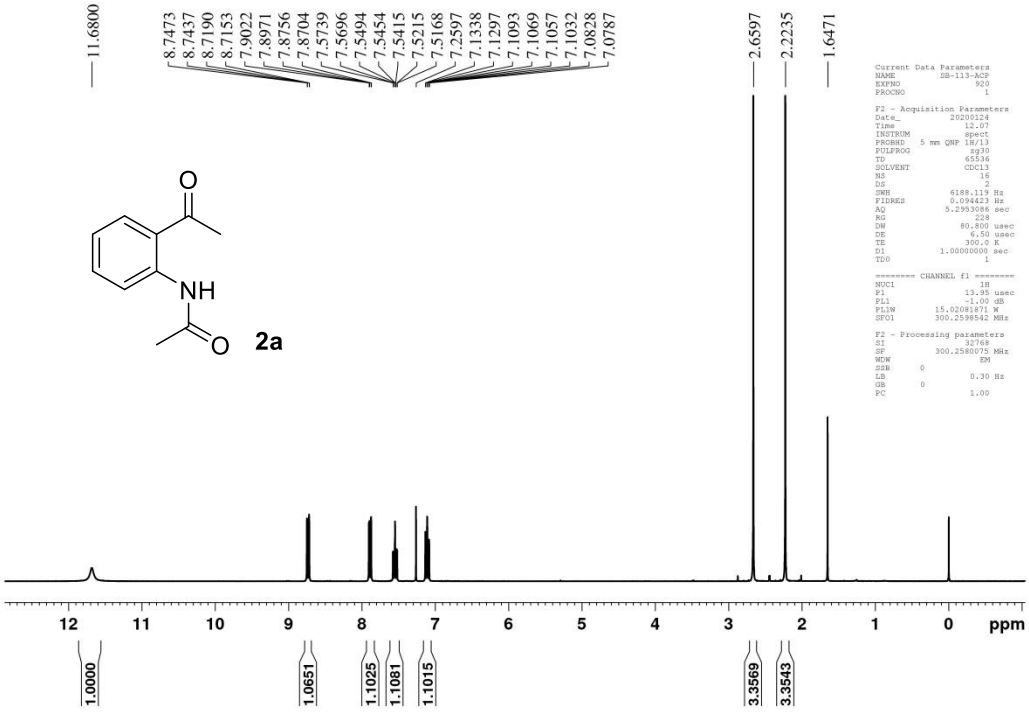
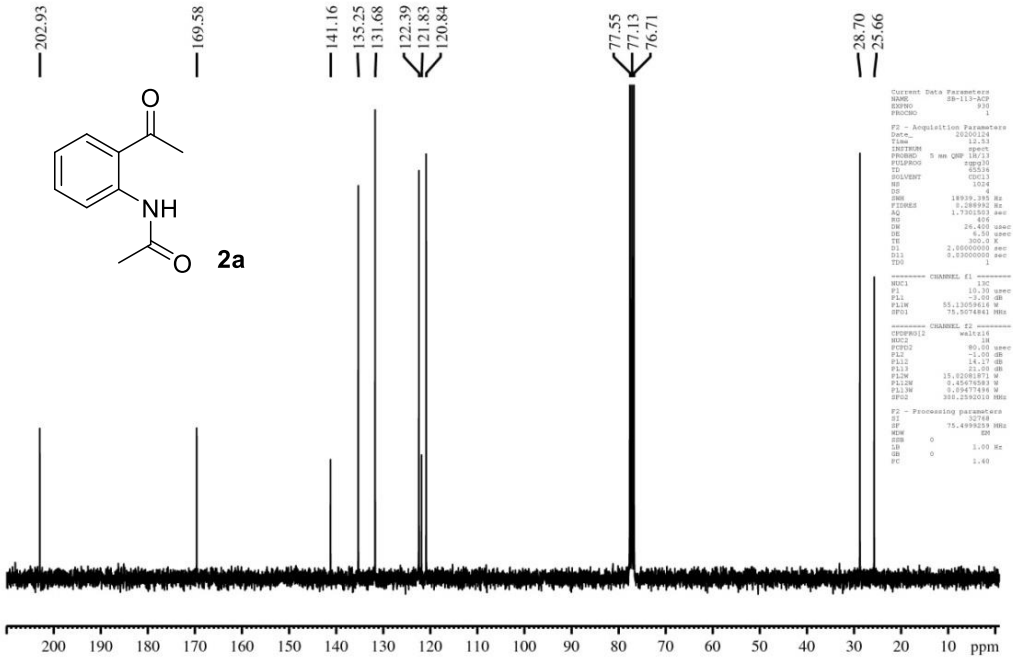
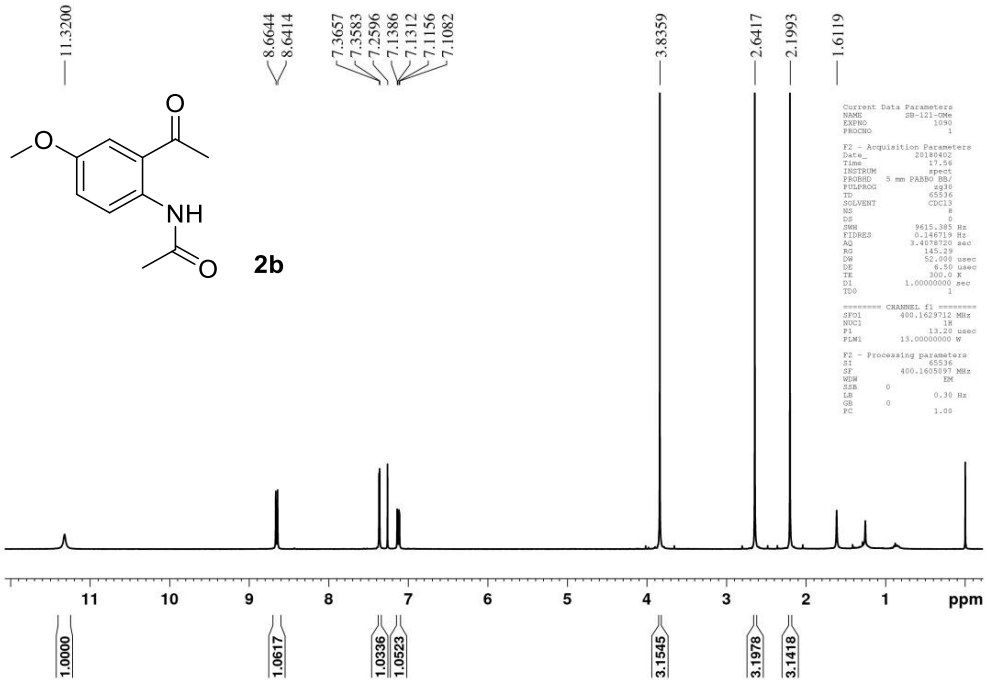
6. NMR Spectra of the Products:



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2b
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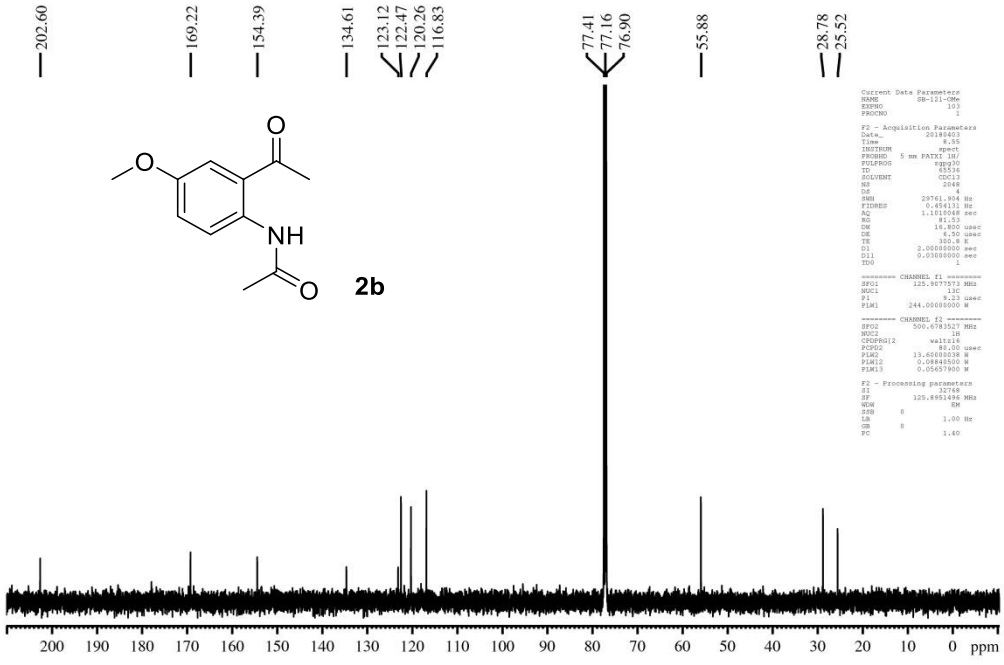
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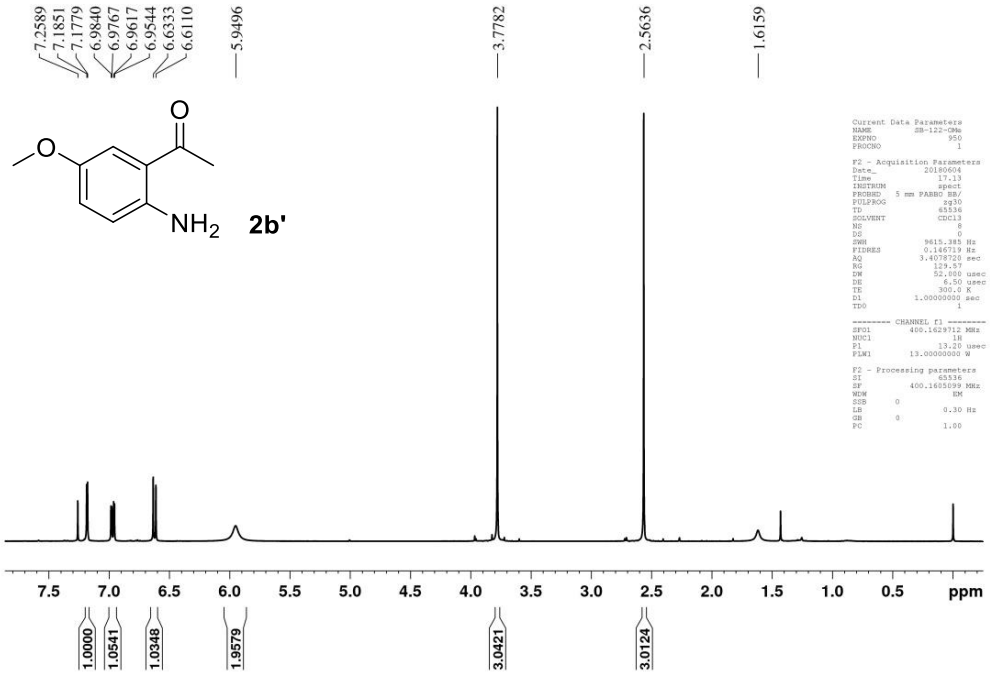
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2.5636
1.6159
O
NH2
2b'
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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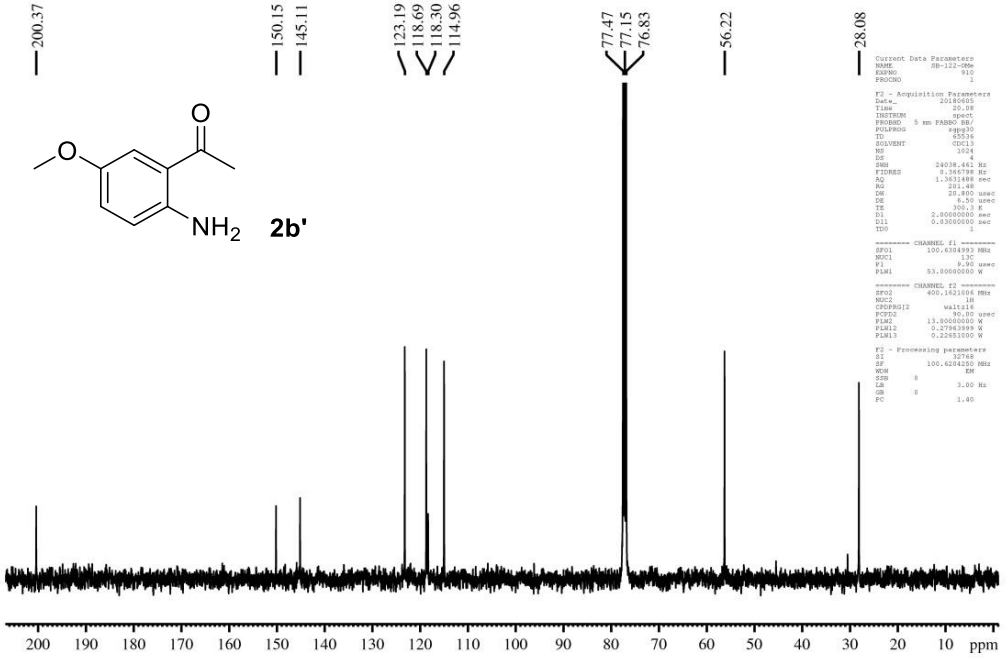
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28.08
O
NH2
2b'
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150
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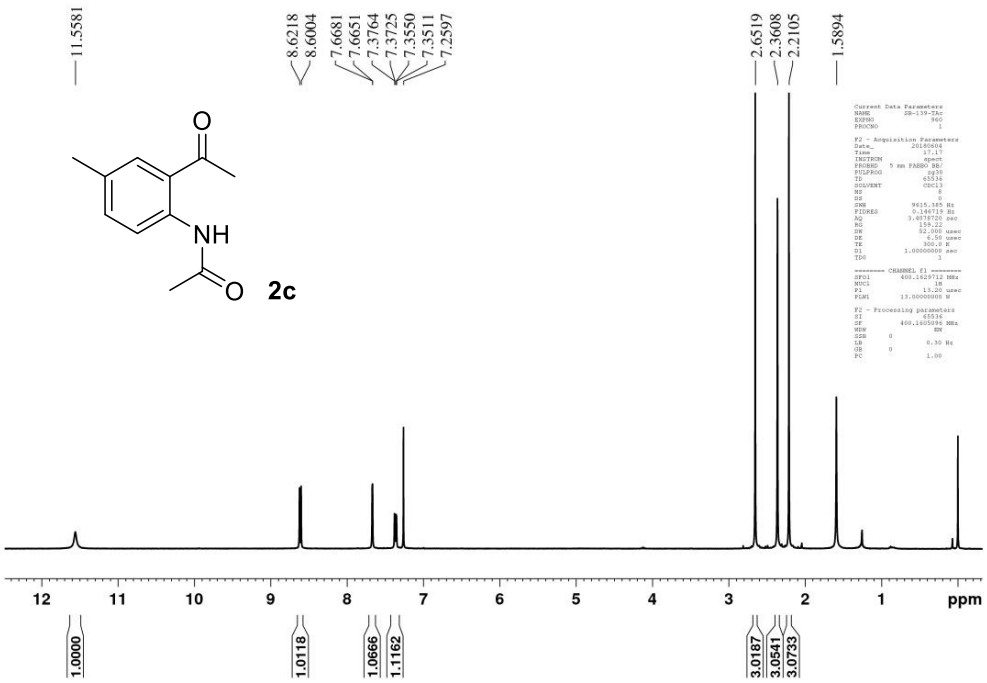
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11
10
9
8
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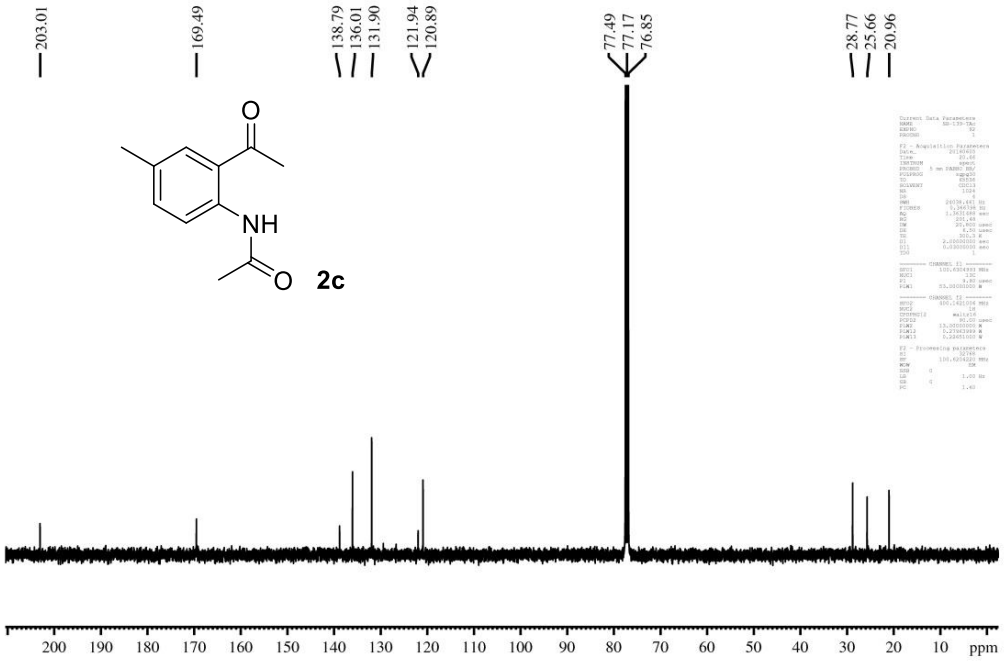
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NH
2c
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10
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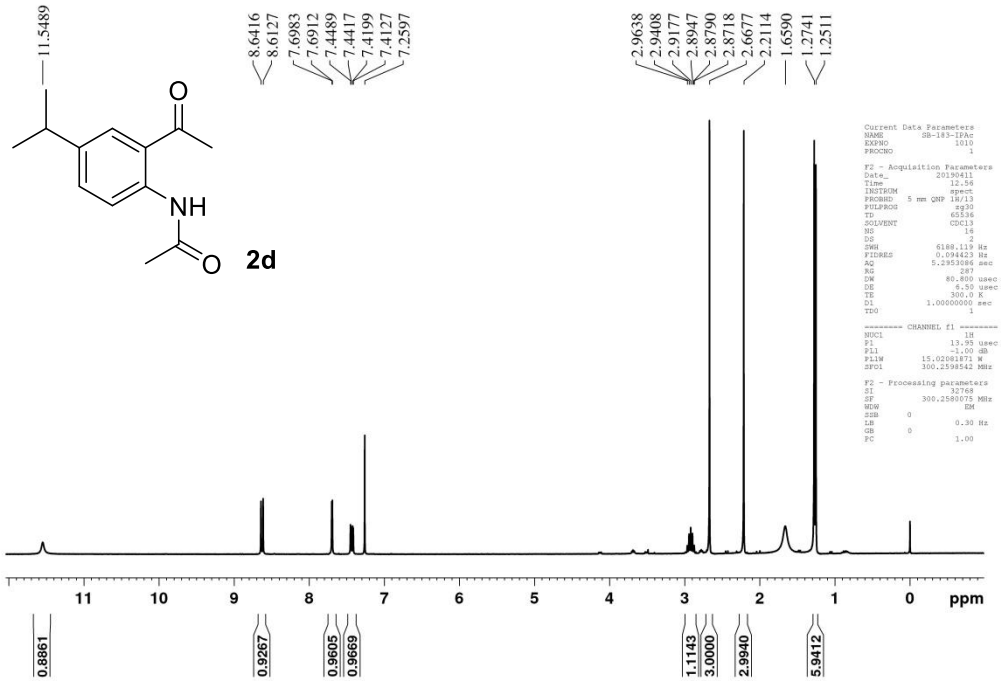
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10
9
8
7
6
5
4
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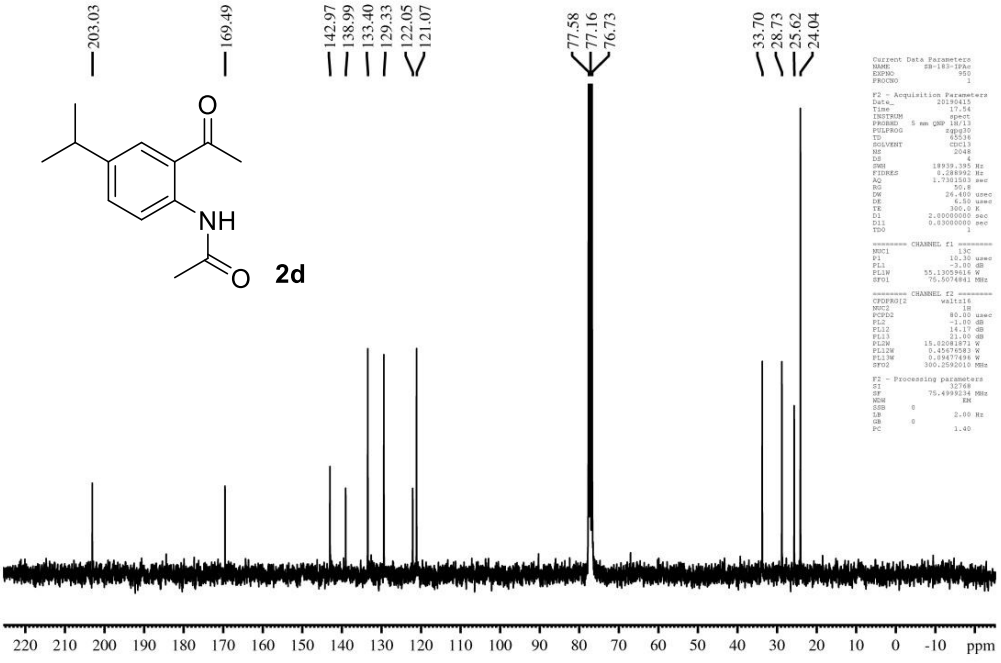
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O
NH
O
2d
220
210
200
190
180
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50
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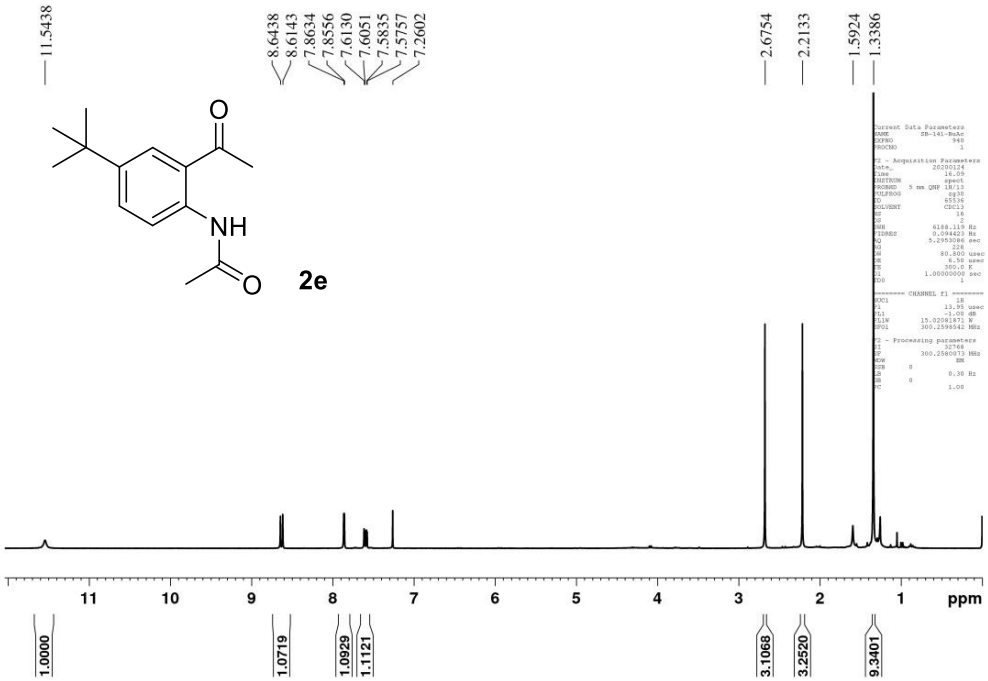
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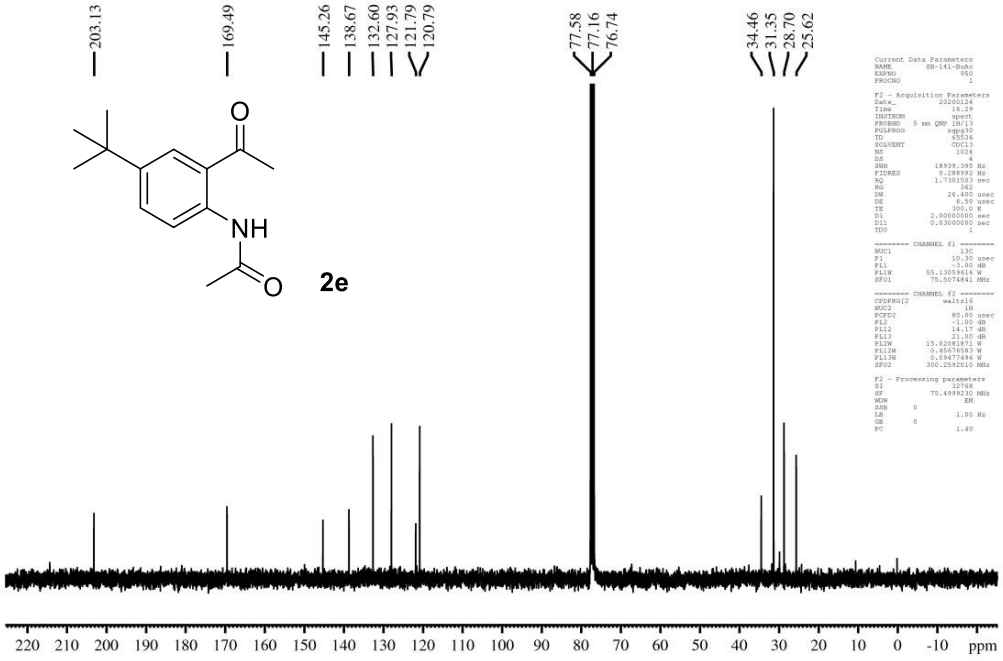
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210
200
190
180
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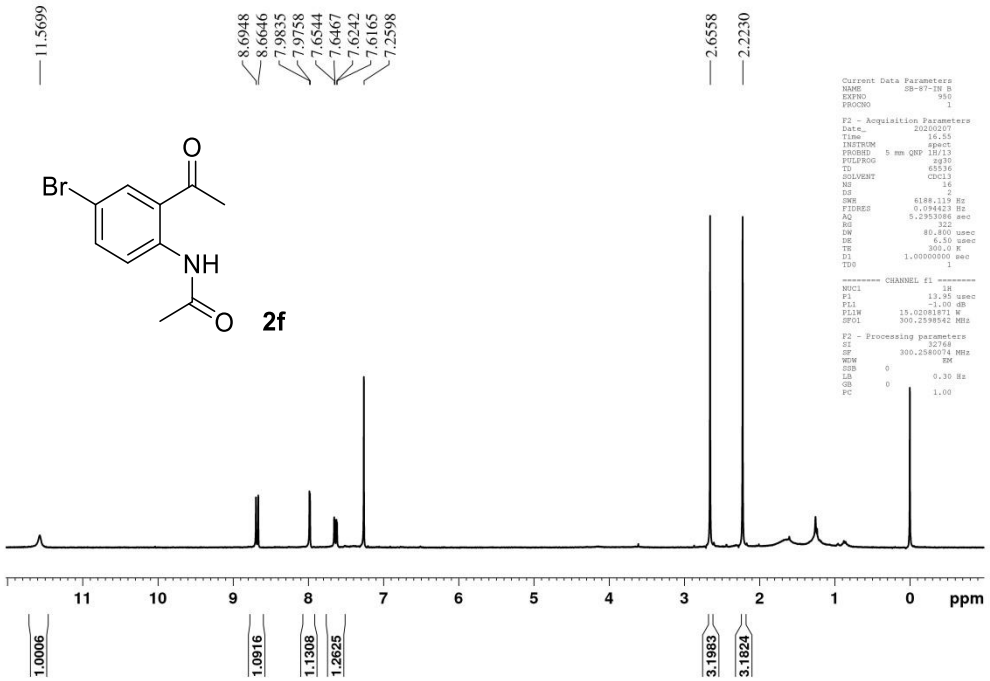
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10
9
8
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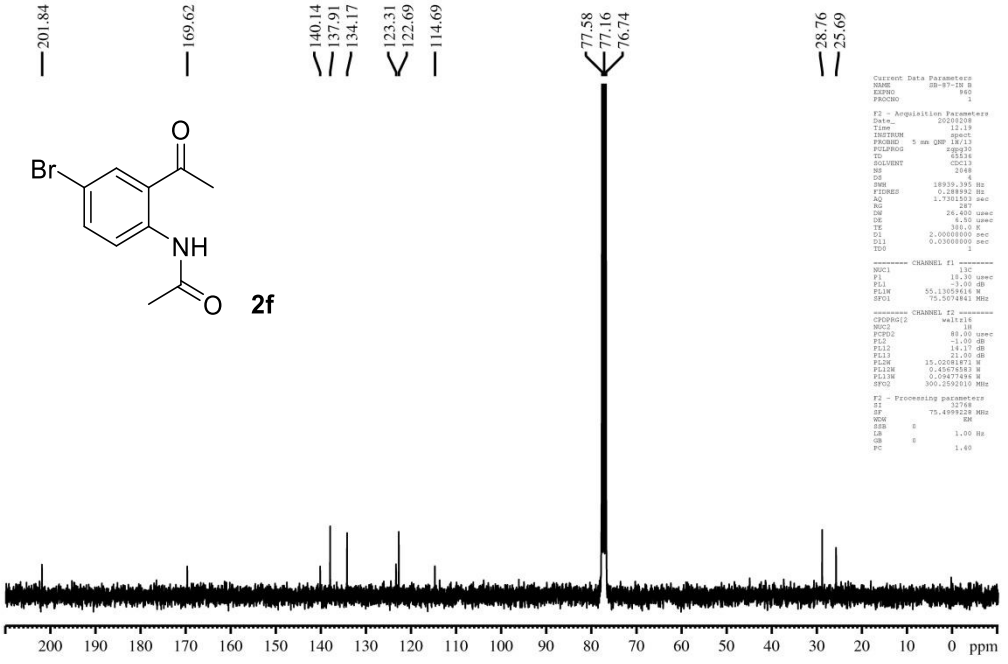
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O
2f
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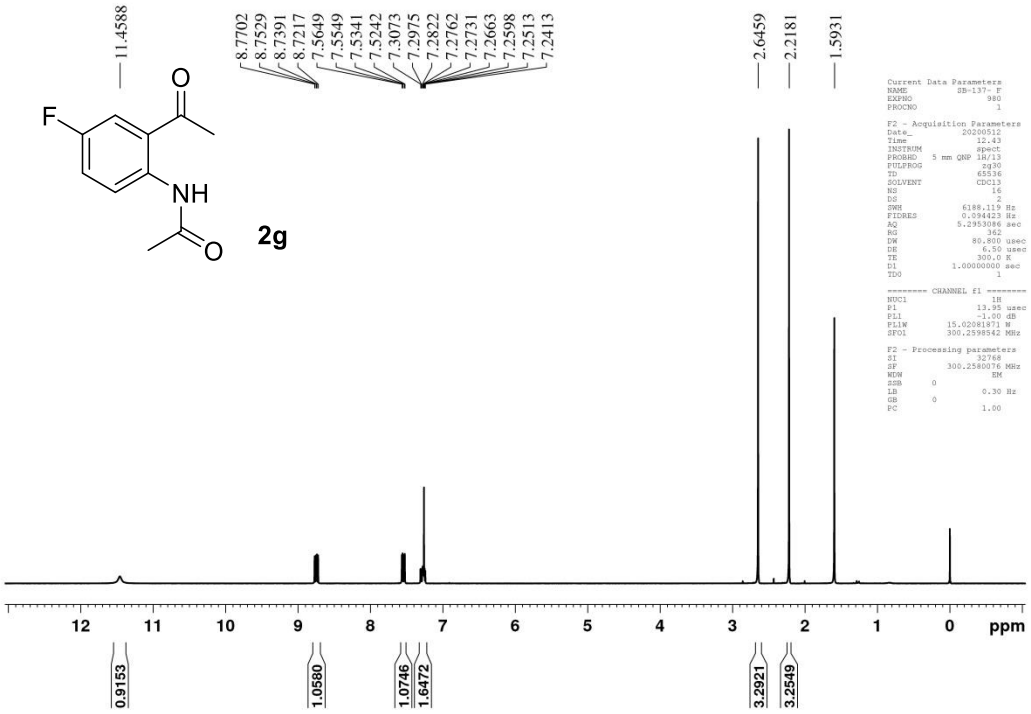
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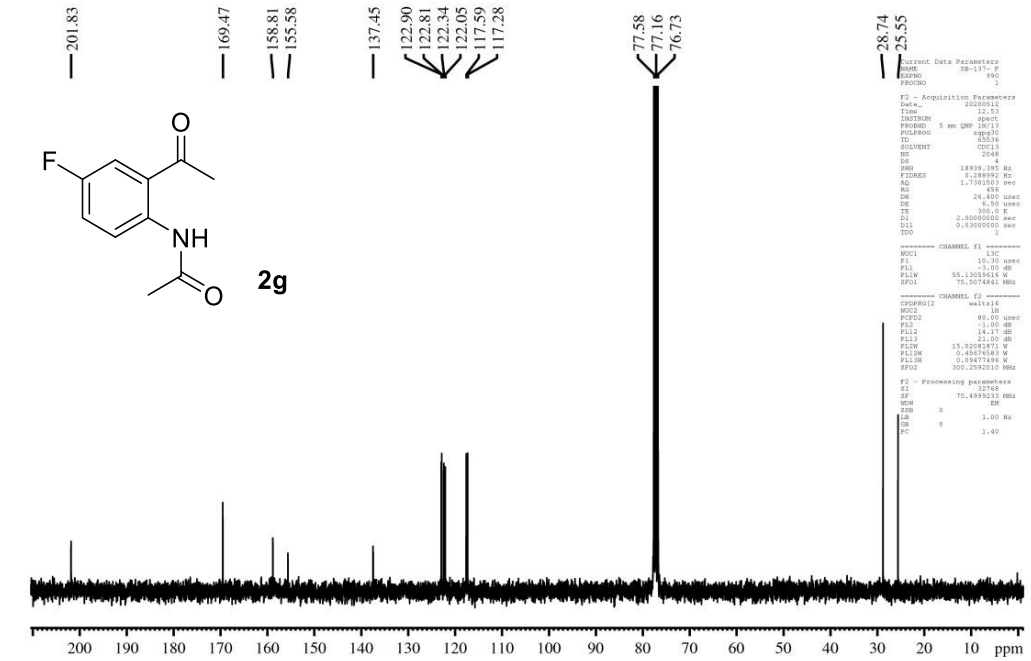
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28.74
