Supporting Information

Microwave-mediated stereocontrolled annulations of diazo(aryl)methyl(diaryl)phosphine oxides with pyridinium 1,4-zwitterionic thiolates

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1. Experimental

1.1. General Information

Microwave reactions were performed using a commercial CEM SP microwave reactor with an external IR sensor and in a closed reaction vessel. Unless otherwise noted, all materials were purchased from commercial suppliers. MeCN, DCE, and DCM were refluxed over CaH_2 and freshly distilled prior to use. THF and toluene were refluxed over sodium with benzophenone as an indicator and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemicals. The thin layer chromatography silica gel preparative plates were purchased from Anhui Liangchen Silicon Material Co. Ltd. Petroleum ether used for column chromatography was 60–90 °C fraction, and the removal of residue solvent was accomplished under rotovap with repeated azeotrope with chloroform, and then evaporation under vacuum (< 1 mmHg pressure). Reactions were monitored by thin-layer chromatography on silica gel 60–F254 coated 0.2 mm plates from Institute of Yantai Chemical Industry. The plates were visualized under UV light. **^{1}H** (400 MHz), **^{13}C** (101 MHz), **^{31}P** (162 MHz), and **^{19}F NMR** (376 MHz) spectra were recorded on a Bruker 400 NMR spectrometer usually with TMS as an internal standard for ^{1}H NMR, $CDCl_3$ as an internal standard (77.16) for ^{13}C NMR, 85% H_3PO_4 as an external standard (0.0) for ^{31}P NMR, and CF_3CO_2H as an external standard (-76.55) for ^{19}F NMR in $CDCl_3$ solution and the chemical shifts (δ) were reported in parts per million (ppm). HRMS measurements were carried out on an LC/MSD TOF mass spectrometer. Melting points were obtained on a melting point apparatus and are uncorrected.

1.2. Synthesis of Diazo Compounds 1

General Procedure for the Synthesis of Diazo(aryl)methyl(diaryl)phosphine Oxides 1a–1i

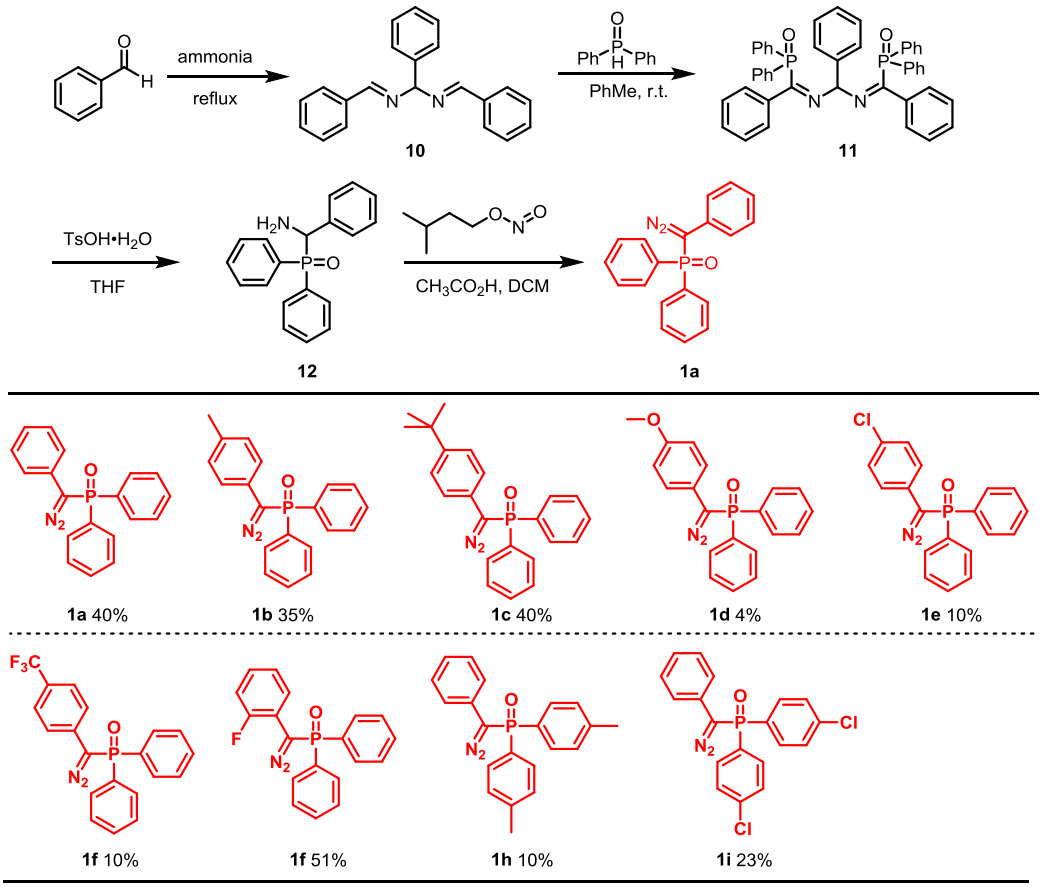
Synthesis of diazo(aryl)methyl(diaryl)phosphine oxides **1a**–**1i** refers to the known literature (Scheme S1).[1-3] To a 100 mL flask were added benzaldehyde (4.24 g, 40 mmol) and 28% ammonia (40 mL). The mixture was refluxed in an oil bath overnight. After cooling to room temperature, the reaction mixture was filtered through a Buchner funnel under reduced pressure to afford colorless crystals **10** after washing with a small amount of petroleum ether (60–90 °C fraction).

To a solution of the colorless crystals **10** (5 mmol, 1.50 g) in toluene (40 mL) in a 100 mL flask was added diphenylphosphine oxide (10 mmol, 2.02 g). The resulting solution was stirred at room temperature for 20 h. White precipitates appeared. After filtration through a Buchner funnel under reduced pressure and washing several times with petroleum ether, colorless crystals **11** were obtained.

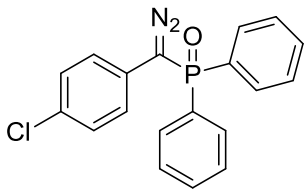
Crystals **11** were further dissolved in 40 mL of tetrahydrofuran in a 100 mL flask. After addition of *p*-toluenesulfonic acid hydrate (12 mmol, 2.28 g), the resulting mixture was stirred at room temperature for 5 h. White solid precipitates were observed. After filtration and washing several times with a small amount of tetrahydrofuran, tosylate of **12** was obtained as colorless crystals and directly added into a 100 mL flask.

After addition of 30 mL of 15% ammonia the solution was stirred at room temperature for 1 h and was extracted with 3×20 mL of chloroform. The combined organic phases were dried over anhydrous sodium sulfate and concentrated to 30 mL with a rotary evaporator. After addition of isoamyl nitrite (12 mmol, 1.44 g) and glacial acetic acid (5 mmol, 0.30 g), the solution was refluxed for 1 h. After cooling

to room temperature, the reaction mixture was washed with 2×20 mL of saturated aqueous sodium bicarbonate solution and 20 mL of saturated brine. The organic phase was dried over anhydrous sodium sulfate and concentrated to give a residue, which was purified by silica gel column chromatography with petroleum ether and ethyl acetate (PE:EA = 4:1, *v*/*v*) as eluent to afford diazo phosphine oxide **1a**. In addition, it can also be recrystallized from a mixture of ethyl acetate and petroleum ether. Other diazo phosphine oxides **1b**–**1i** were synthesized as well according to the above experimental procedure. Their analytic data are identical to those in our previous report.[1-3] **1j** refers to our previous report.[3]



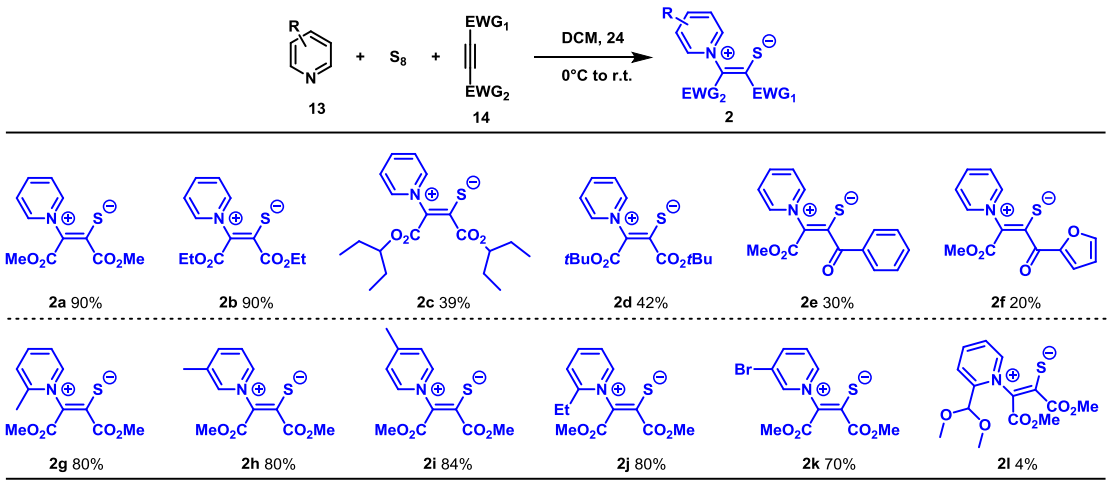
Scheme S1. Synthesis of diazophosphine oxides **1a**–**1i**.

((4-Chlorophenyl)(diazo)methyl)diphenylphosphine oxide (**1e**) [CAS: 26321-51-7]

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v*/*v*) as eluent. Colorless crystals, yield 352 mg (10 %), m.p. = 148–152°C. Lit.[2] 152–154 °C. R_f = 0.30 (PE: EA = 2:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 4H), 7.58 (td, J = 7.3, 1.6 Hz, 2H), 7.50 (td, J = 7.5, 3.3 Hz, 4H), 7.23 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.6.

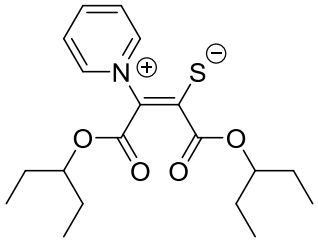
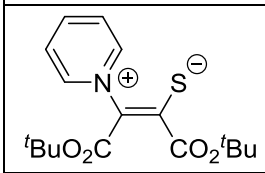
1.3. Synthesis of Pyridinium 1,4-zwitterionic Thiolates 2

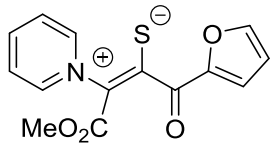
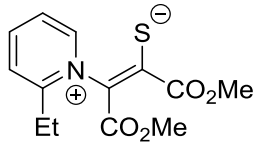
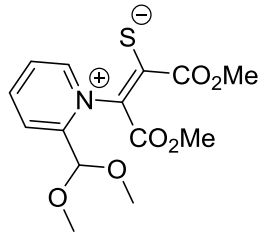
To a 50 mL flask were sequentially added corresponding pyridine **13** (1 mmol), S_8 (0.125 mmol), and corresponding acetylenedicarboxylate **14** (1 mmol) in DCM (5 mL) at 0 °C, then the mixture was stirred for 24 h. After completion, the mixture was filtered and the precipitate was washed with Et_2O (2 × 5 mL) and EtOH (5 mL) to afford pure pyridinium thiloates **2a**–**2l**.[3,4]

The analytic data of **2a**, **2b**, **2e**, **2g-2i**, and **2k** are identical to those in our previous report.[3]



Scheme S2. Synthesis of diazophosphine oxides **2a**–**2l**.

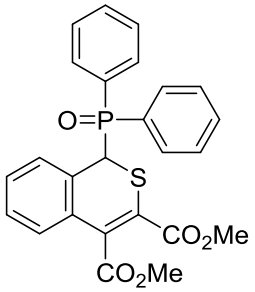
(*Z*)-1,4-Dioxo-1,4-bis(pentan-3-yloxy)-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (**2c**)

The product was recrystallized with petroleum ether (60–90 °C fraction) and ethyl acetate. Yellow crystals, yield 141 mg (39 %), m.p. = 110–112 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.10 Hz, 2H), 8.38 (tt, *J* = 7.81, 1.48 Hz, 1H), 7.93 (dd, *J* = 7.84, 6.45 Hz, 2H), 4.94 (p, *J* = 6.03 Hz, 1H), 4.85–4.74 (m, 1H), 1.76 (qd, *J* = 7.46, 5.94 Hz, 4H), 1.57–1.49 (m, 4H), 1.01 (t, *J* = 7.48 Hz, 6H), 0.83 (t, *J* = 7.41 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) 180.0, 168.9, 160.1, 148.7, 144.4, 127.0, 125.6, 78.2, 78.1, 26.7, 25.7, 9.9, 9.6. **HRMS (ESI)** calcd for $C_{19}H_{28}NO_4S^+$ $[M+H]^+$ *m*/*z*: 366.1734; found 366.1733.
(*Z*)-1,4-Di-tert-butoxy-1,4-dioxo-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (**2d**)[4] [CAS: 1321889-47-7]

The product was recrystallized with petroleum ether (60–90 °C fraction) and ethyl acetate. Yellow crystals, yield 139 mg (42 %), m.p. = 209–210°C. Lit.[4] 240–242°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.29 Hz, 2H), 8.34 (t, *J* = 7.83 Hz, 1H), 7.90 (dd, *J* = 7.82, 6.56 Hz, 2H), 1.62 (s, 9H), 1.44 (s, 9H).
(*Z*)-1-(Furan-2-yl)-4-methoxy-1,4-dioxo-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (**2f**)[5] [CAS: 2417676-86-7]

The product was purified by washing with Et_2O (2 × 5 mL) and EtOH (5 mL). Brown crystals, yield 60 mg (20 %), m.p. = 186–188°C. Lit.[5] 138–139°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.76 (dd, *J* = 6.6, 1.5 Hz, 2H), 8.41 (t, *J* = 7.8 Hz, 1H), 7.99 (t, *J* = 7.1 Hz, 2H), 7.58 (dd, *J* = 1.7, 0.8 Hz, 1H), 7.26–7.25 (M, 1H), 6.54 (dd, *J* = 3.5, 1.7 Hz, 1H), 3.58 (s, 3H)
(*Z*)-3-(2-Ethylpyridin-1-ium-1-yl)-1,4-dimethoxy-1,4-dioxobut-2-ene-2-thiolate (**2j**)[4] [CAS: 1321889-55-7]

The product was purified by washing with Et_2O (2 × 5 mL) and EtOH (5 mL). Brown crystals, yield 224 mg (80 %), m.p. = 182–183°C. Lit.[4] 175–177°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.38–8.32 (m, 2H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.76 (ddd, *J* = 7.7, 6.1, 1.5 Hz, 1H), 3.92 (s, 3H), 3.71 (s, 3H), 3.16–2.94 (m, 2H), 1.38 (t, *J* = 7.5 Hz, 3H).
(*Z*)-3-(2-(Dimethoxymethyl)pyridin-1-ium-1-yl)-1,4-dimethoxy-1,4-dioxobut-2-ene-2-thiolate (**2l**)

The product was purified by washing with Et_2O (2 × 5 mL) and EtOH (5 mL). Brown crystals, yield 24 mg (4 %), m.p. = 161–162°C. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 8.45 (td, *J* = 7.9, 1.5 Hz, 1H), 8.40 (dd, *J* = 6.1, 1.5 Hz, 1H), 8.27 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.93 (ddd, *J* = 7.8, 6.1, 1.6 Hz, 1H), 5.53 (s, 1H), 3.93 (s, 3H), 3.69 (s, 3H), 3.58 (s, 3H), 3.38 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 169.7, 161.0, 156.6, 149.6, 145.6, 143.6, 127.7, 126.3, 105.1, 99.8, 57.4, 55.2, 53.0, 52.0. **HRMS (ESI)** calcd for $C_{14}H_{18}NO_6S^+$ $[M+H]^+$ *m*/*z*: 328.0849; found 328.0852.

1.4. [3+3] Annulation of Diazo Compounds 1 and Pyridinium 1,4-zwitterionic Thiolates 2

To a 10-mL reaction tube were sequentially added diazo compound **1** (0.6 mmol), pyridinium 1,4-zwitterionic thiolate **2** (0.2 mmol), and PhCl (3 mL) at room temperature, then the reaction mixture was stirred at 105°C for 10 min under M.W. irradiation. After completion of the reaction, the organic layer was concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc/petroleum ether) to give the corresponding product **3**.

Dimethyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3aa**)

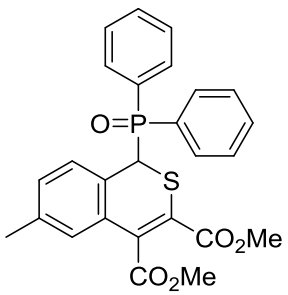


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v/v*) as eluent.

Colorless crystals, yield 65 mg (70%), m.p. = 181–182°C. R_f = 0.20 (PE: EA = 1:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.71 (ddd, J = 11.1, 8.2, 1.3 Hz, 2H), 7.53 (tt, J = 7.1, 3.5 Hz, 2H), 7.45 (ddd, J = 8.6, 6.9, 3.1 Hz, 2H), 7.39 (td, J = 7.7, 3.2 Hz, 2H), 7.31–7.24 (m, 2H), 7.19–7.17 (m, 1H), 6.98 (d, J = 6.8 Hz, 1H), 4.70 (d, J = 13.2 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 163.2, 137.1, 132.7 (d, J = 8.8 Hz), 132.3 (d, J = 1.8 Hz), 132.3 (d, J = 2.2 Hz), 132.1 (d, J = 8.6 Hz), 131.0, 130.9 (d, J = 7.1 Hz), 130.4 (d, J = 97.2 Hz), 130.3 (d, J = 3.2 Hz), 129.4 (d, J = 97.9 Hz), 129.0 (d, J = 2.5 Hz), 128.7 (d, J = 11.6 Hz), 128.4 (d, J = 11.7 Hz), 127.2 (d, J = 2.2 Hz), 125.0, 123.6, 52.9, 52.6, 42.8 (d, J = 63.9 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.1. **HRMS (ESI)** calcd for $C_{25}H_{22}O_5PS^+$ $[M+H]^+$ *m/z*: 465.0920; found 465.0926.

Dimethyl 1-(diphenylphosphoryl)-6-methyl-1*H*-isothiochromene-3,4-dicarboxylate (**3ba**)



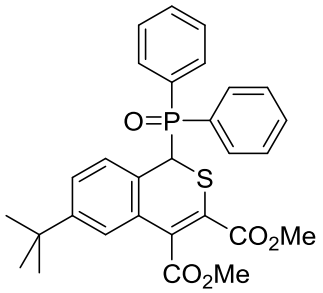
The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v/v*) as eluent.

Yellow oil, yield 72 mg (75%). R_f = 0.18 (PE: EA = 1:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.70 (ddd, J = 11.1, 8.2, 1.4 Hz, 2H), 7.56–7.49 (m, 2H), 7.46–7.41 (m, 2H), 7.37 (td, J = 7.7, 3.1 Hz, 2H), 7.07 (d, J = 7.6 Hz, 1H), 6.95 (s, 1H), 6.87 (dd, J = 7.8, 1.9 Hz, 1H), 4.67 (d, J = 13.0 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 2.29 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 163.2, 138.9, 137.3, 132.7 (d, J = 8.7 Hz), 132.2 (d, J = 1.6 Hz), 132.0 (d,

J = 8.3 Hz), 131.8, 130.7 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 96.8 Hz), 129.5 (d, *J* = 108.7 Hz), 128.6 (d, *J* = 11.3 Hz), 128.3 (d, *J* = 11.8 Hz), 127.7, 123.2, 122.0, 52.8, 52.6, 42.4 (d, *J* = 64.5 Hz), 21.3. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.1. **HRMS (ESI)** calcd for $C_{26}H_{24}O_5PS^+$ $[M+H]^+$ *m*/*z*: 479.1077; found 479.1083.

Dimethyl 6-(*tert*-butyl)-1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ca**)

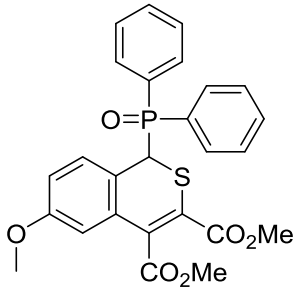


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v*/*v*) as eluent.

Yellow oil, yield 65 mg (63%). R_f = 0.08 (PE: EA = 1:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (ddd, *J* = 11.0, 8.3, 1.3 Hz, 2H), 7.70 (ddd, *J* = 11.1, 8.2, 1.3 Hz, 2H), 7.52 (dddd, *J* = 10.5, 7.3, 2.9, 1.5 Hz, 2H), 7.46–7.36 (m, 4H), 7.29 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 6.92 (dd, *J* = 8.1, 2.0 Hz, 1H), 4.68 (d, *J* = 12.9 Hz, 1H), 3.80 (s, 3H), 3.70 (s, 3H), 1.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.4, 163.3, 152.0, 137.7, 132.7 (d, *J* = 8.7 Hz), 132.2, 132.1 (d, *J* = 8.5 Hz), 130.6 (d, *J* = 98.4 Hz), 130.5 (d, *J* = 3.1 Hz), 129.9, 129.5 (d, *J* = 98.2 Hz), 129.3, 128.6 (d, *J* = 11.5 Hz), 128.3, 128.2, 124.1, 123.1, 122.2, 52.9, 52.5, 42.4 (d, *J* = 64.8 Hz), 34.8, 31.2. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.4. **HRMS (ESI)** calcd for $C_{29}H_{30}O_5PS^+$ $[M+H]^+$ *m*/*z*: 521.1546; found 521.1549.

Dimethyl 1-(diphenylphosphoryl)-6-methoxy-1*H*-isothiochromene-3,4-dicarboxylate (**3da)**

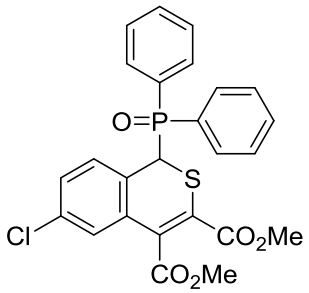


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v*/*v*) as eluent.

Yellow oil, yield 53 mg (54%). R_f = 0.20 (PE: EA = 1:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (ddd, *J* = 10.9, 8.3, 1.4 Hz, 2H), 7.71 (ddt, *J* = 11.1, 6.9, 1.3 Hz, 2H), 7.57–7.50 (m, 2H), 7.45 (ddd, *J* = 8.5, 6.8, 3.1 Hz, 2H), 7.41–7.37 (m, 2H), 6.91 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.81 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 4.67 (d, *J* = 12.7 Hz, 1H), 3.78 (s, 6H), 3.71 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.2, 163.3, 159.8, 136.8, 132.7 (d, *J* = 8.9 Hz), 132.3, 132.1 (d, *J* = 8.4 Hz), 131.9 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 93.3 Hz), 131.2 (d, *J* = 2.9 Hz), 129.9, 129.4 (d, *J* = 88.7 Hz), 128.7 (d, *J* = 11.2 Hz), 128.4 (d, *J* = 11.7 Hz), 124.3, 116.9, 115.9, 113.1, 55.6, 52.9, 52.6, 42.2 (d, *J* = 65.3 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.1. **HRMS (ESI)** calcd for $C_{26}H_{24}O_6PS^+$ $[M+H]^+$ *m*/*z*: 495.1026; found 495.1027.

Dimethyl 6-chloro-1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ea)**

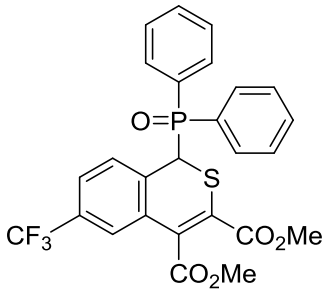


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 3:1 to 1:1, *v/v*) as eluent.

Yellow oil, yield 70 mg (71%). R_f = 0.15 (PE: EA = 3:2, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.77 (m, 2H), 7.75–7.70 (m, 2H), 7.55 (qd, *J* = 7.2, 1.4 Hz, 2H), 7.46 (td, *J* = 7.6, 3.1 Hz, 2H), 7.40 (td, *J* = 7.7, 3.1 Hz, 2H), 7.23 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.19 (d, *J* = 2.1 Hz, 1H), 6.93 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.67 (d, *J* = 12.7 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 163.0, 135.6, 135.0 (d, *J* = 3.1 Hz), 132.6 (d, *J* = 8.8 Hz), 132.5 (d, *J* = 2.8 Hz), 132.0, 132.0, 131.9, 131.8, 131.2 (d, *J* = 108.6 Hz), 129.6, 129.5, 128.8 (d, *J* = 11.6 Hz), 128.5 (d, *J* = 11.8 Hz), 126.9 (d, *J* = 2.3 Hz), 125.6, 123.4, 53.1, 52.8, 42.1 (d, *J* = 63.7 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.1. **HRMS (ESI)** calcd for $C_{25}H_{21}ClO_5PS^+$ $[M+H]^+$ *m/z*: 499.0530; found 499.0535.

Dimethyl 1-(diphenylphosphoryl)-6-(trifluoromethyl)-1*H*-isothiochromene-3,4-dicarboxylate (**3fa**)

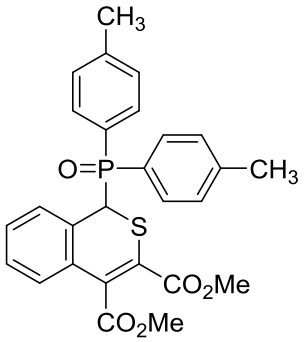


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 1:1, *v/v*) as eluent.

Yellow oil, yield 41 mg (39%). R_f = 0.05 (PE: EA = 2:3, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.78 (m, 2H), 7.76–7.71 (m, 2H), 7.60–7.40 (m, 8H), 7.13 (d, *J* = 8.0 Hz, 1H), 4.73 (d, *J* = 12.7 Hz, 1H), 3.81 (s, 3H), 3.74 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.5, 163.0, 135.6, 132.68 (d, *J* = 11.6 Hz), 132.66, 131.9 (d, *J* = 8.7 Hz), 131.4 (d, *J* = 4.0 Hz), 130.1 (d, *J* = 98.9 Hz), 130.0 (d, *J* = 3.2 Hz), 128.9 (d, *J* = 11.6 Hz), 128.8 (d, *J* = 99.9 Hz), 128.6 (d, *J* = 11.8 Hz), 127.3, 126.3, 123.8, 122.2, 53.2, 52.9, 42.4 (d, *J* = 62.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.3. **^{19}F NMR** (376MHz, $CDCl_3$) δ -63.0. **HRMS (ESI)** calcd for $C_{26}H_{21}F_3O_5PS^+$ $[M+H]^+$ *m/z*: 533.0794; found 533.0789.

Dimethyl 1-(di-*p*-tolylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ha**)

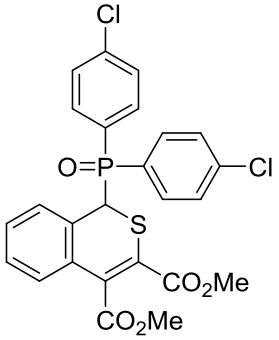


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 1:1, *v/v*) as eluent.

Yellow oil, yield 13 mg (13%). R_f = 0.05 (PE: EA = 2:3, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 10.9, 8.1 Hz, 2H), 7.57 (dd, J = 10.9, 8.0 Hz, 2H), 7.25 (td, J = 8.6, 8.0, 3.4 Hz, 4H), 7.17 (td, J = 7.6, 6.6, 3.8 Hz, 3H), 7.00 (dt, J = 6.5, 2.1 Hz, 1H), 4.66 (d, J = 13.1 Hz, 1H), 3.79 (s, 3H), 3.71 (s, 3H), 2.39 (s, 3H), 2.39 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 163.3, 142.82 (d, J = 2.5 Hz), 142.77 (d, J = 2.6 Hz), 136.9, 132.7 (d, J = 9.1 Hz), 132.1 (d, J = 9.0 Hz), 130.95 (d, J = 3.8 Hz), 130.88, 130.3 (d, J = 2.9 Hz), 129.4 (d, J = 11.8 Hz), 129.1 (d, J = 12.1 Hz), 128.8, 127.14, 127.10 (d, J = 101.3 Hz), 126.1 (d, J = 103.6 Hz), 125.2, 123.7, 52.9, 52.6, 42.8 (d, J = 64.0 Hz), 21.8. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.9. **HRMS (ESI)** calcd for $C_{27}H_{26}O_5PS^+$ $[M+H]^+$ *m/z*: 493.1233; found 493.1237.

Dimethyl 1-(bis(4-chlorophenyl)phosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ia**)

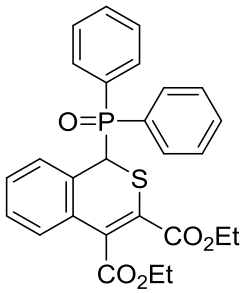


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 4:1, *v/v*) as eluent.

Yellow oil, yield 36 mg (34%). R_f = 0.05 (PE: EA = 2:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, J = 10.6, 8.4 Hz, 2H), 7.57 (dd, J = 10.7, 8.4 Hz, 2H), 7.47 (dd, J = 8.5, 2.4 Hz, 2H), 7.35 (ddd, J = 11.9, 7.1, 2.0 Hz, 4H), 7.19 (dd, J = 7.3, 2.0 Hz, 1H), 7.08 (d, J = 6.7 Hz, 1H), 4.67 (d, J = 14.1 Hz, 1H), 3.81 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 163.1, 139.5, 139.4, 138.8 (d, J = 3.8 Hz), 137.0 (d, J = 9.1 Hz), 134.0 (d, J = 9.6 Hz), 133.5 (d, J = 9.4 Hz), 131.3 (d, J = 2.1 Hz), 131.1 (d, J = 4.1 Hz), 130.6 (d, J = 97.8 Hz), 129.5 (d, J = 93.5 Hz), 129.3 (d, J = 2.5 Hz), 129.2 (d, J = 12.2 Hz), 128.9 (d, J = 12.3 Hz), 127.9 (d, J = 3.3 Hz), 127.4 (d, J = 2.1 Hz), 124.3, 53.1, 52.9, 42.7 (d, J = 65.4 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 24.7. **HRMS (ESI)** calcd for $C_{25}H_{20}Cl_2O_5PS^+$ $[M+H]^+$ *m/z*: 533.0141; found 533.0145.

Diethyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ab**)

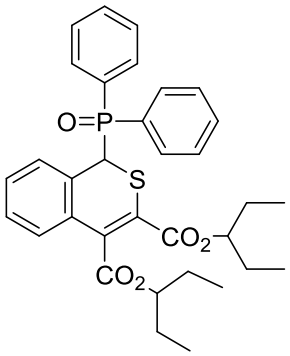


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 1:1, *v/v*) as eluent.

Yellow oil, yield 54 mg (55%). R_f = 0.15 (PE: EA = 2:3, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (ddd, J = 11.0, 8.4, 1.4 Hz, 2H), 7.70 (ddd, J = 11.1, 8.2, 1.3 Hz, 2H), 7.58–7.45 (m, 4H), 7.37 (tdd, J = 7.6, 3.3, 1.8 Hz, 2H), 7.29 (dd, J = 5.8, 3.4 Hz, 2H), 7.15 (dd, J = 5.6, 3.7 Hz, 1H), 7.06–7.03 (m, 1H), 4.71 (d, J = 14.2 Hz, 1H), 4.31–4.22 (m, 2H), 4.16 (q, J = 7.1 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.7, 162.8, 136.7, 132.7 (d, J = 9.0 Hz), 132.3 (d, J = 2.4 Hz), 132.1 (d, J = 8.5 Hz), 131.1 (d, J = 3.4 Hz), 130.9, 130.3, 129.8, 128.9, 128.7 (d, J = 11.7 Hz), 128.3 (d, J = 11.8 Hz), 127.2, 125.0, 123.9, 62.1, 61.7, 42.9 (d, J = 63.8 Hz), 14.2, 14.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.9. **HRMS (ESI)** calcd for $C_{27}H_{26}O_5PS^+$ $[M+H]^+$ *m/z*: 493.1233; found 493.1235.

Di(pentan-3-yl) 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ac**)

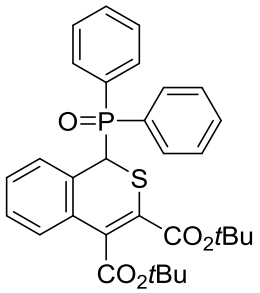


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 4:1, *v/v*) as eluent.

Yellow oil, yield 54 mg (47%). R_f = 0.22 (PE: EA = 2:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.89 (m, 2H), 7.67 (ddd, J = 11.1, 8.2, 1.3 Hz, 2H), 7.55 (dd, J = 7.4, 1.6 Hz, 1H), 7.51–7.45 (m, 3H), 7.34 (td, J = 7.7, 3.1 Hz, 2H), 7.29–7.27 (m, 2H), 7.16–7.13 (m, 1H), 7.10 (dt, J = 6.5, 2.1 Hz, 1H), 4.87 (p, J = 6.0 Hz, 1H), 4.76–4.69 (m, 2H), 1.74–1.51 (m, 8H), 0.94–0.80 (m, 12H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.6, 162.1, 140.1, 137.1, 132.6 (d, J = 8.8 Hz), 132.4 (d, J = 2.8 Hz), 132.3 (d, J = 3.0 Hz), 132.2 (d, J = 8.5 Hz), 131.3 (d, J = 98.0 Hz), 131.1, 130.7 (d, J = 8.5 Hz), 129.4 (d, J = 87.6 Hz), 128.8, 128.6 (d, J = 11.6 Hz), 128.3 (d, J = 11.7 Hz), 127.2 (d, J = 1.9 Hz), 124.9, 123.3, 78.9, 78.8, 43.3 (d, J = 64.2 Hz), 26.30, 26.27, 25.6 , 25.4 , 9.7, 9.61, 9.57, 9.5. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 25.9. **HRMS (ESI)** calcd for $C_{33}H_{38}O_5PS^+$ $[M+H]^+$ *m/z*: 577.2172; found 577.1273.

Di-*tert*-butyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (**3ad**)

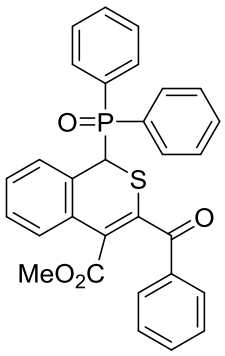


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v*/*v*) as eluent.

Yellow oil, yield 55 mg (51%). R_f = 0.23 (PE: EA = 1:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (ddd, J = 11.0, 8.4, 1.4 Hz, 2H), 7.69–7.64 (m, 2H), 7.56–7.54 (m, 1H), 7.50–7.46 (m, 3H), 7.35 (td, J = 7.7, 3.2 Hz, 2H), 7.28–7.23 (m, 2H), 7.17 (dd, J = 7.5, 1.6 Hz, 1H), 7.01 (d, J = 7.6 Hz, 1H), 4.65 (d, J = 15.8 Hz, 1H), 1.53 (s, 9H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 161.5, 136.1, 132.6 (d, J = 8.7 Hz), 132.3 (d, J = 3.1 Hz), 132.2, 131.7, 131.6, 131.0 (d, J = 3.7 Hz), 130.5 (d, J = 93.8 Hz), 130.3 (d, J = 2.0 Hz), 129.3 (d, J = 90.8 Hz), 129.1, 128.8, 128.6 (d, J = 11.6 Hz), 128.3 (d, J = 12.0 Hz), 127.1 (d, J = 2.3 Hz), 125.3, 82.8, 82.6, 44.0 (d, J = 63.6 Hz), 28.2, 28.1. **^{31}P NMR** (162 MHz, $CDCl_3$) δ 26.4. **HRMS (ESI)** calcd for $C_{31}H_{34}O_5PS^+$ $[M+H]^+$ *m*/*z*: 549.1859; found 549.1857.

Methyl 3-benzoyl-1-(diphenylphosphoryl)-1*H*-isothiochromene-4-carboxylate (**3ae**)

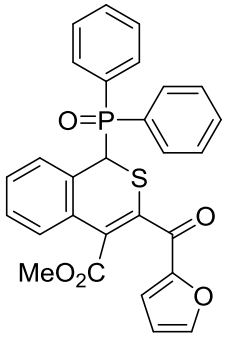


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 2:1, *v*/*v*) as eluent.

Yellow oil, yield 58 mg (57%). R_f = 0.28 (PE: EA = 1:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14–8.12 (m, 2H), 7.85 (ddd, J = 11.0, 8.3, 1.4 Hz, 2H), 7.66 (ddd, J = 11.0, 8.2, 1.4 Hz, 2H), 7.57–7.50 (m, 4H), 7.47 (ddd, J = 7.2, 5.7, 2.3 Hz, 4H), 7.40 (td, J = 7.7, 3.0 Hz, 2H), 7.29 (dt, J = 7.7, 1.5 Hz, 1H), 7.09 (t, J = 7.4 Hz, 1H), 6.60 (dt, J = 7.7, 1.6 Hz, 1H), 4.60 (d, J = 7.5 Hz, 1H), 3.30 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 192.5, 165.0, 140.1, 135.3, 133.6, 132.4 (d, J = 2.8 Hz), 132.3 (d, J = 2.7 Hz), 132.1 (d, J = 8.5 Hz), 132.0 (d, J = 8.8 Hz), 131.0 (d, J = 95.7 Hz), 129.89, 129.85, 129.60, 129.56, 129.31 (d, J = 87.9 Hz), 129.27 (d, J = 1.9 Hz), 128.84 (d, J = 11.6 Hz), 128.83, 128.7 (d, J = 2.6 Hz), 128.6 (d, J = 11.7 Hz), 128.1 (d, J = 2.0 Hz), 124.5, 51.8, 43.5 (d, J = 65.1 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.2. **HRMS (ESI)** calcd for $C_{30}H_{24}O_4PS^+$ $[M+H]^+$ *m*/*z*: 511.1127; found 511.1128.

Methyl 1-(diphenylphosphoryl)-3-(furan-2-carbonyl)-1*H*-isothiochromene-4-carboxylate (**3af**)



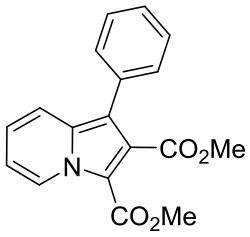
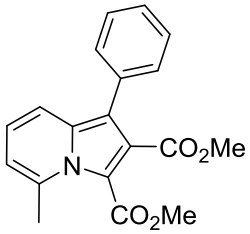
The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 4:1, *v*/*v*) as eluent.

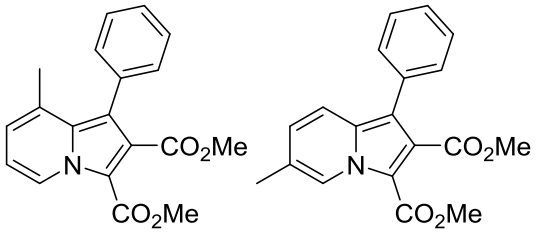
Yellow oil, yield 35 mg (35%). R_f = 0.18 (PE: EA = 2:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, J = 3.6, 0.8 Hz, 1H), 7.83 (ddd, J = 10.9, 8.2, 1.3 Hz, 2H), 7.65–7.59 (m, 3H), 7.55 (dd, J = 7.4, 1.6 Hz, 1H), 7.50 (t, J = 2.5 Hz, 1H), 7.48 (dt, J = 4.0, 1.4 Hz, 1H), 7.45 (d, J = 1.2 Hz, 1H), 7.38 (td, J = 7.6, 3.1 Hz, 2H), 7.29 (tt, J = 7.7, 1.5 Hz, 2H), 7.09 (td, J = 7.6, 1.0 Hz, 1H), 6.59 (d, J = 7.9 Hz, 1H), 6.56 (dd, J = 3.6, 1.7 Hz, 1H), 4.55 (d, J = 7.0 Hz, 1H), 3.50 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 179.2, 165.3, 150.7, 148.2, 132.5 (d, J = 2.7 Hz), 132.3 (d, J = 2.5 Hz), 132.1 (d, J = 8.5 Hz), 131.8 (d, J = 8.6 Hz), 131.6 (d, J = 2.4 Hz), 131.0 (d, J = 91.5 Hz), 130.1 (d, J = 3.1 Hz), 130.0, 129.5 (d, J = 1.8 Hz), 129.2 (d, J = 96.0 Hz), 128.9 (d, J = 11.8 Hz), 128.6 (d, J = 11.8 Hz), 128.2 (d, J = 2.2 Hz), 127.4, 124.8, 122.8, 122.2, 112.8, 52.1, 43.2 (d, J = 64.6 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 28.3. **HRMS (ESI)** calcd for $C_{28}H_{22}O_5PS^+$ $[M+H]^+$ *m*/*z*: 501.0920; found 501.0923.

1.5. ([1+5]-1) Annulation of Diazo Compounds 1 and Pyridinium 1,4-zwitterionic Thiolates 2

To a 10-mL reaction tube were sequentially added diazo compound **1** (0.6 mmol), pyridinium 1,4-zwitterionic thiolate **2** (0.2 mmol), and PhCl (3 mL) at room temperature, then the reaction mixture was stirred at 105°C for 10 min under M.W. irradiation. After completion of the reaction, the organic layer was concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc/petroleum ether) to give the corresponding product **4**.

Dimethyl 1-phenylindolizine-2,3-dicarboxylate (**4aa**)[6] [CAS: 2452307-17-2]

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent. Colorless crystals, yield 7 mg (12%), m.p. 114–115°C. Lit.[6] 104–105 °C. R_f = 0.20 (PE: EA = 10:1, *v/v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.46 (d, J = 7.1 Hz, 1H), 7.66 (d, J = 8.9 Hz, 1H), 7.49 (d, J = 6.9 Hz, 2H), 7.44 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.09 (dd, J = 9.0, 6.5 Hz, 1H), 6.91 (td, J = 7.0, 1.3 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.3, 160.9, 134.5, 132.8, 129.2, 128.8, 127.4, 127.3, 126.9, 123.3, 118.2, 115.1, 114.5, 110.8, 52.7, 51.7.
Dimethyl 5-methyl-1-phenylindolizine-2,3-dicarboxylate (**4ag**)

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent. Colorless crystals, yield 32 mg (50%), m.p. 114–115°C. R_f = 0.58 (PE: EA = 4:1, *v/v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 5H), 7.35 (td, J = 5.8, 2.7 Hz, 1H), 6.89 (dd, J = 9.1, 6.7 Hz, 1H), 6.61 (dt, J = 6.7, 1.1 Hz, 1H), 3.96 (s, 3H), 3.76 (s, 3H), 2.60 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 163.2, 136.0, 134.5, 133.5, 130.4, 128.3, 127.1, 122.9, 121.6, 116.9, 115.9, 115.5, 105.1, 52.8, 52.1, 21.2. **HRMS (ESI)** calcd for $C_{19}H_{18}NO_4^+$ $[M+H]^+$ *m/z*: 324.1230; found 324.1230.
Dimethyl 8-methyl-1-phenylindolizine-2,3-dicarboxylate (**4ah**) and dimethyl 6-methyl-1-phenylindolizine-2,3-dicarboxylate (**4ah'**)

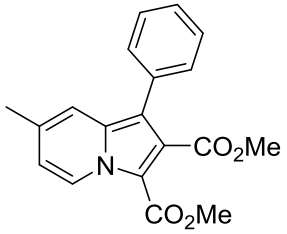


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Colorless oil, yield 16 mg (25%), **3ah**: **3ah'** = 68:32. R_f = 0.38 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) (**3ah, 3ah'**) δ 9.4 (t, J = 8.0 Hz, 1H), 9.29 (d, J = 1.7 Hz, 0.5H), 7.57 (d, J = 9.1 Hz, 0.5H), 7.49–7.41 (m, 3H), 7.36–7.31 (m, 4.5H), 6.97 (dd, J = 9.2, 1.5 Hz, 0.5H), 6.80 (d, J = 4.4 Hz, 2H), 3.90 (s, 1.5H), 3.89 (s, 3H), 3.84 (s, 1.5H), 3.70 (s, 3H), 2.37 (s, 1.5H), 2.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) (**3ah, 3ah'**) δ 168.0, 167.5, 167.0, 161.0, 134.2, 134.1, 133.0, 131.4, 129.7, 129.3, 128.9, 128.6, 127.7, 127.6, 127.2, 126.6, 125.4, 125.3, 124.5, 123.7, 117.6, 116.4, 114.0, 110.5, 52.7, 52.4, 51.71, 51.70, 20.5, 18.8. **HRMS (ESI)** calcd for $C_{19}H_{18}NO_4^+$ $[M+H]^+$ *m/z*: 324.1230; found 324.1231.

Dimethyl 7-methyl-1-phenylindolizine-2,3-dicarboxylate (**4ai**)

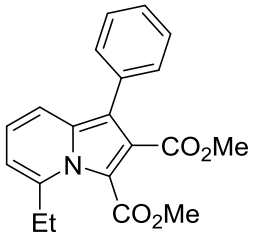


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Colorless oil, yield 16 mg (25%). R_f = 0.37 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (d, J = 7.2 Hz, 1H), 7.49–7.41 (m, 5H), 7.33 (t, J = 7.1 Hz, 1H), 6.76 (dd, J = 7.3, 1.8 Hz, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 2.35 (d, J = 1.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.5, 161.0, 135.1, 134.4, 133.1, 129.3, 128.9, 127.2, 127.1, 127.0, 117.2, 116.6, 113.9, 110.2, 52.7, 51.7, 21.4. **HRMS (ESI)** calcd for $C_{19}H_{18}NO_4^+$ $[M+H]^+$ *m/z*: 324.1230; found 324.1229.

