Manipulating Room-Temperature Phosphorescence by Electron-Phonon Coupling

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General Information. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker AV-400 spectrometer. The electronic spray ionization (ESI) high-resolution mass spectra were tested on a Waters LCT Premier XE spectrometer. The UV-Vis absorption spectra were obtained on a Shimadzu UV-2600 spectrophotometer. Fluorescence, phosphorescence, and lifetime of delayed emission spectra were recorded on an Agilent Cary Eclipse spectrophotometer. Phosphorescence mode; Delay time = 0.1 ms; Gate time = 2.0 ms. Photoluminescence spectra were record on Shimadzu RF-6000 spectrometer. Fluorescence lifetimes were measured on Edinburgh Instruments Fluorescence Spectrometer (FLS1000). Absolute PL quantum yields were determined with a spectrometer C11347-11 (Hamamatsu, Japan). Density functional theory (DFT) and time-dependent (TD) DFT calculations were performed with the Gaussian 09 (Revision E.01) software package. The ground-state (S_0) geometries were optimized with the m062x and aug-cc-pVTZ basis. The energies in the singlet and triplet states were obtained using the time-dependent (TD) DFT method based on the optimized S_0 molecular structure. Femtosecond transient absorption (TA) spectra were obtained on Time-Tech Spectra TA100.

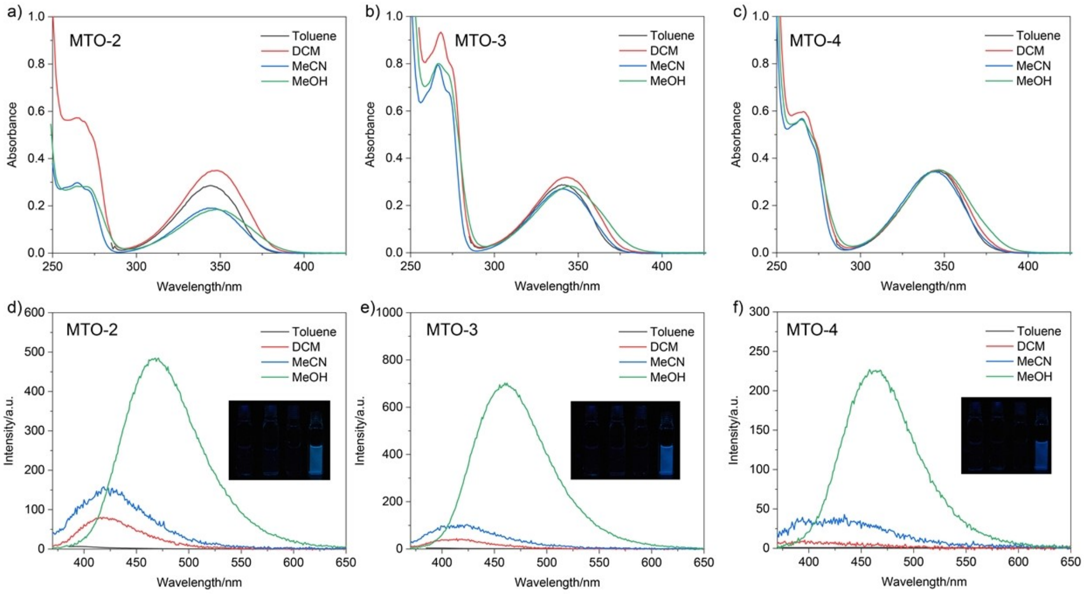


Figure S1. Absorption and emission spectra of MTOs in different solvents; Inset: photograph of MTOs in different solvents under 365 nm light (1.0×10^{-4} M).

Table S1. The Φ_{PL} of MTOs in different solvents (1.0×10^{-4} M)

	Toluene	DCM	MeCN	MeOH
MTO-1	0.27%	1.19%	0.73%	6.67%
MTO-2	0.24%	0.37%	0.29%	3.67%
MTO-3	0.28%	0.31%	0.28%	3.48%
MTO-4	0.23%	0.25%	0.24%	1.43%

Table S2. The singlet and triplet excited states transition configurations (%) and energy level of MTOs revealed by TD-DFT calculation.

	$S_0\rightarrow S_1$	$S_1\rightarrow S_0$	$S_0\rightarrow T_1$	$S_0\rightarrow T_2$	$S_0\rightarrow T_3$
MTO-1	3.87 eV, *f*=0.0165 H-2→L, 64.7% H→L, 20.1%	3.22 eV, *f*=0.1453 H→L, 95.4% H-2→L, 2.2%	2.43 eV H→L, 90.0% H-1→L, 6.1%	3.29 eV H-2→L, 82.0%	3.63 eV H-1→L, 74.2%
MTO-2	3.90 eV, *f*=0.0026 H-2→L, 78.7% H→L, 4.0%	3.38 eV, *f*=0.0237 H→L, 24.1% H-2→L, 62.3%	2.57 eV H→L, 90.0% H-1→L, 6.1%	3.29 eV H-2→L, 82.2%	3.54 eV H-1→L, 80.8%
MTO-3	3.92 eV, *f*=0.0030 H-2→L, 78.1% H→L, 4.5%	3.43 eV, *f*=0.0180 H→L, 18.5% H-2→L, 67.6%	2.58 eV H→L, 86.1% H-1→L, 9.2%	3.33 eV H-2→L, 81.9%	3.66 eV H-1→L, 81.7%

MTO-4	3.84 eV, f=0.0002 H-2→L, 80.6% H→L, 0.0%	3.24 eV, f=0.0057 H→L, 8.6% H-2→L, 76.9%	2.34 eV H→L, 89.8% H-1→L, 5.5%	3.21 eV H-2→L, 69.7% H-1→L, 11.5%	3.53 eV H-1→L, 72.6% H-2→L, 11.1%

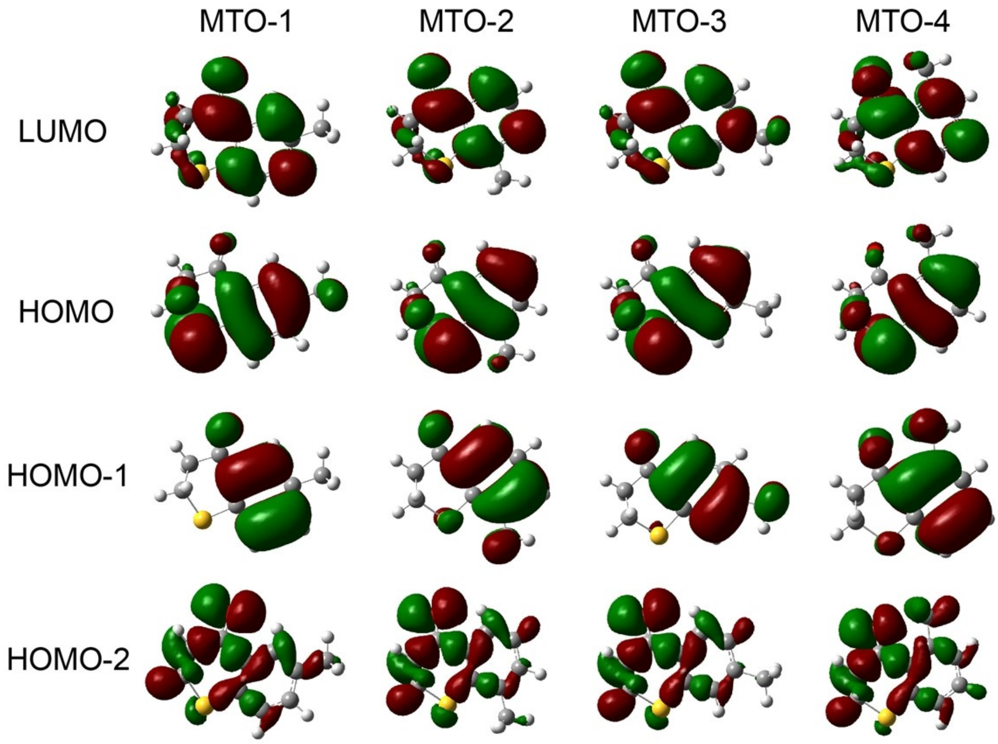


Figure S2. The frontier molecular orbits of MTOs

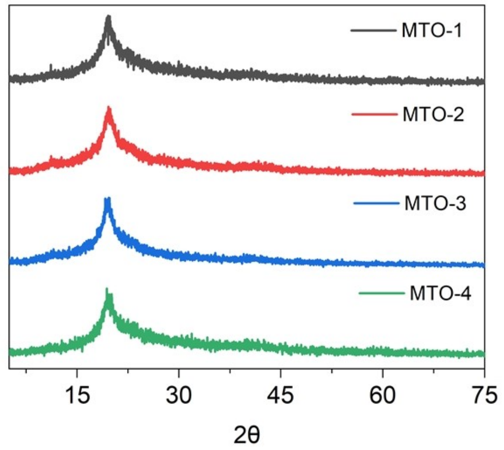


Figure S3. PXRD spectra of MTO-1@PVA, MTO-2@PVA, MTO-3@PVA, and MTO-4@PVA

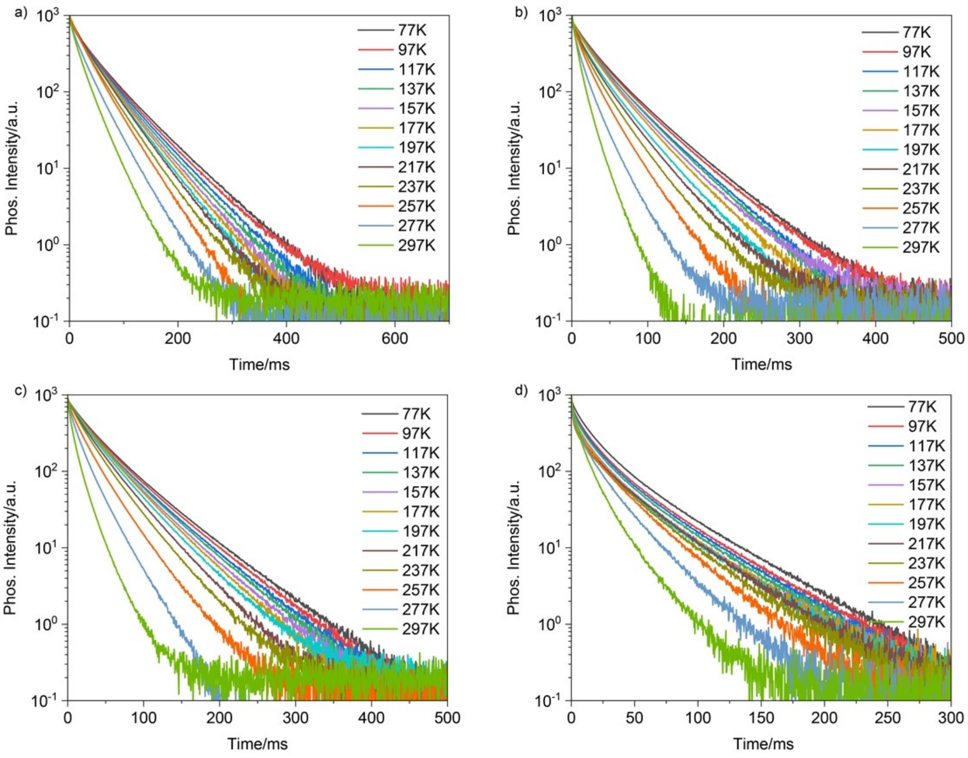
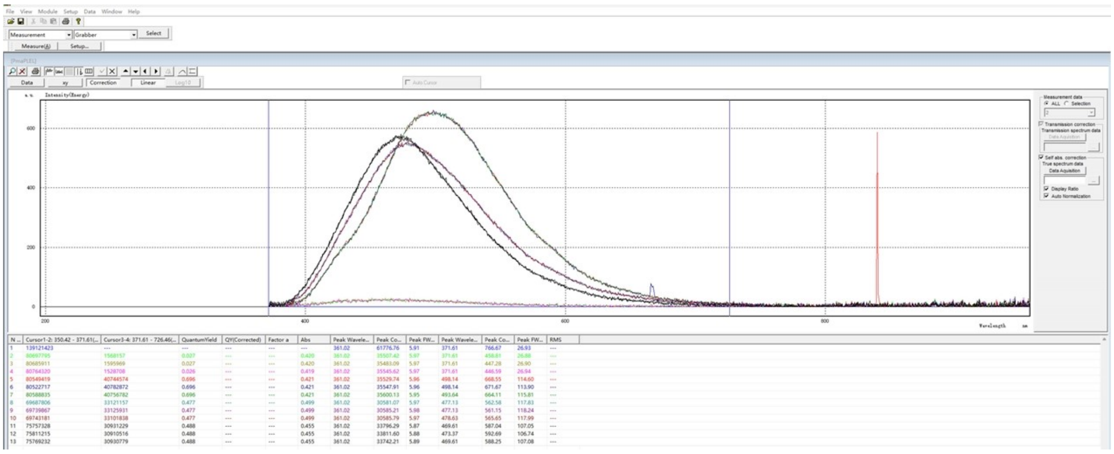


Figure S4 Lifetime spectra of MTO-1@PVA (a), MTO-1@PVA (b), MTO-1@PVA (c), and MTO-1@PVA (d) at different temperature.



N ...	Cursor1-2: 350.42 - 371.61(...	Cursor3-4: 371.61 - 726.46(...	QuantumYield	QY(Corrected)	Factor a	Abs	Peak Wavele...	Peak Co...	Peak FW...	Peak Wavele...	Peak Co...	Peak FW...	RMS
1	139121423	---	---	---	---	---	361.02	61776.76	5.91	371.61	766.67	26.93	---
2	80697795	1568157	0.027	---	---	0.420	361.02	35507.42	5.97	371.61	458.81	26.88	---
3	80685911	1595969	0.027	---	---	0.420	361.02	35483.09	5.97	371.61	447.28	26.90	---
4	80764320	1528708	0.026	---	---	0.419	361.02	35545.62	5.97	371.61	446.59	26.94	---
5	80549419	40744574	0.696	---	---	0.421	361.02	35529.74	5.96	498.14	668.55	114.60	---
6	80522717	40782872	0.696	---	---	0.421	361.02	35547.91	5.96	498.14	671.67	113.90	---
7	80588835	40756782	0.696	---	---	0.421	361.02	35600.13	5.95	493.64	664.11	115.81	---
8	69687806	33121157	0.477	---	---	0.499	361.02	30581.07	5.97	477.13	562.58	117.83	---
9	69739867	33125931	0.477	---	---	0.499	361.02	30585.21	5.98	477.13	561.15	118.24	---
10	69743181	33101838	0.477	---	---	0.499	361.02	30585.79	5.97	478.63	565.65	117.99	---
11	75757328	30931229	0.488	---	---	0.455	361.02	33796.29	5.87	469.61	587.04	107.05	---
12	75811215	30910516	0.488	---	---	0.455	361.02	33811.60	5.88	473.37	592.69	106.74	---
13	75769232	30930779	0.488	---	---	0.455	361.02	33742.21	5.89	469.61	588.25	107.08	---

Figure S5. The PL quantum yield of MTOs in PVA matrix.

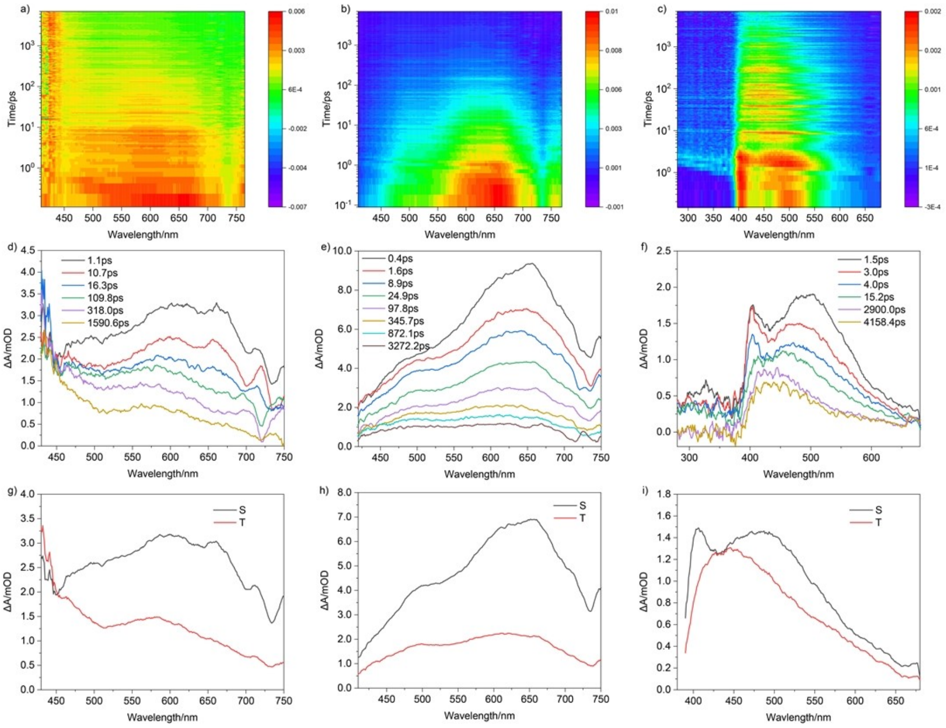


Figure S6. Femtosecond broadband transient absorption spectra of MTO-2 (a), MTO-3 (b), and MTO-4 (4) in PVA under 320 nm excitation; TA spectra of MTO-2@PVA (d), MTO-3@PVA (e), and MTO-4@PVA (f) at different pump-probe delay time; Species associated difference spectra of MTO-2@PVA (g), MTO-3@PVA (h), and MTO-4@PVA (i).

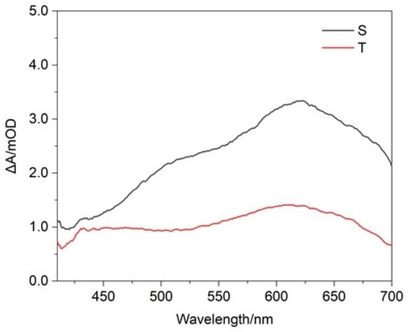


Figure S7. Species associated difference spectra of MTO-1@PVA

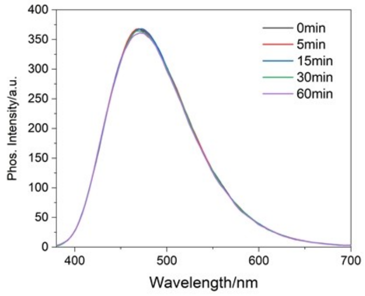


Figure S8. Phosphorescence spectra change of MTO-4@PVA when moved from argon to air atmosphere

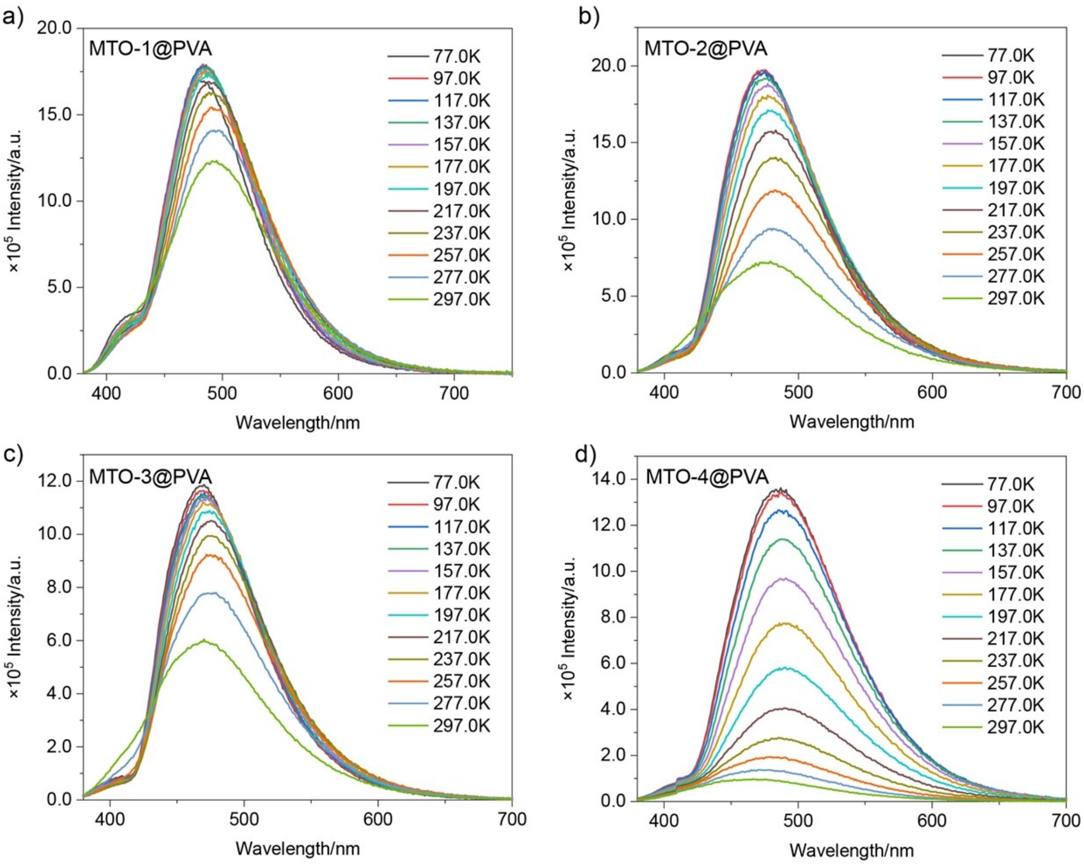
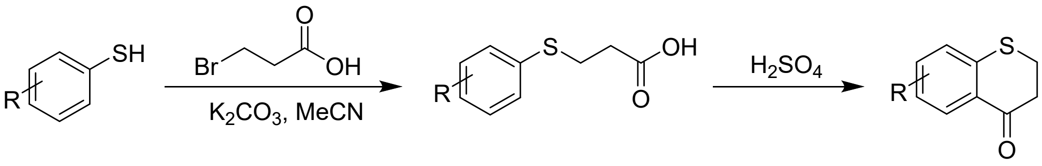


Figure S9. Steady-state spectra of MTOs in PVA matrix at different temperature.

Synthesis of target compounds



Scheme S1. Synthesis route of Compounds

General procedure for the synthesis of 3-(phenylthio)propanoic acid

Potassium Carbonate (24 mmol, 3.31 g) was added to the solution of benzenethiol (10 mmol) and 3-bromopropanoic acid (12 mmol, 1.84 g) in acetonitrile. Then the mixture was brought to reflux after stirring at room temperature for about 2 h. After the reaction was complete, the mixture was acidized to acid condition and the precipitate was removed by filtration. The filtrate was washed with water and dried with magnesium sulfate. After concentration, the desired product was obtained by recrystallization in petroleum ether. The crude product was used for the next step without further purification.

General procedure for the synthesis of thiochroman-4-one

3-(phenylthio) propanoic acid was added to concentrated H_2SO_4 (15 mL) under an ice bath. After the reaction was completed, the mixture was poured into a cold Na_2CO_3 aqueous solution and extracted with DCM. The combined organic phase was washed with water, dried by $MgSO_4$, and concentrated over the rotatory evaporator. The crude product was purified by the column chromatography on silica gel.

6-methylthiochroman-4-one (MTO-1)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.23 – 7.14 (m, 2H), 3.25 – 3.18 (m, 3H), 2.98 – 2.93 (m, 2H), 2.32 (s, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 194.35, 138.79, 134.91, 134.44, 130.71, 129.33, 127.56, 39.76, 26.71, 20.79. HRMS (ESI+) (m/z): $[M+H]^+$ calc. for $[C_{10}H_{11}OS]^+$, 179.0525; found, 179.0522.

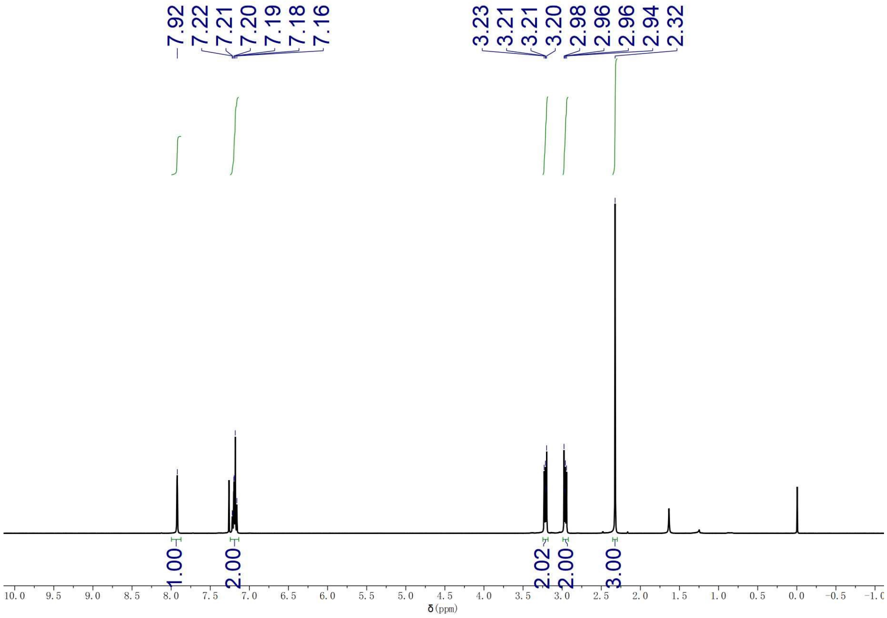


Figure S10. ^{1}H NMR spectra of MTO-1

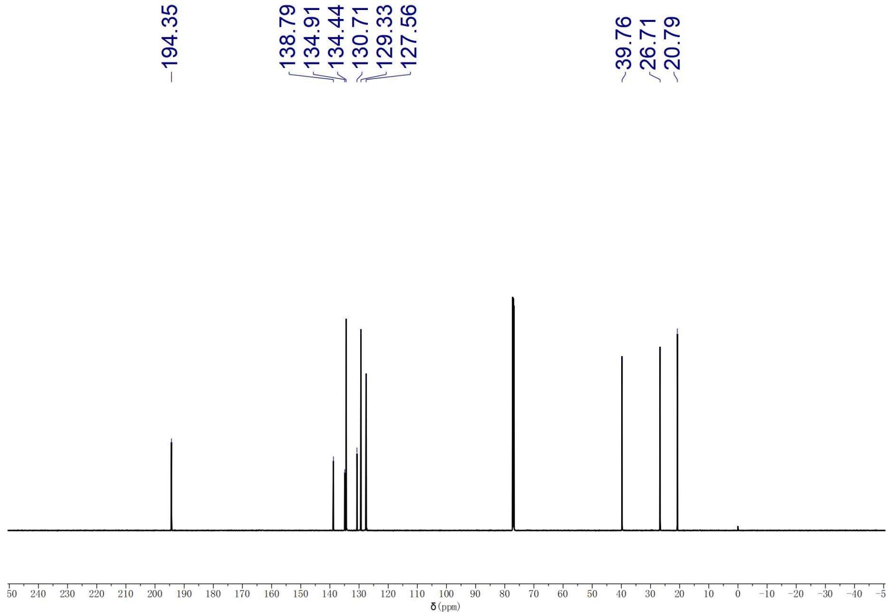
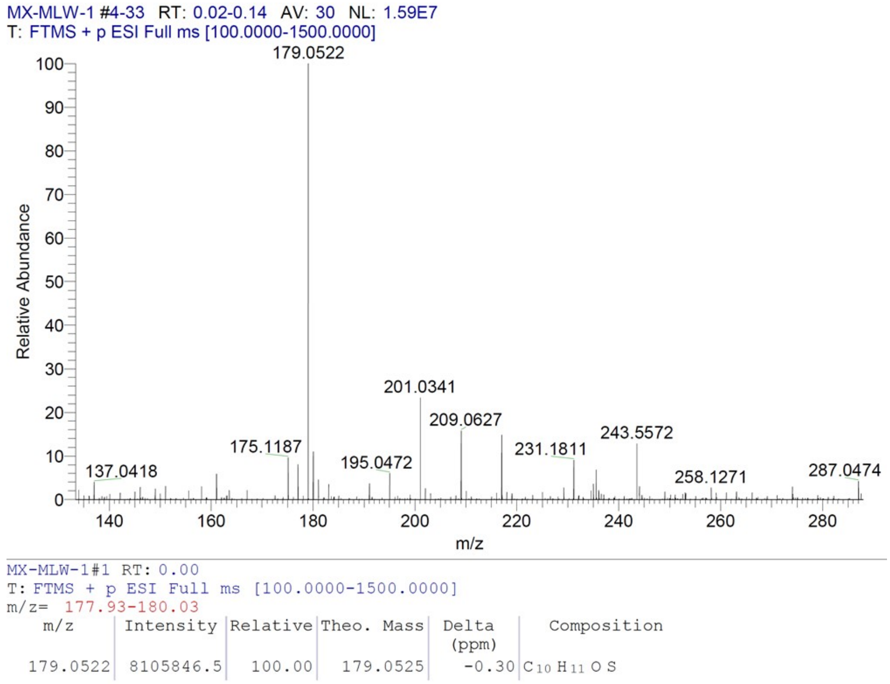


Figure S11. ${}^{13}C$ NMR spectra of MTO-1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T: FTMS + p ESI Full ms [100.0000-1500.0000]
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     m/z   | Intensity |Relative|Theo. Mass| Delta  |    Composition
           |           |        |          | (ppm)  |
  179.0522 | 8105846.5 | 100.00 | 179.0525 |  -0.30 |C10 H11 O S
```

Figure S 12. HRMS spectra of MTO-1

8-methylthiochroman-4-one (MTO-2)

${}^{1}H$ NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.13 (m, 2H), 7.00 – 6.94 (m, 1H), 3.23 – 3.15 (m, 2H), 3.03 – 2.96 (m, 2H), 2.60 (s, 3H). ${}^{13}C$ NMR (151 MHz, $CDCl_3$) δ 194.48, 141.75, 135.48, 134.39, 131.15, 126.95, 124.11, 39.10, 25.93, 20.07. HRMS (ESI+) (m/z): $[M+H]^+$ calc. for $[C_{10}H_{11}OS]^+$, 179.0525; found, 179.0522.

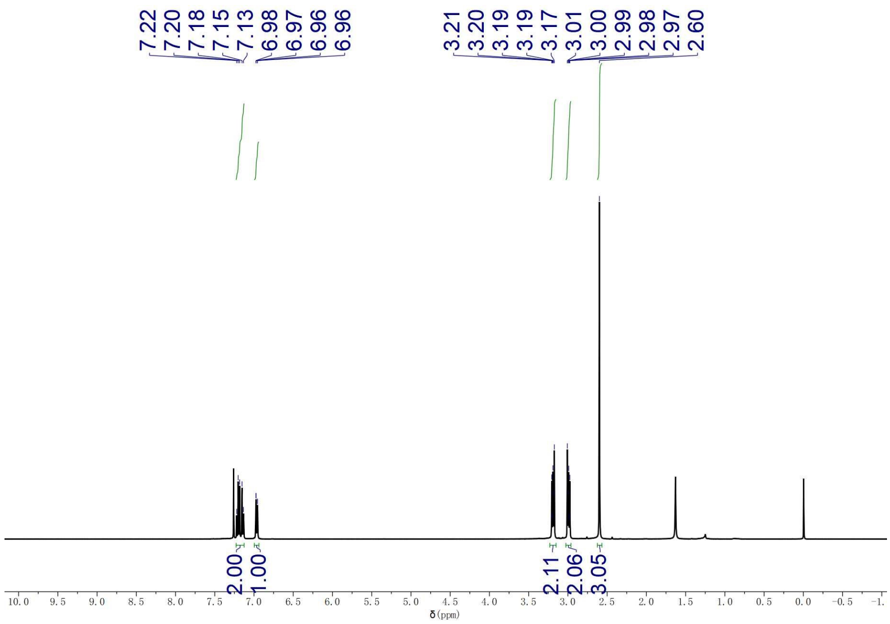


Figure S13. ^{1}H NMR spectra of MTO-2

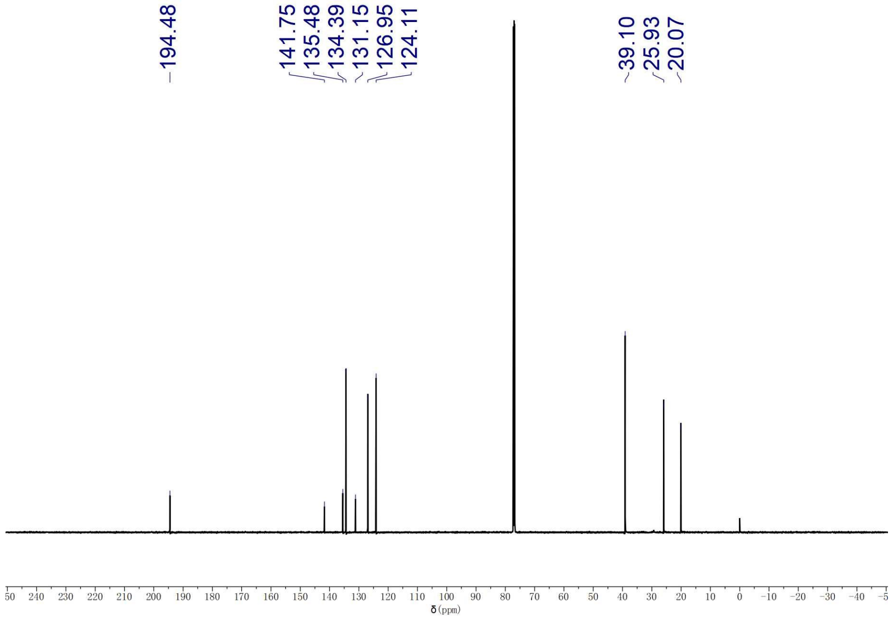
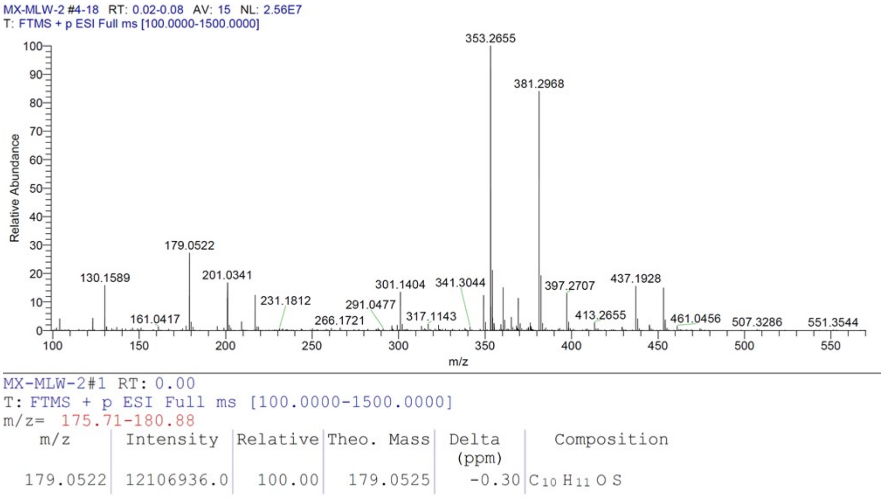


Figure S14. ^{13}C NMR spectra of MTO-2



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          |             |        |          | (ppm)  |
 179.0522 | 12106936.0  | 100.00 | 179.0525 |  -0.30 |C10 H11 O S
```

Figure S15. HRMS spectra of MTO-2

7-methylthiochroman-4-one (MTO-3)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 3.24 – 3.19 (m, 2H), 2.98 – 2.92 (m, 2H), 2.33 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 193.82, 144.35, 142.10, 129.26, 128.69, 127.74, 126.33, 39.59, 26.67, 21.53. HRMS (ESI+) (m/z): [M+H]$^+$ calc. for [C$_{10}$H$_{11}$OS]$^+$, 179.0525; found, 179.0522.

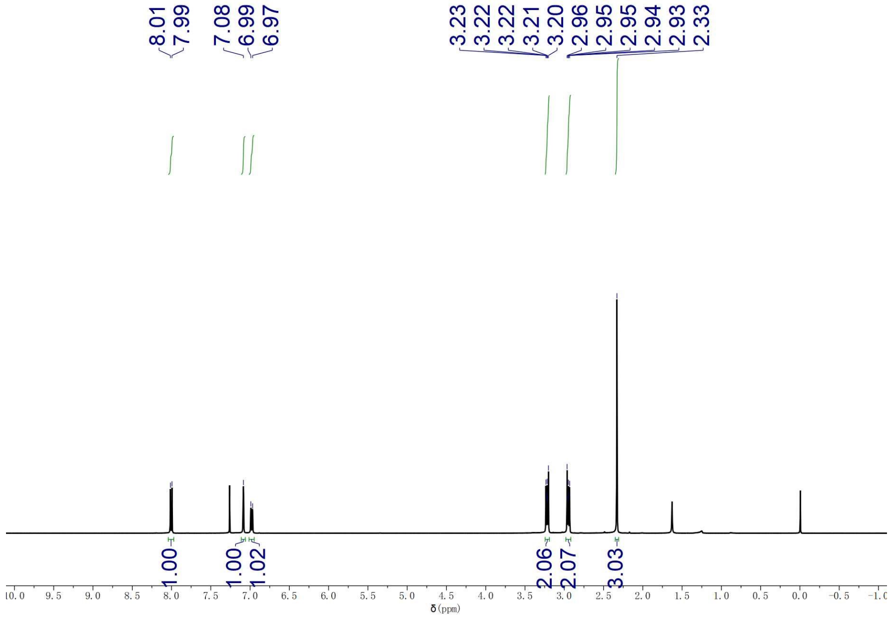


Figure S16. ^{1}H NMR spectra of MTO-3

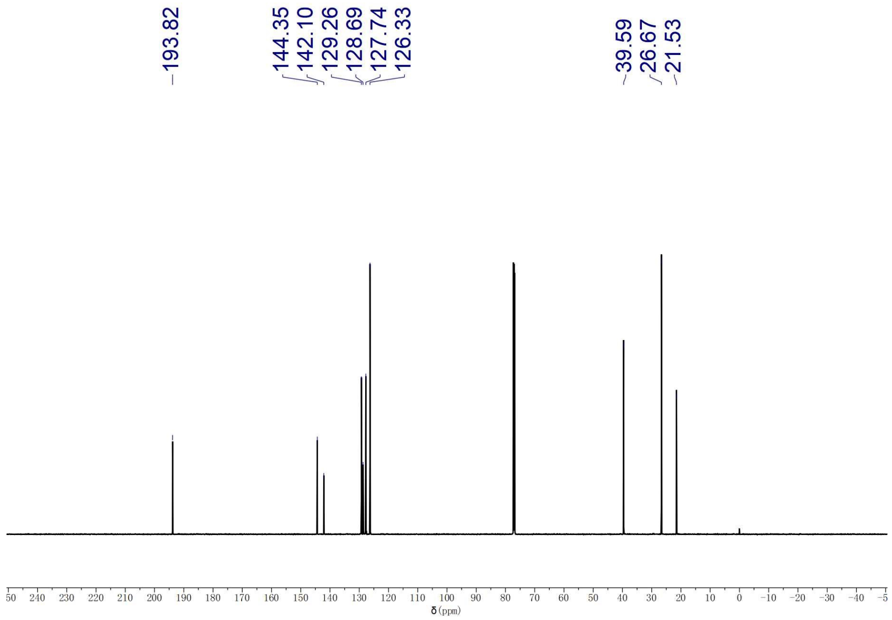
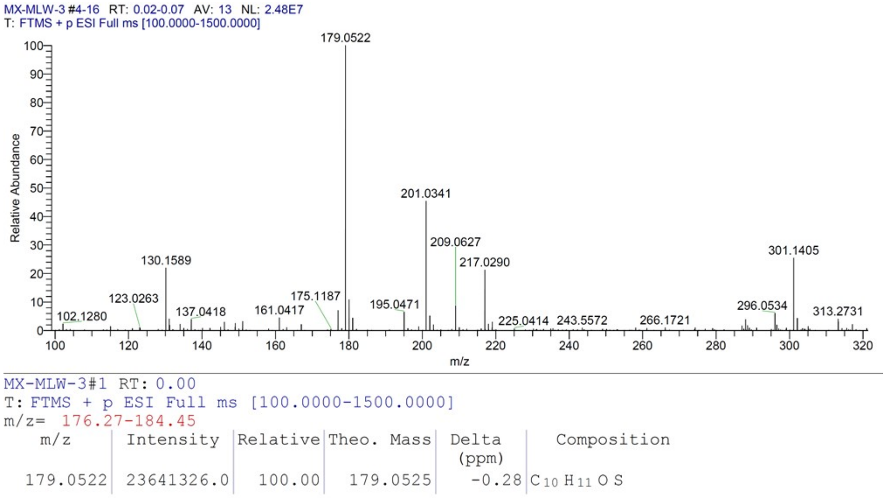


Figure S17 ^{1}H NMR spectra of MTO-3



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         |             |        |          |  (ppm)  |
 179.0522| 23641326.0  | 100.00 | 179.0525 |   -0.28 |C10 H11 O S
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Figure S18 HRMS spectra of MTO-3

5-methylthiochroman-4-one (MTO-4)

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.04 – 7.98 (m, 1H), 7.31 – 7.27 (m, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 3.26 – 3.20 (m, 2H), 2.99 – 2.94 (m, 2H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, CDCl$_3$) δ 196.38, 143.03, 142.88, 131.82, 130.18, 129.18, 125.73, 41.59, 26.22, 23.88. HRMS (ESI+) (m/z): [M+H]$^+$ calc. for [C$_{10}$H$_{11}$OS]$^+$, 179.0525; found, 179.0522.

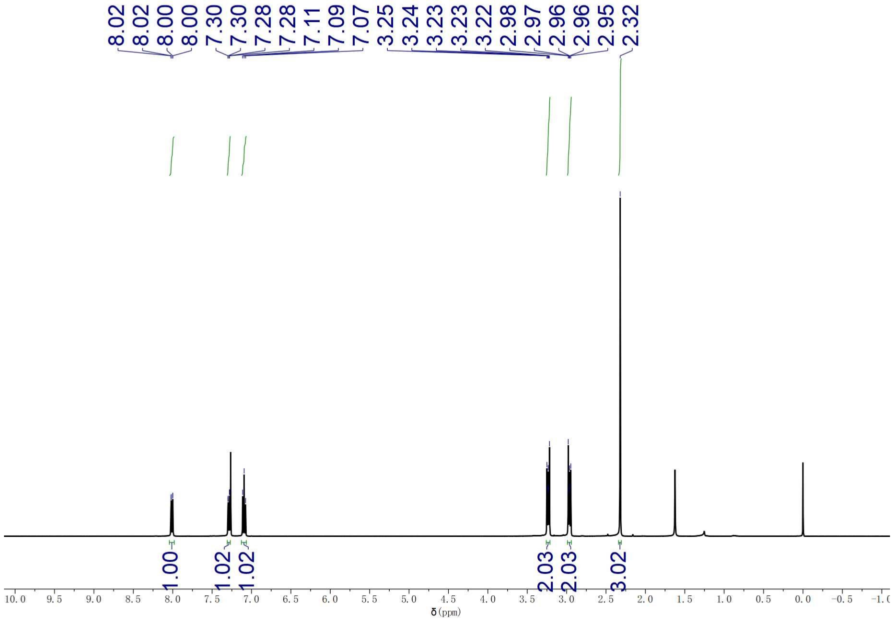


Figure S19. ^{1}H NMR spectra of MTO-4

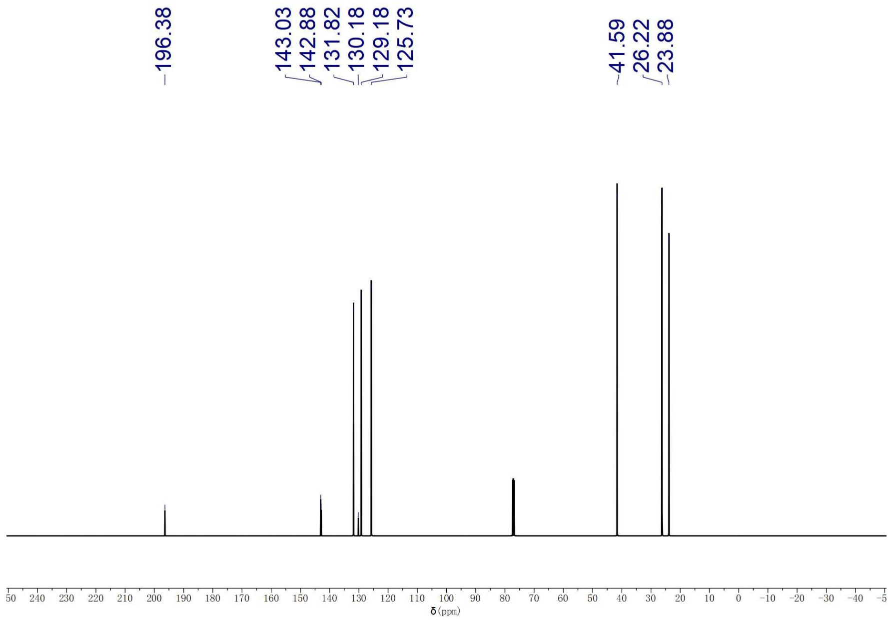
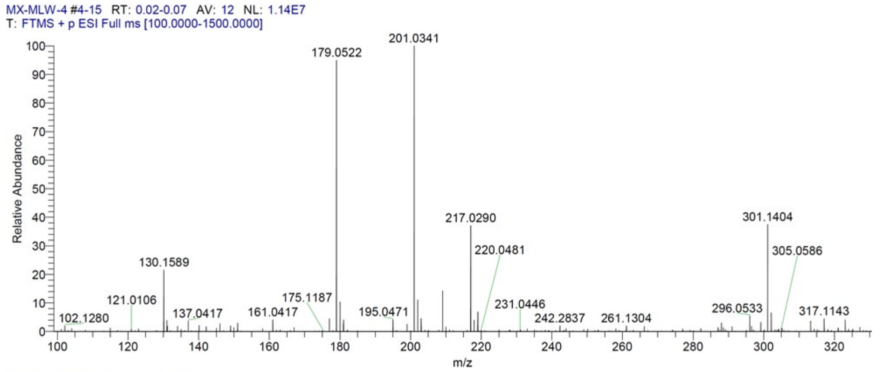
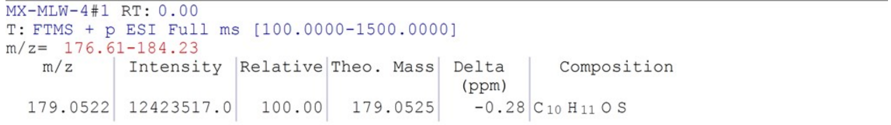


Figure S20. ^{13}C NMR spectra of MTO-4





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           |           |        |          | (ppm)  |
  179.0522 | 12423517.0|  100.00|  179.0525|   -0.28|C10 H11 O S
```

Figure S21. HRMS spectra of MTO-4