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F
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O
2g
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10
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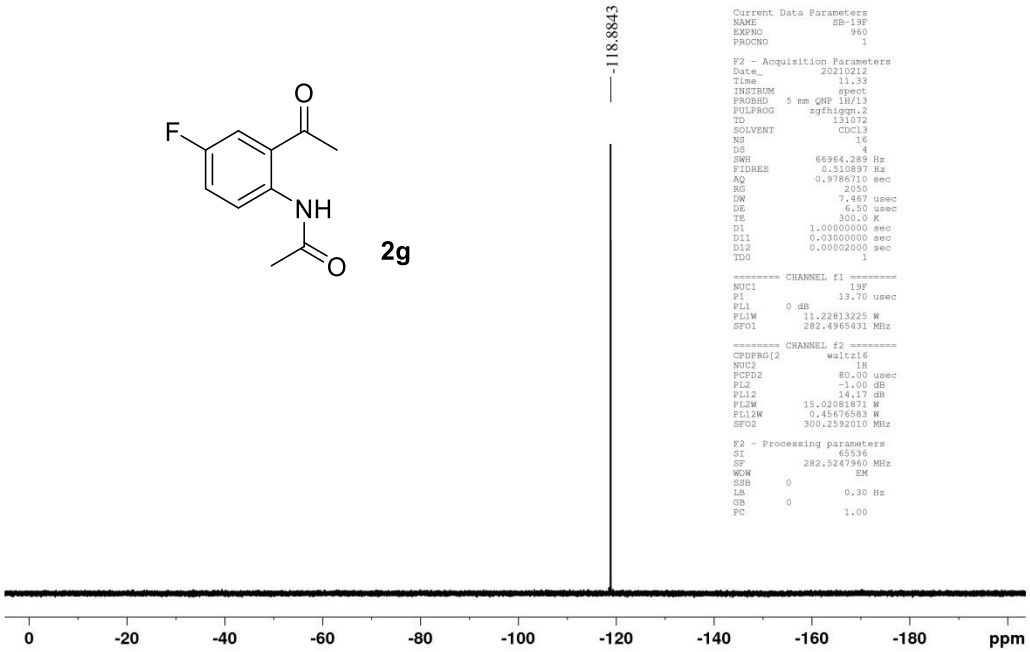
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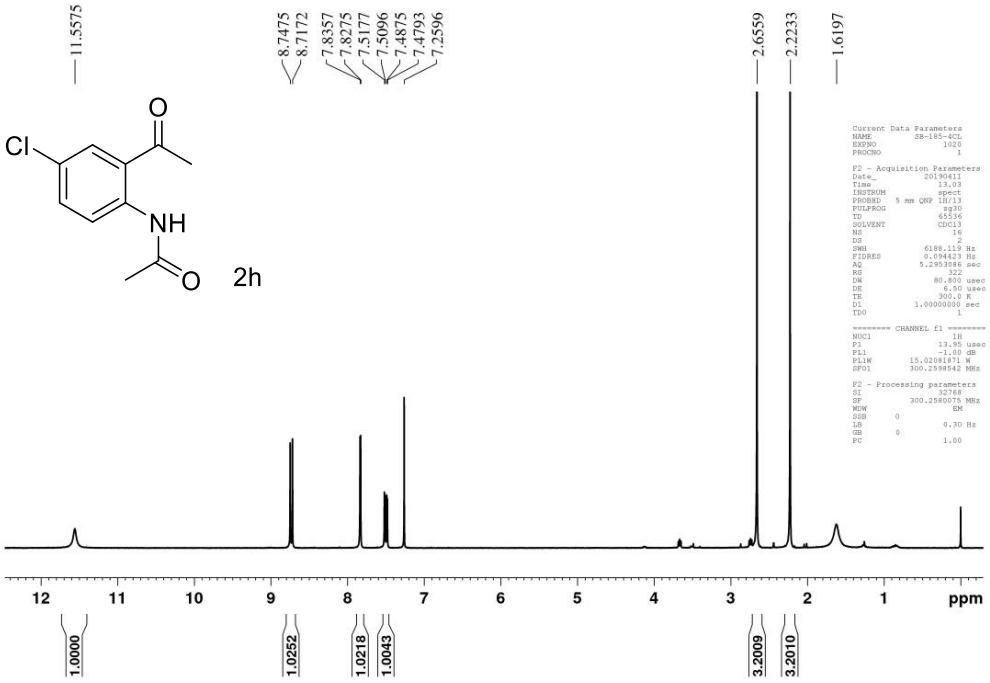
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NH
O
2h
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11
10
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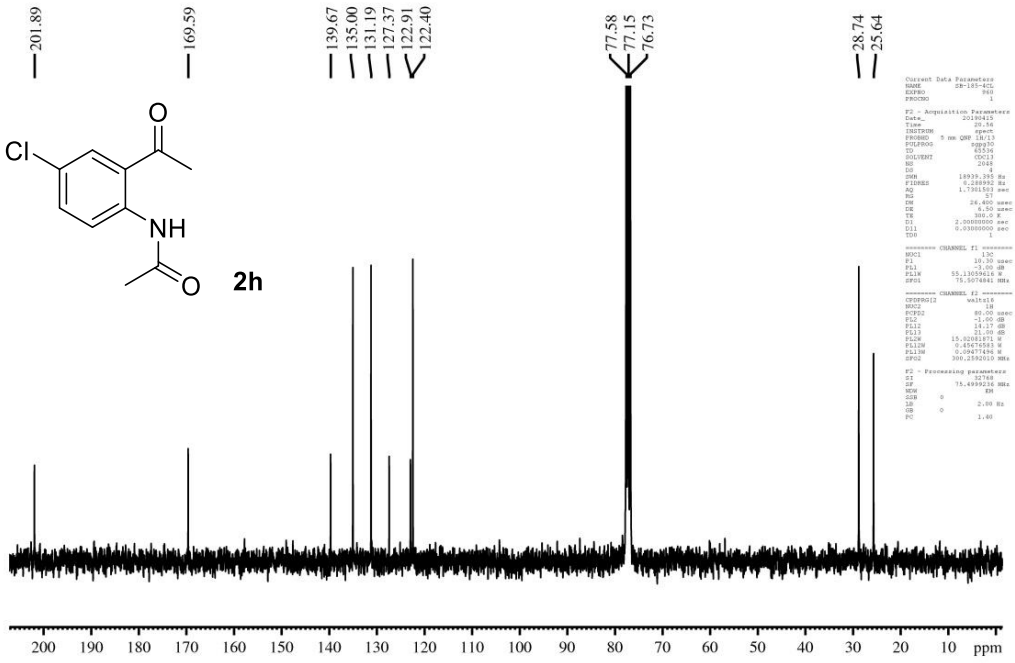
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O
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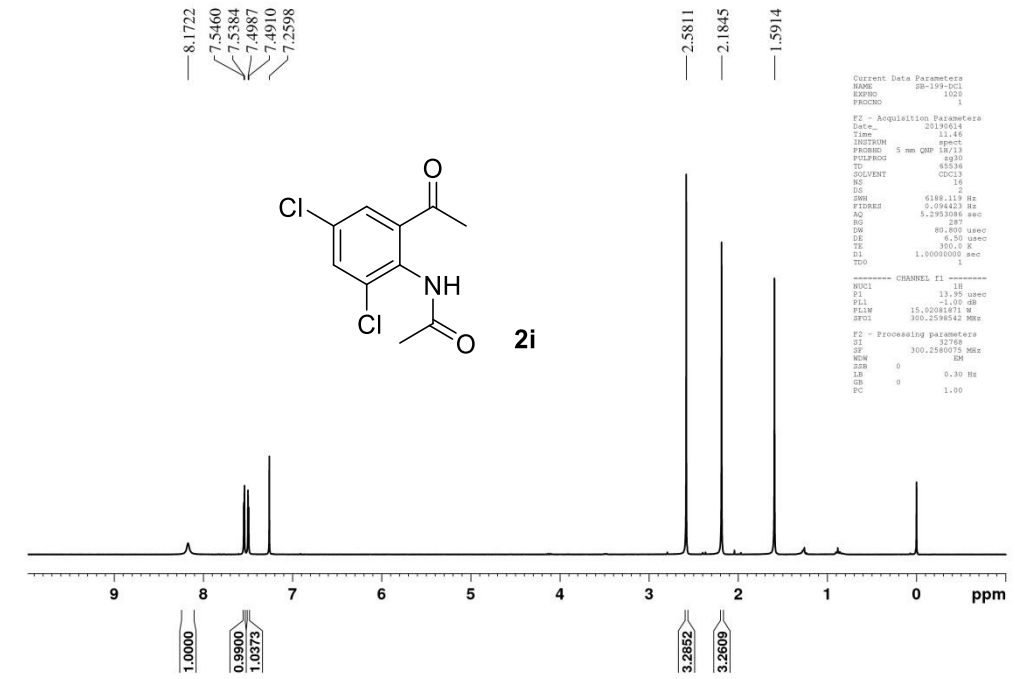
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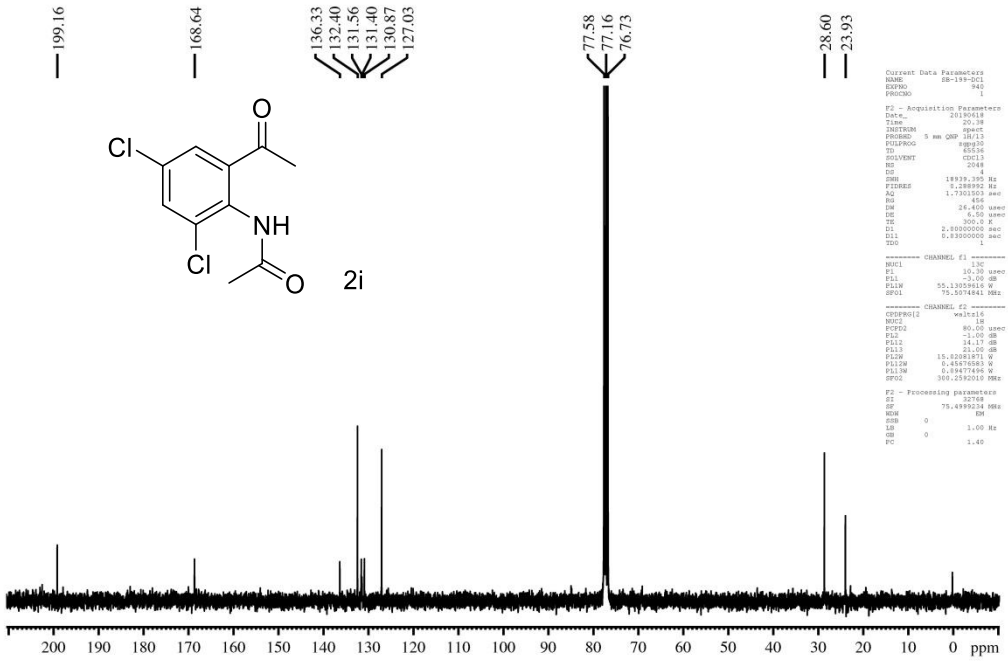
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23.93
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NH
Cl
O
2i
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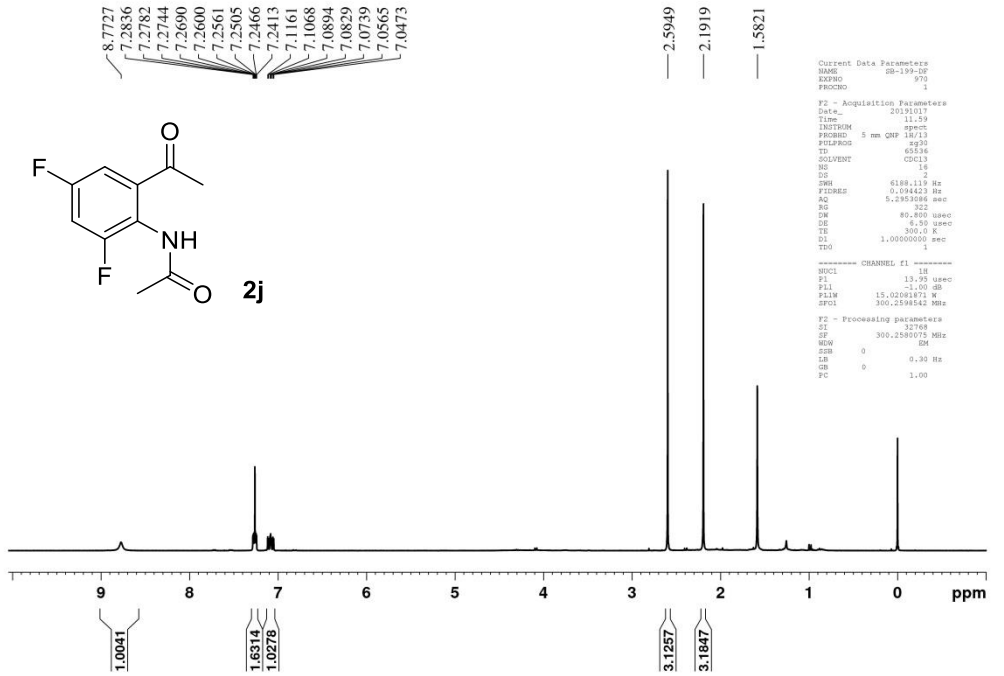
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7.1068
7.0894
7.0829
7.0739
7.0565
7.0473
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2.1919
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O
2j
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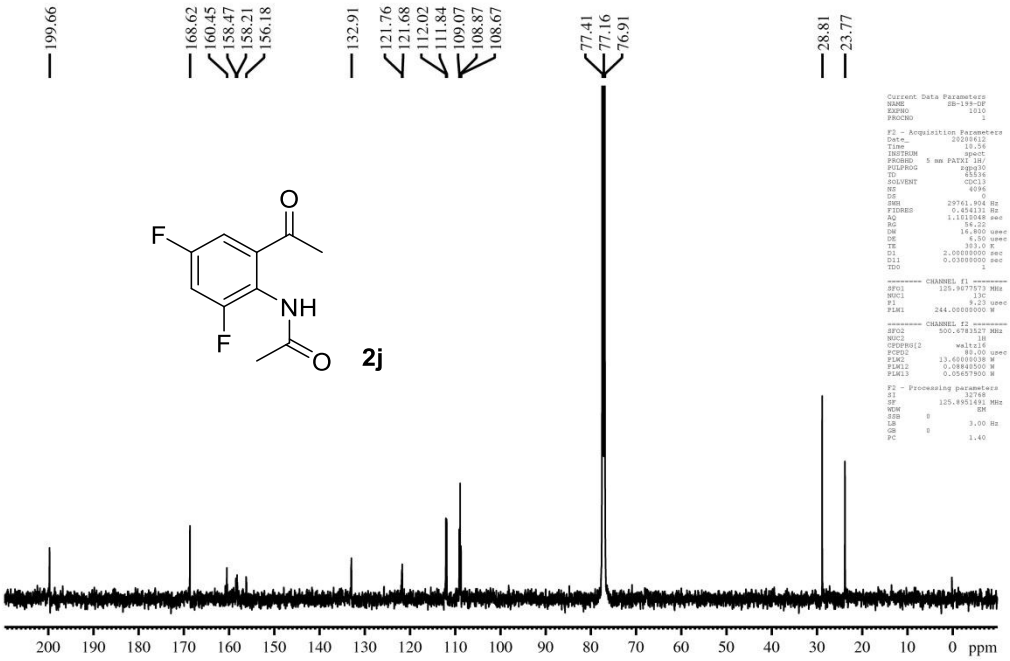
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108.67
77.41
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2j
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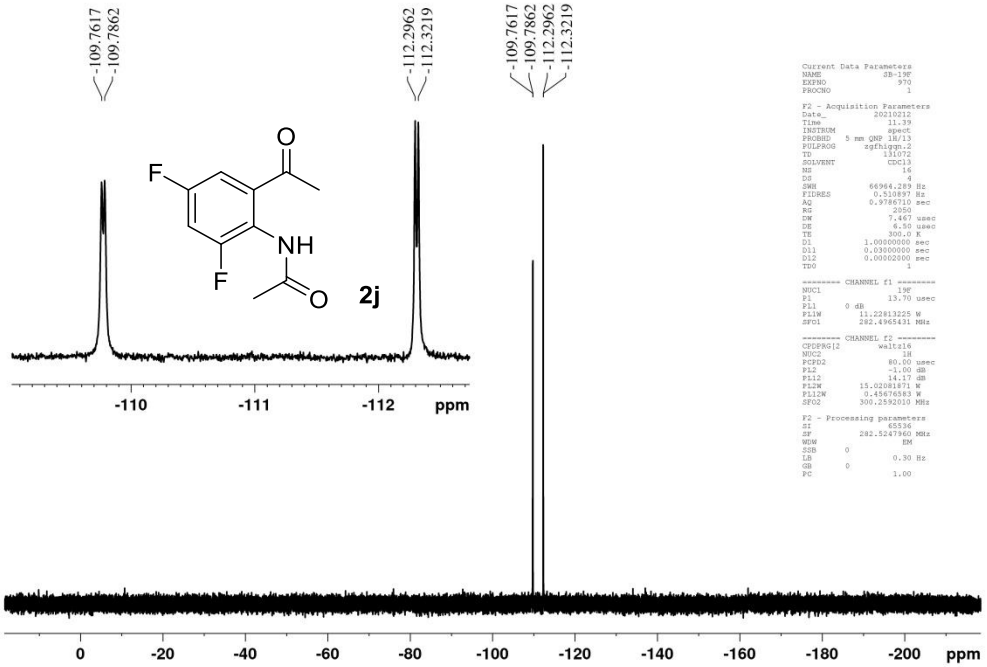
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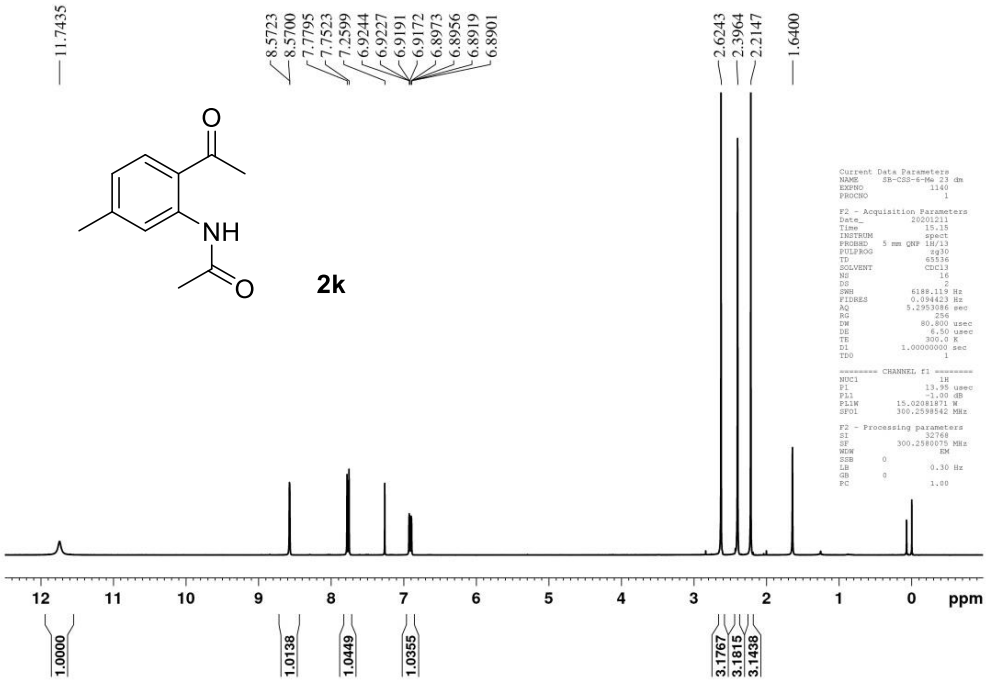
2j
-110 -111 -112 ppm
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm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2.3964
2.2147
1.6400
O
NH
O
2k
12
11
10
9
8
7
6
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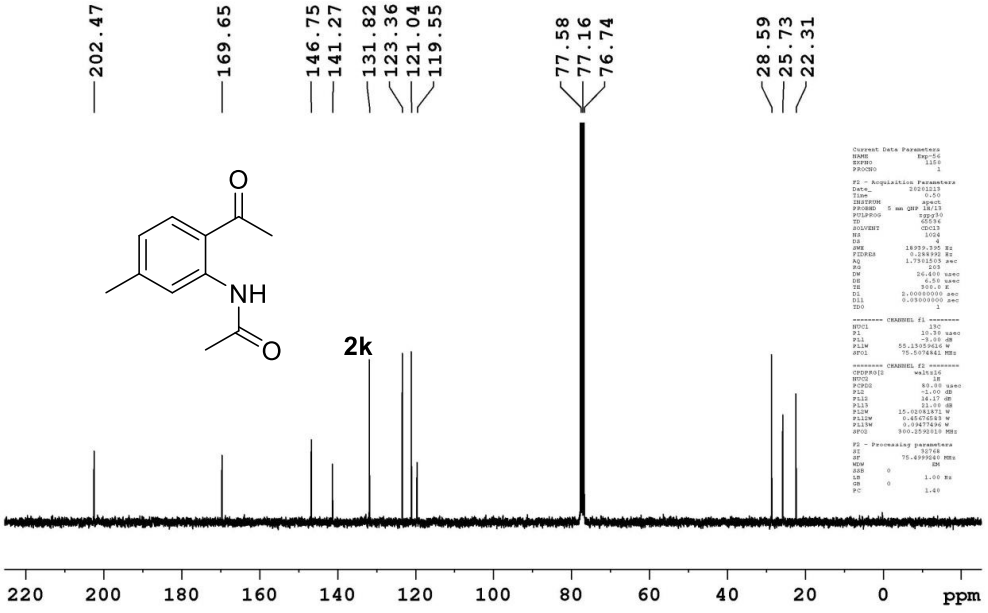
3.1438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0
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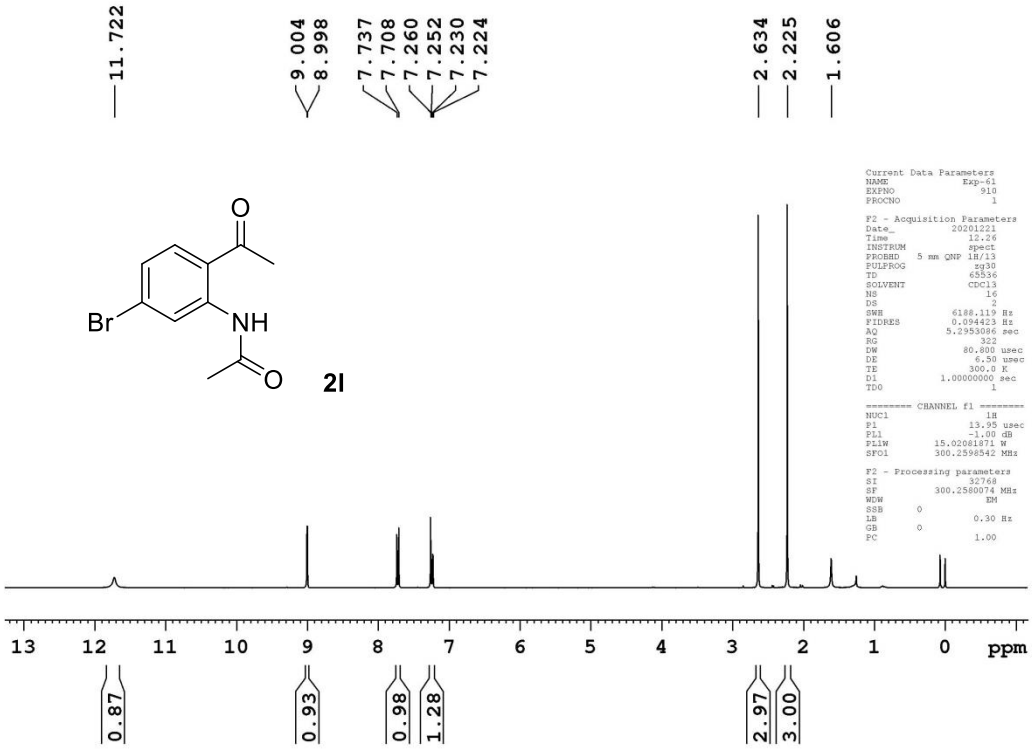
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2l
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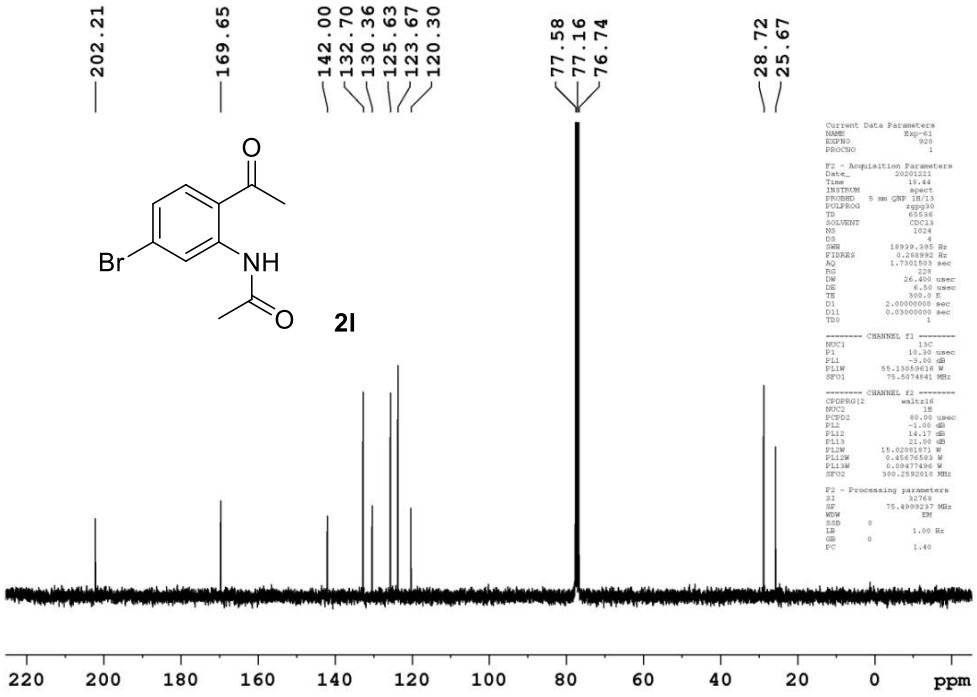
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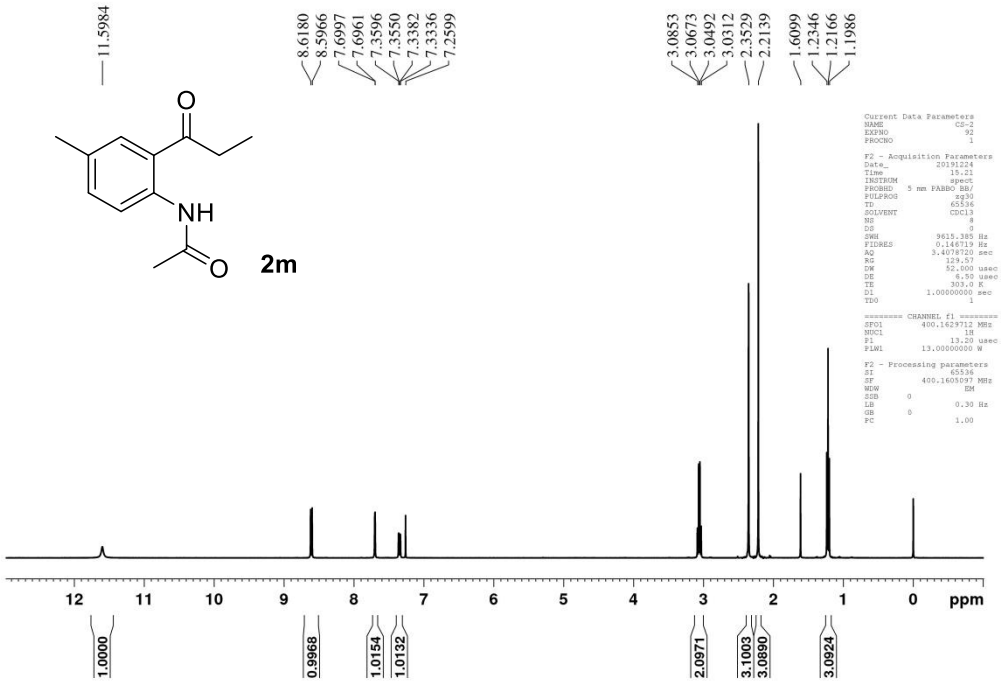
O
2l
ppm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3.0312