Dimethyl 5-ethyl-1-phenylindolizine-2,3-dicarboxylate (**4aj**)



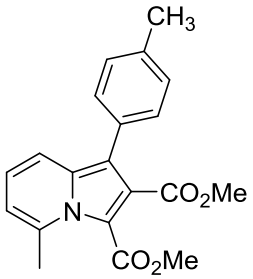
The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Yellow oil, yield 31 mg (46%). R_f = 0.25 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.40 (m, 5H), 7.34 (td, J = 5.9, 2.6 Hz, 1H), 6.94 (dd, J = 9.0,

6.9 Hz, 1H), 6.67 (dt, *J* = 6.8, 1.2 Hz, 1H), 3.96 (s, 3H), 3.76 (s, 3H), 2.98 (q, *J* = 7.3 Hz, 2H), 1.32 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 163.4, 141.4, 134.6, 133.5, 130.3, 128.3, 127.1, 123.3, 121.6, 116.8, 116.5, 115.8, 112.5, 52.9, 52.1, 26.0, 11.3. **HRMS (ESI)** calcd for $C_{20}H_{20}NO_4^+$ $[M+H]^+$ *m*/*z*: 338.1387; found 338.1389.

Dimethyl 5-methyl-1-(*p*-tolyl)indolizine-2,3-dicarboxylate (**4bg**)

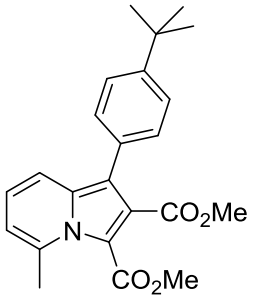


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v*/*v*) as eluent.

Yellow oil, yield 35 mg (52%). R_f = 0.28 (PE: EA = 10:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 9.3 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 6.87 (dd, *J* = 9.0, 6.7 Hz, 1H), 6.60 (dt, *J* = 6.6, 1.2 Hz, 1H), 3.95 (s, 3H), 3.78 (s, 3H), 2.59 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.0, 163.1, 136.7, 135.9, 134.5, 130.4, 130.2, 129.1, 123.0, 121.4, 116.9, 116.3, 115.9, 115.5, 52.7, 52.1, 21.4, 21.2. **HRMS (ESI)** calcd for $C_{20}H_{20}NO_4^+$ $[M+H]^+$ *m*/*z*: 338.1387; found 338.1388.

Dimethyl 1-(4-(*tert*-butyl)phenyl)-5-methylindolizine-2,3-dicarboxylate (**4cg**)

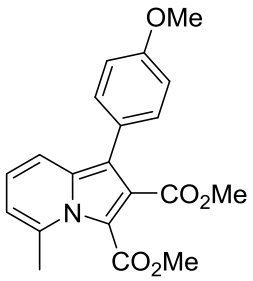


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v*/*v*) as eluent.

Yellow oil, yield 38 mg (51%). R_f = 0.25 (PE: EA = 10:1, *v*/*v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49–7.43 (m, 3H), 7.38 (d, *J* = 8.4 Hz, 2H), 6.88 (dd, *J* = 9.0, 6.7 Hz, 1H), 6.60 (dd, *J* = 6.7, 1.3 Hz, 1H), 3.95 (s, 3H), 3.79 (s, 3H), 2.60 (s, 3H), 1.37 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 163.1, 149.8, 136.0, 134.7, 130.3, 129.9, 125.3, 123.1, 121.5, 117.1, 116.2, 115.8, 115.5, 52.7, 52.2, 34.7, 31.5, 21.2. **HRMS (ESI)** calcd for $C_{23}H_{26}NO_4^+$ $[M+H]^+$ *m*/*z*: 380.1856; found 380.1858.

Dimethyl 1-(4-methoxyphenyl)-5-methylindolizine-2,3-dicarboxylate (**4dg)**

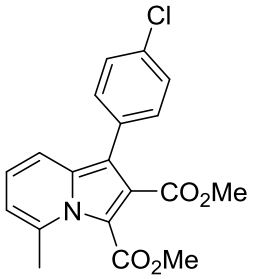


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Yellow oil, yield 31 mg (46%). R_f = 0.22 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 3H), 6.97 (d, J = 8.5 Hz, 2H), 6.87 (dd, J = 9.0, 6.7 Hz, 1H), 6.59 (d, J = 6.7 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.77 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.1, 163.2, 158.8, 135.9, 134.6, 131.5, 125.7, 122.9, 121.3, 116.9, 116.3, 115.7, 115.5, 113.9, 55.4, 52.8, 52.1, 21.2. **HRMS (ESI)** calcd for $C_{20}H_{20}NO_5^+$ $[M+H]^+$ *m/z*: 354.1336; found 354.1338.

Dimethyl 1-(4-chlorophenyl)-5-methylindolizine-2,3-dicarboxylate (**4eg**)

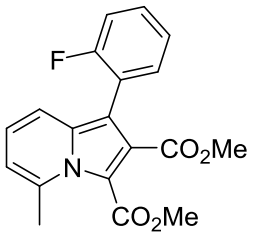


The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Yellow oil, yield 36 mg (51%). R_f = 0.20 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.34 (m, 5H), 6.89 (dd, J = 9.1, 6.7 Hz, 1H), 6.60 (dt, J = 6.6, 1.2 Hz, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 163.4, 135.9, 134.3, 133.1, 132.0, 131.8, 128.5, 122.2, 121.7, 117.1, 116.6, 115.5, 114.6, 52.9, 52.2, 21.0. **HRMS (ESI)** calcd for $C_{19}H_{17}ClNO_4^+$ $[M+H]^+$ *m/z*: 358.0841; found 358.0844.

Dimethyl 1-(2-fluorophenyl)-5-methylindolizine-2,3-dicarboxylate (**4gg**)



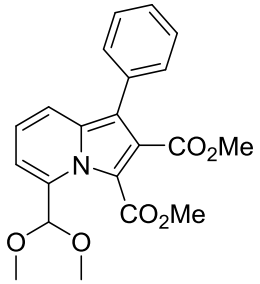
The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Yellow oil, yield 20 mg (30%). R_f = 0.21 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (m, 2H), 7.26 (d, J = 9.2 Hz, 1H), 7.20 (td, J = 7.4, 1.2 Hz, 1H), 7.15 (ddd, J = 9.6, 8.2, 1.3 Hz, 1H), 6.85 (dd, J = 9.1, 6.7 Hz, 1H), 6.58 (d, J = 6.7 Hz, 1H), 3.98 (s, 3H), 3.74 (s, 3H), 2.59 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.1, 164.2, 160.6 (d, J = 246.5 Hz), 135.4, 133.8, 132.6 (d, J = 2.6 Hz), 129.2 (d, J = 8.0 Hz), 123.9 (d, J = 3.4 Hz), 121.5, 121.4,

121.2, 118.2, 117.0, 115.6 (d, J = 22.3 Hz), 115.2, 109.1, 53.1, 52.0, 20.5. **^{19}F NMR** (376MHz, $CDCl_3$) δ -113.7. **HRMS (ESI)** calcd for $C_{19}H_{17}FNO_4^+$ $[M+H]^+$ m/z: 342.1136; found 342.1138.

Dimethyl 5-(dimethoxymethyl)-1-phenylindolizine-2,3-dicarboxylate (**4al**)



The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 20:1, *v/v*) as eluent.

Yellow oil, yield 40 mg (53%). R_f = 0.28 (PE: EA = 10:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 8.9, 1.5 Hz, 1H), 7.44 (s, 2H), 7.43 (d, J = 1.6 Hz, 2H), 7.34 (ddd, J = 7.2, 3.7, 2.2 Hz, 1H), 7.24 (dt, J = 7.0, 1.3 Hz, 1H), 6.97 (dd, J = 9.0, 7.0 Hz, 1H), 5.99 (s, 1H), 3.94 (s, 3H), 3.77 (s, 3H), 3.30 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 166.2, 162.7, 134.9, 134.3, 133.2, 130.3, 128.4, 127.2, 123.8, 120.4, 119.3, 117.8, 116.0, 114.3, 98.5, 53.0, 52.6, 52.2. **HRMS (ESI)** calcd for $C_{21}H_{22}NO_6^+$ $[M+H]^+$ m/z: 384.1442; found 384.1443.

1.6. Gram-scaled Synthesis of 3aa and 4ag

1.6.1. Gram-scaled Synthesis of 3aa

To a 35-mL reaction tube were sequentially added (diazo(phenyl)methyl)diphenylphosphine oxides (**1a**) (9.0 mmol, 2.862 g), (*Z*)-1,4-dimethoxy-1,4-dioxo-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (**2a**) (3.0 mmol, 0.759 g), and dry PhCl (20 mL) at room temperature, then the reaction mixture was stirred at 105°C for 10 min under M.W. irradiation. After completion of the reaction, the organic layer was concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc/Petroleum ether) to give the corresponding product **3aa** (53%, 0.707g).

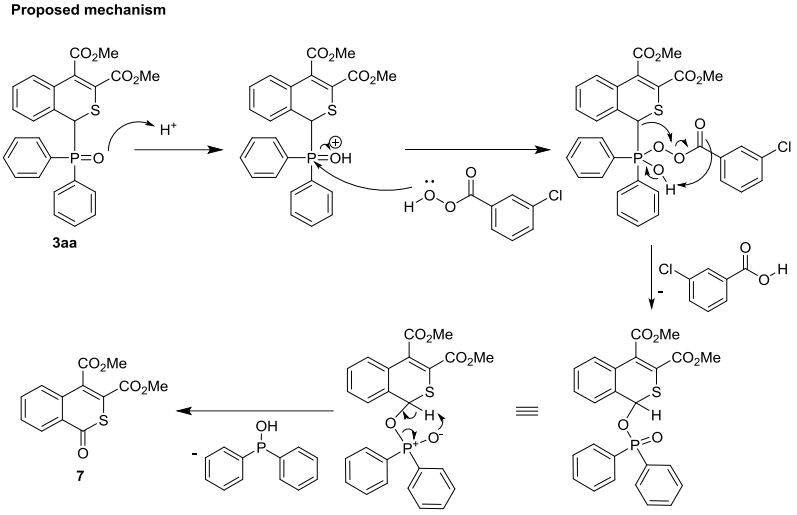
1.6.2. Gram-scaled Synthesis of 4ag

To a 35-mL reaction tube were sequentially added (diazo(phenyl)methyl)diphenylphosphine oxides (**1a**) (12.0 mmol, 3.816 g), (*Z*)-1,4-dimethoxy-3-(2-methylpyridin-1-ium-1-yl)-1,4-dioxobut-2-ene-2-thiolate (**2g**) (4.0 mmol, 1.068 g), and dry PhCl (20 mL) at room temperature, then the reaction mixture was stirred at 105°C for 15 min under M.W. irradiation. After completion of the reaction, the organic layer was concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc/Petroleum ether) to give the corresponding product **4ag** (49%, 0.631g).

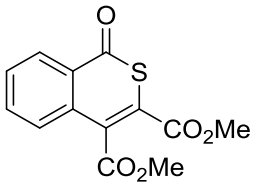
1.7 Applications

(1) To a 10-mL reaction tube were sequentially added dimethyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate **3aa** (0.2 mmol, 92.8 mg) and DCM (2 mL) at 0°C, then *m*CPBA (0.48 mmol, 82.8 mg) was added and the reaction mixture was stirred at 0 °C to room temperature for 12 hours. After completion of the reaction, 2 mL of saturated solution of $NaHCO_3$ was added, and the mixture was stirred well. It was then extracted with DCM (3 × 3 mL). The combined organic layers were washed with brine (1 mL), dried over anhydrous magnesium sulfate, and concentrated under reduced pressure to yield the crude product, which was purified by silica gel column chromatography (EtOAc/petroleum ether 10:1, *v/v*) to give the corresponding product dimethyl 1-oxo-1*H*-isothiochromene-3,4-dicarboxylate **7** (44 %, 24 mg).

The formation mechanism of product **7** was proposed as shown in Scheme S3. **3aa** first underwent a Bayer-Villiger oxidation with *m*CPBA followed by P-Cope elimination to afford product **7**.

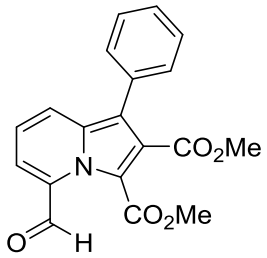


Scheme S3. Proposed mechanism

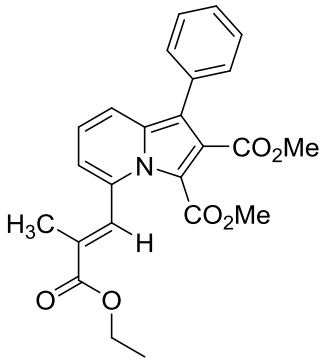
Dimethyl 1-oxo-1*H*-isothiochromene-3,4-dicarboxylate (**7**)

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 10:1, *v/v*) as eluent. Colorless crystals, yield 24 mg (44%), m.p. 90–91°C. R_f = 0.38 (PE: EA = 4:1, *v/v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (dd, J = 7.9, 1.5 Hz, 1H), 7.81 (ddd, J = 8.2, 7.3, 1.5 Hz, 1H), 7.73 (ddd, J = 8.3, 7.3, 1.2 Hz, 1H), 7.61 (dd, J = 8.1, 1.2 Hz, 1H), 4.04 (s, 3H), 3.93 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 184.9, 167.5, 162.0, 134.6, 133.7, 133.4, 131.7, 129.43, 129.36, 127.3, 126.7, 53.8, 53.5. **HRMS (ESI)** calcd for $C_{13}H_{11}O_5S^+$ $[M+H]^+$ *m/z*: 279.0322; found 279.0319.

(2) To a 10-mL reaction tube were sequentially added dimethyl 5-(dimethoxymethyl)-1-phenylindolizine-2,3-dicarboxylate **4al** (0.1 mmol, 38.3 mg) and DCM (1 mL), then TFA (10 eq.) was

added and the reaction mixture was stirred at room temperature for 3 hours. After completion of the reaction, the excess of TFA was neutralized with saturated solution of $NaHCO_3$ and the mixture was extracted with DCM (3 × 3 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product **8** (99%, 34 mg).

Dimethyl 5-formyl-1-phenyl-1,8a-dihydroindolizine-2,3-dicarboxylate (**8**)

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 10:1, *v/v*) as eluent. Yellow oil, yield 34 mg (99%). R_f = 0.25 (PE: EA = 4:1, *v/v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 7.80 (dd, *J* = 8.9, 1.3 Hz, 1H), 7.48 (dd, *J* = 6.9, 1.3 Hz, 1H), 7.46–7.42 (m, 4H), 7.41–7.36 (m, 1H), 7.14 (dd, *J* = 8.9, 6.9 Hz, 1H), 3.95 (s, 3H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 182.0, 165.8, 161.8, 134.1, 133.8, 132.1, 129.8, 128.8, 127.9, 126.1, 124.6, 124.3, 120.8, 118.9, 117.4, 52.6, 52.5. **HRMS (ESI)** calcd for $C_{19}H_{16}NO_5^+$ $[M+H]^+$ *m/z*: 338.1023; found 338.1024.

(3) To a 10-mL reaction tube were sequentially added dimethyl 5-formyl-1-phenyl-1,8a-dihydroindolizine-2,3-dicarboxylate (**8**) (0.1 mmol, 33.7 mg) and DCM (2 mL), then ethyl 2-(triphenylphosphoranylidene)propionate (0.1 mmol, 36.2 mg) was added and the reaction mixture was stirred at room temperature for 6 hours. After completion of the reaction, the mixture was concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the desired product dimethyl (*E*)-5-(3-ethoxy-2-methyl-3-oxoprop-1-en-1-yl)-1-phenylindolizine-2,3-dicarboxylate **9** (86%, 36 mg).

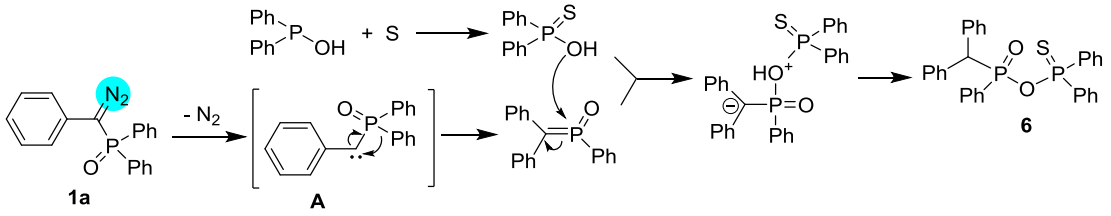
Dimethyl (*E*)-5-(3-ethoxy-2-methyl-3-oxoprop-1-en-1-yl)-1-phenylindolizine-2,3-dicarboxylate (**9**)

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 10:1, *v/v*) as eluent. Yellow oil, yield 36 mg (86 %). R_f = 0.38 (PE: EA = 4:1, *v/v*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dt, J = 9.0, 0.9 Hz, 1H), 7.46–7.41 (m, 4H), 7.39–7.33 (m, 2H), 6.99 (dd, J = 9.0, 6.9 Hz, 1H), 6.82 (dt, J = 6.9, 1.2 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.87 (s, 3H), 3.77 (s, 3H), 2.19 (d, J = 1.6 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.8, 165.6, 162.3, 134.0, 133.4, 132.9, 132.0, 130.7, 130.2, 128.4, 127.3, 123.3, 120.8, 119.2, 117.6, 117.1, 117.0, 61.3, 52.3, 15.0, 14.4. **HRMS (ESI)** calcd for $C_{24}H_{24}NO_6^+$ $[M+H]^+$ m/z: 422.1598; found 422.1601.

2. Control Experiments

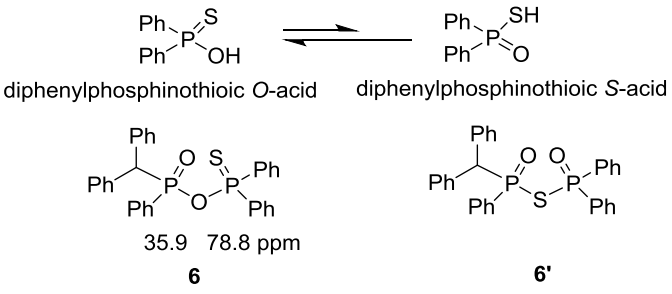
2.1. Control experiments

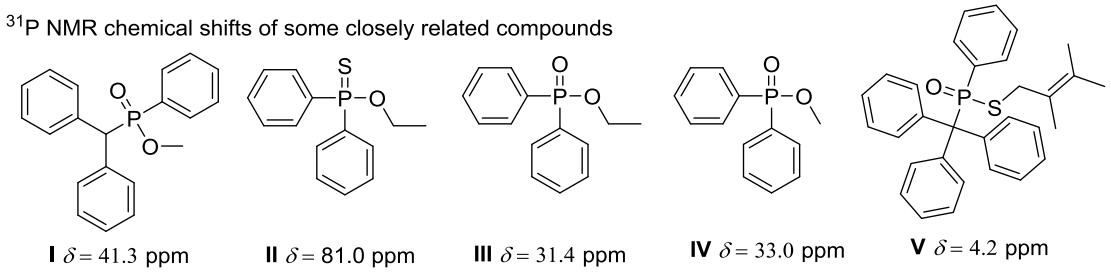
In the control experiment on the formation of product **4ag**, a byproduct **6** was obtained in 45% yield. It was generated from the nucleophilic addition of diphenylphosphinothioic *O*-acid (generated via sulfur oxidation of hydroxydiphenylphosphane to phosphene ((diphenylmethylene)(phenyl)phosphine oxide generated from **1a** via the Wolff rearrangement[11]). This byproduct **6** provided a perfect experimental evidence for our proposed mechanism in Scheme 2. Its formation mechanism is proposed in Scheme S4. As shown in Scheme 2, during the formation of products **4**, both sulfur and hydroxydiphenylphosphane generate and takes place a sulfurization to yield diphenylphosphinothioic *O*-acid. In the same time, diazo compound **1a** undergoes a Wolff rearrangement to form phosphene [(diphenylmethylene)(phenyl)phosphine oxide] under microwave irradiation. The nucleophilic addition of diphenylphosphinothioic *O*-acid to the phosphene generates the byproduct **6** because the phosphene is more oxyphilic.



Scheme S4. Proposed mechanism for the formation of byproduct **6**.

Verification of structure of byproduct **6**.

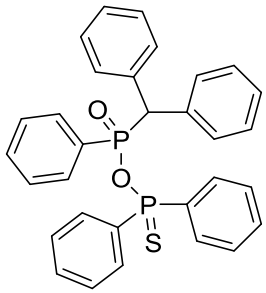




Scheme S5. Structural identification of byproduct **6** and ^{31}P NMR chemical shifts of some closely related compounds

The originally generated diphenylphosphinothioic *O*-acid can tautomerize to diphenylphosphinothioic *O*-acid in the reaction mixture. Both of them can undergo nucleophilic addition with the phosphine to

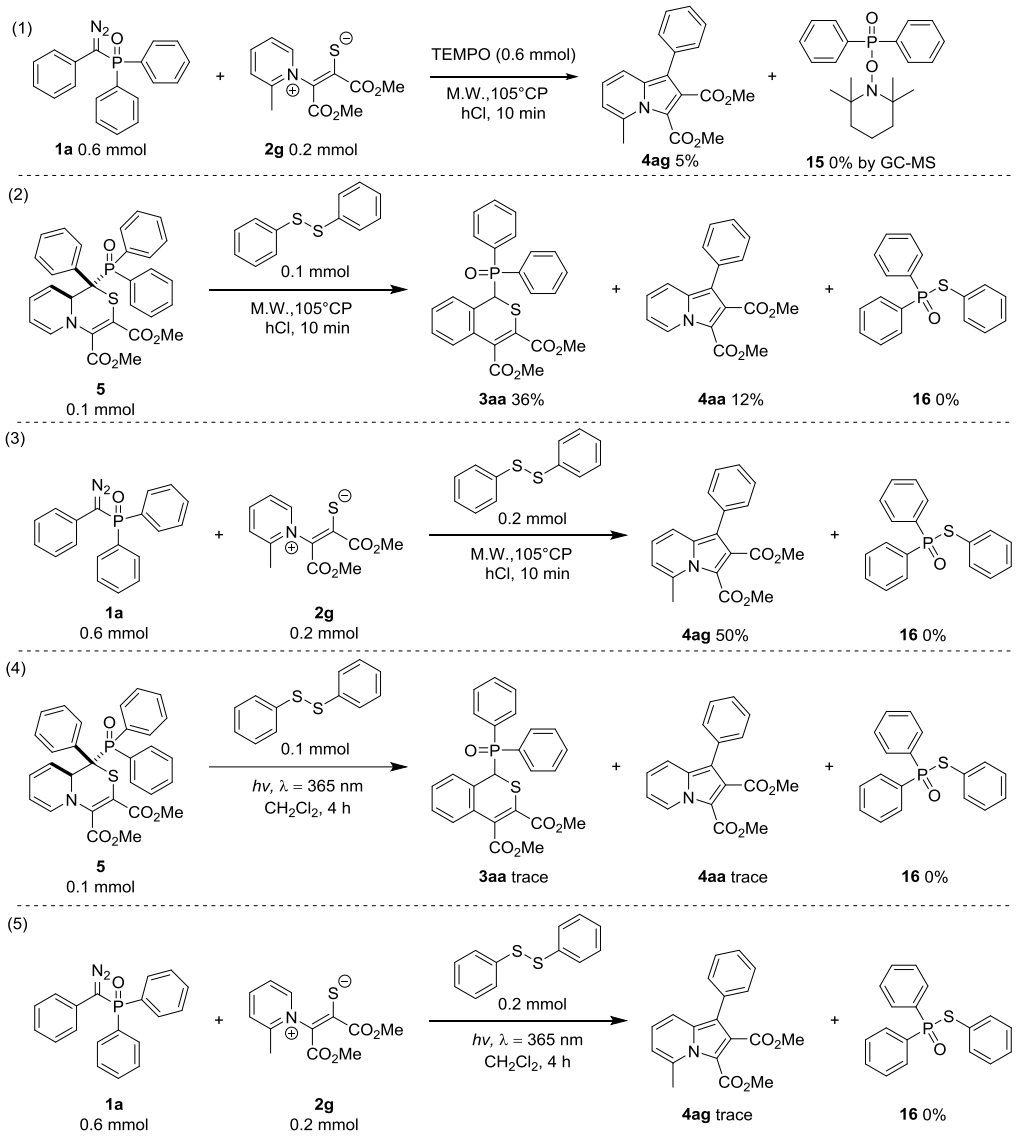
generate benzhydryl(phenyl)phosphinic diphenylphosphinothioic anhydride (**6**) or benzhydryl(phenyl)phosphinic diphenylphosphinic thioanhydride (**6**'). Both the *O*-acid and *S*-acid can possibly generate anhydride **6** or thioanhydride **6**'. The byproduct shows two phosphorus peaks at 35.9 and 78.8 ppm in its ^{31}P NMR spectrum. To identify the structure of the byproduct, we surveyed literature to find some closely related compounds **I** to **V** listed in Scheme S5. Their ^{31}P chemical shifts are 31.4 ppm for methyl benzhydryl(phenyl)phosphinate (**I**),[7] 81.0 ppm for *O*-ethyl diphenylphosphinothioate (**II**),[8] 31.4 and 33.0 ppm for ethyl and methyl diphenylphosphinates (**III** and **IV**),[8] and 4.2 ppm for *S*-(2,3-dimethylbut-2-en-1-yl) phenyl(trityl)phosphinothioate.[9] By referring these reported chemical shifts, the byproduct should be mere likely to benzhydryl(phenyl)phosphinic diphenylphosphinothioic anhydride (**6**) rather than benzhydryl(phenyl)phosphinic diphenylphosphinic thioanhydride (**6**'). The results indicate that the phosphene is more oxyphilic although the sulfur is more nucleophilic than the oxygen in diphenylphosphinothioic *O*-acid. This is very different from the reactions of ketenes and thiolacetic acid, in which the sulfur of thiolacetic acid predominantly nucleophilically attacks ketenes, generating the corresponding thioanhydrides.[10]

Benzhydryl(phenyl)phosphinic diphenylphosphinothioic anhydride (**6**)

The product was purified by silica gel column chromatography with petroleum ether (60–90°C fraction) and ethyl acetate (PE:EA = 10:1, *v*/*v*) as eluent. Red oil, yield 47 mg (45%). R_f = 0.25 (PE: EA = 4:1, *v*/*v*). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71–7.63 (m, 4H), 7.55–7.44 (m, 5H), 7.43–7.36 (m, 4H), 7.35–7.27 (m, 5H), 7.25–7.17 (m, 4H), 7.16–7.07 (m, 3H), 4.90 (d, J = 17.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 136.1 (d, J = 7.9 Hz), 135.5, 134.9, 133.9 (d, J = 26.9 Hz), 133.0, 132.6, 132.2, 132.1, 132.0 (d, J = 2.8 Hz), 131.5 (d, J = 12.7 Hz), 130.9, 130.3 (d, J = 6.8 Hz), 130.1, 129.8 (d, J = 8.3 Hz), 128.8 (d, J = 15.3 Hz), 128.4 (d, J = 14.2 Hz), 128.1 (d, J = 13.9 Hz), 127.4 (d, J = 22.6 Hz), 55.1 (d, J = 93.0 Hz). **^{31}P NMR** (162 MHz, $CDCl_3$) δ 78.8 (d, J = 43.3 Hz), 35.9 (d, J = 43.0 Hz). **HRMS (ESI)** calcd for $C_{31}H_{27}O_2P_2S^+$ $[M+H]^+$ *m*/*z*: 525.1202; found 525.1205.

2.2. Additional control experiments on the possible radical process

It was reported that arenecarbonyl diphenylphosphine oxides or diarenecarbonyl phenylphosphine oxides underwent radical reactions under photo irradiation[10] or under Pd-catalyzed conditions[11] and arenecarbonylphosphonates underwent radical reaction as well under Co-catalyzed conditions.[12] In our current reaction, compound **5** was a possible intermediate in the reaction. If it underwent a radical elimination, it also gave product **4aa**. To examine whether the reaction was a radical process, several control reactions were designed and carried out. Although the reaction of diphenyl(2,4,6-methylbenzoyl)phosphine oxide and 1,2-diphenyldisulfane (phenyl disulfide) produced *S*-phenyl

diphenylphosphinothioate and *S*-phenyl 2,4,6-methylbenzothioate in excellent yields under photo irradiation (330 nm < λ < 400 nm), neither TEMPO-captured product nor *S*-phenyl diphenylphosphinothioate (**16**) were observed in our control experiments (Scheme S5). The results ruled out the radical process and support the P-Cope elimination as the key step.



Scheme S4. Control experiments

Procedures of additional control experiments

(1) To a 10-mL reaction tube were sequentially added (diazo(phenyl)methyl)diphenylphosphine oxide (**1a**) (0.6 mmol, 191 mg), (*Z*)-1,4-dimethoxy-3-(2-methylpyridin-1-ium-1-yl)-1,4-dioxobut-2-ene-2-thiolate (**2g**) (0.2 mmol, 53.4 mg), TEMPO (0.6 mmol, 93.6 mg), and PhCl (3 mL) at room temperature, then the reaction mixture was stirred at 105 °C for 10 min under M.W. irradiation. Product 5% **4ag** was obtained in 5% yield and no 2,2,6,6-tetramethylpiperidin-1-yl diphenylphosphinate (**15**) was observed by GC-MS analysis of the reaction mixture.

(2) To a 10-mL reaction tube were sequentially added dimethyl *rel*-(1*R*,9a*S*)-1-(diphenylphosphoryl)-1-

phenyl-1,9a-dihydropyrido[2,1-*c*][1,4]thiazine-3,4-dicarboxylate (**5**) (0.1 mmol, 54.3 mg), 1,2-diphenyldisulfane (0.1 mmol, 21.8 mg), and PhCl (1 mL) at room temperature, then the reaction mixture was stirred at 105°C for 10 min under M.W. irradiation. **3aa** and **4aa** were obtained in 36% and 12% yields, respectively. But no *S*-phenyl diphenylphosphinothioate (**16)** was found after reaction.

(3) To a 10-mL reaction tube were sequentially added (diazo(phenyl)methyl)diphenylphosphine oxide (**1a**) (0.6 mmol, 191 mg), (*Z*)-1,4-dimethoxy-3-(2-methylpyridin-1-ium-1-yl)-1,4-dioxobut-2-ene-2-thiolate (**2g**) (0.2 mmol, 53.4 mg), 1,2-diphenyldisulfane (0.2 mmol, 43.6 mg), and PhCl (3 mL) at room temperature, then the reaction mixture was stirred at 105°C for 10 min under M.W. irradiation. And **4ag** was obtained in 50% yield without observation of *S*-phenyl diphenylphosphinothioate (**16)** after the reaction.

(4) To a 20-mL reaction tube were sequentially added dimethyl *rel*-(1*R*,9a*S*)-1-(diphenylphosphoryl)-1-phenyl-1,9a-dihydropyrido[2,1-*c*][1,4]thiazine-3,4-dicarboxylate (**5**) (0.2 mmol, 108.6 mg), 1,2-diphenyldisulfane (0.2 mmol, 43.6 mg), and DCM (8 mL) at room temperature, then the reaction mixture was stirred at room temperature for 4 h under photo irradiation (λ = 365nm). After reaction, only a trace amount of **3aa** and **4aa** were observed, but **16** was not by GC-MS analysis of the reaction mixture.

(5) To a 20-mL reaction tube were sequentially added (diazo(phenyl)methyl)diphenylphosphine oxide (**1a**) (0.6 mmol, 191 mg), (*Z*)-1,4-dimethoxy-3-(2-methylpyridin-1-ium-1-yl)-1,4-dioxobut-2-ene-2-thiolate (**2g**) (0.2 mmol, 53.4 mg), 1,2-diphenyldisulfane (0.2 mmol, 43.6 mg), and DCM (8 mL) at room temperature, then the reaction mixture was stirred at room temperature for 4 h under photo irradiation (λ = 365nm). After reaction, only a trace amount of **4ag** was observed, but **16** was not by GC-MS analysis of the reaction mixture.

3. References

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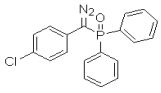
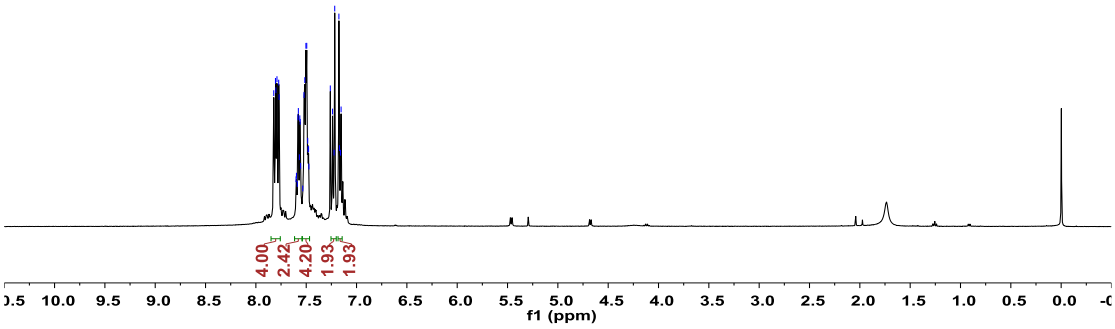
4. Copies of ^{1}H, ^{13}C, ^{31}P, ^{19}F NMR, and HRMS Spectra of Products

4.1. Copies of ^{1}H and ^{31}P NMR Spectra of Diazo Compounds 1

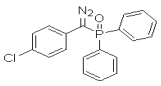
((4-Chlorophenyl)(diazo)methyl)diphenylphosphine oxide (1e)

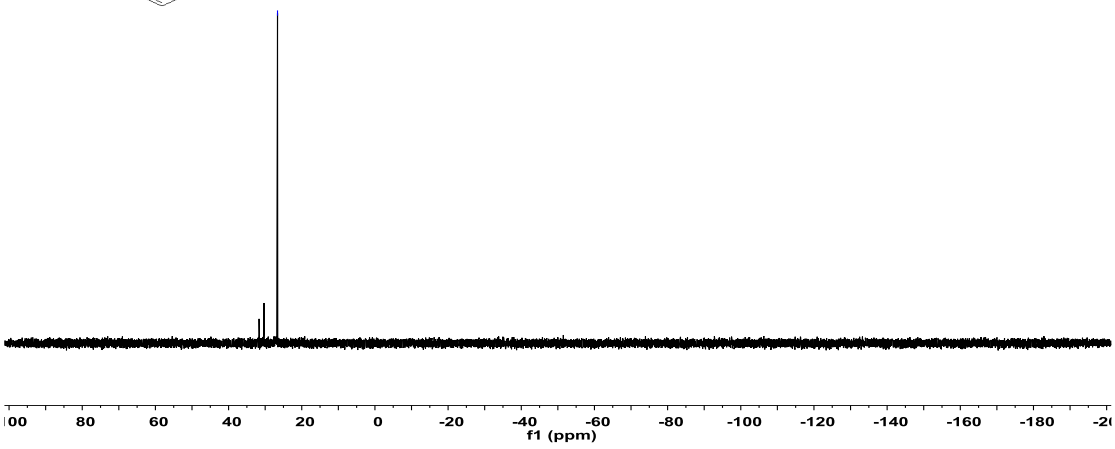
^{1}H NMR (400MHz, $CDCl_3$)





^{31}P NMR (162 MHz, $CDCl_3$)

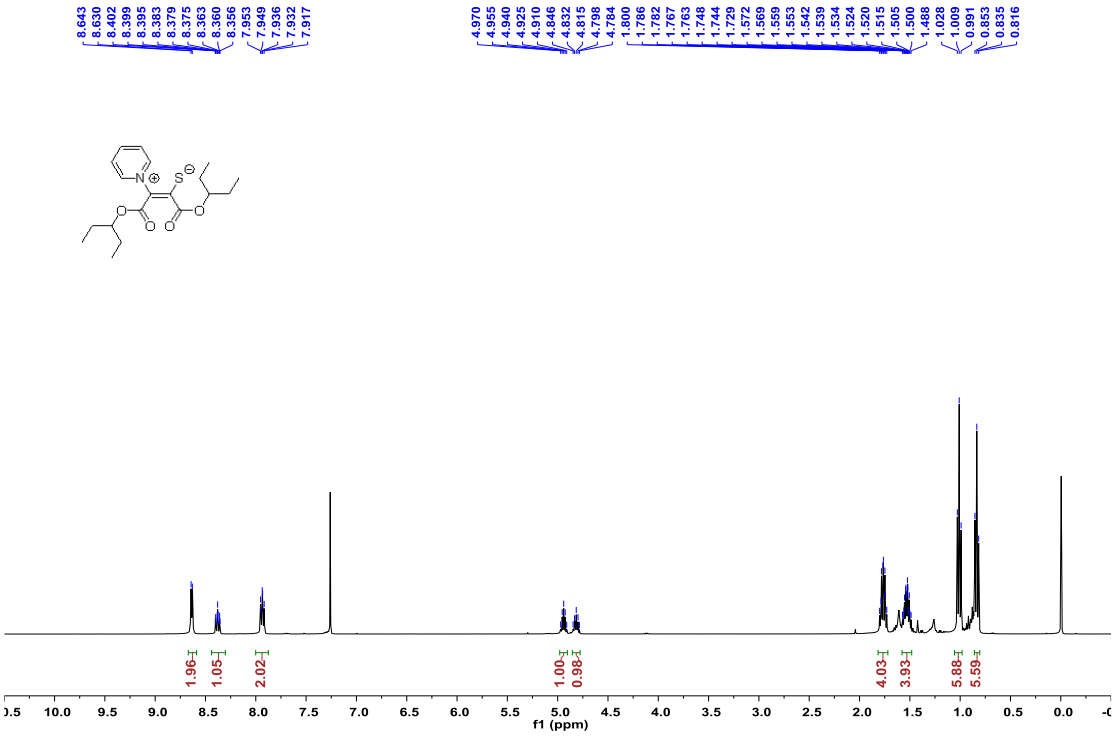




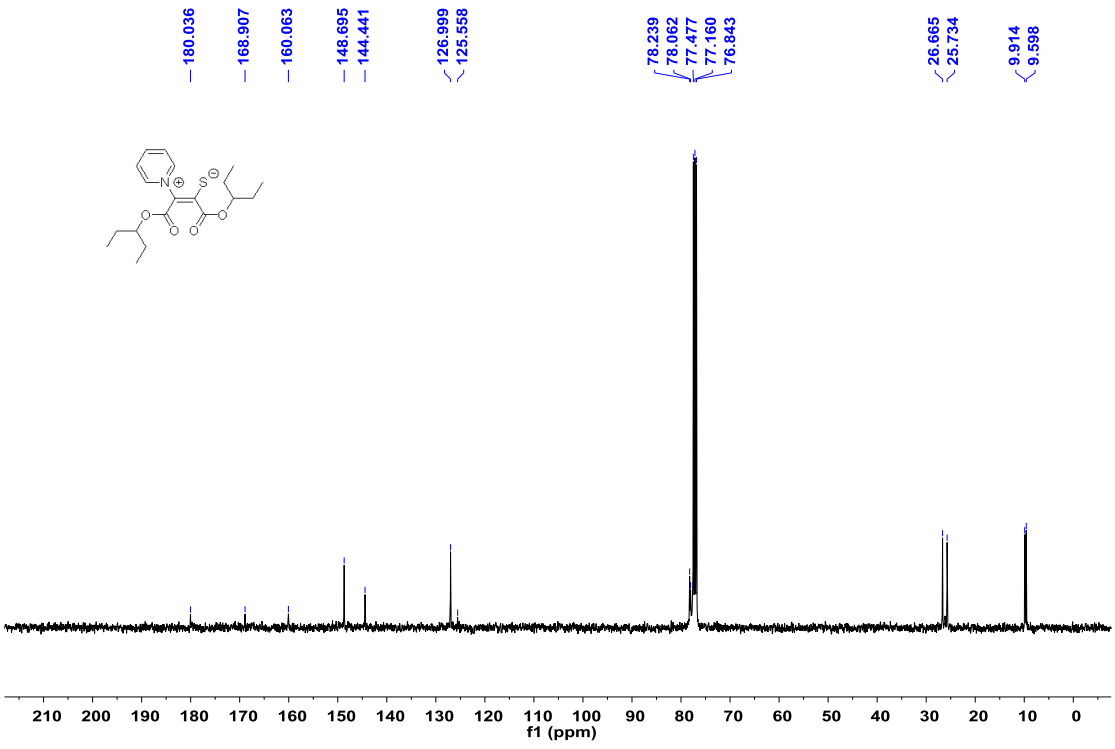
4.2. Copies of ^{1}H, ^{13}C NMR and HRMS Spectra of Pyridinium 1,4-zwitterionic Thiolates 2

(*Z*)-1,4-Dioxo-1,4-bis(pentan-3-yloxy)-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (2c)

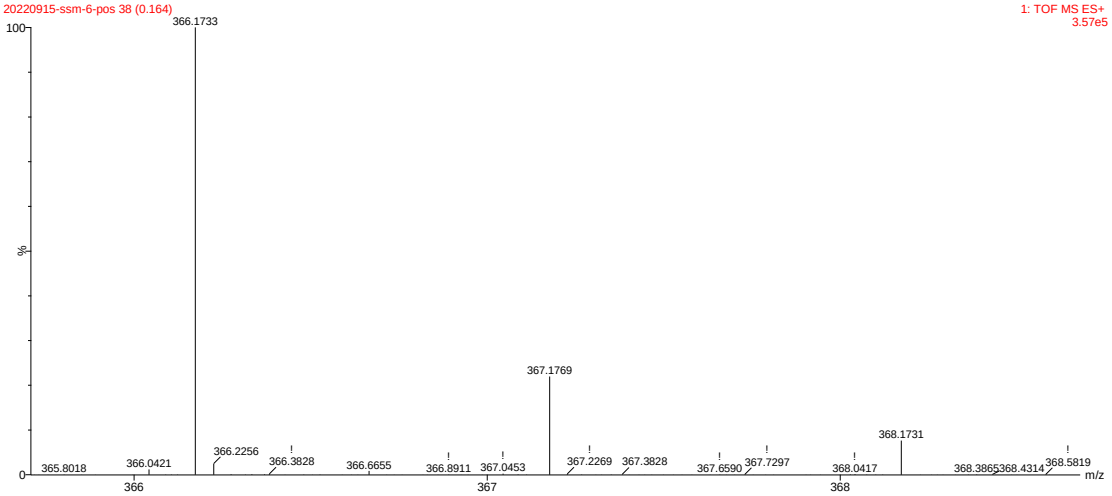
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

