Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Sulfur-Controlled and Rhodium-Catalyzed Formal (3 + 3) Transannulation of Thioacyl Carbenes with Alk-2-enals and Mechanistic Insights

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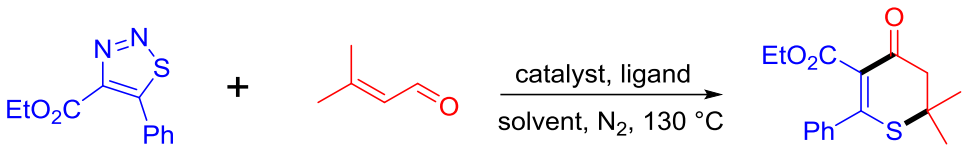
Contents

1. General Information

Unless otherwise noted, all starting materials were purchased from commercial suppliers. Chlorobenzene and acetonitrile were refluxed over CaH_2 and freshly distilled prior to use. Tetrahydrofuran was refluxed over $LiAlH_4$ and freshly distilled prior to use. Toluene was refluxed over Na and freshly distilled prior to use. Column chromatography was performed using silica gel (normal phase, 200–300 mesh) from branch of Anhui Liangchen Silicon Material Co. Ltd, with petroleum ether (60–90 °C fraction), hexane, methylene chloride and ethyl acetate as eluents. Reactions were monitored by thin-layer chromatography (TLC) on GF254 silica gel plates (0.2 mm) from Anhui Liangchen Silicon Material Co. Ltd. The plates were visualized under UV light, as well as other TLC stains (1% potassium permanganate in water; 10 g of iodine absorbed on 30 g of silica gel; 12 g 2,4-dinitrophenylhydrazine dissolved in 60 mL of H_2SO_4 and 80 mL H_2O in 200 mL 95% EtOH.). ^1H, ^{19}F, and $^{13}C\{^1H\}$ NMR spectra were recorded on a 400 MHz spectrometer, usually in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) are reported in parts per million (ppm). And multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplet). Coupling constants (J) are reported in Hertz (Hz). HRMS measurements were carried out on an LC/MSD TOF mass spectrometer. The IR spectra (film, ν [cm^{-1}]) were taken on an FT IR spectrometer. Melting points were obtained on a melting point apparatus and are uncorrected. Single crystal X-ray diffraction analysis (**3aa**) was performed on a single crystal X-ray diffractometer. The enantiomeric excesses were determined by chiral HPLC analysis using an Agilent 1260 LC instrument with Daicel Chiralpak AS-H column with a mixture of isopropyl alcohol and hexane as eluents. PE, EA, PhCl, DCM, MeOH, Et_2O and THF are abbreviated for petroleum ether, ethyl acetate, chlorobenzene, methylene chloride, methanol, diethyl ether and tetrahydrofuran, respectively.

Compounds **3aa**, **3ag**, **3aq**, **3au**, **3av**, **3aw**, **3ax**, **3az**, **3aaa** and **3aab** were reported in our previous work.[1] For their analytical data and spectra, and those of the alkenals (**2q**, **2u**, **2v**, **2w**, **2x**, **2z**, **2aa**, and **2ab**), please see the supporting information of our previous publications.[1]

2. Detailed Optimizations on the Reaction Conditions



1a **2a** **3aa**

Table S1. Optimization of reaction conditions[a]

Entry	Catalyst (mol%)	Ligand (mol%)	Solvent	Yield[b](%)
1	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhCl	72
2	$[Rh(COD)Cl]_2$ (5)	—	PhCl	trace
3	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhCl	trace[c]
4	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhCl	3[d]
5	$[Rh(COD)Cl]_2$ (5)	DPPM (12)	PhCl	trace
6	$[Rh(COD)Cl]_2$ (5)	DPPE (12)	PhCl	6
7	$[Rh(COD)Cl]_2$ (5)	DPPP (12)	PhCl	8
8	$[Rh(COD)Cl]_2$ (5)	DPPB (12)	PhCl	15
9	$[Rh(COD)Cl]_2$ (5)	DPPPenta (12)	PhCl	3
10	$[RhCp^*Cl_2]_2$ (5)	DPPF (12)	PhCl	63
11	$[RhCp^*Cl_2]_2$ (5)	DPPE (12)	PhCl	trace
12	$[RhCp^*Cl_2]_2$ (5)	DPPP (12)	PhCl	8
13	$[RhCp^*Cl_2]_2$ (5)	DPPB (12)	PhCl	7
14	$[RhCp^*Cl_2]_2$ (5)	DPPPenta (12)	PhCl	1
15	$[Rh(COD)Cl]_2$ (5)	PPh_3 (24)	PhCl	trace
16	$[Rh(COD)Cl]_2$ (5)	Triphenyl phosphorus oxychloride (24)	PhCl	trace
17	$[Rh(COD)Cl]_2$ (5)	Triethyl phosphite (24)	PhCl	trace
18	$[Rh(COD)Cl]_2$ (5)	Triphenyl phosphite (24)	PhCl	trace
19	$[Rh(COD)Cl]_2$ (5)	Triphenyl phosphate (24)	PhCl	trace
20	$[Rh(COD)Cl]_2$ (5)	Triethyl phosphate (24)	PhCl	trace
21	$[Rh(COD)Cl]_2$ (5)	Tris(4-trifluoromethylphenyl) phosphine (24)	PhCl	trace
22	$[Rh(COD)Cl]_2$ (5)	Tris(pentafluorophenyl)phosphine (24)	PhCl	trace
23	$[Rh(COD)Cl]_2$ (5)	DPPF (12)	PhMe	54

[a] Reaction was carried out with 1,2,3-thiadiazole **1a** (0.25 mmol) and 3-methyl-2-butenal (**2a**) (0.5 mmol) in the presence of 1.0 mL of solvent for 6 h.

[b] Yield of the isolated product.

[c] Reaction was carried out at 50 °C.

[d] Reaction was carried out at 100 °C.

3. Crystal Data and Structure of Ethyl 2,2-Dimethyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (3aa)

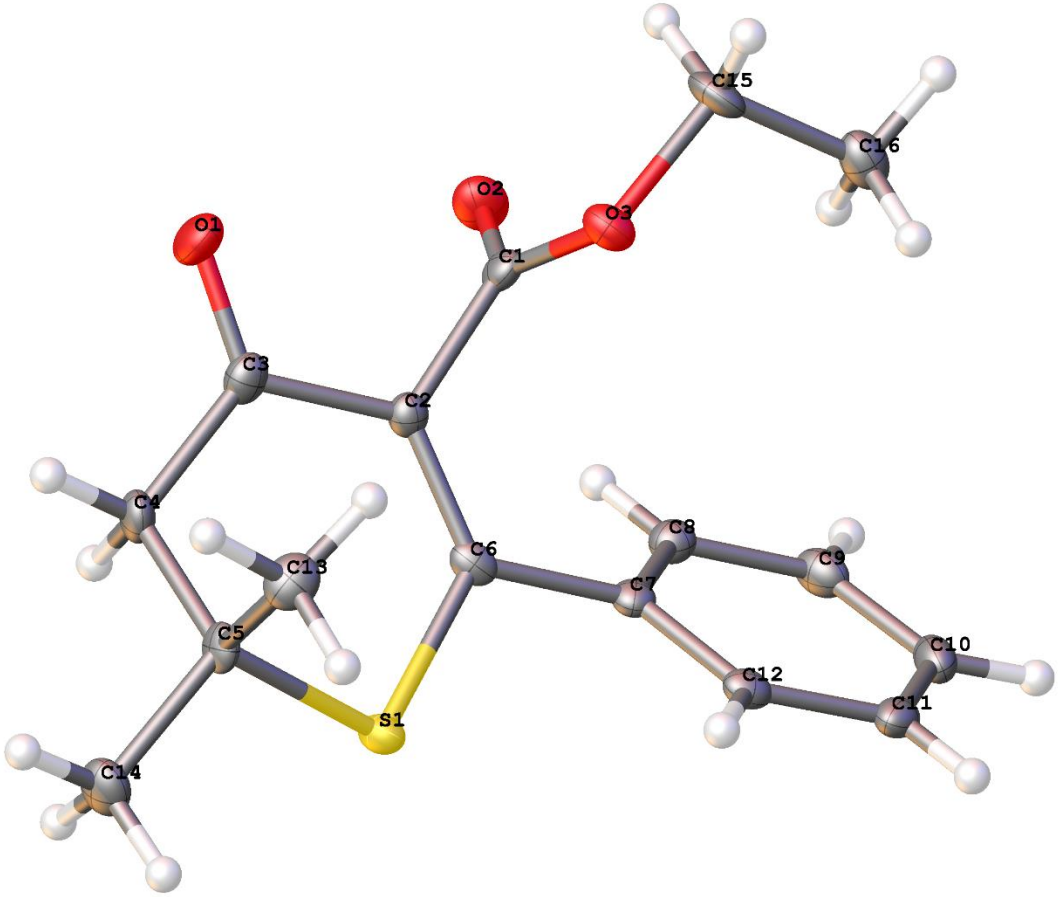


Figure S1. Thermal ellipsoid plot for the crystal structure of **3aa** (at 50% probability level)

Experimental

Single crystals of $C_{16}H_{18}O_3S$ (**3aa**) were recrystallized from diethyl ether, mounted in inert oil, and transferred to the cold gas stream of the diffractometer.

The X-ray intensity data were measured at 105.6 K, on an Agilent Gemini E single crystal X-ray diffractometer. The crystal data of **3aa** has been deposited in CCDC with number 1919688.

Crystal structure determination of 3aa

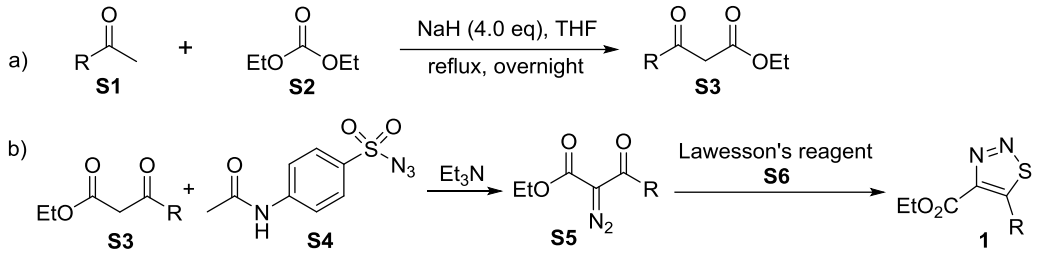
Crystal Data. $C_{16}H_{18}O_3S$, M =290.36, monoclinic, a = 17.860(3) Å, b = 8.4885(4) Å, c = 14.325(2) Å, β = 136.68(3)°, U = 1489.9(7) Å^3, T = 105.6, space group Cc (no. 9), Z = 4, μ (Cu Kα) = 1.968, 2624 reflections measured, 1579 unique (R_{int} = 0.0190) which were used in all calculations. The final $wR(F_2)$ was 0.0755 (all data).

Table S2. Crystal data and structure refinement for **3aa**

Identification code	exp_5184
Empirical formula	$C_{16}H_{18}O_3S$
Formula weight	290.36
Temperature / K	105.6
Crystal system	monoclinic
Space group	Cc
a / Å, b / Å, c / Å	17.860(3), 8.4885(4), 14.325(2)
α/°, β/°, γ/°	90, 136.68(3), 90
Volume / Å^3	1489.9(7)
Z	4
ρ_{calc} / mg mm^{-3}	1.294
μ / mm^{-1}	1.968
F(000)	616
Crystal size / mm^3	0.150 × 0.140 × 0.130
2Θ range for data collection	12.138 to 142.142°
Index ranges	-19 ≤ h ≤ 21, -9 ≤ k ≤ 10, -16 ≤ l ≤ 17
Reflections collected	2624
Independent reflections	1579[R(int) = 0.0190 (inf-0.9Å)]
Data/restraints/parameters	1579/2/184
Goodness-of-fit on F^2	1.082
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0287, wR_2 = 0.0753
Final R indexes [all data]	R_1 = 0.0289, wR_2 = 0.0755
Largest diff. peak/hole / e Å^{-3}	0.227/-0.254
Flack Parameters	0.031(18)
Completeness	0.979

4. General procedure for the synthesis of thiadizaoles 1

Thiadiazoles **1a–1m** were prepared according to Gevorgyan's[2] and Lee's[3] published procedures.



a) An oven-dried 100-mL flask were charged with a stirrer bar, NaH (60% in mineral oil, 1.60 g, 40 mmol), dry THF (25 mL), and diethyl carbonate (**S2**) (4.85 mL, 40 mmol) successively. To the mixture was added a solution of ketone **S1** (10 mmol) in dry THF (15 mL) in 5 min under stirring at 0 °C. After warming up to room temperature, a spherical condenser was put on the flask. The reaction mixture was refluxed overnight, then quenched with 1 M HCl (30 mL) under stirring at 0 °C. When there was no bubble released, solvent THF was removed in vacuo. The mixture was added water (20 mL), and then extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was purified by flash chromatography (silica gel, PE:EA 20:1 to 5:1, *v*/*v*), affording the corresponding *β*-keto ester **S3**.

b) In a flask, the above prepared *β*-keto ester **S3** (10 mmol) and 4-acetamidobenzenesulfonyl azide (**S4**) (2.64 g, 11 mmol) were dissolved in acetonitrile (60 mL). Triethylamine (3.05 g, 30 mmol) was slowly added at 0 °C. The reaction mixture was stirred at room temperature overnight. After removal of the solvent by rotary evaporation, the resulting residue was purified by column chromatography (PE/EA = 3:1, *v/v*) to give ethyl 2-diazo-3-oxo-3-arylpropanoate **S5**. The diazo compound **S5** was then dissolved in toluene (50 mL), followed by addition of Lawesson's reagent (**S6**) (4.85 g, 12 mmol). The mixture was heated at reflux for 4 h. After the reaction was completed, the solvent was removed by rotary evaporation, and the resulting residue was purified by silica gel column chromatography (PE/EA = 10:1 to 20:1 or DCM/MeOH = 100:1, *v/v*) to afford ethyl 5-aryl-1,2,3-thiadiazole-4-carboxylate **1**.

All the thiodiazoles **1** are known compounds. For those without published spectra data, IR and HRMS data are also provided here.

Ethyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1a**) [2,3] [CAS No. 60474-27-3]
Yellow solid, 2.06 g, 88% yield over the last two steps, m.p. 36–37 °C, R_f = 0.45 (PE/EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.55 – 7.44 (m, 5H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 161.9, 160.4, 148.4, 130.6, 129.7, 128.6, 126.1, 62.0, 14.0.

Ethyl 5-(benzo[*d*][1,3]dioxol-5-yl)-1,2,3-thiadiazole-4-carboxylate (**1b**)[3a] [CAS No. 2022219-62-9]

Pale yellow solid, 2.13 g, 77% yield over three steps, m.p. 81–82 °C (Lit.[3a] 84–86 °C), R_f = 0.5 (PE/EA = 3:1, *v*/*v*), R_f = 0.5 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 – 7.01 (m, 2H), 6.89 (dd, *J* = 7.9, 0.6 Hz, 1H), 6.06 (s, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 161.9, 160.6, 149.9, 148.0, 147.9, 124.6, 119.2, 110.0, 108.5, 101.9, 62.1, 14.1.

Ethyl 5-(4-methoxyphenyl)-1,2,3-thiadiazole-4-carboxylate (**1c**) [3b] [CAS No. 2010973-32-5]
Pale yellow solid, 2.05 g, 78% yield over three steps, m.p. 49–50 °C (Lit.[3b] 50–52 °C), R_f = 0.3 (PE/EA = 5:1, *v*/*v*), R_f = 0.45 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 162.1, 161.6, 160.7, 147.6, 131.4, 117.9, 114.1, 62.0, 55.4, 14.1.

Ethyl 5-(4-methylphenyl)-1,2,3-thiadiazole-4-carboxylate (**1d**) [3b] [CAS No. 340260-34-6]
Yellow solid, 1.41 g, 57% yield over three steps, m.p. 46–47 °C (Lit.[3b] 44–46 °C), R_f = 0.3 (PE/EA = 15:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 2.41 (s, 3H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 162.2, 160.5, 148.1, 141.1, 129.6, 129.3, 123.0, 62.0, 21.4, 14.1.

Ethyl 5-(4-fluorophenyl)-1,2,3-thiadiazole-4-carboxylate (**1e**) [1] [CAS No. 2111487-42-2]
White solid, 2.05 g, 81% yield over three steps, m.p. 67–69 °C, R_f = 0.45 (PE/EA = 5:1, *v*/*v*), R_f = 0.55 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.50 (m, 2H), 7.17 (t, *J* = 8.5 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 164.1 (d, $J_{C\text{-}F}$ = 253.5 Hz), 160.9, 160.4, 148.4, 131.9 (d, $J_{C\text{-}F}$ = 7.1 Hz), 122.0 (d, $J_{C\text{-}F}$ = 3.0 Hz), 115.9 (d, $J_{C\text{-}F}$ = 22.2 Hz), 62.2, 14.1. ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ -109.0 (s). IR (film) 2981, 2922, 2359, 2341, 1730, 1684, 1653, 1635, 1601, 1558, 1540, 1520, 1507, 1474, 1457, 1418, 1395, 1371, 1324, 1272, 1236, 1187, 1161, 1132, 1096, 1075, 1052, 1018, 985, 848, 815, 785, 755, 696, 668, 566, 525 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{11}H_{10}FN_2O_2S^+$ 253.0442, found 253.0445.

Ethyl 5-(4-chlorophenyl)-1,2,3-thiadiazole-4-carboxylate (**1f**) [1] [CAS No. 340260-35-7]
White solid, 73% yield over three steps, m.p. 74–75 °C, R_f = 0.45 (PE/EA = 5:1, *v*/*v*), R_f = 0.55 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50–7.41 (m, 4H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 160.6, 160.2, 148.4, 137.0, 131.0, 128.9, 124.4, 62.2, 14.0. IR (film) 2980, 2359, 2341, 1727, 1653, 1592, 1558, 1540, 1507, 1473, 1457, 1399, 1372, 1338, 1272, 1195, 1184, 1092, 1016, 986, 848, 837, 776, 668, 655, 555, 522, 510, 474 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{11}H_{10}ClN_2O_3S^+$ 269.0146, found 269.0145.

Ethyl 5-(3,4-dichlorophenyl)-1,2,3-thiadiazole-4-carboxylate (**1g**) [1] [CAS No. 2342602-62-2]
White solid, 2.25 g, 74% over three steps, m.p. 75–77 °C, R_f = 0.45 (PE/EA = 5:1, *v*/*v*), R_f = 0.45 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 2.2 Hz, 1H),

7.56 (d, *J* = 8.3 Hz, 1H), 7.37 (dd, *J* = 8.3, 2.2 Hz, 1H), 4.44 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 160.0, 159.1, 148.7, 135.2, 133.1, 131.5, 130.6, 129.0, 125.9, 62.4, 14.1. IR (film) 2923, 2359, 2341, 1732, 1718, 1699, 1683, 1652, 1636, 1558, 1541, 1520, 1507, 1489, 1473, 1457, 1436, 1418, 1373, 1321, 1274, 1194, 1132, 1051, 1032, 1015, 971, 847, 680, 555 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{11}H_9Cl_2N_2O_2S^+$ 302.9756, found 302.9751.

Ethyl 5-(4-iodophenyl)-1,2,3-thiadiazole-4-carboxylate (**1h**) [1] [CAS No. 2342602-61-1]
White solid, 2.80 g, 78% yield over three steps, m.p. 149–151 °C, R_f = 0.5 (PE/EA = 5:1, *v*/*v*), R_f = 0.6 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85–7.80 (m, 2H), 7.30–7.25 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 160.8, 160.2, 148.4, 137.8, 131.2, 125.5, 97.2, 62.2, 14.1. IR (film) 2973, 2921, 2358, 2341, 1718, 1684, 1652, 1636, 1577, 1558, 1540, 1520, 1507, 1471, 1457, 1418, 1393, 1369, 1336, 1271, 1193, 1131, 1076, 1056, 1010, 980, 846, 826, 776, 669, 654, 556, 519, 499, 419 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{11}H_{10}IN_2O_2S^+$ 360.9502, found 360.9504.

Ethyl 5-(4-(trifluoromethyl)phenyl)-1,2,3-thiadiazole-4-carboxylate (**1i**) [1] [CAS No. 2342602-63-3]
Brown solid, 2.19 g, 72% yield over three steps, m.p. 29–31 °C, R_f = 0.45 (PE/EA = 5:1, *v*/*v*), R_f = 0.45 (DCM/MeOH = 100:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 2H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 160.10, 160.05, 148.9, 132.5 (q, $J_{C\text{-}F}$ = 33.3 Hz), 130.2, 129.9, 125.5 (q, $J_{C\text{-}F}$ = 4.0 Hz), 123.5 (q, $J_{C\text{-}F}$ = 273.7 Hz), 62.3, 14.0. ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) *δ* -63.05 (s).IR (film) 2984, 2359, 1732, 1684, 1653, 1617, 1558, 1507, 1487, 1457, 1409, 1373, 1325, 1274, 1169, 1130, 1068, 1019, 985, 849, 787, 687, 577 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{12}H_{10}F_3N_2O_2S^+$ 303.0410, found 303.0410.

Ethyl 5-(4-cyanophenyl)-1,2,3-thiadiazole-4-carboxylate (**1j**) [3a] [CAS No. 2022219-64-1]
Pale brown solid, 1.54 g, 59% yield over three steps, m.p. 108–110 °C, R_f = 0.4 (PE/EA = 3:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.78 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 159.9, 159.5, 149.0, 132.2, 131.0, 130.5, 117.8, 114.4, 62.5, 14.1.

Ethyl 5-(furan-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1k**) [3a] [CAS No. 2022219-65-2]
Brown solid, 1.47 g, 67%, yield over three steps, m.p. 109–110 °C, R_f = 0.55 (PE/EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.81 (dd, *J* = 3.7, 0.7 Hz, 1H), 7.60 (dd, *J* = 1.9, 0.8 Hz, 1H), 6.59 (dd, *J* = 3.7, 1.8 Hz, 1H), 4.52 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 160.7, 150.5, 146.5, 144.8, 143.0, 117.1, 113.3, 62.1, 14.2.

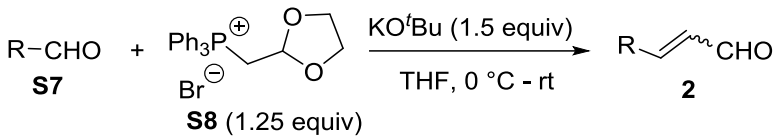
Ethyl 5-(thiophen-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1l**) [3a] [CAS No. 2010973-34-7]
Brown solid, 2.13 g, 89% yield over three steps, m.p. 96–97 °C, R_f = 0.3 (PE/EA = 10:1, *v*/*v*), R_f = 0.40 (DCM/MeOH = 200:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.68 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.59 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.12 (dd, *J* = 5.2, 3.8 Hz, 1H), 4.49 (q, *J* = 7.1

Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 160.7, 155.0, 146.2, 133.1, 131.8, 128.2, 125.9, 62.2, 14.1

Ethyl 5-(naphthalen-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1m**) [1] [CAS No. 2342602-64-4]
Brown solid, 1.47 g, 66% yield over three steps, m.p. 50–52 °C, R_f = 0.4 (PE/EA = 10:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.00–7.97 (m, 1H), 7.90–7.82 (m, 3H), 7.55–7.51 (m, 3H), 4.43–4.36 (m, 2H), 1.31–1.26 (m, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 161.8, 160.2, 148.2, 133.6, 132.4, 129.7, 128.2, 128.1, 127.6, 127.6, 126.9, 126.3, 123.2, 61.9, 13.9. IR (film) 2979, 2924, 2359, 2342, 1731, 1684, 1653, 1636, 1597, 1558, 1541, 1507, 1490, 1473, 1457, 1371, 1320, 1273, 1243, 1195, 1178, 1130, 1076, 1019, 963, 861, 816, 785, 747, 556, 475 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{15}H_{13}N_2O_2S^+$ 285.0692, found 285.0690.

5. General procedure for the synthesis of alk-2-enals 2

Alk-2-enals **2j**, **2l**, **2m**, **2n**, **2o**, **2p** were synthesized according to Christmann's procedure.[4a]



To an oven-dried flask with a stirrer bar was added (1,3-dioxolan-2-ylmethyl) triphenylphosphonium bromide (**S8**) (1.08 g, 2.5 mmol). The vial was sealed with a nitrogen gas balloon and cooled to 0 °C, after which dry THF (7 mL) and KO^{t}Bu (1 M in THF, 3 mL, 3 mmol) were added until the suspension turned a deep yellow color. After 30 min, a solution of aldehyde **S7** (2 mmol) in dry THF (5 mL) was added. The reaction mixture was kept stirring at room temperature for 6 h. After addition of 20% aqueous oxalic acid (20 mL), the resulting solution was kept stirring for another 8 h. The mixture was extracted with EA (10 mL × 3). The combined organic phase was washed with saturated aqueous $NaHCO_3$ and dried over Na_2SO_4. After concentrated *in vacuo*, the resulting residue was purified by silica gel column chromatography with a mixture of PE and EA as eluent to give alk-2-enal **2**.

(*E*)-3-(2,3-Dichlorophenyl)propenal (**2j**)[4b] [CAS No. 78444-18-5]
White solid, 334 mg, 83% yield, m.p. 95–97 °C (Lit.[23b] 94–95 °C), R_f = 0.3 (PE/EA = 10:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.78 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 16.0 Hz, 1H), 7.58–7.53 (m, 2H), 7.30–7.26 (m, 1H), 6.69 (dd, *J* = 16.0, 7.6 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 193.2, 147.7, 134.4, 134.3, 133.2, 132.4, 131.6, 127.6, 126.0.

(*E*)-3-(Naphthalen-2-yl)propenal (**2l**)[4c] [CAS No. 113388-98-0]
Colorless solid, 346 mg, 38 % yield (from 5 mmol scale reaction), m.p. 124–126 °C (Lit.[23c] 125–126 °C), R_f = 0.6 (PE/EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 9.77 (d, *J* = 7.7 Hz, 1H), 8.02–7.98 (m, 1H), 7.91–7.85 (m, 3H), 7.71–7.61 (m, 2H), 7.59–7.51 (m, 2H), 6.84 (dd, *J* = 15.9, 7.7 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 193.7, 152.8, 134.7, 133.2, 131.6, 130.7, 130.0, 128.8, 128.7, 127.9, 127.8, 127.0, 123.5.

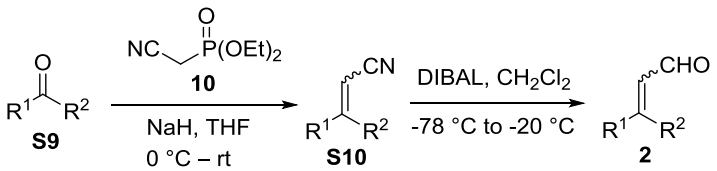
(*E*)-5-Phenylpenta-2,4-dienal (**2m**)[4d] [CAS No. 24163-63-1]
Brown oil, 270 mg, 85% yield, R_f = 0.3 (PE/EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.62 (d, *J* = 8.0 Hz, 1H), 7.53–7.47 (m, 2H), 7.41–7.33 (m, 3H), 7.30–7.22 (m, 1H), 7.03–6.98 (m, 2H), 6.27 (dd, *J* = 15.3, 7.9 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 193.5, 152.0, 142.4, 135.5, 131.6, 129.6, 128.9, 127.5, 126.1.

(*E*)-3-((1*R*,5*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-3-yl)propenal (**2n**)
Pale yellow oil, 318 mg, 90% yield, R_f = 0.6 (PE/EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.57 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 15.6 Hz, 1H), 6.19–6.17 m, 1H), 6.05 (dd, *J* = 15.6, 7.8 Hz, 1H), 2.59–2.44 (m, 4H), 2.19–2.16 (m, 1H), 1.34 (s, 3H), 1.15 (d, *J* = 9.0 Hz, 1H), 0.77 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 194.2, 153.2, 146.2, 136.8, 125.5, 41.4, 40.5, 37.8, 32.9, 31.1, 26.0, 20.7. IR (film): 2926, 2821, 1680, 1612, 1180, 1155, 1121, 1075, 1042, 1011, 969, 581 cm^{-1}; HRMS (ESI-TOF) *m/z* [M + H]$^+$ calcd. for $C_{12}H_7O^+$ 177.1274, found 177.1281.

(*E*)-3-Cyclohexylpropenal (**2o**)[4e] [CAS No. 37868-74-9]
Pale yellow oil, 196 mg, 76% yield, R_f = 0.8 (PE/EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.49 (d, *J* = 7.9 Hz, 1H), 6.77 (dd, *J* = 15.7, 6.5 Hz, 1H), 6.06 (ddd, *J* = 15.7, 7.8, 1.4 Hz, 1H), 2.31–2.22 (m, 1H), 1.87–1.74 (m, 5H), 1.37–1.15 (m, 5H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 194.5, 163.8, 130.5, 40.8, 31.5, 25.8, 25.6.

(*E*)-4-Phenylpent-2-enal (**2p**)[4f] [CAS No. 1259027-51-4]
Pale yellow oil, 225 mg, 70% yield, R_f = 0.2 (PE/EA = 20:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.55 (d, *J* = 7.8 Hz, 1H), 7.39–7.26 (m, 3H), 7.25–7.19 (m, 2H), 6.97 (dd, *J* = 15.7, 6.4 Hz, 1H), 6.13 (ddd, *J* = 15.7, 7.8, 1.5 Hz, 1H), 3.79–3.71 (m, 1H), 1.49 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 194.0, 161.7, 142.6, 131.2, 128.8, 128.1, 127.3, 127.0, 42.5, 19.9.

Alk-2-enals **2s**, **2t**,**2y**, and **12** were synthesized according to Jørgensen's procedure.[5a]



In a flask with a stirrer bar, diethyl cyanomethylphosphonate (**10**) (1.14 g, 6.43 mmol) was dissolved in 10 mL of dry tetrahydrofuran. The flask was cooled to 0 °C and sodium hydride (320 mg, 60% in mineral oil, 8 mmol) was slowly added, followed by addition of a solution of ketone **S9** (6.125 mmol) in 5 mL of dry tetrahydrofuran. The resulting solution was kept stirring under room temperature for 2 h. After the reaction was completed, the mixture was extracted with CH_2Cl_2 (10 mL × 3). The combined organic phase was washed with water (10 mL × 3) and dried over Na_2SO_4. After concentrated *in vacuo*, the resulting residue was dissolved in CH_2Cl_2 (5 mL) and DIBAL (1 M in cyclohexane, 8 mL, 8 mmol) was added dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was kept at -20 °C

for 2 h and monitored by TLC. After reaction was completed, EA (10 mL) was added to quench the remaining DIBAL. The reaction mixture was warmed up to room temperature followed by addition of another 10 mL of EA and 10 mL of saturated potassium sodium tartrate aqueous solution. The suspension was stirred vigorously for 4 ho give a biphasic mixture, which was extracted with EA (10 mL × 3). The organic layer was combined and dried over Na_2SO_4, then concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EA = 10:1~20:1, *v/v*) to give the corresponding alk-2-enal **2**.

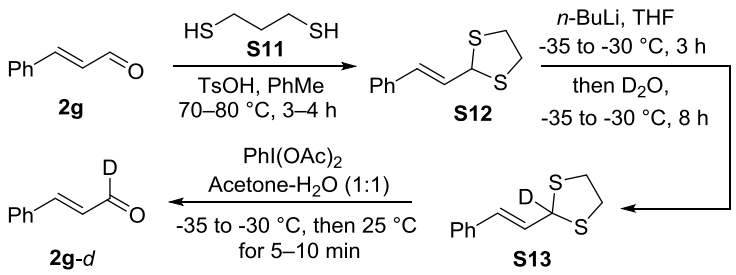
(*E*)-3-Phenylbut-2-enal (**2s**)[5b] [CAS No. 21866-70-6]
Pale yellow oil, 1.13 g, 77% yield over two steps, R_f = 0.3 (PE/EA = 10:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.18 (d, J = 7.9 Hz, 1H), 7.58–7.51 (m, 2H), 7.44–7.39 (m, 3H), 6.40 (dq, *J* = 7.9, 1.3 Hz, 1H), 2.58 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.3, 157.7, 140.5, 130.1, 128.7, 127.2, 126.2, 16.4.

3-Cyclopropylbut-2-enal (**2t**)[5c] [CAS No. 59819-87-3]
Pale yellow oil, 1.00 g, 90% yield over two steps, R_f = 0.4 (pentane/acetone = 10:1, *v*/*v*), *E/Z* = 2/1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.10 (d, *J* = 8.1 Hz, 0.5H), 9.90 (d, *J* = 8.1 Hz, 1H), 5.87 (d, *J* = 8.1 Hz, 0.5H), 5.83 (d, *J* = 8.1 Hz, 1H), 1.96 (s, 3H), 1.59 (s, 1.5H), 0.94–0.79 (m, 5H), 0.77–0.70 (m, 2.5H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.2, 166.0, 164.5, 128.6, 124.9, 20.0, 19.1, 14.2, 13.3, 8.0, 7.1, 5.4, 0.9.

(2-Cyclohexenylidene)acetaldehyde (**2y**)[5e] [CAS No. 106019-07-2]
Pale yellow oil, 691 mg, 57% yield over two steps, R_f = 0.7 (PE/EA = 5:1, *v*/*v*), E/Z = 2/1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.10 (d, *J* = 8.2 Hz, 0.5 H), 10.03 (d, *J* = 8.2 Hz, 1 H), 7.08 (d, *J* = 10.0 Hz, 0.5 H), 6.35–6.28 (m, 1.5 H), 6.20–6.17 (m, 1H), 5.71 (d, *J* = 8.3 Hz, 1H), 5.64 (d, *J* = 8.3 Hz, 0.5 H), 2.90–2.82 (m, 2H), 2.49–2.41 (m, 1 H), 2.28–2.20 (m, 3 H), 1.82–1.75 (m, 3 H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.9, 189.8, 156.1, 140.1, 140.0, 130.2, 125.6, 124.4, 122.8, 32.4, 26.9, 26.0, 25.3, 22.6, 22.2, 21.8.

2-((8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-1,2,7,8,9,10,11,12,13,14,15,16-dodecahydro-17*H*-cyclopenta[*a*]phenanthren-17-ylidene)acetaldehyde (**12**)
Yellow solid, 56 % yield over the last two steps, m.p. 158–159 °C, R_f = 0.7 (PE/EA = 5:1, *v*/*v*), E/Z = 2/1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 10.14 (d, *J* = 8.7 Hz, 0.35H), 9.86 (d, *J* = 8.0 Hz, 0.63H), 5.91 (d, *J* = 9.6 Hz, 1H), 5.82 (d, *J* = 7.9 Hz, 0.34H), 5.75 (d, *J* = 7.9 Hz, 0.68H), 5.59 (t, *J* = 7.7 Hz, 1H), 5.40–5.34 (m, 1H), 3.02–2.77 (m, 1H), 2.41–2.04 (m, 4H), 1.93–1.68 (m, 8H), 1.65–1.26 (m, 4H), 1.24–1.04 (m, 4H), 0.96 (s, 3H), 0.89 (s, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 192.2, 190.6, 180.0, 178.9, 141.4, 128.71, 128.68, 125.2, 125.2, 124.1, 122.3, 122.2, 119.4, 55.7, 53.6, 48.4, 47.7, 46.4, 38.7, 35.2, 34.7, 33.62, 33.56, 33.4, 31.4, 31.31, 31.26, 27.6, 24.2, 22.9, 21.2, 20.7, 18.9, 18.73, 18.67, 18.0. IR (film): 2944, 1668, 1454, 1374, 1264, 1142, 1024, 906, 861, 755, 735, 702, 666 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd. for $C_{12}H_{28}NaO^+$ 319.2032, found 319.2029.

Cinnamaldehyde-1-*d* (**2g**-*d*) was synthesized according to Pierre's procedure.[6]



1) In a flask with a stir-bar, cinnamic aldehyde (**2g**) (1.32 g, 10 mmol), propane-1,3-dithiol (**S11**) (1.30 g, 12 mmol), and 4-methylbenzenesulfonic acid monohydrate (86 mg, 0.5 mmol) were dissolved in 20 mL of toluene. The reaction mixture was heated to 70–80 °C and kept stirring for 3–4 h. After the completion of the reaction and removal of solvent by rotary evaporation the resulting residue was purified by silica gel column chromatography (PE/EA = 50:1, *v/v*) to give pale yellow oil (*E*)-2-styryl-1,3-dithiolane (**S12**).

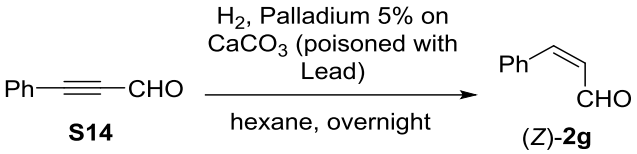
2) To an oven-dried flask with a stirrer bar and sealed with a nitrogen gas balloon were added above prepared (*E*)-2-styryl-1,3-dithiolane (**S12**) and dry THF (10 mL). The reaction mixture was cooled down to -35 to -30 °C. After addition of *n*-BuLi (1.6 M in THF, 12.5 mL, 20 mmol) dropwise the reaction mixture was stirred for 3 h. Then D_2O (1.0 mL, 50 mmol) was added and the reaction mixture was further stirred at -35 to -30 °C for 8 h. After the completion of the reaction and removal of solvent THF by rotary evaporation the resulting residue was extracted with CH_2Cl_2 (10 mL × 3). The organic layer was combined and concentrated *in vacuo*. The residue was purified by silica gel column chromatography (PE/EA = 50:1, *v/v*) to give pale yellow oil (*E*)-2-styryl-1,3-dithiolane-2-*d* (**S13**) 1.345 g (60% yield).

3) To a flask with a stirrer bar were added the above prepared (*E*)-2-styryl-1,3-dithiolane-2-*d* (**S12**) (1.2 g, 6mmol) and solvent (acetone: H_2O = 1:1, 15 mL). The flask was cooled down to -35 to -30 °C. After addition of (diacetoxyiodo)benzene (4.83 g, 15 mmol) the flask was heated in an oil bath at 25 °C for 5–10 mins. After the reaction was completed and removal of solvent acetone by rotary evaporation the resulting residue was extracted with CH_2Cl_2 (10 mL × 3). The organic layer was combined and concentrated *in vacuo.* The residue was purified by silica gel column chromatography (PE/EA = 20:1, *v/v*) to give pale yellow oil cinnamaldehyde-1-*d* (**2g**-*d*) (>99%D) 649 mg (60 % yield).

(*E*)-Cinnamaldehyde-1-*d* (**2g**-*d*) [6] [CAS No. 77249-46-8]

Pale yellow oil, 649 mg, 36% overall yield, R_f = 0.2 (PE/EA = 10/1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61–7.55 (m, 2H), 7.48 (d, J = 16.0 Hz, 1H), 7.44 (dd, J = 5.0, 2.0 Hz, 3H), 6.72 (d, J = 16.0 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): δ 193.4 (t, $J_{C\text{-}D}$ = 26.2 Hz), 152.7, 134.0, 131.2, 129.1, 128.6, 128.5, 128.5. IR (film): 2359, 2341, 1698, 1669, 1654, 1636, 1623, 1575, 1558, 1541, 1520, 1507, 1489, 1456, 1448, 1194, 1144, 1074, 1052, 1032, 997, 975, 739, 687 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_9H_8DO^+$ 134.0711, found 134.0713.

(*Z*)-3-Phenylacrylaldehyde [(*Z*)-**2g**] was synthesized according to Lindlar's procedure.[7]



To an oven-dried vial with a stirrer bar was added palladium 5% on calcium carbonate (poisoned with lead) (10 mg, 0.1 mmol). The vial was sealed with a nitrogen balloon and then gas was exchanged with a hydrogen balloon (1 atm). After addition of 3-phenylpropiolaldehyde (**S14**) (260 mg, 2 mmol) and hexane (1.5 mL), the reaction mixture was stirred overnight at room temperature. After the reaction was completed and removal of solvent hexane by rotary evaporation the resulting residue was purified by silica gel column chromatography to give (*Z*)-3-phenylacrylaldehyde [(*Z)*-**2g**] 165mg (30 % yield).

(*Z*)-3-Phenylacrylaldehyde [(*Z)*-**2g**] [7] [CAS No. 57194-69-1]
Pale yellow oil, 165 mg, 30% yield, R_f = 0.5 (PE/EA = 10:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 9.98 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 11.6 Hz, 1H), 7.45–7.39 (m, 5H), 6.20 (dd, *J* = 11.6, 8.1 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 192.5, 148.6, 134.2, 130.5, 129.8, 129.7, 128.6.

6. General procedure for the synthesis of ethyl 4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylates 3 and 13

Conditions A: This procedure is used for the preparation of **3aa, 3ac-3af, 3ah-3at, 3ay, 3aac, 3aad, 3ba, 3ea**, and **3ma**.
To an oven-dried 10 mL-vial with a stirring bar were added 1,2,3-thiadiazole **1** (0.25 mmol), catalyst $[Rh(COD)Cl]_2$ (6.2 mg, 5 mol%), ligand DPPF (16.6 mg, 12 mol%), and pre-dried solvent PhCl (1 mL). The vial was sealed with a nitrogen gas balloon, then alkenal **2** (0.5 mmol) was added via a syringe. The reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 5:1~20:1, *v/v*) to give desired product **3**.

Conditions B: This modification is used for the preparation of **3ca, 3fa, 3ga, 3ha, 3ia, 3ja 3ka**, and **3la**.
To an oven-dried 10 mL-vial with a stirring bar were added 1,2,3-thiadiazole **1** (0.10 mmol), catalyst $[Rh(COD)Cl]_2$ (12.4 mg, 10 mol%), ligand DPPF (33.2 mg, 24 mol%), additive $AgBF_4$ (9.7 mg, 20 mol%), and pre-dried solvent PhCl (0.5 mL). The vial was sealed with a nitrogen gas balloon, then alkenal **2** (0.3 mmol) was added via a syringe. The reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 5:1~20:1, *v/v*) to give desired product **3**.

Conditions C: This modification was used for the preparation of **3ab.**
To an oven-dried 10 mL-vial with a stirring bar were added 1,2,3-thiadiazole **1a** (0.10 mmol, 23.4 mg), catalyst $[Rh(COD)Cl]_2$ (2.5 mg, 5 mol%), ligand DPPF (6.7 mg, 12 mol%), and

pre-dried solvent PhCl (1 mL). The vial was sealed with a nitrogen gas balloon, then alkenal **2b** (0.4 mmol, 22.4 mg) was added via a syringe. The reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 5:1, *v/v*) to give desired product **3ab**.

Conditions D: This modification was used for the preparation of **3aae.**
To an oven-dried 10 mL-vial with a stirring bar were added 1,2,3-thiadiazole **1a** (0.25 mmol, 58.6 mg), catalyst $[Rh(COD)Cl]_2$ (12.3 mg, 10 mol%), ligand DPPF (33.2 mg, 24 mol%), and pre-dried solvent PhCl (1 mL). The vial was sealed with a nitrogen gas balloon, then alkenal **2ae** (0.5 mmol, 73.0 mg) was added via a syringe. The reaction mixture was kept stirring at 130 °C in an oil-bath for 12 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 10:1, *v/v*) to give desired product **3aae**

Ethyl 2,2-dimethyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aa**)
Prepared under *Condition A* on 0.25 mmol scale. Colorless crystal, 52 mg, 72% yield, R_f = 0.2 (PE/EA = 5:1, *v/v*), m.p. 105–107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.47–7.31 (m, 5H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 2H), 1.52 (s, 6H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.5, 165.9, 160.8, 136.5, 130.4, 128.4, 127.8, 126.9, 61.1, 51.2, 45.6, 27.7, 13.5.

Ethyl 4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ab**)
Prepared under *Conditions C* on 0.10 mmol scale. Brown oil, 17 mg, 65% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.85–7.69 (m, 5H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.64 (dd, *J* = 8.0, 8.0 Hz, 2H), 3.19 (dd, *J* = 8.0, 8.0 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.5, 165.8, 162.1, 136.5, 130.7, 128.5, 128.2, 127.9, 61.2, 36.3, 27.0, 13.6. IR (film): 2960, 2924, 1724, 1657, 1544, 1486, 1443, 1365, 1332, 1298, 1233, 1210, 1173, 1094, 1047, 1017, 940, 914, 840 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{14}H_{15}O_3S^+$ 263.0736, found 263.0738.

Ethyl 2-(4-(dimethylamino)phenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ac**)
Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 73 mg, 77% yield, R_f = 0.15 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.55–7.35 (m, 5H), 7.26 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 4.74 (dd, *J* = 14.8, 3.2 Hz, 1H), 4.04–4.00 (m, 2H), 3.23 (dd, *J* = 15.4, 15.4 Hz 1H), 3.01 (dd, *J* = 16.0, 2.6 Hz, 1H), 2.96 (s, 6H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.7, 166.0, 162.7, 150.6, 136.3, 130.6, 128.5, 128.2, 127.9, 127.8, 123.8, 112.4, 61.1, 46.1, 44.0, 40.3, 13.6. IR (film): 2979, 2897, 2805, 1728, 1658, 1611, 1524, 1484, 1444, 1362, 1323, 1228, 1210, 1166, 1142, 1095, 1038, 945, 915, 847, 818 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{20}H_{24}NO_3S^+$ 382.1471, found 382.1472.

Ethyl 2-(4-methoxyphenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ad**) Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 72 mg, 78% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53–7.35 (m, 5H), 7.33 (d, *J* = 8.3 Hz, 2H), 6.91 (d, *J* = 8.3 Hz, 2H), 4.76 (dd, *J* = 14.5, 2.8 Hz, 1H), 4.03–3.99 (m, 2H), 3.80 (s, 3H), 3.21 (dd, *J* = 16.0, 14.4 Hz, 1H), 3.01 (dd, *J* = 15.9, 2.8 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.2, 165.9, 162.2, 159.8, 136.1, 130.7, 128.8, 128.6, 128.5, 127.890, 127.887, 114.4, 61.2, 55.3, 45.7, 43.9, 13.6. IR (film): 2979, 2932, 1728, 1659, 1609, 1580, 1513, 1486, 1463, 1443, 1365, 1321, 1303, 1254, 1225, 1180, 1144, 1113, 1095, 1037, 946, 915, 852, 833 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{20}H_{21}O_4S^+$ 369.1155, found 369.1154.

Ethyl 2-(3-methoxyphenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ae**) Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 76 mg, 83% yield, R_f = 0.2 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53–7.48 (m, 2H), 7.46–7.34 (m, 3H), 7.32–7.26 (m, 1H), 7.01–6.86 (m, 3H), 4.77 (dd, *J* = 14.3, 3.0 Hz, 1H), 4.03–3.98 (m, 2H), 3.80 (s, 3H), 3.20 (dd, *J* = 15.9, 14.3 Hz, 1H), 3.03 (dd, *J* = 16.0, 3.0 Hz, 1H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.9, 165.7, 161.9, 159.9, 138.4, 136.0, 130.7, 130.2, 128.5, 127.9, 119.6, 114.1, 113.2, 61.2, 55.2, 46.1, 43.6, 13.5. IR (film): 2978, 1729, 1659, 1599, 1585, 1550, 1492, 1463, 1442, 1365, 1321, 1250, 1228, 1211, 1147, 1106, 1039, 1027, 946, 915 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+K]^+$ calcd. for $C_{21}H_{20}KO_4S^+$ 407.0714, found 407.0724.

Ethyl 2-(2-methoxyphenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3af**) Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 73 mg, 80% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.55–7.47 (m, 2H), 7.47–7.28 (m, 5H), 7.02–6.89 (m, 2H), 5.29 (dd, *J* = 13.6, 3.2 Hz, 1H), 4.05–3.99 (m, 2H), 3.87 (s, 3H), 3.22 (dd, *J* = 15.9, 13.6 Hz, 1H), 2.97 (dd, *J* = 16.0, 3.2 Hz, 1H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.6, 166.0, 162.8, 156.8, 136.4, 130.6, 129.7, 128.5, 127.93, 127.88, 127.5, 125.2, 120.9, 111.0, 61.1, 55.5, 42.8, 39.6, 13.6. IR (film): 3057, 2978, 1728, 1660, 1599, 1584, 1550, 1490, 1443, 1365, 1318, 1267, 1232, 1213, 1158, 1094, 1039, 946, 915, 877 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{21}H_{21}O_4S^+$ 369.1155, found 369.1148.

Ethyl 2-(4-fluorophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ah**) Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 67 mg, 75% yield, R_f = 0.3 (PE/PE = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50 (d, *J* = 7.6 Hz, 2H), 7.45–7.36 (m, 5H), 7.10 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 1H), 4.79 (dd, *J* = 14.3, 2.8 Hz, 1H), 4.09–3.93 (m, 2H), 3.19 (dd, *J* = 15.6, 14.8 Hz, 1H), 3.02 (dd, *J* = 16.0, 3.0 Hz, 1H), 0.92 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.8, 165.7, 162.4 (d, $J_{C\text{-}F}$ = 249.5 Hz), 161.8, 135.9, 132.7 (d, $J_{C\text{-}F}$ = 3.3 Hz), 130.8, 129.2 (d, $J_{C\text{-}F}$ = 8.3 Hz), 128.6, 127.95, 127.89, 116.1(d, $J_{C\text{-}F}$ = 21.7 Hz), 61.3, 45.4, 43.7, 13.6.^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) *δ* -112.3 (s). IR (film): 2981, 1728, 1660, 1603, 1550, 1509, 1486, 1444, 1416, 1366, 1319, 1225, 1160, 1144, 1097, 1039, 946, 915, 856, 838 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for

$C_{20}H_{18}FO_3S^+$ 356.0882, found 356.0884.

Ethyl 2-(4-bromophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ai**)
Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 75 mg, 72%, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53–7.48 (m, 4H), 7.47 – 7.29 (m, 5H), 4.76 (dd, *J* = 14.0, 3.1 Hz, 1H), 4.07–3.95 (m, 2H), 3.18 (dd, *J* = 15.9, 14.0 Hz, 1H), 3.01 (dd, *J* = 15.9, 3.1 Hz, 1H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.6, 165.6, 161.5, 136.0, 135.9, 132.3, 130.8, 129.1, 128.6, 128.0, 127.9, 122.8, 61.3, 45.5, 43.4, 13.6. IR (film): 2920, 2850, 1727, 1660, 1591, 1549, 1487, 1470, 1400, 1366, 1316, 1298, 1263, 1223, 1141, 1091, 1074, 1012, 929, 827 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd. for $C_{20}H_{17}BrNaO_3S^+$ 438.9974, found 438.9965.

Ethyl 2-(2,3-dichlorophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aj**)
Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 66 mg, 65% yield, R_f = 0.2 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.57–7.29 (m, 8H), 5.33 (dd, *J* = 12.5, 3.6 Hz, 1H), 4.06–3.99 (m, 2H), 3.19 (dd, *J* = 15.9, 12.5 Hz, 1H), 3.06 (dd, *J* = 15.9, 3.7 Hz, 1H), 0.95 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.2, 165.5, 161.3, 137.0, 135.8, 134.1, 132.1, 130.9, 130.6, 128.6, 128.0, 127.9, 127.8, 126.4, 61.3, 42.9, 42.5, 13.6. IR (film): 3060, 2979, 1729, 1661, 1597, 1553, 1486, 1451, 1421, 1365, 1309, 1279, 1223, 1181, 1159, 1095, 1040, 947, 915, 859 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{20}H_{17}Cl_2O_3S^+$ 407.0270, found 407.0274.

Ethyl 2-(4-nitrophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ak**)
Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 40 mg, 39% yield, R_f = 0.15 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.27 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.55–7.34 (m, 5H), 4.91 (dd, *J* = 13.4, 3.1 Hz, 1H), 4.04–3.99 (m, 2H), 3.24 (dd, *J* = 15.8, 13.5 Hz, 1H), 3.08 (dd, *J* = 15.8, 3.2 Hz, 1H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 189.9, 165.4, 160.8, 148.0, 144.1, 135.6, 131.1, 128.7, 128.6, 128.2, 128.0, 124.4, 61.4, 45.2, 43.0, 13.6. IR (film): 3079, 2981, 2927, 1727, 1660, 1598, 1523, 1490, 1444, 1347, 1320, 1264, 1227, 1212, 1146, 1111, 1038, 946, 916, 856, 833 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{20}H_{18}NO_5S^+$ 384.0900, found 384.0900.

Ethyl 2-(naphthalen-2-yl)-4-oxo-6-phenyl-3,4-dihydro-2H-thiopyran-5-carboxylate (**3al**)
Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 67 mg, 69%, R_f = 0.4 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.93–7.80 (m, 4H), 7.58–7.48 (m, 5H), 7.48–7.35 (m, 3H), 4.97 (dd, *J* = 14.3, 3.0 Hz, 1H), 4.07–7.02 (m, 2H), 3.36 (dd, *J* = 15.9, 14.3 Hz, 1H), 3.13 (dd, *J* = 15.9, 3.0 Hz, 1H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.0, 165.8, 161.9, 136.1, 134.2, 133.2, 130.7, 129.1, 128.5, 127.99, 127.94 127.7, 126.75, 126.69, 124.8, 61.3, 46.4, 43.6, 13.6. IR (film): 2925, 2360, 2341, 1729, 1660, 1598, 1551, 1508, 1487, 1443, 1365, 1307, 1210, 1141, 1038, 946, 914, 858, 818, 751, 720, 697, 669, 568, 477 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{24}H_{21}O_3S^+$ 389.1206, found 389.1207.

Ethyl (*E*)-4-oxo-6-phenyl-2-styryl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3am**)

Prepared under *Conditions A* on 0.25 mmol scale. Brown oil, 67 mg, 74% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52–7.47 (m, 2H), 7.44–7.37 (m, 5H), 7.36–7.31 (m, 2H), 7.31–7.27 (m, 1H), 6.70 (d, *J* = 15.7 Hz, 1H), 6.25 (dd, *J* = 15.7, 8.3 Hz, 1H), 4.39 (ddd, *J* = 12.1, 8.3, 4.3 Hz, 1H), 4.03–3.98 (m, 2H), 3.06–2.91 (m, 2H), 0.93 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 190.6, 165.7, 161.3, 136.2, 135.5, 134.4, 130.7, 128.7, 128.51, 128.46, 128.0, 127.9, 126.6, 124.4, 61.2, 44.5, 42.8, 13.6. IR (film): 3058, 3027, 2980. 1728, 1659, 1598, 1550, 1488, 1445, 1407, 1366, 1324, 1212, 1143, 1095, 1072, 1036, 964, 945, 914 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{22}H_{21}O_3S^+$ 365.1206, found 365.1201.

Ethyl 2-((1*R*,5*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3an**)

Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 76 mg, 80% yield, R_f = 0.5 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.45–7.32 (m, 5H), 5.64–5.62 (m, 1H), 4.23–4.16 (m, 1H), 4.03–3.90 (m, 2H), 2.92 (ddd, *J* = 16.0, 12.5, 7.6 Hz, 1H), 2.81 (ddd, *J* = 16.0, 3.6, 1.8 Hz, 1H), 2.47–2.42 (m, 1H), 2.38–2.08 (m, 4H), 1.30 (d, *J* = 3.4 Hz, 3H), 1.17 (dd, *J* = 8.8, 5.4 Hz, 1H), 0.89 (td, *J* = 7.1, 1.5 Hz, 3H), 0.83 (d, *J* = 4.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.5, 191.3, 165.8, 162.1, 161.9, 143.4, 143.2, 136.6, 136.5, 130.52, 130.50, 128.5, 127.9, 127.8, 122.6, 122.5, 61.1, 47.4, 47.1, 44.0, 43.7, 41.3, 40.9, 40.5, 40.4, 38.2, 38.1, 31.7, 31.6, 31.3, 31.3, 26.0, 21.4, 21.3, 13.6, 13.5. IR (film): 2979, 2932, 1731, 1660, 1611, 1552, 1466, 1444, 1366, 1309, 1212, 1142, 1096, 1038, 945 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{23}H_{27}O_3S^+$ 383.1675, found 383.1671.

Ethyl 2-cyclohexyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ao**)

Prepared under *Conditions A* on 0.25 mmol scale. Pale yellow oil, 62 mg, 72% yield, R_f = 0.5 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.49–7.32 (m, 5H), 4.00–3.93 (m, 2H), 3.48 (ddd, *J* = 12.9, 6.4, 3.3 Hz, 1H), 2.86 (dd, *J* = 15.8, 3.3 Hz, 1H), 2.75 (dd, *J* = 15.8, 12.9 Hz, 1H), 1.92–1.61 (m, 6H), 1.32–1.07 (m, 5H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.9, 165.9, 162.3, 136.8, 130.5, 128.4, 127.8, 127.6, 61.1, 48.2, 40.9, 40.8, 30.1, 29.9, 26.0, 25.92, 25.90, 13.6. IR (film): 2927, 2853, 1730, 1660, 1551, 1486, 1445, 1365, 1322, 1234, 1210, 1095, 1030, 956, 915 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{20}H_{25}O_3S^+$ 345.1519, found 345.1519.

Ethyl 4-oxo-6-phenyl-2-(1-phenylethyl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ap**)

Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 54 mg, 59% yield, R_f = 0.15 (PE/EA = 10:1, *v/v*), dr = 1:1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.54–7.49 (m, 1H), 7.49–7.34 (m, 6H), 7.34–7.18 (m, 4H), 4.07–3.93 (m, 2H), 3.85–3.72 (m, 1H), 3.16–3.08 (m, 1H), 3.04 (dd, *J* = 15.8, 3.1 Hz, 0.5H), 2.78 (dd, *J* = 16, 12.8 Hz, 0.5H), 2.72 (dd, *J* = 16, 3.6 Hz, 0.5H), 2.58 (dd, *J* = 16, 12.4 Hz, 0.5H), 1.52 (d, *J* = 7.0 Hz, 1.5H), 1.47 (d, *J* = 7.0 Hz, 1.5H), 0.924 (t, *J* = 7 Hz, 1.5H), 0.915 (t, *J* = 7 Hz, 1.5H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.24, 191.21, 165.8, 162.2, 161.4, 141.97, 141.95, 136.61, 136.57, 130.63, 130.55, 128.9, 128.7, 128.5, 128.4, 128.1, 127.95, 127.85, 127.7, 127.5, 127.43, 127.40, 61.16, 61.14, 48.7, 48.6, 43.13, 43.11, 41.6, 41.2, 19.2, 18.5, 13.6. IR (film): 3060, 2970, 2928, 1727, 1658, 1599, 1551, 1491, 1444, 1365, 1326, 1304, 1233, 1211, 1075, 1049, 1028,

946, 914 cm^{-1}. HRMS (ESI-TOF) *m/z* $C_{22}H_{23}O_3S^+$ calcd. for 367.1362; found 367.1362.

Ethyl 2-methyl-2-(4-methylpent-3-en-1-yl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ar**)
Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 74 mg, 83% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.46–7.32 (m, 5H), 5.08 (t, *J* = 6.9 Hz, 1H), 3.96 (q, *J* = 7.1 Hz, 2H), 2.84 (d, *J* = 15.4 Hz, 1H), 2.71 (d, *J* = 15.4 Hz, 1H), 2.17–2.10 (m, 2H), 1.87–1.69 (m, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.50 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.5, 165.8, 160.6, 136.6, 132.8, 130.4, 128.4, 127.8, 126.8, 122.6, 61.0, 49.7, 49.1, 40.2, 25.5, 24.9, 22.8, 17.6, 13.5. IR (film): 2974, 2930, 1729, 1659, 1551, 1444, 1366, 1326, 1241, 1211, 1075, 1042, 945, 914 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{21}H_{27}O_3S^+$ 359.1675, found 359.1682.

Ethyl 2-methyl-4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3as**)
Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 76 mg, 86% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.57–7.29 (m, 10H), 3.97 (q, *J* = 7.0 Hz, 2H), 3.44 (d, *J* = 15.6 Hz, 1H), 3.03 (d, *J* = 15.6 Hz, 1H), 1.89 (s, 3H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.1, 165.6, 160.5, 142.0, 136.1, 130.5, 128.8, 128.5, 128.4, 128.0, 127.9, 125.7, 61.0, 51.3, 49.8, 27.4, 13.5. IR (film): 3058, 2979, 2927, 1729, 1659, 1598, 1553, 1493, 1444, 1366, 1325, 1241, 1213, 1069, 1028, 1001, 946, 914, 818 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{21}H_{21}O_3S^+$ 353.1206, found 353.1206.

Ethyl 2-cyclopropyl-2-methyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3at**)
Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 62 mg, 78% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.48–7.31 (m, 5H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.85 (d, *J* = 15.3 Hz, 1H), 2.75 (d, *J* = 15.3 Hz, 1H), 1.34 (s, 3H), 1.21–1.11 (m, 1H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.60–0.51 (m, 3H), 0.49–0.42 (m, 1H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.5, 165.9, 160.9, 136.5, 130.4, 128.4, 127.8, 127.1 , 61.0, 50.0, 49.3, 22.9, 20.0, 13.5, 1.9, 1.5. IR (film): 2979, 1729, 1660, 1598, 1553, 1487, 1444, 1386, 1366, 1325, 1212, 1086, 1051, 1026, 944, 912, 819 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{18}H_{21}O_3S^+$ 317.1206, found 317.1204.

Ethyl 4-oxo-2-phenyl-1-thiaspiro[5.5]undeca-2,7-diene-3-carboxylate (**3ay**)
Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 21 mg, 64% yield, R_f = 0.4 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.51–7.32 (m, 5H), 5.98 (d, *J* = 9.2 Hz, 1H), 5.69 (d, *J* = 9.6 Hz, 1H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.01 (d, *J* = 15.3 Hz, 1H), 2.70 (d, *J* = 15.3 Hz, 1H), 2.33–2.31 (m, 1H), 2.21–1.98 (m, 2H), 1.97–1.76 (m, 2H), 1.72–1.58 (m, 1H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.0, 165.9, 160.9, 136.5, 132.8, 130.5, 128.5, 128.0, 127.9, 127.4, 61.1, 50.2, 49.2, 32.6, 24.9, 19.1, 13.6. IR (film): 2933, 1729, 1660, 1550, 1444, 1365, 1323, 1299, 1248, 1234, 1212, 1095, 1066, 1036, 941 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{19}H_{21}O_3S^+$ 329.1206, found 329.1201.

Ethyl 3-methyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aac**)

Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 19 mg, 28% yield, R_f = 0.2 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53–7.32 (m, 5H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.18 (d, *J* = 7.9 Hz, 2H), 2.81 (tq, *J* = 7.9, 6.8 Hz, 1H), 1.32 (d, *J* = 6.8 Hz, 3H), 0.93 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 193.1, 166.1, 160.8, 136.6, 130.6, 128.5, 127.9, 127.7, 61.2, 39.0, 33.5, 14.3, 13.6. IR (film): 3431, 2975, 2931, 1726, 1660, 1551, 1488, 1444, 1365, 1341, 1324, 1288, 1214, 1194, 1093, 1020, 943, 913, 771, 743, 698 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{15}H_{17}O_3S^+$ 277.0893, found 277.0891.

Ethyl 2,3-dimethyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aad**)
Prepared under *Conditions A* on 0.25 mmol scale. Yellow oil, 22 mg, 31% yield, R_f = 0.2 (PE/EA = 5:1, *v/v*), dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.51–7.31 (m, 5H), 4.01–3.96 (m, 2H), 3.66–3.62 (m, 0.6H), 3.37–3.31 (m, 0.3H), 2.91–2.85 (m, 0.6H), 2.62–2.58 (m, 0.4H), 1.50 (d, *J* = 7.1 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 2H), 1.32 (d, *J* = 6.8 Hz, 1H), 1.26 (d, *J* = 6.8 Hz, 2H), 0.92–0.89 (m, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 166.1, 136.6, 136.5, 130.5, 128.5, 127.88, 127.86, 127.0, 61.1, 46.2, 44.5, 42.5, 41.4, 18.9, 15.1, 13.6, 12.6, 10.3. IR (film): 2968, 2929, 1719, 1701, 1654, 1648, 1629, 1618, 1577, 1559, 1541, 1534, 1508, 1458, 1443, 1364, 1290, 1211, 1094, 1074, 1020, 945, 912, 773, 760, 735, 696 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{16}H_{19}O_3S^+$ 291.1049, found 291.1054.

Ethyl 3-methyl-4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aae**)
Prepared under *Conditions D* on 0.25 mmol scale. Yellow oil, 89 mg, 50% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*), dr = 2:1. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.53–7.48 (m, 2H), 7.45–7.31 (m, 8H), 4.45 (d, *J* = 13.2 Hz, 1H), 4.07–3.99 (m, 2H), 3.17(dq, *J* = 13.2, 6.8 Hz, 0.7H), 3.0 (dq, *J* = 6.8, 4 Hz, 0.3H), 1.26 (d, *J* = 4 Hz, 0.3H), 1.24 (d, *J* = 10 Hz, 1H), 1.23 (d, *J* = 13.6 Hz, 0.7H), 1.05 (d, *J* = 6.7 Hz, 2H), 0.96 (t, *J* = 7.2, 2H), 0.94 (t, *J* = 7.2, 1H).^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 194.2, 193.1, 166.1, 165.9, 160.7, 159.8, 136.5, 136.4, 136.3, 136.0, 130.61, 130.60, 129.0, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.84, 127.81, 127.4, 126.9, 61.2, 52.3, 50.9, 45.4, 45.2, 13.60, 13.58, 12.1. IR (film): 3060, 2979, 2928, 1728, 1658, 1598, 1556, 1489, 1453, 1366, 1325, 1276, 1212, 1193, 1091, 1022, 943, 916, 844 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{21}H_{21}O_3S^+$ 353.1206, found 353.1209.

Ethyl 6-(benzo[*d*][1,3]dioxol-5-yl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ba**)
Prepared under *Conditions A* on 0.25 mmol scale. Pale yellow oil, 56 mg, 67% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.03–6.97 (dd, *J* = 8, 1.2Hz 1H), 6.97–6.91 (d, *J* = 0.8Hz 1H), 6.78 (d, *J* = 8.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.72 (s, 2H), 1.49 (s, 6H), 1.03 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 191.6, 166.3, 160.2, 149.7, 147.8, 130.2, 126.5, 122.6, 108.4, 108.3, 101.6, 61.1, 51.3, 45.2, 27.7, 13.8. IR (film): 2974, 2917, 1726, 1655, 1546, 1503, 1484, 1437, 1367, 1345, 1321, 1299, 1251, 1211, 1101, 1038, 932 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{17}H_{19}O_5S^+$ 335.0948, found 335.0949.

Ethyl 6-(4-methoxyphenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ca**)

Prepared under *Conditions B* on 0.10 mmol scale with reaction time extended to 12 h. Pale yellow oil, 22 mg, 69% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.73 (s, 2H), 1.50 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): δ 191.6, 166.4, 161.6, 160.6, 129.6, 128.8, 126.2, 113.9, 61.1, 55.3, 51.3, 45.0, 27.7, 13.8. IR (film): 2964, 2932, 2840, 1727, 1656,1604, 1574, 1546, 1505, 1461, 1444, 1414, 1388, 1367, 1325, 1294, 1253, 1211, 1176, 1148, 1103, 1040, 949, 933, 836, 813 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{17}H_{21}O_4S^+$ 321.1155, found 321.1158.

Ethyl 2,2-dimethyl-6-(4-methylphenyl)-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3da**)
Prepared under *Conditions A* on 0.25 mmol scale. Pale yellow oil, 56 mg, 74% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, *J* = 7.8 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.73 (s, 2H), 2.35 (s, 3H), 1.50 (s, 6H), 0.94 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): δ 191.5, 166.2, 160.9, 140.9, 133.6, 129.1, 127.8, 126.5, 61.0, 51.3, 45.3, 27.7, 21.3, 13.6. IR (film): 2974, 2927, 1729, 1658, 1608, 1550, 1505, 1460, 1408, 1388, 1367, 1325, 1246, 1215, 1184, 1148, 1103, 1041, 1021, 936, 814 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{17}H_{21}O_3S^+$ 305.1206, found 305.1210.

Ethyl 6-(4-fluorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ea**)
Prepared under *Conditions A* on 0.25 mmol scale. Pale yellow oil, 42 mg, 55% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51–7.40 (m, 2H), 7.09–7.03 (m, 2H), 4.01 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 2H), 1.52 (s, 6H), 0.96 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): δ 191.4, 165.9, 164.0 (d, $J_{C\text{-}F}$ = 252.7 Hz), 159.4, 132.5 (d, $J_{C\text{-}F}$ = 3.2 Hz), 130.1(d, $J_{C\text{-}F}$ = 8.7 Hz), 127.1, 115.6(d, $J_{C\text{-}F}$ = 22.0 Hz), 61.2, 51.2, 45.7, 27.8, 13.7. ^{19}F NMR{^{1}H} (376 MHz, $CDCl_3$) δ -109.3 (s). IR (film): 2974, 2930, 1729, 1661, 1600, 1551, 1503, 1368, 1324, 1299, 1245, 1215, 1160, 1105, 1040, 840 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{16}H_{18}FO_3S^+$ 309.0955, found 309.0952.

Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3fa**)
Prepared under *Conditions B* on 0.10 mmol scale. Pale yellow oil, 24 mg, 74% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 (d, *J* = 8.6 Hz, 2H), 7.35 (d, *J* = 8.5 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.76 (s, 2H), 1.52 (s, 6H), 0.98 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): δ 191.4, 165.8, 159.2, 136.7, 134.9, 129.3, 128.8, 61.3, 51.2, 45.8, 27.8, 13.7, 1.0. IR (film): 2966, 2926, 1729, 1662, 1593, 1549, 1486, 1461, 1398, 1368, 1323, 1298, 1246, 1212, 1091, 1041, 1014, 936, 877, 830 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{16}H_{17}ClO_3S^+$ 325.0660, found 325.0657.

Ethyl 6-(3,4-dichlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ga**)
Prepared under *Conditions B* on 0.10 mmol scale. Pale yellow oil, 26 mg, 72% yield, R_f = 0.3 (hexane/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.76 (s, 2H), 1.53 (s, 6H), 1.04 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): δ 191.3, 165.5, 157.4,

136.2, 134.9, 133.0, 130.6, 129.9, 127.5, 127.2, 61.5, 51.1, 46.2, 27.8, 13.8. IR (film): 2975, 2928, 1729, 1665, 1588, 1560, 1543, 1465, 1369, 1322, 1244, 1210, 1133, 1103, 1033, 943, 883, 824 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{16}H_{17}Cl_2O_3S^+$ 359.0270, found 359.0275.

Ethyl 6-(4-iodophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ha**)
Prepared under *Conditions B* on 0.10 mmol scale. Pale yellow oil, 29 mg, 70% yield, R_f = 0.3 (hexane/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.72 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 2H), 1.52 (s, 6H), 0.98 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.4, 165.7, 159.3, 137.7, 136.0, 129.5, 127.0, 97.0, 61.3, 51.2, 45.9, 27.8, 13.7. IR (film): 2974. 2924, 1727, 1660, 1583, 1560, 1543, 1478, 1460, 1389, 1367, 1323, 1298, 1245, 1212, 1102, 1039, 1005, 936, 821 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{16}H_{18}IO_3S^+$ 417.0016, found 417.0010.

Ethyl 2,2-dimethyl-4-oxo-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ia**)
Prepared under *Conditions B* on 0.10 mmol scale. Pale yellow oil, 28 mg, 78% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.64 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 8.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.78 (s, 2H), 1.55 (s, 6H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.2, 165.4, 158.7, 140.0, 132.2 (q, J_{C-F} = 32.9 Hz), 128.4, 127.6, 125.4 (q, J_{C-F} = 3.9 Hz), 123.6 (q, J_{C-F} = 274.0 Hz), 61.4, 51.2, 46.3, 27.8, 13.6. ^{19}F NMR{^1H} (376 MHz, $CDCl_3$) *δ* -63.0 (s). IR (film): 2967, 1730, 1664, 1557, 1508, 1461, 1407, 1369, 1322, 1246, 1215, 1169, 1129, 1067, 1040, 1016, 939, 842 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{17}H_{18}F_3O_3S^+$ 259.0923, found 259.0924.

Ethyl 6-(4-cyanophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ja**)
Prepared under *Conditions B* on 0.10 mmol scale with reaction time extended to 10 h. Pale yellow oil, 22 mg, 70% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.68 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.78 (s, 2H), 1.54 (s, 6H), 0.95 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.1, 165.2, 157.9, 140.9, 132.2, 128.8, 127.7, 117.9, 114.1, 61.5, 51.1, 46.6, 27.8, 13.7. IR (film): 2966, 2926, 2854, 2230, 1729, 1664, 1565, 1496, 1462, 1389, 1368, 1324, 1273, 1246, 1215, 1148, 1103, 1041, 1019, 841 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+K]^+$ calcd. for $C_{17}H_{17}KNO_3S^+$ 354.0561, found 354.0568.

Ethyl 6-(furan-2-yl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ka**)
Prepared under *Conditions B* on 0.10 mmol scale with reaction time extended to 12 h. Pale yellow oil, 13 mg, 46% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.53 (d, *J* = 1.7 Hz, 1H), 6.95 (d, *J* = 3.6 Hz, 1H), 6.51 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.30 (q, *J* = 7.1 Hz, 2H), 2.74 (s, 2H), 1.50 (s, 6H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^1H} (101 MHz, $CDCl_3$): *δ* 191.9, 166.7, 148.0, 145.9, 144.0, 122.9, 115.8, 112.6, 61.6, 51.8, 44.8, 27.8, 14.1. IR (film): 2973, 2929, 1731, 1654, 1579, 1528, 1462, 1386, 1367, 1326, 1234, 1210, 1104, 1043, 1026, 948, 883 cm^{-1}. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{14}H_{17}O_4S^+$ 281.0842, found 281.0847.

Ethyl 2,2-dimethyl-4-oxo-6-(thiophen-2-yl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3la**)
Prepared under *Conditions B* on 0.10 mmol scale. Pale yellow oil, 21 mg, 72% yield, R_f = 0.4 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.52 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.42 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.07 (dd, *J* = 5.1, 3.8 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 2H), 1.52 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.6, 166.7, 150.8, 137.9, 130.5, 129.8, 128.1, 125.4, 61.6, 51.5, 45.4, 27.6, 13.8. IR (film): 2963, 2927, 1728, 1655, 1546, 1509, 1460, 1415, 1388, 1366, 1320, 1298, 1245, 1213, 1103, 1036, 936, 859 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{14}H_{17}O_3S^+$ 297.0614, found 297.0615.

Ethyl 2,2-dimethyl-6-(naphthalen-2-yl)-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ma**)
Prepared under *Conditions A* on 0.20 mmol scale. Pale yellow oil, 60 mg, 71% yield, R_f = 0.3 (PE/EA = 5:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 8.00 (s, 1H), 7.85 (m, 3H), 7.54 (m, 3H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.81 (s, 3H), 1.57 (s, 6H), 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 191.6, 166.1, 160.9, 134.0, 133.9, 132.6, 128.6, 128.3, 128.0, 127.7, 127.5, 127.2, 126.8, 125.0, 61.2, 51.4, 45.7, 27.8, 13.6. IR (film): 3056, 2963, 2928, 1728, 1659, 1597, 1548, 1502, 1462, 1387, 1367, 1349, 1321, 1298, 1240, 1214, 1180, 1147, 1103, 1041, 1018, 861, 817 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+K]$^+$ calcd. for $C_{20}H_{20}KO_3S^+$ 379.0765, found 379.0770.

Ethyl (10*R*,13*S*)-10,13-dimethyl-4'-oxo-6'-phenyl-1,2,3',4',7,8,9,10,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-thiopyran]-5'-carboxylate (**13**)
Pale yellow oil, 46 mg, 91% yield, R_f = 0.2 (PE/EA = 20:1, *v/v*). ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.50–7.34 (m, 5H), 5.96–5.90 (m, 1H), 5.64–5.58 (m, 1H), 5.42–5.36 (m, 1H), 4.04–3.93 (m, 2H), 2.94 (s, 2H), 2.30–2.19 (m, 3H), 2.15–2.12 (m, 1H), 2.10–2.02 (m, 1H), 1.91–1.65 (m, 8H), 1.50–1.30 (m, 3H), 1.22–1.15 (m, 1H), 1.13–1.10 (m, 1H), 0.96 (s, 3H), 0.90 (s, 3H), 0.89 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$): *δ* 192.1, 165.9, 161.7, 141.5, 136.7, 130.9, 130.5, 128.8, 128.5, 127.9, 125.3, 122.4, 63.1, 61.1, 51.5, 48.0, 47.9, 45.0, 36.4, 35.2, 33.8, 33.6, 32.3, 31.7, 23.9, 23.0, 20.8, 18.8, 14.6, 13.6. IR (film): 3019, 2936, 1724, 1655, 1550, 1444, 1382, 1328, 1216, 1028, 911, 740, 669, 650 cm^{-1}. HRMS (ESI-TOF) *m/z* [M+H]$^+$ calcd. for $C_{32}H_{39}O_3S^+$ 503.2614, found 503.2617.

7. Intermediate Probing Experiments

Dimerization of carbenes

To an oven-dried 10 mL-vial with a stirrer bar were added 1,2,3-thiadiazole **1a** (0.25 mmol, 58.6 mg), catalyst $[Rh(COD)Cl]_2$ (12.3 mg, 10 mol%), ligand DPPF (33.3 mg, 24 mol%), and pre-dried solvent PhCl (1 mL). The vial was sealed with a nitrogen gas balloon. Then the reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the ensuing mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 5:1~20:1, *v/v*) to give 1,2,3-thiadiazole **1a** (14 mg, 21% recovery), dimer of the carbene **4** (22 mg, 46% yield) and phosphine sulfide **5** (11 mg, 7% yield).

Diethyl 2,3-dibenzoylbut-2-enedioate (**4**) [8] [(*E*)-isomer: CAS No. 77249-46-8] [(*Z*)-isomer: CAS No. 60903-90-4]
Pale yellow oil, 22 mg, 46% yield, R_f = 0.55 (PE:EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.54–7.19 (m, 10H), 4.18 (q, *J* = 7.2 Hz, 2H; q, *J* = 7.2 Hz, 0.67H;), 3.94 (q, *J* = 7.1 Hz, 1.33H), 1.17 (t, *J* = 7.2 Hz, 3H; t, *J* = 7.2 Hz, 1H), 0.83 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 164.7, 161.4, 148.6, 147.8, 135.1, 134.8, 132.5, 129.8, 129.2, 129.0, 128.8, 128.6, 127.9, 127.5, 127.4, 127.3, 61.4, 61.13, 61.09, 13.92, 13.90, 13.4. HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd. for $C_{22}H_{20}NaO_6^+$ 403.1152, found 403.1149.

Phosphine sulfide **5** [9] [CAS No. 170656-69-6]
Yellow solid, m.p. 240–250 °C, 11 mg, 7% yield, R_f = 0.4 (PE:EA = 5:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.64–7.58 (m, 8H), *δ* 7.46–7.43 (m, 4H), 7.40–7.36 (m, 8H), 4.64 (dd, *J* = 3.6, 1.6 Hz, 4H), 4.29 (dd, *J* = 4.0, 2.0 Hz, 4H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 134.5, 133.7, 131.5, 131.4, 131.32, 131.29, 128.3, 128.2, 75.04, 74.94, 74.1, 74.0. ^{31}P NMR{^{1}H} (162 MHz, $CDCl_3$) *δ* 40.73. HRMS (ESI-TOF) *m/z* [M+Na]$^+$ calcd. for $C_{34}H_{28}FeNaP_2S_2^+$ 641.0349, found 641.0353.

Decarbonylation of (*E*)-3-(naphthalene-2-yl)propenal (2l)
To an oven-dried 10 mL-vial with a stirrer bar were added (*E*)-3-(naphthalene-2-yl)propenal (**2l**) (0.2 mmol, 36.4 mg), catalyst $[Rh(COD)Cl]_2$ (5 mg, 5 mol%), ligand DPPF (13 mg, 12 mol%), and pre-dried solvent PhCl (1 mL). The vial was sealed with a nitrogen gas balloon. The reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the ensuing mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 20:1, *v*/*v*) to give (*E*)-3-(naphthalene-2-yl)propenal (**2l**) (2 mg, 5% recovery) and 2-vinylnaphthalene (**6**) (28 mg, 91% yield).

2-Vinylnaphthalene (**6**) [10] [CAS No. 827-54-3]
White solid, m.p. 66–67 °C (Lit.[10] 65.5–66 °C), R_f = 0.8 (PE:EA = 10:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.85–7.74 (m, 4H), 7.64 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.50–7.42 (m, 2H), 6.89 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.34 (d, *J* = 10.9 Hz, 1H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) *δ* 136.9, 135.0, 133.1, 128.1, 128.0, 127.7, 126.3, 126.2, 125.9, 123.2, 114.2, 100.0.

8. Isotope Tracing Experiments

To an oven-dried 10 mL-vial with a stirrer bar were added 1,2,3-thiadiazole **1a** (0.2 mmol, 46 mg), catalyst $[Rh(COD)Cl]_2$ (5 mg, 5 mol%), ligand DPPF (13.3 mg, 12 mol%), and pre-dried solvent PhCl (1 mL). The vial was sealed with a nitrogen gas balloon, then alk-2-enal (**2g**-*d*) (0.4 mmol, 53.2 mg) was added. The reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the ensuing mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA 5:1~20:1, *v*/*v*) to give 2,3-dihydro-4*H*-thiopyran-4-one **3ag**-*dh* as brown oil in 85% yield.

Ethyl 4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate-3-*d* (**3ag**-*d/h*)
Brown oil, 57 mg, 85% yield, R_f = 0.3 (PE:EA = 10:1, *v*/*v*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.49 (m, 2H), 7.47–7.32 (m, 8H), 4.83–4.79 (m, 1H), 4.08–3.96 (m, 2H), 3.23 (dd, *J* = 15.2, 15.2 Hz, 0.8H), 3.04 (dd, *J* = 16.0, 3.0 Hz, 0.8H), 0.94 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$) δ 191.06, 191.03, 165.8, 162.0, 136.9, 136.1, 130.7, 129.1, 128.8, 128.5, 127.9, 127.4, 61.2, 46.22, 46.15, 43.6, 13.6. HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd. for $C_{20}H_{18}DO_3S^+$ 340.1112, found 340.1116.

9. KIE Studies

To two oven-dried 10 mL-vials with stirrer bars each were added 1,2,3-thiadiazole **1a** (0.25 mmol, 58.6 mg), catalyst $[Rh(COD)Cl]_2$ (6.2 mg, 5 mol%), ligand DPPF (16.6 mg, 12 mol%), and pre-dried solvent PhCl (1 mL). The vials were sealed with nitrogen gas balloons, then alk-2-enal **2g**-*d* (0.5 mmol, 67 mg) and **2g** (0.5 mmol, 66 mg) were added, respectively. When the reaction mixtures were stirred and heated at 130 °C in an oil-bath for 5 min, a small portion of the reaction mixtures was taken out from reactions 1 and 2 for ^{1}HNMR analysis. Samples of 10 min, 15 min, 20 min, 30 min, 40 min, 50 min and 60 min were made by the same procedure.

Table S3. ^{1}HNMR analysis for reactions 1 and 2

Entry	Time (min)	Yield of **3ag** (%) (Reaction 2)	Yield of **3ag**-*d* (%) (Reaction 1)
1	5 min	12	30
2	10 min	17	39
3	15 min	20	48
4	20 min	28	52
5	30 min	30	59
6	40 min	38	60
7	50 min	44	64
8	60 min	49	65

10. Gram-scale reaction

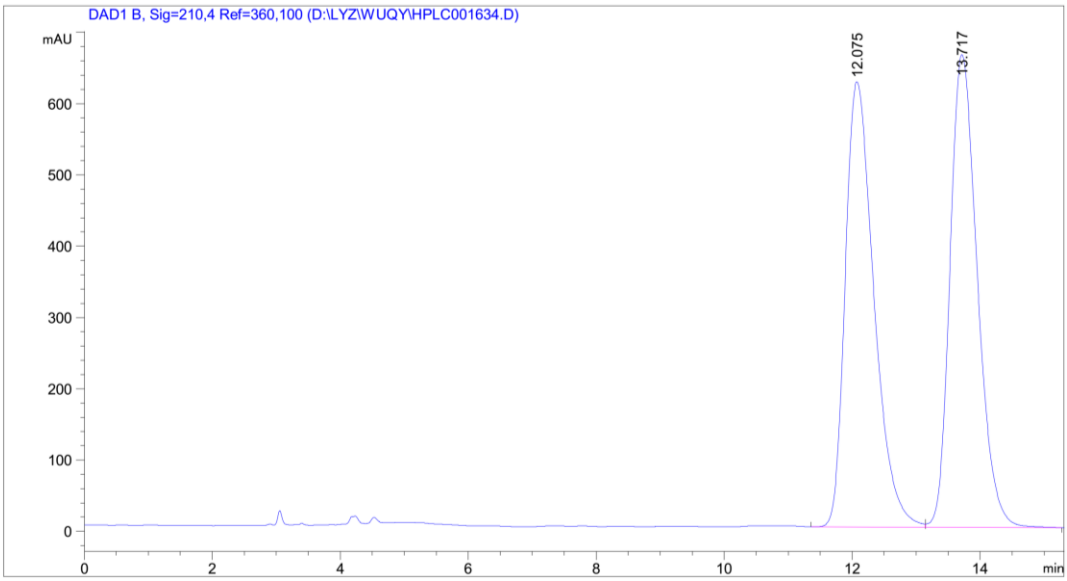
Ethyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1a**) (5 mmol, 1.17g), $[Rh(COD)]_2Cl_2$ (123 mg, 0.25 mmol), and DPPF (333 mg, 0.6 mmol) were added into a three-neck round bottom flask. The flask was equipped with a condenser tube and then sealed with N_2 balloon. PhCl (20 mL) and cinnamaldehyde (**2g**) (10 mmol, 1.32 g) were added. The reaction mixture was then heated in an oil bath at 130 °C for 6 h. After removal of solvent under reduced pressure the residue was purified by silica gel column chromatography (PE/EA = 10:1, *v*/*v*). The product ethyl 4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ag**) was obtained in 1.27 g, 75 % yield.

11. Trials on asymmetric catalysis

(*i*) To an oven-dried 10 mL-vial with a stirring bar were added 1,2,3-thiadiazole **1a** (0.1 mmol, 23.4 mg), catalyst $[Rh(COD)Cl]_2$ (2.5 mg, 5 mol%), ligand (*R*)-BINAP (7.5 mg, 12 mol%) and pre-dried solvent PhCl (0.5 mL). The vial was sealed with a nitrogen gas balloon, then alkenyl aldehyde **2h** (0.2 mmol, 30 mg) was added via a syringe. The reaction mixture was kept stirring at 130 °C in an oil-bath for 6 h. After the reaction mixture was cooled to room temperature, the solvent was removed by rotary evaporation. The resulting residue was purified by silica gel column chromatography (PE/EA = 5:1, *v/v*) to give desired product **3ah** in 17% yield (6 mg). HPLC analysis: Daicel Chiralpak AS-H (*i*-PrOH/hexane = 15/85, *v*/*v*, 1.0 mL/min, 210 nm) major t_R = 12.009 min and 13.647 min.

(*ii*) The same procedure as above but using (*S*)-BINAP (7.5 mg, 12 mol%) as ligand gave desired product **3ah** in 6% yield (2 mg). HPLC analysis: Daicel Chiralpak AS-H (*i*-PrOH/hexane = 15/85, *v*/*v*, 1.0 mL/min, 210 nm) major t_R = 12.042 min and 13.661 min.

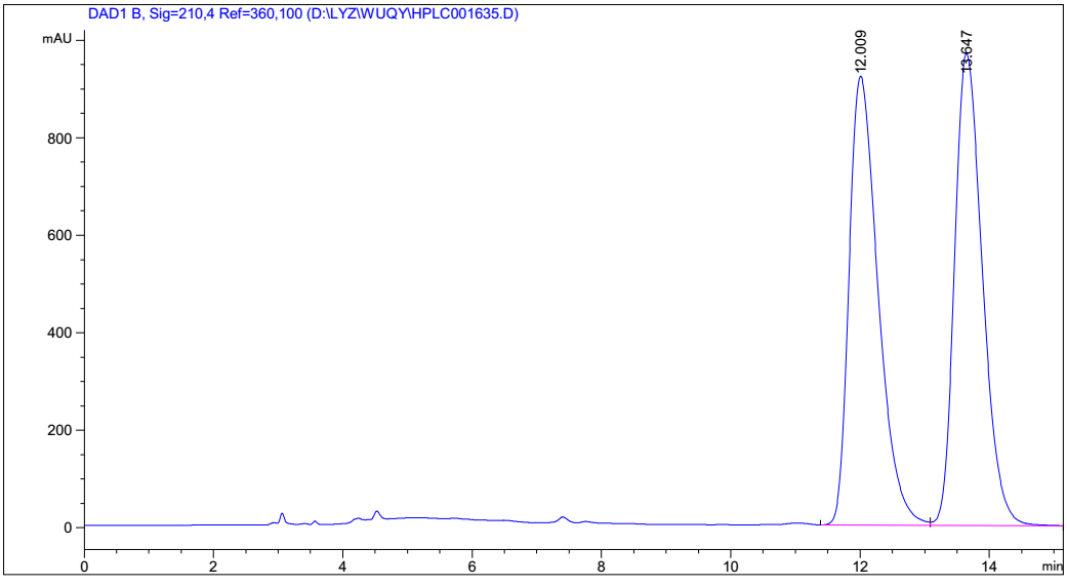
HPLC data of the product obtained using **DPPF** ligand.
Daicel Chiralpak AS-H (*i*-PrOH/hexane = 15/85, *v*/*v*, 1.0 mL/min, 210 nm)



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.075	BV	0.4789	1.94317e4	624.64917	49.7630
2	13.717	VBA	0.4592	1.96168e4	662.95557	50.2370

HPLC data of the product obtained using **(*R*)-BINAP ligand**.

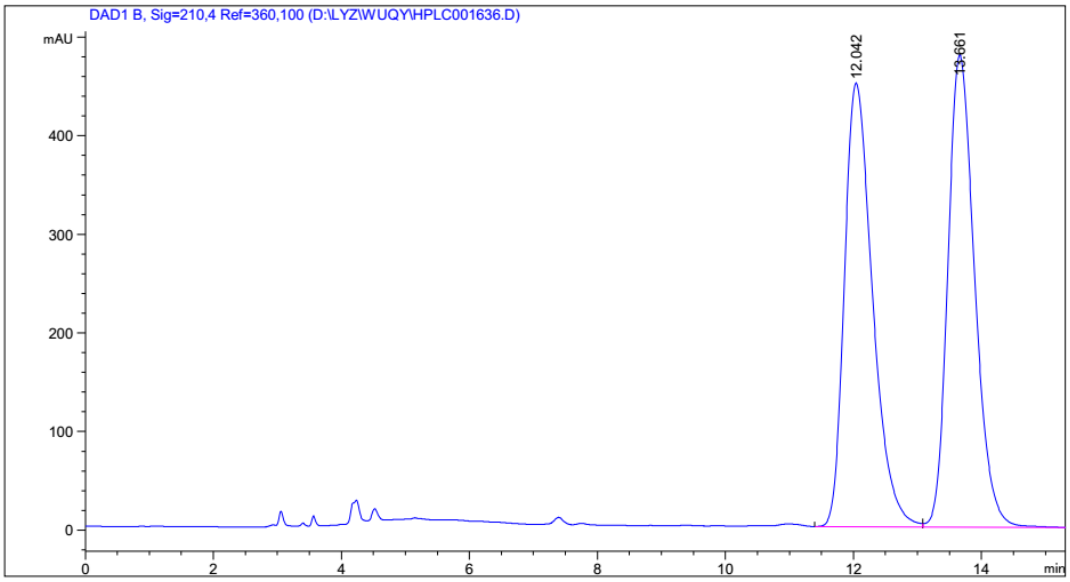
Daicel Chiralpak AS-H (*i*-PrOH/hexane = 15/85, *v*/*v*, 1.0 mL/min, 210 nm)



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.009	BV	0.4814	2.86749e4	920.63379	49.7789
2	13.647	VBA	0.4647	2.89297e4	967.89911	50.2211

HPLC data of the product obtained using **(*S*)-BINAP** ligand.

Daicel Chiralpak AS-H (*i*-PrOH/hexane = 15/85, *v*/*v*, 1.0 mL/min, 210 nm)



Peak #	Ret. Time [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.042	BV	0.4696	1.37233e4	450.22104	49.6819
2	13.661	VBA	0.4485	1.38990e4	478.99881	50.3181

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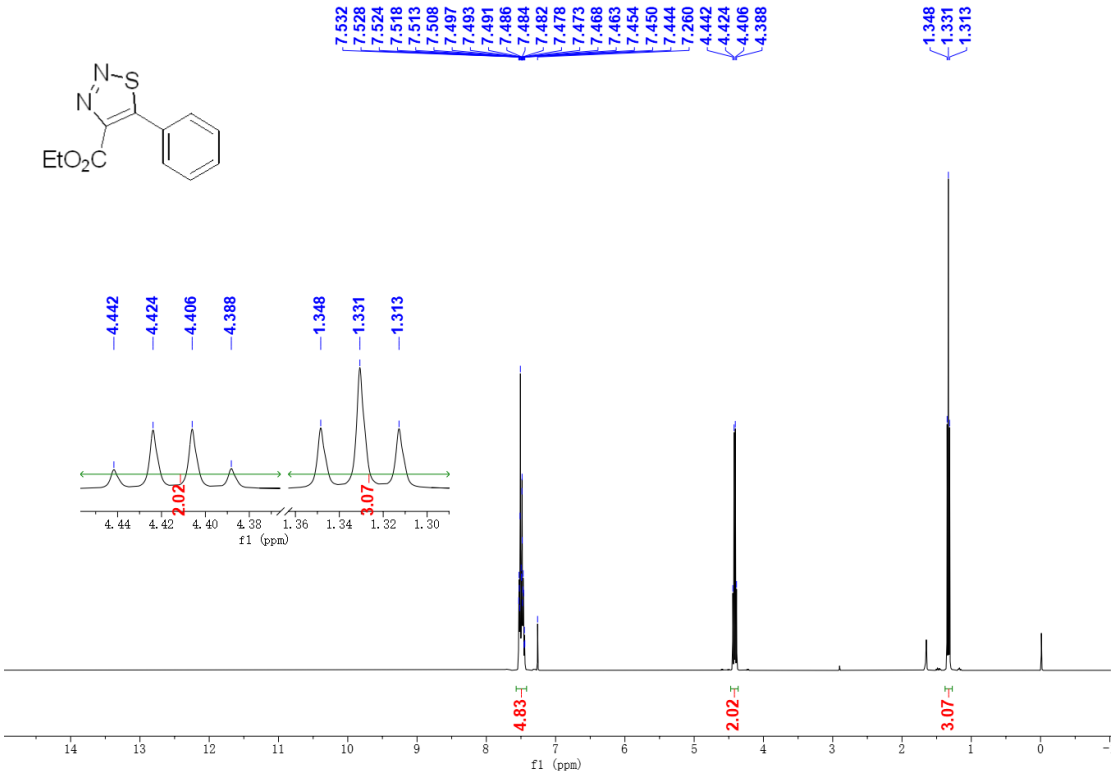
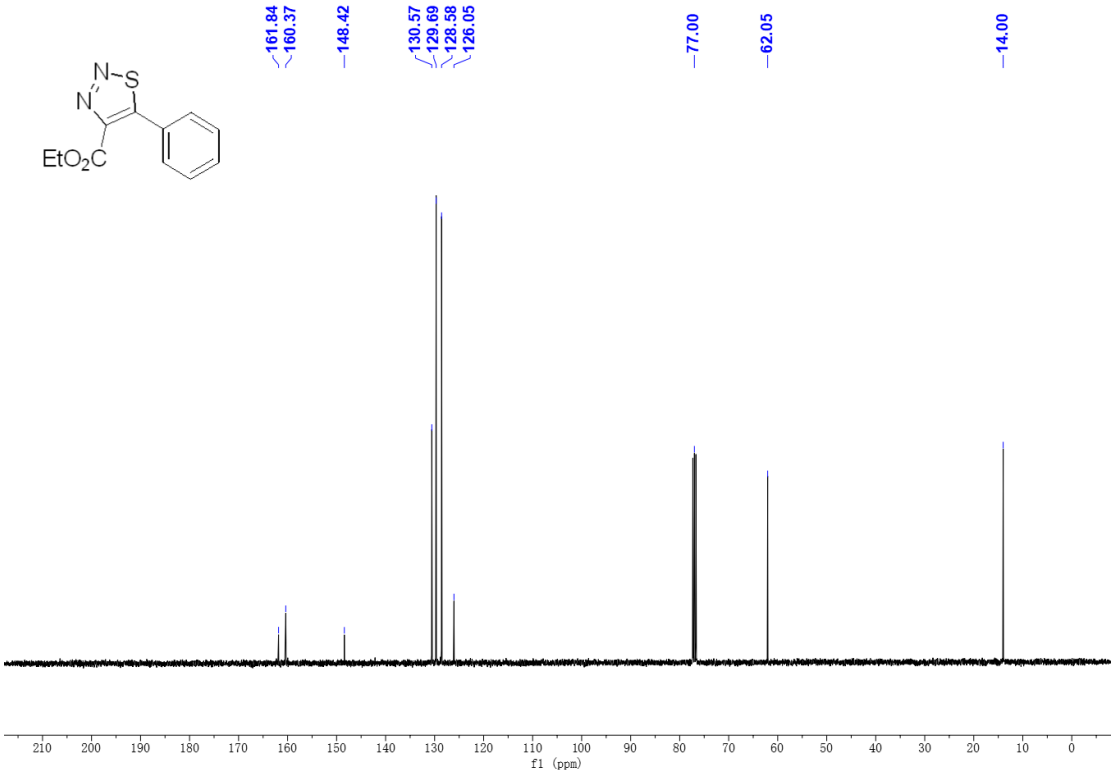
13. Copies of Spectra of Materials, Intermediates, and Products

Ethyl 5-phenyl-1,2,3-thiadiazole-4-carboxylate (**1a**)

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



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



Ethyl 5-(benzo[*d*][1,3]dioxol-5-yl)-1,2,3-thiadiazole-4-carboxylate (**1b**)

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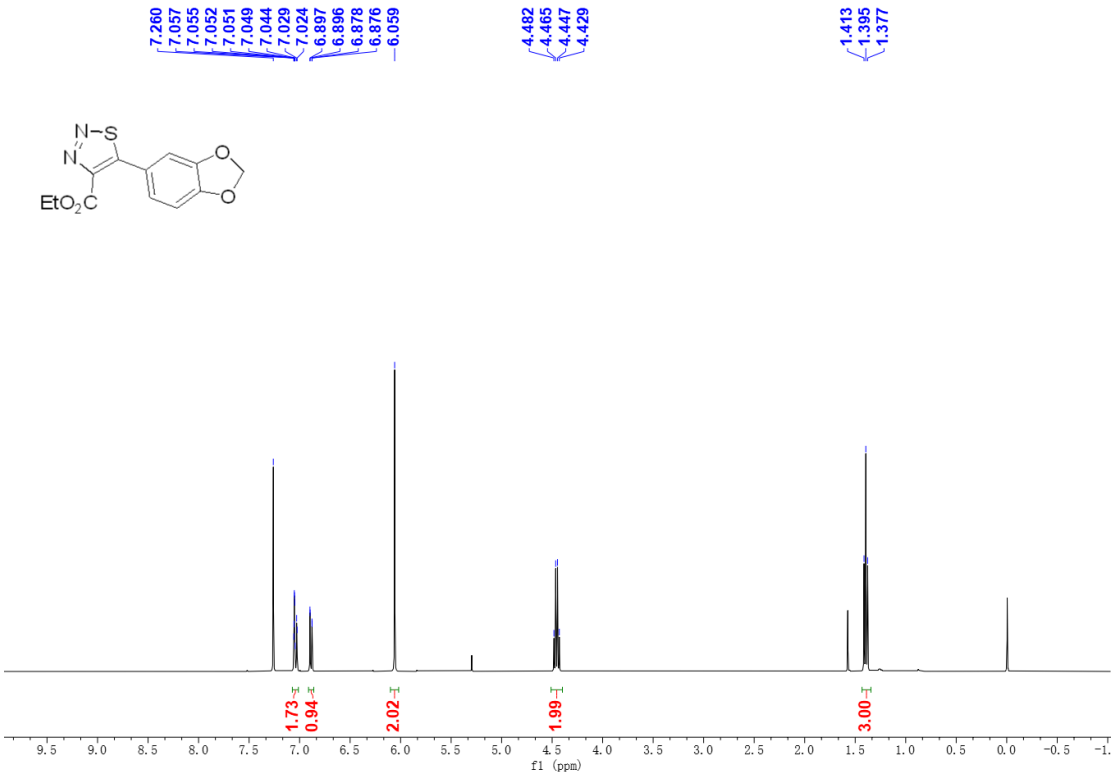

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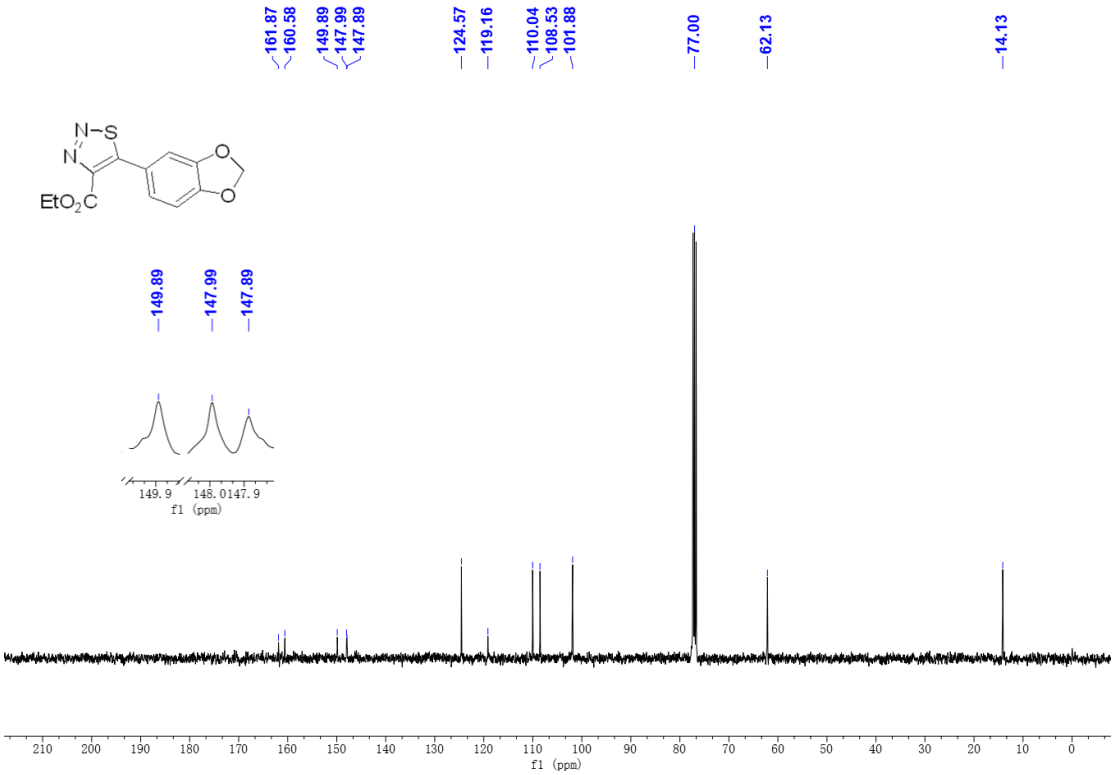

Ethyl 5-(4-methoxyphenyl)-1,2,3-thiadiazole-4-carboxylate (**1c**)

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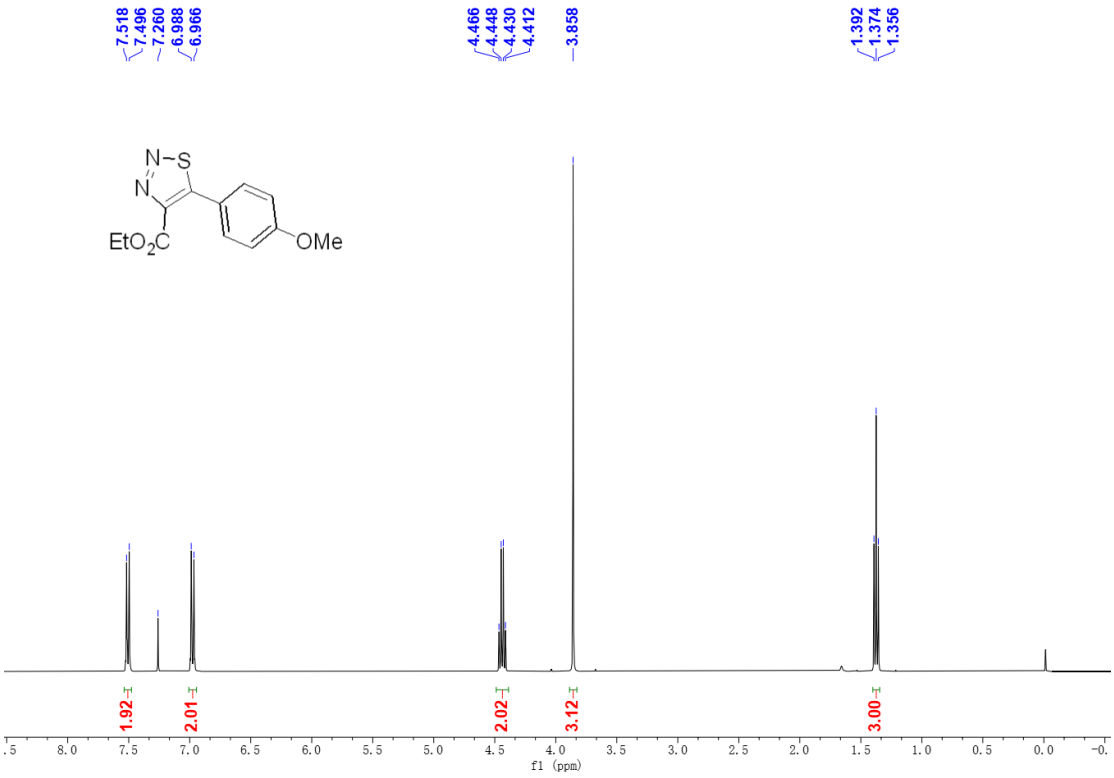

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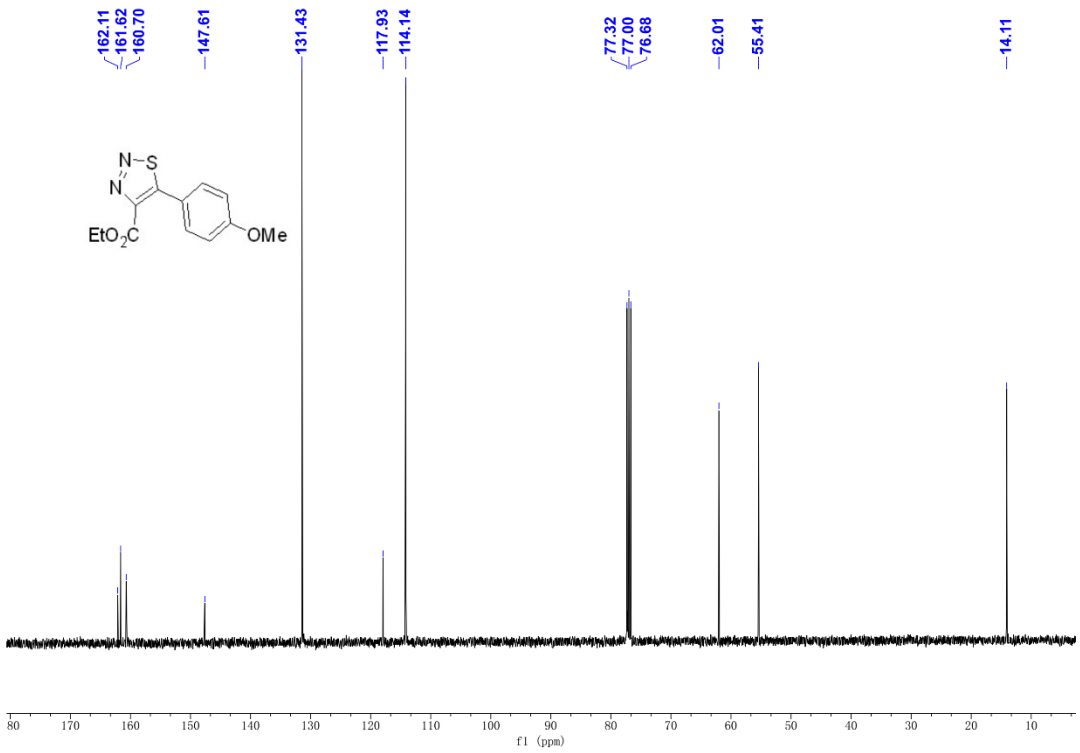

Ethyl 5-(4-methylphenyl)-1,2,3-thiadiazole-4-carboxylate (**1d**)

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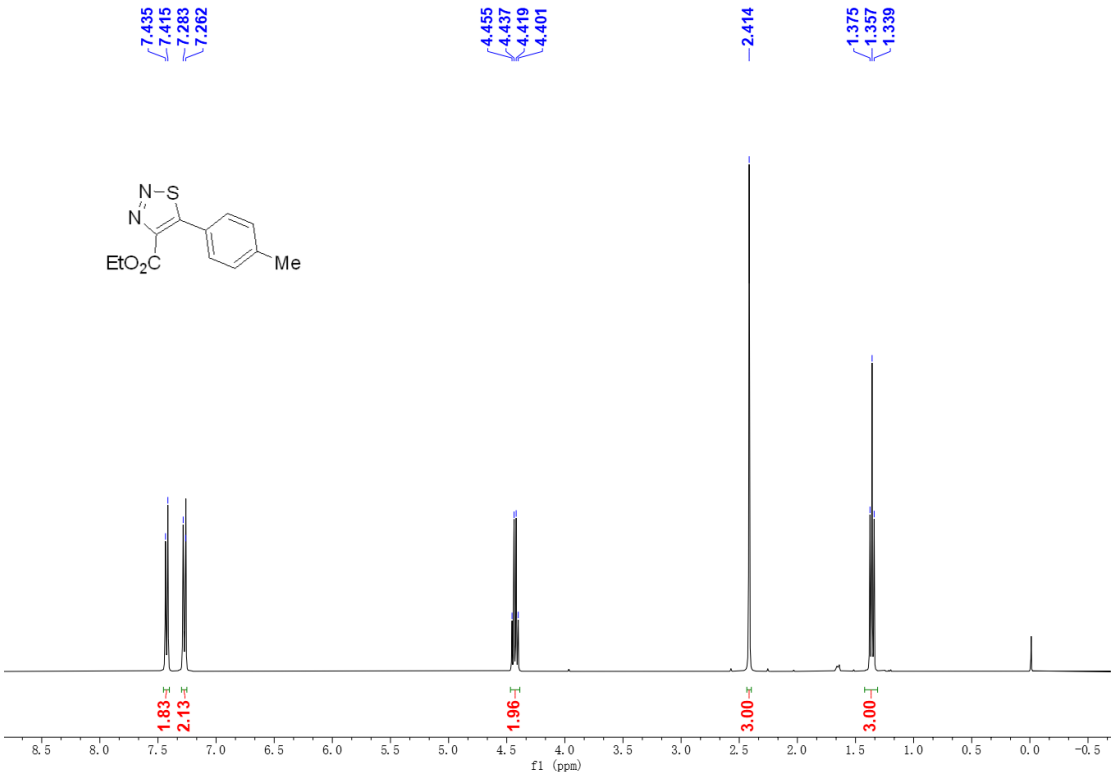
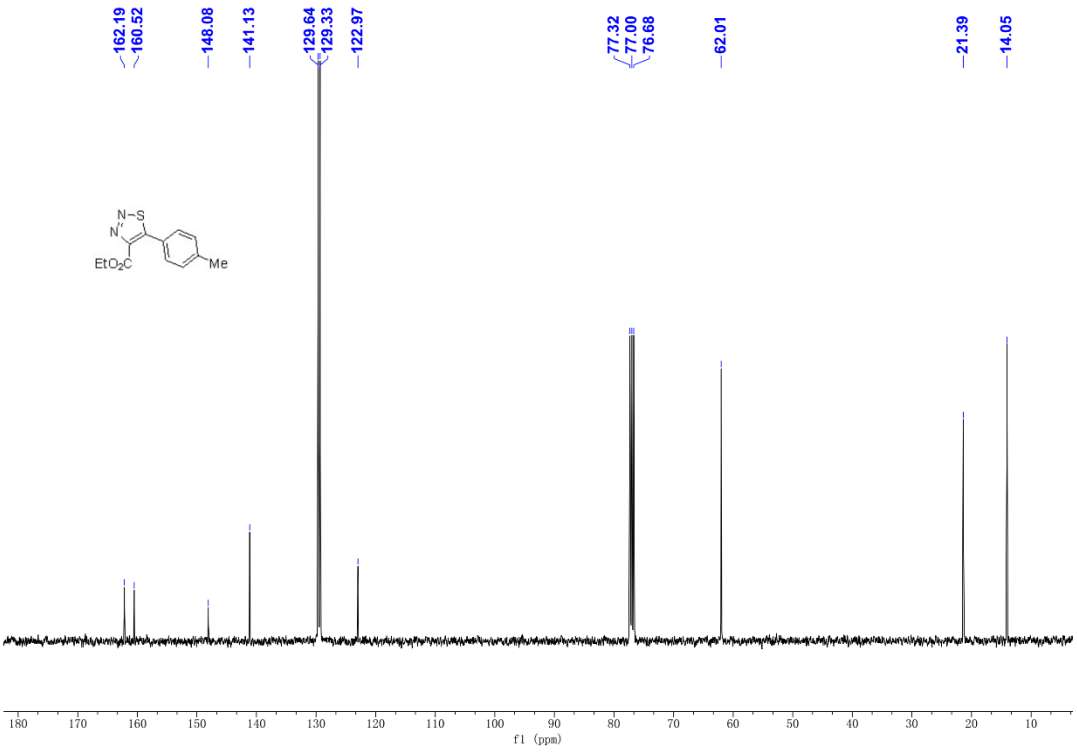


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



Ethyl 5-(4-fluorophenyl)-1,2,3-thiadiazole-4-carboxylate (**1e**)

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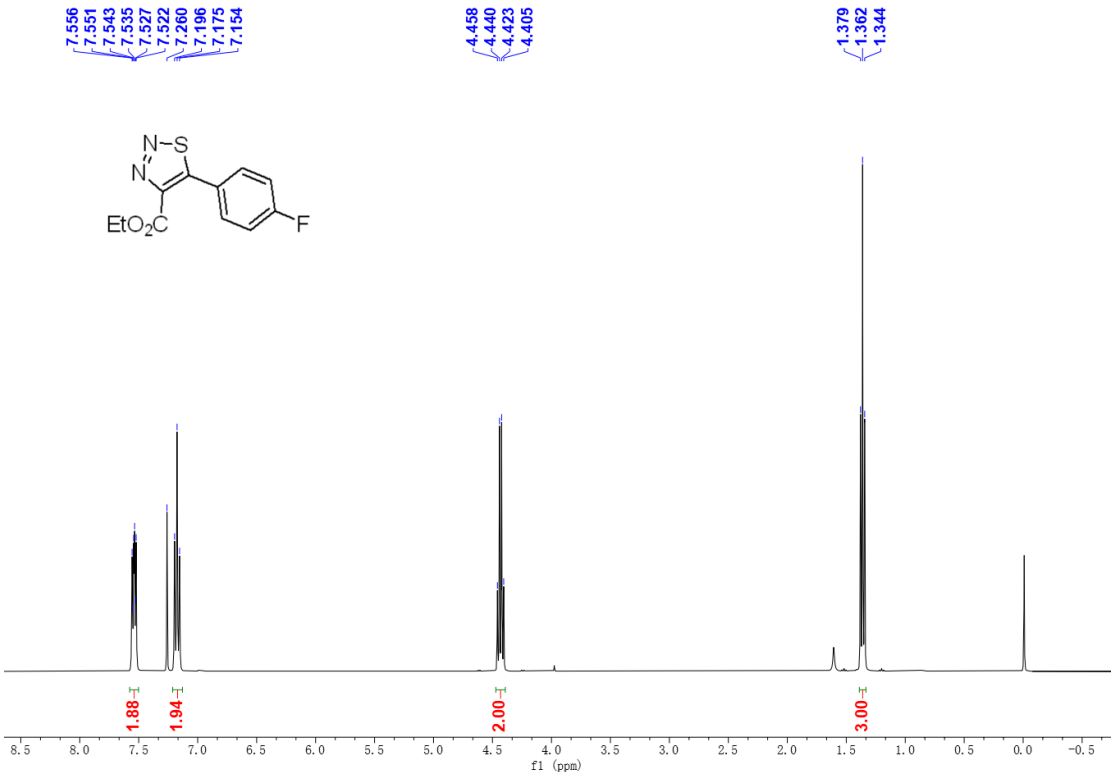
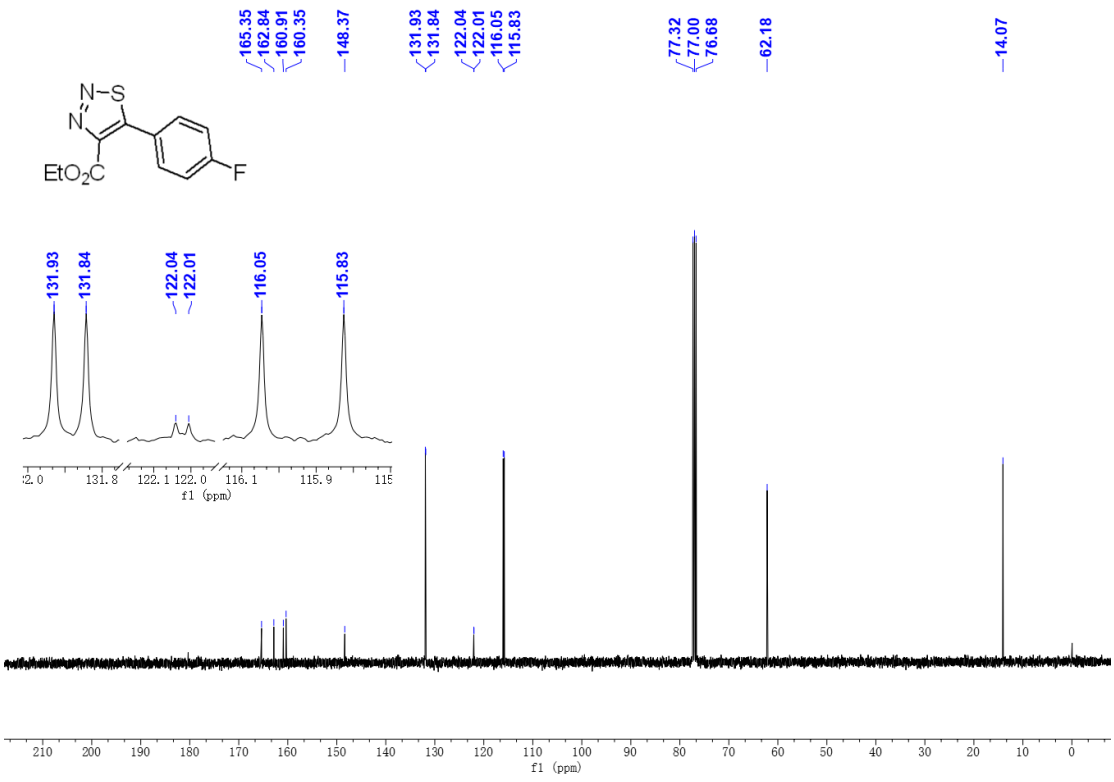
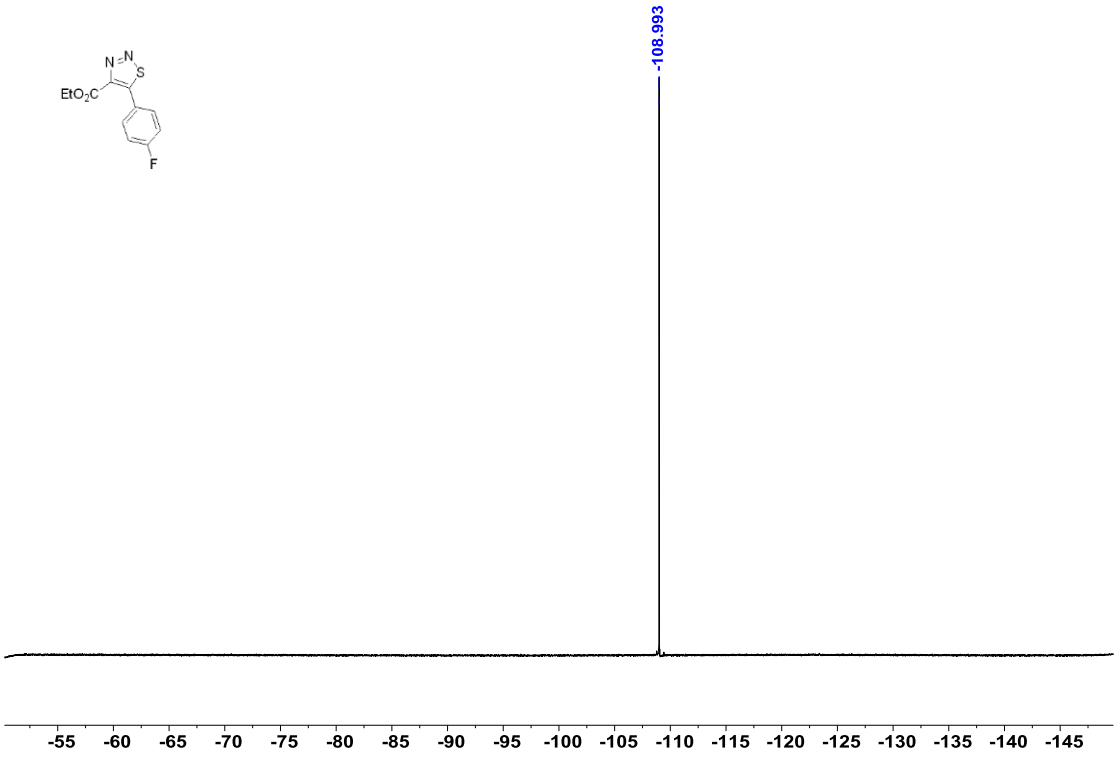


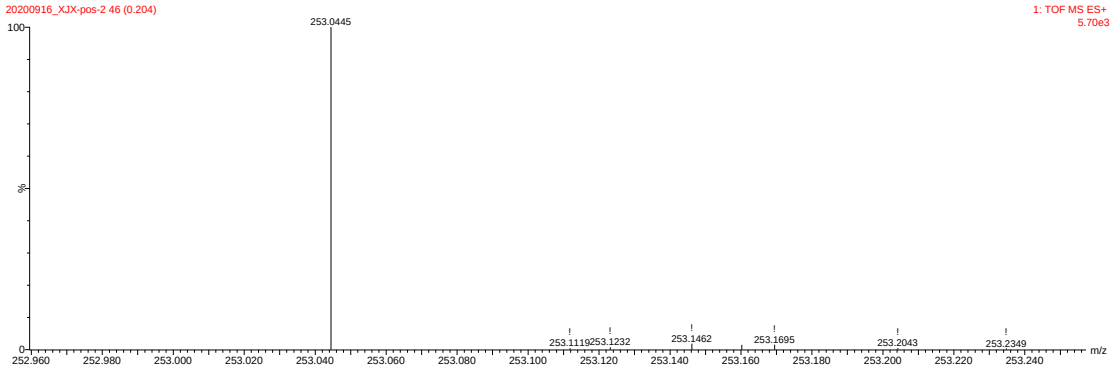
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



^{19}F NMR{^{1}H } (376 MHz, $CDCl_3$)

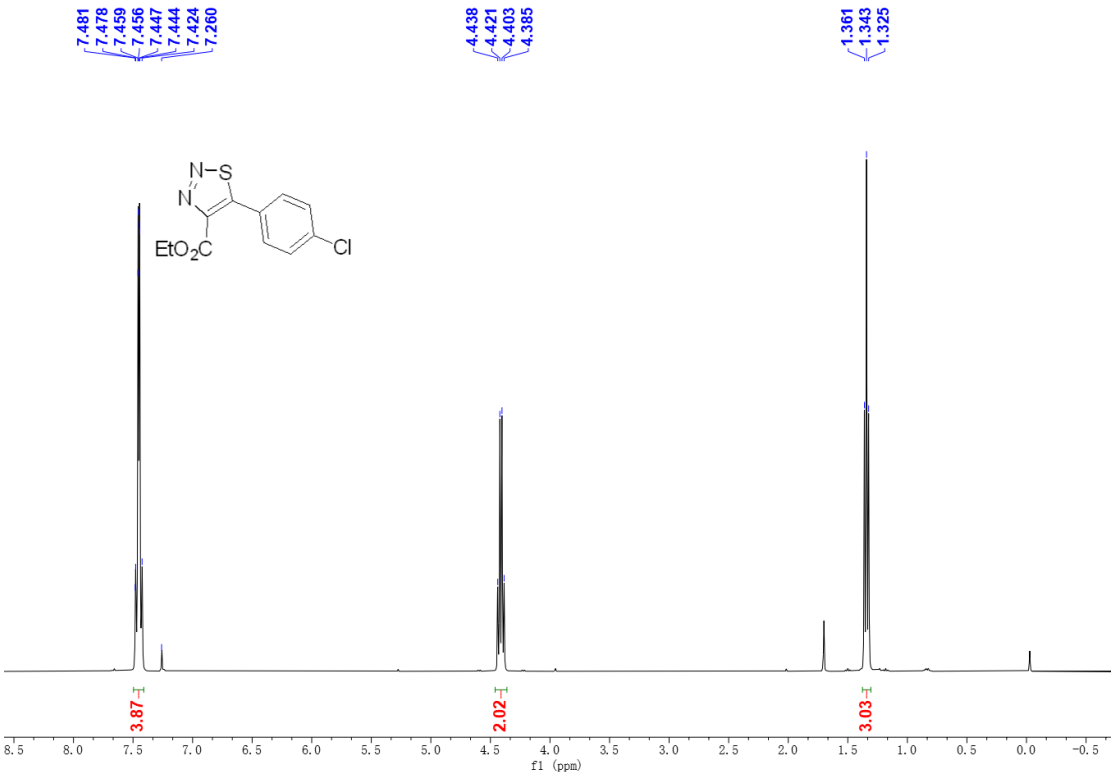


HRMS

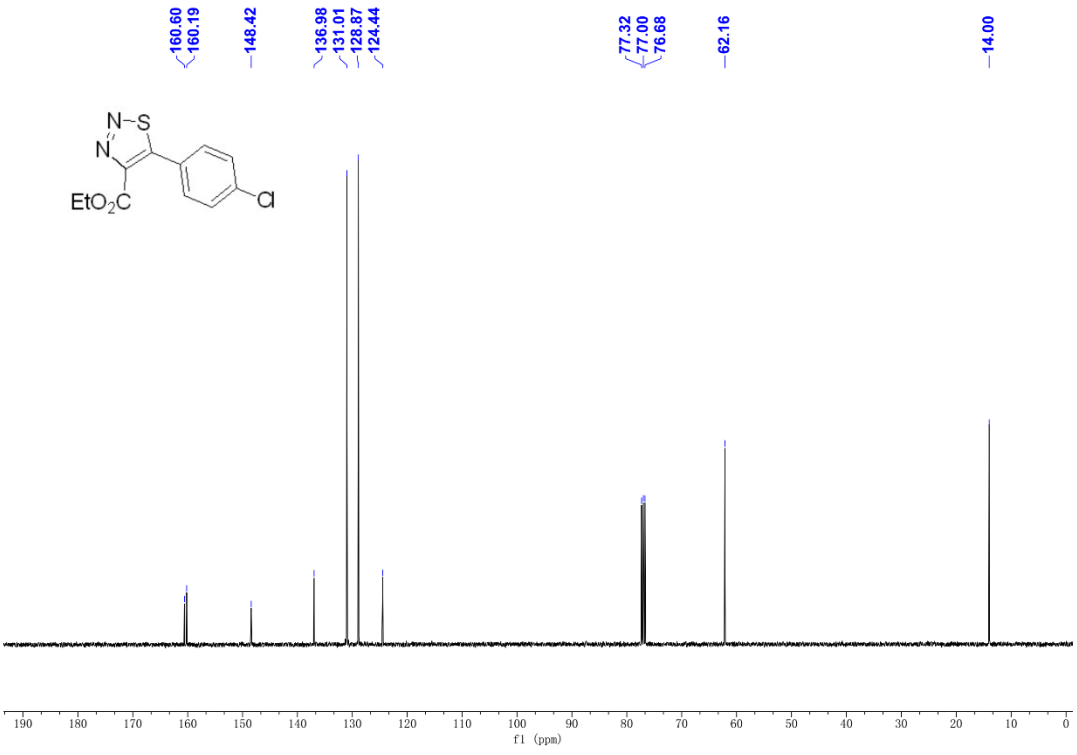


Ethyl 5-(4-chlorophenyl)-1,2,3-thiadiazole-4-carboxylate (**1f**)

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



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



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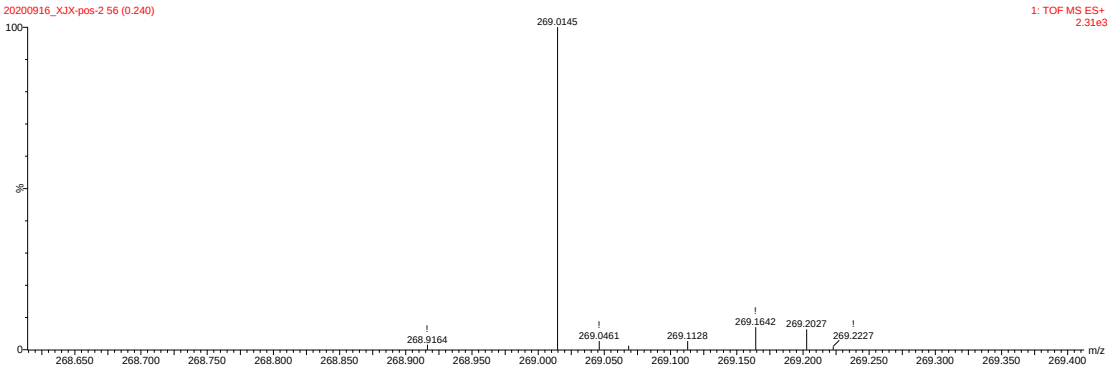
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m/z
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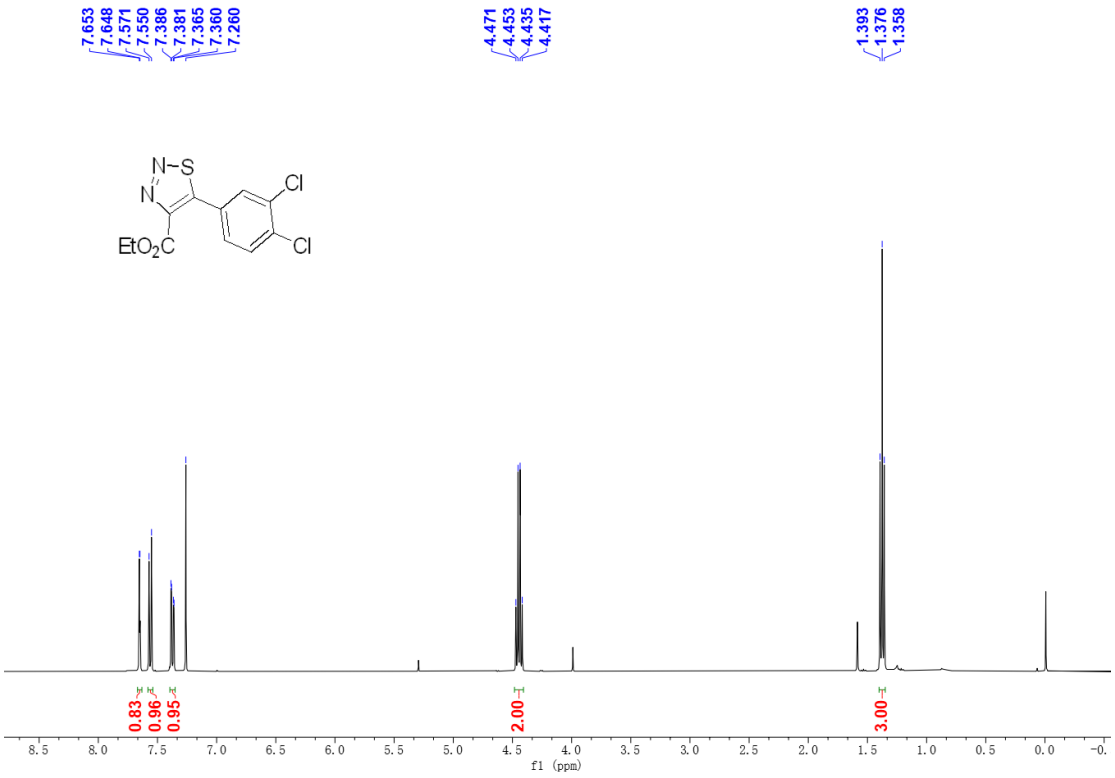
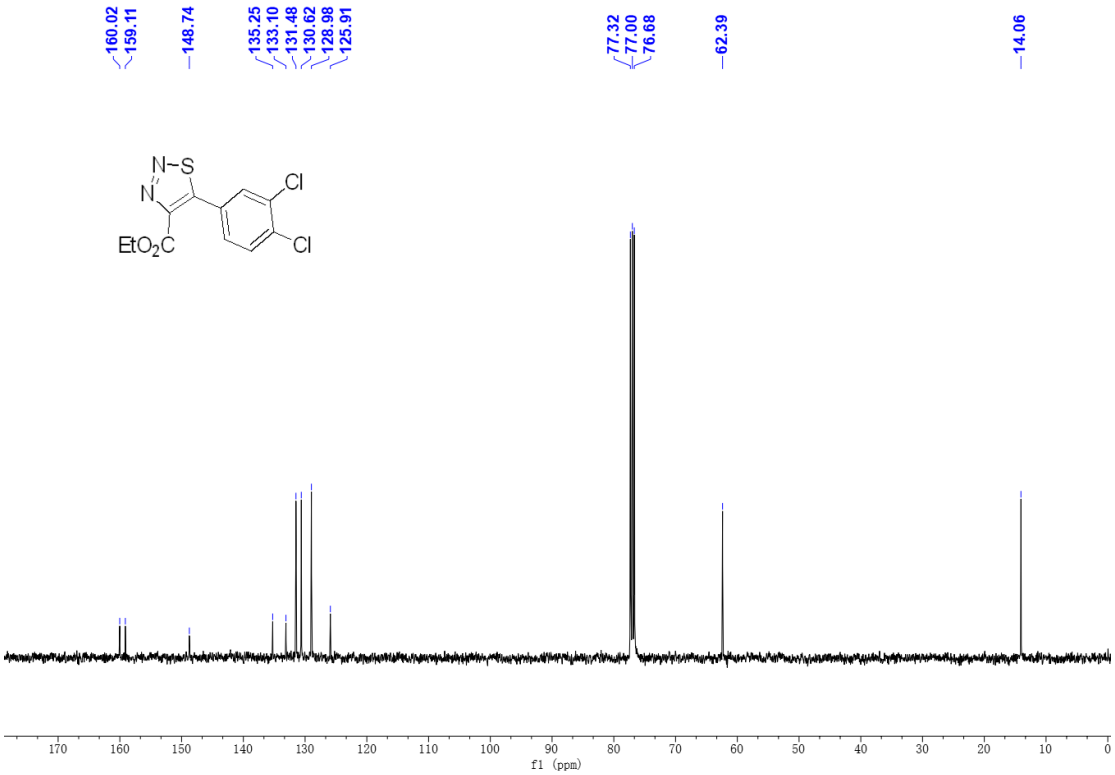
268.700
268.750
268.800
268.850
268.900
268.950
269.000
269.050
269.100
269.150
269.200
269.250
269.300
269.350
269.400

Ethyl 5-(3,4-dichlorophenyl)-1,2,3-thiadiazole-4-carboxylate (**1g**)

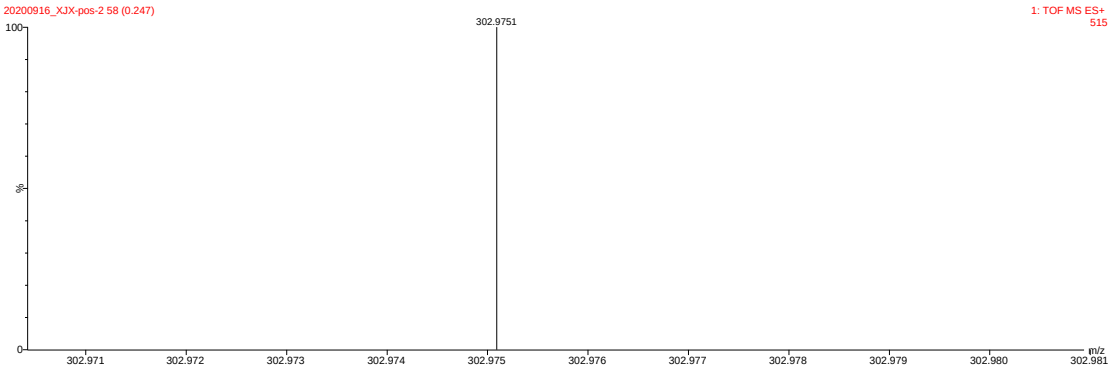
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