2.3529
2.2139
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1.2346
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1.1986
NH
O
O
2m
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11
10
9
8
7
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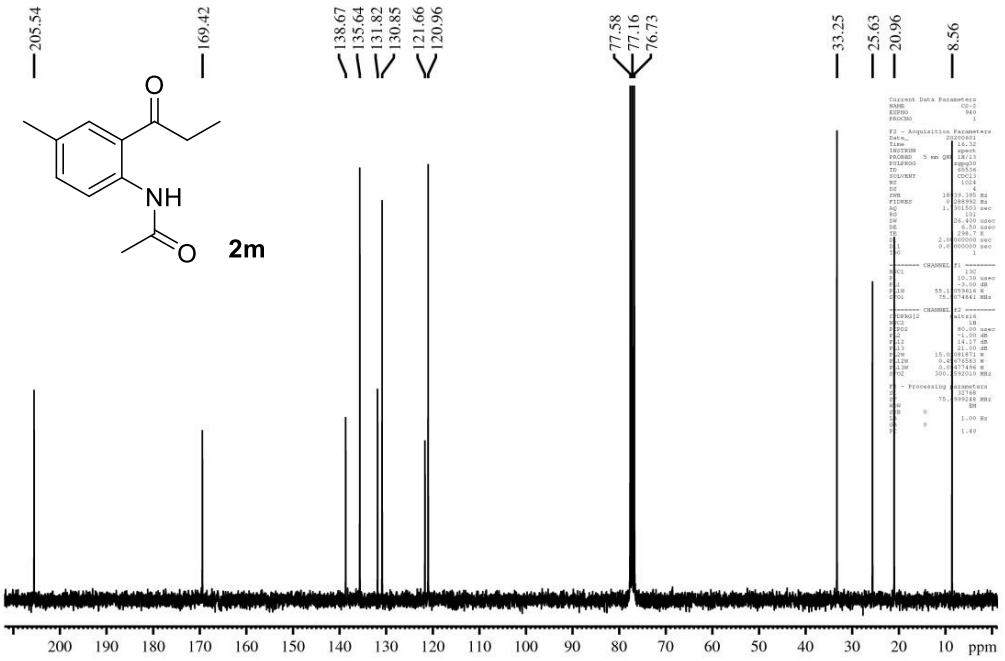
3.0924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76.73
33.25
25.63
20.96
8.56
NH
O
O
2m
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130
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110
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70
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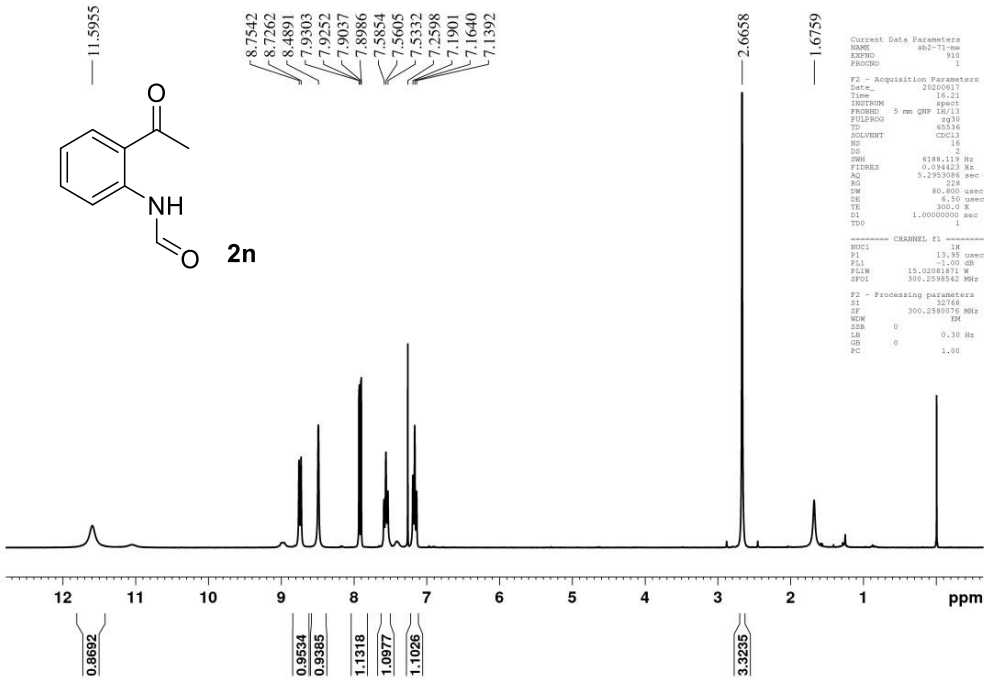
10
ppm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7.5332
7.2598
7.1901
7.1640
7.1392
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NH
O
O
2n
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8
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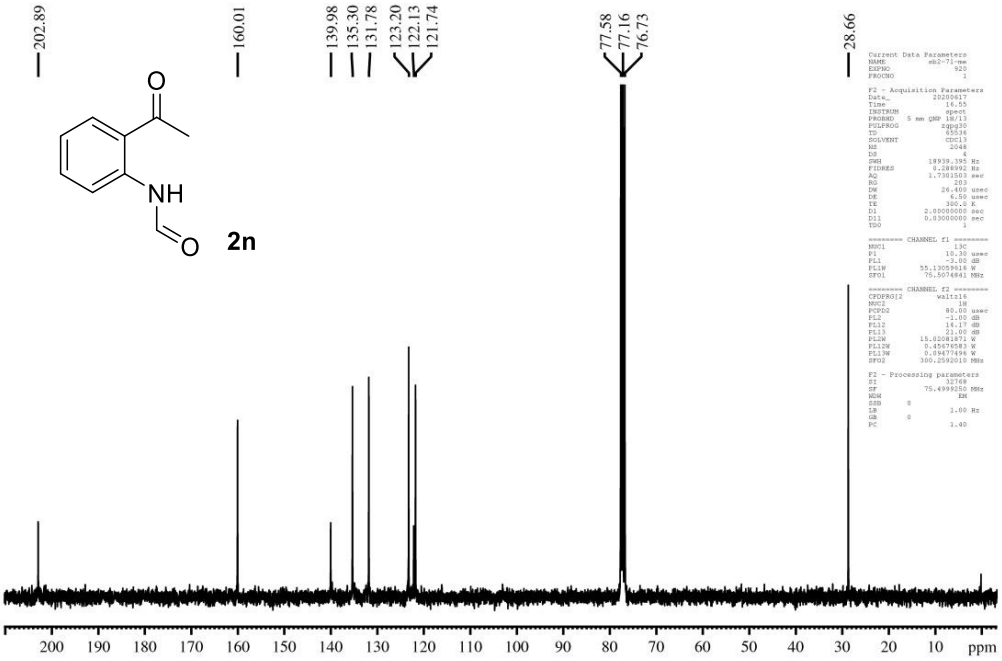
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77.16
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28.66
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O
O
2n
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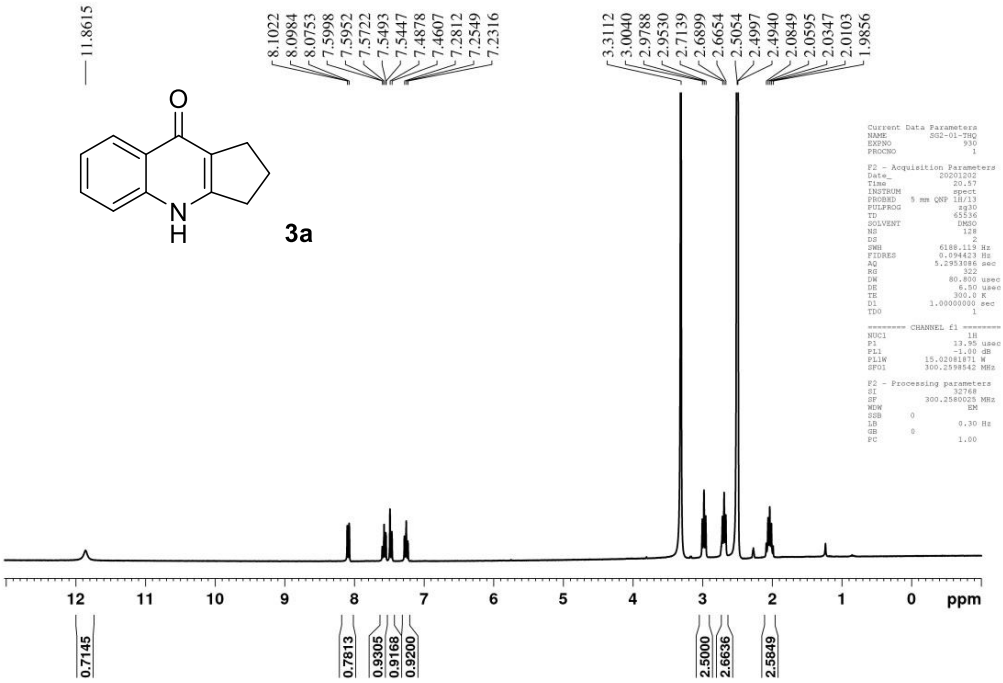
ppm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7.2812
7.2549
7.2316
3.3112
3.0040
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2.9530
2.7139
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2.6654
2.5054
2.4997
2.4940
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10
9
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6
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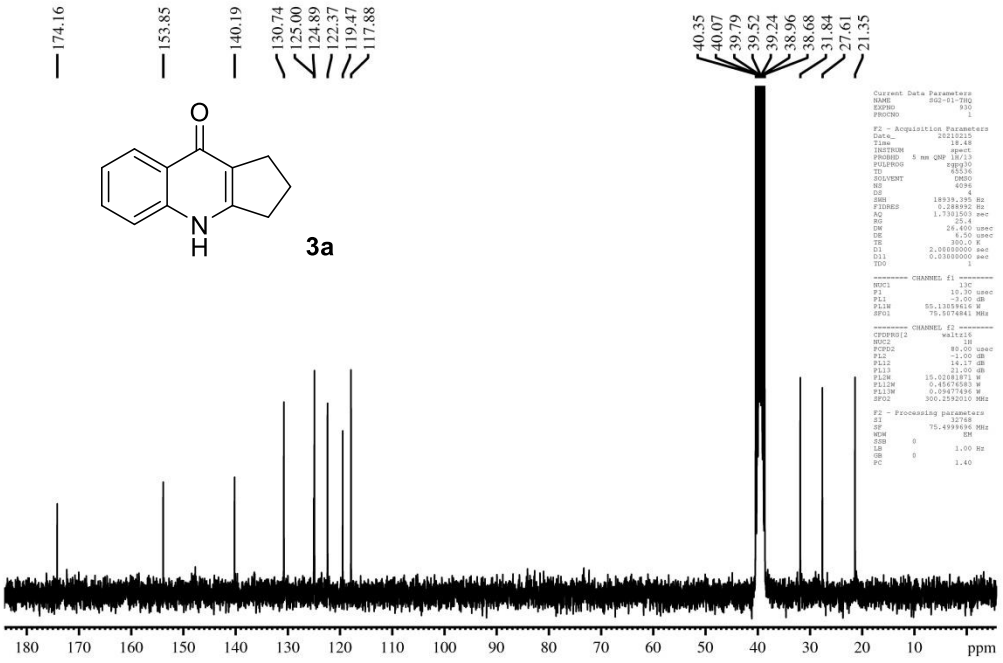
2.5849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119.47
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40.07
39.79
39.52
39.24
38.96
38.68
31.84
27.61
21.35
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150
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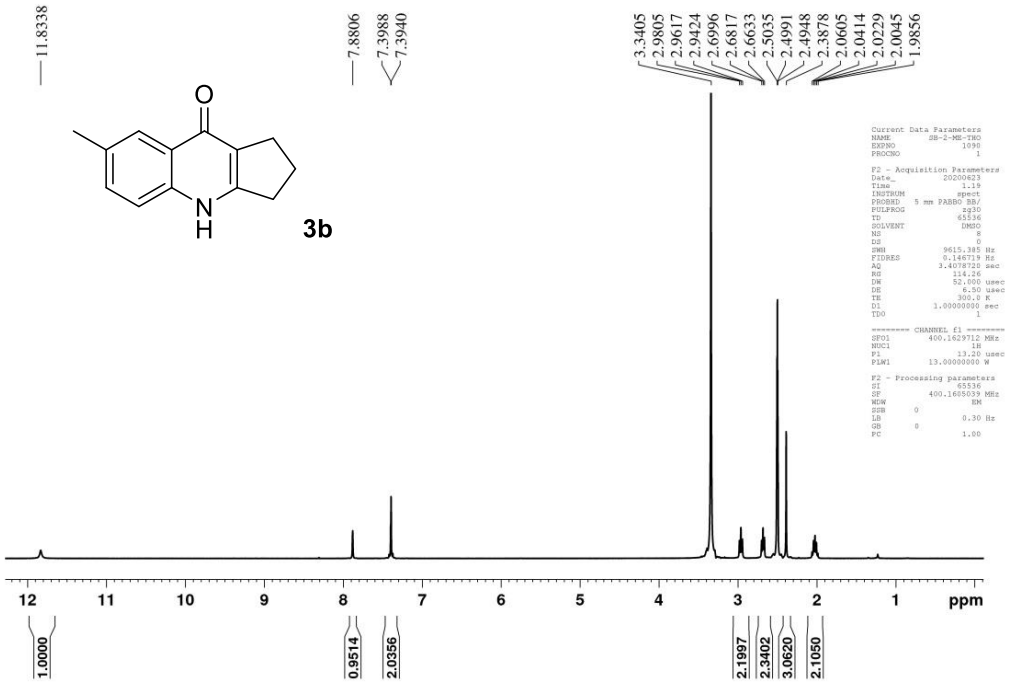
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9
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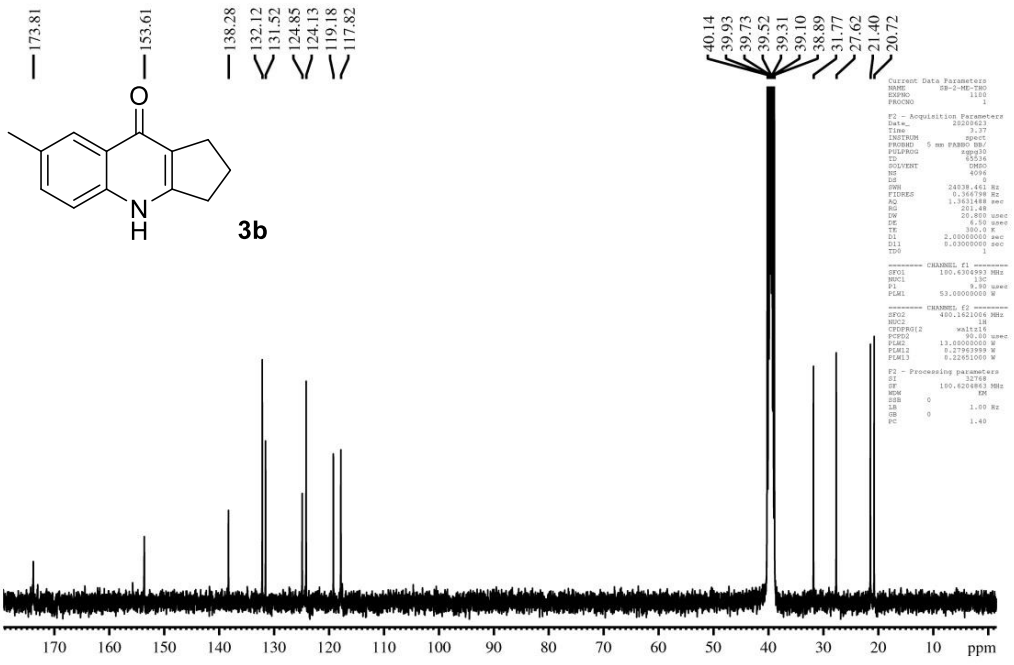
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39.31
39.10
38.89
31.77
27.62
21.40
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150
140
130
120
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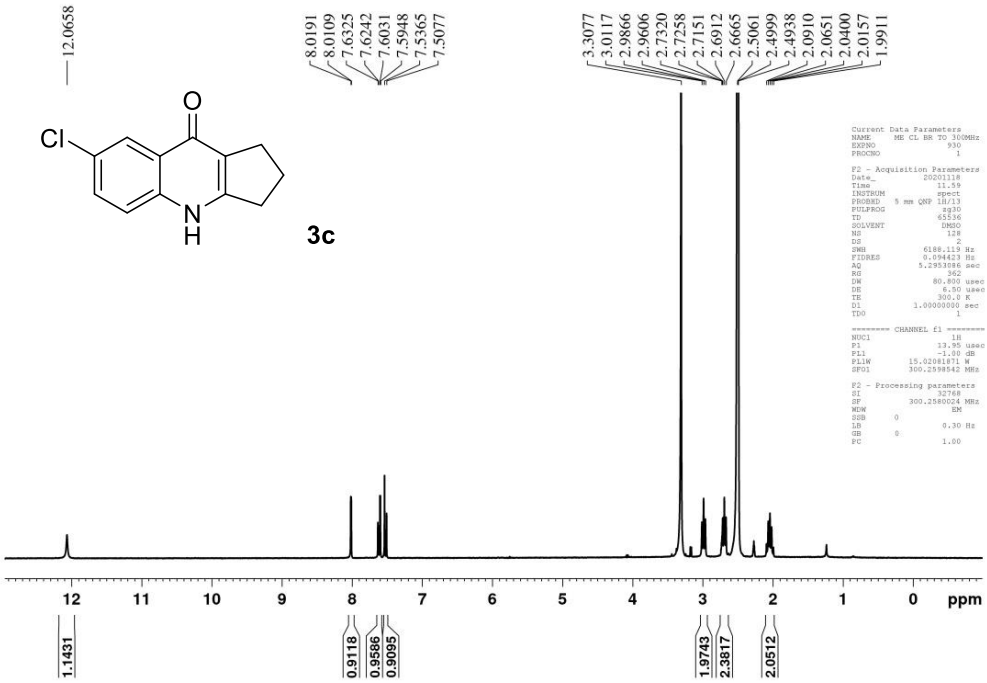
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2.5061
2.4999
2.4938
2.0910
2.0651
2.0400
2.0157
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H
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11
10
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8
7
6
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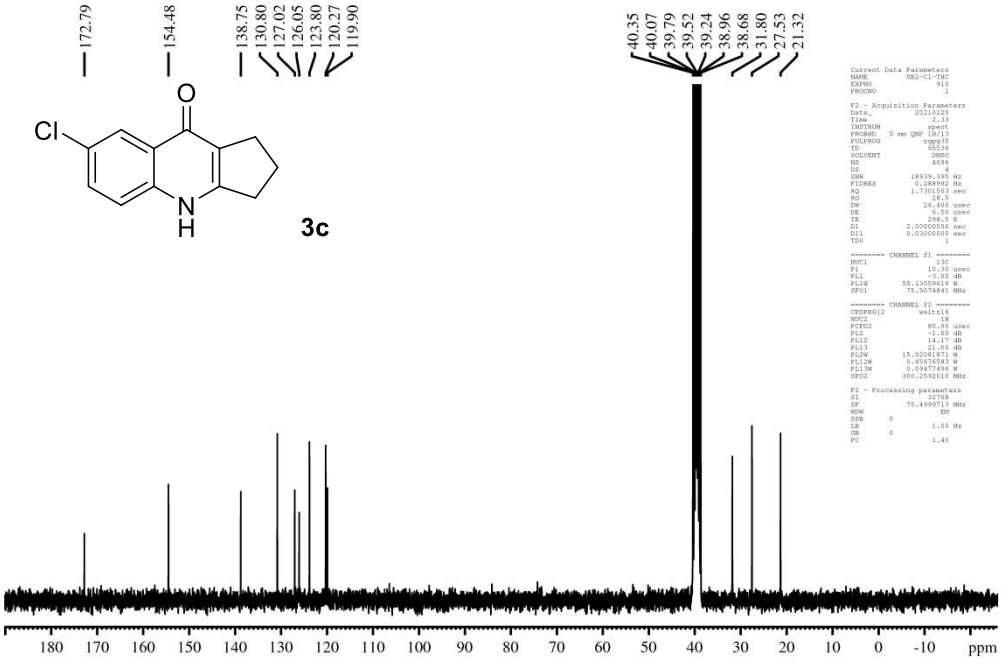
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39.24
38.96
38.68
31.80
27.53
21.32
Cl
O
N
H
3c
180
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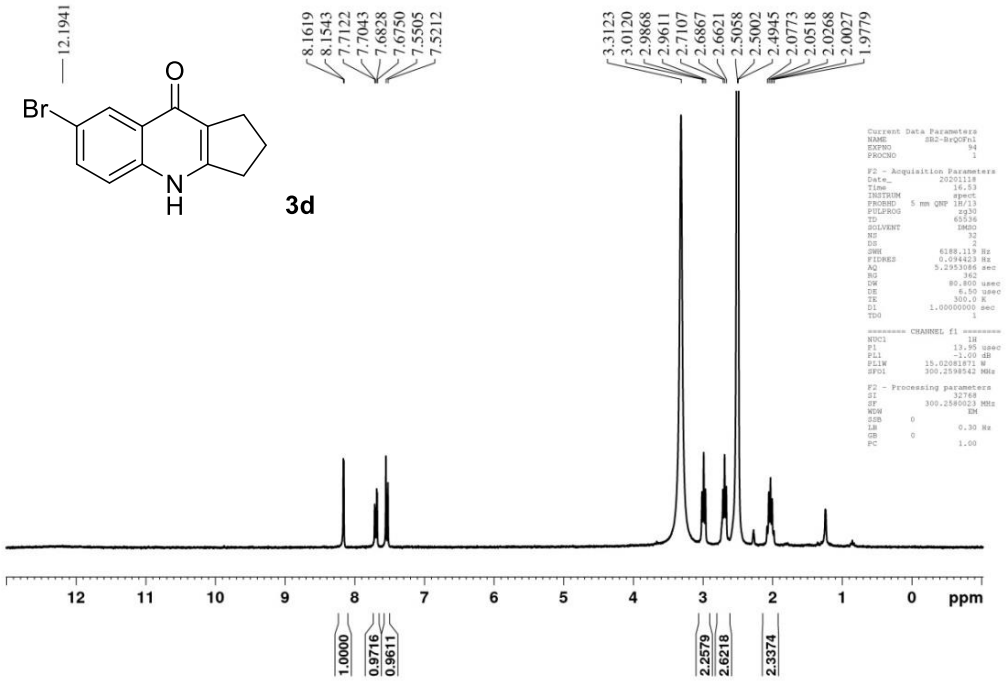
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2.9611
2.7107
2.6867
2.6621
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2.5002
2.4945
2.0773
2.0518
2.0268
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1.9779
Br
O
N
H
3d
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11
10
9
8
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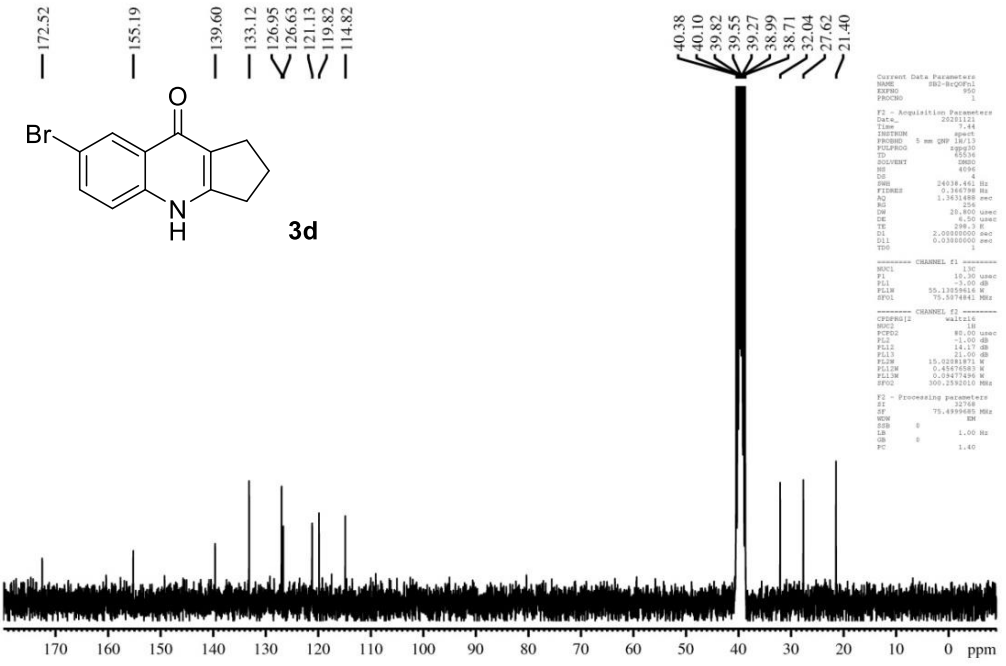
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119.82
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40.10
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39.55
39.27
38.99
38.71
32.04
27.62
21.40
Br
O
N
H
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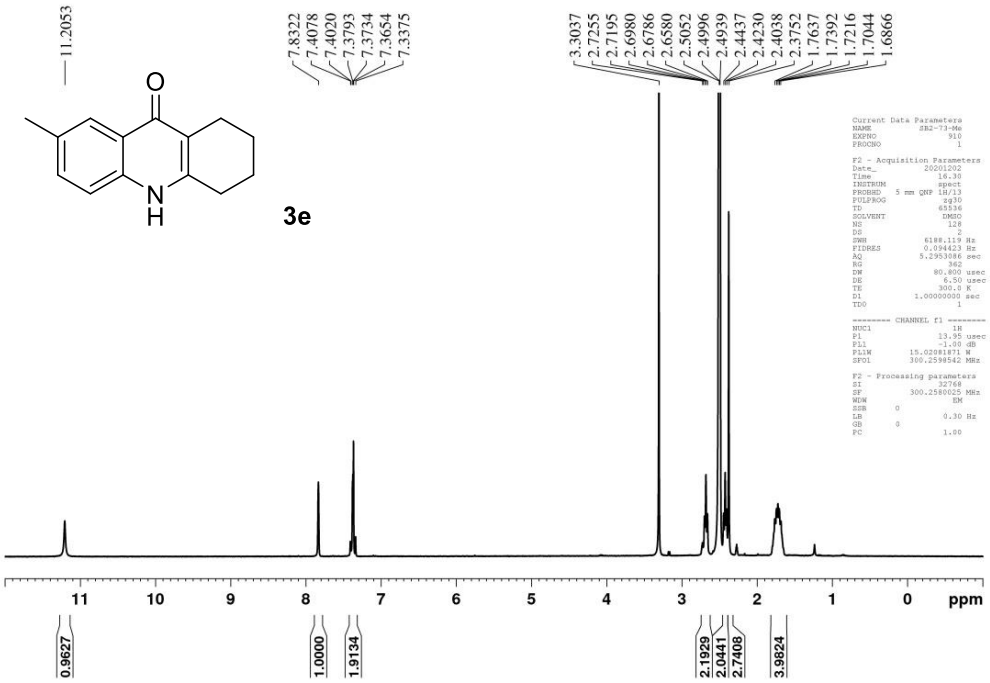
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2.6980
2.6786
2.6580
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2.4996
2.4939
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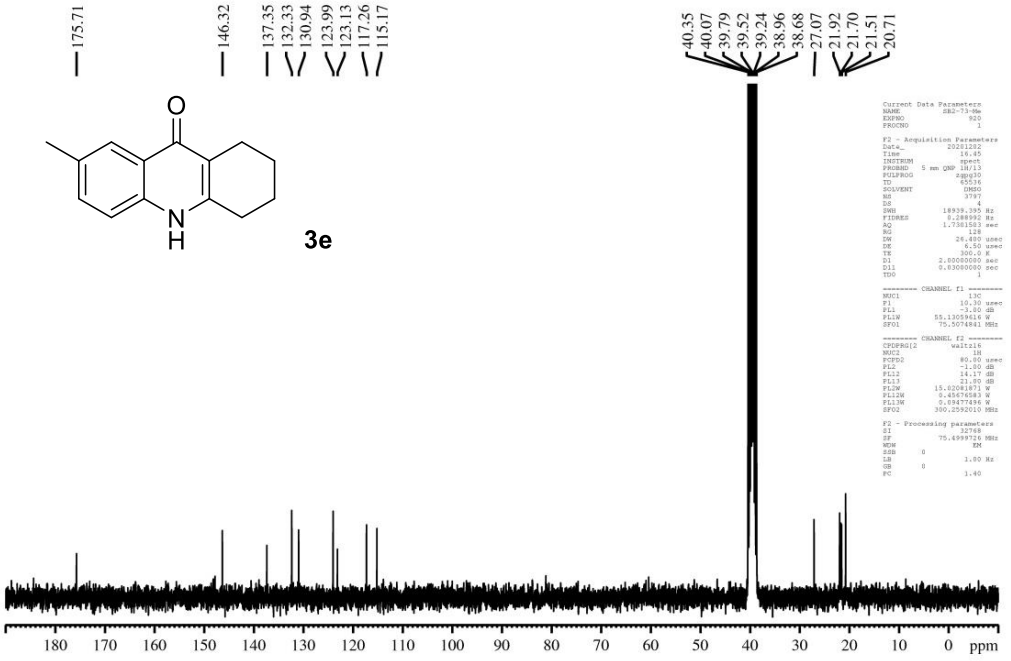
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39.79
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38.96
38.68
27.07
21.92
21.70
21.51
20.71
3e
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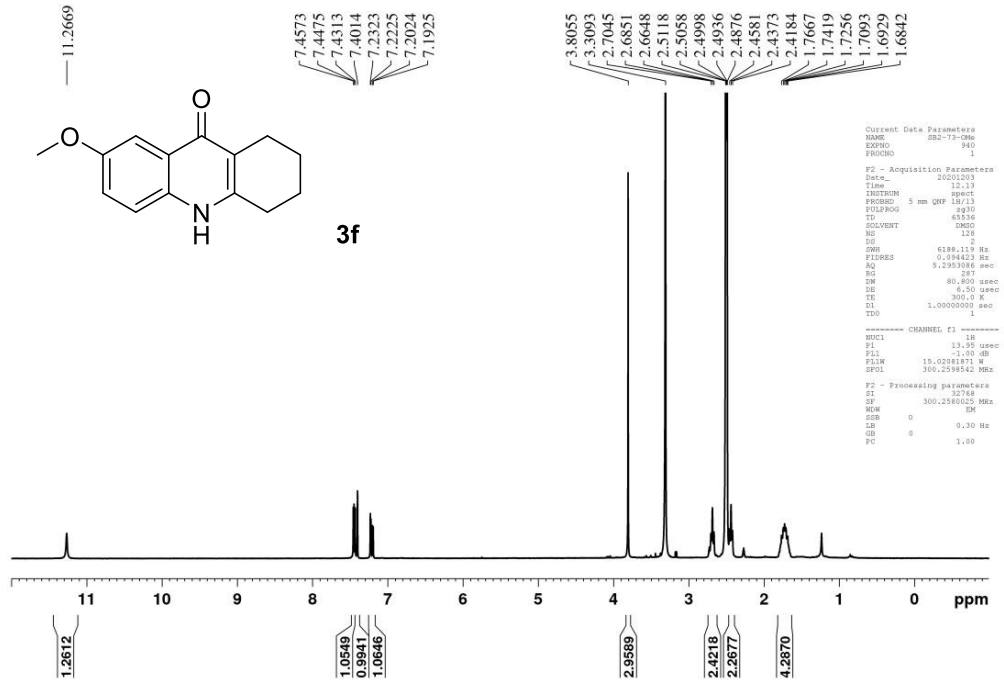
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7.1925
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3.3093
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2.5118
2.5058
2.4998
2.4936
2.4876
2.4581
2.4373
2.4184
1.7667
1.7419
1.7256
1.7093
1.6929
1.6842
3f
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10
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8
7
6
5
4
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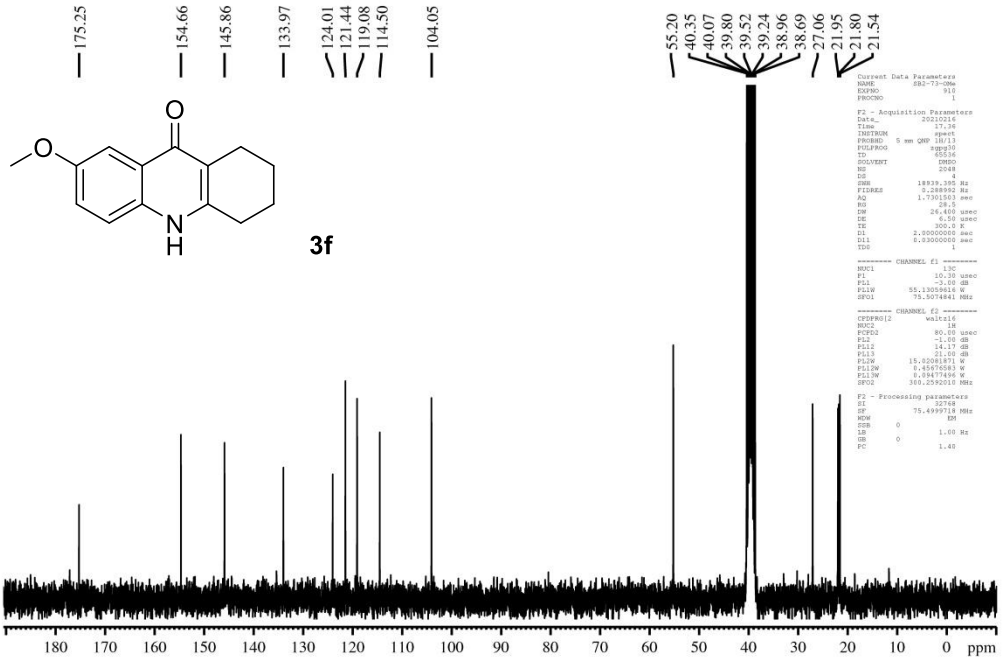
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114.50
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55.20
40.35
40.07
39.80
39.52
39.24
38.96
38.69
27.06
21.95
21.80
21.54
3f
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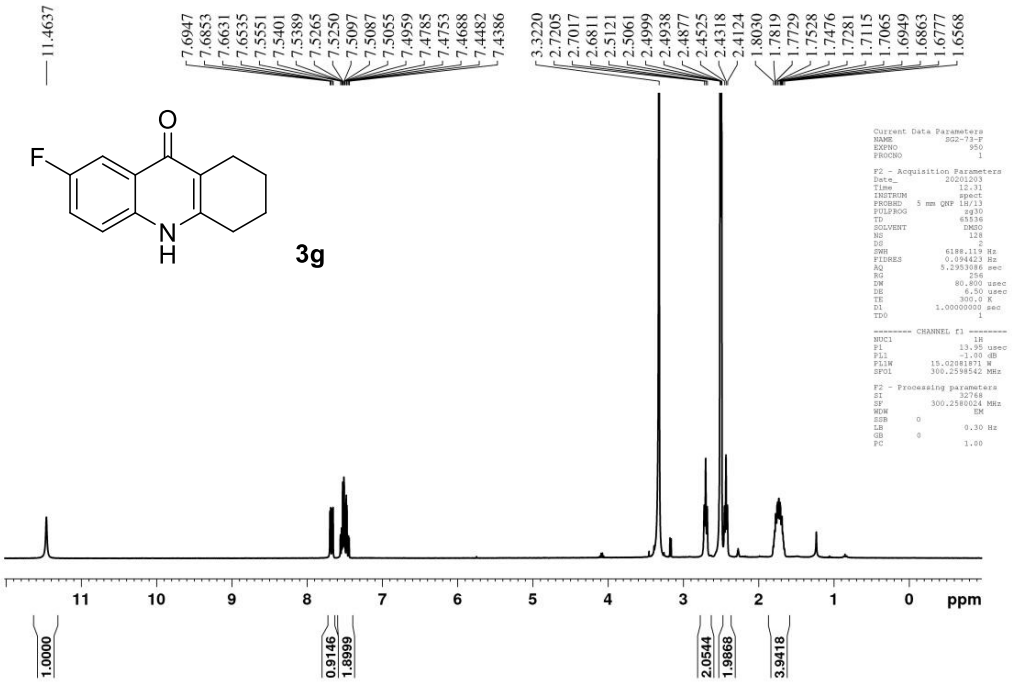
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1.6777
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F
O
N
H
3g
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10
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8
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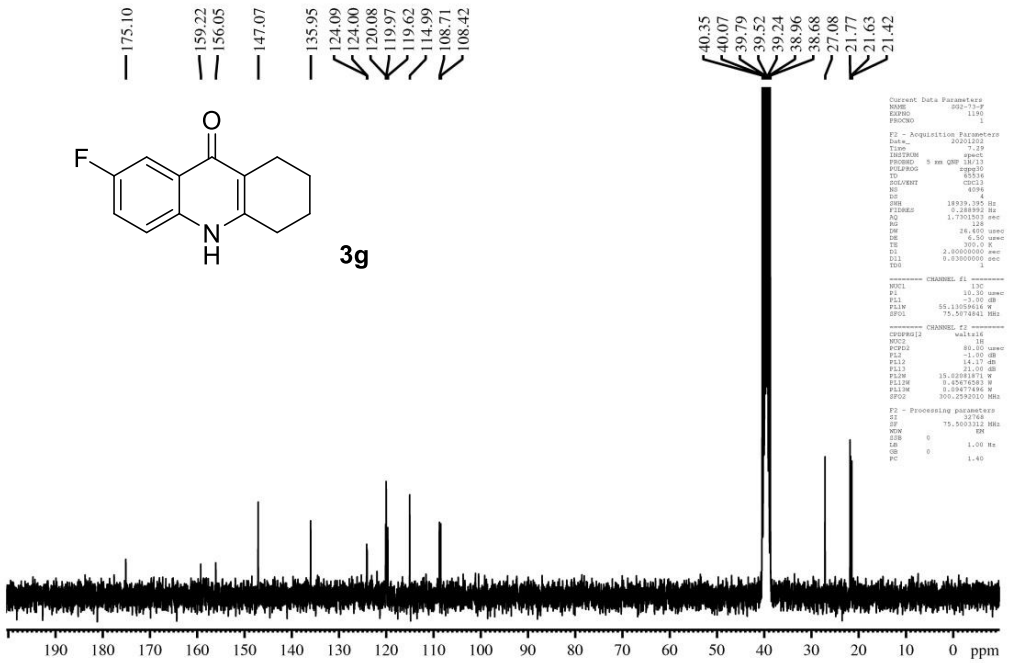
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124.00
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119.62
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40.35
40.07
39.79
39.52
39.24
38.96
38.68
27.08
21.77
21.63
21.42
F
O
N
H
3g
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100
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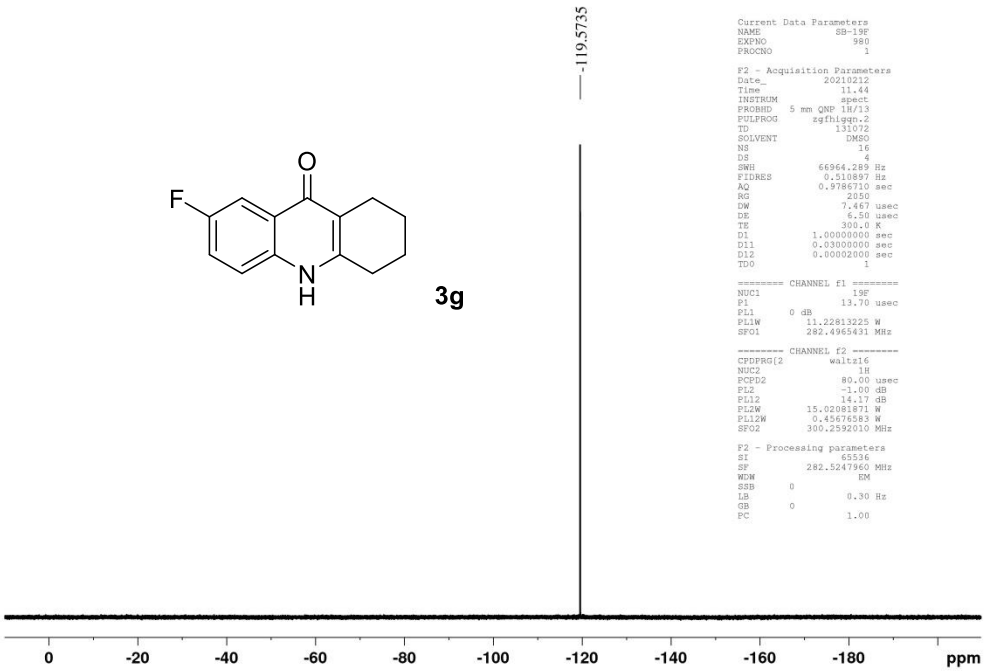
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Time 11.44
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PROBHD 5 mm QNP 1H/13
PULPROG zgfhigqn.2
TD 131072
SOLVENT DMSO
NS 16
DS 4
SWH 66964.289 Hz
FIDRES 0.510897 Hz
AQ 0.9786710 sec
RG 2050
DW 7.467 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
D11 0.03000000 sec
D12 0.00002000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 19F
P1 13.70 usec
PL1 0 dB
PL1W 11.22813225 W
SFO1 282.4965431 MHz
======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.17 dB
PL2W 15.02081871 W
PL12W 0.45676583 W
SFO2 300.2592010 MHz
F2 - Processing parameters
SI 65536
SF 282.5247960 MHz
WDW EM
SSB 0
LB 0.30 Hz
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PC 1.00
0
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-100
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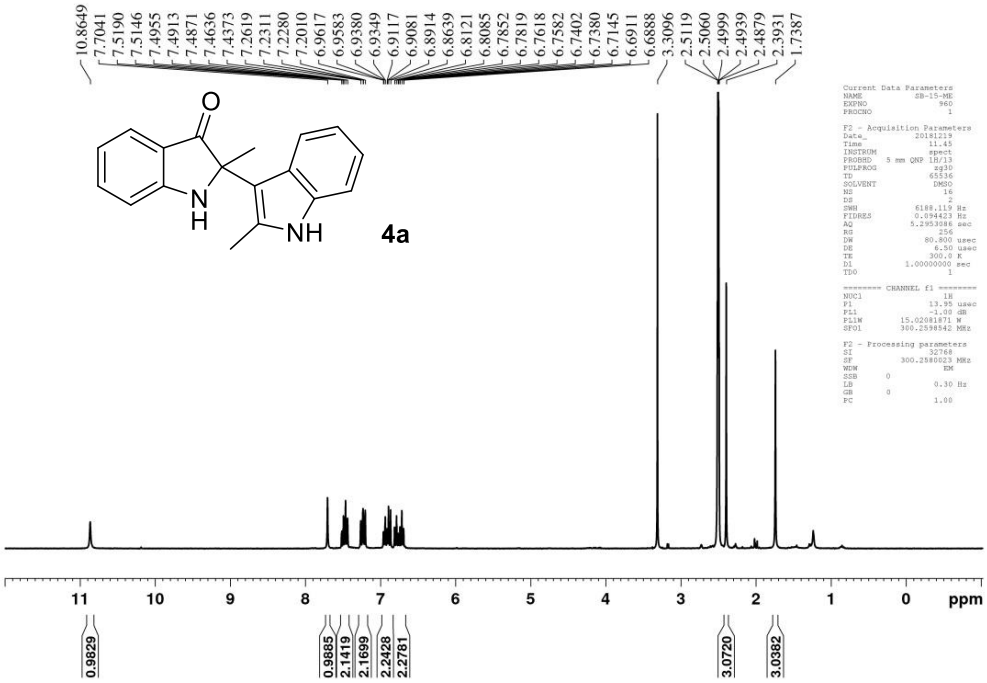
-140
-160
-180
ppm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6.8085
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6.7819
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6.7582
6.7402
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6.6911
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3.3096
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2.5060
2.4999
2.4939
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N
H
NH
4a
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EXPNO 960
PROCNO 1
F2 - Acquisition Parameters
Date_ 20181219
Time 11.45
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PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 6188.119 Hz
FIDRES 0.094423 Hz
AQ 5.2953086 sec
RG 256
DW 80.800 usec
DE 6.50 usec
TE 300.0 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 13.95 usec
PL1 -1.00 dB
PL1W 15.02081871 W
SFO1 300.2598542 MHz
F2 - Processing parameters
SI 32768
SF 300.2580023 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
11
10
9
8
7
6
5
4
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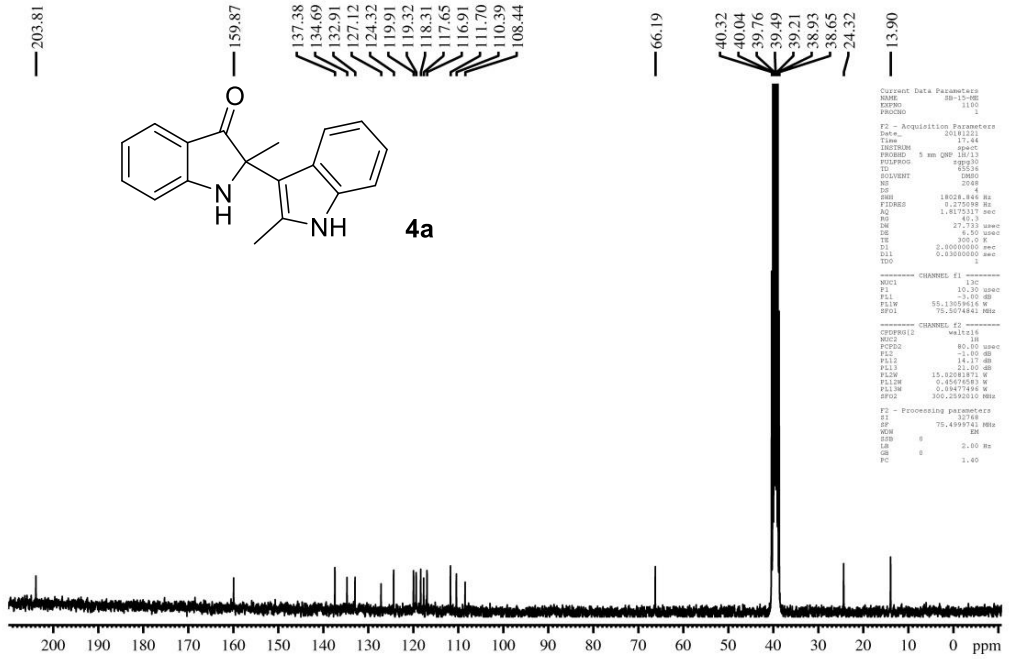
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118.31
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110.39
108.44
66.19
40.32
40.04
39.76
39.49
39.21
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13.90
O
N
H
NH
4a
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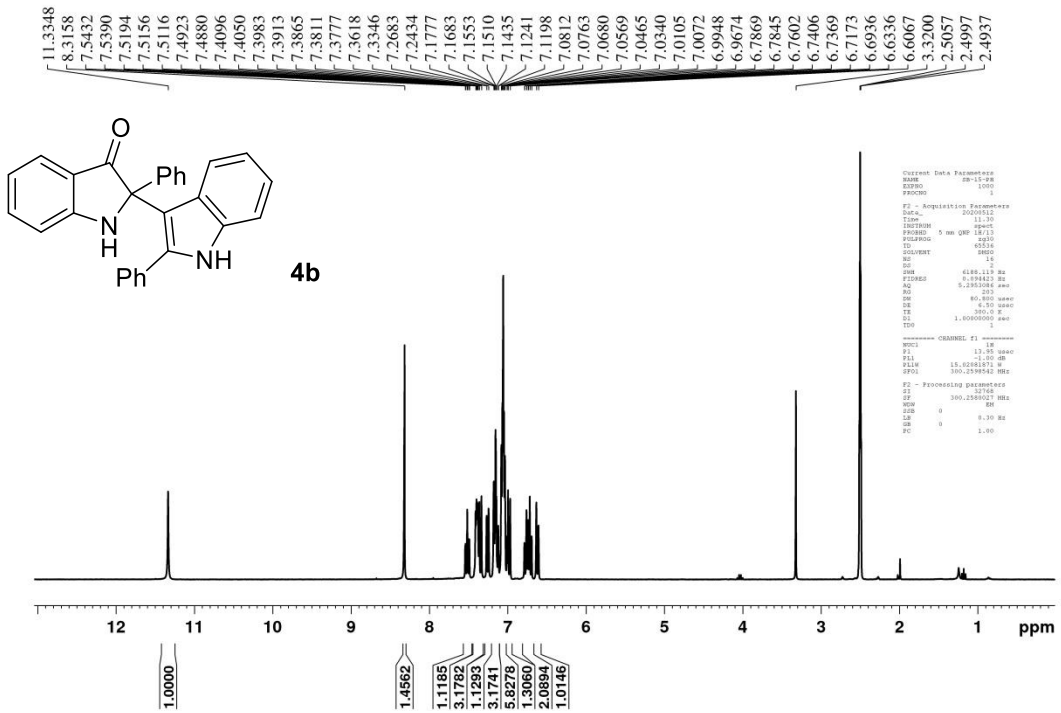
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6.6067
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2.4997
2.4937
O
Ph
N
H
NH
Ph
4b
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1.1293
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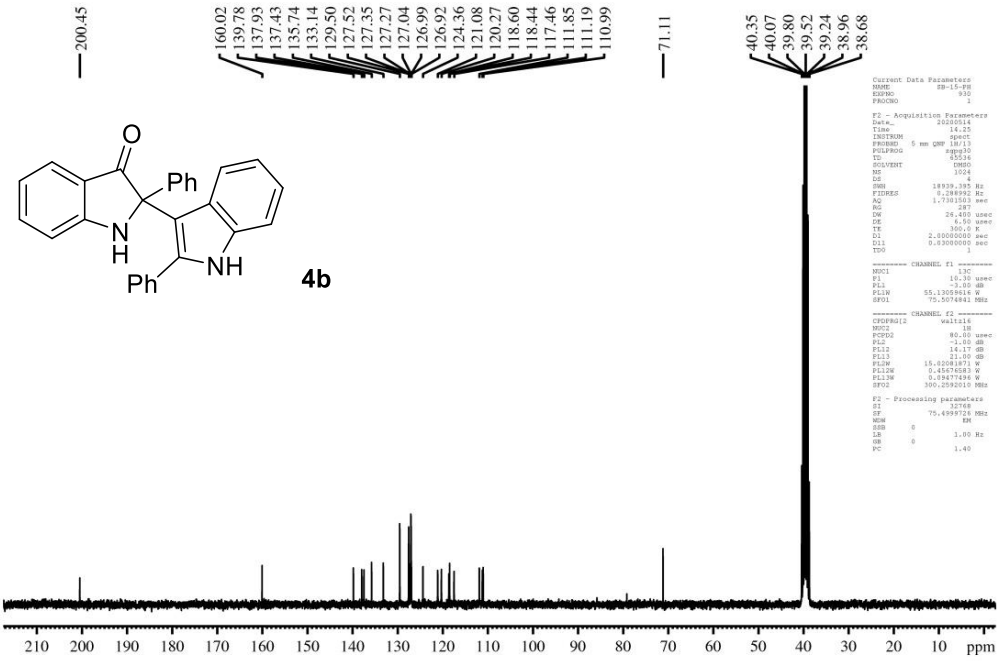
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135.74
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127.27
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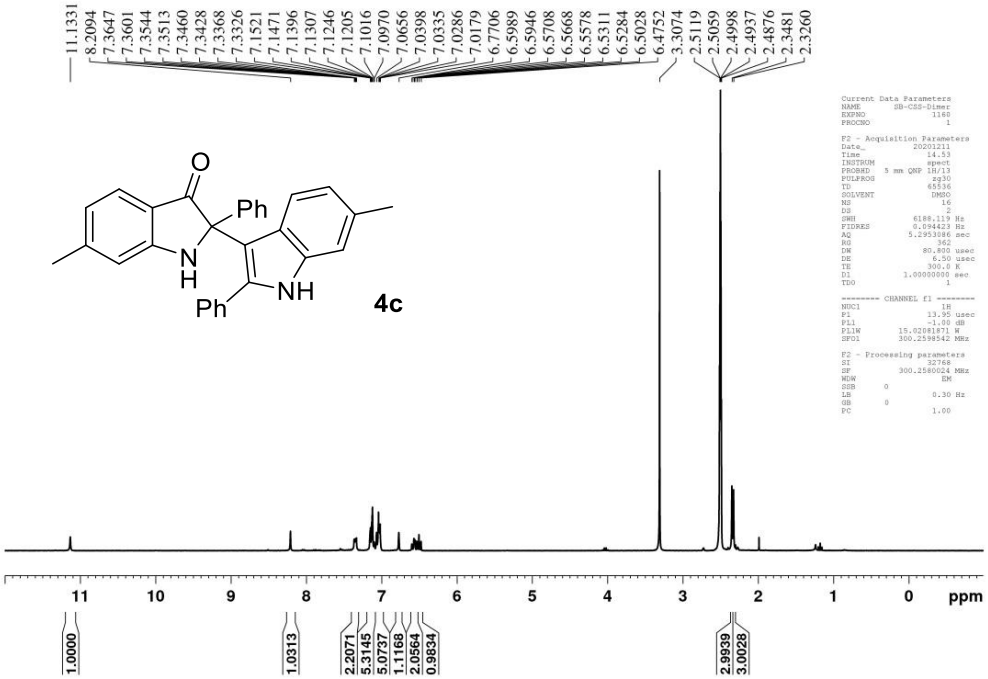
126.99
126.92
124.36
121.08
120.27
118.60
118.44
117.46
111.85
111.19
110.99
71.11
40.35
40.07
39.80
39.52
39.24
38.96
38.68
O
Ph
N
H
NH
Ph
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.3513
7.3460
7.3428
7.3368
7.3326
7.1521
7.1471
7.1396
7.1307
7.1246
7.1205
7.1016
7.0970
7.0656
7.0398
7.0335
7.0286
7.0179
6.7706
6.5989
6.5946
6.5708
6.5668
6.5578
6.5311
6.5284
6.5028
6.4752
3.3074
2.5119
2.5059
2.4998
2.4937
2.4876
2.3481
2.3260
O
Ph
N
H
NH
Ph
4c
11 10 9 8 7 6 5 4 3 2 1 0 ppm
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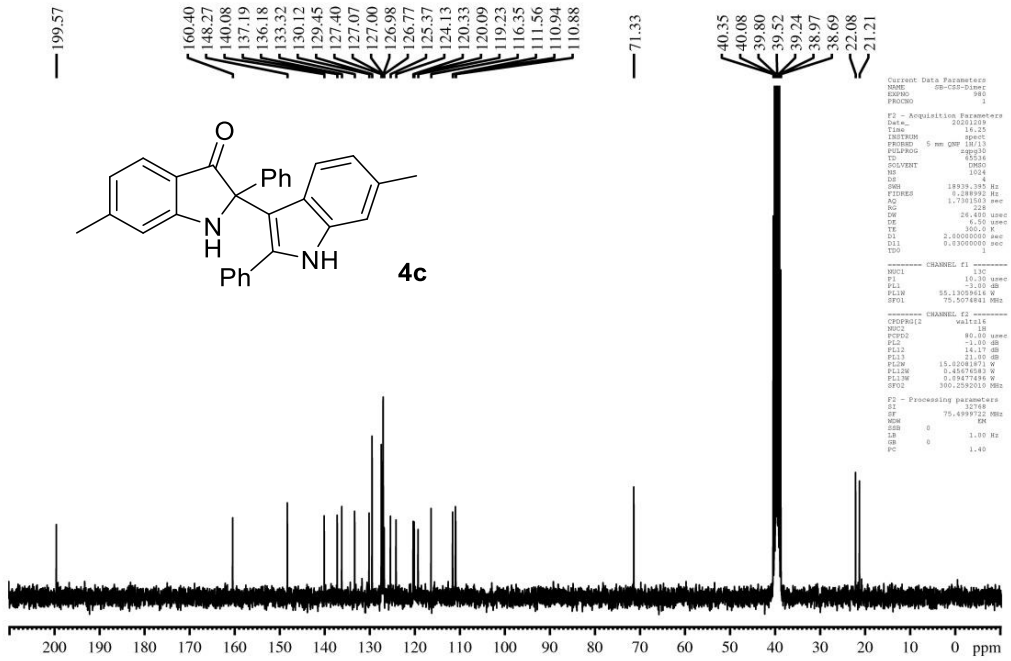
1.0313
2.2071
5.3145
5.0737
1.1168
2.0564
0.9834
2.9939
3.0028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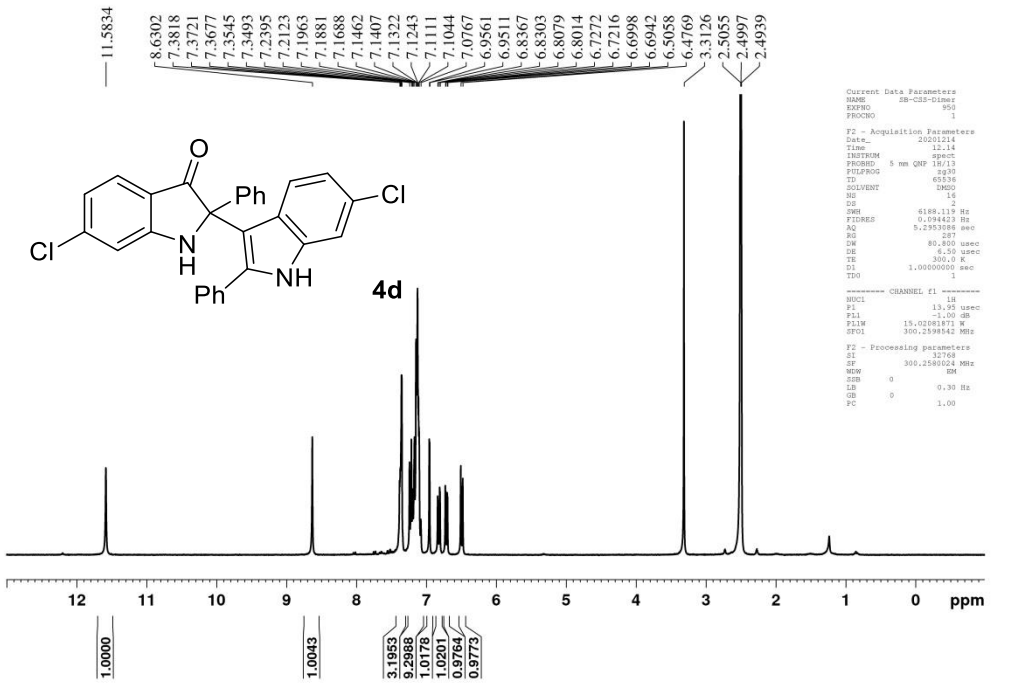
160.40
148.27
140.08
137.19
136.18
133.32
130.12
129.45
127.40
127.07
127.00
126.98
126.77
125.37
124.13