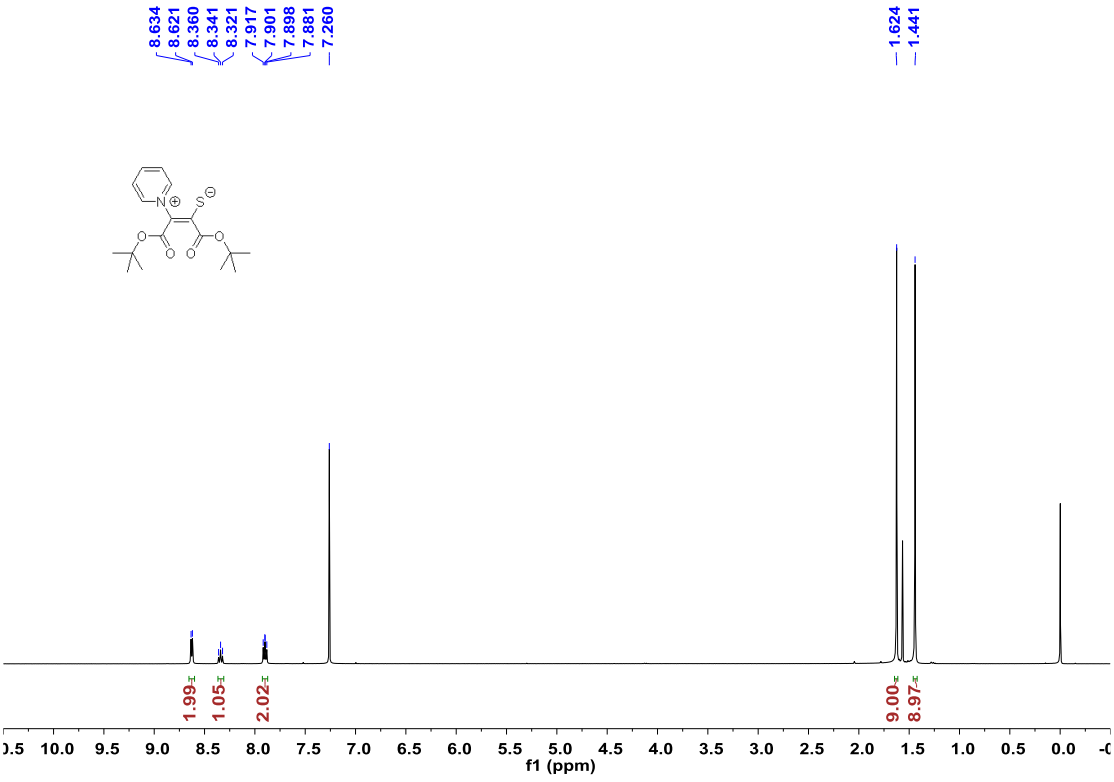


HRMS



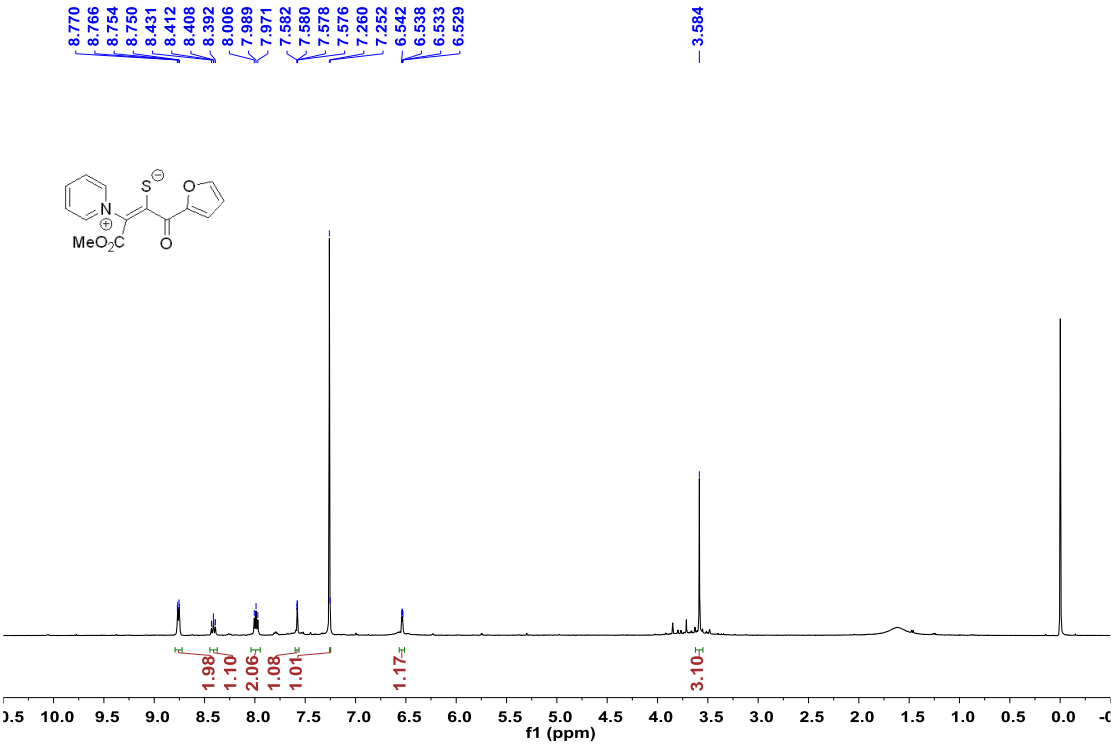
(*Z*)-1,4-Di-tert-butoxy-1,4-dioxo-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (2d)

^{1}H NMR (400MHz, $CDCl_3$)



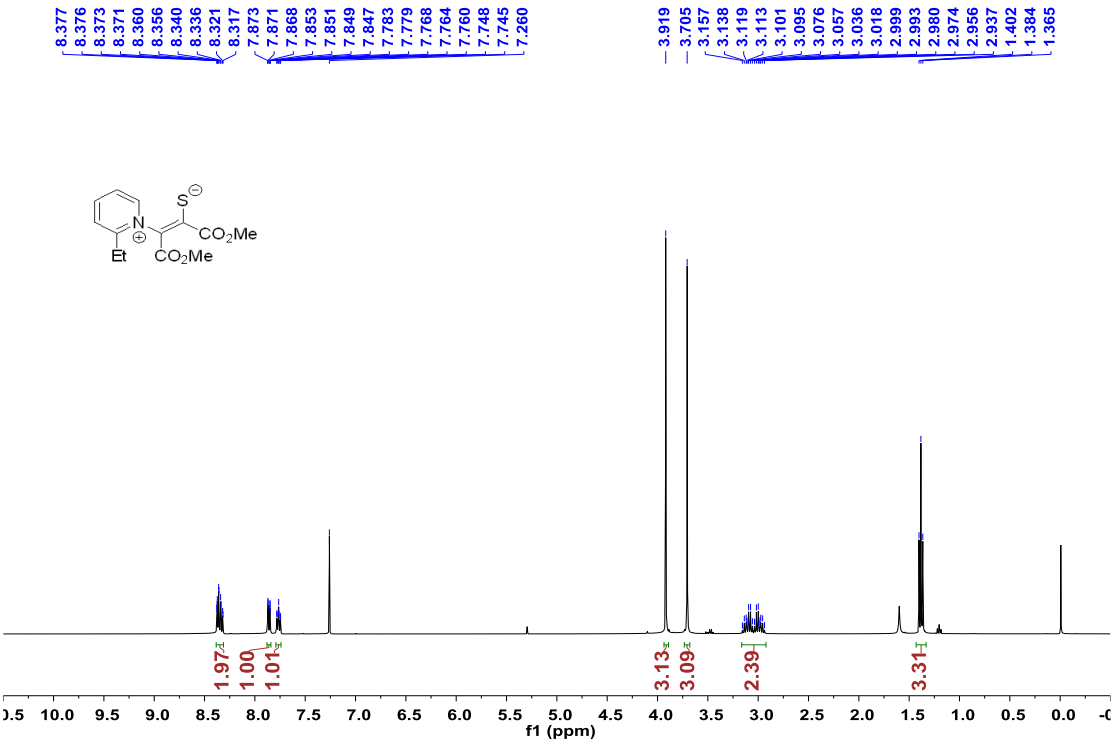
(*Z*)-1-(Furan-2-yl)-4-methoxy-1,4-dioxo-3-(pyridin-1-ium-1-yl)but-2-ene-2-thiolate (2f)

^{1}H NMR (400MHz, $CDCl_3$)



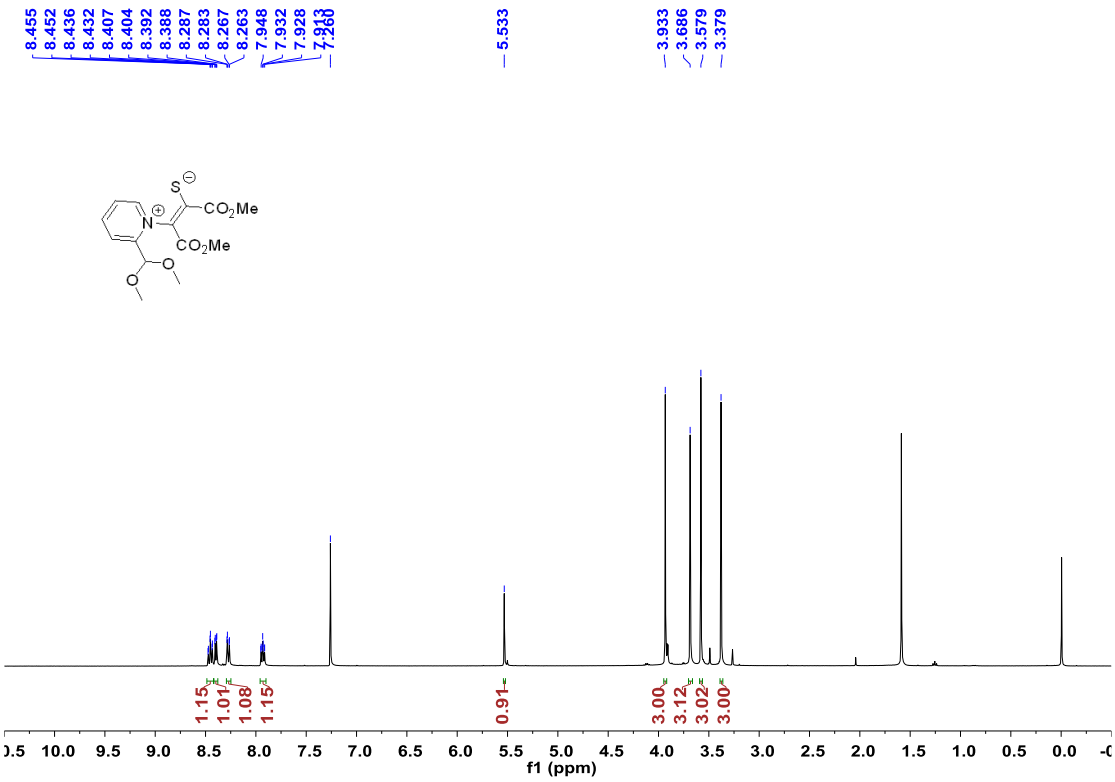
(*Z*)-3-(2-Ethylpyridin-1-ium-1-yl)-1,4-dimethoxy-1,4-dioxobut-2-ene-2-thiolate (2j)

^{1}H NMR (400MHz, $CDCl_3$)

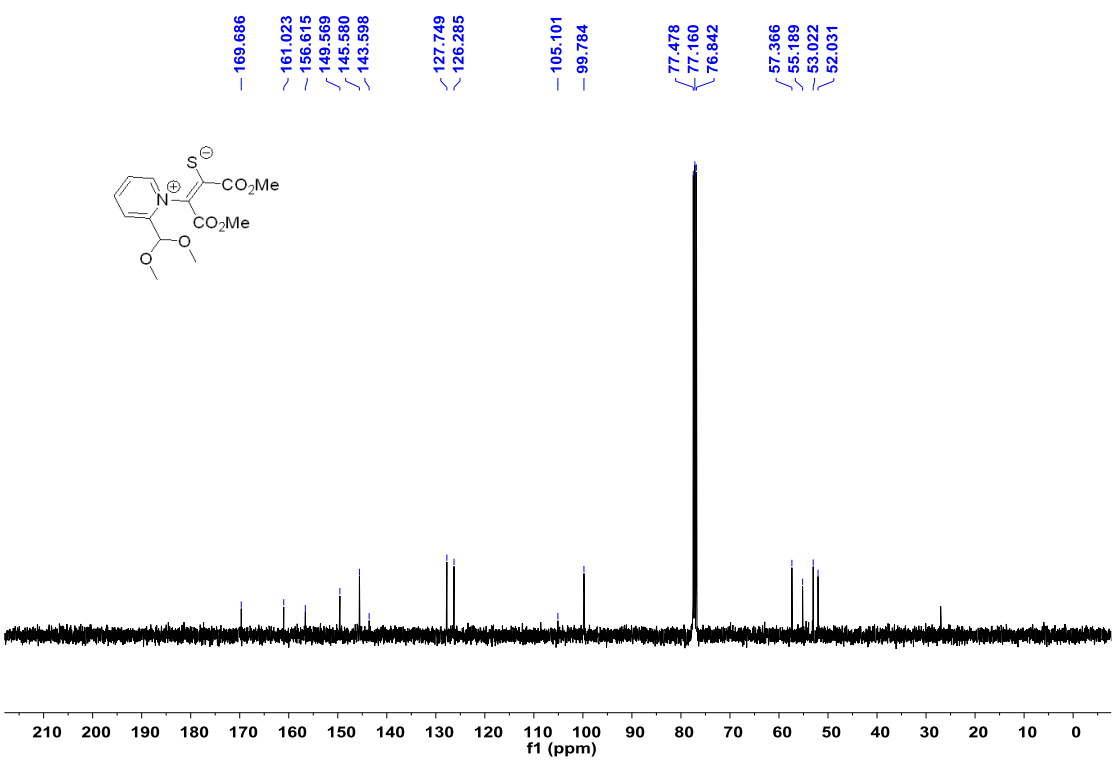


(*Z*)-3-(2-(Dimethoxymethyl)pyridin-1-ium-1-yl)-1,4-dimethoxy-1,4-dioxobut-2-ene-2-thiolate (2l)

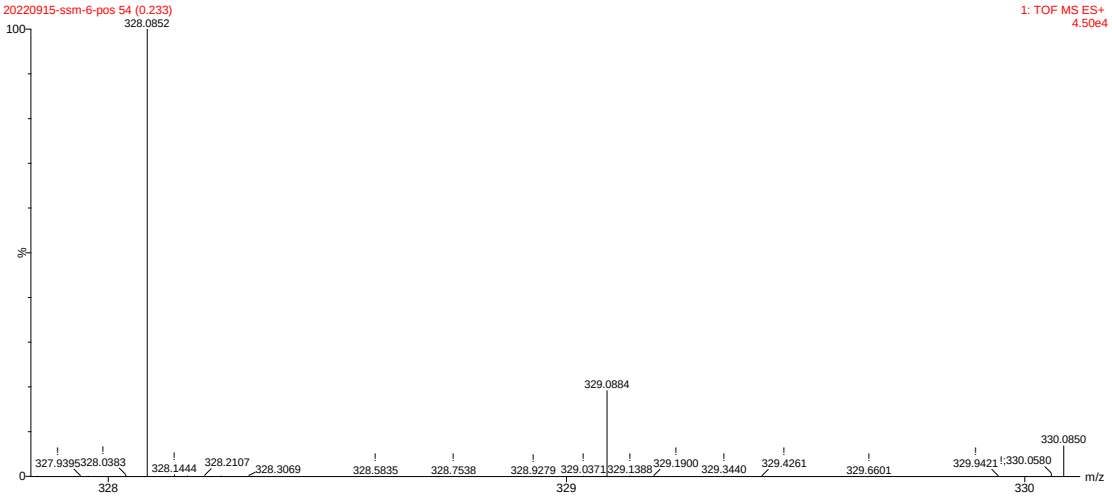
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



HRMS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%
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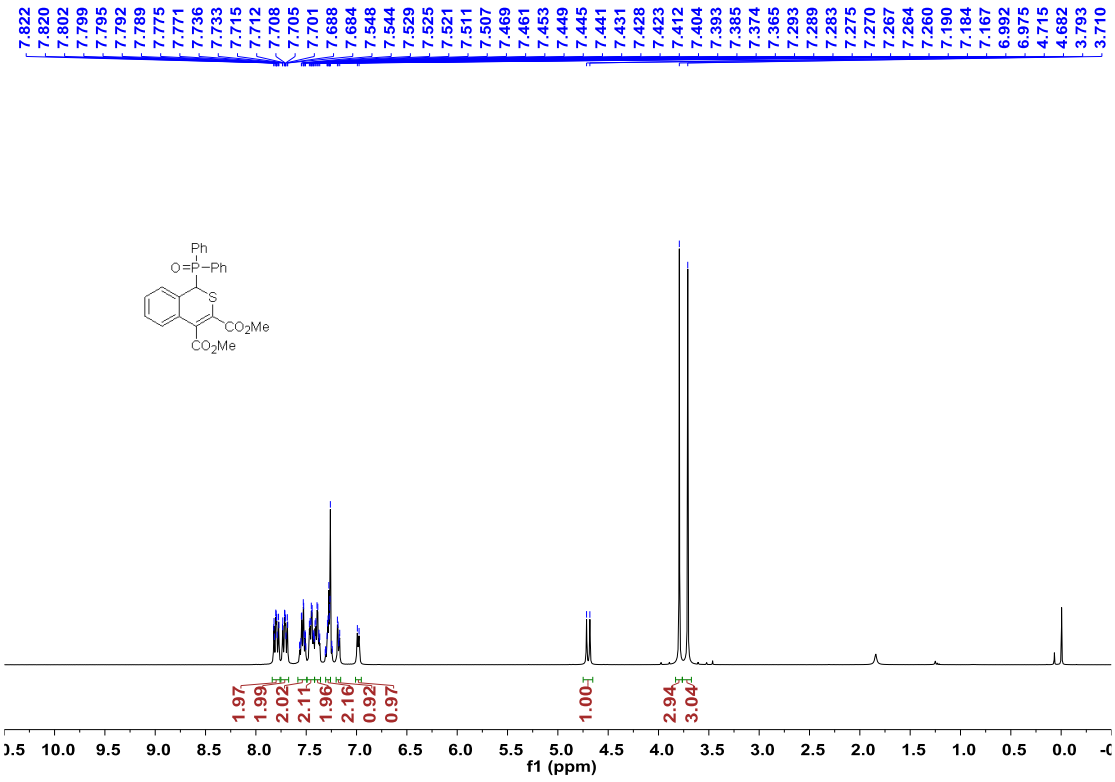
329.0884
330.0850
327.9395
328.0383
328.1444
328.2107
328.3069
328.5835
328.7538
328.9279
329.0371
329.1388
329.1900
329.3440
329.4261
329.6601
329.9421
330.0580
328
329
330
m/z

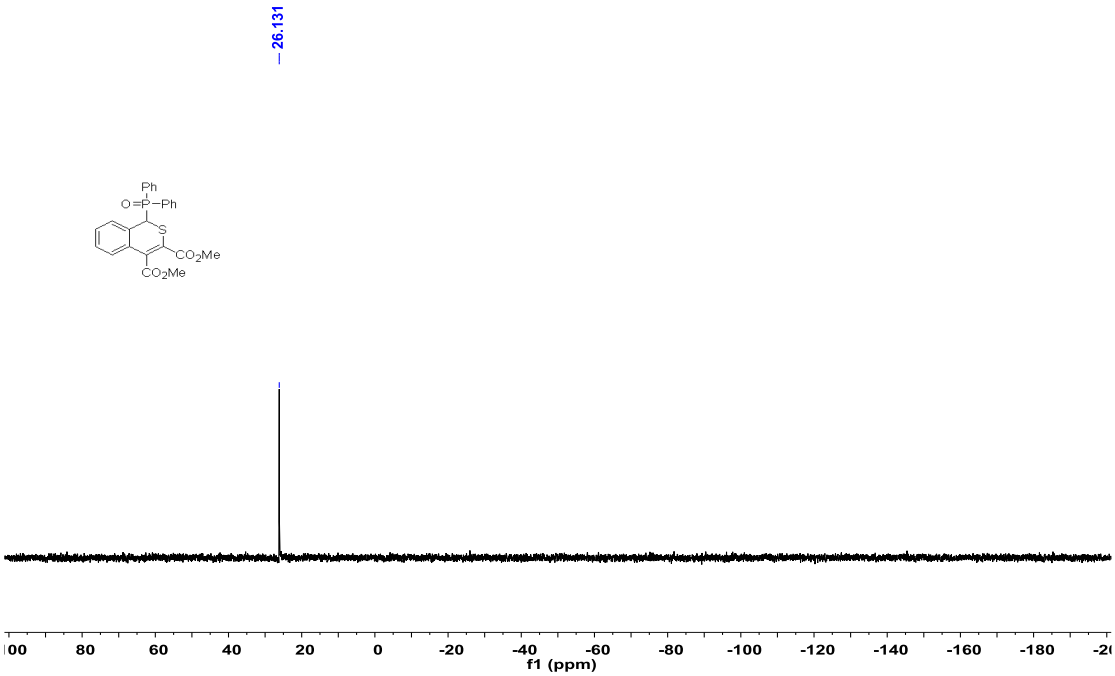
4.3. Copies of ^{1}H, ^{31}P, ^{13}C, ^{19}F NMR and HRMS Spectra of Products 3

Dimethyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3aa)

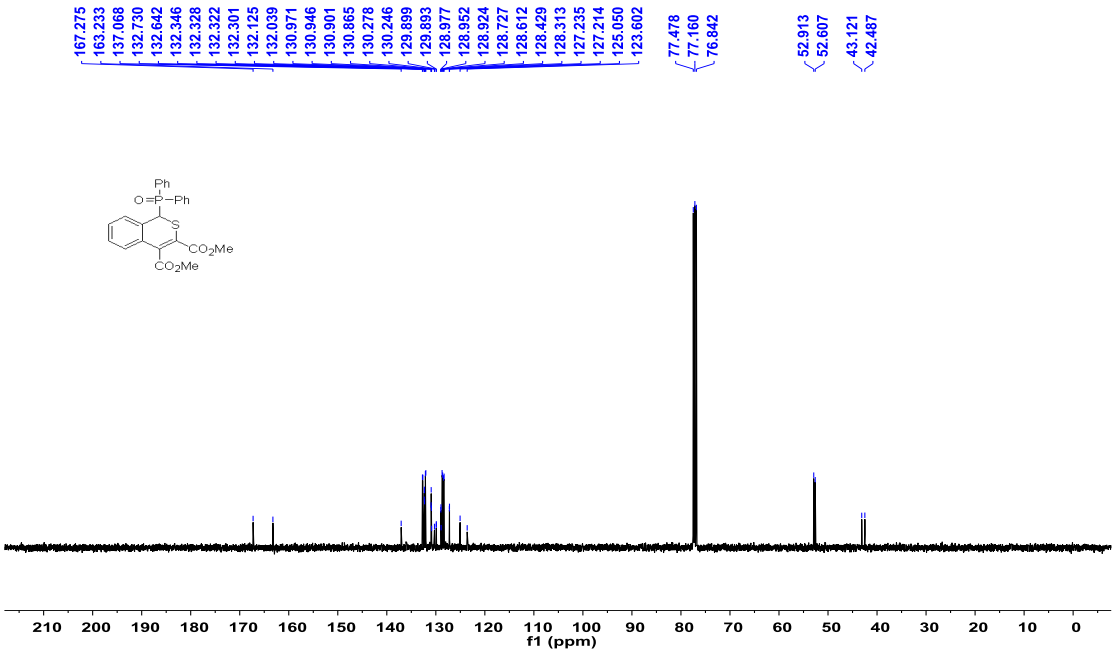
^{1}H NMR (400MHz, $CDCl_3$)



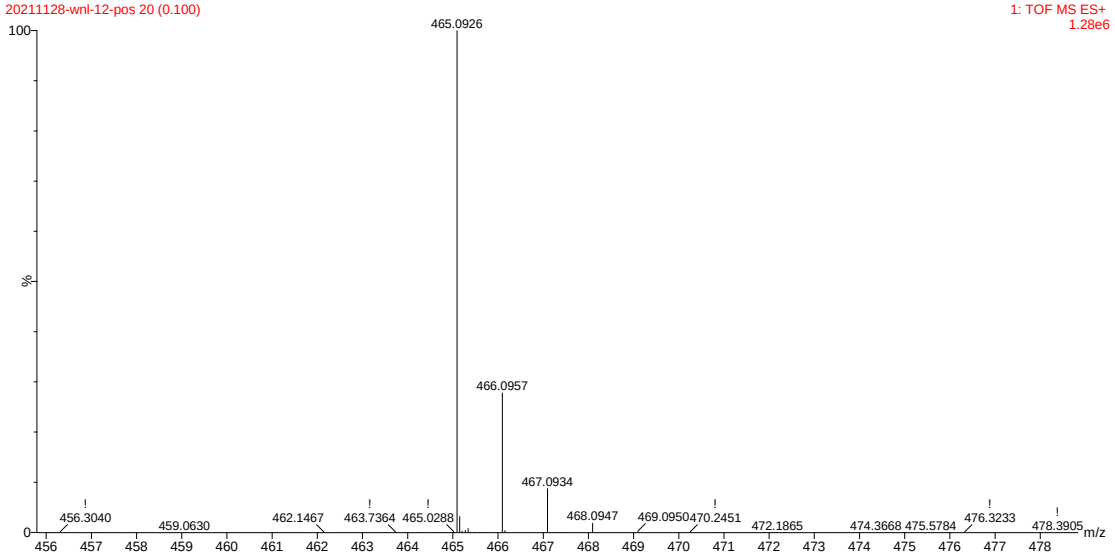
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

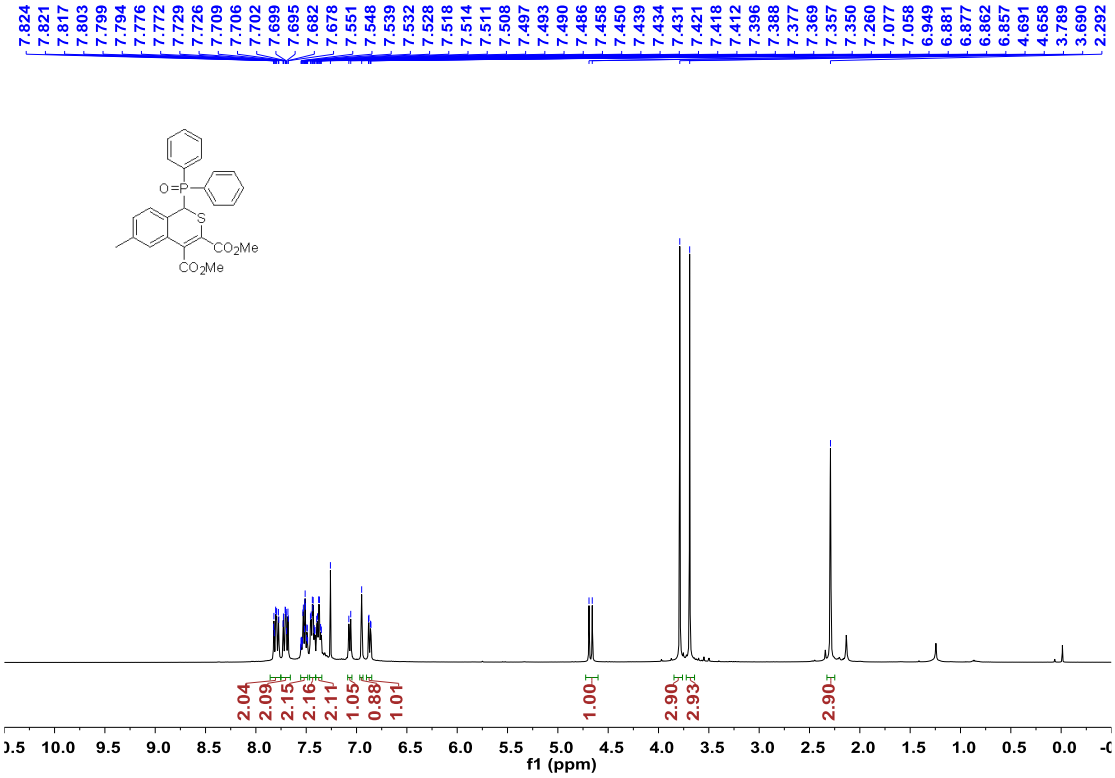


HRMS

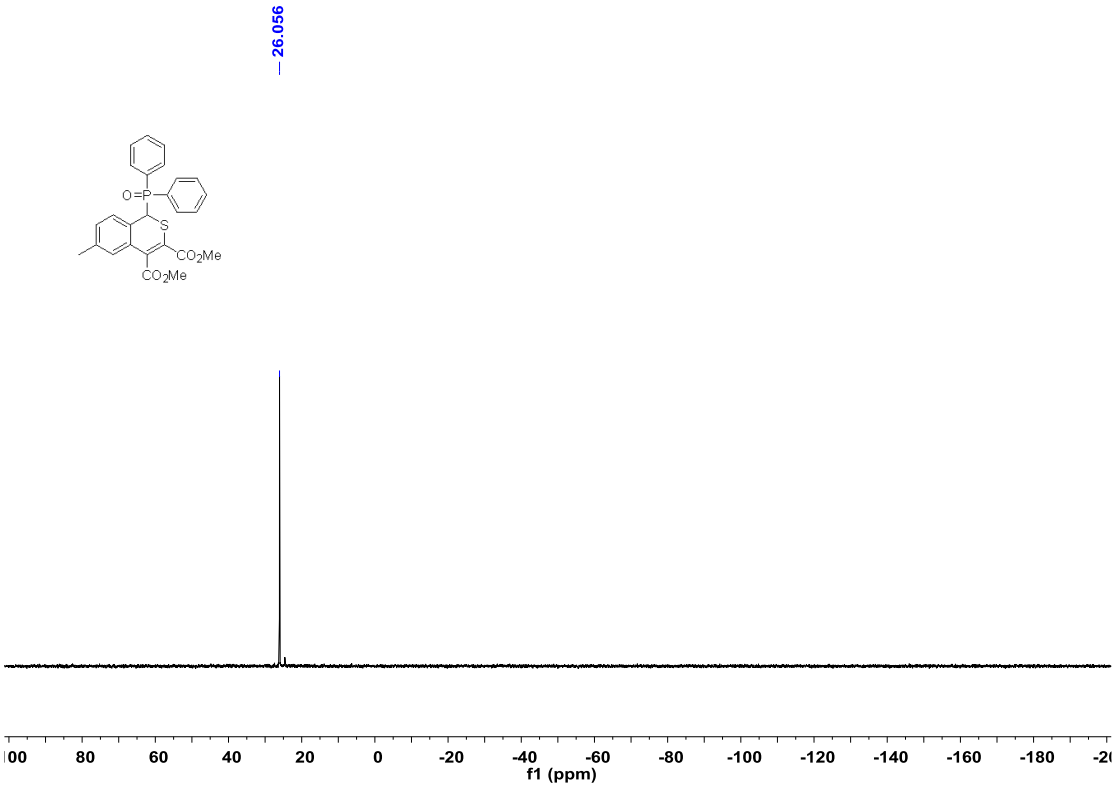


Dimethyl 1-(diphenylphosphoryl)-6-methyl-1*H*-isothiochromene-3,4-dicarboxylate (3ba)

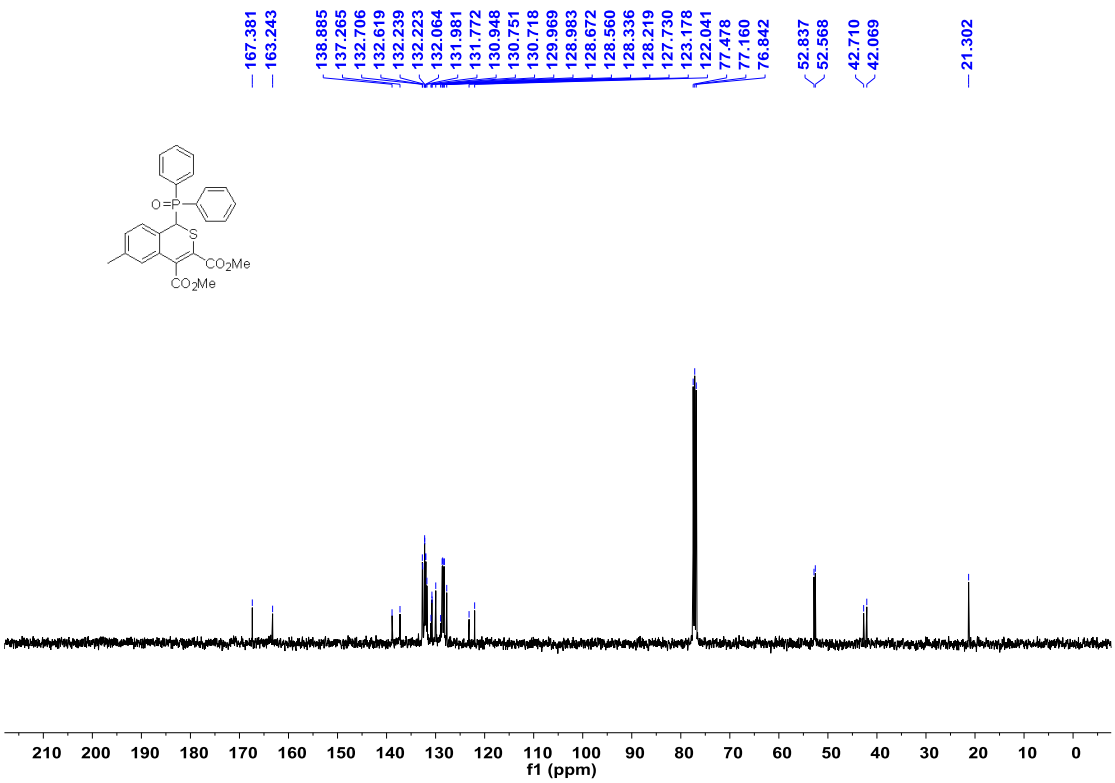
^{1}H NMR (400MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



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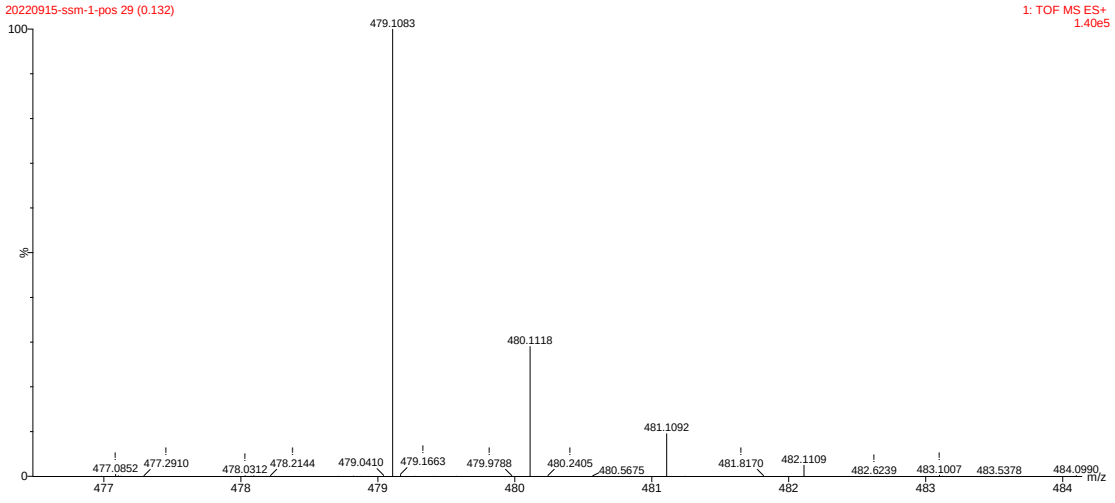
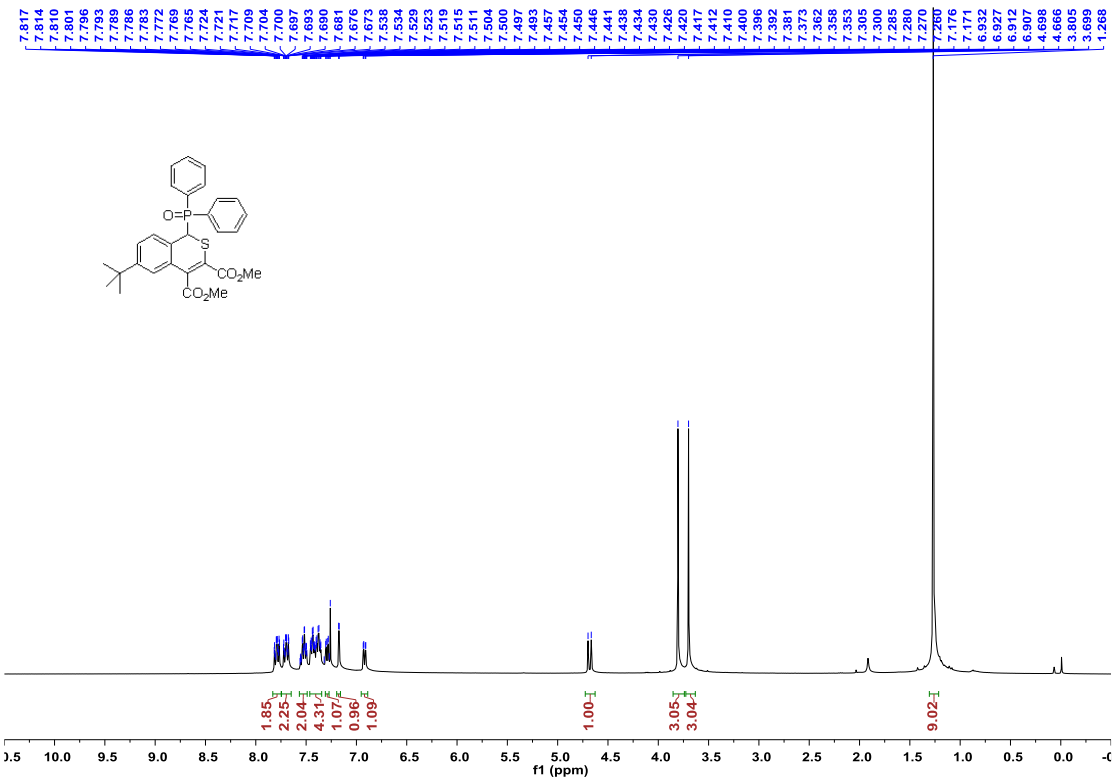
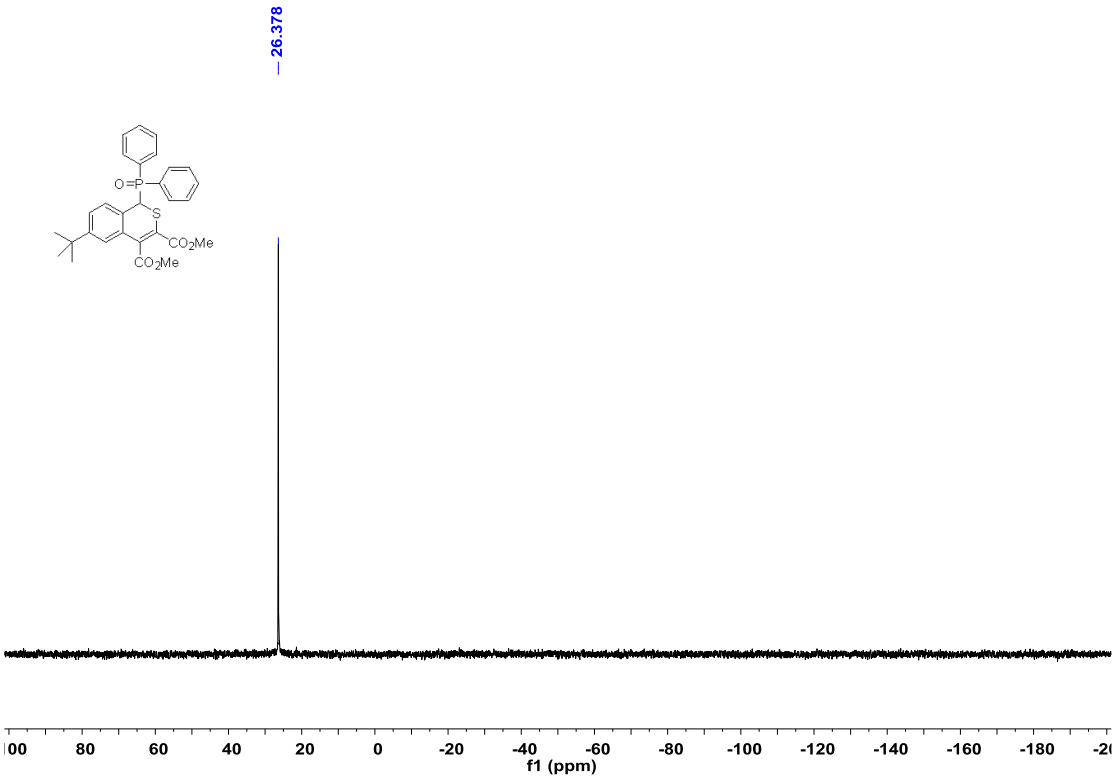


Dimethyl 6-(*tert*-butyl)-1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ca)

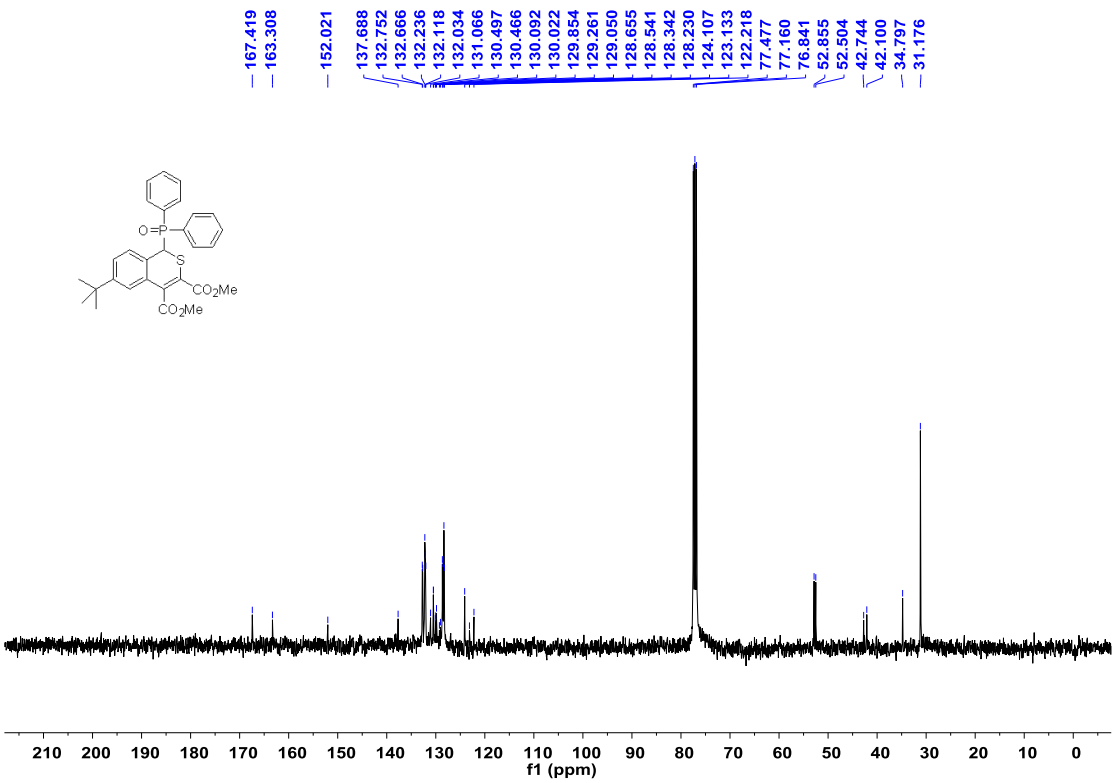
^{1}H NMR (400MHz, $CDCl_3$)



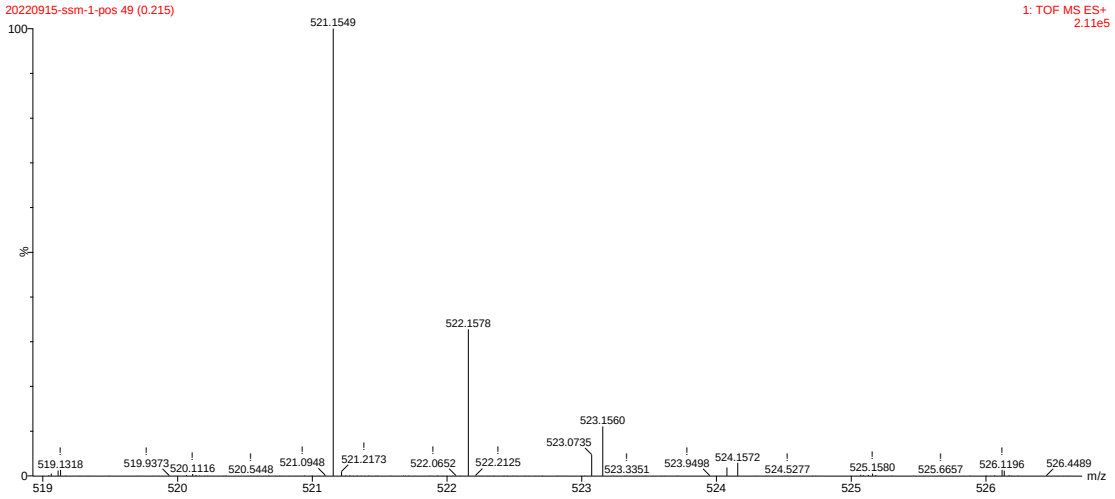
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

