

Supporting Information

Concise synthesis of chiral γ -butenolides via an allylation/lactonization cascade

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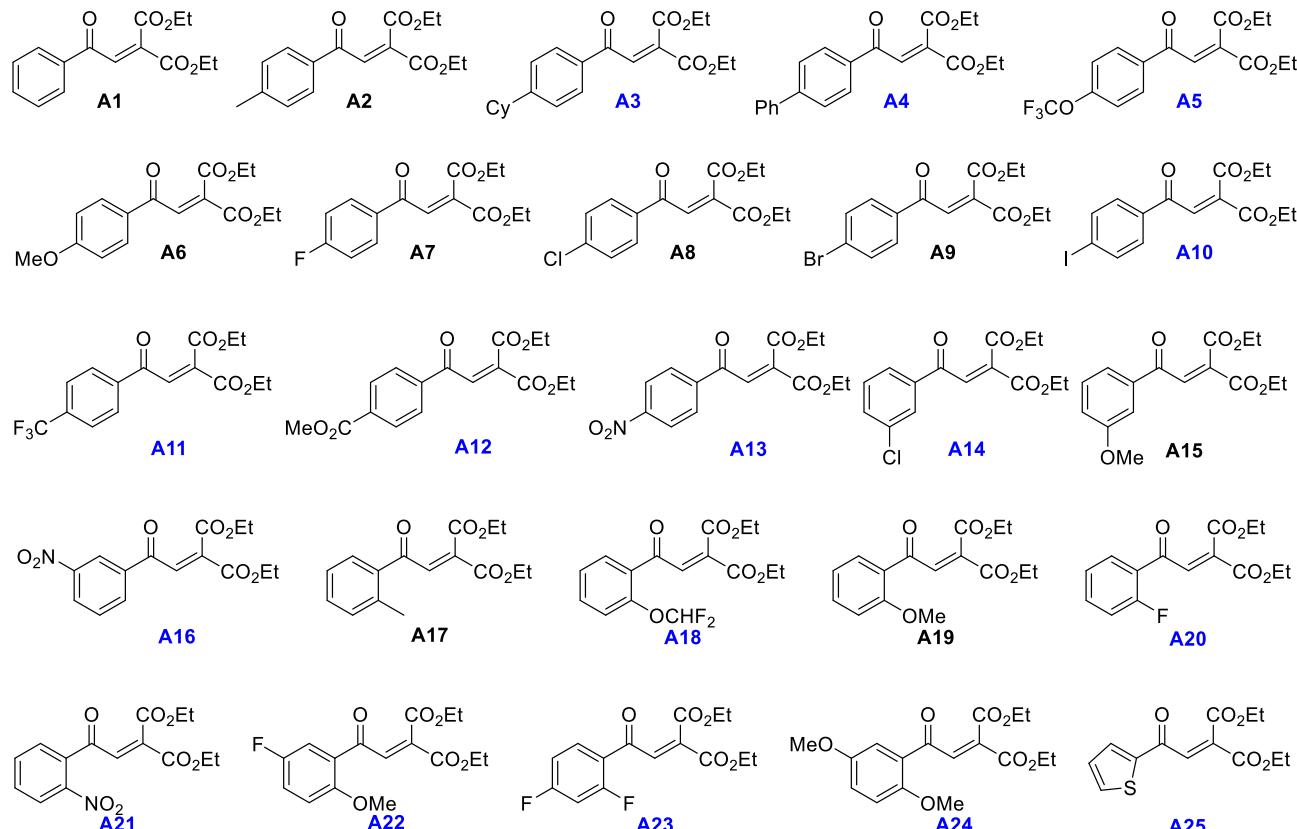
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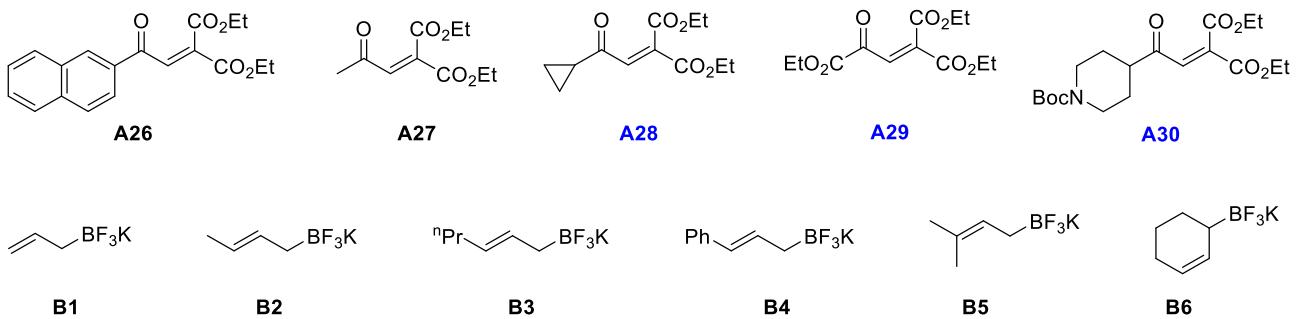
(A) General information

¹H NMR spectra were recorded on Bruker ASCEND™ operating at 400 MHz. Chemical shifts were recorded in ppm from tetramethylsilane with the solvent resonance as the internal standard (CDCl_3 , $\delta = 7.26$). Data were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets), coupling constants (Hz), integration. ¹³C{¹H} NMR data were collected on commercial instruments (101 MHz) with complete proton decoupling. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as internal standard (CDCl_3 , $\delta = 77.0$). ¹⁹F{¹H} NMR spectra were collected on a bruker ASCEND™ 400M (376 MHz) in CDCl_3 with complete proton decoupling. Enantiomeric excesses (ee) were determined by HPLC analysis by using the corresponding commercial chiralpak column as stated in the experimental procedures at 25 °C. Optical rotations were reported as follows: $[\alpha]_D^T = (c = \text{g}/100 \text{ mL}, \text{ in } \text{CH}_2\text{Cl}_2, \text{ unless otherwise noted, } \lambda = 589 \text{ nm})$. IR was detected by Bruker Tensor II spectrometer with Plantium ATR accessory. HRMS was recorded on a Q Exactive hybrid quadrupole-Orbitrap mass spectrometer (ESI). All reactions were carried out in flame-dried reaction flasks, and all reactions involving air-sensitive reagents were performed under nitrogen atmosphere. Solvents were dried and distilled prior to use according to the standard methods. Metal salts obtained from commercial sources were used without further purification. The chiral *N,N'*-dioxide ligands¹, potassium allyltrifluoroborate², and enone diesters³ were synthesized by the same procedure in the literature.

(B) Characterization of the substrates

All the substrates were synthesized according to the methods reported in the literature^{2,3}, and the NMR of the known substrates was also consistent with the literature reports, and the NMR characterization of the other new compounds (the blue-marked ones) were as follows:





A3: 2,2-dimethyl-3-oxo-1-(4-cyano-phenyl)-1,3-butadiene diethyl ester.

1H NMR (400 MHz, Chloroform-*d*): δ 7.93 – 7.88 (m, 2H), 7.85 (s, 1H), 7.37 – 7.30 (m, 2H), 4.34 (q, *J* = 7.2 Hz, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 2.65 – 2.53 (m, 1H), 1.94 – 1.80 (m, 4H), 1.80 – 1.72 (m, 1H), 1.50 – 1.38 (m, 4H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.29–1.26 (m, 1H), 1.25 (t, *J* = 7.2 Hz, 4H); **13C{1H} NMR** (101 MHz, Chloroform-*d*): δ 188.57, 164.66, 162.96, 155.16, 136.26, 135.43, 133.99, 129.09, 127.45, 62.39, 61.91, 44.80, 34.00, 26.65, 25.97, 14.03, 13.75; **ESI-HRMS** calcd for [C₂₁H₂₆NO₅+Na⁺]: 381.1673, found 381.1667;

A4: 2,2-dimethyl-3-oxo-1-(phenyl)-1,3-butadiene diethyl ester.

1H NMR (400 MHz, Chloroform-*d*): δ 8.33 – 7.17 (m, 10H), 4.61 – 4.02 (m, 4H), 1.55 – 1.00 (m, 6H); **13C{1H} NMR** (101 MHz, Chloroform-*d*): δ 188.57, 164.64, 162.94, 146.91, 139.52, 136.55, 135.23, 134.81, 129.48, 129.06, 128.59, 127.56, 127.34, 62.50, 62.03, 14.07, 13.81; **ESI-HRMS** calcd for [C₂₁H₂₀NO₅+Na⁺]: 375.1203, found 375.1195;

A5: 2,2-dimethyl-3-oxo-1-(4-(trifluoromethoxy)phenyl)-1,3-butadiene diethyl ester.

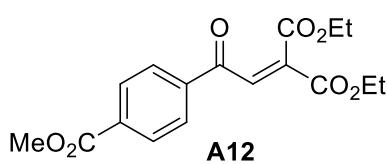
1H NMR (400 MHz, Chloroform-*d*): δ 8.08 – 8.00 (m, 2H), 7.81 (s, 1H), 7.38 – 7.30 (m, 2H), 4.33 (dq, *J* = 19.1, 7.1 Hz, 4H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); **13C{1H} NMR** (101 MHz, Chloroform-*d*): δ 187.68, 164.31, 162.69, 153.34 (q, *J*_{F-C} = 1.8 Hz), 136.99, 134.66, 134.20, 130.91, 120.22 (q, *J*_{F-C} = 259.3 Hz), 116.36, 62.55, 62.06, 13.97, 13.70; **¹⁹F{1H} NMR** (377 MHz, Chloroform-*d*) δ –57.65; **ESI-HRMS** calcd for [C₁₆H₁₅F₃O₆+Na⁺]: 383.0713, found 383.0708;

A10: 2,2-dimethyl-3-oxo-1-(4-iodophenyl)-1,3-butadiene diethyl ester.

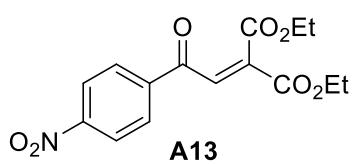
1H NMR (400 MHz, Chloroform-*d*): δ 7.92 – 7.82 (m, 2H), 7.78 (s, 1H), 7.72 – 7.64 (m, 2H), 4.33 (dq, *J* = 18.4, 7.1 Hz, 4H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H); **13C{1H} NMR** (101 MHz, Chloroform-*d*): δ 188.48, 164.38, 162.75, 138.32, 136.93, 135.31, 134.60, 130.03, 102.71, 62.58, 62.09, 14.04, 13.79; **ESI-HRMS** calcd for [C₁₅H₁₅IO₅+Na⁺]: 424.9857, found 424.9849;

A11: 2,2-dimethyl-3-oxo-1-(4-(trifluoromethyl)phenyl)-1,3-butadiene diethyl ester.

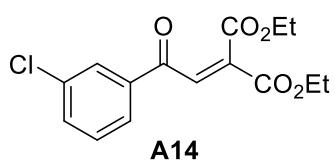
1H NMR (400 MHz, Chloroform-*d*): δ 8.12 – 8.06 (m, 2H), 7.82 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 4.34 (dq, *J* = 21.7, 7.1 Hz, 2H), 1.37 (t, *J* = 7.2 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 1H); **13C{1H} NMR** (101 MHz, Chloroform-*d*): δ 188.36, 164.20, 162.62, 138.64, 137.36, 135.27 (q, *J*_{F-C} = 32.9 Hz), 134.45, 129.12, 126.00 (q, *J* = 3.8 Hz), 123.40 (q, *J* = 272.8 Hz), 62.65, 62.15, 13.98, 13.72; **ESI-HRMS** calcd for [C₁₆H₁₅F₃O₅+Na⁺]: 367.0764, found 367.0757;



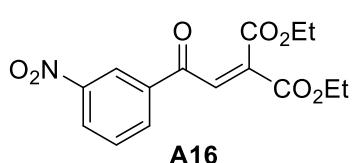
¹H NMR (400 MHz, Chloroform-*d*): δ 8.20 – 8.13 (m, 2H), 8.06 – 7.99 (m, 2H), 7.83 (s, 1H), 4.33 (dq, J = 25.4, 7.1 Hz, 4H), 3.97 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H), 1.27 (t, J = 7.1 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 188.75, 165.97, 164.29, 162.71, 139.14, 137.11, 134.78, 134.72, 130.10, 128.71, 62.62, 62.13, 52.62, 14.04, 13.77; **ESI-HRMS** calcd for [C₁₈H₁₈O₇+Na⁺]: 357.0945, found 357.0939;



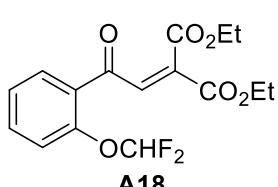
¹H NMR (400 MHz, Chloroform-*d*): δ 8.40 – 8.33 (m, 2H), 8.20 – 8.08 (m, 2H), 7.81 (s, 1H), 4.35 (dq, J = 21.6, 7.1 Hz, 4H), 1.37 (t, J = 7.1 Hz, 3H), 1.29 (t, J = 7.1 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 187.88, 164.04, 162.49, 150.82, 140.34, 137.80, 134.07, 129.81, 124.16, 62.78, 62.28, 14.02, 13.79; **ESI-HRMS** calcd for [C₁₅H₁₅NO₇+Na⁺]: 344.0741, found 344.0735; **ESI-HRMS** calcd for [C₁₅H₁₅NO₇+Na⁺]: 344.0741, found 344.0735;



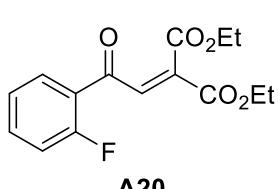
¹H NMR (400 MHz, Chloroform-*d*): δ 7.94 (t, J = 1.9 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.78 (s, 1H), 7.60 (ddd, J = 8.0, 2.1, 1.0 Hz, 1H), 7.46 (t, J = 7.9 Hz, 1H), 4.33 (dq, J = 20.1, 7.2 Hz, 4H), 1.36 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 187.98, 164.29, 162.69, 137.52, 137.14, 135.36, 134.56, 134.13, 130.31, 128.73, 126.92, 62.61, 62.12, 14.03, 13.76; **ESI-HRMS** calcd for [C₁₅H₁₅ClO₅+Na⁺]: 333.0501, 335.0471, found 333.0495, 335.0463;



¹H NMR (400 MHz, Chloroform-*d*): δ 8.80 (t, J = 2.0 Hz, 1H), 8.50 (ddd, J = 8.2, 2.3, 1.1 Hz, 1H), 8.31 (dt, J = 7.9, 1.4 Hz, 1H), 7.83 (s, 1H), 7.76 (t, J = 8.0 Hz, 1H), 4.36 (dq, J = 20.5, 7.2 Hz, 4H), 1.38 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 187.24, 164.11, 162.49, 148.59, 138.03, 137.27, 134.19, 133.73, 130.34, 128.33, 123.57, 62.80, 62.28, 14.03, 13.80; **ESI-HRMS** calcd for [C₁₅H₁₅NO₇+Na⁺]: 344.0741, found 344.0736;

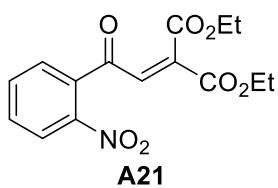


¹H NMR (400 MHz, Chloroform-*d*): δ 7.82 (dd, J = 7.8, 1.8 Hz, 1H), 7.71 (s, 1H), 7.60 (ddd, J = 8.3, 7.4, 1.8 Hz, 1H), 7.34 (td, J = 7.6, 1.1 Hz, 1H), 7.24 (dd, J = 8.3, 1.2 Hz, 1H), 6.60 (t, J_{F-H} = 72.9 Hz, 1H), 4.31 (dq, J = 17.1, 7.1 Hz, 4H), 1.34 (t, J = 7.1 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 188.99, 164.52, 162.89, 149.97 (t, J = 2.8 Hz), 138.07, 134.78, 134.75, 131.14, 129.76, 125.95, 120.04, 115.79 (t, J = 262.6 Hz), 62.35, 61.99, 13.97, 13.76; **¹⁹F{¹H} NMR** (377 MHz, Chloroform-*d*) δ -81.19; **ESI-HRMS** calcd for [C₁₆H₁₆F₂O₆+Na⁺]: 365.0808, found 365.0802;

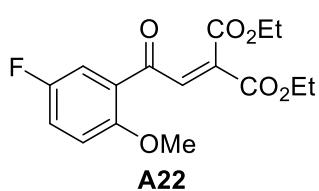


¹H NMR (400 MHz, Chloroform-*d*): δ 7.87 (td, J = 7.6, 1.9 Hz, 1H), 7.77 (d, J = 3.9 Hz, 1H), 7.65 – 7.55 (m, 1H), 7.32 – 7.24 (m, 1H), 7.22 – 7.14 (m, 1H), 4.34 (qd, J = 7.1, 1.8 Hz, 4H), 1.33 (dt, J = 15.1, 7.2 Hz, 6H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 186.86, 186.83, 164.64, 162.87, 162.07 (d, J_{F-C} = 256.4 Hz), 137.01 (d, J_{F-C} = 7.1 Hz), 136.09 (d, J_{F-C} = 1.8 Hz), 135.89 (d, J_{F-C} = 9.1 Hz), 131.09 (d, J_{F-C} = 1.8 Hz), 124.95 (d, J_{F-C} = 11.6 Hz), 124.83 (d, J_{F-C} = 3.4 Hz),

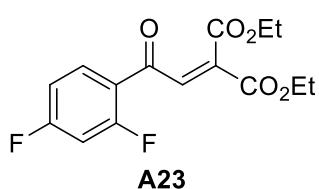
116.85 (d, $J_{F-C} = 22.9$ Hz), 62.43, 62.01, 14.01, 13.81; $^{19}\text{F}\{\text{H}\}$ NMR (377 MHz, Chloroform-*d*) δ -108.90; ESI-HRMS calcd for [C₁₅H₁₅FO₅+Na⁺]: 317.0796, found 317.0792;



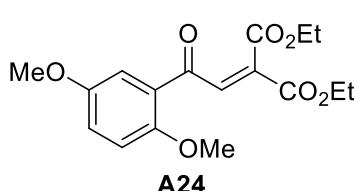
¹H NMR (400 MHz, Chloroform-*d*): δ 8.18 (dd, $J = 8.2, 1.2$ Hz, 1H), 7.82 – 7.76 (m, 1H), 7.74 – 7.68 (m, 1H), 7.56 – 7.51 (m, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 1.31 (td, $J = 7.2, 1.2$ Hz, 6H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 189.68, 164.19, 162.45, 146.18, 136.07, 135.31, 134.59, 134.48, 131.85, 129.16, 124.38, 62.67, 62.18, 13.95, 13.78; **ESI-HRMS** calcd for [C₁₅H₁₅NO₇+Na⁺]: 344.0741, found 344.0735;



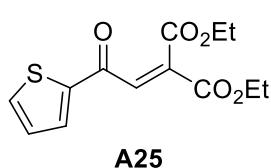
¹H NMR (400 MHz, Chloroform-*d*): δ 7.82 (s, 1H), 7.51 – 7.42 (m, 1H), 7.30 – 7.20 (m, 1H), 7.01 – 6.91 (m, 1H), 4.33 (q, $J = 7.1$ Hz, 4H), 3.91 (s, 3H), 1.33 (dt, $J = 13.9, 7.1$ Hz, 6H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 188.56 (d, $J_{F-C} = 1.8$ Hz), 164.92, 163.25, 156.88 (d, $J_{F-C} = 241.2$ Hz), 155.77 (d, $J_{F-C} = 2.0$ Hz), 138.66, 133.97, 127.30 (d, $J_{F-C} = 6.3$ Hz), 121.73 (d, $J_{F-C} = 23.6$ Hz), 116.97 (d, $J_{F-C} = 24.3$ Hz), 113.37 (d, $J_{F-C} = 7.5$ Hz) 62.21, 61.86, 56.44, 14.02, 13.82; **¹⁹F NMR{¹H}** (377 MHz, Chloroform-*d*) δ -122.56; **ESI-HRMS** calcd for [C₁₆H₁₇FO₆+Na⁺]: 347.0902, found 347.0895;



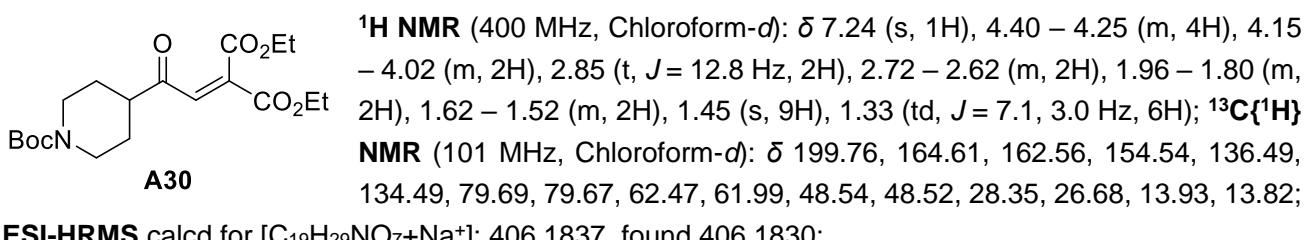
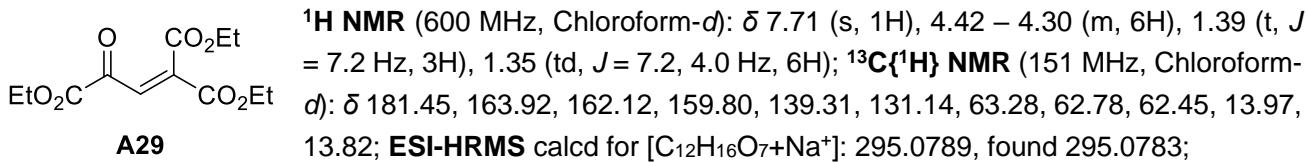
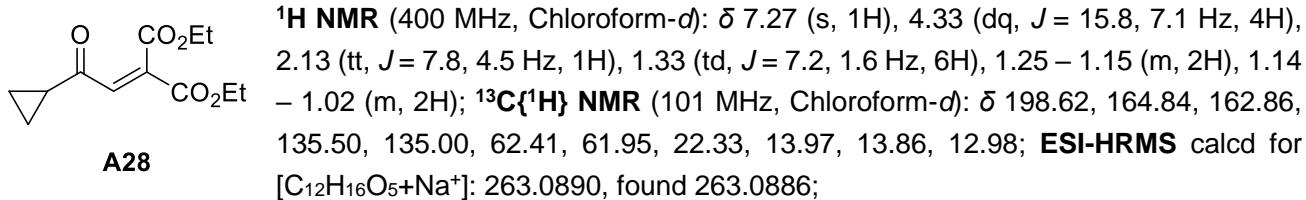
¹H NMR (400 MHz, Chloroform-*d*): δ 7.94 (td, $J = 8.6, 6.4$ Hz, 1H), 7.73 (d, $J = 4.0$ Hz, 1H), 7.07 – 6.97 (m, 1H), 6.93 (ddd, $J = 11.0, 8.6, 2.4$ Hz, 1H), 4.34 (qd, $J = 7.2, 3.1$ Hz, 1H), 1.33 (dt, $J = 14.1, 7.1$ Hz, 1H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 185.35 (d, $J_{F-C} = 3.1$ Hz), 167.89 (d, $J_{F-C} = 12.4$ Hz), 165.31 (d, $J_{F-C} = 12.3$ Hz), 164.54, 164.21 (d, $J_{F-C} = 12.7$ Hz), 162.76, 161.64 (d, $J_{F-C} = 12.8$ Hz), 136.71 (d, $J_{F-C} = 7.4$ Hz), 136.39 (d, $J_{F-C} = 1.9$ Hz), 133.17 (dd, $J_{F-C} = 10.8, 3.4$ Hz), 121.56 (dd, $J_{F-C} = 11.8, 3.5$ Hz), 112.76 (dd, $J_{F-C} = 21.7, 3.4$ Hz), 105.05 (dd, $J_{F-C} = 26.8, 25.5$ Hz), 62.48, 62.03, 13.98, 13.80; **¹⁹F NMR** (377 MHz, Chloroform-*d*) δ -98.99, -99.02, -103.98, -104.01; **ESI-HRMS** calcd for [C₁₅H₁₄F₂O₅+Na⁺]: 335.0702, found 335.0895;



¹H NMR (400 MHz, Chloroform-*d*): δ 7.87 (s, 1H), 7.30 (d, $J = 3.2$ Hz, 1H), 7.11 (dd, $J = 9.1, 3.2$ Hz, 1H), 6.94 (d, $J = 9.1$ Hz, 1H), 4.33 (qd, $J = 7.2, 2.8$ Hz, 4H), 3.88 (s, 3H), 3.79 (s, 3H), 1.33 (dt, $J = 11.9, 7.2$ Hz, 6H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 189.33, 165.15, 163.41, 154.22, 153.73, 139.34, 133.48, 126.69, 122.53, 113.64, 113.60, 62.11, 61.78, 56.40, 55.83, 14.03, 13.86; **ESI-HRMS** calcd for [C₁₇H₂₀O₇+Na⁺]: 359.1102, found 359.1094;

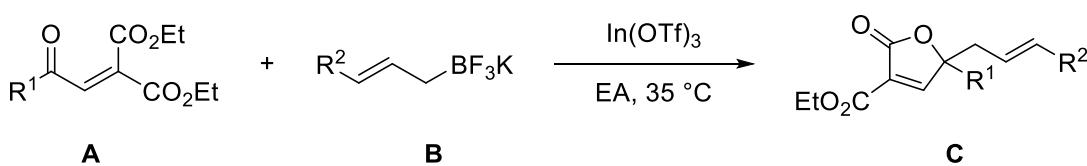


¹H NMR (400 MHz, Chloroform-*d*): δ 7.85 (dd, $J = 3.8, 1.2$ Hz, 1H), 7.79 (dd, $J = 4.9, 1.1$ Hz, 1H), 7.74 (s, 1H), 7.20 (dd, $J = 4.9, 3.9$ Hz, 1H), 4.36 (dq, $J = 10.4, 7.1$ Hz, 4H), 1.34 (dt, $J = 9.5, 7.1$ Hz, 6H); **¹³C{¹H} NMR** (101 MHz, Chloroform-*d*): δ 180.24, 164.72, 162.75, 143.91, 137.15, 136.34, 133.86, 132.94, 128.72, 62.56, 62.06, 14.00, 13.84; **ESI-HRMS** calcd for [C₁₃H₁₄O₅S+Na⁺]: 305.0455, found 305.0450;



(C) General procedures for the preparation of racemic products

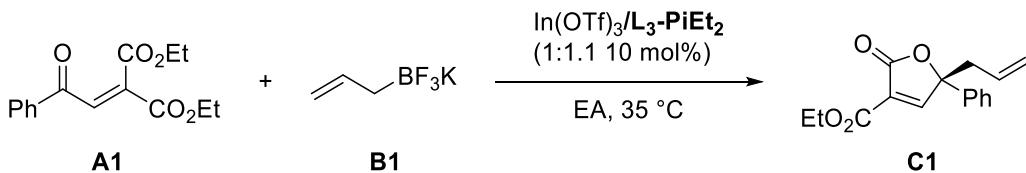
1. General procedure for the racemic allylboration/lactonization.



In(OTf)₃ (10 mol%, 5.6 mg), enone diesters **A** (0.10 mmol) and potassium allyltrifluoroborate **B** (0.20 mmol) were stirred in 1.0 mL of ethyl acetate (EA) at 35 °C in water bath till substrate **A** was fully consumed. The reaction mixture was directly subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate to afford the racemic product **C**.

(D) General procedures for the preparation of chiral products

1. Representative experimental procedure for the reaction of trifluoroacetophenone **A1** and allyl trifluoroborate **B1**



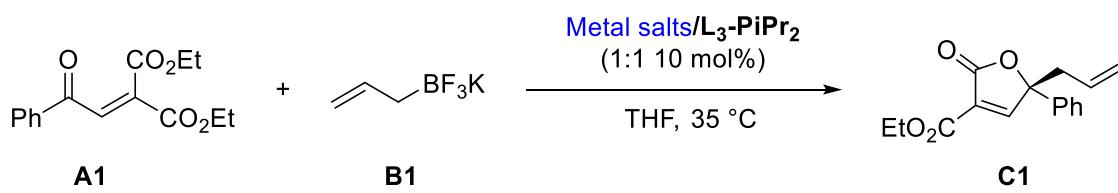
L₃-PiEt₂ (11 mol%, 6.5 mg), In(OTf)₃ (10 mol%, 5.6 mg) and enone diesters **A1** (0.10 mmol, 25 μL) were stirred in 1.0 mL of EA at 35 °C for 30 minutes under N₂ atmosphere. Then potassium allyltrifluoroborate **B1** (0.20 mmol, 30.0 mg) was added in the glovebox as one portion and the mixture was stirred at 35 °C

for another 10 minutes. The above steps and the reactions must be carried out under N₂ atmosphere. After the reaction was completed, the mixture was directly subjected to flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1, v/v) to afford the desired product **C1** as colorless oil.

(E) Optimization of reaction conditions

1. Optimization of the reaction conditions of allylation between enone diesters **A1** and potassium allyltrifluoroborate **B1**

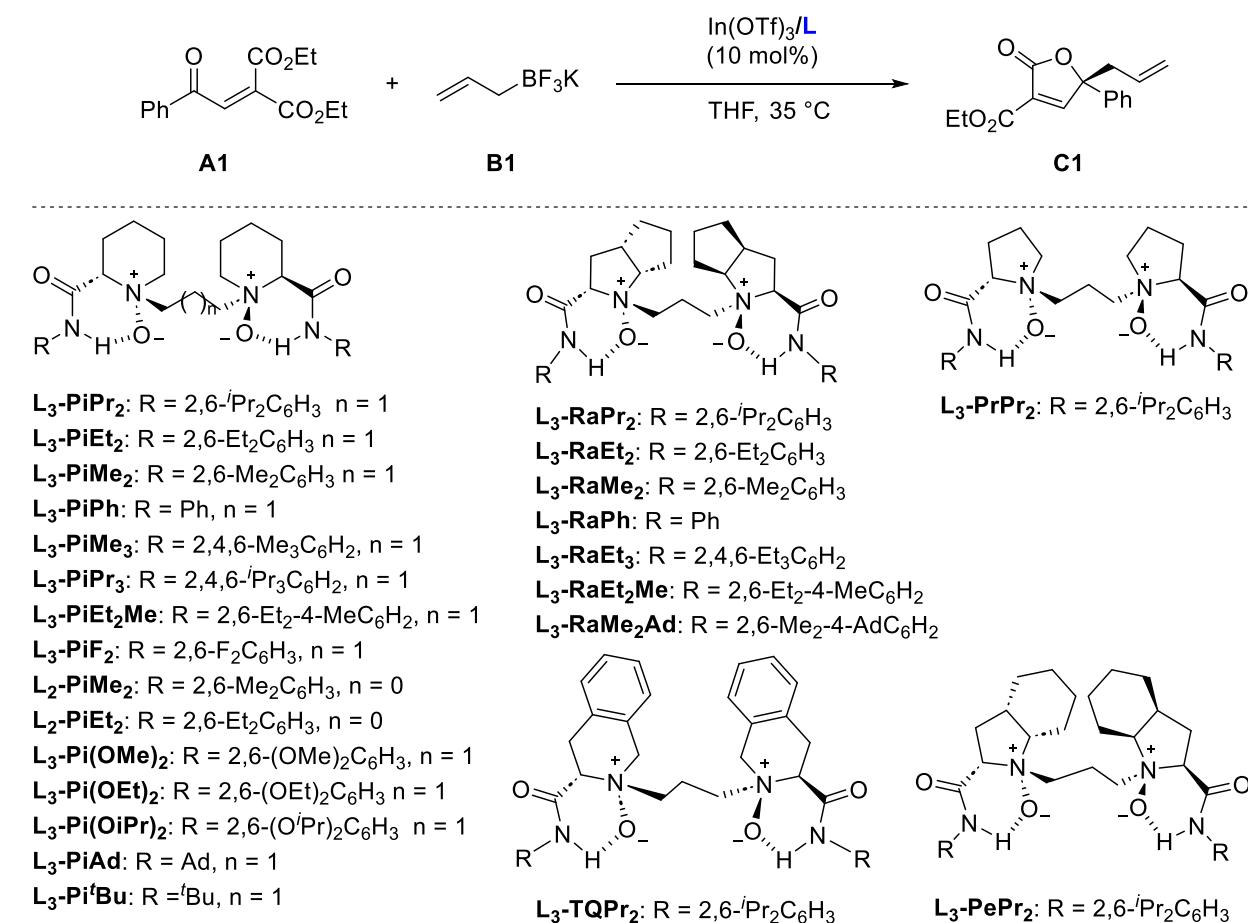
Table S1. Screening of the metal salts.



entry ^a	metal salts	reaction time	yield (%) ^b	ee (%) ^c
1	-	48 h	NR	-
2	Ni(OTf) ₂	48 h	NR	-
3	Cu(OTf) ₂	48 h	94	20
4	Co(OTf) ₂	48 h	NR	-
5	Mg(OTf) ₂	48 h	NR	-
6	Zn(OTf) ₂	48 h	78	13
7	Sc(OTf) ₃	48 h	NR	-
8	In(OTf) ₃	2 h	99	62
9	Ga(OTf) ₃	48 h	trace	-
10	Al(OTf) ₃	48 h	trace	-
11	Yb(OTf) ₃	48 h	NR	-

^aAll reactions were performed with **A1** (0.10 mmol), **B1** (0.20 mmol), metal salt (10 mol%), **L₃-PiPr₂** (10 mol%) and THF (1.0 mL) at 35 °C for indicated time. ^b Isolated yield. ^c Determined by HPLC analysis on Daicel chiralpak ID.

Table S2. Screening of the ligands.

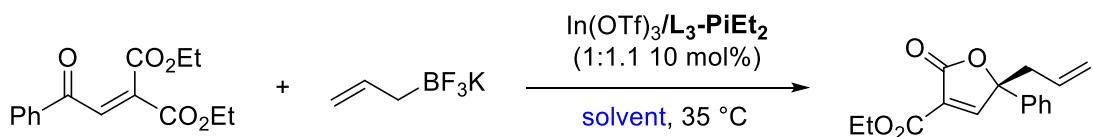


entry ^a	L	yield (%) ^b	ee (%) ^c
1	L₃-PiPr₂	99	62
2	L₃-RaPr₂	78	85
3	L₃-PrPr₂	76	25
4	L₃-PePr₂	96	34
5	L₃-TQPr₂	99	0
6	L₃-PiPh	99	40
7	L₃-PiMe₂	99	90
8	L₃-PiEt₂	99	93
9	L₃-PiPr₃	99	58
10 ^d	L₃-PiPh	99	56
11 ^d	L₃-PiMe₂	99	90
12 ^d	L₃-PiEt₂	99	93
13 ^d	L₃-PrEt₂	99	14
14 ^d	L₃-PeEt₂	99	9
15 ^d	L₃-TQEt₂	99	48
13 ^d	L₃-PiMe₃	99	76
14 ^d	L₃-PiEt₂Me	99	78

15 ^d	L₃-PiF₂	99	12
16 ^d	L₂-PiMe₂	99	18
17 ^d	L₂-PiEt₂	99	84
18 ^d	L₃-Pi(OMe)₂	99	19
19 ^d	L₃-Pi(OEt)₂	99	48
20 ^d	L₃-Pi(OiPr)₂	99	76
21 ^d	L₃-PiAd	99	76
22 ^d	L₃-Pi^tBu	99	72
23 ^d	L₃-RaPh	99	30
24 ^d	L₃-RaMe₂	99	69
25 ^d	L₃-RaEt₂	99	58
26 ^d	L₃-RaEt₂Me	99	70
27 ^d	L₃-RaEt₃	74	45
28 ^d	L₃-RaMe₂Ad	88	58

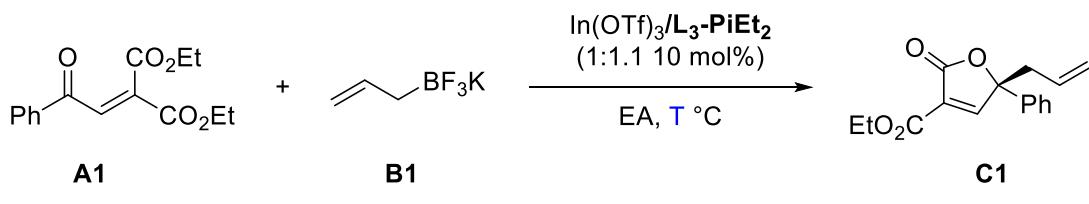
^a All reactions were performed with **A1** (0.10 mmol), **B1** (0.20 mmol), metal salt (10 mol%), **L₃-PiPr₂** (10 mol%) and THF (1.0 mL) at 35 °C and work up after the **A1** was fully consumed (monitored by TLC). ^b Isolated yield. ^c Determined by HPLC analysis on Daicel chiralpak ID. ^d Metal salt/Ligand = 1: 1.1 (10 mol%).

Table S3. Screening of the solvents.



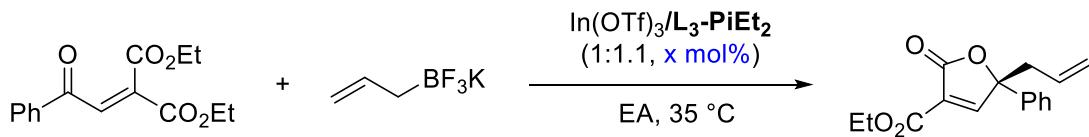
entry ^a	solvent	reaction time	yield (%) ^b	ee (%) ^c
1	DCM	4 h	99	95
2	THF	2 h	99	93
3	toluene	8 h	99	95
4	Et ₂ O	8 h	99	95
5	EA	10 min	99	95
6	MeCN	mess	-	-
7	1,4-dioxane	10 min	99	94
8	MTBE	8 h	99	94
9	2-Me-THF	2 h	99	94
10	DME	10 min	99	95
11	DMF	24 h	99	42

^a All reactions were performed with **A1** (0.10 mmol), **B1** (0.20 mmol), metal salt (10 mol%), **L₃-PiEt₂** (11 mol%) and solvent (1.0 mL) at 35 °C and work up after the **A1** was fully consumed (monitored by TLC). ^b Isolated yield. ^c Determined by HPLC analysis on Daicel chiralpak ID.

Table S4. Screening of the reaction temperature.

entry ^a	T (°C)	t	yield (%) ^b	ee (%) ^c
1	35	10 min	99	95
2	20	2 h	99	95
3	10	2 h	99	94
4	0	3 h	99	94
5	-10	5 h	99	95

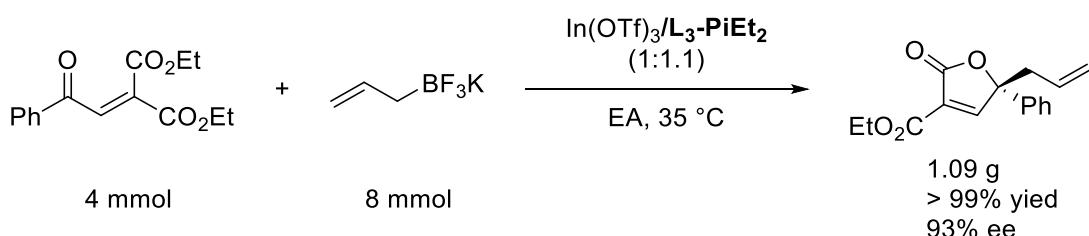
^a All reactions were performed with **A1** (0.10 mmol), **B1** (0.20 mmol), metal salt (10 mol%), **L₃-PiEt₂** (11 mol%) and solvent (1.0 mL) at T °C and work up after the **A1** was fully consumed (monitored by TLC). ^b Isolated yield. ^c Determined by HPLC analysis on Daicel chiralpak ID.

Table S5. Screening of the catalyst loading.

entry ^a	x	t	Yield (%) ^b	ee (%) ^c
1	10	10 min	99	95
2	8	2 h	99	95
3	5	12 h	72	94
4	2	12 h	Trace	-
5	1	12 h	Trace	-

^a All reactions were performed with **A1** (0.10 mmol), **B1** (0.20 mmol), metal salt (10 mol%), **L₃-PiEt₂** (11 mol%) and solvent (1.0 mL) at 35 °C and work up after the **A1** was fully consumed (monitored by TLC). ^b Isolated yield. ^c Determined by HPLC analysis on Daicel chiralpak ID.

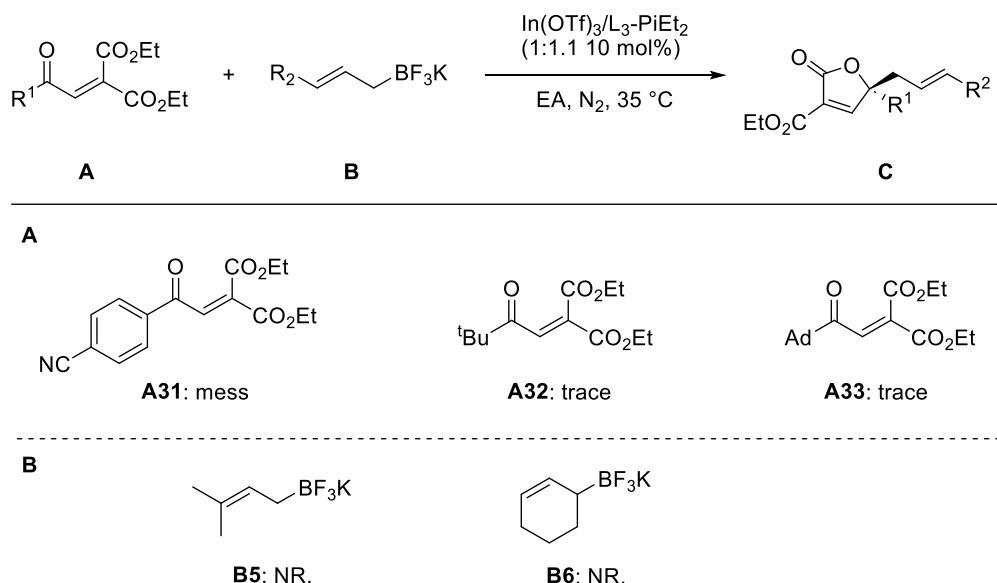
(F) Gram-scale synthesis of compound C1.



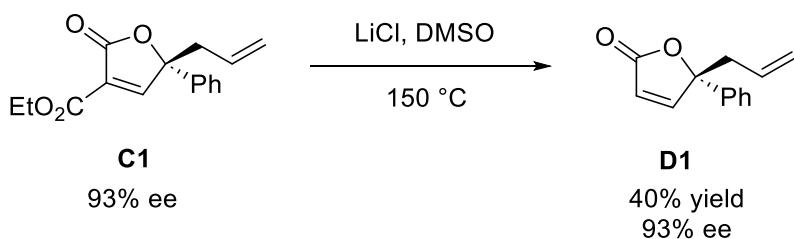
L₃-PiEt₂ (11 mol%, 260 mg), **In(OTf)₃** (10 mol%, 224 mg) and enone diesters **A1** (4 mmol, 1.104 g) were stirred in 40 mL of EA at 35 °C in water bath for 30 minutes under N₂ atmosphere. Then potassium

allyltrifluoroborate **B1** (8 mmol, 1.184 g) was added in the glovebox as one portion and the mixture was stirred at 35 °C for another 30 minutes. The above steps and the reactions must be carried out under N₂ atmosphere. After the reaction was completed, the solvent was removed under vacuum and the mixture was purified by flash column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1, v/v) to afford the desired product **C1** as colorless oil.

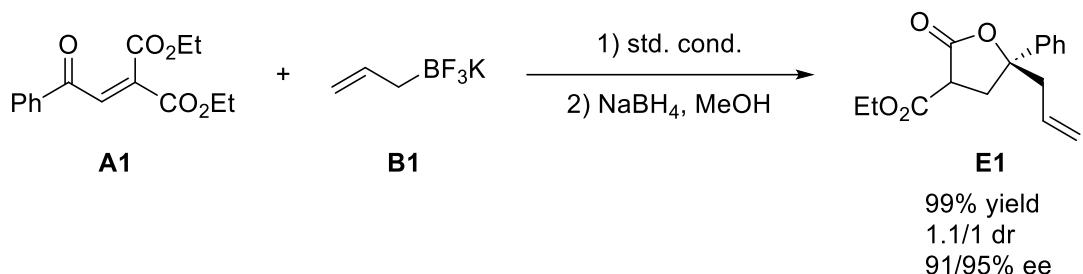
(G) Scope Limitation



(H) Transformation of compound **C1**



The products **C1** (0.2 mmol) and LiCl (2 mmol, 10 equiv) were added sequentially to the pre-dried reaction tube, then 2.0 mL of dimethyl sulfoxide (DMSO) was added, and the reaction was stirred in at 150 °C in an oil bath for 2 h. When the **C1** is fully consumed, the mixture was cooled to room temperature, and then extracted by ethyl acetate (3 * 3 ML). the organic phase was combined and dried over Na₂SO₄, the product **D1** was obtained by column chromatography (petroleum ether/ethyl acetate = 9/1~4/1, v/v).



The catalytic reaction (0.1 mmol scale) was carried out under standard reaction conditions, and after the reaction was completed, 0.2 mL of methanol was added to the reaction system, and the reaction was cooled in an ice water bath at 0 °C, and NaBH_4 (1.5 equiv) was added to the reaction system. After the reaction was completed (about 30 minutes), the reduction product **E1** was obtained directly by column chromatography separation (elute: petroleum ether/ethyl acetate = 6/1, v/v).

(I). Biological activity study

Anti-HCCLM3 cell proliferative activity assay

HCCLM3 cells were cultured to higher than 80% fusion rate in 10 mm dishes, trypsin-digested cells were diluted to the appropriate concentration and inoculated in 96-well plates. After 12-16 h of incubation in 37°C, 5% CO_2 incubator, the medium was aspirated, washed twice with phosphate buffered saline (PBS), and new medium was added, followed by the addition of the compound (20 μM) and dimethyl sulfoxide (DMSO) as a control. The medium was aspirated after 24 h, and a blank medium containing 10% (v/v) Cell Counting Kit-8 reagent (Selleck) was added for 1 h of incubation. Absorbance was then measured at 450 nm using a Varioskan Flash Multimode Reader (Thermo Fisher Scientific) and cell viability was calculated by GraphPad Prism 8.0, the data is represented as mean \pm standard deviation (SD).

Table S6. Structures and activities of synthetic compounds

compound	HCCLM3 cell viability (% of control)	compound	HCCLM3 cell viability (% of control)
sorafeinb	20.70476	C18	120.5925
C1	140.8507	C19	116.0756
C2	137.5647	C20	104.8728
C3	65.44189	C21	133.3856
C4	63.67407	C22	135.5473
C5	95.99829	C23	140.0133
C6	123.491	C24	122.4767
C7	132.8001	C25	110.2258
C8	132.3812	C26	115.407
C9	123.0938	C27	116.0941
C10	107.3269	C28	125.4862
C11	116.404	C29	128.5559
C12	119.8826	C30	119.5556

C13	114.2488	C31	124.0899
C14	140.6541	C32	132.3831
C15	133.9822	C33	107.7849
C16	143.9308	D1	105.4745
C17	118.8482	E1	117.5245

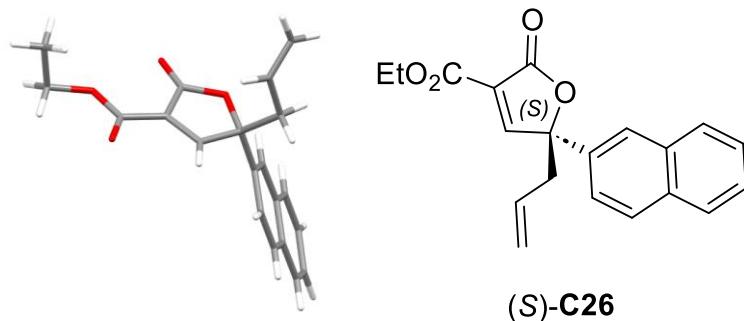
Table S7 IC₅₀ of C3 and C4

entry	IC ₅₀ (μM)	
	HCCLM3	MHCC97L
C3	9.19	93.51
C4	14.99	121

(J). X-ray crystallography data

The absolute configuration of product **C26** and the newly generated chiral center was determined to be (S) by X-ray chromatography analysis. Single crystal of **C26** [C₂₀H₁₈O₄] was obtained by recrystallization in DCM at room temperature with slow vaporization. CCDC 2331720 (**C26**) contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Center.

For CCDC 2331720 (**C26**), The colourless crystal in rod-shape, with approximate dimensions of 0.228 × 0.441 × 0.530 mm³, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source ($K\alpha = 1.54178 \text{ \AA}$). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package^{4a, 4b, 4c, 4d}. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested^{4e}.



Crystallographic Data for **C26**.

Formula	C ₂₀ H ₁₈ O ₄
Formula mass (amu)	322.36
Space group	P2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	6.3415(1)
<i>b</i> (Å)	8.4205(2)
<i>c</i> (Å)	30.8465(7)
α (deg)	90
β (deg)	90
γ (deg)	90
<i>V</i> (Å ³)	1647.16(6)
<i>Z</i>	4
λ (Å)	1.54178
<i>T</i> (K)	173(2)

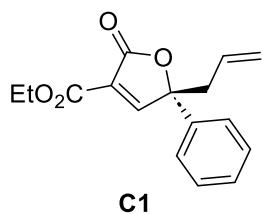
ρ_{calcd} (g cm ⁻³)	1.300
$s\mu$ (mm ⁻¹)	0.735
Transmission factors	0.730-0.910
θ_{max} (deg)	68.267
No. of unique data, including $F_o^2 < 0$	3013
No. of unique data, with $F_o^2 > 2\sigma(F_o^2)$	2993
No. of variables	219
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ ^a	0.0257
$R_w(F_o^2)$ ^b	0.0664
Goodness of fit	1.095

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

^b $R_w(F_o^2) = [\sum [w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$; $w^{-1} = [\sigma^2(F_o^2) + (Ap)^2 + Bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2] / 3$.

(K) Characterization of the products

Ethyl (S)-5-allyl-2-oxo-5-phenyl-2,5-dihydrofuran-3-carboxylate (C1)



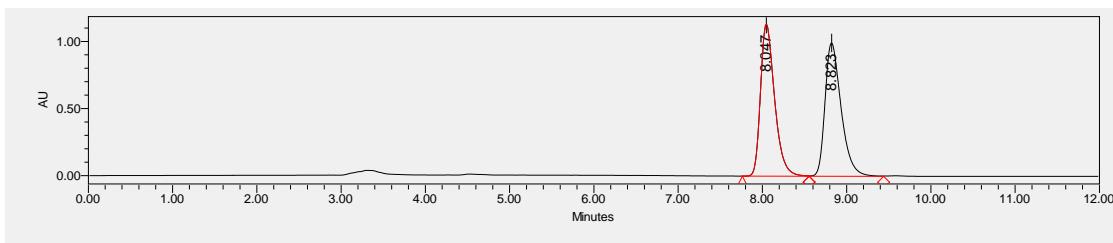
Results: colorless oil, 99% yield, 95 % ee; $[\alpha]^{22}\text{D} = -92.9$ ($c = 0.95 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 8.16 \text{ min}$, $t_{\text{R(major)}} = 8.93 \text{ min}$;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.33 (s, 1H), 7.45 – 7.30 (m, 5H), 5.61 (m, 1H), 5.20 – 5.10 (m, 2H), 4.33 (q, $J = 7.1 \text{ Hz}$, 2H), 2.92 (ddt, $J = 14.4, 7.2, 1.1 \text{ Hz}$, 1H), 2.84 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 1.35 (t, $J = 7.1 \text{ Hz}$, 3H);

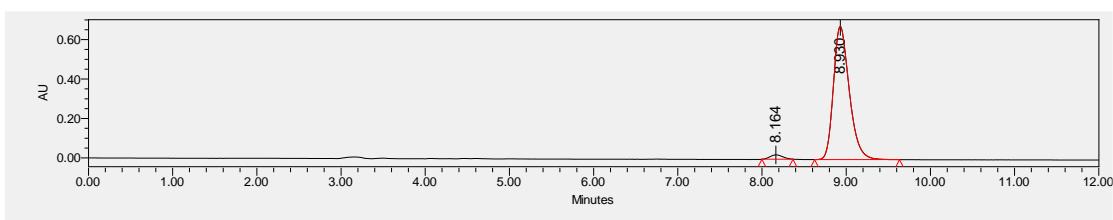
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.59, 164.94, 160.06, 137.23, 129.63, 129.06, 128.74, 125.16, 124.68, 121.23, 87.88, 61.85, 43.86, 14.14;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2983, 2981, 1774, 1721, 1641, 1448, 1370, 1335, 1258, 1066, 1030, 799, 764, 700;

ESI-HRMS calcd for $[\text{C}_{16}\text{H}_{16}\text{O}_4+\text{Na}^+]$: 295.0941, found 295.0938;

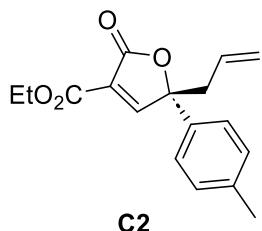


	Retention Time	Area	% Area	Height
1	8.047	13135899	49.94	1131785
2	8.823	13169363	50.06	993255



	Retention Time	Area	% Area	Height
1	8.164	228198	2.52	21984
2	8.930	8829116	97.48	675128

Ethyl (S)-5-allyl-2-oxo-5-(*p*-tolyl)-2,5-dihydrofuran-3-carboxylate (C2)



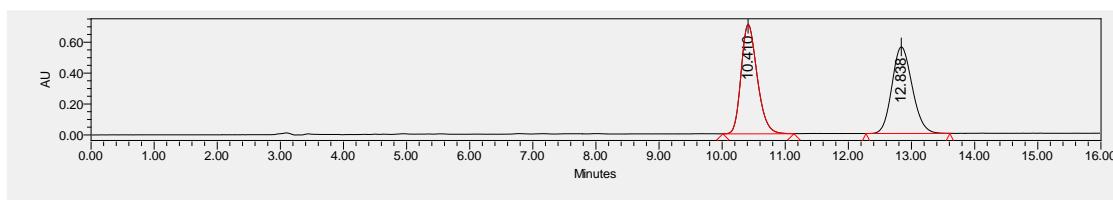
Results: colorless oil, 99% yield, 93 % ee; $[\alpha]^{23}_{\text{D}} = -98.5$ ($c = 0.62 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 10.43 \text{ min}$, $t_{\text{R(major)}} = 12.67 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.30 (s, 1H), 7.41 – 7.01 (m, 4H), 5.68 – 5.52 (m, 1H), 5.18 – 5.10 (m, 2H), 4.33 (q, $J = 7.1 \text{ Hz}$, 2H), 2.90 (ddt, $J = 14.4, 7.3, 1.1 \text{ Hz}$, 1H), 2.82 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 2.35 (s, 3H), 1.35 (t, $J = 7.1 \text{ Hz}$, 3H);

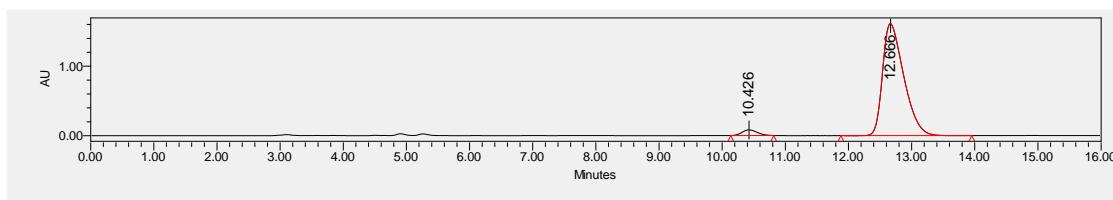
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 166.70, 165.14, 160.12, 138.71, 134.19, 129.77, 129.70, 125.10, 124.50, 121.10, 87.89, 61.81, 43.76, 21.09, 14.14;

IR (film): $\tilde{\nu}$ (cm^{-1}) 2985, 2923, 1780, 1722, 1642, 1264, 1075, 1032, 800, 735, 702;

ESI-HRMS calcd for [C₁₇H₁₈O₄+Na⁺]: 309.1098, found 295. 309.1093;

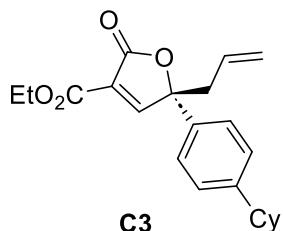


	Retention Time	Area	% Area	Height
1	13.083	22573274	50.13	935385
2	14.877	22454788	49.87	814348



	Retention Time	Area	% Area	Height
1	10.426	1368298	3.52	81847
2	12.666	37498867	96.48	1611753

Ethyl (S)-5-allyl-5-(4-cyclohexylphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C3)



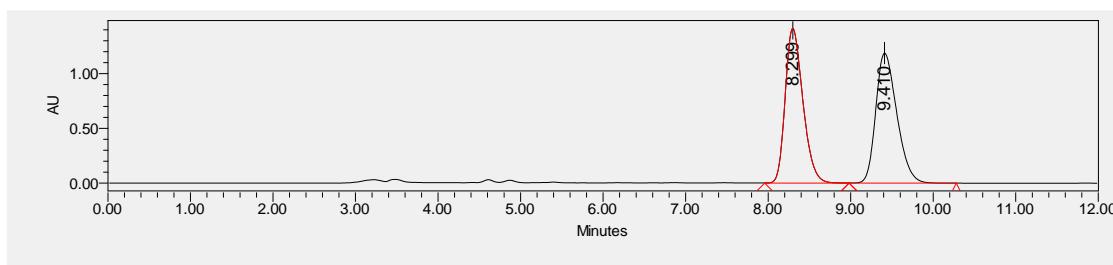
Results: colorless oil, 98% yield, 92 % ee; $[\alpha]^{22}_D = 92.2$ ($c = 1.10$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{minor})} = 8.41$ min, $t_{R(\text{major})} = 9.53$ min;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.30 (s, 1H), 7.36 – 7.18 (m, 4H), 5.67 – 5.53 (m, 1H), 5.17 (s, 1H), 5.15 – 5.12 (m, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.92 (ddt, $J = 14.3, 7.2, 1.1$ Hz, 1H), 2.83 (ddt, $J = 14.4, 7.2, 1.1$ Hz, 1H), 2.50 (m, 1H), 1.89 – 1.65 (m, 6H), 1.46 – 1.38 (m, 4H), 1.35 (t, $J = 7.1$ Hz, 3H);

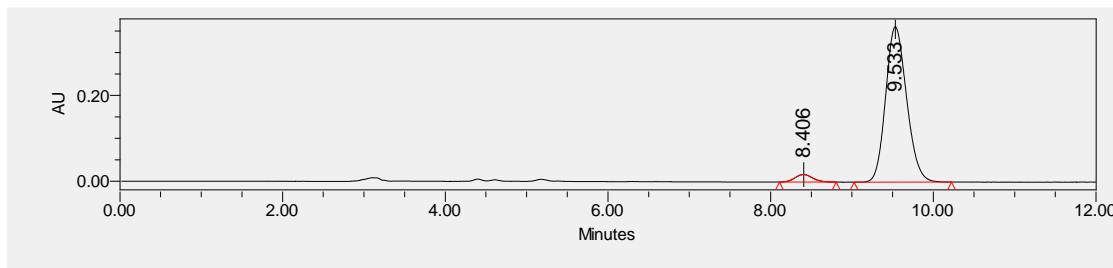
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.75, 165.20, 160.13, 148.82, 134.49, 129.78, 127.48, 125.13, 124.49, 121.10, 87.91, 61.80, 44.19, 43.71, 34.32, 34.31, 26.79, 26.06, 14.14;

IR (film): $\tilde{\nu}$ (cm⁻¹) 2924, 2850, 1782, 1723, 1448, 1370, 1314, 1074, 1032, 828, 799;

ESI-HRMS calcd for [C₂₂H₂₆O₄+Na⁺]: 377.1724, found 377.1717;

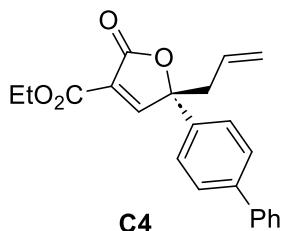


	Retention Time	Area	% Area	Height
1	8.299	21036944	49.98	1413372
2	9.410	21055800	50.02	1187552



	Retention Time	Area	% Area	Height
1	8.406	264158	3.91	17588
2	9.533	6483818	96.09	362040

Ethyl (S)-5-([1,1'-biphenyl]-4-yl)-5-allyl-2-oxo-2,5-dihydrofuran-3-carboxylate (C4)



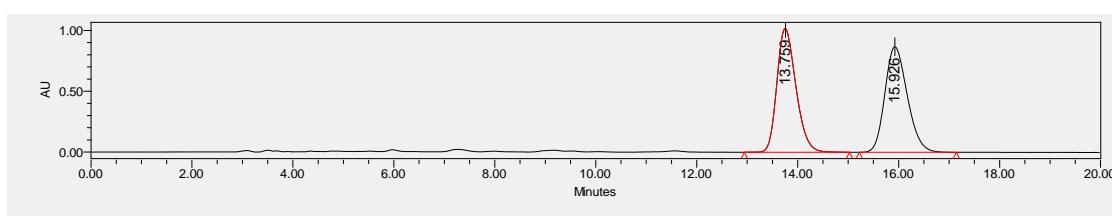
Results: white solid, 99% yield, 94 % ee; $[\alpha]^{23}\text{D} = -129.9$ ($c = 0.668 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R}}(\text{minor}) = 13.82 \text{ min}$, $t_{\text{R}}(\text{major}) = 15.88 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.35 (s, 1H), 7.67 – 7.52 (m, 4H), 7.52 – 7.41 (m, 4H), 7.38 – 7.33 (m, 1H), 5.71- 5.57 (m, 1H), 5.20 (s, 1H), 5.19 – 5.14 (m, 1H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.96 (ddt, $J = 14.3, 7.3, 1.1 \text{ Hz}$, 1H), 2.87 (ddt, $J = 14.4, 7.1, 1.1 \text{ Hz}$, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

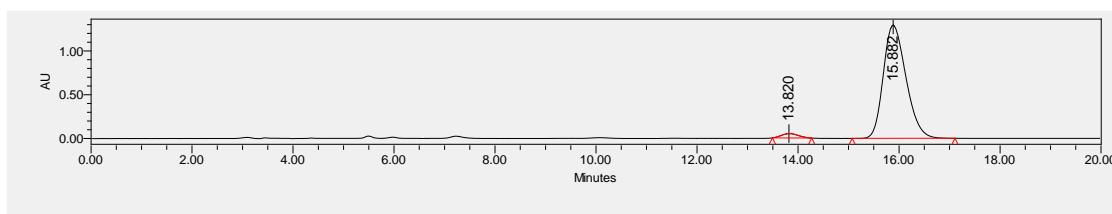
¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 166.61, 164.87, 160.07, 141.72, 140.03, 136.09, 129.62, 128.93, 127.80, 127.74, 127.12, 125.66, 124.72, 121.33, 87.81, 61.88, 43.79, 29.72, 14.16;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3081, 2982, 2919, 1776, 1721, 1486, 1374, 1370, 1337, 1255, 1075, 1031, 840, 799, 767, 732, 697;

ESI-HRMS calcd for [C₂₂H₂₀O₄+Na⁺]: 371.1254, found 371.1248;

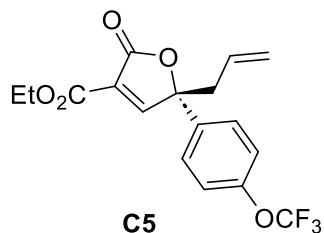


	Retention Time	Area	% Area	Height
1	13.759	26631164	49.87	1016790
2	15.926	26768694	50.13	867633



	Retention Time	Area	% Area	Height
1	13.820	1159021	2.79	50241
2	15.882	40311861	97.21	1295772

Ethyl (S)-5-allyl-2-oxo-5-(4-(trifluoromethoxy)phenyl)-2,5-dihydrofuran-3-carboxylate (C5)



Results: colorless oil, 99% yield, 96 % ee; $[\alpha]^{23}\text{D} = -73.8$ ($c = 1.31 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak ODH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{R(\text{major})} = 7.26 \text{ min}$, $t_{R(\text{minor})} = 8.62 \text{ min}$;

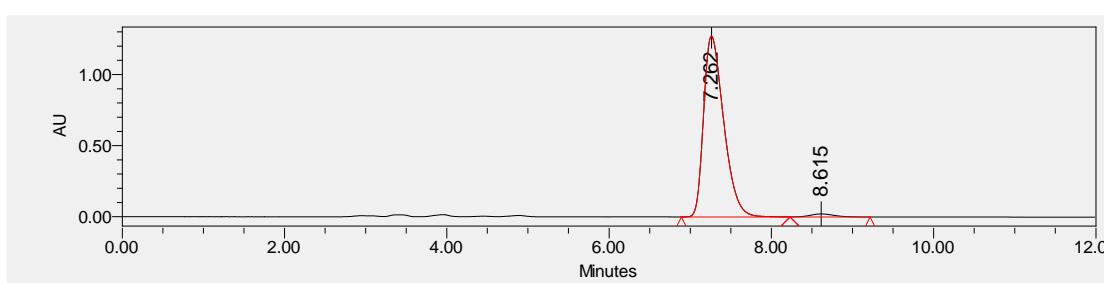
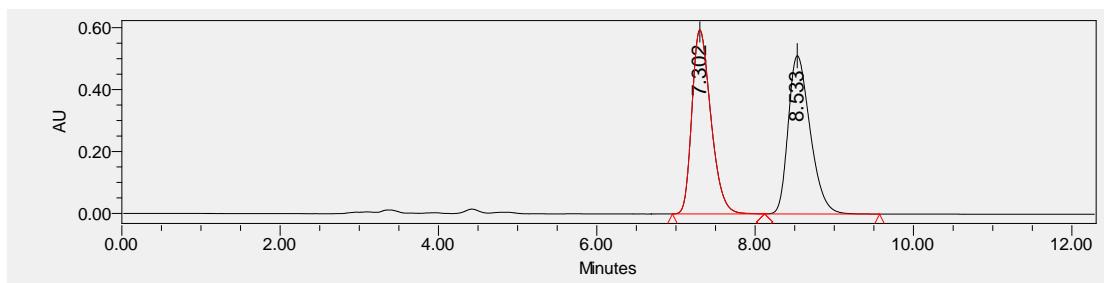
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.31 (s, 1H), 7.50 – 7.40 (m, 2H), 7.30 – 7.22 (m, 2H), 5.67 – 5.53 (m, 1H), 5.24 – 5.11 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.91 (ddt, $J = 14.3, 7.3, 1.1 \text{ Hz}$, 1H), 2.83 (ddt, $J = 14.3, 7.1, 1.2 \text{ Hz}$, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.22, 164.19, 159.87, 149.29 (d, $J_{F-C} = 2.0 \text{ Hz}$), 135.92, 129.21, 126.87, 125.03, 121.64, 121.43, 119.07, 87.28, 61.97, 43.89, 14.10;

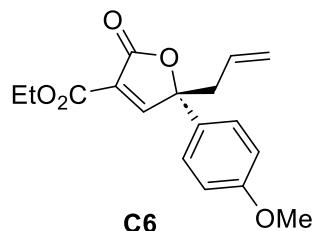
$^{19}\text{F}\{^1\text{H}\} \text{NMR}$ (377 MHz, Chloroform-*d*) δ -57.90.

