Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.


# Nickel catalysed synthesis of 4,4'-bichromenes/ 4,4'-bithiochromenes and their Atropisomerism

*Muthuramalingam Somasundaram,*[a,†] *Jai Anand Garg,*[b,†] *R. Karthick,*[c] *Thomas Fox,*[d] *Olivier Blacque,*[d] *Koushik Venkatesan,*[d,e] *Ramanathan Saiganesh,*[c] *Senthamaraikannan Kabilan,*[a]* *Kalpattu Kuppuswamy Balasubramanian*[b]*

[a] Department of Chemistry, Annamalai University, Annamalainagar-608002, India

[b] Department of Chemistry, Indian Institute of Technology Madras, Chennai-600036, India

[c] Strides-Shasun pharmaceuticals Ltd, Vandalur-Kelambakkan Rd., Chennai-600127, India

[d] Department of Chemistry, University of Zürich, Zürich, CH-8057, Switzerland

[e] Department of Molecular Sciences, Macquarie University, NSW 2109, Australia.

[†] Both the authors contributed equally to the work.

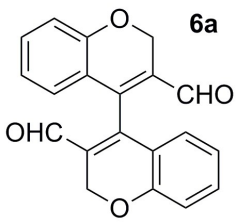
E-mail: profdrskabilanau@gmail.com, kkbalu@hotmail.com

# Supporting information

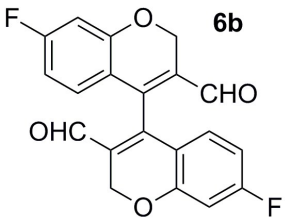
## Table of contents

## Page Nos.

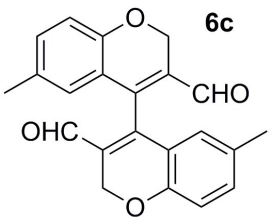
## S1.0 Compounds chemical structure chart.



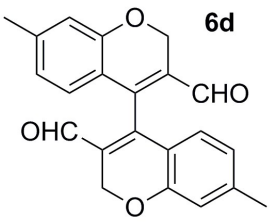

2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbaldehyde



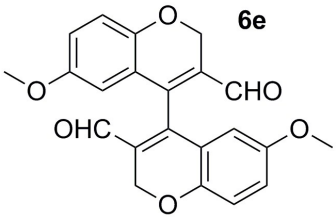

7,7'-difluoro-2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbaldehyde



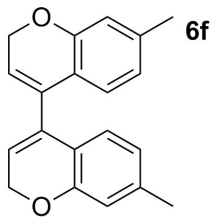

6,6'-dimethyl-2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbaldehyde



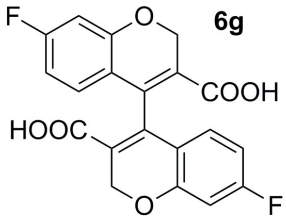

7,7'-dimethyl-2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbaldehyde



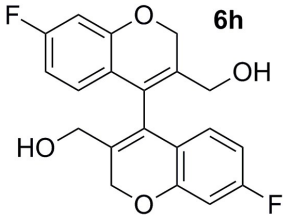

6,6'-dimethoxy-2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbaldehyde



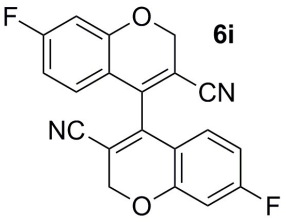

7,7'-dimethyl-2*H*,2'*H*-4,4'-bichromene



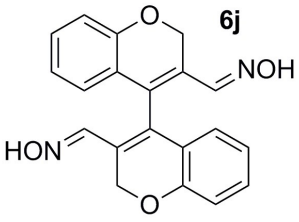

7,7'-difluoro-2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarboxylic acid



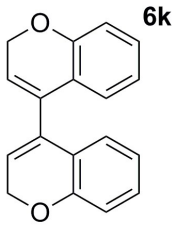

(7,7'-difluoro-2*H*,2'*H*-[4,4'-bichromene]-3,3'-diyl)dimethanol



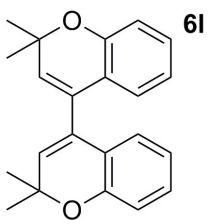

7,7'-difluoro-2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbonitrile




2*H*,2'*H*-[4,4'-bichromene]-3,3'-dicarbaldehyde dioxime

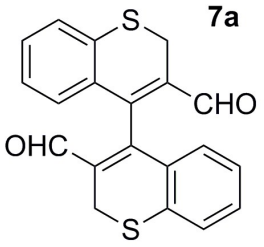



2*H*,2'*H*-4,4'-bichromene



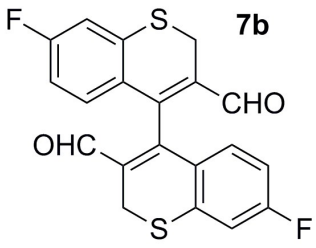

2,2,2',2'-tetramethyl-2*H*,2'*H*-4,4'-bichromene

**7a**



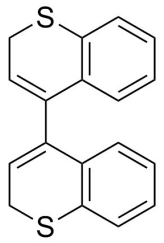

2*H*,2'*H*-[4,4'-bithiochromene]-3,3'-dicarbaldehyde

**7b**



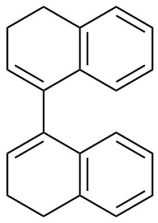

7,7'-difluoro-2*H*,2'*H*-[4,4'-bithiochromene]-3,3'-dicarbaldehyde

**7c**



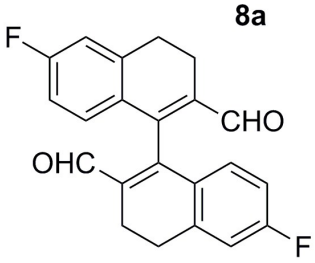

2*H*,2'*H*-4,4'-bithiochromene

**8**



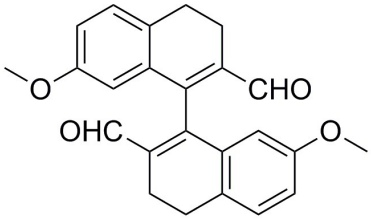
3,3',4,4'-tetrahydro-1,1'-binaphthalene

**8a**



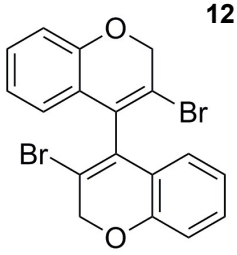

6,6'-difluoro-3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-2,2'-dicarbaldehyde

**8b**




7,7'-dimethoxy-3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-2,2'-dicarbaldehyde

**12**




3,3'-dibromo-2*H*, 2'*H*-4,4'-bichromene

## S.2.0 Experimental Section

### General Considerations

Unless otherwise noted, all reactions were carried out in oven-dried glassware under nitrogen atmosphere using anhydrous solvents. $^{1}H$ NMR spectra were recorded in either 300 or 500 MHz in $CDCl_3$ as the solvent and TMS as an internal standard. $^{13}C$ NMR spectra were recorded in 75 or 125 MHz frequency. Melting points were measured using on Veego VMP-PM apparatus and were uncorrected. Infrared (IR) spectra were recorded on Perkin Elmer FT-IR in KBr for solid compounds. HRMS spectra were obtained in the ESI mode (positive ion) with the mass spectrometer (TOF). Analytical thin layer chromatography (TLC) was carried out using silica gel 60 $F_{254}$ precoated plates, (0.25 mm thickness). Visualization was performed using UV lamp or $I_2$ stain. Silica gel 230−400 mesh size was used for column chromatography using the combination of ethyl acetate and hexane as eluent. Reagents and solvents were purchased from commercial suppliers. Wherever appropriate, all reagents were purified prior to use by standard pocedures. Compound **6k**, *2H,2'H-4,4'-bichromene* was prepared according to a literature known procedure.[S1] *2,2,2',2'-tetramethyl-2H,2'H-4,4'-bichromene* **(6l)** was synthesized following a similar reported procedure. [S2]

### General procedure for the synthesis of 6a-e, 7a-c and 8a-b (Scheme 1 and Table1):

To a stirred solution of 4-chloro-3-formylchromene (2.0 g, 10.0 mmol) in freshly distilled NMP (10.0 mL) was added activated Zinc powder (2.0 g, 30.0 mmol) and $NiCl_2(PPh_3)_2$ (0.67 g, 1.0 mmol) at 45-50 ºC. The reaction mass was stirred at the same temperature for 3-4 h and the progress was monitored by TLC. After completion of the reaction, the reaction mass was cooled to room temperature, and diluted with 20 mL of methyl *tert*-butyl ether (MTBE). It was then filtered through celite bed and further washed with 10 mL of MTBE. The combined organic portions were washed with dilute 5% aqueous HCl (2 x 15 mL), followed by water (1 x 15 mL), dried over anhydrous sodium sulphate and then concentrated under reduced pressure to yield brown pasty solids. The crude products thus obtained were triturated with 8 mL of ethanol,

filtered and dried to get off-white to yellow solids.

*2H,2'H-[4,4'-bichromene]-3,3'-dicarbaldehyde* (**6a**): General procedure described above was followed to obtain **6a** as a pale yellow solid. Yield: 1.14 g, 70%; mp: 132-134 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.68 (s, 2H), 7.32 (t, 2H), 7.06 (dd, $J$ = 7.8 Hz and 5.2 Hz, 2H), 6.98 (d, $J$ = 8.1 Hz, 2H), 6.88 (t, 2H), 5.06 (q, $J$ =14.5 Hz and $J$ = 14.31 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 188.2, 155.7, 143.0, 134.1, 129.5, 127.2, 122.6, 121.6, 117.3, 62.7; IR (KBr): 3447.3, 3056.2, 2970.7, 2843.9, 2738.6, 1668.5, 1644.7, 1598.9, 1569.8, 1538.0 cm$^{-1}$; HRMS-ESI *m/z*: $[M+Na]^+$ calculated for $C_{20}H_{14}O_4$ 341.0790, found 341.0793.; TLC $R_f$. 0.425, eluent: hexane: ethyl acetate (9:1).

*7,7'-difluoro-2H,2'H-[4,4'-bichromene]-3,3'-dicarbaldehyde* **(6b):** General procedure described above was followed to obtain **6b** as a pale yellow solid. Yield: 1.29 g, 78%; mp: 232-236 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.66 (s, 2H), 7.00 (dd, $J$ = 8.7 Hz and 6.3 Hz, 2H), 6.66 (m, 2H), 6.60 (dd, $J$ = 8.4 Hz and 2.26 Hz, 2H), 5.06 (q, $J$ =14.4 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 187.8, 167.7, 164.3, 157.6, 141.9, 128.5, 117.7, 110.3, 105.0, 63.1; IR (KBr): 3316.1, 3078.0, 2925.1, 2884.4, 2846.0, 2835.8, 2738.4, 1667.3, 1607.1, 1573.9, 1493.8, 1469.2, 1433.3 1378.5, 1337.7 cm$^{-1}$; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{20}H_{13}O_4F_2$ 355.0773, found 355.0782.; TLC $R_f$. 0.23, eluent: hexane: ethyl acetate (9:1).

*6,6'-dimethyl-2H,2'H-[4,4'-bichromene]-3,3'-dicarbaldehyde* **(6c):** General procedure described above was followed to obtain **6c** as a pale yellow solid. Yield: 0.99 g, 60%, mp: 228-231°C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.64 (s, 2H), 7.14 (d, $J$ = 6.9 Hz, 2H), 6.89 (d, $J$ = 8.4 Hz, 2H), 6.84 (s, 2H), 5.03 (q, $J$ = 14.4 Hz, 4H), 2.19 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): 188.4, 153.6, 143.4, 134.9, 132.2, 129.4, 127.1, 121.6, 117.1, 62.7, 20.6; IR (KBr): 1763.3, 1660.4, 1651.8, 1613.5, 1568.0 cm$^{-1}$; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{22}H_{19}O_4$ 347.1280, found

347.1283; TLC $R_f$. 0.38, eluent: hexane: ethyl acetate (9:1).

*7,7'-dimethyl-2H,2'H-[4,4'-bichromene]-3,3'-dicarbaldehyde* **(6d):** General procedure described above was followed to obtain **6d** as a pale yellow solid. Yield: 1.03 g, 62%, mp: 208-212 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.64 (s, 2H), 6.93 (d, $J$ = 7.8 Hz, 2H), 6.80 (s, 2H), 6.69 (d, $J$ = 7.8, 2H), 5.03 (q, $J$ = 14.4 Hz, 4H), 2.32 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): 188.3, 155.7, 145.6, 143.5, 128.4, 127.2, 123.7, 119.2, 117.6, 62.8, 21.84; IR (KBr): 3046.8, 2979.5, 2916.6, 2847.5, 2746.4, 1662.6, 1601.9, 1556.7 cm$^{-1}$; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{22}H_{19}O_4$ 347.1279, found 347.1283; TLC $R_f$. 0.41, eluent: hexane: ethyl acetate (9:1).

*6,6'-dimethoxy-2H,2'H-[4,4'-bichromene]-3,3'-dicarbaldehyde* **(6e):** General procedure described above was followed to obtain **6e** as a pale brown solid. Yield: 0.87 g, 52%, mp: 162-166 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.672 (s, 2H), 6.89 (m, 4H), 6.56 (s, 2H), 4.99 (q, $J$ =14.4 Hz, 4H), 3.66 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): 188.2, 154.7, 149.7, 143.0, 130.2, 122.3, 119.4, 117.9, 111.8, 62.7, 55.7; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{20}H_{14}O_4H$ 379.1182, found 379.1195; TLC $R_f$. 0.22, eluent: hexane: ethyl acetate (9:1).

*7,7'-dimethyl-2H,2'H-4,4'-bichromene* **(6f):** An analogous reported procedure was adopted.[S2] To a suspension of $HgCl_2$ (100.0 mmol) in toluene: ethanol mixture (30 vol, 6:1), was slowly added small pieces of aluminium foil (3.0 mol%) in a temperature range of 60-65 °C. After 30 min, it was then cooled to 10 °C and a solution of 7-methylchroman-4-one (1000.0 mmol in 5.0 vol. of toluene) was added maintaining temperature below 10 °C. The mass was then stirred at 80 °C for 2 h and the reaction progress was monitored by TLC. At the end of 2 h, the TLC showed the formation of the diol intermediate and the absence of the chromanone. The reaction mass was subsequently cooled to 5 °C and quenched with dilute HCl. The mass was then filtered through a celite bed and the organic portion was washed twice with water and dried over sodium sulphate.

Upon concentration the crude diol was obtained as a brown pasty mass. It was then refluxed with acetic acid : acetic anhydride mixture (1:1, 3.0 vol) for 1 h, and then poured into crushed ice, extracted with MTBE (5.0 vol) and concentrated to get the crude product. Purification by column chromatography yielded **6f** as brown crystalline solid. Yield: 82%, mp: 144-148 °C; $^{1}$H NMR (300 MHz, $CDCl_3$; $\delta$ (ppm) 6.76 (d, 2H, $J$ = 7.8 Hz), 6.67 (s, 2H), 6.56 (d, 2H, $J$ = 7.5 Hz), 5.74 (t, 2H, $J$ = 4.0 Hz ), 4.84 (d, 4H, $J$ = 4.0 Hz), 2.55 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$): 153.8, 139.7, 133.8, 126.5, 122.9, 120.1, 116.5, 65.3, 21.3; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{20}H_{18}O_2$ 290.1307, found, 290. 1421, TLC $R_f$. 0.61, eluent: hexane: ethyl acetate (8:2).

*2,2,2',2'-tetramethyl-2H,2'H-4,4'-bichromene* **(6l):** The procedure adopted for the synthesis of **6f** was followed to obtain **6l** in 78% yield. $^{1}$H NMR (500 MHz, THF-D8); $\delta$ (ppm) 7.10 (t, 1H, $J$ = 4.0 Hz), 6.80-6.75 (m, 2H), 6.70 (t, 1H, $J$ = 4.0 Hz), 5.70 (s, 2H), 1.51(s, 6H), 1.40 (s, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$): 152.7, 131.4, 130.0, 129.3, 125.4, 121.6, 120.7, 116.6, 75,8, 39.9, 27.5; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{22}H_{22}O_2$ 319.1693, found, 319.1723, TLC: $R_f$ 0.71, eluent: hexane: ethyl acetate (9:1).

*7,7'-difluoro-2H,2'H-[4,4'-bichromene]-3,3'-dicarboxylic acid* **(6g):** To a stirred solution of 7,7'-difluoro-3,3'-diformyl-4,4'-bichromene (**6b**, 250 mg, 0.7 mmol) in acetonitrile (2.0 mL) was slowly added 50% aq. solution of sodium chlorite (3.0 mol equiv.) followed by 50% aq. solution of sodium dihydrogen phosphate (0.6 mol equiv.) at 10-20 $^{o}$C. Cooled to 0 $^{o}$C and slowly added 30% $H_2O_2$ (10.0 mol equiv.). After the addition the reaction mixture was stirred at 25-30 $^{o}$C overnight, and the reaction progress was monitored by TLC. After completion of the reaction, the mass was acidified using dilute HCl (until pH = 3-4), extracted with MTBE (2 x 10.0 vol) and washed the organic portion with water (5.0 vol). Drying over anhydrous sodium sulphate and solvent concentration yielded crude pasty mass. It was further purified by column

chromatography using silica gel (230-400 mesh) and hexane: ethyl acetate (90:10)% as eluting solvent to obtain **6g** as white solid. Yield: 228.0 mg, 84%; mp: 208 - 212 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 12.78 (s, 2H), 6.96 (t, 2H), 6.84 (dd, 2H $J$ = 9.9 Hz), 6.70 (t, 2H), 4.89 (q, $J$ = 14.1 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 164.7, 161.8, 156.0, 138.8, 131.3, 128.0, 118.6, 108.7, 103.5, 65.0; IR (KBr): 3839.4, 3736.0, 3221.5, 2924.6, 2854.0, 1698.2, 1608.7, 1575.0 cm$^{-1}$; HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{20}H_{12}F_2O_6$ 386.0601, found 386.3210; TLC: $R_f$. 0.23, eluent: chloroform : methanol (8:2).

*(7,7'-difluoro-2H,2'H-[4,4'-bichromene]-3,3'-diyl)dimethanol* **(6h):** To a stirred solution of 7,7'-difluoro-3,3'-diformyl-4,4'-bichromene (**6b**, 200 mg, 0.87 mmol) in methanol was slowly added sodium borohydride (1.2 mol. equiv.) at 10-20 $^{o}$C, and stirred the reaction mixture at 25-30 $^{o}$C while monitoring the reaction progress by TLC. After the completion of the reaction, the mass was quenched with saturated ammonium chloride solution and then solvent concentrated. The crude pasty mass which was obtained was dissolved in ethyl acetate (20 mL), and washed with water (20 mL). The organic portion was dried over anhydrous sodium sulphate, concentrated under vacuum and then purified by column chromatography using silica gel (230-400 mesh) with hexane: ethyl acetate (90:10) % as eluting solvent to obtain **6h**. Yield: 213 mg, 68%, mp: 158-162 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 6.70 (t, 2H), 6.56 (dd, $J$ = 9.6 Hz and 2.4 Hz, 2H), 6.44 (t, 2H), 4.89 (q, $J$ = 14.4 Hz, 4H), 3.82 (q, $J$ = 9.0 Hz, 4H), 3.86 (s, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$): 164.7, 161.5, 154.8, 130.9, 126.2, 118.8, 114.8, 108.8, 103.5, 67.5, 59.8; IR (KBr): 3851.7, 3736.0, 3274.3, 2922.9, 2850.6, 2374.8, 1608.6, 1585.2, 1494.6, 1269.7, 1184.2 cm$^{-1}$, HRMS-ESI *m/z*: $[M+H]^+$ calculated for $C_{20}H_{17}F_2O_4$ 359.1094, found 359.1092; TLC: $R_f$. 0.15, eluent: hexane: ethyl acetate (8:2).

*7,7'-difluoro-2H,2'H-[4,4'-bichromene]-3,3'-dicarbonitrile* **(6i):** To a stirred solution of 7,7'-difluoro-3,3'-diformyl-4,4'-bichromene (**6b**, 250 mg, 0.7 mmol) in ethanol was slowly added an aqueous solution of 40% sodium hydroxide (2.0 mol. equiv.) followed by $NH_2OH{\cdot}HCl$ (2.5 mol equiv.) at 10-15 $^oC$. After addition, the reaction mass was stirred at 25-30 $^oC$ and the progress was monitored by TLC. After completion, the reaction mass was acidified using dilute HCl and then solvent concentrated. The crude oxime was taken in acetonitrile (3.0 mL) and to it was slowly added triethyl amine (2.2 equiv.) followed by DMAD (2.0 equiv.) at 10-15 $^oC$ and allowed the reaction mixture to stir at 25-30 $^oC$. After 15 minutes, the starting material was absent by TLC. It was then quenched with water and extracted with ethyl acetate (2 x 15 mL). The combined organic portions were dried over sodium sulphate and concentrated to obtain the crude product. Purification by column chromatography using silica gel (230-400 mesh) and hexane: ethyl acetate (90:10)% as eluent afforded **6i** as white coloured crystalline solid. Yield: 165 mg, 68%, mp: 188 -190 °C; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 6.80 (t, 2H), 6.70 (m, 2H), 6.59 (t, 2H), 5.01 (s, 4H); $^{13}C$ NMR (75 MHz, $CDCl_3$): 167.1, 163.7, 156.0, 143.0, 128.2, 115.7, 114.4, 110.4, 105.2, 103.8, 64.7; IR (KBr): 2922.9, 2851.6, 2216.9, 1605.1, 1579.8, 1495.6, 1449.6, 1381.0, 1308.4, 1270.1 $cm^{-1}$; HRMS-$[M+Na]^+$ *m/z*: calculated for $C_{20}H_{10}F_2N_2O_2$ 371.0608, found 371.0608; TLC $R_f$. 0.38. eluent: hexane: ethyl acetate (8:2).

*2H,2'H-[4,4'-bichromene]-3,3'-dicarbaldehyde dioxime* **(6j):** To a stirred solution of 3,3'-diformyl-4,4'-bichromene (**6a**, 250 mg, 0.78 mmol) in ethanol was slowly added an aqueous solution of 40% NaOH (2.0 equiv.) followed by $NH_2{\cdot}OH{\cdot}HCl$ (2.5 equiv.) at 10-15 $^oC$. After addition, the reaction mixture was stirred at 25-30 $^oC$ and the reaction progress was monitored by TLC. After completion, the reaction mixture was acidified using dilute HCl and then concentrated under vacuum. The crude pasty mass thus obtained was redissolved in ethyl acetate

(20 mL) and washed with water (20 mL). Finally the organic portions were concentrated and purified by column chromatography using silica gel (230-400 mesh) and hexane: ethyl acetate (90:10)% as eluting solvent to obtain **6j** as a white solid. Yield: 218 mg, 80%; mp: 178-182 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.73 (s, 2H), 7.76 (s, 2H), 7.16 (t, 2H), 6.89 (d, $J$ = 7.8 Hz, 4H), 6.76 (t, 2H), 5.09 (q, $J$ = 14.4 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 154.4, 146.2, 130.9, 130.5, 126.0, 125.8, 122.2, 121.9, 116.2, 64.0. IR (KBr): 3384.0, 3380.7, 2870.8, 2854.0, 1596.9, 1482.9, 1460.7, 1346.5, 1299.0 cm$^{-1}$; HRMS-$[M+H]^+$ *m/z*: calculated for $C_{20}H_{17}N_2O_4$ 349.1188, found 349.1187; TLC $R_f$. 0.30. eluent, hexane: ethyl acetate (8:2).

*2H,2'H-[4,4'-bithiochromene]-3,3'-dicarbaldehyde* **(7a):** Starting from 4-chloro-2*H*-thiochromene-3-carbaldehyde the general procedure described above was followed to obtain **7a** as a pale yellow solid. Yield: 80%; mp: 190-194 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.68 (s, 2H), 7.42 (d, $J$ =7.8 Hz, 2H), 7.23 (t, 2H), 7.14 (d, $J$ = 7.5 Hz, 2H), 7.043 (t, $J$ =7.8 Hz and 7.2 Hz, 2H), 3.69 (q, $J$ = 15.0 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 189.6, 148.1, 136.3, 133.7,133.0, 131.5, 129.0, 128.2, 126.6, 21.0; IR (KBr): 3052.8, 2958.29, 2921.12, 2892.92, 2863.0, 1960.75, 1665.41, 1602.15, 1581.35, 1549.59, 1459.22 cm$^{-1}$; HRMS-$[M+H]^+$ *m/z*: calculated for $C_{20}H_{14}O_2S_2$ 351.0513, found 351.0513; TLC $R_f$. 0.53, eluent: hexane: ethyl acetate (9:1).

*7,7'-difluoro-2H,2'H-[4,4'-bithiochromene]-3,3'-dicarbaldehyde* **(7b):** Starting from 4-chloro-7-fluoro-2H-thiochromene-3-carbaldehyde the general procedure described above was followed to obtain **7b** as a yellow solid. Yield: 74%, mp: 168 - 172 °C; $^{1}$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.67 (s, 2H), 7.08 (m, 4H), 6.75 (t, 2H), 3.68 (q, $J$ =15 Hz, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 189.1, 165.3, 161.9, 147.0, 139.4, 139,3, 130.9, 129.1, 115.2, 114.1, 21.7; IR (KBr): 3061.5, 2892.3, 1670.8, 1592.1, 1555.5, 1473.9, cm$^{-1}$; HRMS-$[M+H]^+$ *m/z*: calculated for $C_{20}H_{13}O_2F_2S_2$

387.0308, found 387.0325; TLC $R_f$ 0.52, eluent: hexane: ethyl acetate (8:2).

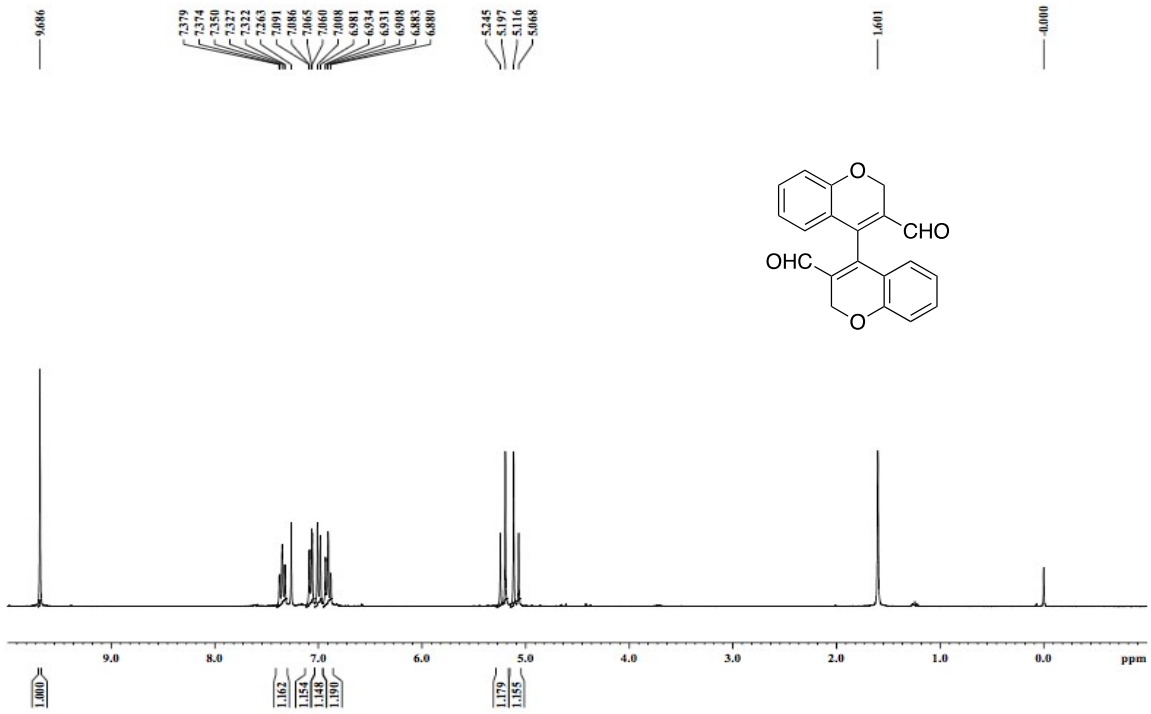
*2H,2'H-4,4'-bithiochromene* **(7c):** Starting from thiochroman-4-one, a procedure analogous to the preparation of **6f** was followed to obtain **7c** yellow solid. Yield: 74%; mp: 168-172 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 7.26 (m, 2H), 6.98 (m, 2H), 6.86 (m, 2H ), 6.09 (t, 2H), 3.45 (br. s, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 139.9, 133.0, 132.3, 127.6, 127.3, 127.0, 125.6, 122.4, 24.9; TLC, $R_f$ 0.53; eluent: hexane: ethyl acetate (9:1).

*6,6'-difluoro-3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-2,2'-dicarbaldehyde* **(8a):** Starting from 1-chloro-6-fluoro-3,4-dihydronaphthalene-2-carbaldehyde (**11a**) the general procedure described above was followed to obtain **8a** as an off white crystalline solid. Yield: 84%; mp: 158-162 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.72 (s, 2H), 7.0 (m, 4H), 6.80 (m, 2H), 2.97 (m, 4H), 2.65(m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 191.1, 165.7, 162.3, 146.8, 141.0-141.12, 136.48, 129.1-129.8, 115.6-115.9, 114.3-114.5, 27.4, 19.4; HRMS-$[M+H]^+$ *m/z*: calculated for $C_{22}H_{16}F_2O_2$ 351.1118, found; TLC, $R_f$. 0.30, eluent: hexane: ethyl acetate (9:1).

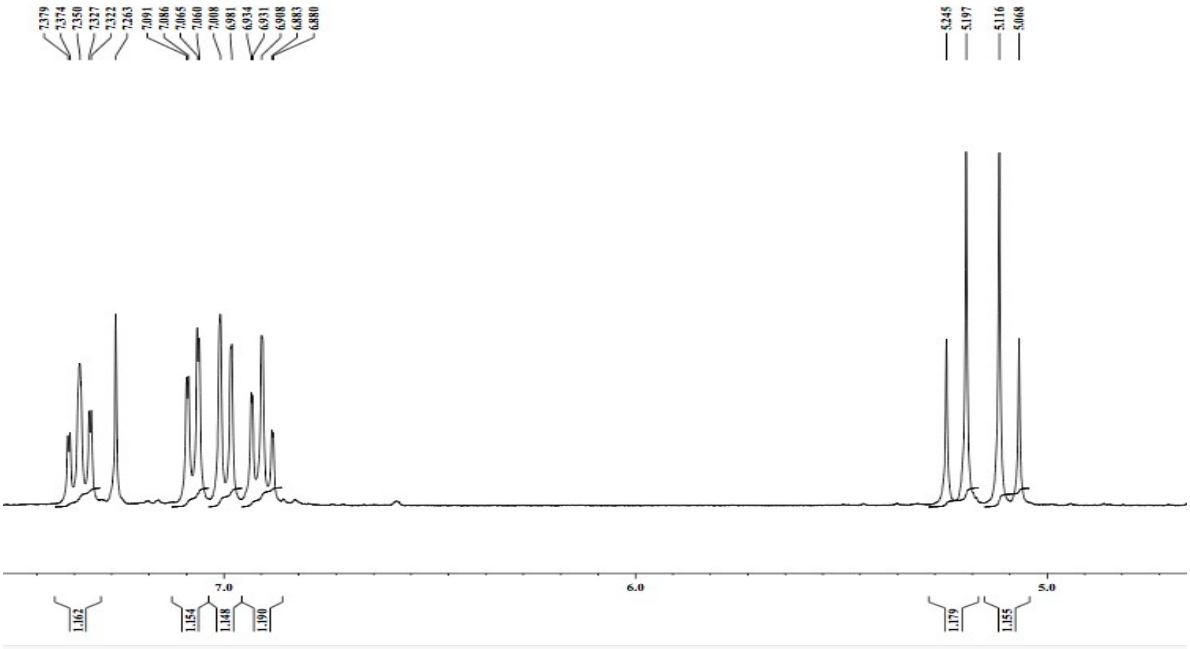
*7,7'-dimethoxy-3,3',4,4'-tetrahydro-[1,1'-binaphthalene]-2,2'-dicarbaldehyde* **(8b):** Starting from 1-chloro-7-methoxy-3,4-dihydronaphthalene-2-carbaldehyde (**11b**) the general procedure was followed to obtain to obtain **8b** as a pale yellow solid. Yield: 78%; mp: 162-166 °C; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 9.69 (s, 2H), 7.05-7.08 (m, 2H), 6.65-6.81 (m, 4H), 3.81 (s, 6H), 2.95 (m, 4H); $^{13}$C NMR (75 MHz, $CDCl_3$): 191.5, 161.8, 148.5, 140.3, 134.6, 129.1, 126.8, 114.1, 112.4, 55.4, 26.9, 19.6; HRMS-$[M+H]^+$ *m/z*: calculated for $C_{24}H_{22}O_4$ 375.1518, found; TLC, $R_f$. 0.225, eluent : hexane: ethyl acetate (9:1).

**S3.0. $^{1}H$ and $^{13}C$ NMR spectra of the synthesized compounds:**

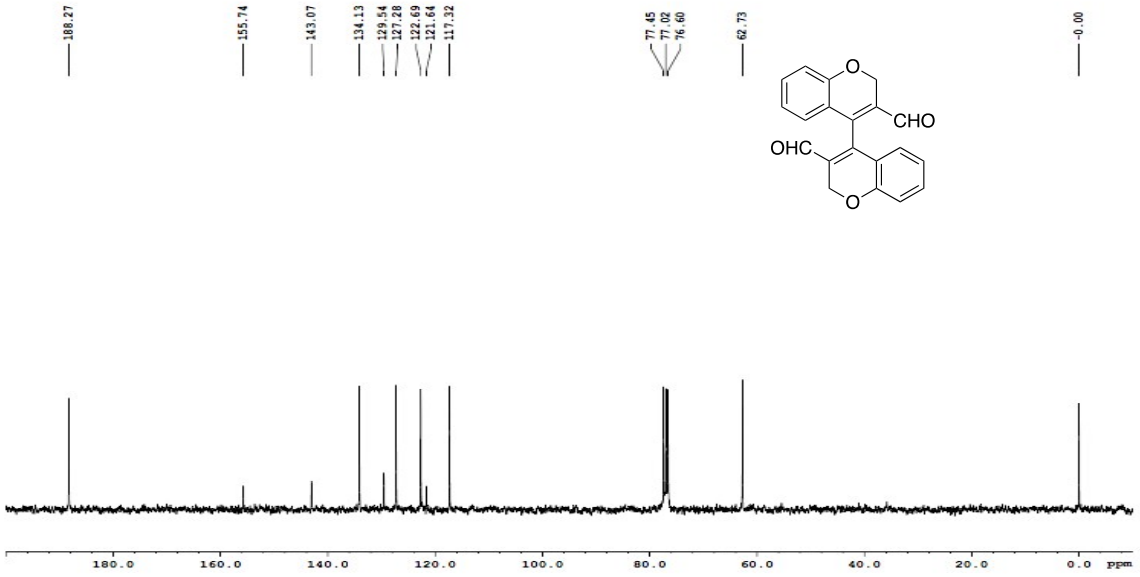
**S3.1.** $^{1}H$ NMR of bichromene **6a**:



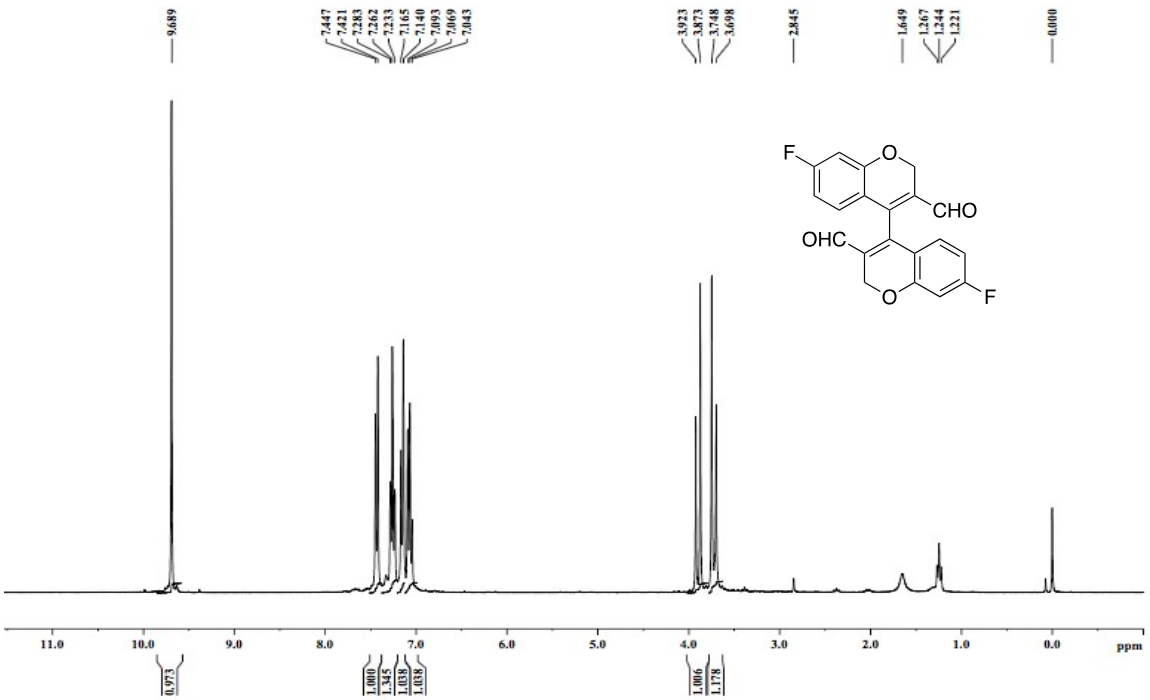

Expansion of aromatic region of $^{1}H$ NMR (**6a**):



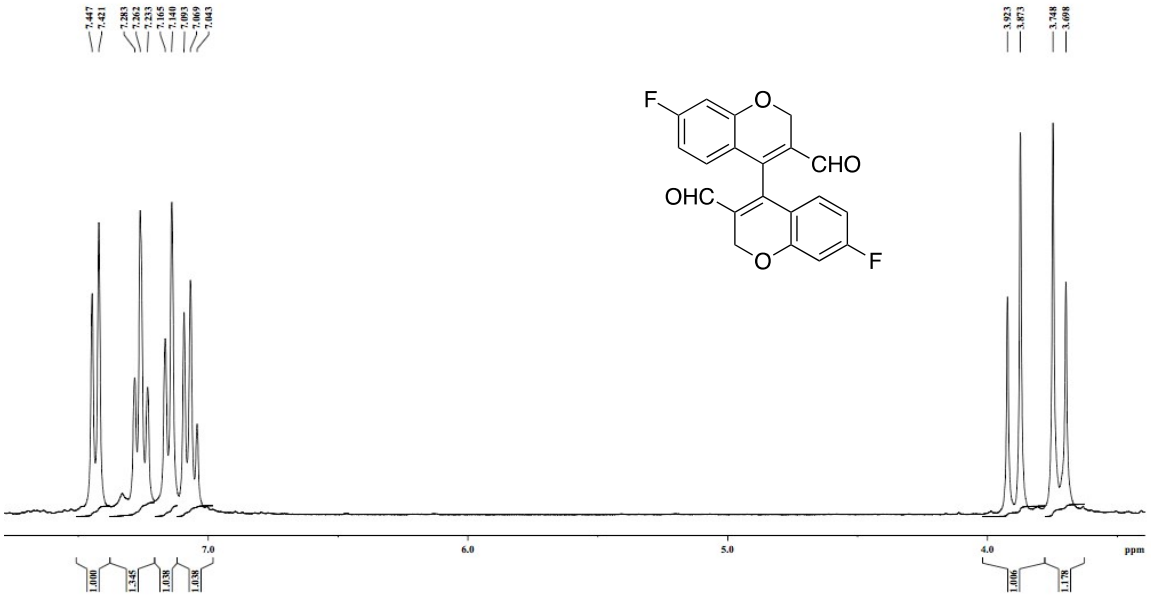
$^{13}$C NMR of of bichromene **6a**:



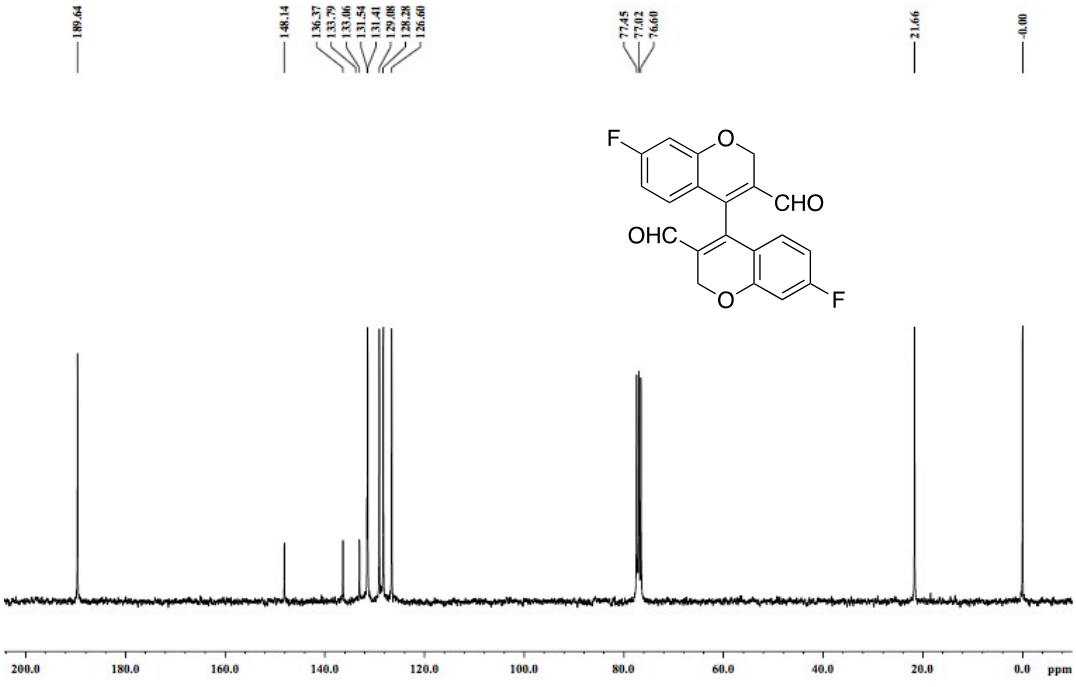

**S3.2.** $^{1}$H NMR of bichromene **6b**:



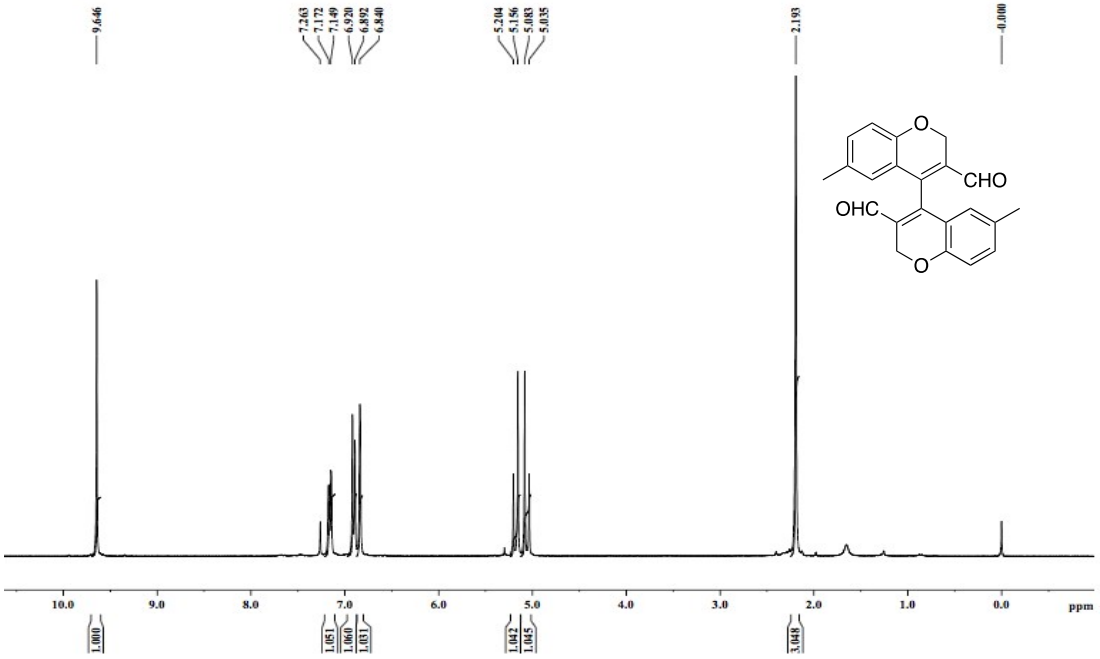
Expansion of aromatic region of $^{1}H$ NMR **6b**:



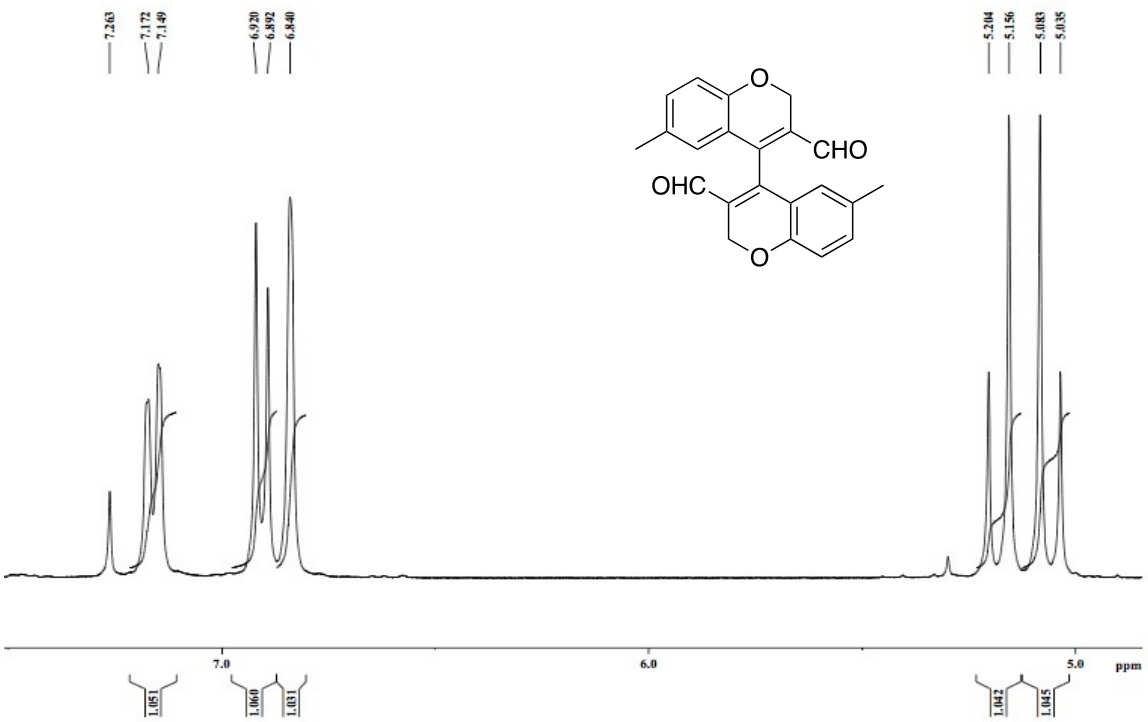

$^{13}C$ NMR of of bichromene **6b**:



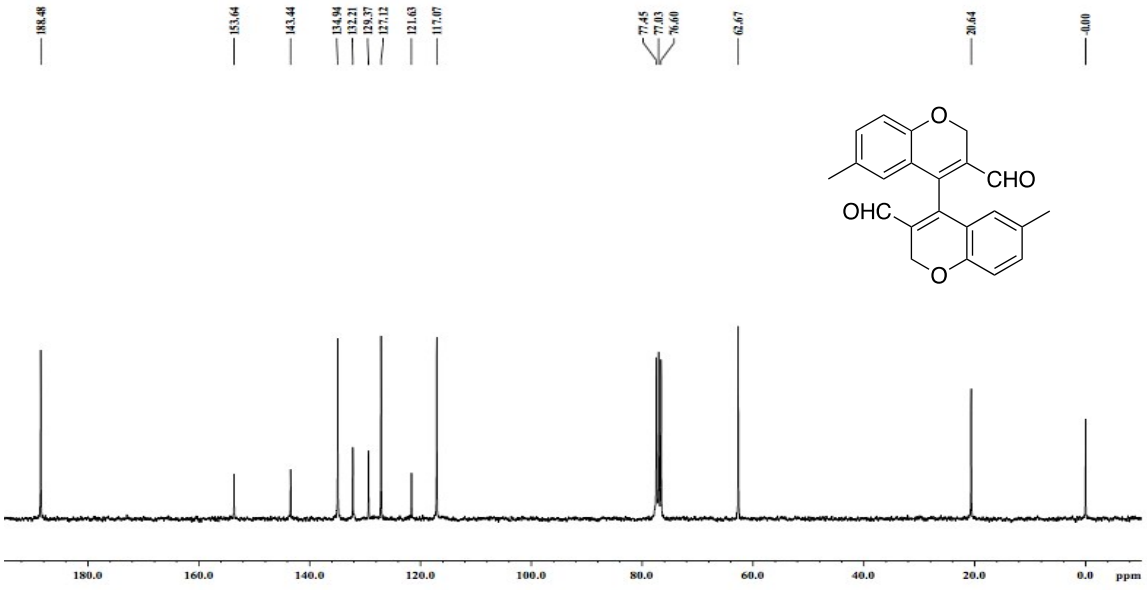
**S3.3.** $^{1}$H NMR of bichromene **6c**:



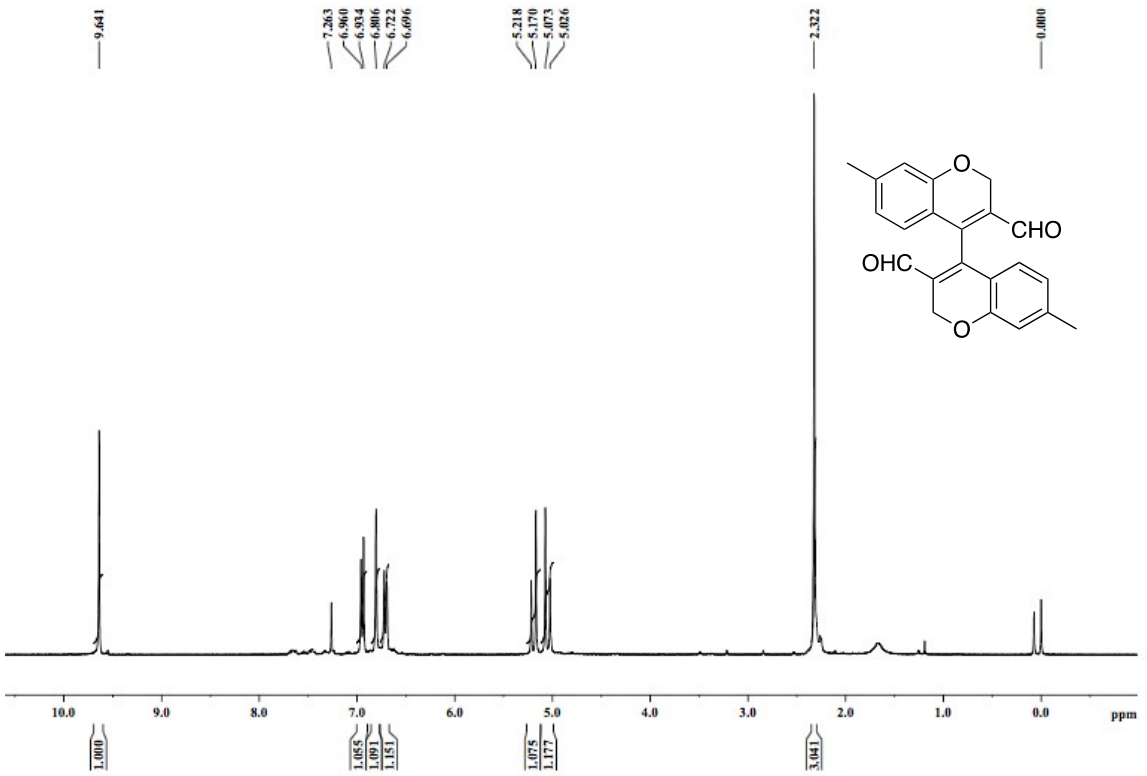

Expansion of $^{1}$H NMR of **6c**:



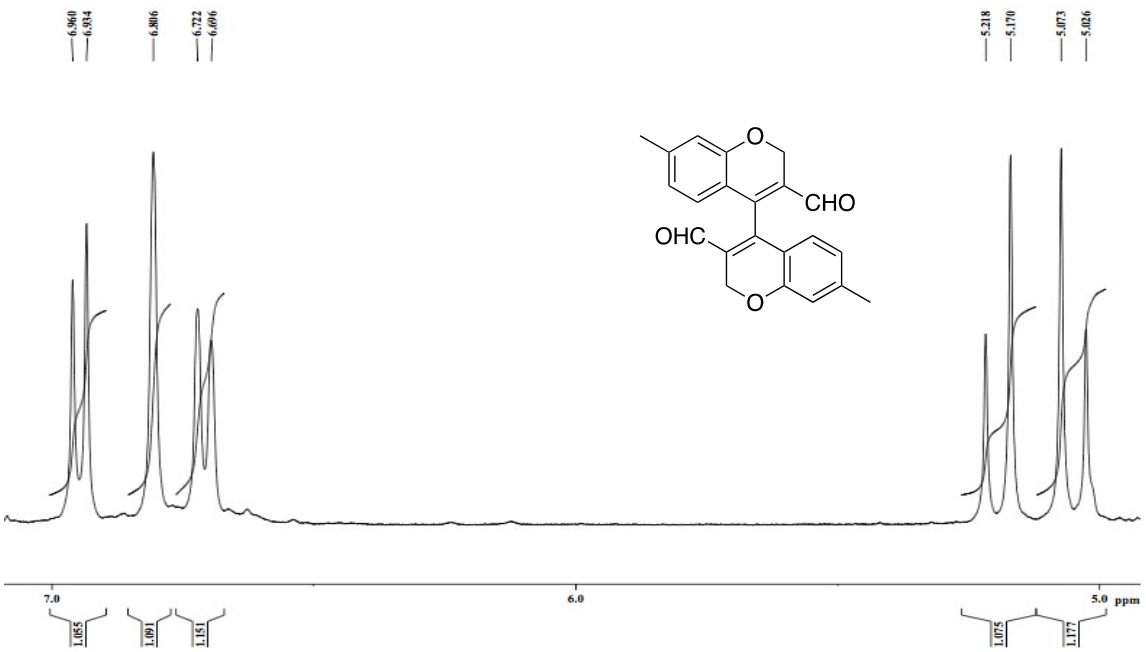
$^{13}$C NMR of of bichromene **6c**:



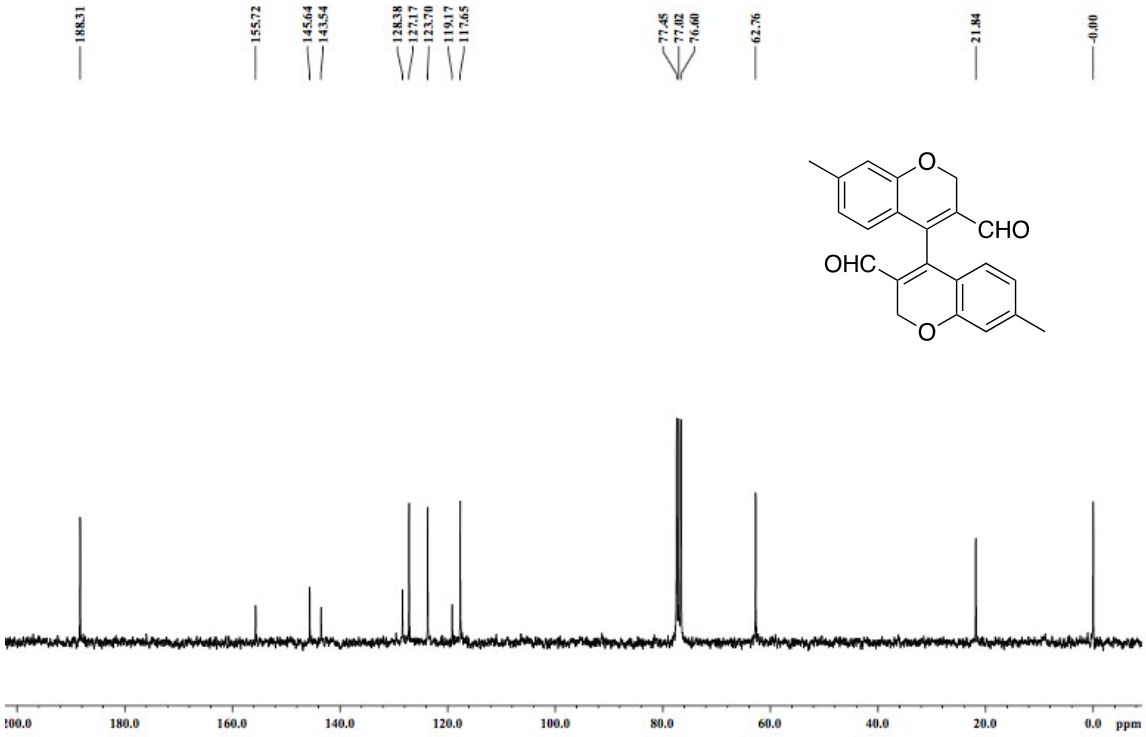

**S3.4** $^{1}$H NMR of bichromene **6d**:



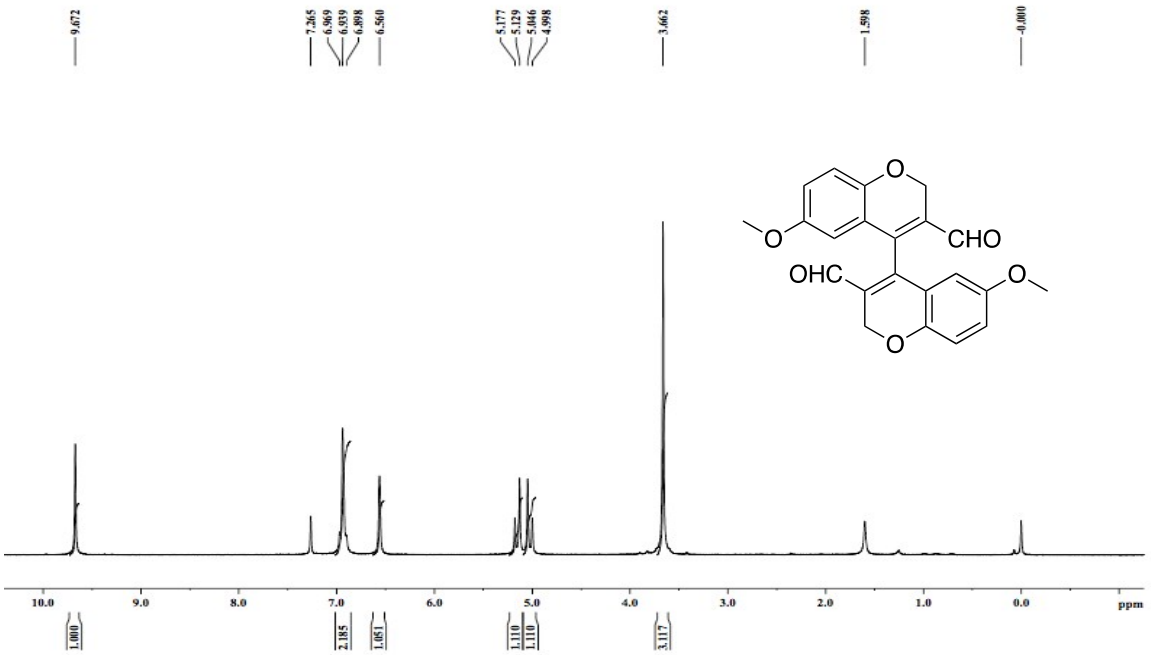
Expansion of $^{1}H$ NMR of **6d**:



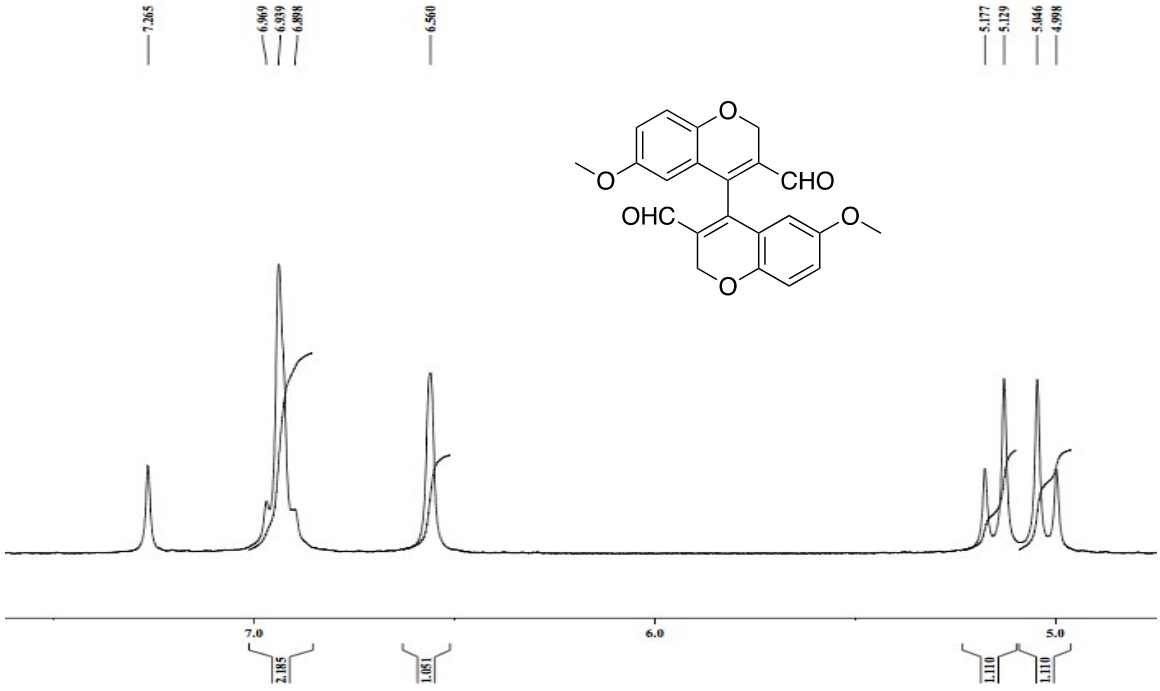

$^{13}C$ NMR of bichromene **6d**:



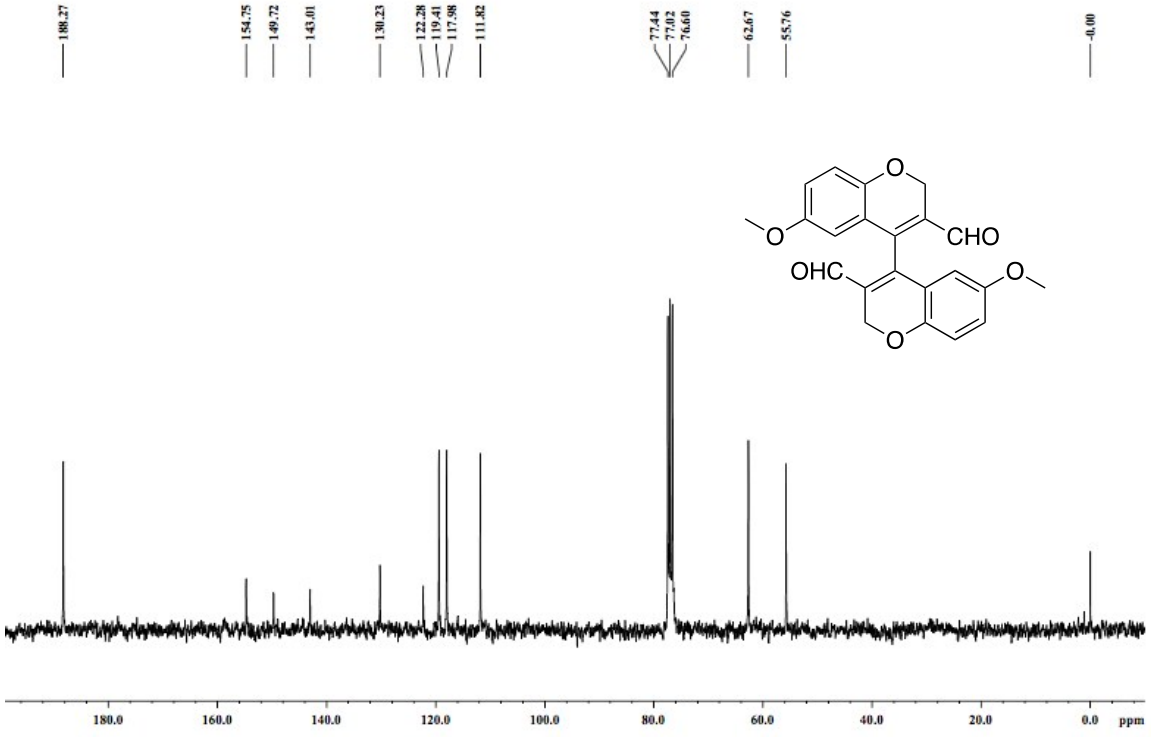
**S3.5** $^{1}$H NMR of bichromene **6e**:



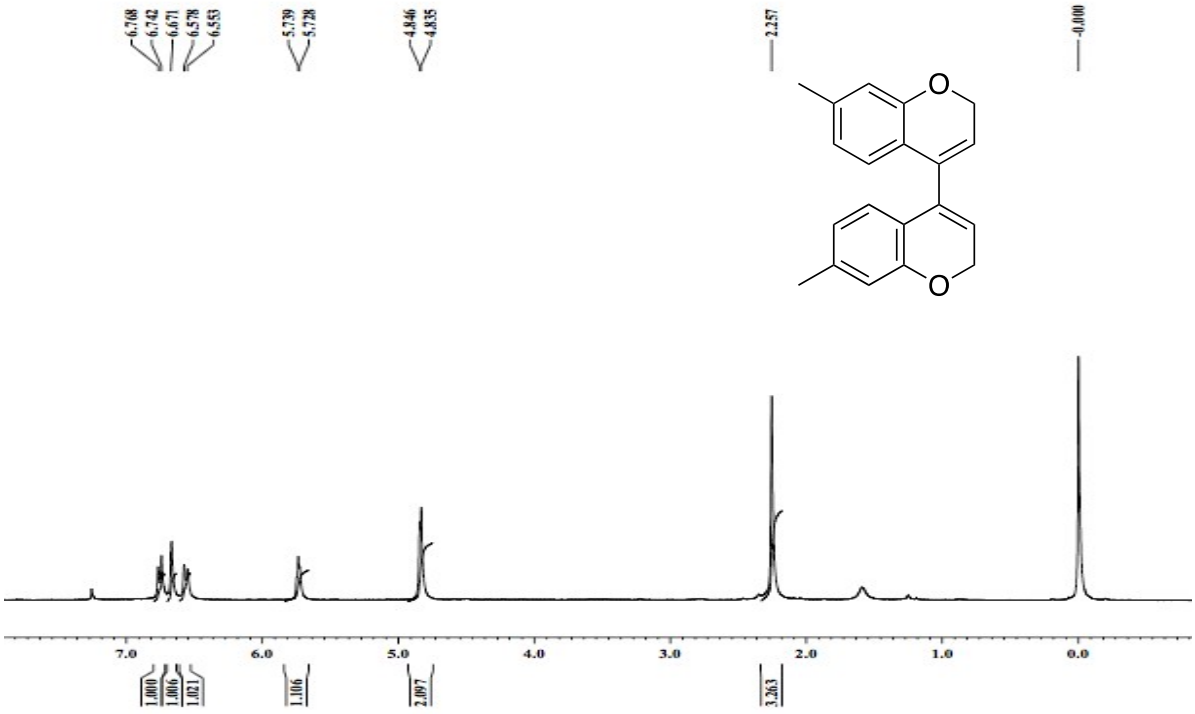

Expansion of $^{1}$H NMR of **6e**:



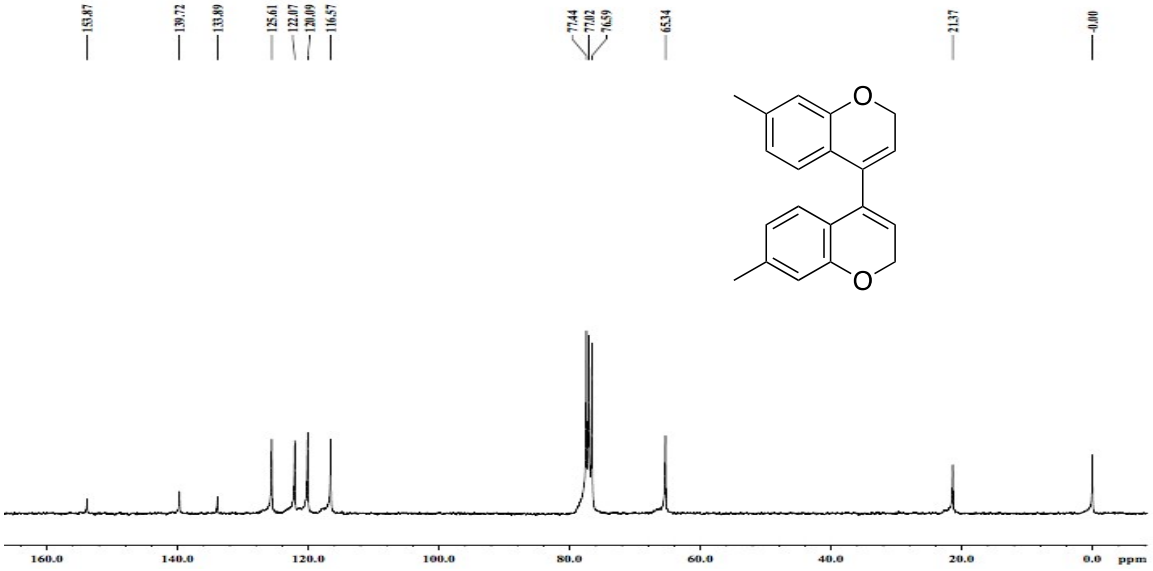
$^{13}$C NMR of bichromene **6e**:



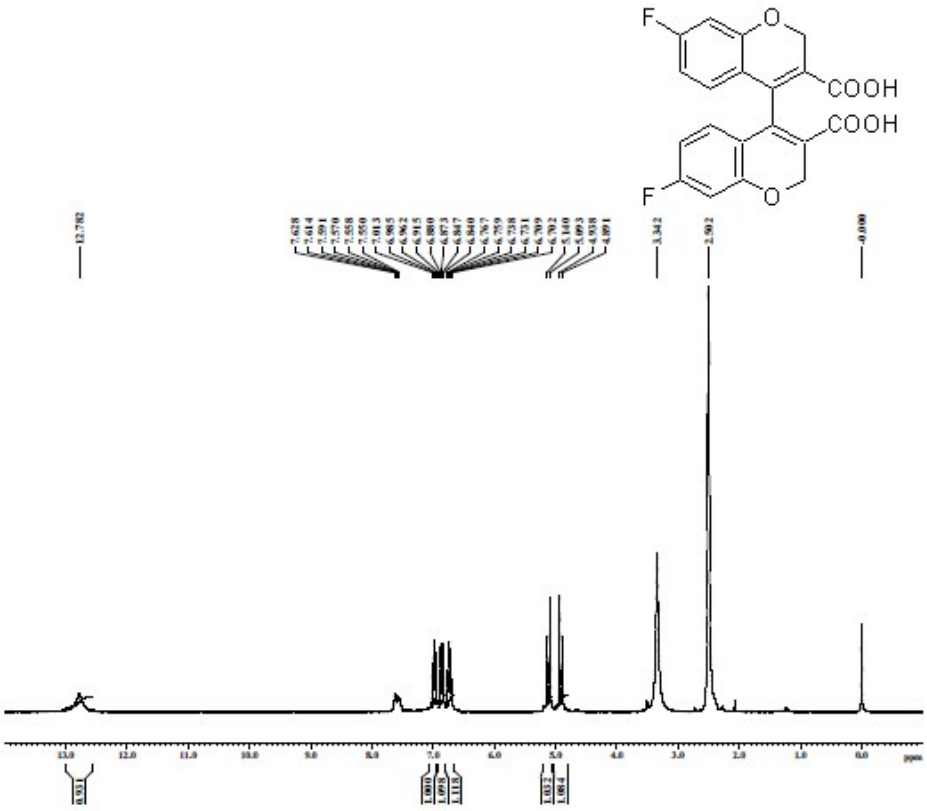

**S3.6** $^{1}$H NMR of bichromene **6f**:



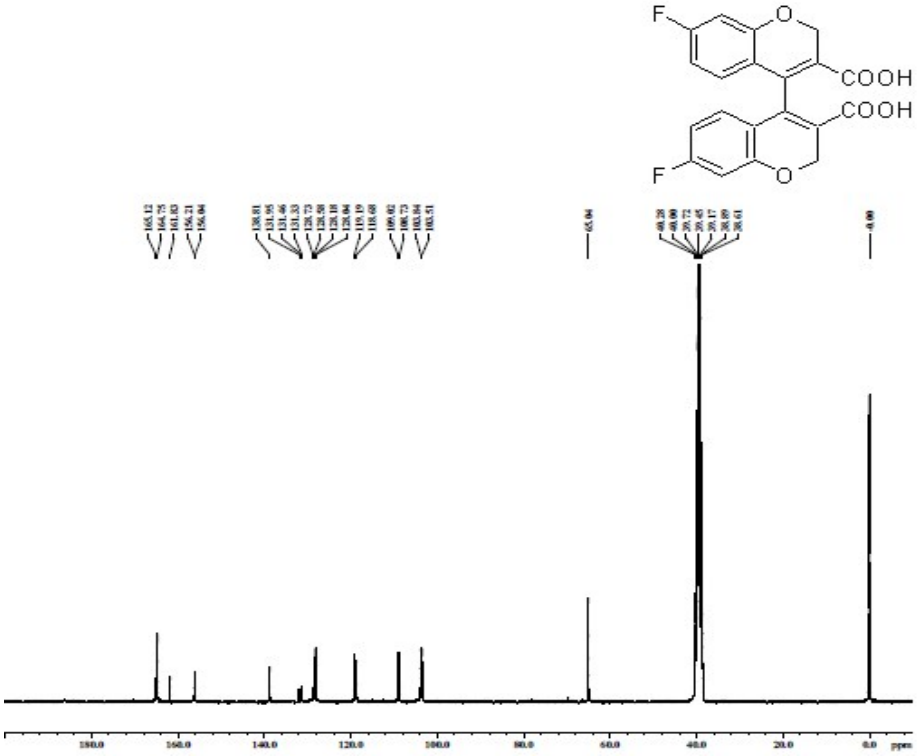
$^{13}$C NMR of bichromene **6f**:



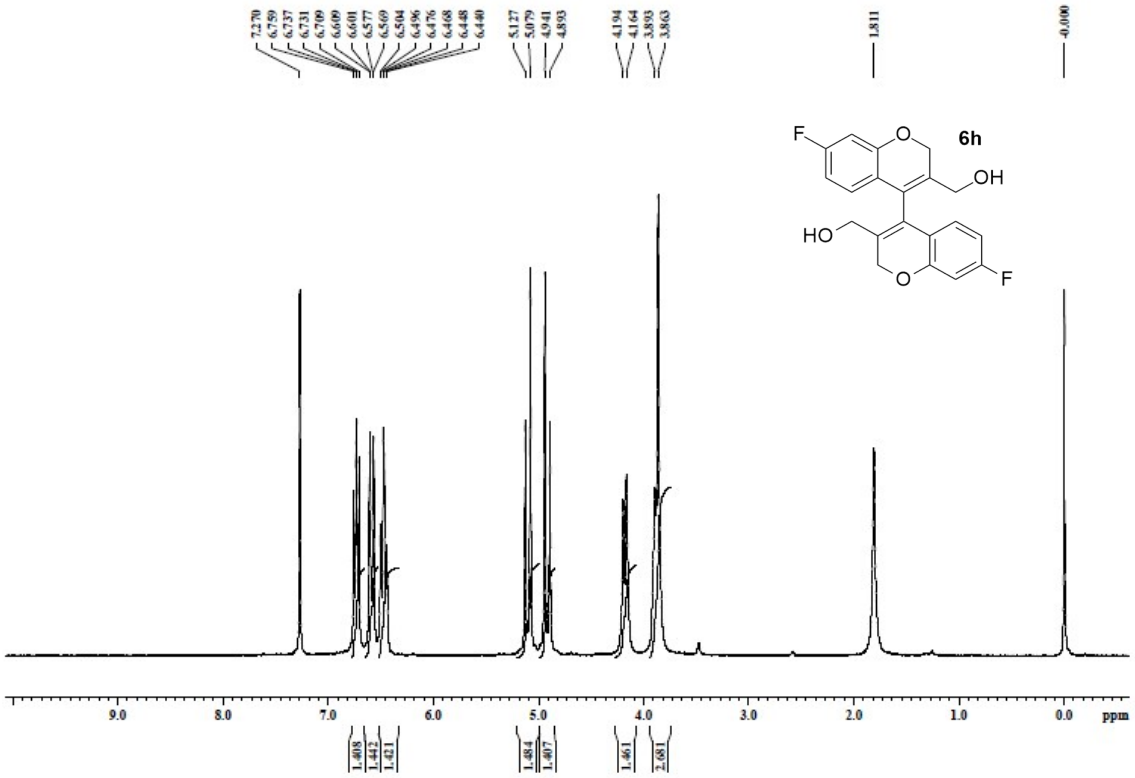

**S3.7** $^{1}$H NMR of bichromene **6g**:



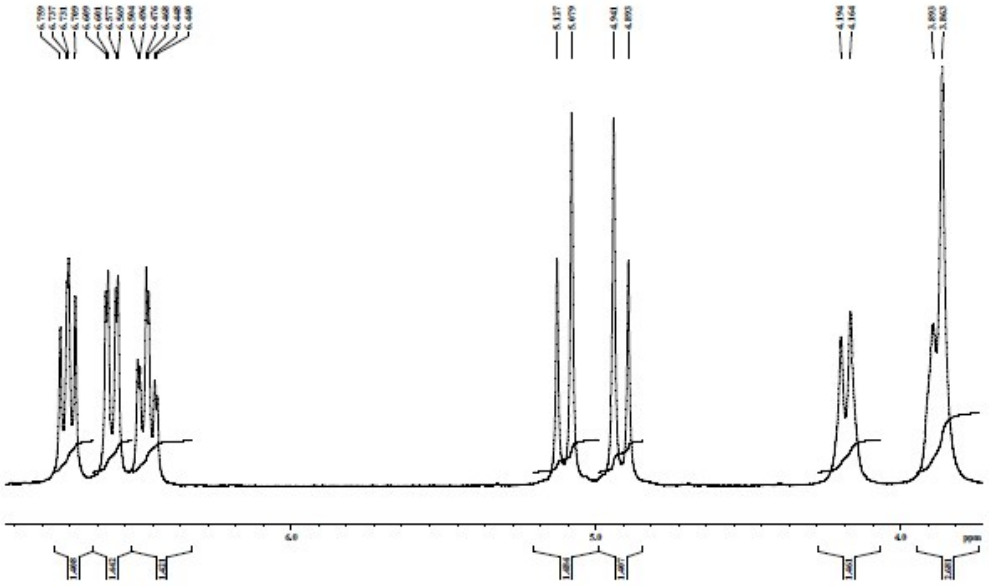
$^{13}$C NMR of bichromene **6g**:



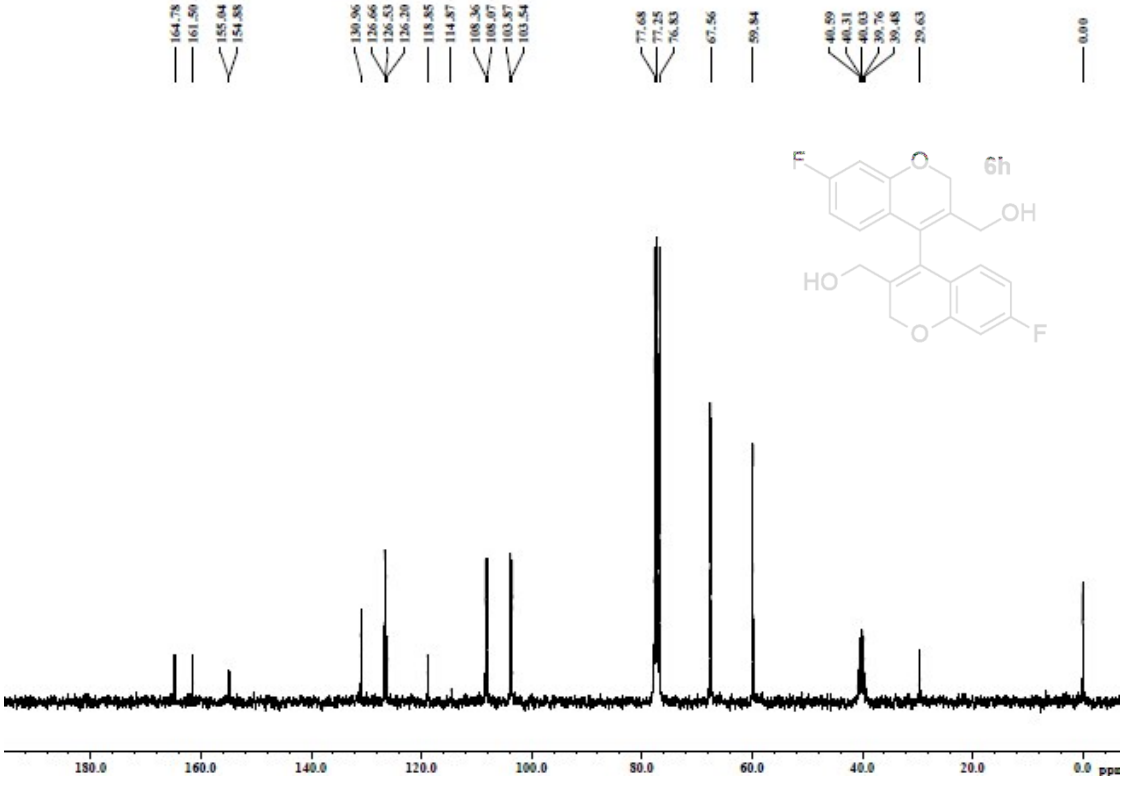

**S3.8** $^{1}$H NMR of bichromene **6h**:



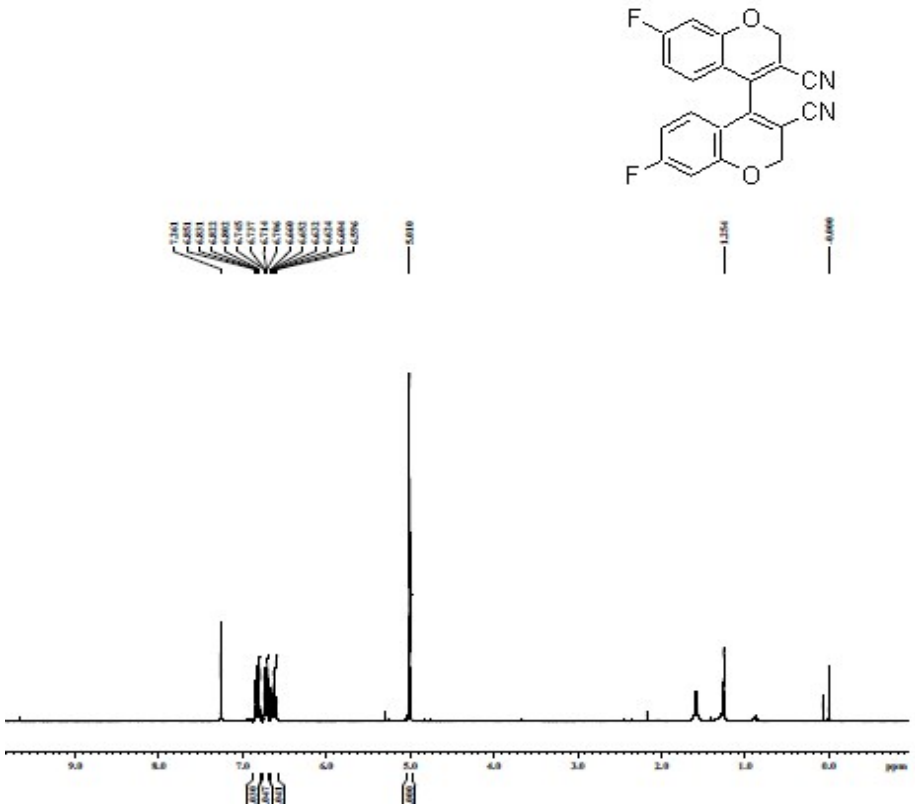
Partial $^{1}H$ NMR of **6h**:



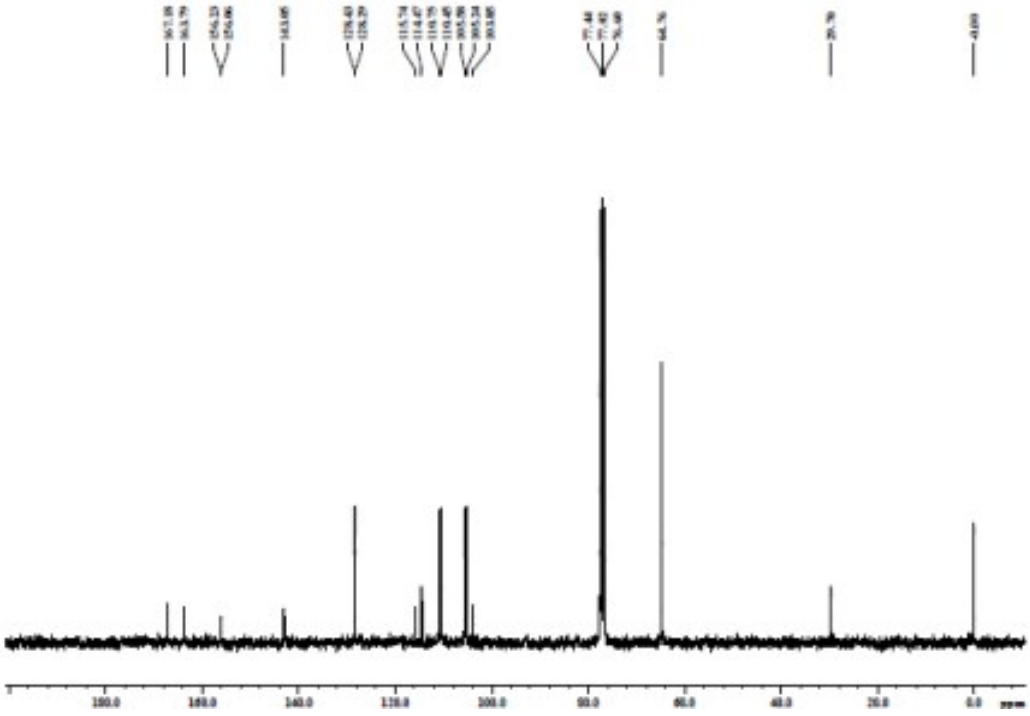
$^{13}C$ NMR of bichromene **6h**:



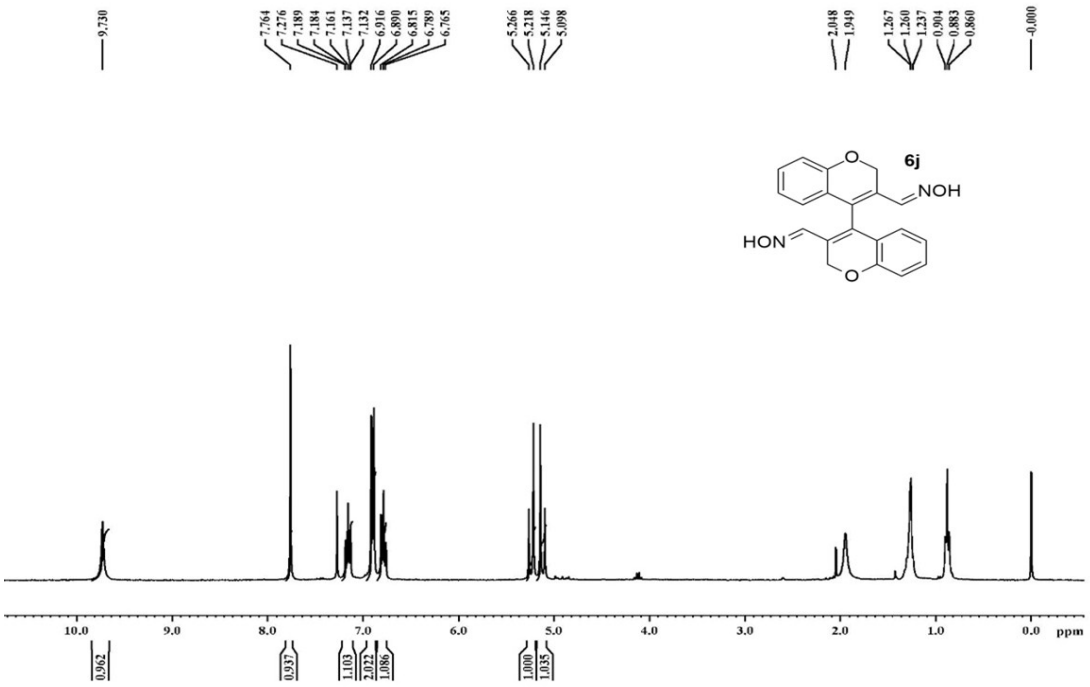
**S3.9** $^{1}$H NMR of bichromene **6i**:



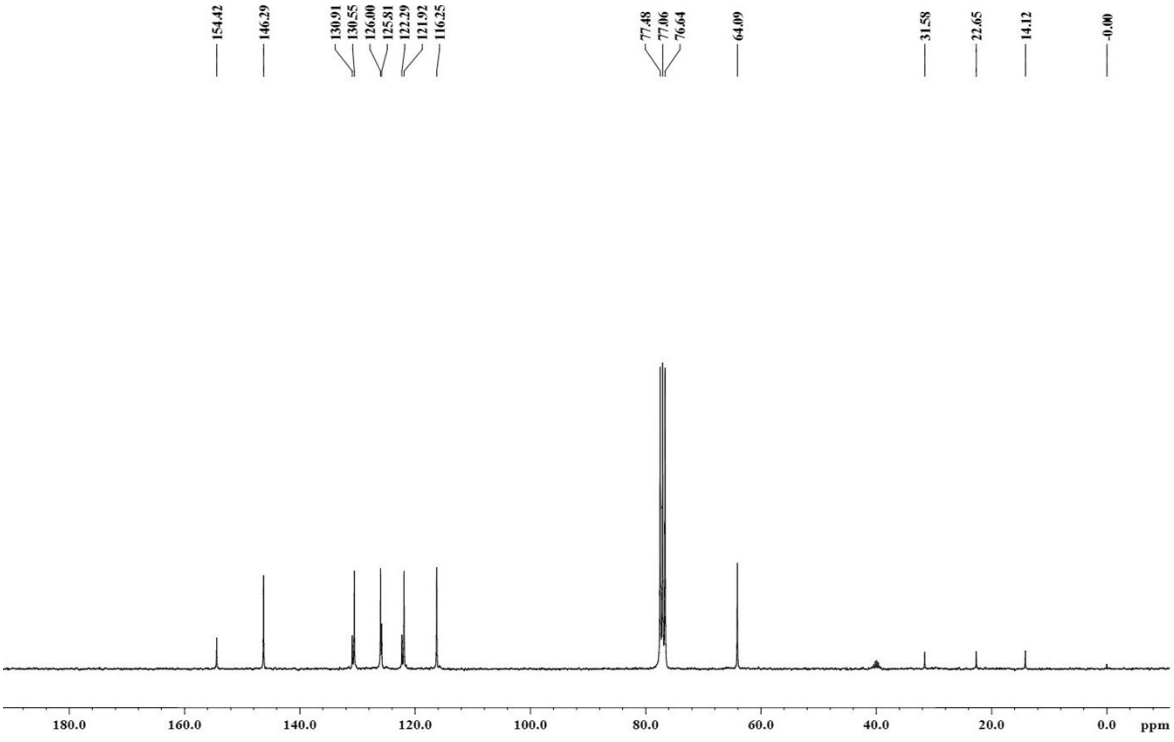

$^{13}$C NMR of of bichromene **6i**:



**S3.10** $^{1}$H NMR of bichromene **6j**:

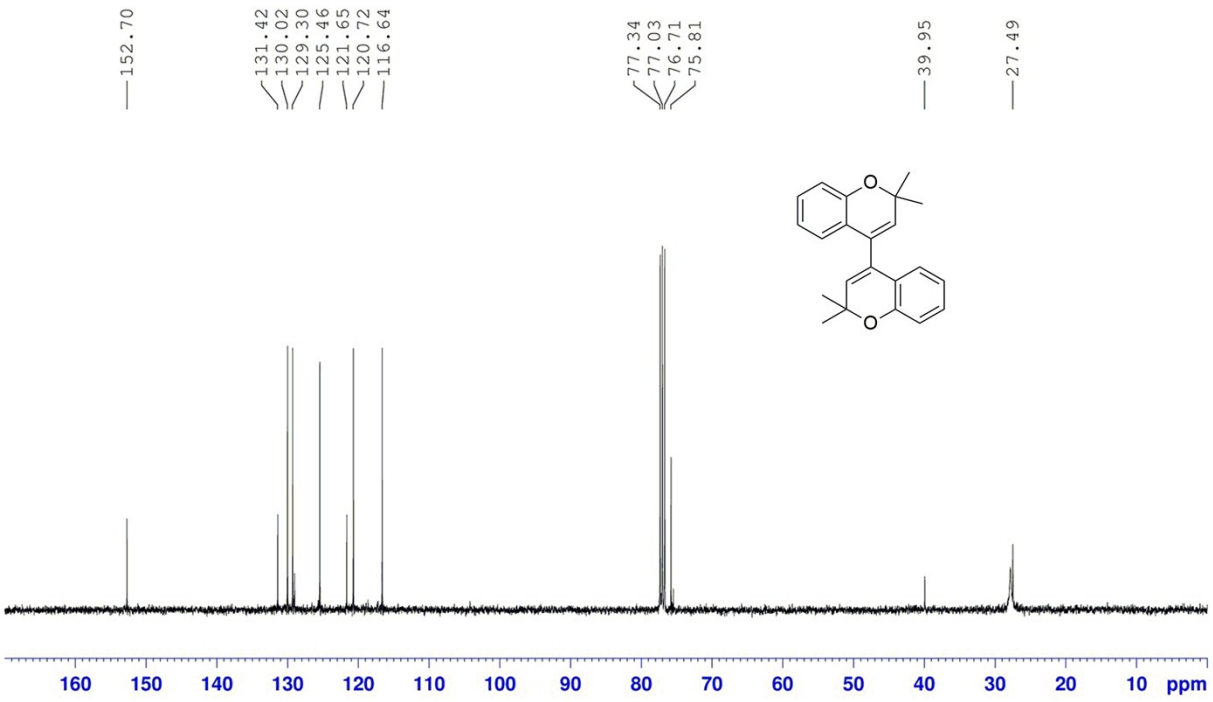



$^{13}$C NMR of bichromene **6j**:

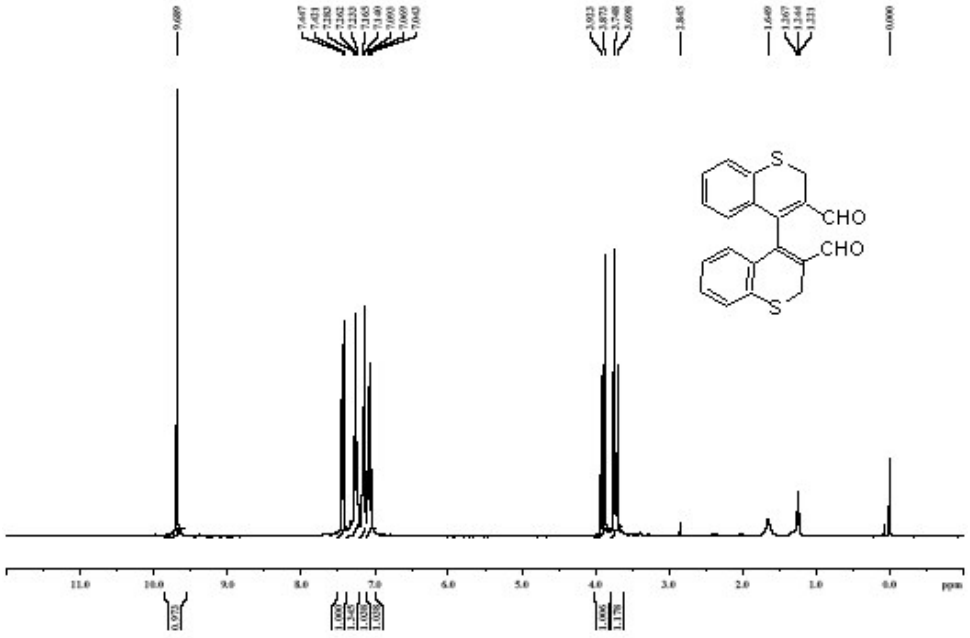


**S3.11** [1]H NMR of bichromene **6l**: (Refer section **S7.0**)

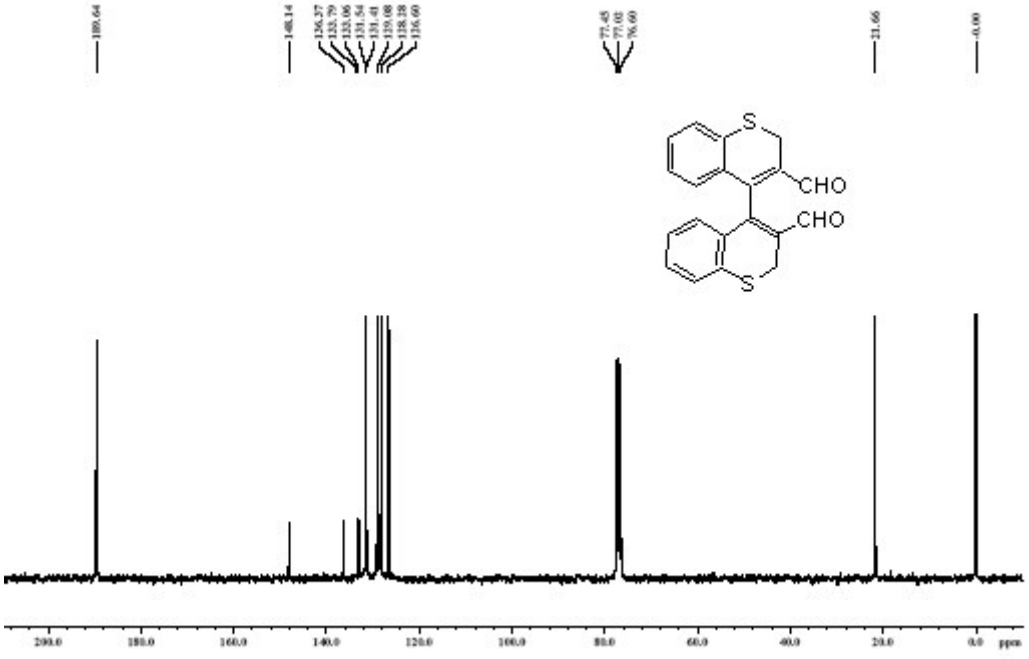
[13]C NMR of bichromene **6l**:



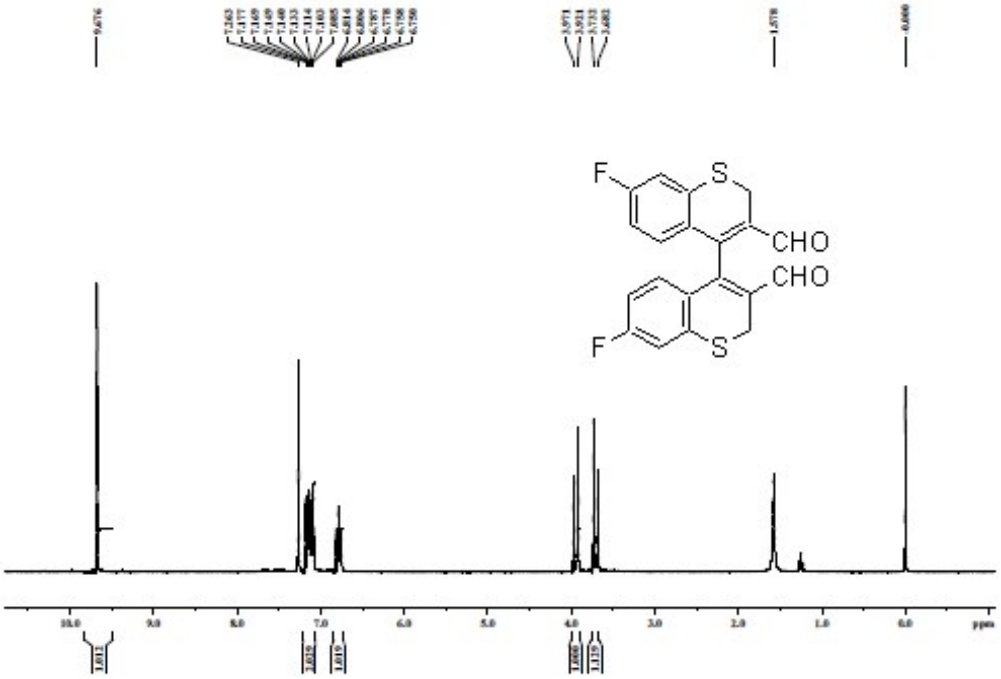

**S3.12** [1]H NMR spectrum of **7a**:



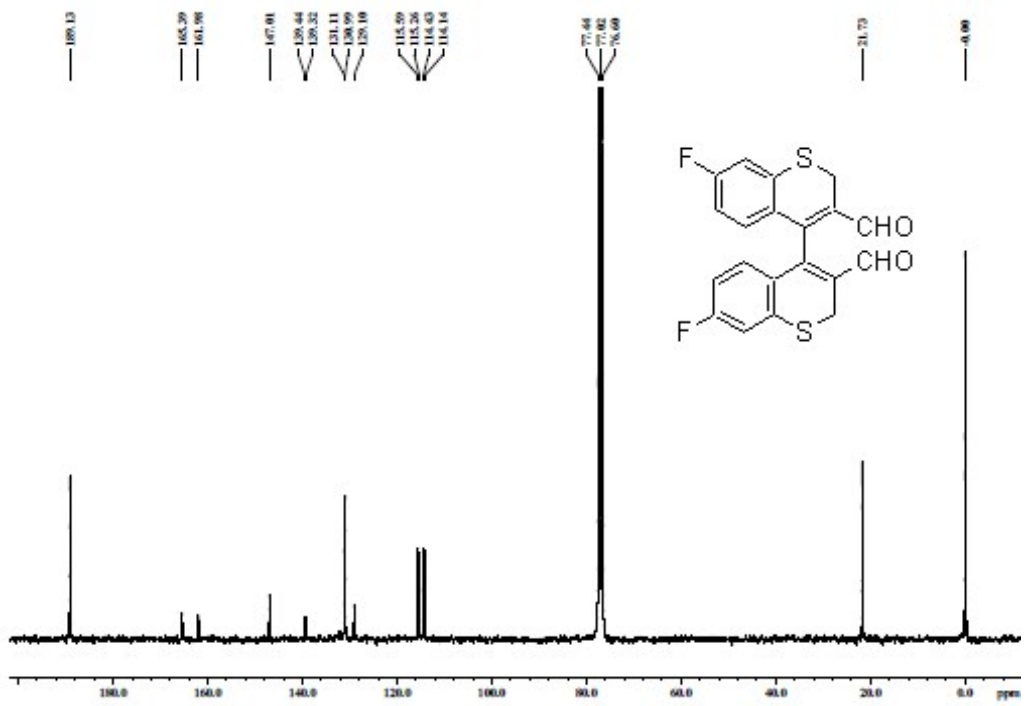
$^{13}$C NMR spectrum of **7a:**



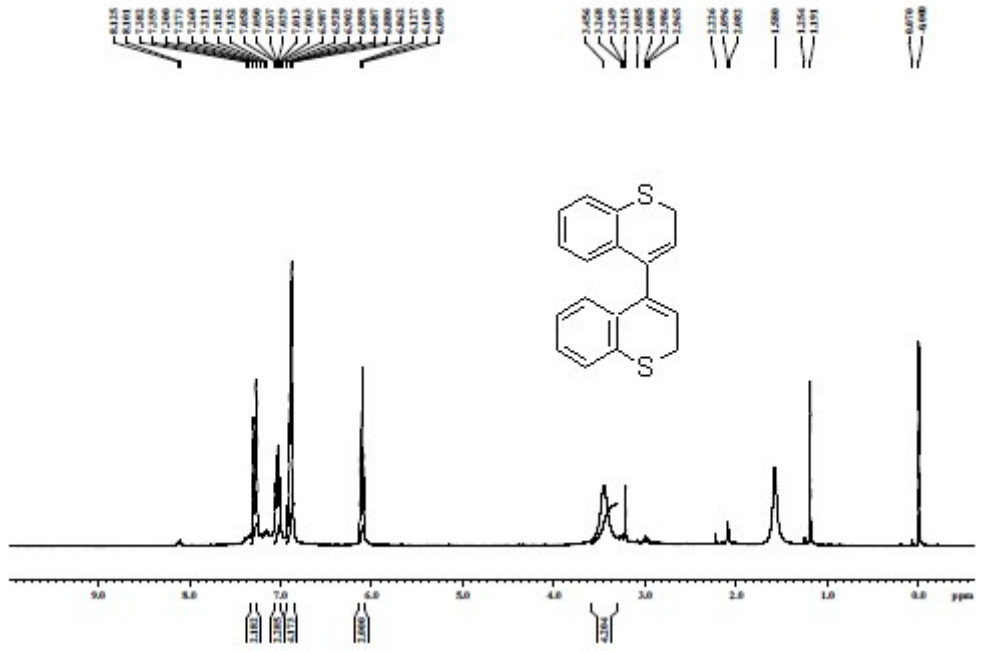

**S3.13** $^{1}$H NMR spectrum of **7b**



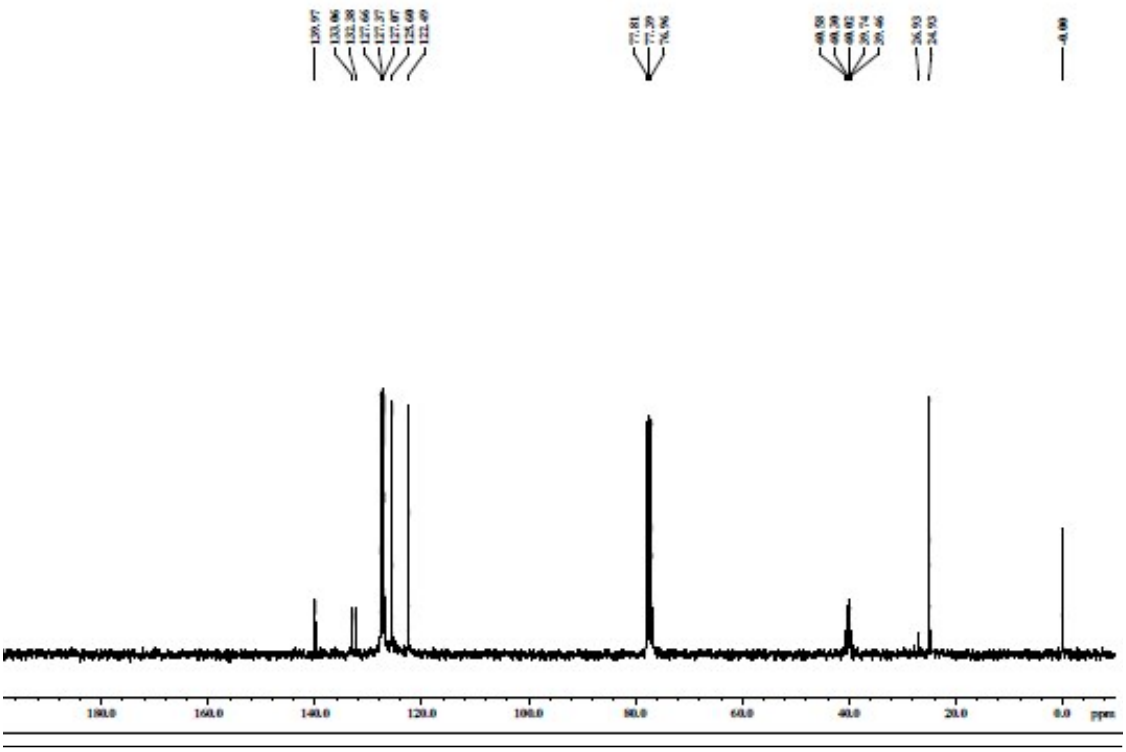
$^{13}$C NMR spectrum of **7b**



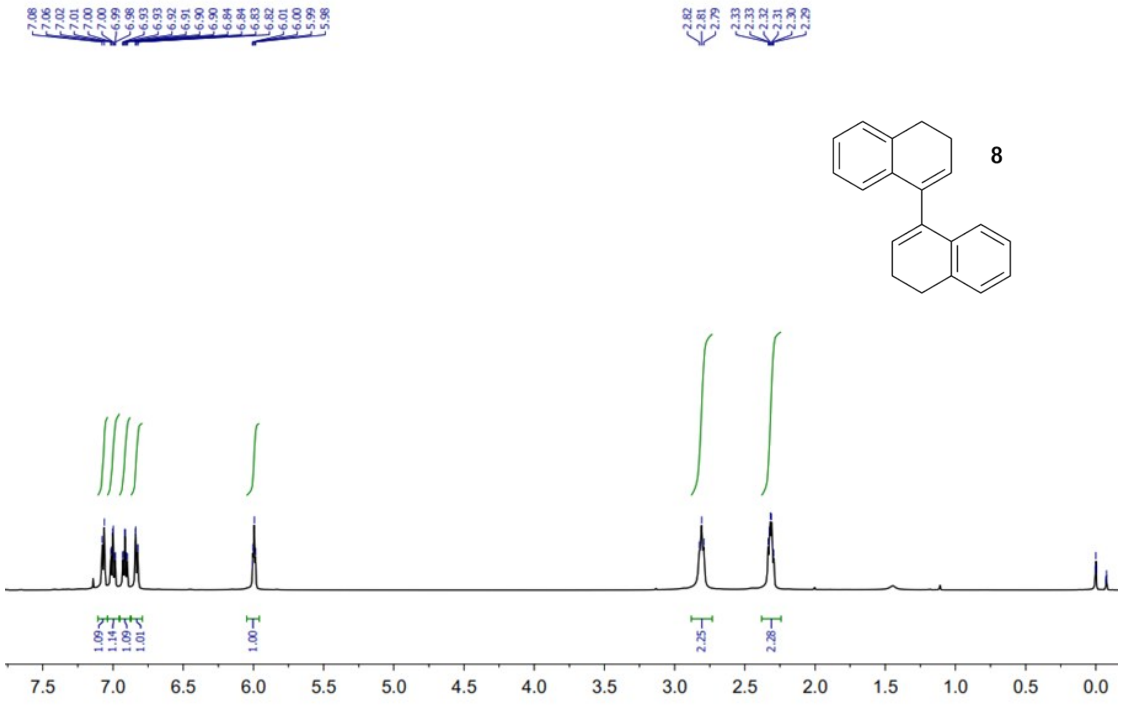

**S3.14** $^{1}$H NMR spectrum of bithiochromene **7c**:



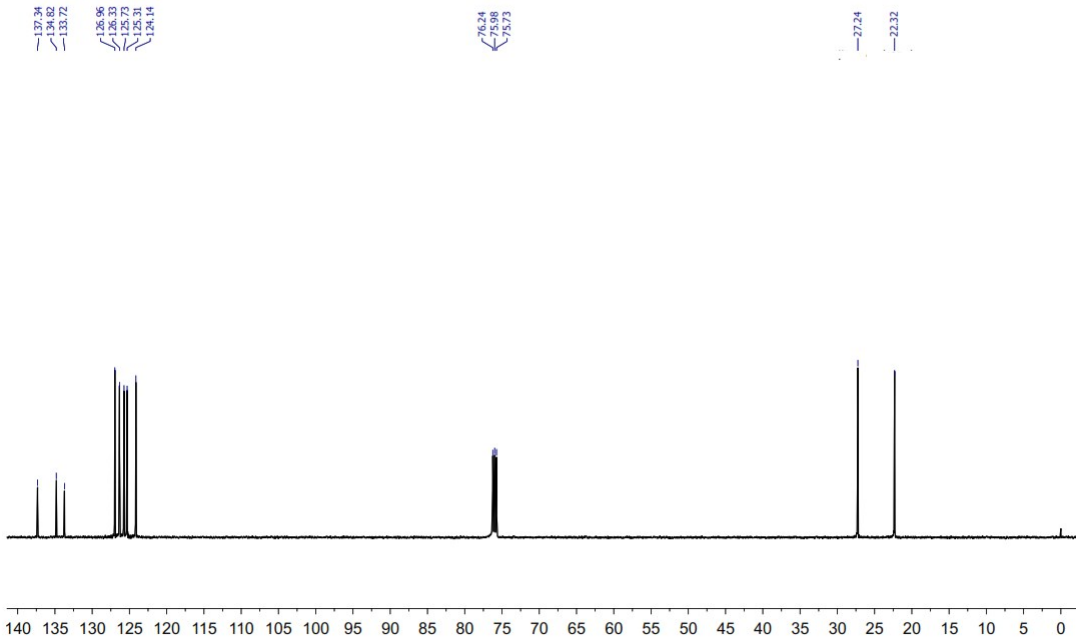
$^{13}$C NMR spectrum of **7c**



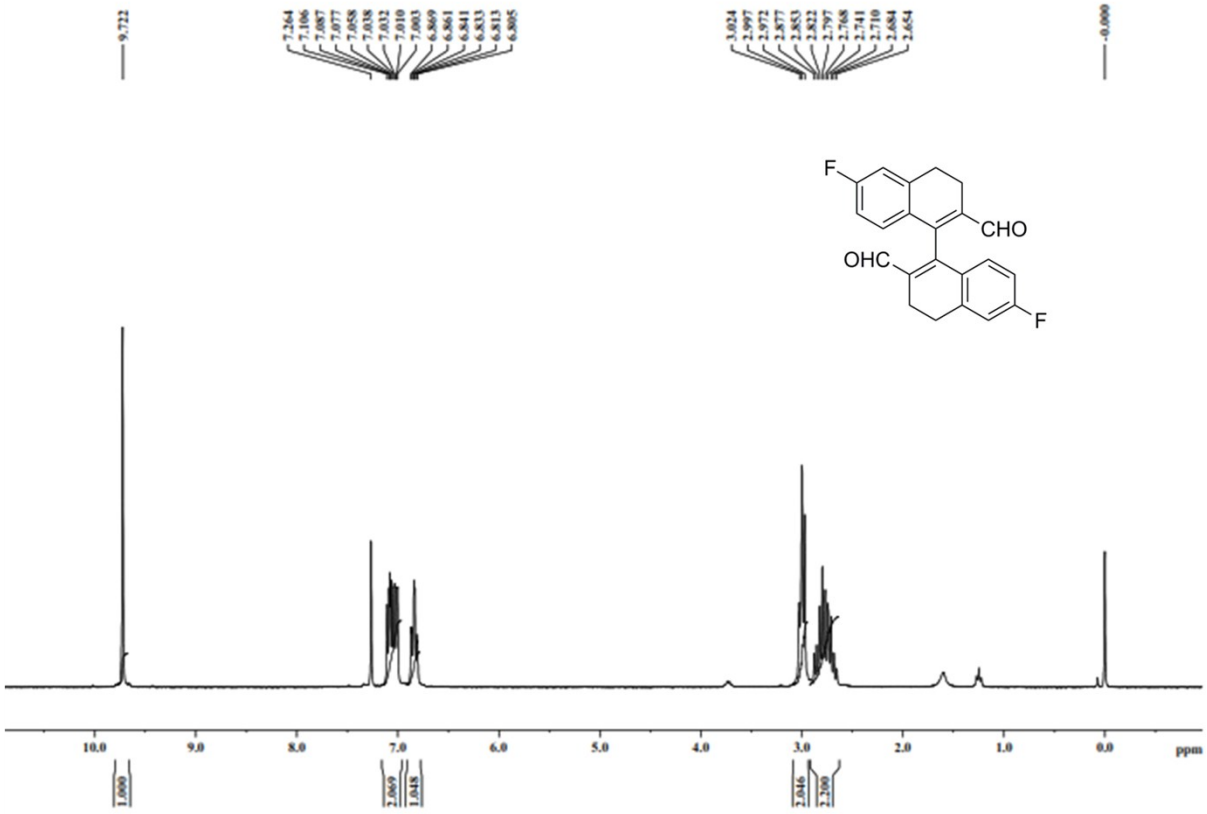
**S3.15** $^{1}$H NMR spectrum of **8**.



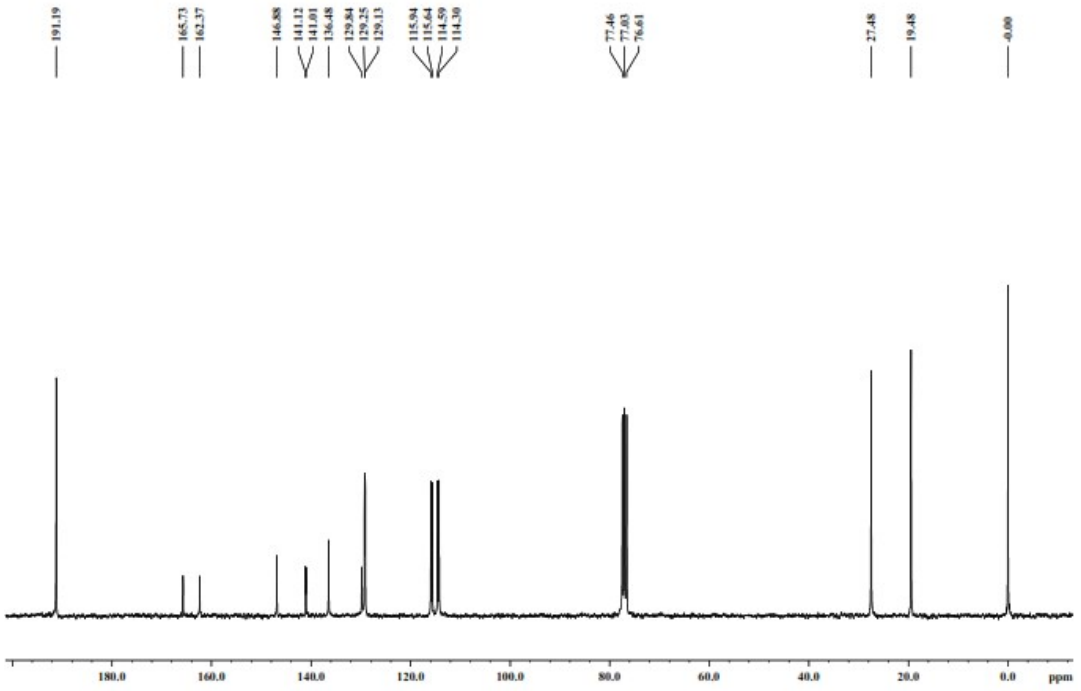
$^{13}$**C** NMR spectrum of **8**.



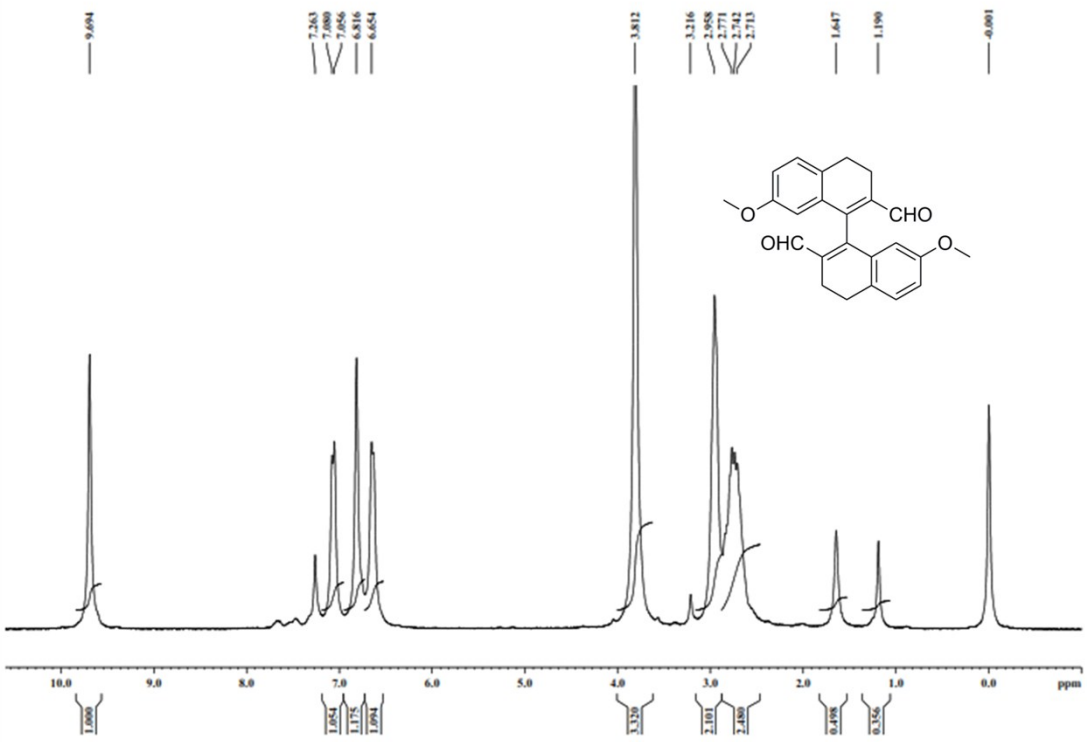

**S3.16** $^{1}$H NMR spectrum of **8a**:



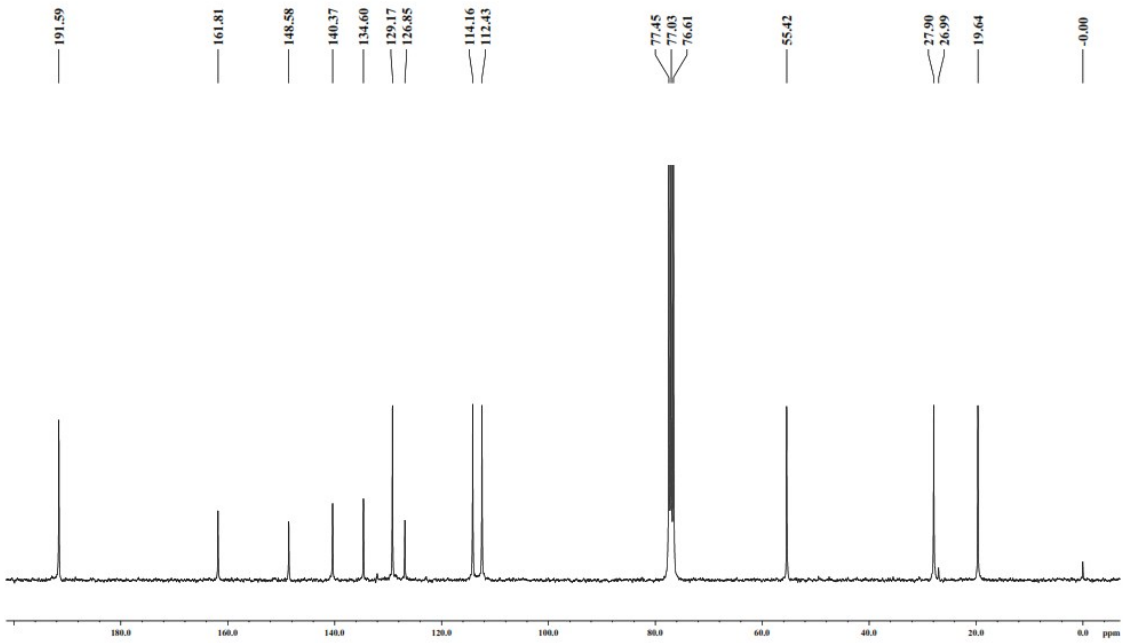
$^{13}$C NMR spectrum of **8a**



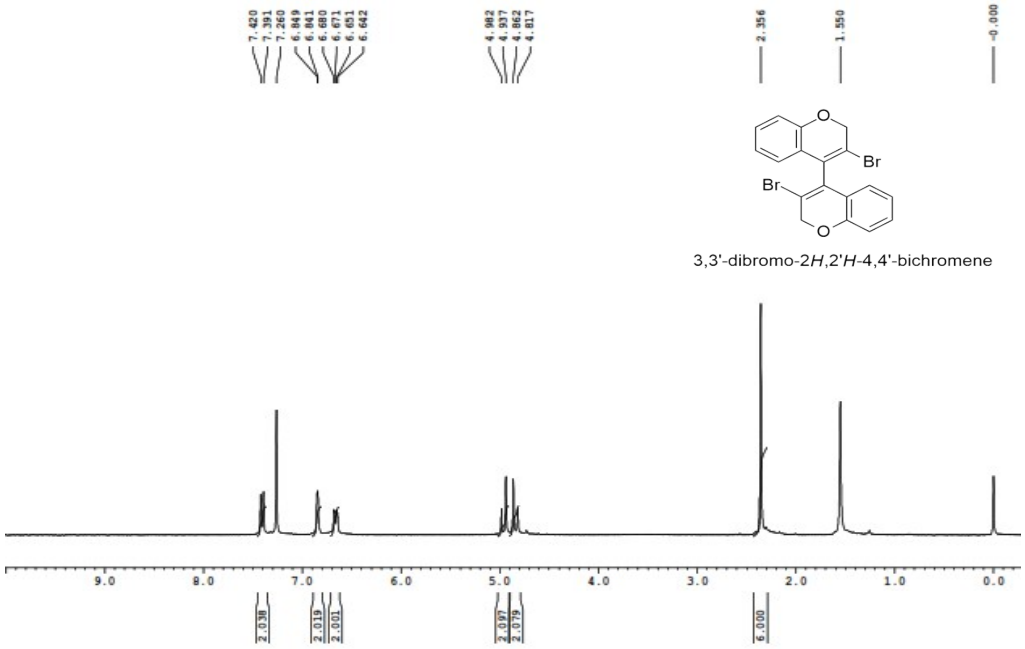

**S3.17** $^{1}$H NMR spectrum of **8b**:



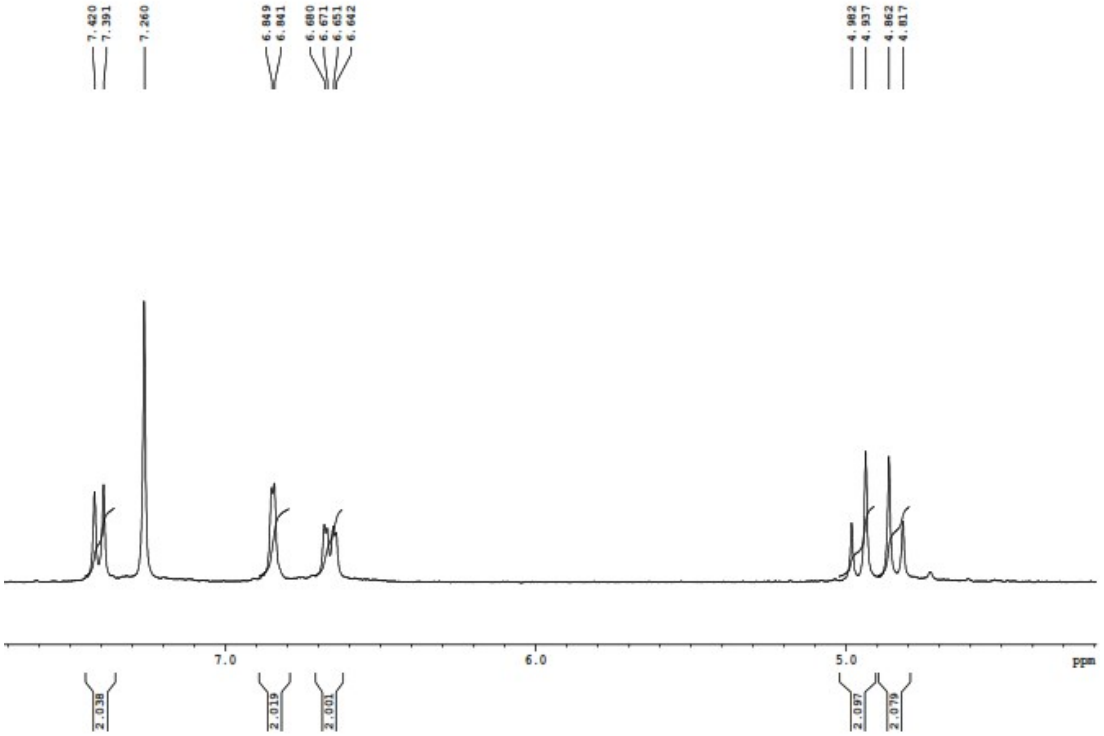
$^{13}$C NMR spectrum of **8b**




**S3.18** $^{1}$H NMR of **12**



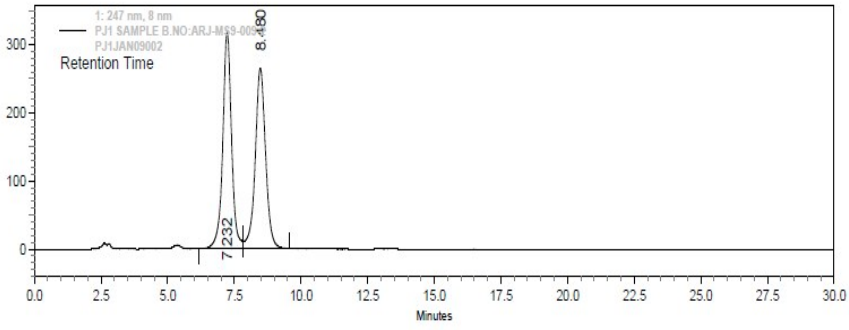
Expansion $^{1}$H NMR of **12**




**S4.0 Chiral stationary phase HPLC analysis:**

**S4.1** Chiral HPLC analysis of **6b:**

Column type: **AD-H**, hexane/IPA (9:1), Flow rate: 0.5 mL/min. Retention time: 30 mins

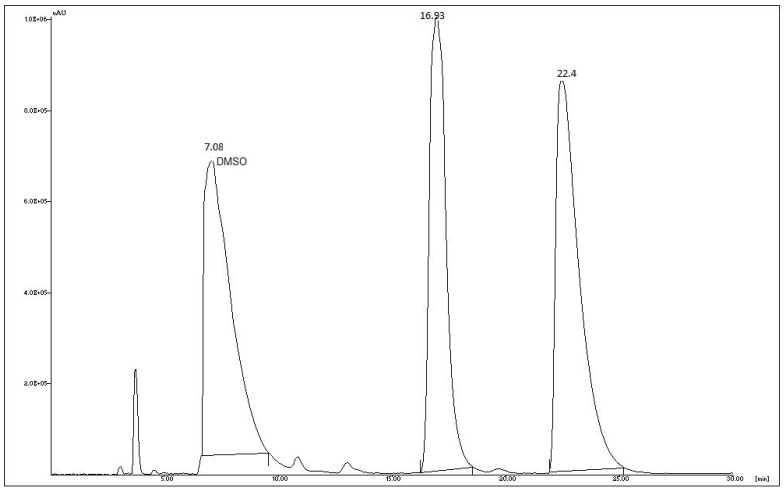



1: 247 nm, 8 nm

| Pk # | Retention Time | Area | Area Percent | Resolution | Asymmetry |
|---|---|---|---|---|---|
| 1 | 7.232 | 7278217 | 50.42 | 0.00 | 1.00 |
| 2 | 8.480 | 7156057 | 49.58 | 1.79 | 0.96 |
| Totals | | 14434274 | 100.00 | | |

**S4.2** Chiral HPLC analysis of **6e:**

Column type: AD-H, hexane/IPA (9:1), Flow rate: 1.0 mL/min. Retention time: 30 mins



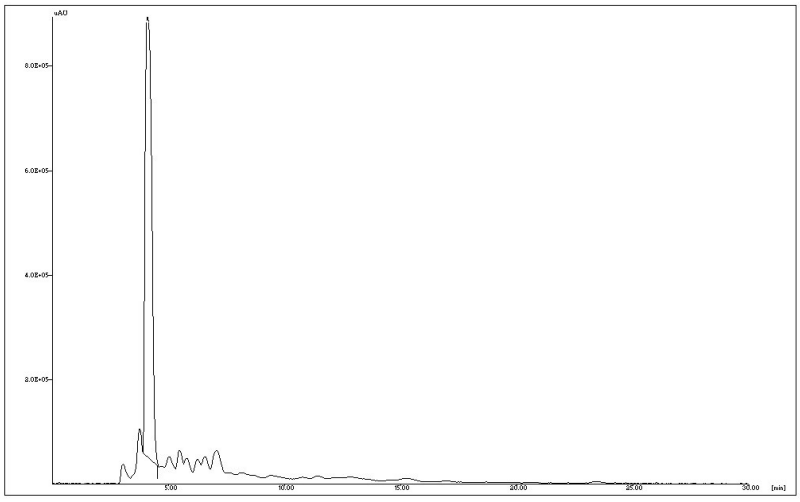

| PK# | Retention time | Area | Area Percent |
|---|---|---|---|
| 1 | 7.080 | 50677608.23 | 31.876 |
| 2 | 16.933 | 48794364.829 | 30.691 |
| 3 | 22.413 | 59513259.287 | 37.433 |

Total Area of Peak = 158985232.350 [uAU.Sec]

Note: The peak at RT 7.08 is due to DMSO solvent which was added to improve solubility of the compound.

**S4.3** Chiral HPLC analysis of **6f:**

Column type: AD-H, hexane/IPA (9:1), Flow rate: 1.0 mL/min. Retention time: 30 mins

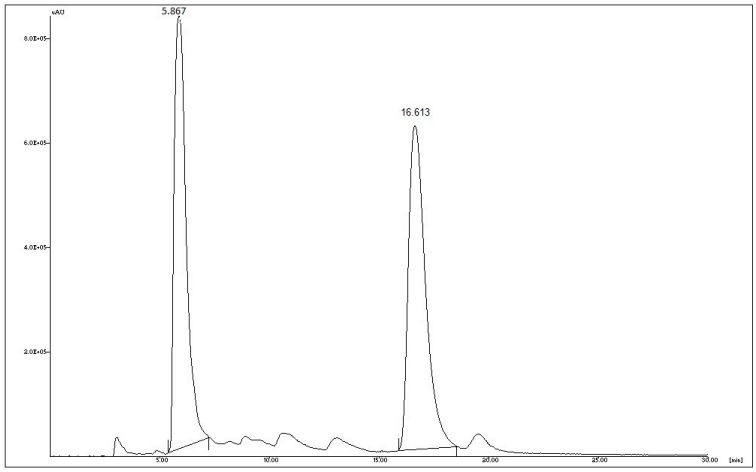



| PK# | Retention time | Area | Area Percent |
|---|---|---|---|
| 1 | 4.093 | 14799428.221 | 100.000 |

Total Area of Peak = 14799428.221 [uAU.Sec]

**S4.4** Chiral HPLC analysis of **6g:**

Column type: AD-H, hexane/IPA (9:1), Flow rate: 1.0 mL/min. Retention time: 30 mins

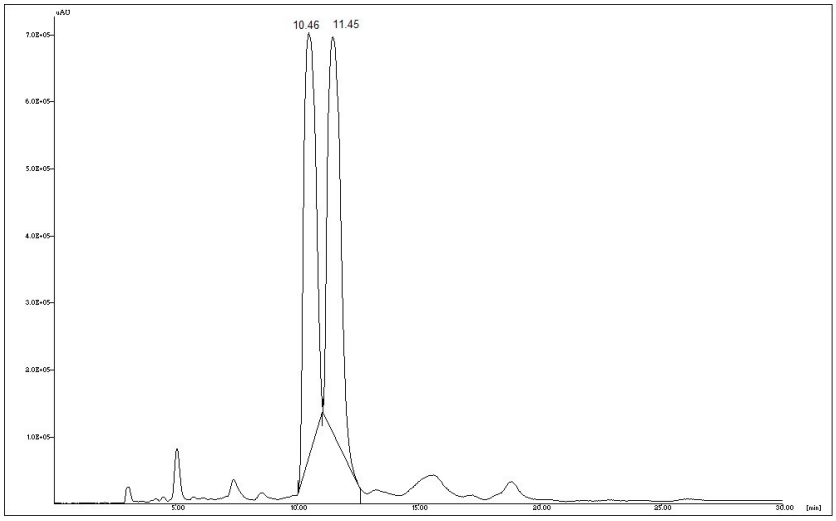



| PK# | Retention time | Area | Area Percent |
|---|---|---|---|
| 1 | 5.867 | 30035802.048 | 48.261 |
| 2 | 16.613 | 32199739.280 | 51.739 |

Total Area of Peak = 62235541.327 [uAU.Sec]

**S4.5** Chiral HPLC analysis of **6h:**

Column type: AD-H, hexane/IPA (9:1), Flow rate: 1.0 mL/min. Retention time: 30 mins.

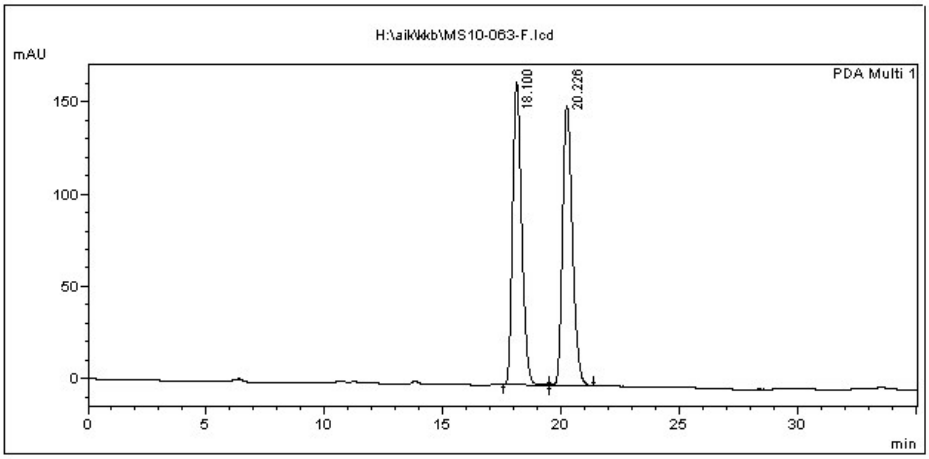



| PK# | Retention time | Area | Area Percent |
|---|---|---|---|
| 1 | 10.467 | 20412045.904 | 49.776 |
| 2 | 11.453 | 20595356.983 | 50.224 |

Total Area of Peak = 41007402.9 [uAU.Sec]

**S4.6** Chiral HPLC analysis of **6i:**

Column type: **AD-H**, hexane/IPA (9:1), Flow rate: 0.5 mL/min. Retention time: 40 mins



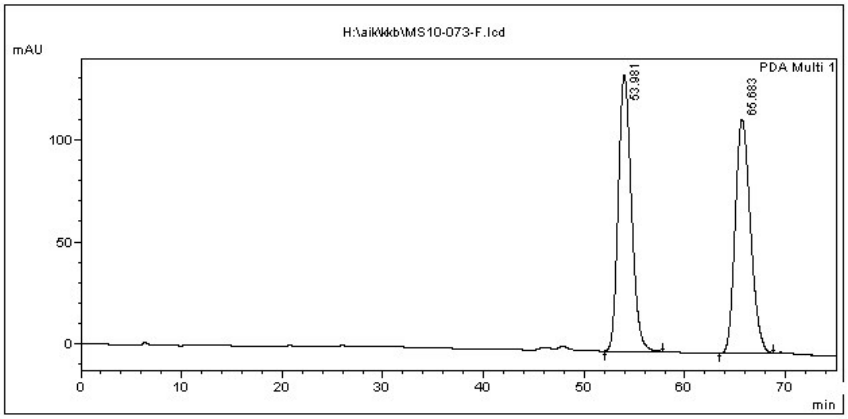

Peak Table

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 18.100 | 4367423 | 163674 | 49.875 | 51.975 |
| 2 | 20.226 | 4389279 | 151235 | 50.125 | 48.025 |
| Total | | 8756702 | 314910 | 100.000 | 100.000 |

**S4.7** Chiral HPLC analysis of compound **6j:**

Column type: **AD-H**, hexane/IPA (9:1), Flow rate: 0.5 mL/min. Retention time: 75 mins



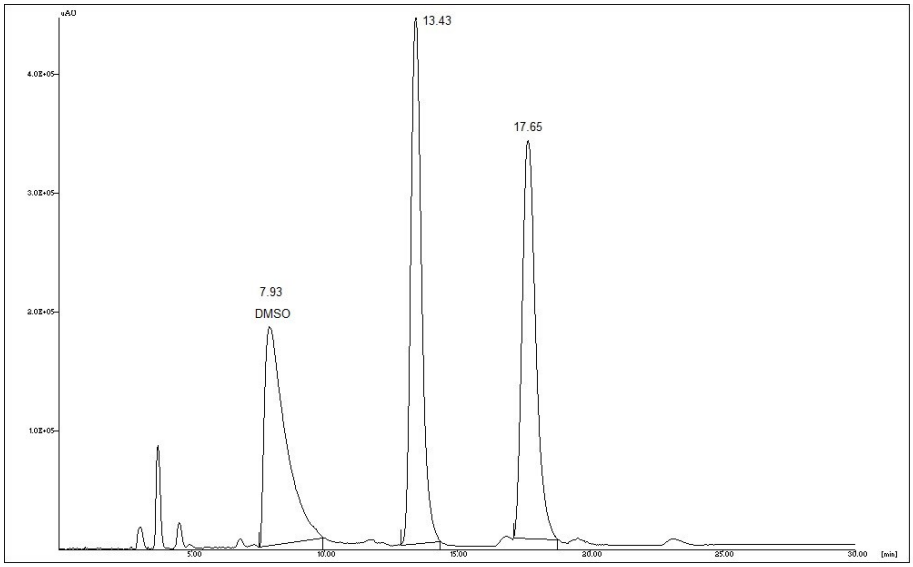

Peak Table

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 53.981 | 12265893 | 135067 | 50.382 | 54.138 |
| 2 | 65.683 | 12079814 | 114421 | 49.618 | 45.862 |
| Total | | 24345707 | 249488 | 100.000 | 100.000 |

**S4.8** Chiral HPLC analysis of **7a:**

Column type: AD-H, hexane/IPA (9:1), Flow rate: 1.0 mL/min. Retention time: 30 mins



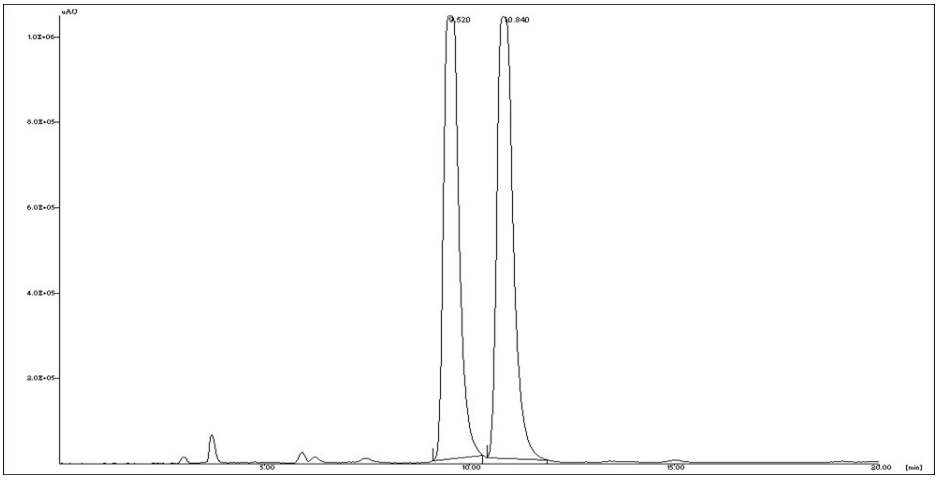

| PK# | Retention time | Area | Area Percent |
|---|---|---|---|
| 1 | 7.933 | 9731446.518 | 29.921 |
| 2 | 13.427 | 11563871.372 | 35.555 |
| 3 | 17.653 | 11228561.767 | 34.524 |

Total Area of Peak = 32523879.658 [uAU.Sec]

Note: The peak at RT 7.93 is due to DMSO solvent which was added to improve solubility of the compound.

## **S4.9** Chiral HPLC analysis of **8a:**

Column type: AD-H, hexane/IPA (9:1), Flow rate: 1.0 mL/min. Retention time: 30 min.

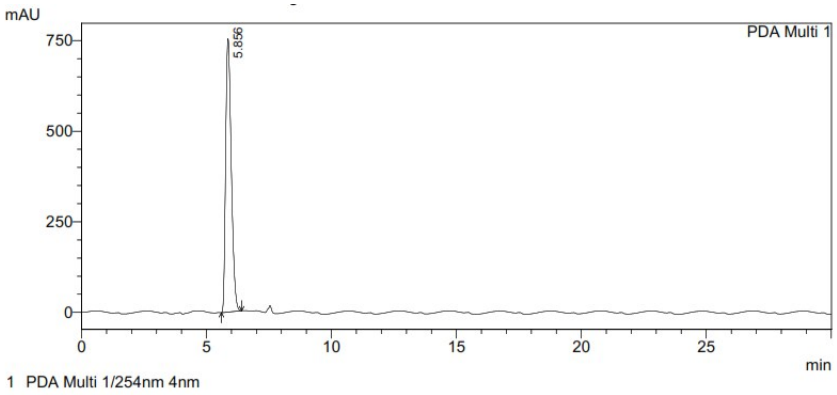


| PK# | Retention time | Area | Area Percent |
|---|---|---|---|
| 1 | 9.520 | 25868328.172 | 48.752 |
| 2 | 10.840 | 27193214.405 | 51.248 |

Total Area of Peak = 53061542.23 [uAU.Sec]

## S4.10 Chiral HPLC of 3,4,3',4'-tetrahydrobinaphthyl (8) using six different chiral columns.

Column type: **OD-H**

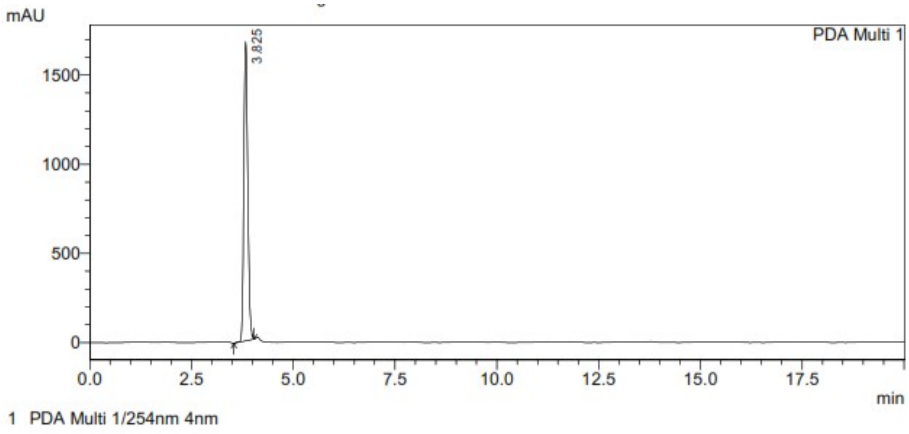



PeakTable

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.856 | 11807608 | 754352 | 100.000 | 100.000 |
| Total | | 11807608 | 754352 | 100.000 | 100.000 |

Column type: **AD-H**

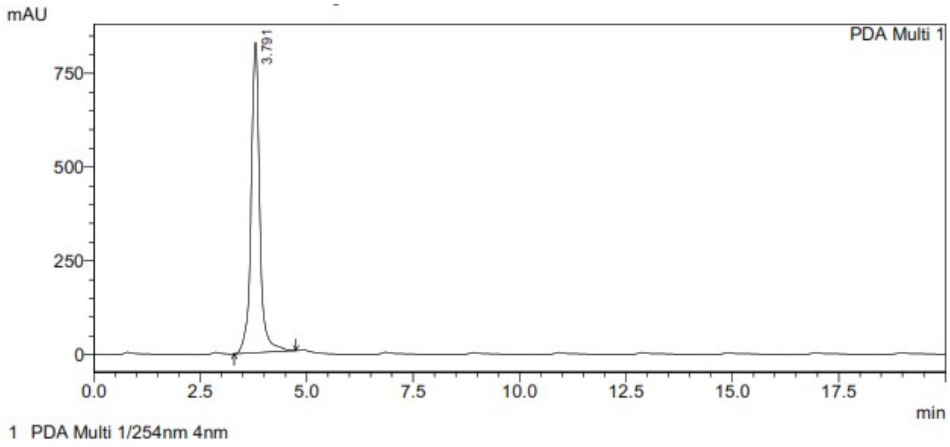



PeakTable

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 3.825 | 11428636 | 1677465 | 100.000 | 100.000 |
| Total | | 11428636 | 1677465 | 100.000 | 100.000 |

Column type: **AS-H**

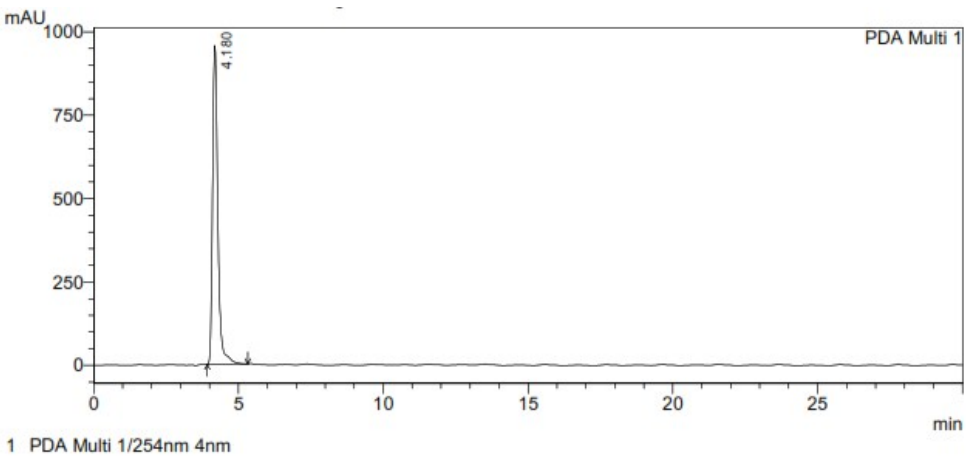



PeakTable

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 3.791 | 11748009 | 828377 | 100.000 | 100.000 |
| Total | | 11748009 | 828377 | 100.000 | 100.000 |

Column type: **OC-H**

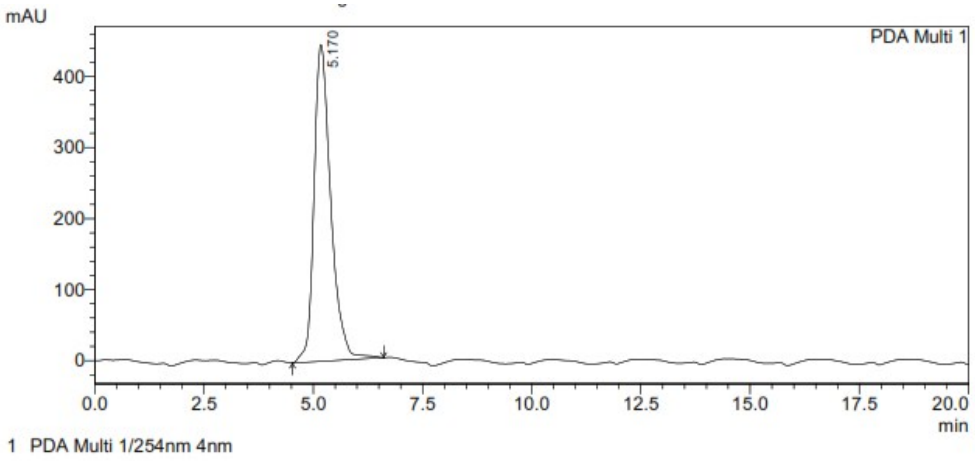



PeakTable

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 4.180 | 12101659 | 956111 | 100.000 | 100.000 |
| Total | | 12101659 | 956111 | 100.000 | 100.000 |

Column type: **OB-H**

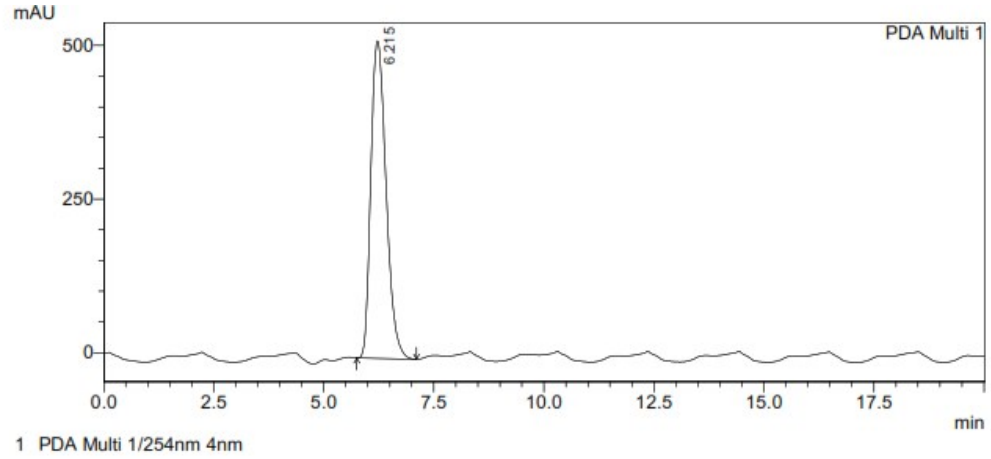



PeakTable

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 5.170 | 11914225 | 445926 | 100.000 | 100.000 |
| Total | | 11914225 | 445926 | 100.000 | 100.000 |

Column type: **OJ-H**




PeakTable

PDA Ch1 254nm 4nm

| Peak# | Ret. Time | Area | Height | Area % | Height % |
|---|---|---|---|---|---|
| 1 | 6.215 | 12454961 | 516644 | 100.000 | 100.000 |
| Total | | 12454961 | 516644 | 100.000 | 100.000 |

**S4.11 Chiral stationary phase HPLC spectral analysis of compound 6b:**

***Purification of P and M isomers of* 6b**

***Separation of P & M isomers by preparative HPLC:***

Pure *P* & *M* form of (2.5 mg) was dissolved in 800 µL of Hexane/ Isopropyl alcohol = 90/10 (v/v) and injected in preparative HPLC, the analytical conditions are given below for preparative and analytical injections.

*Operation parameters for preparative separation:*

| | |
|---|---|
| Condition | Isocratic |
| Column | AD-H |
| Column size | 25 cm x 10 mm (L x I.D) |
| Solvent | Hexane / Isopropyl alcohol = 96/04 (v/v) |
| Flow rate | 1.5 mL / min |
| Detection | UV (254 & 270 nm) |
| Retention time | ~40.58 (min) and ~65.87 (min) |

*Operation parameters for analytical injection:*

| | |
|---|---|
| Condition | Isocratic |
| Column | AD-3 |
| Column size | 15 cm x 4.6 mm (L x I.D) |
| Solvent | Hexane / Isopropyl alcohol = 96/04 (v/v) |
| Flow rate | 1.0 mL /min |
| Detection | UV (254 & 270nm) |
| Retention time | ~8.94 (min) and ~15.42 (min) |

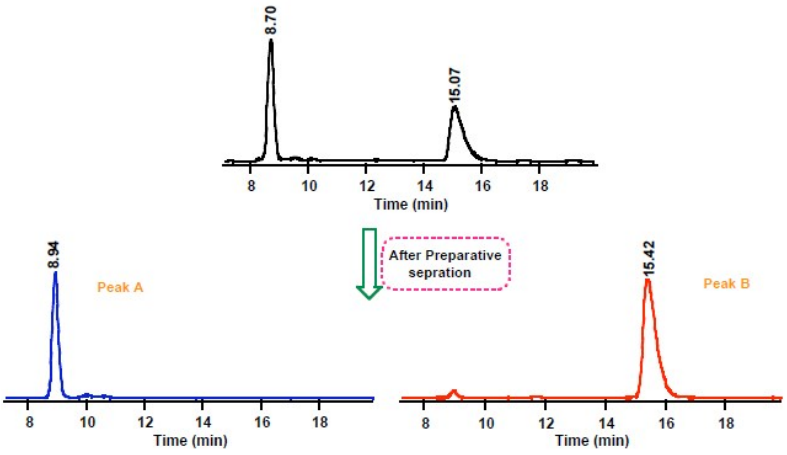



**Figure S1**: Chiral HPLC profiles of pure and racemic forms of **6b**.

**S5.0. Circular dichroism (CD) spectral analysis of compound 6b:**

Optically pure forms of **6b** were separated by HPLC and dissolved in spectrophotometric grade chloroform. $C_A$ = 2.82 x $10^{-6}$ M, $C_B$ = 2.82 x $10^{-6}$ M, pathlength = 1.0 $cm^{-1}$



**Figure S2**: Circular dichroism (CD) spectra of **6b**.

Peak **A** and **B** refer to the first and second peaks that elute from the HPLC column during analytical / preparative separation respectively. *Note: (-) and (+) are assigned to the optically pure isomers A and B respectively based on the sign of the cotton effect at ~300 and 400 nm.*

**S6.0 X-ray crystallography:**

Diffraction intensities were collected with a Bruker AXS Kappa Apex II CCD diffractometer equipped with graphite monochromated MoKα (l = 0.7107 Å) radiation. APEXII-SAINT (Bruker, 2008) program was used for finding the unit cell parameters.[S3] The data were corrected for Lorentz and polarization effects, and absorption corrections were performed using SADABS (Bruker, 2008) program. The structures were solved by direct methods using SHELXS-97, (Sheldrick, 2008)[S4] and refined by full-matrix least squares techniques using SHELXL-97 (Sheldrick, 2013)[S5] computer program. All hydrogen atoms were fixed at chemically meaningful positions and riding model refinement was applied. Molecular graphics were generated using Mercury program. Slow evaporation of methanolic solution of **6a** and **8** was employed for growing single crystals. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 851692 (**6a**), and CCDC 1817591 (**8**). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

*Crystal data and structure refinement for* **6a.**

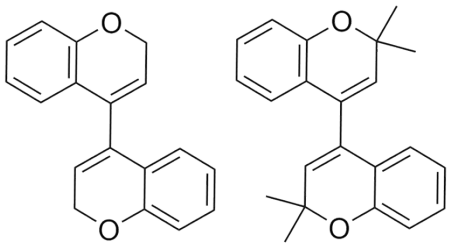
| | | |
|---|---|---|
| Empirical formula | $C_{20}H_{14}O_4$ | |
| Formula weight | 318.31 | |
| Temperature | 298(2) K | |
| Wavelength | 0.71073 Å | |
| Crystal system | Monoclinic | |
| Space group | P2(1)/c | |
| Unit cell dimensions | a = 8.0844(4) Å | α = 90°. |
| | b = 19.8817(10) Å | β = 109.061(2)°. |
| | c = 10.2123(5) Å | γ = 90°. |
| Volume | 1551.44(13) $Å^3$ | |
| Z | 4 | |
| Density (calculated) | 1.363 $Mg/m^3$ | |
| Absorption coefficient | 0.095 $mm^{-1}$ | |
| F(000) | 664 | |
| Crystal size | 0.42 x 0.38 x 0.32 $mm^3$ | |
| Theta range for data collection | 2.05 to 28.43°. | |
| Index ranges | -10<=h<=10, -26<=k<=25, -13<=l<=11 | |
| Reflections collected | 11587 | |
| Independent reflections | 3892 [R(int) = 0.0245] | |
| Completeness to theta = 25.00° | 100.0 % | |
| Absorption correction | None | |
| Max. and min. transmission | 0.9702 and 0.9612 | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 3892 / 0 / 217 | |
| Goodness-of-fit on $F^2$ | 0.988 | |
| Final R indices [I>2 sigma(I)] | R1 = 0.0486, wR2 = 0.1072 | |
| R indices (all data) | R1 = 0.0722, wR2 = 0.1218 | |
| Largest diff. peak and hole | 0.190 and -0.229 e. $Å^{-3}$ | |

*Crystal data and structure refinement for* **8**.

| | |
|---|---|
| Identification code | SSR1 |
| Empirical formula | $C_{20}H_{18}$ |
| Formula weight | 258.34 |
| Temperature | 296(2) K |

| | |
|---|---|
| Wavelength | 71.073 pm |
| Crystal system | Orthorhombic |
| Space group | P n a 21 |
| Unit cell dimensions | a = 1585.3(3) pm α= 90°. |
| | b = 1237.5(2) pm β= 90°. |
| | c = 736.39(12) pm γ= 90°. |
| Volume | 1.4447(4) $nm^3$ |
| Z | 4 |
| Density (calculated) | 1.188 $Mg/m^3$ |
| Absorption coefficient | 0.067 $mm^{-1}$ |
| F(000) | 552 |
| Crystal size | 0.250 x 0.220 x 0.120 $mm^3$ |
| Theta range for data collection | 2.088 to 23.658°. |
| Index ranges | -17<=h<=17, -11<=k<=13, -5<=l<=8 |
| Reflections collected | 7027 |
| Independent reflections | 1836 [R(int) = 0.0666] |
| Completeness to theta = 23.658° | 99.1 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.992 and 0.983 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 1836 / 1 / 182 |
| Goodness-of-fit on $F^2$ | 1.011 |
| Final R indices [I>2sigma(I)] | R1 = 0.0456, wR2 = 0.0892 |
| R indices (all data) | R1 = 0.0757, wR2 = 0.1032 |
| Absolute structure parameter | -5.9(10) |
| Extinction coefficient | 0.008(2) |
| Largest diff. peak and hole | 0.135 and -0.124 $e.Å^{-3}$ |

## S7.0 Derivation of Activation Parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$)



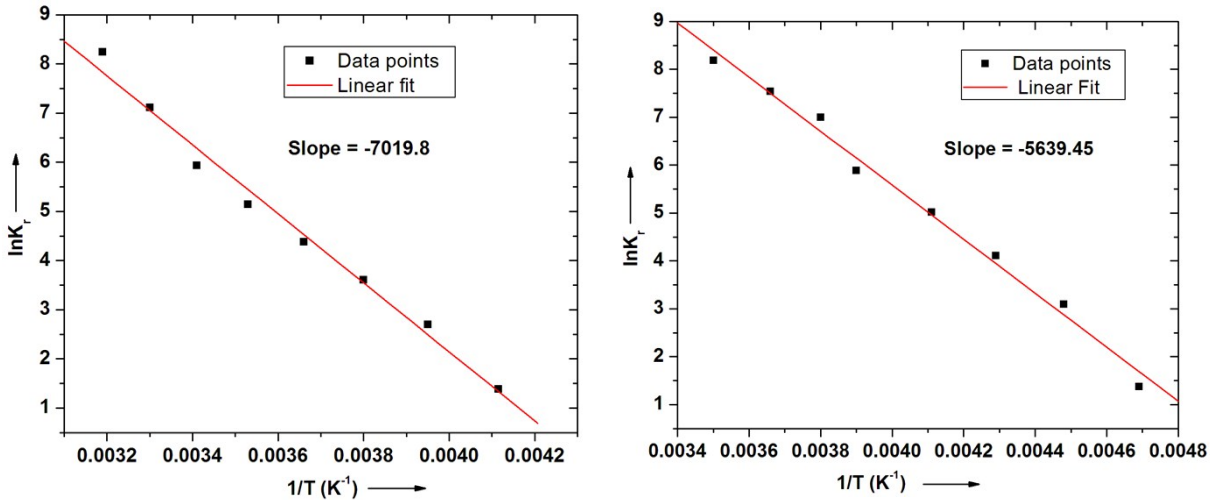
**6k** **6l**

Samples of **6k** and **6l** in THF-D8 were studied for coalacence behaviour of the exchanging isomers using VT-NMR in the temperature range of 213-323 K. For **6k** the methylene protons and **6l** the protons of the methyl group were used as diastereotopic probes. Line-shape stimulation were performed using Bruker WIN-NMR software. Reliable rate constants were obtained by the electronic superimposition of the experimental and stimulated spectra. The activation energy ($E_a$) was calculated from the value of the slope obtained by plotting $\ln(k_r)$ *vs* 1/T, where $k_r$ is the rate determined from dynamic VT-NMR.[S6]

For **6k**: $-E_a/R = -7019.8 = E_a = 58.36$ kJ/mol (or) 14.59 kcal/mol

**6l:** $-E_a/R = -5639.4 = E_a = 46.88$ kJ/mol (or) 11.16 kcal/mol

Accordingly, $E_a$ of **6k** and **6l** was found to be 14.6 kcal/mol and 11.16 kcal/mol respectively. The plots are shown below.




**Figure**

**Figure S3:** Plot for calculation of $E_a$, compound **6k** (*left*) and compound **6l** (*right*)

Next, the Eyring plots [S6] were derived by plotting $\ln(k_r/T)$ *vs* $1/T(K^{-1})$. Here $\Delta H^{\ddagger}$ was calculated from the slope of the linear regression. Accordingly,

For **compound 6k**

$-\Delta H^{\ddagger}/R$ = slope = -6.8246; where R = gas constant = 8.3144621 $JK^{-1}mol^{-1}$

Therefore, $\Delta H^{\ddagger}$ **= 56.94 kJ mol$^{-1}$ (or) 13.3 kcal mol$^{-1}$**,

$\Delta S^{\ddagger}/R + \ln(k'/h) = \Delta S^{\ddagger}/R + 23.76$ = Intercept at the 'Y'axis = 23.82

$\Delta S^{\ddagger}$ = (23.82-23.76) 8.3144621 = 0.498 **J mol$^{-1}$ (or) 0.118 cal mol$^{-1}$**

Fitting it into equation: $\mathbf{\Delta G^{\ddagger}_{(298K)} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}}$

$\mathbf{\Delta G^{\ddagger}_{(298K)}}$ **= 56.94-(298)(0.000498) = 56.79 kJ mol$^{-1}$ (or) 13.52 kcal mol$^{-1}$**.

Also, the average of $\mathbf{\Delta G^{\ddagger}}$ arrived at various temperature by fitting the rate constant $k_r$ in the Eyring formula for $\mathbf{\Delta G^{\ddagger}}$ gives reasonably close estimate as seen below.

$$\Delta G^{\ddagger} = aT\left[10.319 + \log\left(\frac{T}{k_{rate}}\right)\right]$$

where a= 4.575 x $10^{-3}$ for units of kcal/mol
a= 1.914 x $10^{-2}$ for units of kJ/mol

| **Temperature (K)** | **Rate ($k_r$) (Hz)** | **$\Delta G^{\ddagger}$ (kcal/mol)** |
|---|---|---|
| 233 | 0 | - |
| 243 | 4 | 13.45 |
| 253 | 15 | 13.36 |
| 263 | 37 | 13.44 |

| | | |
|---|---|---|
| 273 | 80 | 13.55 |
| 283 | 172 | 13.64 |
| 293 | 383 | 13.68 |
| 303 | 1230 | 13.46 |
| 313 | 3840 | 13.22 |
| 323 | 8300 | 13.16 |
| Average $\Delta G^{\ddagger}$ = 13.44 | | |

**$\Delta G^{\ddagger}$ = 13.44 kcal/mol**

For **compound 6l:**

$-\Delta H^{\ddagger}/R$ = slope = -5.6530; where R = gas constant = 8.3144621 $JK^{-1}mol^{-1}$

Therefore, **$\Delta H^{\ddagger}$ = 47.17 kJ $mol^{-1}$ (or) 11.2 kcal $mol^{-1}$**,

$\Delta S^{\ddagger}/R + \ln(k'/h) = \Delta S^{\ddagger}/R + 23.76$ = Intercept at the 'Y'axis = 22.52

**$\Delta S^{\ddagger}$ =** = (22.52-23.76) 8.3144621 = **-10.3 J $mol^{-1}$ (or) -2.45 cal $mol^{-1}$**

**$\Delta G^{\ddagger}_{(298K)} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$ = 47.17-(298)(-0.0103) = 50.23 kJ $mol^{-1}$ (or) 11.96 kcal $mol^{-1}$**.

Also, the average of **$\Delta G^{\ddagger}$** arrived at various temperature by fitting the rate constant $k_r$ in the Eyring formula as in the previous case gives reasonably close estimate.

| **Temperature (K)** | **Rate ($k_r$) (Hz)** | **$\Delta G^{\ddagger}$ (kcal/mol)** |
|---|---|---|
| 213 | 4 | 8.36 |
| 223 | 22 | 9.50 |
| 233 | 61 | 10.40 |
| 243 | 151 | 10.87 |
| 253 | 362 | 11.38 |
| 263 | 1100 | 11.76 |
| 273 | 1890 | 11.80 |
| 283 | 3610 | 11.92 |
| Average $\Delta G^{\ddagger}$ = 10.75 | | |

**$\Delta G^{\ddagger}$ = 10.75 kcal/mol**

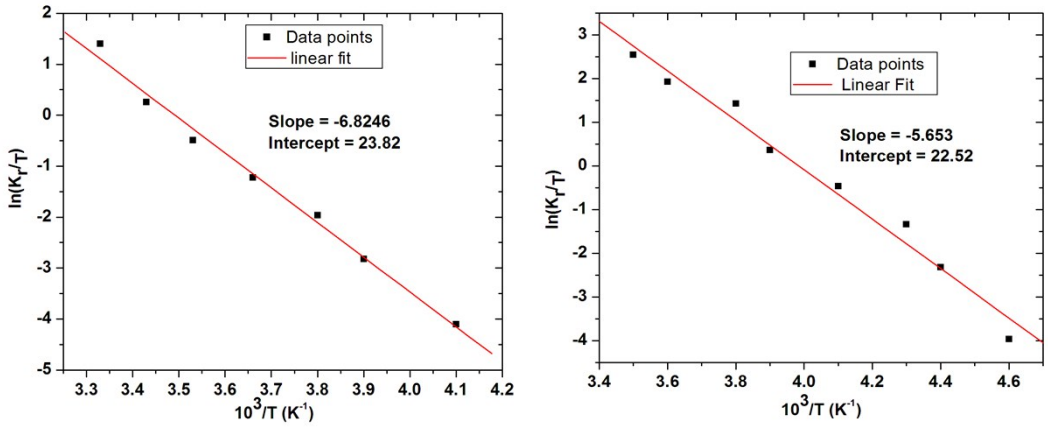
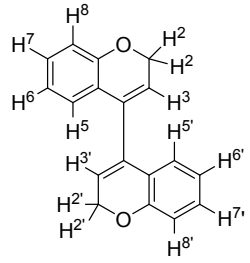
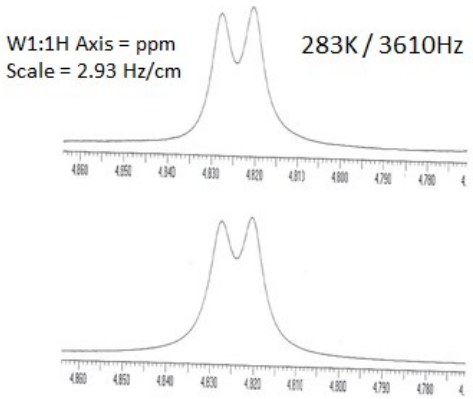


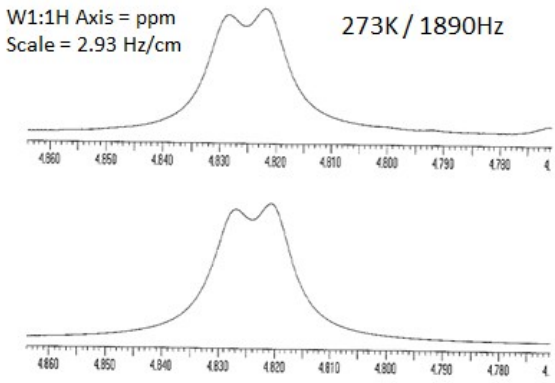

**Figure S4:** Eyring plot for calculation of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$, compound **6k** (*left*) and compound **6l** (*right*)

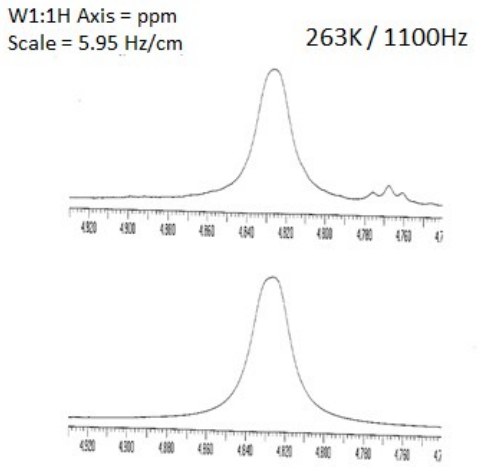
Among the bichromenes **6k** and **6l**, the marginally lower value of $\Delta G^{\ddagger}$ in the case of latter suggests its slightly lower configurational stability.

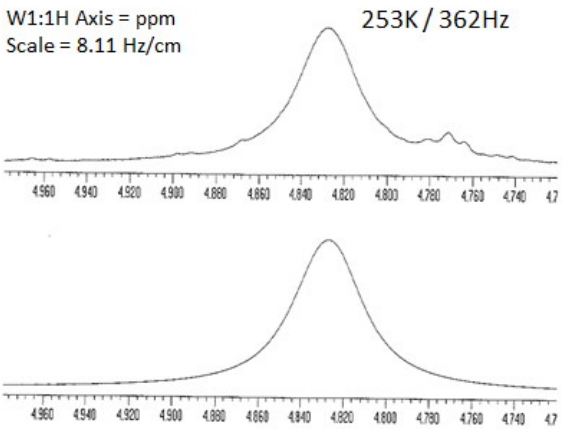
*[1]H NMR line-shape stimulation of the methylene protons $H^2/H^{2'}$ of* **6k** *for determining rate constant.* (**Top**: Experimental, **Bottom**: Stimulated)

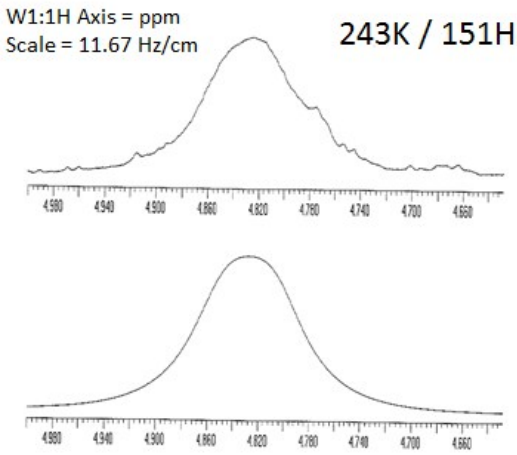


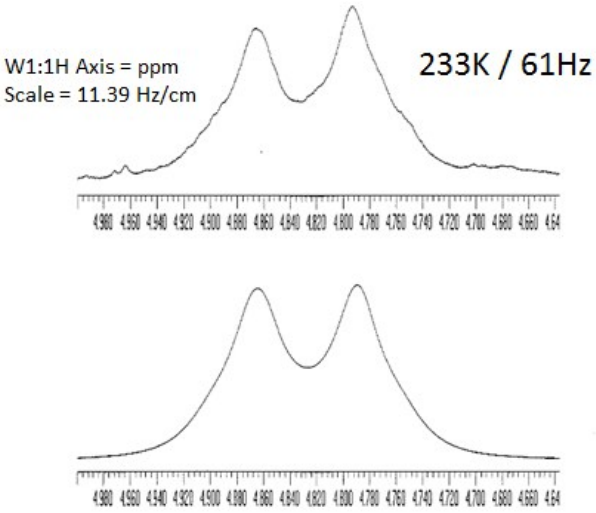



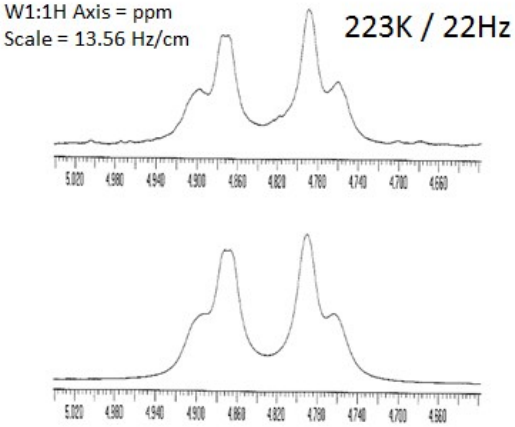



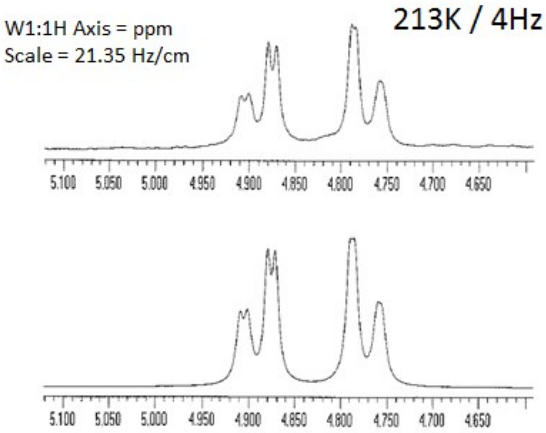



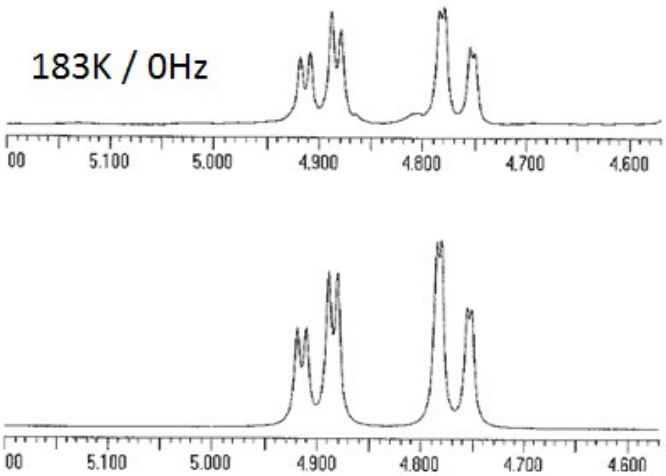




W1:1H Axis = ppm
Scale = 11.67 Hz/cm
243K / 151Hz

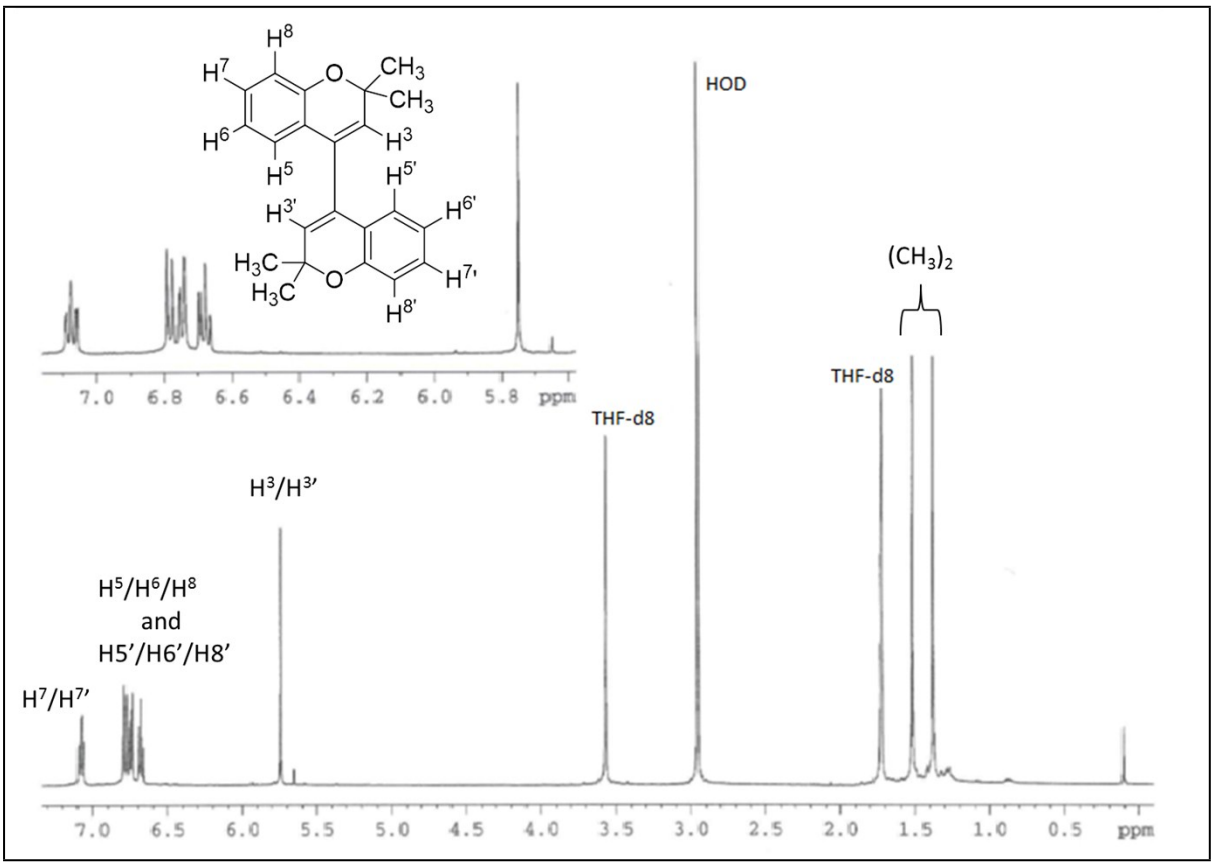

W1:1H Axis = ppm
Scale = 11.39 Hz/cm
233K / 61Hz


W1:1H Axis = ppm
Scale = 13.56 Hz/cm
223K / 22Hz

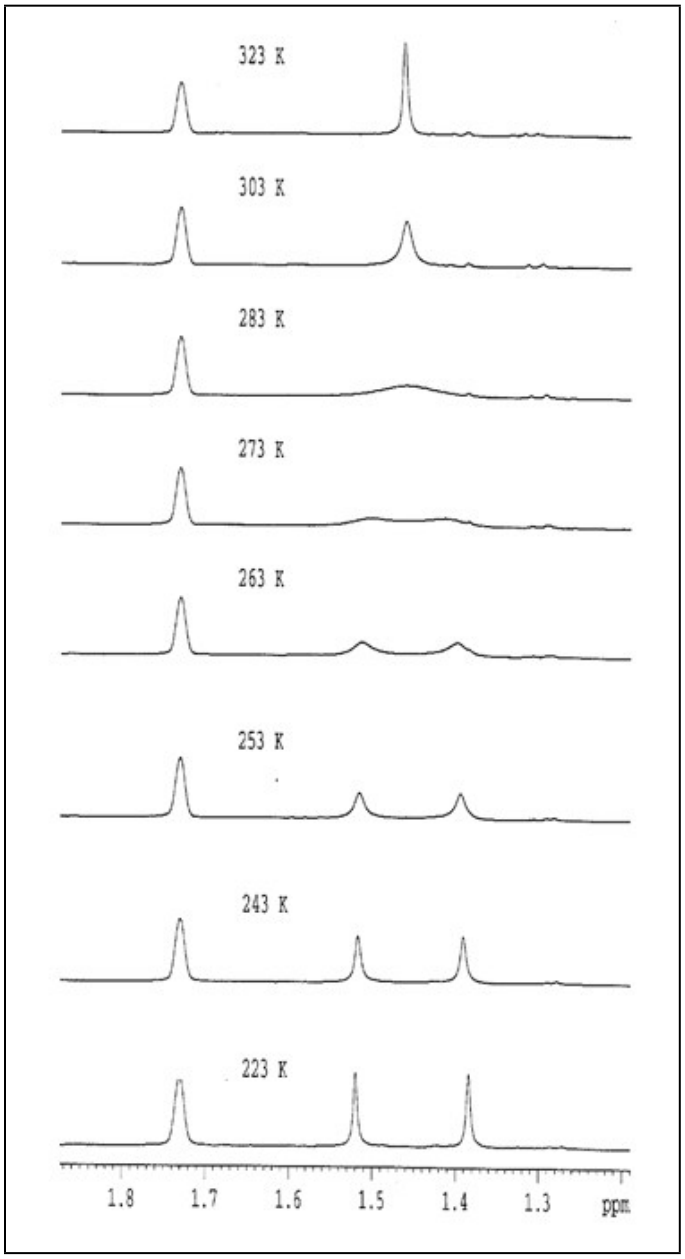

W1:1H Axis = ppm
Scale = 21.35 Hz/cm
213K / 4Hz


183K / 0Hz

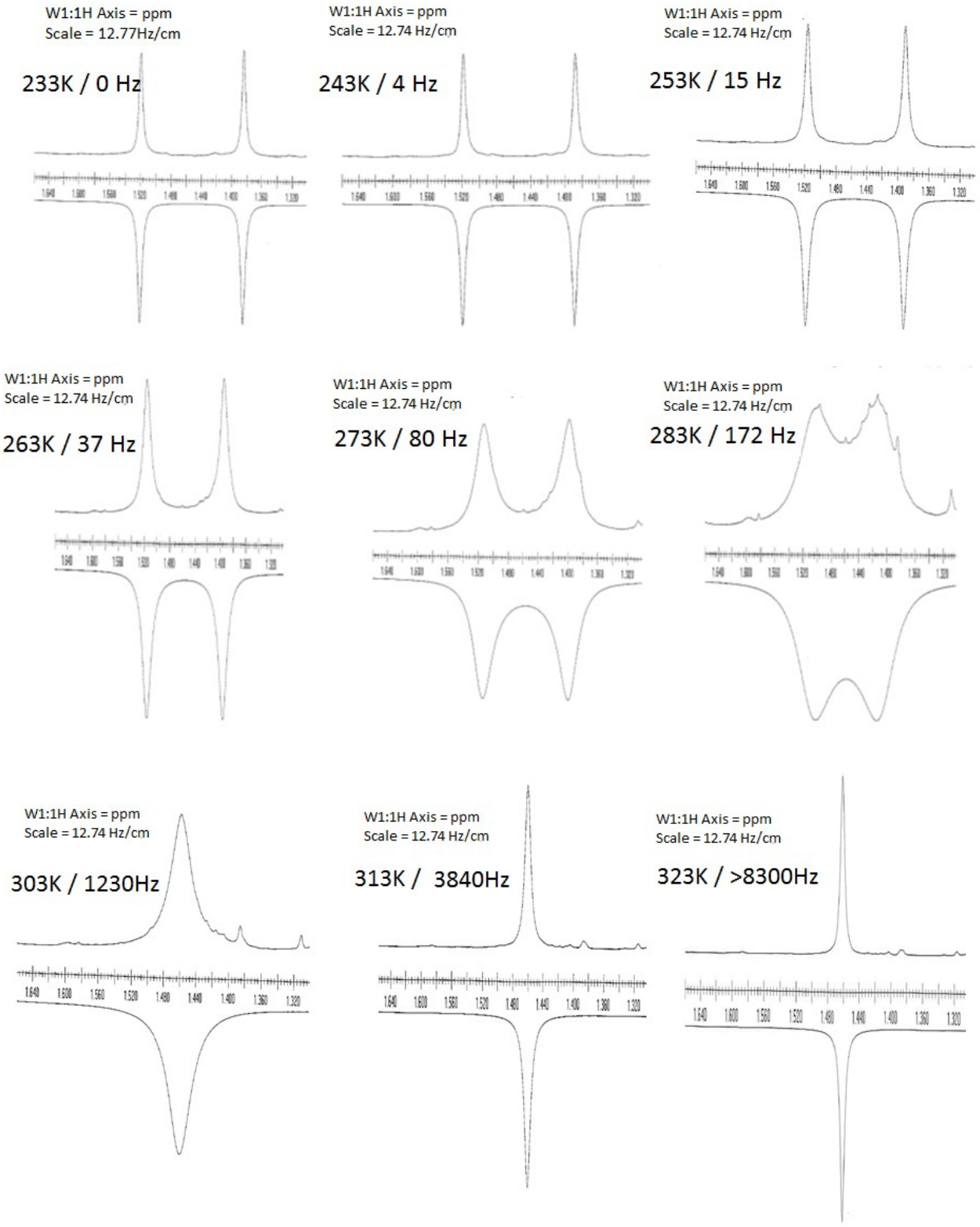
*$^{1}H$ NMR spectrum of* **6l** *at 223K.*



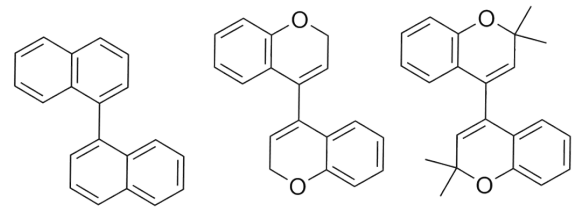
*VT-NMR showing the decoalascence behaviour of methyl protons of* **6l.**



*[1]H NMR line-shape stimulation of the methyl protons of* **6l** *for determining rate constant.* (Top: Experimental, Bottom: Stimulated)



## S8.0 Theoretical studies (Density functional theory)




DFT calculations were performed with the Gaussian 03 program package[S7] using the hybrid functional B3LYP in conjunction with the standard 6-31G (d, p) basis set.[S8,S9] The relaxed potential energy surface (PES) scans were carried out with geometry optimization at each point. A total of 36 optimizations were performed for each scan as the chosen torsional angle (around the chiral) was stepped by 10°. The transition states (TS) encountered during the racemization processes were successfully optimized and characterized (one negative frequency) based on the results of the PES scans. The respective energies of **6k** and **6l** were compared along with that of 1,1'-binapthyl. As seen in Figure S5 below, the rotational about the central sigma bond encounters two energy barriers one being higher (-30 to -50°) than the other one (-200 to -210°). The highest barrier is of interest ( and it corresponds to the "attached" phenyl rings on the same side, all the computed TS corresponds to this highest energetic barrier (rate-limiting TS). Accordingly, the calculated activation energies (*viz*., energy difference between the electronic energies including the zero-point corrections of the optimized ground-state and the optimized transition state) are as follows $E_a$ of 1,1'-binapthyl = 32.0 kcal/mol, $E_a$ of **6k** = 19.15 kcal/mol and $E_a$ of **6l** = 20.66 kcal/mol. The comparative results are summarized in the Table S1 below.

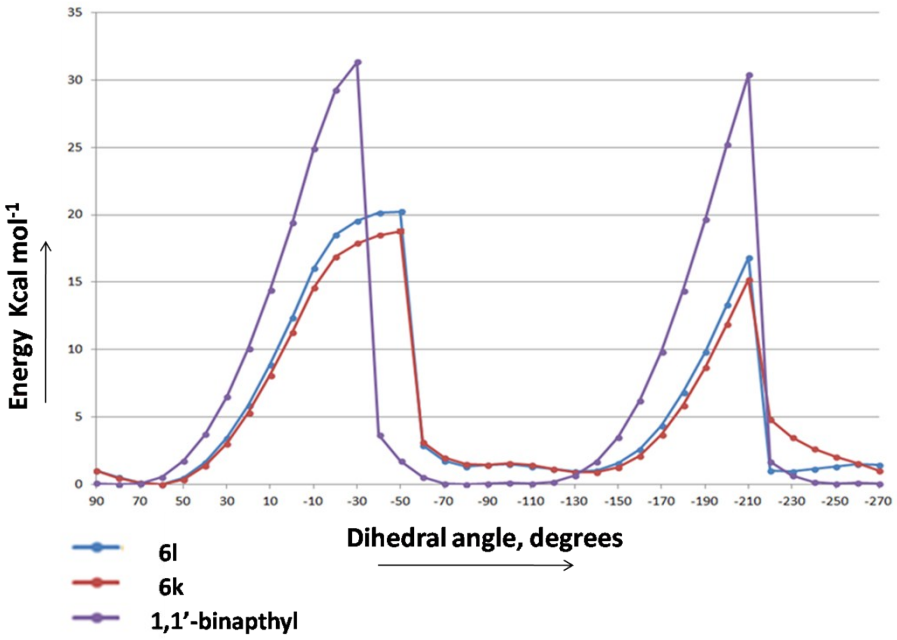



**Figure S5:** DFT computed energy profile of rotation around the central axis.

**Table S1**

| **Energy (kcal/mol)** | **1,1'-binapthyl (kcal/mol)** | **6k (kcal/mol)** | **6l (kcal/mol)** |
|---|---|---|---|
| $E_a$ (Experimental) | - | 14.59 | 11.16 |
| $E_a$ (DFT calculated) in this work | 32.0 | 19.15 | 20.66 |
| | | | |
| $\Delta G^{\ddagger}_{(298K)}$ (Experimental) | 23.5[a] | 13.44 | 10.75 |
| | | | |
| $\Delta H^{\ddagger}_{(298K)}$ (Experimental) | - | 13.30 | 11.2 |

[a] Experimental value of $\Delta G^{\ddagger}$ at 323K (50 °C) in DMF solvent. Ref. [S10]

In order to gain insight into the effect of small substituent such as the methyl group in the 3,3′-position of the bichromene system, the energy barrier of rotation about the central axis was calcuated for 3,3′-dimethyl-*2H,2H′*-4,4′-bichromene and compared with that of 2,2′-dimethyl-1,1′-binapthalene in the procedure described above. The $E_a$ of the bichromene was 80.0 kcal/mol and $E_a$ of binapthalene was 110 kcal/mol. The transition energy profile is depicted in Figure S6 below.

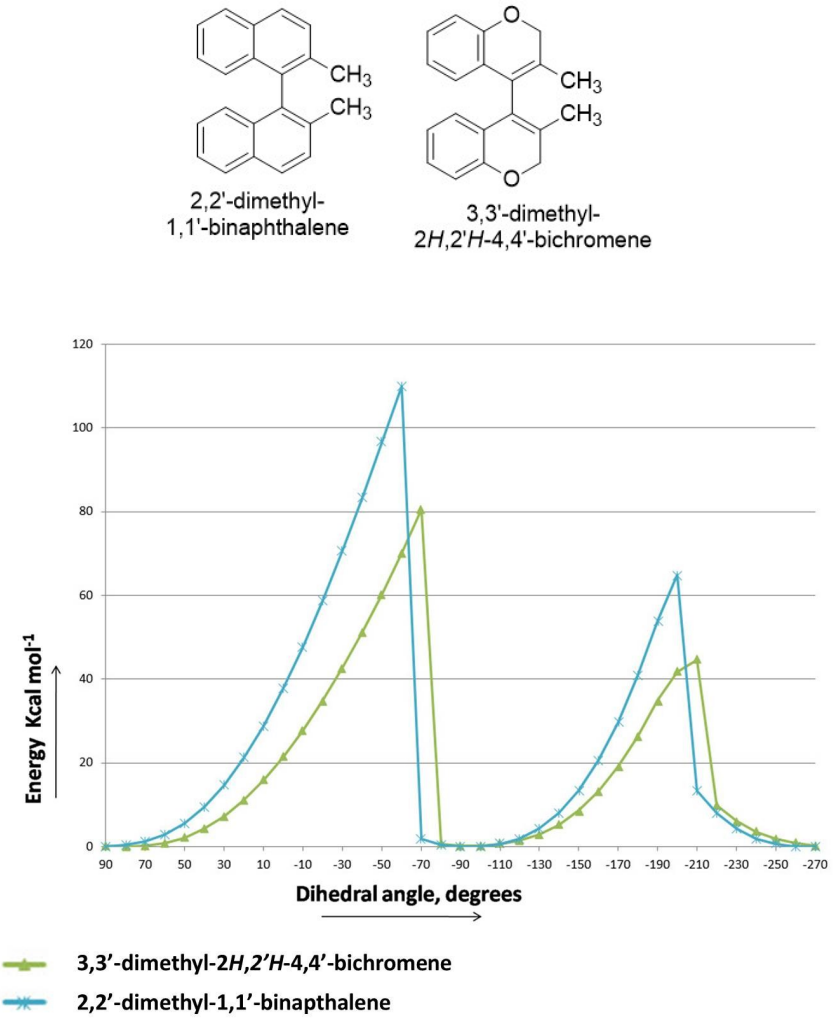



**Figure S6:** DFT computed energy profile of rotation around the central axis for 2,2′-dimethyl -1,1′-binapthalane and 3,3′-dimethyl-4,4′ bichromene.

**References:**


[S1] Mo, J.; Eom, D.; Lee, E.; Lee, P. H. *Org. Lett.* **2012**, *14*, 3684-3687.

[S2] Balasubramanian, K.K.; Reddy, V.; Nagarajan, R. *Tet. Lett.* **1973**, *50*, 5003.

[S3] SAINT, version 7.06 a; Bruker AXS Inc., Madison, Wisconsin, 2008.

[S4] Sheldrick, G. M. Acta Crystallogr. A 2008, 64, 112.

[S5] Sheldrick, G. M. Acta Crystallogr. A 2013, 69, S74.

[S6] (a) H. Eyring, *Chem. Rev.* **1935**, 17, 65–77. For Dynamic NMR calculations: (b) Kost, D.; Carlson, E. H.; Raban, M. *J. Chem. Soc., Chem. Commun.***1971**, 656. (c) For Eyring plots: Zimmer, K. D.; Shoemaker, R.; Ruminski, R. R. *Inorganica Chimica Acta*, **2006**, *359*, 1478-1484.

[S7] Gaussian 03, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

[S8] A. D. Becke, Phys. Rev. A. 1988, 38, 3098.

[S9] Ditchfield, R.; Hehre,W. J.; Pople, J. A. *J. Chem. Phys.*, **54** (1971) 724.

[S10] A. S. Cooke, M. M. Harris, *J. Chem. Soc.,* **1963**, 2365-2373.