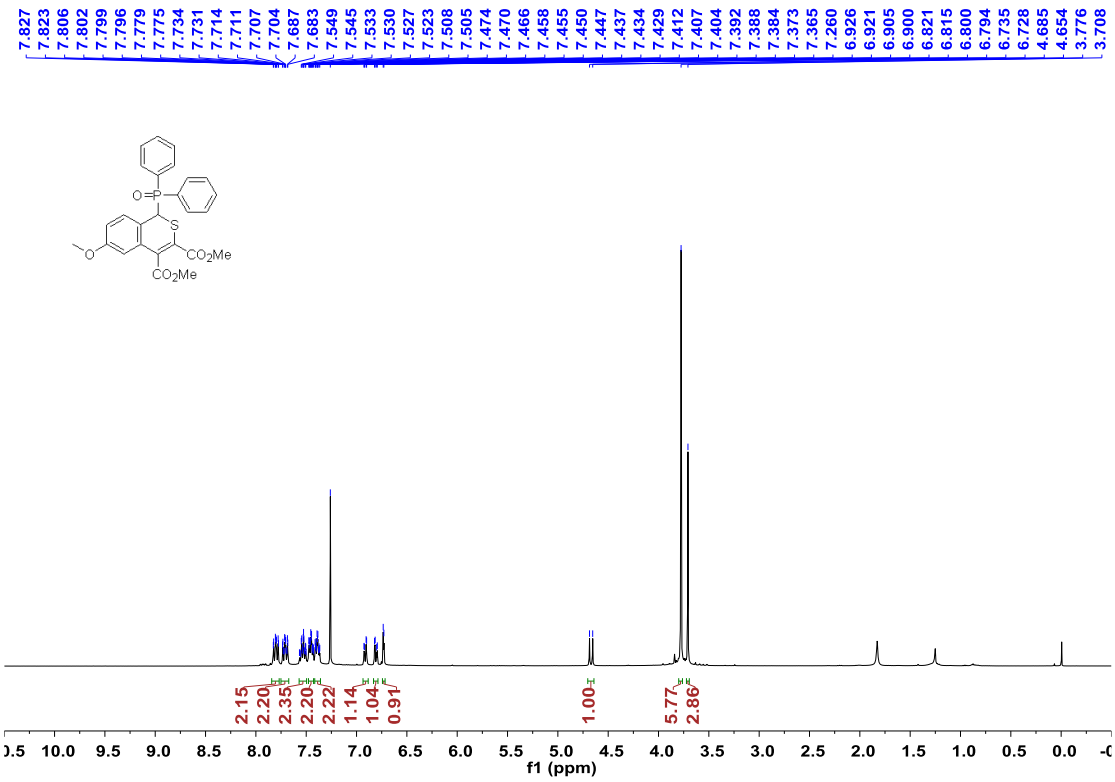


HRMS

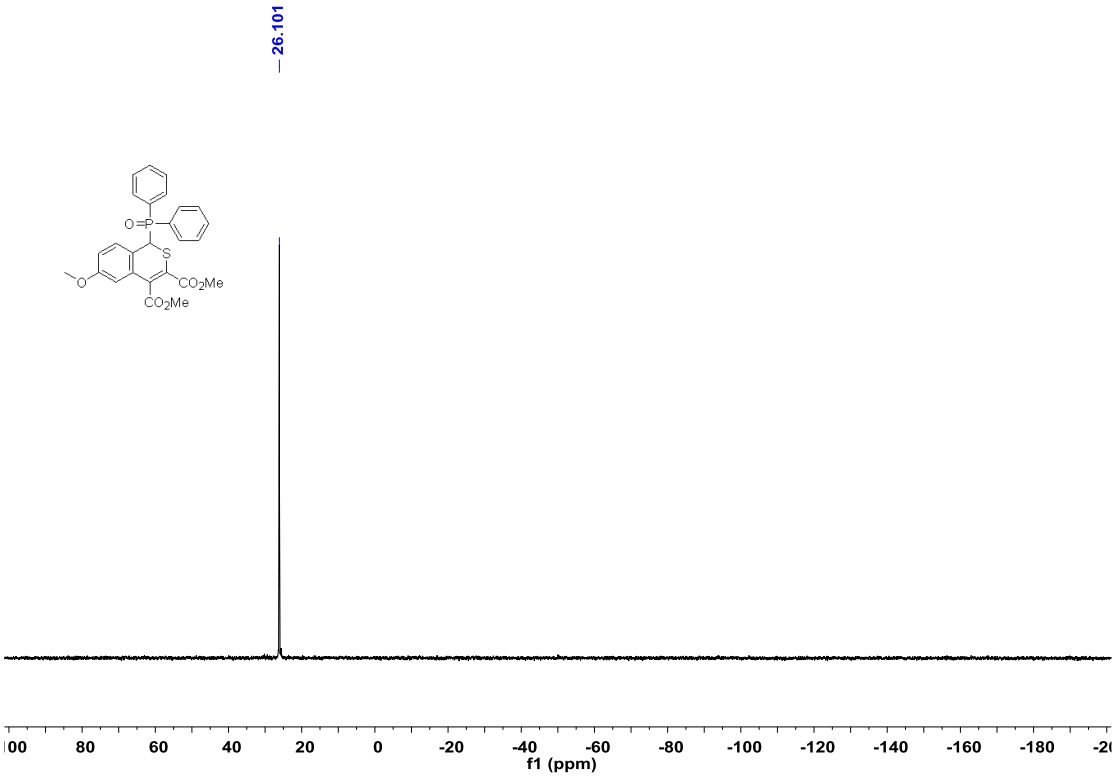


Dimethyl 1-(diphenylphosphoryl)-6-methoxy-1*H*-isothiochromene-3,4-dicarboxylate (3da)

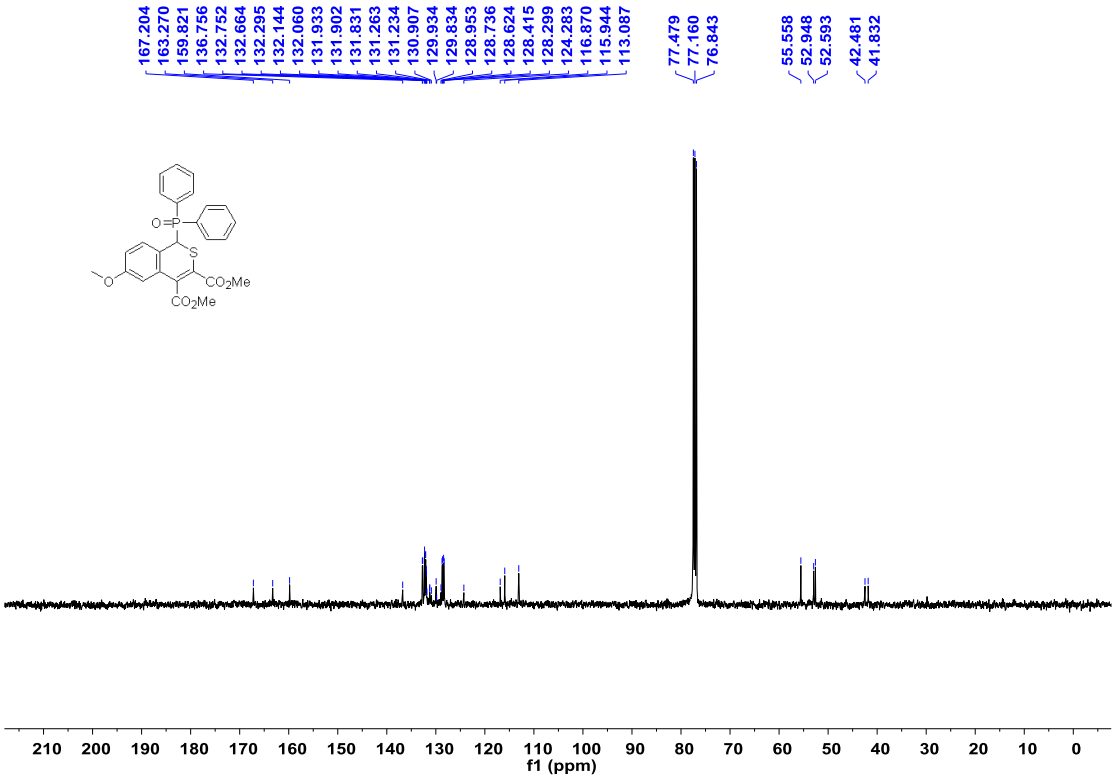
^{1}H NMR (400MHz, $CDCl_3$)



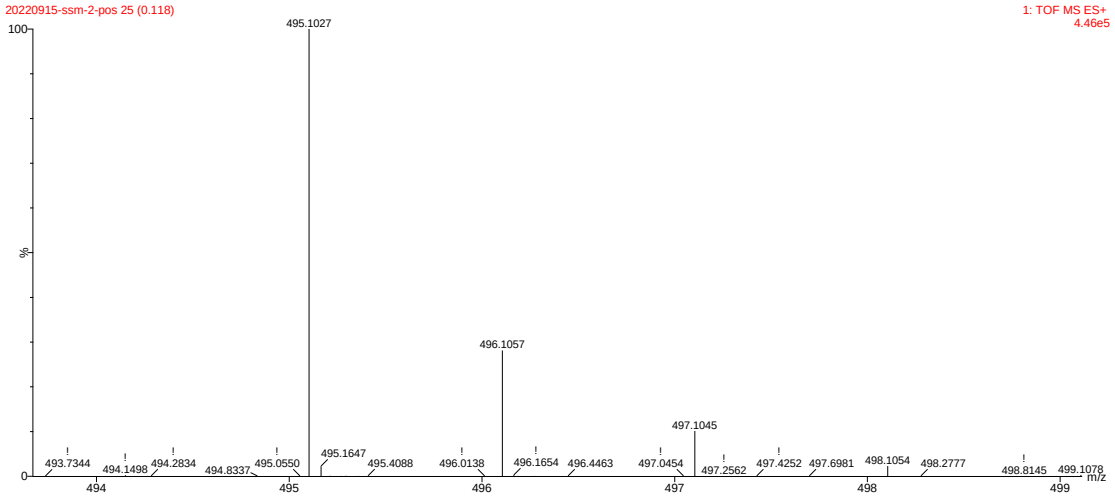
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

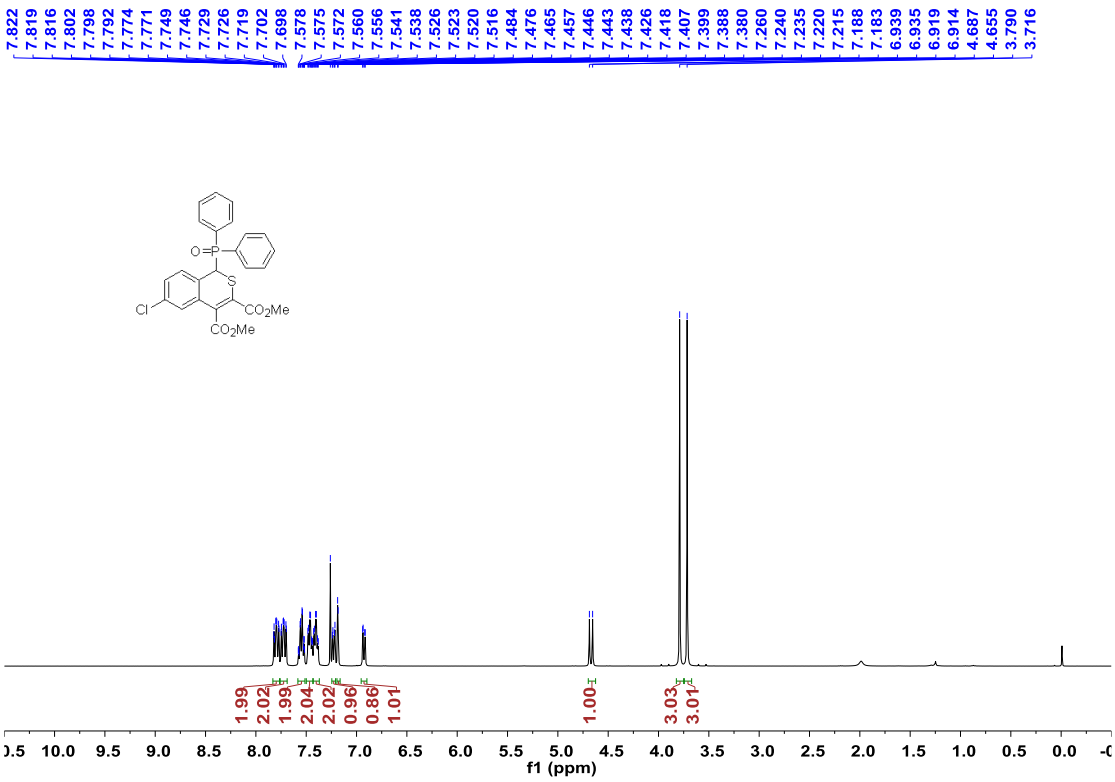


HRMS

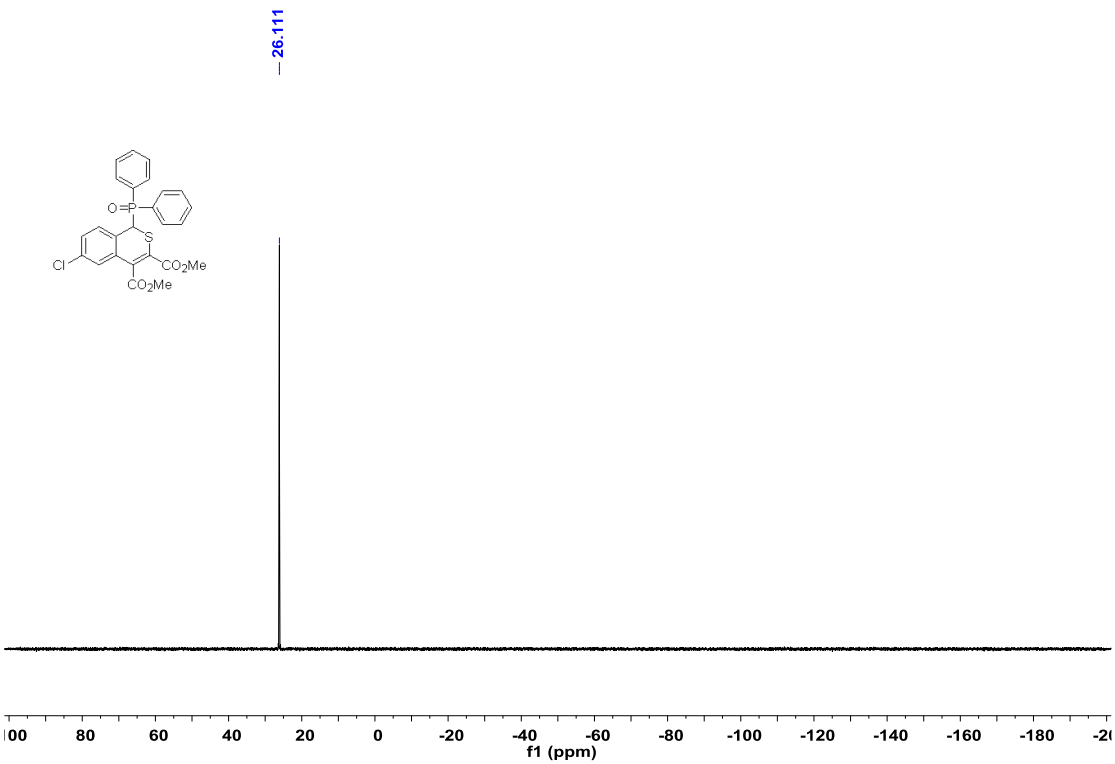


Dimethyl 6-chloro-1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ea)

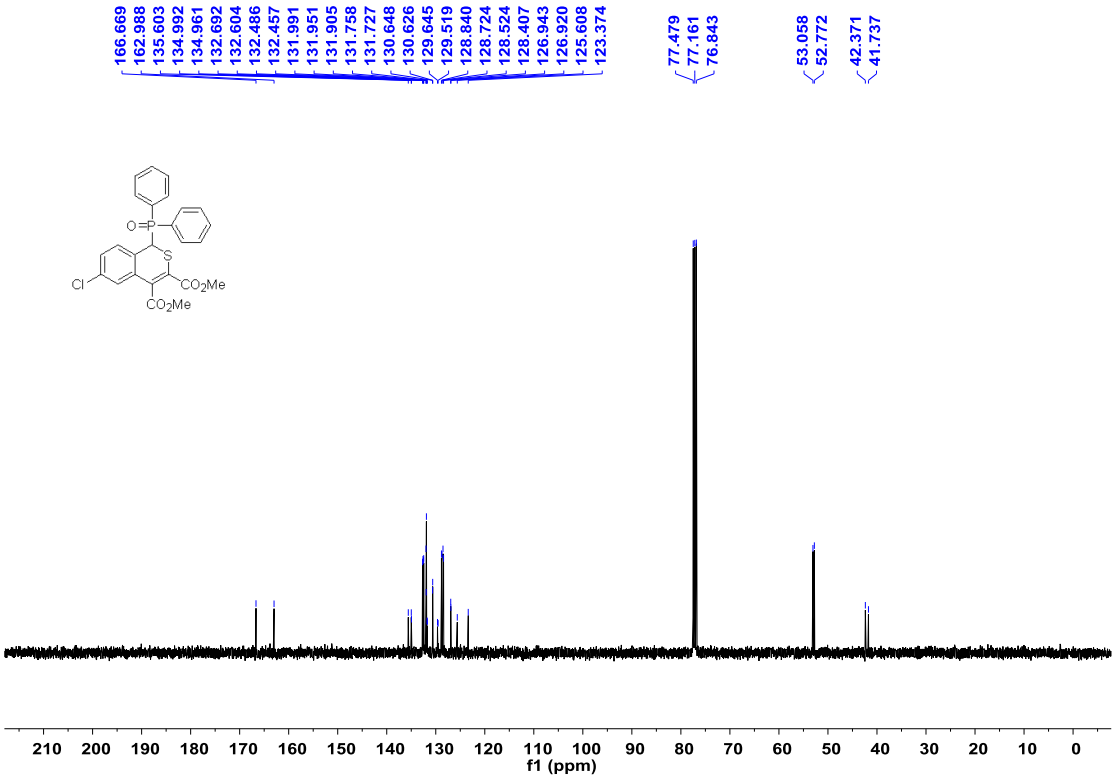
^{1}H NMR (400MHz, $CDCl_3$)



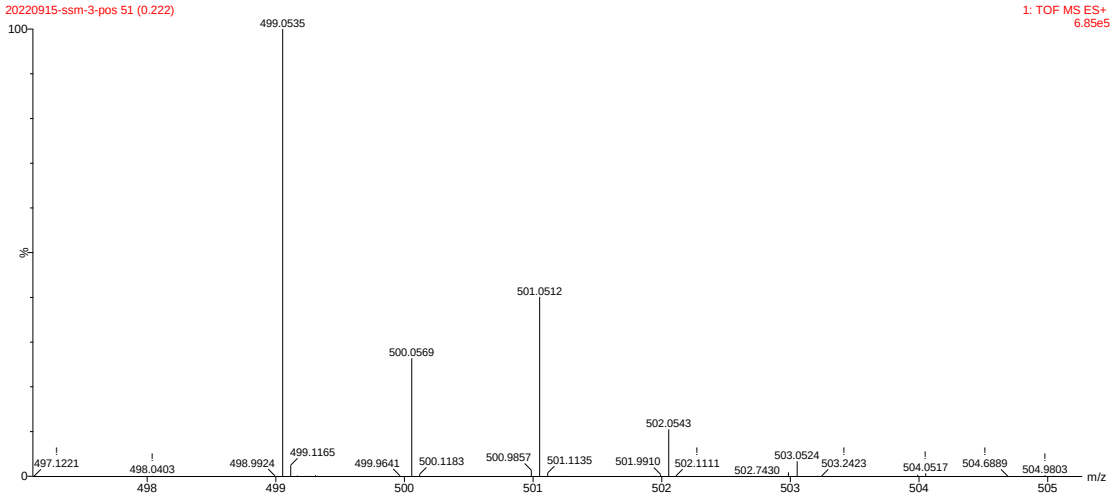
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

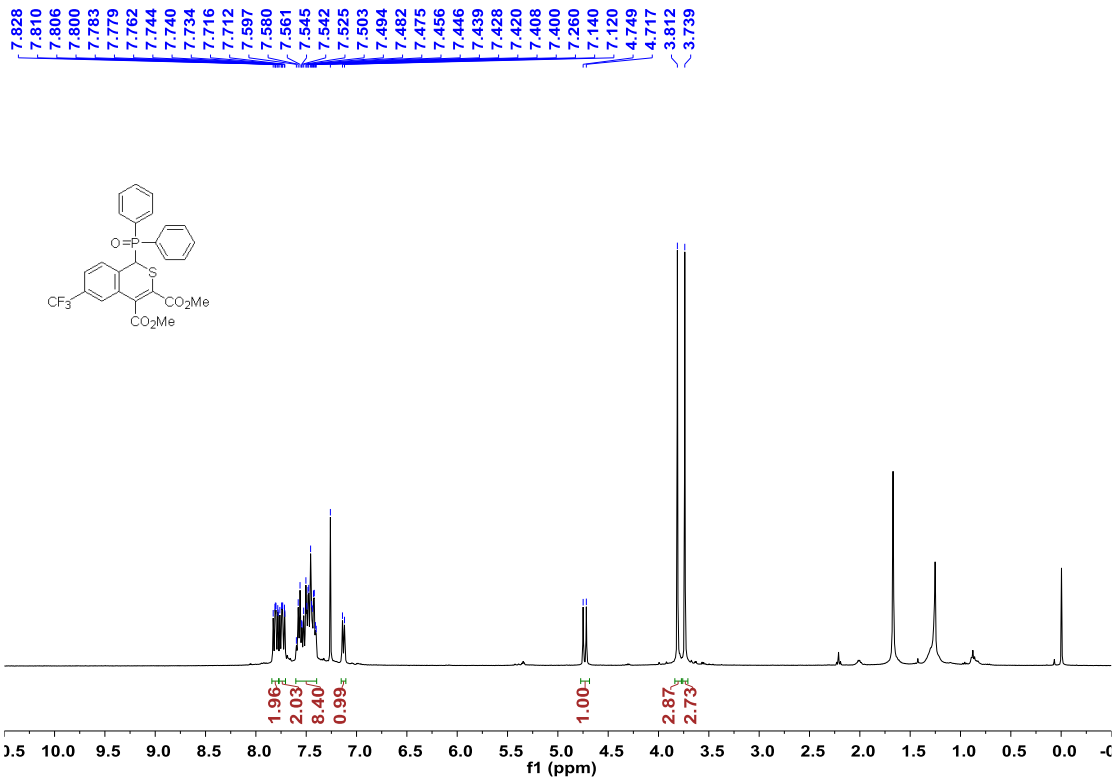


HRMS

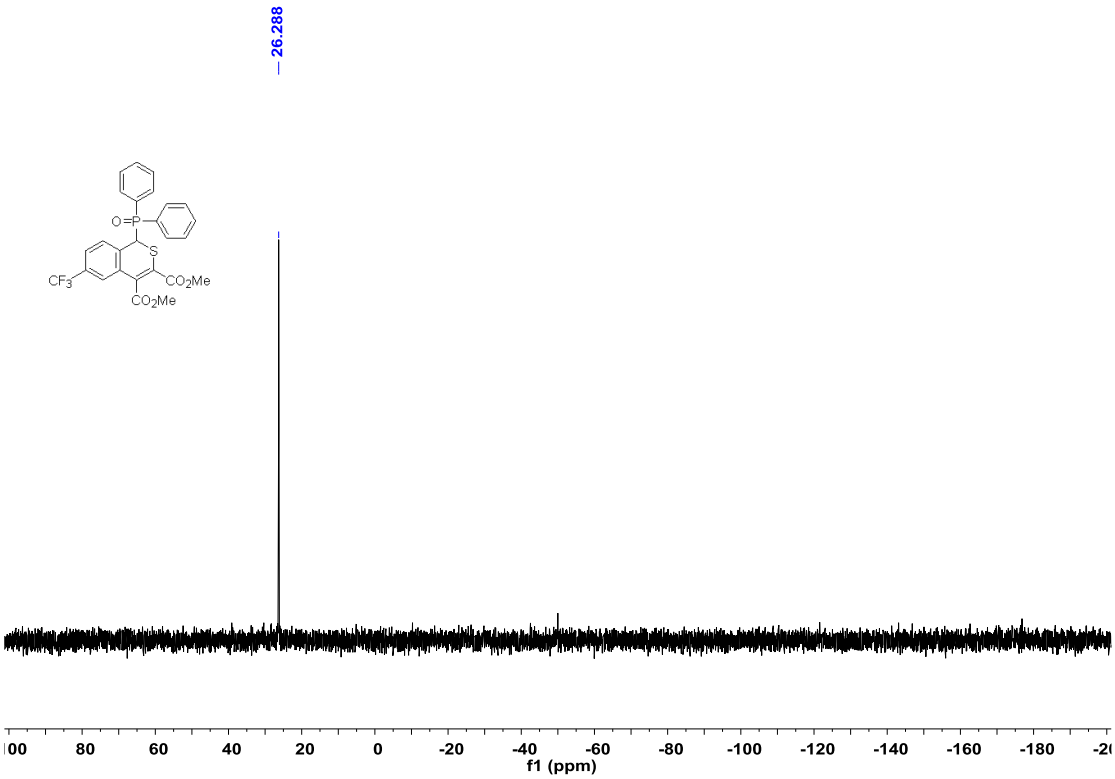


Dimethyl 1-(diphenylphosphoryl)-6-(trifluoromethyl)-1*H*-isothiochromene-3,4-dicarboxylate (3fa)

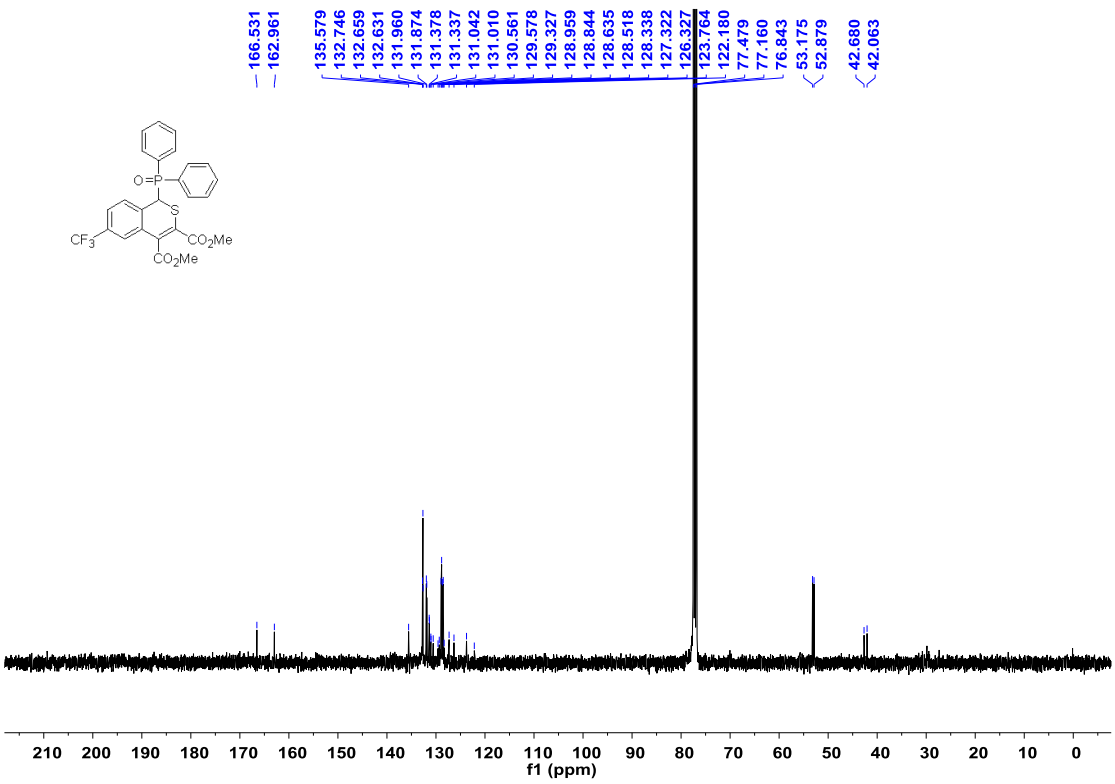
^{1}H NMR (400MHz, $CDCl_3$)



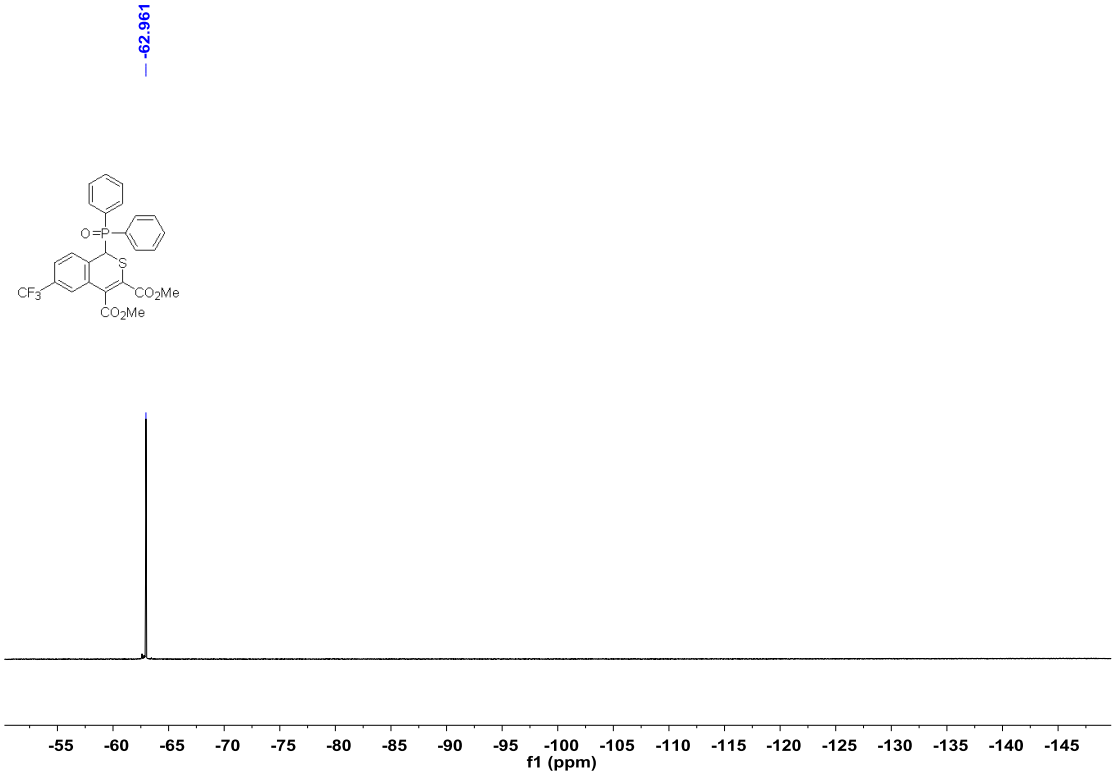
^{31}P NMR (162 MHz, $CDCl_3$)



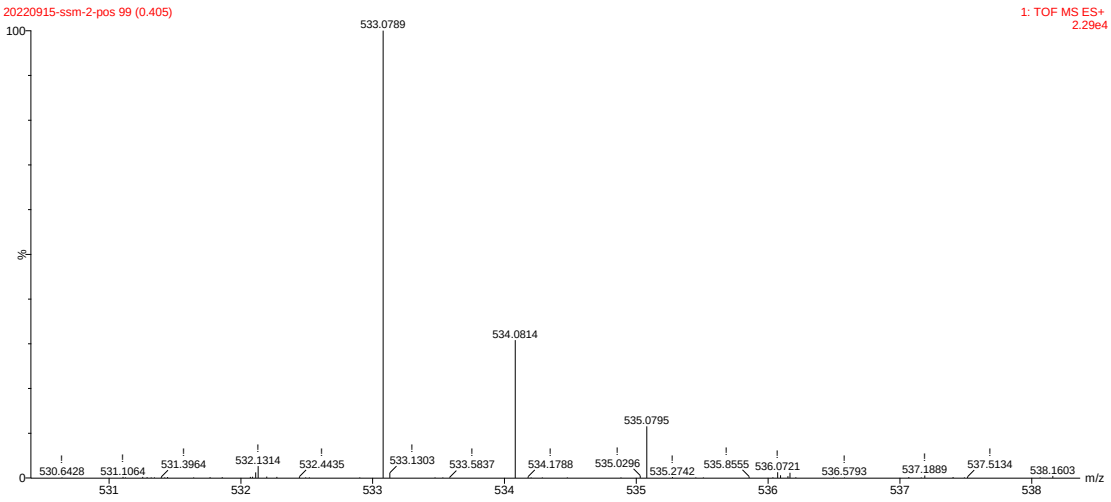
^{13}C NMR (101MHz, $CDCl_3$)



^{19}F NMR (376MHz, $CDCl_3$)



HRMS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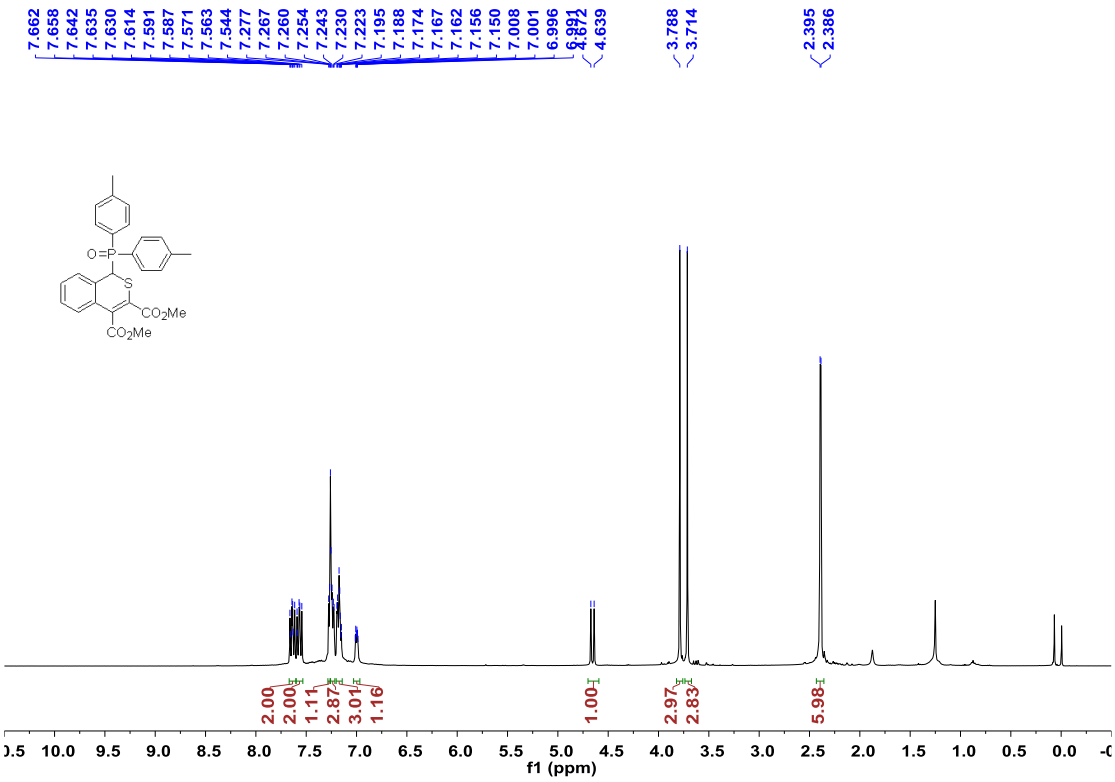
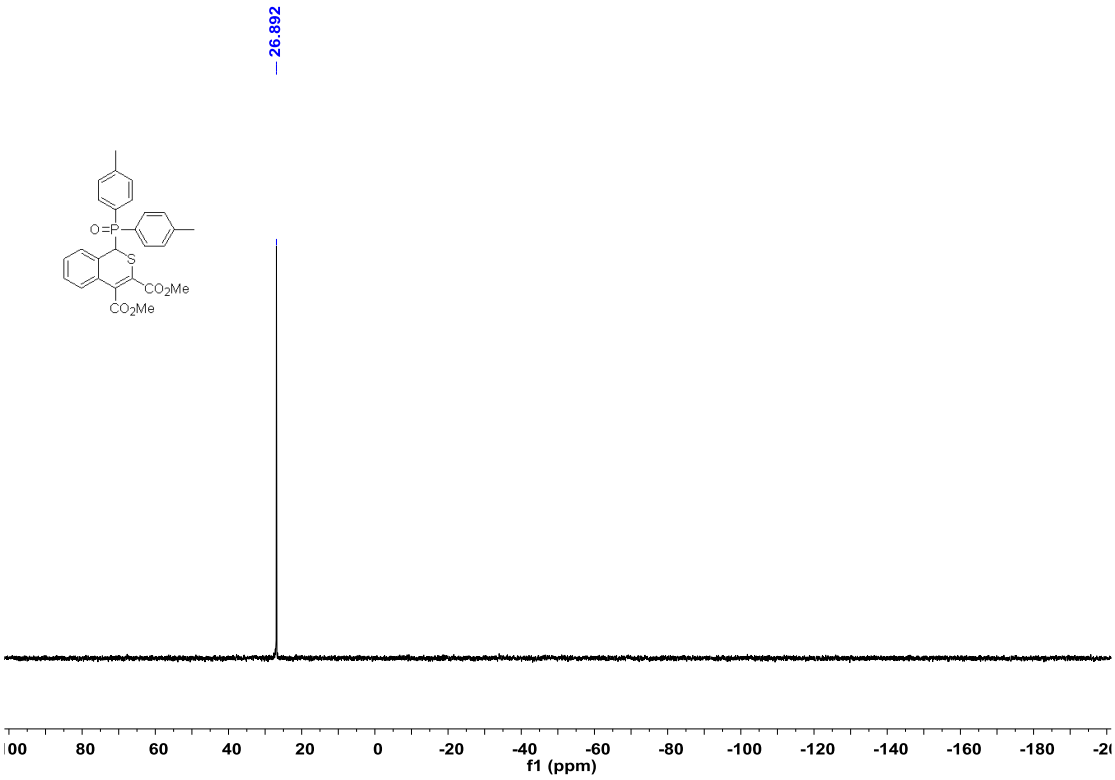
538.1603
531
532
533
534
535
536
537
538
m/z

Dimethyl 1-(di-*p*-tolylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ha)

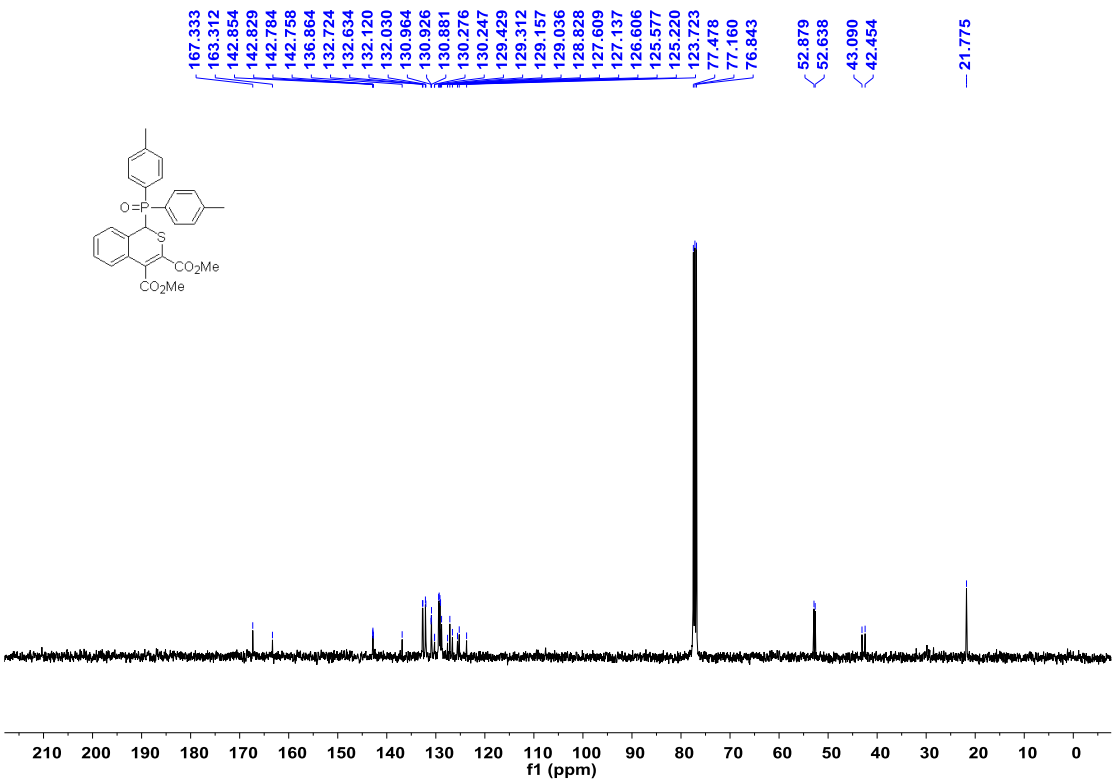
^{1}H NMR (400MHz, $CDCl_3$)



^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



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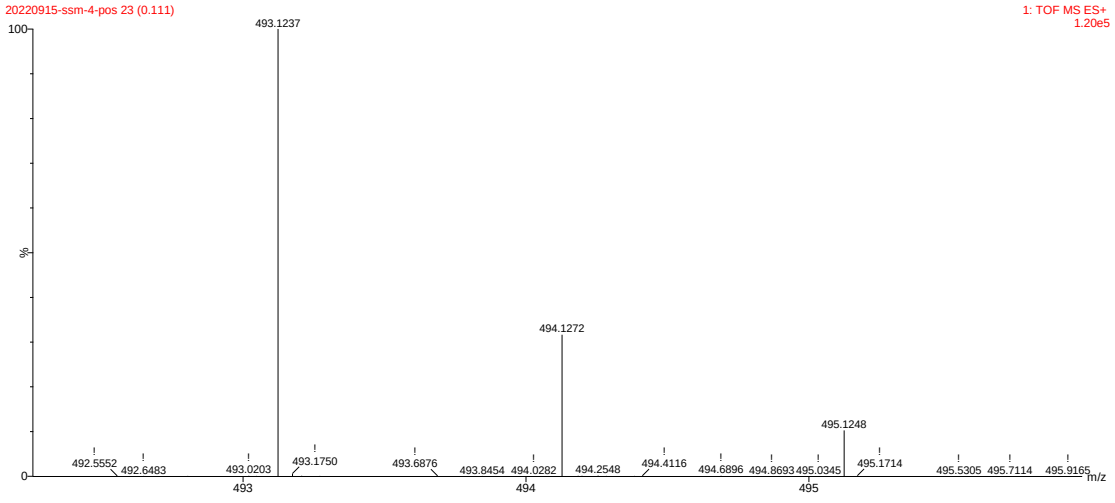
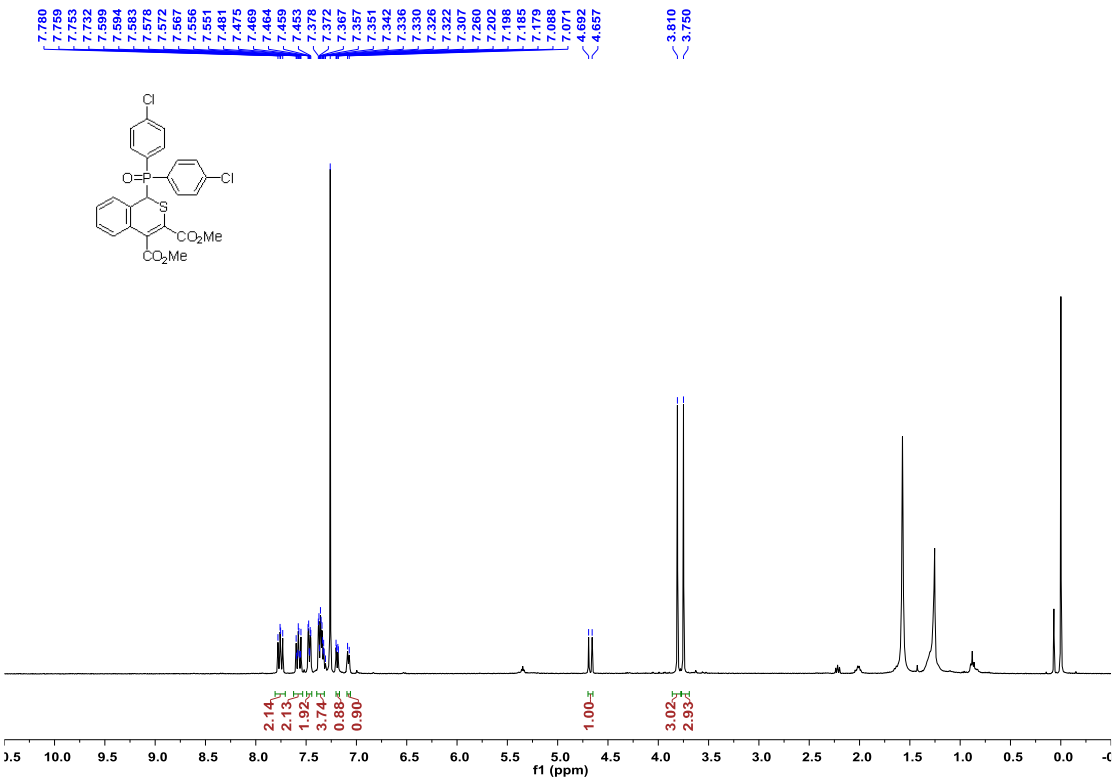
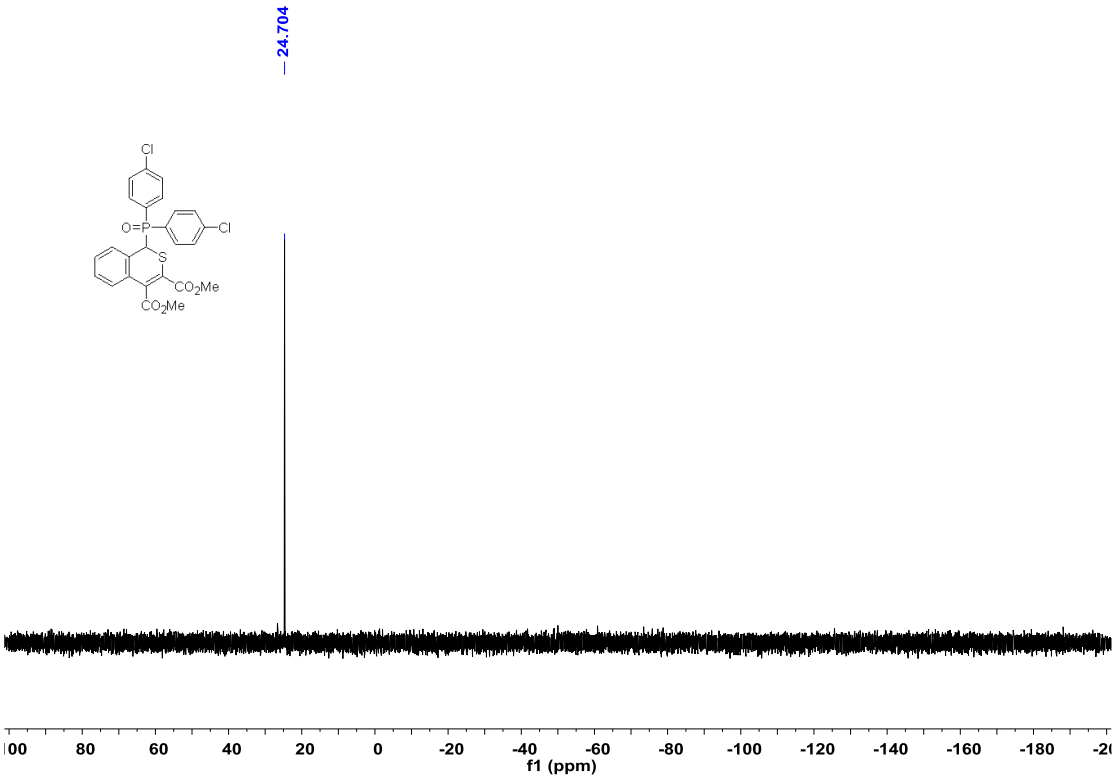