IR (film): $\tilde{\nu}$ (cm^{-1}) 3085, 2985, 2917, 1778, 1723, 1510, 1255, 1212, 1165, 1032, 800, 691;

ESI-HRMS calcd for $[\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_5+\text{Na}^+]$: 379.0764, found 379.0758;



Ethyl (S)-5-allyl-5-(4-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C6)



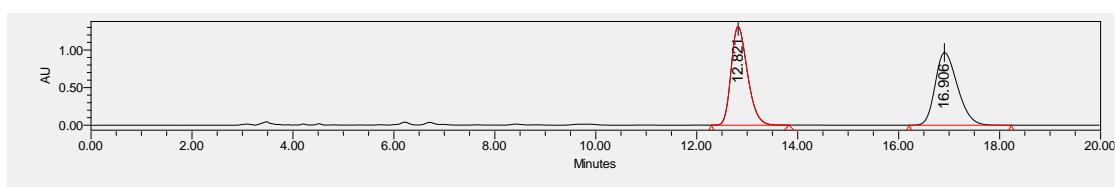
Results: colorless oil, 99% yield, 94 % ee; $[\alpha]^{23}_{\text{D}} = -104.8$ ($c = 0.546$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R(minor)}} = 12.94$ min, $t_{\text{R(major)}} = 17.00$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 (s, 1H), 7.38 – 7.20 (m, 2H), 6.98 – 6.79 (m, 2H), 5.67 – 5.53 (m, 1H), 5.19 – 5.09 (m, 2H), 4.33 (q, $J = 7.1$ Hz, 2H), 3.81 (s, 3H), 2.89 (ddt, $J = 14.3, 7.2, 1.1$ Hz, 1H), 2.82 (ddt, $J = 14.3, 7.0, 1.2$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H);

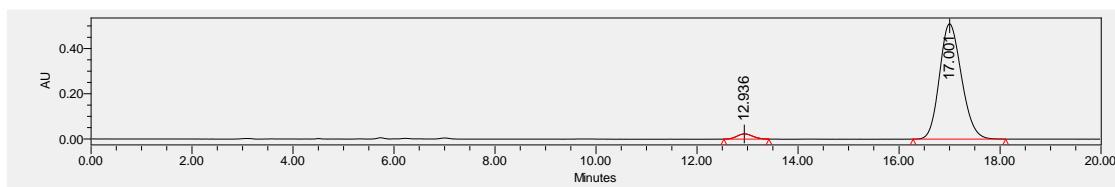
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 166.71, 165.12, 160.14, 159.78, 129.81, 129.03, 126.56, 124.45, 121.08, 114.36, 87.71, 61.81, 55.37, 43.74, 14.14;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3082, 2983, 2935, 1778, 1722, 1514, 1255, 1072, 1032, 800, 750;

ESI-HRMS calcd for [C₁₇H₁₈O₅+Na⁺]: 325.1047, found 325.1041;

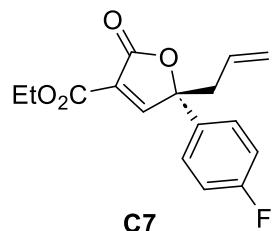


	Retention Time	Area	% Area	Height
1	12.821	29438208	49.86	1310921
2	16.906	29600763	50.14	965599



	Retention Time	Area	% Area	Height
1	12.936	496691	3.12	23024
2	17.001	15435871	96.88	510384

Ethyl (S)-5-allyl-5-(4-fluorophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C7)



Results: colorless oil, 91% yield, 96 % ee; $[\alpha]^{23}\text{D} = -80.8$ ($c = 0.500 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 7.72 \text{ min}$, $t_{\text{R(major)}} = 8.57 \text{ min}$;

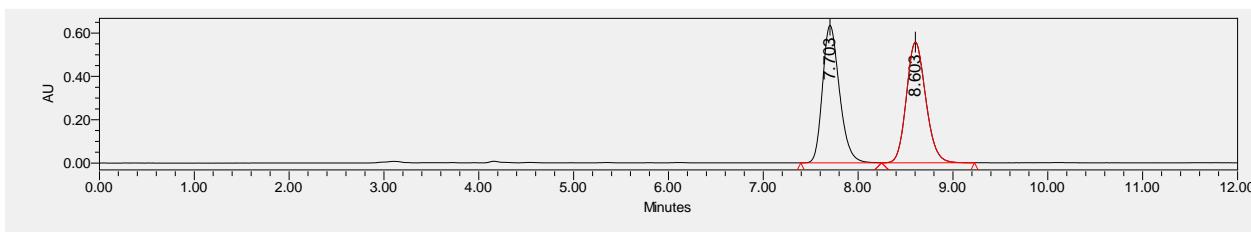
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.30 (s, 1H), 7.43 – 7.32 (m, 2H), 7.16 – 7.04 (m, 2H), 5.66 – 5.52 (m, 1H), 5.21 – 5.07 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.89 (ddt, $J = 14.3, 7.4, 1.1 \text{ Hz}$, 1H), 2.81 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.35, 164.51, 162.67 (d, $J_{\text{F-C}} = 248.7 \text{ Hz}$) 159.97, 133.07 (d, $J_{\text{F-C}} = 3.3 \text{ Hz}$), 129.42, 127.14 (d, $J_{\text{F-C}} = 8.3 \text{ Hz}$), 124.87, 121.45, 116.05 (d, $J_{\text{F-C}} = 21.8 \text{ Hz}$), 87.41, 61.93, 43.96, 14.12;

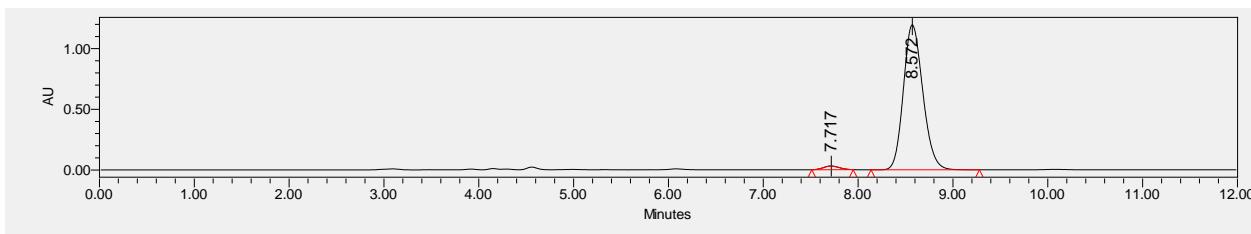
$^{19}\text{F}\{^1\text{H}\} \text{NMR}$ (377 MHz, Chloroform-*d*): δ -112.58;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2985, 2929, 1781, 1723, 1511, 1275, 1260, 1075, 1032, 837, 800, 750;

ESI-HRMS calcd for $[\text{C}_{16}\text{H}_{15}\text{FO}_4+\text{Na}^+]$: 313.0847, found 313.0843;

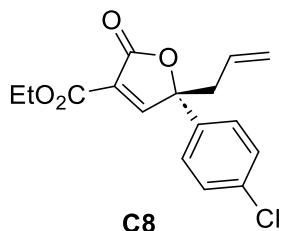


	Retention Time	Area	% Area	Height
1	7.703	7888260	50.05	635069
2	8.603	7871887	49.95	556858



	Retention Time	Area	% Area	Height
1	7.717	351238	2.02	30088
2	8.572	17013165	97.98	1195886

Ethyl (S)-5-allyl-5-(4-chlorophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C8)



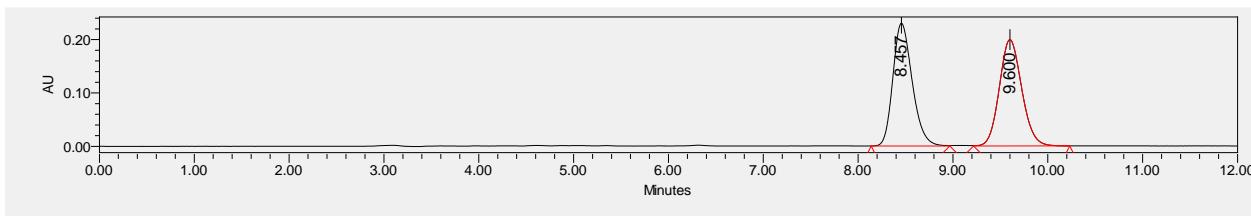
Results: colorless oil, 99% yield, 95 % ee; $[\alpha]^{19}_{\text{D}} = -105.5$ ($c = 0.584$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R(minor)}} = 8.51$ min, $t_{\text{R(major)}} = 9.61$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 (s, 1H), 7.44 – 7.29 (m, 4H), 5.66 – 5.52 (m, 1H), 5.21 – 5.09 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 2.89 (ddt, $J = 14.3, 7.3, 1.1$ Hz, 1H), 2.80 (ddt, $J = 14.3, 7.0, 1.1$ Hz, 1H), 1.36 (t, $J = 7.2$ Hz, 3H);

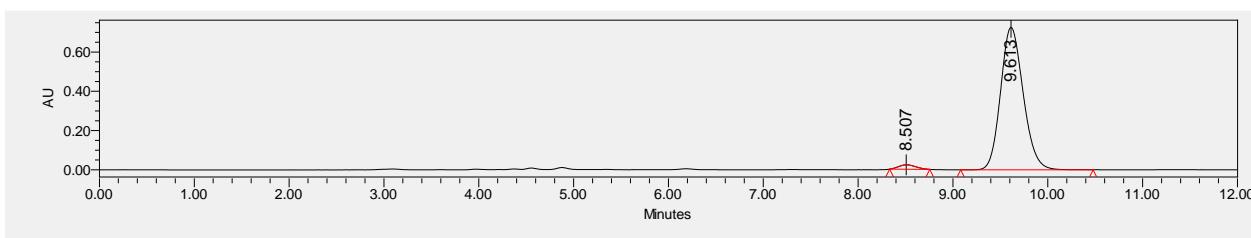
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 166.27, 164.28, 159.91, 135.73, 134.80, 129.29, 129.25, 126.64, 124.93, 121.55, 87.37, 61.95, 43.83, 14.12;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3084, 2983, 2927, 1777, 1722, 1493, 1371, 1314, 1275, 1260, 1093, 1070, 1031, 828, 799, 750;

ESI-HRMS calcd for [C₁₆H₁₅³⁵ClO₄+Na⁺]: 329.0552, found 329.0547; calcd for [C₁₆H₁₅³⁷ClO₄+Na⁺]: 331.0522, found 331.0514;

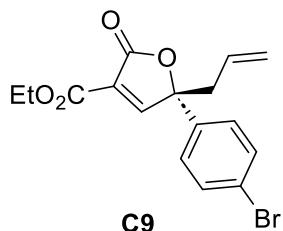


	Retention Time	Area	% Area	Height
1	8.457	3254406	49.98	229875
2	9.600	3257628	50.02	198968



	Retention Time	Area	% Area	Height
1	8.507	285714	2.33	22688
2	9.613	11997296	97.67	725595

Ethyl (S)-5-allyl-5-(4-bromophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C9)



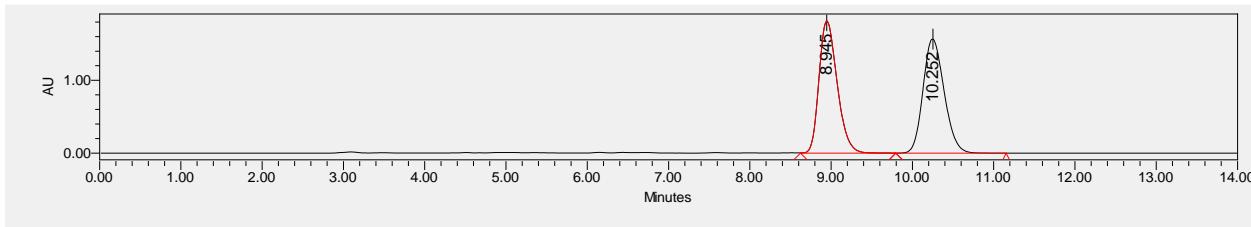
Results: colorless oil, 99% yield, 96 % ee; $[\alpha]^{23}\text{D} = -96.0$ ($c = 0.650 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 9.02 \text{ min}$, $t_{\text{R(major)}} = 10.25 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.28 (s, 1H), 7.59 – 7.50 (m, 2H), 7.33 – 7.23 (m, 2H), 5.65 – 5.51 (m, 1H), 5.21 – 5.09 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.88 (ddt, $J = 14.3, 7.4, 1.1 \text{ Hz}$, 1H), 2.80 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 1.35 (t, $J = 7.1 \text{ Hz}$, 3H);

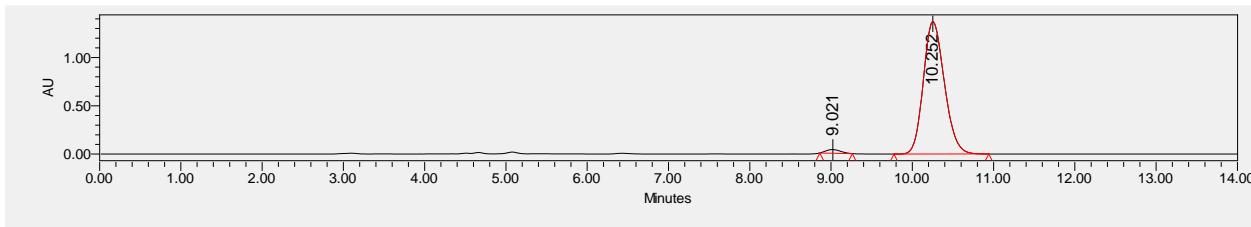
¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 166.25, 164.20, 159.89, 136.27, 132.21, 129.26, 126.92, 124.95, 122.94, 121.58, 87.39, 61.96, 43.78, 14.13;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3085, 2983, 2928, 1778, 1722, 1488, 1396, 1370, 1314, 1275, 1259, 1074, 1030, 1010, 824, 799, 749;

ESI-HRMS calcd for [C₁₆H₁₅⁷⁹BrO₄+Na⁺]: 373.0046, found 373.0041; calcd for [C₁₆H₁₅³⁷ClO₄+Na⁺]: 375.0026, found 375.0020;

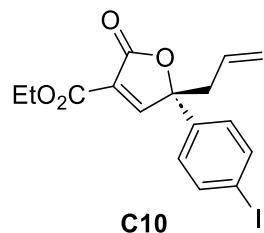


	Retention Time	Area	% Area	Height
1	8.945	28106627	49.85	1818342
2	10.252	28273166	50.15	1565329



	Retention Time	Area	% Area	Height
1	9.021	465659	1.85	37456
2	10.252	24642580	98.15	1371240

Ethyl (S)-5-allyl-5-(4-iodophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C10)



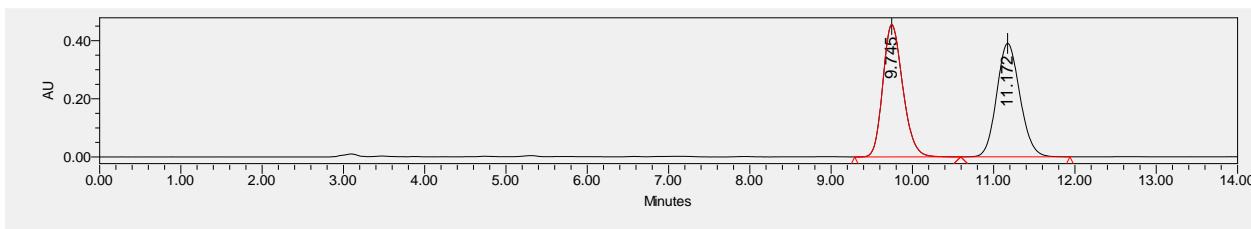
Results: colorless oil, 99% yield, 96 % ee; $[\alpha]^{23}\text{D} = -98.9$ ($c = 0.750 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 9.79 \text{ min}$, $t_{\text{R(major)}} = 11.14 \text{ min}$;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.27 (s, 1H), 7.79 – 7.68 (m, 2H), 7.20 – 7.10 (m, 2H), 5.65 – 5.51 (m, 1H), 5.21 – 5.08 (m, 2H), 4.33 (q, $J = 7.1 \text{ Hz}$, 2H), 2.88 (ddt, $J = 14.3, 7.3, 1.1 \text{ Hz}$, 1H), 2.79 (ddt, $J = 14.4, 7.0, 1.1 \text{ Hz}$, 1H), 1.35 (t, $J = 7.1 \text{ Hz}$, 3H);

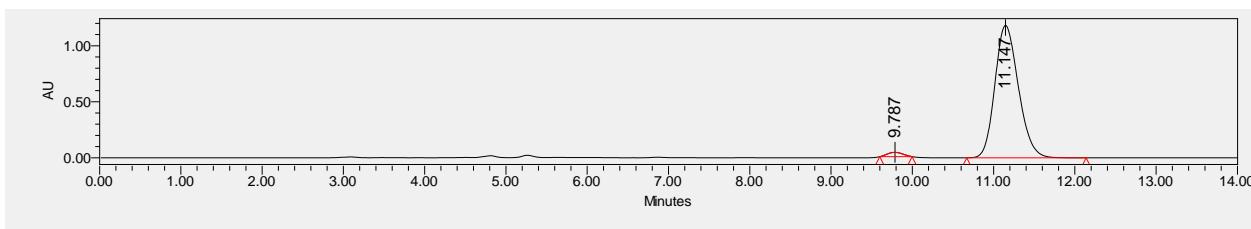
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.25, 164.20, 159.88, 138.16, 136.96, 129.26, 127.05, 124.93, 121.58, 94.60, 87.45, 61.95, 43.72, 14.13;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2982, 2927, 1778, 1722, 1486, 1393, 1370, 1314, 1275, 1259, 1066, 1031, 1005, 821, 799, 750;

ESI-HRMS calcd for $[\text{C}_{16}\text{H}_{15}\text{IO}_4+\text{Na}^+]$: 420.9908, found 420.9899;

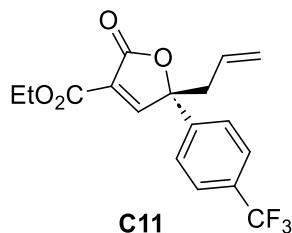


	Retention Time	Area	% Area	Height
1	9.745	7754559	50.00	455709
2	11.172	7755716	50.00	390068



	Retention Time	Area	% Area	Height
1	9.787	511835	2.11	38653
2	11.147	23721220	97.89	1182711

Ethyl (S)-5-allyl-2-oxo-5-(4-(trifluoromethyl)phenyl)-2,5-dihydrofuran-3-carboxylate (C11)



Results: colorless oil, 99% yield, 96 % ee; $[\alpha]^{23}\text{D} = -77.8$ ($c = 0.636 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 7.46 \text{ min}$, $t_{\text{R(major)}} = 8.13 \text{ min}$;

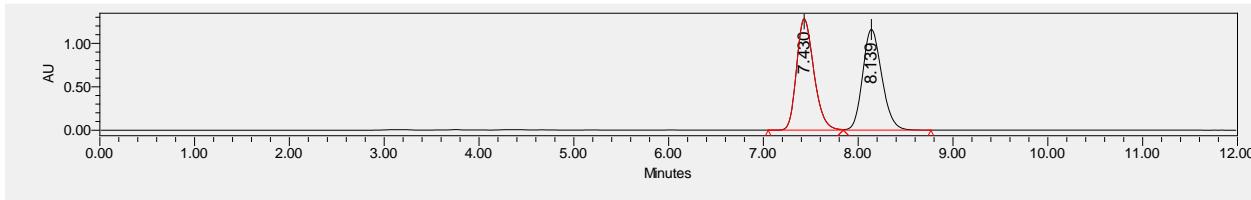
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.32 (s, 1H), 7.68 (d, $J = 8.3 \text{ Hz}$, 2H), 7.55 (d, $J = 8.1 \text{ Hz}$, 2H), 5.67 – 5.53 (m, 1H), 5.23 – 5.11 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.92 (ddt, $J = 14.3, 7.3, 1.1 \text{ Hz}$, 1H), 2.84 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 1.36 (t, $J = 7.2 \text{ Hz}$, 3H);

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.07, 163.84, 159.78, 141.20, 131.00 (d, $J_{\text{F-C}} = 32.8 \text{ Hz}$), 129.02, 126.07 (q, $J_{\text{F-C}} = 3.7 \text{ Hz}$), 125.69, 125.24, 123.68 (d, $J_{\text{F-C}} = 272.2 \text{ Hz}$), 121.81, 87.36, 62.02, 43.89, 14.10;

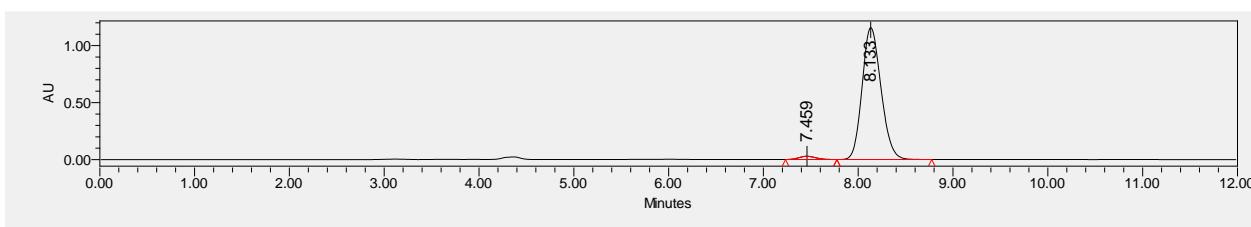
$^{19}\text{F}\{^1\text{H}\} \text{NMR}$ (377 MHz, Chloroform-*d*): δ -62.81;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3085, 2985, 2916, 1778, 1723, 1323, 1276, 1260, 1166, 1123, 1069, 1031, 1017, 842, 800, 750;

ESI-HRMS calcd for $[\text{C}_{17}\text{H}_{15}\text{F}_3\text{O}_4+\text{Na}^+]$: 363.0815, found 363.0808;

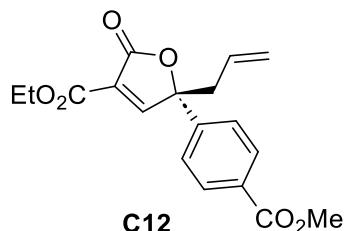


	Retention Time	Area	% Area	Height
1	7.430	16253391	49.94	1281793
2	8.139	16293344	50.06	1158629



	Retention Time	Area	% Area	Height
1	7.459	349526	2.14	28612
2	8.133	16009566	97.86	1157037

Ethyl (S)-5-allyl-5-(4-(methoxycarbonyl)phenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C12)



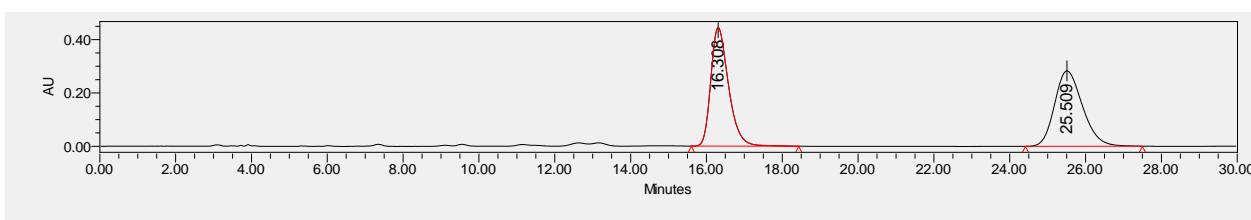
Results: colorless oil, 99% yield, 95 % ee; $[\alpha]^{23}_{\text{D}} = -106.9$ ($c = 0.598$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R(minor)}} = 16.46$ min, $t_{\text{R(major)}} = 25.43$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.33 (s, 1H), 8.11 – 8.02 (m, 2H), 7.53 – 7.44 (m, 2H), 5.66 – 5.52 (m, 1H), 5.21 – 5.09 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.93 (s, 4H), 2.92 (ddt, $J = 14.3, 7.3, 1.1$ Hz, 1H), 2.83 (ddt, $J = 14.4, 7.0, 1.1$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H);

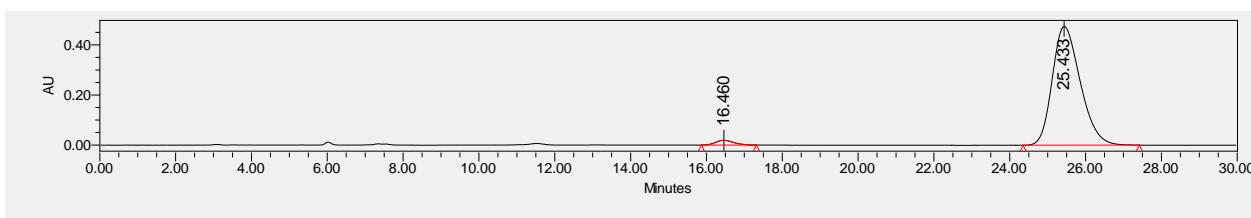
¹³C{¹H NMR} (101 MHz, Chloroform-*d*): δ 166.28, 166.19, 164.04, 159.86, 141.97, 130.52, 130.29, 129.16, 125.27, 125.12, 121.65, 87.62, 61.98, 52.36, 43.89, 14.12;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3083, 2985, 2954, 1782, 1722, 1436, 1279, 1190, 1112, 1070, 1032, 859, 800, 750;

ESI-HRMS calcd for [C₁₈H₁₈O₆+Na⁺]: 353.0996, found 353.0991;

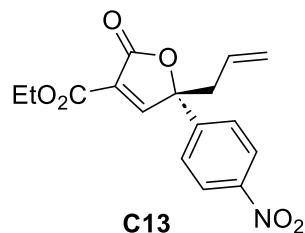


	Retention Time	Area	% Area	Height
1	16.308	14422810	49.94	444750
2	25.509	14454932	50.06	282688



	Retention Time	Area	% Area	Height
1	16.460	628630	2.52	18843
2	25.433	24282732	97.48	474155

Ethyl (S)-5-allyl-5-(4-nitrophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C13)



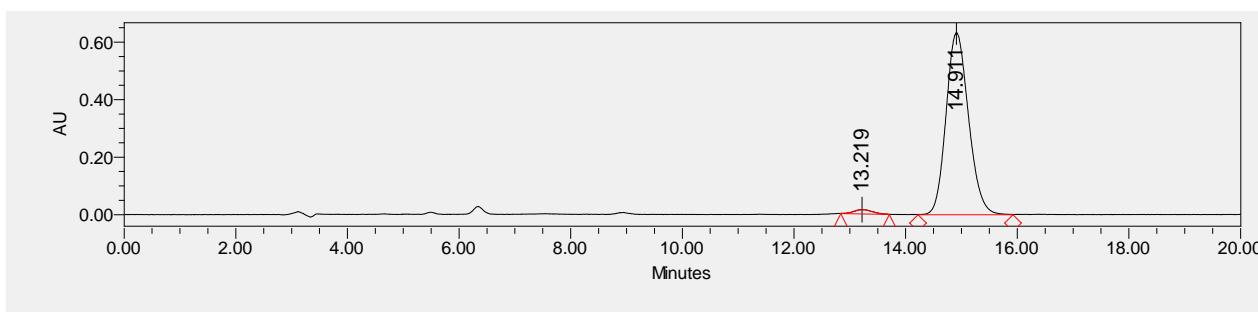
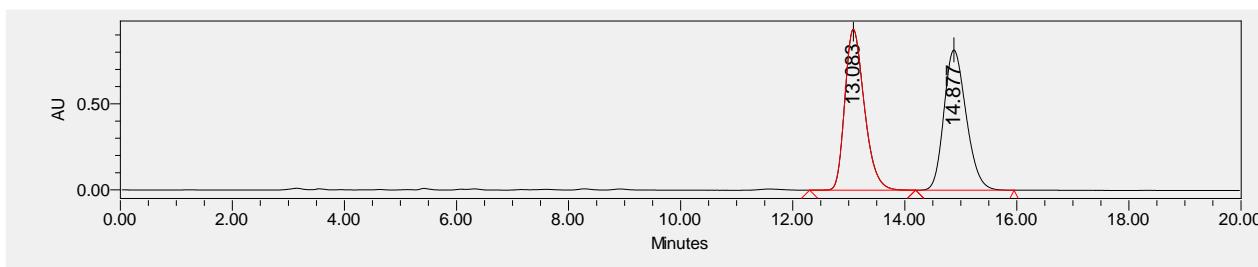
Results: colorless oil, 99% yield, 96% ee; $[\alpha]^{22}\text{D} = -110.5$ ($c = 0.570$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R}}(\text{minor}) = 13.22$ min, $t_{\text{R}}(\text{major}) = 14.91$ min;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.35 (s, 1H), 8.33 – 8.22 (m, 2H), 7.66 – 7.58 (m, 2H), 5.66 – 5.55 (m, 1H), 5.31 – 5.04 (m, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 2.94 (dd, $J = 14.3, 7.5$ Hz, 1H), 2.85 (dd, $J = 14.3, 7.0$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H);

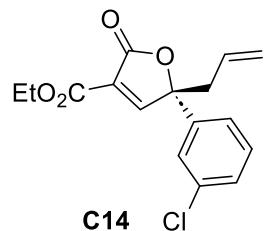
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 165.78, 163.20, 159.63, 147.91, 144.15, 128.71, 126.38, 125.54, 124.26, 122.15, 87.21, 62.13, 43.95, 14.10;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3085, 2983, 2928, 1781, 1722, 1521, 1349, 1315, 1067, 1030, 856, 799, 697;

ESI-HRMS calcd for [C₁₆H₁₅NO₆+Na⁺]: 340.0792, found 340.0787;



Ethyl (S)-5-allyl-5-(3-chlorophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C14)



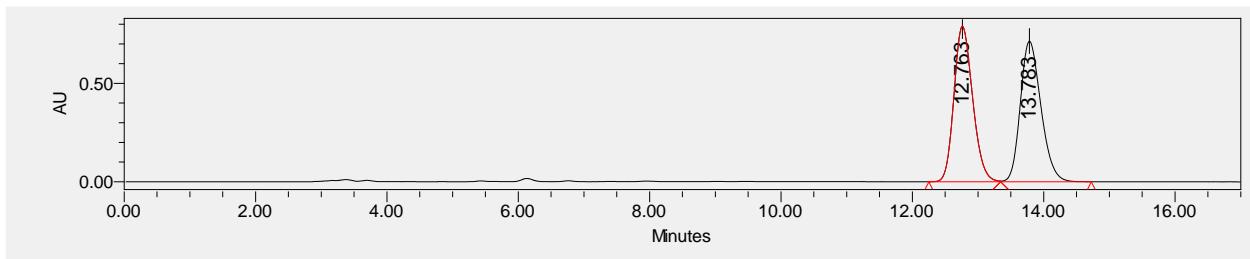
Results: colorless oil, 99% yield, 92% ee; $[\alpha]^{23}\text{D} = -81.6$ ($c = 0.564 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R}}(\text{major}) = 12.80 \text{ min}$, $t_{\text{R}}(\text{minor}) = 13.87 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.29 (s, 1H), 7.43 – 7.23 (m, 4H), 5.66 – 5.51 (m, 1H), 5.24 – 5.11 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.90 (ddt, $J = 14.3, 7.3, 1.1 \text{ Hz}$, 1H), 2.81 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

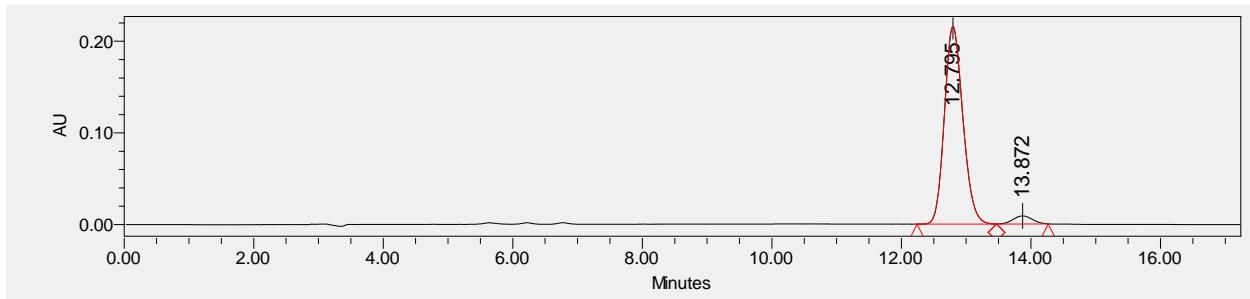
¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 166.21, 164.10, 159.86, 139.20, 135.09, 130.36, 129.18, 128.95, 125.50, 125.03, 123.37, 121.64, 87.23, 61.97, 43.80, 14.12;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3084, 2983, 2927, 1780, 1723, 1371, 1338, 1315, 1259, 1069, 1137, 1032, 799, 749, 697;

ESI-HRMS calcd for [C₁₆H₁₅³⁵ClO₄+Na⁺]: 329.0552, found 329.0562; calcd for [C₁₆H₁₅³⁷ClO₄+Na⁺]: 331.0522, found 331.0530

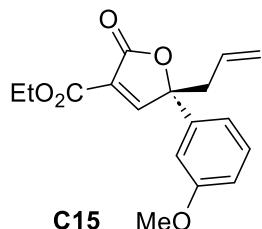


	Retention Time	Area	% Area	Height
1	12.763	15593422	50.07	789474
2	13.783	15551082	49.93	713779



	Retention Time	Area	% Area	Height
1	12.795	4271879	95.94	215580
2	13.872	180764	4.06	8840

Ethyl (S)-5-allyl-5-(3-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C15)



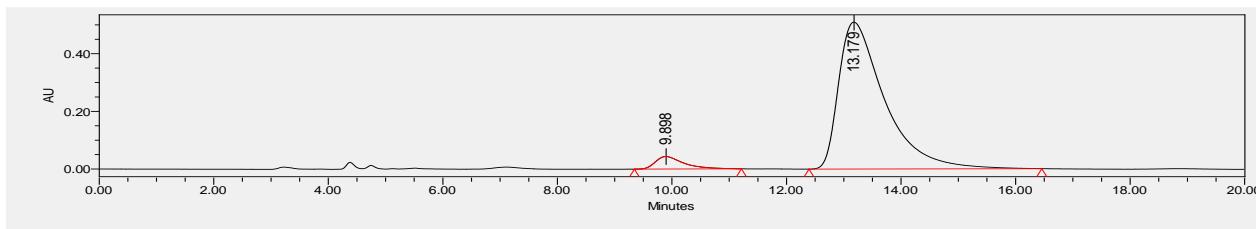
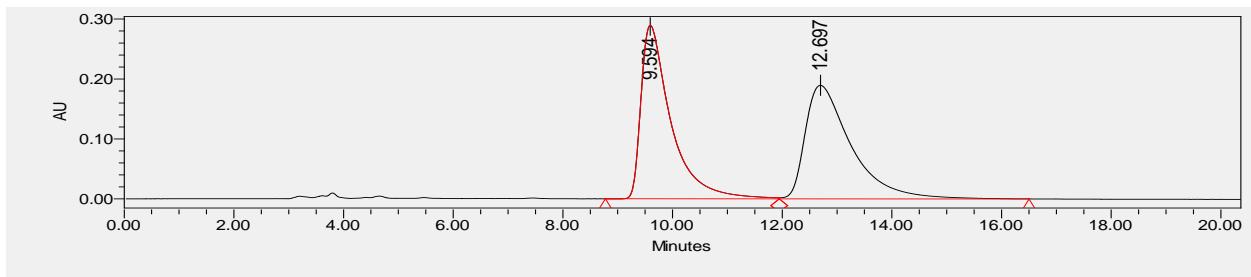
Results: colorless oil, 97% yield, 90% ee; $[\alpha]^{23}\text{D} = -80.4$ ($c = 1.020 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak AYH, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 9.90 \text{ min}$, $t_{\text{R(major)}} = 13.18 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.30 (s, 1H), 7.35 – 7.29 (m, 1H), 6.98 – 6.84 (m, 3H), 5.60 (m, 1H), 5.20 – 5.10 (m, 2H), 4.33 (q, $J = 7.1 \text{ Hz}$, 2H), 3.82 (s, 3H), 2.91 (ddt, $J = 14.3, 7.2, 1.1 \text{ Hz}$, 1H), 2.81 (ddt, $J = 14.3, 7.1, 1.1 \text{ Hz}$, 1H), 1.35 (t, $J = 7.1 \text{ Hz}$, 3H);

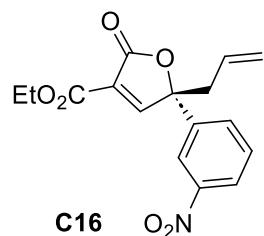
¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 166.58, 164.86, 160.06, 160.04, 138.73, 130.10, 129.61, 124.58, 121.21, 117.36, 113.98, 111.05, 87.78, 61.85, 55.42, 43.88, 14.14;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3082, 2982, 2938, 1774, 1721, 1371, 1601, 1293, 1260, 1030, 991, 798, 750, 700;

ESI-HRMS calcd for $[\text{C}_{17}\text{H}_{18}\text{O}_5+\text{Na}^+]$: 325.1047, found 325.1042;



Ethyl (S)-5-allyl-5-(3-nitrophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C16)

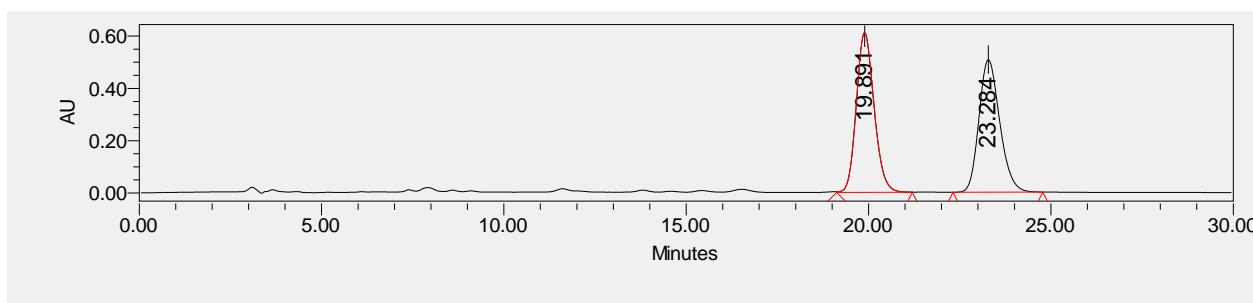


Results: colorless oil, 99% yield, 96% ee; $[\alpha]^{23}\text{D} = -87.1$ ($c = 0.510 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R}}(\text{major}) = 20.07 \text{ min}$, $t_{\text{R}}(\text{minor}) = 23.61 \text{ min}$;

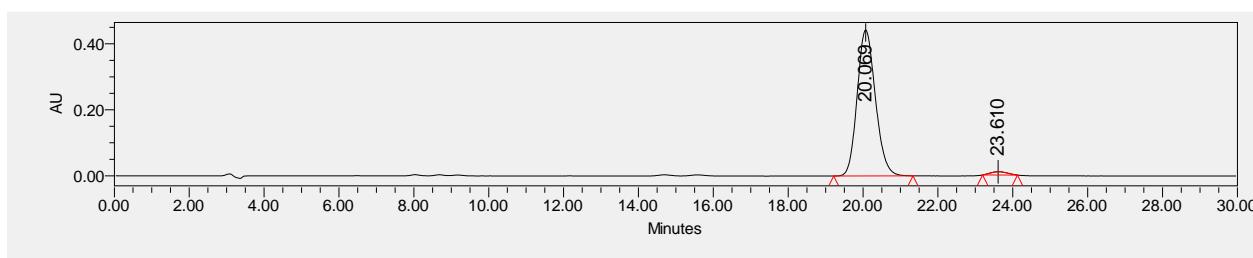
¹H NMR (400 MHz, Chloroform-*d*): δ 8.39 (s, 1H), 8.30 – 8.21 (m, 2H), 7.82 - 7.76 (m, 1H), 7.64 (t, $J = 8.0 \text{ Hz}$, 1H), 5.68 - 5.55 (m, 1H), 5.25 – 5.13 (m, 2H), 4.35 (q, $J = 7.2 \text{ Hz}$, 2H), 2.95 (ddt, $J = 14.4, 7.5, 1.1 \text{ Hz}$, 1H), 2.88 (ddt, $J = 14.3, 6.9, 1.1 \text{ Hz}$, 1H), 1.37 (t, $J = 7.1 \text{ Hz}$, 3H);

¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 165.82, 163.24, 159.65, 148.45, 139.49, 131.30, 130.33, 128.76, 125.57, 123.74, 122.19, 120.50, 86.96, 62.12, 43.96, 14.11;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3088, 2984, 2922, 1779, 1722, 1530, 1348, 1275, 1259, 1067, 1030, 993, 799, 749, 690; **ESI-HRMS** calcd for [C₁₆H₁₅NO₆+Na⁺]: 340.0792, found 340.0786;

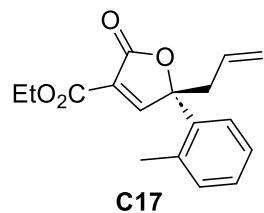


	Retention Time	Area	% Area	Height
1	19.891	20669973	50.73	610461
2	23.284	20075926	49.27	506762



	Retention Time	Area	% Area	Height
1	20.069	14926667	97.96	442305
2	23.610	310644	2.04	9953

Ethyl (S)-5-allyl-2-oxo-5-(o-tolyl)-2,5-dihydrofuran-3-carboxylate (C17)



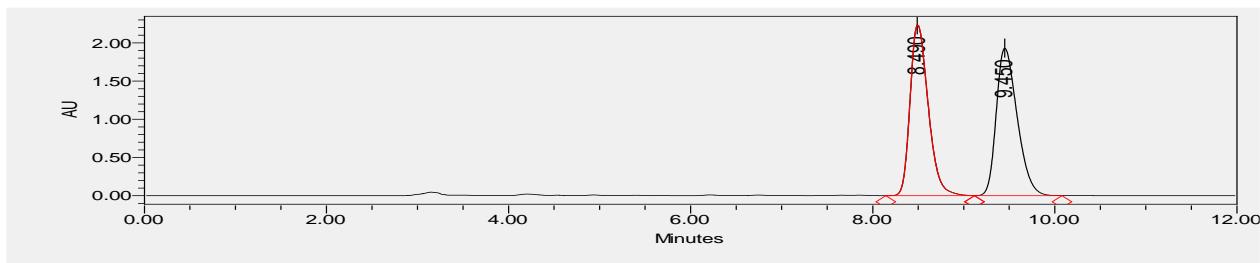
Results: colorless oil, 99% yield, 64% ee; $[\alpha]^{23}\text{D} = -14.1$ ($c = 1.038 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(minor)}} = 8.56 \text{ min}$, $t_{\text{R(major)}} = 9.50 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.57 (s, 1H), 7.36 – 7.14 (m, 4H), 5.64 – 5.49 (m, 1H), 5.19 – 5.08 (m, 2H), 4.35 (q, $J = 7.1 \text{ Hz}$, 2H), 2.96 (ddt, $J = 14.4, 7.4, 1.1 \text{ Hz}$, 1H), 2.90 (ddt, $J = 14.4, 7.1, 1.2 \text{ Hz}$, 1H), 2.58 (s, 3H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

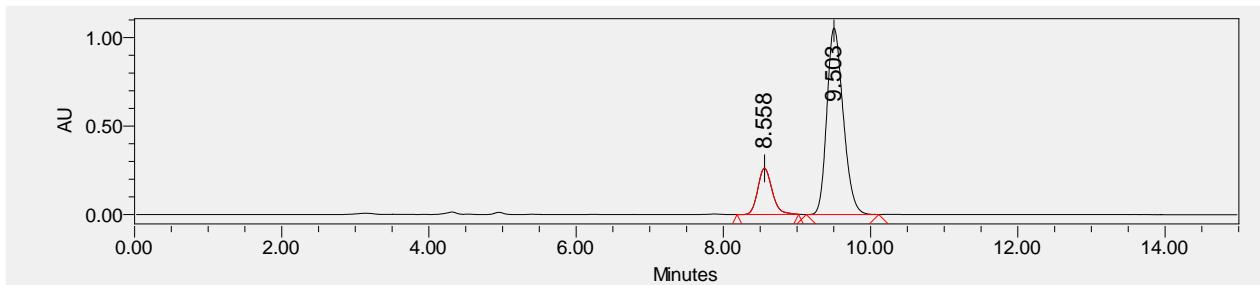
¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 166.24, 164.26, 160.17, 135.56, 135.11, 133.01, 129.84, 128.81, 126.69, 126.35, 125.37, 121.01, 89.07, 61.88, 42.82, 21.85, 14.16;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2981, 2917, 2849, 1775, 1722, 1370, 1340, 1314, 1272, 1067, 1027, 799, 763, 725;

ESI-HRMS calcd for [C₁₇H₁₈O₄+Na⁺]: 309.1098, found 309.1092;

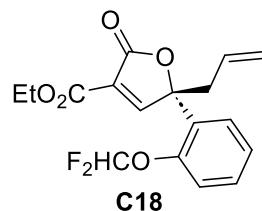


	Retention Time	Area	% Area	Height
1	8.490	30957931	50.14	2234624
2	9.450	30790944	49.86	1930321



	Retention Time	Area	% Area	Height
1	8.558	3521507	17.78	261806
2	9.503	16284902	82.22	1054212

Ethyl (S)-5-allyl-5-(2-(difluoromethoxy)phenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C18)



Results: colorless oil, 99% yield, 98% ee; $[\alpha]^{23}\text{D} = -113.2$ ($c = 0.608$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R(major)}} = 8.33$ min, $t_{\text{R(minor)}} = 9.22$ min;

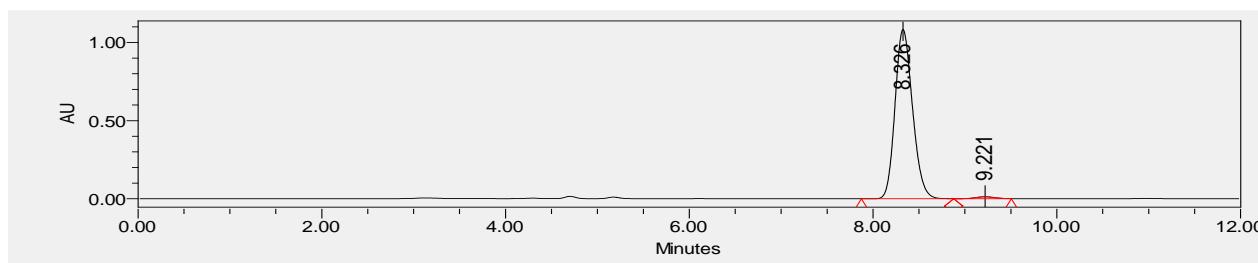
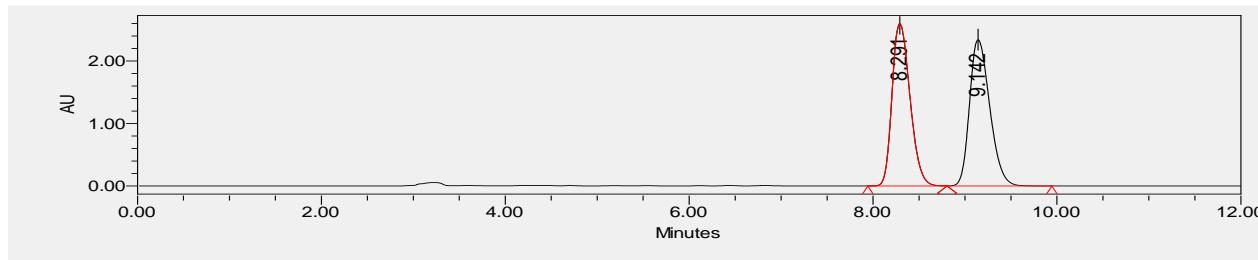
$^1\text{H NMR}$ (400 MHz, Chloroform- δ): δ 8.61 (s, 1H), 7.64 (dd, $J = 7.9, 1.7$ Hz, 1H), 7.44 – 7.33 (m, 1H), 7.23 (td, $J = 7.7, 1.1$ Hz, 1H), 7.10 (dd, $J = 8.2, 1.2$ Hz, 1H), 6.69 (t, $J = 72.9$ Hz, 1H), 5.68 – 5.50 (m, 1H), 5.16 – 5.06 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.00 (ddt, $J = 14.4, 7.7, 1.1$ Hz, 1H), 2.84 (ddt, $J = 14.4, 6.9, 1.2$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H);

$^{13}\text{C}\{^1\text{H}\}\text{NMR}$ (101 MHz, Chloroform- δ): δ 166.26, 163.83, 160.06, 147.88 (t, $J_{\text{F-C}} = 2.4$ Hz), 130.46, 129.77, 127.79, 127.63, 125.74, 124.74, 120.97, 116.61, 116.05 (t, $J_{\text{F-C}} = 259.1$ Hz),, 87.03, 61.87, 41.89, 14.11;

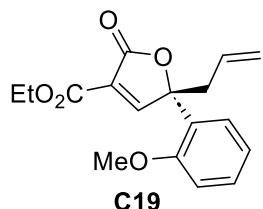
$^{19}\text{F}\{^1\text{H}\}\text{NMR}$ (377 MHz, Chloroform- δ) δ -79.35 ~ -80.31 (m, 2F).

IR (film): $\tilde{\nu}$ (cm $^{-1}$) 3083, 2985, 2917, 2849, 1784, 1724, 1372, 1339, 1316, 1276, 1226, 1117, 1048, 1030, 799, 762;

ESI-HRMS calcd for [C₁₇H₁₆F₂O₅+Na⁺]: 361.0858, found 361.0851;



Ethyl (S)-5-allyl-5-(2-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C19)

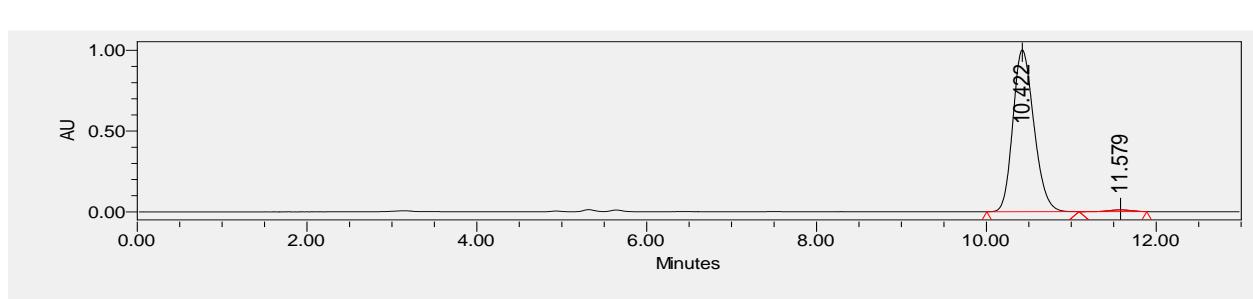
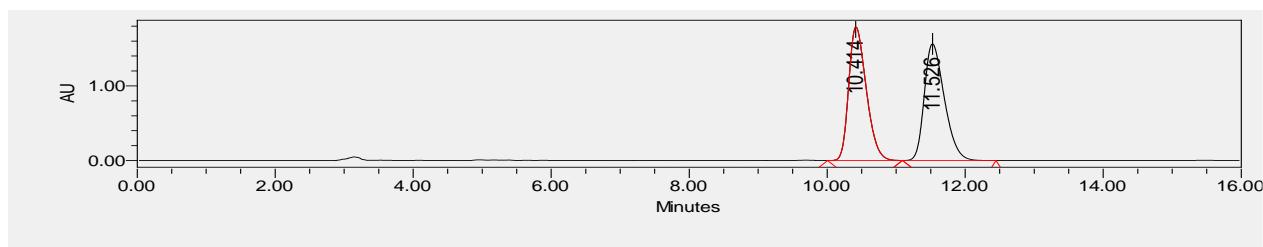


Results: colorless oil, 97% yield, 98% ee; $[\alpha]^{23}\text{D} = -167.8$ ($c = 0.522$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R}}(\text{major}) = 10.42$ min, $t_{\text{R}}(\text{minor}) = 11.58$ min;

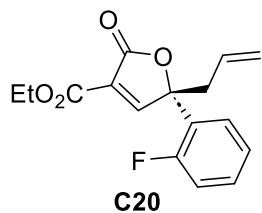
¹H NMR (400 MHz, Chloroform-*d*): δ 8.71 (s, 1H), 7.56 – 7.48 (m, 1H), 7.36 – 7.30 (m, 1H), 7.03 – 6.96 (m, 1H), 6.95 – 6.91 (m, 1H), 5.65 – 5.53 (m, 1H), 5.13 – 5.03 (m, 2H), 4.33 (qd, $J = 7.1, 0.8$ Hz, 2H), 3.94 (s, 3H), 3.00 (ddt, $J = 14.3, 7.4, 1.1$ Hz, 1H), 2.89 (ddt, $J = 14.3, 7.0, 1.1$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H);

¹³C{¹H NMR} (101 MHz, Chloroform-*d*): δ 166.80, 165.37, 160.49, 155.10, 130.44, 130.09, 126.55, 125.51, 124.03, 121.45, 120.38, 111.01, 87.89, 61.69, 55.49, 41.12, 14.17;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3079, 2981, 2918, 2847, 1783, 1723, 1489, 1370, 1336, 1241, 1053, 1030, 799, 756; **ESI-HRMS** calcd for [C₁₇H₁₈O₅+Na⁺]: 325.1047, found 325.1042;



Ethyl (S)-5-allyl-5-(2-fluorophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C20)



Results: colorless oil, 99% yield, 96% ee; $[\alpha]^{23}\text{D} = -92.6$ ($c = 0.568 \text{ g/100 mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(major)}} = 9.33 \text{ min}$, $t_{\text{R(minor)}} = 9.97 \text{ min}$;

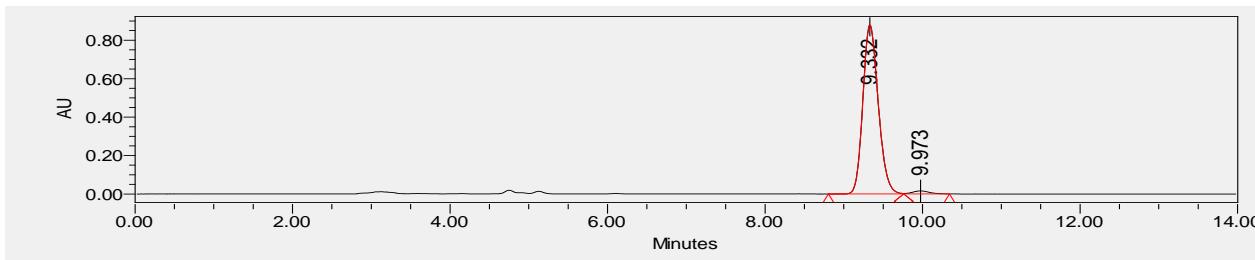
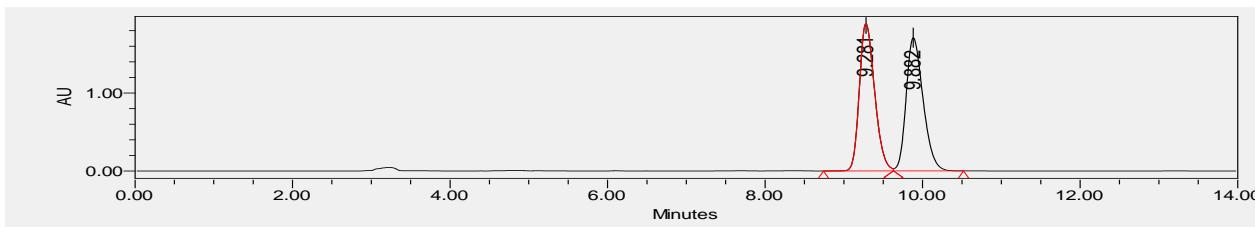
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.52 (d, $J = 3.4 \text{ Hz}$, 1H), 7.57 - 7.51 (m, 1H), 7.40 - 7.32 (m, 1H), 7.21 - 7.16 (m, 1H), 7.14- 7.07 (m, 1H), 5.68 – 5.53 (m, 1H), 5.18 – 5.06 (m, 2H), 4.34 (q, $J = 7.2 \text{ Hz}$, 2H), 3.02 – 2.91 (m, 1H), 2.88 – 2.78 (m, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.28, 163.63 (d, $J_{\text{F-C}} = 6.6 \text{ Hz}$), 159.98, 158.66 (d, $J_{\text{F-C}} = 245.3 \text{ Hz}$), 130.75 (d, $J_{\text{F-C}} = 8.5 \text{ Hz}$), 129.49, 127.11 (d, $J_{\text{F-C}} = 3.5 \text{ Hz}$), 125.13 (d, $J_{\text{F-C}} = 3.2 \text{ Hz}$), 124.76 (d, $J_{\text{F-C}} = 12.4 \text{ Hz}$), 124.70, 121.25, 116.06 (d, $J_{\text{F-C}} = 22.1 \text{ Hz}$), 86.27 (d, $J_{\text{F-C}} = 4.0 \text{ Hz}$), 61.87, 42.29 (d, $J_{\text{F-C}} = 3.1 \text{ Hz}$), 14.13;

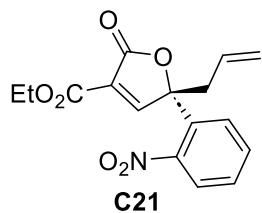
$^{19}\text{F}\{^1\text{H}\} \text{NMR}$ (377 MHz, Chloroform-*d*) δ -114.18;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2982, 2920, 2850, 1787, 1724, 1486, 1370, 1337, 1316, 1221, 1039, 1028, 799, 763;

ESI-HRMS calcd for $[\text{C}_{16}\text{H}_{15}\text{FO}_4+\text{Na}^+]$: 313.0847, found 313.0842;



Ethyl (S)-5-allyl-5-(2-nitrophenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C21)



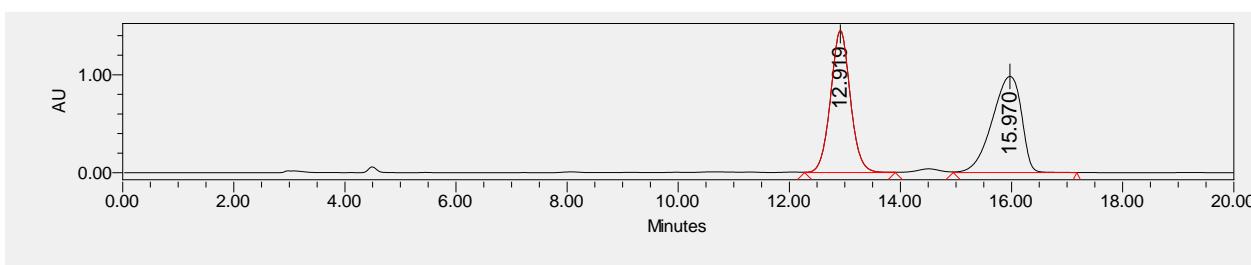
Results: colorless oil, 99% yield, 90% ee; $[\alpha]^{19}\text{D} = +19.5$ ($c = 0.514 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiraldpak ADH, *n*-hexane/*i*-PrOH 90/10, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(major)}} = 12.96 \text{ min}$, $t_{\text{R(minor)}} = 15.77 \text{ min}$;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.64 (s, 1H), 7.69 – 7.62 (m, 1H), 7.57 – 7.51 (m, 1H), 5.68 – 5.53 (m, 1H), 5.19 – 5.10 (m, 3H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 3.04 (dd, $J = 14.5, 7.9 \text{ Hz}$, 1H), 2.91 (dd, $J = 14.5, 6.6 \text{ Hz}$, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

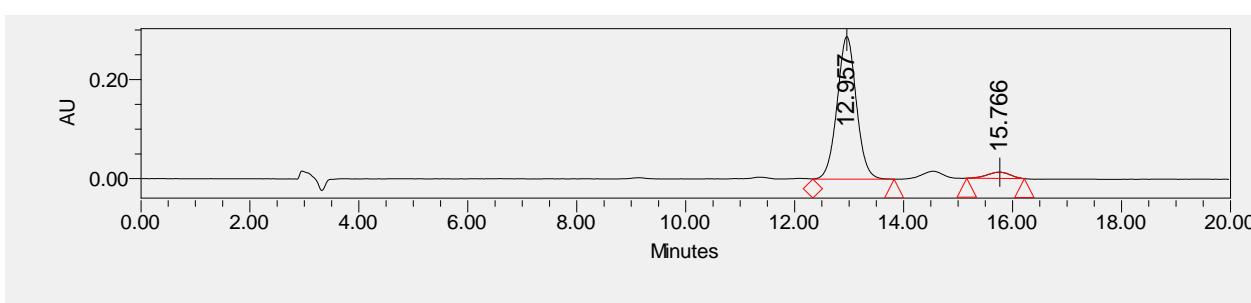
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 165.56, 163.38, 159.72, 148.38, 133.54, 131.04, 130.03, 129.32, 128.47, 125.81, 125.56, 121.77, 87.51, 62.02, 42.17, 14.11;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3089, 2985, 1787, 1725, 1536, 1371, 1260, 1067, 1028, 799, 750;

ESI-HRMS calcd for $[\text{C}_{16}\text{H}_{15}\text{NO}_6+\text{Na}^+]$: 340.0792, found 340.0788;

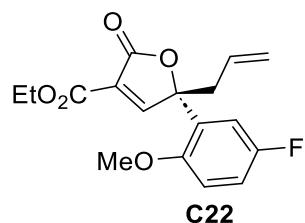


	Retention Time	Area	% Area	Height
1	12.919	35828677	49.94	1448734
2	15.970	35910994	50.06	981022



	Retention Time	Area	% Area	Height
1	12.957	7071941	95.05	287859
2	15.766	368598	4.95	12768

Ethyl (S)-5-allyl-5-(5-fluoro-2-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C22)



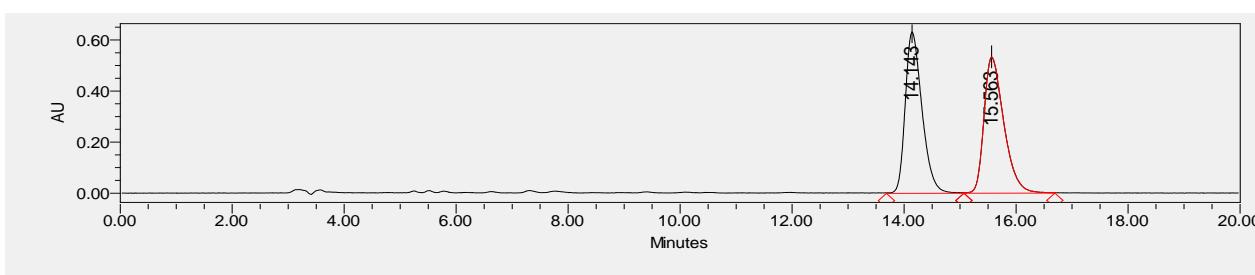
Results: colorless oil, 94% yield, 91% ee; $[\alpha]^{23}\text{D} = -151.3$ ($c = 0.538$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak ID, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R}}(\text{minor}) = 14.27$ min, $t_{\text{R}}(\text{major}) = 15.52$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.67 (s, 1H), 7.30 – 7.23 (m, 1H), 7.05 – 6.97 (m, 1H), 6.86 (dd, $J = 9.0, 4.3$ Hz, 1H), 5.65 – 5.51 (m, 1H), 5.13 – 5.03 (m, 2H), 4.33 (qd, $J = 7.1, 1.3$ Hz, 2H), 3.93 (s, 3H), 2.99 (ddt, $J = 14.2, 7.5, 1.1$ Hz, 1H), 2.85 (ddt, $J = 14.2, 7.0, 1.1$ Hz, 1H), 1.36 (t, $J = 7.1$ Hz, 3H);

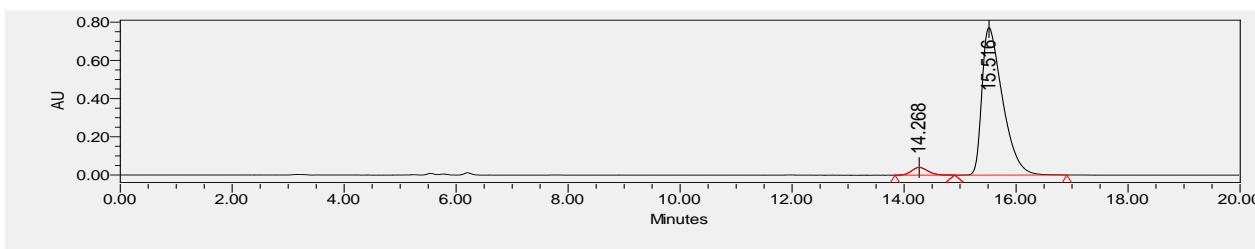
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 166.39, 164.62, 160.33, 157.23 (d, $J_{\text{F-C}} = 240.4$ Hz), 151.18 (d, $J_{\text{F-C}} = 2.2$ Hz), 130.07, 127.08 (d, $J_{\text{F-C}} = 7.2$ Hz), 124.38, 120.71, 115.88 (d, $J_{\text{F-C}} = 23.0$ Hz), 114.03 (d, $J_{\text{F-C}} = 26.3$ Hz), 111.94 (d, $J_{\text{F-C}} = 8.0$ Hz), 87.29, 61.80, 56.00, 40.97, 14.15;

IR (film): $\tilde{\nu}$ (cm⁻¹) 2982, 1786, 1725, 1496, 1274, 1249, 1031, 799, 749;

ESI-HRMS calcd for [C₁₇H₁₇FO₅+Na⁺]: 343.0953, found 343.0947;

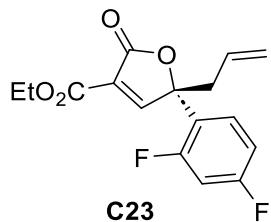


	Retention Time	Area	% Area	Height
1	14.143	13123174	50.04	632365
2	15.563	13104752	49.96	533807



	Retention Time	Area	% Area	Height
1	14.268	821756	4.01	40510
2	15.516	19655736	95.99	772038

Ethyl (S)-5-allyl-5-(5-fluoro-2-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C23)



Results: colorless oil, 99% yield, 98% ee; $[\alpha]^{23}\text{D} = -91.3$ ($c = 0.528 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralkpak IG, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(major)}} = 8.48 \text{ min}$, $t_{\text{R(minor)}} = 9.30 \text{ min}$;

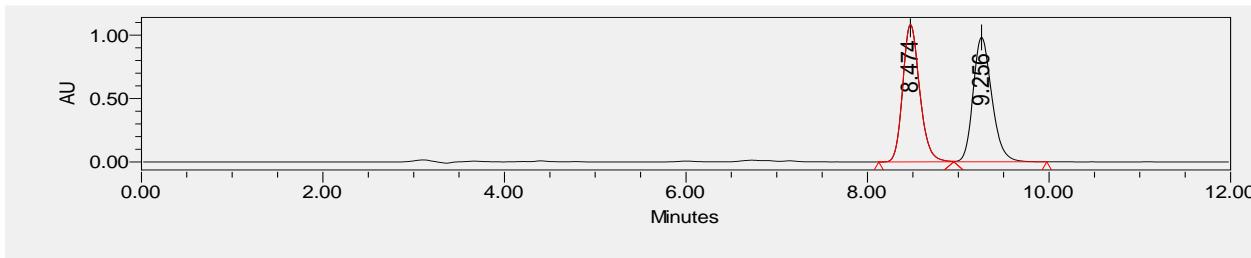
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.48 (d, $J = 3.5 \text{ Hz}$, 1H), 7.53 (td, $J = 8.8, 6.2 \text{ Hz}$, 1H), 7.04 – 6.77 (m, 2H), 5.67 – 5.52 (m, 1H), 5.18 – 5.08 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 2.98 – 2.87 (m, 1H), 2.85 – 2.74 (m, 1H), 1.36 (t, $J = 7.1 \text{ Hz}$, 3H);

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.03, 164.44 (d, $J_{\text{F-C}} = 12.3 \text{ Hz}$), 163.24 (d, $J_{\text{F-C}} = 6.5 \text{ Hz}$), 161.94 (d, $J_{\text{F-C}} = 12.2 \text{ Hz}$), 159.99 (d, $J_{\text{F-C}} = 11.9 \text{ Hz}$), 159.88, 157.52 (d, $J_{\text{F-C}} = 11.9 \text{ Hz}$), 129.28, 128.31 (dd, $J_{\text{F-C}} = 9.7, 5.2 \text{ Hz}$), 124.90, 121.45, 120.88 (dd, $J_{\text{F-C}} = 12.9, 3.9 \text{ Hz}$), 112.25 (dd, $J_{\text{F-C}} = 21.2, 3.4 \text{ Hz}$), 104.63 (t, $J_{\text{F-C}} = 26.0 \text{ Hz}$), 85.88 (d, $J_{\text{F-C}} = 4.2 \text{ Hz}$), 61.95, 42.39 (d, $J_{\text{F-C}} = 3.0 \text{ Hz}$), 14.12;

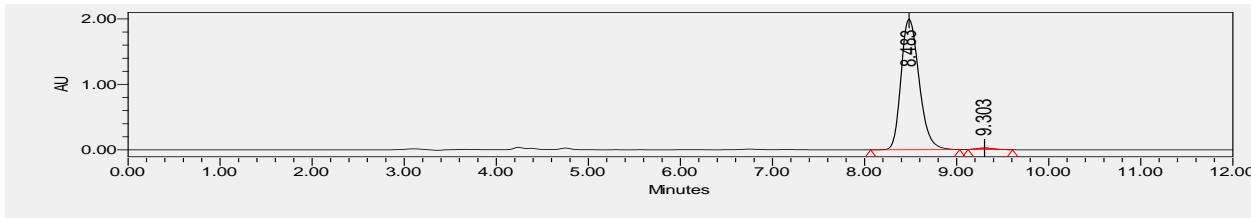
$^{19}\text{F NMR}$ (377 MHz, Chloroform-*d*) δ -108.53 (d, $J = 7.9 \text{ Hz}$), -110.26 (d, $J = 8.2 \text{ Hz}$);

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2985, 2928, 1788, 1724, 1501, 1299, 1275, 1030, 799, 750;

ESI-HRMS calcd for $[\text{C}_{16}\text{H}_{14}\text{F}_2\text{O}_4+\text{Na}^+]$: 331.0753, found 331.0746;

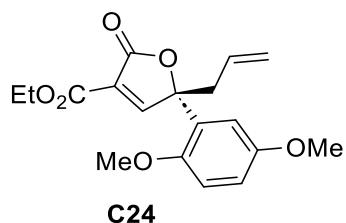


	Retention Time	Area	% Area	Height
1	8.474	14032262	49.92	1083078
2	9.256	14075757	50.08	980285



	Retention Time	Area	% Area	Height
1	8.483	27208458	98.92	1994188
2	9.303	297675	1.08	23586

Ethyl (S)-5-allyl-5-(2,5-dimethoxyphenyl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C24)



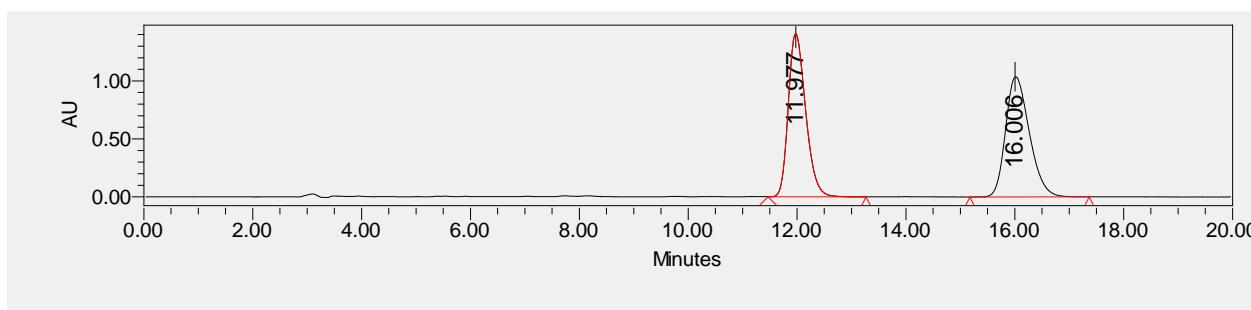
Results: colorless oil, 90% yield, 84% ee; $[\alpha]^{23}\text{D} = -100.3$ ($c = 0.574$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{\text{R}}(\text{major}) = 11.86$ min, $t_{\text{R}}(\text{minor}) = 15.98$ min;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.69 (s, 1H), 7.10 – 7.07 (m, 1H), 6.88 – 6.82 (m, 2H), 5.66 – 5.51 (m, 1H), 5.14 – 5.04 (m, 2H), 4.33 (qd, $J = 7.1, 1.1$ Hz, 2H), 3.89 (s, 3H), 3.76 (s, 3H), 2.99 (ddt, $J = 14.3, 7.3, 1.1$ Hz, 1H), 2.88 (ddt, $J = 14.3, 7.1, 1.1$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H). ;

