Supplementary Material

An efficient and convenient synthesis, characterization and antimicrobial evaluation of some new tetracyclic 1,4-benzothiazines

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Experimental detail, Characterization data, and NMR (^1H and ^{13}C) spectra of **4a–4t**
and 2D-NMR spectra of **4b**

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Experimental Detail

Commercial reagents were utilized as received from suppliers without additional purification. 2-Aminothiophenol was purchased from Sigma-Aldrich. All the synthesized compounds were characterized by ^1H NMR, ^{13}C NMR, IR, ESI-MS and microanalysis. All the melting points ($^{\circ}\text{C}$) were recorded on electrothermal apparatus in open capillary tubes and are uncorrected. Thin layer chromatography was used for monitoring the progress of the reaction and ascertaining the purity of the synthesized compounds on pre-coated TLC plates (Merck Keiselgel F₂₅₄) using hexane-ethyl acetate solvent system of different polarity and visualization was achieved by exposure to UV light. Columns were packed as slurry of silica gel (60–120 mesh) in hexane. Initially, compounds were adsorbed on silica gel in appropriate solvent and then loaded on column as slurry in hexane. The FTIR spectra were scanned on IR Affinity-1 FTIR (Shimadzu) spectrophotometer in KBr and wave numbers (ν) are reported in cm^{-1} . Nuclear Magnetic Resonance spectra (^1H at 400 MHz and ^{13}C at 100 MHz) were recorded on 400 MHz Bruker AVANCE-III spectrometer using CDCl_3 as solvent and tetramethylsilane (TMS) as internal standard. DEPT (Distortionless Enhancement by Polarization Transfer) and 2D-NMR *viz.* COSY (correlation spectroscopy), HSQC (heteronuclear single-quantum coherence) and HMBC (heteronuclear multiple bond correlation) spectra of compound **4b** were also recorded on 400 MHz Bruker AVANCE-III spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) are expressed in Hertz (Hz). Multiplicities in NMR signals are designated as s (singlet), d (doublet), dd (doublet of doublet), t (triplet), q (quartet) and m (multiplet, for unresolved signals). Mass spectra were scanned on Waters Quadrupole Detector (TDQ), Waters gtof micro Mass spectrometer and Agilent 6410B Triple Quad LCMS spectrometer. Microanalyses were performed on Thermo Scientific FLASH-2000 CHN analyser.

All the synthesized compounds were found in good agreement with the elemental analysis. Analytical results for C, H and N were found to be within ± 0.4 % of the theoretical values. Nomenclature of the compounds was assigned with the help of Chem Draw Ultra 12.0.

General procedure for the synthesis of 2-aryl-1H-indene-1,3(2H)-diones (1)

Condensation of equimolar quantities of phthalide and appropriate benzaldehyde under the influence of sodium methoxide and ethylacetate led to the formation of 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**).

General procedure for the synthesis of 2-aryl-2-bromo-1H-indene-1,3(2H)-diones (2)

The 2-aryl-1*H*-indene-1,3(2*H*)-diones (**1**) upon bromination in Br₂/chloroform furnished the corresponding 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-diones (**2**) according to the procedure as illustrated in literature.^[41]

General procedure for the synthesis of 5-substituted-2-aminobenzenethiols (3)

The reaction of potassium thiocyanate and bromine (generating thiocyanogen, [(SCN)₂], *in situ*) on appropriate aniline yielded the corresponding 6-substituted-2-aminobenzothiazoles, which upon subsequent base catalyzed hydrolytic fission afforded the corresponding 5-substituted 2-aminobenzenethiols (**3**) in good yields.^[42–44]

General procedure for the synthesis of benzo[b]indeno[1,2-*e*][1,4]thiazin-11(10*aH*)-ones (4)

A solution of equimolar quantities of 2-aryl-2-bromo-1*H*-indene-1,3(2*H*)-dione (**2**) and 2-aminobenzenethiol/5-substituted 2-aminobenzenethiol (**3**) in dry ethanol (30 mL) was heated at reflux on a water bath for 8–13 h. Thereafter, the reaction mixture was cooled to room temperature and solid thus obtained was filtered, dried and purified on silica gel (60–120 mesh)

column prepacked in hexane. Elution of the column with hexane:ethylacetate (19:1, v/v) gave a homogeneous residue, which upon crystallization from chloroform furnished benzo[*b*]indeno[1,2-*e*][1,4]thiazin-11(10*aH*)-ones (**4**) in high yields (82–95 %).

Characterization data

10a-(4-Nitrophenyl)benzo[*b*]indeno[1,2-*e*][1,4]thiazin-11(10*aH*)-one (**4a**)

Orange solid, yield 85%; mp 250–252 °C; IR (KBr, cm⁻¹): $\nu_{\max}$ 3113, 3065 (aromatic C–H), 1684 (C=O), 1647 (C=N), 1512 (asymmetric N–O stretch.), 1346 (symmetric N–O stretch.); ¹H NMR (400 MHz, CDCl₃): δ 9.14 (d, 1H, *J* = 8.44 Hz, H-6), 8.41 (d, 2H, *J* = 8.20 Hz, H-3', H-5'), 7.97 (d, 1H, *J* = 7.52 Hz, H-1), 7.73 (d, 2H, *J* = 8.20 Hz, H-2', H-6'), 7.55–7.09 (m, 5H, H-2, H-3, H-7, H-8, H-9), 6.48 (d, 1H, *J* = 7.92 Hz, H-4); ¹³C NMR (100 MHz, CDCl₃): δ 165.13 (C-11), 148.69 (C-4'), 141.47 (C-1'), 133.73 (C-5a), 131.87 (C-3), 131.09 (C-2', C-6'), 130.36 (C-4b), 129.03 (C-2), 128.56 (C-4a), 128.14 (C-7), 127.67 (C-11a), 125.77 (C-8), 125.61 (C-9), 124.93 (C-3', C-5'), 123.51 (C-1), 121.46 (C-4), 119.51 (C-6), 119.15 (C-9a), 115.32 (C-10a); ESI-MS *m/z*: [M+H]⁺ calcd. for C₂₁H₁₂N₂O₃S, 373.06; found, 373.14. *Anal.* calcd. for C₂₁H₁₂N₂O₃S: C, 67.73; H, 3.25; N, 7.52; found: C, 67.92; H, 3.48; N, 7.24.

8-Methyl-10a-(4-nitrophenyl)benzo[*b*]indeno[1,2-*e*][1,4]thiazin-11(10*aH*)-one (**4b**)

Orange crystals, yield 87%; mp 252–254 °C; IR (KBr, cm⁻¹): $\nu_{\max}$ 3076, 3045 (aromatic C–H), 2947, 2855 (aliphatic C–H), 1686 (C=O), 1647 (C=N), 1516 (asymmetric N–O stretch.), 1348 (symmetric N–O stretch.); ¹H NMR (400 MHz, CDCl₃): δ 9.03 (d, 1H, *J* = 8.60 Hz, H-6), 8.41 (d, 2H, *J* = 8.80 Hz, H-3', H-5'), 7.96 (d, 1H, *J* = 7.60 Hz, H-1), 7.73 (d, 2H, *J* = 8.80 Hz, H-2', H-6'), 7.45–7.49 (m, 1H, H-2), 7.28–7.32 (m, 1H, H-3), 7.09 (dd, 1H, *J* = 8.60 Hz, 1.44 Hz, H-7), 6.90 (d, 1H, *J* = 1.44 Hz, H-9), 6.47 (d, 1H, *J* = 8.00 Hz, H-4), 2.31 (s, 3H, CH₃); ¹³C NMR

(100 MHz, CDCl₃): δ 164.98 (C-11), 148.65 (C-4'), 141.59 (C-1'), 135.71 (C-5a), 131.70 (C-3), 131.20 (C-8), 131.11 (C-2', C-6'), 130.33 (C-4b), 128.96 (C-2), 128.74 (C-7), 128.64 (C-4a), 127.62 (C-11a), 125.84 (C-9), 124.91 (C-3', C-5'), 123.41 (C-1), 121.44 (C-4), 119.35 (C-6), 118.79 (C-9a), 115.29 (C-10a), 20.68 (CH₃); TOF MS ES m/z : [M+Na]⁺ calcd. for C₂₂H₁₄N₂O₃S 409.0623; found, 409.0620. *Anal.* calcd. for C₂₂H₁₄N₂O₃S: C, 68.38; H, 3.65; N, 7.25; found: C, 68.34; H, 3.34; N, 7.43.

8-Methoxy-10a-(4-nitrophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4c)

Yellow solid, yield 82%; mp 246–248 °C; IR (KBr, cm⁻¹): $\nu_{\max}$ 3107, 3051 (aromatic C–H), 2882 (aliphatic C–H), 1687 (C=O), 1647 (C=N), 1518 (asymmetric N–O stretch.), 1347 (symmetric N–O stretch.); ¹H NMR (400 MHz, CDCl₃): δ 9.14 (d, 1H, J = 8.60 Hz, H-6), 8.40 (d, 2H, J = 8.76 Hz, H-3', H-5'), 7.95 (d, 1H, J = 7.60 Hz, H-1), 7.72 (d, 2H, J = 8.76 Hz, H-2', H-6'), 7.50–6.76 (m, 3H, H-2, H-3, H-7), 6.61 (d, 1H, J = 2.40 Hz, H-9), 6.46 (d, 1H, J = 8.00 Hz, H-4), 3.80 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 165.02 (C-11), 156.58 (C-8), 148.67 (C-4'), 141.56 (C-1'), 131.60 (C-3), 131.10 (C-2', C-6'), 130.33 (C-4b), 129.05 (C-2), 128.67 (C-4a), 127.64 (C-11a), 127.23 (C-5a), 124.92 (C-3', C-5'), 123.48 (C-1), 121.49 (C-4), 121.18 (C-9a), 120.65 (C-6), 115.30 (C-10a), 112.64 (C-9), 110.72 (C-7), 55.66 (OCH₃); ESI-MS m/z : [M+H]⁺ calcd. for C₂₂H₁₄N₂O₄S, 403.08; found, 413.12. *Anal.* calcd. for C₂₂H₁₄N₂O₄S: C, 65.66; H, 3.51; N, 6.96; found: C, 65.98; H, 3.23; N, 7.23.

8-Bromo-10a-(4-nitrophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4d)

Yellow solid, yield 84%; mp 290–296 °C; IR (KBr, cm⁻¹): $\nu_{\max}$ 3111, 3067 (aromatic C–H), 1688 (C=O), 1647 (C=N), 1522 (asymmetric N–O stretch.), 1346 (symmetric N–O stretch.); ¹H NMR (400 MHz, CDCl₃): δ 9.04 (d, 1H, J = 9.08 Hz, H-6), 8.42 (d, 2H, J = 8.76 Hz, H-3', H-5'), 7.96

(d, 1H, $J = 7.64$ Hz, H-1), 7.73 (d, 2H, $J = 8.76$ Hz, H-2', H-6'), 7.51–7.31 (m, 3H, H-2, H-3, H-7), 7.21 (d, 1H, $J = 2.16$ Hz, H-9), 6.48 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, CDCl_3): δ 165.06 (C-11), 148.78 (C-4'), 140.97 (C-1'), 132.78 (C-5a), 132.12 (C-3), 131.10 (C-2', C-6'), 130.88 (C-7), 130.31 (C-4b), 129.31 (C-2), 128.35 (C-4a), 127.84 (C-9), 127.61 (C-11a), 125.03 (C-3', C-5'), 123.59 (C-1), 121.56 (C-4), 121.39 (C-8), 120.70 (C-6), 118.30 (C-9a), 114.52 (C-10a); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{11}\text{BrN}_2\text{O}_3\text{S}$, 450.98 (^{79}Br), 452.98 (^{81}Br); found, 451.02 (^{79}Br), 453.01 (^{81}Br). *Anal.* calcd. for $\text{C}_{21}\text{H}_{11}\text{BrN}_2\text{O}_3\text{S}$: C, 55.89; H, 2.46; N, 6.21; found: C, 55.57; H, 2.74; N, 6.52.

8-Chloro-10a-(4-nitrophenyl)benzo[b]indeno[1,2-*e*][1,4]thiazin-11(10aH)-one (4e)

Orange solid, yield 86%; mp 284–286 °C; IR (KBr, cm^{-1}): ν_{max} 3105, 3054 (aromatic C–H), 1686 (C=O), 1647 (C=N), 1517 (asymmetric N–O stretch.), 1347 (symmetric N–O stretch.); ^1H NMR (400 MHz, CDCl_3): δ 9.15 (d, 1H, $J = 9.12$ Hz, H-6), 8.40 (d, 2H, $J = 8.72$ Hz, H-3', H-5'), 7.96 (d, 1H, $J = 7.64$ Hz, H-1), 7.73 (d, 2H, $J = 8.72$ Hz, H-2', H-6'), 7.51–7.17 (m, 3H, H-2, H-3, H-7), 7.05 (d, 1H, $J = 2.32$ Hz, H-9), 6.48 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, CDCl_3): δ 165.01 (C-11), 148.72 (C-4'), 141.21 (C-1'), 132.52 (C-5a), 132.07 (C-3), 131.09 (C-2', C-6'), 130.49 (C-8), 130.32 (C-4b), 129.26 (C-2), 128.32 (C-4a), 127.63 (C-9), 127.21 (C-11a), 125.01 (C-3', C-5'), 124.88 (C-7), 123.57 (C-1), 121.72 (C-9a), 121.55 (C-4), 120.39 (C-6), 115.18 (C-10a); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{11}\text{ClN}_2\text{O}_3\text{S}$, 407.03 (^{35}Cl), 409.03 (^{37}Cl); found, 407.04 (^{35}Cl), 409.05 (^{37}Cl). *Anal.* calcd. for $\text{C}_{21}\text{H}_{11}\text{ClN}_2\text{O}_3\text{S}$: C, 62.00; H, 2.73; N, 6.89; found: C, 61.78; H, 2.97; N, 6.57.

10a-(4-Ethylphenyl)benzo[b]indeno[1,2-*e*][1,4]thiazin-11(10aH)-one (4f)

Light yellow crystals, yield 83%; mp 190–194 °C; IR (KBr, cm^{-1}): ν_{max} 3109, 3063 (aromatic C–H), 2966, 2870 (aliphatic C–H), 1693 (C=O), 1649 (C=N); ^1H NMR (400 MHz, CDCl_3): δ 9.18 (d, 1H, J = 8.48 Hz, H-6), 7.93 (d, 1H, J = 7.64 Hz, H-1), 7.43–7.06 (m, 9H, H-2, H-3, H-7, H-8, H-9, H-2', H-3', H-5', H-6'), 6.55 (d, 1H, J = 8.00 Hz, H-4), 2.77 (q, 2H, J = 7.60 Hz, CH_2), 1.34 (t, 3H, J = 7.60 Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 165.22 (C-11), 146.24 (C-4'), 133.88 (C-5a), 131.84 (C-1'), 131.43 (C-3), 130.89 (C-4b), 129.33 (C-2', C-6'), 129.09 (C-3', C-5'), 128.29 (C-4a), 128.17 (C-2), 127.63 (C-7), 126.67 (C-11a), 125.44 (C-8), 125.37 (C-9), 122.97 (C-1), 121.93 (C-4), 120.13 (C-9a), 119.36 (C-6), 118.66 (C-10a), 28.79 ($-\text{CH}_2\text{CH}_3$), 15.36 ($-\text{CH}_2\text{CH}_3$); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{23}\text{H}_{17}\text{NOS}$, 356.11; found, 356.10. *Anal.* calcd. for $\text{C}_{23}\text{H}_{17}\text{NOS}$: C, 77.72; H, 4.82; N, 3.94; found: C, 77.43; H, 4.65; N, 4.28.

10a-(4-Ethylphenyl)-8-methylbenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4g)

Light yellow crystals, yield 90%; mp 186–188 °C; IR (KBr, cm^{-1}): ν_{max} 3119, 3057, 3026 (aromatic C–H), 2972, 2936, 2870 (aliphatic C–H), 1682 (C=O), 1647 (C=N); ^1H NMR (400 MHz, CDCl_3): δ 9.08 (d, 1H, J = 8.60 Hz, H-6), 7.93 (d, 1H, J = 7.64 Hz, H-1), 7.43–7.04 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 6.90 (d, 2H, J = 1.48 Hz, H-9), 6.54 (d, 1H, J = 8.00 Hz, H-4), 2.77 (q, 2H, J = 7.60 Hz, CH_2), 2.29 (s, 3H, CH_3), 1.33 (t, 3H, J = 7.60 Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 165.09 (C-11), 146.21 (C-4'), 135.26 (C-5a), 131.96 (C-1'), 131.40 (C-8), 131.30 (C-3), 130.89 (C-4b), 129.39 (C-2', C-6'), 129.10 (C-3', C-5'), 128.42 (C-4a), 128.30 (C-2), 128.14 (C-7), 126.68 (C-11a), 125.72 (C-9), 122.91 (C-1), 121.94 (C-4), 119.82 (C-9a), 119.25 (C-6), 118.67 (C-10a), 28.82 ($-\text{CH}_2\text{CH}_3$), 20.68 (CH_3), 15.41 ($-\text{CH}_2\text{CH}_3$); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{19}\text{NOS}$, 370.13; found, 370.68. *Anal.* calcd. for $\text{C}_{24}\text{H}_{19}\text{NOS}$: C, 78.02; H, 5.18; N, 3.79; found: C, 78.34; H, 5.42; N, 3.45.

10a-(4-Ethylphenyl)-8-methoxybenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4h)

Yellow solid, yield 92%; mp 166–168 °C; IR (KBr, cm^{-1}): ν_{max} 3123, 3073, 3040 (aromatic C–H), 2968, 2934, 2839 (aliphatic C–H), 1676 (C=O), 1649 (C=N); ^1H NMR (400 MHz, CDCl_3): δ 9.16 (d, 1H, $J = 9.28$ Hz, H-6), 7.91 (d, 1H, $J = 7.60$ Hz, H-1), 7.42–6.76 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 6.62 (d, 1H, $J = 1.92$ Hz, H-9), 6.54 (d, 1H, $J = 7.96$ Hz, H-4), 3.79 (s, 3H, OCH_3), 2.77 (q, 2H, $J = 7.60$ Hz, CH_2), 1.33 (t, 3H, $J = 7.60$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 164.87 (C-11), 156.53 (C-8), 146.25 (C-4'), 131.82 (C-1'), 131.21 (C-3), 130.82 (C-4b), 129.44 (C-2', C-6'), 129.10 (C-3', C-5'), 128.47 (C-4a), 128.19 (C-2), 127.28 (C-5a), 126.79 (C-11a), 122.82 (C-1), 121.92 (C-4), 121.43 (C-9a), 120.60 (C-6), 117.92 (C-10a), 112.48 (C-9), 110.66 (C-7), 55.54 (OCH_3), 28.82 ($-\text{CH}_2\text{CH}_3$), 15.40 ($-\text{CH}_2\text{CH}_3$); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{S}$, 386.12; found, 386.14. *Anal.* calcd. for $\text{C}_{24}\text{H}_{19}\text{NO}_2\text{S}$: C, 74.78; H, 4.97; N, 3.63; found: C, 74.43; H, 4.64; N, 3.95.

8-Bromo-10a-(4-ethylphenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4i)

Yellow solid, yield 95%; mp 227–230 °C; IR (KBr, cm^{-1}): ν_{max} 3109, 3059 (aromatic C–H), 2968, 2930 (aliphatic C–H), 1680 (C=O), 1649 (C=N); ^1H NMR (400 MHz, CDCl_3): δ 9.09 (d, 1H, $J = 9.04$ Hz, H-6), 7.92 (d, 1H, $J = 7.56$ Hz, H-1), 7.45–7.27 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 7.19 (d, 1H, $J = 2.28$ Hz, H-9), 6.55 (d, 1H, $J = 8.00$ Hz, H-4), 2.78 (q, 2H, $J = 7.60$ Hz, CH_2), 1.33 (t, 3H, $J = 7.60$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 165.20 (C-11), 146.50 (C-4'), 132.99 (C-5a), 131.71 (C-3), 131.38 (C-1'), 130.88 (C-4b), 130.40 (C-7), 129.34 (C-2', C-6'), 129.22 (C-3', C-5'), 128.47 (C-2), 128.14 (C-4a), 127.67 (C-9), 126.65 (C-11a), 123.09 (C-1), 122.51 (C-8), 122.04 (C-4), 120.63 (C-6), 117.91 (C-9a), 117.88 (C-10a), 28.83 ($-\text{CH}_2\text{CH}_3$), 15.38 ($-\text{CH}_2\text{CH}_3$); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{23}\text{H}_{16}\text{BrNOS}$, 434.02 (^{79}Br),

436.02 (^{81}Br); found, 434.00 (^{79}Br), 436.01 (^{81}Br). *Anal.* calcd. for $\text{C}_{23}\text{H}_{16}\text{BrNOS}$: C, 63.60; H, 3.71; N, 3.22; found: C, 63.28; H, 3.93; N, 3.56.

8-Chloro-10a-(4-ethylphenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4j)

Yellowish orange solid, yield 84%; mp 230–232 °C; IR (KBr, cm^{-1}): ν_{max} 3113, 3061, 3024 (aromatic C–H), 2970, 2934, 2876 (aliphatic C–H), 1680 (C=O), 1649 (C=N); ^1H NMR (400 MHz, CDCl_3): δ 9.16 (d, 1H, $J = 9.04$ Hz, H-6), 7.93 (d, 1H, $J = 7.60$ Hz, H-1), 7.43–7.17 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 7.05 (d, 2H, $J = 2.44$ Hz, H-9), 6.56 (d, 1H, $J = 8.00$ Hz, H-4), 2.78 (q, 2H, $J = 7.60$ Hz, CH_2), 1.33 (t, 3H, $J = 7.60$ Hz, CH_3); ^{13}C NMR (100 MHz, CDCl_3): δ 165.16 (C-11), 146.47 (C-4'), 132.49 (C-5a), 131.66 (C-3), 131.39 (C-1'), 130.87 (C-4b), 130.36 (C-8), 129.33 (C-2', C-6'), 129.19 (C-3', C-5'), 128.43 (C-2), 128.14 (C-4a), 127.42 (C-9), 126.68 (C-11a), 124.86 (C-7), 123.06 (C-1), 122.18 (C-9a), 122.02 (C-4), 120.34 (C-6), 117.77 (C-10a), 28.80 ($-\text{CH}_2\text{CH}_3$), 15.34 ($-\text{CH}_2\text{CH}_3$); TOF MS ES m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{23}\text{H}_{16}\text{ClNOS}$, 390.0719 (^{35}Cl), 391.0735 (^{37}Cl); found, 390.0747 (^{35}Cl), 392.0738 (^{37}Cl); $[\text{M}+\text{Na}]^+$ calcd. for $\text{C}_{23}\text{H}_{16}\text{ClNOS}$, 412.0539 (^{35}Cl), 414.0605 (^{37}Cl); found, 412.0536 (^{35}Cl), 414.0608 (^{37}Cl). *Anal.* calcd. for $\text{C}_{23}\text{H}_{16}\text{ClNOS}$: C, 70.85; H, 4.14; N, 3.59; found: C, 70.52; H, 4.39; N, 3.83.

10a-(4-Fluorophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4k)

Light yellow crystals, yield 87%; mp 160–163 °C; IR (KBr, cm^{-1}): ν_{max} 3069, 3059, 3044 (aromatic C–H), 1690 (C=O), 1649 (C=N); ^1H NMR (400 MHz, CDCl_3): δ 9.17 (d, 1H, $J = 8.88$ Hz, H-6), 7.95 (d, 1H, $J = 7.64$ Hz, H-1), 7.50–7.06 (m, 9H, H-2, H-3, H-7, H-8, H-9, H-2', H-3', H-5', H-6'), 6.50 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, CDCl_3): δ 165.20 (C-11), 163.52 (d, $J = 249$ Hz, C-4'), 133.83 (C-5a), 131.62 (d, $J = 8$ Hz, C-2', C-6'), 131.60 (C-3),

130.72 (C-4b), 130.62 (d, $J = 4$ Hz, C-1'), 128.48 (C-2), 128.42 (C-4a), 127.84 (C-7), 127.18 (C-11a), 125.51 (C-8), 125.48 (C-9), 123.19 (C-1), 121.72 (C-4), 119.80 (C-9a), 119.42 (C-6), 117.13 (C-10a), 116.93 (d, $J = 22$ Hz, C-3', C-5'); ESI-MS m/z : $[M+H]^+$ calcd. for $C_{21}H_{12}FNOS$, 346.09; found, 346.60. *Anal.* calcd. for $C_{21}H_{12}FNOS$: C, 73.03; H, 3.50; N, 4.06; found: C, 73.38; H, 3.18; N, 4.32.

10a-(4-Fluorophenyl)-8-methylbenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4l)

Yellow solid, yield 91%; mp 238–242 °C; IR (KBr, cm^{-1}): ν_{max} 3119, 3067, 3028 (aromatic C–H), 2874, 2793 (aliphatic C–H), 1684 (C=O), 1649 (C=N); 1H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, 1H, $J = 8.60$ Hz, H-6), 7.92 (d, 1H, $J = 7.64$ Hz, H-1), 7.50–7.03 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 6.87 (d, 1H, $J = 1.40$ Hz, H-9), 6.48 (d, 1H, $J = 8.00$ Hz, H-4), 2.28 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.97 (C-11), 163.50 (d, $J = 249$ Hz, C-4'), 135.35 (C-5a), 131.64 (d, $J = 8$ Hz, C-2', C-6'), 131.39 (C-3), 131.31 (C-8), 130.71 (d, $J = 3$ Hz, C-1'), 130.66 (C-4b), 128.49 (C-4a), 128.41 (C-2), 128.36 (C-7), 127.11 (C-11a), 125.68 (C-9), 123.05 (C-1), 121.67 (C-4), 119.43 (C-9a), 119.24 (C-6), 117.05 (C-10a), 116.87 (d, $J = 22$ Hz, C-3', C-5'), 20.64 (CH_3); ESI-MS m/z : $[M+H]^+$ calcd. for $C_{22}H_{14}FNOS$, 360.09; found, 360.10. *Anal.* calcd. for $C_{22}H_{14}FNOS$: C, 73.52; H, 3.93; N, 3.90; found: C, 73.21; H, 4.23; N, 3.65.

10a-(4-Fluorophenyl)-8-methoxybenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4m)

Greenish yellow solid, yield 94%; mp 206–210 °C; IR (KBr, cm^{-1}): ν_{max} 3111, 3042 (aromatic C–H), 2961, 2840 (aliphatic C–H), 1686 (C=O), 1647 (C=N); 1H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, 1H, $J = 9.32$ Hz, H-6), 7.92 (d, 1H, $J = 7.64$ Hz, H-1), 7.50–6.77 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 6.62 (d, 1H, $J = 2.88$ Hz, H-9), 6.48 (d, 1H, $J = 7.96$ Hz, H-4), 3.80 (s, 3H, OCH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.82 (C-11), 163.53 (d, $J = 249$ Hz, C-4'), 156.60

(C-8), 131.70 (d, $J = 8$ Hz, C-2', C-6'), 131.36 (C-3), 130.62 (C-4b), 130.58 (d, $J = 3$ Hz, C-1'), 128.56 (C-4a), 128.47 (C-2), 127.26 (C-11a), 127.18 (C-5a), 123.01 (C-1), 121.69 (C-4), 121.07 (C-9a), 120.63 (C-6), 116.92 (d, $J = 22$ Hz, C-3', C-5'), 116.37 (C-10a), 112.60 (C-9), 110.72 (C-7); ESI-MS m/z : $[M+H]^+$ calcd. for $C_{22}H_{14}FNO_2S$, 376.08; found, 376.15. *Anal.* calcd. for $C_{22}H_{14}FNO_2S$: C, 70.38; H, 3.76; N, 3.73; found: C, 70.63; H, 3.47; N, 3.98.

8-Bromo-10a-(4-fluorophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4n)

Green solid, yield 92%; mp 234–236 °C; IR (KBr, cm^{-1}): ν_{max} 3113, 3061, (aromatic C–H), 1684 (C=O), 1647 (C=N); 1H NMR (400 MHz, $CDCl_3$): δ 9.07 (d, 1H, $J = 9.04$ Hz, H-6), 7.93 (d, 1H, $J = 7.60$ Hz, H-1), 7.50–7.22 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 7.19 (d, 1H, $J = 2.20$ Hz, H-9), 6.50 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.13 (C-11), 163.62 (d, $J = 249$ Hz, C-4'), 132.90 (C-5a), 131.85 (C-3), 131.64 (d, $J = 8$ Hz, C-2', C-6'), 130.68 (C-4b), 130.57 (C-7), 130.14 (d, $J = 3$ Hz, C-1'), 128.75 (C-2), 128.23 (C-4a), 127.70 (C-9), 127.13 (C-11a), 123.27 (C-1), 122.12 (C-8), 121.81 (C-4), 120.64 (C-6), 118.03 (C-9a), 117.06 (d, $J = 21$ Hz, C-3', C-5'), 116.33 (C-10a); ESI-MS m/z : $[M+H]^+$ calcd. for $C_{21}H_{11}BrFNOS$, 423.98 (^{79}Br), 426.02 (^{81}Br); found, 424.32 (^{79}Br), 426.57 (^{81}Br). *Anal.* calcd. for $C_{21}H_{11}BrFNOS$: C, 59.45; H, 2.61; N, 3.30; found: C, 59.72; H, 2.34; N, 3.65.

8-Chloro-10a-(4-fluorophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4o)

Greenish yellow solid, yield 89%; mp 240–242 °C; IR (KBr, cm^{-1}): ν_{max} 3117, 3063, 3022 (aromatic C–H), 1684 (C=O), 1607 (C=N); 1H NMR (400 MHz, $CDCl_3$): δ 9.14 (d, 1H, $J = 9.08$ Hz, H-6), 7.94 (d, 1H, $J = 7.52$ Hz, H-1), 7.50–7.18 (m, 7H, H-2, H-3, H-7, H-2', H-3', H-5', H-6'), 7.05 (d, 1H, $J = 2.40$ Hz, H-9), 6.50 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.11 (C-11), 163.62 (d, $J = 249$ Hz, C-4'), 132.42 (C-5a), 131.82 (C-3), 131.64 (d, $J = 8$ Hz,

C-2', C-6'), 130.68 (C-4b), 130.51 (C-8), 130.16 (d, $J = 3$ Hz, C-1'), 128.74 (C-2), 128.24 (C-4a), 127.61 (C-9), 127.18 (C-11a), 124.90 (C-7), 123.26 (C-1), 121.86 (C-9a), 121.80 (C-4), 120.37 (C-6), 117.04 (d, $J = 21$ Hz, C-3', C-5'), 116.24 (C-10a); ESI-MS m/z : $[M+H]^+$ calcd. for $C_{21}H_{11}ClFNOS$, 380.01 (^{35}Cl), 382.03 (^{37}Cl); found, 380.03 (^{35}Cl), 382.04 (^{37}Cl). *Anal.* calcd. for $C_{21}H_{11}ClFNOS$: C, 66.40; H, 2.92; N, 3.69; found: C, 66.18; H, 3.25; N, 3.32.

10a-(4-Bromophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4p)

Yellow solid, yield 93%; mp 196–198 °C; IR (KBr, cm^{-1}): ν_{max} 3123, 3088, 3055, 3028 (aromatic C–H), 1691 (C=O), 1647 (C=N); 1H NMR (400 MHz, $CDCl_3$): δ 9.15 (d, 1H, $J = 8.52$ Hz, H-6), 7.93 (d, 1H, $J = 7.44$ Hz, H-1), 7.67 (d, 2H, $J = 8.52$ Hz, H-3', H-5'), 7.44–7.03 (m, 7H, H-2, H-3, H-7, H-8, H-9, H-2', H-6'), 6.56 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.14 (C-11), 133.77 (C-5a), 133.62 (C-1'), 133.00 (C-3', C-5'), 131.66 (C-3), 131.29 (C-2', C-6'), 130.61 (C-4b), 128.55 (C-2), 128.38 (C-4a), 127.81 (C-7), 127.04 (C-11a), 125.52 (C-8), 125.48 (C-9), 124.23 (C-4'), 123.20 (C-1), 121.74 (C-4), 119.64 (C-9a), 119.40 (C-6), 116.85 (C-10a); ESI-MS m/z : $[M+H]^+$ calcd. for $C_{21}H_{12}BrNOS$, 405.99 (^{79}Br), 407.98 (^{81}Br); found, 406.02 (^{79}Br), 408.07 (^{81}Br). *Anal.* calcd. for $C_{21}H_{12}BrNOS$: C, 62.08; H, 2.98; N, 3.45; found: C, 62.36; H, 2.63; N, 3.72.

10a-(4-Bromophenyl)-8-methylbenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4q)

Yellow solid, yield 90%; mp 224–226 °C; IR (KBr, cm^{-1}): ν_{max} 3088, 3049, 3032 (aromatic C–H), 2972, 2947, 2920 (aliphatic C–H), 1684 (C=O), 1645 (C=N); 1H NMR (400 MHz, $CDCl_3$): δ 9.05 (d, 1H, $J = 8.60$ Hz, H-6), 7.94 (d, 1H, $J = 7.56$ Hz, H-1), 7.68 (d, 2H, $J = 8.52$ Hz, H-3', H-5'), 7.47–7.05 (m, 5H, H-2, H-3, H-7, H-8, H-9, H-2', H-6'), 6.89 (d, 1H, $J = 1.36$ Hz, H-9), 6.56 (d, 1H, $J = 7.96$ Hz, H-4), 2.29 (s, 3H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.02 (C-11),

135.44 (C-5a), 133.75 (C-1'), 132.98 (C-3', C-5'), 131.51 (C-3), 131.32 (C-2', C-6'), 131.23 (C-8), 130.62 (C-4b), 128.51 (C-2), 128.49 (C-7), 128.42 (C-4a), 127.08 (C-11a), 125.74 (C-9), 124.18 (C-4'), 123.13 (C-1), 121.73 (C-4), 119.33 (C-9a), 119.28 (C-6), 116.82 (C-10a), 20.66 (CH₃); ESI-MS *m/z*: [M+H]⁺ calcd. for C₂₂H₁₄BrNOS, 420.01 (⁷⁹Br), 422.03 (⁸¹Br); found, 420.02 (⁷⁹Br), 422.05 (⁸¹Br). *Anal.* calcd. for C₂₂H₁₄BrNOS: C, 62.87; H, 3.36; N, 3.33; found: C, 62.51; H, 3.62; N, 3.64.

10a-(4-Bromophenyl)-8-methoxybenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4r)

Yellow solid, yield 83%; mp 176–180 °C; IR (KBr, cm⁻¹): $\nu_{\max}$ 3086, 3028 (aromatic C–H), 2965, 2941 (aliphatic C–H), 1682 (C=O), 1649 (C=N); ¹H NMR (400 MHz, CDCl₃): δ 9.13 (d, 1H, *J* = 9.28 Hz, H-6), 7.92 (d, 1H, *J* = 7.64 Hz, H-1), 7.67 (d, 2H, *J* = 8.40 Hz, H-3', H-5'), 7.45–6.76 (m, 5H, H-2, H-3, H-7, H-2', H-6'), 6.60 (d, 1H, *J* = 2.88 Hz, H-9), 6.55 (d, 1H, *J* = 7.96 Hz, H-4), 3.79 (s, 3H, OCH₃); ¹³C NMR (100 MHz, CDCl₃): δ 164.80 (C-11), 156.63 (C-8), 133.63 (C-1'), 133.00 (C-3', C-5'), 131.43 (C-3), 131.38 (C-2', C-6'), 130.91 (C-4b), 128.77 (C-4a), 128.56 (C-2), 127.18 (C-11a), 127.15 (C-5a), 124.24 (C-4'), 123.04 (C-1), 121.73 (C-4), 120.93 (C-9a), 120.64 (C-6), 116.08 (C-10a), 112.66 (C-9), 110.74 (C-7), 55.56 (OCH₃); TOF MS ES *m/z*: [M+H]⁺ calcd. for C₂₂H₁₄BrNO₂S, 436.0007 (⁷⁹Br), 438.0013 (⁸¹Br); found, 435.9982 (⁷⁹Br), 438.0025 (⁸¹Br); [M+Na]⁺ calcd. for C₂₂H₁₄BrNO₂S, 457.9826 (⁷⁹Br), 459.9859 (⁸¹Br); found, 457.9824 (⁷⁹Br), 459.9857 (⁸¹Br). *Anal.* calcd. for C₂₂H₁₄BrNO₂S: C, 60.56; H, 3.23; N, 3.21; found: C, 60.23; H, 3.51; N, 3.49.

8-Bromo-10a-(4-bromophenyl)benzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4s)

Greenish yellow solid, yield 85%; mp 236–240 °C; IR (KBr, cm⁻¹): $\nu_{\max}$ 3059, 3113 (aromatic C–H), 1697 (C=O), 1651 (C=N); ¹H NMR (400 MHz, CDCl₃): δ 9.07 (d, 1H, *J* = 9.08 Hz, H-6),

7.95 (d, 1H, $J = 7.64$ Hz, H-1), 7.70 (d, 2H, $J = 8.44$ Hz, H-3', H-5'), 7.50–7.32 (m, 5H, H-2, H-3, H-7, H-2', H-6'), 7.21 (d, 1H, $J = 2.28$ Hz, H-9), 6.58 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, CDCl_3): δ 165.14 (C-11), 133.16 (C-1'), 133.12 (C-3', C-5'), 132.90 (C-5a), 131.94 (C-3), 131.26 (C-2', C-6'), 130.66 (C-4b), 130.63 (C-7), 128.86 (C-2), 128.26 (C-4a), 127.74 (C-9), 127.09 (C-11a), 124.47 (C-4'), 123.33 (C-1), 121.99 (C-8), 121.85 (C-4), 120.67 (C-6), 118.08 (C-9a), 116.07 (C-10a); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{11}\text{Br}_2\text{NOS}$, 483.90 (^{79}Br and ^{79}Br), 485.88 (^{79}Br and ^{81}Br), 487.92 (^{81}Br and ^{81}Br); found, 483.93 (^{79}Br and ^{79}Br), 485.91 (^{79}Br and ^{81}Br), 487.95 (^{81}Br and ^{81}Br). *Anal.* calcd. for $\text{C}_{21}\text{H}_{11}\text{Br}_2\text{NOS}$: C, 51.98; H, 2.29; N, 2.89; found: C, 51.62; H, 2.58; N, 3.15.

10a-(4-Bromophenyl)-8-chlorobenzo[b]indeno[1,2-e][1,4]thiazin-11(10aH)-one (4t)

Greenish yellow crystals, yield 87%; mp 214–216 °C; IR (KBr, cm^{-1}): ν_{max} 3074 (aromatic C–H), 1697 (C=O), 1651 (C=N); ^1H NMR (CDCl_3): δ 9.14 (d, 1H, $J = 9.08$ Hz, H-6), 7.95 (d, 1H, $J = 7.68$ Hz, H-1), 7.70 (d, 2H, $J = 8.44$ Hz, H-3', H-5'), 7.48–7.19 (m, 5H, H-2, H-3, H-7, H-2', H-6'), 7.07 (d, 2H, $J = 2.00$ Hz, H-9), 6.58 (d, 1H, $J = 8.00$ Hz, H-4); ^{13}C NMR (100 MHz, CDCl_3): δ 165.13 (C-11), 133.16 (C-1'), 133.12 (C-3', C-5'), 132.39 (C-5a), 131.92 (C-3), 131.26 (C-2', C-6'), 130.61 (C-4b), 130.56 (C-8), 128.86 (C-2), 128.24 (C-4a), 127.67 (C-9), 127.11 (C-11a), 124.95 (C-7), 124.47 (C-4'), 123.31 (C-1), 121.85 (C-4), 121.68 (C-9a), 120.40 (C-6), 116.00 (C-10a); ESI-MS m/z : $[\text{M}+\text{H}]^+$ calcd. for $\text{C}_{21}\text{H}_{11}\text{BrClNOS}$, 439.95 (^{79}Br and ^{35}Cl), 441.98 (^{81}Br or ^{37}Cl), 443.89 (^{81}Br and ^{37}Cl); found, 439.93 (^{79}Br and ^{35}Cl), 441.92 (^{81}Br or ^{37}Cl), 443.74 (^{81}Br and ^{37}Cl). *Anal.* calcd. for $\text{C}_{21}\text{H}_{11}\text{BrClNOS}$: C, 57.23; H, 2.52; N, 3.18; found: C, 57.54; H, 2.18; N, 3.47.

General procedure for *in vitro* Antimicrobial evaluation

All the newly synthesized twenty tetracyclic 1,4-benzothiazines (**4a–4t**) were screened for their *in vitro* antimicrobial activity against two Gram-positive bacteria viz. *B. subtilis* (MTCC 441) and *S. epidermidis* (MTCC 6880), two Gram-negative bacteria viz. *E. coli* (MTCC 1652) and *P. aeruginosa* (MTCC 424), and two fungi viz. *A. niger* (MTCC 8189) and *C. albicans* (MTCC 227) by employing serial dilution technique.^[45] Initially, stock solutions were prepared by dissolving weighed amounts of synthesized compounds in DMSO (1.0 mg of the test compound in 10 mL DMSO) to get a final concentration of 100 µg/mL. Fresh cultures were obtained by inoculation of respective microorganisms in suitable media viz. nutrient broth for bacterial strains and potato dextrose broth for fungal strains, followed by incubation at 37 ± 1 °C for 24 h (all bacteria), 25 ± 1 °C for 7 days (*A. niger*) and 37 ± 1 °C for 48 h (*C. albicans*). The stock solutions of the test compounds were then serially diluted in test tubes containing 1 mL of sterile medium to get the concentrations of 50–0.39 µg/mL. Then 100 µL of the respective microorganism in sterile saline was inoculated to different dilutions of test compounds (each dilution in triplicates). The inoculated test tubes were incubated at 37 ± 1 °C for 24 h (bacteria), 25 ± 1 °C for 7 days (*A. niger*) and 37 ± 1 °C for 48 h (*C. albicans*). Ciprofloxacin and Fluconazole were used as standard antibacterial and antifungal drugs, respectively which were also assessed under similar conditions for comparison with the tested compounds. After incubation, microbial growth was monitored visually and spectrophotometrically and the results were recorded in terms of Minimum Inhibitory Concentration (MIC, µmol/mL). The data for the antibacterial activity are presented in Table 1 and Fig. 2, and results of antifungal activity are depicted in Table 2 and Fig. 3.

^1H and ^{13}C NMR Spectra of 4a–4t

Fig. S1 ^1H NMR spectra of compound **4a**

Fig. S2 ¹³C NMR spectra of compound **4a**

Fig. S3 ¹H NMR spectra of compound **4b**

Fig. S4 ¹³C NMR spectra of compound **4b**

Fig. S5 ¹H NMR spectra of compound **4c**

Fig. S6 ¹³C NMR spectra of compound **4c**

Fig. S7 ¹H NMR spectra of compound **4d**

Fig. S8 ¹³C NMR spectra of compound **4d**

Fig. S9 ¹H NMR spectra of compound **4e**

Fig. S10 ¹³C NMR spectra of compound **4e**

Fig. S11 ¹H NMR spectra of compound **4f**

Fig. S12 ¹³C NMR spectra of compound **4f**

Fig. S13 ¹H NMR spectra of compound **4g**

Fig. S14 ¹³C NMR spectra of compound **4g**

Fig. S15 ¹H NMR spectra of compound **4h**

Fig. S16 ^{13}C NMR spectra of compound **4h**

Fig. S17 ¹H NMR spectra of compound **4i**

Fig. S18 ¹³C NMR spectra of compound **4i**

Fig. S19 ¹H NMR spectra of compound **4j**

Fig. S20 ¹³C NMR spectra of compound **4j**

Fig. S21 ¹H NMR spectra of compound **4k**

Fig. S22 ¹³C NMR spectra of compound **4k**

Fig. S23 ¹H NMR spectra of compound **41**

Fig. S24 ¹³C NMR spectra of compound **4l**

Fig. S25 ¹H NMR spectra of compound **4m**

Fig. S26 ^{13}C NMR spectra of compound **4m**

Fig. S27 ¹H NMR spectra of compound **4n**

Fig. S28 ¹³C NMR spectra of compound **4n**

Fig. S29 ¹H NMR spectra of compound **4o**

Fig. S30 ¹³C NMR spectra of compound **4o**

Fig. S31 ¹H NMR spectra of compound **4p**

Fig. S32 ¹³C NMR spectra of compound **4p**

Fig. S33 ¹H NMR spectra of compound **4q**

Fig. S34 ¹³C NMR spectra of compound **4q**

Fig. S35 ¹H NMR spectra of compound **4r**

Fig. S36 ¹³C NMR spectra of compound **4r**

Fig. S37 ¹H NMR spectra of compound **4s**

Fig. S38 ¹³C NMR spectra of compound **4s**

Fig. S39 ¹H NMR spectra of compound **4t**

Fig. S40 ¹³C NMR spectra of compound **4t**

2D NMR Spectra of 4b

Fig. S41 DEPT-135 spectra of compound 4b

Fig. S42 DEPT-135 spectra of compound **4b**

Fig. S43 COSY spectra of compound **4b**

Fig. S44 COSY spectra of compound **4b**

Fig. S45 HSQC spectra of compound **4b**

Fig. S46 HSQC spectra of compound **4b**

Fig. S47 HMBC spectra of compound **4b**

Fig. S48 HMBC spectra of compound **4b**

HMBC of **4b**

Fig. S49 HMBC spectra of compound **4b**

Fig. S50 HMBC spectra of compound **4b**