Dimethyl 1-(bis(4-chlorophenyl)phosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ia)

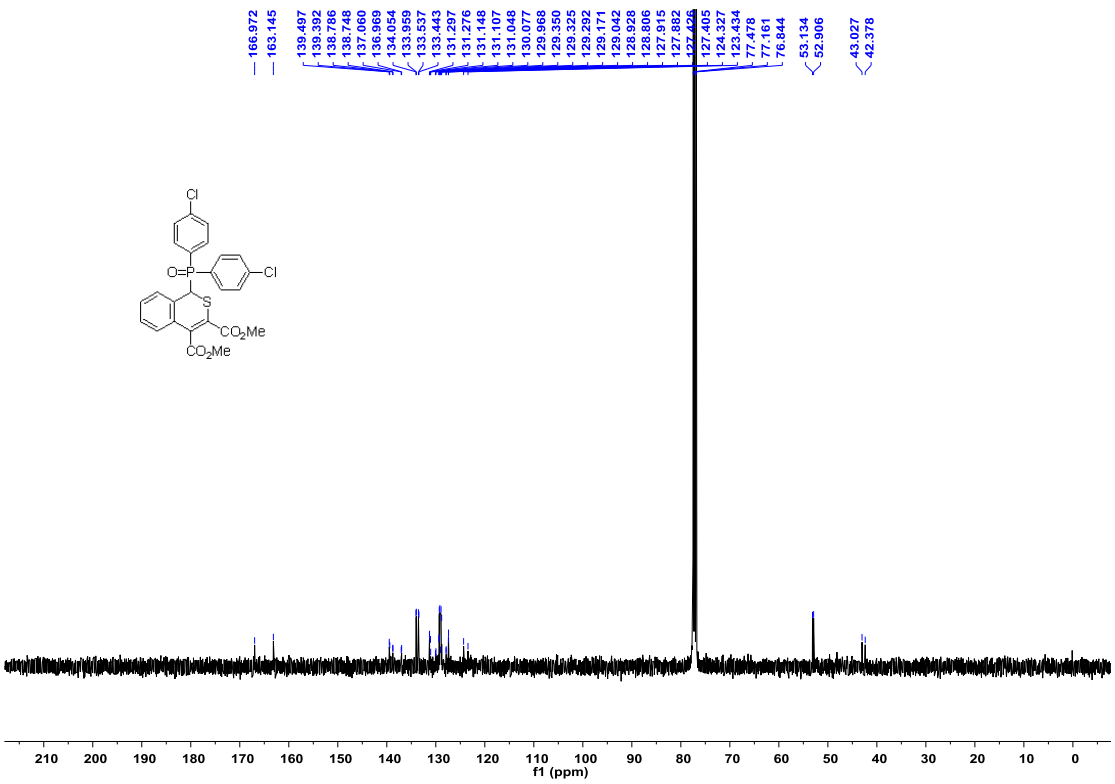
^{1}H NMR (400MHz, $CDCl_3$)



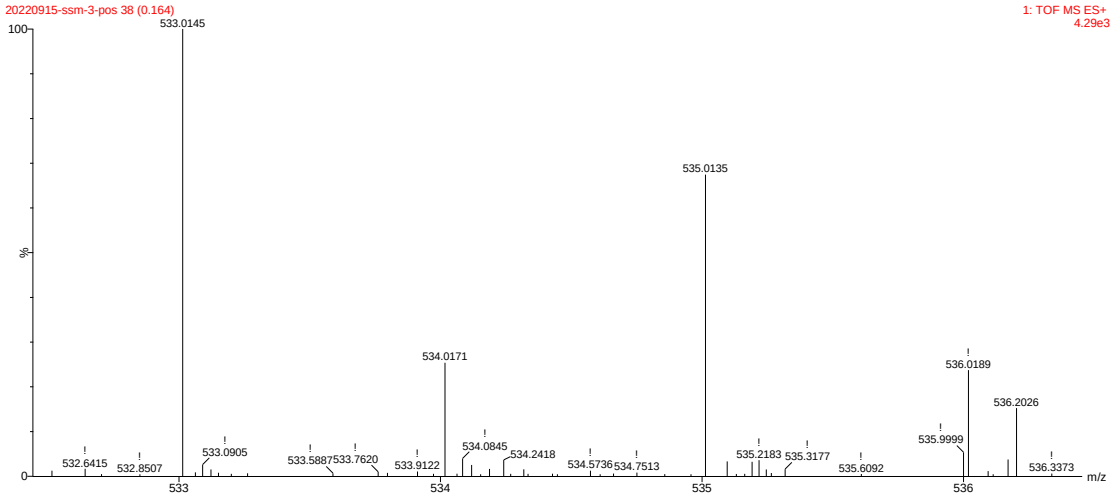
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

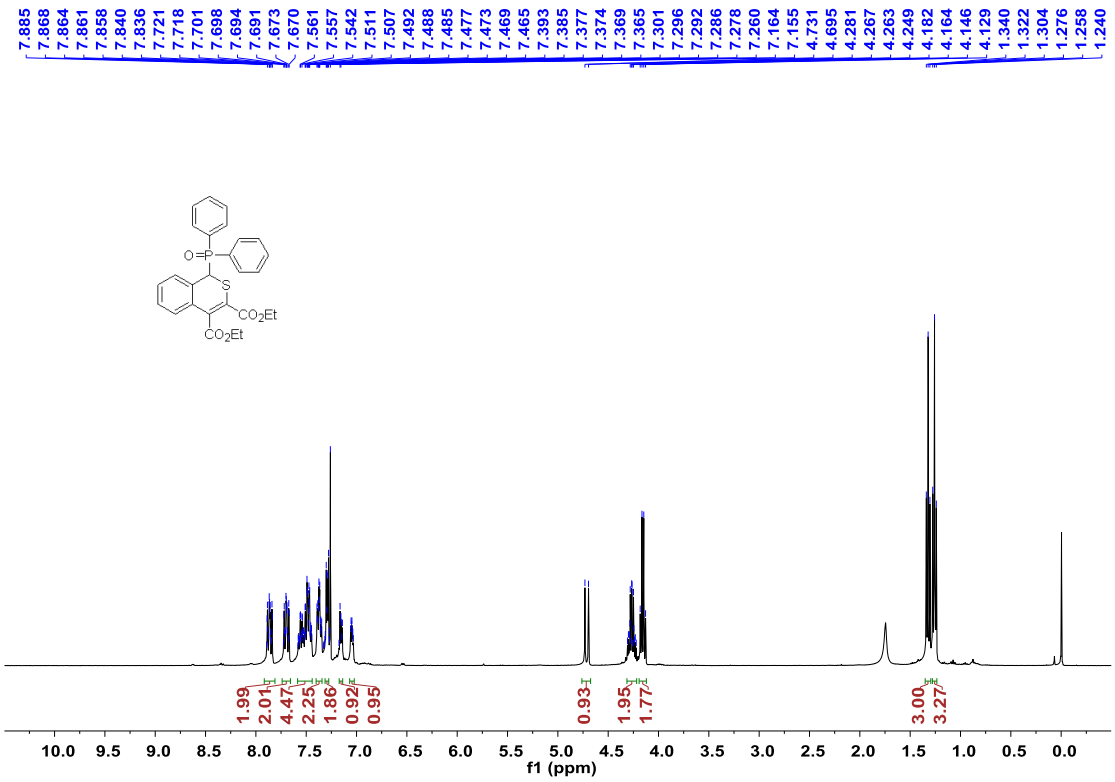


HRMS

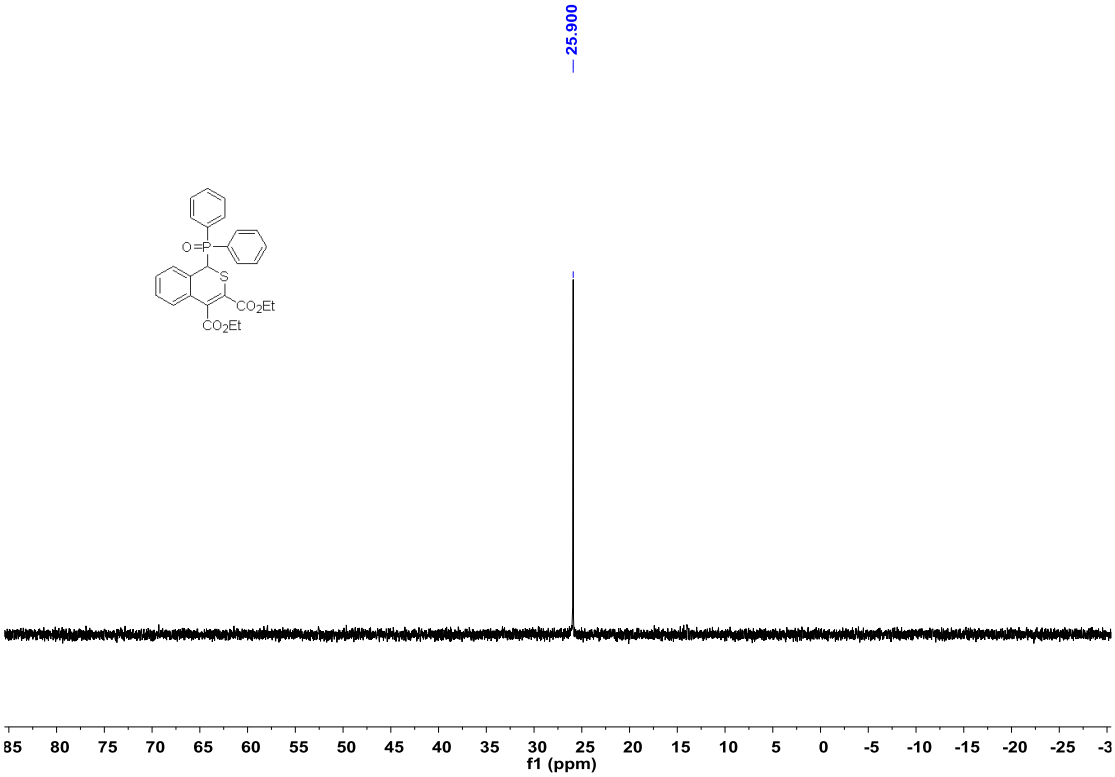


Diethyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ab)

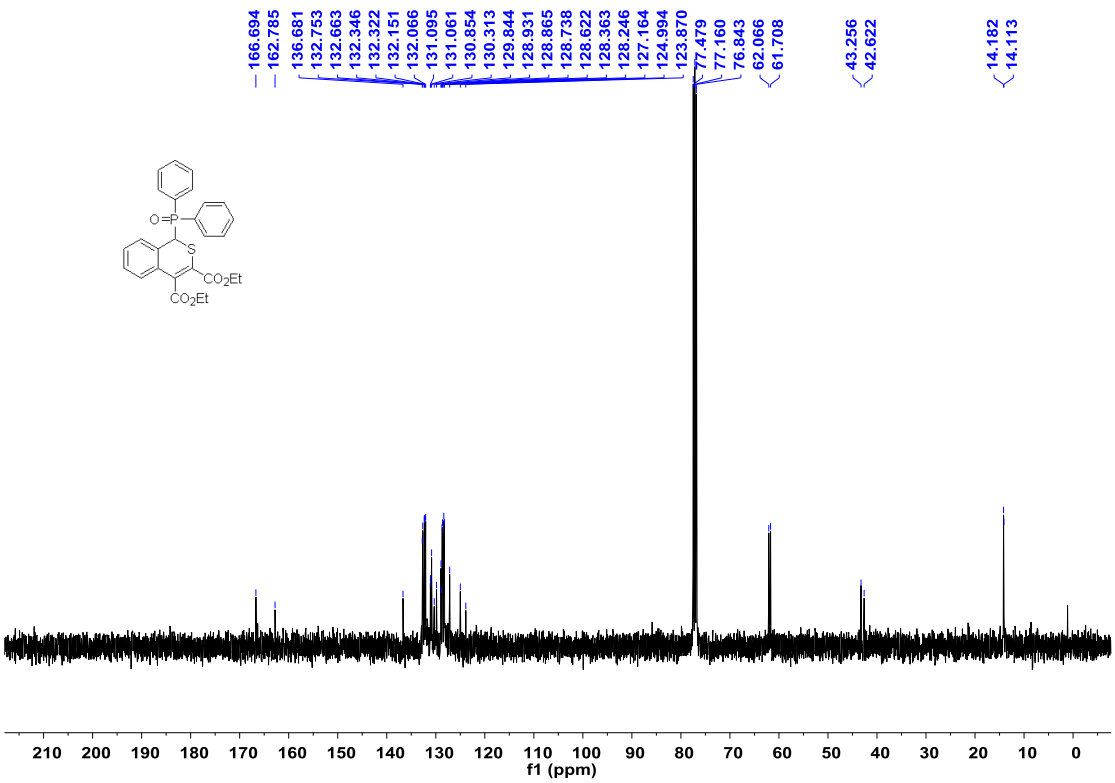
^{1}H NMR (400MHz, $CDCl_3$)



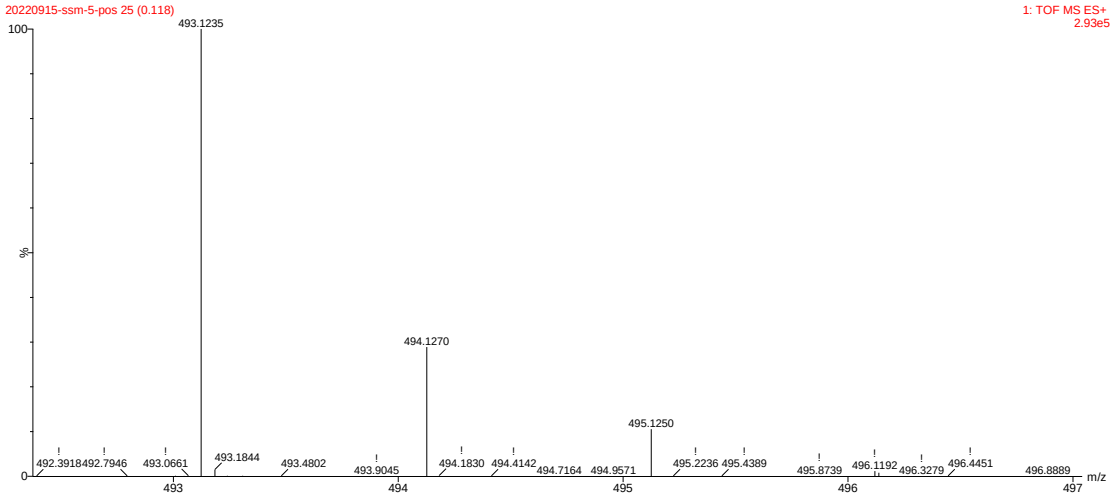
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

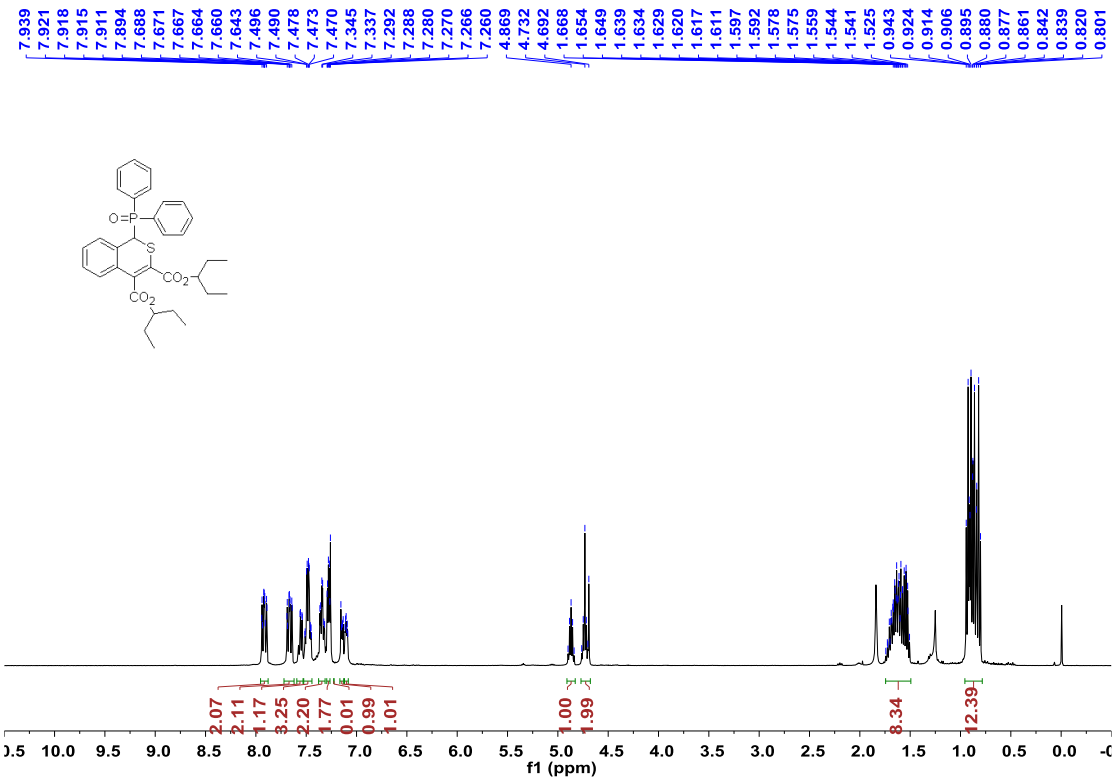


HRMS

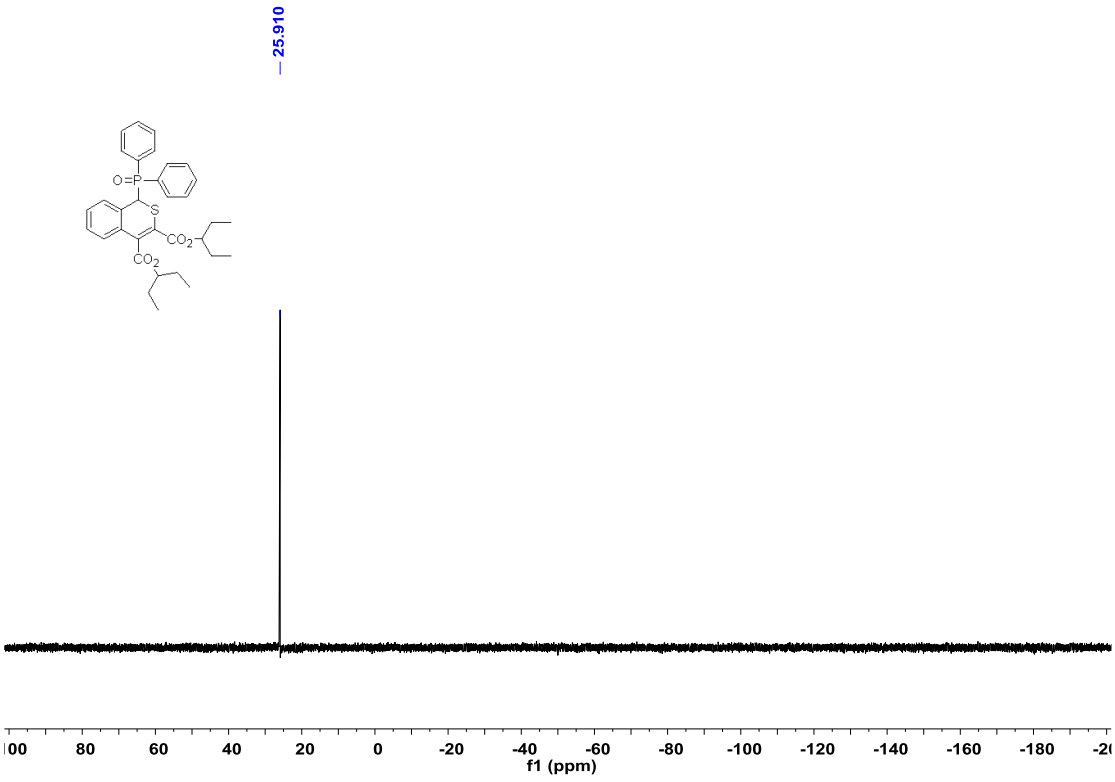


Di(pentan-3-yl) 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ac)

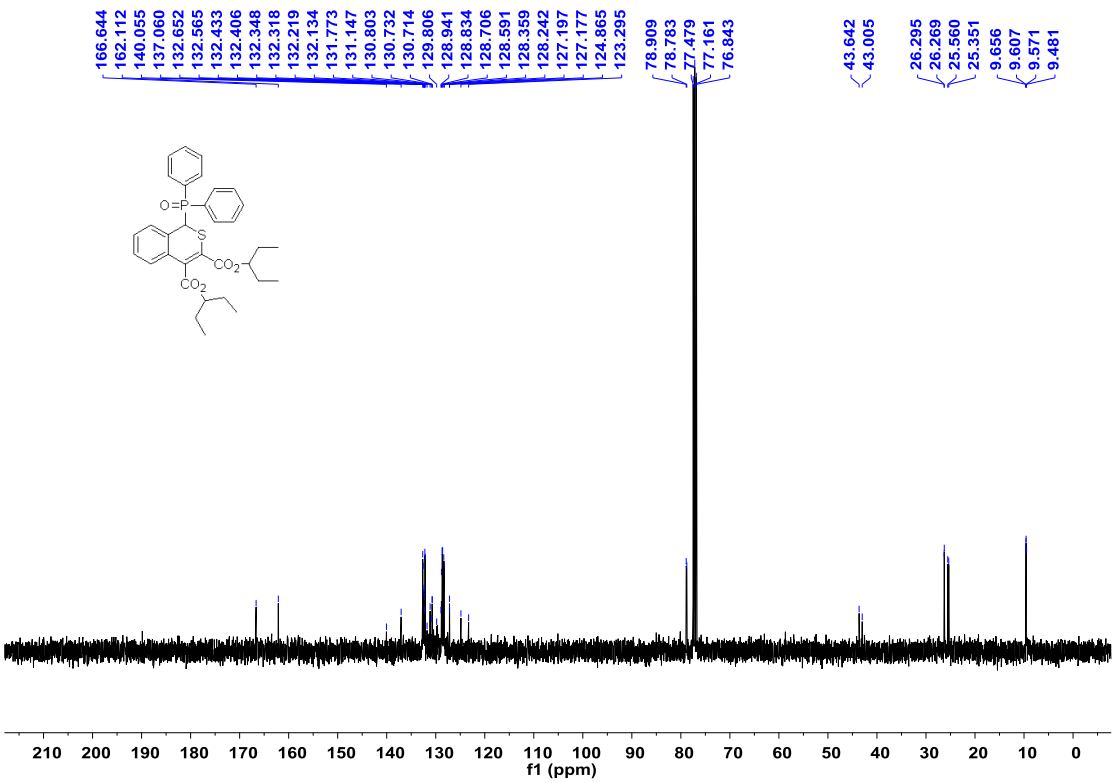
^{1}H NMR (400MHz, $CDCl_3$)



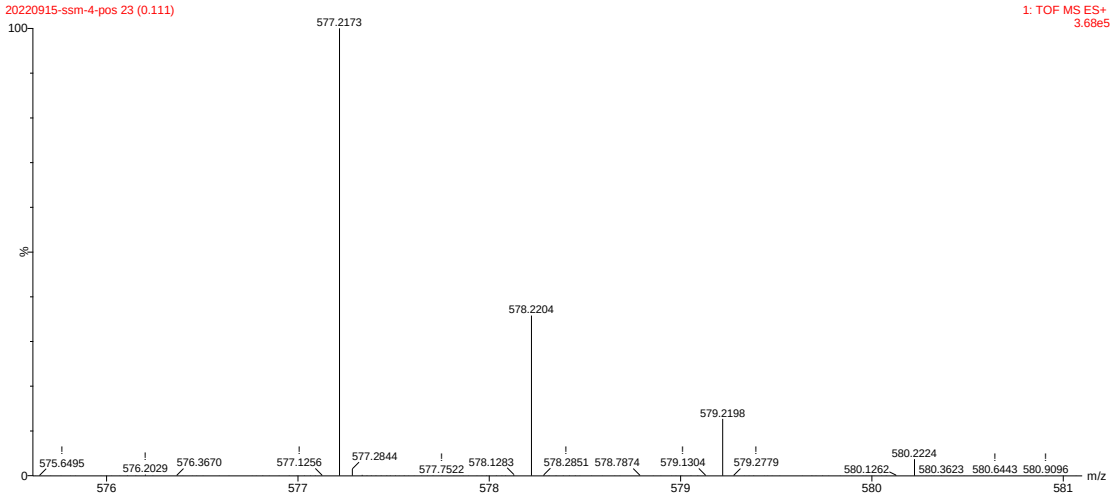
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

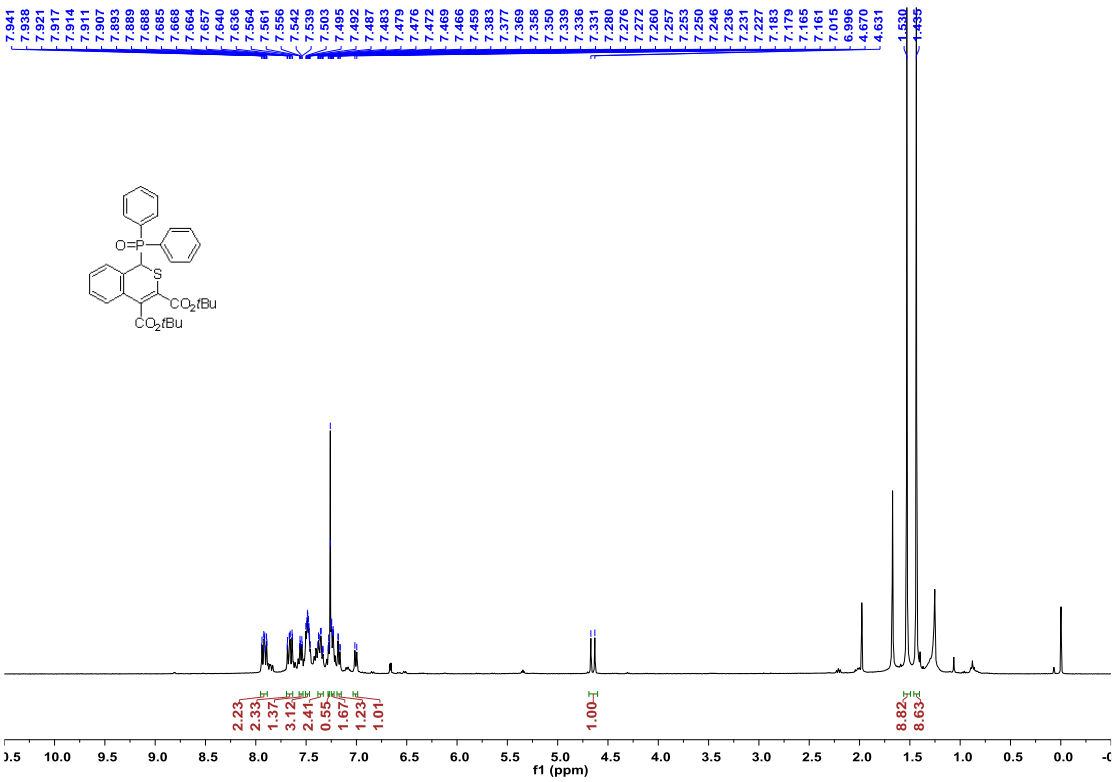


HRMS

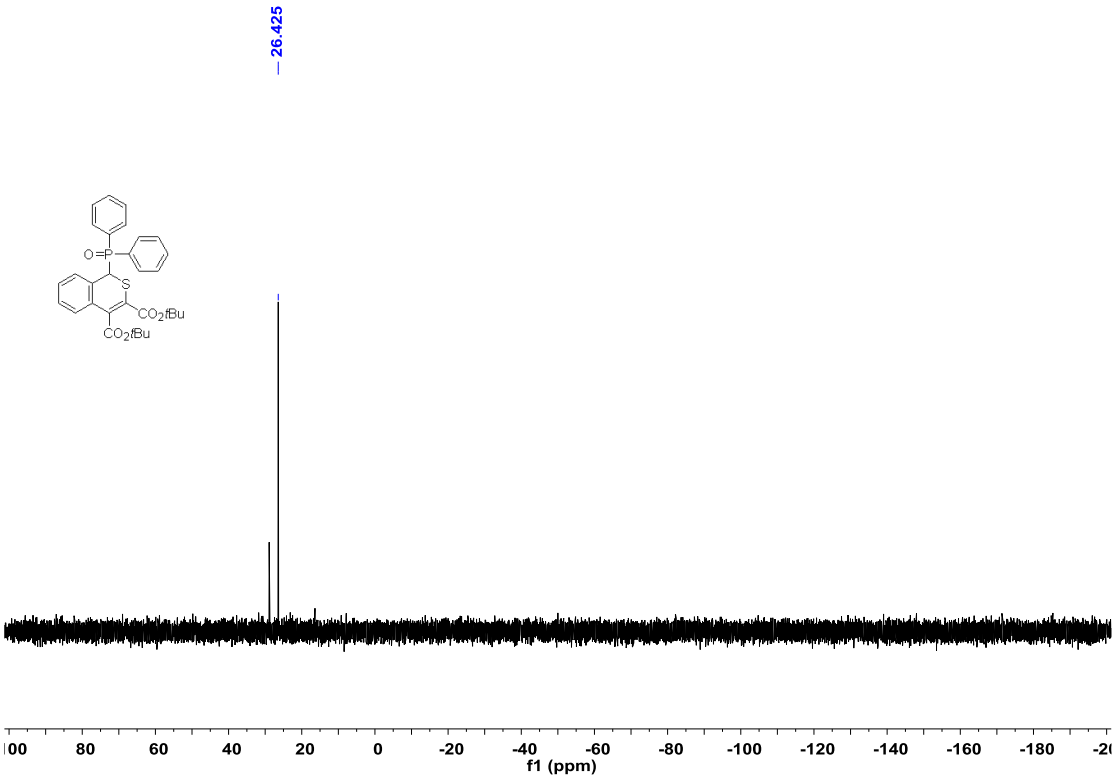


Di-*tert*-butyl 1-(diphenylphosphoryl)-1*H*-isothiochromene-3,4-dicarboxylate (3ad)

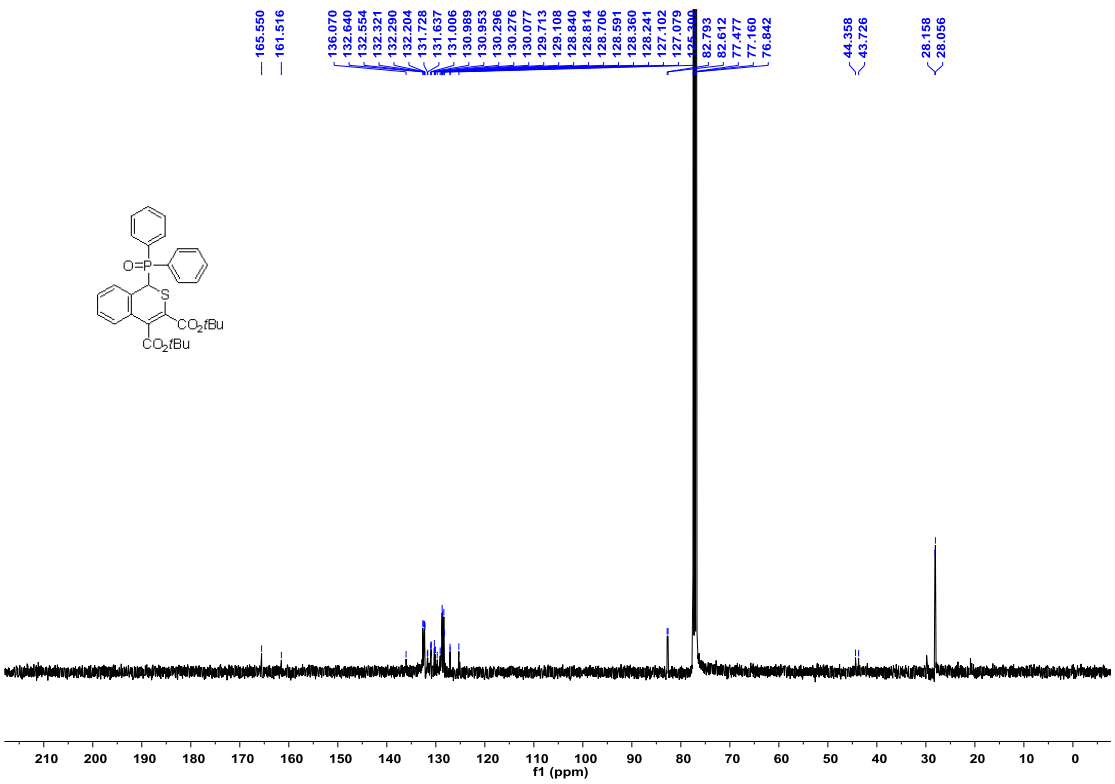
^{1}H NMR (400MHz, $CDCl_3$)



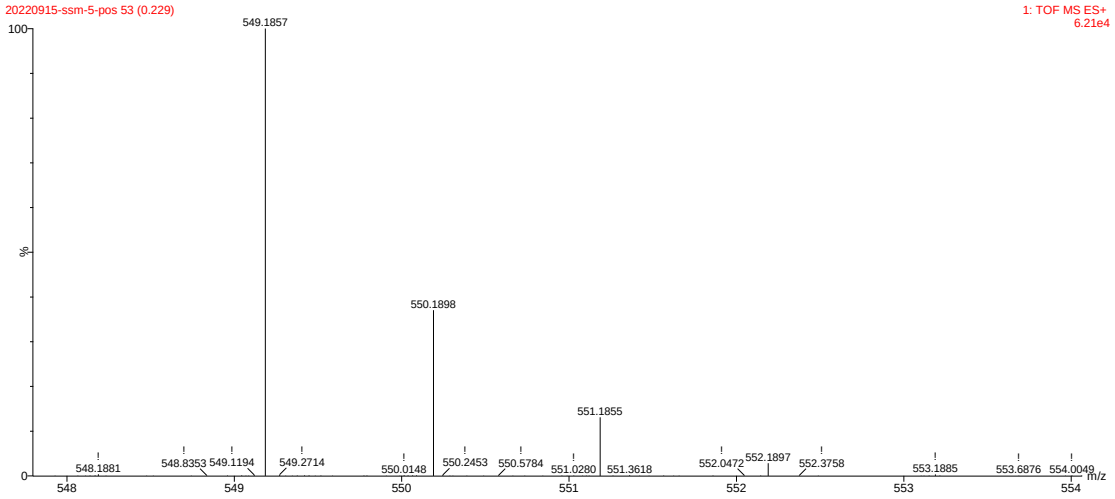
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

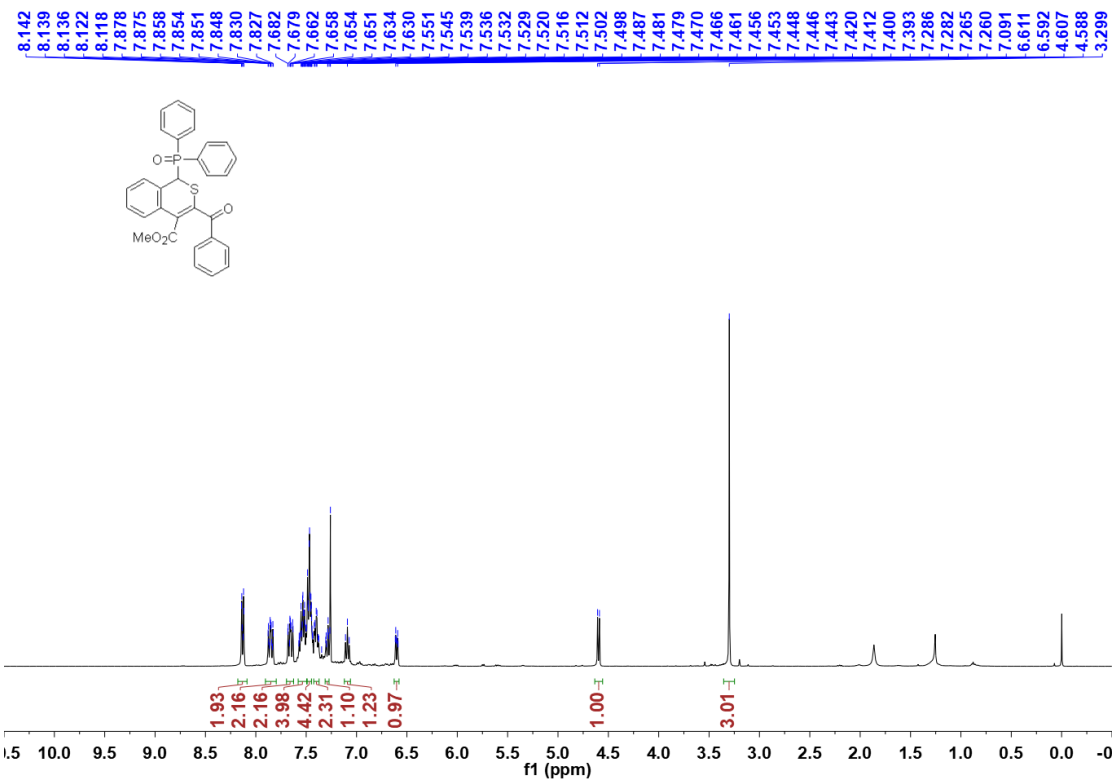


HRMS

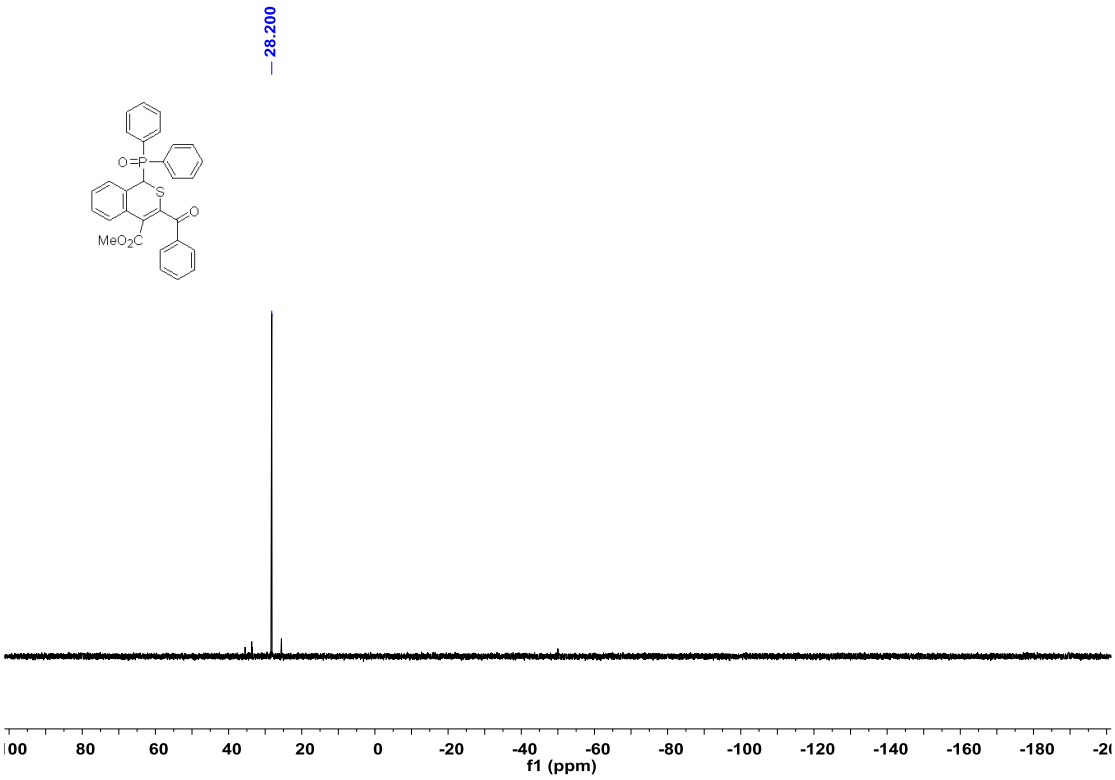


Methyl 3-benzoyl-1-(diphenylphosphoryl)-1*H*-isothiochromene-4-carboxylate (3ae)

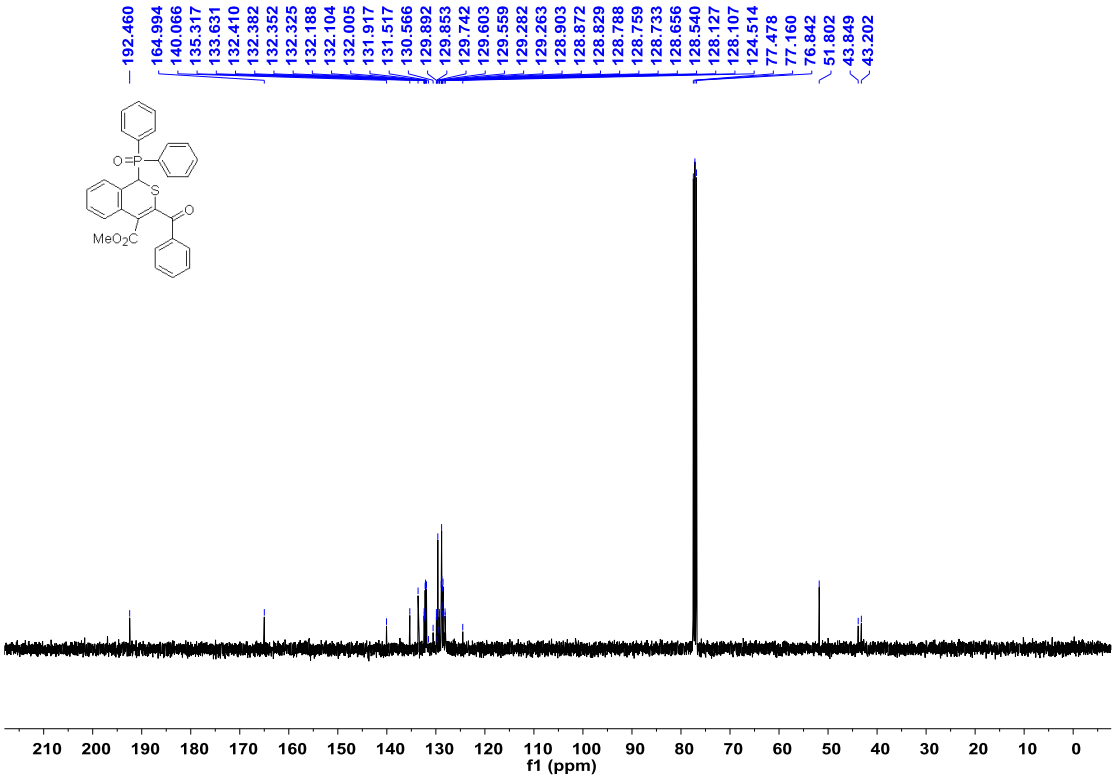
^{1}H NMR (400MHz, $CDCl_3$)



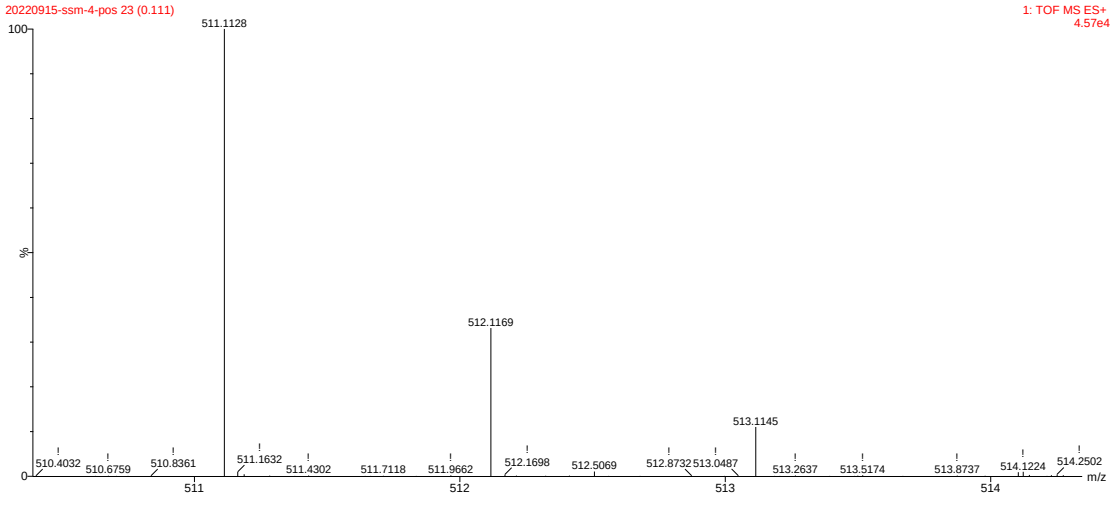
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

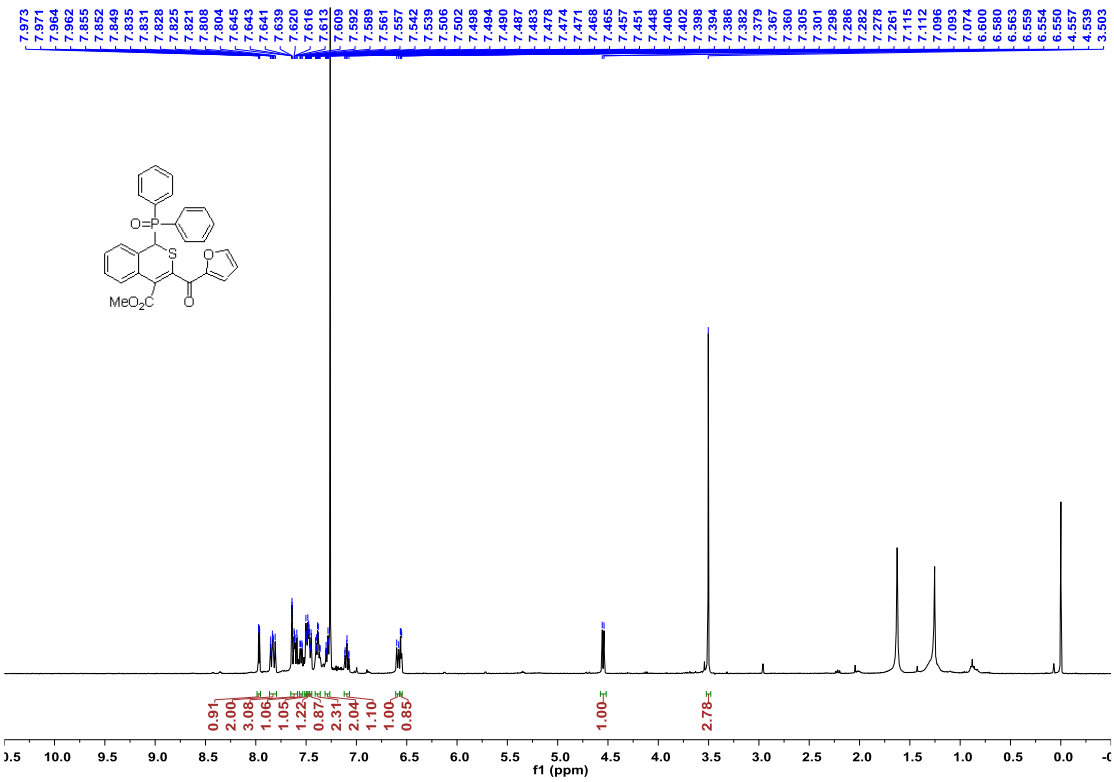


HRMS

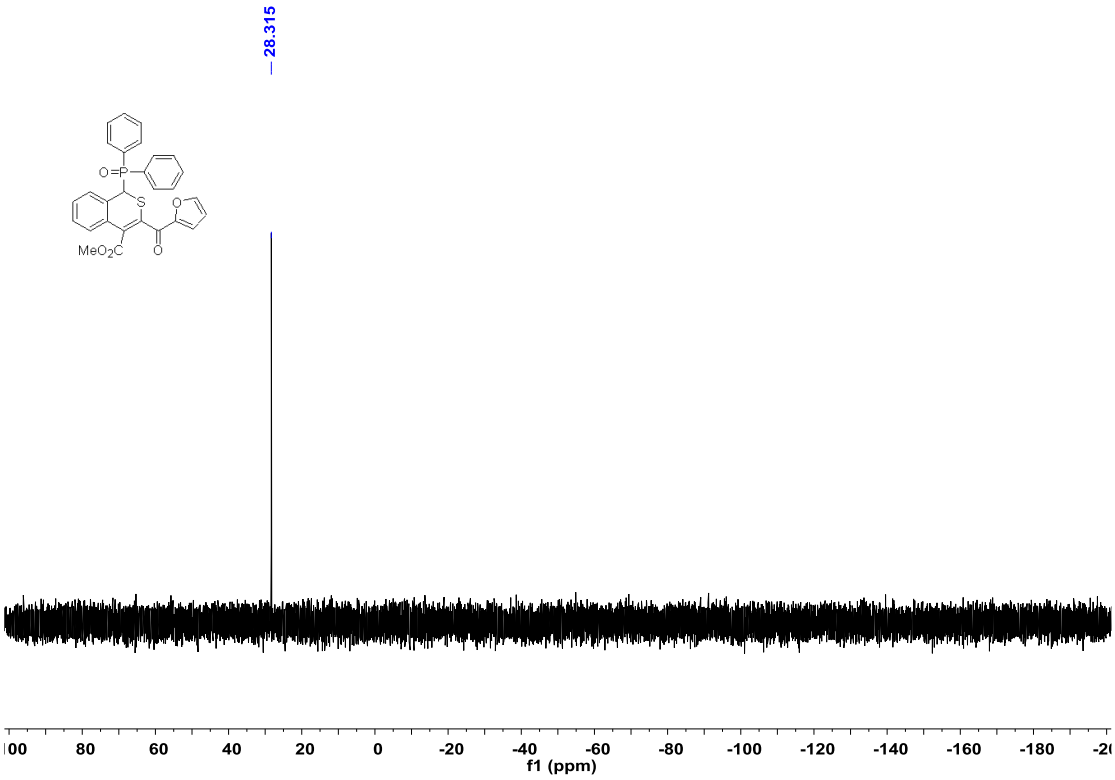


Methyl 1-(diphenylphosphoryl)-3-(furan-2-carbonyl)-1*H*-isothiochromene-4-carboxylate (3af)

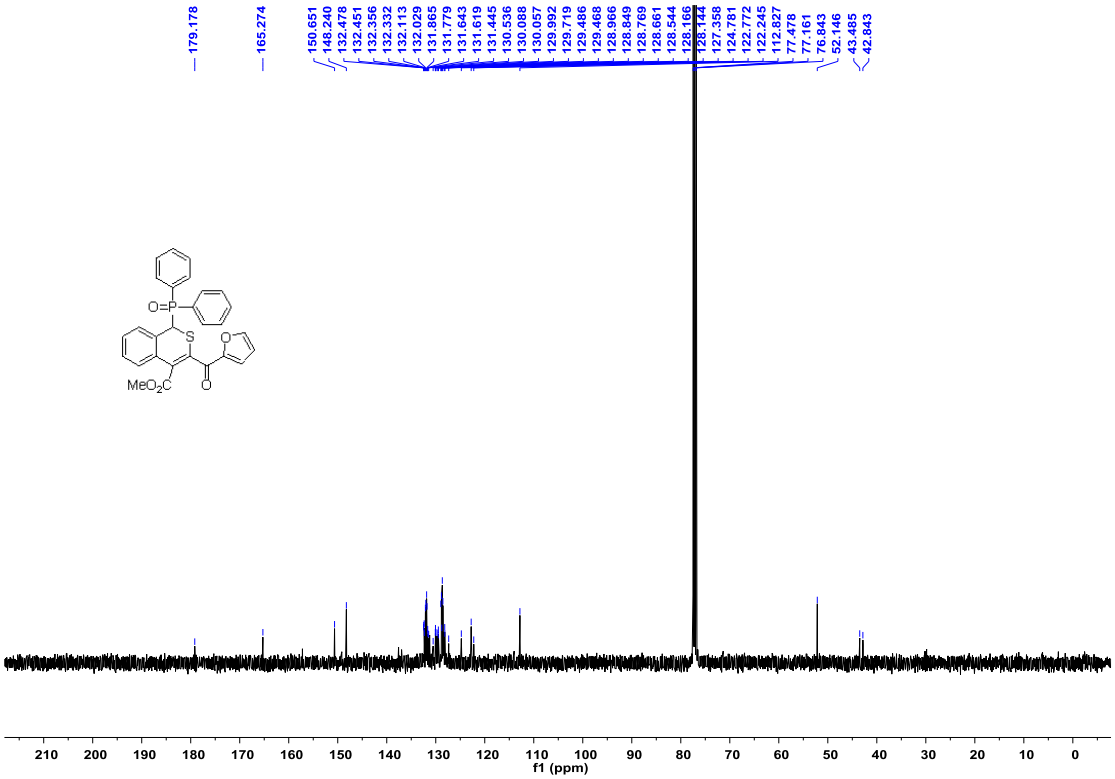
^{1}H NMR (400MHz, $CDCl_3$)



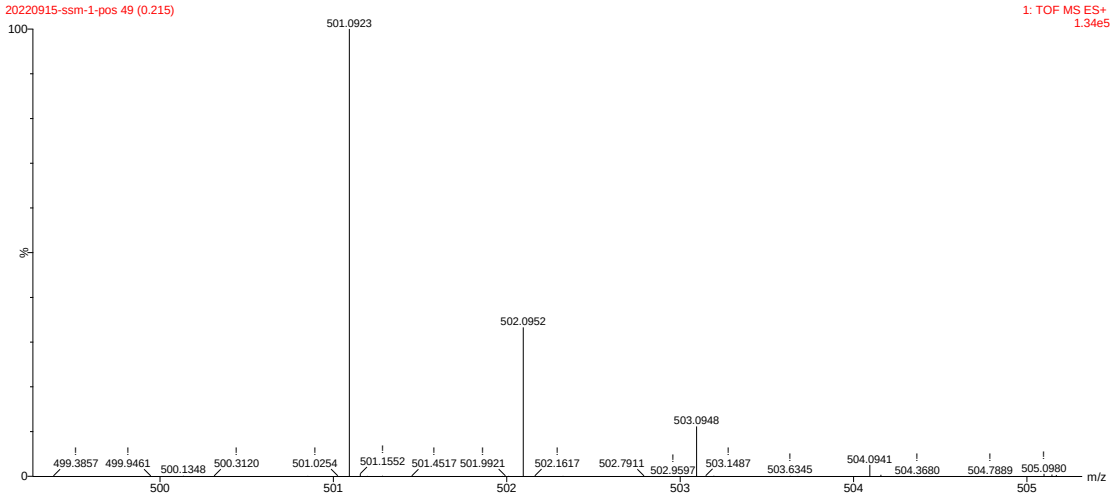
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



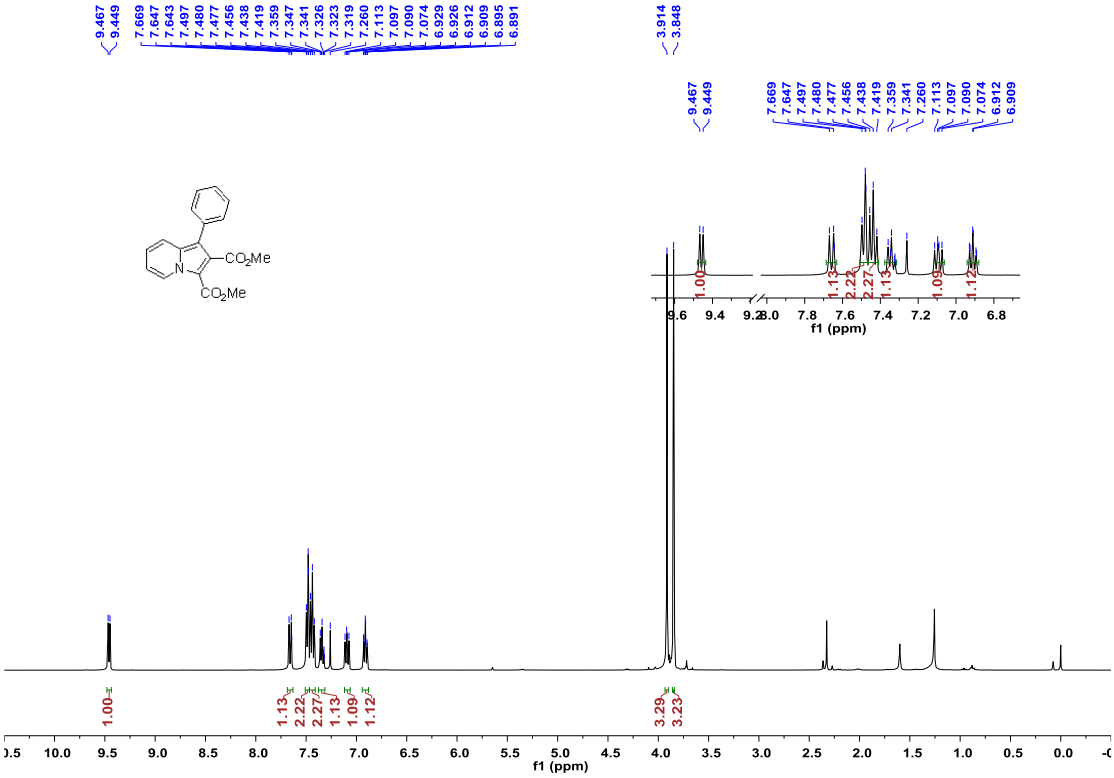
HRMS



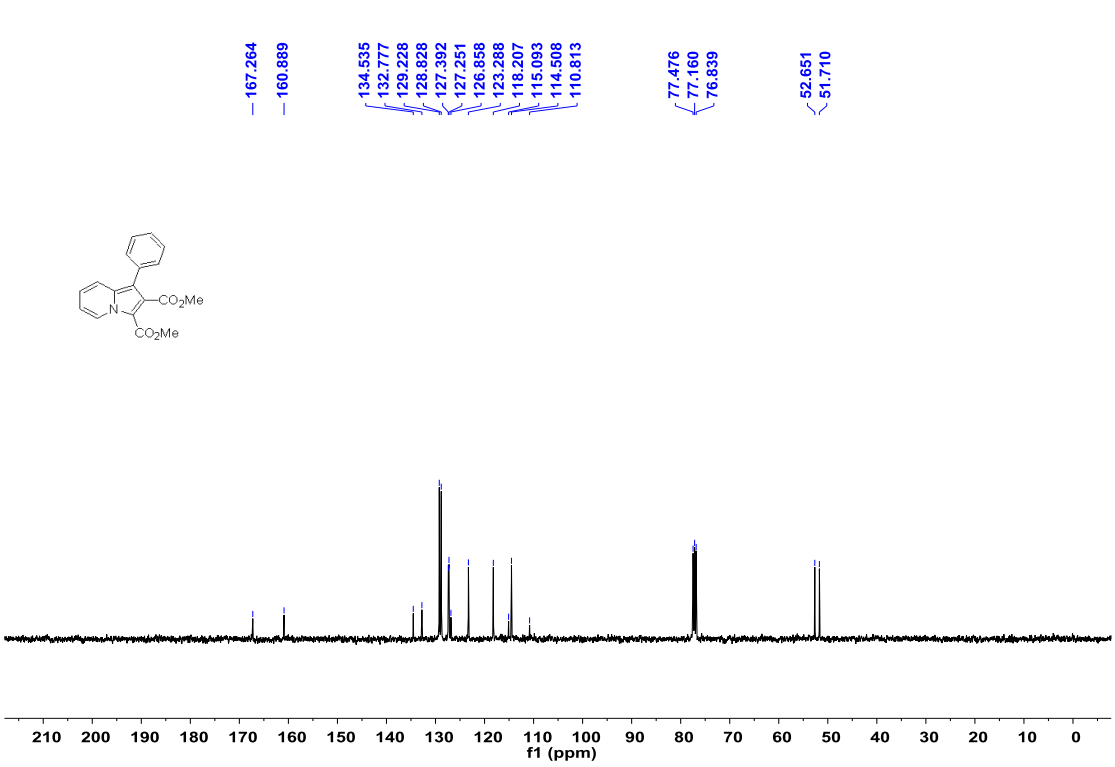
4.4. Copies of ^{1}H, ^{13}C, ^{19}F NMR and HRMS Spectra of Products 4

Dimethyl 1-phenylindolizine-2,3-dicarboxylate (4aa)

^{1}H NMR (400MHz, $CDCl_3$)

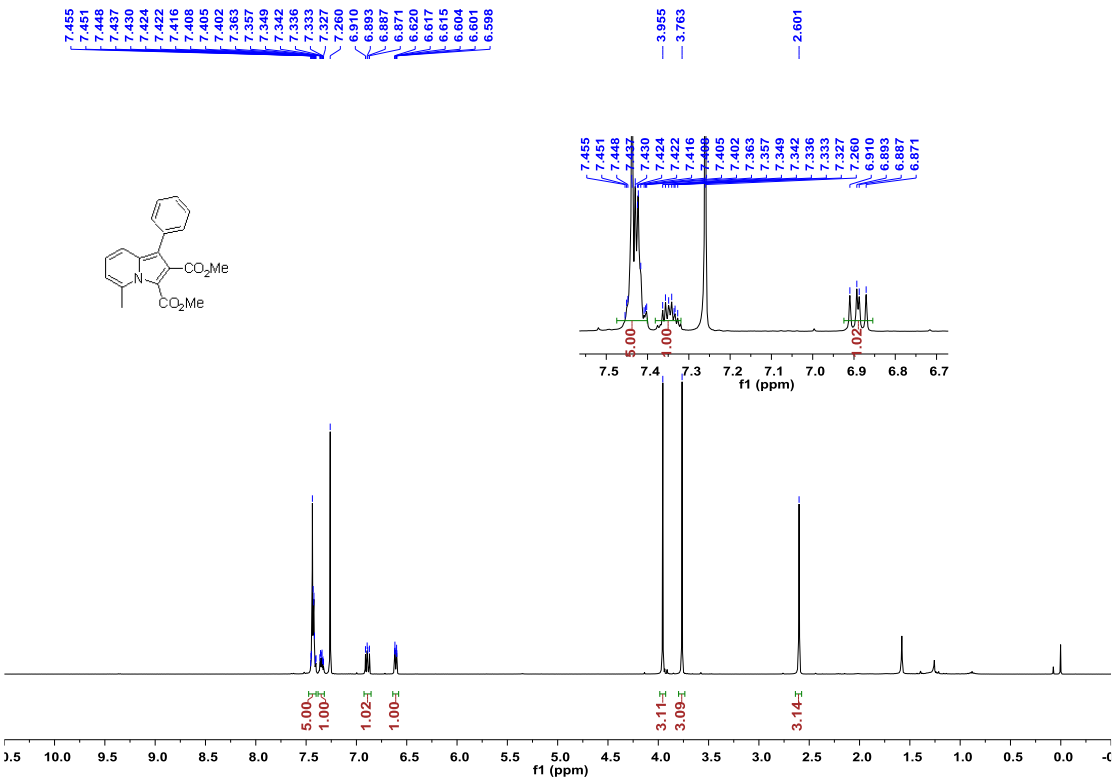


^{13}C NMR (101MHz, $CDCl_3$)

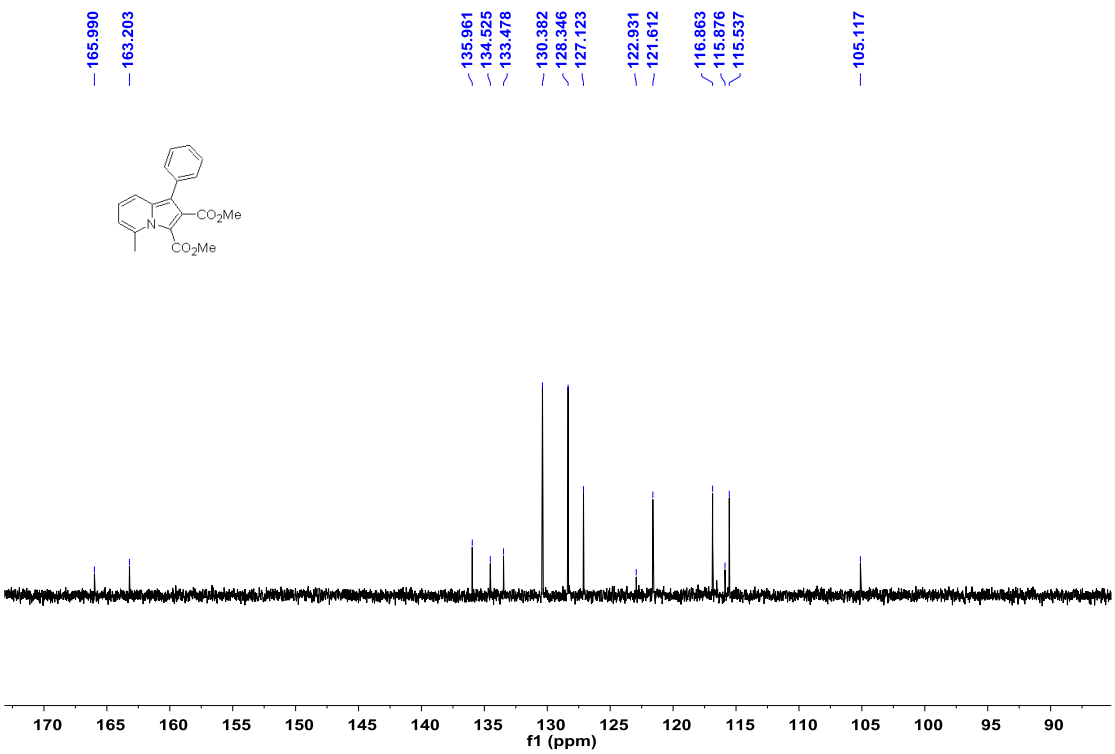


Dimethyl 5-methyl-1-phenylindolizine-2,3-dicarboxylate (4ag)

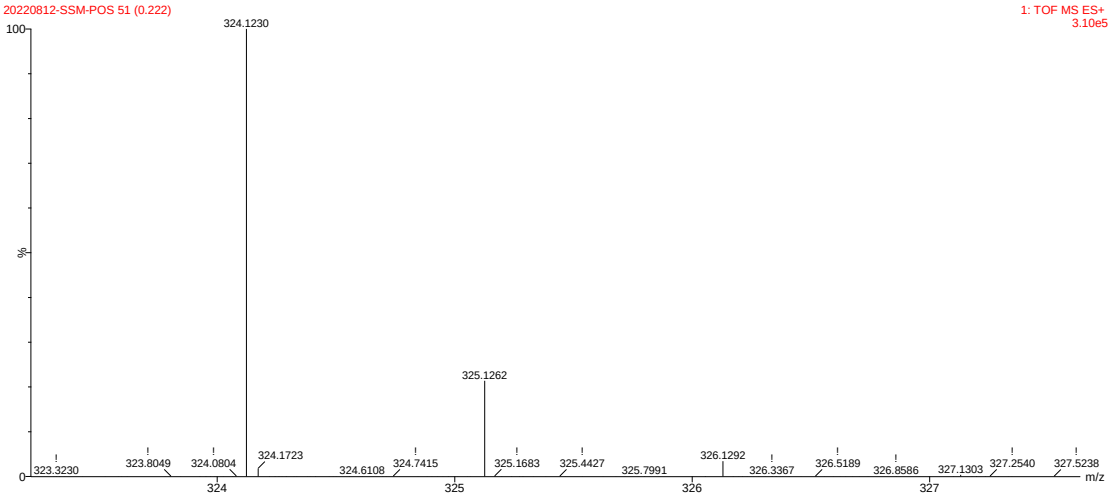
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



HRMS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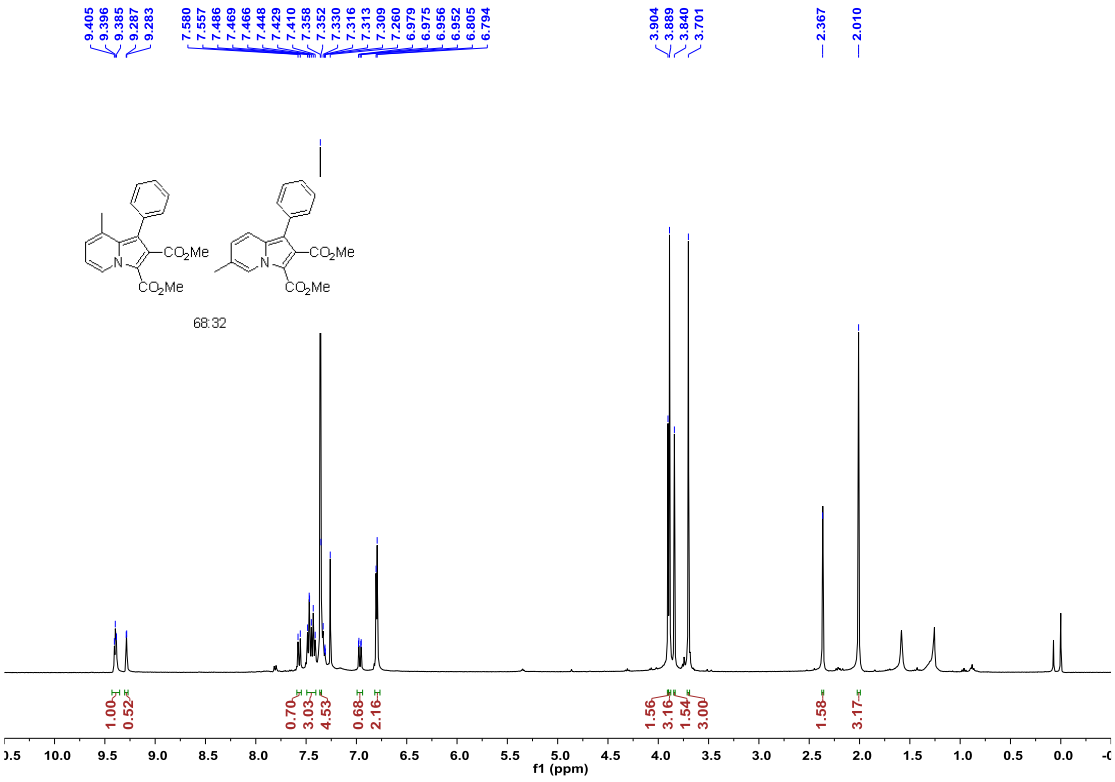
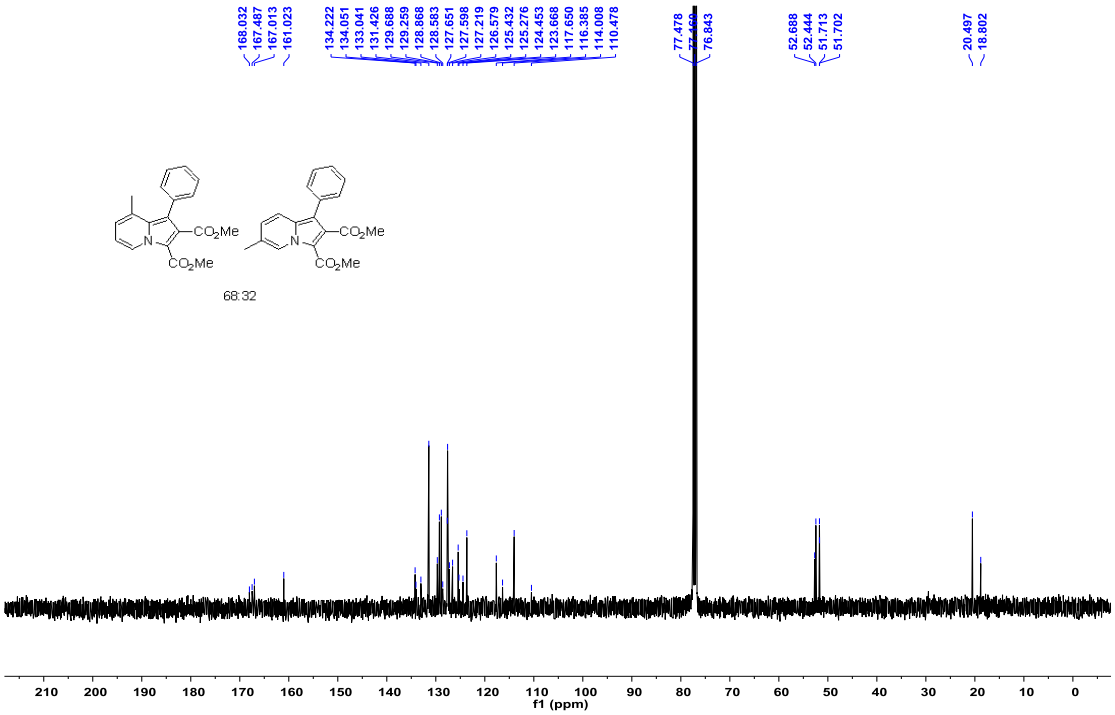
326.8586
327.1303
327.2540
327.5238
324
325
326
327
m/z

Dimethyl 8-methyl-1-phenylindolizine-2,3-dicarboxylate (4ah) and dimethyl 6-methyl-1-phenylindolizine-2,3-dicarboxylate (4ah')

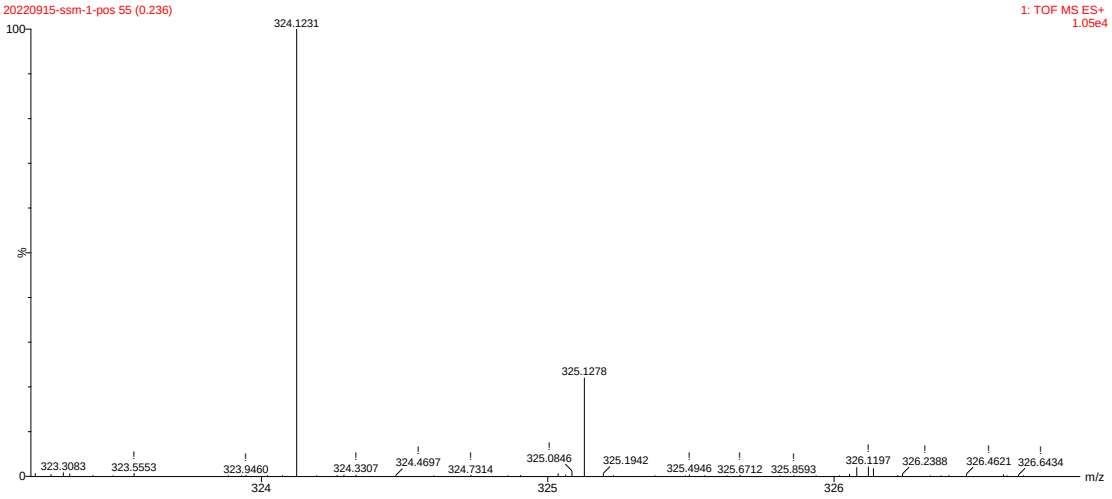
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



HRMS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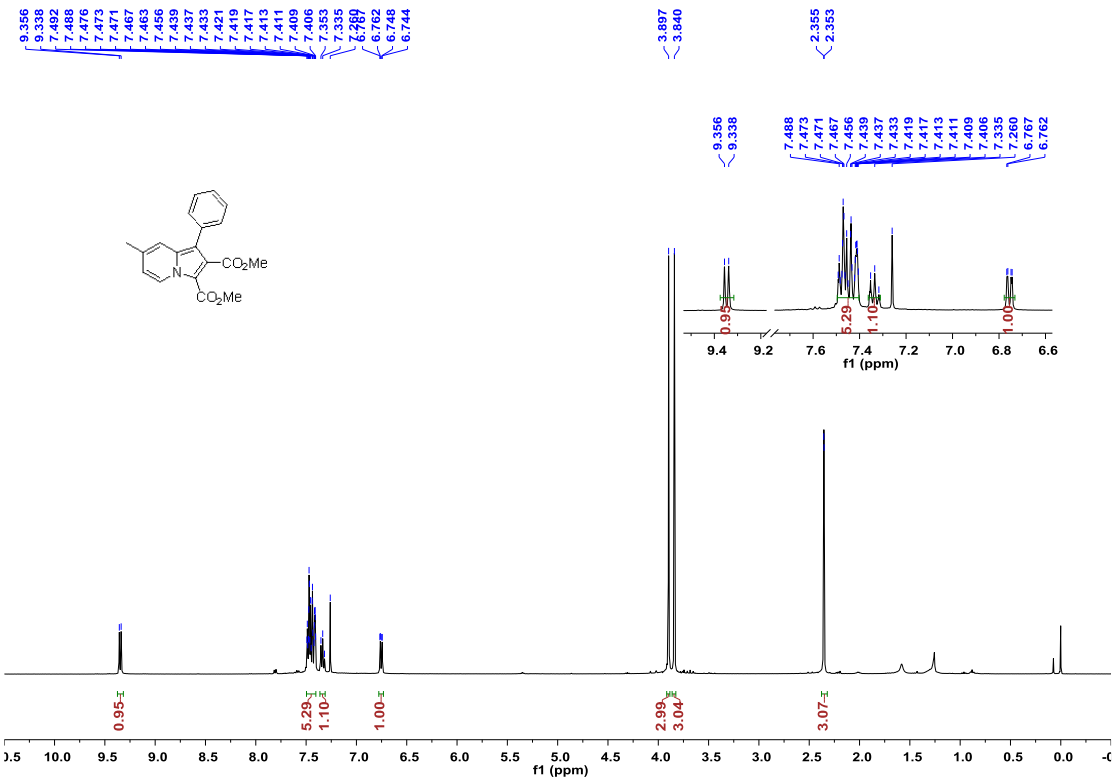
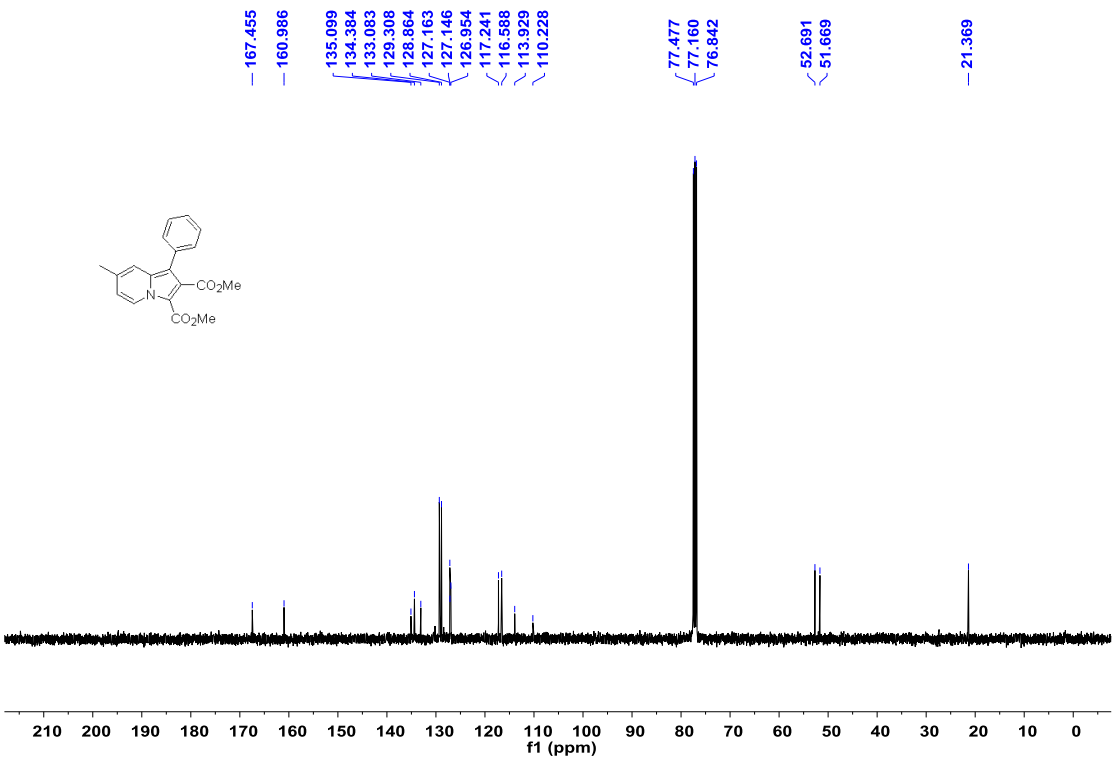
326.1197
326.2388
326.4621
326.6434
324
325
326
m/z

Dimethyl 7-methyl-1-phenylindolizine-2,3-dicarboxylate (4ai)

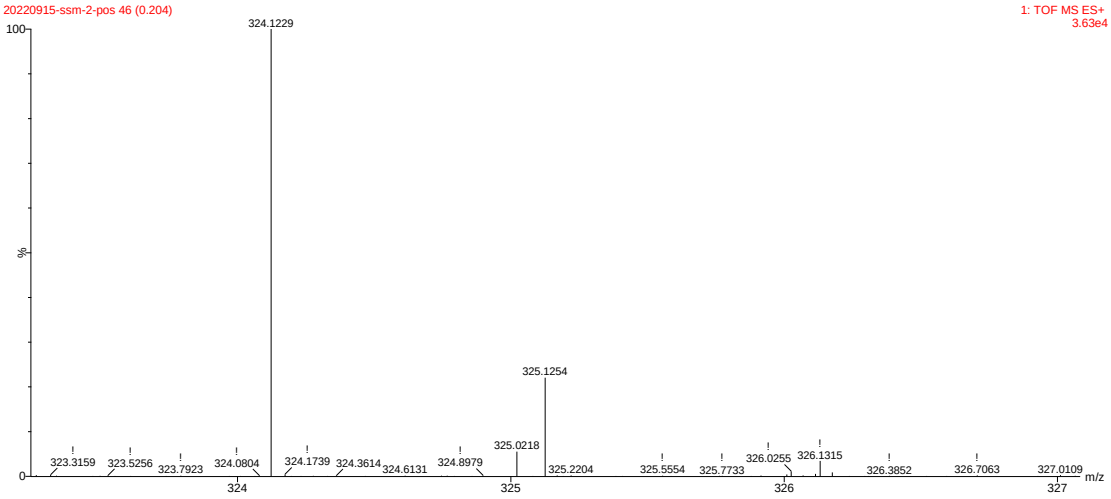
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



HRMS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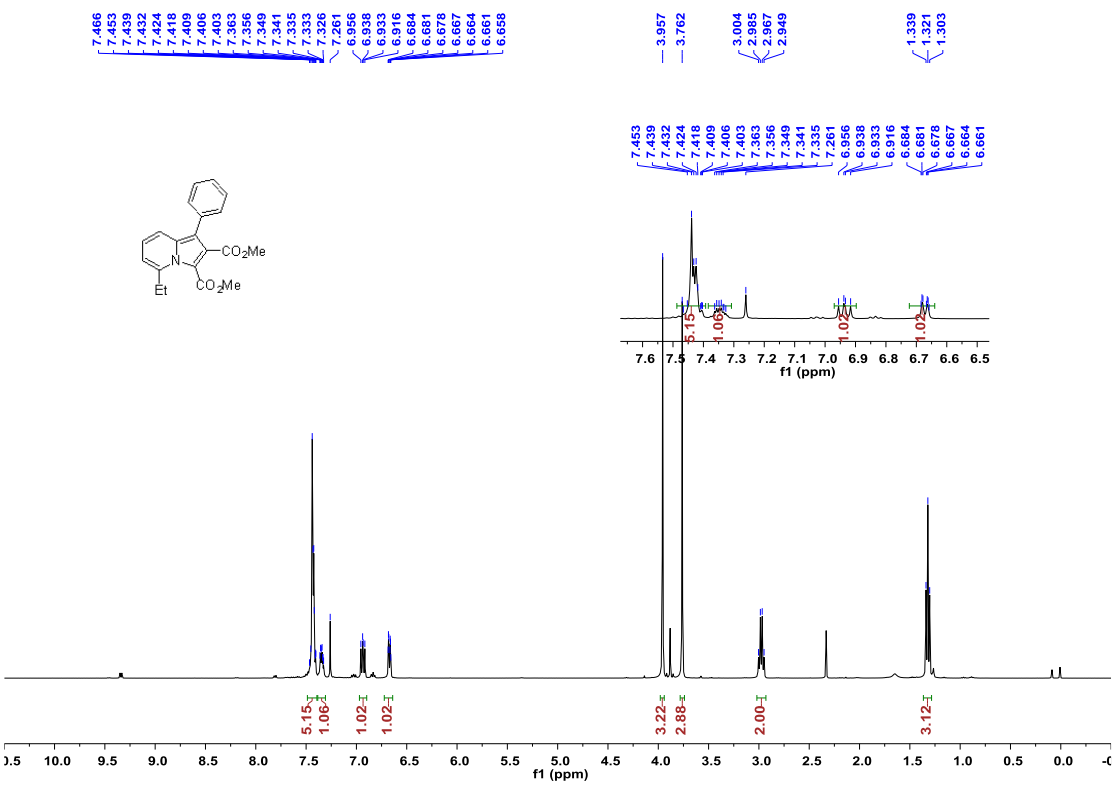
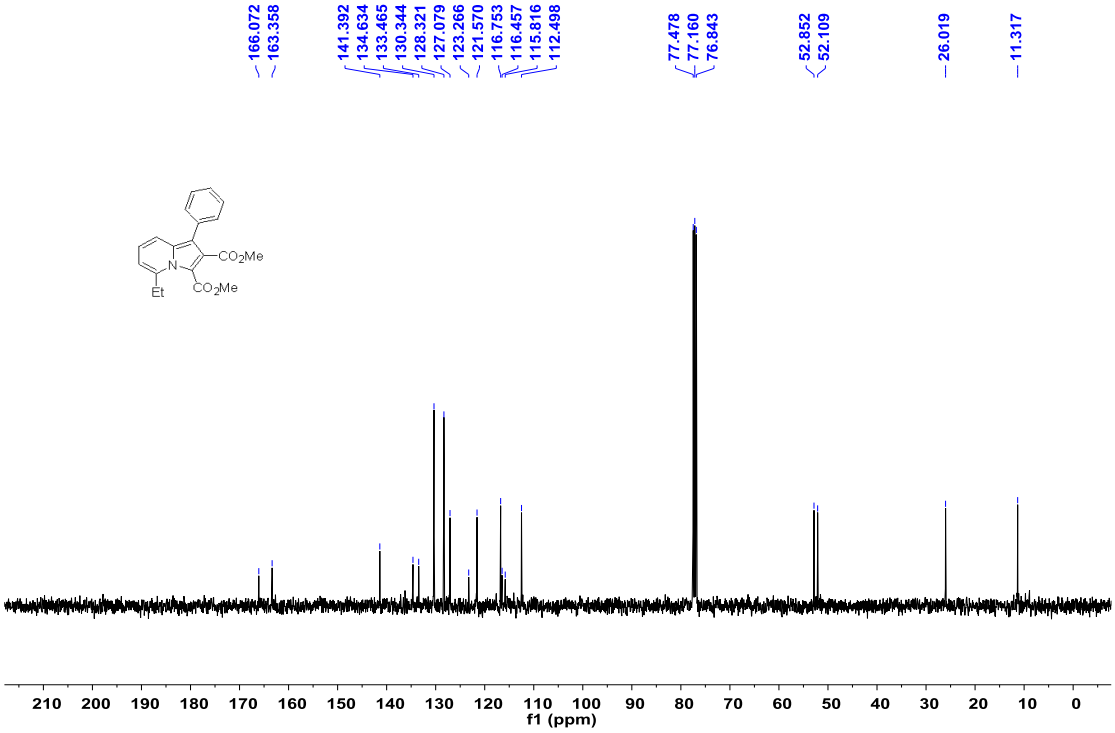
326.3852
326.7063
327.0109
324
325
326
327
m/z

Dimethyl 5-ethyl-1-phenylindolizine-2,3-dicarboxylate (4aj)