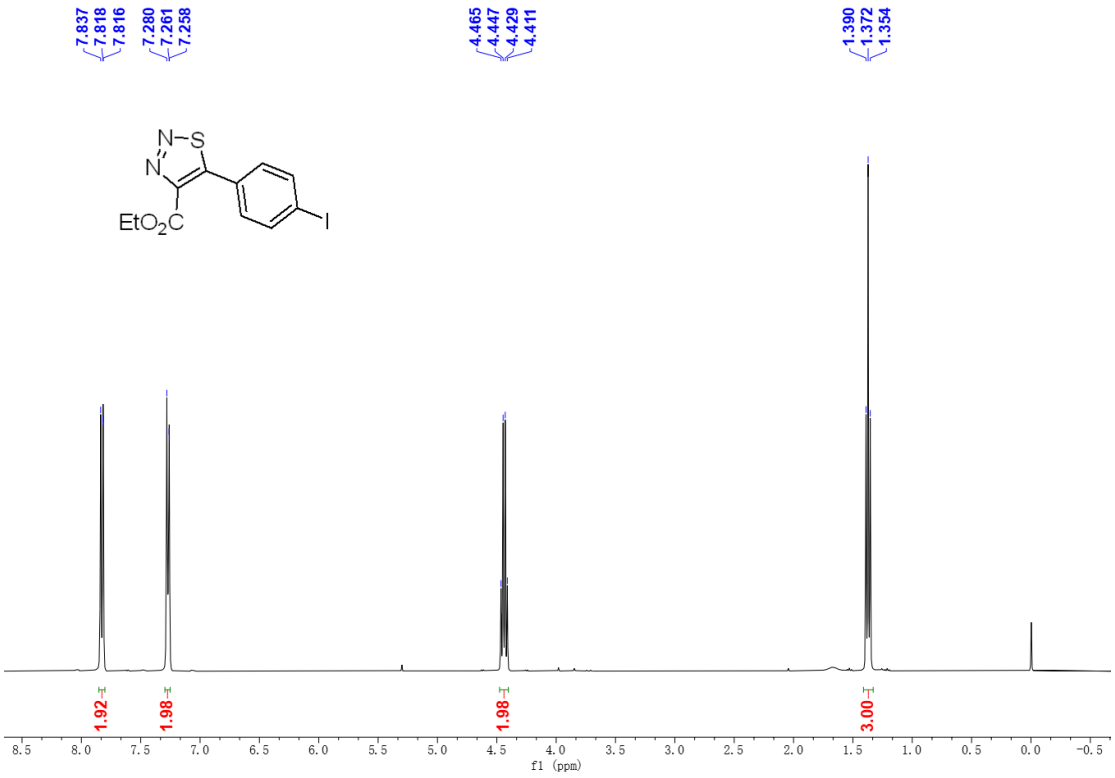


HRMS

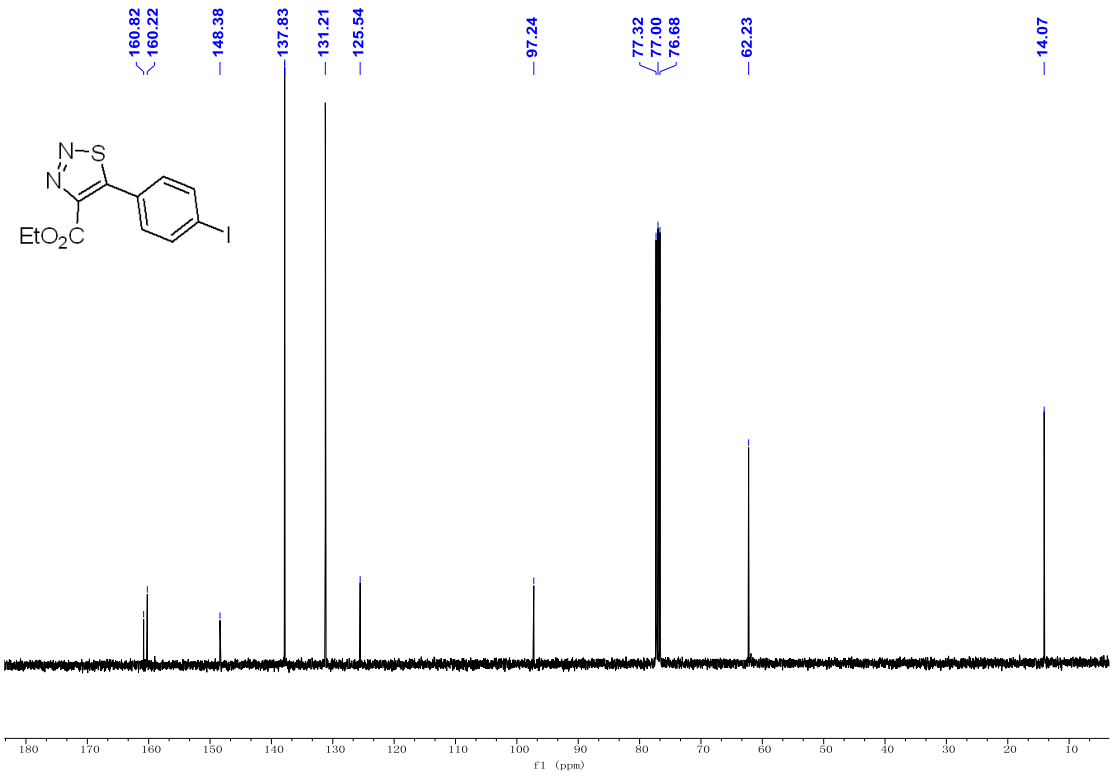

20200916_XJX-pos-2 58 (0.247)
1: TOF MS ES+
515
302.9751
100
%
0
302.971
302.972
302.973
302.974
302.975
302.976
302.977
302.978
302.979
302.980
302.981
m/z

Ethyl 5-(4-iodophenyl)-1,2,3-thiadiazole-4-carboxylate (**1h**)

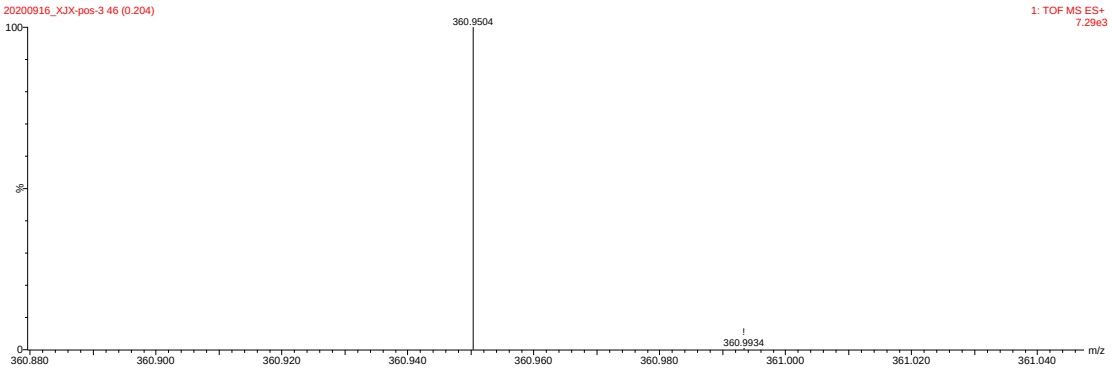
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



HRMS


20200916_XJX-pos-3 46 (0.204)
1: TOF MS ES+
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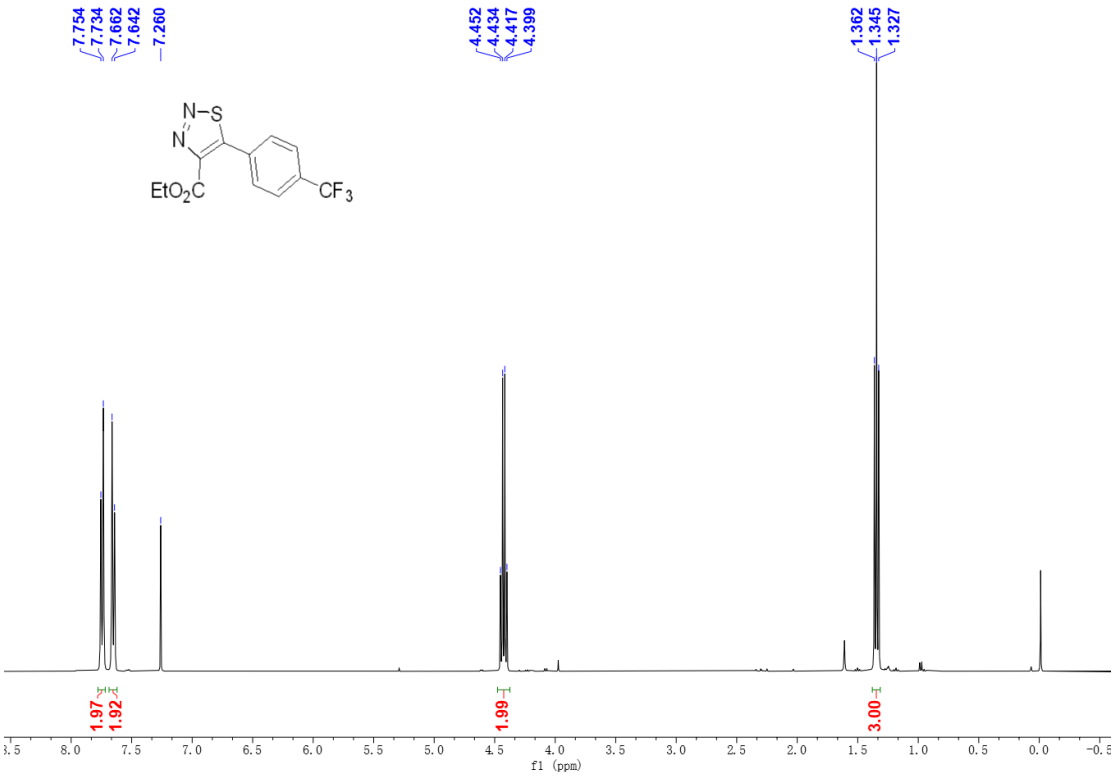
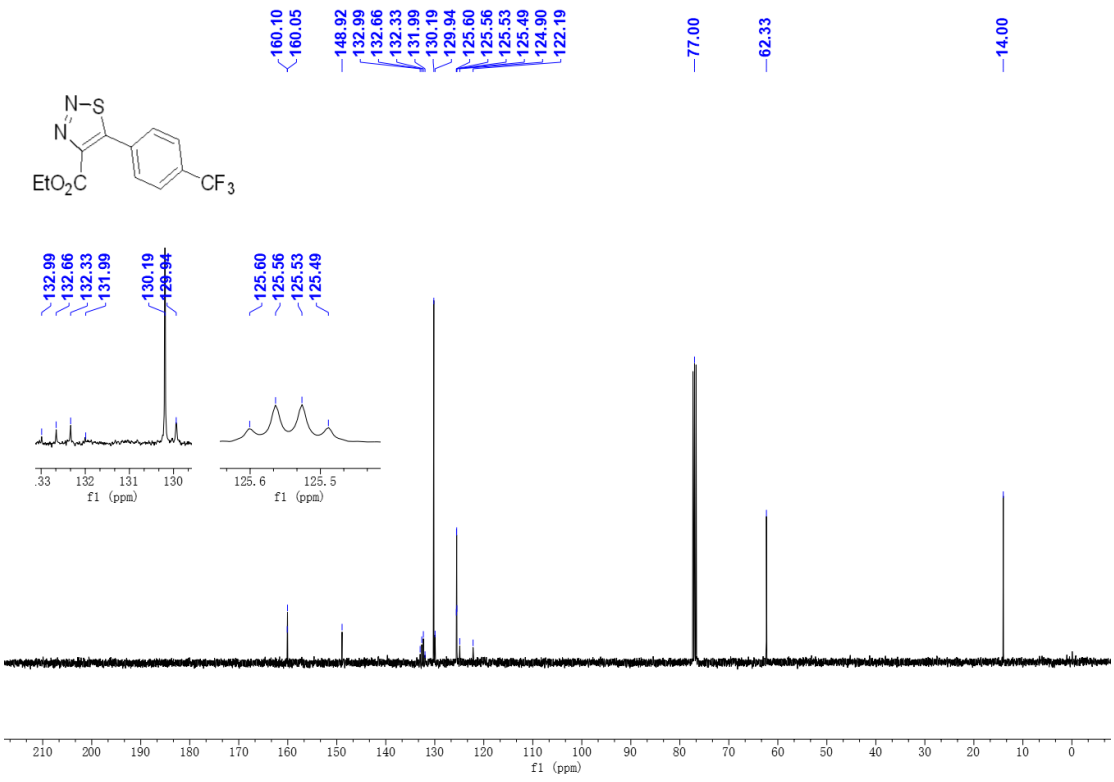
100
%
0
360.9504
360.9934
360.880
360.900
360.920
360.940
360.960
360.980
361.000
361.020
361.040
m/z

Ethyl 5-(4-(trifluoromethyl)phenyl)-1,2,3-thiadiazole-4-carboxylate (**1i**)

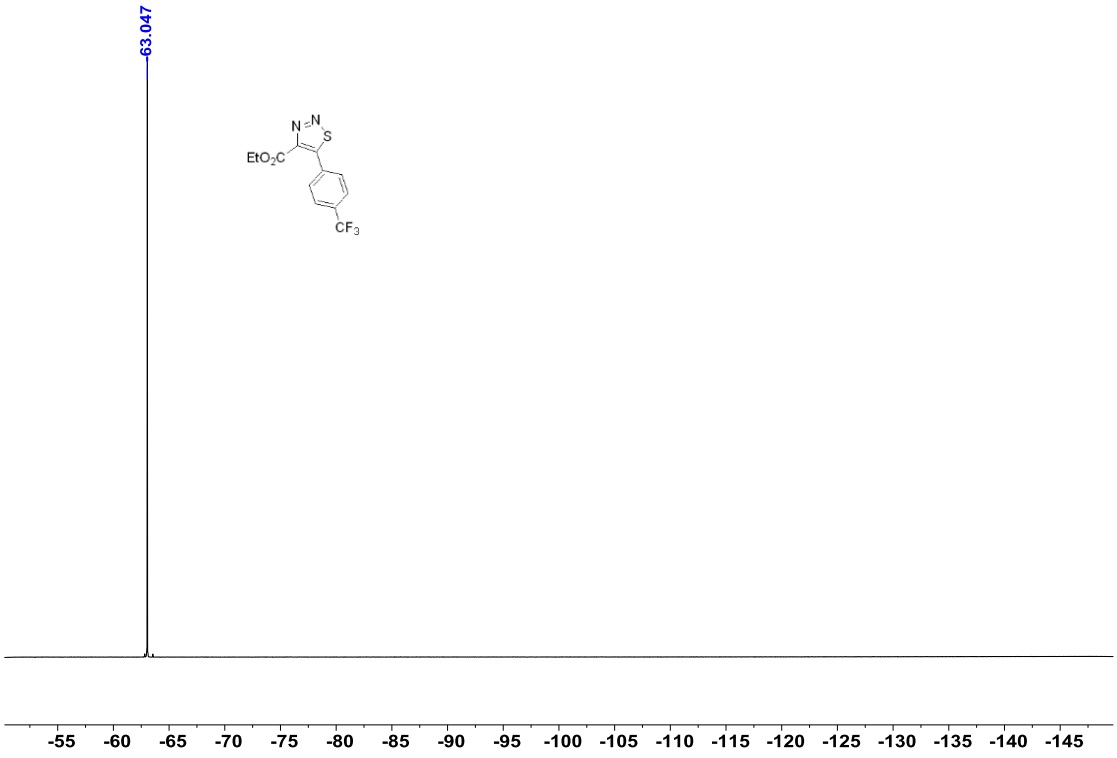
^{1}H MNR (400 MHz, $CDCl_3$)



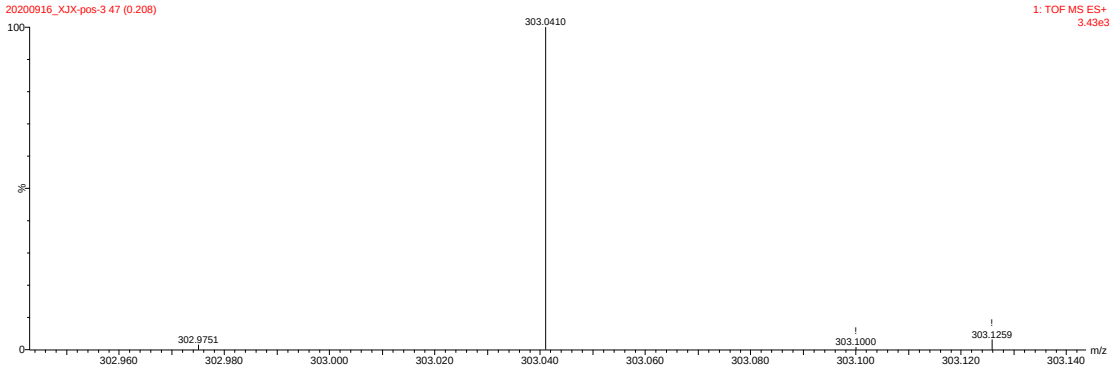
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



^{19}F NMR{^{1}H } (376 MHz, $CDCl_3$)

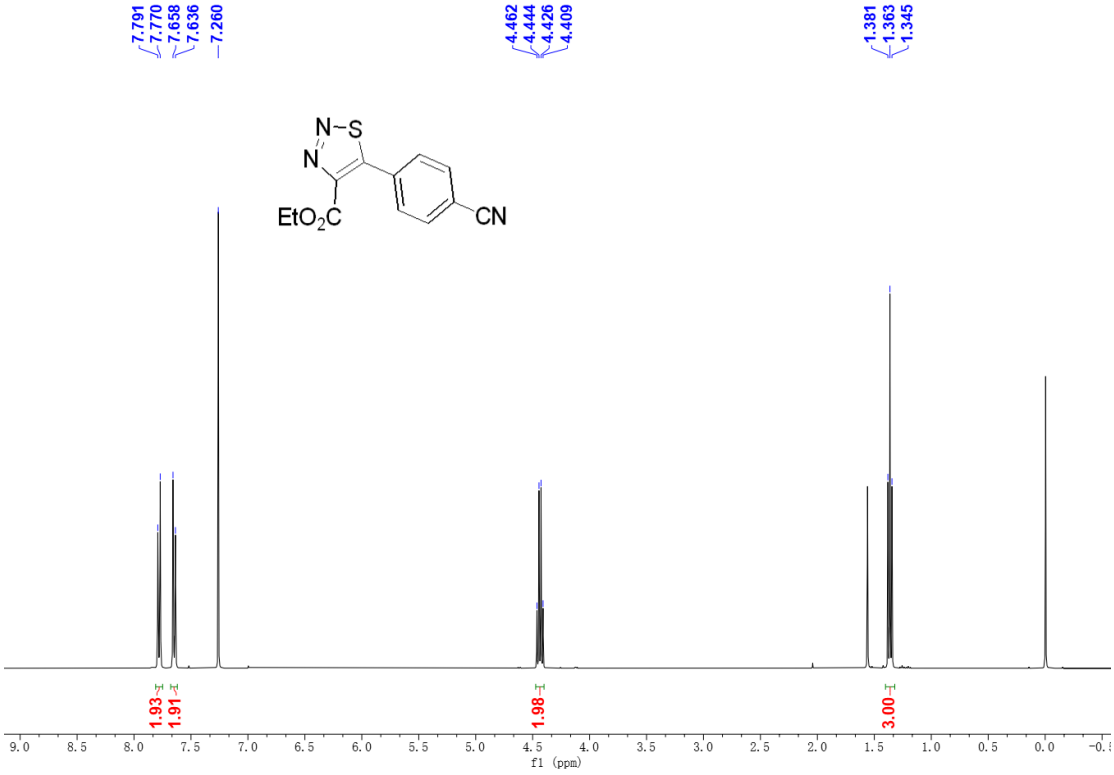


HRMS

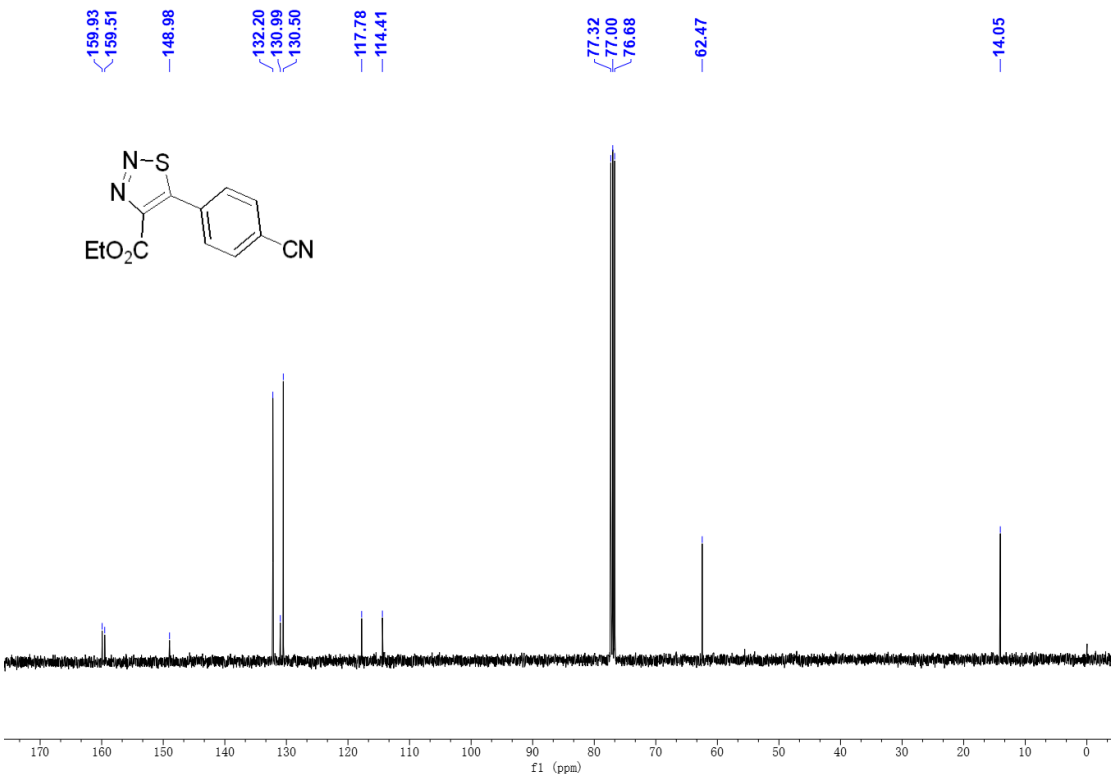


Ethyl 5-(4-cyanophenyl)-1,2,3-thiadiazole-4-carboxylate (**1j**)

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

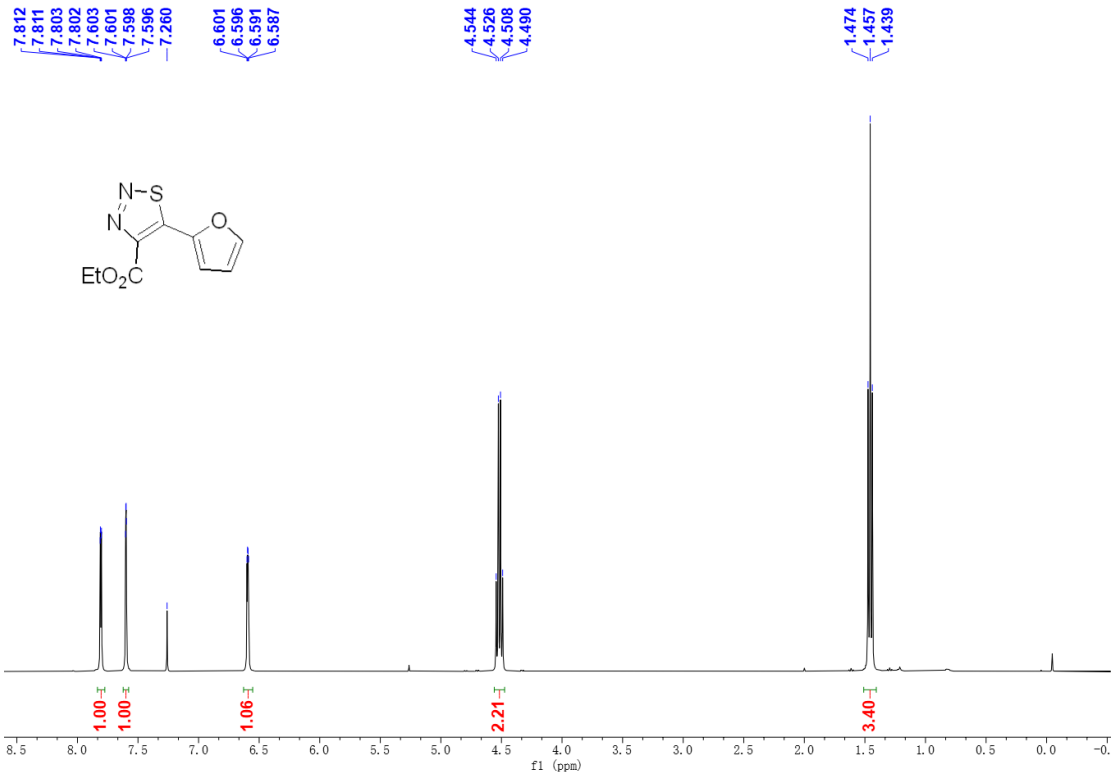


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

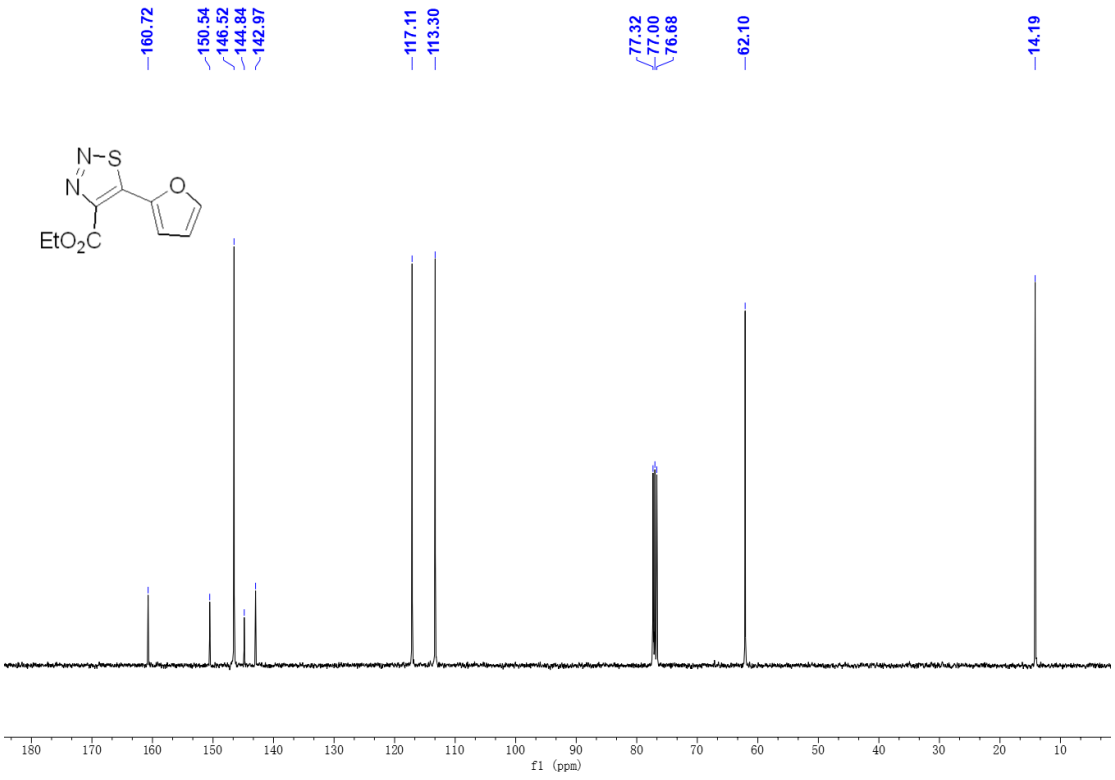


Ethyl 5-(furan-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1k**)

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

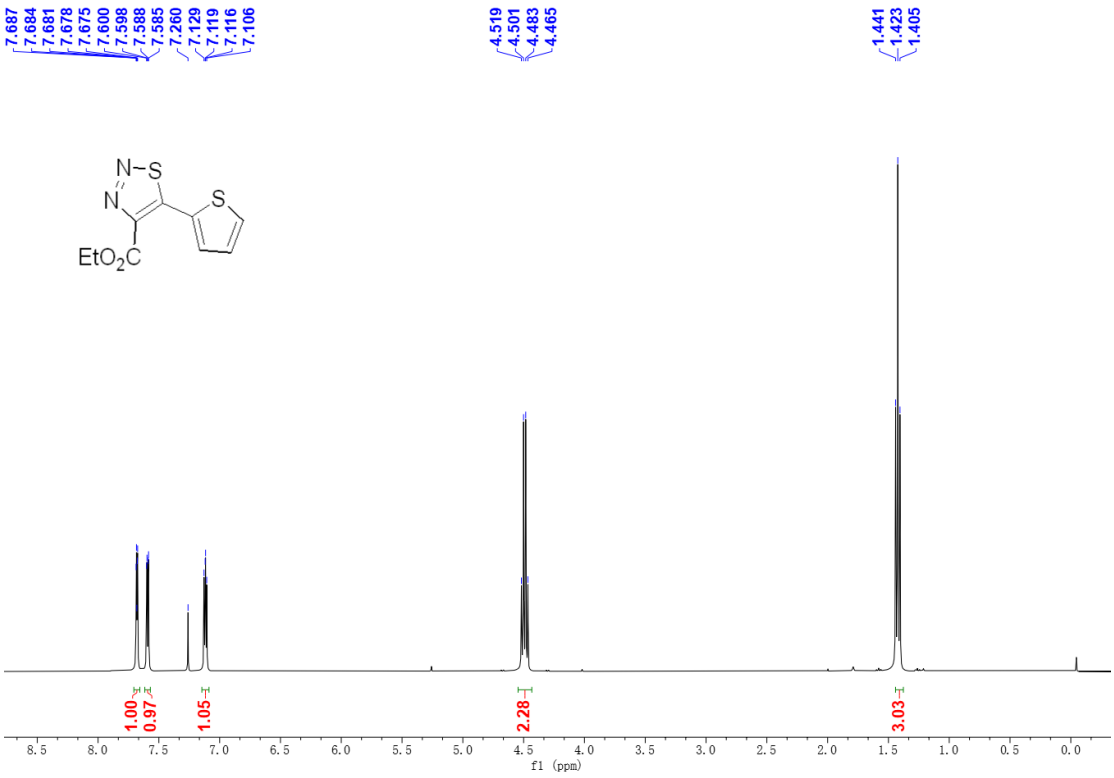


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

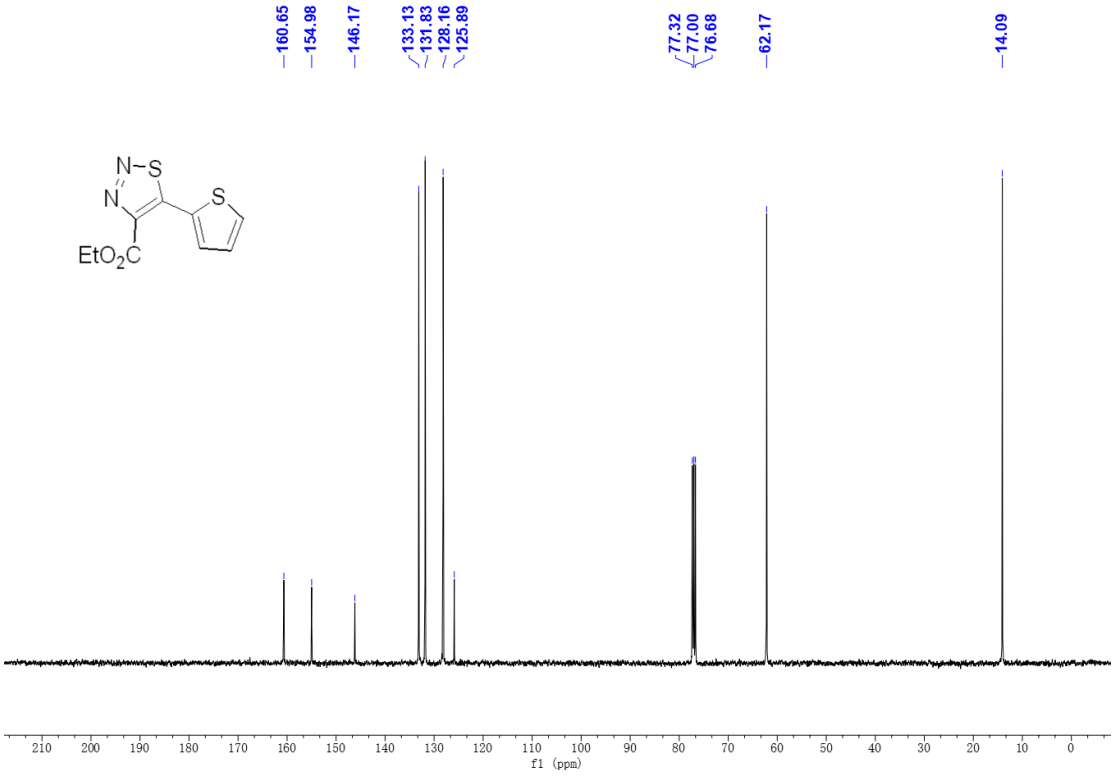


Ethyl 5-(thiophen-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1l**)

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

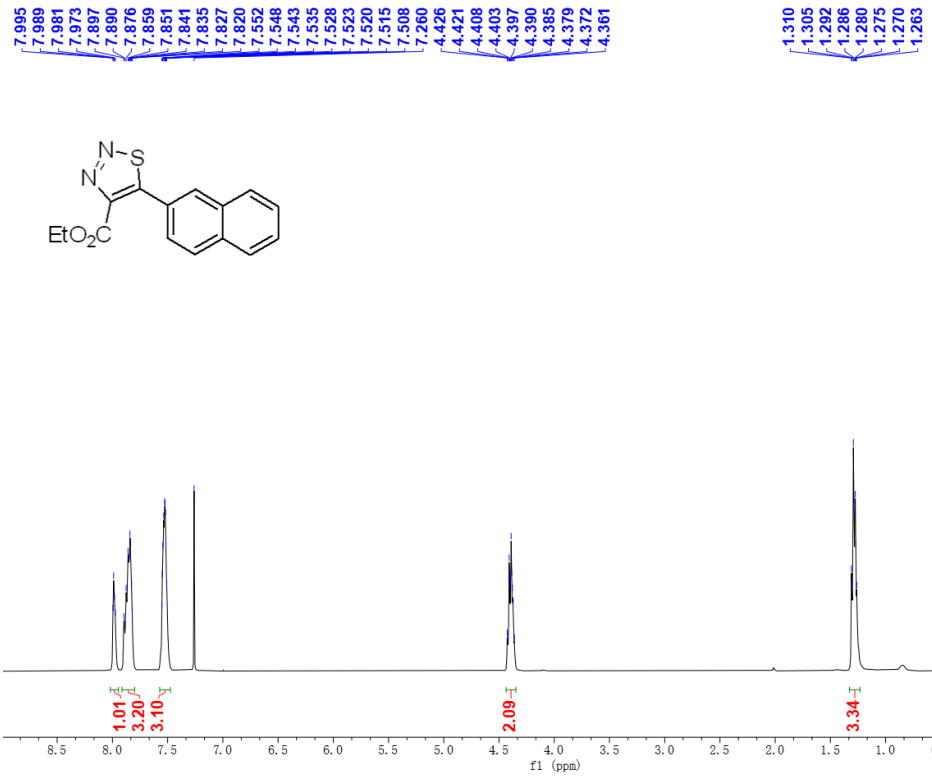


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

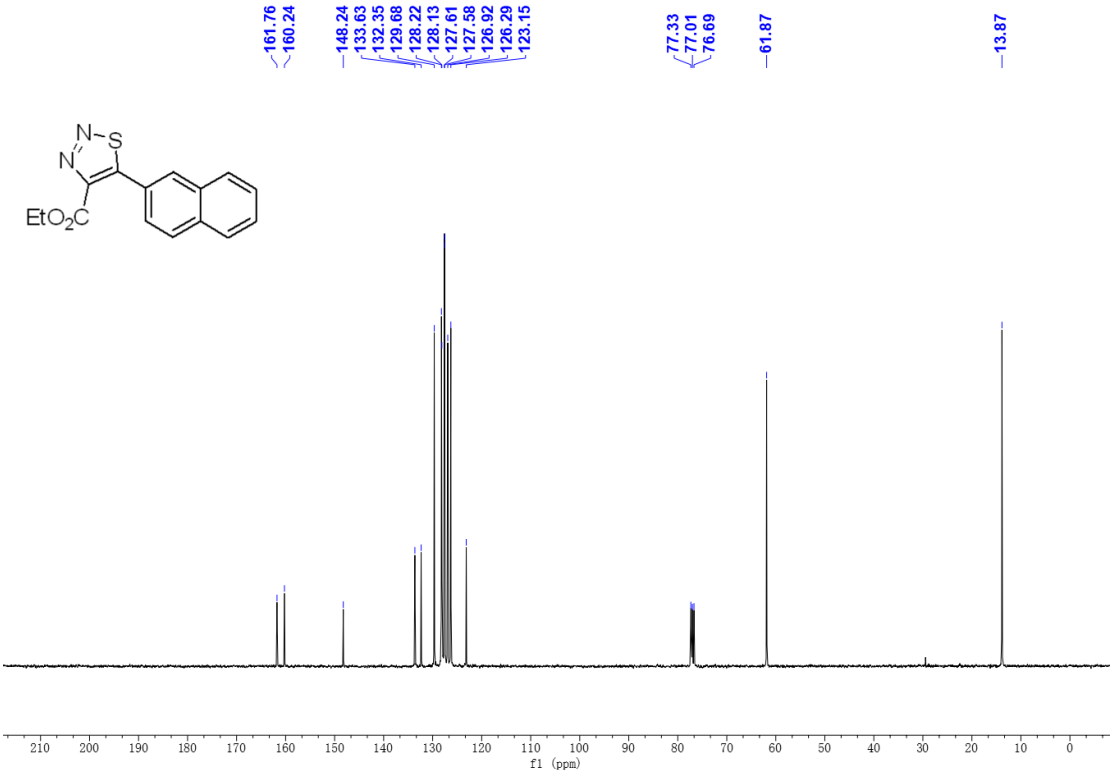


Ethyl 5-(naphthalen-2-yl)-1,2,3-thiadiazole-4-carboxylate (**1m**)

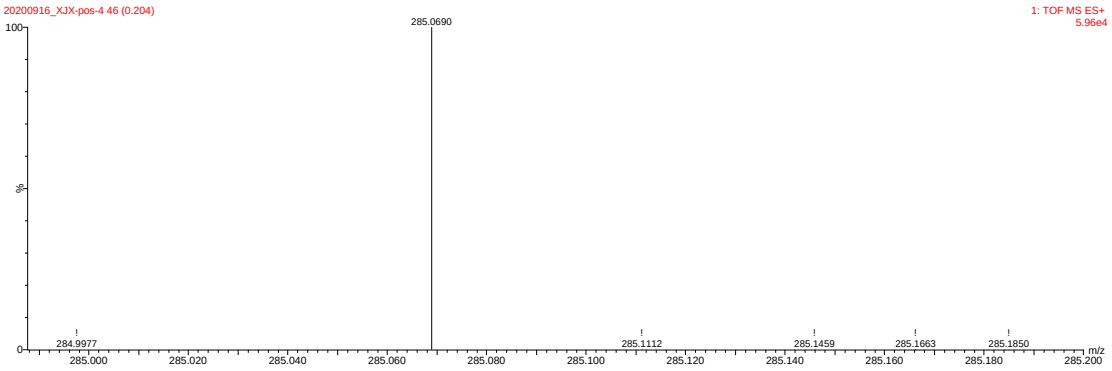
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

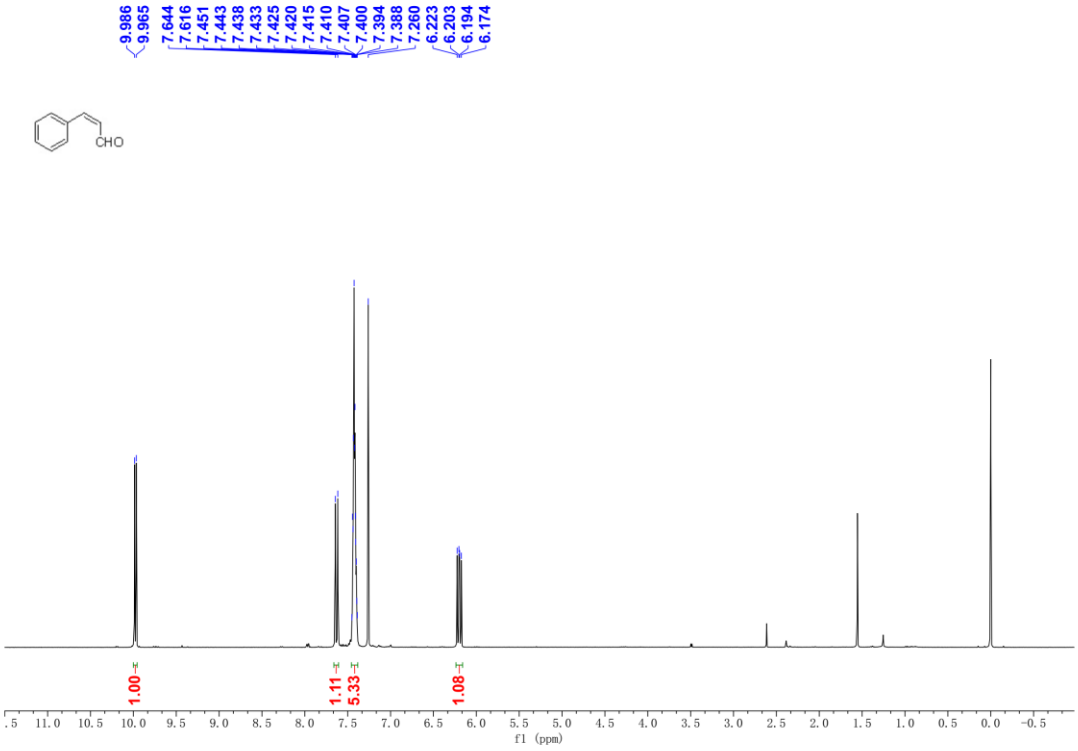


HRMS

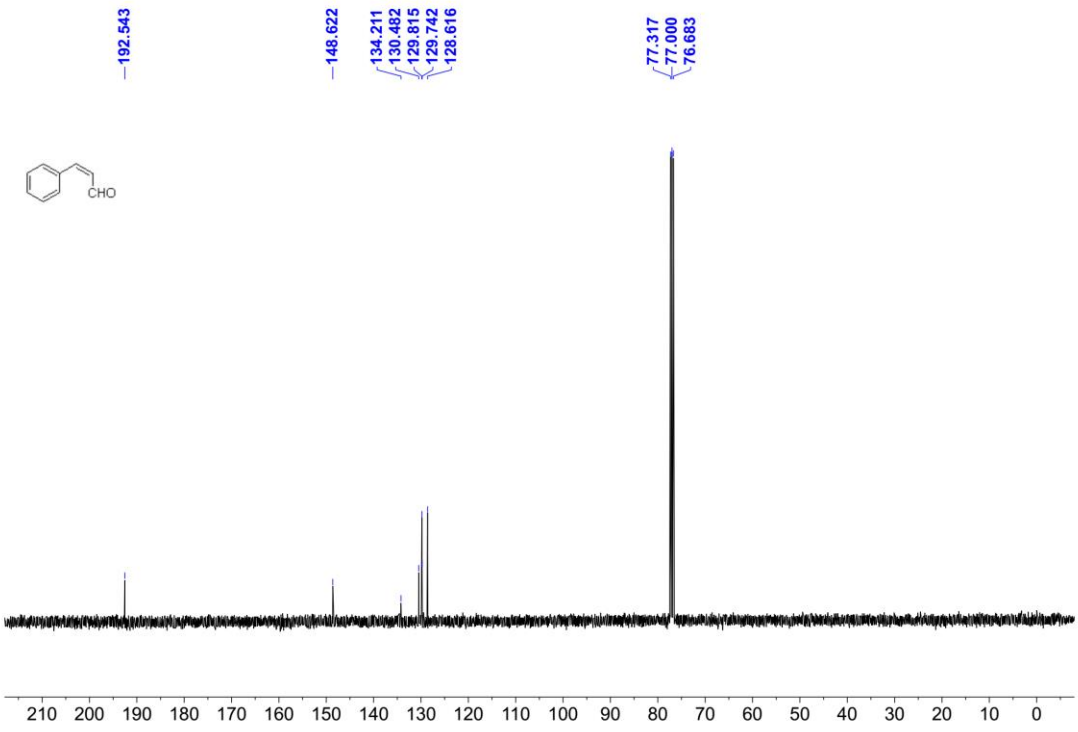

20200916_XJX-pos-4 46 (0.204)
1: TOF MS ES+
5.96e4
285.0690
100
%
0
284.9977
285.1112
285.1459
285.1663
285.1850
285.000
285.020
285.040
285.060
285.080
285.100
285.120
285.140
285.160
285.180
285.200
m/z

(*Z*)-3-Phenylacrylaldehyde [(*Z*)-**2g**]

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

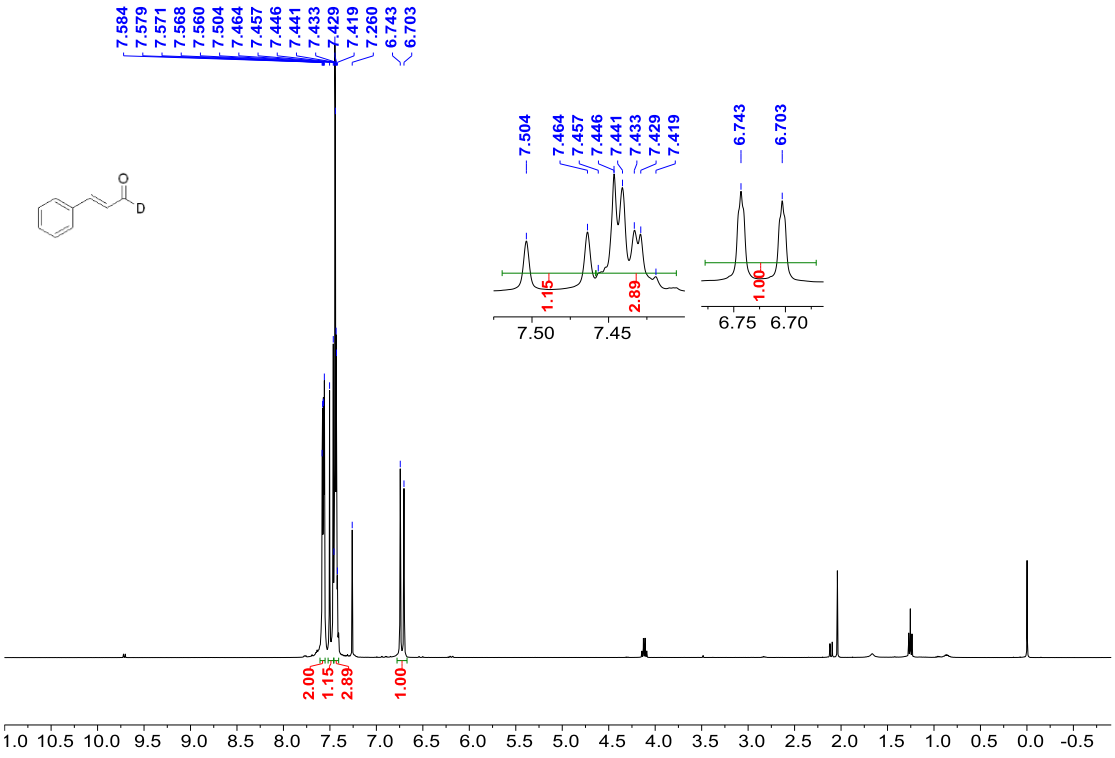


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

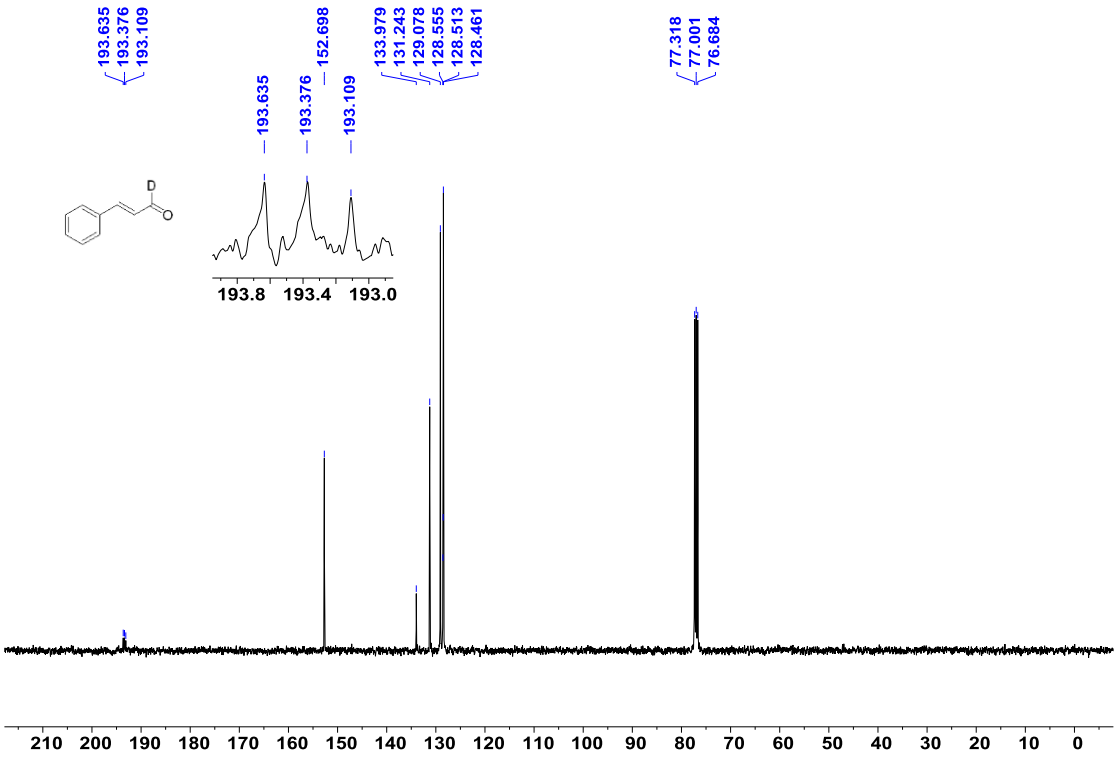


Cinnamaldehyde-1-*d* (**2g**-*d*)

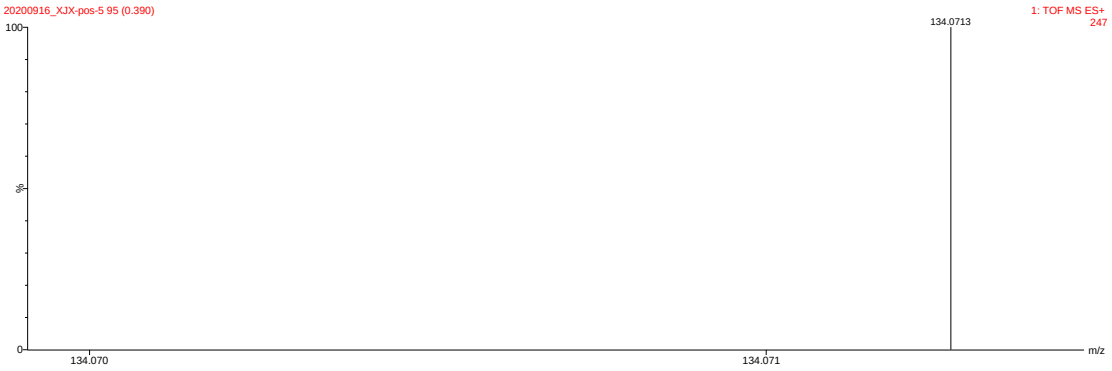
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

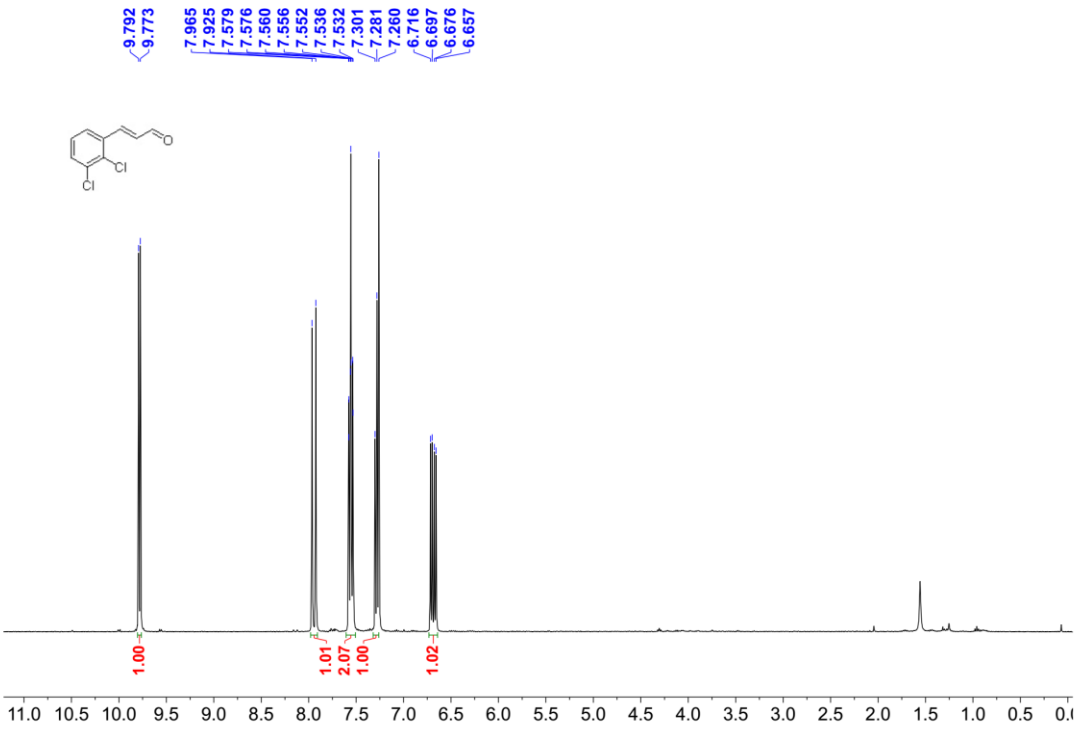


HRMS

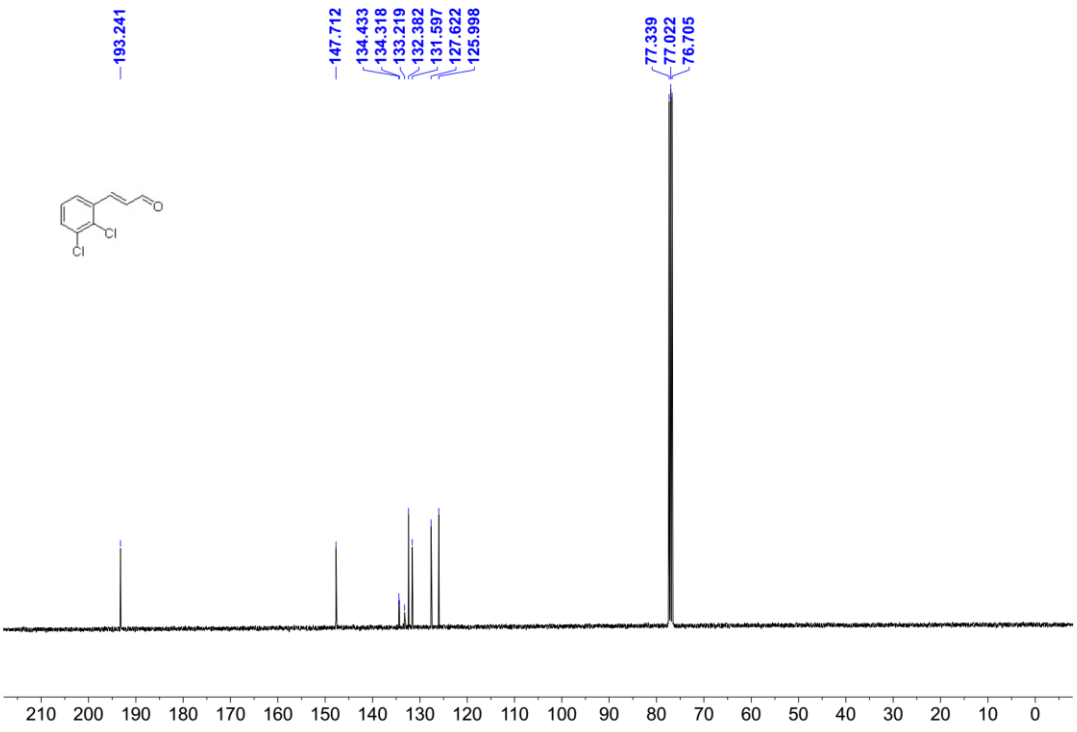

20200916_XJX-pos-5 95 (0.390)
1: TOF MS ES+
247
100
%
0
134.0713
134.070
134.071
m/z

3-(2,3-Dichlorophenyl)acrylaldehyde (**2j**)

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

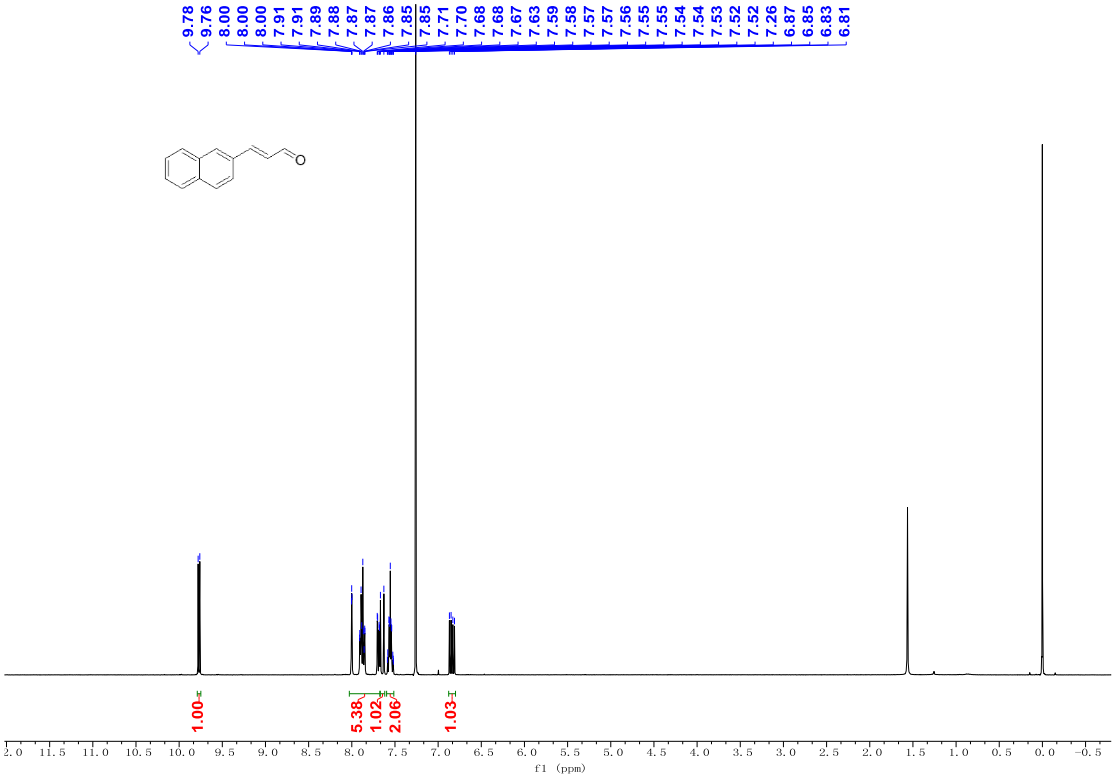


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

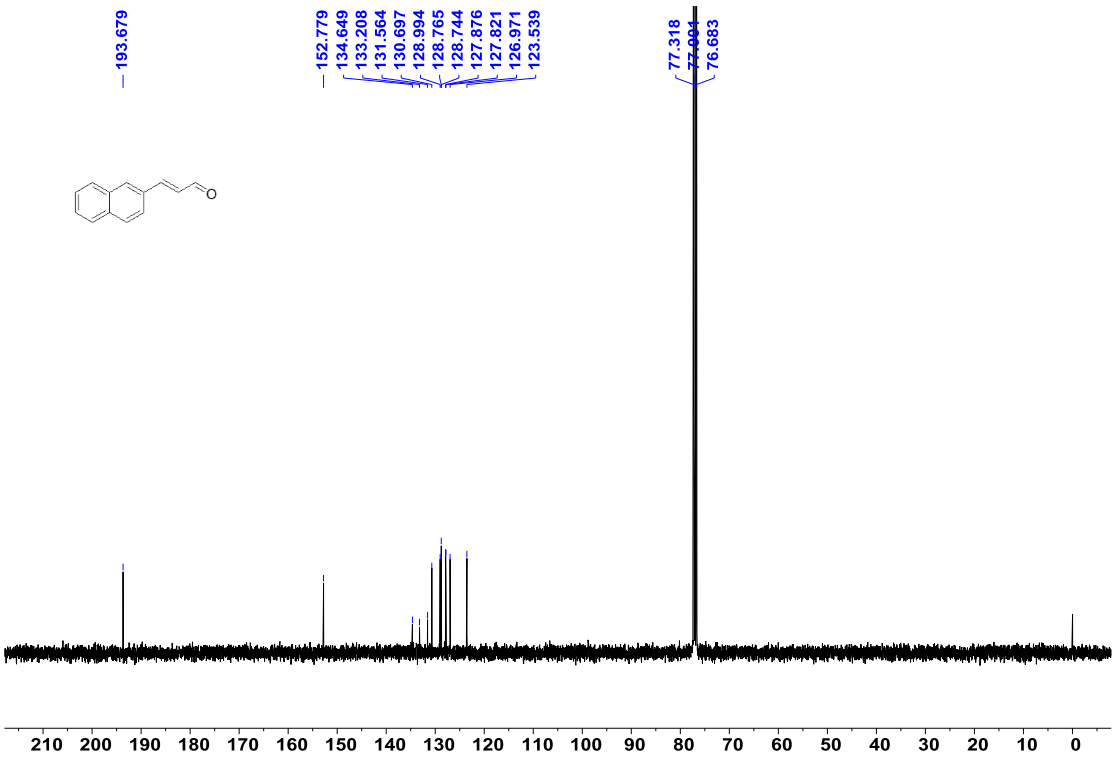


(*E*)-3-(Naphthalen-2-yl)propenal (**2l**)

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

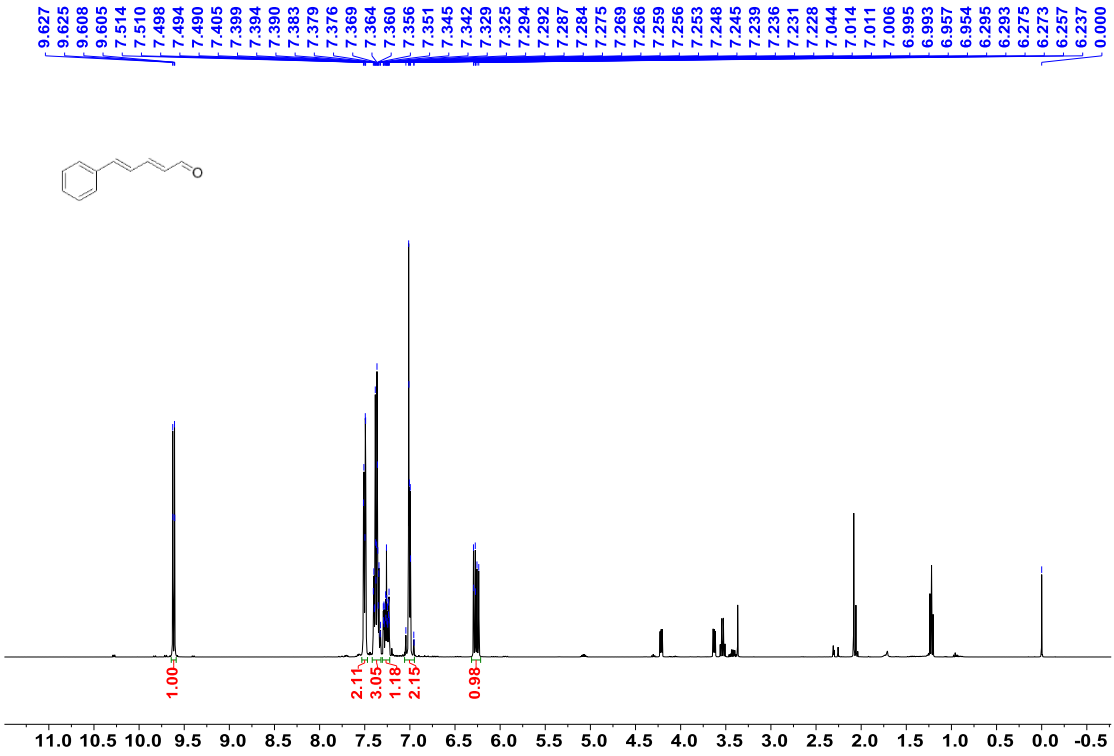


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

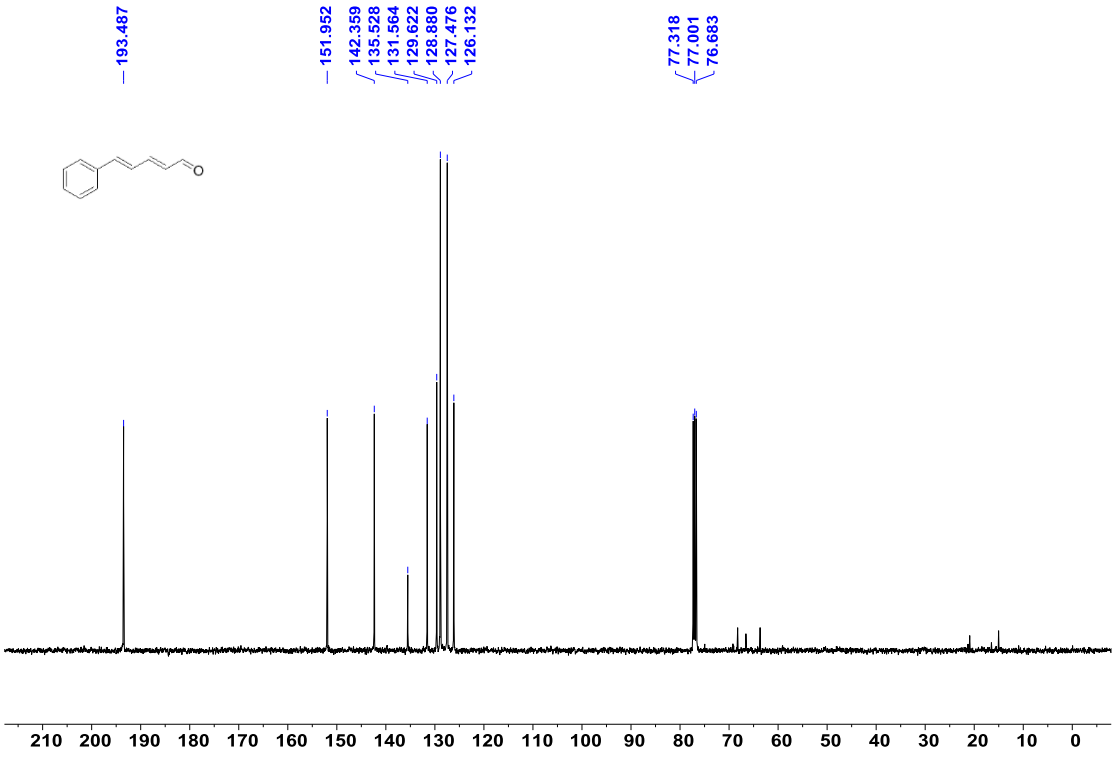


(E)-5-Phenylpenta-2,4-dienal (**2m**)