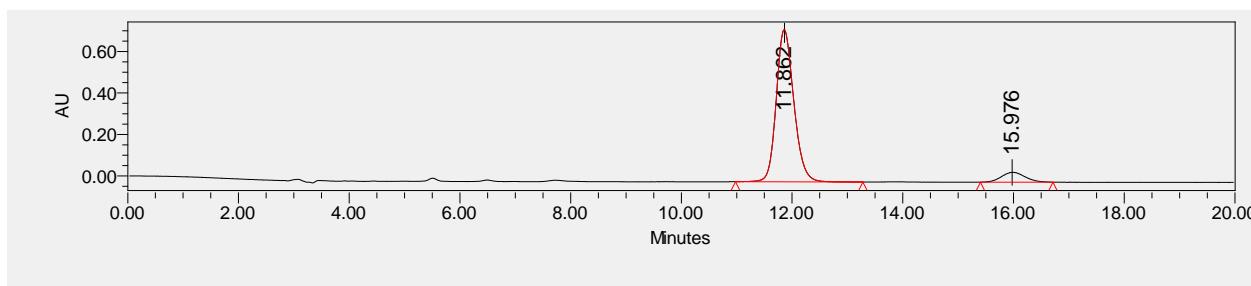
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.76, 165.27, 160.45, 154.06, 149.12, 130.35, 126.27, 124.02, 120.46, 114.87, 112.10, 112.05, 87.75, 61.70, 55.84, 41.11, 29.71, 14.16;

IR (film): $\tilde{\nu}$ (cm⁻¹) 2980, 2917, 2837, 1783, 1724, 1498, 1277, 1224, 1032, 799, 749;

ESI-HRMS calcd for [C₁₈H₂₀O₆+Na⁺]: 355.1153, found 355.1147;

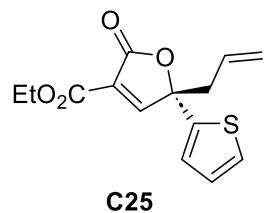


	Retention Time	Area	% Area	Height
1	11.977	31246040	49.80	1409772
2	16.006	31497367	50.20	1037208



	Retention Time	Area	% Area	Height
1	11.862	16180919	92.00	733742
2	15.976	1407213	8.00	47642

Ethyl (S)-5-allyl-2-oxo-5-(thiophen-2-yl)-2,5-dihydrofuran-3-carboxylate (C25)



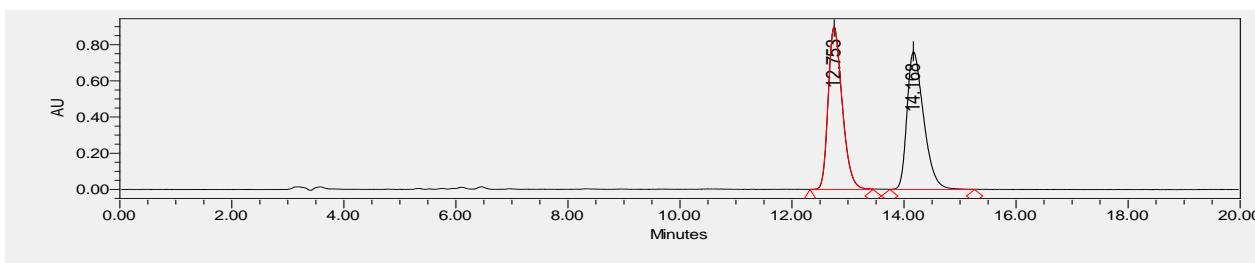
Results: colorless oil, 99% yield, 81% ee; $[\alpha]^{23}\text{D} = -39.1$ ($c = 1.040 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak IG, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R}}(\text{minor}) = 12.85 \text{ min}$, $t_{\text{R}}(\text{major}) = 14.24 \text{ min}$;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.21 (s, 1H), 7.35 (dd, $J = 4.9, 1.4 \text{ Hz}$, 1H), 7.07 – 6.99 (m, 2H), 5.72 – 5.57 (m, 1H), 5.25 – 5.16 (m, 2H), 4.35 (q, $J = 7.1 \text{ Hz}$, 2H), 2.99 (dq, $J = 14.3, 7.2 \text{ Hz}$, 2H), 1.37 (t, $J = 7.1 \text{ Hz}$, 3H);

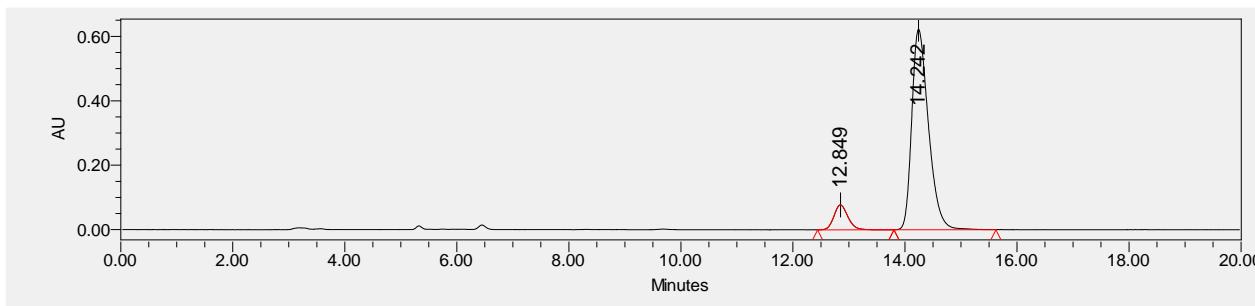
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 166.16, 163.75, 159.95, 139.53, 129.30, 127.35, 126.47, 125.39, 124.96, 121.65, 85.63, 61.97, 43.69, 14.13;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3083, 2982, 2917, 2837, 1777, 1722, 1641, 1370, 1336, 1311, 1252, 1062, 1024, 799, 708;

ESI-HRMS calcd for [C₁₄H₁₄O₄S +Na⁺]: 301.0505, found 301.0503;

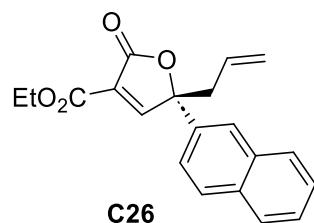


	Retention Time	Area	% Area	Height
1	12.753	15677683	49.88	898878
2	14.168	15755163	50.12	764329



	Retention Time	Area	% Area	Height
1	12.849	1349241	9.48	77479
2	14.242	12882167	90.52	622682

Ethyl (S)-5-allyl-5-(naphthalen-2-yl)-2-oxo-2,5-dihydrofuran-3-carboxylate (C26)

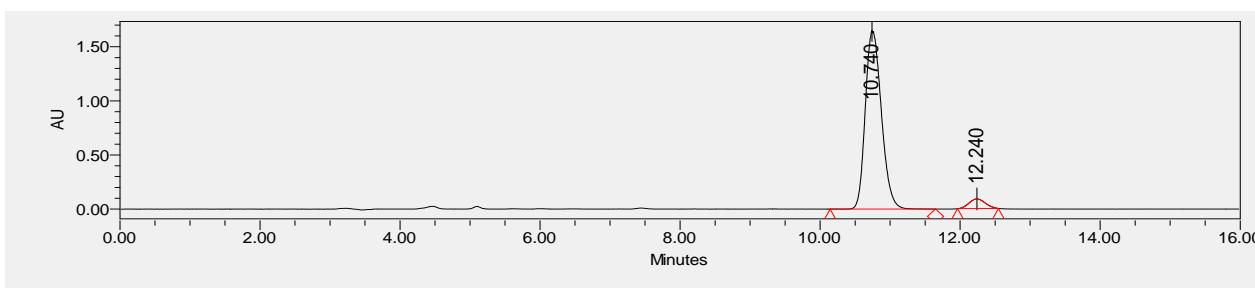
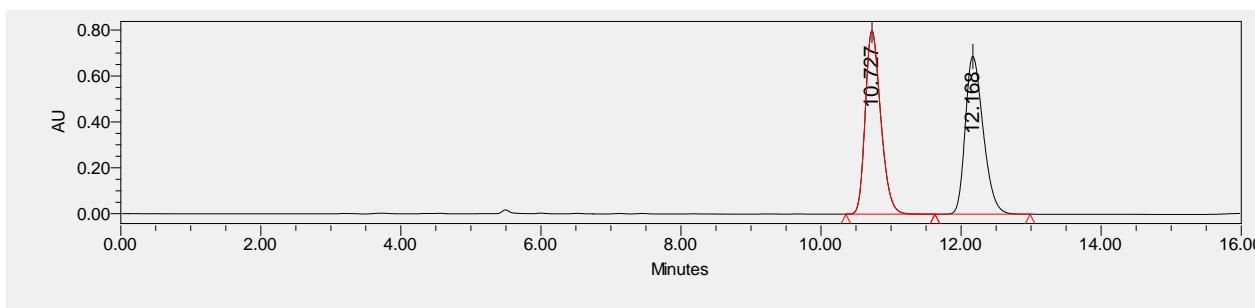


Results: white solid, 99% yield, 90% ee; $[\alpha]^{23}\text{D} = -107.8$ ($c = 0.476 \text{ g}/100 \text{ mL}$, $\lambda = 589 \text{ nm}$, in DCM), HPLC (Daicel Chiralpak OXH, *n*-hexane/*i*-PrOH 80/20, 1.0 mL/min, $\lambda = 210 \text{ nm}$, $t_{\text{R(major)}} = 10.74 \text{ min}$, $t_{\text{R(minor)}} = 12.24 \text{ min}$;

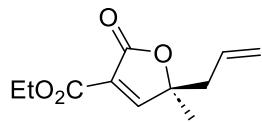
¹H NMR (400 MHz, Chloroform-*d*): δ 8.44 (s, 1H), 7.92 – 7.79 (m, 4H), 7.57 – 7.43 (m, 3H), 5.70 – 5.56 (m, 1H), 5.22 – 5.11 (m, 2H), 4.34 (q, $J = 7.1 \text{ Hz}$, 2H), 3.01 (ddt, $J = 14.4, 7.3, 1.2 \text{ Hz}$, 1H), 2.93 (ddt, $J = 14.3, 7.0, 1.1 \text{ Hz}$, 1H), 1.35 (t, $J = 7.1 \text{ Hz}$, 3H);

¹³C{¹H NMR (101 MHz, Chloroform-*d*): δ 166.68, 164.93, 160.09, 134.43, 133.09, 132.99, 129.65, 129.03, 128.25, 127.70, 126.94, 126.91, 124.74, 124.51, 122.56, 121.29, 88.09, 61.89, 43.75, 14.15;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3082, 2983, 2931, 1777, 1722, 1641, 1370, 1275, 1260, 1069, 1032, 994, 800, 750; **ESI-HRMS** calcd for [C₂₀H₁₈O₄ +Na⁺]: 345.1098, found 345.1092;



Ethyl (S)-5-allyl-5-methyl-2-oxo-2,5-dihydrofuran-3-carboxylate (C27)



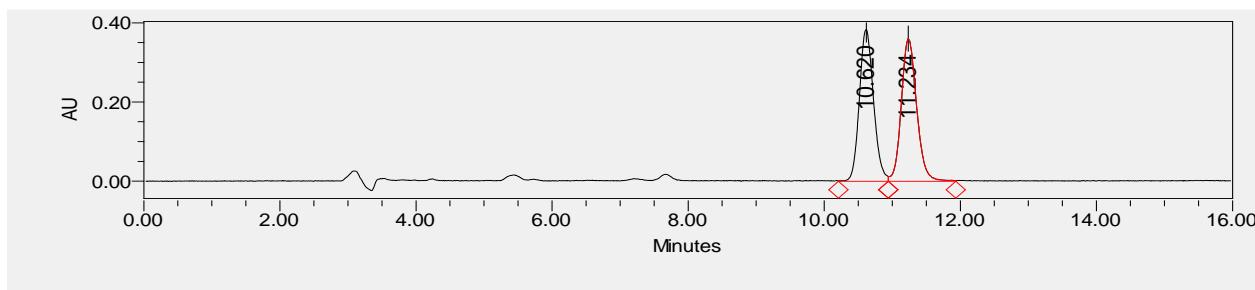
C27

Results: colorless oil, 99% yield, 68% ee; $[\alpha]^{24}_D = +22.8$ ($c = 0.316$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak AZH, *n*-hexane/*i*-PrOH 85/15, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{minor})} = 10.64$ min, $t_{R(\text{major})} = 11.24$ min;

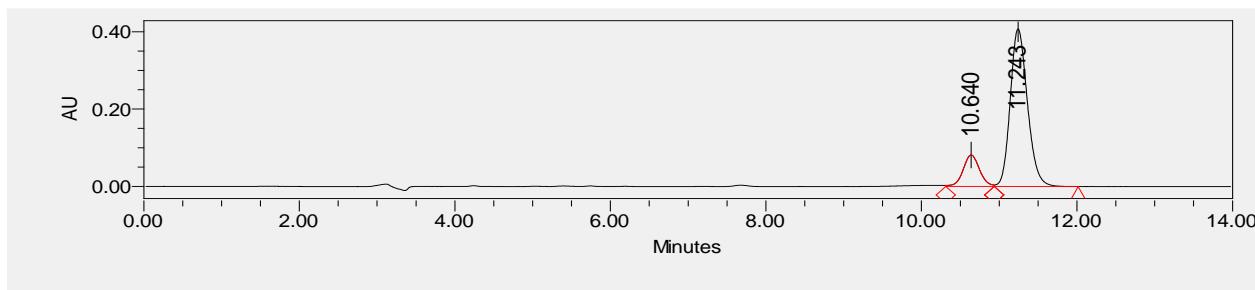
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.05 (s, 1H), 5.66 (ddt, $J = 17.5, 10.3, 7.3$ Hz, 1H), 5.20 – 5.11 (m, 2H), 4.32 (q, $J = 7.1$ Hz, 2H), 2.53 (dt, $J = 7.4, 1.1$ Hz, 1H), 1.50 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H);

$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.75, 166.33, 160.22, 130.23, 125.33, 120.93, 85.26, 61.77, 42.63, 23.13, 14.13;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3082, 2984, 2919, 1776, 1722, 1642, 1450, 1338, 1314, 1275, 1260, 1036, 800, 764, 750; **ESI-HRMS** calcd for [C₁₁H₁₄O₄+Na⁺]: 233.0785, found 233.0782;

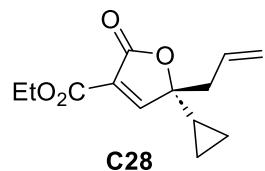


	Retention Time	Area	% Area	Height
1	10.620	5531467	49.48	382856
2	11.234	5647411	50.52	360186



	Retention Time	Area	% Area	Height
1	10.640	1193109	16.00	81434
2	11.243	6264700	84.00	407738

Ethyl (R)-5-allyl-5-cyclopropyl-2-oxo-2,5-dihydrofuran-3-carboxylate (C28)



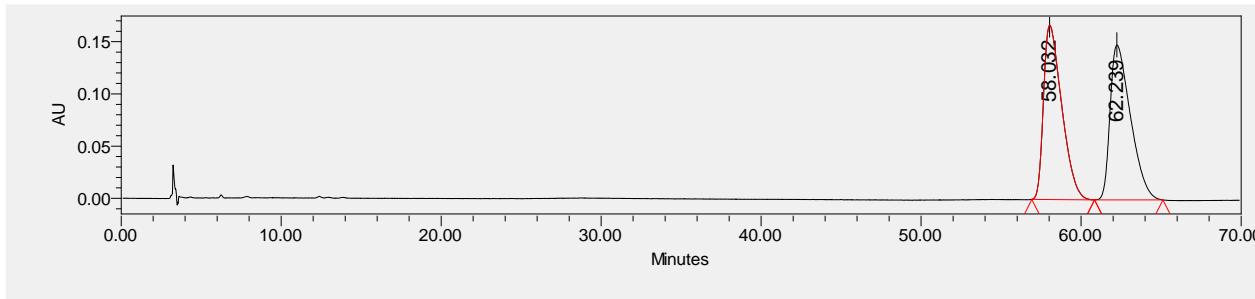
Results: colorless oil, 99% yield, 86% ee; $[\alpha]^{24}_D = +24.6$ ($c = 0.390$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiraldex IC, *n*-hexane/*i*-PrOH 95/5, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{major})} = 57.79$ min, $t_{R(\text{minor})} = 62.72$ min;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.02 (s, 1H), 5.78 – 5.62 (m, 1H), 5.23 – 5.13 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 2.67 (d, $J = 7.3$ Hz, 1H), 1.37 (t, $J = 7.1$ Hz, 3H), 0.66 – 0.43 (m, 3H), 0.31 – 0.21 (m, 1H);

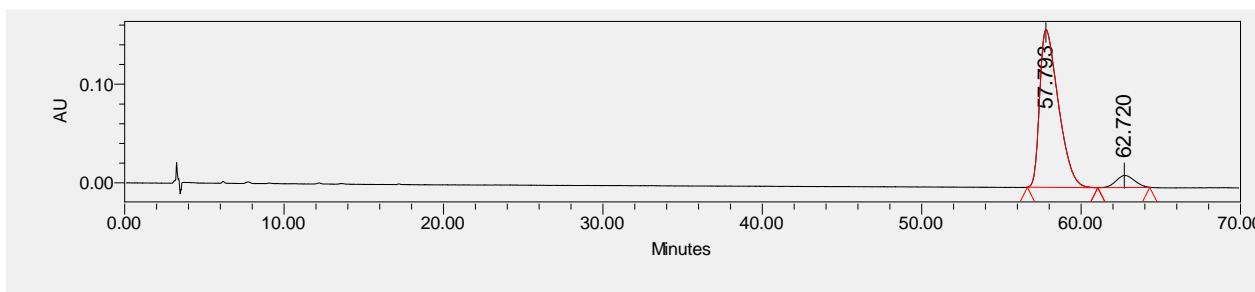
$^{13}\text{C}\{^1\text{H}\} \text{NMR}$ (101 MHz, Chloroform-*d*): δ 166.09, 164.45, 159.28, 129.33, 124.60, 119.85, 85.30, 60.93, 41.14, 15.88, 13.29, 1.16, 0.00;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3082, 3006, 2986, 2917, 2349, 1777, 1722, 1275, 1260, 1048, 995, 764, 750;

ESI-HRMS calcd for [C₁₃H₁₆O₄+Na⁺]: 259.0941, found 259.0938;

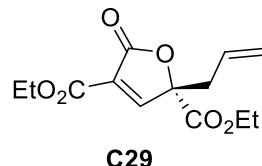


	Retention Time	Area	% Area	Height
1	58.032	13207767	50.09	167089
2	62.239	13161258	49.91	148402



	Retention Time	Area	% Area	Height
1	57.793	12998197	92.98	159771
2	62.720	982096	7.02	12190

Diethyl (S)-2-allyl-5-oxo-2,5-dihydrofuran-2,4-dicarboxylate (C29)



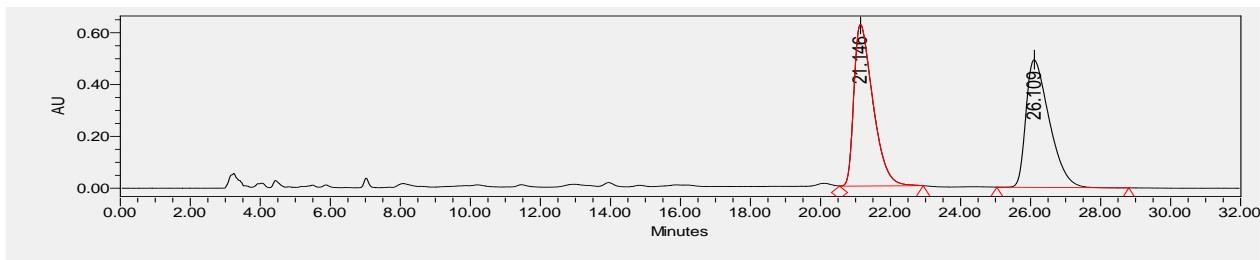
Results: colorless oil, 97% yield, 81% ee; $[\alpha]^{24}_D = -80.6$ ($c = 0.360$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{major})} = 21.51$ min, $t_{R(\text{minor})} = 26.58$ min;

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*): δ 8.08 (s, 1H), 5.73 – 5.61 (m, 1H), 5.28 – 5.18 (m, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 3H), 2.92 (dd, $J = 14.2, 7.6$ Hz, 1H), 2.77 (dd, $J = 14.3, 6.9$ Hz, 1H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.31 (t, $J = 7.2$ Hz, 3H);

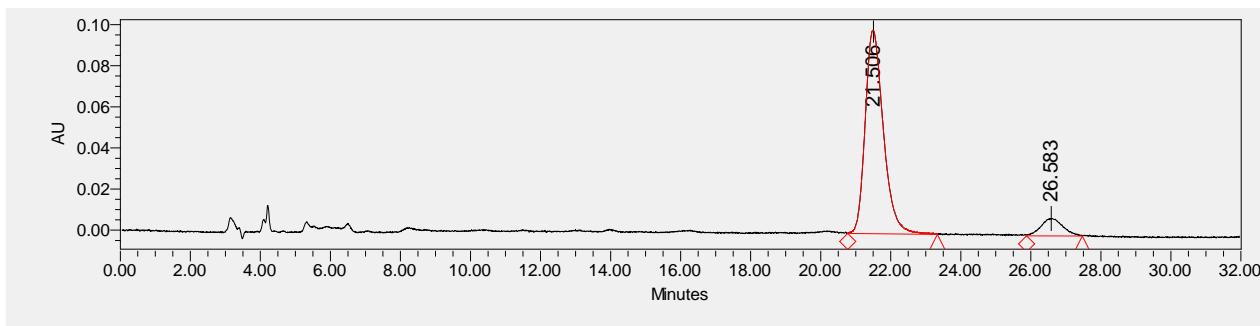
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, Chloroform-*d*): δ 166.08, 165.81, 160.18, 159.50, 128.53, 126.55, 121.92, 86.56, 63.18, 62.08, 39.74, 14.09, 14.07;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3087, 2985, 2937, 1792, 1722, 1643, 1370, 1336, 1259, 1032, 764, 750;

ESI-HRMS calcd for [C₁₃H₁₆O₆+Na⁺]: 291.0840, found 291.0834;

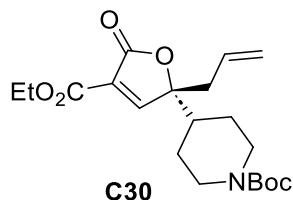


	Retention Time	Area	% Area	Height
1	21.146	23500919	50.79	624252
2	26.109	22768981	49.21	492343



	Retention Time	Area	% Area	Height
1	21.506	3566549	90.64	99022
2	26.583	368120	9.36	8504

tert-Butyl (R)-4-(2-allyl-4-(ethoxycarbonyl)-5-oxo-2,5-dihydrofuran-2-yl)piperidine-1-carboxylate (C30)



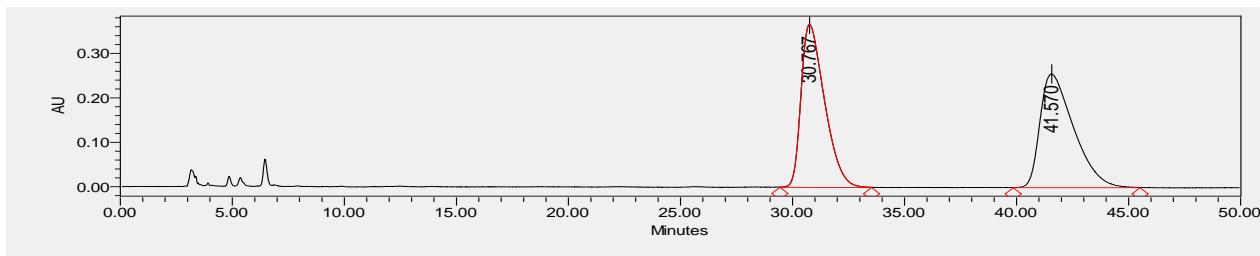
Results: colorless oil, 88% yield, 86% ee; $[\alpha]^{24}_D = -19.6$ ($c = 0.628$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak IC, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{minor})} = 31.46$ min, $t_{R(\text{major})} = 42.03$ min;

^1H NMR (400 MHz, Chloroform-*d*): δ 8.03 (s, 1H), 5.68 – 5.56 (m, 1H), 5.23 – 5.12 (m, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 4.19 (s, 3H), 2.69 – 2.50 (m, 4H), 2.03 – 1.91 (m, 1H), 1.85 – 1.62 (m, 2H), 1.45 (s, 9H), 1.37 (t, $J = 7.1$ Hz, 3H), 1.33 – 1.22 (m, 3H);

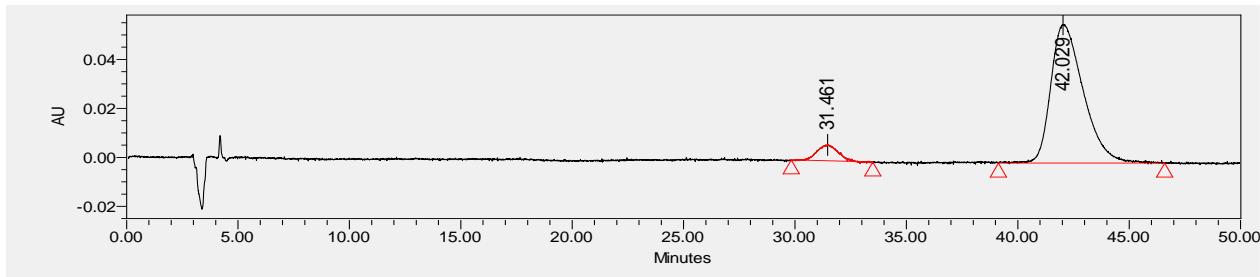
$^{13}\text{C}\{\text{H}\}$ NMR (101 MHz, Chloroform-*d*): δ 166.64, 164.60, 159.87, 154.46, 129.63, 126.64, 121.12, 89.20, 79.80, 61.87, 42.13, 38.80, 28.41, 26.84, 26.05, 14.13;

IR (film): $\tilde{\nu}$ (cm⁻¹) 2982, 1778, 1689, 1425, 1275, 1260, 1167, 764, 750;

ESI-HRMS calcd for [C₂₀H₂₉NO₆+Na⁺]: 402.1888, found 402.1881;

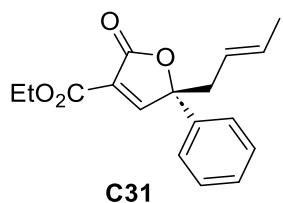


	Retention Time	Area	% Area	Height
1	30.767	26731085	50.02	366964
2	41.570	26706821	49.98	255823



	Retention Time	Area	% Area	Height
1	31.461	431040	6.97	6541
2	42.029	5755563	93.03	56630

Ethyl (S,E)-5-(but-2-en-1-yl)-2-oxo-5-phenyl-2,5-dihydrofuran-3-carboxylate (C31)

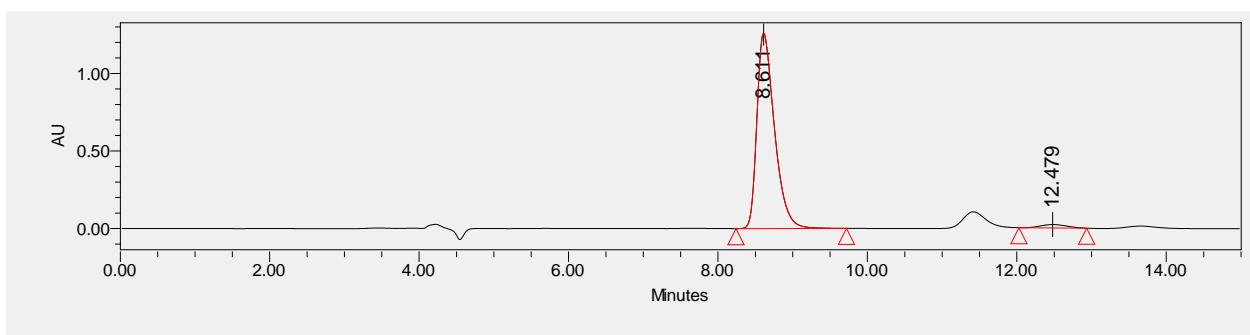
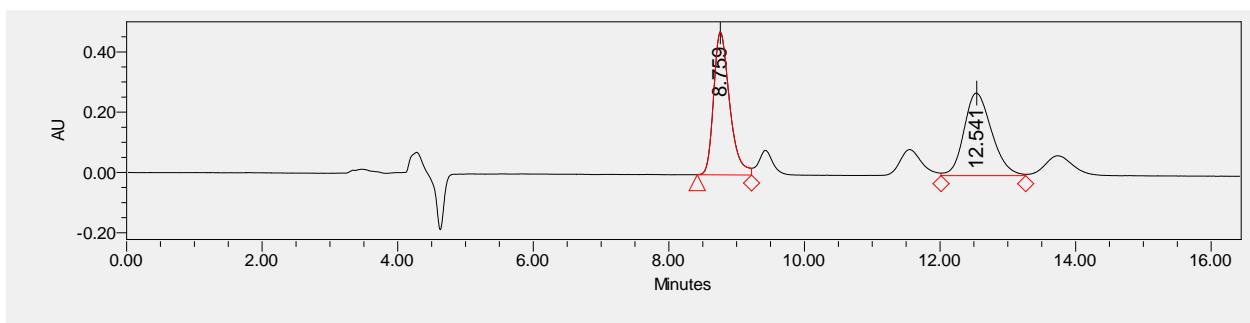


Results: colorless oil, 99% yield, 95% ee; $[\alpha]^{24}_D = -75.4$ ($c = 0.516$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak OJH, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{major})} = 8.61$ min, $t_{R(\text{minor})} = 12.48$ min;

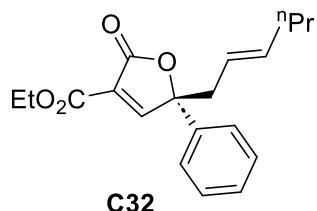
¹H NMR (400 MHz, Chloroform-*d*): δ 8.32 (s, 1H), 7.45 – 7.29 (m, 5H), 5.63 – 5.49 (m, 1H), 5.29 – 5.15 (m, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 2.81 (qdt, $J = 14.3, 7.2, 1.2$ Hz, 2H), 1.66 – 1.54 (m, 3H), 1.35 (t, $J = 7.1$ Hz, 3H);

¹³C{¹H NMR} (101 MHz, Chloroform-*d*): δ 166.73, 165.28, 160.15, 137.47, 132.17, 128.99, 128.63, 125.19, 124.58, 121.94, 88.27, 61.81, 42.93, 18.05, 14.15;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3086, 2984, 2918, 1778, 1723, 1371, 1334, 1315, 1275, 1065, 1032, 800, 750, 700; **ESI-HRMS** calcd for [C₁₇H₁₈O₄+Na⁺]: 309.1098, found 309.1092;



Ethyl (S,E)-5-(hex-2-en-1-yl)-2-oxo-5-phenyl-2,5-dihydrofuran-3-carboxylate (C32)



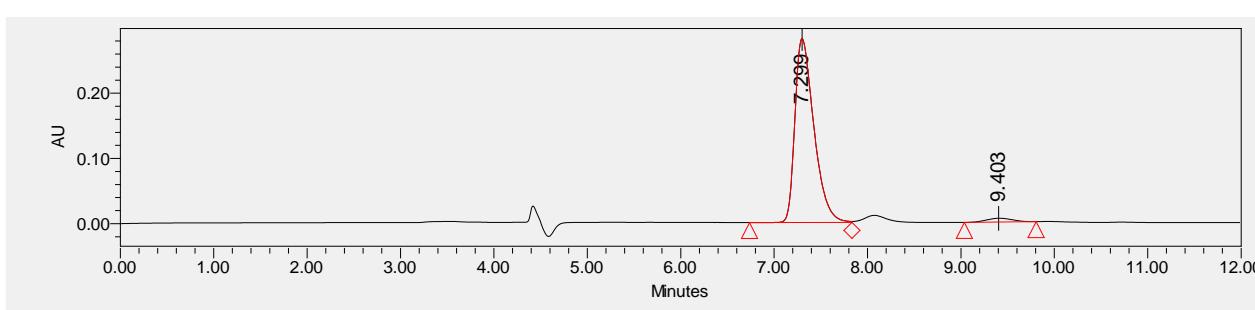
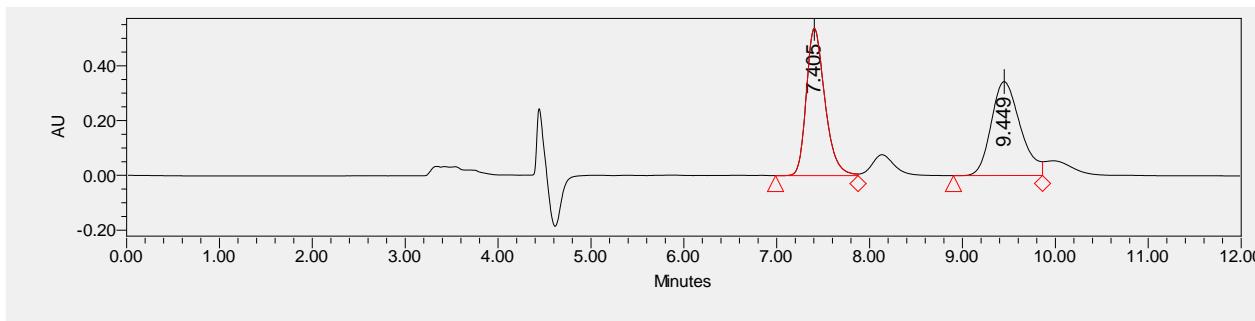
Results: colorless oil, 99% yield, 95% ee; $[\alpha]^{24}_D = -60.8$ ($c = 0.592$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak OJH, *n*-hexane/*i*-PrOH 75/25, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{major})} = 7.30$ min, $t_{R(\text{minor})} = 9.40$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.31 (s, 1H), 7.44 – 7.29 (m, 5H), 5.60 – 5.45 (m, 1H), 5.27 – 5.15 (m, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 2.95 – 2.72 (m, 2H), 1.92 (q, $J = 7.1$ Hz, 1H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.29 (q, $J = 7.3$ Hz, 2H), 0.80 (t, $J = 7.3$ Hz, 3H);

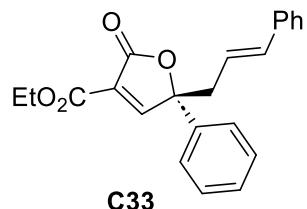
¹³C{¹H NMR} (101 MHz, Chloroform-*d*): δ 166.71, 165.29, 160.12, 137.60, 137.48, 128.97, 128.61, 125.19, 124.63, 120.99, 88.34, 61.78, 42.96, 34.55, 22.25, 14.15, 13.50;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3086, 2959, 2928, 2871, 1779, 1723, 1370, 1334, 1314, 1260, 1066, 1032, 800, 763, 750, 700;

ESI-HRMS calcd for [C₁₉H₂₂O₄+Na⁺]: 337.1411, found 337.1405;



Ethyl (S)-5-cinnamyl-2-oxo-5-phenyl-2,5-dihydrofuran-3-carboxylate (C33)



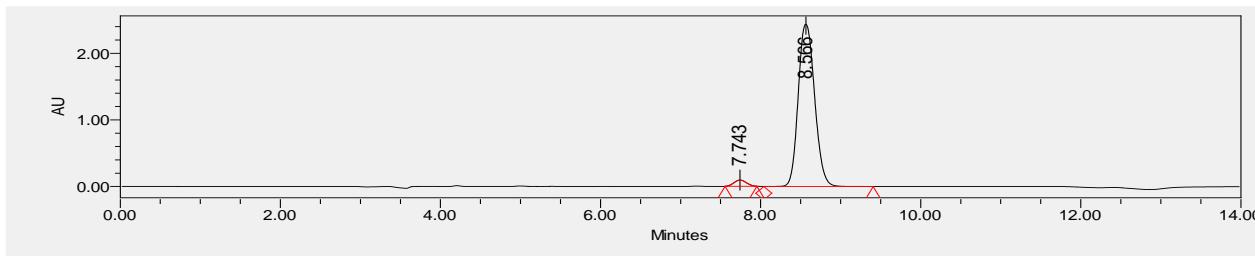
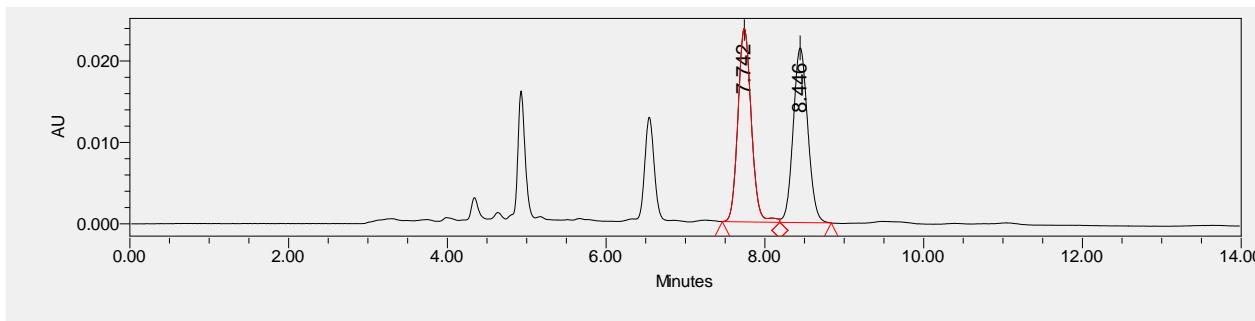
Results: white solid, 84% yield, 94% ee; $[\alpha]^{24}_D = -52.6$ ($c = 0.542$ g/100 mL, $\lambda = 589$ nm, in DCM), HPLC (Daicel Chiralpak ADH, *n*-hexane/*i*-PrOH 70/30, 1.0 mL/min, $\lambda = 210$ nm, $t_{R(\text{minor})} = 7.74$ min, $t_{R(\text{major})} = 8.57$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 8.39 (s, 1H), 7.47 – 7.33 (m, 5H), 7.31 – 7.19 (m, 5H), 6.45 (d, $J = 15.8$ Hz, 1H), 5.96 (dt, $J = 15.7, 7.3$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 3.06 (ddd, $J = 14.3, 7.4, 1.3$ Hz, 1H), 2.98 (ddd, $J = 14.4, 7.2, 1.3$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H);

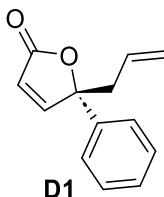
¹³C{¹H NMR} (101 MHz, Chloroform-*d*): δ 166.54, 165.05, 160.05, 137.21, 136.48, 135.81, 129.11, 128.80, 128.59, 127.84, 126.38, 125.23, 124.69, 120.86, 88.24, 61.88, 43.38, 14.13;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3083, 3029, 2982, 2928, 1777, 1722, 1494, 1448, 1370, 1315, 1274, 1068, 1031, 800, 749, 700;

ESI-HRMS calcd for [C₂₂H₂₀O₄+Na⁺]: 371.1254, found 371.1247;



(S)-5-Allyl-5-phenylfuran-2(5H)-one (D1)



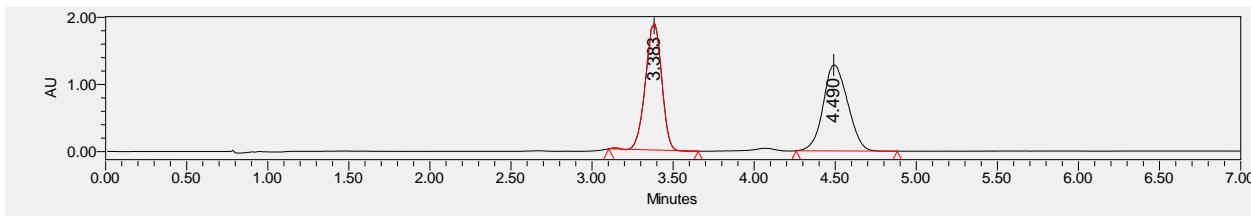
Results: colorless oil, 40% yield, 93% ee; $[\alpha]^{24}_D = -128.5$ ($c = 0.474$ g/100 mL, $\lambda = 589$ nm, in DCM), UPC² (Daicel Chiralpak IG, CO₂/MeOH 90/10, 1.5 mL/min, $\lambda = 210$ nm, $t_{R(\text{minor})} = 3.37$ min, $t_{R(\text{major})} = 4.51$ min;

¹H NMR (400 MHz, Chloroform-*d*): δ 7.65 (d, $J = 5.6$ Hz, 1H), 7.47 – 7.29 (m, 5H), 6.10 (d, $J = 5.6$ Hz, 1H), 5.61 (ddt, $J = 16.6, 10.7, 7.2$ Hz, 1H), 5.17 – 5.07 (m, 2H), 2.89 (ddt, $J = 14.3, 7.2, 1.2$ Hz, 1H), 2.79 (ddt, $J = 14.3, 7.0, 1.1$ Hz, 1H);

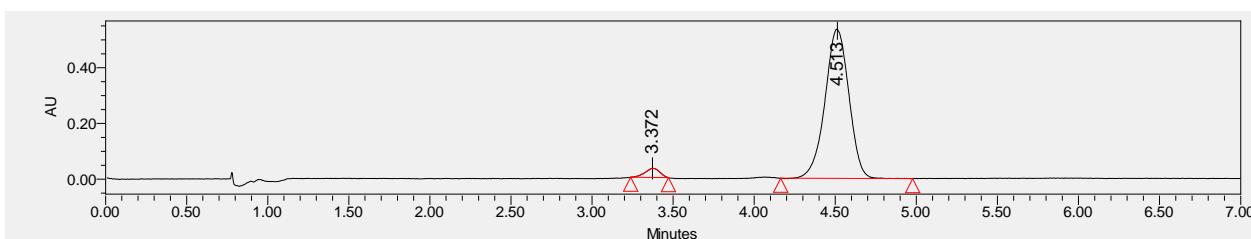
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): δ 172.08, 158.68, 138.58, 130.41, 128.83, 128.35, 125.12, 120.61, 120.47, 90.73, 44.05;

IR (film): $\tilde{\nu}$ (cm⁻¹) 3006, 2988, 1761, 1722, 1275, 1260, 1197, 930, 764, 750;

ESI-HRMS calcd for [C₁₃H₁₂O₂+Na⁺]: 223.0730, found 223.0727;

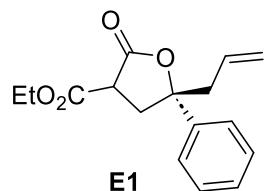


	Retention Time	Area	% Area	Height
1	3.383	13140011	49.45	1889894
2	4.490	13431946	50.55	1277987



	Retention Time	Area	% Area	Height
1	3.372	204929	3.60	32945
2	4.513	5479843	96.40	536495

Ethyl (5S)-5-allyl-2-oxo-5-phenyltetrahydrofuran-3-carboxylate (E1)



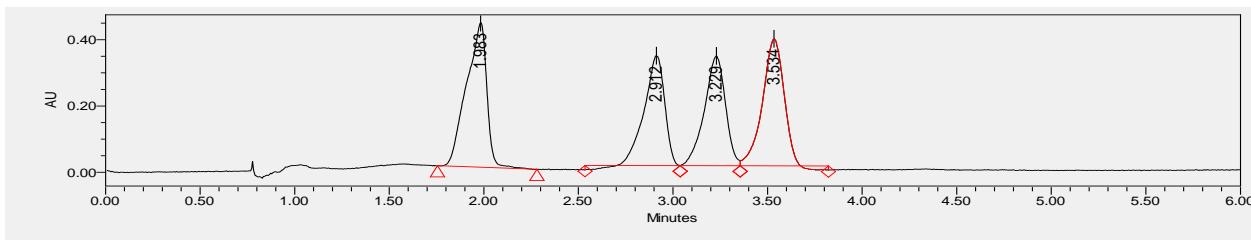
Results: colorless oil, 99% yield, 1.1/1 dr, 91/95% ee; $[\alpha]^{24}_D = -17.5$ ($c = 0.514$ g/100 mL, $\lambda = 589$ nm, in DCM), UPC² (Daicel Chiralpak IG, CO₂/MeOH 90/10, 1.5 mL/min, $\lambda = 210$ nm, $t_{R(\text{minor})} = 1.99$ min, $t_{R(\text{minor})} = 2.93$ min $t_{R(\text{major})} = 3.24$ min, $t_{R(\text{major})} = 3.55$ min);

¹H NMR (400 MHz, Chloroform-*d*): diastereomer mixture, δ 7.43 – 7.26 (m, 5H), 5.73 – 5.56 (m, 1H), 5.20 – 5.05 (m, 2H), 4.26 (qd, $J = 7.2, 1.6$ Hz, 2H), 4.12 (q, $J = 7.1$ Hz, 2H), 3.78 (t, $J = 9.4$ Hz, 1H), 3.47 (dd, $J = 11.4, 8.8$ Hz, 1H), 2.96 – 2.57 (m, 4H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.19 (t, $J = 7.1$ Hz, 3H);

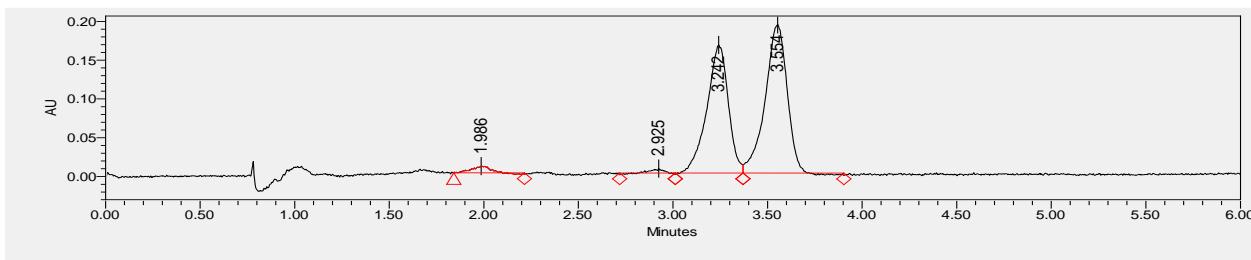
¹³C{¹H} NMR (101 MHz, Chloroform-*d*): diastereomer mixture δ 171.26, 171.08, 167.62, 167.36, 142.90, 141.68, 131.17, 131.09, 128.70, 128.50, 128.07, 127.86, 124.73, 124.56, 120.80, 120.14, 87.52, 87.42, 62.24, 62.21, 47.41, 46.92, 46.63, 46.46, 37.63, 36.78, 14.09, 13.94;

IR (film): $\tilde{\nu}$ (cm⁻¹) 2983, 2928, 1777, 1734, 1275, 1260, 1177, 1019, 969, 764, 750, 702;

ESI-HRMS calcd for [C₁₆H₁₈O₄+Na⁺]: 297.1098, found 297.1094;

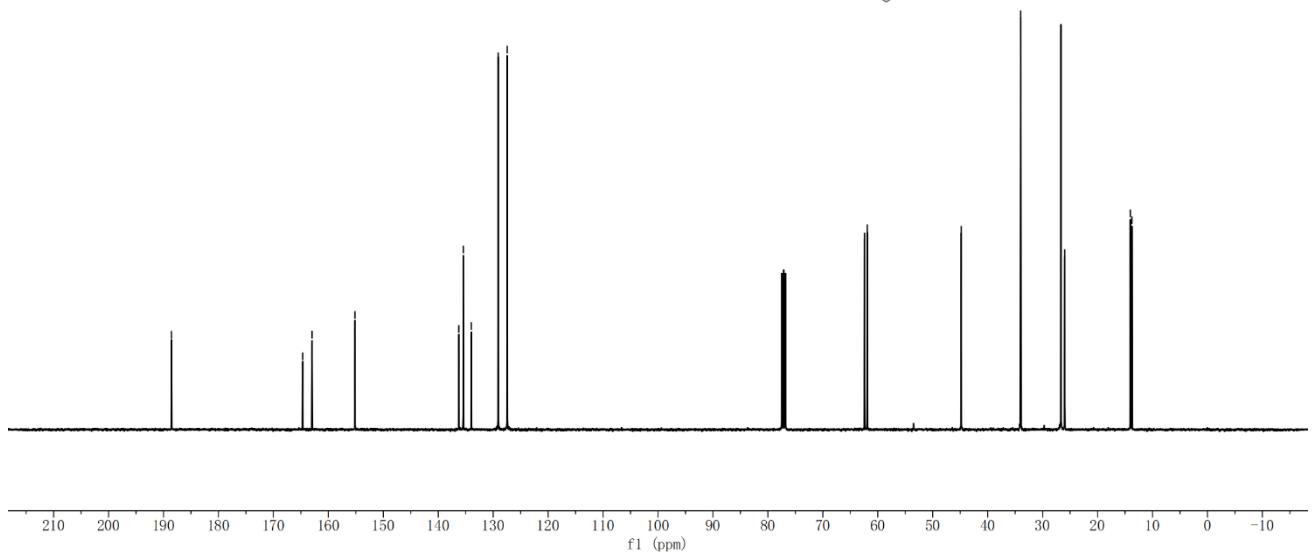
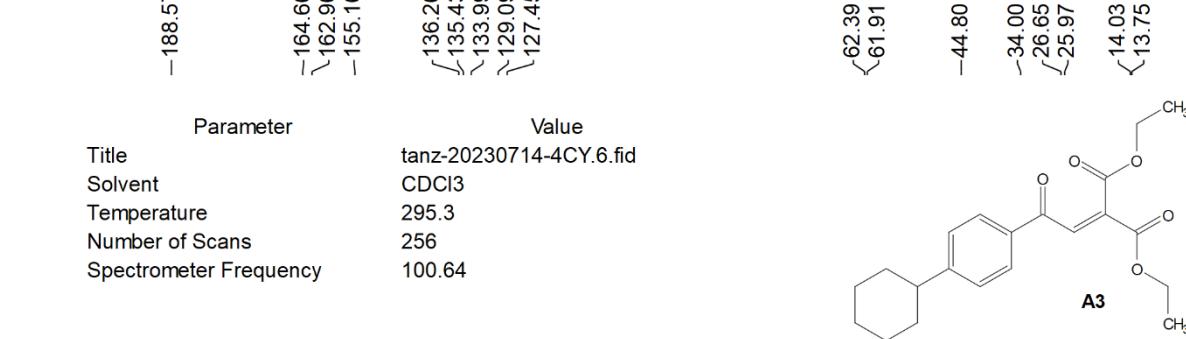
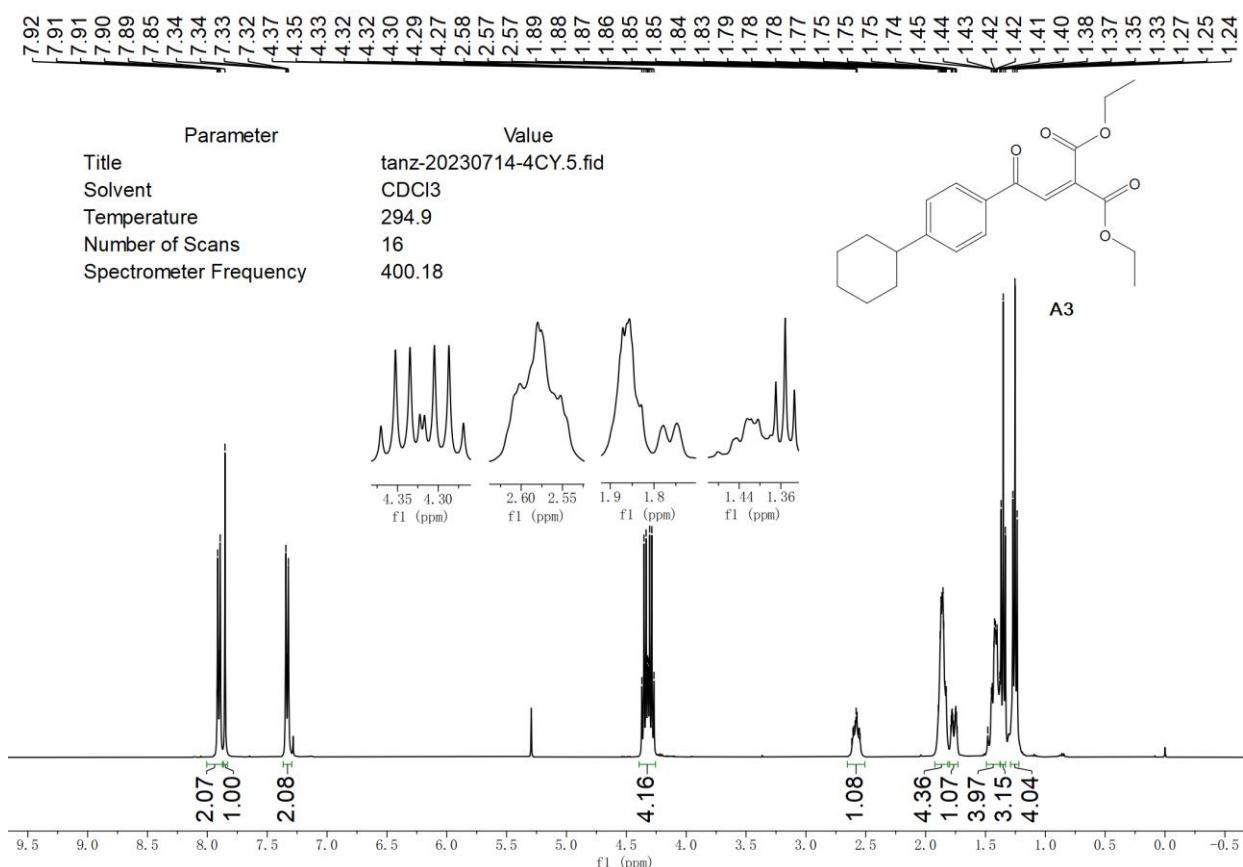


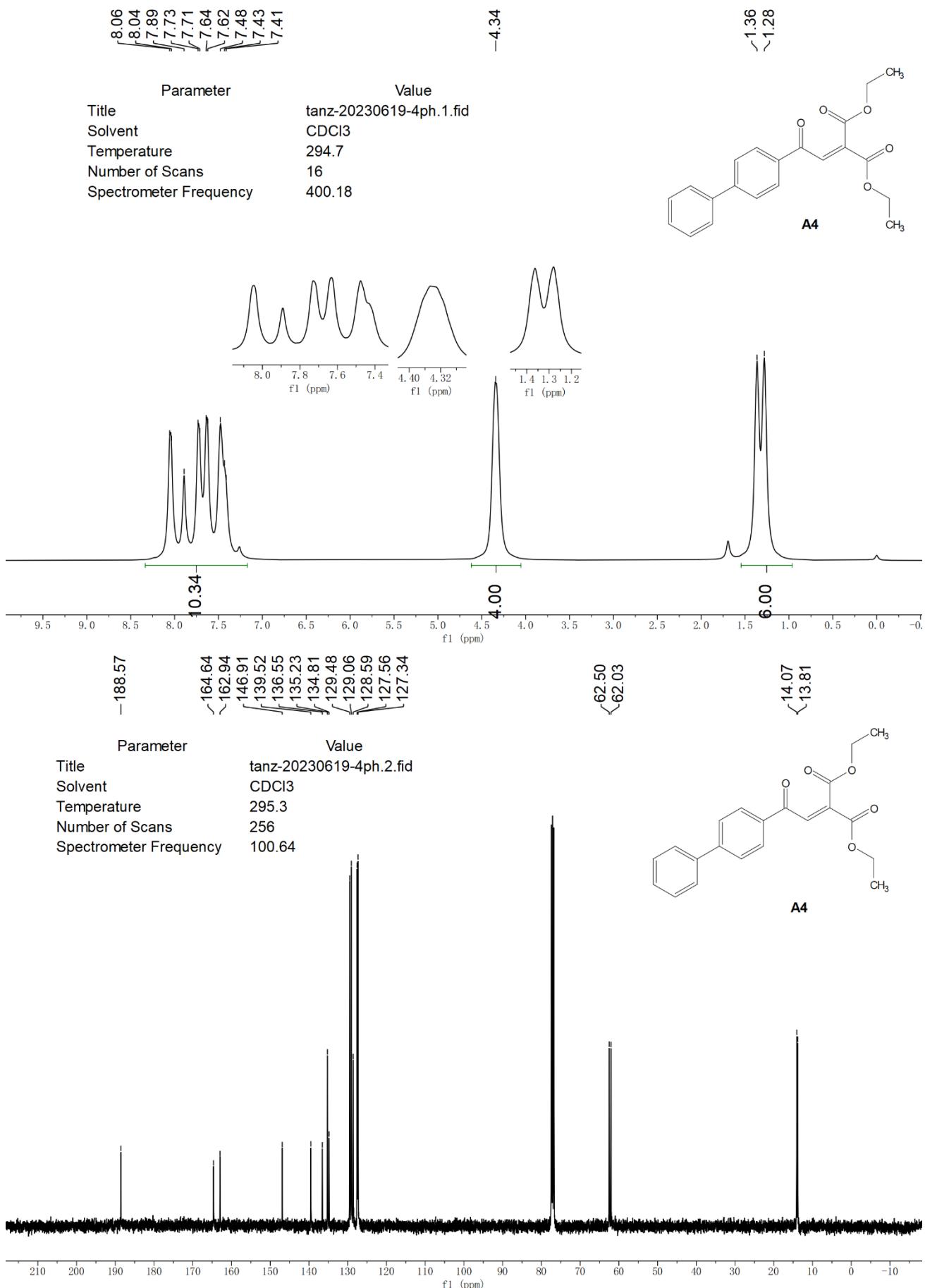
	Retention Time	Area	% Area	Height
1	1.983	3255850	28.24	436069
2	2.912	2592223	22.49	331467
3	3.229	2557871	22.19	331512
4	3.534	3122627	27.09	383318

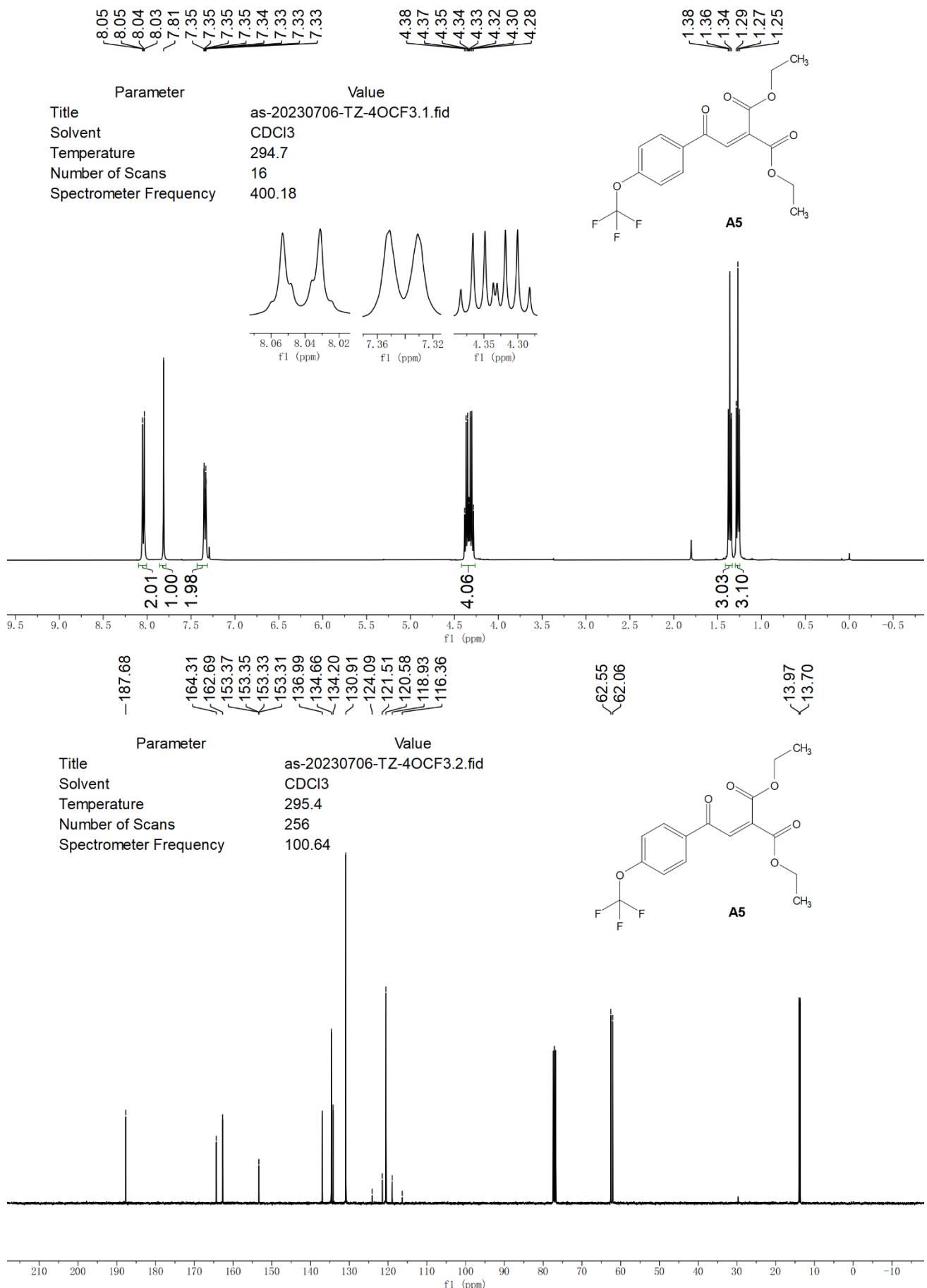


	Retention Time	Area	% Area	Height
1	1.986	66986	2.26	8669
2	2.925	31899	1.08	5877
3	3.242	1302012	43.90	165046
4	3.554	1564683	52.76	191612

(K) Copies of NMR spectra

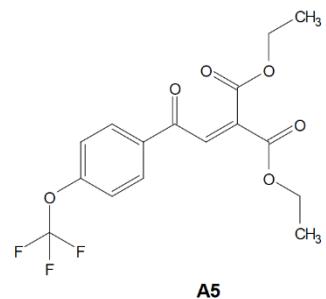




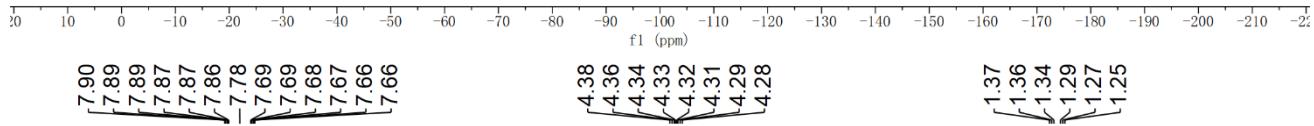
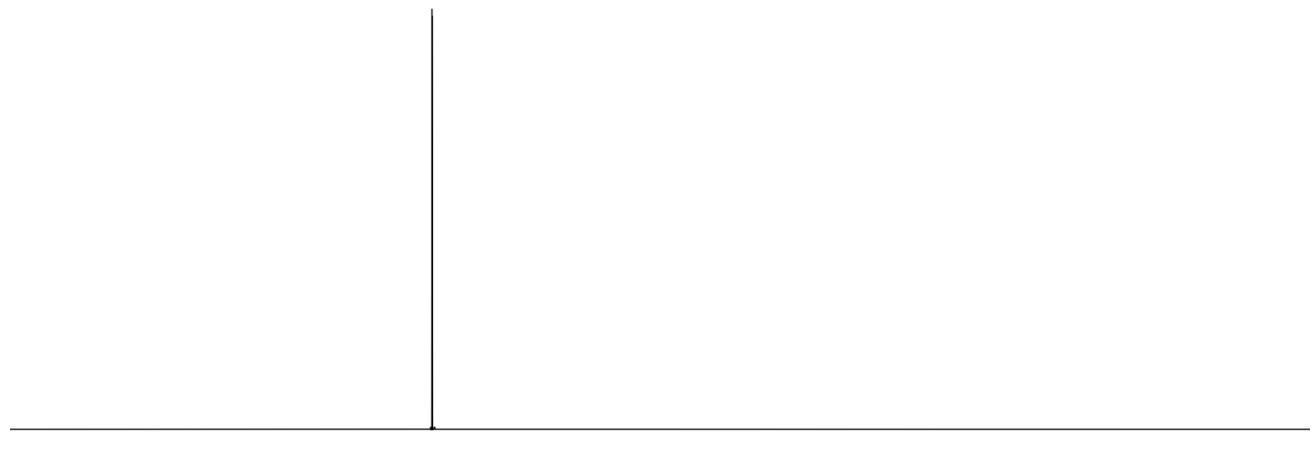


-57.65

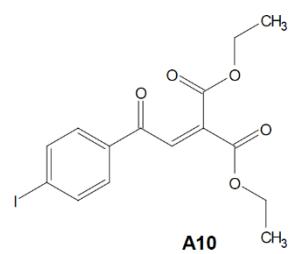
Parameter	Value
Title	as-20230706-TZ-4OCF3.3.fid
Solvent	CDCl ₃
Temperature	295.1
Number of Scans	16
Spectrometer Frequency	376.51



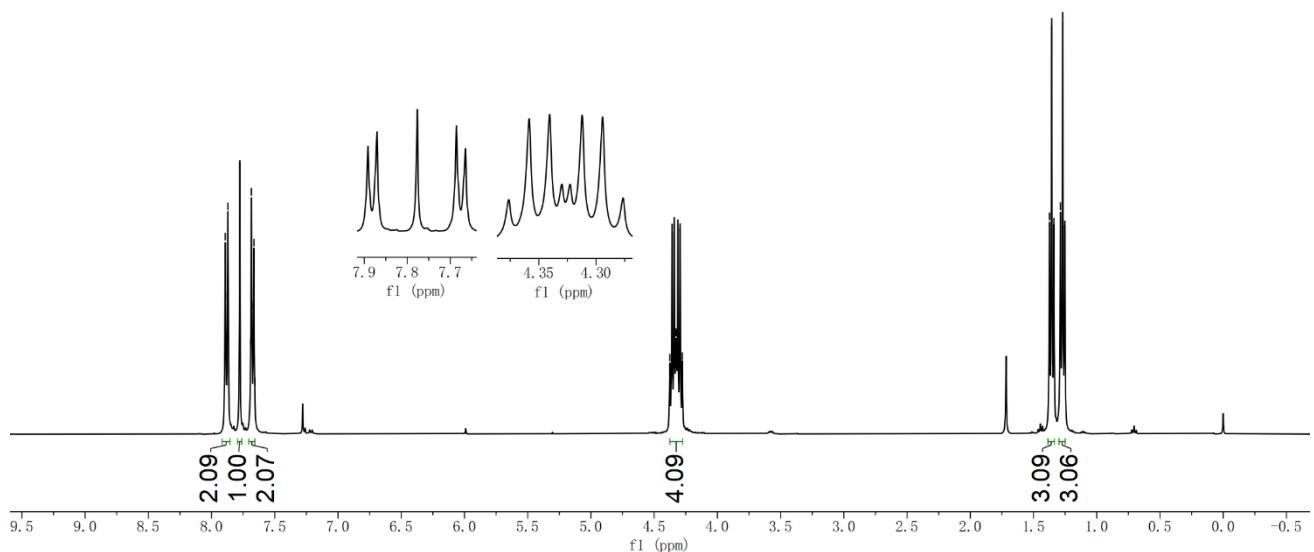
A5

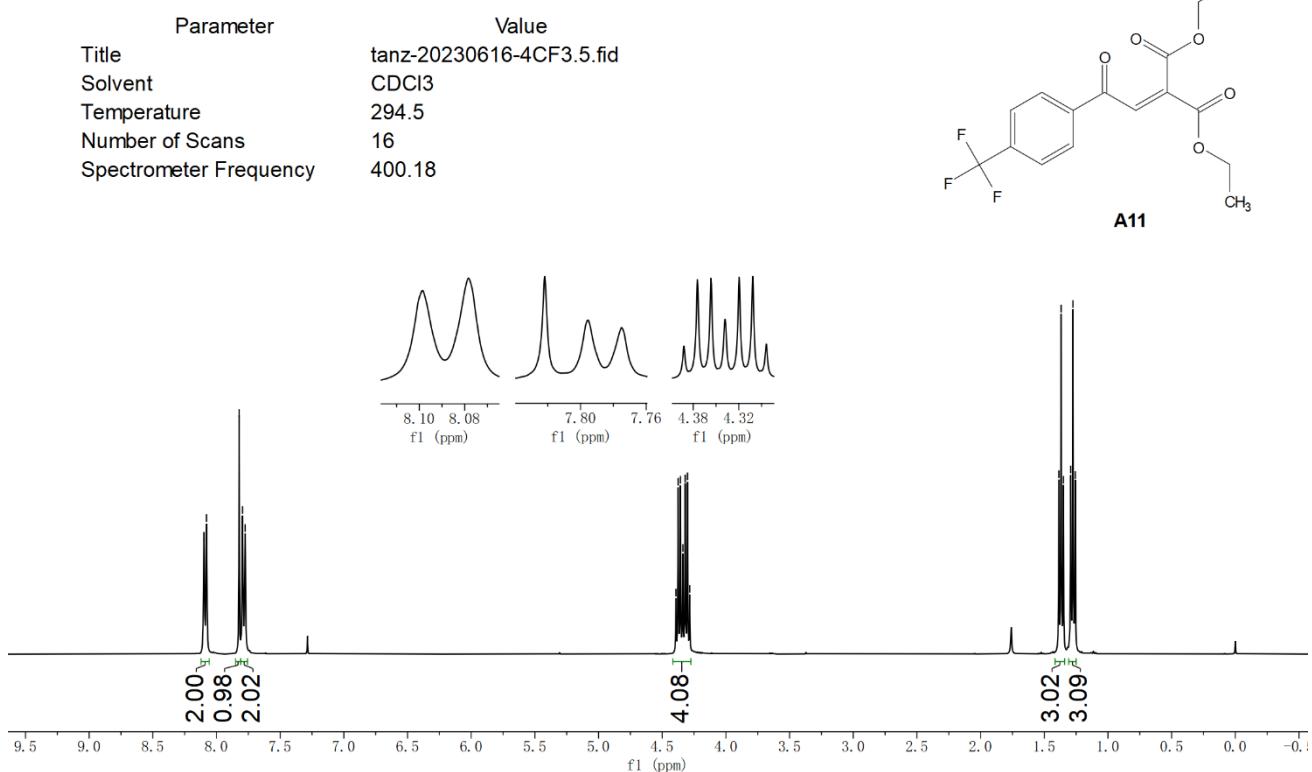
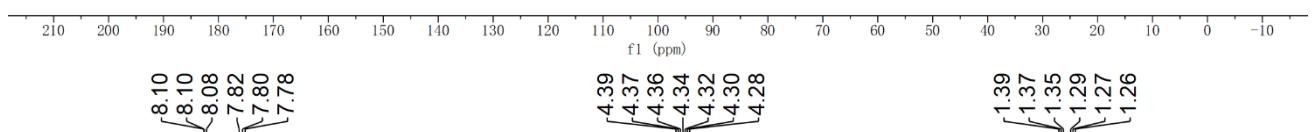
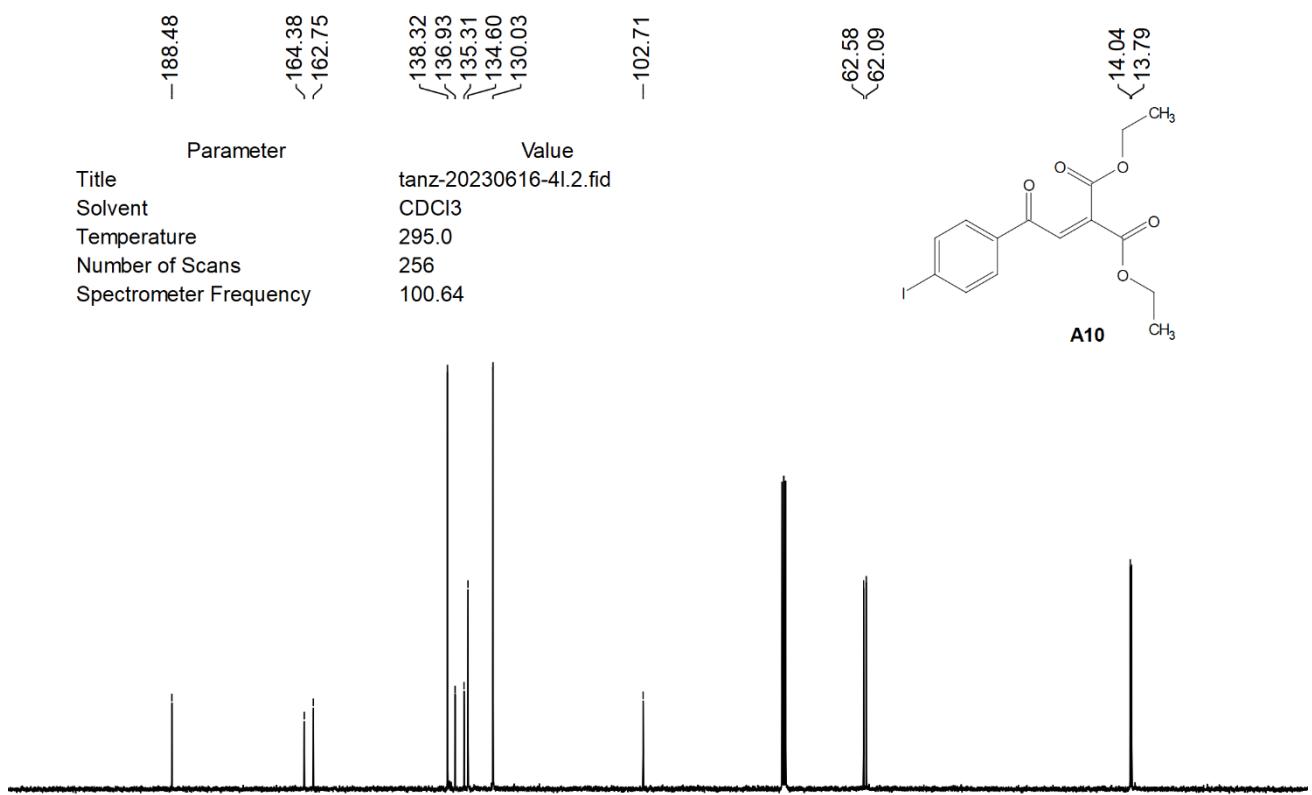


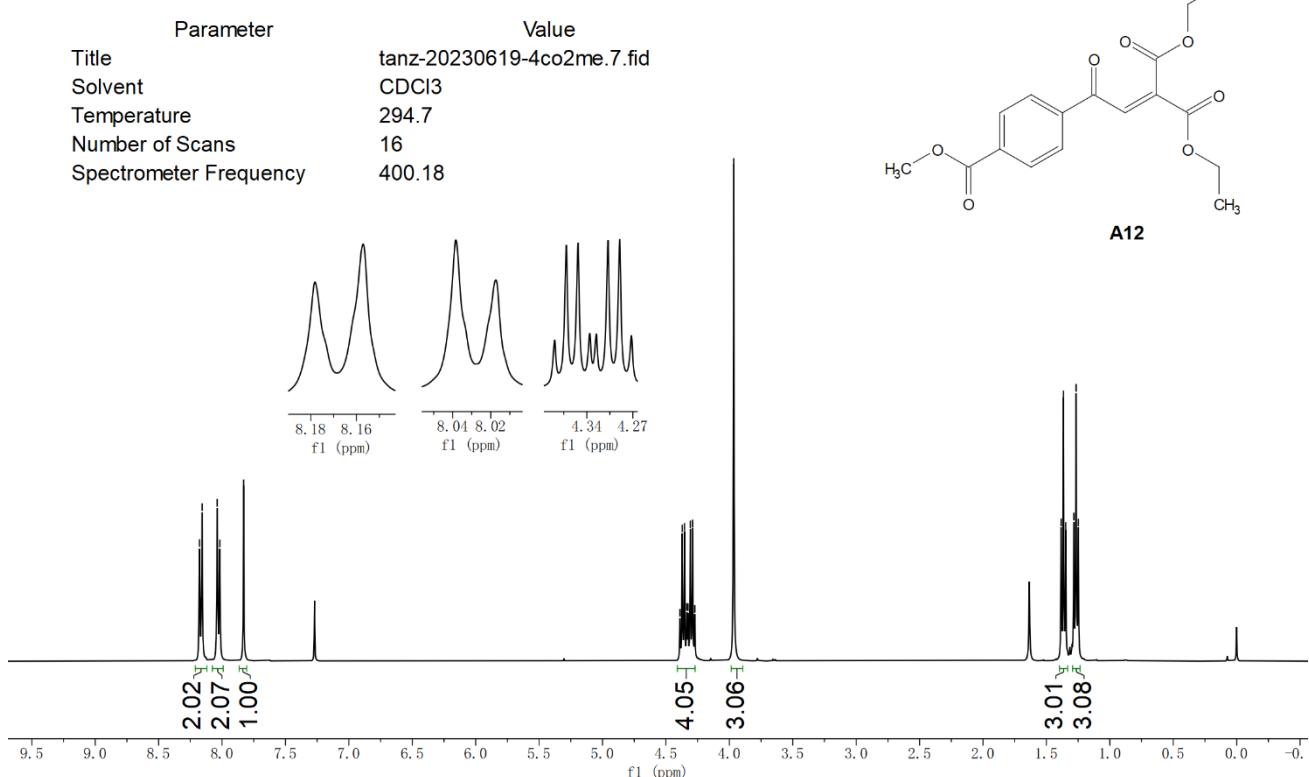
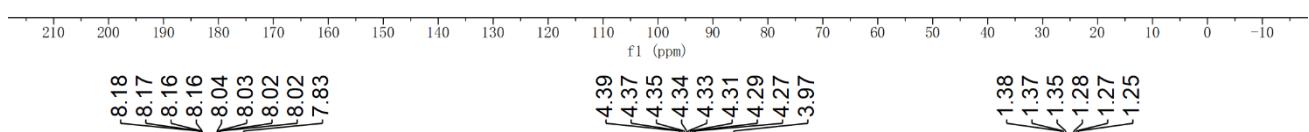
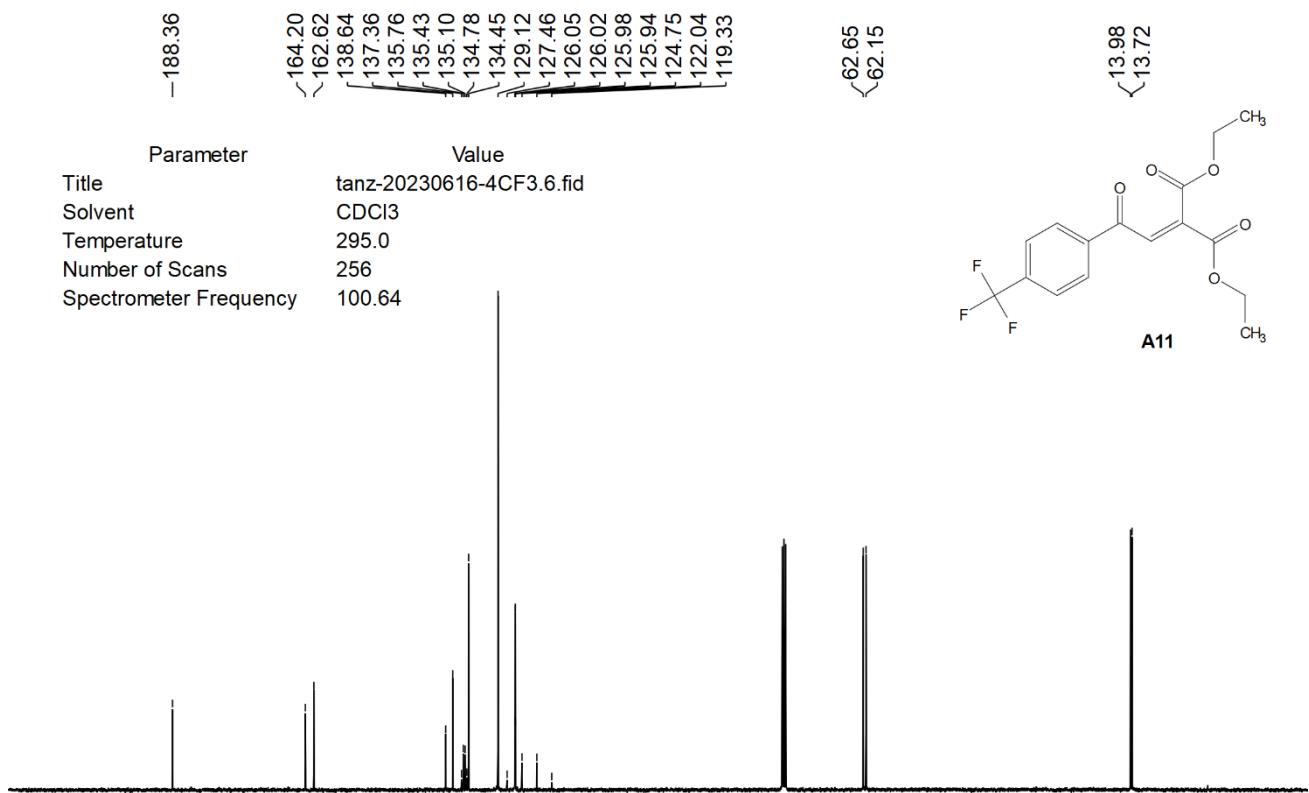
Parameter	Value
Title	tanz-20230616-4I.1.fid
Solvent	CDCl ₃
Temperature	294.5
Number of Scans	16
Spectrometer Frequency	400.18

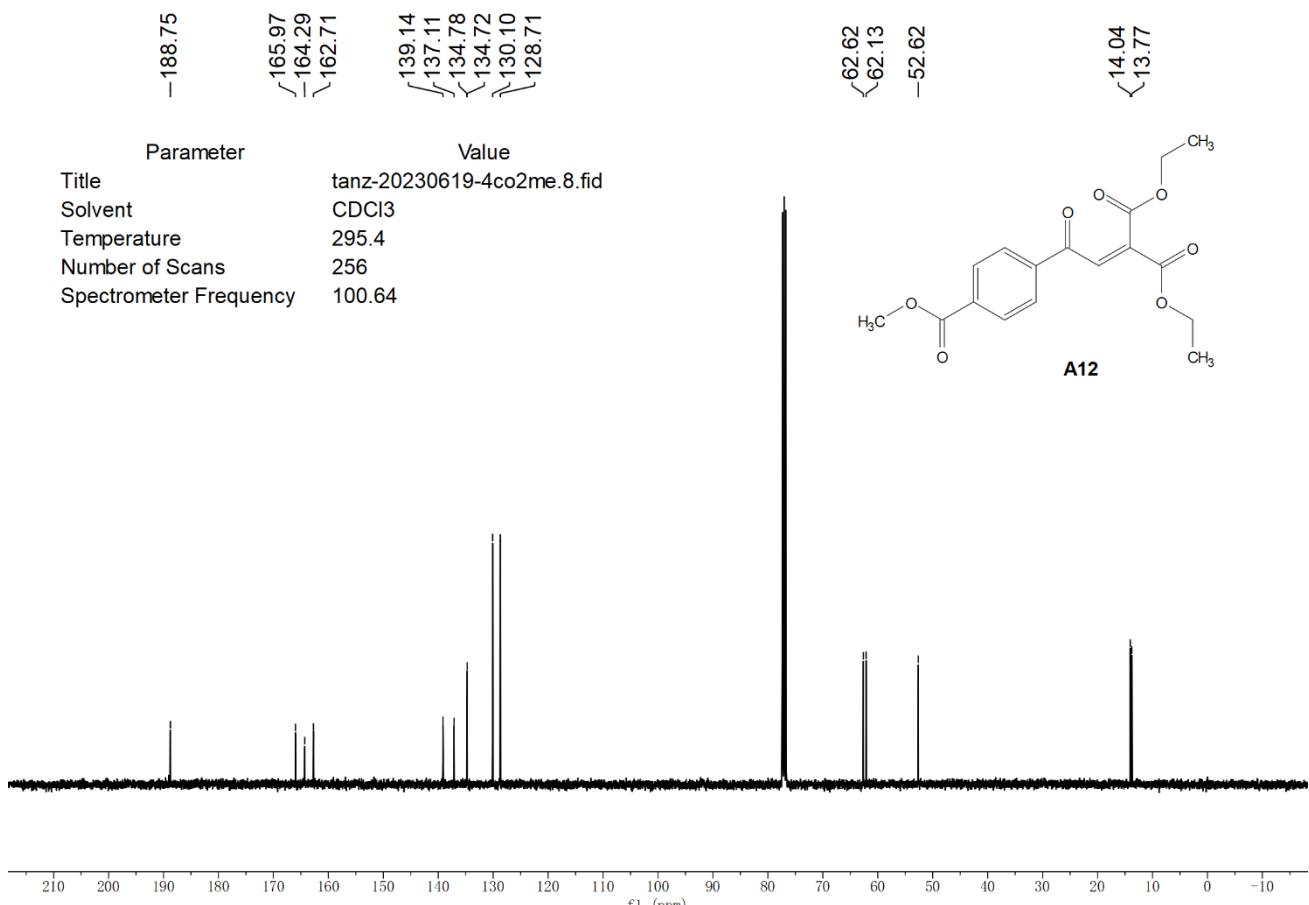


A10









210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

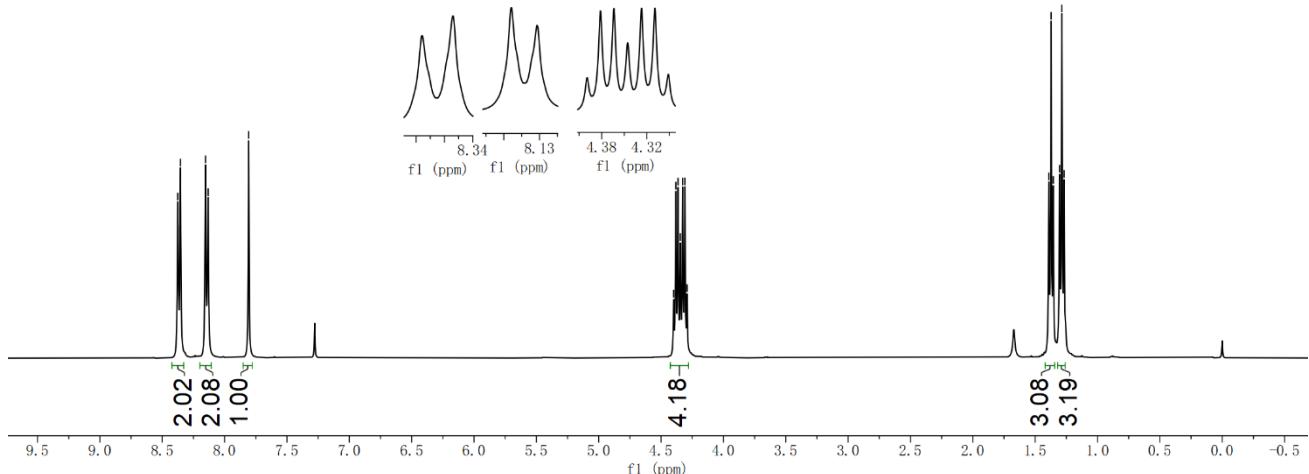
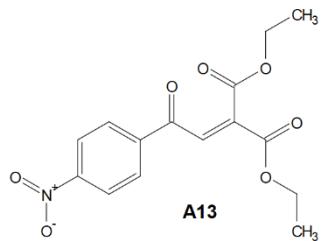
f1 (ppm)

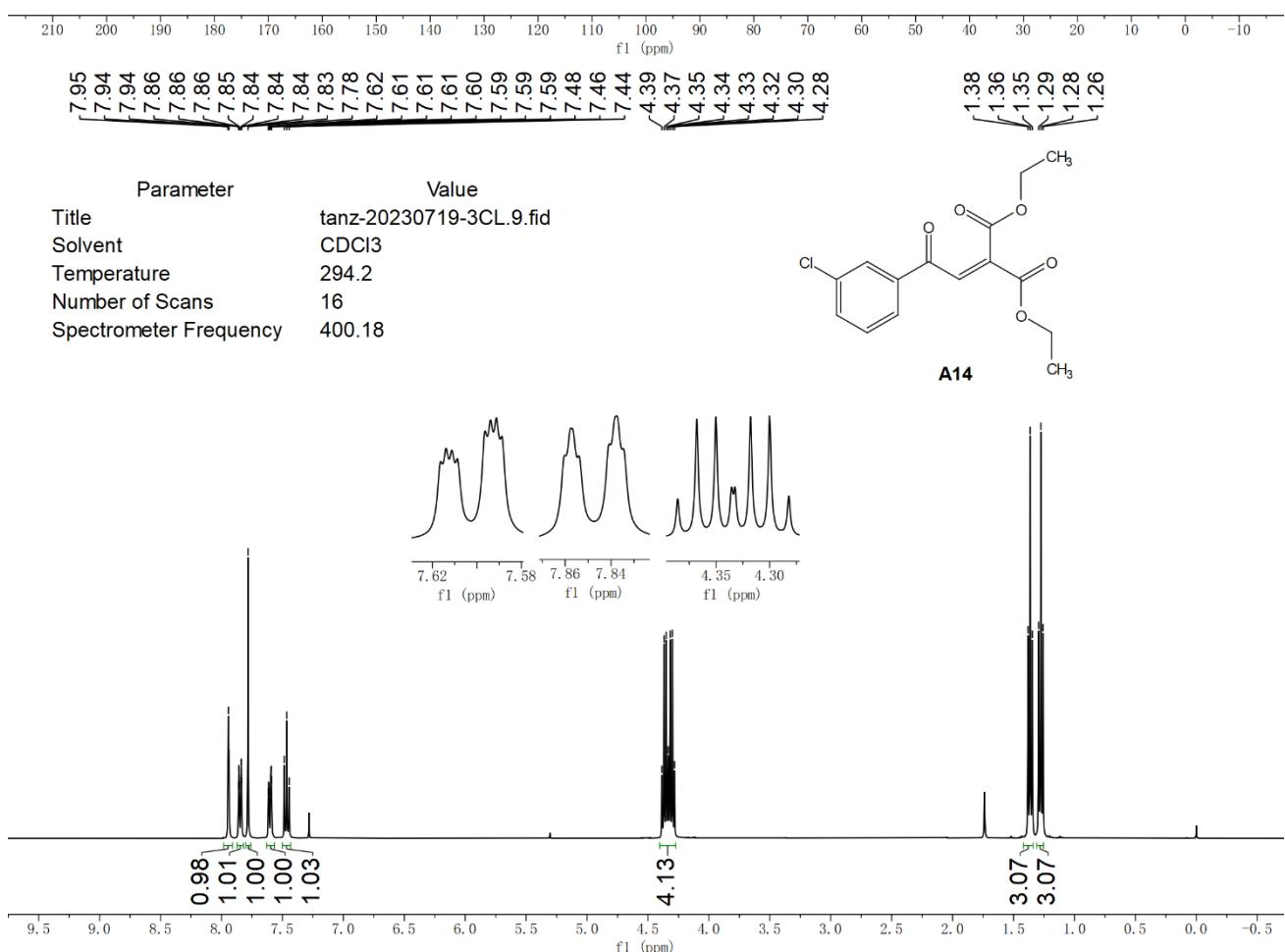
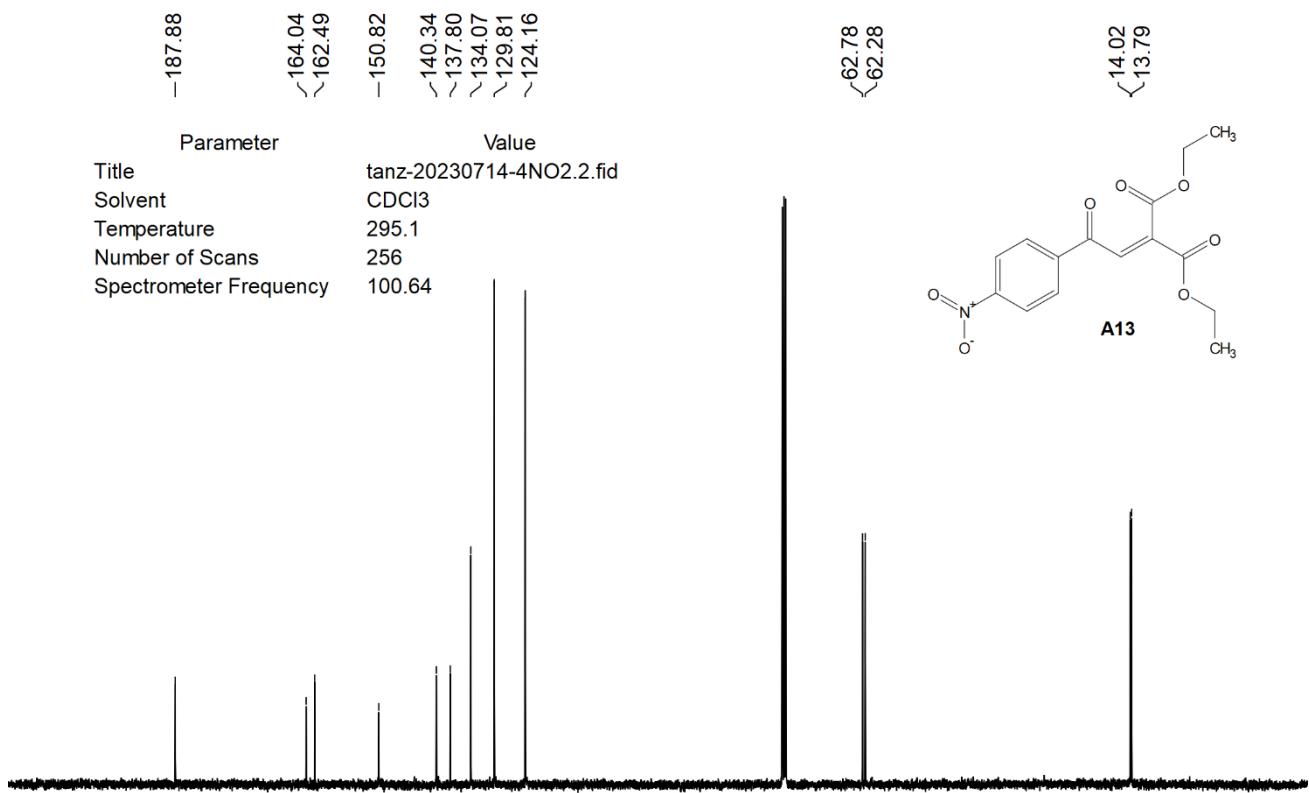
8.38
8.36
8.35
8.15
8.14
8.13
7.81

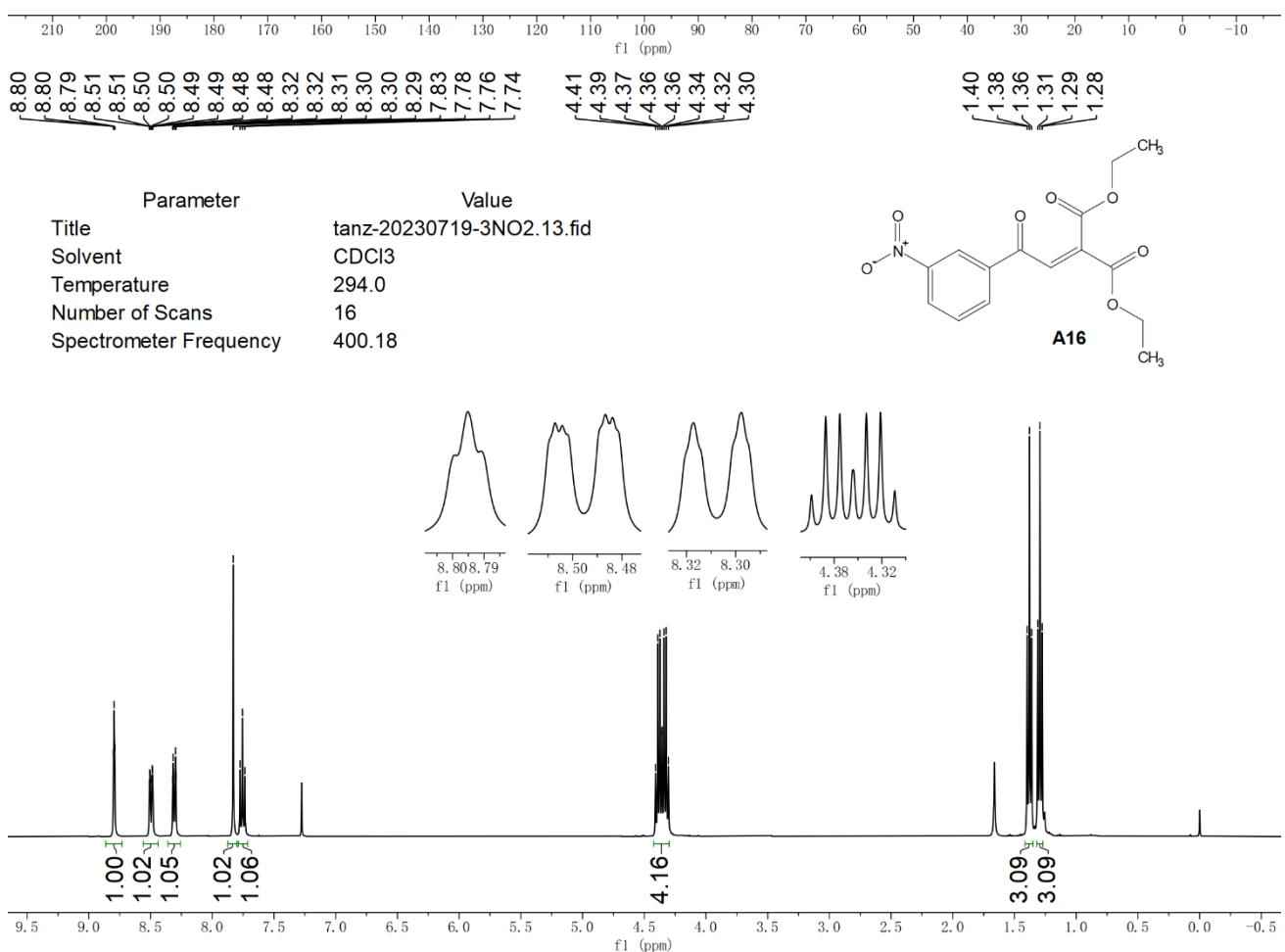
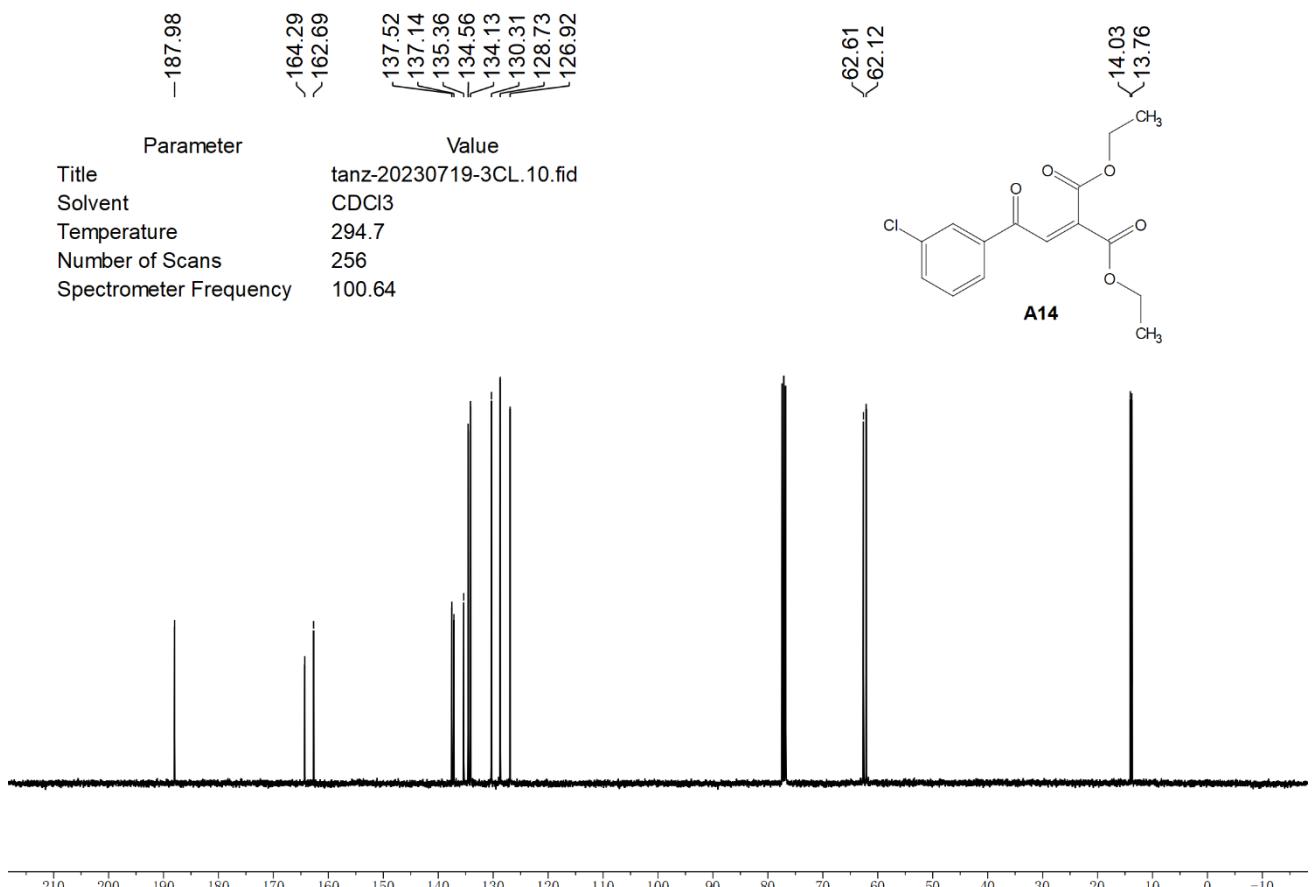
4.40
4.38
4.36
4.35
4.33
4.31
4.29

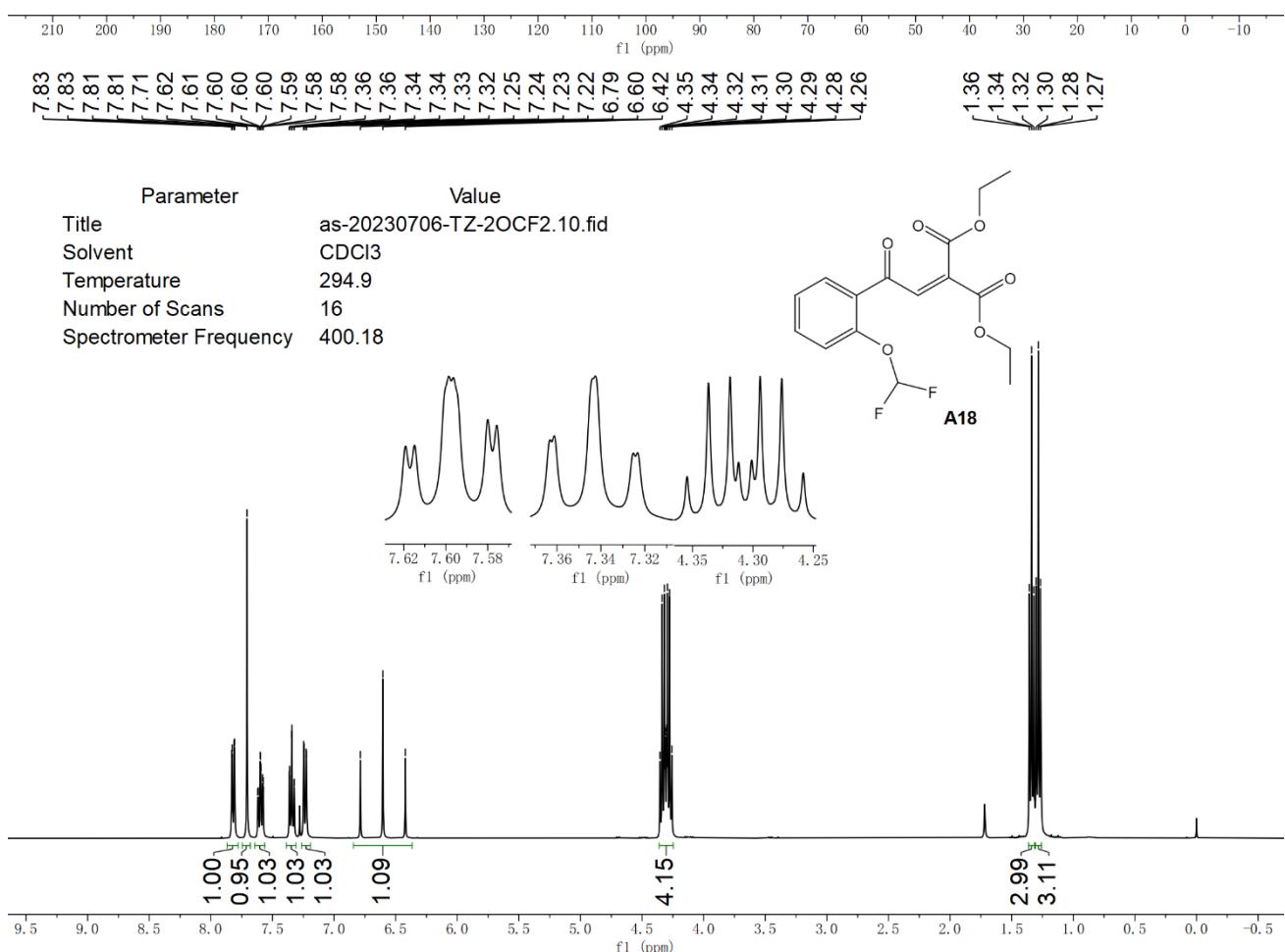
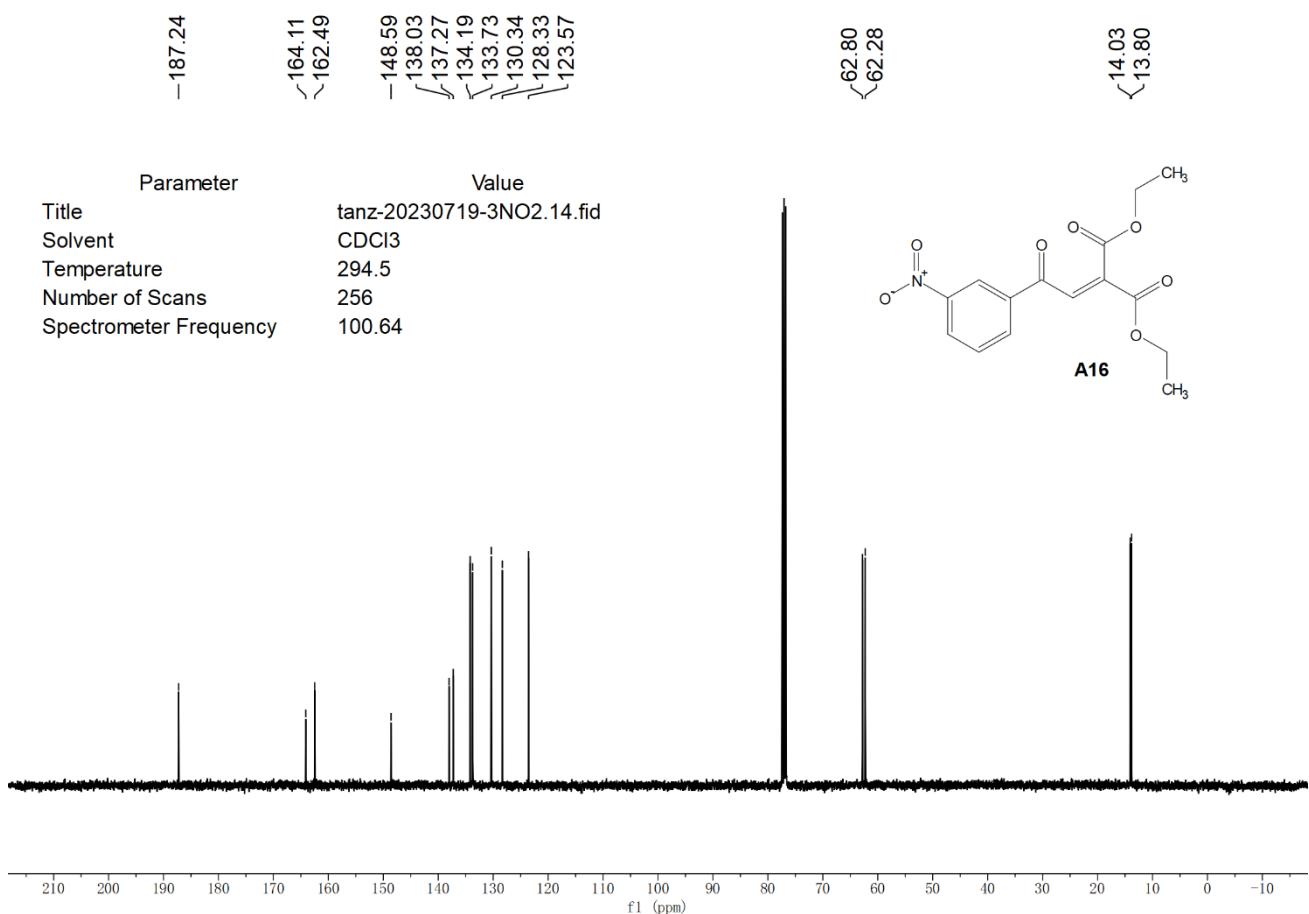
1.39
1.37
1.35
1.30
1.29
1.27

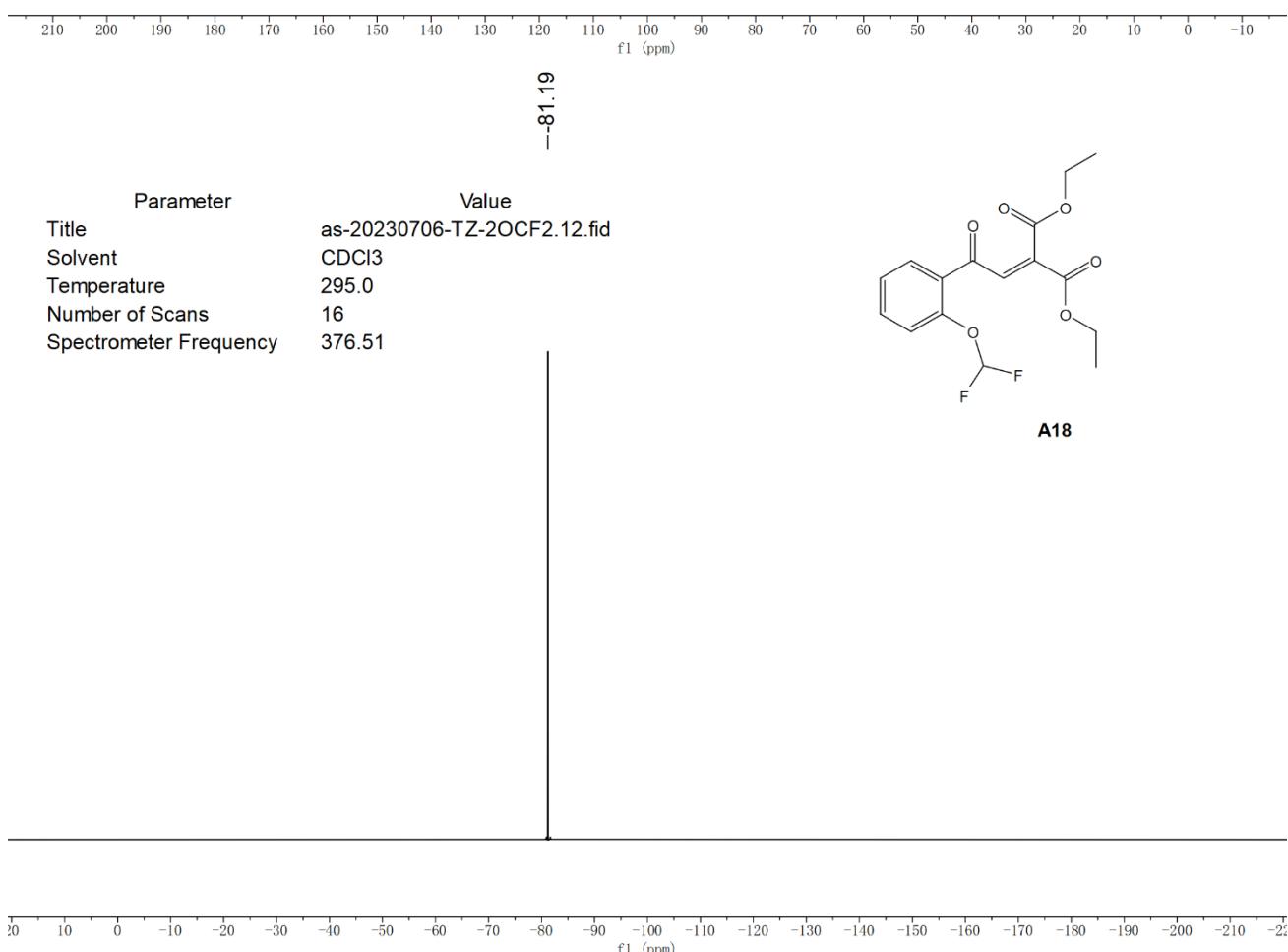
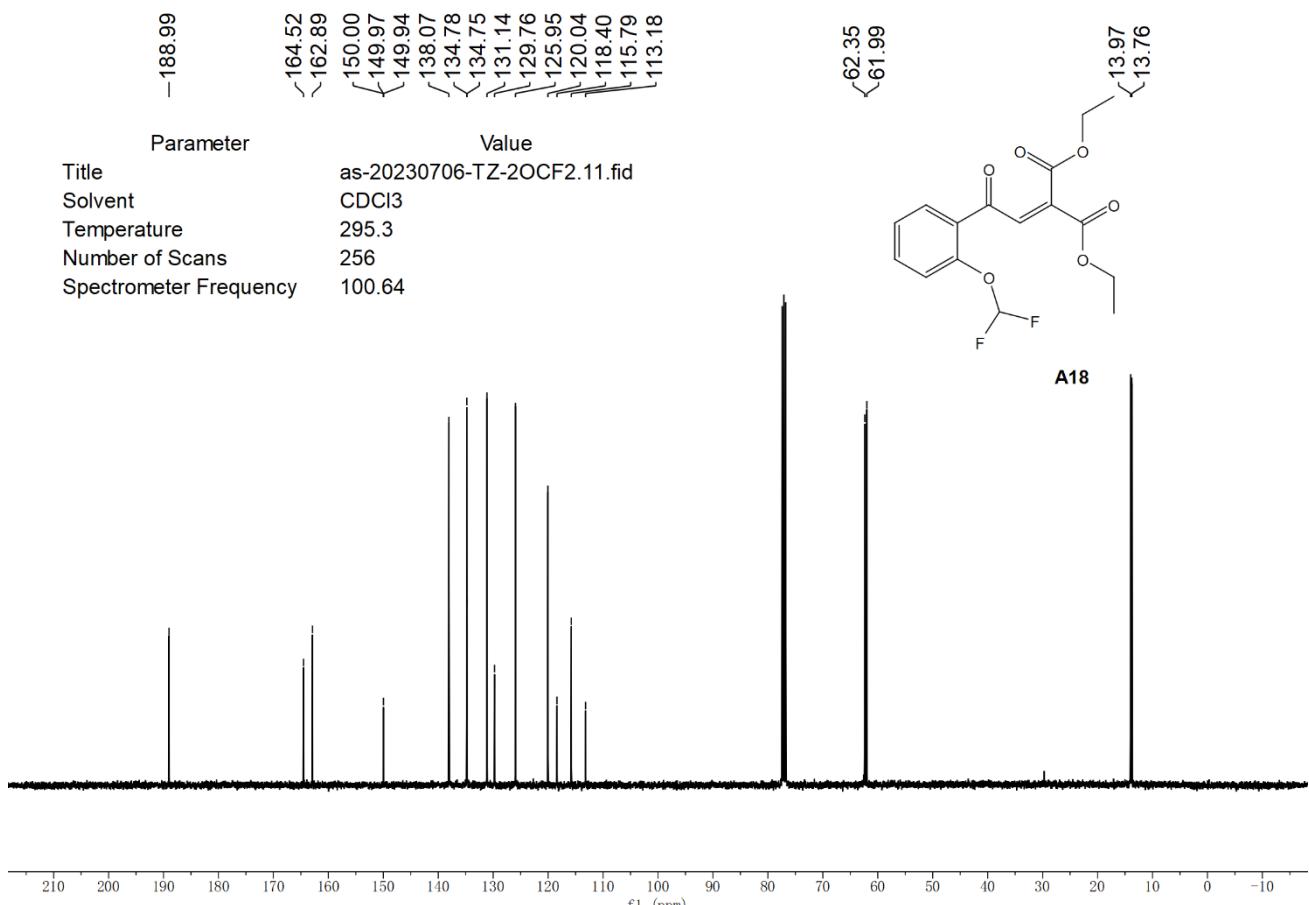
Parameter	Value
Title	tanz-20230714-4NO2.1.fid
Solvent	CDCl ₃
Temperature	294.6
Number of Scans	16
Spectrometer Frequency	400.18

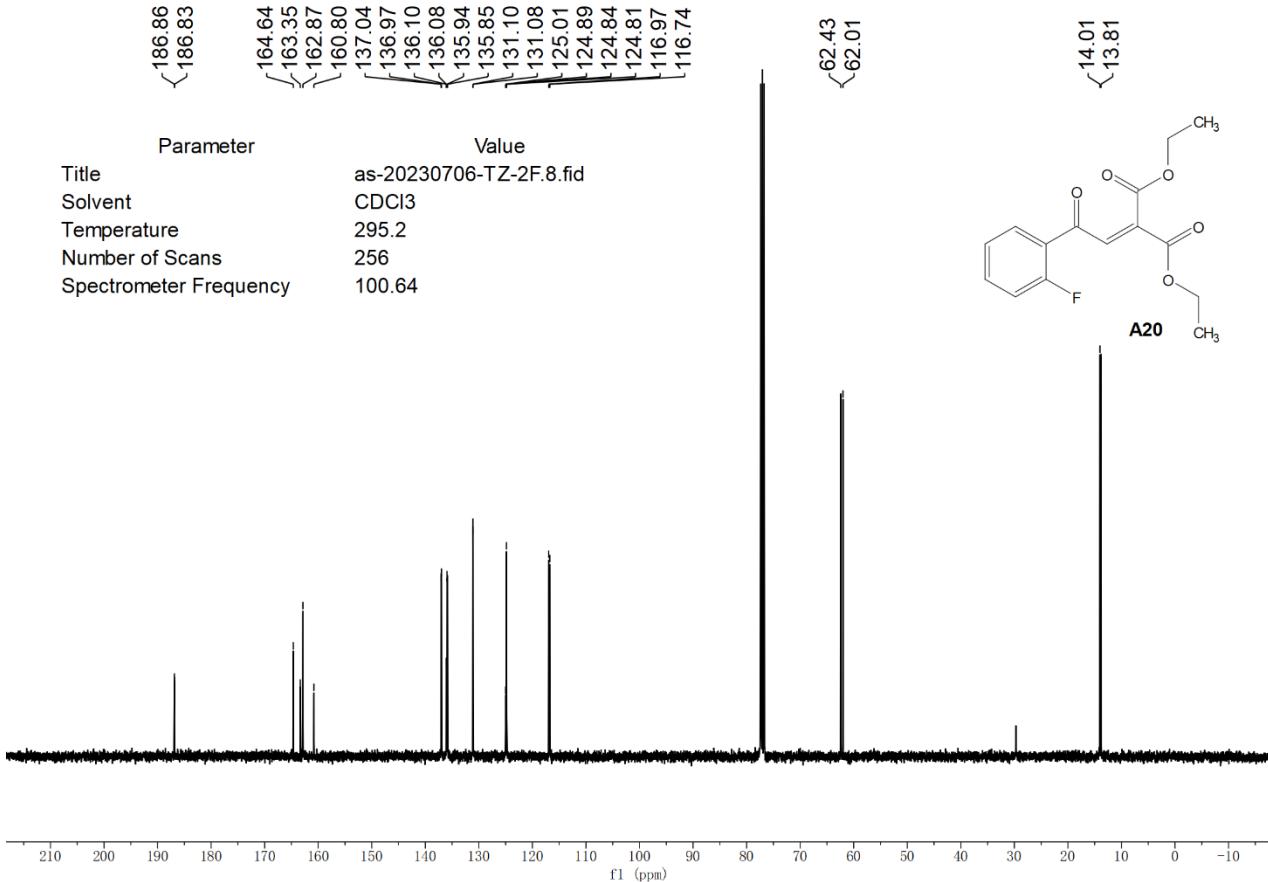
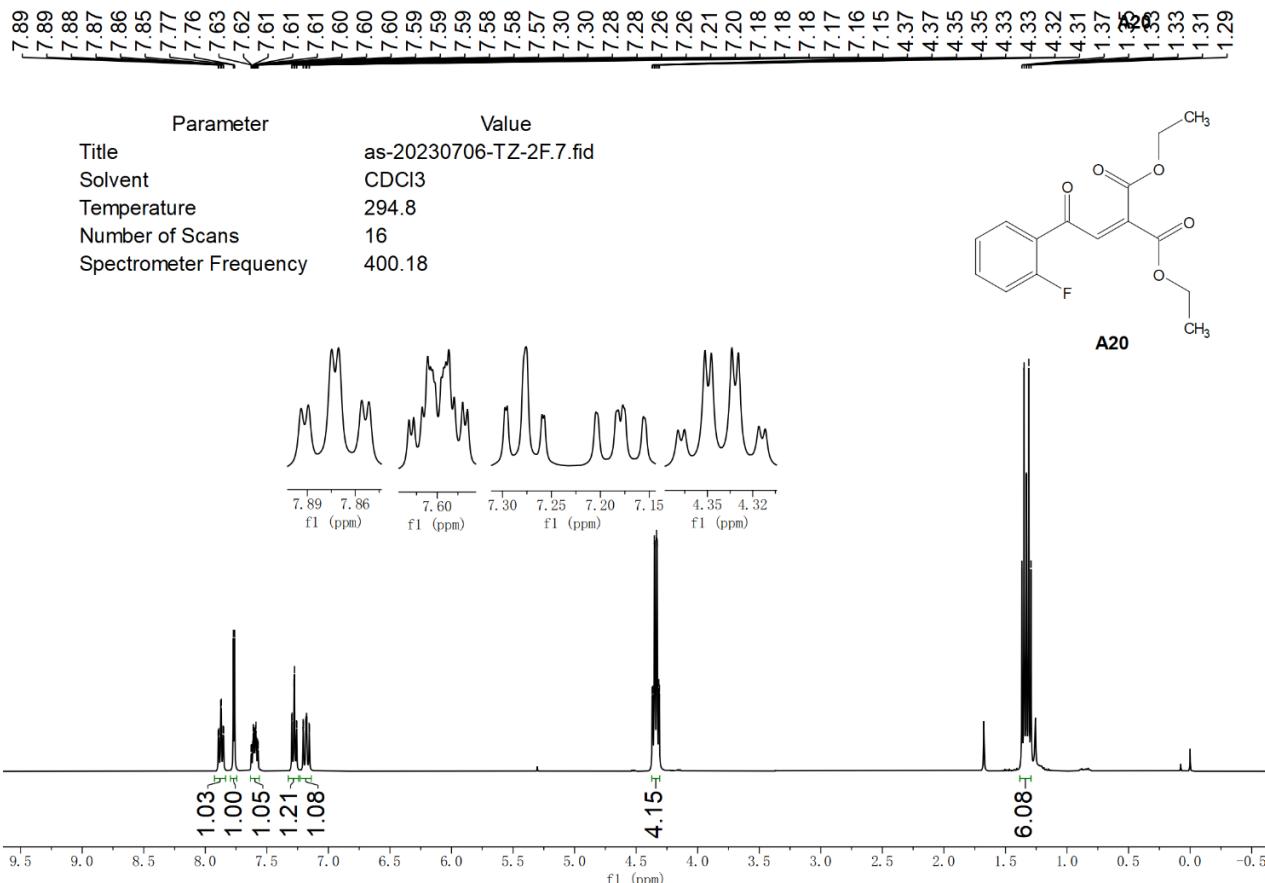


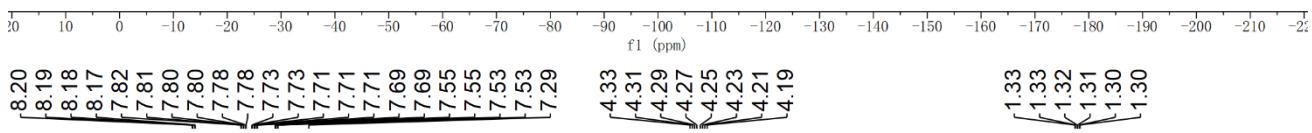






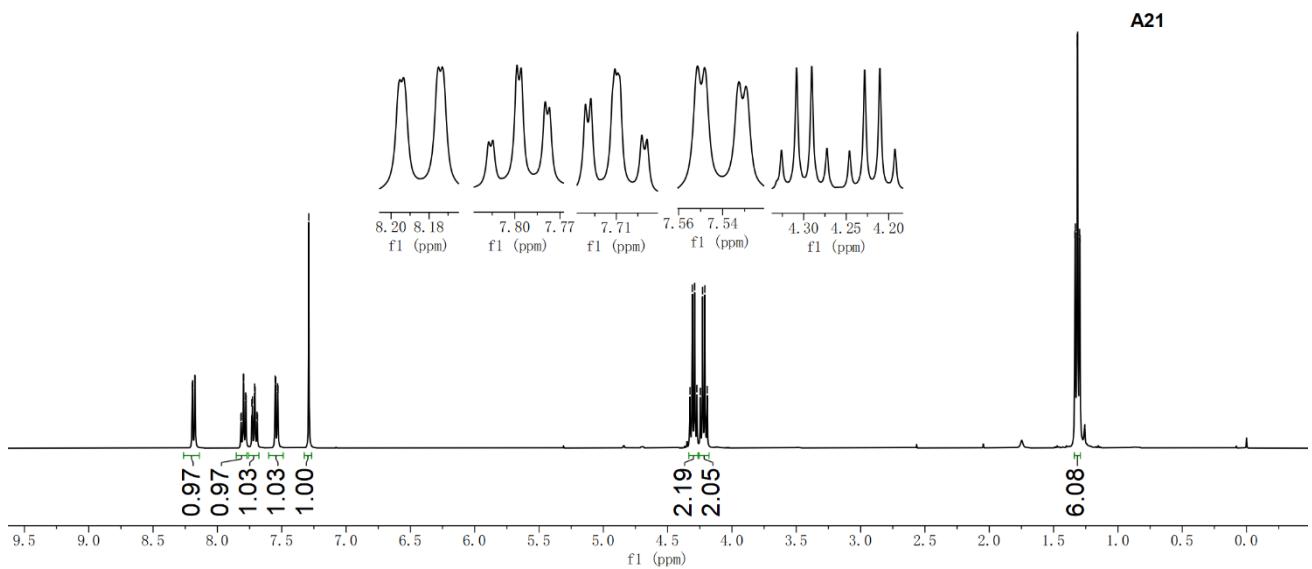
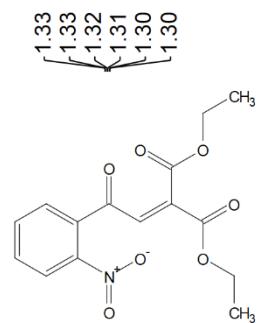


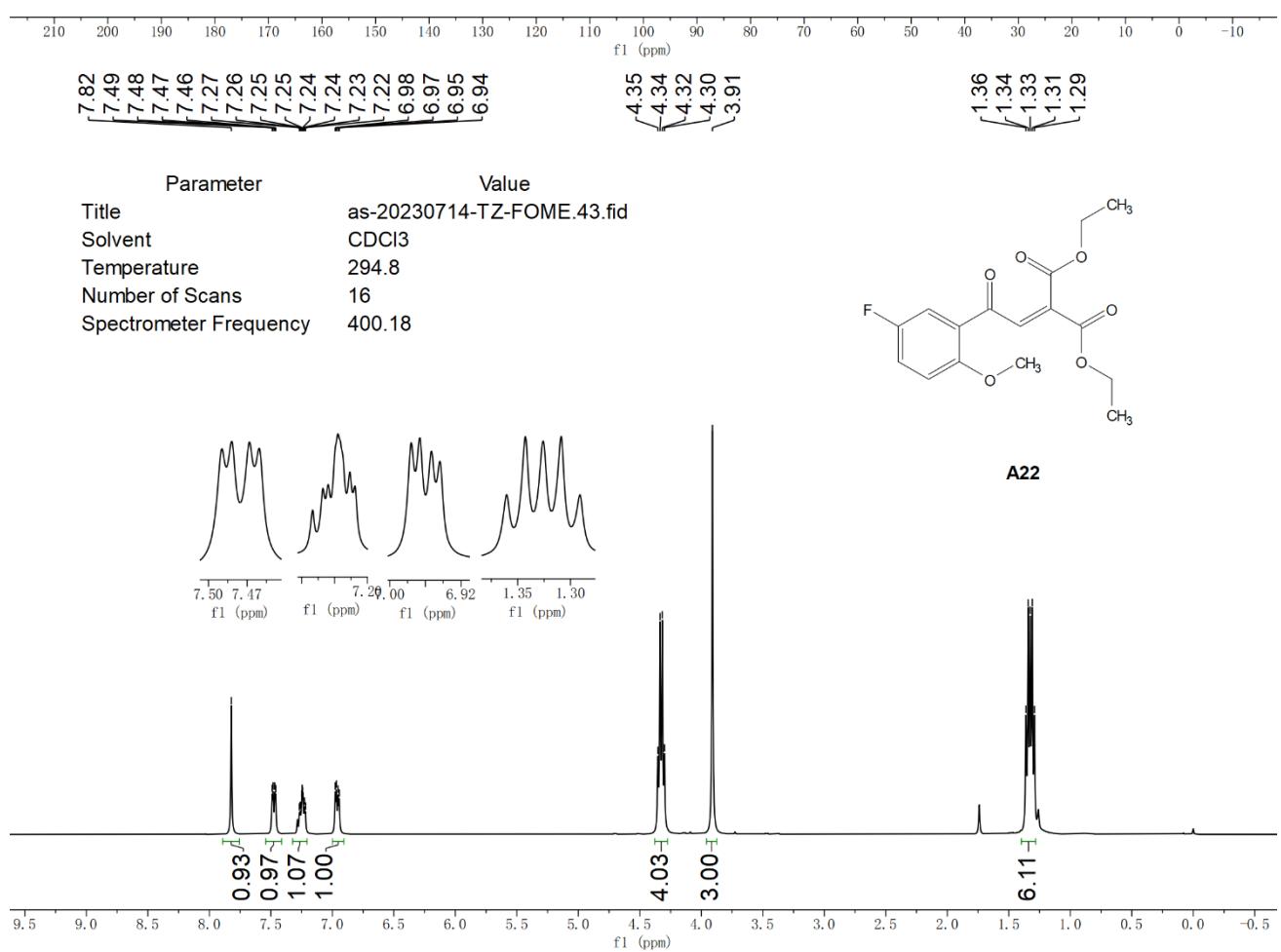
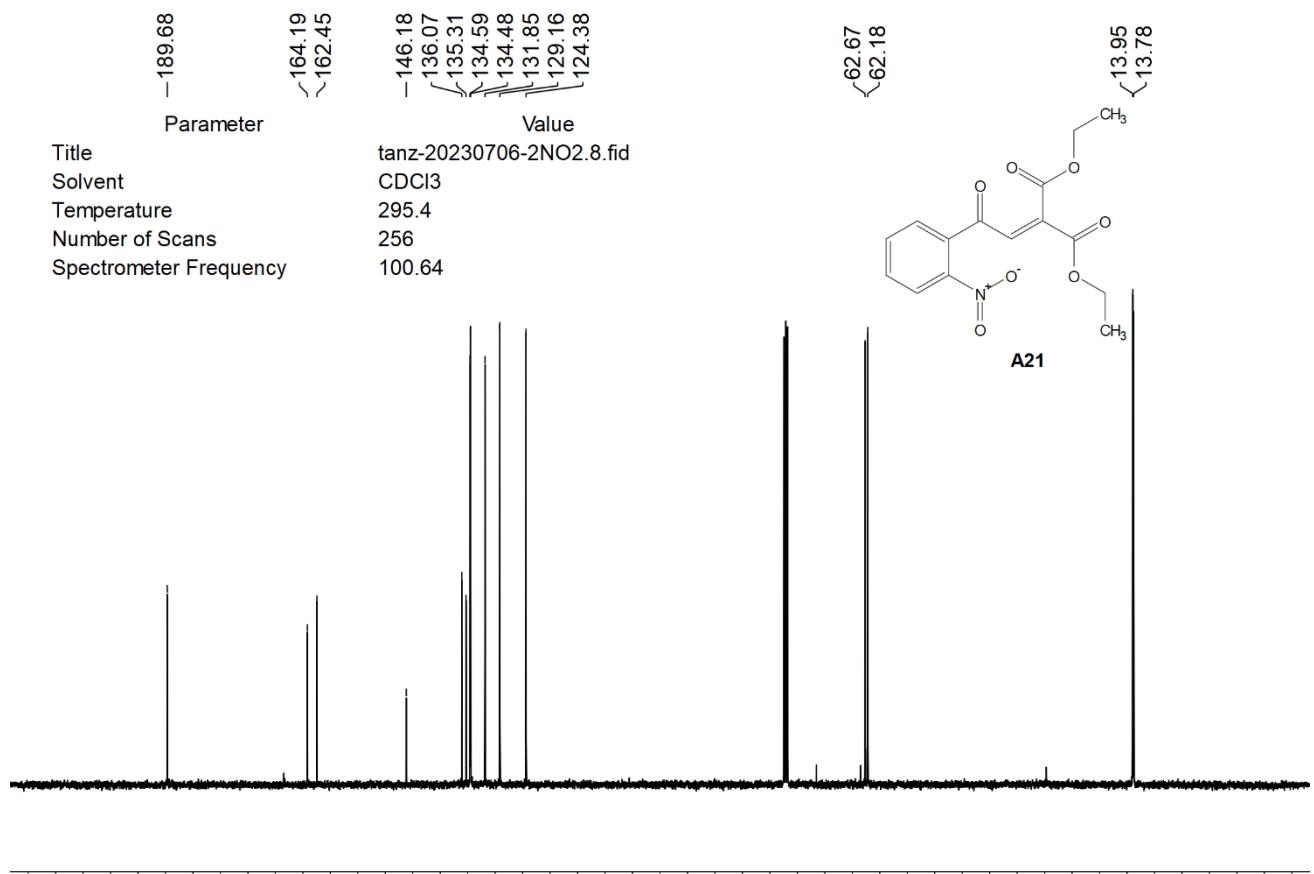


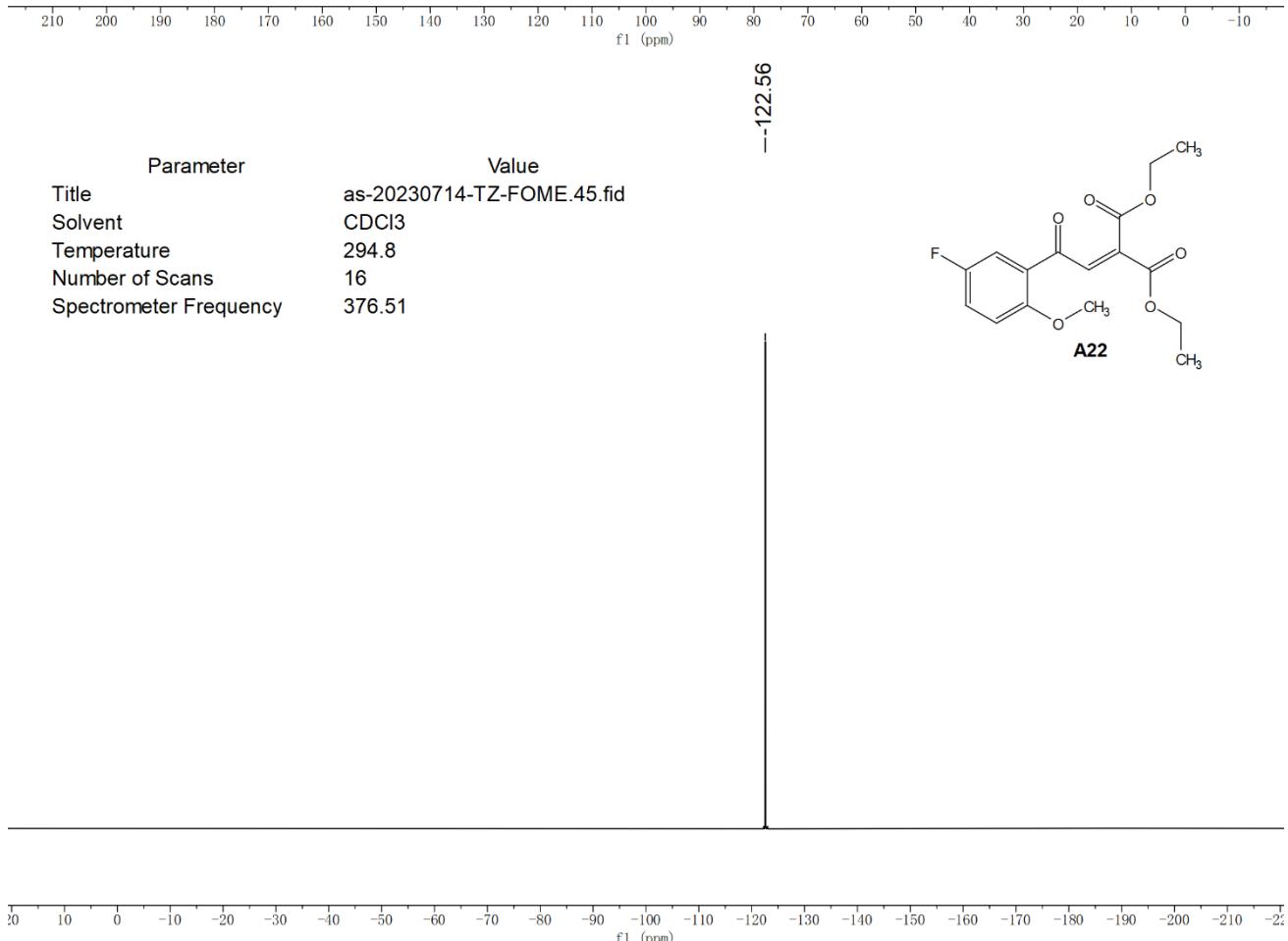
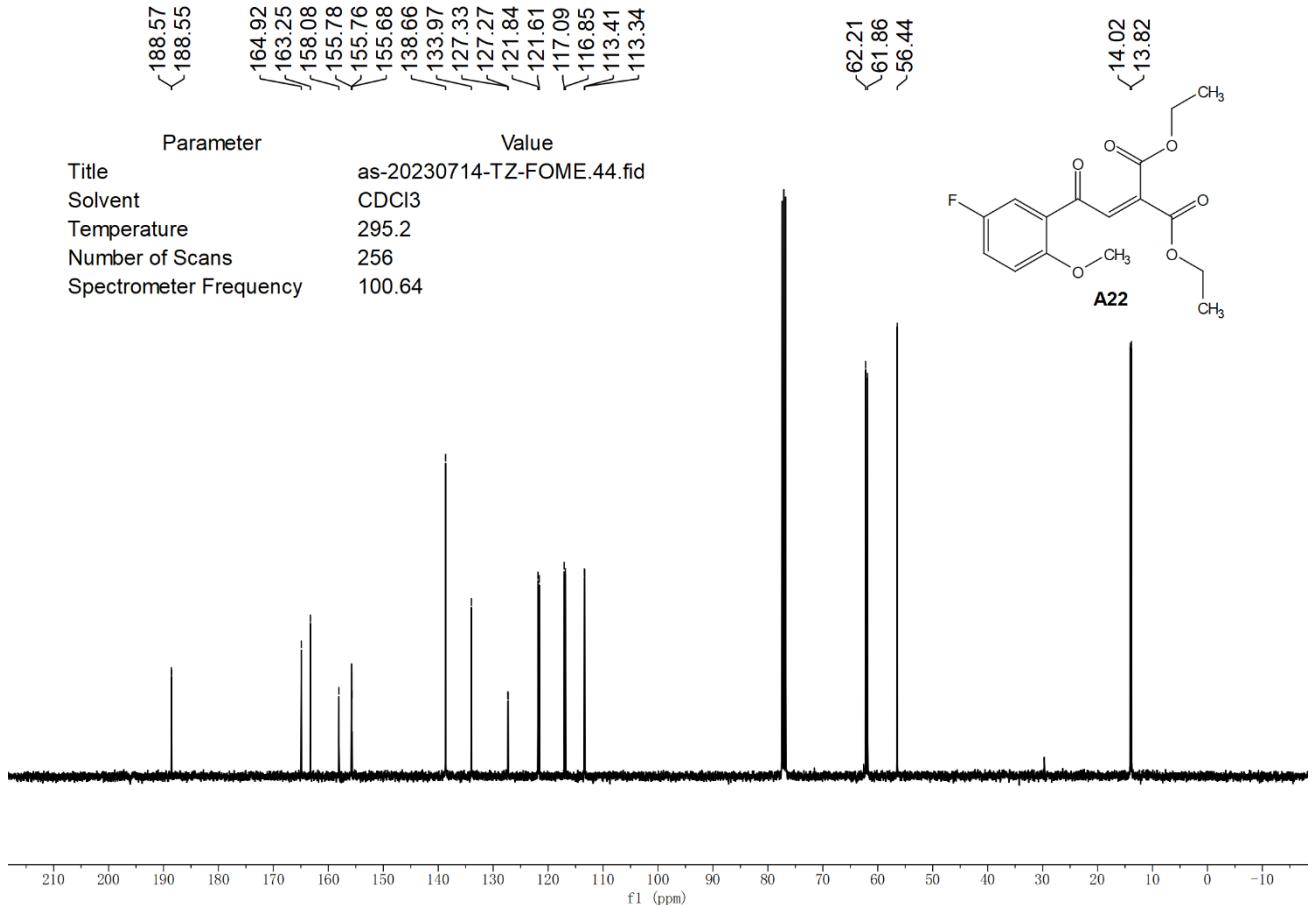


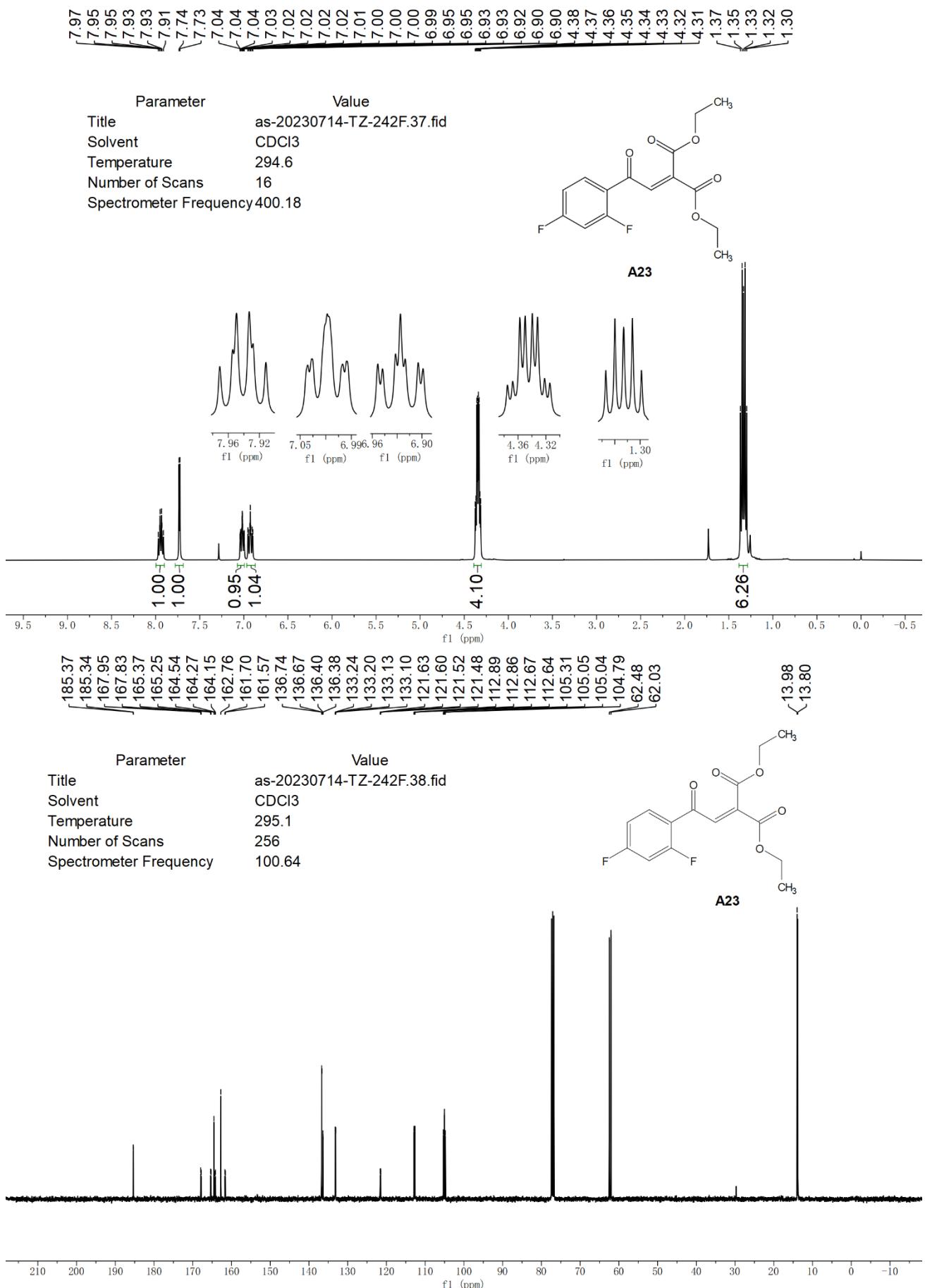
Parameter Value

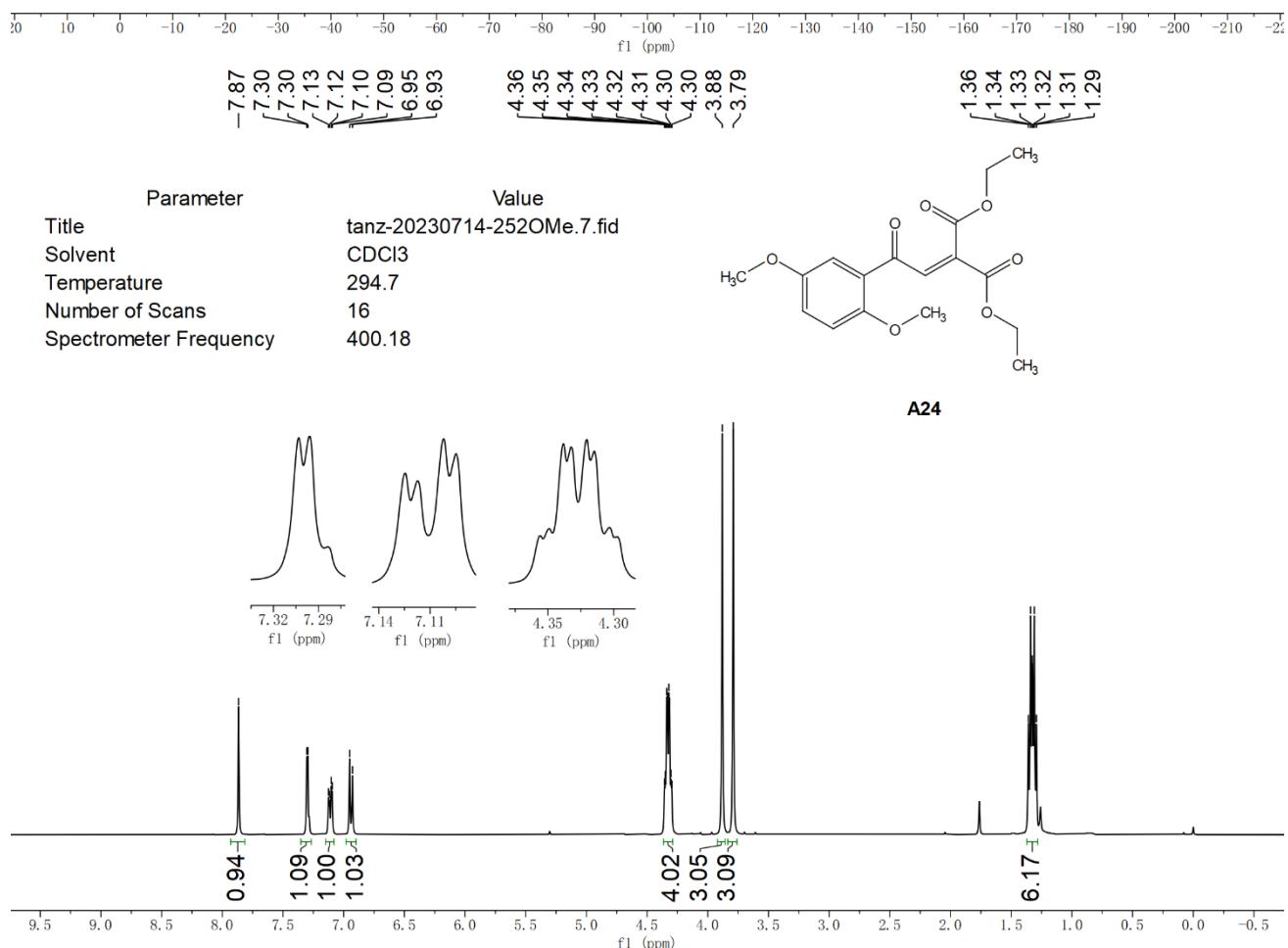
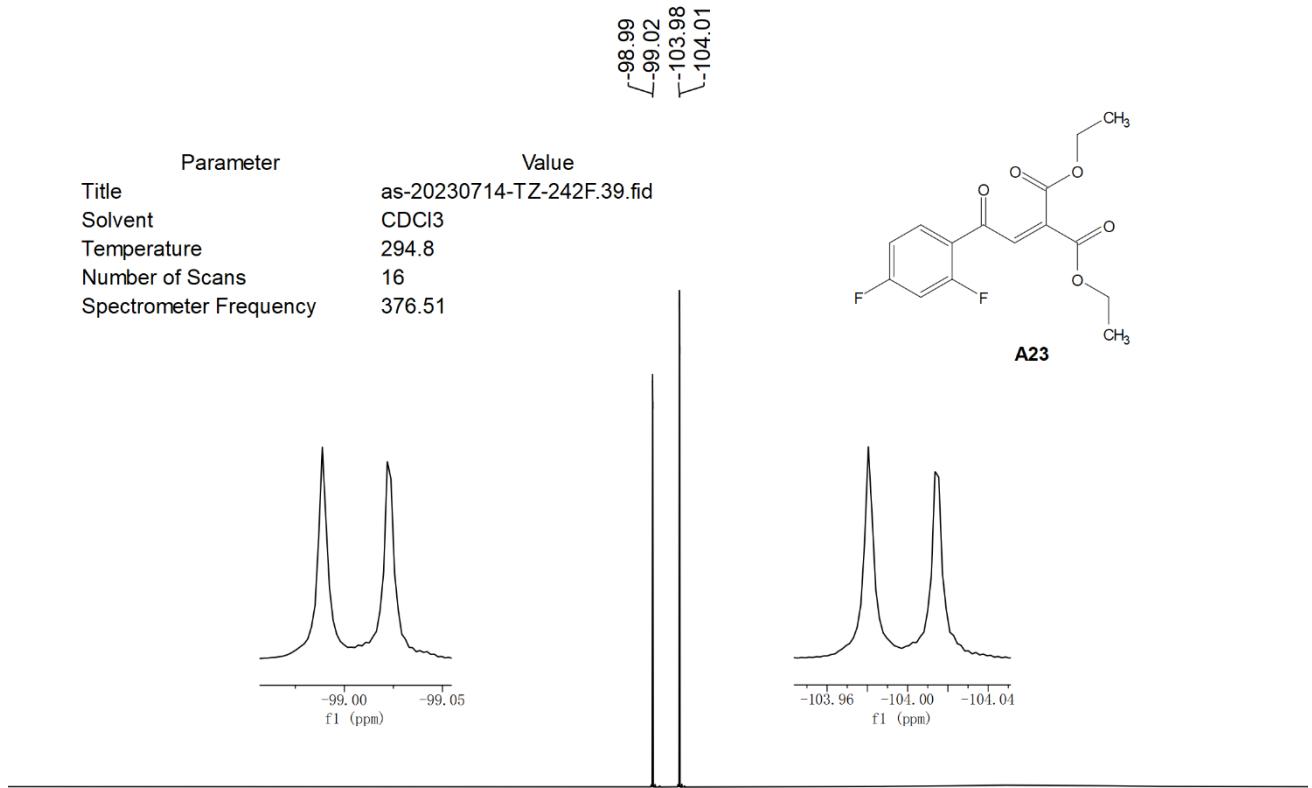
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Solvent	CDCl ₃
Temperature	294.8
Number of Scans	16
Spectrometer Frequency	400.18

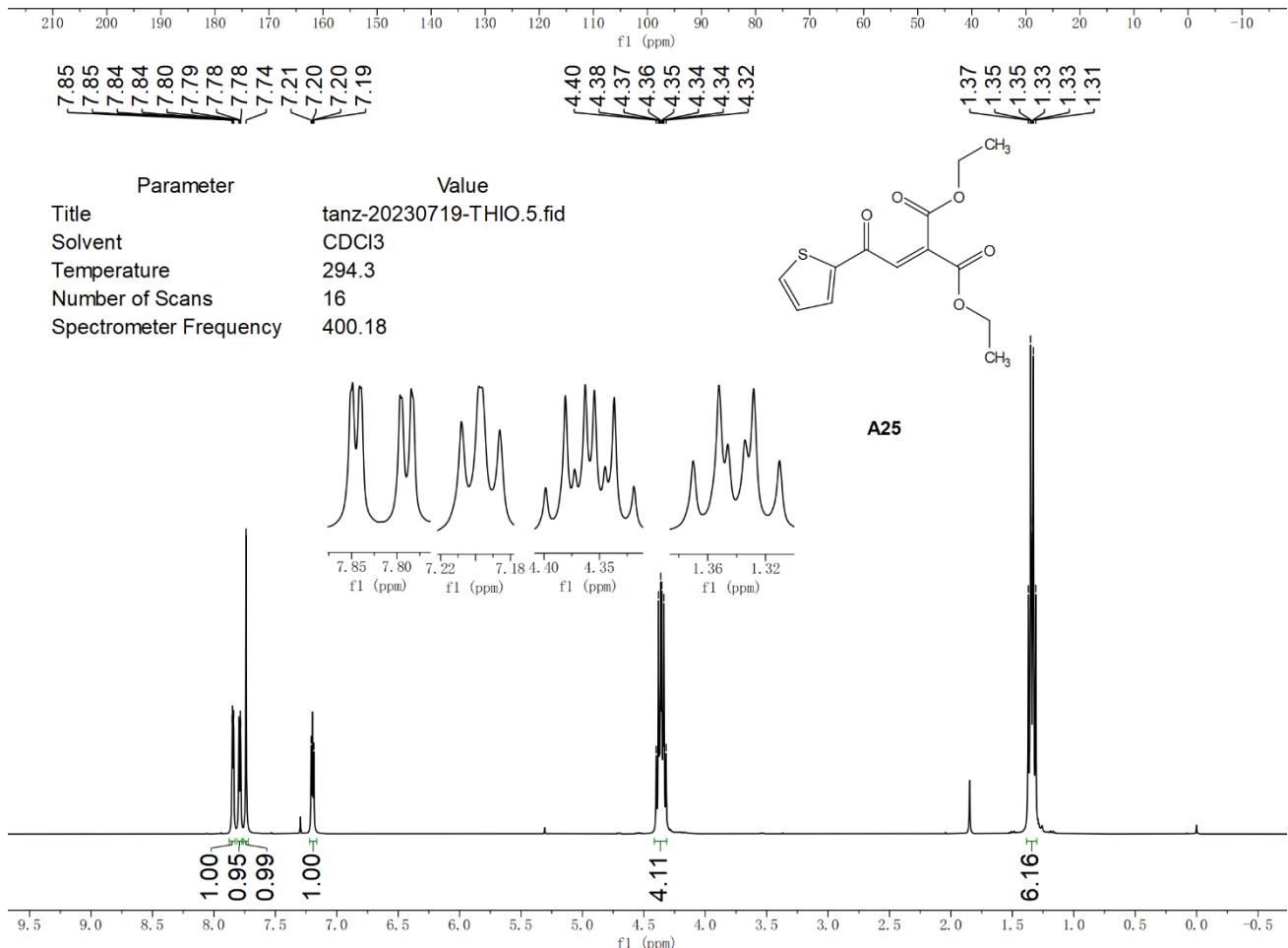
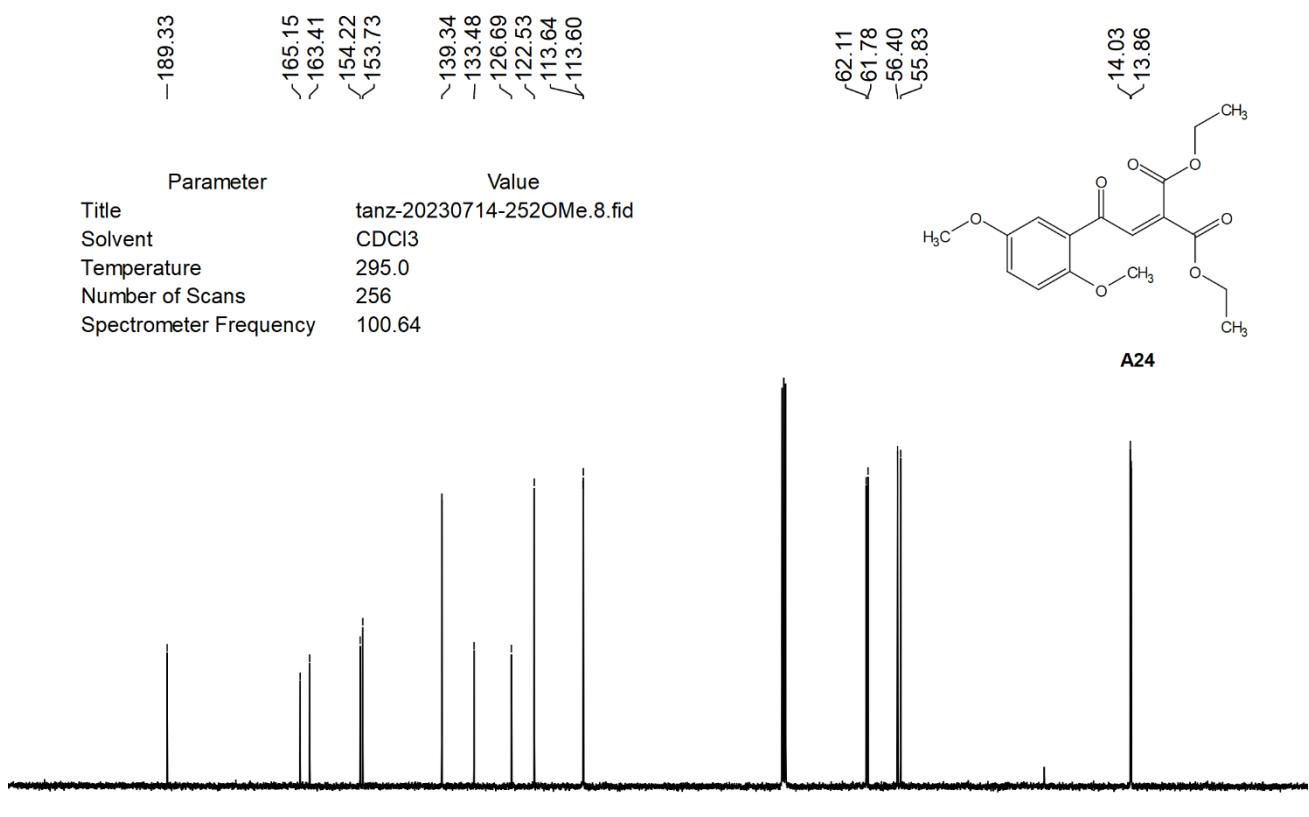


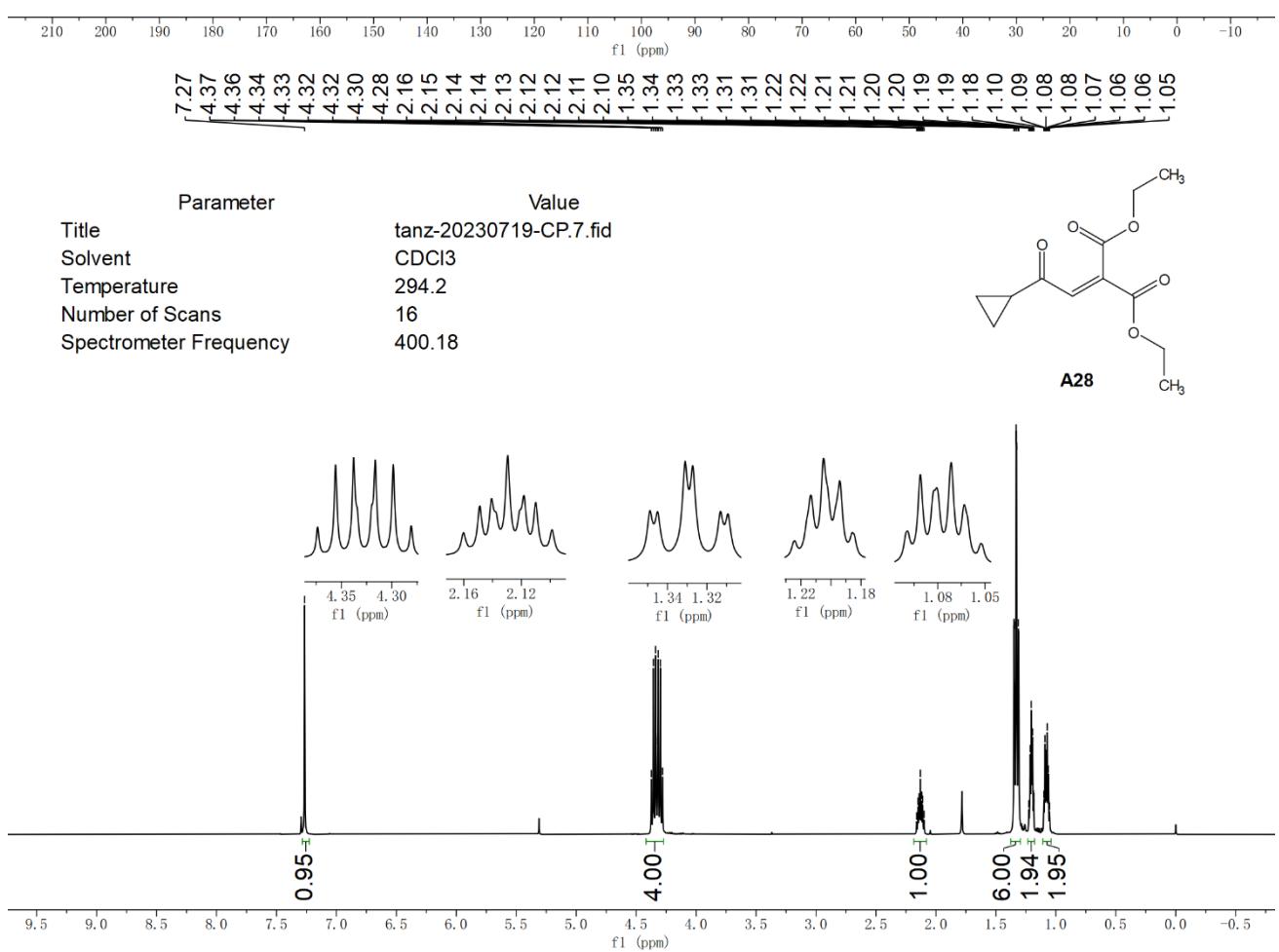
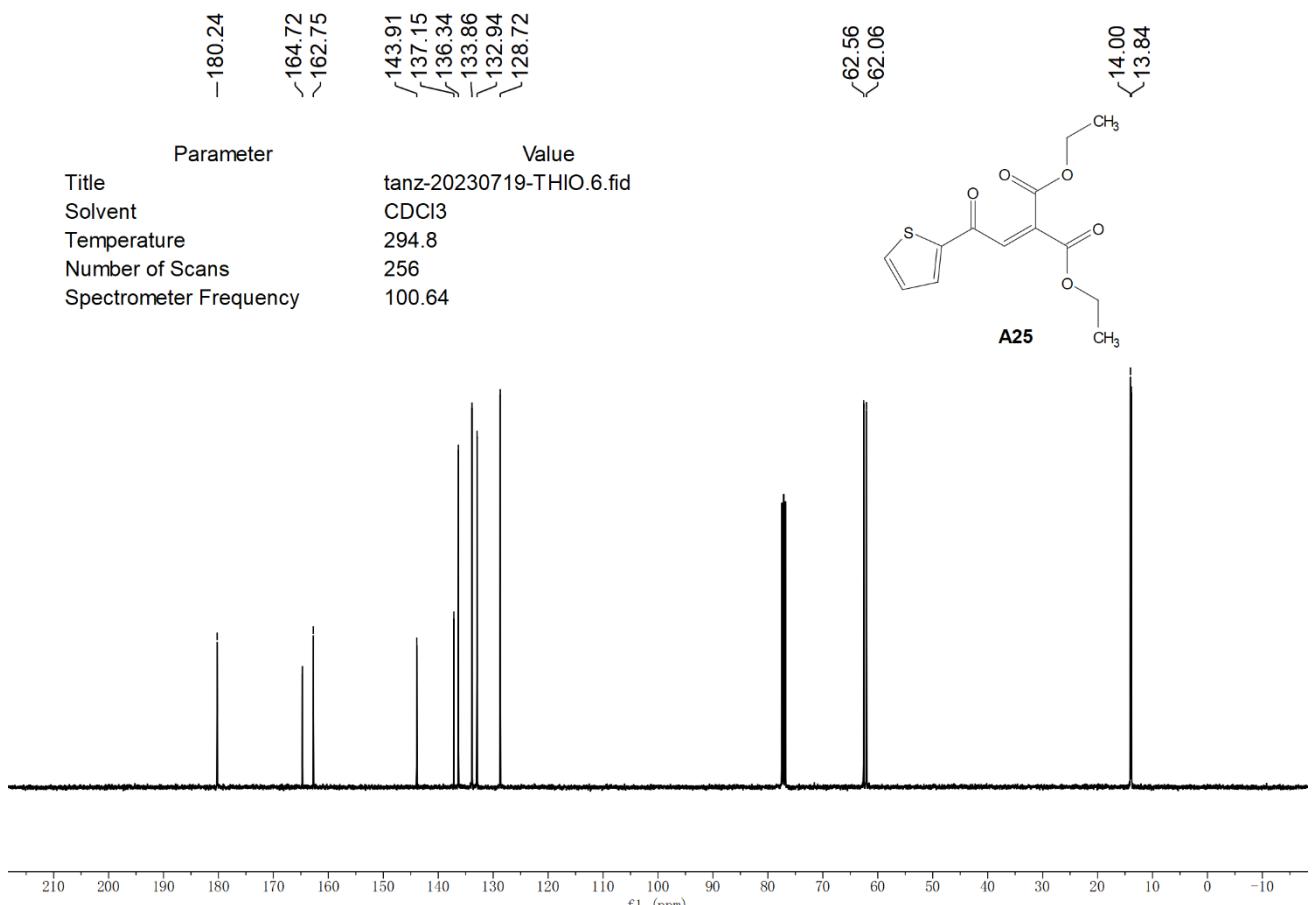


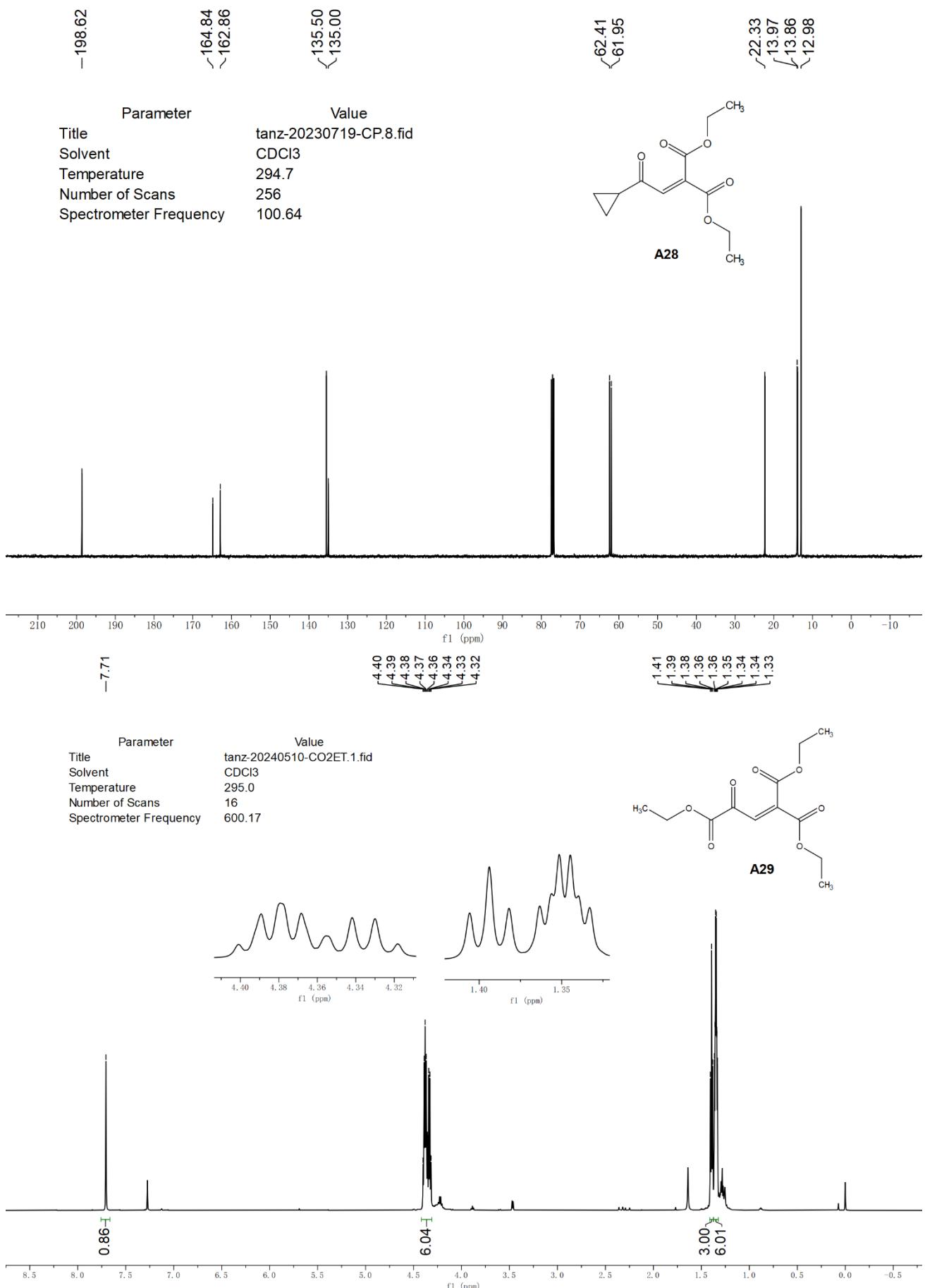


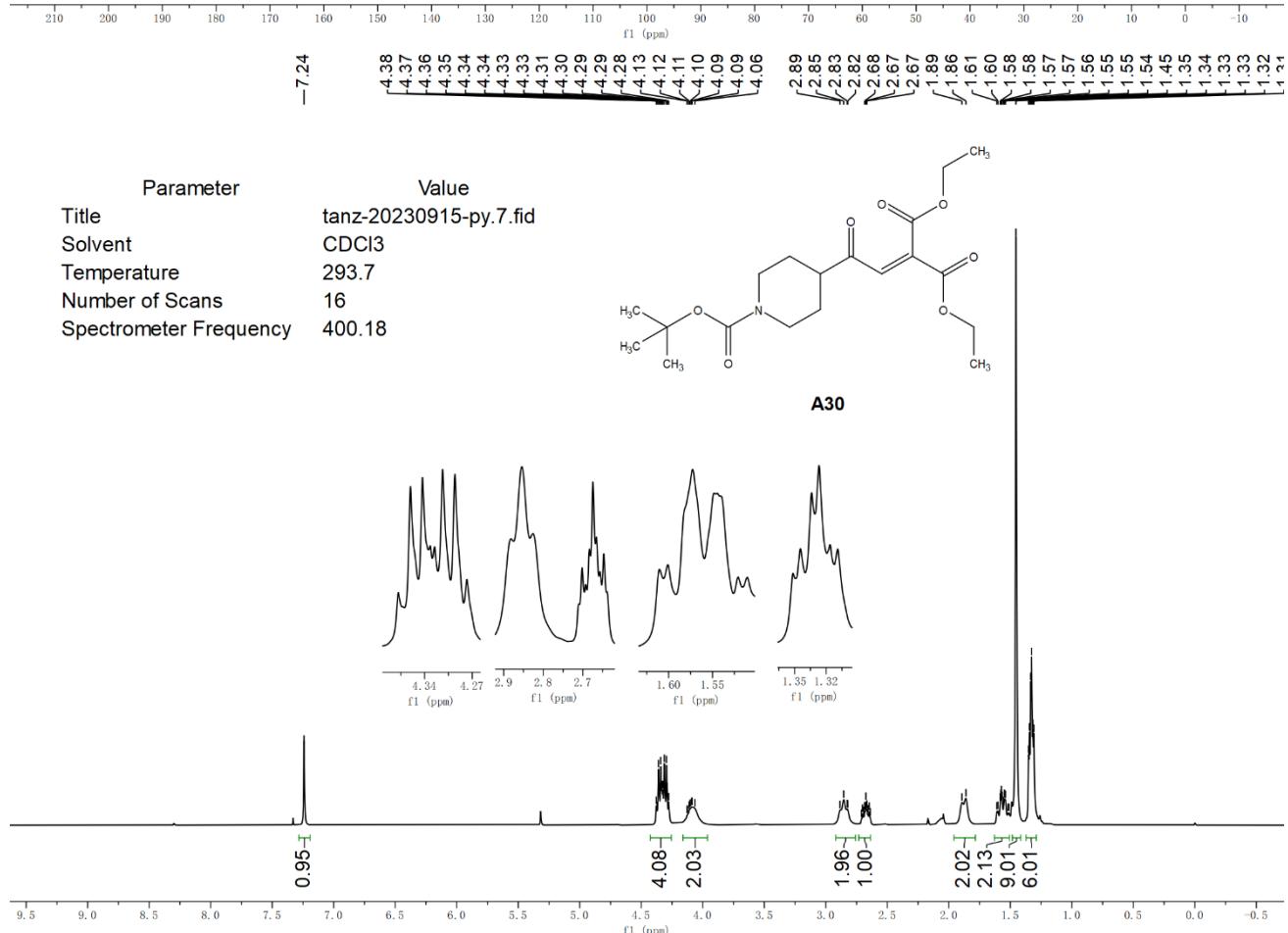
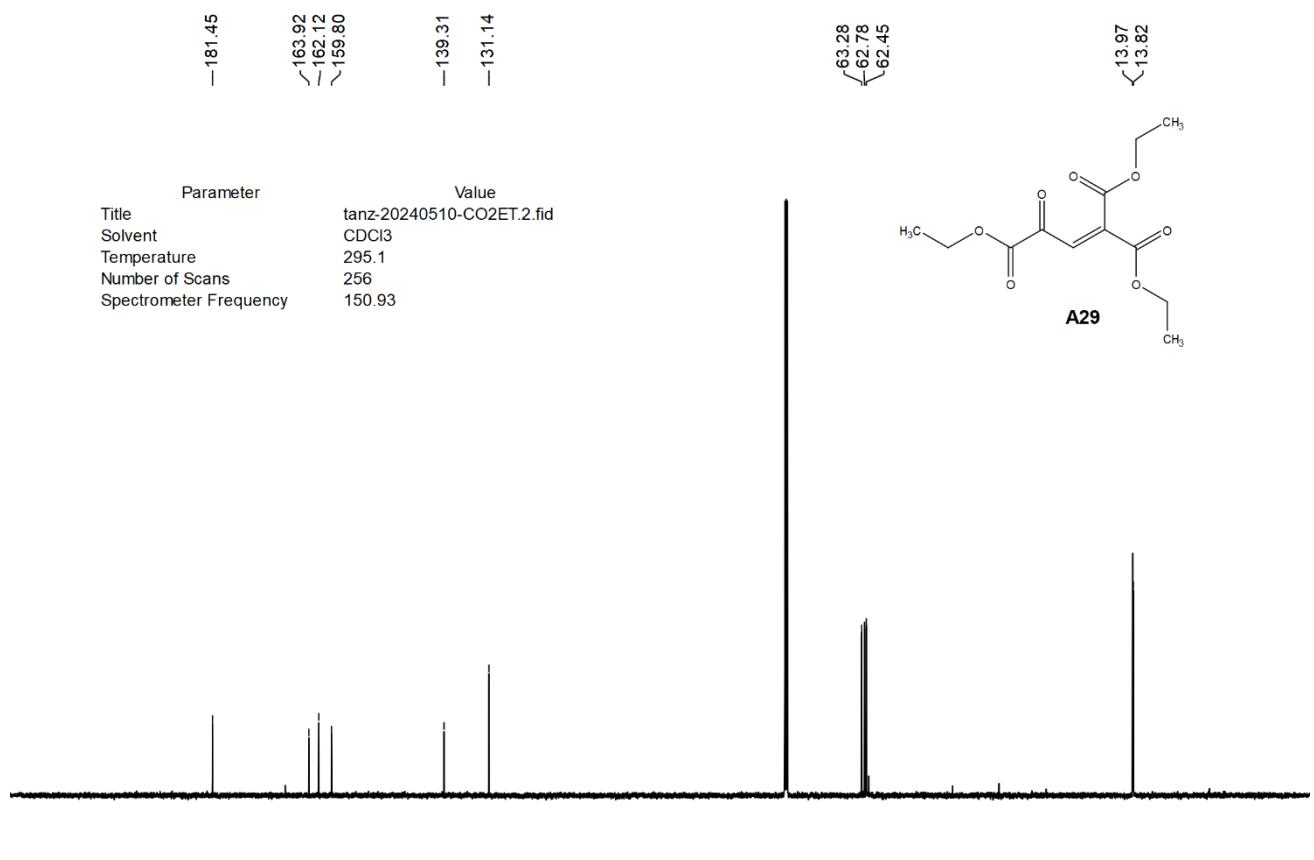


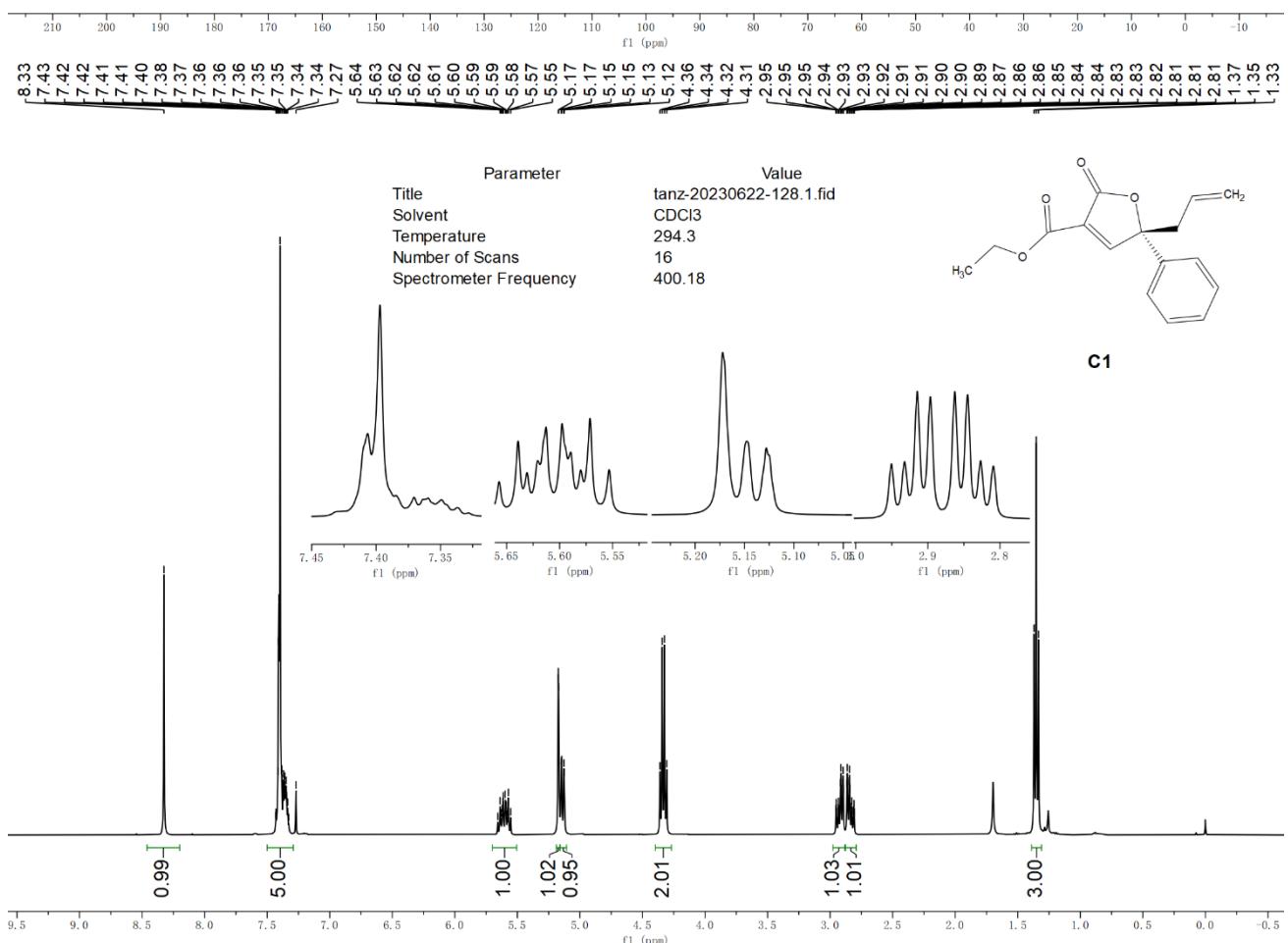
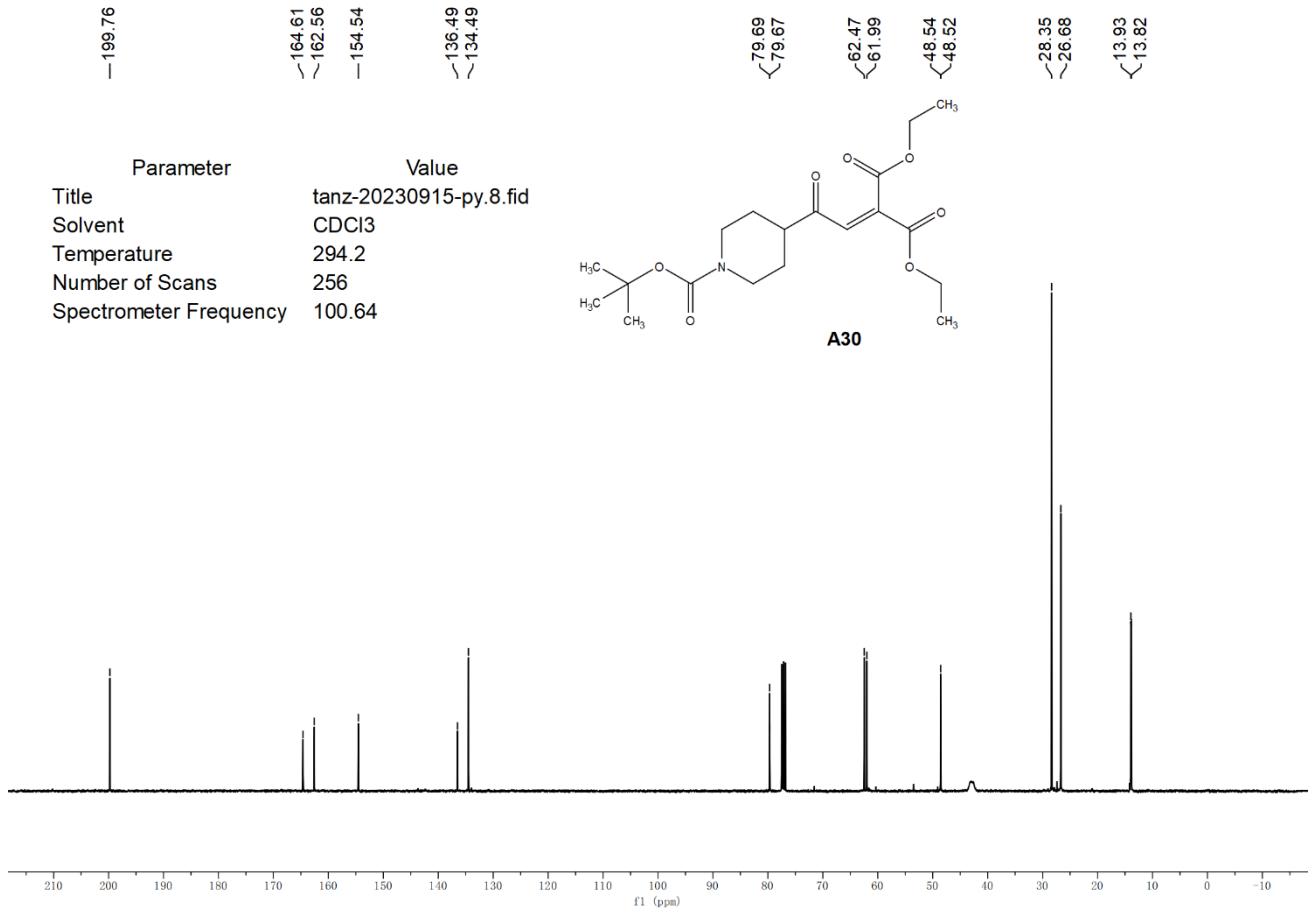


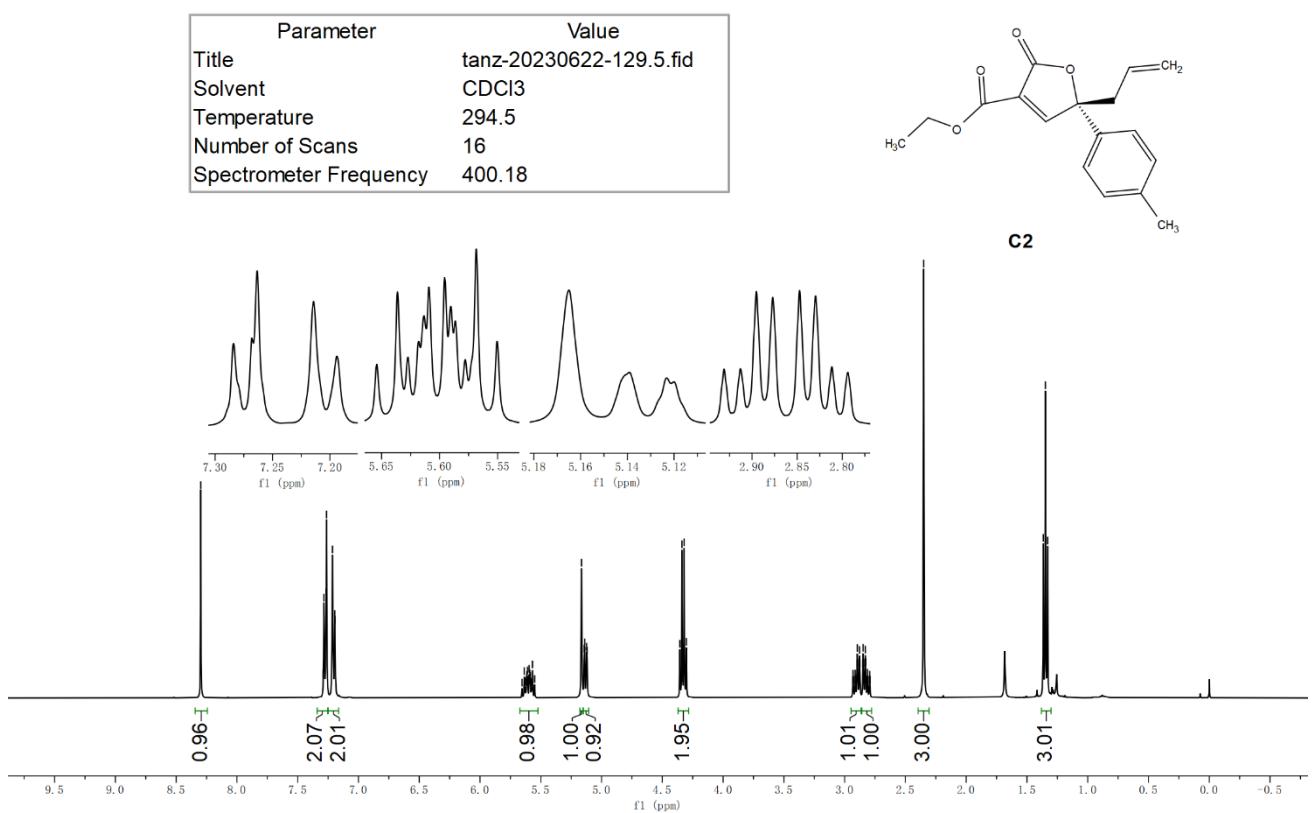
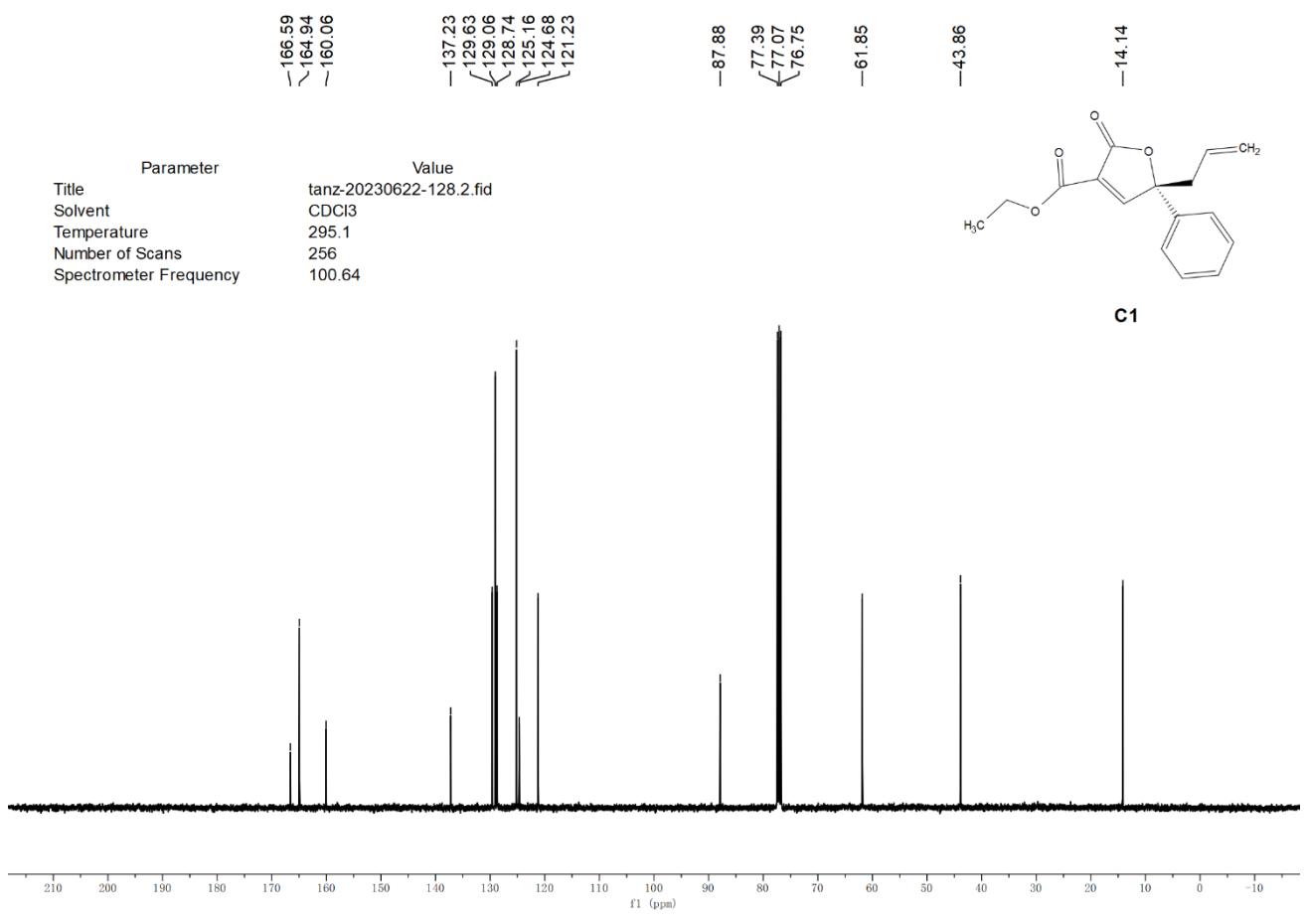


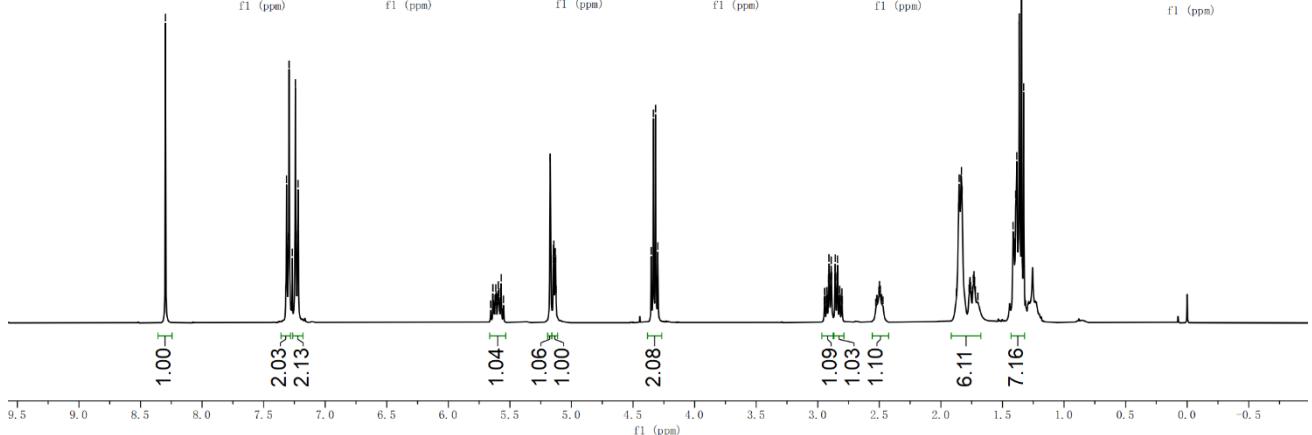
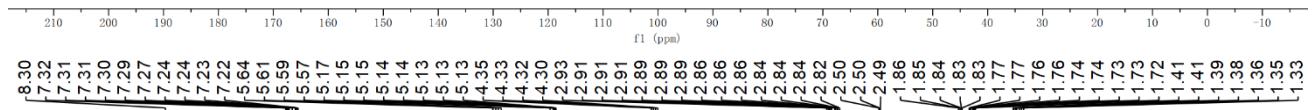
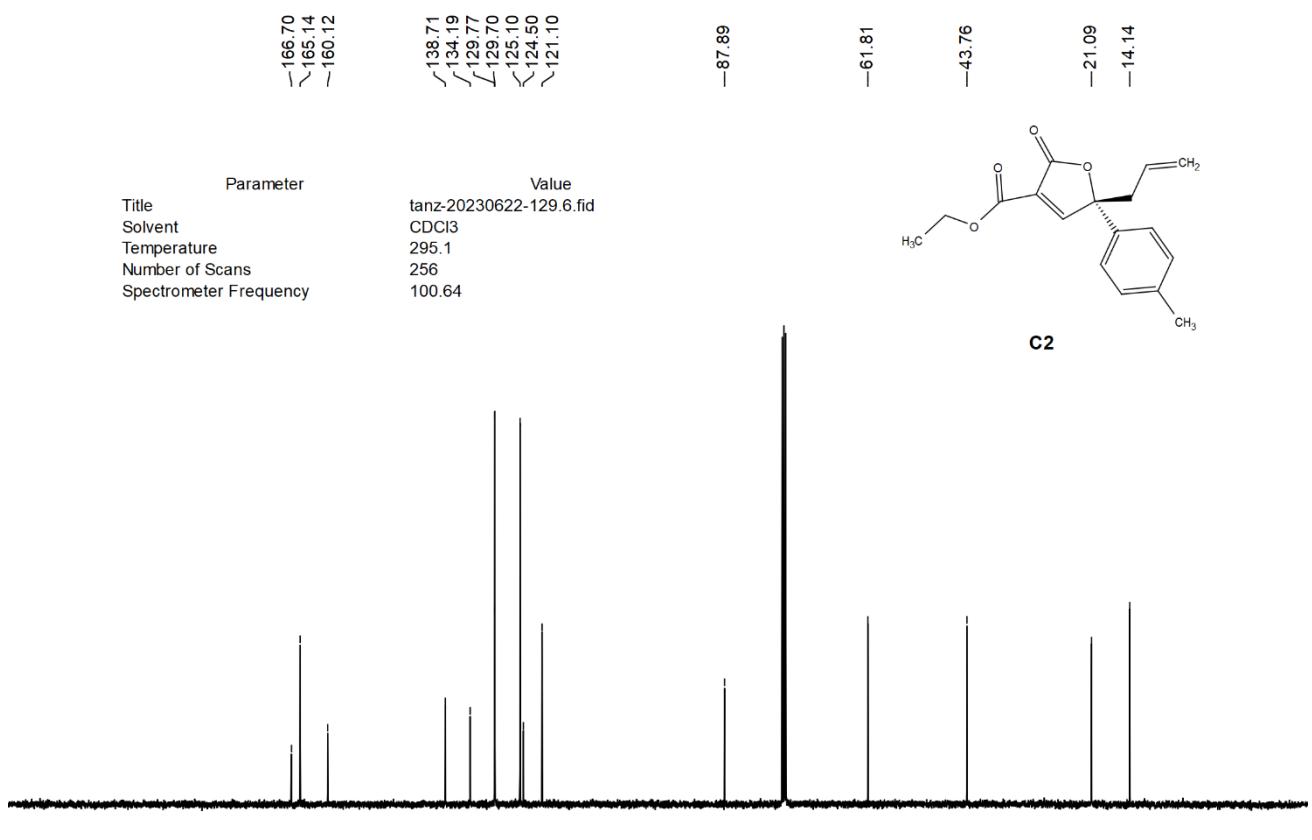


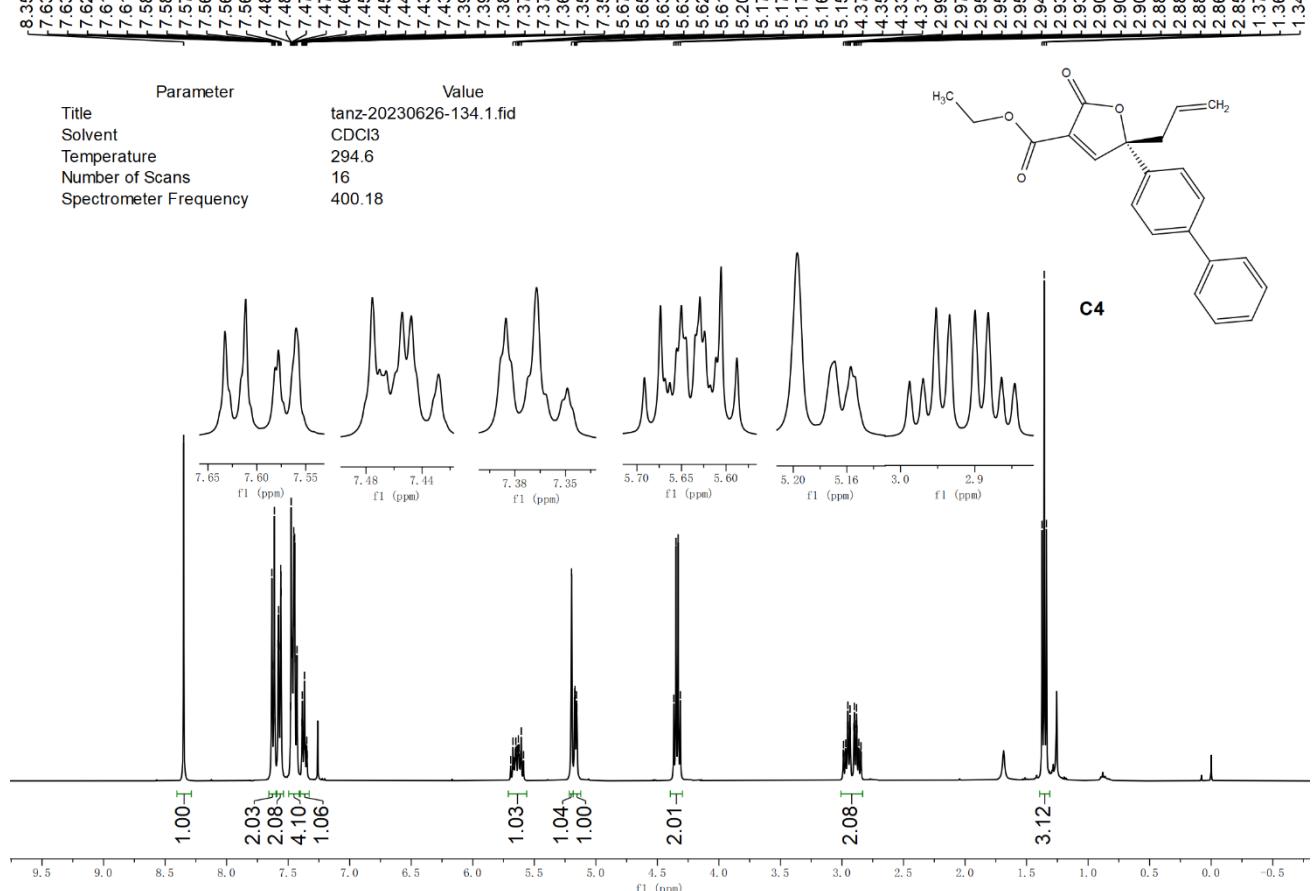
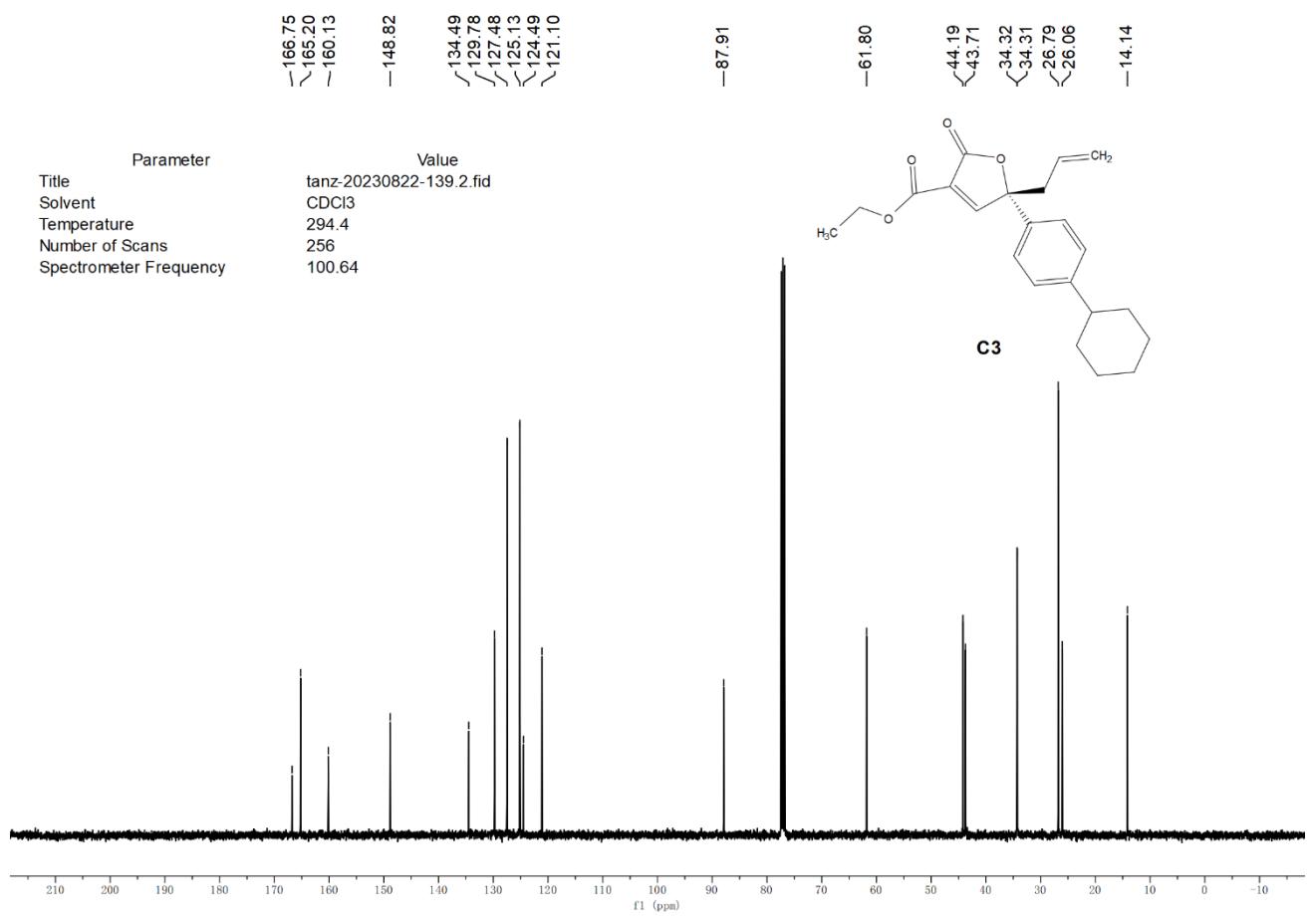


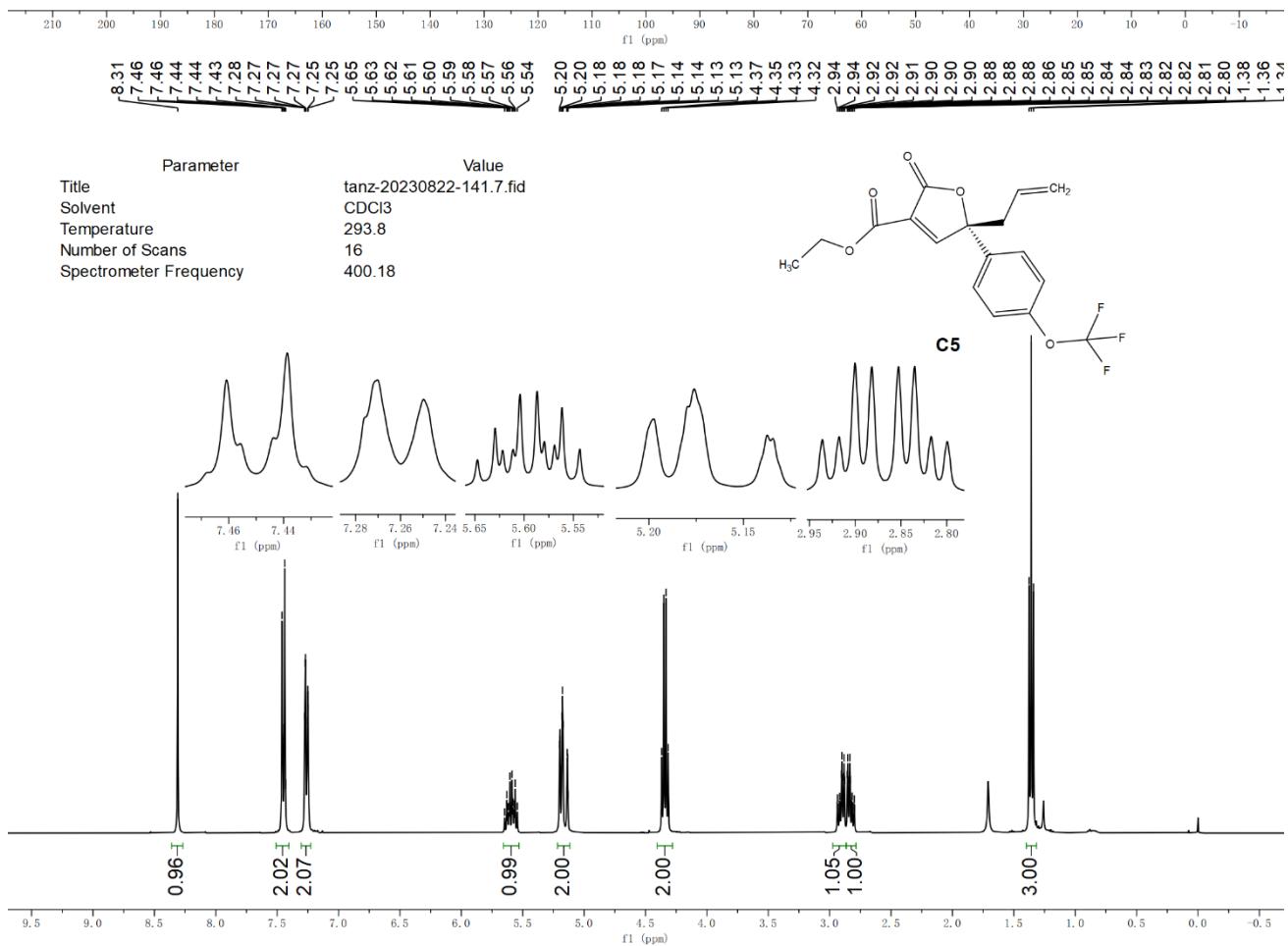
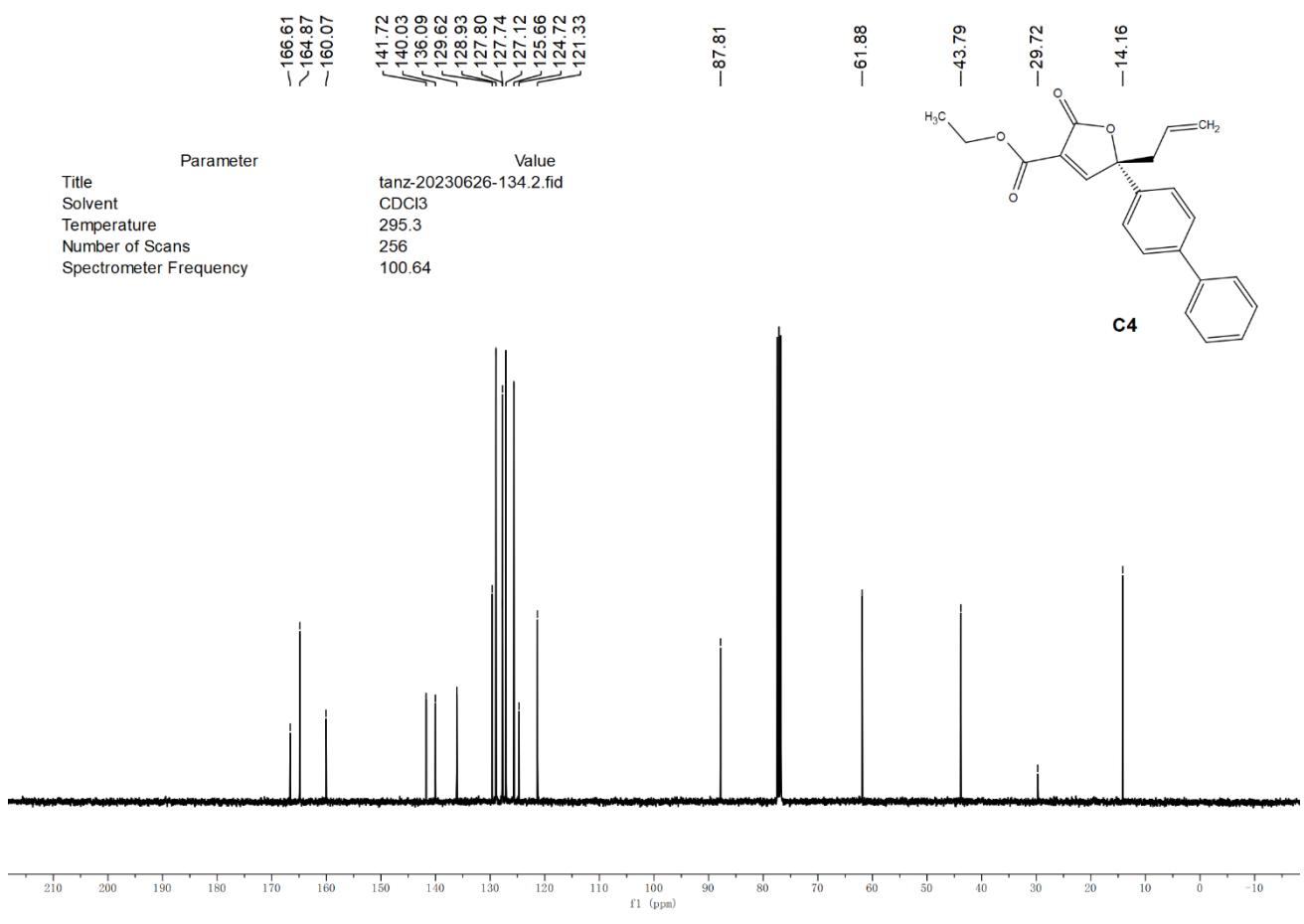


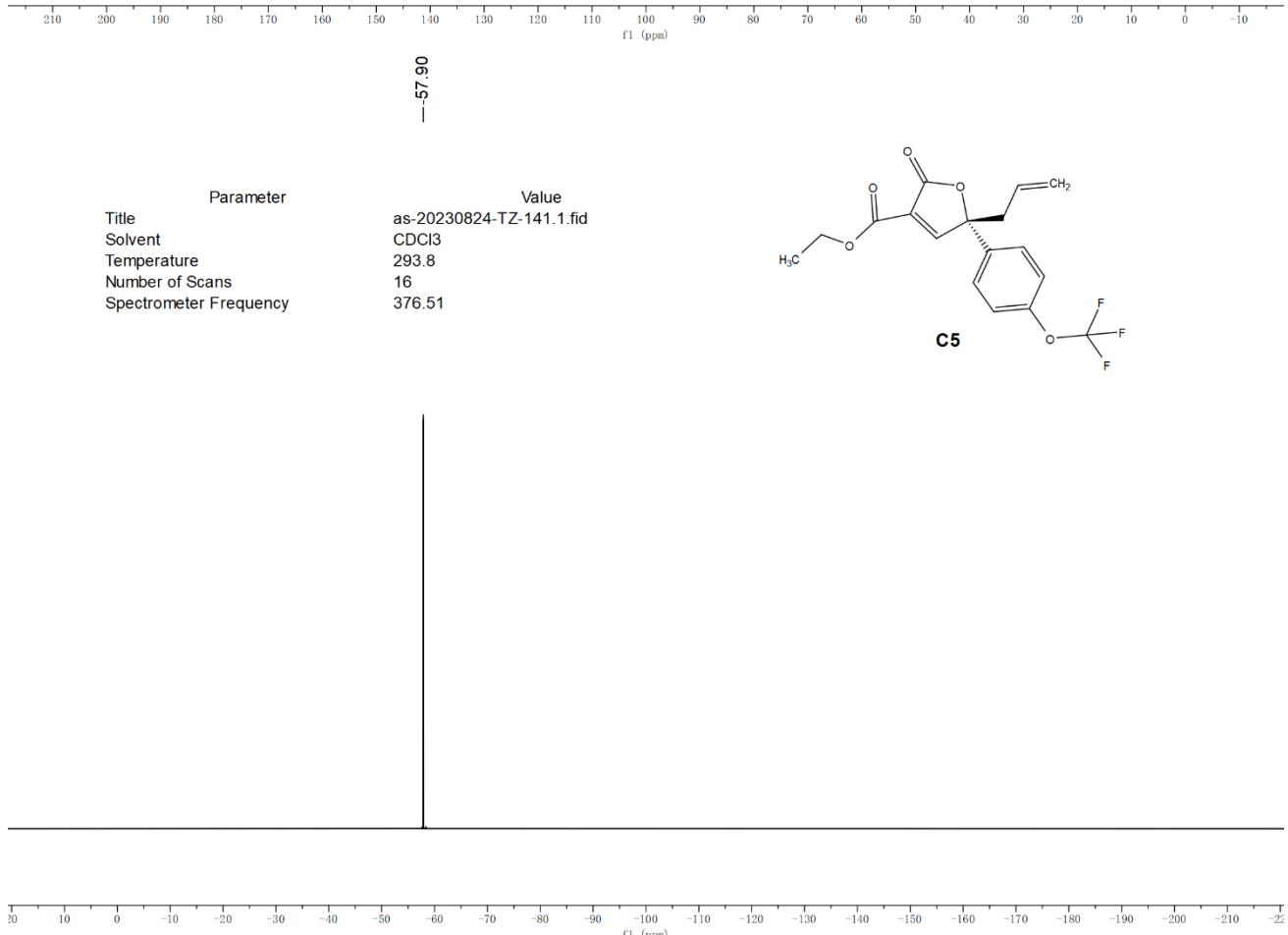
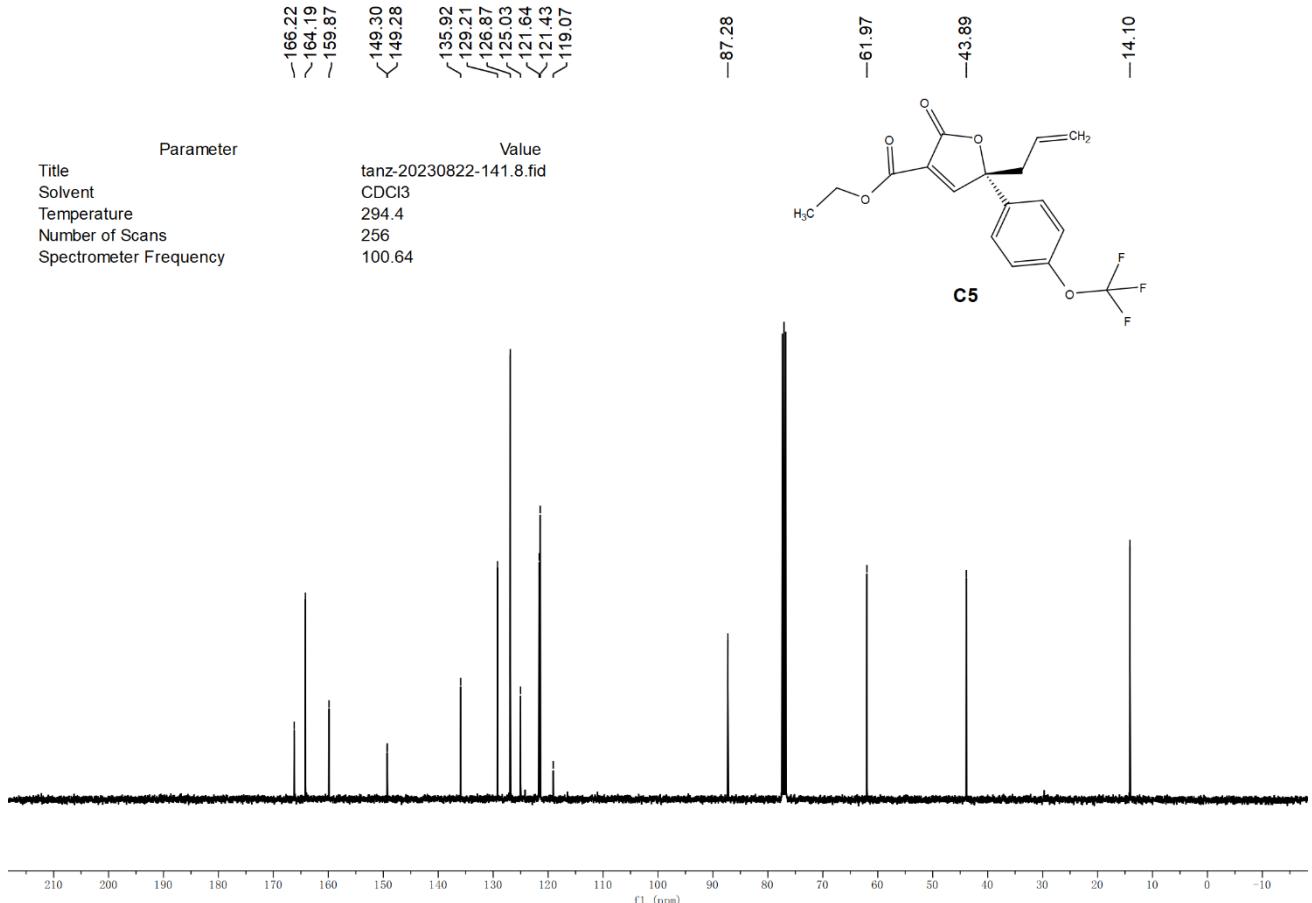


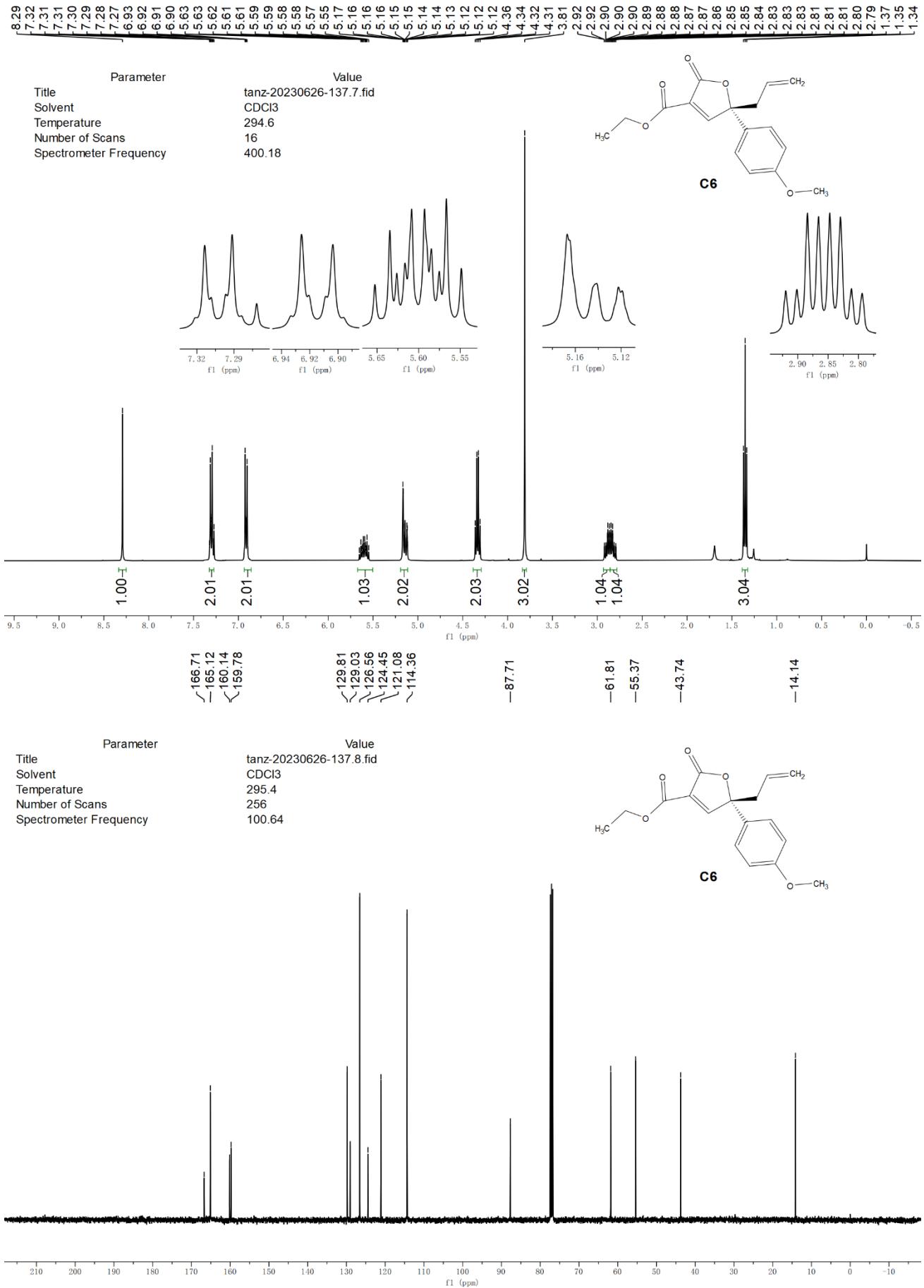








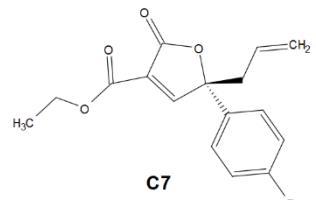




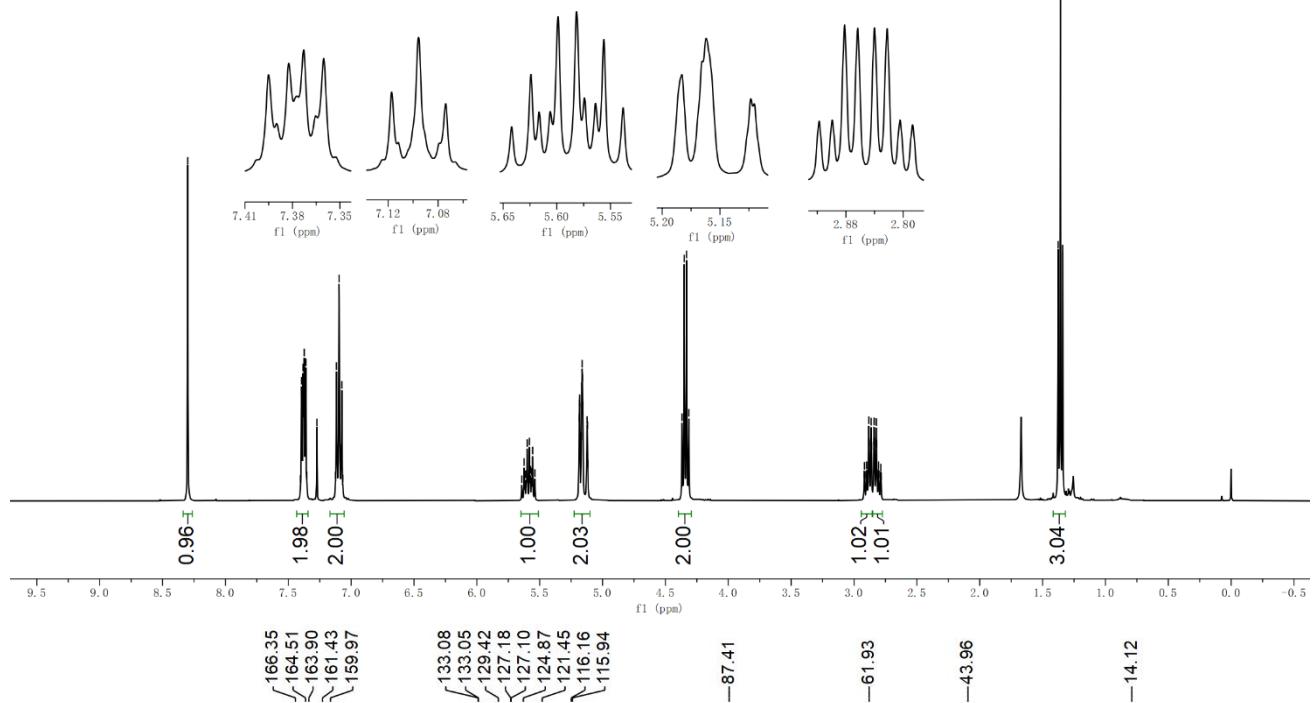
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Parameter

Title as-20230622-TZ-130.1.fid
Solvent CDCl₃
Temperature 294.7
Number of Scans 16
Spectrometer Frequency 400.18

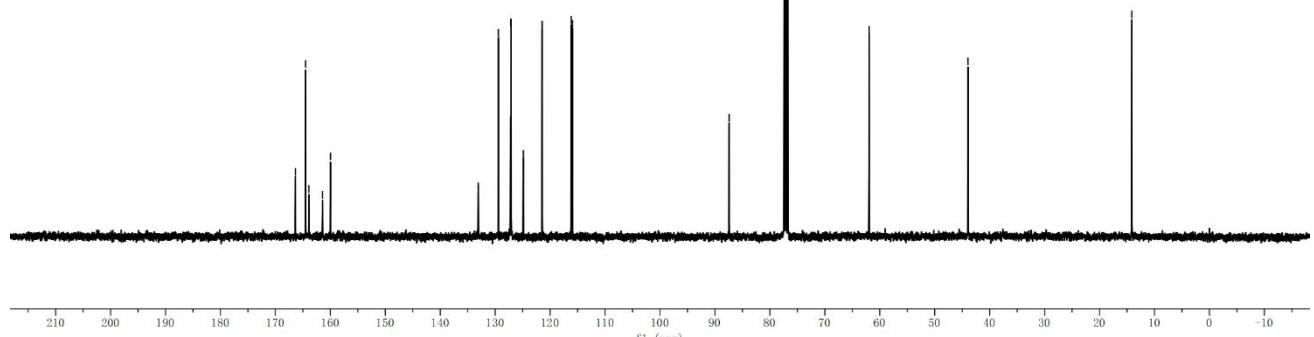
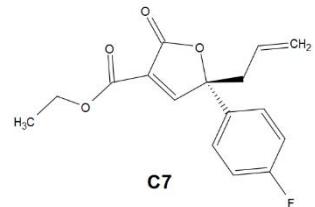


C7

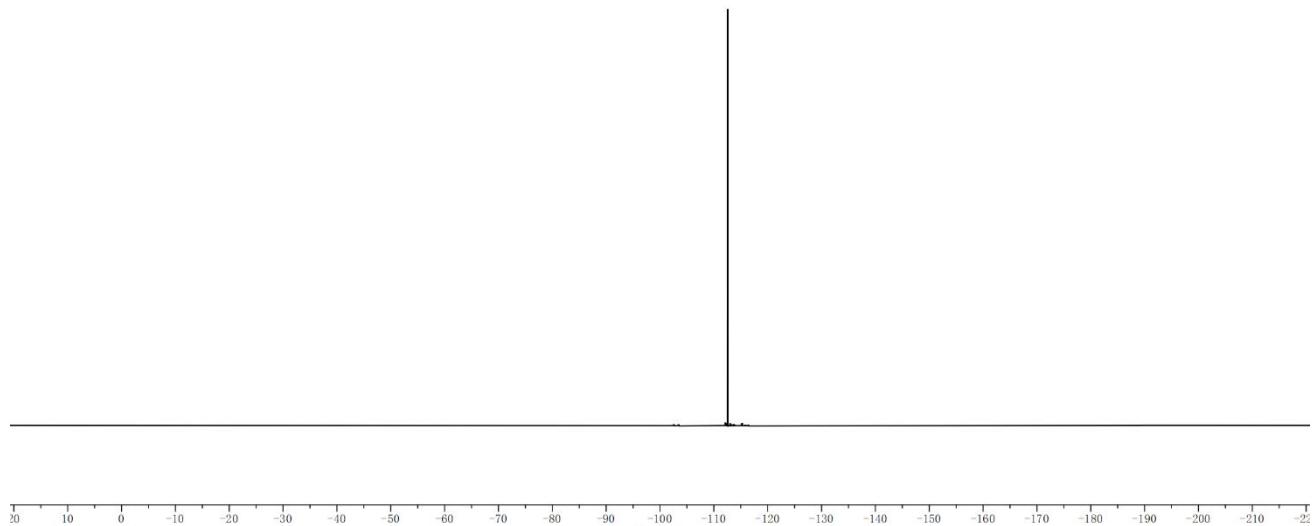
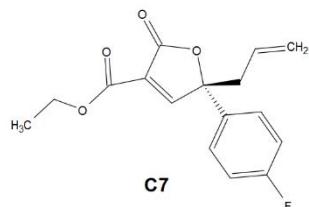


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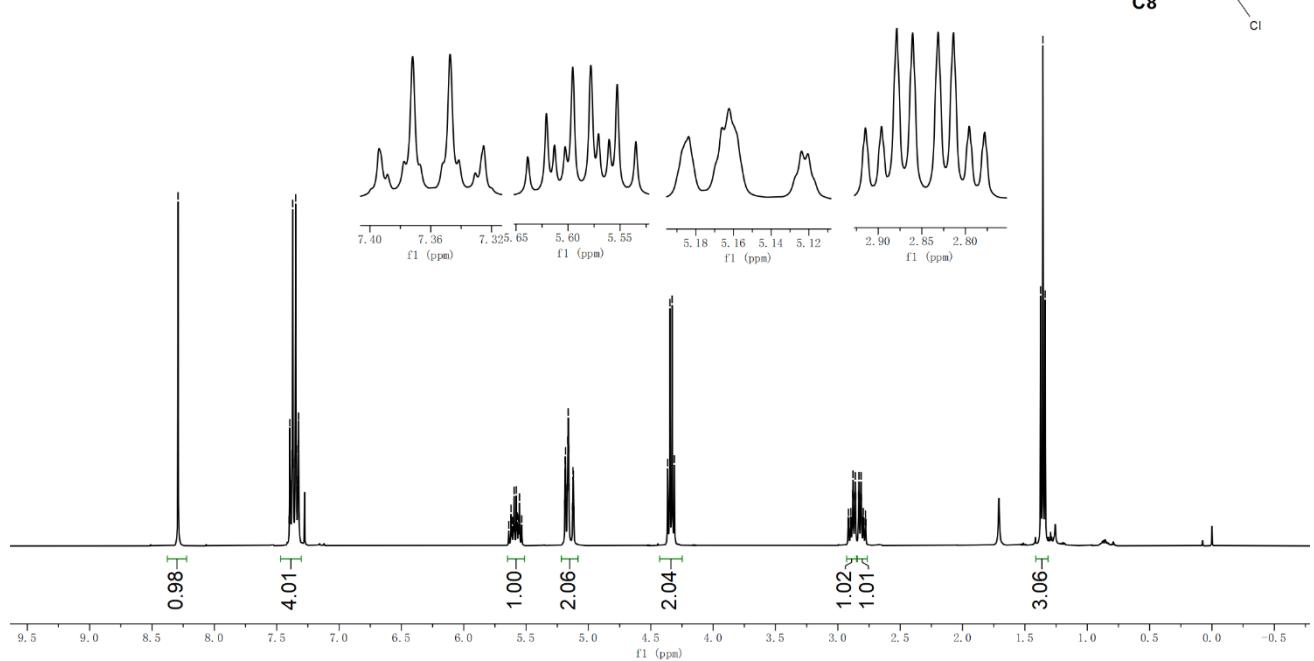
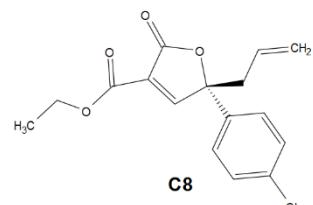
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Solvent CDCl₃
Temperature 295.2
Number of Scans 256
Spectrometer Frequency 100.64

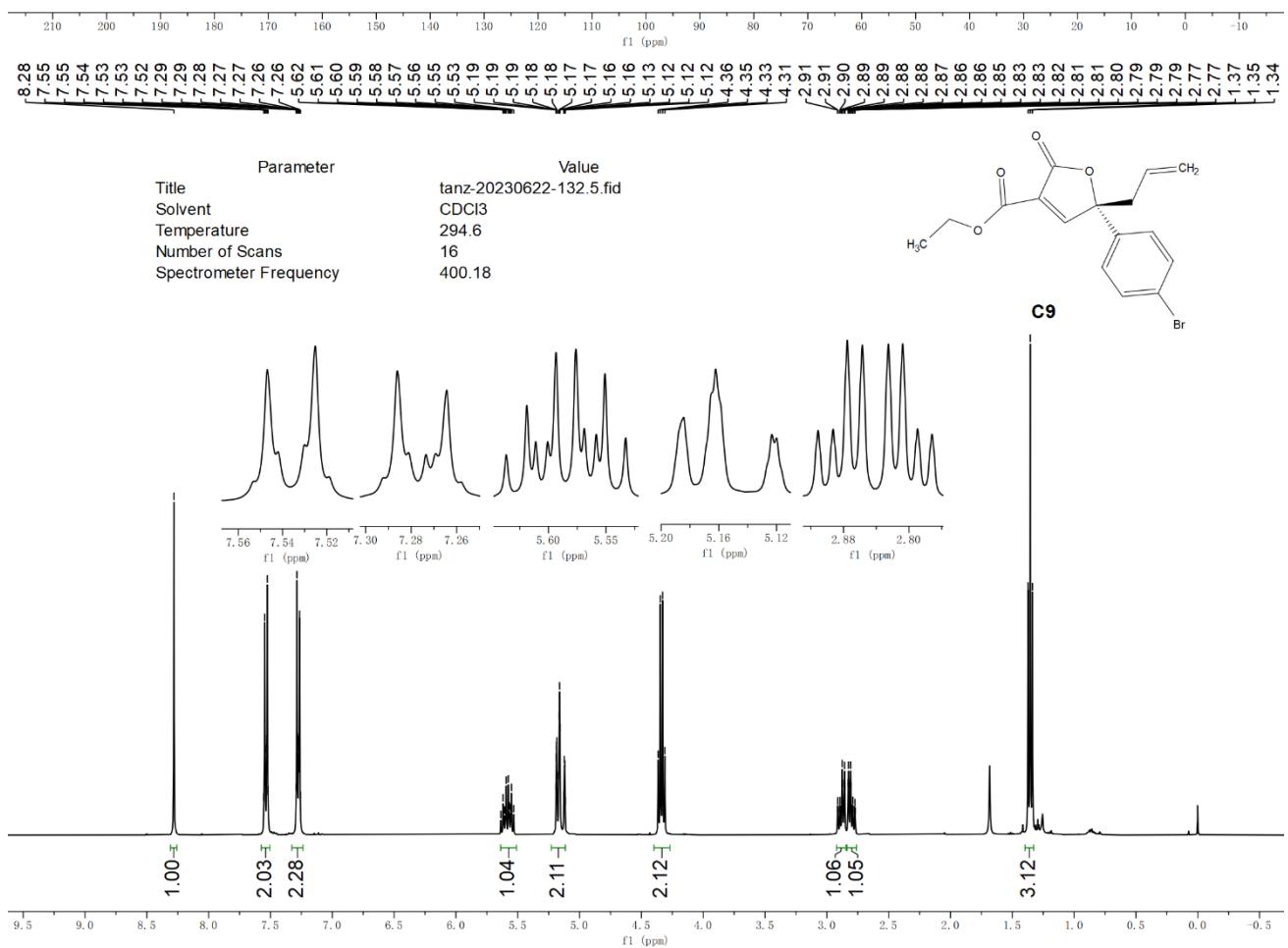
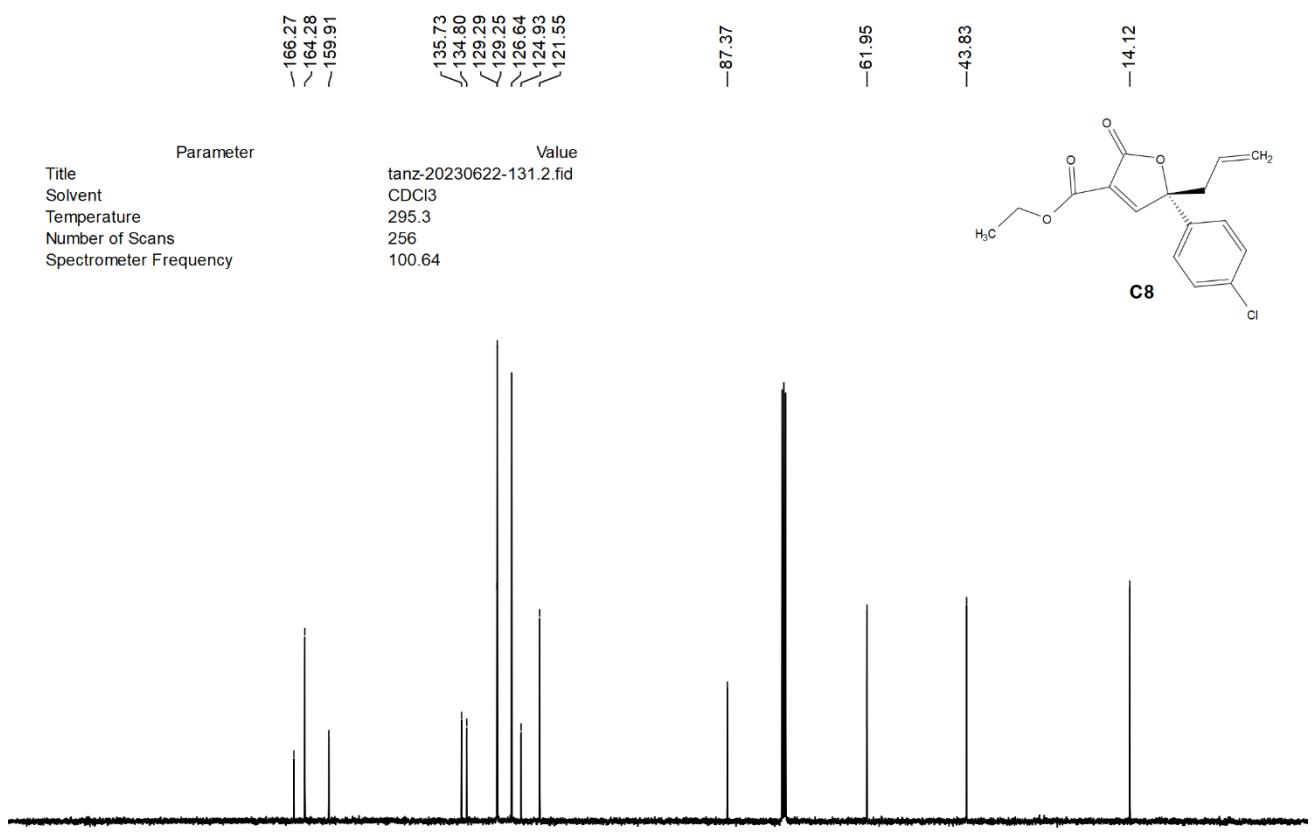


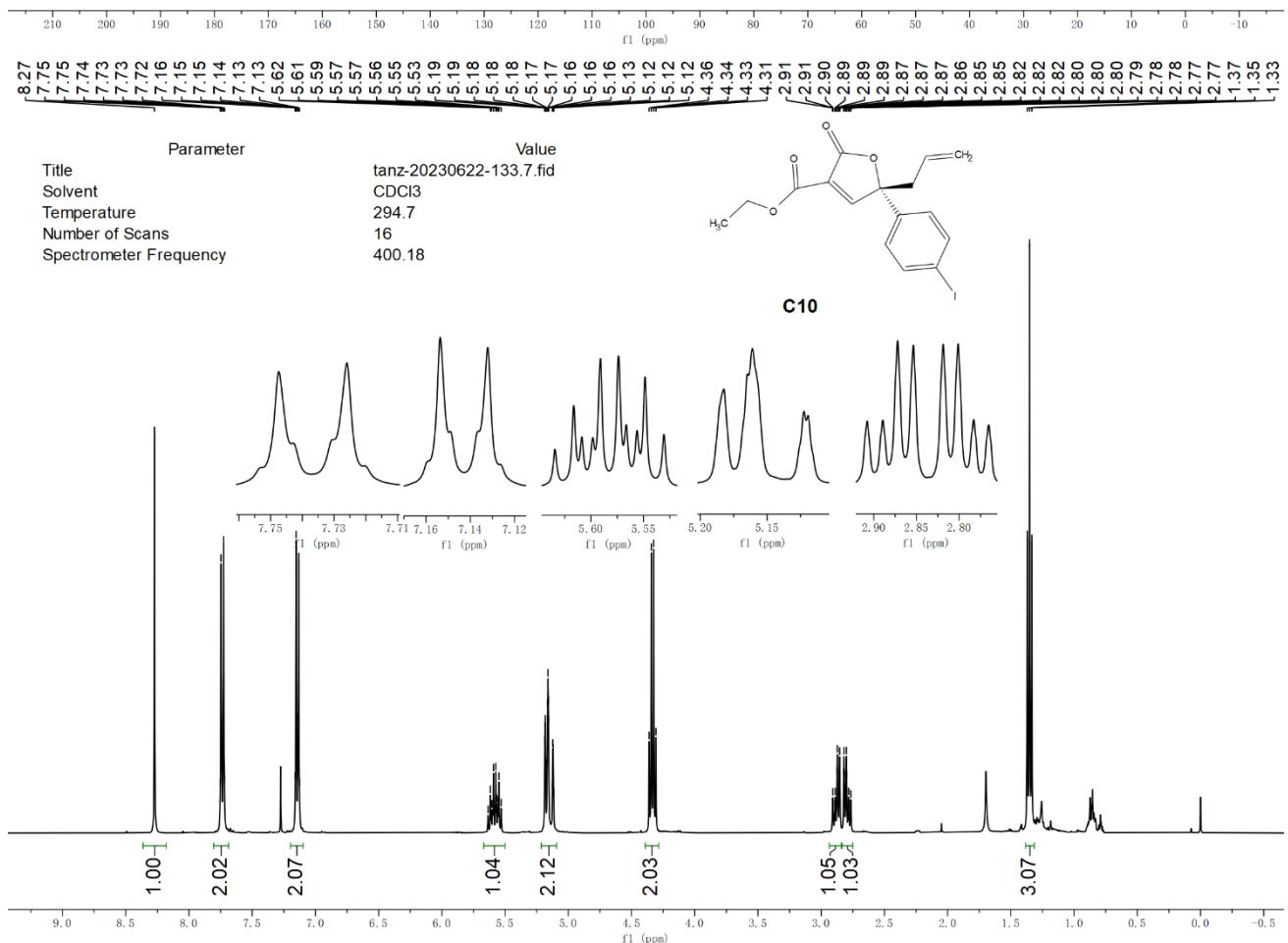
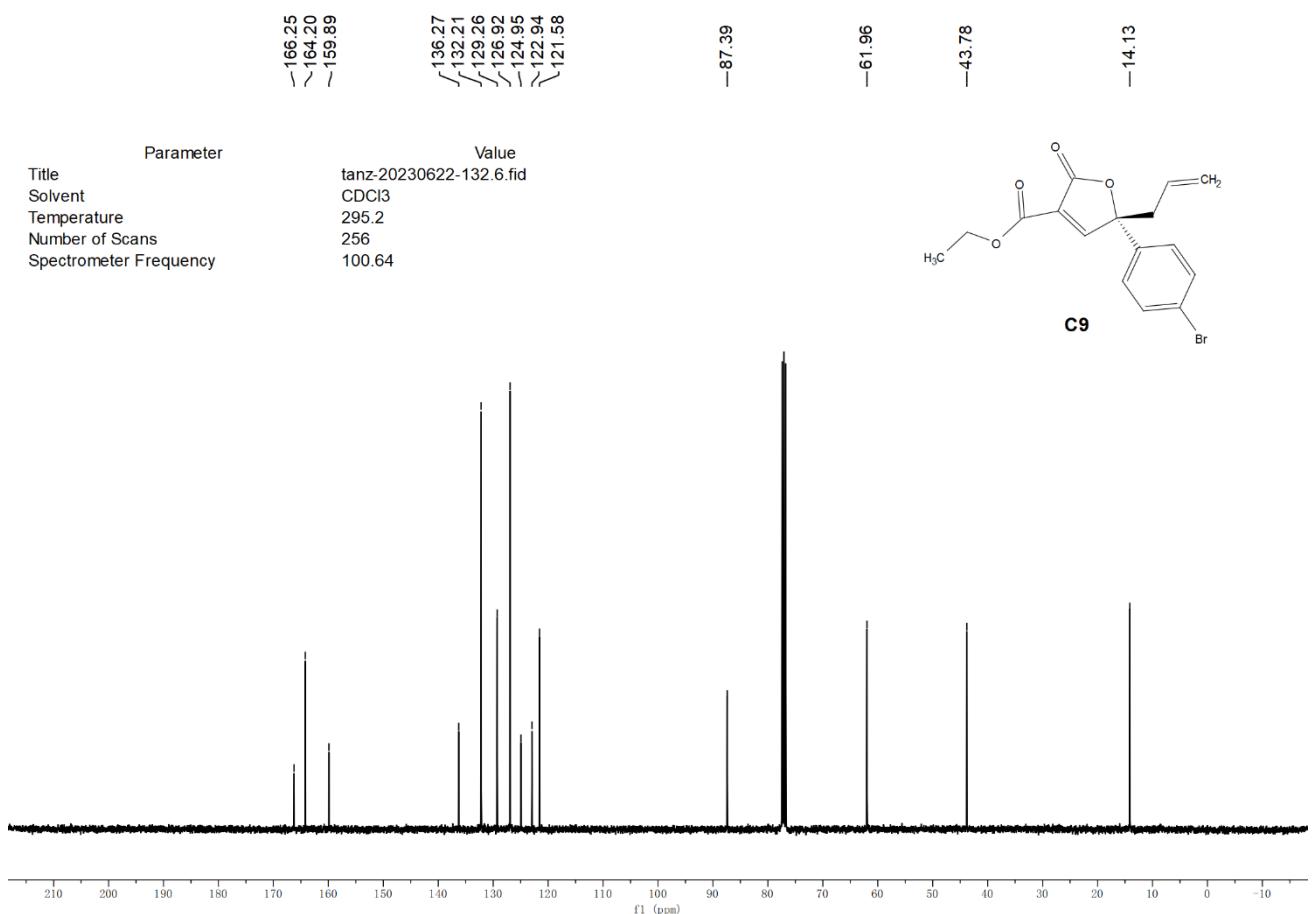
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Number of Scans	16
Spectrometer Frequency	376.51

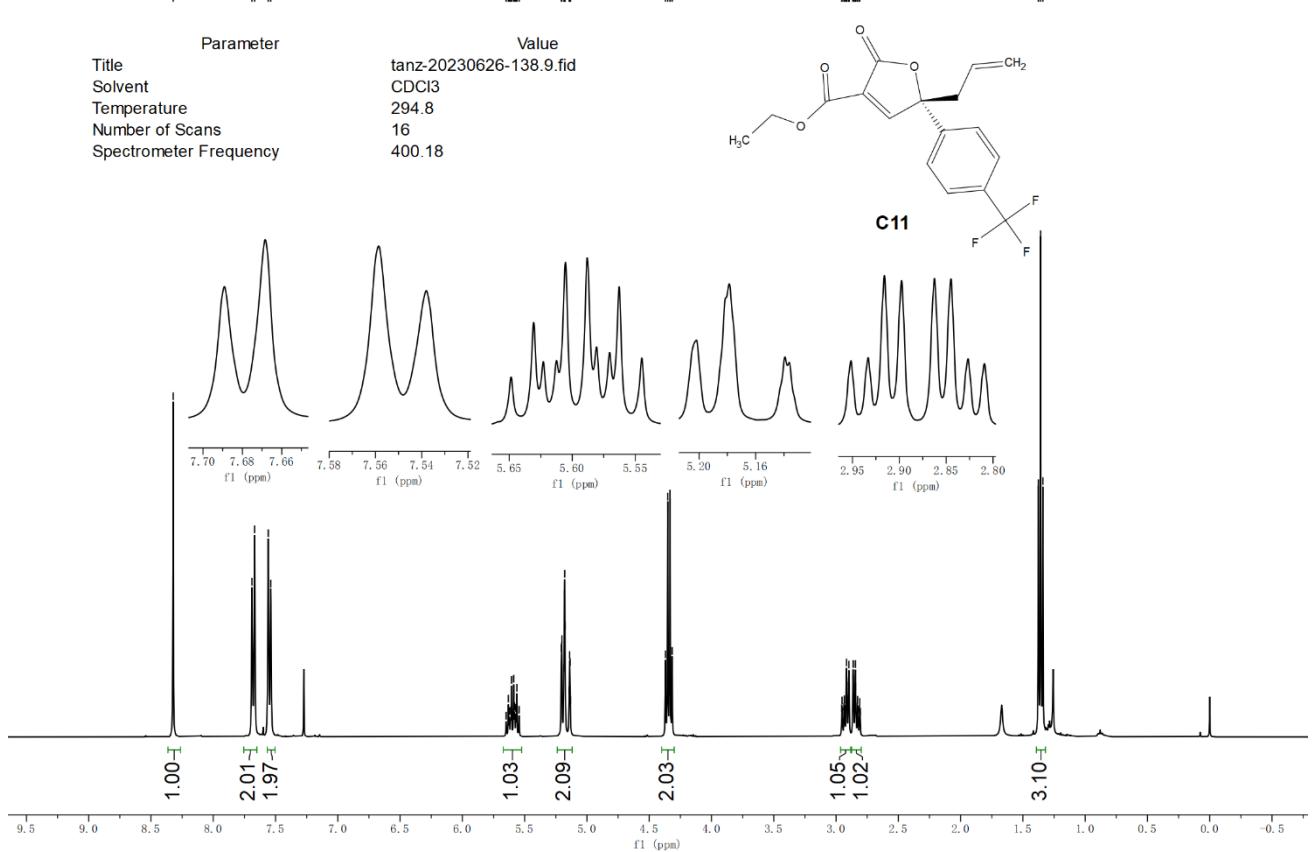
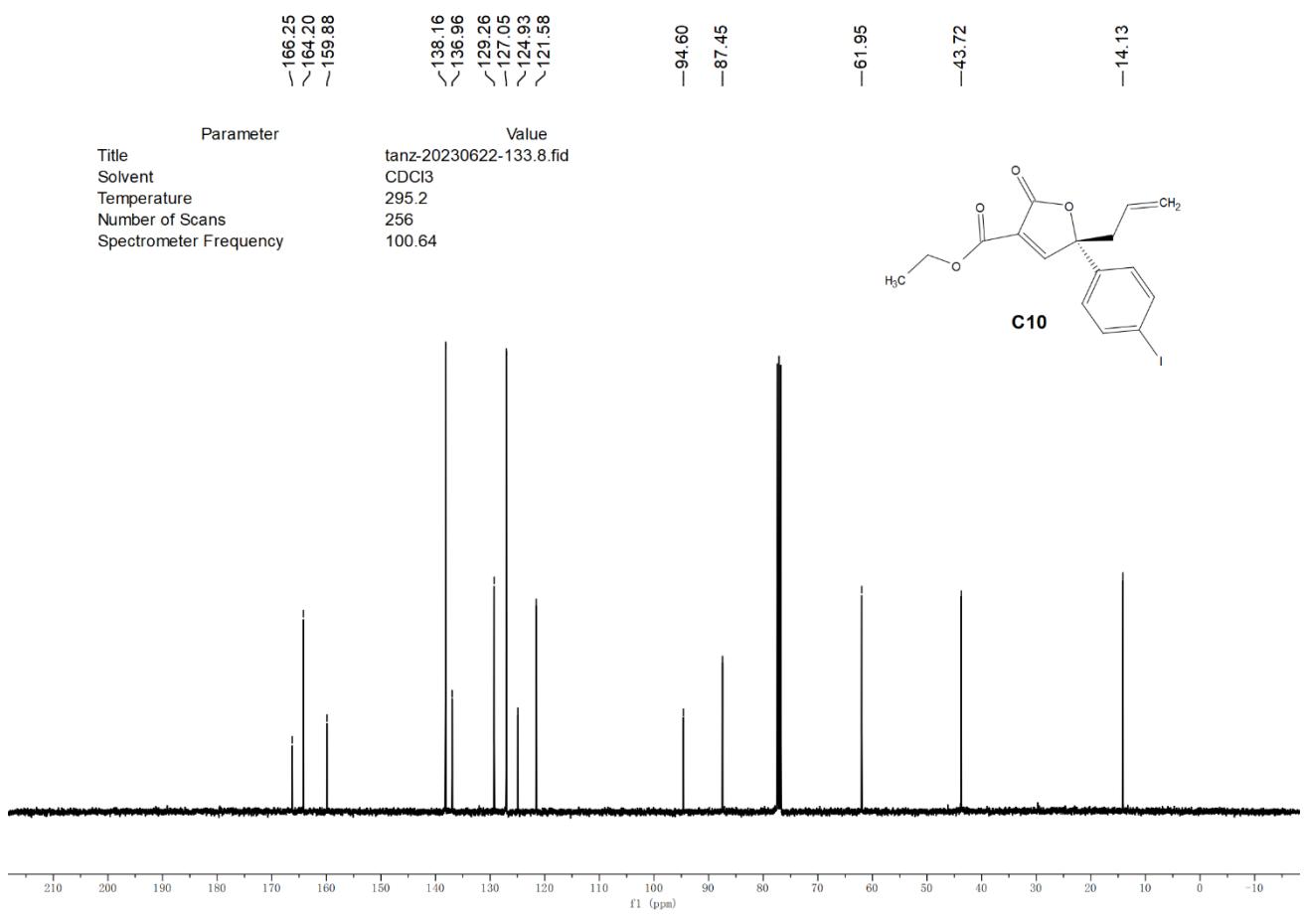


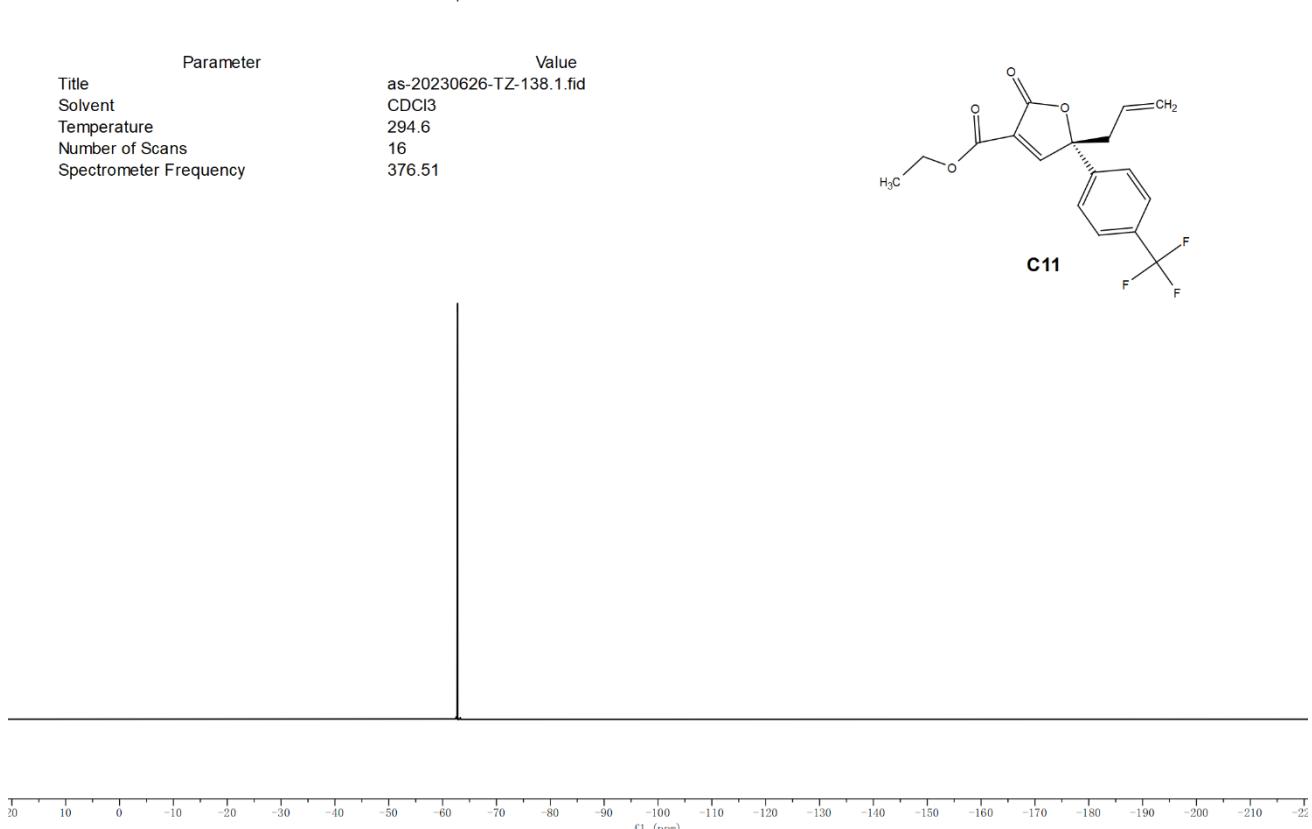
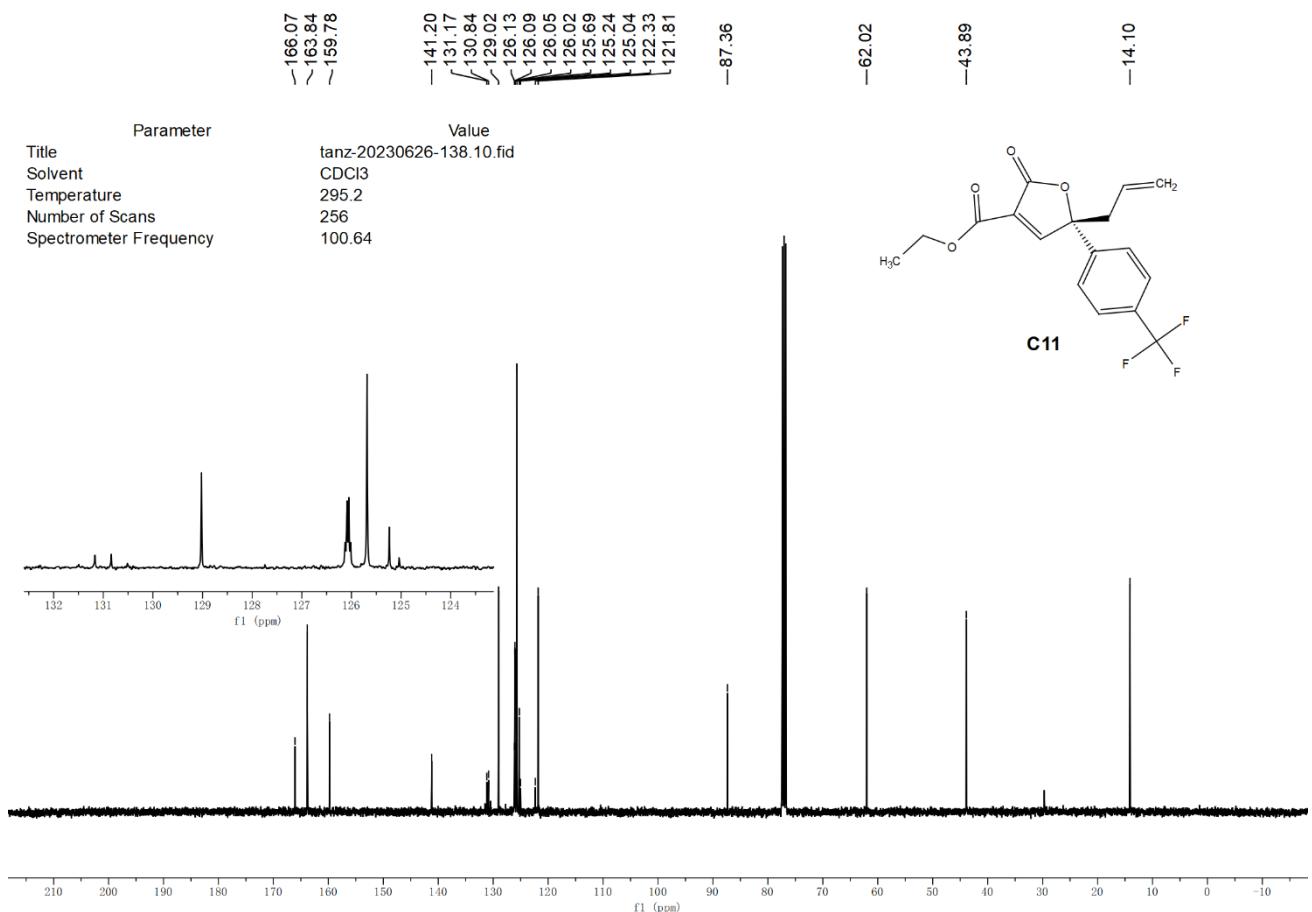
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Solvent	CDCl3
Temperature	294.6
Number of Scans	16
Spectrometer Frequency	400.18

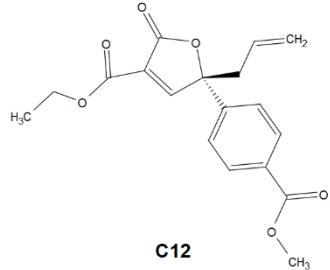
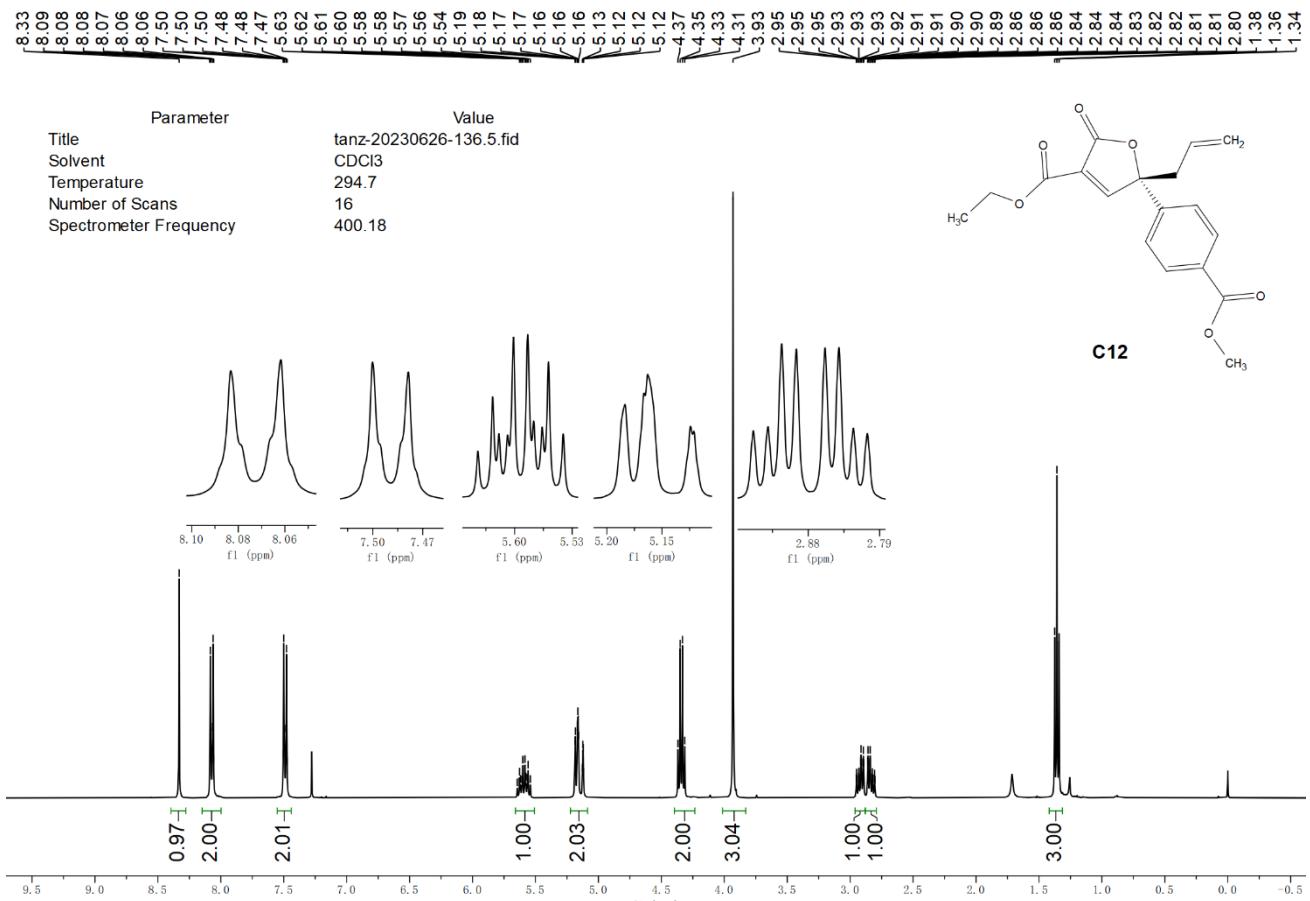






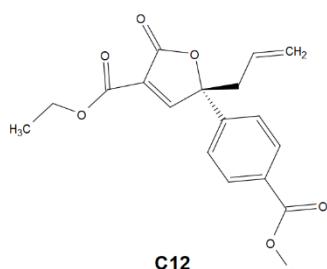
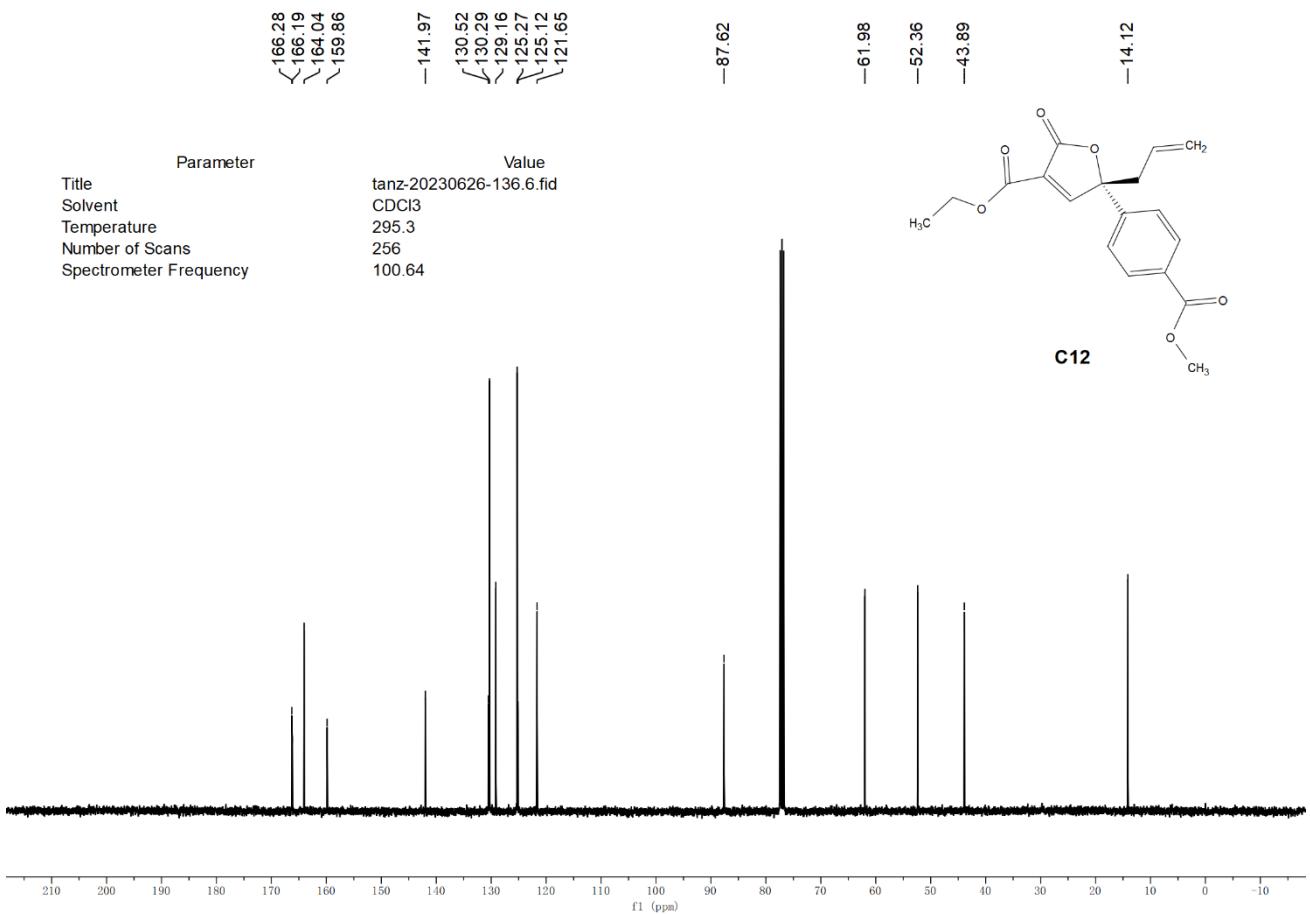






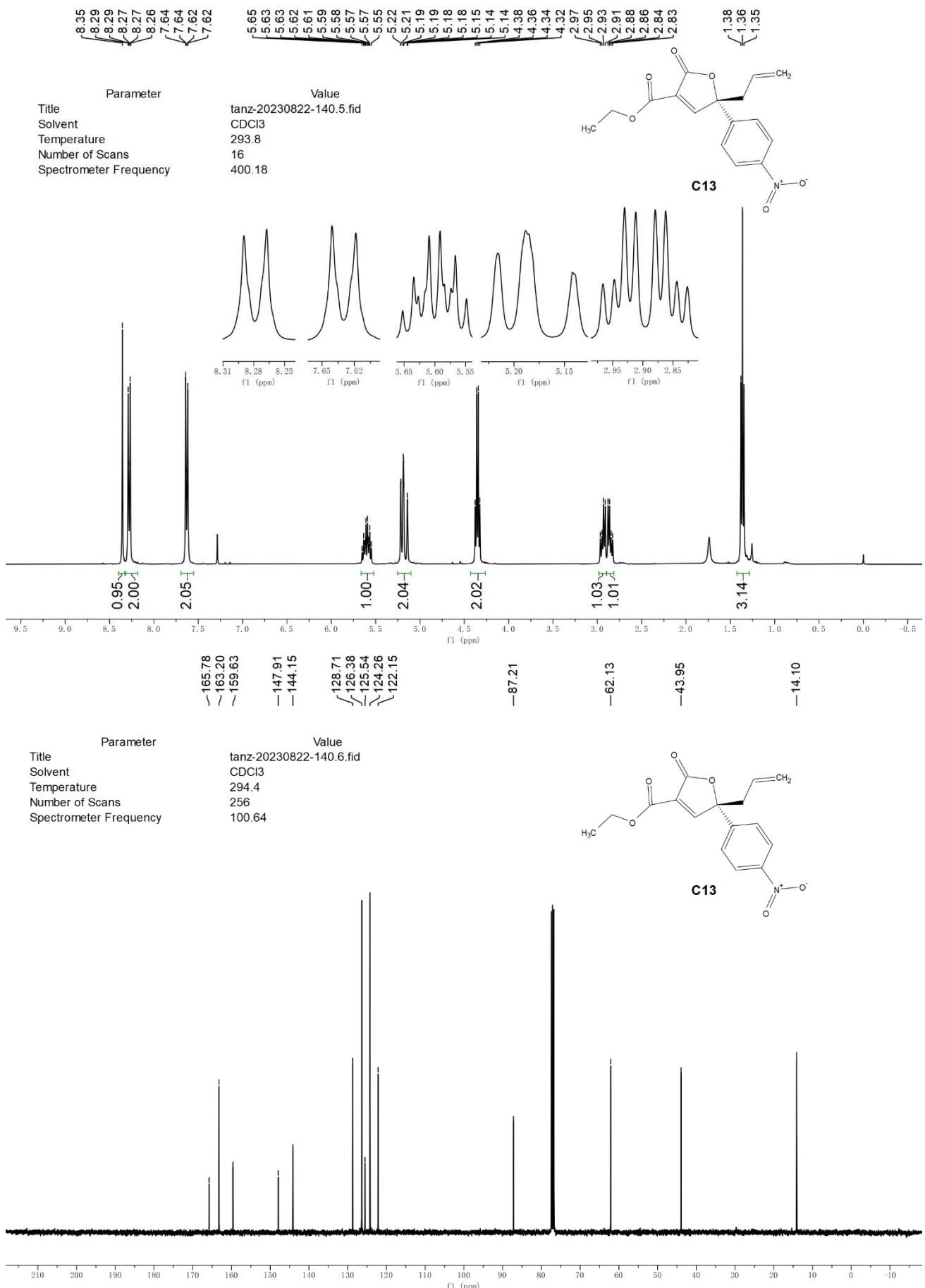
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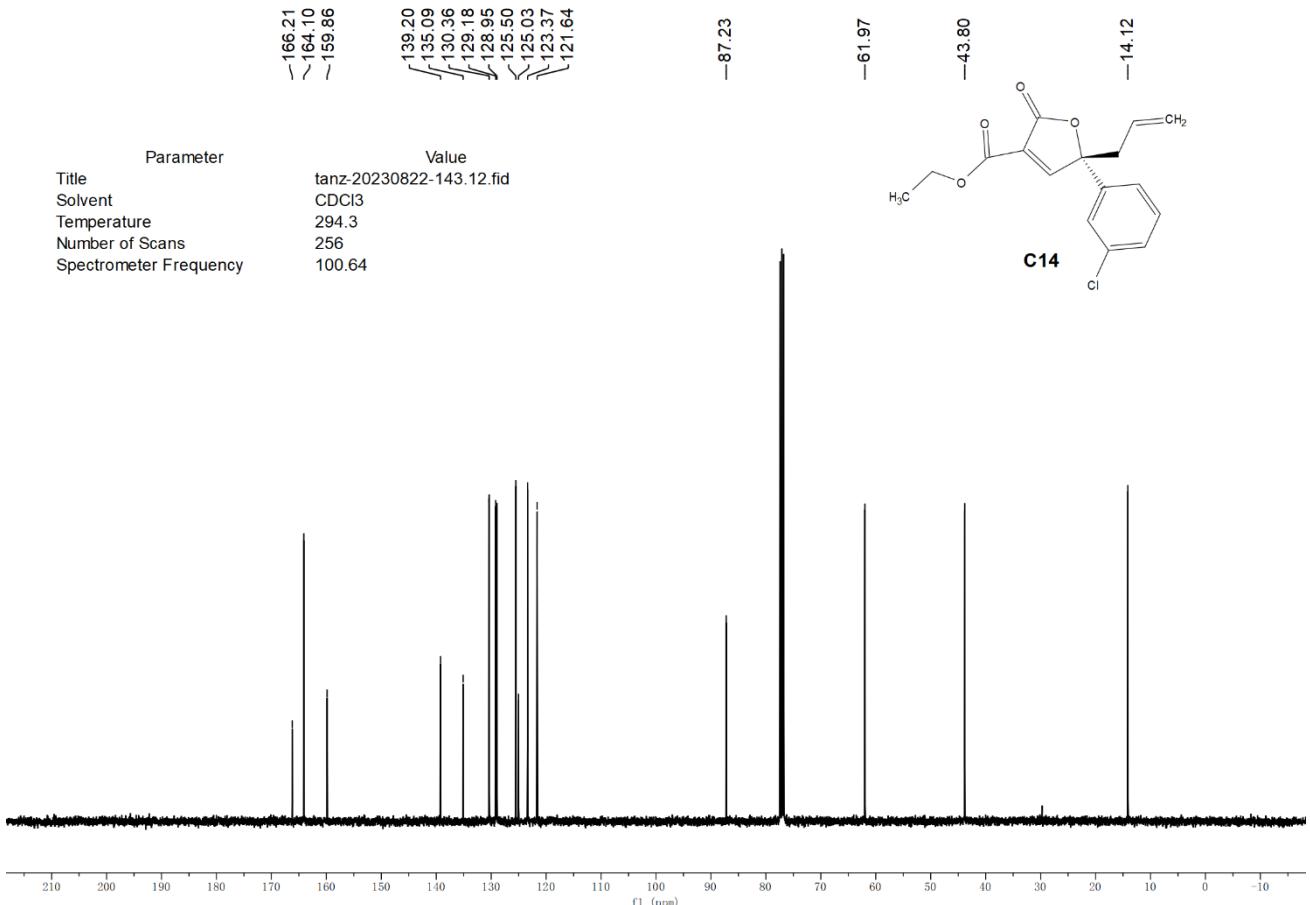
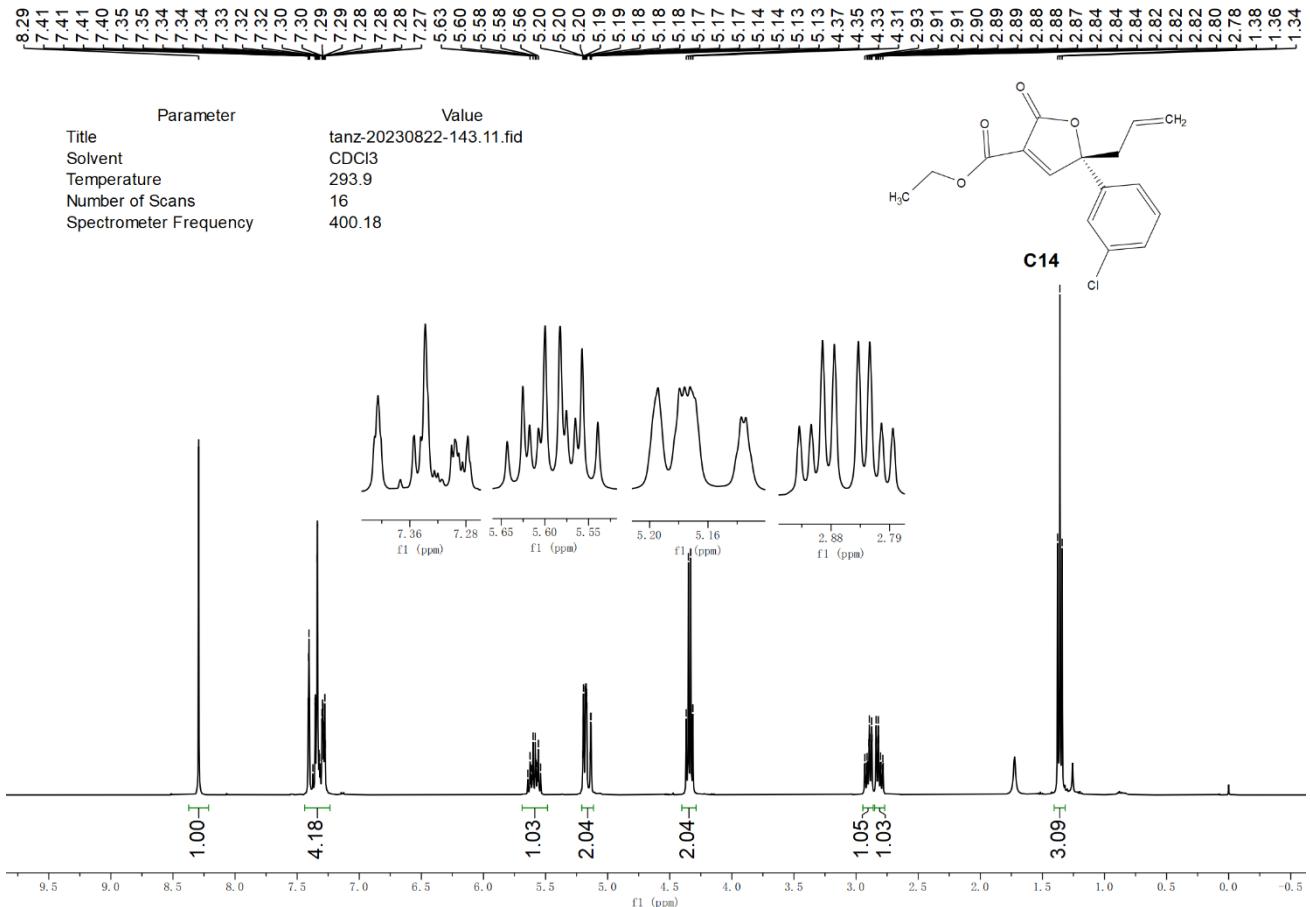
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Solvent	CDC13
Temperature	294.7
Number of Scans	16
Spectrometer Frequency	400.18

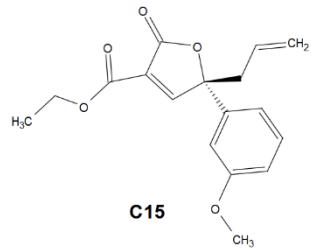
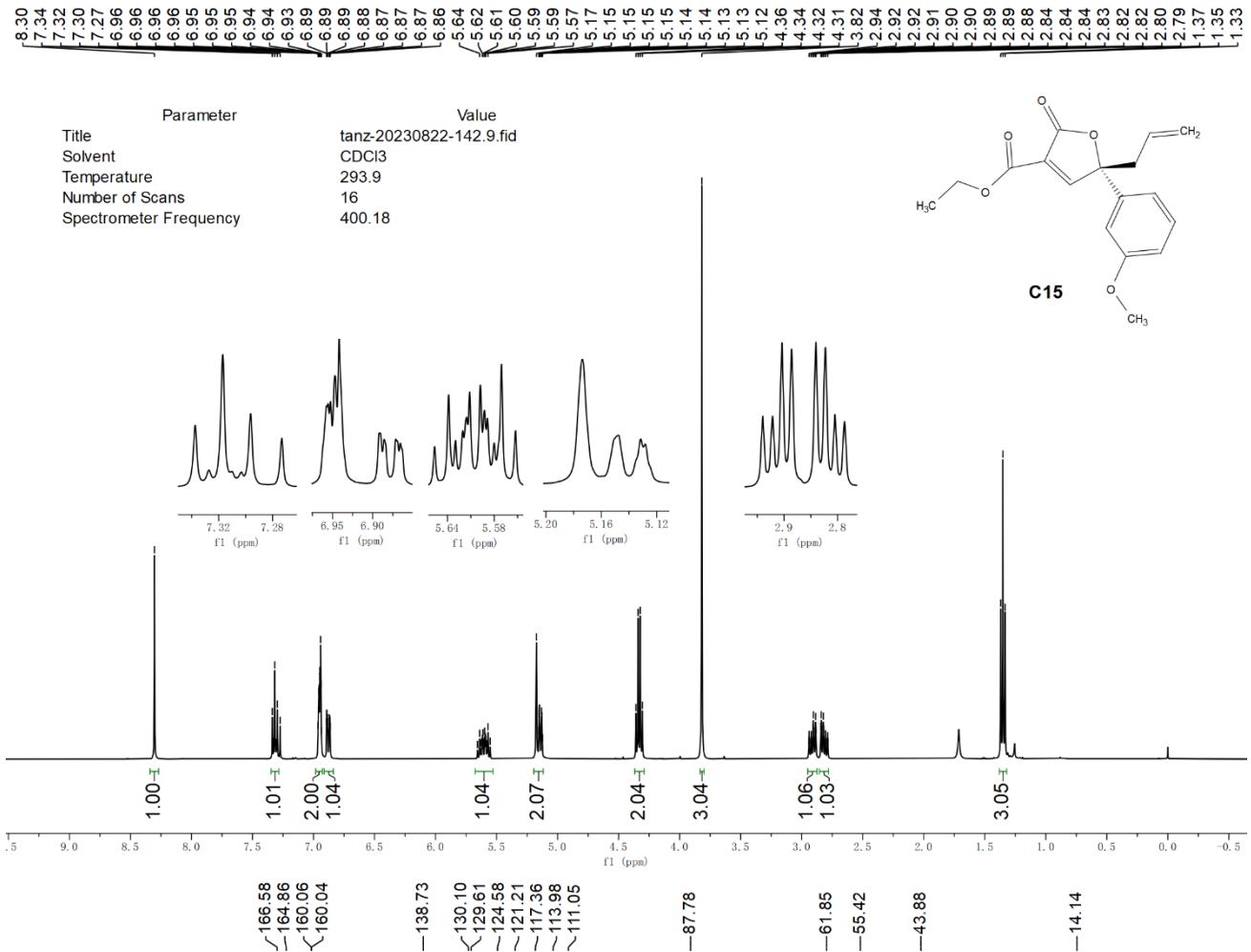


C12

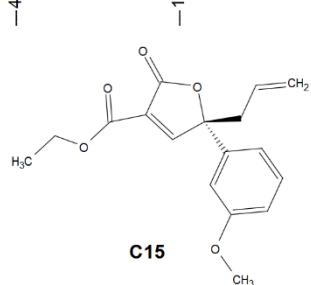
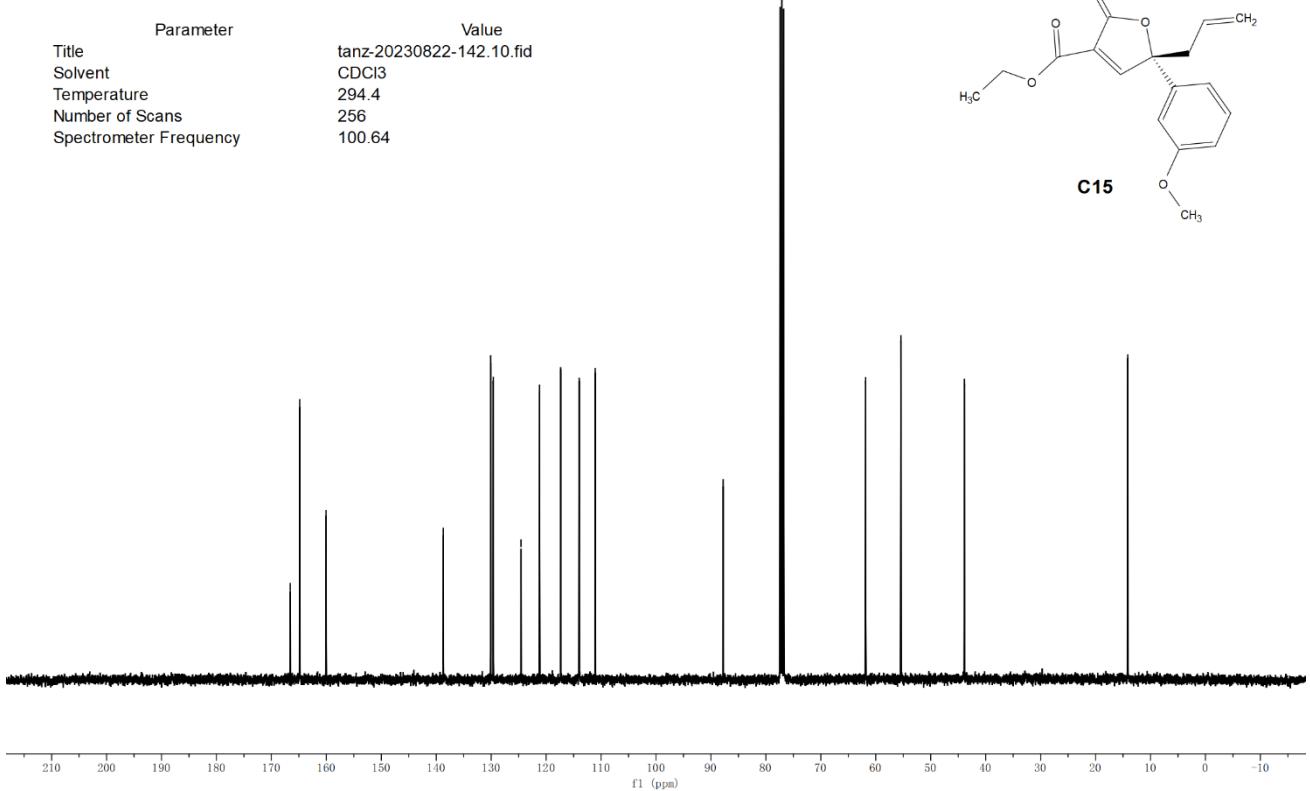
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Temperature	295.3
Number of Scans	256
Spectrometer Frequency	100.64





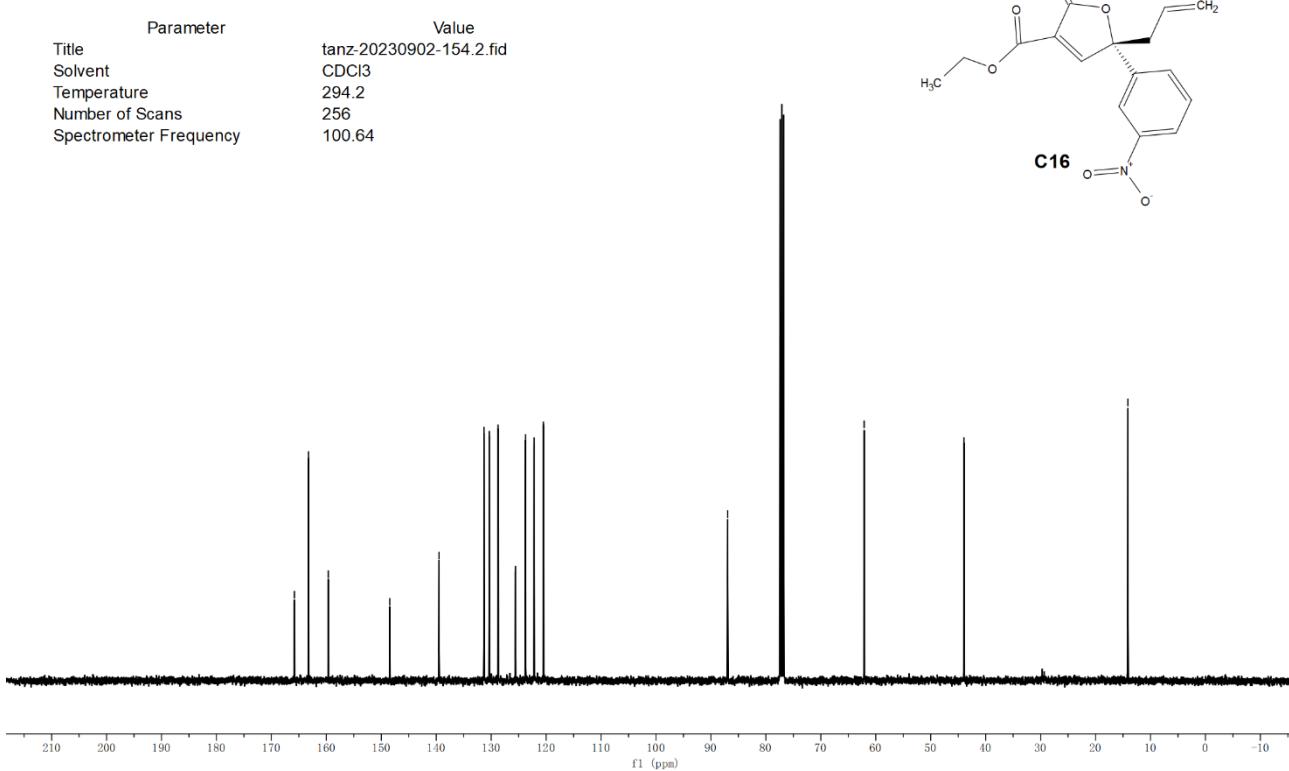
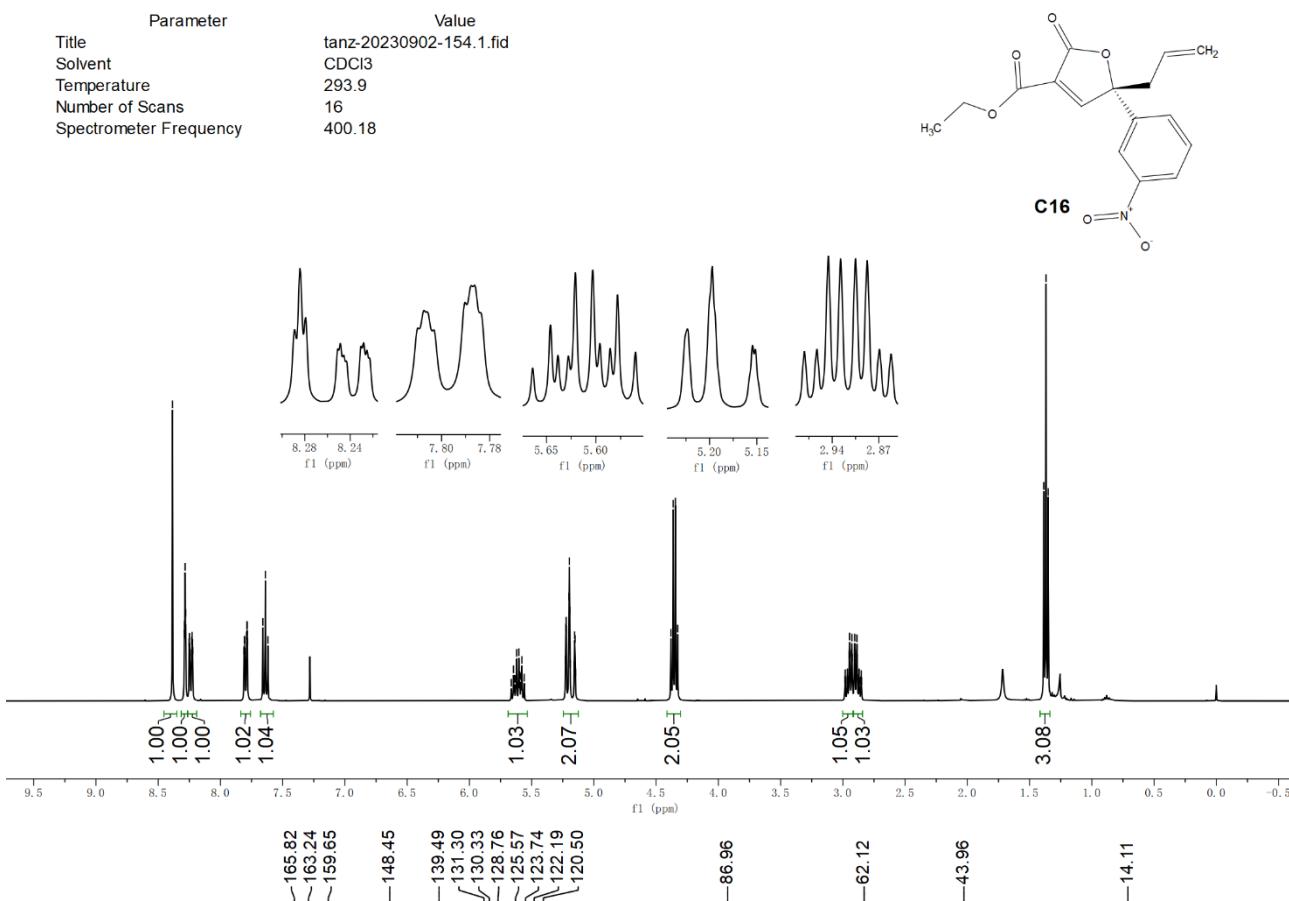


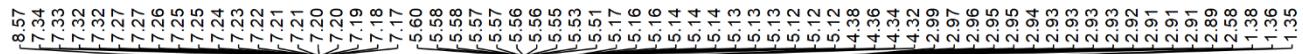
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Solvent	CDC13
Temperature	293.9
Number of Scans	16
Spectrometer Frequency	400.18



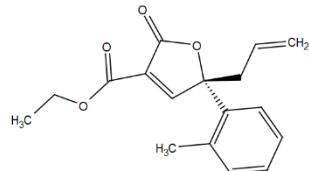
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Solvent	CDCl3
Temperature	294.4
Number of Scans	256
Spectrometer Frequency	100.64

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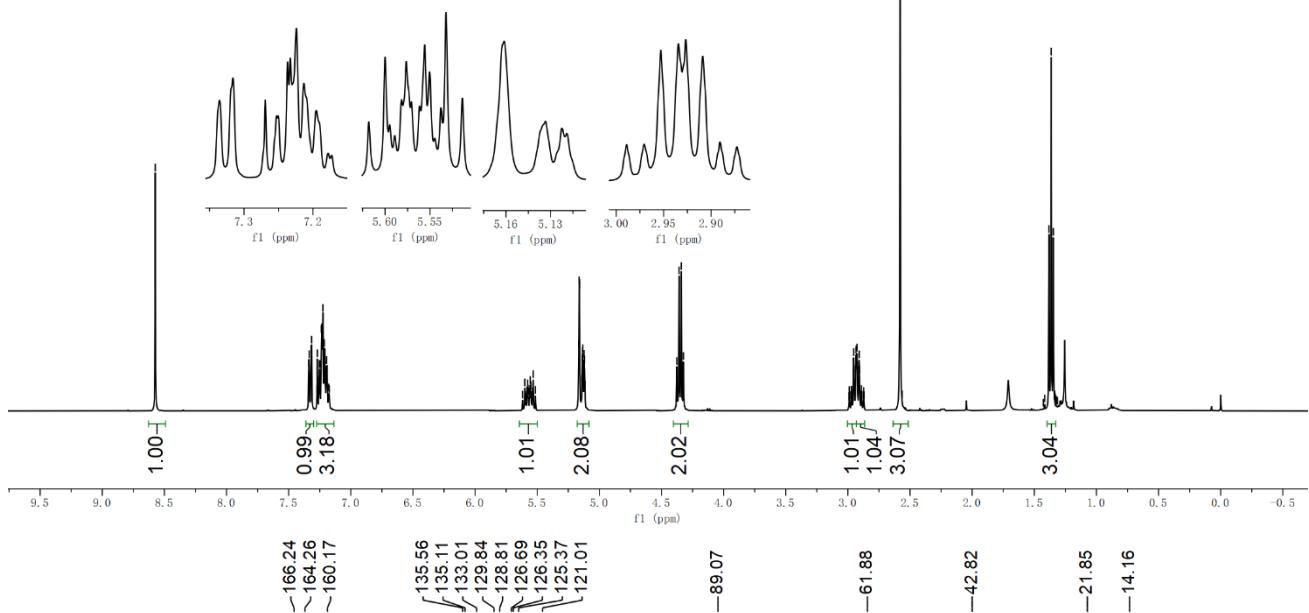




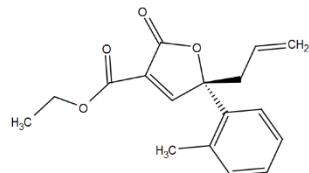
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Solvent	CDCl ₃
Temperature	293.7
Number of Scans	16
Spectrometer Frequency	400.18



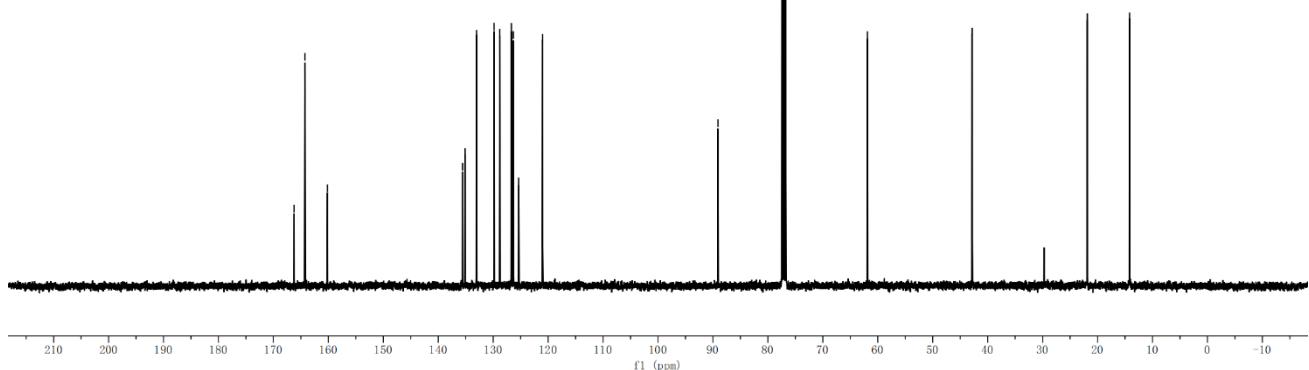
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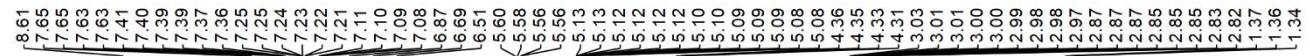


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Spectrometer Frequency	100.64

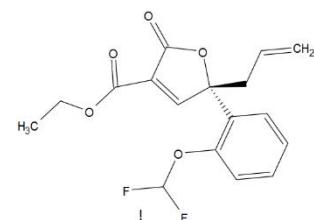


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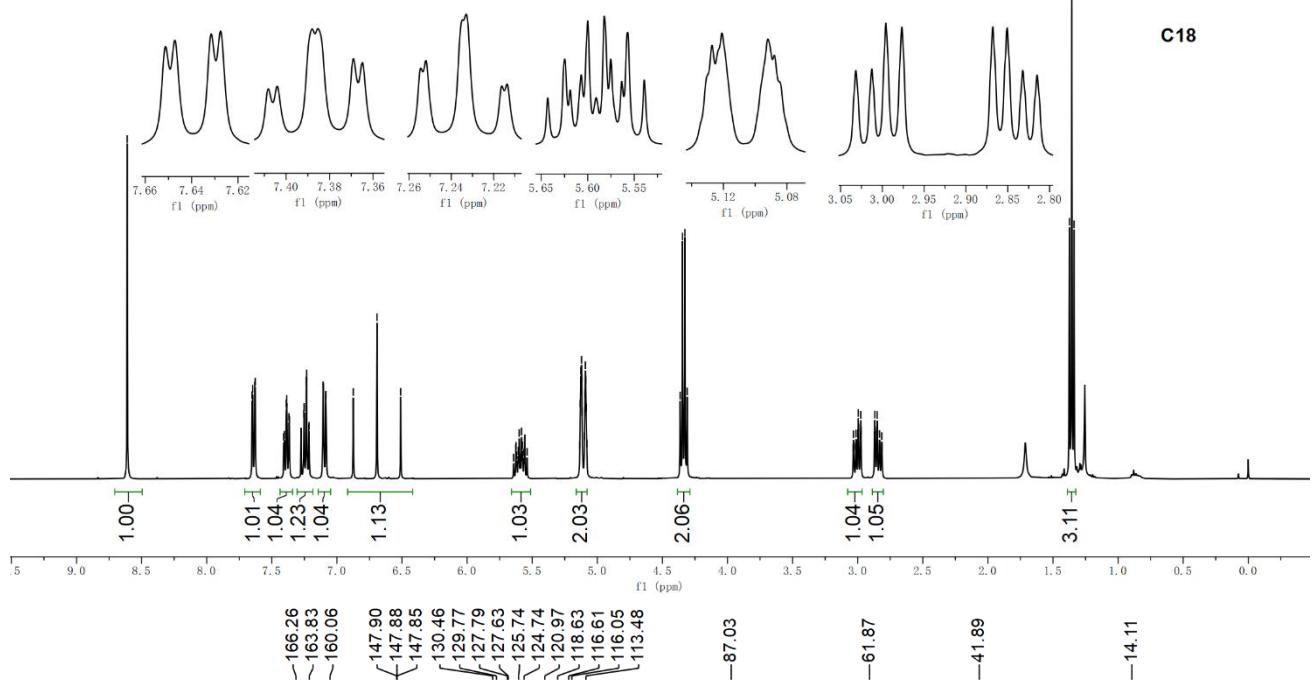




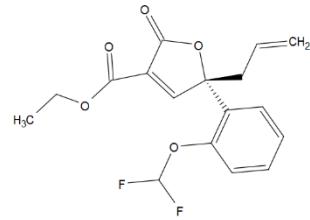
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Temperature	293.7
Number of Scans	16
Spectrometer Frequency	400.18



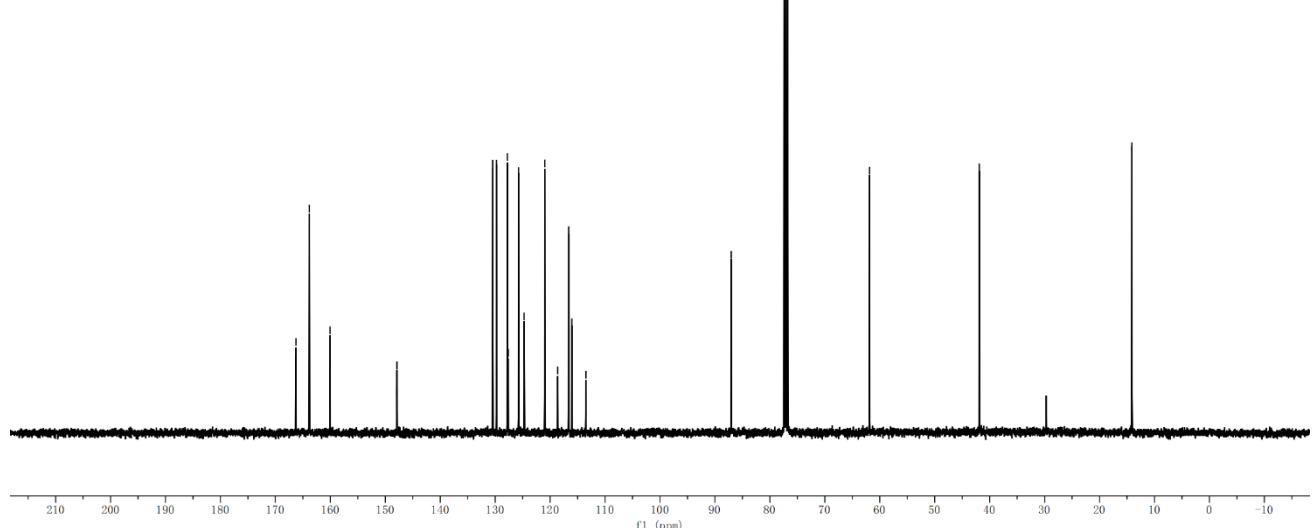
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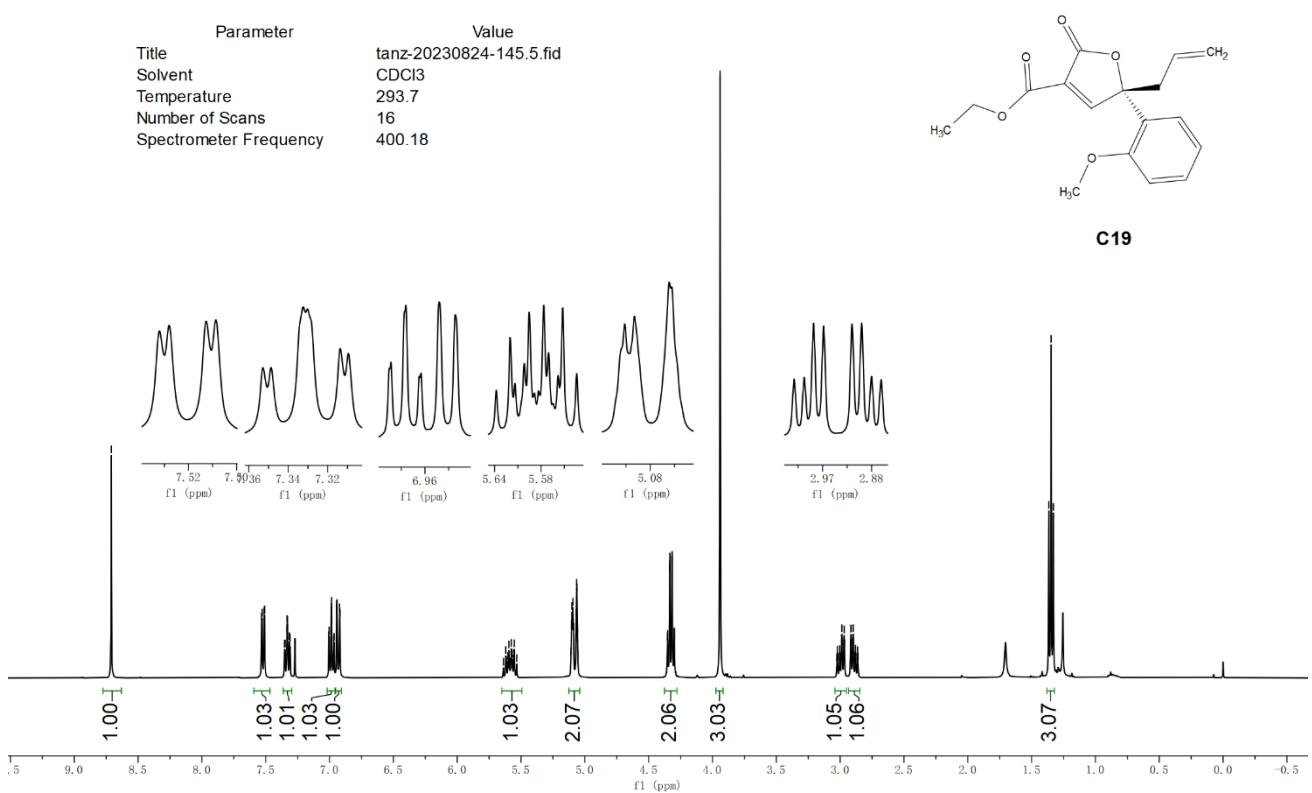
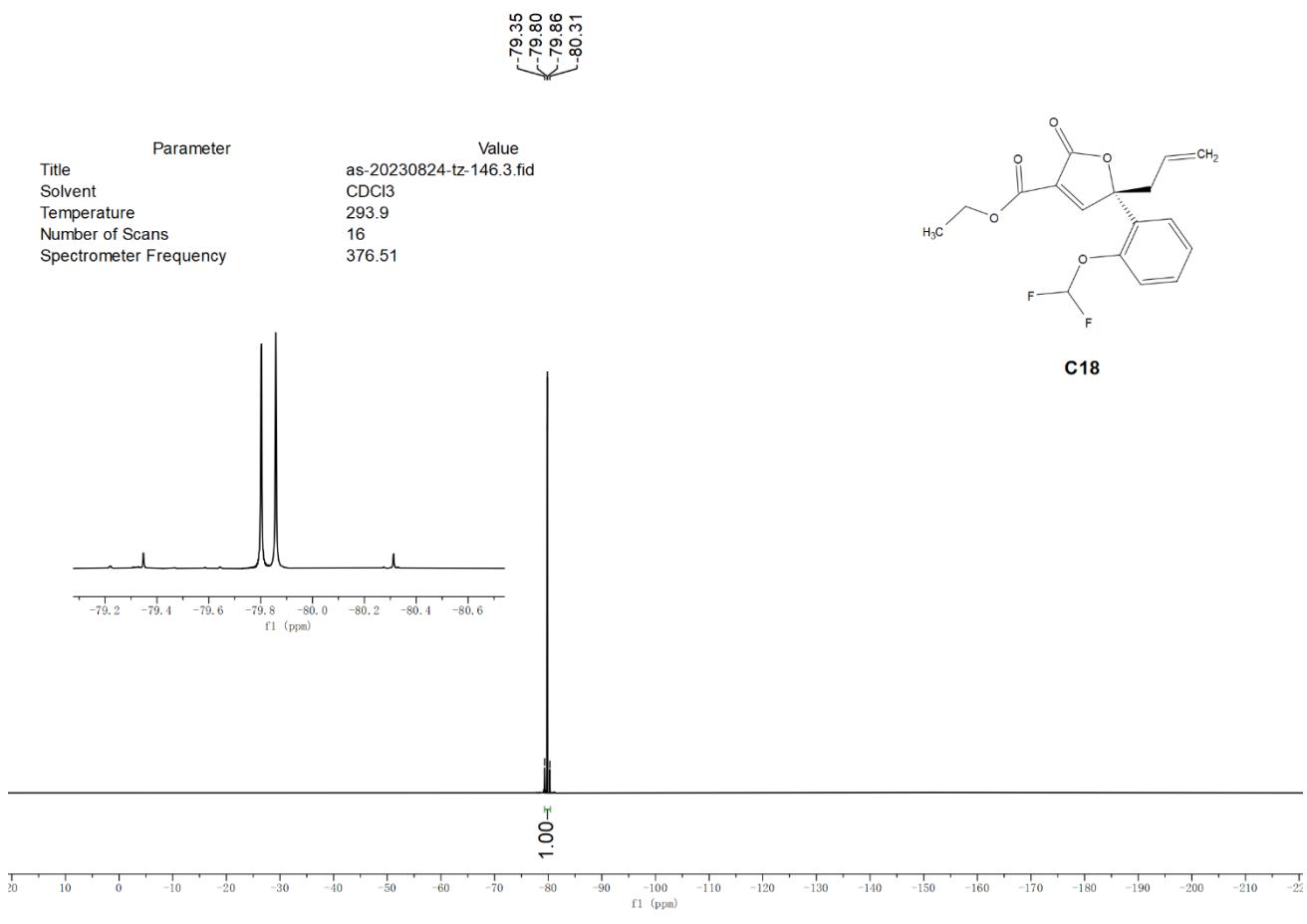


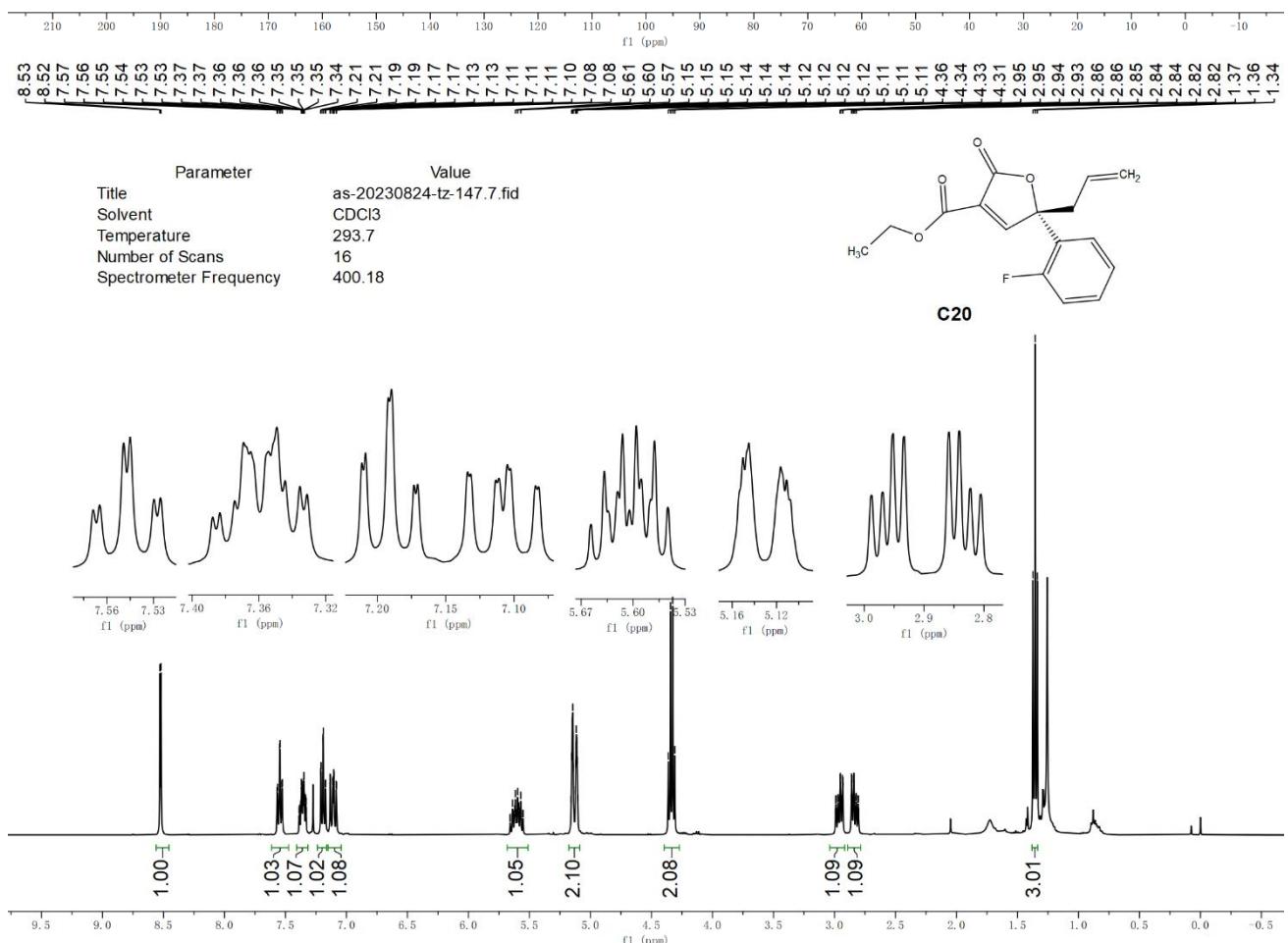
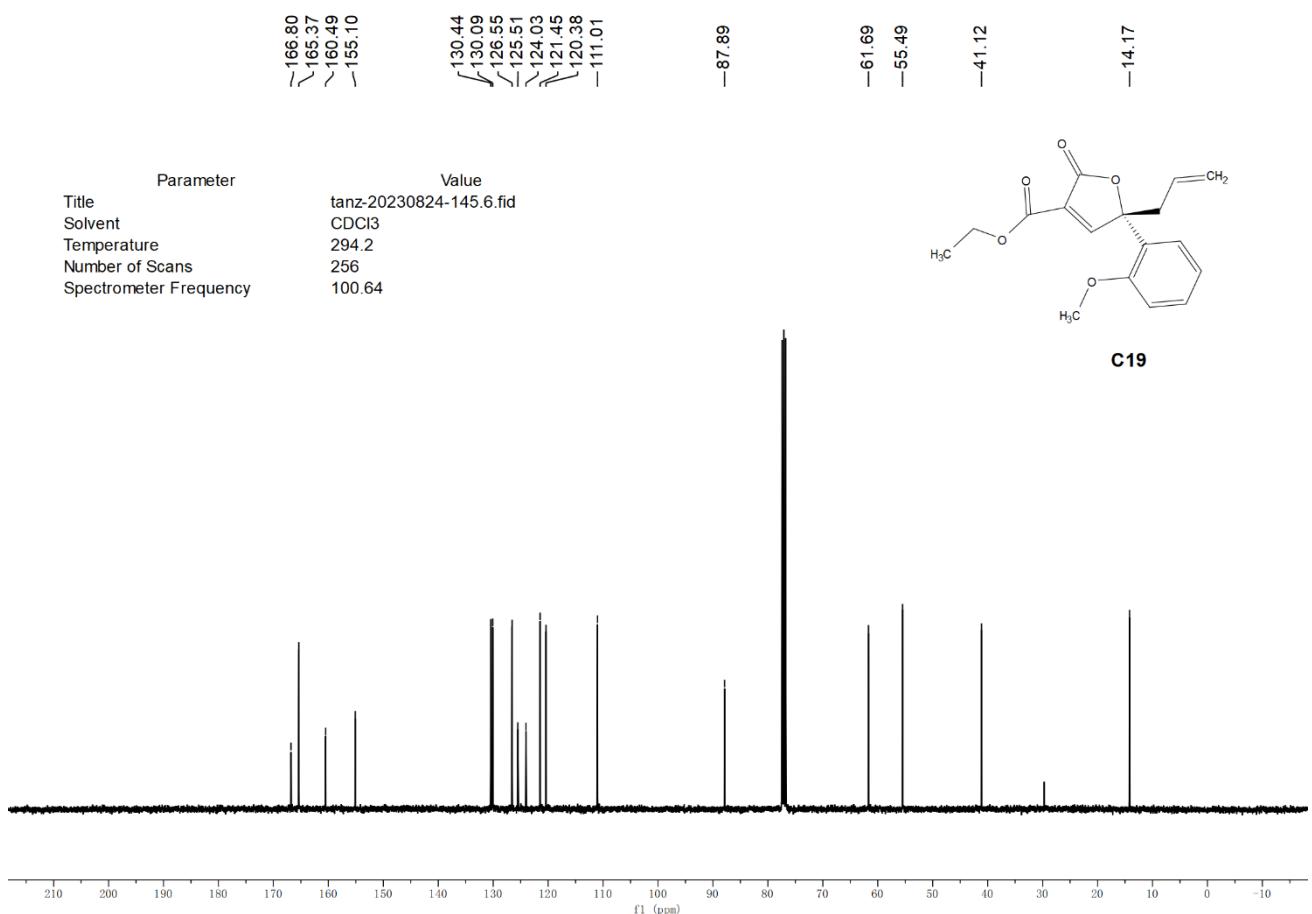
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Solvent	CDCl ₃
Temperature	294.3
Number of Scans	256
Spectrometer Frequency	100.64

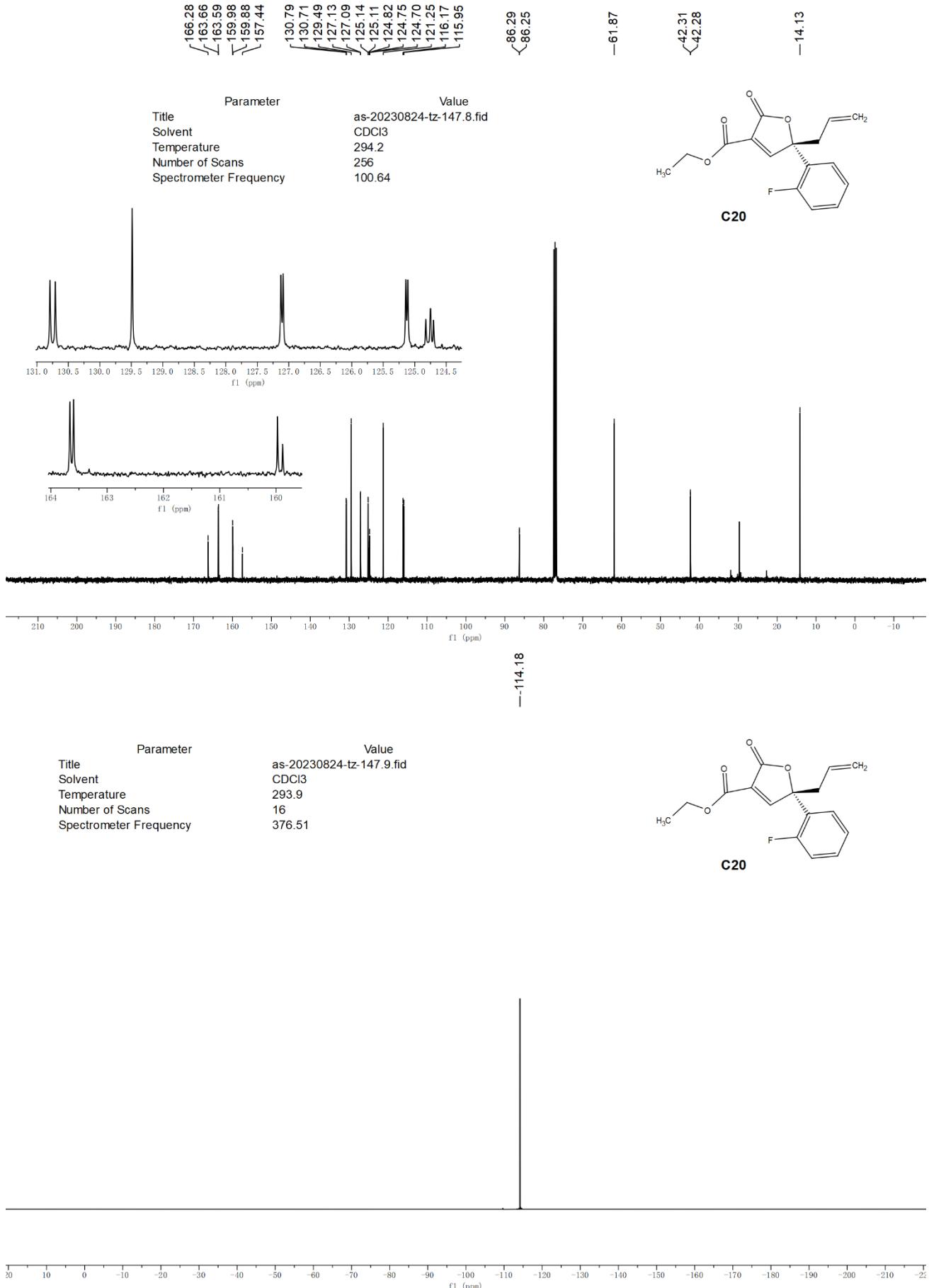


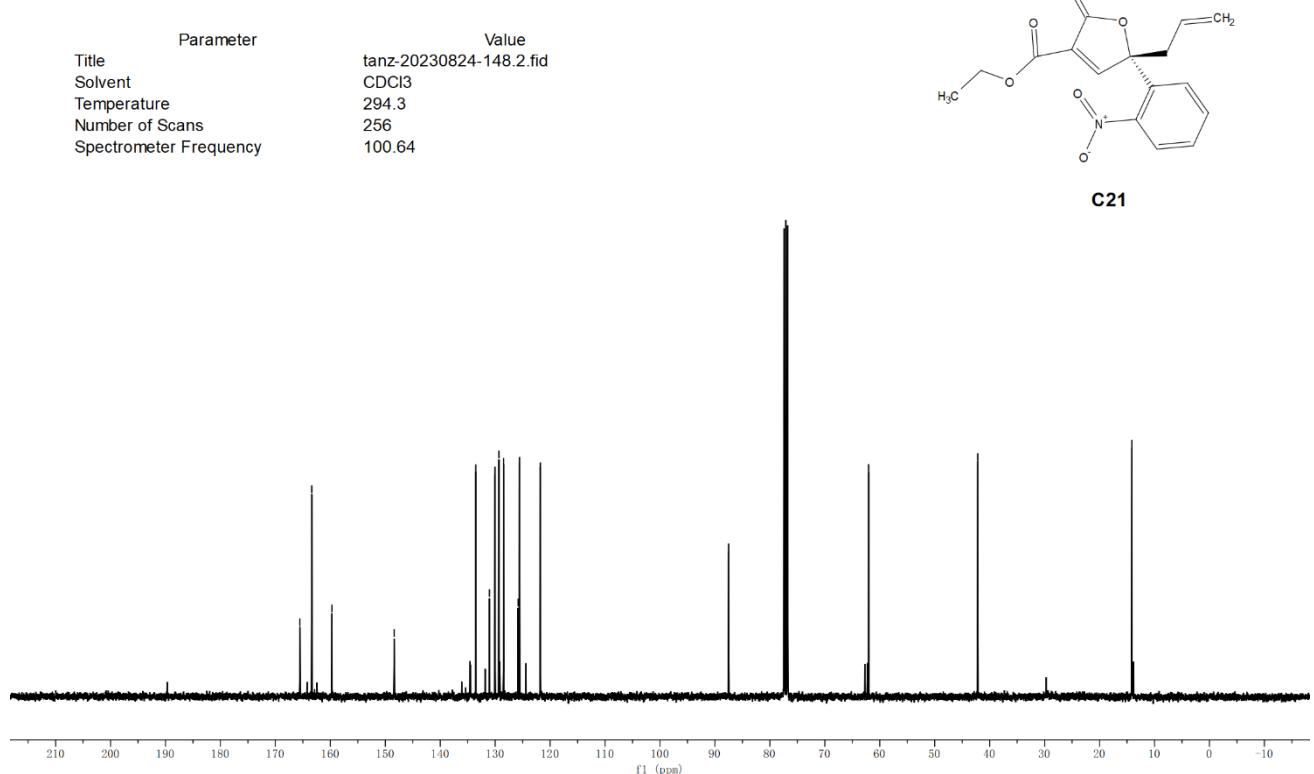
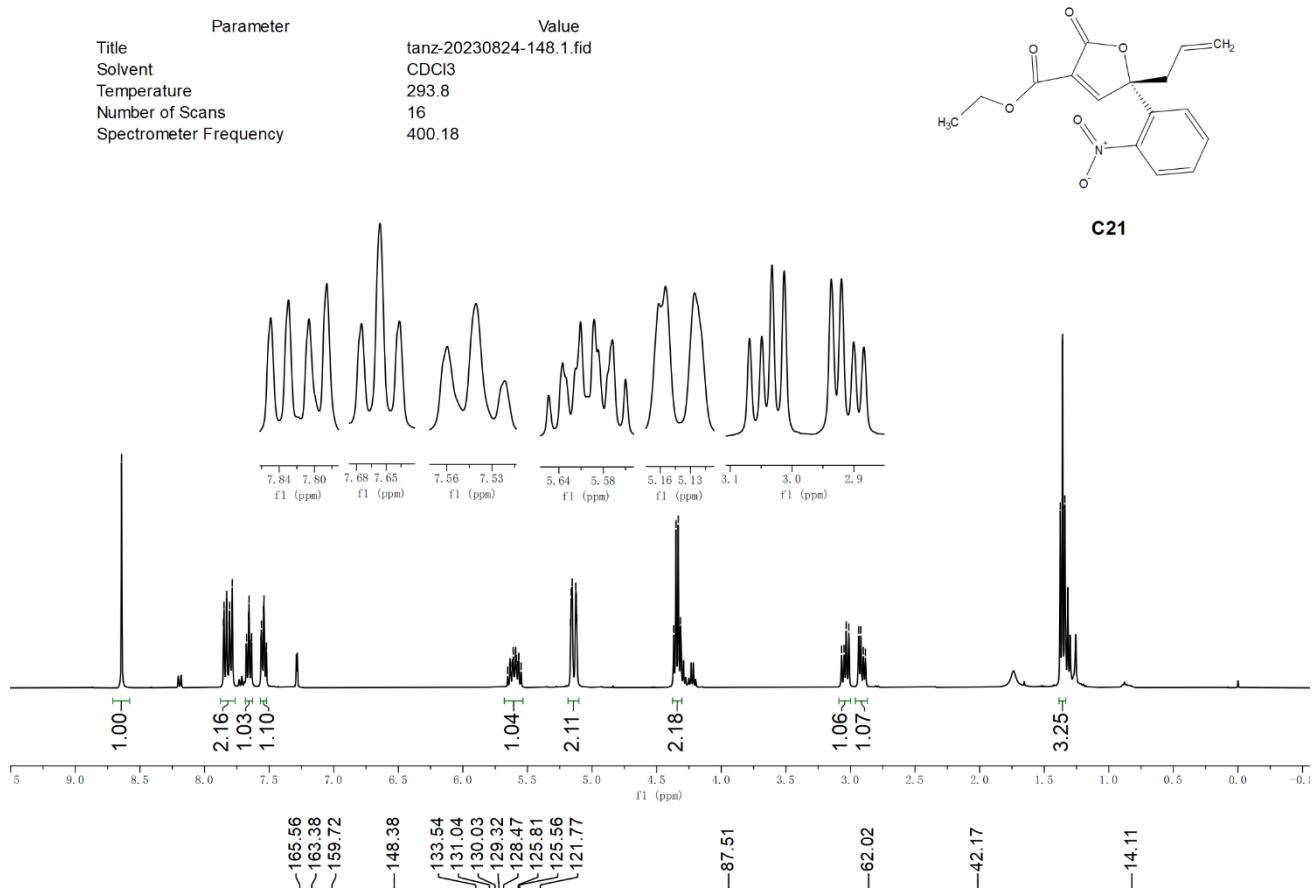
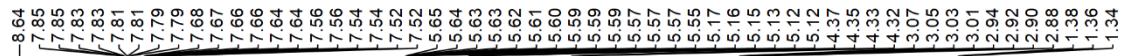
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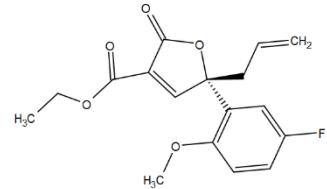




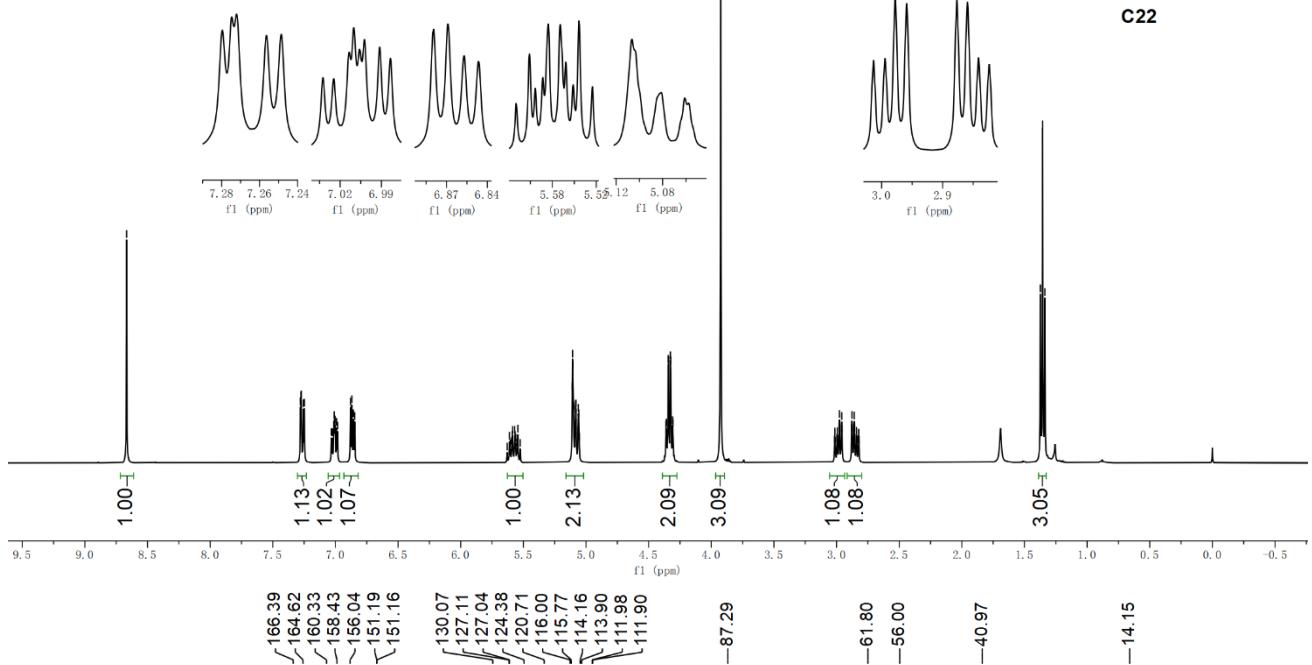


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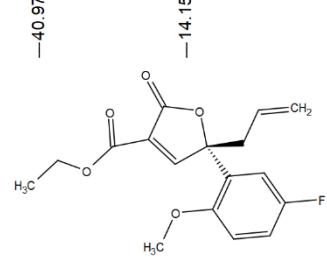
Parameter	Value
Title	as-20230902-TZ-157.1.fid
Solvent	CDCl ₃
Temperature	293.8
Number of Scans	16
Spectrometer Frequency	400.18



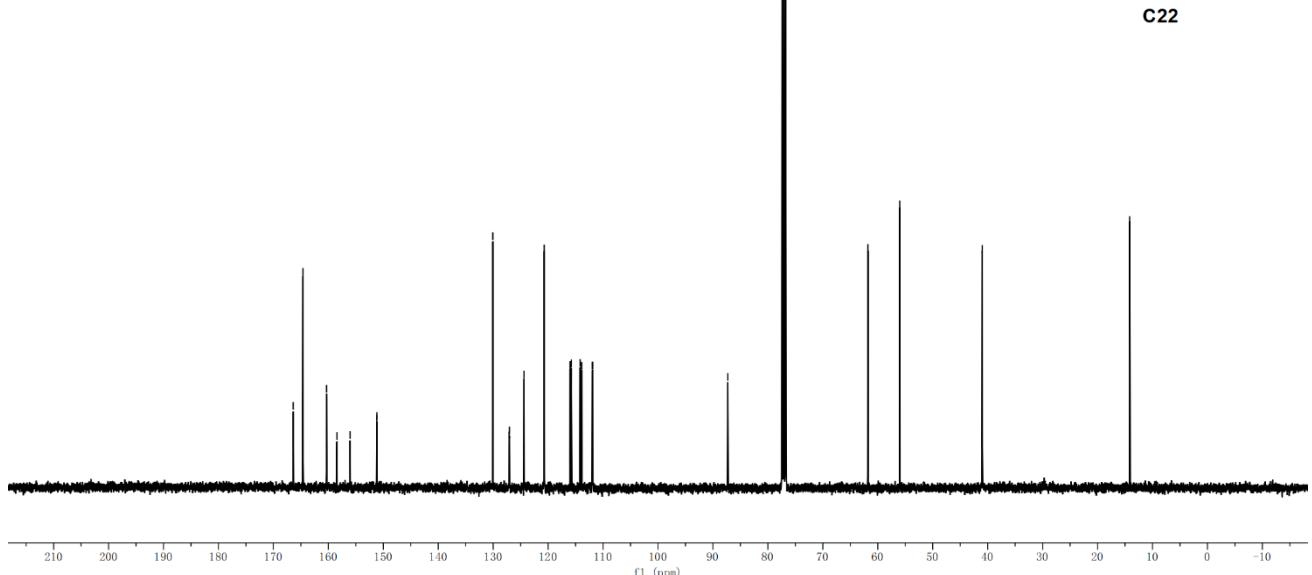
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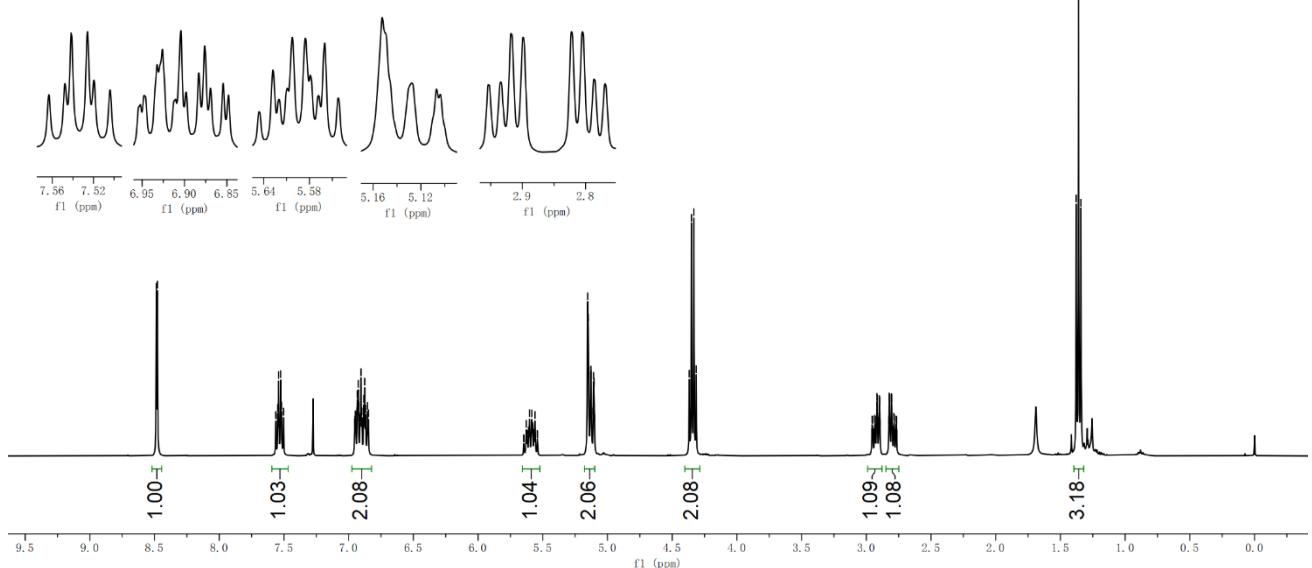
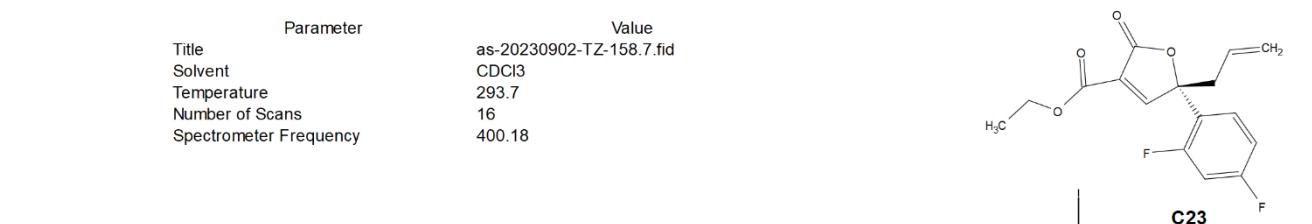
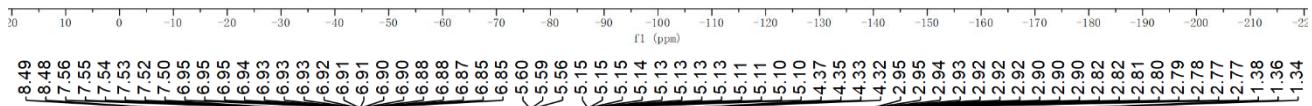
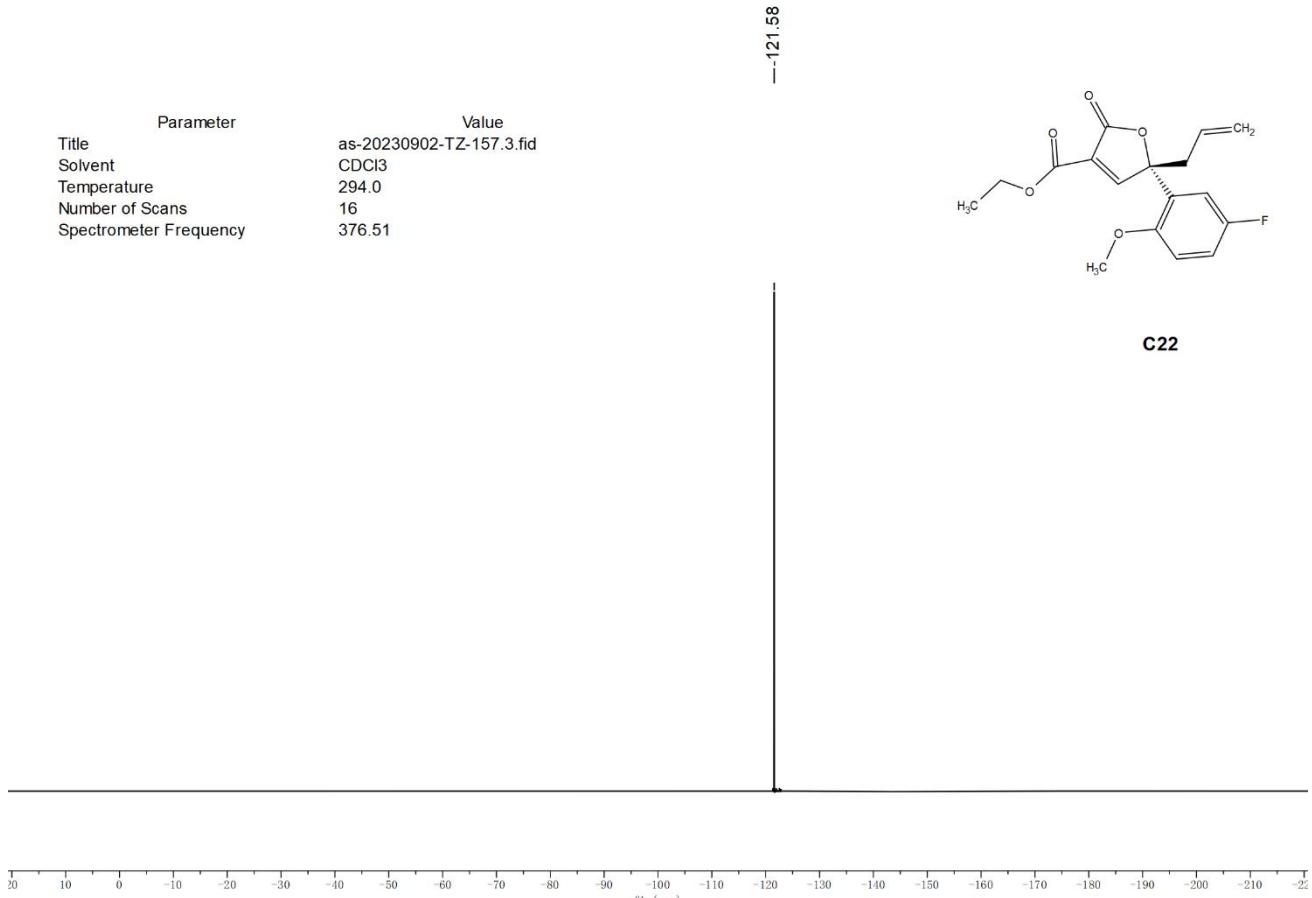


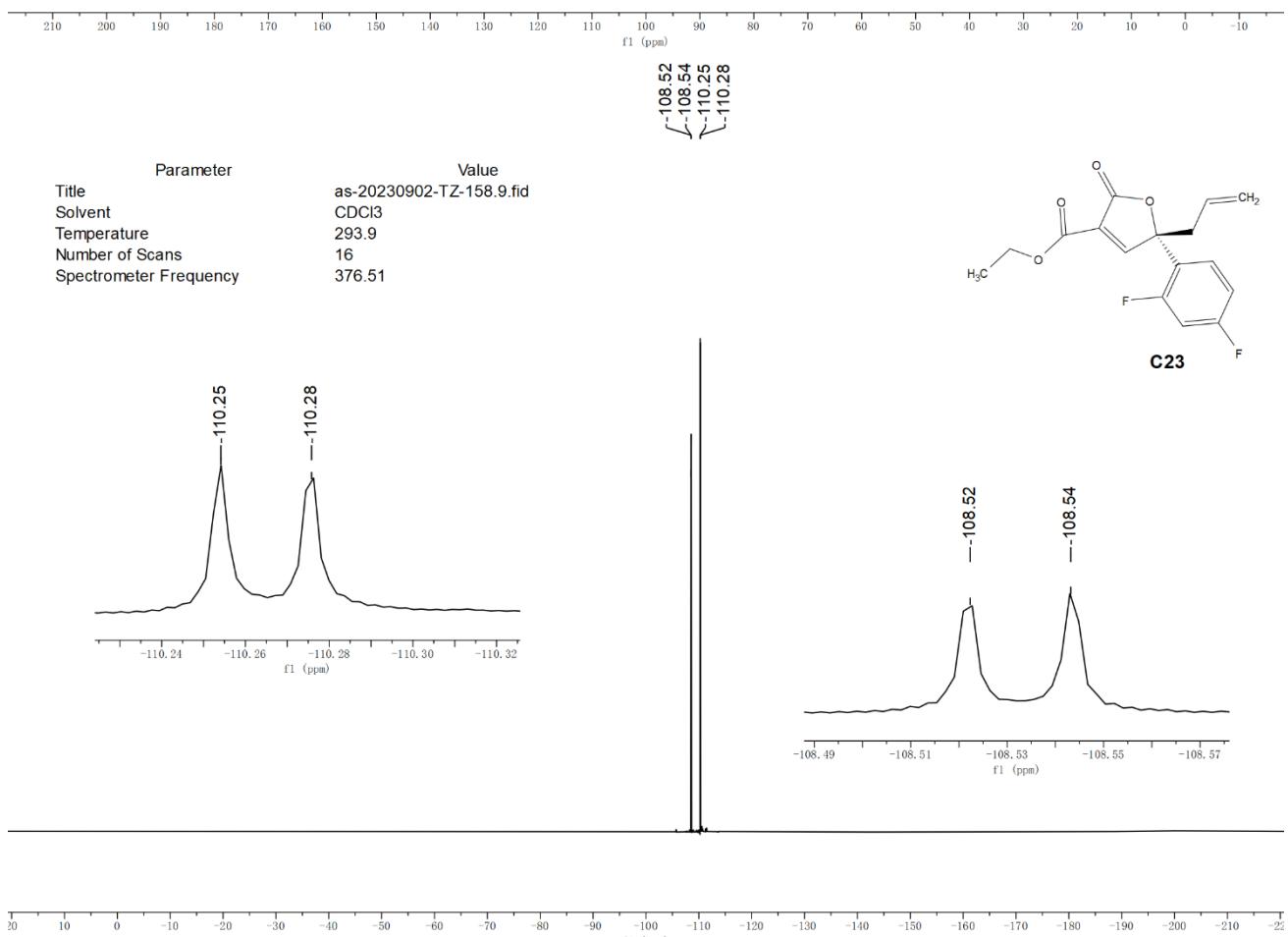
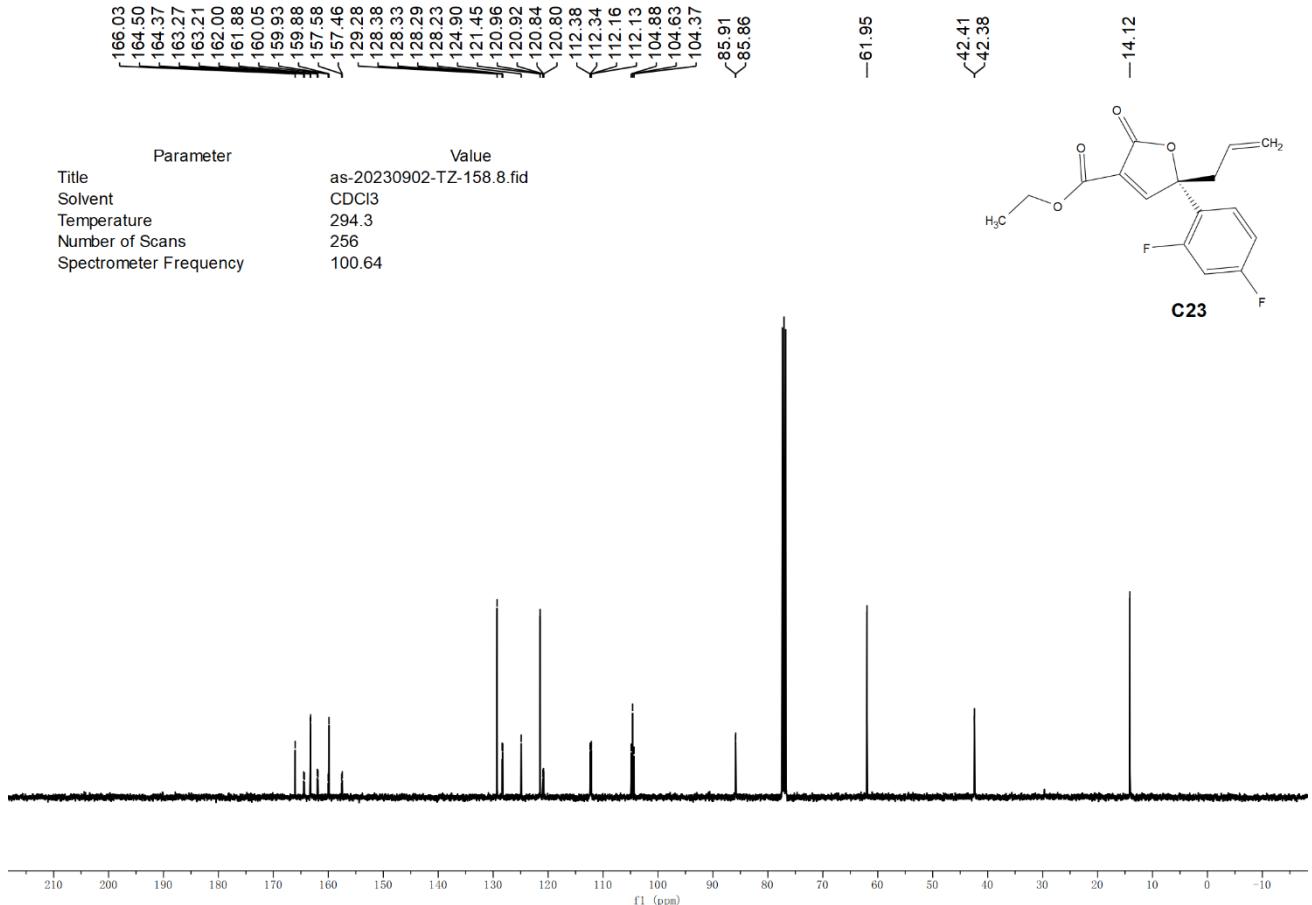
Parameter	Value
Title	as-20230902-TZ-157.2.fid
Solvent	CDCl ₃
Temperature	294.4
Number of Scans	256
Spectrometer Frequency	100.64



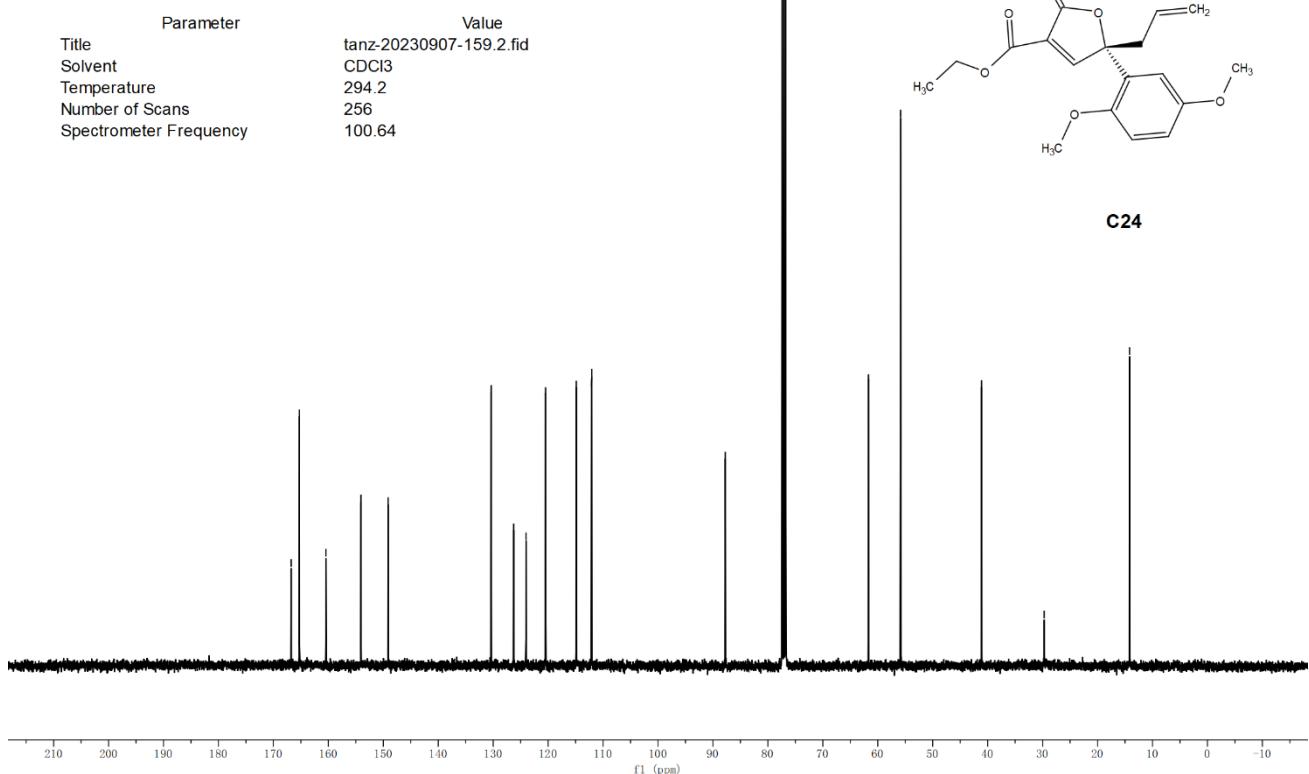
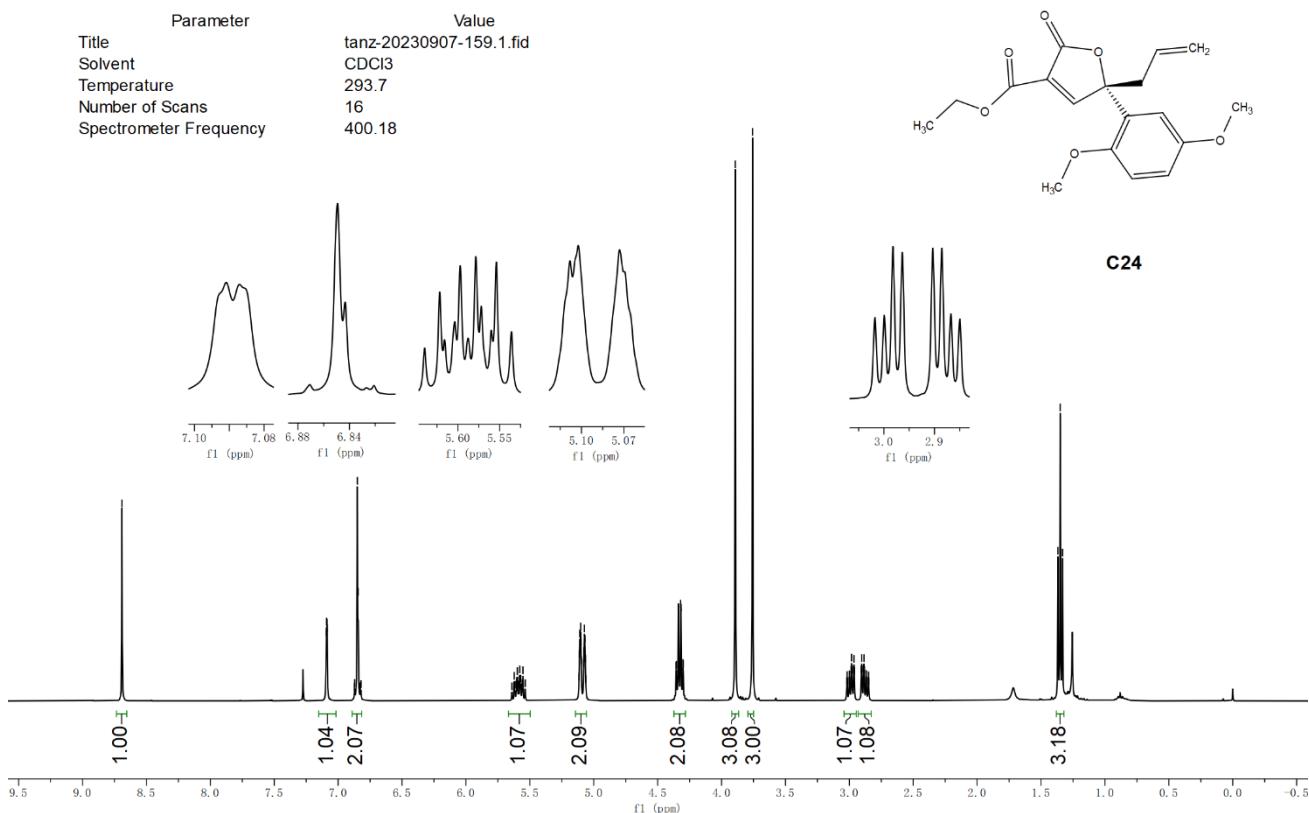
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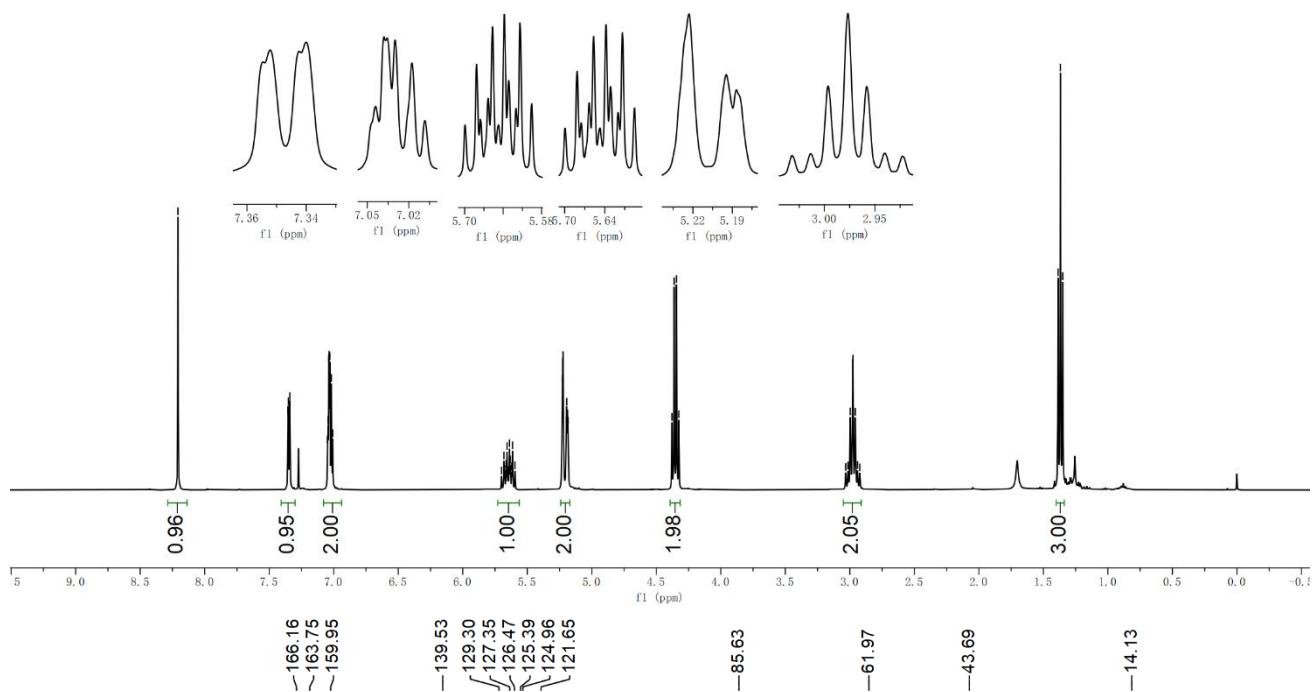
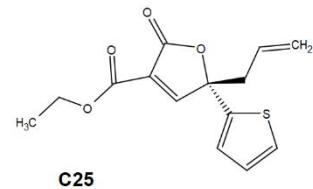


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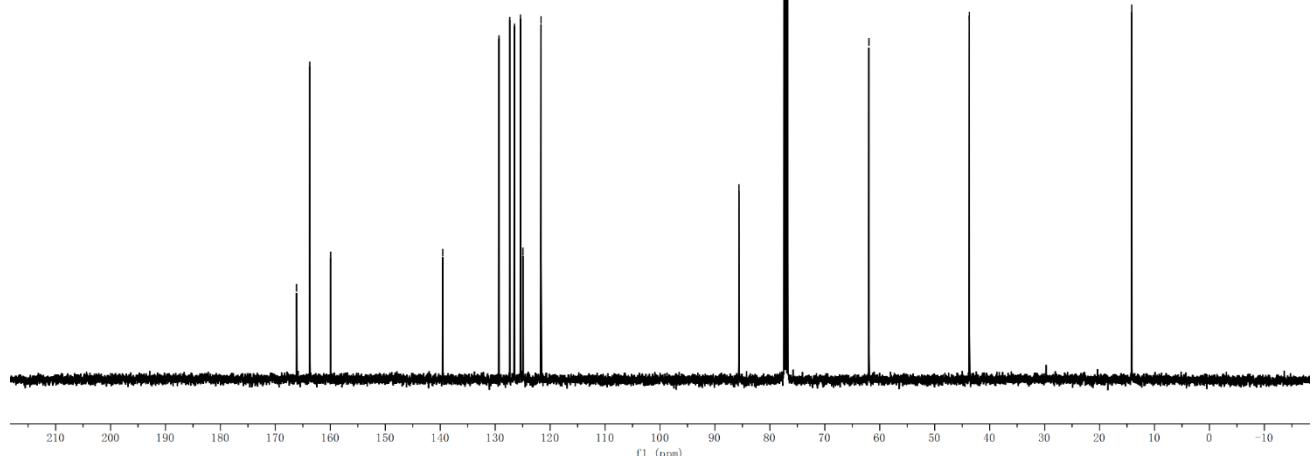
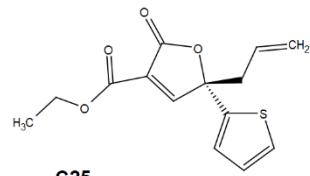




Parameter	Value
Title	tanz-20230902-156.7.fid
Solvent	CDCl ₃
Temperature	293.8
Number of Scans	16
Spectrometer Frequency	400.18



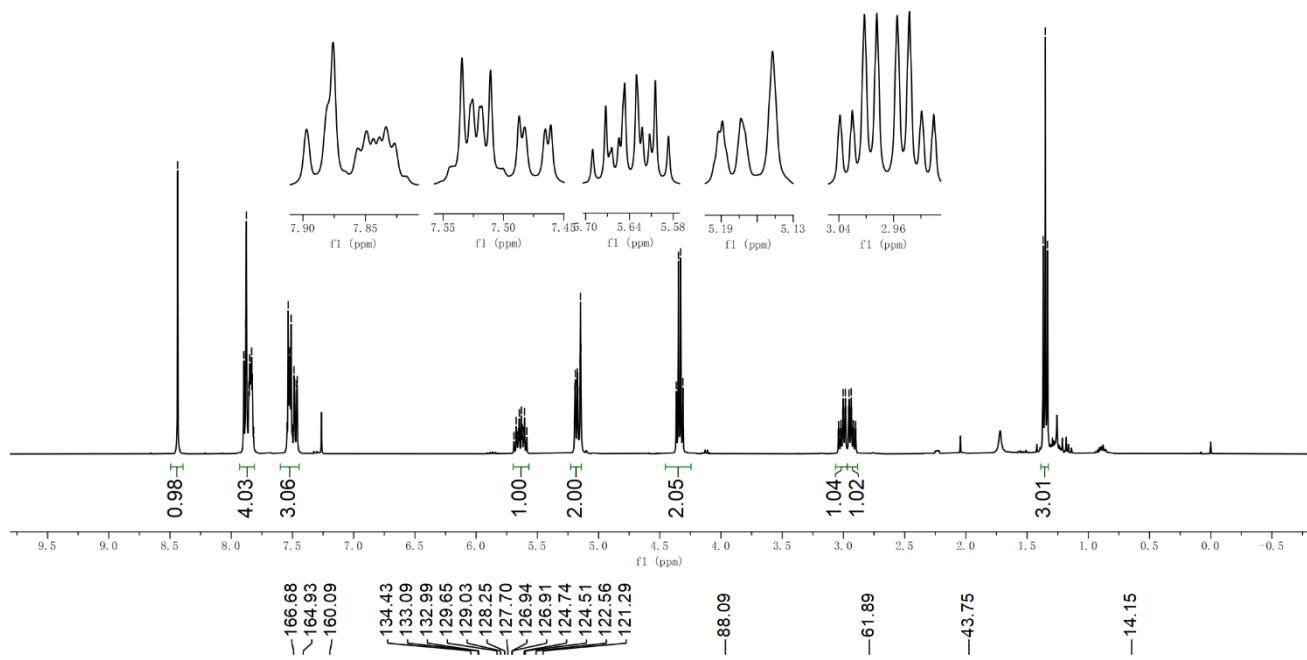
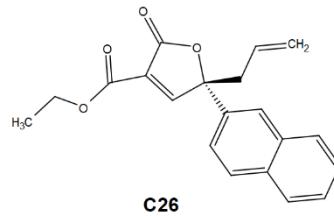
Parameter	Value
Title	tanz-20230902-156.8.fid
Solvent	CDCl ₃
Temperature	294.3
Number of Scans	256
Spectrometer Frequency	100.64



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7.87
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7.51
7.50
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7.46
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5.18
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5.17
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4.35
4.33
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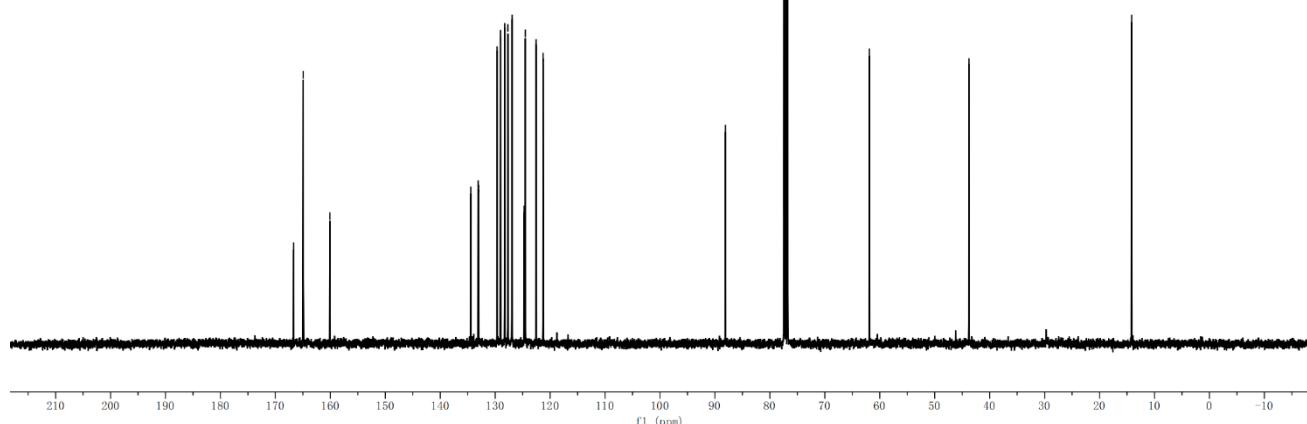
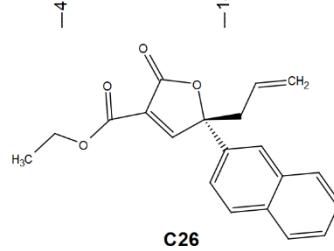
Parameter
Title
Solvent
Temperature
Number of Scans
Spectrometer Frequency

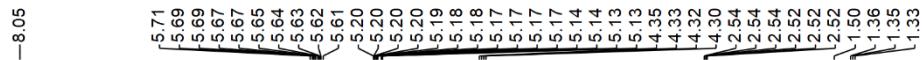
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CDCl₃
293.9
16
400.18



Parameter
Title
Solvent
Temperature
Number of Scans
Spectrometer Frequency

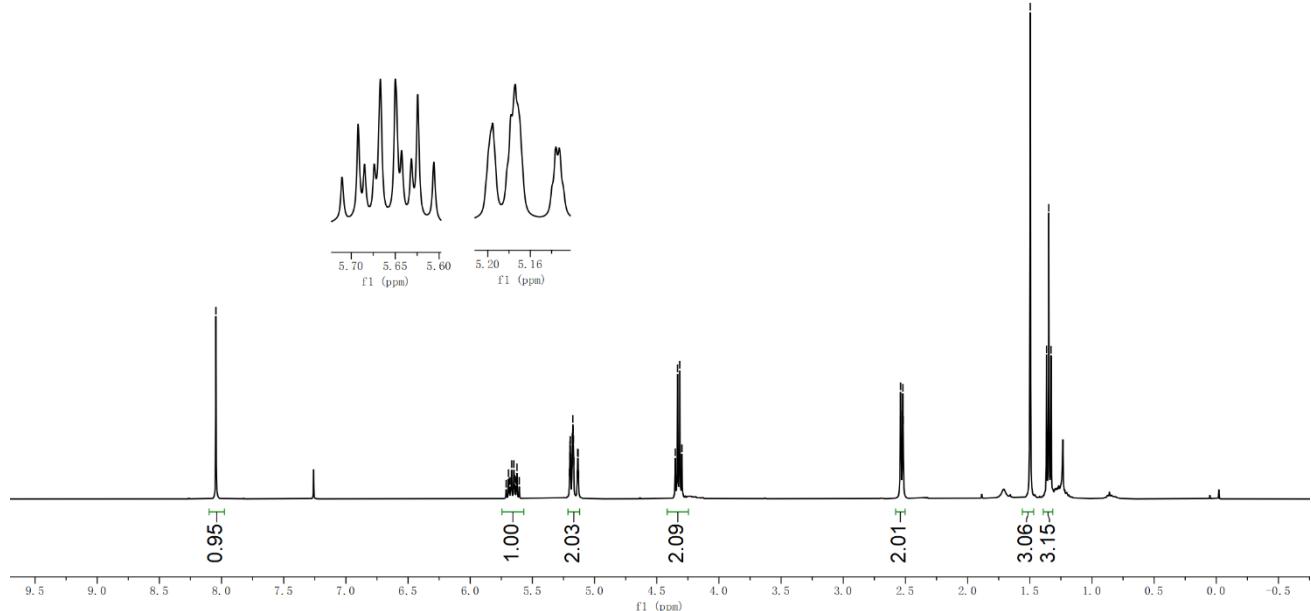
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CDCl₃
294.3
256
100.64





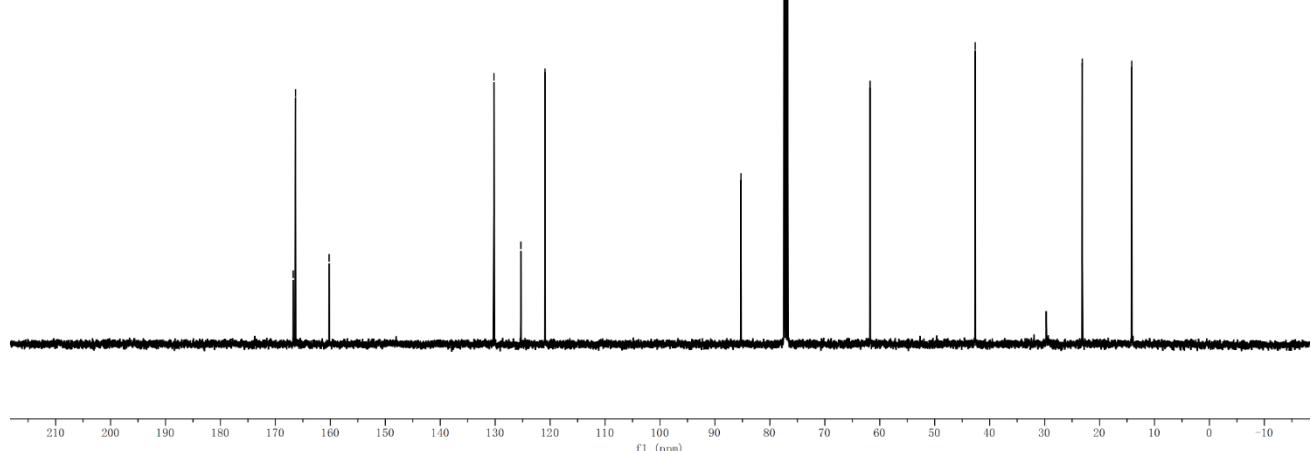
Parameter	Value
Title	tanz-20230907-161.9.fid
Solvent	CDCl ₃
Temperature	293.8
Number of Scans	16
Spectrometer Frequency	400.18

C27



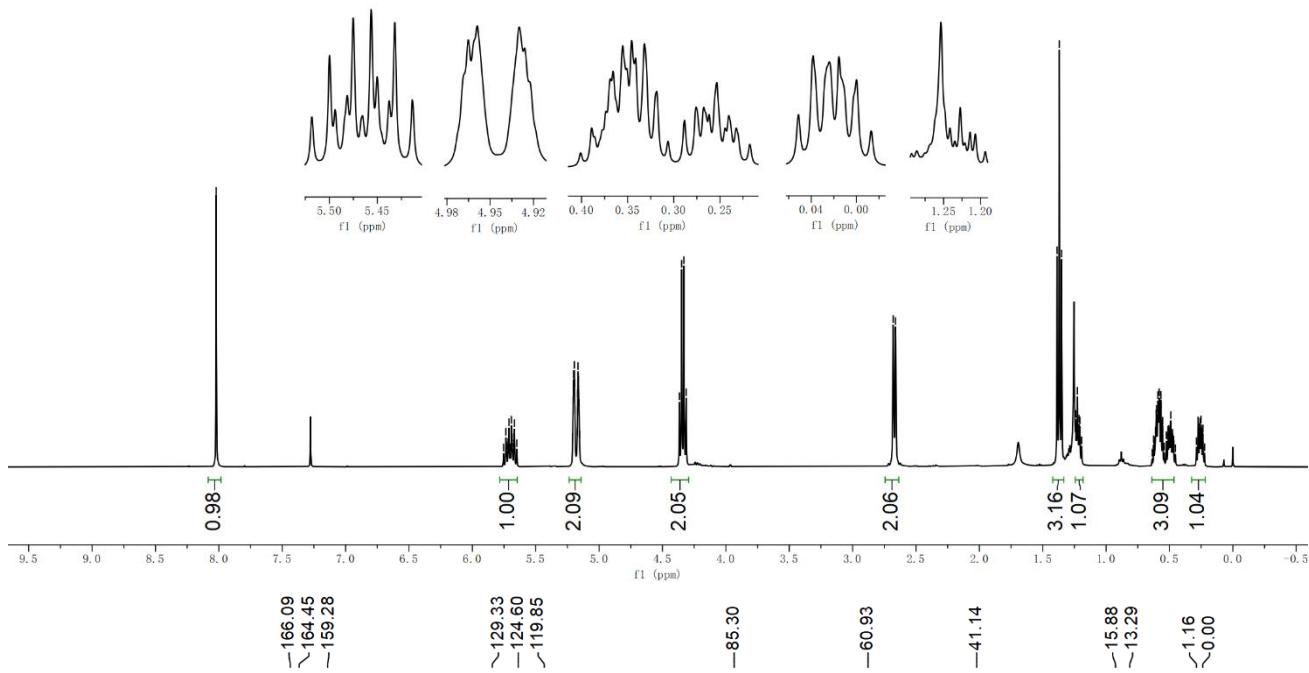
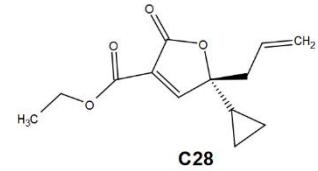
Parameter	Value
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Solvent	CDCl ₃
Temperature	294.1
Number of Scans	256
Spectrometer Frequency	100.64

C27

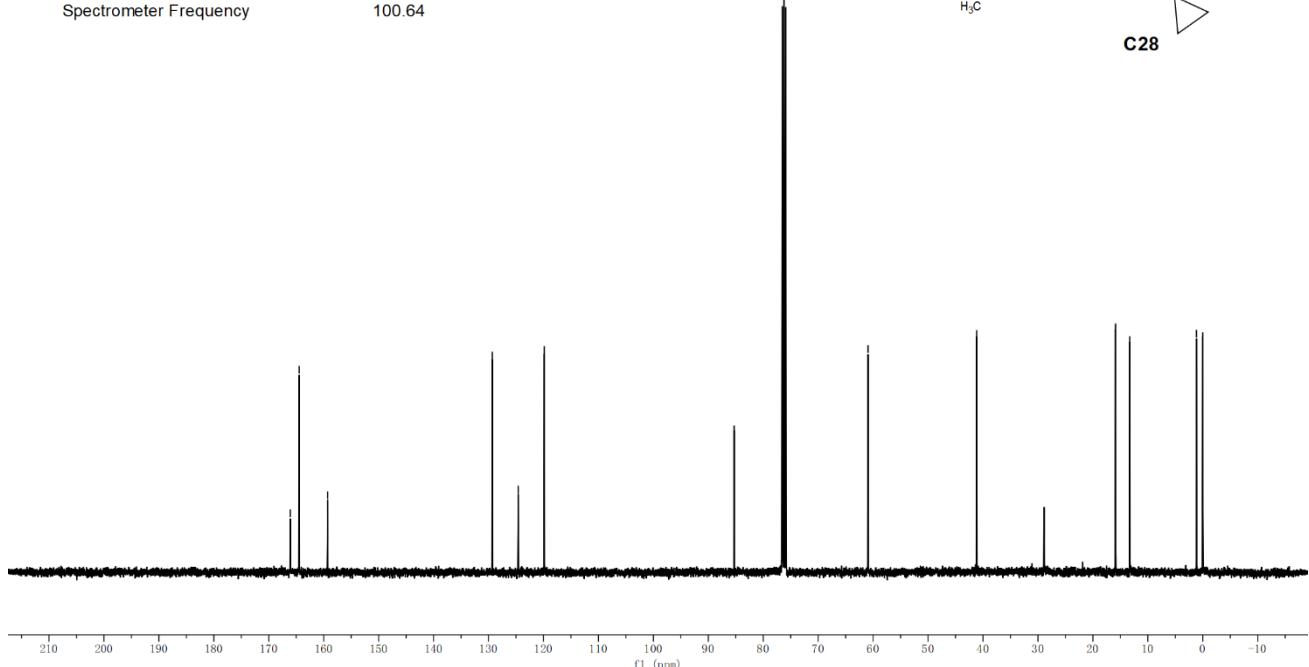
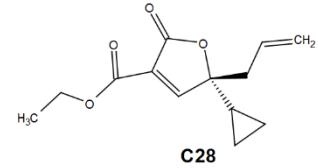


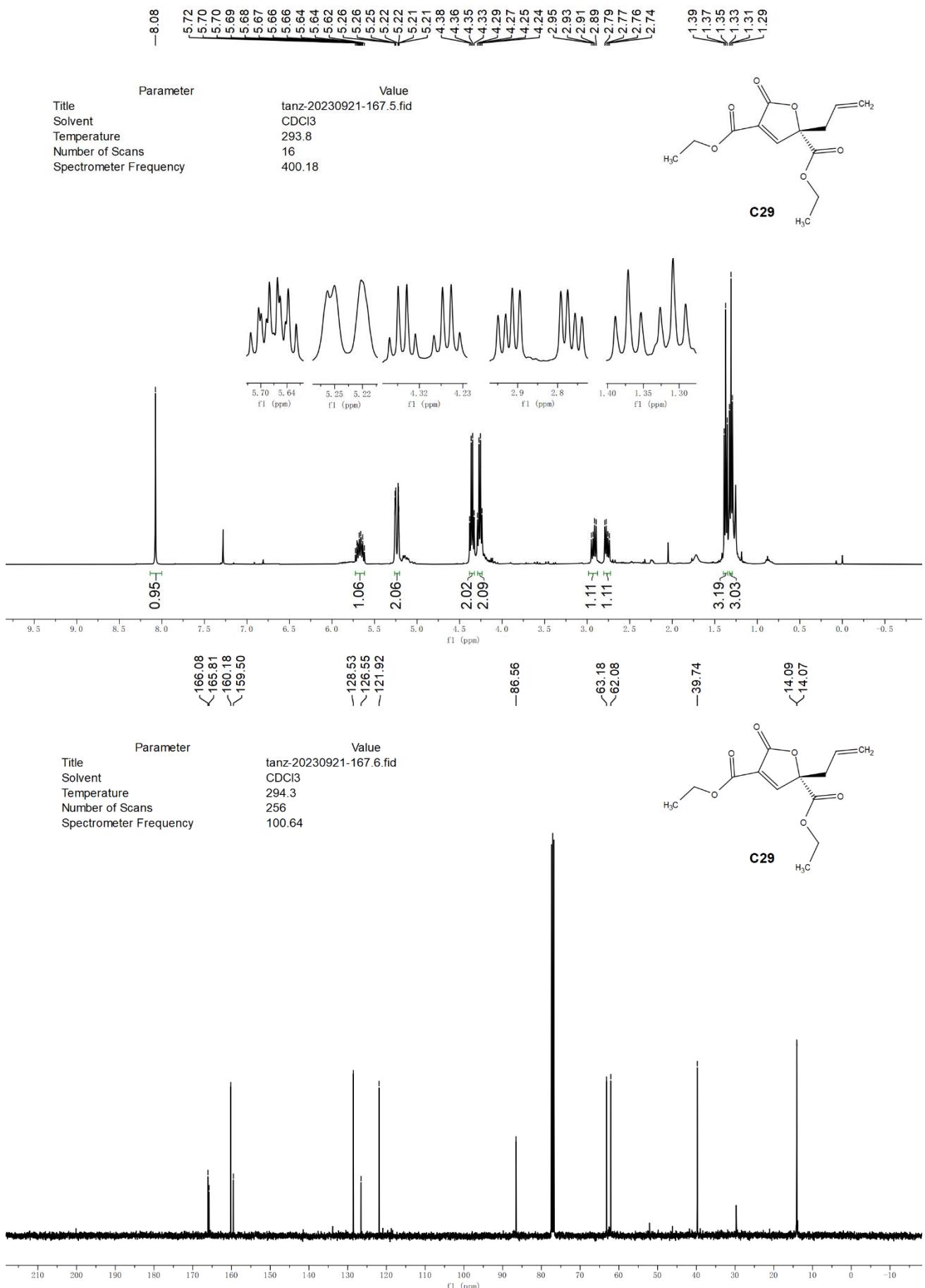
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5.17
5.17
5.17
4.37
4.35
4.33
4.31
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2.66
1.39
1.37
1.35
1.24
1.23
1.23
1.22
1.21
1.21
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0.61
0.60
0.60
0.57
0.57
0.56
0.56
0.55
0.55
0.52
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0.51
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0.26
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0.24
0.24

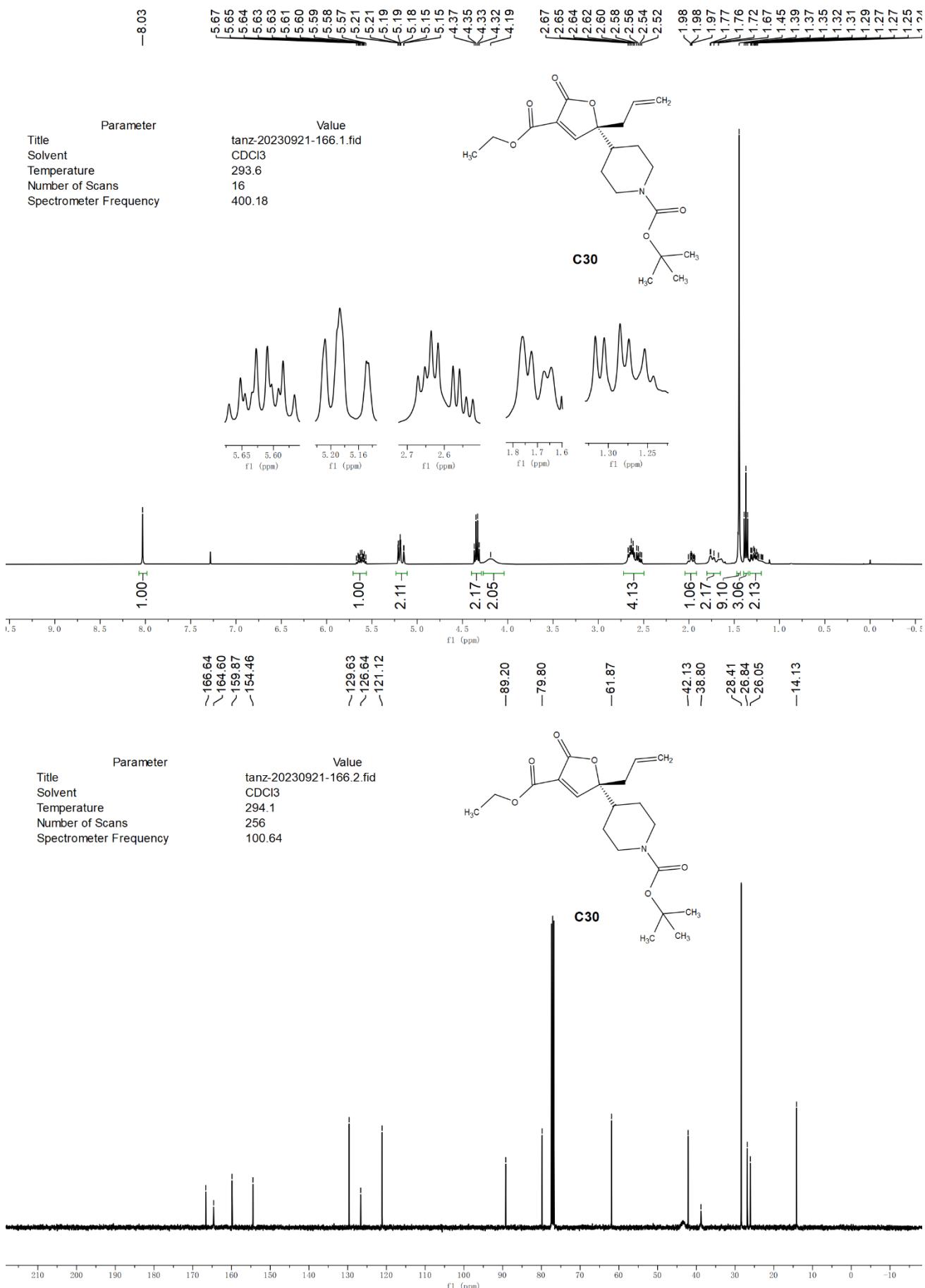
Parameter	Value
Title	tanz-20230907-162.9.fid
Solvent	CDCl ₃
Temperature	293.8
Number of Scans	16
Spectrometer Frequency	400.18



Parameter	Value
Title	tanz-20230907-162.10.fid
Solvent	CDCl ₃
Temperature	294.2
Number of Scans	256
Spectrometer Frequency	100.64

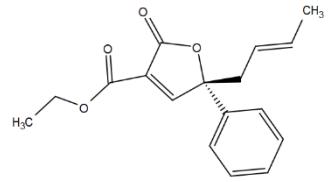




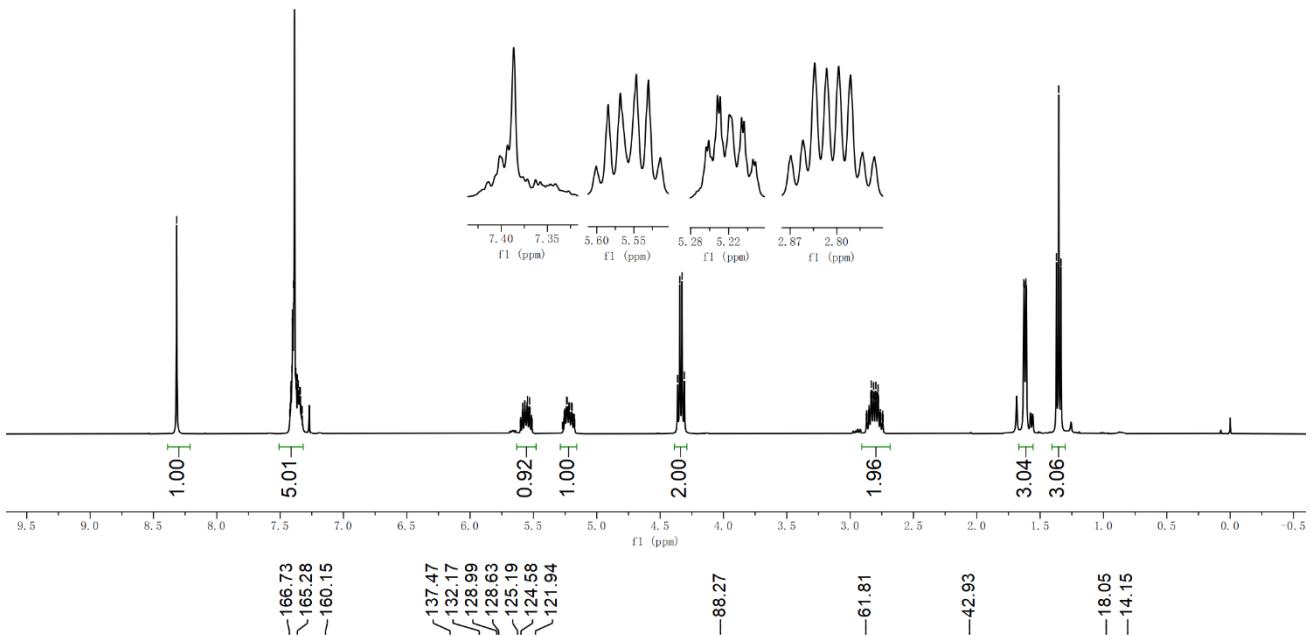




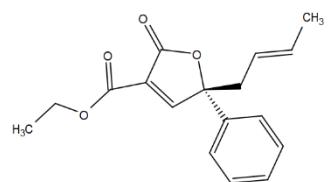
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Title	tanz-20231122-168.1.fid
Solvent	CDCl3
Temperature	293.3
Number of Scans	16
Spectrometer Frequency	400.18



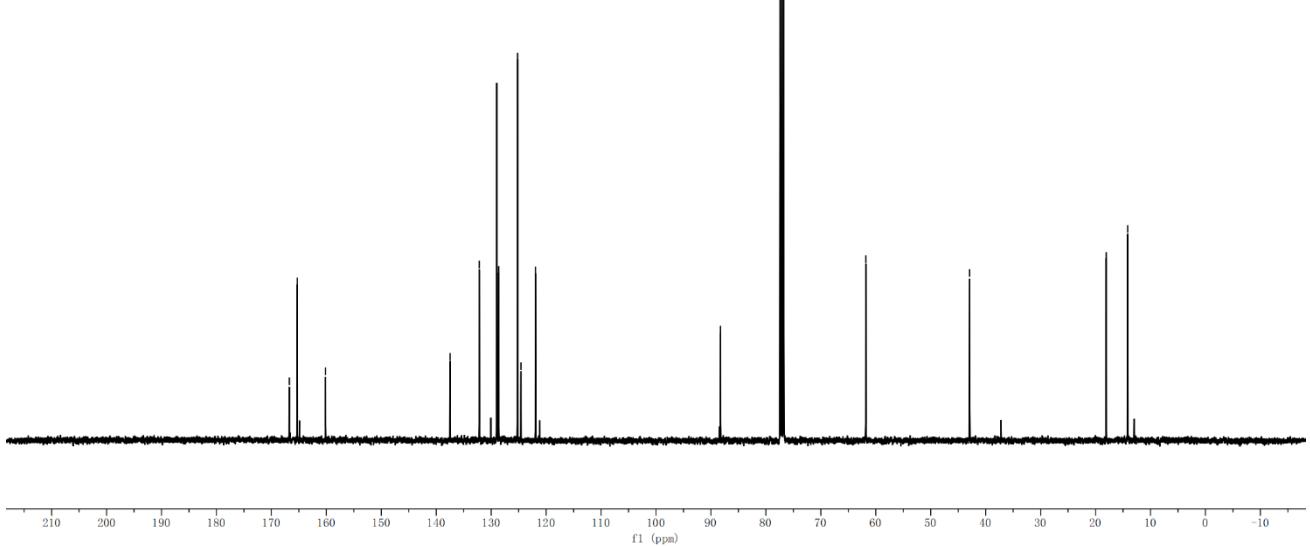
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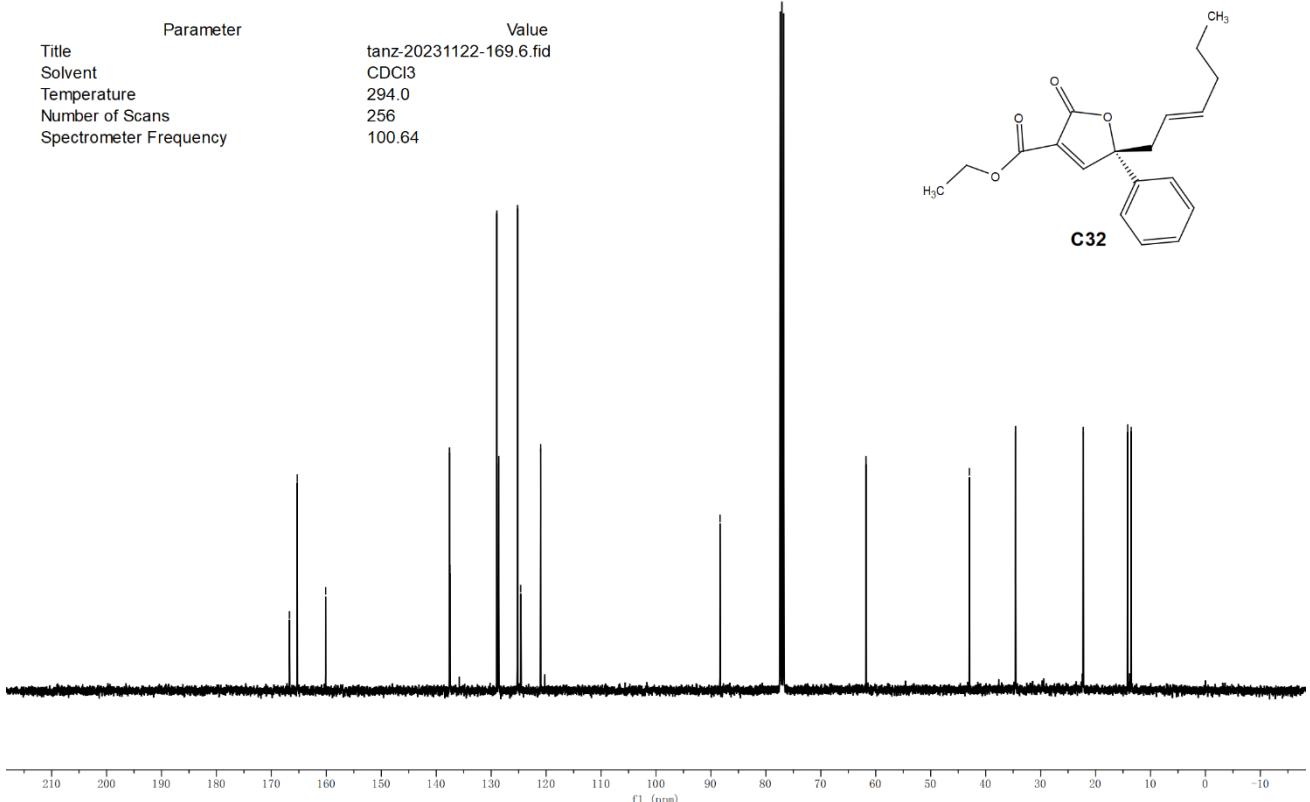
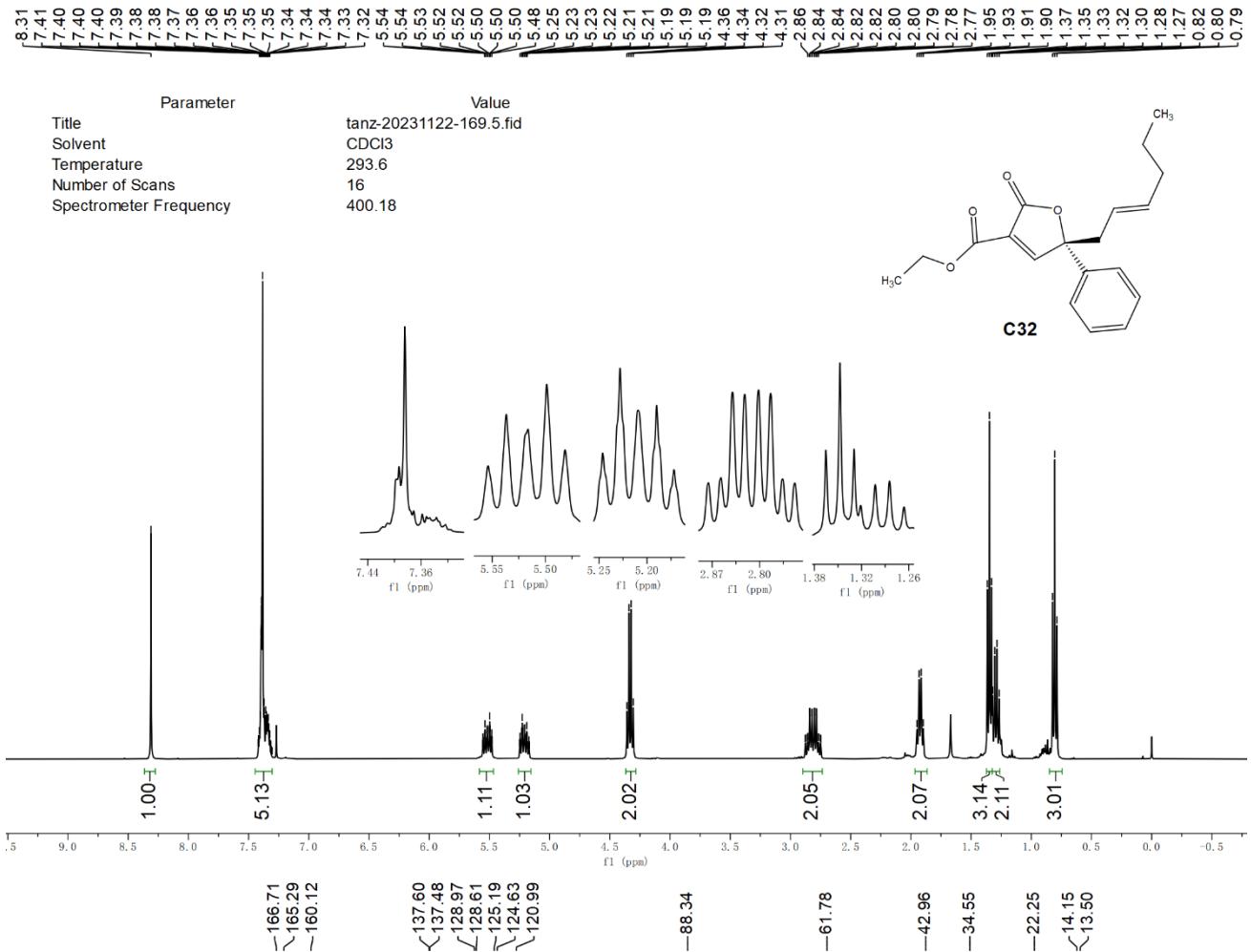


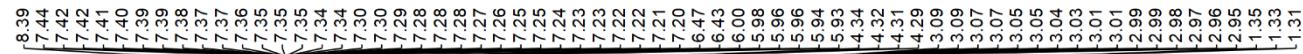
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Title	tanz-20231122-168.2.fid
Solvent	CDCl3
Temperature	293.9
Number of Scans	256
Spectrometer Frequency	100.64



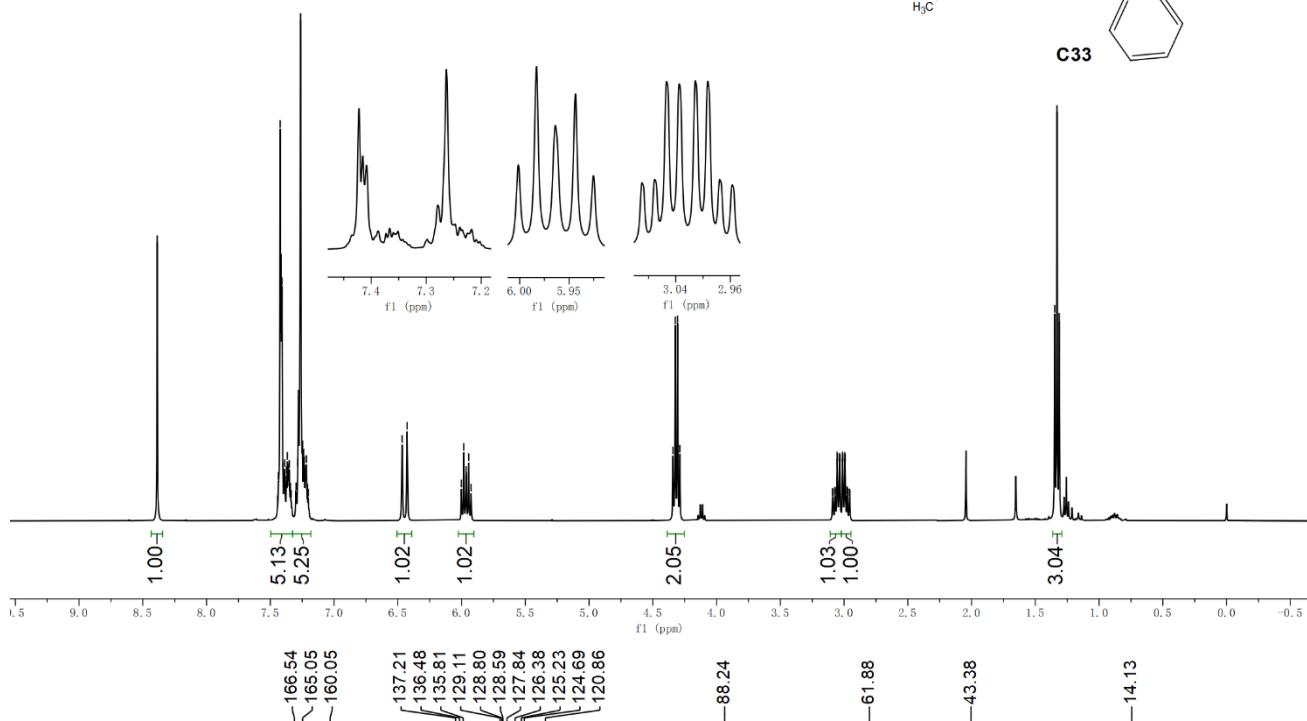
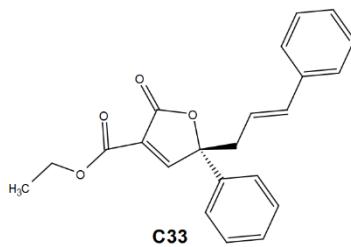
C31



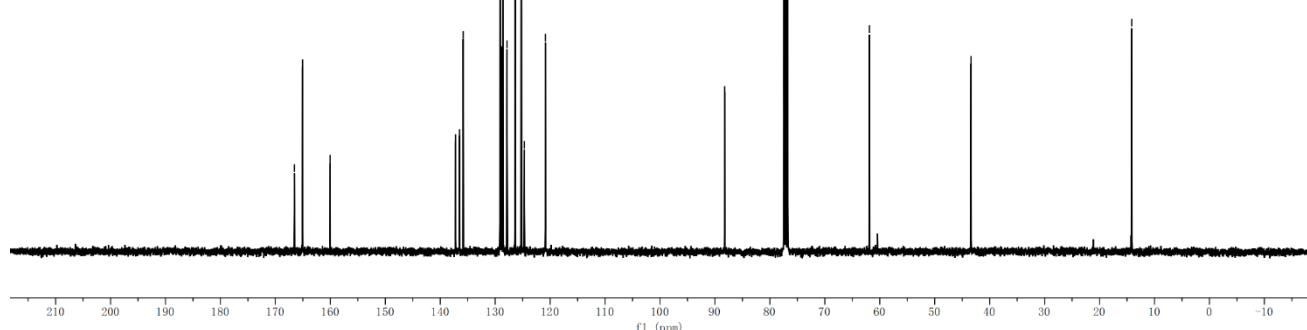
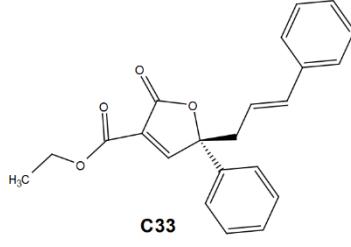


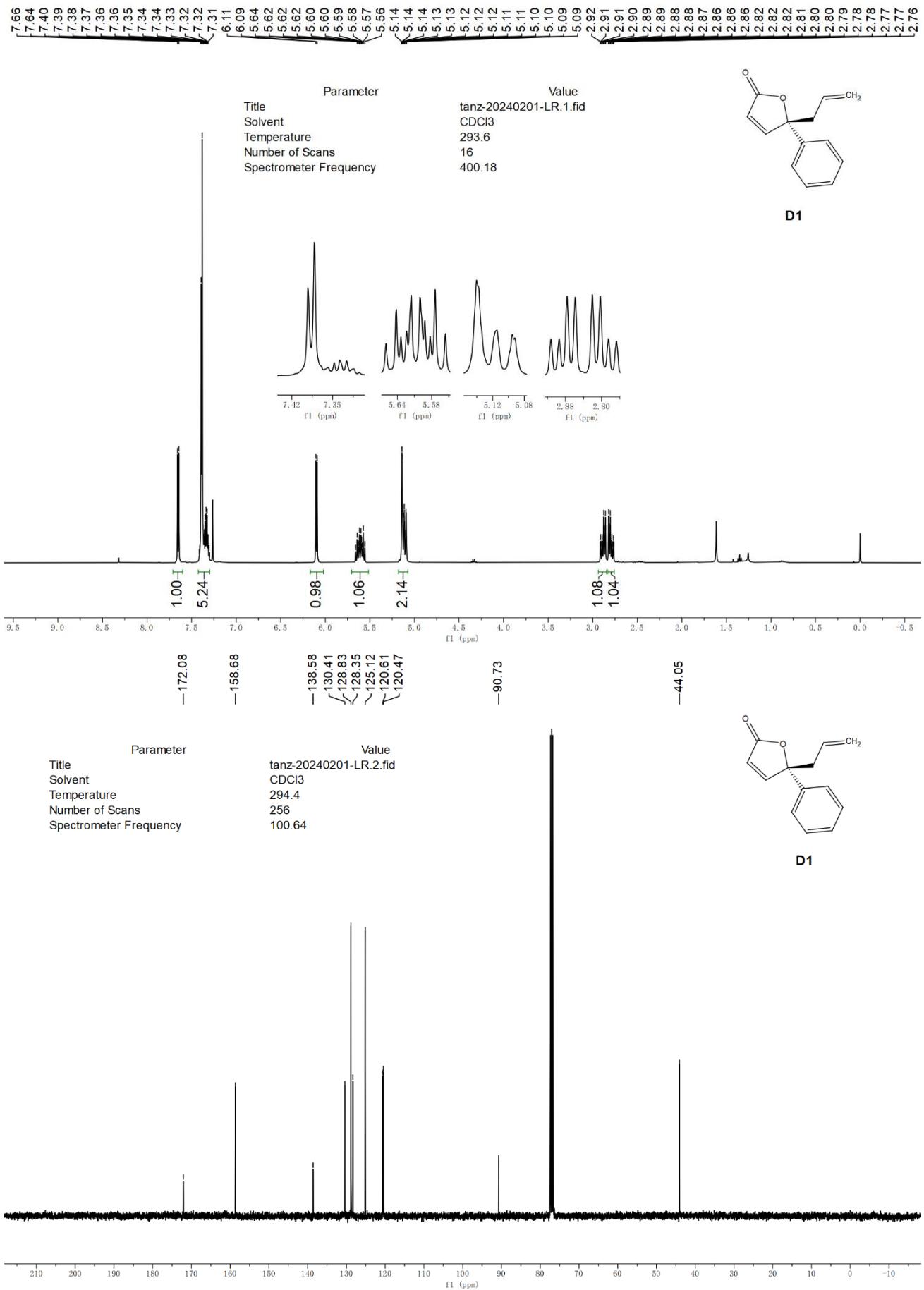


Parameter	Value
Title	tanz-20231220-YHAY-tz-1.1.fid
Solvent	CDCl ₃
Temperature	293.6
Number of Scans	16
Spectrometer Frequency	400.18



Parameter	Value
Title	tanz-20231220-YHAY-tz-1.2.fid
Solvent	CDCl ₃
Temperature	293.8
Number of Scans	256
Spectrometer Frequency	100.64

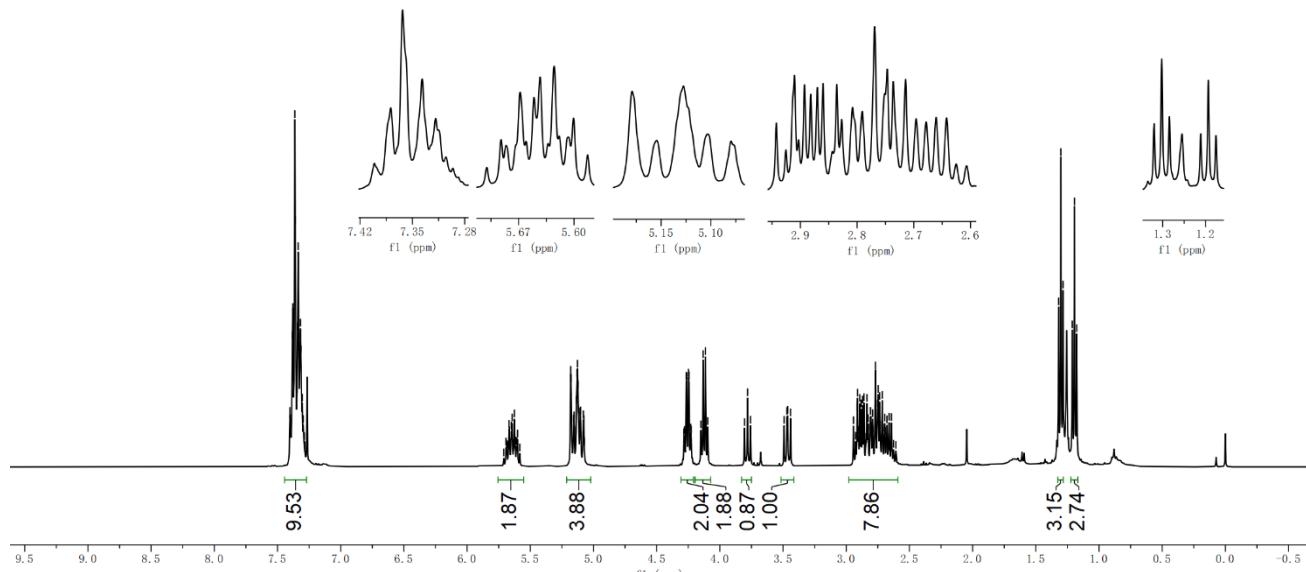
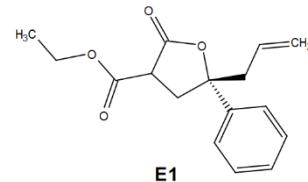




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7.33
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5.63
5.18
5.18
5.17
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5.14
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5.13
5.12
5.11
5.10
5.08
5.08
4.27
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4.25
4.24
4.13
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2.75
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2.66
2.64
1.32
1.30
1.28
1.21
1.19
1.18

Parameter

Value
tanz-20240201-199.1.fid
CDCl₃
293.8
16
400.18



171.26
171.08
167.62
167.36

141.68
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128.07
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124.56
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120.14

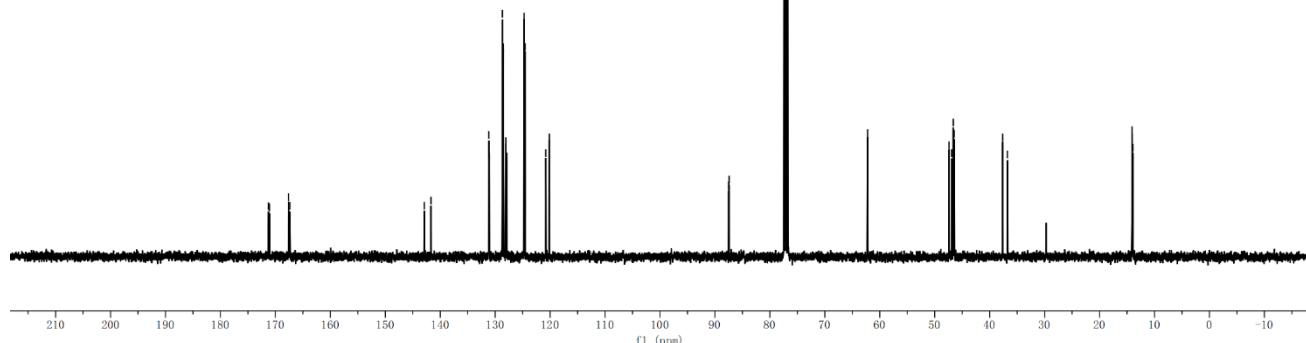
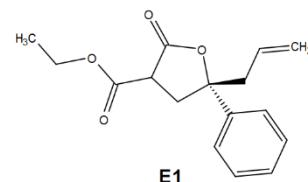
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87.42

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47.41
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46.63
46.46
37.63
36.78

14.09
13.94

Parameter
Title
Solvent
Temperature
Number of Scans
Spectrometer Frequency

Value
tanz-20240201-199.2.fid
CDCl₃
294.3
256
100.64



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- [1] Y. H. Wen, X. Huang, J. L. Huang, Y. Xiong, B. Qin and X. M. Feng, *Synlett*, 2005, **16**, 2445–2448.
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(c) G. M. Sheldrick, *Acta Cryst.* 2015, **C71**, 3–8. (d) O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339–341. (e) A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7–13.