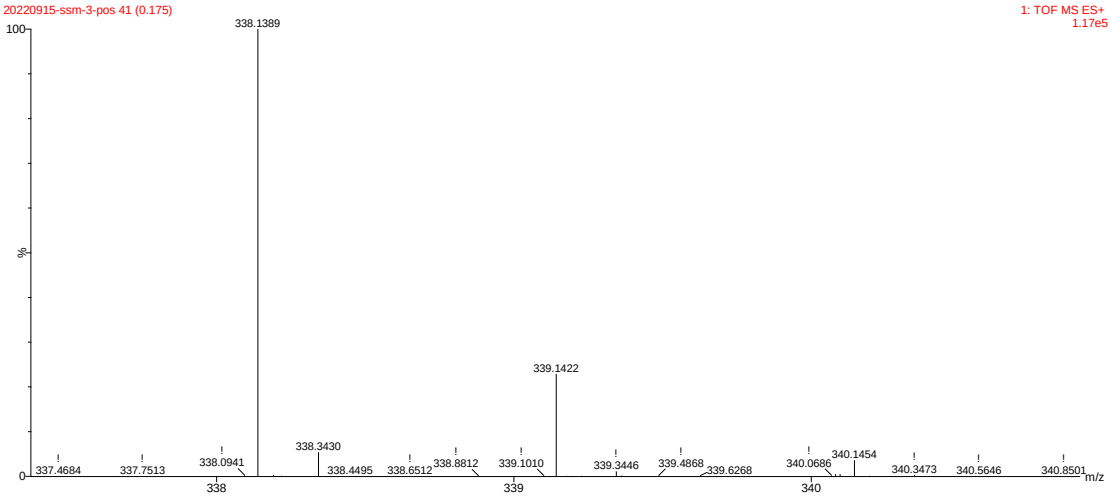
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

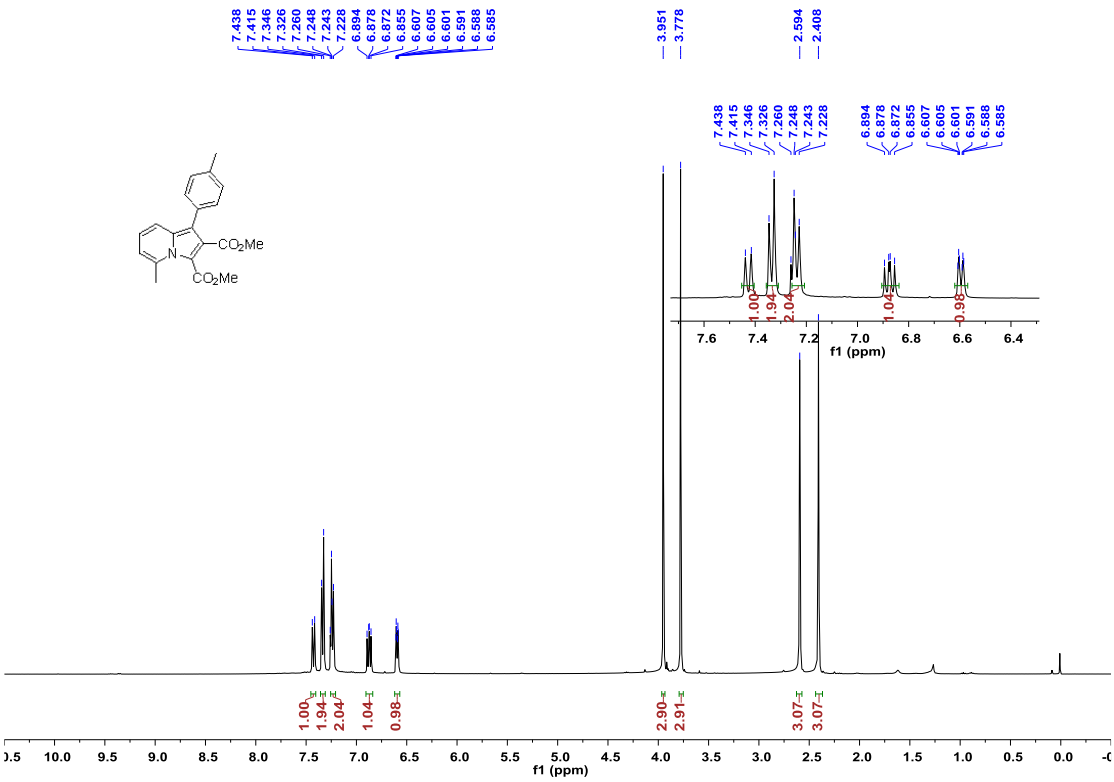


HRMS

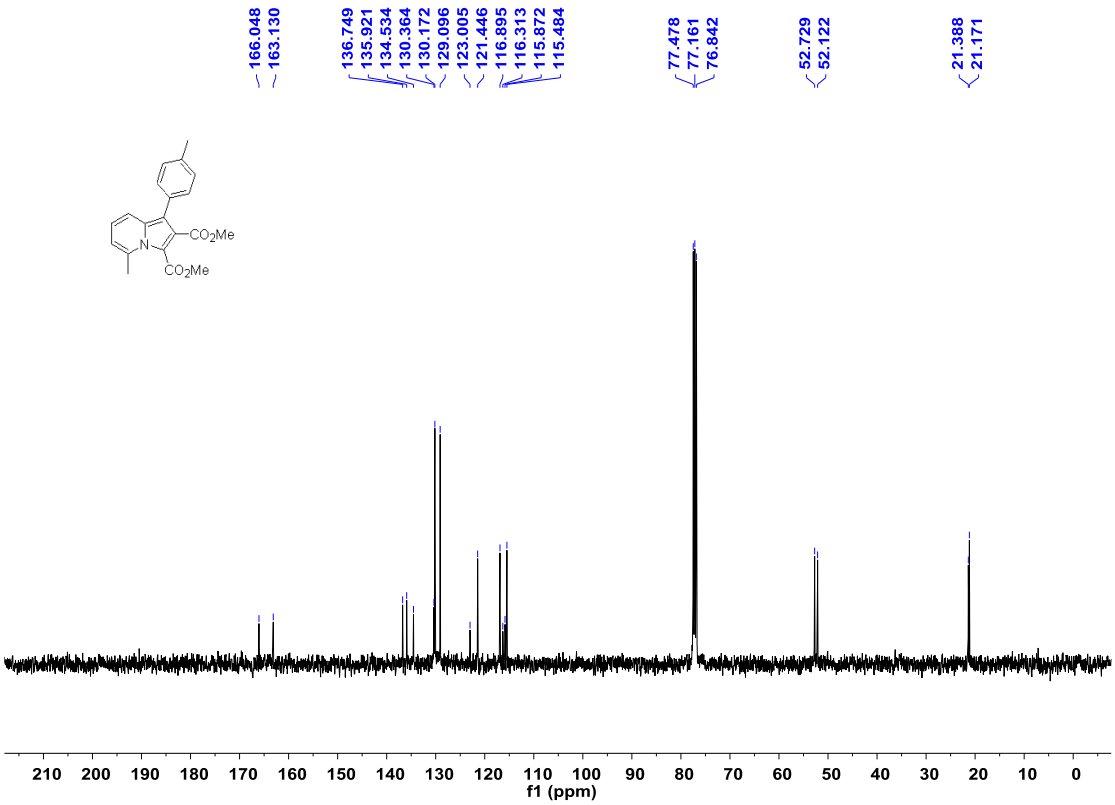

20220915-ssm-3-pos 41 (0.175)
1: TOF MS ES+
1.17e5
100
%
0
338.1389
339.1422
338.3430
337.4684
337.7513
338.0941
338.4495
338.6512
338.8812
339.1010
339.3446
339.4868
339.6268
340.0686
340.1454
340.3473
340.5646
340.8501
338
339
340
m/z

Dimethyl 5-methyl-1-(*p*-tolyl)indolizine-2,3-dicarboxylate (4bg)

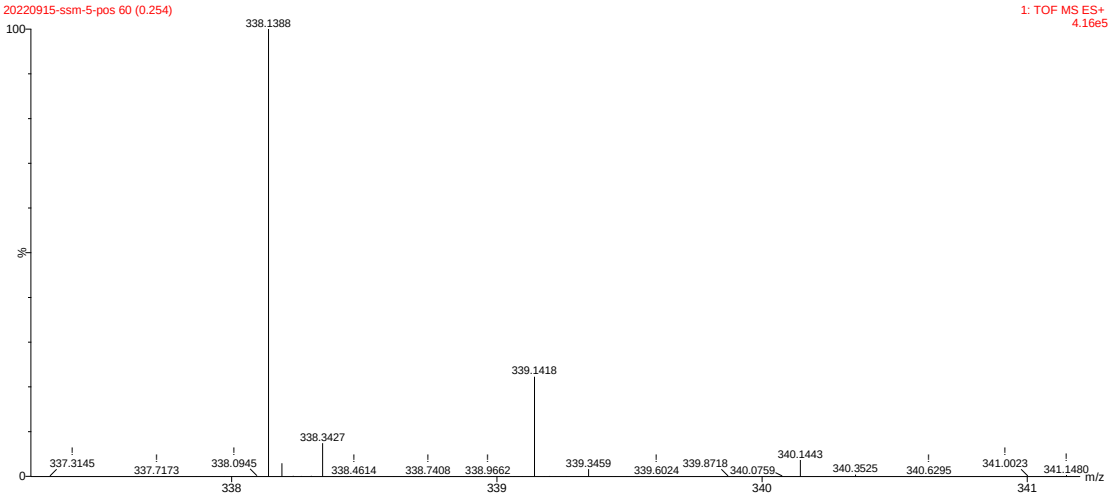
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

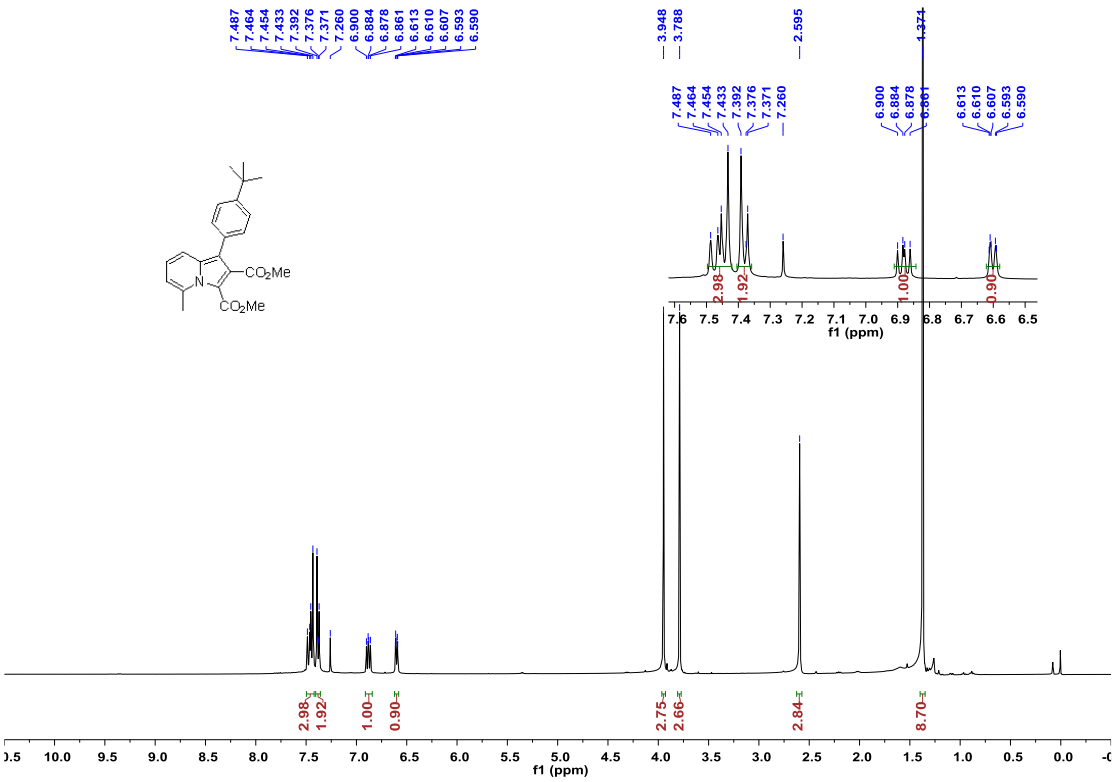


HRMS

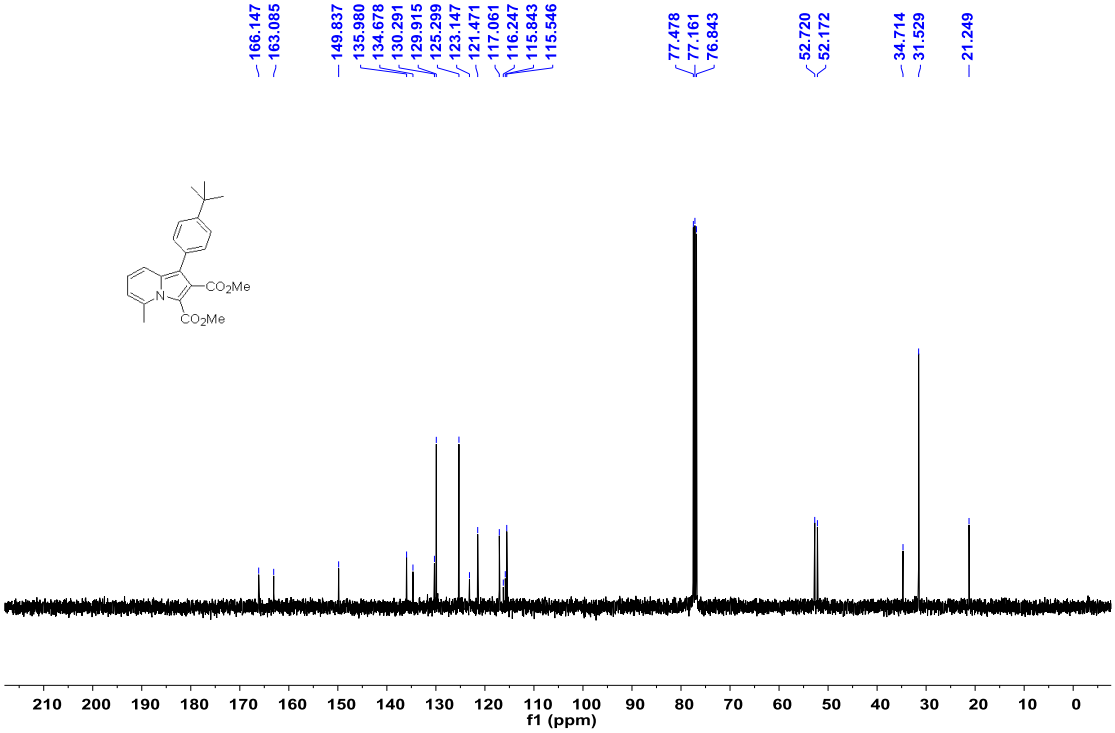

20220915-ssm-5-pos 60 (0.254)
1: TOF MS ES+
4.16e5
100
%
0
338.1388
339.1418
338.3427
337.3145
337.7173
338.0945
338.4614
338.7408
338.9662
339.3459
339.6024
339.8718
340.0759
340.1443
340.3525
340.6295
341.0023
341.1480
338
339
340
341
m/z

Dimethyl 1-(4-(*tert*-butyl)phenyl)-5-methylindolizine-2,3-dicarboxylate (4cg)

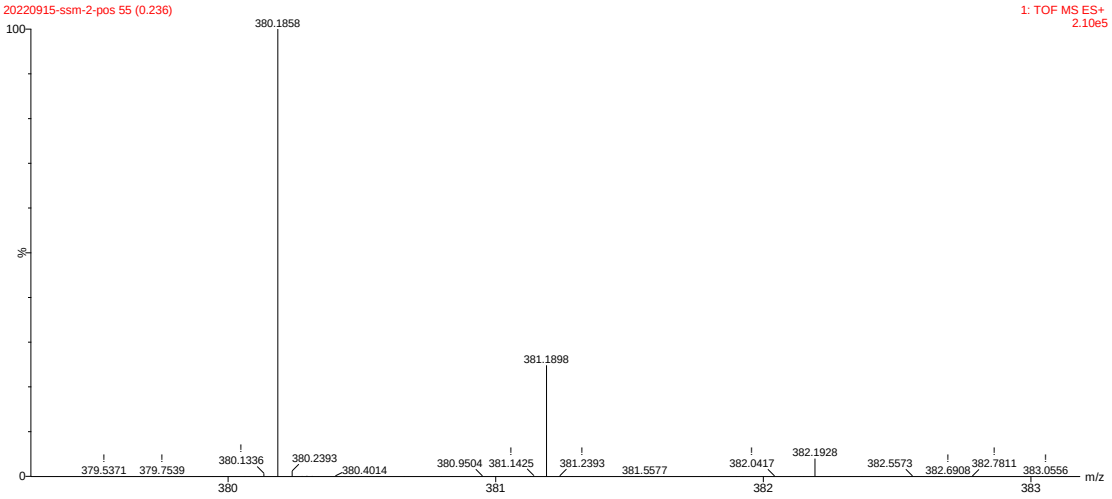
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

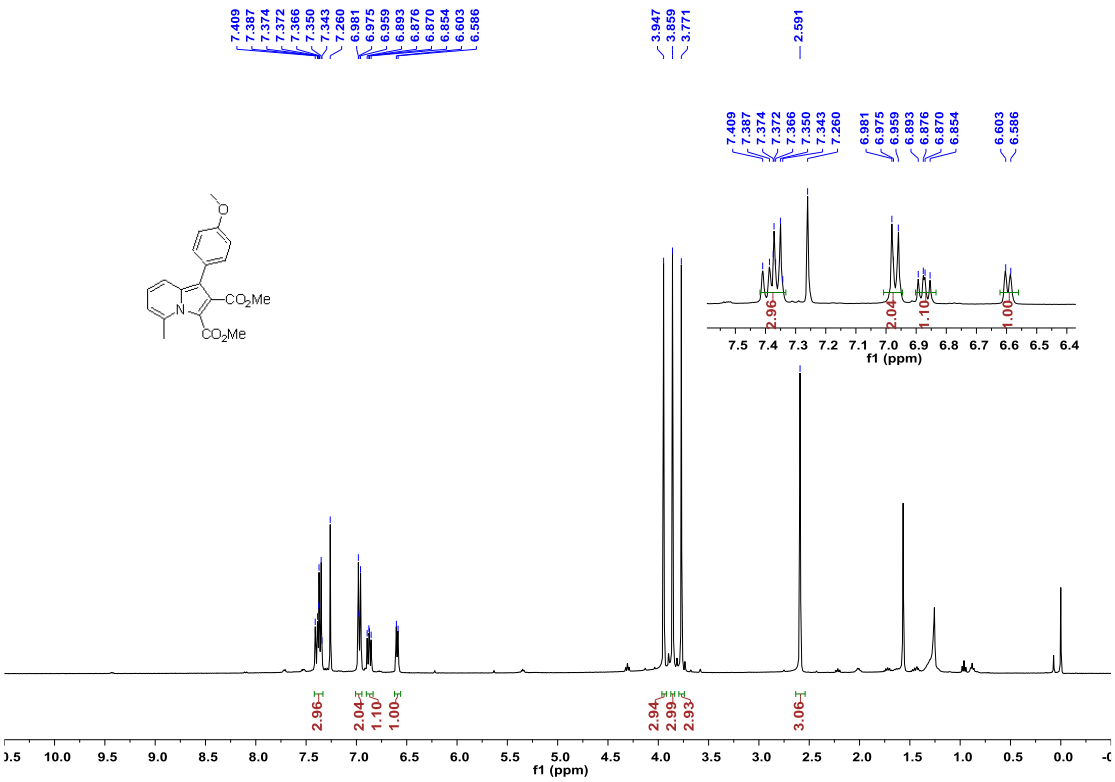


HRMS

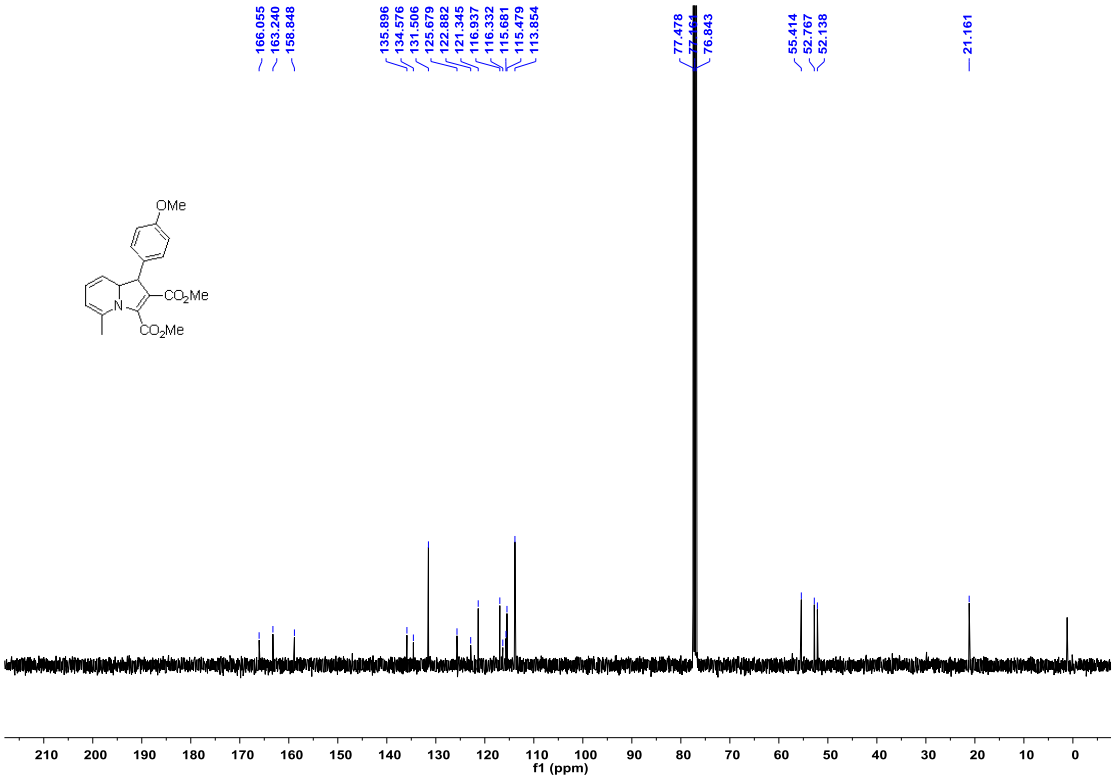

20220915-ssm-2-pos 55 (0.236)
1: TOF MS ES+
2.10e5
100
%
0
380.1858
381.1898
382.1928
379.5371
379.7539
380.1336
380.2393
380.4014
380.9504
381.1425
381.2393
381.5577
382.0417
382.5573
382.6908
382.7811
383.0556
380
381
382
383
m/z

Dimethyl 1-(4-methoxyphenyl)-5-methylindolizine-2,3-dicarboxylate (4dg)

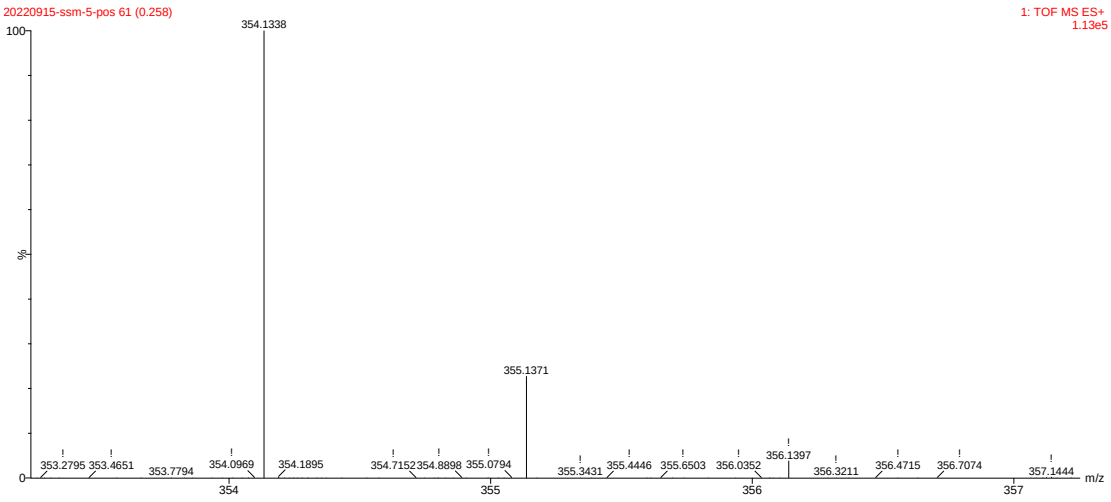
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

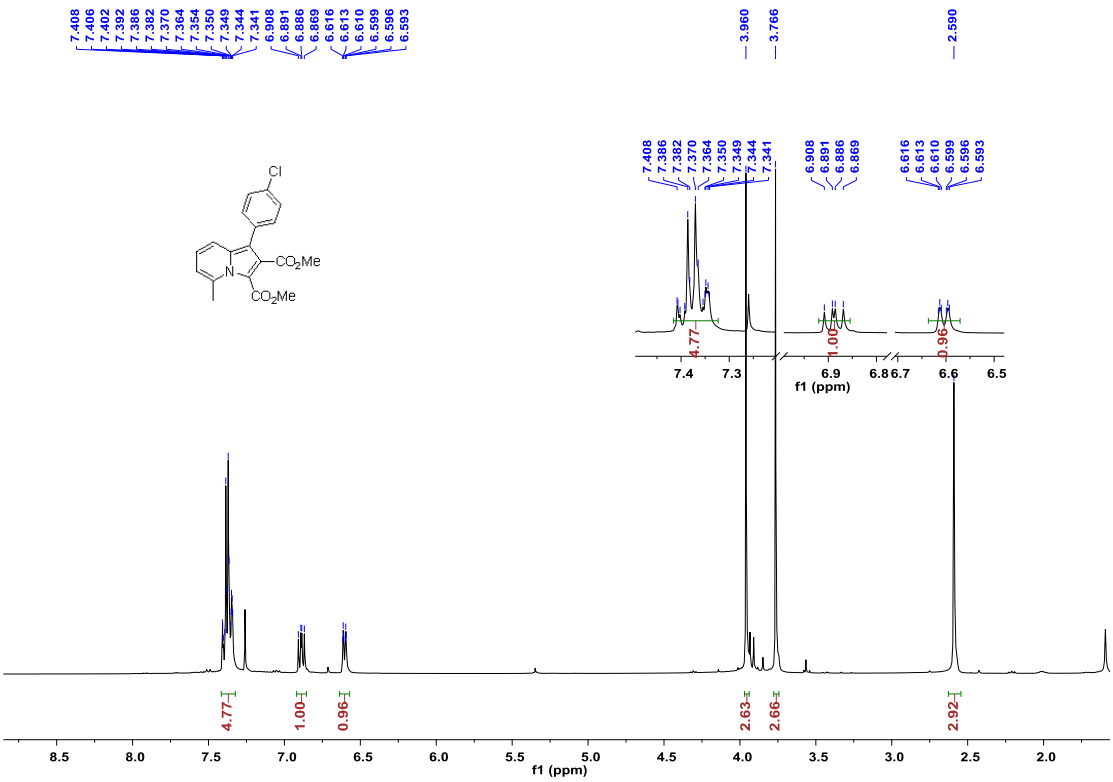


HRMS

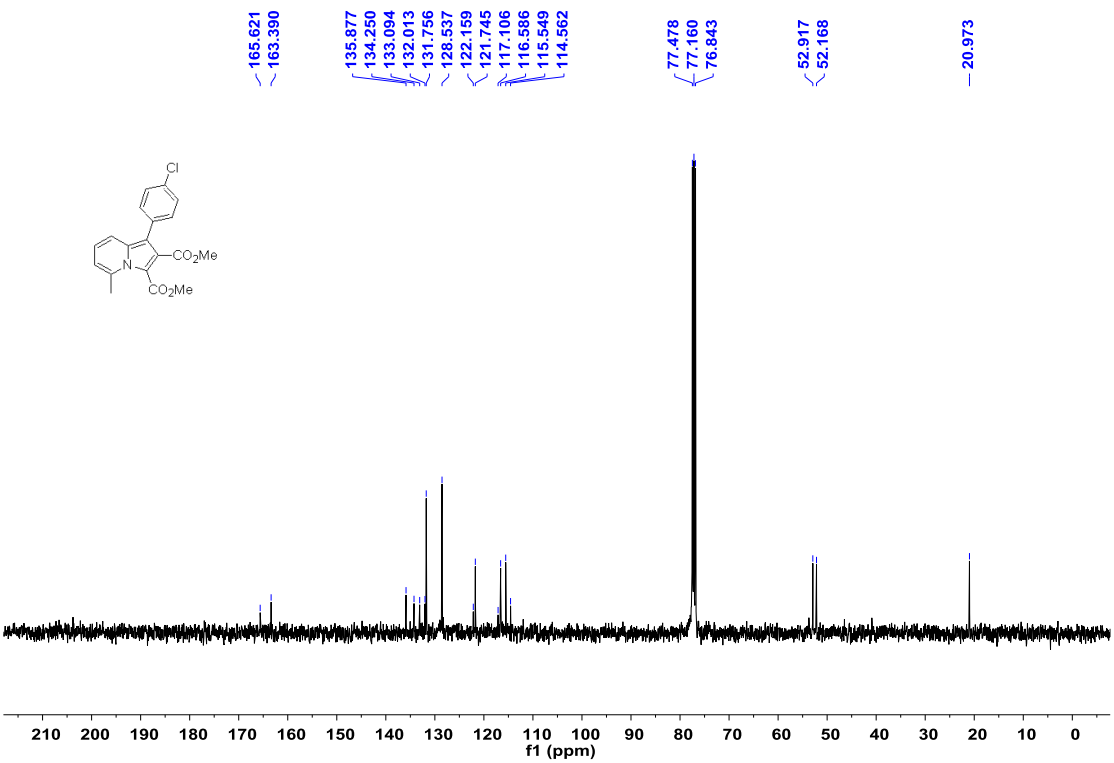

20220915-ssm-5-pos 61 (0.258)
1: TOF MS ES+
1.13e5
100
%
0
354.1338
355.1371
353.2795
353.4651
353.7794
354.0969
354.1895
354.7152
354.8898
355.0794
355.3431
355.4446
355.6503
356.0352
356.1397
356.3211
356.4715
356.7074
357.1444
354
355
356
357
m/z

Dimethyl 1-(4-chlorophenyl)-5-methylindolizine-2,3-dicarboxylate (4eg)

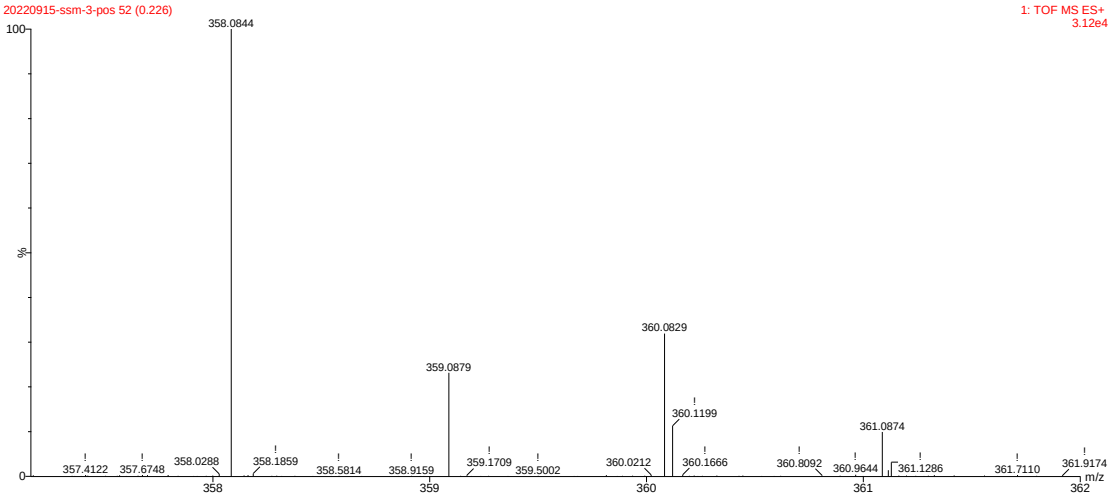
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

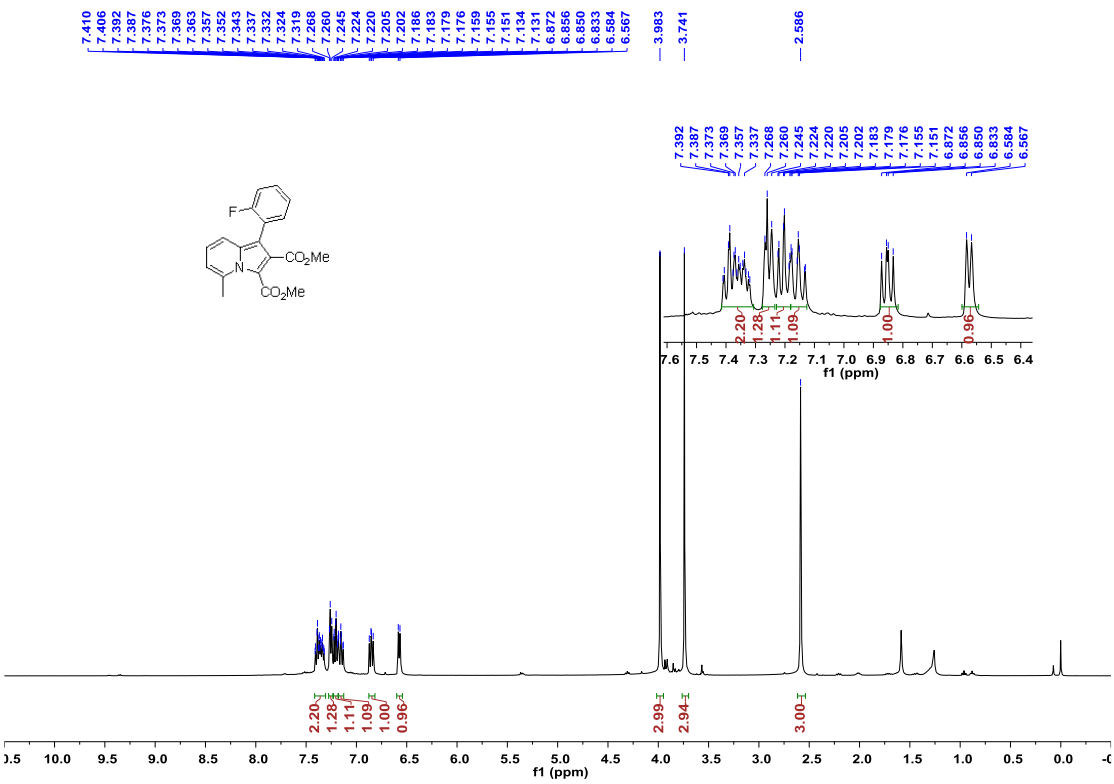


HRMS

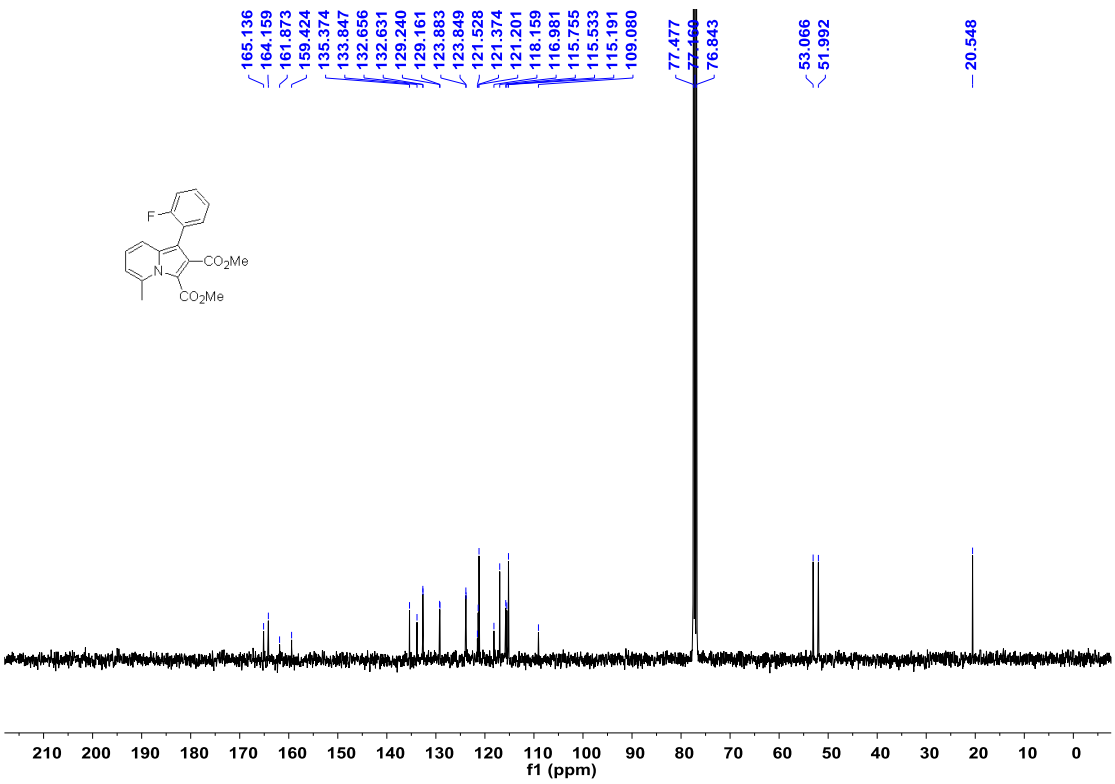

20220915-ssm-3-pos 52 (0.226)
1: TOF MS ES+
3.12e4
100
%
0
358.0844
360.0829
359.0879
360.1199
361.0874
357.4122
357.6748
358.0288
358.1859
358.5814
358.9159
359.1709
359.5002
360.0212
360.1666
360.8092
360.9644
361.1286
361.7110
361.9174
358
359
360
361
362
m/z

Dimethyl 1-(2-fluorophenyl)-5-methylindolizine-2,3-dicarboxylate (4gg)

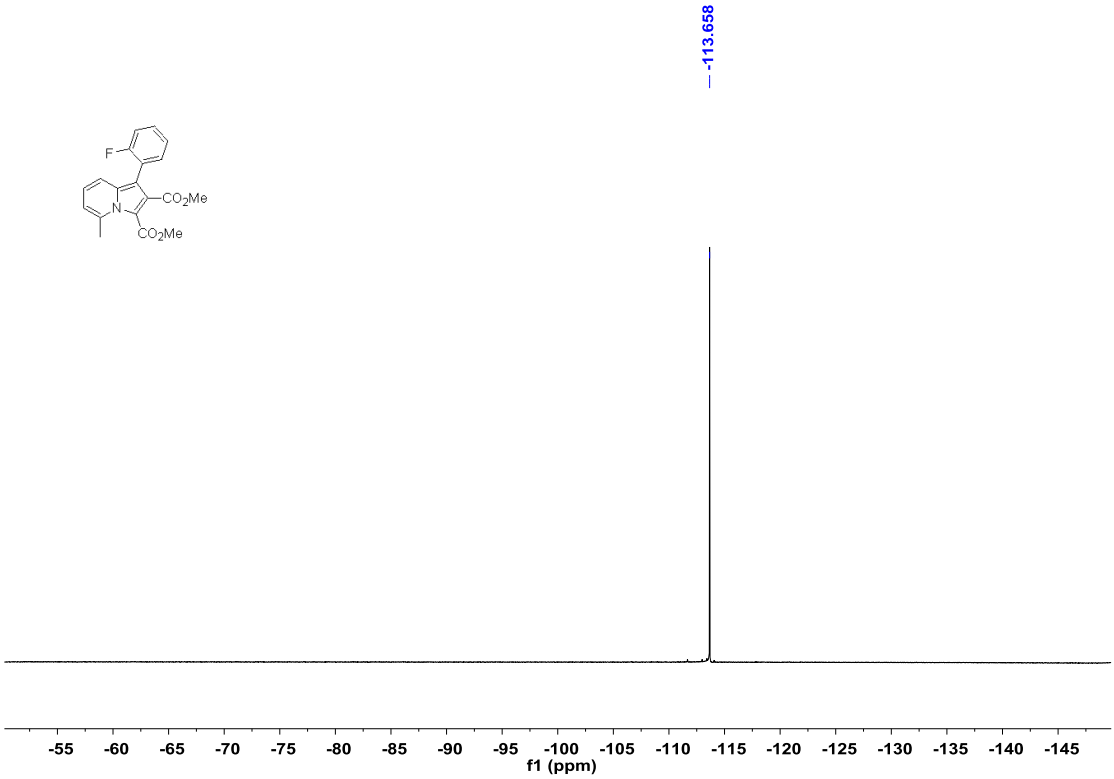
^{1}H NMR (400MHz, $CDCl_3$)



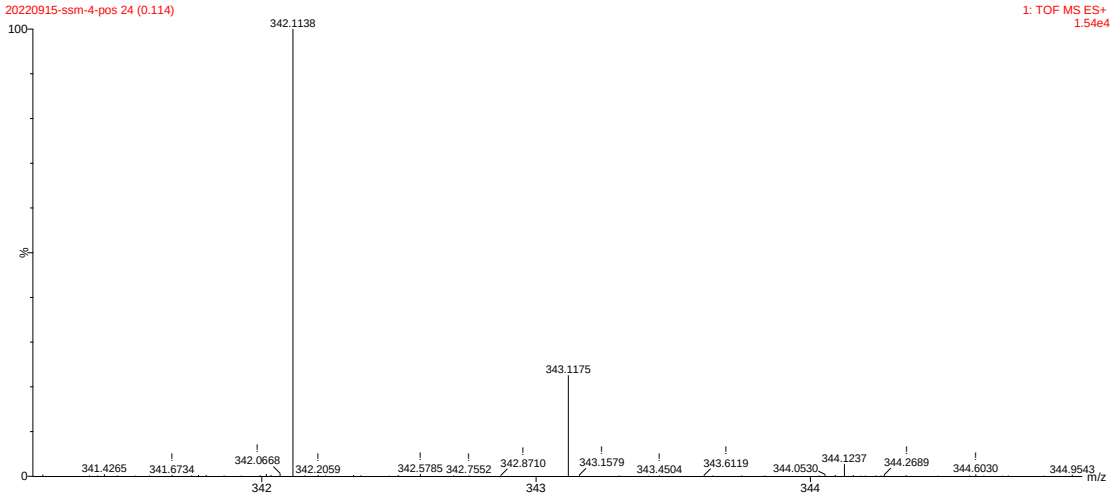
^{13}C NMR (101MHz, $CDCl_3$)



^{19}F NMR (376MHz, $CDCl_3$)