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

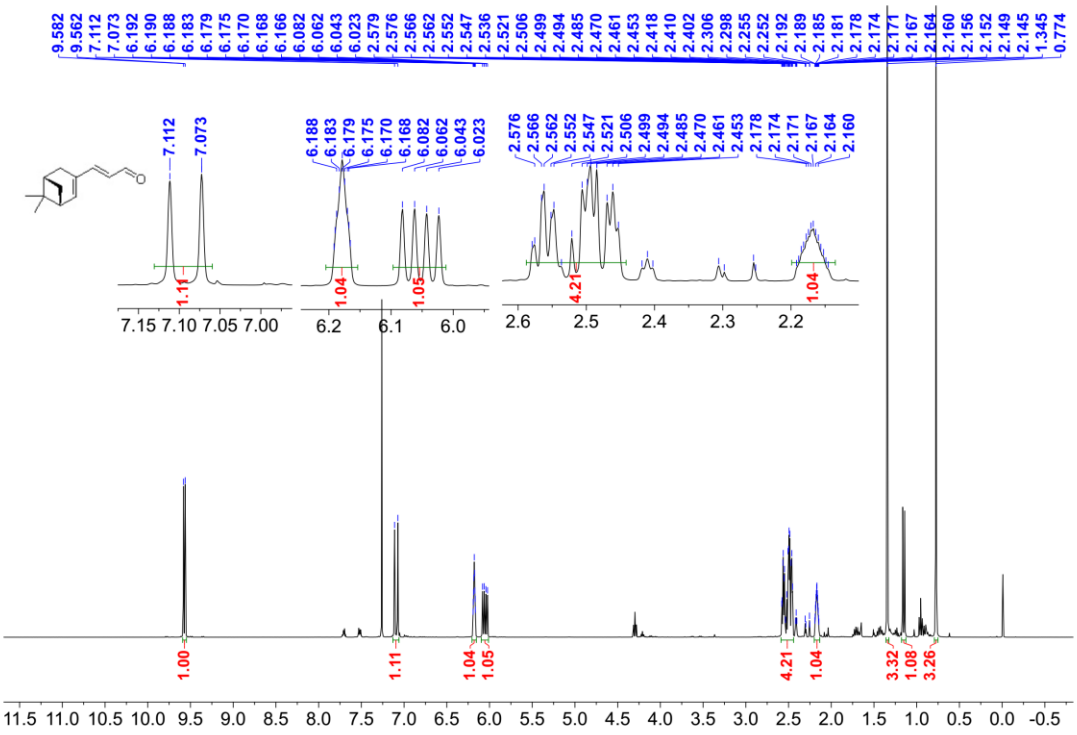


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

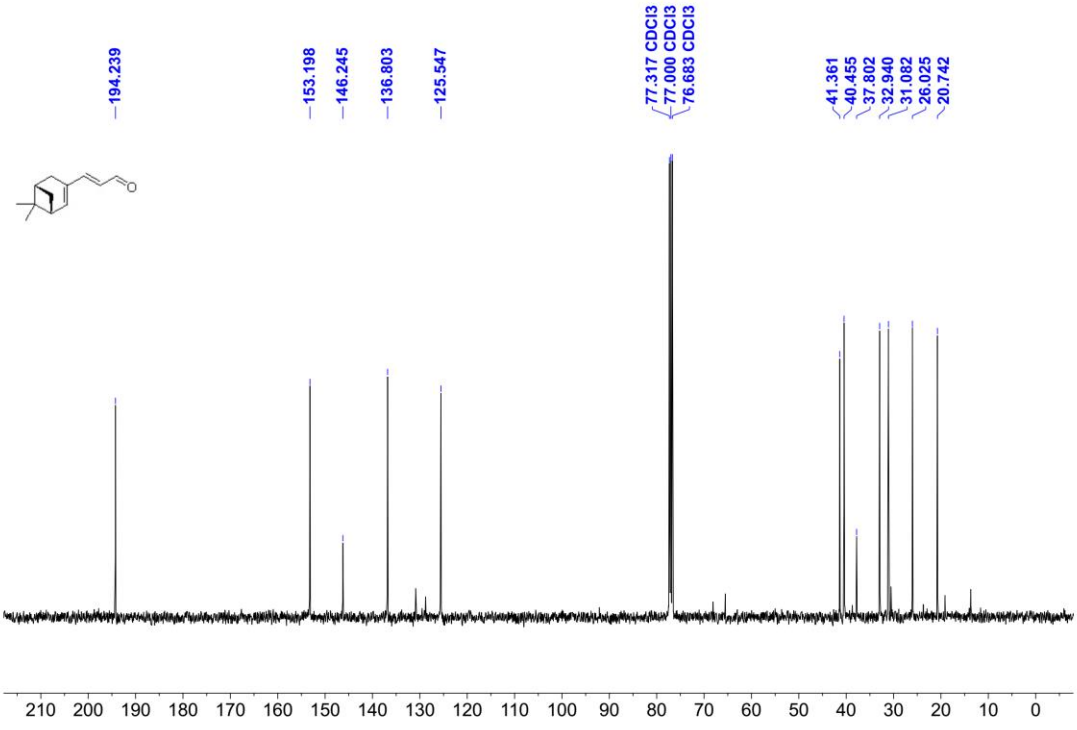


3-((1*R*,5*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-3-yl)acrylaldehyde (**2n**)

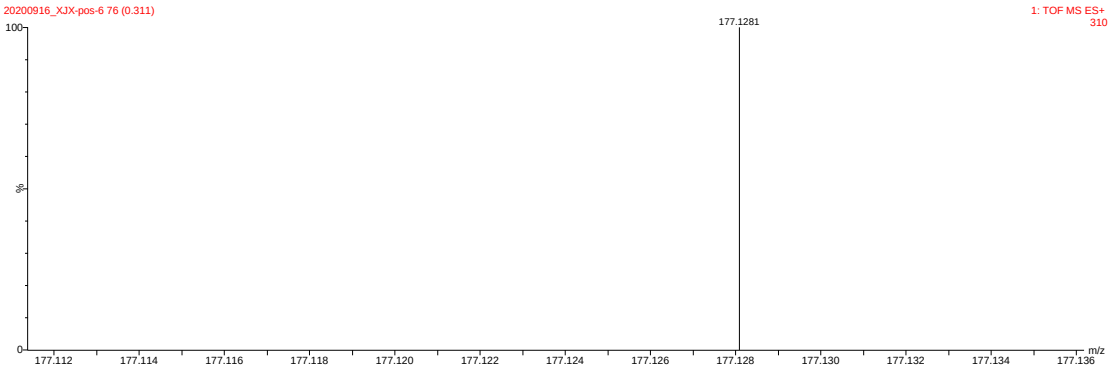
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

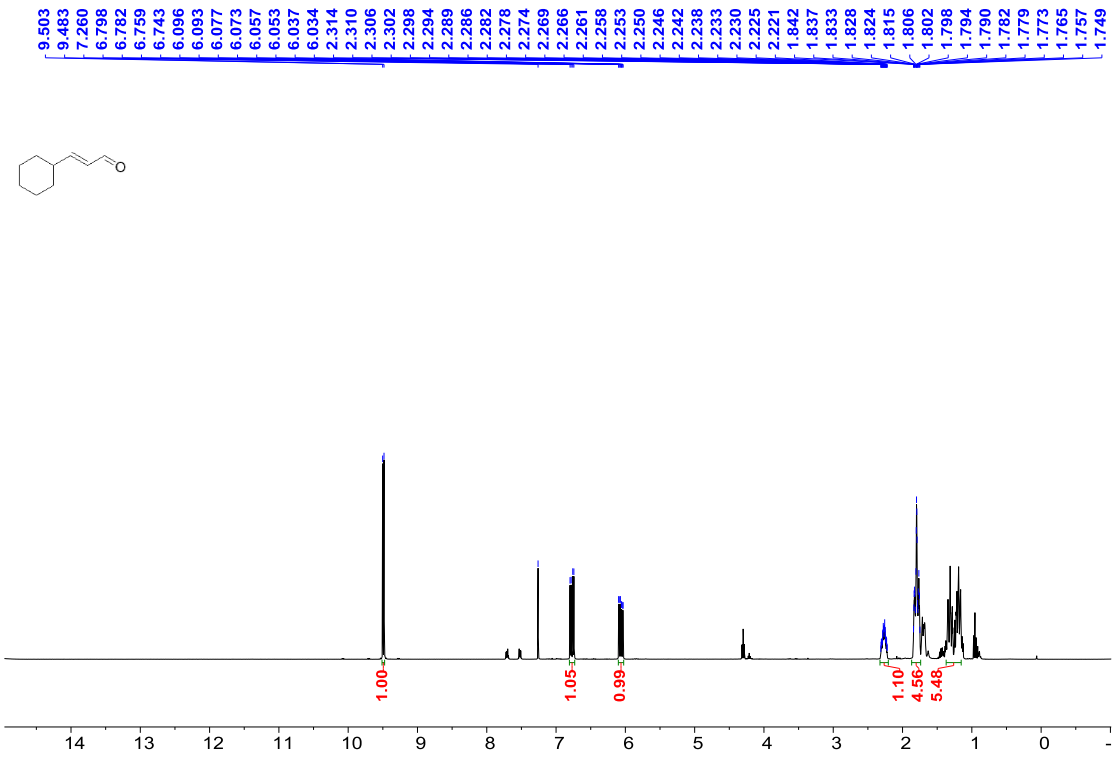


HRMS

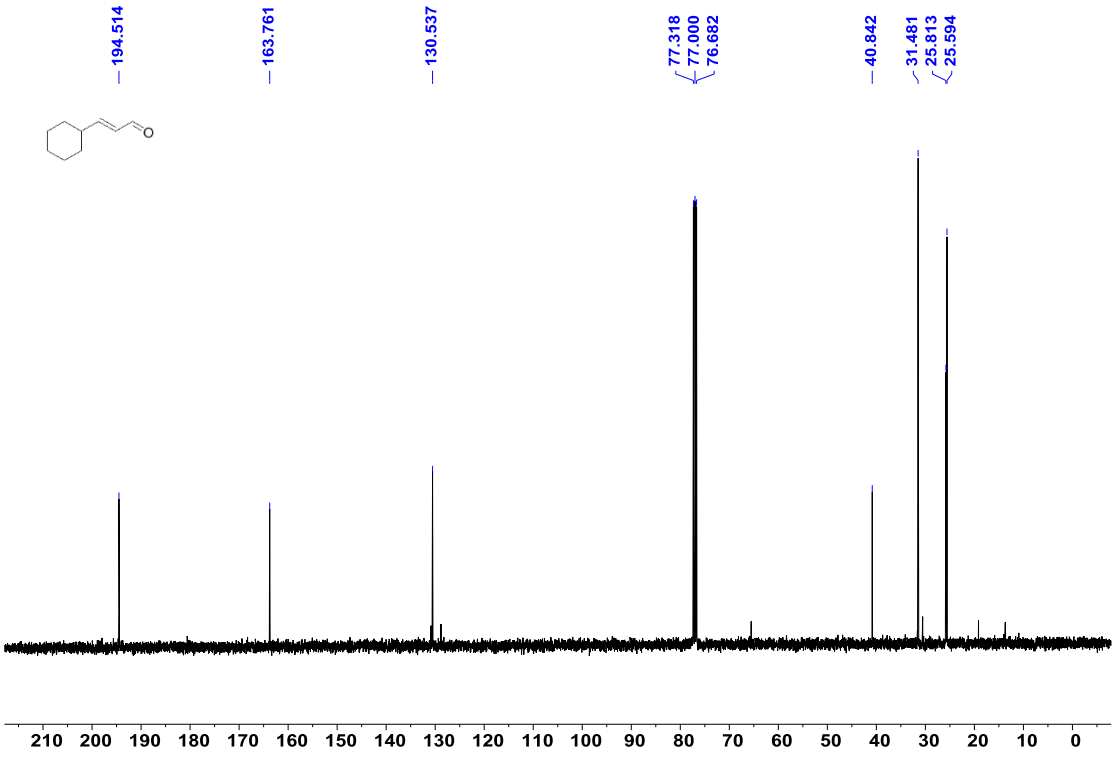

20200916_XJX-pos-6 76 (0.311)
1: TOF MS ES+
310
177.1281
100
%
0
177.112
177.114
177.116
177.118
177.120
177.122
177.124
177.126
177.128
177.130
177.132
177.134
177.136
m/z

(*E*)-3-Cyclohexylpropenal (**2o**)

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

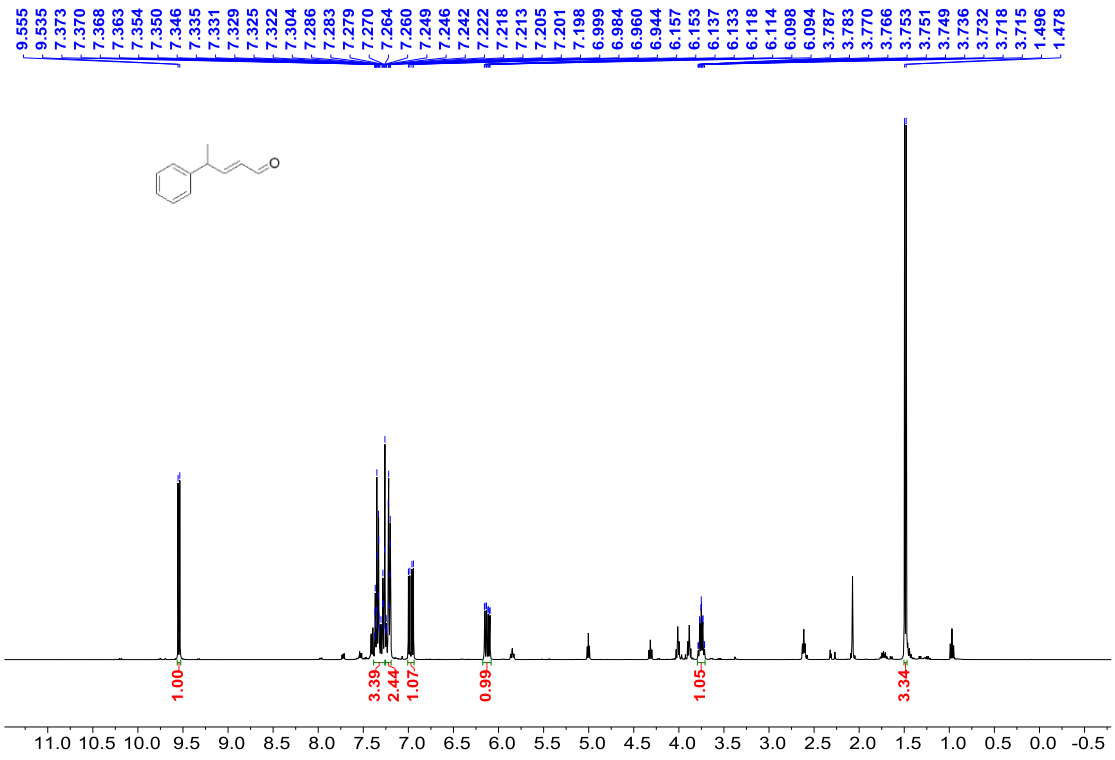


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

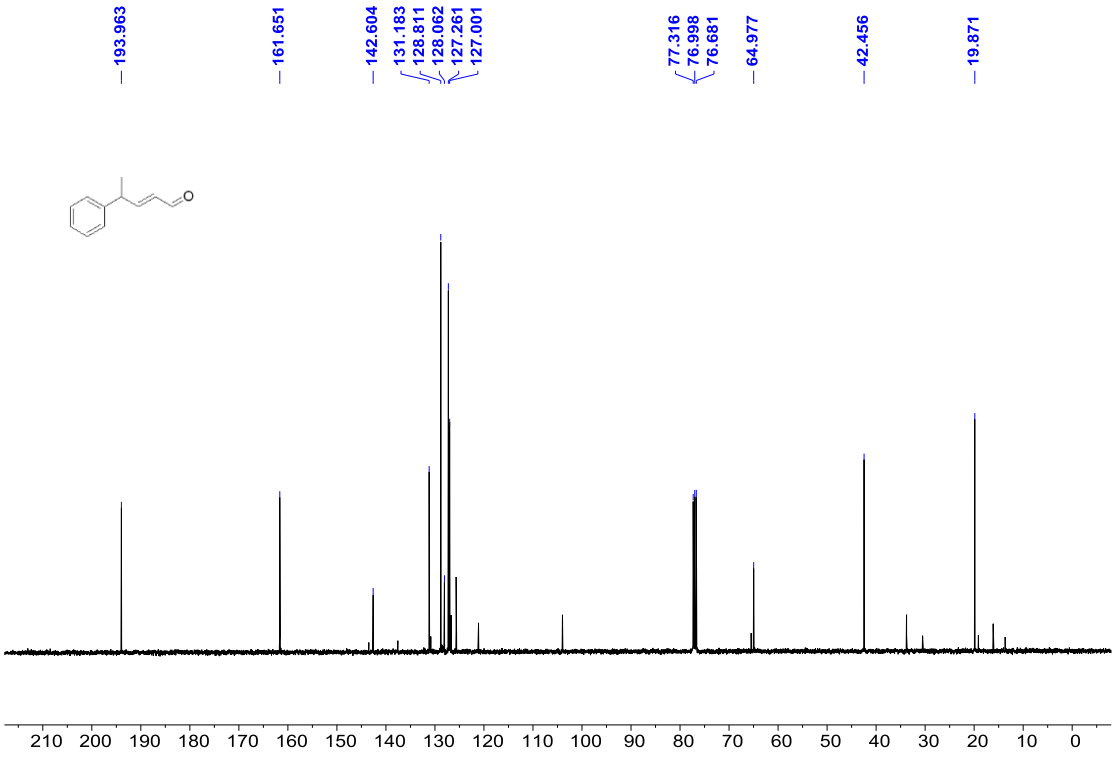


(*E*)-4-Phenylpent-2-enal (**2p**)

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

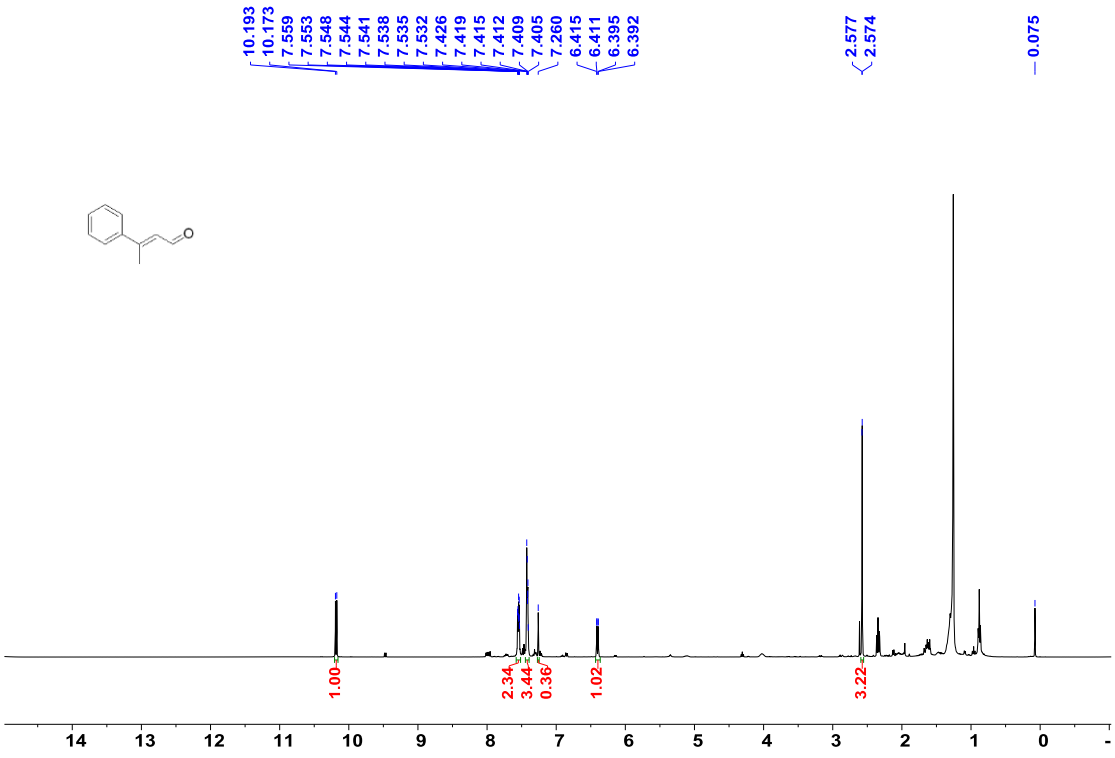


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

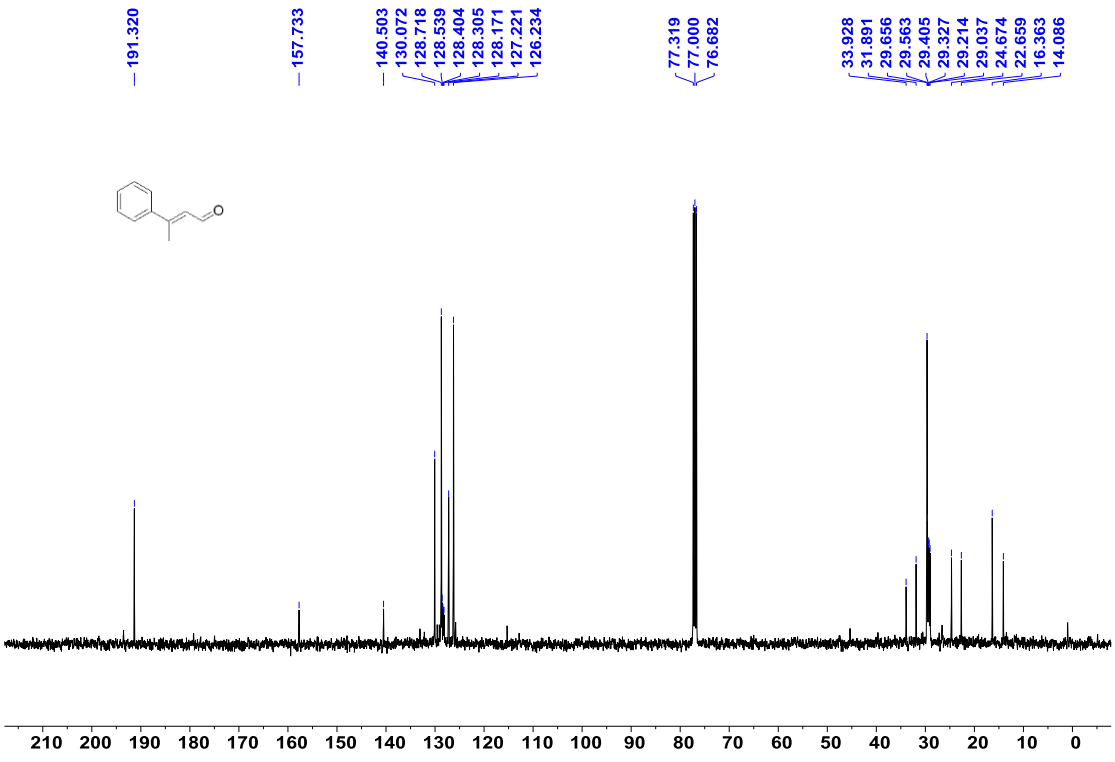


(*E*)-3-Phenylbut-2-enal (**2s**)

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

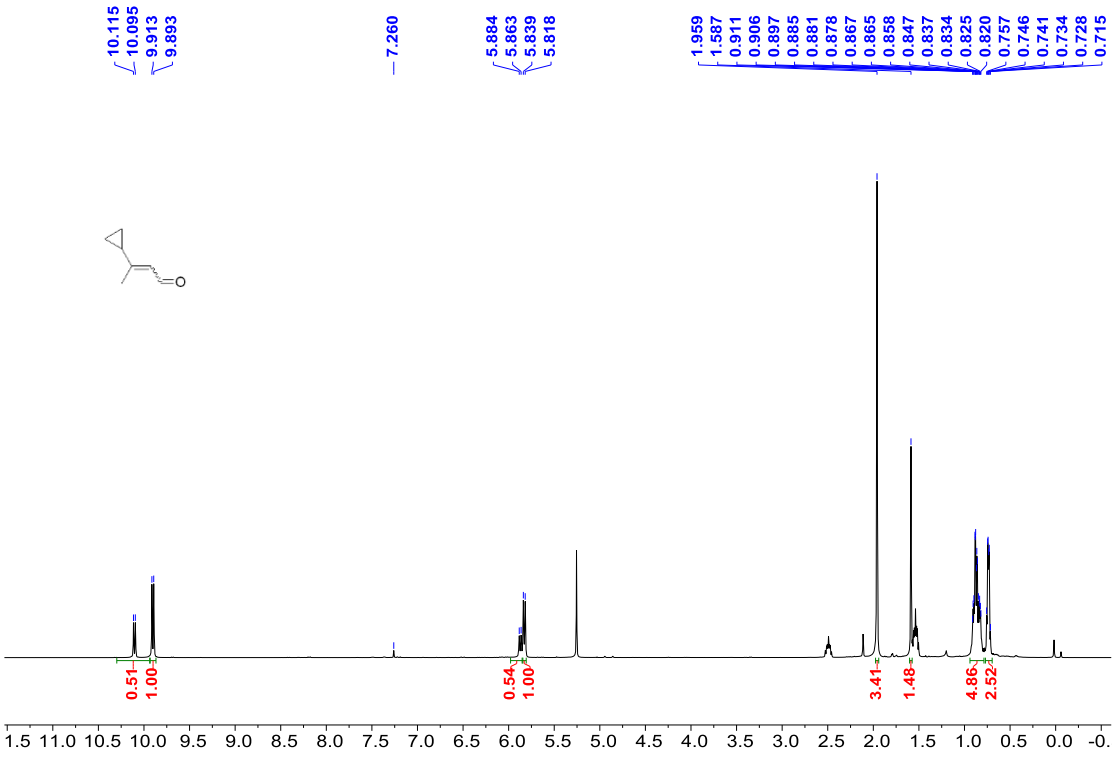


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

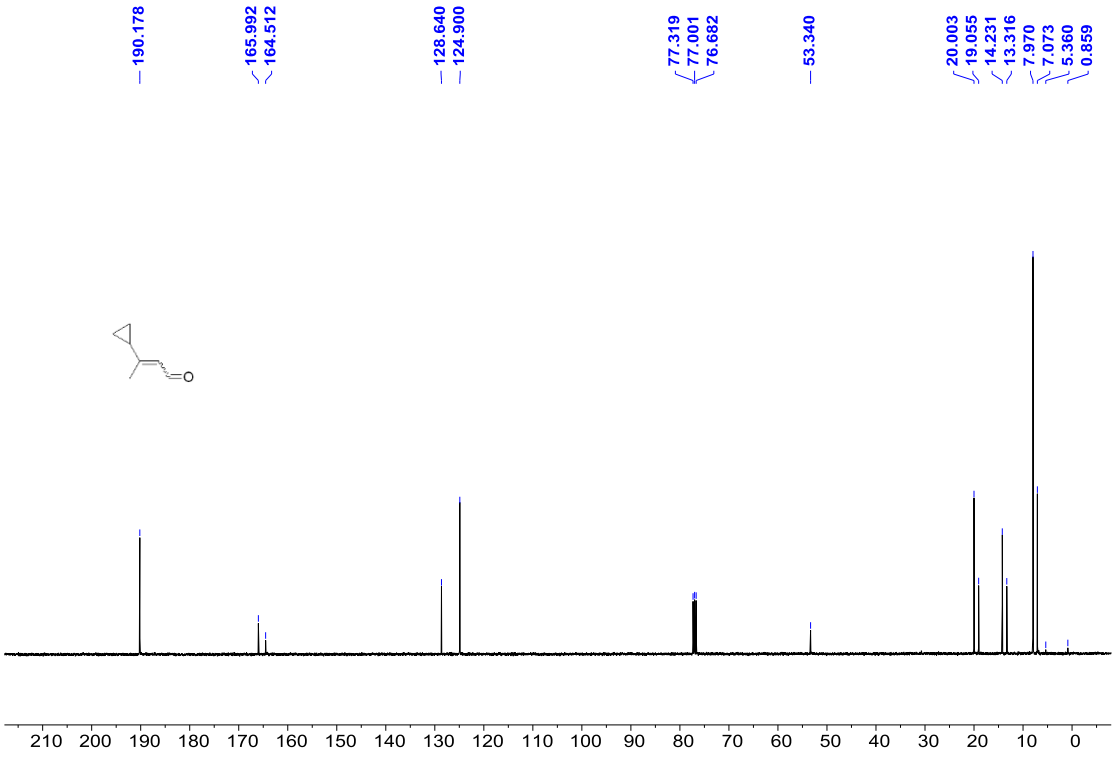


3-Cyclopropylbut-2-enal (**2t**)

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

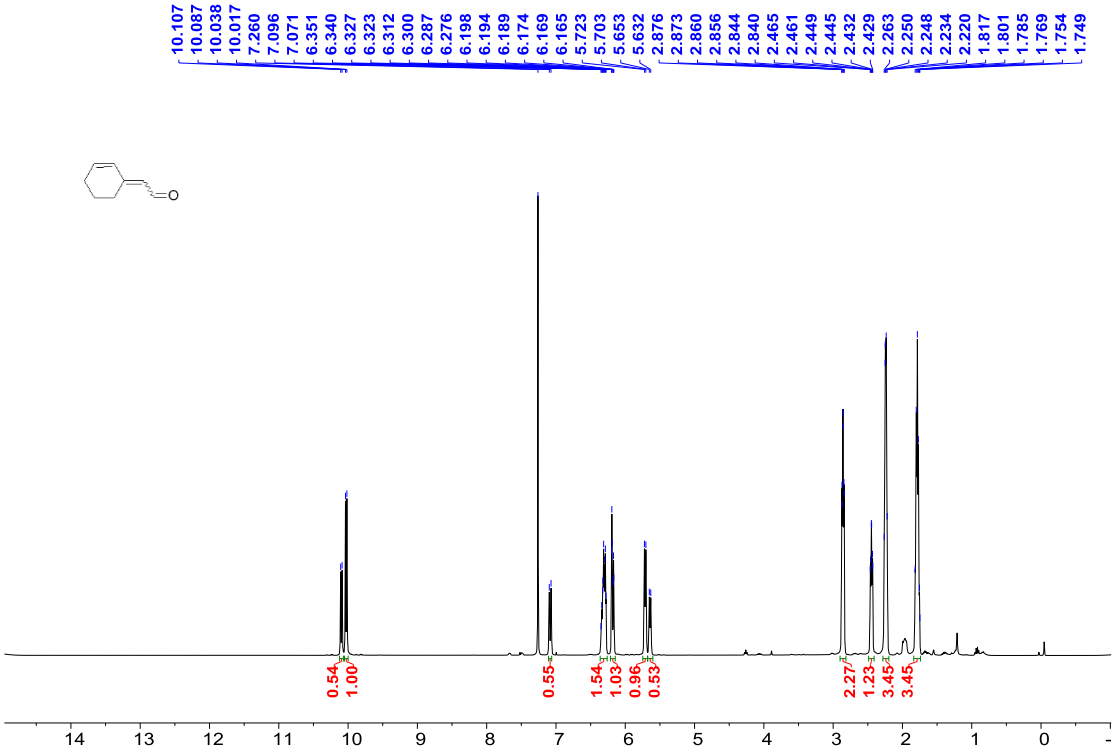


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

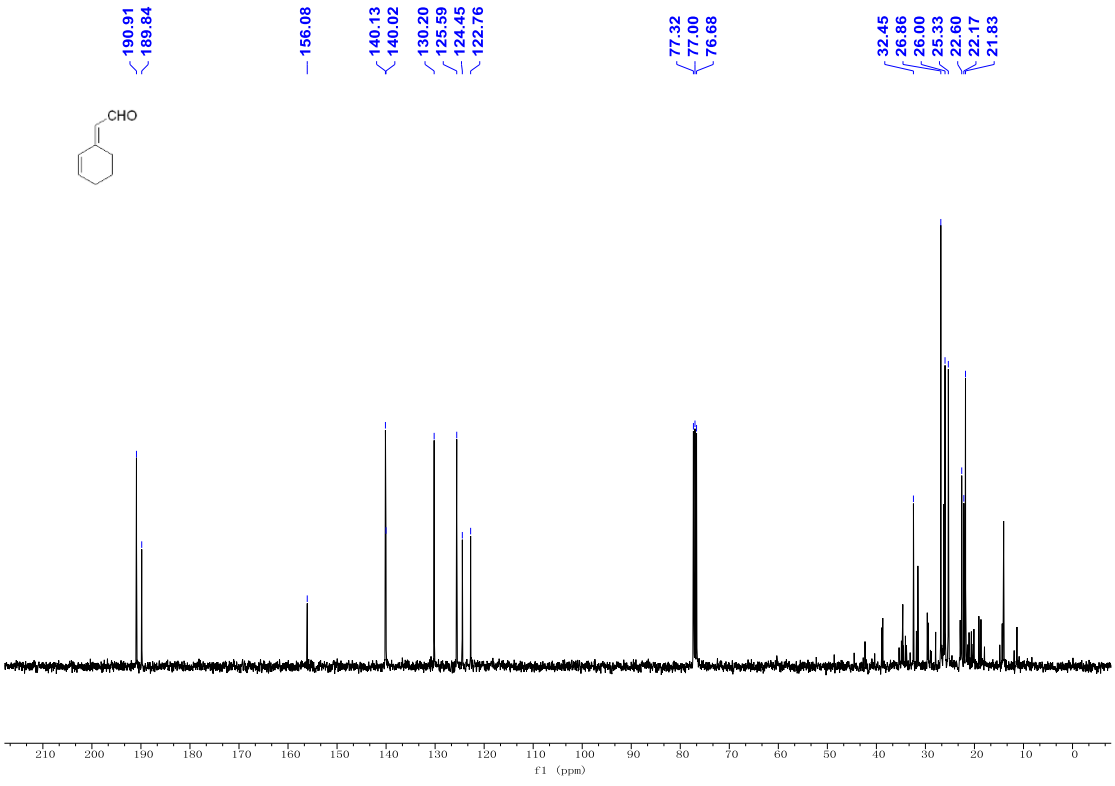


(2-Cyclohexenylidene)acetaldehyde (**2y**)

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

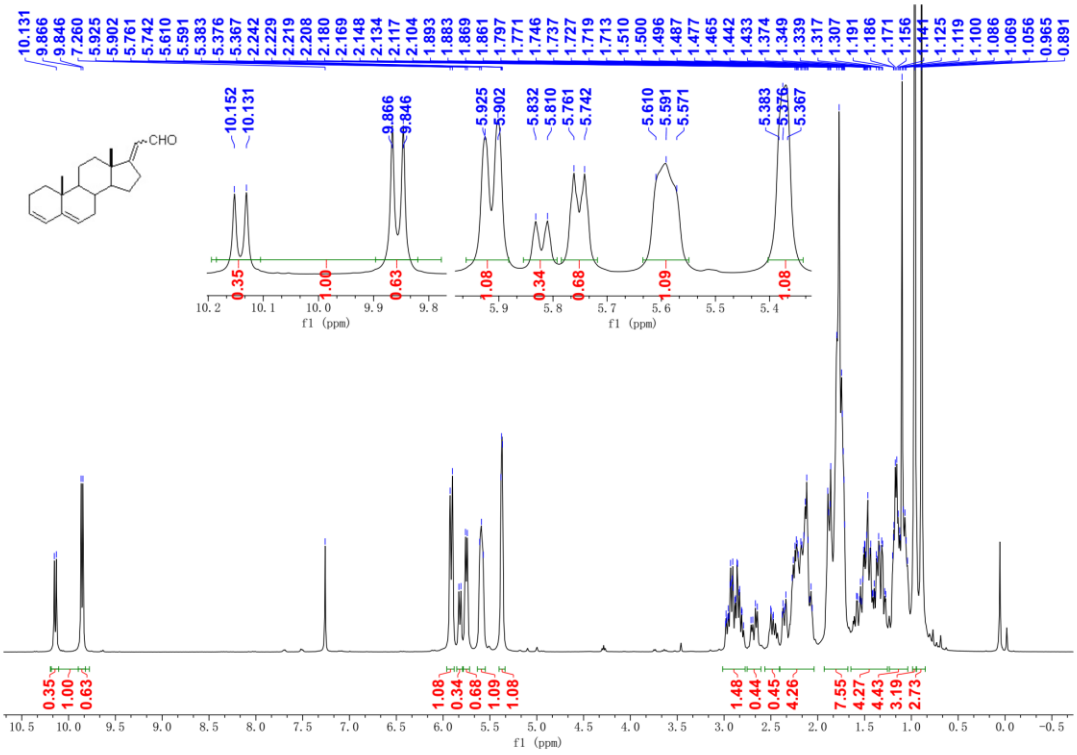


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

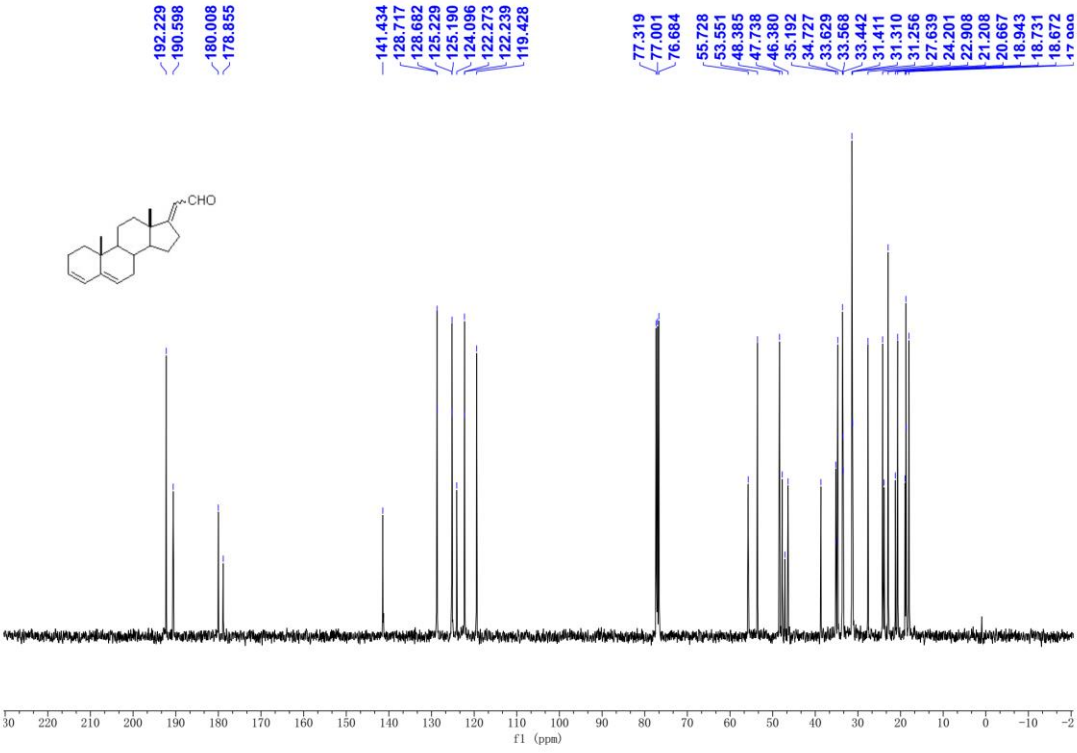


2-((8*S*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-1,2,7,8,9,10,11,12,13,14,15,16-dodecahydro-17*H*-cyclopenta[*a*]phenanthren-17-ylidene)acetaldehyde (**12**)

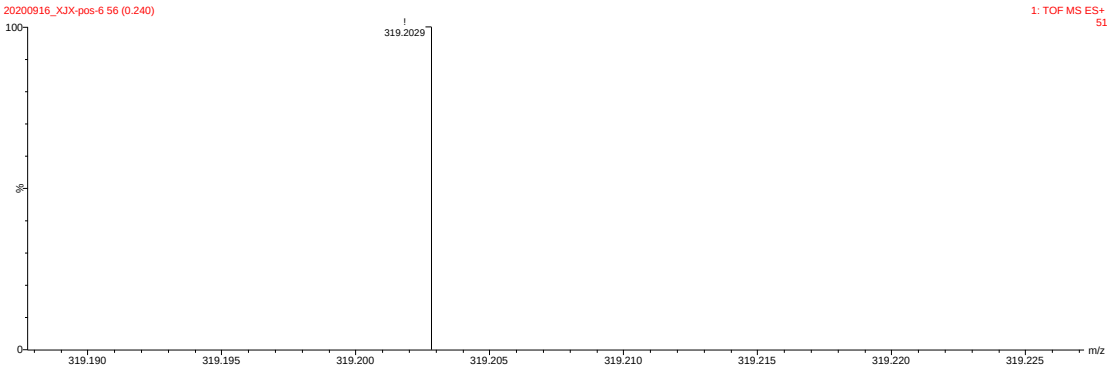
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

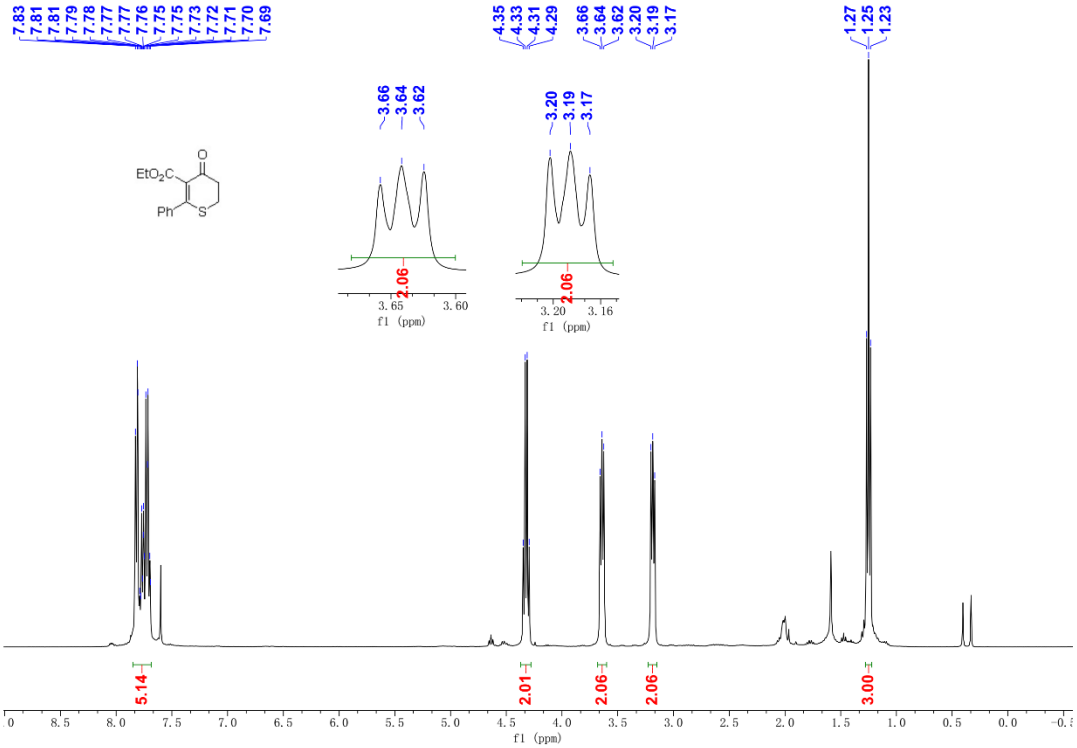


HRMS

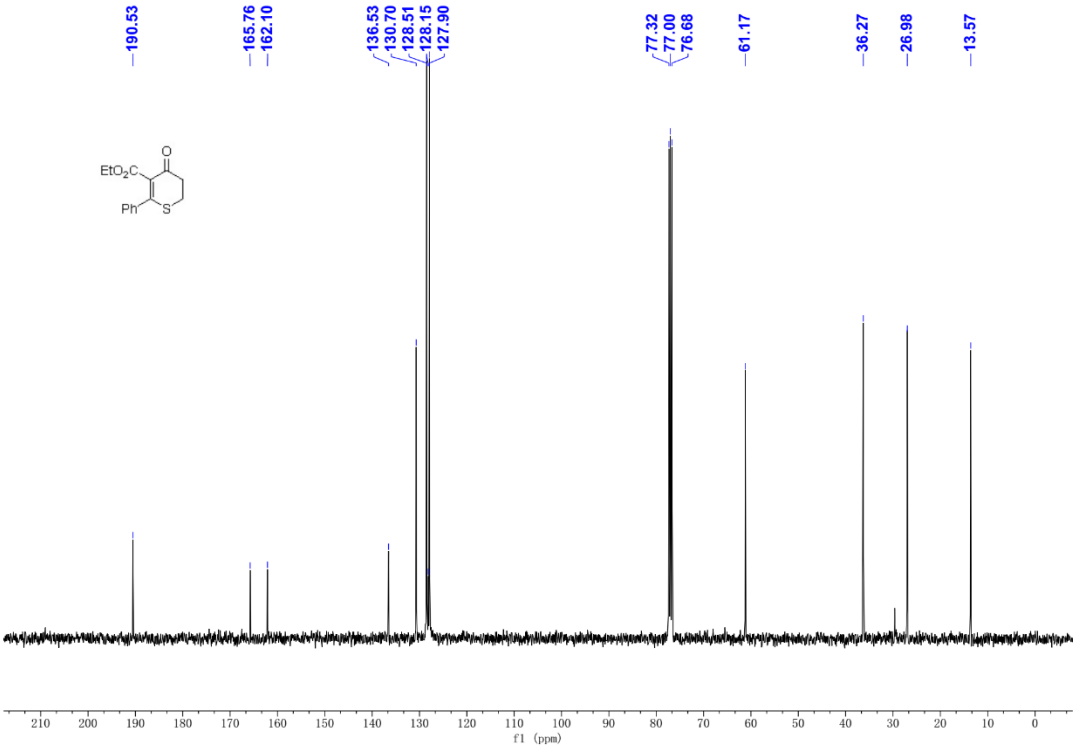

20200916_XJX-pos-6 56 (0.240)
1: TOF MS ES+
51
319.2029
100
%
0
319.190
319.195
319.200
319.205
319.210
319.215
319.220
319.225
m/z

Ethyl 4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ab**)

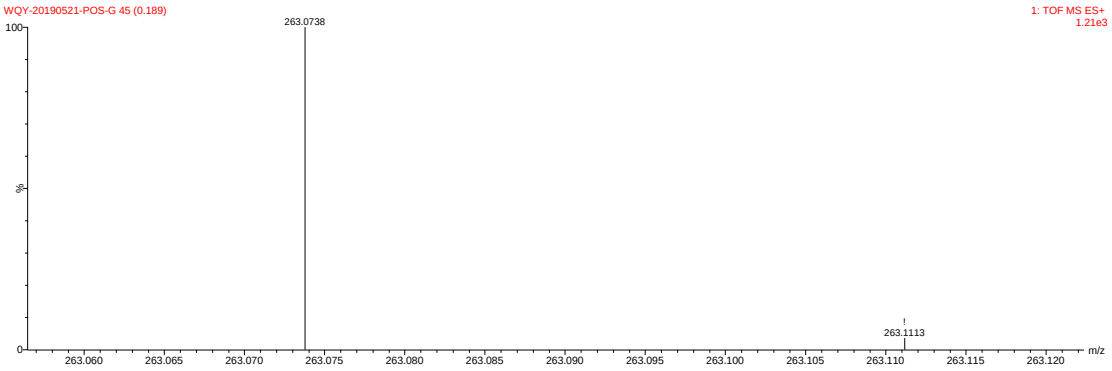
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

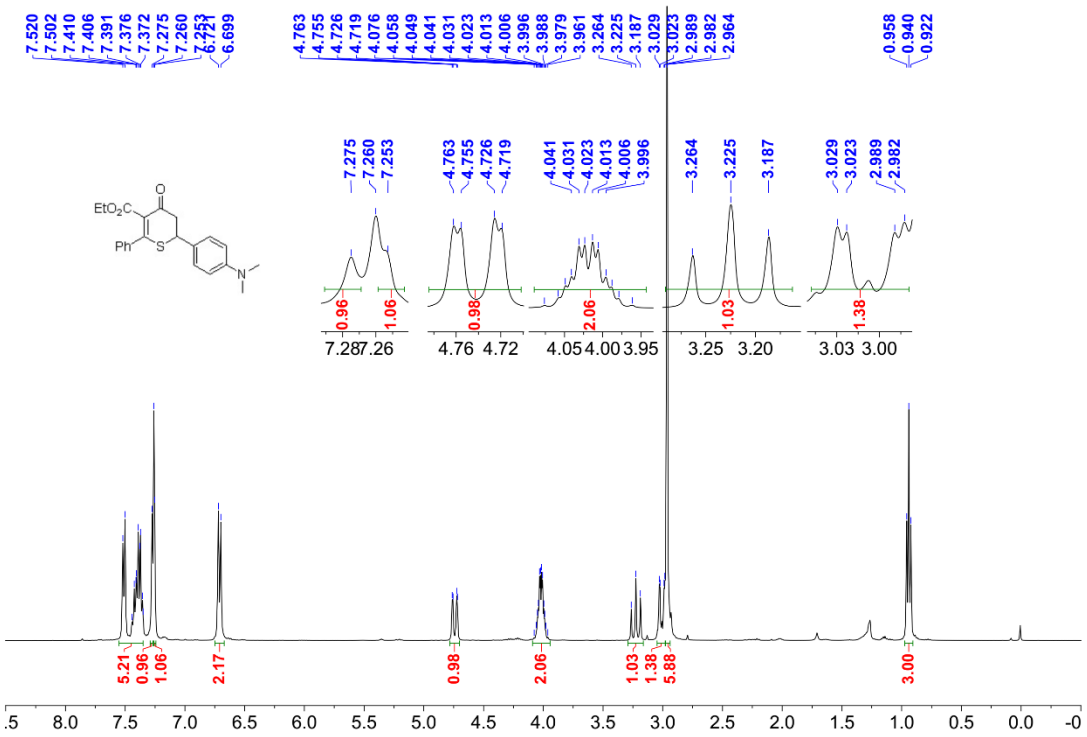


HRMS

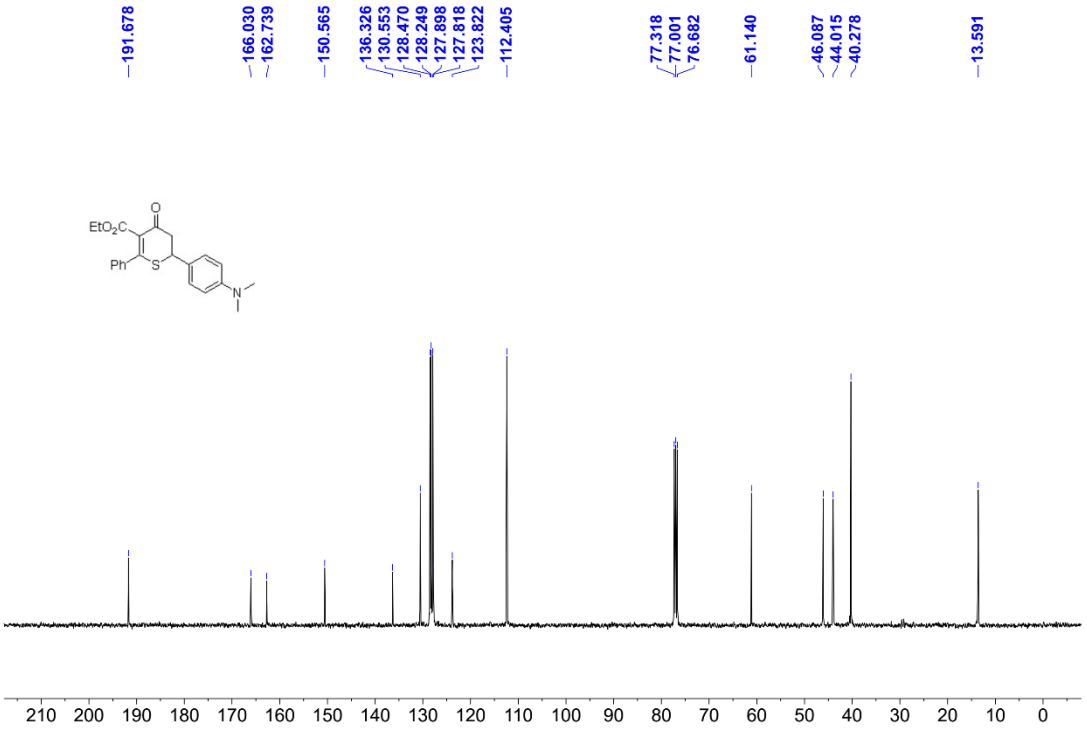

WQY-20190521-POS-G 45 (0.189)
1: TOF MS ES+
1.21e3
100
%
0
263.0738
263.1113
263.060
263.065
263.070
263.075
263.080
263.085
263.090
263.095
263.100
263.105
263.110
263.115
263.120
m/z

Ethyl 2-(4-(dimethylamino)phenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ac**)

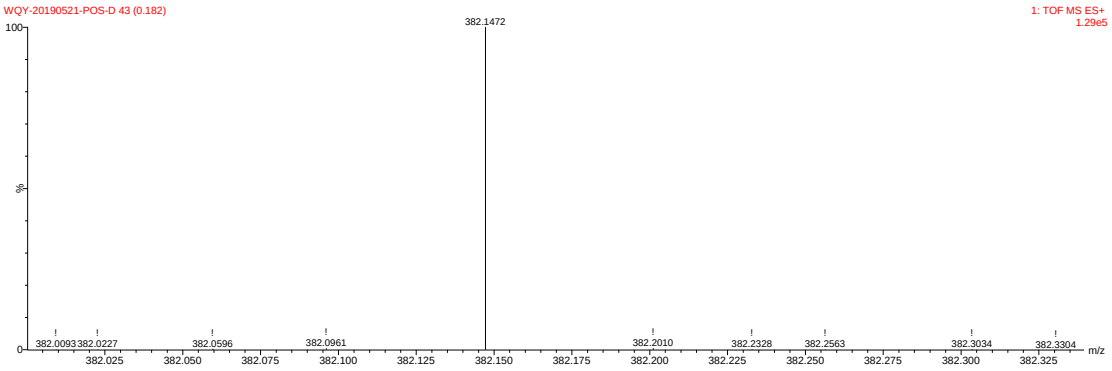
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

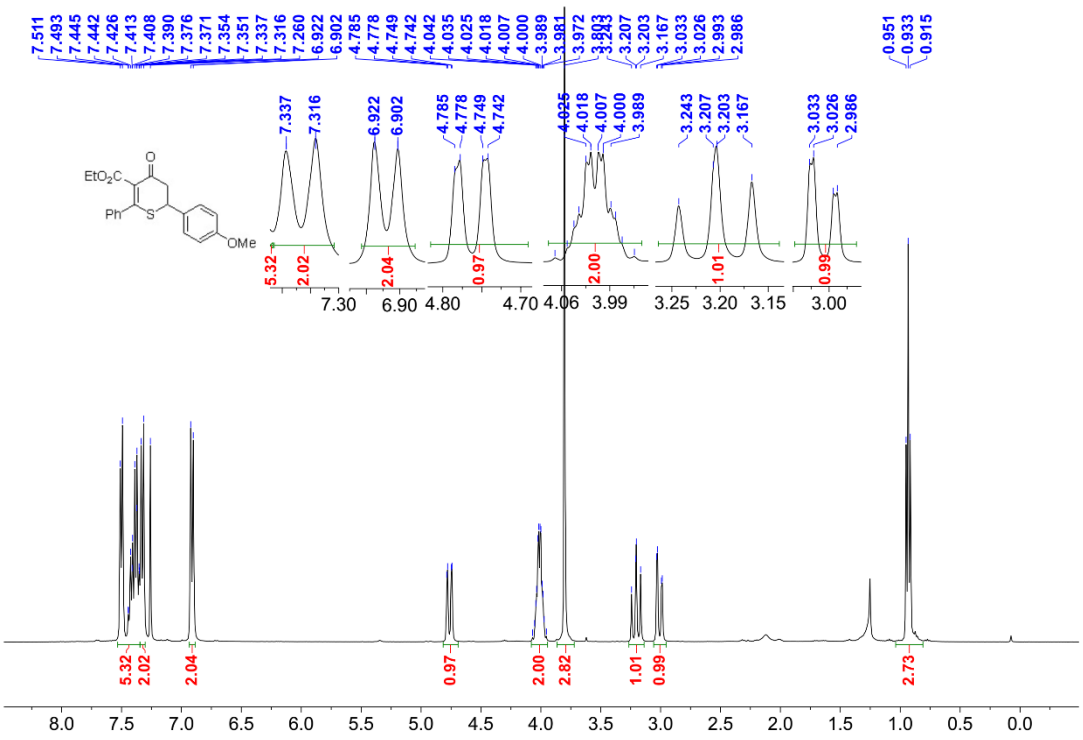


HRMS

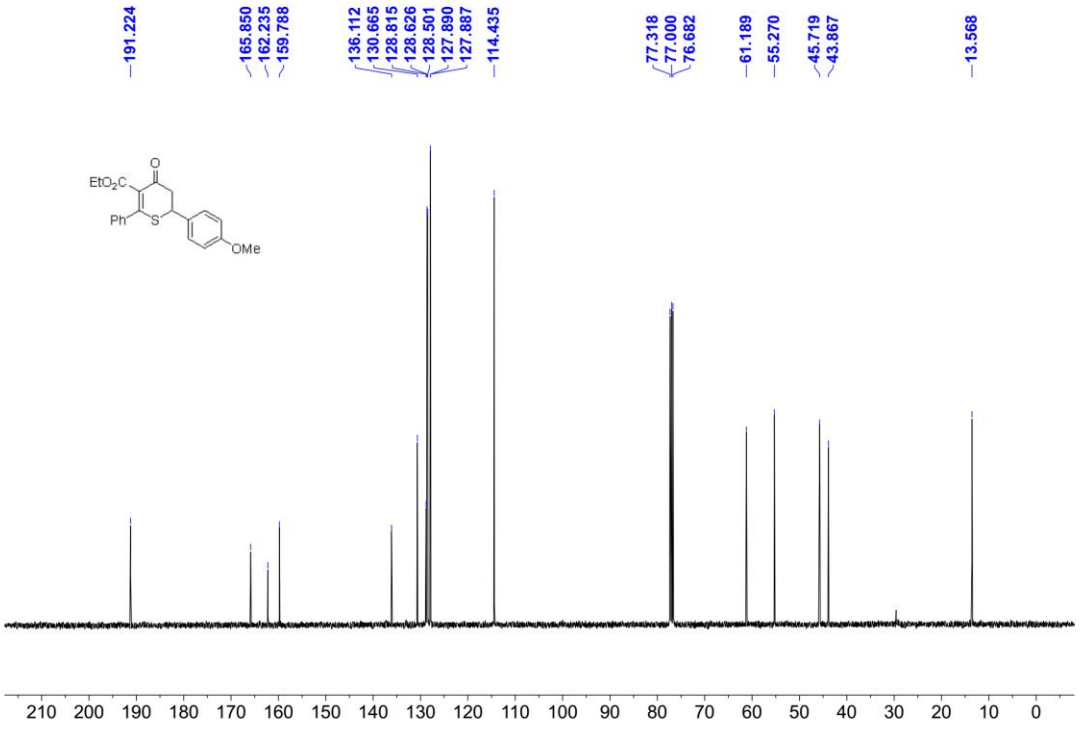

WQY-20190521-POS-D 43 (0.182)
1: TOF MS ES+
1.29e5
100
%
0
382.1472
382.0093
382.0227
382.0596
382.0961
382.2010
382.2328
382.2563
382.3034
382.3304
382.025
382.050
382.075
382.100
382.125
382.150
382.175
382.200
382.225
382.250
382.275
382.300
382.325
m/z

Ethyl 2-(4-methoxyphenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ad**)

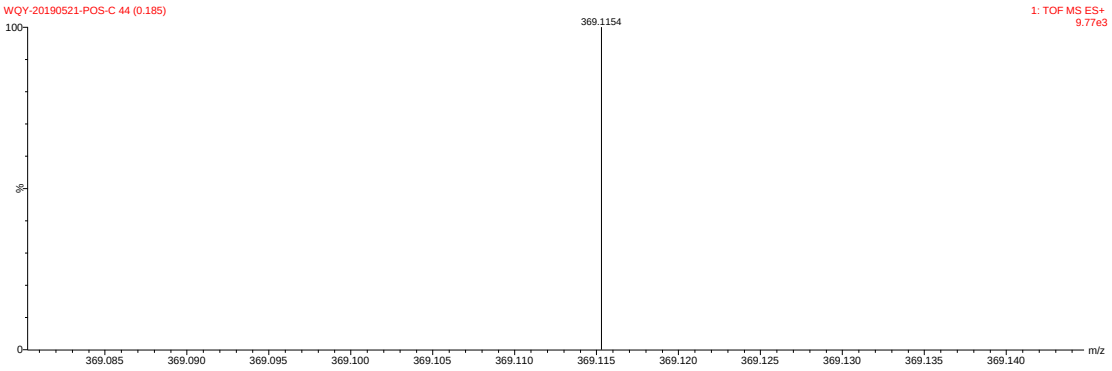
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

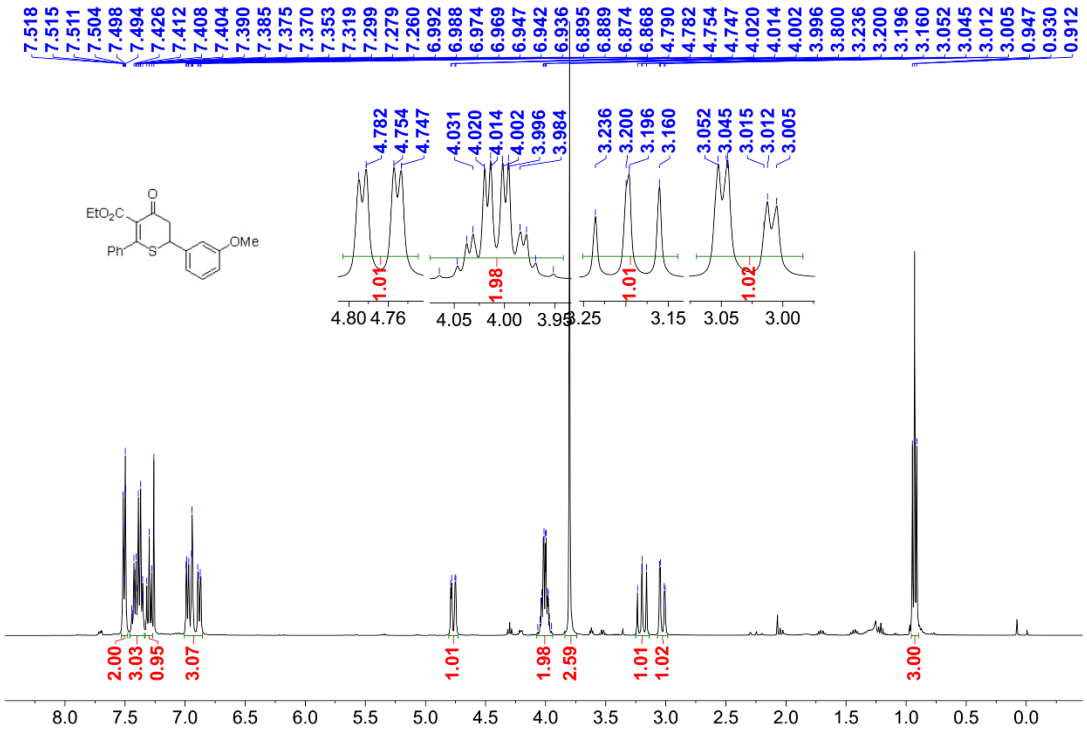


HRMS

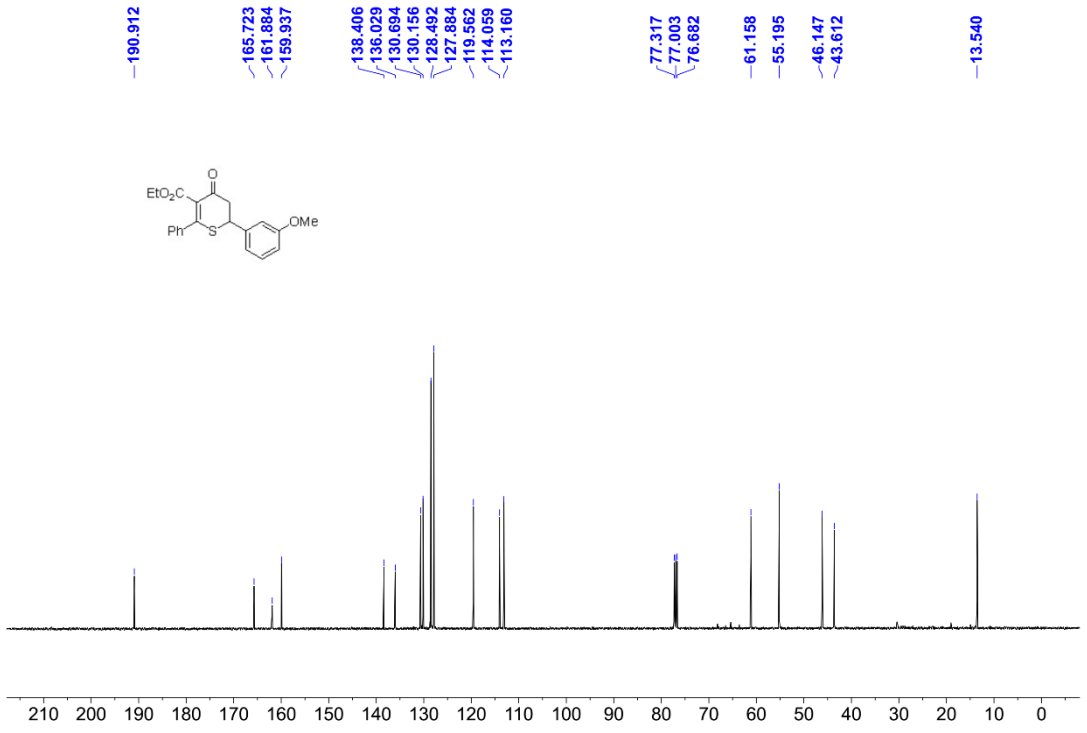

WQY-20190521-POS-C 44 (0.185)
1: TOF MS ES+
9.77e3
369.1154
100
%
0
369.085
369.090
369.095
369.100
369.105
369.110
369.115
369.120
369.125
369.130
369.135
369.140
m/z

Ethyl 2-(3-methoxyphenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ae**)

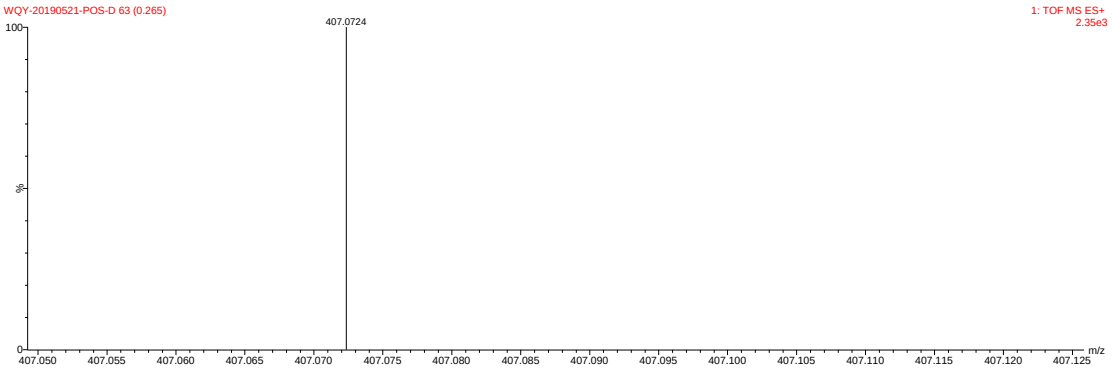
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

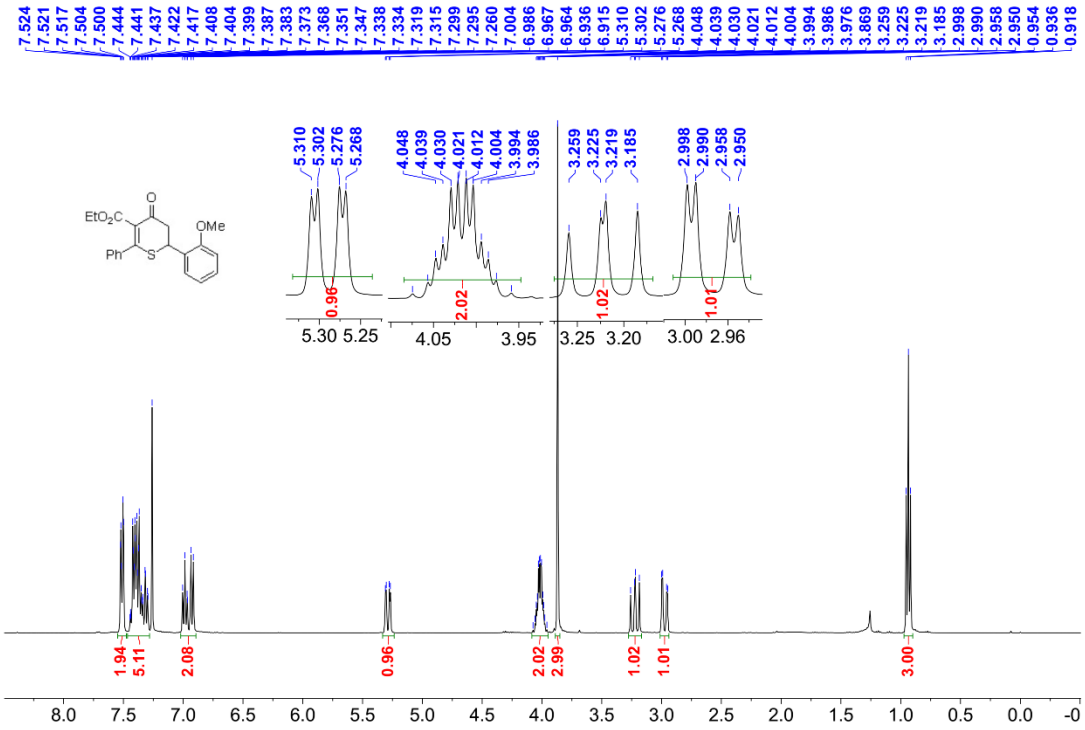


HRMS

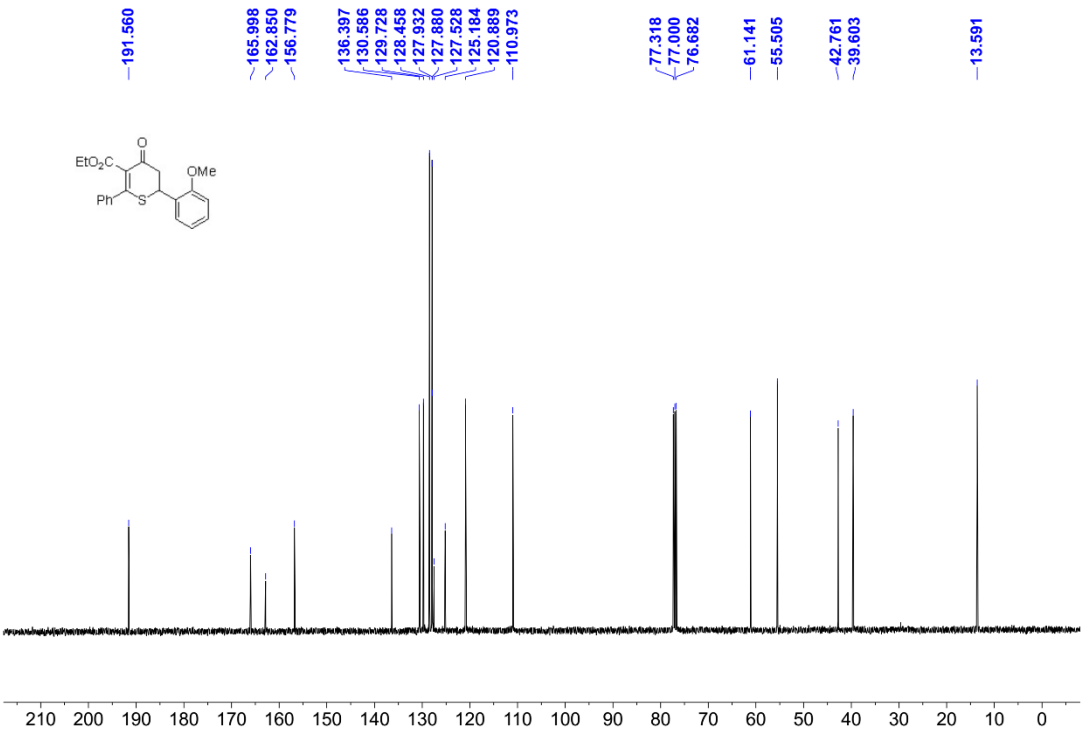

WQY-20190521-POS-D 63 (0.265)
1: TOF MS ES+
2.35e3
407.0724
100
%
0
407.050
407.055
407.060
407.065
407.070
407.075
407.080
407.085
407.090
407.095
407.100
407.105
407.110
407.115
407.120
407.125
m/z

Ethyl 2-(2-methoxyphenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3af**)

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



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

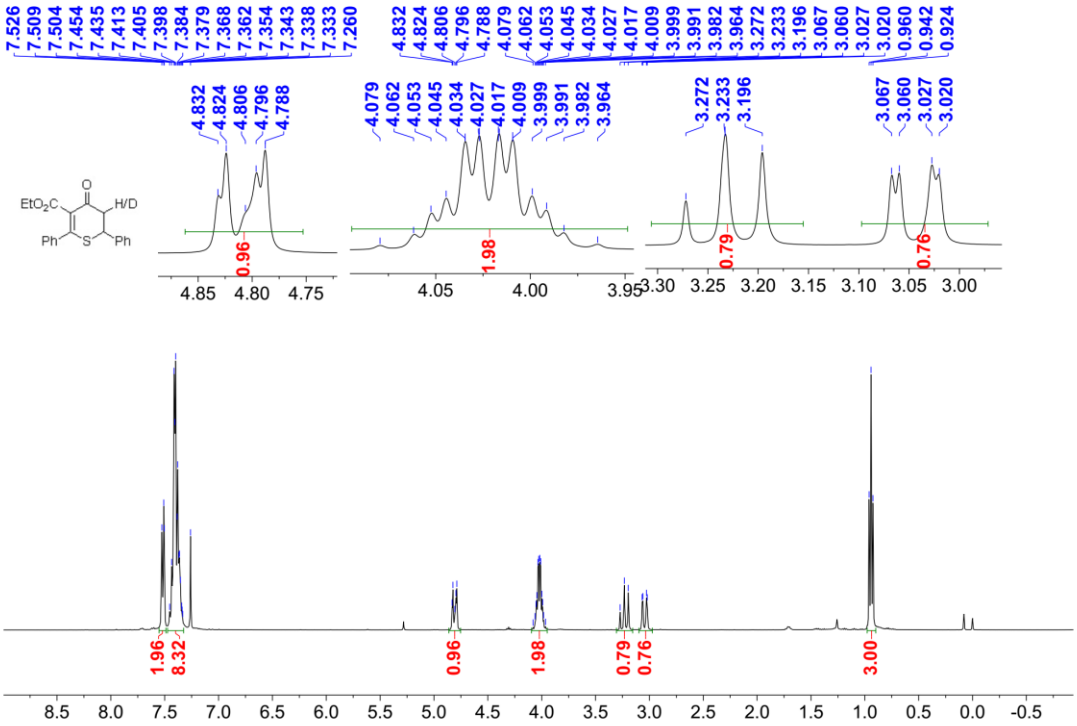


HRMS

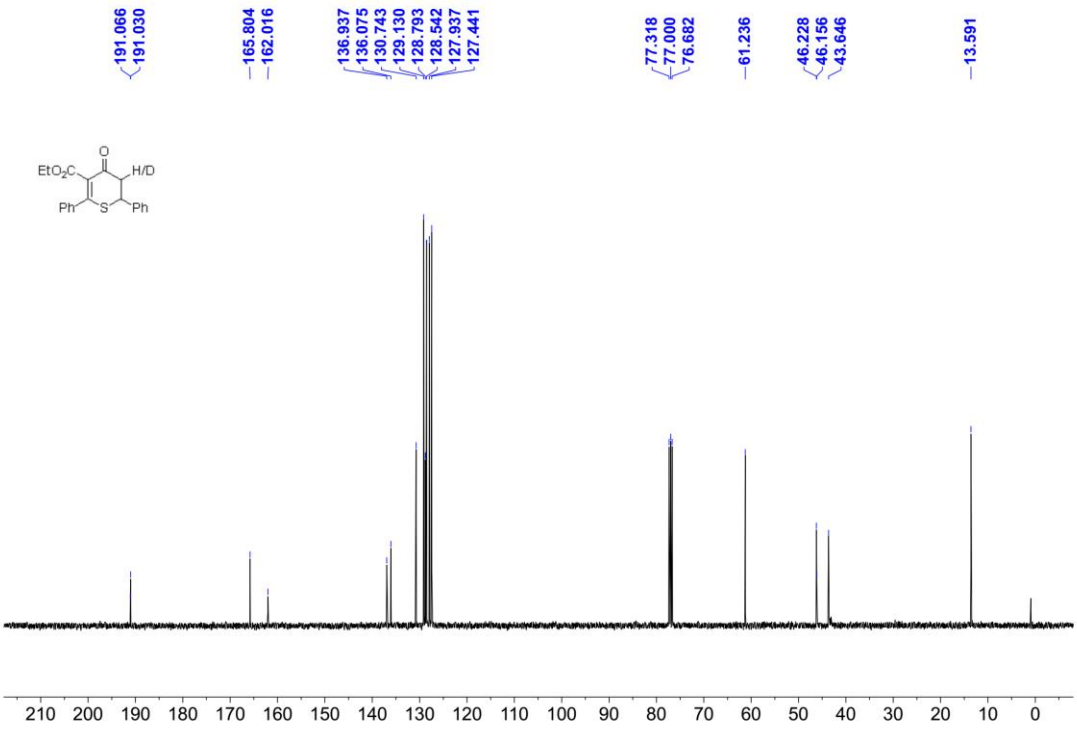

WQY-20190521-POS-E 127 (0.505)
1: TOF MS ES+
438
100
%
0
369.1148
369.114
369.115
m/z

Ethyl 4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ag**-*d/h*)

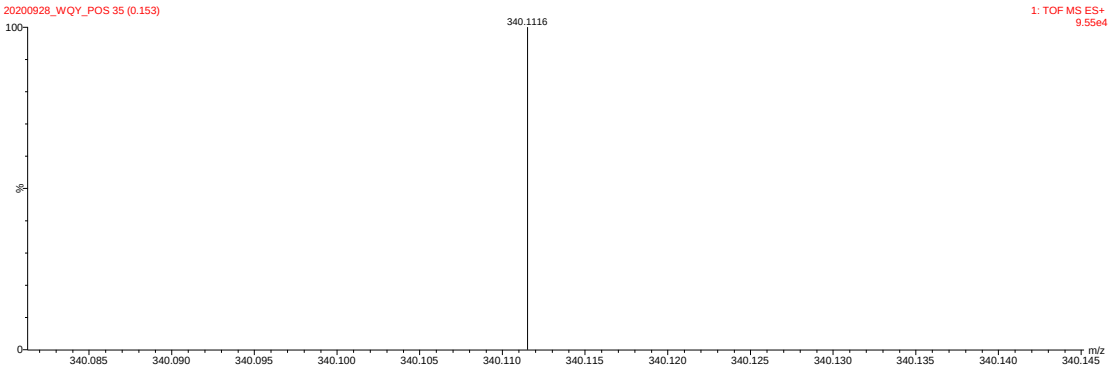
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

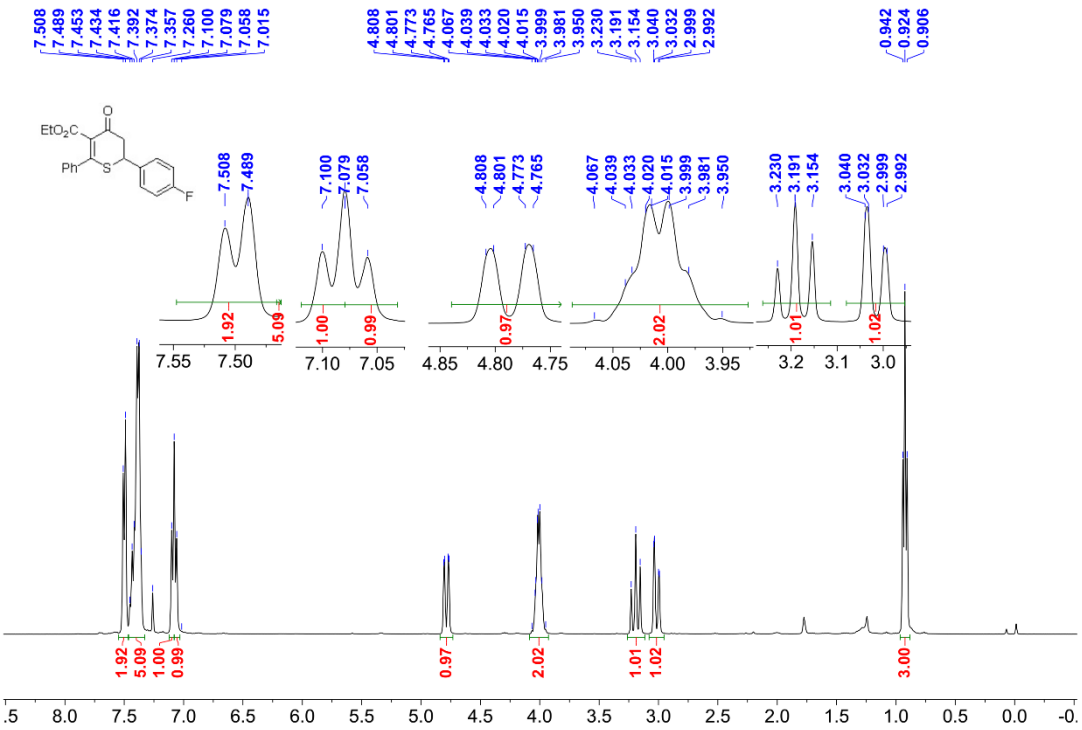


HRMS

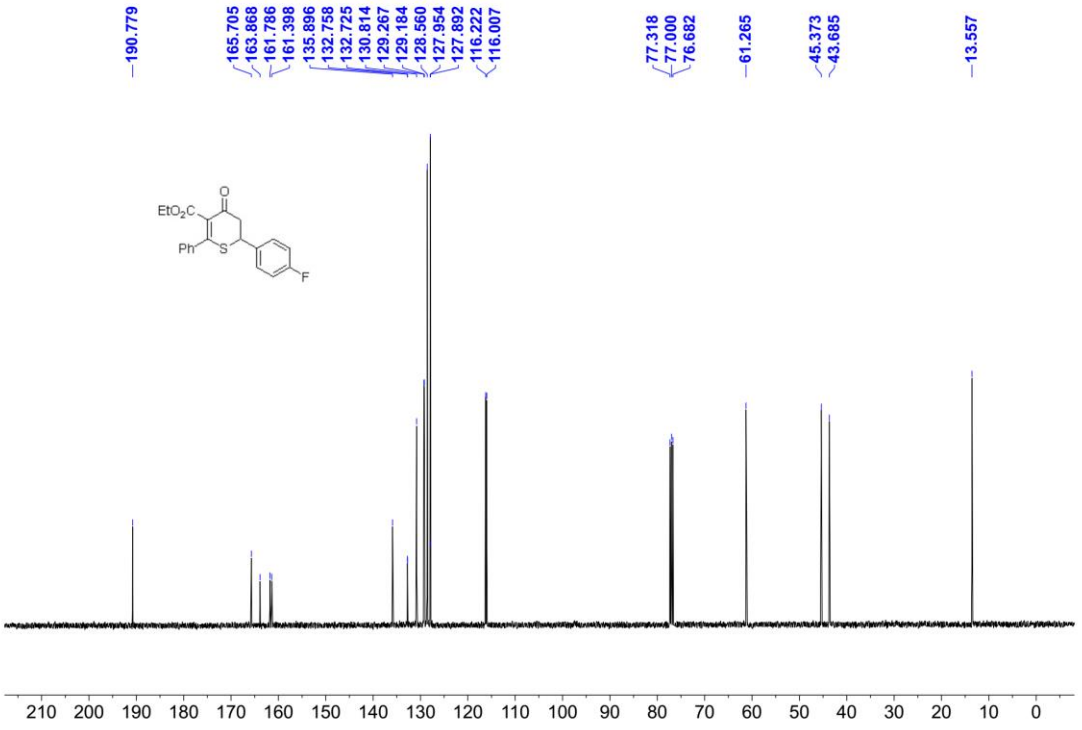

20200928_WQY_POS 35 (0.153)
1: TOF MS ES+
9.55e4
340.1116
100
%
0
340.085
340.090
340.095
340.100
340.105
340.110
340.115
340.120
340.125
340.130
340.135
340.140
340.145
m/z

Ethyl 2-(4-fluorophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ah**)

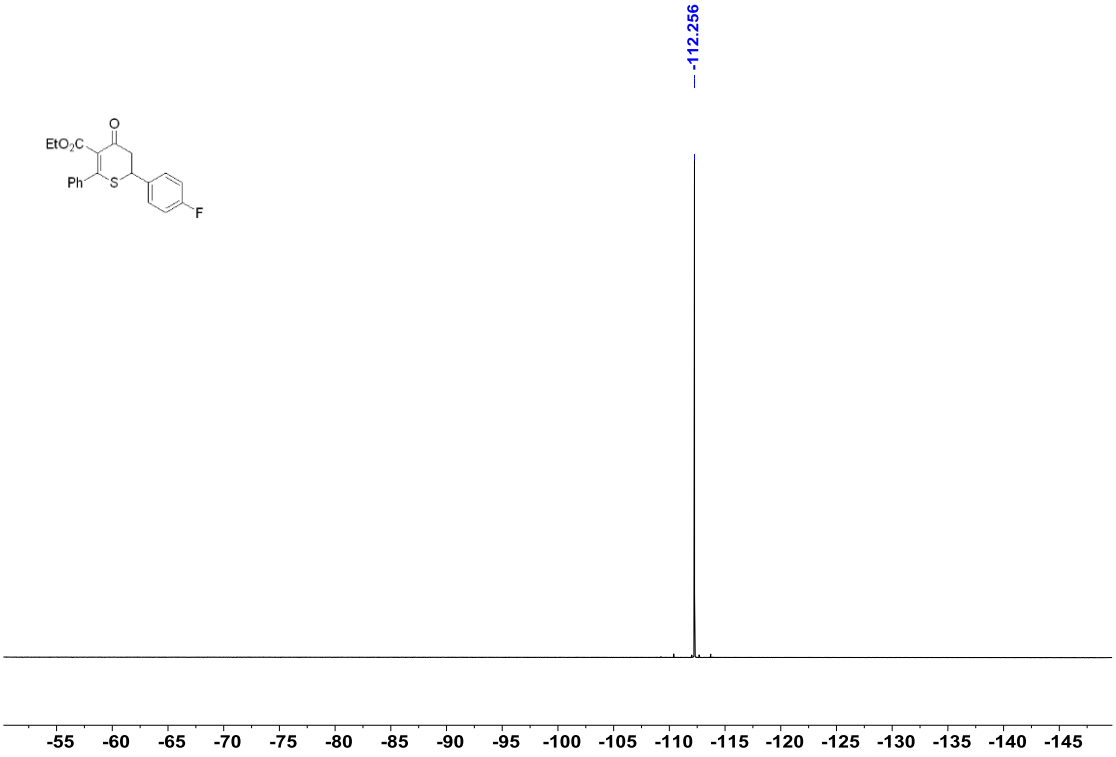
^{1}H MNR (400 MHz, $CDCl_3$)



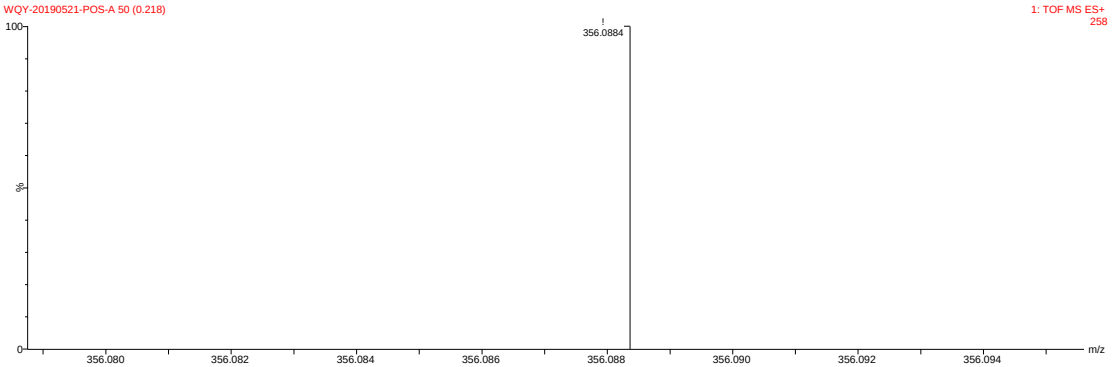
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



^{19}F NMR{^{1}H } (376 MHz, $CDCl_3$)

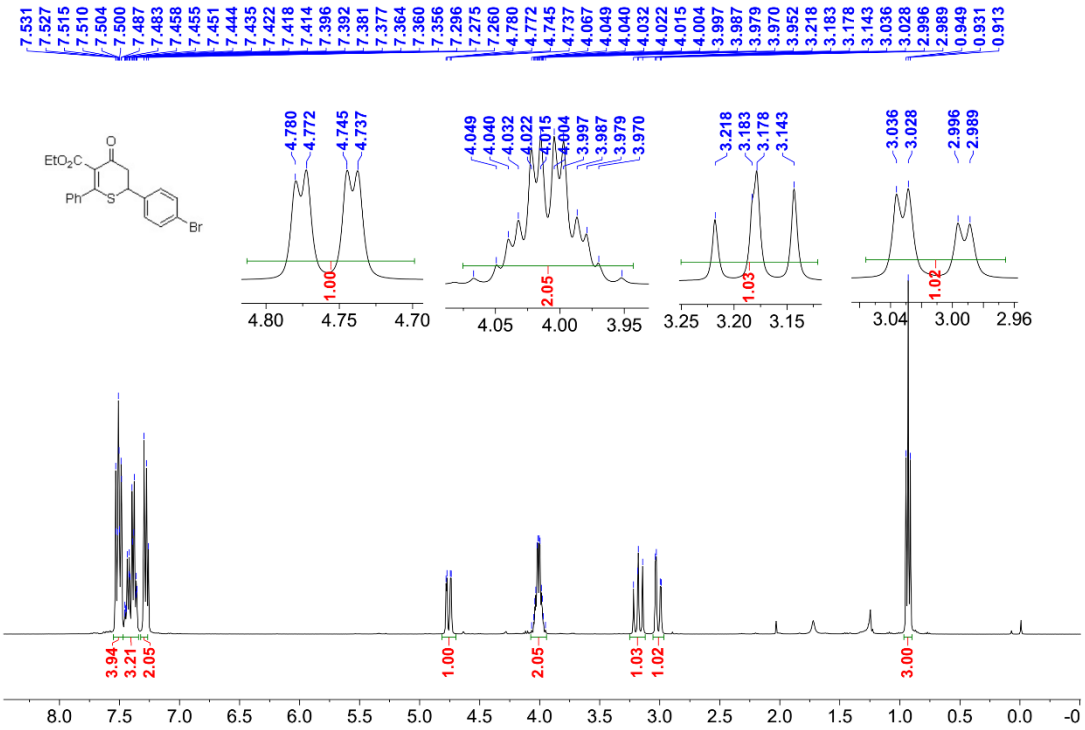


HRMS

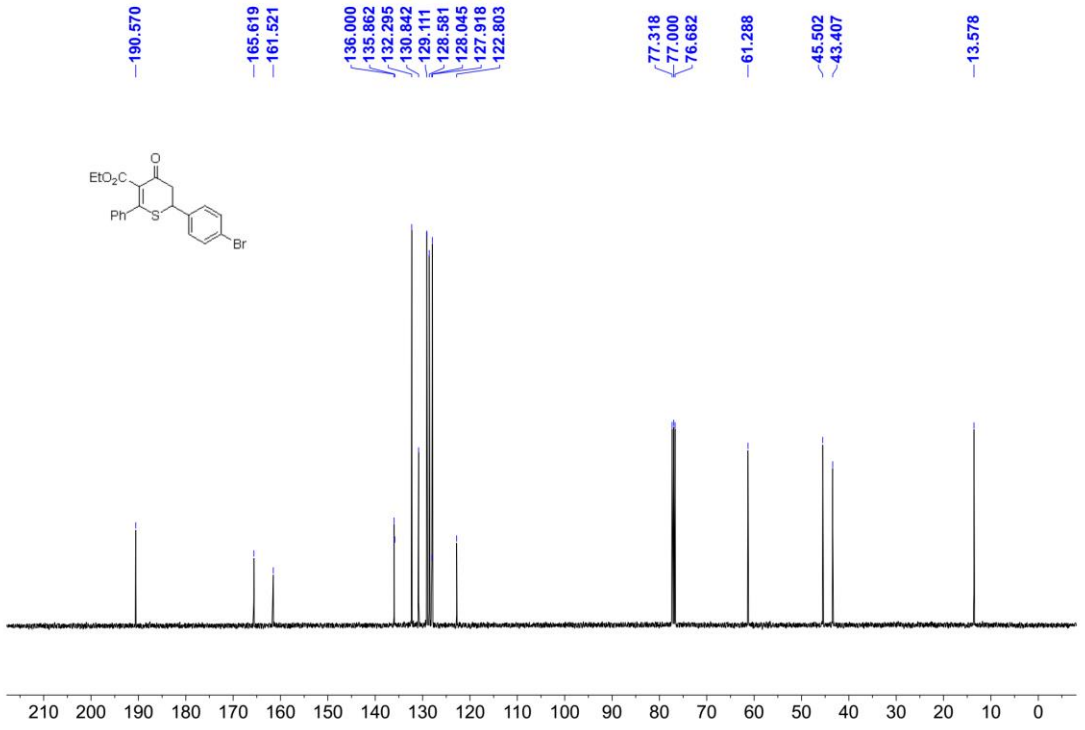


Ethyl 2-(4-bromophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ai**)

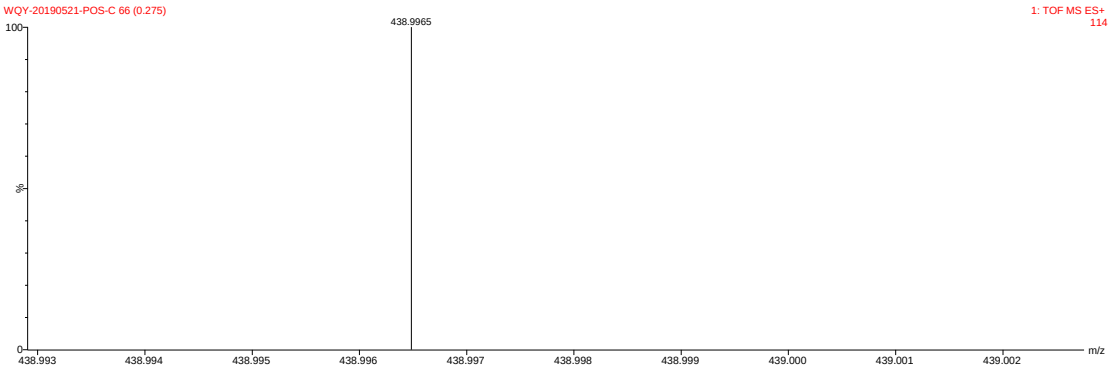
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

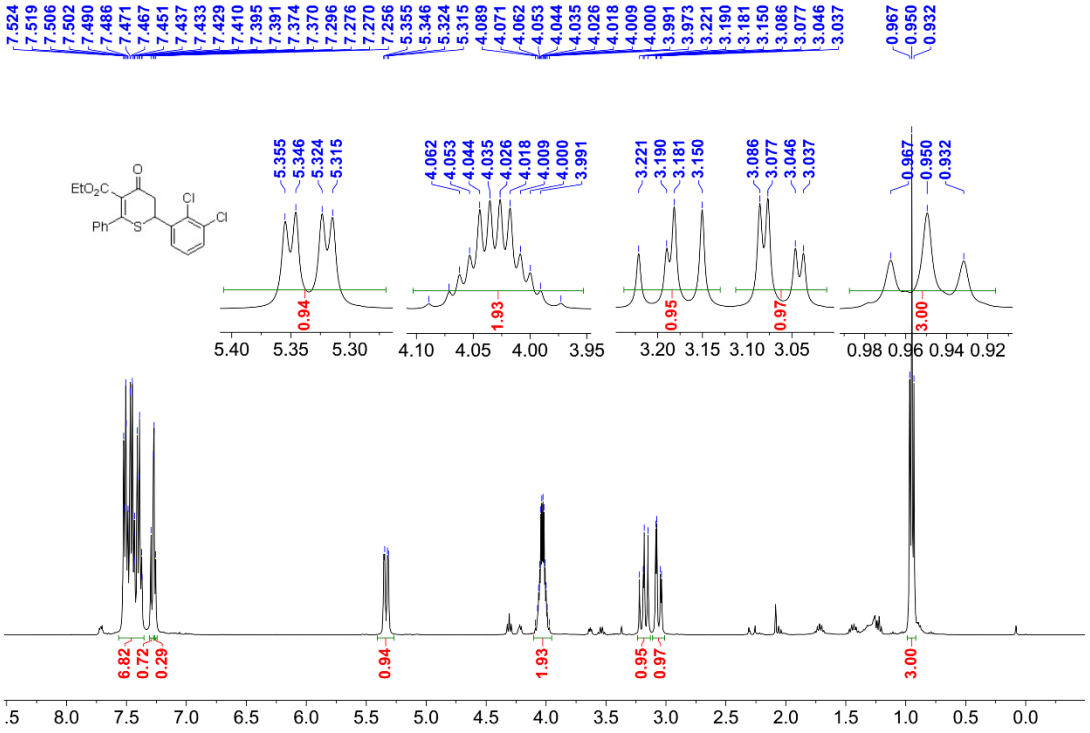


HRMS

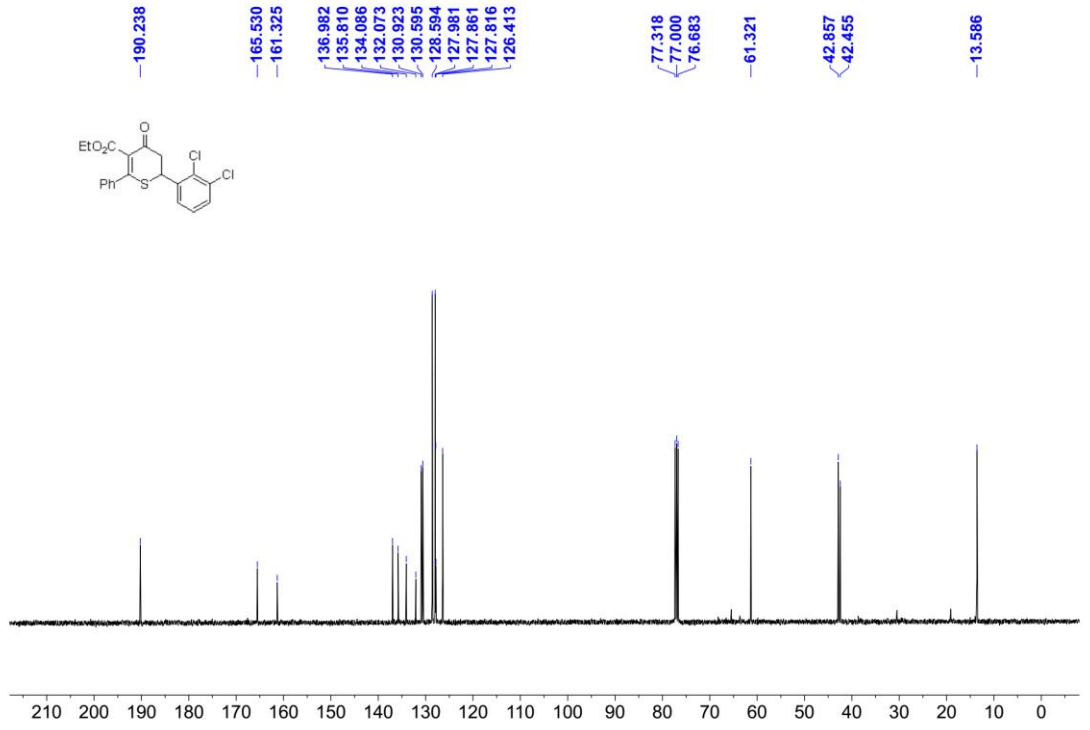

WQY-20190521-POS-C 66 (0.275)
1: TOF MS ES+
114
438.9965
100
%
0
438.993
438.994
438.995
438.996
438.997
438.998
438.999
439.000
439.001
439.002
m/z

Ethyl 2-(2,3-dichlorophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aj**)

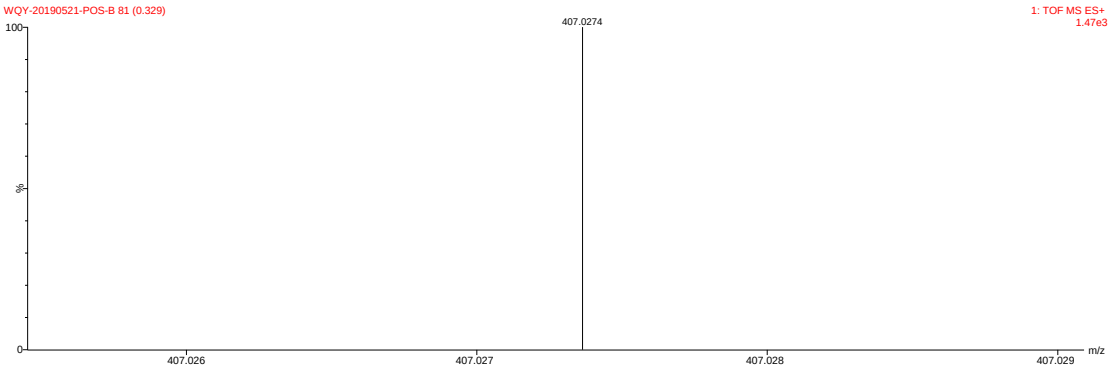
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

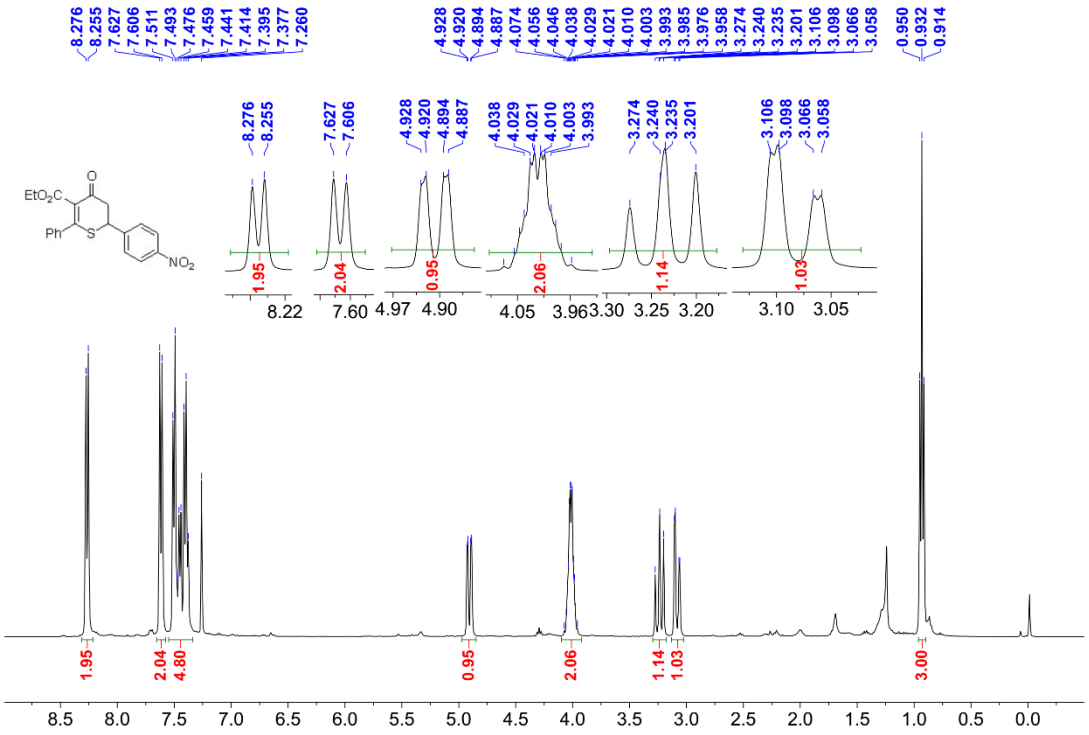


HRMS

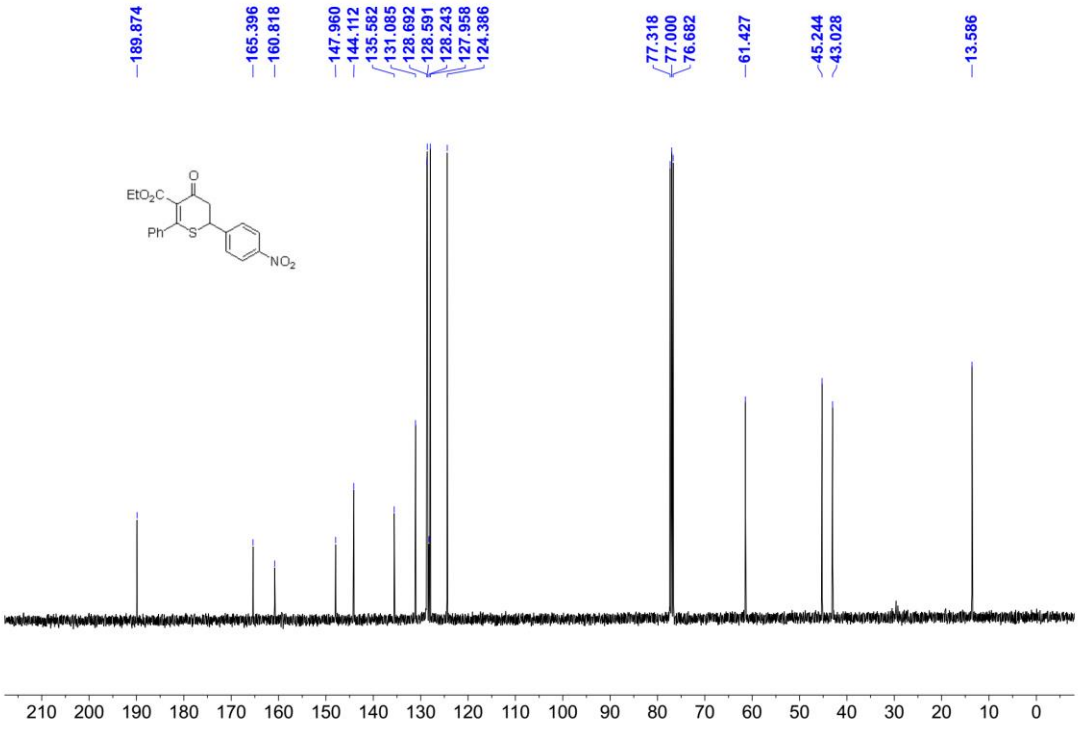

WQY-20190521-POS-B 81 (0.329)
1: TOF MS ES+
1.47e3
407.0274
100
%
0
407.026
407.027
407.028
407.029
m/z

Ethyl 2-(4-nitrophenyl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ak**)

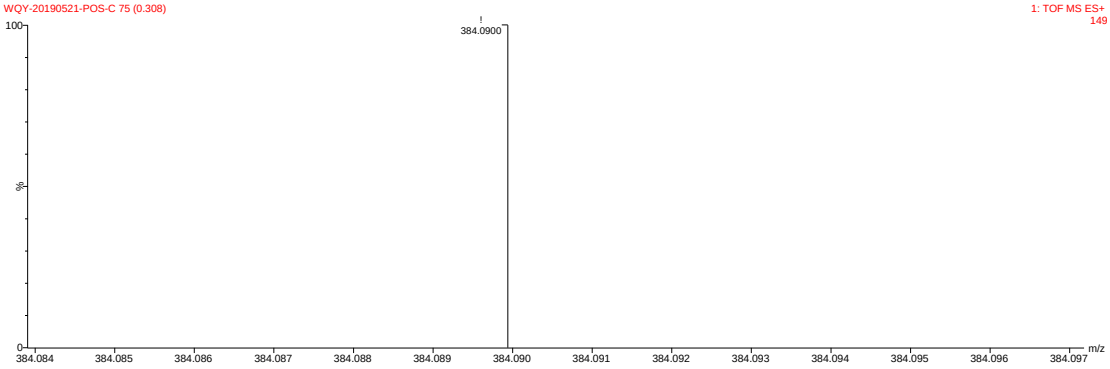
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

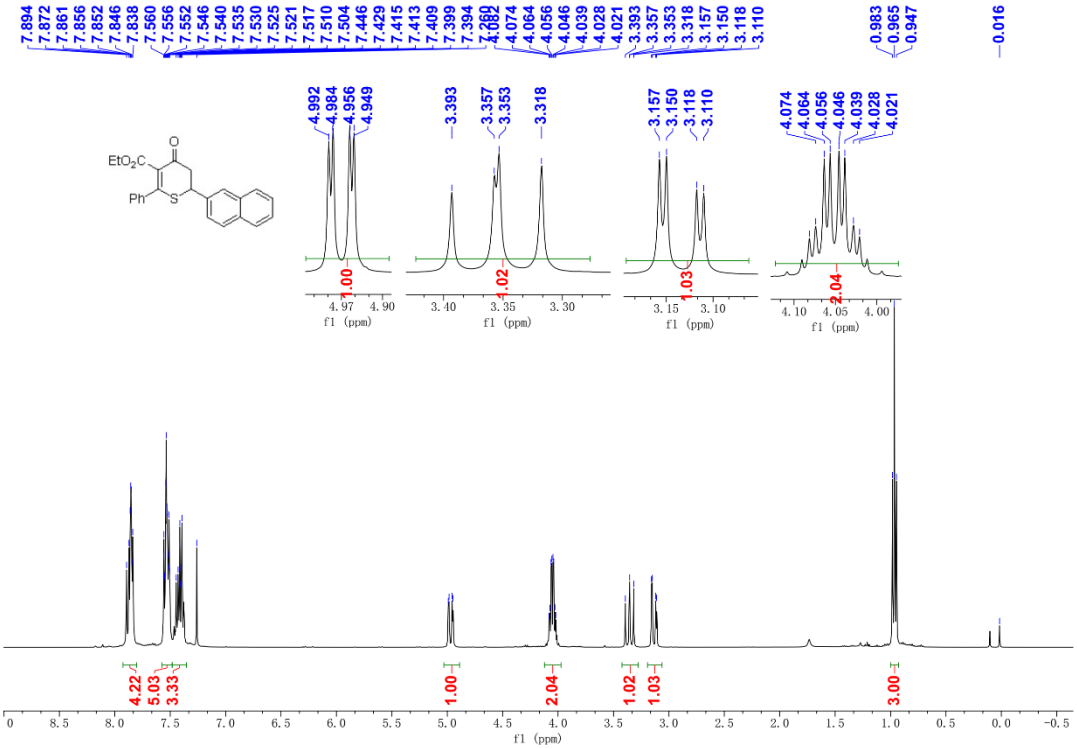


HRMS

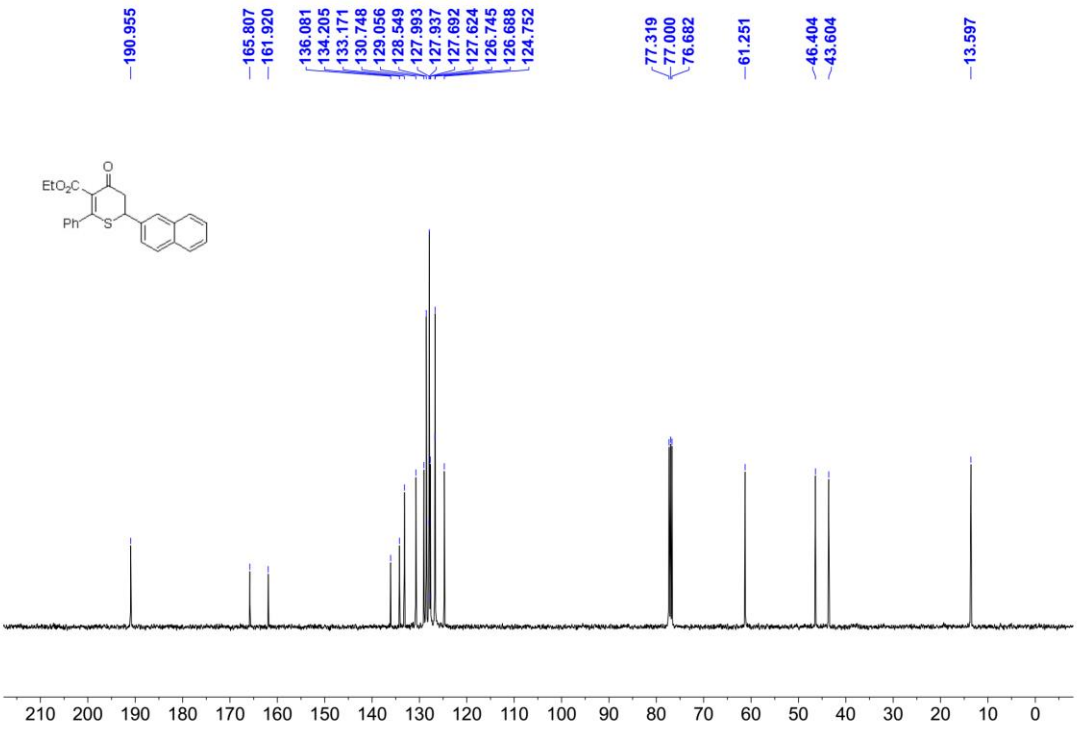

WQY-20190521-POS-C 75 (0.308)
1: TOF MS ES+
149
384.0900
100
%
0
384.084
384.085
384.086
384.087
384.088
384.089
384.090
384.091
384.092
384.093
384.094
384.095
384.096
384.097
m/z

Ethyl 2-(naphthalen-2-yl)-4-oxo-6-phenyl-3,4-dihydro-2H-thiopyran-5-carboxylate (**3al**)

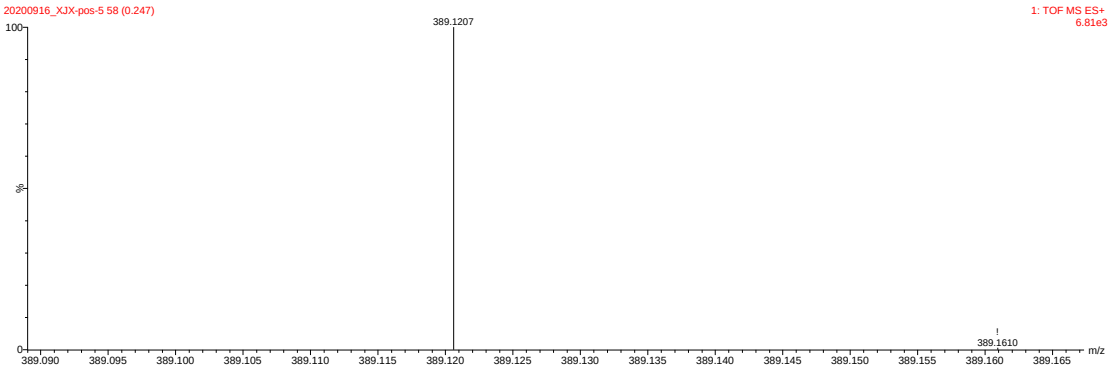
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

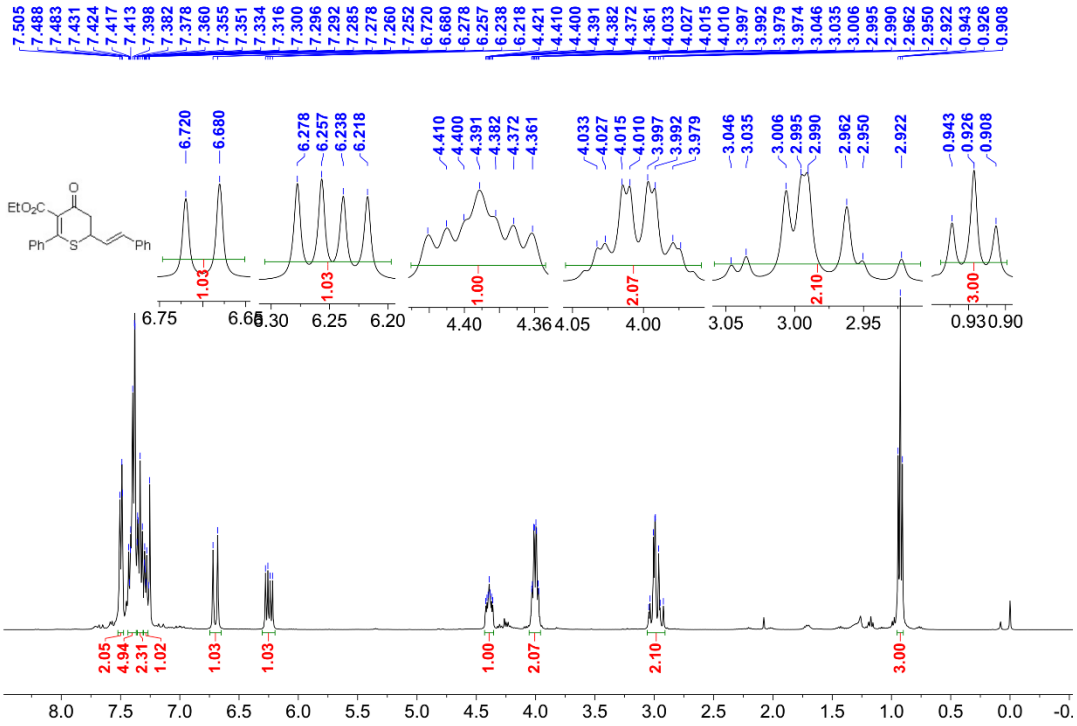


HRMS

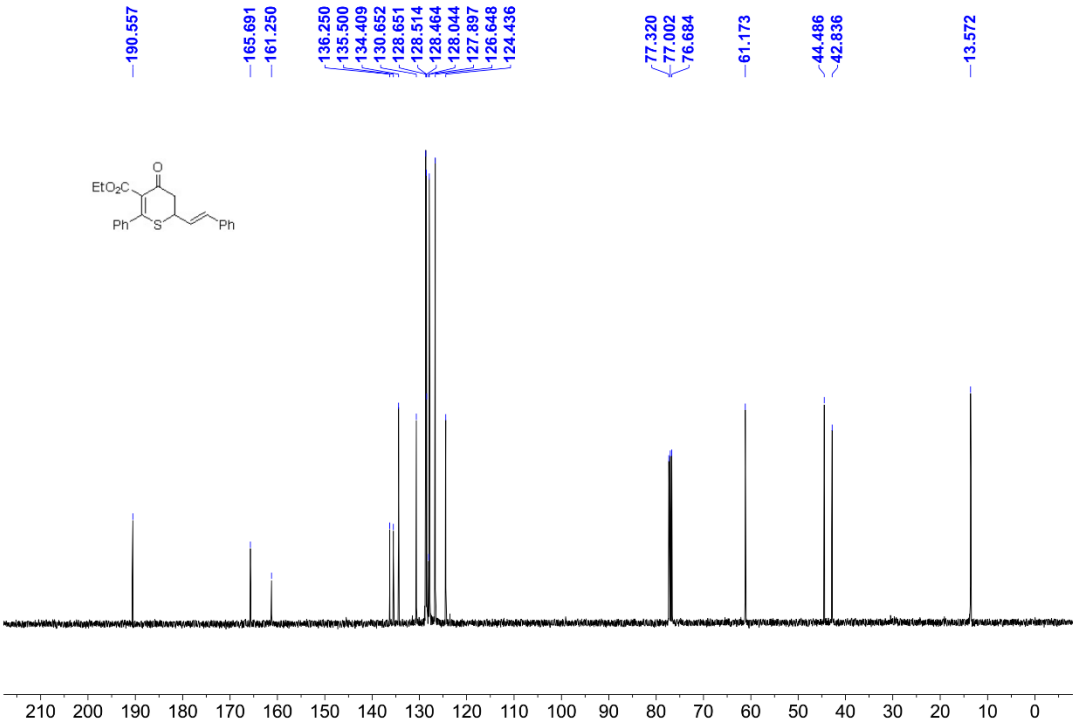

20200916_XJX-pos-5 58 (0.247)
1: TOF MS ES+
6.81e3
100
%
0
389.1207
389.1610
389.090
389.095
389.100
389.105
389.110
389.115
389.120
389.125
389.130
389.135
389.140
389.145
389.150
389.155
389.160
389.165
m/z

Ethyl (*E*)-4-oxo-6-phenyl-2-styryl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3am**)

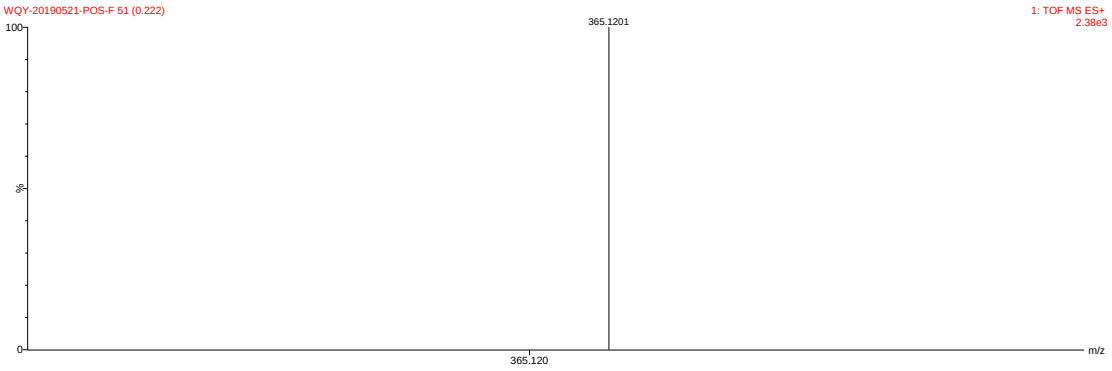
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

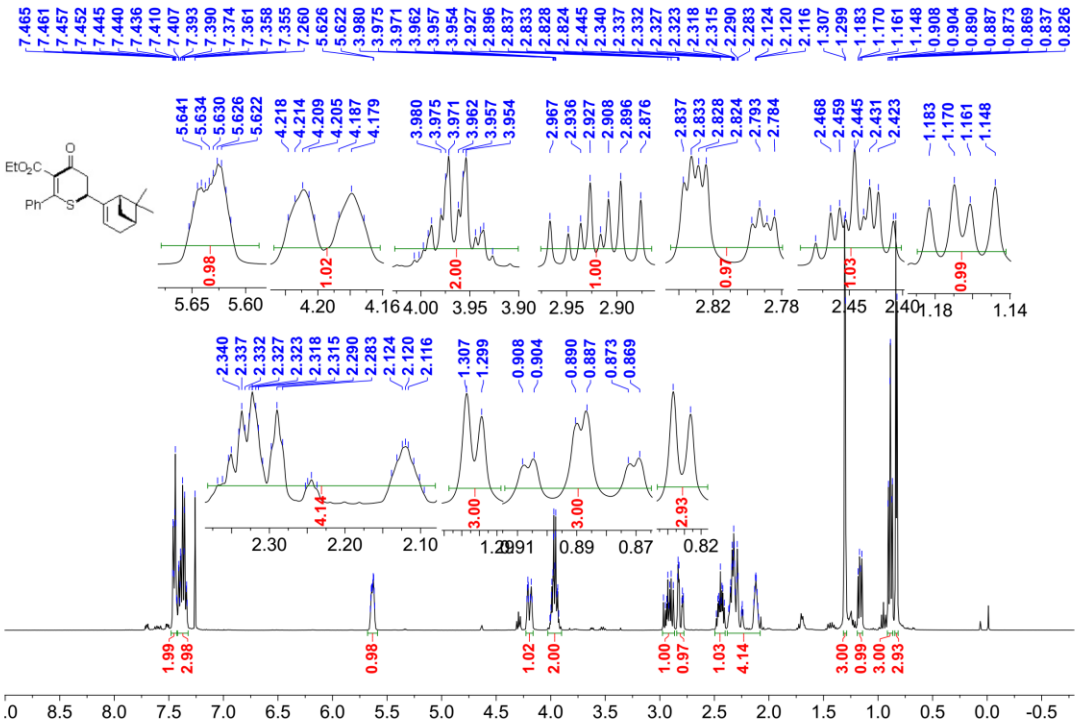


HRMS

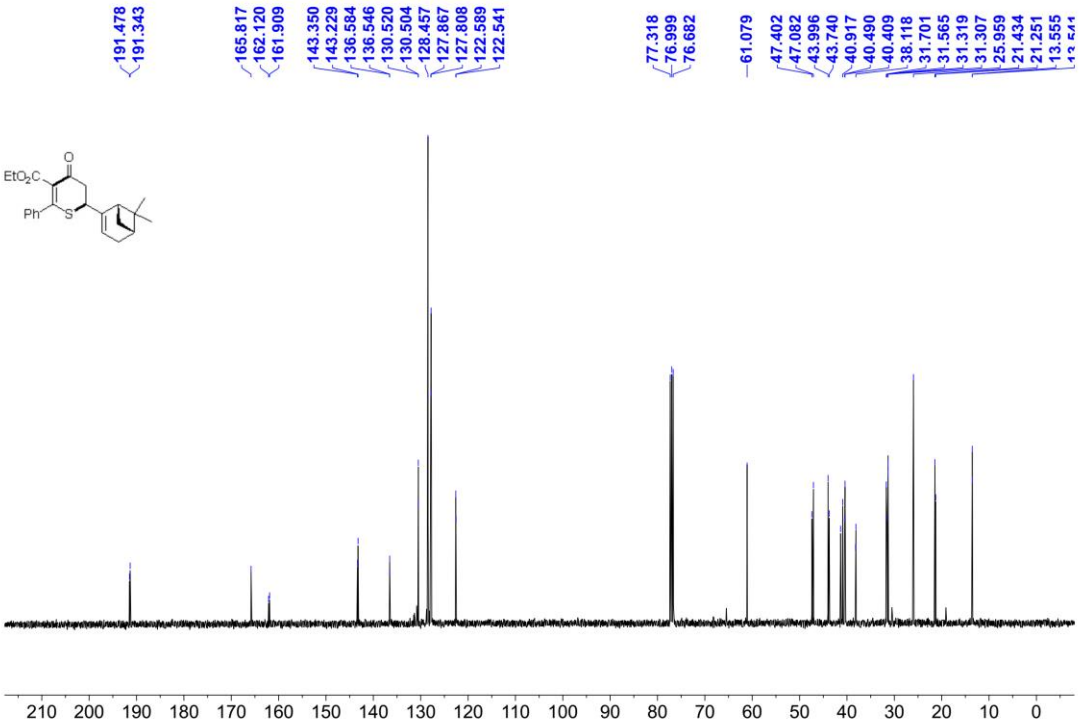

WQY-20190521-POS-F 51 (0.222)
1: TOF MS ES+
2.38e3
100
%
0
365.1201
365.120
m/z

Ethyl 2-((1*R*,5*R*)-6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3an**)

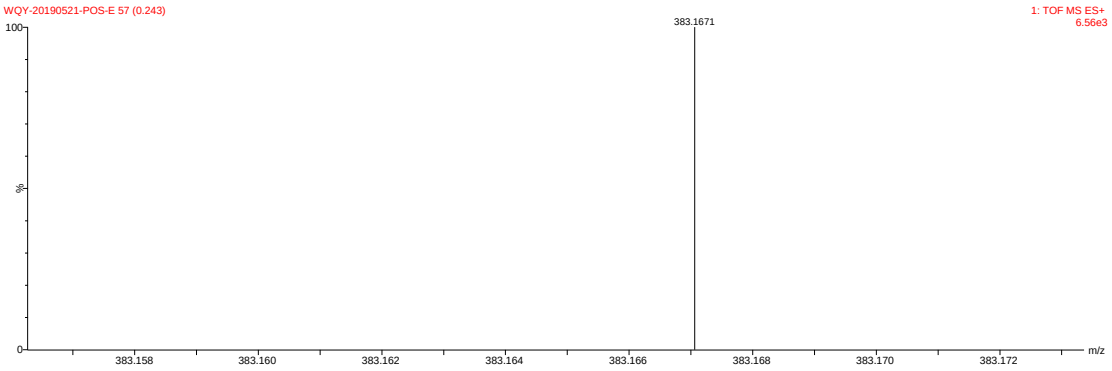
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

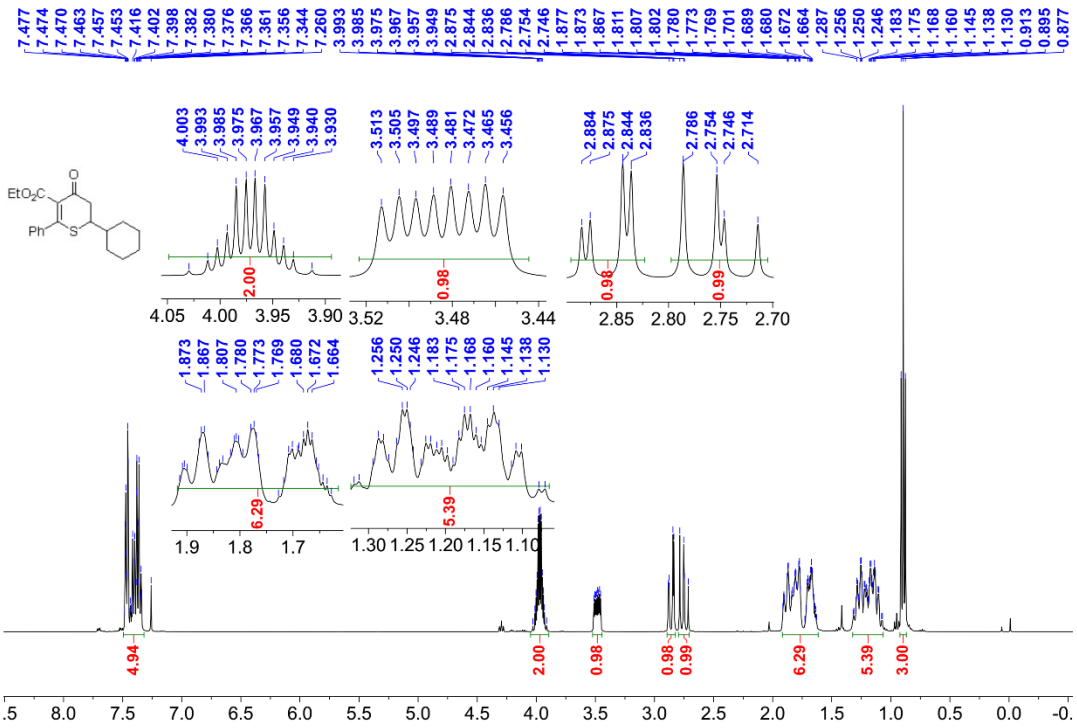


HRMS

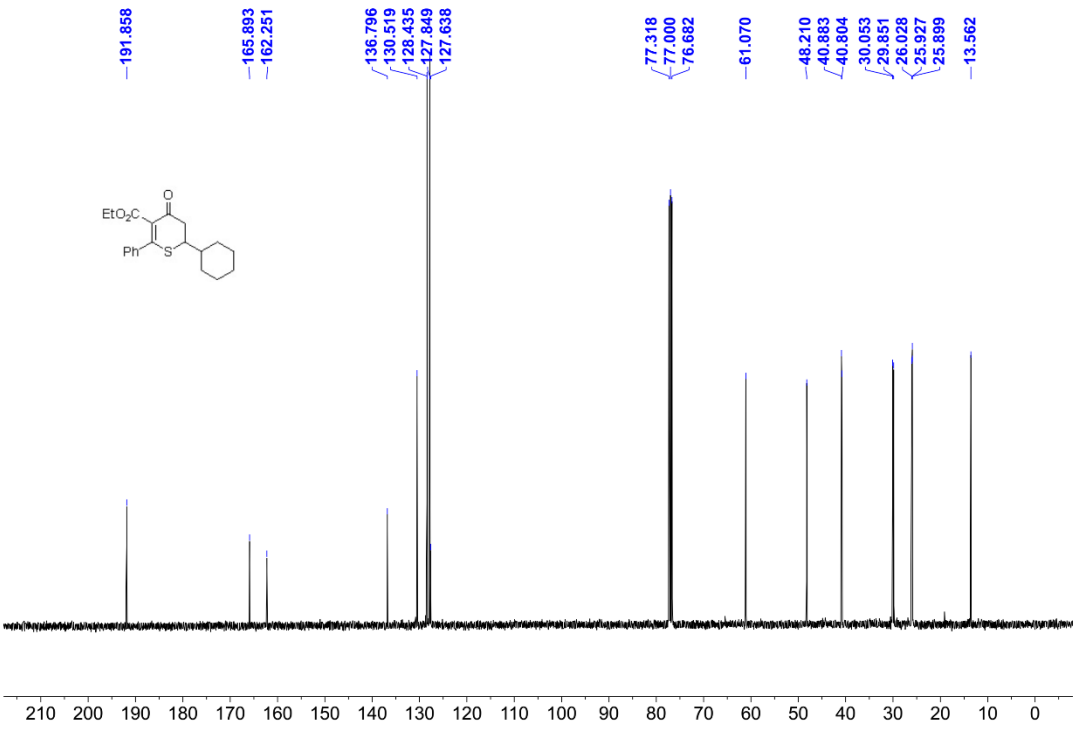

WQY-20190521-POS-E 57 (0.243)
1: TOF MS ES+
6.56e3
383.1671
100
%
0
383.158
383.160
383.162
383.164
383.166
383.168
383.170
383.172
m/z

Ethyl 2-cyclohexyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ao**)

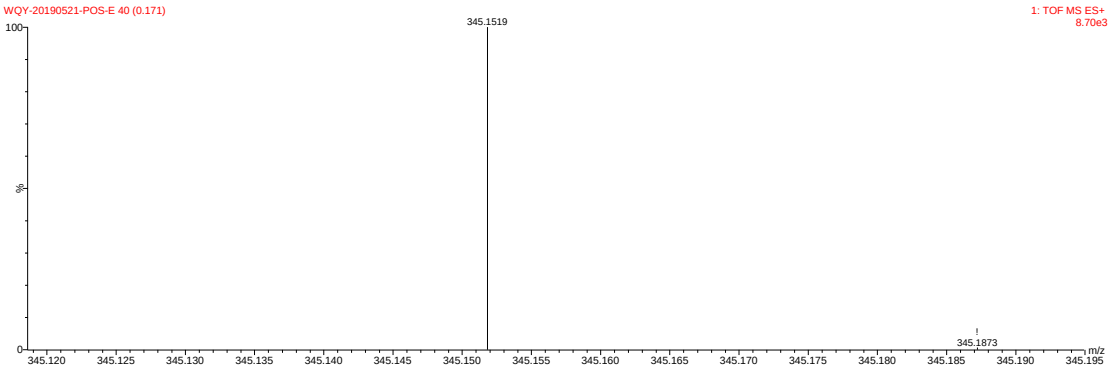
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

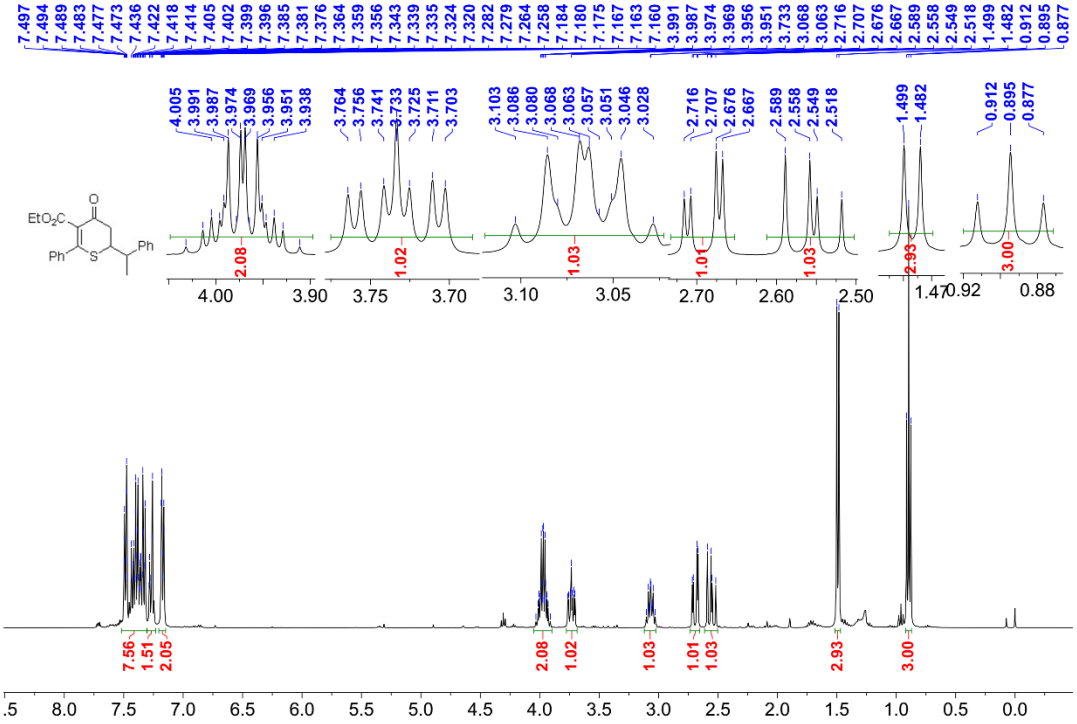


HRMS

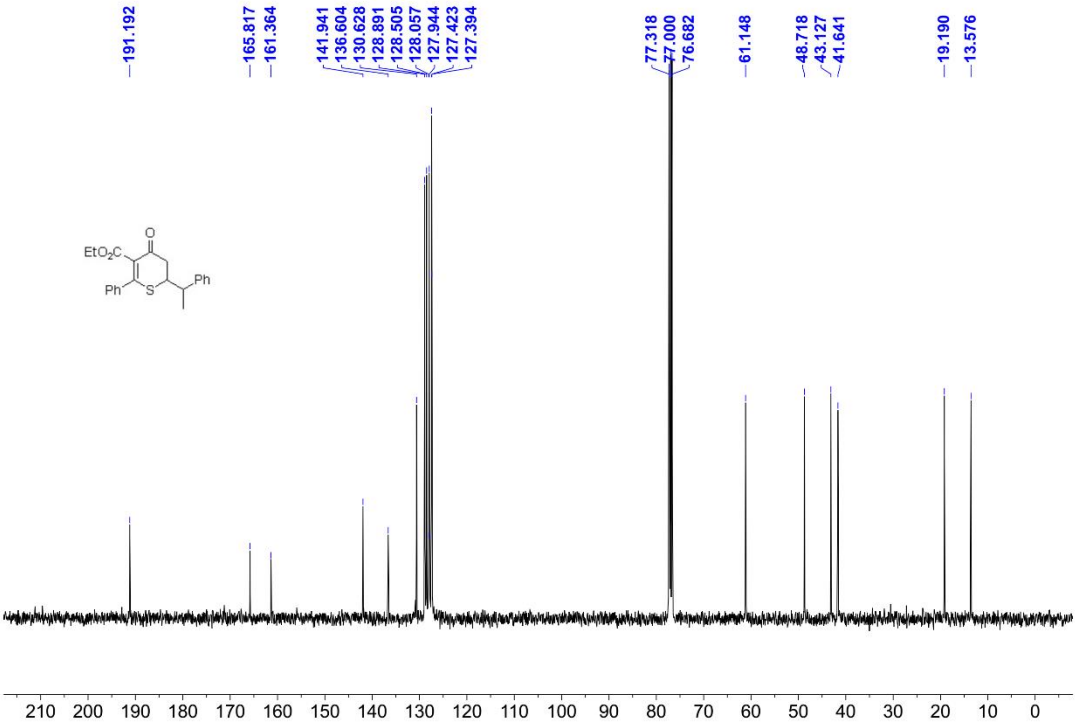

WQY-20190521-POS-E 40 (0.171)
1: TOF MS ES+
8.70e3
345.1519
100
%
0
345.1873
345.120
345.125
345.130
345.135
345.140
345.145
345.150
345.155
345.160
345.165
345.170
345.175
345.180
345.185
345.190
345.195
m/z

Ethyl 4-oxo-6-phenyl-2-(1-phenylethyl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ap**)

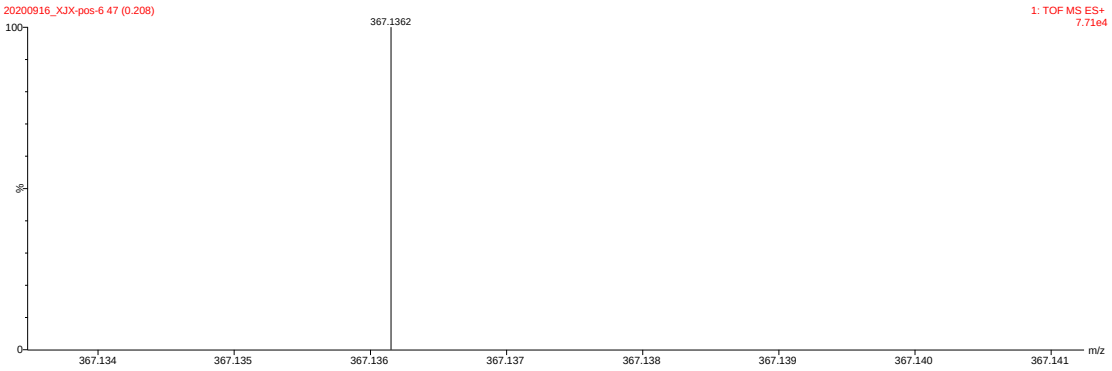
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

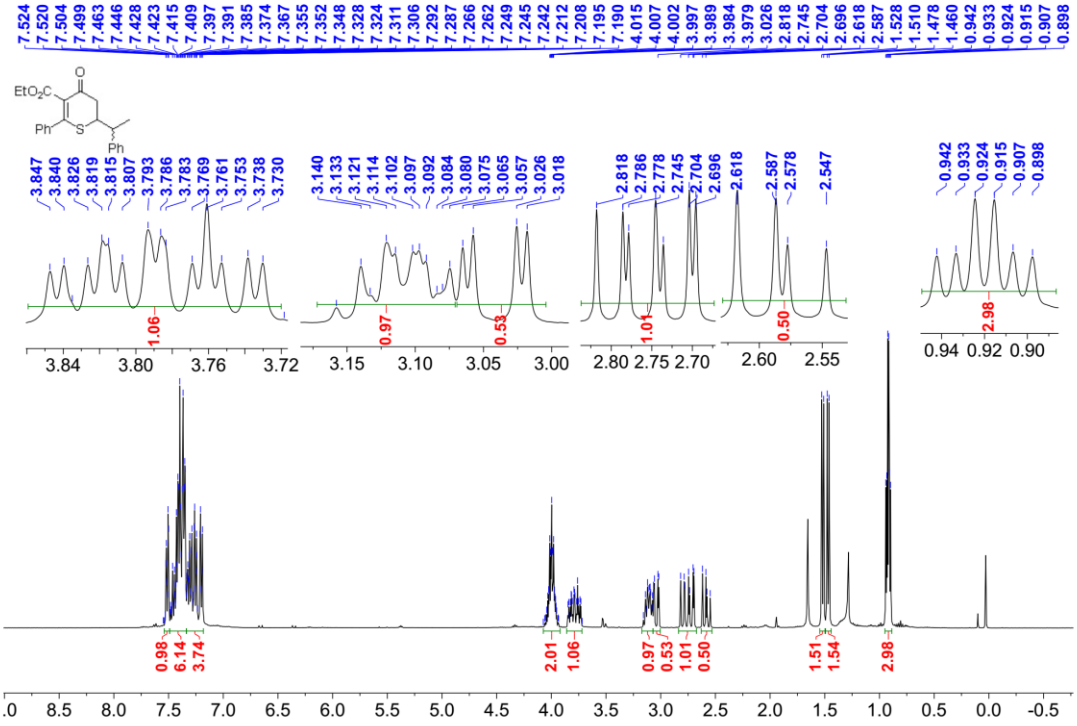


HRMS

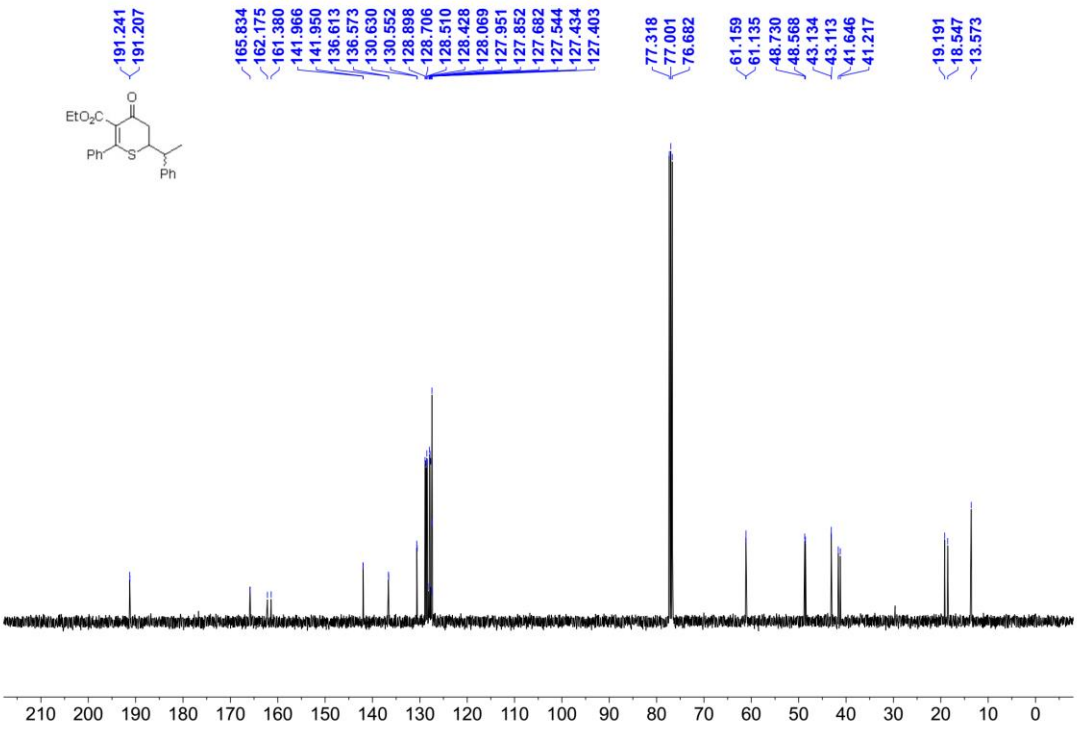

20200916_XJX-pos-6 47 (0.208)
1: TOF MS ES+
7.71e4
367.1362
100
%
0
367.134
367.135
367.136
367.137
367.138
367.139
367.140
367.141
m/z

Ethyl 4-oxo-6-phenyl-2-(1-phenylethyl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate **3ap** (*dr* = 1:1)

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



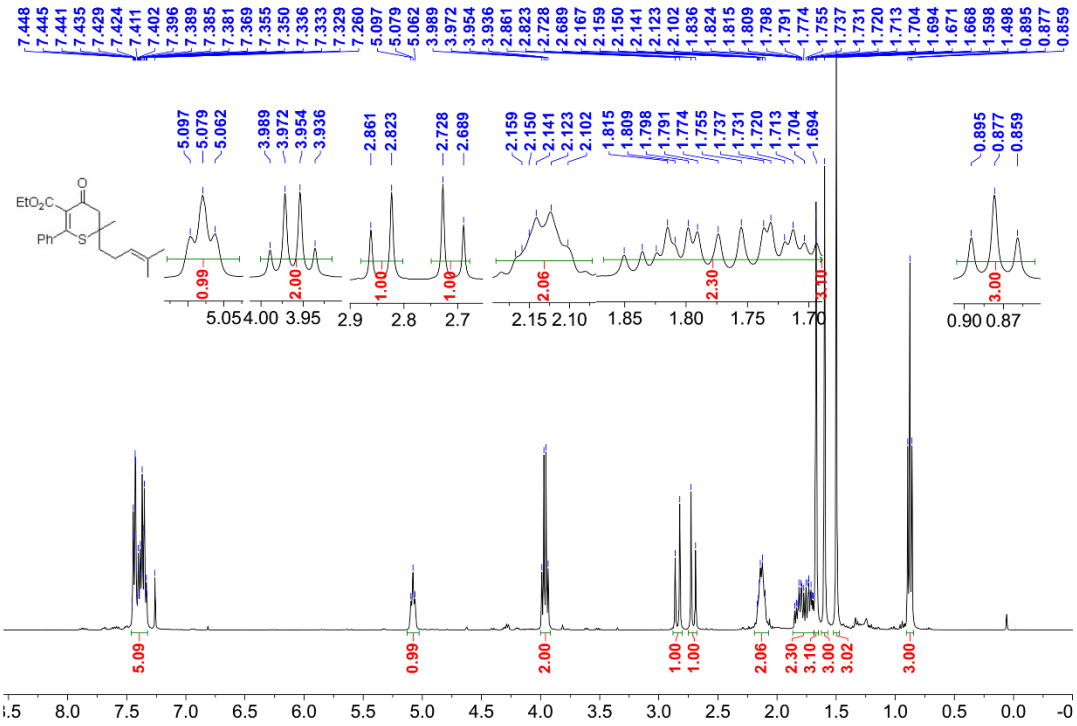
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



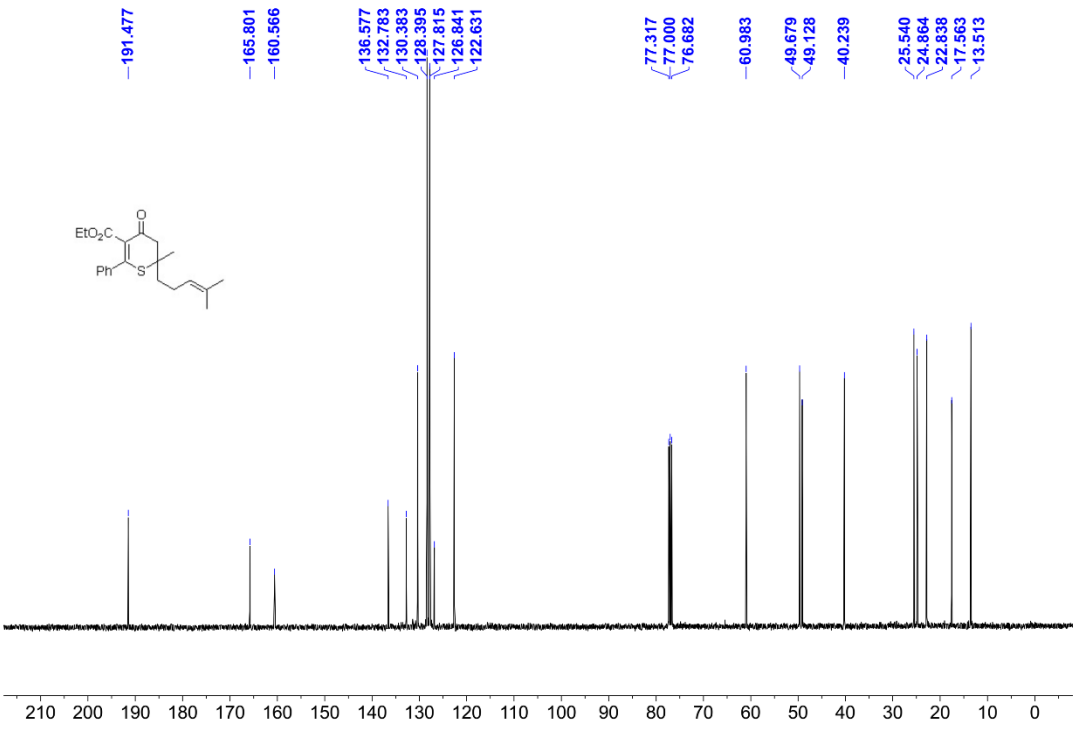
HRMS

Ethyl 2-methyl-2-(4-methylpent-3-en-1-yl)-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ar**)

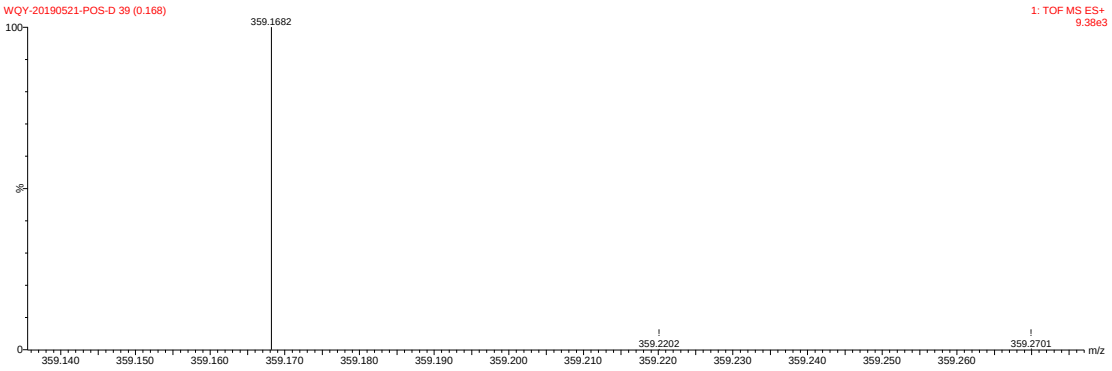
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

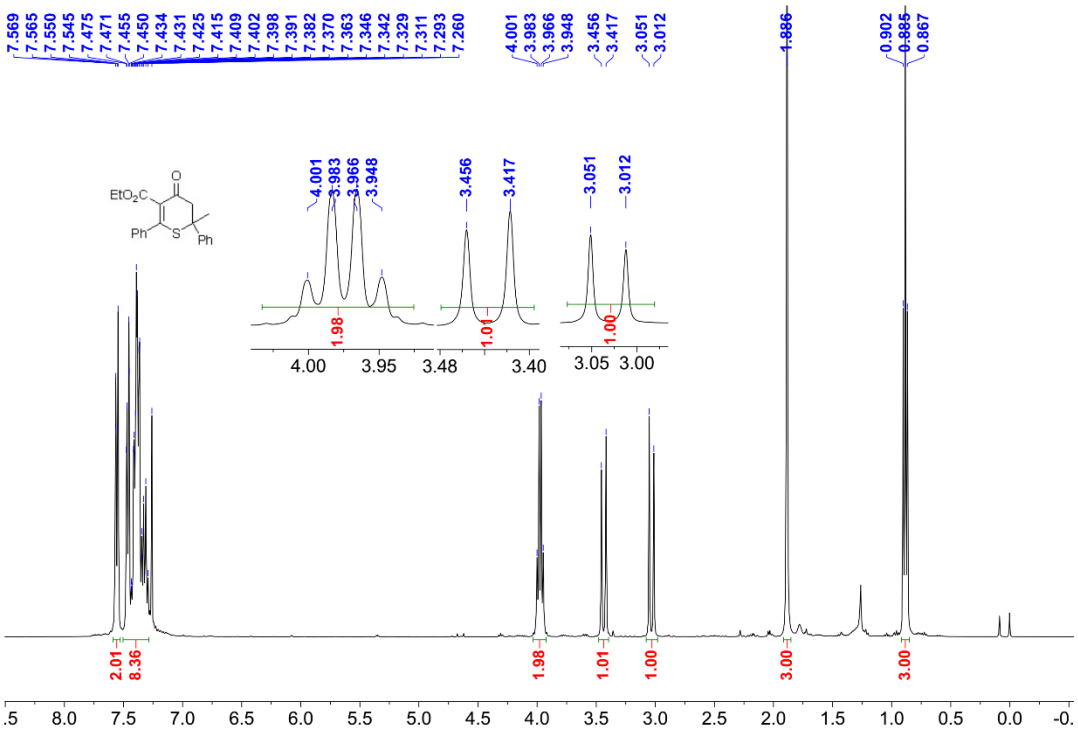


HRMS

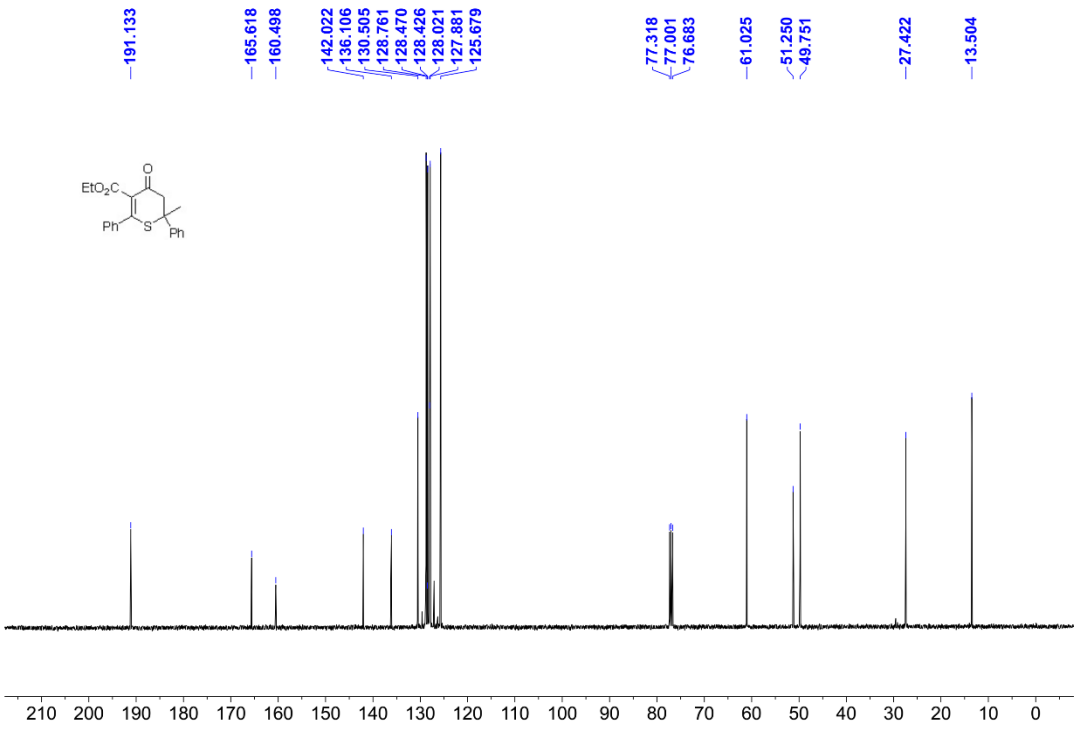

WQY-20190521-POS-D 39 (0.168)
1: TOF MS ES+
9.38e3
100
%
0
359.1682
359.2202
359.2701
359.140
359.150
359.160
359.170
359.180
359.190
359.200
359.210
359.220
359.230
359.240
359.250
359.260
m/z

Ethyl 2-methyl-4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3as**)

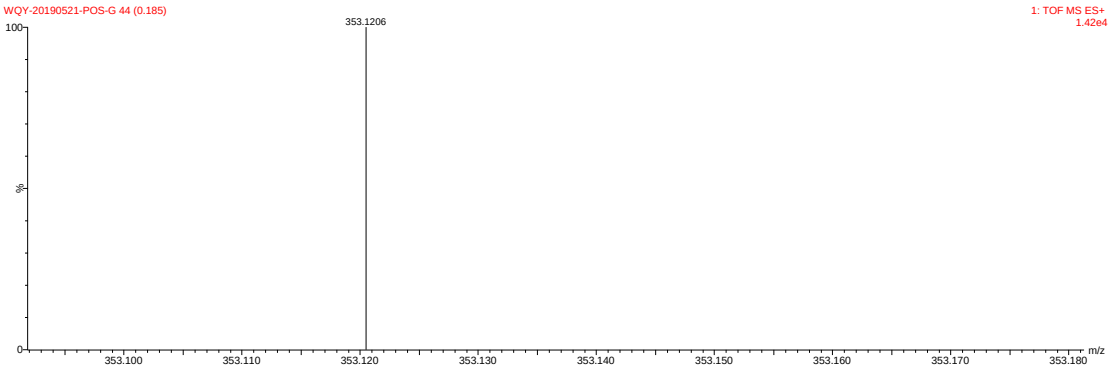
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

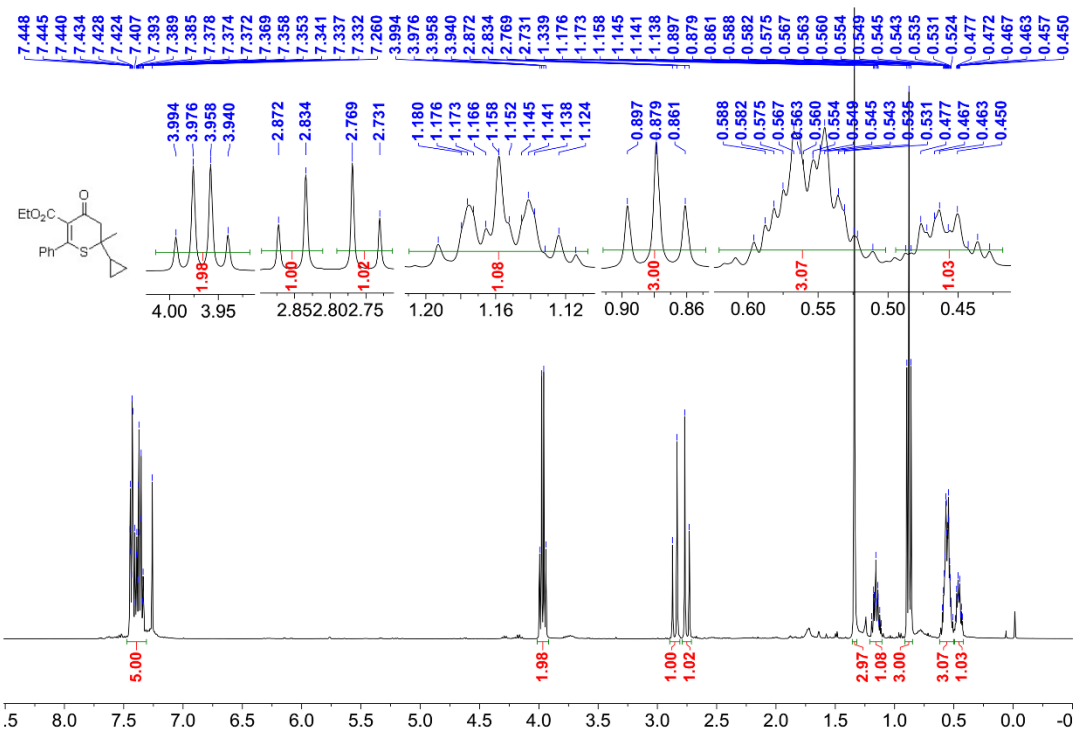


HRMS

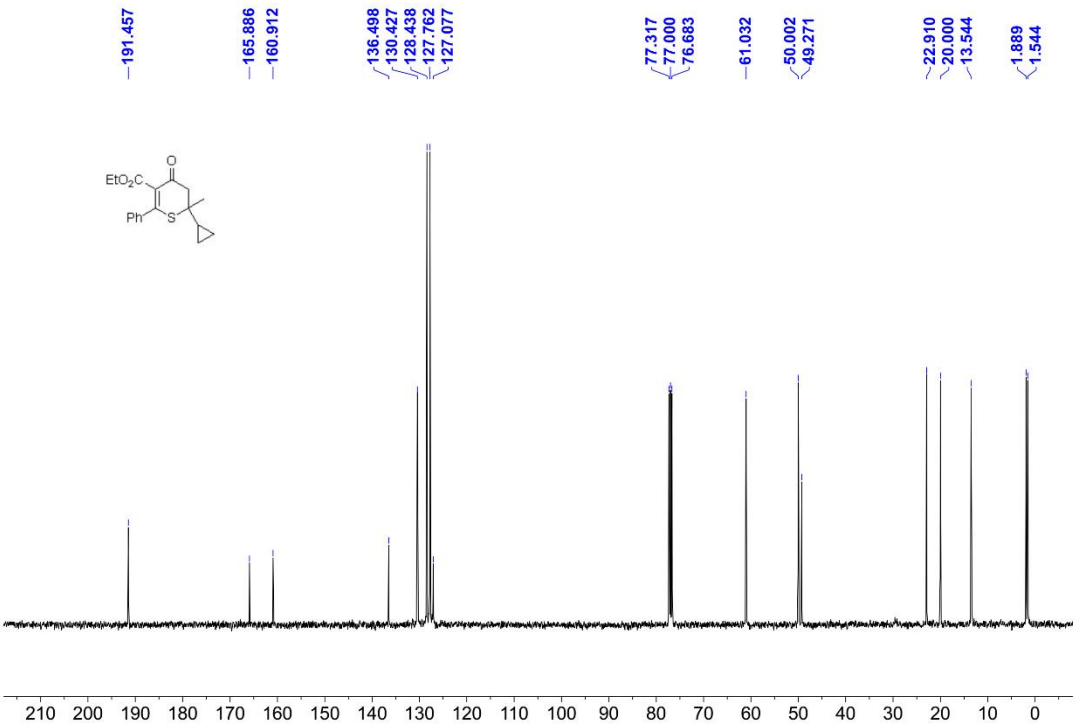

WQY-20190521-POS-G 44 (0.185)
1: TOF MS ES+
1.42e4
353.1206
100
%
0
353.100
353.110
353.120
353.130
353.140
353.150
353.160
353.170
353.180
m/z

Ethyl 2-cyclopropyl-2-methyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3at**)

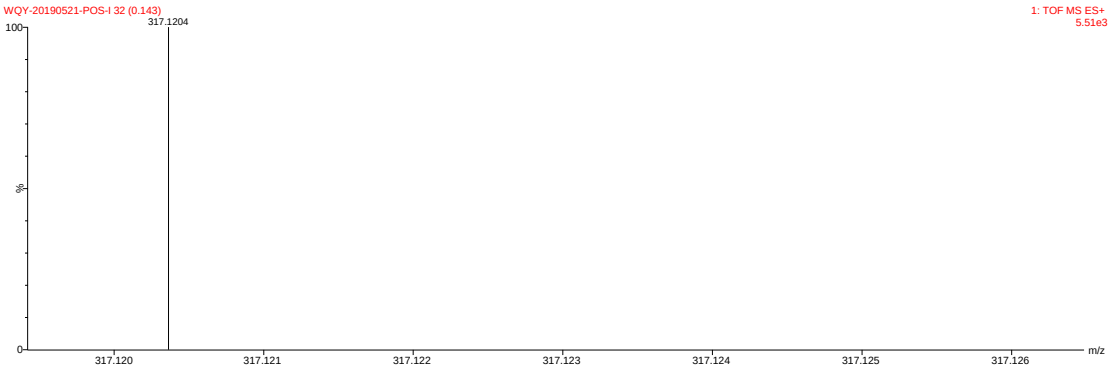
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

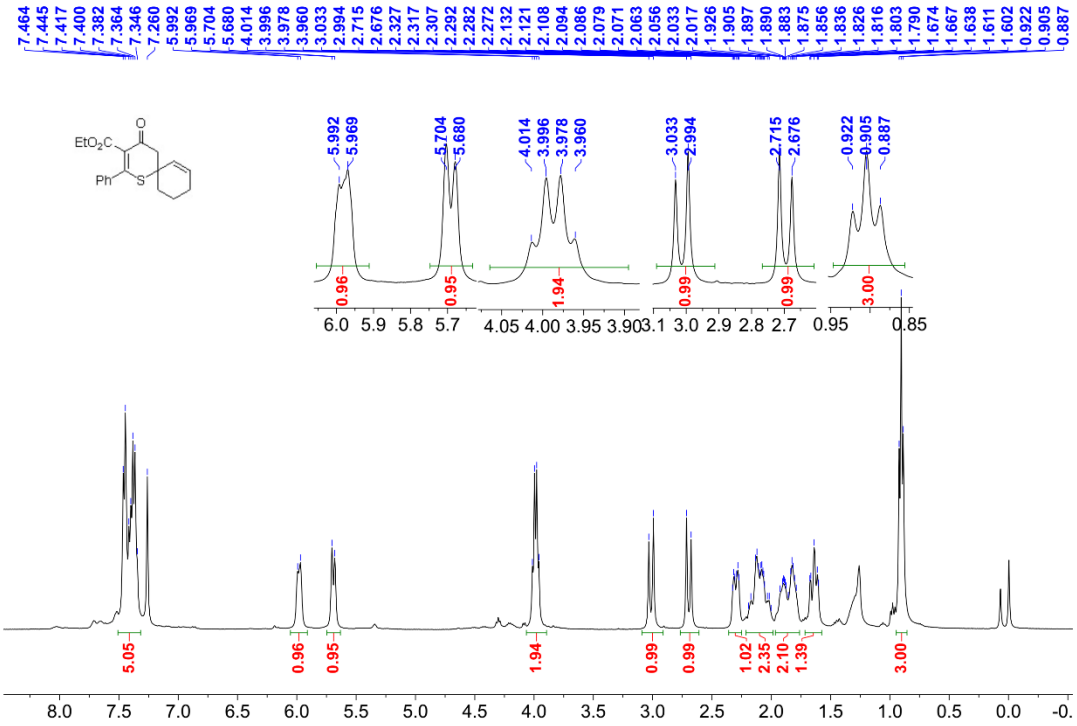


HRMS

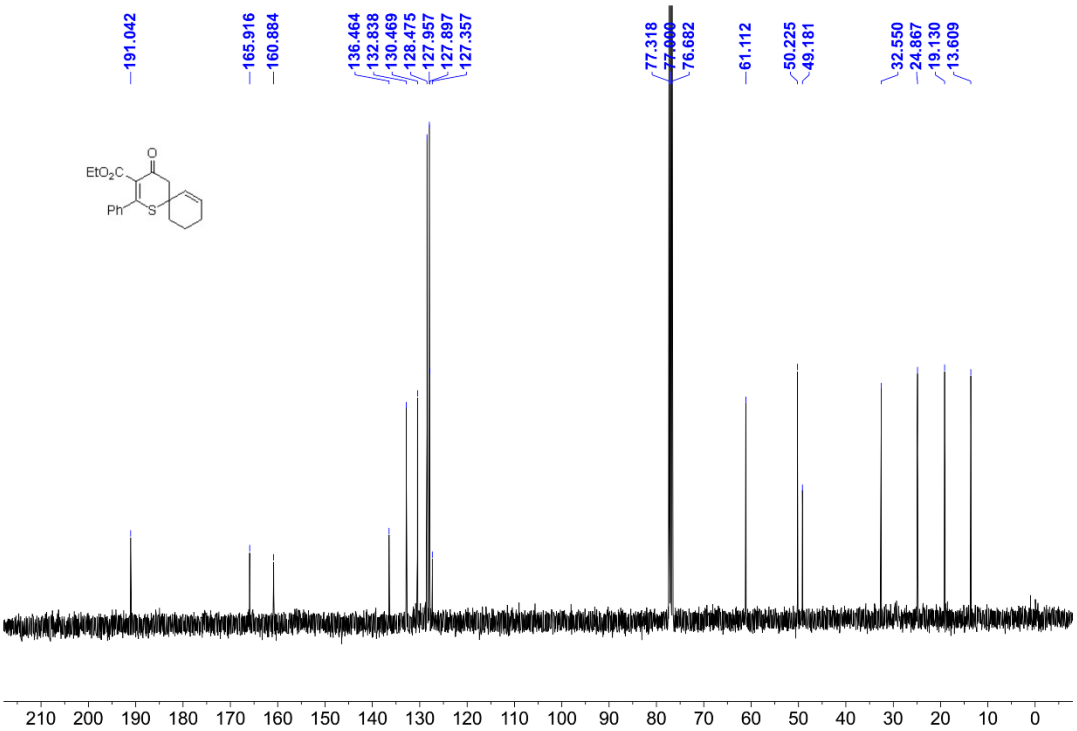

WQY-20190521-POS-I 32 (0.143)
1: TOF MS ES+
5.51e3
317.1204
100
%
0
317.120
317.121
317.122
317.123
317.124
317.125
317.126
m/z

Ethyl 4-oxo-2-phenyl-1-thiaspiro[5.5]undeca-2,7-diene-3-carboxylate (**3ay**)

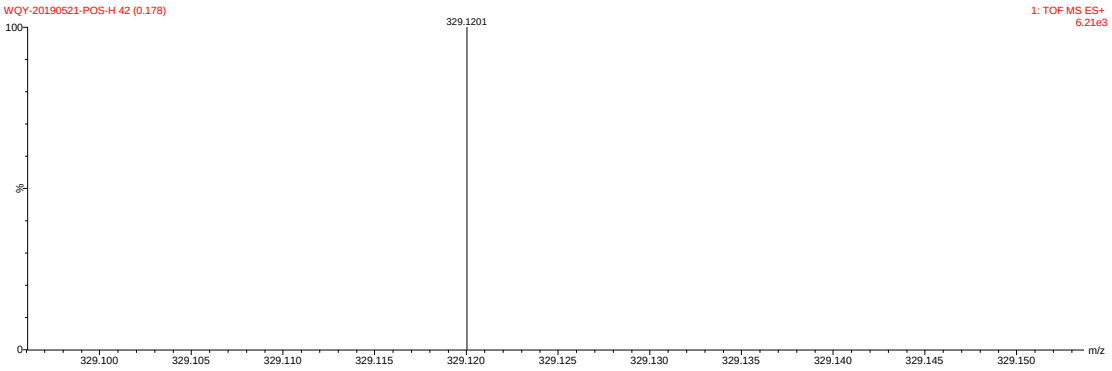
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

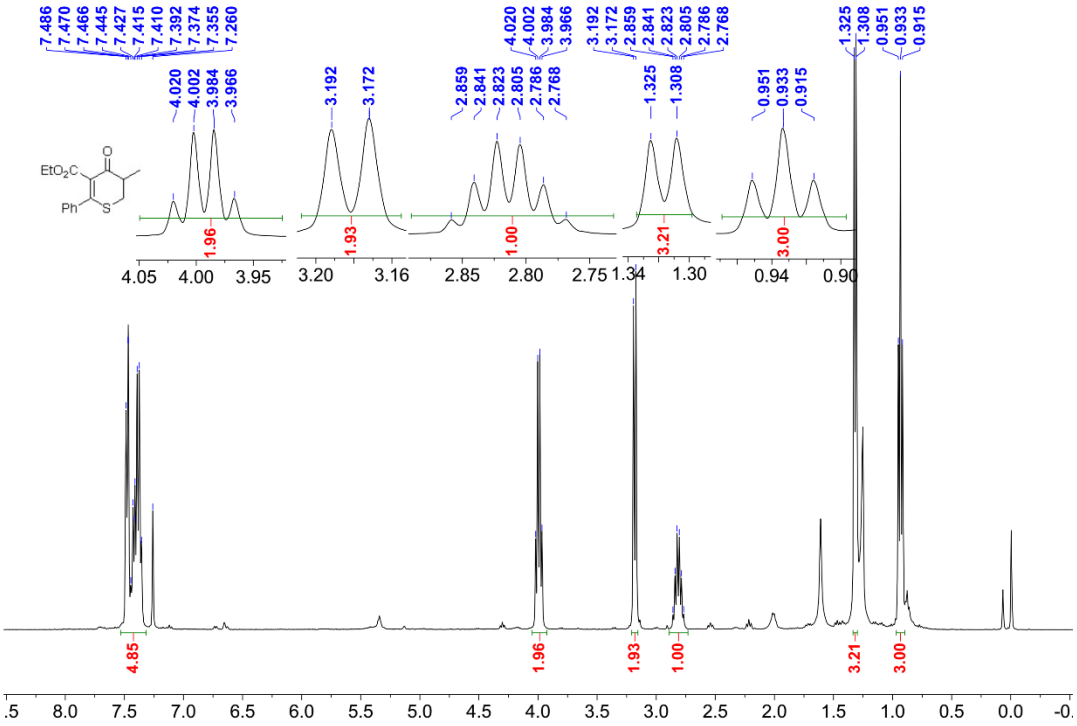


HRMS

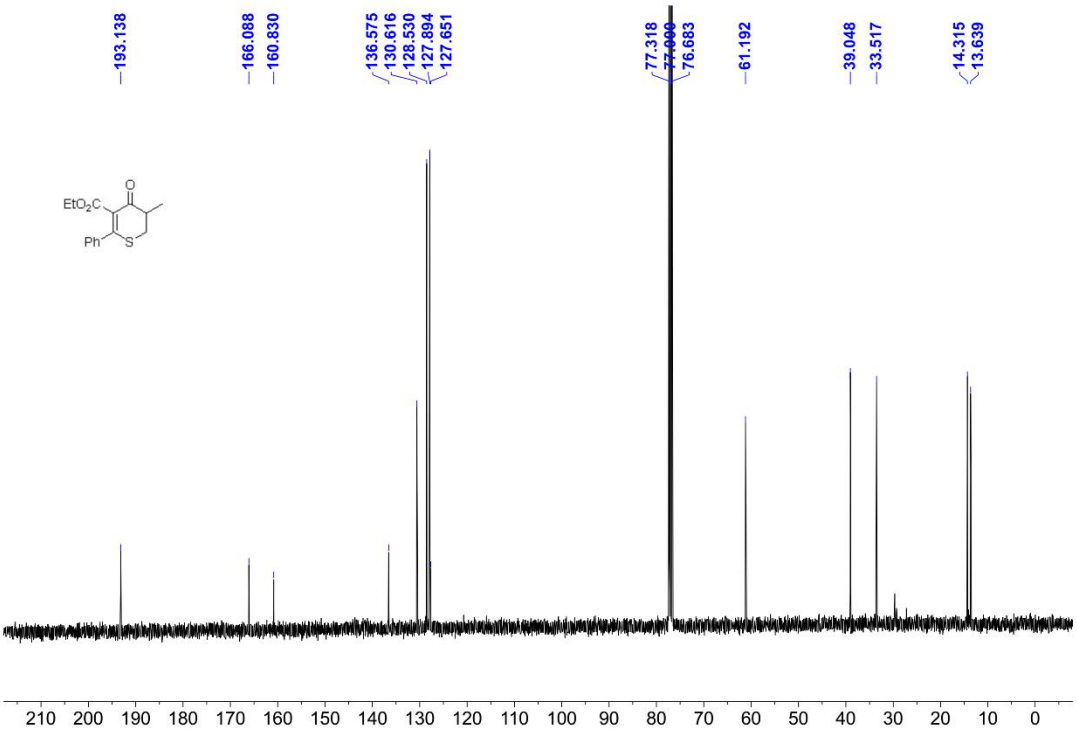

WQY-20190521-POS-H 42 (0.178)
1: TOF MS ES+
6.21e3
329.1201
100
%
0
329.100
329.105
329.110
329.115
329.120
329.125
329.130
329.135
329.140
329.145
329.150
m/z

Ethyl 3-methyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aac**)

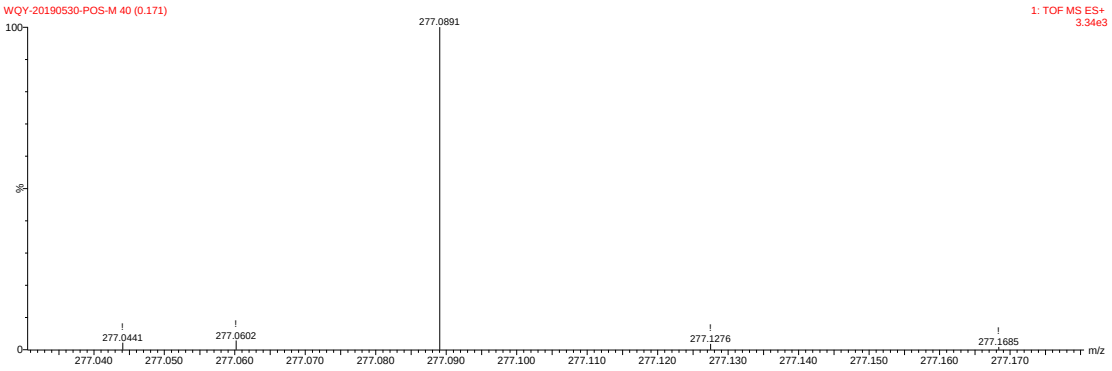
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

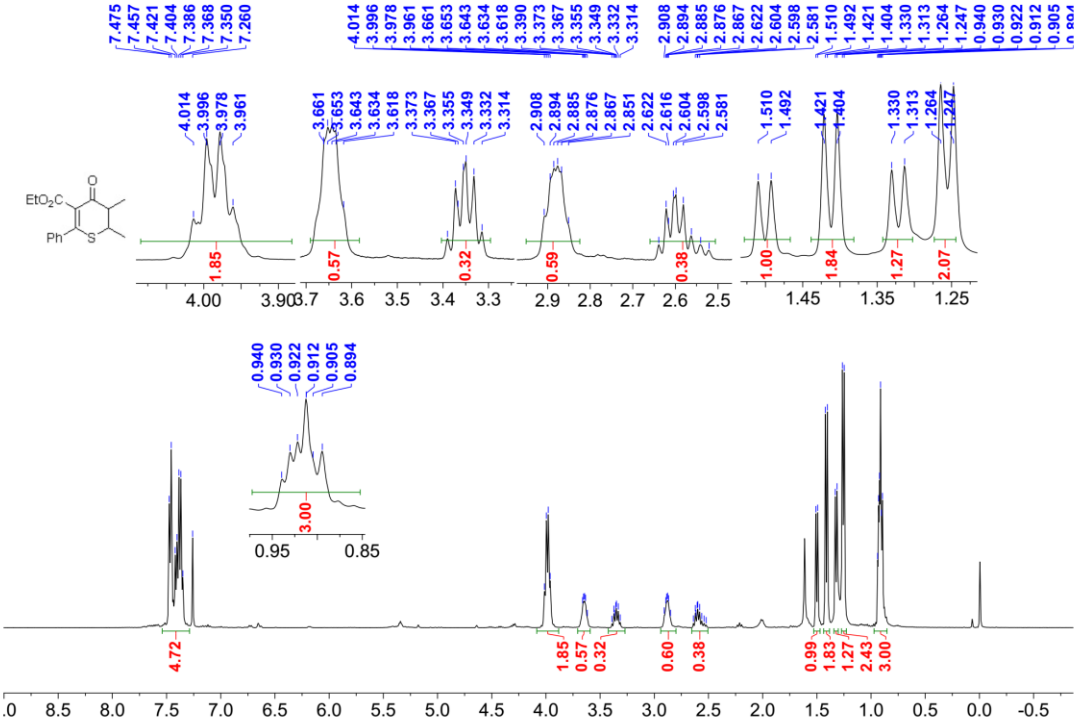


HRMS

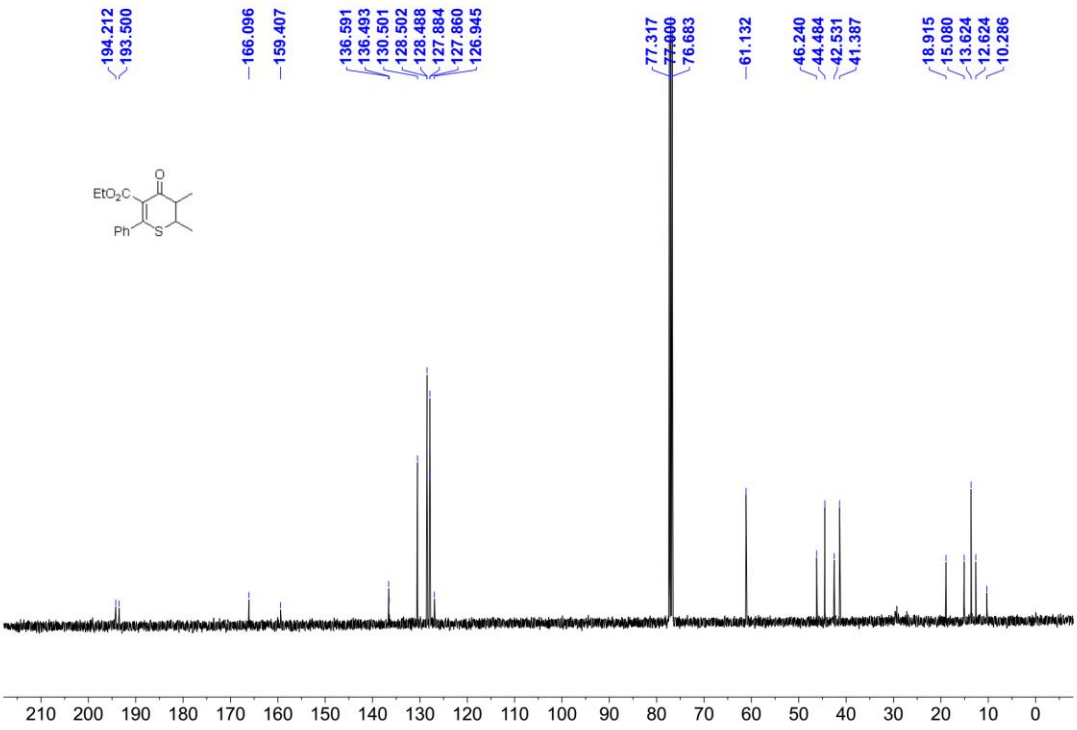

WQY-20190530-POS-M 40 (0.171)
1: TOF MS ES+
3.34e3
100
%
0
277.0891
277.0441
277.0602
277.1276
277.1685
277.040
277.050
277.060
277.070
277.080
277.090
277.100
277.110
277.120
277.130
277.140
277.150
277.160
277.170
m/z

Ethyl 2,3-dimethyl-4-oxo-6-phenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aad**, dr = 2:1)

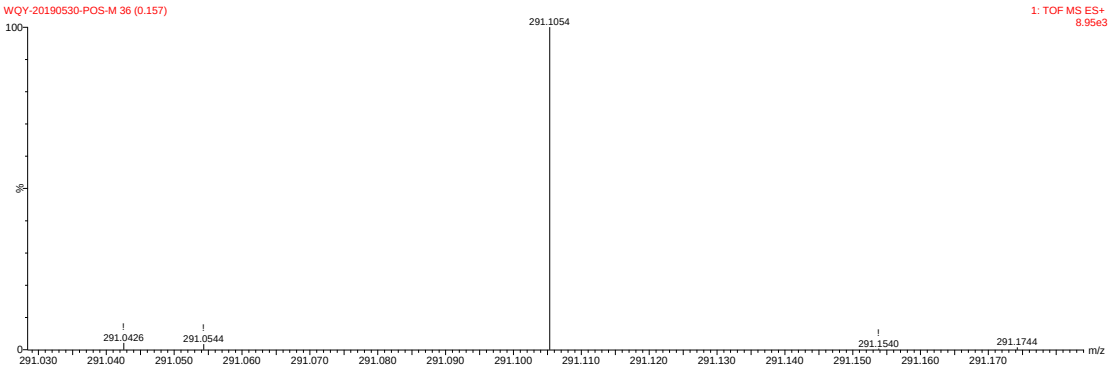
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

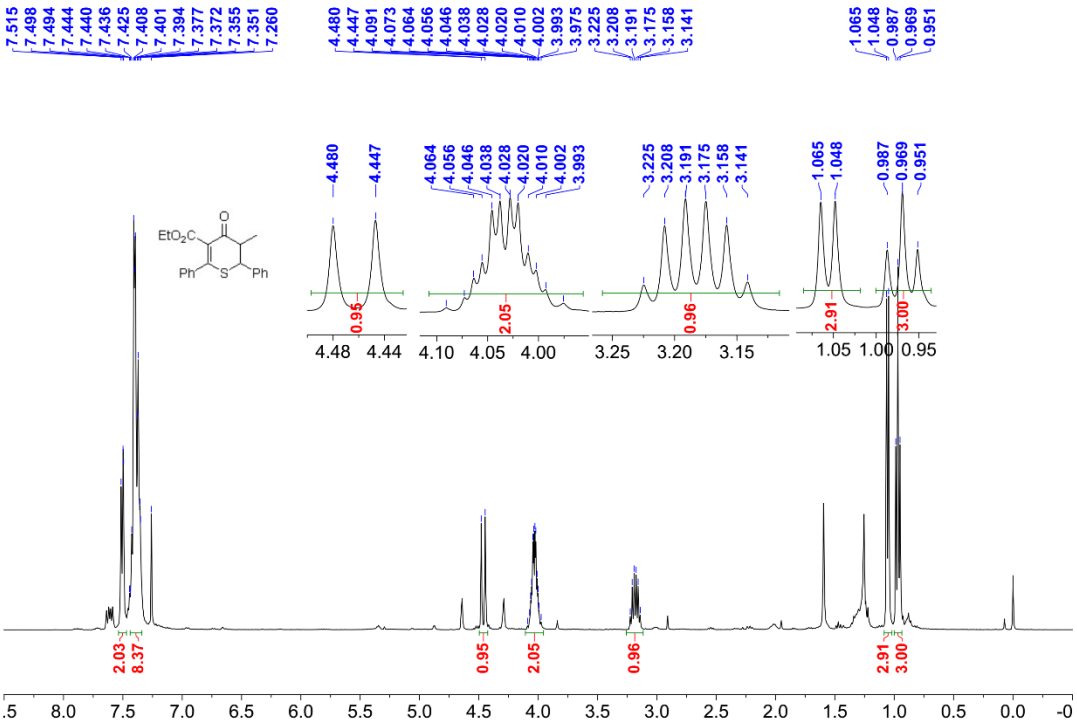


HRMS

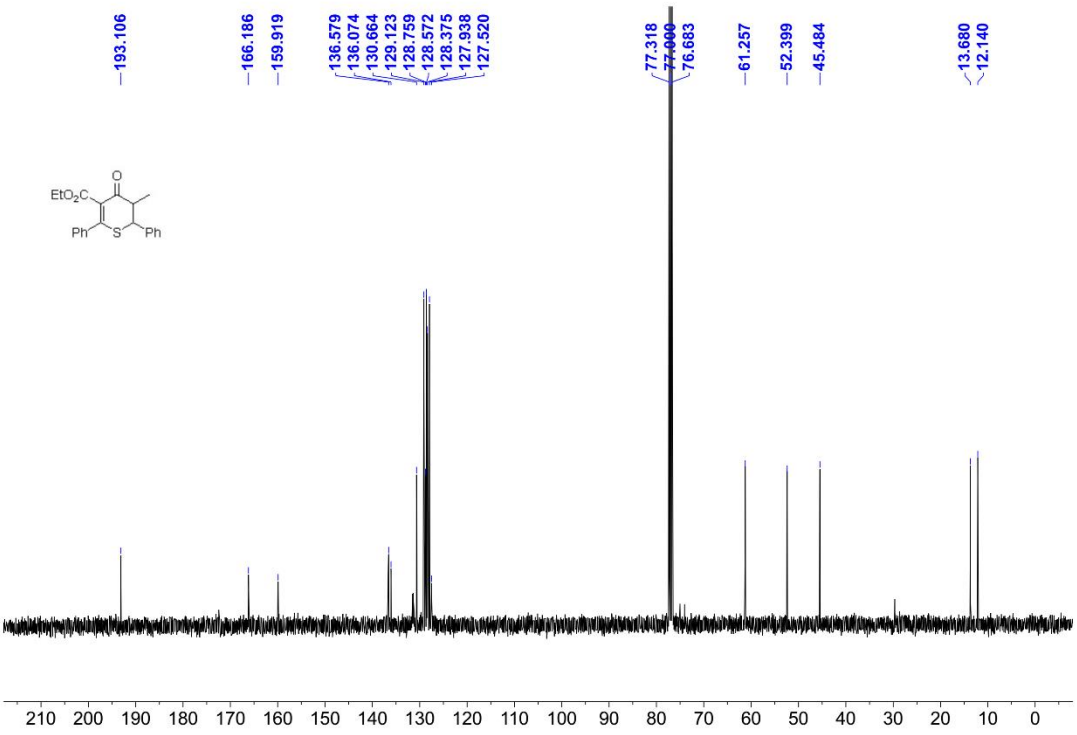

WQY-20190530-POS-M 36 (0.157)
1: TOF MS ES+
8.95e3
100
%
0
291.1054
291.0426
291.0544
291.1540
291.1744
291.030
291.040
291.050
291.060
291.070
291.080
291.090
291.100
291.110
291.120
291.130
291.140
291.150
291.160
291.170
m/z

Ethyl 3-methyl-4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aae-***single isomer*)

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

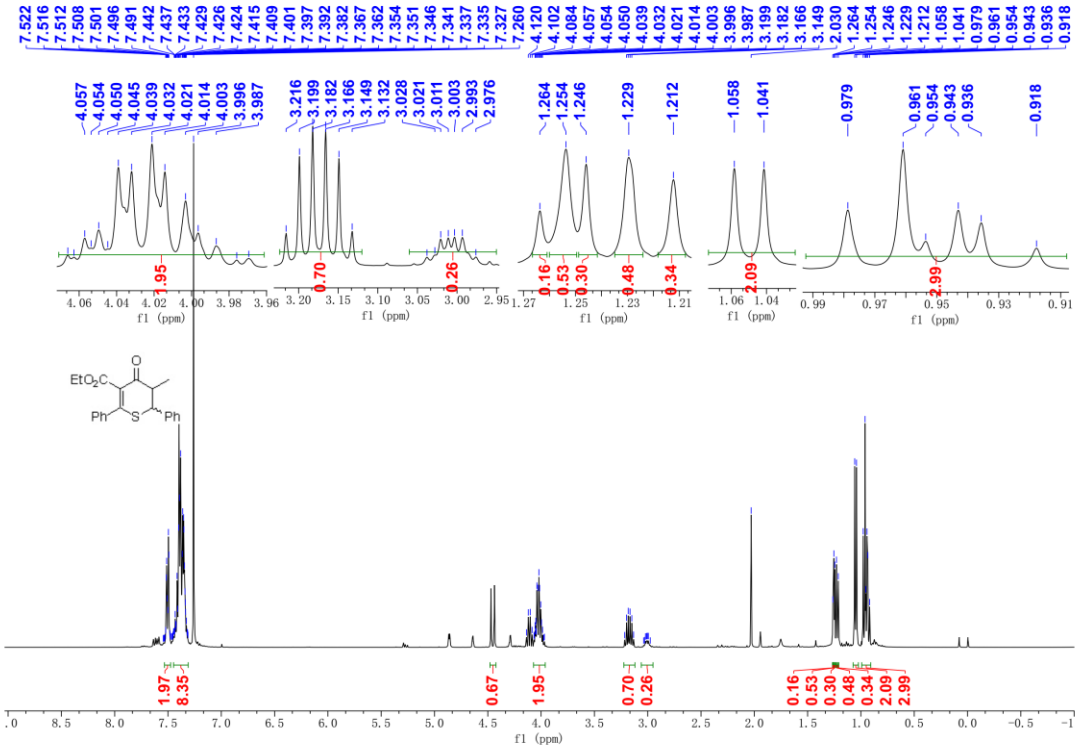


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

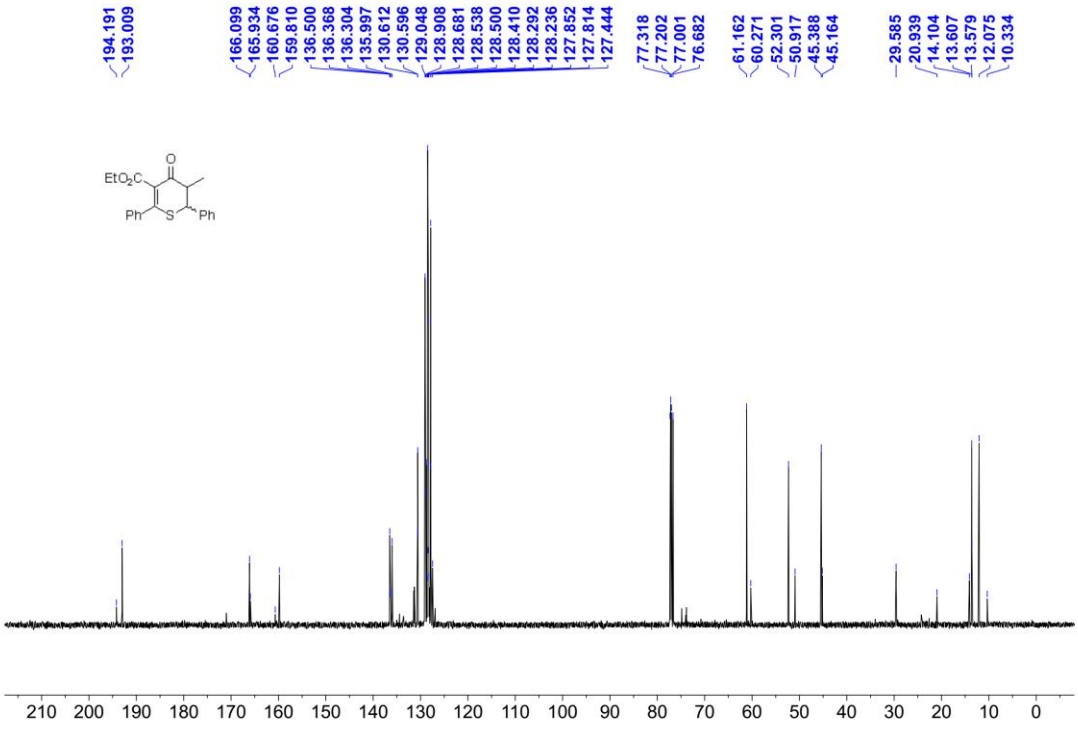


Ethyl 3-methyl-4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aae**, dr = 2:1)

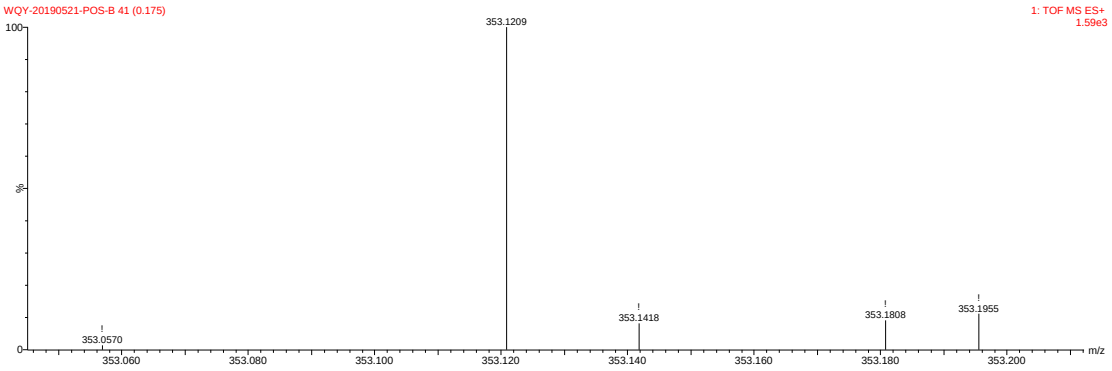
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

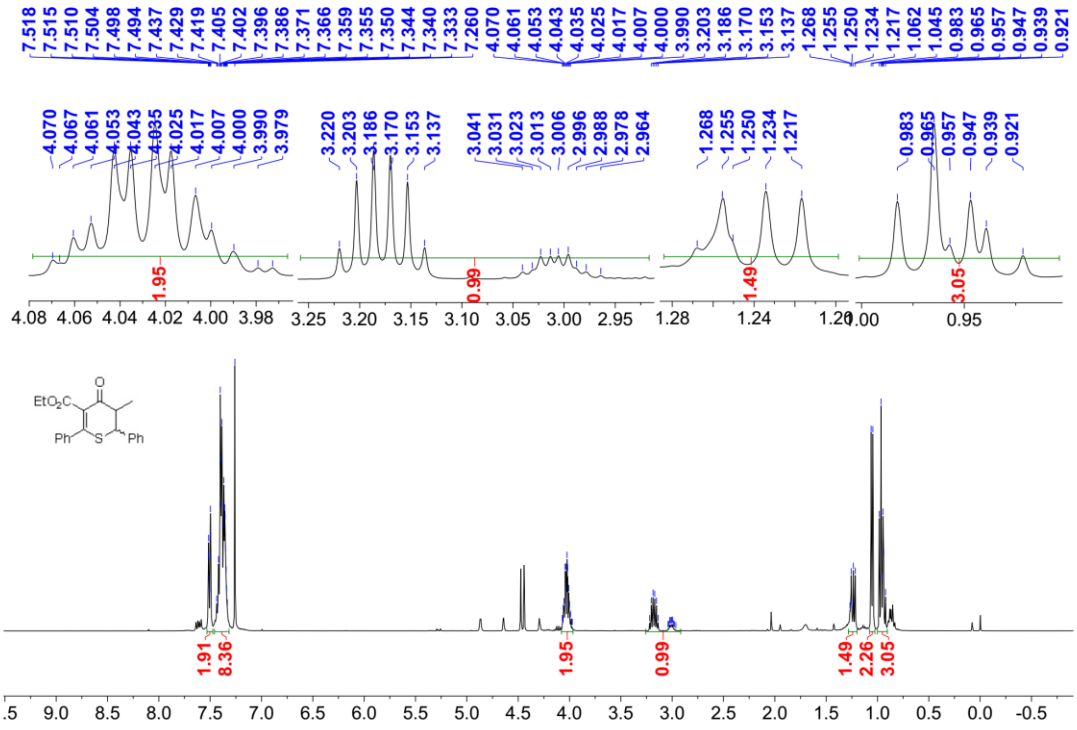


HRMS

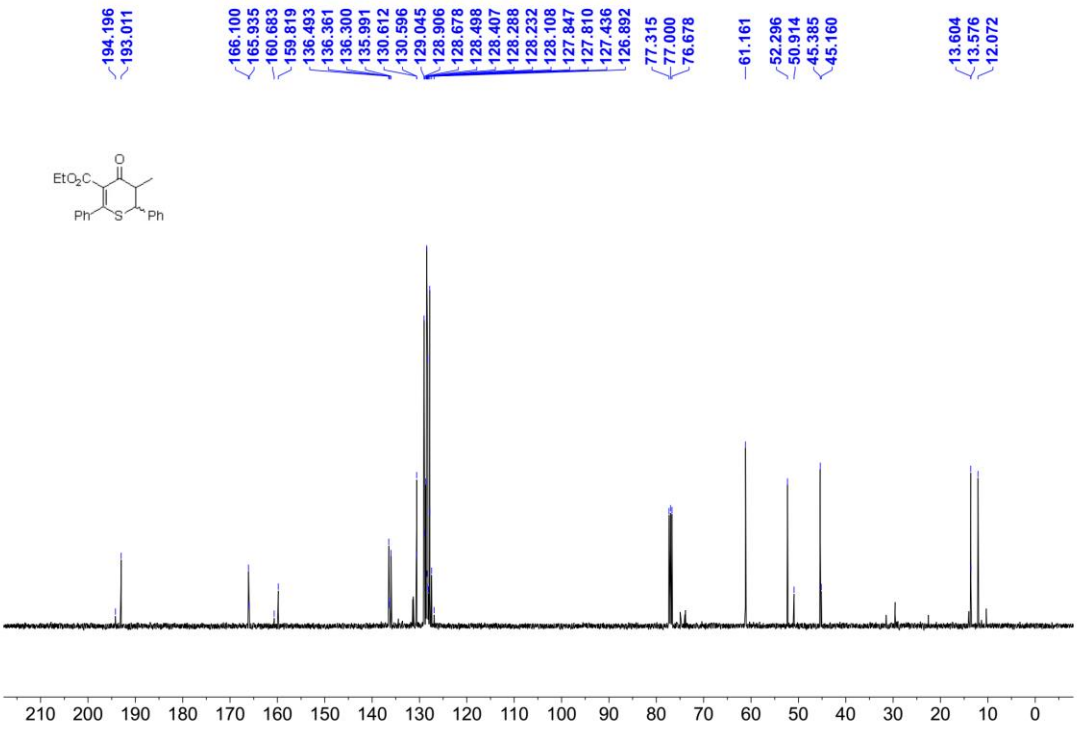

WQY-20190521-POS-B 41 (0.175)
1: TOF MS ES+
1.59e3
100
%
0
353.1209
353.0570
353.1418
353.1808
353.1955
353.060
353.080
353.100
353.120
353.140
353.160
353.180
353.200
m/z

Ethyl 3-methyl-4-oxo-2,6-diphenyl-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3aae**, diastereomers repurified)

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

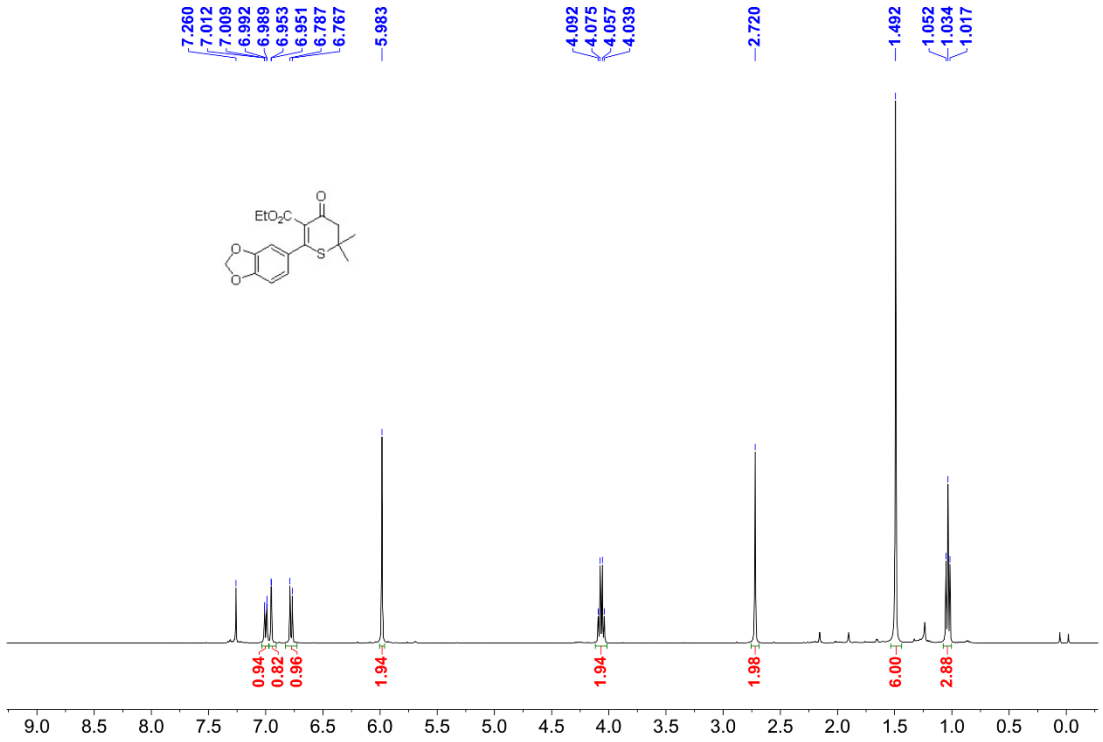


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

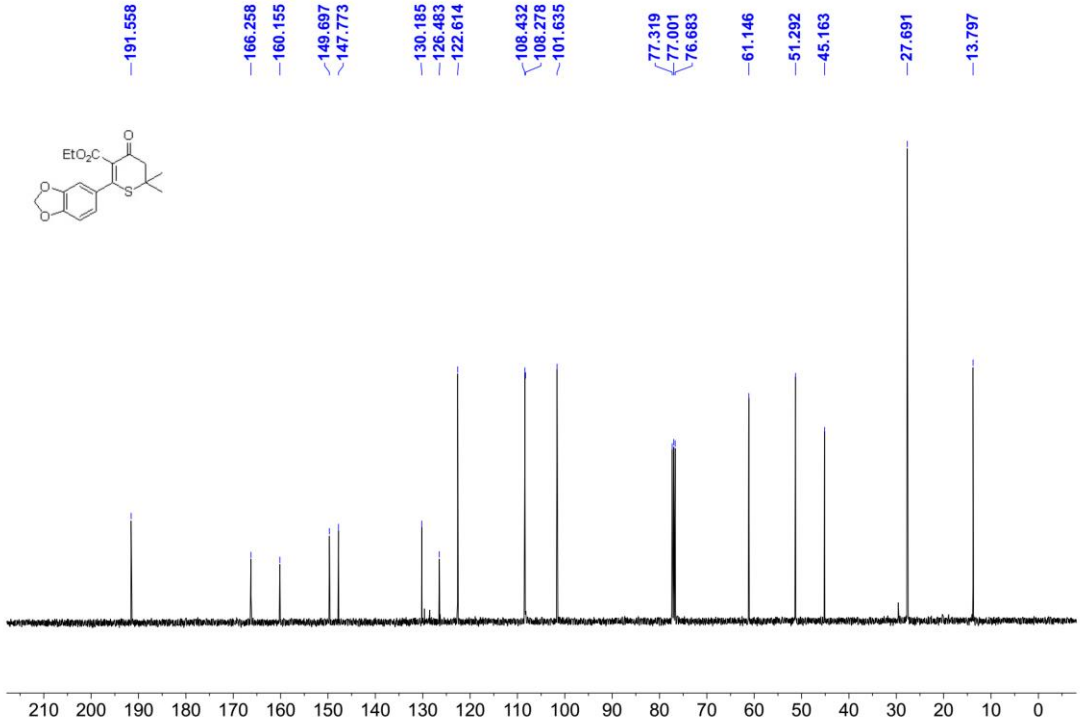


Ethyl 6-(benzo[*d*][1,3]dioxol-5-yl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ba**)

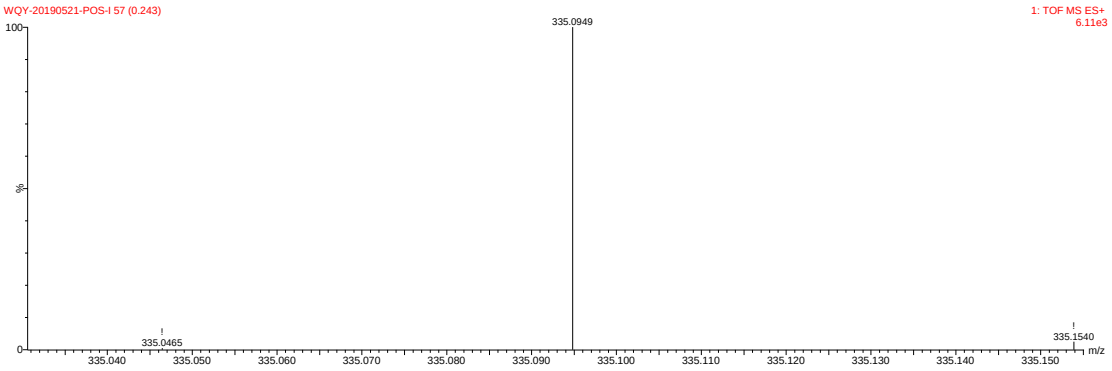
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

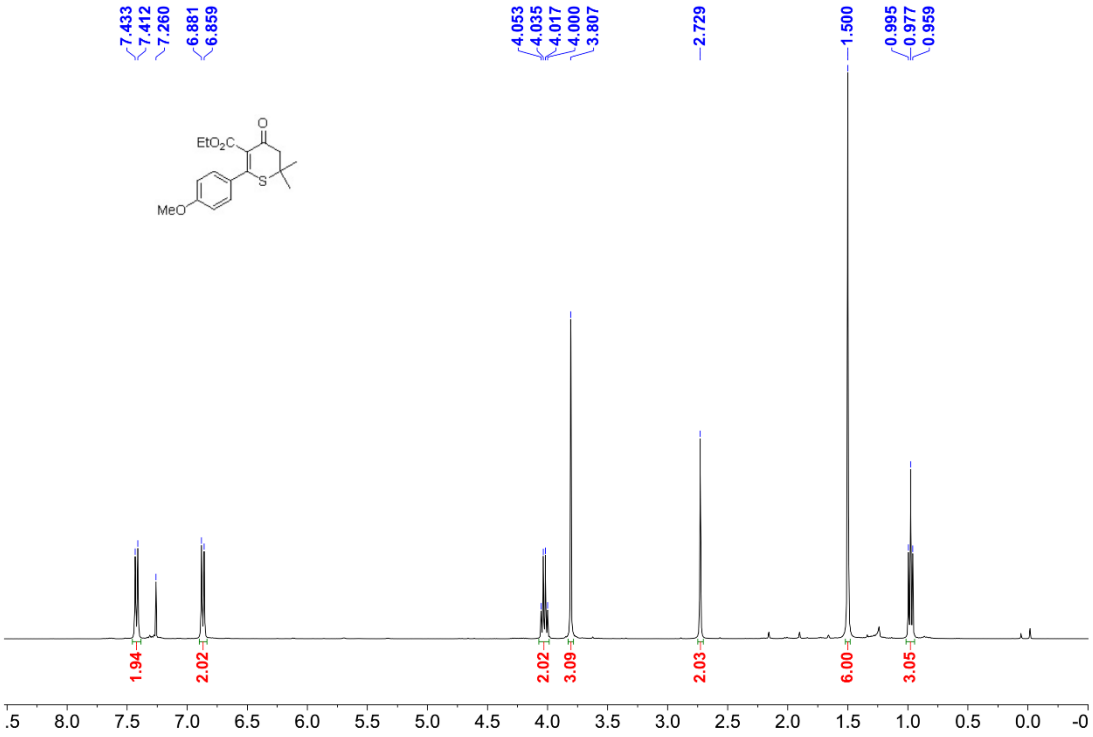


HRMS

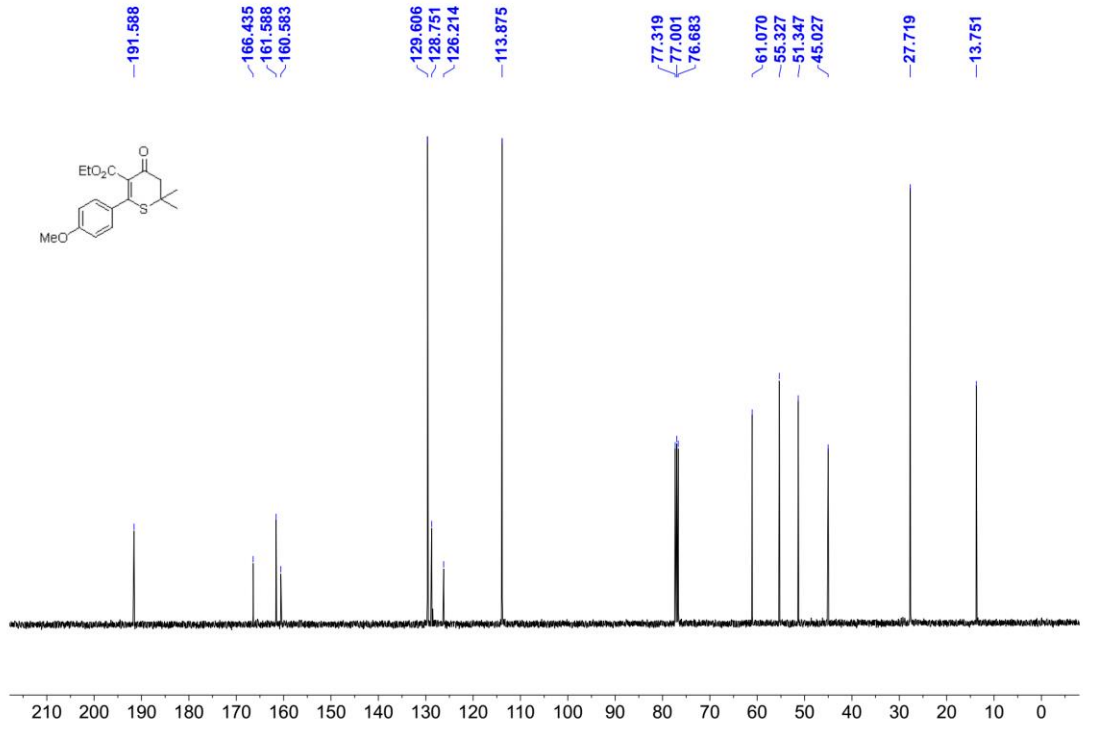

WQY-20190521-POS-I 57 (0.243)
1: TOF MS ES+
6.11e3
100
%
0
335.0949
335.0465
335.1540
335.040
335.050
335.060
335.070
335.080
335.090
335.100
335.110
335.120
335.130
335.140
335.150
m/z

Ethyl 6-(4-methoxyphenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ca**)

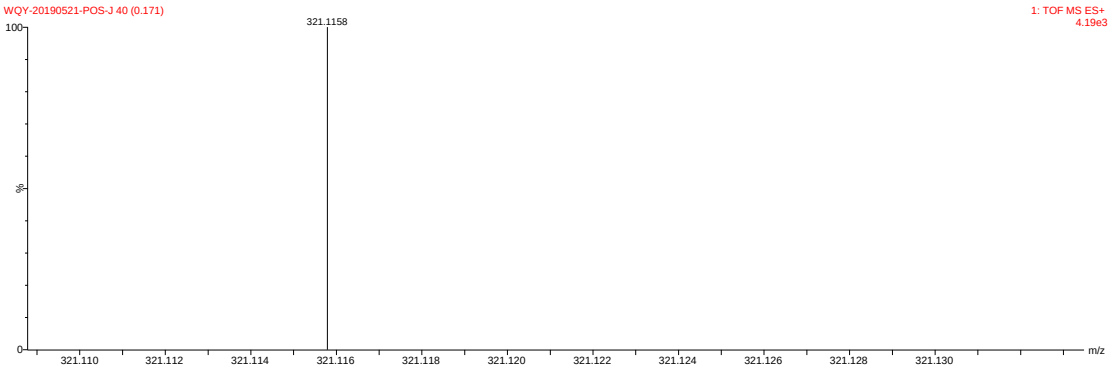
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

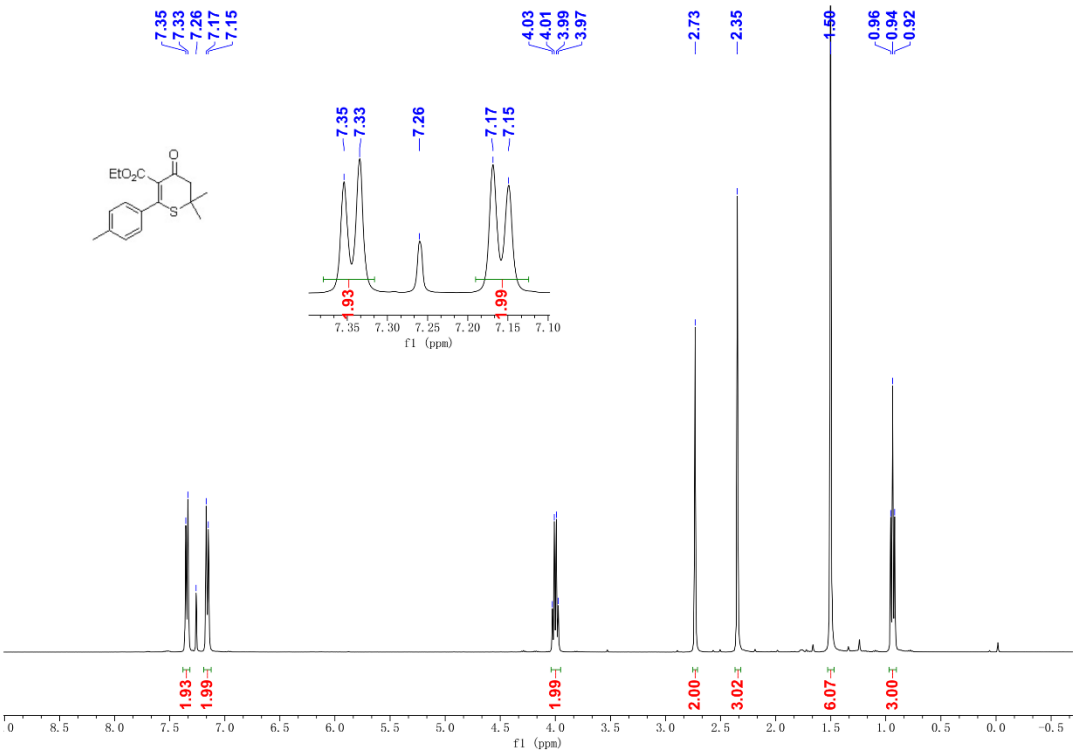


HRMS

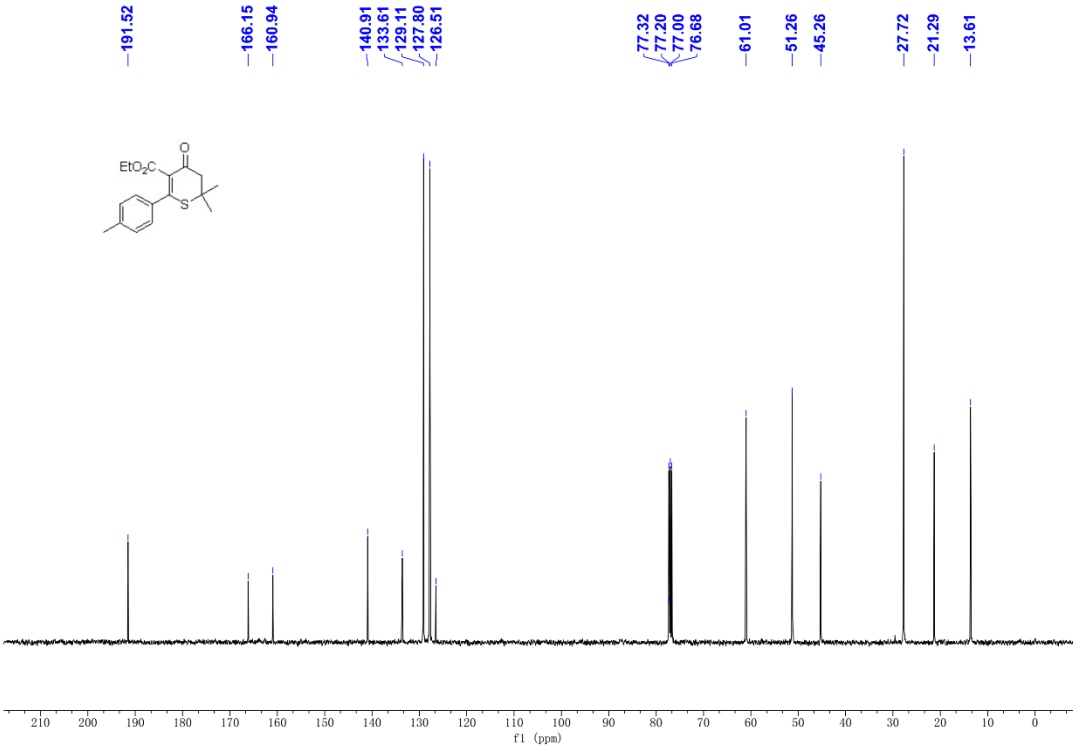

WQY-20190521-POS-J 40 (0.171)
1: TOF MS ES+
4.19e3
321.1158
100
%
0
321.110
321.112
321.114
321.116
321.118
321.120
321.122
321.124
321.126
321.128
321.130
m/z

Ethyl 2,2-dimethyl-4-oxo-6-(p-tolyl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3da**)

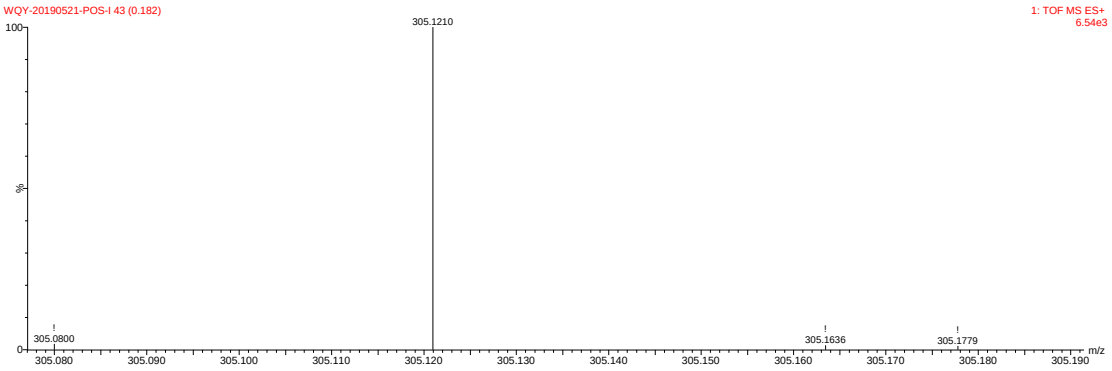
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

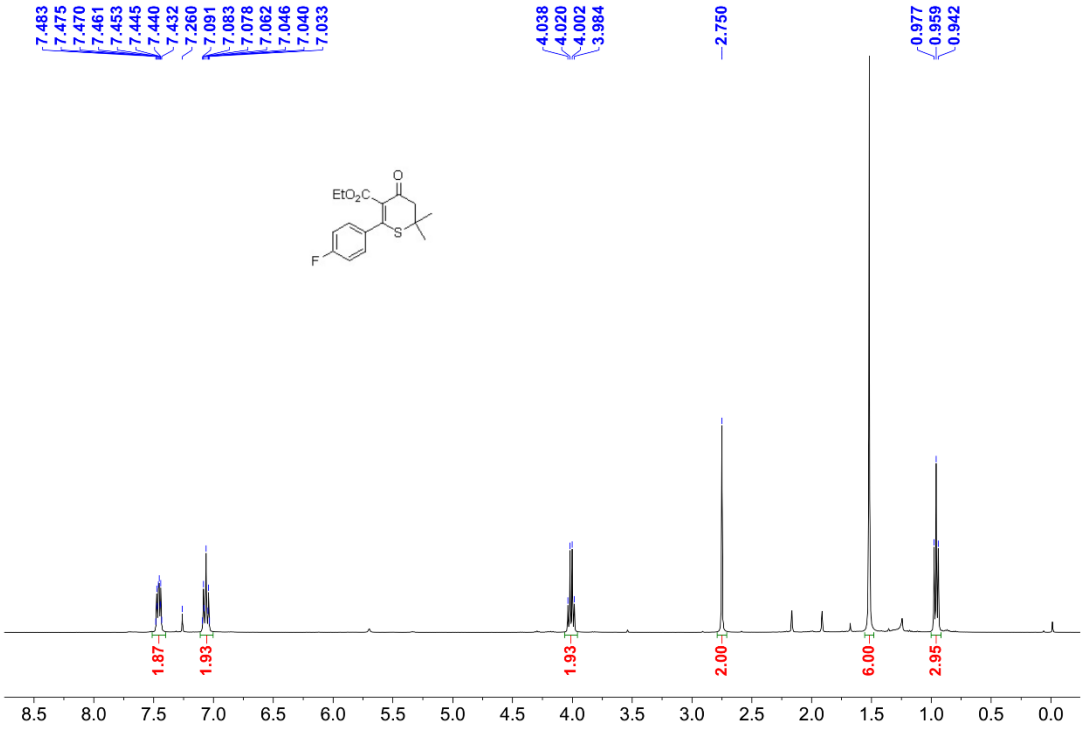


HRMS

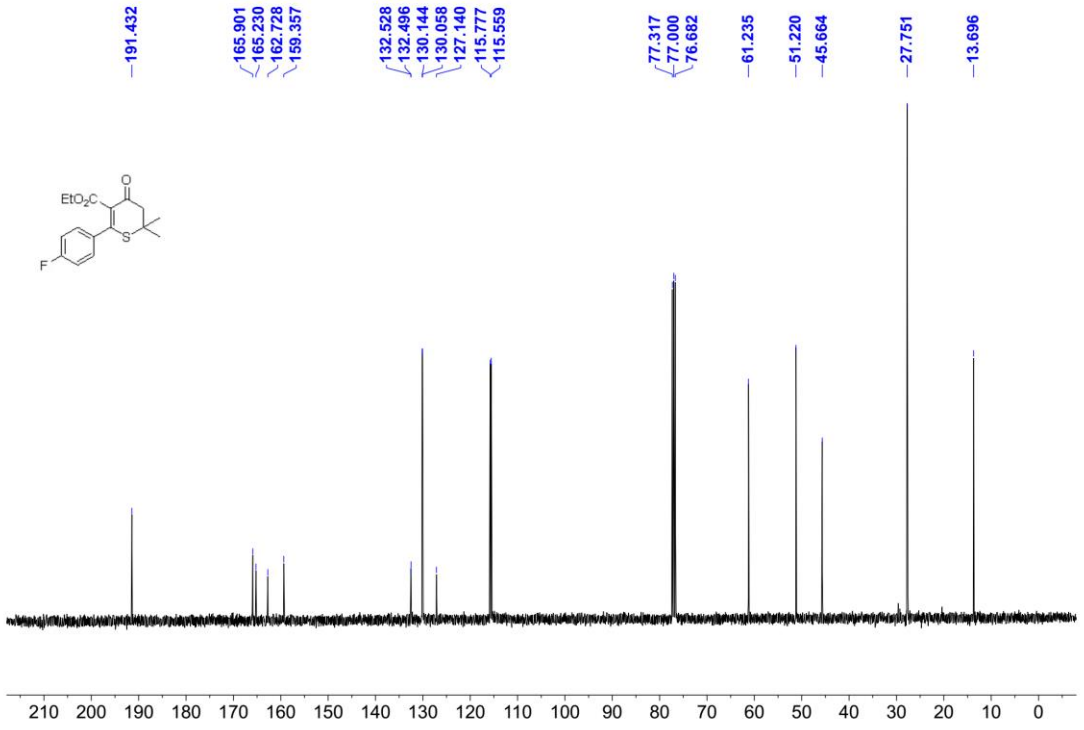

WQY-20190521-POS-I 43 (0.182)
1: TOF MS ES+
6.54e3
100
%
0
305.1210
305.0800
305.1636
305.1779
305.080
305.090
305.100
305.110
305.120
305.130
305.140
305.150
305.160
305.170
305.180
305.190
m/z

Ethyl 6-(4-fluorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ea**)

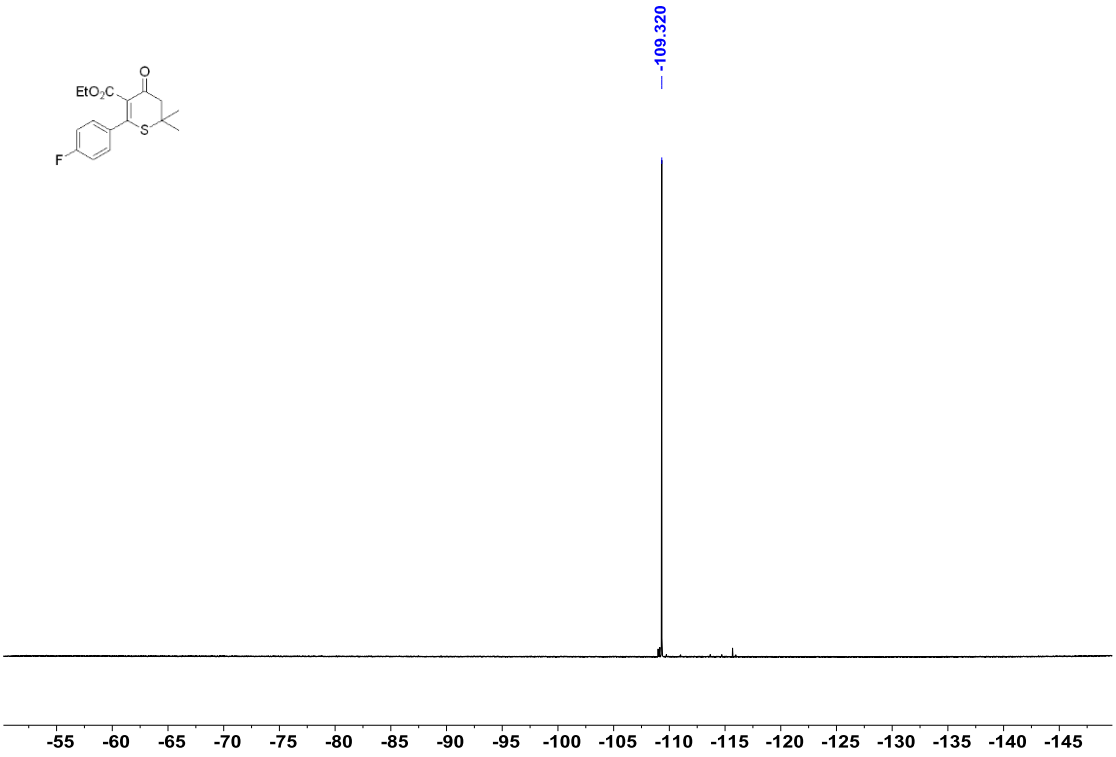
^{1}H MNR (400 MHz, $CDCl_3$)



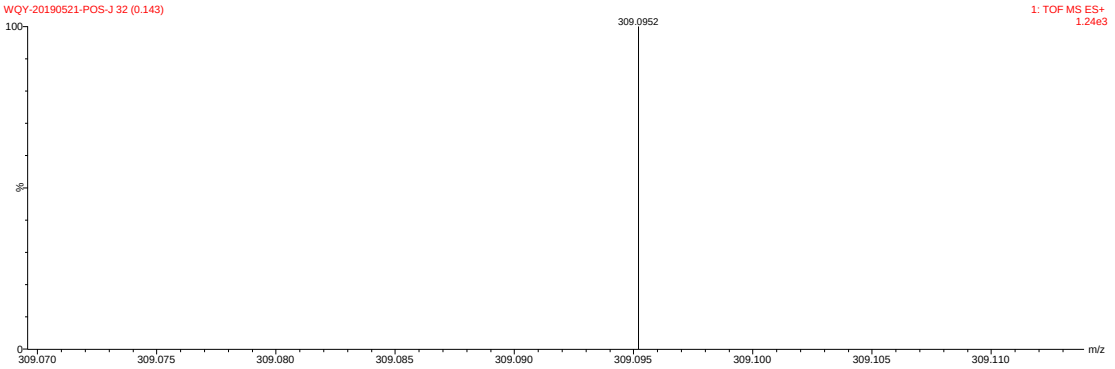
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



^{19}F NMR{^{1}H } (376 MHz, $CDCl_3$)

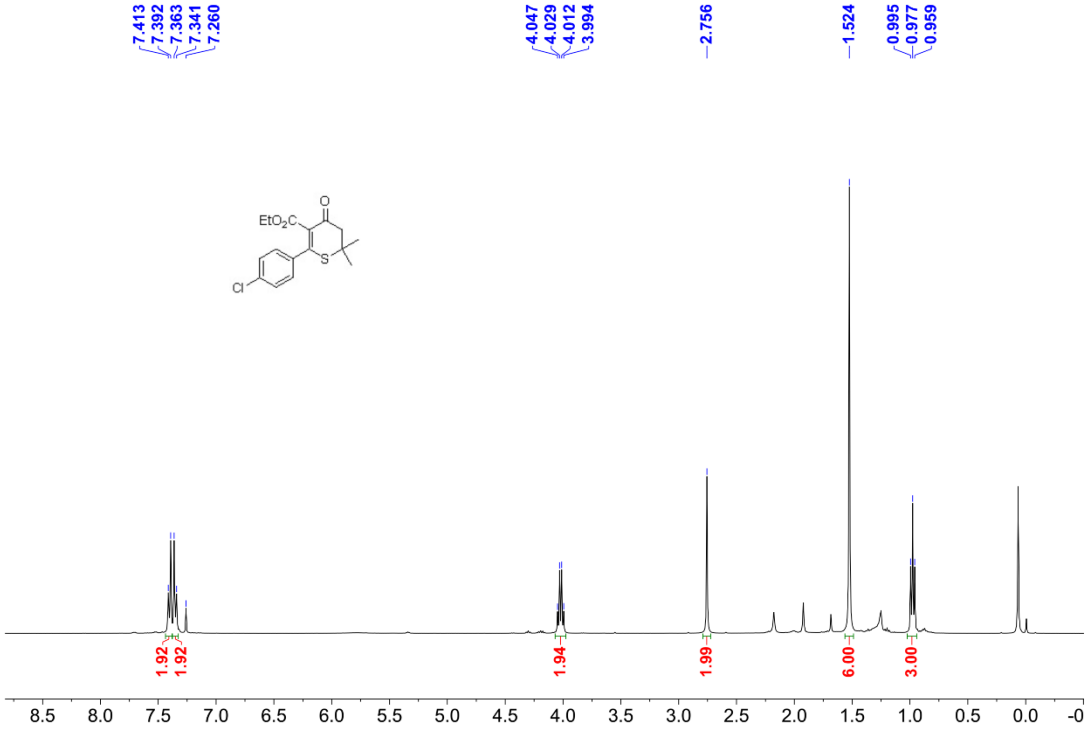


HRMS

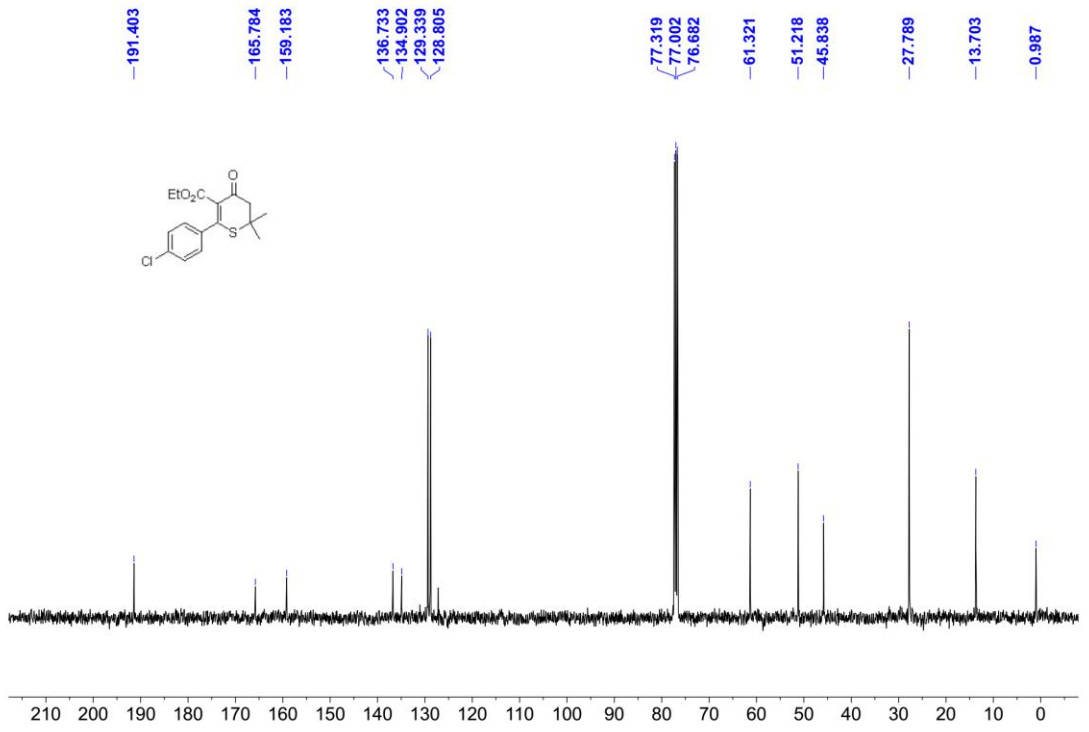


Ethyl 6-(4-chlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3fa**)

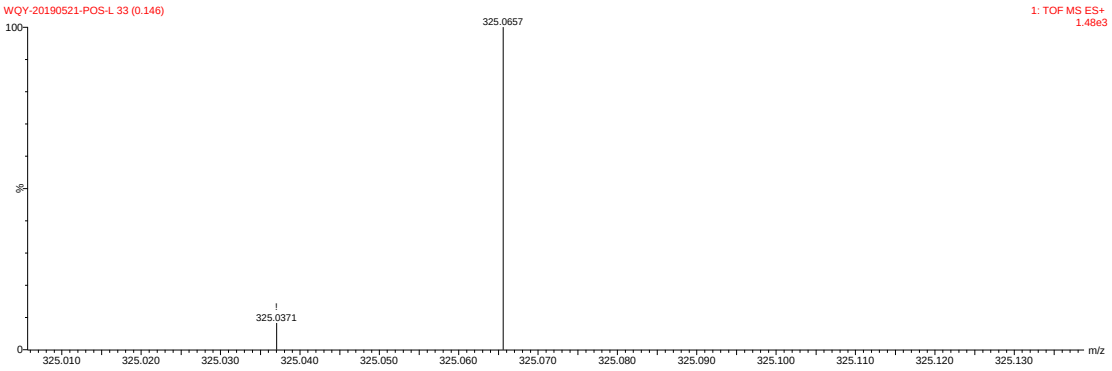
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

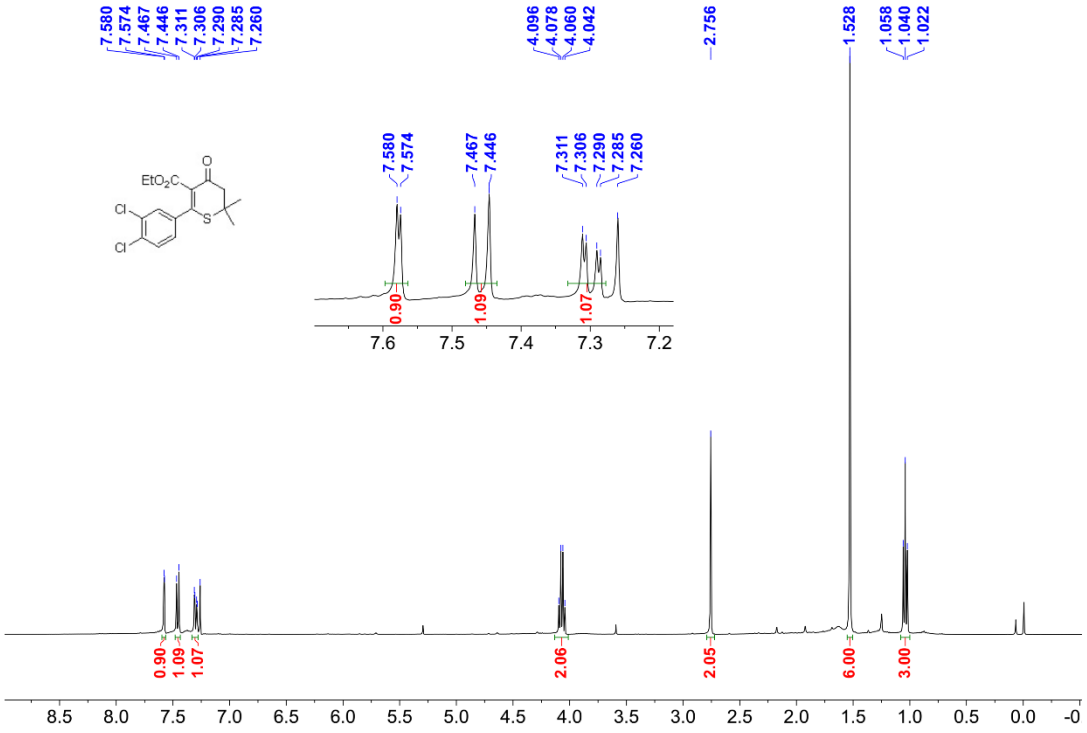


HRMS

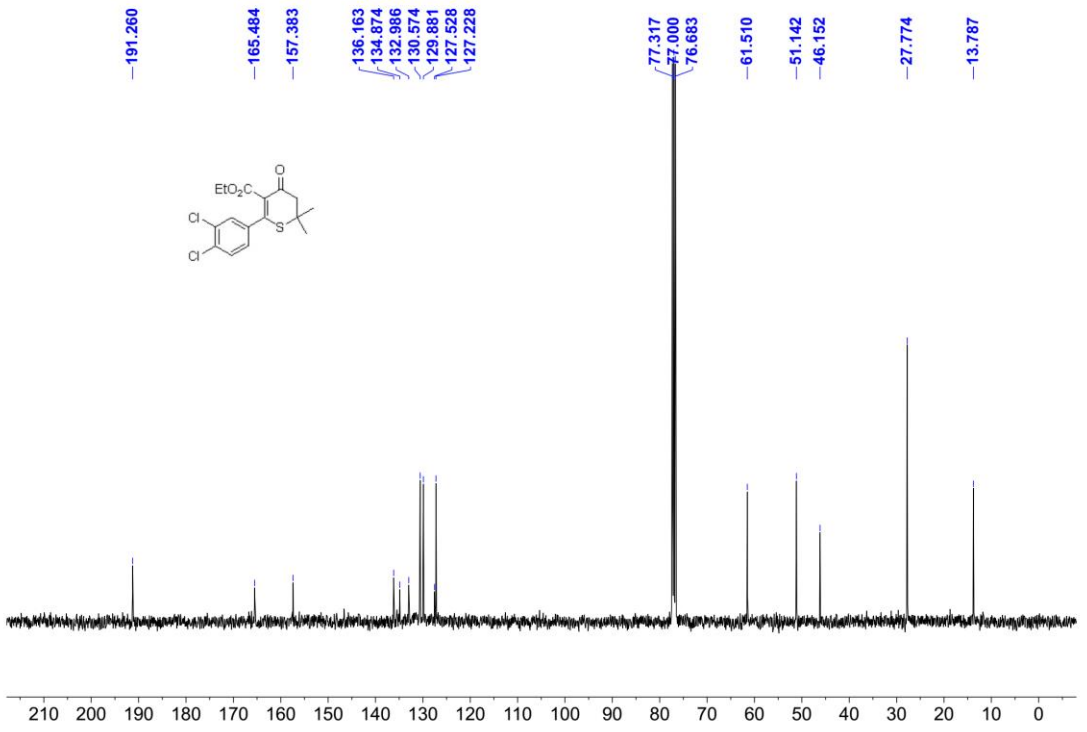

WQY-20190521-POS-L 33 (0.146)
1: TOF MS ES+
1.48e3
100
%
0
325.0657
325.0371
325.010
325.020
325.030
325.040
325.050
325.060
325.070
325.080
325.090
325.100
325.110
325.120
325.130
m/z

Ethyl 6-(3,4-dichlorophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ga**)

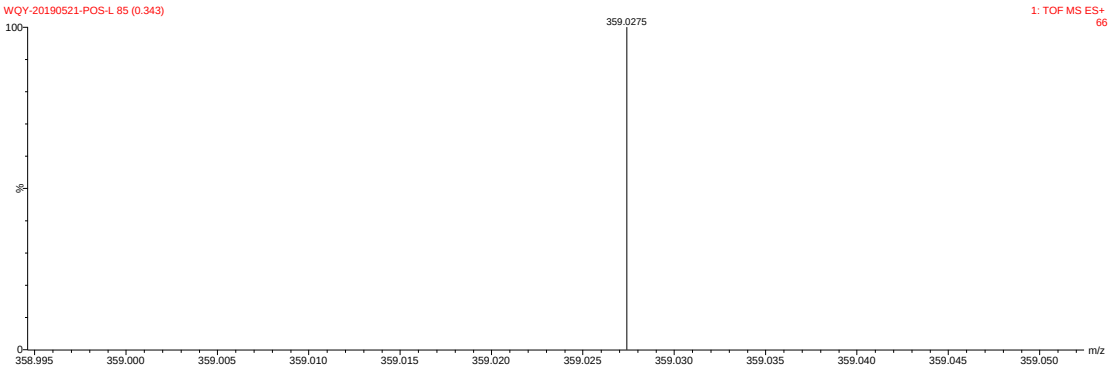
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

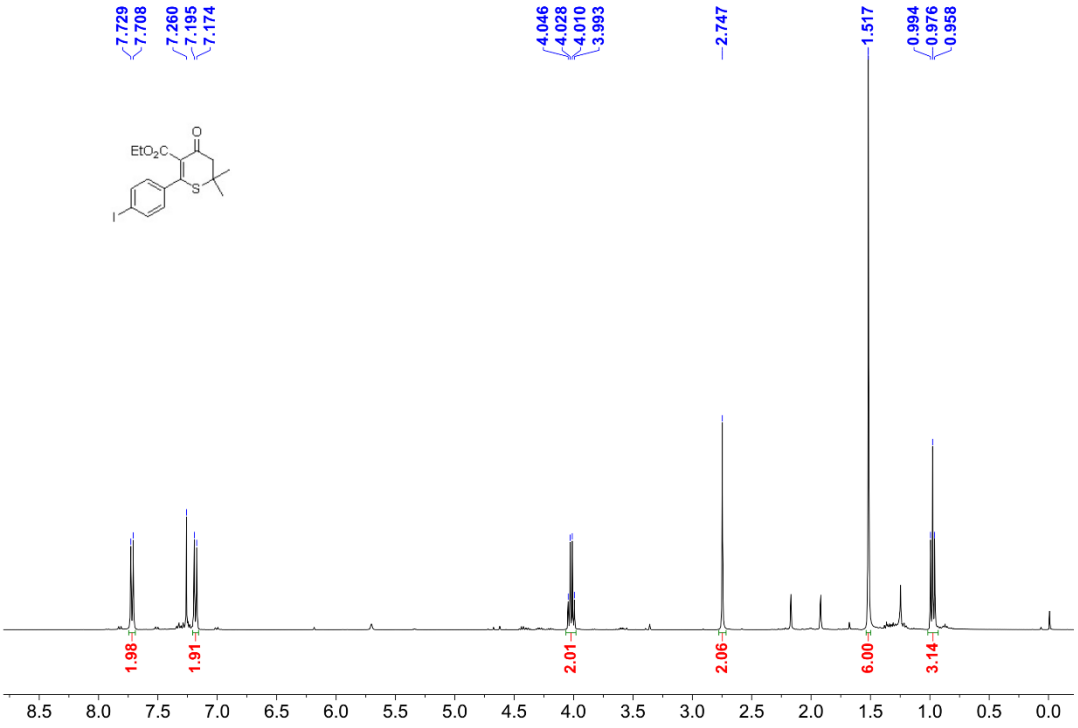


HRMS

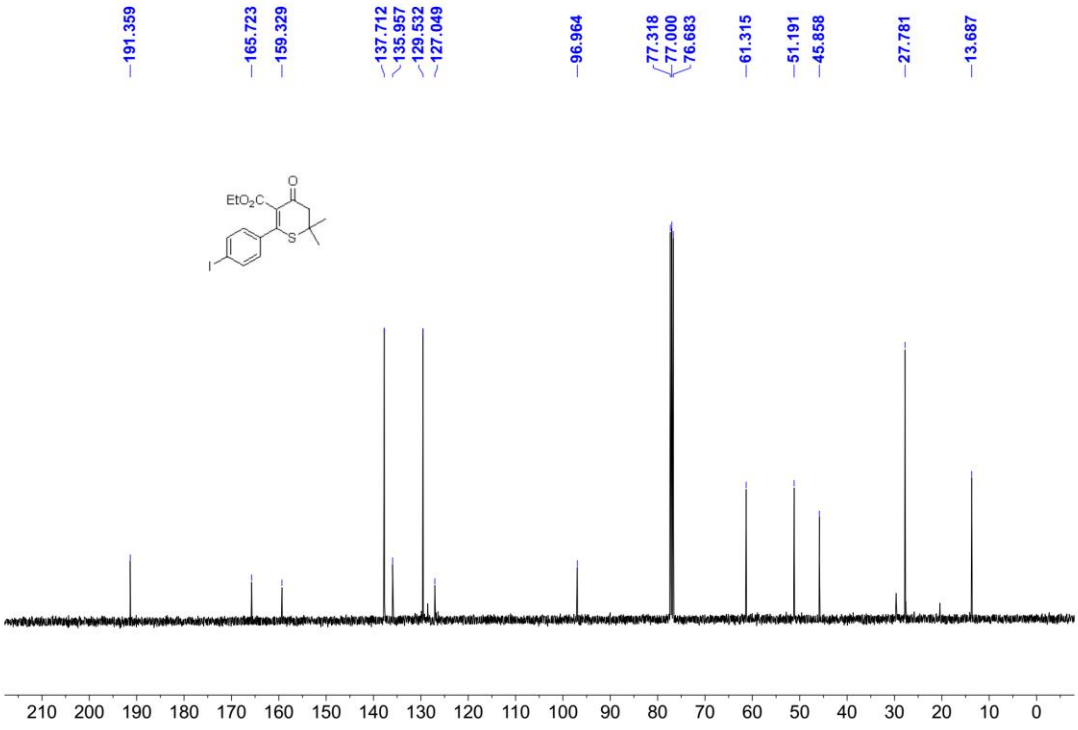

WQY-20190521-POS-L 85 (0.343)
1: TOF MS ES+
66
359.0275
100
%
0
358.995
359.000
359.005
359.010
359.015
359.020
359.025
359.030
359.035
359.040
359.045
359.050
m/z

Ethyl 6-(4-iodophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ha**)

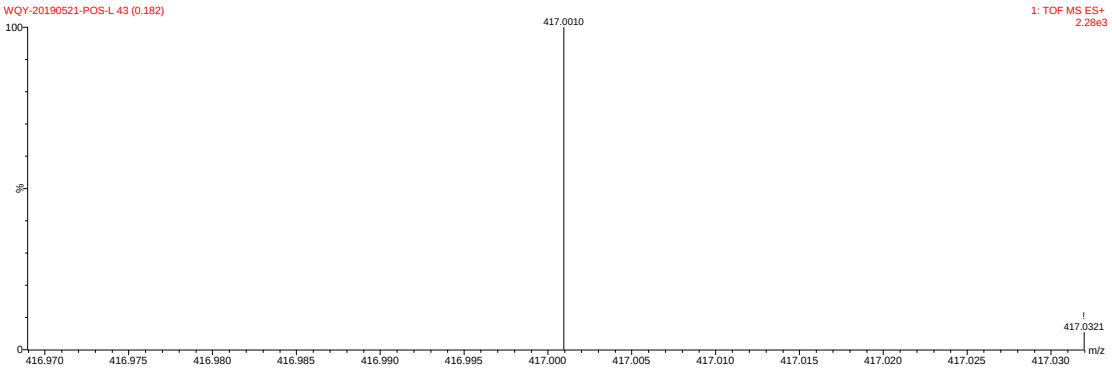
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

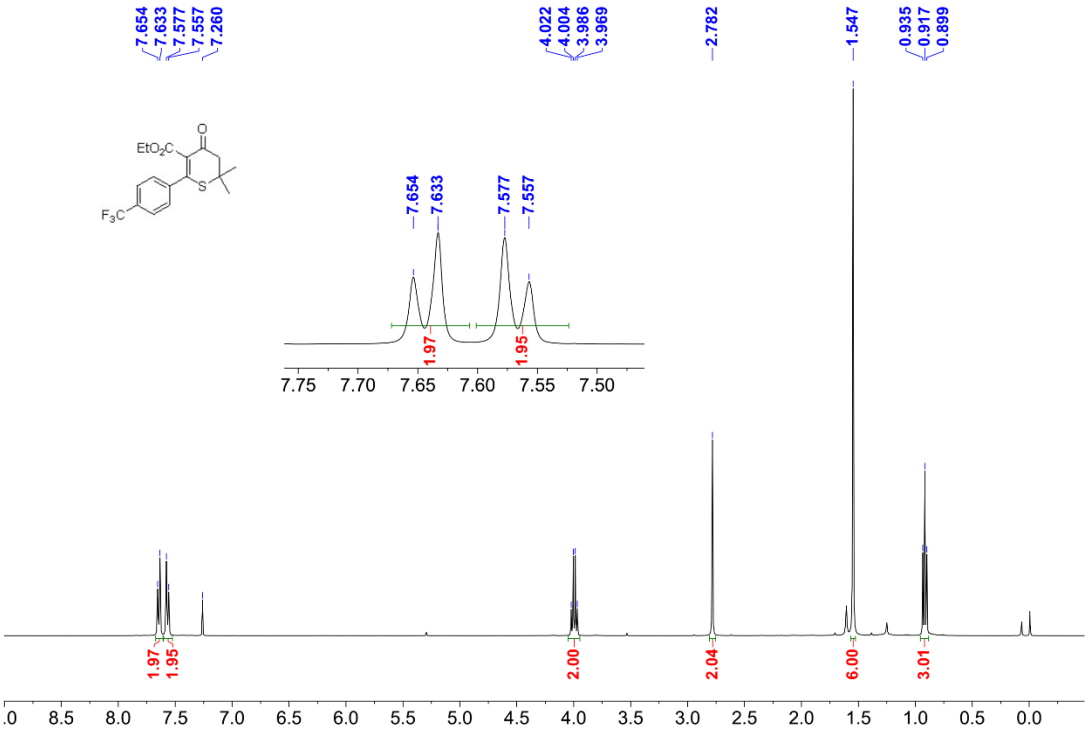


HRMS

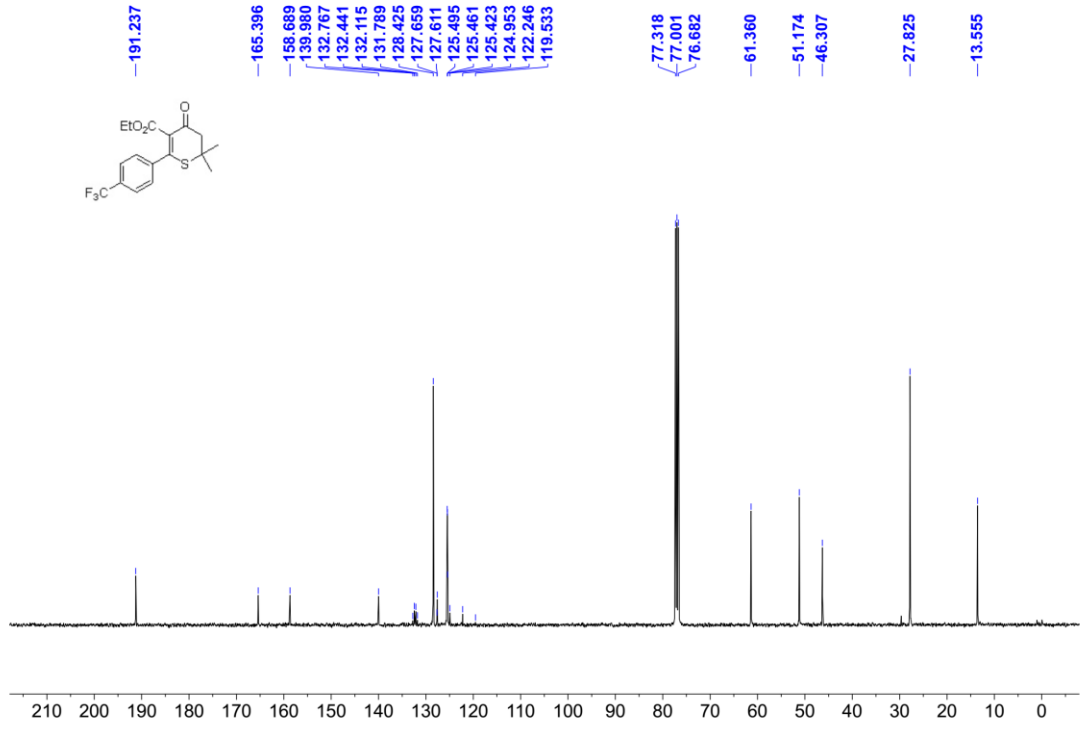

WQY-20190521-POS-L 43 (0.182)
1: TOF MS ES+
2.28e3
417.0010
100
%
0
417.0321
m/z
416.970
416.975
416.980
416.985
416.990
416.995
417.000
417.005
417.010
417.015
417.020
417.025
417.030

Ethyl 2,2-dimethyl-4-oxo-6-(4-(trifluoromethyl)phenyl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ia**)

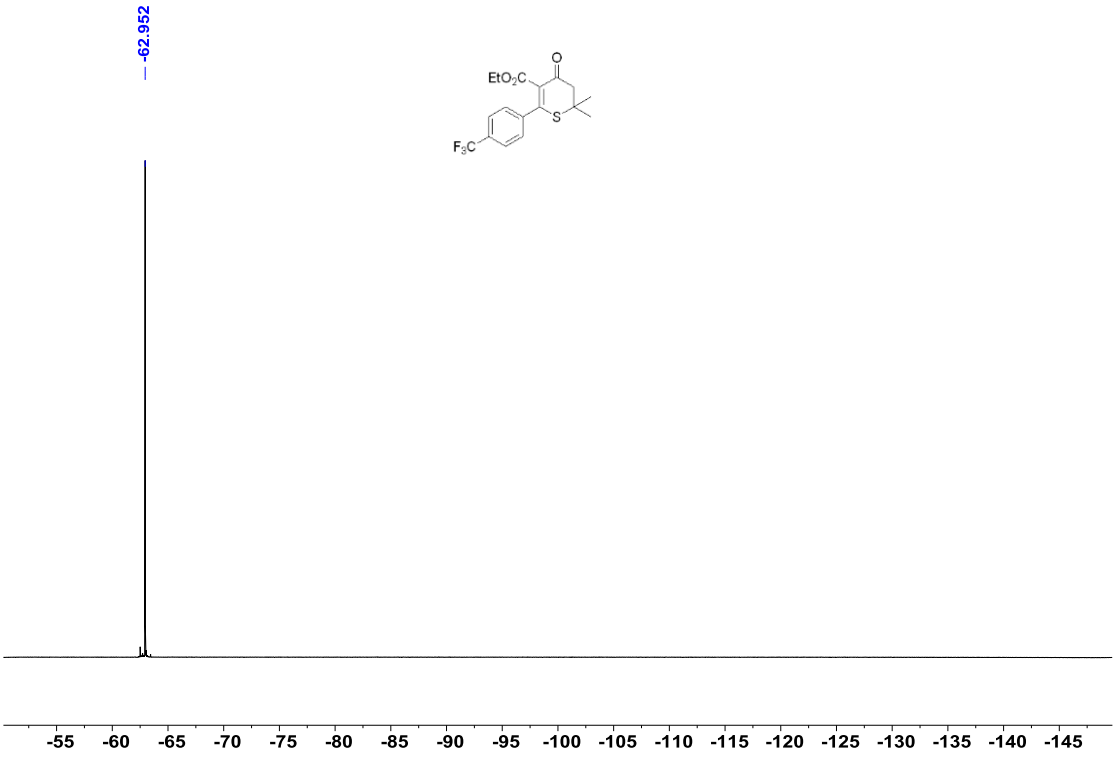
^{1}H MNR (400 MHz, $CDCl_3$)



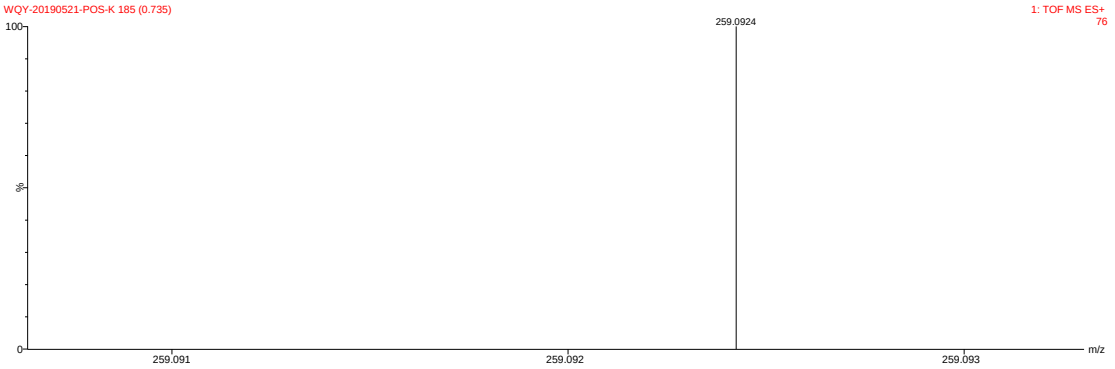
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



^{19}F NMR{^{1}H } (376 MHz, $CDCl_3$)

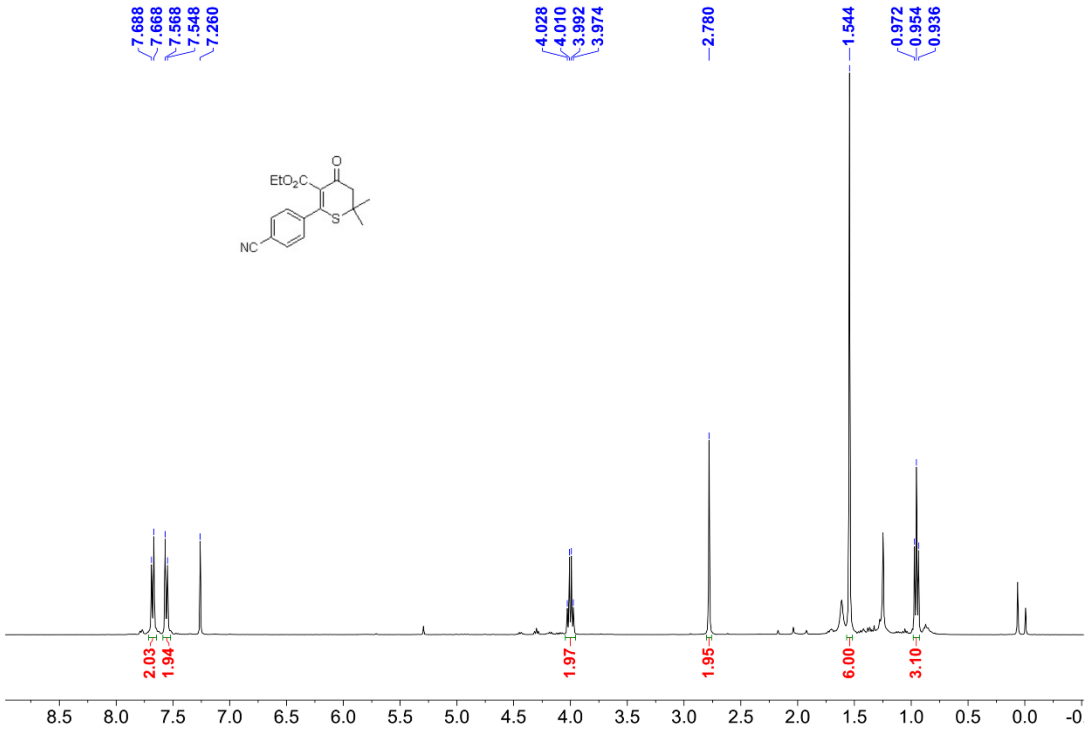


HRMS

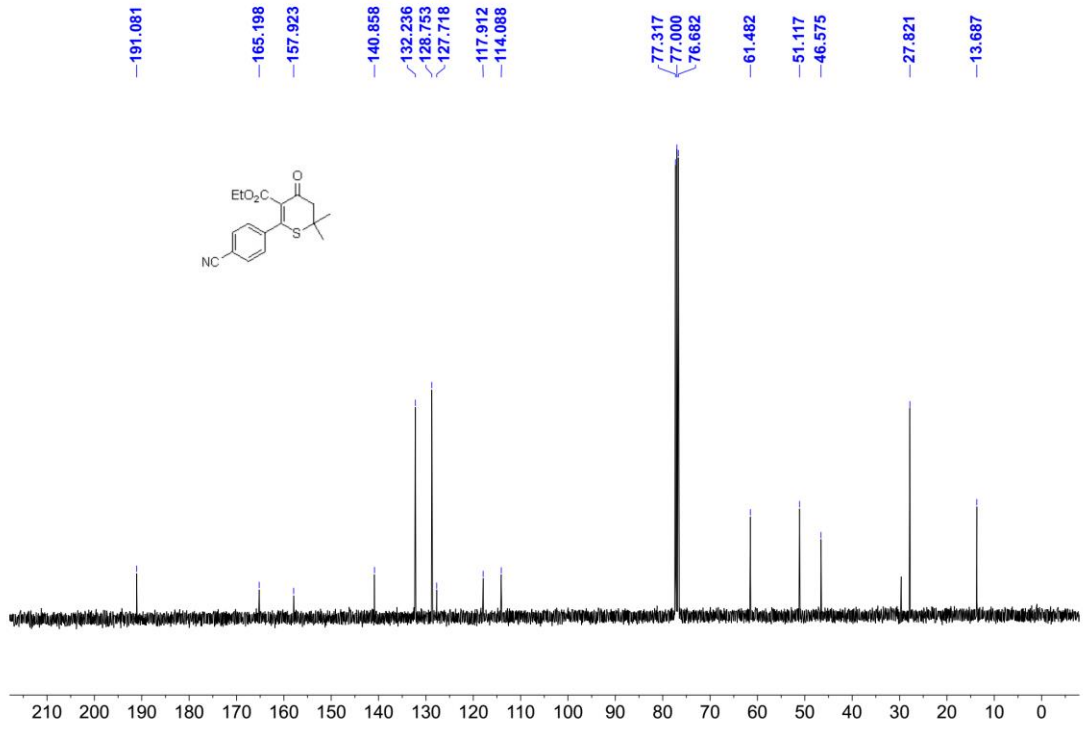


Ethyl 6-(4-cyanophenyl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ja**)

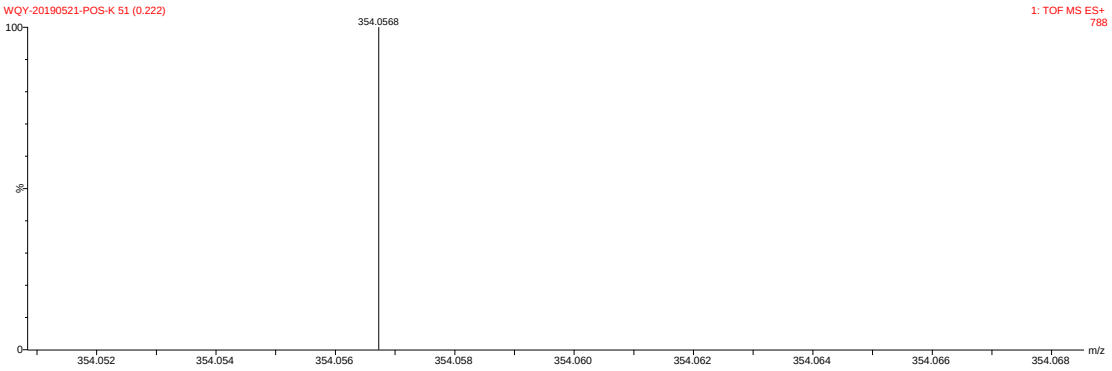
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

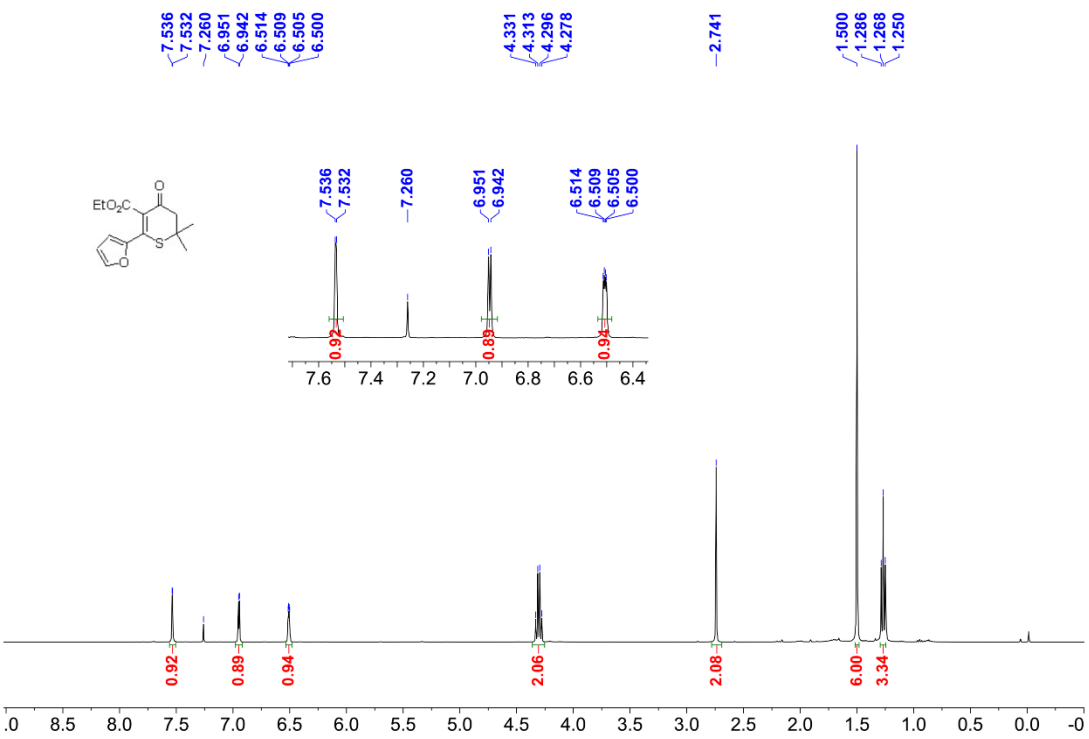


HRMS

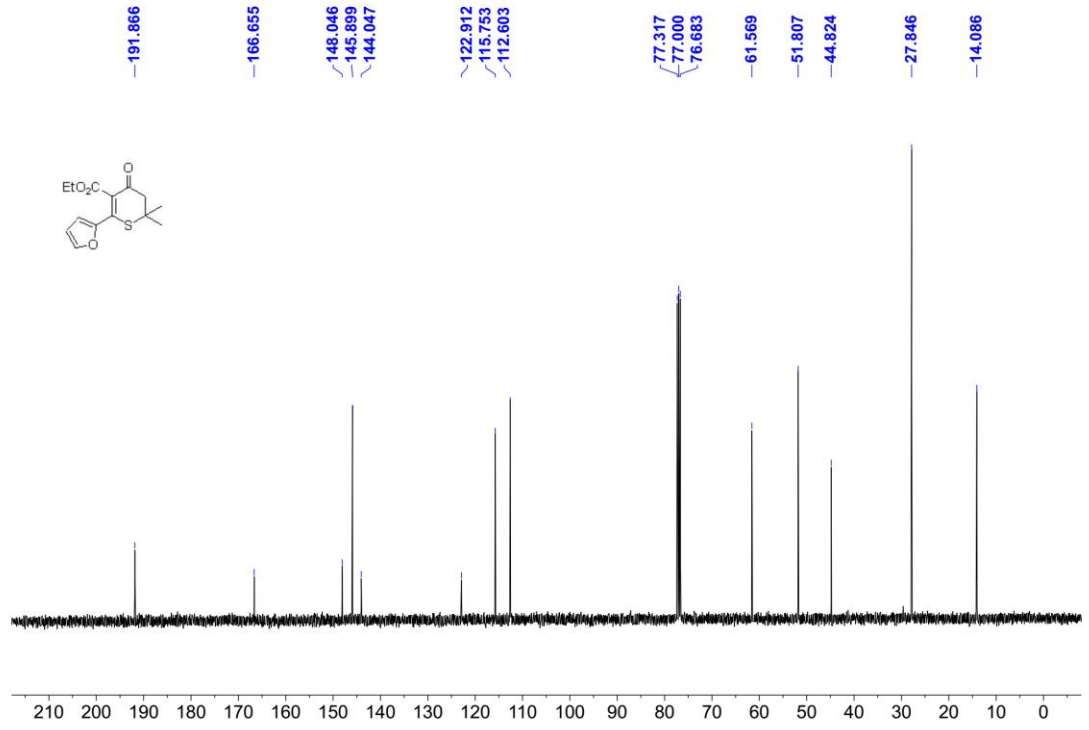

WQY-20190521-POS-K 51 (0.222)
1: TOF MS ES+
788
354.0568
100
%
0
354.052
354.054
354.056
354.058
354.060
354.062
354.064
354.066
354.068
m/z

Ethyl 6-(furan-2-yl)-2,2-dimethyl-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ka**)

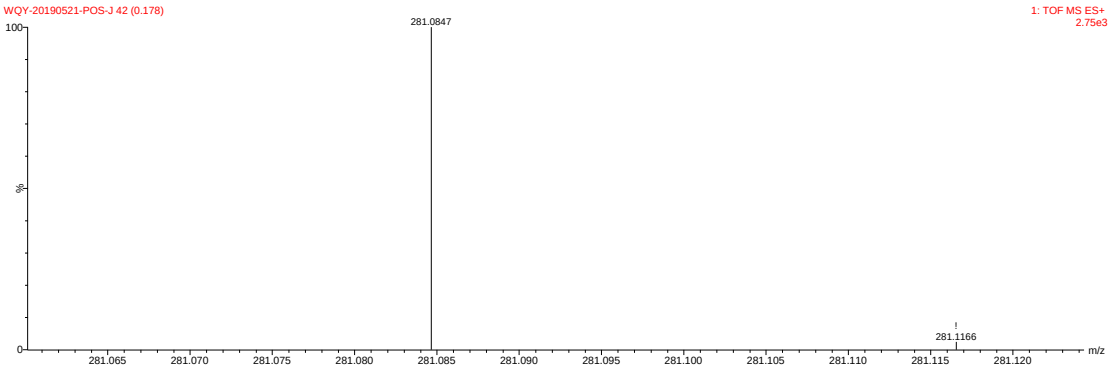
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

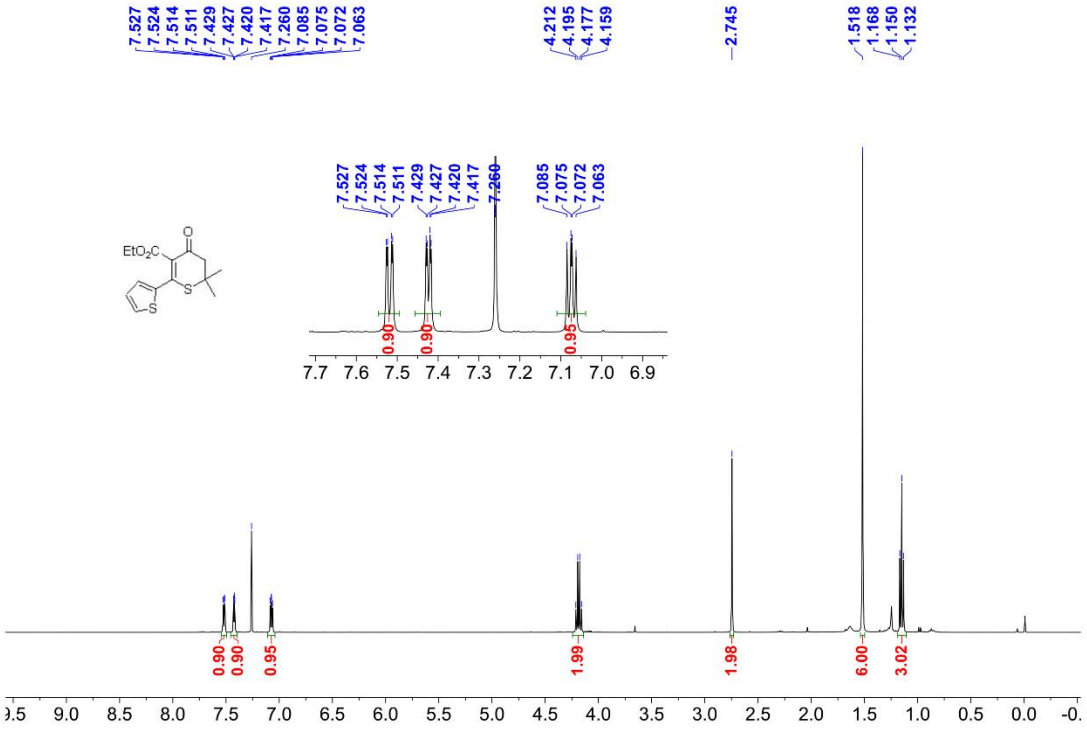


HRMS

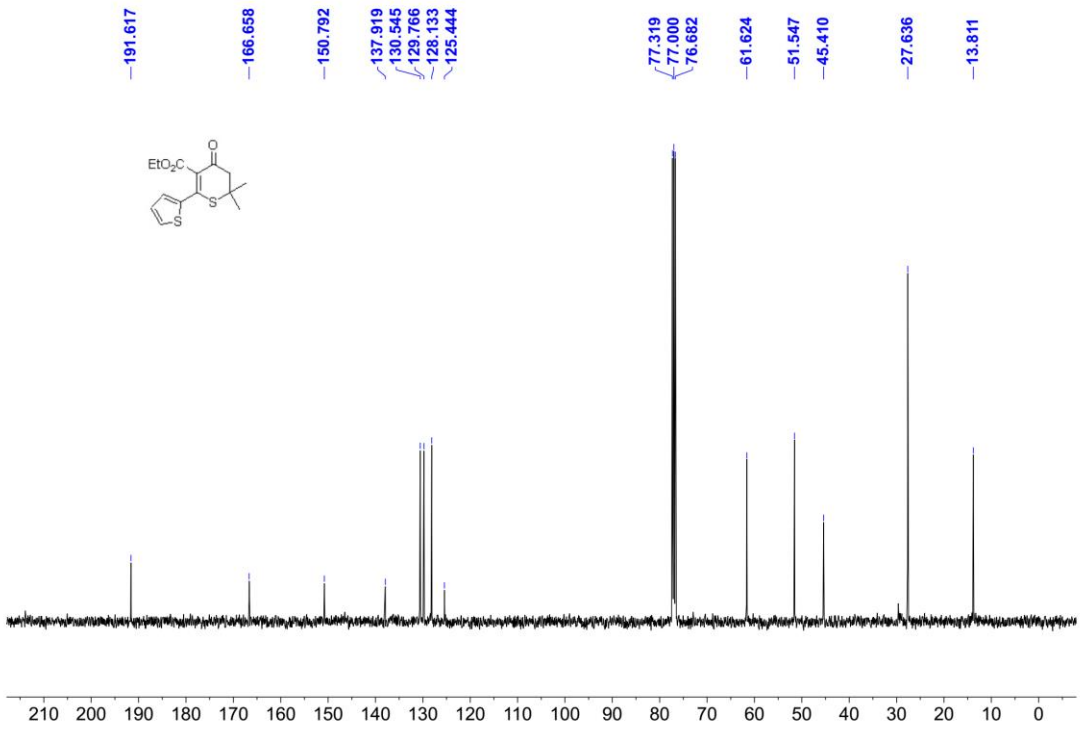

WQY-20190521-POS-J 42 (0.178)
1: TOF MS ES+
2.75e3
100
%
0
281.0847
281.1166
281.065
281.070
281.075
281.080
281.085
281.090
281.095
281.100
281.105
281.110
281.115
281.120
m/z

Ethyl 2,2-dimethyl-4-oxo-6-(thiophen-2-yl)-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3la**)

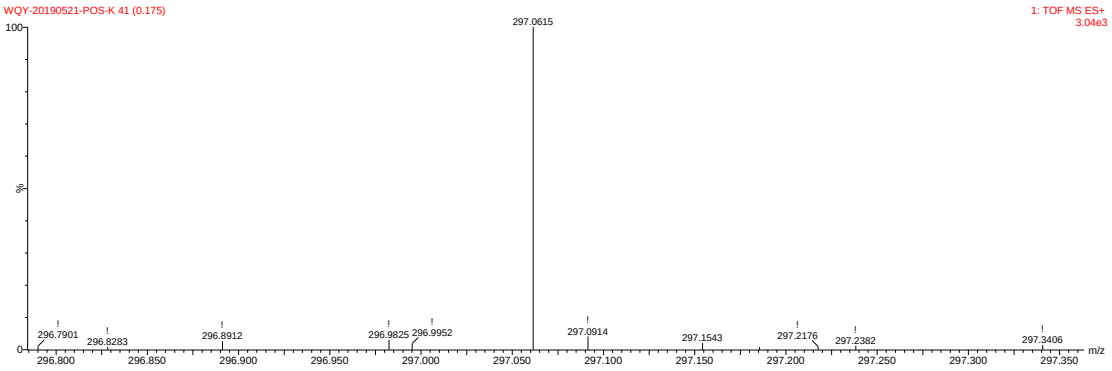
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

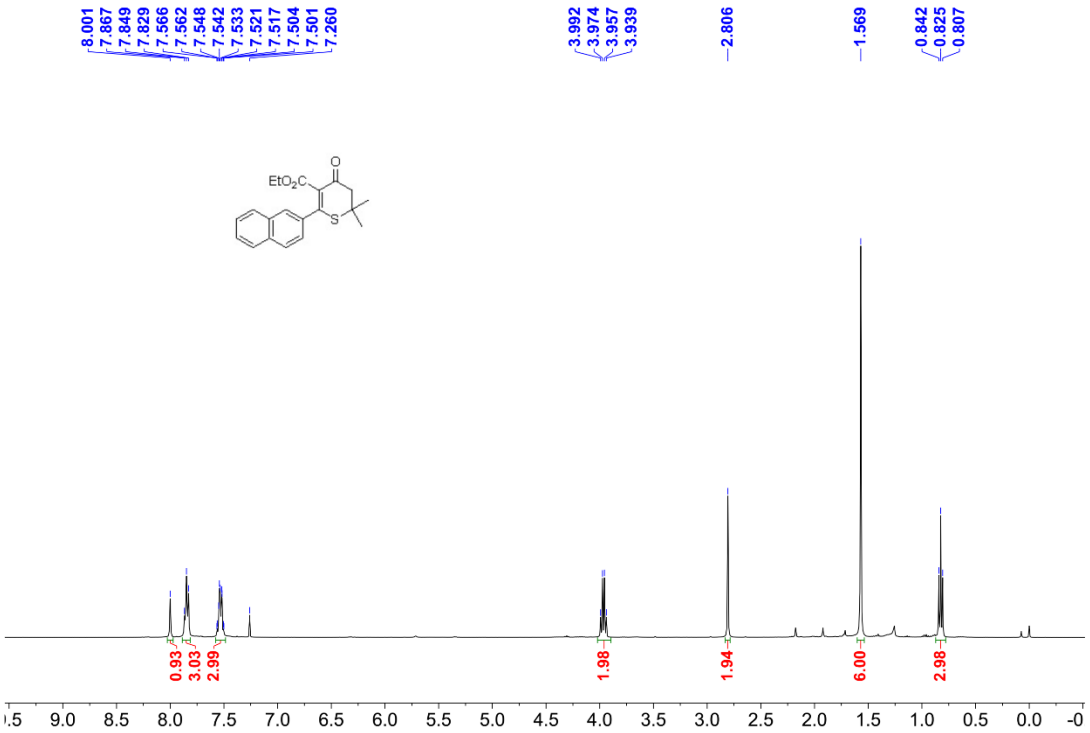


HRMS

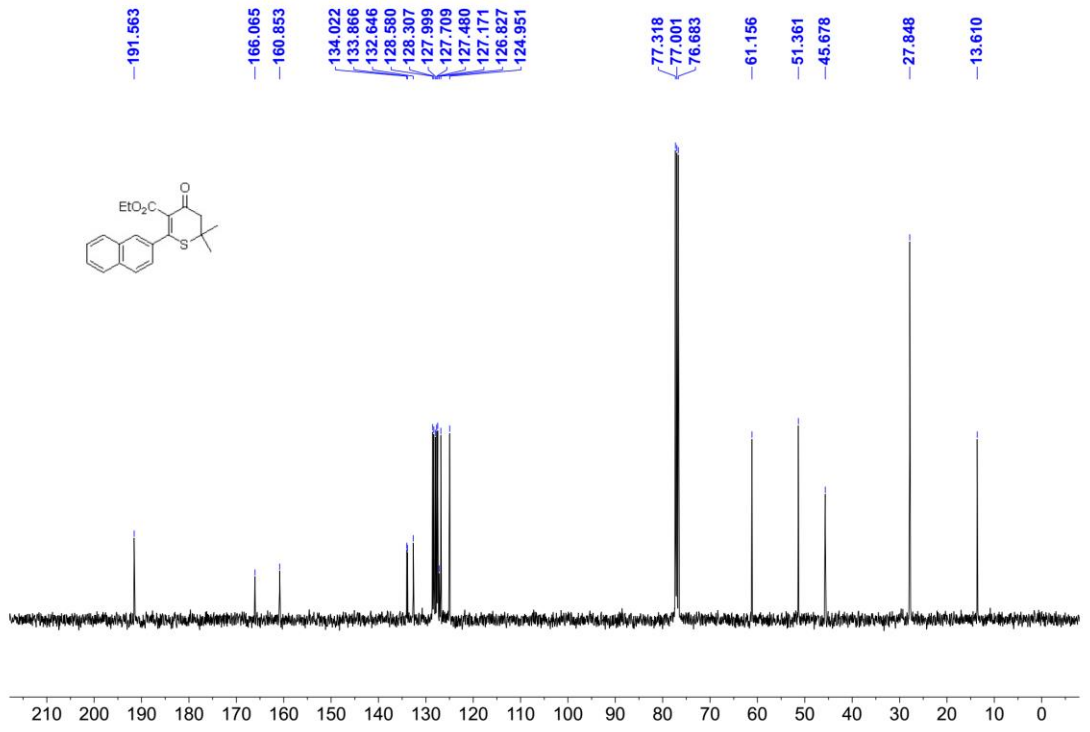

WQY-20190521-POS-K 41 (0.175)
1: TOF MS ES+
3.04e3
100
%
0
297.0615
296.7901
296.8283
296.8912
296.9825
296.9952
297.0914
297.1543
297.2176
297.2382
297.3406
m/z
296.800
296.850
296.900
296.950
297.000
297.050
297.100
297.150
297.200
297.250
297.300
297.350

Ethyl 2,2-dimethyl-6-(naphthalen-2-yl)-4-oxo-3,4-dihydro-2*H*-thiopyran-5-carboxylate (**3ma**)

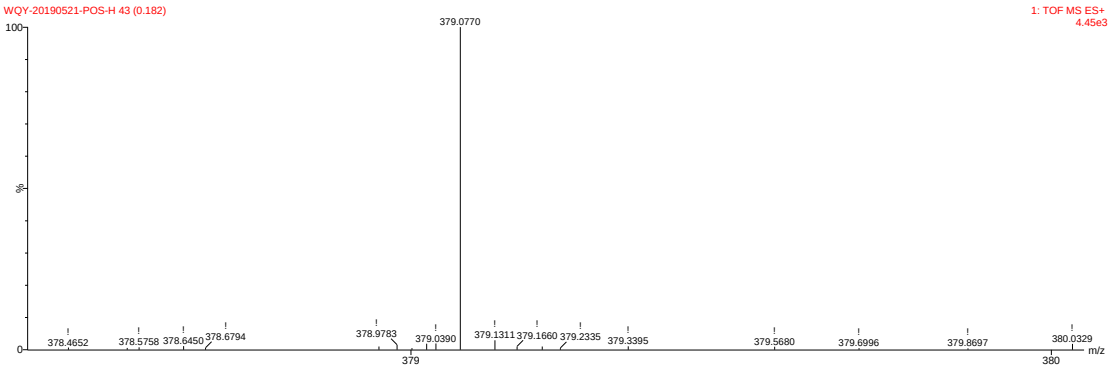
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

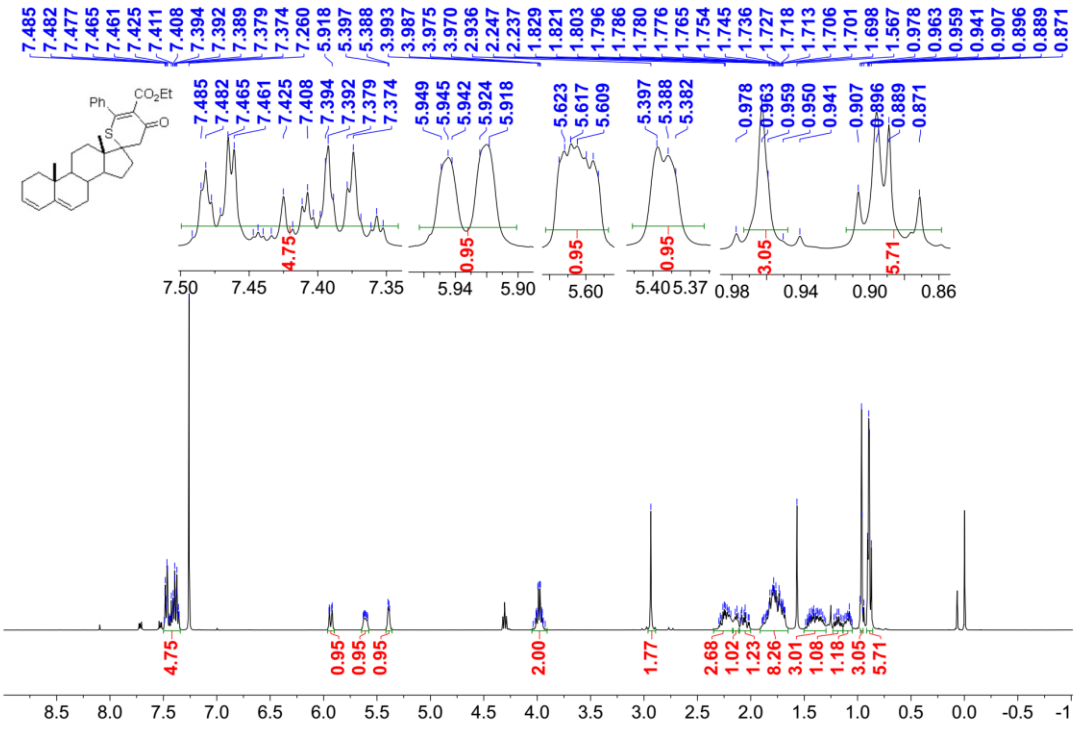


HRMS

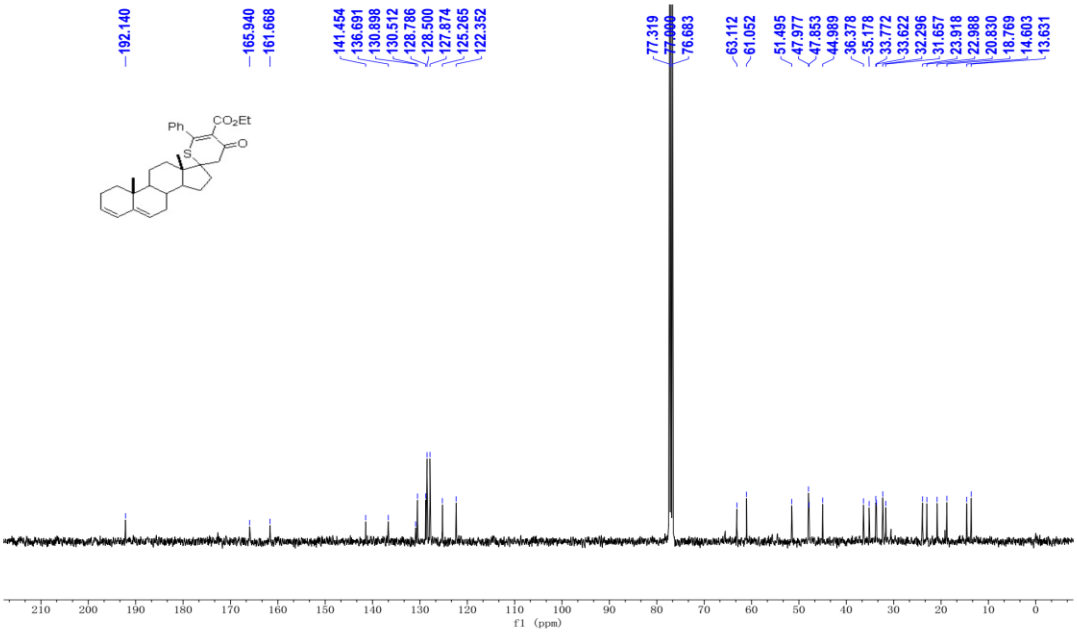

WQY-20190521-POS-H 43 (0.182)
1: TOF MS ES+
4.45e3
100
%
0
379.0770
378.4652
378.5758
378.6450
378.6794
378.9783
379.0390
379.1311
379.1660
379.2335
379.3395
379.5680
379.6996
379.8697
380.0329
379
380
m/z

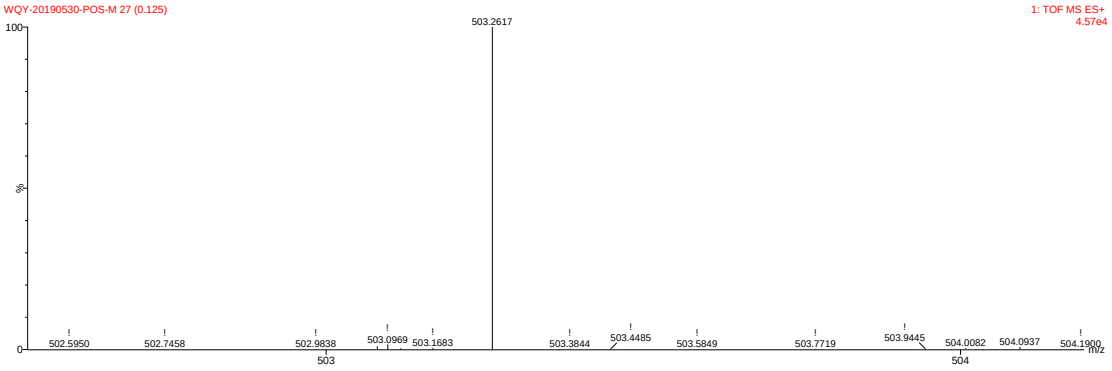
Ethyl (10R,13S)-10,13-Dimethyl-4'-oxo-6'-phenyl-1,2,3',4',7,8,9,10,11,12,13,14,15,16-tetradecahydrospiro[cyclopenta[a]phenanthrene-17,2'-thiopyran]-5'-carboxylate (13)

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



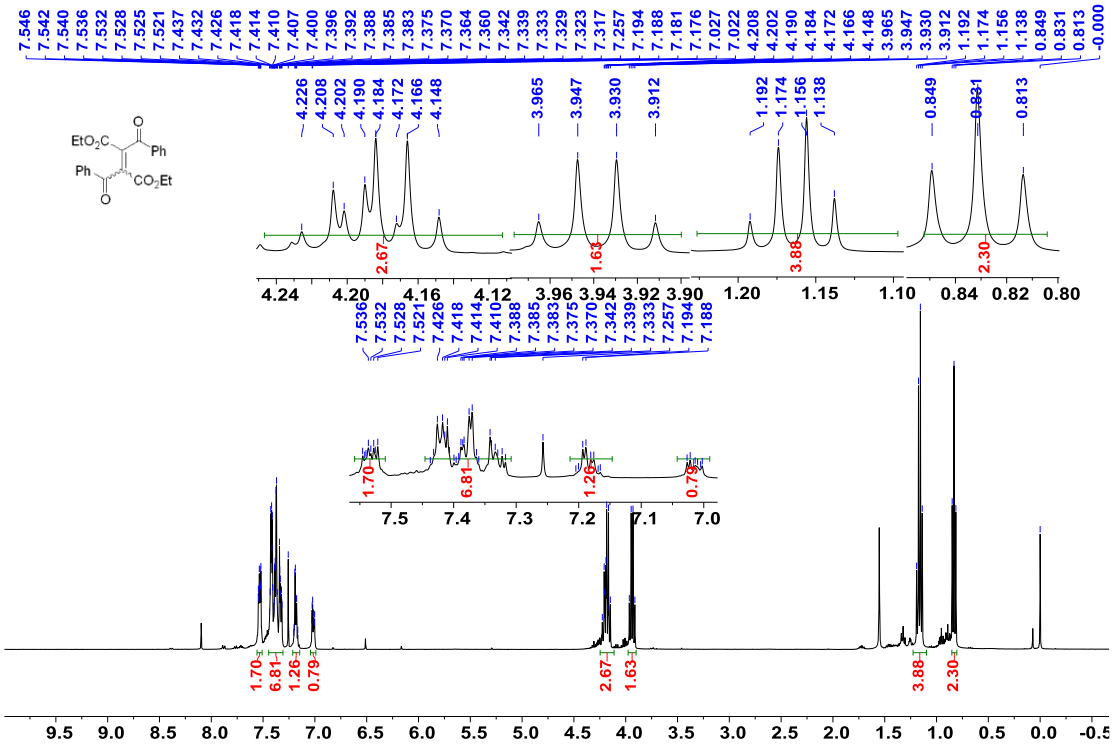
^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



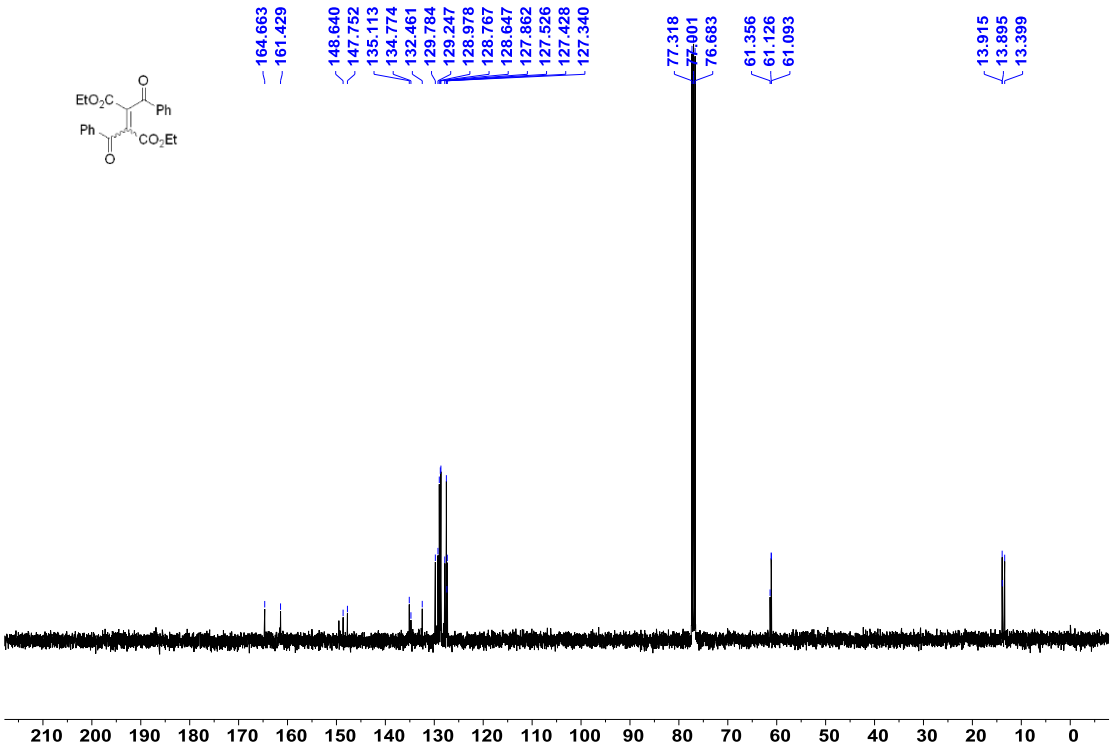

WQY-20190530-POS-M 27 (0.125)
1: TOF MS ES+
4.57e4
100
%
0
503.2617
502.5950
502.7458
502.9838
503.0969
503.1683
503.3844
503.4485
503.5849
503.7719
503.9445
504.0082
504.0937
504.1900
503
504
m/z

Diethyl 2,3-Dibenzoylbut-2-enedioate (4)

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

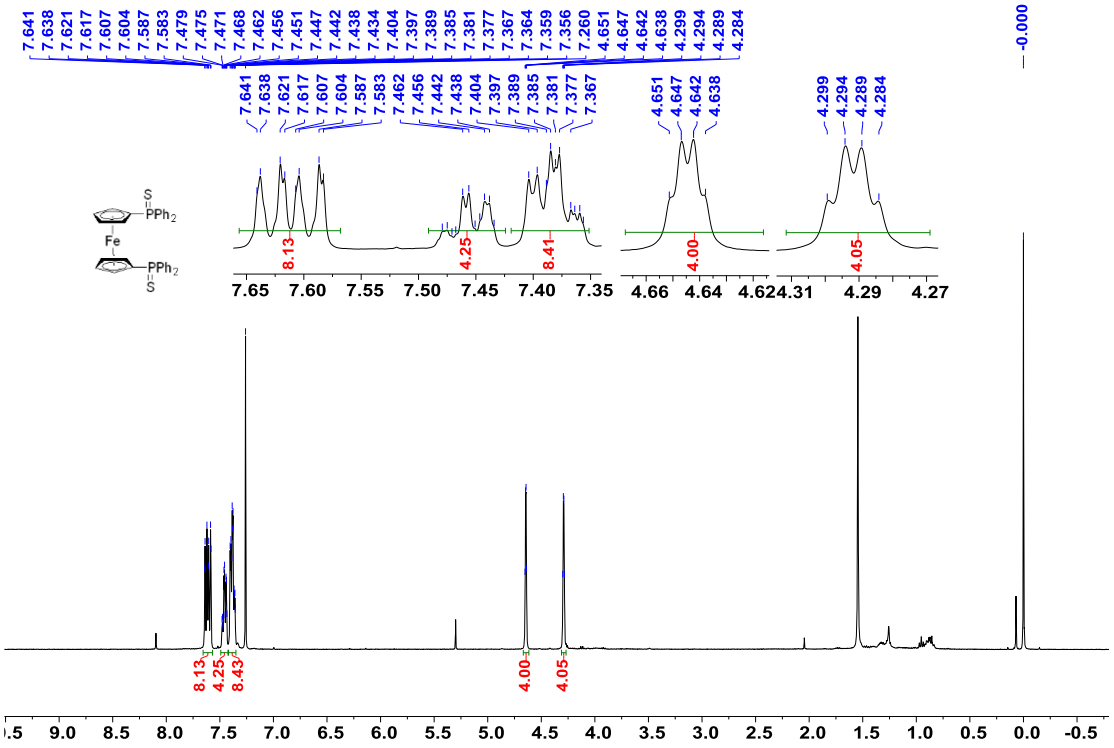


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

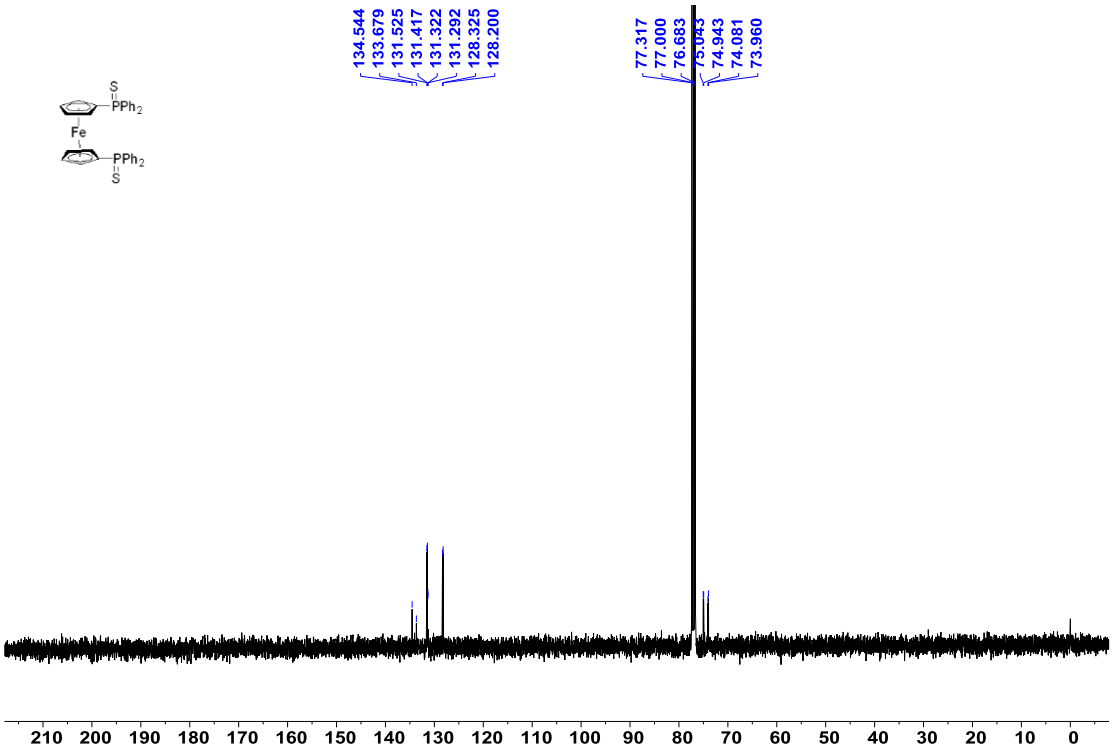


Phosphine sulfide (5)

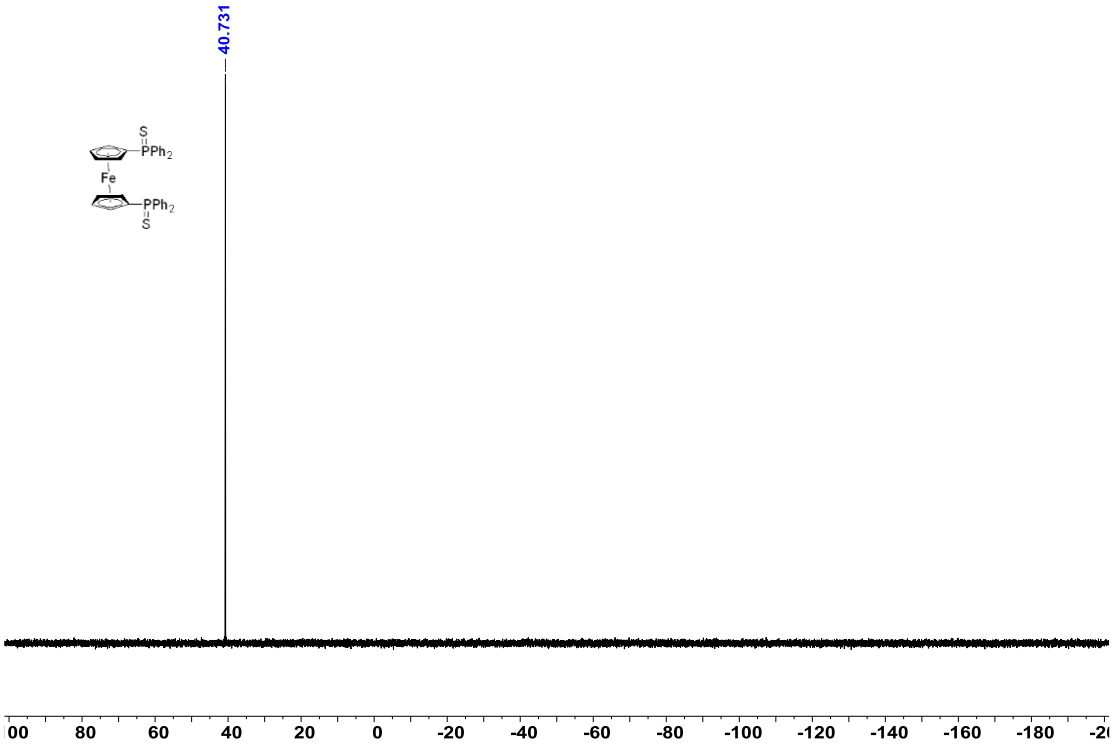
^{1}H MNR (400 MHz, $CDCl_3$)



^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)

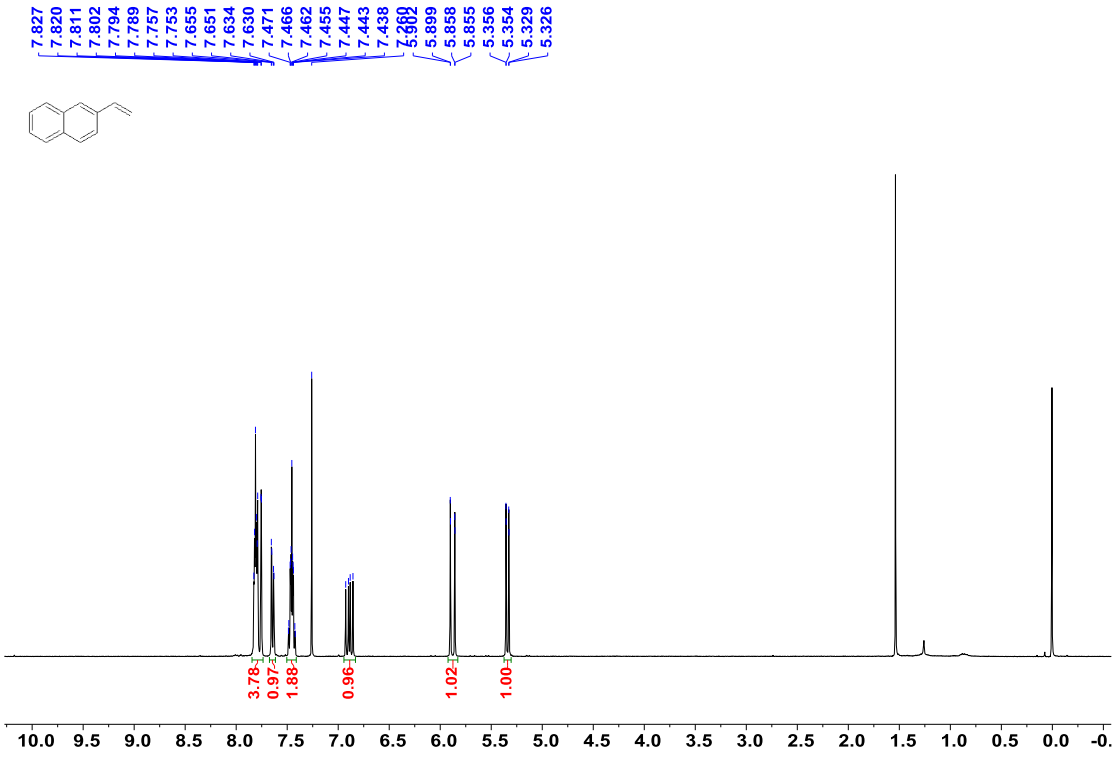


^{31}P NMR{^{1}H} (162 MHz, $CDCl_3$)

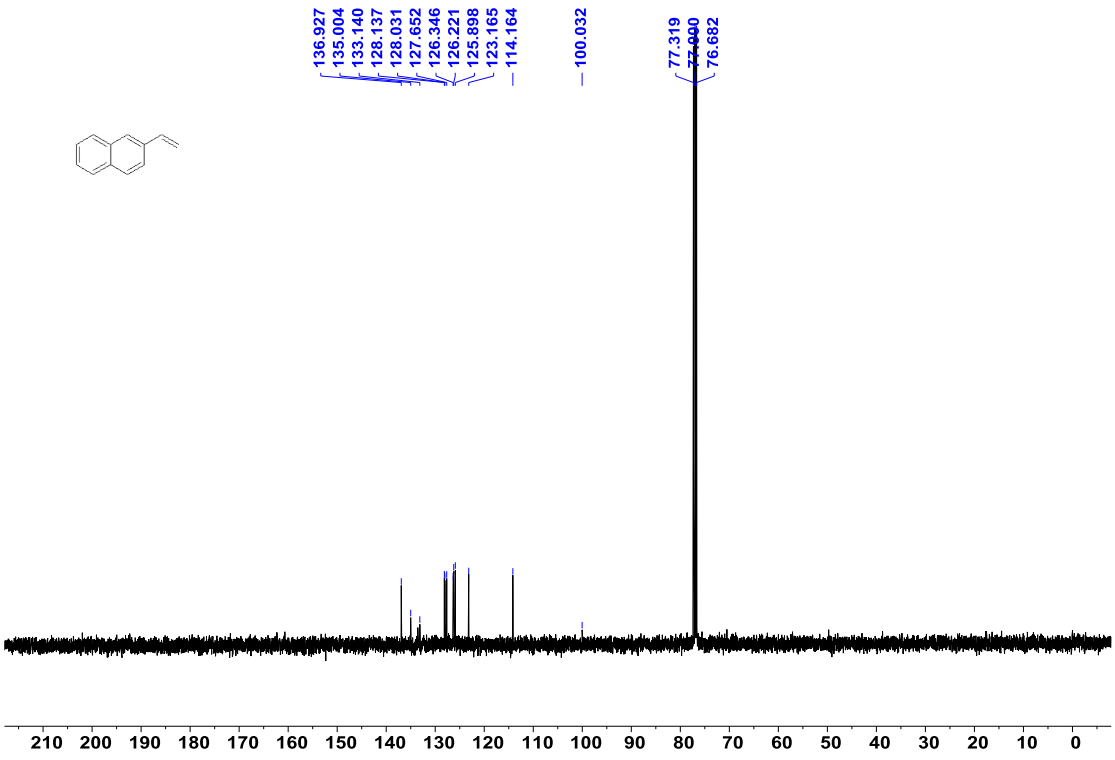

40.731
S
PPh2
Fe
PPh2
S
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180

2-vinylnaphthalene (6)

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

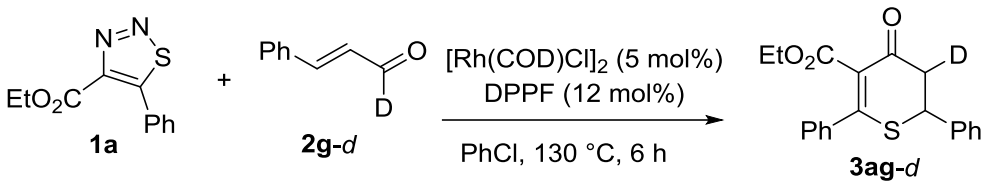


^{13}C NMR{^{1}H} (101 MHz, $CDCl_3$)



14. Copies of NMR Spectra of the Crude Reaction Mixtures in KIE Studies

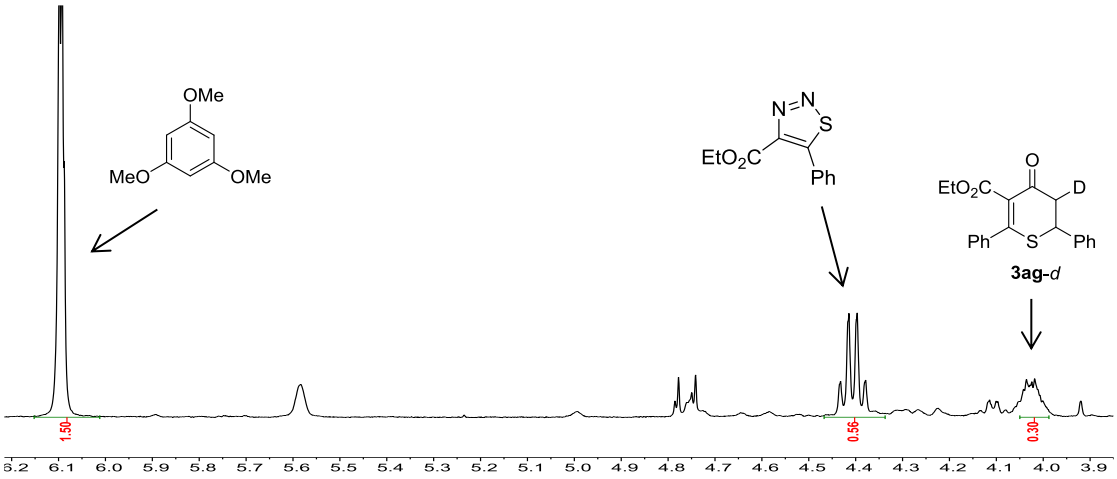
Reaction 1



Reaction 2

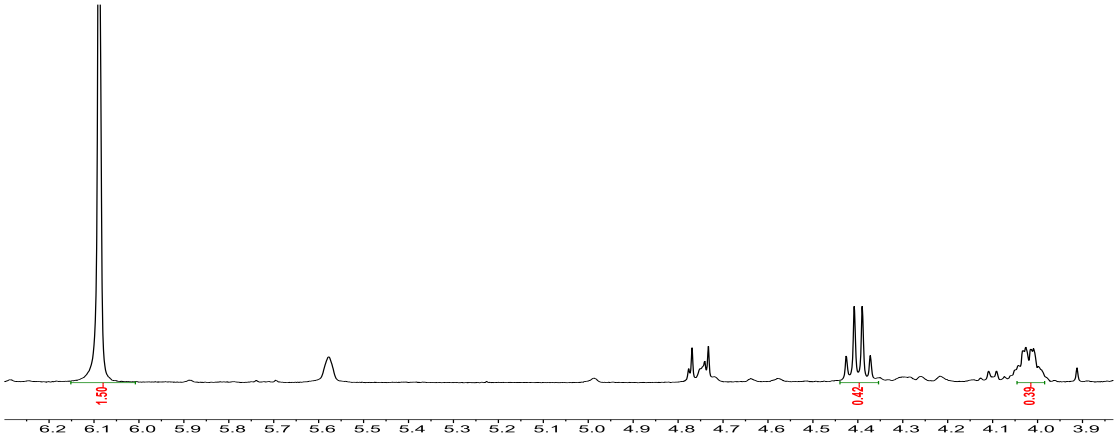
Reaction 1 (5 min)

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



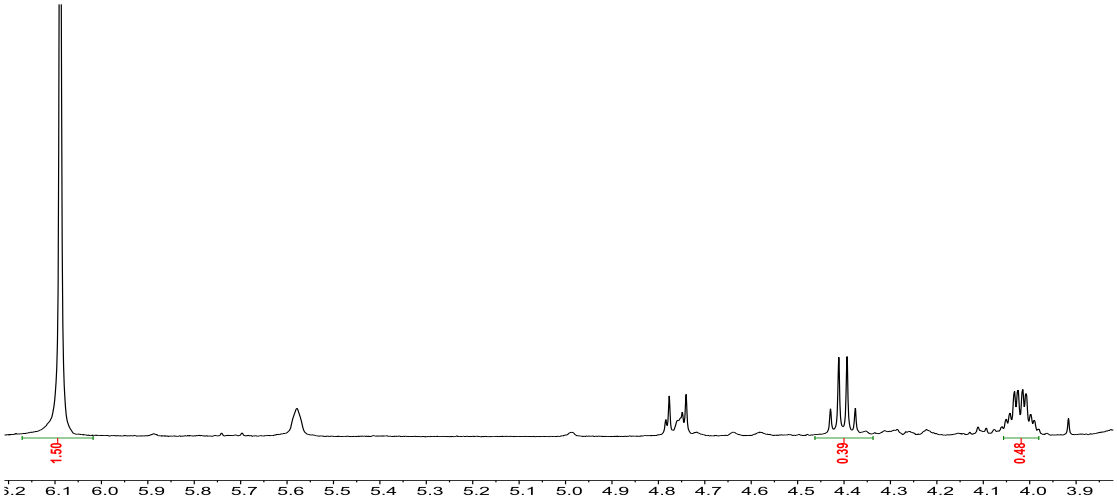
Reaction 1 (10 min)

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



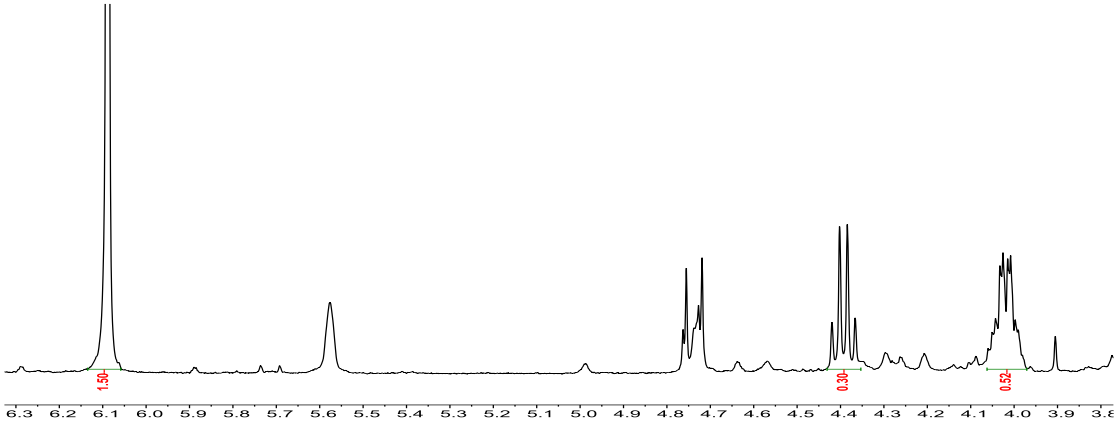
Reaction 1 (15 min)

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



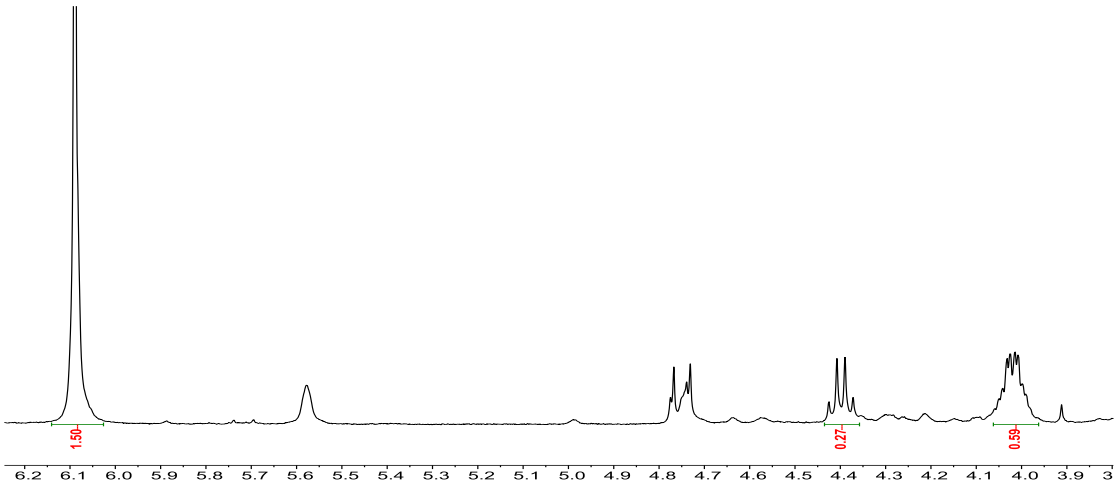
Reaction 1 (20 min)

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



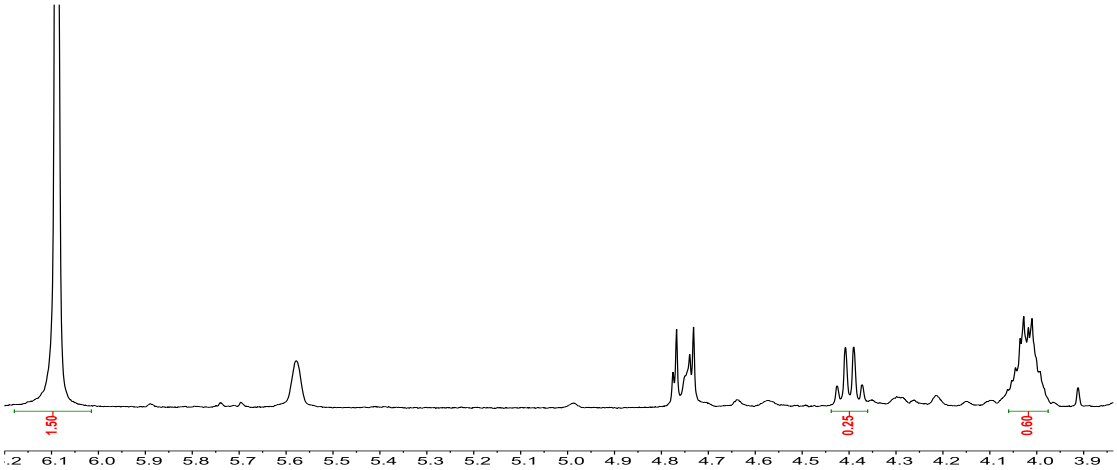
Reaction 1 (30 min)

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



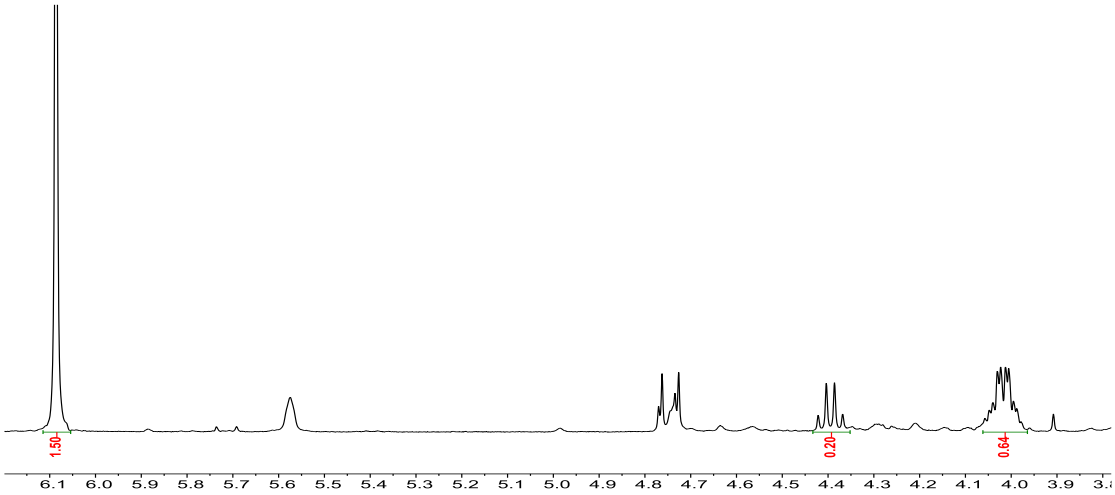
Reaction 1 (40 min)

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



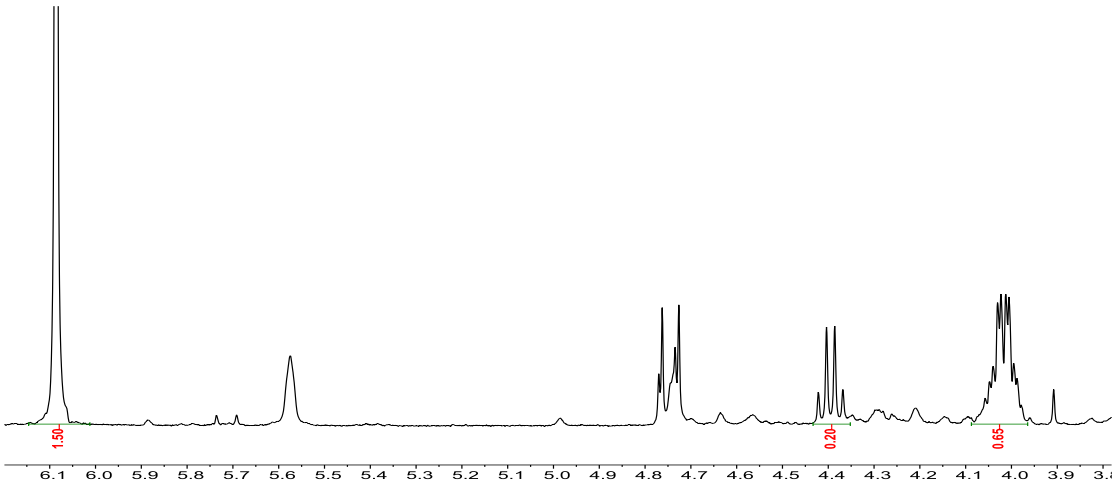
Reaction 1 (50 min)

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



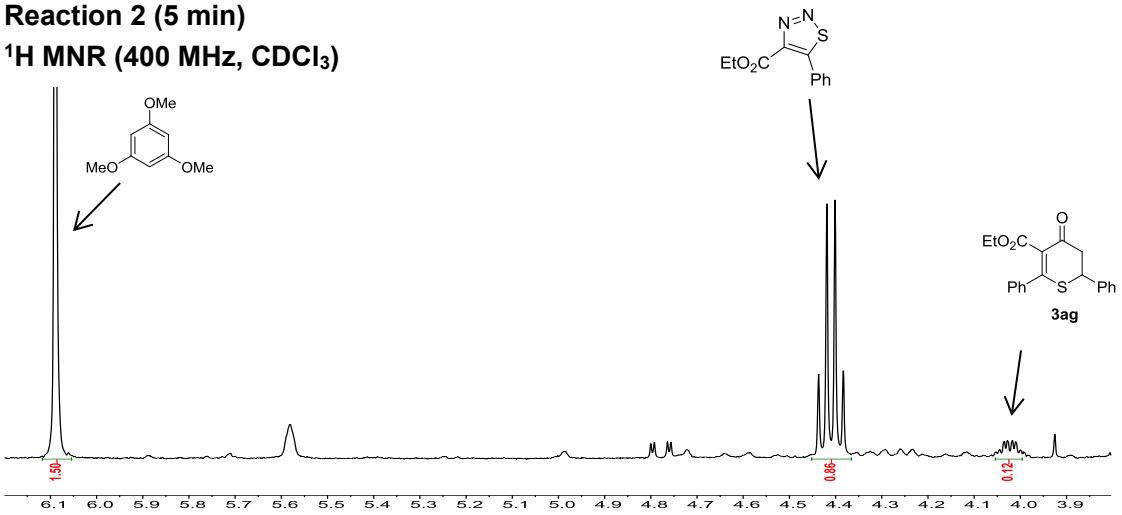
Reaction 1 (60 min)

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



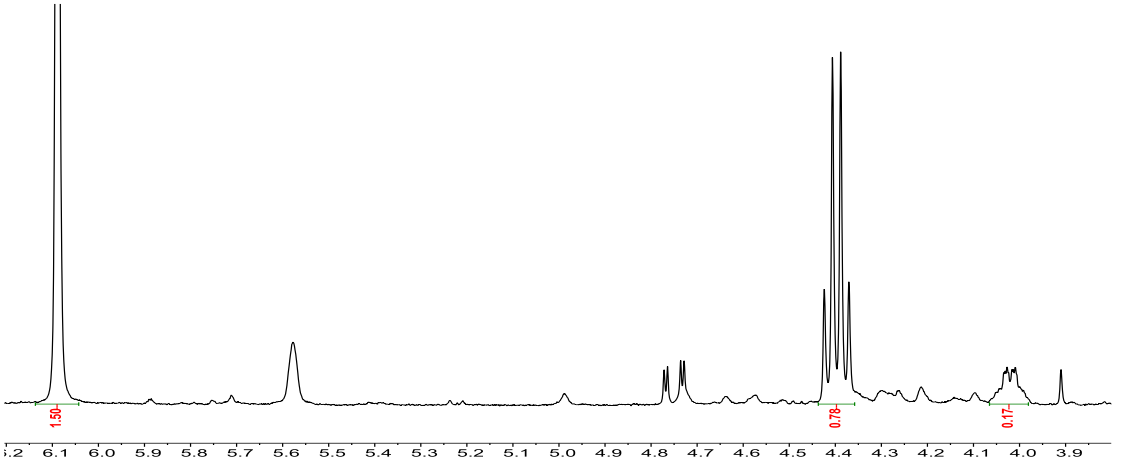
Reaction 2 (5 min)

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



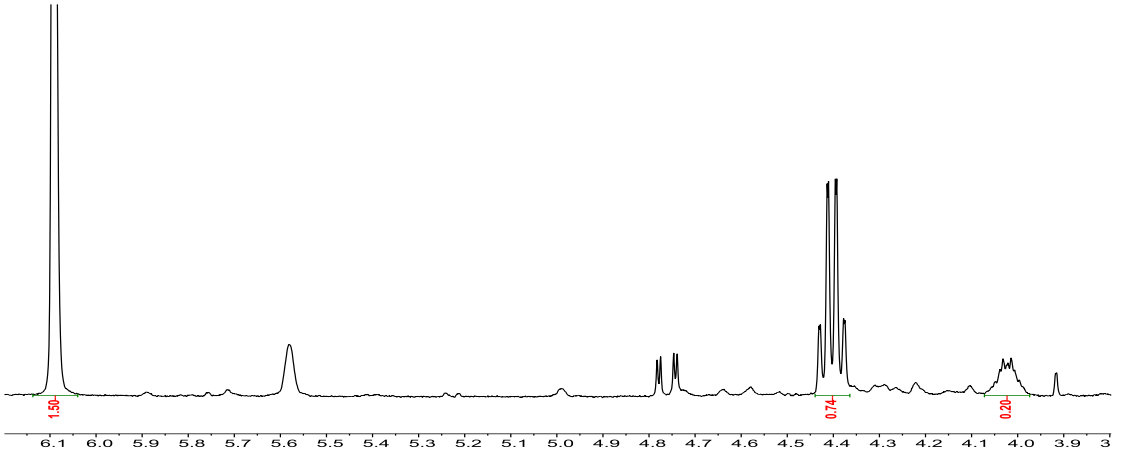
Reaction 2 (10 min)

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



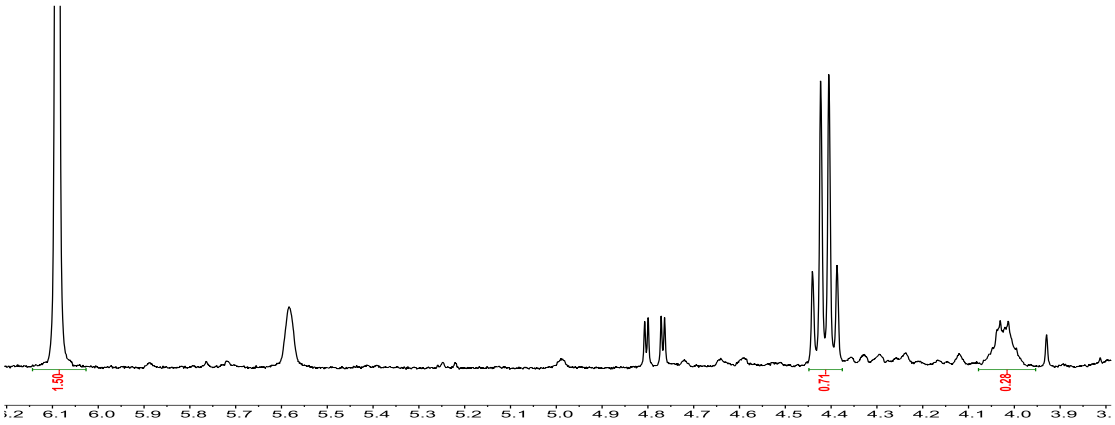
Reaction 2 (15 min)

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



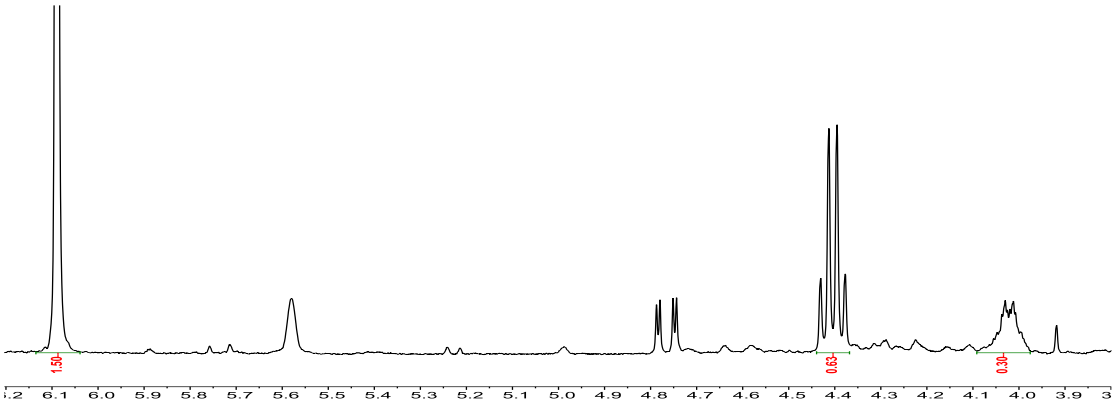
Reaction 2 (20 min)

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



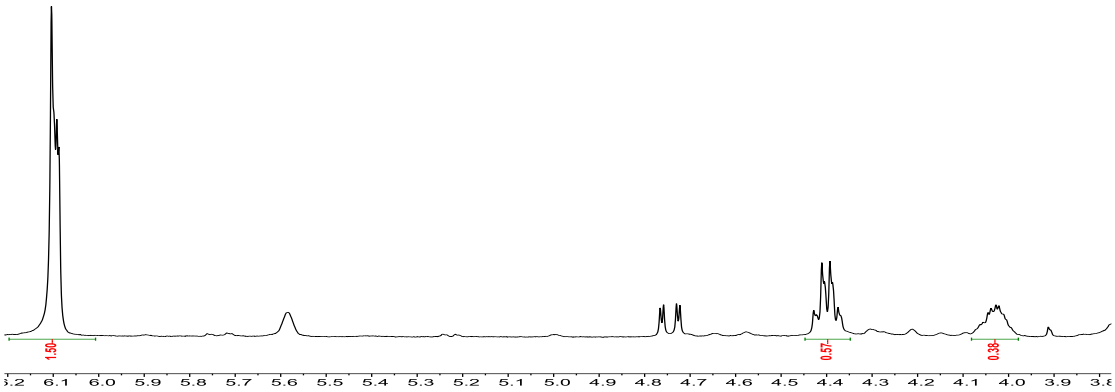
Reaction 2 (30 min)

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



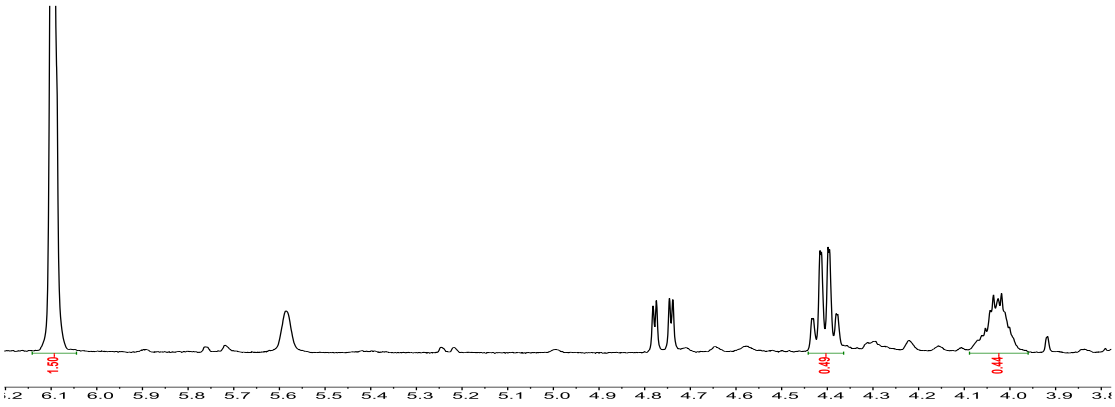
Reaction 2 (40 min)

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



Reaction 2 (50 min)

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



Reaction 2 (60 min)

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