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A convenient synthesis of furo[3,2-*c*]pyran-3-carboxylates from 3-bromo-3-nitroacrylates

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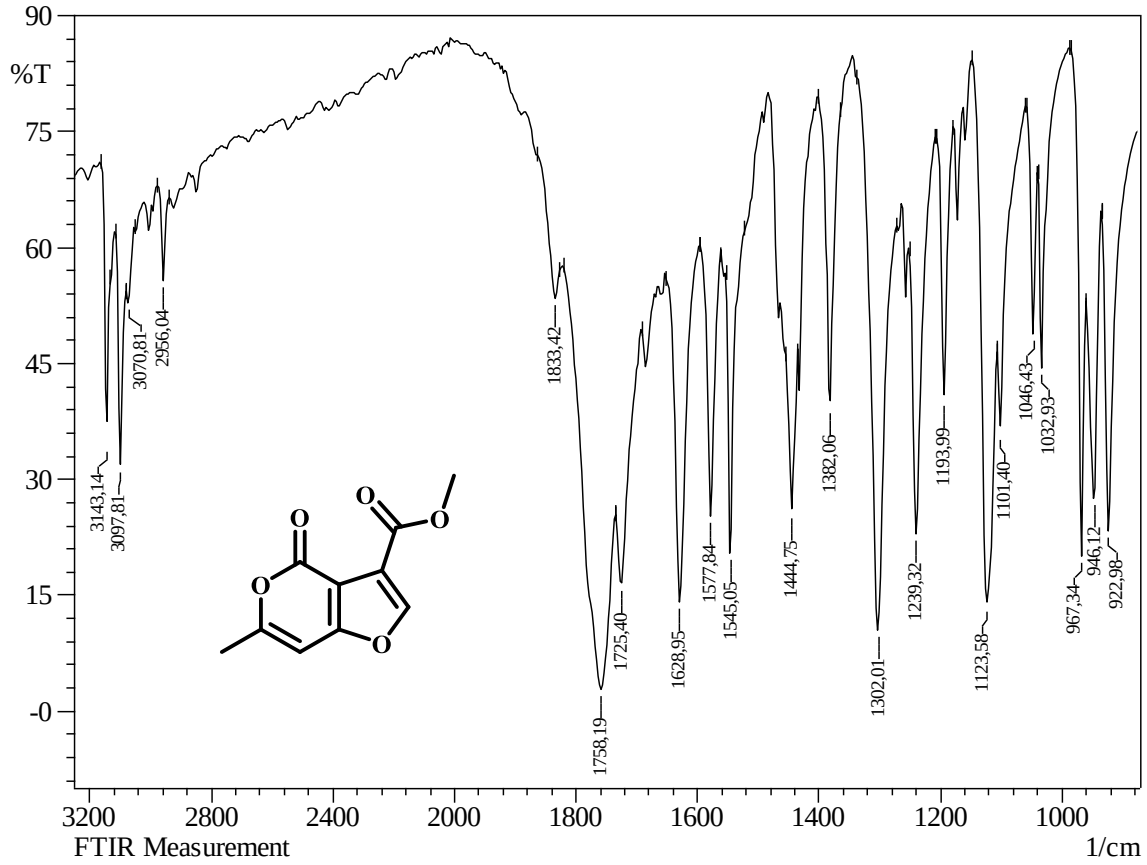
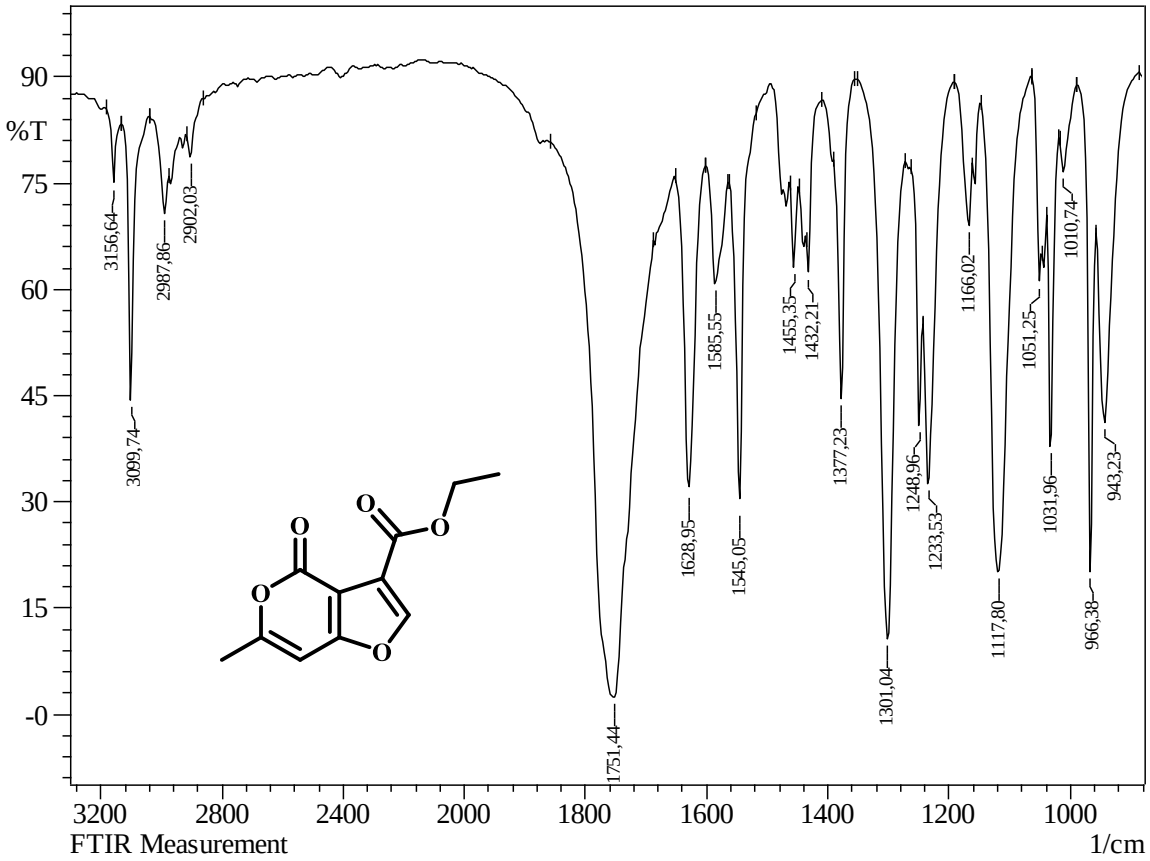


Figure S1. IR spectrum of methyl 6-methyl-4-oxo-4*H*-furo[3,2-*c*]pyran-3-carboxylate **2a** in KBr.



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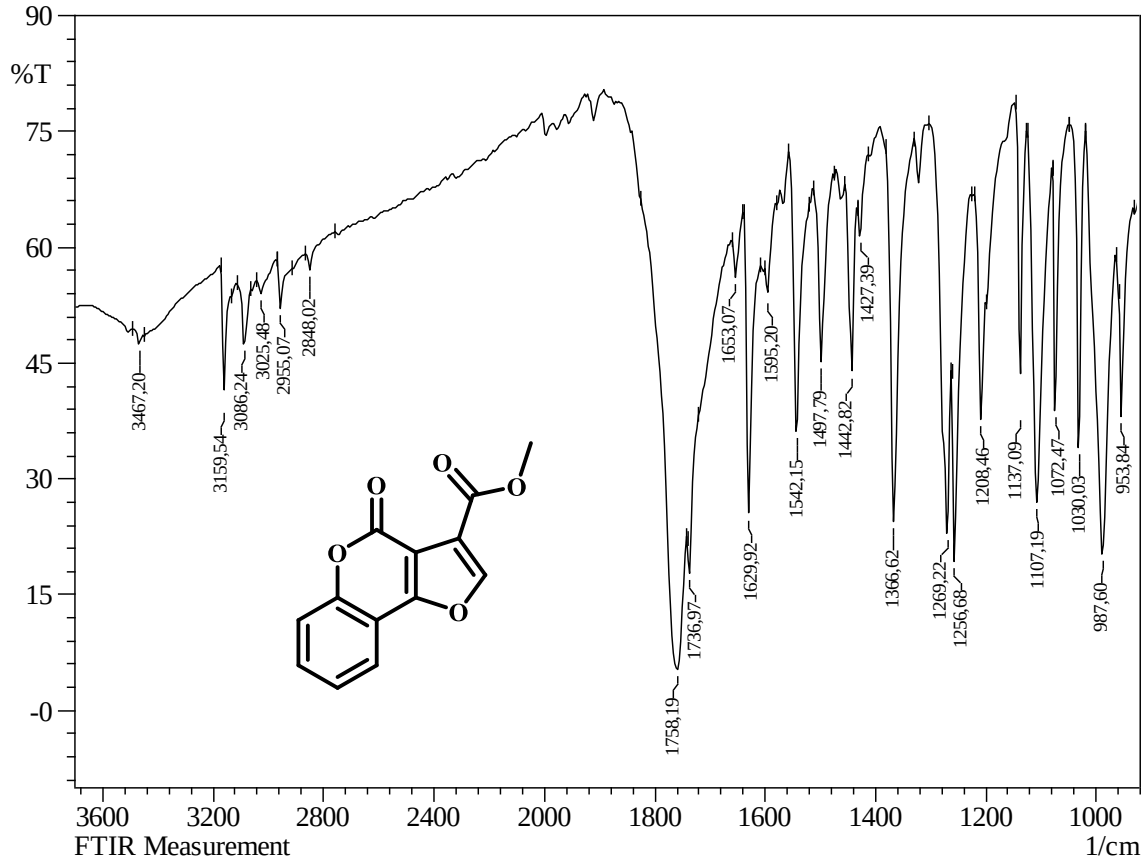
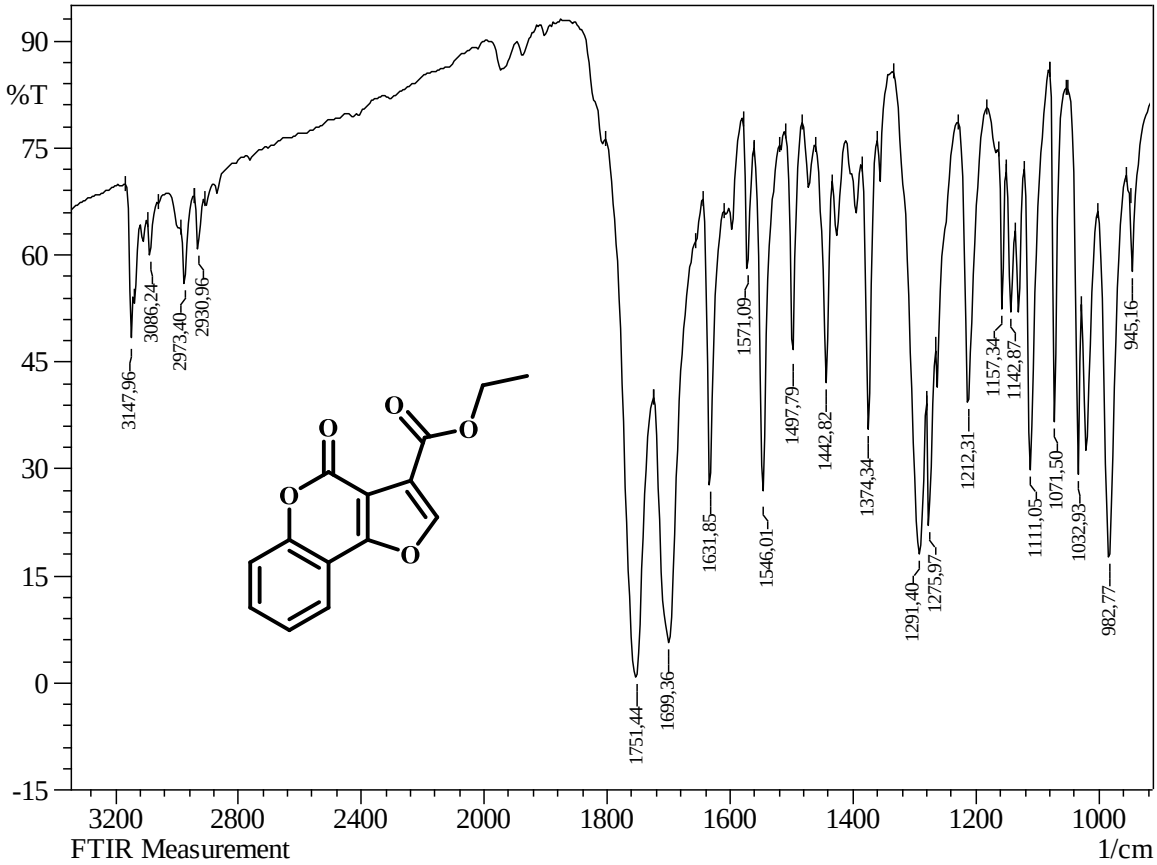


Figure S3. IR spectrum of methyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3a** in KBr.



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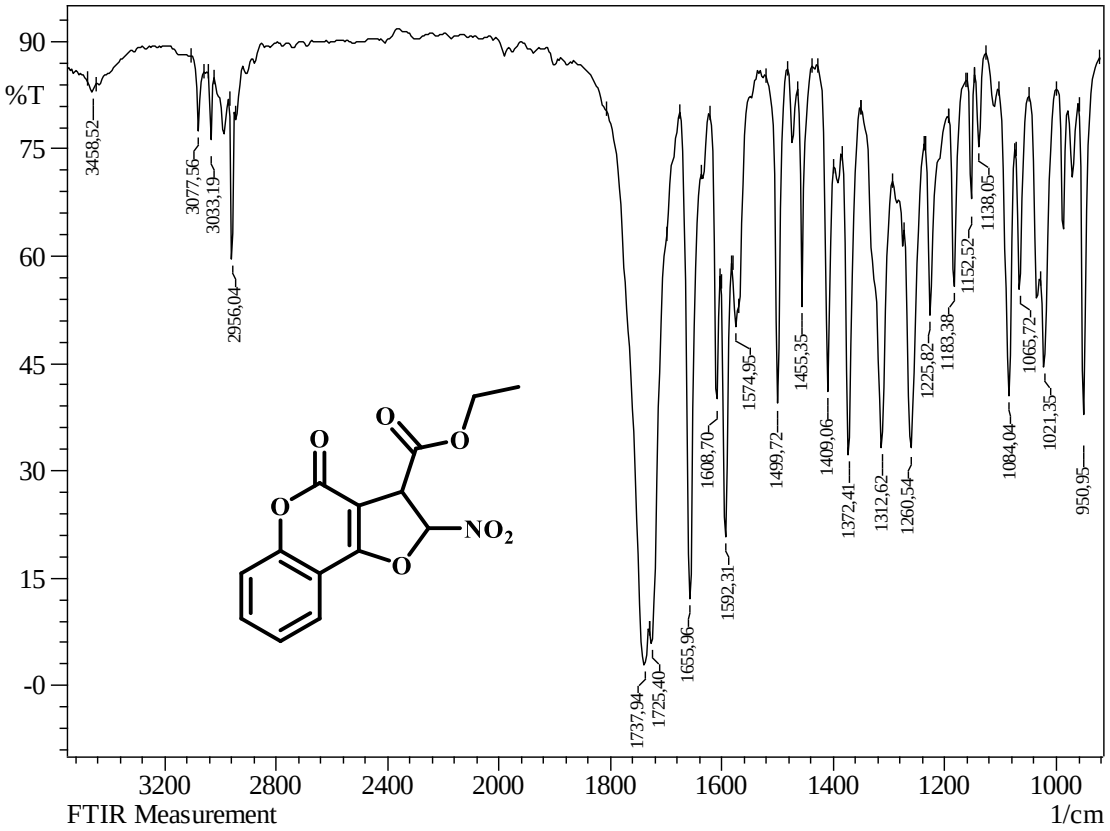

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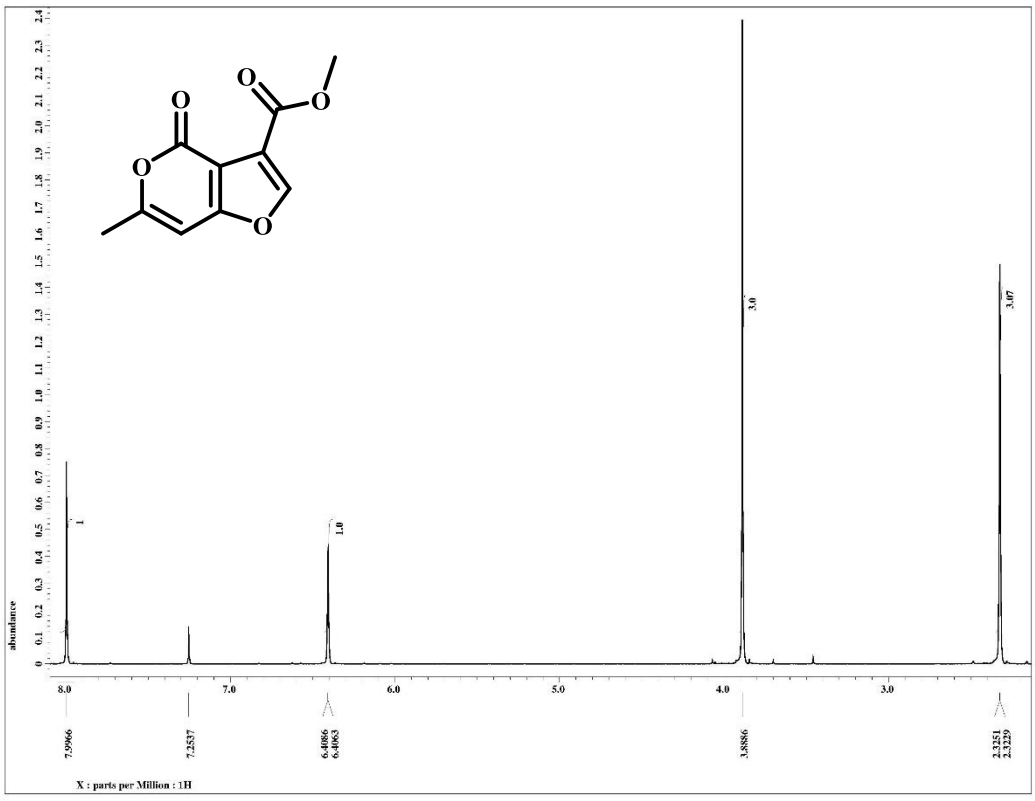

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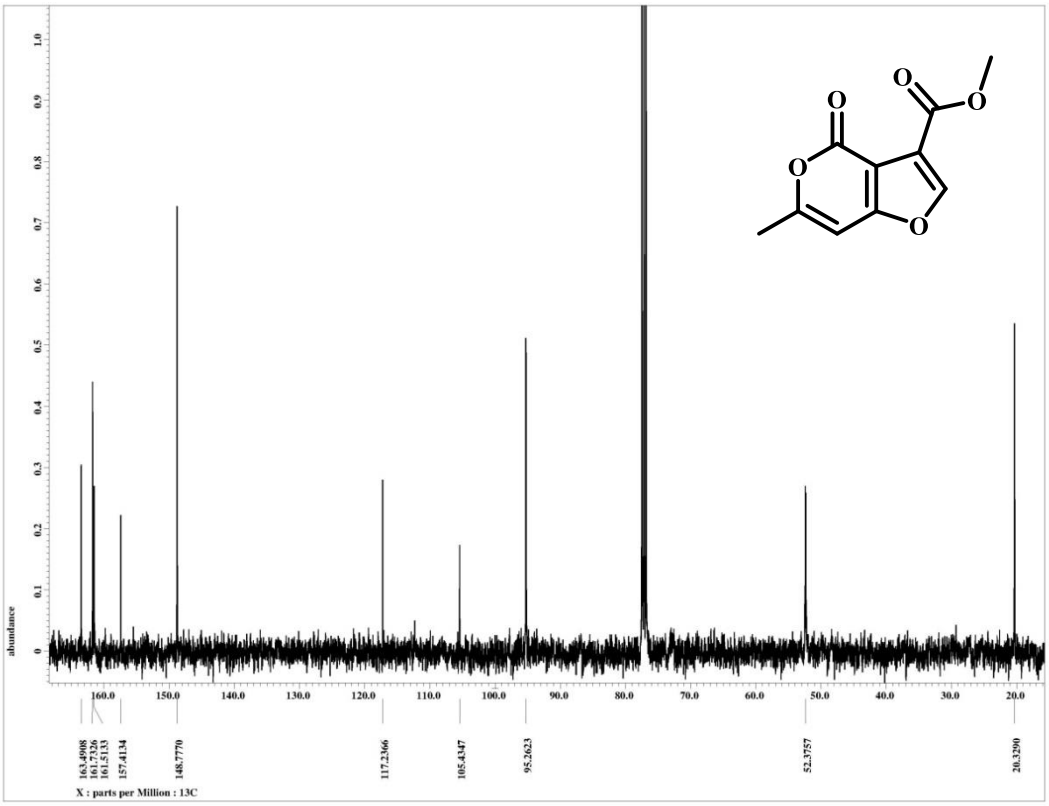

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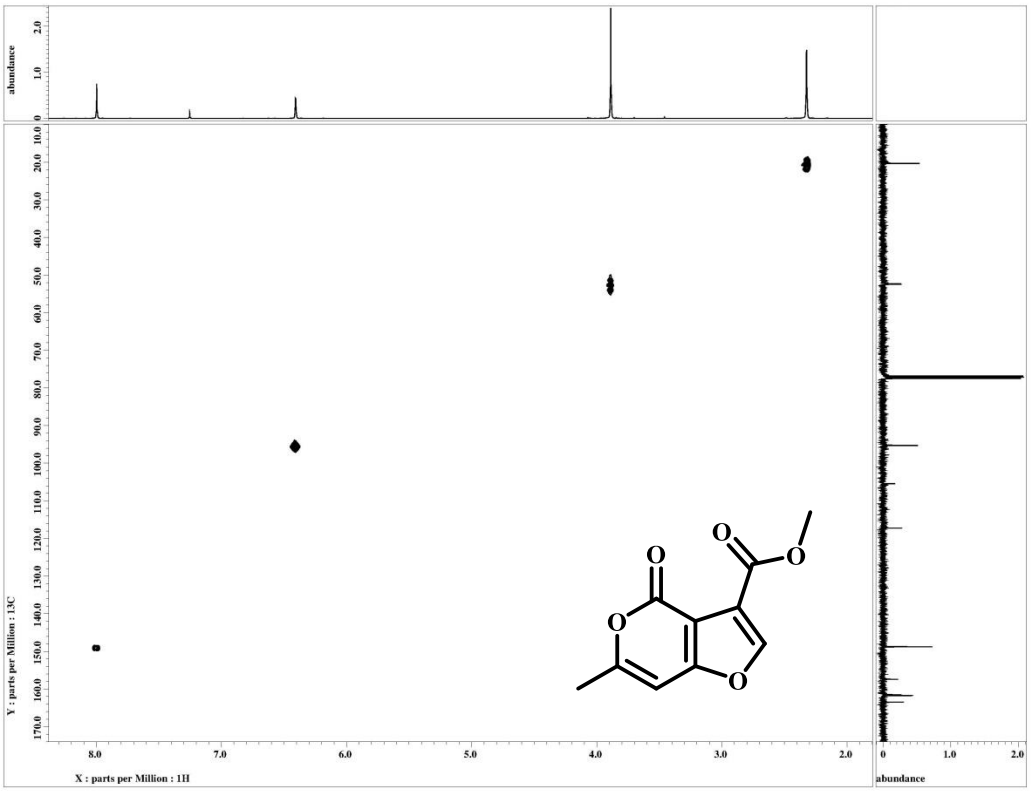

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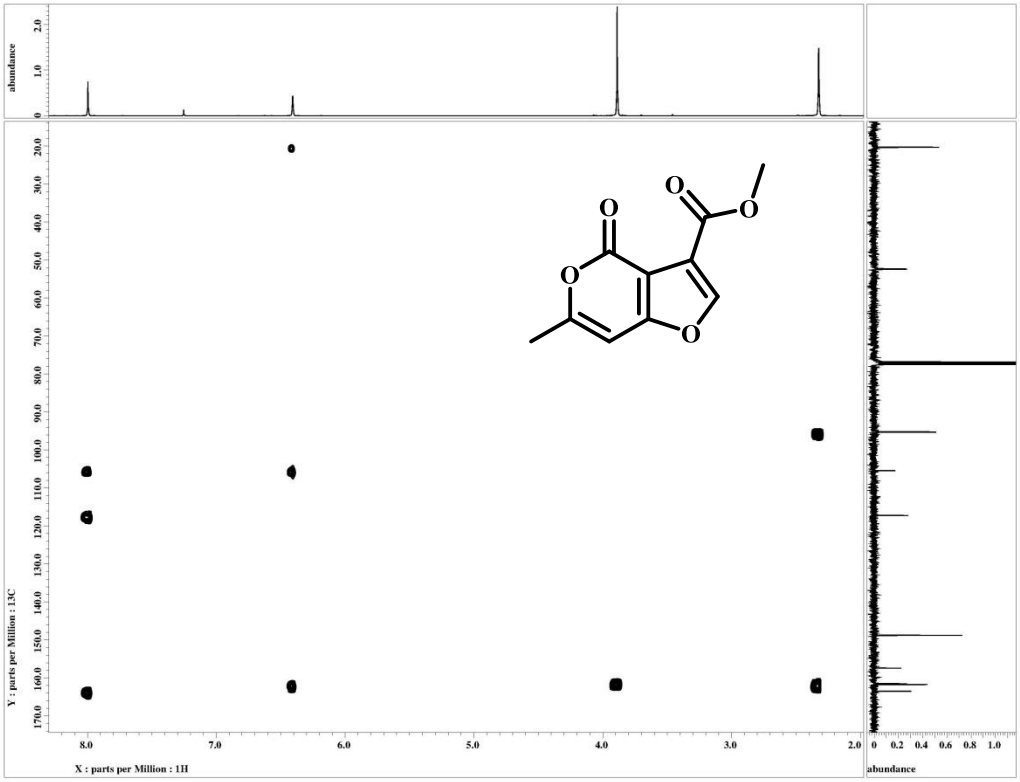

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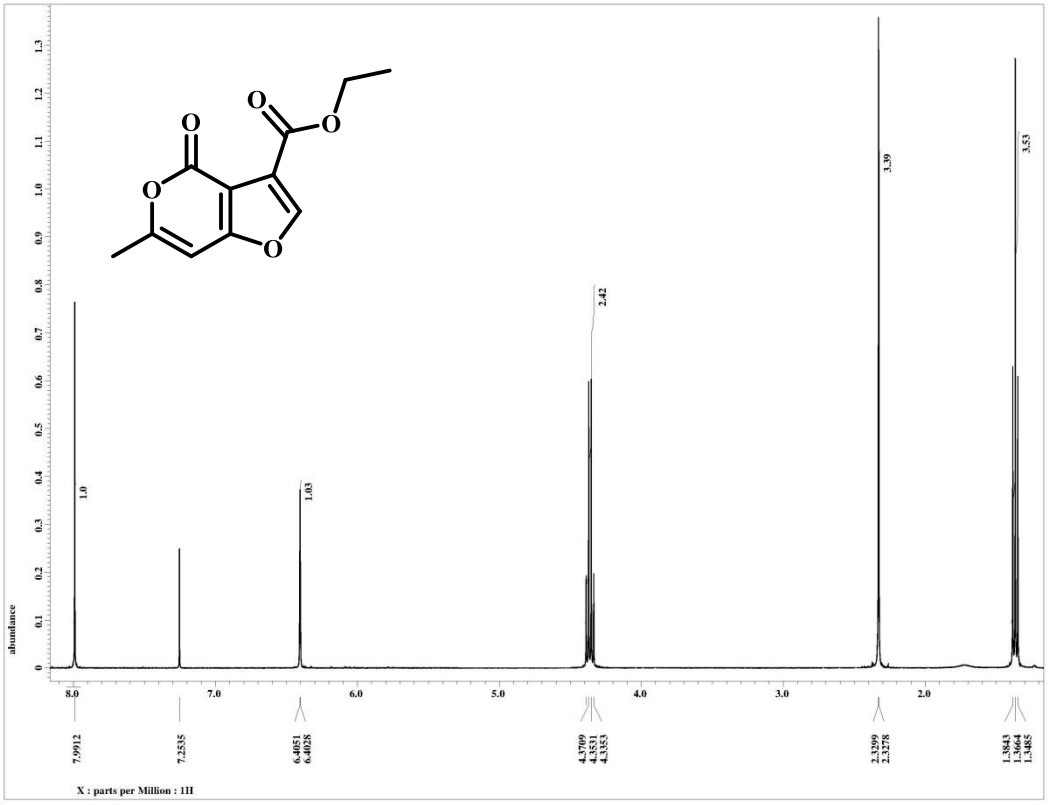


Figure S10. ^{1}H NMR spectrum of ethyl 6-methyl-4-oxo-4*H*-furo[3,2-*c*]pyran-3-carboxylate **2b** in $CDCl_3$.

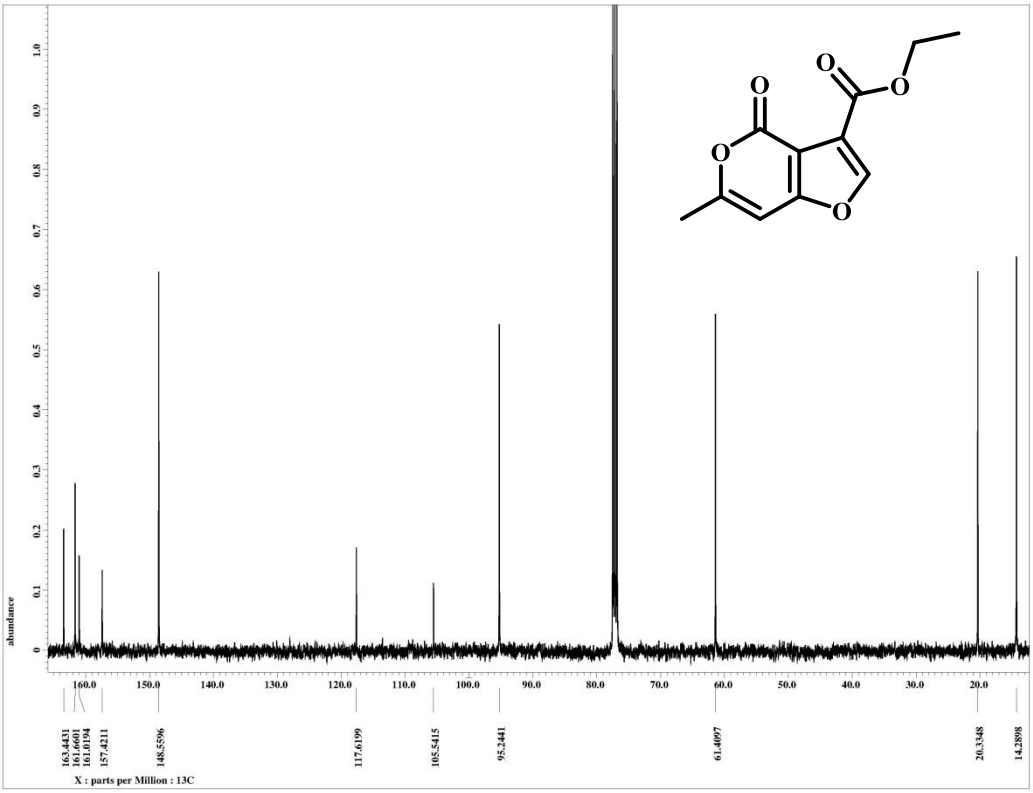
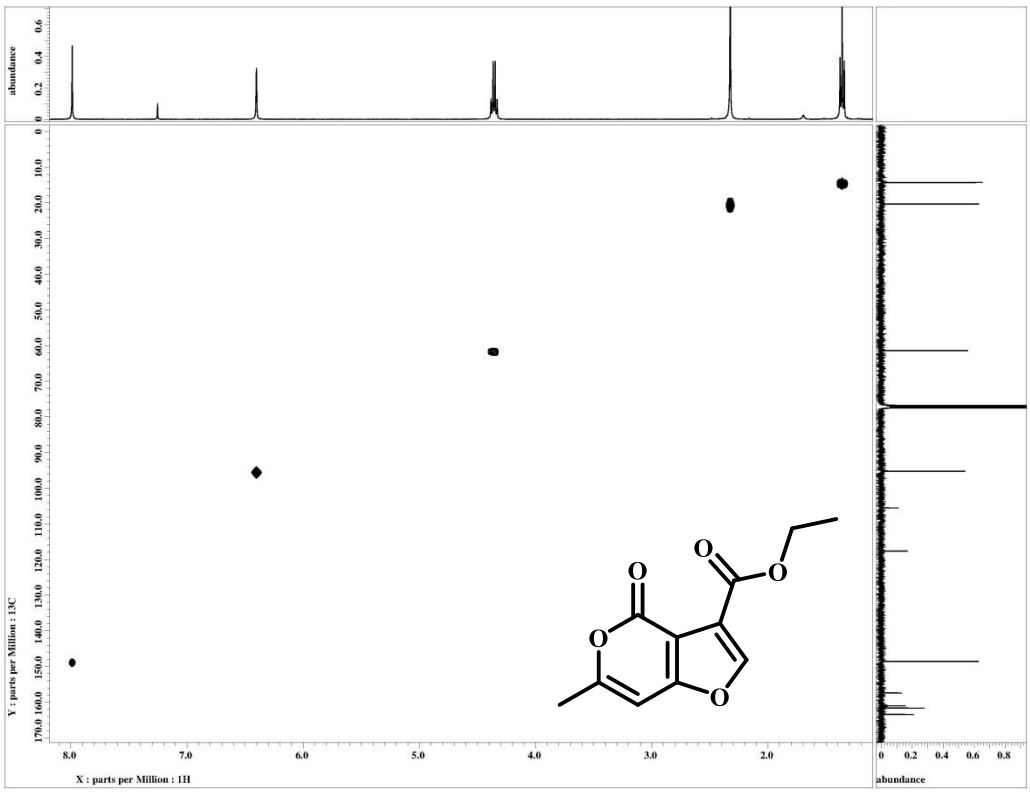


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 6-methyl-4-oxo-4*H*-furo[3,2-*c*]pyran-3-carboxylate **2b** in $CDCl_3$.



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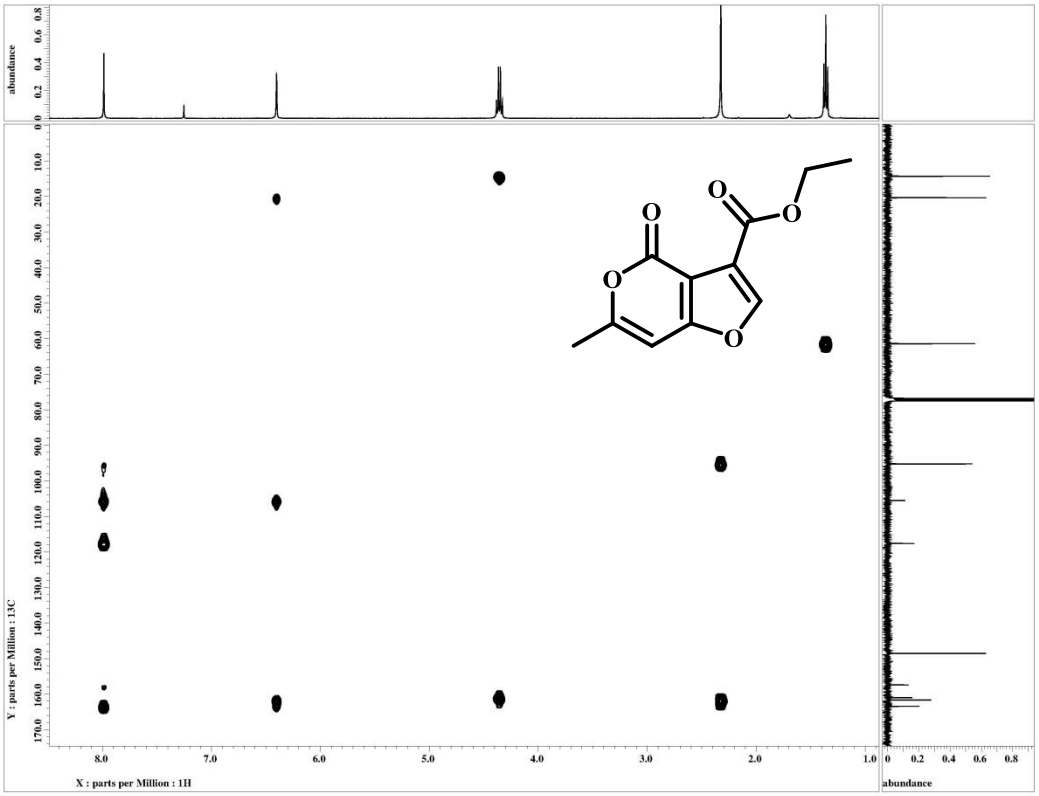

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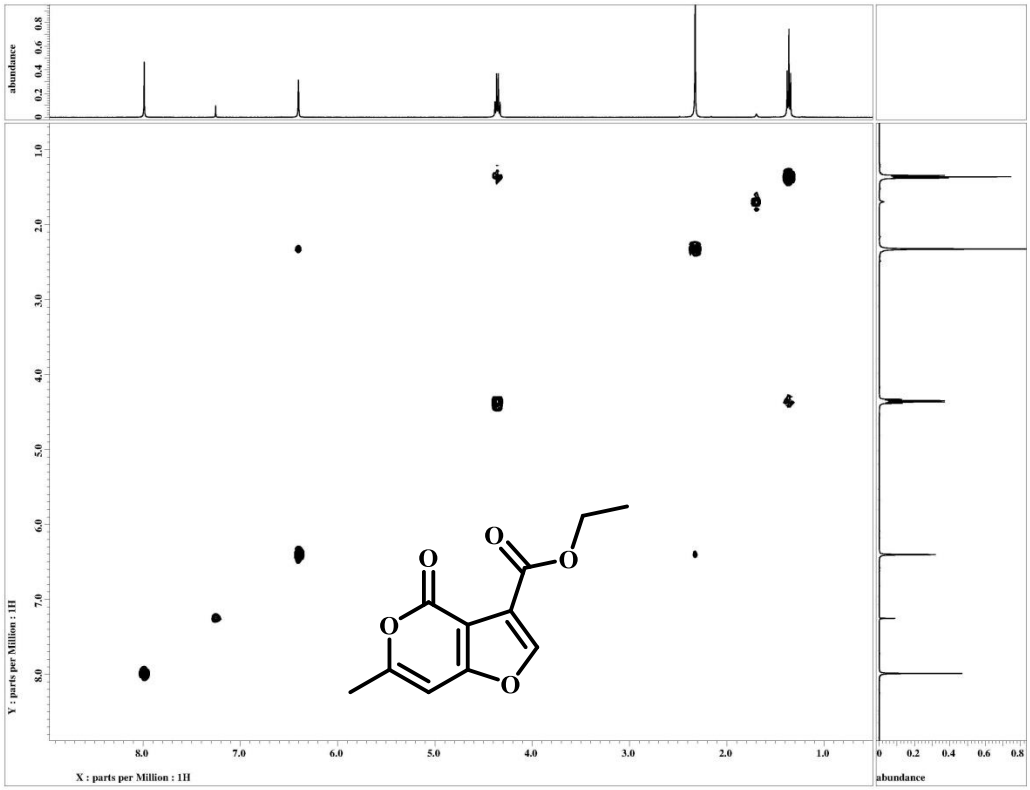

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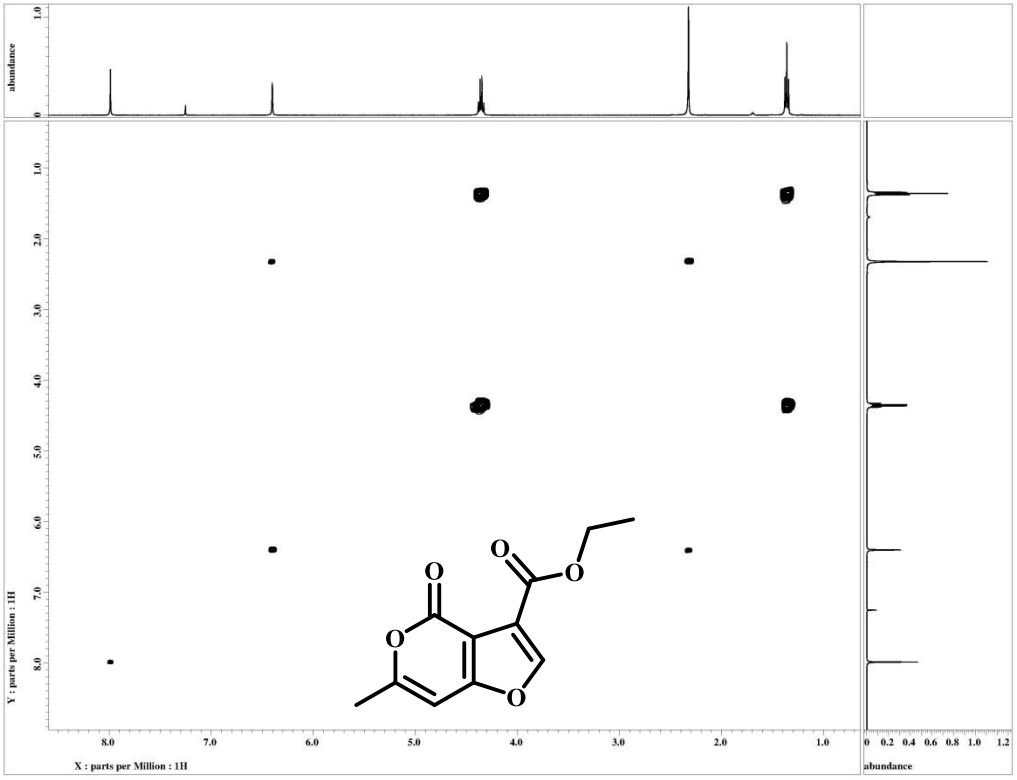

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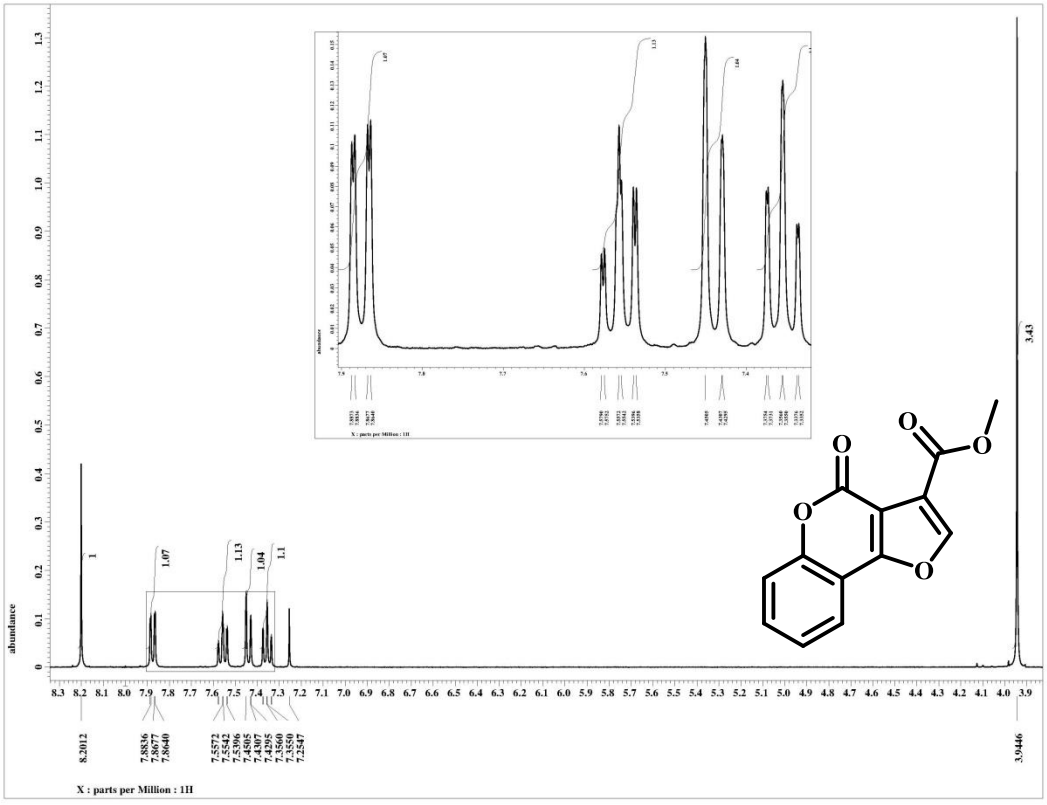


Figure S16. ^{1}H NMR spectrum of methyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3a** in $CDCl_3$.

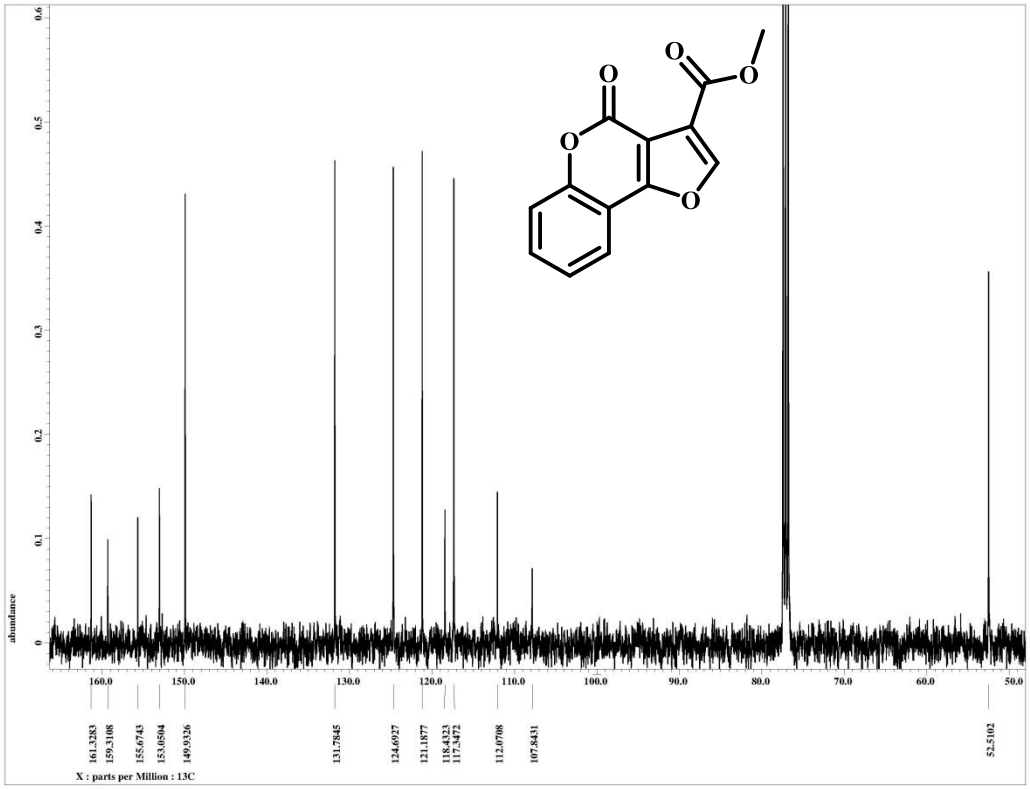


Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of methyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3a** in $CDCl_3$.

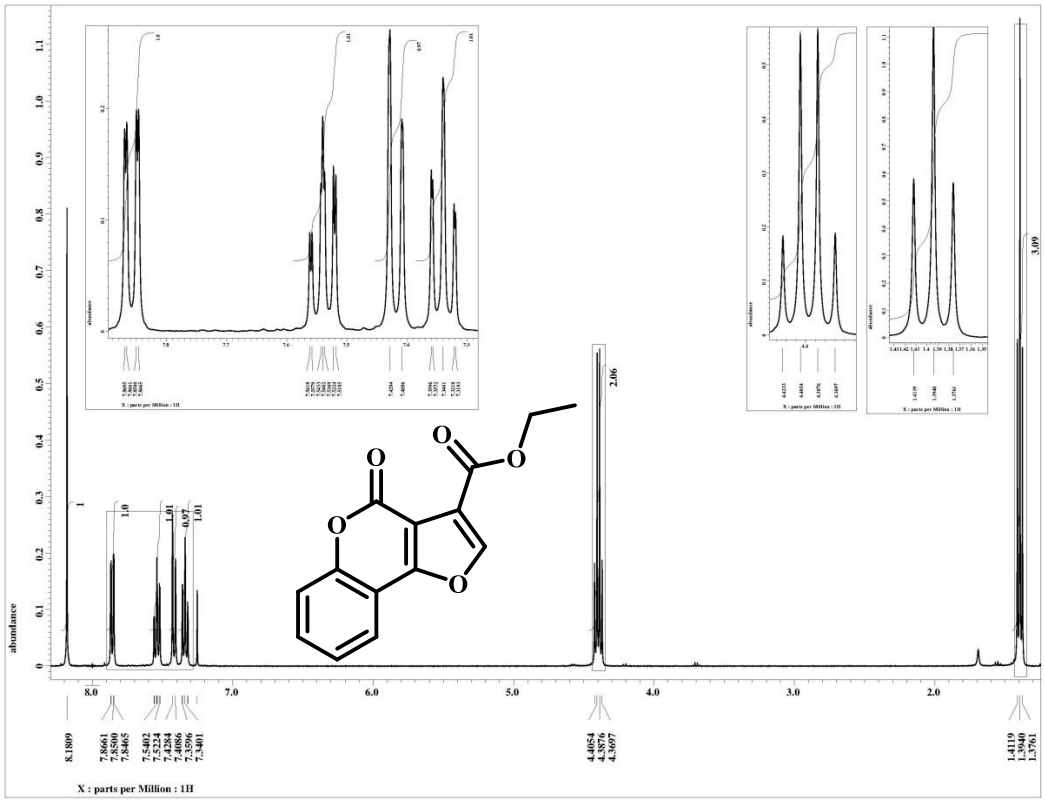


Figure S18. ^{1}H NMR spectrum of ethyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3b** in $CDCl_3$.

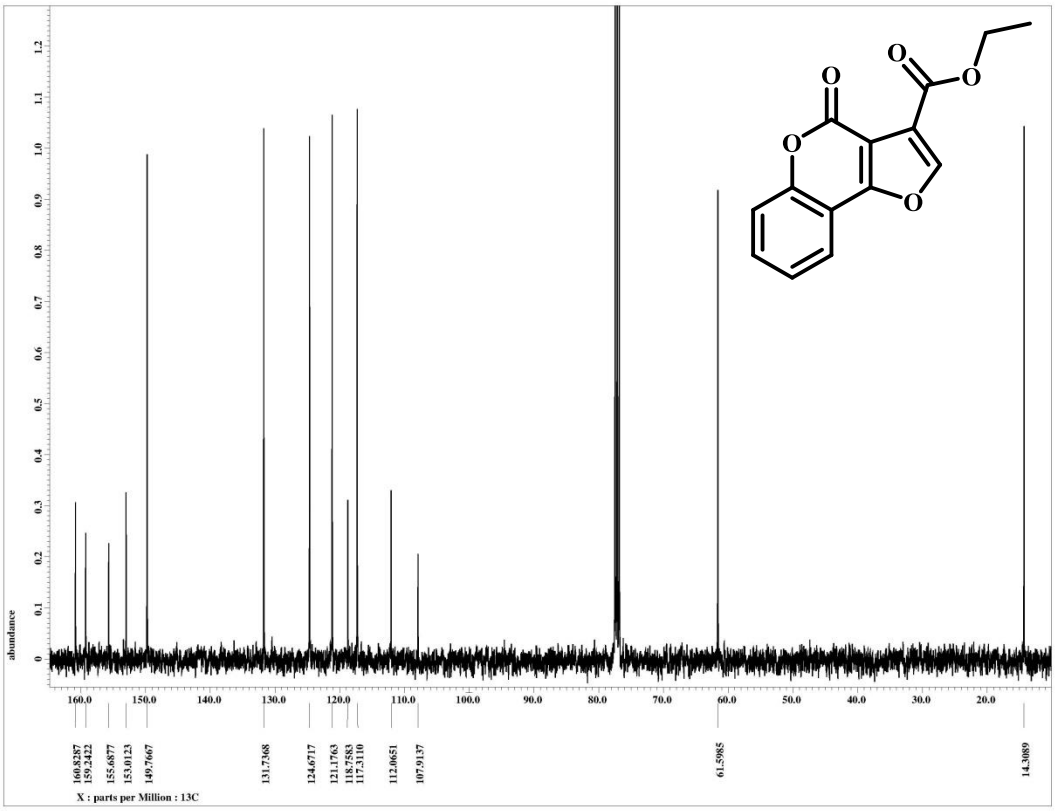


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3b** in $CDCl_3$.

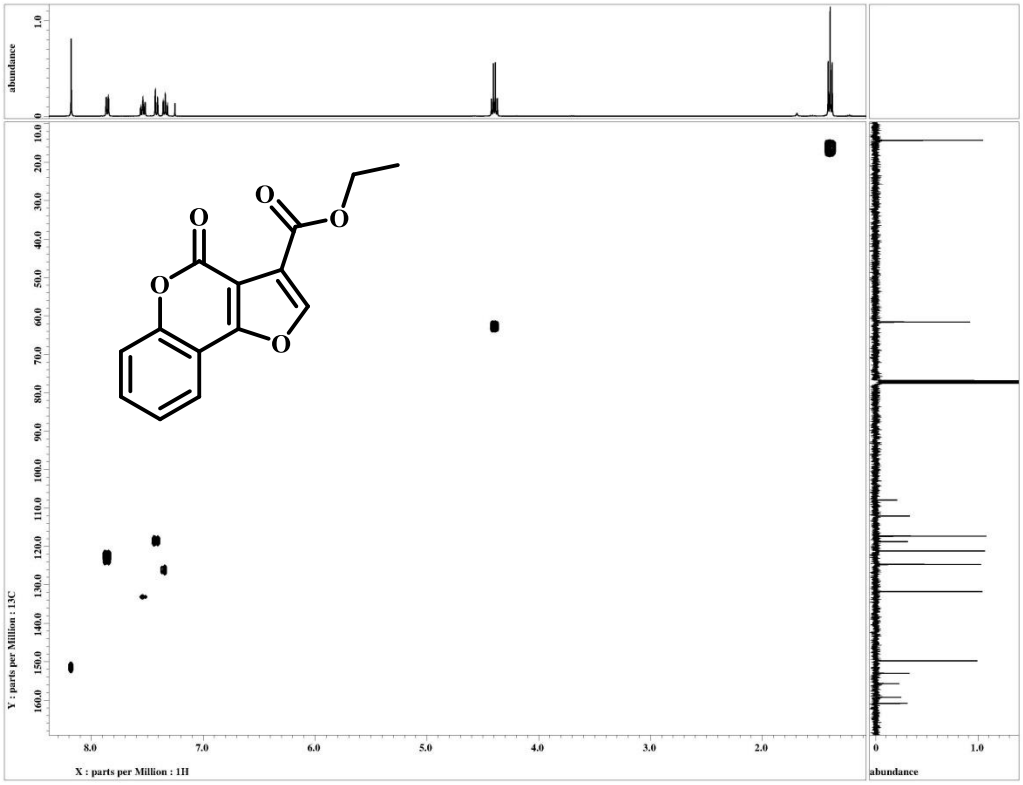


Figure S20. ^{1}H-^{13}C HMQC spectrum of ethyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3b** in $CDCl_3$.

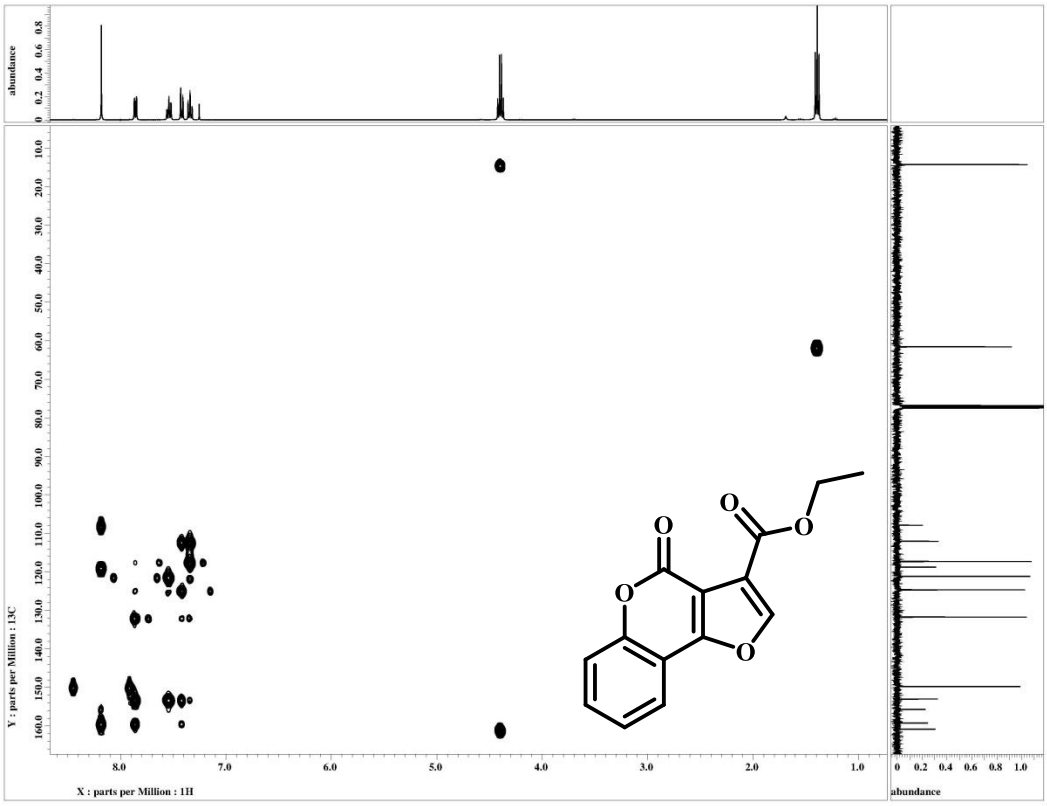


Figure S21. ^{1}H-^{13}C HMBC spectrum of ethyl 4-oxo-4*H*-furo[3,2-*c*]chromene-3-carboxylate **3b** in $CDCl_3$.

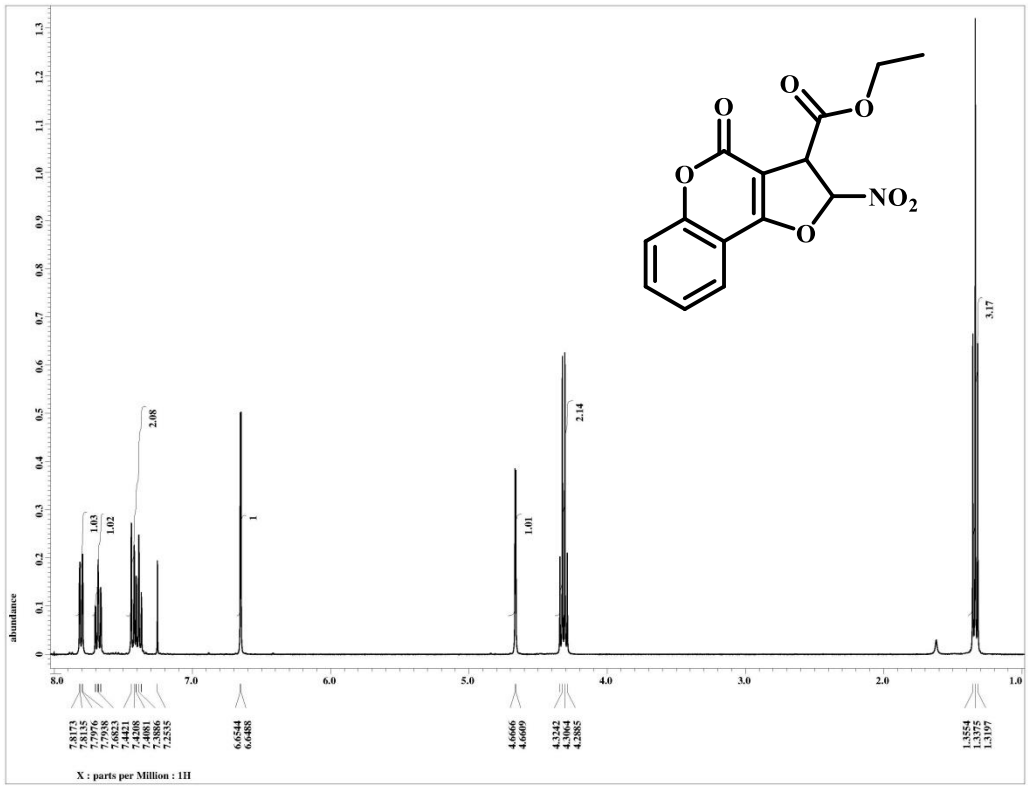


Figure S22. ^{1}H NMR spectrum of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** in $CDCl_3$.

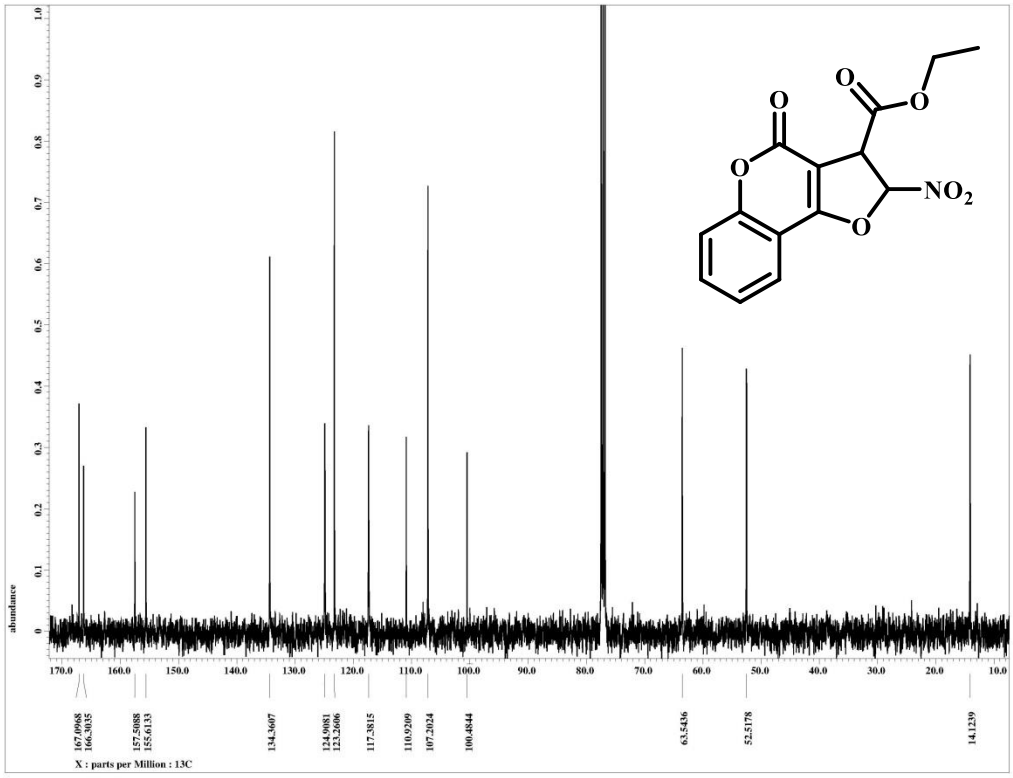


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** in $CDCl_3$.

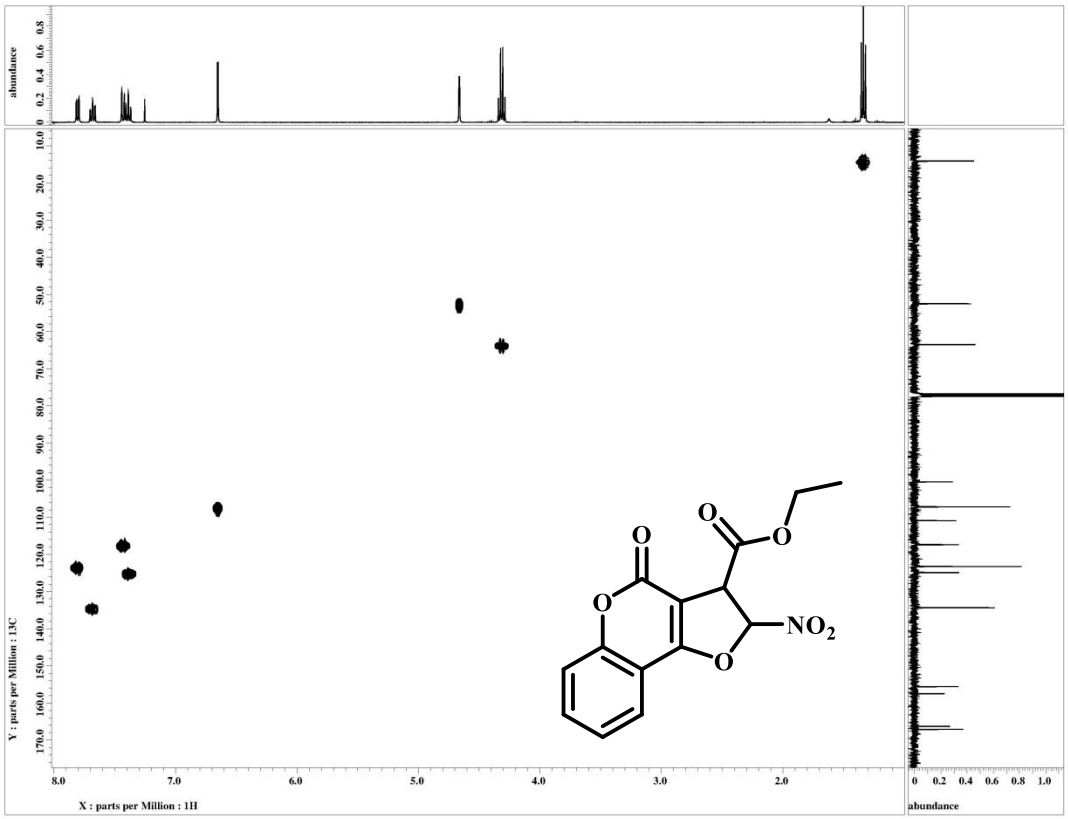


Figure S24. ^{1}H-^{13}C HMQC spectrum of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** in $CDCl_3$.

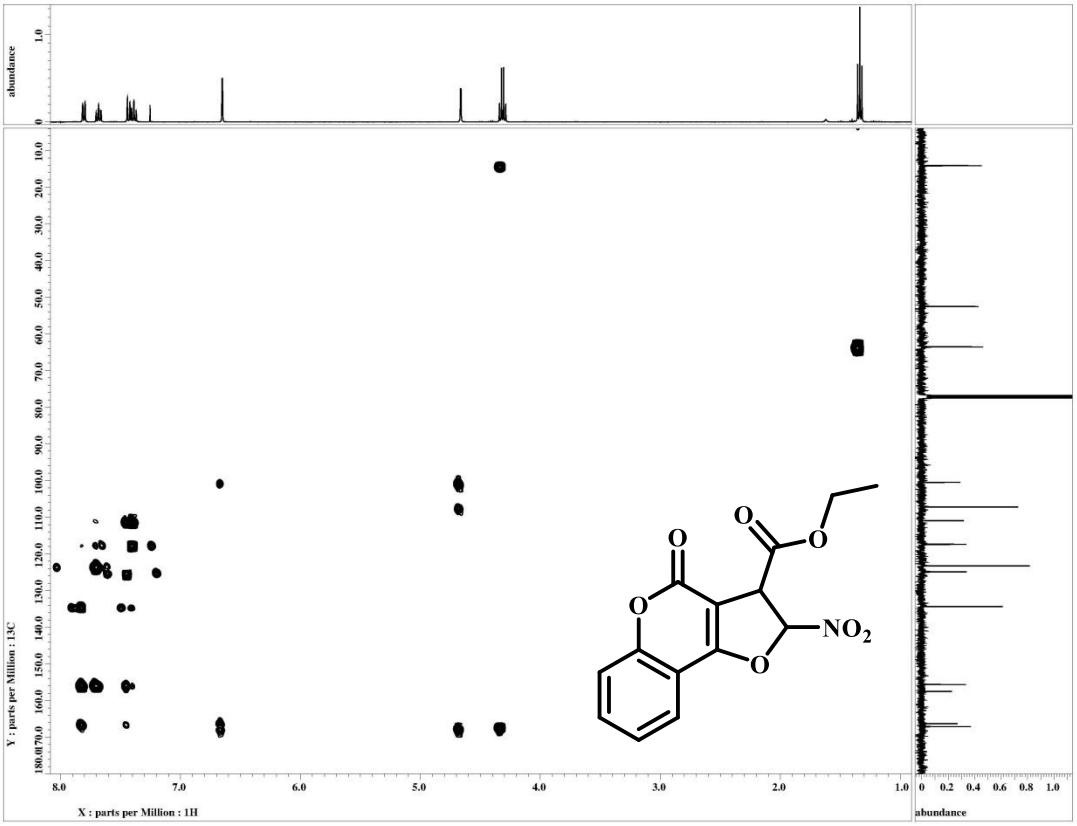


Figure S25. ^{1}H-^{13}C HMBC spectrum of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** in $CDCl_3$.

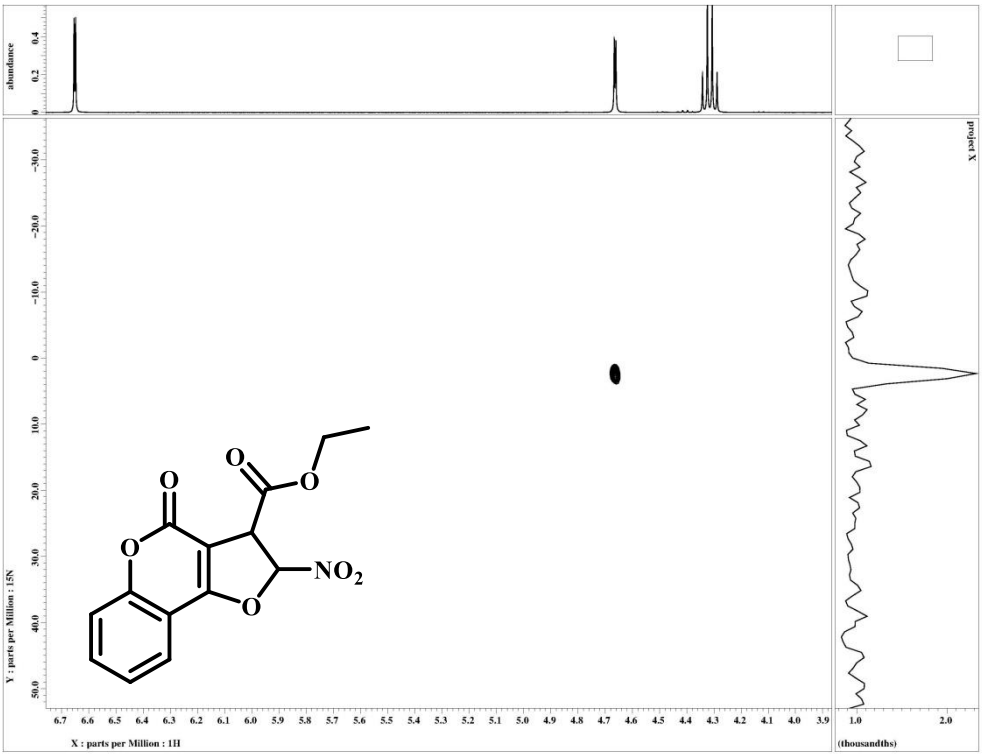
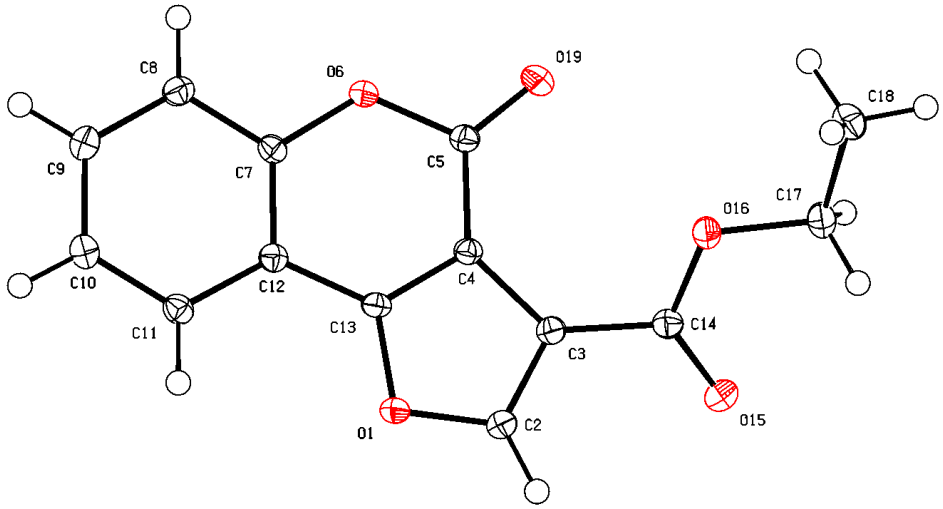


Figure S26. ^{1}H-^{15}N HMBC spectrum of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** in $CDCl_3$.

Table S1. Torsion angles (τ) in the molecule of compound **3b**



Angle	τ/deg	Angle	τ/deg
C13–O1–C2–H2	-178.68	C8–C7–C12–C13	179.39(8)
C13–O1–C2–C3	1.3(1)	C7–C8–C9–H9	-179.78
C2–O1–C13–C4	-1.0(1)	C7–C8–C9–C10	0.2(1)
C2–O1–C13–C12	177.88(8)	H8–C8–C9–H9	0.2
O1–C2–C3–C4	-1.1(1)	H8–C8–C9–C10	-179.8
O1–C2–C3–C14	175.80(8)	C8–C9–C10–H10	179.2
H2–C2–C3–C4	178.86	C8–C9–C10–C11	-0.8(2)
H2–C2–C3–C14	-4.2	H9–C9–C10–H10	-0.8
C2–C3–C4–C5	-174.0(1)	H9–C9–C10–C11	179.2
C2–C3–C4–C13	0.5(1)	C9–C10–C11–H11	-179.57
C14–C3–C4–C5	9.5(2)	C9–C10–C11–C12	0.4(1)
C14–C3–C4–C13	-175.9(1)	H10–C10–C11–H11	0.4
C2–C3–C14–O15	31.4(1)	H10–C10–C11–C12	-179.58
C2–C3–C14–O16	-145.79(9)	C10–C11–C12–C7	0.5(1)
C4–C3–C14–O15	-152.7(1)	C10–C11–C12–C13	179.95(9)
C4–C3–C14–O16	30.2(1)	H11–C11–C12–C7	-179.50
C3–C4–C5–O6	174.61(9)	H11–C11–C12–C13	-0.1
C3–C4–C5–O19	-5.1(2)	C7–C12–C13–O1	-175.56(8)
C13–C4–C5–O6	0.7(1)	C7–C12–C13–C4	3.1(1)
C13–C4–C5–O19	-179.03(9)	C11–C12–C13–O1	5.0(1)
C3–C4–C13–O1	0.3(1)	C11–C12–C13–C4	-176.34(9)
C3–C4–C13–C12	-178.55(8)	C3–C14–O16–C17	178.61(8)
C5–C4–C13–O1	175.75(8)	O15–C14–O16–C17	1.5(1)
C5–C4–C13–C12	-3.1(1)	C14–O16–C17–H17A	69.1
C4–C5–O6–C7	1.4(1)	C14–O16–C17–H17B	-50.9
O19–C5–O6–C7	-178.85(8)	C14–O16–C17–C18	-170.88(8)
C5–O6–C7–C8	178.41(8)	O16–C17–C18–H18A	-175.52
C5–O6–C7–C12	-1.3(1)	O16–C17–C18–H18B	64.5
O6–C7–C8–H8	1.0	O16–C17–C18–H18C	-55.5
O6–C7–C8–C9	-178.95(8)	H17A–C17–C18–H18A	-55.5
C12–C7–C8–H8	-179.29	H17A–C17–C18–H18B	-175.50
C12–C7–C8–C9	0.7(1)	H17A–C17–C18–H18C	64.5
O6–C7–C12–C11	178.57(8)	H17B–C17–C18–H18A	64.5
O6–C7–C12–C13	-0.9(1)	H17B–C17–C18–H18B	-55.5
C8–C7–C12–C11	-1.1(1)	H17B–C17–C18–H18C	-175.53

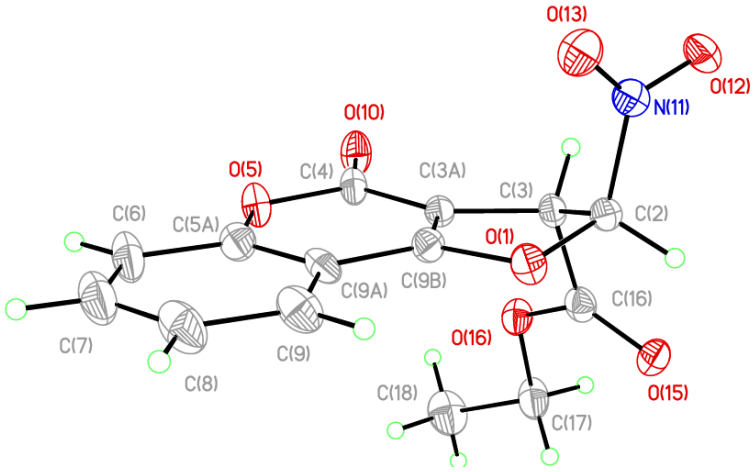
Table S2. Angles (τ) in the molecule of compound **3b**

Angle	τ/deg	Angle	τ/deg
C2–O1–C13	106.06(7)	C10–C11–H11	120.27
O1–C2–H2	124.34	C10–C11–C12	119.47(9)
O1–C2–C3	111.32(8)	H11–C11–C12	120.26
H2–C2–C3	124.34	C7–C12–C11	119.68(8)
C2–C3–C4	105.52(8)	C7–C12–C13	113.69(8)
C2–C3–C14	121.54(8)	C11–C12–C13	126.63(8)
C4–C3–C14	132.85(8)	O1–C13–C4	111.23(8)
C3–C4–C5	133.97(8)	O1–C13–C12	123.78(8)
C3–C4–C13	105.85(8)	C4–C13–C12	124.98(8)
C5–C4–C13	119.97(8)	C3–C14–O15	123.22(9)
C4–C5–O6	114.67(7)	C3–C14–O16	112.19(8)
C4–C5–O19	128.19(9)	O15–C14–O16	124.53(9)
O6–C5–O19	117.14(8)	C14–O16–C17	116.02(8)
C5–O6–C7	124.28(7)	O16–C17–H17A	110.34
O6–C7–C8	116.64(8)	O16–C17–H17B	110.34
O6–C7–C12	122.32(8)	O16–C17–C18	106.91(8)
C8–C7–C12	121.03(8)	H17A–C17–H17B	108.6
C7–C8–H8	120.74	H17A–C17–C18	110.34
C7–C8–C9	118.52(9)	H17B–C17–C18	110.34
H8–C8–C9	120.74	C17–C18–H18A	109.47
C8–C9–H9	119.4	C17–C18–H18B	109.47
C8–C9–C10	121.22(9)	C17–C18–H18C	109.47
H9–C9–C10	119.4	H18A–C18–H18B	109.5
C9–C10–H10	120.0	H18A–C18–H18C	109.5
C9–C10–C11	120.06(9)	H18B–C18–H18C	109.5
H10–C10–C11	120.0		

Table S3. Bond lengths (*d*) in the molecule of compound **3b**

Bond	*d*/Å	Bond	*d*/Å
O1–C2	1.370(1)	C9–C10	1.400(1)
O1–C13	1.358(1)	C10–H10	0.9500
C2–H2	0.9499	C10–C11	1.385(1)
C2–C3	1.360(1)	C11–H11	0.9500
C3–C4	1.443(1)	C11–C12	1.403(1)
C3–C14	1.479(1)	C12–C13	1.427(1)
C4–C5	1.454(1)	C14–O15	1.212(1)
C4–C13	1.365(1)	C14–O16	1.330(1)
C5–O6	1.389(1)	O16–C17	1.457(1)
C5–O19	1.202(1)	C17–H17A	0.990
O6–C7	1.3789(9)	C17–H17B	0.990
C7–C8	1.390(1)	C17–C18	1.505(2)
C7–C12	1.403(1)	C18–H18A	0.9801
C8–H8	0.9499	C18–H18B	0.980
C8–C9	1.389(1)	C18–H18C	0.980
C9–H9	0.950		

Table S4. Torsion angles (τ) in the molecule of compound **4**



Angle	τ/deg	Angle	τ/deg
C9B–O1–C2–H2A	-144.4	C4–O5–C5A–C9A	-0.7(8)
C9B–O1–C2–C3	-23.9(5)	O5–C5A–C6–H6A	0.8
C9B–O1–C2–N11	94.2(5)	O5–C5A–C6–C7	-179.1(5)
C2–O1–C9B–C3A	13.1(6)	C9A–C5A–C6–H6A	-179.5
C2–O1–C9B–C9A	-168.6(5)	C9A–C5A–C6–C7	0.5(9)
O1–C2–C3–C3A	24.7(5)	O5–C5A–C9A–C9B	-0.2(8)
O1–C2–C3–H3A	142.7	O5–C5A–C9A–C9	179.6(5)
O1–C2–C3–C16	-92.8(5)	C6–C5A–C9A–C9B	-179.9(5)
H2A–C2–C3–C3A	145.2	C6–C5A–C9A–C9	-0.1(9)
H2A–C2–C3–H3A	-96.9	C5A–C6–C7–H7A	178.9
H2A–C2–C3–C16	27.7	C5A–C6–C7–C8	-1.1(9)
N11–C2–C3–C3A	-92.8(5)	H6A–C6–C7–H7A	-1
N11–C2–C3–H3A	25.2	H6A–C6–C7–C8	178.9
N11–C2–C3–C16	149.7(4)	C6–C7–C8–H8A	-178.8
O1–C2–N11–O12	173.9(4)	C6–C7–C8–C9	1(1)
O1–C2–N11–O13	-5.5(6)	H7A–C7–C8–H8A	1
H2A–C2–N11–O12	52.5	H7A–C7–C8–C9	-178.8
H2A–C2–N11–O13	-126.9	C7–C8–C9–C9A	-0.7(9)
C3–C2–N11–O12	-69.5(5)	C7–C8–C9–H9A	179.3
C3–C2–N11–O13	111.1(5)	H8A–C8–C9–C9A	179.3
C4–C3A–C3–C2	163.8(5)	H8A–C8–C9–H9A	-1
C4–C3A–C3–H3A	45.9	O1–C9B–C9A–C5A	-179.9(5)
C4–C3A–C3–C16	-80.4(7)	O1–C9B–C9A–C9	0.3(9)
C9B–C3A–C3–C2	-17.0(5)	C3A–C9B–C9A–C5A	-1.8(8)
C9B–C3A–C3–H3A	-135.0	C3A–C9B–C9A–C9	178.5(6)
C9B–C3A–C3–C16	98.7(5)	C5A–C9A–C9–C8	0.2(9)
C3–C3A–C4–O5	174.0(5)	C5A–C9A–C9–H9A	-179.9
C3–C3A–C4–O10	-7(1)	C9B–C9A–C9–C8	179.9(6)
C9B–C3A–C4–O5	-5.0(7)	C9B–C9A–C9–H9A	-0
C9B–C3A–C4–O10	174.5(5)	C17–O16–C16–C3	-177.5(4)
C3–C3A–C9B–O1	3.6(6)	C17–O16–C16–O15	1.7(8)
C3–C3A–C9B–C9A	-174.6(5)	C16–O16–C17–H17A	42.9
C4–C3A–C9B–O1	-177.2(5)	C16–O16–C17–H17B	-76.8
C4–C3A–C9B–C9A	4.6(8)	C16–O16–C17–C18	163.1(5)
C2–C3–C16–O15	-20.4(7)	O16–C17–C18–H18A	176.6

Table S4 *(continued)*

C2–C3–C16–O16	158.9(4)	O16–C17–C18–H18B	56.5
C3A–C3–C16–O15	-129.6(5)	O16–C17–C18–H18C	-63.5
C3A–C3–C16–O16	49.7(6)	H17A–C17–C18–H18A	-63.3
H3A–C3–C16–O15	104.1	H17A–C17–C18–H18B	176.7
H3A–C3–C16–O16	-76.6	H17A–C17–C18–H18C	56.7
C3A–C4–O5–C5A	3.2(7)	H17B–C17–C18–H18A	56.4
O10–C4–O5–C5A	-176.3(5)	H17B–C17–C18–H18B	-63.6
C4–O5–C5A–C6	179.0(5)	H17B–C17–C18–H18C	176.4

Table S5. Angles (τ) in the molecule of compound **4**

Angle	**τ/deg**	**Angle**	**τ/deg**
C2–O1–C9B	105.5(4)	C7–C8–C9	120.2(6)
O1–C2–H2A	110.5	H8A–C8–C9	119.9
O1–C2–C3	107.1(4)	O1–C9B–C3A	113.4(5)
O1–C2–N11	108.5(4)	O1–C9B–C9A	122.2(5)
H2A–C2–C3	110.5	C3A–C9B–C9A	124.4(5)
H2A–C2–N11	110.5	C5A–C9A–C9B	113.4(5)
C3–C2–N11	109.5(4)	C5A–C9A–C9	120.5(5)
C3–C3A–C4	130.7(5)	C9B–C9A–C9	126.1(5)
C3–C3A–C9B	108.3(5)	C8–C9–C9A	118.9(5)
C4–C3A–C9B	121.0(5)	C8–C9–H9A	120.5
C2–C3–C3A	99.2(4)	C9A–C9–H9A	120.6
C2–C3–H3A	111.8	C2–N11–O12	114.3(4)
C2–C3–C16	109.7(4)	C2–N11–O13	120.5(4)
C3A–C3–H3A	111.7	O12–N11–O13	125.1(4)
C3A–C3–C16	112.0(4)	C16–O16–C17	116.0(4)
H3A–C3–C16	111.8	C3–C16–O15	123.0(5)
C3A–C4–O5	115.1(5)	C3–C16–O16	111.0(4)
C3A–C4–O10	127.5(5)	O15–C16–O16	126.0(5)
O5–C4–O10	117.4(5)	O16–C17–H17A	110.2
C4–O5–C5A	122.9(4)	O16–C17–H17B	110.2
O5–C5A–C6	116.6(5)	O16–C17–C18	107.5(5)
O5–C5A–C9A	123.1(5)	H17A–C17–H17B	108.5
C6–C5A–C9A	120.4(5)	H17A–C17–C18	110.2
C5A–C6–H6A	121.0	H17B–C17–C18	110.2
C5A–C6–C7	118.1(6)	C17–C18–H18A	109.5
H6A–C6–C7	120.9	C17–C18–H18B	109.5
C6–C7–H7A	119.1	C17–C18–H18C	109.5
C6–C7–C8	121.9(6)	H18A–C18–H18B	109.5
H7A–C7–C8	119.0	H18A–C18–H18C	109.5
C7–C8–H8A	119.9	H18B–C18–H18C	109.5

Table S6. Bond lengths (*d*) in the molecule of compound **4**

Bond	*d*/Å	Bond	*d*/Å
O1–C2	1.417(6)	C7–C8	1.382(9)
O1–C9B	1.377(6)	C8–H8A	0.950
C2–H2A	1.000	C8–C9	1.375(8)
C2–C3	1.531(7)	C9B–C9A	1.432(7)
C2–N11	1.508(7)	C9A–C9	1.399(8)
C3A–C3	1.506(7)	C9–H9A	0.949
C3A–C4	1.426(7)	N11–O12	1.232(6)
C3A–C9B	1.345(7)	N11–O13	1.217(6)
C3–H3A	1.000	O15–C16	1.208(7)
C3–C16	1.532(7)	O16–C16	1.316(6)
C4–O5	1.399(6)	O16–C17	1.457(7)
C4–O10	1.210(7)	C17–H17A	0.990
O5–C5A	1.369(7)	C17–H17B	0.990
C5A–C6	1.389(8)	C17–C18	1.494(8)
C5A–C9A	1.395(8)	C18–H18A	0.980
C6–H6A	0.950	C18–H18B	0.980
C6–C7	1.386(9)	C18–H18C	0.980
C7–H7A	0.949		

Figure S27. Key correlations in the ^{1}H-^{13}C HMBC NMR spectrum of compound **2a** ($CDCl_3$).

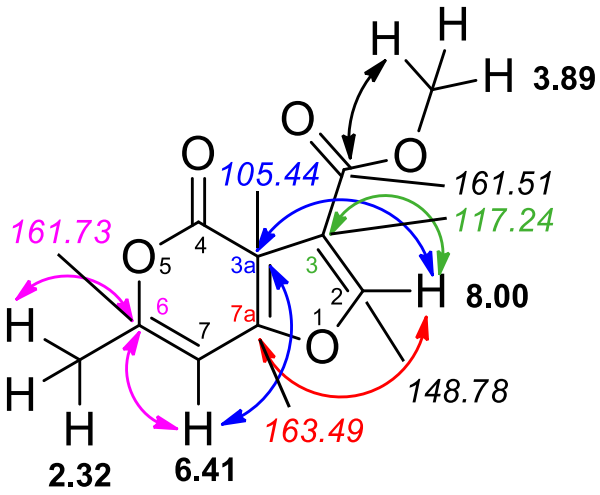
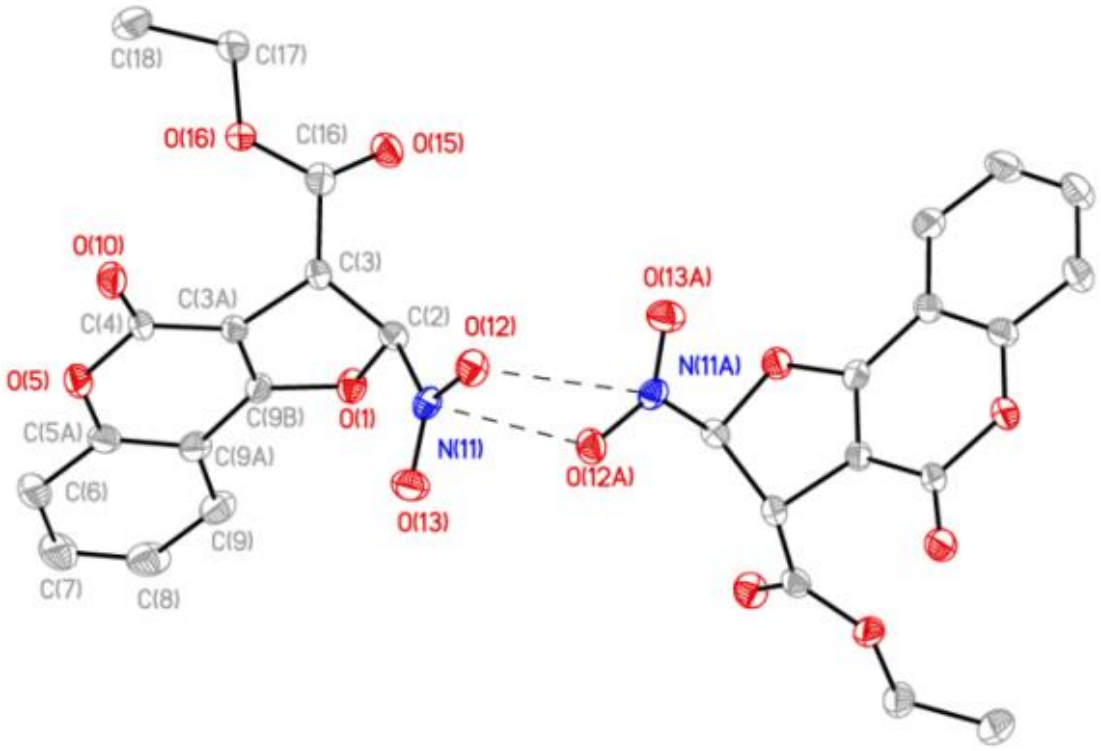
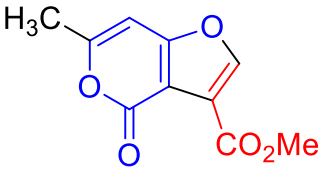


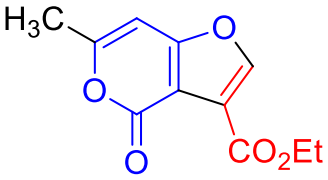
Figure S28. Intermolecular $NO_2 \cdots NO_2$ contacts in the crystals of **4**.



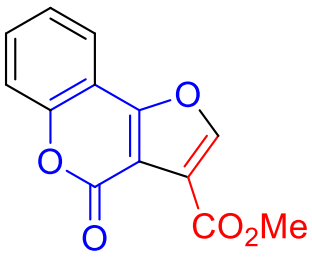
General procedure for the synthesis of 3-alkoxycarbonyl-4-oxo-4H-furo[3,2-c]pyranes and -chromenes **2, 3.** To a solution of 4-hydroxy-6-methyl-2*H*-pyran-2-one or 4-hydroxycoumarin (1.43 mmol) and freshly molten AcOK (210 mg, 2.14 mmol) in anhydrous MeOH (5 ml), a solution of the corresponding 3-bromo-3-nitroacrylate **1a,b** (1.43 mmol) in anhydrous MeOH (5 ml) was added dropwise. The resulted mixture was stirred at 18-20 °C for 3 h and then poured on crushed ice. The product was extracted with $CHCl_3$ (3×20 ml). The combined extracts were dried over $MgSO_4$, filtered and evaporated to dryness to give **2, 3** as crystalline solids.



***Methyl 6-methyl-4-oxo-4H-furo[3,2-c]pyran-3-carboxylate (2a)*:** Colorless crystalline powder, yield was 230 mg (77%), mp 174-177 °C (MeOH). IR (KBr): 1725 (C=O), 1758 (C=O) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.32 (d, 3H, ^4J = 0.9 Hz, C(6)CH_3), 3.89 (s, 3H, OCH_3), 6.41 (q, 1H, ^4J = 0.9 Hz, H-7), 8.00 (s, 1H, H-2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (C(6)CH_3), 52.4 (OCH_3), 95.3 (C-7), 105.4 (C-3a), 117.2 (C-3), 148.8 (C-2), 157.4 (C-4), 161.5 ($C{=}O_{ester}$), 161.7 (C-6), 163.5 (C-7a) ppm. Anal. Calcd for $C_{10}H_8O_5$ (M 208.17): C, 57.70; H, 3.87. Found: C, 58.1; H 3.64.

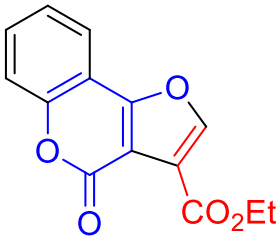


***Ethyl 6-methyl-4-oxo-4H-furo[3,2-c]pyran-3-carboxylate (2b)*:** colorless powder, yield 81%, mp 105-107 °C (EtOH). IR (KBr): 1751 (C=O) cm^{-1}; UV, λ_{max}, nm (ε, $l{\times}mol^{-1}{\times}cm^{-1}$): 228 (4900), 289 (9500). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.36 (t, 3H, ^3J = 7.1 Hz, $OCH_2C\underline{H_3}$), 2.33 (d, 3H, ^4J = 0.9 Hz, C(6)CH_3), 4.37 (q, 2H, ^3J = 7.1 Hz, $OC\underline{H_2}CH_3$), 6.40 (q, 1H, ^4J = 0.9 Hz, H-7), 7.99 (s, 1H, H-2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.3 (C(6)$\underline{C}H_3$), 14.3 ($OCH_2\underline{C}H_3$), 61.4 ($O\underline{C}H_2CH_3$), 95.3 (C-7), 105.5 (C-3a), 117.6 (C-3), 148.6 (C-2), 157.4 (C-4), 161.0 ($C{=}O_{ester}$), 161.7 (C-6), 163.5 (C-7a) ppm. Anal. Calcd for $C_{11}H_{10}O_5$ (M 222.05): C, 59.46; H, 4.54. Found: C, 60.0; H 4.27.

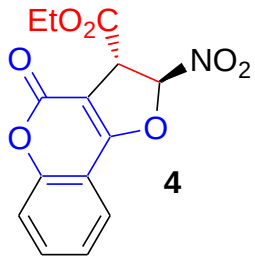


Methyl 4-oxo-4H-furo[3,2-c]chromene-3-carboxylate (3a) was prepared by analogy with the procedure for **1a** starting from 232 mg (1.43 mmol) of 4-hydroxycoumarin, 210 mg (2.14 mmol) of fused AcOK and 300 mg (1.43 mmol) of methyl 3-bromo-3-nitroacrylate **1a**. The solid resulted from the reaction mixture was filtered off, and the mother liquor was poured on ice to give additional portion of product. Overall yield was 270 mg (77%), colorless crystals, mp 171-173 °C (MeOH). IR (KBr): 1737 (C=O), 1758 (C=O) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3H, OCH_3), 7.36 (td, 1H, J = 0.9, J = 7.7 Hz, H-8), 7.44 (dd, 1H, J = 0.4, J = 8.4 Hz, H-9), 7.56 (td, 1H, J = 1.5, J = 7.9 Hz, H-7), 7.88 (dd, 1H, J = 1.5, J = 7.8 Hz, H-6), 8.20 (s, 1H, H-2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 107.8 (C-3), 112.1

(C-9a), 117.4 (C-9), 118.4 (C-3a),121.2 (C-6), 124.7 (C-8), 131.8 (C-7), 149.9 (C-2), 153.1 (C-5a), 155.7 (C-4), 159.3 (C-9b), 161.3 ($C{=}O_{ester}$) ppm. Anal. Calcd for $C_{13}H_8O_5$ (M 244.04): C, 63.94; H, 3.30. Found: C, 64.33; H 3.23.

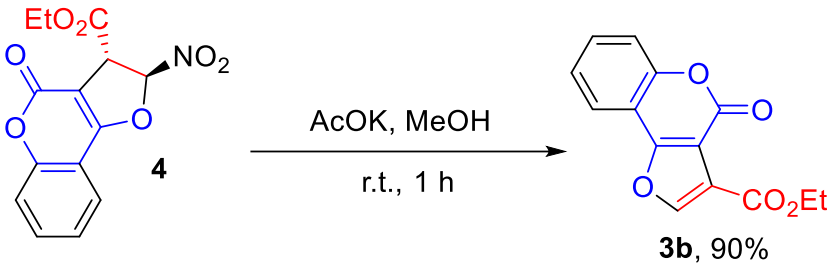


Ethyl 4-oxo-4H-furo[3,2-c]chromene-3-carboxylate (3b) was prepared by analogy with the procedure for **2a** starting from 217 mg (1.34 mmol) of 4-hydroxycoumarin, 197 mg (2.01 mmol) of freshly molten AcOK and 300 mg (1.34 mmol) of ethyl 3-bromo-3-nitroacrylate **1b**. The reaction mixture was stirred for 3 h and poured on crushed ice. The solid was filtered off and recrystallized from EtOH to give **3b** as light yellow crystals, yield 280 mg (80%), mp 118-120 °C (EtOH). IR (KBr): 1699 (C=O), 1751 (C=O) cm^{-1}; UV, λ_{max}, nm (ε, $l{\times}mol^{-1}{\times}cm^{-1}$): 272 (11500), 284 (12700), 310 (12700), 325 (8600). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.39 (t, 3H, ^{3}J = 7.1 Hz, $OCH_2C\underline{H_3}$), 4.40 (q, 2H, ^{3}J = 7.1 Hz, $OC\underline{H_2}CH_3$), 7.34 (td, 1H, J = 1.0, J = 7.6 Hz, H-8), 7.42 (dd, 1H, J = 0.4, J = 8.3 Hz, H-9), 7.54 (td, 1H, J = 1.6, J = 7.9 Hz, H-7), 7.86 (dd, 1H, J = 1.4, J = 7.8 Hz, H-6), 8.18 (s, 1H, H-2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.3 ($OCH_2\underline{C}H_3$), 61.6 ($O\underline{C}H_2CH_3$), 107.9 (C-3), 112.1 (C-9a), 117.3 (C-9), 118.8 (C-3a), 121.2 (C-6), 124.7 (C-8), 131.7 (C-7), 149.8 (C-2), 153.0 (C-5a), 155.7 (C-4), 159.2 (C-9b), 160.8 ($C{=}O_{ester}$) ppm. Anal. Calcd for $C_{14}H_{10}O_5$ (M 258.23): C, 65.12; H, 3.90. Found: C, 65.38; H 3.86.



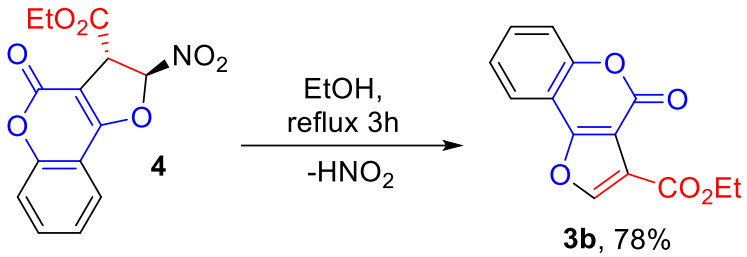
4

Ethyl 2-nitro-4-oxo-2,3-dihydro-4H-furo[3,2-c]chromene-3-carboxylate (4). To a solution of 4-hydroxycoumarin (362 mg, 2.23 mmol) and freshly fused potassium acetate (218 mg, 2.23 mmol) in anhydrous MeOH (16 mL), a solution of ethyl 3-bromo-3-nitroacrylate **1b** (500 mg, 2.23 mmol) in anhydrous MeOH (14 mL) was added dropwise. The reaction mixture was stirred for 1 h and then poured on crushed ice. The formed solid was filtered off and recrystallized from EtOH to furnish nitro compound **4** as light yellow crystals, yield 530 mg (78%), mp 141-144°C (EtOH). IR (KBr): 1372 (NO_2), 1592 (NO_2), 1725 (C=O), 1738 (C=O). UV, λ_{max}, nm (ε, $l{\times}mol^{-1}{\times}cm^{-1}$): 274 (9800), 285 (10300), 313 (8000), 327 (5500). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, 3H, ^{3}J = 7.1 Hz, $OCH_2C\underline{H_3}$), 4.32 (q, 2H, ^{3}J = 7.1 Hz, $OC\underline{H_2}CH_3$), 4.66 (d, 1H, ^{3}J = 2.3 Hz, H-3), 6.65 (d, 1H, ^{3}J = 2.3 Hz, H-2), 7.39 (td, 1H, J = 0.9, J = 7.6 Hz, H-8), 7.43 (dd, 1H, J = 0.3, J = 8.4 Hz, H-9), 7.68 (td, 1H, J = 1.5, J = 7.9 Hz, H-7), 7.81 (dd, 1H, J = 1.5, J = 7.9 Hz, H-6) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.1 ($OCH_2\underline{C}H_3$), 52.5 (C-3), 63.5 ($O\underline{C}H_2CH_3$), 100.5 (C-3a), 107.2 (C-2), 110.9 (C-9a), 117.4 (C-9), 123.3 (C-6), 124.9 (C-8), 134.4 (C-7), 155.6 (C-5a), 157.5 (C-9b), 166.3 (C-4), 167.1 ($C{=}O_{ester}$) ppm. ^{15}N NMR (40 MHz, $CDCl_3$): δ = 2.3 (NO_2) ppm. Anal. Calcd for $C_{14}H_{11}NO_7$ (M 305.05): C, 55.09; H, 3.63; N, 4.59. Found: C, 55.31; H, 3.57; N, 4.21.



3b, 90%

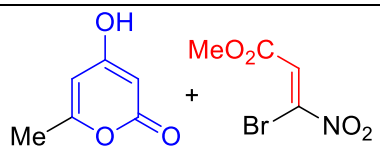
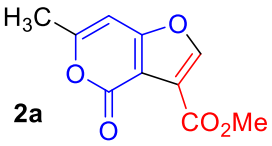
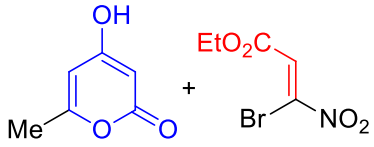
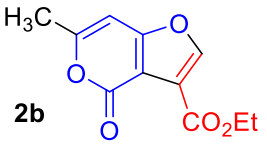
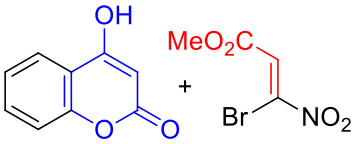
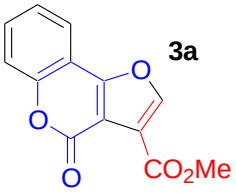
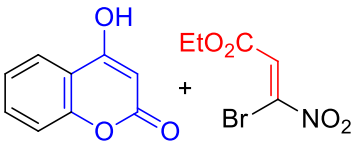
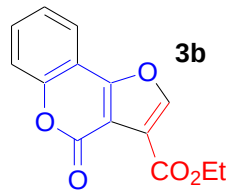
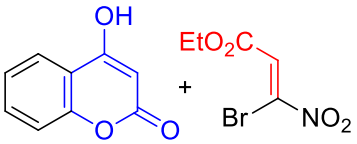
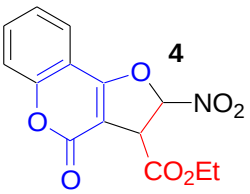
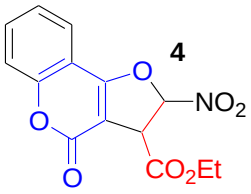
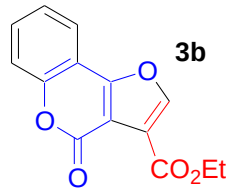
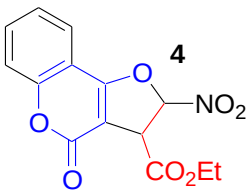
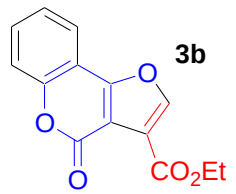
Preparation of compound 3b from nitro intermediate 4 in the presence of AcOK: To a solution of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** (70 mg, 0.23 mmol) in anhydrous MeOH (6 mL), a solution of 22.5 mg (0.23 mmol) of freshly fused AcOK in anhydrous MeOH (4 mL) was added dropwise. The resulted mixture was stirred for 1 h at ambient temperature and then poured on crushed ice. The solid was filtered off and recrystallized from EtOH to give 53 mg (90%) of **3b** as light yellow crystals, mp 118-120 °C (EtOH).



3b, 78%

Preparation of compound 1d from nitro intermediate 4 by refluxing in EtOH: A solution of ethyl 2-nitro-4-oxo-2,3-dihydro-4*H*-furo[3,2-*c*]chromene-3-carboxylate **4** (200 mg, 0.66 mmol) in EtOH (10 mL) was refluxed for 3 h. The reaction mixture was cooled, the resulted solid was filtered off and recrystallized from EtOH to give 132 mg (78%) of compound **3b** as light yellow crystals, mp 118-120 °C (EtOH).

Table S7. Structures and yields of compounds **2a,b, 3a,b** and **4**

Starting compound(s)	Procedure*	Product	Yield (%)
	**A**		77
	**A**		77
	**A**		77
	**A**		80
	**B**		78
	**B**		90
	**C**		78

*Procedure: **A** – AcOK (1.5 eq.), anhydrous MeOH, r.t., 3 h; **B** – AcOK (1.0 eq.), anhydrous MeOH, r.t., 1 h; **C** – EtOH, reflux 3 h.