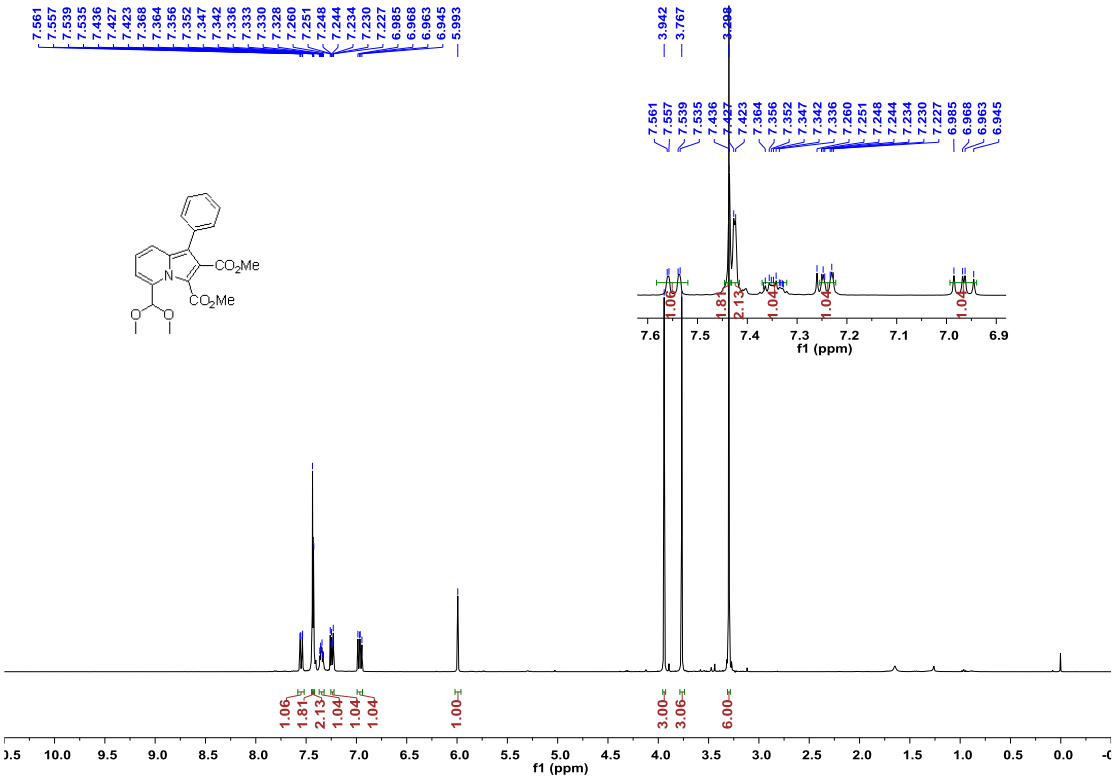


HRMS

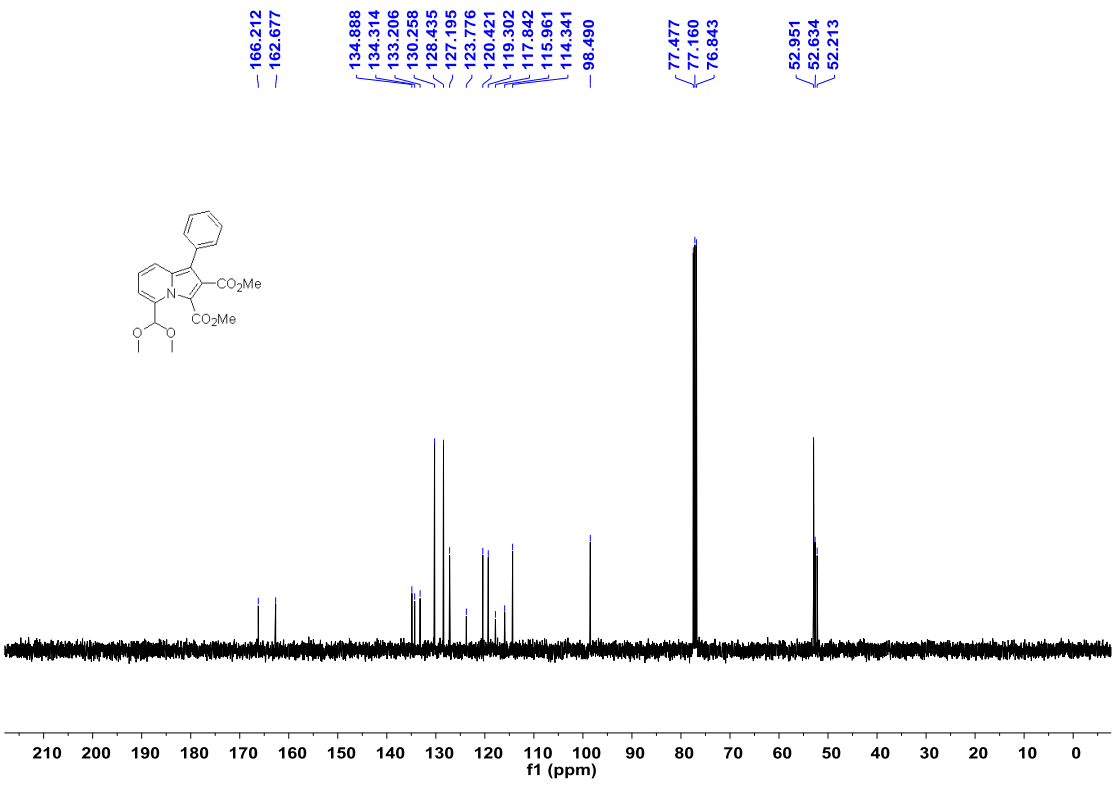


Dimethyl 5-(dimethoxymethyl)-1-phenylindolizine-2,3-dicarboxylate (4al)

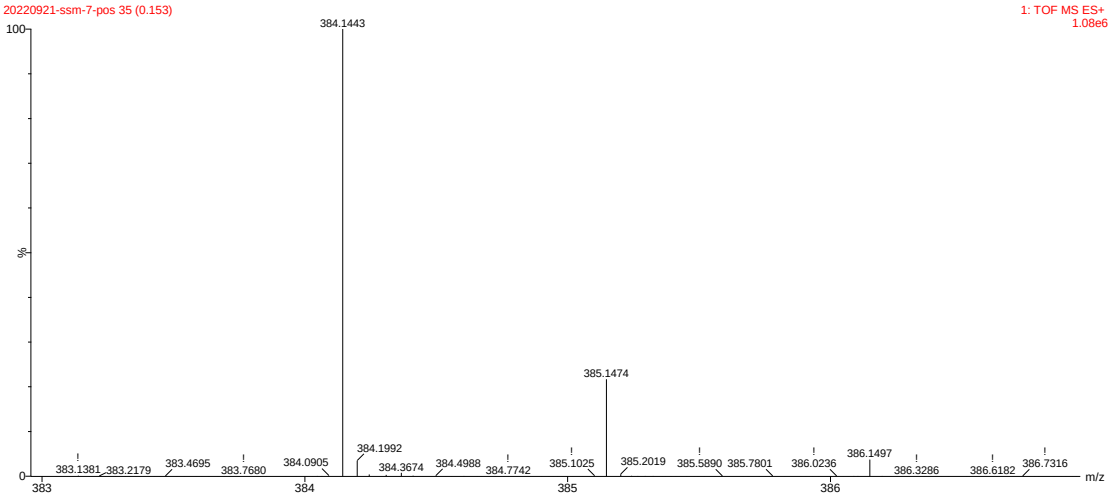
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



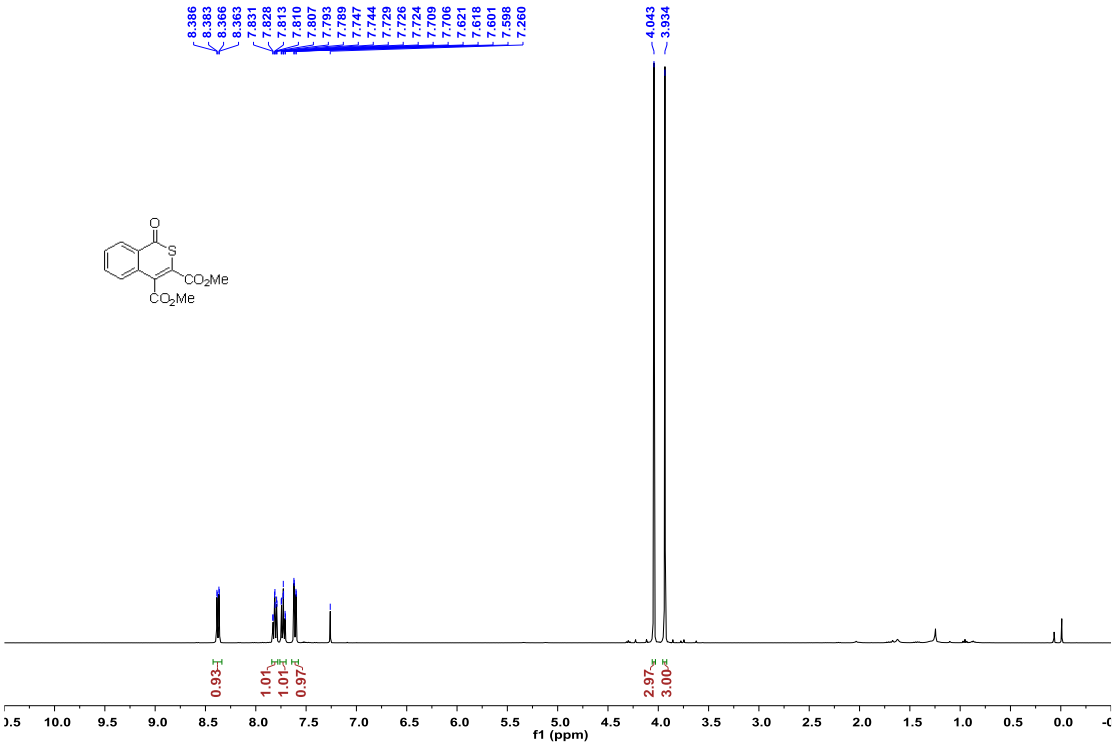
HRMS


20220921-ssm-7-pos 35 (0.153)
1: TOF MS ES+
1.08e6
100
%
0
384.1443
385.1474
384.1992
383.1381
383.2179
383.4695
383.7680
384.0905
384.3674
384.4988
384.7742
385.1025
385.2019
385.5890
385.7801
386.0236
386.1497
386.3286
386.6182
386.7316
383
384
385
386
m/z

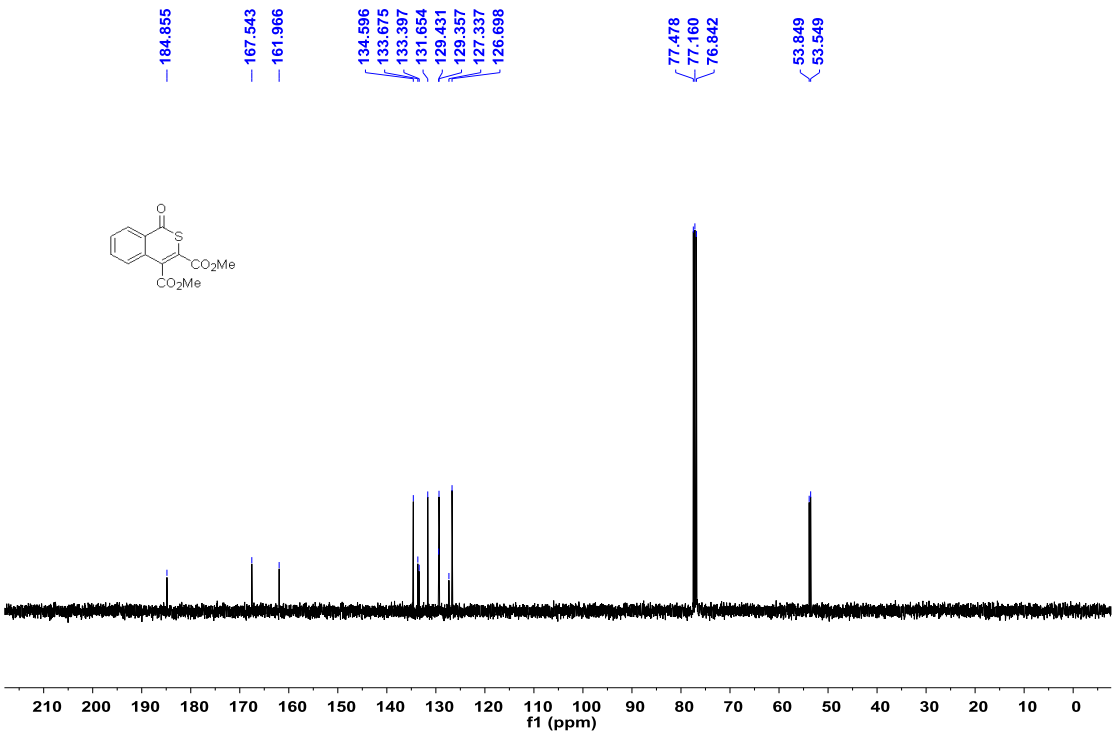
4.5. Copies of ^{1}H, ^{13}C NMR and HRMS Spectra of Applications

Dimethyl 1-oxo-1*H*-isothiochromene-3,4-dicarboxylate (7)

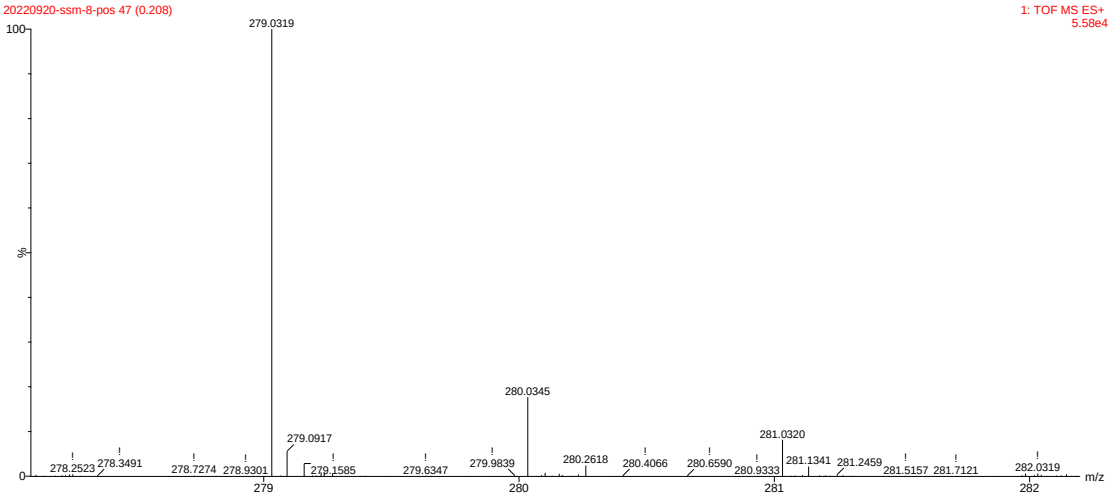
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

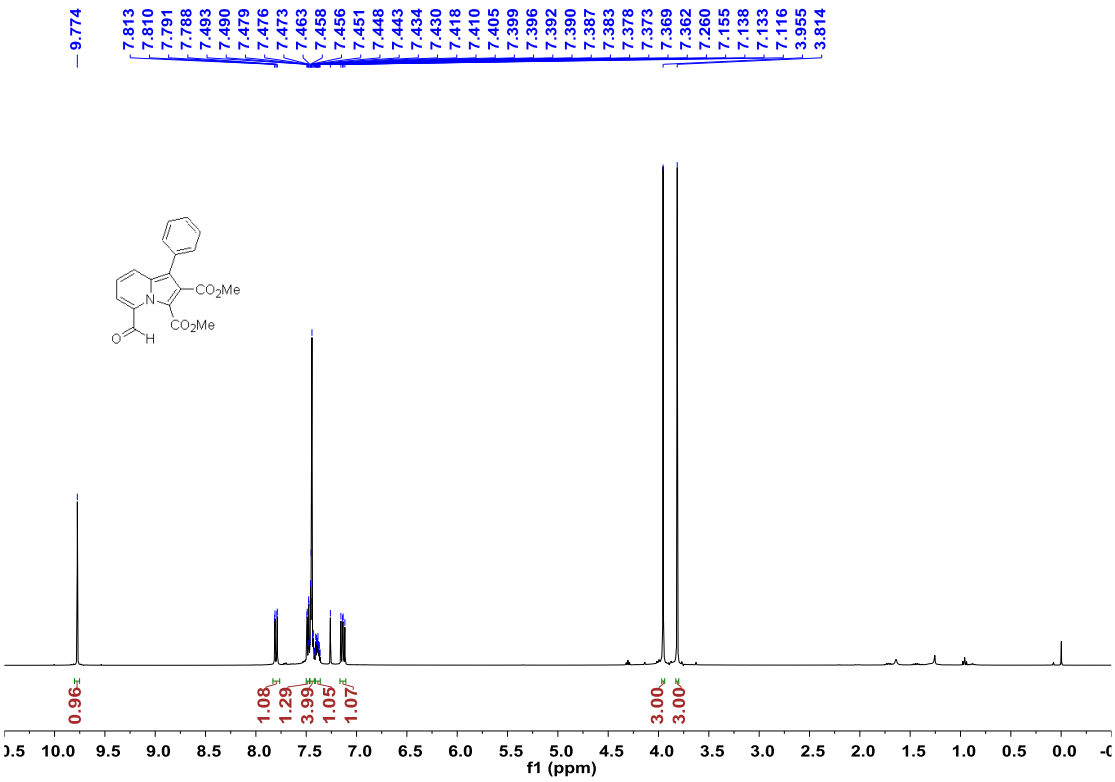


HRMS

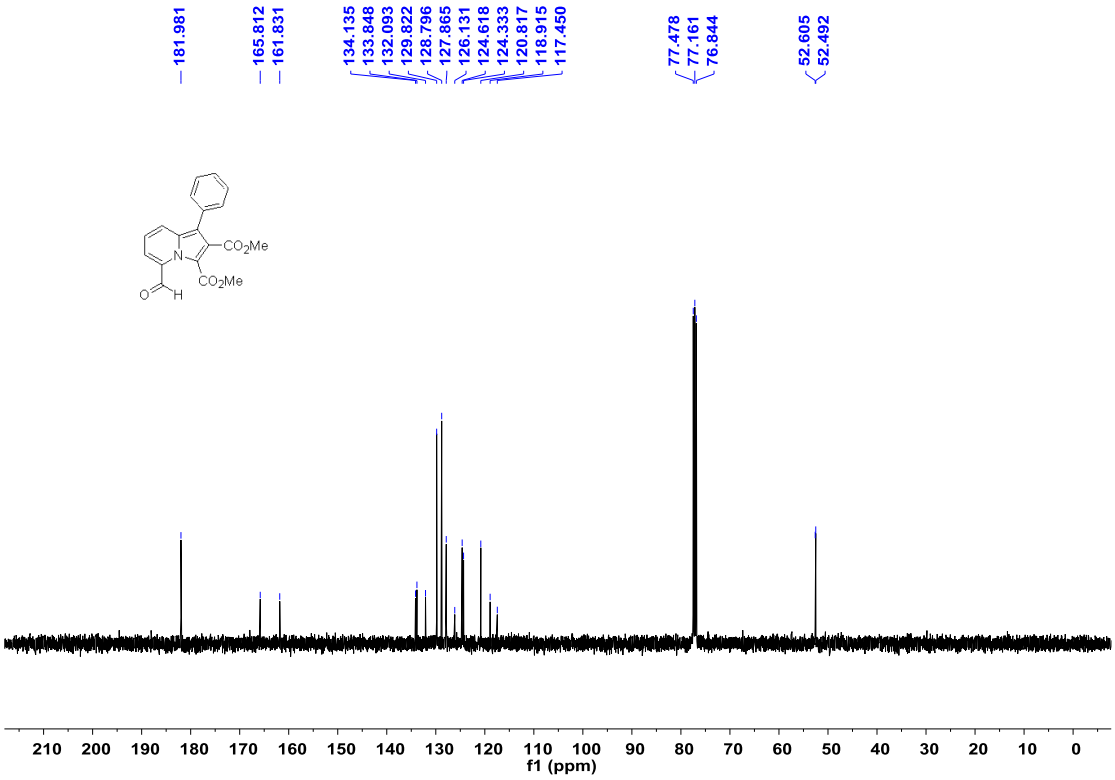

20220920-ssm-8-pos 47 (0.208)
1: TOF MS ES+
5.58e4
100
%
0
279.0319
280.0345
279.0917
281.0320
278.2523
278.3491
278.7274
278.9301
279.1585
279.6347
279.9839
280.2618
280.4066
280.6590
280.9333
281.1341
281.2459
281.5157
281.7121
282.0319
279
280
281
282
m/z

Dimethyl 5-formyl-1-phenyl-1,8a-dihydroindolizine-2,3-dicarboxylate (8)

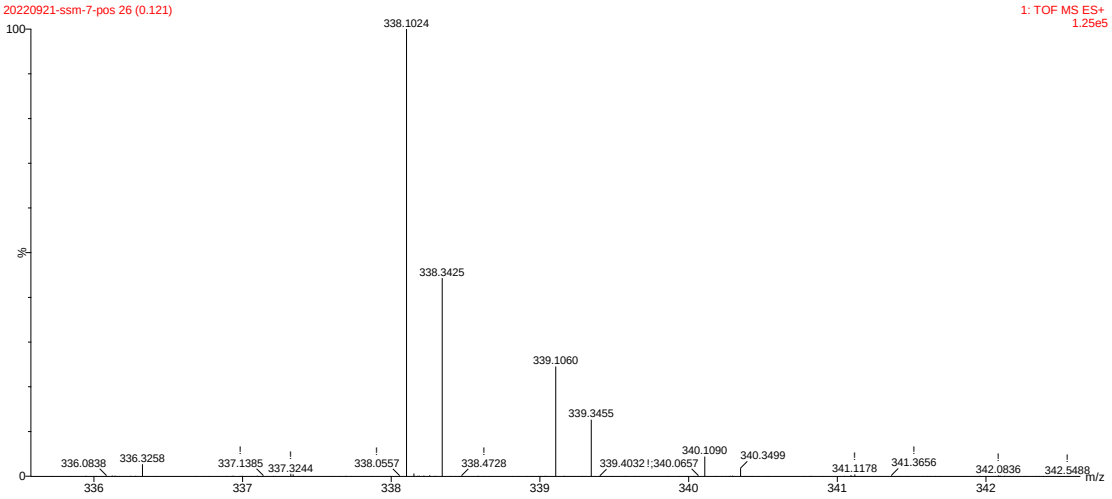
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)

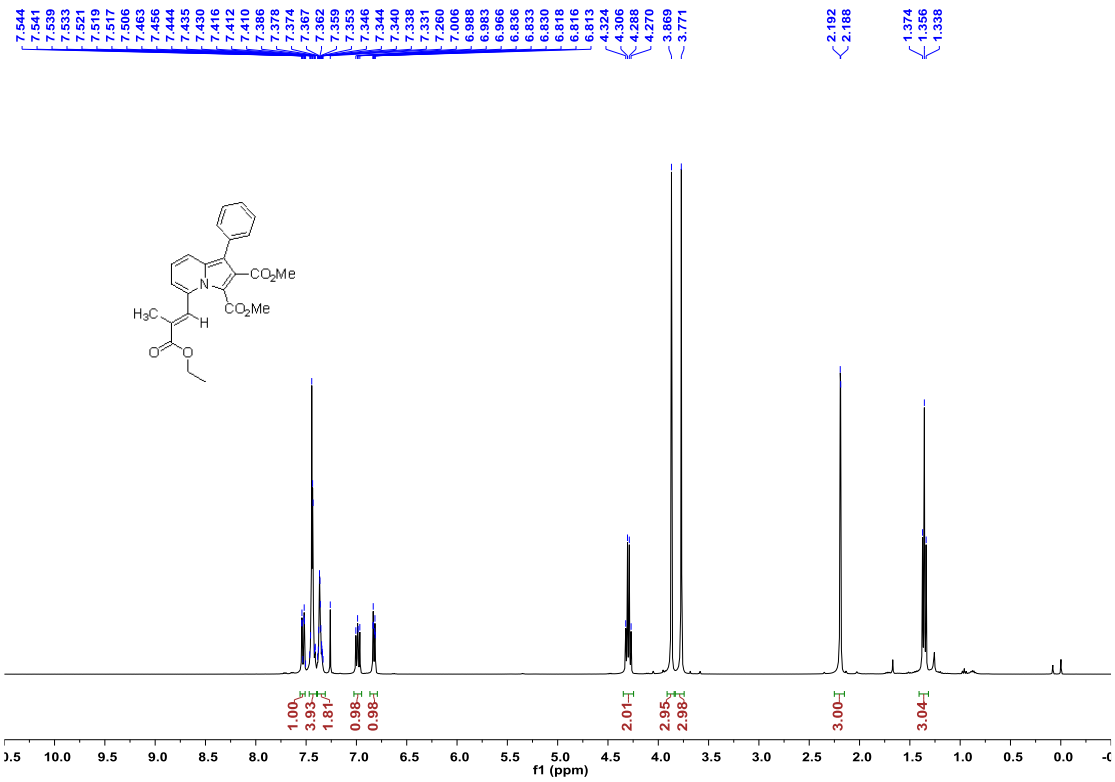


HRMS

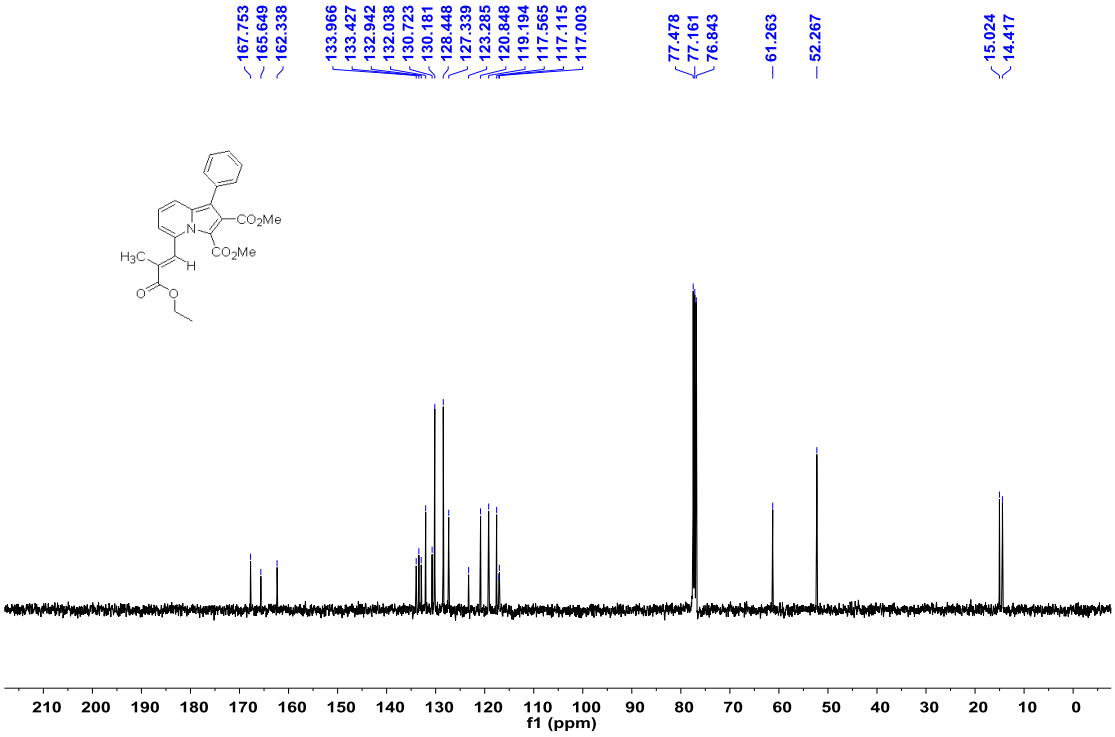

20220921-ssm-7-pos 26 (0.121)
1: TOF MS ES+
1.25e5
100
%
0
338.1024
338.3425
339.1060
339.3455
336.0838
336.3258
337.1385
337.3244
338.0557
338.4728
339.4032
340.0657
340.1090
340.3499
341.1178
341.3656
342.0836
342.5488
336
337
338
339
340
341
342
m/z

Dimethyl (*E*)-5-(3-ethoxy-2-methyl-3-oxoprop-1-en-1-yl)-1-phenylindolizine-2,3-dicarboxylate (9)

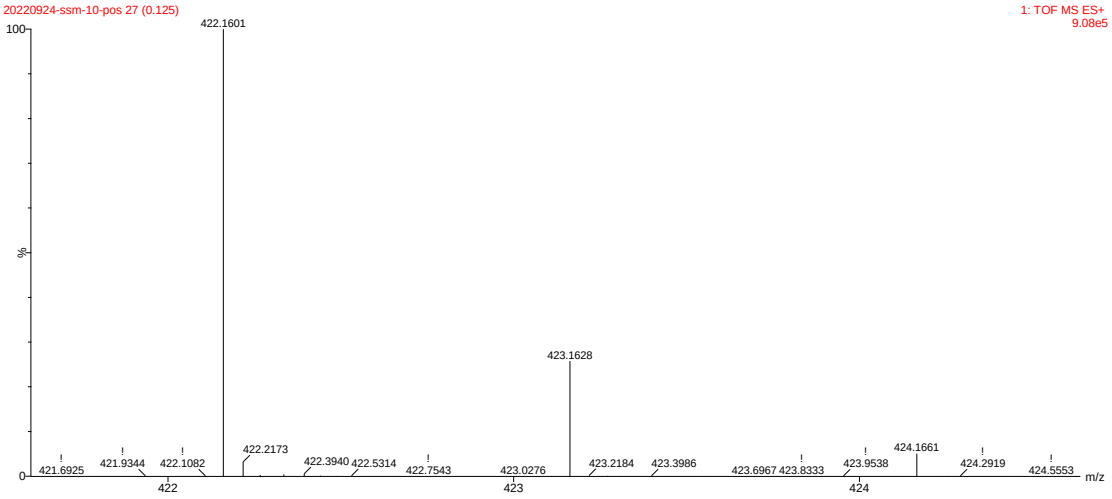
^{1}H NMR (400MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



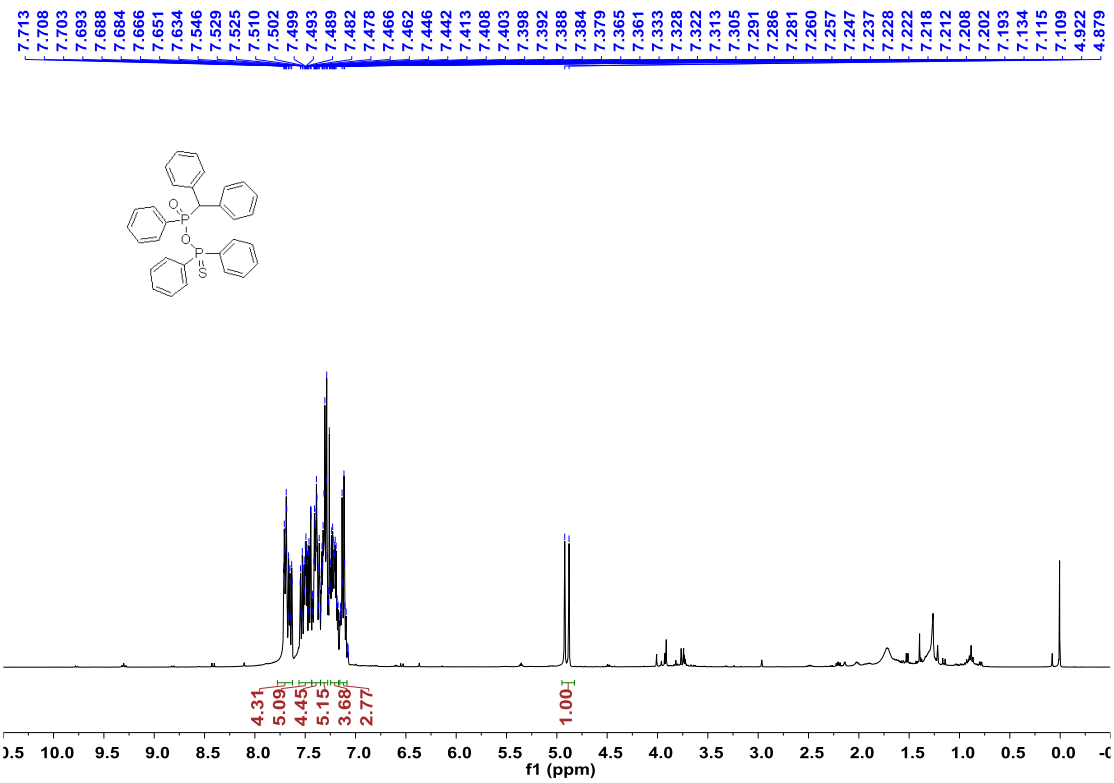
HRMS


20220924-ssm-10-pos 27 (0.125)
1: TOF MS ES+
9.08e5
100
%
0
422.1601
423.1628
424.1661
421.6925
421.9344
422.1082
422.2173
422.3940
422.5314
422.7543
423.0276
423.2184
423.3986
423.6967
423.8333
423.9538
424.2919
424.5553
422
423
424
m/z

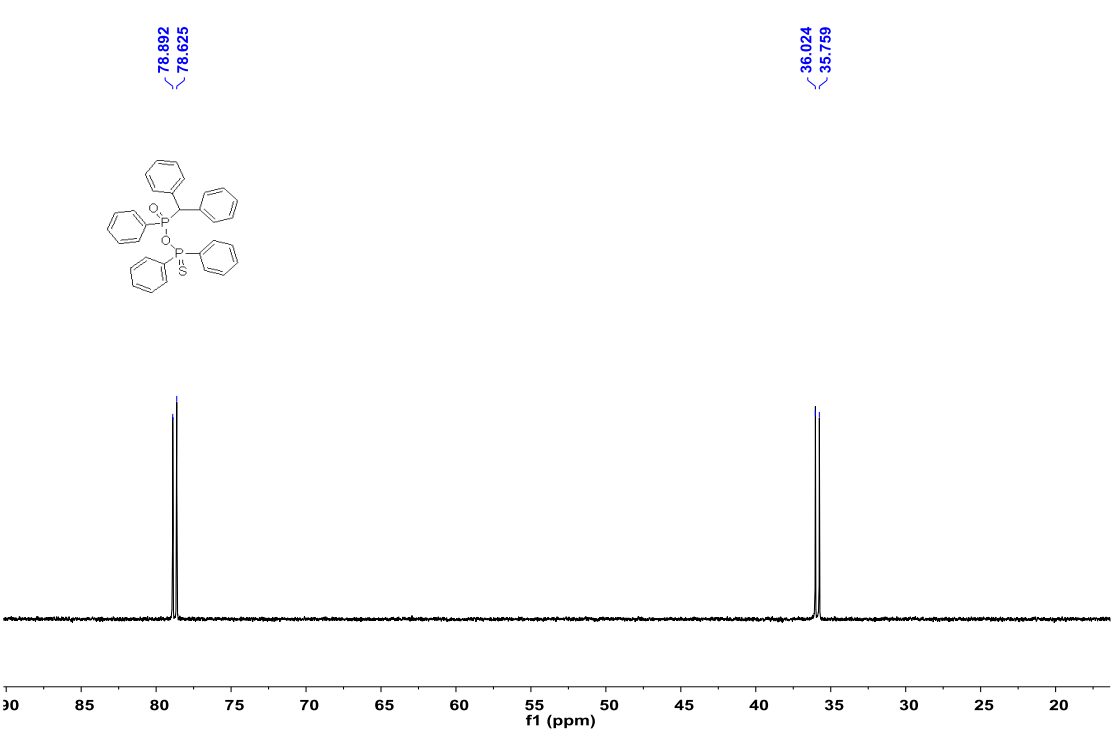
4.6. Copies of ^{1}H, ^{13}C NMR and HRMS Spectra of Control Experiments

Benzhydryl(phenyl)phosphinic diphenylphosphinothioic anhydride (6)

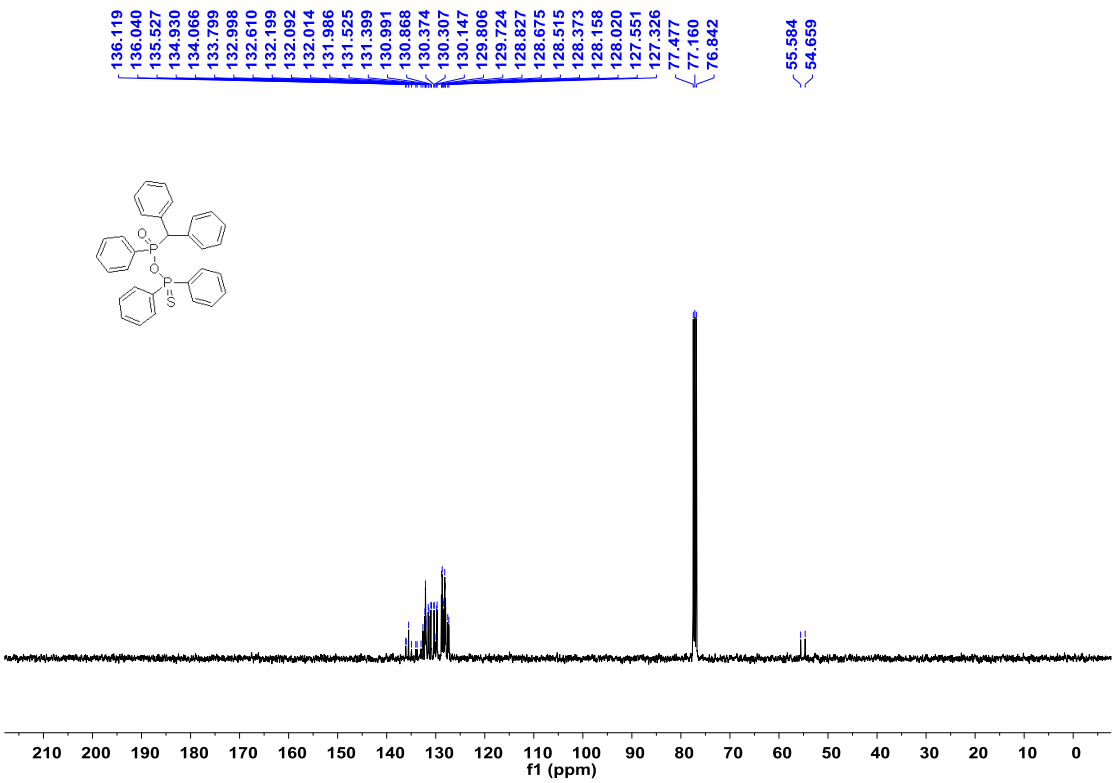
^{1}H NMR (400MHz, $CDCl_3$)



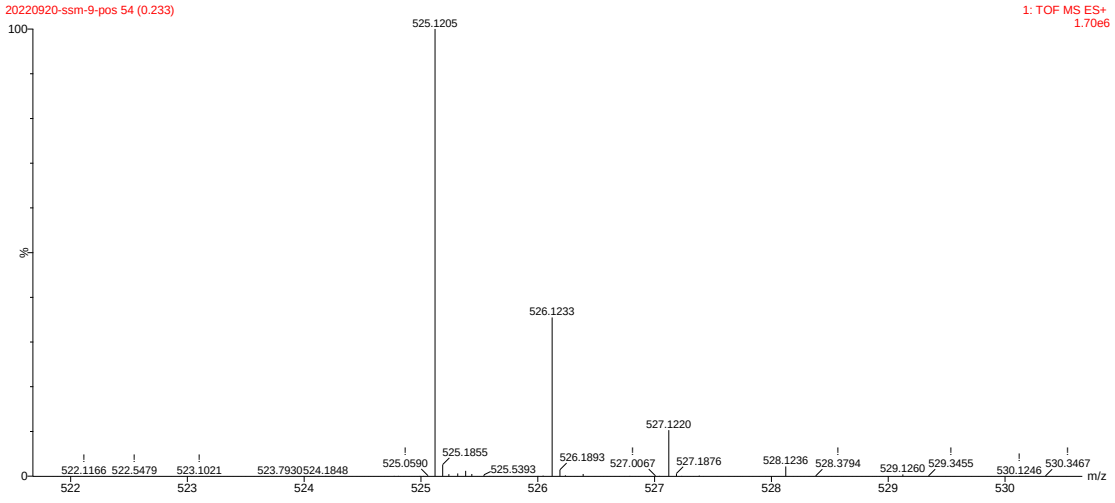
^{31}P NMR (162 MHz, $CDCl_3$)



^{13}C NMR (101MHz, $CDCl_3$)



HRMS



5. X-Ray Crystallographic Data of 3aa and 4ag

5.1. X-Ray Crystallographic Data of 3aa

Experimental

Single crystals of $C_{25}H_{21}O_5PS$ [**3aa**] were recrystallized from dichloromethane and diethyl ether. One crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal Structure Determination of 3aa

Crystal Data. $C_{25}H_{21}O_5PS$, M=464.45, monoclinic, a = 9.9928(5) Å, b = 17.2209(6) Å, c = 13.4103(5) Å, β = 105.451(4)°, U = 2224.31(16) Å^3, T = 114.85(10), space group $P2_1/c$ (no. 14), Z = 4, μ(Mo Kα) = 0.253, 18570 reflections measured, 4339 unique (R_{int} = 0.0643) which were used in all calculations. The final $wR(F_2)$ was 0.1054 (all data)

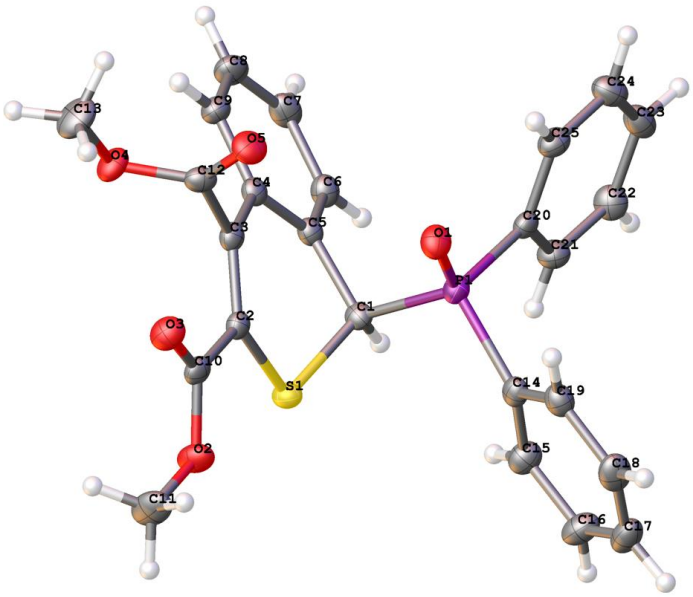


Figure S1. X-Ray Structure of 3aa (50% probability)

Table S1: Crystal Data and Structure Refinement for 3aa

Identification code	exp_7669
Empirical formula	$C_{25}H_{21}O_5PS$
Formula weight	464.45
Temperature / K	114.85(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a / Å, b / Å, c / Å	9.9928(5), 17.2209(6), 13.4103(5)
α/°, β/°, γ/°	90.00, 105.451(4), 90.00
Volume / Å^3	2224.31(16)
Z	4
ρ_{calc} / mg mm^{-3}	1.387
μ / mm^{-1}	0.253
F(000)	968
Crystal size / mm^3	0.38 × 0.21 × 0.19
2Θ range for data collection	6.3 to 52°
Index ranges	-12 ≤ h ≤ 10, -21 ≤ k ≤ 21, -16 ≤ l ≤ 16
Reflections collected	18570
Independent reflections	4339[R(int) = 0.0643 (inf-0.9Å)]
Data/restraints/parameters	4339/0/291
Goodness-of-fit on F^2	1.048
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0458, wR_2 = 0.0935
Final R indexes [all data]	R_1 = 0.0684, wR_2 = 0.1054
Largest diff. peak/hole / e Å^{-3}	0.400/-0.357
Flack Parameters	N
Completeness	0.9976

5.2. X-Ray Crystallographic Data of 4ag

Experimental

Single crystals of $C_{19}H_{17}NO_4PS$ [**4ag**] were recrystallized from petroleum ether (60–90 °C fraction) and ethyl acetate. One crystal was mounted in inert oil and transferred to the cold gas stream of the diffractometer.

Crystal Structure Determination of 4ag

Crystal Data. $C_{19}H_{17}NO_4$, M = 323.34, orthorhombic, a = 38.4079(16) Å, b = 10.3454(5) Å, c = 7.9044(4) Å, U = 3140.8(2) Å^3, T = 112.85(10), space group Pbca (no. 61), Z = 8, μ(Mo Kα) = 0.096, 12029 reflections measured, 3052 unique (R_{int} = 0.0496) which were used in all calculations. The final $wR(F_2)$ was 0.1135 (all data).

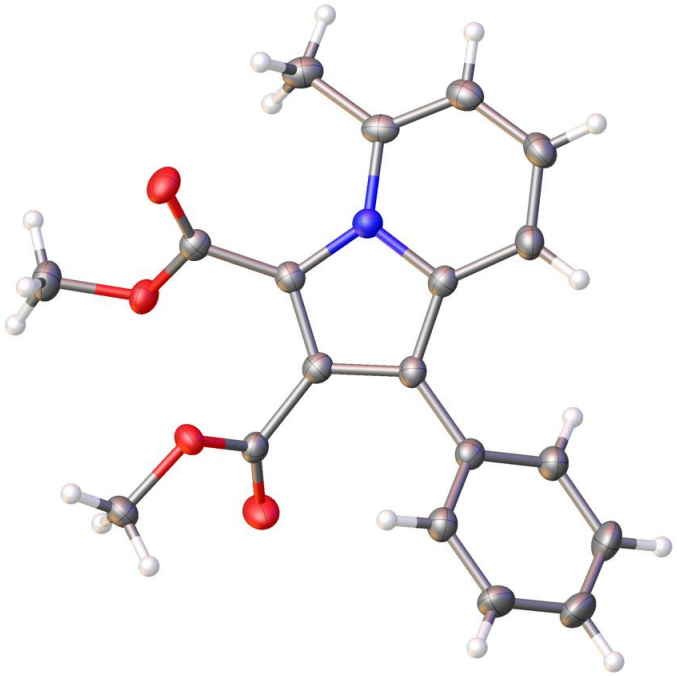


Figure S2. X-Ray Structure of 4ag (50% probability)

Table S2: Crystal Data and Structure Refinement for 4ag

Table 1: Crystal data and structure refinement for exp_8106

Identification code	exp_8106
Empirical formula	$C_{19}H_{17}NO_4$
Formula weight	323.34
Temperature / K	112.85(10)
Crystal system	orthorhombic
Space group	Pbca
a / Å, b / Å, c / Å	38.4079(16), 10.3454(5), 7.9044(4)
α/°, β/°, γ/°	90.00, 90.00, 90.00
Volume / Å^3	3140.8(2)
Z	8
ρ_{calc} / mg mm^{-3}	1.368
μ / mm^{-1}	0.096
F(000)	1360
Crystal size / mm^3	0.24 × 0.23 × 0.22
2Θ range for data collection	6.58 to 52°
Index ranges	-34 ≤ h ≤ 46, -10 ≤ k ≤ 12, -9 ≤ l ≤ 8
Reflections collected	12029
Independent reflections	3052[R(int) = 0.0496 (inf-0.9Å)]
Data/restraints/parameters	3052/0/220
Goodness-of-fit on F^2	1.084
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0496, wR_2 = 0.1021
Final R indexes [all data]	R_1 = 0.0676, wR_2 = 0.1135
Largest diff. peak/hole / e Å^{-3}	0.212/-0.216
Flack Parameters	N
Completeness	0.9936