NHC-Catalyzed Reaction of Enals with Hydroxy Chalcones: Diastereoselective Synthesis of Functionalized Coumarins

Anup Bhunia,[†] Atanu Patra,[†] Vedavati G. Puranik,[‡] and Akkattu T. Biju*[†]

[†]Organic Chemistry Division, [‡]Centre for Material Characterization CSIR-National Chemical Laboratory (CSIR-NCL), Dr. Homi Bhabha Road, Pune - 411008, India at.biju@ncl.res.in

Supporting Information

1. General Information	S2
2. General Procedure for the Optimization of the Reaction Conditions	S3
3. Optimization Studies	S4
4. General Procedure for the NHC-Catalyzed Synthesis of Functionalized Coumarins	S5
5. Mechanistic Experiments	S 6
6. Synthesis and Characterization of 2'-Hydroxy Chalcones	S25
7. Synthesis and Characterization Functionalized Coumarins	S34
8. ¹ H and ¹³ C NMR Spectra 2'-Hydroxy Chalcones	S51
9. ¹ H and ¹³ C NMR Spectra Functionalized Coumarins	S67

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw cap. Dry DME was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The 2'-hydroxy acetophenone was purchased from commercial sources, 2-acetyl-1-napthol was purchased from Sigma Aldrich, 5'- bromo-2'-hydroxy acetophenone was purchased from Acros Organics and they were used without any further purification. The α , β -unsaturated aldehydes were synthesized from corresponding aldehydes following the literature procedure.¹ DBU was purchased from Sigma Aldrich and was distilled, prior to use. The imidazolium salt **4** was synthesized following the literature procedure.²

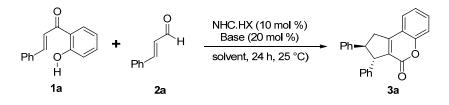
Analytical thin layer chromatography was performed on TLC Silica gel 60 F_{254} . Visualization was accomplished with short wave UV light or KMnO4 staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with solvents as indicated.

All compounds were fully characterized. ¹H and ¹³C NMR spectra were recorded on Bruker AV 400, AV 500, and JEOL 400 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 (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm). Infrared spectra were recorded on a Perkin-Elmer 1615 FT Infrared Spectrophotometer Model 60B. The wave numbers (n) of recorded IR-signals are quoted in cm⁻¹. HRMS mass spectra were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump.

¹ (a) Wube, A. A.; Hüfner, A.; Thomaschitz, C.; Blunder, M.; Kollroser, M.; Bauer, R.; Bucar, F. *Bioorg. Med. Chem.* **2011**, *19*, 567. (b) Orita, A.; Uehara, G.; Miwa, K.; Otera, J. *Chem. Commun.* **2006**, 4729. (c) Gadakh, S. K.; Reddy, R. S.; Sudalai, A. *Tetrahedron: Asymmetry*, **2012**, *23*, 898.

² (a) Arduengo, A. J.; Krafczyk, R.; Schmutzler, R.; Craig, H. A.; Goerlich, J. R.; Marshall, W. J.; Unverzagt, M. *Tetrahedron* **1999**, *55*, 14523. (b) Cooke , J.; Lightbody, O. C. J. Chem. Educ. **2009**, *86*, 610.

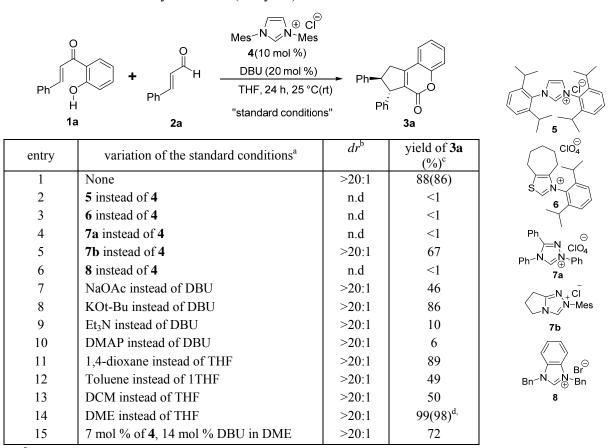
2. General Procedure for the Optimization of Reaction Conditions



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the azolium salt NHC.HX (0.025 mmol) and (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (56 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (33 mg, 31 μ L, 0.25 mmol) followed by the addition of DBU (7.6 mg, 7.5 μ L, 0.05 mmol). After 24 hour stirring, the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard.

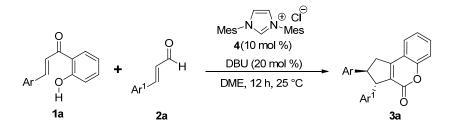
3. Optimization Studies

Our optimization study commenced with treatment of (E)-1-(2-hydroxyphenyl)-3phenylprop-2-en-1-one **1a** with *trans* cinnamaldehyde **2a**. Treatment of **1a** with **2a** in the presence of the carbene generated from **4** by deprotonation using DBU resulted in the formation of functionalized coumarin derivative **3a** in 88% yield (based on ¹H NMR spectroscopy). Notably, in contrast to this NHC, other common NHCs derived from precursors **5-8** are less effective (entries 2-5). Other bases such as NaOAc, KO*t*-Bu, NEt₃, and DMAP furnished the desired product in reduced yields (Table 1, entries 6-9). Among the various solvents screened, THF and 1,4-dioxane resulted in comparable result (entries 1 and 10). Gratifyingly, reaction carried out in DME shows excellent reactivity to get almost quantitative yield (Table 1, entry 13). Additionally, reaction carried out using 7 mol % of **4** and 14 mol % loadings of DBU, resulted in reduced the yield of **3a** (entry 14).



^a Standard conditions: **1a** (0.25 mmol), **2a** (0.25 mmol), NHC·HX (10 mol $\frac{1}{9}$), DBU (20 mol $\frac{9}{9}$), THF (1.0 mL), 25 °C and 24 h. ^b Determined by ¹H-NMR analysis of crude products. ^cThe yields were determined by ¹H-NMR analysis of crude products using CH₂Br₂ as the internal standard, Isolated yield in 1.0 mmol scale in parentheses. ^d The reaction was completed in 12 h.

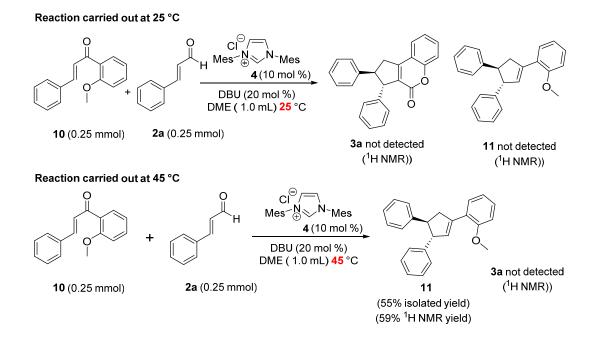
4. General Procedure for the NHC-Catalyzed Annulation Reaction



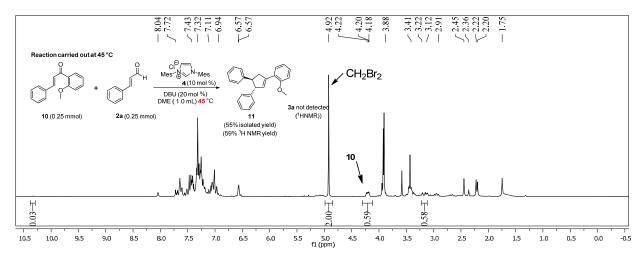
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (0.034 g, 0.1 mmol) and the 2'-hydroxychalcone **1a** (1.0 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. To this mixture was added DME (4.00 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the aldehyde **2a** (1.0 mmol) (*solid* aldehydes were transferred to the screw-capped tube by closing the argon flow and *liquid* aldehydes were transferred via syringe under argon flow) and the DBU (0.030 gm, 30 μ L, 0.20 mmol) were successively added. Then the reaction mixture was stirred at 25° C for 12 h. When the reaction is complete, the solvent was evaporated and the crude residue was purified by flash column chromatography on silica gel to afford the corresponding functionalized coumarin derivatives.

5. Mechanistic Experiments

a) Reaction Employing 2'-Methoxy Chalcone as Substrate



To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the (*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one **10** (60 mg, 0.25 mmol) and the *trans* cinnamaldehyde **2a** (33 mg, 31 μ L, 0.25 mmol) was successively added followed by DBU (7.6 mg, 7.5 μ L, 0.05 mmol). Then the reaction mixture is placed in a preheated oil bath at 45 °C. After 12 h, the reaction mixture cooled and the mixture was diluted with CH₂Cl₂ (5.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂. The solvent was evaporated and the crude residue purified by flash column chromatography on silica gel to afford (4-(2-methoxyphenyl)cyclopent-3-ene-1,2-diyl)dibenzene **11** (45 mg, 55%).



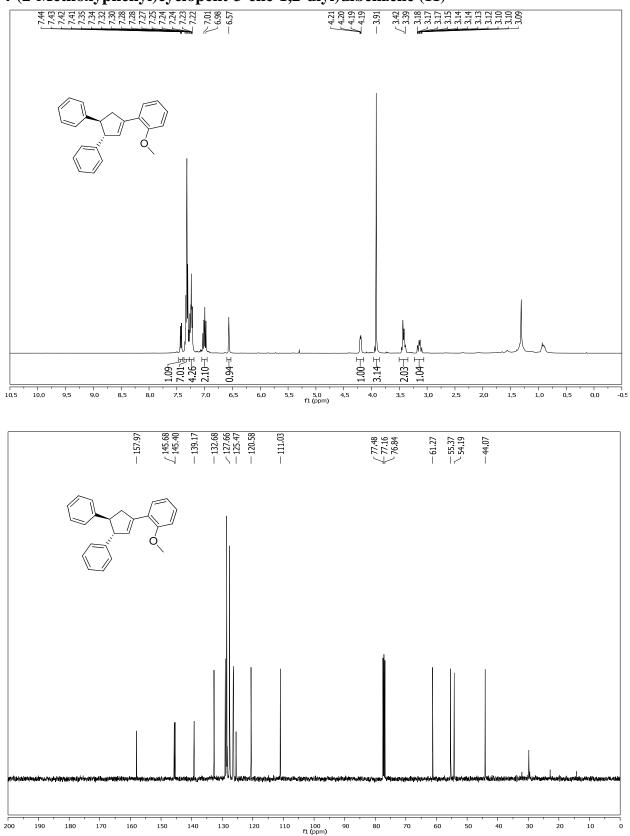
¹H-NMR of Crude Reaction Mixture after 12 h at 45 °C (CDCl₃)

4-(2-Methoxyphenyl)cyclopent-3-ene-1,2-diyl)dibenzene (11)

 R_f (Pet. ether /EtOAc = 80/20): 0.85 ¹H NMR (400 MHz, CDCl₃) δ 7.44-7.41 (m, 1H, H_{ar}), 7.35-7.28 (m, 7H, H_{ar}), 7.27-7.22 (m, 4H, H_{ar}), 7.03-6.98 (m, 2H, H_{ar}), 6.57 (bs, 1H, CH), 4.21-4.19 (m, 1H, CH), 3.91 (s, 3H, CH₃), 3.46-3.39 (m, 2H), 3.18-3.09 (m, 1H, CH). ¹³C NMR (100

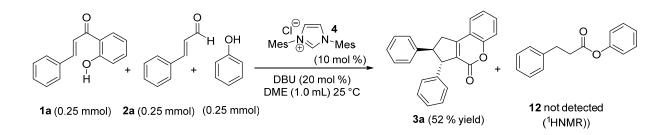
MHz, CDCl₃) δ 157.97, 145.68, 145.40, 139.17, 132.68, 129.00, 128.54, 128.51, 128.36, 127.66, 127.57, 126.40, 126.27, 125.47, 120.58, 111.03, 61.27, 55.37, 54.19, 44.07. **HRMS** calculated [M+H]⁺ for C₂₄H₂₃O: 327.1743, found: 327.1735. **FTIR** (**cm⁻¹**) 3060, 3026, 2925, 2852, 1600, 1576, 1492, 1454, 1435, 1295, 1251, 1181, 1161, 1125, 1077, 1057, 1028, 992, 868, 751, 700, 668, 563, 493.

This experiment reveals that in the absence of free OH group at the 2'-position of chalcone, the reaction does not proceed at all. However the reaction leads to the formation of cyclopentene derivative **11** at 45 °C without the formation of the functionalized coumarin **3a**.

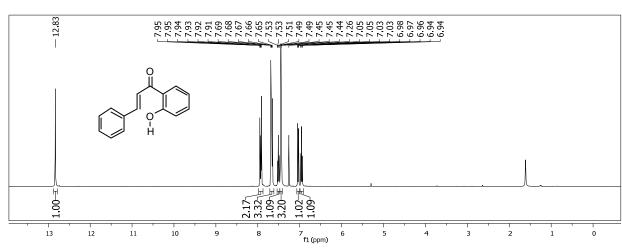


4-(2-Methoxyphenyl)cyclopent-3-ene-1,2-diyl)dibenzene (11)

b) Reaction Carried out in the Presence of Phenol

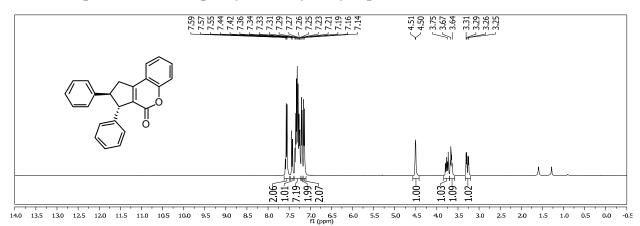


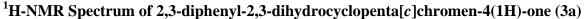
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol), (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (56 mg, 0.25 mmol) and phenol (23.6 mg, 0.25 mmol) was added. Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (33 mg, 31 µL, 0.25 mmol) followed by DBU (7.6 mg, 7.5 µL, 0.05 mmol). After 12 hour stirring the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 µL, 0.25 mmol) as the internal standard. ¹H NMR analaysis shows that the crude mixture contains 52% product, 33% unreacted hydroxyl chalcone **1a**, and 30% unreacted *trans* cinnamaldehyde **2a**, but there is no detectable amounts of phenyl 3-phenylpropanoate **12**.³



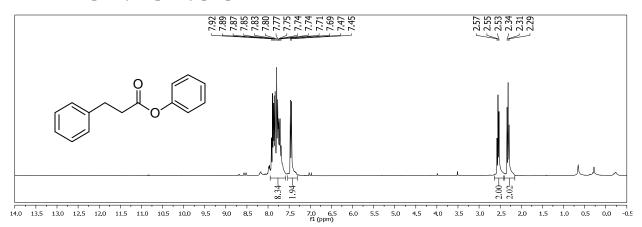
¹H-NMR Spectrum of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1a)

³ Chan, A.; Scheidt, K. A. Org. Lett. 2004, 7, 905.

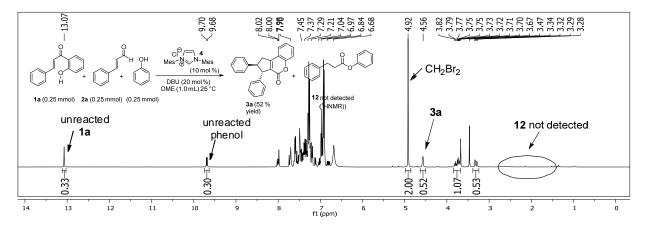




¹H-NMR of phenyl 3-phenylpropanoate (12)

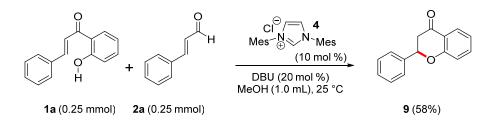


¹H-NMR of Crude Reaction Mixture after 12 h (CDCl₃)

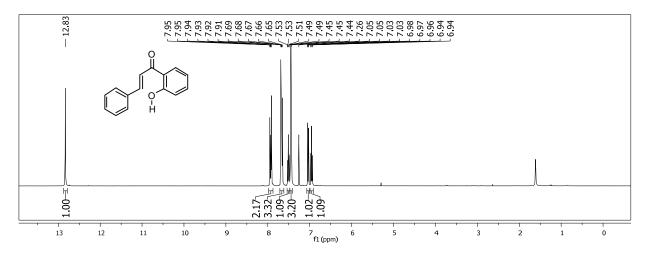


This result tends to indicate that the proton transfer events are intramolecular (Scheme 4 of manuscript) and the nucleophilic attack of homoenolate equivalent **A** onto 2'-hydroxy chalcone is more important than its protonation (leading to redox-esterification product).

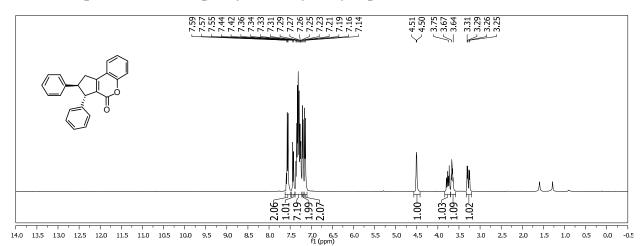
c) Reaction Employing Methanol as a Solvent

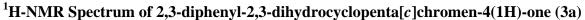


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol) and (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (56 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in MeOH (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (33 mg, 31 μ L, 0.25 mmol) followed by DBU (7.6 mg, 7.5 μ L, 0.05 mmol). After 12 hour stirring, the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard. ¹H NMR analysis shows that the crude mixture contains 58% of 2-phenylchroman-4-one **9**.

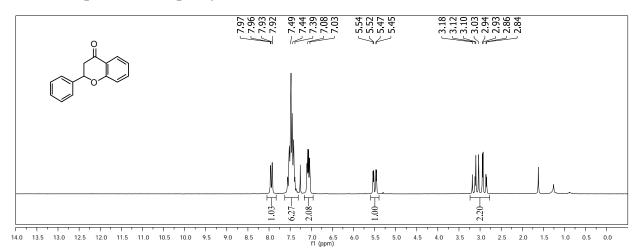


¹H-NMR Spectrum of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1a)

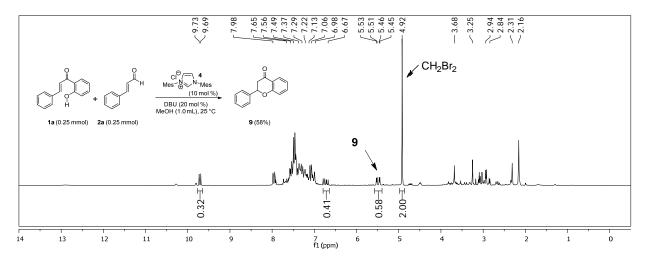




¹H-NMR Spectrum of 2-phenylchroman-4-one (9)

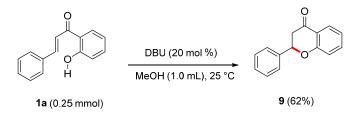


¹H-NMR of Crude Reaction Mixture after 12 h (CDCl₃)



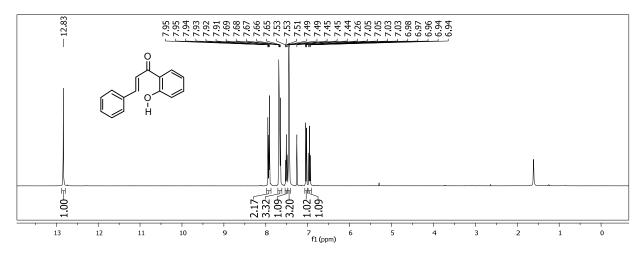
d) Blank reaction in Methanol as a Solvent and DBU as a catalyst

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (56 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in MeOH (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added DBU (7.6 mg, 7.5 μ L, 0.05 mmol). After 12 hour stirring the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard. ¹H NMR analaysis shows that the crude mixture contains 62% 2-phenylchroman-4-one **9**.

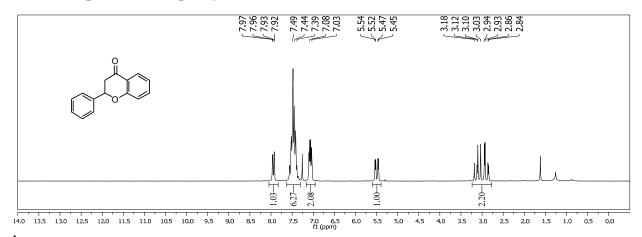


This indicates that in methanol as solvent, **1a** undergoes intramolecular cyclization catalyzed by DBU leading to the formation of **9**.

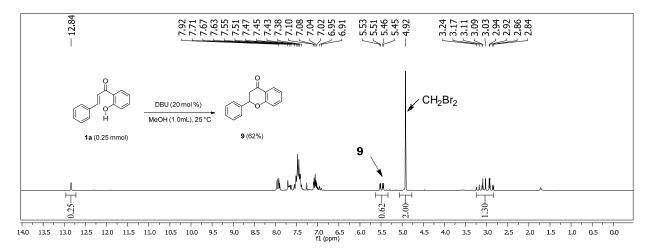
¹H-NMR Spectrum of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1a)



¹H-NMR Spectrum of 2-phenylchroman-4-one (9)



¹H-NMR of Crude Reaction Mixture after 12 h (CDCl₃)

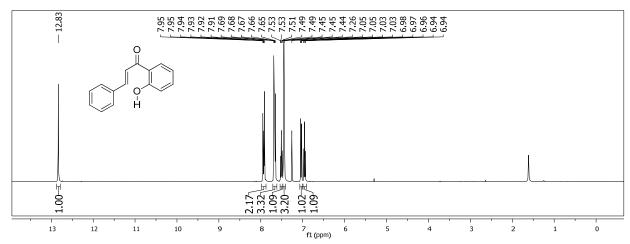


e) Blank reaction in DME as a Solvent

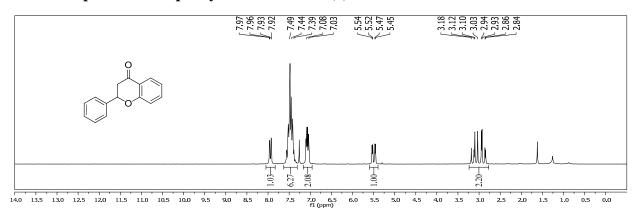
To a flame-dried screw-capped test tube equipped with a magnetic stir bar was (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (56 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added DBU (7.6 mg, 7.5 μ L, 0.05 mmol). After 12 hour stirring the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard. ¹H NMR study shows that the crude mixture contains 20% 2-phenylchroman-4-one.



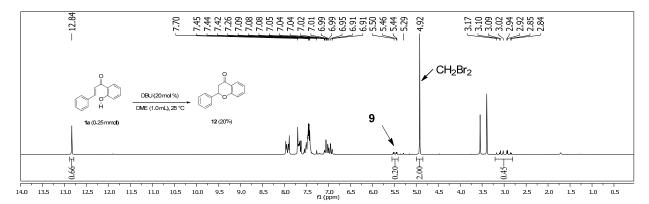
¹H-NMR Spectrum of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1a)

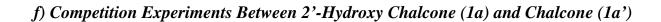


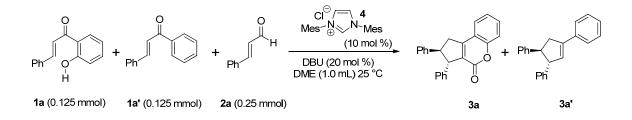
¹H-NMR Spectrum of 2-phenylchroman-4-one (9)



¹H-NMR of Crude Reaction Mixture after 12 h (CDCl₃)







entry	Time (min)	Yield of 3a (%)	Yield of 3a' (%)
1	5	46	not detected
2	10	60	not detected
3	15	76	~1
4	30	90	10
5	45	98	14
6	60	>99	24
7	120	>99	48

The yields were determined by ¹H-NMR analysis of crude products using CH₂Br₂ as the internal standard.

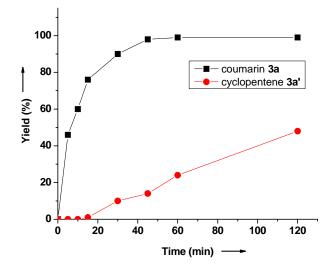
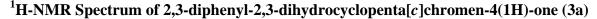
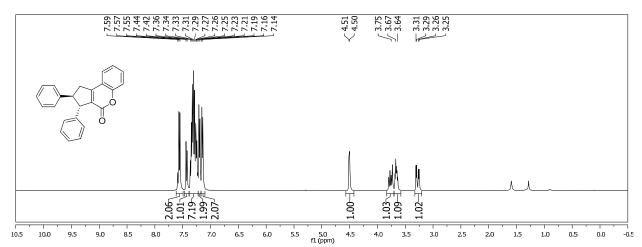


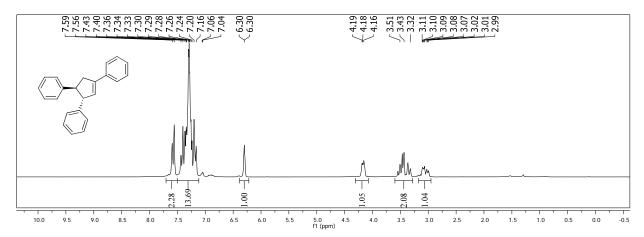
Figure 1. Intermolecular competition experiments between 2'-hydroxy chalcone 1a and chalcone 1a'

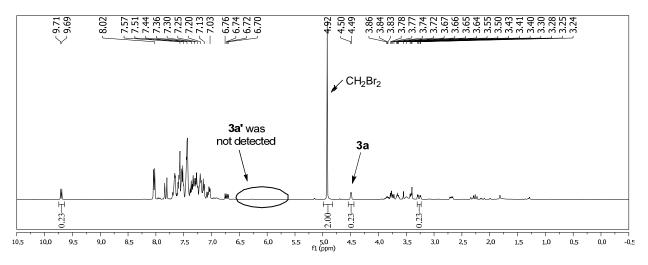
Seven reactions were carried out parallel. To each of the flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol) (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (28 mg, 0.125 mmol) and (*E*)-chalcone **1a'** (26 mg, 0.125 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (33 mg, 31 μ L, 0.25 mmol) followed by DBU (7.6 mg, 7.5 μ L, 0.05 mmol). After 5 minutes stirring the reaction is quenched and the mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard. The same procedure is followed for other six reactions and they were quenched at 10 min, 15 min, 30 min, 45 min, 60 min, and 120 min respectively.





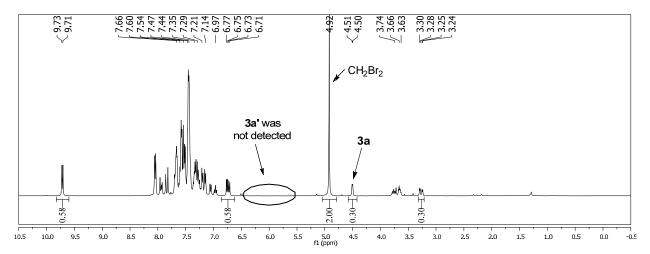
¹H-NMR Spectrum of cyclopent-3-ene-1,2,4-triyltribenzene (3a')



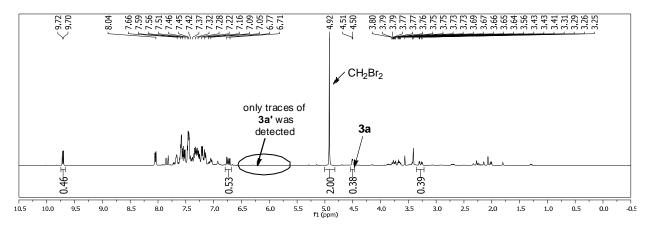


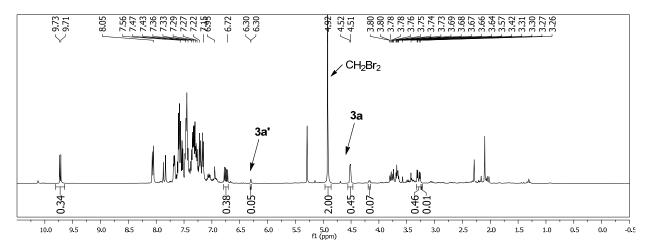
¹H-NMR of Crude Reaction Mixture after 5 minutes (CDCl₃)

¹H-NMR of Crude Reaction Mixture after 10 minutes (CDCl₃)



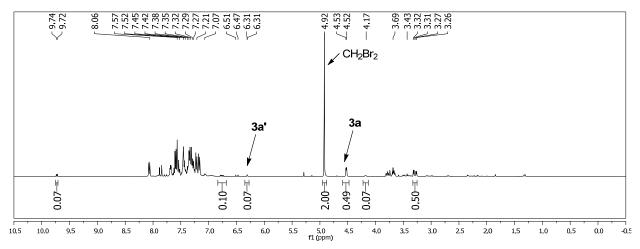
¹H-NMR of Crude Reaction Mixture after 15 minutes (CDCl₃)



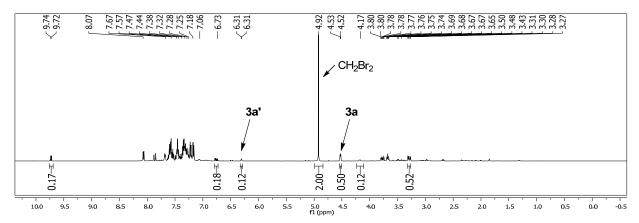


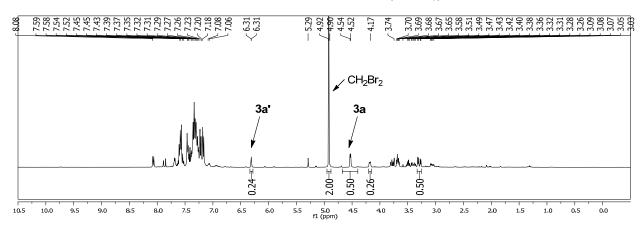
¹H-NMR of Crude Reaction Mixture after 30 minutes (CDCl₃)





H-NMR of Crude Reaction Mixture after 60 minutes (CDCl₃)

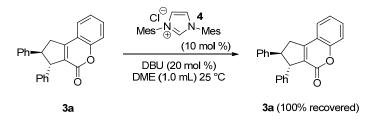




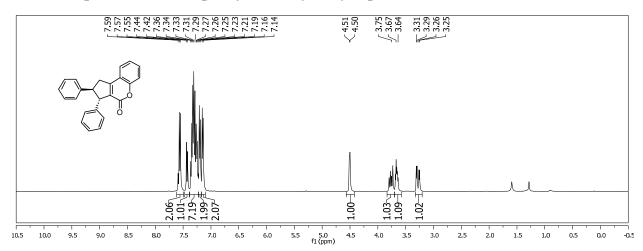
¹H-NMR of Crude Reaction Mixture after 120 minutes (CDCl₃)

It is interesting to note, that the formation of 3a proceeds first and the formation of cyclopentene 3a' begins when most of 1a has been consumed. Thus, it is reasonable to assume that the thermodynamically more feasible δ -lactonization proceeds over the β -lactonization.

g) Test for Product Stability

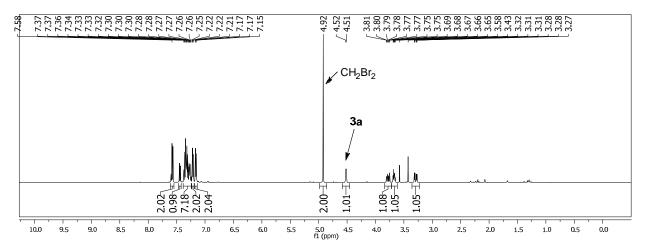


To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol) and 2,3-diphenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1H)-one **3a** (84.6 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture, DBU (7.6 mg, 7.5 μ L, 0.05 mmol) was added. After 12 hour stirring the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica gel and eluted with CH₂Cl₂ (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH₂Br₂ (18.0 μ L, 0.25 mmol) as the internal standard.



¹H-NMR Spectrum of 2,3-diphenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1H)-one (3a)

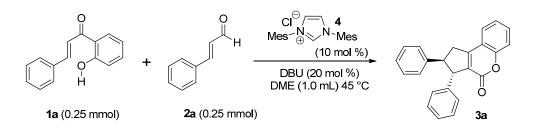
¹H-NMR of Crude Reaction Mixture after 12 hour (CDCl₃)



h) Kinetics Study of the Reaction

To a flame-dried screw-capped test tube equipped with a magnetic stir bar was added the imidazolium salt **4** (8.5 mg, 0.025 mmol) and (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (56 mg, 0.25 mmol). Then the screw-capped tube was evacuated and backfilled with argon. The mixture was dissolved in DME (1.0 mL) under argon atmosphere. The resultant reaction mixture was kept stirring at 25 °C. To this mixture was added the *trans* cinnamaldehyde **2a** (33 mg, 31 μ L, 0.25 mmol) followed by DBU (7.6 mg, 7.5 μ L, 0.05 mmol). After 15 minutes stirring the reaction mixture was diluted with CH₂Cl₂ (2.0 mL) and filtered through a short pad of silica

gel and eluted with CH_2Cl_2 (10 mL). The solvent was evaporated to obtain the crude product, which was analyzed using ¹H NMR using CH_2Br_2 (18.0 µL, 0.25 mmol) as the internal standard. Similar procedure followed for other three reactions, which were analyzed after 30 min, 45 min, and 60 min respectively.



entry	Time (min)	Yield of 3a (%)
1	15	11
2	30	25
3	45	43
4	60	50

The yields were determined by ¹H-NMR analysis of crude products using CH₂Br₂ as the internal standard.

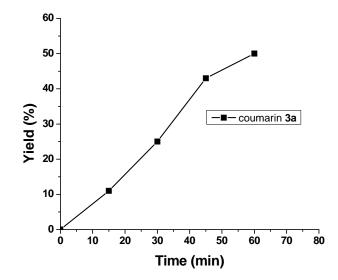
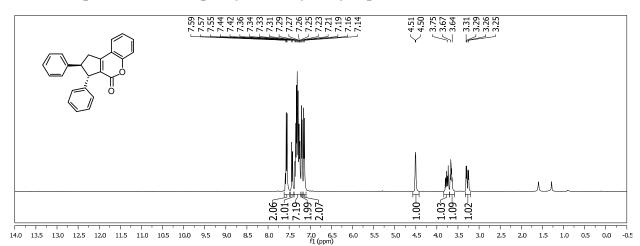
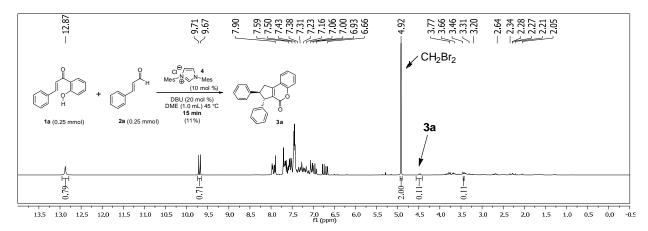


Figure 2. Kinetics study

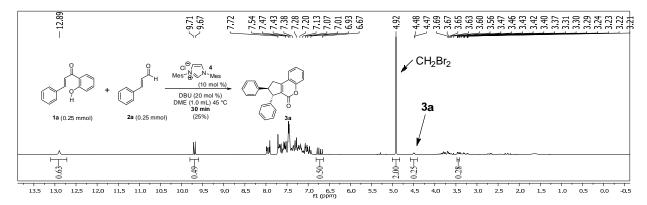


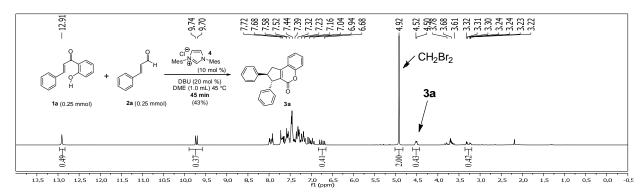
¹H-NMR Spectrum of 2,3-diphenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1H)-one (3a)

¹H-NMR of Crude Reaction Mixture after 15 minutes (CDCl₃)



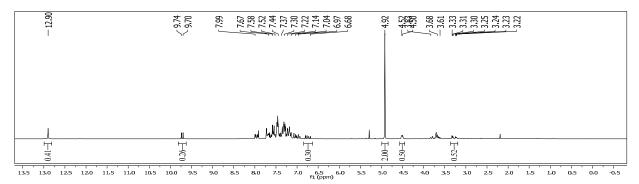
¹H-NMR of Crude Reaction Mixture after 30 minutes (CDCl₃





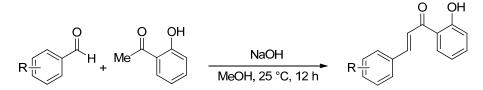
¹H-NMR of Crude Reaction Mixture after 45 minutes (CDCl₃)

¹H-NMR of Crude Reaction Mixture after 60 minutes (CDCl₃)

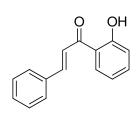


6. Synthesis and Characterization of 2'-Hydroxy Chalcones

The 2'-hydroxy chalcones used in the present study were prepared following the procedure by Bai and coworkers.⁴



(E)-1-(2-Hydroxyphenyl)-3-phenylprop-2-en-1-one (1a)

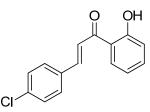


Following the known procedure, 1-(2-hydroxyphenyl)ethanone (1.36 g, 1.2 mL, 10.0 mmol) and benzaldehyde (1.06 g, 1.01 mL, 10 mmol) were treated with NaOH (10.0 g, in 20 mL water) in methanol (50.0 mL) at 25 °C for 12 h. The reaction mixture was poured into ice cold water and was subsequently neutralized with dropwise addition of Conc. HCl. The solid

obtained was collected by filtration and was purified by crystallization in ethanol to afford (E)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** as a crystalline yellow solid (1.58 g, 70%).

R_f (Pet. ether/EtOAc = 80/20): 0.80; ¹H NMR (400 MHz, CDCl₃) δ 12.83 (s, 1H, OH), 7.95-7.91 (m, 2H, H_{ar}), 7.69-7.65 (m, 3H, H_{ar}), 7.53-7.49 (m, 1H, H_{ar}), 7.45-7.44 (m, 3H, H_{ar}), 7.04 (d, *J* = 8.5 Hz, 1H, H_{ar}), 6.96 (t, *J* = 7.1 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.88, 163.73, 145.63, 136.57, 134.71, 131.09, 129.80, 129.19, 128.81, 120.22, 119.01, 118.78. HRMS calculated [M+H]⁺ for C₁₅H₁₃O₂: 225.0910, found: 225.0909. FTIR (cm⁻¹) 3057, 2925, 1638, 1487, 1440, 1487, 1366, 1340, 1308, 1268, 1235, 1206, 1154, 1030, 1020, 999, 864, 837, 778, 754, 740, 694, 665, 578, 478.

(E)-3-(4-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1b)



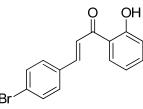
Following the known procedure, 1-(2-hydroxyphenyl) ethanone (1.36 g, 1.2 mL, 10.0 mmol) and 4-chlorobenzaldehyde (1.40 g, 10 mmol) were treated with NaOH (10 g, in 20 mL water) in methanol (50.0 mL) at 25 °C for 12 h. The reaction mixture was poured into ice cold water

⁴ Liu, B.; Wang, H.; Wang, T.; Bao, Y.; Du, F.; Tian, J.; Li, Q.; Bai, R. Chem. Commun. 2012, 48, 2867.

and was subsequently neutralized with dropwise addition of Conc. HCl. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1b** as a crystalline yellow solid (1.61 g, 62%).

R_f (Pet. ether /EtOAc = 80/20): 0.73; ¹H NMR (400 MHz, CDCl₃) δ 12.76 (s, 1H, OH), 7.92-7.84 (m, 2H, H_{ar}), 7.65-7.59 (m, 3H, H_{ar}), 7.53-7.49 (m, 1H, H_{ar}), 7.41 (d, *J* = 8.5 Hz, 2H, H_{ar}), 7.04 (d, *J* = 8.5 Hz, 1H, H_{ar}), 6.95 (t, *J* = 8.1 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.52, 163.70, 144.00, 136.94, 136.65, 133.14, 129.88, 129.71, 129.42, 120.59, 119.99, 119.01, 118.76. HRMS calculated [M+H]⁺ for C₁₅H₁₂O₂Cl: 259.0520, found: 259.0521. FTIR (cm⁻¹) 2298, 1644, 1579, 1486, 14440, 1406, 1369, 1342, 1301, 1262, 1205, 1091, 1011, 984, 862, 819, 785, 754, 646, 488.

(*E*)-3-(4-Bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1c)

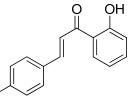


Following the known procedure, 1-(2-hydroxyphenyl) ethanone (0.68 g, 0.6 mL, 5.0 mmol) and 4-bromobenzaldehyde (0.925 g, 5.0 mmol) were treated with NaOH (5 g, in 10 mL water) in methanol (25.0 mL) for 12 h, before the reaction mixture was poured into ice cold water

and made neutralized with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-3-(4-bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1c** as a crystalline yellow solid (0.8 g, 65%).

R_f (Pet. ether /EtOAc = 80/20): 0.81. ¹H NMR (400 MHz, CDCl₃) δ 12.75 (s, 1H, OH), 7.91-7.89 (m, 1H, H_{ar}), 7.84 (d, *J* = 15.4 Hz, 1H, H_{ar}), 7.63 (d, *J* = 15.5 Hz, 1H, H_{ar}), 7.58-7.49 (m, 5H, H_{ar}), 7.03 (d, *J* = 8.4 Hz, 1H, H_{ar}), 6.95 (t, *J* = 8.0 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.57, 163.74, 144.12, 136.71, 133.60, 132.43, 130.10, 129.74, 125.40, 120.75, 120.02, 119.05, 118.82. HRMS calculated [M+H]⁺ for C₁₅H₁₂O₂Br: 304.9986, found: 304.9986. FTIR(cm¹) 2985, 2113, 1645, 1575, 1486, 1439, 1401, 1370, 1339, 1265, 1206, 1179, 1150, 107 0, 1023, 1007, 982, 816, 781, 754, 669.

(E)-3-(4-Fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1d)

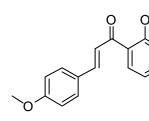


Following the known procedure, 1-(2-hydroxyphenyl) ethanone (0.68 g, 0.6 mL, 5.0 mmol) and 4-fluorobenzaldehyde (0.62 g, 0.53 mL, 5 mmol) were treated with NaOH (5 g, in 10 ml water) in methanol (25.0 mL) for 12 h, before the reaction mixture was poured into ice cold water

and made neutralized with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-3-(4-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1d** as a crystalline yellow solid (0.666 g, 70%).

R_f (Pet. ether /EtOAc = 80/20): 0.72 ¹H NMR (400 MHz, CDCl₃) δ 12.75 (s, 1H, OH), 7.93-7.89 (m, 1H, H_{ar}), 7.84 (d, *J* = 15.4 Hz, 1H, H_{ar}), 7.63 (d, *J* = 15.5 Hz, 1H, H_{ar}), 7.59-7.49 (m, 5H, H_{ar}), 7.04 (d, *J* = 8.4 Hz, 1H, H_{ar}), 6.96 (t, *J* = 8.0 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.63, 165.40, 163.72, 163.39, 144.24, 136.59, 130.98 (d, *J*_{C-F} = 3.2 Hz), 130.73 (d, *J*_{C-F} = 8.6 Hz), 120.05, 119.91, 118.79 (d, *J*_{C-F} = 26.7 Hz), 117.67, 116.37 (d, *J*_{C-F} = 22.0 Hz), 114.63. HRMS calculated [M+H]⁺ for C₁₅H₁₂O₂F: 243.0816, found: 243.0813. FTIR(cm¹) 3019, 2106, 1637, 1578, 1491, 1442, 1366, 1340, 1299, 1204, 1156, 1022, 984, 868, 827, 762, 749, 660.

(E)-1-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (1e)



Following the known procedure, 1-(2-hydroxyphenyl) ethanone (1.36 g, 1.2 mL, 10.0 mmol) and 4-methoxybenzaldehyde (1.36 g, 1.22 mL, 10 mmol) were treated with NaOH (10 g, in 20 mL water) in methanol (50.0 mL) at 25 °C for 12 hr, followed by pouring the reaction mixture into ice cold water and made neutralized with Conc.

HCl. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one **1e** as a crystalline yellow solid (1.65 g, 65%)

R_f (Pet. ether /EtOAc = 80/20): 0.7 ¹H NMR (400 MHz, CDCl₃) δ 12.97 (s, 1H, OH), 7.92-7.87 (m, 2H, H_{ar}), 7.61 (d, *J* = 8.7 Hz, 2H, H_{ar}), 7.54-7.46 (m, 2H, H_{ar}), 7.02 (d, *J* = 8.4 Hz, 1H, H_{ar}), 6.95-6.91 (m, 3H, H_{ar}), 3.85 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 193.74, 163.63, 162.11, 145.45, 136.24, 130.66, 129.64, 127.39, 120.19, 118.66, 118.65, 117.60, 114.60, 55.53. HRMS calculated [M+H]⁺ for C₁₆H₁₅O₃: 255.1016, found: 255.1015. FTIR (cm⁻¹) 3262, 2843, 2205, 2053, 1699, 1637, 1605, 1583, 1511, 1442, 1489, 1424, 1343, 1303, 1258, 1204, 1174, 1157, 1128, 1114, 1024, 981, 940, 863, 829, 805, 764, 720, 660.

(E)-1-(2-Hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (1f)

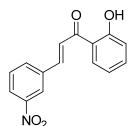
QН

Following the known procedure, 1-(2-hydroxyphenyl) ethanone (1.36 g, 1.2 mL, 10.0 mmol) and 3-methoxybenzaldehyde (1.36 g, 1.22 mL, 10 mmol) were treated with NaOH (10 g, in 20 mL water) with methanol (50.0 mL) at 25 °C for 12 h. The reaction mixture was poured into ice cold water and was subsequently neutralized with dropwise addition of Conc. HCl. The solid obtained was collected by filtration and was purified by

crystallization in ethanol to afford (*E*)-1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1one **1f** as yellow solid (1.71 g, 67%).

R_f (Pet. ether /EtOAc = 80/20): 0.7 ¹H NMR (400 MHz, CDCl₃) δ 12.92 (s, 1H, OH), 8.02-7.95 (m, 2H, H_{ar}), 7.72 (d, *J* = 15.5 Hz, 1H, H_{ar}), 7.60 (t, *J* = 8.5 Hz, 1H, H_{ar}), 7.45 (t, *J* = 7.6 Hz, 1H, H_{ar}), 7.35 (d, *J* = 7.6 Hz, 1H, H_{ar}), 7.26(s, 1H, H_{ar}), 7.14-7.02 (m, 3H, H_{ar}), 3.96 (s, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 193.79, 163.70, 160.08, 145.48, 136.54, 136.04, 130.14, 129.78, 121.38, 120.47, 120.09, 118.97, 118.73, 116.71, 113.83, 55.48. HRMS calculated [M+H]⁺ for C₁₆H₁₅O₃: 255.1016, found: 255.1014. FTIR (cm⁻¹) 3004, 2940, 2836, 1640, 1579, 1488, 1443, 1363, 1341, 1317, 1292, 1273, 1247, 1202, 1158, 1129, 1047, 1024, 978, 861, 817, 788, 757, 736, 697, 664, 594.

(*E*)-1-(2-Hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one (1g)



Following the known procedure, 1-(2-hydroxyphenyl) ethanone (0.68 g, 0.6 mL, 5.0 mmol) and 3-nitrobenzaldehyde (0.756 g, 5 mmol) were treated with NaOH (5 g, in 10 mL water) in methanol (25.0 mL) for 12 h, before the reaction mixture was poured into ice cold water and made neutralised with Conc. HCl. The solid was collected by filtration followed

by crystallization in ethanol to afford (*E*)-1-(2-hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one **1g** as a crystalline yellow solid (1.00 g, 77%).

 R_f (Pet. ether /EtOAc = 80/20): 0.70 ¹H NMR (400 MHz, CDCl₃) δ 12.62 (s, 1H, OH), 8.54, (bs, 1H, H_{ar}), 8.30-8.27 (m, 1H, H_{ar}), 7.95-7.91 (m, 3H, H_{ar}), 7.77 (d, J = 15.6 Hz, 1H, H_{ar}), 7.64

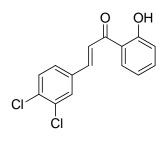
(t, J = 8.0 Hz, 1H, H_{ar}), 7.56-7.52 (m, 1H, H_{ar}), 7.05 (d, J = 8.3 Hz, 1H, H_{ar}), 7.01-6.97 (m, 1H, H_{ar}), ¹³C NMR (100 MHz, CDCl₃) δ 193.17, 163.84, 148.88, 142.39, 137.12, 136.46, 134.72, 130.30, 129.88, 125.12, 123.11, 122.58, 119.88, 119.26, 118.93. HRMS calculated [M+H]⁺ for C₁₅H₁₁O₄N: 270.0761, found: 270.0760. FTIR (cm⁻¹) 3419, 2101, 1645, 1590, 1524, 1487, 1439, 1358, 1289, 1211, 1157, 1020, 973, 756, 730, 659, 483.

(E)-3-(2-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1h)

Following the known procedure, 1-(2-hydroxyphenyl)ethanone (0.68 g, 0.6 mL, 5.0 mmol) and 2-chlorobenzaldehyde (0.70 g, 0.56 mL, 5.0 mmol) were treated with NaOH (5 g, in 10 ml water) in methanol (25.0 mL) for 12 h, before the reaction mixture was poured into ice cold water and made neutralized with Conc. HCl. Solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-3-(2-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1h** as a crystalline yellow solid (0.86 g, 66%).

R_f (Pet. ether /EtOAc = 80/20): 0.73. ¹H NMR (400 MHz, CDCl₃) δ 12.74 (s, 1H, OH), 8.30 (d, J = 15.4 Hz 1H, H_{ar}), 7.90 (dd, $J_I = 8 \text{ Hz} \& J_2 = 1.4 \text{ Hz}$, 1H, H_{ar}), 7.76 (dd, $J_I = 7.3 \text{ Hz} \& J_2 = 2.0 \text{ Hz}$, 1H, H_{ar}), 7.63 (d, J = 15.5 Hz, 1H, H_{ar}), 7.53-7.49 (m, 1H, H_{ar}), 7.46-7.45 (m, 1H, H_{ar}), 7.37-7.31 (m, 2H, H_{ar}), 7.04-7.03 (m, 1H, H_{ar}), 6.96-6.93 (m, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.61, 163.75, 141.27, 136.73, 135.85, 133.02, 131.67, 130.53, 129.85, 128.04, 127.26, 122.81, 120.00, 119.06, 118.80. HRMS calculated [M+H]⁺ for C₁₅H₁₂O₂Cl: 259.0520, found:259.0520.FTIR(cm¹) 2922, 1639, 1582, 1486, 1467, 1441, 1339, 1317, 1262, 1 233, 1205, 1157, 1020, 972, 864, 753, 659, 589.

(E)-3-(3,4-Dichlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1i)

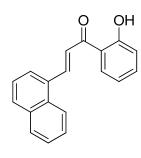


Following the known procedure, 1-(2-hydroxyphenyl) ethanone (0.68 g, 0.6 mL, 5.0 mmol) and 3,4-dichlorobenzaldehyde (0.875 g, 5 mmol) were treated with NaOH (5 g, in 10 ml water) in methanol (25.0 mL) for 12 hr, before the reaction mixture was poured into ice cold water and made neutralised with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-3-(3,4-

dichlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1i** as a crystalline yellow solid (0.987 g, 68%).

R_f (Pet. ether /EtOAc = 80/20): 0.80 ¹H NMR (400 MHz, CDCl₃) δ 12.67 (s, 1H, OH), 7.90 (dd, $J_1 = 8.1 \text{ Hz} \& J_2 = 1.0 \text{ Hz}$, 1H, H_{ar}), 7.80-7.73 (m, 2H, H_{ar}), 7.61 (d, J = 15.5 Hz, 1H, H_{ar}), 7.53-7.50 (m, 2H, H_{ar}), 7.47-7.45 (m, 1H, H_{ar}), 7.03 (d, J = 8.4 Hz, 1H, H_{ar}), 6.96 (t, J = 7.8 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.26, 163.79, 142.61, 136.89, 134.93, 134.73, 133.56, 131.17, 130.01, 129.76, 127.84, 121.84, 119.93, 119.13, 118.87. HRMS calculated [M+H]⁺ for C₁₅H₁₁O₂Cl₂: 293.0131, found: 293.0129. FTIR (cm⁻¹) 2923, 1644, 1571, 1439, 1363, 1341, 1208, 1156, 1020, 981, 811, 756, 648.

(E)-1-(2-Hydroxyphenyl)-3-(naphthalene-1-yl)prop-2-en-1-one (1j)

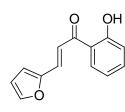


Following the known procedure, 1-(2-hydroxyphenyl) ethanone (0.68 g, 0.6 mL, 5.0 mmol) and 1-naphthaldehyde (0.781 g, 0.68 mL, 5 mmol) were treated with NaOH (5 g, in 10 ml water) in methanol (25.0 mL) for 12 hr, before the reaction mixture was poured into ice cold water and made neutralised with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-1-(2-hydroxyphenyl)-

R_f (Pet. ether /EtOAc = 80/20): 0.71 ¹H NMR (400 MHz, CDCl₃) δ 12.89 (s, 1H, OH), 8.78 (d, J = 15.2 Hz, 1H, H_{ar}), 8.28 (d, J = 8.4 Hz, 1H, H_{ar}), 7.96 (t, J = 7.2 Hz, 2H, H_{ar}), 7.91 (t, J = 7.1 Hz, 1H, H_{ar}), 7.74 (d, J = 15.2 Hz, 1H, H_{ar}), 7.63-7.60 (m, 1H, H_{ar}), 7.58-7.51 (m, 3H, H_{ar}), 7.07 (d, J = 8.5 Hz, 1H, H_{ar}), 6.96 (t, J = 7.5 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.74, 163.84, 142.55, 136.64, 133.90, 132.22, 131.93, 131.39, 129.90, 128.98, 127.31, 126.57, 125.58, 125.50, 123.57, 122.88, 120.14, 119.08, 118.83. HRMS calculated [M+H]⁺ for C₁₉H₁₅O₂: 275.1067, found:275.1066.FTIR(cm¹) 3058, 1945, 1688, 1637, 1579, 1487, 1443, 1398, 1307, 1279, 1250, 1201, 1157, 1023, 973, 860, 799, 774, 755, 662, 601.

3-(naphthalene-1-yl)prop-2-en-1-one **1**j as a crystalline yellow solid (1.04 g, 73% yield)

(E)-3-(Furan-2-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1k)

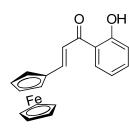


Following the known procedure, 1-(2-hydroxyphenyl)ethanone (1.36 g, 1.2 mL, 10.0 mmol) and furan-2-carbaldehyde (0.97 g, 0.83 mL, 10 mmol) were treated with NaOH (10 g, in 20 mL water) in methanol (50.0 mL) at

25 °C for 12 h. The reaction mixture was poured into ice cold water and was subsequently neutralized with dropwise addition of Conc. HCl. The solid obtained was collected by filtration and was purified by crystallization in ethanol to afford (*E*)-3-(furan-2-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1k** as yellow solid (1.40 g, 65%).

R_f (Pet. ether /EtOAc = 80/20): 0.66 ¹H NMR (400 MHz, CDCl₃) δ 12.91 (s, 1H, OH), 7.91 (d, J = 8.0 Hz, 1H, H_{ar}), 7.68 (d, J = 15.0 Hz, 1H, H_{ar}), 7.57-7.46 (m, 3H, H_{ar}), 7.01 (d, J = 8.5 Hz, 1H, H_{ar}), 6.93 (t, J = 7.3 Hz, 1H, H_{ar}), 6.76 (d, J = 3.3 Hz, 1H, H_{ar}), 6.54-6.53 (m, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.43, 163.64, 151.61, 145.55, 136.42, 131.24, 129.75, 120.14, 118.97, 118.63, 117.68, 117.29, 113.02. HRMS calculated [M+H]⁺ for C₁₃H₁₁O₃: 215.0703, found: 215.0701. FTIR (cm⁻¹) 3149, 3129, 2924, 1643, 1582, 1554, 1488, 1474, 1441, 1363, 1337, 1308, 1271, 1259, 1236, 1215, 1189, 1160, 1079, 1016, 969, 929, 883, 858, 831, 745, 720, 696, 653.

(E)-1-(2-Hydroxyphenyl)-3-(ferrocenyl)prop-2-en-1-one (11)

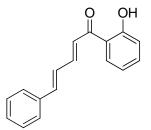


Following the known procedure, 1-(2-hydroxyphenyl)ethanone (0.68 g, 0.6 mL, 5.0 mmol) and ferrocene carboxaldehyde (1.07 g, 5.0 mmol) were treated with NaOH (5.0 g, in 10 mLwater) in methanol (25 mL) at 25 °C for 12 h. The reaction mixture was poured into ice cold water and was subsequently neutralized with dropwise addition of Conc. HCl. The solid obtained was collected by filtration and was purified by crystallization in

ethanol to afford (*E*)-1-(2-hydroxyphenyl)-3-(ferroceniyl)prop-2-en-1-one **11** as a crystalline red solid (772 mg, 46%).

 R_f (Pet. ether /EtOAc = 80/20): 0.6 ¹H NMR (200 MHz, CDCl₃) δ 13.07 (s, 1H, OH), 7.94-7.84 (m, 2H, H_{ar}), 7.53-7.44 (m, 1H, Har), 7.28-7.21 (m, 1H, Har), 7.04-6.89 (m, 2H, H_{ar}), 4.65-4.63 (m, 2H, bs), 4.55-4.53 (m, 2H, bs), 4.22-4.18 (m, 5H, bs). ¹³C NMR (100 MHz, CDCl₃) δ 192.84, 163.70, 148.10, 136.23, 136.01, 129.51, 127.06, 121.44, 120.13, 118.80, 118.68, 118.16, 116.79, 72.07, 70.13, 69.47. HRMS calculated [M+H]⁺ for C₁₉H₁₆O₂Fe: 332.0494, found: 332.0497. FTIR (cm⁻¹) 3053, 2926. 2855, 1955, 1692, 1639, 1615, 1582, 1487, 1463, 1448, 1369, 1323, 1303, 1244, 1220, 1158, 1066, 1025, 1003, 961, 836, 818, 756, 738, 648, 620, 596, 562, 522, 487.

(2E,4E)-1-(2-Hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one (1m)



Following the known procedure, 1-(2-hydroxyphenyl) ethanone (0.68 g, 0.6 ml, 5.0 mmol) and *trans* cinnamaldehyde (0.66 g, 0.62 ml, 5 mmol) were treated with NaOH (5 g, in 10 ml water) in methanol (25.0 mL) for 12 hr, before the reaction mixture was poured into ice cold water and made neutralized with Conc. HCl. The solid was collected by filtration

followed by crystallization in ethanol to afford (2E,4E)-1-(2-hydroxyphenyl)-5-phenylpenta-2,4dien-1-one **1m** as a crystalline orange solid (0.80 g, 66%).

R_f (Pet. ether /EtOAc = 80/20): 0.70 ¹H NMR (400 MHz, CDCl₃) δ 12.95 (s, 1H, OH), 7.90 (d, J = 7.9 Hz, 1H, H_{ar}), 7.79-7.74 (m, 1H, H_{ar}), 7.58-7.55 (m, 2H, H_{ar}), 7.53 (d, J = 7.2 Hz, 1H, H_{ar}), 7.46-7.43 (m, 2H, H_{ar}), 7.41-7.38 (m, 1H, H_{ar}), 7.30 (d, J = 9.6 Hz, 1H, H_{ar}), 7.12-7.10 (m, 2H, H_{ar}), 7.07 (d, J = 8.4 Hz, 1H, H_{ar}), 6.98 (t, J = 7.4 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.86, 163.73, 145.67, 143.09, 136.41, 136.10, 129.66, 129.07, 127.60, 126.83, 123.61, 120.16, 118.95, 118.75. HRMS calculated [M+H]⁺ for C₁₇H₁₅O₂: 251.1067, found: 251.1066. FTIR (cm¹) 2925, 1635, 1574, 1563, 1488, 1444, 1371, 1340, 1301, 1278, 1227, 1148, 1004, 803, 760, 691.

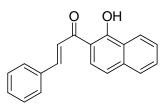
(E)-1-(5-Bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one (1n)

Following the known procedure, 1-(5-bromo-2-hydroxyphenyl) ethanone (1.075 g, 5.0 mmol) and benzaldehyde (0.530 g, 0.50 mL, 5 mmol) were treated with NaOH (5 g, in 10 ml water) in methanol (25.0 mL) for 12 h, before the reaction mixture was poured into ice cold water and made neutralised with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1n** as a crystalline yellow solid (1.515 g, 69%).

 R_f (Pet. ether /EtOAc = 80/20): 0.75 ¹H NMR (400 MHz, CDCl₃) δ 12.75 (s, 1H, OH), 8.01 (d, J = 2.4 Hz, 1H, H_{ar}), 7.94 (d, J = 15.3 Hz, 1H, H_{ar}), 7.69-7.68 (m, 2H, H_{ar}), 7.57 (s, 1H, H_{ar}), 7.56-7.54 (m, 1H, H_{ar}), 7.47-7.44 (m, 3H, H_{ar}), 6.94 (d, J = 8.8 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 192.86, 162.64, 146.71, 139.09, 134.43, 131.97, 131.42, 129.25, 129.00, 121.37, 120.79, 119.52, 110.59. HRMS calculated [M+H]⁺ for C₁₅H₁₂O₂Br: 303.0015, found:

303.0008.**FTIR(cm¹)** 3391, 1642, 1576, 1471, 1449, 1398, 1361, 1341, 1307, 1292, 1269, 1191, 1183, 1019, 977, 848, 809, 731, 701, 689, 626, 581.

(E)-1-(1-Hydroxynaphthalen-2-yl)-3-phenylprop-2-en-1-one (10)

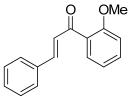


Following the known procedure, 1-(1-hydroxynaphthalen-2-yl) ethanone (1.862 g, 10.0 mmol) and benzaldehyde (1.061 g, 1.01 ml, 10 mmol) were treated with NaOH (10 g, in 20 ml water) in methanol (50.0 mL) for 12 h, before the reaction mixture was poured into ice

cold water and made neutralised with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford(E)-1-(1-hydroxynaphthalen-2-yl)-3-phenylprop-2-en-1-one **10** as a crystalline red solid (2.0 g, 74%).

R_f (Pet. ether /EtOAc = 80/20): 0.74 ¹H NMR (400 MHz, CDCl₃) δ 14.89 (s, 1H, OH), 8.53 (d, J = 8.4 Hz, 1H, H_{ar}), 8.03-7.99 (m, 1H, H_{ar}), 7.86 (d, J = 8.9 Hz, 1H, H_{ar}), 7.81-7.65 (m, 5H, H_{ar}), 7.59-7.55 (m, 1H, H_{ar}), 7.48-7.47 (m, 3H, H_{ar}), 7.33 (d, J = 8.9 Hz, 1H, H_{ar}), 6.96 (t, J = 7.8 Hz, 1H, H_{ar}). ¹³C NMR (100 MHz, CDCl₃) δ 193.39, 164.57, 145.23, 137.53, 134.91, 130.99, 130.37, 129.19, 128.82, 127.55, 126.09, 125.63, 124.66, 124.06, 120.60, 118.38, 113.60. HRMS calculated [M+H]⁺ for C₁₅H₁₁O₂Cl₂: 293.0131,found: 293.0129. FTIR (cm¹) 2923, 1644, 1571, 1439, 1363, 1341, 1208, 1156, 1020, 981, 811, 756, 648.

(*E*)-1-(2-Methoxyphenyl)-3-phenylprop-2-en-1-one (9)



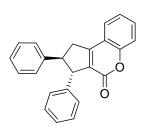
Following the general procedure, 1-(2-methoxyphenyl) ethanone (1.50 g, 1.4 mL, 10.0 mmol) and benzaldehyde (1.17 g, 1.12 mL, 11 mmol) were treated with NaOH (10 g, in 20 ml water) in methanol (50.0 mL) for 12 hr, before the reaction mixture was poured into ice cold water and made

neutralised with Conc. HCl. The solid was collected by filtration followed by crystallization in ethanol to afford (*E*)-1-(2-methoxyphenyl)-3-phenylprop-2-en-1-one **9** as a colourless liquid (2.1 g, 88%).

 R_f (Pet. ether /EtOAc = 80/20): 0.72; ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.64 (m, 1H, H_{ar}), 7.63-7.62 (m, 1H, H_{ar}), 7.59-7.57 (m, 2H, H_{ar}), 7.48-7.44 (m, 1H, H_{ar}), 7.41-7.37 (m, 4H, H_{ar}) 7.03 (t, J = 7.4 Hz, 1H, H_{ar}), 6.99 (d, J = 8.2 Hz, 1H, H_{ar}), 3.87 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.90, 158.11, 143.16, 135.08, 132.92, 130.30, 130.25, 129.22, 128.87, 128.37, 127.05, 120.71, 111.65, 55.71. **HRMS** calculated [M+H]⁺ for C₁₆H₁₅O₂: 239.1067, found: 239.1063.**FTIR(cm¹)** 3015, 2966, 2839, 2401, 1658, 1604, 1485, 1464, 1436, 1333, 1289, 1244, 1216, 1180, 1163, 1114, 1059, 1032, 978, 891, 869, 812, 754, 698, 667, 601, 568, 483.

7. Synthesis and Characterization Functionalized Coumarins

2,3-Diphenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3a)



Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography

afforded 2,3 diphenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one **3a** as a white solid (0.336 g, 98%).

R_f (Pet. ether /EtOAc = 80/20): 0.62; ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.55 (m, 2H, H_{ar}), 7.43 (d, *J* = 8.2 Hz, 1H, H_{ar}), 7.36-7.25 (m, 7H, H_{ar}), 7.20 (d, *J* = 7.6 Hz, 2H, H_{ar}), 7.15 (d, *J* = 7.4 Hz, 2H, H_{ar}) 4.51 (d, *J* = 4.6 Hz, 1H, CH), 3.80-3.75 (m, 1H, CH), 3.68-3.64 (m, 1H, CH), 3.27 (dd, *J*₁ = 5.0 Hz, *J*₂ = 17.8 Hz, 1H, CH). ¹³C NMR (125 MHz, CDCl₃) δ 158.96, 155.65, 154.92, 144.69, 142.50, 131.61, 129.01, 128.86, 128.76, 127.19, 127.08, 126.96, 125.17, 124.39, 118.47, 117.11, 59.29, 53.52, 39.63. HRMS calculated [M+H]⁺ for C₂₄H₁₉O₂: 339.1380, found: 339.1380. FTIR (cm⁻¹) 3063, 3028, 2927, 2853, 1728, 1627, 1607, 1568, 1494, 1453, 1432, 1388, 1322, 1274, 1250, 1218, 1134, 1078, 1059, 1037, 925, 883, 754, 700, 666, 527.

X-ray Crystal Structure Analysis of 3a.⁵

Single crystals of the compound were grown by slow evaporation from a mixture of ethyl acetate and Pet. ether. Data was collected on SMART APEX-II CCD using Mo-K α radiation (λ = 0.7107 Å) to a maximum θ range of 25.00°. Colourless plate like crystal of approximate size

⁵ Sheldrick, G. M. SHELX-97 program for crystal structure solution and refinement, University of Gottingen, Germany, 1997; 2008

0.44 x 0.13 x 0.02 mm³, was used for data collection. Crystal to detector distance 5.00 cm, 512 x 512 pixels / frame, Oscillation / frame -0.5°, maximum detector swing angle = -30.0° , beam center = (260.2, 252.5), in plane spot width = 1.24, Multi run data acquisition. Total scans = 3, total frames = 1800, exposure / frame = 15.0 sec / frame, θ range = 1.86 to 25.00°, completeness to θ of 25.00°, is 100.0 %. C₂₄ H₁₈ O₂, *M* = 338.38. Crystals belong to Monoclinic, space group P2₁/c, *a* = 12.9452(6), *b* = 8.9427(4), *c* = 31.393(2) Å, β = 101.7470(8)°, *V* = 3558.1(3) Å³, *Z* = 8, D_c = 1.263 g /cc, μ (Mo–K α) = 0.079 mm⁻¹, 27804 reflections measured, 6270 unique [I>2 σ (I)], R value 0.0567, wR2 = 0.1164. Largest diff. peak and hole 0.151 and -0.233 e. Å⁻³. All the data were corrected for Lorentzian, polarisation and absorption effects. SHELX-97 (ShelxTL)^{ref} was used for structure solution and full matrix least squares refinement on F². Hydrogen atoms were included in the refinement as per the riding model. There are two molecules in the asymmetric unit. The overlap shows that the phenyl rings are differently oriented in two molecules.

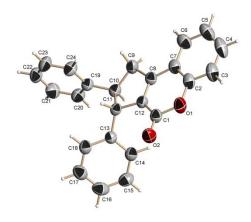


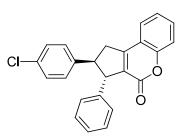
Figure 3. ORTEP diagram of one of the molecules of 3a drawn at 50 % probability.

Crystal data and structure refinement for 3a.

Empirical formula	$C_{24}H_{18}O_2$
Formula weight	338.38
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P21/c	
Unit cell dimensions	a = 12.9452(6) Å	α= 90°.
	b = 8.9427(4) Å	β= 101.7470(8)°.
	c = 31.393(2) Å	$\gamma = 90^{\circ}$.
Volume	3558.1(3) Å ³	
Z	8	
Density (calculated)	1.263 g/cc	
Absorption coefficient	0.079 mm ⁻¹	
F(000)	1424	
Crystal size	0.44 x 0.13 x 0.02 mm ³	
Theta range for data collection	1.86 to 25.00°.	
Index ranges	-15<=h<=15, -10<=k<=10, -34<=l<=37	
Reflections collected	27804	
Independent reflections	6270 [R(int) = 0.0359]	
Completeness to theta = 25.00°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9981 and 0.9658	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6270 / 0 / 469	
Goodness-of-fit on F ²	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1164	
R indices (all data)	R1 = 0.0762, wR2 = 0.1245	
Largest diff. peak and hole	0.151 and -0.233 e.Å ⁻³	

2-(4-Chlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3b)

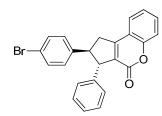


Following the general procedure, treatment of (*E*)-3-(4-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1b** (0.259 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h

followed by flash column chromatography afforded 2-(4-chlorophenyl)-3-phenyl-2,3dihydrocyclopenta[c]chromen-4(1H)-one **3b** as a white solid (0.356 g, 96%).

R_f (Pet. ether /EtOAc = 80/20): 0.63; ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.54 (m, 2H, H_{ar}), 7.42 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.37-7.23 (m, 6H, H_{ar}), 7.13-7.08 (m, 4H, H_{ar}), 4.43 (d, *J* = 5.0 Hz, 1H, CH), 3.79-3.72 (m, 1H, CH), 3.65-3.60 (m, 1H, CH), 3.22 (dd, *J*₁ = 5.7 Hz, *J*₂ = 18.1 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.75, 155.42, 154.80, 142.84, 142.06, 132.67, 131.67, 129.01, 128.83, 128.35, 127.12, 127.09, 125.12, 124.41, 118.25, 116.99, 59.24, 53.02, 39.40. HRMS calculated [M+Na]⁺ for C₂₄H₁₇O₂ClNa: 395.0809, found: 395.0803. FTIR (cm⁻¹) 3020, 2401, 1725, 1629, 1608, 1569, 1511, 1454, 1389, 1322, 1272, 1216, 1079, 1040, 927, 823, 757, 701, 669, 528.

2-(4-Bromophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3c)

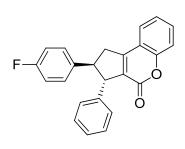


Following the general procedure, treatment of (*E*)-3-(4-bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1c** (0.303 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography

afforded 2-(4-bromophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one 3c as a white solid (0.391 g, 94%).

R_f (Pet. ether /EtOAc = 80/20): 0.59; ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.55 (m, 2H, H_{ar}), 7.44 (t, *J* = 8.2 Hz, 3H, H_{ar}), 7.37-7.24 (m, 4H, H_{ar}), 7.13 (d, *J* = 7.0 Hz, 2H, H_{ar}), 7.08 (d, *J* = 8.5 Hz, 2H, H_{ar}) 4.45 (d, *J* = 5.2 Hz, 1H, CH), 3.80-3.73 (m, 1H, CH), 3.64-3.60 (m, 1H, CH), 3.23 (dd, *J*₁ = 5.6 Hz, *J*₂ = 18.0 Hz, 1H, CH). ¹³C NMR (125 MHz, CDCl₃) δ 158.76, 155.35, 154.90, 143.46, 142.09, 132.05, 131.71, 128.89, 128.75, 128.50, 127.20, 127.13, 125.12, 124.43, 120.82, 118.31, 117.10, 59.25, 53.10, 39.43. HRMS calculated [M+Na]⁺ for C₂₄H₁₇O₂BrNa: 439.0304, found: 439.0301. FTIR (cm⁻¹) 3061, 3027, 2930, 1724, 1627, 1607, 1567, 1491, 1453, 1407, 1388, 1273, 1217, 1134, 1077, 1037, 1010, 923, 883, 819, 753, 700, 663, 525.

2-(4-Fluorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3d)

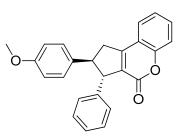


Following the general procedure, treatment of (*E*)-3-(4-fluorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1d** (0.121 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.066 g, 63 μ L, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 μ L, 0.1 mmol) in DME (2.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 2-(4-fluorophenyl)-3-phenyl-2,3-

dihydrocyclopenta[c]chromen-4(1H)-one **3d** as a white solid (0.159 g, 89%).

R_f (Pet. ether /EtOAc = 80/20): 0.55; ¹H NMR (400 MHz, CDCl₃) δ 8.18-8.11 (m, 2H, H_{ar}), 7.96 (d, *J* = 10.4 Hz, 1H, H_{ar}), 7.89-7.71 (m, 4H, H_{ar}), 7.64-7.56 (m, 4H, H_{ar}), 7.47-7.41 (m, 2H, H_{ar}), 4.21 (d, *J* = 6.4 Hz, 1H, CH), 3.44-3.33 (m, 1H, CH), 3.26-3.19 (m, 1H, CH), 2.76-2.68 (m 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 161.89 (d, *J* = 244.8 Hz), 158.88, 155.48, 154.92, 142.22, 140.26 (d, *J* = 3.0 Hz), 131.71, 128.90, 128.58, 128.48 (d, *J* = 8.1 Hz), 127.18, 127.15, 125.15, 124.44, 118.38, 117.14, 115.80 (d, *J* = 21.7 Hz), 59.45, 52.94, 39.66. HRMS calculated [M+Na]⁺ for C₂₄H₁₇O₂FNa: 379.1105, found: 379.1099. FTIR (cm⁻¹) 3062, 3018, 2928, 2855, 1725, 1608, 1569, 1511, 1496, 1454, 1388, 1301, 1248, 1217, 1178, 1158, 1064, 1038, 923, 909, 831, 756, 701, 667, 557.

2-(4-Methoxyphenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3e)

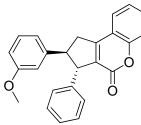


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one **1e** (0.255 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 2-(4-

methoxyphenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one **3e** as a white solid (0.339 g, 92%).

 R_f (Pet. ether /EtOAc = 80/20): 0.56; ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.57 (m, 2H, H_{ar}), 7.45 (d, J = 7.8 Hz, 1H, H_{ar}), 7.39-7.25 (m, 4H, H_{ar}), 7.18-7.11 (m, 4H, H_{ar}), 6.89 (d, J = 8.6 Hz, 2H, H_{ar}), 4.49 (d, J = 4.9 Hz, 1H, CH), 3.84-3.74 (m, 4H, CH), 3.66-3.61 (m, 1H, CH), 3.26 (dd, $J_1 = 5.6$ Hz, $J_2 = 17.9$ Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.88, 158.56, 155.64, 154.83, 142.48, 136.53, 131.51, 128.74, 128.62, 127.93, 127.14, 126.94, 125.14, 124.32, 118.43, 116.98, 114.24, 59.35, 55.33, 52.91, 39.62. HRMS calculated [M+H]⁺ for C₂₅H₂₁O₃: 369.1485, found: 369.1485. FTIR (cm⁻¹) 3438, 3060, 3027, 2934, 2836, 1729, 1625, 1607, 1584, 1492, 1453, 1388, 1320, 1288, 1263, 1215, 1156, 1078, 1038, 1001, 924, 887, 761, 737, 699.

2-(3-Methoxyphenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3f)

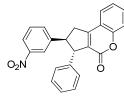


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one **1f** (0.255 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column

chromatography afforded 2-(3-methoxyphenyl)-3-phenyl-2,3-dihydrocyclopenta [c]chromen-4(1H)-one **3f** as a white solid (0.335 g, 91%)

R_f (Pet. ether /EtOAc = 80/20): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 6.9 Hz, 2H, Har), 7.41 (d, *J* = 8.4 Hz, 1H, Har), 7.35-7.23 (m, 5H, Har), 7.16 (d, *J* = 6.6.Hz, 2H, Har), 6.83-6.75 (m, 3H, Har), 4.51 (bs, 1H, CH), 3.77-3.71 (m, 4H, CH), 3.64-3.63 (m, 1H, CH), 3.27 (dd, *J*₁ = 4.5 Hz, *J*₂ = 17.8 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 159.90, 158.82, 155.57, 154.78, 146.16, 142.45, 131.52, 129.95, 128.74, 128.55, 127.12, 126.97, 125.12, 124.32, 119.13, 118.34, 116.92, 113.03, 111.83, 59.07, 55.22, 53.45, 39.42. HRMS calculated [M+H]⁺ for C₂₅H₂₁O₃: 369.1485, found: 369.1478. FTIR (cm⁻¹) 3060, 3028, 2935, 2837, 2251, 1947, 1725, 1607, 1492, 1454, 1388, 1320, 1263, 1217, 1157, 1078, 1039, 1001, 911, 888, 754, 704, 667, 573, 550, 520.

2-(3-Nitrophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3g)



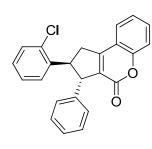
Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one **1g** (0.269 g 1.0 mmol) and *trans*cinnamaldehyde **1a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.0304 g, 30 μ L, 0.2 mmol) in DME (4.0

mL) at 25 °C for 12 h followed by flash column chromatography afforded 2-(3-nitrophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one **3g** as a white solid (0.322 g, 84%).

R_f (Pet. ether /EtOAc = 60/40): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 8.15-8.12 (m, 1H, H_{ar}), 8.09 (s, 1H, H_{ar}), 7.61-7.55 (m, 2H, H_{ar}), 7.51-7.50 (m, 2H, H_{ar}), 7.44 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.38-7.28 (m, 4H, H_{ar}), 7.13-7.11 (m, 2H, H_{ar}), 4.47 (d, *J* = 4.2 Hz, 1H, CH), 3.84-3.75 (m, 2H, CH), 3.31-3.26 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.68, 154.98, 148.68, 146.39, 141.61, 133.31, 131.97, 130.12, 129.11, 128.35, 127.53, 127.15, 125.12, 124.58, 122.32, 122.06, 118.16, 117.27, 59.32, 53.27, 39.35. HRMS calculated [M+H]⁺ for C₂₄H₁₈O₄N: 384.1230, found: 384.1226. FTIR (cm⁻¹) 3028, 2926, 1727, 1626, 1607, 1528, 1495, 1453, 1388, 1349, 1218, 1038, 925, 889, 754, 700.

2-(2-Chlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3h)

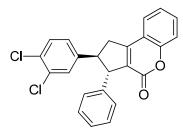
dihydrocyclopenta[c] chromen-4(1H)-one **3h** as a white solid (0.356 g, 95%).



Following the general procedure, treatment of (*E*)-3-(2-chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1h** (0.259 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded2-(2-chlorophenyl)-3-phenyl-2,3-

R_f (Pet. ether /EtOAc = 80/20): 0.56; ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 2H, H_{ar}), 7.45-7.41 (m, 2H, H_{ar}), 7.38-7.30 (m, 3H, H_{ar}), 7.27-7.19 (m, 6H, H_{ar}), 4.64 (d, *J* = 3.6 Hz, 1H, CH), 4.20-4.16 (m, 1H, CH), 3.85-3.78 (m, 1H, CH), 3.25 (dd, *J*₁ = 4.6 Hz, *J*₂ = 18.3 Hz, 1H, CH). ¹³C NMR (125 MHz, CDCl₃) δ 158.93, 155.40, 154.91, 142.08, 141.74, 133.74, 131.66, 130.12, 128.90, 128.83, 128.23, 127.76, 127.44, 127.22, 127.16, 125.18, 124.42, 118.38, 117.09, 57.29, 49.51, 38.45. HRMS calculated [M+H]⁺ for C₂₄H₁₈O₂Cl: 373.0990, found: 373.0988. FTIR (cm⁻¹) 3019, 2928, 2401, 1951, 1725, 1628, 1608, 1570, 1494, 1475, 1454, 1389, 1276, 1216, 1134, 1038, 926, 754, 700, 668, 482.

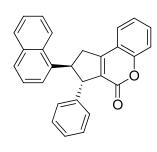
3,4-(Dichlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3i)



Following the general procedure, treatment of (*E*)-3-(3,4dichlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one **3i** (0.147 g 0.5 mmol) and *trans* cinnamaldehyde **2a** (0.066 g, 63 μ L, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 μ L, 0.1mmol) in DME (2.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3,4-(dichlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one **3i** as a white solid (0.183 g, 90%).

R_f (Pet. ether /EtOAc = 80/20): 0.54; ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.53 (m, 2H, H_{ar}), 7.43 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.38 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.35-7.31 (m, 2H, H_{ar}), 7.29-7.24 (m, 3H, H_{ar}), 7.13-7.11 (m, 2H, H_{ar}), 7.01 (dd, *J*₁ = 2.0 Hz, *J*₂ = 8.4 Hz, 1H, H_{ar}), 4.43 (d, *J* = 5.2 Hz, 1H, CH), 3.80-3.73 (m, 1H, CH), 3.62-3.57 (m, 1H, CH), 3.24-3.18 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.70, 155.09, 154.93, 144.72, 141.84, 132.93, 131.85, 131.10, 130.97, 129.01, 128.41, 127.38, 127.12, 126.47, 125.13, 124.51, 118.21, 117.18, 59.20, 52.77, 39.45. HRMS calculated [M+Na]⁺ for C₂₄H₁₇O₂Cl₂Na: 429.0420, found: 429.0419. FTIR (cm⁻¹) 3063, 3019, 2936, 1727, 1628, 1608, 1493, 1468, 1454, 1389, 1216, 1133, 1079, 1133, 1079, 1038, 886, 820, 756, 701, 668, 529.

2-(Naphthalen-1-yl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3j)

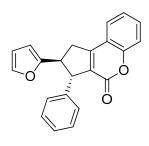


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1j** (0.275 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 2-(naphthalen-1-yl)-3-phenyl-2,3-

dihydrocyclopenta [c]chromen-4(1H)-one **3j** as a white solid (0.353 g, 91%).

R_f (Pet. ether /EtOAc = 80/20): 0.50; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (d, *J* = 8.4 Hz, 2H, H_{ar}), 7.83 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.62-7.44 (m, 6H, H_{ar}), 7.40-7.35 (m, 4H, H_{ar}), 7.33-7.28 (m, 3H, H_{ar}), 4.79 (bs, 1H, CH), 4.51 (bs, 1H, CH), 3.98-3.93 (m, 1H, CH), 3.46 (dd, *J*₁ = 3.7 Hz, *J*₂ = 18.2 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 179.45, 175.16, 174.27, 158.99, 159.19, 148.50, 145.18, 144.63, 142.24, 142.14, 141.84, 140.25, 139.71, 139.61, 138.55, 137.95, 137.73, 137.17, 136.16, 134.93, 134.76, 128.73, 126.98, 77.41, 53.13, 29.63. HRMS calculated [M+H]⁺ for C₂₈H₂₁O₂: 389.1536, found: 389.1526. FTIR (cm⁻¹) 3059, 2928, 1728, 1628, 1607, 1493, 1453, 1388, 1322, 1225, 1078, 1058, 1036, 925, 884, 797, 778, 760, 737, 700, 561, 473.

2-(Furan-2-yl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3k)

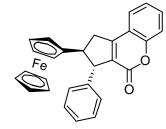


Following the general procedure, treatment of (*E*)-3-(furan-2-yl)-1-(2-hydroxyphenyl)prop-2-en-1-one **1k** (0.215 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 2-(Furan-2-yl)-3-phenyl-2,3-dihydrocyclopenta[*c*]chromen-

4(1*H*)-one **3k** as a gray solid (0.303 g, 92%).

R_f (Pet. ether /EtOAc = 80/20): 0.65; ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.53 (m, 2H, H_{ar}), 7.41-7.37 (m, 2H, H_{ar}), 7.35-7.30 (m, 3H, H_{ar}), 7.26-7.23 (m, 1H, H_{ar}), 7.20-7.18 (m, 1H, H_{ar}), 6.32-6.30 (m, 1H, H_{ar}), 6.10 (d, *J* = 3.2 Hz), 4.61 (d, *J* = 5.2 Hz, 1H, CH), 3.76-3.71 (m, 1H, CH), 3.68-3.60 (m, 1H, CH), 3.36 (dd, *J*₁ = 5.4 Hz, *J*₂ = 17.7 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.92, 156.20, 155.25, 154.81, 142.20, 141.98, 131.58, 128.80, 128.35, 127.24, 127.18, 125.09, 124.37, 118.43, 117.04, 110.35, 105.38, 55.93, 46.71, 36.58. HRMS calculated [M+H]⁺ for C₂₂H₁₇O₃: 329.1172, found: 329.1167. FTIR (cm⁻¹) 3113, 3063, 3019, 2927, 2854, 1725, 1630, 1608, 1570, 1494, 1454, 1390, 1321, 1276, 1217, 1148, 1135, 1078, 1063, 1039, 1013, 927, 894, 753, 700, 667.

2-(Ferroceniyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3l)

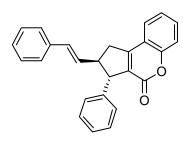


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-(ferroceniyl)prop-2-en-1-one **11** (0.083 g 0.25 mmol) and *trans* cinnamaldehyde **2a** (0.033 g, 31 μ L, 0.25 mmol) with imidazolium salt **4** (0.0085 mg, 0.025 mmol) and DBU (0.0076 mg, 7.5 μ L, 0.05 mmol) in DME (1.0 mL) at 25 °C for 12 h

followed by flash column chromatography afforded 2-(ferroceniyl)-3-phenyl-2,3-dihydrocyclop enta[c]chromen-4(1H)-one **3l** as a yellow solid (0.101 g, 91%).

 R_f (Pet. ether /EtOAc = 80/20): 0.53; ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.55 (m, 2H, H_{ar}), 7.42-7.34 (m, 4H, H_{ar}), 7.29-7.26 (m, 3H, H_{ar}), 4.42 (d, J = 3.6 Hz, 1H, CH), 4.16-4.05 (m, 9H), 3.76-3.69 (m, 1H, CH), 3.54-3.50 (m, 1H, CH), 3.27 (dd, J_1 = 4.8 Hz, J_2 = 17.7 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 159.02, 155.14, 154.74, 142.78, 131.43, 129.09, 128.82, 127.41, 127.02, 125.12, 124.29, 118.52, 117.00, 92.30, 68.56, 67.99, 67.88, 67.25, 65.90, 58.52, 47.47, 38.91. **HRMS** calculated [M]⁺ for C₂₈H₂₂O₂Fe: 446.0964, found: 446.0962. **FTIR** (**cm**⁻¹) 3025, 2923, 2841, 1718, 1628, 1607, 1492, 1452, 1388, 1214, 1134, 1033, 964, 924, 754, 697, 667, 527, 503.

3-Phenyl-2-((*E*)-styryl)-2,**3**-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3m)

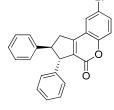


Following the general procedure, treatment of (2E,4E)-1-(2-hydroxyphenyl)-5-phenylpenta-2,4-dien-1-one **1m** (0.251 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 µL, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3-phenyl-2-((*E*)-styryl)-2,3-

dihydrocyclopenta[c]chromen-4(1H)-one **3m** as a yellow solid (0.289 g, 79%).

R_f (Pet. ether /EtOAc = 80/20): 0.50; ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.58 (m, 2H, H_{ar}), 7.46-7.44 (m, 1H, H_{ar}), 7.42-7.34 (m, 7H, H_{ar}), 7.32-7.25 (m, 4H, H_{ar}), 6.44 (d, *J* = 5.6 Hz, 2H, H_{ar}), 4.36 (d, *J* = 5.6 Hz, 1H, CH), 3.65-3.58 (m, 1H, CH), 3.36-3.29 (m, 1H, CH), 3.14-3.08 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.89, 155.61, 154.67, 141.85, 136.87, 131.46, 131.42, 130.56, 128.72, 128.62, 128.47, 127.53, 127.29, 126.95, 126.25, 125.10, 124.27, 118.43, 116.87, 56.86, 51.71, 37.44. HRMS calculated [M+H]⁺ for C₂₆H₂₁O₂: 365.1536, found: 365.1535. FTIR (cm⁻¹) 3061, 3026, 2928, 2061, 1984, 1735, 1651, 1608, 1569, 1493, 1452, 1429, 1388, 1322, 1276, 1216, 1134, 1078, 1063, 1039, 1001, 965, 925, 888, 753, 699, 667, 523.

8-bromo-2,3-diphenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3n)



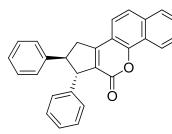
Following the general procedure, treatment of (*E*)-1-(5-bromo-2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1n** (0.303 g 1.0 mmol) and *trans*-cinnamaldehyde **1a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.0304 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 8-

bromo-2,3-diphenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one **3n** as a white solid (0.363 g, 87%).

 R_f (Pet. ether /EtOAc = 60/40): 0.54 ¹H NMR (400 MHz, CDCl₃) δ 7.69-7.66 (m, 2H, H_{ar}), 7.36-7.27 (m, 8H, H_{ar}), 7.21-7.20 (m, 1H, H_{ar}), 7.14 (d, J = 7.1 Hz, 2H, H_{ar}), 4.51-4.50 (m, 1H,

CH), 3.78-3.67 (m, 2H, CH), 3.29-3.24 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.25, 154.35, 153.76, 144.35, 142.13, 134.32, 129.99, 129.07, 128.93, 127.75, 127.23, 127.19, 126.90, 120.12, 118.81, 117.06, 59.32, 53.39, 39.51. HRMS calculated [M+H]⁺ for C₂₄H₁₈O₂Br: 417.0485, found: 417.0479. FTIR (cm⁻¹) 3027, 2923, 1729, 1601, 1492, 1453, 1414, 1373, 1265, 1218, 1078, 1029, 932, 818, 761, 698.

7,8-Diphenyl-8,9-dihydrobenzo[h]cyclopenta[c]chromen-6(7H)-one (3o)

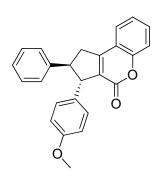


Following the general procedure, treatment of (*E*)-1-(1hydroxynaphthalen-2-yl)-3-phenylprop-2-en-1-one **10** (0.274 g 1.0 mmol) and *trans* cinnamaldehyde **2a** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.0304 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by

flash column chromatography afforded 7,8-diphenyl-8,9-dihydrobenzo[h]cyclopenta[c]chromen-6(7H)-one **30** as a white solid (0.354 g, 91%).

R_f (Pet. ether /EtOAc = 60/40): 0.56 ¹H NMR (400 MHz, CDCl₃) δ 8.57- 8.54 (m, 1H, H_{ar}), 7.69 (d, *J* = 8.7 Hz,1H, H_{ar}), 7.61-7.59 (m, 2H, H_{ar}), 7.49 (d, *J* = 8.6 Hz, 1H, H_{ar}), 7.29-7.11 (m, 10H, H_{ar}), 4.51-4.50 (m, 1H, CH), 3.81-3.74 (m, 1H, CH), 3.65-3.61 (m, 1H, CH), 3.29 (dd, *J*₁ = 5.3 Hz, *J*₂ = 18.0 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.99, 156.77, 152.07, 144.73, 142.55, 134.82, 129.02, 128.86, 128.63, 127.99, 127.92, 127.35, 127.23, 127.07, 127.02, 124.50, 123.37, 122.92, 121.11, 113.73, 59.15, 53.71, 39.97. HRMS calculated [M+H]⁺ for C₂₈H₂₁O₂: 389.1536, found: 389.1536. FTIR (cm⁻¹) 3019, 2400, 1722, 1611, 1565, 1531, 1495, 1370, 1353, 1216, 1080, 1030, 962, 929, 768, 668.

3-(4-methoxyphenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3p)

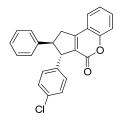


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (*E*)-3-(4-methoxyphenyl)acrylaldehyde **2p** (0.162 g, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3-(4-methoxyphenyl)-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one **3s** as a white solid (0.327 g,

89%).

R_f (Pet. ether /EtOAc = 80/20): 0.51; ¹H NMR (400 MHz, CDCl₃) δ 8.22-8.17 (m, 2H, H_{ar}), 8.02 (d, *J* = 10.8 Hz, 1H, H_{ar}), 7.94-7.89 (m, 3H, H_{ar}), 7.85-7.81 (m, 1H, H_{ar}), 7.75 (d, *J* = 9.3 Hz, 2H, H_{ar}), 7.59 (d, *J* = 10.3 Hz, 2H, H_{ar}), 7.30 (d, *J* = 10.3 Hz, 2H, H_{ar}), 4.33 (d, *J* = 6.0 Hz, 1H, CH), 3.47-3.39 (m, 4H, CH), 3.32-3.26 (m, 1H, CH), 2.83 (dd, *J*₁ = 6.7 Hz, *J*₂ = 22.4 Hz, 1H, CH). ¹³C NMR (125 MHz, CDCl₃) δ 179.18, 178.13, 174.79, 174.03, 161.21, 148.79, 144.93, 141.69, 141.50, 140.76, 139.24, 137.01, 136.00, 128.59, 126.69, 123.26, 53.70, 49.63, 47.68, 29.80. HRMS calculated [M+Na]⁺ for C₂₅H₂₀O₃Na: 391.1305, found: 391.1299. FTIR (cm⁻¹) 3062, 3016, 2935, 2837, 1727, 1608, 1585, 1568, 1512, 1495, 1454, 1388, 1322, 1302, 1249, 1217, 1134, 1065, 1038, 923, 908, 831, 755, 701, 667, 556.

3-(4-Chlorophenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3q)

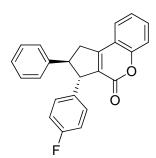


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (*E*)-3-(4chlorophenyl)acrylaldehyde **2q** (0.167 g, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.0304 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3-(4-

chlorophenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one **3q** as a white solid (0.338 g, 91%).

R_f (Pet. ether /EtOAc = 60/40): 0.61 ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.54 (m, 2H, H_{ar}), 7.42 (d, *J* = 8.3 Hz, 1H, H_{ar}), 7.36-7.24 (m, 6H, H_{ar}), 7.19-7.17 (m, 2H, H_{ar}), 7.06-7.04 (m, 2H, H_{ar}), 4.47-4.45 (m, 1H, CH), 3.78-3.70 (m, 1H, CH), 3.61-3.56 (m, 1H, CH), 3.31-3.25 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.88, 155.96, 154.91, 143.88, 140.90, 132.78, 131.81, 129.06, 128.99, 128.59, 128.11, 127.24, 127.04, 125.19, 124.49, 118.33, 117.14, 58.71, 53.87, 39.58. HRMS calculated [M+H]⁺ for C₂₄H₁₈O₂Cl: 373.0990, found: 373.0990. FTIR (cm⁻¹) 3019, 2939, 2400, 1722, 1628, 1607, 1493, 1457, 1388, 1325, 1216, 1064, 1044, 927, 828, 756, 668.

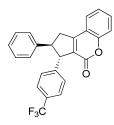
3-(4-Fluorophenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3r)



Following the general procedure, treatment of (E)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (E)-3-(4fluorophenyl)acrylaldehyde 2r (0.150 g, 1.0 mmol) with imidazolium salt 4 (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 µL, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3-(4-fluorophenyl)-2-phenyl-2,3dihydrocyclopenta[c]chromen-4(1H)-one 3r as a white solid (0.307 g, 86%).

 R_f (Pet. ether /EtOAc = 80/20): 0.63; ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.55 (m, 2H, H_{ar}), 7.44 (d, J = 8.2 Hz, 1H, H_{ar}), 7.37-7.27 (m, 4H, H_{ar}), 7.20 (d, J = 7.1 Hz, 2H, H_{ar}), 7.12-7.08 (m, 2H, H_{ar}), 6.99 (t, J = 8.5 Hz, 2H, H_{ar}), 4.48 (d, J = 5.3 Hz, 1H, CH), 3.79-3.72 (m, 1H, CH), 3.63-3.58 (m, 1H, CH), 3.29 (dd, $J_1 = 5.9$ Hz, $J_2 = 18.1$ Hz, 1H, CH). ¹³C NMR (100 MHz, **CDCl₃**) δ 161.94 (d, J = 241.8 Hz), 158.85, 155.73, 154.90, 144.08, 138.15 (d, J = 2.8 Hz), 131.72, 129.03, 128.69 (d, J = 8.5 Hz), 128.39, 127.17, 127.01, 125.18, 124.45, 118.37, 117.10, 115.64 (d, J = 21.16 Hz), 58.57, 53.87, 39.50. **HRMS** calculated $[M+Na]^+$ for $C_{24}H_{17}O_2FNa$: 379.1105, found: 379.1101. FTIR (cm⁻¹) 3030, 2925, 2854, 1728, 1683, 1625, 1601, 1509, 1455. 1378, 1298, 1275, 1236, 1158, 1124, 1097, 1037, 973, 818, 758, 723, 701, 495.

3-(4-(Trifluromethyl)phenyl)-2,3-dihydro-2-phenylcyclopenta[c]chromen-4(1H)-one (3s)

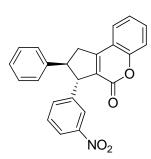


Following the general procedure, treatment of (E)-1-(2-hydroxyphenyl)-3phenylprop-2-en-1-one 1a (0.112 g 0.5 mmol) and (E)-3-(4-(trifluromethyl) phenyl)acrylaldehyde 2s (0.100 g, 0.5 mmol) with imidazolium salt 4 (0.017 g, 0.05 mmol) and DBU (0.0152 g, 15 µL, 0.1 mmol) in DME (2.0 mL) at 25 for 12 h followed by flash column chromatography afforded 3-(4-°C

(trifluromethyl)phenyl)-2,3-dihydro-2-phenylcyclopenta[c]chromen-4(1H)-one 3s as a white solid (0.197 g, 97%).

 R_f (Pet. ether /EtOAc = 60/40): 0.58; ¹H NMR (400 MHz, CDCl₃) δ 7.61-7.54 (m, 4H, H_{ar}), 7.44 (d, J = 8.2 Hz, 1H, H_{ar}), 7.37-7.33 (m, 3H, H_{ar}), 7.30-7.29 (m, 1H, H_{ar}), 7.23 (d, J = 7.9 Hz, 2H, H_{ar}), 7.18 (d, J = 7.2 Hz, 2H, H_{ar}), 4.55-4.54 (m, 1H, CH), 3.80-3.74 (m, 1H, CH), 3.63-3.60 (m, 1H, CH), 3.31 (dd, $J_1 = 6.2$ Hz, $J_2 = 18.2$ Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.84, 156.26, 154.98, 146.42, 143.70, 131.94, 129.14, 127.82, 127.59, 127.37, 127.06, 125.86, 125.83, 125.24, 124.56, 118.29, 117.20, 59.08, 53.81, 39.75. **HRMS** calculated [M+H]⁺ for C₂₅H₁₈O₂F₃: 407.1253, found: 407.1249. **FTIR** (cm⁻¹) 3029, 2029, 1726, 1620, 1607, 1496, 1454, 1420, 1389, 1326, 1218, 1164, 1110, 1064, 1018, 925, 842, 757, 701, 602, 459.

3-(3-Nitrophenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3t)

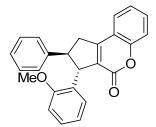


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.112 g 0.5 mmol) and (*E*)-3-(3nitrophenyl)acrylaldehyde **2t** (0.088 g, 0.5 mmol) with imidazolium salt **4** (0.017 g, 0.05 mmol) and DBU (0.015 g, 15 μ L, 0.1 mmol) in DME (2.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3-(3-nitrophenyl)-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-

4(1*H*)-one **3t** as a white solid (0.167 g, 87%).

R_f (Pet. ether /EtOAc = 60/40): 0.61; ¹H NMR (400 MHz, CDCl₃) δ 8.12-8.09 (m, 1H, H_{ar}), 7.98 (bs, 1H, H_{ar}), 7.62-7.56 (m, 2H, H_{ar}), 7.47-7.42 (m, 3H, H_{ar}), 7.39-7.29 (m, 4H, H_{ar}), 7.20-7.18 (m, 2H, H_{ar}), 4.60-4.58 (m, 1H, CH), 3.84-3.77 (m, 1H, CH), 3.66-3.61 (m, 1H, CH), 3.37-3.30 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.78, 156.58, 154.97, 148.69, 144.47, 143.01, 132.12, 129.71, 129.21, 127.52, 127.29, 127.06, 125.30, 124.65, 122.29, 122.00, 118.18, 117.22, 58.85, 54.04, 39.75. HRMS calculated [M+H]⁺ for C₂₄H₁₈O₄N: 384.1230, found: 384.1229. FTIR(cm⁻¹) 3020, 2930, 2401, 1957, 1723, 1627, 1608, 1530, 1496, 1454, 1389, 1352, 1216, 1065, 1046, 942, 883, 805, 757, 701, 668.

3-(2-Methoxyphenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3u)

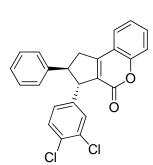


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (*E*)-3-(2methoxyphenyl)acrylaldehyde **2u** (0.162 g, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column

chromatography 3-(2-methoxyphenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one**3u**as a white solid (0.331 g, 89%).

 R_f (Pet. ether /EtOAc = 80/20): 0.59; ¹H NMR (400 MHz, CDCl₃) δ 7.60-7.56 (m, 2H, H_{ar}), 7.46 (d, J = 8.5 Hz, 1H, H_{ar}), 7.38-7.30 (m, 3H, H_{ar}), 7.27-7.22 (m, 4H, H_{ar}), 6.95-6.86 (m, 3H, H_{ar}), 4.84 (d, J = 2.7 Hz, 1H, CH), 3.73-3.64 (m, 5H), 3.29-3.23 (m, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 159.86, 157.28, 156.05, 154.84, 145.65, 131.34, 130.24, 128.66, 128.47, 128.15, 127.55, 126.87, 126.69, 125.07, 124.29, 120.64, 118.59, 117.04, 111.06, 55.35, 53.60, 51.85, 39.04. HRMS calculated [M+H]⁺ for C₂₅H₂₁O₃: 369.1485, found: 369.1482. FTIR (cm⁻¹) 3062, 3027, 2936, 2837, 1725, 1626, 1607, 1493, 1454, 1439, 1389, 1272, 1288, 1246, 1134, 1110, 1092, 1033, 974, 926, 754, 701, 667, 475.

3-(3,4-Dichlorophenyl)-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3v)

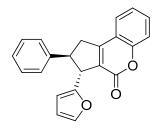


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.056 g 0.25 mmol) and (*E*)-3-(3,4dichlorophenyl)acrylaldehyde **2v** (0.050 g, 0.25 mmol) with imidazolium salt **4** (0.0085 g, 0.025 mmol) and DBU (0.0076 g, 7.5 μ L, 0.050 mmol) in DME (1.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3-(3,4-Dichlorophenyl)-2-phenyl-2,3-

dihydrocyclopenta[c]chromen-4(1H)-one **3v** as a white solid (0.082 g, 81% after crystalisation in Pet. ether).

R_f (Pet. ether /EtOAc = 80/20): 0.49; ¹H NMR (400 MHz, CDCl₃) δ 7.62-7.60 (m, 2H, H_{ar}), 7.44-7.26 (m, 7H, H_{ar}), 7.15 (d, *J* = 6.9 Hz, 2H, H_{ar}), 7.05 (dd, *J*₁ = 2.0 Hz, *J*₂ = 8.3 Hz, 1H, H_{ar}) 4.45 (d, *J* = 5.1 Hz, 1H, CH), 3.82-3.75 (m, 1H, CH), 3.65-3.60 (m, 1H, CH), 3.23 (dd, *J*₁ = 5.7 Hz, *J*₂ = 18.1 Hz, 1H, CH). ¹³C NMR (125 MHz, CDCl₃) δ 158.58, 155.08, 154.81, 144.60, 141.78, 132.77, 131.75, 130.94, 130.86, 128.96, 128.89, 128.22, 127.26, 127.06, 126.45, 125.10, 124.43, 118.12, 117.00, 59.09, 52.72, 39.30. HRMS calculated [M+H]⁺ for C₂₄H₁₇O₂Cl₂: 407.0600, found: 407.0601. FTIR (cm⁻¹) 3029, 1726, 1683, 1625m 1607, 1568, 1494, 1470, 1454, 1400, 1288, 1217, 1133, 1066, 1030, 935, 819, 757, 719, 700, 670, 479.

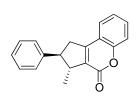
3-(Furan-2-yl)-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3w)



Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (*E*)-3-(furan-2yl)acrylaldehyde **2w** (0.122 g, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h followed by flash column chromatography afforded 3(furan-2-yl)-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one **3w** as a white solid (0.271 g, 82%).

R_f (Pet. ether /EtOAc = 80/20): 0.62; ¹H NMR (400 MHz, CDCl₃) δ 7.59-7.53 (m, 2H, H_{ar}), 7.42 (d, *J* = 8.2 Hz, 1H, H_{ar}), 7.35-7.31 (m, 4H, H_{ar}), 7.26 (d, *J* = 6.8 Hz, 1H, H_{ar}), 7.25-7.21 (m, 2H, H_{ar}), 6.33-6.32 (m, 1H, H_{ar}), 6.15 (d, *J* = 3.2 Hz, 1H, H_{ar}), 4.59 (d, *J* = 4.7 Hz, 1H, CH), 3.92-3.87 (m, 1H, CH), 3.80-3.73 (m, 1H, CH), 3.26 (dd, *J*₁ = 4.8 Hz, *J*₂ = 17.8 Hz, 1H, CH). ¹³C NMR (100 MHz, CDCl₃) δ 158.84, 155.91, 154.82, 154.14, 144.19, 141.87, 131.74, 129.00, 127.13, 126.81, 126.42, 125.21, 124.40, 118.41, 117.07, 110.60, 106.42, 51.99, 49.63, 39.05. HRMS calculated [M+H]⁺ for C₂₂H₁₇O₃: 329.1172, found: 329.1165. FTIR (cm⁻¹) 3165, 3004, 2943, 2628, 2411, 2293, 2253, 1726, 1625, 1602, 1452, 1416, 1376, 1147, 1070, 1039, 1007, 918, 758.

3-Methyl-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3x)

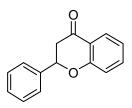


Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3-phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (*E*)-but-2-enal **2x** (0.0702 g, 82 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C

for 12 h followed by flash column chromatography afforded 3-methyl-2-phenyl-2,3dihydrocyclopenta[c]chromen-4(1H)-one **3x** as a white solid (0.205 g, 74%) along with 2phenylchroman-4-one **12** as a white solid (0.050 g, 22%).

R_f (Pet. ether /EtOAc = 60/40): 0.61; ¹H NMR (400 MHz, CDCl₃) δ 7.55-7.51 (m, 1H, H_{ar}), 7.47-7.45 (m, 1H, H_{ar}), 7.41-7.32 (m, 3H, H_{ar}), 7.32-7.25 (m, 4H, H_{ar}), 3.57 (dq, *J*₁ = 1.9 Hz, *J*₂ = 18.7 Hz, *J*₃ = 17.7 Hz, *J*₄ = 26.5, Hz, 1H, CH), 3.43-3.38 (m, 1H, CH), 3.29-3.23 (m, 1H, CH), 3.15-3.09 (m, 1H, CH), 1.46 (d, *J* = 6.9 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 159.58, 154.51, 154.09, 144.23, 131.13, 130.29, 128.86, 127.27, 126.90, 124.87, 124.22, 118.60, 116.84, 52.26, 47.90, 39.19, 18.47. HRMS calculated [M+H]⁺ for C₁₉H₁₆O₂Na: 299.1043, found: 299.1041. FTIR (cm⁻¹) 3062, 3020, 2960, 2930, 2871, 1950, 1720, 1625, 1608, 1584, 1571, 1493, 1430, 1453, 1389, 1373, 1320, 1288, 1217, 1135, 1078, 1092, 1033, 1019, 976, 948, 884, 756, 702, 667, 539.

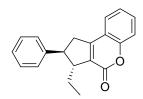
2-Phenylchroman-4-one (9)⁶



 R_f (Pet. ether /EtOAc = 80/20): 0.65 ¹H NMR (200 MHz, CDCl₃) δ 7.95 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.2$ Hz, 1H, H_{ar}), 7.57-7.36 (m, 6H, H_{ar}), 7.10-7.03 (m, 2H, H_{ar}), 5.50 (dd, $J_1 = 3.3$ Hz, $J_2 = 13.0$ Hz, 1H, CH), 3.19-2.85 (m, 2H, CH₂). ¹³C NMR (100 MHz, CDCl₃) δ 192.16, 161.70, 138.86, 136.37, 129.00, 128.93, 127.20, 126.29, 121.77, 121.05, 118.28, 79.75,

44.82. **HRMS** calculated $[M+H]^+$ for C₁₅H₁₃O₂: 225.0910, found: 225.0910. **FTIR** (**cm**⁻¹) 3066, 3035, 1692, 1606, 1577, 1498, 1472, 1463, 1371, 1321, 1304, 1228, 1149, 1116, 1066, 1027, 988, 906, 760, 699, 590.

3-Ethyl-2-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (**3**y)



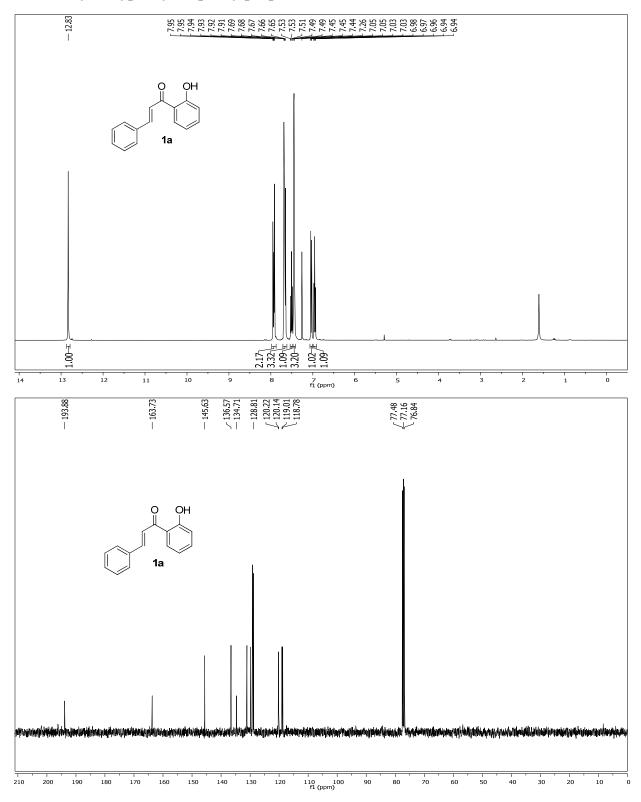
Following the general procedure, treatment of (*E*)-1-(2-hydroxyphenyl)-3phenylprop-2-en-1-one **1a** (0.224 g 1.0 mmol) and (*E*)-pent-2-enal **2y** (0.132 g, 126 μ L, 1.0 mmol) with imidazolium salt **4** (0.034 g, 0.1 mmol) and DBU (0.030 g, 30 μ L, 0.2 mmol) in DME (4.0 mL) at 25 °C for 12 h

followed by flash column chromatography afforded 3-ethyl-2-phenyl-2,3-dihydrocyclopenta [c]chromen-4(1*H*)-one **3y** as a white solid (0.251 g, 86% yield).

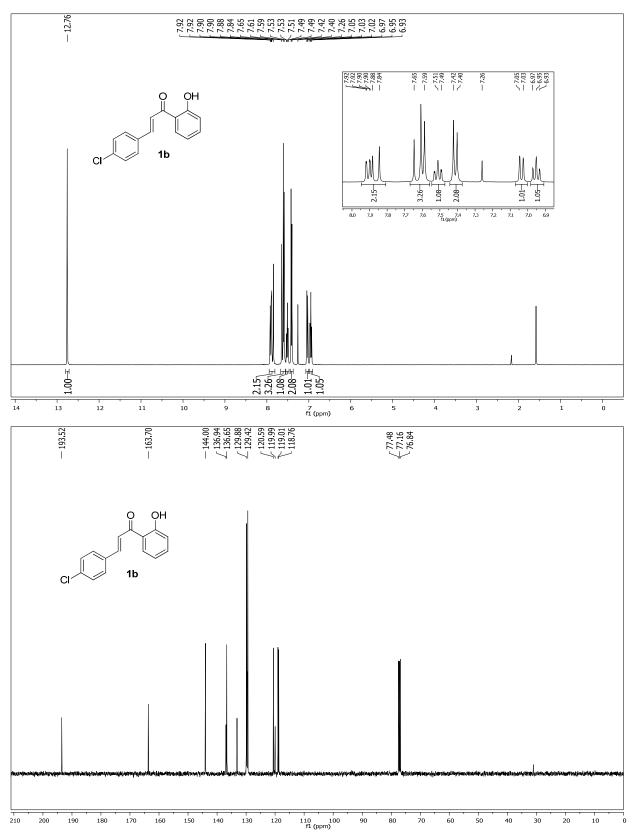
R_f (Pet. ether /EtOAc = 80/20): 0.56 ¹H NMR (500 MHz, CDCl₃) δ 7.54-7.51 (m, 1H, H_{ar}), 7.45 (dd, $J_1 = 1.5$ Hz, $J_2 = 7.8$ Hz , 1H, H_{ar}), 7.41 (d, J = 7.9 Hz, 1H, H_{ar}), 7.32-7.28 (m, 3H, H_{ar}), 7.24-7.21 (m, 3H, H_{ar}), 3.59 (qd, $J_1 = 2.3$ Hz, $J_2 = 9.2$ Hz, $J_3 = 18.2$ Hz, 1H, CH), 3.48-3.45 (m, 1H, CH), 3.39-3.38 (m, 1H, CH), 3.13-3.08 (m, 1H, CH), 2.07-2.02 (m, 1H, CH), 1.78-1.72 (m, 1H, CH), 0.98 (t, J = 7.7 Hz, 3H, CH₃), ¹³C NMR (125 MHz, CDCl₃) δ 159.65, 154.59, 146.25, 131.19, 129.53, 128.94, 126.94, 126.72, 124.92, 124.27, 118.62, 116.93, 54.62, 47.59, 39.91, 25.44, 11.12. HRMS calculated [M+H]⁺ for C₂₀H₁₉O₂: 291.1380, found: 291.1378. FTIR (cm⁻¹) 3062, 3029, 2963, 2932, 2252, 1719, 1630, 1607, 1577, 1494, 1454, 1389, 1321, 1305, 1282, 1268, 1227, 1198, 1156, 1100, 1076, 1065, 1036, 1020, 910, 886, 756, 735, 701, 648.

⁶ Han, F.; Chen, G.; Zhang, X.; Liao, J. Eur. J. Org. Chem. 2011, 2928.

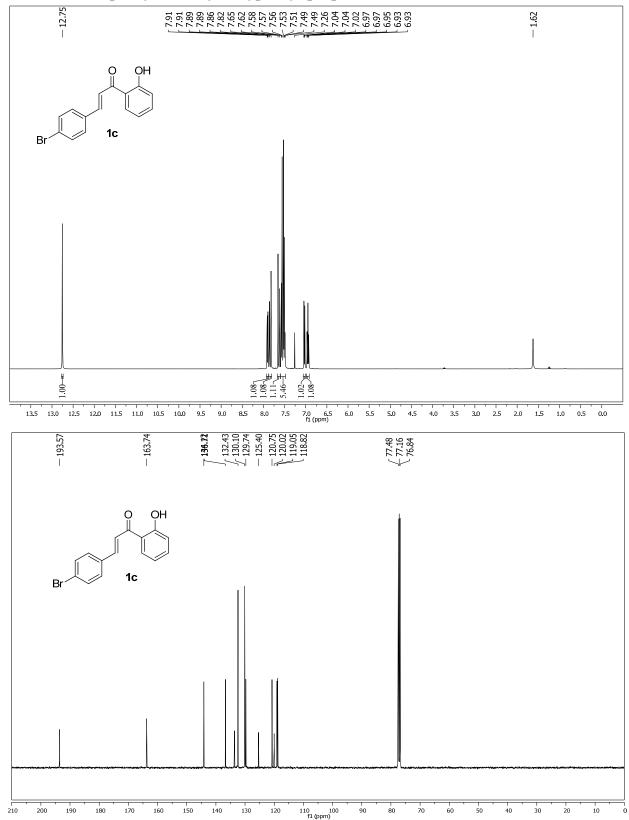
8. ¹H and ¹³C NMR Spectra 2'-Hydroxy Chalcones



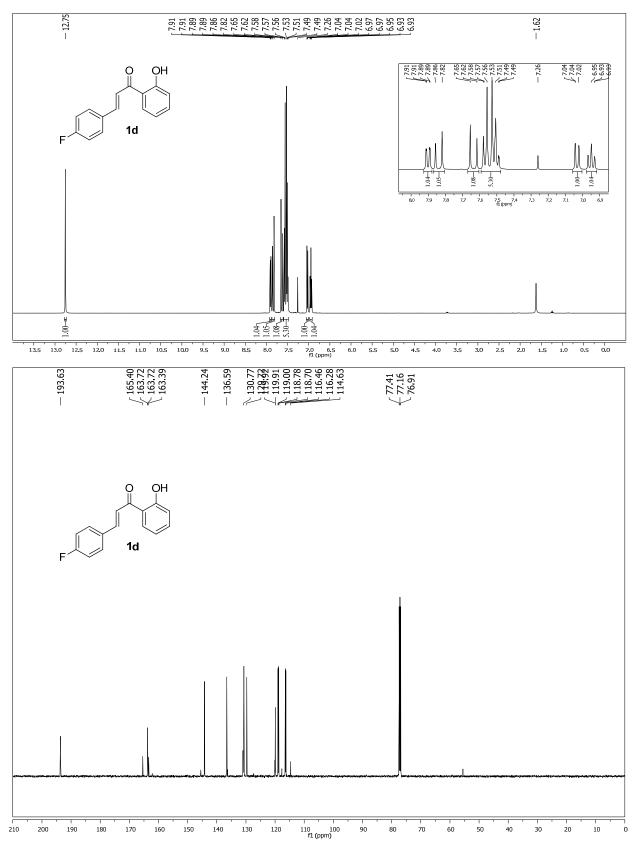
(*E*)-1-(2-Hydroxyphenyl)-3-phenylprop-2-en-1-one (1a)

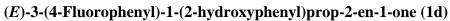


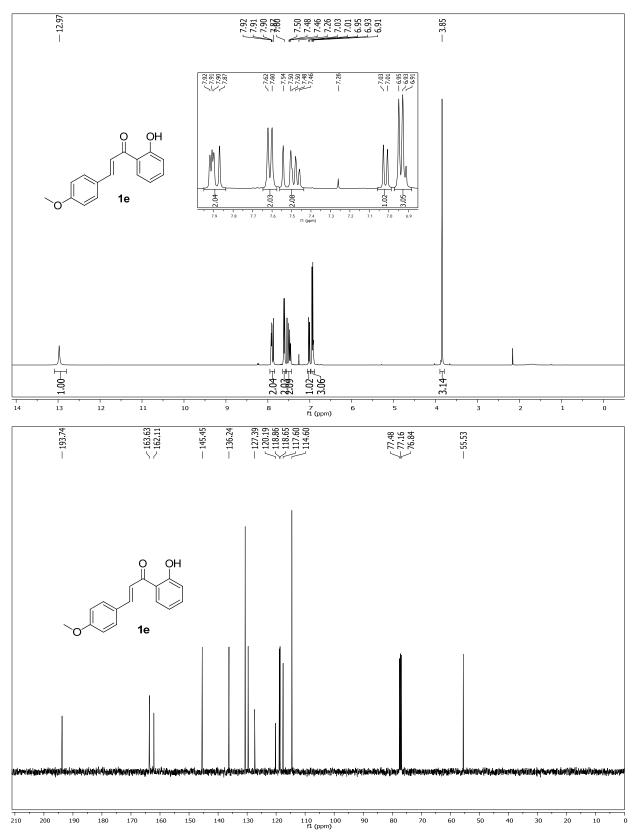
(*E*)-3-(4-Chlorophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1b)



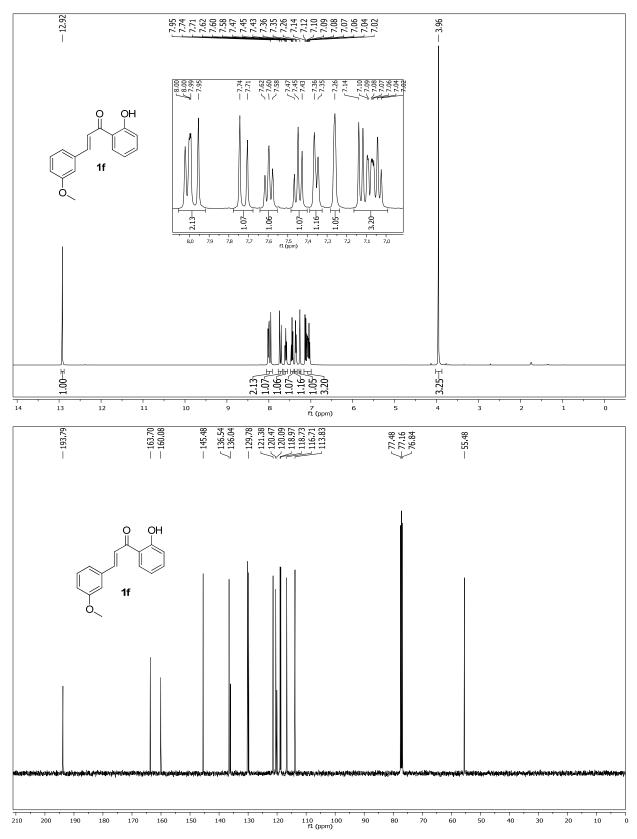
(*E*)-3-(4-Bromophenyl)-1-(2-hydroxyphenyl)prop-2-en-1-one (1c)



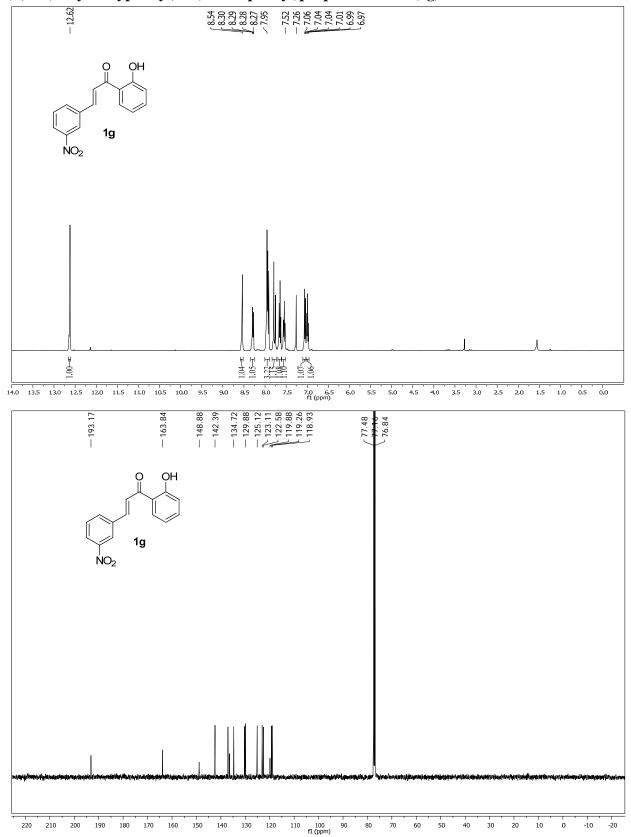




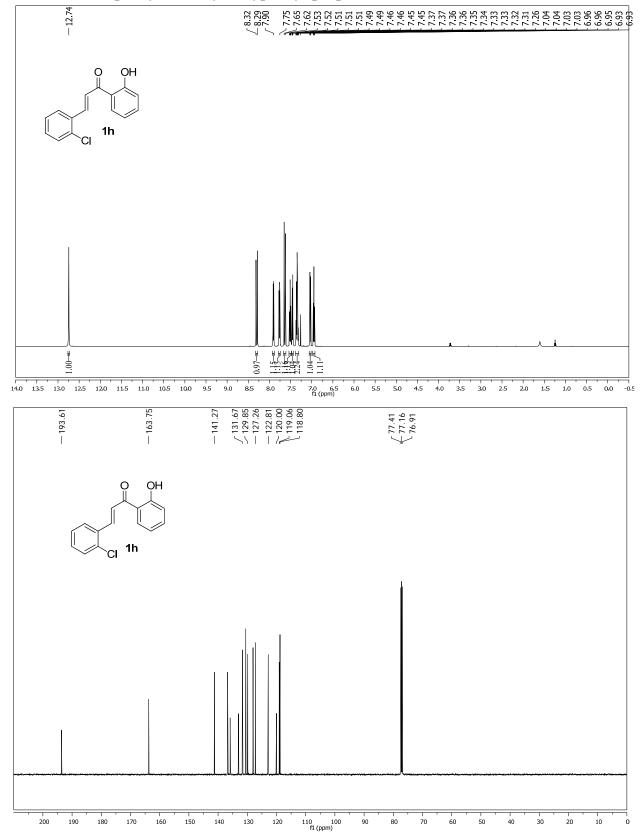
(E)-1-(2-Hydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (1e)

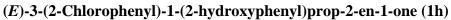


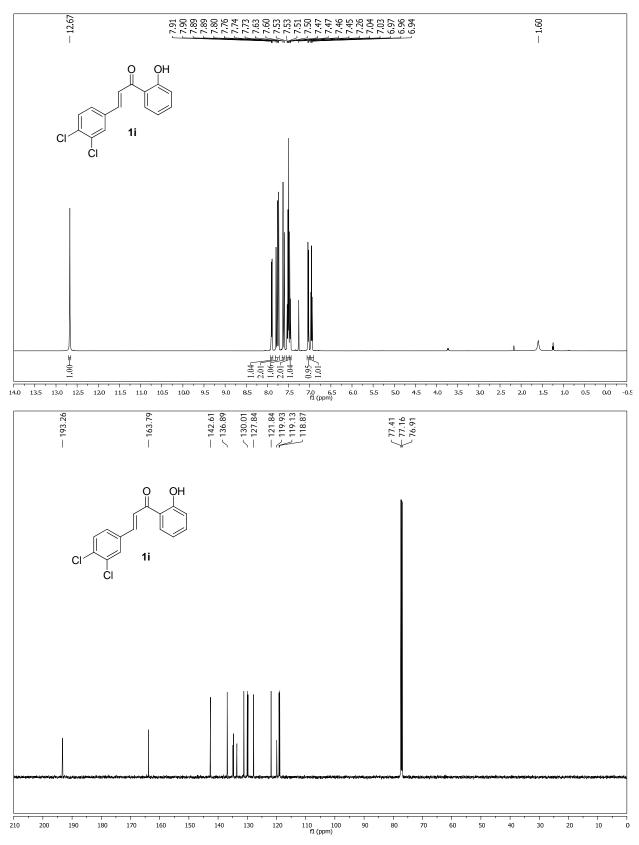
(E)-1-(2-Hydroxyphenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (1f)

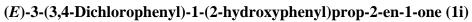


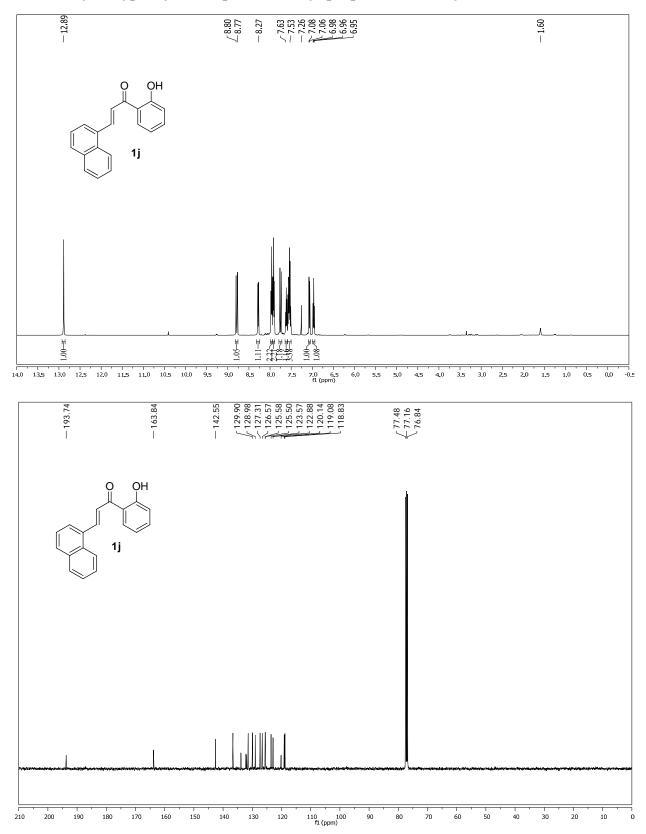
(*E*)-1-(2-Hydroxyphenyl)-3-(3-nitrophenyl)prop-2-en-1-one (1g)



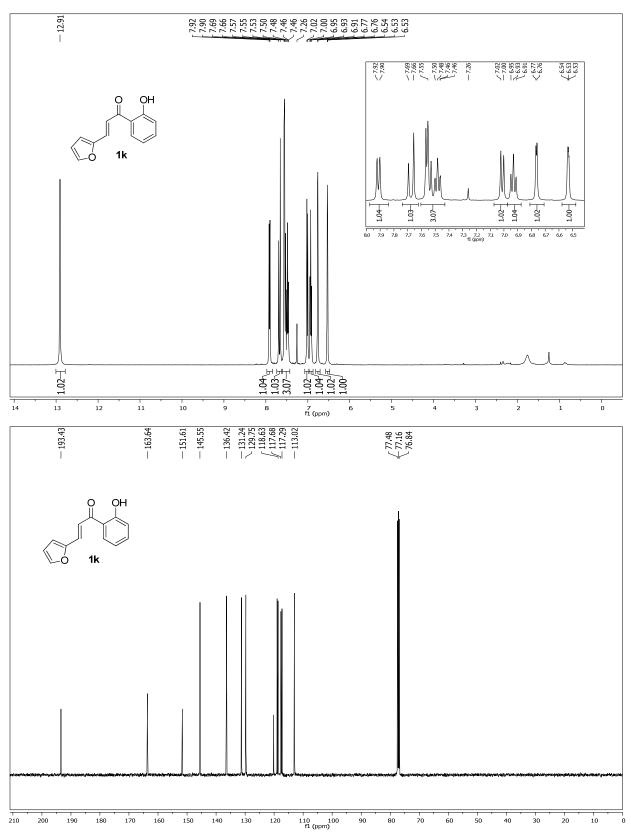


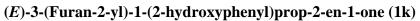


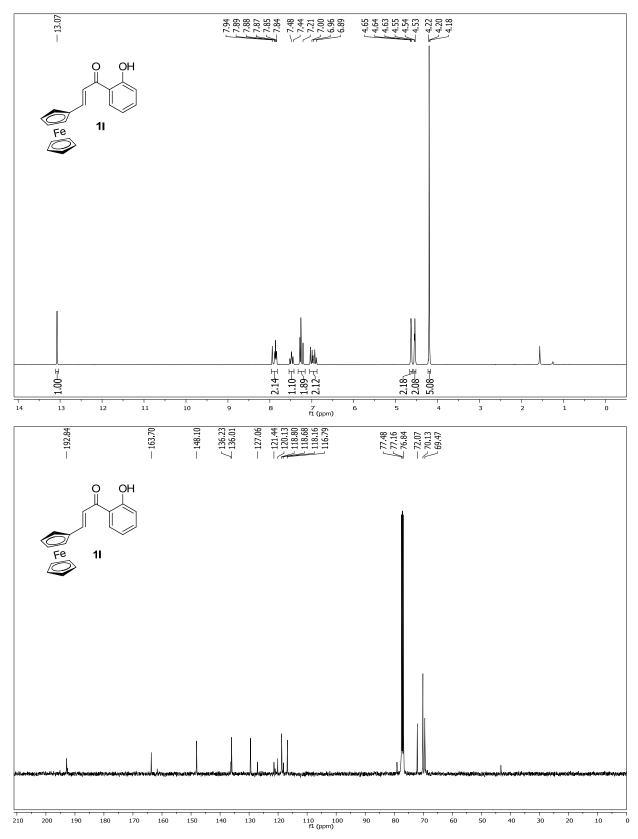


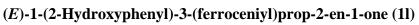


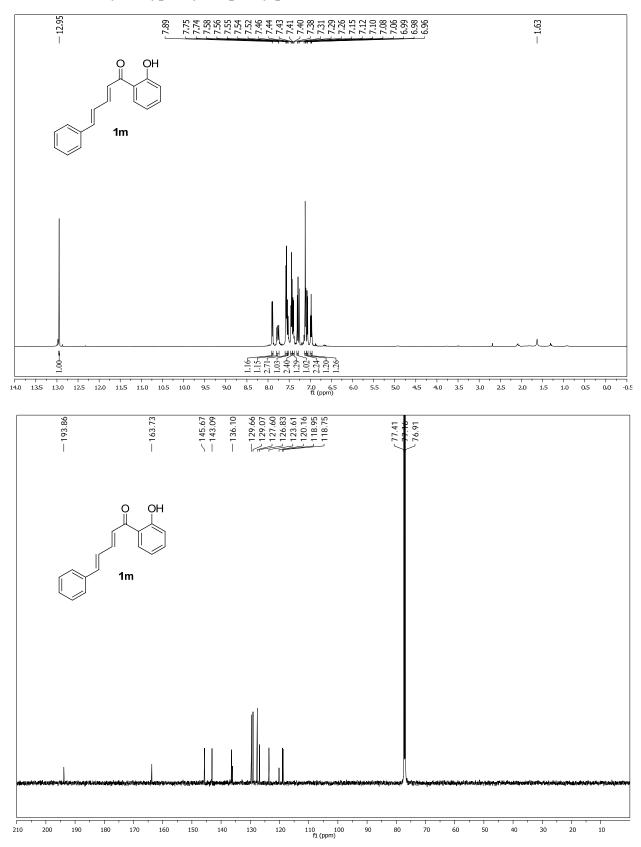


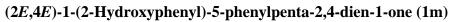


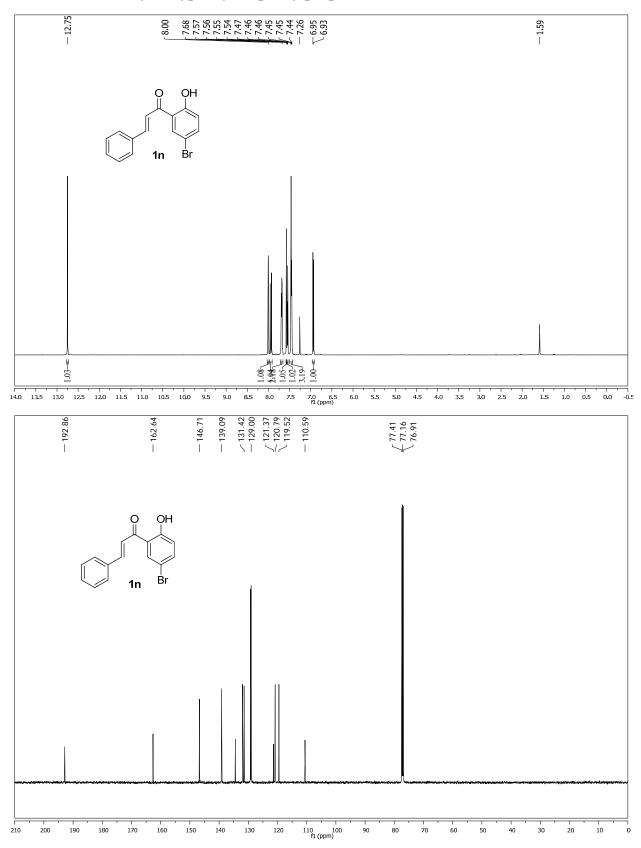


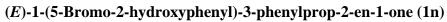


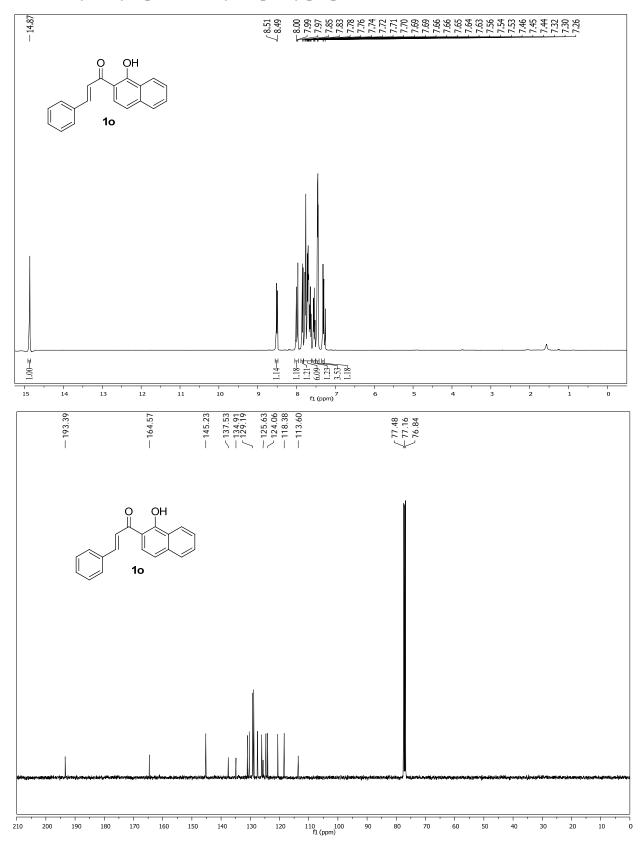


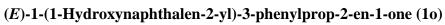


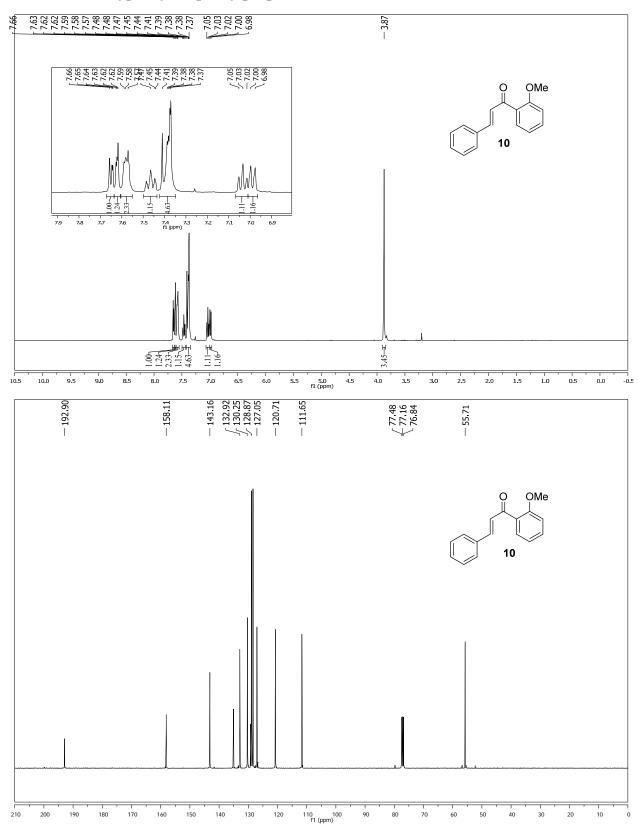








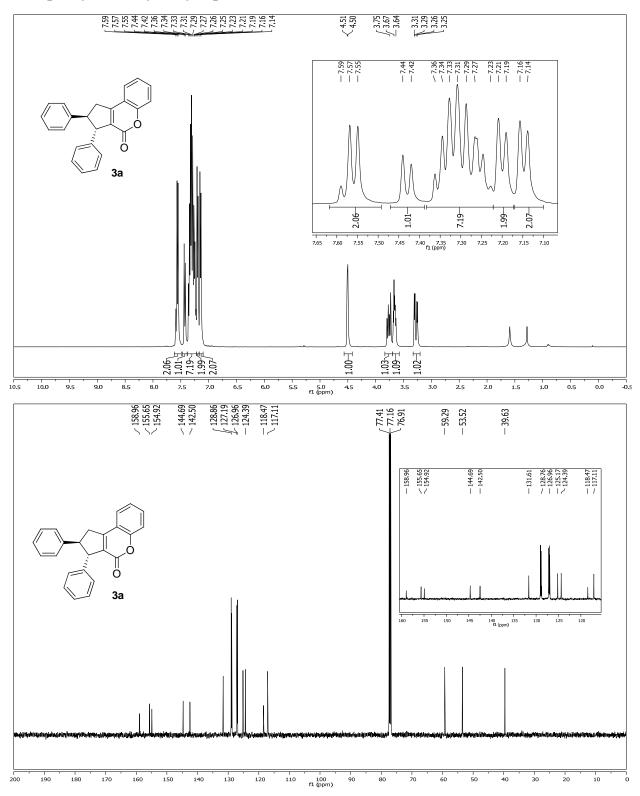


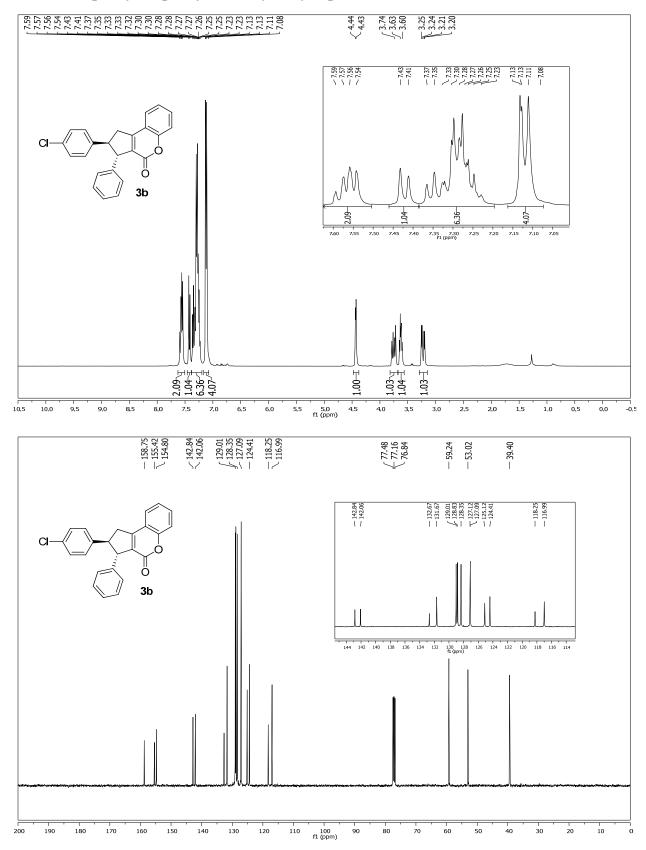


(*E*)-1-(2-Methoxyphenyl)-3-phenylprop-2-en-1-one (10)

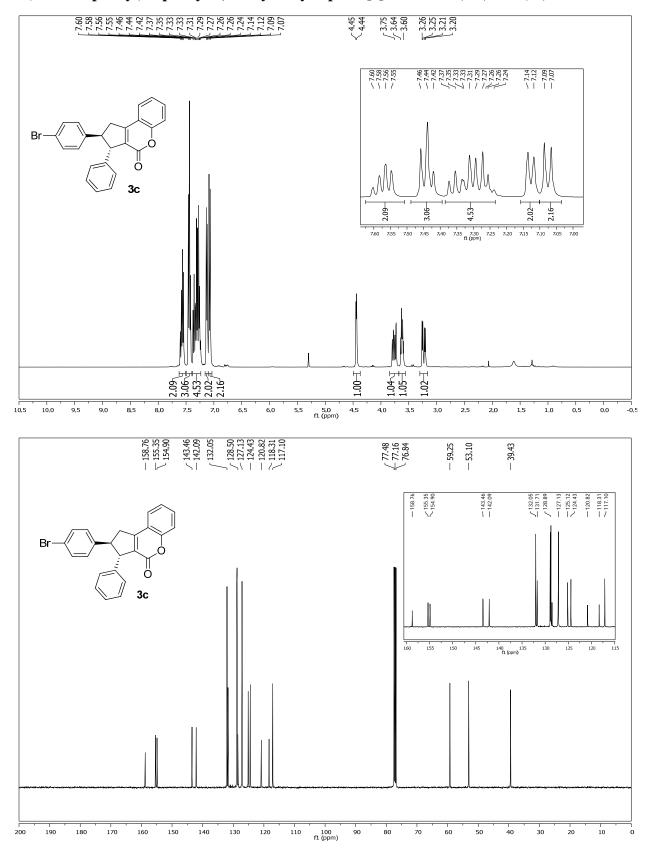
9. ¹H and ¹³C NMR Spectra Functionalized Coumarins

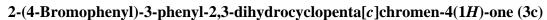
2,3-Diphenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3a)

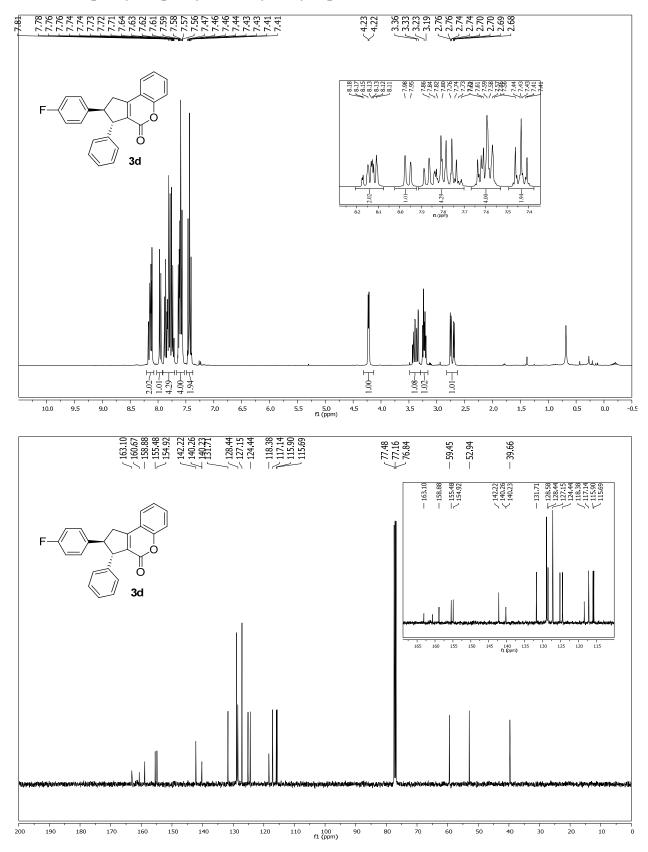




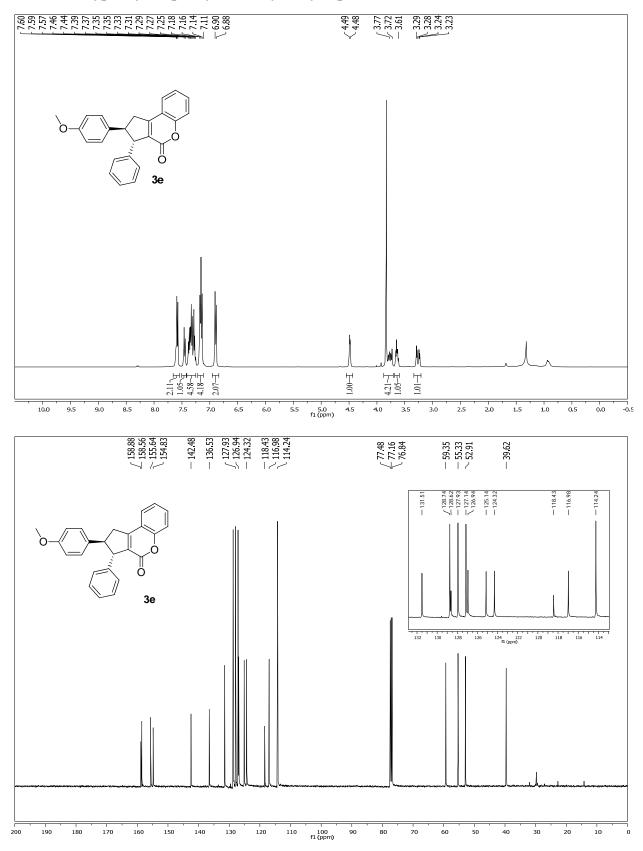
2-(4-Chlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3b)



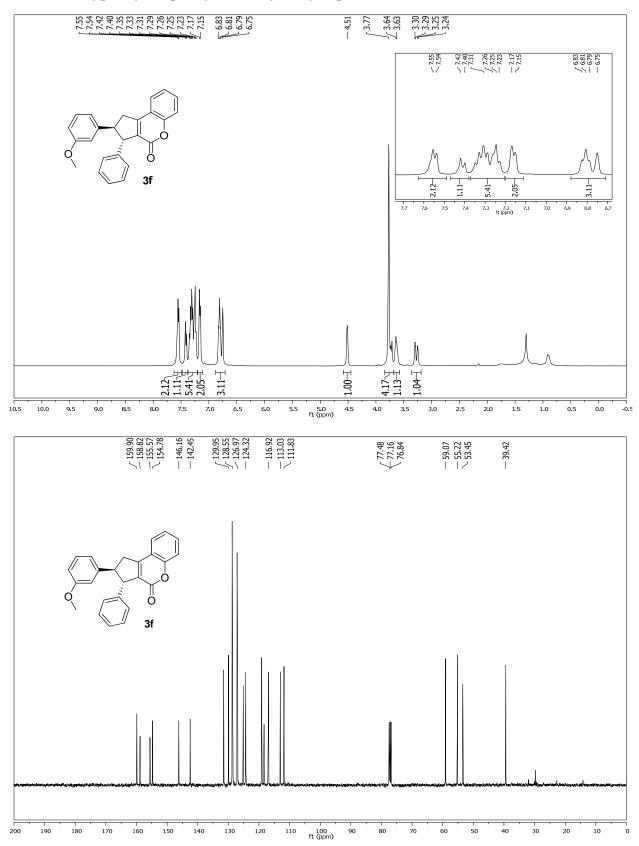


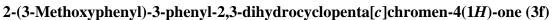


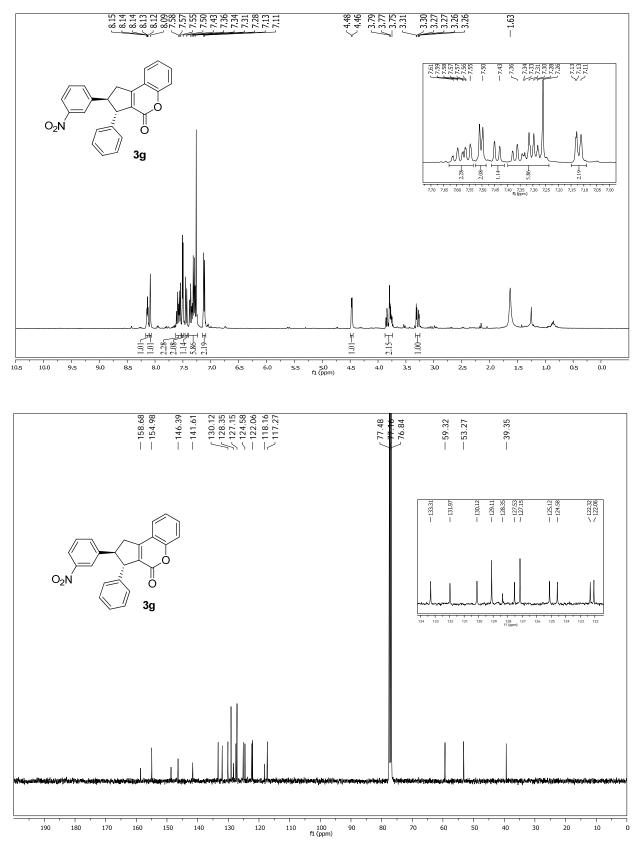
2-(4-Fluorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3d)



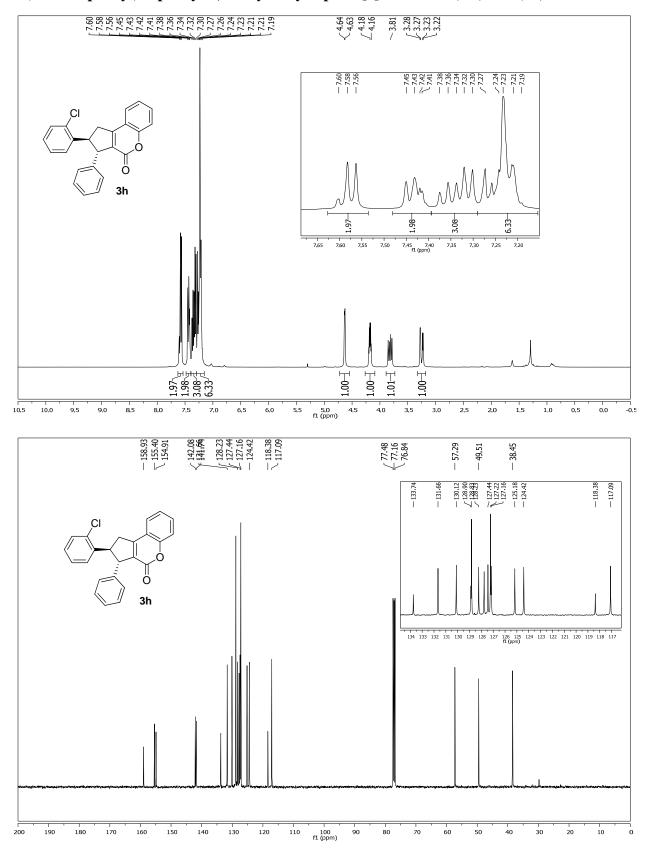
2-(4-Methoxyphenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3e)



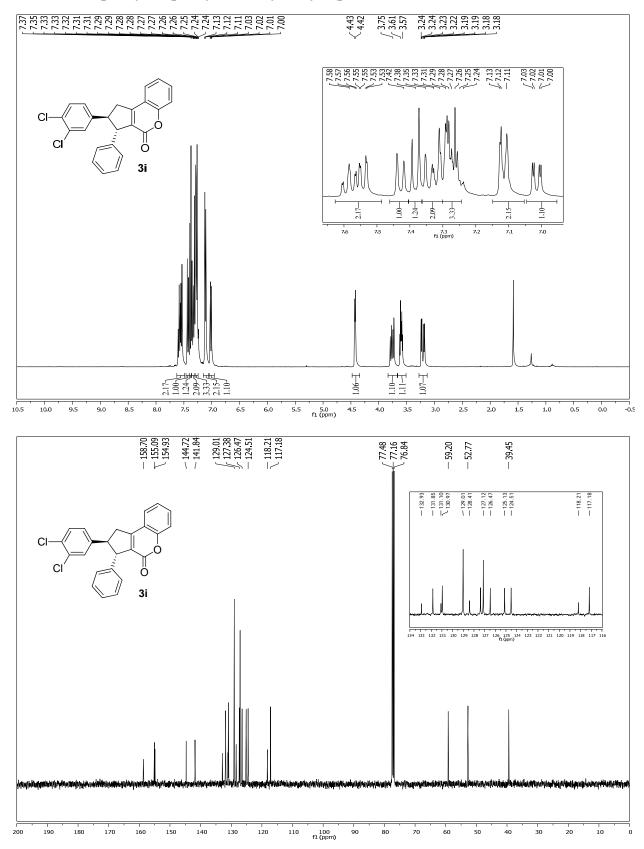




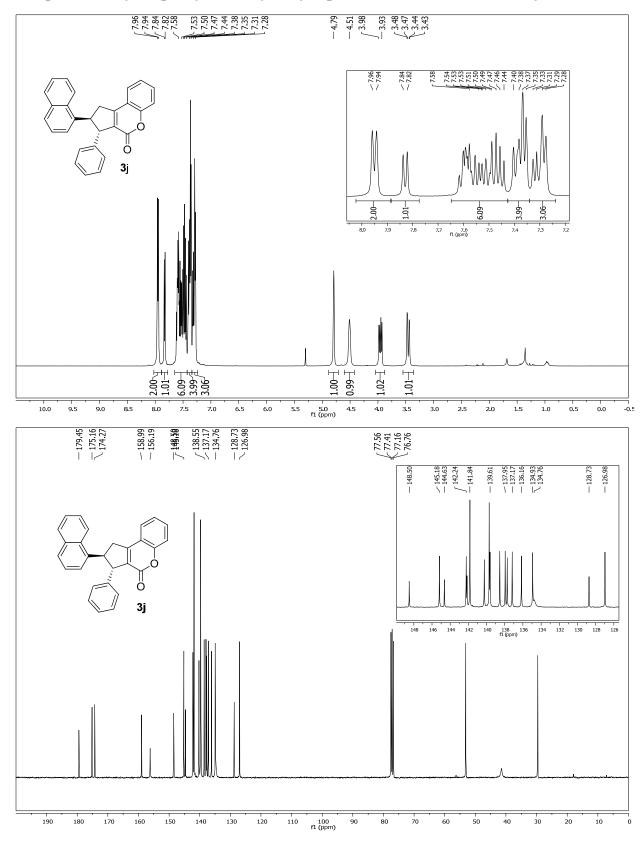


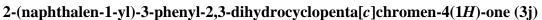


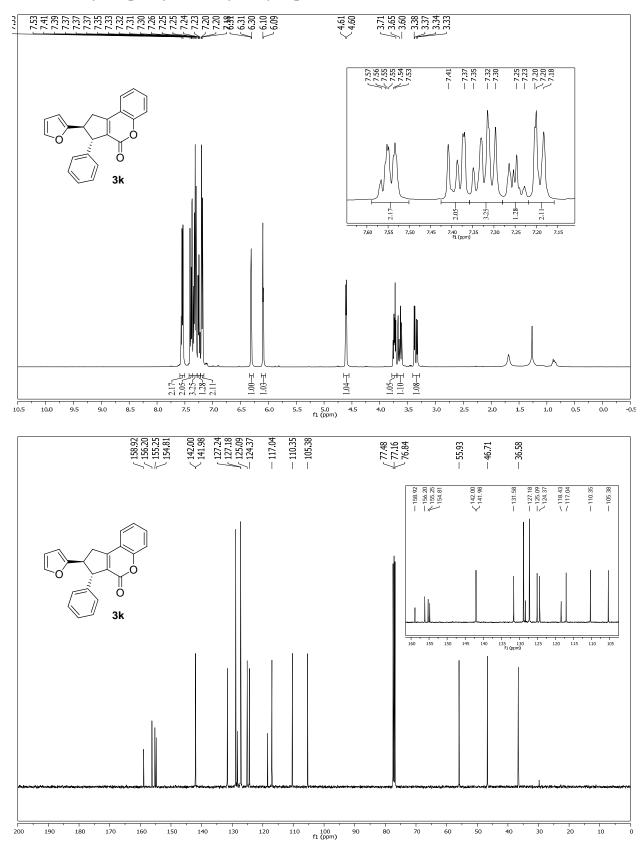
2-(2-chlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3h)

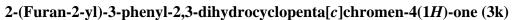


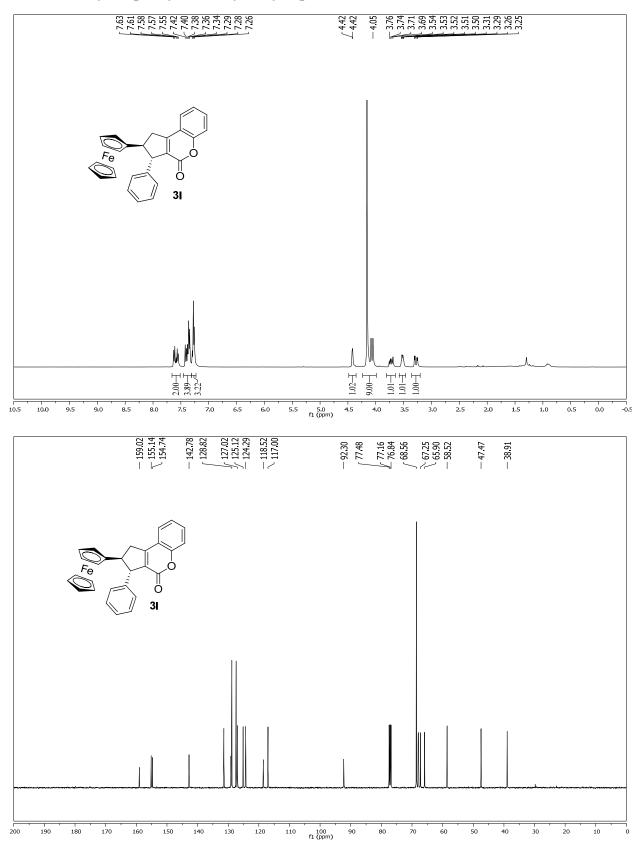
3,4-(Dichlorophenyl)-3-phenyl-2,3-dihydrocyclopenta[*c*]chromen-4(1*H*)-one (3i)



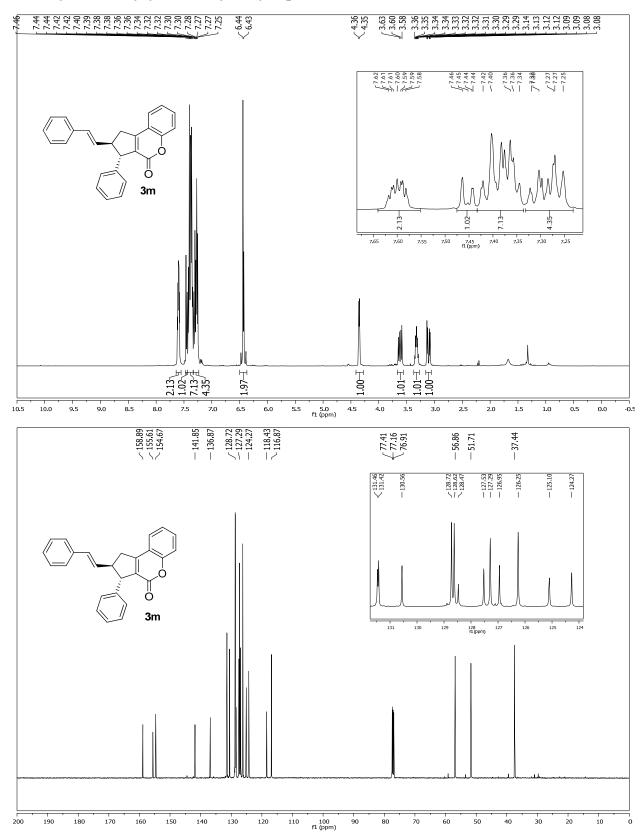




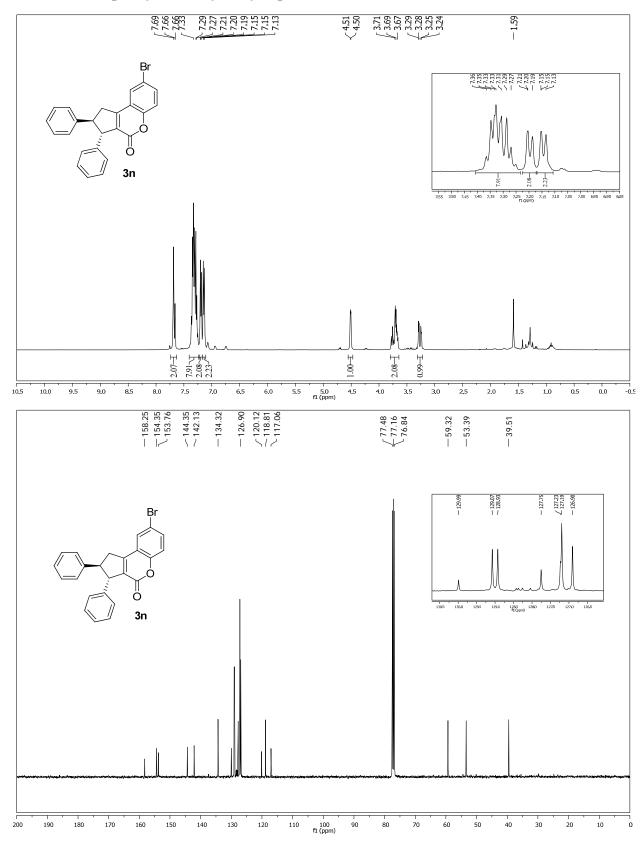




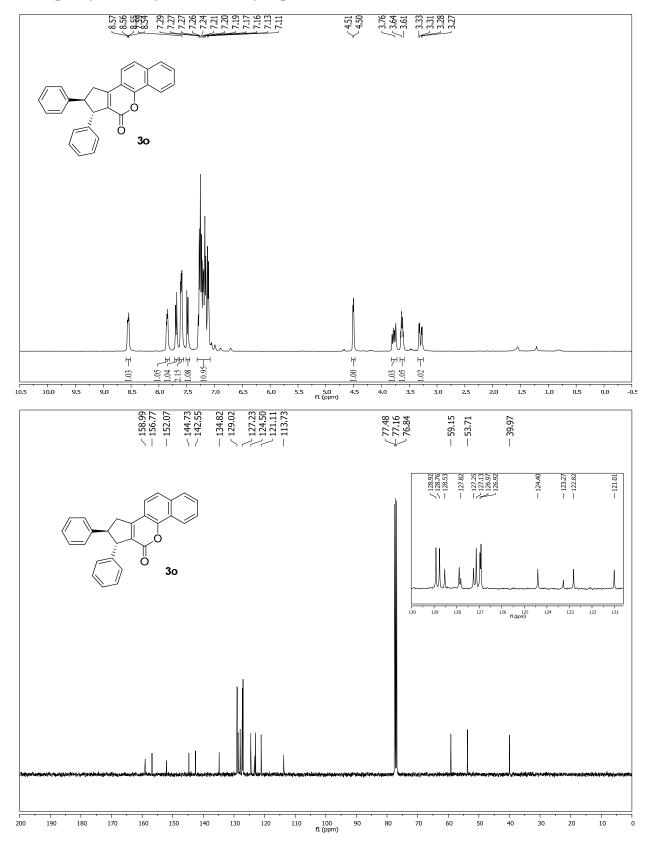
2-(Ferroceniyl)-3-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3l)



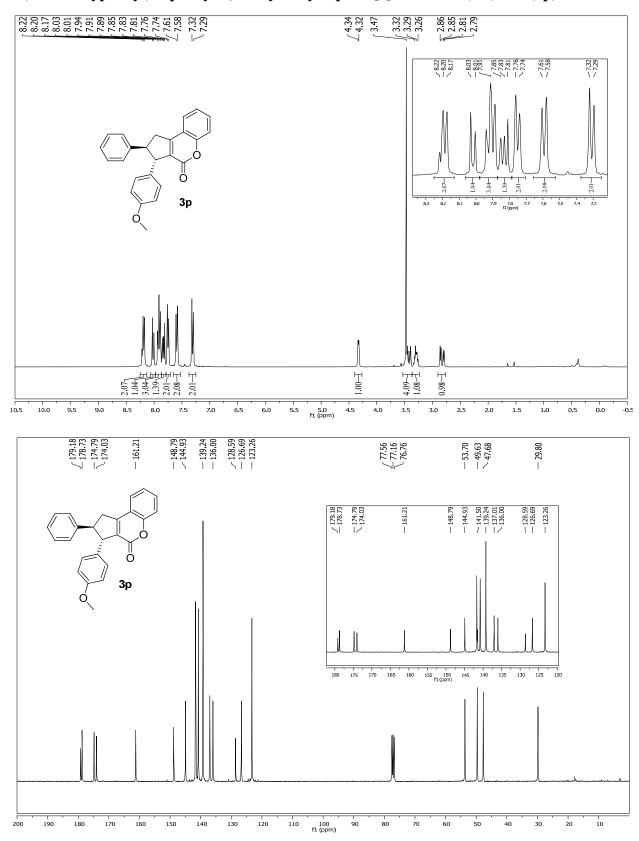




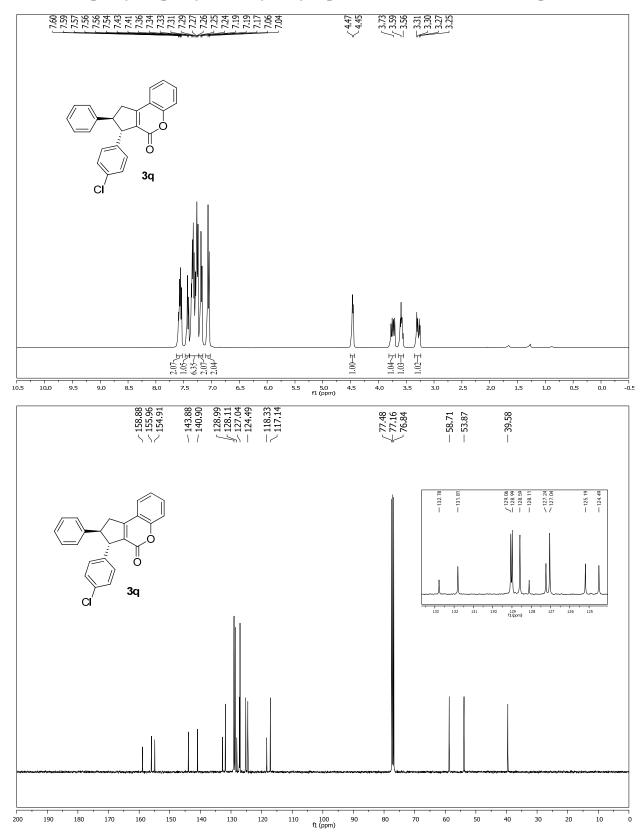
8-bromo-2,3-diphenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3n)



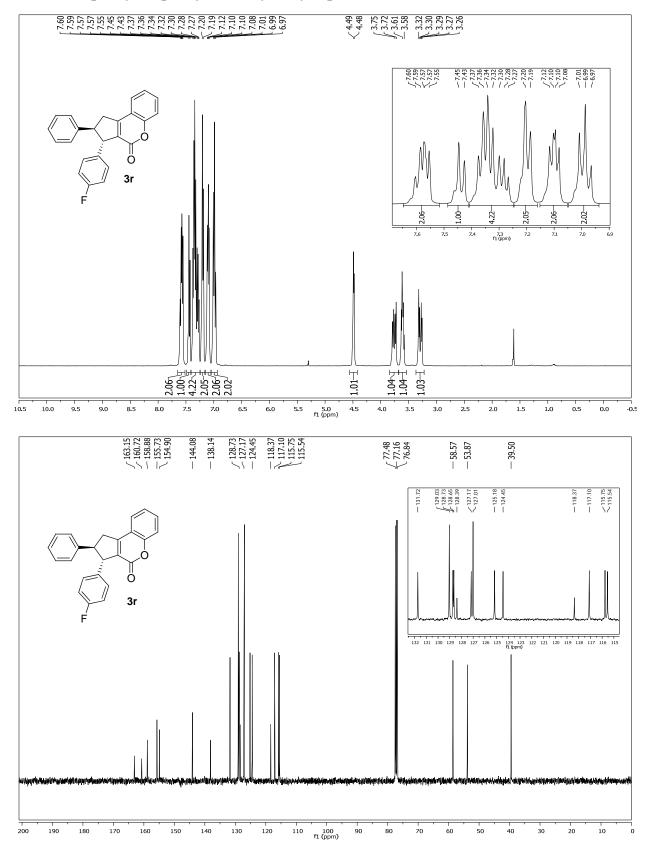
7,8-Diphenyl-8,9-dihydrobenzo[h]cyclopenta[c]chromen-6(7H)-one (3o)

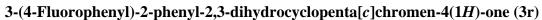


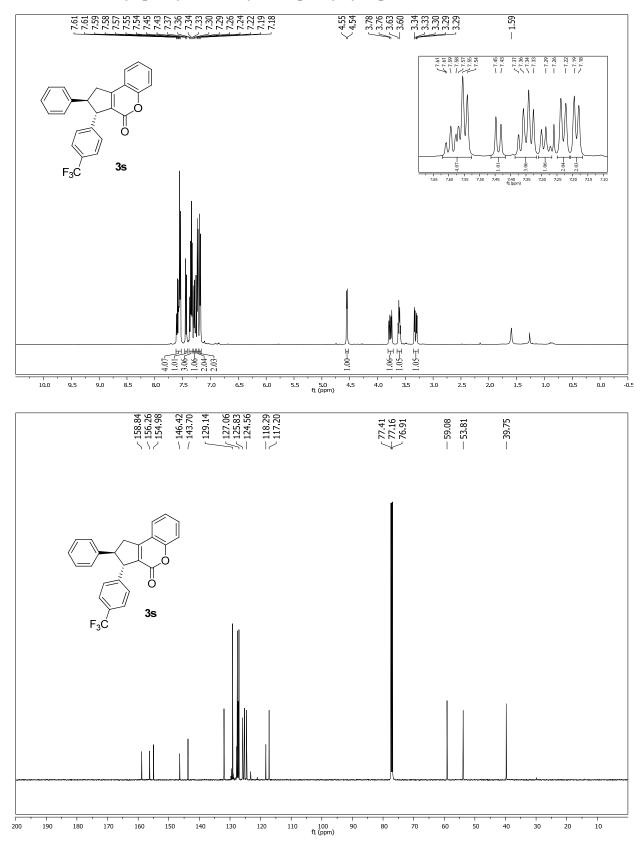
3-(4-methoxyphenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3p)

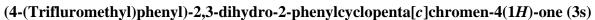


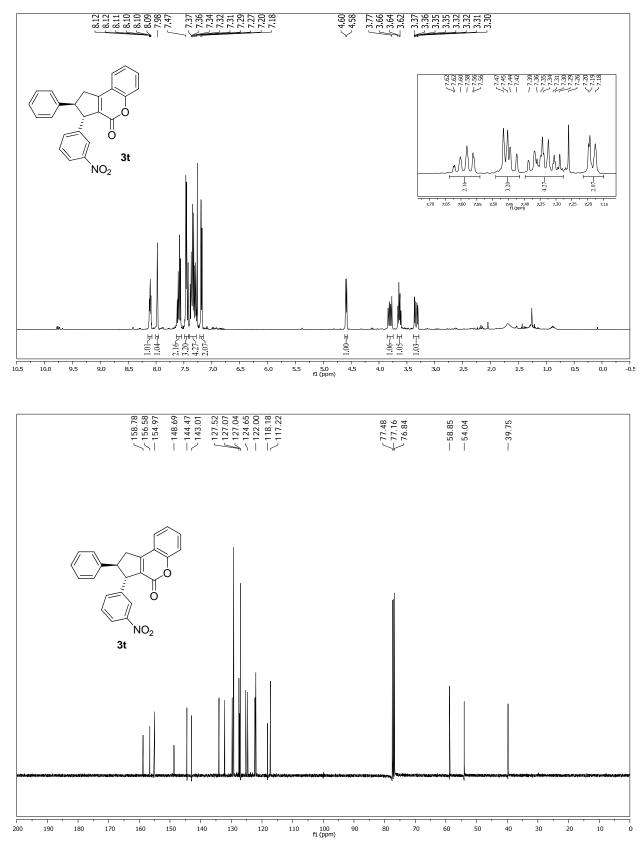
3-(4-Chlorophenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3q)



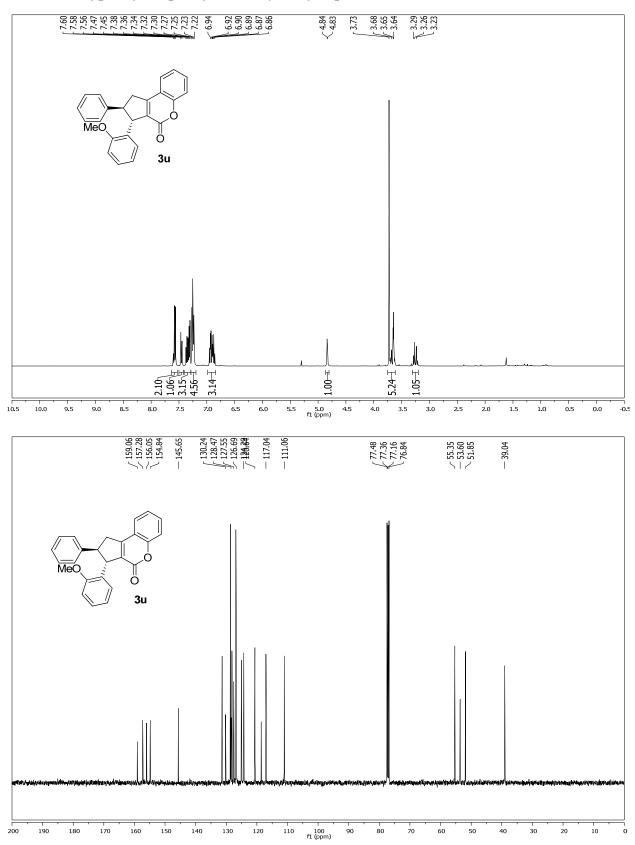




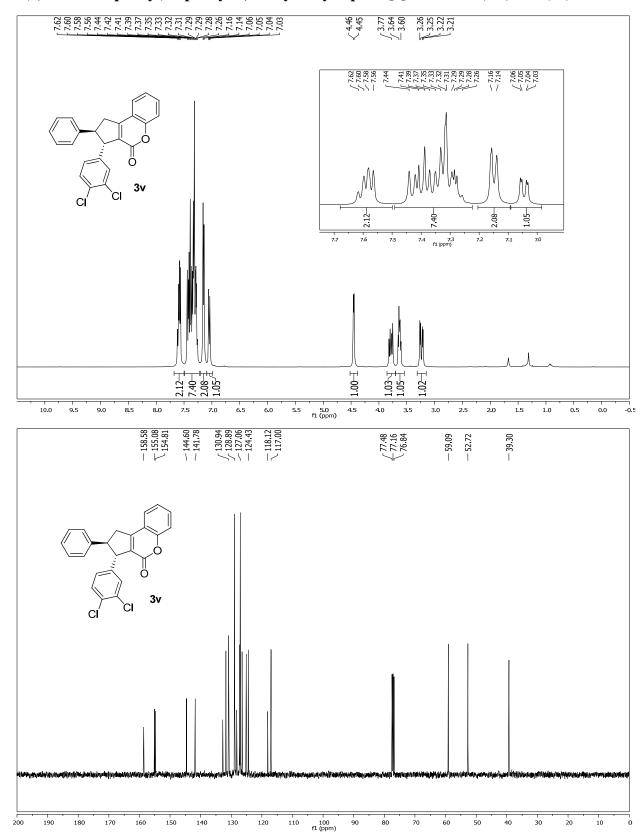


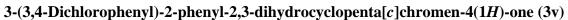


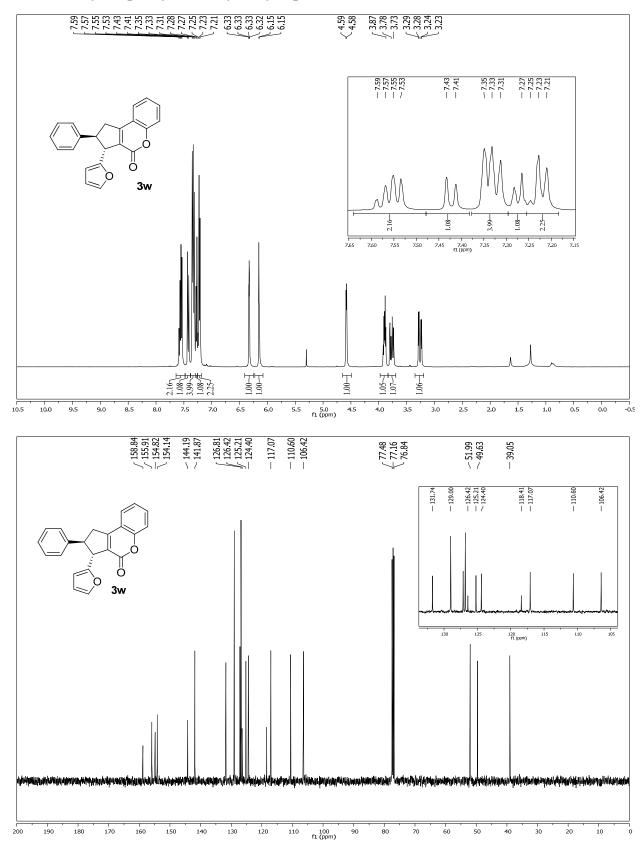


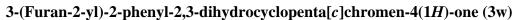


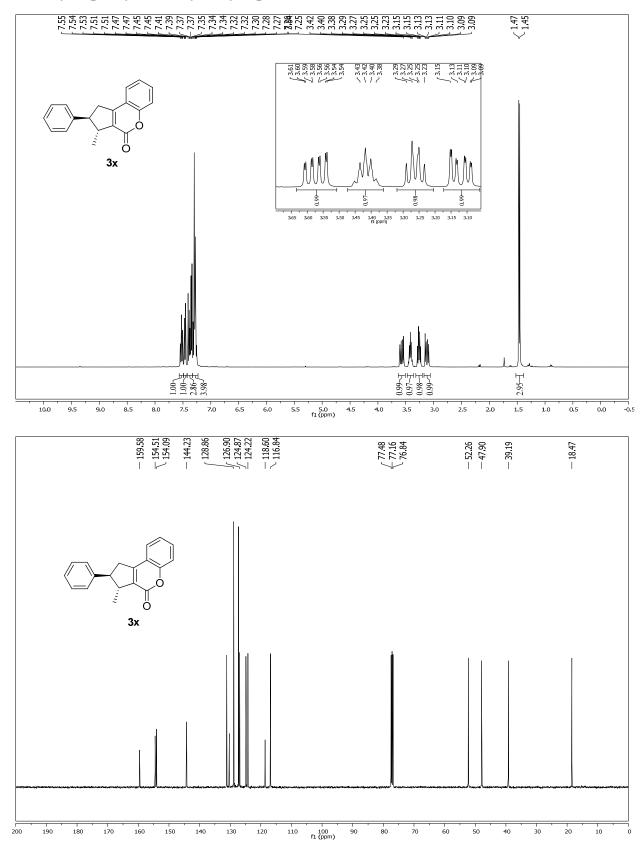
3-(2-Methoxyphenyl)-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3u)

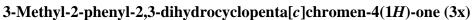




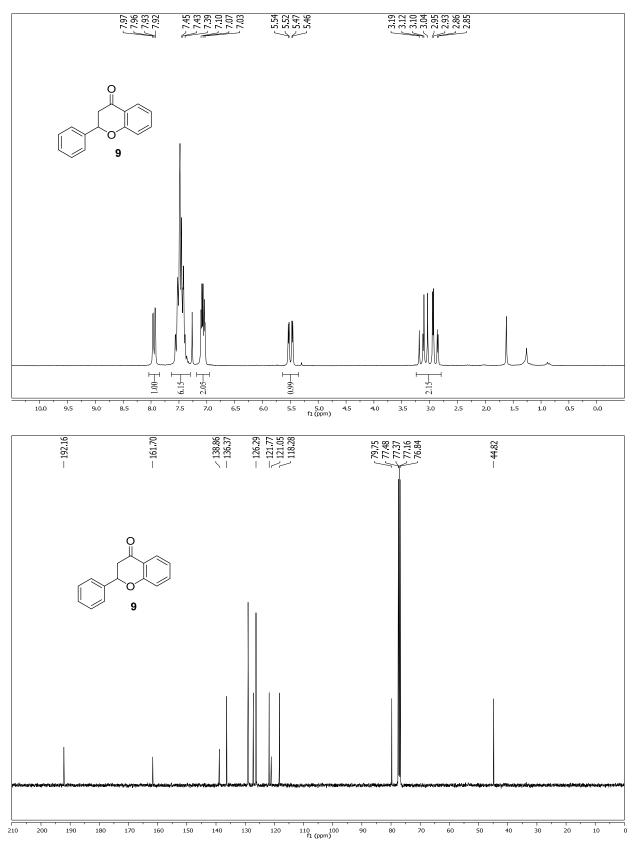


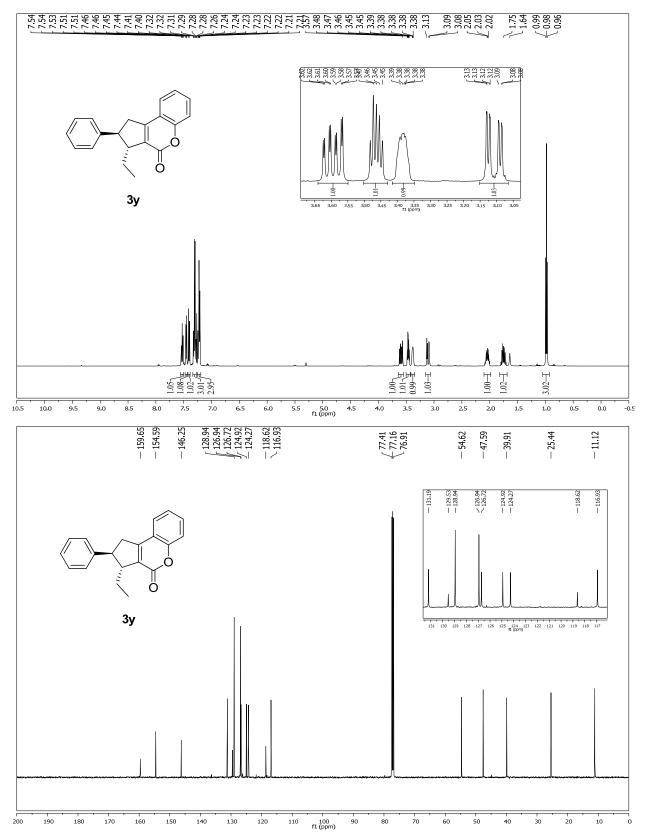






2-Phenylchroman-4-one (9)





3-Ethyl-2-phenyl-2,3-dihydrocyclopenta[c]chromen-4(1H)-one (3y)