120.33
120.09
119.23
116.35
111.56
110.94
110.88
71.33
40.35
40.08
39.80
39.52
39.24
38.97
38.69
22.08
21.21
O
Ph
N
H
NH
Ph
4c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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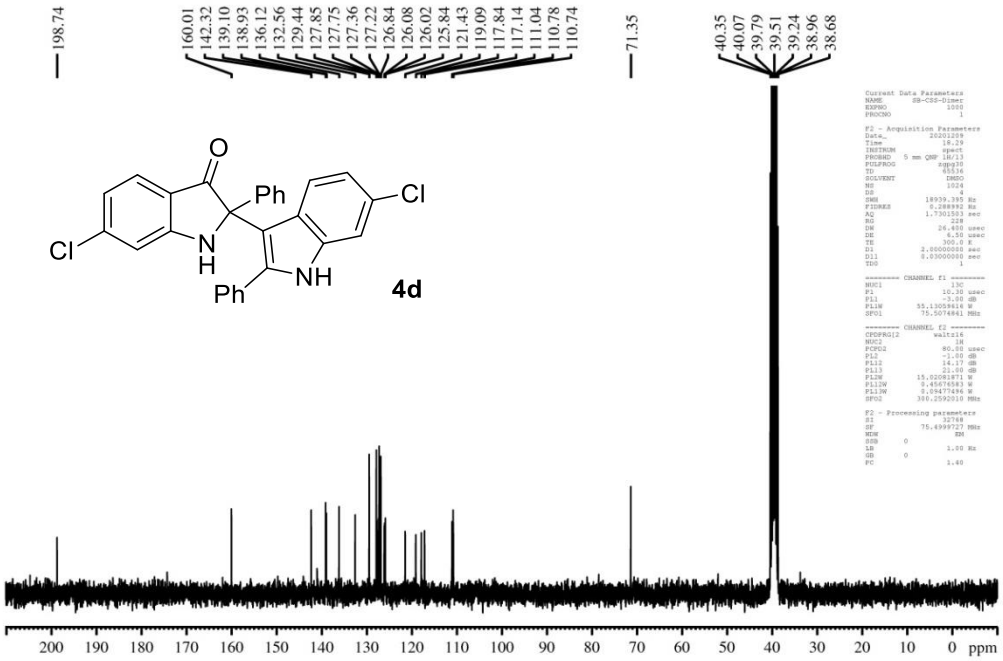
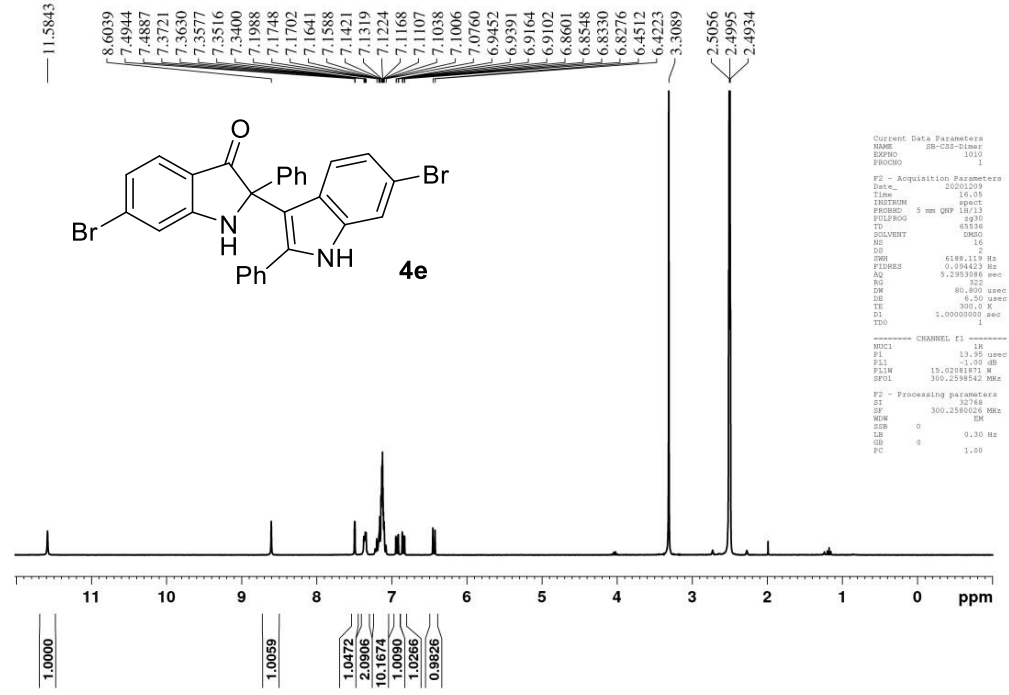
8.6302
7.3818
7.3721
7.3677
7.3545
7.3493
7.2395
7.2123
7.1963
7.1881
7.1688
7.1462
7.1407
7.1322
7.1243
7.1111
7.1044
7.0767
6.9561
6.9511
6.8367
6.8303
6.8079
6.8014
6.7272
6.7216
6.6998
6.6942
6.5058
6.4769
3.3126
2.5055
2.4997
2.4939
O
Ph
Cl
Cl
N
H
NH
Ph
4d
12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.0000
1.0043
3.1953
9.2988
1.0178
1.0201
0.9764
0.9773


198.74
160.01
142.32
139.10
138.93
136.12
132.56
129.44
127.85
127.75
127.36
127.22
126.84
126.08
126.02
125.84
121.43
119.09
117.84
117.14
111.04
110.78
110.74
71.35
40.35
40.07
39.79
39.51
39.24
38.96
38.68
O
Ph
Cl
N
H
Cl
NH
Ph
4d
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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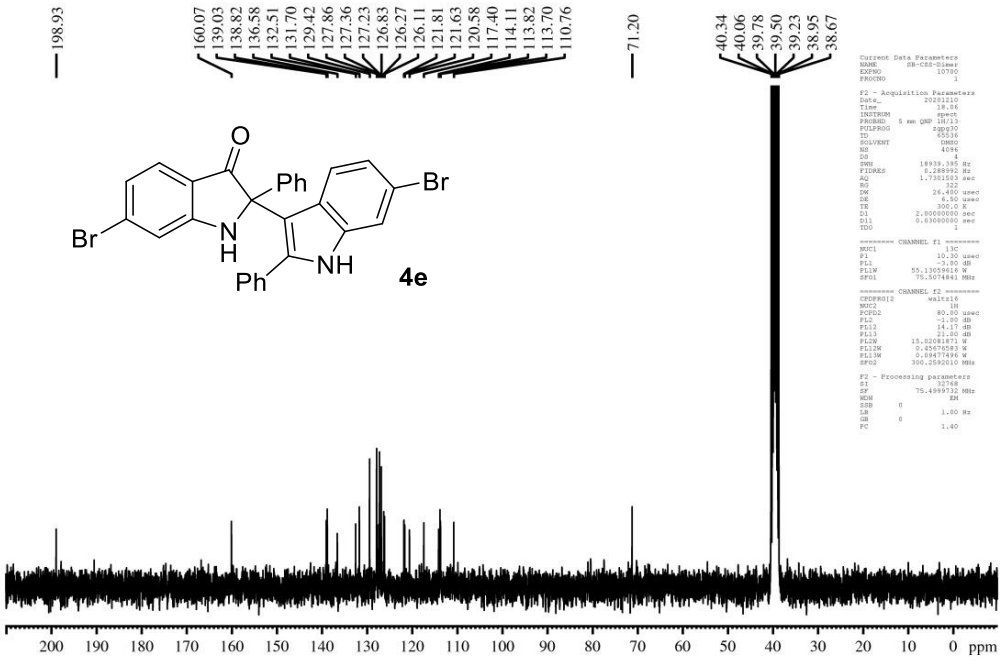
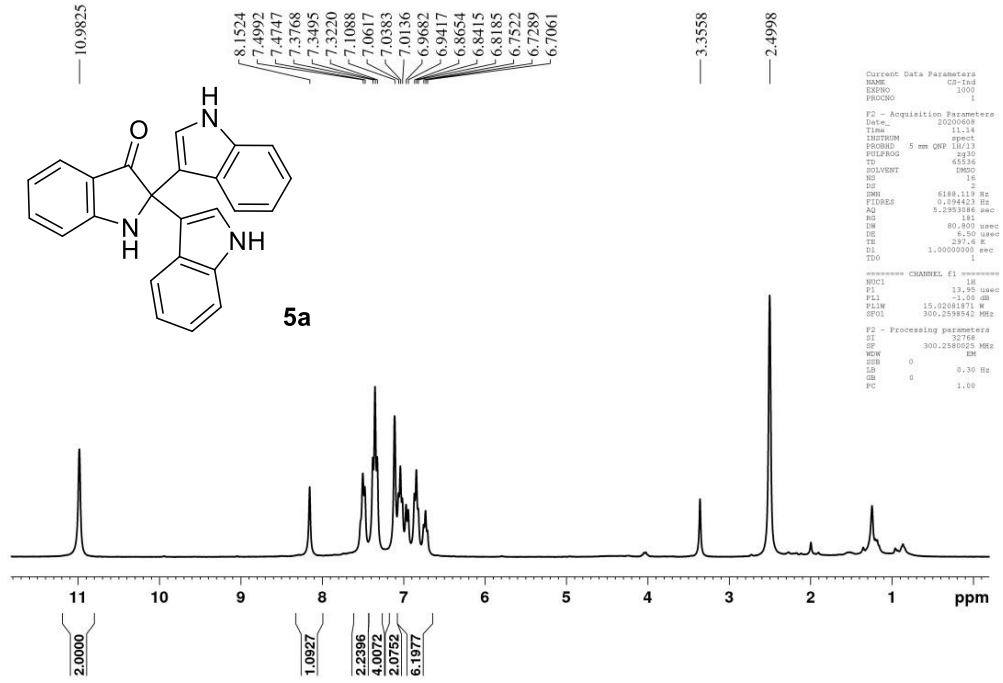
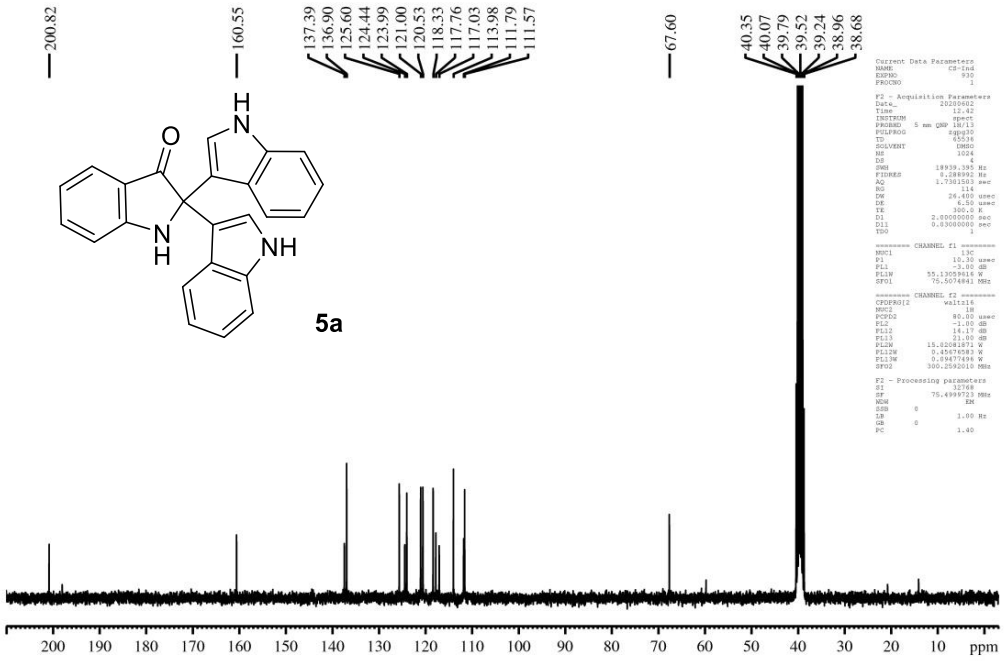
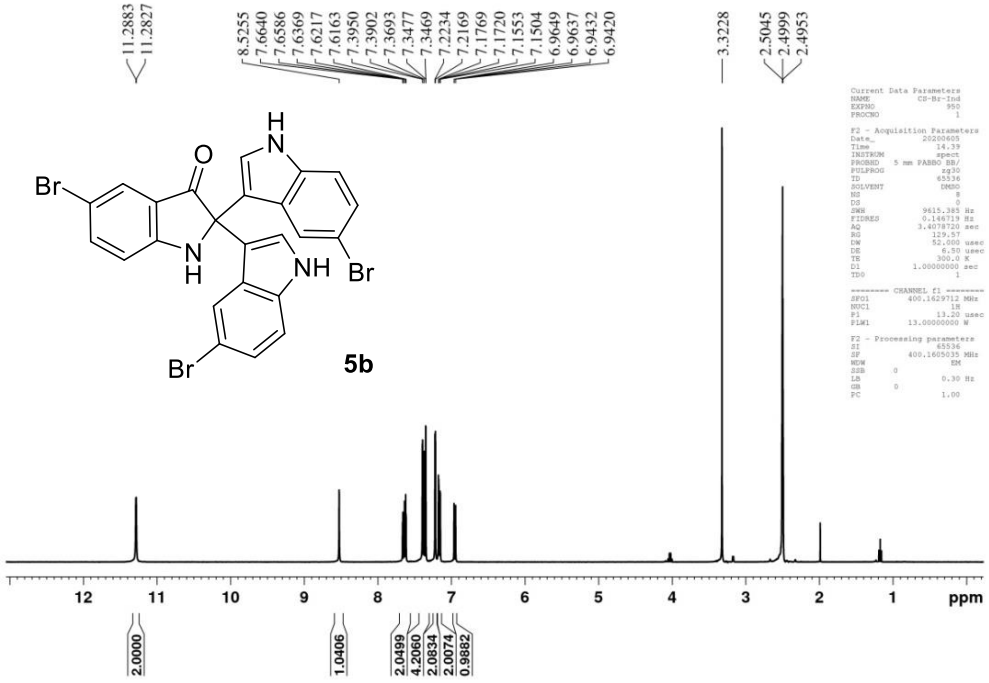
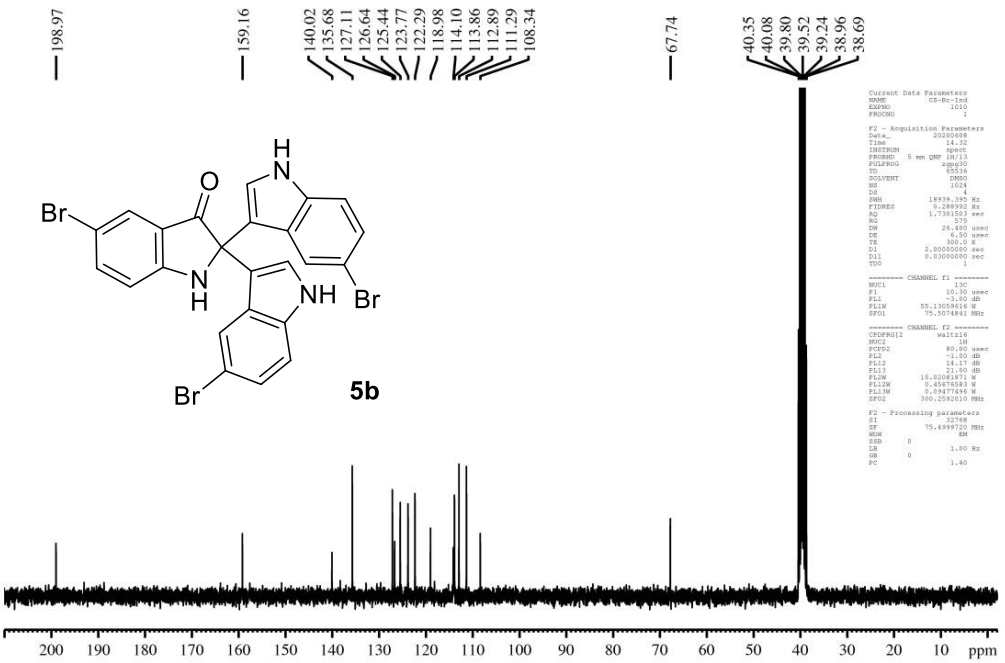
7.4944
7.4887
7.3721
7.3630
7.3577
7.3516
7.3400
7.1988
7.1748
7.1702
7.1641
7.1588
7.1421
7.1319
7.1224
7.1168
7.1107
7.1038
7.1006
7.0760
6.9452
6.9391
6.9164
6.9102
6.8601
6.8548
6.8330
6.8276
6.4512
6.4223
3.3089
2.5056
2.4995
2.4934
O
Ph
Br
N
H
Br
NH
Ph
4e
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.0000
1.0059
1.0472
2.0906
10.1674
1.0090
1.0266
0.9826

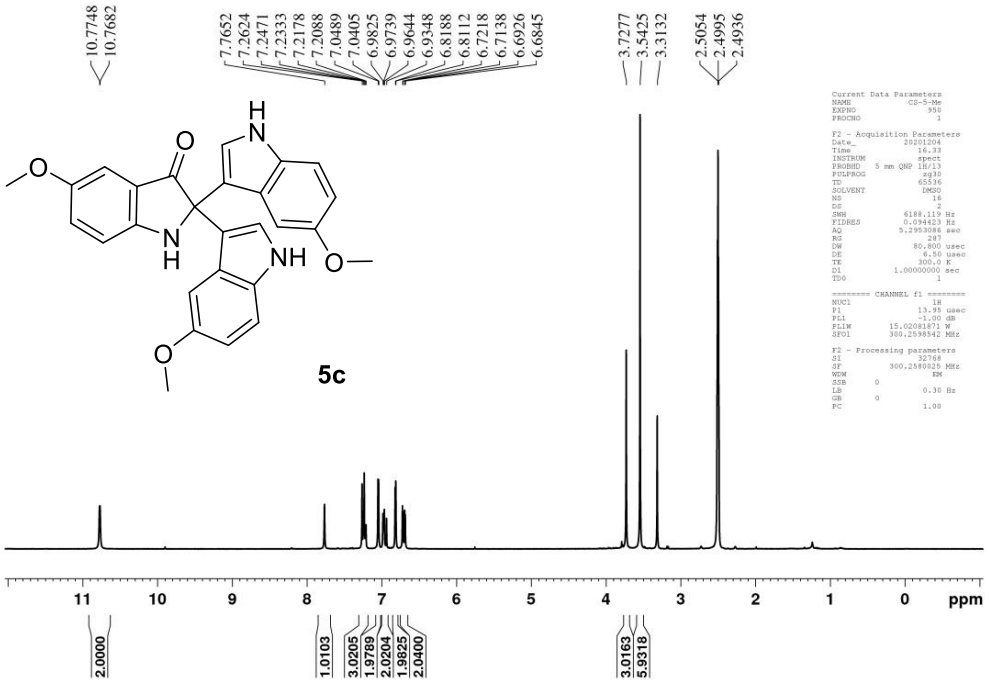

198.93
160.07
139.03
138.82
136.58
132.51
131.70
129.42
127.86
127.36
127.23
126.83
126.27
126.11
121.81
121.63
120.58
117.40
114.11
113.82
113.70
110.76
71.20
40.34
40.06
39.78
39.50
39.23
38.95
38.67
Br
Br
O
Ph
N
H
Ph
NH
4e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

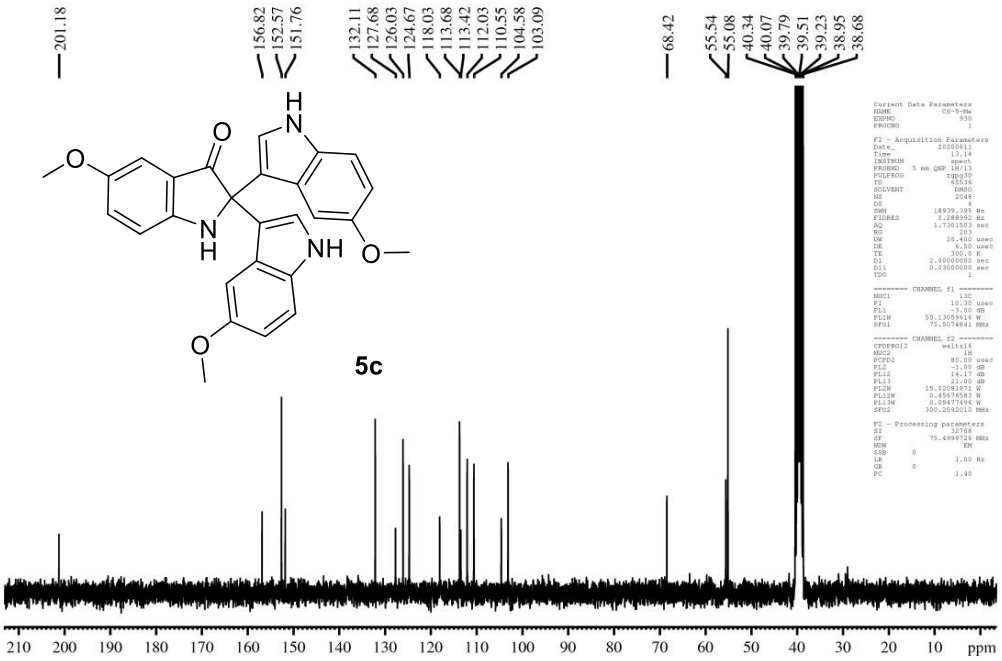

10.9825
8.1524
7.4992
7.4747
7.3768
7.3495
7.3220
7.1088
7.0617
7.0383
7.0136
6.9682
6.9417
6.8654
6.8415
6.8185
6.7522
6.7289
6.7061
3.3558
2.4998
H
N
O
N
H
NH
5a
11 10 9 8 7 6 5 4 3 2 1 ppm
2.0000
1.0927
2.2396
4.0072
2.0752
6.1977

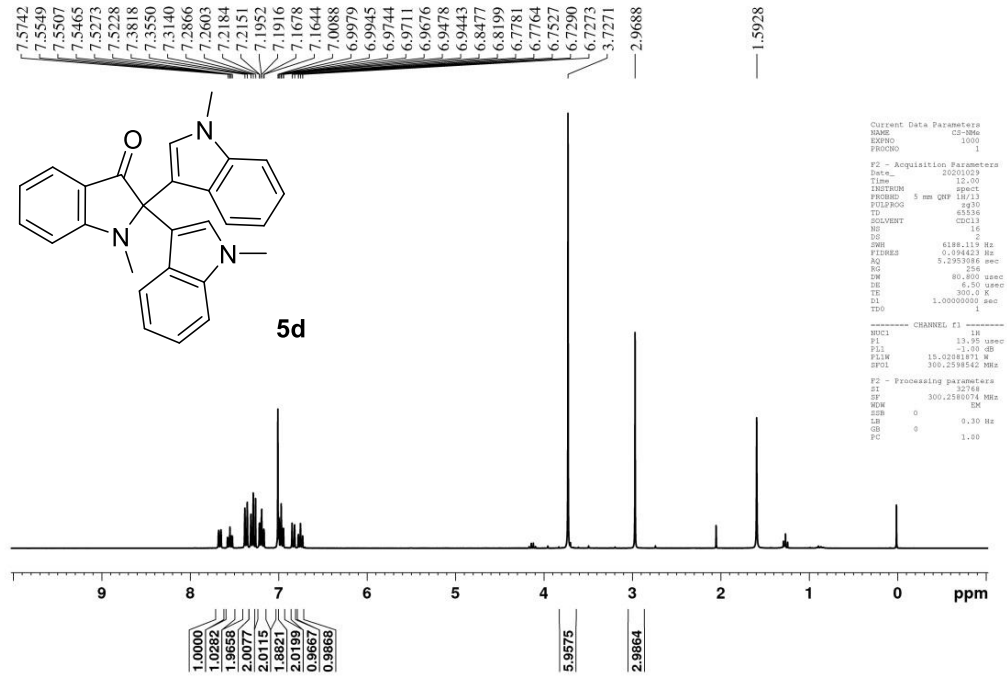

200.82
160.55
137.39
136.90
125.60
124.44
123.99
121.00
120.53
118.33
117.76
117.03
113.98
111.79
111.57
67.60
40.35
40.07
39.79
39.52
39.24
38.96
38.68
5a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

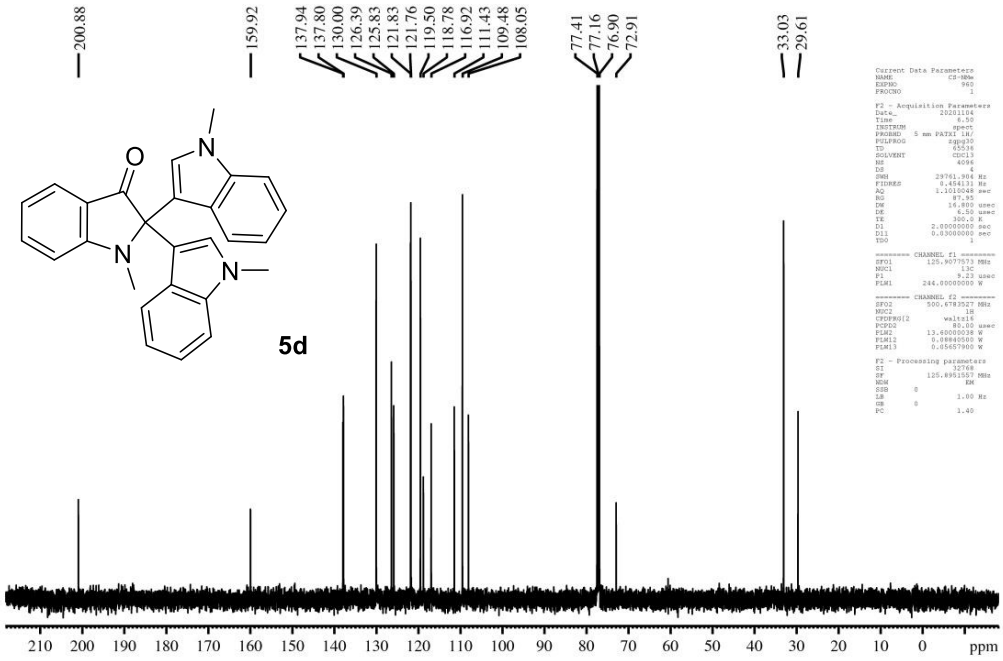

11.2883
11.2827
8.5255
7.6640
7.6586
7.6369
7.6217
7.6163
7.3950
7.3902
7.3693
7.3477
7.3469
7.2234
7.2169
7.1769
7.1720
7.1553
7.1504
6.9649
6.9637
6.9432
6.9420
3.3228
2.5045
2.4999
2.4953
Br
Br
Br
5b
12 11 10 9 8 7 6 5 4 3 2 1 ppm
2.0000
1.0406
2.0499
4.2060
2.0834
2.0074
0.9882


198.97
159.16
140.02
135.68
127.11
126.64
125.44
123.77
122.29
118.98
114.10
113.86
112.89
111.29
108.34
67.74
40.35
40.08
39.80
39.52
39.24
38.96
38.69
Br
Br
Br
5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


10.7748
10.7682
7.7652
7.2624
7.2471
7.2333
7.2178
7.2088
7.0489
7.0405
6.9825
6.9739
6.9644
6.9348
6.8188
6.8112
6.7218
6.7138
6.6926
6.6845
3.7277
3.5425
3.3132
2.5054
2.4995
2.4936
5c
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.0000
1.0103
3.0205
1.9789
2.0204
1.9825
2.0400
3.0163
5.9318


201.18
156.82
152.57
151.76
132.11
127.68
126.03
124.67
118.03
113.68
113.42
112.03
110.55
104.58
103.09
68.42
55.54
55.08
40.34
40.07
39.79
39.51
39.23
38.95
38.68
5c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.5742
7.5549
7.5507
7.5465
7.5273
7.5228
7.3818
7.3550
7.3140
7.2866
7.2603
7.2184
7.2151
7.1952
7.1916
7.1678
7.1644
7.0088
6.9979
6.9945
6.9744
6.9711
6.9676
6.9478
6.9443
6.8477
6.8199
6.7781
6.7764
6.7527
6.7290
6.7273
3.7271
2.9688
1.5928
5d
9 8 7 6 5 4 3 2 1 0 ppm
1.0000
1.0282
1.9658
2.0077
2.0115
1.8821
2.0199
0.9667
0.9868
5.9575
2.9864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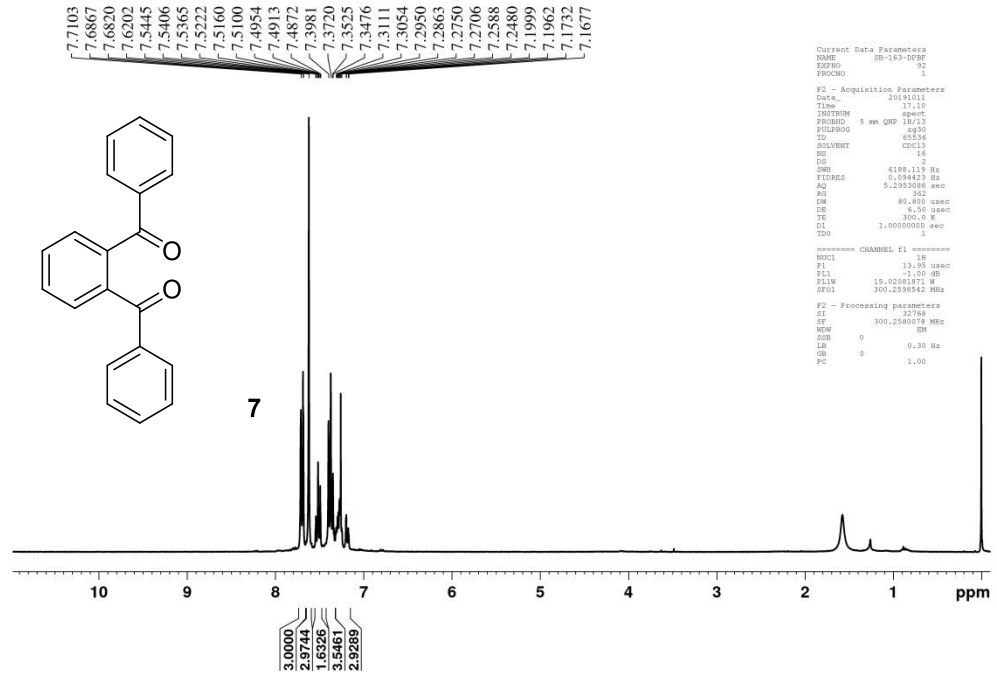
159.92
137.94
137.80
130.00
126.39
125.83
121.83
121.76
119.50
118.78
116.92
111.43
109.48
108.05
77.41
77.16
76.90
72.91
33.03
29.61
O
N
N
N
5d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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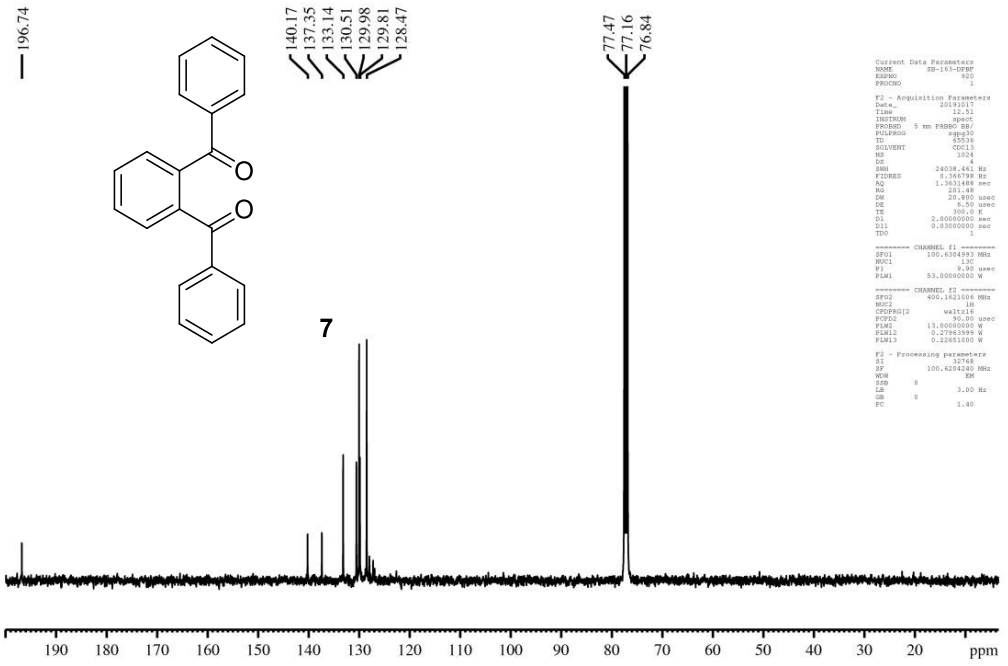
7.6867
7.6820
7.6202
7.5445
7.5406
7.5365
7.5222
7.5160
7.5100
7.4954
7.4913
7.4872
7.3981
7.3720
7.3525
7.3476
7.3111
7.3054
7.2950
7.2863
7.2750
7.2706
7.2588
7.2480
7.1999
7.1962
7.1732
7.1677
O
O
7
10
9
8
7
6
5
4
3
2
1
ppm
3.0000
2.9744
1.6326
3.5461
2.9289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140.17
137.35
133.14
130.51
129.98
129.81
128.47
77.47
77.16
76.84
O
O
7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm