Note

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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.5b02920 • Publication Date (Web): 18 Mar 2016

One Pot Synthesis of Benzothiazole Tethered Chromanones / Coumarins via Claisen Rearrangement Using Solid State Melt Reaction

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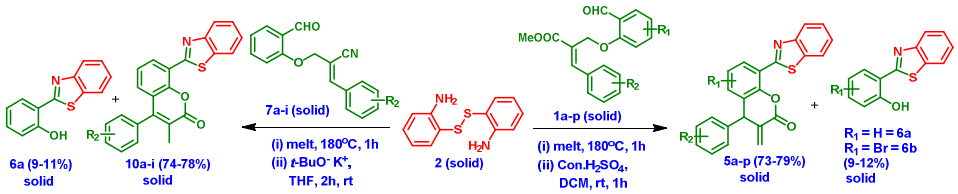


ABSTRACT

A novel protocol has been successfully established for the efficient synthesis of benzothiazole tethered chromanone / coumarin scaffolds via Claisen rearrangement using a solid state melt reaction (SSMR) in one pot manner. Benzothiazole formation and Claisen rearrangement involves the cleavage of S–S and C–O bonds, formation of C–S, C=N and C–C bonds in a single operation without using catalyst and solvent.

The rapid synthesis of functionalized organic molecular building blocks, intermediates and bioactive molecular entities represents an important endeavor in organic synthesis,[1a-d] particularly in target-oriented synthesis. Among pericyclic reactions, [3,3]-sigmatropic rearrangements are the most powerful and straightforward synthetic tool utilized for the atom-economical synthesis of many natural and bioactive molecules.[1e,1f] For instance, the Claisen rearrangement is a very important and useful synthetic tool widely exploited for the synthesis of library of natural products and bioactive scaffolds through C–C bond formation.[1g] It is well clear from the literature that the Claisen rearrangement is found to be one of the prominent reaction in

synthetic chemistry since its introduction in 1972[1e] and known to delineate widespread applications in preparative chemistry.[2]

Benzothiazole derivatives are known to be the integral part of a wide variety of natural products, bioactive compounds and industrial chemicals. They are widely used in many industries, for example, 2-mercaptobenzothiazole, cambendazole, and thiabendazole[3] are effectively utilized as rubber vulcanization accelerators and as slimicides in paper and pulp industry.[3]

Chromanone and coumarin units belong to privileged scaffold of various natural products. Most of these compounds are well screened for their biological properties and found to be useful in cancer treatment,[4a] antibacterial,[4b] antifungal,[4b] autoimmune,[4b] inflammatory diseases,[5] estrogenic,[5] antilipoperoxidant,[5] antiplatelet,[5] antiviral,[5] antihemolytic[5] and antiallergic.[5]

Claisen rearrangement is one of the key reactions available for the synthesis of numerous natural products[1f] such as acorone, homogynolide B and pancratistatin. Benzothiazole, chromanone and coumarin moieties are identified as the core unit of several natural products and bioactive molecules particularly, Geiparvarin (**I**),[6a] 1-isopropyl-2-methylene-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one (**II**) [anti-tumor agent],[6b] isodispar B (**III**),[6c] 3-(benzo[*d*]thiazol-2-yl)-7-hydroxycoumarin (**IV**) [anti-proliferative agent],[6d] D-luciferin (**V**)[6e] and CJM 126 (**VI**) [anti-cancer agent][6f] are shown in Figure **1** as representatives. Due to the significance of these interesting bioactivities, several research groups have been interested towards the syntheses of chromanones,[6g] coumarins[6h] and benzothiazole based heterocycles.[6i]

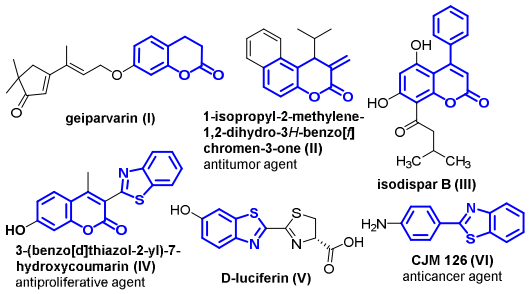


Figure 1. Natural products and bioactive molecules containing chromanone, coumarin and benzothiazole units.

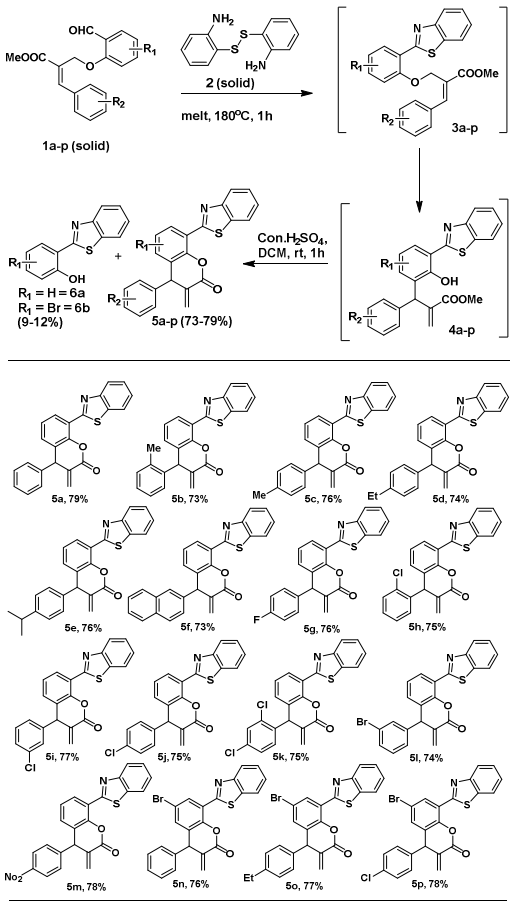
Since the Claisen rearrangement is widely exploited for the synthesis of variety of heterocyclic compounds with various biological applications,[1e,1f] we envisaged that the Baylis-Hillman derivatives[8c-e,9] can be utilized for the synthesis of chromanone / coumarin frameworks through Claisen rearrangement. As a part of our continual effort in the field of solid-state melt reaction (SSMR)[7] and heterocyclic chemistry,[8] here in, we describe a simple and novel method for the synthesis of benzothiazole tethered chromanone / coumarin scaffolds using Solid State Melt Reaction (SSMR). This new protocol involves benzothiazole formation, Claisen rearrangement and intramolecular lactonization for the formation of benzothiazole tethered chromanone / coumarin scaffolds via SSMR in one pot manner for the first time. We envisaged that the Baylis-Hillman[8c-e,9] derivative **1a** and disulfide **2** will be the suitable substrates for making an array of benzothiazole tethered chromanone / coumarin scaffolds.

To execute our idea, we have prepared disulfide **2** from aminothiophenol under aerobic oxidation[10] and melted with Baylis-Hillman[9] derivative **1a** at different temperature levels, the best result was obtained when we carried out the reaction without catalyst and solvent at 180^{o}C for 1 h which successfully led to the formation of Claisen rearrangement product (**4a**). The reaction probably proceeded via benzothiazole formation and Claisen rearrangement.

Interestingly, the benzothiazole formation and Claisen rearrangement carried out by the cleavage of disulfide S–S, *O*-allyl C–O bonds and formation of thiazole C–S, C=N and aryl-allylic C–C bonds in a single step process. After the formation of compound **4a**, the crude reaction mixture was further treated with Con. H_2SO_4 (1 mmol) in DCM as a solvent at room temperature for 1 h in one-pot manner which successfully afforded the desired benzothiazole tethered chromanone (**5a**) in 79% yield (Table 1) along with minor benzothiazole product (**6a**) in 9% yield. This type of domino benzothiazole formation and Claisen rearrangement followed by lactonization in one pot is new and not known so far in the literature. It is surprising to note that this novel protocol provides a single product even though multiple reaction sites are present in the reactants with comparable reactivities. Interestingly, the first two parts of the protocol does not involve any solvent and catalyst even though both the reactants (**1a** and **2**) are solid in nature.

Delighted by this result, we have employed various Baylis–Hillman derivatives[8c-e,9] (**1b-p**) under the optimized reaction conditions which smoothly provided the desired functionalized chromanones (**5b-p**) in very good yields (73–78%) along with minor benzothiazoles (**6a** and **6b**) in 9-12% yields. The results are summarized in Table 1. Based on the results, electron donating and withdrawing group in the aryl moiety does not have any remarkable difference in the reactivities on Claisen rearrangement. Further, the structure of compound **5b** was confirmed by single-crystal X-ray[11] analysis (see the Supporting Information - Figure S1).

Table 1. Synthesis of Benzothiazole Tethered Chromanones (5a-p)[a,b,c]

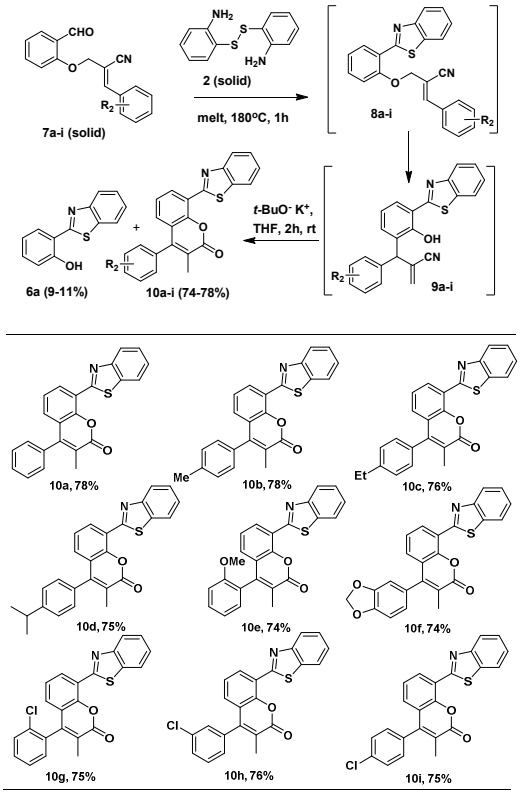


[a]All reactions were carried out on 1 mmol of B-H derivative (**1a-p**) with 0.5 mmol of compound **2** at 180 °C for 1 h. Further, 1 mmol of Con. H_2SO_4 was added. [b]Isolated yields of the pure products. [c]All the new compounds were fully characterized (see the Supporting Information).

Based on this successful result, we have employed several Baylis–Hillman derivatives[8c-e,9] (**7a-i**), possessing nitrile functionality. Accordingly, we melted B-H derivatives (**7a-i**) with disulfide (**2**) in the round bottom flask at 180°C for 1 h which successfully led to the Claisen rearrangement products tethered with benzothiazole moiety (**9**). In the same round bottom flask, potassium *tert*-butoxide (2 equiv.) was added in THF as a solvent and stirred at room temperature for 2 h which successfully afforded the benzothiazole tethered coumarin scaffolds

10a-i in 74-78% yields (Table 2) along with minor benzothiazole (**6a**) in 9-11% yields. It is interesting to note that, the olefinic double bond in the Claisen rearrangement product (**9**) got isomerized and formed coumarin moiety **10**. The structure of **10d** was confirmed by single-crystal X-ray[11] analysis (see the Supporting Information - Figure S2).

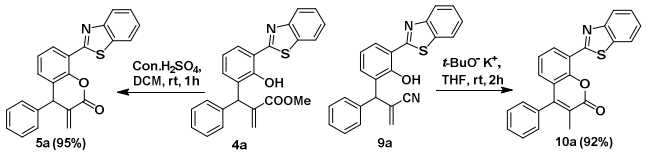
Table 2. Synthesis of Benzothiazole Tethered Coumarins (10a-i)[a,b,c]



[a]All reactions were carried out on 1 mmol of B-H derivative (**7a-i**) with 0.5 mmol of compound **2** at 180 °C for 1 h. Further, 2 mmol of potassium *tert*-butoxide was added. [b]Isolated yields of the pure products. [c]All the new compounds were fully characterized (see the Supporting Information).

To understand the reaction pathway, we have isolated Claisen rearrangement product **4a** and treated with Con. H_2SO_4 (1 mmol) which efficiently led to anticipated chromanone derivative (**5a**) in excellent yield (95%). Subsequently, we also treated Claisen product **9a** containing nitrile functionality with 2 equivalent potassium tertiary butoxide smoothly provided the coumarin derivative (**10a**) in excellent yield (92%) as shown in Scheme 1. It is remarkable, to note that the Claisen rearrangement products on B-H derivatives with ester functionality led to chromanone derivative (**5a**) with *exo* methylene double bond, whereas the Claisen rearrangement on B-H derivatives with nitrile functionality led to the formation of coumarin derivative (**10a**) in which the double bond migrated to the lactone ring system.

Scheme 1. Synthesis of Chromanone and Coumarin Derivatives (5a and 10a) from Claisen Rearrangement Products (4a and 9a)

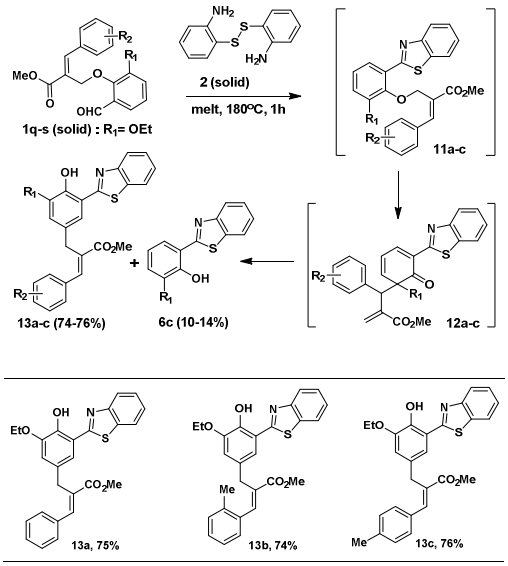


After the successful synthesis of *ortho*-migrated Claisen rearrangement products from Baylis-Hillman derivatives, we turned our attention towards the *para* migrated Claisen rearrangement product which can be achieved from the *ortho* substituted Baylis-Hillman derivatives[8c-e,9] via Claisen rearrangement using SSMR.

To accomplish this idea, we treated *ortho* substituted Baylis-Hillman derivative **1q** with disulfide (**2**) at 180°C for 1 h which successfully afforded the desired *para* migrated Claisen rearrangement product tethered with benzothiazole (**13a**) in 75% yield along with minor product **6c** (benzothiazole) in 12% yield. Encouraged by this result, we have treated couple of *ortho* substituted Baylis-Hillman derivatives (**1r** and **1s**) with disulfide (**2**) at 180°C for 1 h, which

smoothly afforded the anticipated *para* migrated Claisen rearrangement products (**13b** and **13c**) in 74 and 76% yields (Table 3) along with minor product **6c** (benzothiazole) in 10-14% yields.

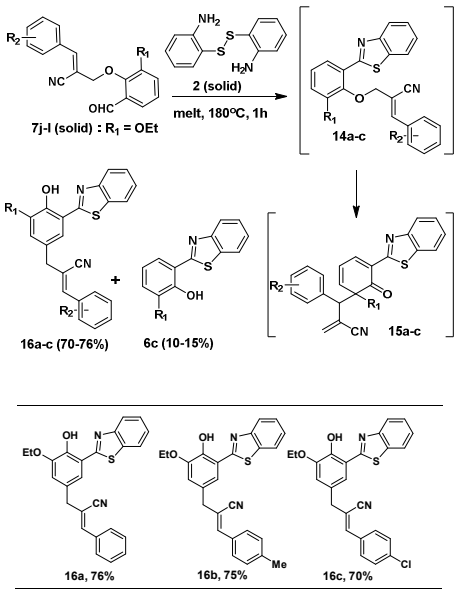
Table 3. *para* Claisen Rearrangement Products (13a-c)[a,b] via Solid State Melt Reaction



[a]All reactions were carried out on 1 mmol of B-H derivative (**1q-s**) with 0.5 mmol of compound (**2**) at 180 °C for 1 h. [b]Isolated yields of the pure products.

To further expand the generality of the *para* migration in the Claisen rearrangement, we have decided to engage the *ortho* substituted Baylis–Hillman derivatives[8c-e,9] bearing nitrile functionality. Accordingly, we subjected the *ortho* substituted Baylis–Hillman derivatives (**7j-l**) with disulfide (**2**) at 180°C for 1 h which smoothly led to the desired *para* migrated Claisen rearrangement products (**16a-c**) in 70-76% yields (Table 4) along with minor benzothiazole (**6c**) product in 10-15% yields. The structure of **16c** was confirmed by single-crystal X-ray[11] analysis (see the Supporting Information - Figure S3).

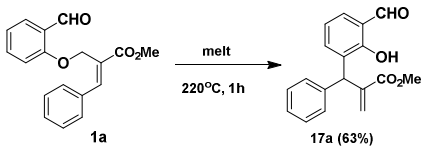
Table 4. *para* Claisen Rearrangement Products (16a-c)[a,b] via Solid State Melt Reaction



[a]All reactions were carried out on 1 mmol of B-H derivative (**7j-l**) with 0.5 mmol of compound (**2**) at 180 °C for 1 h. [b]Isolated yields of the pure products.

Finally, we also examined the Baylis-Hillman derivative (**1a**) for the Claisen rearrangement without disulfide (**2**). Accordingly, the B-H derivative **1a** melted at 220°C for 1 h which led to the desired diaryl vinyl methane derivative (**17a**) in 63% yield via Claisen rearrangement as shown in Scheme 2.

Scheme 2. Claisen Rearrangement in B-H Derivative 1a.



In conclusion, we have developed a novel and efficient protocol for the facile construction of benzothiazole tethered chromanone and coumarin frameworks via benzothiazole formation, Claisen rearrangement and lactonization reaction sequence in one pot fashion utilizing

Baylis-Hillman derivatives (B-H) for the first time. Notably, the first two steps of the protocol carried out through a solid state melt reaction which does not require catalyst and solvent even though all the starting materials are solids. We also utilized *ortho* substituted Baylis-Hillman derivatives for the *para* Claisen rearrangement products (*para* migration) with diverse functionalities in good yields. It is surprising to note that this new protocol provides a single product even though various reactive functionalities are present in the reactants with comparable reactivities. This novel protocol also opens new avenues for making a library of wide variety of diversified chromanone/coumarin scaffolds for biological screening.

EXPERIMENTAL SECTION

General Information. All reagents were procured from commercial sources and utilized without further purification. Solvents were distilled prior to use. Silica gel used for Column chromatography purification as stationary phase. FTIR- spectrophotometer was used for IR spectral studies. ^{1}H NMR (300 and 400 MHz) and ^{13}C NMR (75 and 100 MHz) were recorded using $CDCl_3$ as solvent and TMS as an internal standard; chemical shifts are reported in δ (ppm). Mass spectra were recorded on a QTOF mass spectrometer using the electrospray ionization (ESI) mode. Melting points were uncorrected. Thin-layer chromatography (TLC) was performed using glass plates coated with silica gel (254F). Spots were visualized using UV lamp and iodine vapour. The single crystal X-ray diffraction measurements were carried on a graphite monochromatic MoKα radiation and CCD detector.

Typical Experimental Procedure for the Synthesis of Compound 5a

A mixture of (*E*)-methyl-2-((2-formylphenoxy)methyl)-3-phenylacrylate (**1a**, 1mmol), and 2-(2-(2-minophenyl)disulfanyl)benzenamine (**2**, 0.5 mmol) was placed in a round bottom flask and melted at 180 ºC for 1 h. After formation of the Claisen rearrangement product as indicated by

TLC, the crude product was further treated with Con.H_2SO_4 in DCM at room temperature for 1 h. After completion of the reaction as indicated by TLC, the reaction mixture was concentrated and the resulting crude mass was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (2 x 10 mL) and dried over anhydrous Na_2SO_4. The crude reaction mass was purified by column chromatography on silica gel (Acme 60-120 mesh), using ethyl acetate : hexanes (1 : 9) to afford **5a** as a colourless solid in 79% yield.

Methyl 2-((3-(benzo[*d*]thiazol-2-yl)-2-hydroxyphenyl)(phenyl)methyl)acrylate (**4a**).

White solid: (84%, 0.337g); mp: 143-145 °C; Reaction time: 1h; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (s, 3H), 5.28 (s, 1H), 5.93 (s, 1H), 6.45 (s, 1H), 6.84 – 7.90 (m, 12H), 13.00 (s, 1H) ; ^{13}C NMR (75 MHz, $CDCl_3$) : δ 45.6, 52.0, 116.5, 118.9, 121.5, 122.0, 125.5, 126.6, 126.7, 127.0, 127.1, 128.4, 129.1, 130.9, 132.4, 132.6, 140.8, 142.8, 151.6, 155.5, 167.3, 169.4; IR (KBr): 1623, 1712, 3415 cm^{-1}; HRMS calculated for $C_{24}H_{20}NO_3S$ $[M+H]^+$ 402.1164, found 402.1174.

8-(Benzo[*d*]thiazol-2-yl)-3-methylene-4-phenylchroman-2-one (**5a**).

White solid: (79%, 0.29g); mp: 137-139 °C; Reaction time: 2h; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.03 (s, 1H), 5.82 (s, 1H), 6.55 (s, 1H), 7.17 – 8.52 (m, 12H) ; ^{13}C NMR (75 MHz, $CDCl_3$) : δ 48.3, 121.5, 122.5. 123.1, 124.9, 125.2, 125.7, 126.2, 127.8, 127.8, 129.2, 130.1, 130.7, 135.8, 136.4, 139.7, 148.1, 152.1, 161.4, 161.6; IR (KBr): 1631, 1724, 3015 cm^{-1}; HRMS calculated for $C_{23}H_{16}NO_2S$ $[M+H]^+$ 370.0902, found 370.0894.

8-(Benzo[*d*]thiazol-2-yl)-3-methylene-4-*o*-tolylchroman-2-one (**5b**).

White solid : (73%, 0.27g); mp : 148-150 °C; Reaction time : 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.28 (s, 3H), 5.29 (s, 1H), 5.55 (s, 1H), 6.58 (s, 1H), 6.95 – 8.48 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.3, 45.1, 121.5, 122.3, 123.1, 124.8, 125.2, 125.7, 126.2, 126.9, 128.0, 129.0, 129.9,

130.1, 130.3, 131.5, 135.0, 136.4, 136.5, 137.4, 148.1, 152.2, 161.3, 161.5; IR (KBr) : 1632, 1720, 3026 cm^{-1}; HRMS calculated for $C_{24}H_{18}NO_2S$ $[M+H]^+$ 384.1058, found 384.1052.

8-(Benzo[*d*]thiazol-2-yl)-3-methylene-4-*p*-tolylchroman-2-one (**5c**).

White solid : (76%, 0.29g); mp : 147-149 °C; Reaction time : 2h; ^1H NMR (400 MHz, $CDCl_3$) : δ 2.36 (s, 3H), 5.03 (s, 1H), 5.84 (s, 1H), 6.57 (s, 1H), 7.08 -8.53 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 21.1, 48.0, 121.6, 122.6, 123.2, 125.0, 125.3, 126.1, 126.3, 127.8, 129.2, 130.0, 130.1, 130.8, 136.1, 136.5, 136.8, 137.7, 148.2, 152.3, 161.5, 161.9; IR (KBr) : 1636, 1794, 3018 cm^{-1}; HRMS calculated for $C_{24}H_{18}NO_2S$ $[M+H]^+$ 384.1058, found 384.1048.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-ethylphenyl)-3-methylenechroman-2-one (**5d**).

White solid : (74%, 0.29g); mp : 146-148°C; Reaction time : 2h; ^1H NMR (300 MHz, $CDCl_3$) : δ 1.21 (t, J = 7.5 Hz, 3H), 2.62 (q, J = 7.5 Hz, 2H), 4.99 (s, 1H), 5.81 (s, 1H), 6.53 (s, 1H), 7.06 - 8.51 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 15.4, 28.4, 48.0, 121.5, 123.1, 124.8, 125.2, 126.0, 126.2, 126.7, 127.7, 128.6, 129.1, 129.9, 130.7, 136.0, 136.4, 136.9, 143.9, 148.1, 152.1, 161.4, 161.7; IR (KBr) : 1635, 1728, 3025 cm^{-1}; HRMS calculated for $C_{25}H_{20}NO_2S$ $[M+H]^+$ 398.1215, found 398.1216.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-isopropylphenyl)-3-methylenechroman-2-one (**5e**).

White solid: (76%, 0.31g); mp: 145-147 °C; Reaction time: 2h; ^1H NMR (400 MHz, $CDCl_3$): δ 1.15 (d, J = 6.4 Hz, 6H), 2.80 (sep, J = 6.8 Hz, 1H), 4.93 (s, 1H), 5.75 (s, 1H), 6.43 (s, 1H), 7.00 – 8.42 (m, 11H). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 24.0, 33.8, 48.1, 121.6, 122.6, 123.2, 125.0, 125.3, 126.1, 126.3, 127.3, 127.8, 129.2, 130.0, 130.8, 136.1, 136.5, 137.0, 148.2, 148.6, 152.3, 161.6, 162.0; IR (KBr): 1625, 1738, 3030 cm^{-1}; HRMS calculated for $C_{26}H_{22}NO_2S$ $[M+H]^+$ 412.1371, found 412.1382.

8-(Benzo[*d*]thiazol-2-yl)-3-methylene-4-(naphthalen-2-yl)chroman-2-one (**5f**).

White solid : (73%, 0.30g); mp : 136-138 °C; Reaction time : 2h; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 5.55 (d, J = 1.5 Hz, 1H), 5.76 (s, 1H), 6.57 (d, J = 1.8 Hz, 1H), 6.91-8.48 (m, 14H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 45.9, 121.7, 122.5, 123.3, 125.0, 125.0, 125.4, 125.8, 125.8, 126.0, 126.3, 126.4, 128.8, 129.2, 129.3, 129.5, 130.4, 130.5, 131.1, 134.6, 134.8, 134.9, 136.6, 148.0, 152.4, 161.6, 161.7; IR (KBr) : 1635, 1730, 3026 cm^{-1}; HRMS calculated for $C_{27}H_{18}NO_2S$ $[M+H]^+$ 420.1058, found 420.1062.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-fluorophenyl)-3-methylenechroman-2-one (**5g**).

White solid : (76%, 0.29g); mp : 139-141 °C; Reaction time : 2h; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 5.02 (s, 1H), 5.81 (s, 1H), 6.55 (s, 1H), 7.02 - 8.51 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 47.6, 116.2 (d, 2JC-F = 21 Hz), 121.7, 122.8, 123.3, 125.1, 125.6, 126.3, 127.6, 129.2, 129.5, 129.6, 129.7, 130.3, 130.6, 135.4, 135.9, 136.5, 148.2, 152.3, 161.7, 161.7, 162.6 (d, 1JC-F = 223 Hz); IR (KBr) : 1630, 1740, 3033 cm^{-1}; HRMS calculated for $C_{23}H_{15}FNO_2S$ $[M+H]^+$ 388.0808, found 388.0825.

8-(Benzo[*d*]thiazol-2-yl)-4-(2-chlorophenyl)-3-methylenechroman-2-one (**5h**).

White solid : (75%, 0.30g); mp : 143-145 °C; Reaction time : 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.66 (s, 1H), 5.90 (s, 1H), 6.61 (s, 1H), 7.12 -8.51 (11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 44.5, 121.5, 122.4, 123.1, 124.8, 125.0, 125.2, 126.2, 127.8, 129.1, 129.3, 130.0, 130.4, 131.2, 133.5, 134.1, 136.4, 138.1, 148.3, 152.2, 161.0, 161.4; IR (KBr): 1645, 1730, 3026 cm-1; HRMS calculated for $C_{23}H_{15}ClNO_2S$ $[M+H]^+$ 404.0512, found 404.0500.

8-(Benzo[*d*]thiazol-2-yl)-4-(3-chlorophenyl)-3-methylenechroman-2-one (**5i**).

White solid : (77%, 0.31g); mp : 142-144 °C; Reaction time : 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.00 (s, 1H), 5.85 (s, 1H), 6.58 (s, 1H), 7.04 -8.54 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ

47.9, 121.5, 122.7, 123.1, 124.9, 125.0, 125.3, 125.9, 126.2, 128.0, 128.1, 129.5, 130.49, 130.6, 130.7, 135.1, 135.2, 136.4, 141.7, 148.1, 152.1, 161.2, 161.3; IR (KBr) : 1645, 1740, 3031 cm^{-1}; HRMS calculated for $C_{23}H_{15}ClNO_2S$ $[M+H]^+$ 404.0512, found 404.0503.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-chlorophenyl)-3-methylenechroman-2-one (**5j**).

White solid : (75%, 0.30g); mp : 141-143 °C, Reaction time : 2h; ^1H NMR (300 MHz, $CDCl_3$) : δ 5.00 (s, 1H), 5.82 (s, 1H), 6.56 (s, 1H), 7.09 -8.53 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 47.7, 121.5, 122.7, 123.2, 125.0, 125.2, 125.3, 126.2, 129.2, 129.4, 129.4, 130.3, 130.5, 133.8, 135.5, 136.4, 138.1, 148.1, 152.2, 161.2, 161.3; IR (KBr) : 1647, 1741, 3031 cm^{-1}; HRMS calculated for $C_{23}H_{15}ClNO_2S$ $[M+H]^+$ 404.0512, found 404.0504.

8-(Benzo[*d*]thiazol-2-yl)-4-(2,4-dichlorophenyl)-3-methylenechroman-2-one (**5k**).

White solid : (75%, 0.32g); mp : 140-142 °C; Reaction time : 2h; ^1H NMR (300 MHz, $CDCl_3$) : δ 5.61 (s, 1H), 5.89 (s, 1H), 6.61 (s, 1H), 7.02 – 8.52 (m, 10 H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 44.1, 121.5, 122.6, 123.2, 124.3, 125.1, 125.3, 126.3, 128.2, 129.6, 130.2, 130.2, 130.8, 131.5, 133.7, 134.2, 134.4, 136.4, 136.7, 148.2, 152.1, 160.8, 161.2; IR (KBr) : 1650, 1743, 3036 cm^{-1}; HRMS calculated for $C_{23}H_{14}Cl_2NO_2S$ $[M+H]^+$ 438.0122, found 438.0123.

8-(Benzo[*d*]thiazol-2-yl)-4-(3-bromophenyl)-3-methylenechroman-2-one (**5l**).

White solid : (74%, 0.33g); mp : 152-156 °C; Reaction time : 2h; ^1H NMR (300 MHz, $CDCl_3$) : δ 4.99 (s, 1H), 5.85 (s, 1H), 6.58 (s, 1H), 7.07 – 8.54 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 47.8, 121.5, 122.7, 123.2, 123.2, 124.8, 125.0, 125.3, 126.2, 126.4, 129.5, 130.6, 130.7, 130.9, 131.0, 135.2, 136.4, 142.0, 148.0, 152.2, 161.2, 161.3; IR (KBr) : 1625, 1730, 3026 cm^{-1}; HRMS calculated for $C_{23}H_{15}BrNO_2S$ $[M+H]^+$ 448.0007, found 448.0012.

8-(Benzo[*d*]thiazol-2-yl)-3-methylene-4-(4-nitrophenyl)chroman-2-one (**5m**).

White solid : (78%, 0.32g); mp : 156-158 °C; Reaction time : 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.16 (s, 1H), 5.92 (s, 1H), 6.63 (s, 1H), 7.22-8.57 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 48.0, 121.5, 123.0, 123.2, 124.2, 124.4, 125.2, 125.4, 126.3, 128.7, 129.9, 130.4, 131.2, 134.6, 136.4, 146.9, 147.5, 148.0, 152.2, 160.9; IR (KBr) : 1635, 1720, 3029 cm^{-1}; HRMS calculated for $C_{23}H_{15}N_2O_4S$ $[M+H]^+$ 415.0753, found 415.0754.

8-(Benzo[*d*]thiazol-2-yl)-6-bromo-3-methylene-4-phenylchroman-2-one (**5n**).

White solid: (76%, 0.33g); mp: 151-153 °C; Reaction time: 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.00 (s, 1H), 5.82 (s, 1H), 6.57 (s, 1H), 7.16 – 8.68 (11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 48.1, 117.8, 121.6, 123.3, 124.2, 125.5, 126.4, 127.7, 127.8, 128.1, 129.4, 130.9, 131.5, 132.9, 135.1, 136.5, 139.0, 147.1, 152.0, 159.7, 161.0; IR (KBr): 1635, 1737, 3026 cm^{-1}; HRMS calculated for $C_{23}H_{15}BrNO_2S$ $[M+H]^+$ 448.0007, found 448.0005.

8-(Benzo[*d*]thiazol-2-yl)-6-bromo-4-(4-ethylphenyl)-3-methylenechroman-2-one (**5o**).

White solid: (77%, 0.36g); mp: 150-152 °C; Reaction time: 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.35 (t, J = 7.5 Hz, 3H), 2.78 (q, J = 7.5 Hz, 2H), 4.97 (s, 1H), 5.82 (s, 1H), 6.55 (s, 1H), 7.06 – 8.15 (9H), 8.79 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 15.0, 28.7, 47.8, 117.1, 121.5, 121.6, 123.2, 123.3, 124.4, 125.6, 126.5, 127.7, 128.2, 128.6, 128.8, 131.3, 131.4, 132.8, 132.9, 136.5, 145.3, 152.1, 159.4; IR (KBr) : 1625, 1734, 3026 cm^{-1}; HRMS calculated for $C_{25}H_{19}BrNO_2S$ $[M+H]^+$ 476.0320, found 476.0323.

8-(Benzo[*d*]thiazol-2-yl)-6-bromo-4-(4-chlorophenyl)-3-methylenechroman-2-one (**5p**).

White solid : (78%, 0.37g); mp : 149-151 °C; Reaction time : 2h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 4.98 (s, 1H), 5.82 (s, 1H), 6.59 (s, 1H), 7.10 – 8.15 (m, 9H), 8.69 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.5, 117.9, 121.6, 122.2, 123.3, 125.6, 126.0, 126.5, 127.0, 128.8, 129.2, 129.6,

130.4, 131.8, 132.8, 134.7, 137.4, 147.0, 151.9, 159.6, 160.7; IR (KBr) : 1628, 1740, 3029 cm^{-1}; HRMS calculated for $C_{23}H_{14}BrClNO_2S$ $[M+H]^+$ 481.9617, found 481.9612.

Typical Experimental Procedure for the Synthesis of Compound 10a.

A mixture of (*E*)-2-((2-formylphenoxy)methyl)-3-phenylacrylonitrile (**7a**, 1mmol), 2-(2-(2-minophenyl)disulfanyl)benzenamine (**2**, 0.5 mmol) was placed in a round bottom flask and melted at 180 ºC for 1 h. After formation of the Claisen product as indicated by TLC, the crude product was further treated with potassium tertiary butoxide in THF at room temperature for 2 h. After the completion of the reaction as showed by TLC, the reaction mixture was concentrated and the resulting crude mass was diluted with water (10 mL) and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with brine (2 x 10 mL) and dried over anhydrous Na_2SO_4. The crude reaction mass was purified by column chromatography on silica gel (Acme 60-120 mesh), using ethyl acetate : hexanes (1 : 9) to afford **10a** as a colourless solid in 78% (0.28 g) yield.

2-((3-(Benzo[*d*]thiazol-2-yl)-2-hydroxyphenyl)(phenyl)methyl)acrylonitrile (**9a**).

White solid: (86%, 0.31g); mp : 140-142 °C, Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.58 (s, 1H), 5.62 (d, J = 1.5Hz, 1H), 6.14 (d, J = 0.9Hz, 1H), 6.92 – 7.94 (12H), 13.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 48.2, 116.8, 118.8, 119.3, 121.5, 122.1, 125.2, 125.7, 126.8, 127.4, 127.8, 128.1, 128.8, 128.9, 132.4, 132.4, 132.6, 138.5, 151.6, 155.6, 169.2; IR (KBr) : 1625, 2230, 3421 cm^{-1}; HRMS calculated for $C_{23}H_{17}N_2OS$ $[M+H]^+$ 369.1062, found 369.1069.

8-(Benzo[*d*]thiazol-2-yl)-3-methyl-4-phenyl-*2H*-chromen-2-one (**10a**).

White solid : (78%, 0.28g); mp : 161-163 °C, Reaction time : 3h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.03 (s, 3H), 7.08 – 8.63 (12H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 121.3, 121.6, 123.1,

123.2, 123.9, 125.2, 126.2, 128.2, 128.3, 128.8, 129.0, 129.3, 130.7, 134.8, 136.4, 149.7, 150.6, 152.1, 160.7, 160.8; IR (KBr) : 1625, 1740, 3036 cm^{-1}; HRMS calculated for $C_{23}H_{16}NO_2S$ $[M+H]^+$ 370.0902, found 370.0907.

8-(Benzo[*d*]thiazol-2-yl)-3-methyl-4-*p*-tolyl-*2H*-chromen-2-one (**10b**).

White solid: (78%, 0.29g); mp: 160-162 °C; Reaction time: 3h; ^1H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H), 2.46 (s, 3H), 6.98 – 8.49 (m, 11H) ; ^{13}C NMR (75 MHz, $CDCl_3$) : δ 15.6, 21.3, 120.4, 121.4, 122.1, 122.9, 123.1, 124.2, 125.2, 126.2, 128.7, 129.0, 129.5, 129.6, 132.5, 136.0, 138.2, 143.3, 149.5, 152.2, 159.5, 161.2; IR (KBr) : 1624, 1728, 3026 cm^{-1}; HRMS calculated for $C_{24}H_{18}NO_2S$ $[M+H]^+$ 384.1058, found 384.1048.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-ethylphenyl)-3-methyl-*2H*-chromen-2-one (**10c**).

White solid : (76%, 0.30g); mp : 159-161 °C; Reaction time : 3h; ^1H NMR (300 MHz, $CDCl_3$) : δ 1.34 (t, J = 7.5 Hz, 3H), 2.06 (s, 3H), 2.77 (q, J = 7.5 Hz, 2H), 7.17 – 8.66 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 15.3, 28.7, 121.5, 121.6, 123.1, 123.2, 123.8, 125.2, 126.2, 128.3, 128.4, 129.4, 130.6, 132.0, 136.4, 145.0, 149.7, 150.9, 152.2, 160.8, 161.0; IR (KBr) : 1621, 1720, 3016 cm^{-1}; HRMS calculated for $C_{25}H_{20}NO_2S$ $[M+H]^+$ 398.1215, found 398.1221.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-isopropylphenyl)-3-methyl-*2H*-chromen-2-one (**10d**).

White solid : (75%, 0.30g); mp : 156-158 °C; Reaction time : 3h; ^1H NMR (400 MHz, $CDCl_3$) : δ 1.34 (d, J = 6.8 Hz, 6H), 2.07 (s, 3H), 3.02 (sep, J = 6.8 Hz, 1H), 7.15 – 8.65 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 15.1, 24.1, 34.1, 121.6, 121.8, 123.3, 123.4, 124.0, 125.4, 126.4, 127.0, 127.1, 128.5, 128.9, 129.6, 130.8, 132.2, 136.6, 149.8, 151.1, 152.3, 161.1, 161.1; IR (KBr) : 1631, 1731, 3027 cm^{-1}; HRMS calculated for $C_{26}H_{22}NO_2S$ $[M+H]^+$ 412.1371, found 412.1395.

8-(Benzo[*d*]thiazol-2-yl)-4-(2-methoxyphenyl)-3-methyl-*2H*-chromen-2-one (**10e**).

White solid: (74%, 0.29g); mp : 166-168 °C; Reaction time : 3h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.02 (s, 3H), 3.79 (s, 3H), 6.91 – 7.96 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 18.6, 55.6, 111.0, 111.3, 111.5, 117.0, 118.9, 120.5, 121.0, 121.5, 122.2, 123.1, 125.7, 126.8, 127.7, 128.6, 129.1, 129.7, 130.1, 130.6, 132.6., 133.1, 154.6, 156.6; IR (KBr) : 1641, 1730, 3041 cm^{-1}; HRMS calculated for $C_{24}H_{18}NO_3S$ $[M+H]^+$ 400.1007, found 400.1016.

4-(Benzo[*d*][1,3]dioxol-5-yl)-8-(benzo[*d*]thiazol-2-yl)-3-methyl-*2H*-chromen-2-one (**10f**).

White solid: (74%, 0.30g); mp : 168-170 °C; Reaction time : 3h; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.09 (s, 3H), 6.09 (s, 2H), 6.72 – 8.64 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 15.0, 101.7, 109.0, 121.6, 121.8, 121.8, 122.2, 123.3, 123.7, 124.1, 125.4, 126.4, 128.3, 129.4, 130.9, 136.9, 140.6, 148.1, 148.3, 152.3, 160.9, 160.9; IR (KBr) : 1631, 1739, 3046 cm^{-1}; HRMS calculated for $C_{24}H_{16}NO_4S$ $[M+H]^+$ 414.0800, found 414.0795.

8-(Benzo[*d*]thiazol-2-yl)-4-(2-chlorophenyl)-3-methyl-*2H*-chromen-2-one (**10g**).

White solid : (75%, 0.30g); mp : 163-165 °C; Reaction time : 3h; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 2.05 (s, 3H), 7.09 – 8.68 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 15.0, 121.2, 121.8, 123.3, 123.4, 123.8, 124.2, 125.5, 126.4, 129.1, 129.5, 129.9, 130.0, 131.0, 131.1, 133.4, 135.2, 136.7, 138.7, 138.9, 149.9, 160.7, 160.9; IR (KBr) : 1634, 1747, 3031 cm^{-1}; HRMS calculated for $C_{23}H_{15}ClNO_2S$ $[M+H]^+$ 404.0512, found 404.0515.

8-(Benzo[*d*]thiazol-2-yl)-4-(3-chlorophenyl)-3-methyl-*2H*-chromen-2-one (**10h**).

White solid : (76%, 0.30g); mp : 162-164 °C; Reaction time : 3h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.00 (s, 3H), 6.88 – 8.49 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 15.6, 120.6, 121.4, 121.5, 122.2, 123.1, 123.2, 125.2, 126.3, 127.0, 128.6, 128.7, 128.8, 129.9, 130.3, 132.9, 135.0, 136.0,

137.3, 141.7, 149.4, 152.1, 161.0; IR (KBr) : 1639, 1740, 3036 $cm^{-1;}$ HRMS calculated for $C_{23}H_{15}ClNO_2S$ $[M+H]^+$ 404.0512, found 404.0538.

8-(Benzo[*d*]thiazol-2-yl)-4-(4-chlorophenyl)-3-methyl-*2H*-chromen-2-one (**10i**).

White solid : (75%, 0.30g); mp : 163-165 °C; Reaction time : 3h; ^1H NMR (300 MHz, $CDCl_3$) : δ 2.01 (s, 3H), 6.97 – 7.95 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 121.6, 122.2, 123.2, 124.0, 125.3, 125.9, 126.9, 128.6, 129.4, 129.8, 130.0, 130.9, 133.0, 135.0, 137.6, 149.4, 151.5, 154.7, 160.5, 160.7 ; IR (KBr) : 1639, 1740, 3036 $cm^{-1;}$ HRMS calculated for $C_{23}H_{15}ClNO_2S$ $[M+H]^+$ 404.0512, found 404.0548.

Typical Experimental Procedure for the Synthesis of Compound 13a.

A mixture of (*E*)-methyl 2-((3-ethoxy-2-formylphenoxy)methyl)-3-phenylacrylate (**1r**, 1mmol), and 2-(2-(2-minophenyl)disulfanyl)benzenamine (0.5 mmol) was placed in a round bottom flask and melted at 180 ºC for 1 h. After completion of the reaction as indicated by TLC, The crude reaction mass was purified by column chromatography on silica gel (Acme 60-120 mesh), using ethylacetate : hexanes (0.5 : 9.5) to afford **13a** as a colourless solid in 75% (0.33 g) yield.

(*E*)-Methyl 2-(3-(benzo[*d*]thiazol-2-yl)-5-ethoxy-4-hydroxybenzyl)-3-phenylacrylate (**13a**).

White solid: (75%, 0.33g); mp : 147-149 °C; Reaction time : 1h; ^1H NMR (300 MHz, $CDCl_3$) : δ 1.48 (t, J = 6.9 Hz, 3H), 3.80 (s, 3H), 3.92 (s, 2H), 4.10 (q, J = 6.9 Hz, 2H), 6.81 – 7.97 (m, 12H), 12.64 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 32.5, 52.2, 64.7, 115.9, 116.6, 118.9, 121.4, 122.1, 125.4, 126.6, 128.7, 128.8, 129.1, 130.1, 130.8, 132.7, 135.3, 141.1, 146.9, 148.2, 151.8, 168.5, 169.4; IR (KBr) : 1625, 1715, 3426 cm^{-1}; HRMS calculated for $C_{26}H_{24}NO_4S$ $[M+H]^+$ 446.1426, found 446.1437.

(*E*)-Methyl 2-(3-(benzo[*d*]thiazol-2-yl)-5-ethoxy-4-hydroxybenzyl)-3-*o*-tolylacrylate (**13b**).

White solid : (74%, 0.33g); mp : 144-146 °C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.47 (t, J = 6.9 Hz, 3H), 2.30 (s, 3H), 3.71 (s, 3H), 3.80 (s, 2H), 4.07 (q, J = 6.9 Hz, 2H), 6.46 – 7.94 (m, 11H), 12.61 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 20.0, 32.4, 52.1, 64.7, 116.5, 119.2, 121.4, 122.1, 125.4, 125.9, 126.6, 128.1, 128.6, 130.2, 130.6, 132.6, 134.9, 136.6, 140.3, 143.2, 146.8, 148.0, 148.3, 151.8, 168.3, 169.4; IR (KBr) : 1625, 1720, 3421 cm^{-1}; HRMS calculated for $C_{27}H_{26}NO_4S$ $[M+H]^+$ 460.1583, found 460.1585.

(*E*)-Methyl 2-(3-(benzo[*d*]thiazol-2-yl)-5-ethoxy-4-hydroxybenzyl)-3-*p*-tolylacrylate (**13c**).

White solid : (76%, 0.34g); mp : 142-144 °C; Reaction time : 1h; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.47 (t, J = 6.6 Hz, 3H), 2.35 (s, 3H), 3.79 (s, 3H), 3.93 (s, 2H), 4.09 (q, J = 6.6 Hz, 2H), 6.83 – 7.94 (m, 11H), 12.53 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 21.3, 32.5, 52.1, 64.7, 116.0, 116.7, 118.9, 121.4, 122.1, 125.4, 126.6, 129.2, 129.4, 129.8, 130.2, 132.5 132.7, 139.1, 141.3, 147.0, 148.2, 151.8, 168.7, 169.5; IR (KBr) : 1619, 1710, 3410 cm$^{-1;}$ HRMS calculated for $C_{27}H_{26}NO_4S$ $[M+H]^+$ 460.1583, found 460.1596.

Typical Experimental Procedure for the Synthesis of Compound 16a.

A mixture of (*E*)-2-((2-ethoxy-6-formylphenoxy)methyl)-3-phenylacrylonitrile (**7j**, 1mmol), and 2-(2-(2-minophenyl)disulfanyl)benzenamine (0.5 mmol) was placed in a round bottom flask and melted at 180 ºC for 1 h. After completion of the reaction as indicated by TLC, The crude reaction mass was purified by column chromatography on silica gel (Acme 60-120 mesh), using ethylacetate : hexanes (0.5 : 9.5) to afford **16a** as a colourless solid in 76% (0.31 g) yield.

(*Z*)-2-(3-(Benzo[*d*]thiazol-2-yl)-5-ethoxy-4-hydroxybenzyl)-3-phenylacrylonitrile (**16a**).

White solid : (76%, 0.31g); mp : 139-141°C; Reaction time : 1h; ^{1}H NMR (400 MHz, $CDCl_3$) : δ 1.57 (t, J = 6.8 Hz, 3H), 3.75 (s, 2H), 4.22 (q, J = 6.8 Hz, 2H), 6.94 – 8.04 (m, 12H); ^{13}C NMR

(100 MHz, $CDCl_3$) : δ 14.9, 41.8, 65.0, 110.7, 116.3, 116.9, 120.1, 121.6, 122.3, 125.7, 126.8, 127.2, 128.8, 129.0, 130.3, 132.8, 133.5, 144.1, 148.0, 148.7, 151.8, 169.1; IR (KBr) : 1635, 2239, 3426 cm^{-1} ; HRMS calculated for $C_{25}H_{21}N_2O_2S$ $[M+H]^+$ 413.1324, found 413.1322.

(*Z*)-2-(3-(Benzo[*d*]thiazol-2-yl)-5-ethoxy-4-hydroxybenzyl)-3-*p*-tolylacrylonitrile (**16b**).

White solid : (75%, 0.31g); mp : 138-140 °C; Reaction time : 1h; ^1H NMR (400 MHz, $CDCl_3$) : *δ* 1.51 (t, *J* = 6.8 Hz, 3H), 2.37 (s, 3H), 3.68 (s, 2H), 4.17 (q, *J* = 6.8 Hz, 2H), 6.87 – 8.00 (m, 11H), 12.76 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) : δ 14.9, 21.6, 41.8, 65.0, 109.4, 116.3, 117.0, 120.2, 121.6, 122.4, 125.7, 126.9, 127.4, 128.9, 129.7, 130.9, 132.8, 140.8, 144.2, 148.0, 151.8, 169.1; IR (KBr) : 1632, 2231, 3410 cm^{-1}; HRMS calculated for $C_{26}H_{23}N_2O_2S$ $[M+H]^+$ 427.1480, found 427.1493.

(*Z*)-2-(3-(Benzo[*d*]thiazol-2-yl)-5-ethoxy-4-hydroxybenzyl)-3-(4-chlorophenyl)acrylonitrile (**16c**).

White solid : (70%, 0.31g); mp : 138-140 °C; Reaction time : 1h; ^1H NMR (300 MHz, $CDCl_3$) : *δ* 1.50 (t, *J* = 6.9 Hz, 3H), 3.66 (s, 2H), 4.13 (q, *J* = 6.9 Hz, 2H), 6.86 – 7.97 (m, 11H), 12.77 (br s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.8, 41.6, 64.9, 111.3, 116.9, 120.0, 121.5, 122.2, 125.6, 125.7, 126.7, 126.9, 129.1, 129.2, 129.9, 130.0, 131.9, 132.6, 136.1, 142.6, 148.6, 151.6, 168.8; IR (KBr) : 1633, 2246, 3424 cm^{-1}; HRMS calculated for $C_{25}H_{20}ClN_2O_2S$ $[M+H]^+$ 447.0934, found 447.0937.

Typical Experimental Procedure for the Synthesis of Compound 17a.

(*E*)-Methyl-2-((2-formylphenoxy)methyl)-3-phenylacrylate (**1a**, 1mmol), was placed in a round bottom flask and melted at 220 ºC for 1 h. After completion of the reaction as indicated by TLC, The crude reaction mass was purified by column chromatography on silica gel (Acme 60-120

mesh), using ethylacetate : hexanes (0.5 : 9.5) to afford **17a** as a semi-solid in 63% (0.18 g) yield.

Methyl 2-((3-formyl-2-hydroxyphenyl)(phenyl)methyl)acrylate (**17a**).

White semi-solid: (63%, 0.18g); Reaction time: 1h; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.69 (s, 3H), 5.23 (s, 1H), 5.79 (s, 1H), 6.44 (s, 1H), 6.93 – 7.48 (m, 8H), 9.89 (s, 1H), 11.41 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 44.8, 52.0, 119.3, 120.4, 126.8, 127.4, 128.5, 129.0, 130.8, 132.3, 136.4, 140.2, 142.3, 159.1, 167.0, 196.5; IR (KBr): 1613, 1710, 3411 cm^{-1}; HRMS calculated for $C_{18}H_{17}O_4$ $[M+H]^+$ 297.1127, found 297.1111.

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website at DOI:.

^{1}H NMR, ^{13}C NMR and mass spectra of all new compounds.

X-ray crystallographic data (CIF files) for compounds **5b, 10d** and **16c**

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ACKNOWLEDGMENT

We thank DST, New Delhi for the financial support. We also thank DST-FIST for the NMR facility. R.S thanks CSIR for his SRF fellowship.

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