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Supporting information

One-Pot Construction of Highly Functionalized 4*H*-Chromenes Using K-10 Montmorillonite in Aqueous Medium

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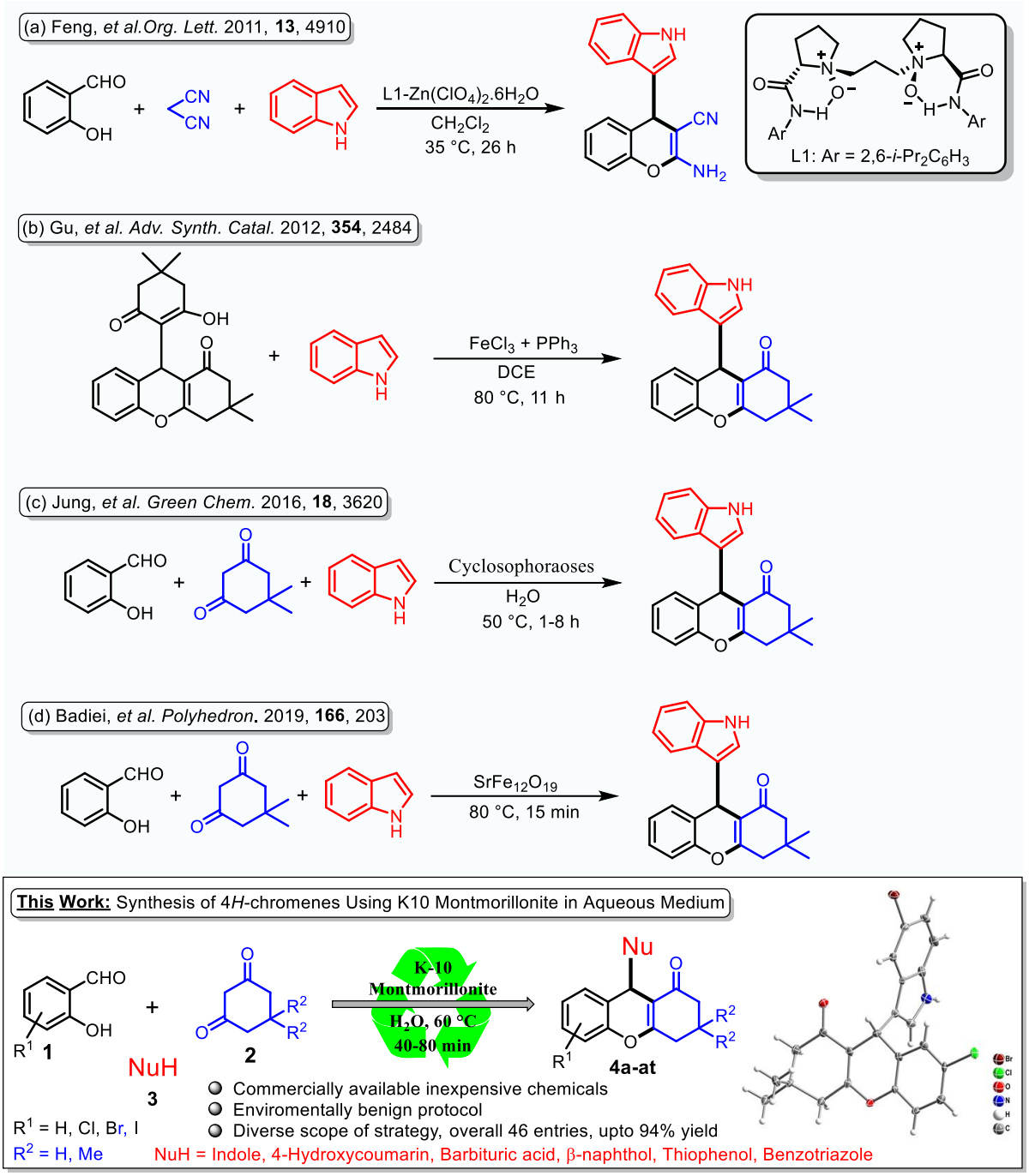
(1) General remarks:

All the reagents and solvents were purchased from Sigma-Aldrich or Merck chemical Co. and were used directly without any further purification. TLC (Thin Layer Chromatography) was performed on Merck-percoated silica gel, and 100-200 mesh silica gel was used for column chromatography. The chromatographic solvents are mentioned as v/v ratios. All the synthesized compounds were fully characterized by ^{1}H, ^{13}C NMR, IR, and further confirmed through ESI-MS and HRMS analyses. IR spectra were recorded on a Perkin-Elmer FT-IR RXI spectrophotometer and values reported in cm^{-1}. NMR spectra were recorded with 400 MHz spectrometers for ^{1}H NMR, 100 MHz for ^{13}C NMR respectively. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H), $CDCl_3$ and DMSO-d_6 (^{13}C) as internal standards. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), doublet of triplets (dt), triplet (t), triplet of doublets (td), quartet (q), multiplet (m), broad singlet (bs). Integrals are in accordance with assignments, coupling constants are given in Hz. ESI-MS spectra were obtained on a LCQ Advantage Ion trap mass spectrometer (Finnigan thermo fischer scientific), and HRMS spectra were performed using a mass spectrometer Q-TOF (Agilent 6520). Melting points were measured with a Büchi B-540 apparatus and are uncorrected. A good quality single crystal of size 0.029 × 0.026 × 0.023 mm, was selected under a polarizing microscope and was mounted on a glass fiber for data collection. The colorless crystals of **4t** were obtained in methanol by slow evaporation, at room temperature. The **4t** is crystallized in $P2_1$space group. The single-crystal X-ray diffraction data of **4t** was collected from Rigaku XtaLAB Oxford Diffraction system by using a MoKα radiation ($\lambda\alpha$ = 0.71073 Å) at 100K. The structure solution and refinements were performed by using SHELXT[1], SHELXL[2] program in the Olex 2[3] software. The crystallographic Figure was drawn by using Diamond 3.2k software.[4] The crystallographic details of **4t** can be access from Cambridge Crystallographic Data Center by using, 2016011, CCDC number. The Crystallographic parameters of **4t** are summarized in Table 1.

1. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3-8.
2. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.
3. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.

4. Brandenburg, K.; DIAMOND. Version 3.2k, Crystal Impact GbR, Bonn, Germany, **2014**.

(2) Approaches for the synthesis of 4*H*-chromenes (Scheme S1)



(3) Recycling experiment of K-10 montmorillonite (Figure S1)

Catalyst reusability is another crucial factor from environmental and economic points of view. For this purpose, the reusability of K-10 montmorillonite was investigated for a model reaction between 5-bromosalicylaldehyde (**1a**), dimedone (**2a**) and indole (**3a**) under optimized condition (Table 1, Entry 12). After the reaction was completed (checked by TLC), by filtration K-10 montmorillonite was isolated from the reaction mixture and then washed with EtOAc containing formic acid (small amount) to reactivate the catalyst as well as to remove the impurities from its surface. The air-dried K-10 montmorillonite was reused for five more rounds of subsequent reaction, and the outcomes of reactions shown in figure indicate that there was no significant loss in its catalytic efficiency.

(4) A typical procedure of multi-component reaction of salicylaldehyde 1,3-cyclohexanedione and indole/Benzotriazole:

A mixture of salicylaldehyde (0.5 mmol), 1,3-cyclohexanedione (0.5 mmol), indole/Benzotriazole (0.5 mmol) and montmorillonite K-10 (300 mg), in H_2O (1.2 mL) was stirred at 60 °C for the stipulated time mentioned in Scheme1/3. After reaction completion (indicated by TLC), the reaction mixture was allowed to cool to room temperature and washed with 20 mL (2 × 10 mL) of ethyl acetate to dissolve the product and the catalyst was removed by filtration. The organic layer of filtrate was evaporated under reduced pressure; the product thus obtained was recrystallized from ethanol to get pure compounds as white or pale yellow solid. The isolated compounds were well characterized by IR, ^{1}H NMR, ^{13}C NMR, HRMS, and an X-ray crystallographic study.

A typical procedure of three-component reaction of salicylaldehyde 1,3-cyclohexanedione and other nucleophile:

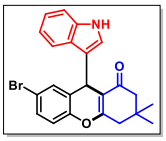
A mixture of salicylaldehyde (0.5 mmol), 1,3-cyclohexanedione (0.5 mmol), nucleophile (0.5 mmol) and K-10 montmorillonite (300 mg), in H_2O (1.2 mL) was stirred at 60 °C for the stipulated time mentioned in Scheme 2. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and then filtered. The ethyl acetate layer was concentrated to obtain a crude product. This was purified by column chromatography by using *n*-hexane/ethyl acetate (10% ethyl acetate in *n*-hexane) as an eluent to afford final product.

Catalyst recycling:

The portion of K-10 that was used in the previous cycle was stirred in 5 mL of ethyl acetate and 200 µL of formic acid for 4 h. The clay was then filtered and rinsed using two portions of 15 mL of ethyl acetate. Before reusing the catalyst for another reaction, it was dried overnight at 90 °C.

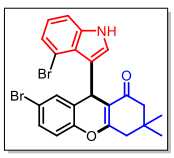
(5). Characterization data of all the synthesized compounds:

7-bromo-9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4a):



White solid; yield 88 %; **mp:** 181-183 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.24 (s, 1H), 7.39 (d, *J* = 7.9, 1H), 7.30-7.28 (m, 2H), 7.26-7.25 (m, 1H), 7.14-7.09 (m, 2H), 7.02-6.99 (m, 2H), 5.28 (s, 1H), 2.64 (q, *J* = 17.4, 2H), 2.30 (q, *J* = 16.2, 2H), 1.13 (s, 3H), 0.96 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.2, 164.0, 148.6, 136.6, 132.8, 130.5, 127.3, 125.4, 122.6, 121.7, 119.6, 119.4, 118.7, 118.0, 117.2, 112.3, 111.4, 50.8, 41.4, 32.0, 29.6, 29.0, 27.5; **IR (KBr) max** 3344, 2960, 1641, 1479, 1376, 1232, 1178, 1097, 752; **ESI-MS (m/z)** = 422 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{20}BrNO_2$; [M+H$^+$]**, 422.0750; found: m/z 422.0735.

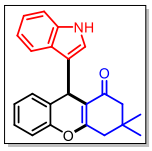
7-bromo-9-(4-bromo-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4b):



Light yellow solid; yield 87%; **mp:** 184-186 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.25 (s, 1H), 7.49 (s, 1H), 7.30-7.25 (m, 2H), 7.26-7.18 (m, 1H), 7.16-7.14 (m, 2H), 7.03 (d, *J* = 8.6, 1H), 5.22 (s, 1H), 2.65-2.54 (m, 2H), 2.30 (q, *J* = 16.3, 2H), 1.13 (s, 3H), 0.99 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.1, 164.2, 148.5, 135.1, 132.7, 130.7, 127.2, 126.9, 124.6, 123.7, 121.4, 119.6, 118.2, 117.3, 112.8,

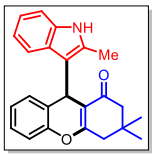
112.0, 50.8, 41.4, 32.0, 29.4, 29.1, 27.3; **IR (KBr) max** 3840, 3742, 3395, 2920, 1632, 1378, 1096; **ESI-MS (m/z)** = 499 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{19}Br_2NO_2$; [M+H$^+$]**, 499.9856; found: m/z 499.9854.

9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4c):



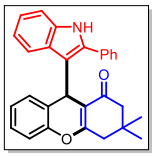
White solid; yield 90%; **mp:** 178-180 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.98 (s, 1H), 7.41 (d, *J* = 7.9, 1H), 7.27-7.25 (m, 1H), 7.18-7.12 (m, 3H), 7.09-7.05 (m, 2H), 7.00-6.94 (m, 2H), 5.32 (s, 1H), 2.62 (q, *J* = 17.3, 2H), 2.27 (q, *J* = 16.2, 2H), 1.10 (s, 3H), 0.96 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.2, 164.2, 149.6, 136.5, 130.1, 127.4, 125.7, 125.2, 124.8, 122.3, 121.6, 120.5, 119.3, 119.0, 116.2, 112.7, 111.1, 50.9, 41.5, 32.0, 29.4, 29.0, 27.6; **IR (KBr) max** 3839, 3739, 3406, 2953, 1638, 1457, 1377, 1229, 1176, 1024, 753; **ESI-MS (m/z)** = 344 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{21}NO_2$; [M+H$^+$]**, 344.1645; found: m/z 344.1602.

3,3-dimethyl-9-(2-methyl-1H-indol-3-yl)-2,3,4,9-tetrahydro-1H-xanthen-1-one (4d):



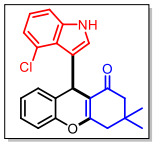
Light yellow solid; yield 93%; **mp:** 174-176 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.81 (s, 1H), 7.23 (d, *J* = 7.8, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.11-7.03 (m, 3H), 6.99-6.87 (m, 3H), 5.24 (s, 1H), 2.64-2.61 (m, 3H), 2.59-2.51 (m, 2H), 2.24 (q, *J* = 16.2, 2H), 1.10 (s, 3H), 0.93 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.5, 164.0, 149.5, 135.2, 131.3, 130.2, 127.3, 127.0, 125.2, 124.8, 120.4, 119.0, 117.9, 116.1, 115.8, 112.3, 110.2, 50.9, 41.5, 32.0, 29.0, 28.5, 27.6, 11.9; **IR (KBr) max** 3398, 2953, 1635, 1582, 1456, 1376, 1228, 1179, 759; **ESI-MS (m/z)** = 358 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{23}NO_2$; [M+H$^+$]**, 358.1802; found: m/z 358.1806.

3,3-dimethyl-9-(2-phenyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4e):



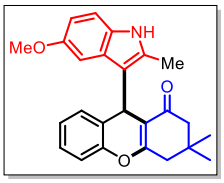
Light yellow solid; yield 90%; **mp:** 185-187 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.07-8.04 (m, 3H), 7.55-7.52 (m, 2H), 7.45-7.39 (m, 2H), 7.28-7.26 (m, 1H), 7.09-7.02 (m, 2H), 7.00-6.94 (m, 2H), 6.84-6.83 (m, 2H), 5.53 (s, 1H), 2.64-2.51 (m, 2H), 2.27 (q, *J* = 16.1, 2H), 1.11 (s, 3H), 1.02 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.7, 164.7, 148.8, 135.9, 134.4, 133.4, 130.0, 129.4, 128.8, 127.9, 127.3, 127.1, 125.2, 124.7, 121.7, 119.5, 119.0, 116.9, 116.1, 111.9, 110.9, 51.0, 41.7, 31.9, 28.9, 28.6, 28.0; **IR (KBr) max** 3324, 2962, 1627, 1581, 1378, 1229, 1180, 753; **ESI-MS (m/z)** = 420 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{29}H_{25}NO_2$; [M+H$^+$]**, 420.1958; found: m/z 420.1952.

9-(4-chloro-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4f):



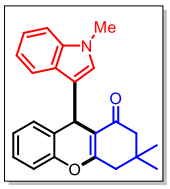
Light yellow solid; yield 91%; **mp:** 192-194 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.22 (s, 1H), 7.35 (d, *J* = 1.8, 1H), 7.19-7.15 (m, 2H), 7.13-7.10 (m, 3H), 7.02-6.97 (m, 2H), 5.26 (s, 1H), 2.64 (d, *J* = 17.4 Hz, 2H), 2.29 (q, *J* = 16.2, 2H), 1.12 (s, 3H), 0.98 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 164.6, 149.4, 134.8, 130.0, 127.6, 126.7, 125.0, 124.8, 123.8, 121.9, 120.3, 118.5, 116.4, 112.4, 112.2, 50.9, 41.5, 32.0, 29.3, 29.1, 27.4; **IR (KBr) max** 3839, 3739, 3415, 2924, 2635, 1458, 1378, 1229, 759; **ESI-MS (m/z)** = 378 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{20}ClNO_2$; [M+H$^+$]**, 378.1256; found: m/z 378.1248.

9-(5-methoxy-2-methyl-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4g):



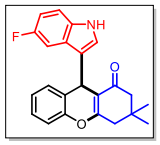
White solid; yield 94%; **mp:** 190-192 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.64 (s, 1H), 7.14-7.09 (m, 1H), 7.07-7.02 (m, 3H), 6.97-6.93 (m, 1H), 6.72 (d, *J* = 2.0, 1H), 6.63 (dd, *J* = 8.6, 2.4 Hz, 1H), 5.21 (s, 1H), 3.71 (s, 3H), 2.61 (s, 3H), 2.57-2.56 (m, 2H), 2.25 (q, *J* = 16.2, 2H), 1.10 (s, 3H), 0.94 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 163.9, 153.4, 149.6, 132.1, 130.3, 130.2, 127.4, 127.3, 125.0, 124.9, 115.9, 115.7, 112.2, 110.7, 110.0, 100.4, 55.6, 50.8, 41.5, 32.0, 29.1, 28.4, 27.6, 12.0; **IR (KBr) max** 3840, 3740, 3394, 2923, 1637, 1476, 1376, 1225, 757; **ESI-MS (m/z)** = 388 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{25}H_{25}NO_3$; [M+H$^+$]**, 388.1907; found: m/z 388.1903.

3,3-dimethyl-9-(2-methyl-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4h):



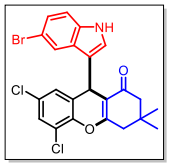
White solid; yield 93 %; **mp:** 180-182 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.40 (d, *J* = 8.0 Hz, 1H), 7.19-7.17 (m, 2H), 7.14-7.07 (m, 3H), 7.03 (s, 1H), 6.99-6.93 (m, 2H), 5.29 (s, 1H), 3.69 (m, 3H), 2.62 (q, *J* = 17.4, 2H), 2.27 (q, *J* = 16.2 Hz, 2H), 1.10 (s, 3H), 0.97 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 164.1, 149.6, 137.2, 130.1, 127.3, 127.0, 126.1, 125.5, 124.8, 121.1, 119.1, 119.0, 118.8, 116.2, 112.9, 109.1, 50.9, 41.5, 32.6, 32.0, 29.3, 29.0, 27.7; **IR (KBr) max** 3841, 3740, 3396, 2922, 1632, 1066; **ESI-MS (m/z)** = 358 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{23}NO_2$; [M+H$^+$]**, 358.1802; found: m/z 358.1800.

9-(5-fluoro-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4i):



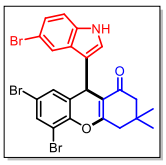
White solid; yield 88%; **mp:** 198-200 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.19 (s, 1H), 7.18-7.09 (m, 5H), 7.01-6.97 (m, 2H), 6.83 (td, *J* = 9.0, 2.4 Hz, 1H), 5.26 (s, 1H), 2.64 (q, *J* = 17.4, 2H), 2.29 (q, *J* = 16.2 Hz, 2H), 1.11 (s, 3H), 0.96 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 164.5, 158.4, 156.6, 149.5, 133.1, 130.0, 127.5, 125.9, 124.9, 124.8, 124.2, 120.5, 116.3, 112.4, 111.8, 111.7, 110.0, 109.8, 103.9, 103.8, 50.9, 41.5, 32.0, 29.4, 29.1, 27.4; **IR (KBr) max** 3839, 3739, 3415, 2924, 2662, 1458, 1378, 1229, 753; **ESI-MS (m/z)** = 362 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{20}FNO_2$; [M+H$^+$]**, 362.1551; found: m/z 362.1550.

9-(5-bromo-1*H*-indol-3-yl)-5,7-dichloro-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4j):



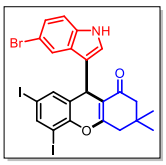
Off White solid; yield 86%; **mp:** 186-188 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.15 (s, 1H), 7.53 (d, *J* = 1.7, 1H), 7.24-7.23 (m, 1H), 7.21-7.18 (m, 1H), 7.16-7.14 (m, 1H), 7.11 (d, *J* = 2.5 Hz, 1H), 7.02 (dd, *J* = 2.4, 0.7 Hz, 1H), 5.21 (s, 1H), 2.72-2.60 (m, 2H), 2.29-2.18 (m, 2H), 1.13 (s, 3H), 0.99 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 196.8, 163.8, 144.2, 135.0, 129.5, 128.2, 128.1, 127.9, 127.1, 124.9, 123.7, 122.6, 121.4, 119.5, 113.1, 112.7, 112.3, 50.8, 41.1, 32.1, 29.7, 29.1, 27.3; **IR (KBr) max** 3839, 3739, 3396, 2962, 1632, 1450, 1375, 1237, 1032, 753; **ESI-MS (m/z)** = 489 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{18}BrClNO_2$; [M+H$^+$]**, 489.9971; found: m/z 489.9968.

5,7-dibromo-9-(5-bromo-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro 1*H*-xanthen-1-one (4k):



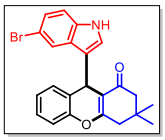
White solid; yield 85%; **mp:** 192-190 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.17 (s, 1H), 7.54-7.53 (m, 2H), 7.21-7.18 (m, 2H), 7.15-7.13 (m, 1H), 7.09 (d, *J* = 2.4, 1H), 5.21 (s, 1H), 2.72 (q, *J* = 17.6 Hz, 2H), 2.29 (d, *J* = 16.3, 2H), 1.13 (s, 3H), 0.99 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 196.9, 163.9, 145.7, 135.0, 133.8, 131.8, 128.2, 127.1, 124.9, 123.7, 121.4, 119.5, 117.1, 113.1, 112.8, 112.5, 111.5, 50.8, 41.1, 32.1, 29.7, 29.1, 27.3; **IR (KBr) max** 3836, 3739, 3362, 2922, 1641, 1450, 1375, 1237, 1032, 761; **ESI-MS (m/z)** = 577 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{18}Br_3NO_2$; [M+H$^+$]**, 577.8961; found: m/z 577.8958.

9-(5-bromo-1*H*-indol-3-yl)-5,7-diiodo-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4l):



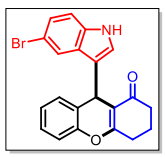
White solid; yield 84%; **mp:** 187-189 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.09 (s, 1H), 7.92 (d, *J* = 1.9, 1H), 7.52-7.52 (m, 1H), 7.39-7.38 (m, 1H), 7.21-7.19 (m, 1H), 7.16-7.14 (m, 1H), 7.10 (d, *J* = 2.5 Hz, 1H), 5.18 (s, 1H), 2.71-2.62 (m, 2H), 2.28-2.20 (m, 2H), 1.12 (s, 3H), 0.98 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 145.0, 138.8, 128.0, 124.9, 123.7, 121.5, 112.9, 112.7, 50.8, 41.1, 32.1, 29.6, 29.1, 27.3; **IR (KBr) max** 3836, 3739, 3362, 2922, 1632, 1450, 1375, 1239, 1033, 753; **ESI-MS (m/z)** = 673 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{18}BrI_2NO_2$; [M+H$^+$]**, 673.8683; found: m/z 673.8679.

9-(5-bromo-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4m):



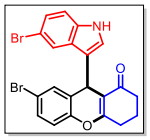
White solid; yield 90%; **mp:** 180-182 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.22 (s, 1H), 7.52-7.51 (m, 1H), 7.19-7.15 (m, 2H), 7.13-7.10 (m, 3H), 7.08-7.07 (m, 1H), 7.01-6.97 (m, 1H), 5.25 (s, 1H), 2.64 (q, *J* = 17.4 Hz, 2H), 2.29 (d, *J* = 16.2, 2H), 1.12 (s, 3H), 0.99 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 164.6, 149.4, 135.1, 130.0, 127.6, 127.3, 125.0, 124.8, 124.4, 123.6, 121.6, 120.3, 116.4, 112.6, 112.4, 50.9, 41.5, 32.0, 29.3, 29.1, 27.4; **IR (KBr) max** 3362, 2952, 1641, 1450, 1375, 1236, 1173, 1049, 735; **ESI-MS (m/z)** = 422 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{20}BrNO_2$; [M+H$^+$]**, 422.0750; found: m/z 422.0748.

9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4n):



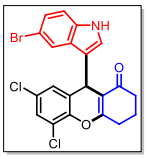
White solid; yield 86%; **mp:** 170-172 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.20 (s, 1H), 7.53 (d, *J* = 1.6, 1H), 7.18-7.14 (m, 3H), 7.12-7.10 (m, 2H), 7.08 (d, *J* = 2.4 Hz, 1H), 7.02-6.98 (m, 1H), 5.29 (s, 1H), 2.80-2.73 (m, 1H), 2.69-2.61 (m, 1H), 2.39-2.34 (m, 2H), 2.08-1.95 (m, 2H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.5, 166.3, 149.4, 135.0, 129.9, 127.6, 127.4, 125.0, 124.9, 124.5, 123.8, 121.7, 120.4, 116.3, 113.8, 112.7, 112.6, 37.0, 29.2, 27.8, 20.4; **IR (KBr) max** 3838, 3742, 3396, 2921, 1634, 1380, 1067; **ESI-MS (m/z)** = 394 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{21}BrNO_2$; [M+H$^+$]**, 394.0437; found: m/z 394.0431.

7-bromo-9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4o):



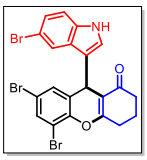
Off White solid; yield 84%; **mp:** 181-183 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.08 (s, 1H), 7.48-7.48 (m, 1H), 7.27-7.26 (m, 1H), 7.25-7.24 (m, 1H), 7.18-7.15 (m, 3H), 7.02 (d, *J* = 8.6, 1H), 5.23 (s, 1H), 2.79-2.72 (m, 1H), 2.68-2.61 (m, 1H), 2.37-2.33 (m, 2H), 2.07-1.95 (m, 2H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.0, 165.7, 148.5, 135.1, 132.6, 130.7, 127.3, 126.9, 124.7, 123.8, 121.5, 119.8, 118.1, 117.3, 113.3, 112.9, 112.7, 36.9, 29.3, 27.7, 20.3; **IR (KBr) max** 3840, 3740, 3395, 2922, 1635, 1379, 1096; **ESI-MS (m/z)** = 471 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{15}Br_2NO_2$; [M+H$^+$]**, 471.9543; found: m/z 471.9539.

9-(5-bromo-1*H*-indol-3-yl)-5,7-dichloro-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4p):



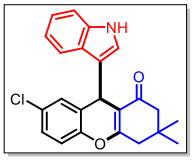
White solid; yield 85%; **mp:** 186-188 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.16 (s, 1H), 7.55-7.54 (m, 1H), 7.24-7.20 (m, 2H), 7.17 (d, *J* = 8.6, 1H), 7.08 (d, *J* = 2.5 Hz, 1H), 7.02 (dd, *J* = 2.4, 0.6 Hz, 1H), 5.24 (s, 1H), 2.88-2.81 (m, 1H), 2.75-2.67 (m, 1H), 2.40-2.35 (m, 2H), 2.10-1.99 (m, 2H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 165.5, 144.2, 135.0, 129.5, 128.2, 128.1, 128.0, 127.1, 124.9, 123.9, 122.6, 121.4, 119.5, 113.6, 113.1, 112.8, 36.9, 29.6, 27.5, 20.3; **IR (KBr) max** 3838, 3738, 3395, 2961, 1632, 1450, 1375, 1237, 1033, 754; **ESI-MS (m/z)** = 461 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{14}BrCl_2NO_2$; [M+H$^+$]**, 461.9658; found: m/z 461.9651.

5,7-dibromo-9-(5-bromo-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4q):



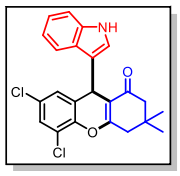
White solid; yield 83%; **mp:** 184-186 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.04 (s, 2H), 7.52-7.50 (m, 2H), 7.10 (s, 1H), 6.68 (s, 1H), 6.12-5.73 (m, 1H), 4.13-4.11 (m, 1H), 2.04 (s, 2H), 1.26 (m, 3H), 0.88 (s, 1H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 149.1, 135.3, 132.6, 132.4, 131.7, 128.3, 125.3, 124.7, 117.1, 113.0, 112.7, 111.2, 33.4; **IR (KBr) max** 3839, 3739, 3360, 2921, 1642, 1450, 1375, 1238, 1033, 762; **ESI-MS (m/z)** = 549 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{14}Br_3NO_2$; [M+H$^+$]**, 549.8648; found: m/z 549.8645.

7-chloro-9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4r):



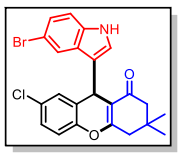
Off White solid; yield 90%; **mp:** 180-182 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.02 (s, 1H), 7.41 (d, *J* = 7.8, 1H), 7.26-7.24 (m, 1H), 7.18-7.12 (m, 2H), 7.09-7.05 (m, 2H), 7.00-6.95 (m, 2H), 5.32 (s, 1H), 2.62 (q, *J* = 17.4, 2H), 2.27 (q, *J* = 16.2, 2H), 1.11 (s, 3H), 0.96 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.3, 164.2, 149.6, 136.5, 130.1, 127.4, 125.7, 125.2, 124.9, 122.3, 121.6, 120.5, 119.3, 119.0, 116.2, 112.7, 111.1, 50.9, 41.5, 32.0, 29.4, 29.0, 27.6; **IR (KBr) max** 3840, 3742, 3396, 2955, 1635, 1377, 1096, 762; **ESI-MS (m/z)** = 378 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{20}ClNO_2$; [M+H$^+$]**, 378.1256; found: m/z 378.1250.

5,7-dichloro-9-(1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4s):



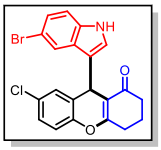
Light yellow solid; yield 88%; **mp:** 185-187 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.06 (s, 1H), 7.37 (d, *J* = 7.6, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21-7.17 (m, 2H), 7.13-7.09 (m, 1H), 7.04-7.02 (m, 2H), 5.26 (s, 1H), 2.71 (q, *J* = 17.8 Hz, 2H), 2.27 (q, *J* = 15.9 Hz, 2H), 1.12 (s, 3H), 0.96 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 196.8, 128.3, 128.0, 122.5, 122.4, 121.9, 119.7, 119.4, 118.6, 112.5, 111.3, 50.8, 41.1, 32.1, 29.6, 29.0, 27.5; **IR (KBr) max** 3839, 3739, 3395, 2920, 1632, 1378, 1096; **ESI-MS (m/z)** = 412 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{19}Cl_2NO_2$; [M+H$^+$]**, 412.0863; found: m/z 412.0866.

9-(5-bromo-1*H*-indol-3-yl)-7-chloro-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4t):



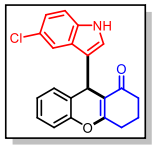
Dark brown solid; yield 89% (148.05 mg); **mp:** 189-191 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.16 (s, 1H), 7.46-7.46 (m, 1H), 7.18-7.11 (m, 4H), 7.09-7.04 (m, 2H), 5.20 (s, 1H), 2.63-2.52 (m, 2H), 2.27 (q, *J* = 16.3, 2H), 1.11 (s, 3H), 0.97 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.1, 164.2, 147.9, 135.1, 129.8, 129.7, 127.8, 127.2, 126.4, 124.7, 123.6, 121.5, 119.6, 117.8, 112.8, 112.7, 111.9, 50.8, 41.4, 32.0, 29.5, 29.1, 27.3; **IR (KBr) max** 3839, 3738, 3348, 2926, 1640, 1468, 1375, 1233, 1178, 1095, 880, 754; **ESI-MS (m/z)** = 456 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{19}BrClNO_2$; [M+H$^+$]**, 456.0361; found: m/z 456.0364.

9-(5-bromo-1*H*-indol-3-yl)-7-chloro-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4u):



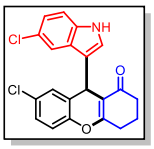
Off White solid; yield 85%; **mp:** 178-180 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.22 (s, 1H), 7.48-7.47 (m, 1H), 7.19-7.15 (m, 2H), 7.13-7.09 (m, 3H), 7.07-7.05 (m, 1H), 5.23 (s, 1H), 2.80-2.73 (m, 1H), 2.69-2.61 (m, 1H), 2.38-2.34 (m, 2H), 2.07-1.95 (m, 2H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.2, 165.9, 148.0, 135.1, 129.8, 129.7, 127.8, 127.2, 126.5, 124.7, 123.9, 121.4, 119.6, 117.8, 113.2, 112.9, 112.7, 37.0, 29.4, 27.7, 20.3; **IR (KBr) max** 3842, 3740, 3349, 2926, 1637, 1468, 1376, 1234, 1178, 1097, 880, 755; **ESI-MS (m/z)** = 428 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{15}BrClNO_2$; [M+H$^+$]**, 428.0018; found: m/z 428.0021.

9-(5-chloro-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4v):



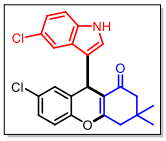
Light yellow solid; yield 87%; **mp:** 196-198 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.17 (s, 1H), 7.35 (d, *J* = 1.9, 1H), 7.26-7.14 (m, 3H), 7.12-7.11 (m, 2H), 7.04-6.98 (m, 2H), 5.29 (s, 1H), 2.80-2.73 (m, 1H), 2.69-2.61 (m, 1H), 2.39-2.34 (m, 2H), 2.05-1.96 (m, 2H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 166.2, 149.5, 134.8, 129.8, 127.6, 126.8, 125.1, 125.0, 124.9, 123.9, 122.0, 120.4, 118.6, 116.3, 113.8, 112.1, 37.0, 29.2, 27.8, 20.4; **IR (KBr) max** 3841, 3740, 3356, 2928, 1635, 1456, 1377, 1232, 1098, 755; **ESI-MS (m/z)** = 350 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{16}ClNO_2$; [M+H$^+$]**, 350.0943; found: m/z 350.0939.

7-chloro-9-(5-chloro-1*H*-indol-3-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4w):



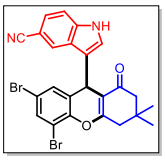
Light yellow solid; yield 85 %; **mp:** 198-200 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.22 (s, 1H), 7.30 (d, *J* = 1.9, 1H), 7.19 (d, *J* = 8.6, 1H), 7.15-7.09 (m, 3H), 7.07-7.03 (m, 2H), 5.23 (s, 1H), 2.80-2.73 (m, 1H), 2.69-2.61 (m, 1H), 2.38-2.34 (m, 2H), 2.06-1.94 (m, 2H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.0, 165.7, 148.5, 135.0, 132.6, 130.7, 127.3, 126.9, 124.7, 123.8, 121.5, 119.7, 118.1, 117.3, 113.3, 112.9, 112.7, 36.9, 29.3, 27.6, 20.3; **IR (KBr) max** 3840, 3740, 3359, 2924, 1636, 1467, 1376, 1234, 1178, 1097, 757; **ESI-MS (m/z)** = 384 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{15}ClNO_2$; [M+H$^+$]**, 384.0553; found: m/z 384.0550.

7-chloro-9-(5-chloro-1*H*-indol-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4x):



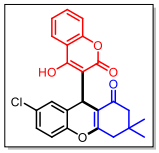
Off White solid; yield 84%; **mp:** 178-180 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.10 (s, 1H), 7.40-7.40 (m, 1H), 7.24 (d, *J* = 8.5, 1H), 7.17-7.10 (m, 3H), 7.08-7.04 (m, 1H), 7.01-6.97 (m, 1H), 5.27 (s, 1H), 2.61-2.51 (m, 2H), 2.28 (q, *J* = 16.2, 2H), 1.11 (s, 3H), 0.95 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.3, 164.3, 148.6, 135.3, 132.8, 130.9, 127.3, 127.0, 124.8, 123.8, 121.6, 119.7, 118.4, 117.5, 112.9, 112.1, 50.9, 41.5, 32.2, 29.5, 29.3, 27.4; **IR (KBr) max** 3839, 3740, 3396, 2920, 1632, 1378, 1096, 760; **ESI-MS (m/z)** = 412 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{23}H_{19}Cl_2NO_2$; [M+H$^+$]**, 412.0866; found: m/z 412.0861.

3-(5,7-dibromo-3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1*H*-indole-5-carbonitrile (4y):



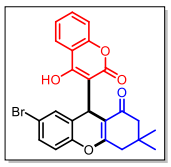
Yellow solid; yield 86%; **mp:** 188-190 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.78 (s, 1H), 7.71 (s, 1H), 7.55 (d, *J* = 2.2 Hz, 1H), 7.35-7.30 (m, 2H), 7.19 (d, *J* = 2.4 Hz, 1H), 7.15-7.15 (m, 1H), 5.25 (s, 1H), 2.75-2.62 (m, 2H), 2.30 (q, *J* = 16.3, 2H), 1.13 (s, 3H), 0.97 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.3, 164.5, 145.8, 138.3, 134.3, 131.9, 127.9, 125.3, 125.2, 125.1, 124.4, 120.8, 120.5, 117.5, 112.6, 112.4, 111.9, 103.1, 51.0, 41.3, 32.3, 30.0, 29.8, 27.5; **IR (KBr) max** 3838, 3739, 3362, 2920, 1662, 1452, 1375, 1239, 1033, 753; **ESI-MS (m/z)** = 524 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{18}Br_2N_2O_2$; [M+H$^+$]**, 524.9808; found: m/z 524.9807.

7-chloro-9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4z):



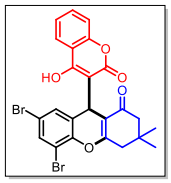
White solid; yield 92%; **mp:** 217-219 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 11.00 (s, 1H), 8.04 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.53-7.49 (m, 1H), 7.33-7.29 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.20 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.06-7.03 (m, 2H), 5.03 (s, 1H), 2.69 (q, *J* = 17.7, 2H), 2.45 (q, *J* = 16.8, 2H), 1.17 (s, 3H), 1.07 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 201.2, 169.8, 161.2, 161.1, 153.0, 149.8, 131.8, 129.8, 128.2, 124.2, 124.1, 123.8, 117.3, 116.9, 116.2, 109.6, 108.6, 49.8, 41.5, 32.3, 29.2, 28.5, 27.1; **IR (KBr) max** 3839, 3741, 3391, 2925, 1711, 1619, 1482, 1384, 1238, 1036; **ESI-MS (m/z)** = 423 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{19}ClO_5$; [M+H$^+$]**, 423.0994; found: m/z 423.0989.

7-bromo-9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4aa):



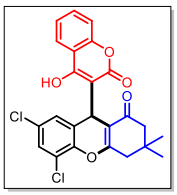
White solid; yield 89% ; **mp:** 234-236 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 10.9 (s, 1H), 8.03 (d, *J* = 7. 4 Hz, 1H), 7.53 (t, *J* = 7. 3 Hz, 1H), 7.33-7.29 (m, 2H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.17 (s, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 5.03 (s, 1H), 2.68 (q, *J* = 17.7 Hz, 2H), 2.45 (q, *J* = 16.9, 2H), 1.17 (s, 3H), 1.06 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 201.2, 169.7, 161.2, 161.1, 153.0, 150.4, 131.8, 131.1,124.5, 124.3, 123.8, 117.7, 117.3, 116.9, 116.3, 109.7, 108.6, 49.8, 41.5, 32.3, 29.2, 28.4, 27.1; **IR (KBr) max** 3838, 3740, 3391, 2924, 1712, 1619, 1384, 1237, 1037, 757; **ESI-MS (m/z)** = 467 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{19}BrO_5$; [M+H$^+$]**, 467.0489; found: m/z 467.0483.

5,7-dibromo-9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4ab):



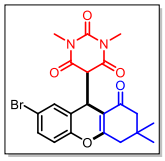
White solid; yield 85%; **mp:** 212-214 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 10.9 (s, 1H), 8.04 (dd, *J* = 1.4 Hz, 1H), 7.54-7.49 (m, 1H), 7.34-7.32 (m, 1H), 7.24 (d, *J* = 8.2 Hz, 1H), 7.18 (d, *J* = 2.1 Hz, 1H), 7.00 (d, *J* = 6.8 Hz, 1H), 5.03 (s, 1H), 2.69 (q, *J* = 17.7 Hz, 2H), 2.45 (q, *J* = 16.8, 2H), 1.17 (s, 3H), 1.07 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 201.2, 169.7, 161.2, 161.1, 153.0, 150.4, 131.8, 131.1, 124.5, 124.2, 123.8, 117.7, 117.3, 116.9, 116.2, 109.7, 108.6, 49.8, 41.5, 32.3, 29.2, 28.4, 27.1; **IR (KBr) max** 3839, 3740, 3391, 2923, 1712, 1619, 1385, 1239, 1035, 757; **ESI-MS (m/z)** = 544 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{18}Nr_2O_5$; [M+H$^+$]**, 544.9594; found: m/z 544.9598.

5,7-dichloro-9-(4-hydroxy-2-oxo-2*H*-chromen-3-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4ac):



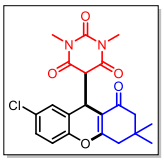
White solid; yield 90%; **mp:** 218-220 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 10.89 (s, 1H), 8.04-8.02 (m, 1H), 7.55-7.51 (m, 1H), 7.34-7.29 (m, 2H), 7.25 (d, *J* = 8.2 Hz, 1H), 6.94 (d, *J* = 2.2 Hz, 1H), 5.02 (s, 1H), 2.78 (q, *J* = 17.9, 2H), 2.46 (q, *J* = 16.9, 2H), 1.19 (s, 3H), 1.08 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 201.3, 169.3, 161.3, 161.1, 153.0, 146.1, 132.0, 129.5, 128.8, 126.6, 125.5, 124.3, 123.9, 122.2, 116.8, 116.3, 109.8, 108.3, 49.8, 41.3, 32.3, 29.2, 28.8, 27.0; **IR (KBr) max** 3838, 3740, 3392, 2926, 1712, 1620, 1482, 1385, 1235, 1036, 756; **ESI-MS (m/z)** = 457 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{24}H_{18}Cl_2O_5$; [M+H$^+$]**, 457.0604; found: m/z 457.0601.

5-(7-bromo-3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4ad):



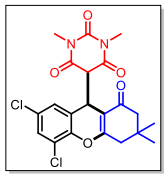
White solid; yield 90%; **mp:** 160-162 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.37 (d, *J* = 8.5 Hz, 1H), 7.31-7.28 (m, 1H), 6.94 (d, *J* = 8.6, Hz, 1H), 4.84 (s, 1H), 3.85-3.84 (m, 1H), 3.25 (s, 3H), 3.16 (s, 3H), 2.56 (q, *J* = 17.5 Hz, 2H), 2.37 (q, *J* = 16.1 Hz, 2H), 1.15 (s, 3H), 1.13 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 167.8, 167.1, 166.8, 151.1, 149.5, 131.9, 130.9, 123.3, 118.4, 117.4, 108.6, 55.1, 50.5, 41.5, 35.6, 32.1, 29.3, 28.4, 28.3, 27.1; **IR (KBr) max** 3839, 3738, 3391, 2928, 1681, 1382, 1238, 1105; **ESI-MS (m/z)** = 461 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{21}BrN_2O_5$; [M+H$^+$]**, 461.0707; found: m/z 461.0703.

5-(7-chloro-3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4ae):



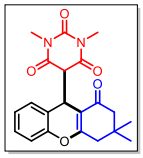
White solid; yield 90%; **mp:** 168-170 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.24 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 4.86 (s, 1H), 3.87 (d, *J* = 2.5 Hz, 1H), 3.26 (s, 3H), 3.18 (s, 3H), 2.57 (q, *J* = 17.6 Hz, 2H), 2.38 (q, *J* = 16.1 Hz, 2H), 1.16 (s, 3H), 1.14 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 167.9, 167.0, 151.1, 149.0, 130.1, 129.0, 127.9, 122.9, 118.0, 108.5, 55.1, 50.6, 41.5, 35.6, 32.1, 29.3, 28.4, 28.3, 27.1; **IR (KBr) max** 3838, 3739, 3391, 2924, 1682, 1382, 1238, 1106; **ESI-MS (m/z)** = 417 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{21}ClN_2O_5$; [M+H$^+$]**, 417.1212; found: m/z 417.1215.

5-(5,7-dichloro-3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethylpyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4af):



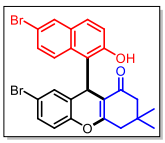
Off white solid; yield 87%; **mp:** 165-167 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.34 (d, *J* = 2.3 Hz, 1H), 7.12 (d, *J* = 2.0 Hz, 1H), 4.88 (s, 1H), 3.85 (d, *J* = 2.3 Hz, 1H), 3.26 (s, 3H), 3.22 (s, 3H), 2.66 (q, *J* = 17.8 Hz, 2H), 2.38 (q, *J* = 16.1 Hz, 2H), 1.16 (s, 6H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 167.5, 166.7, 166.6, 151.1, 145.3, 129.8, 129.5, 126.4, 124.6, 123.1, 108.8, 55.2, 50.6, 41.2, 35.4, 32.1, 29.3, 28.5, 28.4, 27.0; **IR (KBr) max** 3838, 3741, 3391, 2940, 1632, 1497, 1382, 1234, 757; **ESI-MS (m/z)** = 451 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{20}Cl_2N_2O_5$; [M+H$^+$]**, 451.0822; found: m/z 451.0819.

5-(3,3-dimethyl-1-oxo-2,3,4,9-tetrahydro-1*H*-xanthen-9-yl)-1,3-dimethyl pyrimidine-2,4,6(1*H*,3*H*,5*H*)-trione (4ag):



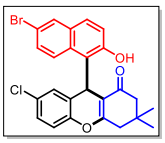
White solid; yield 92%; **mp:** 171-173 °C; **^{1}H NMR (400 MHz; $CDCl_3$)** δ 7.28-7.25 (m, 1H), 7.11-7.10 (m, 2H), 7.05 (d, *J* = 6.4 Hz, 1H), 4.89 (s, 1H), 3.88 (d, *J* = 2.2 Hz, 1H), 3.24 (s, 3H), 3.09 (s, 3H), 2.59-2.47 (m, 2H), 2.39-2.35 (m, 2H), 1.20 (s, 3H), 1.14 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 197.4, 168.1, 167.3, 167.0, 150.5, 129.1, 128.0, 125.1, 120.5, 116.7, 109.0, 55.0, 50.6, 41.6, 36.4, 32.1, 29.3, 28.3, 28.2, 27.3; **IR (KBr) max** ,3838, 3740, 3391, 2939, 1631, 1497, 1382, 1234, 757; **ESI-MS (m/z)** = 383 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{22}N_2O_5$**; **[M+H$^+$],** 383.1602; found: m/z 383.1600.

7-bromo-9-(6-bromo-2-hydroxynaphthalen-1-yl)-3,3-dimethyl-2,3,4,9-tetra hydro-1*H*-xanthen-1-one (4ah):



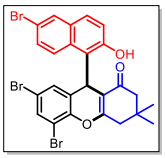
White solid; yield 85%; **mp:** 230-232 °C; **^{1}H NMR (400 MHz; $CDCl_3$)** δ 9.30 (s, 1H), 7.96 (s, 1H), 7.74 (d, *J* = 9.0 Hz, 1H), 7.51-7.46 (m, 2H), 7.38 (d, *J* = 8.9 Hz, 1H), 7.14 (dd, *J* = 8.6, 2.4 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.63 (d, *J* = 2.4 Hz, 1H), 5.68 (s, 1H), 2.70 (q, *J* = 17.6 Hz, 2H), 2.46 (q, *J* = 16.6 Hz, 2H), 1.17 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 200.6, 167.1, 152.1, 147.9, 134.7, 132.7, 131.2, 130.9, 130.4, 129.5, 128.6, 125.0, 121.0, 119.5, 117.9, 116.9, 113.8, 113.2, 50.2, 41.5, 32.4, 28.9, 28.0, 27.4; **IR (KBr) max** 3838, 3740, 3390, 2925, 1633, 1474, 1381, 1227, 757; **ESI-MS (m/z)** = 526 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{25}H_{20}Br_2O_3$**; **[M+H$^+$],** 526.9852; found: m/z 526.9549.

9-(6-bromo-2-hydroxynaphthalen-1-yl)-7-chloro-3,3-dimethyl-2,3,4,9-tetra hydro-1*H*-xanthen-1-one (4ai):



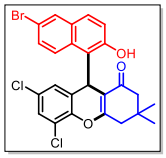
White solid; yield 87%; **mp:** 234-236 °C; **^{1}H NMR (400 MHz; $CDCl_3$)** δ 9.28 (s, 1H), 7.97 (s, 1H), 7.74 (d, *J* = 8.8 Hz, 1H), 7.49 (s, 2H), 7.39 (d, *J* = 8.9 Hz, 1H), 6.98 (s, 2H), 6.50 (s, 1H), 5.69 (s, 1H), 2.70 (q, *J* = 17.6 Hz, 2H), 2.46 (q, *J* = 16.5 Hz, 2H), 1.17 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 200.6, 167.1, 152.1, 147.9, 134.1, 132.7, 131.2, 130.9, 130.4, 129.5, 128.6, 128.3, 126.3, 125.0, 120.0, 119.5, 117.9, 116.9, 113.2, 113.2, 50.2, 41.5, 32.4, 28.9, 28.1, 27.3; **IR (KBr) max** 3840, 3740, 3390, 2922, 1380, 1075, 757; **ESI-MS (m/z)** = 483 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{25}H_{20}BrClO_3$**; **[M+H$^+$],** 483.0357; found: m/z 483.0349.

5,7-dibromo-9-(6-bromo-2-hydroxynaphthalen-1-yl)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4aj):



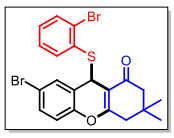
White solid; yield 82 %; **mp:** 208-210 °C; **^{1}H NMR (400 MHz; $CDCl_3$)** δ 9.91 (s, 1H), 7.96 (d, *J* = 1.7 Hz, 1H), 7.73 (d, *J* = 8.9 Hz, 1H), 7.52-7.49 (m, 1H), 7.44-7.41 (m, 2H), 7.37 (d, *J* = 8.9 Hz, 1H), 6.57 (d, *J* = 2.2 Hz, 1H), 5.69 (s, 1H), 2.69 (q, *J* = 17.6 Hz, 2H), 2.45 (q, *J* = 16.7 Hz, 2H), 1.15 (s, 3H), 1.02 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 200.8, 167.6, 147.9, 135.3, 134.0, 132.8, 131.2, 130.6, 130.5, 129.3, 128.8, 124.8, 119.7, 117.9, 116.5, 114.6, 113.5, 112.9, 50.1, 41.5, 32.4, 29.7, 28.9, 27.4; **IR (KBr) max** 3839, 3739, 3614, 2923, 1381, 1076, 757; **ESI-MS (m/z)** = 604 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{25}H_{19}Br_3O_3$**; **[M+H$^+$],** 604.8913; found: m/z 604.8915.

9-(6-bromo-2-hydroxynaphthalen-1-yl)-5,7-dichloro-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4ak):



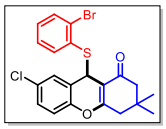
White solid; yield 82%; **mp:** 199-201 °C; **^{1}H NMR (400 MHz; $CDCl_3$)** δ 9.79 (s, 1H), 7.98 (d, *J* = 1.0 Hz, 1H), 7.76 (d, *J* = 8.9 Hz, 1H), 7.54-7.52 (m, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.39 (d, *J* = 8.9 Hz, 1H), 7.14 (d, *J* = 2.2 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 5.72 (s, 1H), 2.70 (q, *J* = 17.6 Hz, 2H), 2.47 (q, *J* = 16.7 Hz, 2H), 1.18 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 200.7, 167.5, 148.1, 147.9, 135.1, 132.7, 131.1, 130.5, 129.4, 128.8, 128.5, 127.0, 126.0, 124.9, 124.8, 119.7, 117.9, 116.5, 112.9, 50.1, 41.5, 32.4, 28.9, 28.7, 27.3; **IR (KBr) max** 3838, 3739, 3614, 2926, 1380, 1076, 757; **ESI-MS (m/z)** = 516 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{25}H_{19}Cl_2O_3$**; **[M+H$^+$],** 516.9968; found: m/z 516.9961.

7-bromo-9-((2-bromophenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4al):



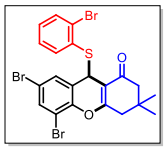
Light yellow solid; yield 88%; mp: 102-104 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.62-7.60 (m, 1H), 7.32-7.30 (m, 1H), 7.22-7.21 (m, 1H), 7.18-7.17 (m, 2H), 7.13 (s, 1H), 6.81 (d, *J* = 8.6 Hz, 2H), 5.43 (s, 1H), 2.54-2.46 (m, 2H), 2.36-2.30 (m, 2H), 1.19 (s, 3H), 1.08 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.6, 166.7, 149.7, 138.2, 133.4, 133.1, 131.9, 131.4, 131.2, 130.5, 127.4, 124.0, 117.9, 117.2, 109.5, 50.7, 41.5, 40.6, 32.4, 28.7, 28.1; **IR (KBr) max** 3838, 3740, 3390, 2935, 1638, 1458, 1382, 1232, 1021, 757; **ESI-MS (m/z)** = 492 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{18}Br_2O_2S$; [M+H$^+$]**, 492.9467; found: m/z 492.9463.

9-((2-bromophenyl)thio)-7-chloro-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4am):



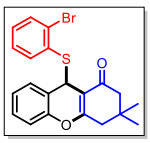
Light yellow solid; yield 90%; mp: 107-109 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.61-7.60 (m, 1H), 7.21 (s, 1H), 7.18-7.17 (m, 3H), 7.01 (s, 1H), 6.87 (d, *J* = 7.9 Hz, 1H), 5.43 (s, 1H), 2.54 (t, *J* = 16.7 Hz, 2H), 2.36-2.30 (m, 2H), 1.19 (s, 3H), 1.08 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.6, 166.8, 149.2, 138.1, 133.4, 133.1, 131.3, 130.4, 129.8, 128.9, 128.3, 127.4, 123.6, 117.5, 109.4, 50.7, 41.5, 40.7, 32.4, 28.7, 28.1; **IR (KBr) max** 3838, 3740, 3390, 2925, 1648, 1448, 1380, 1232, 1021, 757; **ESI-MS (m/z)** = 448 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{18}BrClO_2S$; [M+H$^+$]**, 448.9972; found: m/z 448.9975.

5,7-dibromo-9-((2-bromophenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4an):



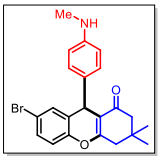
Light yellow solid; yield 85%; mp: 89-91 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.64-7.58 (m, 2H), 7.28-7.20 (m, 3H), 7.04 (s, 1H), 5.39 (s, 1H), 2.62-2.47 (m, 2H), 2.42-2.33 (m, 2H), 1.20 (s, 3H), 1.09 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.4, 166.6, 146.9, 138.3, 134.1, 133.2, 132.9, 131.5, 131.0, 130.8, 127.5, 125.2, 117.0, 111.1, 109.8, 50.6, 41.2, 40.9, 32.4, 28.7, 28.1; **IR (KBr) max** 3838, 3741, 3391, 2925, 1647, 1446, 1376, 1239, 1025, 754; **ESI-MS (m/z)** = 570 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{17}Br_3O_2S$; [M+H$^+$]**, 570.5872; found: m/z 570.5869.

9-((2-bromophenyl)thio)-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4ao):



Orange liquid; yield 90%; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.56-7.55 (m, 1H), 7.21-7.17 (m, 1H), 7.12-7.04 (m, 5H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.51 (s, 1H), 2.52-2.44 (m, 2H), 2.33-2.27 (m, 2H), 1.16 (s, 3H), 1.05 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.9, 166.9, 150.8, 137.9, 133.8, 132.9, 131.1, 130.0, 129.3, 128.3, 127.2, 125.0, 122.1, 116.2, 109.8, 50.7, 41.5, 41.0, 32.4, 28.8, 28.0; **IR (KBr) max** 3839, 3742, 3391, 2926, 1647, 1446, 1376, 1238, 1025, 754; **ESI-MS (m/z)** = 415 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{19}BrO_2S$; [M+H$^+$]**, 414.0289; found: m/z 414.0291.

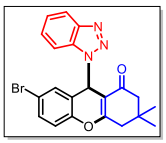
7-bromo-3,3-dimethyl-9-(4-(methylamino)phenyl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4ap):



Off white solid; yield 82%; **mp:** 179-181 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.18-7.16 (m, 1H), 7.14 (s, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 1H), 2.68 (s, 3H), 2.48-2.39 (m, 2H),

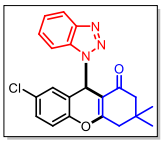
2.20 (q, *J* = 16.2 Hz, 2H), 1.02 (s, 3H), 0.95 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 196.6, 163.7, 148.5, 147.9, 134.6, 132.7, 130.3, 128.6, 128.2, 118.2, 117.2, 113.5, 112.4, 50.8, 41.4, 36.9, 32.1, 30.7, 29.2, 27.4; **IR (KBr) max** 3089, 2957, 2889, 2839, 1647, 1611, 1583, 1518, 1481, 1375, 1272, 1225, 1189, 1117, 1089, 950, 912, 837, 785; **ESI-MS (m/z)** = 412 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{22}H_{22}BrNO_2$; [M+H$^+$]**, 412.0907; found: m/z 412.0910.

9-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-7-bromo-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4aq):



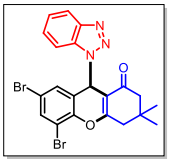
Off white solid; yield 90% ; **mp:** 195-197 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 1H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.45 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.36-7.33 (m, 2H), 7.16 (d, *J* = 8.7 Hz, 1H), 7.00 (s, 1H), 2.77 (q, *J* = 17.7 Hz, 2H), 2.33 (q, *J* = 16.4 Hz, 2H), 1.14 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.9, 167.5, 149.2, 145.7, 133.2, 132.3, 131.8, 127.6, 123.9, 121.3, 120.0, 119.1, 117.9, 109.5, 108.3, 50.3, 48.0, 41.5, 32.2, 29.0, 27.5; **IR (KBr) max** 3843, 3741, 3404, 2954, 1642, 1475, 1379, 1236, 1179, 1074, 1027, 819, 755; **ESI-MS (m/z)** = 424 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{18}BrN_3O_2$; [M+H$^+$]**, 424.0655; found: m/z 424.0650.

9-(1H-benzo[*d*][1,2,3]triazol-1-yl)-7-chloro-3,3-dimethyl-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (4ar):



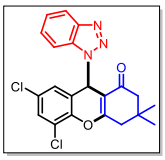
Light yellow solid; yield 92%; **mp:** 210-212 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.8 Hz, 1H), 7.36-7.32 (m, 1H), 7.30 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.21 (s, 1H), 7.19-7.18 (m, 1H), 7.00 (s, 1H), 2.78 (q, *J* = 17.6 Hz, 2H), 2.33 (q, *J* = 16.4 Hz, 2H), 1.15 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.9, 167.6, 148.7, 145.7, 132.3, 130.5, 130.3, 128.8, 127.6, 123.9, 120.9, 120.0, 118.8, 109.5, 108.2, 50.3, 48.2, 41.5, 32.2, 29.0, 27.5; **IR (KBr) max** 3842, 3740, 3404, 2955, 1645, 1475, 1380, 1235, 1180, 1074, 1027, 816, 756; **ESI-MS (m/z)** = 380 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{18}ClN_3O_2$; [M+H$^+$]**, 380.1161; found: m/z 380.1158.

9-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-5,7-dibromo-3,3-dimethyl-2,3,4,9-tetra hydro-1*H*-xanthen-1-one (4as):



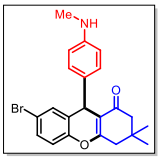
White solid; yield 88%; **mp:** 207-209 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.01 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.69 (d, *J* = 2.2 Hz, 1H), 7.54-7.50 (m, 1H), 7.36-7.32 (m, 1H), 7.28 (d, *J* = 2.2 Hz, 1H), 6.98 (s, 1H), 2.85 (q, *J* = 17.8 Hz, 2H), 2.33 (q, *J* = 16.4 Hz, 2H), 1.14 (s, 3H), 1.04 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.8, 167.4, 146.5, 145.7, 136.2, 132.3, 130.9, 127.8, 124.1, 122.5, 120.1, 117.8, 112.4, 109.5, 108.7, 50.3, 48.1, 41.2, 32.3, 29.0, 27.4; **IR (KBr) max** 3840, 3741, 3403, 2952, 1642, 1476, 1379, 1235, 1179, 1075, 1027, 819, 756; **ESI-MS (m/z)** = 501 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{17}Br_2N_3O_2$; [M+H$^+$]**, 501.9761; found: m/z 501.9758.

9-(1*H*-benzo[*d*][1,2,3]triazol-1-yl)-5,7-dichloro-3,3-dimethyl-2,3,4,9-tetra hydro-1*H*-xanthen-1-one (4at):



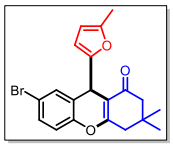
White solid; yield 92%; **mp:** 197-199 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.4 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.40-7.34 (m, 2H), 7.09 (s, 1H), 6.98 (s, 1H), 2.86 (q, *J* = 17.4 Hz, 2H), 2.34 (q, *J* = 16.2 Hz, 2H), 1.16 (s, 3H), 1.05 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 195.8, 167.3, 145.7, 145.1, 132.3, 130.6, 130.3, 127.8, 127.2, 124.1, 123.7, 122.1, 120.1, 109.4, 108.5, 50.3, 48.1, 41.2, 32.3, 29.0, 27.5; **IR (KBr) max** 3843, 3740, 3405, 2955, 1642, 1476, 1379, 1236, 1179, 1074, 1028, 821, 755; **ESI-MS (m/z)** = 414 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{21}H_{17}Cl_2N_3O_2$; [M+H$^+$]**, 414.0771; found: m/z 414.0770.

7-bromo-3,3-dimethyl-9-(4-(methylamino)phenyl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5a):



Off white solid; yield 78% ; **mp:** 179-181 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.18-7.16 (m, 1H), 7.14 (s, 2H), 6.94 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.41 (d, *J* = 8.4 Hz, 2H), 4.77 (s, 1H), 2.68 (s, 3H), 2.48-2.39 (m, 2H), 2.20 (q, *J* = 16.2 Hz, 2H), 1.02 (s, 3H), 0.95 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 196.6, 163.6, 148.4, 147.9, 134.5, 132.6, 130.2, 128.5, 128.2, 118.1, 117.1, 113.5, 112.4, 50.7, 41.4, 36.9, 32.1, 30.6, 29.2, 27.4; **IR (KBr) max** 3089, 2957, 2889, 2839, 1647, 1611, 1583, 1518, 1481, 1375, 1272, 1225, 1189, 1117, 1089, 950, 912, 837, 785; **ESI-MS (m/z)** = 412 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{22}H_{22}BrNO_2$; [M+H$^+$]**, 412.0907; found: m/z 412.0910.

7-bromo-3,3-dimethyl-9-(5-methylfuran-2-yl)-2,3,4,9-tetrahydro-1*H*-xanthen-1-one (5b):



Brown solid; yield 86%; **mp:** 136-138 °C; **^{1}H NMR (400 MHz; $CDCl_3$):** δ 7.54 (d, *J* = 2.3 Hz, 1H), 7.75 (dd, *J* = 5.6, 2.4 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 1H), 5.99 (d, *J* = 3.0 Hz, 1H), 5.89-5.88 (m, 1H), 5.04 (s, 1H), 2.66-2.55 (m, 2H), 2.35 (m, 2H), 2.11 (s, 3H), 1.08 (s, 3H), 1.06 (s, 3H); **^{13}C NMR (100 MHz; $CDCl_3$)** δ 196.1, 165.9, 154.8, 150.8, 148.7, 132.5, 131.4, 125.8, 119.2, 116.8, 109.5, 107.0, 106.3, 50.5, 32.3, 30.9, 29.2, 26.8, 13.7; **IR (KBr) max** 3838, 3740, 3394, 2953, 1649, 1474, 1375, 1230, 1171, 1022, 817; **ESI-MS (m/z)** = 387 [M+H$^+$]; **ESI-HRMS** for cald. **$C_{20}H_{19}BrO_3$; [M+H$^+$]**, 387.0591; found: m/z 387.0589.

(6) ^{1}H, ^{13}C NMR and HRMS Spectra of Compounds

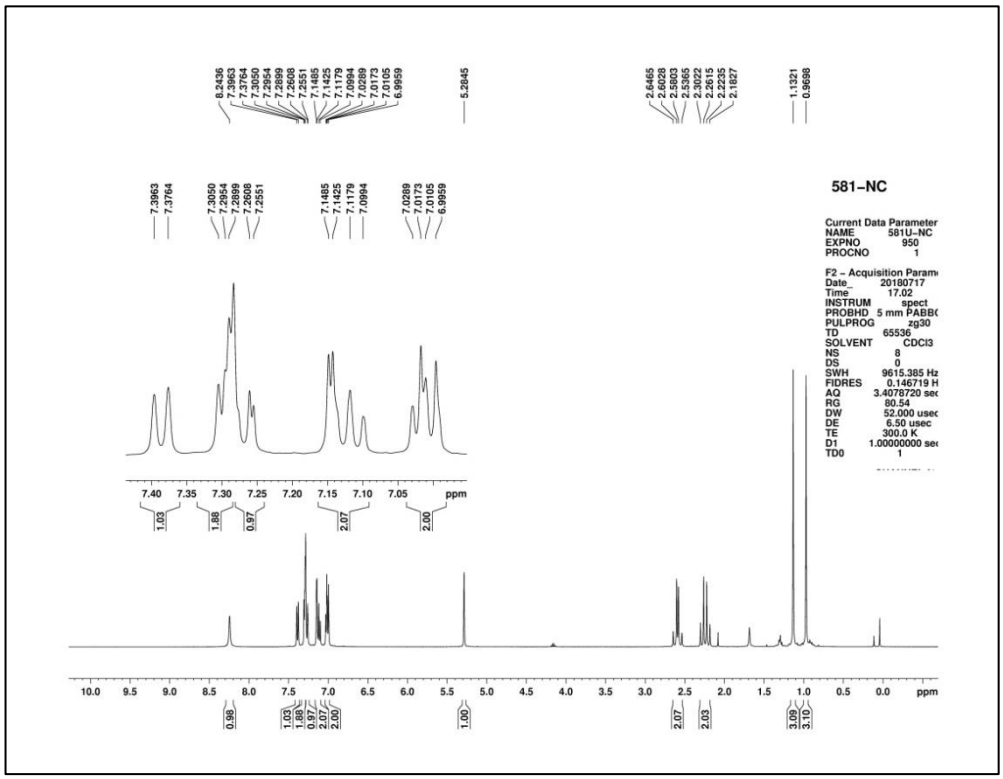


Figure S1: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4a)

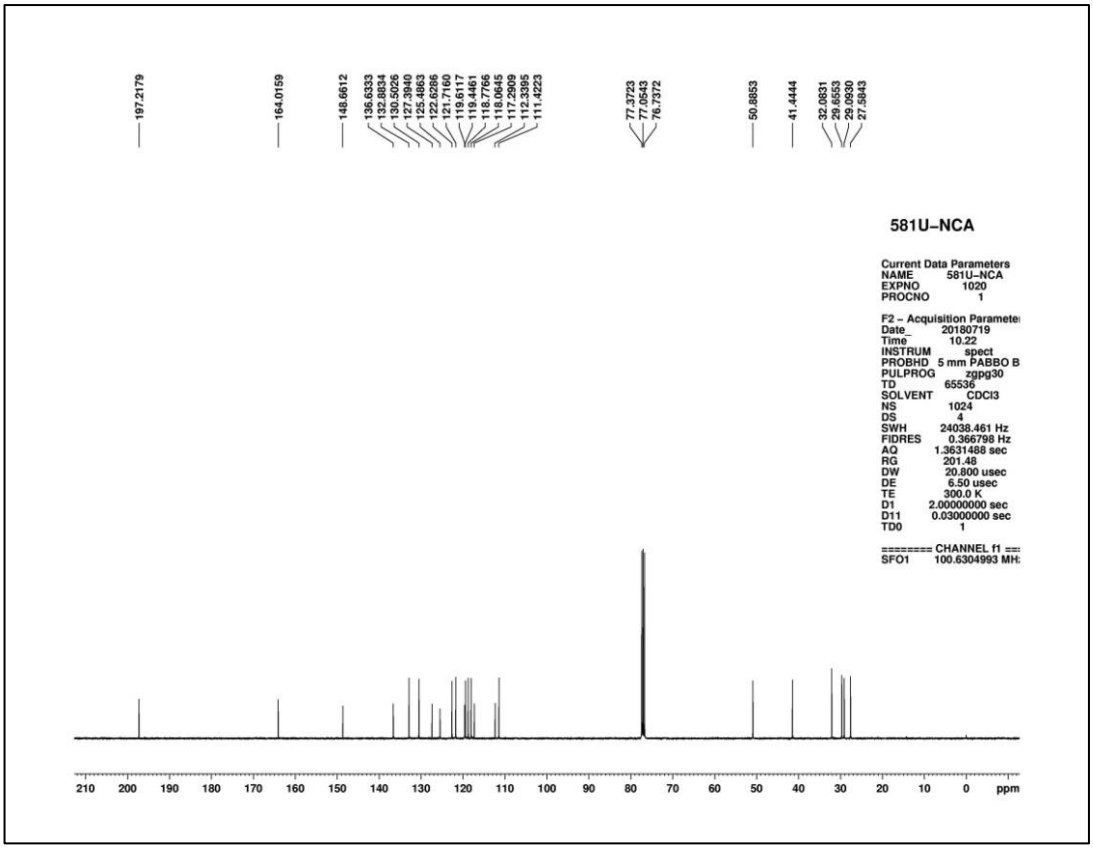


Figure S2: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4a)

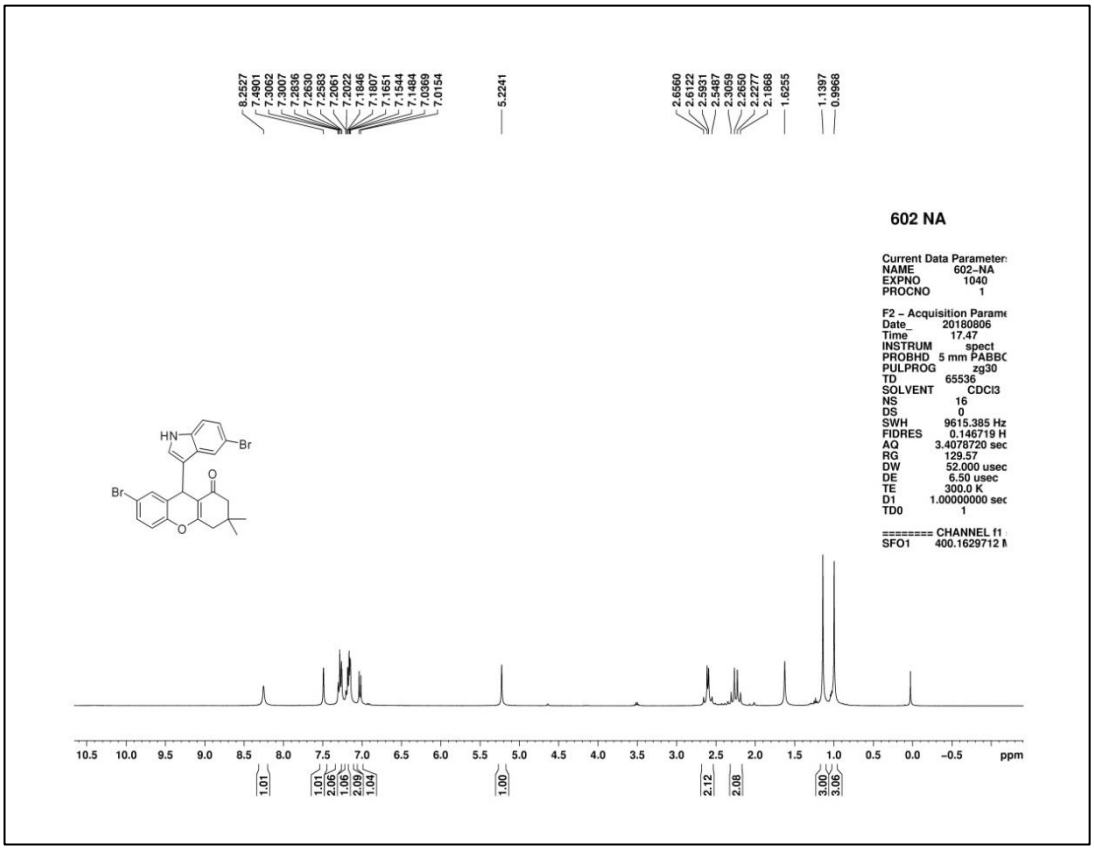


Figure S3: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4b)

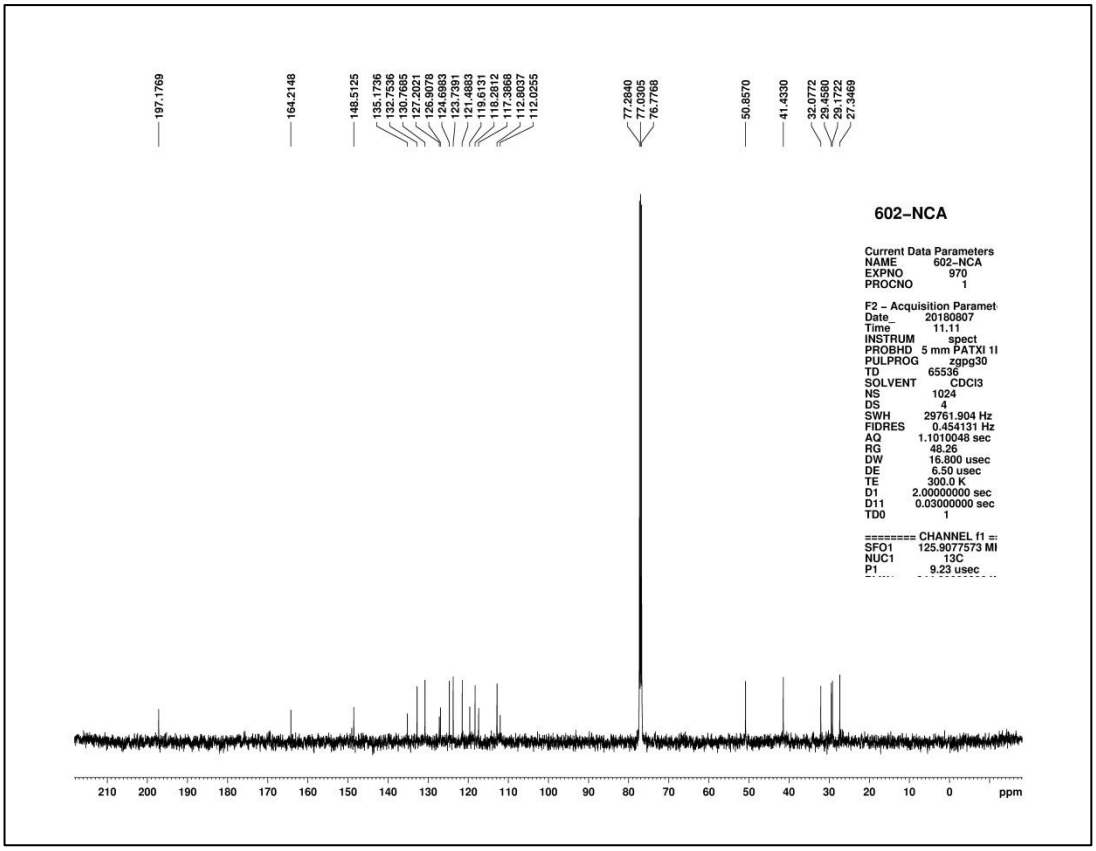


Figure S4: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4b)

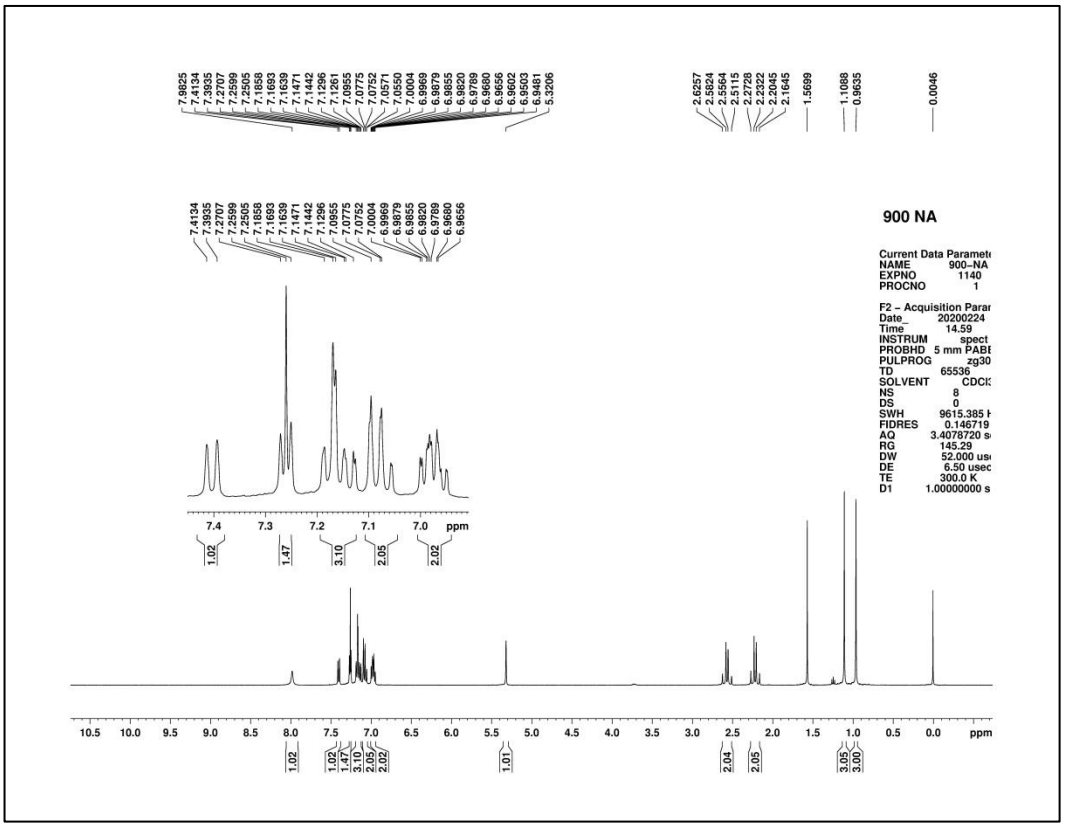


Figure S5: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4c)

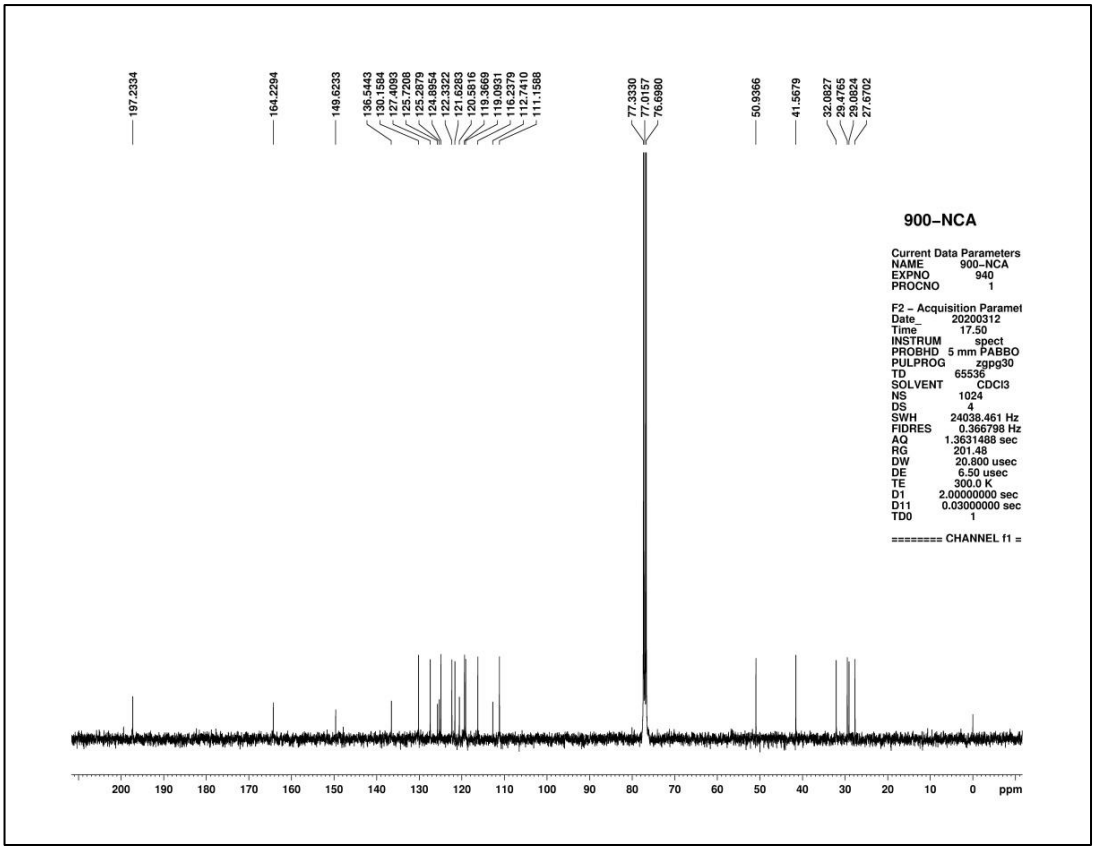


Figure S6: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4c)

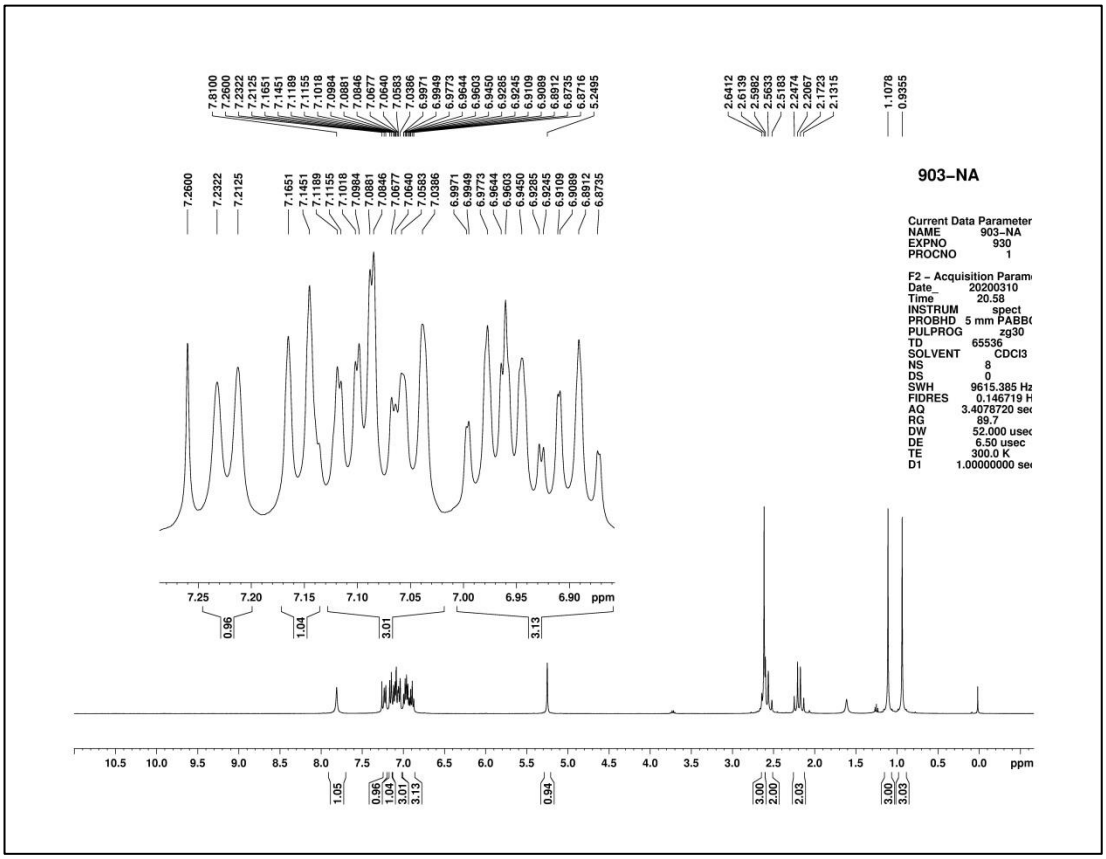


Figure S7: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4d)

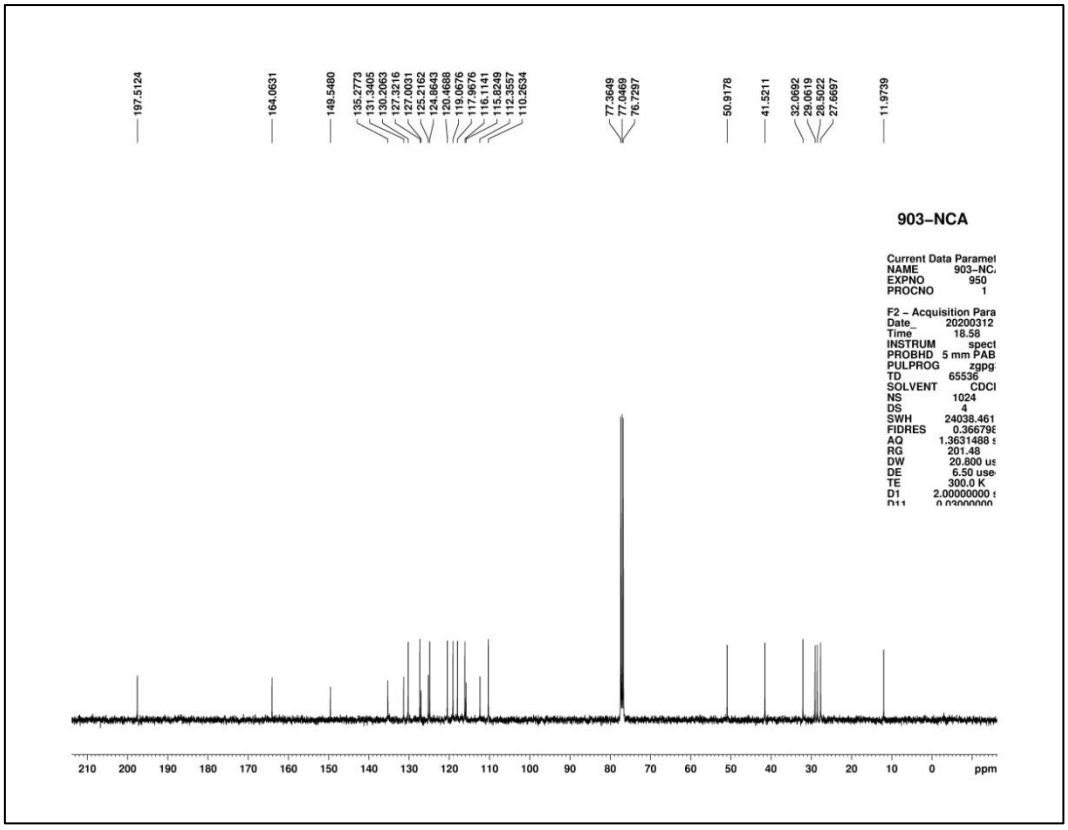


Figure S8: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4d)

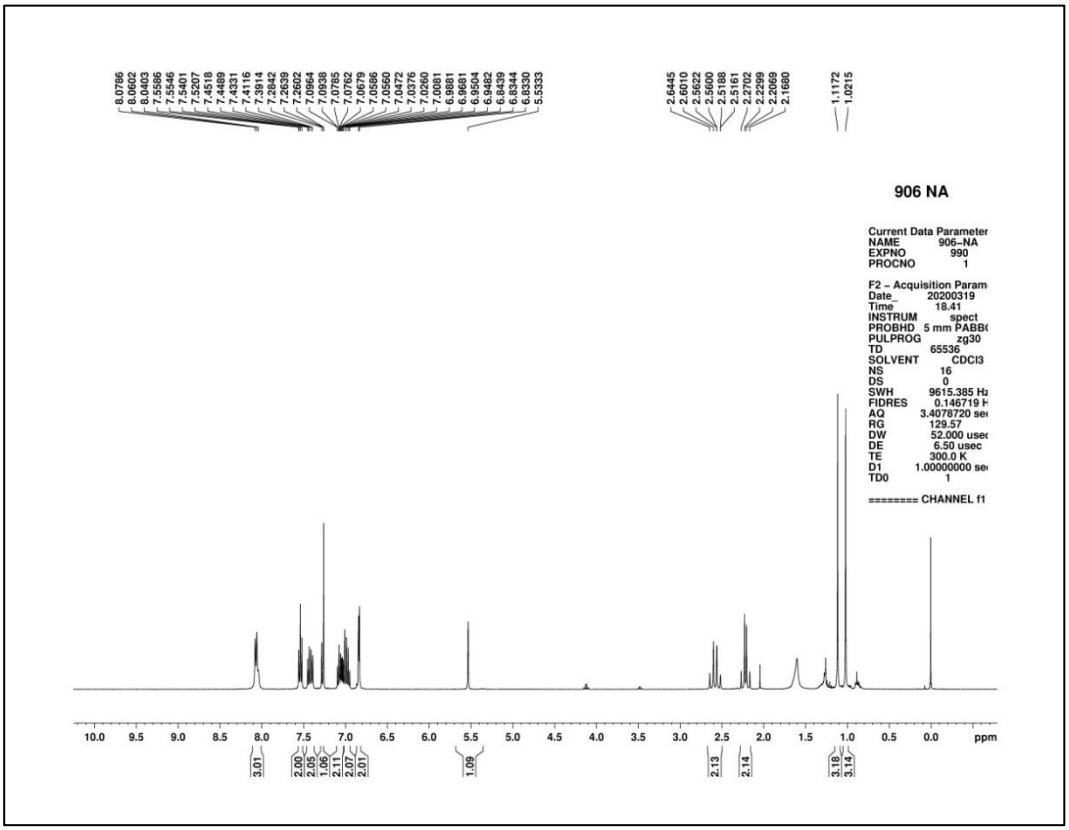


Figure S9: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4e)

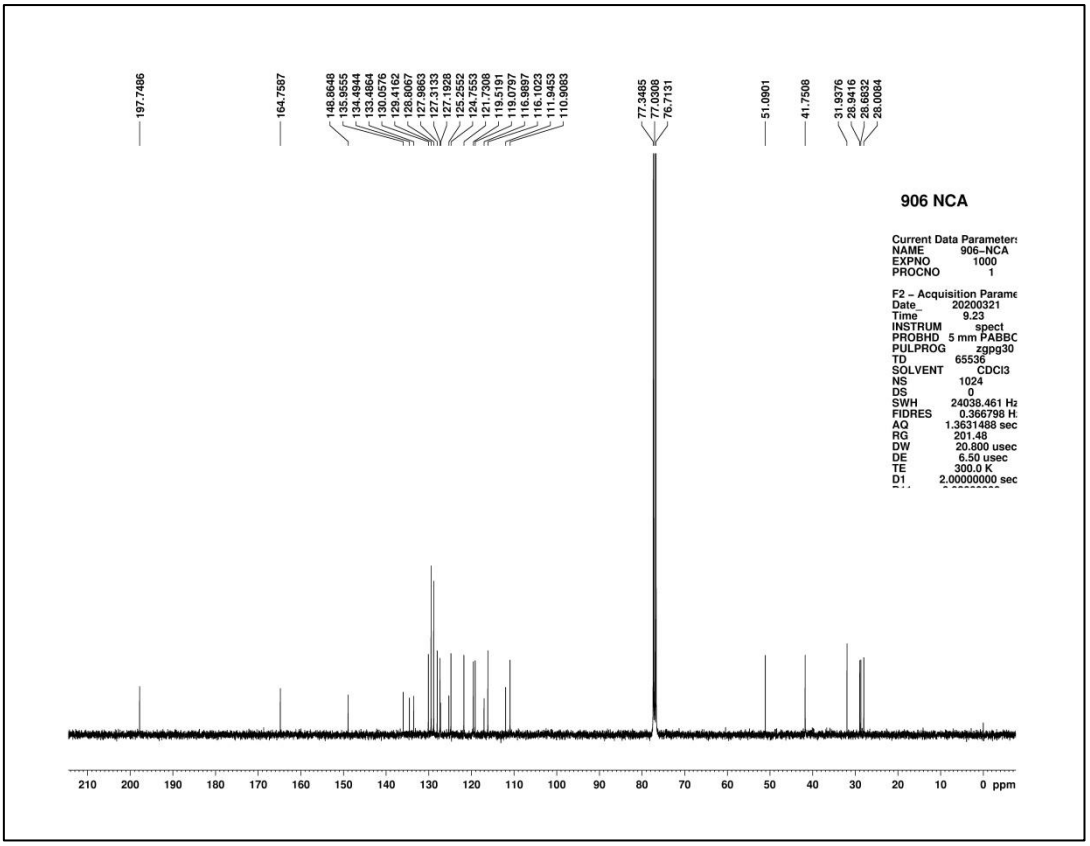


Figure S10: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4e)

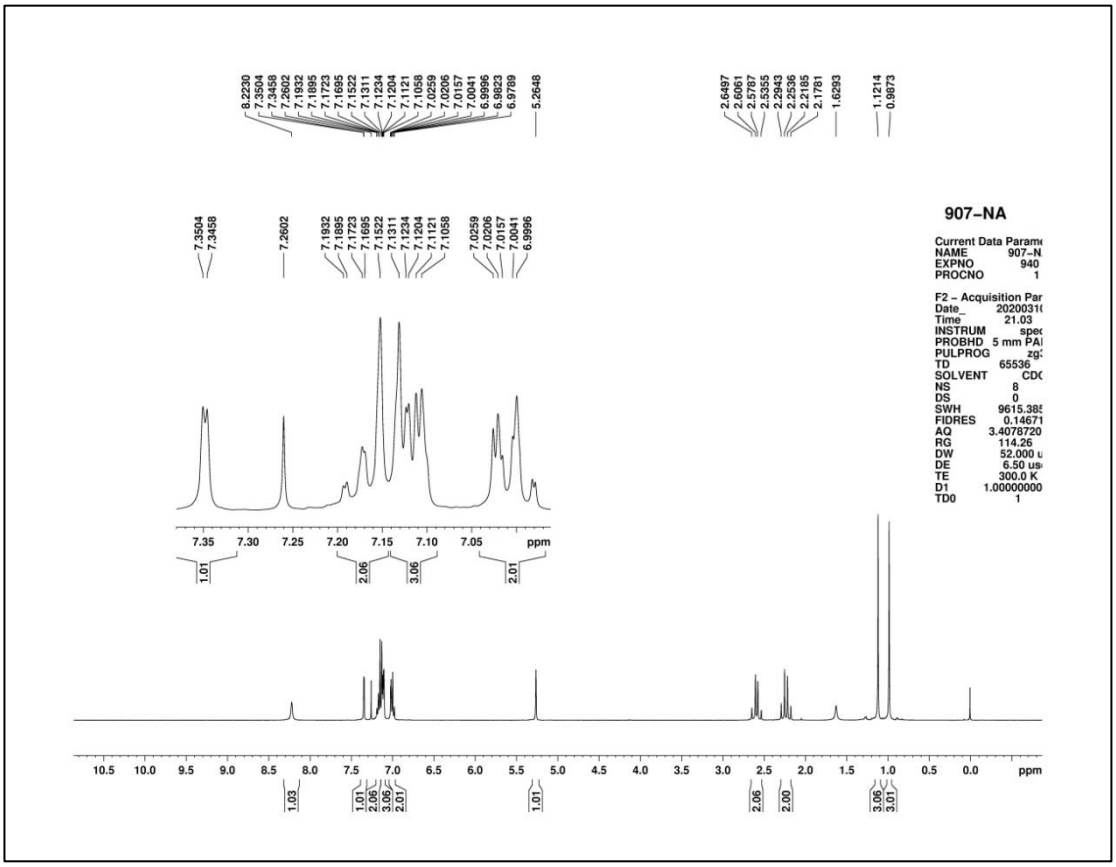


Figure S11: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4f)

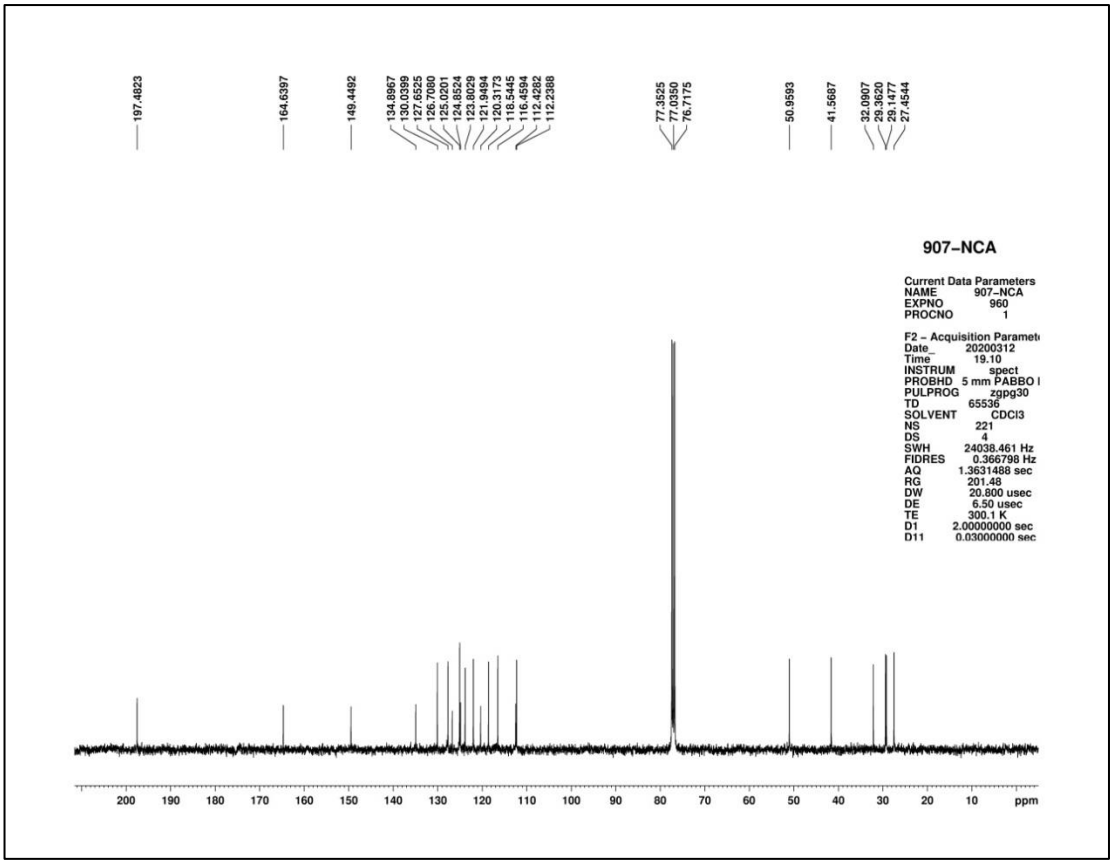


Figure S12: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4f)

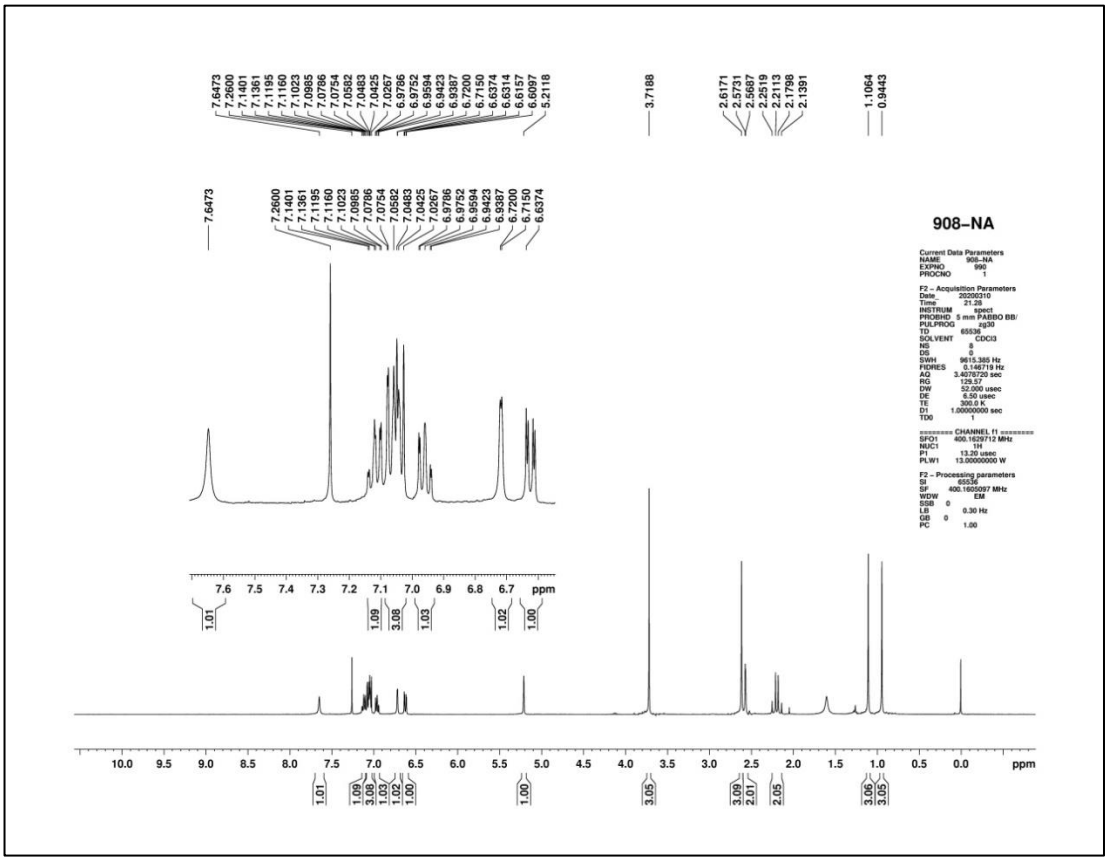


Figure S13: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4g)

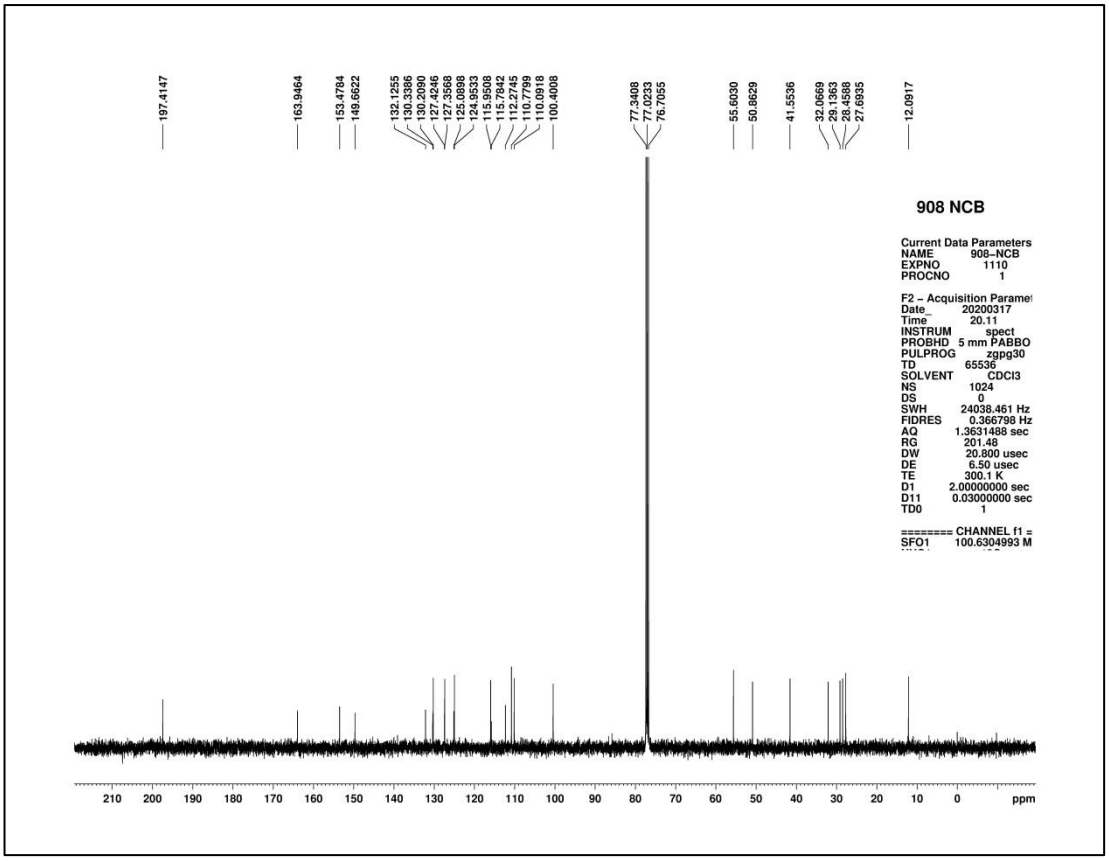


Figure S14: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4g)

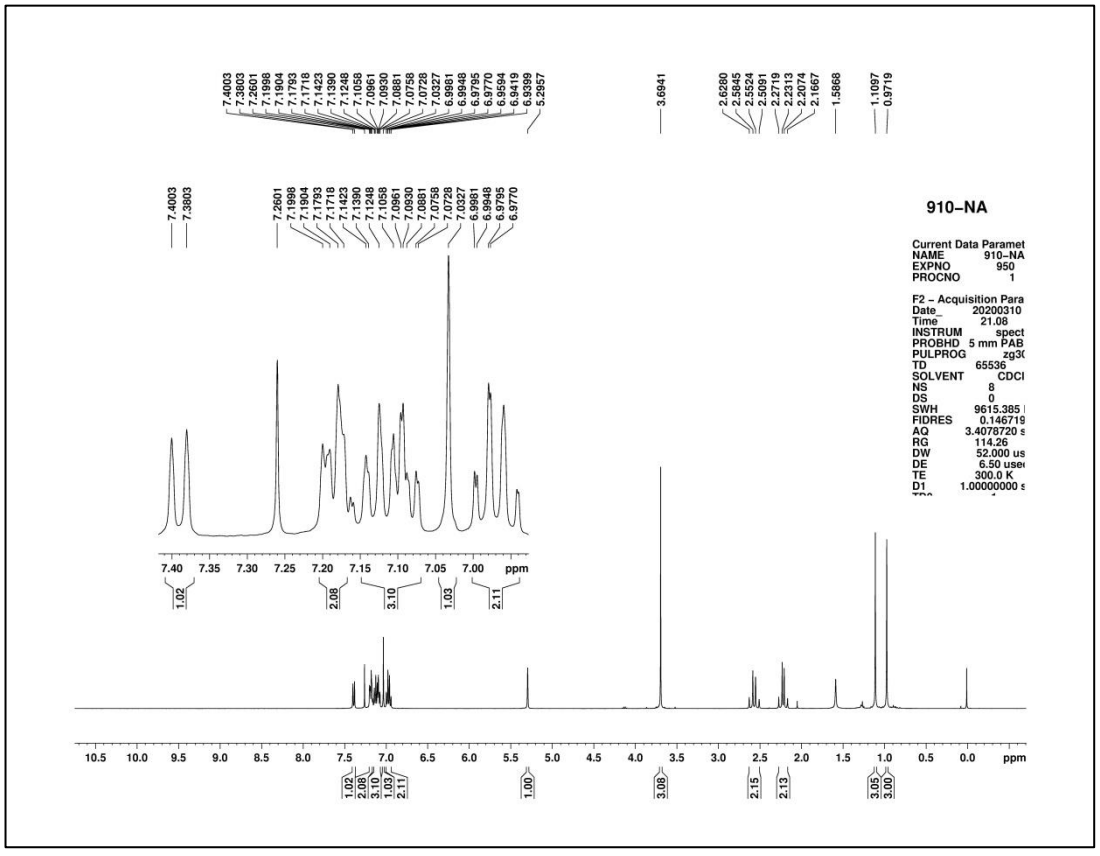


Figure S15: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4h)

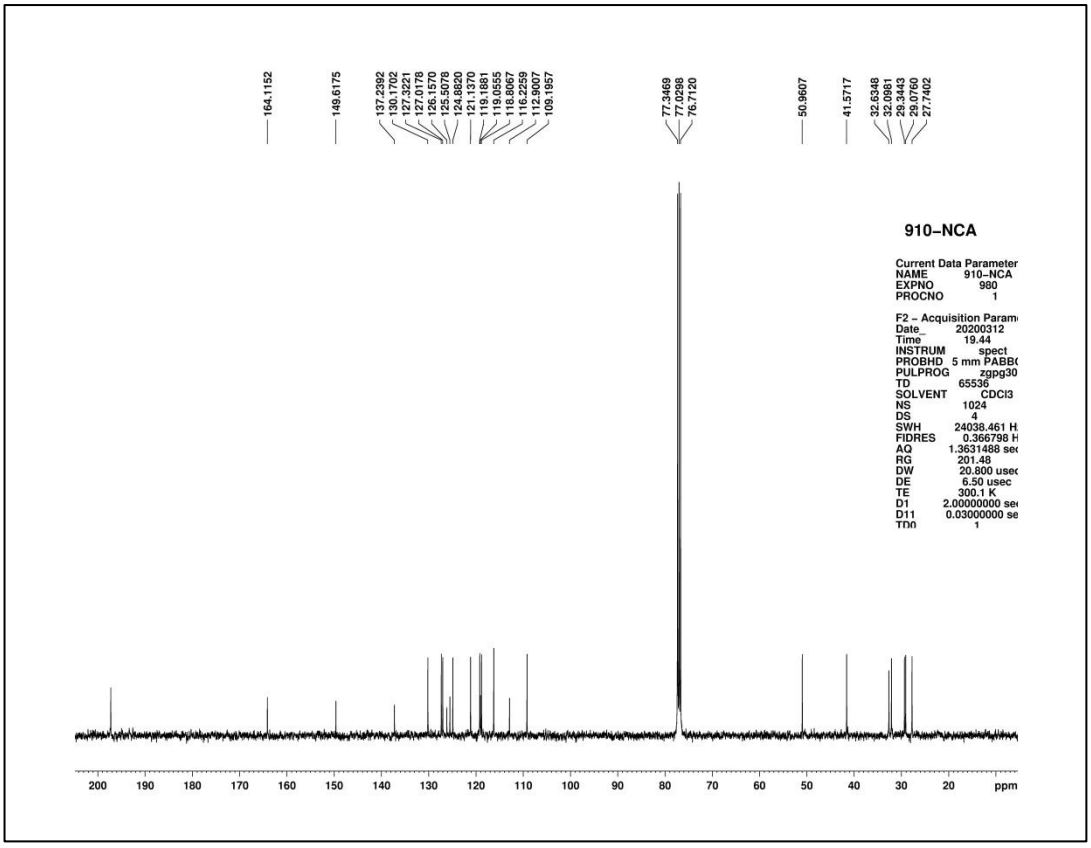


Figure S16: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4h)

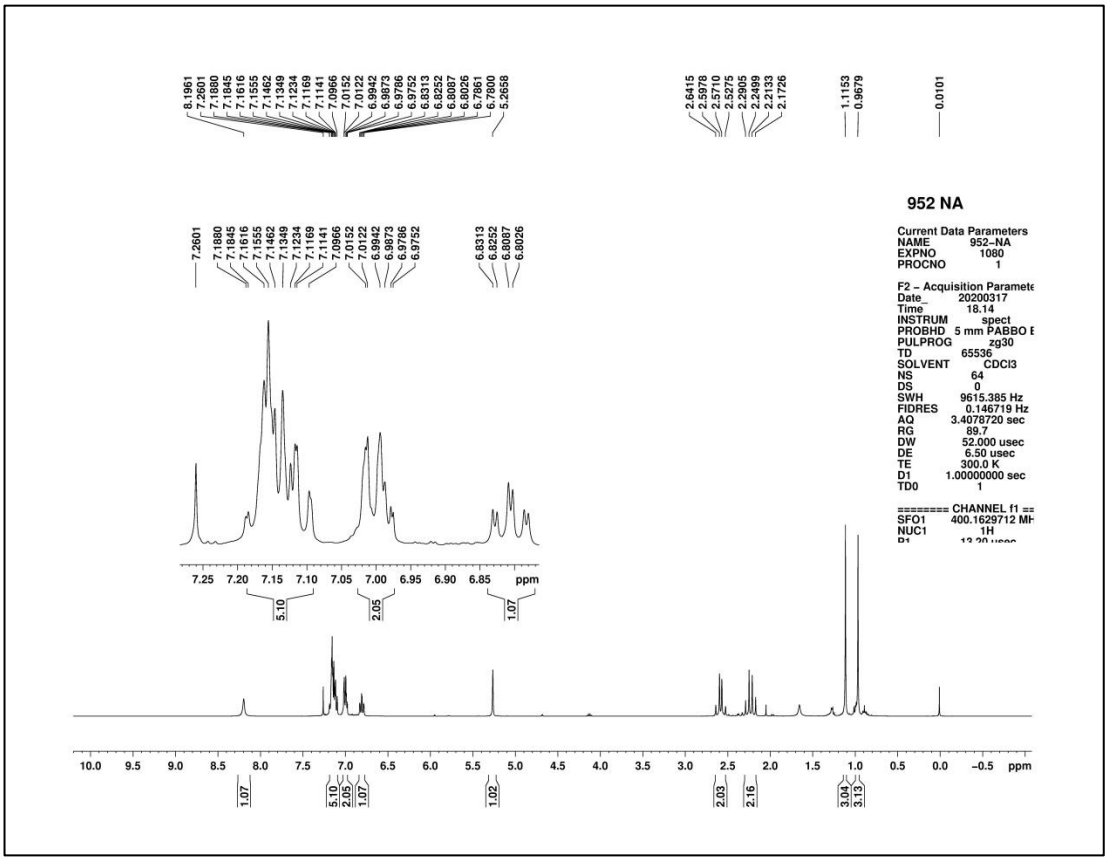


Figure S17: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4i)

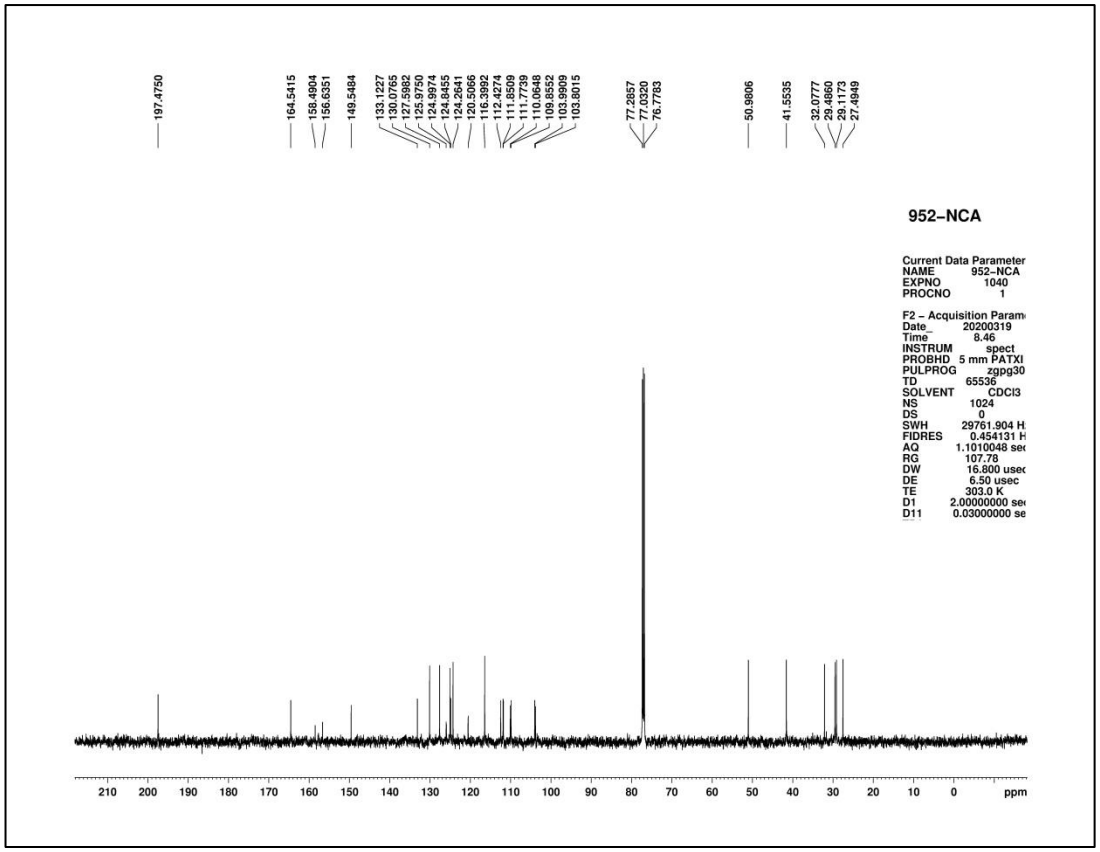


Figure S18: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4i)

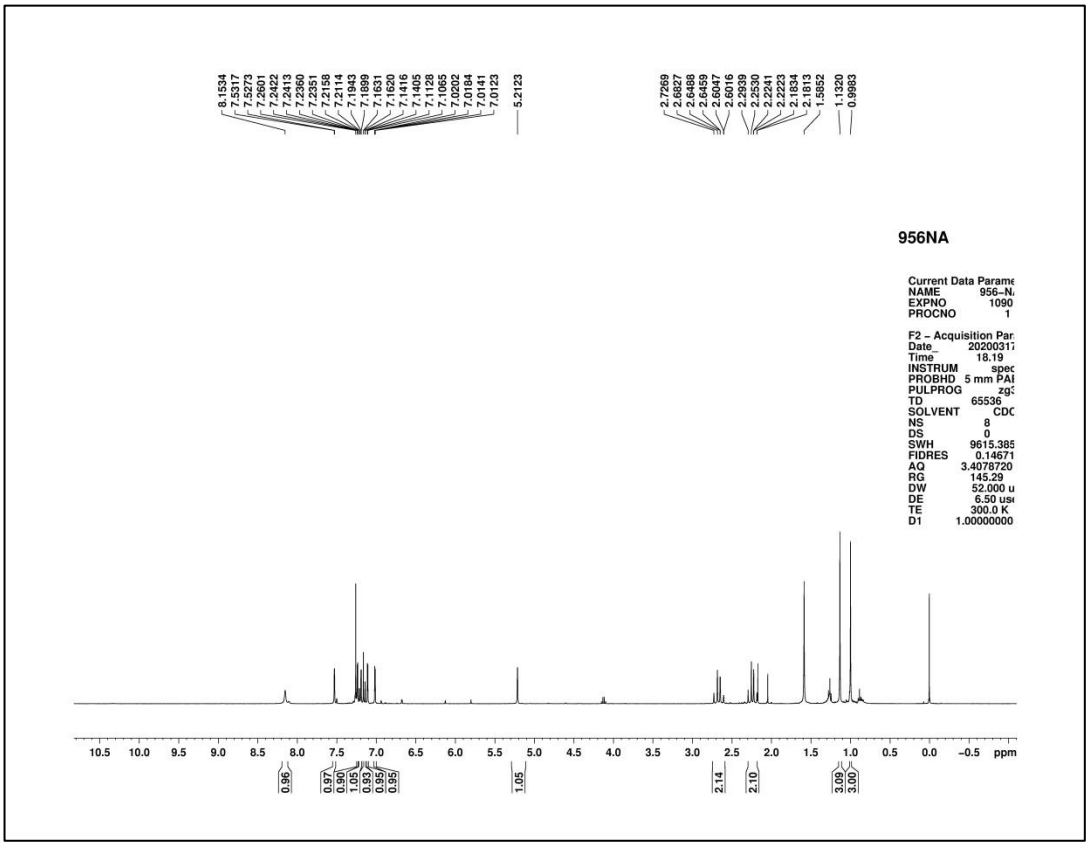


Figure S19: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4j)

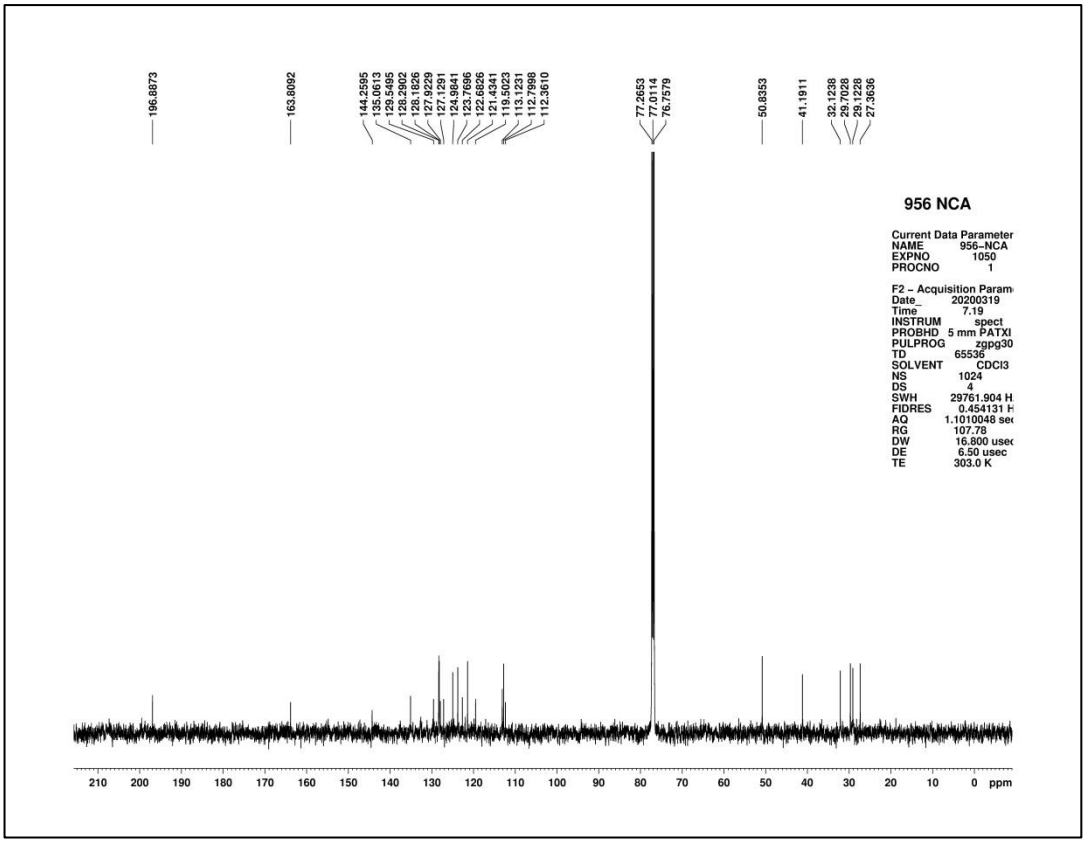


Figure S20: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4j)

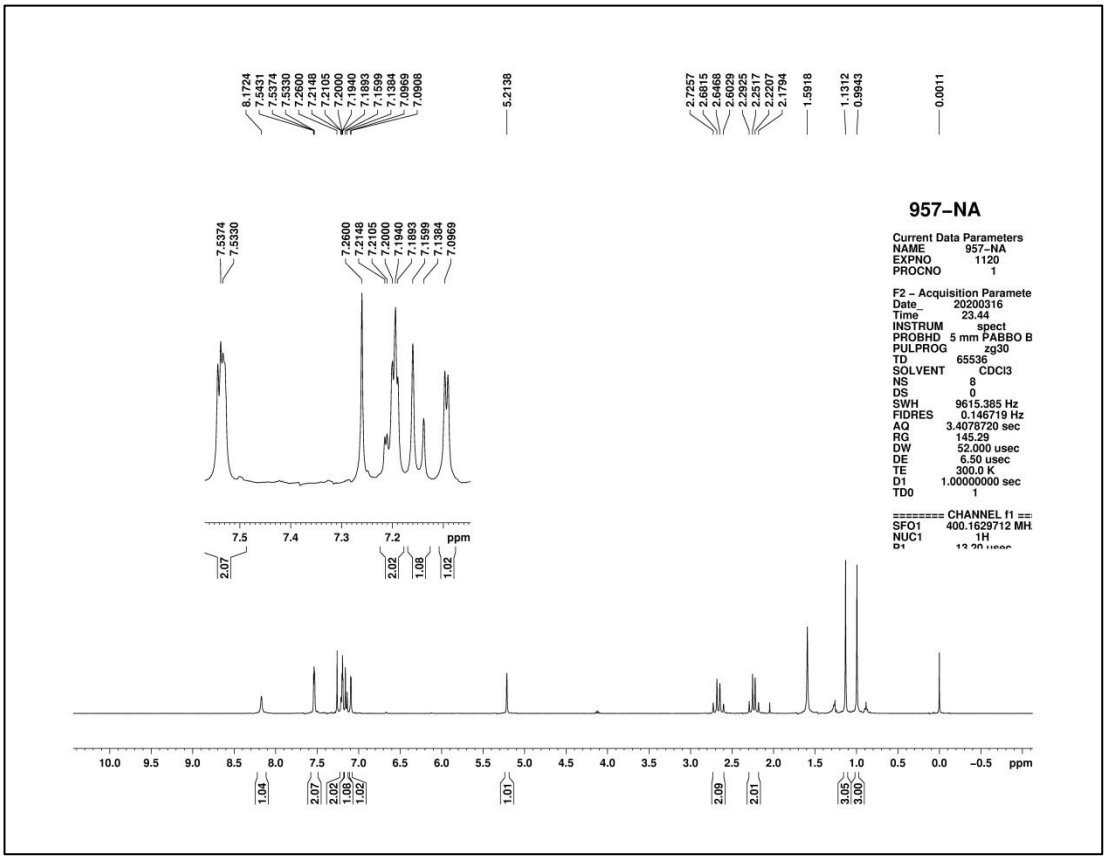


Figure S21: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4k)

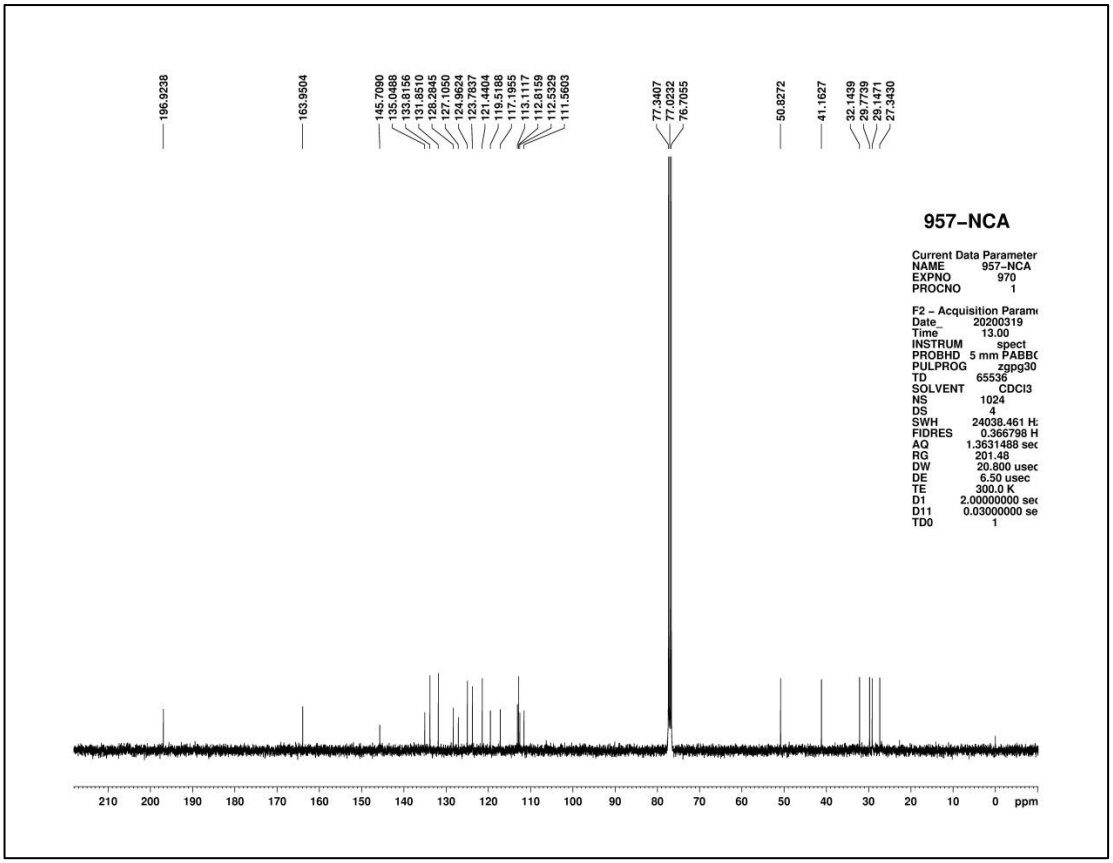


Figure S22: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4k)

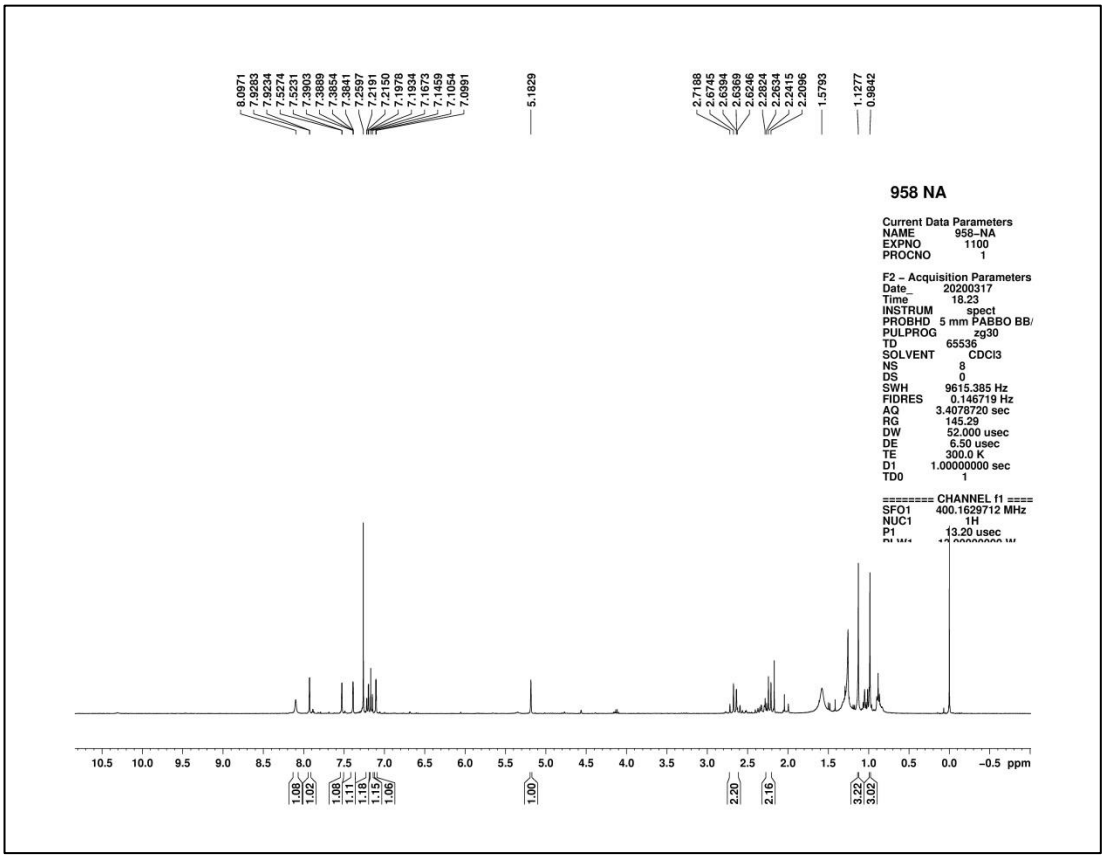


Figure S23: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4l)

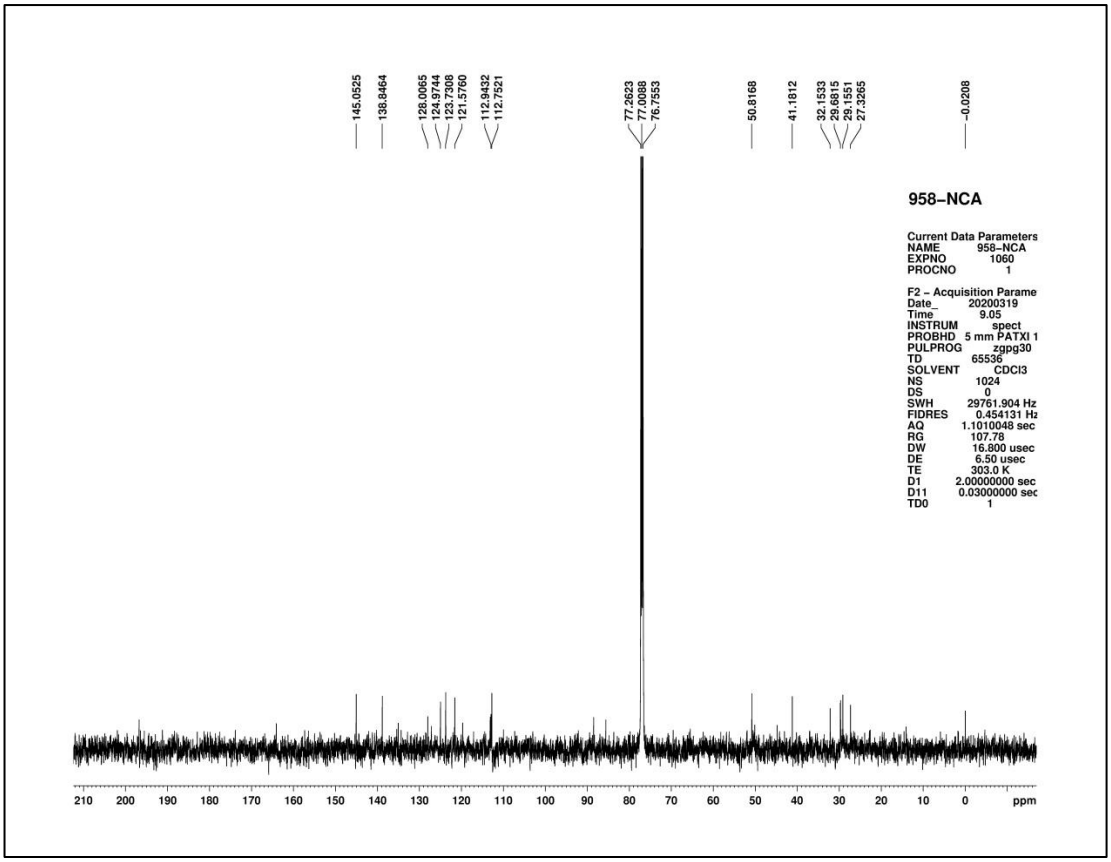


Figure S24: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4l)

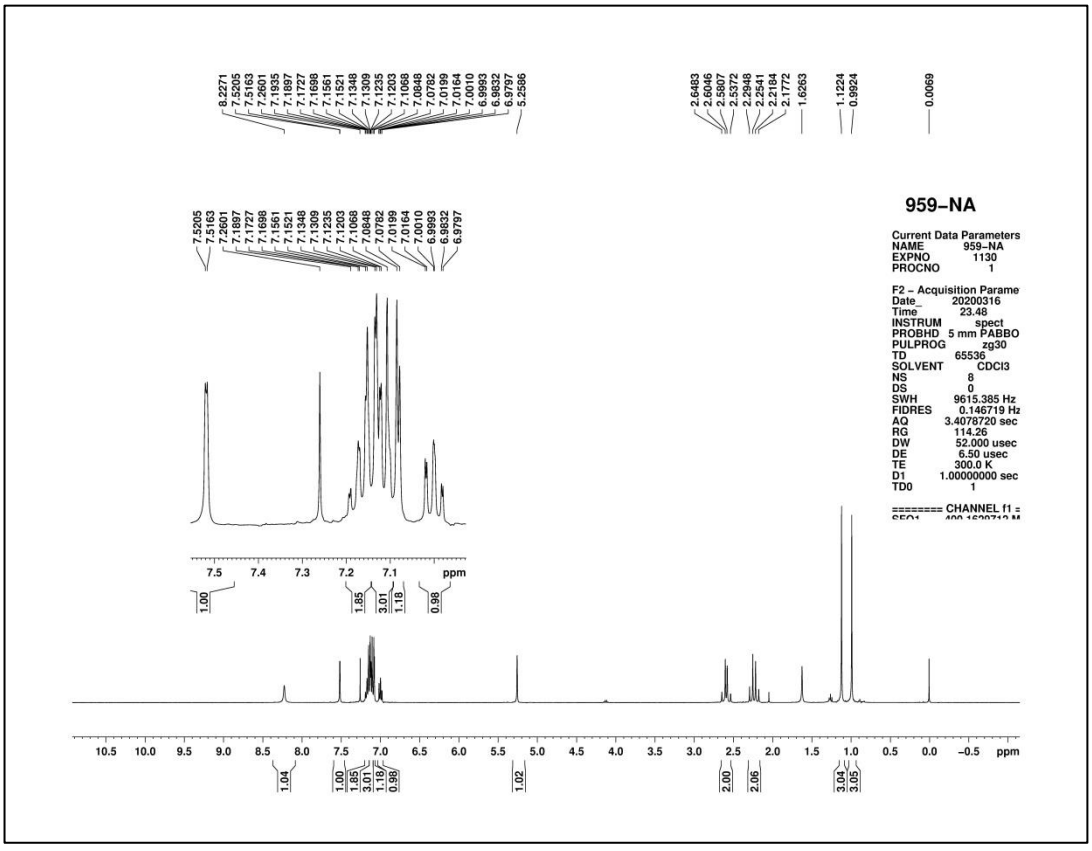


Figure S25: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4m)

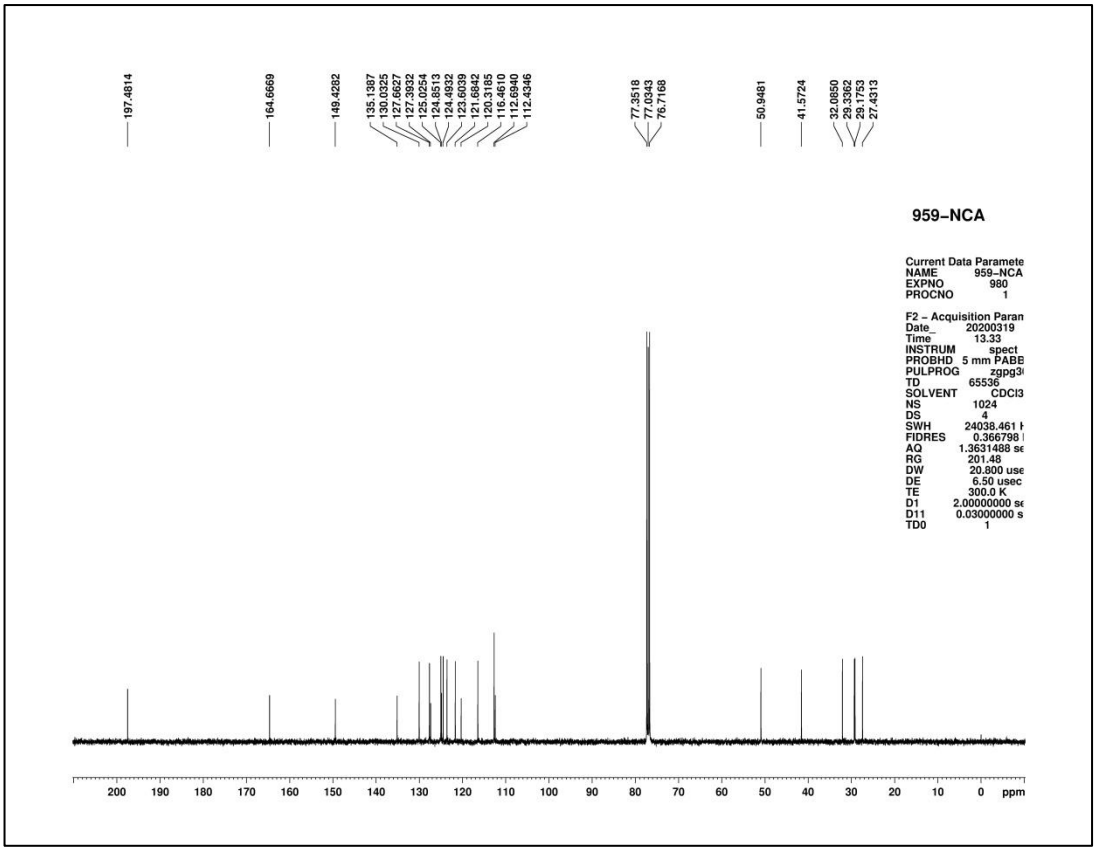


Figure S26: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4m)

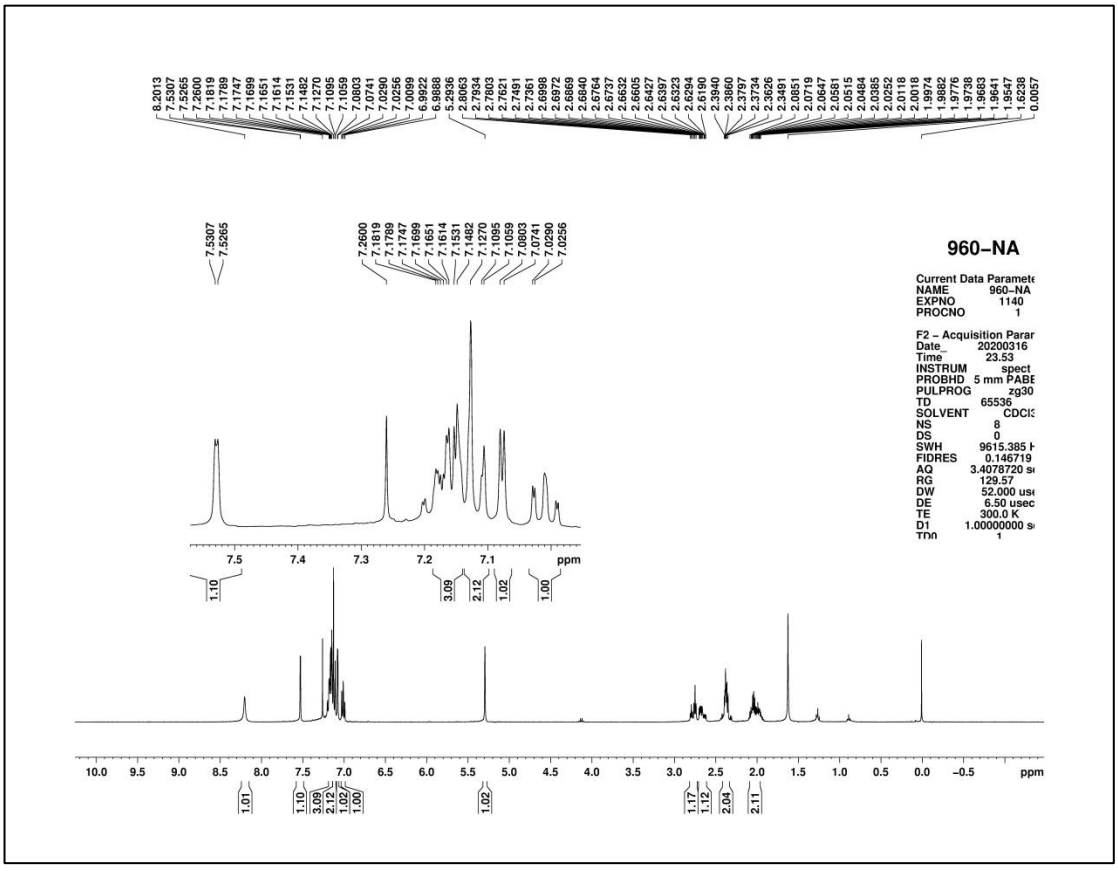


Figure S27: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4n)

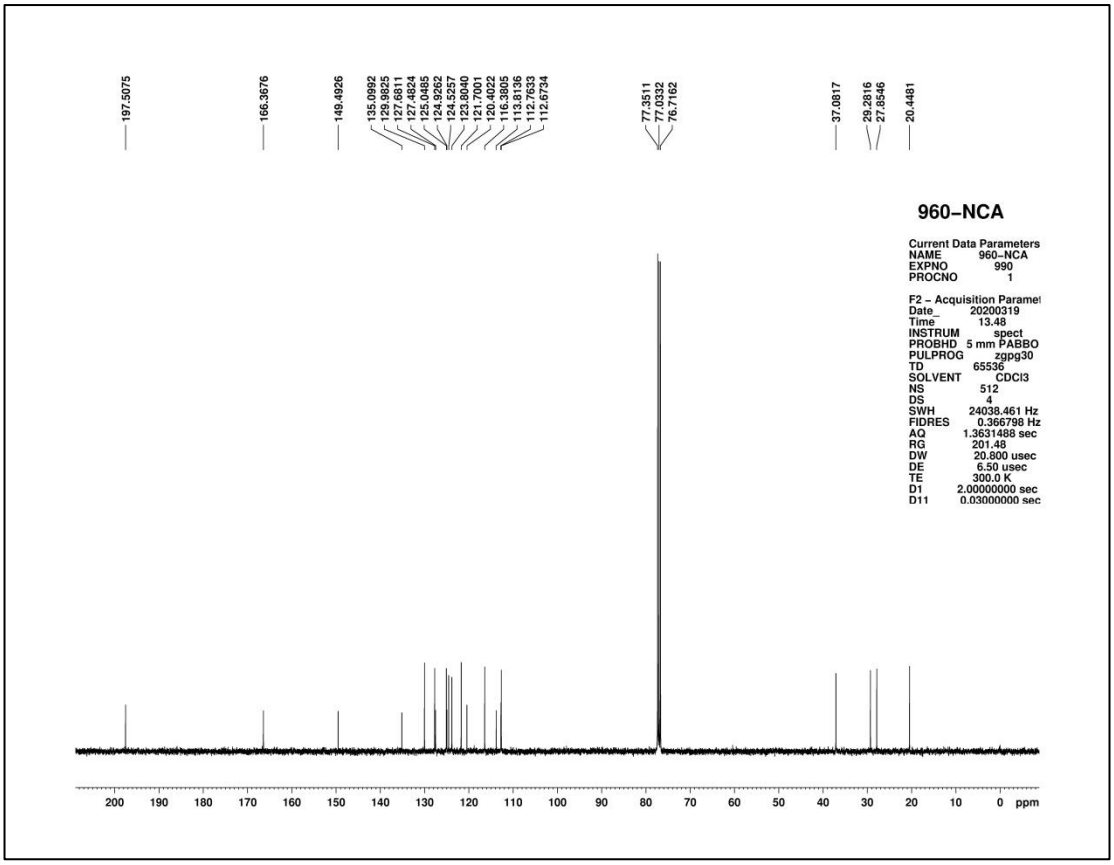


Figure S28: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4n)

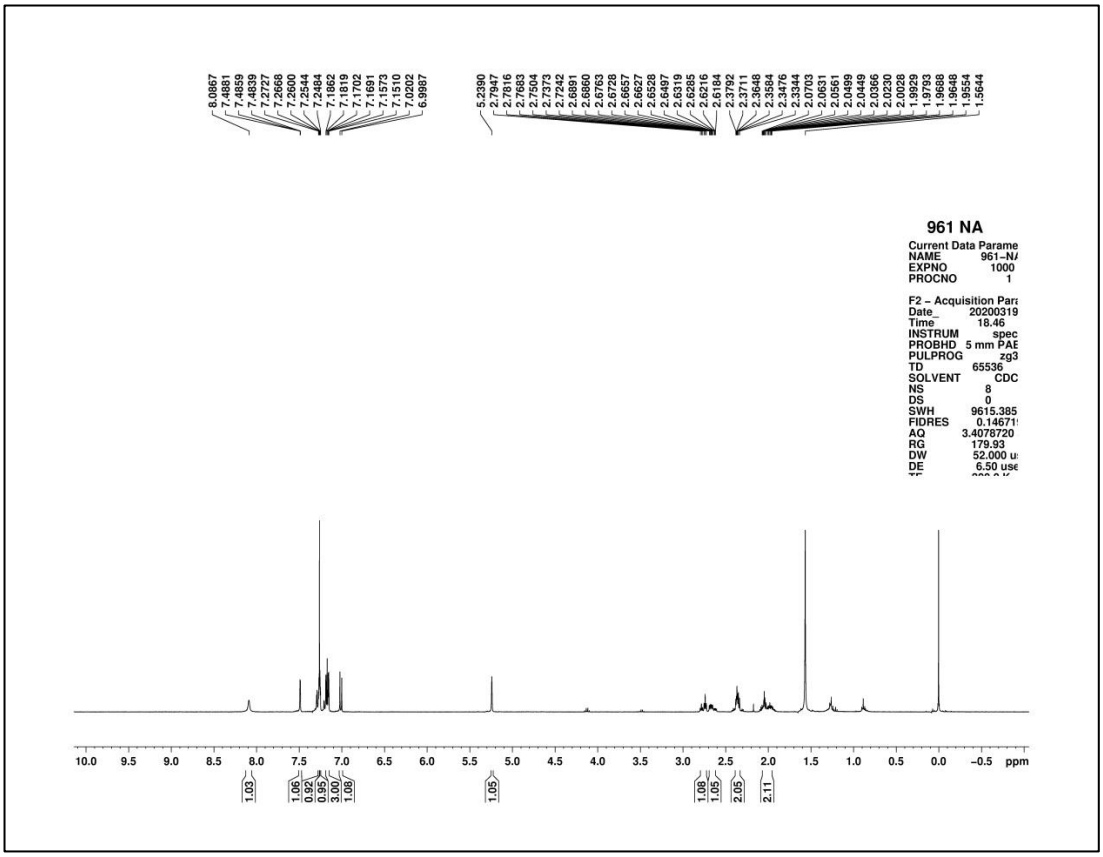


Figure S29: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4o)

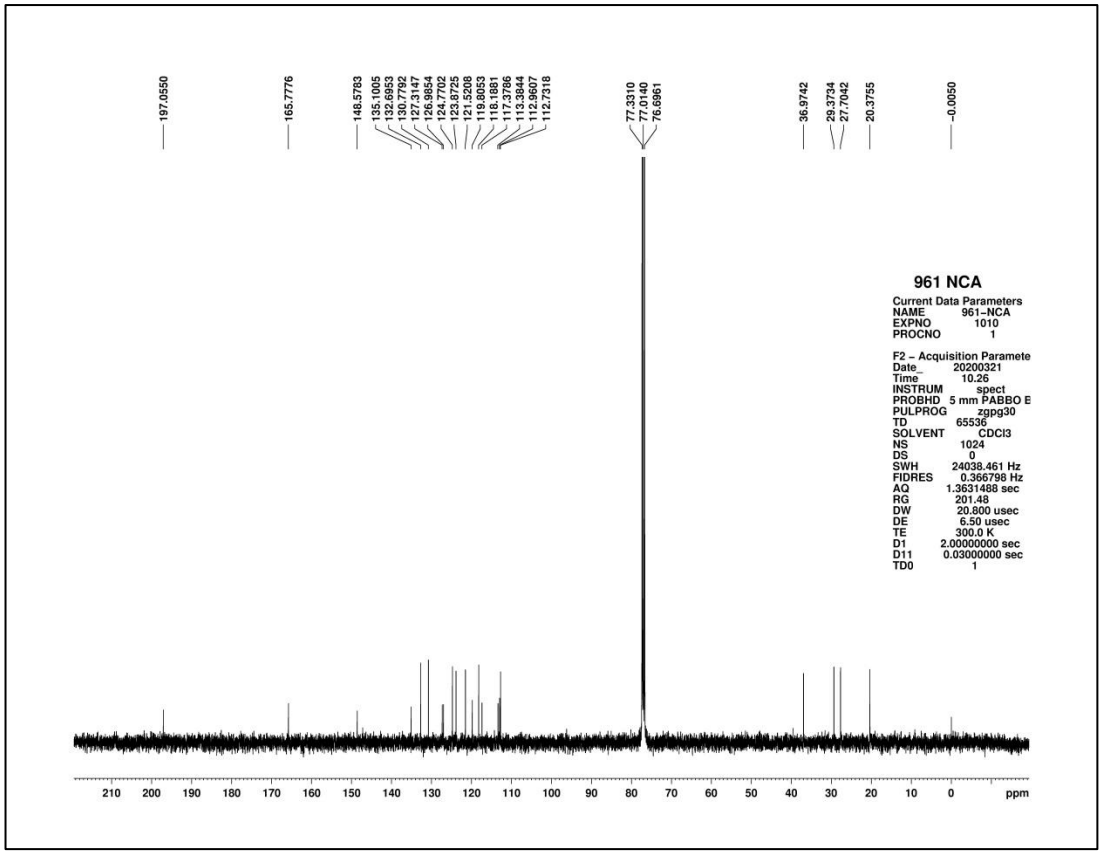


Figure S30: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4o)

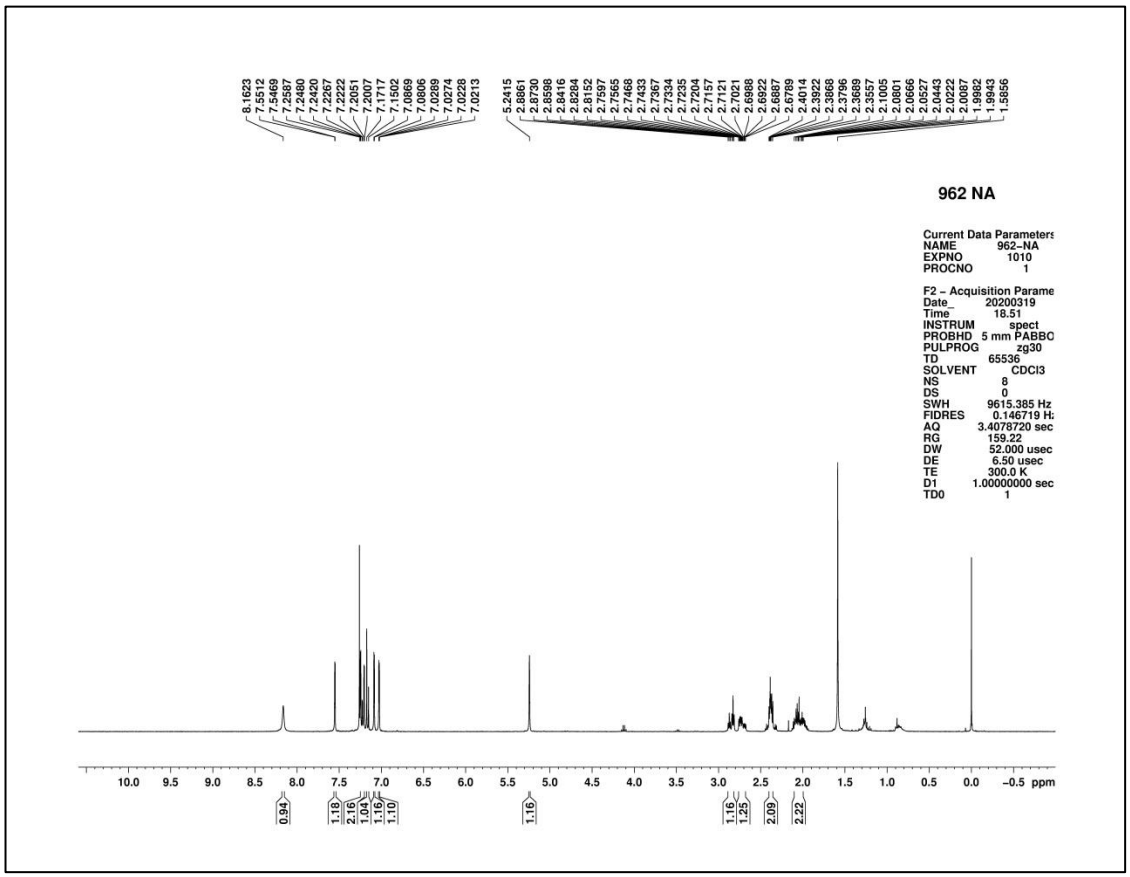


Figure S31: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4p)

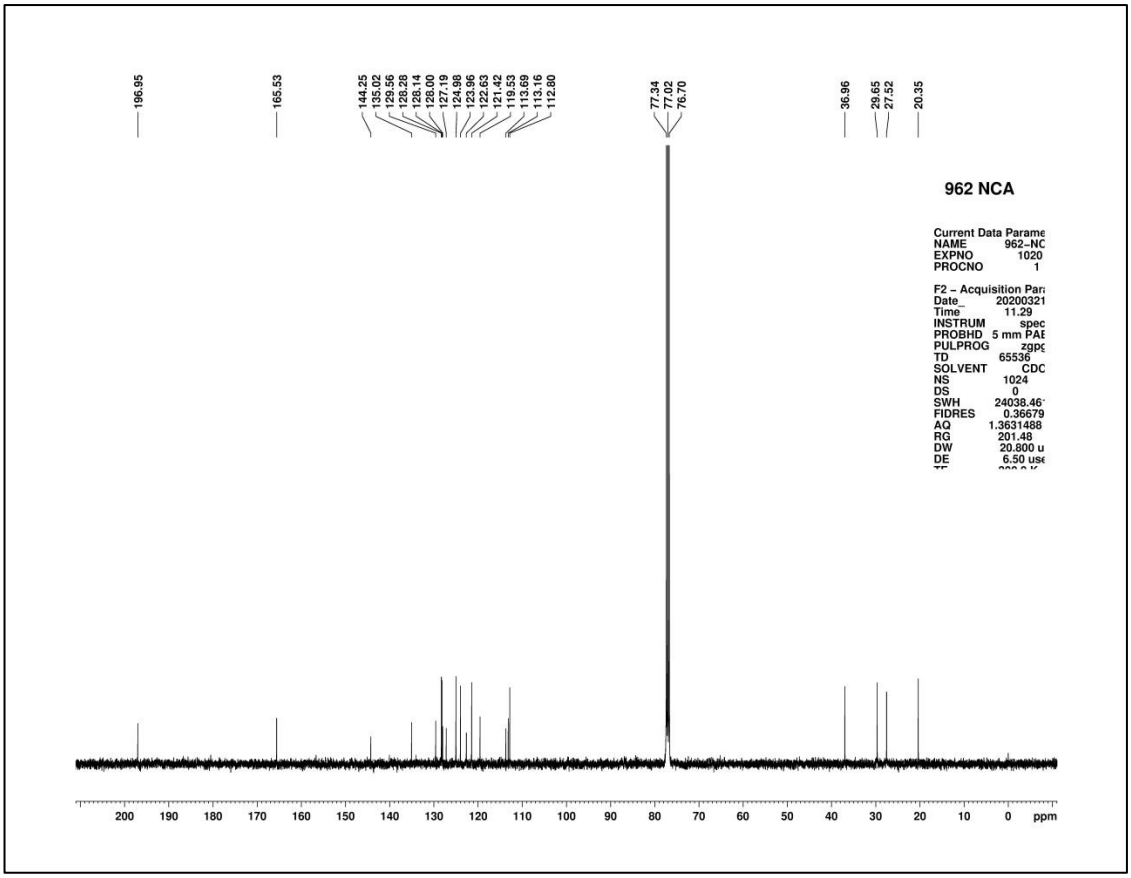


Figure S32: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4p)

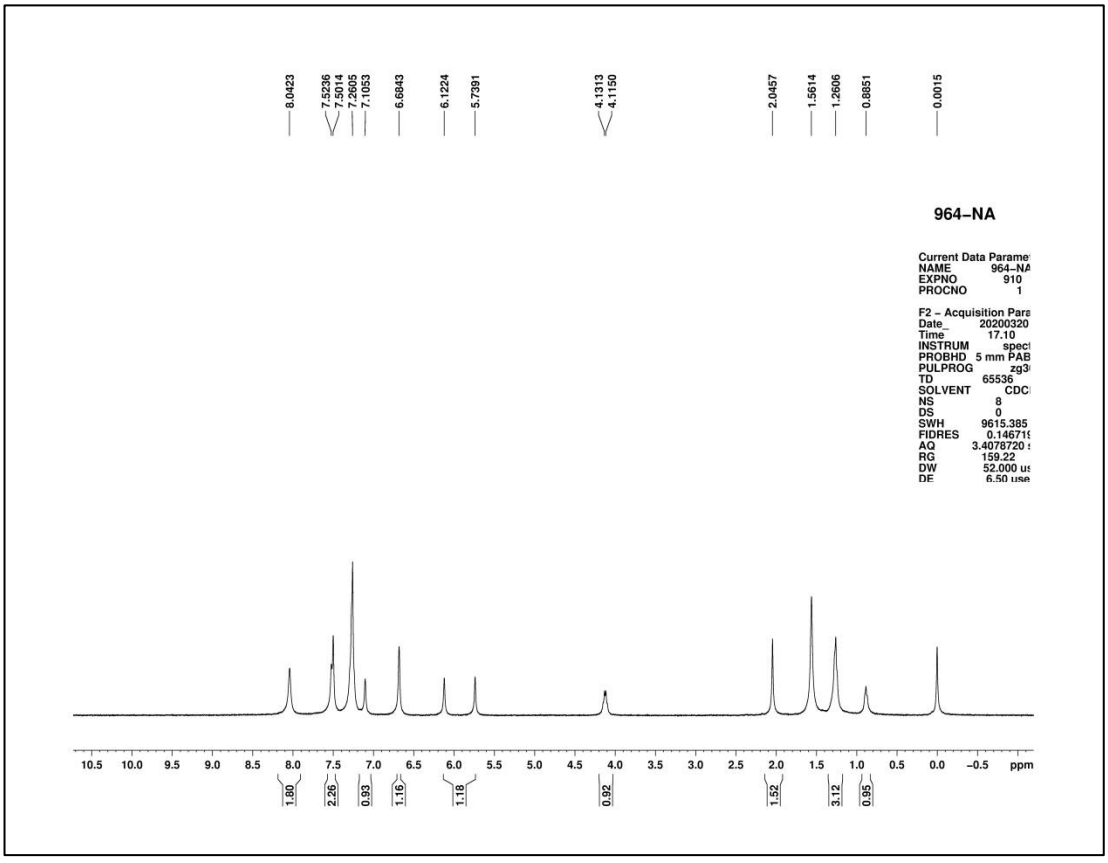


Figure S33: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4q)

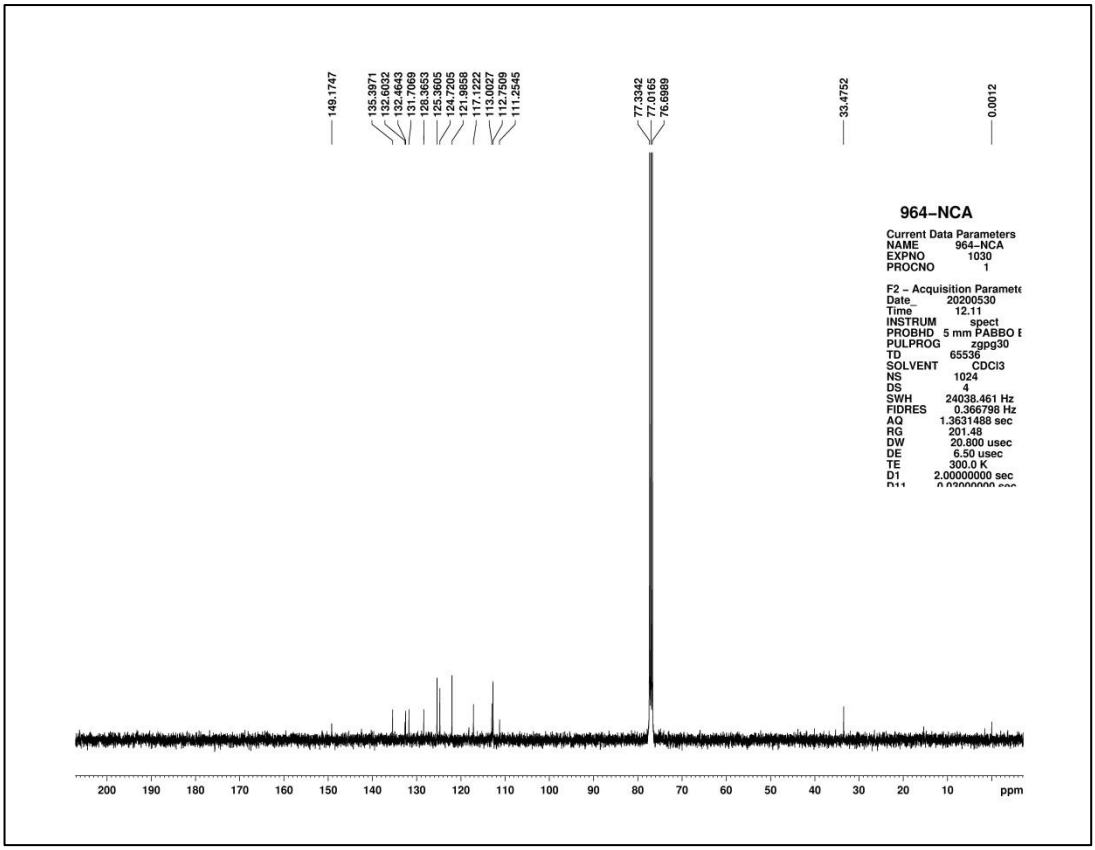


Figure S34: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4q)

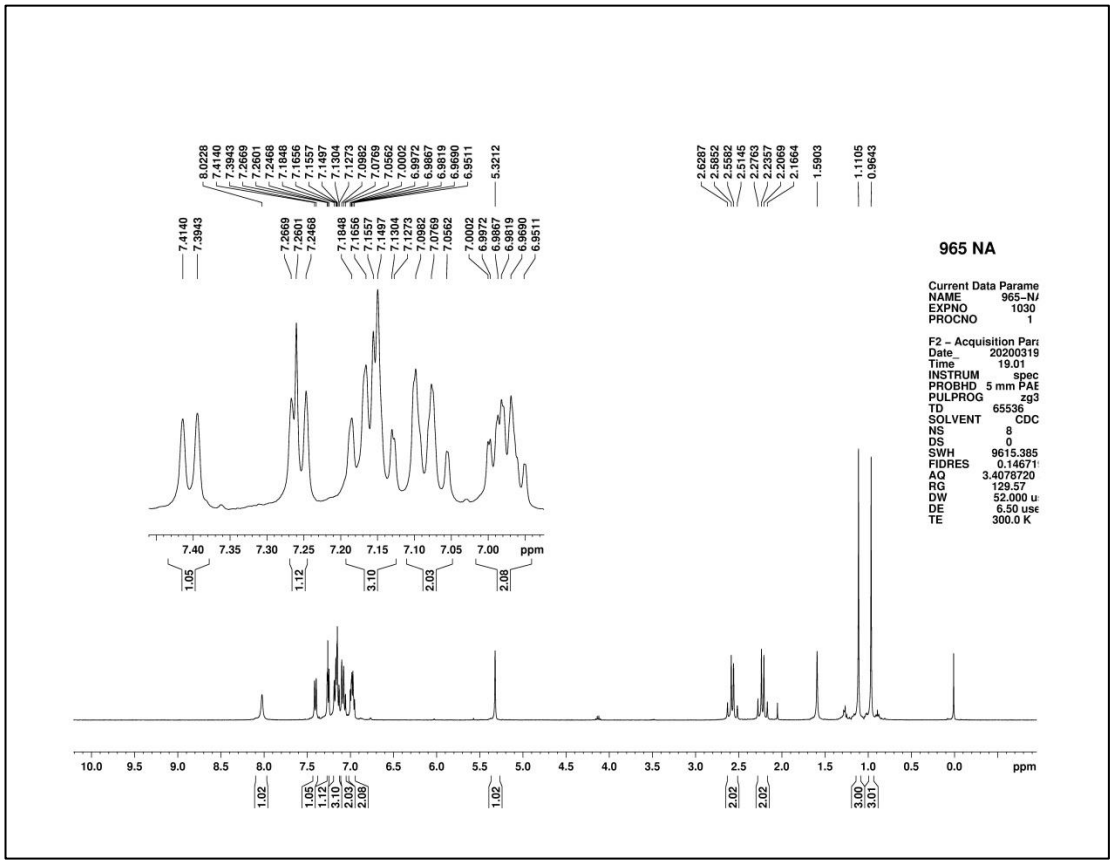


Figure S35: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4r)

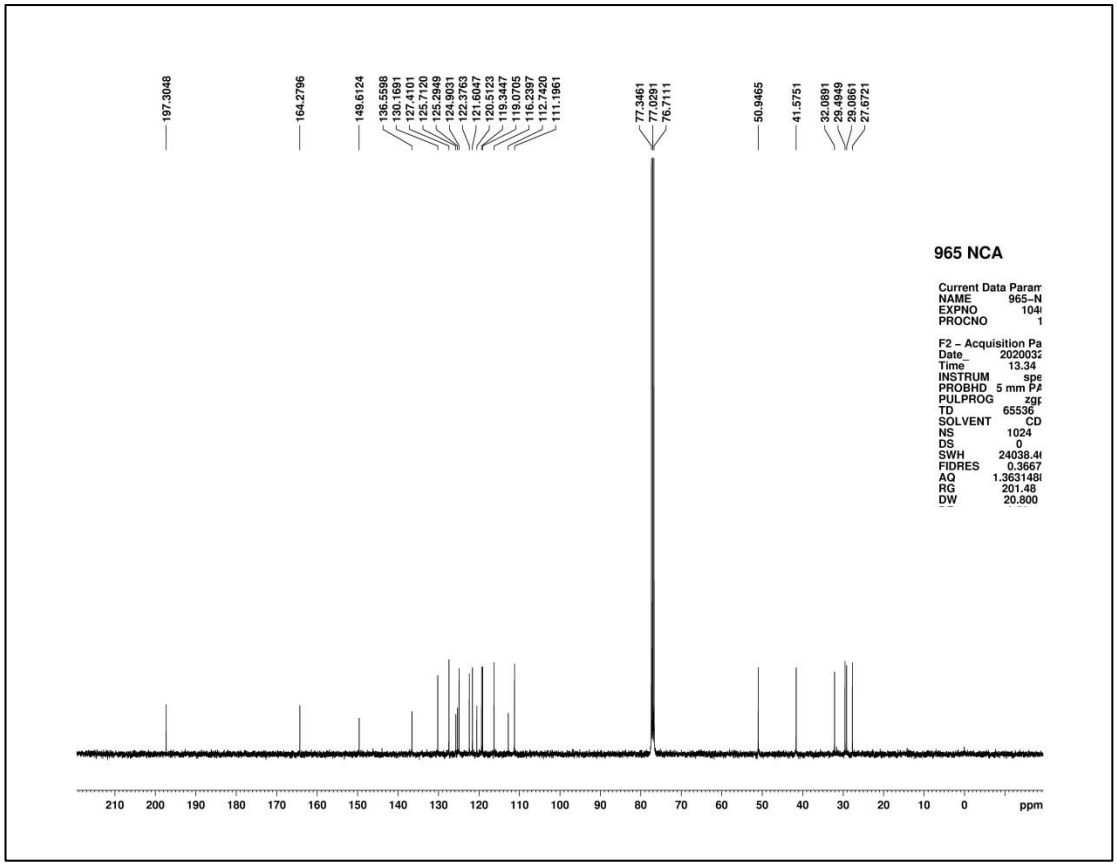


Figure S36: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4r)

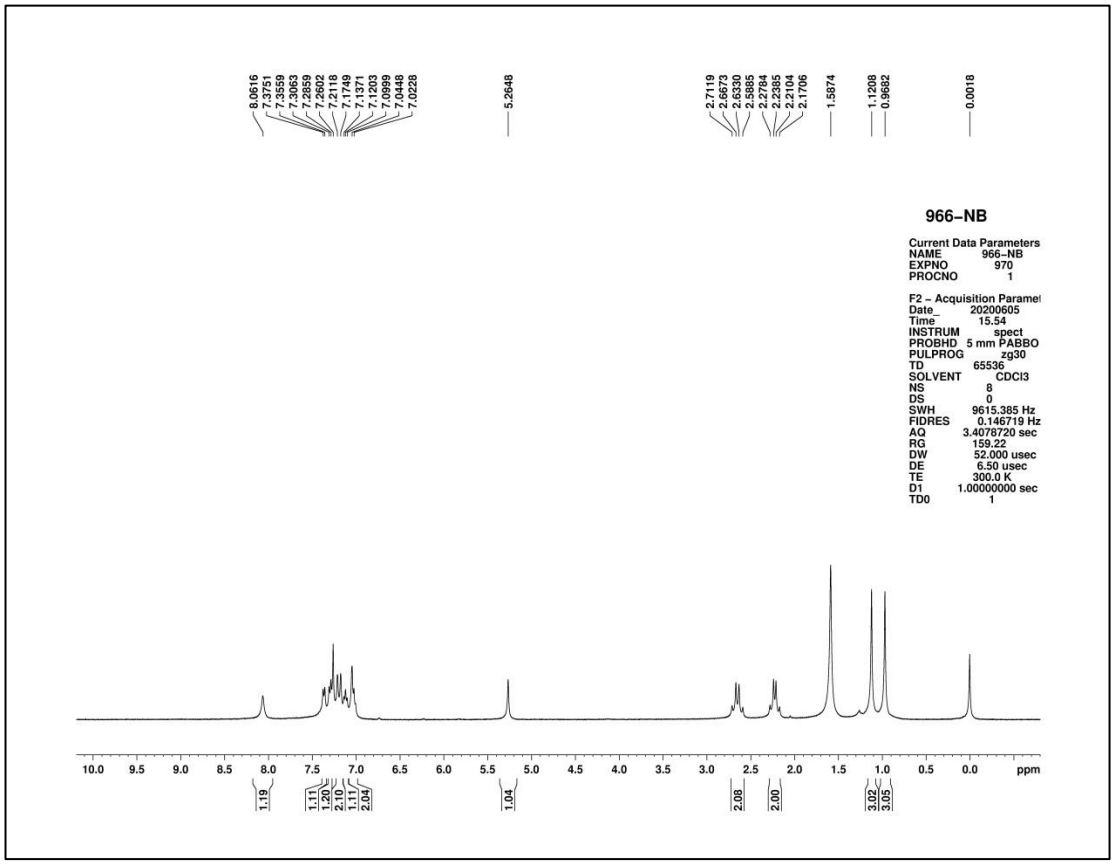


Figure S37: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4s)

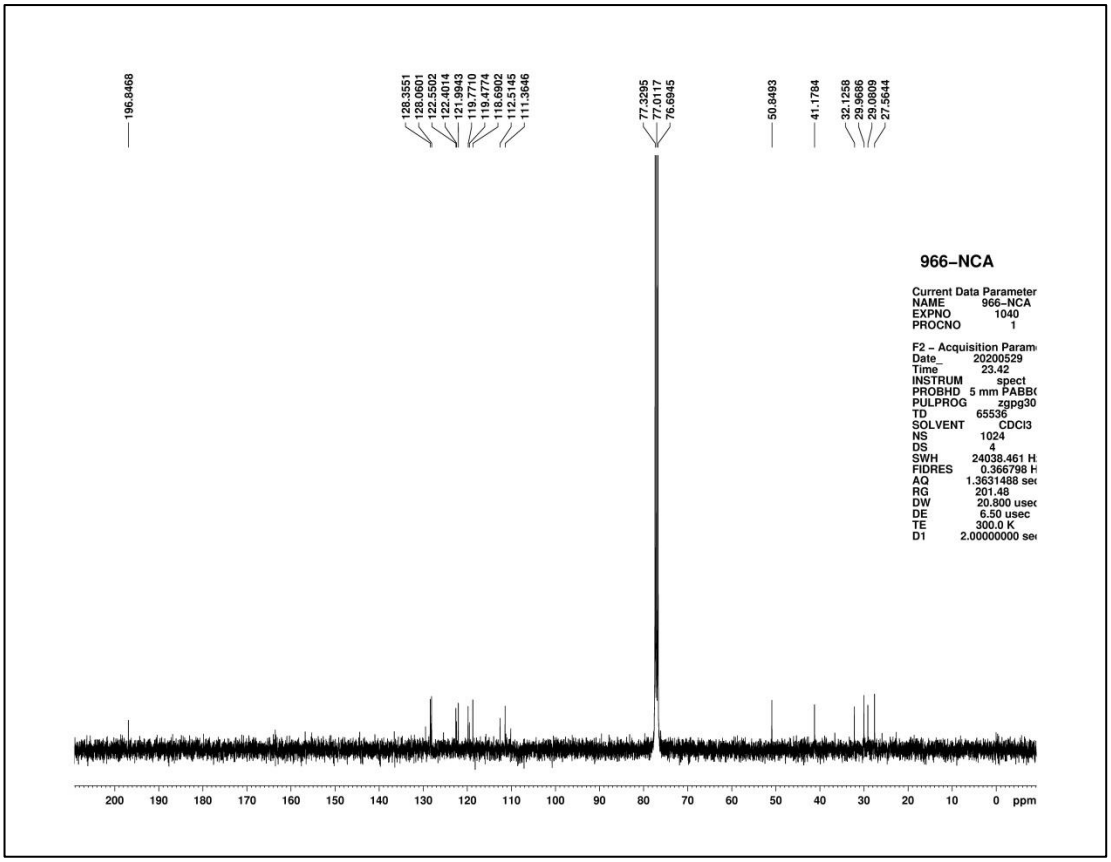


Figure S38: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4s)

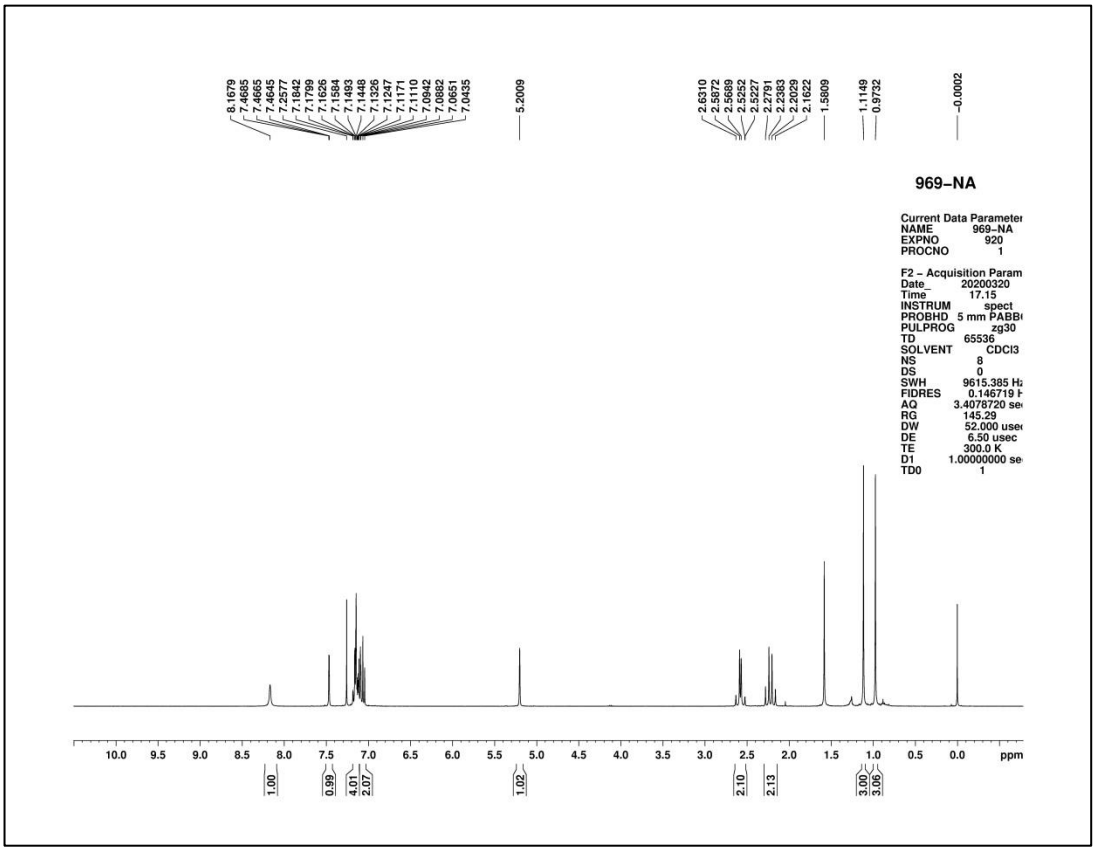


Figure S39: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4t)

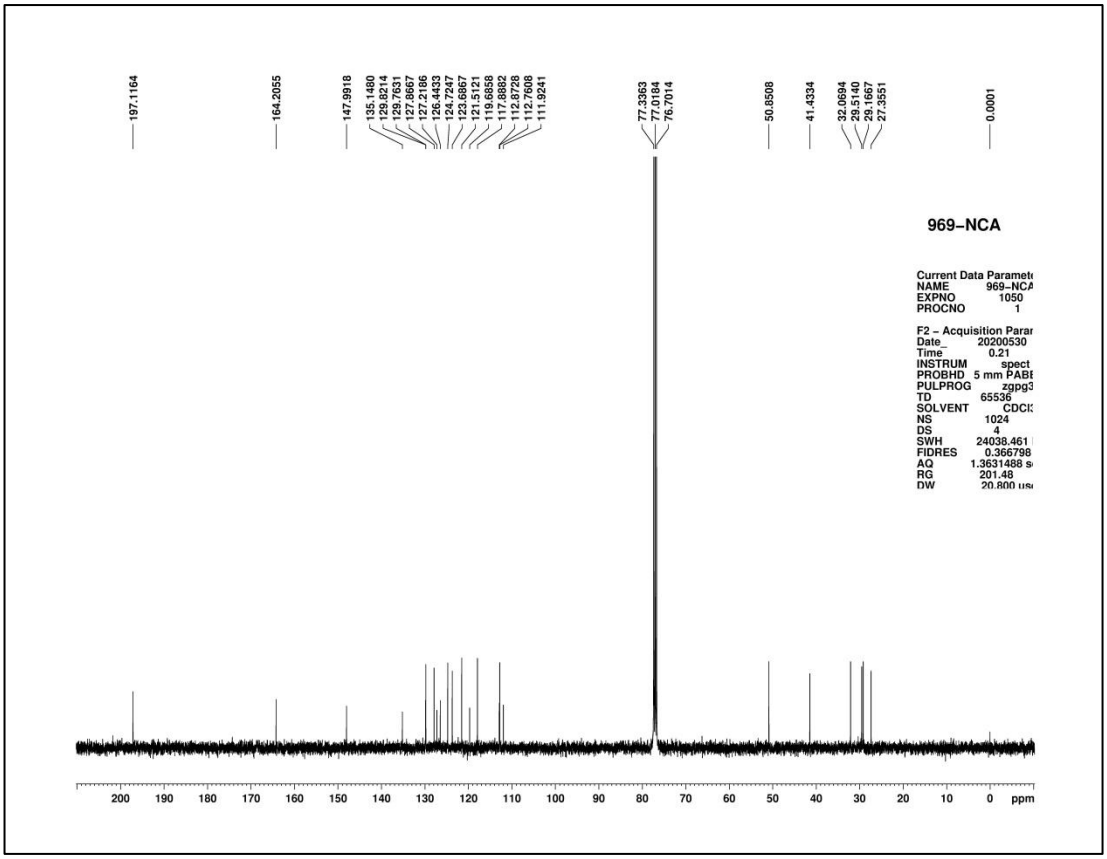


Figure S40: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4t)

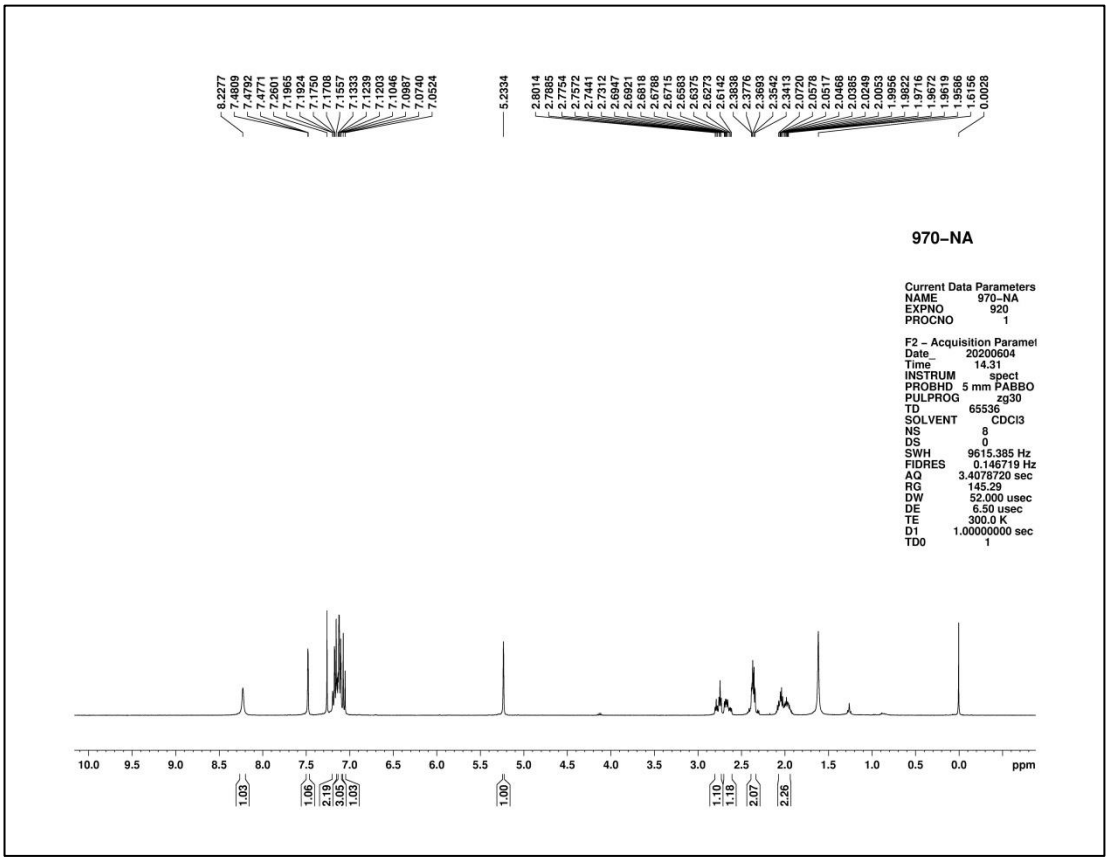


Figure S41: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4u)

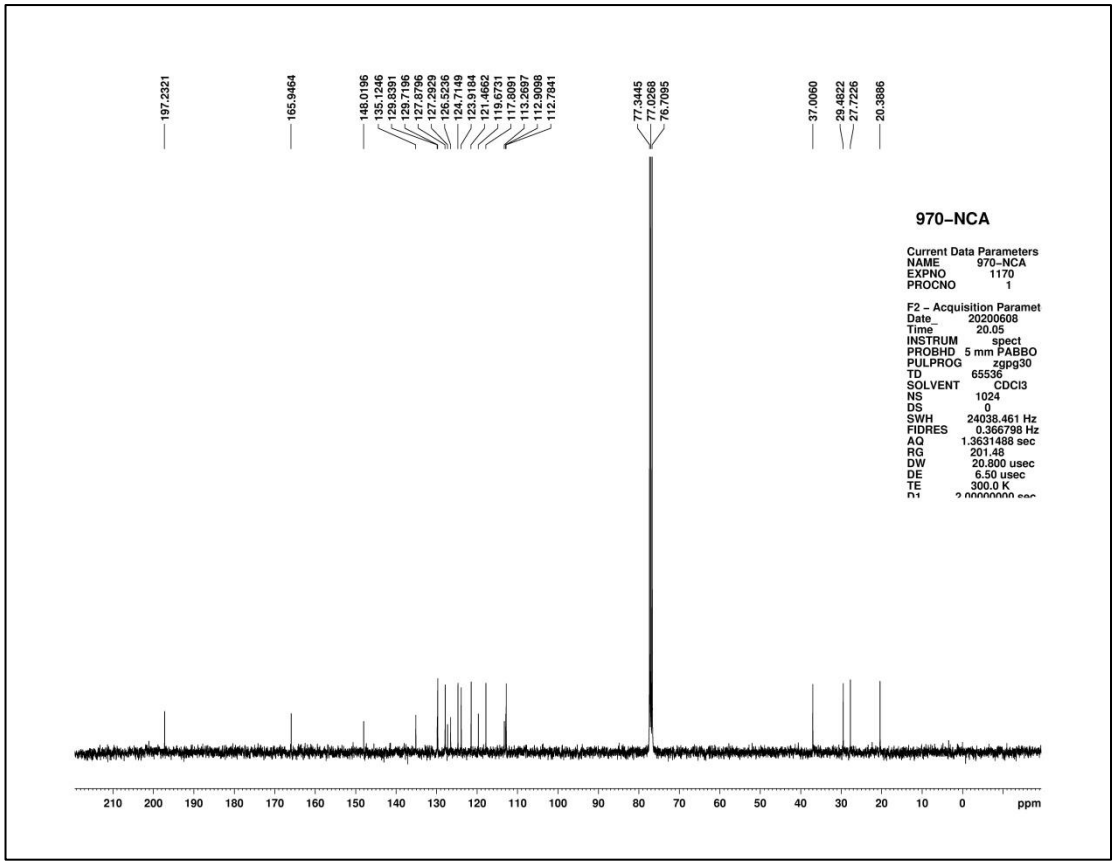


Figure S42: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4u)

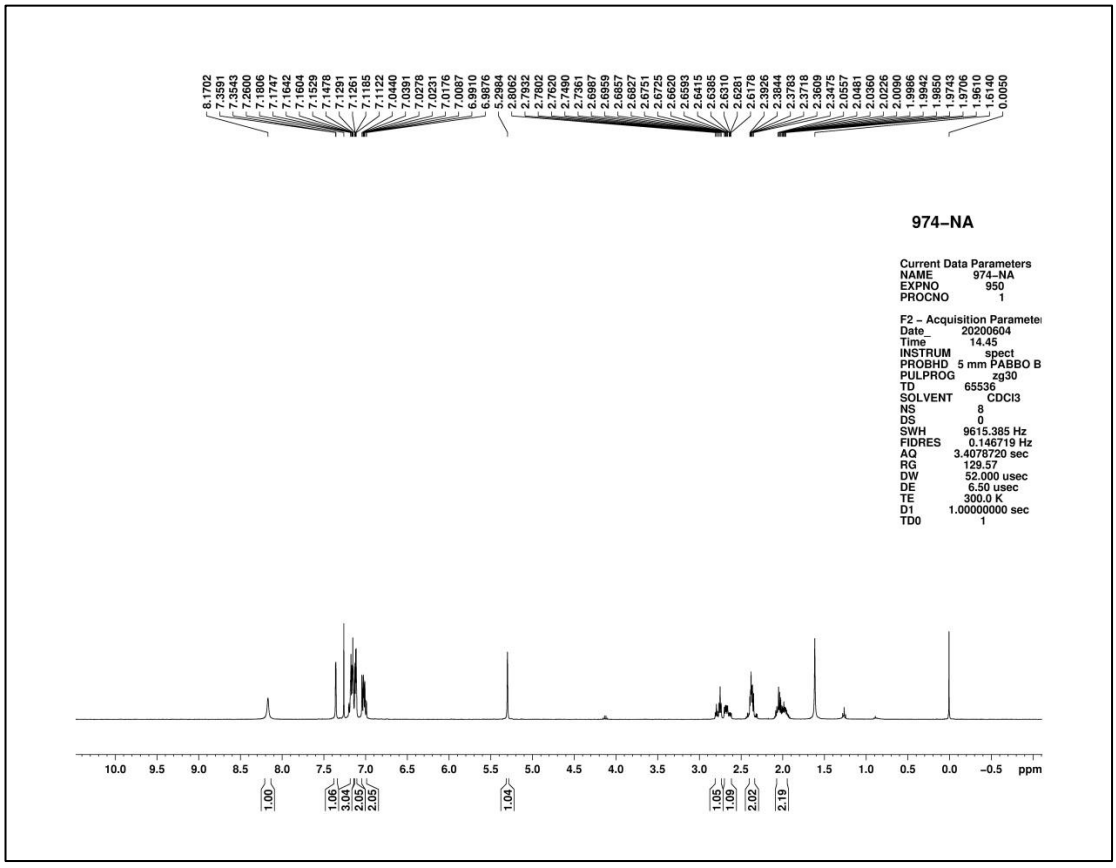


Figure S43: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4v)

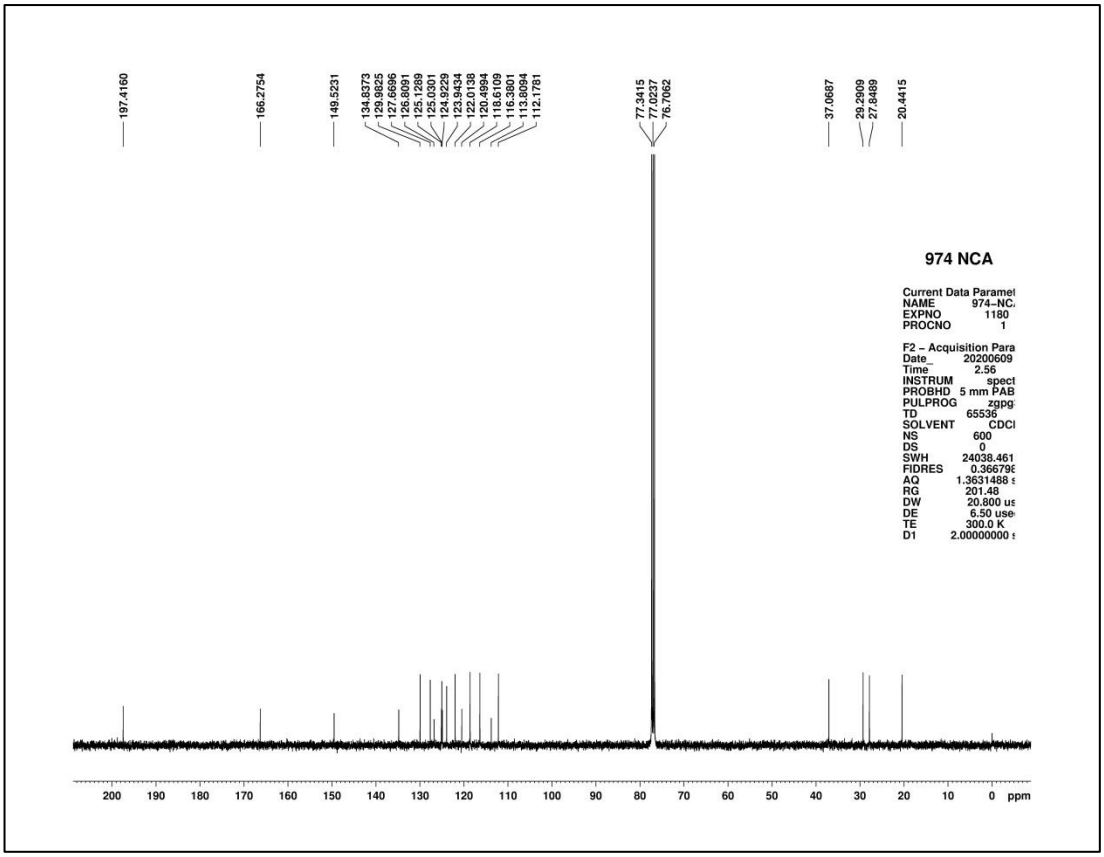


Figure S44: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4v)

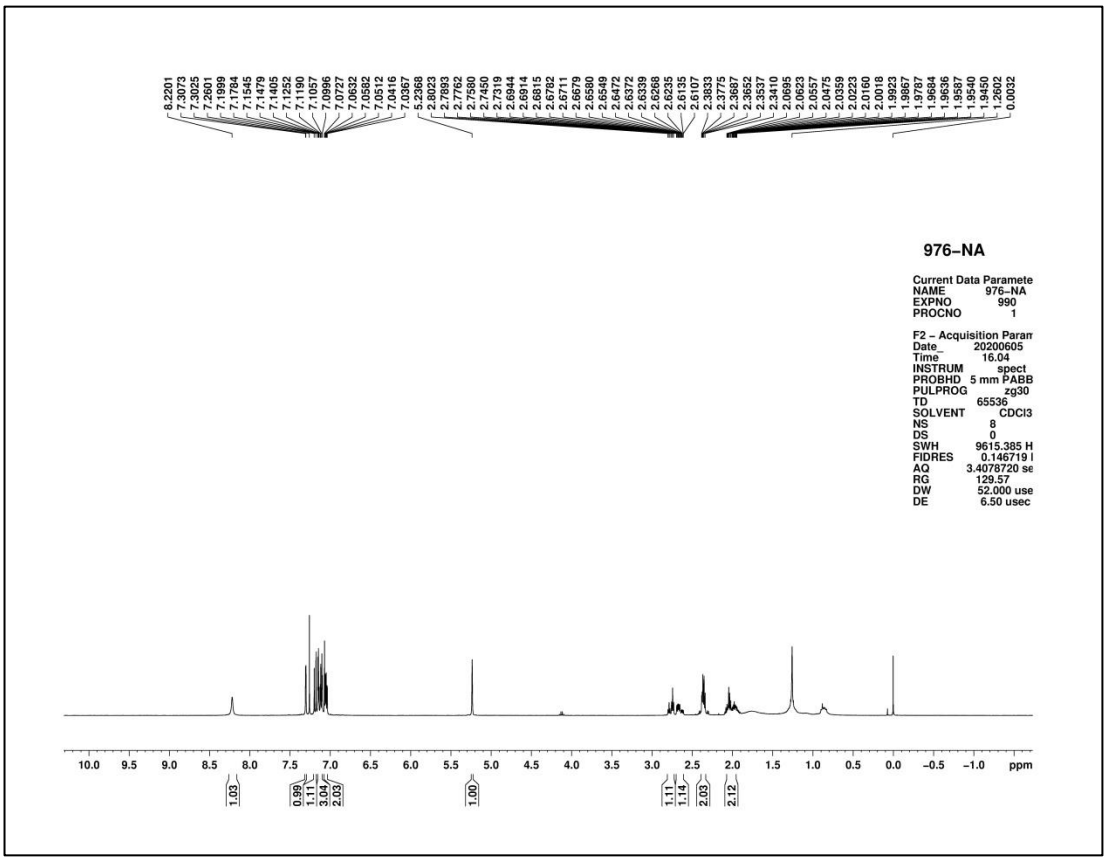


Figure S45: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4w)

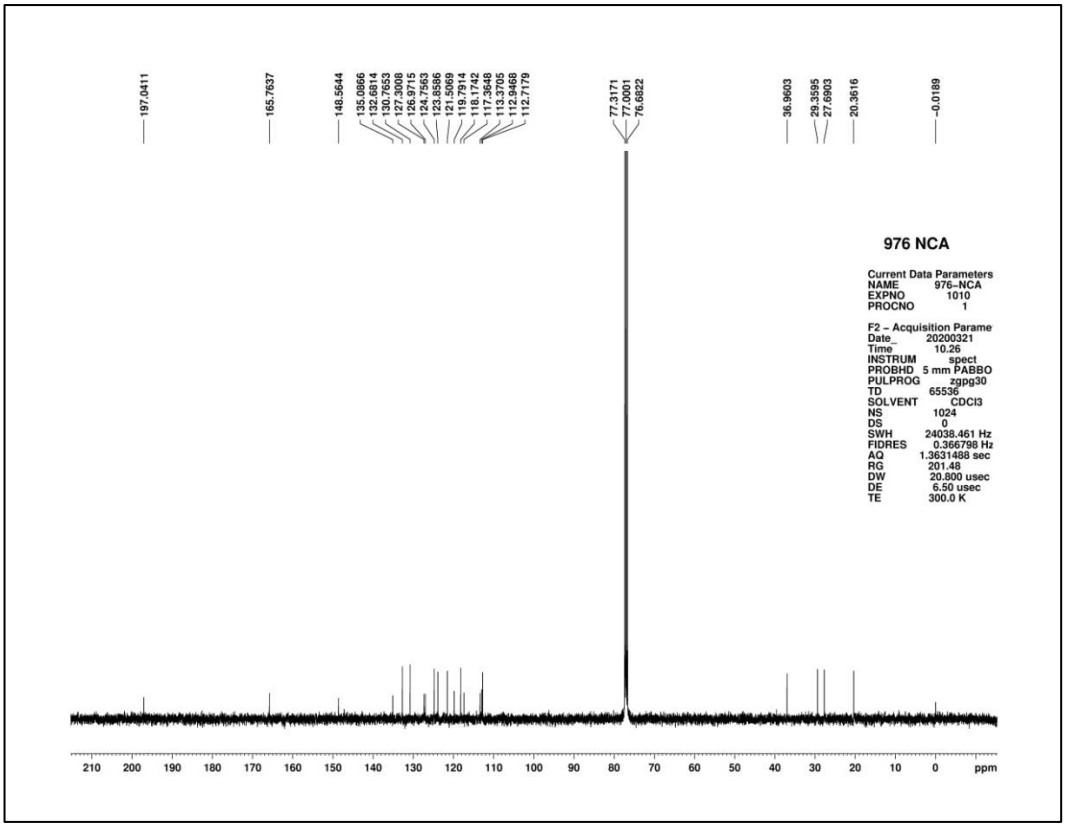


Figure S46: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4w)

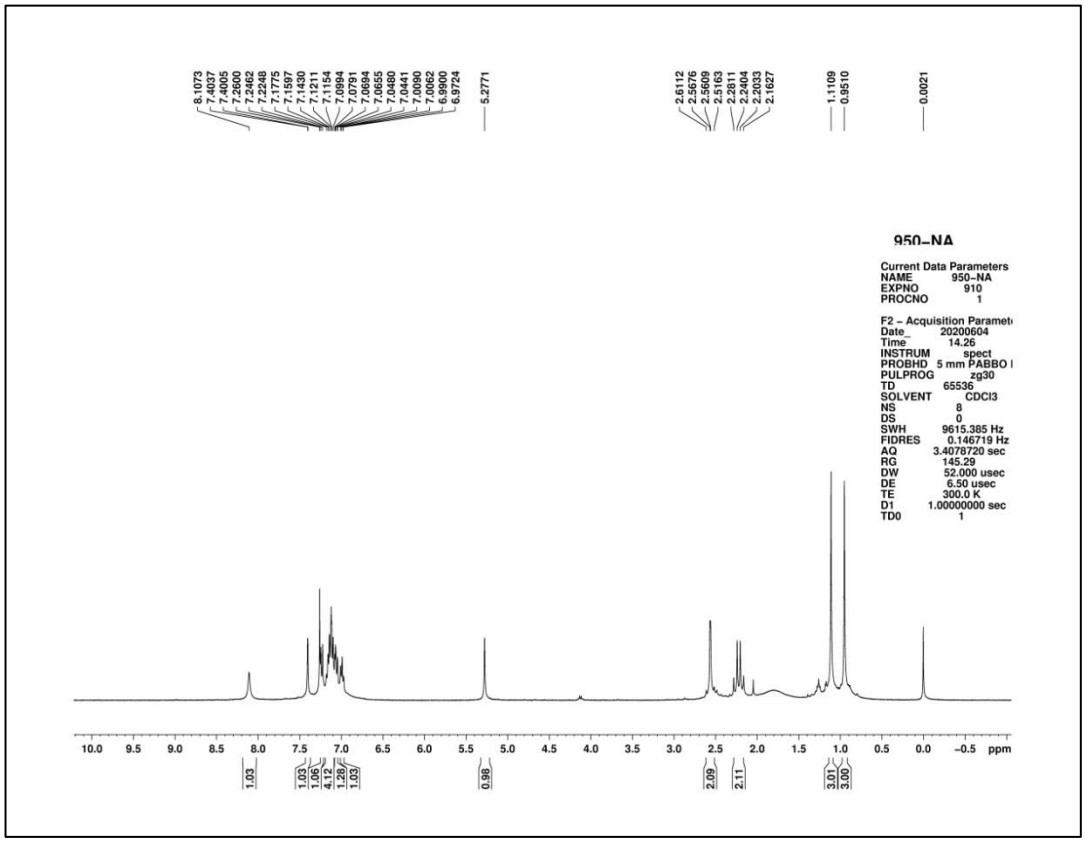


Figure S47: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4x)

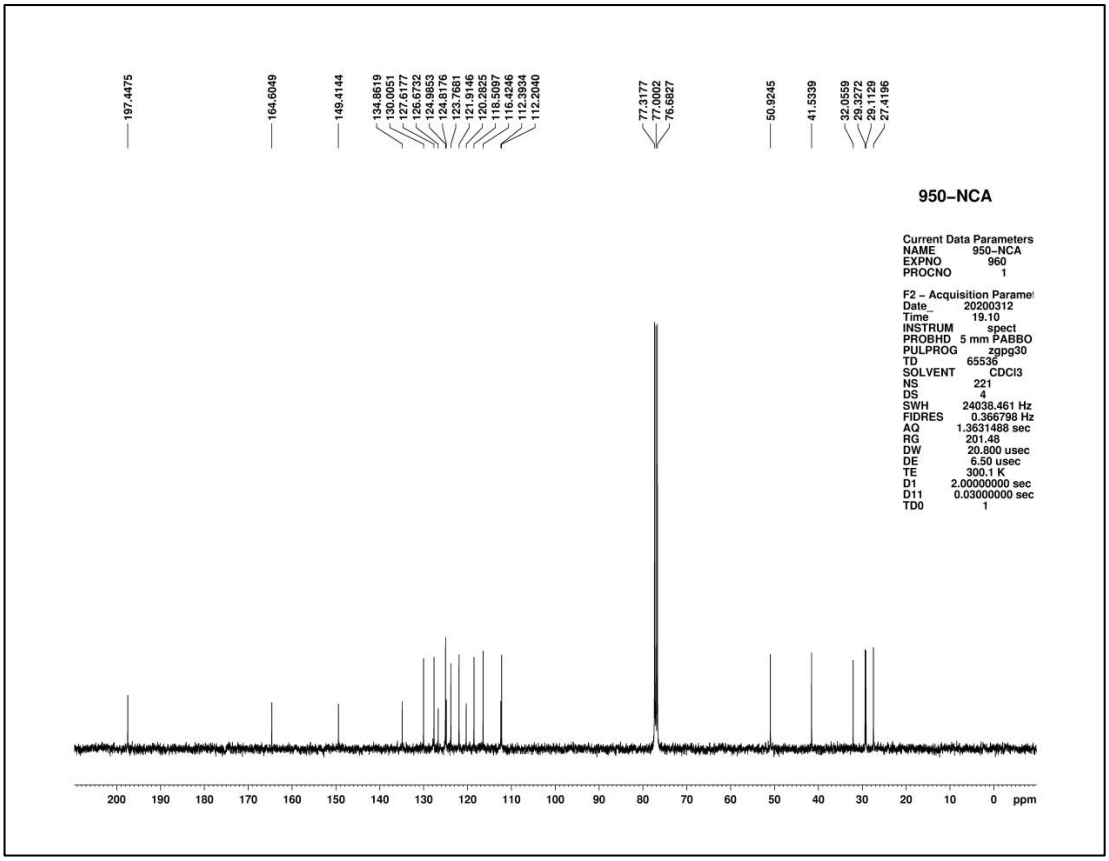


Figure S48: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4x)

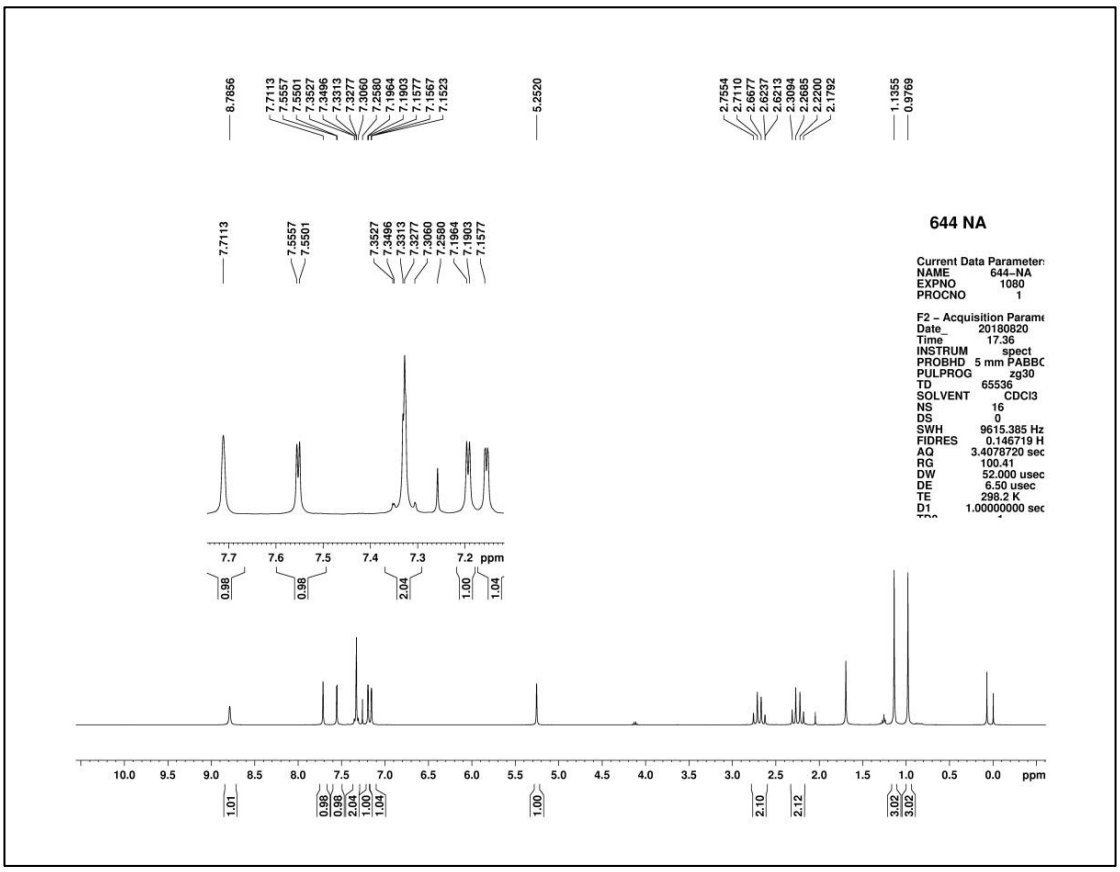


Figure S49: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4y)

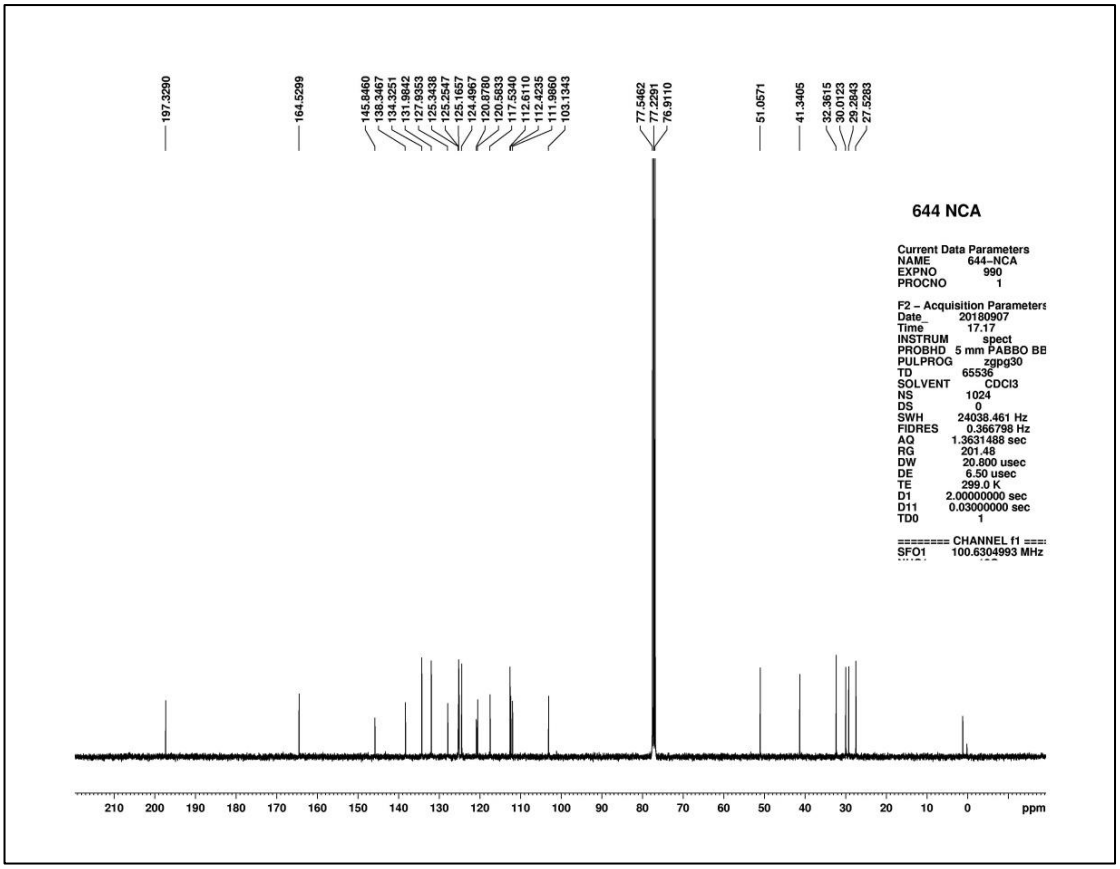


Figure S50: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4y)

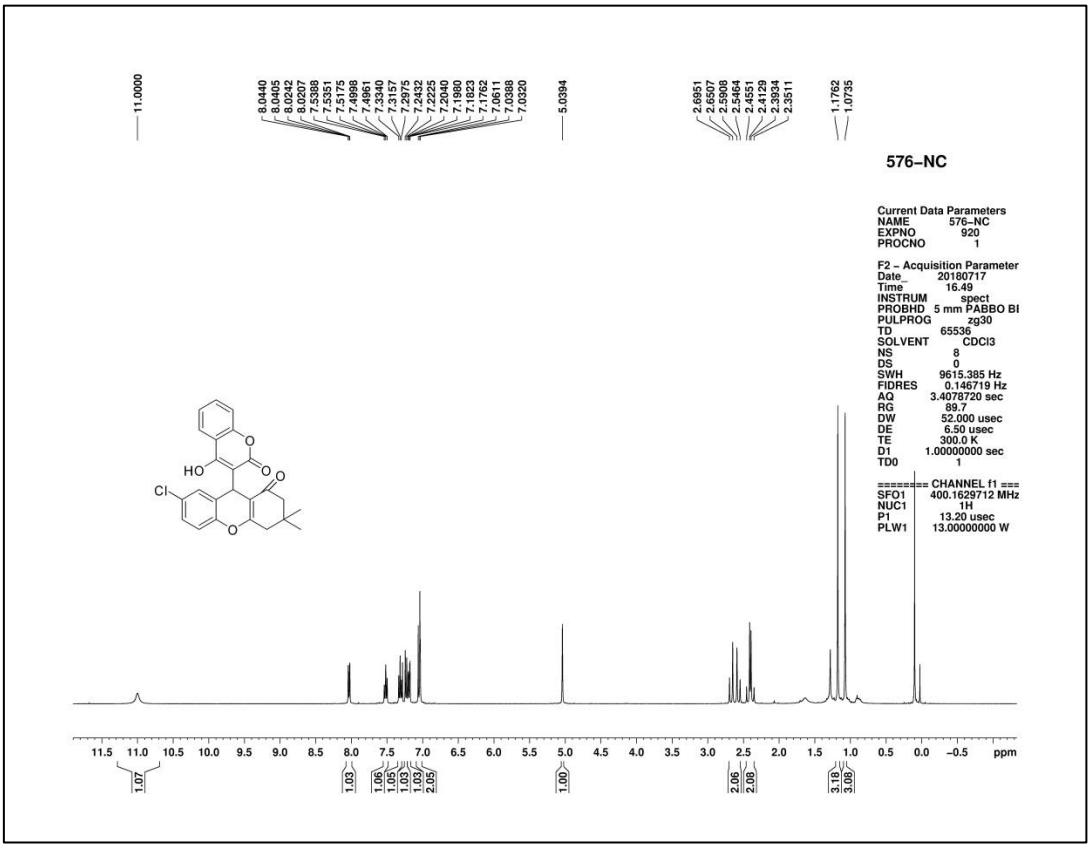


Figure S51: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4z)

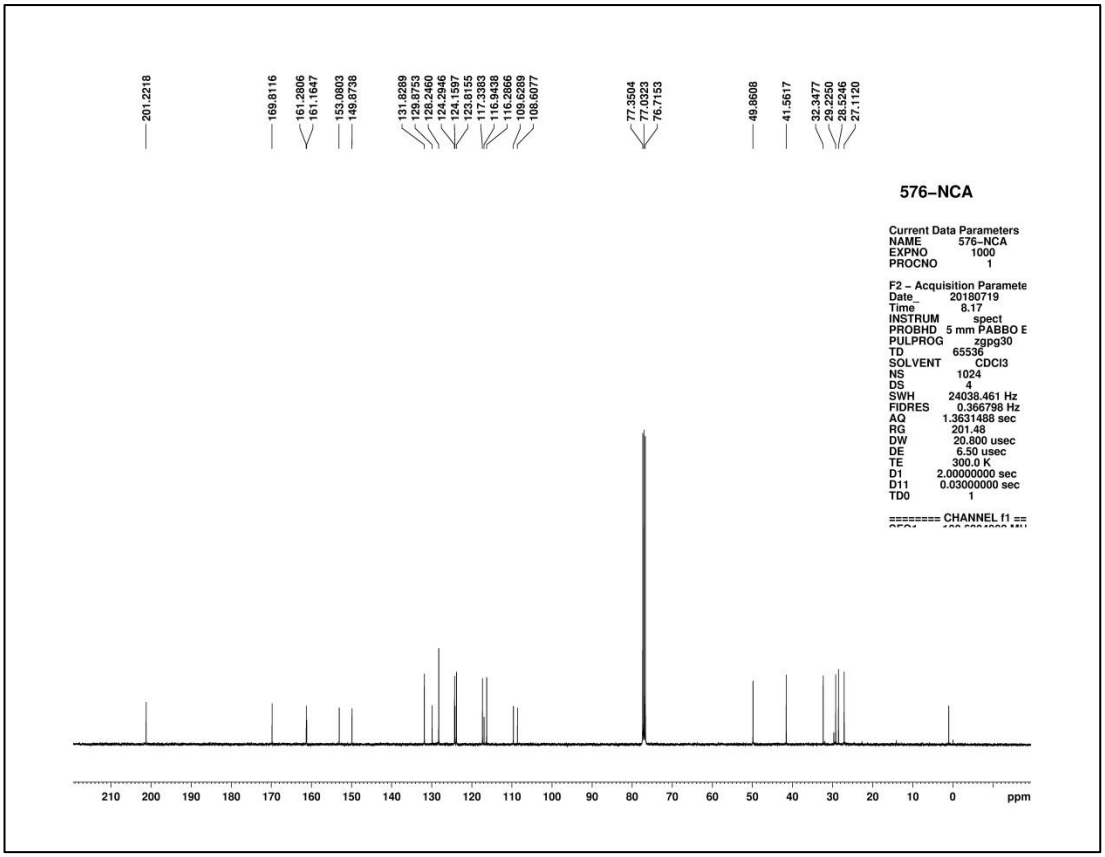


Figure S52: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4z)

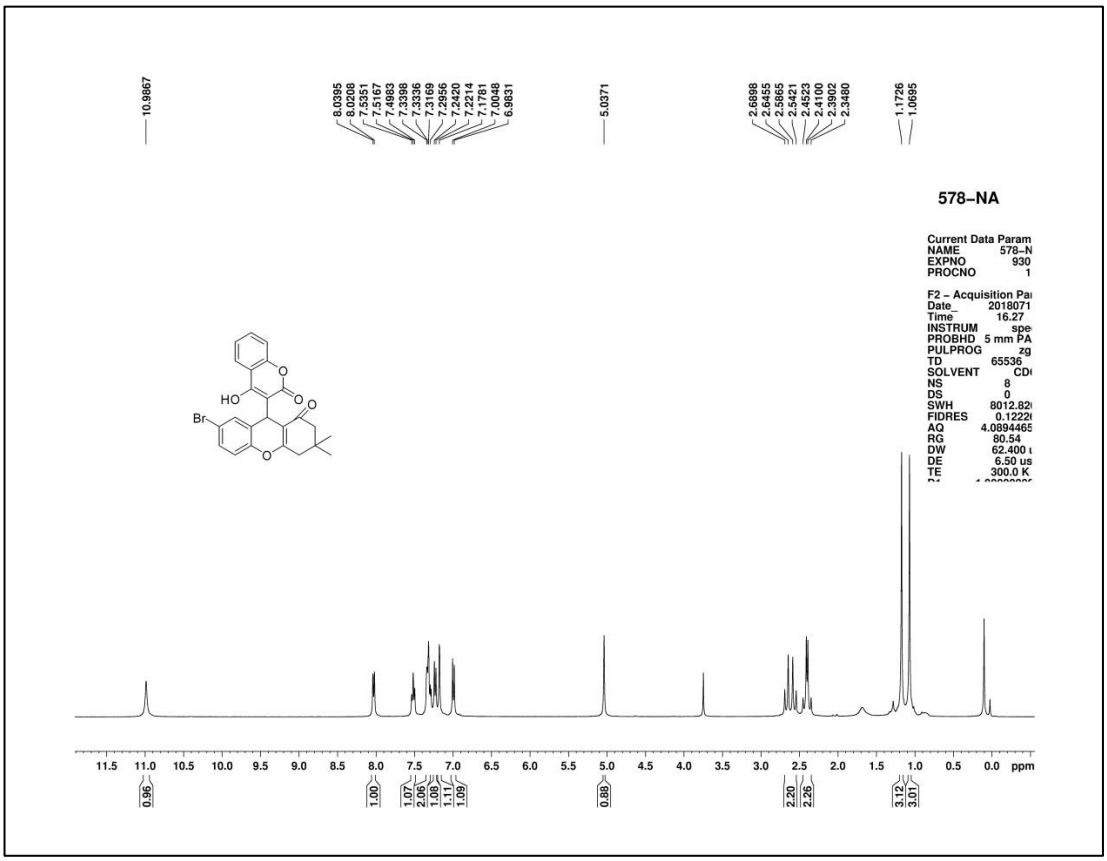


Figure S53: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4aa)

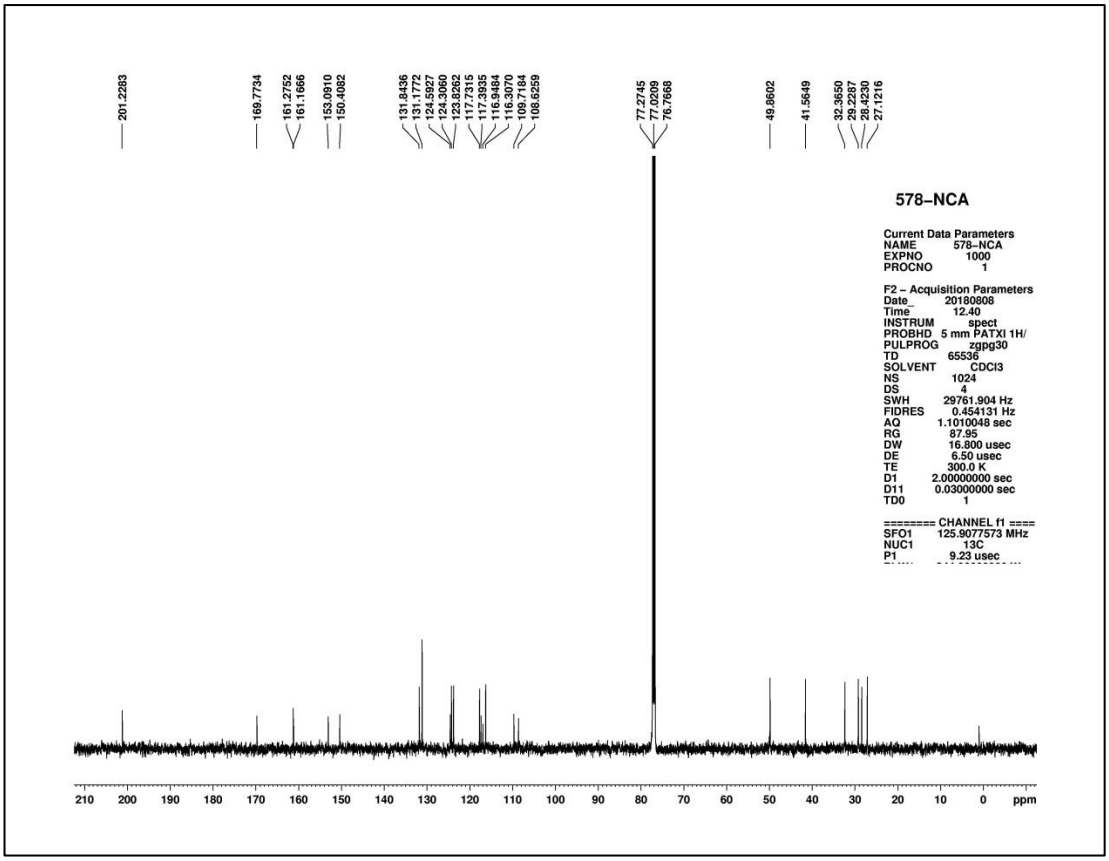


Figure S54: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4aa)

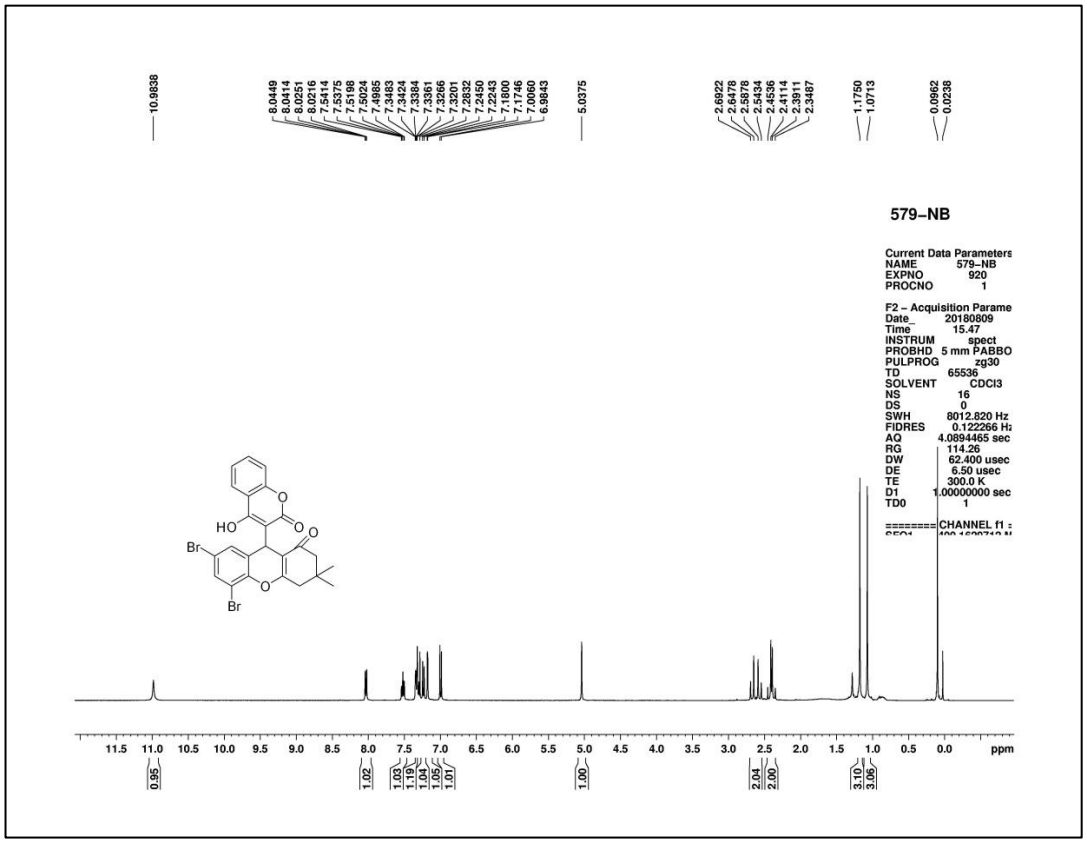


Figure S55: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ab)

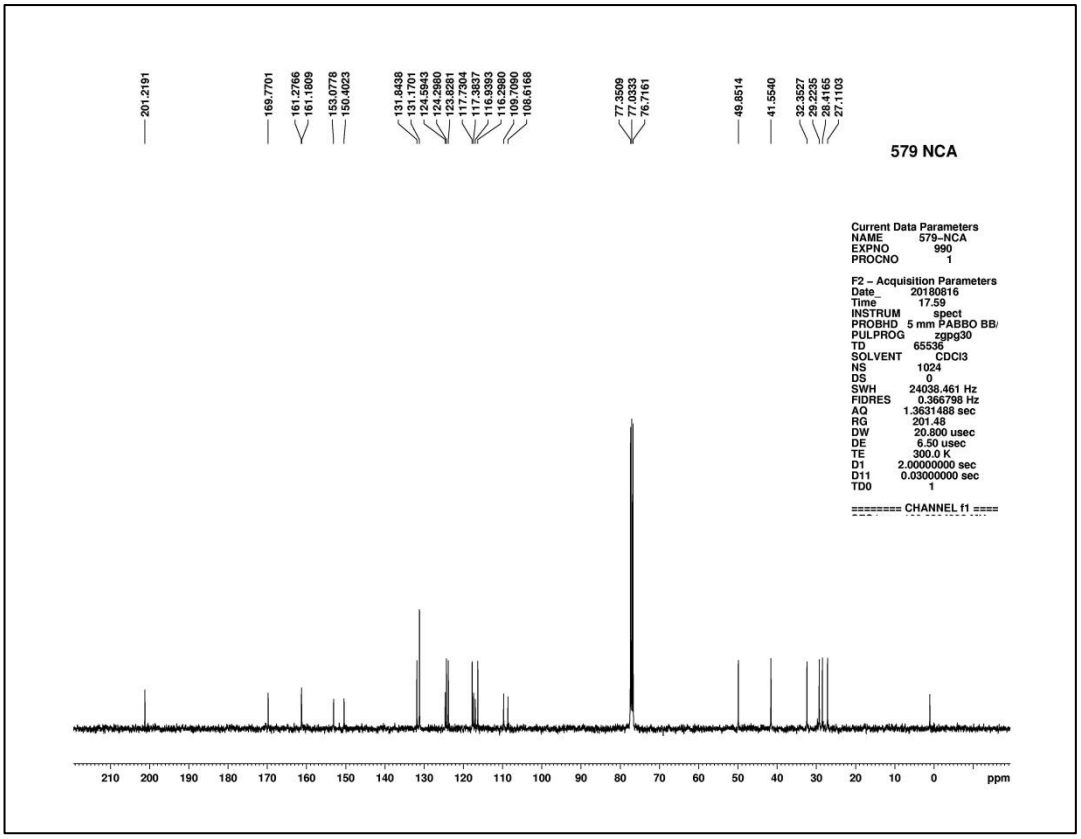


Figure S56: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ab)

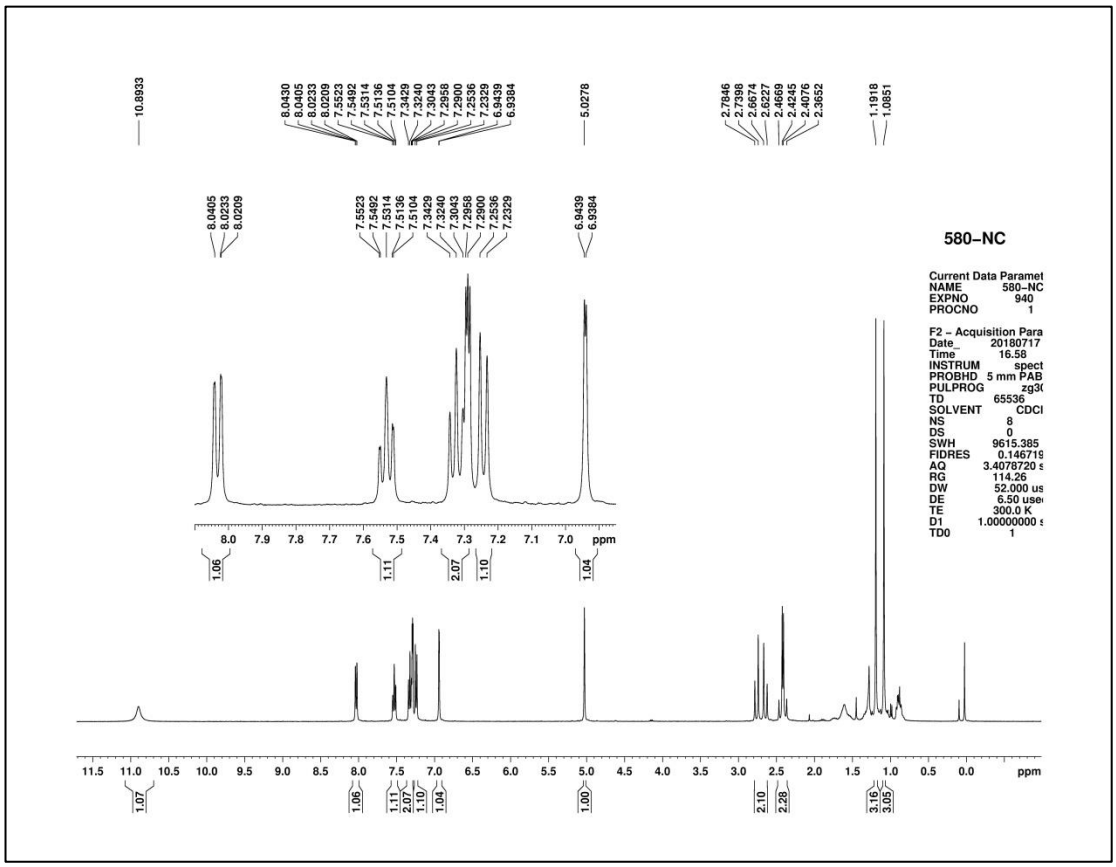


Figure S57: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ac)

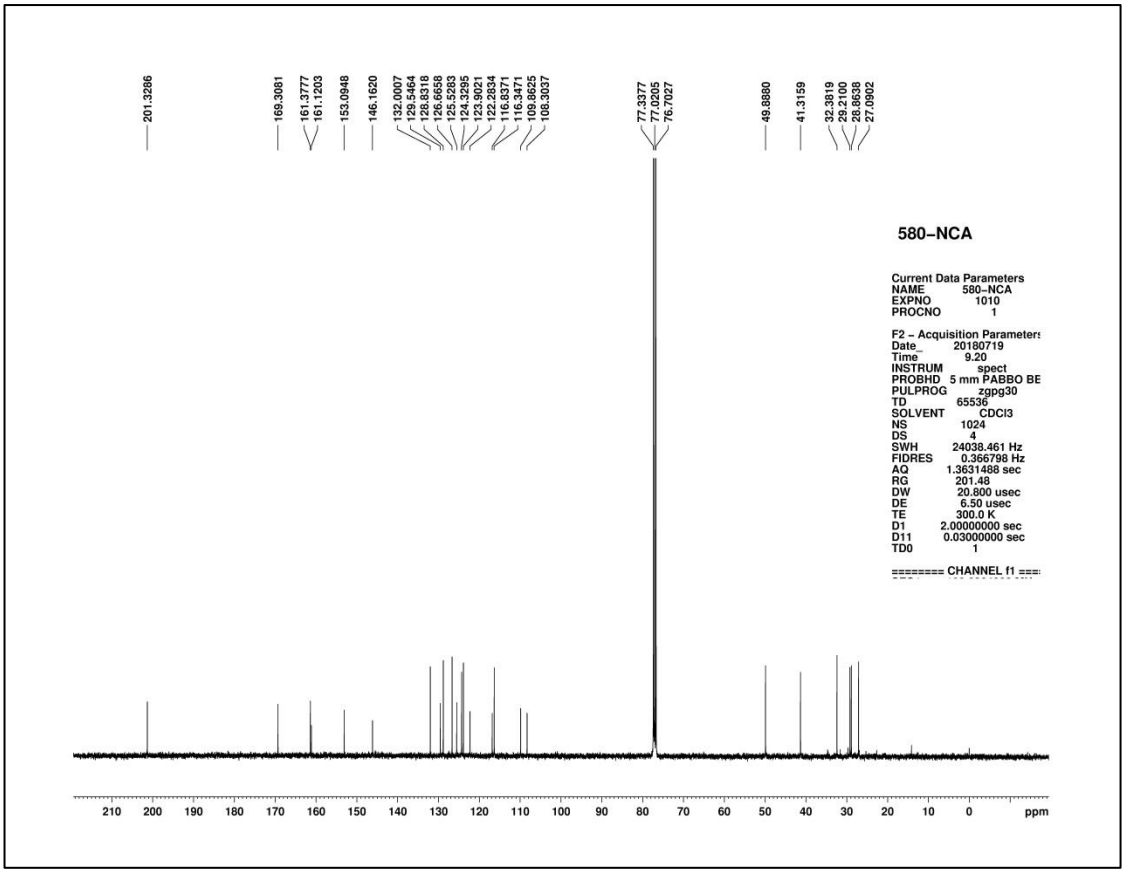


Figure S58: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ac)

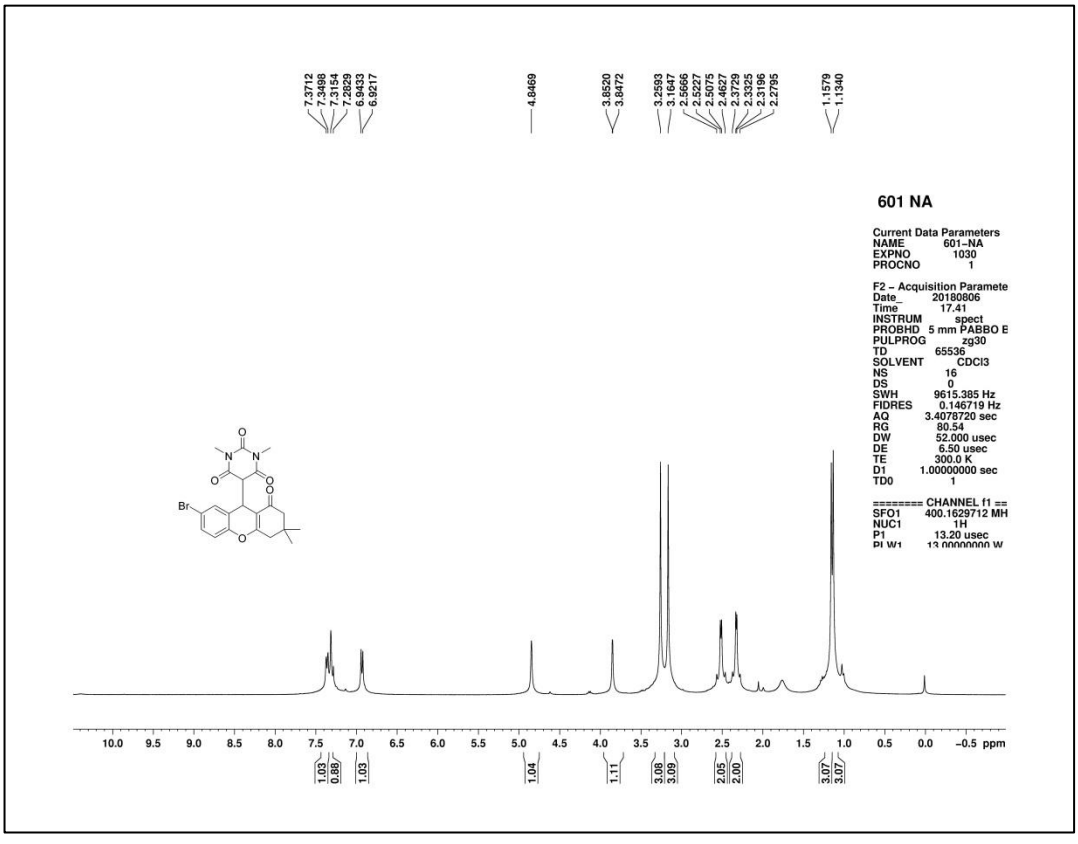


Figure S59: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ad)

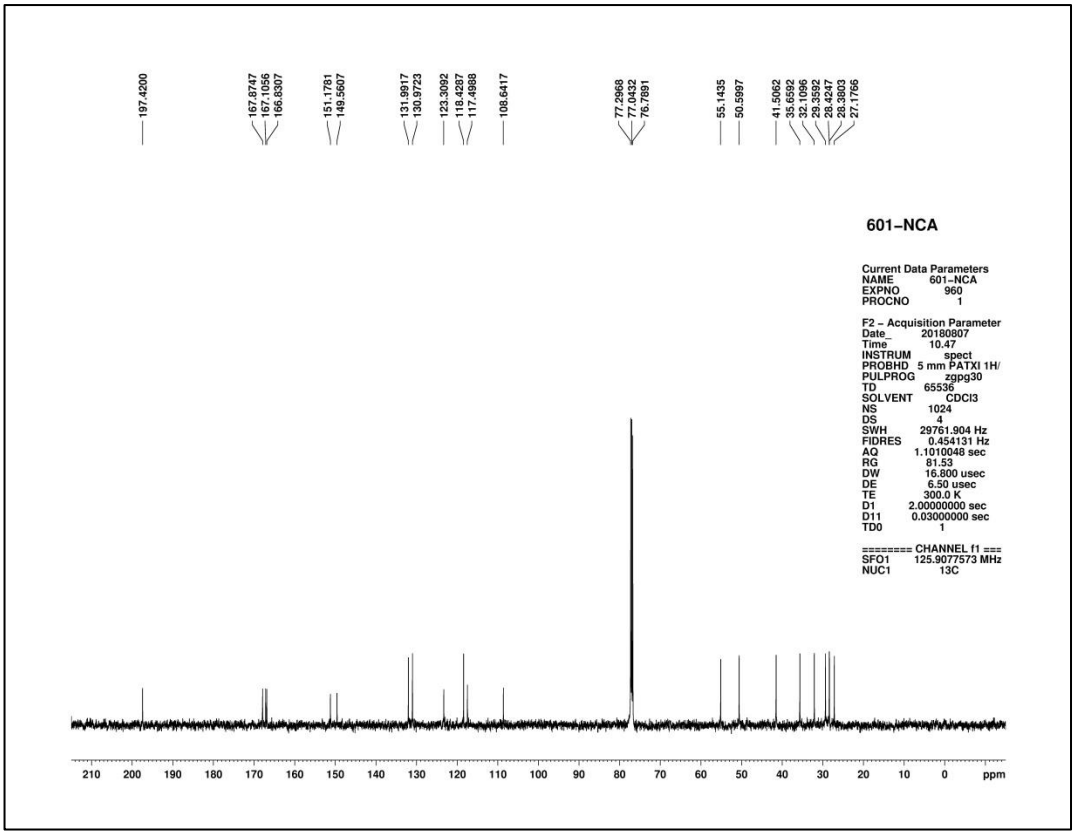


Figure S60: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ad)

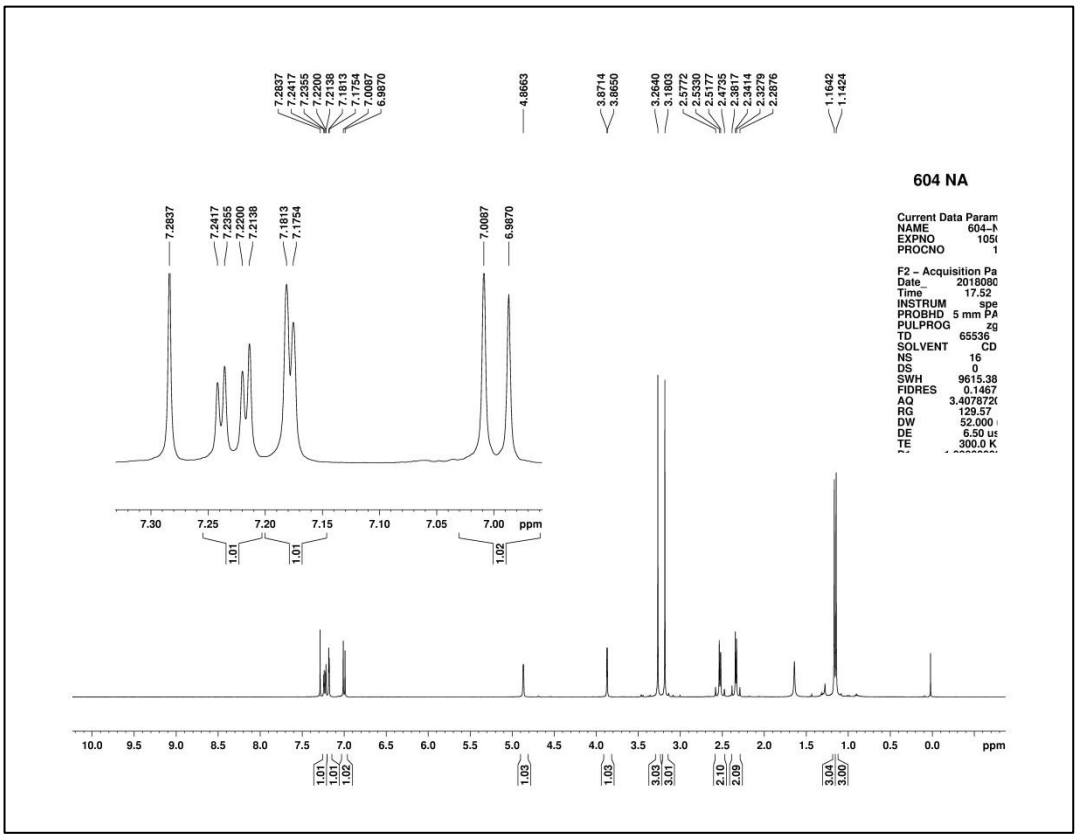


Figure S61: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ae)

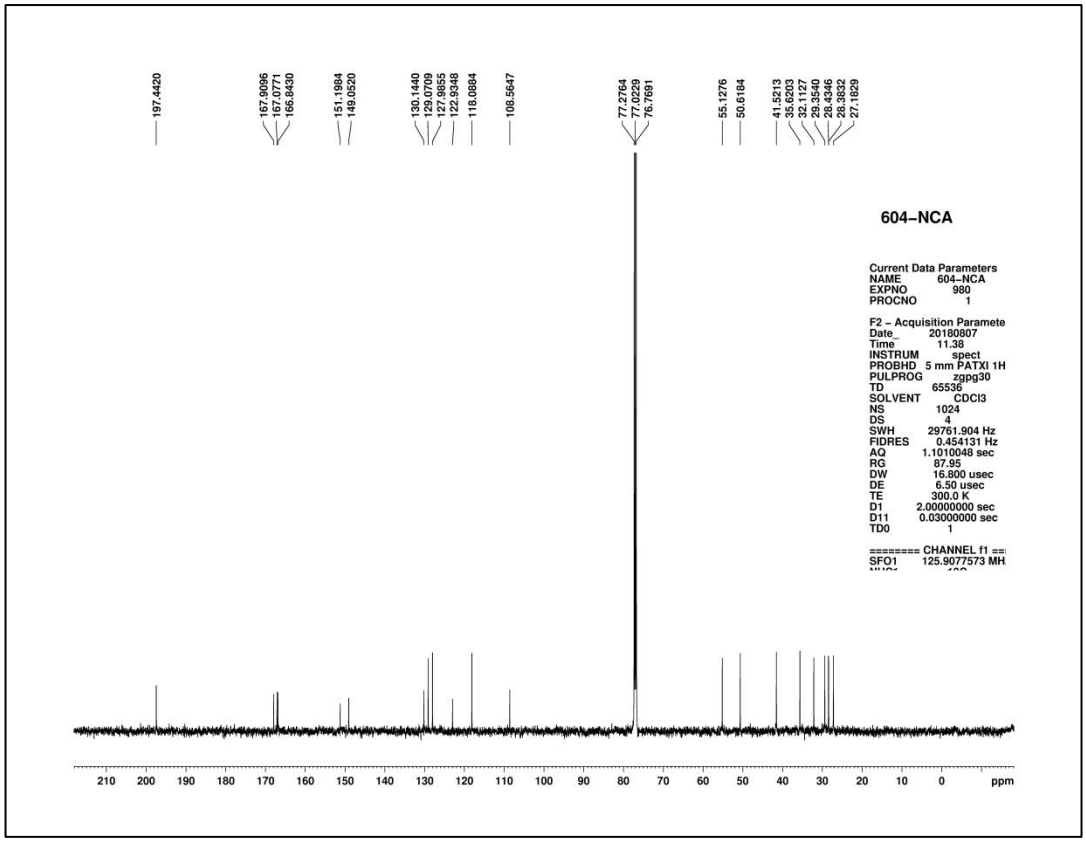


Figure S62: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ae)

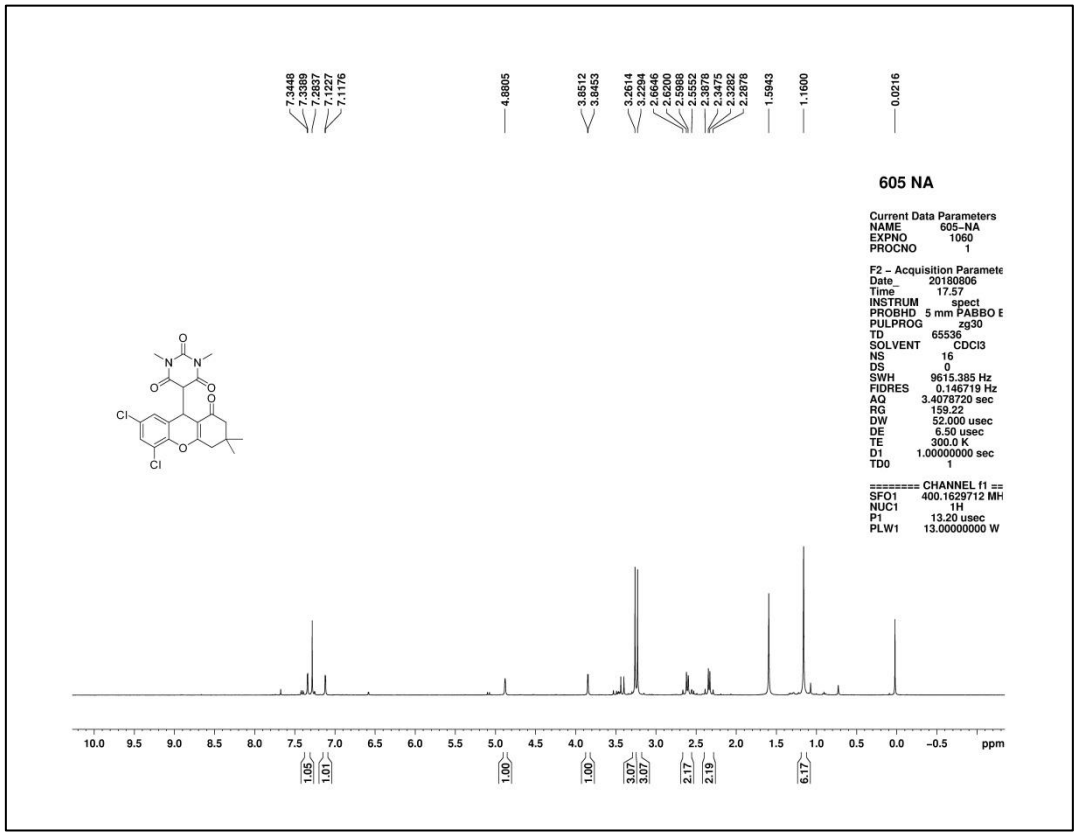


Figure S63: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4af)

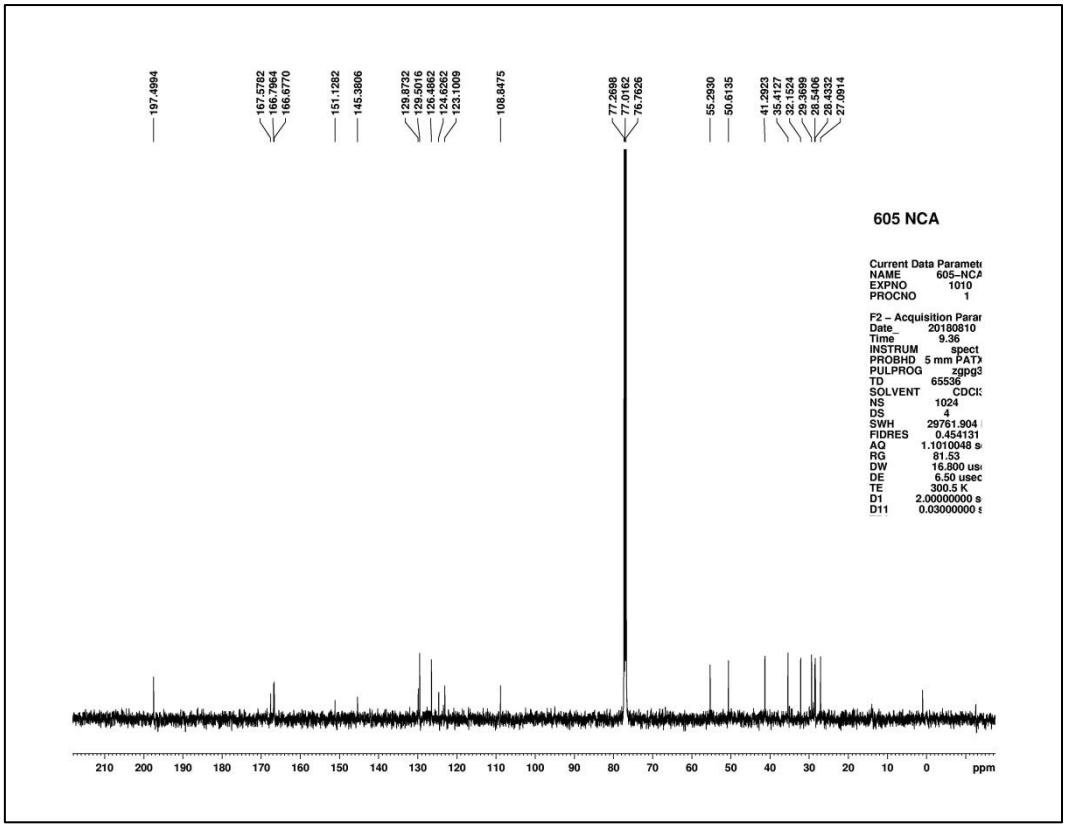


Figure S64: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4af)

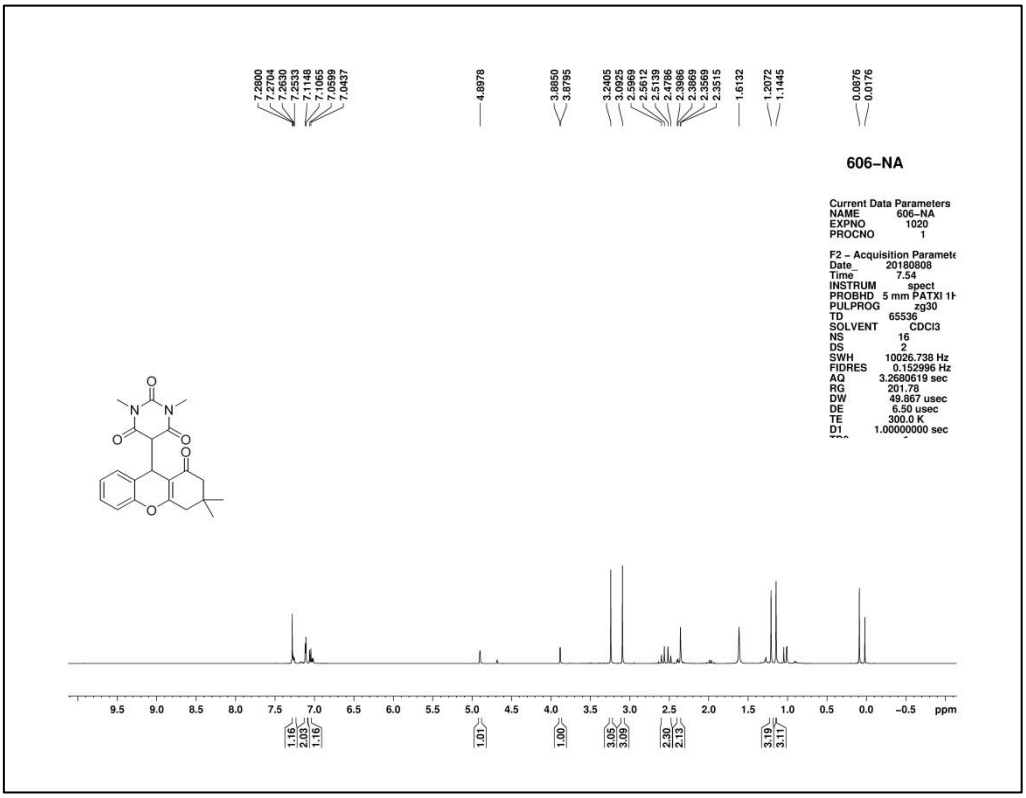


Figure S65: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ag)

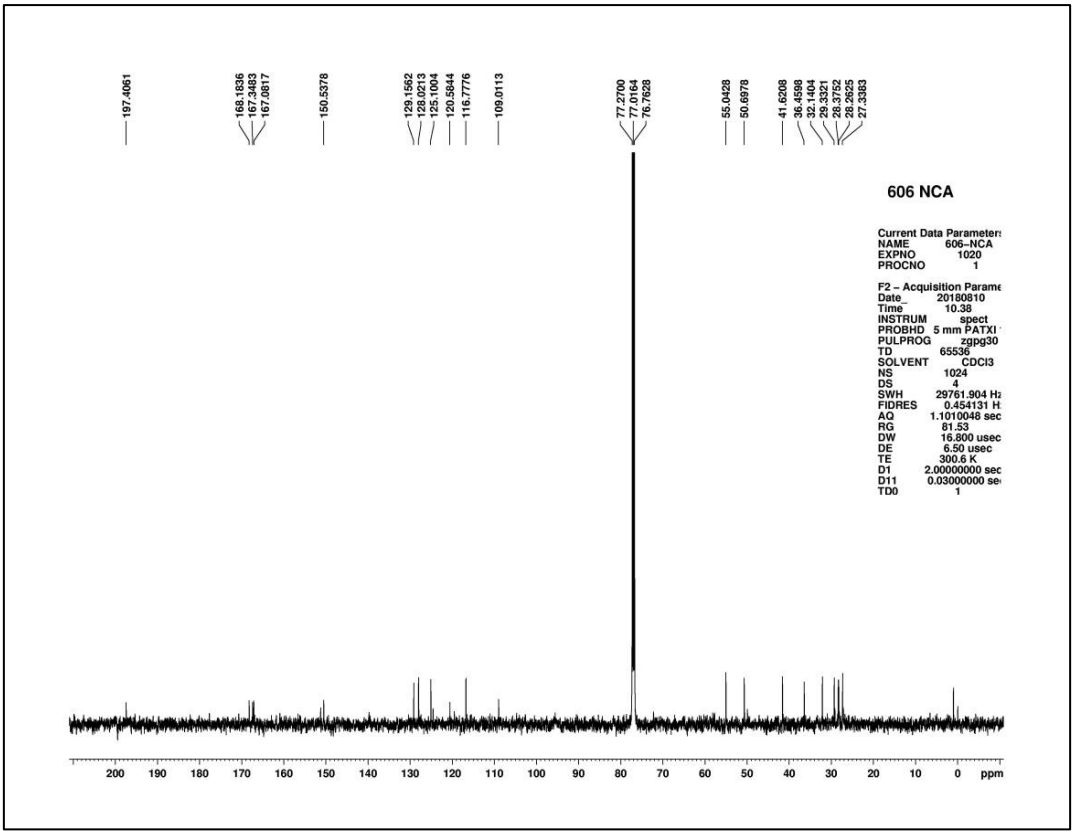


Figure S66: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ag)

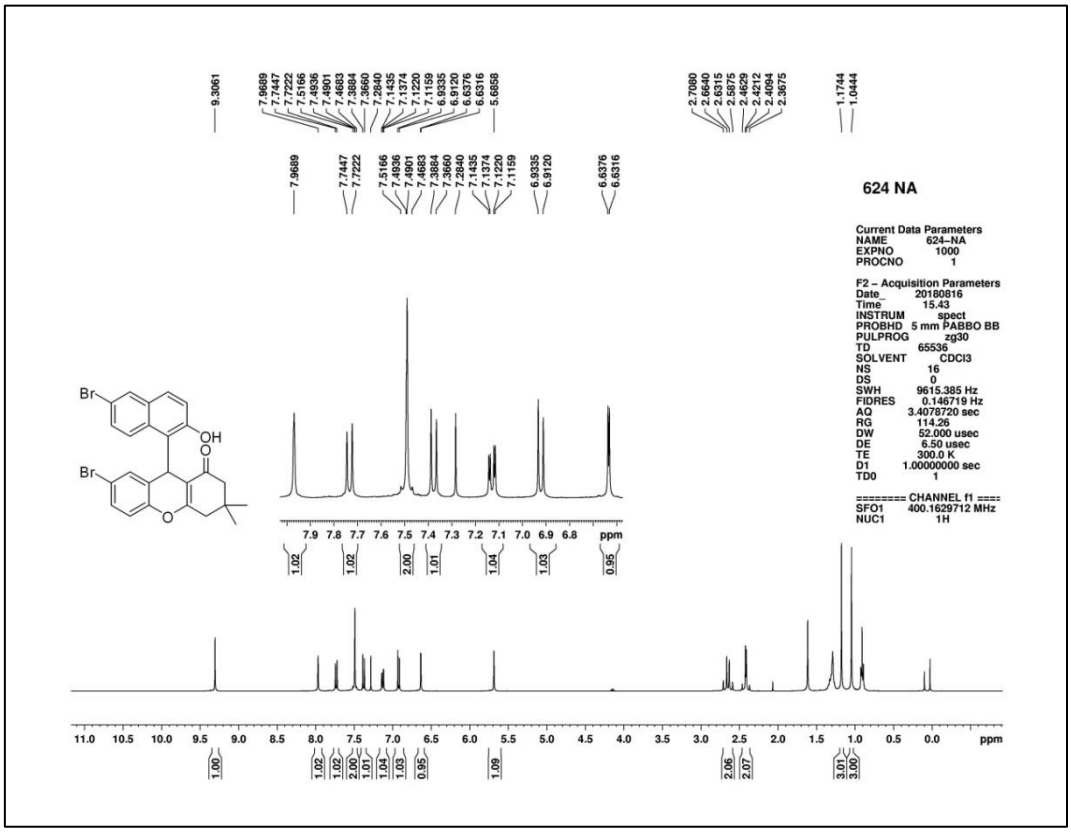


Figure S67:^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ah)

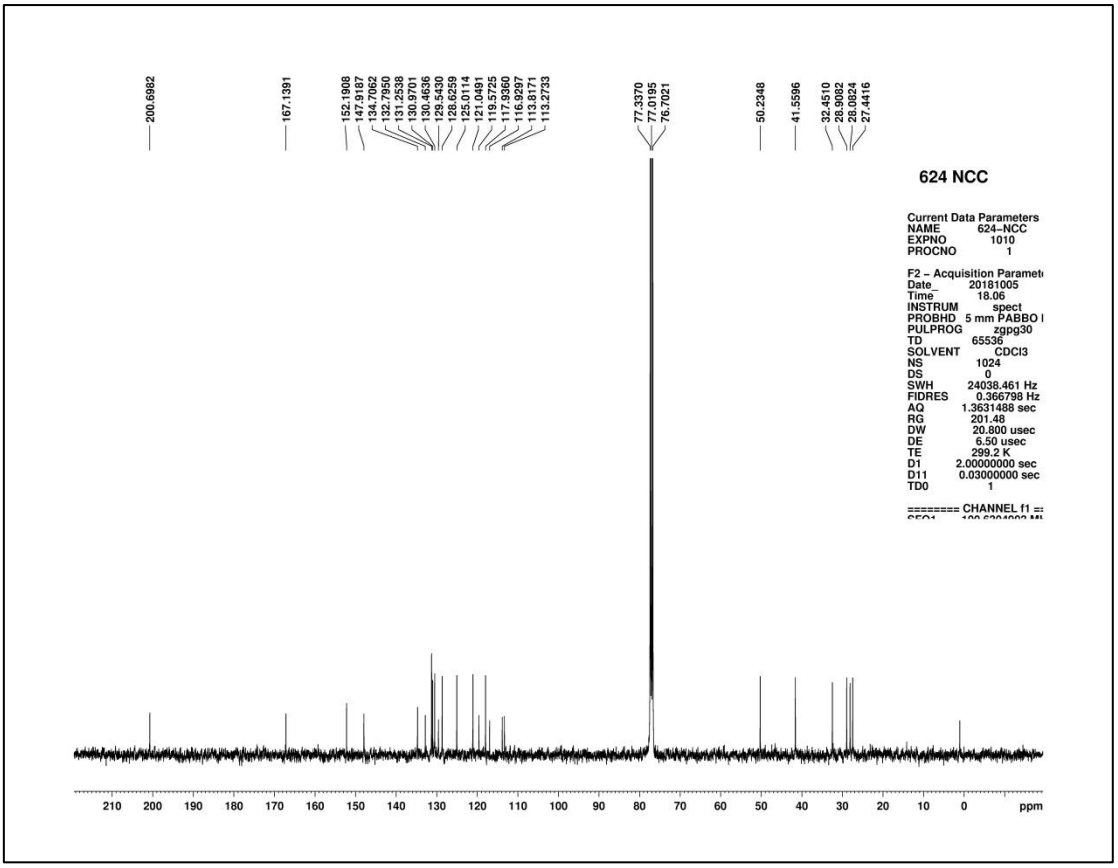
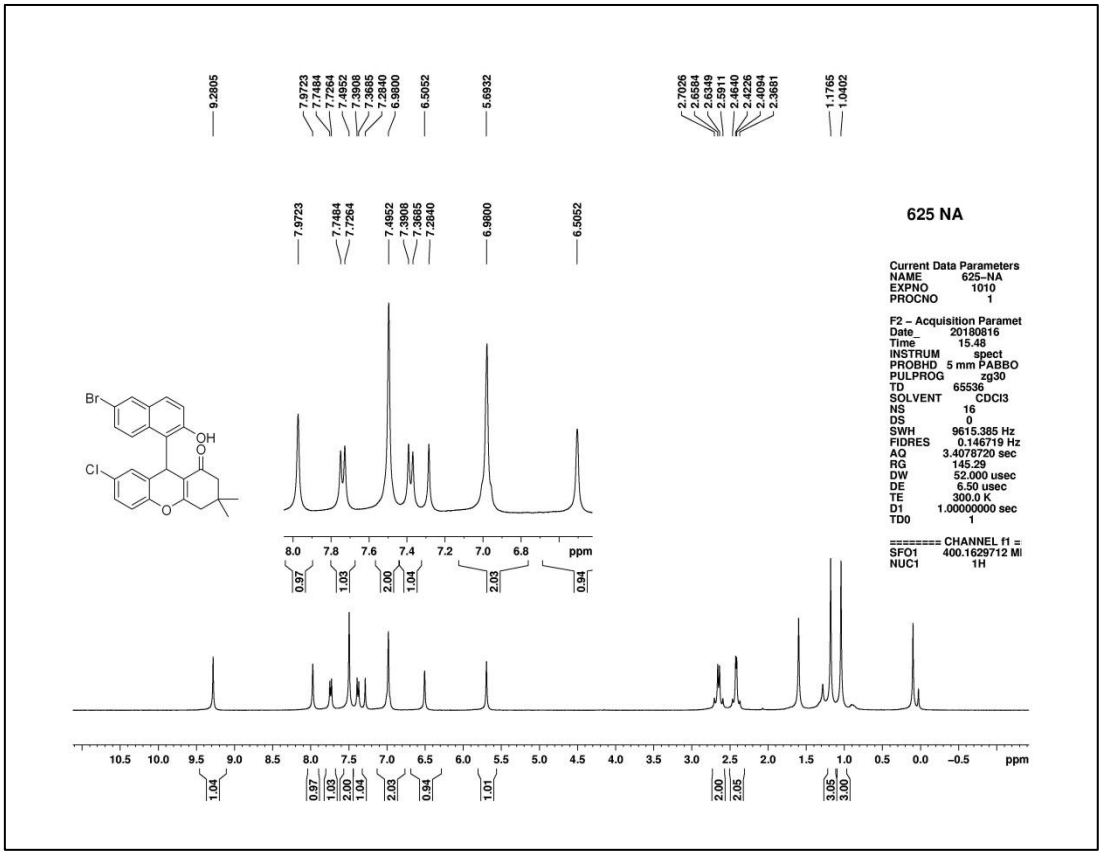


Figure S68: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ah)



Figur S69:^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ai)

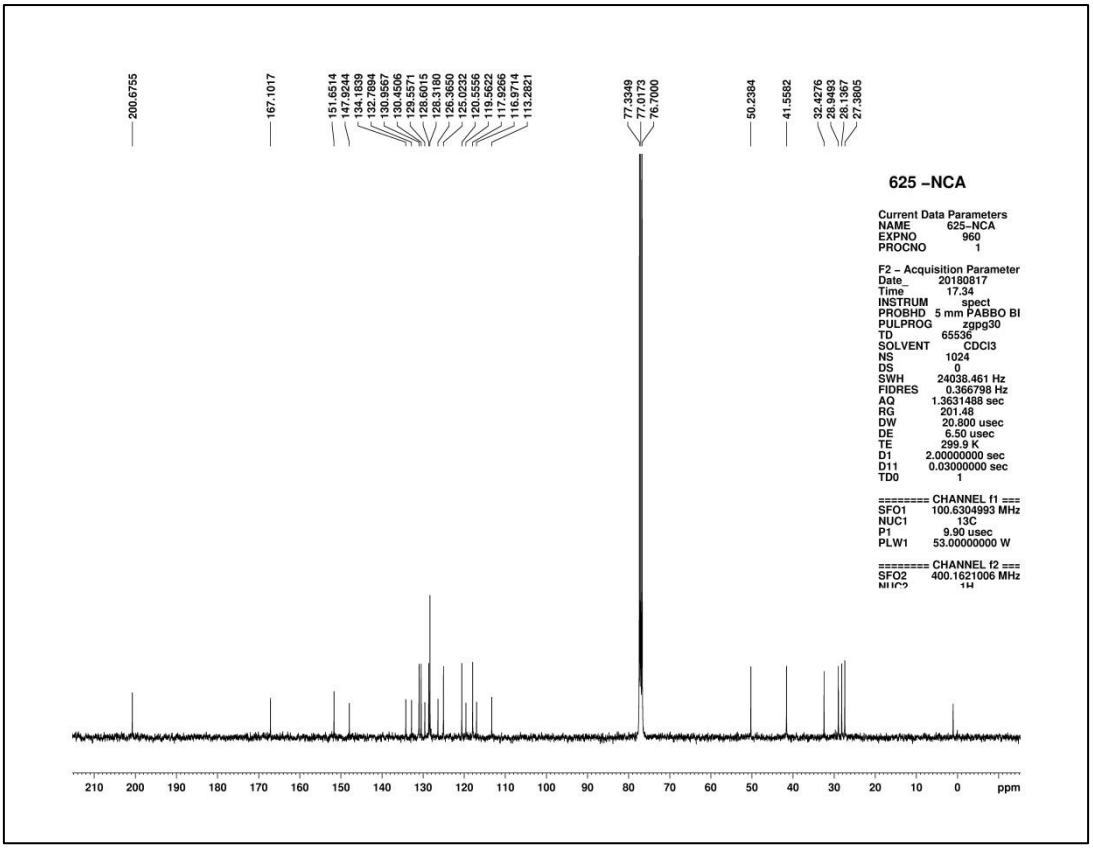


Figure S70: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ai)

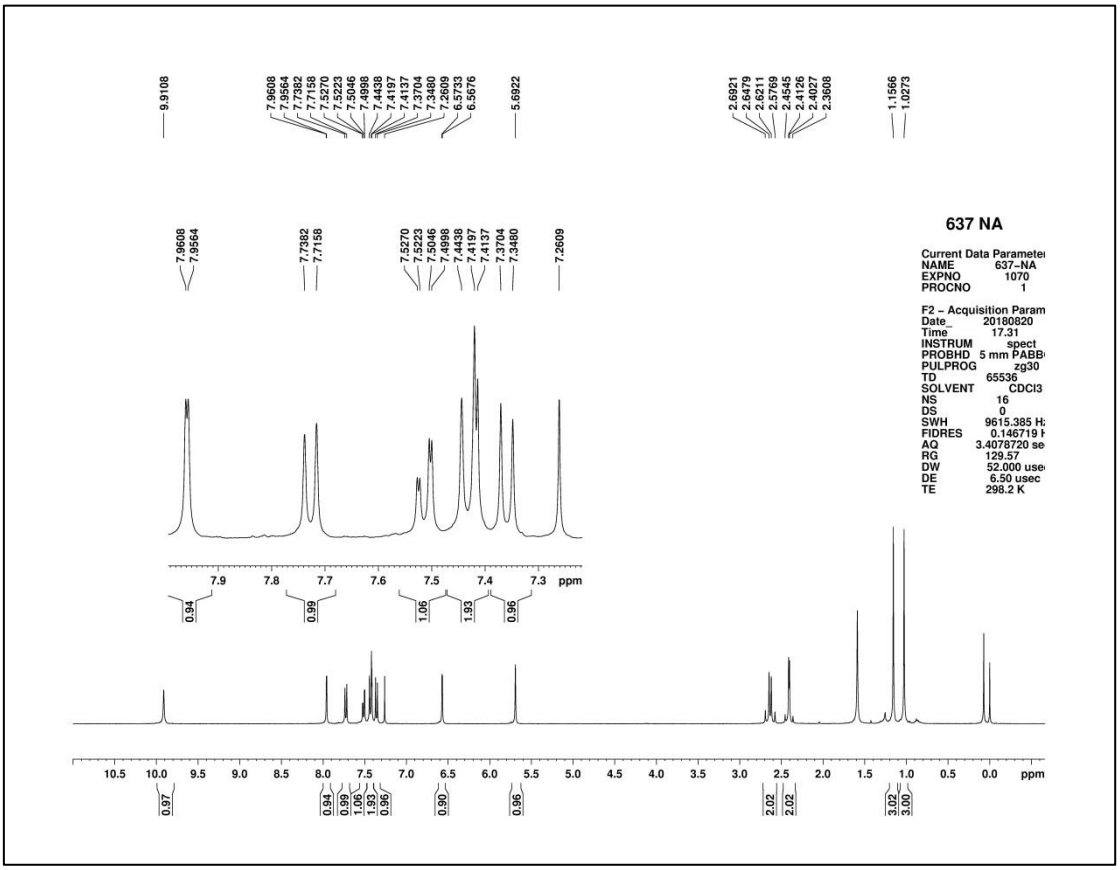


Figure S71: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4aj)

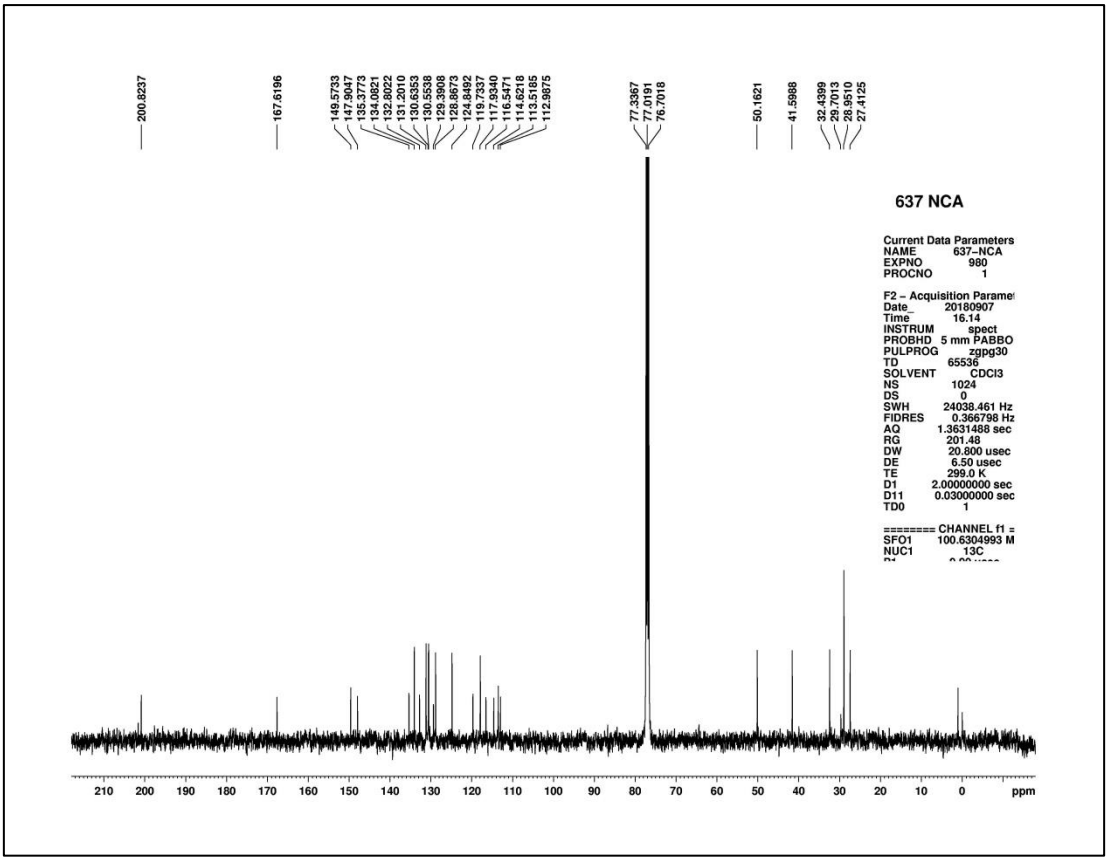


Figure S72: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4aj)

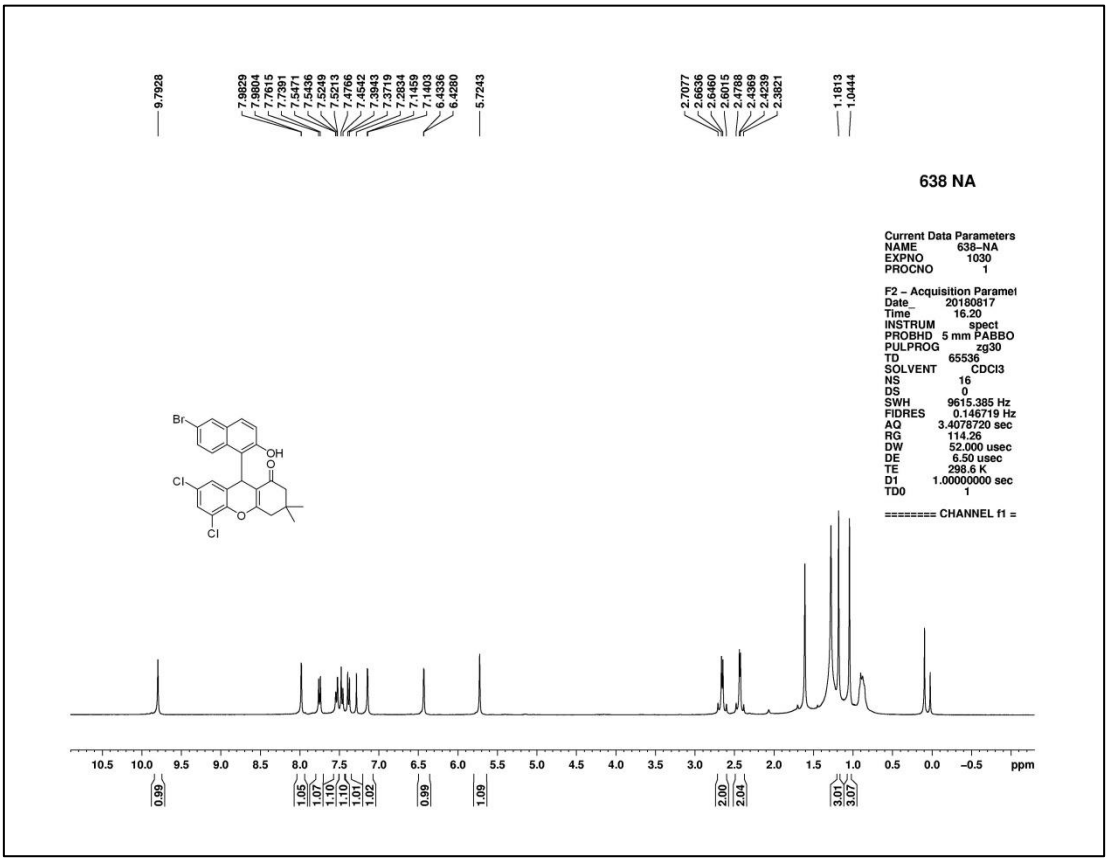


Figure S73: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ak)

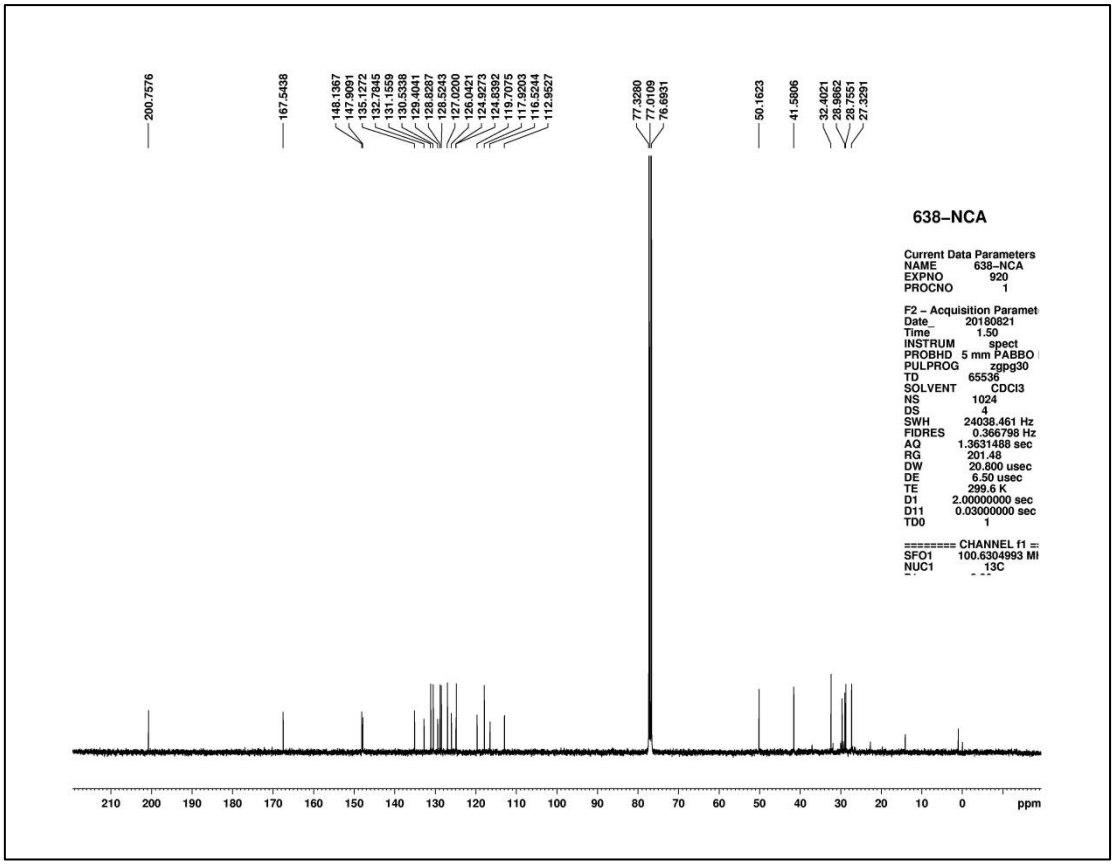


Figure S74: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ak)

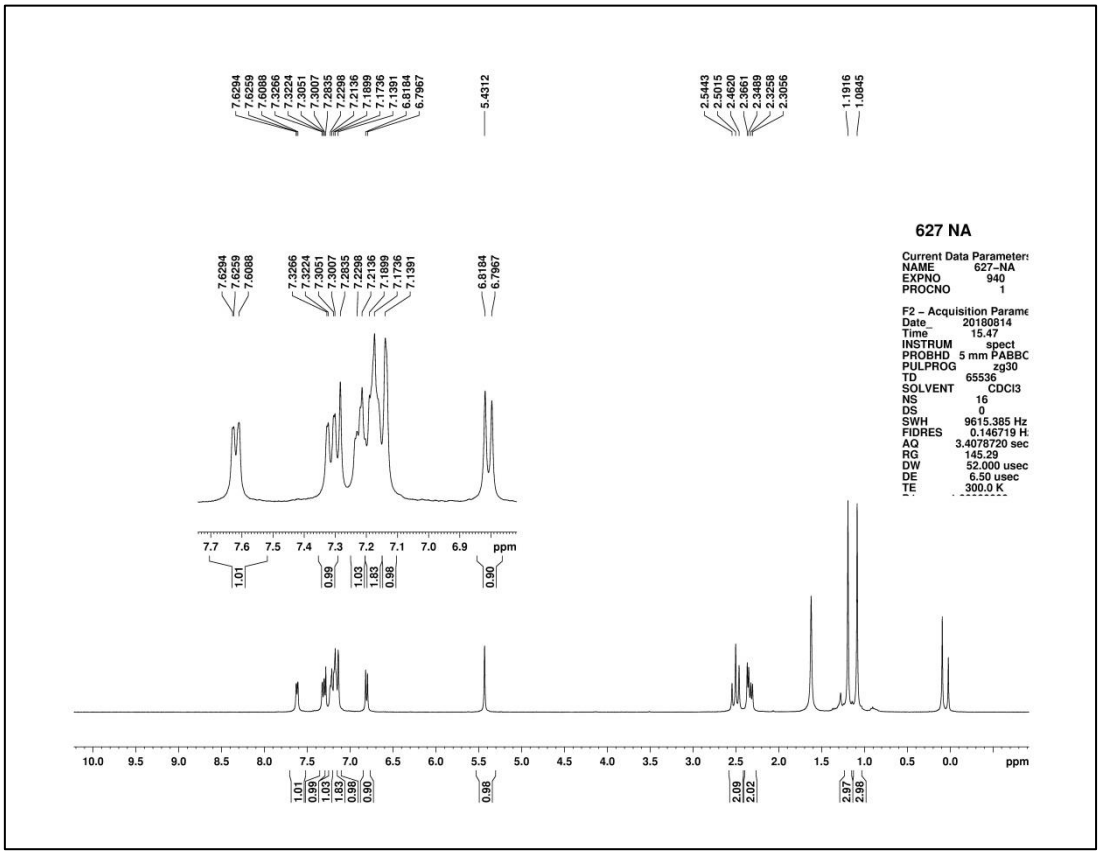


Figure S75: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4al)

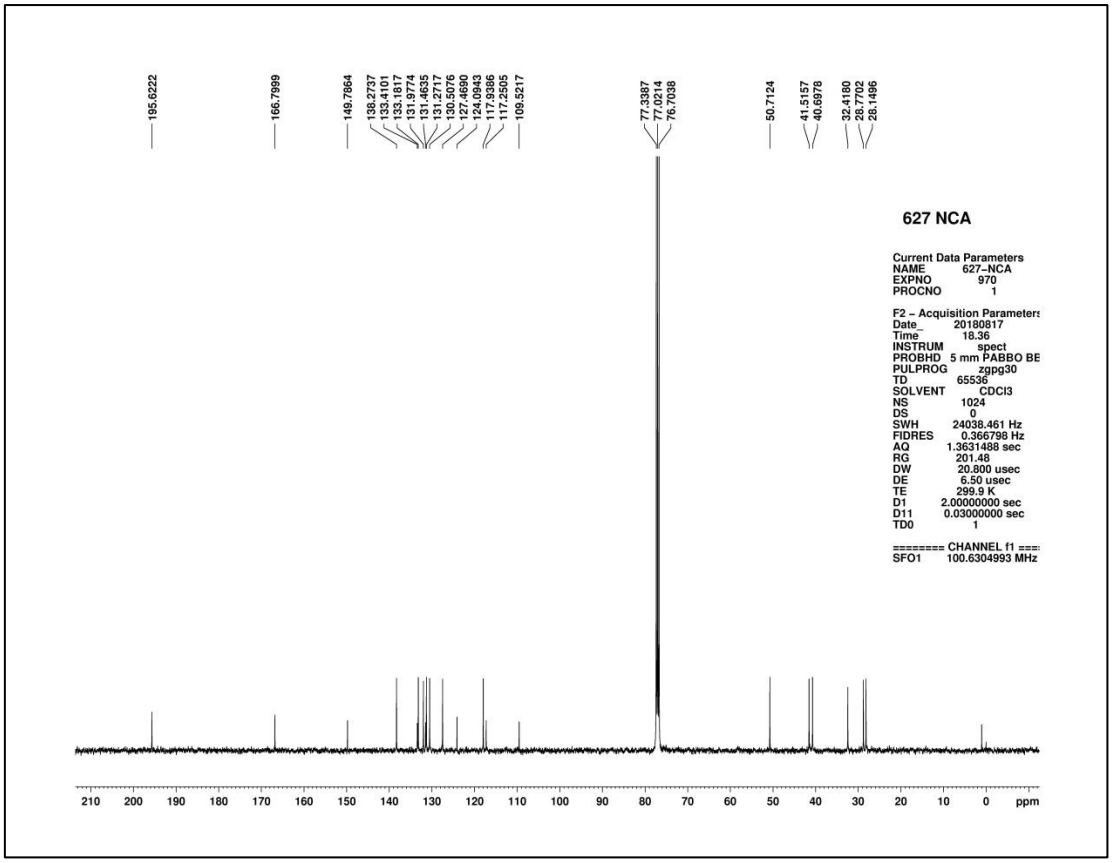


Figure S76: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4al)

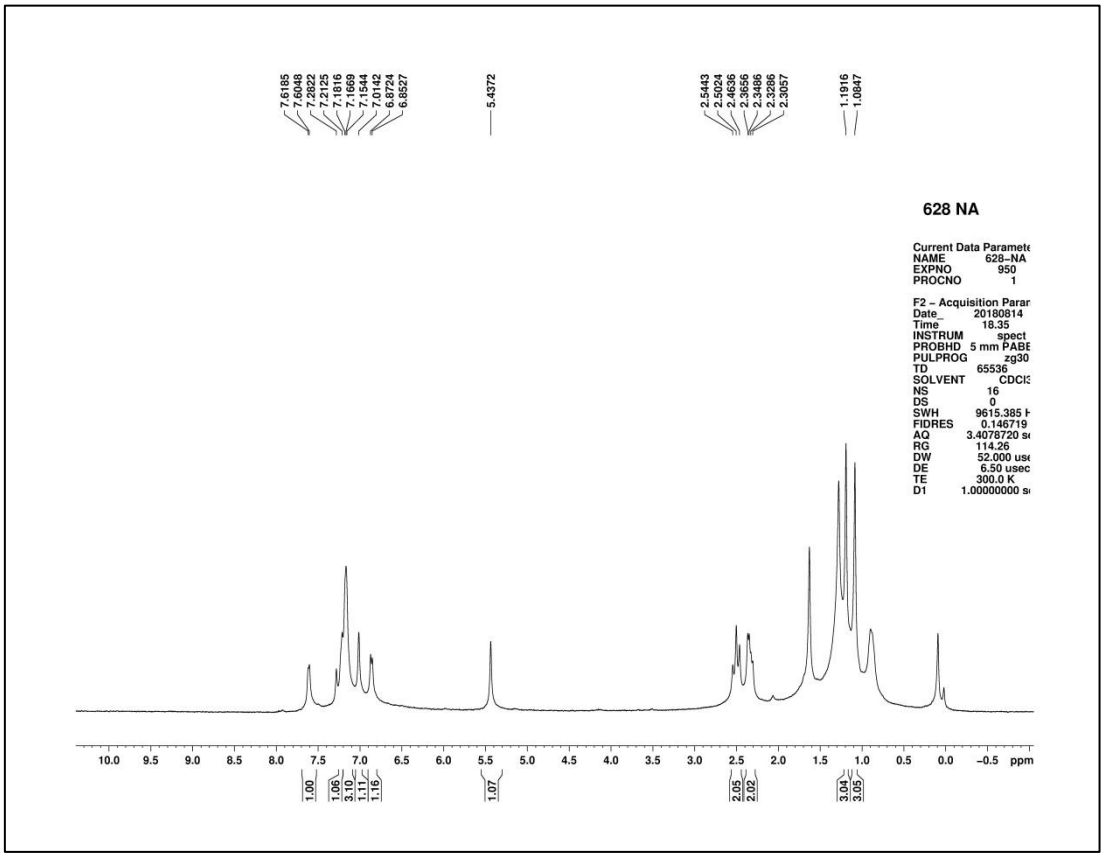


Figure S77: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4am)

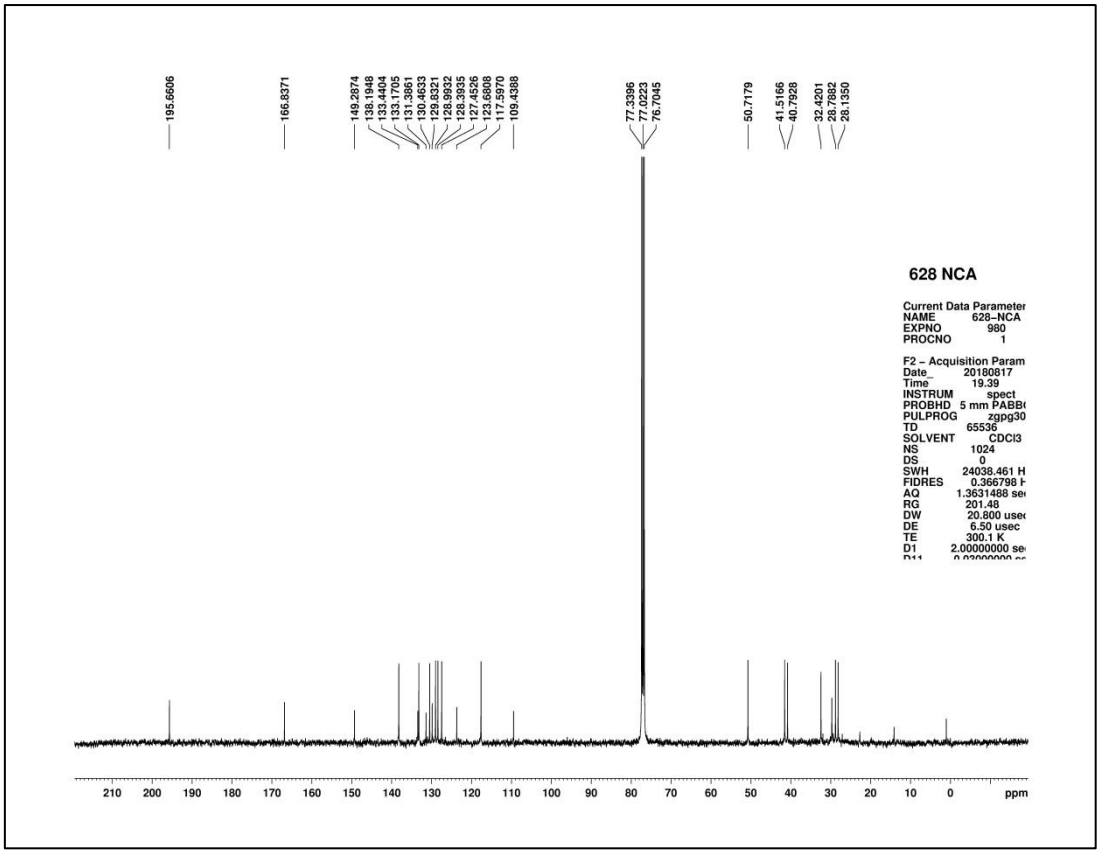


Figure S78: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4am)

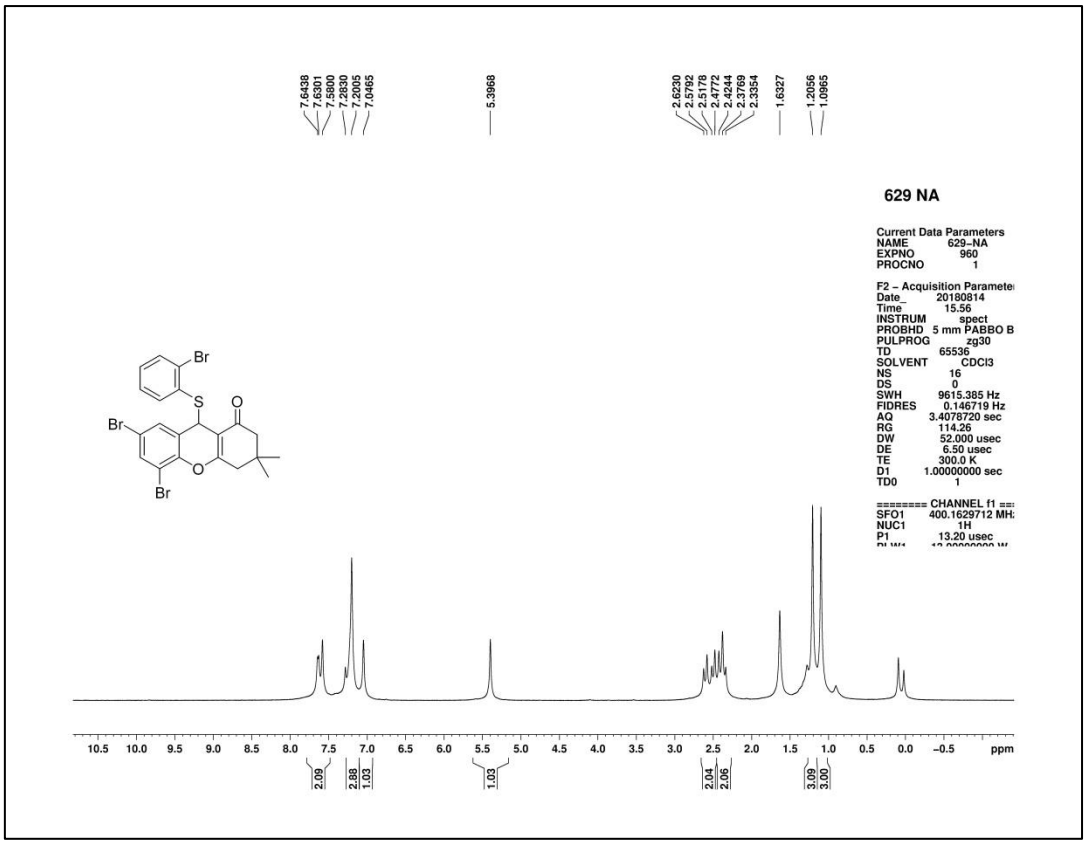


Figure S79: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4an)

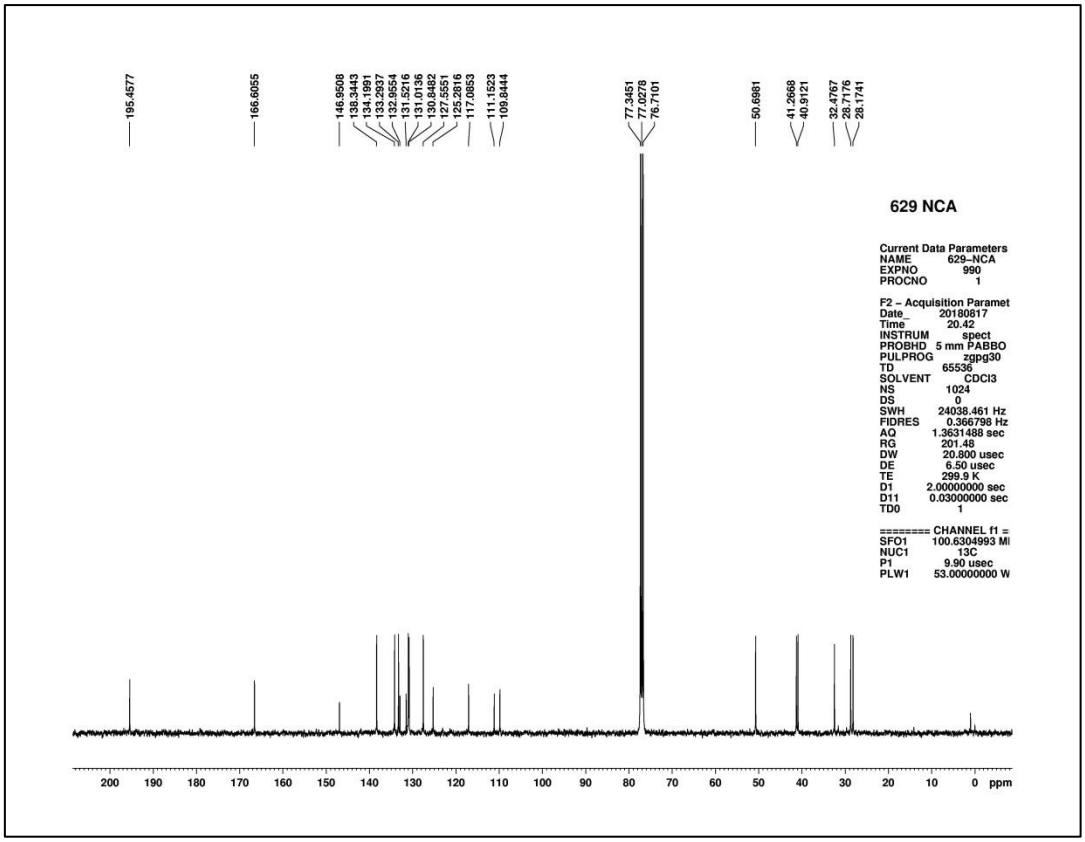


Figure S80: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4an)

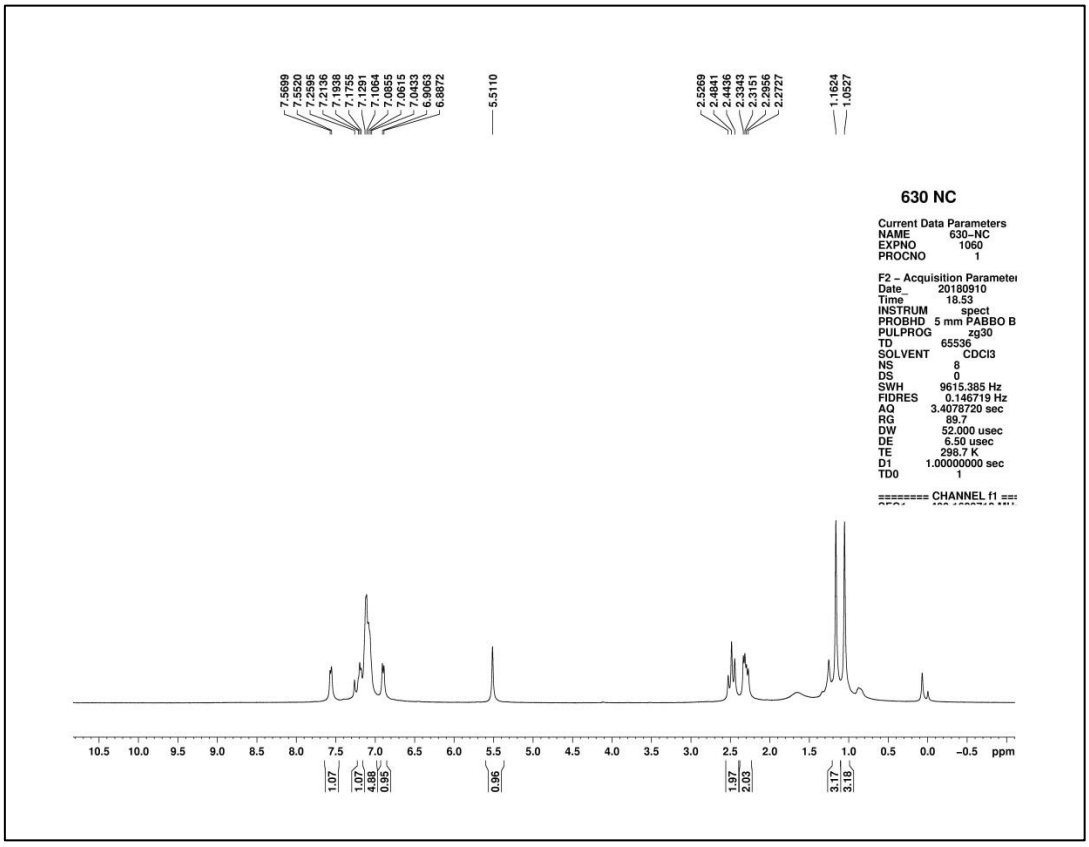


Figure S81: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ao)

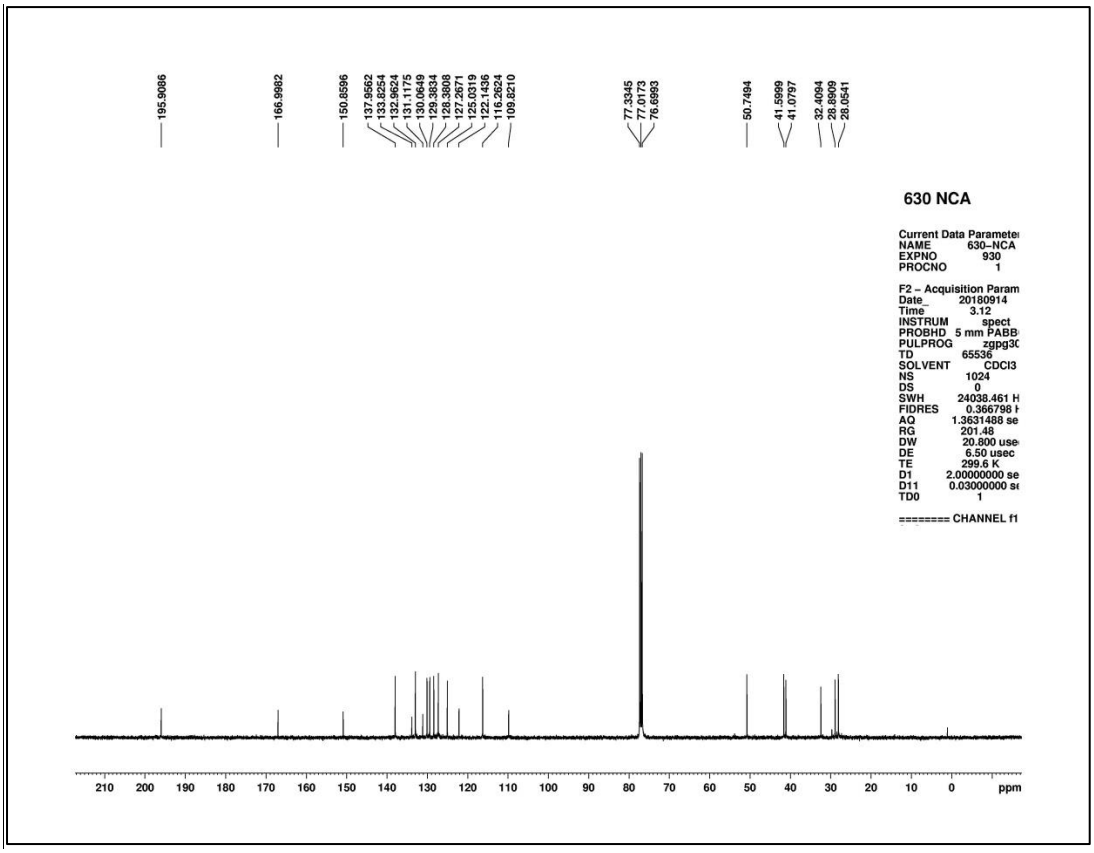


Figure S82: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ao)

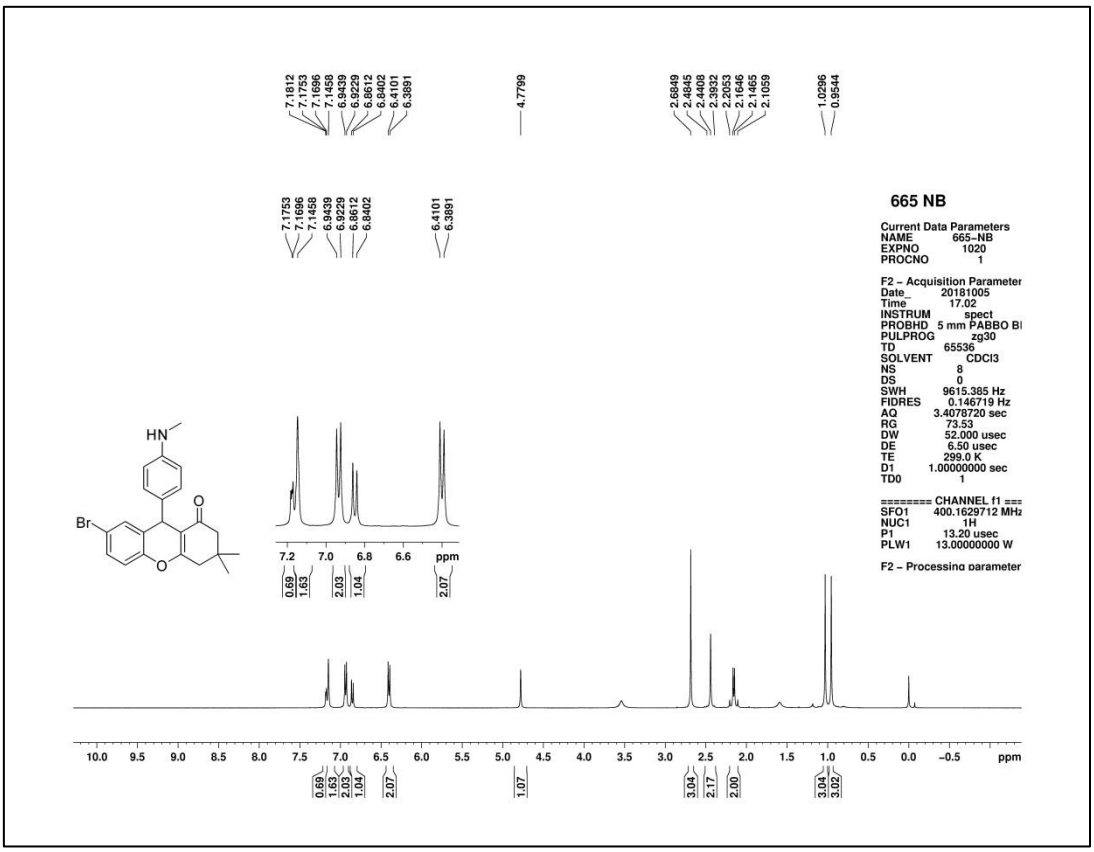


Figure S83: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ap)

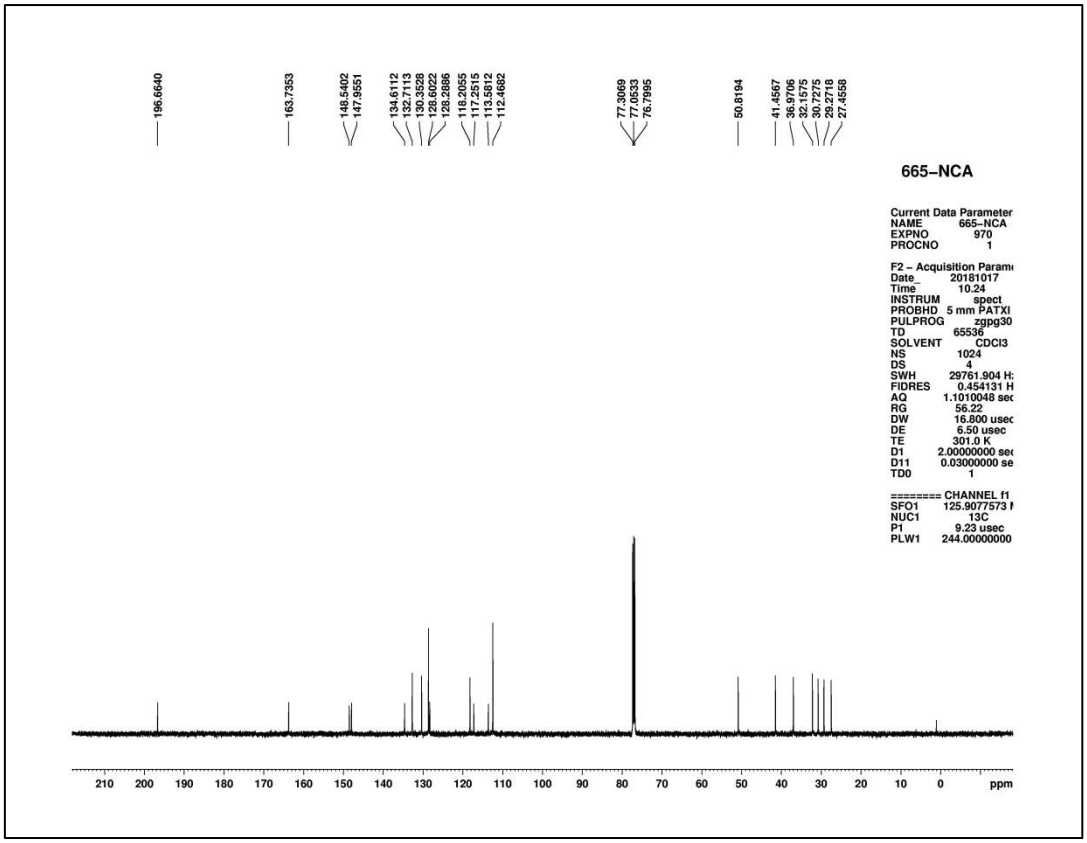


Figure S84: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ap)

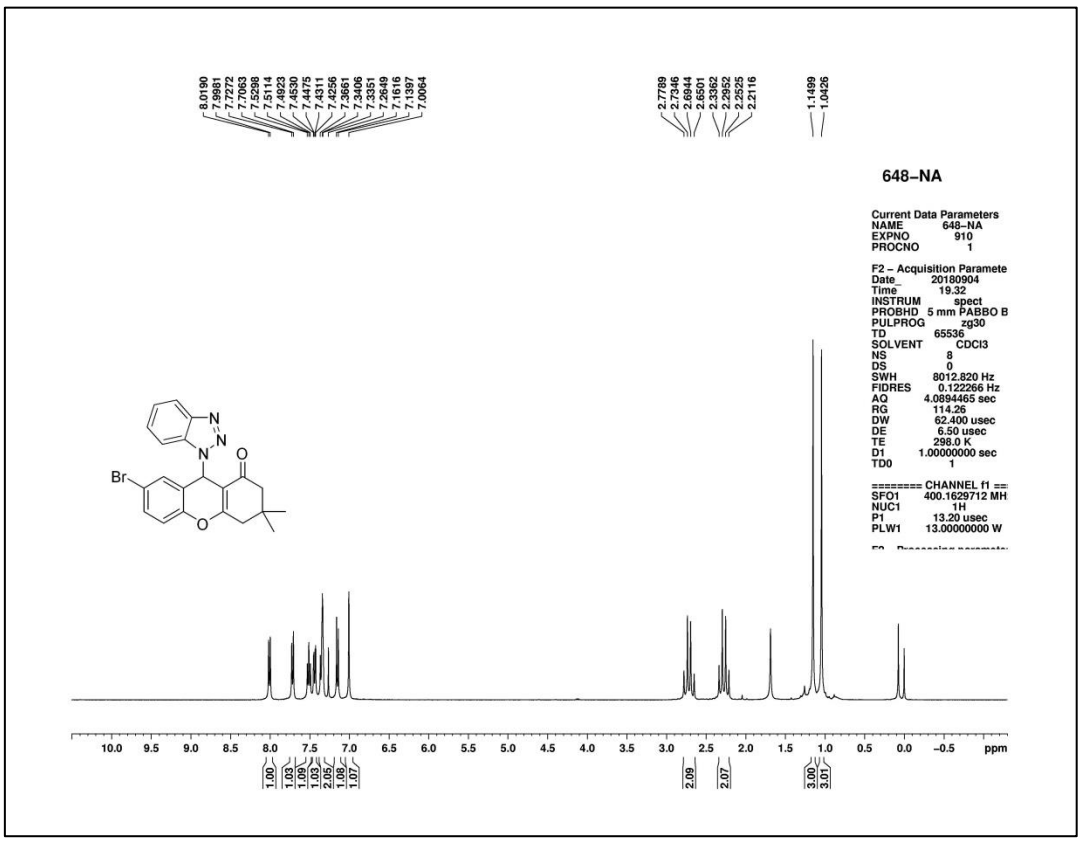


Figure S85: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4aq)

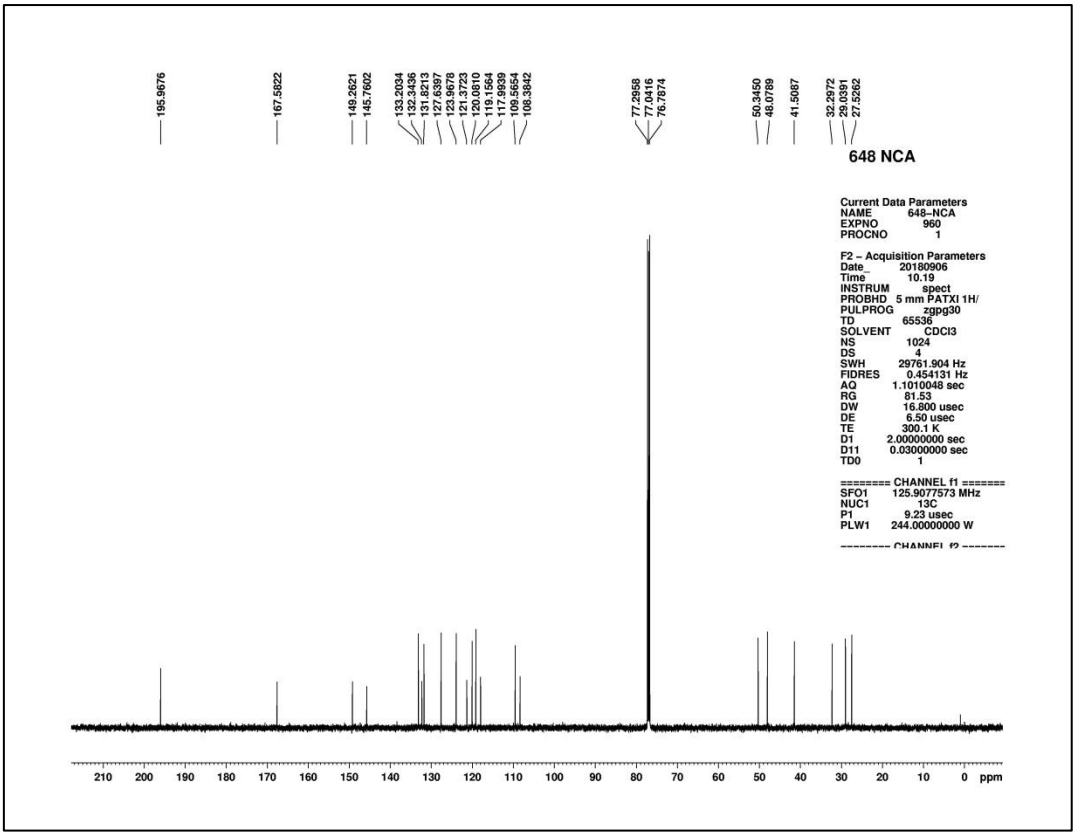


Figure S86: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4aq)

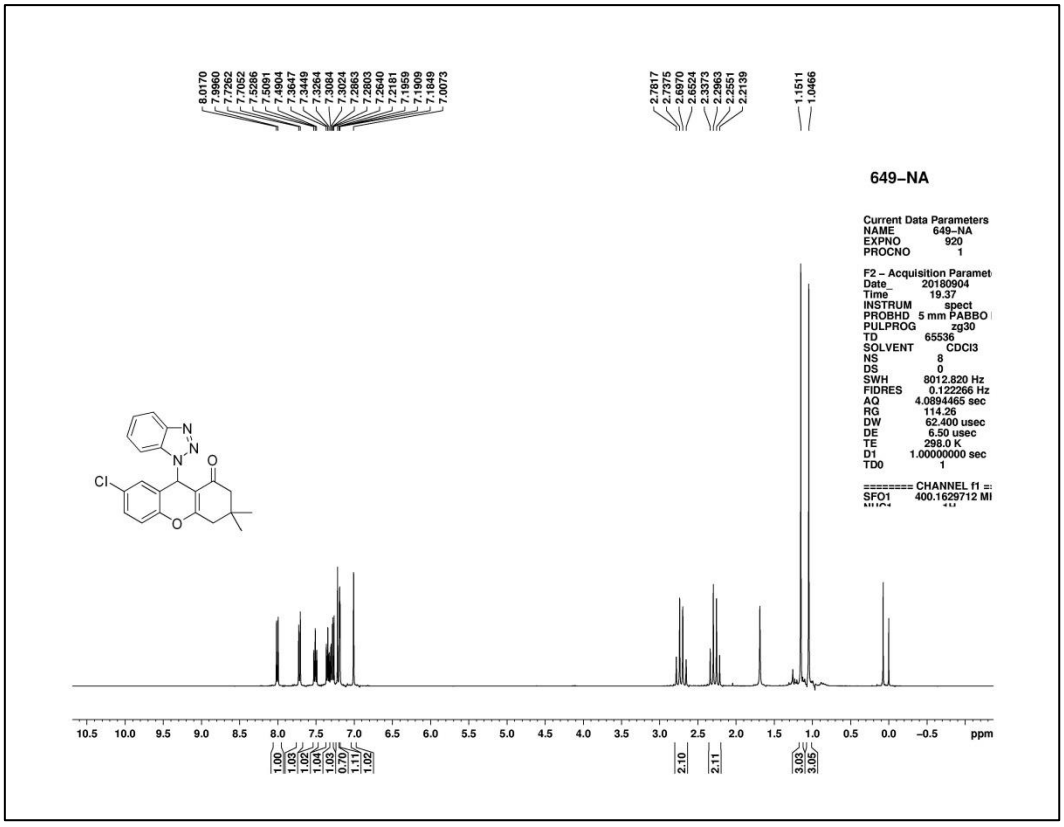


Figure S87: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4ar)

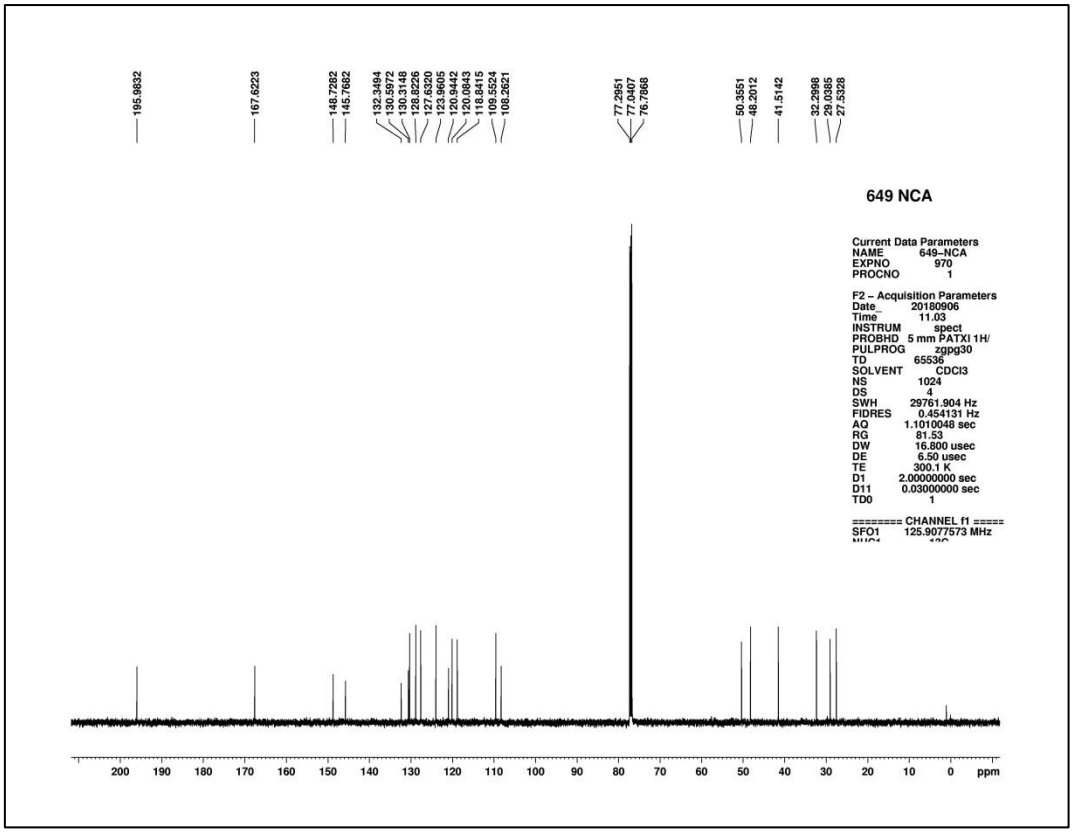


Figure S88: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4ar)

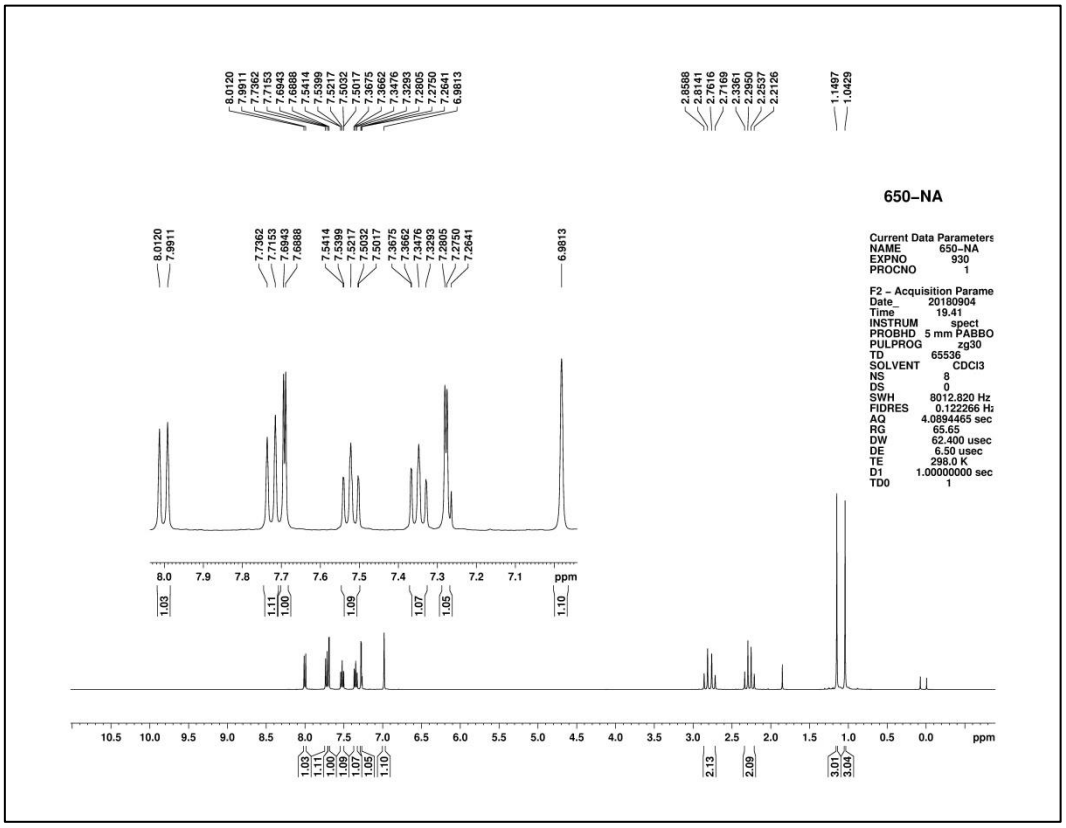


Figure S89: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4as)

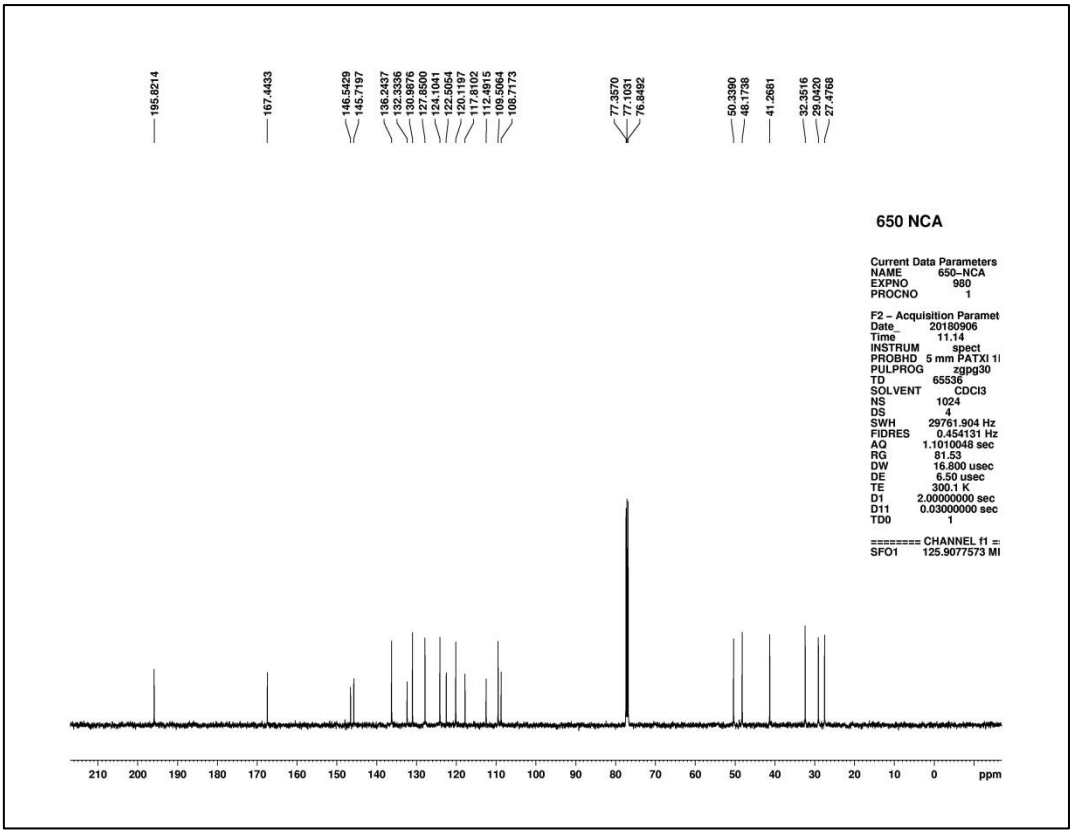


Figure S90: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4as)

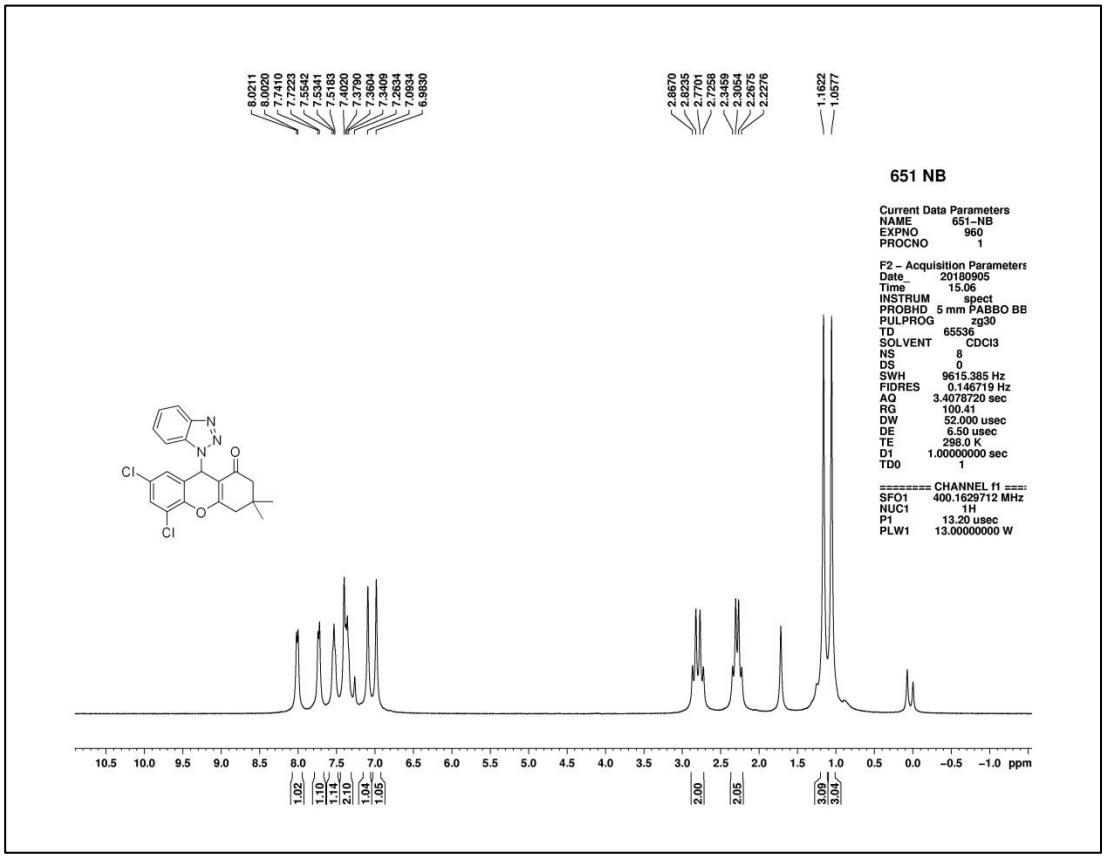


Figure S91: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (4at)

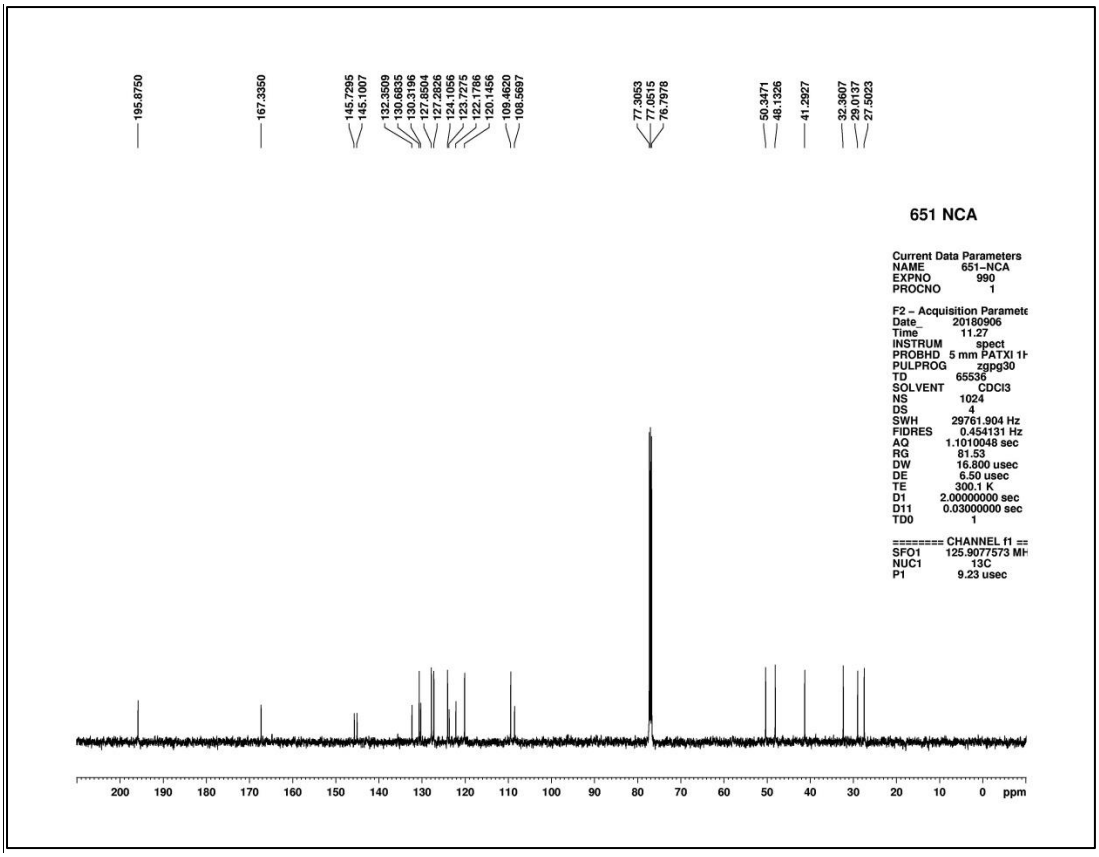


Figure S92: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (4at)

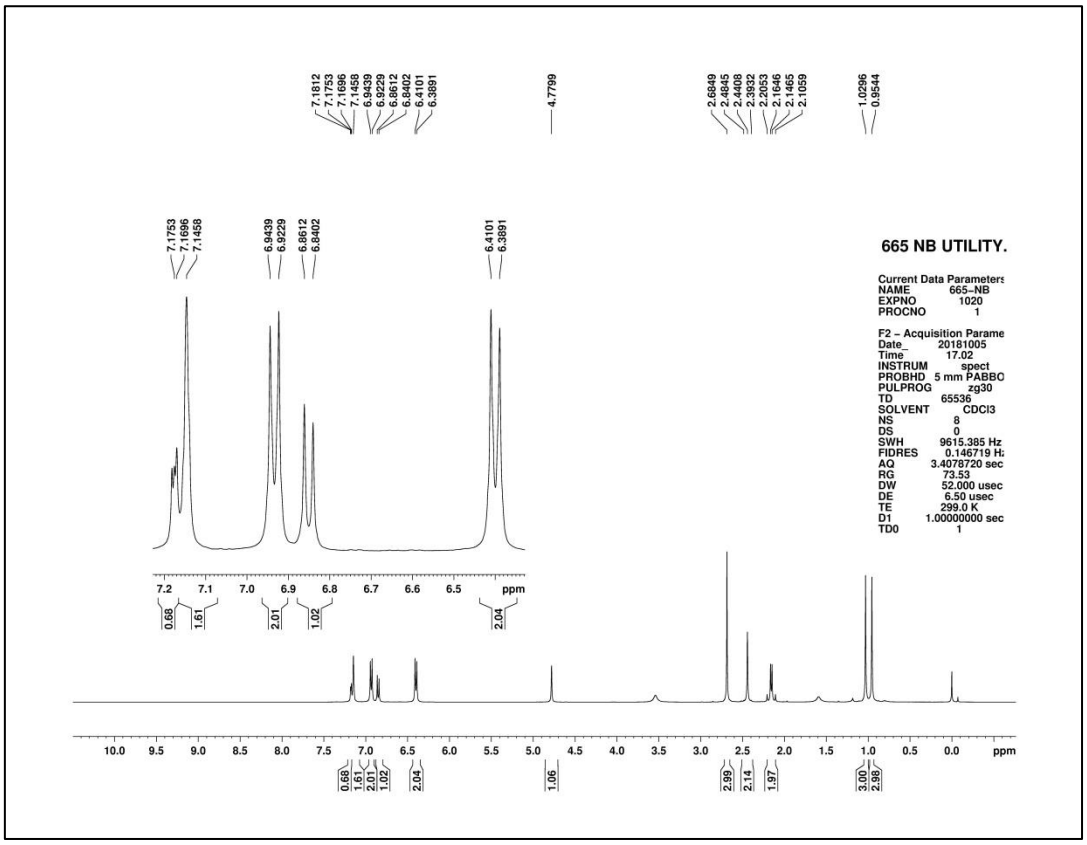


Figure S93: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (5a)

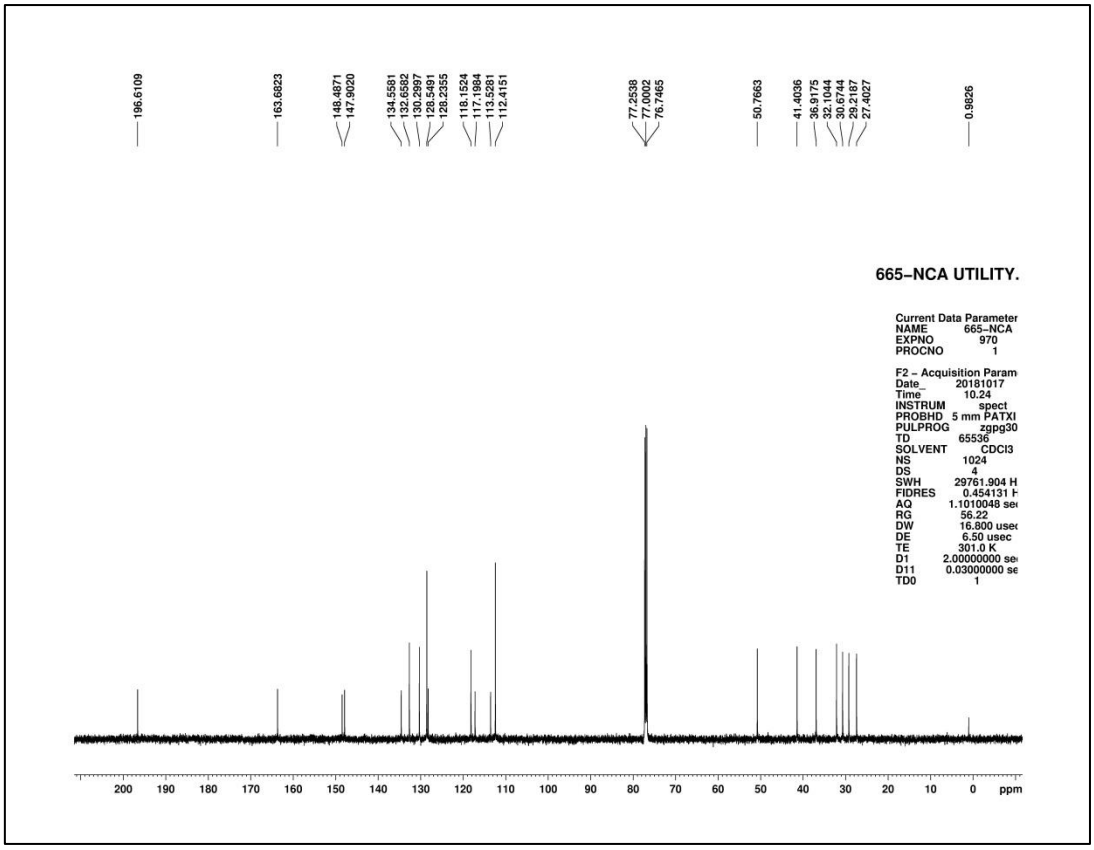


Figure S94: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (5a)

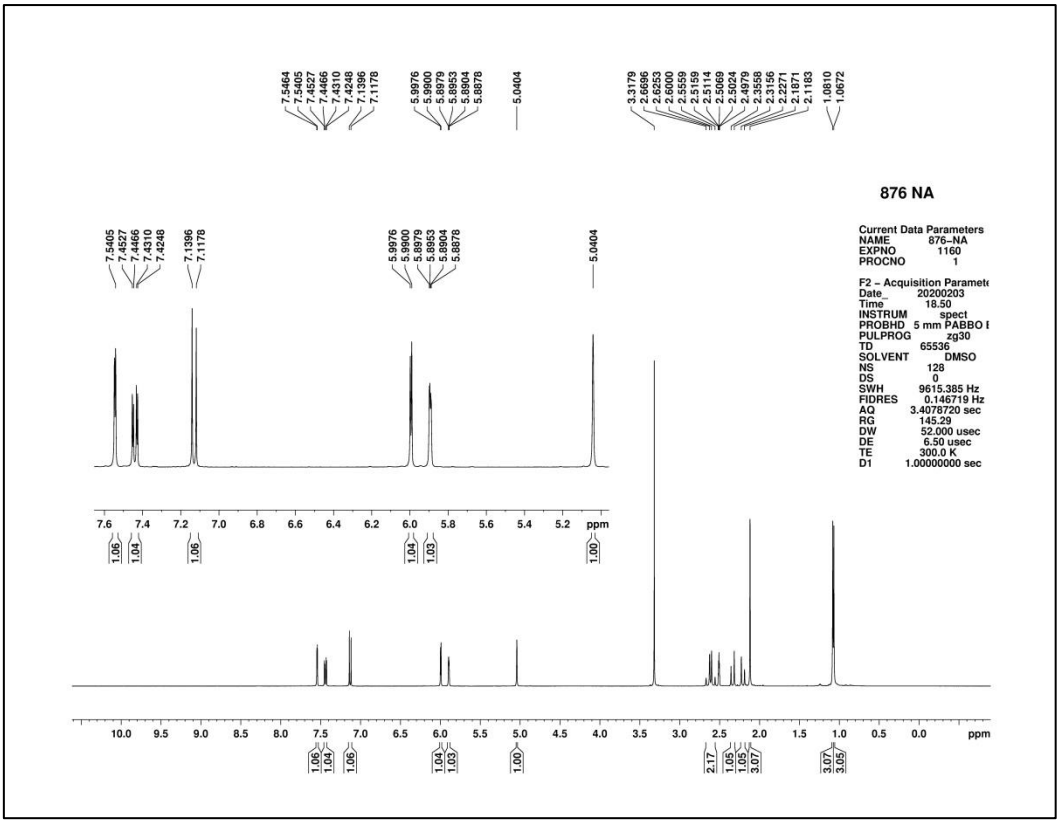


Figure S95: ^{1}H NMR (400 MHz, $CDCl_3$) spectra of compound (5b)

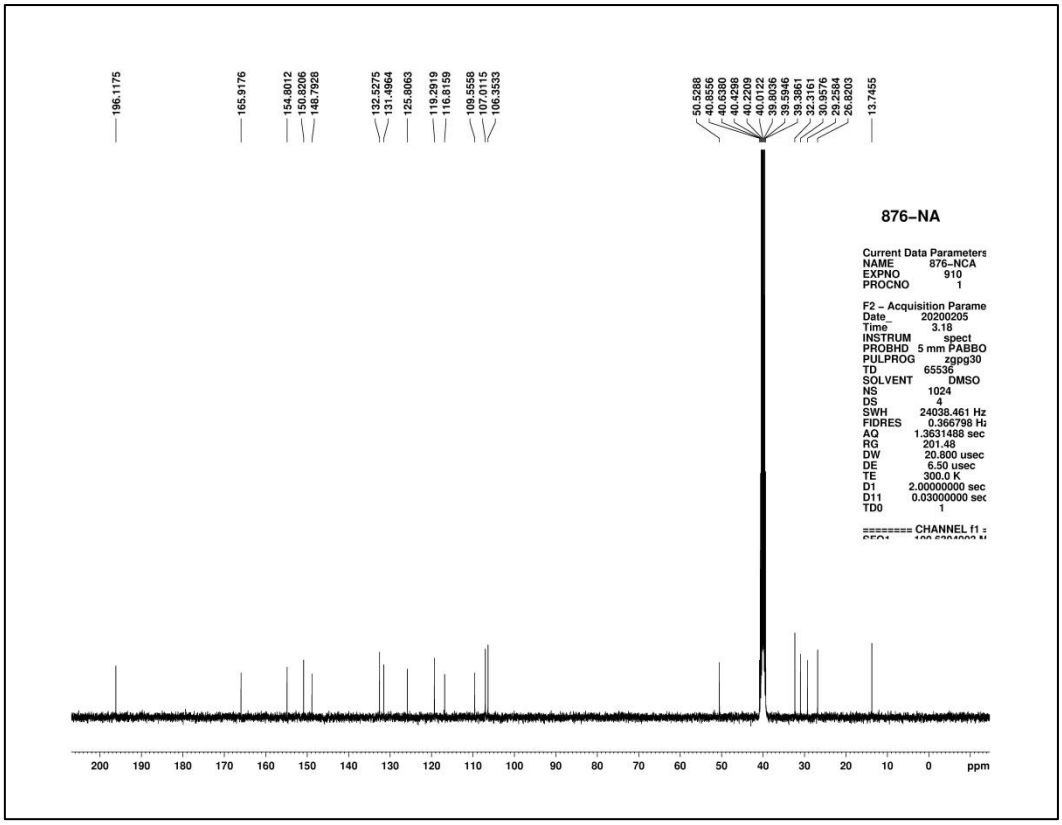
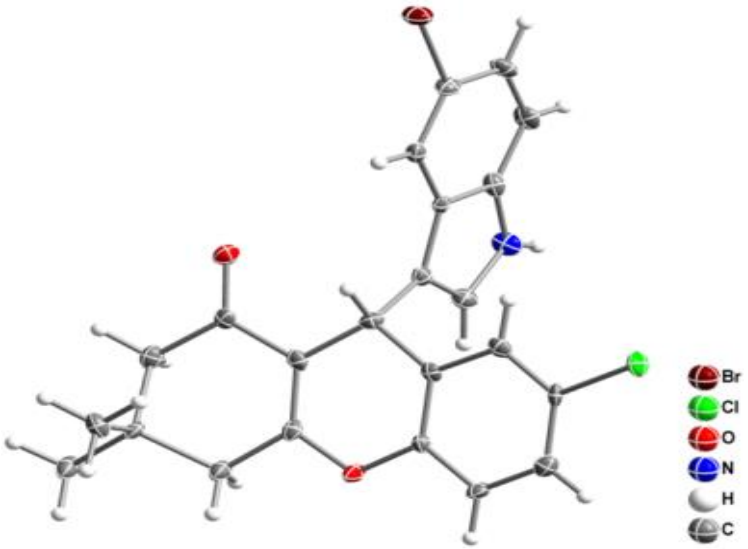


Figure S96: ^{13}C NMR (100 MHz, $CDCl_3$) spectra of compound (5b)

(7). X-Ray Data for compound (4t)



Structure of **4t** with 50% ellipsoid probability for non-H atoms.

X-Ray Data Collection and Structure Refinement Details:

The colorless crystals of **4t** were obtained in methanol by slow evaporation, at room temperature. The **4t** is crystallized in $P2_1$space group. The single-crystal X-ray diffraction data of **4t** was collected from Rigaku XtaLAB Oxford Diffraction system by using a MoKα radiation ($\lambda\alpha$ = 0.71073 Å) at 100K. The structure solution and refinements were performed by using SHELXT[1], SHELXL[2] program in the Olex 2[3] software. The crystallographic Figure was drawn by using Diamond 3.2k software.[4] The crystallographic details of ,**4t**, can be access from Cambridge Crystallographic Data Center by using, 2016011, CCDC number.

5. Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3-8.
6. Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3-8.
7. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* **2009**, *42*, 339-341.
8. Brandenburg, K.; DIAMOND. Version 3.2k, Crystal Impact GbR, Bonn, Germany, **2014**.

Supplementary:

Table 1. Crystal data and structure refinement details for **4t**

Compound	**4t**
CCDC number	2016011
Empirical formula	$C_{23}H_{19}BrClNO_2$
Formula weight	456.75
Temperature/K	100.00(10)
Crystal system	Monoclinic
Space group	$P2_1$
a/Å	10.9206(4)
b/Å	6.2585(2)
c/Å	14.4384(4)
α/°	90
β/°	99.980(3)
γ/°	90
Volume/Å^3	971.88(6)
Z	2
ρ_{calc}g/cm^3	1.561
μ/mm^{-1}	2.272
F(000)	464.0
Crystal size/mm^3	0.029 × 0.026 × 0.023
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	5.566 to 58.17
Index ranges	-12 ≤ h ≤ 12, -7 ≤ k ≤ 7, -16 ≤ l ≤ 16
Reflections collected	7966
Independent reflections	3140 [R_{int} = 0.0296, R_{sigma} = 0.0331]
Data/restraints/parameters	3140/1/255
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0251, wR_2 = 0.0636
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0640
Largest diff. peak/hole / e Å^{-3}	0.56/-0.41

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) 969

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: 969

Bond precision: C-C = 0.0057 A Wavelength=0.71073

Cell: a=10.9206(4) b=6.2585(2) c=14.4384(4)
alpha=90 beta=99.980(3) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	971.88(6)	971.88(6)
Space group	P 21	P 1 21 1
Hall group	P 2yb	P 2yb
Moiety formula	C23 H19 Br Cl N O2	C23 H19 Br Cl N O2
Sum formula	C23 H19 Br Cl N O2	C23 H19 Br Cl N O2
Mr	456.74	456.75
Dx,g cm-3	1.561	1.561
Z	2	2
Mu (mm-1)	2.272	2.272
F000	464.0	464.0
F000’	463.89	
h,k,lmax	12,7,16	12,7,16
Nref	3310[1822]	3140
Tmin,Tmax	0.936,0.949	0.459,1.000
Tmin’	0.936	

Correction method= # Reported T Limits: Tmin=0.459 Tmax=1.000
AbsCorr = MULTI-SCAN

Data completeness= 1.72/0.95 Theta(max)= 24.712

R(reflections)= 0.0251(3064) wR2(reflections)= 0.0640(3140)

S = 1.065 Npar= 255

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

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THETM01_ALERT_3_C  The value of sine(theta_max)/wavelength is less than 0.590
           Calculated sin(theta_max)/wavelength =    0.5882
PLAT090_ALERT_3_C Poor Data / Parameter Ratio (Zmax > 18) ........       7.13 Note
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.588          2 Report
PLAT915_ALERT_3_C No Flack x Check Done: Low Friedel Pair Coverage         89 %
PLAT987_ALERT_1_C The Flack x is >> 0 -  Do a BASF/TWIN Refinement     Please Check
```

Alert level G

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PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          1 Report
PLAT033_ALERT_4_G Flack x Value Deviates > 3.0 * sigma from Zero .      0.038 Note
PLAT791_ALERT_4_G Model has Chirality at C1          (Sohnke SpGr)          S Verify
PLAT883_ALERT_1_G No Info/Value for _atom_sites_solution_primary .     Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still         94% Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          4 Note
PLAT913_ALERT_3_G Missing # of Very Strong Reflections in FCF ....          1 Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        4.4 Low
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          5 Info
```

0 **ALERT level A** = Most likely a serious problem - resolve or explain
0 **ALERT level B** = A potentially serious problem, consider carefully
5 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
9 **ALERT level G** = General information/check it is not something unexpected

2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
1 ALERT type 2 Indicator that the structure model may be wrong or deficient
8 ALERT type 3 Indicator that the structure quality may be low
2 ALERT type 4 Improvement, methodology, query or suggestion
1 ALERT type 5 Informative message, check

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E* or *IUCrData*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 08/07/2020; check.def file version of 17/06/2020

Datablock 969 - ellipsoid plot