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Supporting Information

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Reactions of Keto–Enol Tautomers of 2-Thiazolyl-, 2-Oxazolyl-, 2-Benzoxazolyl-, or 2-Benzothiazolyl-1-phenylethenols with α,β-Alkynyl Esters: Syntheses of Highly Functionalized Fused-Ring Heterocycles:

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Supporting Information

Chemicals and solvents were purchased from commercial suppliers and used as received, except that acetonitrile and triethylamine were distilled from calcium hydride under nitrogen. All reactions were carried out under nitrogen. Silica gel (230-400 mesh and a pore size 60 Å) purchased from Sorbent Technologies, was used as the stationary phase for flash chromatography analyses. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE III -300 or -600 spectrometers operating at 300 MHz and 600 MHz for proton, and 75 MHz and 150 MHz for carbon. Chemical shifts were reported in parts per million (ppm) on the delta (δ) scale relative to the internal standard, tetramethylsilylane for ^{1}H ($\delta = 0$ ppm) and the center line of the deuterated solvent for ^{13}C ($CDCl_3$: $\delta = 77.0$ ppm and DMSO-d_6: $\delta = 39.43$ ppm). Splitting patterns are designed as “s, d, t, q, and m”, and these symbols indicate “singlet, doublet, triplet, quartet, and multiplet,” respectively. Coupling constants, *J*, were reported in Hertz (Hz). High-resolution mass spectra were recorded on a Bruker UHPLC-micro-Q/T MS/MS spectrometer in the ESI mode. Melting points were recorded with a Mel-Temp apparatus and were uncorrected. IR spectra were recorded on a Nicolet 6700 FT-IR spectrometer. A Bruker AXS Smart 1000 diffractometer, upgraded with an APEX II detector and software which incorporates

SHELX components,[1] was employed for crystal structure determinations at -173 °C. All reactions were carried out under nitrogen.

Preparation of enol-esters of thiazoles, oxazoles, benzoxazoles and benzothiazoles

(*Z*)-1-Phenyl-2-(thiazol-2-yl)vinyl benzoate (4)[2]

Triethylamine (1.83 g, 18.1 mmol, 3.6 eq.) was added to a stirred solution of 2-methylthiazole **1** (0.496 g, 5 mmol, 1 eq.) in CH_3CN (25 mL) at room temperature under nitrogen. Benzoyl chloride (2.13 g, 15 mmol, 3 eq.) in acetonitrile (20 mL) was added dropwise into this solution at room temperature under nitrogen. This solution was refluxed for 7 h. After cooling to room temperature, acetonitrile was removed by rotary evaporation. The residue was dissolved in dichloromethane (30 mL), washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and dried over anhydrous sodium sulfate and filtered. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:3) to give the title compound **4** (1.364 g, 88.8%). This general procedure was also used for the syntheses of compounds **5**, **6**, **15-17** discussed in this section.

R_f = 0.39 (ethyl acetate/hexane = 1:3); yellow solid; mp = 105-106 °C.

IR (neat): 3116, 3069, 3032, 2981, 1732, 1642, 1599, 1448, 1235, 1175, 1076, 1058, 1023, 762, 707, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, J = 7.48 Hz, $-OCOC_6\underline{H}_5$ *ortho*, 2H), 7.82 (d, J = 3.0 Hz, $=NC\underline{H}=CHS-$, 1H), 7.71 (t, J = 7.40 Hz, $-OCOC_6\underline{H}_5$ *para*, 1H), 7.63-7.55 and 7.37-7.40 (m, $-OCOC_6\underline{H}_5$ *meta*, $-CH=C(C_6\underline{H}_5)O-$ *ortho*, *meta* and *para*, and N,S≥ $C\underline{H}=$, 8H), 7.25 (d, J = 3.0 Hz, $=NCH=C\underline{H}S-$, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 163.68 ($-O\underline{C}OC_6H_5$), 161.42 ($N,S\geq\underline{C}-$), 150.18 ($-CH=\underline{C}(C_6H_5)O-$), 142.77 ($=N\underline{C}H=CHS-$), 134.13 ($-OCOC_6\underline{H}_5$ *para*), 133.85 ($-OCO\underline{C}_6H_5$ *ipso*), 130.57 ($-OCO\underline{C}_6H_5$ *ortho*), 129.63 ($-CH=\underline{C}(C_6H_5)O-$ *para*), 128.89 ($-OCOC_6\underline{H}_5$ *meta*), 128.85 ($-CH=C(\underline{C}_6H_5)O-$ *meta*), 128.82 ($-CH=C(\underline{C}_6H_5)O-$ *ipso*), 124.96 ($-CH=C(\underline{C}_6H_5)O-$ *ortho*), 119.66 ($=NCH=\underline{C}HS-$), 112.08 ($N,S\geq C\underline{C}H=$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 142.86, 134.23, 130.62, 129.73, 128.99, 128.92, 125.06, 119.76, 112.18.

(*Z*)-2-(4,5-dimethylthiazol-2-yl)-1-phenylvinyl benzoate (5)[2]

The title compound **5** (1.11 g, 66.1%) was obtained using 2,4,5-trimethylthiazole **2** (0.636 g, 5 mmol, 1 eq.), triethylamine (1.84 g, 18 mmol, 3.6 eq.) and benzoyl chloride (2.13 g, 15 mmol, 3 eq.) by the general procedure used for the synthesis and purification of **4**. Ethyl acetate/hexane = 1:3 was used as the eluent for column chromatography.

$R_f = 0.50$ (ethyl acetate/hexane =1:3); yellow solid; mp = 156-158 °C.

IR (neat): 3066, 3045, 2951, 2915, 1741, 1655, 1537, 1450, 1432, 1227, 1076, 1050, 1023, 885, 767, 694 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, $J = 7.55$ Hz, $-OCOC_6\underline{H}_5$ *ortho*, 2H), 7.72 (t, $J = 7.40$ Hz, $-OCOC_6\underline{H}_5$ *para*, 1H), 7.62-7.56 and 7.38-7.35 (m, $-OCOC_6\underline{H}_5$ *meta*, and $-CH=C(C_6\underline{H}_5)O-$ *ortho*, *meta* and *para*, 7H), 7.23 (s, $N,S\geq C\underline{C}\underline{H}=$, 1H), 2.31 (s, $=NC(CH_3)=C(C\underline{H}_3)S-$ or $=NC(C\underline{H}_3)=C(CH_3)S-$, 3H), 2.28 (s, $=NC(CH_3)=C(C\underline{H}_3)S-$ or $=NC(C\underline{H}_3)=C(CH_3)S-$, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 163.84 ($-O\underline{C}OC_6H_5$ or $N,S\geq\underline{C}-$), 156.69 ($-O\underline{C}OC_6H_5$ or $N,S\geq\underline{C}-$), 148.75 ($-CH=\underline{C}(C_6H_5)O-$ or $=N\underline{C}(CH_3)=C(CH_3)S-$), 148.38 ($-CH=\underline{C}(C_6H_5)O-$ or $=N\underline{C}(CH_3)=C(CH_3)S-$), 134.03 ($-OCO\underline{C}_6H_5$ *ipso*), 134.01

($-OCO\underline{C}_6H_5$ *para*), 130.54 ($-OCO\underline{C}_6H_5$ *ortho*), 129.29 ($-CH=C(\underline{C}_6H_5)O-$ *para*), 129.00 ($-OCO\underline{C}_6H_5$ *ipso*), 128.85 ($-OCO\underline{C}_6H_5$ *meta* or $-CH=C(\underline{C}_6H_5)O-$ *meta*), 128.79 ($-OCO\underline{C}_6H_5$ *meta* or $-CH=C(\underline{C}_6H_5)O-$ *meta*), 127.80 ($=NC(CH_3)=\underline{C}(CH_3)S-$), 124.73 ($-CH=C(\underline{C}_6H_5)O-$ *ortho*), 112.24 ($N,S\geq C\underline{C}H=$), 14.54 ($=NC(\underline{C}H_3)=C(CH_3)S-$ or $=NC(CH_3)=C(\underline{C}H_3)S-$), 11.35 ($=NC(\underline{C}H_3)=C(CH_3)S-$ or $=NC(CH_3)=C(\underline{C}H_3)S-$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 134.09, 130.81, 129.37, 128.93, 128.87, 124.81, 112.32, 14.62, 11.43.

(*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylvinyl benzoate (6)[2]

The title compound **6** (1.26 g, 78.9%) was obtained using 2,4,5-trimethyloxazole **3** (0.585 g, 5 mmol, 1 eq.), triethylamine (1.87 g, 18.5 mmol, 3.7 eq.) and benzoyl chloride (2.15 g, 15.1 mmol, 3 eq.). The general procedure used for both the synthesis and purification of **4** was followed. The crude product was purified by column chromatography using ethyl acetate/hexane = 1:4 over silica gel.

$R_f = 0.54$ (ethyl acetate/hexane =1:3); sticky oil.

IR (neat): 3062, 2978, 2953, 2923, 2858, 1738, 1633, 1449, 1236, 1175, 1082, 1064, 1024, 1000, 760, 705, 689 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, $J = 7.47$ Hz, $-OCOC_6\underline{H}_5$ ortho, 2H), 7.69-7.37 (m, $-OCOC_6\underline{H}_5$ *meta* and *para*, and $-CH=C(C_6\underline{H}_5)O-$ ortho, *meta* and *para*, 8H), 6.83 (s, $N,S\geq CC\underline{H}=$, 1H), 2.01 (s, $=NC(CH_3)=C(C\underline{H}_3)O-$ or $=NC(C\underline{H}_3)=C(CH_3)O-$, 3H), 1.92 (s, $=NC(CH_3)=C(C\underline{H}_3)O-$ or $=NC(C\underline{H}_3)=C(CH_3)O-$, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.62 ($-O\underline{C}OC_6H_5$ or $N,O\geq\underline{C}-$), 155.83 ($-O\underline{C}OC_6H_5$ or $N,O\geq\underline{C}-$), 149.71 ($-CH=\underline{C}(C_6H_5)O-$ or $=NC(CH_3)=\underline{C}(CH_3)O-$), 143.42 ($-CH=\underline{C}(C_6H_5)O-$ or $=NC(CH_3)=\underline{C}(CH_3)O-$), 133.82 ($-OCO\underline{C}_6H_5$ *ipso*), 133.42

($-OCO\underline{C}_6H_5$ *para*), 132.00 ($-CH=C(\underline{C}_6H_5)O-$ *ipso*), 130.16 ($-OCO\underline{C}_6H_5$ *ortho*), 129.54 ($-CH=\underline{C}(C_6H_5)O-$ *para*), 129.73 ($=N\underline{C}(CH_3)=C(CH_3)O-$), 128.69 ($-OCO\underline{C}_6H_5$ *meta* or $-CH=C(\underline{C}_6H_5)O-$ *meta*), 128.37 ($-OCO\underline{C}_6H_5$ *meta* or $-CH=C(\underline{C}_6H_5)O-$ *meta*), 124.86 ($-CH=C(\underline{C}_6H_5)O-$ *ortho*), 103.10 ($N,O\geq C\underline{C}H=$), 10.92 ($=NC(\underline{C}H_3)=C(CH_3)O-$ or ($=NC(CH_3)=C(\underline{C}H_3)O-$), 9.59 ($=NC(\underline{C}H_3)=C(CH_3)O-$ or ($=NC(CH_3)=C(\underline{C}H_3)O-$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.62, 130.35, 129.73, 128.88, 128.56, 125.05, 103.29, 11.11, 9.78.

(*Z*)-2-(4-methylthiazol-2-yl)-1-phenylvinyl benzoate (15)

The title compound **15** (3.95 g, 61.5%) was obtained by reacting 2,4-dimethylthiazole **14** (2.29 g, 20 mmol, 1 eq.), triethylamine (7.29 g, 72 mmol, 3.6 eq.) and benzoyl chloride (8.54 g, 61 mmol, 3 eq.) using the general procedure for the synthesis and purification of **4**. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:4.

$R_f = 0.40$ (ethyl acetate/hexane = 1:4); yellow solid; mp = 125-126 °C.

IR (neat): 3107, 3073, 2971, 2929, 1731, 1635, 1599, 1510, 1448, 1421, 1232, 1079, 1059, 1025, 1000, 968, 871, 765, 750, 692 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (d, *J* = 7.19 Hz, $-OCOC_6\underline{H}_5$ ortho, 2H), 7.71 (t, *J* = 7.42 Hz, $-OCOC_6\underline{H}_5$ *para*, 1H), 7.62-7.57 and 7.42-7.36 (m, $-OCOC_6\underline{H}_5$ *meta*, and $-CH=C(C_6\underline{H}_5)O-$ *ortho*, *meta* and *para*, 7H), 7.30 (s, $=NC(CH_3)=C\underline{H}S-$, 1H), 6.80 (s, $N,S\geq C\underline{C}H=$, 1H), 2.43 (s, $=NC(C\underline{H}_3)=CHS-$, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 163.73 ($-O\underline{C}OC_6H_5$ or $N,S\geq\underline{C}-$), 160.64 ($-O\underline{C}OC_6H_5$ or $N,S\geq\underline{C}-$), 152.69 ($-CH=\underline{C}(C_6H_5)O-$ or $=N\underline{C}(CH_3)=CHS-$), 149.87 ($-CH=\underline{C}(C_6H_5)O-$ or $=N\underline{C}(CH_3)=CHS-$), 134.06 ($-OCO\underline{C}_6H_5$ *para*), 133.88 ($-OCO\underline{C}_6H_5$ *ipso*), 130.50 ($-OCO\underline{C}_6H_5$ *ortho*), 129.52 ($-CH=C(\underline{C}_6H_5)O-$ *para*), 128.88 (–

$OCO\underline{C}_6H_5$ *meta*), 128.78 ($-CH=C(\underline{C}_6H_5)O-$ *meta*, 3C), 124.84 ($-CH=C(\underline{C}_6H_5)O-$ *ortho*), 114.63 ($=NC(CH_3)=\underline{C}HS-$), 111.95 ($N,S\geq C\underline{C}H=$), 16.90 ($=NC(\underline{C}H_3)=CHS-$). The *ipso* carbon is overlapping with other peaks.

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 134.15, 130.61, 129.62, 128.98, 128.87, 124.94, 114.71, 112.05, 17.00.

HRMS (ESI, M+H): calcd for $C_{19}H_{15}NO_2S$: 322.0900; found: 322.0880.

(*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylvinyl benzoate (16)

The title compound **16** (2.94 g, 43%) was obtained by the reaction of 2-methylbenzoxazole **7** (2.69 g, 20 mmol, 1 eq.), triethylamine (7.48 g, 74 mmol, 3.7 eq.) and benzoyl chloride (8.51 g, 60.5 mmol, 3 eq.). The general procedure used for the synthesis and purification of **4** was employed. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:5.

$R_f = 0.58$ (ethyl acetate/hexane = 1:4); white crystalline solid; mp = 97-98 °C.

IR (neat): 3078, 1731, 1644, 1605, 1540, 1451, 1234, 1181, 1152, 1084, 1067, 1027, 946, 848, 790, 746, 701, 687 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.32 (d, *J* = 7.68 Hz, $-OCOC_6\underline{H}_5$ *ortho*, 2H), 7.71-7.67, 7.60-7.54, 7.41-7.40 and 7.24-7.18 (m, $-OCOC_6\underline{H}_5$ *meta* and *para*, $-CH=C(C_6\underline{H}_5)O-$ *ortho*, *meta* and the four aromatic C$\underline{H}$s on the benzoxazole ring, 11H), 7.11 (d, *J* = 8.04 Hz, $-CH=C(C_6\underline{H}_5)O-$ *para*, 1H) 7.04 (s, $-C\underline{H}=C(C_6H_5)O-$, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 164.47 ($-O\underline{C}OC_6H_5$ or $N,O\geq\underline{C}-$), 159.75 ($-O\underline{C}OC_6H_5$ or $N,O\geq\underline{C}-$), 154.09 ($-CH=\underline{C}(C_6H_5)O-$ or $\underline{C}$ next to O in the benzoxazole ring), 150.06 ($-CH=\underline{C}(C_6H_5)O-$ or $\underline{C}$ next to O on the benzoxazole ring), 141.57 ($\underline{C}$ next to N on the benzoxazole ring), 133.67 ($-OCO\underline{C}_6H_5$ *para*), 133.58 ($-OCO\underline{C}_6H_5$ *ipso*), 130.45 ($-CH=C(\underline{C}_6H_5)O-$ *para*), 130.41 ($-OCO\underline{C}_6H_5$ *ortho*), 129.37 ($-CH=C(\underline{C}_6H_5)O-$

ipso), 128.87 (–OCO$\underline{C}_6H_5$ *meta* or –CH=C($\underline{C}_6H_5$)O– *meta*), 128.56 (–OCO$\underline{C}_6H_5$ *meta* or (–CH=C($\underline{C}_6H_5$)O– *meta*), 125.48 (–CH=C($\underline{C}_6H_5$)O– *ortho*), 125.19, 124.39, 119.95 and 110.12 (aromatic $\underline{C}$Hs on the benzoxazole ring), 103.22 (N,O≥C$\underline{C}$H=).

DEPT 135 NMR (150 MHz, CDCl$_3$): δ 133.84, 130.61, 130.58, 129.04, 128.72, 125.64, 125.36, 124.56, 120.11, 110.29. 103.38.

(Z)-2-(benzo[*d*]thiazol-2-yl)-1-phenylvinyl benzoate (17)

The title compound **17** (1.89 g, 53%) was prepared from 2-methylbenzothiazole **8** (1.51 g, 10 mmol, 1 eq.), triethylamine (3.71 g, 36.7 mmol, 3.7 eq.) and benzoyl chloride (4.26 g, 30 mmol, 3 eq.) by the general procedure used for the synthesis and purification of **4**. Ethyl acetate/hexane = 1:6 was used as the eluent for column chromatography over silica gel.

R$_f$ = 0.54 (ethyl acetate/hexane = 1:4); yellow solid; mp = 146-148 °C.

IR (neat): 3061, 2981, 1739, 1641, 1596, 1452, 1445, 1432, 1227, 1209, 1175, 1080, 1055, 1023, 1000, 850, 754, 656 cm^{-1}.

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.36 (d, *J* = 7.80 Hz, –OCOC$_6\underline{H}_5$ *ortho*, 2H), 7.97 (d, *J* = 8.19 Hz, aromatic H in benzothiazole ring, 1H), 7.73 (dd, *J* = 7.80 and 7.61 Hz, –OCOC$_6\underline{H}_5$ *meta*, 2H) 7.65 (d, *J* = 7.65 Hz, –CH=C(C$_6\underline{H}_5$)O– *ortho*, 2H), 7.60 (dd, *J* = 7.65 and 7.56 Hz, –CH=C(C$_6\underline{H}_5$)O– *meta*, 2H), 7.45-7.39 (m, –OCOC$_6\underline{H}_5$ *para*, three aromatic C$\underline{H}$s on the benzothiazole ring and –C$\underline{H}$=C(C$_6$H$_5$)O–, 5H), 7.31 (t, *J* = 7.56 Hz, –CH=C(C$_6\underline{H}_5$)O– *para*, 1H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 163.71 (–O$\underline{C}$OC$_6$H$_5$ or N,S≥$\underline{C}$–), 161.38 (–O$\underline{C}$OC$_6$H$_5$ or N,S≥$\underline{C}$–), 152.57 (–CH=$\underline{C}$(C$_6$H$_5$)O– or $\underline{C}$ next to S in the benzothiazole ring), 152.48 (–CH=$\underline{C}$(C$_6$H$_5$)O– or $\underline{C}$ next to S in the benzothiazole ring), 135.05 ($\underline{C}$ next to N in the benzothiazole ring), 134.20 (–OCO$\underline{C}_6$H$_5$ *para*), 133.73 (–OCO$\underline{C}_6$H$_5$ *ipso*), 130.63 (–OCO$\underline{C}_6H_5$ *ortho*), 130.05 (–CH=C($\underline{C}_6H_5$)O– *para*), 128.95 (–OCO$\underline{C}_6H_5$ *meta* or (–CH=C($\underline{C}_6H_5$)O– *meta*), 128.88 (–OCO$\underline{C}_6H_5$ *meta* or (–CH=C($\underline{C}_6H_5$)O– *meta*), 128.80 (–CH=C($\underline{C}_6H_5$)O– *ipso*), 126.25 and 125.32 (aromatic $\underline{C}$Hs on the benzothiazole ring), 125.21 (–CH=C($\underline{C}_6H_5$)O– *ortho*), 123.00 and 121.29 (aromatic $\underline{C}$Hs on the benzothiazole ring), 112.44 (N,S≥C$\underline{C}$H=).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 134.32, 130.74, 130.17, 129.07, 129.00, 126.37, 125.44, 124.33, 123.12, 121.41. 112.56.

Synthesis of the equilibrating tautomers of 2-(thiazole, oxazole, benzoxazole and benzothiazole)-1-phenylethenols

(*Z*)-1-phenyl-2-(thiazol-2-yl)ethenol (18a) and 1-phenyl-2-(thiazol-2-yl)ethanone (18b)

(*Z*)-1-Phenyl-2-(thiazol-2-yl)vinyl benzoate **4** (2.144 g, 6.98 mmol, 1 eq.) was dissolved in anhydrous MeOH (15 mL). KOH (0.788 g, 14.04 mmol, 2 eq.), dissolved in MeOH (10 mL), was added dropwise into this solution and stirred for 24 h at room temperature. Then MeOH was removed by rotary evaporation. The residue was dissolved in water (30 mL), neutralized with 1M H_2SO_4 and extracted with dichloromethane (25 mL × 2). The organic layer was further washed with water (30 mL), dried over anhydrous sodium sulfate and filtered. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:4) to isolate the titled compounds (1.273 g, 89.8%). ^1H and ^{13}C NMR in $CDCl_3$ confirmed that the isolated product consists of the equilibrating tautomers (*Z*)-1-phenyl-2-(thiazol-2-yl)ethenol **18a** and 1-phenyl-2-(thiazol-2-yl)ethanone **18b** in a 1:2.0 ratio.

Tautomers **18a** and **18b** (0.971 g, 97%) were isolated in another batch by reacting (*Z*)-1-phenyl-2-(thiazol-2-yl)vinyl benzoate **4** (1.509 g, 4.9 mmol) and KOH (0.554 g, 9.87 mmol, 2 eq.) in 30 mL of anhydrous MeOH. This general procedure was used for the hydrolysis of enol-esters **15**, **5**, **6**, **16** and **17** to isolate corresponding equilibrating tautomers of **19-23**, respectively.

R_f = 0.48 (ethyl acetate/hexane = 1:3); dark green oil.

IR (neat): 3117, 3084, 3060, 1687, 1622, 1598, 1576, 1494, 1483, 1449, 1263, 1210, 1100, 1070, 752, 686, 632 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 13.18 (broad, OH, 1H), 7.99 (d, *J* = 7.56 Hz, C_6H_5 *ortho* in **18b**, 2H), 7.74 (d, *J* = 7.95 Hz, *ortho* in **18a**, 2H), 7.70 (d, *J* = 3.25, =NC$\underline{H}$=CHS– in **18b**, 1H), 7.61 (d, *J* = 3.32 Hz, =NC$\underline{H}$=CHS– in **18a**, 1H), 7.53 (t, *J* = 7.37 Hz, C_6H_5 *meta* in **18a**, 2H), 7.42 (t, *J* = 7.70 Hz, C_6H_5 *meta* in **18b**, 2H), 7.35-7.31 (m, *para* in both **18a** and **18b**, 2H), 7.26 (d, *J* = 3.25 Hz, =NCH=C$\underline{H}$S– in **18b**, 1H), 7.00 (d, *J* = 3.32 Hz, =NCH=C$\underline{H}$S– in **18a**, 1H), 6.28 (s, =C$\underline{H}$– in **18a**, 1H), 4.69 (s, –C$\underline{H}_2$– in **18b**, 2H).

The areas of the peaks for **18a** and **18b** were considered separately since their mole ratio in the solution was not 1:1. All peaks were first integrated by setting the area of the vinyl proton (=CH) peak of the enol tautomer **18a** at 6.28 ppm at one versus the rest of the resonances for **18a**. The area of the methylene protons (–CH_2) of the keto tautomer **18b** at 4.69 ppm was set at two versus the rest of the resonances for **18b**. The integration values of each peak and coupling patterns were used when assigning proton signals for the each tautomer. To obtain the mole ratio between **18a** and **18b** in $CDCl_3$, the integrated area of the –CH_2 at 4.69 ppm was set at two and then the =CH peak at 6.28 ppm was integrated and found to have an area of 0.5 versus the integrated area of the methylene proton peak of the keto form. The enol =CH peak corresponds to one proton per molecule and the keto CH_2 peak corresponds to two protons per molecule. Therefore, to calculate the mole ratio between **18a** and **18b**, half of the keto CH_2 integrated area (1.0) of **18b** was divided by the enol =CH integrated area (0.5). This gave 1:2.0 ratio for **18a**:**18b**.

^{13}C NMR (150 MHz, $CDCl_3$): δ 194.46 (−$CH_2\underline{C}O$− in **18b**), 168.35 (=$\underline{C}(OH)$− in **18a**), 162.15 and 160.64 (N,S≥$\underline{C}$− in **18a** and **18b**), 142.10 and 140.11 (>N$\underline{C}$H=CHS− in **18a** and **18b**), 135.71 and 134.60 (−$CO\underline{C}_6H_5$, *ipso* in **18a** and **18b**), 133.71 and 129.63 (−$CO\underline{C}_6H_5$, *para* in **18a** and **18b**), 128.74 (−$CO\underline{C}_6H_5$, *ortho* in **18b**), 128.52 (−$CO\underline{C}_6H_5$, *meta* in **18b**), 128.34 (−$CO\underline{C}_6H_5$, *ortho* in **18a**), 125.42 (−$CO\underline{C}_6H_5$, *meta* in **18a**), 120.04 and 114.39 (=NCH=$\underline{C}$HS− in **18a** and **18b**), 90.99 (N,S≥C$\underline{C}$H= in **18a**), 42.65 (N,S≥ C$\underline{C}H_2$− in **18b**).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 142.24, 140.25, 133.85, 129.77, 128.88, 128.66, 128.52, 125.56, 120.18, 114.53, 91.13, 42.78.

(*Z*)-2-(4-methylthiazol-2-yl)-1-phenylethenol (19a) and 2-(4-methylthiazol-2-yl)-1-phenylethanone (19b)

Tautomers (*Z*)-2-(4-methylthiazol-2-yl)-1-phenylethenol **19a** and 2-(4-methylthiazol-2-yl)-1-phenylethanone **19b** were synthesized by reacting (*Z*)-2-(4-methylthiazol-2-yl)-1-phenylvinyl benzoate **15** (1.045 g, 3.25 mmol, 1 eq.) in 15 mL of anhydrous MeOH and KOH (0.365 g, 6.51 mmol) in 10 mL MeOH by the general procedure used for the synthesis and purification of hydrolyzed product **18**. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:7. Tautomers **19a** and **19b** (0.473 g, 66.9%) were isolated. ^1H and ^{13}C NMR in $CDCl_3$ confirmed that the isolated product consists of equilibrating tautomers (*Z*)-2-(4-methylthiazol-2-yl)-1-phenylethenol **19a** and 2-(4-methylthiazol-2-yl)-1-phenylethanone **19b** in a 1:1.32 ratio.

R_f = 0.42 (ethyl acetate/hexane = 1:7); yellow solid; mp = 96-97 °C.

IR (neat): 3106, 3053, 2956, 2918, 1608, 1574, 1519, 1492, 1454, 1259, 1035, 836, 758 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 13.44 (broad, OH, 1H), 7.98 (d, *J* = 7.23 Hz, $C_6\underline{H}_5$ *ortho* in **19b**, 2H), 7.74-7.72 (d, *J* = 7.73 Hz, $C_6\underline{H}_5$ *ortho* in **19a**, 2H), 7.52 (t, *J* = 6.90 Hz, $C_6\underline{H}_5$ *para* in **19b**, 1H), 7.42 (t, *J* = 7.79 Hz, $C_6\underline{H}_5$ *meta* in **19b**, 2H), 7.37-7.42 (m, $C_6\underline{H}_5$ *meta* and *para* in **19a**, 3H), 6.79 (d, *J* = 0.71 Hz, $=NC(CH_3)=C\underline{H}S$ in **19b**, 1H), 6.53 (d, *J* = 0.74 Hz, $=NC(CH_3)=C\underline{H}S$ in **19a**, 1H), 6.21 (s, $=C\underline{H}-$ in **19a**, 1H), 4.63 (s, $-C\underline{H}_2-$ in **19b**, 2H), 2.37 (s, *J* = 0.75 Hz, $=NC(C\underline{H}_3)=CHS-$ in **19b**, 3H), 2.35 (d, *J* = 0.78 Hz, $=NC(C\underline{H}_3)=CHS-$ in **19a**, 3H).

The areas of the peaks for **19a** and **19b** were considered separately since their mole ratio in the solution was not 1:1. All peaks were first integrated by setting the area of the vinyl proton (=CH) peak of the enol tautomer **19a** at 6.21 ppm at one versus the rest of the resonances for **19a**. The area of the methylene protons ($-CH_2$) of the keto tautomer **19b** at 4.63 ppm was set at two versus the rest of the resonances for **19b**. The integration values of each peak and coupling patterns were used when assigning proton signals for the each tautomer. To obtain the mole ratio between **19a** and **19b** in $CDCl_3$, the integrated area of the $-CH_2$ at 4.63 ppm was set at two and then the =CH peak at 6.21 ppm was integrated and found to have an area of 0.76 versus the integrated area of the methylene proton peak of the keto form. The enol =CH peak corresponds to one proton per molecule and the keto CH_2 peak corresponds to two protons per molecule. Therefore, to calculate the mole ratio between **19a** and **19b**, half of the keto CH_2 integrated area (1.0) of **19b** was divided by the enol =CH integrated area (0.76). This gave 1:1.32 ratio for **19a**:**19b**.

^{13}C NMR (75 MHz, $CDCl_3$): δ 194.58 ($-CH_2\underline{C}O-$ in **19b**), 167.58 ($=\underline{C}(OH)-$ in **19a**), 161.37 and 160.52 (N,S≥$\underline{C}-$ in **19a** and **19b**), 152.02 and 150.11 ($=N\underline{C}(CH_3)=CHS-$ in **19a** and **19b**), 135.61 and 134.67 ($-CO\underline{C}_6H_5$, *ipso* in **19a** and **19b**), 133.70 and 129.53 ($-CO\underline{C}_6H_5$, *para* in **19a** and **19b**), 128.27 ($-CO\underline{C}_6H_5$, *ortho* in **19b**), 128.44 and 128.37 ($-CO\underline{C}_6H_5$, *meta* in **19a** and **19b**), 125.30 ($-CO\underline{C}_6H_5$, *ortho* in **19a**), 114.56 ($=NC(CH_3)=\underline{C}HS-$ in **19b**), 108.92 ($=NC(CH_3)=\underline{C}HS-$ in **19a**), 91.06 (N,S ≥$C\underline{C}H=$ in **19a**), 42.68 (N,S≥$C\underline{C}H_2-$ in **19b**), 16.95 ($=NC(\underline{C}H_3)=CHS-$ in **19b**), 16.68 ($=NC(\underline{C}H_3)=CHS-$ in **19b**).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.74, 129.64, 128.83, 128.61, 128.48, 125.49, 114.6, 108.98, 91.19, 42.86, 17.01, 16.75.

(*Z*)-2-(4,5-dimethylthiazol-2-yl)-1-phenylethenol (20a) and 2-(4,5-dimethyl- thiazol-2-yl)-1-phenylethanone (20b)

Tautomers (*Z*)-2-(4,5-dimethylthiazol-2-yl)-1-phenylethenol **20a** and 2-(4,5-dimethylthiazol-2-yl)-1-phenylethanone **20b** were synthesized by reacting (*Z*)-2-(4,5-dimethylthiazol-2-yl)-1-phenylvinyl benzoate **5** (0.502 g, 1.50 mmol, 1 eq.) in 10 mL of anhydrous MeOH and KOH (0.168 g, 2.99 mmol, 2 eq.) in 10 mL MeOH by the general procedure used for the synthesis and purification of equilibrating tautomers of **18**. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:7. Tautomers **20a** and **20b** (0.308 g, 84.8%) were isolated. ^{1}H and ^{13}C NMR in $CDCl_3$ confirmed that the isolated product consists of equilibrating tautomers (*Z*)-2-(4-methylthiazol-2-yl)-1-phenylethenol **20a** and 2-(4-methylthiazol-2-yl)-1-phenylethanone **20b** in a 1:1.41 ratio.

$R_f = 0.44$ (ethyl acetate/hexane = 1:6); yellow solid; mp = 80-81 °C.

IR (neat): 3089, 3055, 3038, 2980, 2918, 1630, 1573, 1555, 1492, 1454, 1268, 1146, 1060, 817, 770, 747, 687, 648 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 13.52 (broad, OH, 1H), 8.04 (d, *J* = 7.66 Hz, $C_6\underline{H}_5$ *ortho* in **20b**, 2H), 7.79 (d, *J* = 7.41 Hz, $C_6\underline{H}_5$ *ortho* in **20a**, 2H), 7.58 (t, *J* = 7.38 Hz, $C_6\underline{H}_5$ *para* in **20b**, 1H), 7.48 (t, *J* = 7.57 Hz, $C_6\underline{H}_5$ *meta* in **20b**, 2H), 7.41-7.35 (m, $C_6\underline{H}_5$ *meta* and *para* in **20a**, 3H), 6.19 (s, $=C\underline{H}-$ in **20a**, 1H), 4.61 (s, $-C\underline{H}_2-$ in **20b**, 2H), 2.32, 2.31 and 2.30 (s, $=NC(CH_3)=C(C\underline{H}_3)S-$ and $=NC(C\underline{H}_3)=C(CH_3)S-$ in both **20a** and **20b**, 12H).

The areas of the peaks for **20a** and **20b** were considered separately since their mole ratio in the solution was not 1:1. All peaks were first integrated by setting the area of the vinyl proton (=CH) peak of the enol tautomer **20a** at 6.19 ppm at one versus the rest of the resonances for **20a**. The area of the methylene protons ($-CH_2$) of the keto tautomer **20b** at 4.61 ppm was set at two versus the rest of the resonances for **20b**. The integration values of each peak and coupling patterns were used when assigning proton signals for the each tautomer. To obtain the mole ratio between **20a** and **20b** in $CDCl_3$, the integrated area of the $-CH_2$ at 4.61 ppm was set at two and then the =CH peak at 6.19 ppm was integrated and found to have an area of 0.71 versus the integrated area of the methylene proton peak of the keto form. The enol =CH peak corresponds to one proton per molecule and the keto CH_2 peak corresponds to two protons per molecule. Therefore, to calculate the mole ratio between **20a** and **20b**, half of the keto CH_2 integrated area (1.0) of **20b** was divided by the enol =CH integrated area (0.71). This gave 1:1.41 ratio for **20a**:**20b**.

^{13}C NMR (75 MHz, $CDCl_3$): δ 194.79 ($-CH_2\underline{C}O-$ in **20b**), 164.01 ($=\underline{C}(OH)-$ in **20a**), 160.45 and 157.33 ($N,S\geq\underline{C}-$ in both **20a** and **20b**), 147.50 and 145.00

($=N\underline{C}(CH_3)=C(CH_3)S-$ in both **20a** and **20b**), 135.86 and 135.10 ($-CO\underline{C}_6H_5$, *ipso* in both **20a** and **20b**), 133.57 and 129.32 ($-CO\underline{C}_6H_5$, *para* in both **20a** and **20b**), 128.69 and 128.52 ($-CO\underline{C}_6H_5$, *ortho* in both **20a** and **20b**), 128.33 ($-CO\underline{C}_6H_5$, *meta* in **20a** or **20b**), 127.27 ($=NC(CH_3)=\underline{C}(CH_3)S-$ in **20a** or **20b**), 125.25 ($-CO\underline{C}_6H_5$, *meta* in **20a** or **20b**), 121.56 ($=NC(CH_3)=\underline{C}(CH_3)S-$ in **20a** or **20b**), 90.64 ($N,S\geq C\underline{C}H-$ in **20a**), 42.92 ($N,S\geq C\underline{C}H_2-$ in **20b**), 14.52 ($=NC(\underline{C}H_3)=C(CH_3)S-$ in **20b**), 14.24 ($=NC(\underline{C}H_3)=C(CH_3)S-$ in **20a**), 11.23 ($=NC(CH_3)=C(\underline{C}H_3)S-$ in **20b**), 11.14 ($=NC(CH_3)=C(\underline{C}H_3)S-$ in **20a**).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.68, 129.42, 128.80, 128.44, 125.35, 90.75, 43.02, 14.63, 14.34, 11.34, 11.25.

(*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylethenol (21a) and 2-(4,5-dimethyl-oxazol-2-yl)-1- phenylethanone (21b)

Tautomers (*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylethenol **21a** and 2-(4,5-dimethyloxazol-2-yl)-1- phenylethanone **21b** were synthesized by reacting (*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylvinyl benzoate **6** (1.6 g, 5.1 mmol, 1 eq.) in 15 mL of anhydrous MeOH and KOH (0.578 g, 10.3 mmol, 2 eq.) in 10 mL MeOH by the general procedure used for the synthesis and purification of equilibrating tautomers of **18**. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:7. Tautomers **21a** and **21b** (0.811 g, 73.8%) were isolated. ^1H and ^{13}C NMR in $CDCl_3$ confirmed that the isolated product consists of equilibrating tautomers (*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylethenol **21a** and 2-(4,5-dimethyloxazol-2-yl)-1-phenylethanone **21b** in 1:3.57 ratio.

$R_f = 0.57$ (ethyl acetate/hexane = 1:6); dark green oil.

IR (neat): 3059, 2980, 2953, 2924, 2882, 1693, 1633, 1598, 1578, 1532, 1496, 1449, 1293, 1201, 1066, 1012, 756, 713, 688, 639, 618 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ –OH peak was not seen, 7.94 (d, *J* = 7.66 Hz, $C_6\underline{H}_5$ *ortho* in **21b**, 2H), 7.71 (d, *J* = 7.72, $C_6\underline{H}_5$ *ortho* in **21a** 2H), 7.51 (m, $C_6\underline{H}_5$ *meta* and *para* in **21a**, and $C_6\underline{H}_5$ *meta* in **21b**, 5H), 7.32 (t, *J* = 7.56, *para* in **21b**, 1H), 5.91 (s, $=C\underline{H}-$ in **21a**, 0.40H), 4.37 (s, $-C\underline{H}_2-$ in **21b**, 2H), 2.17 (s, $=NC(C\underline{H}_3)=C(CH_3)S-$ or $=NC(CH_3)=C(C\underline{H}_3)O-$ in **21a**, 3H), 2.14 (s, $=NC(C\underline{H}_3)=C(CH_3)O-$ or $=NC(CH_3)=C(C\underline{H}_3)O-$ in **21b**, 3H), 2.03 (s, $=NC(C\underline{H}_3)=C(CH_3)O-$ or $=NC(CH_3)=C(C\underline{H}_3)O-$ in **21a**, 3H), 2.02 (s, $=NC(C\underline{H}_3)=C(CH_3)O-$ or $=NC(CH_3)=C(C\underline{H}_3)O-$ in **21b**, 3H).

The areas of the peaks for **21a** and **21b** were considered separately since their mole ratio in the solution was not 1:1. All peaks were first integrated by setting the area of the vinyl proton (=CH) peak of the enol tautomer **21a** at 5.91 ppm at one versus the rest of the resonances for **21a**. The area of the methylene protons ($-CH_2$) of the keto tautomer **21b** at 4.37 ppm was set at two versus the rest of the resonances for **21b**. The integration values of each peak and coupling patterns were used when assigning proton signals for the each tautomer. To obtain the mole ratio between **21a** and **21b** in $CDCl_3$, the integrated area of the $-CH_2$ at 4.37 ppm was set at two and then the =CH peak at 5.91 ppm was integrated and found to have an area of 0.28 versus the integrated area of the methylene proton peak of the keto form. The enol =CH peak corresponds to one proton per molecule and the keto CH_2 peak corresponds to two protons per molecule. Therefore, to calculate the mole ratio between **21a** and **21b**, half of the keto CH_2 integrated area (1.0) of **21b** was divided by the enol =CH integrated area (0.28). This gave 1:3.57 ratio for **21a**:**21b**.

^{13}C NMR (75 MHz, $CDCl_3$): δ 193.28 (–$CH_2\underline{C}O$– in **21b**), 161.23 (=$\underline{C}(OH)$– in **21a**), 160.92 (N,S≥$\underline{C}$– in **21a**), 155.28 (N,S≥$\underline{C}$– in **21b**), 143.98 (=$NC(CH_3)=\underline{C}(CH_3)O$– in **21b**), 140.21 (=$NC(CH_3)=\underline{C}(CH_3)O$– in **21a**), 135.63 (–$CO\underline{C}_6H_5$, *ipso* in **21b**), 134.42 (–$CO\underline{C}_6H_5$, *ipso* in **21a**), 133.49 (–$CO\underline{C}_6H_5$, *para* in **21b**), 130.61 (–$CO\underline{C}_6H_5$, *para* in **21a**), 129.41 (=$N\underline{C}(CH_3)=C(CH_3)O$– in **21b**), 128.88 (=$N\underline{C}(CH_3)=C(CH_3)O$– in **21a**), 128.57 (–$CO\underline{C}_6H_5$, *ortho* in **21b**), 128.36 (–$CO\underline{C}_6H_5$, *meta* in **21b**), 128.22 (–$CO\underline{C}_6H_5$, *ortho* in **21a**), 125.08 (–$CO\underline{C}_6H_5$, *meta* in **21a**), 84.01 (N,O≥$C\underline{C}H$= in **21a**), 38.81 (N,O≥$C\underline{C}H_2$– in **21b**), 10.88 (=$NC(\underline{C}H_3)=C(CH_3)O$– in **21b**), 10.73 (=$NC(\underline{C}H_3)=C(CH_3)O$– in **21a**), 9.75 (=$NC(CH_3)=C(\underline{C}H_3)O$– in **21b**), 9.63 (=$NC(CH_3)=C(\underline{C}H_3)O$– in **21a**).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.71, 129.62, 128.78, 128.58, 128.42, 125.30, 84.23, 39.04, 11.05, 10.95, 9.97, 9.86.

(*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylethenol (22a) and 2-(benzo[*d*]oxazol-2-yl)-1-phenylethanone (22b)

Tautomers (*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylethenol **22a** and 2-(benzo[*d*]oxazol-2-yl)-1-phenylethanone **22b** were synthesized by reacting (*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylvinyl benzoate **16** (0.844 g, 2.47 mmol, 1 eq.) in 15 mL of anhydrous MeOH and KOH (0.28 g, 5.2 mmol, 2.1 eq.) in 10 mL MeOH by the general procedure used for the synthesis and purification of equilibrating tautomers of **18**. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:5. Tautomers **22a** and **22b** (0.541 g, 92.2%) were isolated. ^{1}H and ^{13}C NMR in $CDCl_3$ confirmed that the isolated product consists of equilibrating tautomers (*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylethenol **22a** and 2-(benzo[*d*]oxazol-2-yl)-1-phenylethanone **22b** in a 1.06:1 ratio.

$R_f = 0.64$ (ethyl acetate/hexane = 1:5); greenish white solid; mp = 87-89 °C.

IR (neat): 3065, 3032, 3044, 2979, 1625, 1576, 1530, 1453, 1277, 1250, 1164, 1064, 850, 792, 743, 762, 702, 685 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 12.62 (broad, OH, 1H), 8.05 (d, J = 7.74 Hz, $–C_6\underline{H}_5$ *ortho* , 2H), 7.88 (m, aromatic $C\underline{H}$, 2H), 7.72 (m, aromatic $C\underline{H}$, 1H), 7.61 (m, aromatic $C\underline{H}$, 2H), 7.52-7.45 (m, aromatic $C\underline{H}$, 7H), 7.34-7.31 (m, aromatic $C\underline{H}$, 3H), 7.28 (t, *J* = 7.66 Hz, aromatic $C\underline{H}$, 1H), 6.21 (s, $=C\underline{H}–$ in **22a**, 1H), 4.64 (s, $–C\underline{H}_2–$ in **22b**, 2H).

The areas of the peaks for **22a** and **22b** were considered separately since their mole ratio in the solution was not 1:1. All peaks were first integrated by setting the area of the vinyl proton (=CH) peak of the enol tautomer **22a** at 6.21 ppm at one versus the rest of the resonances for **22a**. The area of the methylene protons ($–CH_2$) of the keto tautomer **22b** at 4.64 ppm was set at two versus the rest of the resonances for **22b**. The integration values of each peak and coupling patterns were used when assigning proton signals for the each tautomer. To obtain the mole ratio between **22a** and **22b** in $CDCl_3$, the integrated area of the $–CH_2$ at 4.64 ppm was set at two and then the =CH peak at 6.21 ppm was integrated and found to have an area of 1.06 versus the integrated area of the methylene proton peak of the keto form. The enol =CH peak corresponds to one proton per molecule and the keto CH_2 peak corresponds to two protons per molecule. Therefore, to calculate the mole ratio between **22a** and **22b**, half of the keto CH_2 integrated area (1.0) of **22b** was used respect to the enol =CH integrated area (1.06). This gave 1.06:1 ratio for **22a**:**22b**.

^{13}C NMR (150 MHz, $CDCl_3$): δ 192.38 ($–CH_2\underline{C}O–$ in **22b**), 166.19 ($=\underline{C}(OH)–$ in **22a**), 165.68 (N,O≥$\underline{C}$– in **22b**), 160.41 (N,O≥$\underline{C}$– in **22a**), 151.24 (C next to O in benzoxazole rings of **22b),** 148.69 (C next to O in benzoxazole rings of **22a**), 141.26 (C next to N in benzoxazole rings of **22b**), 139.85 (C next to N in benzoxazole rings of **22a**), 135.66 (–CO$\underline{C}_6H_5$, *ipso* in **22b**), 134.03 (–CO$\underline{C}_6H_5$, *ipso* in **22a**), 133.71 (–CO$\underline{C}_6H_5$, *para* in **22b**, 130.56 (–CO$\underline{C}_6H_5$, *meta* in **22a**), 128.85 (–CO$\underline{C}_6H_5$, *ortho* in **22b**, 128.59 (–CO$\underline{C}_6H_5$, *meta* in **22b**, 128.53 (–CO$\underline{C}_6H_5$, *meta* in **22a**), 125.82 (–CO$\underline{C}_6H_5$, *ortho* in **22a**), 124.98 (aromatic $\underline{C}H$ on the benzoxazole ring in **22b**), 124.61, 124.32 (aromatic $\underline{C}H$ on the benzoxazole ring in **22b**), 124.08 (aromatic $\underline{C}H$ on the benzoxazole ring in **22a**), 119.95 (aromatic $\underline{C}H$ on the benzoxazole ring in **22b**), 117.85 (aromatic $\underline{C}H$ on the benzoxazole ring in **22a**), 110.61 (aromatic $\underline{C}H$ on the benzoxazole ring in **22b**), 110.19 (aromatic $\underline{C}H$ on the benzoxazole ring in **22a**), 83.66 (N,O≥C$\underline{C}$H= in **22a**), 39.56 (N,O≥C$\underline{C}H_2$– in **22b**).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.99, 130.64, 128.93, 128.67, 128.61, 125.90, 125.07, 124.69, 124.16, 120.03, 117.93, 110.69, 110.27, 83.74, 39.64.

(*Z*)-2-(benzo[*d*]thiazol-2-yl)-1-phenylethenol (23a) and 2-(benzo[*d*]thiazol-2-yl)-1-phenylethanone (23b)

Tautomers (*Z*)-2-(benzo[*d*]thiazol-2-yl)-1-phenylethenol **23a** and 2-(benzo[*d*]thiazol-2-yl)-1-phenylethanone **23b** were synthesized by reacting (*Z*)-2-(benzo[*d*]thiazol-2-yl)-1-phenylvinyl benzoate **17** (1.008 g, 2.82 mmol, 1 eq.) in 15 mL of anhydrous MeOH and KOH (0.316 g, 5.63 mmol, 2 eq.) in 10 mL MeOH by the general procedure used for the synthesis and purification of equilibrating tautomers of **18b**. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:5. Tautomers **23a** and **23b** (0.516 g, 72.8%) were isolated. ^1H and ^{13}C NMR in $CDCl_3$ confirmed that the isolated product consists of equilibrating tautomers **23a** and **23b** in a 1.63:1 ratio.

R_f = 0.64 (ethyl acetate/hexane = 1:5); yellowish green solid; mp = 111-112 °C.

IR (neat): 3057, 2922, 1610, 1596, 1573, 1494, 1473, 1436, 1378, 1264, 1249, 1136, 1057, 751, 729, 687, 668 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 13.91 (broad, OH, 1H), 8.07 (d, J = 7.68 Hz, $-C_6\underline{H}_5$ *ortho* in **23b**, 2H), 7.99 (d, J = 8.13 Hz, aromatic C$\underline{H}$ in the benzothiazole ring of **23b**, 1H), 7.85-7.87 (m, $-C_6\underline{H}_5$ *ortho* in **23a** and aromatic C$\underline{H}$ in the benzothiazole ring of **23b**, 3H), 7.80 (d, J = 8.10 Hz, aromatic C$\underline{H}$ in the benzothiazole ring of **23a**, 1H), 7.76 (d, J = 7.93 Hz, aromatic C$\underline{H}$ in the benzothiazole ring of **23a**, 1H), 7.58 (dd, J = 8.13 and 7.91 Hz, aromatic C$\underline{H}$ in benzothiazole ring in **23b**, 1H), 7.48 (dd, J = 7.68 and 7.53 Hz $-C_6\underline{H}_5$ *meta* in **23b**, 2H), 7.41-7.46 (m, $-C_6\underline{H}_5$ *meta* in **23a** and C$\underline{H}$ in the benzothiazole ring of **23a** and **23b**, 5H), 7.36 (t, J = 7.53 Hz, $-C_6\underline{H}_5$ *para* in **23b**, 1H), 7.27 (t, J = 7.53 Hz, $-C_6\underline{H}_5$ *para* in **23a**, 1H), 6.35 (s, =C$\underline{H}$– in **23a**, 1H), 4.81 (s, $-C\underline{H}_2-$ in **23b**, 2H).

The areas of the peaks for **23a** and **23b** were considered separately since their mole ratio in the solution was not 1:1. All peaks were first integrated by setting the area of the vinyl proton (=CH) peak of the enol tautomer **23a** at 6.35 ppm at one versus the rest of the resonances for **23a**. The area of the methylene protons ($-CH_2$) of the keto tautomer **23b** at 4.81 ppm was set at two versus the rest of the resonances for **23b**. The integration values of each peak and coupling patterns were used when assigning proton signals for the each tautomer. To obtain the mole ratio between **23a** and **23b** in $CDCl_3$, the integrated area of the $-CH_2$ at 4.81 ppm was set at two and then the =CH peak at 6.35 ppm was integrated and found to have an area of 1.63 versus the integrated area of the methylene proton peak of the keto form. The enol =CH peak corresponds to one proton per molecule and the keto CH_2 peak corresponds to two protons per molecule. Therefore, to calculate the mole ratio between **23a** and **23b**, half of the keto CH_2 integrated area

(1.0) of **23b** was used with respect to the enol =CH integrated area (1.63). This gave 1:1.63 ratio for **23a**:**23b**.

^{13}C NMR (150 MHz, $CDCl_3$): δ 194.05 ($–CH_2\underline{C}O–$ in **23b**), 168.07 ($N,S\geq\underline{C}–$ in **23b**), 165.46 ($N,S\geq\underline{C}–$ in **23a**), 163.44 ($=\underline{C}(OH)–$ in **23a**), 152.68 (C next to N in the benzothiazole rings in **23b**), 150.38 (C next to N in the benzothiazole rings in **23a**), 135.88 and 135.78 (C next to S in the benzothiazole rings and $–CO\underline{C}_6H_5$, *ipso* in **23b**), 134.74 ($–CO\underline{C}_6H_5$, *ipso* in **23a**), 133.82 ($–CO\underline{C}_6H_5$, *para* **23b**), 131.37 (C next to S in the benzothiazole rings of **23a**), 130.28 ($–CO\underline{C}_6H_5$, *para* **23a**), 128.81 and 128.64 ($–CO\underline{C}_6H_5$, *meta* and *ortho* in **23b**, 4C), 128.48 ($–CO\underline{C}_6H_5$, *meta* in **23a**, 2C), 126.46 and 125.96 (aromatic $\underline{C}H$ in the benzothiazole ring of **23a** and **23b**, 2C), 125.89 ($–CO\underline{C}_6H_5$, *ortho* in **23a**, 2C), 125.05, 124.11, 122.85, 121.51, 121.37 and 119.95 (aromatic $\underline{C}H$ in the benzothiazole ring of **23a** and **23b**, 6C), 90.83 ($N,S\geq C\underline{C}H=$ in **23a**), 43.81 ($N,S\geq C\underline{C}H_2–$ in **23b**).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.91, 130.38, 128.90, 128.73, 128.58, 126.56, 126.06, 125.98, 125.15, 124.20, 122.95, 121.60, 121.46, 120.04, 90.92, 43.91.

Reaction of Tautomers 18a,b with Dimethyl Acetylenedicarboxylate

MADC (0.63 g, 4.4 mmol, 2.5 eq.) in 5 mL of anhydrous MeOH was added dropwise to a stirred solution of the tautomers, (*Z*)-1-phenyl-2-(thiazol-2-yl)ethanol **18a** and 1-phenyl-2-(thiazol-2-yl)ethanone **18b**, (0.357 g, 1.76 mmol, 1 eq.) in 5 mL of anhydrous MeOH at room temperature under nitrogen. The molarities of DMAD and the tautomers are 0.44 M and 0.18 M, respectively. This solution was refluxed for 24 h under nitrogen and then MeOH was removed by rotary evaporation. The residue was dissolved in dichloromethane (40 mL), washed with water (2 × 40 mL) and dried over anhydrous sodium sulfate. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:3 → 3:1) and isolated. The open chain intermediate product **24** (0.079 g, 13%) eluted first followed by the 5,6-ring-fused product **25** (0.278 g, 50.5%). 0.135 g of orange color solid was isolated which is not identified. This general procedure was also used for the syntheses of compounds **24**–**40**.

Synthesis of compounds 24 and 25 under other reaction conditions

Compounds **24** (0.054 g, 8.8%) and **25** (0.584 g, 69.8%) were prepared by combining solutions of DAMDC (0.378 g, 2.63 mmol, 1.49 eq.) in anhydrous MeOH (5 mL), and the tautomers **18a** and **18b** (0.357 g, 1.76 mmol, 1 eq.) in anhydrous MeOH (5 mL) and then following the general procedure mentioned above. The molarities of DMAD and the tautomers are 0.26 M and 0.18 M, respectively.

DAMDC (0.77 g, 5.36 mmol, 1.1 eq.) in anhydrous MeOH (10 mL) was added dropwise to a solution of the tautomers **18a** and **18b** (0.99 g, 4.87 mmol, 1 eq.) in anhydrous MeOH (20 mL) at room temperature under nitrogen. The molarities of DMAD and the tautomers are 0.18 M and 0.16 M, respectively. After stirring for 24 h at room temperature, **24** (0.426 g, 25.8%) and **25** (0.639 g, 41.9%) were isolated along with 10% of the starting tautomers at a **18a**:**18b** ratio of 1:1.89. The products were worked up by the general procedure.

Dimethyl (2*E*)-2-[2-Oxo-2-phenyl-1-(1,3-thiazol-2-yl)ethylidene]succinate (24)

R_f = 0.42 (ethyl acetate/hexane = 1:2); yellow solid; mp = 130-131 °C.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08 (d, *J* = 7.73 Hz, $C_6\underline{H}_5$ *ortho*, 2H), 7.96 (d, *J* = 2.64 Hz, =NC$\underline{H}$=CHS–, 1H), 7.55 (t, *J* = 7.26 Hz, $C_6\underline{H}_5$ *para*, 1H), 7.45 (m, $C_6\underline{H}_5$ *meta* and =NCH=C$\underline{H}$S–, 3H), 4.12 (s, –C$\underline{H}_2$CO$_2$CH$_3$, 2H), 3.79 (s, =C(CO$_2$C$\underline{H}_3$)–, 3H), 3.57 (s, –CH$_2$CO$_2$C$\underline{H}_3$, 3H).

IR (neat): 3134, 3112, 3096, 3040, 3001, 2951, 2843, 1733, 1712, 1679, 1663, 1612, 1448, 1256, 1198, 1176, 1113, 1102 cm^{-1}.

^{13}C NMR (150 MHz, CDCl$_3$): δ 194.59 (–$\underline{C}$OC$_6$H$_5$), 171.01 (–CH$_2\underline{C}$O$_2$CH$_3$), 166.17 (=C($\underline{C}$O$_2$CH$_3$)–), 160.50 (N,S≥$\underline{C}$–), 144.62 (=N$\underline{C}$H=CHS–), 143.84 (–CH$_2\underline{C}$(CO$_2$CH$_3$)=), 135.55 (–CO$\underline{C}_6$H$_5$, *ipso*), 133.55 (–CO$\underline{C}_6$H$_5$, *para*), 128.97 (–CO$\underline{C}_6$H$_5$), *ortho*), 128.80 (–CO$\underline{C}_6$H$_5$, *meta*), 127.17 (=$\underline{C}$(COC$_6$H$_5$)–), 122.73 (=NCH=$\underline{C}$HS–), 52.54 (–CH$_2$CO$_2\underline{C}$H$_3$), 52.54 (=C(CO$_2\underline{C}$H$_3$)–), 35.11 (–C$\underline{H}_2$CO$_2$CH$_3$).

DEPT 135 NMR (150 MHz, CDCl$_3$): δ 144.72, 133.65, 129.06, 128.90, 122.83, 52.63, 52.31, 35.20.

HRMS (ESI, [M+H]$^+$): calcd for $C_{17}H_{16}NO_5S$: 346.0749; found: 346.0740.

Methyl 8-Benzoyl-5-oxo-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-7-carboxylate (25)

R$_f$ = 0.42 (ethyl acetate/hexane = 1:1); yellow solid; mp = 145-146 °C.

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.36 (d, *J* = 4.27 Hz, >NC$\underline{H}$=CHS–, 1H), 7.59 (d, *J* = 7.95 Hz, C$_6\underline{H}_5$ *ortho*, 2H), 7.53 (t, *J* = 7.28 Hz, C$_6\underline{H}_5$ *para*, 1H), 7.46 (m, C$_6\underline{H}_5$ *meta*, 2H), 7.31 (d, *J* = 4.27 Hz, >NCH=C$\underline{H}$S–, 1H), 6.67 (s, –C$\underline{H}$=C(CO$_2$CH$_3$)–, 1H), 3.18 (s, –CO$_2$C$\underline{H}_3$, 3H).

IR (neat): 3158, 3125, 3091, 3062, 3030, 3008, 2953, 1725, 1681, 1663, 1619, 1595, 1472, 1439, 1409, 1331, 1252, 1159, 1096, 1077 cm^{-1}.

^{13}C NMR (150 MHz, CDCl$_3$): δ 191.20 (–$\underline{C}$OC$_6$H$_5$), 166.43 (–$\underline{C}$O$_2$CH$_3$), 158.12 (>N$\underline{C}$OCH= or N,S>$\underline{C}$=), 154.89 (>N$\underline{C}$OCH= or N,S>$\underline{C}$=), 142.89 (=$\underline{C}$(CO$_2$CH$_3$)–), 139.37 (–CO$\underline{C}_6$H$_5$, *ipso*), 131.86 (–CO$\underline{C}_6$H$_5$, *para*), 128.54 (–CO$\underline{C}_6$H$_5$, *ortho*), 127.85 (–CO$\underline{C}_6$H$_5$, *meta*), 124.14 (>N$\underline{C}$H=CHS–

), 117.00 (>NCO$\underline{C}$H=), 109.81 (>NCH=$\underline{C}$HS–), 108.09 (=$\underline{C}$(COC$_6$H$_5$)–), 52.39 (–CO$_2\underline{C}$H$_3$).

DEPT 135 NMR (150 MHz, CDCl$_3$): δ 131.95, 128.62, 127.93, 124.22, 117.85, 109.90, 52.48.

HRMS (ESI, $[M+H]^+$): calcd for $C_{16}H_{12}NO_4S$: 314.0487; found: 314.0455.

Single crystals were grown for X-ray crystallography by the vapor diffusion method. Hexane was diffused into a solution of compound **25** dissolved in chloroform.

Reaction of Tautomers 19a,b with Dimethyl Acetylenedicarboxylate

The open chain intermediate product **26** and the 5,6-ring-fused product **27** were synthesized by reacting DMAD (0.638 g, 4.44 mmol, 2.49 eq.) in anhydrous MeOH (5 mL) with the tautomers, (*Z*)-2-(4-methylthiazol-2-yl)-1-phenylethenol **19a** and 2-(4-methylthiazol-2-yl)-1-phenylethanone **19b**, (0.386 g, 1.78 mmol) in MeOH (5 mL) by the general procedure used for the synthesis and purification of **24** and **25**. The molarities of DMAD and tautomers are 0.44 M and 0.18 M, respectively. The eluent used for column chromatography over silica gel was ethyl acetate/hexane = 1:1. The compound **26** (0.073 g, 11.5%), eluted first followed by the compound **27** (0.379 g, 65.2%). Trace amounts of (*E*) and (*Z*)-dimethyl 2-methoxymaleate **28** and **29** were also isolated as byproducts.

Syntheses of compounds 26 and 27 under other reaction conditions

DAMD (0.233 g, 1.62 mmol, 1 eq.) in anhydrous MeOH (10 mL) was added dropwise to a solution of the tautomers **19a** and **19b** (0.352 g, 1.62 mmol, 1 eq.) in anhydrous MeOH (10 mL) at room temperature under nitrogen. The molarities of DMAD and tautomers are 0.08 M and 0.08 M, respectively. After stirring for 24 h at room temperature, **26** (0.147 g, 25.2%) and **27** (0.169 g, 31.9%) were isolated along with 15% of the starting tautomers at a **19a**:**19b** ratio of 1:1.25. The products were worked up by the general procedure.

Dimethyl (2*E*)-2-[1-(4-Methyl-1,3-thiazol-2-yl)-2-oxo-2-phenylethylidene]succinate (26)

$R_f = 0.47$ (ethyl acetate/hexane = 1:2); yellow solid; mp = 114-115 °C.

IR (neat): 3100, 2997, 2949, 2933, 1733, 1711, 1679, 1604, 1505, 1446, 1257, 1231, 1198, 1172 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 8.07 (d, $J = 6.74$ Hz, $C_6\underline{H}_5$ *ortho*, 2H), 7.54 (t, $J = 6.39$Hz, $C_6\underline{H}_5$ *para*, 1H), 7.45 (dd, $J = 6.74$ and 6.39 Hz, $C_6\underline{H}_5$ *meta*, 2H), 7.26 (s, $=NC(CH_3)=C\underline{H}S-$, 1H), 4.12 (s, $-C\underline{H}_2CO_2CH_3$, 2H), 3.80 (s, $=C(CO_2C\underline{H}_3)-$, 3H), 3.57 (s, $-CH_2CO_2C\underline{H}_3$, 3H), 2.47 (s, $=NC(C\underline{H}_3)=CHS-$, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 194.52 ($-\underline{C}OC_6H_5$), 171.19 ($-CH_2\underline{C}O_2CH_3$), 166.23 ($=C(\underline{C}O_2CH_3)-$), 159.22 ($N,S\geq\underline{C}-$ or $=\underline{C}(COC_6H_5)-$), 155.04 ($N,S\geq\underline{C}-$ or $=\underline{C}(COC_6H_5)-$), 143.81 ($=\underline{C}(CO_2CH_3)-$), 135.54 ($-CO\underline{C}_6H_5$, *ipso*), 133.42 ($-CO\underline{C}_6H_5$, *para*), 128.86 ($-CO\underline{C}_6H_5$, *ortho*), 128.69 ($-CO\underline{C}_6H_5$, *meta*), 126.30 ($=N\underline{C}(CH_3)=CHS-$), 117.87 ($=NC(CH_3)=\underline{C}HS-$), 52.42 ($=C(CO_2\underline{C}H_3)-$), 51.98 ($-CH_2CO_2\underline{C}H_3$), 35.15 ($-\underline{C}H_2CO_2CH_3$), 17.02 ($=N(\underline{C}H_3)C=CHS-$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.57, 129.06, 128.86, 117.95, 52.60, 52.16, 35.34.

IHRMS (ESI, $[M+H]^+$): calcd for $C_{18}H_{18}NO_5S$: 360.0906; found: 360.0908.

Methyl 8-Benzoyl-3-methyl-5-oxo-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-7-carboxylate (27)

$R_f = 0.53$ (ethyl acetate/hexane = 1:1); yellow solid; mp = 203-204 °C.

IR (neat): 3128, 3066, 2981, 2951, 1723, 1667, 1625, 1594, 1475, 1435, 1406, 1304, 1255, 1144, 1126 $\mathrm{cm^{-1}}$.

^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 7.57 (d, J = 7.14 Hz, $\mathrm{C_6H_5}$ *ortho*, 2H), 7.51 (t, J = 7.38 Hz, $\mathrm{C_6H_5}$ *para*, 1H), 7.44 (dd, J = 7.14 and 7.38 Hz, $\mathrm{C_6H_5}$ *meta*, 2H), 6.74 (s, $\mathrm{>NC(CH_3)=C\underline{H}S-}$, 1H), 6.53 (s, $\mathrm{-C\underline{H}=CCO_2CH_3}$, 1H), 3.16 (s, $\mathrm{-CO_2CH_3}$, 3H), 2.92 (s, $\mathrm{>NC(C\underline{H}_3)=CHS-}$, 3H).

^{13}C NMR (150 MHz, $\mathrm{CDCl_3}$): δ 190.97 ($\mathrm{-\underline{C}OC_6H_5}$), 166.35 ($\mathrm{-\underline{C}O_2CH_3}$), 161.18 ($\mathrm{>N\underline{C}OCH=}$ or $\mathrm{N,S>\underline{C}=}$), 157.55 ($\mathrm{>N\underline{C}OCH=}$ or $\mathrm{N,S>\underline{C}=}$), 142.18 ($\mathrm{=\underline{C}CO_2CH_3}$), 139.56 ($\mathrm{>N\underline{C}(CH_3)=CHS-}$ or $\mathrm{-CO\underline{C}_6H_5}$ *ipso*), 138.93 ($\mathrm{>N\underline{C}(CH_3)=CHS-}$ or $\mathrm{-CO\underline{C}_6H_5}$ *ipso*), 131.64 ($\mathrm{-CO\underline{C}_6H_5}$, *para*), 128.42 ($\mathrm{-CO\underline{C}_6H_5}$, *ortho*), 127.78 ($\mathrm{-CO\underline{C}_6H_5}$, *meta*), 112.36 ($\mathrm{>NCO\underline{C}H=}$), 111.34 ($\mathrm{>NC(CH_3)=\underline{C}HS-}$), 107.46 ($\mathrm{=\underline{C}(COC_6H_5)-}$), 52.26 ($\mathrm{-CO_2\underline{C}H_3}$), 18.25 ($\mathrm{>NC(\underline{C}H_3)=CHS-}$).

DEPT 135 NMR (150 MHz, $\mathrm{CDCl_3}$): δ 131.77, 128.55, 127.91, 112.50, 111.48, 52.40, 18.40.

HRMS (ESI, $[\mathrm{M+H}]^+$): calcd for $\mathrm{C_{17}H_{13}NO_4S}$: 328.0663; found: 328.0644.

(*E*)-Dimethyl 2-methoxymaleate (28)[2]

Brown oil

^{1}H NMR (600 MHz, $\mathrm{CDCl_3}$): δ 5.21 (s, $\mathrm{=C\underline{H}(CO_2CH_3)}$, 1H), 3.89, 3.75 (s, two $\mathrm{-CO_2C\underline{H}_3}$, 6H), 3.71 (s, $\mathrm{-OC\underline{H}_3}$, 3H).

^{13}C NMR (600 MHz, $\mathrm{CDCl_3}$): δ 166.38, 164.08 (two $\mathrm{-\underline{C}O_2CH_3}$), 162.59 ($\mathrm{=\underline{C}(CO_2CH_3)OCH_3}$), 93.26 ($\mathrm{=\underline{C}H(CO_2CH_3)}$, 57.08, 53.04 (two $\mathrm{-CO_2\underline{C}H_3}$), 51.78 ($\mathrm{-O\underline{C}H_3}$).

(*Z*)-Dimethyl 2-methoxymaleate (29)[2]

Brown oil

^{1}H NMR (600 MHz, $CDCl_3$): δ 6.19 (s, $=C\underline{H}(CO_2CH_3)$, 1H), 3.95, 3.85 (s, two $-CO_2C\underline{H}_3$, 6H), 3.76 (s, $-OC\underline{H}_3$, 3H).

^{13}C NMR (600 MHz, $CDCl_3$): δ 164.70, 163.21 (two $-\underline{C}O_2CH_3$), 154.74 ($=\underline{C}(CO_2CH_3)OCH_3$), 107.69 ($=\underline{C}H(CO_2CH_3)$), 61.05, 52.85 (two $-CO_2\underline{C}H_3$) , 51.70 ($-O\underline{C}H_3$).

Reaction of Tautomeric Pair 21a,b with Dimethyl Acetylenedicarboxylate

The open chain intermediate product **30**, the 5,6-ring-fused product **31** and the 5,7-ring-fused product **32** were synthesized by reacting DMAD (0.638 g, 4.44 mmol, 2.49 eq.) in 5 mL of anhydrous MeOH with the tautomers, (*Z*)-2-(4,5-dimethylthiazol-2-yl)-1-phenylethenol **20a** and 2-(4,5-dimethylthiazol-2-yl)-1-phenylethanone **20b**, (0.337 g, 1.46 mmol) in 5 mL MeOH by the general procedure used for the synthesis and purification of **24** and **25**. The molarities of DMAD and tautomers are 0.44 M and 0.15 M, respectively. The eluent used for column chromatography over silica gel was silica gel, 1:2→ 3:1 ethyl acetate: hexane. The compound **30**, (0.175 g, 32.3%), eluted first followed by the compound **31** (0.08 g, 16%) and compound **32** (0.173 g, 23.1%). Trace amount of (*E*) and (*Z*)-dimethyl 2-methoxymaleate **28** and **29** were also isolated as by products.

Synthesis of compounds 30, 31 and 32 under other reaction conditions

The open chain intermediate **30** (0.249 g, 45.8%), the 5,6-ring-fused compound **31**, (0.102 g, 20.5%) and the 5,7-ring-fused compound **32** (0.05 g, 7%) were prepared by combining solutions of DAMDC (0.313 g, 2.18 mmol, 1.5 eq.) in anhydrous MeOH

(5 mL), and the tautomers **20a** and **20b** (0.336 g, 1.45 mmol, 1 eq.) in anhydrous MeOH (5 mL) and then the general procedure mentioned above was followed. The molarities of DMAD and tautomers are 0.22 M and 0.15 M, respectively.

Dimethyl (2*E*)-2-[1-(4,5-Dimethyl-1,3-thiazol-2-yl)-2-oxo-2-phenylethylidene]succinate (30)

$R_f = 0.50$ (ethyl acetate/hexane = 2:1); brown sticky oil.

IR (neat): 3060, 3023, 2997, 2981, 2951, 2925, 2847, 1736, 1714, 1672, 1628, 1294, 1254, 1491, 1407, 1205, 1170, 1121, 939, 785, 729, 689 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.06 (d, $J = 7.50$ Hz, C_6H_5 *ortho*, 2H), 7.55 (t, $J = 7.21$ Hz, C_6H_5 *para*, 1H), 7.45 (dd, $J = 7.50$ and 7.21 Hz, C_6H_5 *meta*, 2H), 4.12 (s, $-C\underline{H}_2CO_2CH_3$, 2H), 3.79 (s, $=C(CO_2C\underline{H}_3)-$, 3H), 3.55 (s, $-CH_2CO_2C\underline{H}_3$, 3H), 2.33 (s, $=NC(CH_3)=C(C\underline{H}_3)S-$, 3H), 2.30 (s, $=NC(C\underline{H}_3)=C(CH_3)S-$, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 194.67 ($-\underline{C}OC_6H_5$), 171.33 ($-CH_2\underline{C}O_2CH_3$), 166.34 ($=C(\underline{C}O_2CH_3)-$), 154.98 ($N,S{\geq}\underline{C}-$ or $=N\underline{C}(CH_3)=C(CH_3)S-$), 151.20 ($N,S{\geq}\underline{C}-$ or $=N\underline{C}(CH_3)=C(CH_3)S-$), 144.00 ($=\underline{C}(COC_6H_5)-$), 135.61 ($=\underline{C}(CO_2CH_3)-$ or $-CO\underline{C}_6H_5$ *ipso*), 133.32 ($=\underline{C}(CO_2CH_3)-$ or $-CO\underline{C}_6H_5$ *ipso*), 131.79 ($-CO\underline{C}_6H_5$, para), 128.83 ($-CO\underline{C}_6H_5$, o*rtho*), 128.66 ($-CO\underline{C}_6H_5$, *meta*), 129.95 ($NC(CH_3)=\underline{C}(CH_3)S-$), 52.35 ($=C(CO_2\underline{C}H_3)-$), 51.94 ($-CH_2CO_2\underline{C}H_3$), 35.10 ($-\underline{C}H_2CO_2CH_3$), 14.70 ($=NC(\underline{C}H_3)=C(CH_3)S-$), 11.17 ($=NC(CH_3)=C(\underline{C}H_3)S-$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.47, 128.96, 128.81, 52.49, 52.08, 35.23, 14.84, 11.37.

HRMS (ESI, $[M+H]^+$): calcd for $C_{19}H_{20}NO_5S$: 374.1062; found: 374.1074.

Methyl 8-Benzoyl-2,3-dimethyl-5-oxo-5*H*-[1,3]thiazolo[3,2-*a*]pyridine-7-carboxylate (31)

R_f = 0.58 (ethyl acetate/hexane = 1:1); yellow solid; mp = 172-174 °C.

IR (neat): 3081, 3030, 2970, 2981, 2951, 2936, 1733, 1683, 1608, 1598, 1539, 1480, 1443, 1413, 1323, 1310, 1280, 1249, 1174, 1123, 981, 947, 847, 780, 694 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 7.84 Hz, $C_6\underline{H}_5$ *ortho*, 2H), 7.51 (t, J = 7.02 Hz, C_6H_5 *para*, 1H), 7.44 (dd, J = 7.84 and 7.02 Hz, C_6H_5 *meta*, 2H), 6.53 (s, $-C\underline{H}=C(CO_2CH_3)-$, 1H), 3.15 (s, $-CO_2C\underline{H}_3$, 3H), 2.82 (s, $>NC(CH_3)=C(C\underline{H}_3)S-$, 3H), 2.35 (s, $>NC(C\underline{H}_3)C(CH_3)S-$, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 191.07 ($-\underline{C}OC_6H_5$), 166.55 ($-\underline{C}O_2CH_3$), 161.06 ($>N\underline{C}OCH=$) or N,S>$\underline{C}$=), 155.57 ($>N\underline{C}OCH=$) or N,S>$\underline{C}$=), 141.50 ($=\underline{C}(CO_2CH_3)-$), 139.73 ($-CO\underline{C}_6H_5$, *ipso*), 133.24 ($>N\underline{C}(CH_3)=C(CH_3)S-$), 131.61 ($-CO\underline{C}_6H_5$, *para*), 128.44 ($-CO\underline{C}_6H_5$, *ortho*), 127.85 ($-CO\underline{C}_6H_5$, *meta*), 122.59 ($>NC(CH_3)=\underline{C}(CH_3)S-$), 111.68 ($>NCO\underline{C}H=$), 107.19 ($=\underline{C}(COC_6H_5)-$), 52.25 ($-CO_2\underline{C}H_3$), 15.11 ($>NC(CH_3)=C(\underline{C}H_3)S-$), 11.61 ($>NC(\underline{C}H_3)=C(CH_3)S-$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 131.71, 128.53, 127.94, 111.77, 52.34, 15.21, 11.71.

HRMS (ESI, $[M+H]^+$): calcd for $C_{18}H_{16}NO_4S$: 342.0800; found: 342.0773.

Tetramethyl (5*S**,6*S**)-9-Benzoyl-2,3-dimethyl-5,6-dihydro[1,3]thiazolo[3,2-*a*]azepine-5,6,7,8-tetracarboxylate (32)

R_f = 0.45 (ethyl acetate/hexane = 3:1); yellowish orange solid; mp = 216-218 °C.

IR (neat): 1996, 2949, 2840, 1738, 1709, 1549, 1449, 1333, 1348, 1213, 1137, 997, 786, 740, 700, 662 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.53 (d, J = 7.16 Hz, C_6H_5 *ortho*, 2H), 7.38 (t, J = 7.34 Hz, C_6H_5 *para*, 1H), 7.31 (dd, J = 7.16 and 7.34 Hz, C_6H_5 *meta*, 2H), 5.76 (d, J =

5.2 Hz, $>NC\underline{H}(CO_2CH_3)–$, 1H), 4.98 (d, J = 5.2 Hz, $–C\underline{H}(CO_2CH_3)–C(CO_2CH_3)=$, 1H), 3.71 (s, $–CH(CO_2CH_3)–C(CO_2C\underline{H}_3)=$, 3H), 3.68 (s, $=C(CO_2C\underline{H}_3)–C(COC_6H_5)=$, 3H), 3.67 (s, $–CH(CO_2C\underline{H}_3)–C(CO_2CH_3)=$, 3H) 3.03 (s, $>NCH(CO_2C\underline{H}_3)–$, 3H), 2.24, 2.21 (s, $>NC(C\underline{H}_3)=C(\underline{C}H_3)S–$, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.64 ($–\underline{C}OC_6H_5$), 169.06, 167.73, 167.70, 167.08 (four $–\underline{C}O_2CH_3$), 160.25 (N,S>$\underline{C}$=), 142.15 ($=\underline{C}(CO_2CH_3)–C(COC_6H_5)=$ or $–CO\underline{C}_6H_5$ *ipso*), 140.86 ($=\underline{C}(CO_2CH_3)–C(COC_6H_5)=$ or $–CO\underline{C}_6H_5$ *ipso*), 132.81 ($>NC(CH_3)=\underline{C}(CH_3)S–$), 130.45 ($–CO\underline{C}_6H_5$, *para*), 129.34 ($–CO\underline{C}_6H_5$, *ortho*), 127.53 ($–CO\underline{C}_6H_5$, *meta*), 119.90 ($–CH(CO_2CH_3)–\underline{C}(CO_2CH_3)=$), 116.90 ($>N\underline{C}(CH_3)=C(CH_3)S–$), 97.59 ($=\underline{C}(COC_6H_5)–$), 64.12 ($>N\underline{C}HCO_2CH_3$), 53.16, 53.07, 52.35, 51.93, (four $–CO_2\underline{C}H_3$), 46.32 ($–\underline{C}H(CO_2CH_3)–C(CO_2CH_3)=$), 12.51 and 11.43 ($>NC(\underline{C}H_3)=C(\underline{C}H_3)S–$, 2C).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 130.52, 129.41, 127.60, 64.19, 53.23, 53.15, 52.43, 52.00, 46.39, 12.58, 11.50.

HRMS (ESI, $[M+H]^+$): calcd for $C_{25}H_{26}NO_9S$: 516.1328; found: 516.1286.

Reaction of Tautomeric Pair 21a,b with Dimethyl Acetylenedicarboxylate

The open chain intermediate product **33**, the 5,6-ring-fused product **34** and the 5,7-ring-fused product **35** were synthesized by reacting DMAD (0.601 g, 4.19 mmol, 2.51 eq.) in anhydrous MeOH (5 mL) and the tautomers, (*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylethenol **21a** and 2-(4,5-dimethyloxazol-2-yl)-1-phenylethanone **21b**, (0.360 g, 1.67 mmol, 1 eq.) in MeOH (5 mL) by the general procedure used for the synthesis and purification of **24** and **25.** The molarities of DMAD and the tautomers are 0.42 M and 0.17 M, respectively. The eluent used for column chromatography over silica gel was 1:2→ 4:1 ethyl acetate: hexane. The intermediate product **33** (0.212 g, 35.5%), eluted first followed by **36** (0.011 g, 1.3%), 5,6-ring-fused compound **34** (0.023 g, 4.3%) and 5,7 ring-fused compound **35** (0.392 g, 47%). Trace amount of (*E*) and (*Z*)-dimethyl 2-methoxymaleate **28** and **29** were also isolated.

Synthesis of compounds 33 and 35 under other reaction conditions

The open chain intermediate product **33** (0.206 g, 44.2%) and 5,7-ring-fused product **35** (0.166 g, 19.8%) were prepared by stirring the tautomers **21a** and **21b** (0.363 g, 1.68 mmol, 1 eq.) and DAMDC (0.242 g, 1.68 mmol, 1 eq.) in anhydrous MeOH (10 mL) at room temperature for 24 h. The starting tautomers (16.5%) were recovered at a **21a**:**21b** ratio of 1 : 2.73. The molarities of both DMAD and tautomers are 0.17 M. The 5,6-ring-fused compound was not detected on TLC.

Dimethyl (2*Z*)-2-[1-(4,5-Dimethyl-1,3-oxazol-2-yl)-2-oxo-2-Phenylethylidene]succinate (33)

R_f = 0.65 (ethyl acetate/hexane = 1:1); yellow solid, mp = 110-111 °C.

IR (neat): 3084, 3066, 3029, 2959, 2935, 2850, 1736, 1708, 1601, 1434, 1361, 1335, 1279, 1248, 1216, 1195, 1174, 1120, 942, 968, 896, 866 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.92 Hz, C_6H_5 *ortho*, 2H), 7.55 (t, *J* = 7.30 Hz, C_6H_5 *para*, 1H), 7.46 (dd, *J* = 7.92 and 7.30 Hz, C_6H_5 *meta*, 2H), 4.22 (s, –$C\underline{H}_2CO_2CH_3$, 2H), 3.78 (s, =$C(CO_2C\underline{H}_3)$–, 3H), 3.55 (s, –$CH_2CO_2C\underline{H}_3$, 3H), 2.16 (s, =$NC(CH_3)=C(C\underline{H}_3)O$–, 3H), 2.07 (s, =$NC(C\underline{H}_3)=C(CH_3)O$–, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 192.63 (–$\underline{C}OC_6H_5$), 171.13 (–$CH_2\underline{C}O_2CH_3$), 166.14 (=$C(\underline{C}O_2CH_3)$–), 154.61 (N,O≥$\underline{C}$–), 145.93 (=$\underline{C}(COC_6H_5)$–), 138.17 (=$\underline{C}(CO_2CH_3)$– or –$CO\underline{C}_6H_5$ *ipso* or =$NC(CH_3)=\underline{C}(CH_3)O$–), 136.16 (=$\underline{C}(CO_2CH_3)$– or –$CO\underline{C}_6H_5$ *ipso* or =$NC(CH_3)=\underline{C}(CH_3)O$–), 134.06 (=$\underline{C}(CO_2CH_3)$– or –$CO\underline{C}_6H_5$, *ipso* or

$=NC(CH_3)=\underline{C}(CH_3)O$–), 133.22 (–$CO\underline{C}_6H_5$, *para*), 128.77 (–$CO\underline{C}_6H_5$, *ortho*), 128.65 (–$CO\underline{C}_6H_5$, *meta*), 126.95 ($N\underline{C}(CH_3)=C(CH_3)O$–), 52.44 ($=C(CO_2\underline{C}H_3)$–), 52.09 (–$CH_2CO_2\underline{C}H_3$), 34.94 (–$\underline{C}H_2CO_2CH_3$), 11.19 ($=NC(\underline{C}H_3)=C(CH_3)O$–), 10.05 ($=NC(CH_3)=C(\underline{C}H_3)O$–).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.30, 128.86, 128.74, 52.52, 52.17, 35.02, 11.28, 10.14.

HRMS (ESI, $[M+H]^+$): calcd for $C_{19}H_{20}NO_6$: 358.1291; found: 358.1261.

Single crystals were grown for X-ray crystallography by the vapor diffusion method. Hexane was diffused into a solution of compound **33** dissolved in chloroform.

Methyl 8-Benzoyl-2,3-dimethyl-5-oxo-5*H*-[1,3]oxazolo[3,2-*a*]pyridine-7-carboxylate (34)

$R_f = 0.44$ (ethyl acetate/hexane = 2:1); yellow solid; mp = 162-164 °C.

IR (neat): 3079, 2993, 2973, 2950, 2933, 1733, 1706, 1663, 1640, 1444, 1428, 1270, 1154, 971 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, $J = 8.42$ Hz, $C_6\underline{H}_5$ *ortho*, 2H), 7.50 (t, $J = 7.38$ Hz, $C_6\underline{H}_5$ *para*, 1H), 7.44 (dd, $J = 8.42$ and 7.38 Hz, $C_6\underline{H}_5$ *meta*, 2H), 6.54 (s, –$C\underline{H}=C(CO_2CH_3)$–, 1H), 3.16 (s, –$CO_2C\underline{H}_3$, 3H), 2.83, 2.35 (s, $>OC(C\underline{H}_3)=C(\underline{C}H_3)N<$, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.57 (–$\underline{C}OC_6H_5$), 166.08 (–$\underline{C}O_2CH_3$), 158.48 ($>N\underline{C}OCH=$ or ($N,O>\underline{C}=$), 153.22 ($>N\underline{C}OCH=$ or ($N,O>\underline{C}=$), 142.76 ($=\underline{C}(CO_2CH_3)$–), 142.10 ($>N\underline{C}(CH_3)=C(CH_3)O$–), 138.43 (–$CO\underline{C}_6H_5$, *ipso*), 132.84 (–$CO\underline{C}_6H_5$, *para*), 128.69 (–$CO\underline{C}_6H_5$, *ortho*), 128.45 (–$CO\underline{C}_6H_5$, *meta*), 119.38 ($>NC(CH_3)=\underline{C}(CH_3)O$–), 109.85 ($>NCO\underline{C}H=$), 97.77 ($=\underline{C}(COC_6H_5)$–), 52.62 (–$CO_2\underline{C}H_3$), 9.95, 9.79 ($>NC(\underline{C}H_3)=C(\underline{C}H_3)O$–).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 132.91, 128.76, 128.52, 109.92, 52.68, 10.00, 9.85.

HRMS (ESI, $[M+H]^+$): calcd for $C_{18}H_{16}NO_5$: 326.1028; found: 326.0998.

Single crystals were obtained for X-ray crystallography by the vapor diffusion method. Hexane was diffused into a solution of compound **34** dissolved in chloroform.

Tetramethyl (5*S**,6*S**)-9-Benzoyl-2,3-dimethyl-5,6-dihydro[1,3]oxazolo[3,2-*a*]azepine-5,6,7,8-tetracarboxylate (35)

R_f = 0.35 (ethyl acetate/hexane = 4:1); intense yellow solid; mp = decompose at 170 °C.

IR (neat): 2997, 2991, 2980, 2930, 1729, 1683, 1657, 1570, 1515, 1430, 1232, 1227, 1225, 1170, 1120, 1097, 1000, 855, 768, 716, 695 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, *J* = 7.58 Hz, C_6H_5 *ortho*, 2H), 7.39 (t, *J* = 7.25 Hz, C_6H_5 *para*, 1H), 7.31 (dd, *J* = 7.58 and 7.25 Hz, C_6H_5 *meta*, 2H), 5.42 (d, *J* = 4.9 Hz, $>NC\underline{H}(CO_2CH_3)–$, 1H), 5.26 (d, *J* = 4.9 Hz, $–C\underline{H}(CO_2CH_3)–C(CO_2CH_3)=$, 1H), 3.74 (s, $–CH(CO_2CH_3)–C(CO_2C\underline{H}_3)=$, 3H), 3.73 (s, $=C(CO_2C\underline{H}_3)–C(COC_6H_5)=$, 3H), 3.69 (s,

$–CH(CO_2C\underline{H}_3)–C(CO_2CH_3)=$, 3H) 3.65 (s, $>NCH(CO_2C\underline{H}_3)–$, 3H), 2.05, 1.83 (s, $>NC(C\underline{H}_3)=C(\underline{C}H_3)O–$, 6H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 192.37 ($–\underline{C}OC_6H_5$), 170.38, 168.76, 167.08, 166.58 (four $–\underline{C}O_2CH_3$), 158.96 ($N,S>\underline{C}=$), 144.31 ($=\underline{C}(CO_2CH_3)–C(COC_6H_5)=$ or $–CO\underline{C}_6H_5$ *ipso*), 141.85 ($=\underline{C}(CO_2CH_3)–C(COC_6H_5)=$ or $–CO\underline{C}_6H_5$ *ipso*), 138.12 ($–CH(CO_2CH_3)–\underline{C}(CO_2CH_3)=$ or ($>NC(CH_3)=\underline{C}(CH_3)O–$), 130.69 ($–CO\underline{C}_6H_5$, *para*), 128.40 ($–CO\underline{C}_6H_5$, *ortho*), 127.71 ($–CO\underline{C}_6H_5$, *meta*), 121.44 ($–CH(CO_2CH_3)–\underline{C}(CO_2CH_3)=$ or ($>NC(CH_3)=\underline{C}(CH_3)O–$), 110.70 ($>N\underline{C}(CH_3)=C(CH_3)O–$), 89.79 ($=\underline{C}(COC_6H_5)–$), 60.29 ($>N\underline{C}HCO_2CH_3$), 53.28, 53.16, 52.32, 52.25, (four $-\mathrm{CO_2\underline{C}H_3}$), 44.93 ($-\mathrm{\underline{C}H(CO_2CH_3)-C(CO_2CH_3)=}$), 9.59, 7.59 ($\mathrm{>NC(\underline{C}H_3)=C(\underline{C}H_3)O-}$, 2C).

DEPT 135 NMR (150 MHz, $\mathrm{CDCl_3}$): δ 130.75, 128.49, 127.78, 60.40, 53.31, 53.21, 52.36, 52.30, 45.06, 9.64, 7.65.

HRMS (ESI, $[\mathrm{M+H}]^+$): calcd for $\mathrm{C_{25}H_{26}NO_{10}}$: 500.1557; found: 500.1530.

Single crystals were grown for X-ray crystallography by the vapor diffusion method. Hexane was diffused into a solution of compound **35** dissolved in acetone.

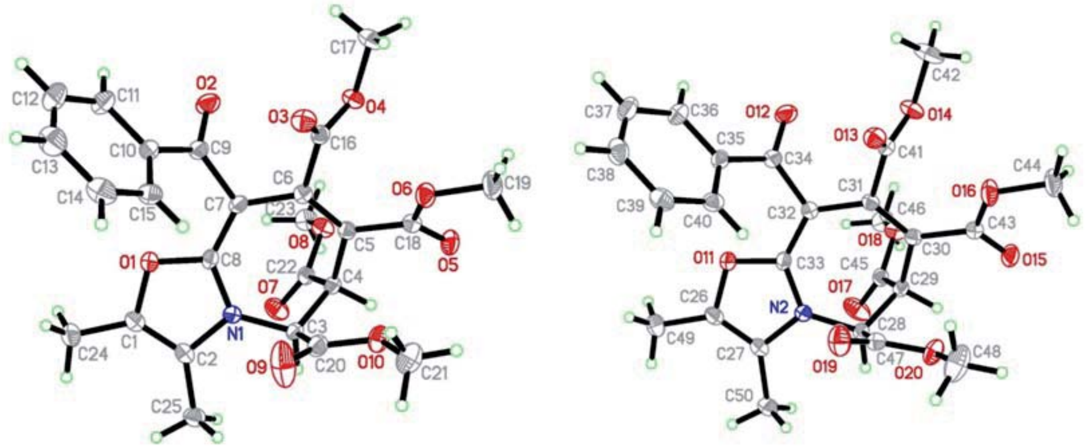

Figure S1 The X-ray crystal structures of two independent molecules of **35**. Solvent molecules (acetone) are not shown for clarity. CCDC: 888332.

Tetramethyl 6-(4,5-Dimethyl-1,3-oxazol-2-yl)biphenyl-2,3,4,5-tetracarboxylate (36)

$R_f = 0.35$ (ethyl acetate/hexane = 2:3); off white solid; mp = 124-126 °C.

IR (neat): 3023, 3018, 3001, 2981, 2956, 2928, 1735, 1438, 1335, 1209, 1187, 1176, 1153, 1094, 924, 857, 824, 715 $\mathrm{cm^{-1}}$.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (m, $C_6\underline{H}_5$ *para* and *meta*, 3H), 7.06 (d, *J* = 7.19 Hz, $C_6\underline{H}_5$ *ortho*, 2H), 3.90, 3.88, 3.76, 3.50 (s, four $-CO_2C\underline{H}_3$, 12H), 1.99, 1.92 (s, $>NC(C\underline{H}_3)=C(\underline{C}H_3)O-$, 6H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 166.71, 166.42, 165.85, 165.82 (four $-\underline{C}O_2CH_3$), 154.26 ($N,O>\underline{C}=$), 144.52, 142.90, 136.44, 135.98, 135.27, 131.75, 131.48, 130.99, 129.89 (aromatic, 7C and $>N\underline{C}(CH_3)=\underline{C}(CH_3)O-$, 2C), 53.24, 53.20, 52.88, 52.51 (four $-CO_2\underline{C}H_3$), 11.08, 9.57 ($>NC(\underline{C}H_3)=C(\underline{C}H_3)O-$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 128.47, 128.03, 127.88, 53.30, 53.26, 52.57, 11.14, 9.63.

HRMS (ESI, $[M+H]^+$): calcd for $C_{25}H_{24}NO_9$: 482.1451; found: 482.1435.

Reaction of Tautomeric pair 22a,b with Dimethyl Acetylenedicarboxylate

The open chain intermediate product **37** and the 5,6-ring-fused product **38**, were synthesized by reacting DMAD (0.308 g, 2.15 mmol, 1.5 eq.) in anhydrous MeOH (5 mL) with the tautomers (*Z*)-2-(benzo[*d*]oxazol-2-yl)-1-phenylethenol **22a** and 2-(benzo[*d*]oxazol-2-yl)-1-phenylethanone **22b** (0.339 g, 1.43 mmol, 1 eq.) in MeOH (5 mL) by the general procedure used for the synthesis and purification of **24** and **25**. The molarities of DMAD and tautomers are 0.22 M and 0.14 M, respectively. The eluent used for column chromatography over silica gel was ethyl acetate: hexane = 1:3. The compound **37** (0.01 g, 2%), eluted first followed by the compound **38** (0.46 g, 93%).

Syntheses of compounds 37 and 38 under other reaction conditions

(*Z*)-Dimethyl 2-(1-(benzo[*d*]oxazol-2-yl)-2-oxo-2-phenylethylidene)succinate **37** 0.172 g, 35.3%) and methyl 4-benzoyl-1-oxo-1*H*-benzo[4,5]oxazolo[3,2-*a*]pyridine-3-carboxylate **38** (0.049 g, 11%) were prepared by combining solutions of DAMDC (0.279 g, 1.94 mmol, 1.51 eq.) in anhydrous MeOH (10 mL), and the tautomers **22a** and

22b (0.305 g, 1.28 mmol, 1 eq.) in anhydrous MeOH (15 mL) and then following the general procedure mentioned above. The molarities of DMAD and tautomers are 0.08 M and 0.05 M, respectively. The starting tautomers (40.6%) were recovered in a **22a**:**22b** ratio of 1.11:1.

Dimethyl (2*Z*)-2-[1-(1,3-Benzoxazol-2-yl)-2-oxo-2-phenylethylidene]succinate (37)

$R_f = 0.48$ (ethyl acetate/hexane = 1:2); yellow solid; mp = 130-132 °C.

IR (neat): 3086, 3067, 2981, 2952, 2923, 2849, 1743, 1720, 1694, 1596, 1534, 1449, 1434, 1296, 1243, 1209, 1181, 1001, 944, 753, 725, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.53 Hz, C_6H_5 *ortho*, 2H), 7.77-7.73 (m, aromatic H), 7.57 (t, *J* = 7.93 Hz, C_6H_5 *para*, 1H), 7.50-7.47 (m, aromatic H), 7.37-7.33 (m, aromatic H), 4.38 (s, $-C\underline{H}_2CO_2CH_3$, 2H), 3.81 (s, $=C(CO_2C\underline{H}_3)-$, 3H), 3.61 (s, $-CH_2CO_2C\underline{H}_3$, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 192.12 ($-\underline{C}OC_6H_5$), 170.72 ($-CH_2\underline{C}O_2CH_3$), 165.75 ($=C(\underline{C}O_2CH_3)-$), 158.21 ($N,O\geq\underline{C}-$), 150.05 ($=NC\geq\underline{C}O-$), 141.13 ($=\underline{C}(COC_6H_5)-$), 138.43 ($=\underline{C}(CO_2CH_3)-$ or $=NC\geq\underline{C}O-$), 135.96 ($-CO\underline{C}_6H_5$, *ipso*), 133.64 ($-CO\underline{C}_6H_5$, *para*), 132.39 ($=\underline{C}(CO_2CH_3)-$ or $=NC\geq\underline{C}O-$), 128.93 ($-CO\underline{C}_6H_5$, *ortho*), 128.90 ($-CO\underline{C}_6H_5$, *meta*), 126.92, 125.25, 121.12, 111.10 (aromatic C) 52.86 ($=C(CO_2\underline{C}H_3)-$), 52.47 ($-CH_2CO_2\underline{C}H_3$), 35.45 ($-\underline{C}H_2CO_2CH_3$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.64, 128.97, 128.92, 126.93, 125.28, 121.15, 111.13, 52.85, 52.48, 35.45.

HRMS (ESI, $[M+H]^+$): calcd for $C_{21}H_{18}NO_6$: 380.1134; found: 380.1115.

Methyl 4-Benzoyl-1-oxo-1*H*-pyrido[2,1-*b*][1,3]benzoxazole-3-carboxylate (38)

$R_f = 0.48$ (ethyl acetate/hexane = 1:1); pale yellow solid; mp = 193-195 °C.

IR (neat): 3081, 3040, 3006, 2952, 1739, 1687, 1648, 1634, 1599, 1516, 1441, 1418, 1297, 1250, 1164, 1050, 1000, 850, 790, 782, 757, 623 cm^{-1}.

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.63 (d, $J = 7.49$ Hz, C_6H_5 *ortho*, 2H), 7.85 (d, $J = 7.74$ Hz, aromatic, 1H), 7.61 (t, $J = 7.31$ Hz, C_6H_5 *para*, 1H), 7.50-7.44 (m, aromatic, 5H), 6.89 (s, $-C\underline{H}=C(CO_2CH_3)-$, 1H). 3.61 (s, $-CH=C(CO_2C\underline{H}_3)-$, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 189.40 ($-\underline{C}OC_6H_5$), 165.57 ($-\underline{C}O_2CH_3$ or $>N\underline{C}OCH=$ or $N,O>\underline{C}=$), 158.07 ($-\underline{C}O_2CH_3$ or $>N\underline{C}OCH=$ or $N,O>\underline{C}=$), 152.87 ($>N\underline{C}OCH=$), 147.03 ($=\underline{C}(CO_2CH_3)-$ or ($>NC\geq\underline{C}O-$), 143.08 ($=\underline{C}(CO_2CH_3)-$ or ($>NC\geq\underline{C}O-$), 137.96 ($-CO\underline{C}_6H_5$, *ipso*), 133.34 ($-CO\underline{C}_6H_5$, *para*), 128.99 ($-CO\underline{C}_6H_5$, *ortho*), 128.69 ($-CO\underline{C}_6H_5$, *meta*), 127.72 (aromatic $\underline{C}H$) , 126.44 ($>N\underline{C}\geq CO-$), 125.56 117.37, 112.76 (aromatic $\underline{C}H$), 110.96 ($>NCO\underline{C}H=$), 98.16 ($=\underline{C}(COC_6H_5)-$), 52.94 ($-CO_2\underline{C}H_3$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 133.40, 129.04, 128.75, 127.78, 125.62, 117.42, 112.82, 111.02, 52.99.

HRMS (ESI, $[M+H]^+$): calcd for $C_{20}H_{14}NO_5$: 348.0872; found: 348.0829.

Single crystals of **38** were obtained for X-ray crystallography by the vapor diffusion method. Hexane was diffused into a solution of compound **38** dissolved in chloroform.

Reaction of Tautomeric pair 23a,b with Dimethyl Acetylenedicarboxylate

The 5,6-ring-fused product **40** was synthesized by reacting DMAD (0.226 g, 1.57 mmol, 1.5 eq.) in anhydrous MeOH (5 mL) and the tautomers, (*Z*)-2-(benzo[*d*]thiazol-2-yl)-1-phenylethenol **23a** and 2-(benzo[*d*]thiazol-2-yl)-1-phenylethanone **23b**, (0.261g, 1.03 mmol, 1 eq.) in MeOH (15 mL) by the general procedure used for the synthesis and purification of **24** and **25.** The molarities of tautomers : DMAD = 0.05 : 0.08. The eluent used for column chromatography over silica gel was ethyl acetate: hexane = 1:2. The compound **40** (0.317 g, 84.8%) was isolated as the only product.

Synthesis of compound 40 under other reaction conditions

DAMDC (0.141 g, 0.98 mmol, 1 eq.) in anhydrous MeOH (5 mL) was added dropwise to a solution of the tautomers **23a** and **23b** (0.261g, 1.03 mmol, 1 eq.), (0.247 g, 0.98 mmol) in anhydrous MeOH (15 mL) at room temperature under nitrogen. The molarities of both DMAD and tautomers are 0.05 M. After 24 h stirring at room temperature, the 5,6-ring-fused product **40** (0.230 g, 64.7%) was isolated along with 21.8% starting tautomers at **23a**:**23b** = 1.62:1. The products were worked up by the general procedure.

Methyl 4-Benzoyl-1-oxo-1*H*-pyrido[2,1-*b*][1,3]benzothiazole-3-carboxylate (40)

$R_f = 0.43$ (ethyl acetate/hexane = 1:2); intense yellow solid; mp = 234-236 °C.

IR (neat): 3126, 3094, 3068, 3013, 2981, 2952, 1719, 1672, 1621, 1559, 1492, 1434, 1409, 1289, 1264, 1244, 1196, 1120, 1066, 996, 945, 858, 805, 762, 679, 620 cm^{-1}.

^1H NMR (600 MHz, $CDCl_3$): δ 9.32 (d, *J* = 8.14 Hz, C_6H_5 *ortho*, 2H), 7.81 (d, *J* = 7.32 Hz, aromatic, 1H), 7.63 (t, *J* = 7.5 Hz, C_6H_5 *para*, 1H), 7.60-7.53 (m, aromatic, 3H), 7.47 (dd, *J* = 7.5 and 8.14 Hz, C_6H_5 *meta*, 2H), 6.83 (s, $-C\underline{H}=C(CO_2CH_3)-$, 1H), 3.23 (s, $-CH=C(CO_2C\underline{H}_3)-$, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 191.72 ($-\underline{C}OC_6H_5$), 166.09 ($-\underline{C}O_2CH_3$), 161.13 ($>N\underline{C}OCH=$), 154.90 ($N,S>\underline{C}=$, 141.70 ($=\underline{C}(CO_2CH_3)-$), 139.25 ($>N\underline{C}\geq\underline{C}S-$) or $-CO\underline{C}_6H_5$, *ipso*), 137.20 ($>N\underline{C}\geq CS-$) or $-CO\underline{C}_6H_5$, *ipso*), 132.12 ($-CO\underline{C}_6H_5$, *para*), 128.61 ($-CO\underline{C}_6H_5$, *ortho*), 128.35 ($>NC\geq\underline{C}S-$), 127.98 ($-CO\underline{C}_6H_5$, *meta*), 127.48 127.06, 121.66, 120.34 (aromatic $\underline{C}H$), 113.92 (>NCO$\underline{C}$H=), 108.16 (=$\underline{C}$(COC_6H_5)–), 52.46 (–$CO_2\underline{C}H_3$).

DEPT 135 NMR (150 MHz, $CDCl_3$): δ 132.19, 128.68, 128.05, 127.54, 127.13, 121.41, 120.41, 113.98, 52.53.

HRMS (ESI, $[M+H]^+$): calcd for $C_{20}H_{14}NO_4S$: 364.0644; found: 364.0600.

Conversion of the Open-Chain Product 37 into the 5,6-Ring-Fused Product 38

The open chain product **37** (0.20 g, 0.53 mmol) was dissolved in anhydrous MeOH (3 mL) and refluxed. The reaction was monitored by TLC. The spot for **37** was not observed after 15 h. MeOH was removed by rotary evaporation and residue was dissolved in dichloromethane (10 mL) and washed with water (2 × 10 mL). Organic layer was dried with anhydrous sodium sulfate. Sodium sulphate was filtered and dichloromethane was removed. The 5,6-ring-fused compound **38** was isolated in 98.9% (0.182 g) yield.

Synthesis of the 5,6-Fused-Ring Product 25 from the Open-Chain Product 24 by Treatment with Sodium Hydride

The open chain intermediate **24** (0.301 g, 0.84 mmol) in THF (10 mL) was added to a suspension of NaH (in 60% mineral oil) (0.051, 1.28 mmol, 1.5 eq.) in THF (10 mL) at room temperature under nitrogen. Hydrogen bubbles were evolved. The unreacted **24** was not observed on the TLC after refluxing for 7 h. Then THF was removed by rotary evaporation. The residue was dissolved in 30 mL dichloromethane, washed with water (2 × 20 mL) and dried over anhydrous sodium sulfate. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:1). The 5,6-ring-fused product **25** (0.086 g, 76%) was isolated.

This general procedure was also used for the syntheses of compounds **31, 34** and **38** from **30, 25** and **37**, respectively, discussed in this section.

Synthesis of the 5,6-Fused-Ring Product 31 from the Open-Chain Product 30 by Treatment with Sodium Hydride

The 5,6-ring-fused product **31** (0.064 g, 61%) was synthesized by refluxing the open chain intermediate product **30** (0.114 g, 0.31 mmol, 1 eq.) and NaH (0.02 g, 0.5 mmol, 1.6 eq.) in THF (20 mL) for 8 h. The unreacted **30** was not observed on the TLC. The product was purified by the general procedure used in synthesizing **31** from **30**. The eluent used for column chromatography over silica gel was 1:2 ethyl acetate: hexane.

Synthesis of the 5,6-Fused-Ring Product 34 from the Open-Chain Product 33 by Treatment with Sodium Hydride

The 5,6-ring-fused product **34** (0.073 g, 40%) was synthesized by refluxing the open chain intermediate product **33** (0.203 g, 0.57 mmol) and NaH (0.034 g, 0.85 mmol, 1.5 eq.) in THF (20 mL) for 24 h. The products were purified by the general procedure used in synthesizing **25** from **24**. The eluent used for column chromatography over silica gel was 1:1 ethyl acetate: hexane. 38.6% of **33** was recovered.

The 5,6-ring-fused product **33** (0.013 g, 7%) was synthesized by refluxing the open chain intermediate product **34** (0.208 g, 0.58 mmol) and NaH (0.035 g, 0.88 mmol, 1.5 eq.) in 1,4-dioxane (20 mL) for 24 h. The products were purified by the general procedure used in synthesizing **25** from **24**. The eluent used for column chromatography over silica gel was 1:1 ethyl acetate: hexane. 31.6% of **33** was recovered. Reaction solution became very dark brown while refluxing. A dark brown spot was seen on the base line on the TLC.

Synthesis of the 5,6-Fused-Ring Product 38 from the Open-Chain Product 37 by Treatment with Sodium Hydride

The 5,6-ring-fused product **38** (0.088 g, 79%) was synthesized by refluxing the open chain intermediate product **37** (0.121 g, 0.32 mmol) and NaH (0.02 g, 0.5 mmol, 1.6 eq.) in THF (20 mL) for 8 h. The unreacted **37** was not observed on the TLC after refluxing for 8 h. The products were purified by the general procedure used in synthesizing **24** from **25**. The eluent used for column chromatography over silica gel was 1:1 ethyl acetate: hexane.

Reaction of the Tautomeric Pair 20a,b with Dimethyl Acetylenedicarboxylate in the presence of Sodium Methoxide in Methanol

DMAD (0.523 g, 3.64 mmol, 2.5 eq.) in anhydrous MeOH (5 mL) was added dropwise to a solution of the tautomers **20a** and **20b** (0.337 g, 1.46 mmol) in anhydrous MeOH (5 mL) at room temperature under nitrogen. Then, 25 wt% NaOMe in MeOH (0.1 ml, 0.5 mmol, 0.32 eq.) was added. This solution was refluxed for 24 h under nitrogen and then MeOH was removed by rotary evaporation. The residue was dissolved in 40 mL dichloromethane, washed with water (2 × 40 mL) and dried over anhydrous sodium sulfate. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:2) and isolated. The the 5,6-ring-fused product **31** (0.221 g, 44.4%) eluted first followed by **59** (0.067 g, 9.2%). A mixture (0.069 g) of (*E*)-dimethyl 2-methoxymaleate **28** and (*Z*)-dimethyl 2-methoxymaleate **29** was also isolated. The 5,7-ring-fused product **32** was not detected on TLC.

Tetramethyl 6-(4,5-Dimethyl-1,3-thiazol-2-yl)biphenyl-2,3,4,5-tetracarboxylate (59)

R_f = 0.50 (ethyl acetate/hexane =1:2); off white solid; mp = 165-166 °C.

IR (neat): 3081, 3030, 2981, 2951, 2936, 1733, 1683, 1608, 1598, 1539, 1480, 1443, 1310, 1413, 1323, 1280, 1249, 947, 789, 747, 726, 694 cm^{-1}.

^{1}H NMR (600 MHz, CDCl$_3$): δ 7.36–7.29 (m, $C_6\underline{H}_5$ *para* and *meta*, 3H), 7.11 (d, *J* = 7.68 Hz, $C_6\underline{H}_5$ *ortho*, 2H), 3.89, 3.87, 3.72, 3.47 (s, four $-CO_2C\underline{H}_3$, 12H), 2.26, 2.20 (s, $>NC(C\underline{H}_3)=C(\underline{C}H_3)S-$, 6H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 166.95, 166.81, 166.08, 165.78 (four $-\underline{C}O_2CH_3$), 156.93 ($N,S>\underline{C}=$), 148.01, 141.68, 135.96, 135.81, 135.28, 134.94, 131.41, 130.18, 130.99 (aromatic, 7C and $>N\underline{C}(CH_3)=\underline{C}(CH_3)S-$, 2C), 129.50 ($-\underline{C}_6H_5$, *ortho*), 128.55 ($-\underline{C}_6H_5$, *para*), 128. 14 ($-\underline{C}_6H_5$, *meta*), 53.15, 53.10, 52.49, 52.40 (four $-CO_2\underline{C}H_3$), 14.41, 11.18 ($>NC(\underline{C}H_3)=C(\underline{C}H_3)S-$).

DEPT 135 NMR (150 MHz, CDCl$_3$): δ 129.63, 128.67, 128.26, 53.27, 52.22, 52.61, 52.52, 14.54, 11.31.

HRMS (ESI, $[M+H]^+$): calcd for $C_{25}H_{24}NO_8S$: 498.1223; found: 498.1182.

Reaction of Tautomeric pair 21a,b with Dimethyl Acetylenedicarboxylate in the presence of Sodium Methoxide in Methanol

The 5,6-ring-fused product **34** and the substituted biphenyl derivative **36** were synthesized by reacting DMAD (0.599 g, 4.17 mmol, 2.5 eq.), tautomers **21a** and **21b** (0.359 g, 1.67 mmol), and NaOMe (0.1 mL, 0.5 mmol, 0.28 eq.) in MeOH (10 mL). Products were purified by the procedure used for the synthesis and purification of **31** and **59**. The eluent used for column chromatography over silica gel was 1:1 ethyl acetate: hexane. The compound **34** (0.286 g, 36.1%) eluted first followed by compound **36** (0.089 g, 17%). The 5,7-ring-fused product **35** was not detected on TLC.

Reaction of Succinate 33 with Dimethyl Acetylenedicarboxylate in the presence of Sodium Methoxide

DMAD (0.112 g, 0.78 mmol, 1.1 eq.) in anhydrous MeOH (2 mL) was added dropwise to a solution of **33** (0.255 g, 0.71 mmol) in anhydrous MeOH (3 mL) at room temperature under nitrogen. Then, 25 wt% NaOMe in MeOH (1.5 µL, 0.01 eq.) was added. This solution was refluxed for 24 h under nitrogen and then MeOH was removed by rotary evaporation. The residue was dissolved in 40 mL dichloromethane, washed with water (2 × 40 mL) and dried over anhydrous sodium sulfate. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:2) and isolated. The 5,7-ring-fused product **35** was not detected on TLC. Instead the 5,6-ring-fused product **34** (0.15 g, 65%) and **36** (0.012 g, 3.6%) was isolated. Further, 18% of the starting ring open intermediate **33** was recovered.

Reaction of 5,7-Ring-Fused Product 35 with Sodium Methoxide in Methanol

NaOMe in MeOH (0.09 ml, 0.4 mmol, 0.9 eq.) was added to **35** (0.2 g, 0.4 mmol) in MeOH at room temperature. The intense yellow color of the **35** in MeOH changed to dark brown color. The solution was analyzed by TLC after stirring for 15 minutes at room temperature. The spot for the starting 5,7-ring-fused compound **35** disappeared while a new spot appeared on TLC plate. The new spot was identified as compound **36**. After 15 minutes, MeOH was removed by rotary evaporation. Products were purified by the procedure used for the synthesis and purification of **31** and **59**. The eluent used for column chromatography over silica gel was 1:1 ethyl acetate: hexane. Compound **36** (0.072 g, 37.1%) was isolated.

Reaction of Tautomeric Pair 18a,b with Methyl Propiolate in Refluxing Methanol

Methyl propiolate (0.691 g, 8.14 mmol, 1.5 eq.) in 10 mL of anhydrous MeOH was added dropwise to a stirred solution of the tautomers **18a**,**b** (1.1 g, 5.4 mmol, 1 eq.) in 15 mL of anhydrous MeOH at room temperature under nitrogen. The molarities of methyl propiolate and the starting tautomers are 0.33 M and 0.22 M, respectively. This solution was refluxed for 24 h under nitrogen and then MeOH was removed by rotary evaporation. The residue was dissolved in dichloromethane (40 mL), washed with water (2 × 40 mL) and dried over anhydrous sodium sulfate. Two very close spots were detected on the TLC ($R_f = 0.65, 0.62$; ethyl acetate:hexane = 3:2) in addition to the spot for unreacted **18a,b**. After removal of dichloromethane by rotary evaporation, the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane = 1:4 → 1:2) and isolated. The starting tautomers **18a,b** were recovered in 14% yield as the first fraction. The compounds corresponding to the two very close spots seen on TLC were collected as a single fraction (yellow solid; 0.21 g) This fraction had a complex ^{1}H NMR spectra. The compounds representing the two TLC spots could not be separated by column chromatography by changing the eluting solvent's polarity using different ethyl acetate/hexane or acetone/hexane ratios. Further purification of this fraction was attempted by crystallization which was carried out by diffusion of hexane vapor into a solution of this yellow solid in chloroform. A yellow solid was formed as a precipitate and this had a very broad melting point range from 178 °C-190 °C. The ^{1}H NMR spectra of this solid is exactly the same as that of the solid before recrystallization. The ^{1}H, ^{13}C and DEPT 135 NMR spectra of this unidentified solid are given in Figures S3 and S4, respectively. This general purification procedure was used in the other reactions discussed below.

Reaction of Tautomeric Pair 21a,b with Methyl Propiolate in Refluxing Methanol

Methyl propiolate (0.264 g, 3.11 mmol, 1.51 eq.) in 5 mL of anhydrous MeOH was added dropwise to a stirred solution of the tautomers **21a** and **21b** (0.444 g, 2.06 mmol, 1 eq.) in 10 mL of anhydrous MeOH at room temperature under nitrogen. The molarities of methyl propiolate and tautomers are 0.21 M and 0.14 M, respectively. This solution was refluxed for 24 h under nitrogen and then MeOH was removed by rotary evaporation. Two new spots were detected on TLC in addition to the spot for unreacted **21a,b** (ethyl acetate:hexane = 1:2). The above-mentioned general procedure was used for the purification and isolation of products. The crude product was purified by column chromatography using ethyl acetate/hexane = 1:3 and then 1:1 over silica gel. The unreacted starting tautomers **21a,b** (0.291, 65.5%) were collected first in a **21a**:**21b** ratio of 1:3.03 in $CDCl_3$. Next, compound **65** (0.022 g, 4.3%) was isolated. A more polar high-intense yellow solid (0.026 g) corresponding to the third spot was also isolated. The R_f of this last fraction is 0.29 (ethyl acetate:hexane = 1:2). Figure S5 shows its ^{1}H NMR spectrum.

This reaction was repeated with **21a,b** (0.37 g, 1.7 mmol, 1 eq.), methyl propiolate (0.222 g, 2.61 mmol, 1.52 eq.) in refluxing MeOH (10 mL) for 27 h. The unreacted starting tautomers **21a,b** (0.15 g, 40.5%), **65** (0.03 g, 5.8%) and the same intense yellow solid (0.058 g) described in the above reaction were isolated.

Methyl (2*E*)-3-[4,5-Dimethyl-2-(2-oxo-2-phenylethylidene)-1,3-oxazol-3(2*H*)-yl]acrylate (65)

R_f = 0.40 (ethyl acetate/hexane = 1:2); yellow solid, mp = 150-152°C.

IR (neat): 3084, 3001, 2951, 2850, 1699, 1635, 1597, 1573, 1450, 1351, 1326, 1289, 1239, 1222, 1152, 1123, 1064, 978, 924, 861, 834, 763, 680 cm^{-1}.

^{1}H NMR (600 MHz, CDCl$_3$): δ 8.09 (d, *J* = 14.95 Hz, >NC$\underline{\text{H}}$=, 1H), 7.46 (m, C$_6$H$_5$, 5H), 6.70 (s, =C$\underline{\text{H}}$(COPh), 1H), 5.32 (d, *J* = 14.95 Hz, =C$\underline{\text{H}}$(CO$_2$CH$_3$), 1H), 3.75 (s, =CH(CO$_2$C$\underline{\text{H}}_3$), 3H), 2.03 and 1.72 (s, =NC(C$\underline{\text{H}}_3$)=C(C$\underline{\text{H}}_3$)O–, 6H).

^{13}C NMR (150 MHz, CDCl$_3$): δ 203.52 (–$\underline{\text{C}}$OC$_6$H$_5$), 168.84 (=CH($\underline{\text{C}}$O$_2$CH$_3$), 167.46 (N,O>$\underline{\text{C}}$=), 162.13 (–CO$\underline{\text{C}}_6$H$_5$ *ipso*), 134.10 (>NC$\underline{\text{H}}$=), 131.51 (–CO$\underline{\text{C}}_6$H$_5$ *para*), 129.44 (–CO$\underline{\text{C}}_6$H$_5$ *ortho*), 129.39 (=NC(CH$_3$)=$\underline{\text{C}}$(CH$_3$)O–), 127.24 (–CO$\underline{\text{C}}_6$H$_5$, *meta*), 120.34 (=$\underline{\text{C}}$H(CO$_2$CH$_3$), 99.73 (=C$\underline{\text{H}}$(COPh)), 75.44 (=N$\underline{\text{C}}$(CH$_3$)=C(CH$_3$)O–), 51.57 (=CH(CO$_2$C$\underline{\text{H}}_3$), 23.39 (=NC(CH$_3$)=C($\underline{\text{C}}$H$_3$)O–), 18.21 (=NC($\underline{\text{C}}$H$_3$)=C(CH$_3$)O–).

DEPT 135 NMR (150 MHz, CDCl$_3$): δ 134.16, 131.53, 129.49, 127.29, 120.44, 99.85, 51.58, 23.41, 18.25

HRMS (ESI, [M+2H]$^+$): calcd for C$_{17}$H$_{19}$NO$_4$: 301.1314; found: 301.1407.

Note: The NOESY spectrum of **65** does not show clear evidence for a NOE interaction between the vinyl protons on the β–carbon and on the carbon next to nitrogen of the side chain alkene. This might be due to the low rotational barrier about the exocyclic double bond which could prevent observation of the NOE interaction. Therefore, the *exo*-ring double bond geometry ((*Z*) or (*E*)) at the β-carbon of **65** is unknown.

Reaction of Tautomeric pair 21a,b with Methyl Propiolate in MeOH at Room Temperature

Methyl propiolate (0.097 g, 1.1 mmol, 1 eq.) in 10 mL of anhydrous MeOH was added dropwise to a stirred solution of the tautomers **21a** and **21b** (0.24 g, 1.1 mmol, 1 eq.) in 15 mL of anhydrous MeOH at room temperature under nitrogen. The molarities of methyl propiolate and **18a,b** were both 0.05 M. Then this solution was stirred for 18 h under nitrogen. MeOH was removed by rotary evaporation. The general work up procedure mentioned above was then employed. The crude product was purified by column chromatography using ethyl acetate/hexane = 1:3 then 2:1 over silica gel. The title compound **68** (0.042 g, 16%) was isolated along with the un-reacted starting tautomers **21a,b** (0.096 g, 38.9%) in a **21a**:**21b** ratio of 1:2.86.

Reaction of **21a,b** (0.269 g, 1.25 mmol, 1 eq.) with methyl propiolate (0.109 g, 1.28 mmol, 1 eq.) in 20 mL MeOH at room temperature for 24 h afforded **68** in 13% (0.036 g) yield.

A control reaction was carried out in the presence of water without methyl propiolate to see if **68** would form from **21a,b** in the presence of water. Water (10 mL) was added to tautomers **21a,b** (0.282 g, 1.31 mmol) in methanol (10 mL). Then solution was refluxed for 24 h at about 80 °C. The crude product mixture was purified according to the general procedure used for purification and isolation of products **24** and **25**. Compound **68** (0.032 g, 11%) was isolated showing that methyl propiolate was not involved in its formation.

2-Acetyl-2-methyl-6-phenyl-2,3-dihydro-4*H*-1,3-oxazin-4-one (68)

R_f = 0.45 (ethyl acetate/hexane = 1:2); pale yellow solid, mp = 142-144 °C.

IR (neat): 3168, 3055, 2895, 1727, 1652, 1451, 1394, 1197, 1108, 1053, 1021, 952, 900, 825, 769, 684, 664 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ 8.37 (s, $>N\underline{H}$, 1H), 7.78 (d, *J* = 7.37 Hz, $C_6\underline{H}_5$ *ortho*, 2H), 7.54-7.44 (m, $C_6\underline{H}_5$ *meta* and *para*, 3H), 5.83 (s, $=C\underline{H}-$, 1H), 2.33 (s, $-COC\underline{H}_3$, 3H), 1.79 (s, $>C C\underline{H}_3-$, 3H).

^{13}C NMR (75 MHz, $CDCl_3$): δ 205.48 ($-\underline{C}OCH_3$), 165.55 ($-\underline{C}ONH-$ or $=\underline{C}(C_6H_5)O-$), 164.12 ($-\underline{C}ONH-$ or $=\underline{C}(C_6H_5)O-$), 131.67 ($-\underline{C}_6H_5$ *para*) , 131.45 ($-\underline{C}_6H_5$

ipso), 128.76 (–$\underline{C}_6H_5$ *meta*), 126.56 (–$\underline{C}_6H_5$ *ortho*), 96.55 (=$\underline{C}$H–), 91.09 (>$\underline{C}CH_3$–), 24.80 (–CO$\underline{C}H_3$), 22.09 (>C$\underline{C}H_3$–).

HRMS (ESI, $[M+H]^+$): calcd for $C_{13}H_{14}NO_3$: 232.0974; found: 232.0992.

Single crystals were grown for X-ray crystallography by the vapor diffusion method. Hexane was diffused into a solution of compound **68** dissolved in chloroform.

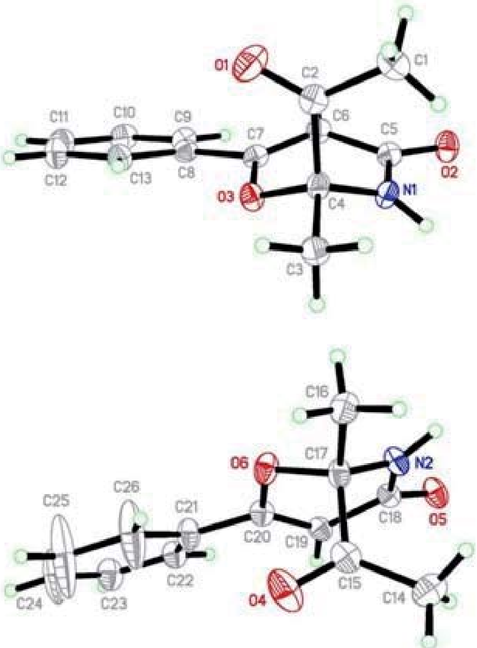

Figure S2 The crystal structure of 6**8**. This crystal structure contains two independent molecules, which are enantiomers

Reaction of (*Z*)-2-(benzo[*d*]thiazol-2-yl)-1-phenylethenol (23a) and 2-(benzo[*d*]thiazol-2-yl)-1-phenylethanone (23b) with methyl propiolate in refluxing MeOH

A solution of the tautomers **23a**,**b** (0.202 g, 0.80 mmol, 1 eq.) and methyl propiolate (0.102 g, 1.20 mmol, 1.5 eq.) in 10 mL of anhydrous MeOH was refluxed for 23 h. The molarities of the tautomers **23a,b** and methyl propiolate are 0.08 M and 0.12 M, respectively. Two new spots were seen on TLC in addition to the spot for **23a,b** after

23 h. Then the general work up procedure mentioned above was followed. The crude product was purified by column chromatography using ethyl acetate/hexane = 1:3 over silica gel. The starting tautomers **23a,b** (fraction 1) were recovered in 58.9% (0.119 g) yield. Fraction 2 ($R_f = 0.44$; ethyl acetate/hexane = 1:3) and fraction 3 ($R_f = 0.29$; ethyl acetate/hexane = 1:3) were separated and each fraction weighted 0.03 g each. These two fractions were unidentified. The ^{1}H NMR spectra of these two fractions are given in Figures S6 and S7.

NMR spectra of unidentified fractions collected from column separation

Reaction of the tautomers (Z)-1-phenyl-2-(thiazol-2-yl)ethenol (18a) and 1-phenyl-2-(thiazol-2-yl)ethanone (18b) with methyl propiolate

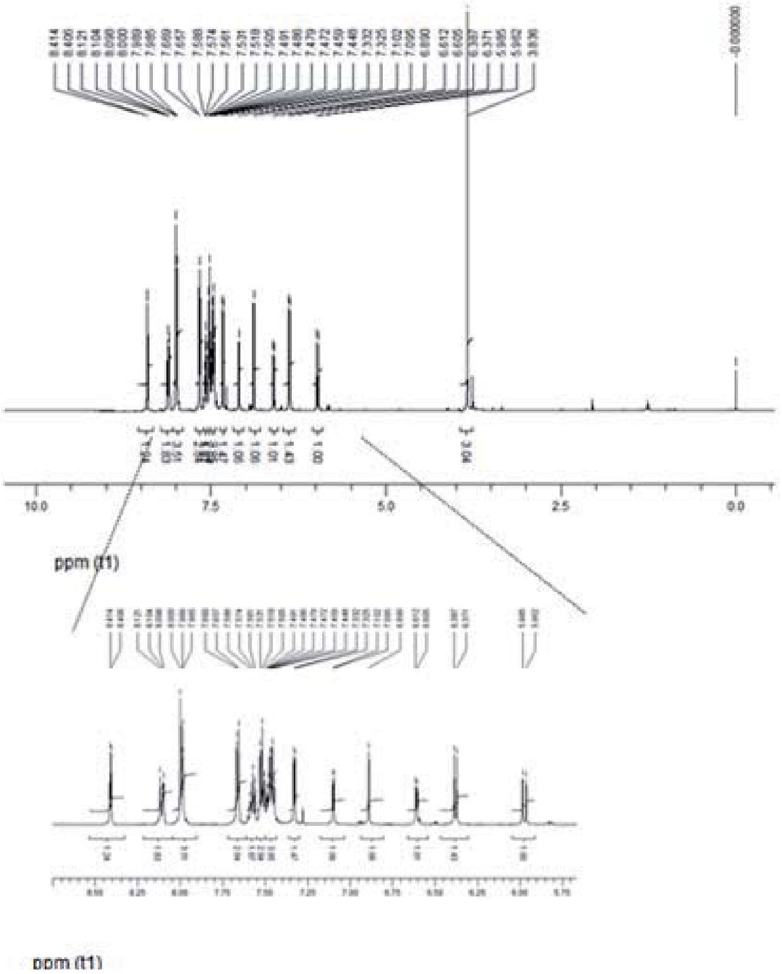

Figure S3: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of two inseparable spots collected as one fraction

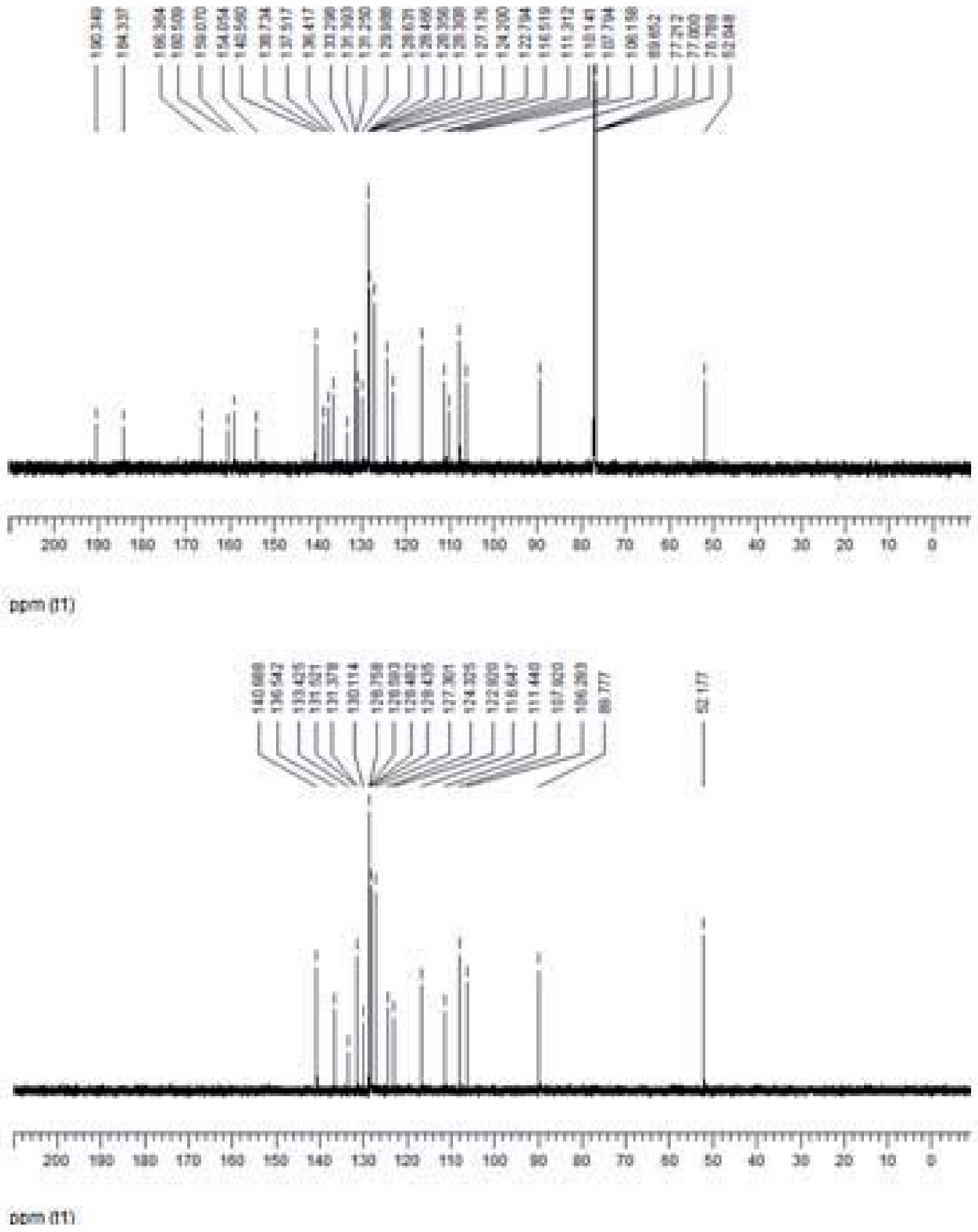

Figure S4: ^{13}C and DEPT 135 NMR spectra (150 MHz, $CDCl_3$) of two inseparable spots collected as one fraction

Reaction of the tautomers (*Z*)-2-(4,5-dimethyloxazol-2-yl)-1-phenylethenol (21a) and 2-(4,5-dimethyloxazol-2-yl)-1- phenylethanone (21b) with methyl propiolate

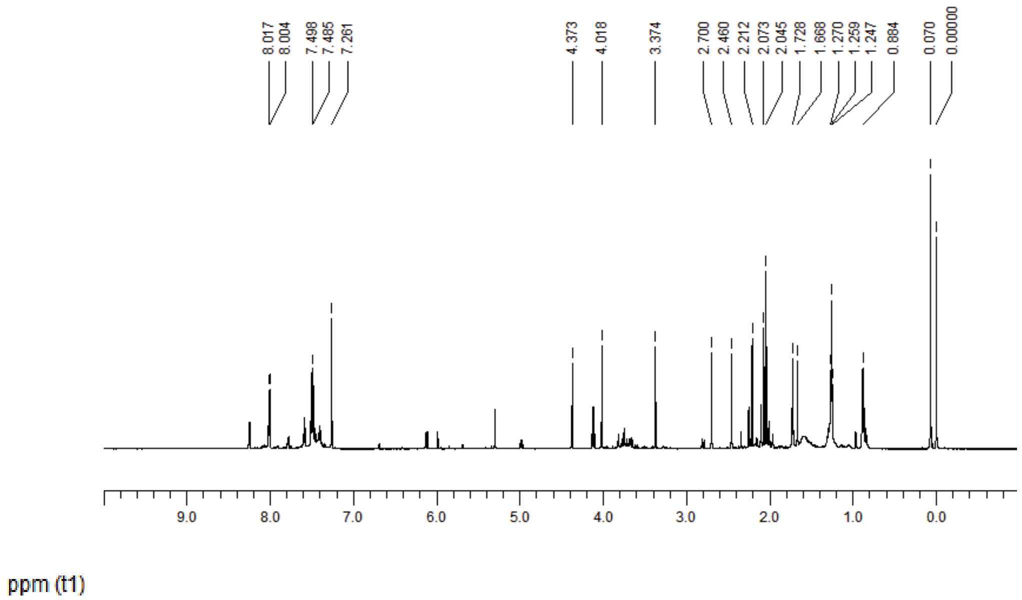

Figure S5: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the last fraction (R_f = 1:2; ethyl acetate-hexane)

Reaction of the tautomers (*Z*)-2-(benzo[*d*]thiazol-2-yl)-1-phenylethenol (23a) and 2-(benzo[*d*]thiazol-2-yl)-1-phenylethanone (23b) with methyl propiolate

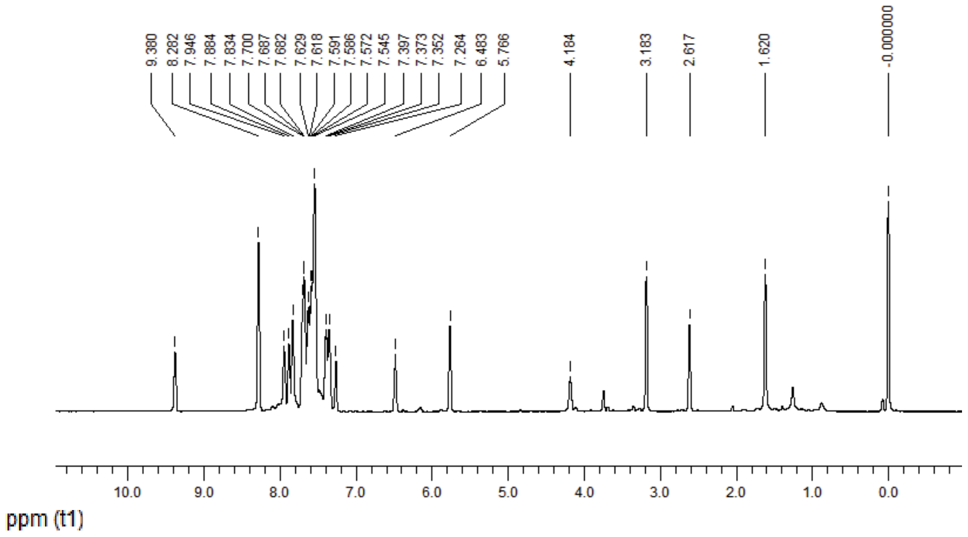

Figure S6: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the fraction 2 (R_f = 0.44; ethyl acetate-hexane = 1:3)

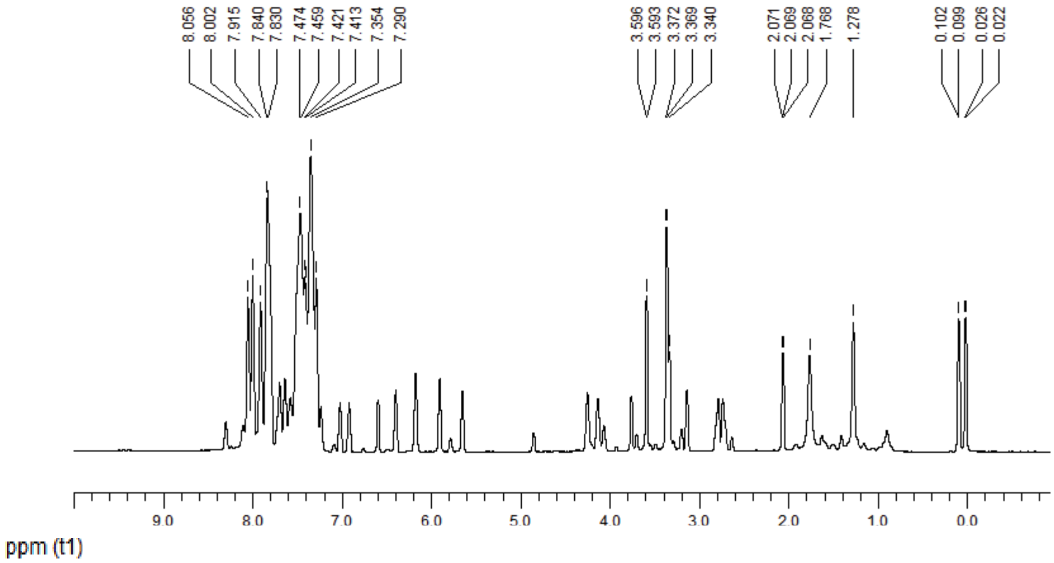

Figure S7: ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of the fraction 3 (R_f = 0.29; ethyl acetate-hexane = 1:3)

References

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