Supplementary Information

Silver-catalyzed [3+3]-annulation cascade of alkynyl alcohols and α,β-unsaturated ketones for the regioselective assembly of chromanes

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1. *General Information*:

All reactions were performed under argon atmosphere with oven (80 ºC) or flame-dried glassware with a septum seal. Tetrahydrofuran (THF) was distilled from sodium-benzophenone under the argon atmosphere immediately before use. Anhydrous dichloromethane, dichloroethane, methanol, and fluorobenzene were purchased from commercial sources and used without any further treatment. Reaction temperatures are reported as the temperature of the bath surrounding the reaction vessel, and 30 °C corresponds to the room temperature (rt) of the laboratory when the experiments were carried out. Analytical thin-layer chromatography (TLC) was performed on TLC Silica gel 60 F254. Visualization was accomplished with short wave UV light, anisaldehyde or $KMnO_4$ staining solutions followed by heating. Chromatography was performed on silica gel (100-200 mesh) by standard techniques eluting with solvents as indicated. ^1H and ^{13}C NMR spectra were recorded on Bruker AV 200, 400, and 500 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ H = 7.27 ppm, δ C = 77.00 ppm), the following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doublet of doublet; td, triplet doublet; and br, broad. HRMS data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump, FT-IR instrument (Bruker Alpha Model) at normal temperature with a NaCl pellet (IR grade). Experimental procedures for all new compounds and known compounds without published experimental procedures are described below. Compounds that are not presented in the main text (manuscript) are numbered starting from **S1**.

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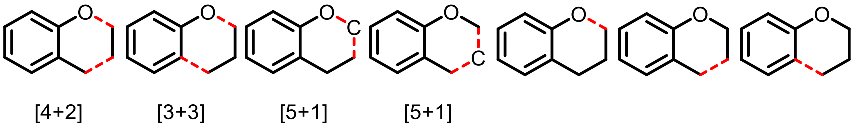
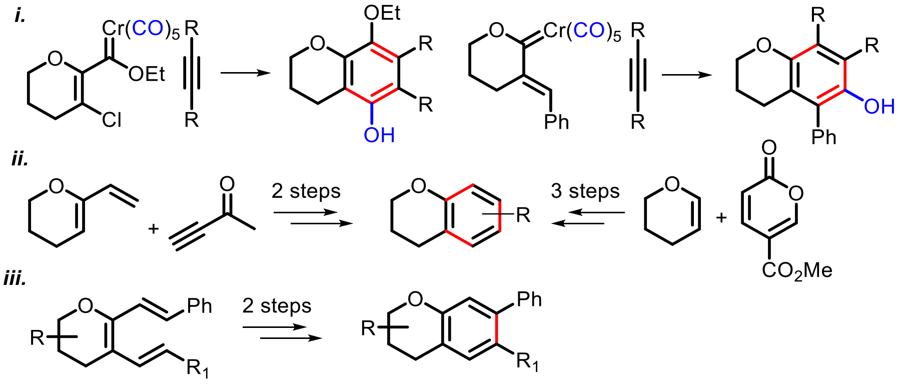
2. Scheme S1. Known synthetic strategies for chromanes 5.

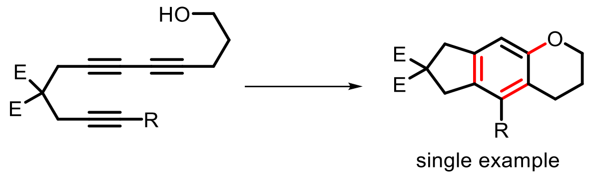
a. From pre-functionalized arenes



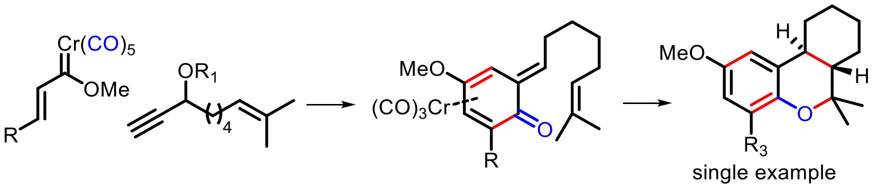
b. From dihydropyran derivatives



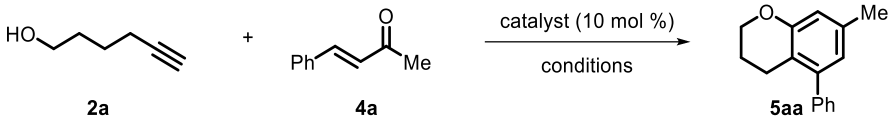
c. Through hexadehydro Diels-Alder reaction of triynes



d. Through Wulff-Dötz reaction



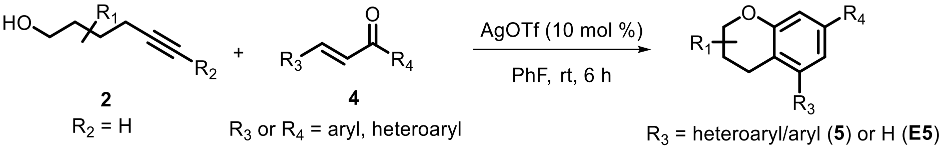
3. Table S1. Reaction optimization studies[a]



Entry	Catalyst	Solvent	Yield[b](%)
1	AgCl	PhF, rt, 12 h	-[c]
2	AgBr	PhF, rt, 12 h	-[c]
3	AgI	PhF, rt, 12 h	-[c]
4	$AgNO_3$	PhF, rt, 12 h	-[c]
5	Ag_2O	PhF, rt, 12 h	-[c]
6	AuCl	CH_2Cl_2, 12 h	70
7	$Hg(OTf)_2$	CH_2Cl_2, 12 h	68
8	$Bi(OTf)_3$	CH_2Cl_2, 12 h	53
9	$Bi(OTf)_3$	PhF, 85 °C	65
10	$Sc(OTf)_3$	CH_2Cl_2	15
11	$Fe(OTf)_3$	CH_2Cl_2	15
12	$Fe(OTf)_3$	PhF, 85 °C	42
13	$Ni(OTf)_2$	CH_2Cl_2	-[c]
14	$Cu(OTf)_2$	CH_2Cl_2	43
15	$Zn(OTf)_2$	CH_2Cl_2	-[c]
16	$In(OTf)_3$	CH_2Cl_2	52
17	$Yb(OTf)_3$	CH_2Cl_2	-[c]

[a]Unless otherwise noted all reactions were carried out with **4a** (1 mmol), **2a** (2 mmol), and catalyst (10 mol %) at rt for 6 h. [b]Isolated yields of **5aa**. [c]No reaction was observed, both starting materials **2a** and **3a** were found to be intact. Tf = triflate (CF_3SO_2).

4. *General Procedure* for the synthesis of chromanes (5 or E5) from alkynols (2) and *α,β*-unsaturated ketones (4):



Alkynol **2**(1.01 mmol) and α,β-unsaturated ketone**4**(0.505mmol) were taken into a single neck 10 mL round bottom flask equipped with positive argon flow, then dissolved in 2 mL of anhydrous PhF. Catalyst (AgOTf, 0.101mmol) was added under an argon atmosphere at room temperature. The resulting reaction mixture was stirred at rt for six h. After completion of the reaction (monitored by TLC, visualized using UV, anisaldehyde, and $KMnO_4$ staining solutions), quenched with saturated aqueous $NaHCO_3$solution, then extracted with CH_2Cl_2 (2x5 mL), then washed with brine solution (10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and filtered through a sintered glass funnel. The filtrate was concentrated under reduced pressure and purified using silica-gel column chromatography (SiO_2, 100-200 mesh) to afford the corresponding chromanes **5** or **E5**.

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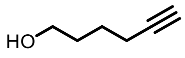
5. Synthesis of alkynols (2):

5.1. Synthesis of alkynols 2a, 2b, 2d, 2e, and 2f: Prepared using reported procedures[1,2,3]



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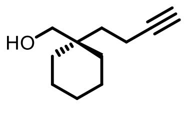
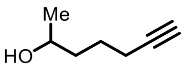


2b[2]



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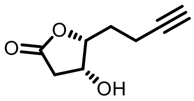
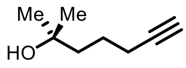
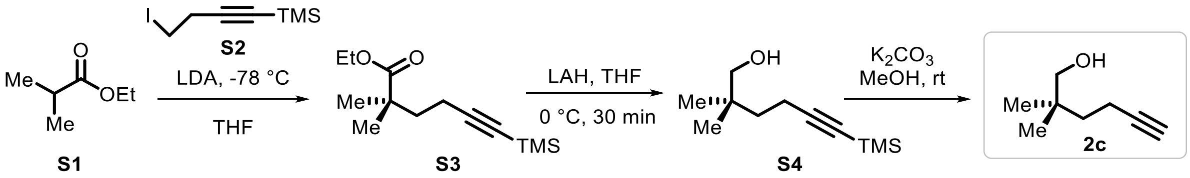


2e[3]



2f[2]

5.2. Synthesis of alkynol 2c:



2,2-Dimethyl-6-(trimethylsilyl)hex-5-yn-1-ol (S4): To a flame dried (100 mL) two neck round bottom flask, anhydrous THF (20 mL) was added under argon atmosphere and cooled to 0 °C, to this diisopropylamine (1.18 g, 11.74mmol) followed by *n*-butyllithium (1.6 M in hexanes, 7.95 mL, 12.7 mmol) was added dropwise at 0 °C and stirred for 45 min at 0 °C to generate LDA solution. To this LDA solution, was added ethyl isobutyrate (**S1**)(1 g, 9.79 mmol) in THF (3 mL) and stirred the reaction mixture at -78 °C for 30 min, then warmed to 0 °C and stirred for another 30 min. The reaction mixture was cooled back to -78 °C and (4-

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[1] 1a were purchased from commercial sources.

[2] Thorat, S. S.; Kataria, P.; Kontham, R. *Org. Lett.***2018**, 20, 872-875.

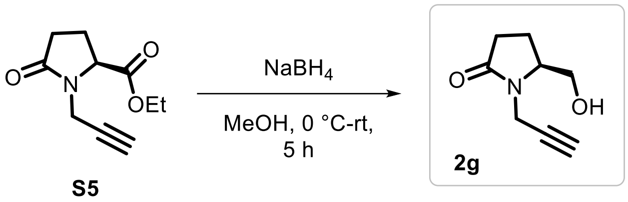
[3] Nakate, A. K.; Pratapure, M. S.; Kontham, R. *Org. Biomol. Chem.*,**2018**, 16, 3229–3240

iodobut-1-yn-1-yl)trimethylsilane (**S2**) (3.69 g, 14.68 mmol) was added dropwise. The resulting mixture was stirred at -78 °C for 1 h and warmed to rt and stirred overnight. Then, the reaction was quenched with saturated aqueous NH_4Cl solution, and extracted with EtOAc (3x20 mL), combined organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure to afford ethyl 2,2-dimethyl-6-(trimethylsilyl)hex-5-ynoate (**S3**) TLC: R_f = 0.7 (SiO_2, 10% EtOAc/hexanes), this crude product was subjected to the next step without further purification.

Lithium aluminium hydride (0.74 g, 19.58 mmol) was dissolved in a 20 mL of anhydrous THF in a 100 mL two neck round bottom flask under argon atmosphere, then ethyl 2,2-dimethyl-6-(trimethylsilyl)hex-5-ynoate (**S3**) in (5 mL) THF was added drop by drop at 0 °C, and the reaction mixture was stirred for 30 min at the same temperature, after completion of the reaction monitored by TLC quenched with a saturated aqueous solution of sodium sulphate (very carefully). After quenching the reaction, the mixture diluted with 50 mL EtOAc and stirred for 1h to obtain the white powder, which was filtered through Celite. The solvent was evaporated under reduced pressure and the resulting crude product was purified by silica gel column chromatography (SiO_2, 8% EtOAc/hexanes) to afford 2,2-dimethyl-6-(trimethylsilyl)hex-5-yn-1-ol (**S4**) (0.726 g, 43% for two steps) as a colorless liquid. TLC: R_f = 0.8 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.35 (s, 2H), 2.23 (t, J = 7.32 Hz, 2H), 1.55 (t, J = 7.32 Hz, 2H), 0.88 (s, 6H), 0.15 (s, 9H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 108.3, 84.2, 70.9, 37.3, 35.2, 23.9, 14.9, 0.04.

2,2-Dimethylhex-5-yn-1-ol (2c): To a stirred solution of 2,2-dimethyl-6-(trimethylsilyl)hex-5-yn-1-ol (**S4**) (0.8 g, 4.03 mmol) in MeOH (20 mL) was added K_2CO_3 (1.2 g, 8.68 mmol) at room temperature. The reaction mixture was stirred for 6 h. After quenched with H_2O, the mixture was extracted twice with ether. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (SiO_2, 5% EtOAc /hexanes) to give 2,2-dimethylhex-5-yn-1-ol (**2c**) (0.402 g, 79%) as a colourless oil. TLC: R_f = 0.5 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.35 (s, 2H), 2.19 (td, J = 7.63, 3.05 Hz, 2H), 1.97-1.95 (m, 1H), 1.60-1.54 (m,2H), 0.89 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 85.4, 71.1, 67.9, 37.3, 35.1, 23.7, 13.5.

3.3. (*S*)-5-(Hydroxymethyl)-1-(prop-2-yn-1-yl)pyrrolidin-2-one(2g):



To a solution of ethyl (*S*)-5-oxo-1-(prop-2-yn-1-yl)pyrrolidine-2-carboxylate (**S5**)[4](0.4 g, 2.05 mmol) in methanol (10 mL), sodium borohydride (0.155 g, 4.1 mmol) was added batch wise at 0 °C. The reaction mixture was stirred at 0 °C for 30 min. and then at rt for 5 h after which the solvent was evaporated under reduced pressure. Aqueous NH$_4$Cl solution (5 mL) was added to the resulting suspension, and then extracted with EtOAc (3×5 mL). Organic phases were combined and dried over anhydrous Na$_2$SO$_4$, filtered and the solvent was evaporated under reduced pressure, and the resulting crude product was purified by silica gel column chromatography (SiO$_2$, 10% MeOH/CH$_2$Cl$_2$) to afford (*S*)-5-(hydroxymethyl)-1-(prop-2-yn-1-yl)pyrrolidin-2-one (**2g**) (0.302 g, 96%) as a colourless liquid. TLC: R_f = 0.1 (SiO$_2$, 70% EtOAc/hexanes);^{1}H NMR (CDCl$_3$, 400 MHz): δ 4.32 (d, J = 17.70 Hz, 1H) , 4.02-3.82 (m, 3H), 3.69-3.56 (m, 1H), 2.86 (br.s., 1H), 2.53-2.43 (m, 1H), 2.37-2.29 (m, 1H), 2.18-2.07 (m, 1H), 2.04-1.95 (m, 1H);^{13}C NMR (CDCl$_3$, 101 MHz): δ175.5, 78.3, 71.9, 62.5, 59.2, 30.5, 30.3, 20.7.

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6. Synthesis of *α,β*-unsaturated ketones (4): Prepared using reported procedures (see below details of chemical structures with related referenes.[5,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20]

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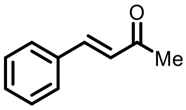

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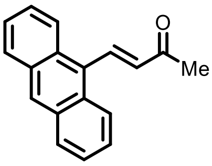

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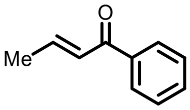

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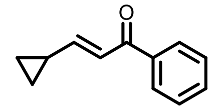

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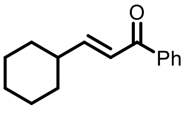

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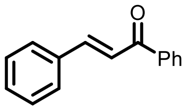

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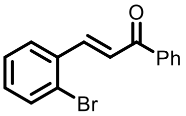

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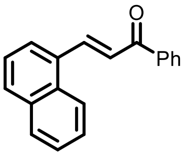

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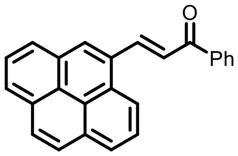

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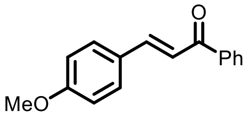

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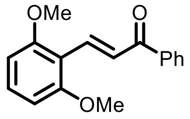

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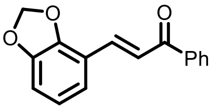

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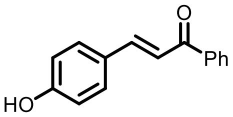

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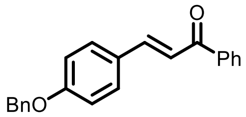

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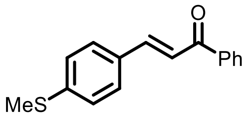

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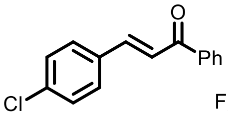

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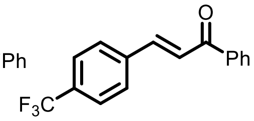

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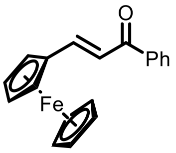

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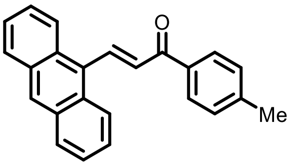

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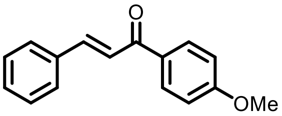

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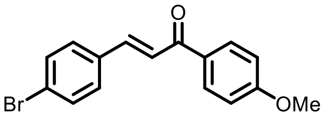

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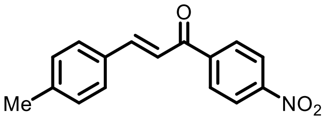

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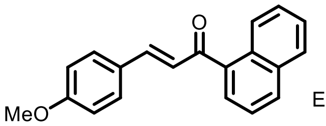

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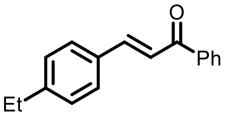
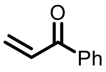
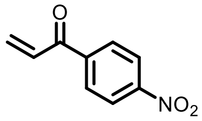


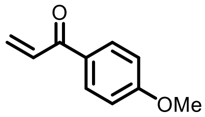
4b'[5]



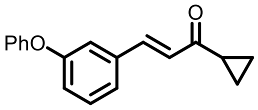
4c'[17]



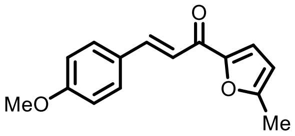
4d'[17]



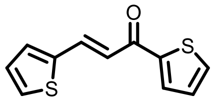
4e'[17]



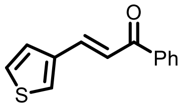
4f'[15]



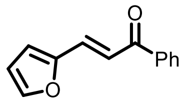
4g'[5]



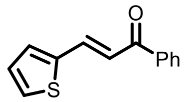
4h'[16]



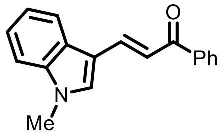
4i'[16]



4j'[9]



4k'[8]



4l'[14]

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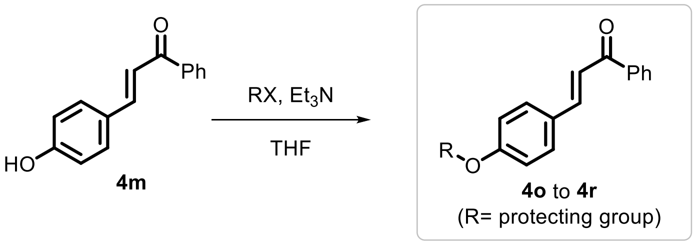
[17] Cheng, S.; Yu, S. *Org. Biomol. Chem.*, **2014**, *12*, 8607-8610.

[18] Thomson, C. J.; Barber, D. M.; Dixon, D. J. *Angew. Chem. Int. Edi.,***2019**, *58*, 8, 2469-2473.

[19] Salfeena, C. T.; Basavaraja, Ashitha, K. T.; Kumar, V. P.; Varughese, S.; Cherumuttathu, H. S.; Sasidhar, B. S. *Chem. Commun*., **2018**, *54*, 12463-12466**.**

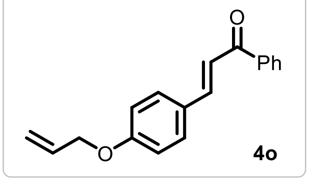
[20] Wang, D.; Li, L.; Feng, H.; Sun, H.; Almedida-Velodo, F.; Charavin, M.; Yu, P.; Désaubry, L. *Green Chemistry*, **2018**, 20, 2775-2780.

7. ***General procedure*** for the synthesis of protected chalcones (4o-4r):



To a solution of 4-hydroxychalcone (**4m**) (10.0 mmol) and triethylamine (12.0 mmol) in anhydrous THF (20 ml)was added drop wise organo-halide (12.0 mmol) and the mixture was stirred at ambient temperature. After a certain reaction time the volatile was concentrated under reduced pressure. The residue was extracted with ethyl acetate (20 ml) and water (20 ml). The organic layer was washed with saturated aqueous solution of sodium hydrogen carbonate (20 mL), 10% aqueous solution of sodium hydrogen sulfonate (20 mL), and brine (20 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The solid was purified by recrystallization.

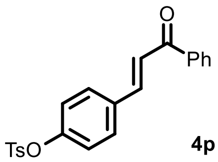
(*E*)-3-(4-(Allyloxy)phenyl)-1-phenylprop-2-en-1-one (4o):



4o

(*E*)-3-(4-(Allyloxy)phenyl)-1-phenylprop-2-en-1-one (**4o**) was prepared by using general procedureas a yellow crystalline solid in 57% yield.^{1}H NMR ($CDCl_3$,200 MHz): δ 8.20-7.97 (m, 2H),7.78 (d, *J*=15.66 Hz, 1H),7.69-7.43 (m, 6H),7.10-6.86 (m, 2H),6.21-5.91 (m, 1H),5.59-5.20 (m, 2H),4.53 (d, *J*=5.18 Hz, 2H).

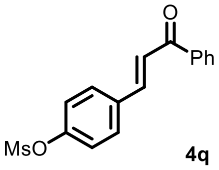
(*E*)-4-(3-Oxo-3-phenylprop-1-en-1-yl)phenyl 4-methylbenzenesulfonate (4p):



4p

(*E*)-4-(3-Oxo-3-phenylprop-1-en-1-yl)phenyl 4-methylbenzenesulfonate (**4p**) was prepared by using general procedureas a yellow crystalline solidin 68% yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.00 (d, *J* = 7.17 Hz, 2H), 7.85-7.66 (m, 3H), 7.66-7.41 (m, 6H), 7.31 (d, *J* = 8.38 Hz, 2H), 7.03 (d, *J* = 8.60 Hz, 2H), 2.44 (s, 3H).

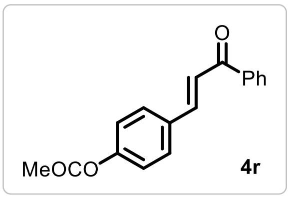
(*E*)-4-(3-Oxo-3-phenylprop-1-en-1-yl)phenylmethanesulfonate (4q):



4q

(*E*)-4-(3-Oxo-3-phenylprop-1-en-1-yl)phenylmethanesulfonate (**4q**) was prepared by using general procedureas a yellow crystalline solidin 80% yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.14-7.94 (m, 2H), 7.81-7.47 (m, 7H), 7.33 (d, *J*=8.71 Hz, 2H), 3.18 (s, 3H).

(*E*)-4-(3-Oxo-3-phenylprop-1-en-1-yl)phenyl acetate (4r):



4r

(*E*)-4-(3-Oxo-3-phenylprop-1-en-1-yl)phenyl acetate (**4r**) was prepared by using general procedureas a light yellow solidin 77% yield. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.16-7.97 (m, 2H), 7.86-7.43 (m, 7H), 7.14 (d, *J*=8.49 Hz, 2H),2.30 (s, 3H).

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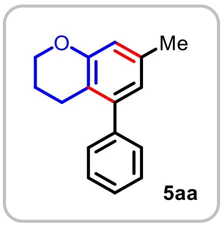
8. Synthesis and characterization of chromanes (5) from alkynols (2) and α,β-unsaturated ketones (4)

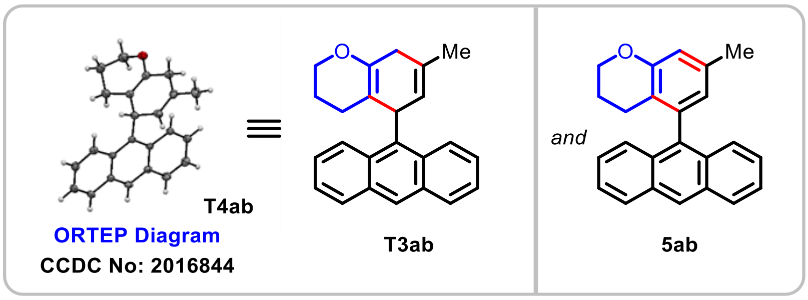
7-Methyl-5-phenylchromane (5aa):



5aa

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-4-phenylbut-3-en-2-one (**4a**) (0.073 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-methyl-5-phenylchromane (**5aa**) (0.086 g, 87%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.43-7.38(m, 2H), 7.37-7.31 (m, 3H),6.67 (d, *J* = 4.96 Hz, 2H), 4.22-4.18 (m,2H), 2.62-2.58 (m, 2H), 2.32 (s, 3H), 1.94-1.88 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 154.8, 142.8, 141.3, 136.7, 129.1, 127.9, 126.8, 122.7, 116.9, 116.3, 66.2, 23.9, 22.6, 21.0; HRMS (ESI) *m/z* calcdfor $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, found 225.1273.

5-(Anthracen-9-yl)-7-methyl-3,4,5,8-tetrahydro-2*H*-chromene (T3ab) and 5-(Anthracen-9-yl)-7-methylchromane (5ab):



T4ab

ORTEP Diagram

CCDC No: 2016844

T3ab

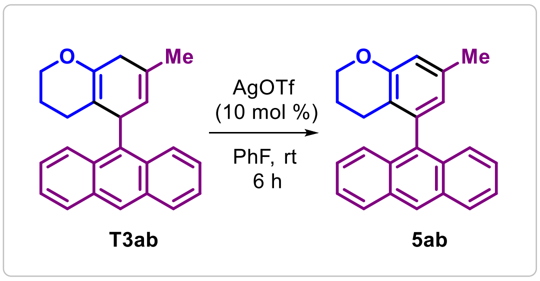
5ab

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g,1.01 mmol) and (*E*)-4-(anthracen-9-yl)but-3-en-2-one (**4b**) (0.124 g,0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded a mixture of two product5-(anthracen-9-yl)-7-methyl-3,4,5,8-tetrahydro-2H-chromene (**T3ab**) (0.056 g, 34%) as a yellow crystalsand 5-(anthracen-9-yl)-7-methylchromane (**5ab**) as a yellow powder (0.063 g, 39%). TLC: R_f = 0.9(SiO_2, 10% EtOAc/hexanes).

T3ab: ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.56-8.52 (m, 1H), 8.46 (d, *J* = 9.14 Hz, 1H), 8.38 (s, 1H), 8.04-7.97 (m, 2H), 7.53-7.41 (m, 3H), 7.39-7.34 (m, 1H), 5.63-5.57 (m, 1H), 5.54-5.51 (m, 1H), 4.06-3.99 (m, 1H), 3.91-3.85 (m, 1H), 2.93 (d, *J* = 8.20 Hz, 2H), 1.78 (s, 3H), 1.77-1.59 (m, 4H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 144.3, 134.6, 131.8, 131.6, 130.9, 130.6, 129.5, 129.3, 129.0, 127.0, 125.8, 125.2, 124.8, 124.5, 124.2, 123.6, 106.8, 65.7, 41.7, 33.6, 22.9, 22.7, 22.4; HRMS (ESI) *m/z* calcd for $C_{24}H_{23}O$ $[M+H]^+$ 327.1743, found 327.1745.

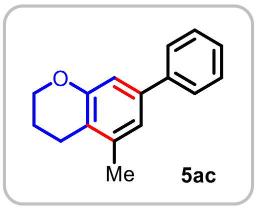
5ab: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.49 (s, 1H), 8.06 (d, *J* = 8.39 Hz, 2H), 7.62 (d, *J* = 9.16 Hz, 2H), 7.51-7.44 (m, 2H), 7.41-7.35 (m, 2H), 6.84 (s, 1H), 6.70 (s, 1H),4.17 (t, *J* = 5.34 Hz, 2H), 2.37 (s, 3H), 2.08-2.03 (m, 2H), 1.84-1.73 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.5, 139.8, 139.4, 137.6, 137.0, 131.4, 129.9, 129.4, 128.5, 126.7, 126.5,125.6, 125.2, 121.8, 121.3, 114.3, 66.4, 22.5, 22.3, 21.1; IR (KBr, cm^{-1}): υ 2929, 2860, 1612, 1575, 1454, 1215, 1138, 908, 733, 642; HRMS (ESI) *m/z* calcd for $C_{24}H_{21}O$ $[M+H]^+$ 325.1587, found 325.1586.

5-(Anthracen-9-yl)-7-methylchromane (5ab)(prepared from **T3ab**):



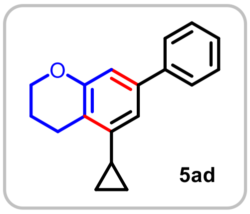
Following the *General Procedure*, to the mixture of 5-(anthracen-9-yl)-7-methyl-3,4,5,8-tetrahydro-2H-chromene (**T3ab**) (0.050 g, 0.15 mmol) in anhydrous PhF (2.0 mL) was added AgOTf (0.003 g, 0.015 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(anthracen-9-yl)-7-methylchromane (**5ab**) (0.035 g, 71%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.49 (s, 1H), 8.06 (d, *J*= 7.94 Hz, 2H), 7.62 (d, *J*= 9.16 Hz, 2H), 7.54-7.32 (m, 4H), 7.41-7.35 (m, 2H), 6.84 (s, 1H), 6.70 (s, 1H), 4.18 (t, *J*= 5.07 Hz, 2H),2.37 (s, 3H), 2.06 (t, *J*=6.39 Hz, 2H), 1.88-1.72 (m, 2H).

5-Methyl-7-phenylchromane (5ac):



Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-1-phenylbut-2-en-1-one (**4c**) (0.073 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-methyl-5-phenylchromane (**5ac**) (0.73 g, 68%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.55 (m, 2H), 7.46-7.40 (m, 2H), 7.36-7.30 (m, 1H), 7.03-6.94 (m, 2H), 4.23-4.17 (m, 2H), 2.70 (t, J = 6.63 Hz, 2H), 2.30 (s, 3H), 2.13-2.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 141.0, 139.8, 138.0, 128.6, 127.0, 126.9, 120.6, 120.2, 113.1, 66.0, 22.5, 22.4, 19.3; HRMS (ESI) *m/z* calcd for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, found 225.1276.

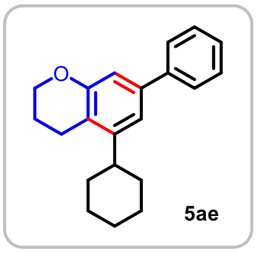
5-Cyclopropyl-7-phenylchromane (5ad):



Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-cyclopropyl-1-phenylprop-2-en-1-one (**4d**) (0.086 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded5-cyclopropyl-7-phenylchromane (**5ad**) (0.085 g, 67%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.59-7.53 (m, 2H), 7.46-7.39 (m, 2H), 7.37-7.30 (m, 1H), 6.93 (d, J = 1.88 Hz, 1H), 6.83 (d, J = 1.50 Hz, 1H), 4.21 (t, J = 5.13 Hz, 2H), 2.93 (t, J = 6.63 Hz, 2H), 2.15-2.07 (m, 2H), 1.90-1.83 (m, 1H), 0.99-0.92 (m, 2H) 0.77-0.65 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.1, 142.7, 141.2, 139.8, 128.6, 127.1, 126.9, 121.4, 116.7, 113.3, 66.0, 22.5, 22.2, 13.1, 6.8; IR (KBr, cm^{-1}): υ 3019, 2955, 2927, 2855, 1663, 1612, 1600, 1583, 1565, 1518, 1502, 1410, 1172, 962, 850, 771, 699, 625; HRMS (ESI) *m/z* calcd for $C_{18}H_{19}O$ $[M+H]^+$ 251.1430 found 251.1432.

5-Cyclohexyl-7-phenylchromane (5ae):

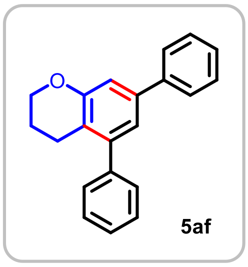
Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-cyclohexyl-1-phenylprop-2-en-1-one (**4e**) (0.108 g, 0.505 mmol) in anhydrous PhF (2 mL) was add AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 8h at rt. Purification of the crude product by column



5ae

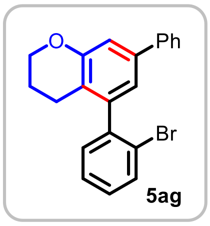
chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-cyclohexyl-7-phenylchromane (**5ae**) (0.083 g, 56%). TLC: R_f = 0.9 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.56 (m, 2H), 7.45-7.39 (m, 2H), 7.35-7.30 (m, 1H), 7.05 (d, *J* = 2.3 Hz, 1H), 6.92 (d, *J* = 2.3 Hz, 1H), 4.23-4.18 (m, 2H), 2.84-2.78 (m, 2H), 2.73-2.65 (m, 1H), 2.11-2.04 (m, 2H), 1.92-1.76 (m, 5H), 1.55-1.33 (m, 5H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.2, 147.5, 141.4, 140.0, 128.6, 127.0, 118.8, 116.6, 113.0, 65.8, 39.5, 33.8, 27.2, 26.3, 22.6, 21.8; HRMS (ESI) *m/z* calcd for $C_{21}H_{25}O$ $[M+H]^+$ 293.1900, found 293.1897.

5,7-Diphenylchromane (5af):



5af

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-chalcone (**4f**) (0.105 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5,7-diphenylchromane (**5af**) (0.111 g, 77%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.62 (d, *J* = 7.63 Hz, 2H), 7.48-7.32 (m, 8H), 7.10 (d, *J* = 4.20 Hz, 2H), 4.33-4.20 (m, 2H), 2.68 (t, *J* = 6.10 Hz, 2H), 2.03-1.90 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.2, 143.3, 141.1, 140.6, 140.0, 129.1, 128.7, 128.1, 127.2, 127.1, 127.0, 120.6, 119.2, 114.3, 66.3, 24.0, 22.5; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}O$ $[M+H]^+$ 287.1430 found 287.1430.



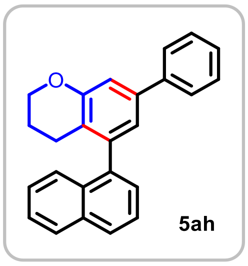
5ag

5-(2-Bromophenyl)-7-phenylchromane (5ag):

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2-bromophenyl)-1-phenylprop-2-en-1-one (**4g**) (0.144 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf(0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(2-bromophenyl)-7-phenylchromane (**5ag**) (0.126 g, 69%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.66-7.60 (m, 2H), 7.46-7.21 (m, 6H), 7.14 (d, *J* = 1.88 Hz, 1H), 6.99 (d, *J* = 1.88 Hz, 1H), 4.26-4.23(m, 2H), 2.60-2.52 (m, 1H), 2.43-2.36 (m, 1H), 2.02-1.97 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.1, 142.3, 141.8, 140.5, 139.7, 132.6, 130.8, 128.9, 128.7, 127.2 (2C), 126.9, 123.6, 120.0, 119.8, 114.7, 66.3, 23.0, 22.3; IR (KBr, cm^{-1}): υ 3018, 2952, 2880, 1612, 1603, 1583, 1566, 1479, 1216, 1177, 1053, 1009, 772, 669.

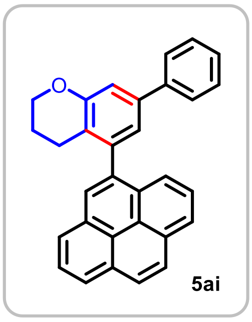
5-(Naphthalen-1-yl)-7-phenylchromane (5ah):

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one (**4h**) (0.130 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded 5-(naphthalen-1-yl)-7-phenylchromane (**5ah**) (0.127 g, 75%). TLC: R_f = 0.90 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.91-7.83 (m, 2H), 7.60 (d, *J* = 7.25 Hz, 3H), 7.54-7.44 (m, 2H), 7.42-7.35 (m, 4H), 7.32-7.28 (m, 1H), 7.23 (s, 1H), 7.13 (dd, *J* = 1.75, 22.3 Hz, 2H) 4.24-4.18 (m, 2H), 2.44-2.34 (m, 1H), 2.32-2.22 (m, 1H), 1.91-1.82 (m, 2H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 155.2, 141.5, 140.6, 139.7, 138.8, 133.5, 131.9, 128.7, 128.2, 127.6, 127.2, 126.9, 126.5, 126.1, 126.0, 125.8, 125.4, 121.2, 120.6, 114.4, 66.4, 23.1, 22.3; HRMS (ESI) *m/z* calcd for $C_{25}H_{21}O$ [M+H]$^+$ 337.1587 found 337.1587.



5ah

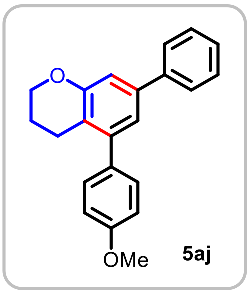
7-Phenyl-5-(pyren-4-yl)chromane(5ai):



5ai

Following the *General Procedure*,to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-1-phenyl-3-(pyren-4-yl)prop-2-en-1-one (**4i**) (0.167 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 8 h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded 7-Phenyl-5-(pyren-4-yl)chromane (**5ai**) (0.136 g, 66%). TLC: R_f = 0.9 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.28-8.16 (m, 4H), 8.13 (d, *J* = 0.9 Hz, 2H), 8.07-8.00 (m, 3H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.89 (d, *J* = 9.3 Hz, 1H), 7.71-7.65 (m, 2H), 7.47-7.40 (m, 2H), 7.35-7.28 (m, 1H), 4.26-4.22 (m, 2H), 2.41-2.36 (m, 2H), 1.93-1.87 (m, 2H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 155.3, 142.0, 140.6, 139.8, 136.3, 131.4, 131.0, 130.6, 128.9, 128.7, 128.3, 127.6, 127.4, 127.3, 127.2, 127.0, 126.0, 125.8, 125.3, 125.2, 125.1, 125.0, 124.8, 124.7, 124.5, 121.5, 120.8, 114.5, 66.4, 23.4, 22.3; HRMS (ESI): *m/z* calcd for $C_{31}H_{23}O$ [M+H]$^+$ 411. 1743, found 411.1741.

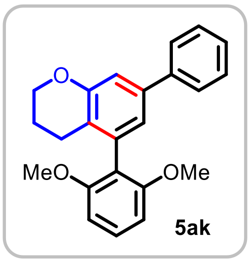
5-(4-Methoxyphenyl)-7-phenylchromane (5aj):



5aj

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**4j**) (0.120 g, 0.505 mmol)in anhydrous PhF (2 mL) was addedAgOTf(0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded5-(4-methoxyphenyl)-7-phenylchromane(**5aj**)(0.116 g, 73%).TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.60 (m, 2H), 7.45-7.40 (m, 2H), 7.36-7.30 (m, 3H), 7.08 (s, 2H), 7.01-6.96 (m, 2H), 4.27-4.23 (m, 2H), 3.87 (s, 3H), 2.71-2.65 (m, 2H), 2.01-1.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.7, 155.2, 143.0, 140.7, 139.9, 133.5, 130.2, 128.7, 127.2, 127.0, 120.7, 119.3, 114.1, 113.5, 66.3, 55.3, 24.1, 22.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}O_2$ $[M+H]^+$ 317.1536, found 317.1530.

5-(2,6-Dimethoxyphenyl)-7-phenylchromane (5ak):

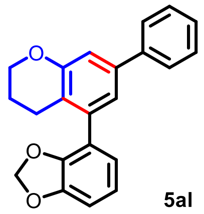


5ak

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(2,6-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**4k**) (0.135 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(2,6-dimethoxyphenyl)-7-phenylchromane (**5ak**) (0.149 g, 85%). TLC: R_f = 0.70 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.63-7.60 (m, 2H), 7.42-7.37 (m, 2H), 7.34-7.29 (m, 2H), 7.08 (d, J = 1.53 Hz, 1H), 7.00 (d, J = 1.91 Hz, 1H), 6.67 (d, J = 8.4 Hz, 2H), 4.26-4.19 (m, 2H), 3.75 (s, 6H), 2.46 (t, J = 6.49 Hz, 2H), 2.01-1.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 157.8, 155.0, 141.1, 139.2, 135.5, 128.8, 128.5, 127.0, 126.8, 121.7, 121.3, 118.0, 114.3, 104.0, 66.3, 55.9, 22.6, 22.4; HRMS (ESI) *m/z* calcd for $C_{23}H_{23}O_3$ $[M+H]^+$347.1642, found 347.1645.

5-(Benzo[d][1,3]dioxol-4-yl)-7-phenylchromane (5al):

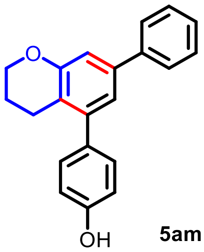
Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(benzo[d][1,3]dioxol-4-yl)-1-phenylprop-2-en-1-one (**4l**) (0.127 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at



5al

room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded5-(benzo[d][1,3]dioxol-4-yl)-7-phenylchromane (**5al**) (0.117 g, 70%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.65-7.56 (m, 2H), 7.47-7.40 (m, 2H), 7.35-7.32 (m, 1H), 7.10-7.03 (m, 2H), 6.90-6.86 (m, 2H), 6.85-6.81 (m, 1H), 6.02 (s, 2H), 4.24 (t, J = 5.04 Hz, 2H), 2.68 (t, J = 6.41 Hz, 2H), 2.02-1.91 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 147.3, 146.7, 142.9, 140.6, 139.9, 134.9, 128.7, 127.2, 127.0, 122.5, 120.6, 119.3, 114.3, 109.7, 108.1, 101.1, 66.3, 24.1, 22.5;HRMS (ESI) *m/z* calcd for $C_{22}H_{19}O_3$ $[M+H]^+$ 331.1329, found 331.1337.

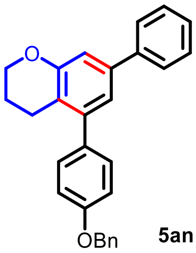
4-(7-Phenylchroman-5-yl)phenol(5am):



5am

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-3-(4-(hydroxy)phenyl)-1-phenylprop-2-en-1-one (**4m**) (0.113 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded4-(7-Phenylchroman-5-yl)phenol(**5am**)(0.124 g, 81%).TLC: R_f = 0.7 (SiO_2, 10% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.63-7.58 (m, 2H), 7.45-7.39 (m, 2H), 7.36-7.31 (m, 1H), 7.28-7.23 (m, 2H), 7.08 (dd, J = 8.4, 1.9 Hz, 2H), 6.92-6.88 (m, 2H), 5.36 (br. s, 1H), 4.25 (t, J = 5.0 Hz, 2H), 2.73-2.67 (m, 2H), 1.99-1.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.1, 154.7, 142.9, 140.6, 139.9, 133.5, 130.4, 128.7, 127.2, 126.9, 120.7, 119.3, 115.0, 114.0, 66.3, 24.1, 22.5; IR (KBr, cm^{-1}): υ 3019, 2953, 2881, 1611, 1563, 1515, 1424, 1347, 1321, 1257, 1215, 1173, 1048, 1009, 869, 835, 760, 699, 669; HRMS (ESI) *m/z* calcd for $C_{21}H_{19}O_2$ $[M+H]^+$ 303.1380, found 303.1379.

5-(4-(Benzyloxy)phenyl)-7-phenylchromane(5an):

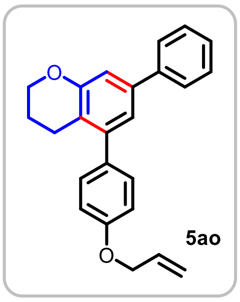


5an

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-(benzyloxy)phenyl)-1-phenylprop-2-en-1-one (**4n**) (0.158 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 2%

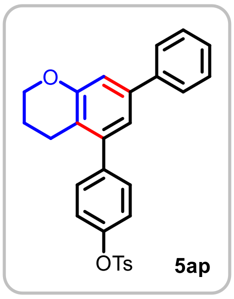
EtOAc/hexanes) afforded 5-(4-(benzyloxy)phenyl)-7-phenylchromane (**5an**) (0.140 g, 70%). TLC: R_f = 0.7 (SiO_2, 10% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.59 (m, 2H), 7.50-7.46 (m, 2H), 7.45-7.39 (m, 4H), 7.38-7.30 (m, 4H), 7.08-7.03 (m, 4H), 5.13 (s, 2H), 4.27-4.23 (m,2H), 2.68 (t, J = 6.4 Hz, 2H), 2.00-1.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.0, 155.2, 142.9, 140.7, 139.9, 137.0, 133.7, 130.2, 128.7, 128.6, 128.0, 127.5, 127.2, 127.0, 120.7, 119.3, 114.4, 114.1, 70.1, 66.3, 24.1, 22.5; IR (KBr, cm^{-1}): υ 3019, 2935, 1608, 1563, 1512, 1401, 1347, 1287, 1218, 1176, 1141, 1076, 1018, 929, 903, 868, 772, 697, 669; HRMS (ESI) *m/z* calcd for $C_{28}H_{25}O_2$ $[M+H]^+$ 393.1849, found 393.1850.

5-(4-(Allyloxy)phenyl)-7-phenylchromane (5ao):


5ao

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-allyloxyphenyl)-1-phenylprop-2-en-1-one (**4o**) (0.133 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded5-(4-(allyloxy)phenyl)-7-phenylchromane (**5ao**) (0.131 g, 76%). TLC: R_f = 0.7 (SiO_2, 10% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.61 (m, 2H), 7.48-7.41 (m, 2H), 7.38-7.30 (m, 3H), 7.13-7.09 (m, 2H), 7.04-6.98 (m, 2H), 6.19-6.08 (m, 1H), 5.53-5.46 (m, 1 H), 5.38-5.33 (m, 1H), 4.64-4.60 (m, 2H), 4.27 (t, J = 5.0 Hz, 2H), 2.70 (t, J = 6.4 Hz, 2H), 2.02-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 157.7, 155.2, 142.9, 140.7, 139.9, 133.6, 133.2, 130.1, 128.6, 127.2, 126.9, 120.6, 119.2, 117.7, 114.3, 114.0, 68.8, 66.2, 24.1, 22.5;IR (KBr, cm^{-1}): υ 3019, 1609, 1563, 1512, 1466, 1424, 1347, 1321, 1286, 1215, 1177, 1076, 929, 834, 760, 669; HRMS (ESI) *m/z* calcd for $C_{24}H_{23}O_2$ $[M+H]^+$ 343.1693, found 343.1689.

4-(7-Phenylchroman-5-yl)phenyl 4-methylbenzenesulfonate (5ap):

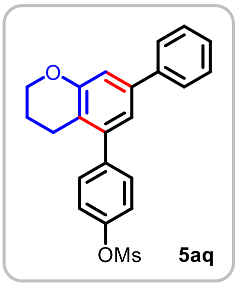


5ap

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-4-(3-oxo-3-phenylprop-1-en-1-yl)phenyl 4-methylbenzenesulfonate (**4p**) (0.191 g, 0.505 mmol) in anhydrous PhF (2 mL) was add AgOTf(0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 4-(7-phenylchroman-5-yl)phenyl 4-methylbenzenesulfonate (**5ap**)

(0.195 g, 85%). TLC: R_f = 0.60 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.76 (m, 2H), 7.60-7.56 (m, 2H), 7.45-7.39 (m, 2H), 7.37-7.33 (m, 3H), 7.32-7.28 (m, 2H), 7.09 (d, *J* = 2.3 Hz, 1H), 7.07-7.03 (m, 2H), 7.01 (d, *J* = 1.8 Hz, 1H), 4.24 (t, *J* = 5.0 Hz, 2H), 2.60 (t, *J* = 6.4 Hz, 2H), 2.47 (s, 3H), 1.99-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 148.7, 145.4, 141.9, 140.4, 140.1, 140.0, 132.5, 130.3, 129.8, 128.7, 128.5, 127.4, 126.9, 122.1, 120.4, 119.0, 114.7, 66.3, 24.0, 22.4, 21.7; HRMS (ESI) *m/z* calcd for $C_{28}H_{25}O_4S$ [M+H]$^+$ 457.1468, found 457.1467.

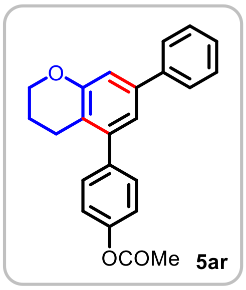
4-(7-Phenylchroman-5-yl)phenylmethanesulfonate (5aq):



5aq

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-4-(3-oxo-3-phenylprop-1-en-1-yl)phenyl methanesulfonate (**4q**) (0.152 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf(0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 4-(7-phenylchroman-5-yl)phenyl methanesulfonate (**5aq**) (0.167 g, 87%). TLC: R_f = 0.60 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.59 (m, 2H), 7.46-7.41 (m, 4H), 7.38-7.34 (m, 3H), 7.12 (d, *J* = 2.3 Hz, 1H), 7.05 (d, *J* = 1.5 Hz, 1H), 4.28-4.24 (m, 2H), 3.21 (s, 3H), 2.68-2.63 (m, 2H), 2.08-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 148.2, 141.7, 140.4, 140.3, 140.1, 130.7, 128.7, 127.4, 126.9, 121.7, 120.4, 119.0, 114.7, 66.3, 37.4, 24.0, 22.3; IR (KBr, cm^{-1}): υ 3019, 2939, 2877, 1723, 1601, 1583, 1565, 1467, 1412, 1372, 1351, 1321, 1287, 1215, 1149, 1101, 1048, 1011, 969, 929, 903, 871, 849, 758, 669; HRMS (ESI): calcd for $C_{22}H_{21}O_4S$ [M+H]$^+$ 381.1155, found 381.1149.

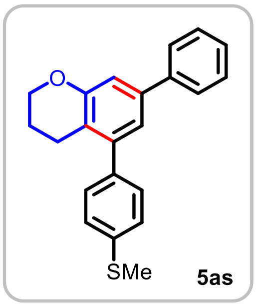
4-(7-Phenylchroman-5-yl)phenyl acetate (5ar):



5ar

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-4-(3-oxo-3-phenylprop-1-en-1-yl)phenyl acetate (**4r**) (0.134 g, 0.505 mmol) in anhydrous PhF (2 mL) was add AgOTf (0.012 g, 0.05mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded4-(7-phenylchroman-5-yl)phenyl acetate (**5ar**) (0.145 g, 83%). TLC: R_f = 0.70 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ7.65-7.57 (m, 2H), 7.46-7.38 (m, 4H), 7.37-7.31 (m, 1H), 7.18-7.14 (m, 2H), 7.10 (d, *J*= 1.88 Hz, 1H), 7.08 (d, *J*= 1.88 Hz, 1H), 4.28-4.23 (m, 2H), 2.68 (t, *J*=6.38 Hz, 2H), 2.35 (s, 3H), 2.01-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 169.6, 155.3, 149.8, 142.4, 140.5, 140.0, 138.6, 130.1, 128.7, 127.3, 126.9, 121.2, 120.6, 119.2, 114.5, 66.3, 24.0, 22.3, 21.2; HRMS (ESI) *m/z* calcd for $C_{23}H_{21}O_3$ $[M+H]^+$ 345.1485, found 345.1476.

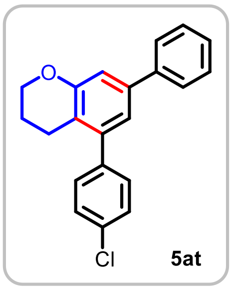
5-(4-(Methylthio)phenyl)-7-phenylchromane(5as):



5as

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-3-(4-(methylthio)phenyl)-1-phenylprop-2-en-1-one (**4s**) (0.128 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(4-(methylthio)phenyl)-7-phenylchromane (**5as**) (0.100 g, 60%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.59 (m, 2H), 7.46-7.39 (m, 2H), 7.37-7.30 (m, 5H), 7.08 (d, *J* = 1.83 Hz, 1H), 7.06 (d, *J* = 1.83 Hz, 1H), 4.27-4.23 (m, 2H), 2.68 (t, *J* = 6.41 Hz, 2H), 2.54 (s, 3H), 2.03-1.89 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 142.7, 140.6, 140.1, 137.9, 137.3, 129.6, 128.7, 127.3, 126.9, 126.2, 120.5, 119.2, 114.4, 66.3, 24.1, 22.5, 15.8; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}OS$ $[M+H]^+$ 333.1308 found 333.1306.

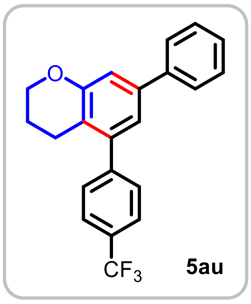
5-(4-Chlorophenyl)-7-phenylchromane (5at):



5at

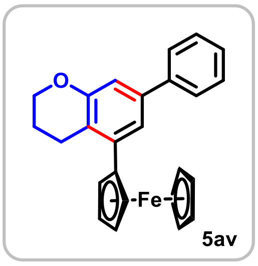
Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (**4t**) (0.122 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded5-(4-chlorophenyl)-7-phenylchromane (**5at**) (0.094 g, 58%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.61-7.58 (m, 2H), 7.45-7.39 (m, 4H), 7.36-7.30 (m, 3H), 7.10 (d, *J* = 1.9 Hz, 1H), 7.03 (d, *J* = 2.0 Hz, 1H), 4.25 (t, *J* = 5.13 Hz, 2H), 2.67-2.62 (m, 2H), 2.01-1.93 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.3, 142.1, 140.5, 140.1, 139.5, 133.1, 130.4, 128.7, 128.3, 127.3, 126.9, 120.4, 119.0, 114.6, 66.3, 24.0, 22.4; HRMS (ESI) *m/z* calcd for $C_{21}H_{18}OCl$ $[M+H]^+$ 321.1041, found 321.1039.

7-Phenyl-5-(4-(trifluoromethyl)phenyl)chromane(5au):



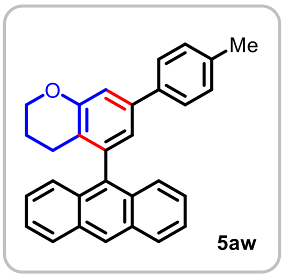
Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**4u**) (0.139 g, 0.505 mmol)in anhydrous PhF (2 mL) was addedAgOTf(0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-phenyl-5-(4-(trifluoromethyl)phenyl)chromane (**5au**) (0.178 g, 69%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, *J* = 8.1 Hz, 2H), 7.63-7.58 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.47-7.40 (m, 2H), 7.38-7.32 (m, 1H), 7.13 (d, *J* = 1.75 Hz, 1H), 7.05 (d, *J* = 1.9 Hz, 1H), 4.30-4.24 (m, 2H), 2.64 (t, *J* = 6.5 Hz, 2H), 2.02-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.4, 144.8, 141.9, 140.4, 140.3, 129.5, 128.8, 127.4, 126.9, 125.2, 125.1 (2C), 125.0 120.3, 118.9, 115.0, 66.3, 23.9, 22.3; HRMS (ESI) *m/z* calcd for $C_{22}H_{18}OF_3$ $[M+H]^+$ 355.1304, found 355.1304.

7-Phenyl-5-(ferrocenyl)chromane (5av):



Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-3-(ferrocene)-1-phenylprop-2-en-1-one (**4v**) (0.156 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded7-phenyl-5-(ferrocenyl)chromane (**5av**) (0.134 g, 67%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.63 (m, 2H), 7.61 (d, *J* = 2.3 Hz, 1H), 7.50-7.45 (m, 2H), 7.40-7.34 (m, 1H), 6.97 (d, *J* = 1.5 Hz, 1H), 4.49-4.48 (m, 2H), 4.32-4.30 (m, 2H), 4.24-4.21 (m, 2H), 4.19 (s, 5H), 2.83-2.78 (m, 2H), 2.00-1.94 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.0, 141.0, 139.5, 139.1, 128.8, 127.2, 126.9, 121.7, 119.9, 113.5, 87.1, 70.2, 69.6, 67.8, 66.1, 24.4, 22.6; HRMS (ESI) *m/z* calcd for $C_{25}H_{23}OFe$ $[M+H]^+$ 395.1093, found 395.1066.

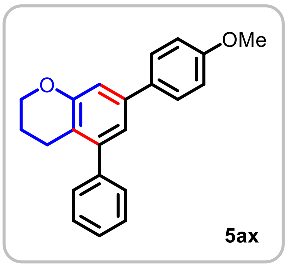
5-(Anthracen-9-yl)-7-(*p*-tolyl)chromane(5aw):



5aw

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(anthracen-9-yl)-1-(*p*-tolyl)prop-2-en-1-one (**4w**) (0.162 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(anthracen-9-yl)-7-(*p*-tolyl)chromane (**5aw**) (0.142 g, 71%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.52 (s, 1H), 8.08 (d, *J* = 8.39 Hz, 2H), 7.69 (d, *J* = 8.39 Hz, 2H), 7.55 (d, *J* = 8.39 Hz, 2H), 7.51-7.46 (m, 2H), 7.42-7.34 (m, 2H), 7.28-7.27 (m, 1H), 7.21 (d, *J* = 8.39 Hz, 2H), 7.15 (d, *J* = 1.53 Hz, 1H),4.24 (t, *J* = 5.34 Hz, 2H), 2.37 (s, 3H), 2.16-2.11 (m, 2H), 1.88-1.80 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.5, 139.8, 139.4, 137.6, 137.0, 135.5, 131.4, 129.9, 129.4, 128.5, 126.7, 126.5, 125.6, 125.2, 121.8, 121.3, 114.3, 66.4, 22.5, 22.3, 21.1; HRMS (ESI) *m/z* calcd for $C_{30}H_{25}O$ $[M+H]^+$ 401.1900 found 401.1899.

7-(4-Methoxyphenyl)-5-phenylchromane (5ax):

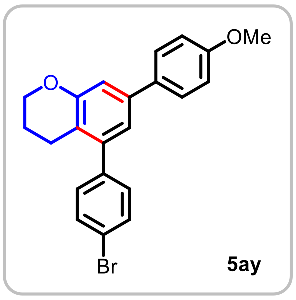


5ax

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (**4x**) (0.120 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-(4-methoxyphenyl)-5-phenylchromane (**5ax**) (0.126 g, 79%). TLC: R_f = 0.80 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60-7.51 (m, 2H), 7.48-7.33 (m, 5H), 7.06-7.04 (m, 2H), 6.99-6.91 (m, 2H), 4.25 (t, *J* = 5.34 Hz, 2H), 3.85 (s, 3H) 2.69-2.64 (m, 2H), 2.01-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 159.1, 155.2, 143.3, 141.2, 139.6, 133.2, 129.1, 128.1, 127.9, 127.0, 120.2, 118.5, 114.1, 113.8, 66.3, 55.3, 24.0, 22.5; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}O_2$ $[M+H]^+$317.1536, found 317.1531.

5-(4-Bromophenyl)-7-(4-methoxyphenyl)chromane (5ay):

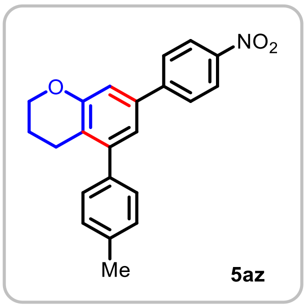
Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-3-(4-bromophenyl)-1-(4-methoxyphenyl)prop-2-en-1-one (**4y**) (0.160 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol) under argon atmosphere at



5ay

room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(4-bromophenyl)-7-(4-methoxyphenyl)chromane (**5ay**) (0.135 g, 67%). TLC: R_f = 0.80 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.76-7.73 (m, 1H), 7.54-7.50 (m, 1H), 7.47-7.43 (m, 1H), 7.32-7.25 (m, 3H), 7.03-7.00 (m, 2H), 6.99-6.95 (m, 2H), 4.25 (t, J = 5.13 Hz, 2H), 3.87 (s, 3H), 2.68 (t, J = 6.50 Hz, 2H), 2.00-1,92 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.8, 155.4, 143.2, 142.9, 138.3, 133.2, 130.2 (2C), 130.1, 130.0, 125.5, 122.8, 120.5, 120.,0 114.0, 113.6, 66.3, 55.3, 24.1, 22.4; HRMS (ESI) m/z calcd for $C_{22}H_{20}O_2Br$ $[M+H]^+$ 395.0641, found 395.0645.

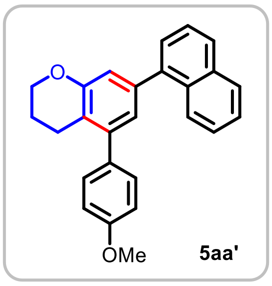
7-(4-Nitrophenyl)-5-(*p*-tolyl)chromane (5az):



5az

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-1-(4-nitrophenyl)-3-(*p*-tolyl)prop-2-en-1-one (**4z**) (0.134 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 7-(4-nitrophenyl)-5-(*p*-tolyl)chromane (**5az**) (0.120 g, 69%). TLC: R_f = 0.70 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.47 (m, 2H), 7.36-7.30 (m, 2H), 7.23 (d, J = 7.9 Hz, 2H), 7.15-7.08 (m, 2H), 7.05 (dd, J = 19.4, 1.9 2H), 4.24 (t, J = 5.1 Hz, 2H), 2.63 (t, J = 6.4 Hz, 2H), 2.39 (s, 3H), 2.00-1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 163.3, 160.8, (unidentified aromatic impurity) 155.3, 142.2, 140.0, 137.6, 137.1, 137.0, 130.7, 130.6, 129.4, 126.8, 120.4, 118.9, 115.1, 114.9, 114.2, 66.3, 29.7 (grease), 24.0, 22.5, 21.1.

5-(4-Methoxyphenyl)-7-(naphthalen-1-yl)chromane(5aa'):

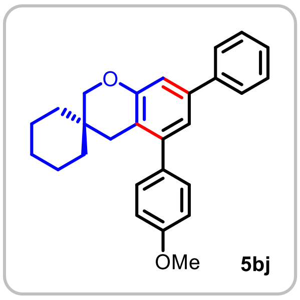


5aa'

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-methoxyphenyl)-1-(naphthalen-1-yl)prop-2-en-1-one (**4a'**) (0.145 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded5-(4-methoxyphenyl)-7-(naphthalen-1-yl)chromane (**5aa'**)

(0.155 g, 84%). TLC: $R_f = 0.80$ (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.11-8.09 (m, 1H), 7.93-7.88 (m, 1H), 7.85 (d, J = 7.79 Hz, 1H), 7.54-7.43 (m, 4H), 7.37-7.32 (m, 2H), 7.02-6.93 (m, 4H), 4.31-4.27 (m, 2H), 3.86 (s, 3H), 2.76 (t, J = 6.41 Hz, 2H), 2.08-1.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.7, 154.8, 142.4, 139.8, 139.4, 133.8, 133.3, 131.5, 130.3, 128.2, 127.5, 126.8, 126.2, 125.9, 125.7, 125.4, 123.7, 119.1, 117.1, 113.5, 66.3, 55.3, 24.3, 22.6; HRMS (ESI) *m/z* calcd for $C_{26}H_{23}O_2$ $[M+H]^+$367.1693, found 367.1696.

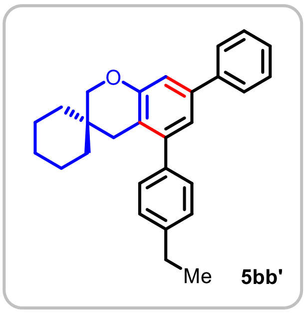
5-(4-Methoxyphenyl)-7-phenylspiro[chromane-3,1'-cyclohexane] (5bj):



5bj

Following the *General Procedure*, to the mixture of (1-(but-3-yn-1-yl)cyclohexyl)methanol (**2b**) (0.1 g, 0.60 mmol) and (*E*)3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (**4j**) (0.071 g, 0.30 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.007 g, 0.03mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(4-methoxyphenyl)-7-phenylspiro[chromane-3,1'-cyclohexane] (**5bj**) (0.088 g, 77%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.62 (m, 1H), 7.61-7.59 (m, 1H), 7.46-7.39 (m, 2H), 7.36-7.29 (m, 3H), 7.10-7.06 (m, 2H), 7.01-6.99 (m, 1H), 6.99-6.98 (m, 1H), 3.94 (s, 2H), 3.89 (s, 3H), 2.50 (s, 2H), 1.49-1.34 (m, 10H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.6, 154.4, 143.2, 140.7, 133.5, 130.2, 128.7, 127.2, 126.9, 121.0, 118.2, 113.5 (2C), 73.3, 55.3, 33.2, 31.2, 26.4, 21.5; IR (KBr, cm^{-1}): υ 3019, 2932, 2855, 1609, 1563, 1514, 1466, 1341, 1215, 1150, 929, 869, 767, 669; HRMS (ESI) *m/z* calcd for $C_{27}H_{29}O_2$ $[M+H]^+$ 385.2162, found 385.2168.

5-(4-Ethylphenyl)-7-phenylspiro[chromane-3,1'-cyclohexane] (5bb'):

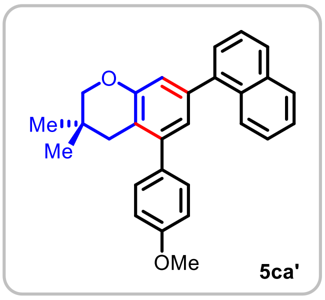


5bb'

Following the *General Procedure*, to the mixture of (1-(but-3-yn-1-yl)cyclohexyl)methanol (**2b**)(0.1 g, 0.60 mmol) and (*E*)-3-(4-ethylphenyl)-1-phenylprop-2-en-1-one (**4b'**) (0.070 g, 0.30 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.007 g, 0.030 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(4-ethylphenyl)-7-phenylspiro[chromane-3,1'-cyclohexane] (**5bb'**) (0.075 g, 66%). TLC: R_f = 0.90 (SiO_2, 10%

EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.61-7.57 (m, 2H), 7.42-7.36 (m, 2H), 7.33-7.25 (m, 5H), 7.08-7.05 (m, 2H), 3.93 (s, 2H), 2.72 (q, *J* = 7.63 Hz, 15.26 Hz, 2H), 2.48 (s, 2H), 1.51-1.34 (m, 9H), 1.33-1.28 (m, 4H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 154.4, 143.6, 142.9, 140.7, 139.6, 138.4, 129.0, 128.6, 127.6, 127.1, 126.9, 121.0, 118.1, 113.6, 73.5, 35.9, 33.2, 31.2, 28.6, 26.4, 21.5, 15.4; HRMS (ESI) *m/z* calcd for $C_{28}H_{31}O$ [M+H]$^+$ 383.2369, found 383.2374.

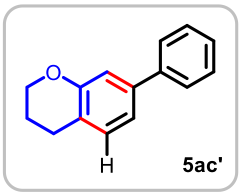
5-(4-Methoxyphenyl)-3,3-dimethyl-7-(naphthalen-1-yl)chromane (5ca'):



5ca'

Following the *General Procedure*, to the mixture of 2,2-dimethylhex-5-yn-1-ol (**2c**) (0.1 g, 0.79 mmol) and (*E*)-3-(4-methoxyphenyl)-1-(naphthalen-1-yl)prop-2-en-1-one (**4a'**) (0.112 g, 0.39 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.010 g, 0.039mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded 5-(4-methoxyphenyl)-3,3-dimethyl-7-(naphthalen-1-yl)chromane (**5ca'**) (0.110 g, 72%). TLC: R_f = 0.90 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.13 (d, *J* = 8.39 Hz, 1H), 7.93-7.84 (m, 2H), 7.54-7.46 (m, 4H), 7.37-7.33 (m, 2H), 7.06-6.94 (m, 4H), 3.87 (s, 5H), 2.55 (s, 2H), 1.06 (s, 6H); ^{13}C NMR (CDCl$_3$, 126 MHz): δ 158.7, 153.6, 142.6, 139.8, 139.3, 133.8, 133.4, 131.5, 130.3, 129.0, 128.2, 127.5, 126.9, 126.2, 125.9, 125.7, 125.4, 124.1, 118.3, 116.8, 113.9, 113.5, 75.4, 55.3, 38.2, 28.8, 24.9.

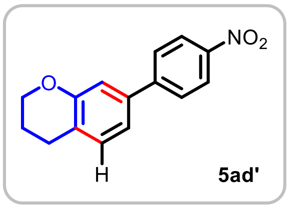
7-Phenylchromane(5ac'):



5ac'

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and1-phenylprop-2-en-1-one (**4c'**) (0.066 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded7 -phenylchromane (**5ac'**)(0.057 g, 54%). TLC: R_f = 0.90 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.63-7.57 (m, 2H), 7.48-7.41 (m, 2H), 7.38-7.32 (m, 1H), 7.16-7.10 (m, 2H), 7.09-7.06 (m, 1H), 4.25 (t, *J* = 5.13 Hz, 2H), 2.85 (t, *J* = 6.5 Hz, 2H), 2.11-2.02 (m, 2H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 155.1, 140.9, 140.5, 130.1, 128.7, 127.1, 126.9, 121.3, 119.0, 115.2, 66.5, 24.6, 22.4; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O$ [M+H]$^+$ 211.1117, found 211.1110.

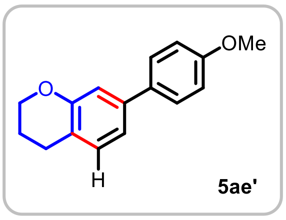
7-(4-Nitrophenyl)chromane (5ad'):



5ad'

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and 1-(4-nitrophenyl)prop-2-en-1-one (**4d'**) (0.089 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded 7-(4-nitrophenyl)chromane (**5ad'**) (0.078 g, 60%). TLC: R_f = 0.90 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.33-8.22 (m, 2H), 7.75-7.65 (m, 2H), 7.18-7.05 (m, 3H), 4.31-4.21 (m, 2H), 2.85 (t, J = 6.50 Hz, 2H), 2.13-1.99 (m, 2H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 155.4, 147.3, 146.9, 137.8, 130.6, 127.5, 124.0, 123.3, 119.0. 115.5, 66.6, 24.7, 22.2.

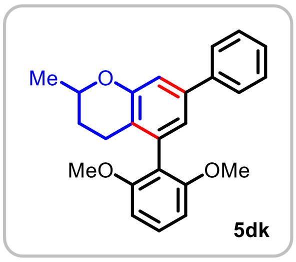
7-(4-Methoxyphenyl)chromane(5ae'):



5ae'

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and1-(4-methoxyphenyl)prop-2-en-1-one (**4e'**) (0.081 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded 7-(4-methoxyphenyl)chromane (**5ae'**) (0.071 g, 59%). TLC: R_f = 0.90 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.58-7.42 (m, 2H), 7.11-7.03 (m, 2H), 7.02-6.94 (m, 3H), 4.23 (t, J = 5.13 Hz, 2H), 3.85 (s, 3H), 2.86-2.80 (m, 2H), 2.13-2.00 (m, 2H); ^{13}C NMR (CDCl$_3$, 101 MHz): δ 159.0, 155.1, 140.1, 133.5, 130.1, 127.9, 120.7, 118.6, 114.7, 114.1, 66.5, 55.3, 24.6, 22.4.

5-(2,6-Dimethoxyphenyl)-2-methyl-7-phenylchromane (5dk):

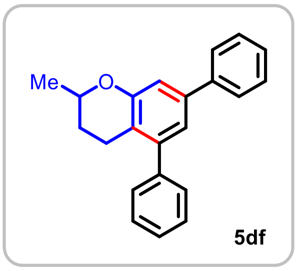


5dk

Following the *General Procedure*, to the mixture of hept-6-yn-2-ol (**2d**) (0.1 g, 0.8 mmol) and (*E*)-3-(2,6-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**4k**) (0.119 g, 0.4 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.011 g, 0.04mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO$_2$, 1% EtOAc/hexanes) afforded 5-(2,6-dimethoxyphenyl)-2-methyl-7-phenylchromane (**5dk**) (0.138 g, 86%). TLC: R_f = 0.70 (SiO$_2$, 10% EtOAc/hexanes); ^{1}H NMR (CDCl$_3$, 400 MHz): δ

7.65 (d, J=7.63 Hz, 2H), 7.41 (t, J = 7.63 Hz, 2H), 7.37-7.28 (m, 2H), 7.12 (d, J = 1.53 Hz, 1H), 7.03 (d, J = 1.53 Hz, 1H), 6.69 (d, J = 8.39 Hz, 2H), 4.25-4.21 (m, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.59-2.53 (m, 1H), 2.46-2.38 (m, 1H), 1.99-1.81 (m, 1H), 1.81-1.67 (m, 1H), 1.45 (d, J = 6.10 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 157.9, 157.6, 155.1, 141.1, 139.2, 135.3, 128.8, 128.5, 127.0, 126.8, 121.5, 120.9, 118.1, 114.2, 104.0, 103.9, 71.9,55.9, 55.8, 29.3, 22.6, 21.6; HRMS (ESI) *m/z* calcd for $C_{24}H_{25}O_3$ $[M+H]^+$ 361.1798 found, 361.1800.

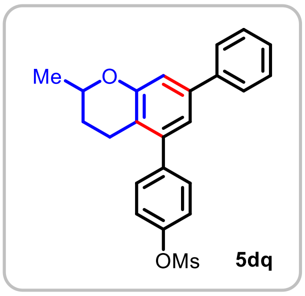
2-Methyl-5,7-diphenylchromane (5df):



5df

Following the *General Procedure*, to the mixture of hept-6-yn-2-ol (**2d**) (0.1 g, 0.8 mmol) and (*E*)-chalcone (**4f**) (0.092 g, 0.4mmol) in anhydrous PhF (2 mL) was added AgOTf (0.011 g, 0.04 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded2-methyl-5,7-diphenylchromane (**5df**) (0.093 g, 70%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.64-7.59 (m, 2H), 7.47-7.30 (m, 8H), 7.13-7.07 (m, 2H), 4.28-4.19 (m, 1H), 2.84-2.73 (m, 1H), 2.63-2.54 (m, 1H), 2.02-1.94 (m, 1H), 1.72-1.60 (m, 1H), 1.43 (d, J = 6.25 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.5, 143.1, 141.3, 140.7, 139.9, 129.1, 128.7, 128.1, 127.2, 127.0, 126.9, 120.4, 118.8, 114.3, 72.1, 29.4, 24.0, 21.4; HRMS (ESI) *m/z* calcd for $C_{22}H_{21}O$ $[M+H]^+$ 301.1587, found 301.1587.

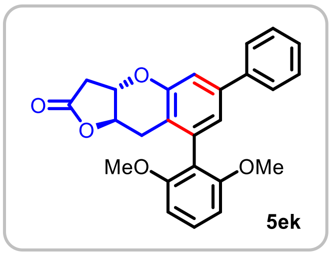
4-(2-Methyl-7-phenylchroman-5-yl)phenylmethanesulfonate(5dq):



5dq

Following the *General Procedure*, to the mixture of hept-6-yn-2-ol (**2d**) (0.1 g, 0.8 mmol) and(*E*)-4-(3-oxo-3-phenylprop-1-en-1-yl)phenyl methanesulfonate (**4q**) (0.134 g, 0.4 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.011 g, 0.04mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 2% EtOAc/hexanes) afforded 4-(2-methyl-7-phenylchroman-5-yl)phenyl methanesulfonate (**5dq**) (0.116 g, 67%). TLC: R_f = 0.70 (SiO_2, 20% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.58 (m, 2H), 7.46-7.39 (m, 4H), 7.37-7.31 (m, 3H), 7.14-7.11 (m, 1H), 7.05-7.03 (m, 1H), 4.34-4.12 (m, 1H), 3.21 (s, 3H), 2.80-2.71 (m, 1H), 2.65-2.52 (m, 1H), 2.06-1.95 (m, 1H), 1.73-1.60 (m, 1H), 1.45 (d, J = 6.25 Hz, 3H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.6, 148.2, 141.6, 140.6, 140.4, 140.1, 130.7, 128.7, 127.4, 126.9, 121.7, 120.4, 118.7, 115.3, 114.8, 72.1, 37.5, 26.9, 24.0, 21.4; HRMS (ESI) *m/z* calcd for $C_{23}H_{23}O_4S$ $[M+H]^+$ 395.1312, found 395.1305.

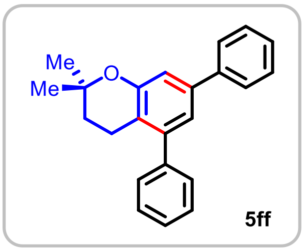
(*3aS*,*9aR*)-8-(2,6-Dimethoxyphenyl)-6-phenyl-3,3a,9,9a-tetrahydro-2*H*-furo[3,2-b]chromen-2-one (5ek):



5ek

Following the *General Procedure*, to the mixture of (*4S*,*5R*)-5-(but-3-yn-1-yl)-4-hydroxydihydrofuran-2(3*H*)-one (**2e**)(0.1 g, 0.64 mmol) and (*E*)-3-(2,6-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**4k**) (0.085 g, 0.32 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.008 g, 0.032 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded (*3aS*,*9aR*)-8-(2,6-dimethoxyphenyl)-6-phenyl-3,3a,9,9a-tetrahydro-2*H*-furo[3,2-*b*]chromen-2-one (**5ek**)(0.058 g, 45%).TLC: R_f = 0.70 (SiO_2, 10% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.52-7.58 (m, 2H), 7.44-7.38 (m, 2H), 7.37-7.29 (m, 2H), 7.17-7.15 (m, 2H), 6.68 (dd, *J* = 8.4, 1.63 Hz, 2H), 4.92-4.87 (m, 1H), 4.83-4.80 (m, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 2.98-2.81 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 174.8, 157.9, 157.6, 153.6, 140.6, 140.1, 135.2, 129.3, 128.6, 127.2, 127.1, 124.3, 119.4, 116.5, 114.8, 104.2, 103.8, 78.3, 73.1, 55.9, 55.8 37.4, 25.7; HRMS (ESI) *m/z* calcd for $C_{25}H_{23}O_5$ $[M+H]^+$ 403.1540, found 403.1536.

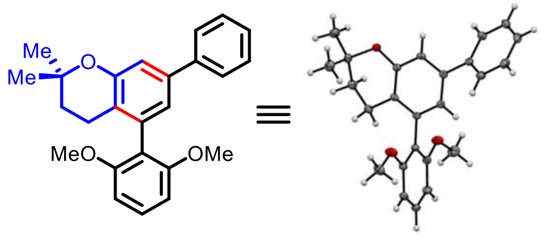
2,2-Dimethyl-5,7-diphenylchromane (5ff):



5ff

Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.1 g, 0.79 mmol) and (*E*)-chalcone (**4f**) (0.081 g, 0.39 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.010 g, 0.039mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 2,2-dimethyl-5,7-diphenylchromane (**5ff**) (0.082 g, 67%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.72-7.66 (m, 2H), 7.51-7.43 (m, 6H), 7.41-7.34 (m, 2H), 7.20-7.14 (m, 2H), 2.75-2.69 (m, 2H), 1.84-1.79 (m, 2H), 1.47 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.4, 143.0, 141.3, 140.7, 140.0, 129.1, 128.6, 128.1, 127.1, 127.0, 126.9, 120.1, 117.9, 114.8, 73.9, 32.9, 26.9, 21.5;IR (KBr, cm^{-1}): υ 3019, 2978, 1600, 1563, 1526, 1468, 1440, 1402, 1332, 1217, 1164, 1029, 967, 929, 772, 702, 669; HRMS (ESI) *m/z* calcd for $C_{23}H_{23}O$ $[M+H]^+$ 315.1743, found 315.1740.

5-(2,6-Dimethoxyphenyl)-2,2-dimethyl-7-phenylchromane (5fk):



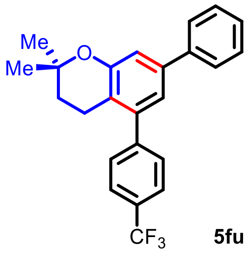
5fk

ORTEP Diagram

CCDC No: 2016842

Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.1 g, 0.79 mmol) and (*E*)-3-(2,6-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**4k**) (0.105 g, 0.39 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.010 g, 0.039mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(2,6-dimethoxyphenyl)-2,2-dimethyl-7-phenylchromane (**5fk**) as a white crystal (0.130 g, 89%).TLC: R_f = 0.60 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.65 (d, *J* = 7.33 Hz, 2H), 7.43-7.38 (m, 2H), 7.37-7.28 (m, 2H), 7.11 (d, *J* = 1.37 Hz, 1H), 7.03 (d, *J* = 1.37 Hz, 1H), 6.73-6.65 (m, 2H), 3.76 (s, 6H), 2.49-2.44 (m, 2H), 1.79 (t, *J* = 6.87 Hz, 2H), 1.40 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 157.8, 154.1, 141.1, 139.2, 135.2, 128.8, 128.4, 127.0, 126.7, 121.1, 120.2, 118.2, 114.6, 104.0, 73.9, 55.8, 32.8, 26.8, 20.3; HRMS (ESI) *m/z* calcd for $C_{25}H_{27}O_3$ $[M+H]^+$ 375.1955, found 375.1956.

2,2-Dimethyl-7-phenyl-5-(4-(trifluoromethyl)phenyl)chromane (5fu):

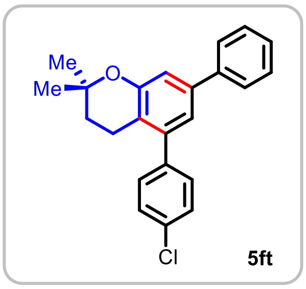


5fu

Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**)(0.1 g, 0.79 mmol) and (*E*)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**4u**) (0.109 g, 0.39 mmol) in anhydrous PhF (2 mL) was added Ag OTf (0.010 g, 0.039 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 2,2-dimethyl-7-phenyl-5-(4-(trifluoromethyl)phenyl)chromane (**5fu**) (0.097 g, 64%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70 (d, *J* = 8.00 Hz, 2H), 7.63-7.58 (m, 2H), 7.51 (d, *J* = 8.00 Hz, 2H), 7.44-7.40 (m, 2H), 7.36-7.32 (m, 1H), 7.13 (d, *J* = 1.88 Hz, 1H), 7.04 (d, *J* = 2.00 Hz, 1H), 2.65-2.59 (m, 2H), 1.80-1.75 (m, 2H), 1.41 (s, 6H); ^{13}C NMR

($CDCl_3$, 101 MHz): δ 154.6, 145.1, 145.0, 141.6, 140.4, 140.3, 129.5, 128.7, 127.4, 126.9, 125.1 (2C), 119.9, 117.7, 115.5, 74.1, 32.8, 26.9, 21.4.

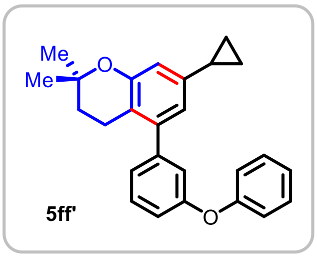
5-(4-Chlorophenyl)-2,2-dimethyl-7-phenylchromane (5ft):



5ft

Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.1 g, 0.79 mmol) and (*E*)-1-phenyl-3-(4-(chloro)phenyl)prop-2-en-1-one (**4t**) (0.095 g, 0.39mmol)in anhydrous PhF (2 mL) was added AgOTf (0.010 g, 0.039 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(4-chlorophenyl)-2,2-dimethyl-7-phenylchromane (**5ft**) (0.081 g, 59%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.62-7.59 (m, 2H), 7.43-7.39 (m, 4H), 7.35-7.31 (m, 3H), 7.10 (d, *J* = 1.88 Hz, 1H), 7.02 (d, *J* = 2.0 Hz, 1H), 2.63 (t, *J* = 6.75 Hz, 2H), 1.79-1.75 (m, 2H), 1.40 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.6, 141.8, 140.5, 140.2, 139.8, 133.1, 130.5, 128.7, 128.3, 127.6, 127.3, 126.9, 120.0, 117.8, 115.2, 74.0, 32.9, 26.9, 21.5; HRMS (ESI) *m/z* calcd for $C_{23}H_{22}OCl$ $[M+H]^+$ 349.1554, found 349.1353.

7-Cyclopropyl-2,2-dimethyl-5-(3-phenoxyphenyl)chromane(5ff’):



5ff'

Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.1 g, 0.79 mmol) and(*E*)-1-cyclopropyl-3-(3-phenoxyphenyl)prop-2-en-1-one (**4f’**) (0.103 g, 0.39 mmol) in anhydrous PhF (2 mL) was add AgOTf (0.010 g, 0.039 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-cyclopropyl-2,2-dimethyl-5-(3-phenoxyphenyl)chromane (**5ff’**) (0.086 g, 71%). TLC: R_f = 0.80 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41-7.34 (m, 3H), 7.11-7.15 (m, 1H), 7.11-7.07 (m, 3H), 7.02-6.98 (m, 2H), 6.59 (d, *J* = 1.91 Hz, 1H), 6.51 (d, *J* = 1.91 Hz, 1H), 2.59-2.55 (m, 2H), 1.89-1.81 (m, 1H), 1.73-1.68 (m, 2H), 1.36 (s, 6H), 0.96-0.91 (m, 2H), 0.74-0.69 (m, 2H); ^{13}C NMR ($CDCl_3$,126 MHz): δ 157.1, 156.9, 154.2, 143.3, 143.1, 141.8, 129.8, 129.3, 124.0, 123.3, 119.6, 119.1, 118.9, 117.1, 115.7, 113.0, 73.8, 33.0, 26.9, 21.3, 15.0, 9.13.

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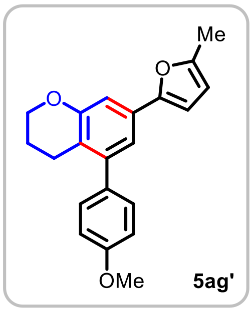
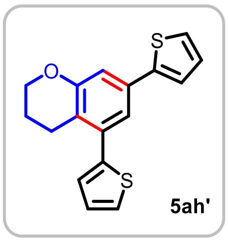
9. Synthesis and characterization of heterocyclic chromanes (5 or E5) fromalkynols (2) and α,β-unsaturated ketone (4)

5-(4-Methoxyphenyl)-7-(5-methylfuran-2-yl)chromane(5ag’):



Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(4-methoxyphenyl)-1-(5-methylfuran-2-yl)prop-2-en-1-one (**4g’**) (0.122 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(4-methoxyphenyl)-7-(5-methylfuran-2-yl)chromane (**5ag’**) (0.130 g, 80%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.30-7.23 (m, 2H), 7.09-7.01 (m, 2H), 6.99-6.82 (m, 2H), 6.45 (d, *J* = 3.09 Hz, 1H), 6.07-5.90 (m, 1H), 4.23-4.15 (m, 2H), 3.84 (s, 3H), 2.59 (t, *J* = 6.39 Hz, 2H), 2.32 (s, 3H), 2.01-1.81 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 158.7, 155.1, 152.0, 151.7, 142.8, 133.4, 130.1, 129.9, 118.9, 117.1, 113.5, 110.3, 107.5, 105.7,66.2, 55.3, 24.2, 22.5, 13.7; HRMS (ESI) *m/z* calcd for $C_{21}H_{21}O_3$ $[M+H]^+$ 321.1485, found 321.1485.

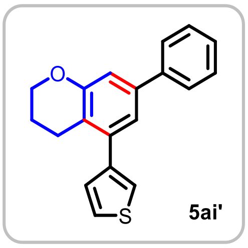
5,7-Di(thiophen-2-yl)chromane(5ah’):



Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**)(0.1 g, 1.01 mmol) and (*E*)-1,3-di(thiophen-2-yl)prop-2-en-1-one (**4h’**) (0.111 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded5,7-di(thiophen-2-yl)chromane (**5ah’**) (0.108 g, 72%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.38-7.37(m, 1H), 7.31-7.29 (m, 1H), 7.27-7.24 (m, 2H), 7.16-7.04 (m, 4H), 4.30-4.20 (m, 2H), 2.82 (t, *J* = 6.49 Hz, 2H), 2.03-1.95 (m, 2H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 155.4, 143.7, 141.8, 135.6, 133.2, 127.9, 127.1,126.8, 125.5, 124.8, 123.2, 120.3, 120.1, 113.8, 66.2, 24.3, 22.4; HRMS (ESI) *m/z* calcd for $C_{17}H_{15}OS_2$ $[M+H]^+$ 299.0559 found 299.0558.

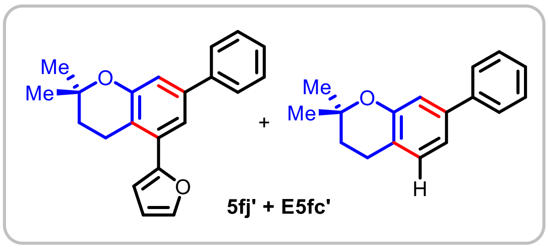
7-Phenyl-5-(thiophen-3-yl)chromane(5ai’):

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-1-phenyl-3-(thiophen-3-yl)prop-2-en-1-one (**4i’**) (0.108 g, 0.505 mmol)in anhydrous PhF


5ai'

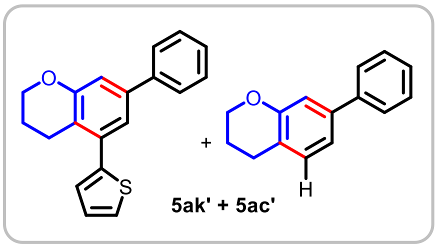
(2 mL) was added AgOTf (0.012 g, 0.05 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-phenyl-5-(thiophen-3-yl)chromane (**5ai'**) (0.093 g, 63%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.63-7.58 (m, 2H), 7.46-7.37 (m, 3H), 7.36-7.31 (m, 1H), 7.28 (s, 1H), 7.21-7.18 (m, 1H), 7.15 (d, *J* = 1.5 Hz, 1H), 7.07 (d, *J* = 1.5 Hz, 1H), 4.28-2.23 (m, 2H), 2.78-2.73 (m, 2H), 2.03-1.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.3, 141.3, 140.6, 140.0, 138.0, 128.8, 128.7, 127.3, 127.0, 125.0, 122.9, 120.6, 119.4, 114.5, 66.3, 24.1, 22.4; IR (KBr, cm^{-1}): υ 3019, 2929, 1600, 1566, 1528, 1474, 1310, 1216, 1017, 772, 669.

5-(furan-2-yl)-2,2-dimethyl-7-phenylchromane(5fj')and 2,2-Dimethyl-7-phenylchromane (E5fc'):


5fj' + E5fc'

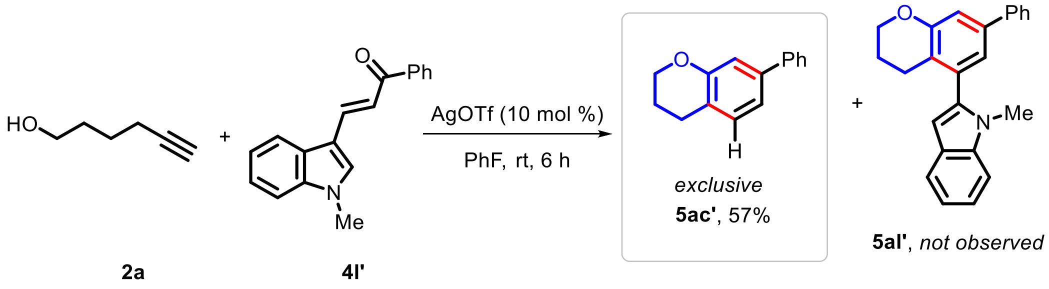
Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol (**2f**) (0.1 g, 0.79 mmol) and (*E*)-3-(furan-2-yl)-1-phenylprop-2-en-1-one (**4j'**) (0.077 g, 0.39 mmol) in anhydrous PhF (2 mL) was add AgOTf(0.010 g, 0.039 mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 5-(furan-2-yl)-2,2-dimethyl-7-phenylchromane (**5fj'**) and 2,2-dimethyl-7-phenylchromane (**E5fc'**) (0.089 g, 70%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.56 (m, 3H), 7.47-7.39 (m, 4H), 7.37-7.30 (m, 2H), 7.16-7.01 (m, 4H), 2.98-2.92 (m, 1H), 2.83 (t, *J* = 6.75 Hz, 2H), 1.89-1.83 (m, 3H), 1.41 (s, 3H), 1.38 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.2, 141.0, 140.5, 129.8, 128.7, 128.6, 127.2, 127.0 (3C), 126.9, 120.0, 118.5, 117.4, 115.7, 115.0, 74.3, 73.6, 32.8, 27.0, 22.2.

7-Phenyl-5-(thiophen-2-yl)chromane(5ak')and 7-phenylchromane (5ac'):


5ak' + 5ac'

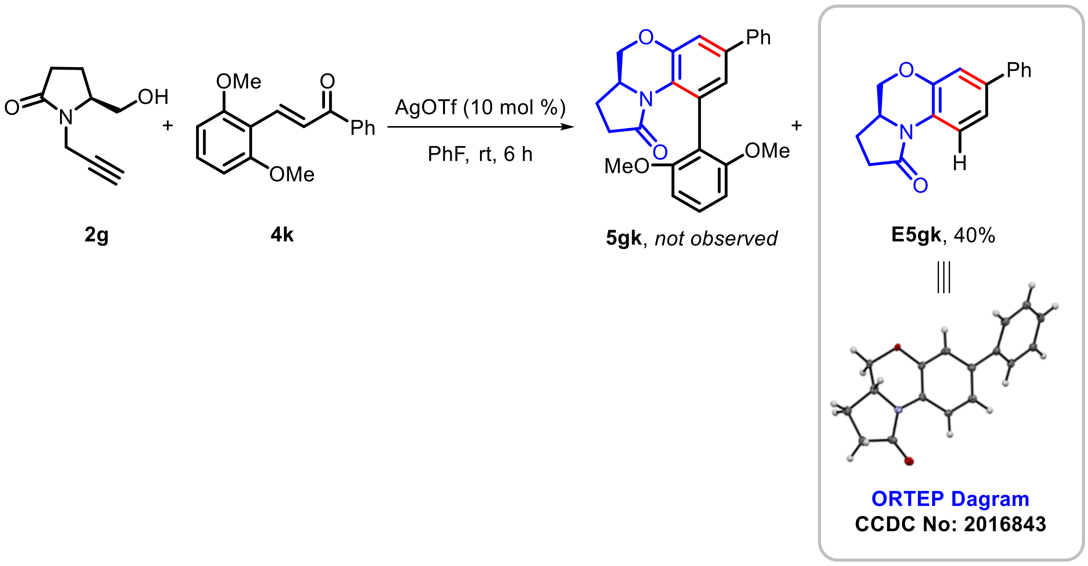
Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (**4k'**) (0.108 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.010 g, 0.05 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded a mixture of 7-phenyl-5-(thiophen-2-yl)chromane (**5ak'**) and 7-phenylchromane (**5ac'**) (0.079 g, 90%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.59-7.51(m, 4H), 7.42-7.35 (m, 4H), 7.34-7.26 (m, 3H), 7.23-7.20 (m, 1H), 7.11-6.99 (m, 6H), 4.27-4.13 (m, 4H), 2.84-2.78 (m, 4H), 2.06-1.92 (m, 4H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.5, 155.1, 142.1, 140.9, 140.5,140.4, 140.0, 135.5, 130.1, 128.7, 128.7, 127.4, 127.1, 127.0, 126.9, 126.6, 125.3, 121.4, 121.3, 119.7, 118.9, 115.2, 115.1, 66.5, 66.1, 24.6, 24.3, 22.4.

7-Phenylchromane (5ac'):



Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-3-(1-methyl-1H-indol-2-yl)-1-phenylprop-2-en-1-one (**4l'**) (0.131 g, 0.505 mmol)in anhydrous PhF (2 mL) was added AgOTf (0.012 g, 0.05mmol)under argon atmosphere at room temperature and reaction mixture was stirred for 6h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded 7-phenylchromane (**5ac'**) (0.060g, 57%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 7.56-7.44 (m, 2H), 7.39-7.27 (m, 2H), 7.25-7.17 (m, 1H), 7.06-6.92 (m, 3H), 4.20-4.12 (m, 2H), 2.81-2.71 (m, 2H), 2.05-1.82 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.1, 140.9, 140.5, 130.1, 128.7, 127.1, 126.9, 121.3, 119.0, 115.2, 66.5, 24.7, 22.4; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}O$ $[M+H]^+$ 211.1117, found 211.1116.

(*S*)-7-Phenyl-2,3,3a,4-tetrahydro-1H-benzo[b]pyrrolo[1,2-d][1,4]oxazin-1-one (E5gk):



Following the *General Procedure,* to the mixture of (*S*)-5-(hydroxymethyl)-1-(prop-2-yn-1-yl)pyrrolidin-2-one (**2g**) (0.1 g, 0.63 mmol) and (*E*)-3-(2,6-dimethoxyphenyl)-1-phenylprop-2-en-1-one (**4k**) (0.084 g, 0.31mmol)in anhydrous PhF (2 mL) was added AgOTf (0.008 g, 0.031 mmol) under argon atmosphere at room temperature and reaction mixture was stirred for 6h at 85 °C. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes)afforded(*S*)-7-phenyl-2,3,3a,4-tetrahydro-1H-benzo[b]pyrrolo[1,2-d][1,4]oxazin-1-one (**E5gk**) as a white crystal (0.034 g, 40%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 200 MHz): δ 8.59 (d, *J* = 8.60 Hz, 1H), 7.61-7.57 (m, 1H), 7.55-7.33 (m, 3H), 7.33-7.17 (m, 3H), 4.54 (dd, *J* = 10.58, 2.98 Hz, 1H), 4.20-4.02 (m, 1H), 3.90-3.74 (m, 1H), 2.82-2.47 (m, 2H), 2.45-2.27 (m, 1H), 1.85-1.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ 172.5, 144.7, 140.2, 137.7, 128.8, 127.3, 126.8, 124.21 120.2, 119.5, 115.2, 69.6, 54.0, 31.1, 21.0;HRMS (ESI) *m/z* calcd for $C_{17}H_{16}O_2N$ $[M+H]^+$ 266.1176, found 266.1173.

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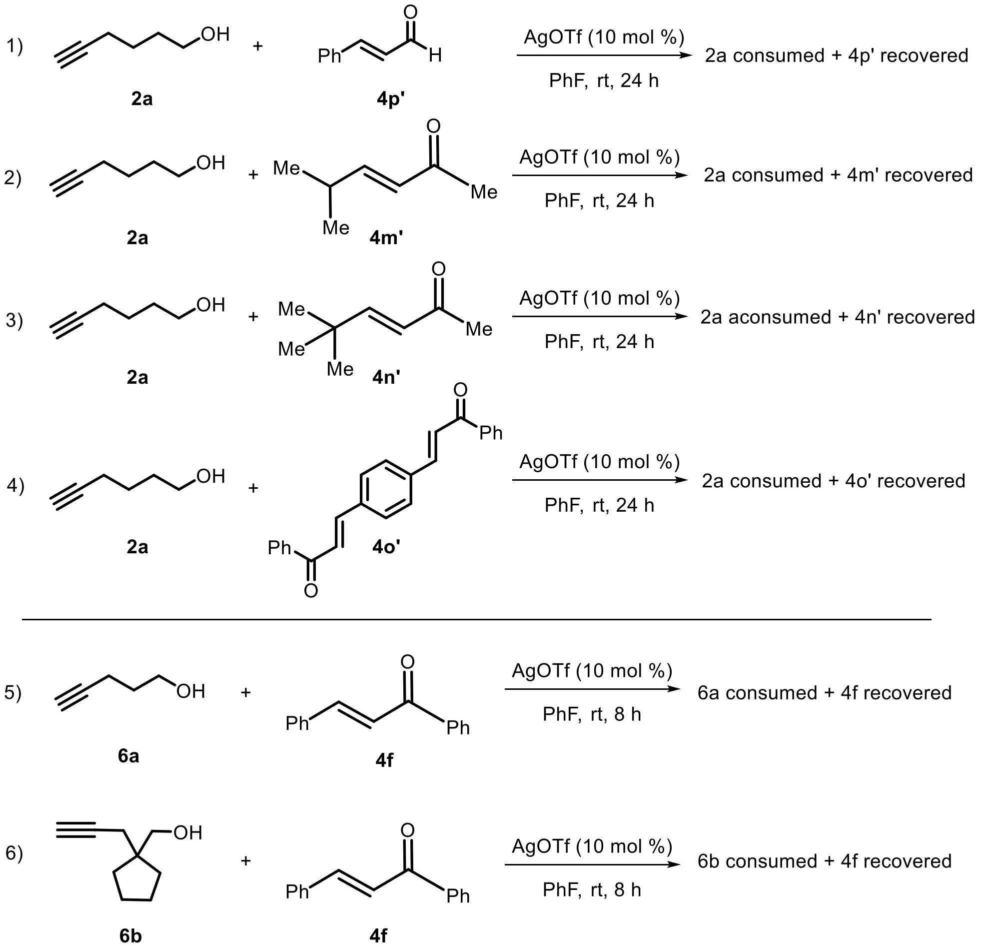
10. Scheme S2. Unsuccessful [3+3]-annulation experiments:



11. X-ray crystallography data:

The single crystal X-ray diffraction measurements were performed for **5fk**, **E5gk** and **T3ab** at 100 K using APEX3 (Bruker, 2016; Bruker D8 VENTURE Kappa Duo PHOTON II CPAD) diffractometer having graphite-monochromatized (Mo = 0.71073 Å). The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of unit cell parameters and an orientation matrix were calculated from a total of 36 frames, and the cell refinement was performed by SAINT-Plus (Bruker, 2016). An optimized strategy used for data collection consisted of different sets of φ and ω scans with 0.5 ^{o}steps φ/ω. The data were collected with a time frame of 10 Sec for all the three components by setting the sample to detector distance fixed at 40 cm. All the data points were corrected for Lorentzian, polarization, and absorption effects using SAINT-Plus and SADABS programs (Bruker, 2016). SHELXS-97 (Sheldrick, 2008) was used for structure solution and full-matrix least-squares refinement on F^2. The molecular graphics of ORTEP diagrams of all three components were performed by Mercury software. The crystal symmetry of all the three components of single crystals are cross-checked by running the cif files through PLATON (Spek, 2020) software, and notified that there is no additional symmetry was observed. The Encifer software was used to correct the cif files (Figures 1, 2 and 3).

All the three compounds **5fk**, **E5gk** and **T3ab** have been crystallized in Monoclinic space group $P2_1/c$, $P2_1$ and $P2_1/c$ respectively from the 1% EtOAc/pet.ether solvent by the slow evaporation method. The asymmetric unit contains one molecule in compound **5fk** and **T3ab**, while two molecules are present in **E5gk** component (Tables 1 and 2).

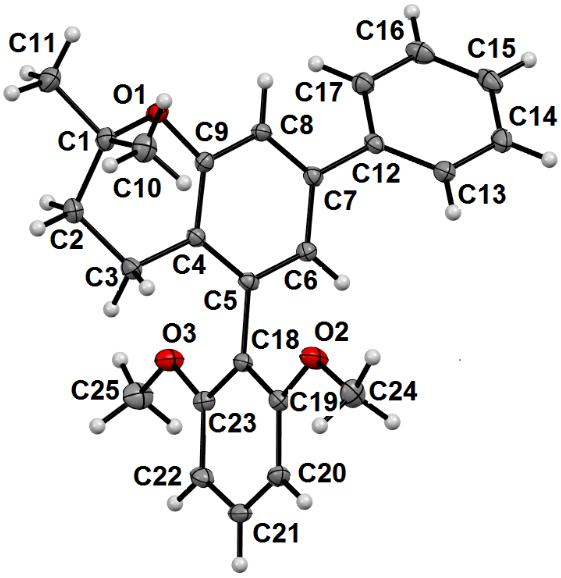


Figure S1. ORTEP diagram of **5fk**, herein, the thermal ellipsoids are drawn with 50% of probability. Moreover, the asymmetric unit contains a single molecule.

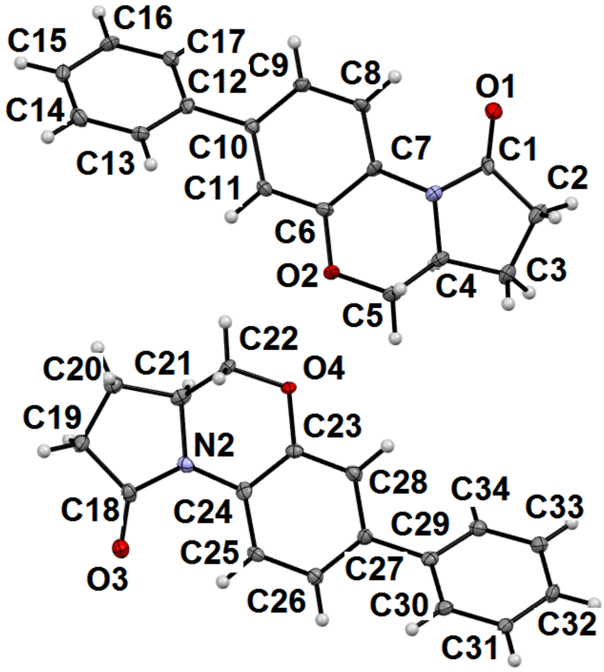


Figure S2. ORTEP diagram of **E5gk**, herein, the thermal ellipsoids are drawn with 50% of probability. Moreover, the asymmetric unit contains two molecules.

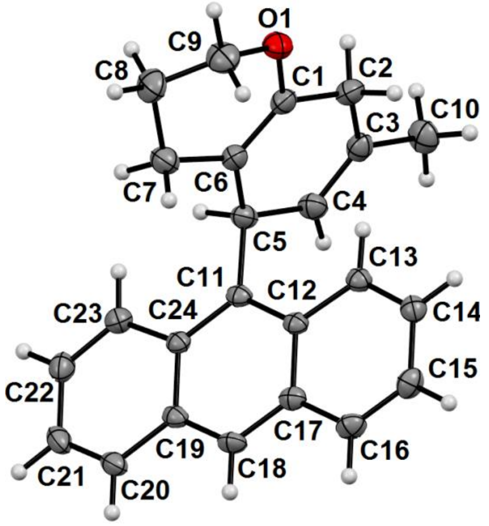


Figure S3. ORTEP diagram of **T3ab**, herein, the thermal ellipsoids are drawn with 50% of probability. Moreover, the asymmetric unit contains a single molecule.

Table S2. Crystallographic information details about the compound **5fk**, **E5gk** and **T3ab**.

Crystal data	Compound **5fk**	Compound **E5gk**	Compound **T3ab**
Chemical formula	$C_{25}H_{26}O_3$	$C_{17}H_{15}NO_2$	$C_{24}H_{22}O$
Formula weight (M_r)	374.46	265.30	326.42
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1$	$P2_1/c$
Temperature T (K)	100 (2)	100 (2)	100 (2)
a (Å)	14.6475(7)	7.2766(18)	9.9695(5)
b (Å)	10.4651(5)	14.676(4)	7.7193(4)
c (Å)	13.6161(6)	12.381(4)	22.7874(10)
α (°)	90	90	90
β (°)	103.479(2)	101.962(13)	101.538(2)
γ (°)	90	90	90
Z	4	4	4
Volume (Å^3)	2029.69(16)	1293.5(6)	1718.22(15)
Source of radiation	MoKα	MoKα	MoKα
D_{calc} (g cm^{-3})	1.225	1.362	1.262
Crystal size (mm)	0.5x0.19x0.16	0.56x0.24x0.22	0.42Xx0.2x0.12
μ (mm^{-1})	0.079	0.090	0.075
Data collection			
Diffractometer	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD	Bruker D8 VENTURE Kappa Duo PHOTON II CPAD
Absorption correction	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)	Multi-scan (SADABS; Bruker, 2016)
$T_{\min}$, $T_{\max}$	0.3929, 0.7455	0.6561, 0.7451	0.4158, 0.7455
No. of measured, independent and observed [I > 2σ(I)] reflections	63797, 4351, 3979	46945, 5615, 5525	32959, 3351, 3027
Theta range (°)	2.41-27.11	2.78-27.16	2.48-27.11
R_{int}	0.0596	0.0790	0.0765
Refinement			
R[F^2> 2σ (F^2)], wR(F^2)	0.0551	0.0782	0.0721
GOF on F^2	1.216	1.129	1.056
No. of independent reflections	4351	5615	3351
No. of parameters	258	362	227
No. of restraints	0	1	0
H-atom treatment	constr	constr	constr
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e A$^{\circ-3}$)	0.570, -0.564	0.665, -0.373	0.709, -0.328
CCDC number	**2016842**	**2016843**	**2016844**

Table S3. Hydrogen-bond geometry (A˚, °) of compound **5fk**, **E5gk** and **T3ab**.

Name of the compound	*D*–H···*A*	*D*–H	H···*A*	*D*···*A*	*D*–H···*A*
Compound **5fk**	C21−H21···O2	0.95	2.57	3.2738(15)	131
Compound **E5gk**	C4−H4···O3	1.00	2.59	3.317(8)	130
	C8−H8···O1	0.95	2.44	2.995(8)	117
	C25−H25···O3	0.95	2.33	2.946(8)	122
Compound **T3ab**	There is no prominent hydrogen bond				

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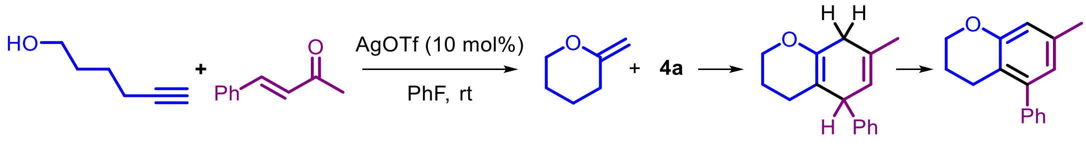
12. Supporting experiments for the postulated reaction mechanism:

12.a. Real-time GC-MS analyses: To gain insight into the probable reaction pathway, the following experiment was carried out under optimized reaction conditions using alkynol **2a** (hex-5-yn-1-ol) and enone **4a** ((*E*)-4-phenylbut-3-en-2-one) in PhF solvent at room temperature, which was monitored through GC-MS analyses at 1 h, 3 h and 5 h reaction times. To our delight we were able to find cyclic eno-lether intermediate (**T1aa**) as a major product at t_1 = 1 h with *m/z* value of 99.1 (Figure 4), 1,3-cyclohexadiene intermediate (**T3aa**) at t_2 = 2 h with *m/z* value of 226.2 (Figure 5) and also the final desired product **5aa**at t_3 = 2 h 37 min h with *m/z* value of 224.2 (Figure 6). This investigation results were in accordance with the proposed mechanistic sequence.



2a **4a** **T1aa** **T3aa** **5aa**

GC-MS*Method Details:*

1. Instrument name: Agilent 7890N 5977MSD
2. Column: HP-5MS column
3. Diameter: 30 m X 0.25 micro meter X 0.25 mm
4. temperature: $\underset{(1\ \text{min.})}{80\ ^{o}\text{C}} \xrightarrow{20\ \text{min.}} \underset{(10\ \text{min.})}{280\ ^{o}\text{C}}$
5. Injected temp: 250 ^{o}C
6. Detector temp: 280 ^{o}C
7. Solvent: MeOH

```
File       :D:\NCL\DATA\OCD\Year_2019\190445.D
Operator   : Dr. Borikar
Acquired   : 20 Jun 2019  19:40     using AcqMethod OCD2019.M
Instrument :    GCMS
Sample Name: F
Misc Info  :
Vial Number: 3
```

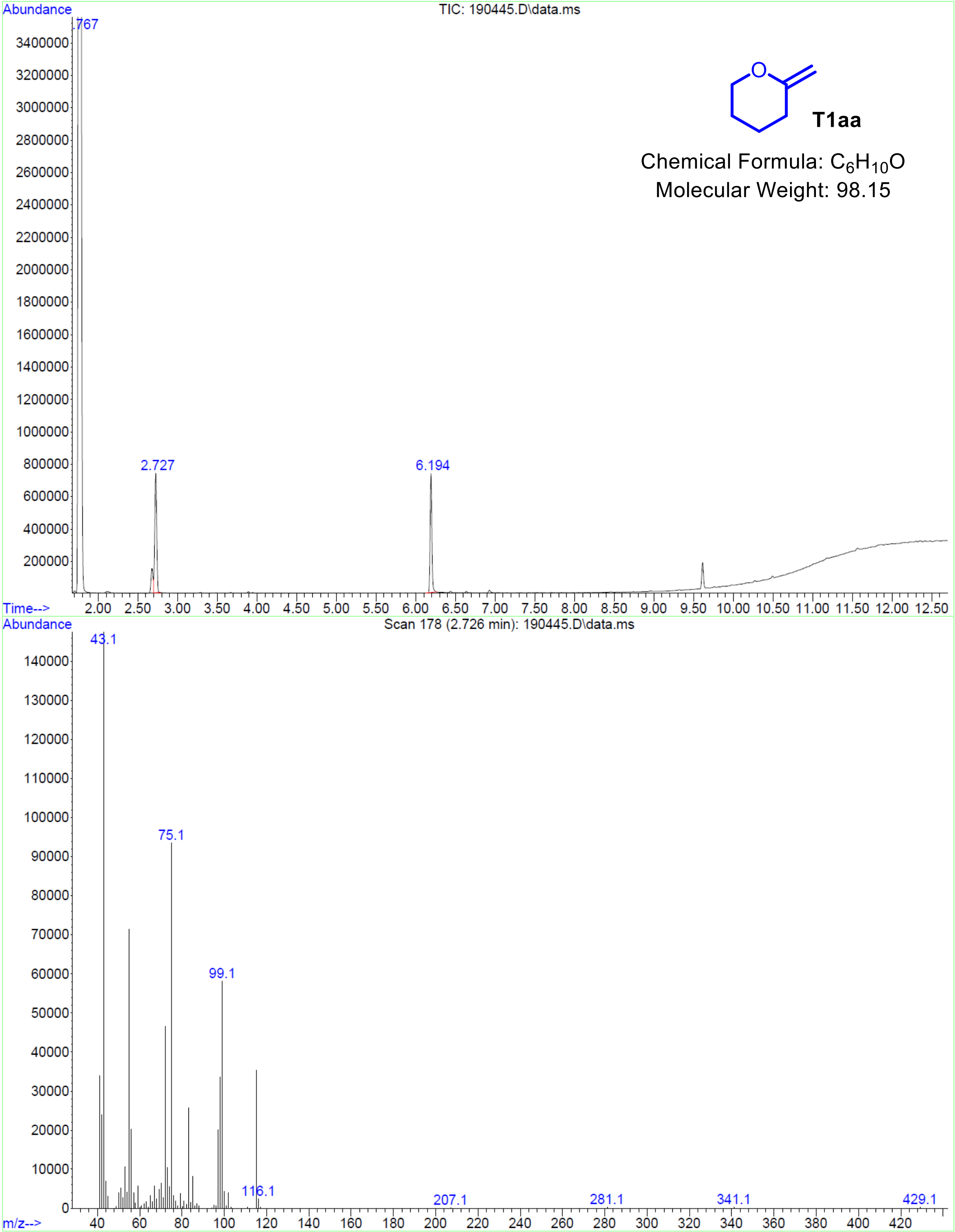


Figure S4. GC-MS chromatogram at t_1 = 1h of the reaction mixture of **2a** and **4a**.

```
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Operator   : Dr. Borikar
Acquired   : 20 Jun 2019  20:35     using AcqMethod OCD2019.M
Instrument :    GCMS
Sample Name: I
Misc Info  :
Vial Number: 6
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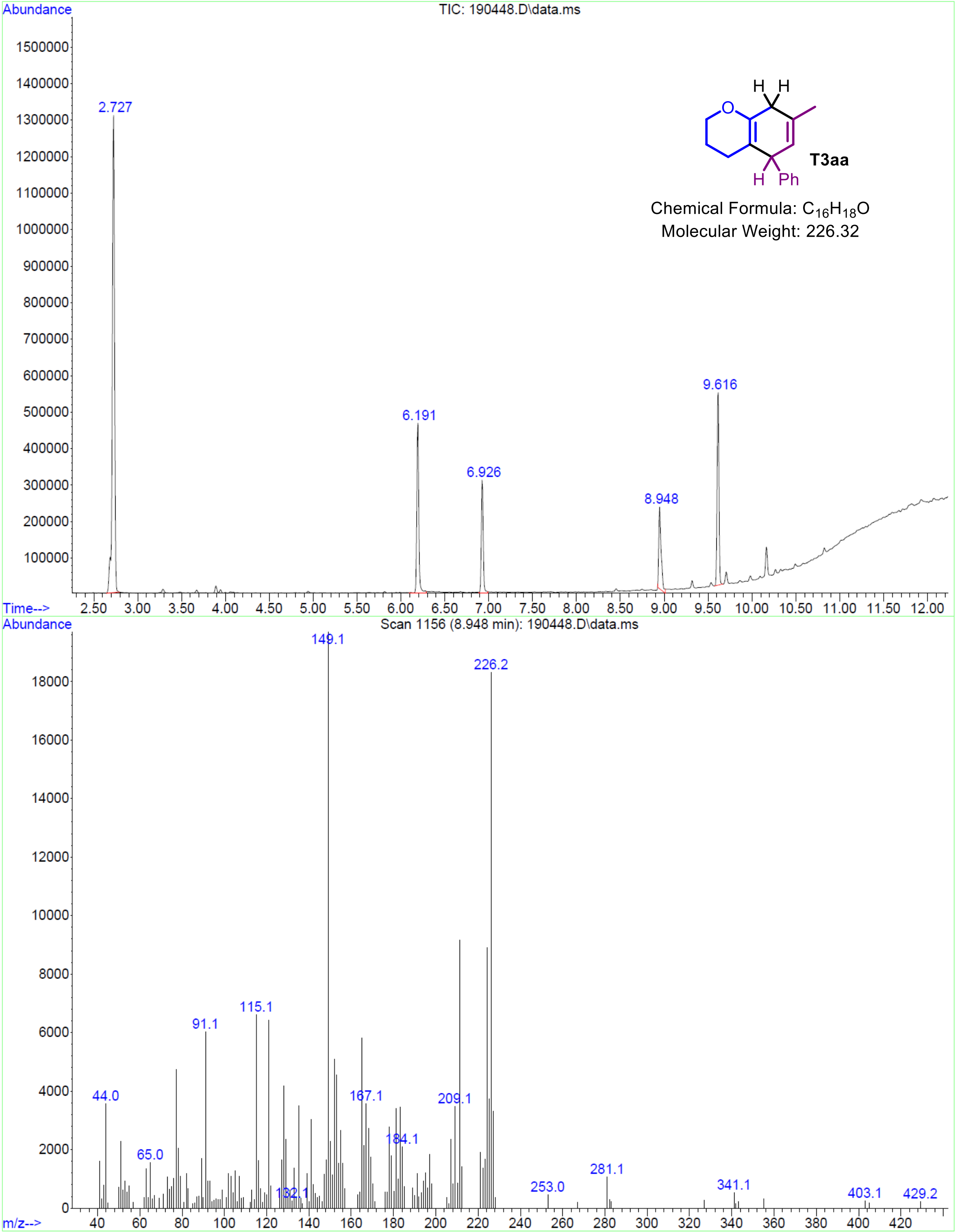

Figure S5. GC-MS chromatogram at t_2 = 2h of the reaction mixture of **2a** and **4a**.

```
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Operator    : Dr. Borikar
Acquired    : 20 Jun 2019  21:12     using AcqMethod OCD2019.M
Instrument :     GCMS
Sample Name: K
Misc Info  :
Vial Number: 8
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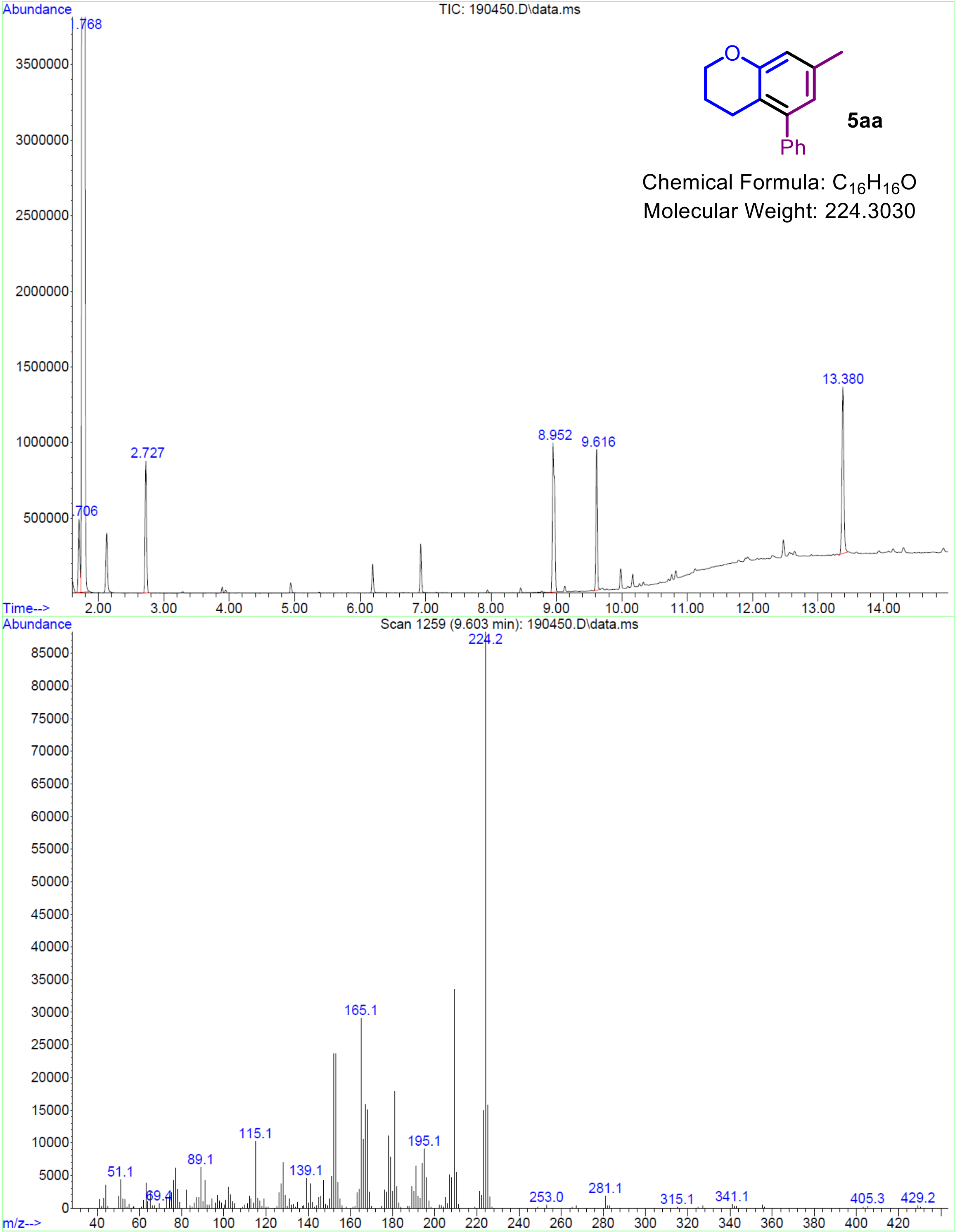
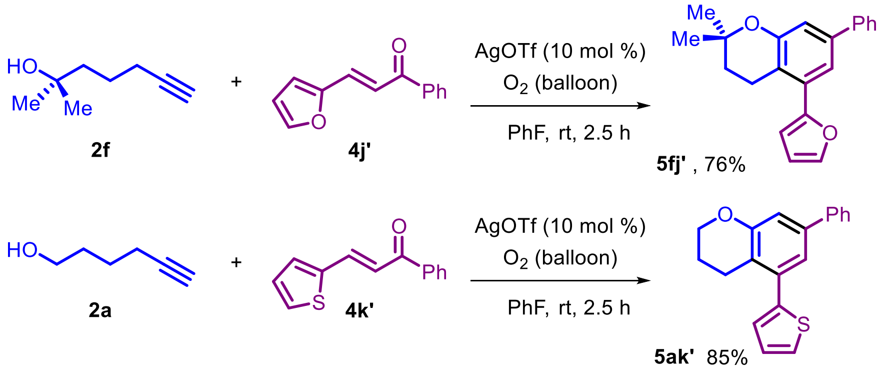
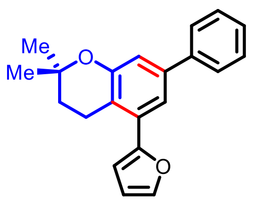


Figure S6. GC-MS chromatogram at t$_3$ = 2h37 min of the reaction mixture of **2a** and **4a**.

12.b. Reactions under oxygen atmosphere:

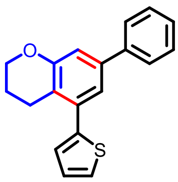


5-(Furan-2-yl)-2,2-dimethyl-7-phenylchromane(5fj'):


5fj'

Following the *General Procedure*, to the mixture of 2-methylhept-6-yn-2-ol **(2f)** (0.1 g, 0.79 mmol) and (*E*)-3-(furan-2-yl)-1-phenylprop-2-en-1-one (**4j'**) (0.077 g, 0.39 mmol)in anhydrous PhF (2 mL) was add AgOTf (0.010 g, 0.039 mmol) under oxygen atmosphere (O_2 balloon pressure) at room temperature and reaction mixture was stirred for 6 h at rt. Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded **5fj'** (0.147 g, 76%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.62 (m, 2H), 7.55-7.49 (m, 2H), 7.46-7.41 (m, 2H), 7.36-7.31 (m, 1H), 7.06 (d, *J* = 1.88Hz, 1H), 6.58 (dd, *J* = 3.38, 0.63 Hz, 1H), 6.53 (dd, *J* = 3.38, 1.88 Hz, 1H), 2.98-2.90 (m, 2H), 1.89-1.85 (m, 2H), 1.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 154.7, 153.4,141.8, 140.6, 140.1, 131.2, 129.8, 128.7, 128.6, 127.2, 127.0, 126.9, 120.9, 117.9, 117.3, 115.5, 111.2, 73.7, 32.8, 26.9, 26.8, 21.9.

7-Phenyl-5-(thiophen-2-yl)chromane(5ak'):


5ak'

Following the *General Procedure*, to the mixture of 5-hexyn-1-ol (**2a**) (0.1 g, 1.01 mmol) and (*E*)-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one (**4k'**) (0.108 g, 0.505 mmol) in anhydrous PhF (2 mL) was added AgOTf (0.010 g, 0.05 mmol) under oxygen atmosphere (O_2 balloon pressure) at room temperature and reaction mixture was stirred for 2.5 h at rt (both starting materials were completely consumed as per the TLC visualization). Purification of the crude product by column chromatography (SiO_2, 1% EtOAc/hexanes) afforded **5ak'** (0.125 g, 85%). TLC: R_f = 0.90 (SiO_2, 10% EtOAc/hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.57 (m, 2H), 7.48-7.42 (m, 2H), 7.40-7.33 (m, 2H), 7.26 (d, *J* = 1.9 Hz, 1H), 7.16-7.05 (m, 3H), 4.26 (t, *J* = 5.1 Hz, 2H), 2.87 (t, *J* = 6.5 Hz, 2H), 2.06-1.98 (m, 2H); ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.5, 142.1, 140.4, 140.0, 135.5, 128.7, 127.4, 127.0 (2C), 126.6, 125.3, 121.4, 119.7, 115.1, 66.2, 24.3, 22.4.

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13. Quantum chemical calculations:

The quantum chemical calculations have been performed using density functional theory (DFT), as a tool with the aid of the Turbomole 7.2 suite of programs.[1] The PBE functional,[2] and the TZVP[3] basis set has been employed. The resolution of identity (RI),[4] along with the multipole accelerated resolution of identity (marij)[5] approximations have been used for an accurate and efficient treatment of the electronic Coulomb term in the DFT calculations. Solvent effects were introduced by using the COSMO model[6] with the dielectric constant $\varepsilon = 2.38$ for toluene.The option “disp” provided in the Turbomole package (DFT-D3) was employed for dispersion-corrected DFT calculations.[7] The values reported are ΔG values, with zero point energy corrections, internal energy and entropic contributions included through frequency calculations on the optimized minima with the temperature taken to be 298.15 K. Harmonic frequency calculations were performed for all stationary points to confirm them as local minima.

References and notes:

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6. A. Klamt and G. Schuurmann, *J. Chem. Soc.Perkin Trans.*, 1993,**2**, 799-805.
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XYZ coordinates for optimized geometries of all the compounds at PBE/TZVP level of theory.

T0

38

O	-0.416898	-2.717829	-1.487655
C	-0.115974	-1.316846	-1.430287
C	-0.141249	-0.689150	-2.794112
C	0.749653	-1.450979	-3.791797
C	0.381110	-2.937227	-3.796693
C	0.444169	-3.498971	-2.389911
C	0.088052	-0.759365	-0.232504
Ag	0.370742	1.248730	0.094947
O	-1.282382	-3.725228	0.626926
S	-1.024130	-5.291000	0.806155
O	-0.888204	-5.974358	-0.502987
O	-1.929896	-5.799091	1.854795
C	0.739013	-5.269378	1.566820
F	1.594616	-4.720754	0.682815
F	1.118032	-6.527529	1.832576
F	0.746990	-4.548067	2.696055
F	-0.786397	6.797410	-0.753288
C	-0.446439	7.899397	-0.017903
C	0.207753	7.713759	1.196023
C	0.551486	8.846495	1.941833
C	0.241778	10.127194	1.469982
C	-0.416737	10.279274	0.244482
C	-0.769251	9.158266	-0.515232
H	-1.182654	-0.699815	-3.163769
H	0.168214	0.361013	-2.706371
H	1.469995	-3.465354	-1.985857
H	0.062087	-4.524573	-2.322854
H	1.068514	-3.516613	-4.432383
H	-0.635409	-3.077864	-4.199715
H	1.806802	-1.333032	-3.499383
H	0.639550	-1.019242	-4.797482
H	0.065567	-1.398926	0.655993
H	-0.882490	-3.338217	-0.294646
H	0.438723	6.705956	1.543371
H	-0.661006	11.275833	-0.127817
H	1.064301	8.722569	2.897336
H	0.512984	11.005819	2.057418
H	-1.283026	9.251287	-1.472889

T0'

38

H	-19.275972	-5.203827	-10.754047
C	-18.602067	-5.821057	-10.132325
H	-17.969005	-6.408271	-10.811584
C	-17.721670	-4.909782	-9.325908
O	-18.507593	-4.168831	-8.360057
C	-19.290049	-5.005425	-7.434785
H	-18.578479	-5.592851	-6.830320
H	-19.820343	-4.294844	-6.789090
C	-20.232352	-5.902041	-8.214977
H	-20.770821	-6.543726	-7.500067

H	-20.983838	-5.278768	-8.726632
C	-19.454778	-6.738640	-9.235661
H	-18.793782	-7.446357	-8.707186
H	-20.143588	-7.333343	-9.853682
C	-16.407854	-4.679350	-9.415634
H	-15.991755	-3.962816	-8.696794
H	-17.918033	-3.076843	-7.831422
F	-16.138166	-9.131578	-13.680262
C	-15.355238	-8.074149	-13.342115
C	-14.476176	-8.210486	-12.276647
H	-14.416463	-9.150644	-11.728324
C	-15.473211	-6.896478	-14.085663
C	-14.666029	-5.812657	-13.748718
H	-14.732380	-4.887881	-14.323008
C	-13.744113	-5.909530	-12.680814
H	-12.893899	-7.233584	-11.172398
C	-13.657253	-7.114347	-11.943264
H	-13.026322	-5.105279	-12.506050
Ag	-15.143501	-5.494034	-10.826869
O	-17.393353	-2.160685	-7.478954
F	-15.774350	-2.210386	-4.895013
C	-17.091875	-2.445426	-4.806497
F	-17.315534	-3.768401	-4.940410
O	-19.460705	-1.874759	-6.024237
F	-17.539309	-2.039440	-3.608476
S	-18.032927	-1.499742	-6.186486
O	-17.596906	-0.090812	-6.092659
H	-16.185729	-6.843234	-14.909339

T2

17

C	0.096050	1.173950	-4.879263
C	0.020407	1.084053	-3.377988
C	0.189619	-0.068478	-2.698969
O	0.527179	-1.265594	-3.300902
C	0.978100	-1.150847	-4.673018
C	0.080557	-0.232662	-5.490588
C	0.033040	-0.240774	-1.221065
H	-0.221228	1.980917	-2.804533
H	2.014173	-0.766325	-4.663856
H	0.987206	-2.178482	-5.059003
H	0.424689	-0.221931	-6.535703
H	-0.943630	-0.639276	-5.483971
H	1.005787	1.717099	-5.194682
H	-0.752325	1.764334	-5.263692
H	-0.725692	-1.008877	-1.002028
H	0.977121	-0.575960	-0.763191
H	-0.275626	0.700696	-0.749985

T'

21

F	-13.945875	-5.547477	-9.139749
C	-14.800869	-4.545765	-8.821436
C	-15.318347	-3.761682	-9.843057
H	-15.045766	-3.954384	-10.880746
C	-15.123732	-4.351391	-7.473771
C	-16.007459	-3.331694	-7.135736
H	-16.280128	-3.172824	-6.091978
C	-16.578700	-2.513958	-8.141877
H	-16.749652	-2.199543	-10.299262
C	-16.225152	-2.733436	-9.503978

H	-17.387253	-1.824249	-7.889778
Ag	-14.900018	-1.018523	-8.631149
O	-13.405966	0.504582	-8.362987
F	-14.254106	0.322043	-5.497586
C	-13.022253	0.838605	-5.716883
F	-13.123121	2.176565	-5.800209
O	-11.033358	0.844520	-7.578197
F	-12.230430	0.520713	-4.677658
S	-12.303747	0.111904	-7.340424
O	-12.257098	-1.364216	-7.098107
H	-14.678864	-4.994268	-6.713867

4

21

C	-16.746530	-17.710864	4.079011
C	-15.725709	-16.992157	4.739729
C	-14.969026	-17.659221	5.727228
C	-15.217828	-18.995315	6.043235
C	-16.231707	-19.692577	5.378324
C	-16.994079	-19.044074	4.395919
C	-15.415286	-15.595731	4.449527
C	-16.008417	-14.796885	3.529473
C	-15.646273	-13.392188	3.284615
C	-14.548490	-12.741620	4.102987
O	-16.247387	-12.750905	2.411313
H	-14.620176	-19.493743	6.808645
H	-16.429630	-20.737962	5.622906
H	-17.786402	-19.585442	3.875437
H	-17.350822	-17.222257	3.312743
H	-14.176629	-17.115120	6.247124
H	-14.607009	-15.175789	5.057984
H	-16.817629	-15.163553	2.891306
H	-13.603008	-13.297164	4.012128
H	-14.400666	-11.714055	3.752450
H	-14.816919	-12.724708	5.170445

4'

42

C	-16.722440	-17.716602	4.053633
C	-15.699825	-17.002181	4.722203
C	-14.937603	-17.654644	5.731823
C	-15.199879	-19.003208	6.057306
C	-16.213053	-19.656271	5.374919
C	-16.979089	-19.045122	4.374360
Ag	-16.566465	-16.308055	6.800808
O	-17.242763	-18.686954	8.866115
S	-16.091822	-17.968647	9.507038
O	-14.780549	-18.685475	9.530810
F	-16.476228	-20.953225	5.678483
O	-18.221917	-14.790619	6.953063
C	-19.162096	-14.751040	7.789906
C	-19.420825	-15.904194	8.716021
C	-19.954609	-13.533615	7.843096
C	-20.957733	-13.309432	8.732948
C	-21.753215	-12.099276	8.870975
C	-22.722030	-12.047035	9.898403
C	-23.509204	-10.911336	10.083440
C	-23.346301	-9.805219	9.241933
C	-22.391567	-9.842360	8.215732
C	-21.601906	-10.973294	8.030425
C	-16.581530	-17.814054	11.353440
F	-16.719269	-19.039869	11.898194

O	-16.004074	-16.499761	9.086629
F	-17.755467	-17.155205	11.482408
F	-15.634792	-17.140983	12.036936
H	-14.634903	-19.515416	6.834908
H	-14.057747	-17.167809	6.157517
H	-15.398348	-16.017903	4.358418
H	-17.297849	-17.225618	3.268029
H	-17.759165	-19.613802	3.867847
H	-24.250897	-10.887552	10.883681
H	-23.962001	-8.914990	9.383439
H	-22.265183	-8.979966	7.558108
H	-20.863688	-10.983710	7.227084
H	-22.847830	-12.911069	10.554715
H	-21.208487	-14.101746	9.445490
H	-19.657398	-12.772060	7.117819
H	-20.489007	-16.054224	8.916623
H	-18.989855	-16.827818	8.309363
H	-18.921234	-15.709012	9.678416

T2a

59

C	-11.904320	-4.072698	-3.808188
C	-10.803185	-4.485261	-4.562759
C	-10.822692	-5.607951	-5.379350
C	-12.001848	-6.376282	-5.431301
C	-13.137328	-5.993437	-4.669491
C	-13.072602	-4.829377	-3.865698
F	-9.664383	-3.742863	-4.501823
Ag	-13.645570	-5.161493	-6.741383
O	-15.776116	-6.839881	-6.691579
S	-15.406287	-8.254273	-7.098420
C	-15.718390	-8.230617	-8.990626
F	-15.565493	-9.459121	-9.523151
O	-14.160971	-4.276064	-8.570985
C	-14.742462	-3.100549	-8.746716
C	-15.775421	-2.952962	-9.635802
C	-16.263534	-4.132587	-10.442730
C	-15.790094	-4.019222	-11.887581
C	-14.848929	-4.928219	-12.392184
C	-14.378090	-4.819508	-13.705264
C	-14.848317	-3.799825	-14.537696
C	-15.789120	-2.886726	-14.045150
C	-16.251390	-2.994533	-12.731490
C	-14.227172	-1.936027	-7.934930
C	-17.794762	-4.377387	-10.390276
C	-18.259114	-5.499417	-11.380703
C	-19.666744	-6.022444	-11.059467
C	-20.416675	-5.032389	-10.189658
O	-19.645225	-4.850163	-8.939801
C	-18.373063	-4.615227	-9.041155
C	-17.636650	-4.561023	-7.793758
O	-13.939791	-8.555272	-6.988951
O	-16.342946	-9.307818	-6.596728
F	-16.986649	-7.809444	-9.257136
F	-14.864649	-7.386356	-9.610153
H	-21.391424	-5.387992	-9.843633
H	-20.524346	-4.042300	-10.657119
H	-19.615660	-6.979119	-10.518560
H	-20.250682	-6.196166	-11.973959
H	-18.211553	-5.074899	-12.390002
H	-17.524624	-6.314235	-11.335168

H	-18.320677	-3.450004	-10.711155
H	-17.005288	-3.647217	-7.825802
H	-18.288283	-4.622985	-6.916945
H	-16.185565	-1.961349	-9.841689
H	-16.975493	-2.264760	-12.357590
H	-16.159751	-2.084563	-14.687318
H	-14.483904	-3.714425	-15.563370
H	-13.642950	-5.536369	-14.077753
H	-14.478780	-5.726476	-11.743994
H	-16.887526	-5.382194	-7.760058
H	-15.775131	-5.022804	-10.015688
H	-9.938603	-5.888885	-5.952523
H	-12.022252	-7.314510	-5.989226
H	-13.992322	-6.667590	-4.590861
H	-13.937721	-4.538079	-3.269174
H	-11.832899	-3.176915	-3.190855
H	-14.743903	-0.996431	-8.174881
H	-14.357836	-2.144870	-6.858401
H	-13.147147	-1.804476	-8.106730

T2b

59

C	-3.972005	-1.818608	1.445549
C	-4.279875	-0.412341	0.978700
C	-5.265738	-0.509410	-0.216448
C	-6.288310	-1.645046	0.003679
C	-6.361708	-2.018605	1.476494
O	-5.071840	-2.505825	1.932446
C	-3.034559	0.444368	0.653740
C	-3.400019	1.717451	-0.090433
C	-2.981075	1.902207	-1.416008
C	-3.309814	3.067252	-2.117227
C	-4.071869	4.064298	-1.502688
C	-4.501787	3.888304	-0.181656
C	-4.165518	2.726928	0.517042
C	-2.786633	-2.450488	1.423958
C	-2.240883	0.752757	1.970082
C	-0.781927	0.961131	1.666799
C	-0.334099	2.282848	1.132383
O	0.001042	0.008500	1.833527
Ag	1.995802	-0.343482	0.827639
O	1.490837	0.605164	-1.235259
S	0.440488	-0.097073	-2.099873
O	-0.110103	0.771799	-3.180990
C	4.978344	-0.059296	0.204323
C	5.388536	0.808931	1.202828
C	5.047706	0.638876	2.550631
C	4.253673	-0.444838	2.908423
C	3.804750	-1.360907	1.927282
C	4.172462	-1.162730	0.566288
F	6.163342	1.873155	0.866863
C	1.492367	-1.412290	-3.015656
F	0.726593	-2.126434	-3.862115
F	2.048372	-2.265367	-2.118755
F	2.485089	-0.826188	-3.714480
O	-0.536172	-0.910570	-1.305606
H	-7.057899	-2.846882	1.661376
H	-6.678256	-1.160618	2.096600
H	-5.990593	-2.543814	-0.558736
H	-7.287533	-1.356268	-0.353985
H	-5.772323	0.458795	-0.333327

H	-4.691946	-0.685858	-1.138937
H	-4.816441	0.084789	1.809035
H	-2.715377	-3.489832	1.746102
H	-2.665355	1.645339	2.450532
H	-4.509577	2.606182	1.548057
H	-5.099954	4.661101	0.306151
H	-4.328685	4.975386	-2.047022
H	-2.963213	3.193733	-3.145057
H	-2.380920	1.131214	-1.903990
H	-1.877757	-1.948335	1.100545
H	-2.390466	-0.149965	-0.013208
H	5.278949	0.104959	-0.830406
H	3.962015	-1.934349	-0.177337
H	3.315555	-2.288188	2.232675
H	3.989449	-0.602865	3.954716
H	5.407556	1.352682	3.292218
H	-2.324233	-0.101390	2.653540
H	-0.647086	3.085893	1.816908
H	0.750592	2.311722	0.975122
H	-0.847153	2.480172	0.175961

T2C

59

C	-16.492364	-4.223584	-8.427505
C	-15.268176	-3.375653	-8.786891
C	-15.361894	-2.961771	-10.257381
C	-15.440449	-4.158709	-11.230455
C	-16.259626	-5.314443	-10.690800
C	-16.749463	-5.305539	-9.433237
O	-17.510547	-6.313609	-8.881676
C	-18.010012	-7.283145	-9.833390
C	-16.920443	-7.729232	-10.794948
C	-16.406843	-6.521858	-11.582918
O	-14.039679	-4.158965	-8.579765
Ag	-13.775263	-5.236954	-6.601630
C	-15.486679	-6.885121	-4.951125
C	-16.758253	-6.328299	-5.052307
C	-16.921865	-4.970736	-4.760025
C	-15.868257	-4.144401	-4.396177
C	-14.579692	-4.703739	-4.309085
C	-14.377694	-6.086088	-4.571978
F	-18.166932	-4.436544	-4.854677
C	-15.133962	-2.169395	-7.868404
C	-15.953592	-3.676093	-12.583126
C	-15.080189	-3.494202	-13.663444
C	-15.550794	-3.018938	-14.893581
C	-16.906741	-2.721172	-15.058269
C	-17.788837	-2.902549	-13.985293
C	-17.313792	-3.375507	-12.760290
O	-13.334065	-6.498579	-9.847855
S	-12.474706	-7.349297	-8.945304
O	-12.201977	-6.706870	-7.589671
C	-13.627825	-8.806526	-8.477101
F	-13.022180	-9.621789	-7.590485
F	-13.952912	-9.522619	-9.571105
F	-14.766913	-8.336217	-7.915931
O	-11.287494	-7.991210	-9.574116
H	-18.395526	-8.110504	-9.223662
H	-18.850819	-6.824560	-10.385590
H	-16.100222	-8.177106	-10.216630
H	-17.316967	-8.506427	-11.465404

H	-17.077305	-6.293614	-12.429941
H	-15.422489	-6.750358	-12.027342
H	-13.987351	-4.922724	-9.215994
H	-17.376590	-3.573049	-8.316045
H	-14.505746	-2.323219	-10.522421
H	-18.005554	-3.529982	-11.927341
H	-18.851002	-2.677742	-14.106595
H	-17.277058	-2.354316	-16.017758
H	-14.856094	-2.885536	-15.725726
H	-14.019984	-3.731573	-13.540188
H	-16.334879	-4.693684	-7.439603
H	-14.414198	-4.537101	-11.402765
H	-16.043873	-3.090685	-4.178832
H	-13.755429	-4.093927	-3.934769
H	-13.424340	-6.559790	-4.324587
H	-15.341937	-7.947085	-5.151811
H	-17.619450	-6.924892	-5.353093
H	-14.228435	-1.598656	-8.115726
H	-16.007281	-1.512027	-7.972131
H	-15.070574	-2.490602	-6.816832
H	-16.269627	-2.347736	-10.363346

T3

35

C	-15.900242	-4.278734	-8.426346
C	-15.463608	-4.424599	-9.859640
C	-16.322108	-4.817730	-10.813223
C	-17.778008	-5.131774	-10.581934
C	-18.168051	-5.142627	-9.119925
C	-17.310588	-4.713731	-8.172888
O	-17.614422	-4.632475	-6.826818
C	-19.025715	-4.725253	-6.518710
C	-19.685616	-5.874169	-7.264905
C	-19.547103	-5.645781	-8.773478
C	-14.027474	-4.087760	-10.147160
C	-18.659700	-4.158841	-11.374109
C	-19.497289	-4.604959	-12.403807
C	-20.304233	-3.704561	-13.111398
C	-20.280262	-2.343568	-12.794227
C	-19.443942	-1.888048	-11.766268
C	-18.642015	-2.789662	-11.064799
H	-19.074608	-4.850511	-5.429214
H	-19.502649	-3.765647	-6.789598
H	-19.193642	-6.816080	-6.972989
H	-20.742332	-5.947744	-6.966322
H	-20.311937	-4.931801	-9.128607
H	-19.738991	-6.585267	-9.321262
H	-15.775941	-3.226413	-8.103893
H	-15.976113	-4.896502	-11.849298
H	-17.993084	-2.436240	-10.259413
H	-19.418190	-0.825885	-11.512422
H	-20.910104	-1.639689	-13.342393
H	-20.953986	-4.069245	-13.910279
H	-19.520440	-5.669734	-12.652728
H	-15.224631	-4.853631	-7.764166
H	-17.983322	-6.138367	-10.998223
H	-13.345522	-4.722405	-9.556484
H	-13.786497	-4.216133	-11.211329
H	-13.805029	-3.044360	-9.865533

5

33

C	-16.553635	-4.642184	-8.223386
C	-15.731527	-4.413359	-9.338638
C	-16.240577	-4.687202	-10.619626
C	-17.537502	-5.183169	-10.780916
C	-18.345527	-5.415335	-9.662266
C	-17.850658	-5.140875	-8.383225
C	-14.348640	-3.878113	-9.160500
C	-14.181472	-2.518598	-8.865096
C	-12.904010	-1.961895	-8.692410
C	-11.795997	-2.805598	-8.796360
C	-11.955929	-4.171228	-9.071345
C	-13.231758	-4.734905	-9.276112
O	-10.790189	-4.901366	-9.139187
C	-10.933920	-6.341414	-9.116366
C	-12.040136	-6.805651	-10.047085
C	-13.373243	-6.209875	-9.588684
C	-12.731208	-0.487686	-8.425154
H	-9.949424	-6.727465	-9.409851
H	-11.142531	-6.657532	-8.078002
H	-11.805902	-6.480468	-11.073591
H	-12.080988	-7.905017	-10.049606
H	-13.730195	-6.743723	-8.690131
H	-14.147130	-6.361497	-10.354534
H	-10.783439	-2.421149	-8.652467
H	-15.066530	-1.883354	-8.778612
H	-16.167571	-4.430772	-7.223605
H	-18.475803	-5.315404	-7.504857
H	-19.357544	-5.805927	-9.787320
H	-17.919383	-5.386280	-11.783781
H	-15.613674	-4.501430	-11.495085
H	-11.806147	-0.285928	-7.866781
H	-12.675813	0.077819	-9.369676
H	-13.577494	-0.083441	-7.851688

H_2

2

H	0.000000	0.000000	-0.001151
H	0.000000	0.000000	0.751151

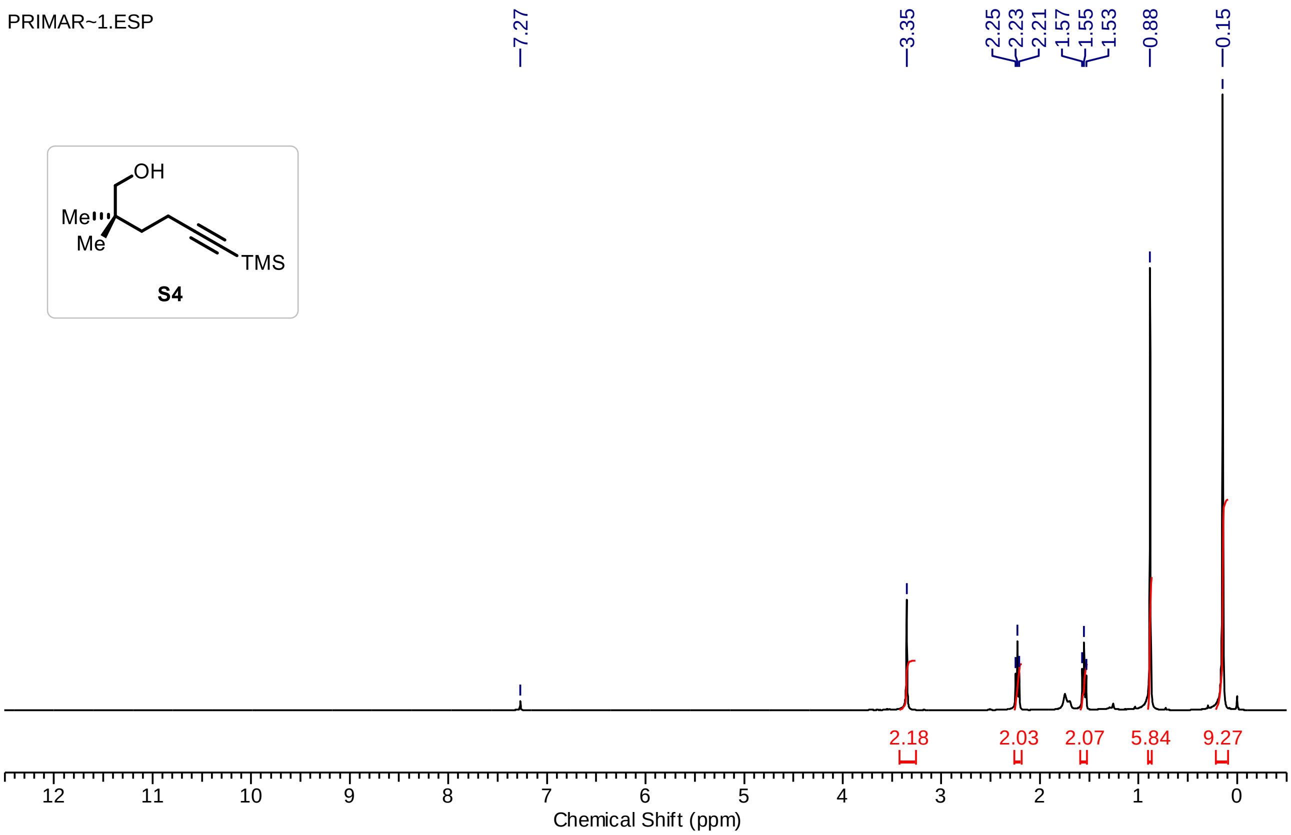
H_2O

3

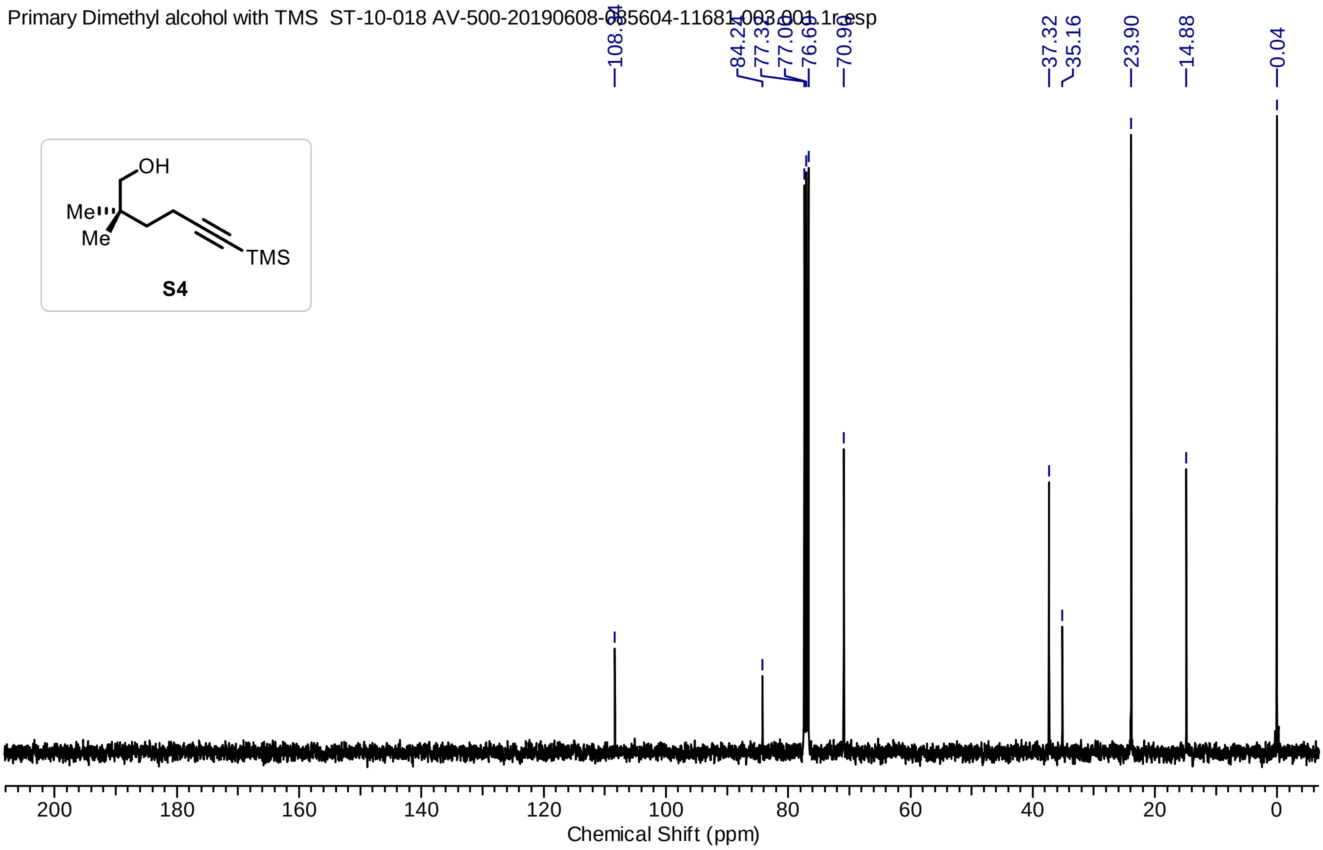
O	-0.027895	0.000000	-0.019709
H	0.019953	0.000000	0.951352
H	0.903612	0.000000	-0.298306

14. ^{1}H, ^{13}C and 2D NMR Spectra

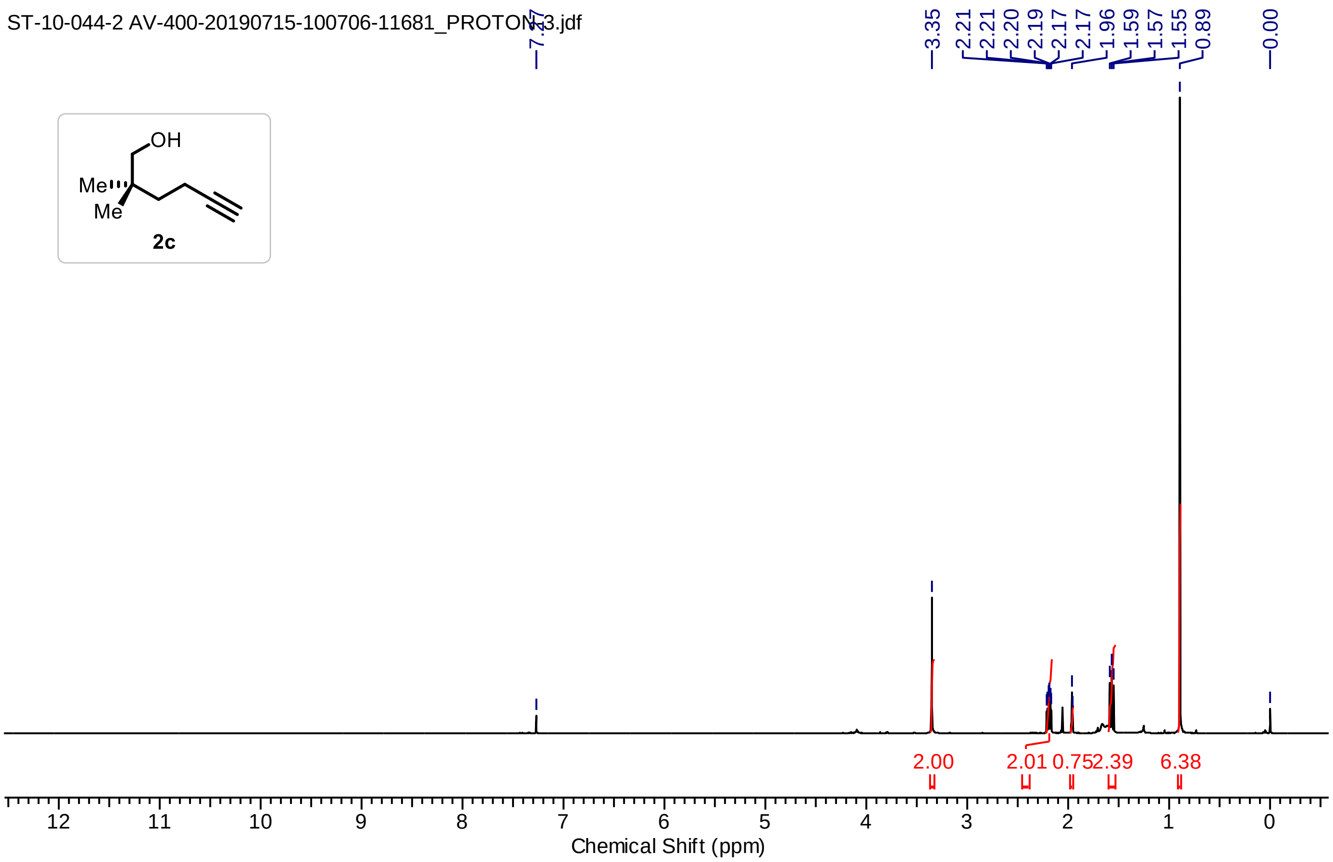
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **S4**:



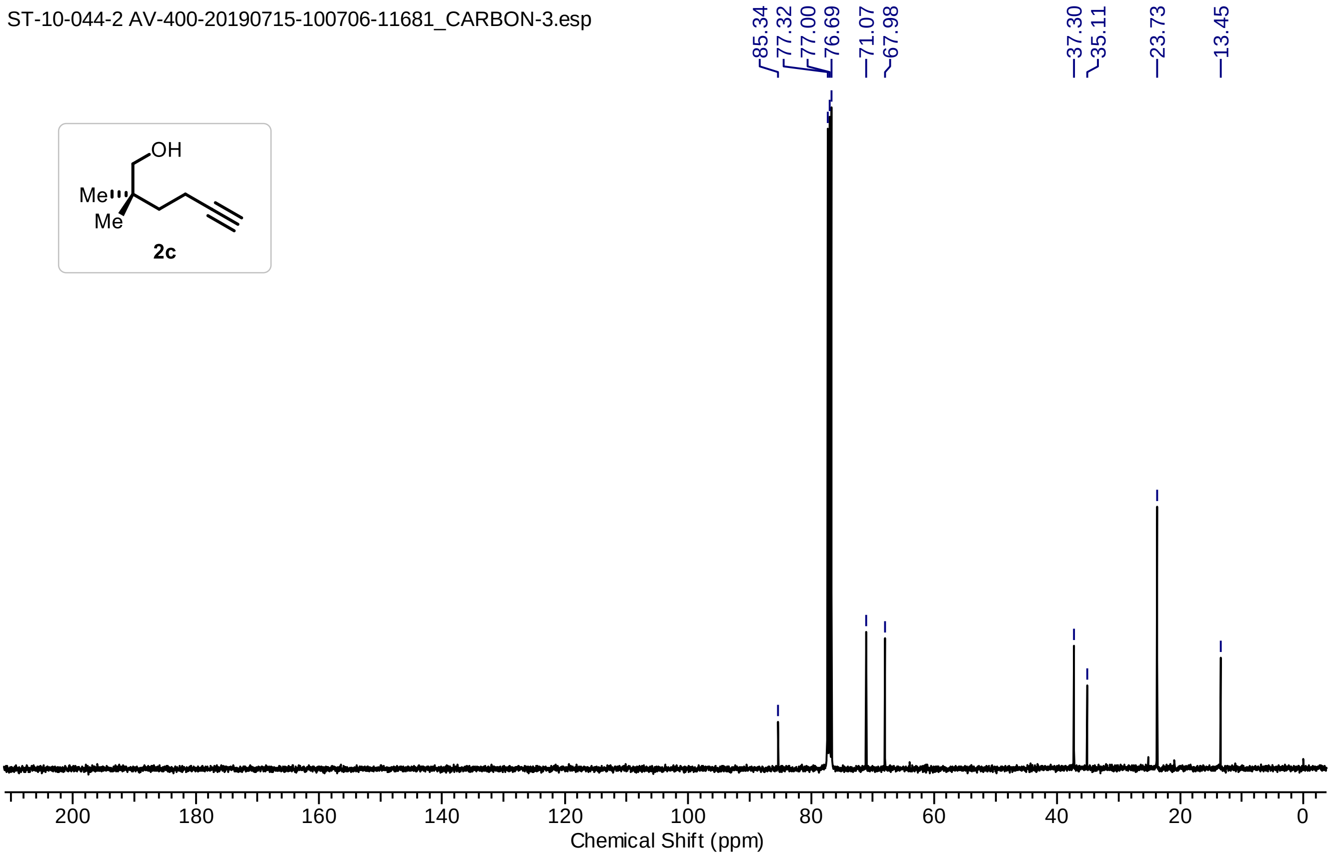
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **S4**:



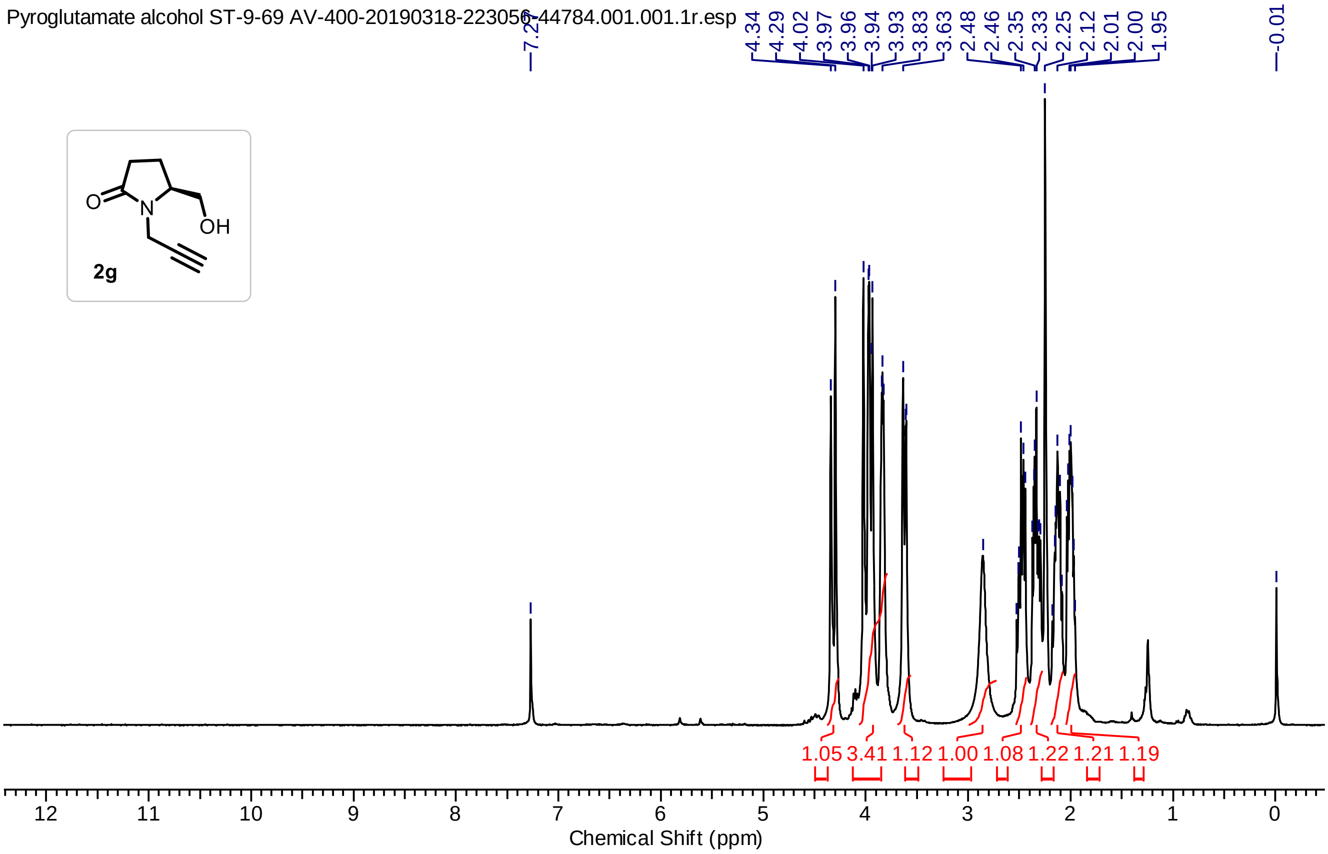
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **2c**:



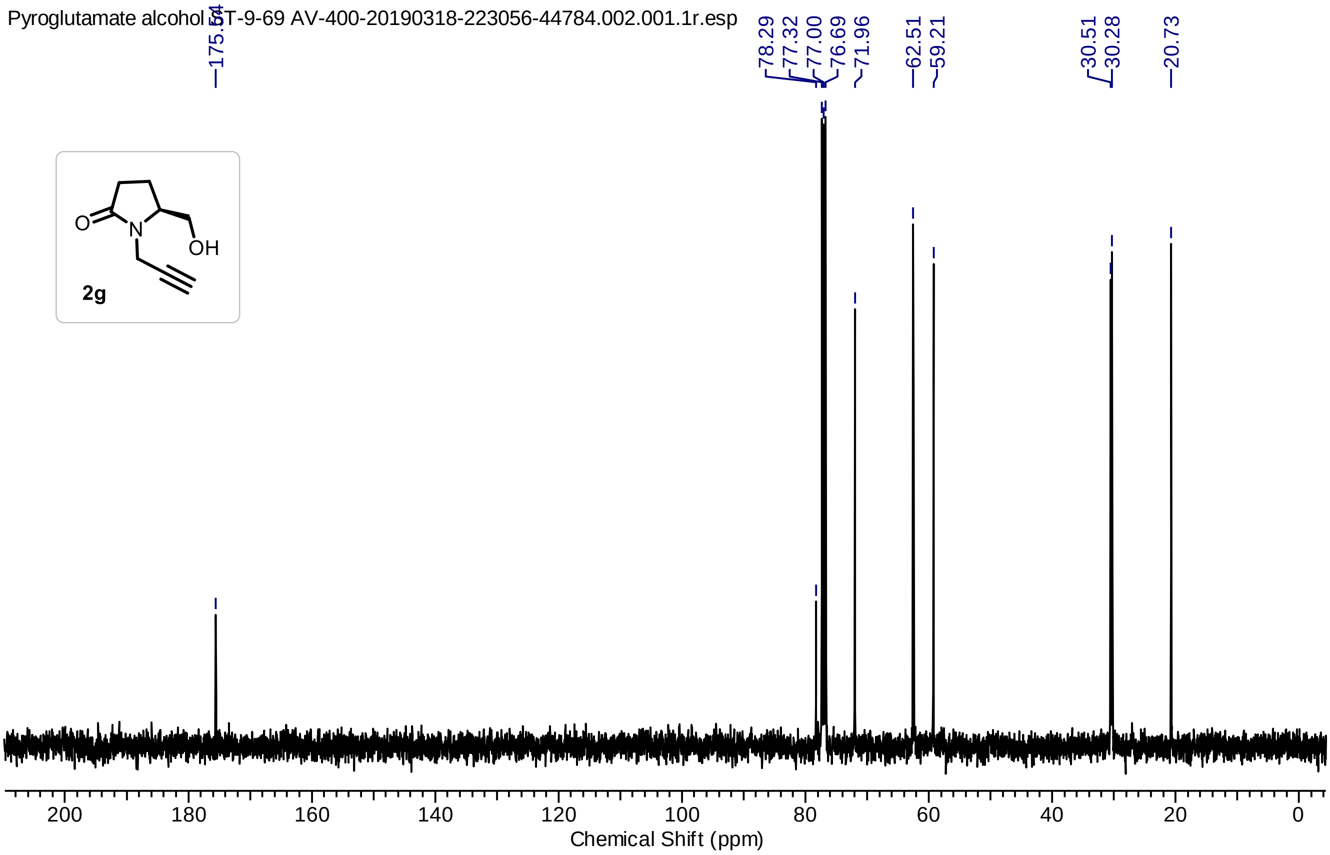
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **2c**:



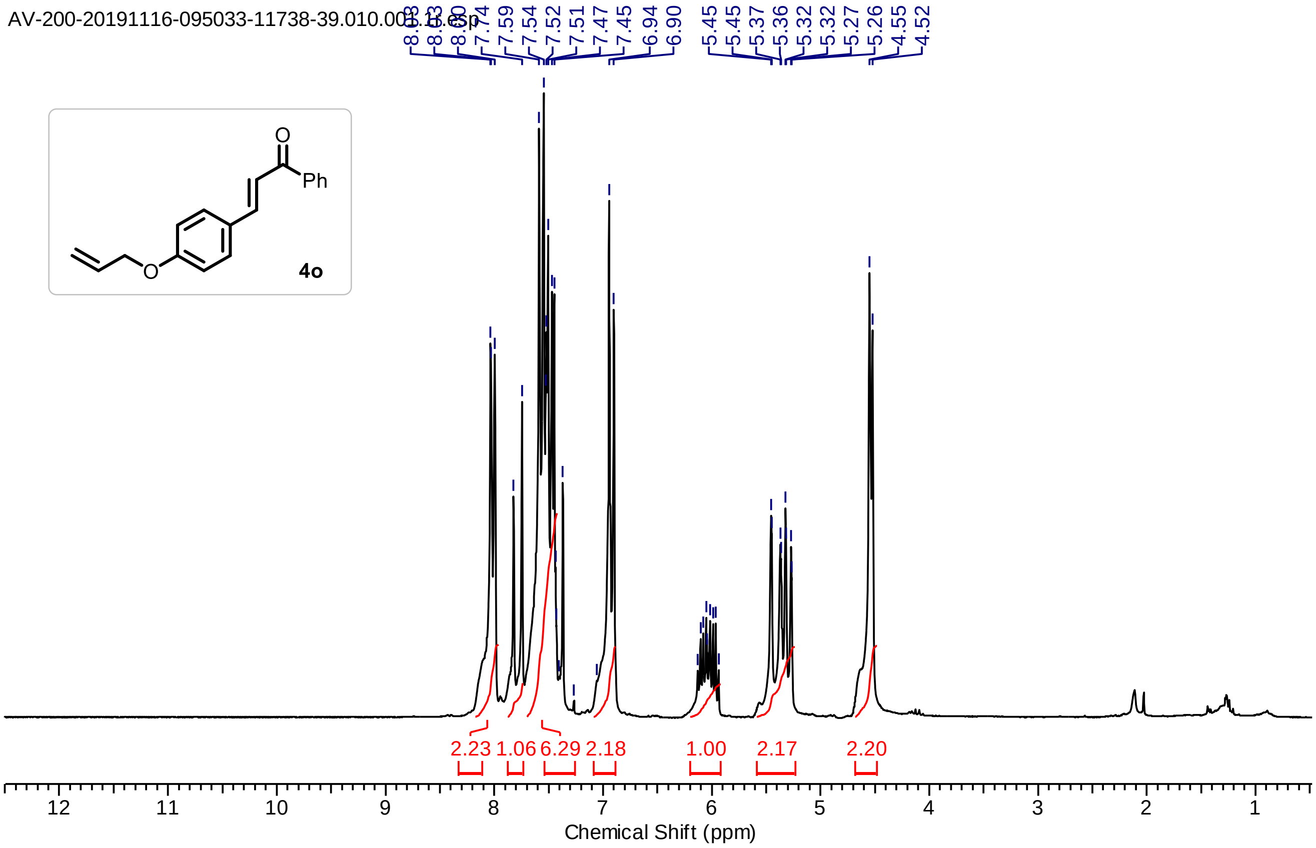
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **2g**:



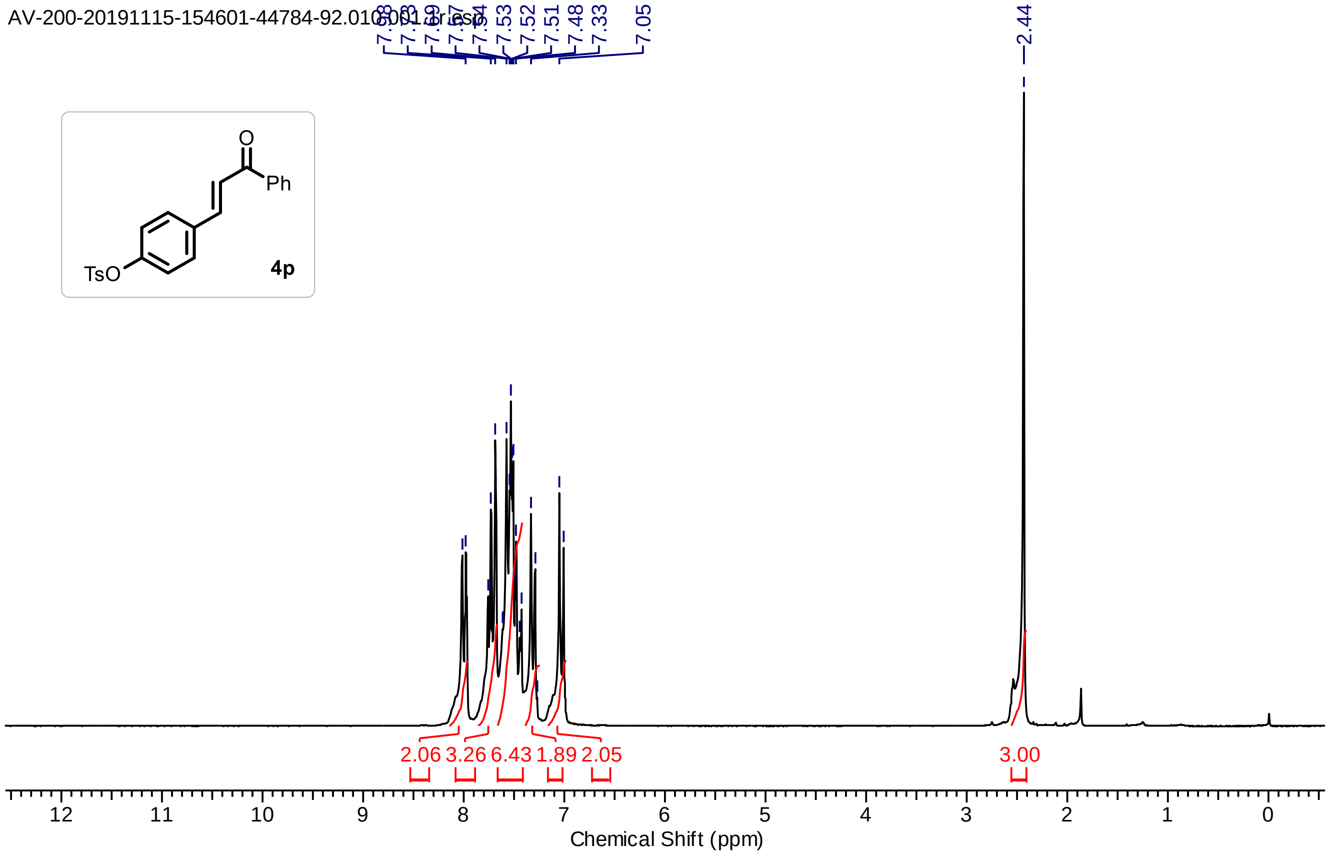
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$) of **2g**:



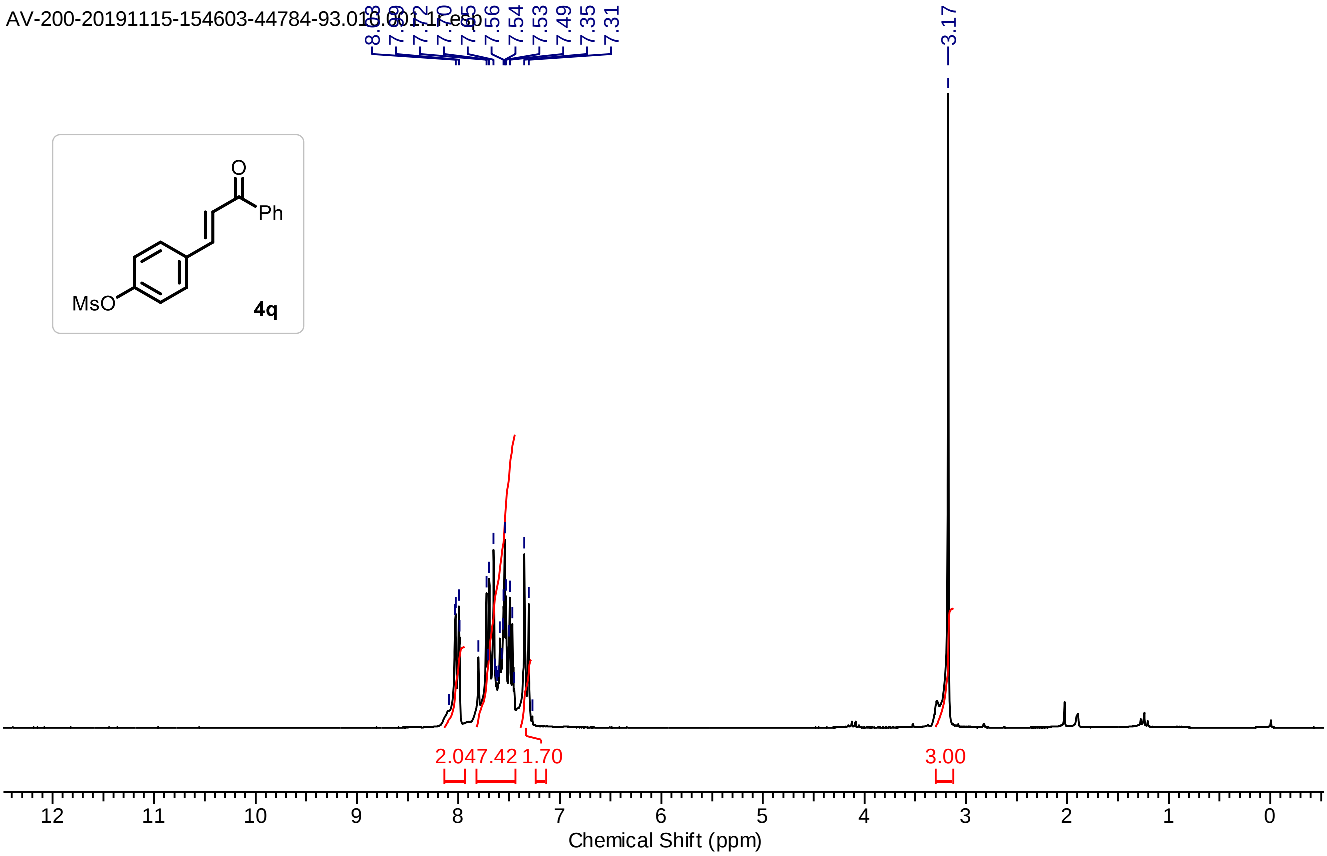
^{1}H NMR-Spectrum (200 MHz, $CDCl_3$) of **4o**:



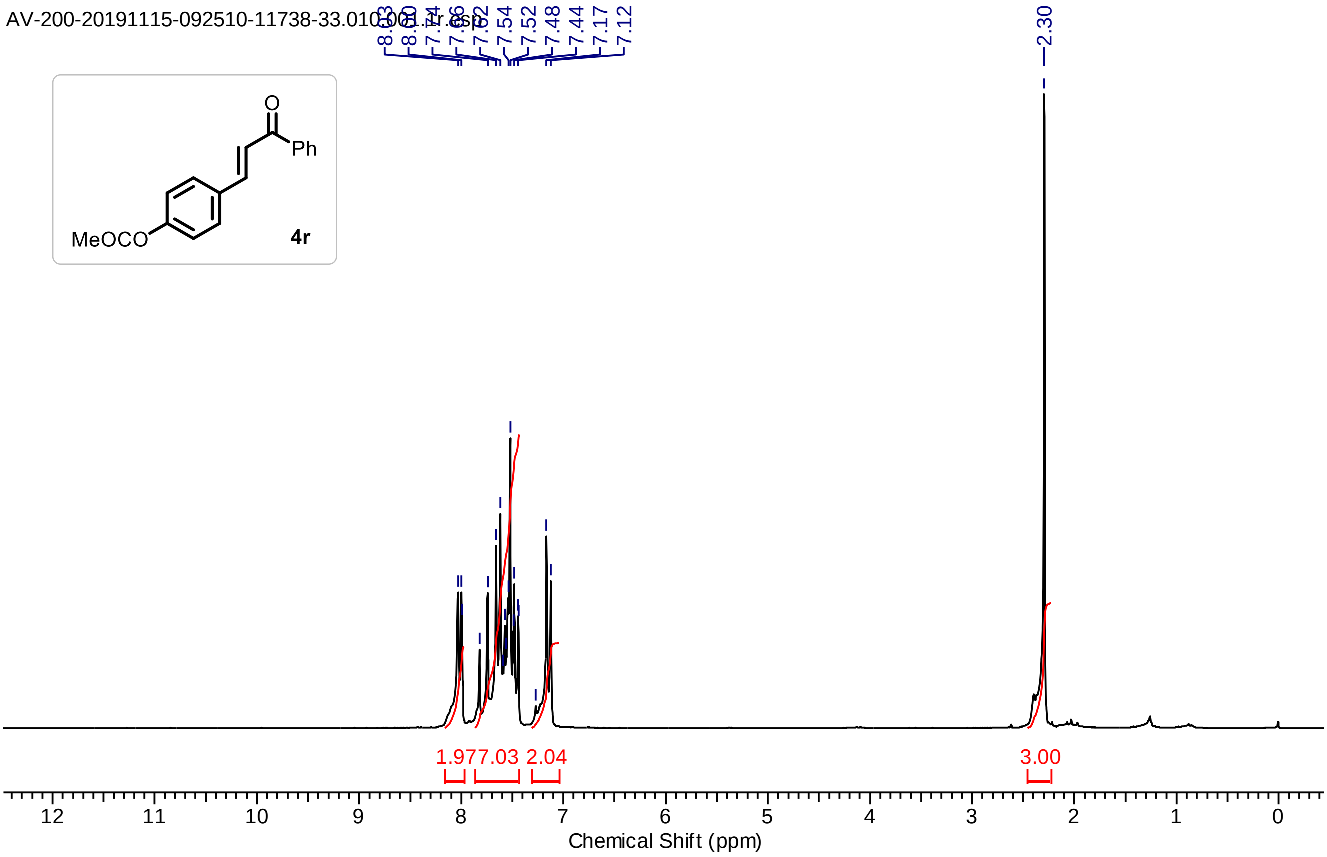
^{1}H NMR-Spectrum (200 MHz, $CDCl_3$) of **4p**:



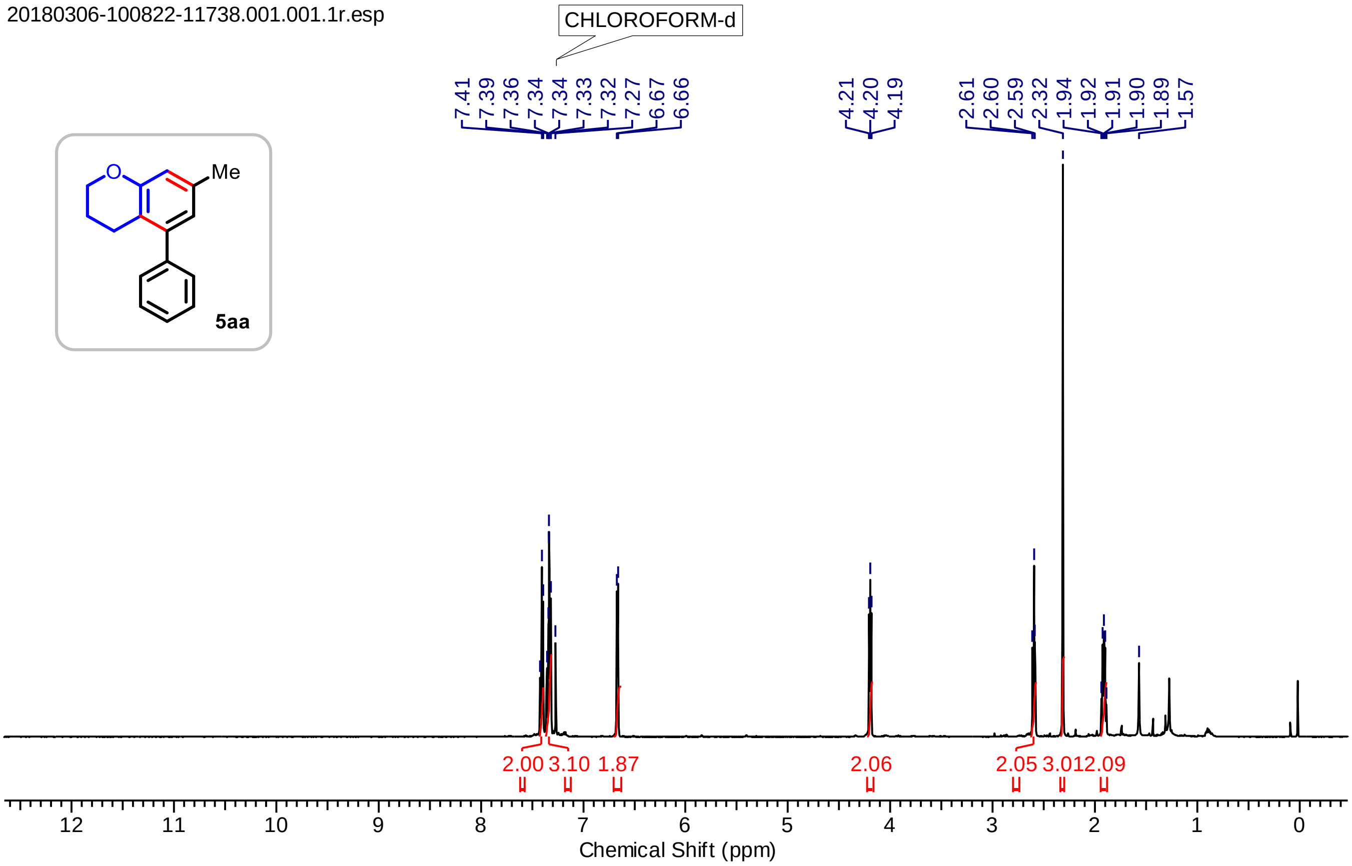
^{1}H NMR-Spectrum (200 MHz, CDCl$_3$) of **4q**:



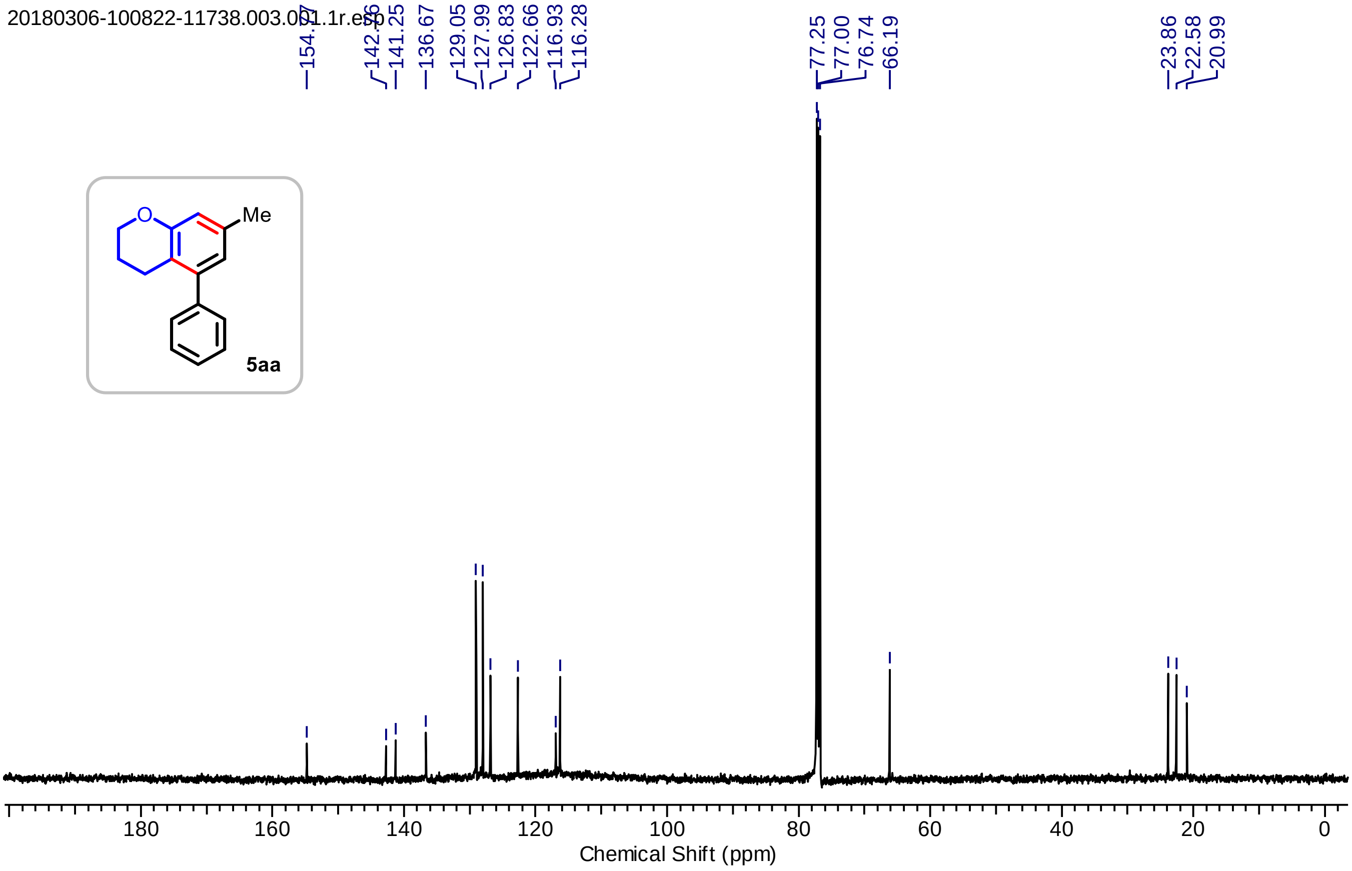
^{1}H NMR-Spectrum (200 MHz, CDCl$_3$) of **4r**:



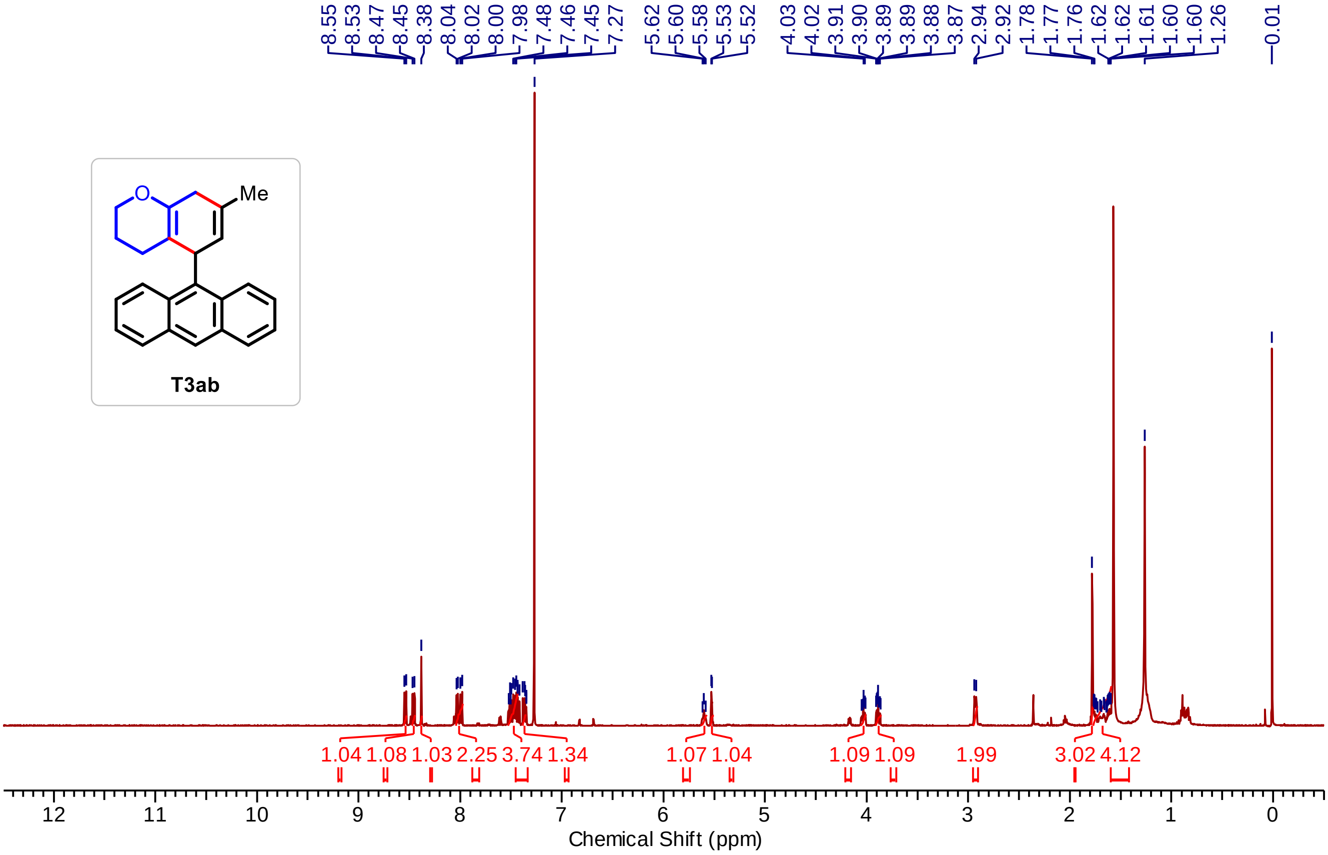
^{1}H NMR-Spectrum (500 MHz, $CDCl_3$) of **5aa**:



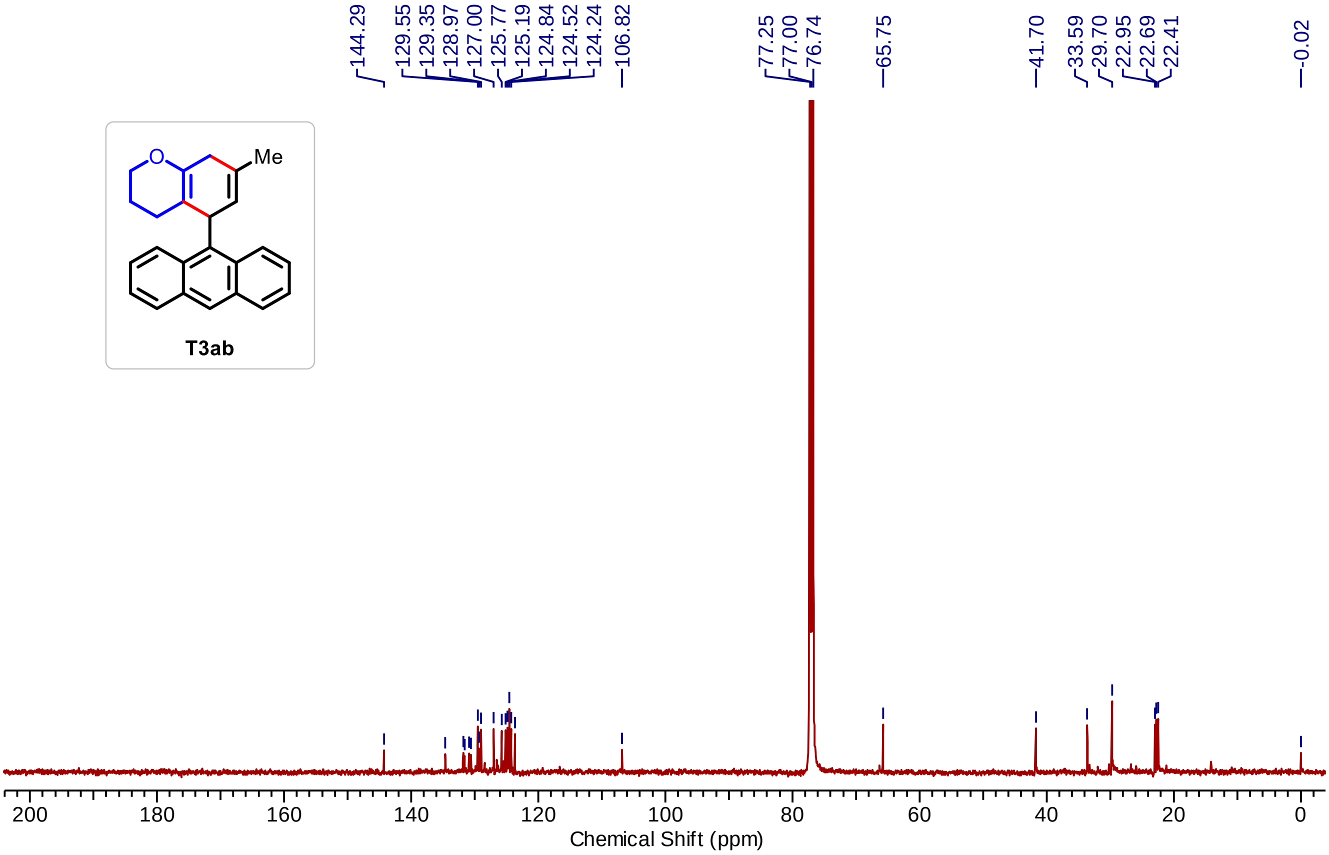
^{13}C NMR-Spectrum (126 MHz, $CDCl_3$)of **5aa**:



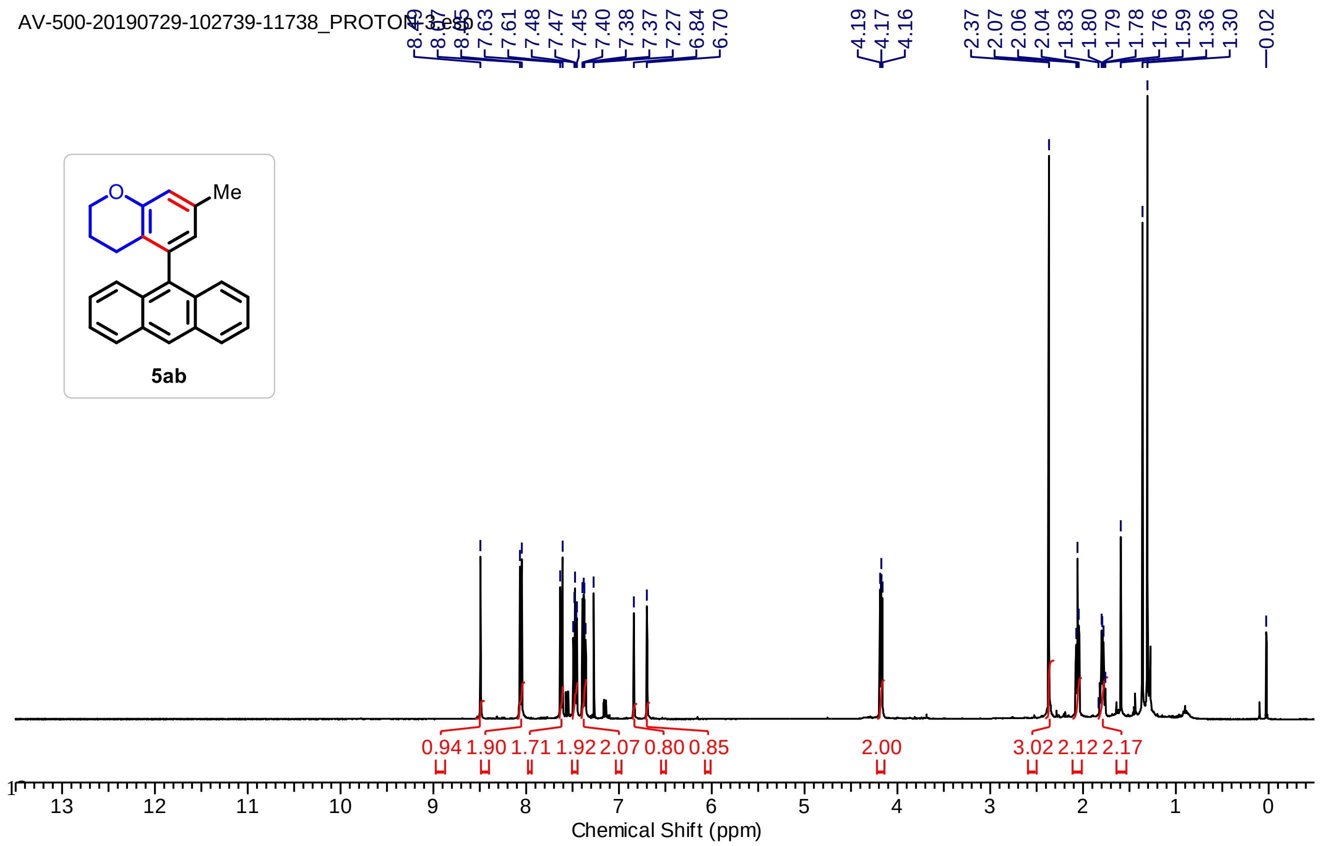
^{1}H NMR-Spectrum (500 MHz, CDCl$_3$) of **T3ab**:



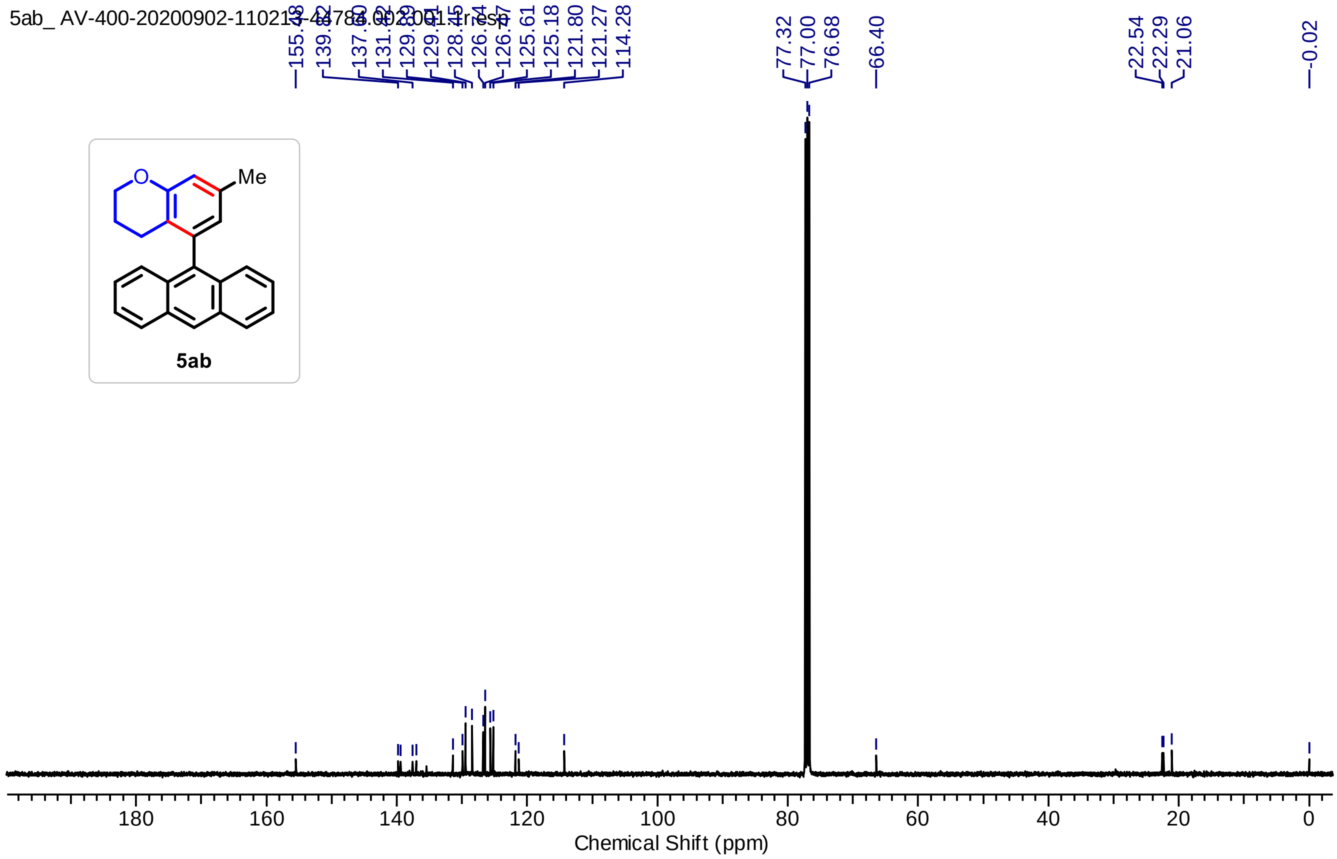
^{13}C NMR-Spectrum (126 MHz, CDCl$_3$)of **T3ab**:



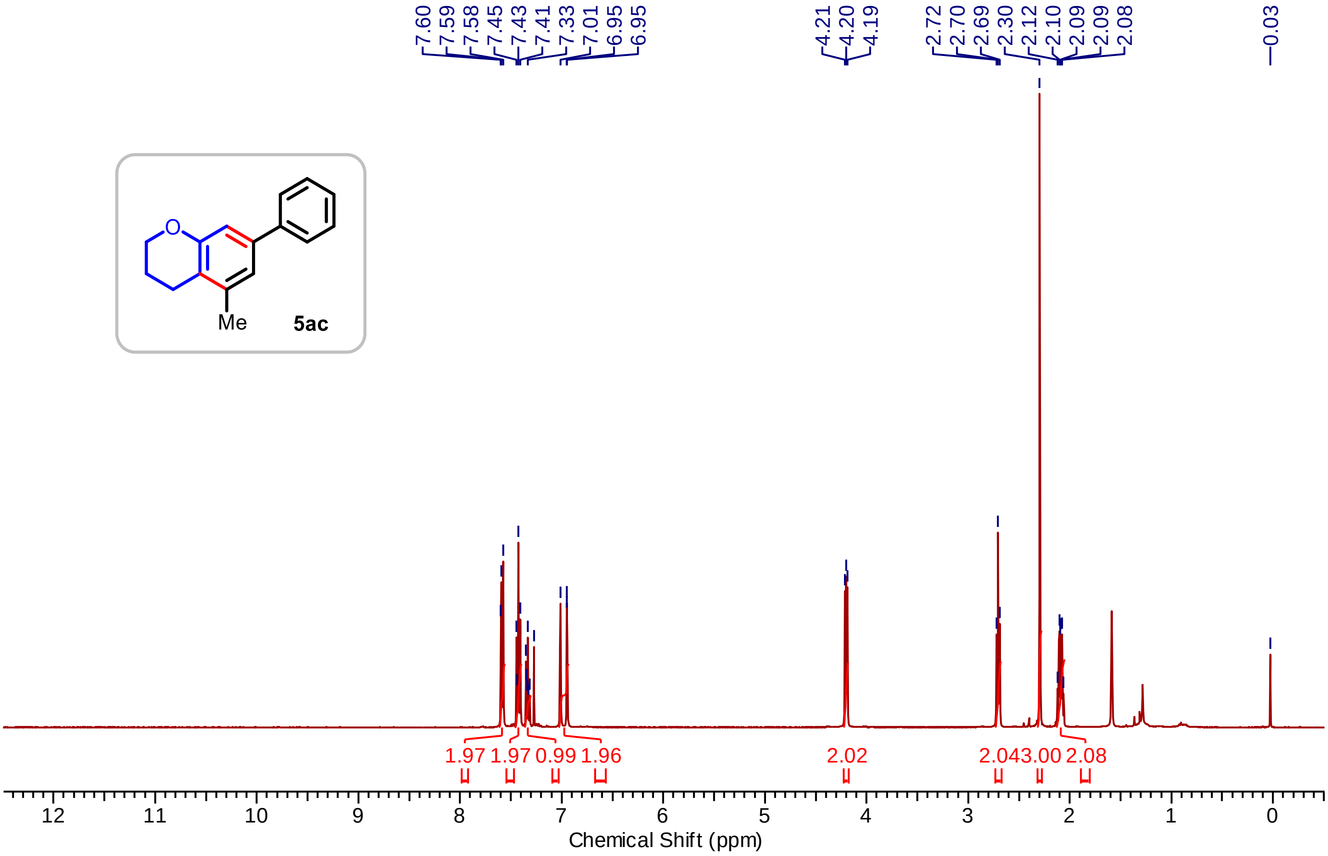
^{1}H NMR-Spectrum (500 MHz, CDCl$_3$) of **5ab**:



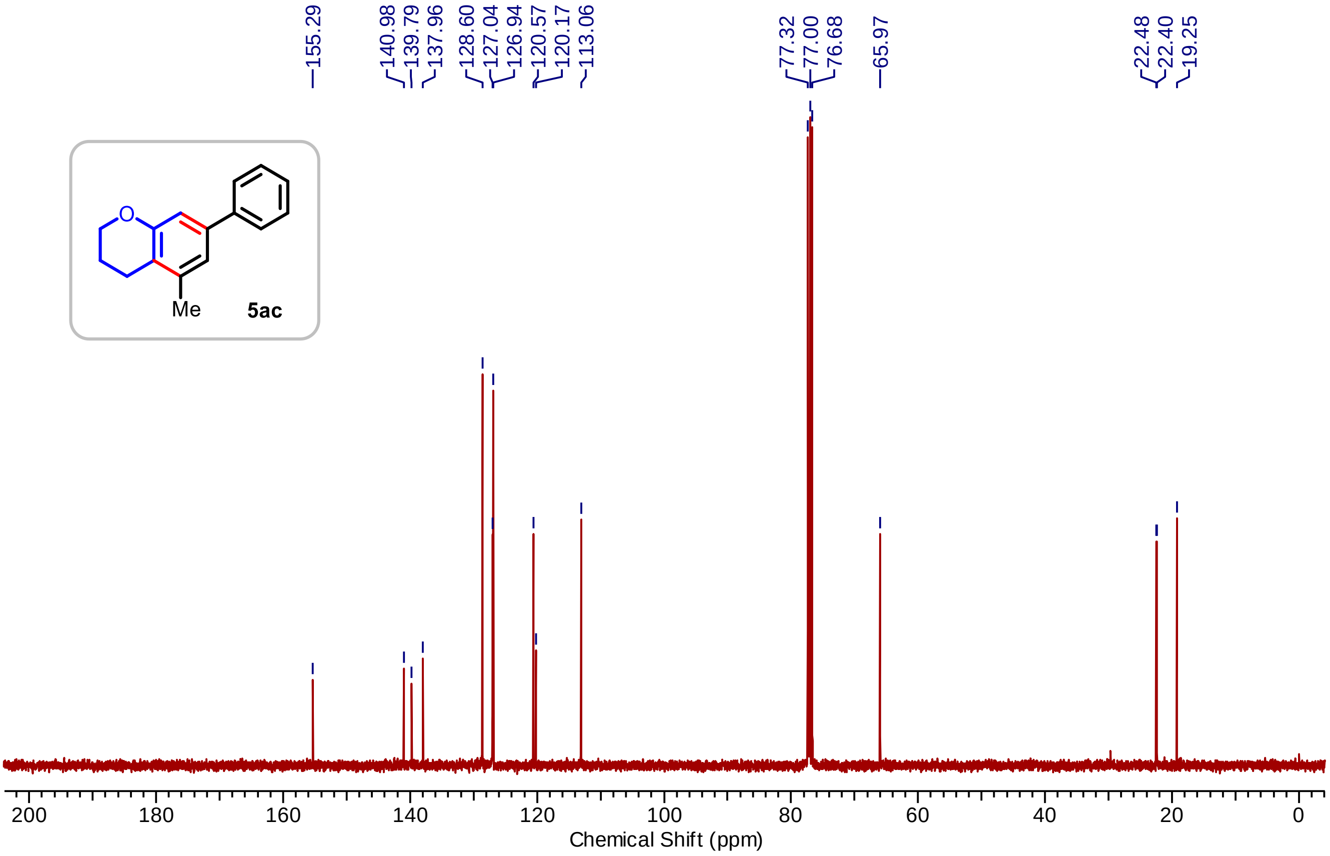
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5ab**:



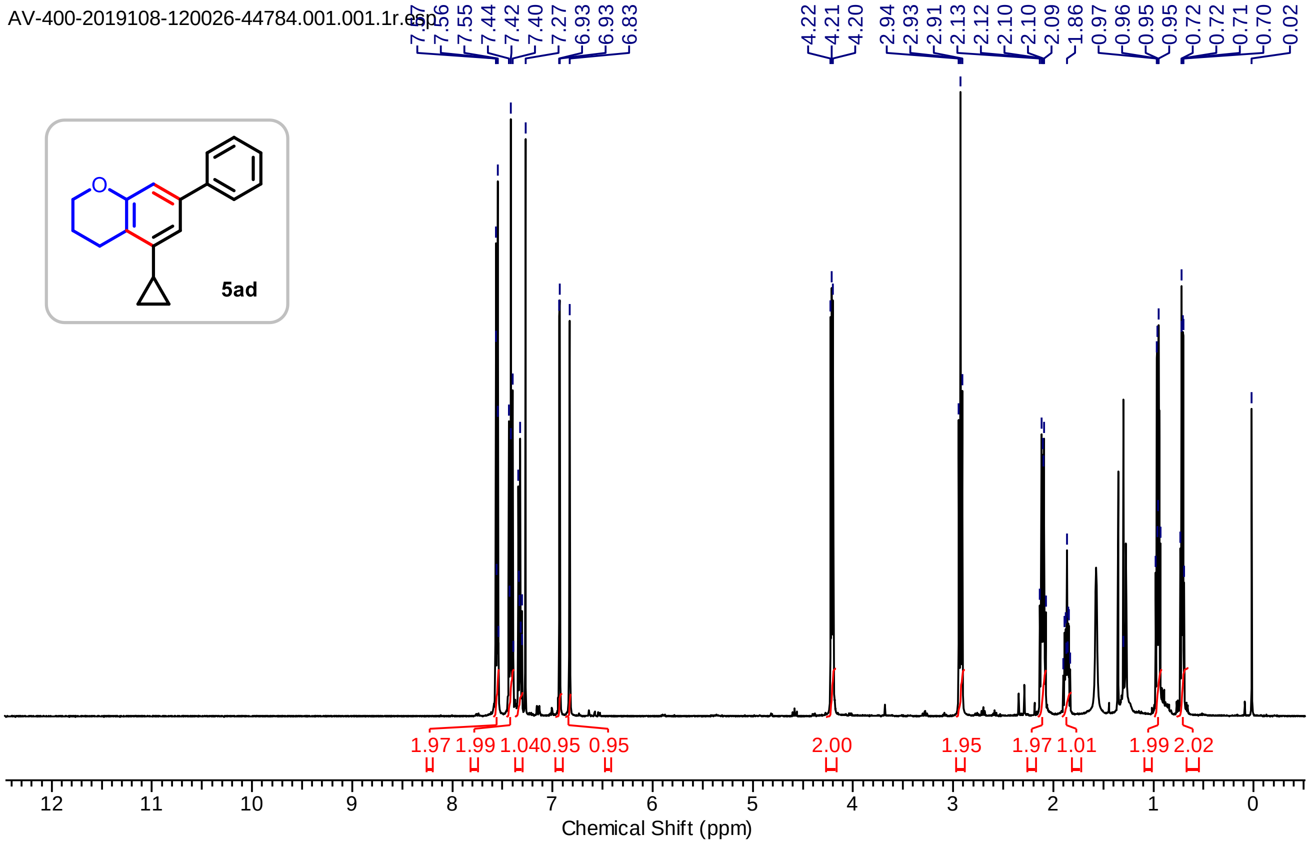
^{1}H NMR-Spectrum (200 MHz, CDCl$_3$) of **5ac**:



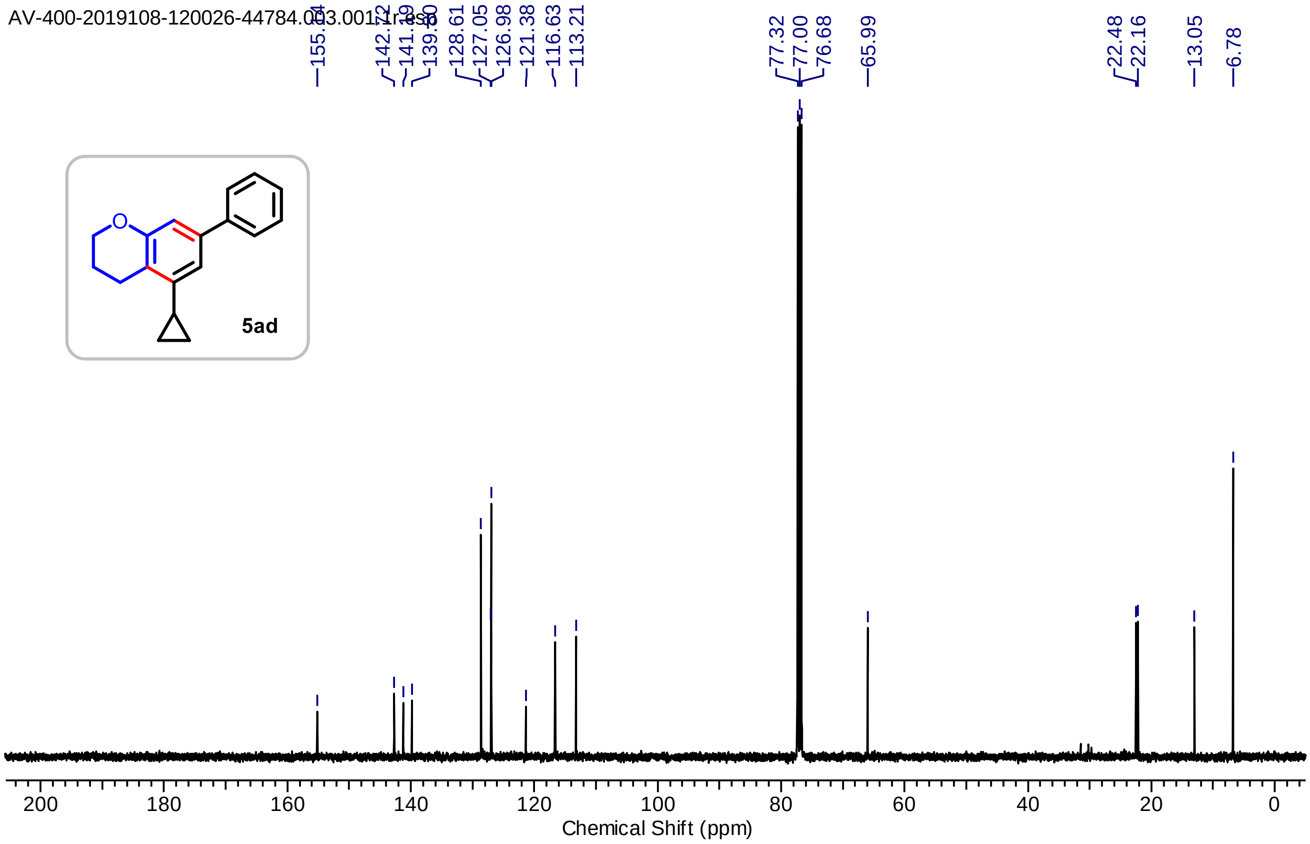
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ac**:



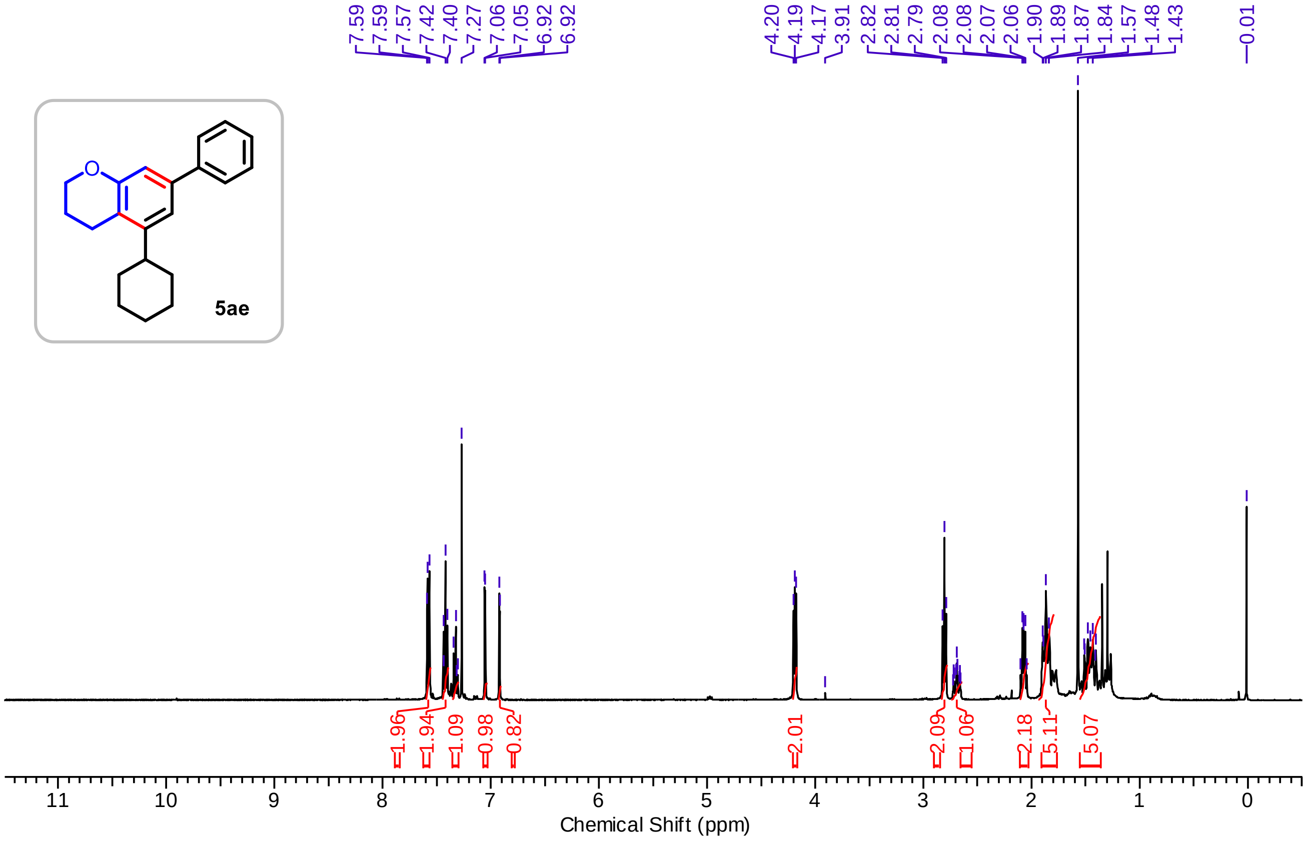
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ad**:



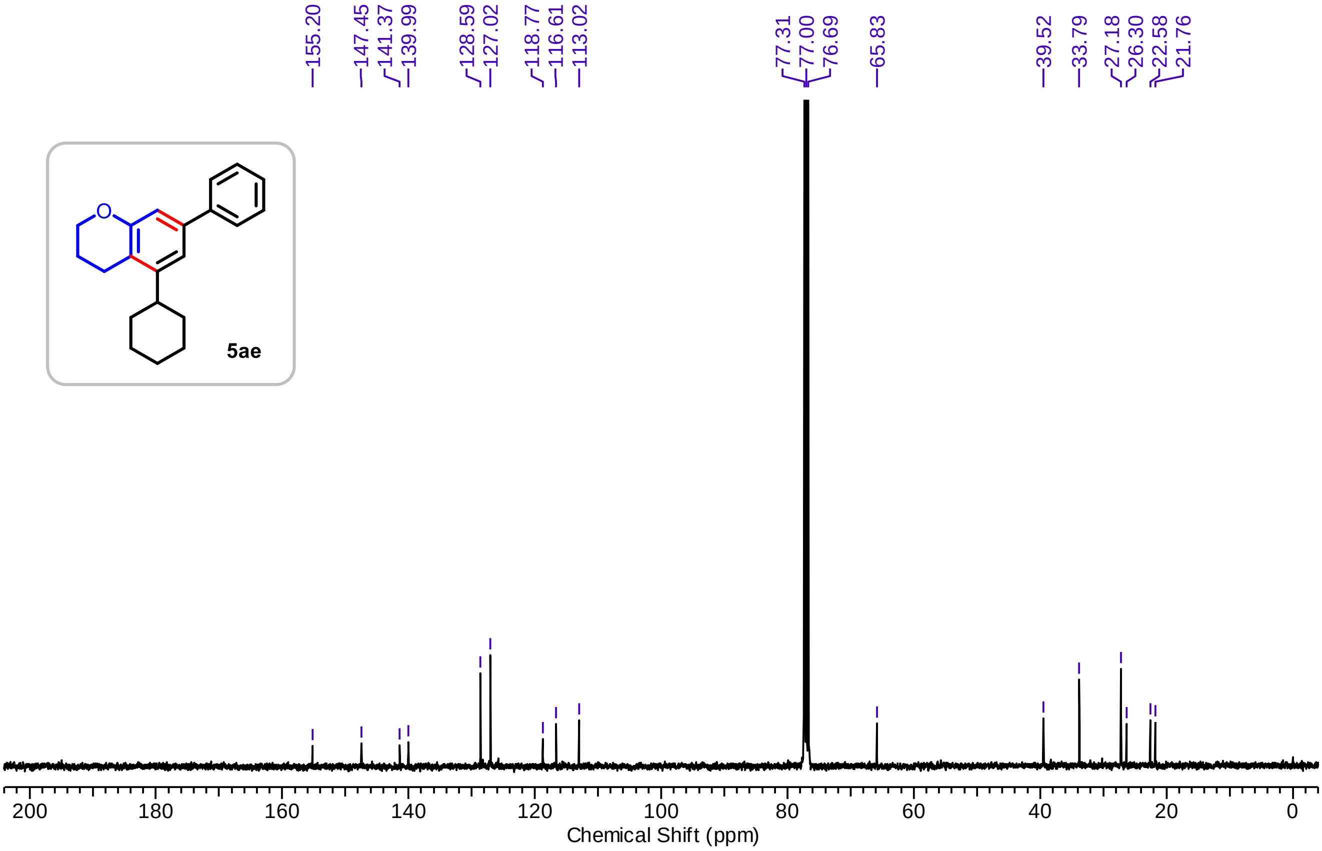
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ad**:



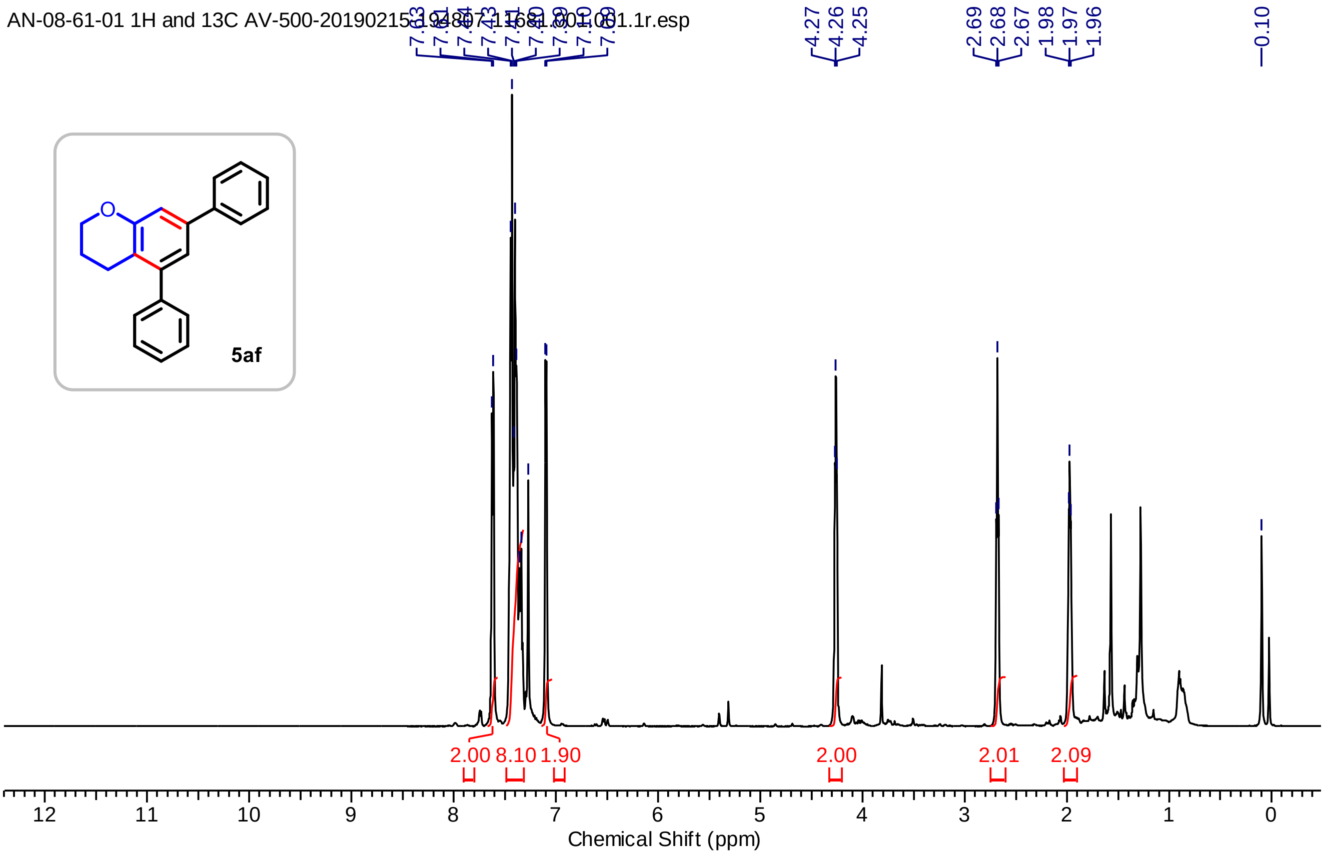
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5ae**:



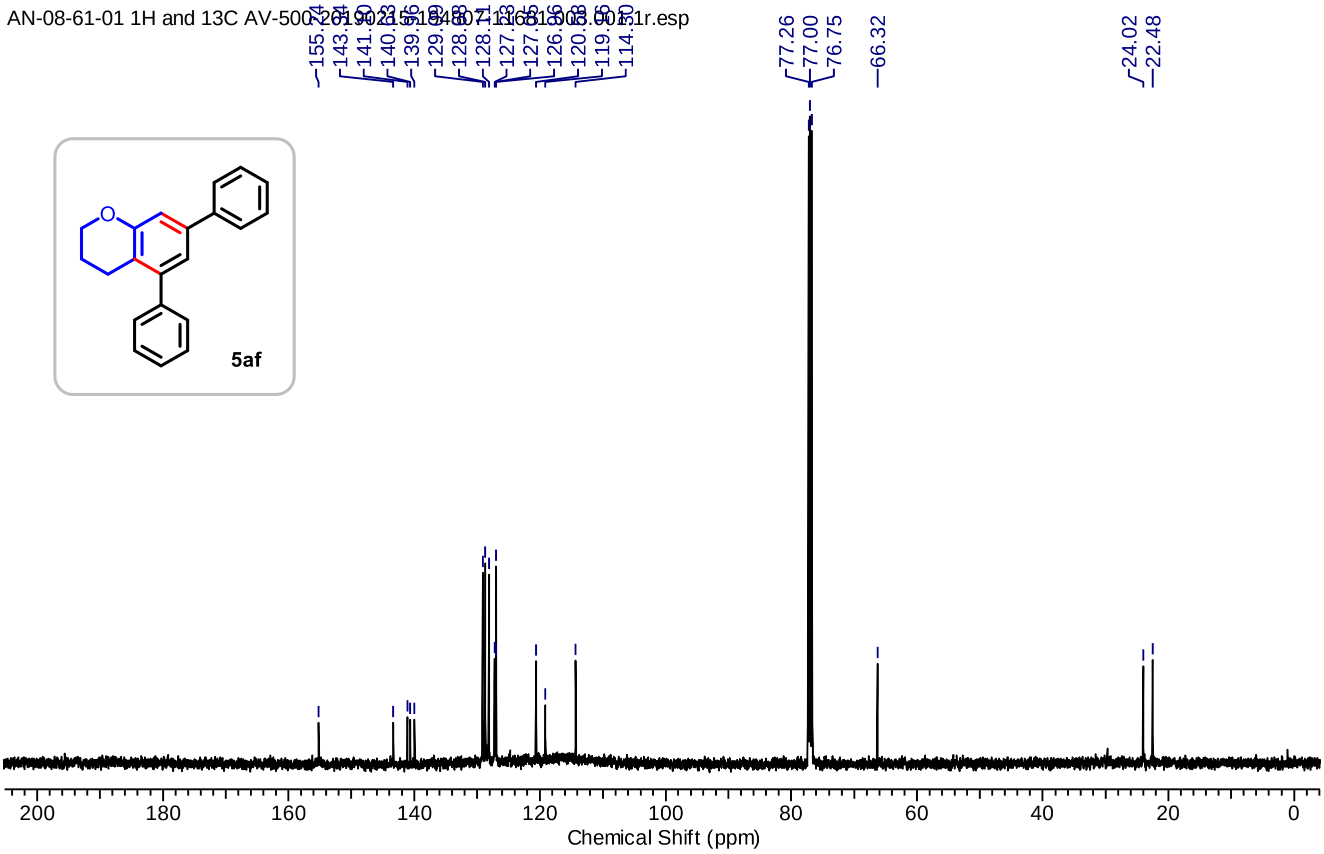
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$)of **5ae**:



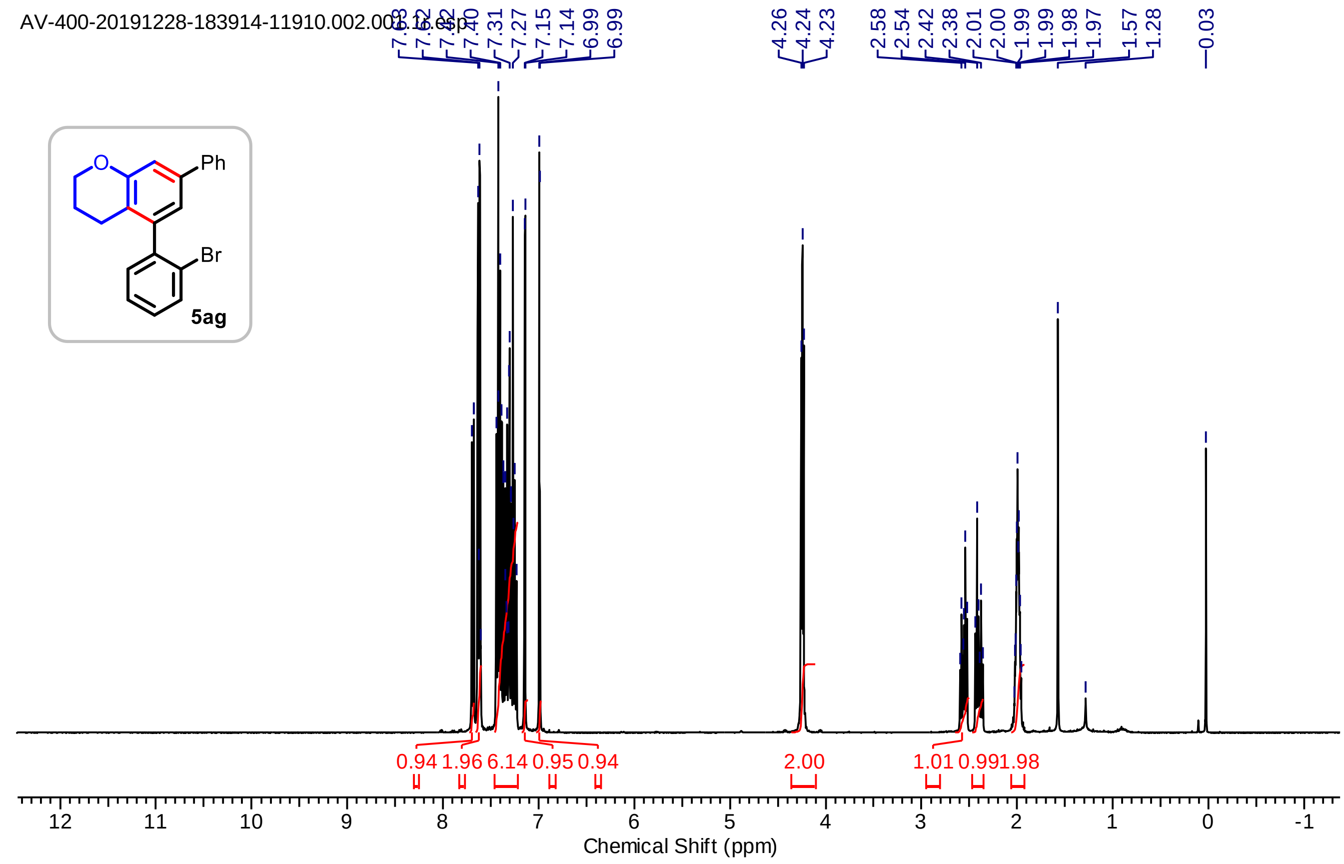
^{1}H NMR-Spectrum (500 MHz, $CDCl_3$) of **5af**:



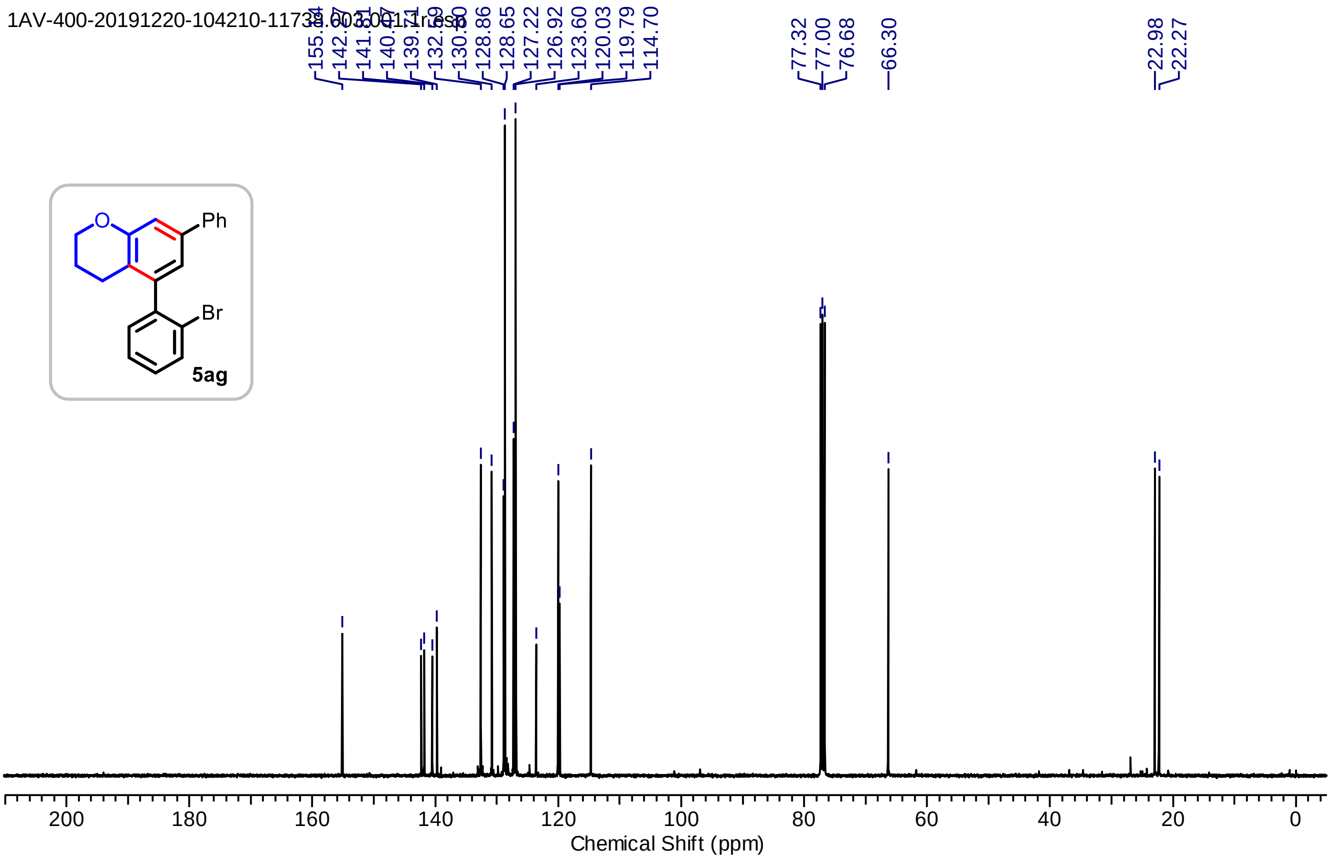
^{13}C NMR-Spectrum (126 MHz, $CDCl_3$)of **5af**:



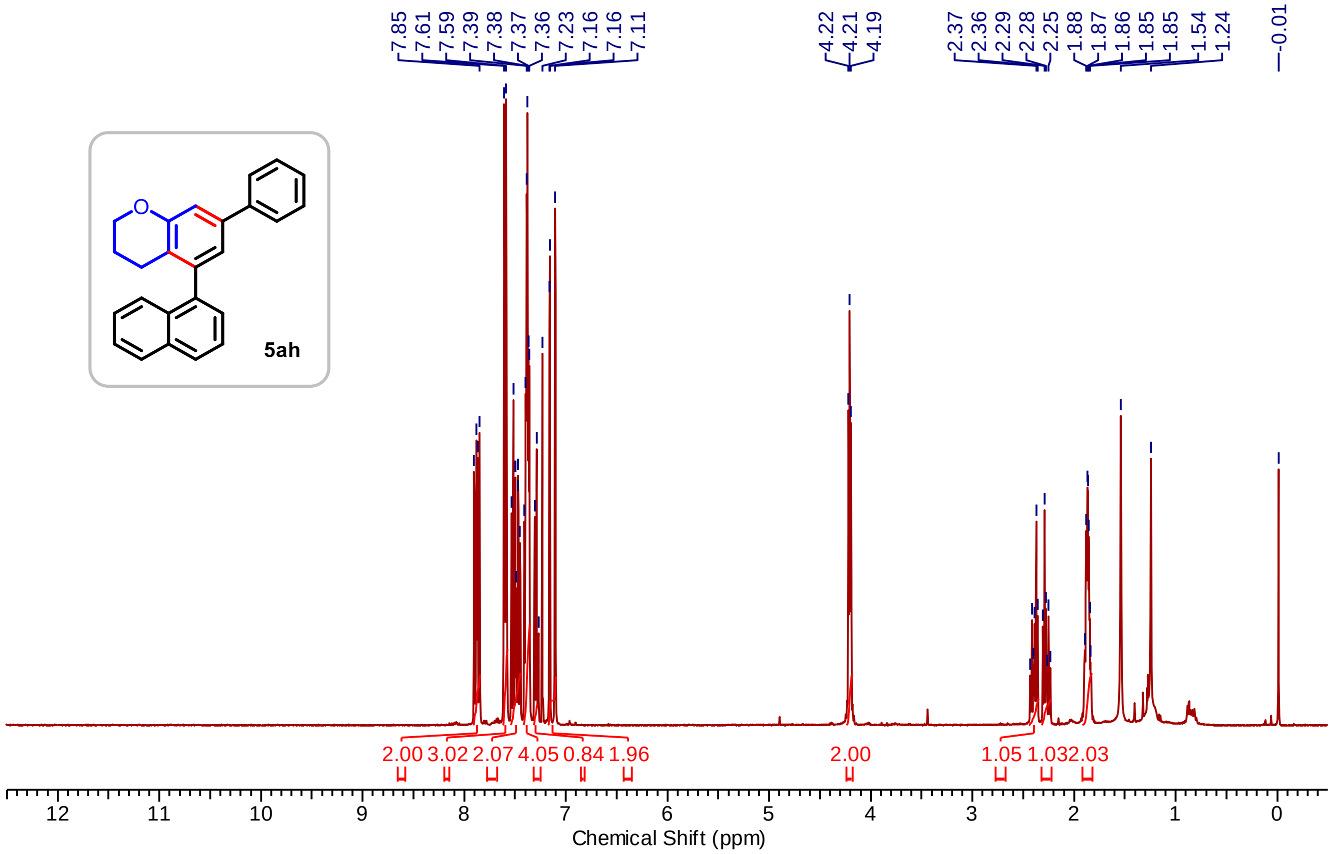
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ag**:



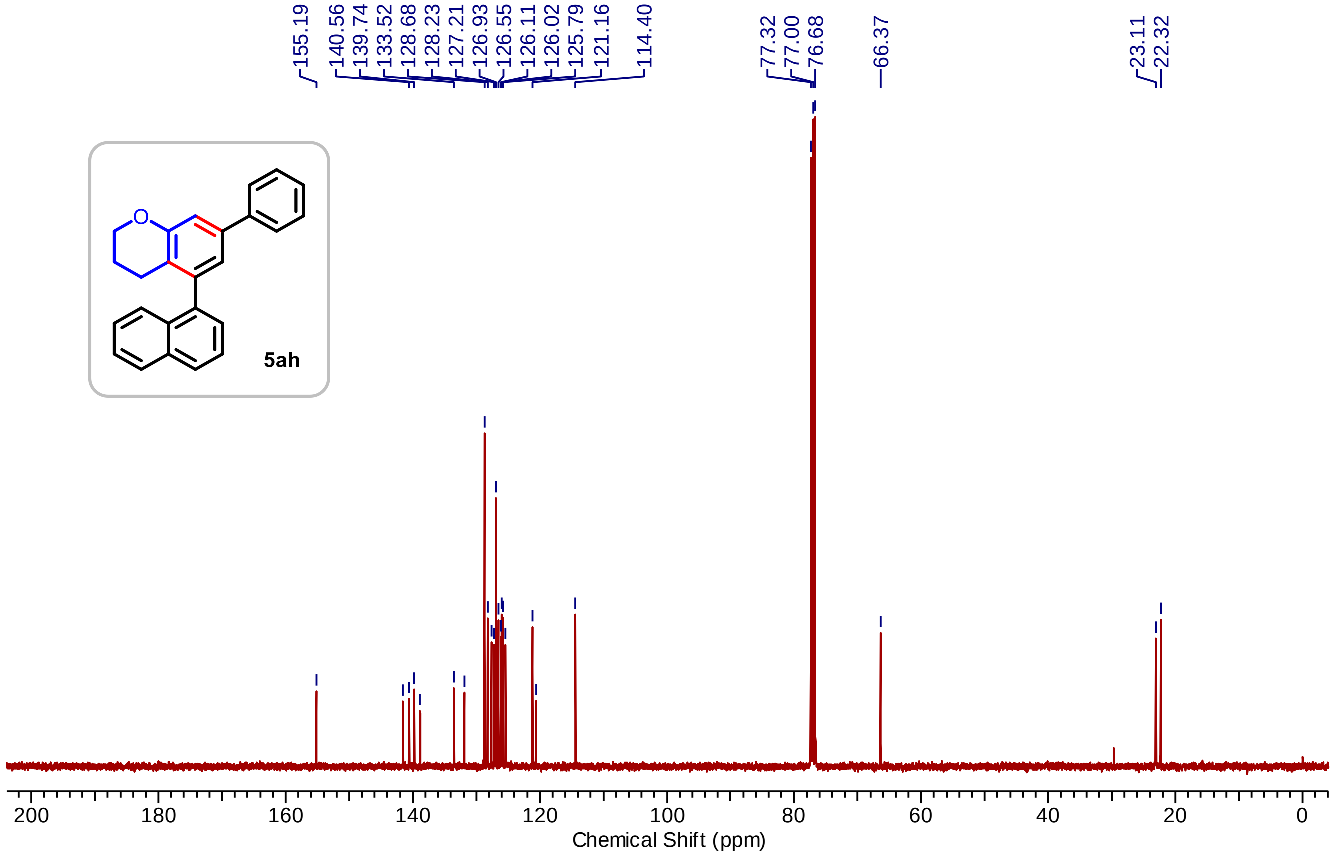
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5ag**:



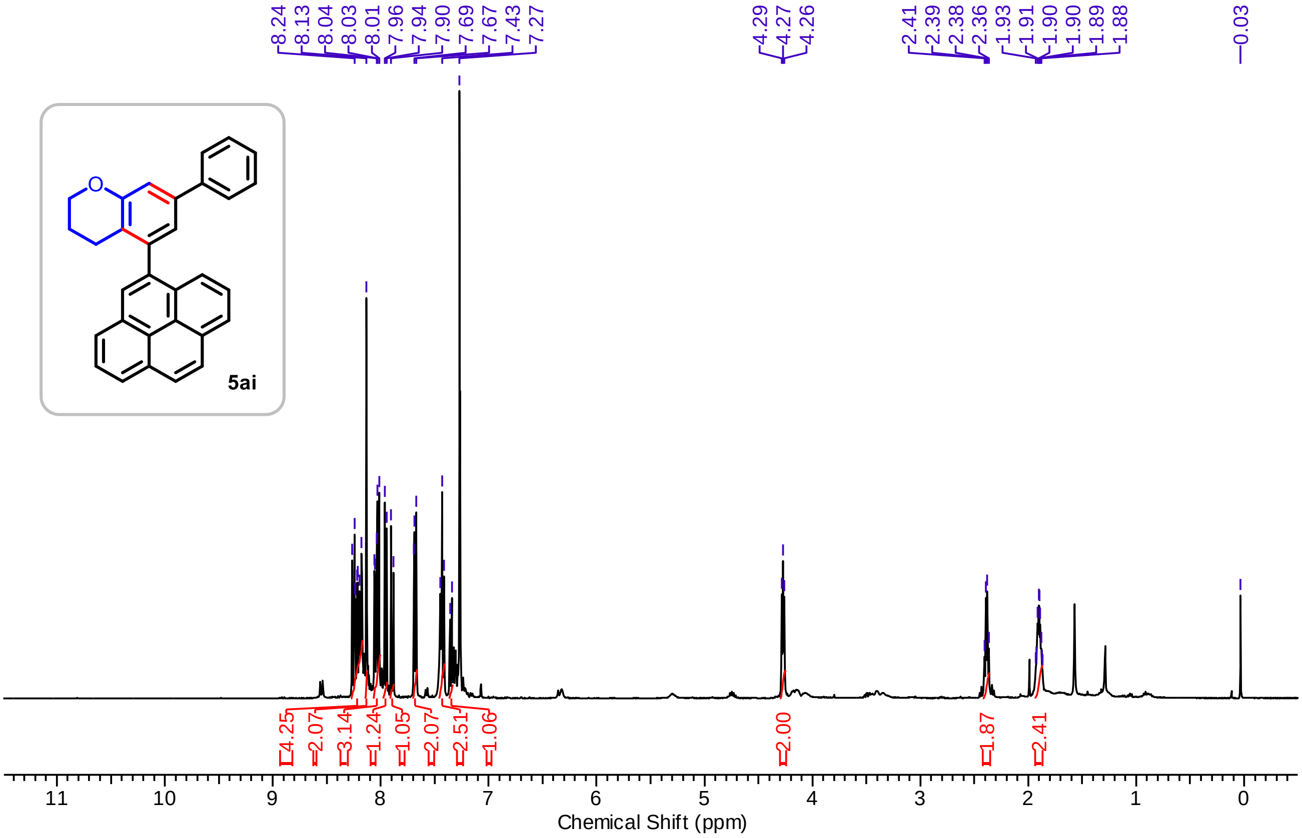
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ah**:



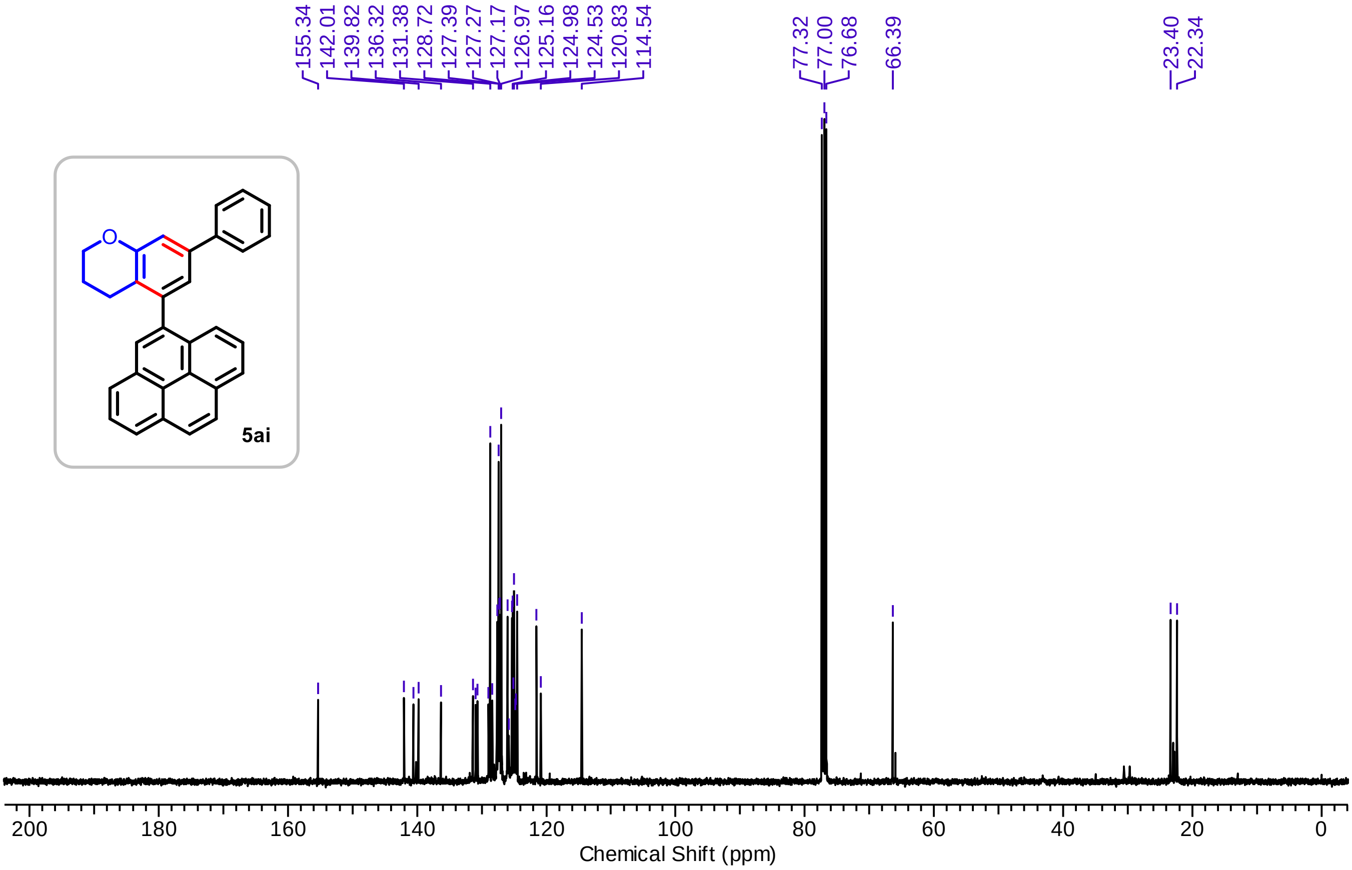
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5ah**:



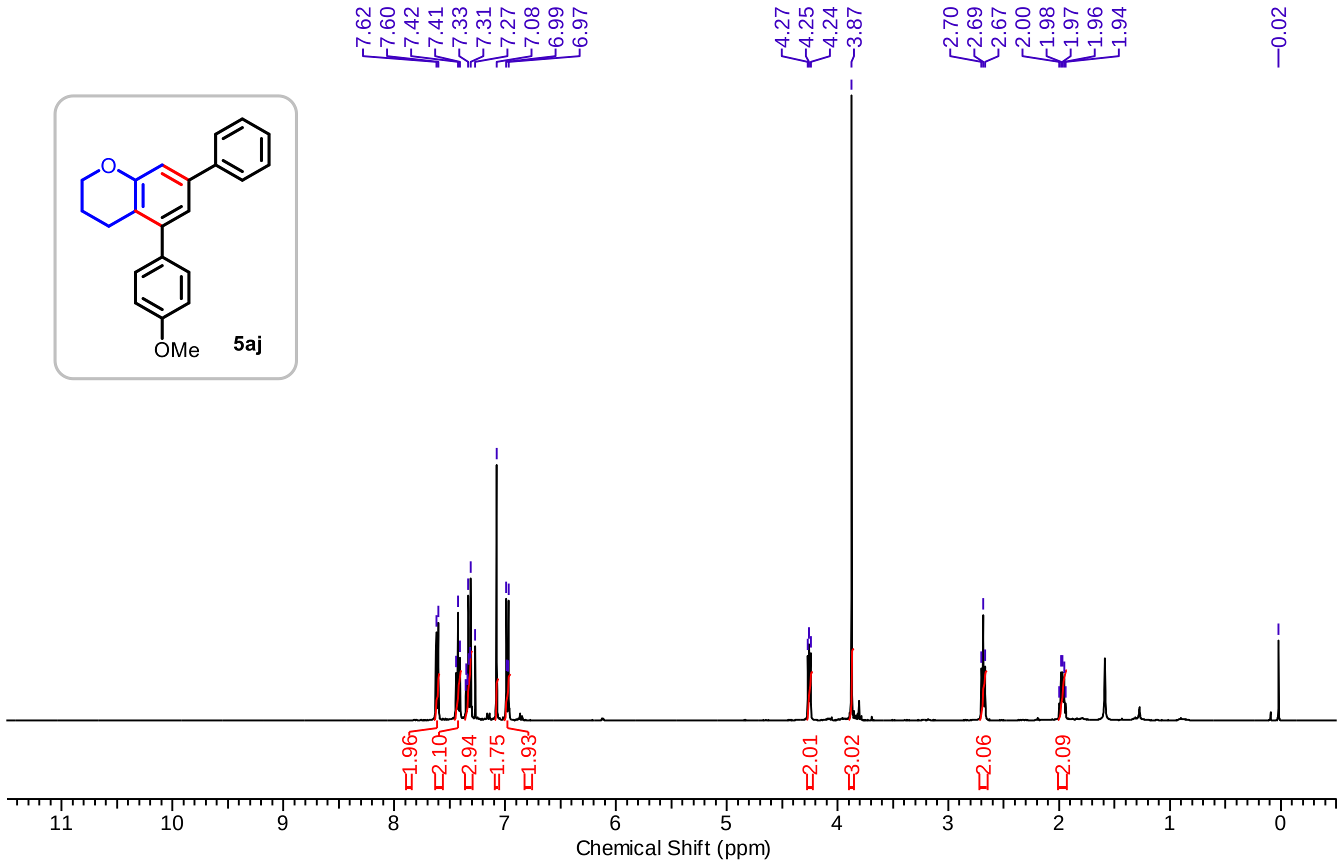
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5ai**:



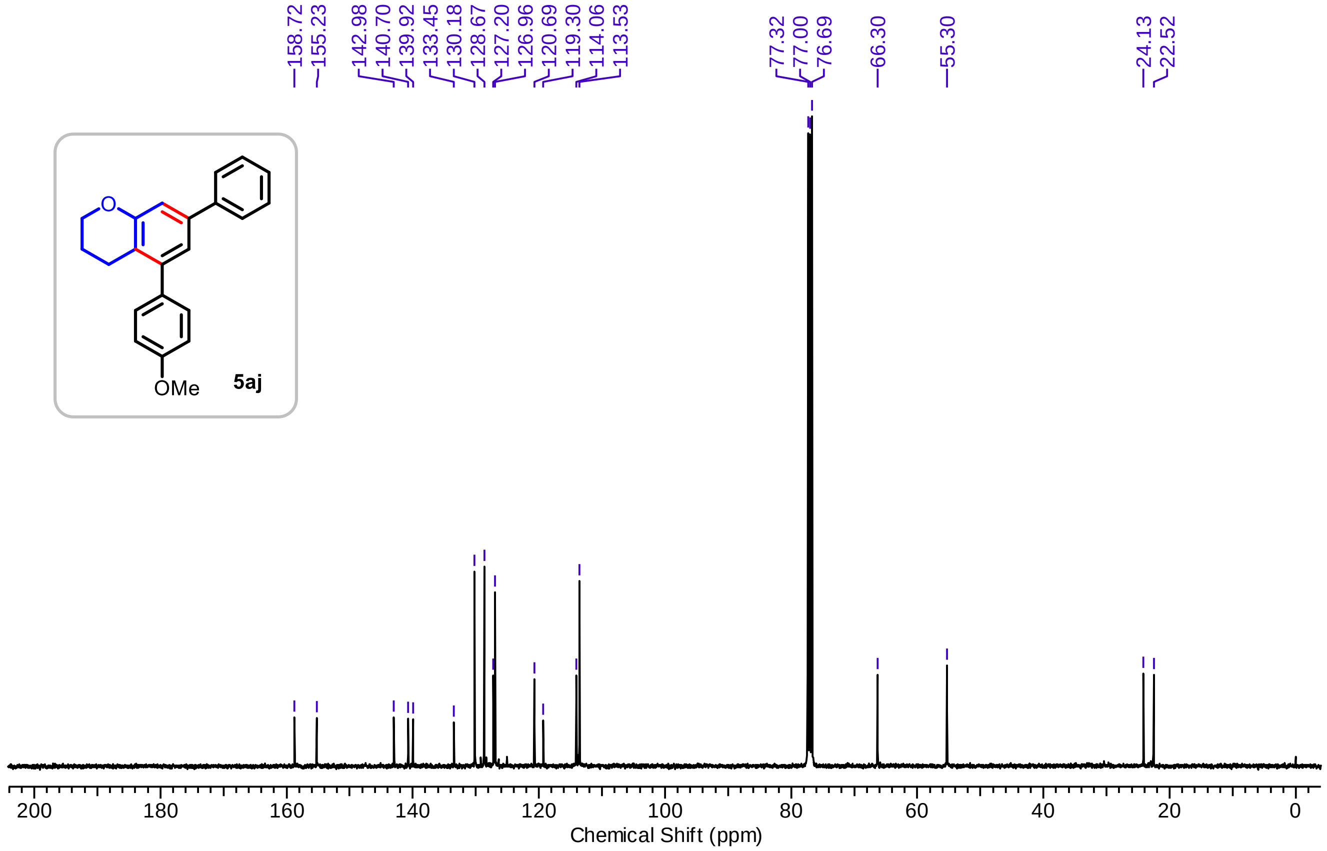
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$)of **5ai**:



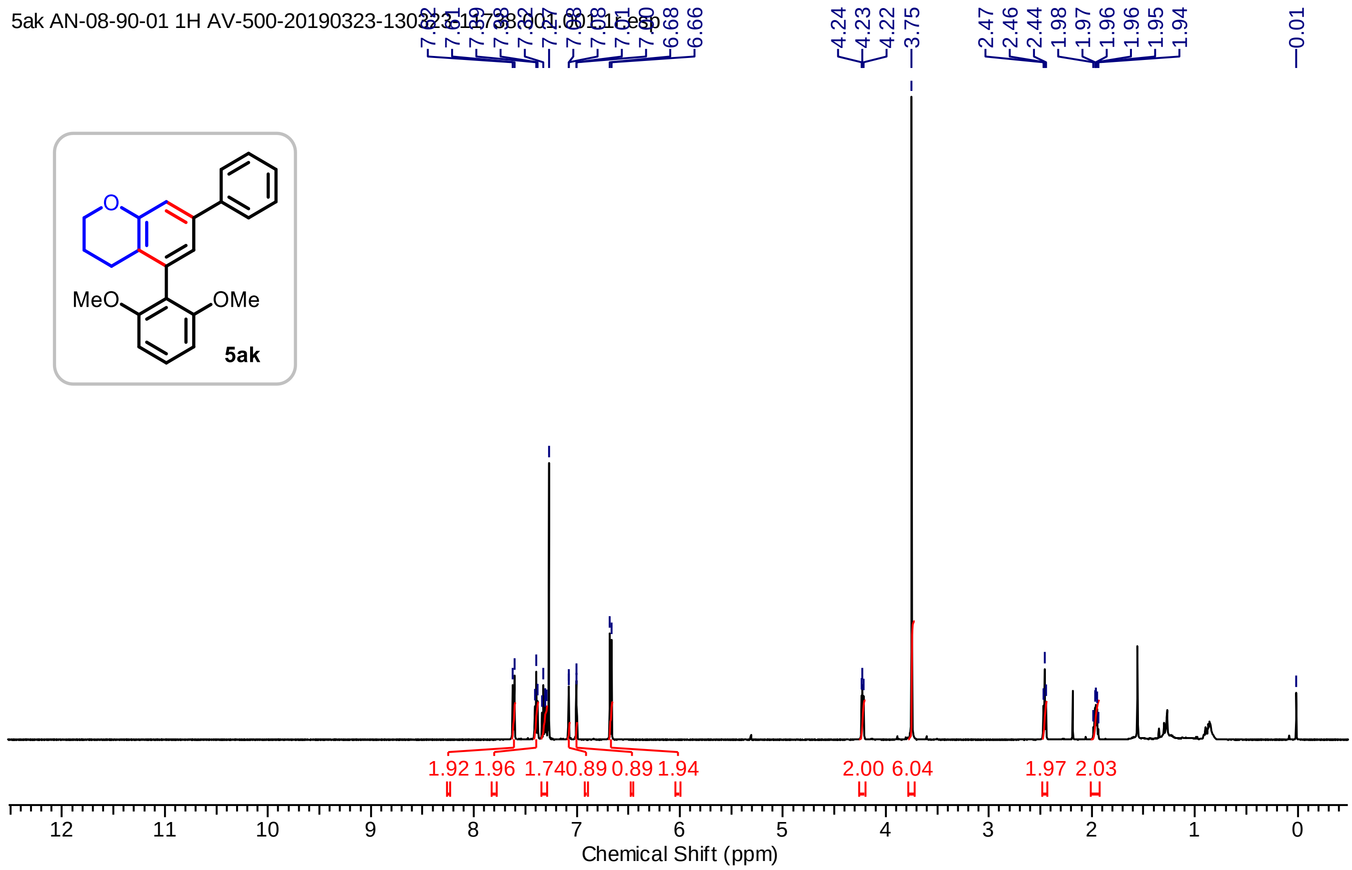
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5aj**:



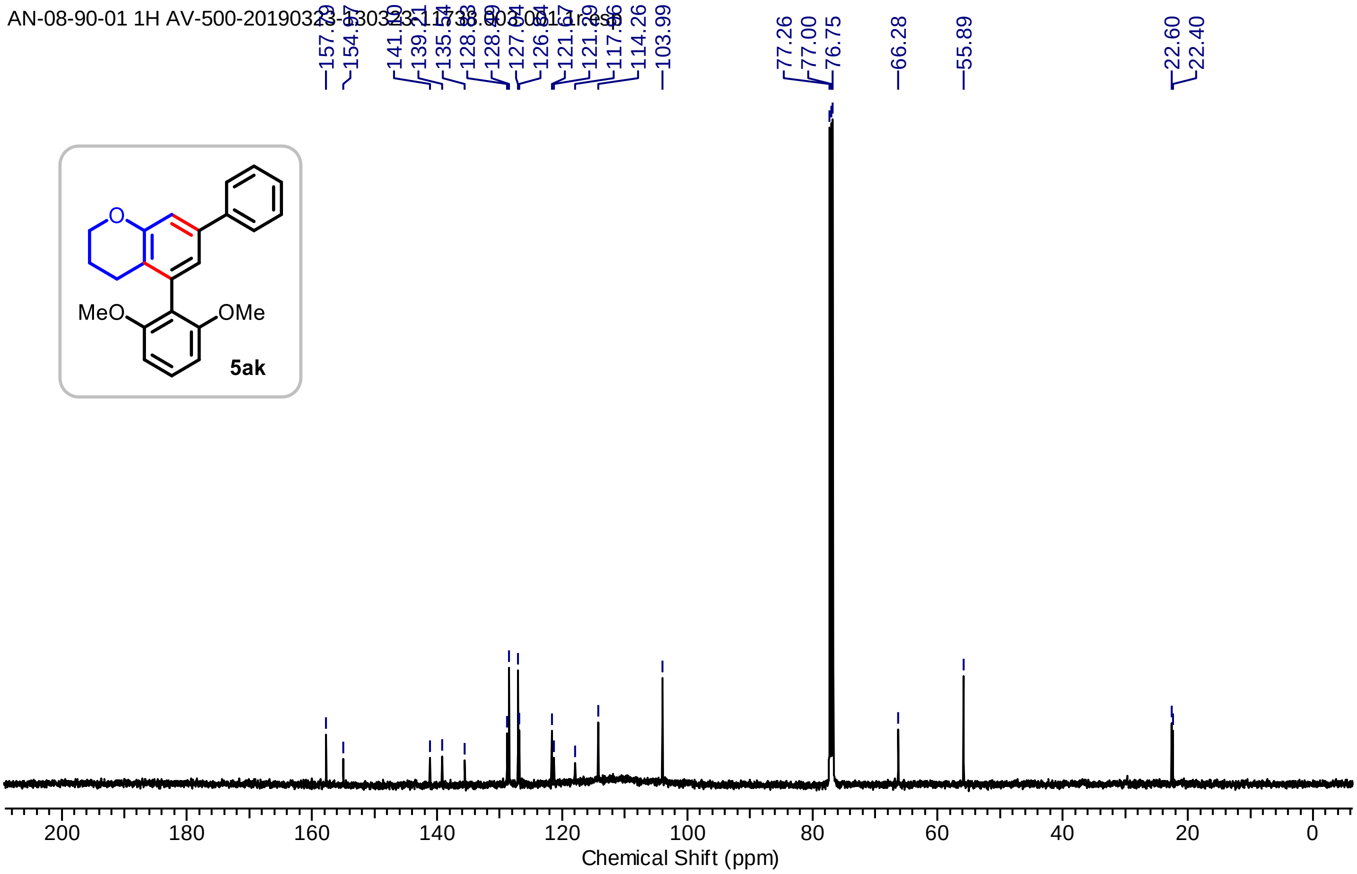
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5aj**:



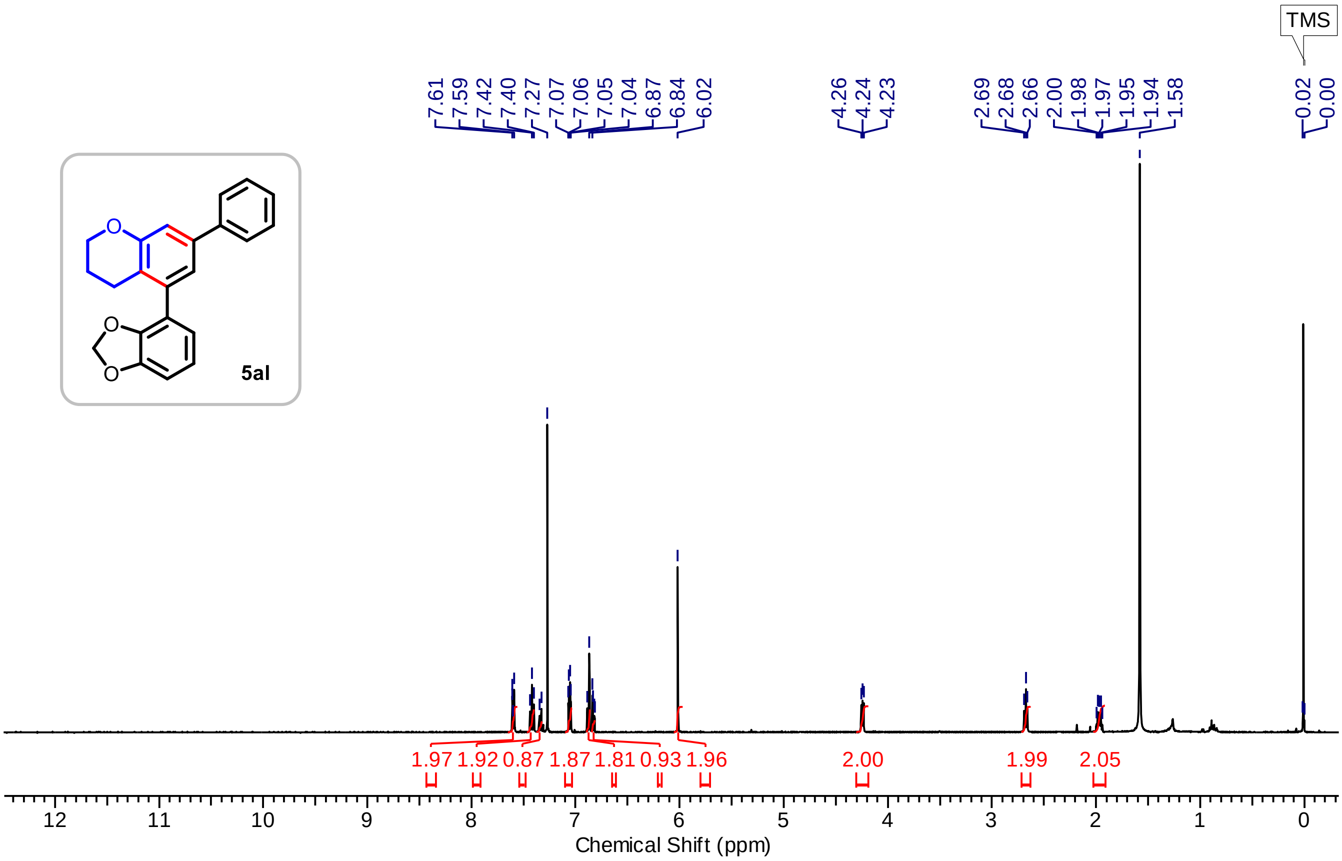
^{1}H NMR-Spectrum (500 MHz, $CDCl_3$) of **5ak**:



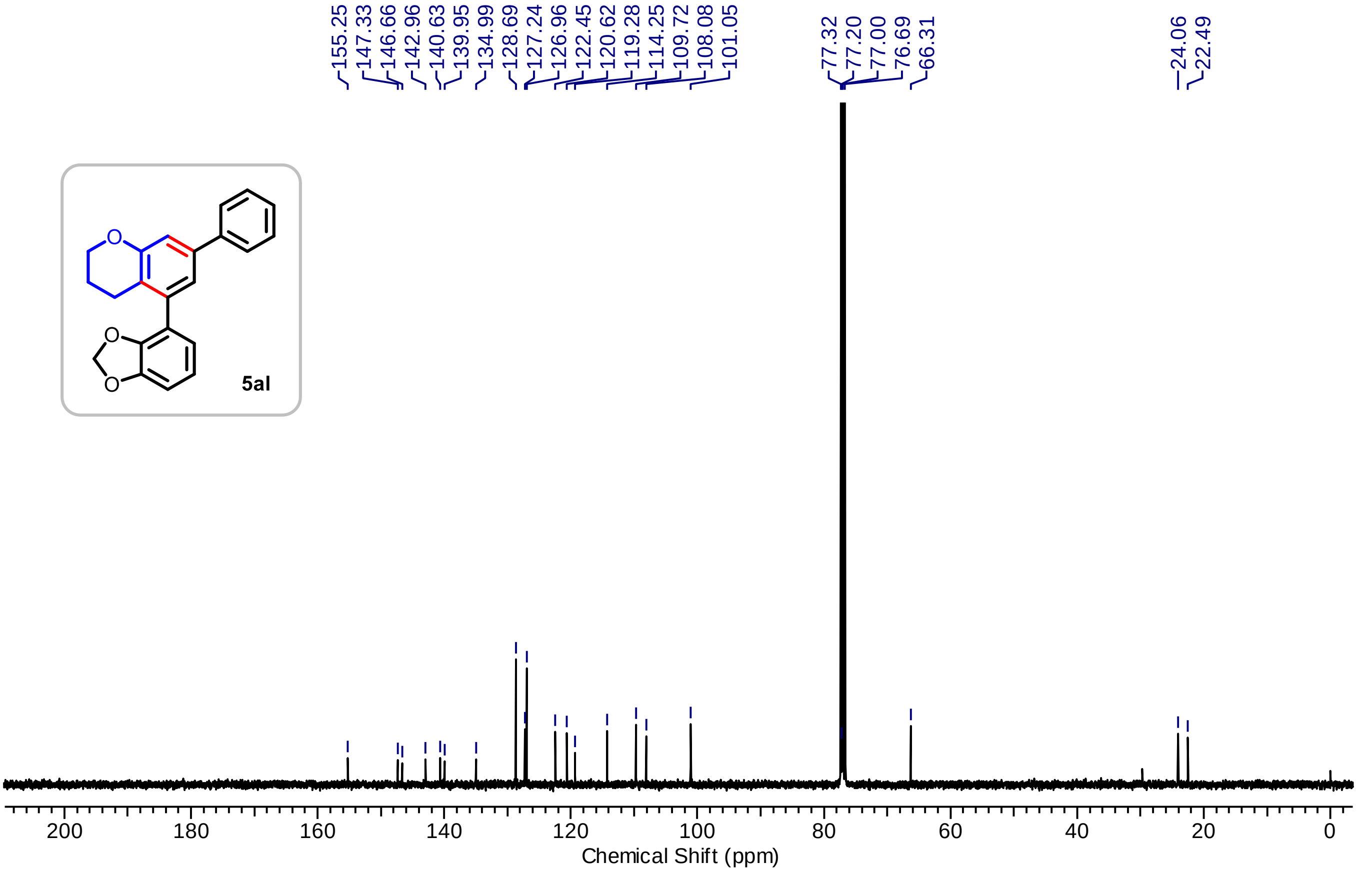
^{13}C NMR-Spectrum (126 MHz, $CDCl_3$)of **5ak**:



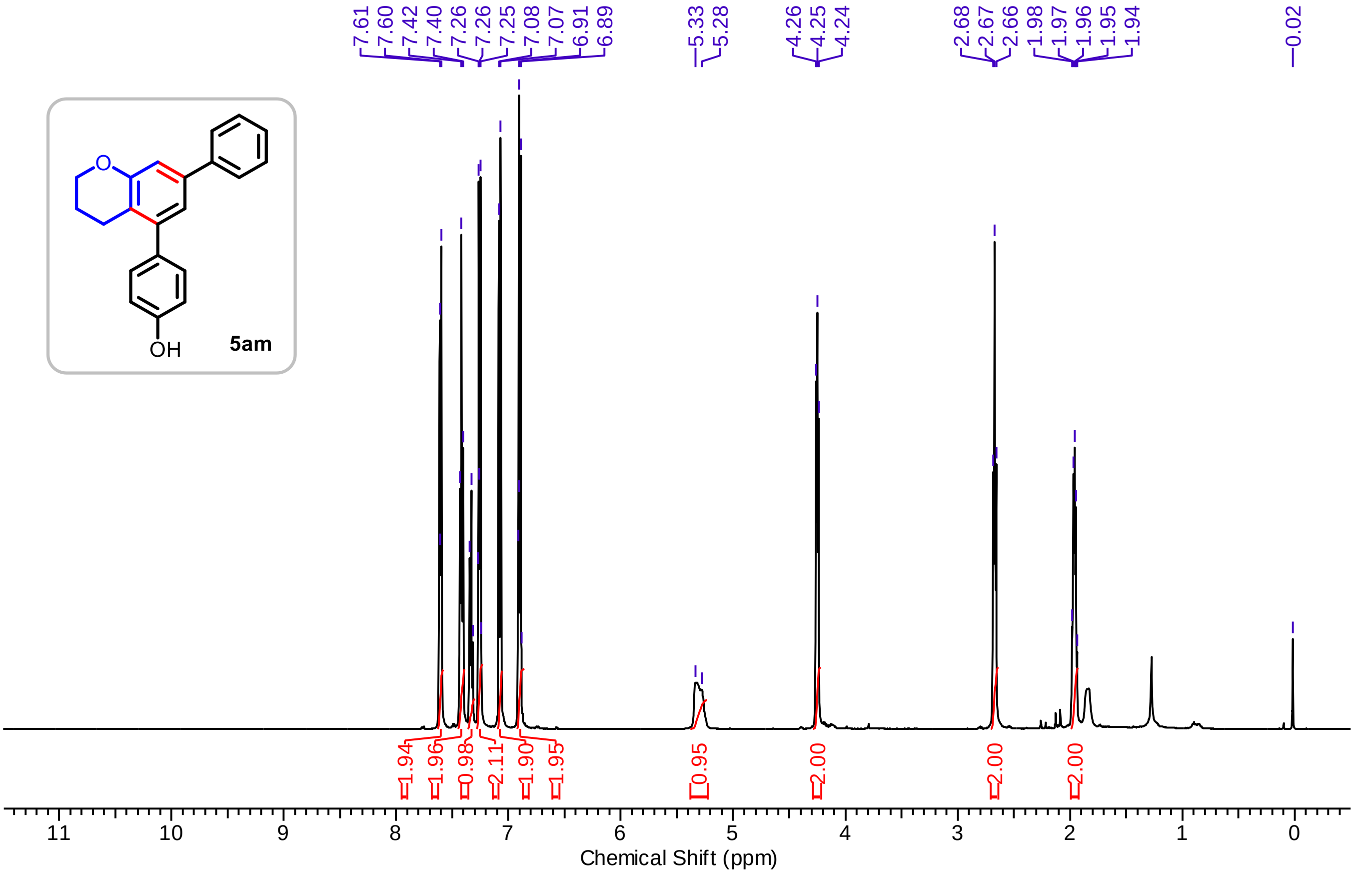
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5al**:



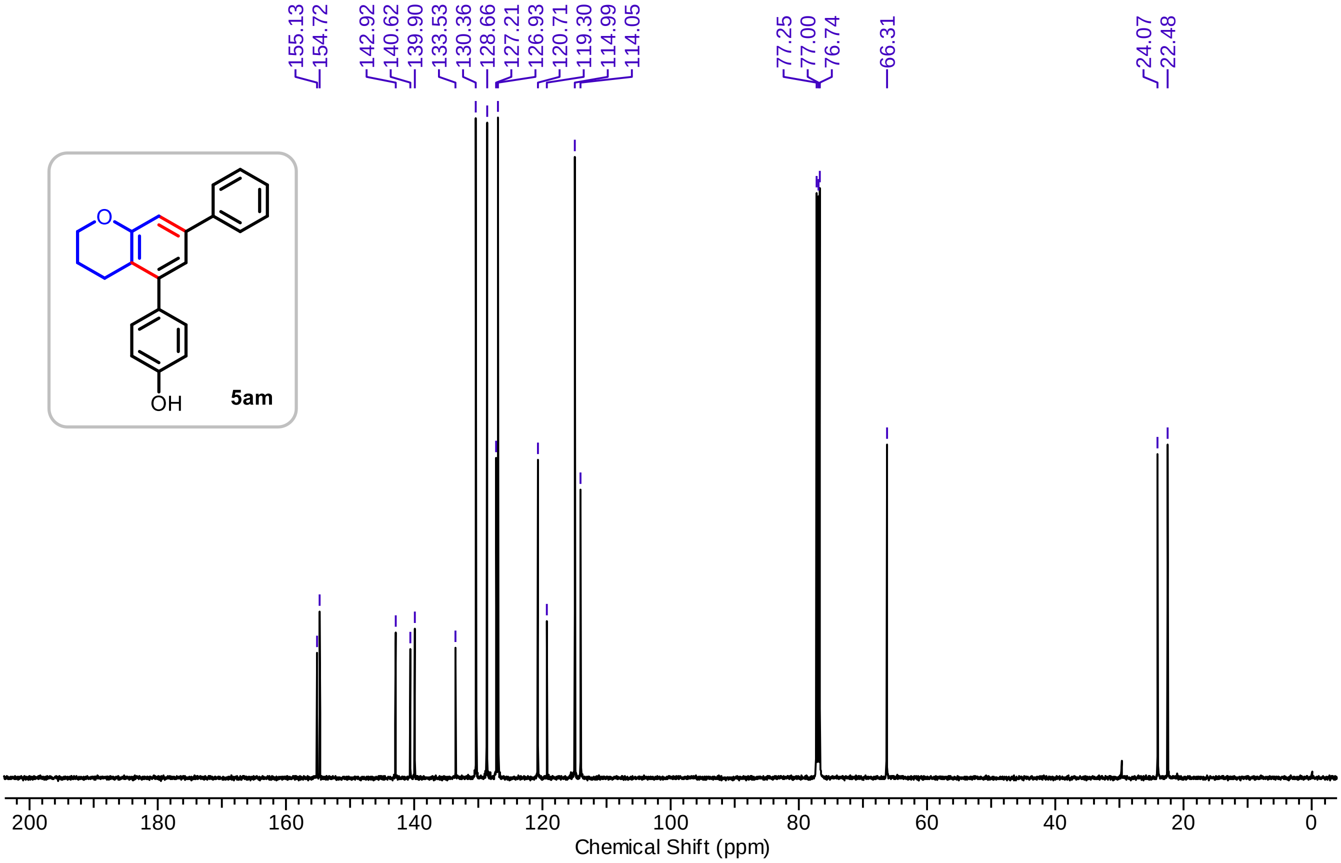
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5al**:



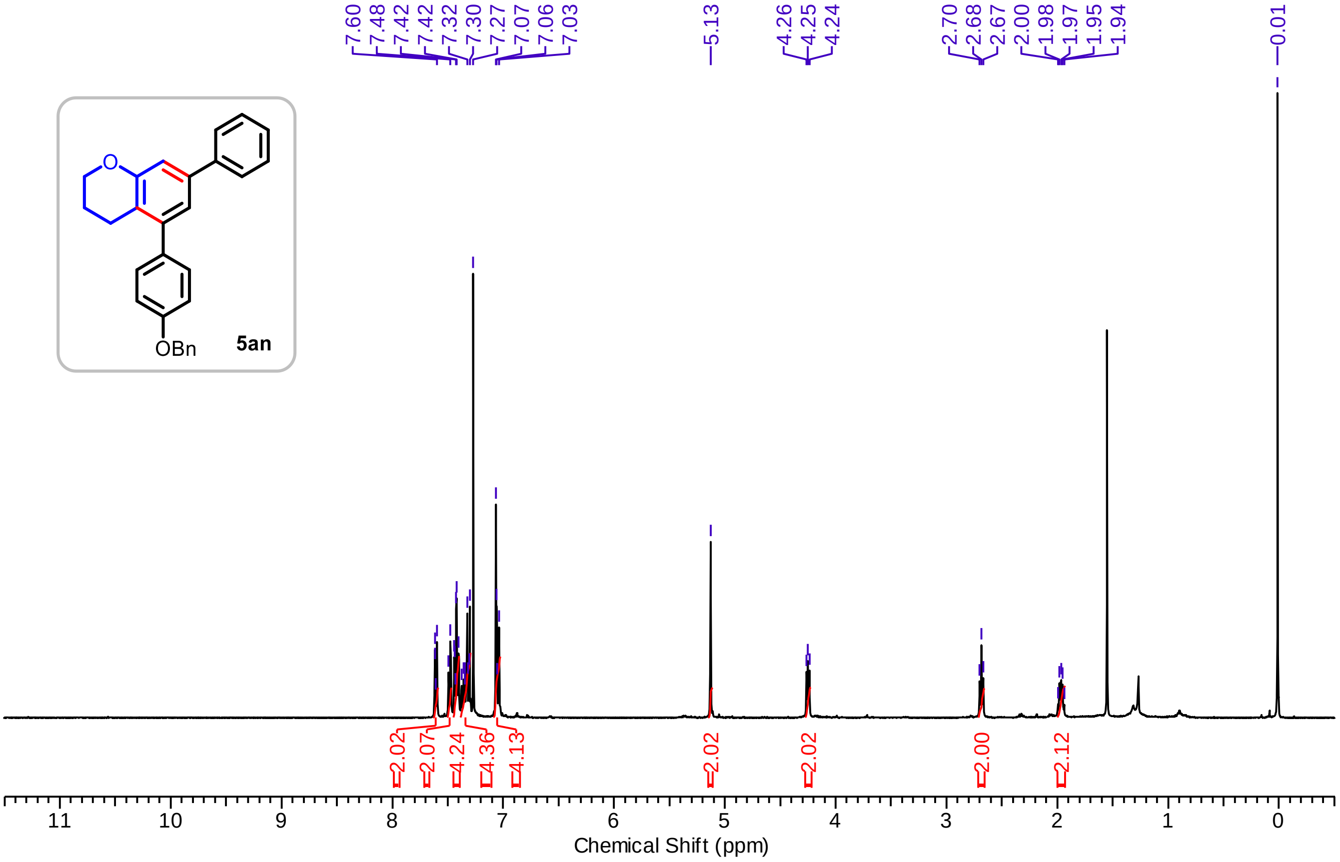
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5am**:



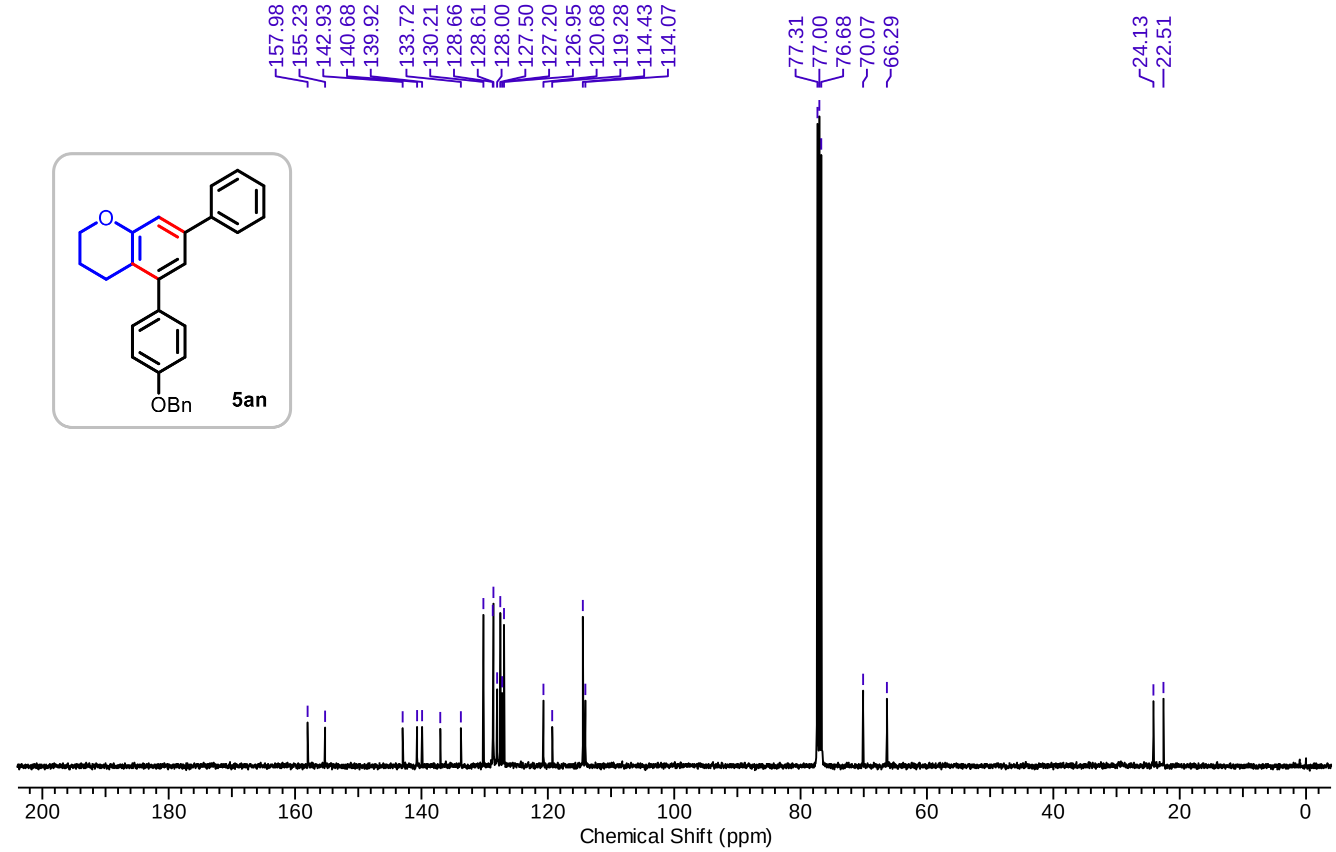
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5am**:



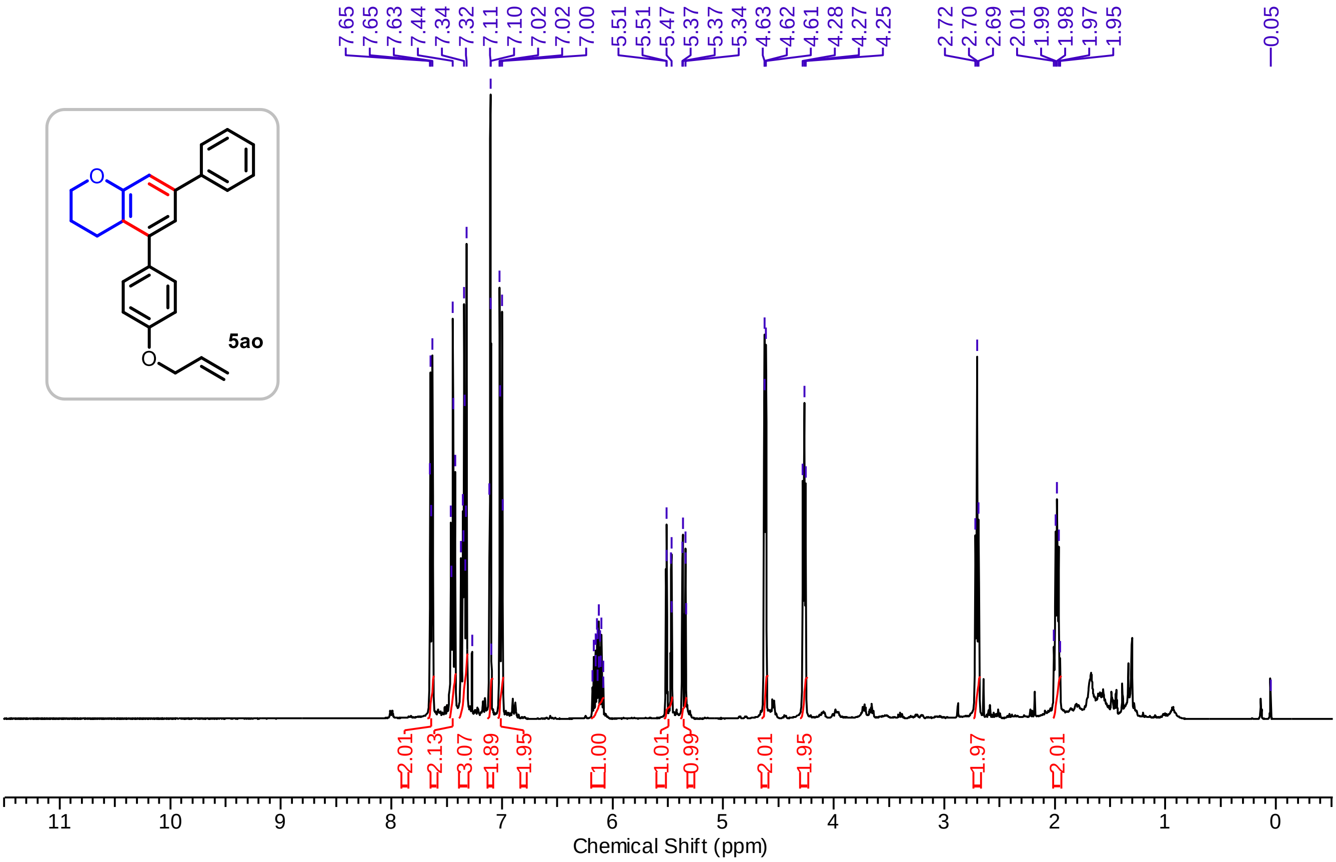
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5an**:



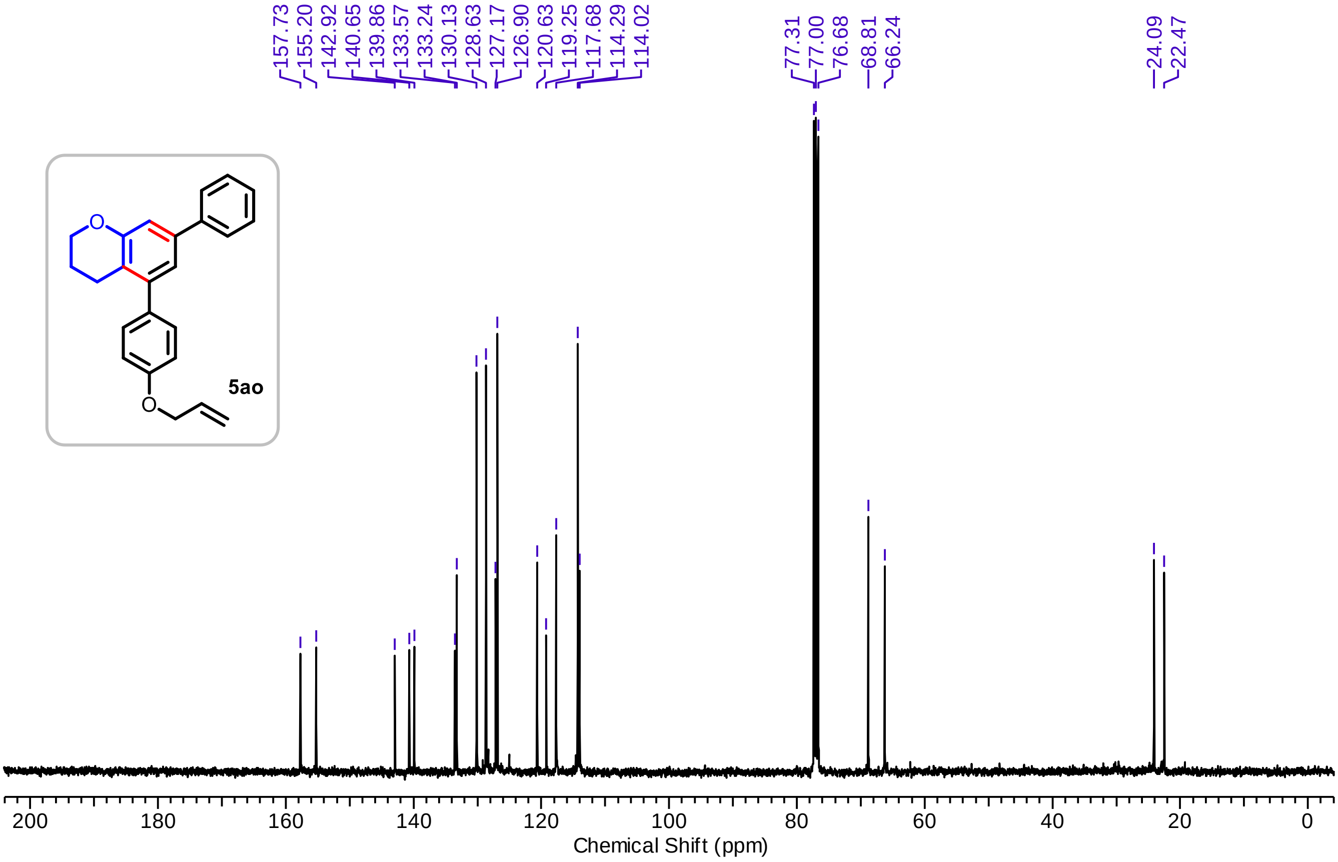
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5an**:



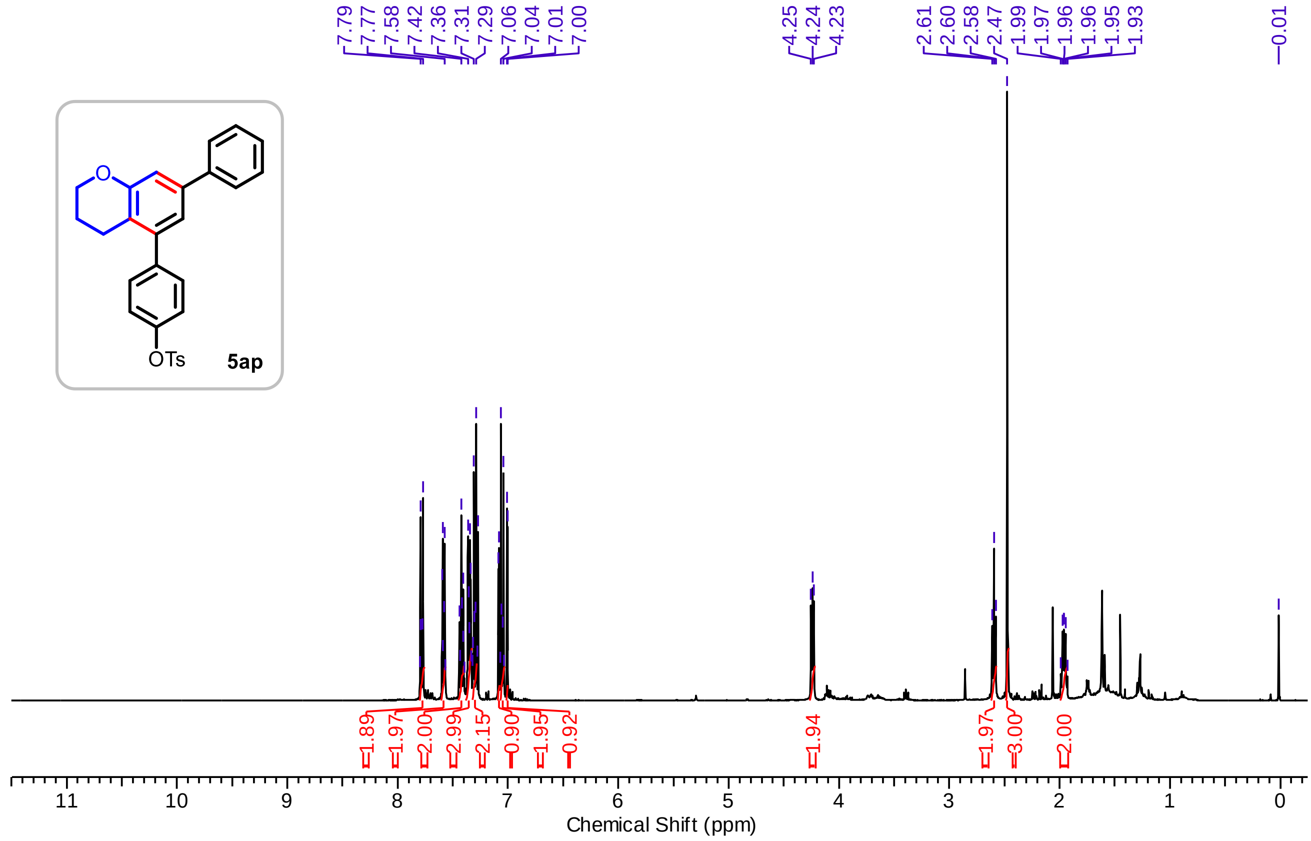
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5ao**:



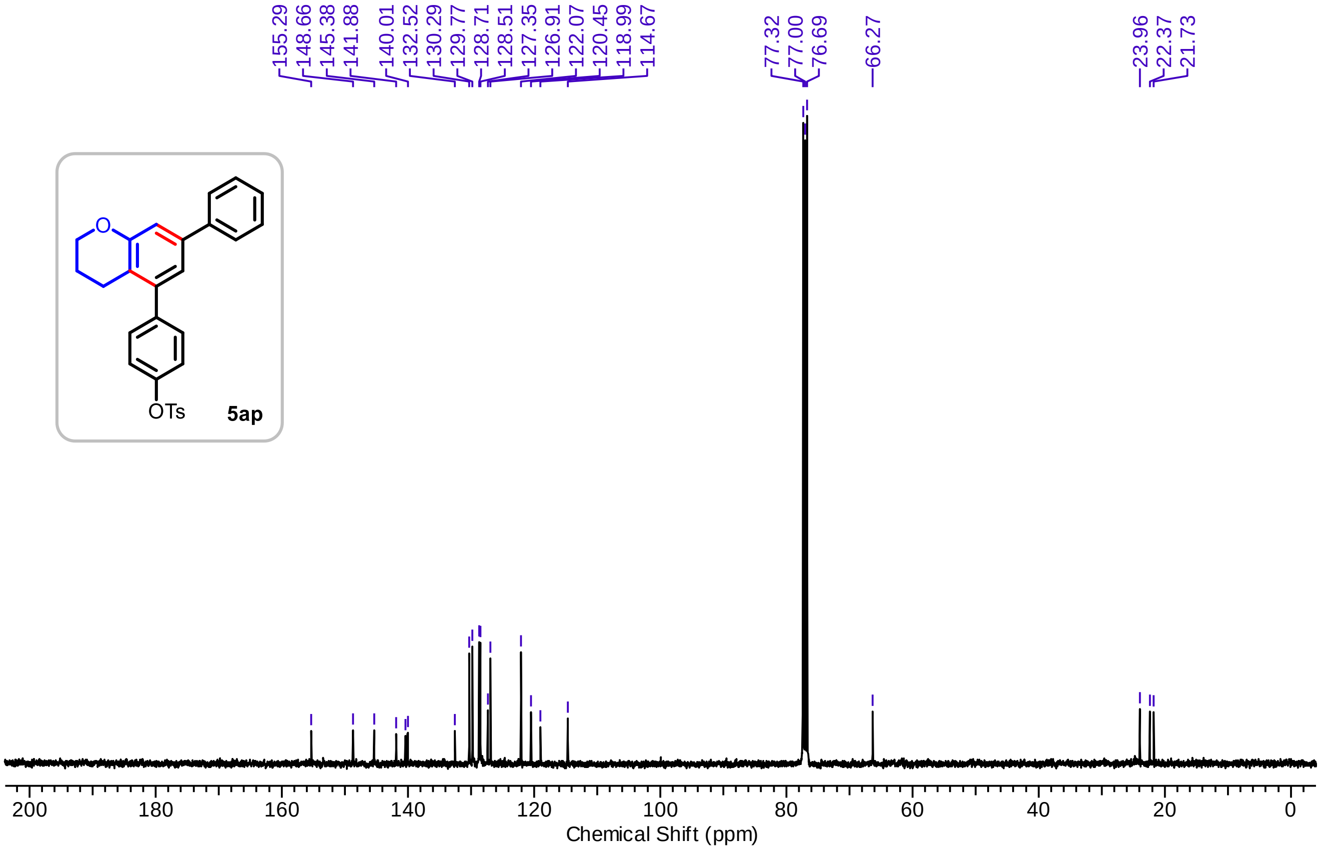
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$)of **5ao**:



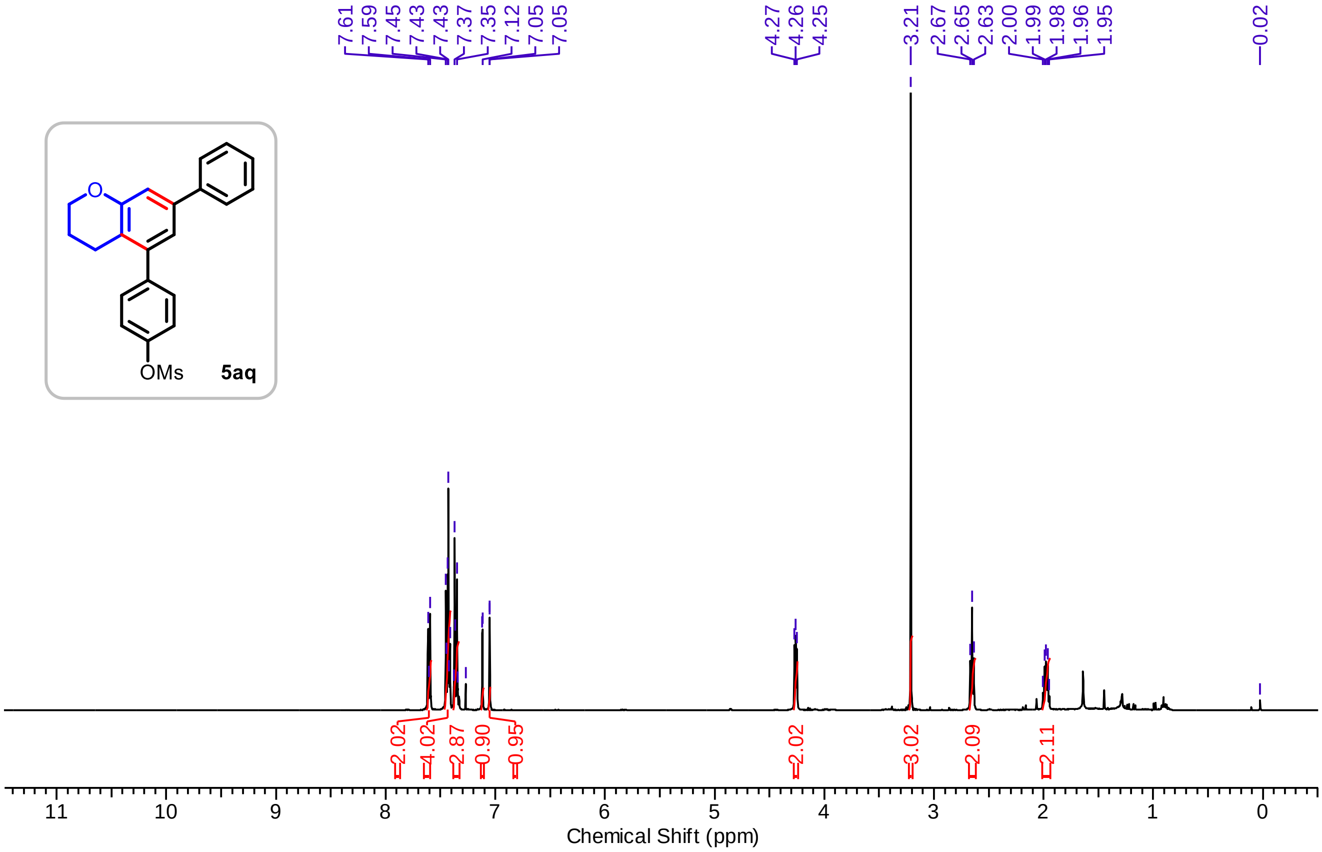
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ap**:



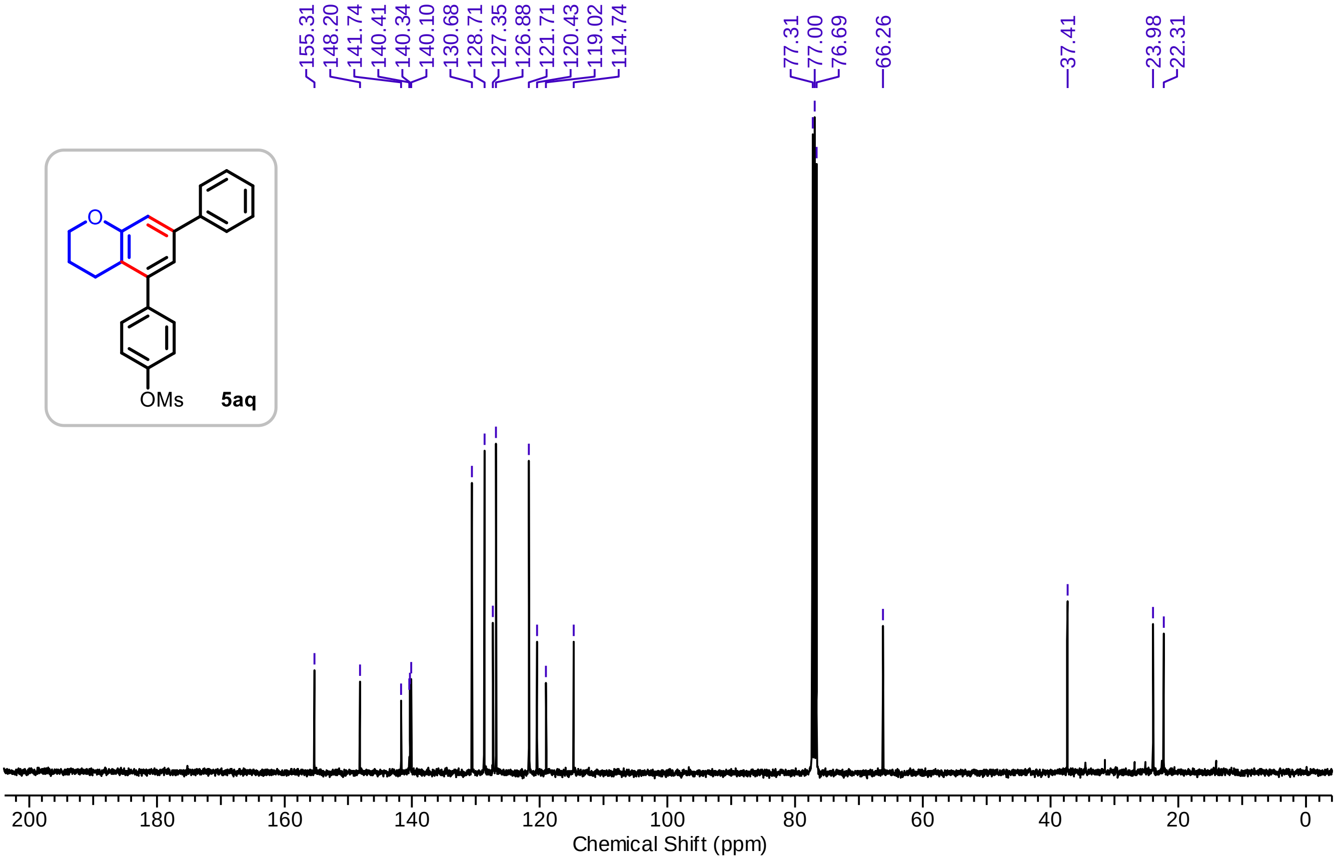
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5ap**:



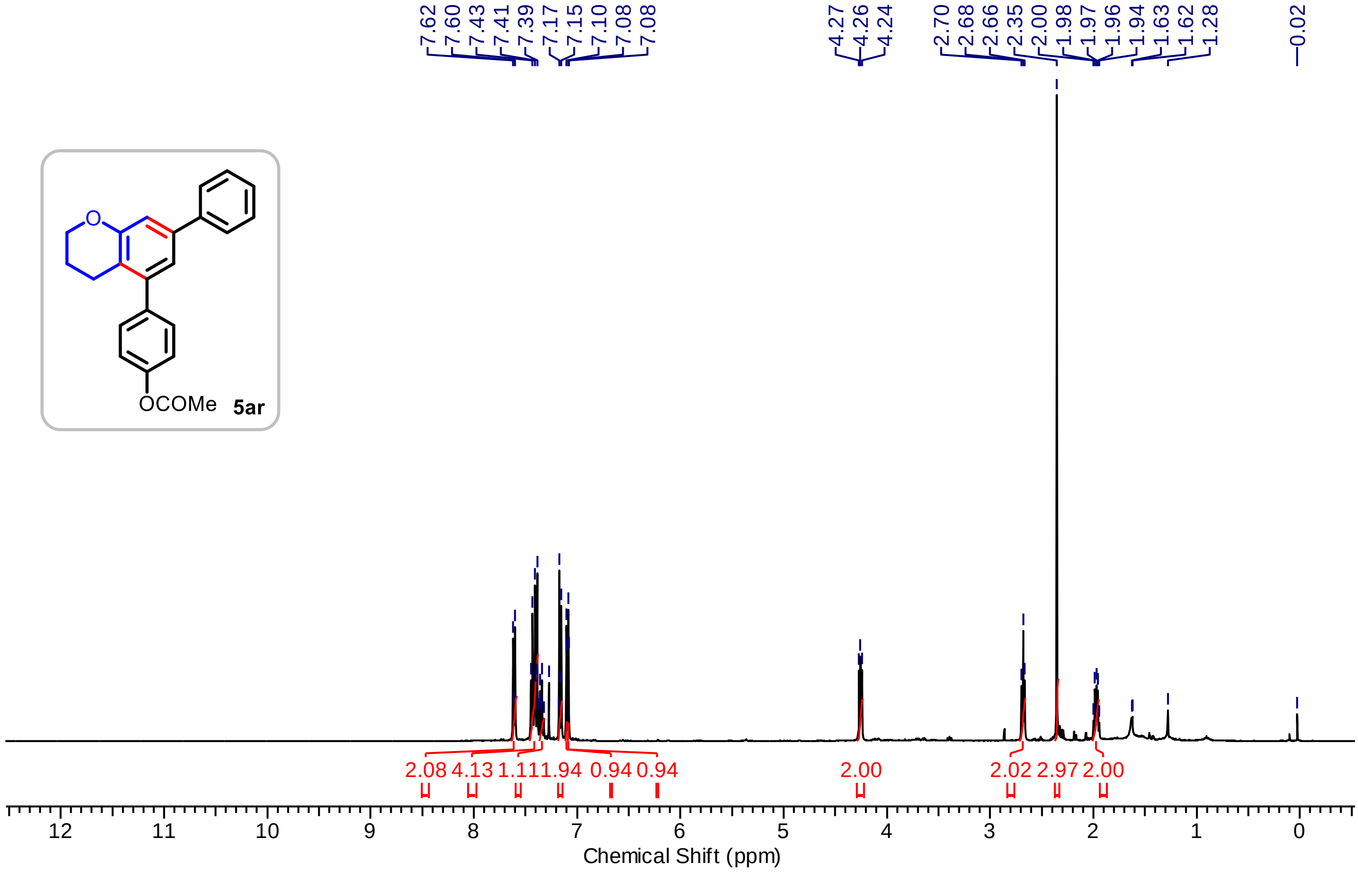
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5aq**:



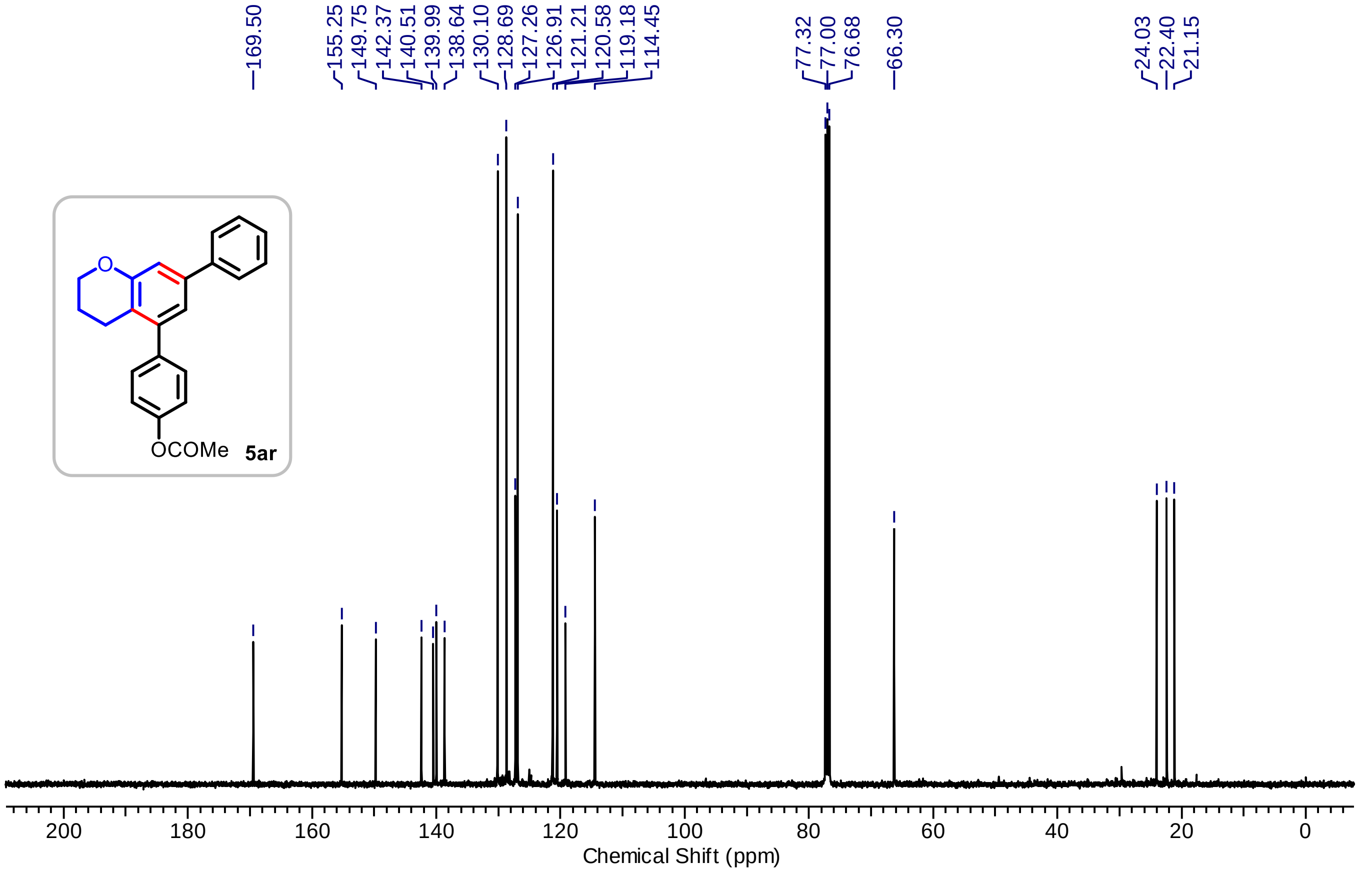
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5aq**:



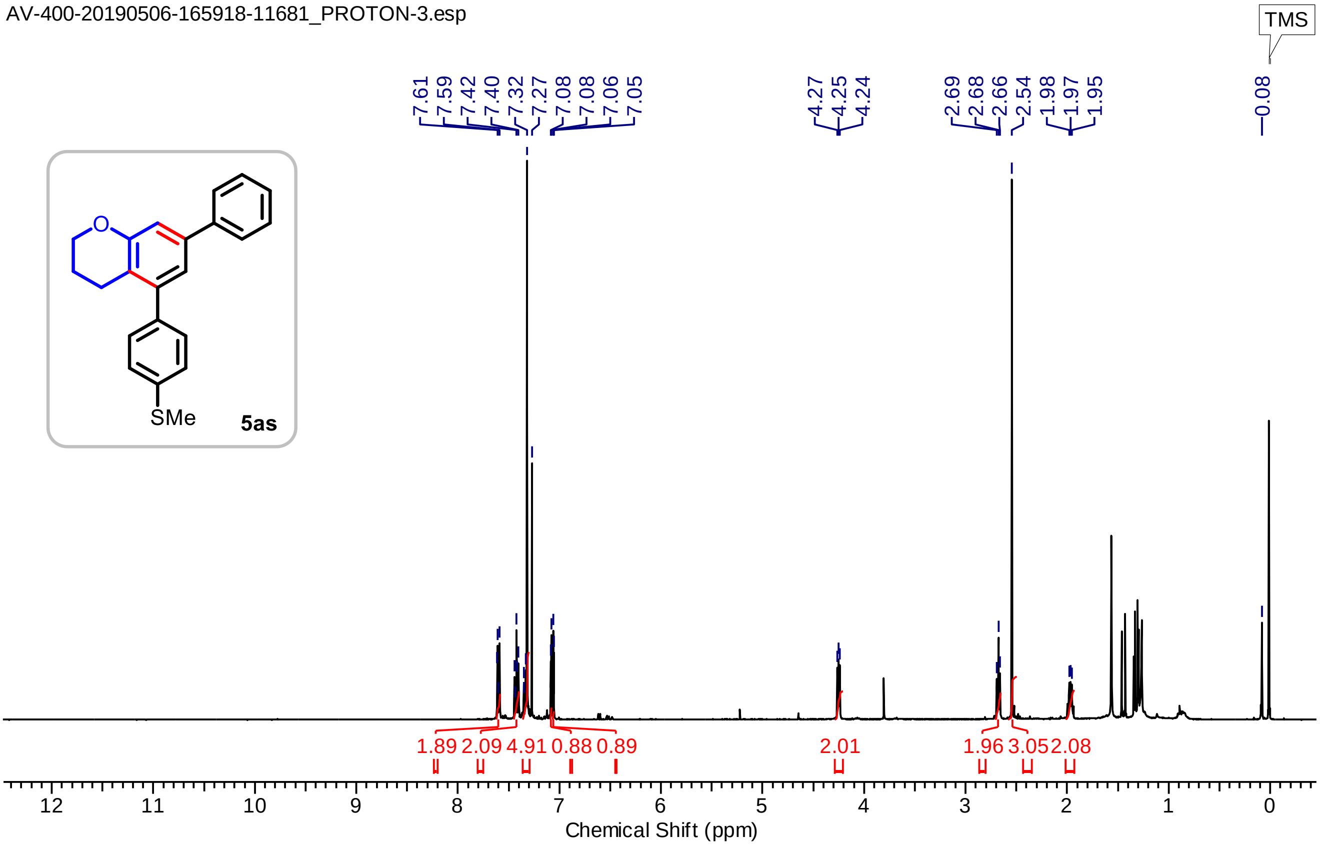
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5ar**:



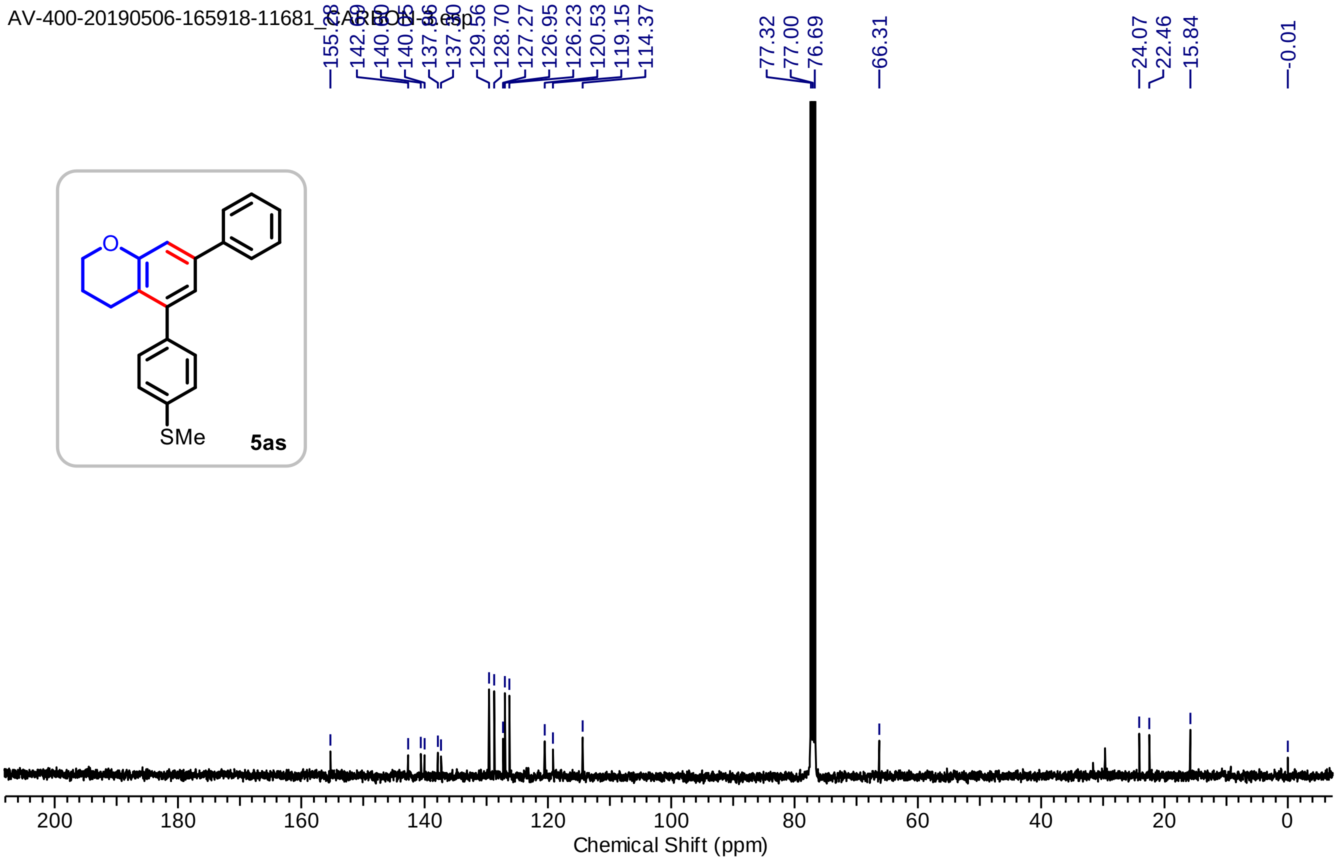
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$) of **5ar**:



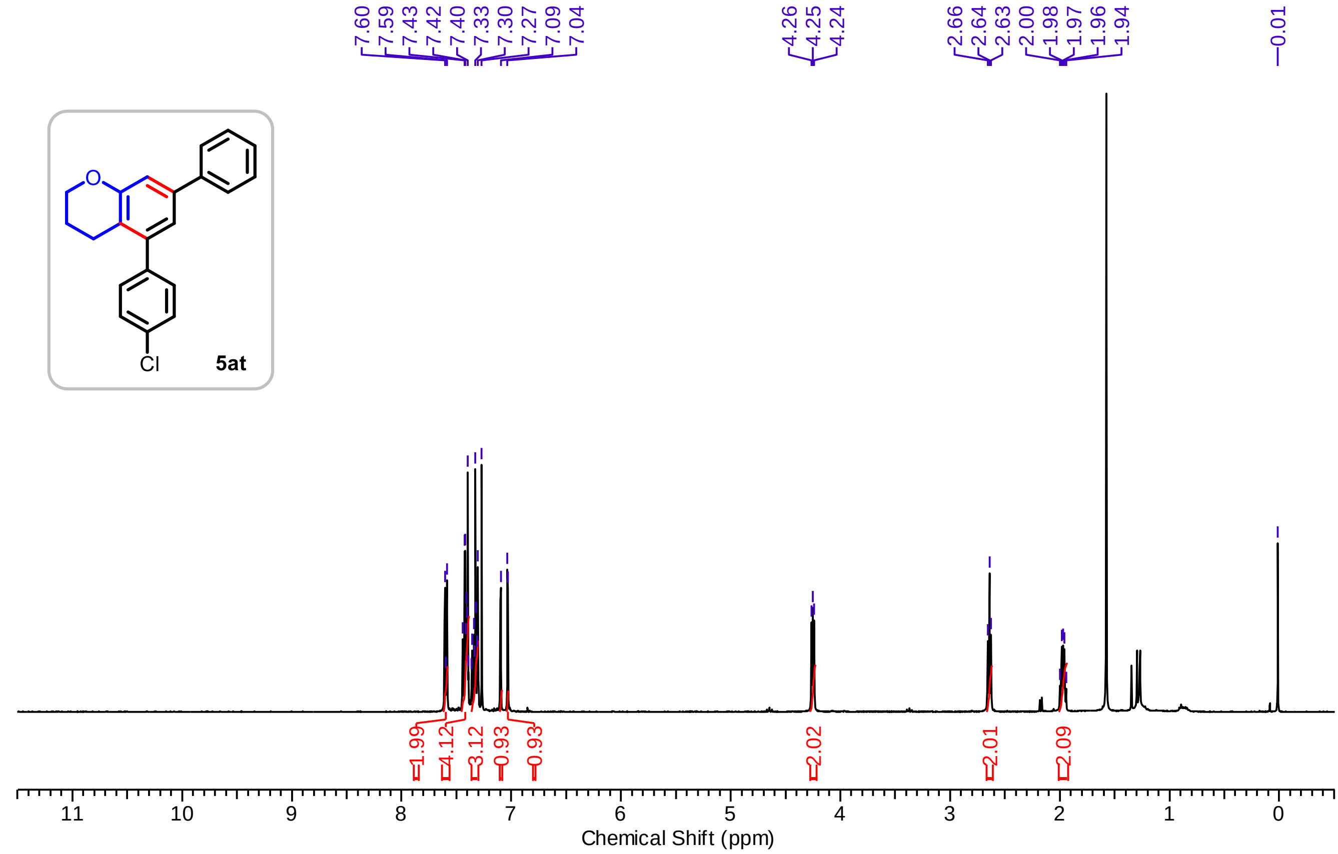
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5as**:



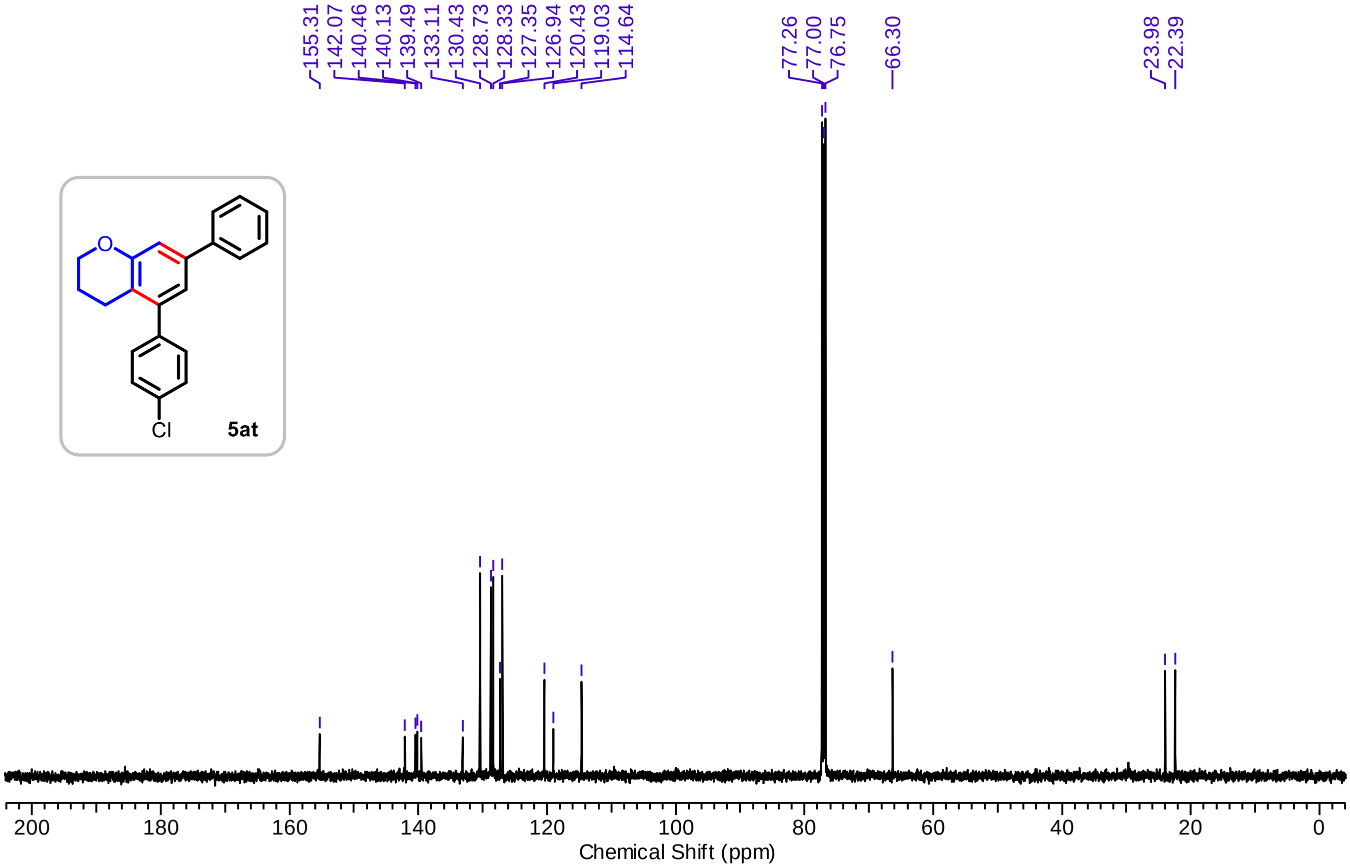
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5as**:



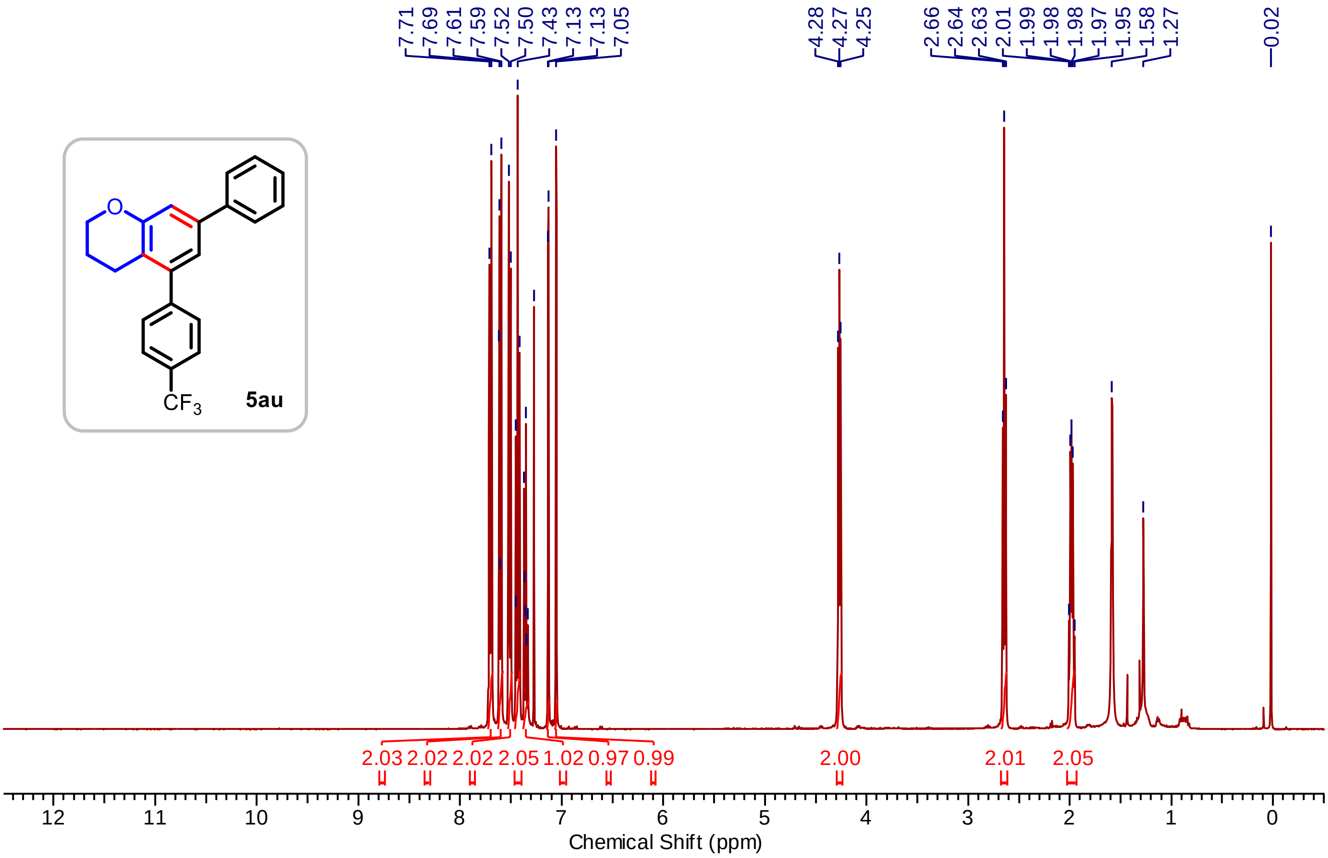
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5at**:



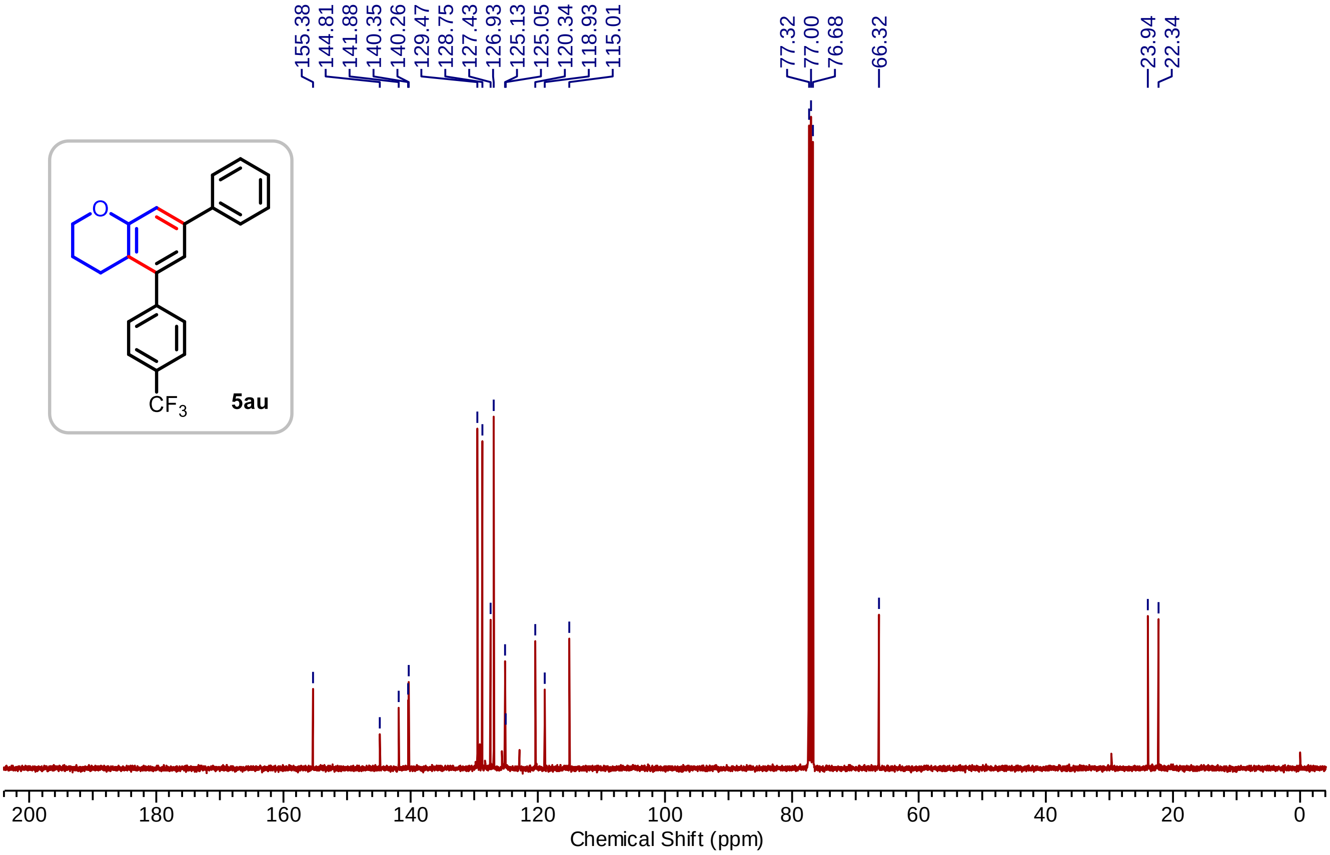
^{13}C NMR-Spectrum (126 MHz, $CDCl_3$) of **5at**:



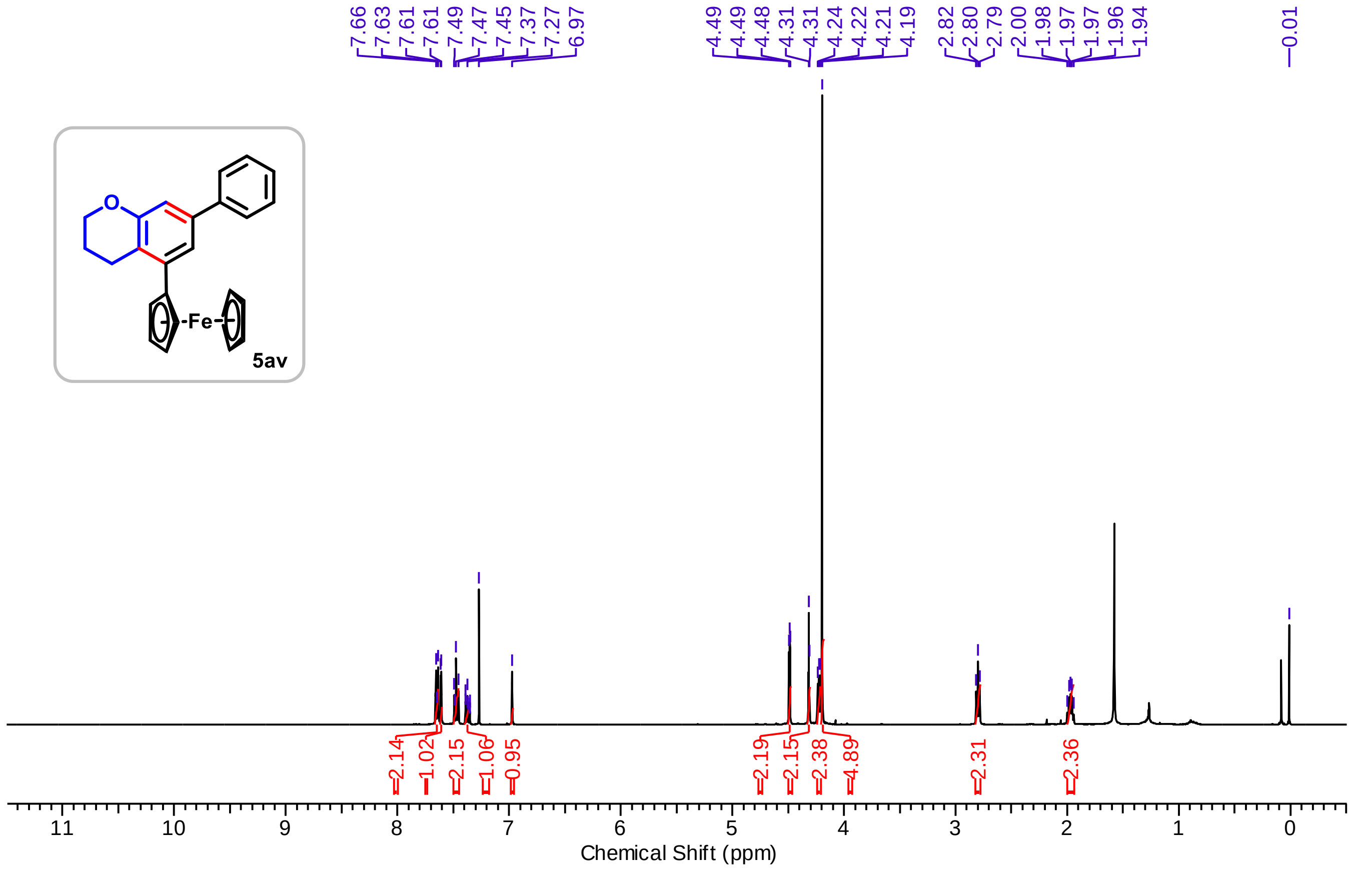
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5au**:



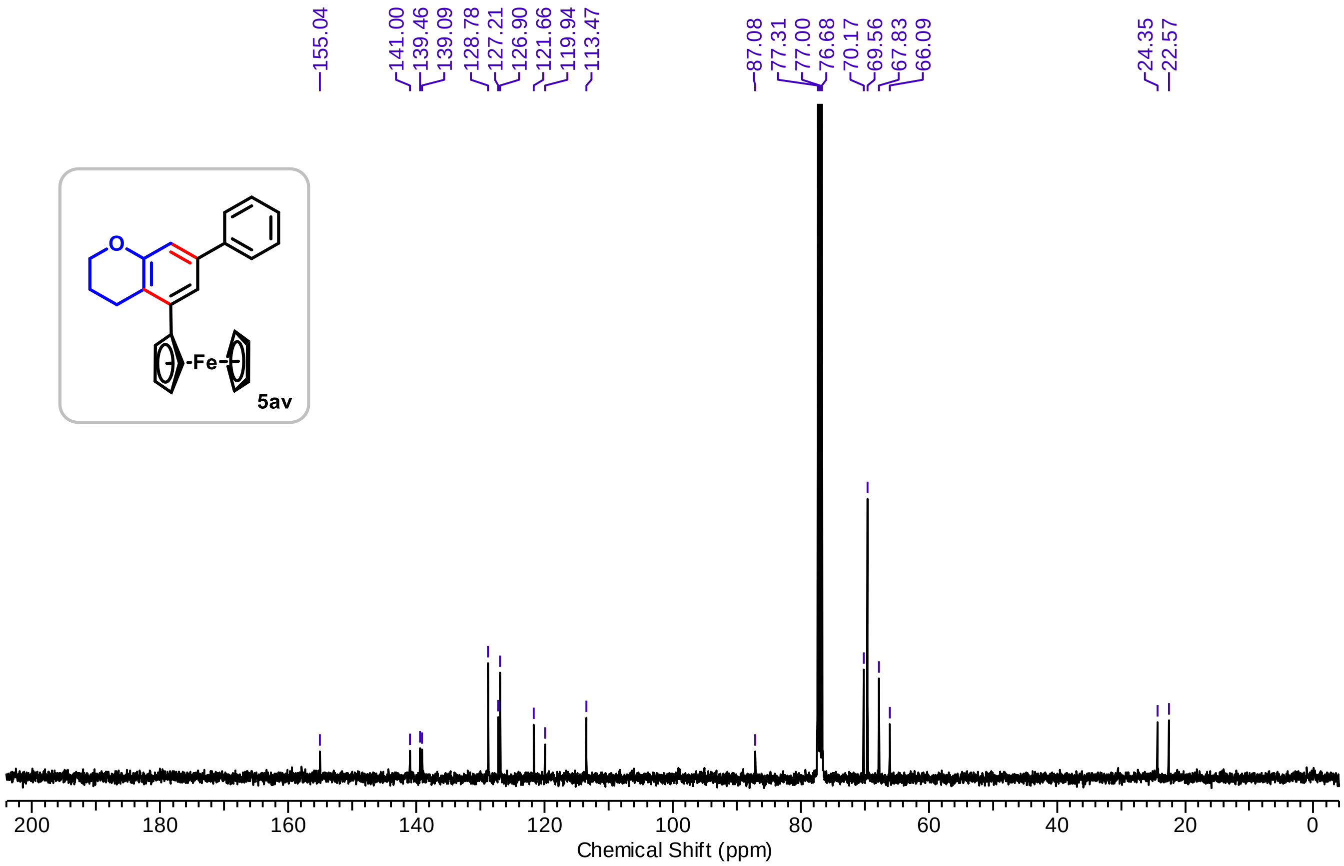
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5au**:



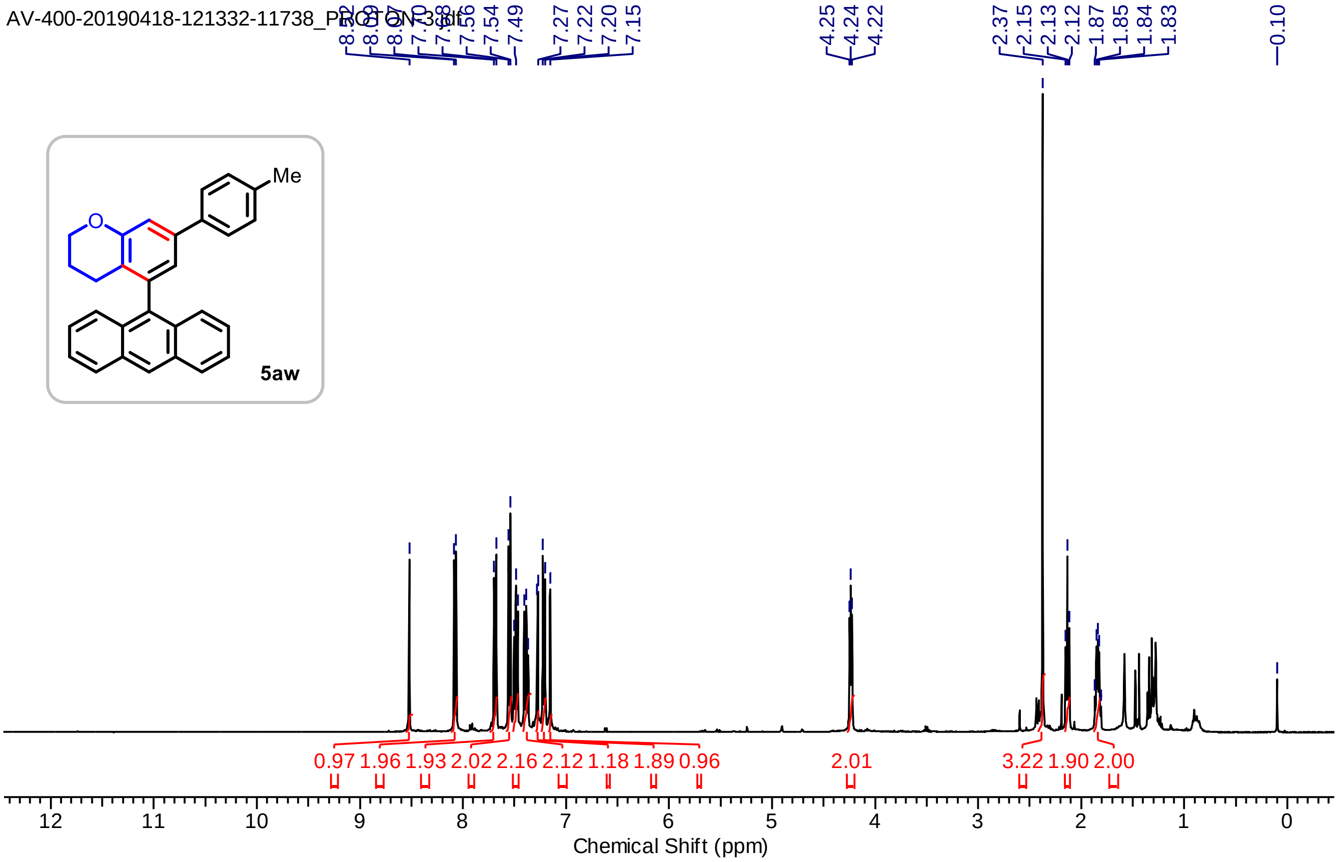
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5av**:



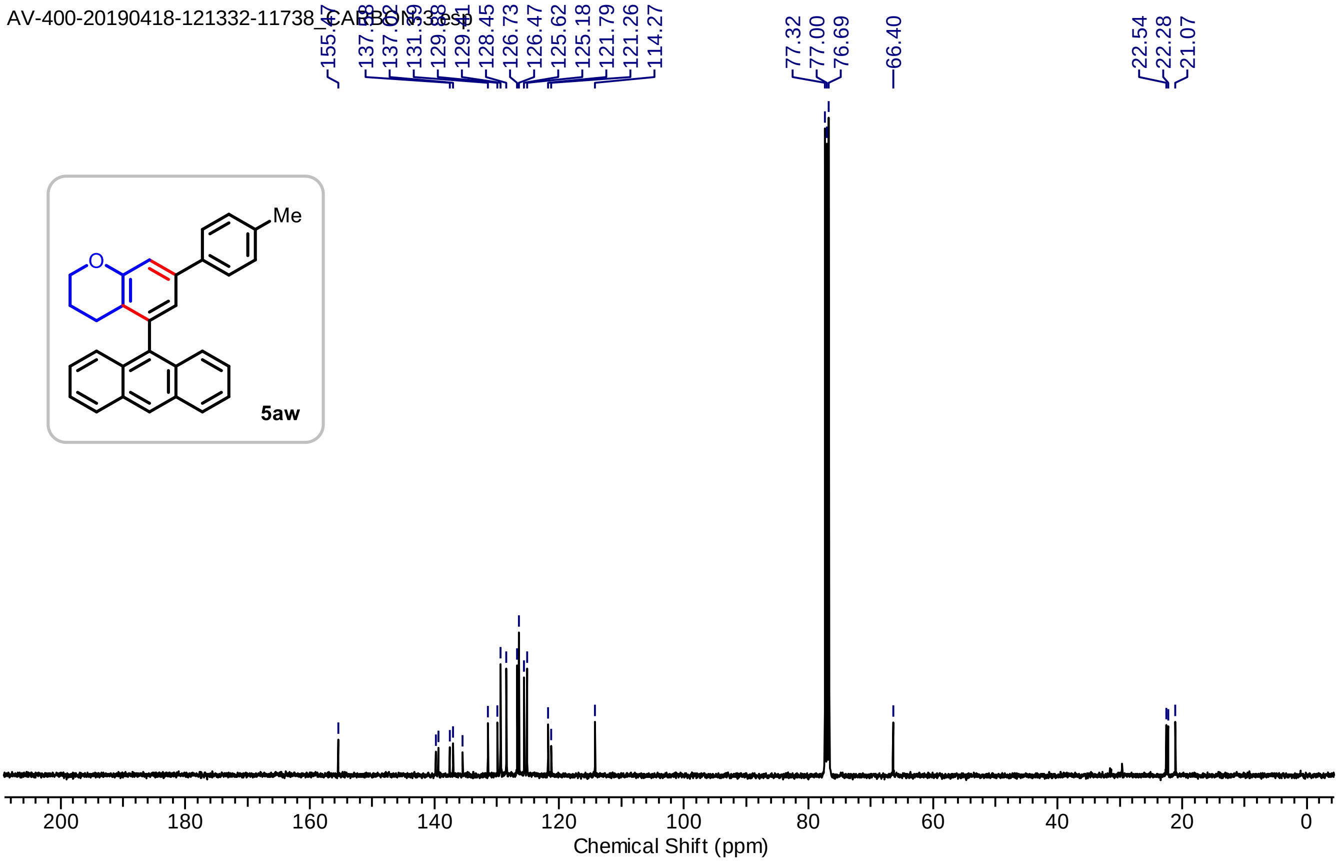
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5av**:



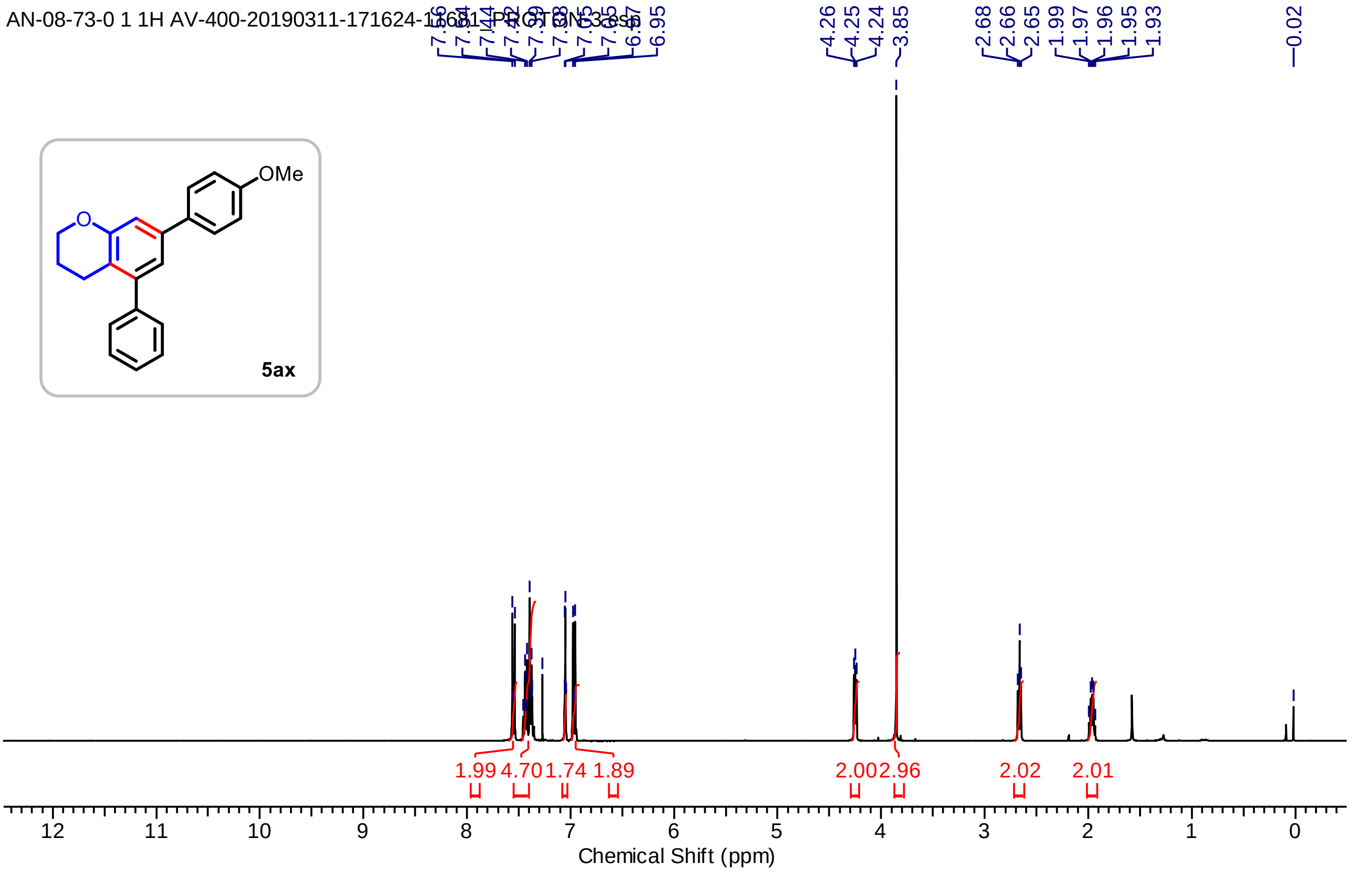
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5aw**:



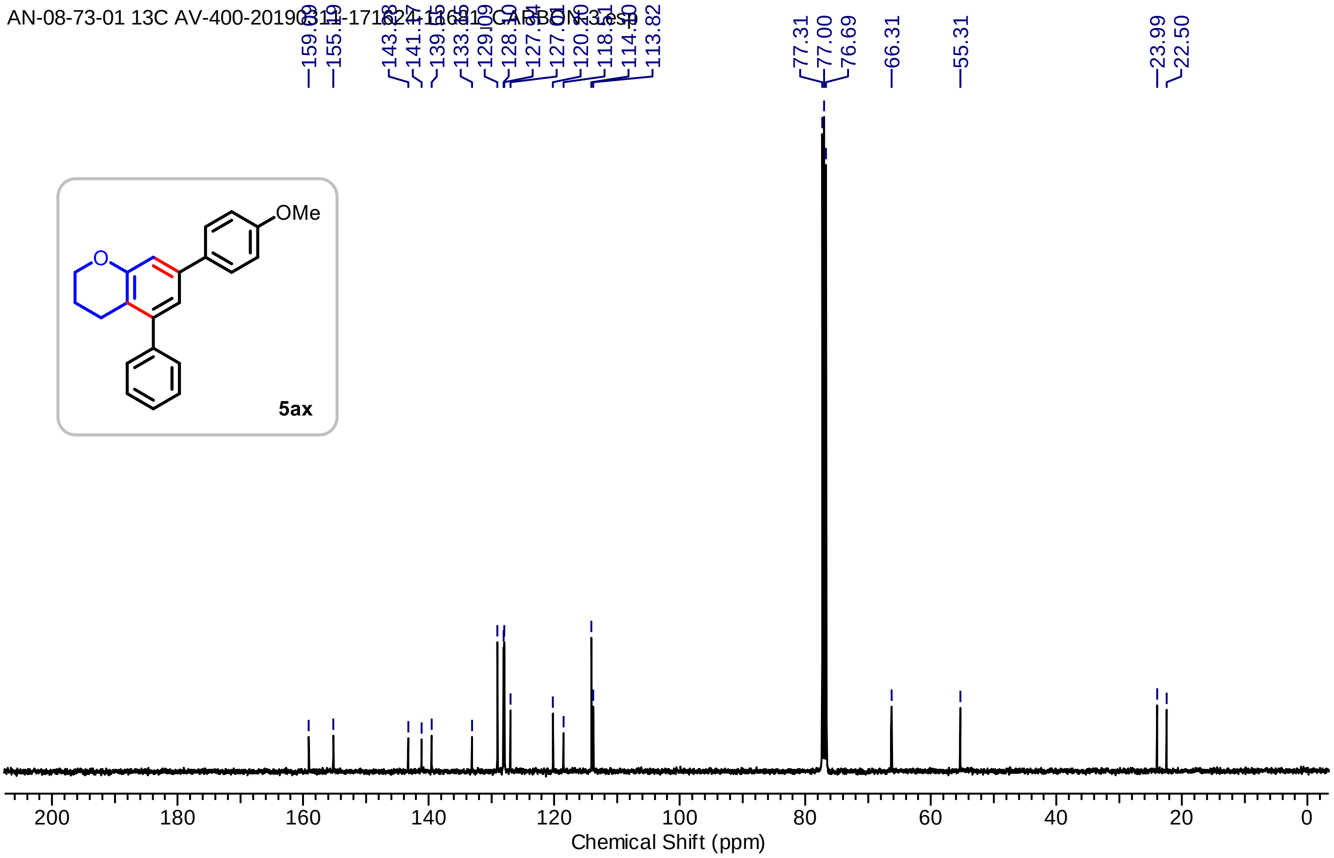
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5aw**:



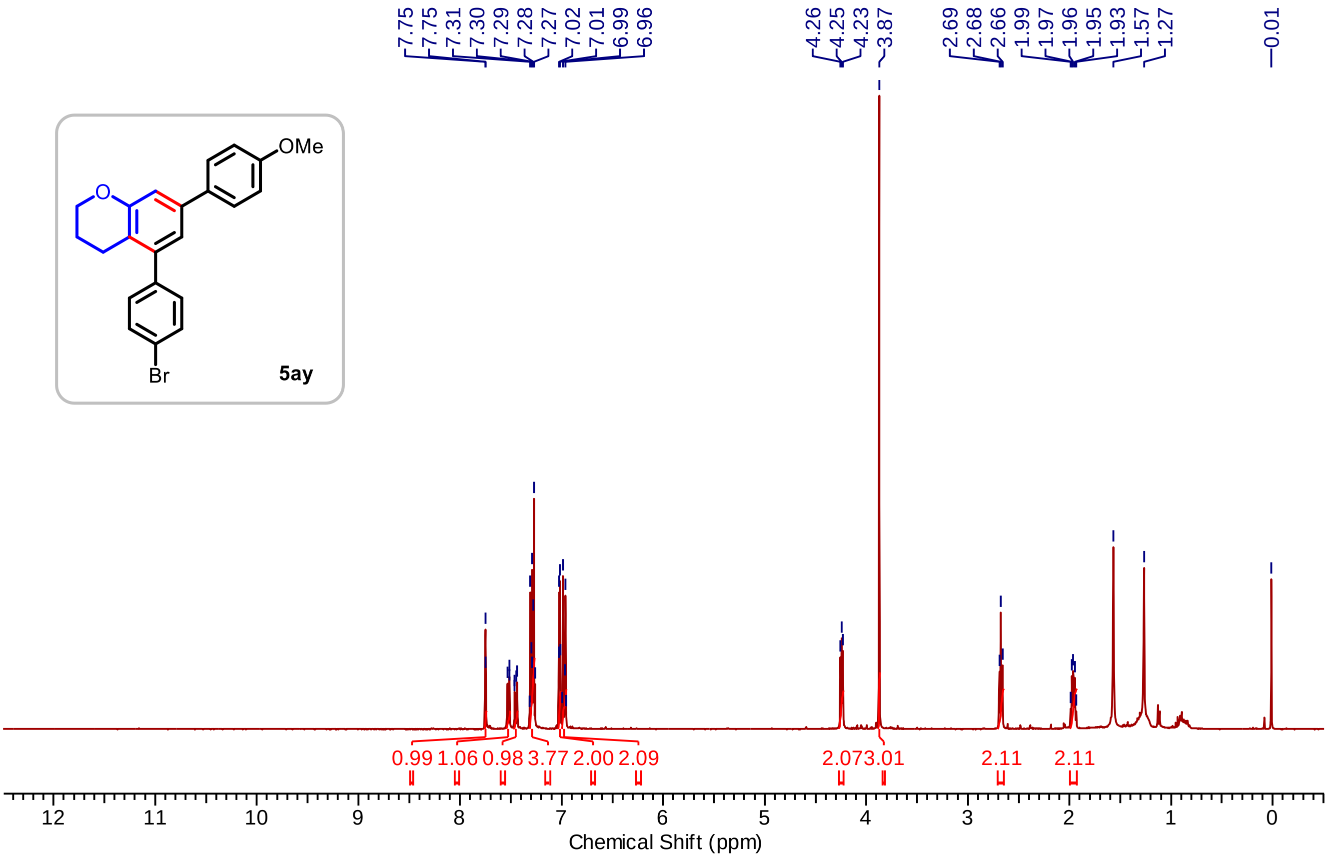
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ax**:



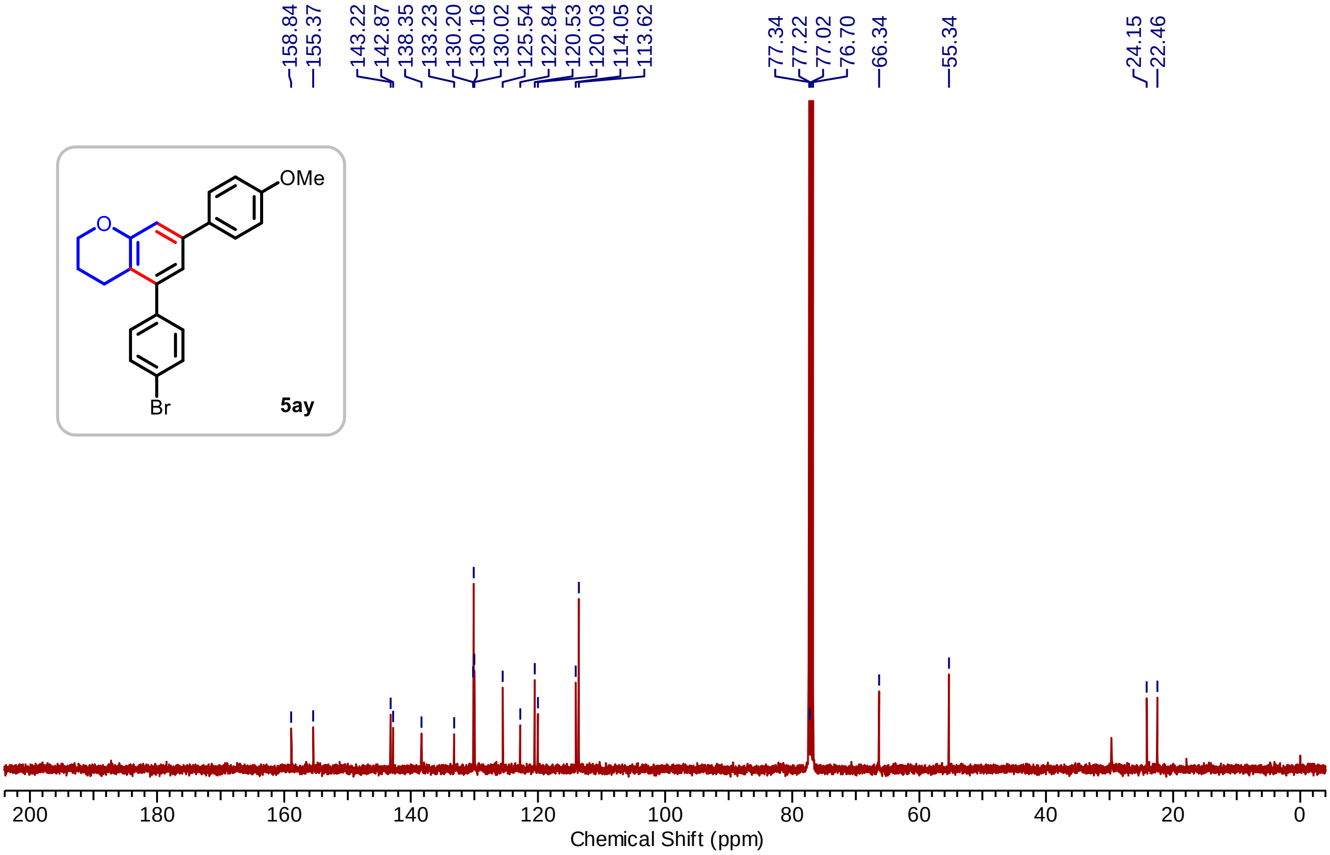
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ax**:



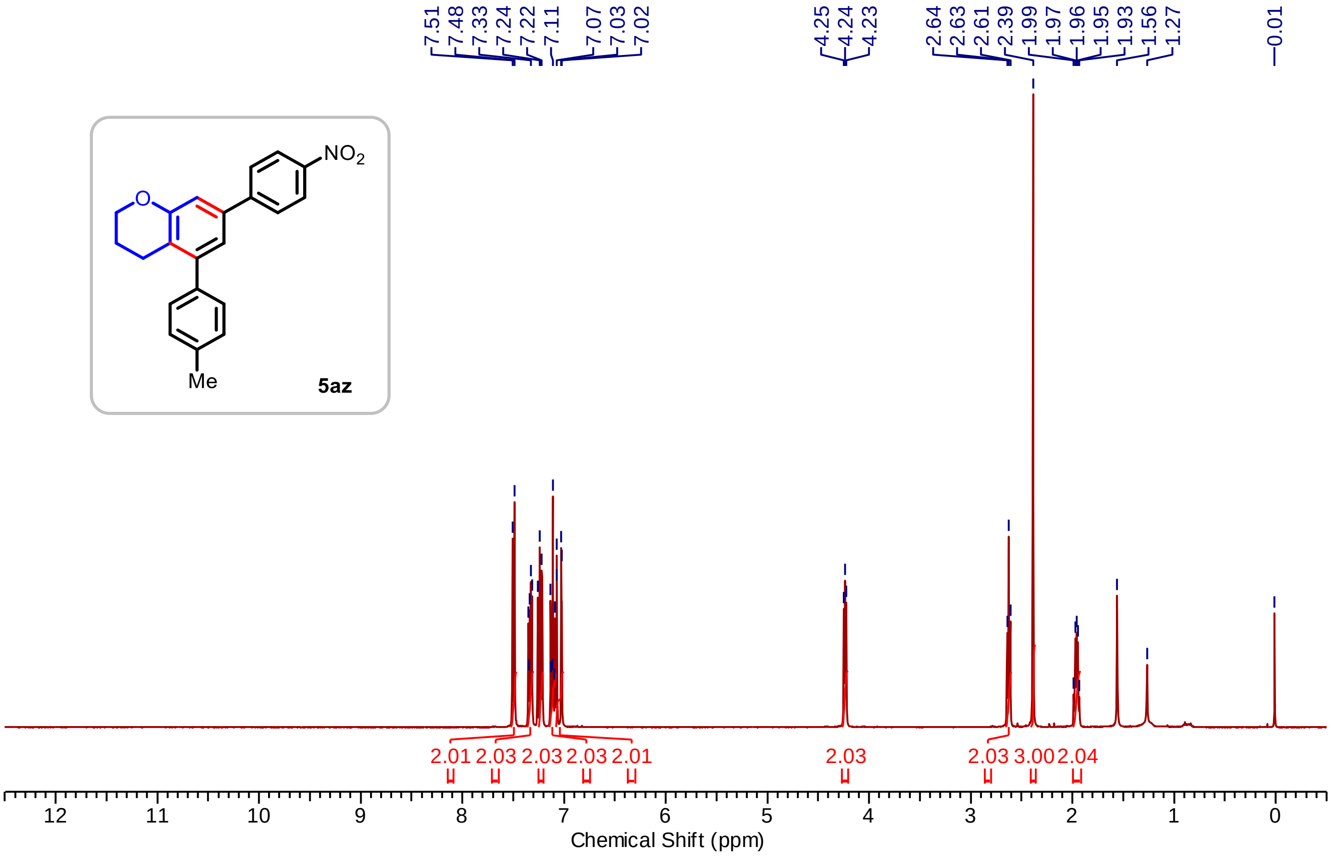
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ay**:



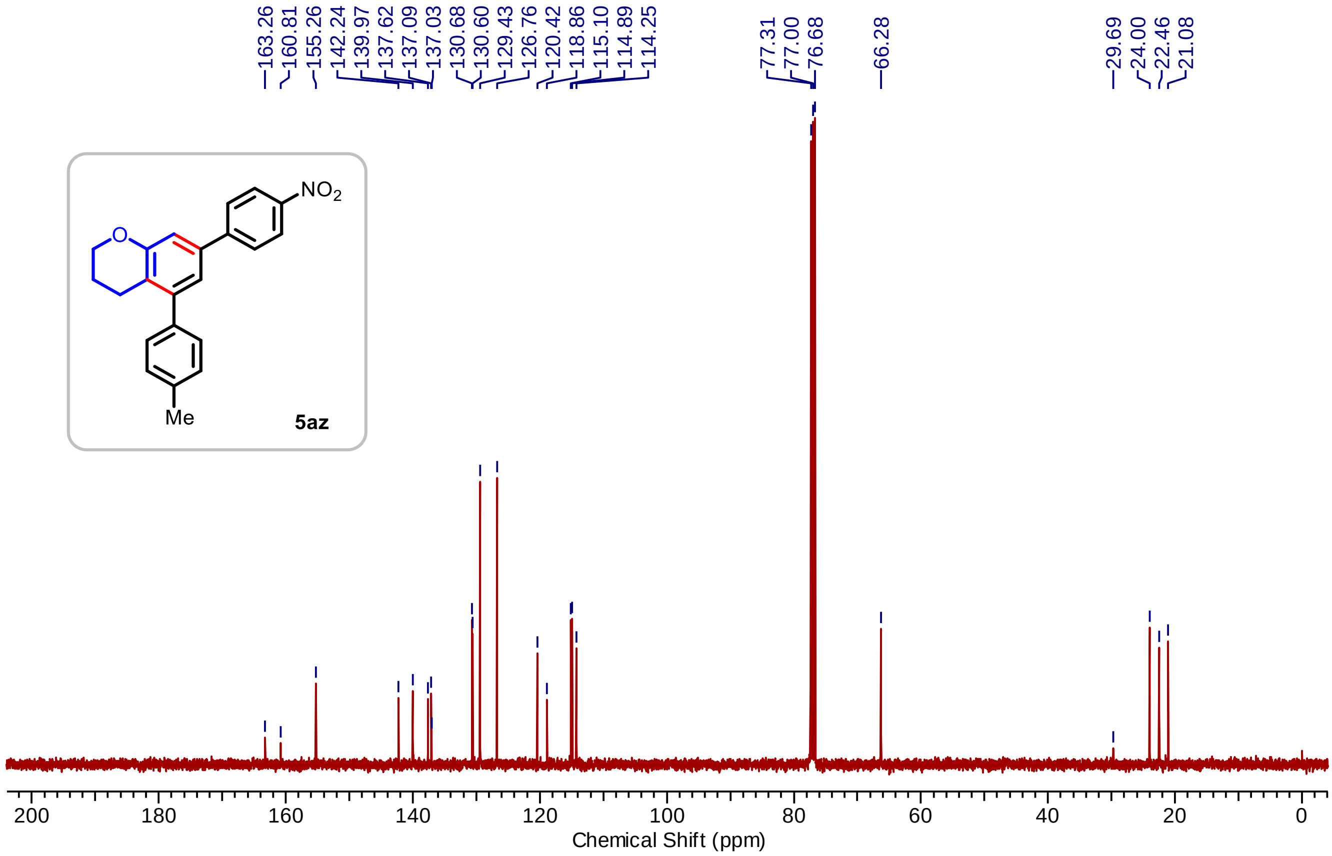
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ay**:

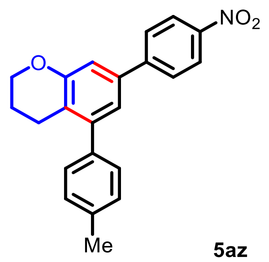


^{1}H NMR-Spectrum (400MHz, CDCl$_3$) of **5az**:



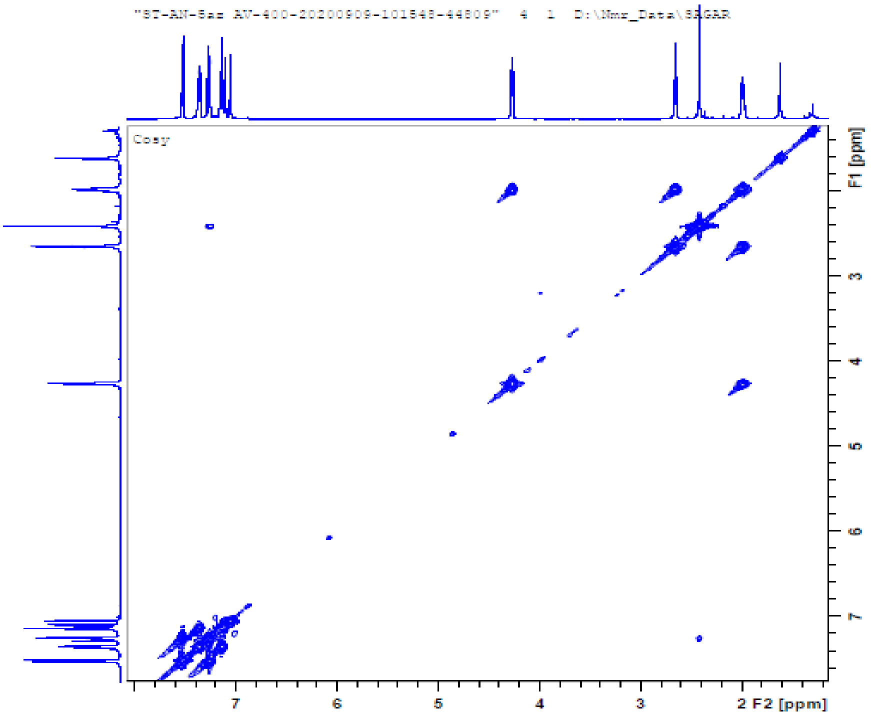
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5az**:



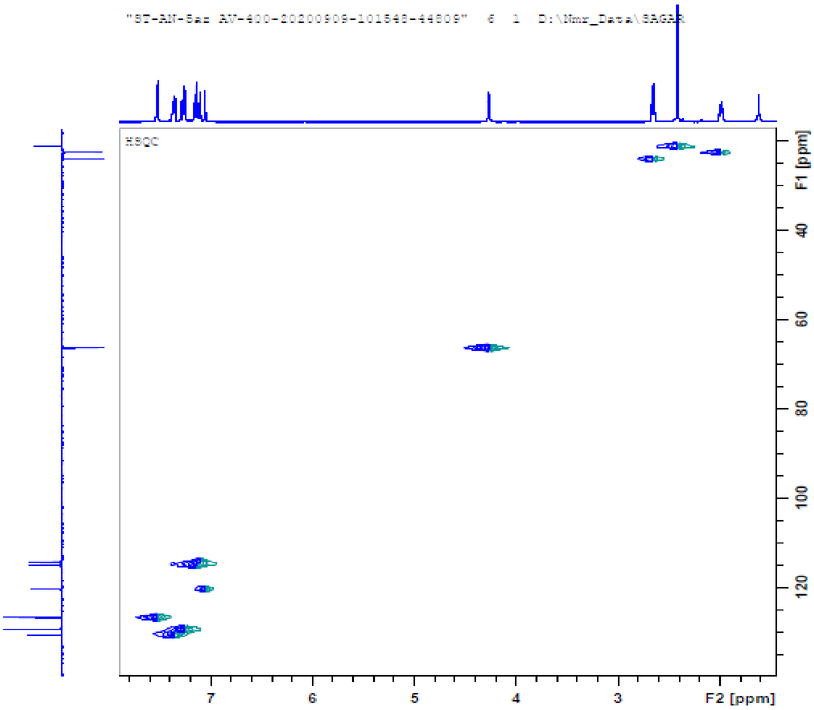


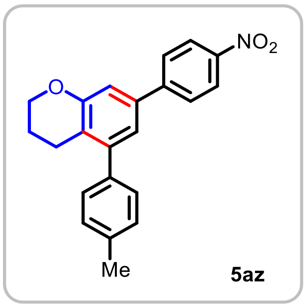
5az

COSY Spectrum of**5az**:



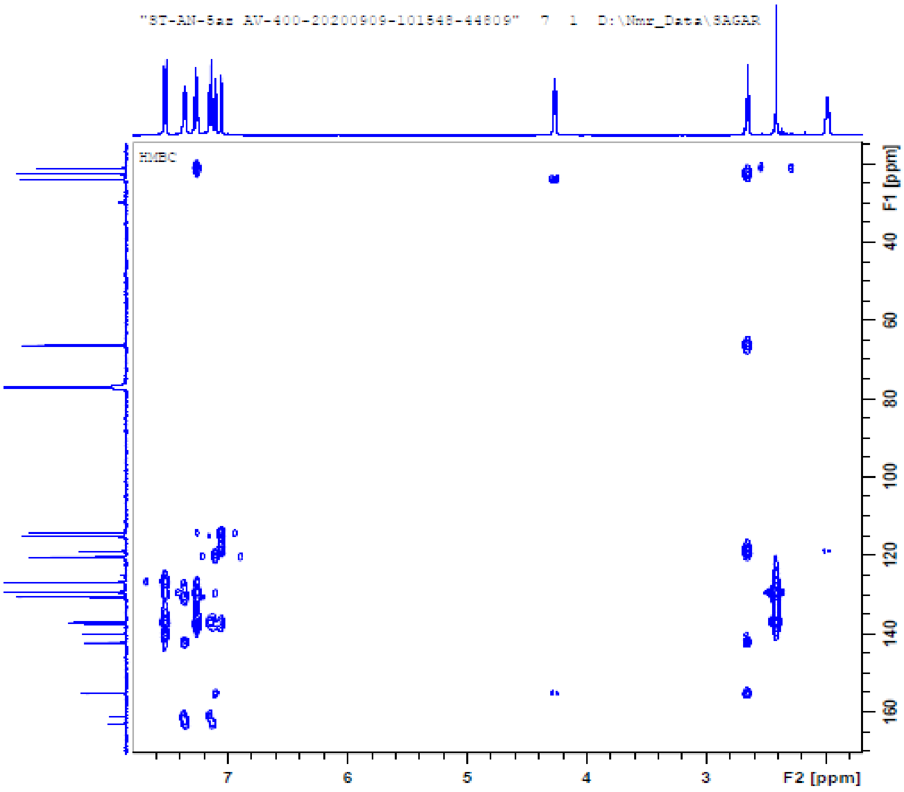
HSQC Spectrum of**5az**:



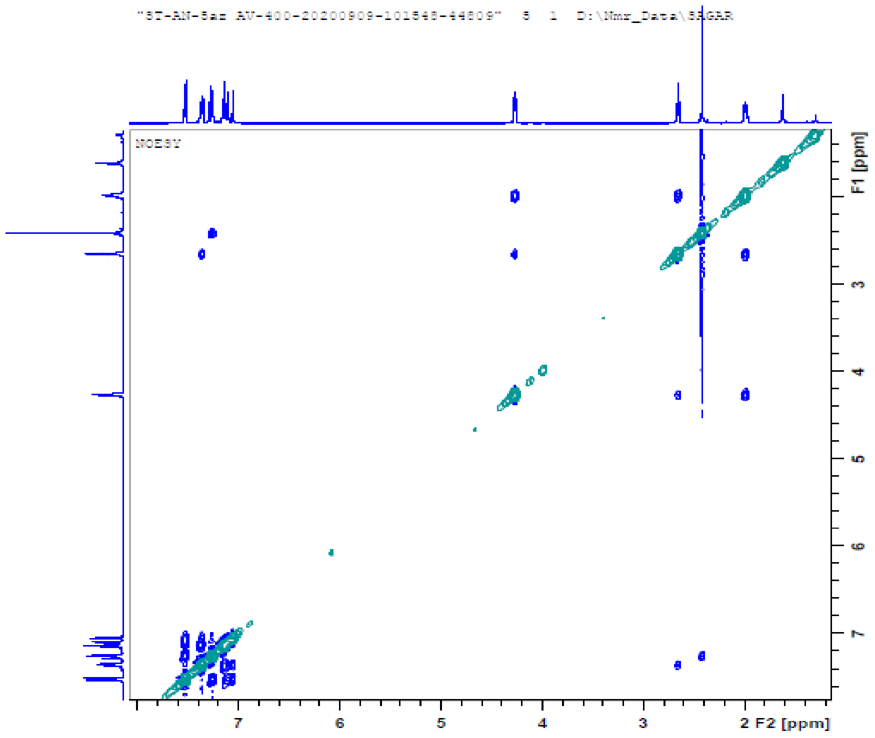


5az

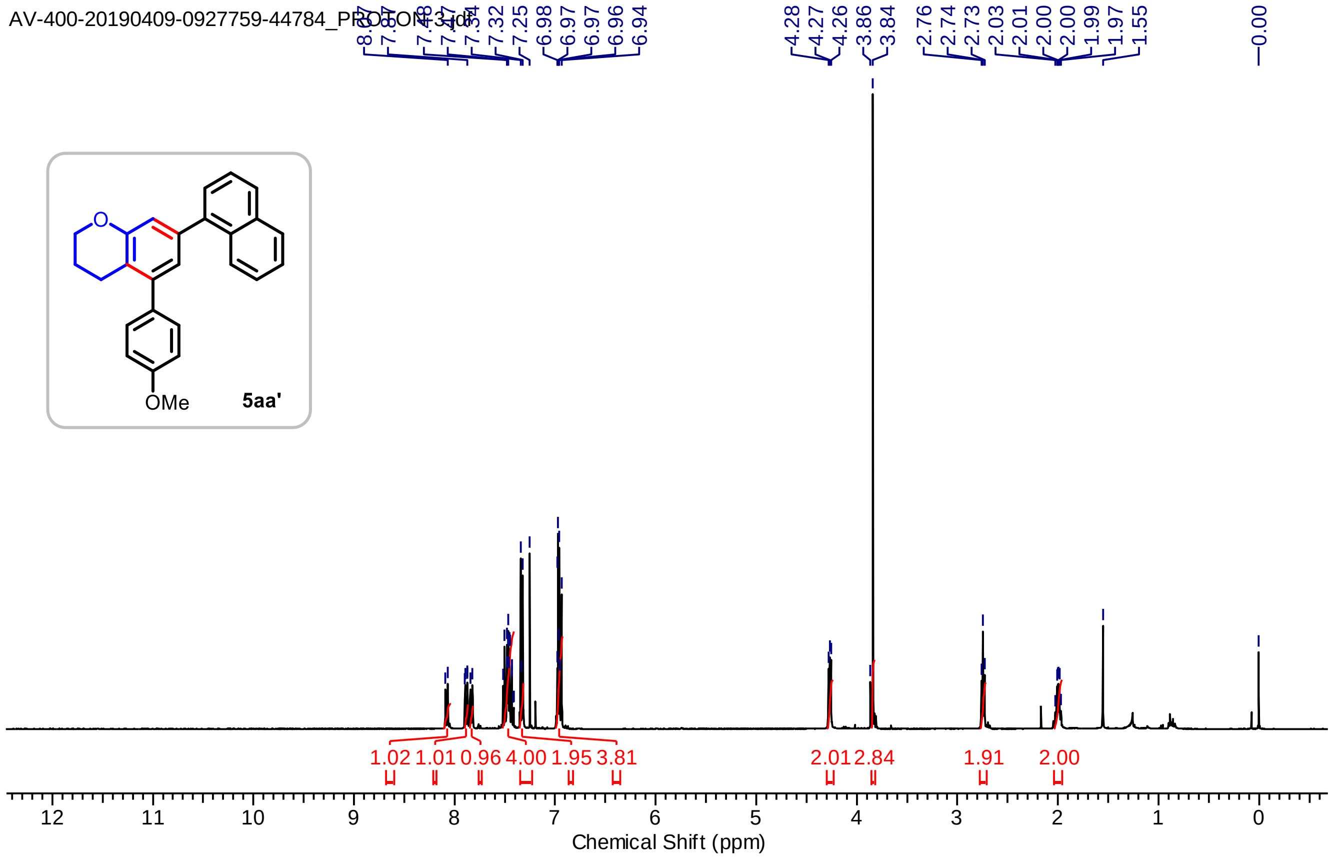
HMBC Spectrum of **5az**:



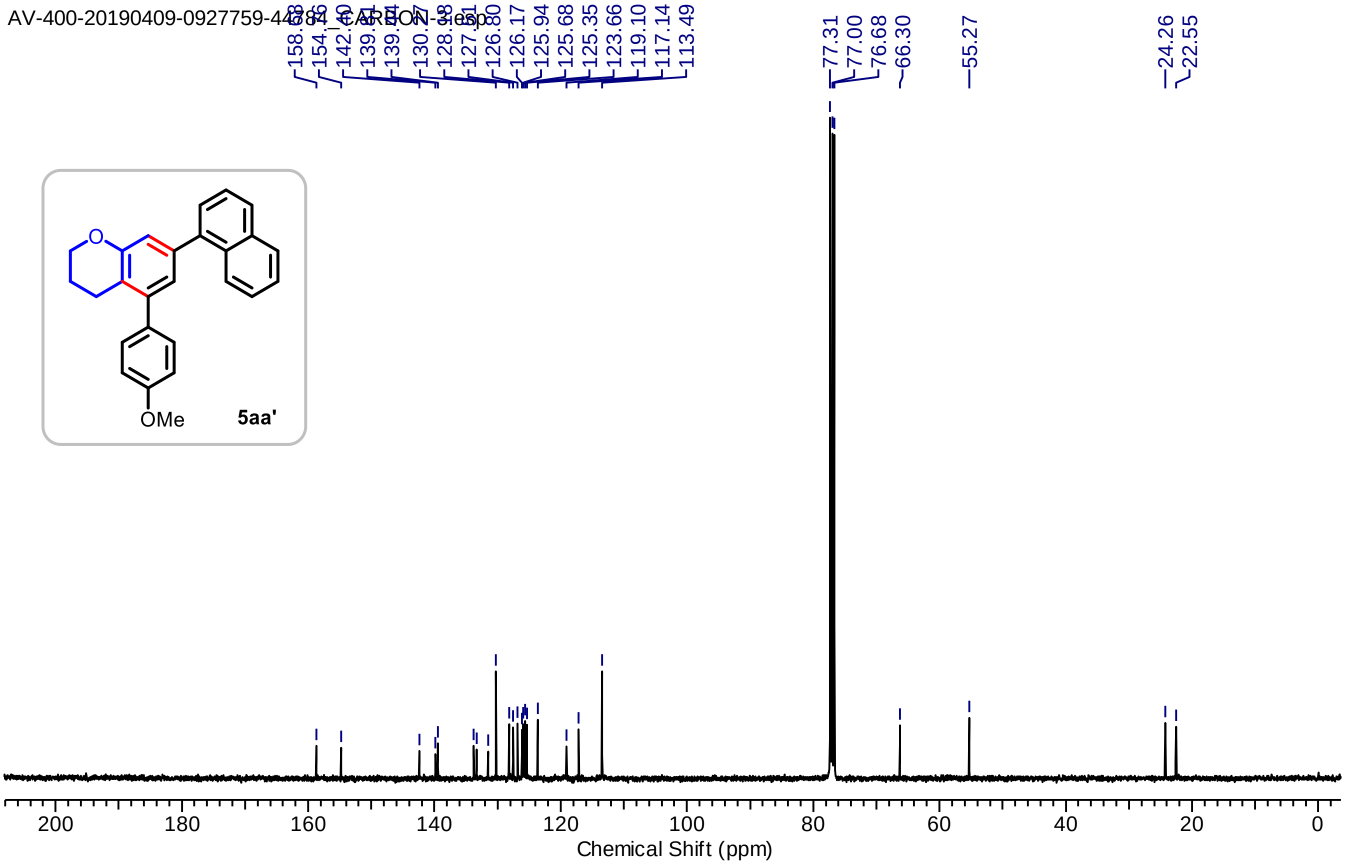
NOESY Spectrum of **5az**:



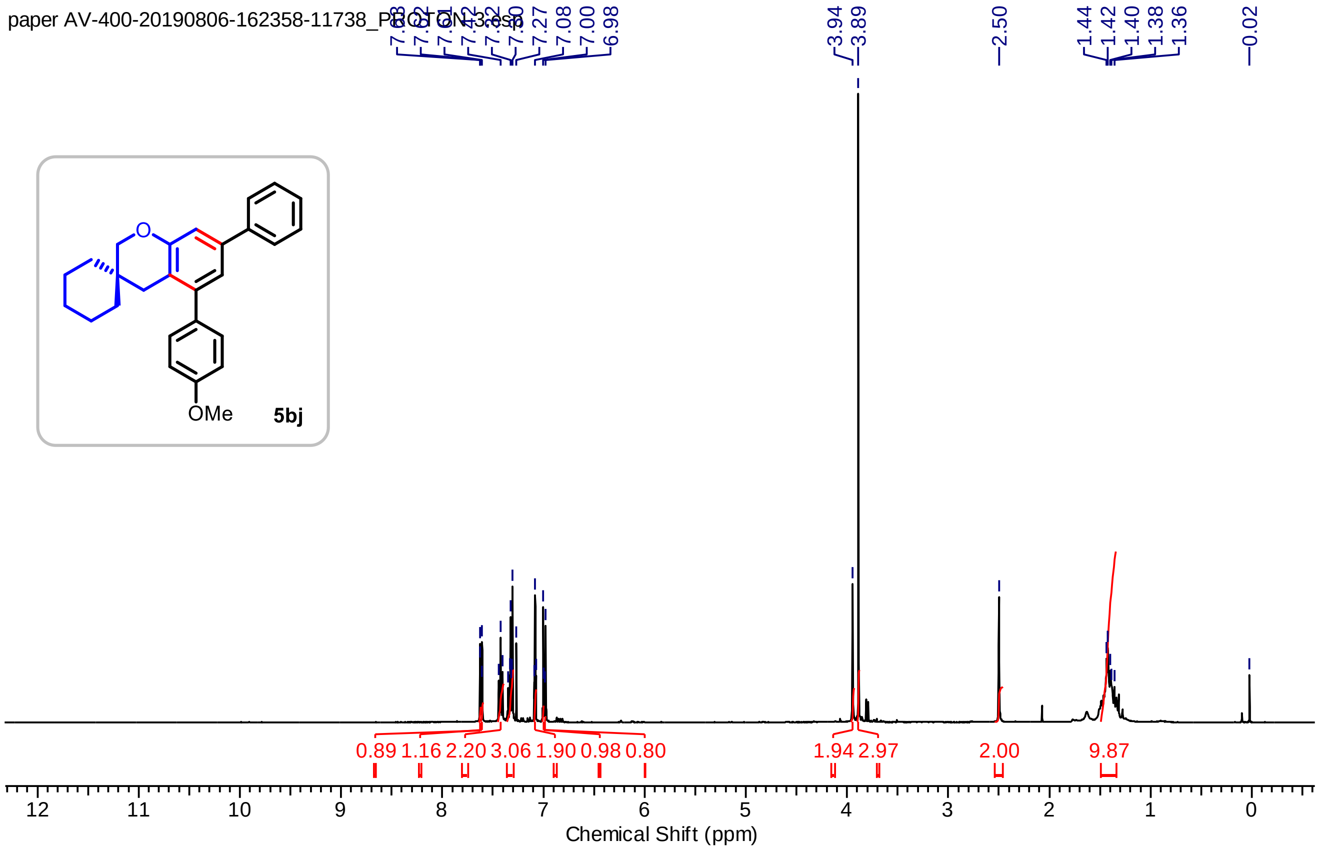
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5aa’**:



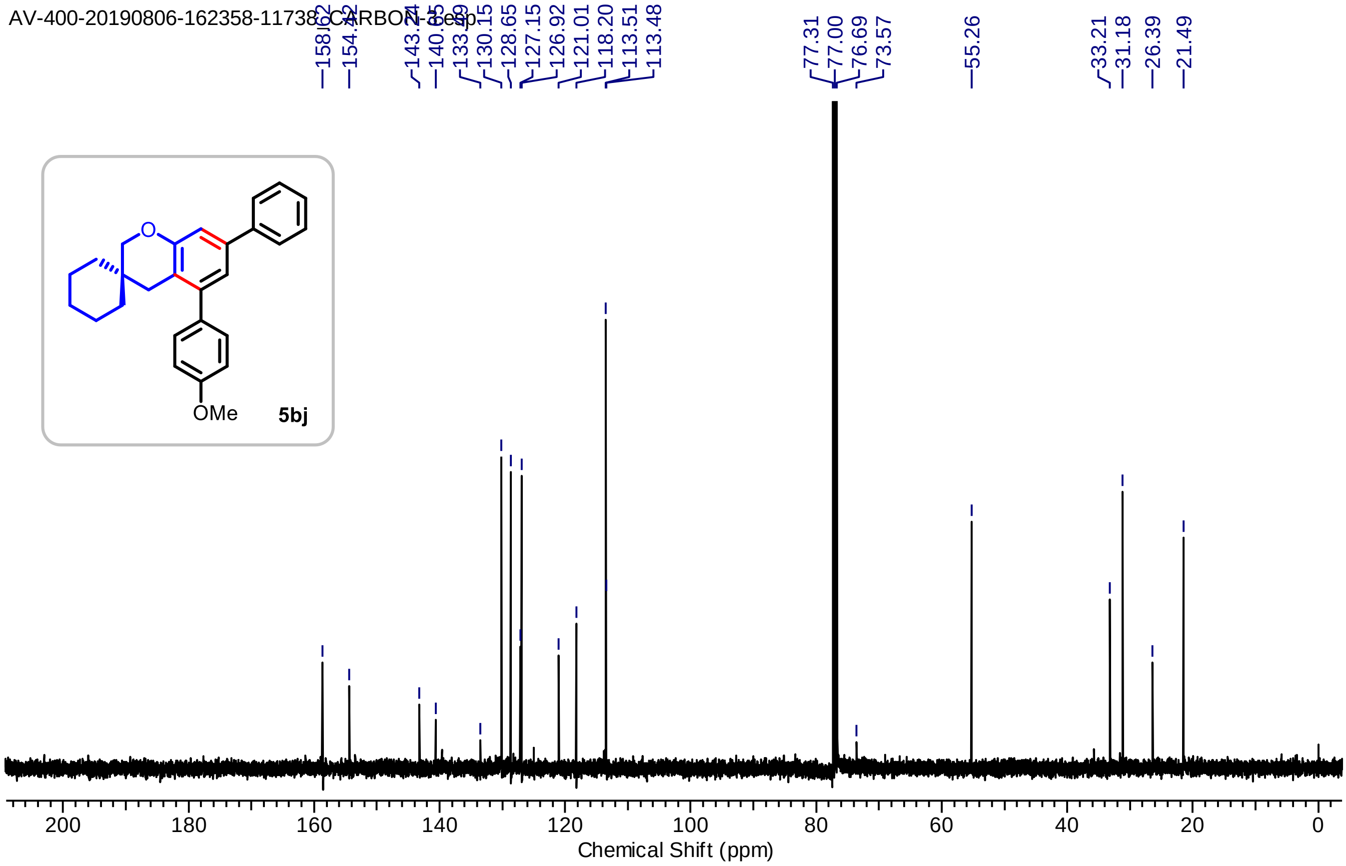
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5aa’**:



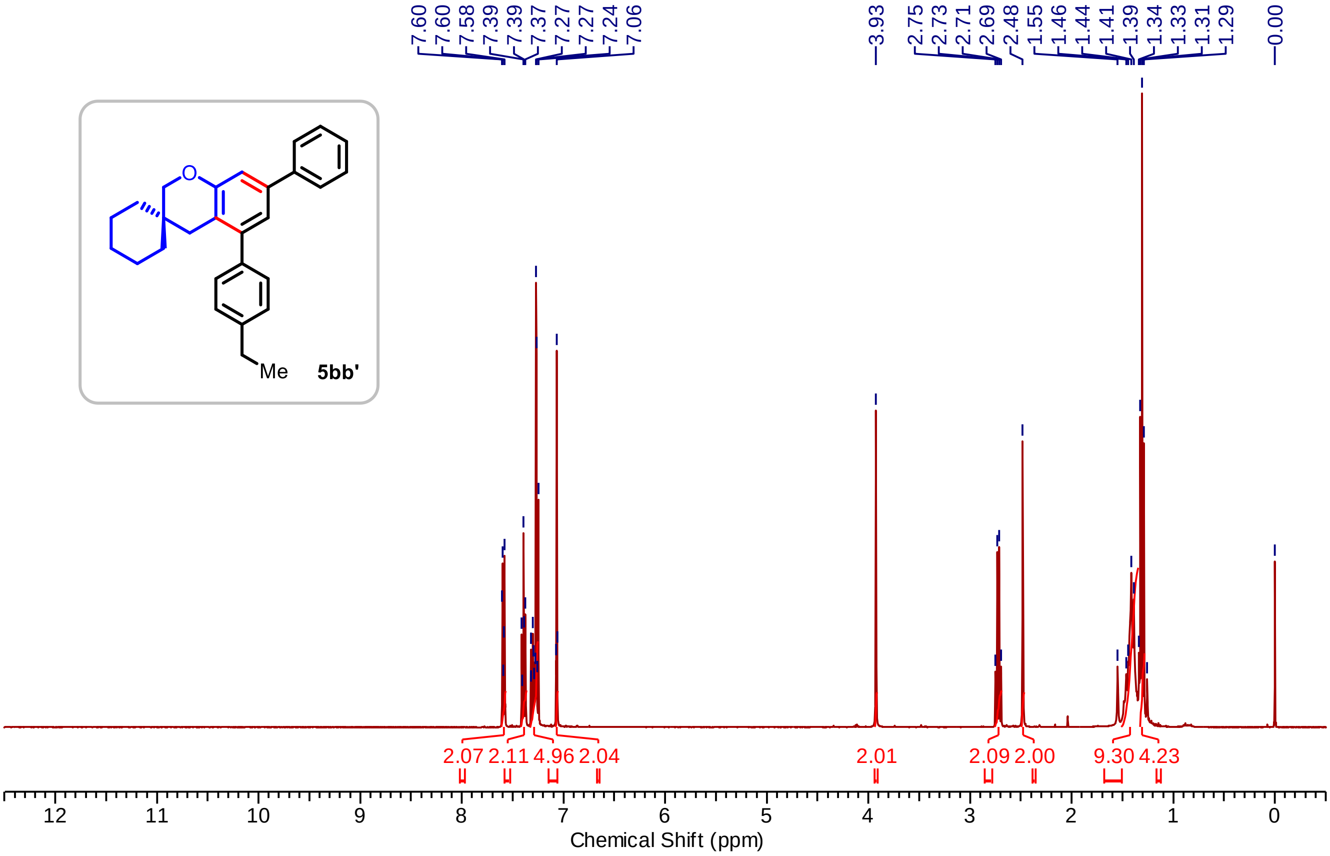
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5bj**:



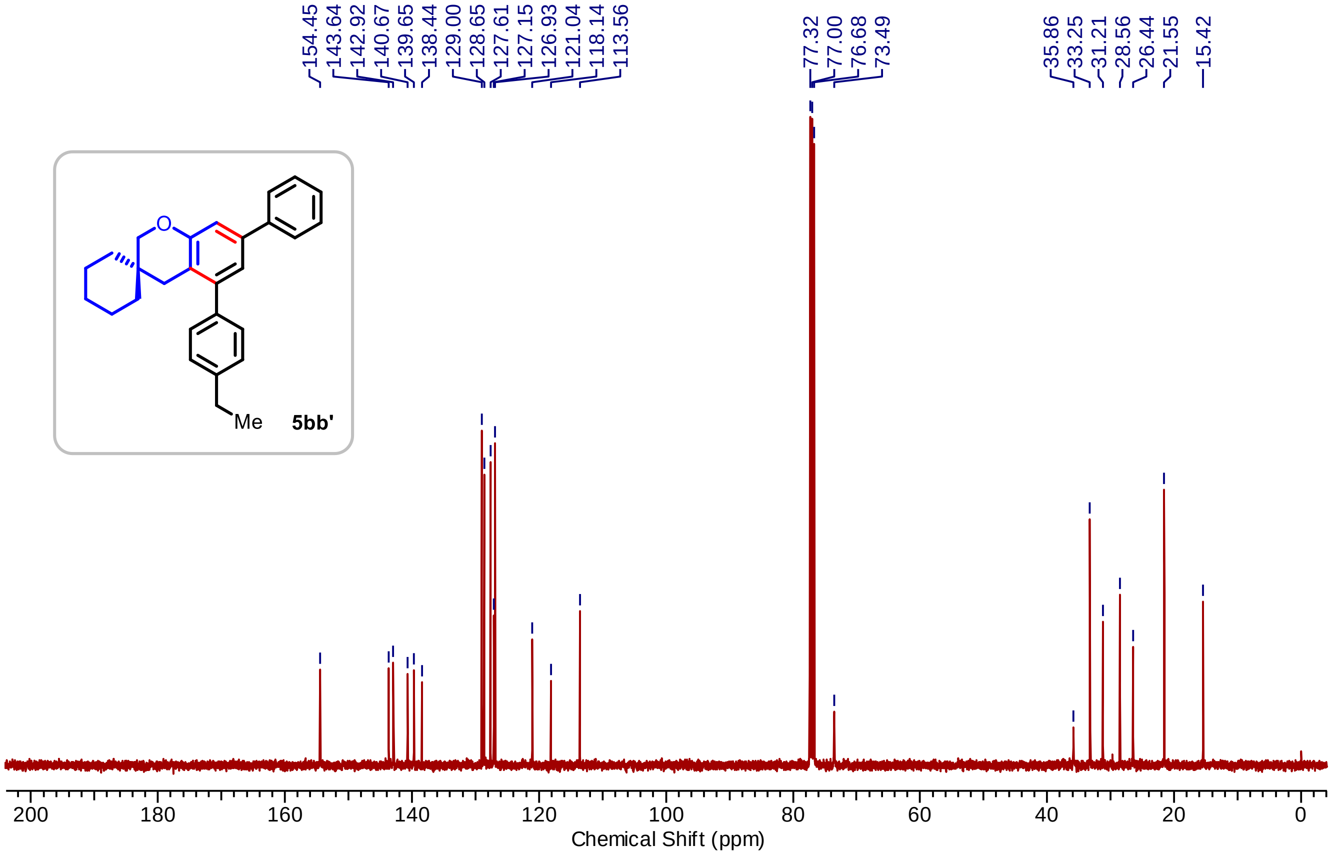
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5bj**:



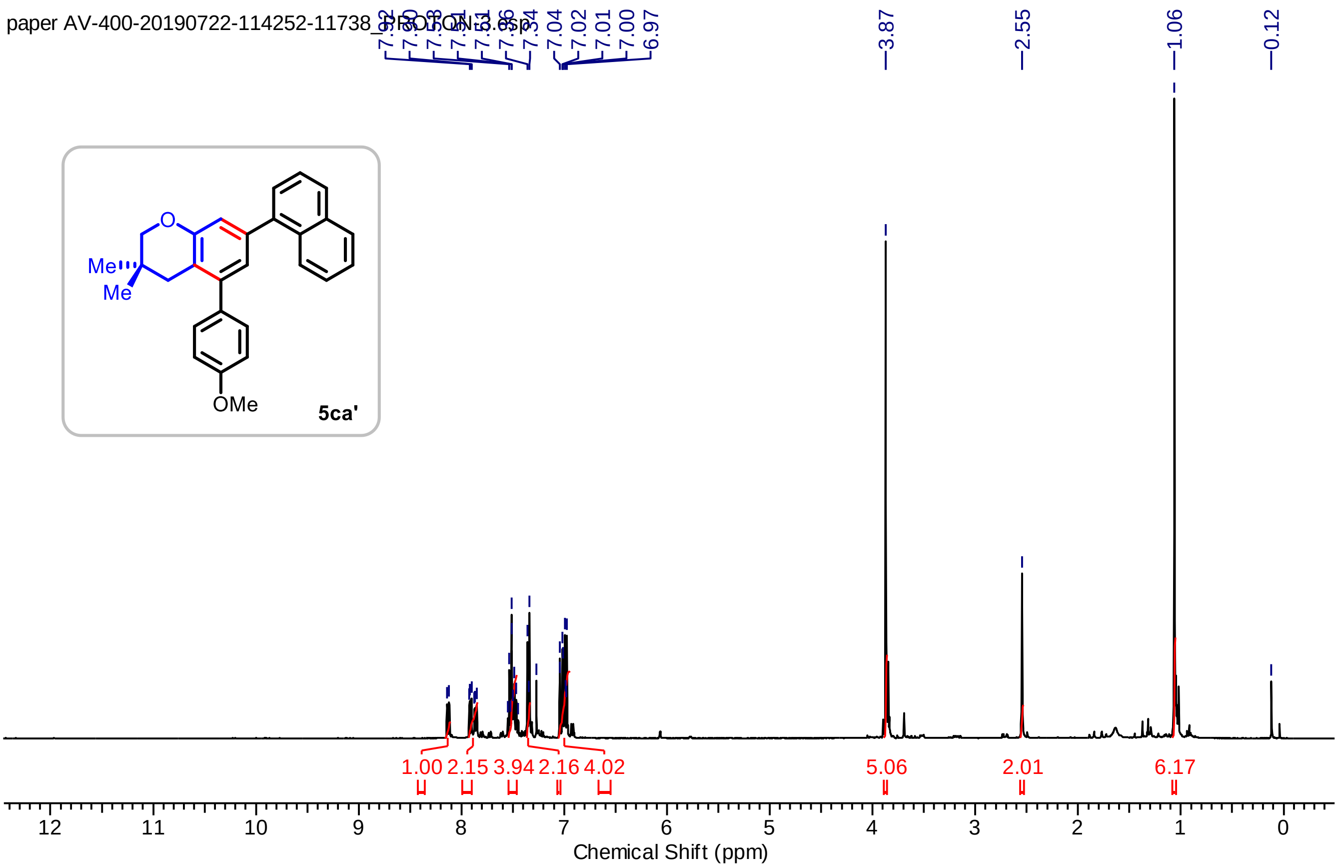
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5bb’**:



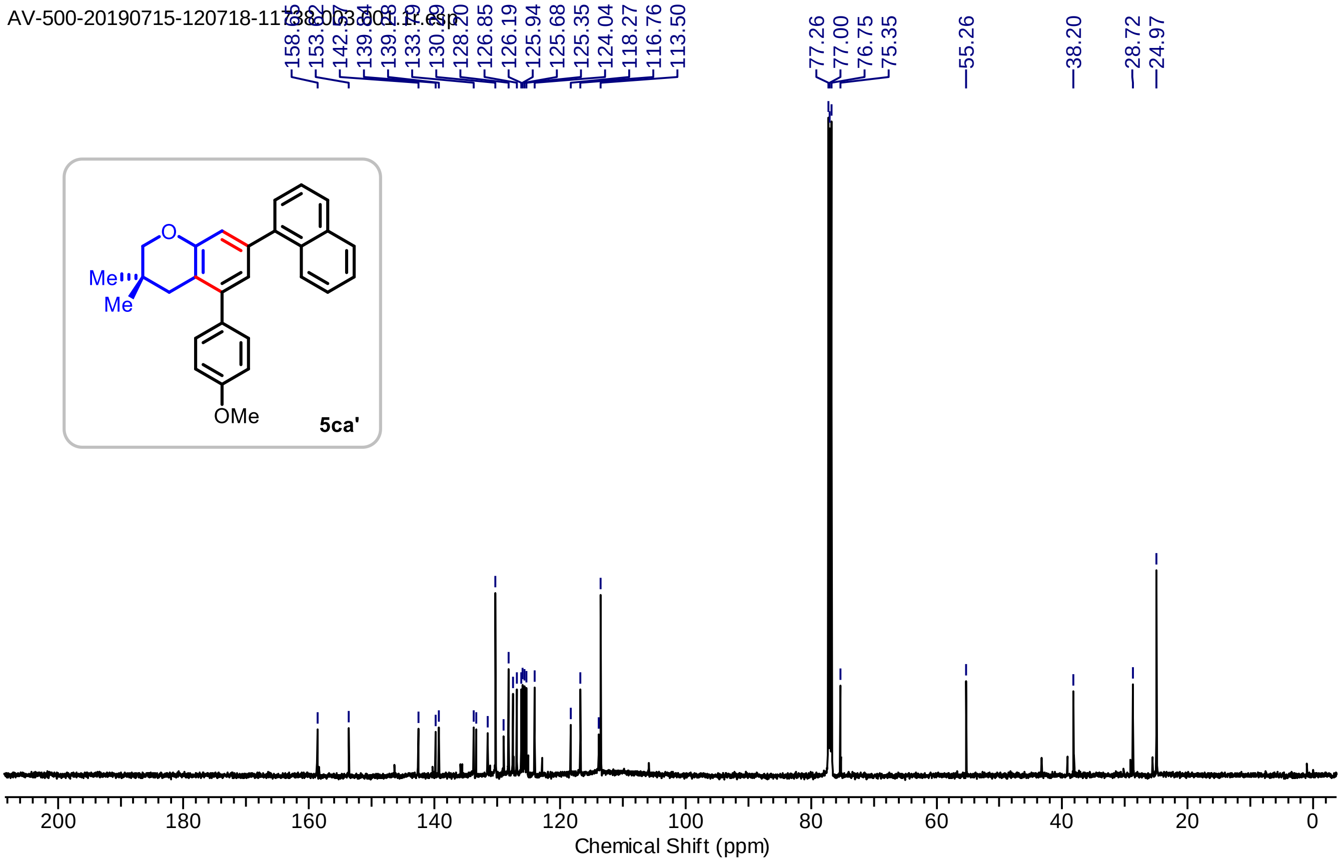
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5bb’**:



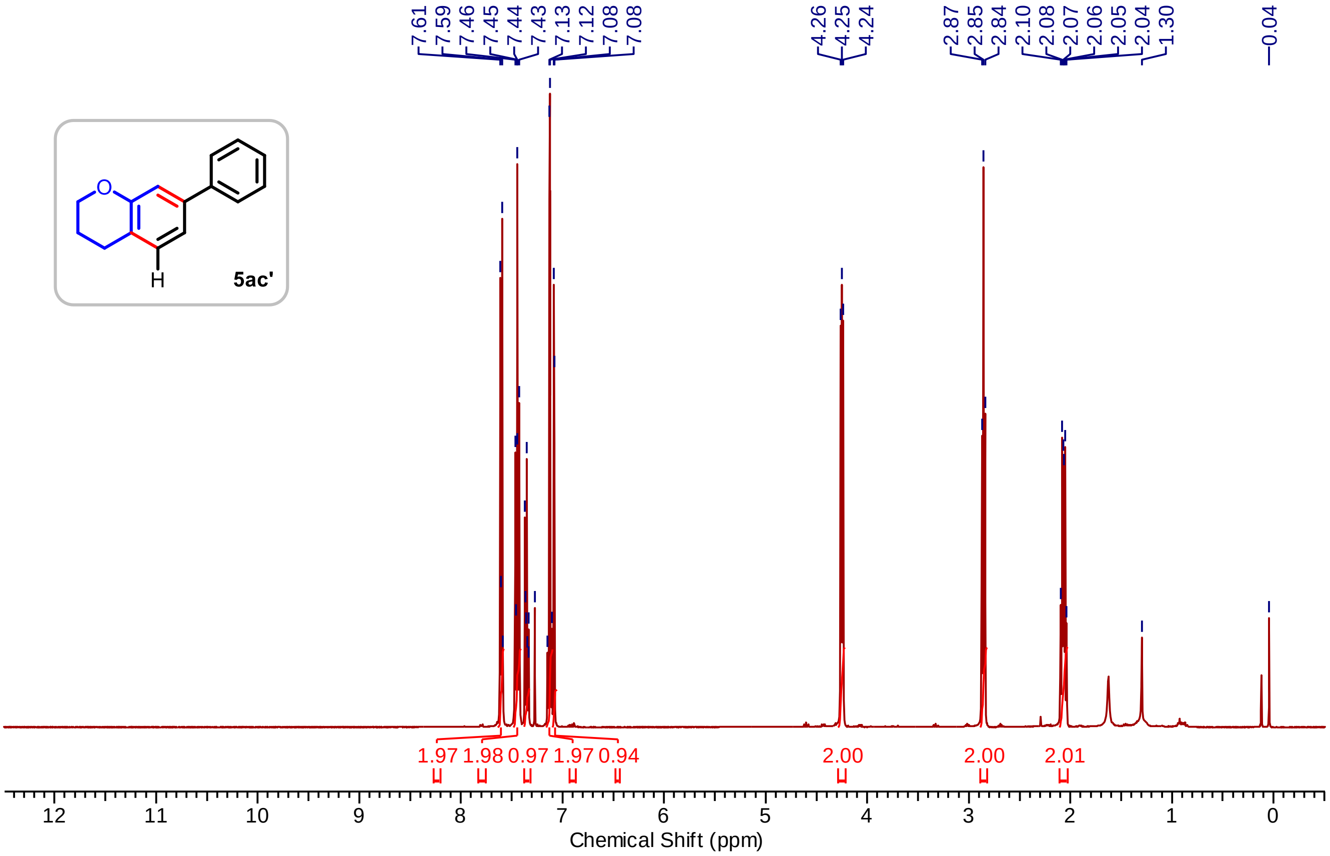
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ca'**:



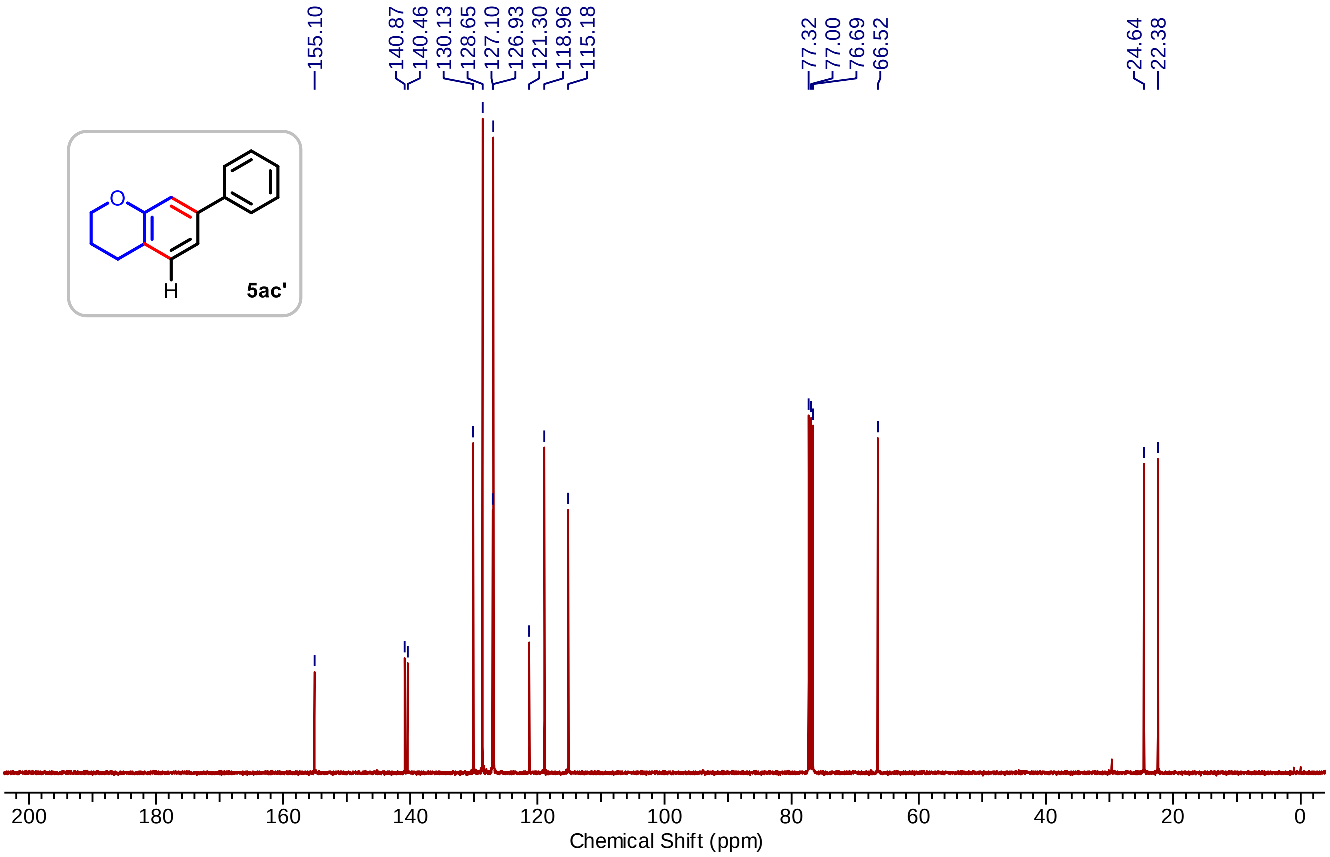
^{13}C NMR-Spectrum (126 MHz, CDCl$_3$) of **5ca'**:



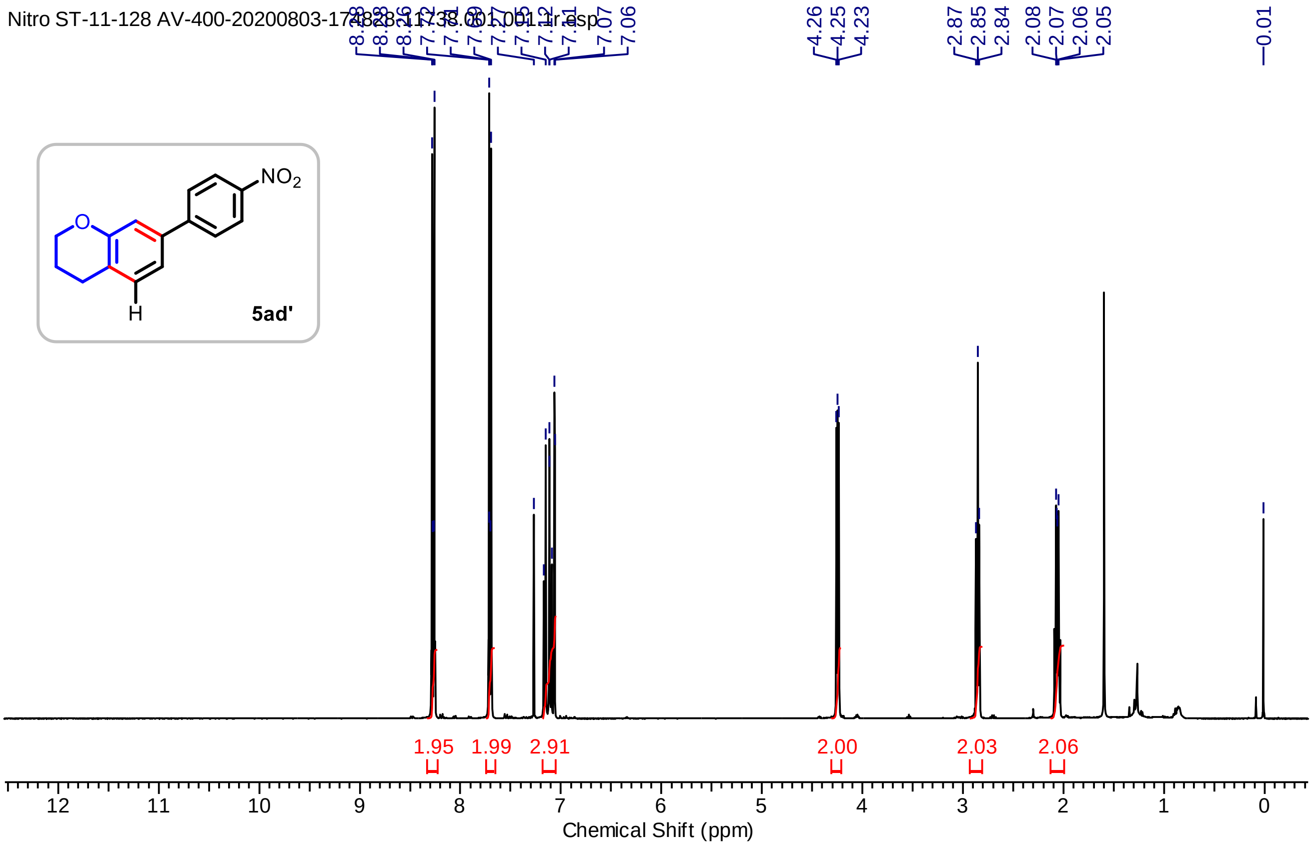
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ac’**:



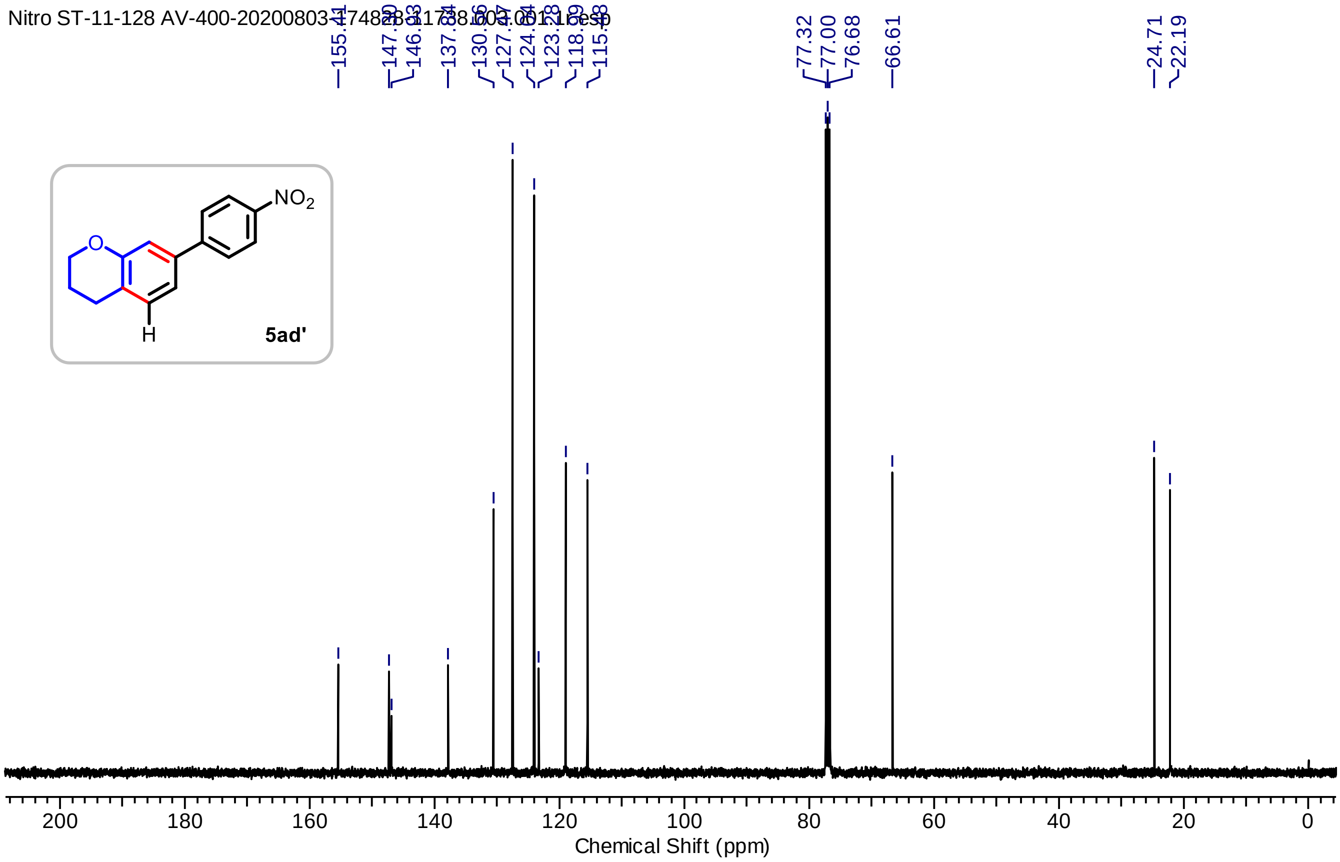
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ac’**:



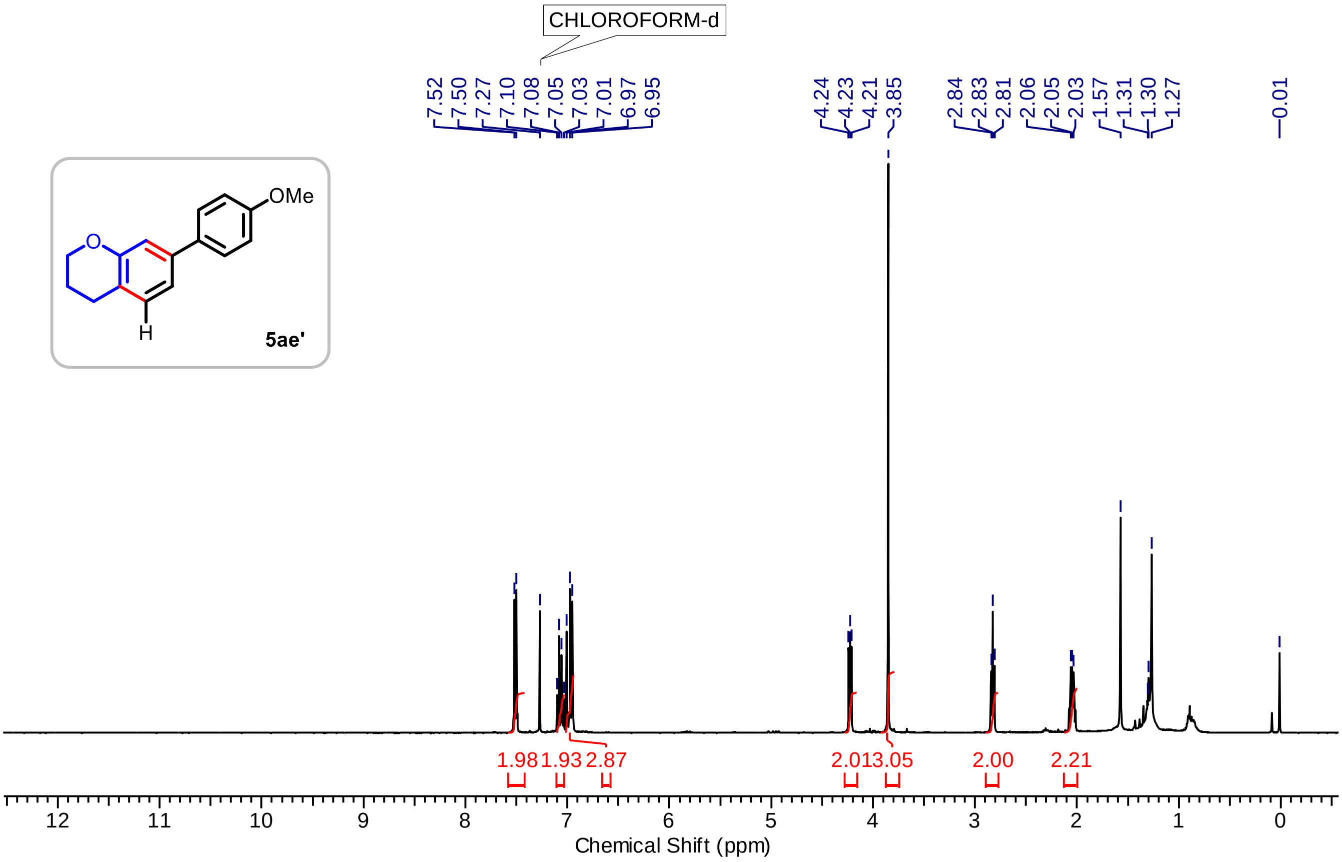
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ad’**:



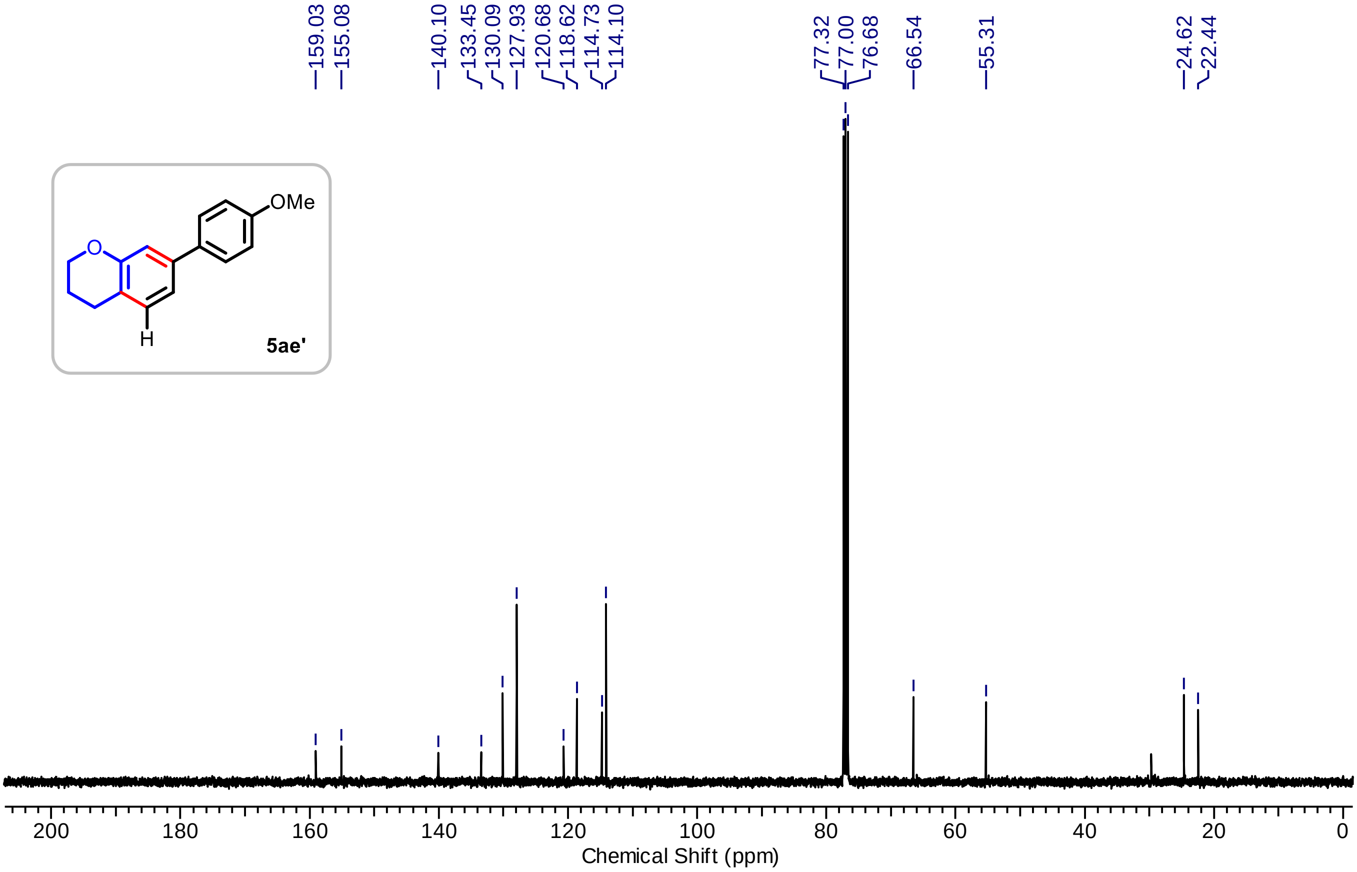
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ad’**:



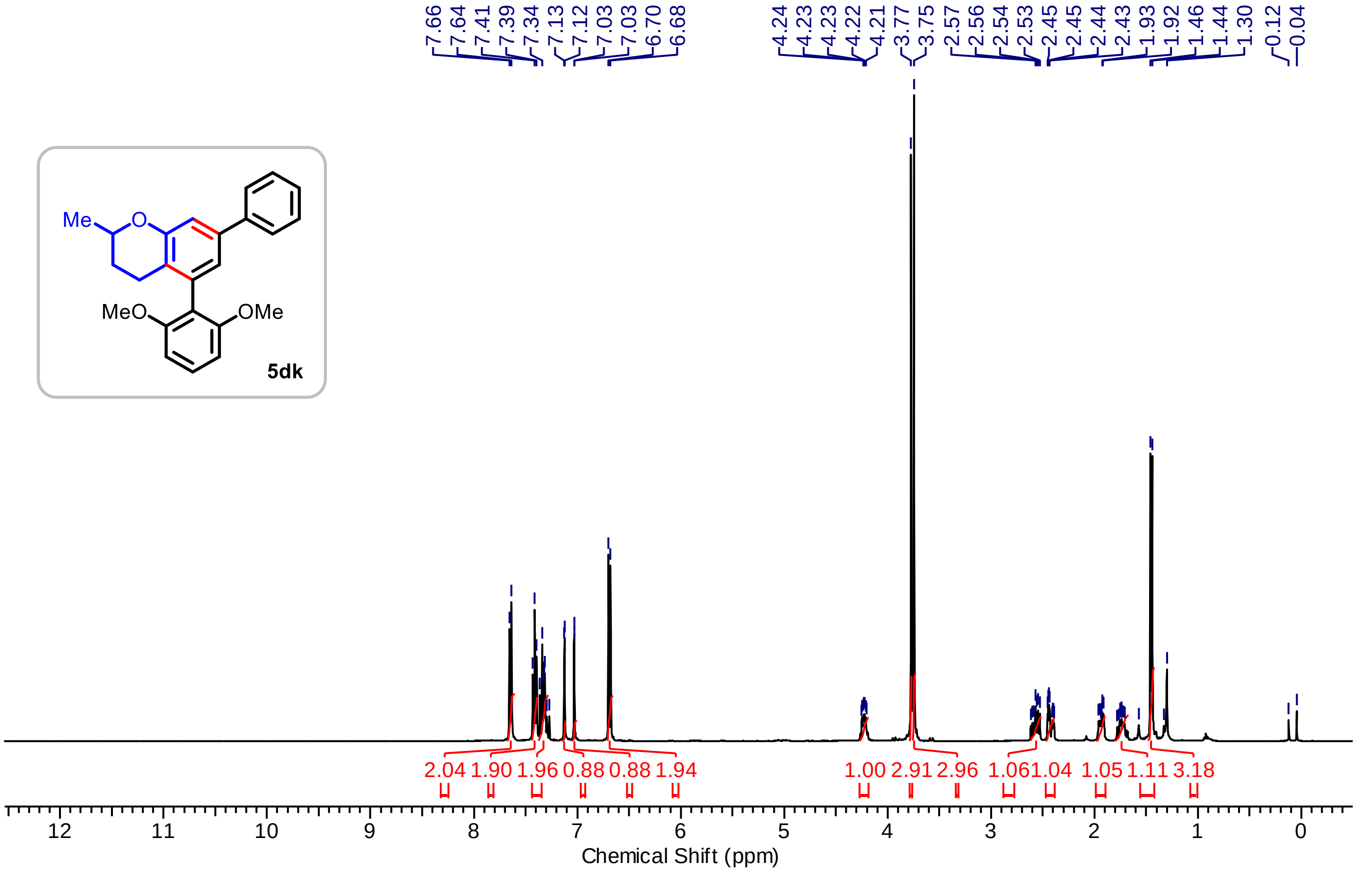
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5ae'**:



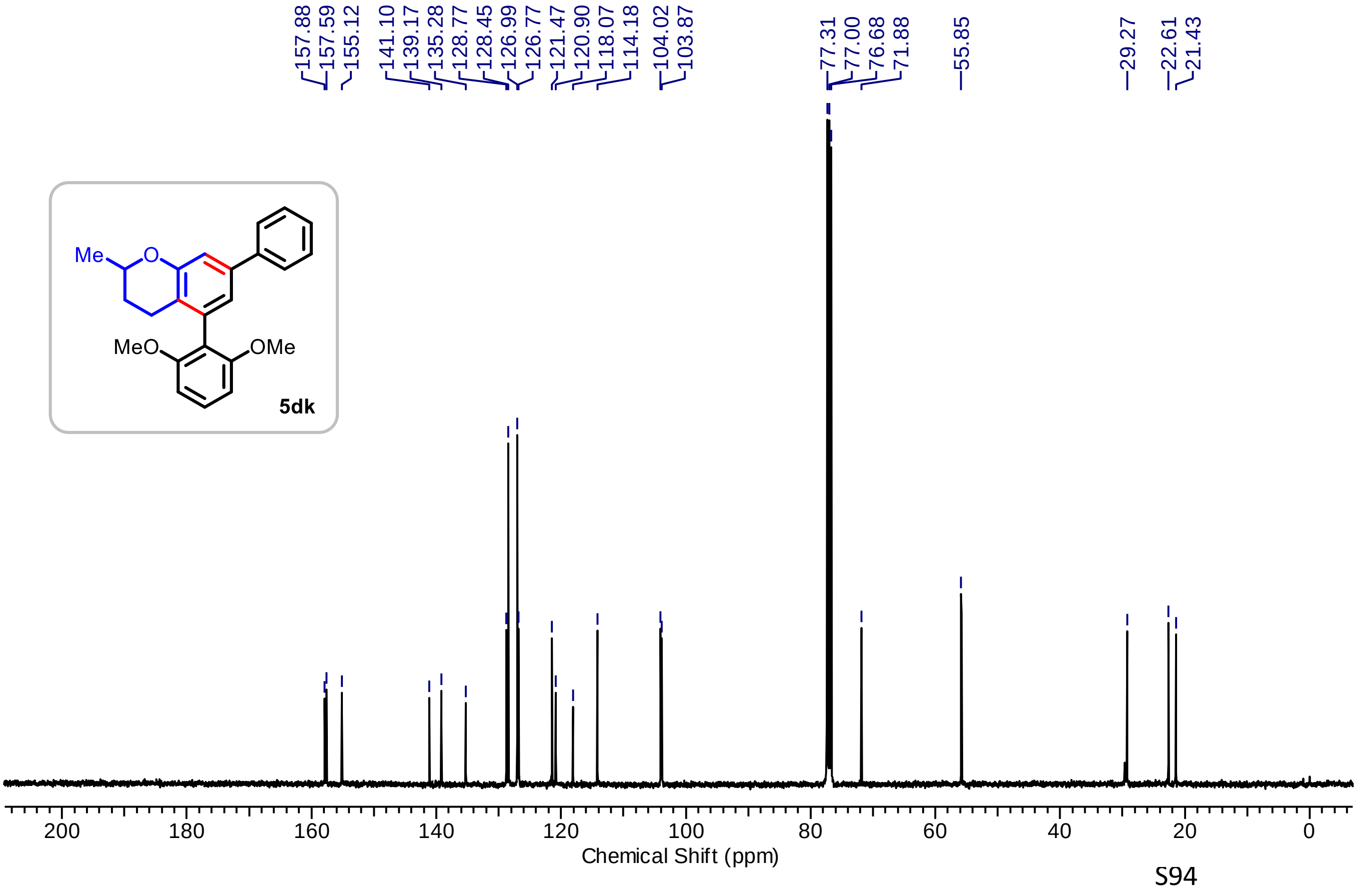
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$)of **5ae'**:



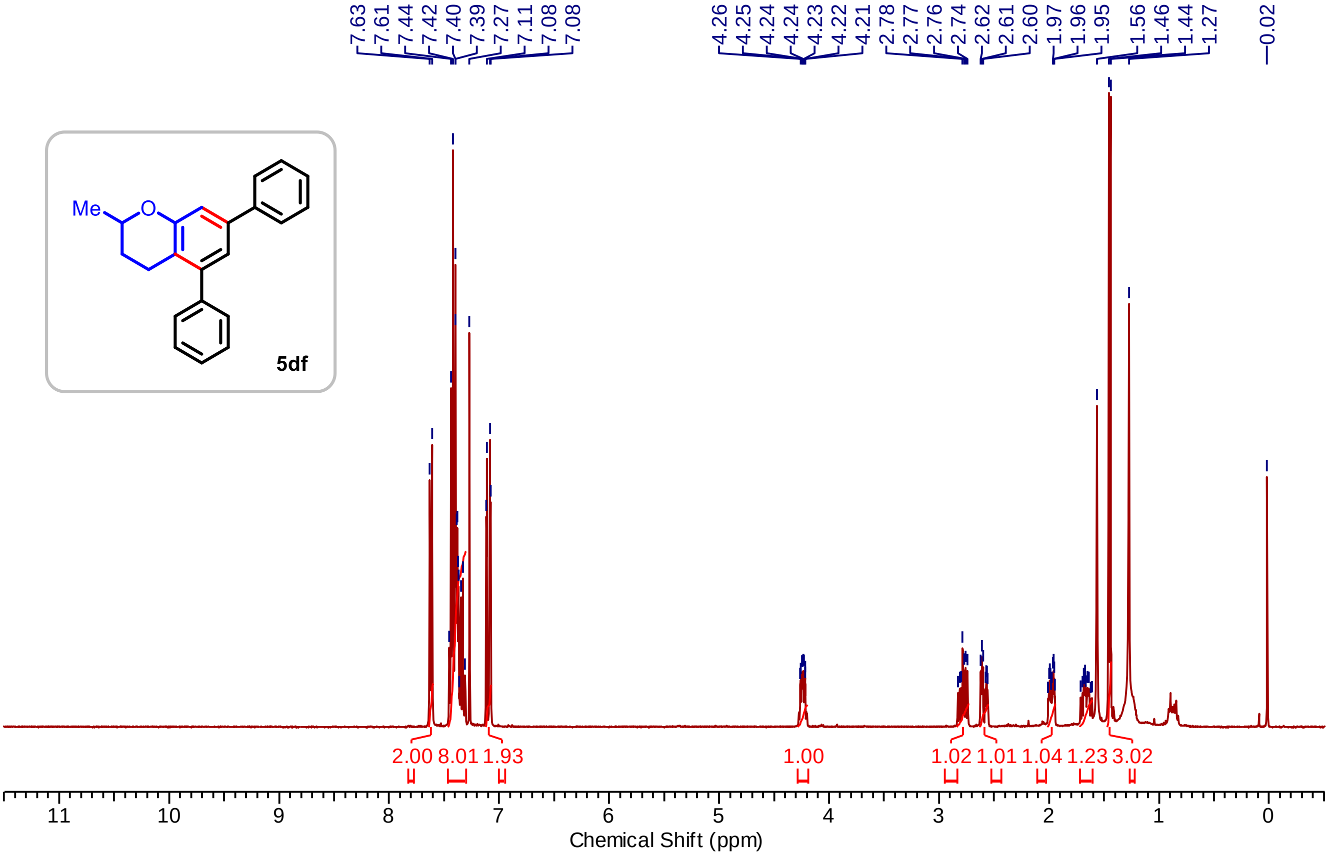
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5dk**:



^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5dk**:



^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5df**:



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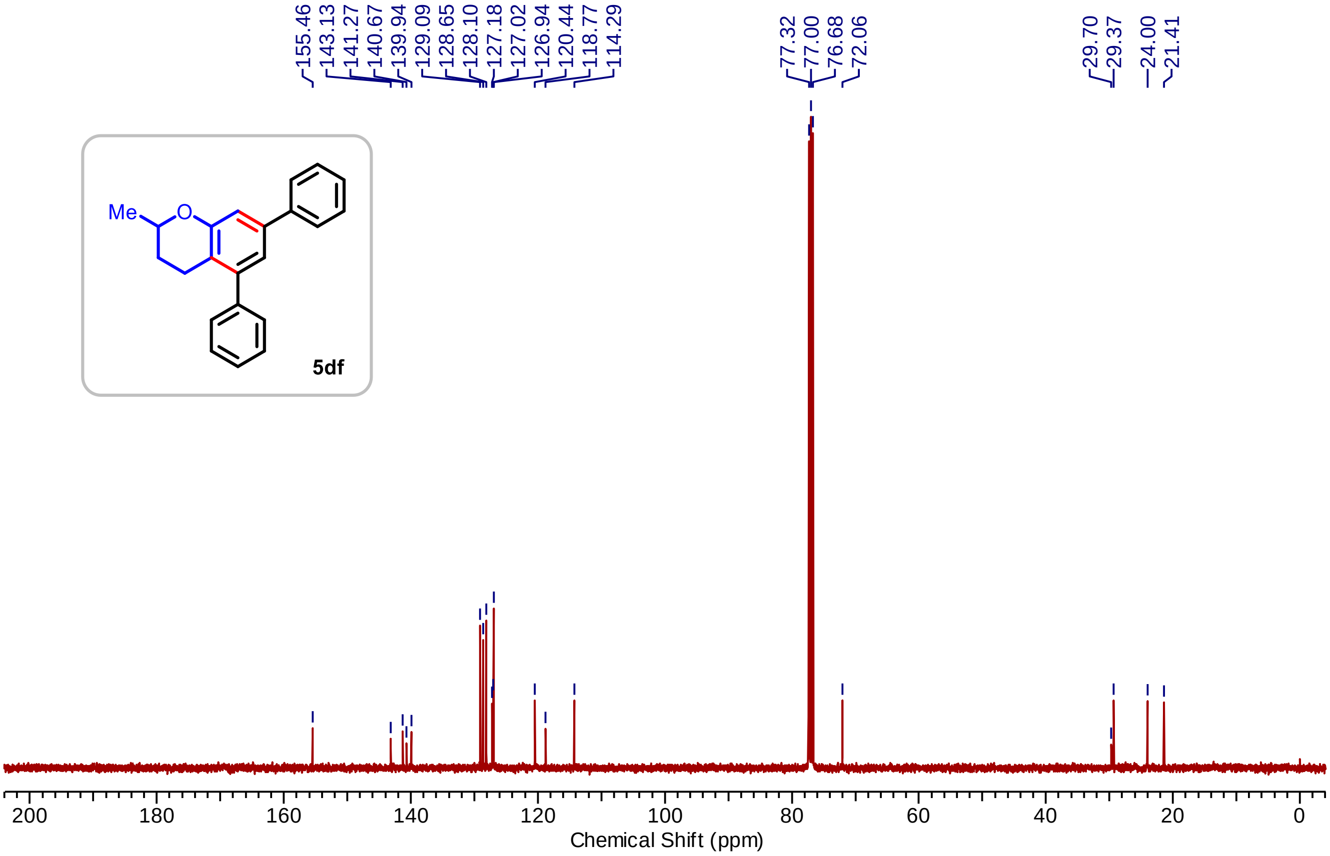
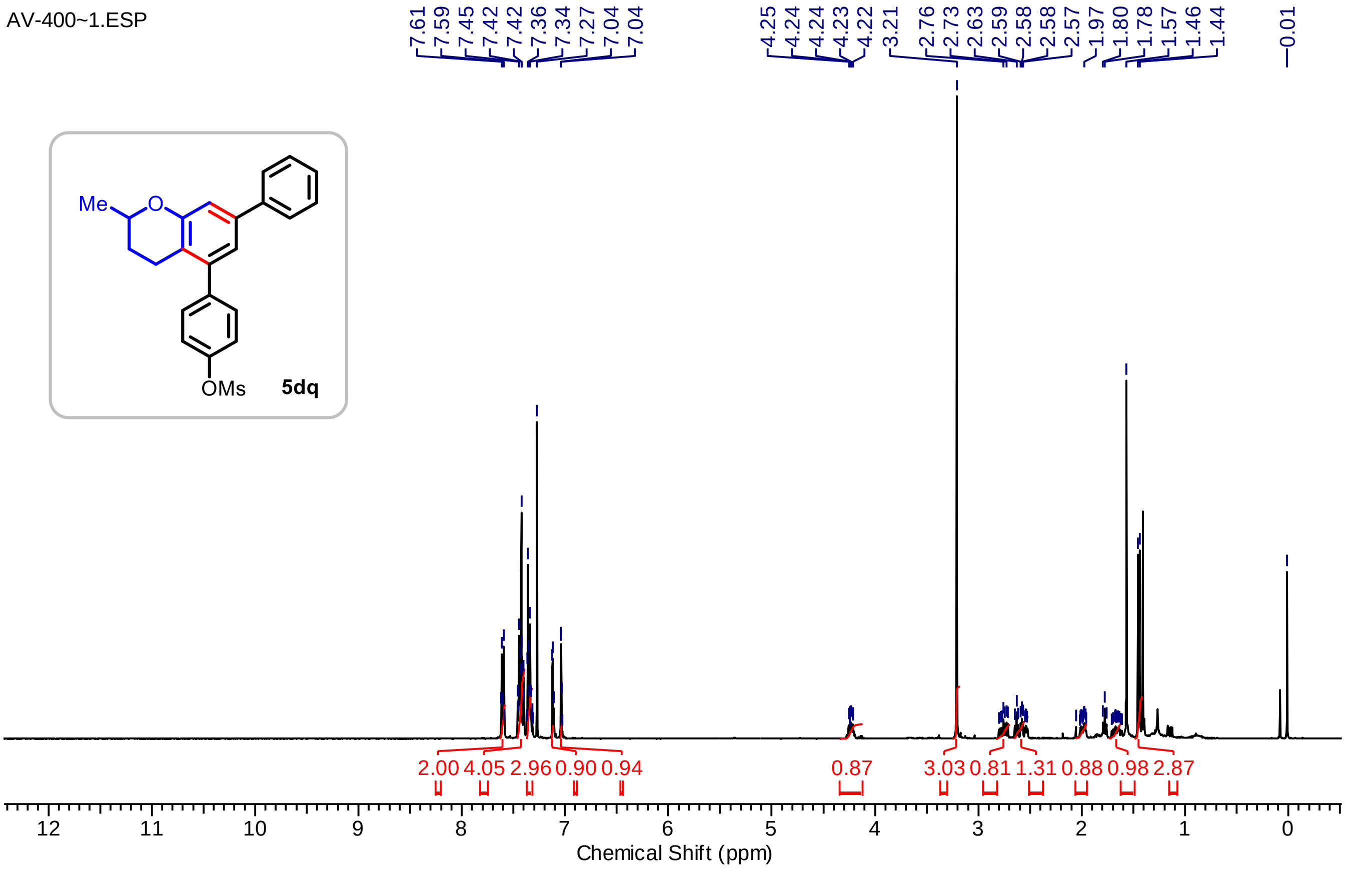
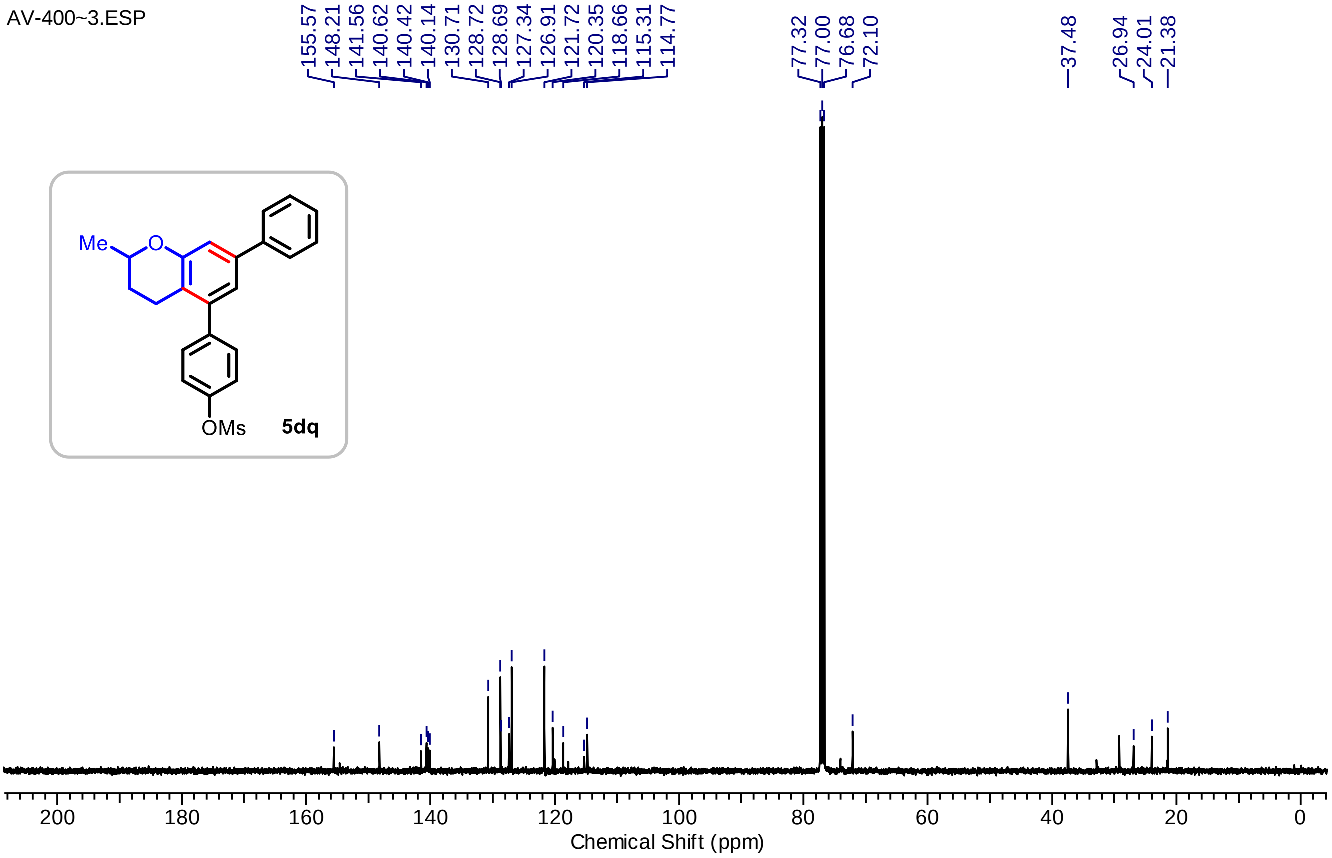


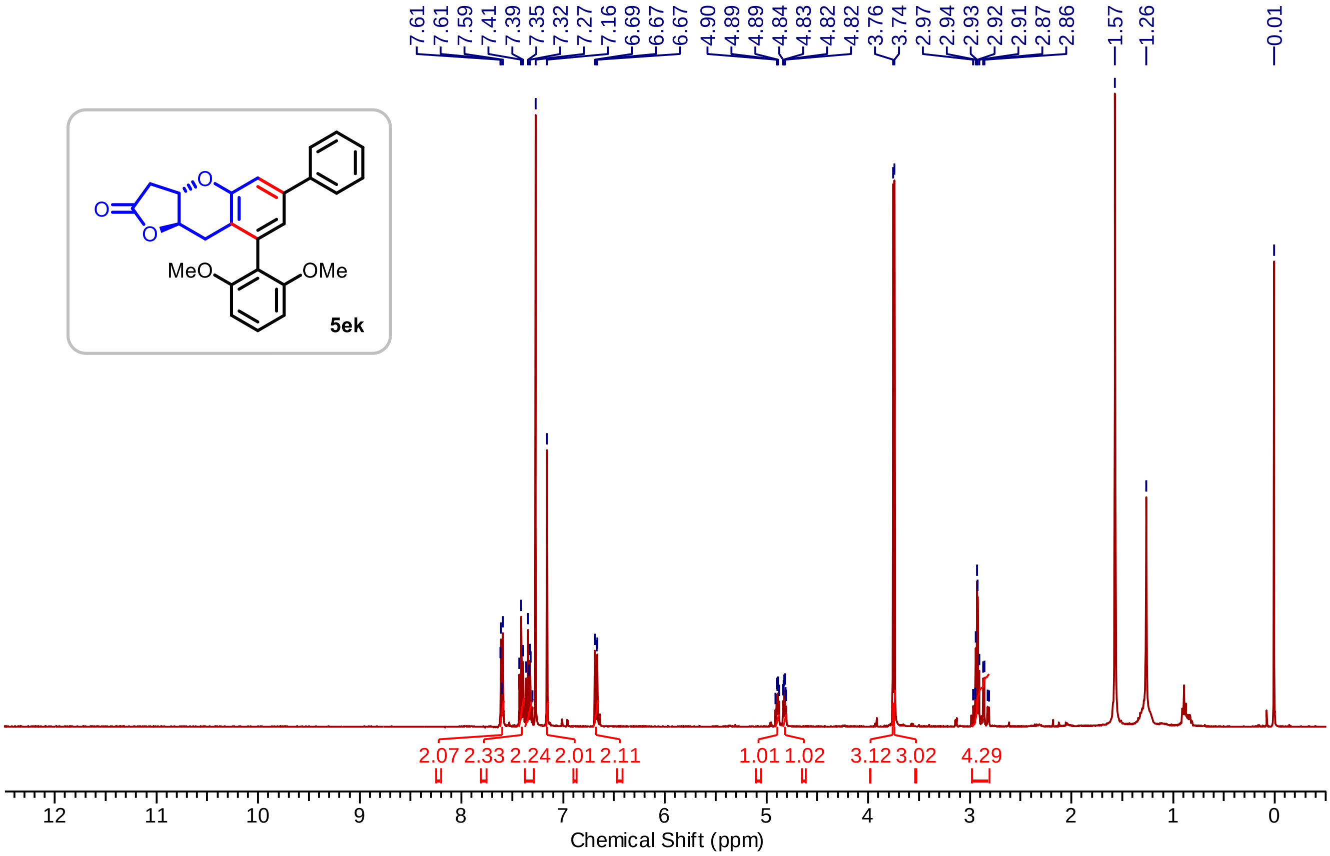
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5dq**:



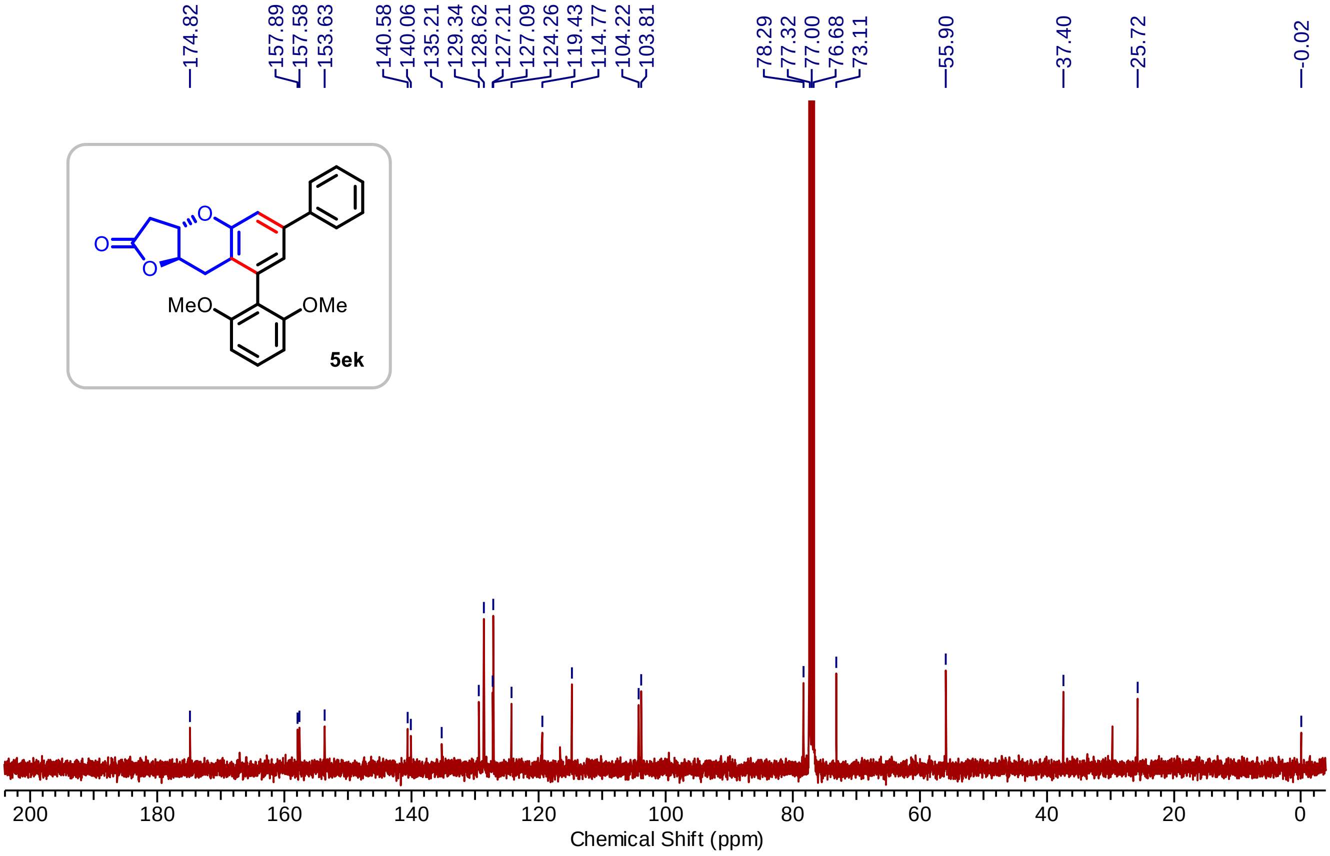
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5dq**:



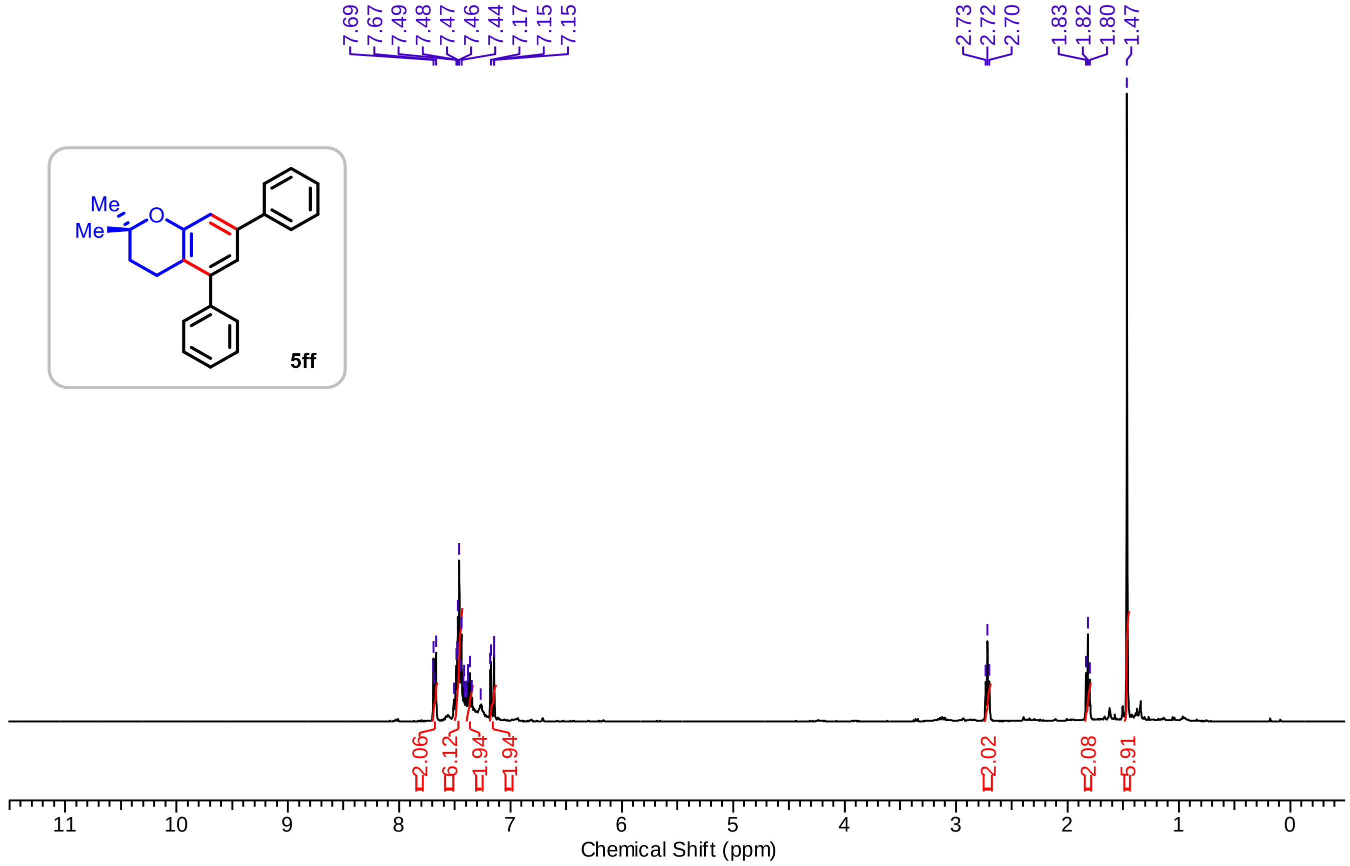
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ek**:



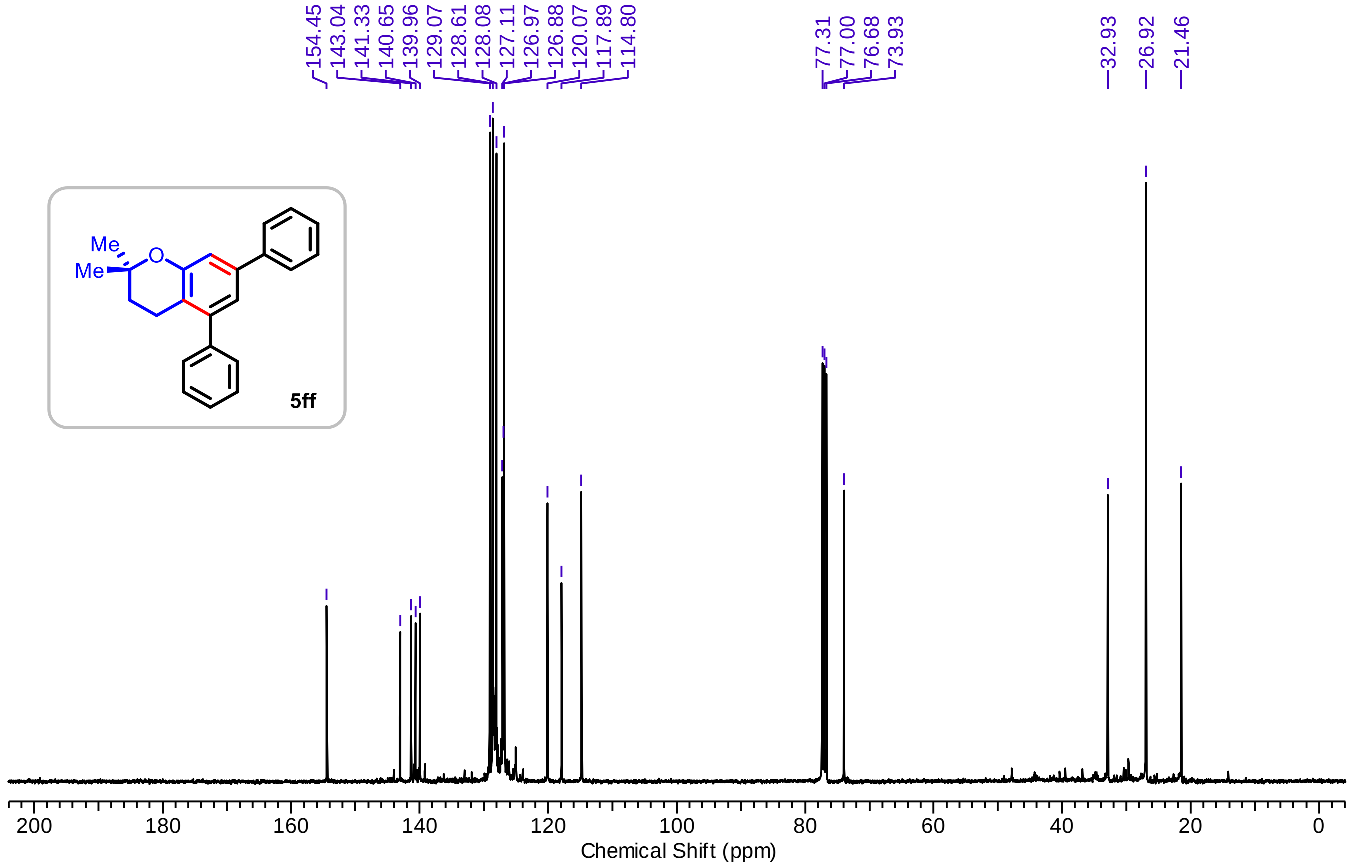
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ek**:



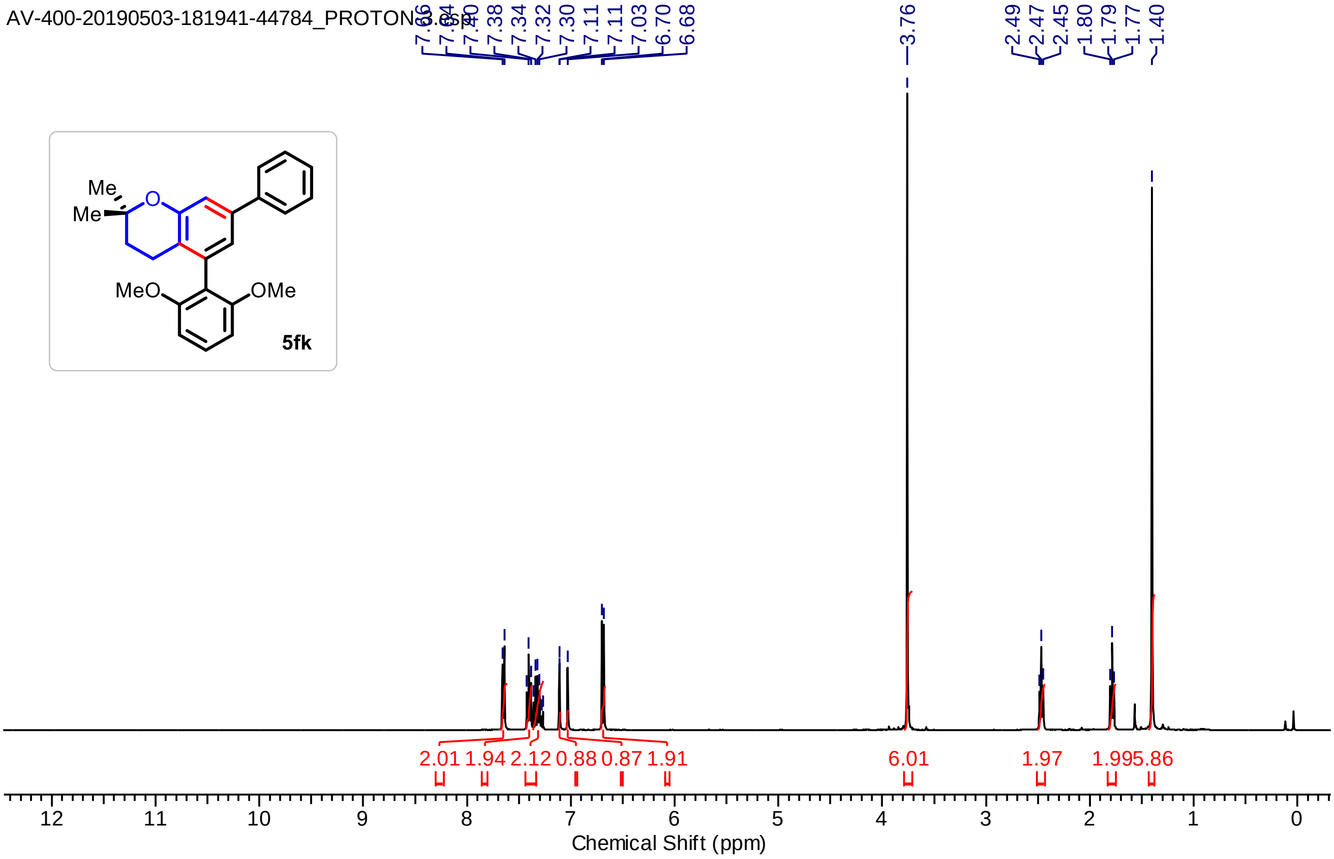
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ff**:



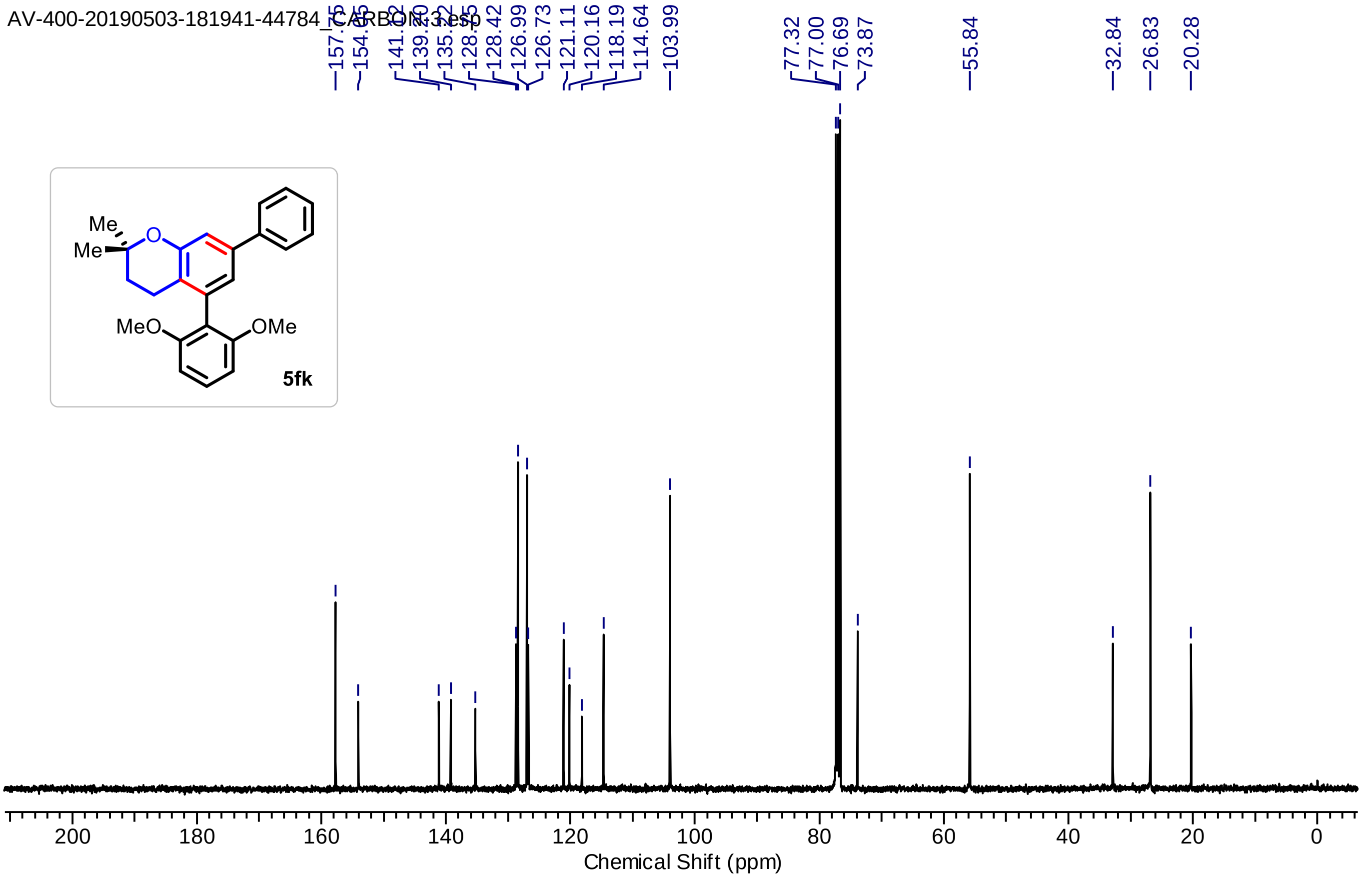
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ff**:



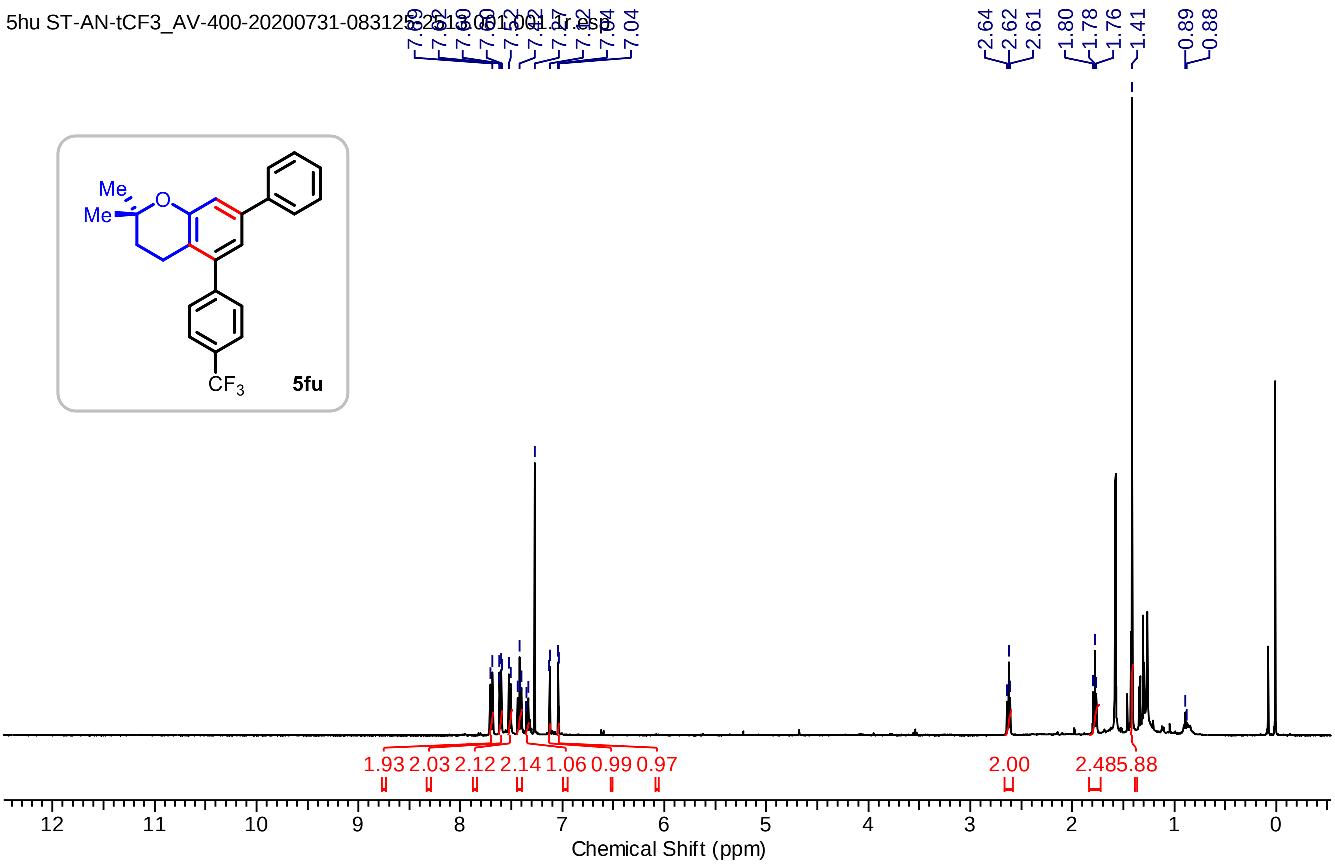
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5fk**:



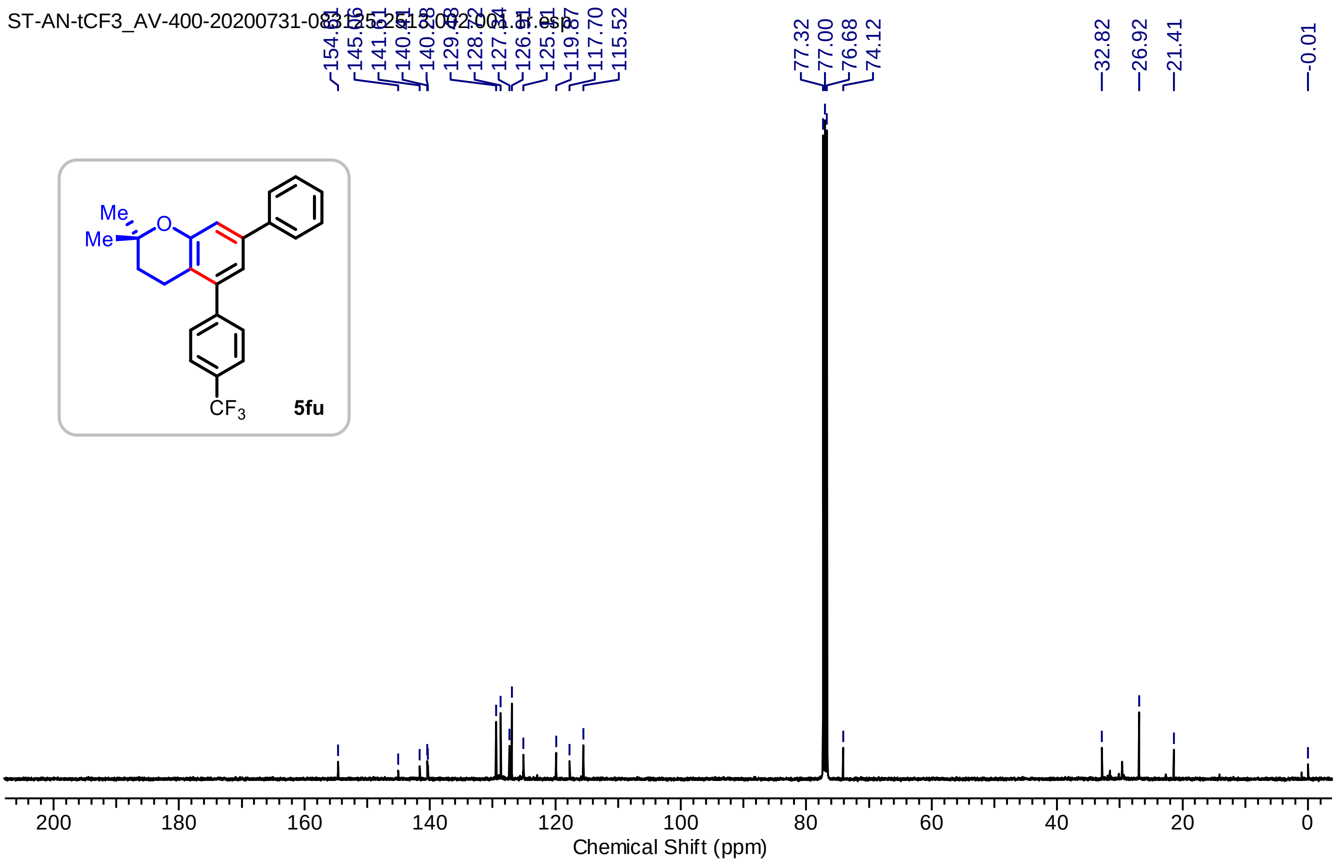
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$) of **5fk**:



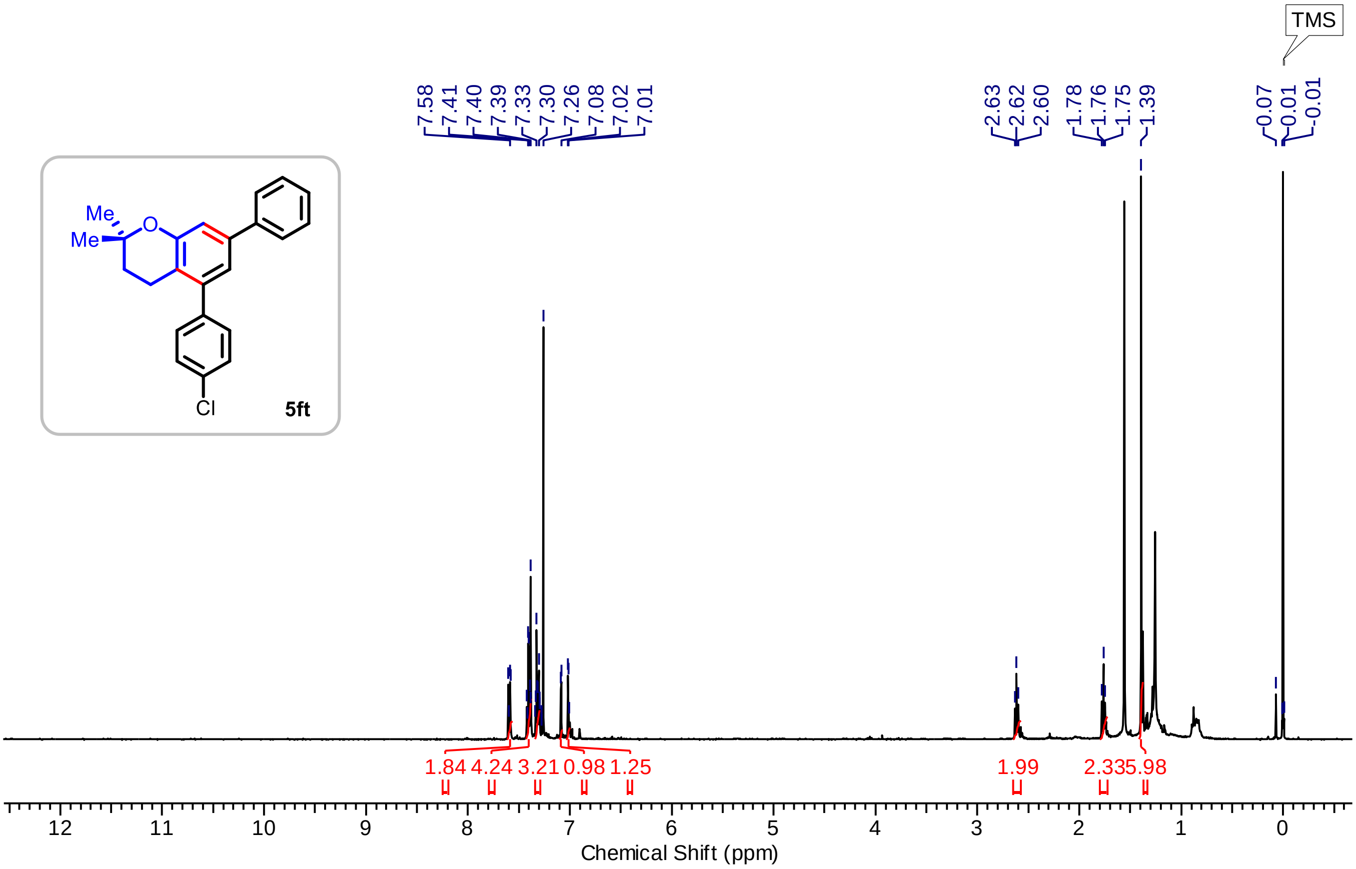
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5fu**:



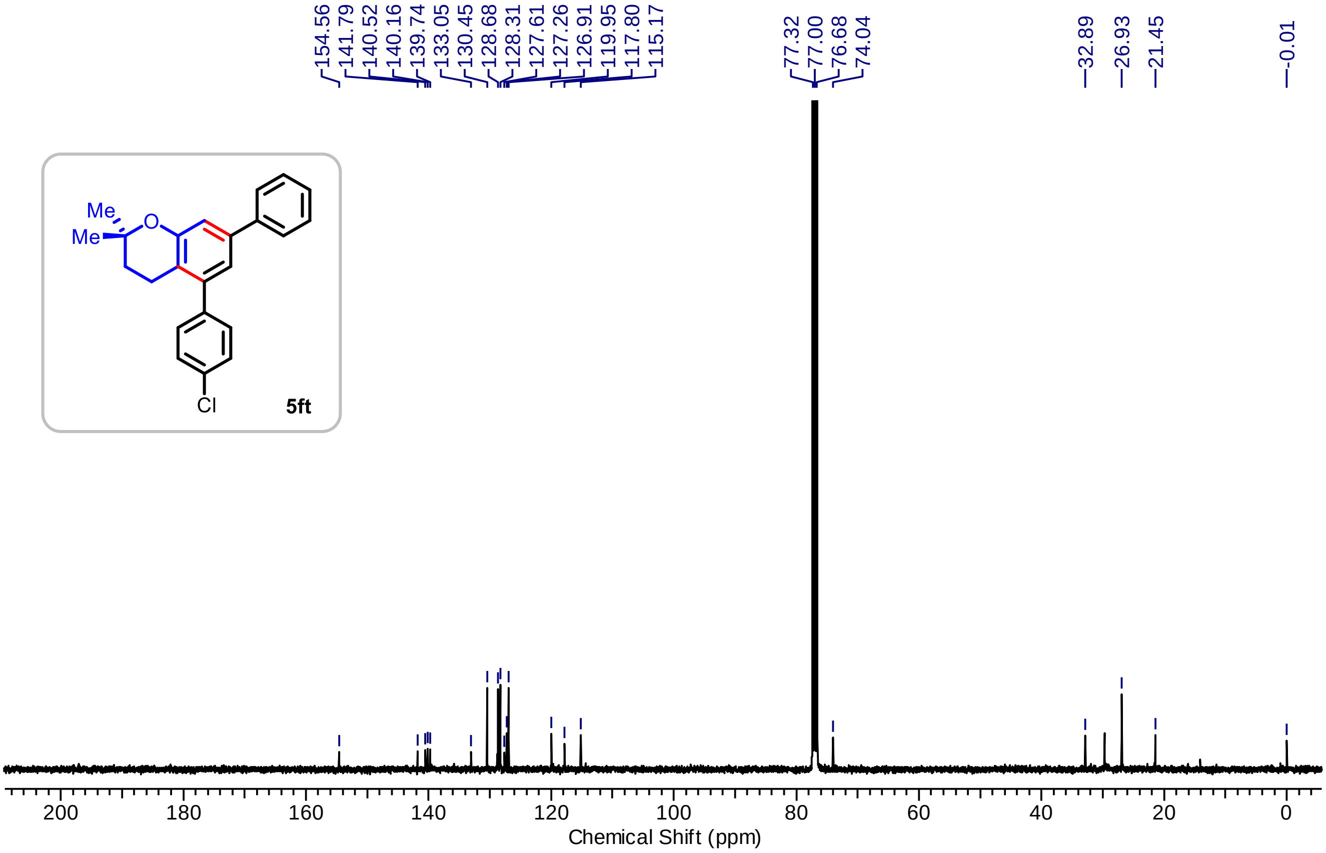
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5fu**:



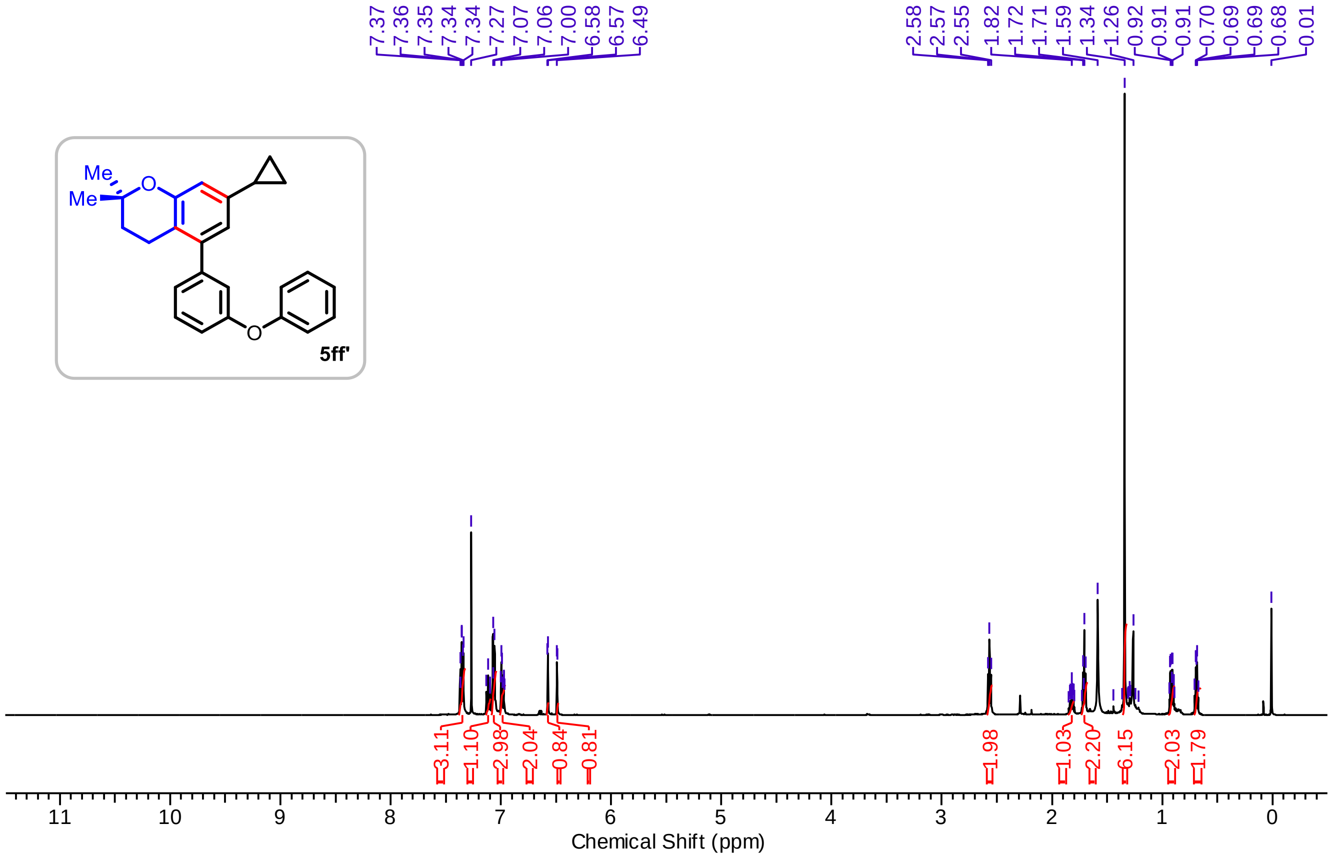
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of **5ft**:



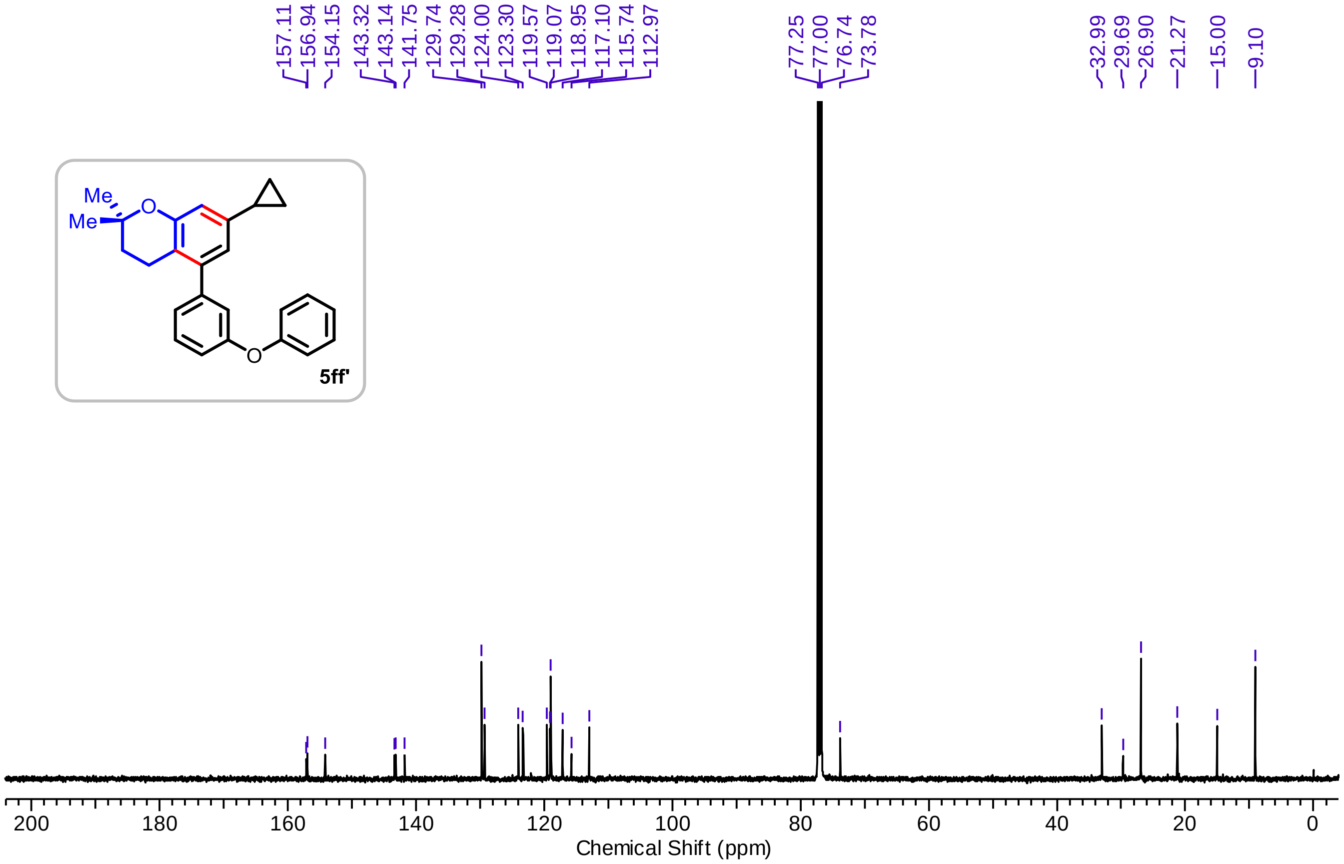
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$) of **5ft**:



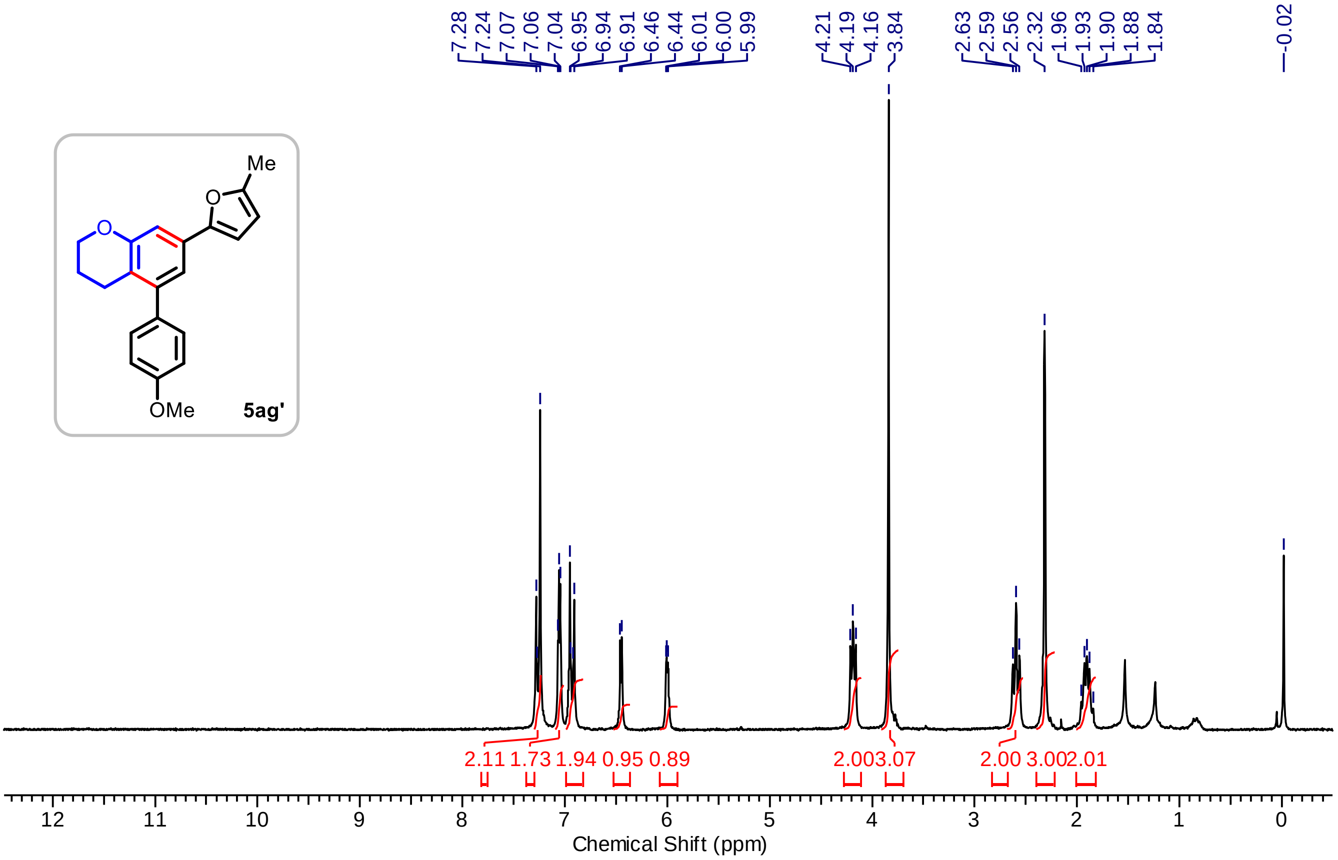
^{1}H NMR-Spectrum (500 MHz, CDCl$_3$) of **5ff'**:



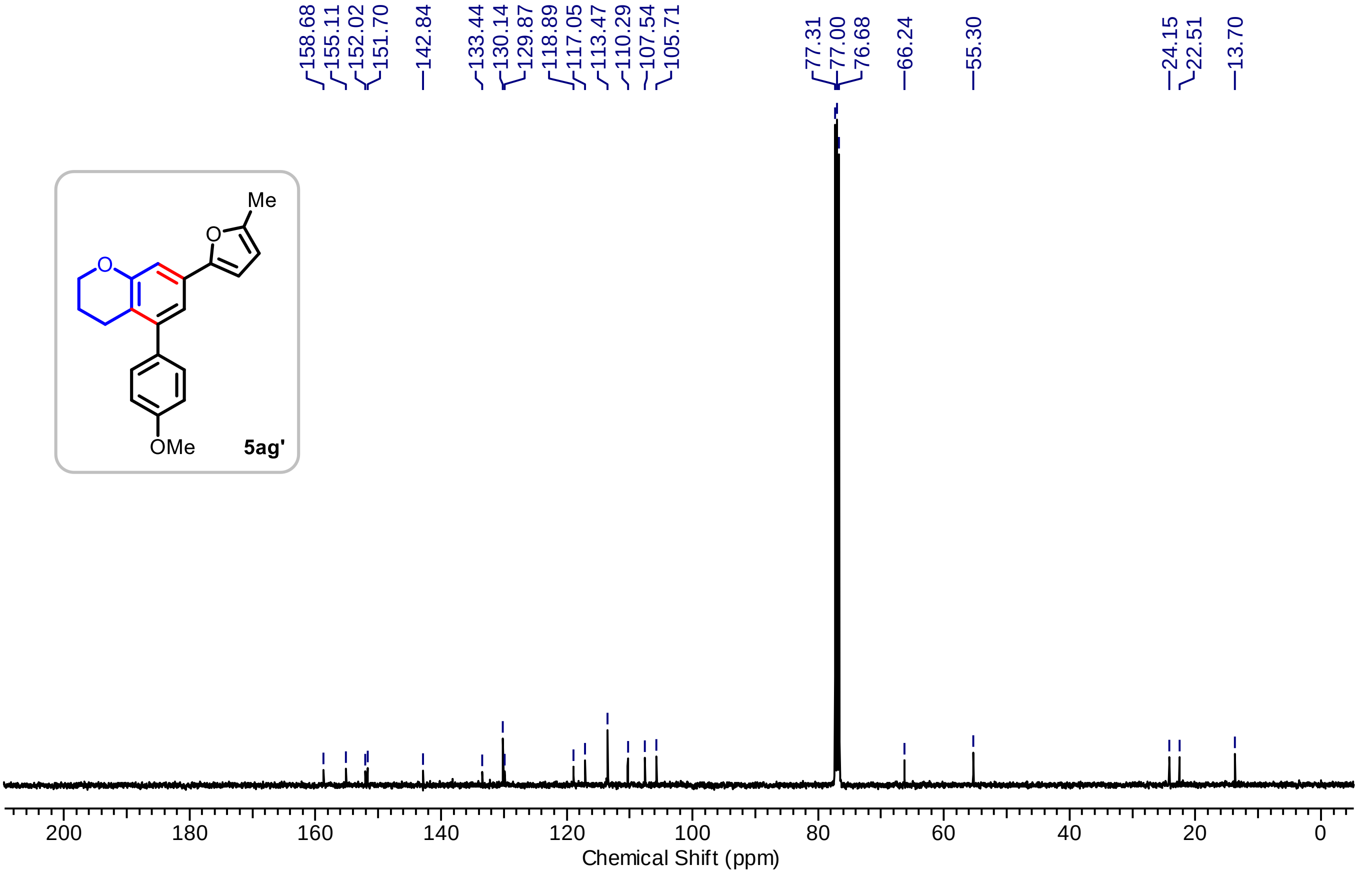
^{13}C NMR-Spectrum (126 MHz, CDCl$_3$) of **5ff'**:



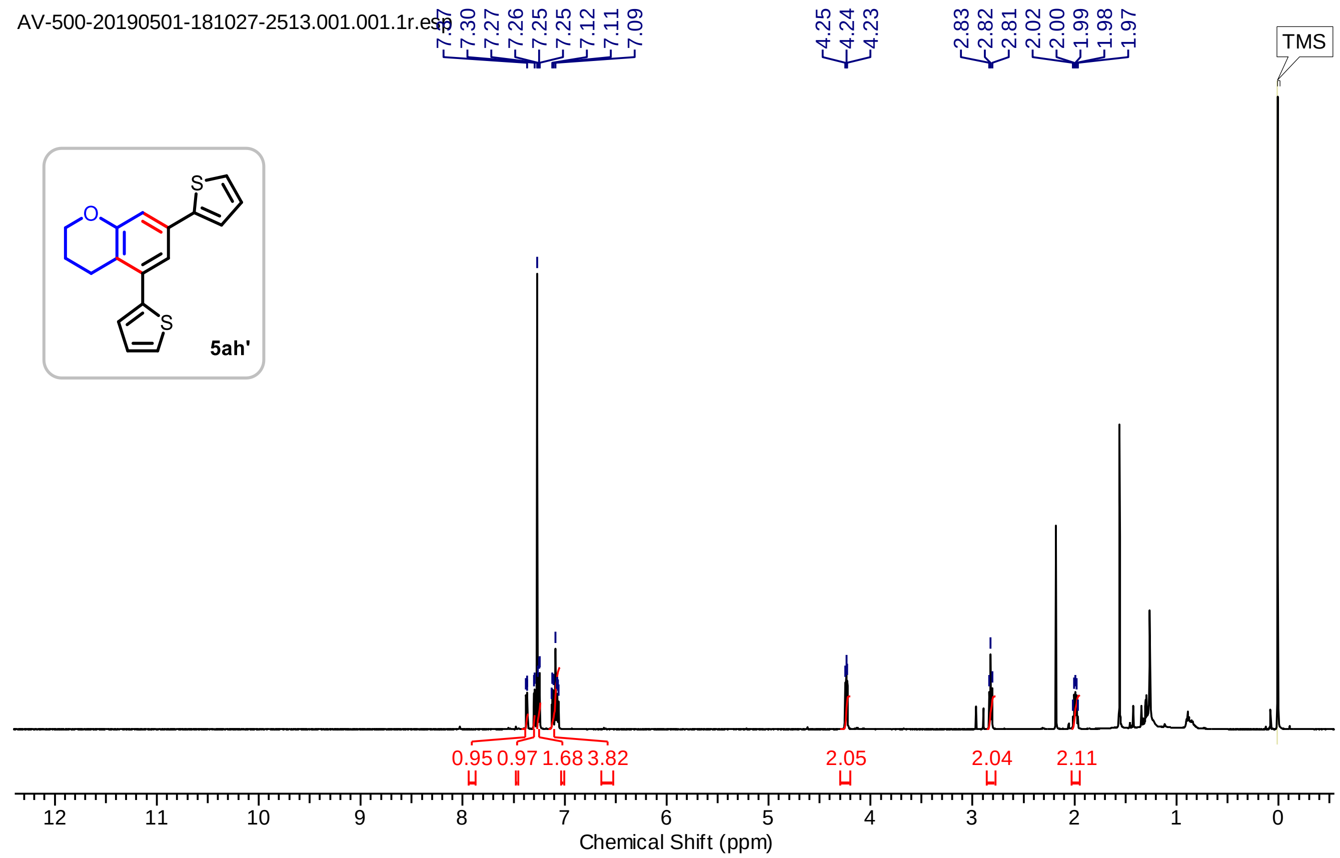
^{1}H NMR-Spectrum (200 MHz, CDCl$_3$) of **5ag’**:



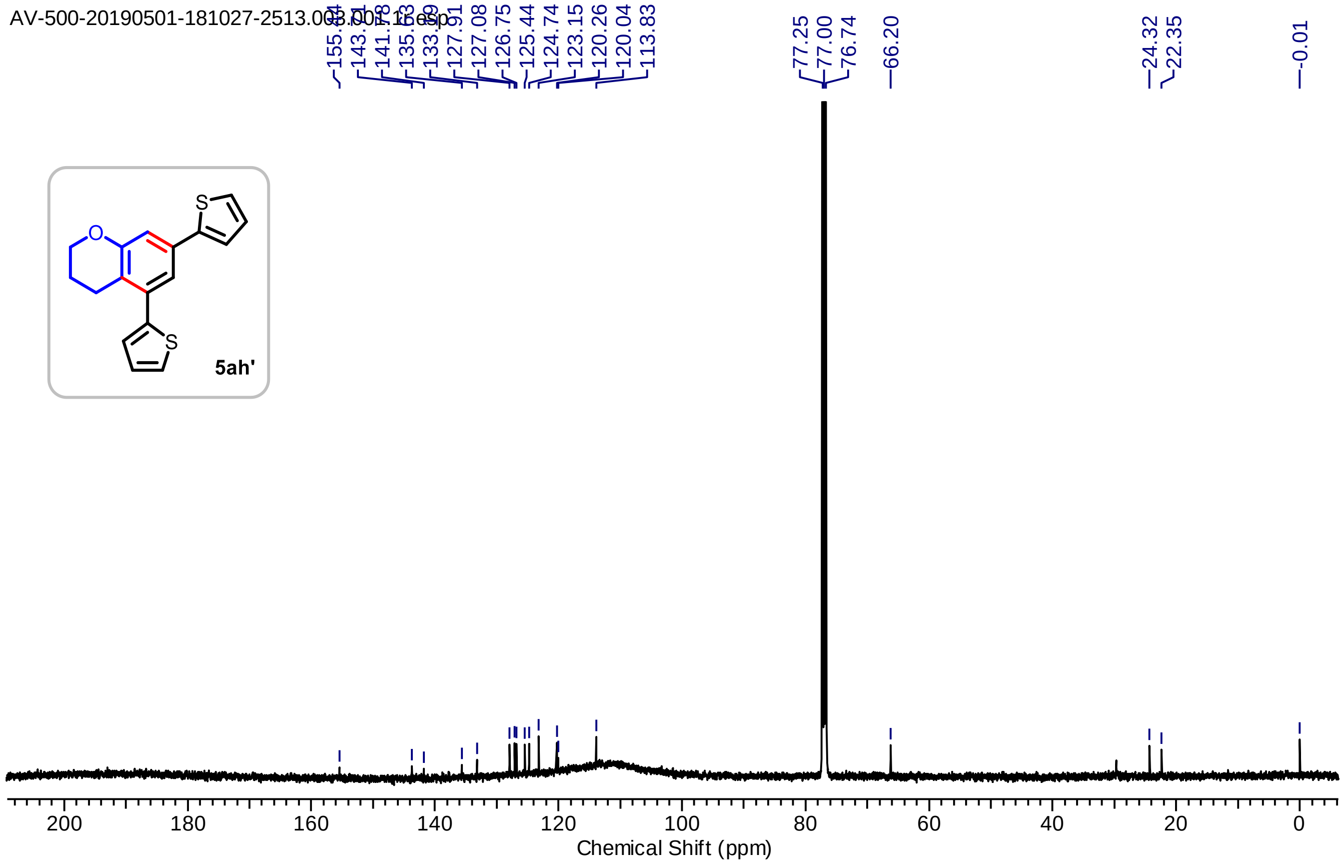
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ag’**:



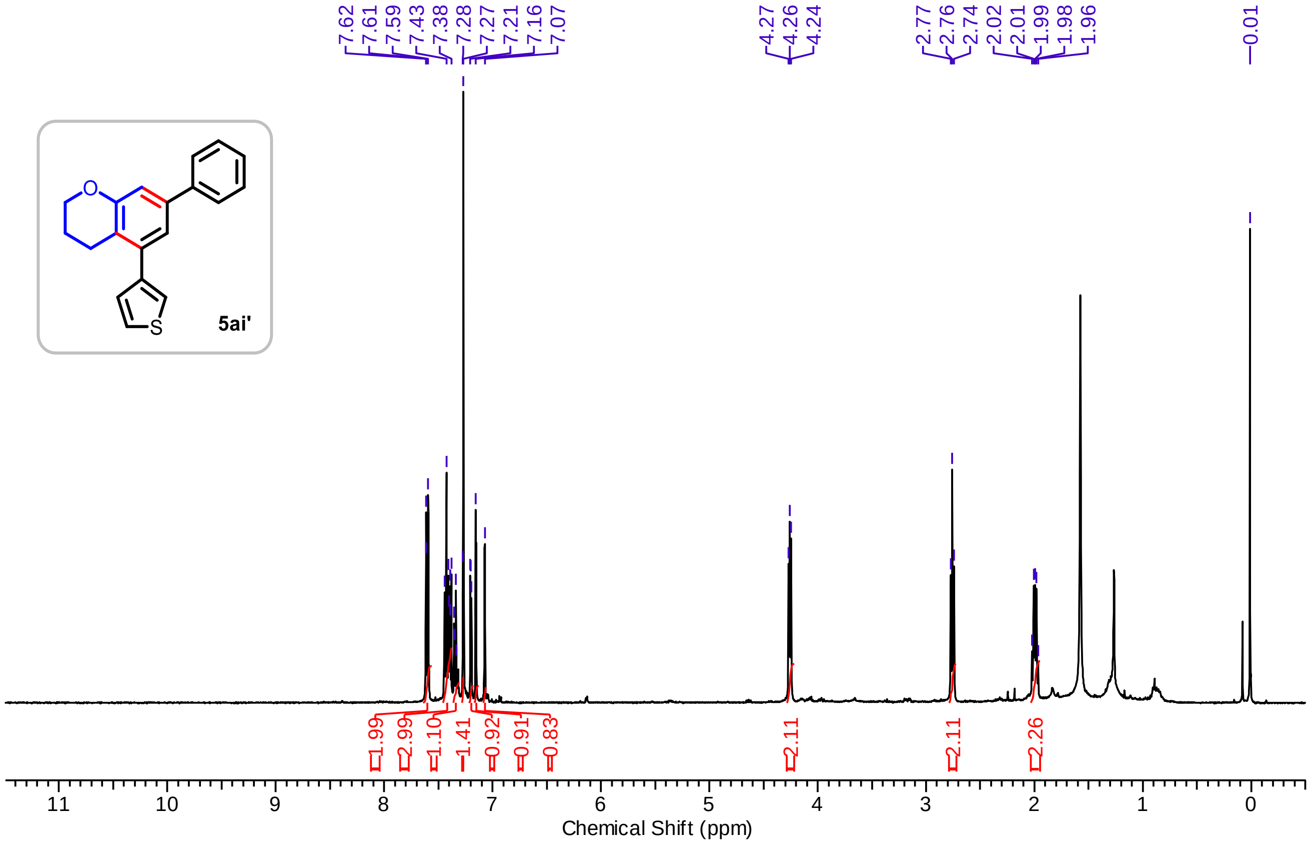
^{1}H NMR-Spectrum (500 MHz, CDCl$_3$) of **5ah'**:



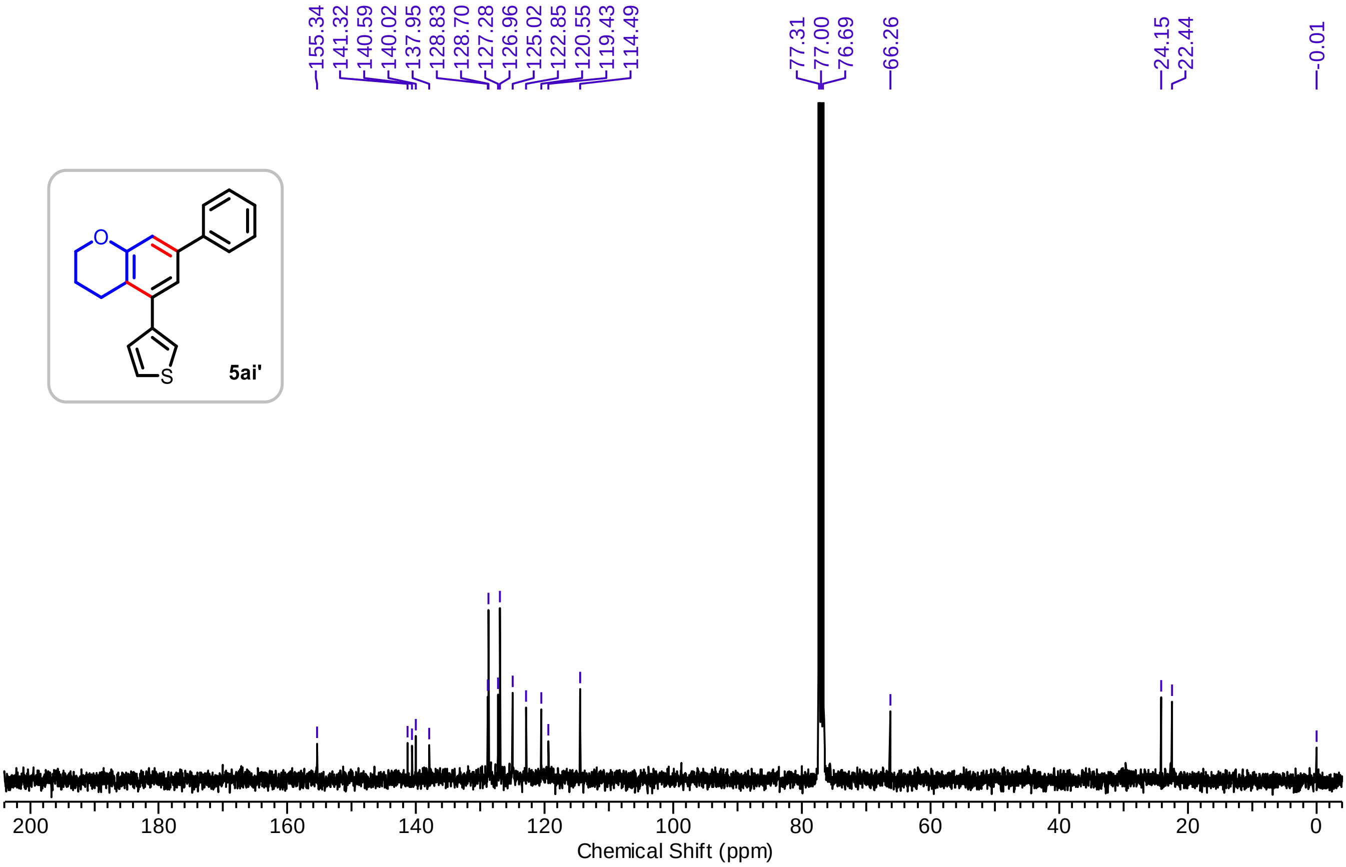
^{13}C NMR-Spectrum (126 MHz, CDCl$_3$) of **5ah'**:



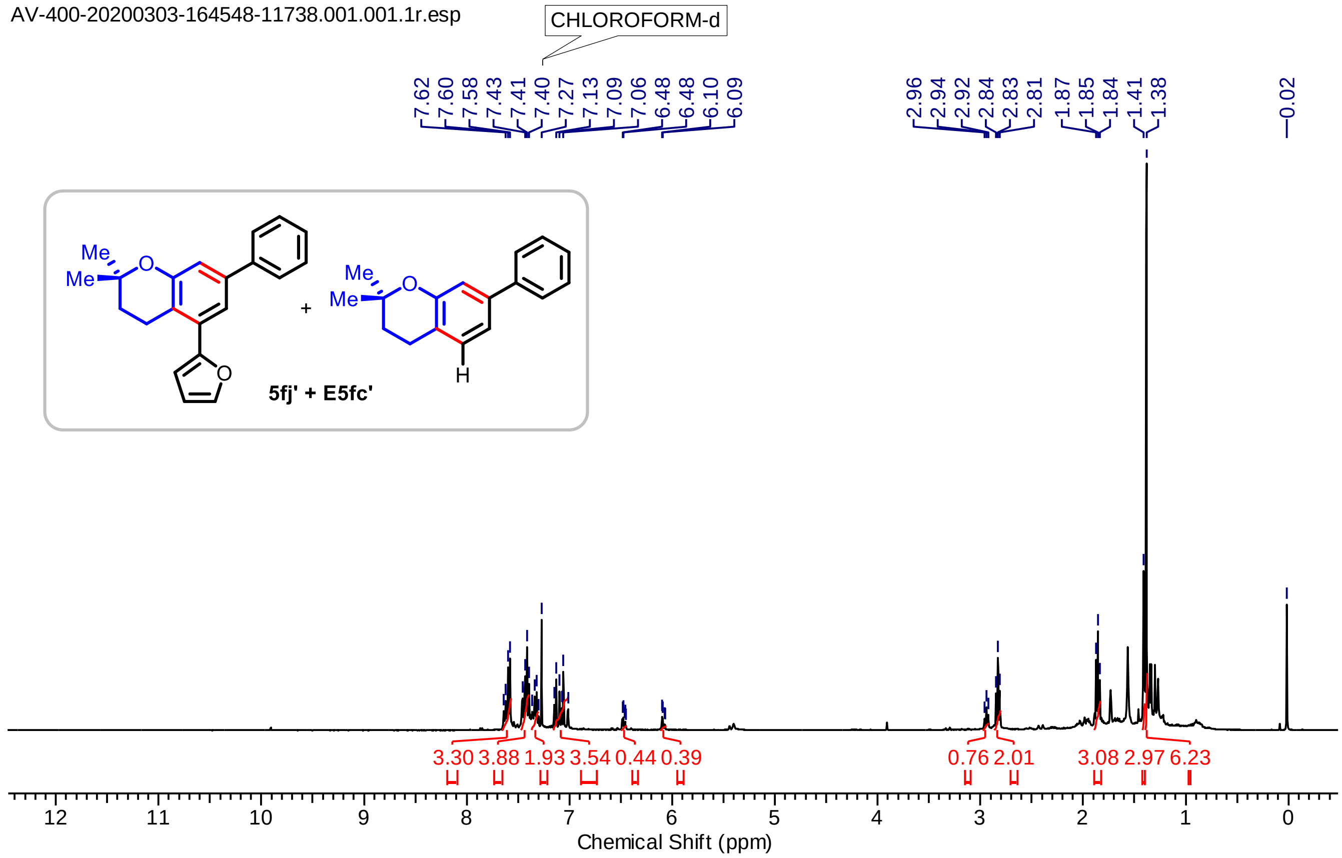
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ai’**:



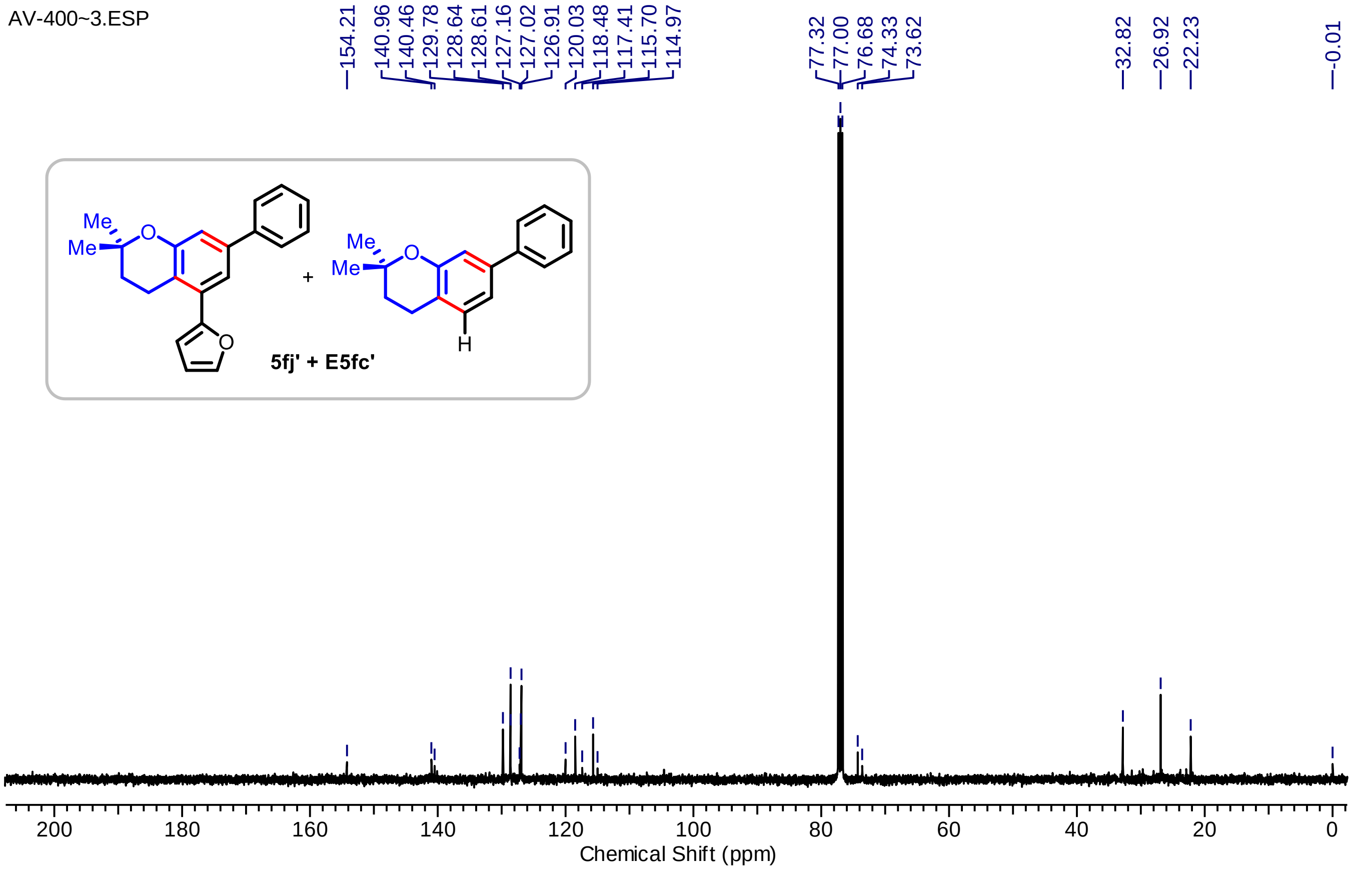
^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ai’**:



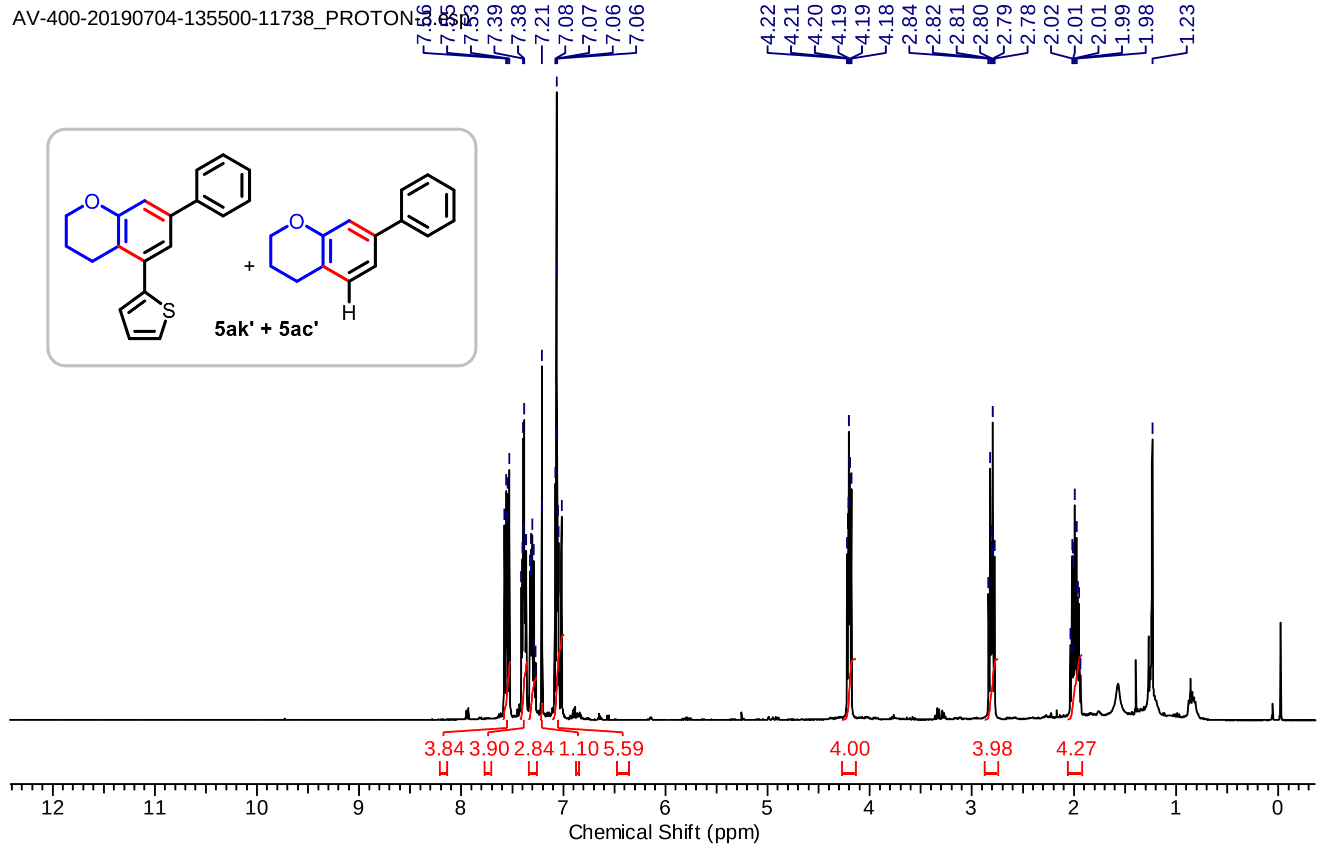
^{1}H NMR-Spectrum (400 MHz, $CDCl_3$) of a mixture of **5fj’**and**E5fc’**:



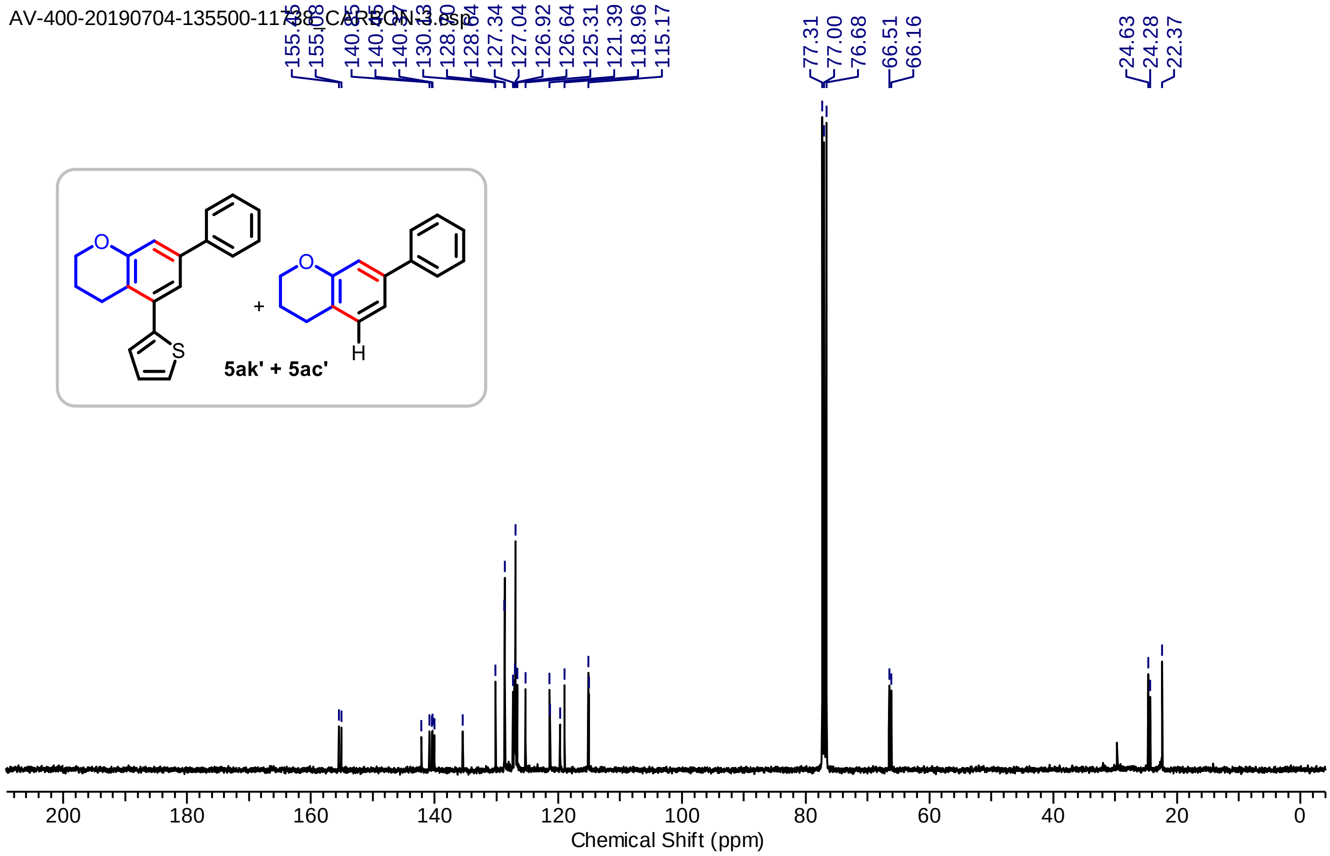
^{13}C NMR-Spectrum (101 MHz, $CDCl_3$)of a mixture of **5fj’**and **E5fc’**:



^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of a mixture of **5ak'** and **5ac'**:

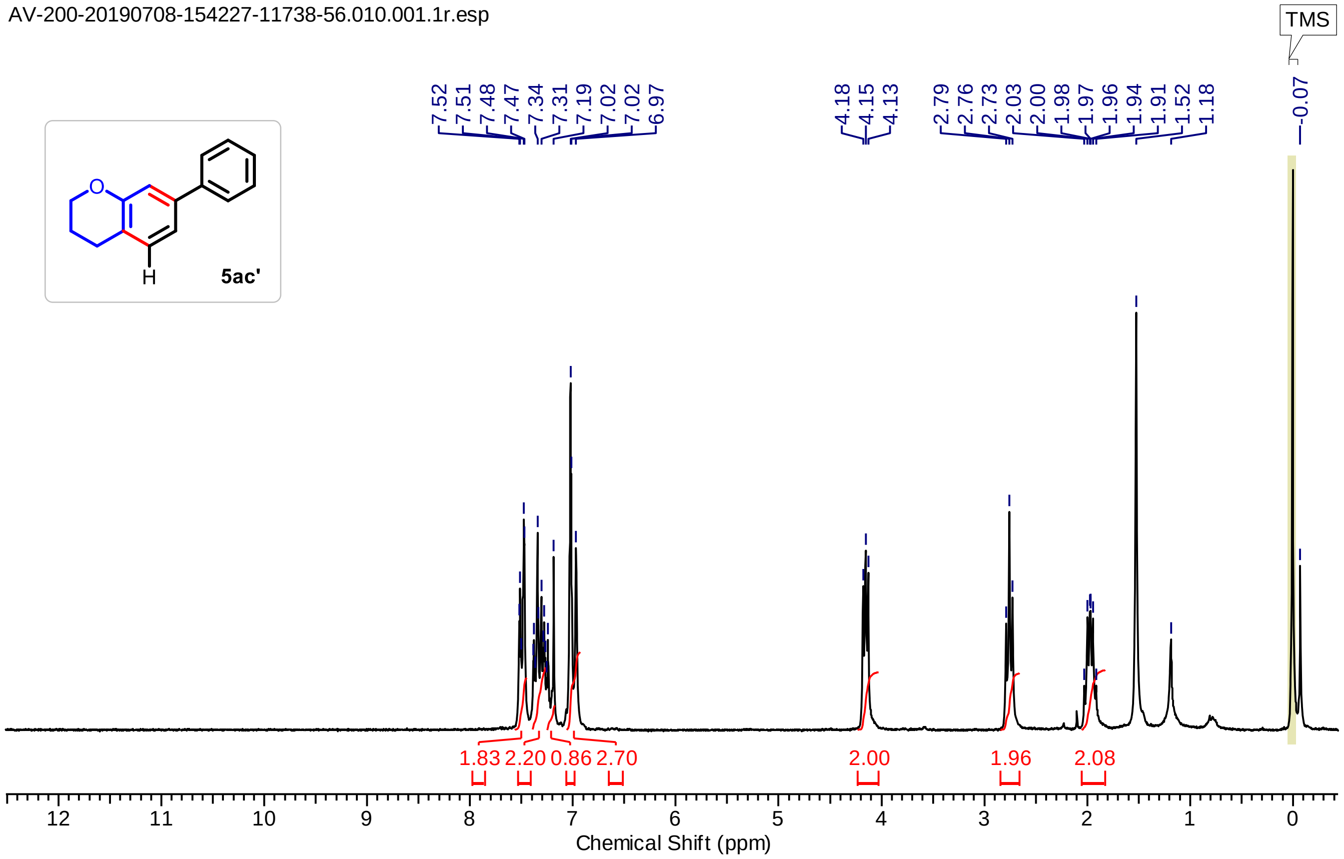


^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of a mixture of **5ak'** and **5ac'**:



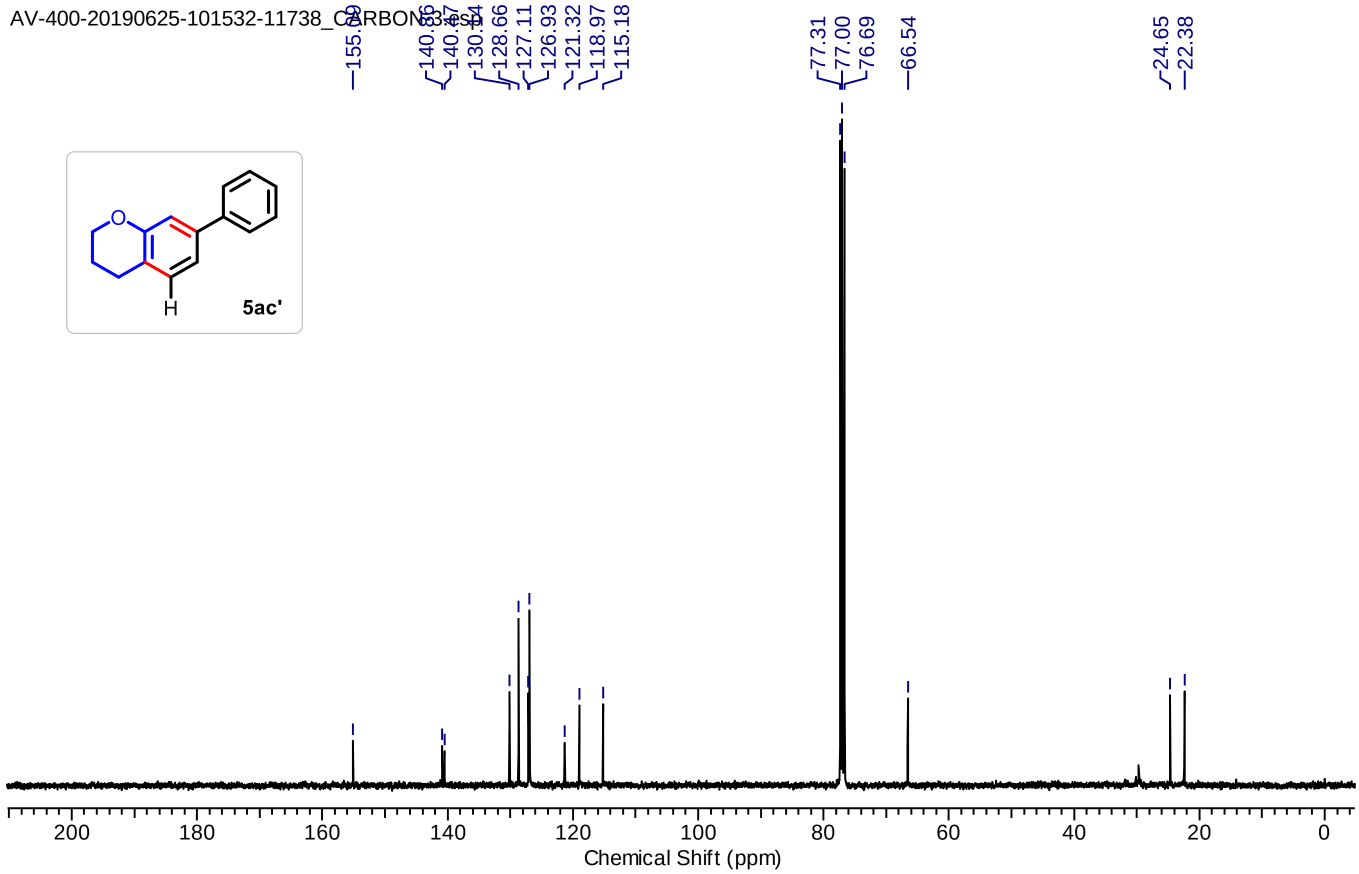
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ac'**(prepared from **2a** and **4l'**):

AV-200-20190708-154227-11738-56.010.001.1r.esp

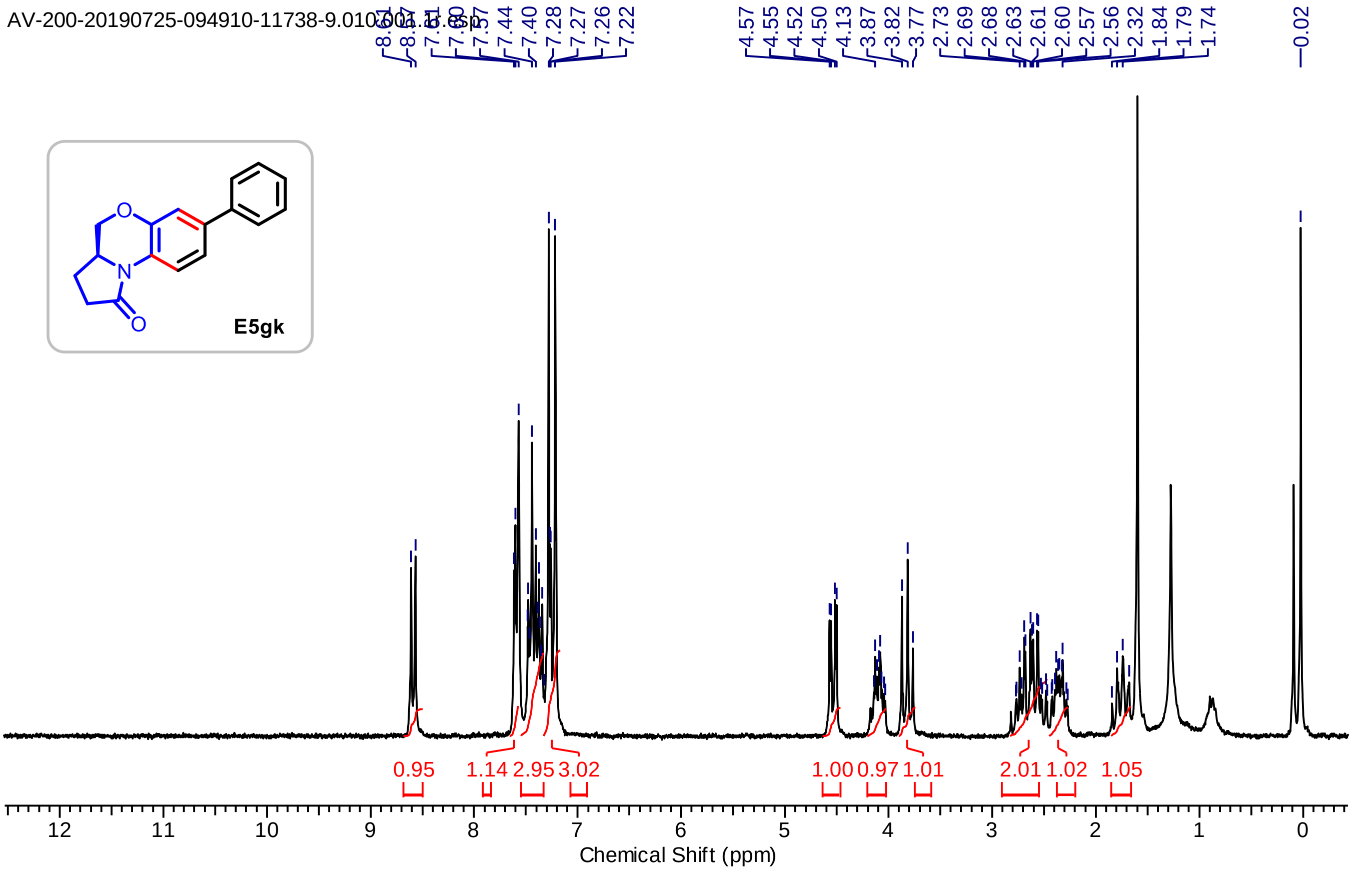


^{13}C NMR-Spectrum (101 MHz, CDCl$_3$)of **5ac'**(prepared from **2a** and **4l'**):

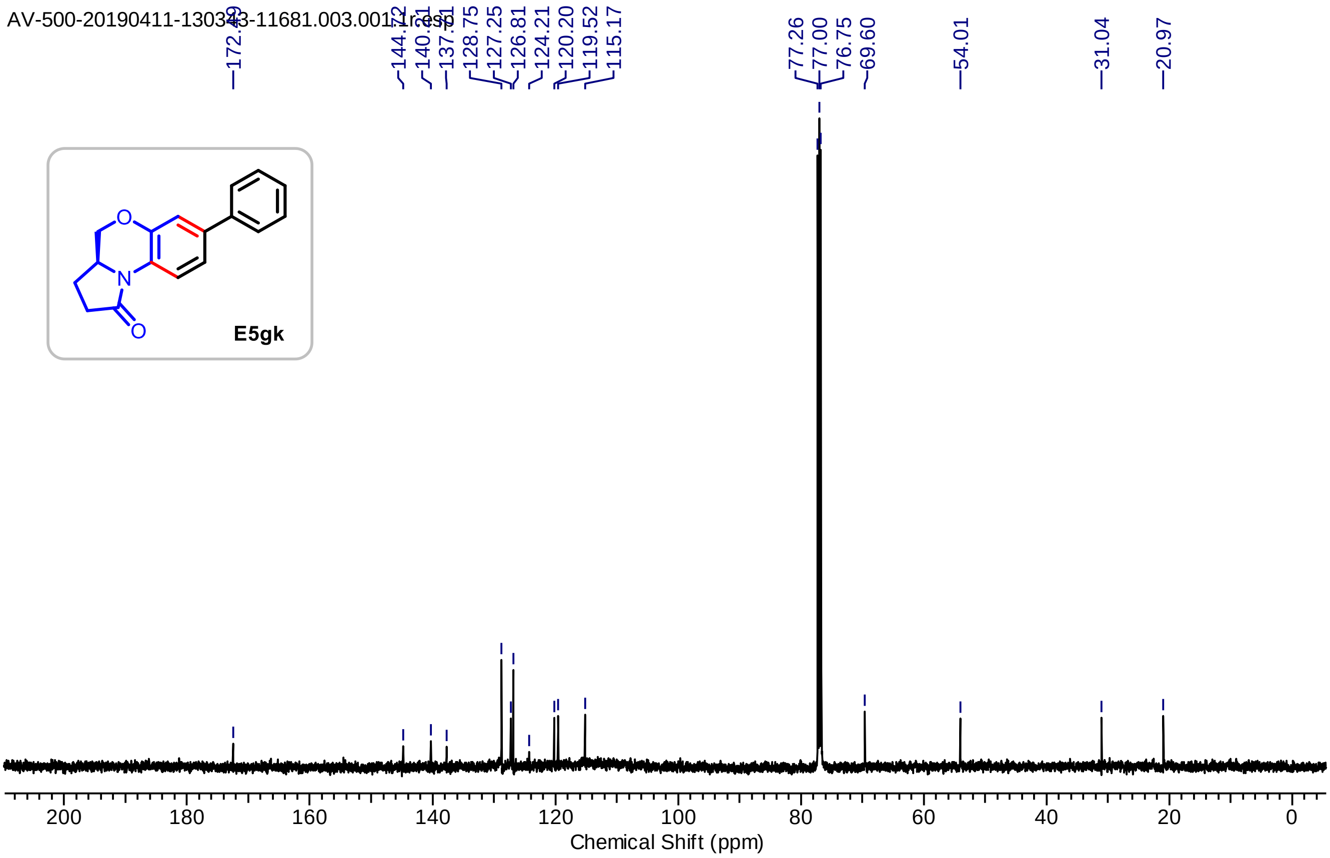
AV-400-20190625-101532-11738_CARBON-3.esp



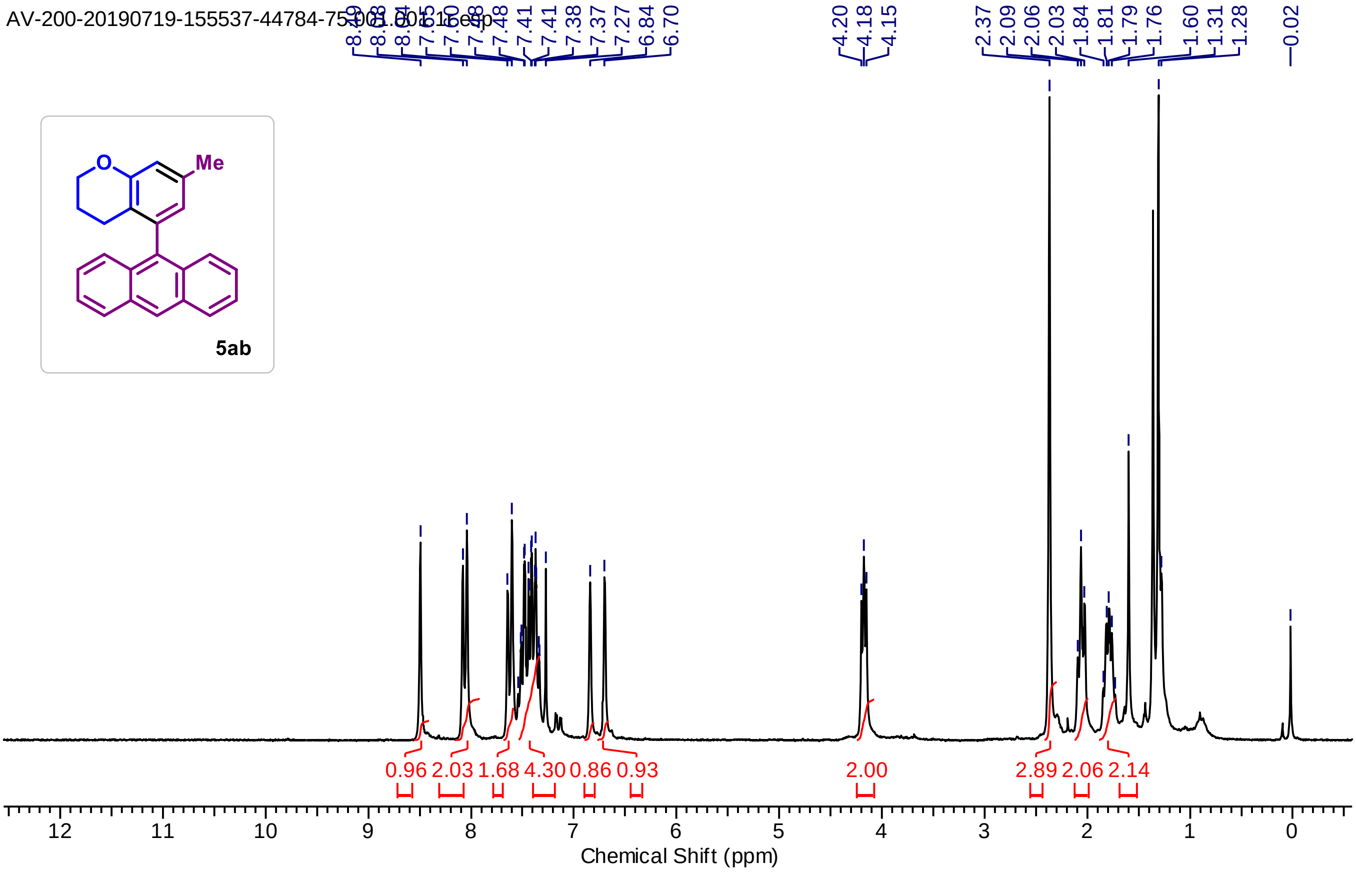
^{1}H NMR-Spectrum (200 MHz, $CDCl_3$) of **E5gk**(prepared from **2g** and **4k**):



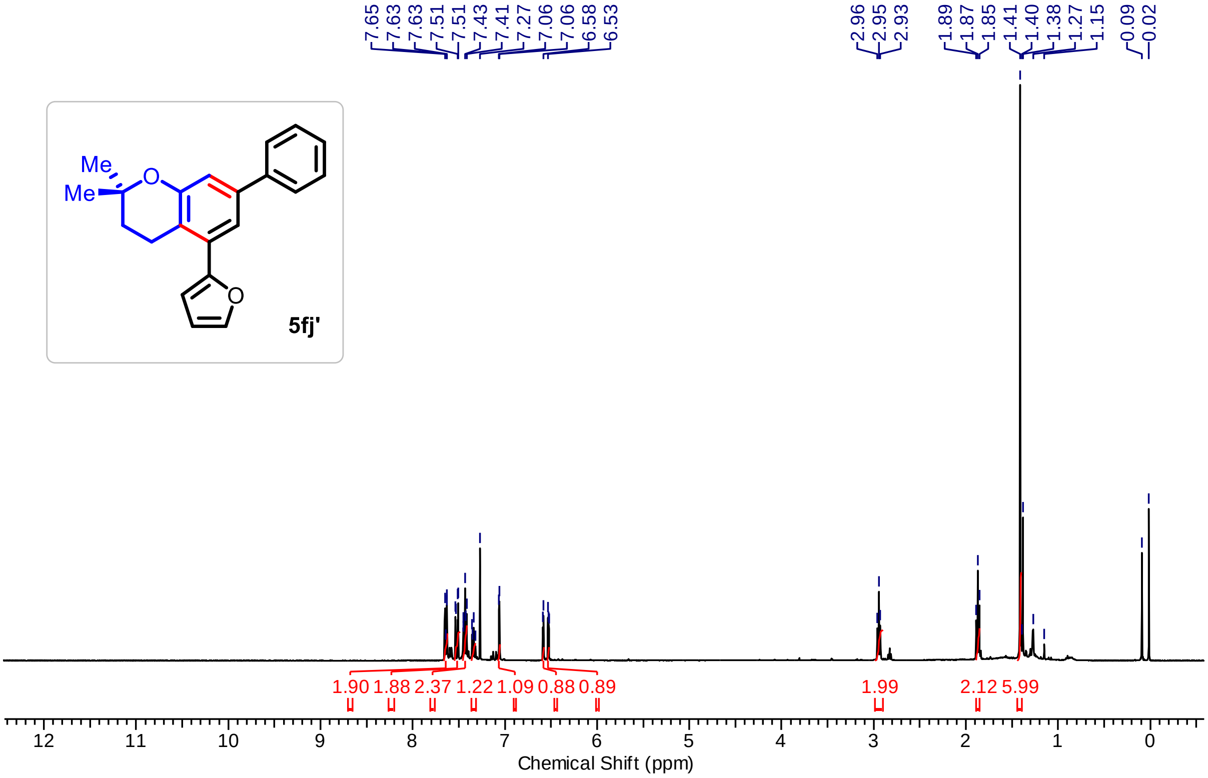
^{13}C NMR-Spectrum (126 MHz, $CDCl_3$)of **E5gk**(prepared from **2g** and **4k**):



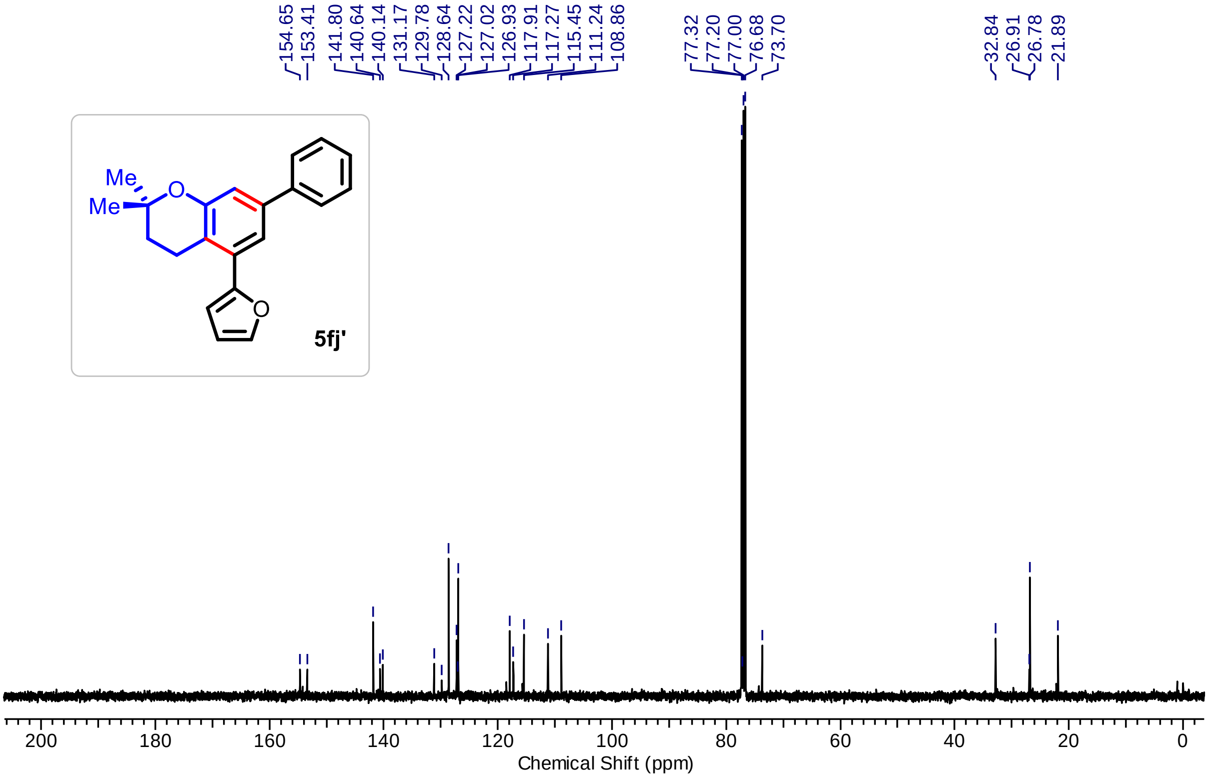
^{1}H NMR-Spectrum (200 MHz, CDCl$_3$) of **5ab** (prepared from **T3ab**):



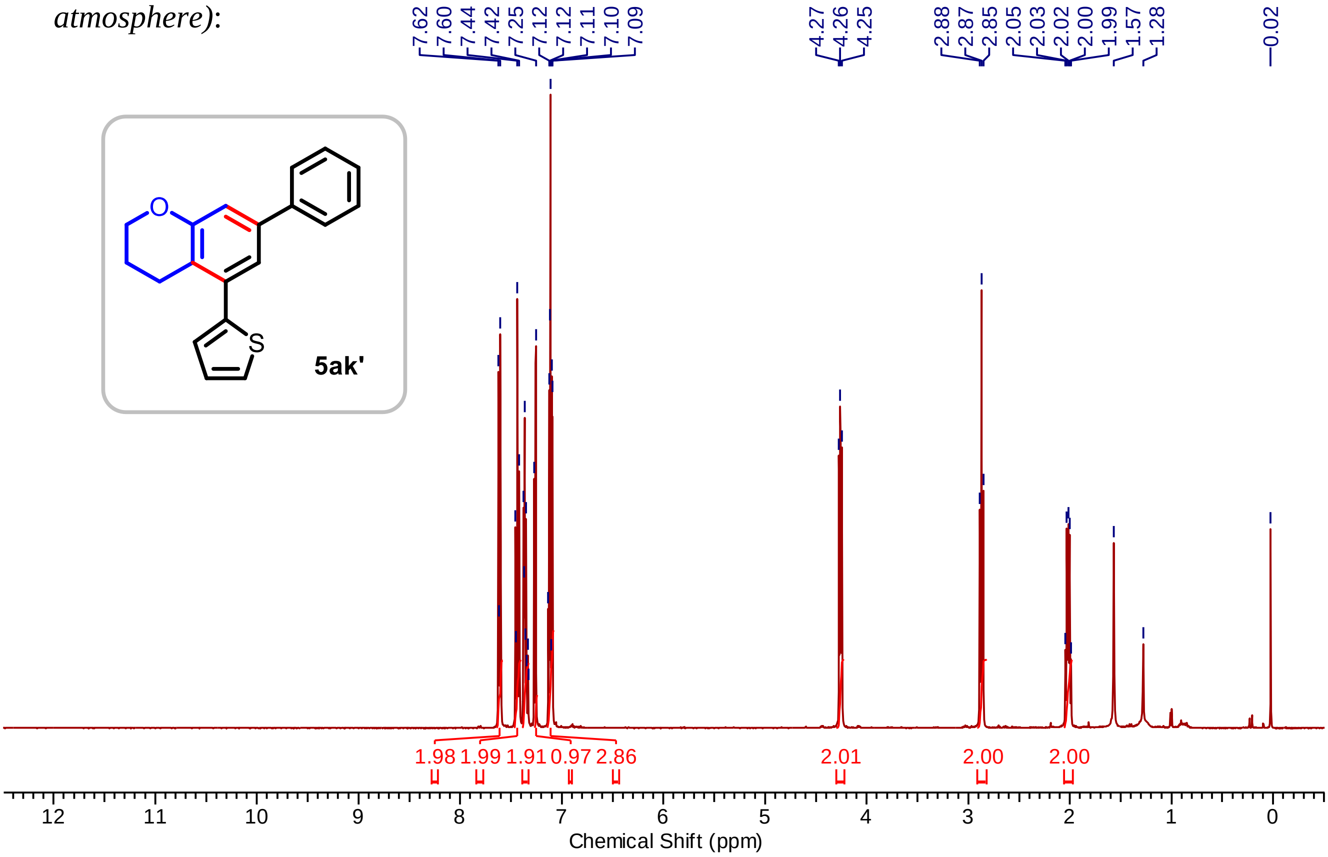
^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5fj’** *(obtained from the reaction under oxygen atmosphere)*:



^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5fj’**:



^{1}H NMR-Spectrum (400 MHz, CDCl$_3$) of **5ak’***(obtained from the reaction under oxygen atmosphere)*:



^{13}C NMR-Spectrum (101 MHz, CDCl$_3$) of **5ak’**: