Supporting Information

Direct C_{sp2}-H Enolization: An Allenoate Alkylation Cascade Toward the Assembly of Multi-substituted Furans

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1. General Information.

All the reactions were performed in flame dried glassware using dry solvents. DMF was distilled from neutral alumina and CaH_2 prior to use. All other chemicals were obtained from commercial sources and used directly without further purification. Yields refer to chromatographically pure material. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Merck TLC Silica gel $60F_{254}$, precoated on aluminium sheets using UV light as a visualizing agent and $KMnO_4$ stain, and heat as developing agents. Merck silica gel (particle size 100-200 and 230-400 mesh) was used for flash column chromatography.

NMR spectra were recorded on Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz) or 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) in $CDCl_3$ having TMS 0.03% as internal standard. Mass spectrometric data were obtained using WATERS-Q-TOF Premier-ESI-MS.

The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, ddd = doublet of a doublet of doublet.

2. Synthesis of Starting Materials.

The bromo- and iodo-electrophiles were synthesized using known procedures.[1a-d] Allene-1,3-dicarboxylate was prepared as reported by Node et. al.[2]

3. General Procedures for Furan Formation:

Method-A: Allenoate **1**, TBAB (1 equiv.) and α-bromo or α-iodo ketone (2 equiv.) were added in vial. Toluene (2 mL) was added followed by the addition of K_2CO_3 (10 equiv.). The reaction mixture was stirred in a closed vial for 24 h. After completion of the reaction (as monitored by TLC analysis), the reaction mixture was poured in a separating funnel and extracted with EtOAc thrice. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (solvent system - EtOAc/ petroleum ether) on silica gel.

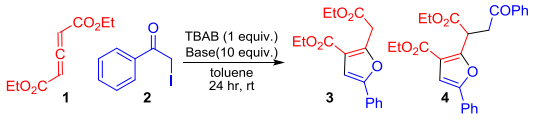
Method-B: Allenoate **1**, 18-Crown-6 (2 equiv.), AgOTf (2 equiv.) and α-bromo ketone (2 equiv.) were added in vial. Toluene (2 ml) was added followed by the addition of K_2CO_3 (10 equiv.). The reaction mixture was stirred in a closed vial for 24 h. After completion of the reaction (as monitored by TLC analysis), the reaction mixture was poured in a separating funnel and extracted with EtOAc thrice. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (solvent system - EtOAc/ petroleum ether) on silica gel.

Method-C: Allenoate **1**, TBAB (3 equiv.) and α-iodo ketone (2.5 equiv.) were added in vial. Acetonitrile (2 ml) was added followed by the addition of K_2CO_3 (3 equiv.). The reaction mixture was stirred in a closed vial for 24 hrs. After completion of the reaction (as monitored by TLC analysis), the reaction mixture was poured in a separating funnel and extracted with EtOAc thrice. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (solvent system - EtOAc/ petroleum ether) on silica gel.

4. Additional Optimization Experiments

In addition to experiments in table 1, various bases and ammonium salts were evaluated in this reaction in order to explore the improvement in the selectivity favoring products **3**. The outcome of those experiments is shown below in table 1s and table 2s.

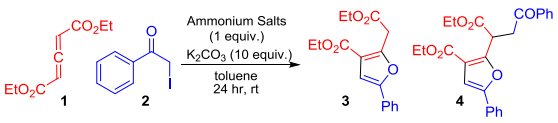
Table 1s: Evaluation of other bases in the reaction



entry[a]	**2** (equiv.)	Base	TBAB (equiv.)	% yield (**3**)	% yield (**4**)
1[b,c]	2	^{t}BuOK	1	-	-
2[c]	2	DBU	1	-	-
3[d]	2	Cs_2CO_3	1	36	32
4[e]	2	K_2CO_3	1	62	23
5	2	K_3PO_4	1	34	16

[a]Reaction Conditions: **1** (0.22 mmol), **2** (0.44 mmol), TBAB (0.22 mmol), base (2.2 mmol), solvent (2 mL; 0.11 M) for 24 h at rt.
[b] 2 equiv. of ^{t}BuOK was employed.
[c]Complex mixture was obtained
[d]Reaction was complete after 6 hrs.
[e]When performed at 100 °C, this reaction reaction provided **3** (33%) and **4** (22%)

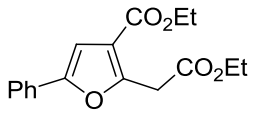
Table 2s: Evaluation of other ammonium salts in the reaction



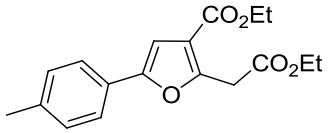
entry	**2** (equiv.)	Ammonium Salts	% yield (**3**)	% yield (**4**)
1	2	$TBAClO_4$	47	18
2	2	$TBAHSO_4$	40	12
3	2	$TBANO_3$	35	9
4	2	TBAI	46	12
5	2	TBAB	62	23
6	2	TMAI[b]	20	38

[a]Reaction Conditions: **1** (0.22 mmol), **2** (0.44 mmol), ammonium salts (0.22 mmol), base (2.2 mmol), $PhCH_3$ (2 mL; 0.11 M) for 24 h at rt.
[b]TMAI = tetramethylammonium iodide

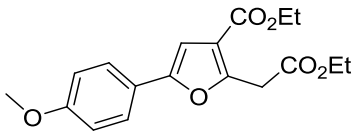
Characterization of Products:



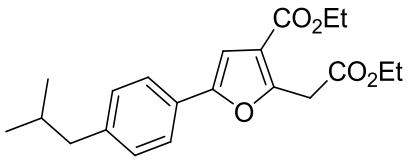
Ethyl 2-(2-ethoxy-2-oxoethyl)-5-phenylfuran-3-carboxylate (3a): According to the method A, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-phenylethanone (107 mg, 434 µmol) provided **3a** as a colorless oil (44 mg, 67%) and **4a** as a yellow oil (20 mg, 22%) after flash column chromatography (5% ethyl acetate in petroleum ether). R_f = 0.70 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 3130, 2982, 1745, 1714. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.64 (d, *J* =7.2 Hz, 2H), 7.37 (t, *J* =7.6 Hz, 2H), 7.30 – 7.25 (m, 1H), 6.93 (s, 1H), 4.30 (q, *J* =7.1 Hz, 2H), 4.19 (q, *J* =7.1 Hz, 2H), 4.11 (s, 2H), 1.35 (t, *J* =7.1 Hz, 3H), 1.26 (t, *J* =7.1 Hz, 3H). ^{13}C NMR (100 MHz Chloroform-*d*) δ 168.7, 163.5, 153.5, 153.1, 129.9, 128.8, 128.1, 124.0, 117.6, 105.6, 77.5, 77.1, 76.8, 61.4, 60.6, 34.1, 14.4, 14.2. Exact mass calculated $C_{17}H_{19}O_5^+$ $[M+H]^+$: 303.1232; found: 303.1237.



Ethyl 2-(2-ethoxy-2-oxoethyl)-5-p-tolylfuran-3-carboxylate (3b): According to the method A, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-p-tolylethanone (113 mg, 434 µmol) provided **3b** as a colorless oil (36 mg, 52%) and **4b** as a yellow liquid (20 mg, 20%) after flash column chromatography (5% ethyl acetate in petroleum ether). R_f = 0.51 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2927, 2981, 1716, 1742. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 6.86 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 2.35 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}CNMR (100 MHz, Chloroform-*d*) δ 168.8, 163.6, 153.4, 153.1, 138.0, 129.5, 127.2, 124.0, 117.5, 104.9, 61.4, 60.5, 34.1, 21.4, 14.4, 14.2. Exact mass calculated $C_{18}H_{21}O_5^+$ $[M+H]^+$: 317.1389; found: 317.1389.

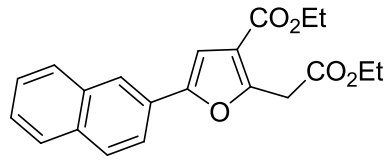


Ethyl 2-(2-ethoxy-2-oxoethyl)-5-(4-methoxyphenyl)furan-3-carboxylate (3c): According to the method A, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-(4-methoxyphenyl)ethanone (120 mg, 434 µmol) provided **3c** as a colorless oil (27 mg, 38%) and **4c** as a yellow liquid (24 mg, 23%) after flash column chromatography (10% ethyl acetate in petroleum ether). R_f = 0.31 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2932, 2981, 1741, 1714, 1234. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 9.0 Hz, 2H), 6.78 (s, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 3.82 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}CNMR (100 MHz, Chloroform-*d*) δ 168.8, 163.6, 159.6, 153.2, 152.8, 125.5, 122.9, 117.5, 114.2, 104.0, 61.4, 60.5, 55.4, 34.1, 14.4, 14.2. Exact mass calculated $C_{18}H_{21}O_6^+$ $[M+H]^+$: 333.1338; found: 333.1336.

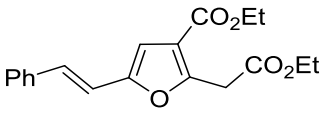


Ethyl 2-(2-ethoxy-2-oxoethyl)-5-(4-isobutylphenyl)furan-3-carboxylate (3d): According to the method A, allenoate **1** (40 mg, 217µmol)and 2-iodo-1-(4-isobutylphenyl)ethanone (131 mg, 434 µmol) provided **3d** as a colorless oil (31 mg, 40%) and **4d** as a yellow liquid (33 mg, 28%) after flash column chromatography (5% ethyl

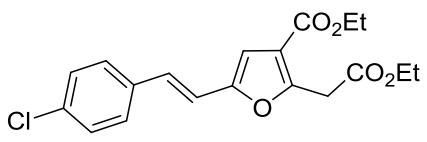
acetate in petroleum ether). R_f = 0.54 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2958, 2927, 1744, 1716, 1233.^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.55 (d, *J* =8.3, 2H), 7.15 (d, *J* =8.3 Hz, 2H), 6.87 (s, 1H), 4.30 (q, *J* =7.1 Hz, 2H), 4.18 (q, *J* =7.1 Hz, 2H), 4.10 (s, 2H), 2.47 (d, *J* =7.2 Hz, 2H), 1.91 – 1.80 (m, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* =7.1 Hz, 3H), 0.89 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.8, 163.6, 153.4, 153.1, 141.9, 129.6, 127.4, 123.8, 117.5, 104.9, 61.4, 60.6, 45.3, 34.2, 30.3, 22.4, 14.4, 14.3..Exact mass calculated $C_{21}H_{27}O_5^+$ $[M+H]^+$: 359.1858; found: 359.1857.



Ethyl 2-(2-ethoxy-2-oxoethyl)-5-(naphthalen-2-yl)furan-3-carboxylate (3e): According to the method A, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-(naphthalen-2-yl)ethanone (129 mg, 434 µmol) provided **3e** as a colorless oil (39mg, 51%) and **4e** as a yellow liquid (26 mg, 23%) after flash column chromatography (5% ethyl acetate in petroleum ether). R_f = 0.70 (10% ethyl acetate in petroleum ether) **IR** (neat): ν_{max}/cm^{-1} 2981, 2931, 1741, 1714. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.12 (s, 1H), 7.86 – 7.78 (m, 3H), 7.72 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.51 – 7.42 (m, 2H), 7.05 (s, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.16 (s, 2H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.28 (t, *J* = 7.1 Hz, 3H).^{13}CNMR (100 MHz, Chloroform-*d*) δ 168.7, 163.5, 153.7, 153.2, 133.4, 133.0, 128.6, 128.3, 127.9, 127.1, 126.7, 126.3, 122.6, 122.1, 117.8, 106.2, 61.5, 60.6, 34.2, 14.4, 14.3. Exact mass calculated $C_{21}H_{21}O_5^+$ $[M+H]^+$: 353.1389; found: 353.1387.

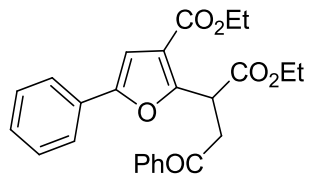


Ethyl -2-(2-ethoxy-2-oxoethyl)-5-styrylfuran-3-carboxylate (3f) : According to the method A allenoate **1** (40 mg, 217 µmol) and 1-iodo-4-phenylbut-3-en-2-one (118 mg, 434 µmol) provided **3f** as a colorless oil (28mg, 40%) and **4f** as a yellow liquid (27 mg, 26%) after flash column chromatography (5% ethyl acetate in petroleum ether). R_f = 0.50 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2961, 2926, 1714, 1738, 1259. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.25 (d, *J* = 6.9 Hz, 1H), 7.03 (d, *J* = 16.3 Hz, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 6.62 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.08 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}CNMR(100 MHz, Chloroform-*d*) δ 168.7, 163.4, 153.6, 152.4, 136.6, 128.8, 128.0, 126.5, 117.5, 115.6, 108.7, 61.5, 60.6, 34.2, 14.4, 14.3. Exact mass calculated $C_{19}H_{21}O_5^+$ $[M+H]^+$: 329.1389; found: 329.1389.

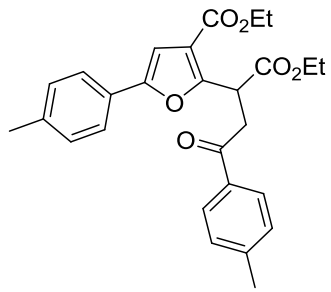


Ethyl -5-(4-chlorostyryl)-2-(2-ethoxy-2-oxoethyl)furan-3-carboxylate (3g): According to the method A, allenoate **1** (40 mg, 217 µmol) and 4-(4-chlorophenyl)-1-iodobut-3-en-2-one (133 mg, 434 µmol) provided **3g** as a colorless oil (32 mg, 40%) and **4g** as a yellow liquid (24 mg, 20%)after flash column chromatography (10% ethyl acetate in petroleum ether). R_f = 0.36 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2980, 2927, 1741, 1715, 1230, 1188. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.97 (d, *J* = 16.3 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 6.62 (s, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.19 (q, *J* = 7.2 Hz, 2H), 4.07 (s, 2H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H). ^{13}CNMR (100 MHz,

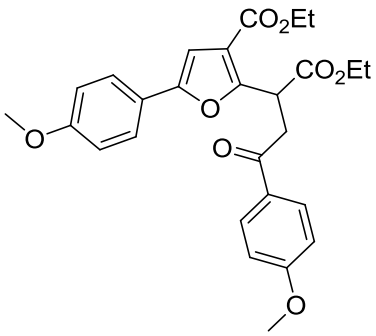
Chloroform-*d*) δ 168.6, 163.3, 153.8, 152.0, 135.1, 133.6, 129.5, 129.4, 129.0, 127.7, 127.3, 117.6, 116.1, 109.2, 61.5, 60.6, 34.1, 14.4. Exact mass calculated $C_{19}H_{20}ClO_5^+$ $[M+H]^+$: 363.0999; found: 363.0990.



Ethyl 2-(1-ethoxy-1,4-dioxo-4-phenylbutan-2-yl)-5-phenylfuran-3-carboxylate (4a): According to the method C, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-phenylethanone (134 mg, 542 µmol) provided **4a** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (70 mg, 78%). R_f = 0.45 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 3051, 2960, 2925, 1715, 1738. ^{1}H NMR (500 MHz, Chloroform-*d*) δ = 8.00 (d, *J* = 7.6 Hz, 2H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* =7.5 Hz, 1H), 7.46 (t, *J* =7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.28 (t, *J* = 7.3 Hz, 1H), 6.95 (s, 1H), 5.27 (dd, *J* = 8.7, 5.2 Hz, 1H), 4.39 – 4.28 (m, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.04 (dd, *J* = 17.7, 8.7 Hz, 1H), 3.43 (dd, *J* = 17.7, 5.2 Hz, 1H), 1.37 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (125 MHz, Chloroform-*d*) δ 196.7, 170.3, 163.3, 156.3, 153.0, 136.5, 133.4, 129.7, 128.8, 128.7, 128.2, 128.2, 124.0, 116.9, 105.9, 61.7, 60.7, 40.2, 39.2, 14.4, 14.2.Exact mass calculated $C_{25}H_{25}O_6^+$ $[M+H]^+$: 421.1651; found: 421.1650.

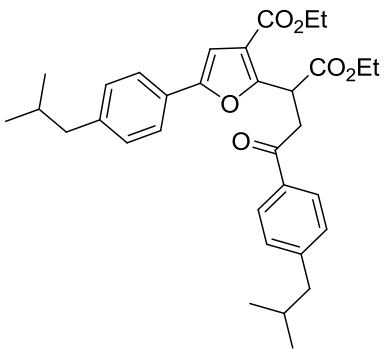


Ethyl 2-(1-ethoxy-1,4-dioxo-4-p-tolylbutan-2-yl)-5-p-tolylfuran-3-carboxylate (4b): According to the method C, allenoate **1** (40 mg, 217µmol) and 2-iodo-1-p-tolylethanone (141 mg, 543 µmol) provided **4b** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (70 mg, 72%). R_f = 0.37 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2960, 2922, 1714, 1681. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.89 (d, *J* =8.2 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.87 (s, 1H), 5.24 (dd, *J* = 8.7, 5.1, 1H), 4.31 (m, 2H), 4.19 (q, *J* = 7.1, 2H), 4.00 (dd, *J* = 17.7, 8.8 Hz, 1H), 3.40 (dd, *J* = 17.6, 5.1 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* =7.1, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.3, 170.5, 163.4, 156.0, 153.2, 144.2, 138.1, 134.0, 129.5, 129.4, 128.4, 127.1, 123.9, 116.8, 105.1, 77.5, 61.6, 60.7, 40.2, 39.1, 21.8, 21.4, 14.4, 14.2. Exact mass calculated $C_{27}H_{29}O_6^+$$[M+H]^+$: 449.1964; found:449.1961.

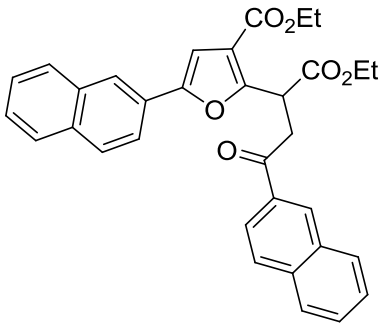


Ethyl 2-(1-ethoxy-4-(4-methoxyphenyl)-1,4-dioxobutan-2-yl)-5-(4-methoxyphenyl)furan-3-carboxylate (4c): According to the method C, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-(4-methoxyphenyl)ethanone (150 mg, 543 µmol) provided **4c** after flash column chromatography (20% ethyl acetate in petroleum ether) as a yellow liquid (73 mg, 70%). R_f = 0.15 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2979, 2935, 1714, 1680, 1258, 1173. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.9 Hz, 2H), 7.51 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* =

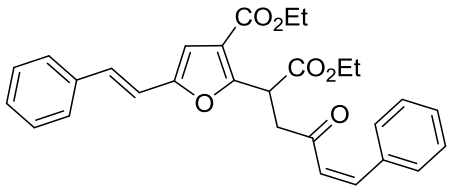
8.9 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.78 (s, 1H), 5.21 (dd, *J* = 8.8, 5.1 Hz, 1H), 4.31 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.96 (dd, *J* = 17.5, 8.8 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 3.36 (dd, *J* = 17.5, 5.2 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 195.2, 170.5, 163.7, 163.4, 159.6, 155.8, 153.0, 130.5, 130.1, 129.6, 125.5, 122.8, 116.8, 114.3, 113.8, 104.2, 77.5, 61.6, 60.6, 55.5, 55.4, 40.2, 38.9, 14.4, 14.2.Exact mass calculated $C_{27}H_{29}O_8^+$ $[M+H]^+$: 481.1862; found: 481.1863.



Ethyl 2-(1-ethoxy-4-(4-isobutylphenyl)-1,4-dioxobutan-2-yl)-5-(4-isobutylphenyl)furan-3-carboxylate (4d): According to the method C, allenoate **1** (40 mg, 217µmol) and 2-iodo-1-(4-isobutylphenyl)ethanone (164 mg, 543 µmol) provided **4d** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (65 mg, 57%). R_f = 0.63 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2957, 2927, 2869, 1715, 1742. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 7.90 (d, *J* =8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* =8.2 Hz, 2H), 6.88 (s, 1H), 5.24 (dd, *J* = 8.7, 5.2 Hz, 1H), 4.37 – 4.27 (m, 2H), 4.18 (m, 2H), 4.00 (dd, *J* = 17.7, 8.7 Hz, 1H), 3.40 (m, *J* = 17.6, 5.2 Hz, 1H), 2.51 (d, *J* = 7.1 Hz, 2H), 2.46 (d, *J* =7.2 Hz, 2H), 1.86 (m, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* =7.1 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 12H) .^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.4, 170.5, 163.4, 156.0, 153.2, 147.9, 142.0, 134.3, 129.6, 129.4, 128.2, 127.3, 123.8, 116.8, 105.1, 61.6, 60.7, 45.5, 45.3, 40.2, 39.1, 30.3, 30.2, 22.4, 14.4, 14.2. Exact mass calculated $C_{33}H_{41}O_6^+$ $[M+H]^+$: 533.2898; found: 533.2891.

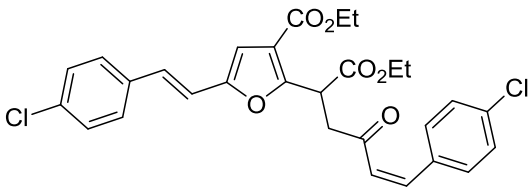


Ethyl 2-(1-ethoxy-4-(naphthalen-2-yl)-1,4-dioxobutan-2-yl)-5-(naphthalen-2-yl)furan-3-carboxylate (4e): According to the method C, allenoate **1** (40 mg, 217 µmol) and 2-iodo-1-(naphthalen-2-yl)ethanone (161 mg, 543 µmol) provided **4e** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (84 mg, 74%). R_f = 0.36 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2928, 2980, 1735, 1717. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 8.56 (s, 1H), 8.09 – 8.03 (m, 2H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.91 – 7.85 (m, 2H), 7.83 – 7.72 (m, 3H), 7.69 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.62 – 7.51 (m, 3H), 7.46 – 7.43 (m, 1H), 7.08 (s, 1H), 5.38 (dd, *J* = 8.6, 5.4 Hz, 1H), 4.37 (qq, *J* = 8.0, 3.6 Hz, 2H), 4.29 – 4.18 (m, 3H), 3.64 (dd, *J* = 17.6, 5.3 Hz, 1H), 1.39 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.7, 170.5, 163.3, 156.6, 153.2, 135.8, 133.9, 133.4, 133.0, 132.6, 130.1, 129.7, 128.6, 128.3, 127.9, 127.9, 127.0, 126.9, 126.7, 126.4, 123.9, 122.6, 122.1, 117.2, 106.5, 77.5, 77.2, 76.8, 61.8, 60.8, 40.4, 39.3, 14.4, 14.2.Exact mass calculated $C_{33}H_{29}O_6^+$ $[M+H]^+$: 521.1964; found: 521.1967.

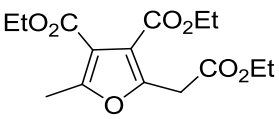


Ethyl 2-(1-ethoxy-1,4-dioxo-6-phenylhex-5-en-2-yl)-5-styrylfuran-3-carboxylate (4f): According to the method C, allenoate **1** (40 mg, 217 µmol) and 1-iodo-4-phenylbut-

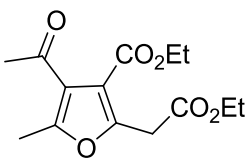
3-en-2-one (148 mg, 543 µmol) provided **4f** after flash column chromatography (5% ethyl acetate in petroleum ether) as a yellow liquid (62 mg, 60%). R_f = 0.26 (10% ethyl acetate in petroleum ether)**. IR** (neat): ν_{max}/cm^{-1} 2981, 2960, 1739, 1715, 1231. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 16.2 Hz, 1H), 7.54 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.42 – 7.37 (m, 5H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.23 (m, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.78 (dd, *J* = 16.2, 1.9 Hz, 2H), 6.62 (s, 1H), 5.16 (dd, *J* = 8.6, 5.4 Hz, 1H), 4.32 (m, 2H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.69 (dd, *J* = 17.4, 8.7 Hz, 1H), 3.15 (dd, *J* = 17.4, 5.4 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ^{13}CNMR (100 MHz, Chloroform-*d*) δ 196.6, 170.4, 163.2, 156.4, 152.3, 152.3, 143.4, 136.5, 134.4, 130.7, 129.1, 128.8, 128.8, 128.5, 128.1, 126.5, 125.8, 116.8, 115.5, 109.0, 77.5, 77.1, 76.8, 61.7, 60.8, 40.8, 40.1, 14.4, 14.2. Exact mass calculated $C_{29}H_{29}O_6^+$ $[M+H]^+$: 473.1964; found: 473.1970.



Ethyl 2-(6-(4-chlorophenyl)-1-ethoxy1,4-dioxohex-5-en-2-yl)-5-(4-chlorostyryl)furan-3-carboxylate (4g): According to the method C, allenoate **1** (40 mg, 217 µmol) and 4-(4-chlorophenyl)-1-iodobut-3-en-2-one (167 mg, 543 µmol) provided **4g** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (29mg, 40%). R_f = 0.28 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2982, 2927, 1714, 1215, 1177. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, *J* = 16.2 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.35 (d, *J* = 8.6 Hz, 3H), 7.30 (d, *J* = 9.5 Hz, 3H), 6.92 (d, *J* = 16.3 Hz, 1H), 6.74 (dd, *J* = 16.2, 2.1 Hz, 2H), 6.63 (s, 1H), 5.14 (dd, *J* = 8.6, 5.4 Hz, 1H), 4.31 (m, 2H), 4.18 (m, 2H), 3.67 (dd, *J* = 17.4, 8.6 Hz, 1H), 3.11 (dd, *J* = 17.4, 5.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.2, 170.2, 163.1, 156.5, 152.0, 141.9, 136.7, 135.0, 133.7, 132.9, 129.6, 129.4, 129.0, 127.7, 127.4, 126.1, 116.9, 116.0, 109.4, 61.8, 60.8, 41.0, 40.1, 14.4, 14.2. Exact mass calculated $C_{29}H_{27}Cl_2O_6^+$ $[M+H]^+$: 541.1185; found : 541.1184.

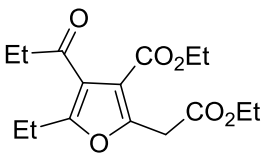


Diethyl 2-(2-ethoxy-2-oxoethyl)-5-methylfuran-3,4-dicarboxylate (3h): According to the method A, allenoate **1** (40 mg, 217 µmol) and ethyl 2-bromo-3-oxobutanoate (90 mg, 434 µmol) provided **3h** after flash column chromatography (10% ethyl acetate in petroleum ether) as a colorless oil (43 mg, 63%). **IR** (neat): ν_{max}/cm^{-1} 2983, 2934, 1739, 1731. R_f = 0.25 (10% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.32 – 4.22 (m, 4H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 2.44 (s, 3H), 1.30 (td, *J* = 7.1, 5.9 Hz, 6H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.4, 163.4, 162.9, 156.8, 151.1, 116.0, 114.1, 61.5, 60.8, 33.6, 14.3, 14.2, 13.3. Exact mass calculated $C_{15}H_{21}O_7^+$ $[M+H]^+$: 313.1287; found : 313.1281.

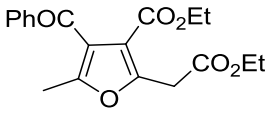


Ethyl 4-acetyl-2-(2-ethoxy-2-oxoethyl)-5-methylfuran-3-carboxylate (3i): According to the method A, allenoate **1** (40 mg, 217 µmol) and 3-bromohexane-2,4-dione (78 mg, 434 µmol) provided **3i** after flash column chromatography (10% ethyl acetate in petroleum ether) as a colorless oil

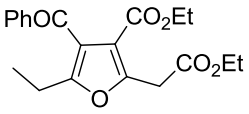
(40mg, 65%). R_f = 0.26 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2963, 2926, 1743, 1715, 1260. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 4.27 (q, *J* = 6.8 Hz, 2H), 4.15 (q, *J* = 6.8 Hz, 2H), 3.90 (s, 2H), 2.42 (s, 3H), 2.35 (s, 3H), 1.30 (t, *J* = 6.9 Hz, 3H), 1.26 – 1.21 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.8, 168.4, 163.0, 155.0, 152.3, 123.0, 114.9, 61.5, 61.0, 34.0, 31.1, 14.2, 13.2. Exact mass calculated $C_{14}H_{19}O_6^+$ $[M+H]^+$: 283.1182; found : 283.1183.



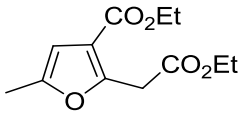
Ethyl 2-(2-ethoxy-2-oxoethyl)-5-ethyl-4-propionylfuran-3-carboxylate (3j): According to the method A, allenoate **1** (40 mg, 217 µmol) and 4-bromoheptane-3,5-dione (90 mg, 434 µmol) provided **3j** after flash column chromatography (10% ethyl acetate in petroleum ether) as a colorless oil (40mg, 65%). R_f = 0.44 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2980, 2938, 1744, 1717, 1275, 1182. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 2H), 2.73 (q, *J* = 7.3 Hz, 2H), 2.66 (q, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.17 (t, *J* = 7.5 Hz, 3H), 1.10 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.0, 168.5, 163.0, 158.1, 152.4, 122.0, 114.7, 77.5, 77.1, 76.8, 61.5, 61.0, 36.9, 34.0, 20.5, 14.2, 14.2, 12.7, 8.4. Exact mass calculated $C_{16}H_{23}O_6^+$ $[M+H]^+$: 311.1494; found : 311.1490.



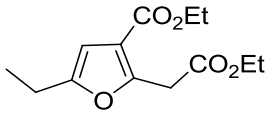
Ethyl 4-benzoyl-2-(2-ethoxy-2-oxoethyl)-5-methylfuran-3-carboxylate (3k): According to the method A, allenoate **1** (40 mg, 217 µmol) and 2-bromo-1-phenylbutane-1,3-dione (77 mg, 434 µmol) provided **3k** after flash column chromatography (5% ethyl acetate in petroleum ether) as a yellow liquid (54mg, 72%). R_f = 0.29 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2926, 2982, 1731, 1651, 1276, 1175. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 7.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.03 (dd, *J* = 14.1, 6.8 Hz, 4H), 2.21 – 2.17 (m, 3H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.14 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.0, 170.2, 158.9, 158.6, 140.3, 138.6, 133.2, 129.2, 128.8, 128.0, 123.9, 61.2, 61.0, 30.2, 14.8, 14.4, 14.2.Exact mass calculated $C_{19}H_{20}NaO_6^+$ $[M+H]^+$: 367.1158; found : 367.1163.



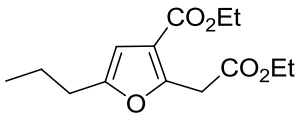
Ethyl 4-benzoyl-2-(2-ethoxy-2-oxoethyl)-5-ethylfuran-3-carboxylate (3l): According to the method A, allenoate **1** (40 mg, 217 µmol) and 2-bromo-1-phenylpentane-1,3-dione (77 mg, 406 µmol) provided **3l** after flash column chromatography (5% ethyl acetate in petroleum ether) as a yellow liquid (35 mg, 60%). R_f = 0.31 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2923, 2851, 1735, 1269, 1174. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.06 – 3.97 (m, 4H), 2.51 (q, *J* = 7.5 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.14 (q, *J* = 7.4 Hz, 6H).Exact mass calculated $C_{20}H_{22}NaO_6^+$ $[M+Na]^+$: 381.1314; found : 381.1310.



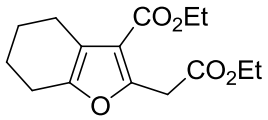
Ethyl 2-(2-ethoxy-2-oxoethyl)-5-methylfuran-3-carboxylate (3m): According to the method B, allenoate **1** (40 mg, 217 µmol) and 1-bromopropan-2-one (60 mg, 434 µmol) provided **3m** after flash column chromatography (10% ethyl acetate in petroleum ether) as a colorless oil (36 mg, 68%). R_f = 0.54 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2983, 2930, 1746, 1714, 1238. ^{1}H NMR (400 MHz, Chloroform-*d*) δ = 6.26 (s, 1H), 4.23 (q, *J* =7.2 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 2H), 2.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.0, 163.7, 152.5, 151.5, 116.4, 106.6, 61.3, 60.3, 33.9, 14.3, 14.2, 13.4. Exact mass calculated $C_{12}H_{16}NaO_5^+$ $[M+Na]^+$: 263.0895; found : 263.0899.



Ethyl 2-(2-ethoxy-2-oxoethyl)-5-ethylfuran-3-carboxylate (3n): According to the method B, allenoate **1** (40 mg, 217 µmol) and 1-bromobutan-2-one (66 mg, 434 µmol) provided **3n** after flash column chromatography (10% ethyl acetate in petroleum ether) as a colorless oil (29mg, 52%). R_f = 0.47 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2980, 2936, 2856, 1746, 1714. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.27 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 2H), 2.60 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.22 (dt, *J* = 15.1, 7.3 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.1, 163.9, 157.2, 152.4, 116.1, 105.0, 61.3, 60.3, 33.9, 21.2, 14.4, 14.2, 11.8. Exact mass calculated $C_{13}H_{18}NaO_5^+$ $[M+Na]^+$: 277.1051; found : 277.1054.

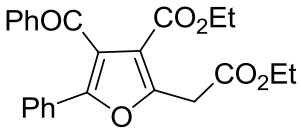


Ethyl 2-(2-ethoxy-2-oxoethyl)-5-propylfuran-3-carboxylate: According to the method B, allene-1,3-dicarboxylates (40 mg, 217.17µmol) and 1-bromopentan-2-one (72 mg, 434.33µmol) at r.t. provided 14 after flash column chromatography (5% ethyl acetate in petroleum ether) as a yellow liquid (21 mg, 35%). R_f = 0.6 (10% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.27 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 2.54 (t, *J* = 7.4 Hz, 2H), 1.63 (t, *J* = 7.4 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.0, 163.8, 155.8, 152.4, 116.1, 105.9, 61.3, 60.3, 33.9, 29.7, 21.1, 14.4, 14.2, 13.7. Exact mass calculated $C_{14}H_{20}NaO_5^+$ $[M+Na]^+$: 291.1208; found : 291.1205.

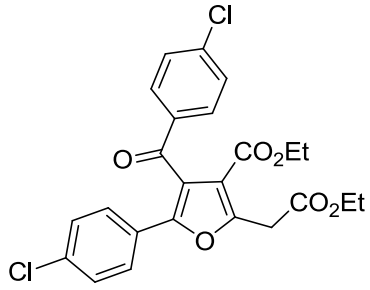


Ethyl2-(2-ethoxy-2-oxoethyl)-4,5,6,7-tetrahydrobenzo furan-3-carboxylate (3q): Allenoate **1** (40 mg, 217 µmol), 2-bromocyclohexanone (77 mg, 434 µmol), 18-Crown-6 (57 mg, 217 µmol), Ag_2CO_3 (60 mg, 217 µmol) were added in vial . 2 ml toluene was added followed by the addition of K_2CO_3 (300 mg, 2 mmol). The reaction mixture was stirred in a close vial for 24 hrs. After completion of the reaction (as monitored by TLC analysis), the reaction mixture was poured in separating funnel and extracted with EtOAc and brine. The combined organic layer was collected and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (10% ethyl acetate in petroleum ether) on silica gel to afford **3o** as a colorless

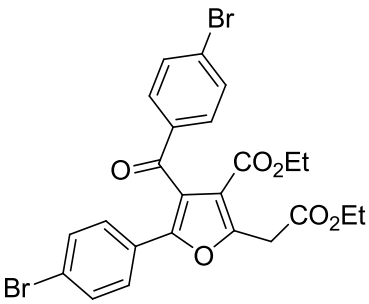
oil (22mg, 36%). R_f = 0.52 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2937, 2855, 1745, 1714, 1272. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.23 (q, *J* = 7.1 Hz, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 2.59 (t, *J* = 6.0 Hz, 2H), 2.53 (t, *J* = 6.1 Hz, 2H), 1.78 (qd, *J* = 7.7, 6.2, 3.9 Hz, 2H), 1.74 – 1.66 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.3, 164.4, 152.4, 150.8, 117.8, 115.1, 77.4, 77.1, 76.8, 61.3, 60.0, 34.2, 23.0, 22.8, 22.7, 22.2, 14.3, 14.2. Exact mass calculated $C_{15}H_{20}NaO_5^+$ $[M+Na]^+$: 303.1208; found : 303.1200.



Ethyl 4-benzoyl-2-(2-ethoxy-2-oxoethyl)-5-phenylfuran-3-carboxylate (3r): According to the method B, allenoate **1** (40 mg, 217μmol) and 2-bromo-1,3-diphenylpropane-1,3-dione (132 mg, 434 μmol) provided **3p** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (76 mg, 86%). R_f = 0.42 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2962, 2928, 1736, 1708, 1176. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 8.1 Hz, 4H), 7.26 (d, *J* = 7.7 Hz, 2H), 7.18 (q, *J* = 8.3, 6.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.05 – 3.96 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.2, 170.0, 159.0, 156.2, 140.9, 137.1, 133.5, 129.9, 129.8, 128.8, 128.5, 128.4, 128.1, 122.9, 61.3, 61.1, 30.2, 14.4, 14.1. Exact mass calculated $C_{24}H_{23}O_6^+$ $[M+H]^+$: 407.1495; found : 407.1499.

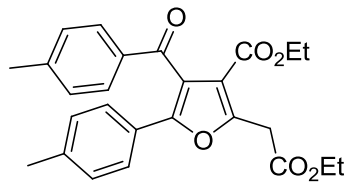


Ethyl 4-(4-chlorobenzoyl)-5-(4-chlorophenyl)-2-(2-ethoxy-2-oxoethyl)furan-3-carboxylate (3s): According to the method B, allenoate **1** (40 mg, 217μmol) and 2-bromo-1,3-bis(4-chlorophenyl)propane-1,3-dione (162 mg, 434 μmol) provided **3q** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (82 mg, 80%). R_f = 0.38 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2981, 2929, 1732, 1250, 1177. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 8.7 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.01 (t, *J* = 3.6 Hz, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.7, 169.9, 158.8, 154.6, 141.1, 140.3, 136.2, 135.3, 131.2, 129.1, 129.1, 129.0, 128.7, 126.8, 122.9, 61.5, 61.2, 30.0, 14.4, 14.1. Exact mass calculated $C_{24}H_{21}Cl_2O_6^+$ $[M+H]^+$: 475.0715; found: 475.0712.

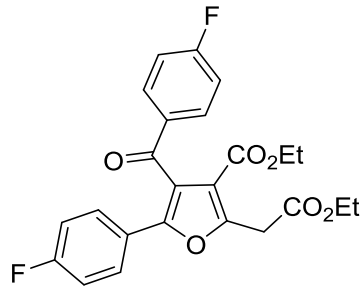


Ethyl 4-(4-bromobenzoyl)-5-(4-bromophenyl)-2-(2-ethoxy-2-oxoethyl)furan-3-carboxylate (3t): According to the method B, allenoate **1** (40 mg, 217 μmol) and 2-bromo-1,3-bis(4-bromophenyl)propane-1,3-dione (200 mg, 434 μmol) provided **3r** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (75 mg, 61%). R_f = 0.43 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2963, 2927, 1732, 1260, 1177. ^{1}H NMR (400 MHz, Chloroform-*d*) δ =

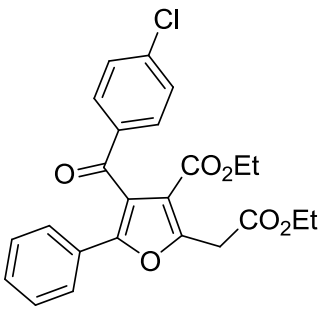
7.63 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.05 – 3.95 (m, 4H), 1.39 (t, *J* = 7.1, 3H), 1.11 (t, *J* = 7.1, 3H).^{13}C NMR (100 MHz, Chloroform-*d*) δ 1900.9, 169.9, 158.8, 154.6, 141.2, 135.7, 132.1, 131.9, 131.3, 129.3, 129.2, 128.7, 127.2, 124.6, 122.9, 61.5, 61.3, 30.0, 14.4, 14.1. Exact mass calculated $C_{24}H_{21}Br_2O_6^+$ $[M+H]^+$: 562.9705; found : 562.9709.



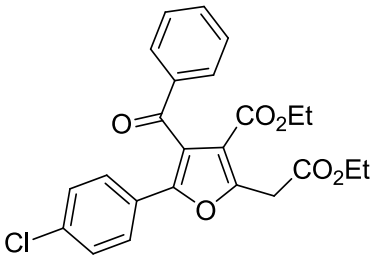
Ethyl 2-(2-ethoxy-2-oxoethyl)-4-(4-methylbenzoyl)-5-p-tolylfuran-3-carboxylate (3u): allenoate 1 (40 mg, 217 µmol) , 2-bromo-1-(4-chlorophenyl)-3-phenylpropane-1,3-dione (72 mg, 217 µmol), and TBAB (70 mg, 217 µmol) were added in vial. 2 ml toluene was added followed by the addition of K_2CO_3 (300 mg, 2 mmol). The reaction mixture was stirred in a closed vial for 24 h. After completion of the reaction (as monitored by TLC analysis), the reaction mixture was poured in a separating funnel and extracted with EtOAc and brine. The combined organic layers were collected and dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography (10% ethyl acetate in petroleum ether) on silica gel to afford **3t** as a yellow liquid (46mg, 48%). R_f = 0.33 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2981, 2927, 1737, 1710. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.99 (dd, *J* = 13.9, 6.8 Hz, 4H), 2.31 (s, 3H), 2.25 (s, 3H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.9, 169.9, 159.1, 155.8, 144.5, 140.5, 139.9, 134.7, 130.1, 129.3, 129.2, 128.7, 127.8, 125.9, 122.6, 100.0, 61.2, 61.0, 30.3, 21.8, 21.4, 14.4, 14.1. Exact mass calculated $C_{26}H_{26}NaO_6^+$ $[M+H]^+$: 457.1627; found : 457.1627.



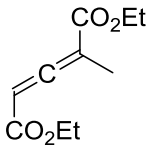
Ethyl 2-(2-ethoxy-2-oxoethyl)-4-(4-fluorobenzoyl)-5-(4-fluorophenyl)furan-3-carboxylate (3v): According to the method B, allenoate **1** (40 mg, 217 µmol) and 2-bromo-1,3-bis(4-fluorophenyl)propane-1,3-dione (147 mg, 434 µmol) provided **3t** after flash column chromatography (10% ethyl acetate in petroleum ether) as a yellow liquid (60 mg, 62%). R_f = 0.36 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2925, 2981, 2851, 1734, 12327, 1178. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.41 (dd, *J* = 8.9, 5.2 Hz, 2H), 6.93 (dt, *J* = 17.5, 8.6 Hz, 4H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.04 – 3.97 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.41 , 169.94 , 167.27 , 163.47 (d, *J* = 251.7 Hz), 158.88 , 155.07 , 140.98 , 133.42 (d, *J* = 3.1 Hz), 132.53 (d, *J* = 9.6 Hz), 130.11 (d, *J* = 8.7 Hz), 128.70 , 124.75 (d, *J* = 3.6 Hz), 122.61 , 115.84 (d, *J* = 22.3 Hz), 61.38 , 61.18 , 30.04 , 14.39 , 14.11 . Exact mass calculated $C_{24}H_{20}F_2NaO_6^+$ $[M+Na]^+$: 465.1126; found : 465.1120.



Ethyl 4-(4-chlorobenzoyl)-2-(2-ethoxy-2-oxoethyl)-5-phenylfuran-3-carboxylate (3w): According to the method B, allenoate **1** (40 mg, 217 µmol) and 2-bromo-1-(4-chlorophenyl)-3-phenylpropane-1,3-dione (77 mg, 406 µmol) provided **3u** after flash column chromatography (5% ethyl acetate in petroleum ether) as a yellow liquid (46 mg, 48%). R_f = 0.38 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2928, 2960, 2852, 1733, 1250, 1180. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 7.1 Hz, 2H), 7.26 – 7.18 (m, 5H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.97 (m, 4H), 1.39 (t, *J* = 7.1 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 192.0, 169.8, 158.9, 154.7, 141.0, 137.0, 135.9, 133.8, 129.8, 129.1, 128.8, 128.7, 128.7, 127.0, 123.3, 61.4, 61.2, 30.2, 14.4, 14.1.Exact mass calculated $C_{24}H_{22}ClO_6^+[M+H]^+$: 441.1105; found : 441.1104.

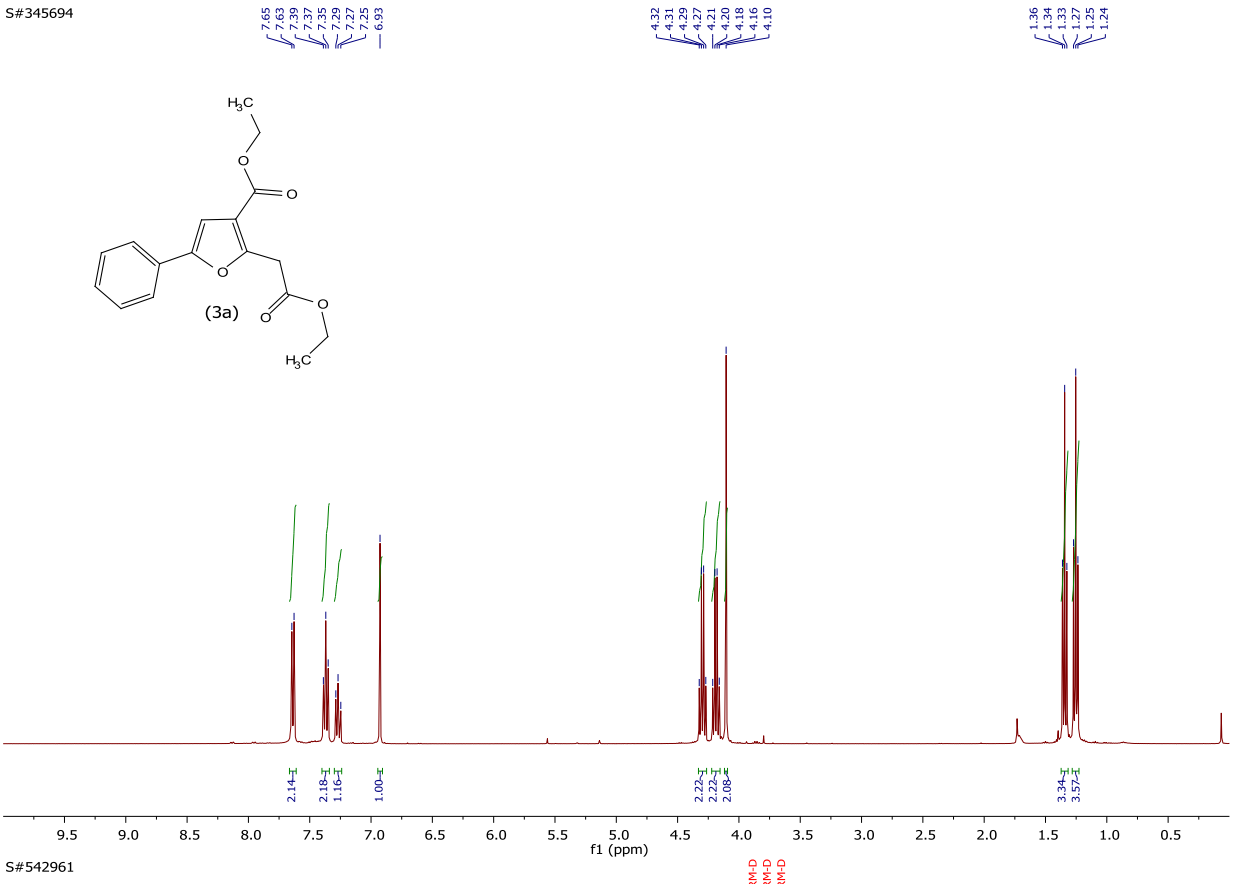


Ethyl 4-benzoyl-5-(4-chlorophenyl)-2-(2-ethoxy-2-oxoethyl)furan-3-carboxylate (3x): According to the method B, allenoate **1** (40 mg, 217µmol) and 2-bromo-1-(4-chlorophenyl)-3-phenylpropane-1,3-dione (77 mg, 406 µmol) provided **3v** after flash column chromatography (5% ethyl acetate in petroleum ether) as a yellow liquid (34 mg, 36%). R_f = 0.41 (10% ethyl acetate in petroleum ether). **IR** (neat): ν_{max}/cm^{-1} 2925, 2958, 2854, 1738, 1259, 1180. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 7.8 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 4.00 (d, *J* = 5.4 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.0, 170.0, 159.0, 156.3, 141.0, 139.9, 135.4, 131.2, 130.0, 128.9, 128.8, 128.6, 128.3, 128.1, 122.6, 100.0, 61.4, 61.2, 30.0, 14.4, 14.1. Exact mass calculated $C_{24}H_{22}ClO_6^+[M+H]^+$: 441.1105; found : 441.1104.



Diethyl 2-methylpenta-2,3-dienedioate (13): According to the method B, allenoate **1** (40 mg, 217µmol) and methyliodide (300 mg, 2 mmol) provided **13** after flash column chromatography (5% ethyl acetate in petroleum ether) as a colorless oil (15 mg, 35%). R_f = 0.38 (10% ethyl acetate in petroleum ether). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.85 (q, *J* = 3.0 Hz, 1H), 4.18 (q, *J* = 9.4, 7.1, 2.3 Hz, 4H), 1.93 (d, *J* = 3.0 Hz, 2H), 1.24 (td, *J* = 7.1, 5.6 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 218.3, 165.6, 164.2, 100.3, 90.9, 61.6, 61.3, 14.3, 14.2, 14.2. The spectral data match as reported previously.[3]

S#345694



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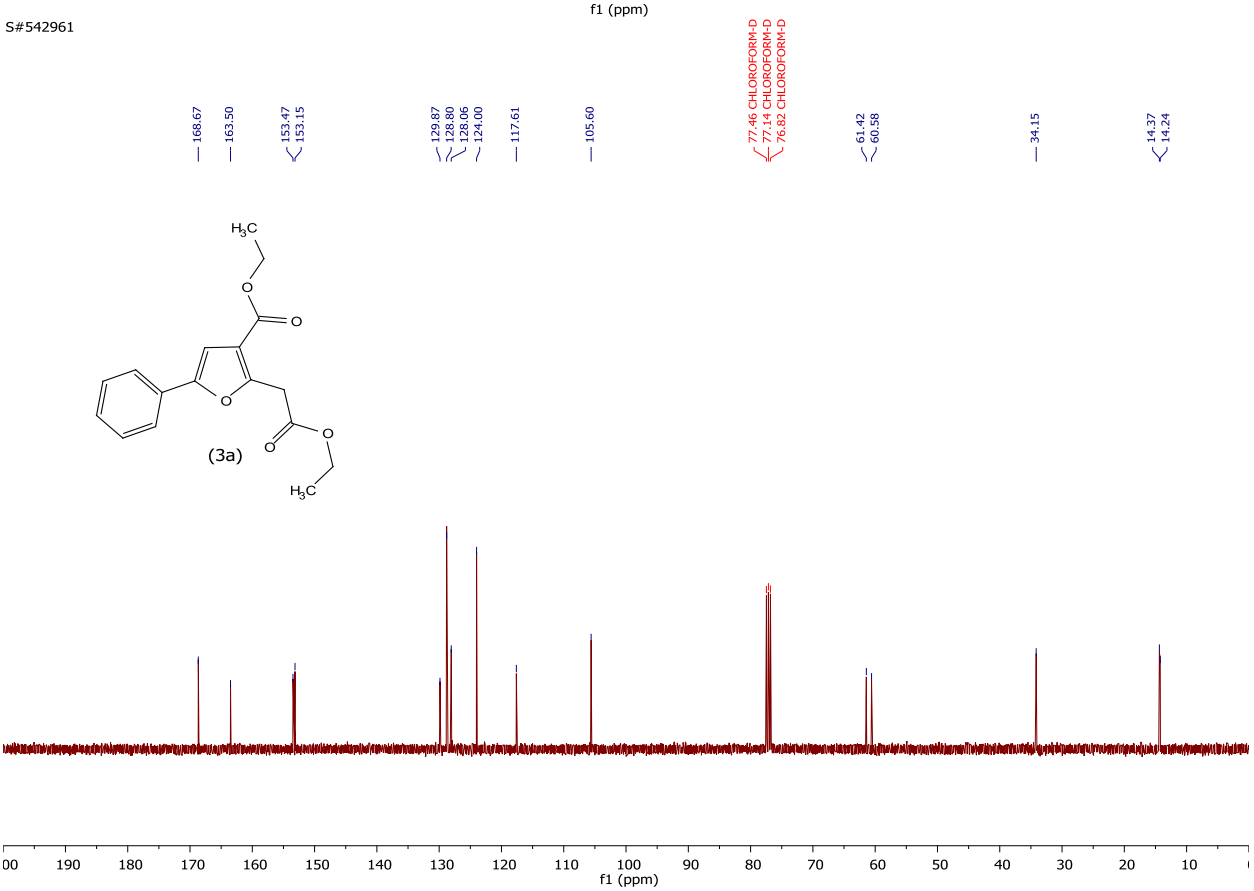
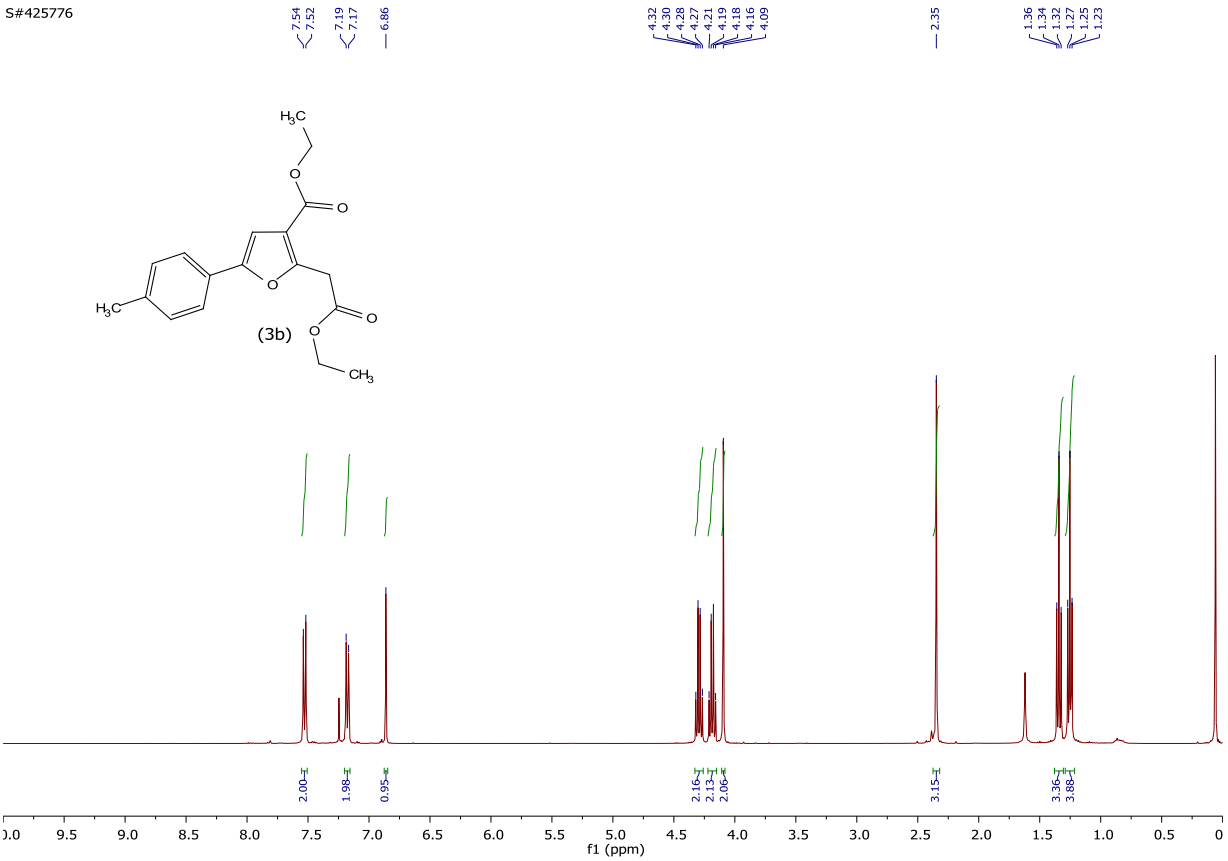


S#425776



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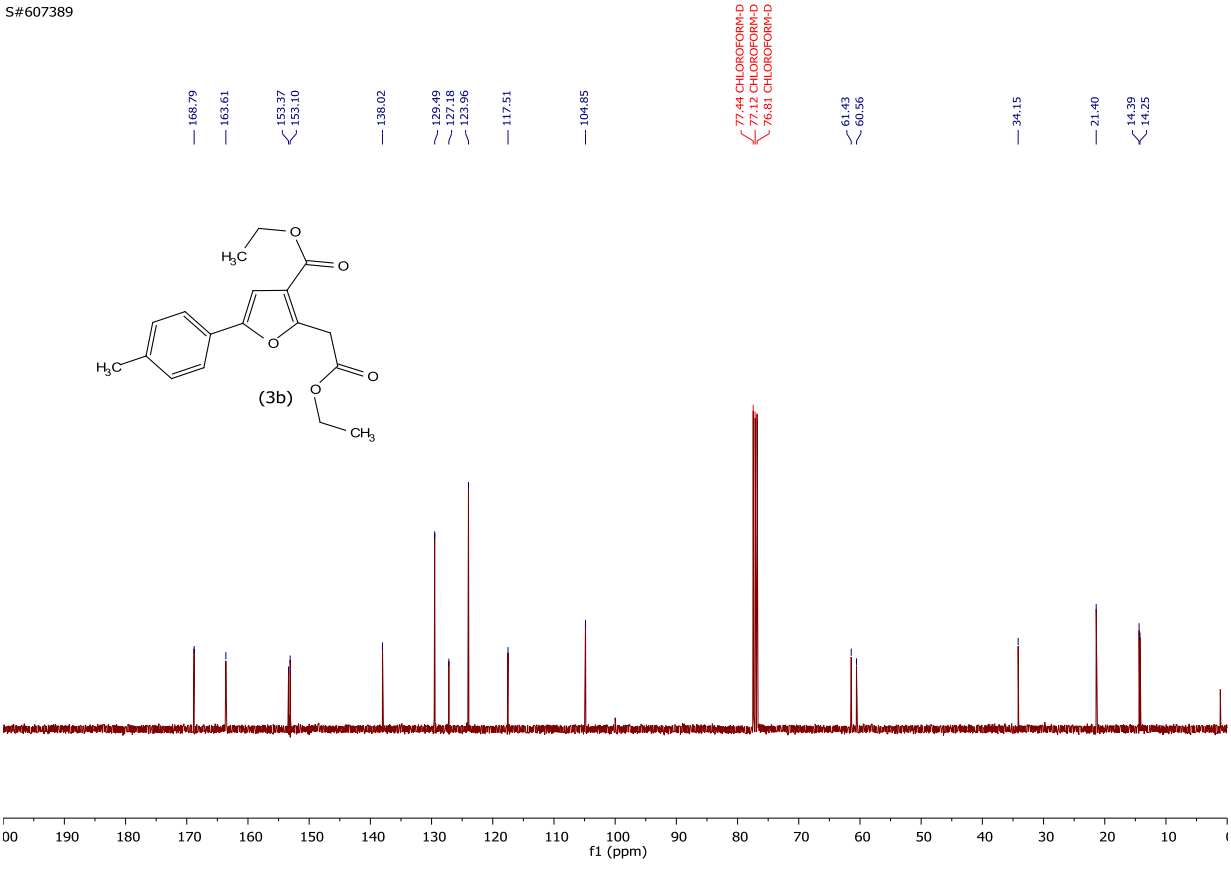

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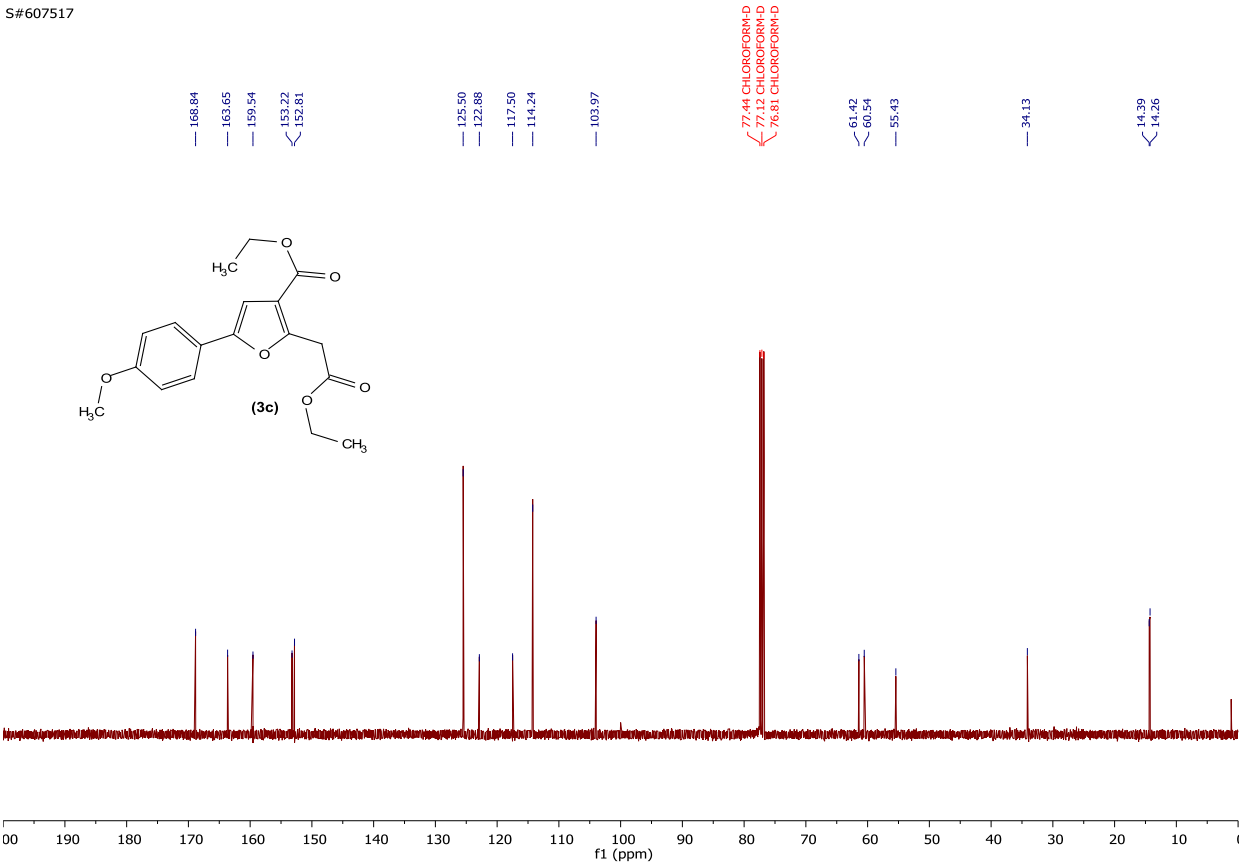

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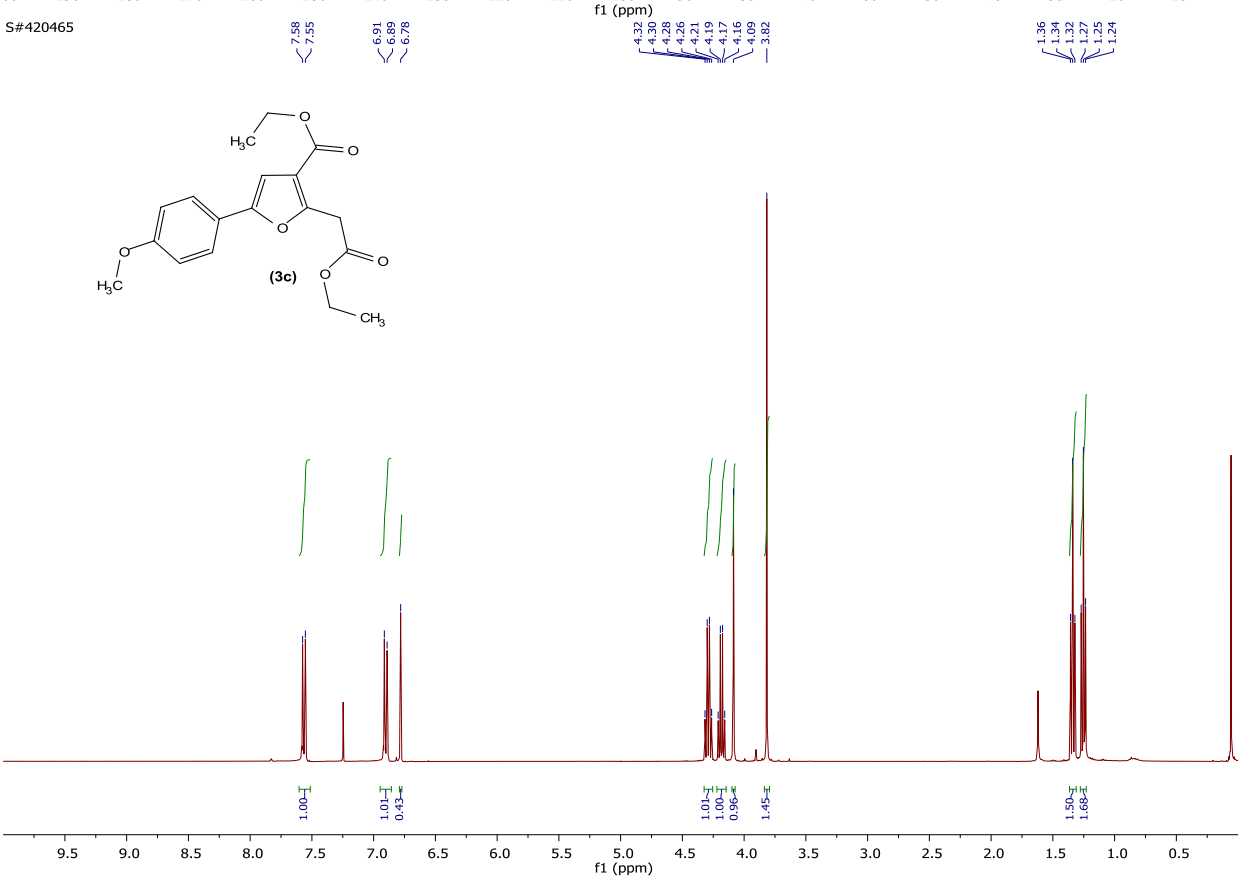

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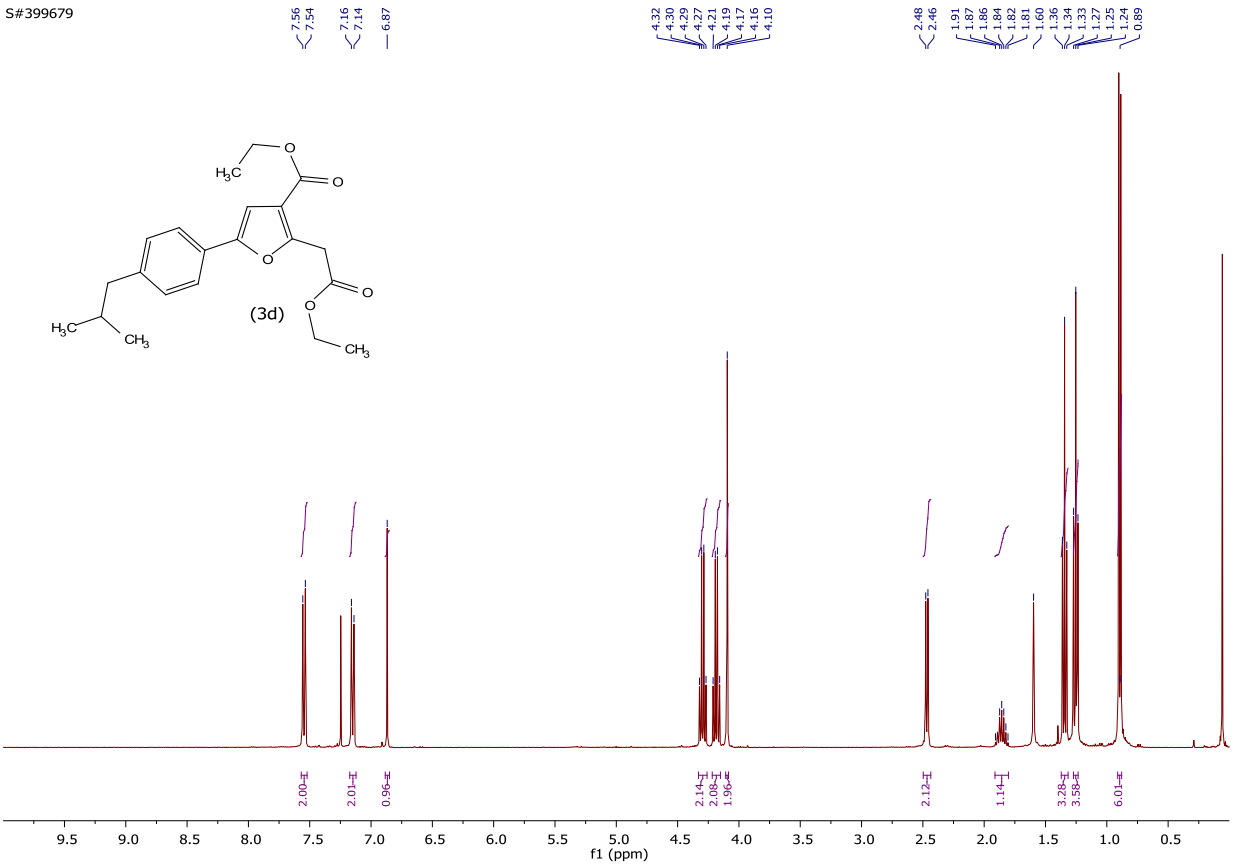
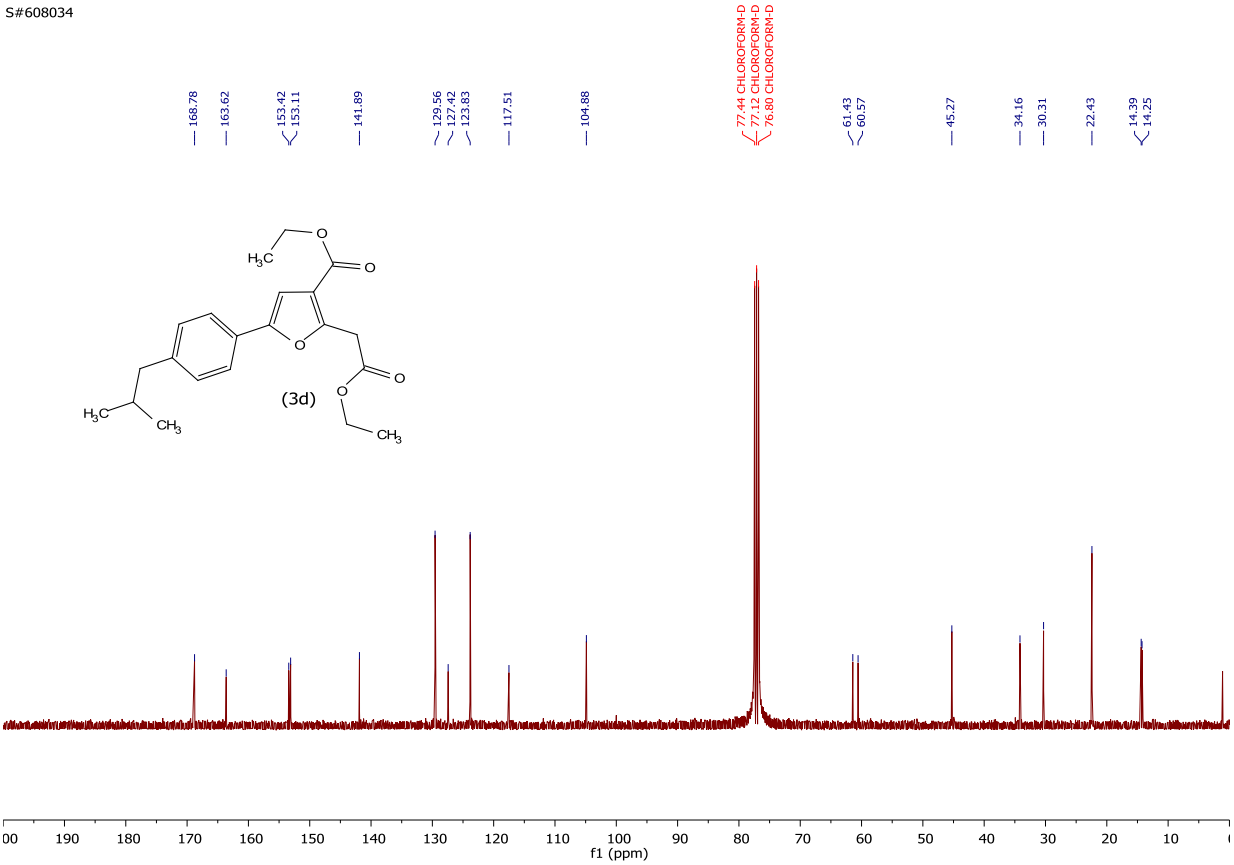


S#608034



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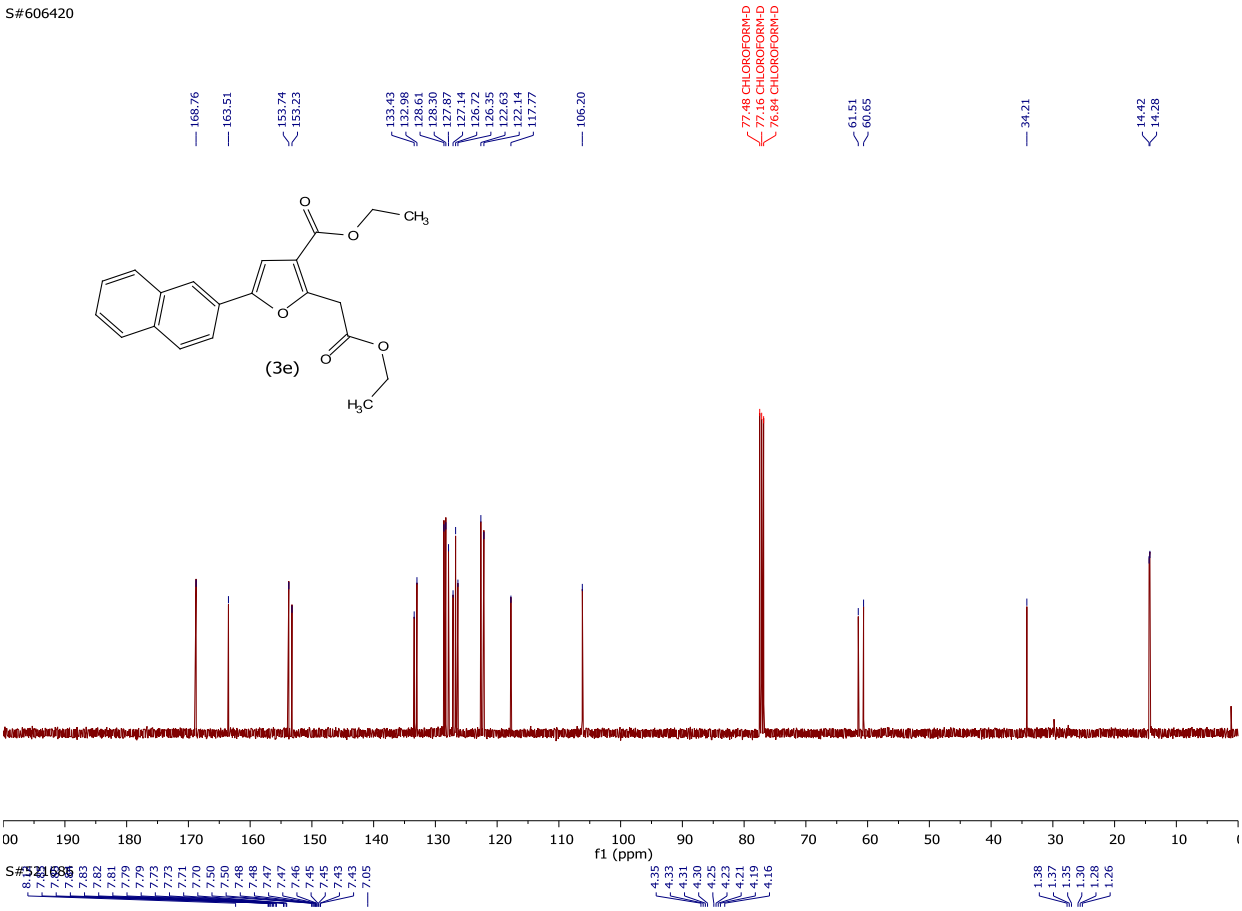

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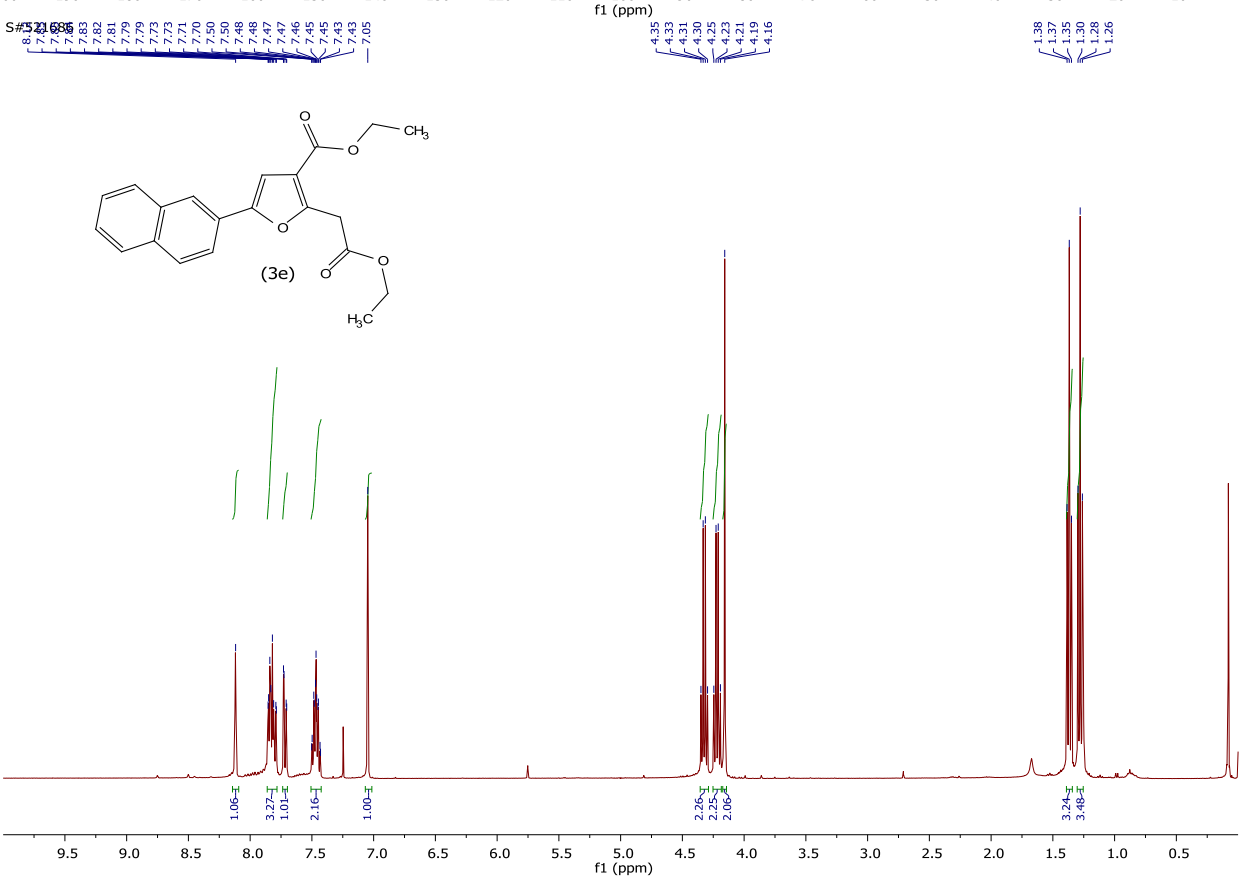

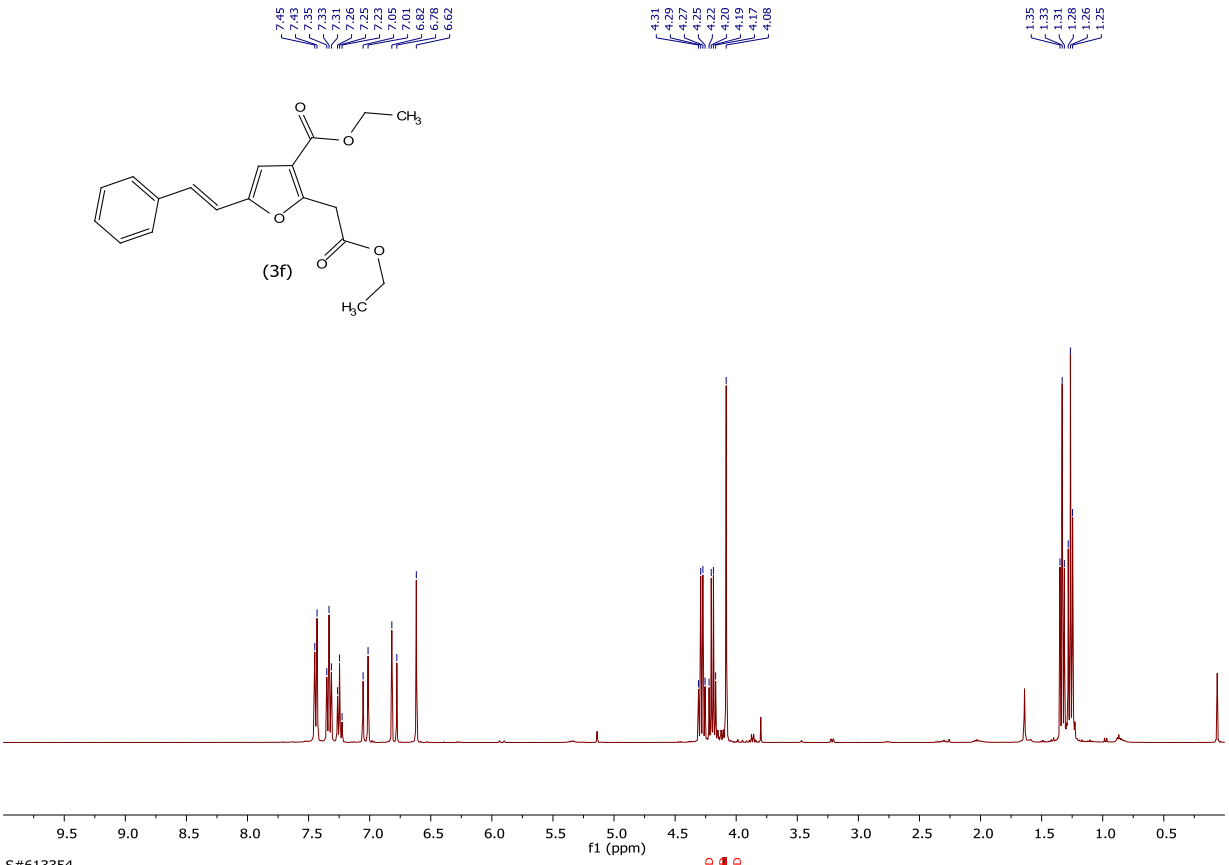
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1.26
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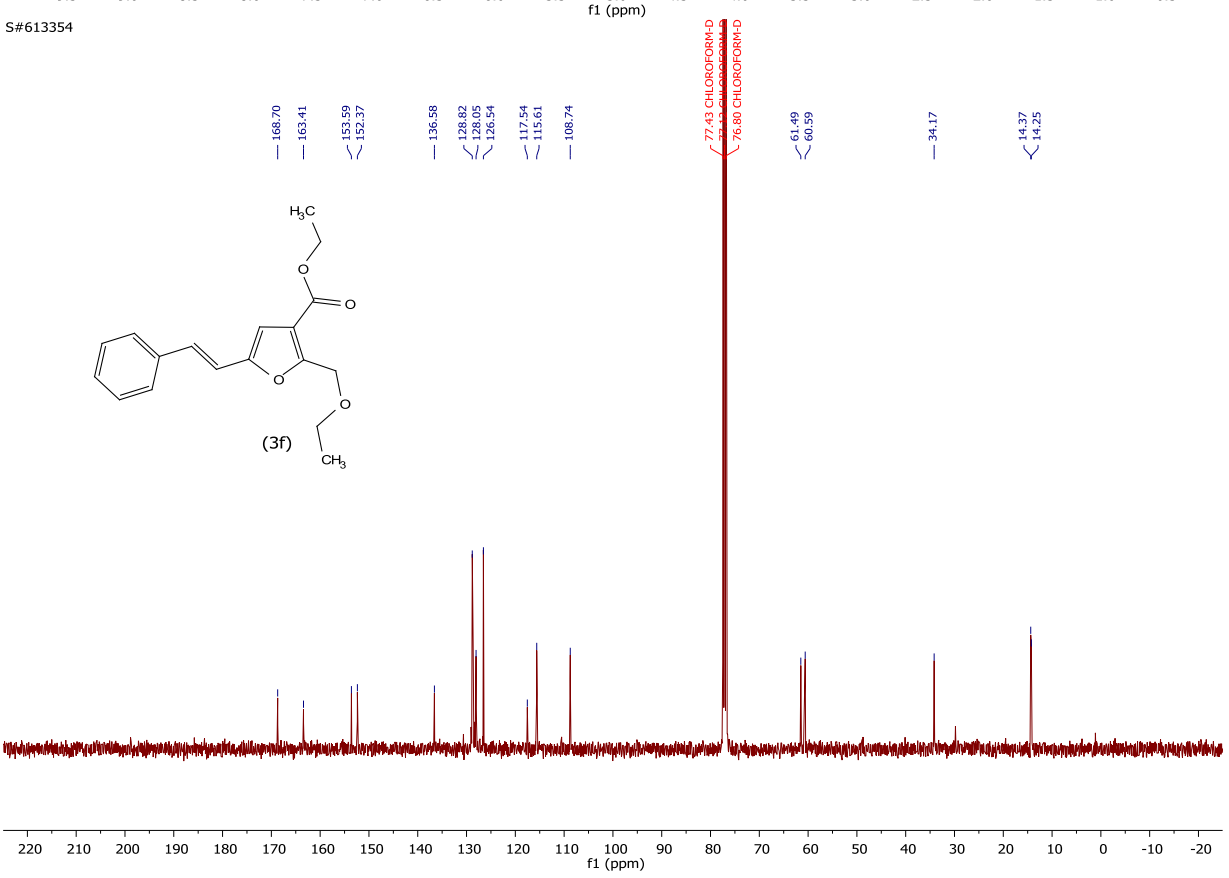
(3f)
f1 (ppm)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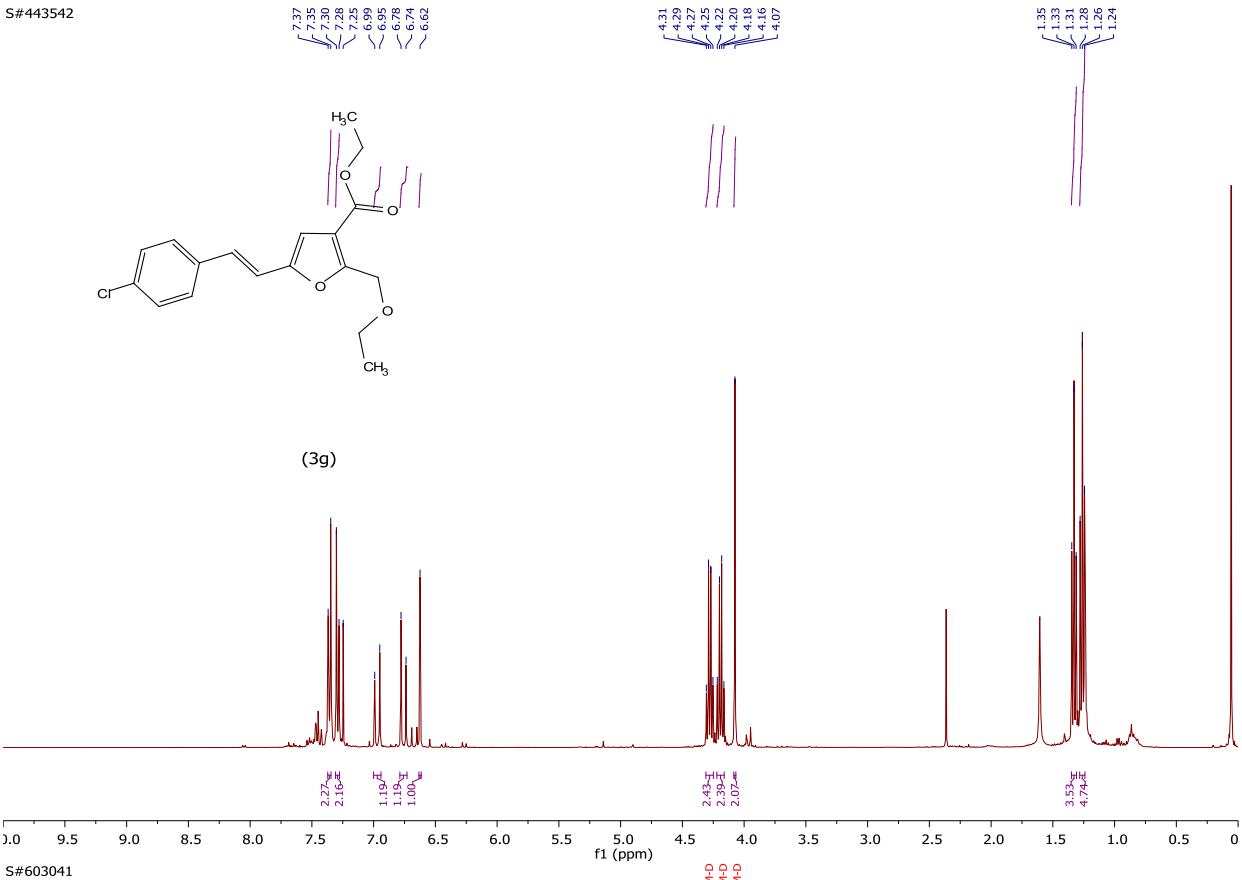
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1.28
1.26
1.24
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Cl
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O
CH3
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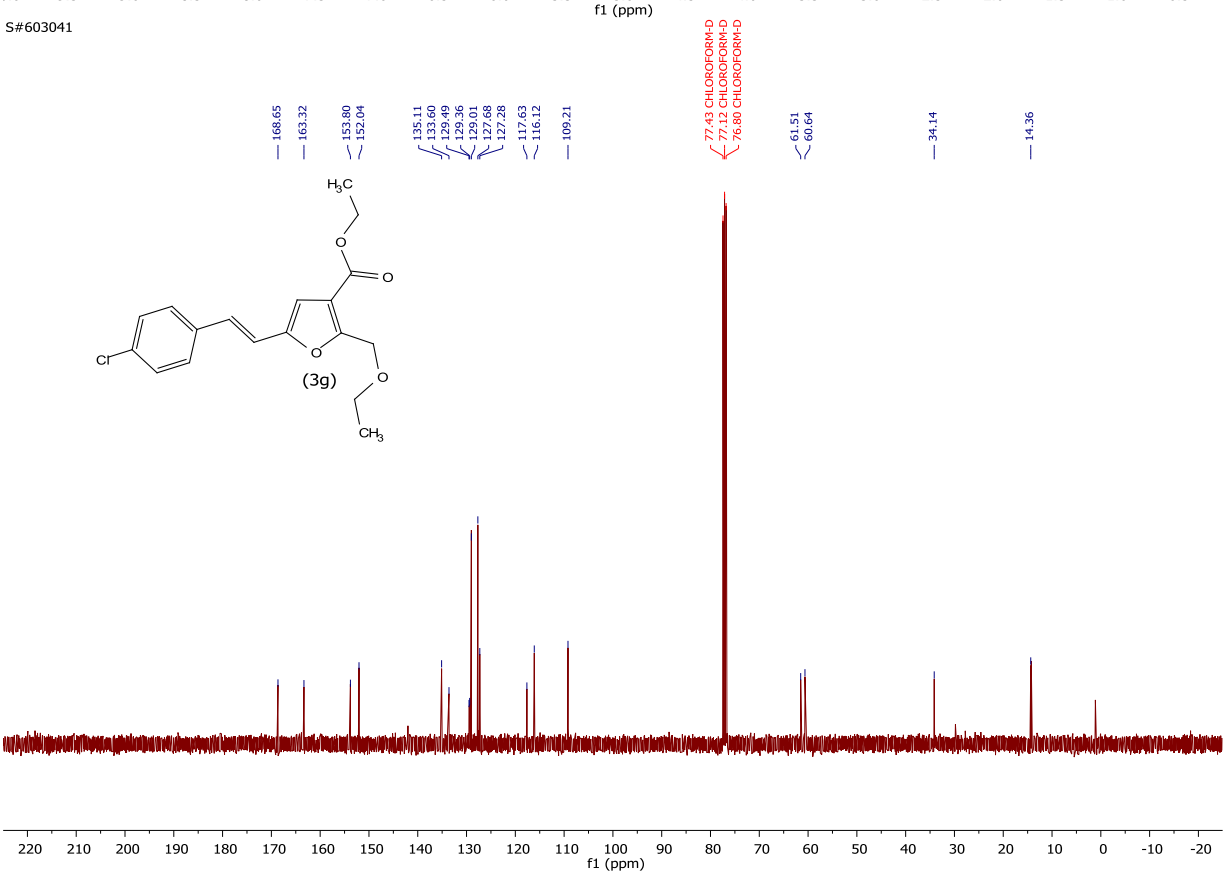
f1 (ppm)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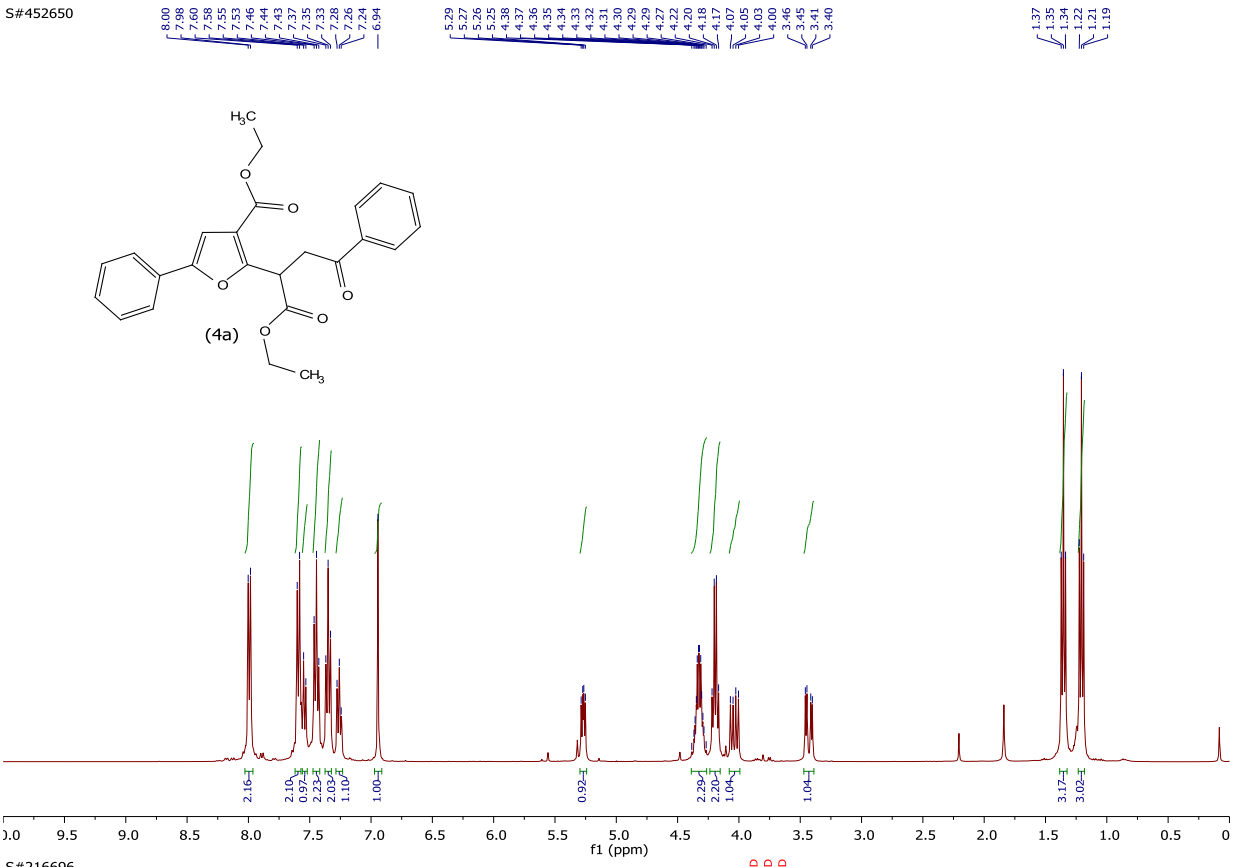
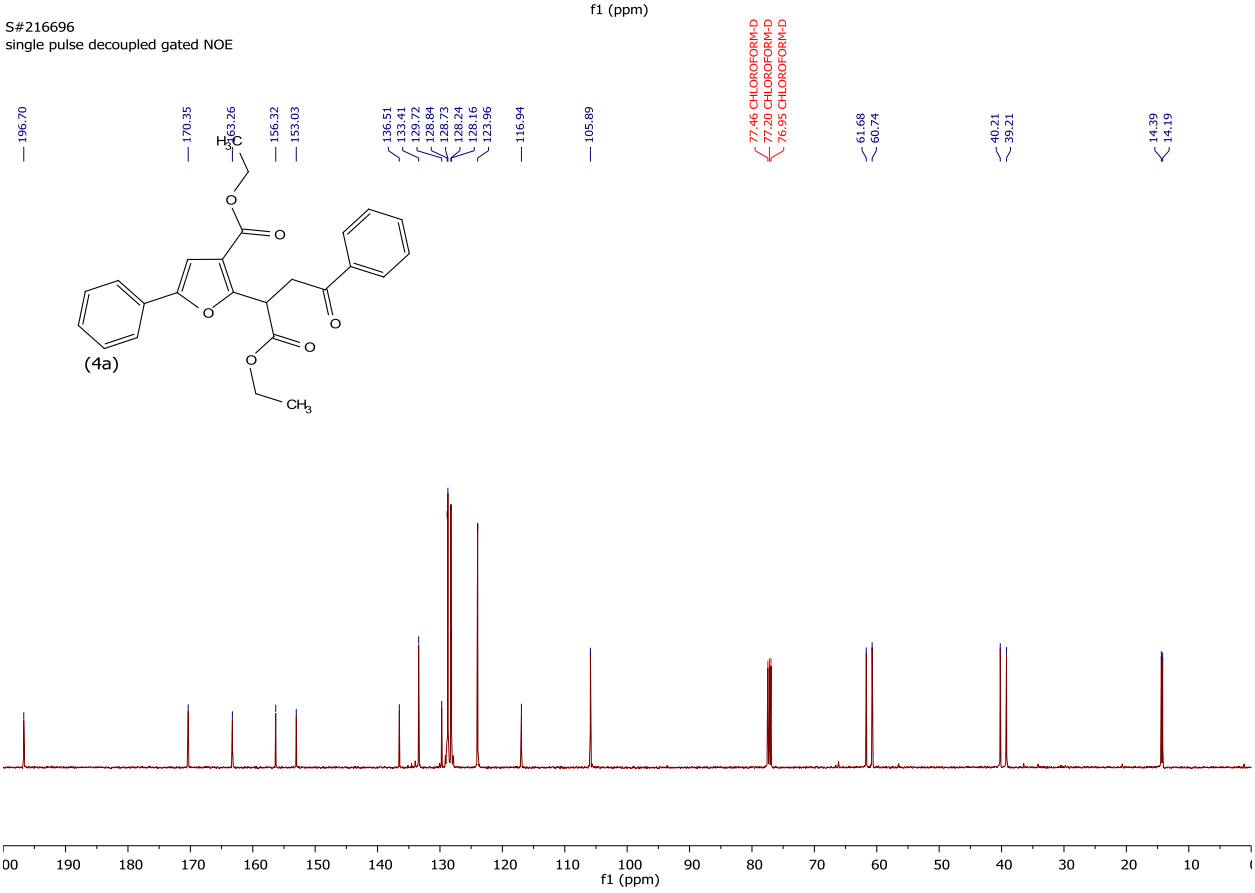
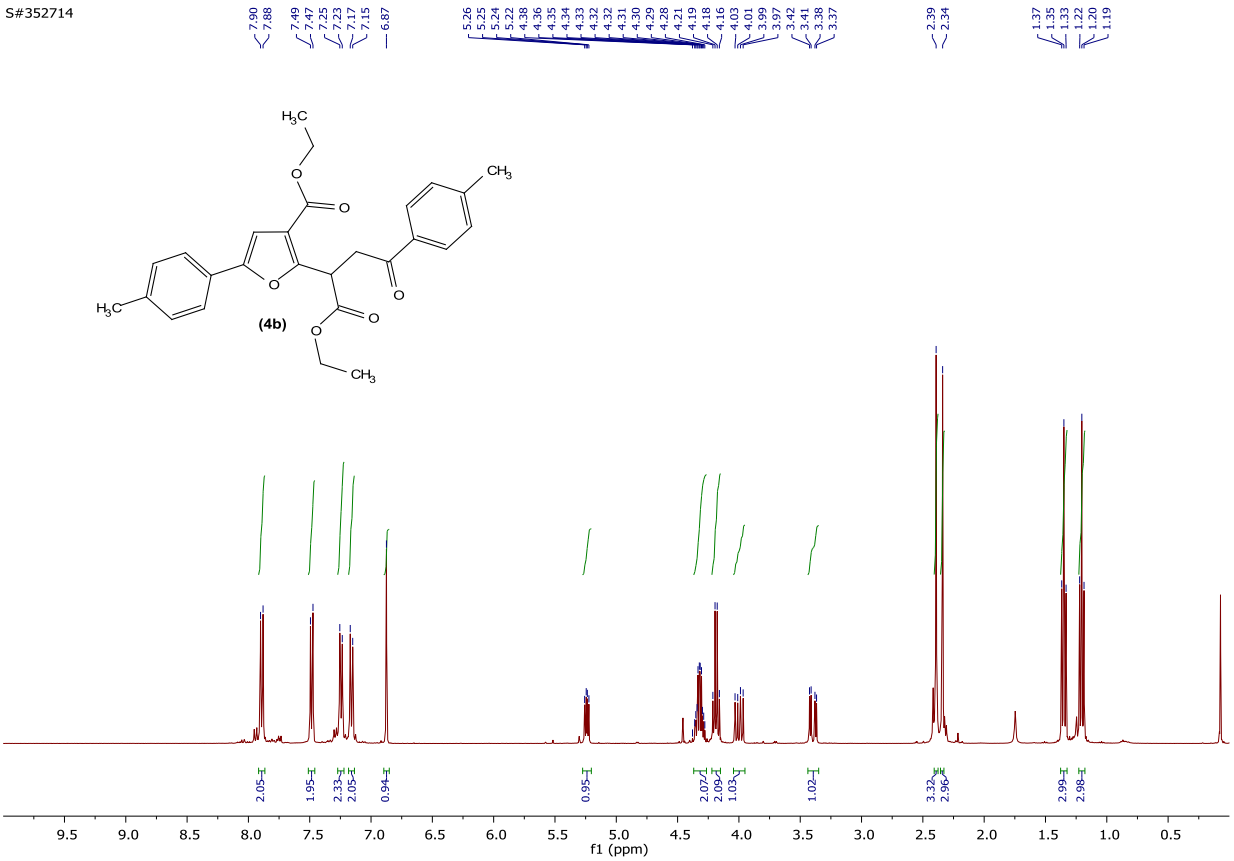
S#452650



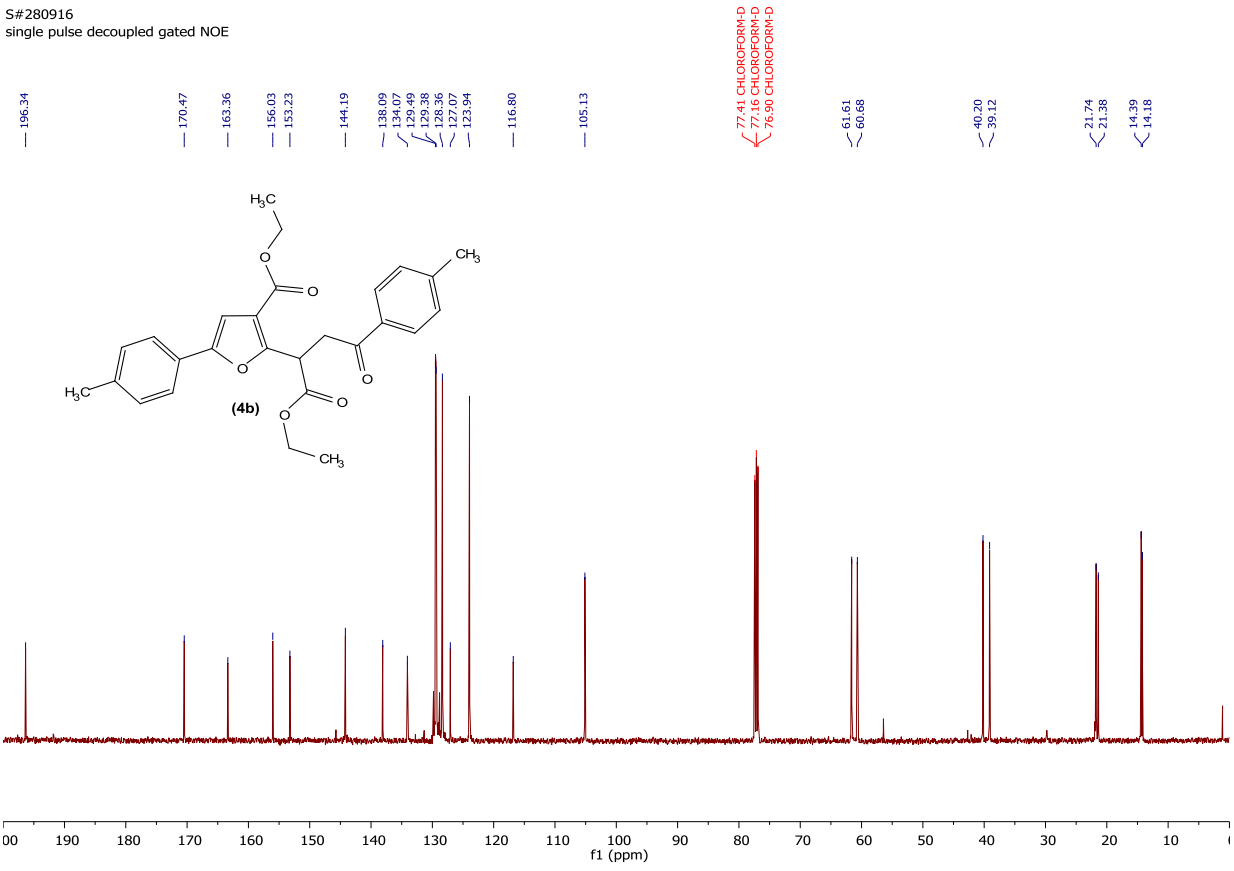
S#216696
single pulse decoupled gated NOE

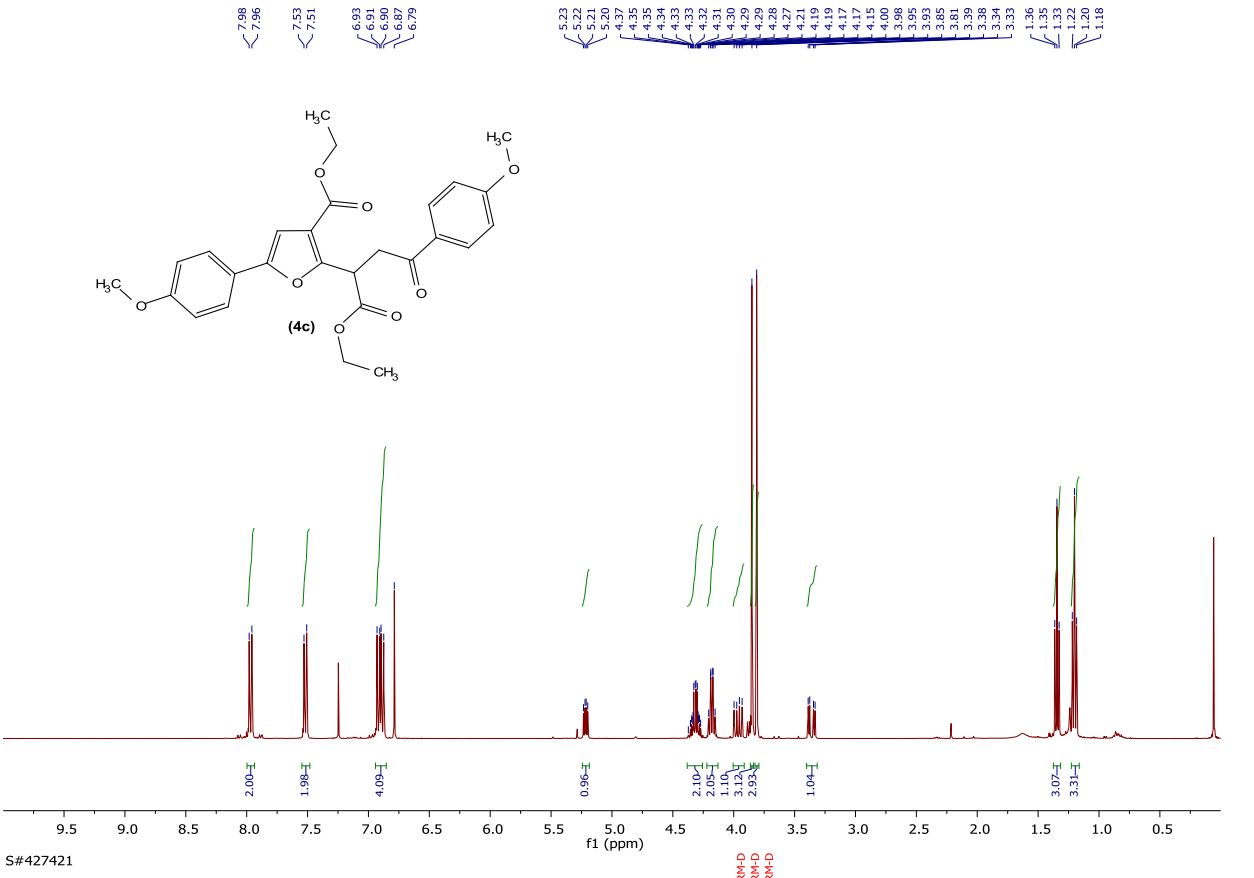


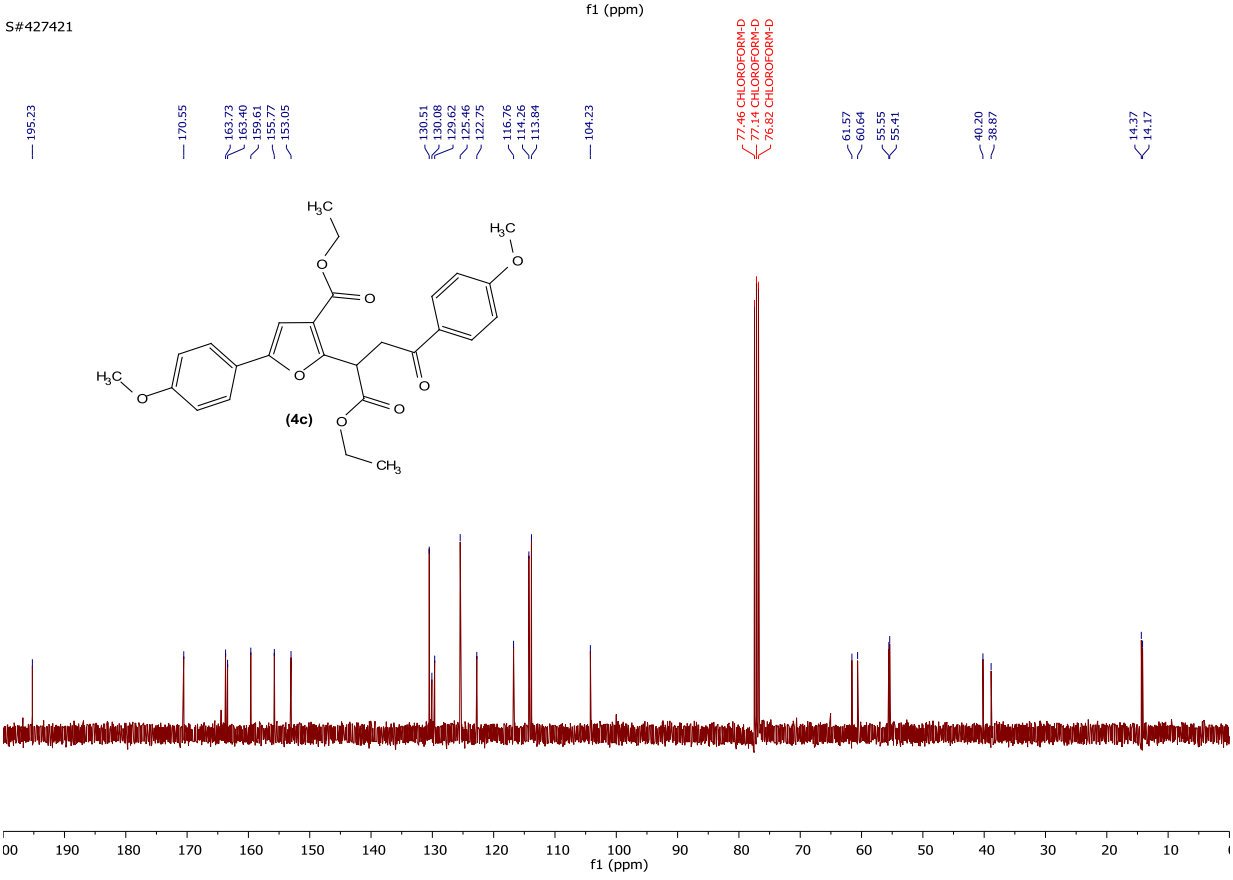
S#352714



S#280916
single pulse decoupled gated NOE




7.98
7.96
7.53
7.51
6.93
6.91
6.90
6.87
6.79
5.23
5.22
5.21
5.20
4.37
4.35
4.35
4.34
4.33
4.33
4.32
4.31
4.30
4.29
4.29
4.28
4.27
4.21
4.19
4.19
4.17
4.17
4.15
4.00
3.98
3.95
3.93
3.85
3.81
3.39
3.38
3.34
3.33
1.36
1.35
1.33
1.22
1.20
1.18
(4c)
2.00
1.98
4.09
0.96
2.10
2.05
1.10
3.12
2.93
1.04
3.07
3.31
f1 (ppm)


S#427421
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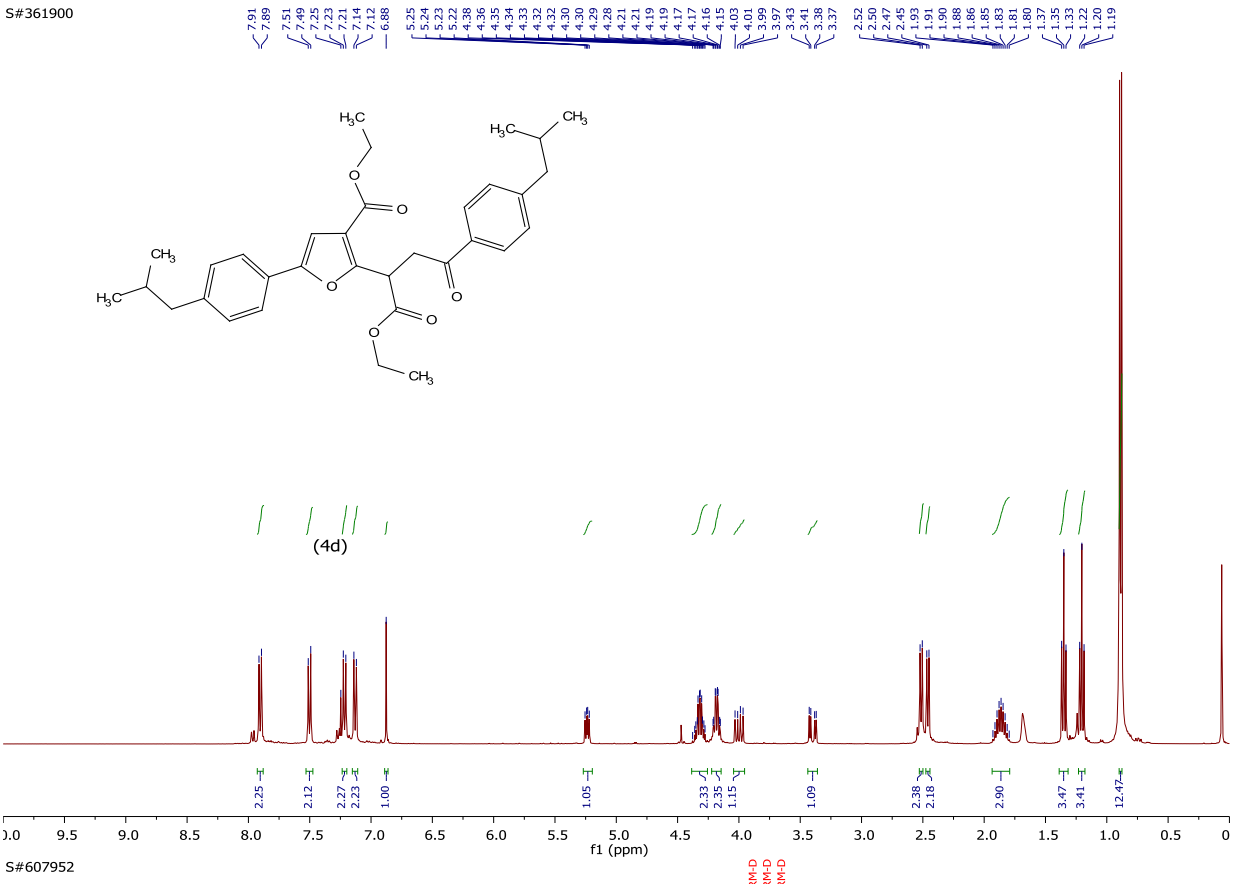
170.55
163.73
163.40
159.61
155.77
153.05
130.51
130.08
129.62
125.46
122.75
116.76
114.26
113.84
104.23
77.46 CHLOROFORM-D
77.14 CHLOROFORM-D
76.82 CHLOROFORM-D
61.57
60.64
55.55
55.41
40.20
38.87
14.37
14.17
(4c)
f1 (ppm)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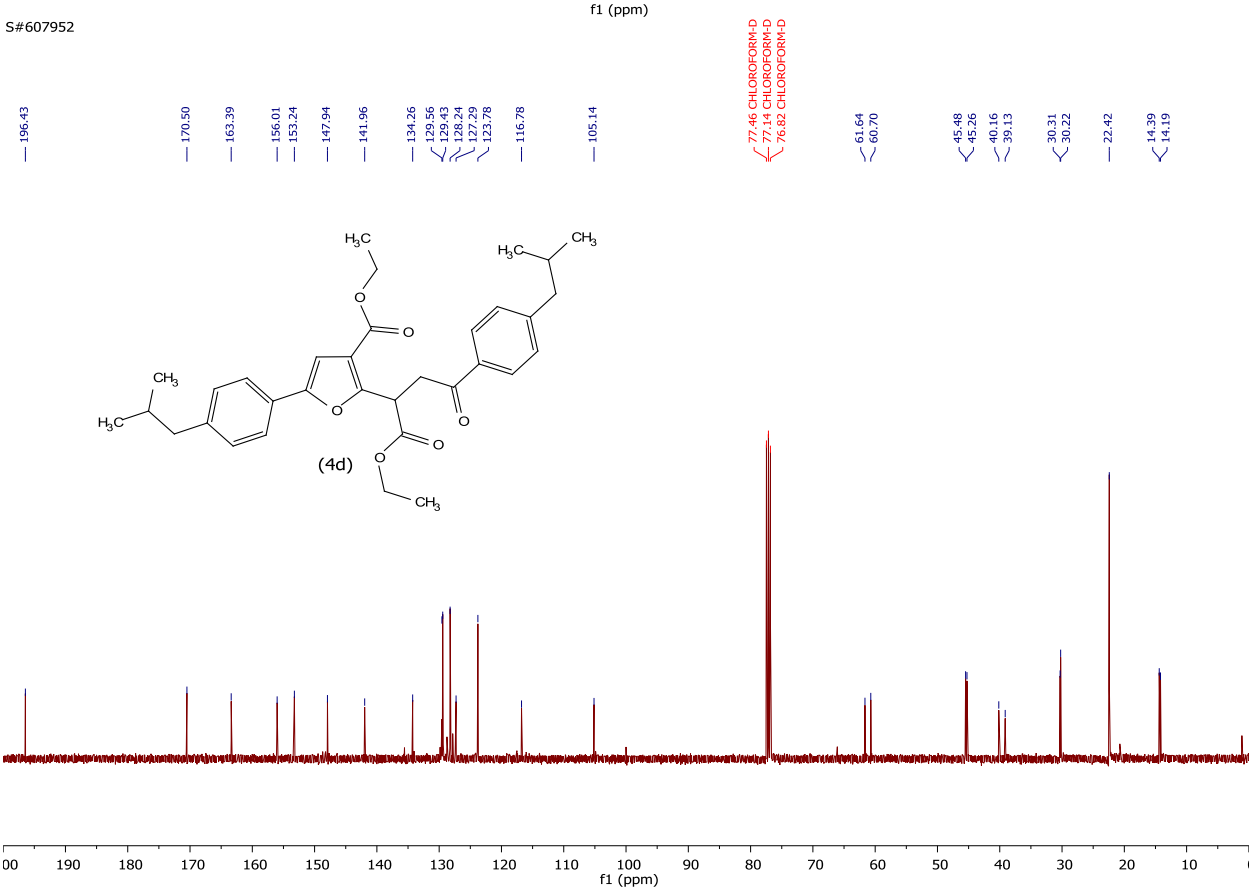
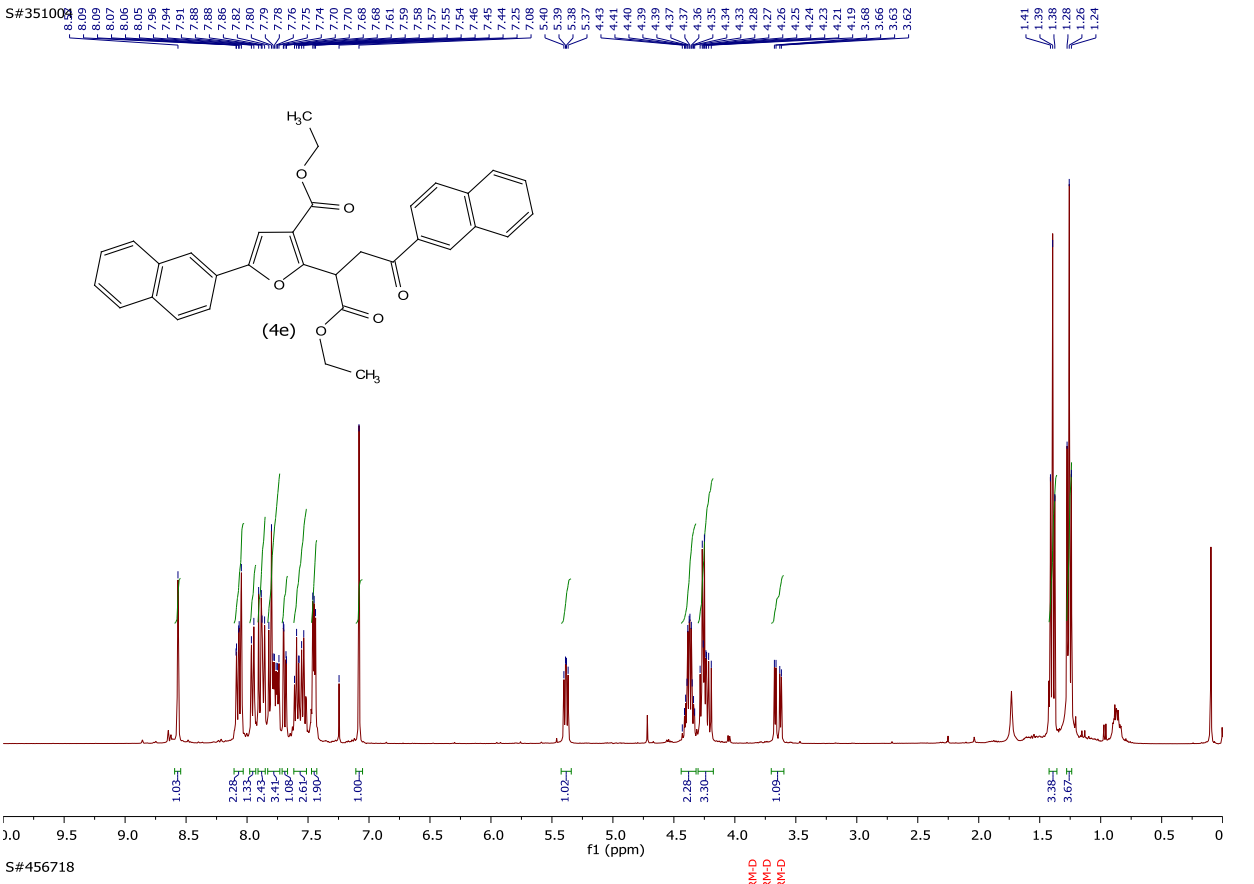
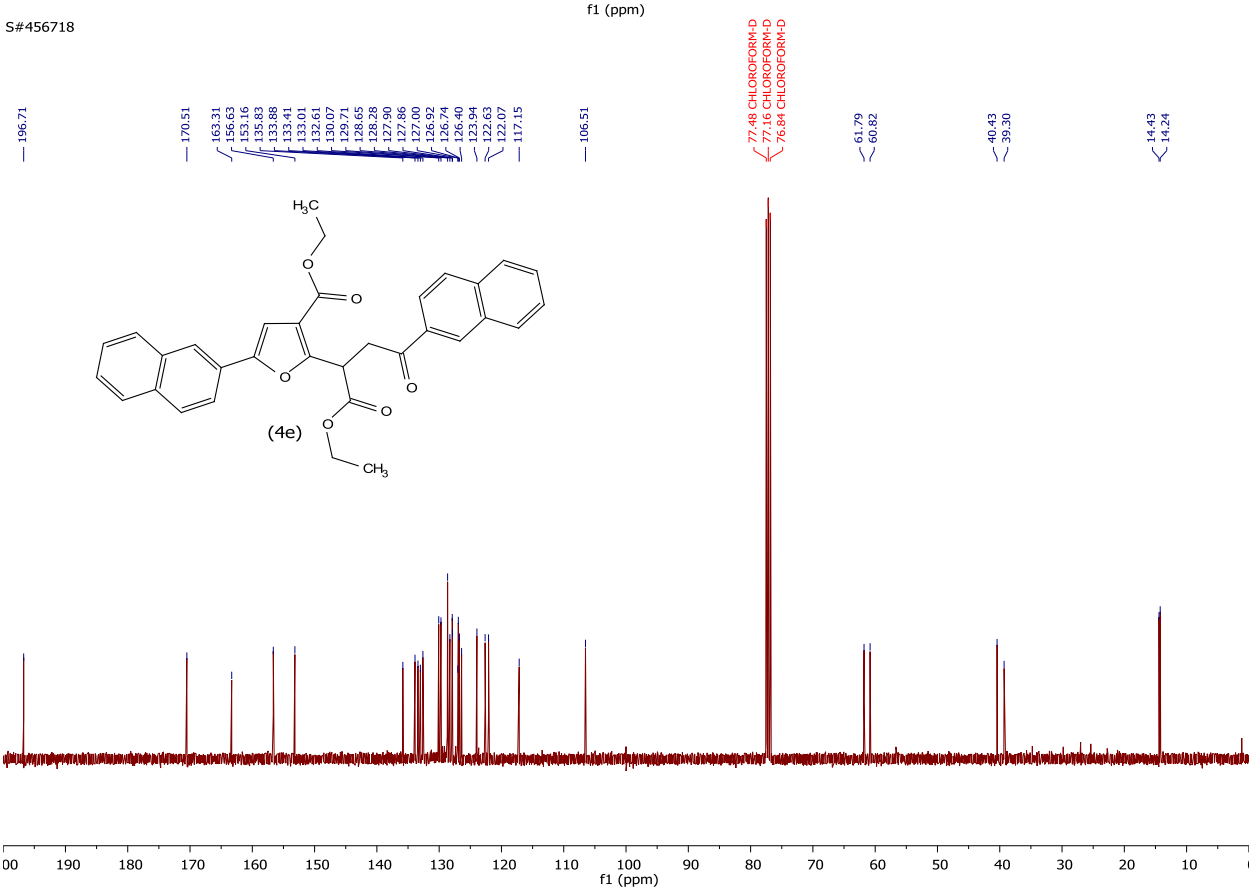
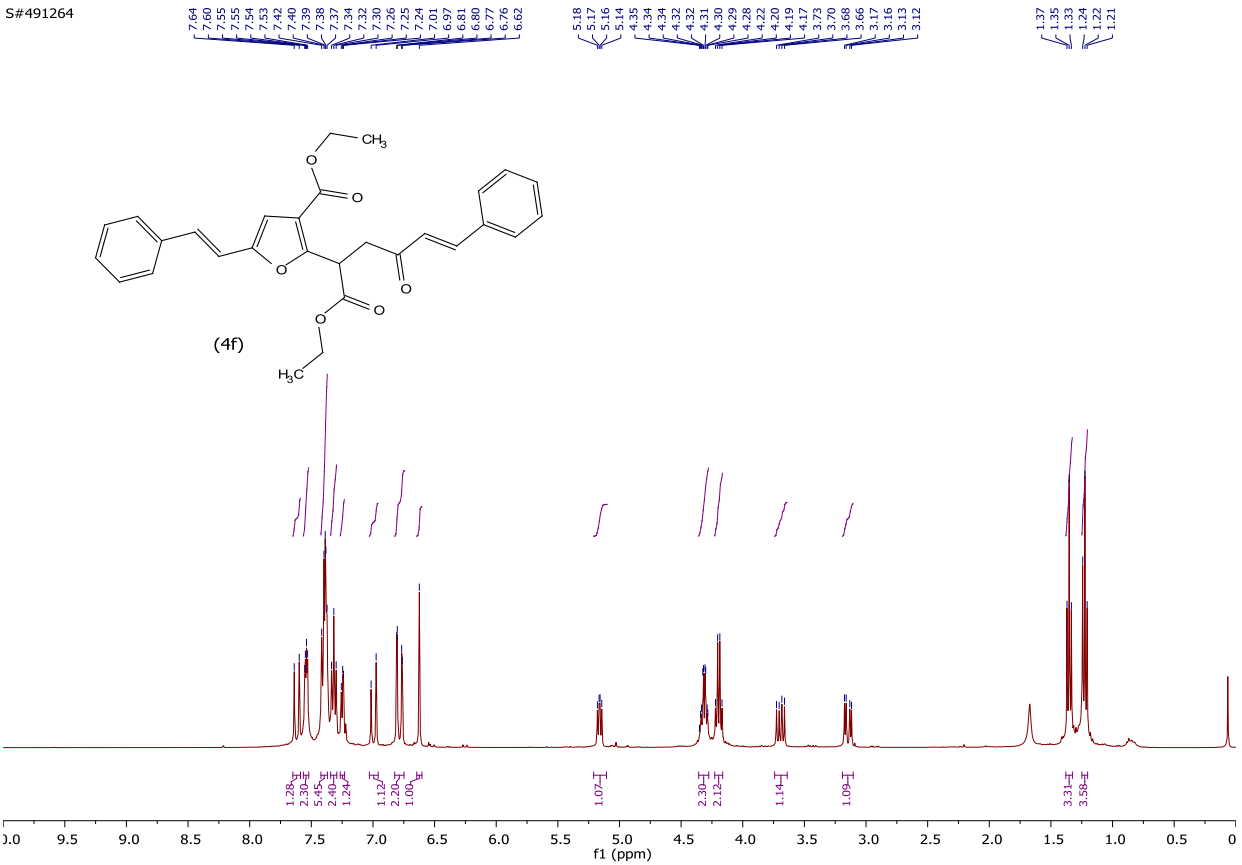
(4d)
f1 (ppm)


S#607952
(4d)
f1 (ppm)

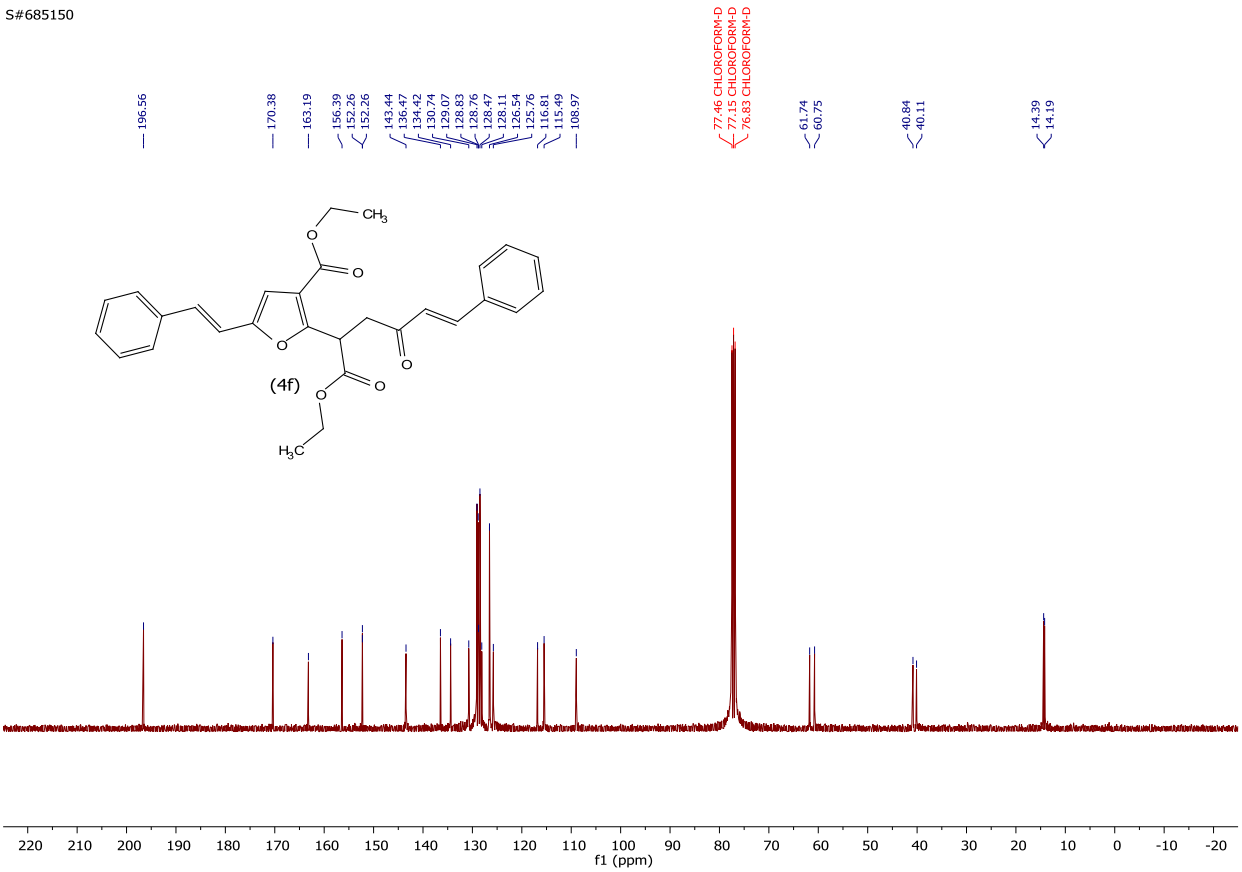

S#351008
(4e)
f1 (ppm)


S#456718
77.48 CHLOROFORM-D
77.16 CHLOROFORM-D
76.84 CHLOROFORM-D
(4e)
f1 (ppm)

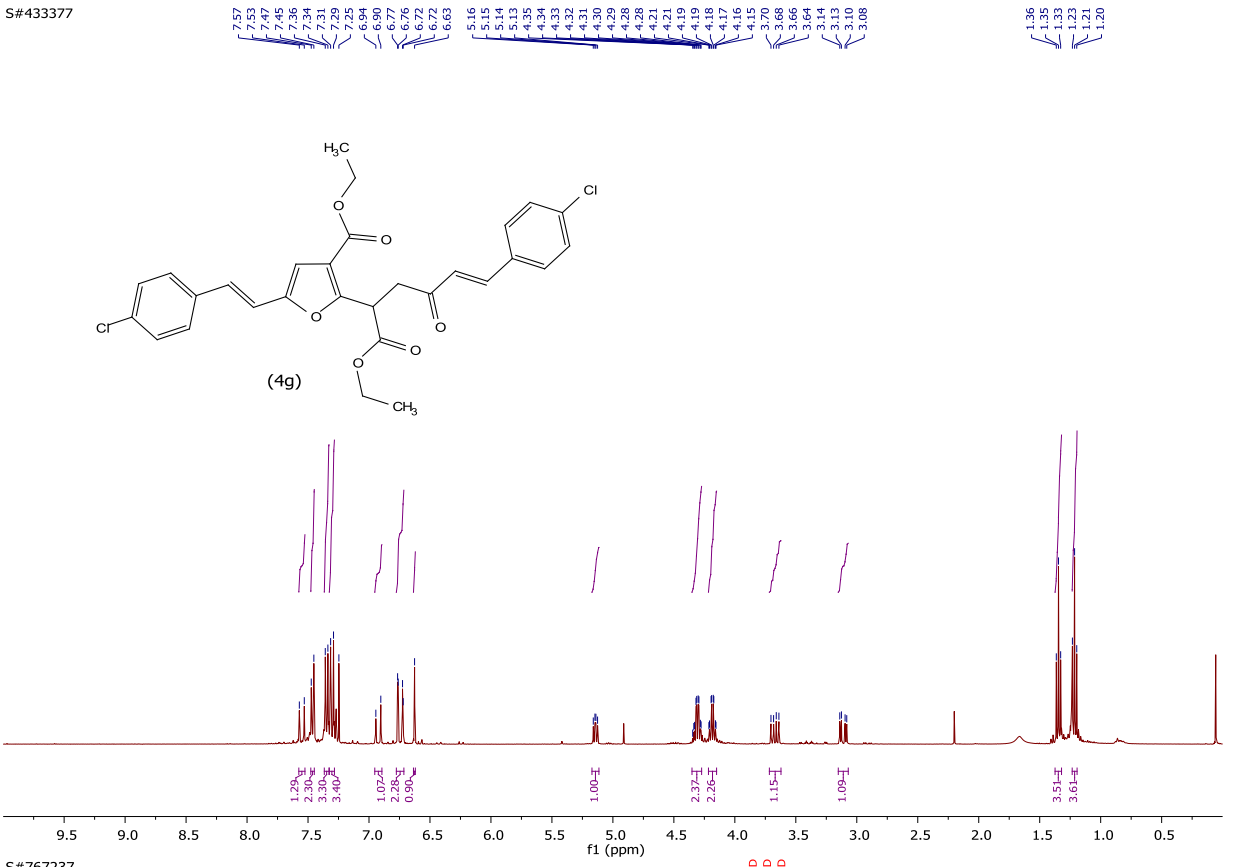
S#491264



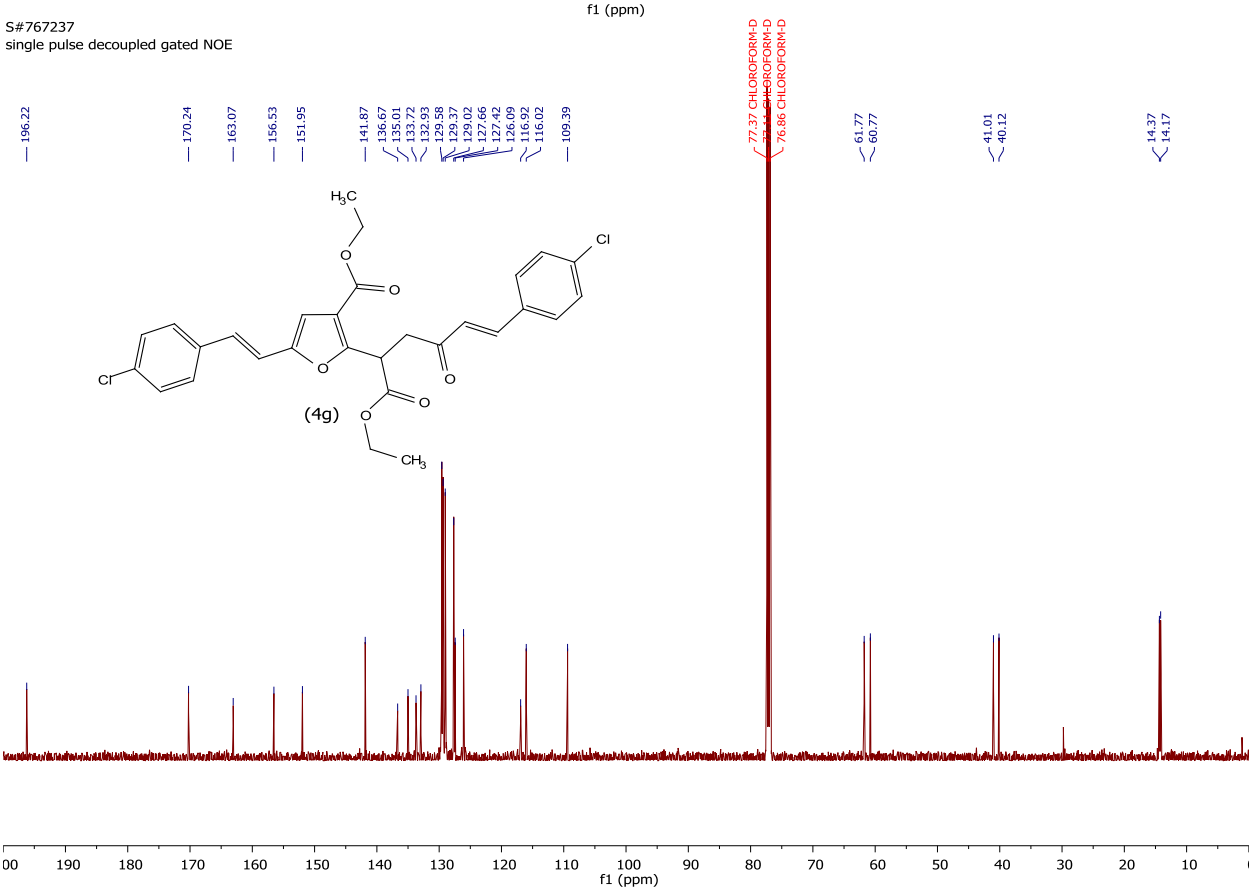
S#685150



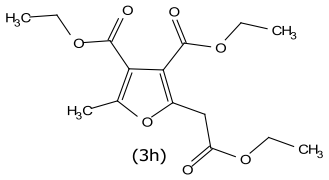
S#433377



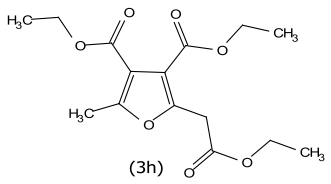
S#767237
single pulse decoupled gated NOE



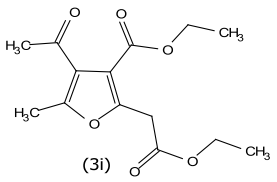
S#471370



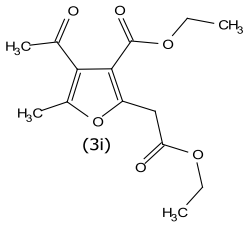
S#605750



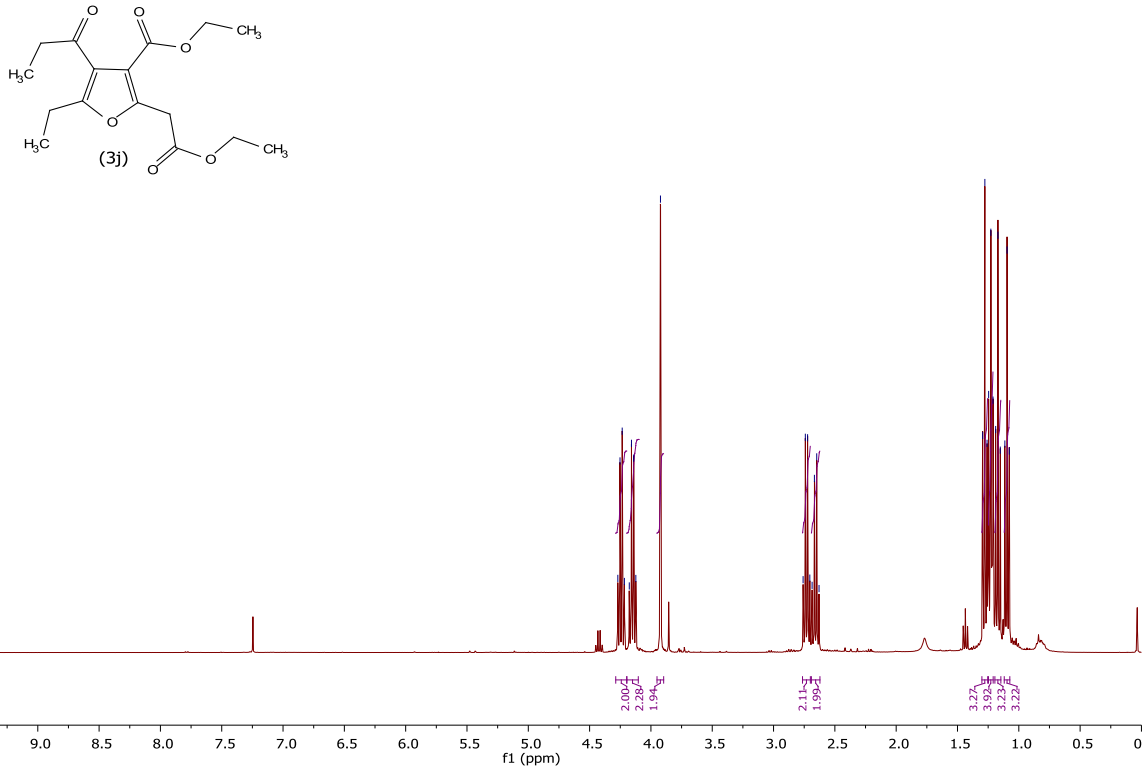
S#417287



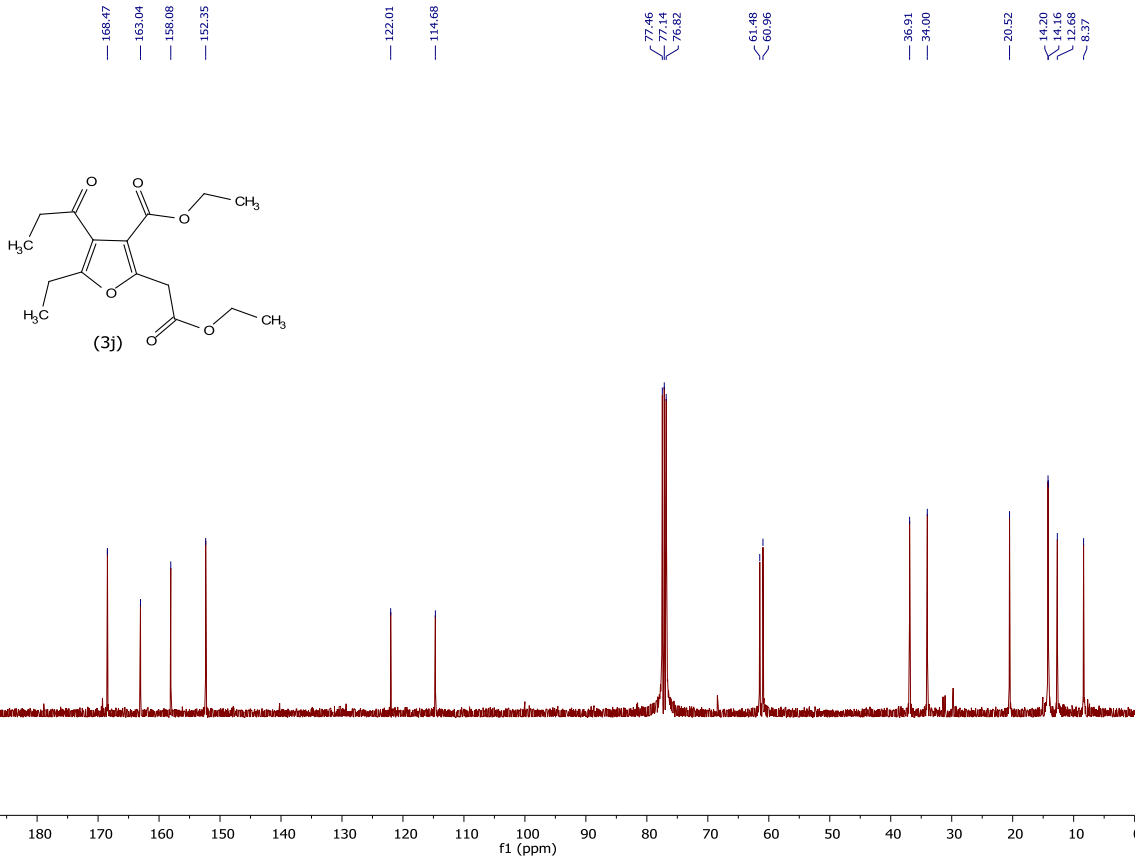
S#441779



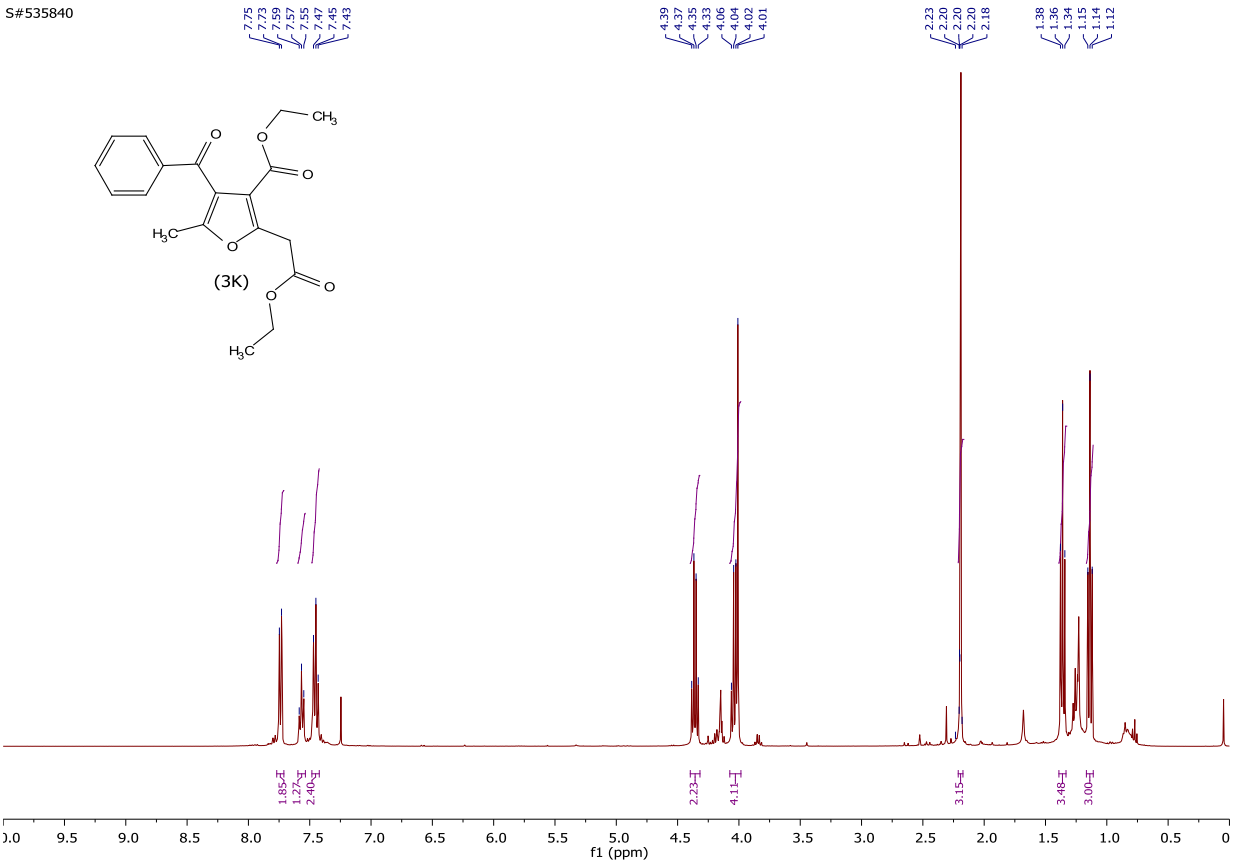
S#437874



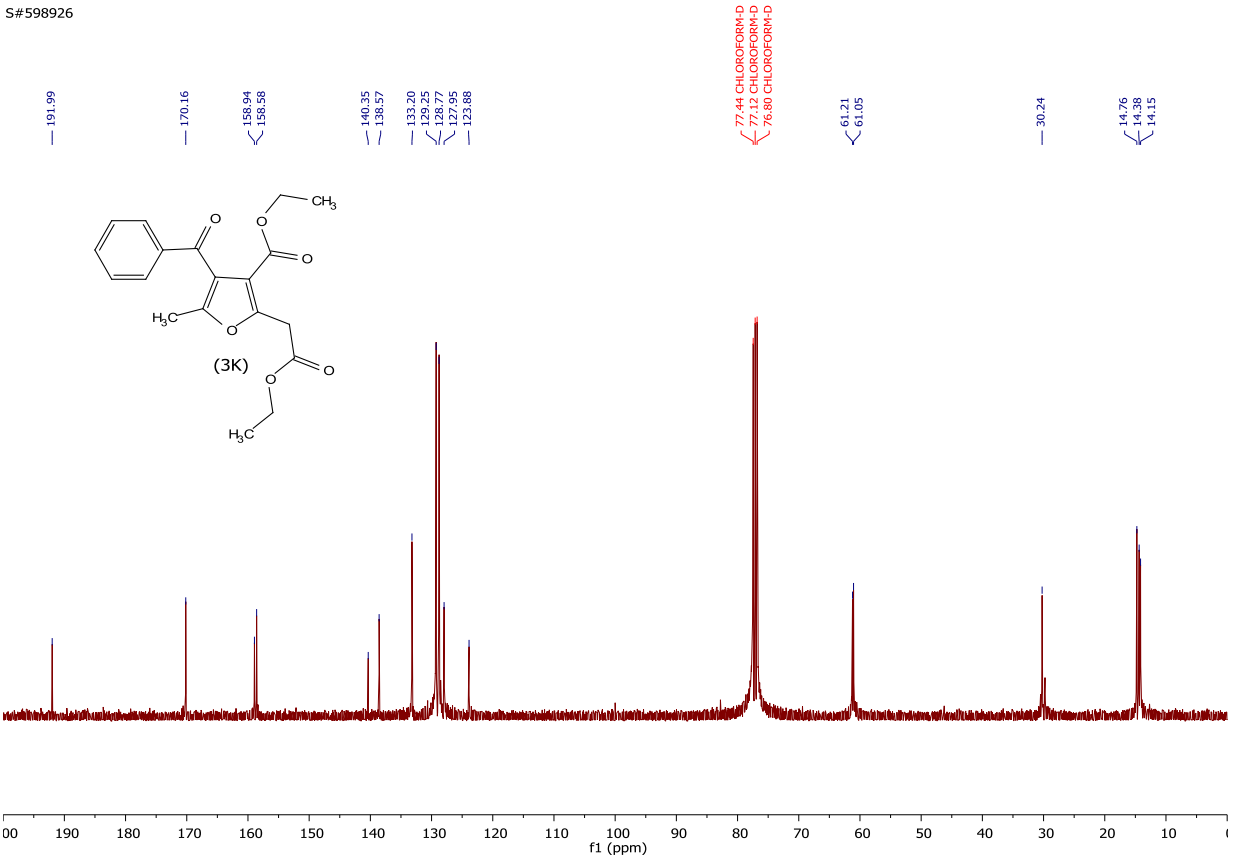
S#603663



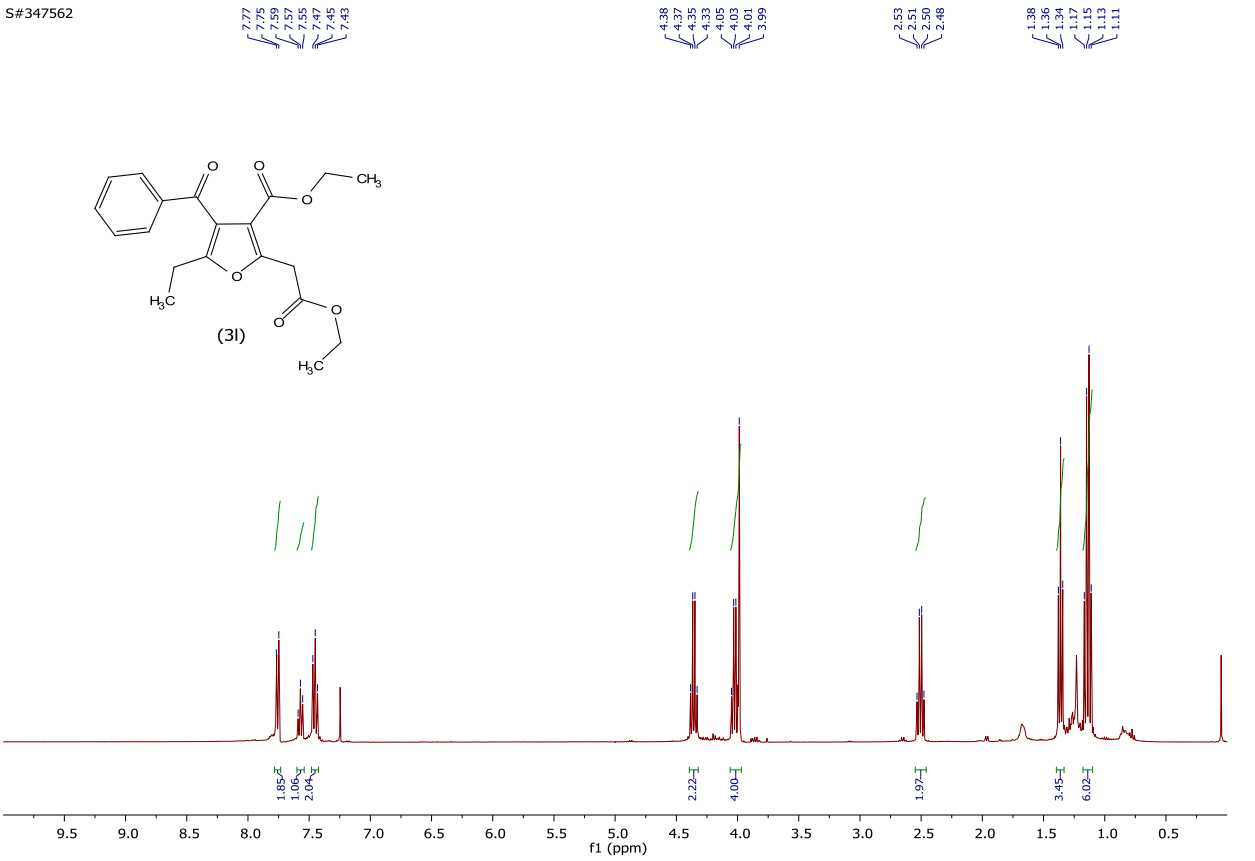
S#535840



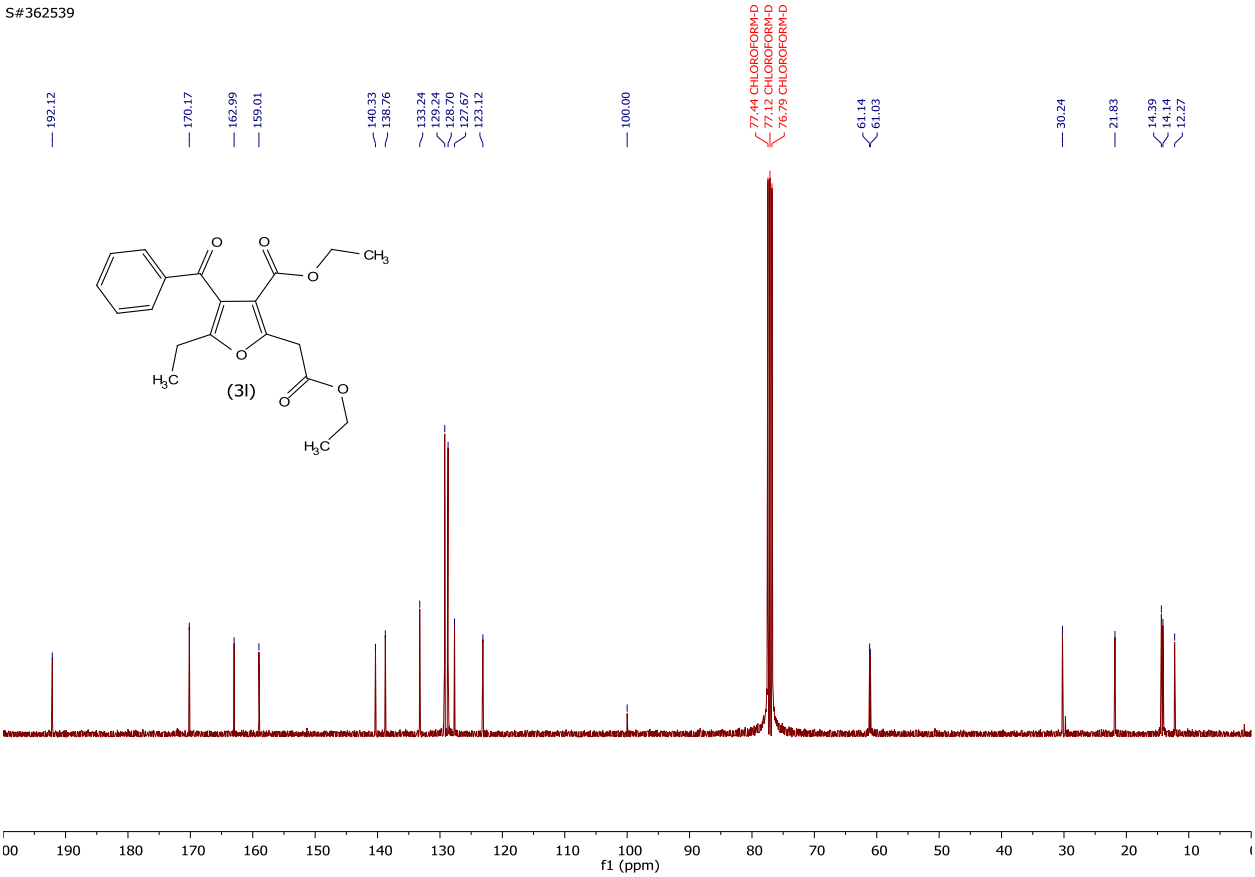
S#598926

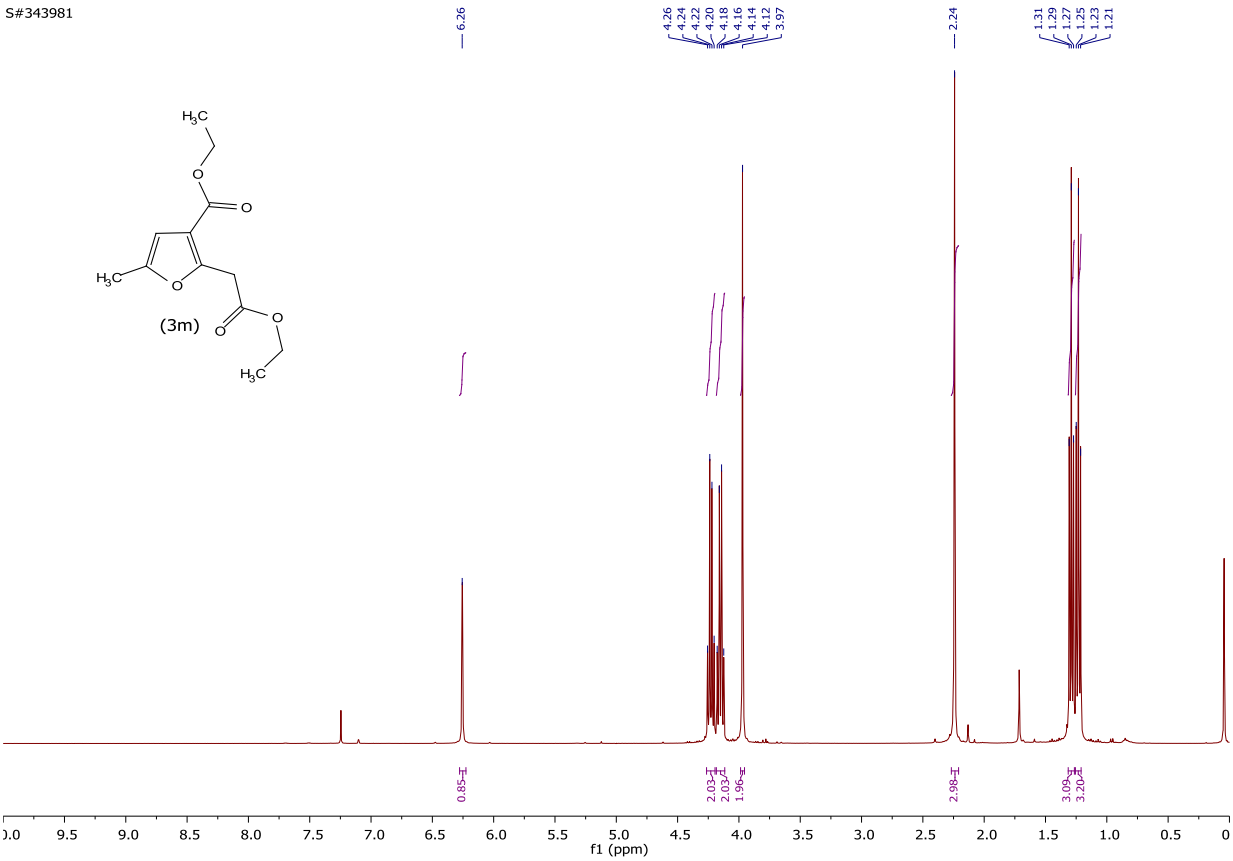


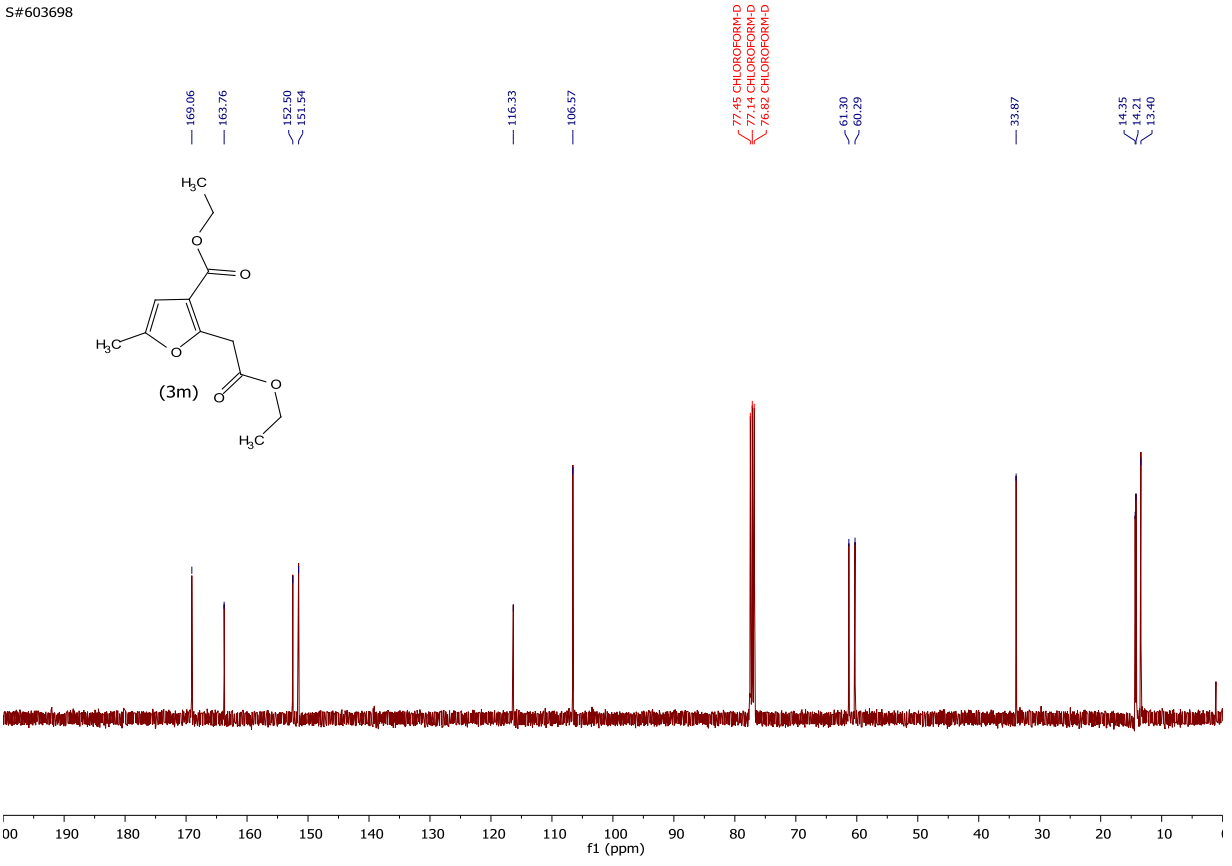
S#347562



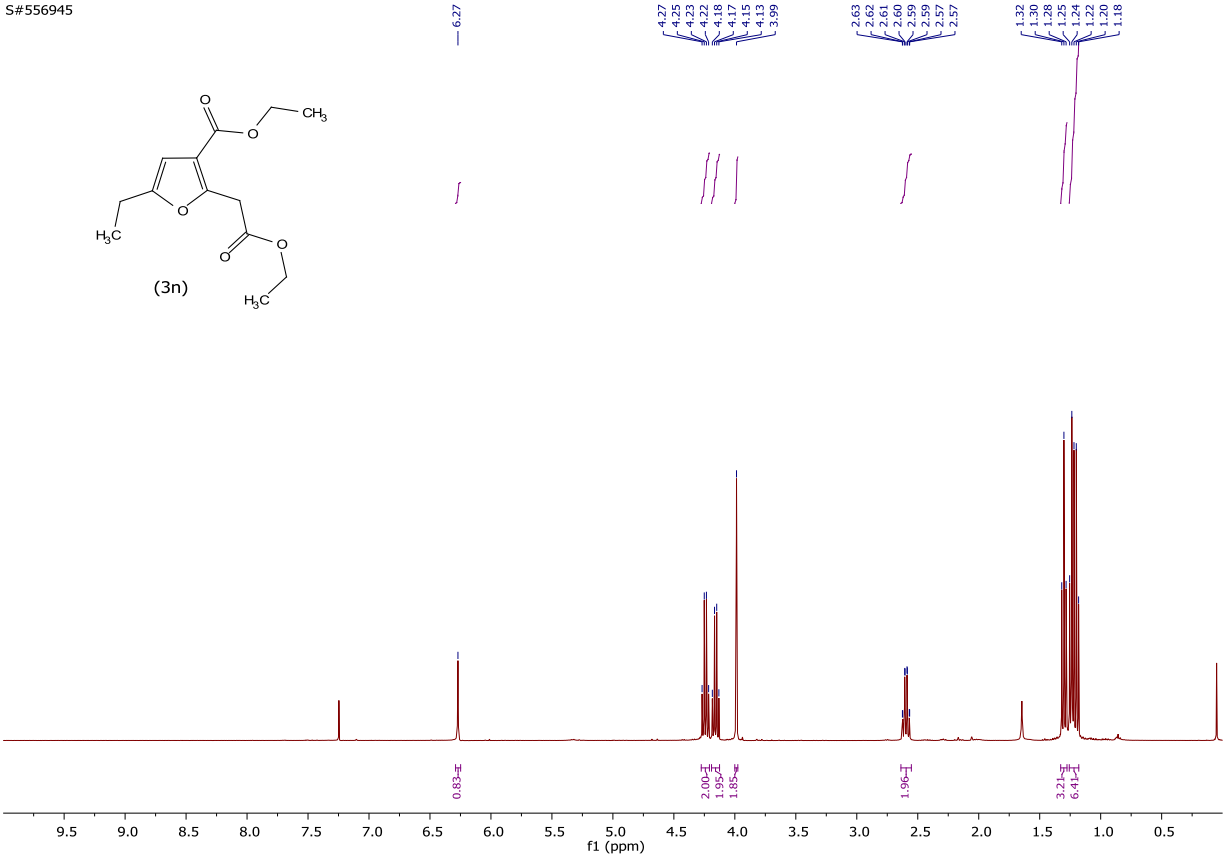
S#362539



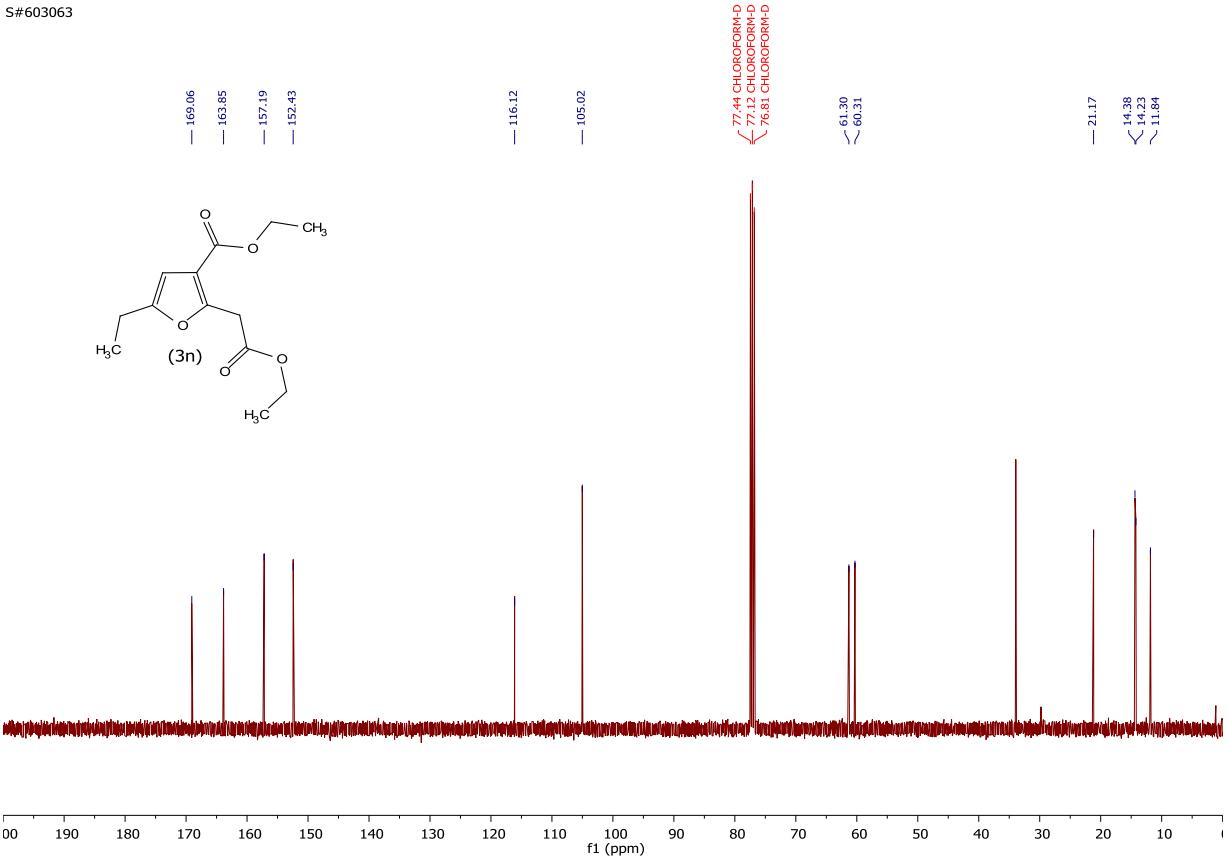

S#343981
6.26
4.26
4.24
4.22
4.20
4.18
4.16
4.14
4.12
3.97
2.24
1.31
1.29
1.27
1.25
1.23
1.21
(3m)
0.85
2.03
2.03
1.96
2.98
3.09
3.20
f1 (ppm)


S#603698
169.06
163.76
152.50
151.54
116.33
106.57
77.45 CHLOROFORM-D
77.14 CHLOROFORM-D
76.82 CHLOROFORM-D
61.30
60.29
33.87
14.35
14.21
13.40
(3m)
f1 (ppm)

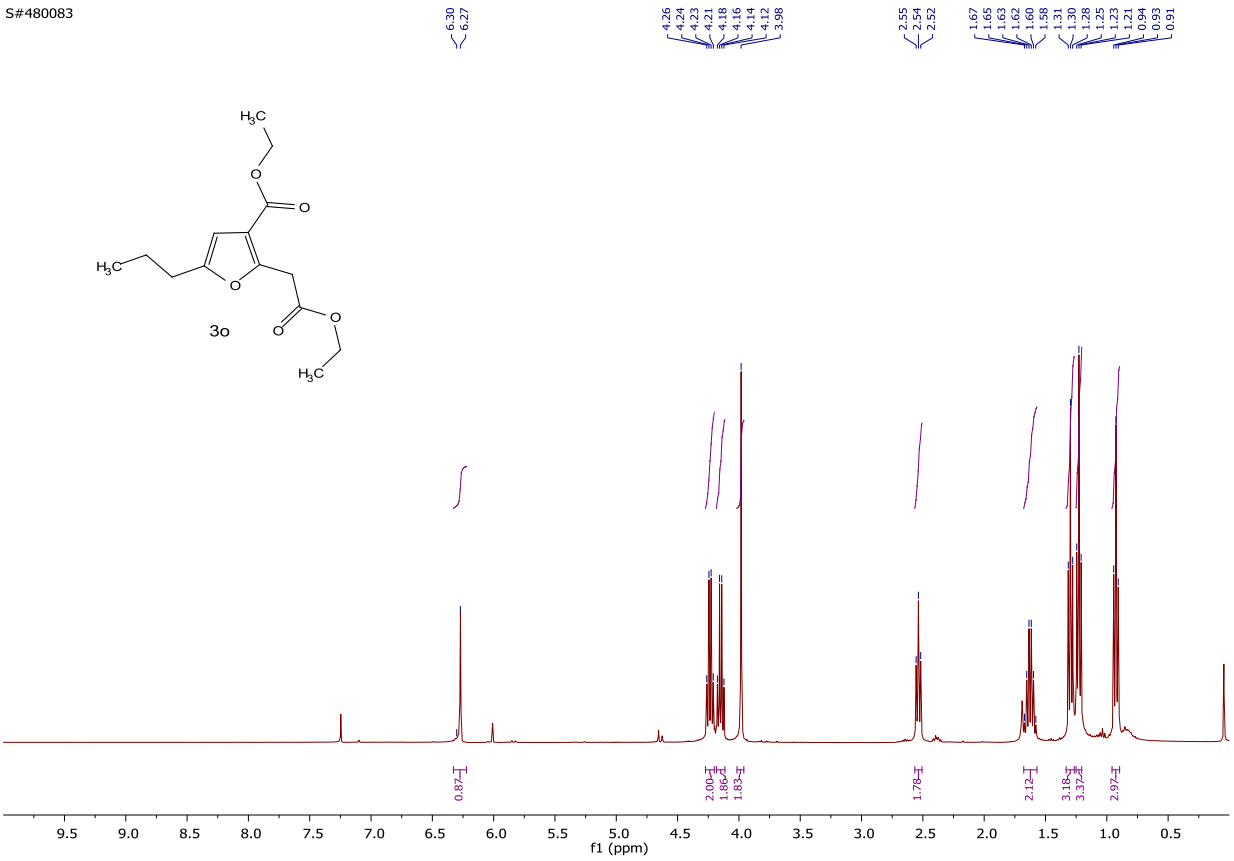
S#556945



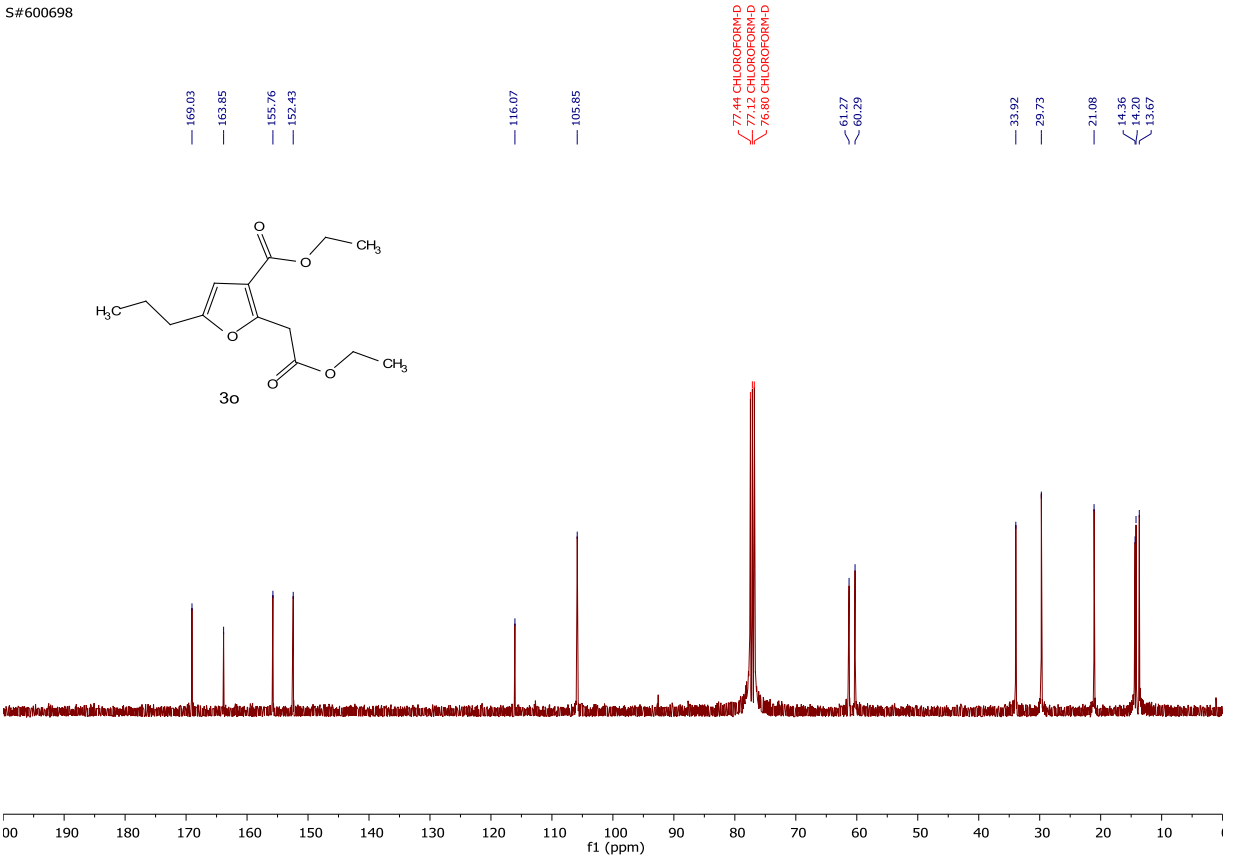
S#603063



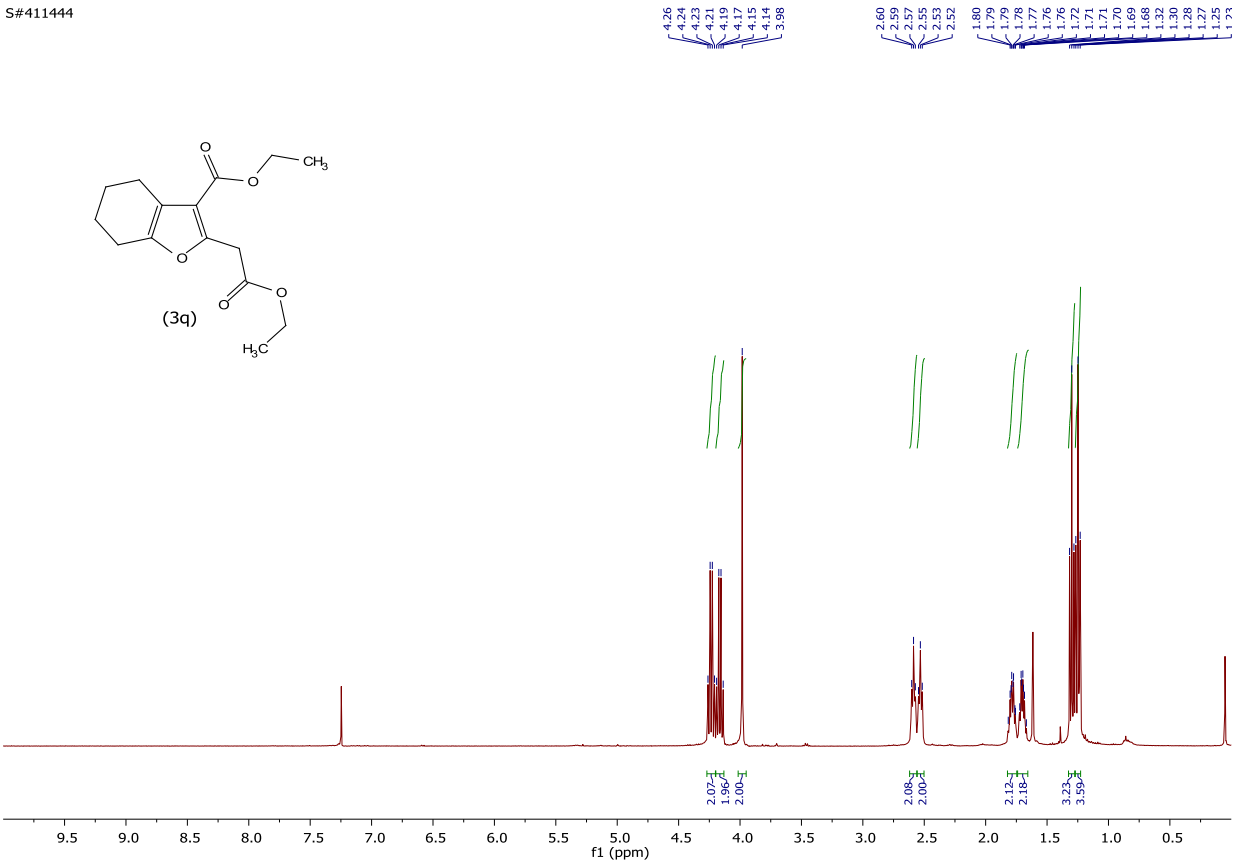
S#480083



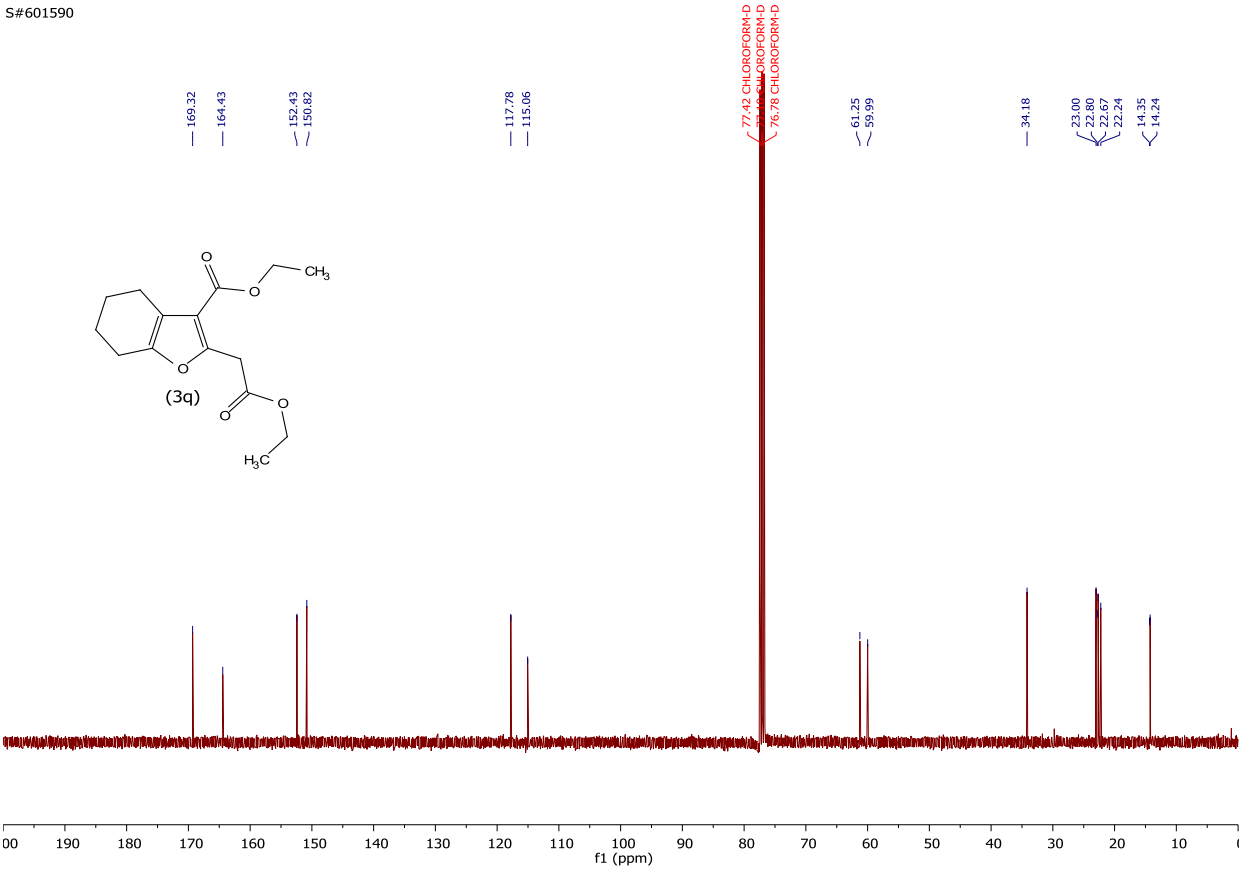
S#600698



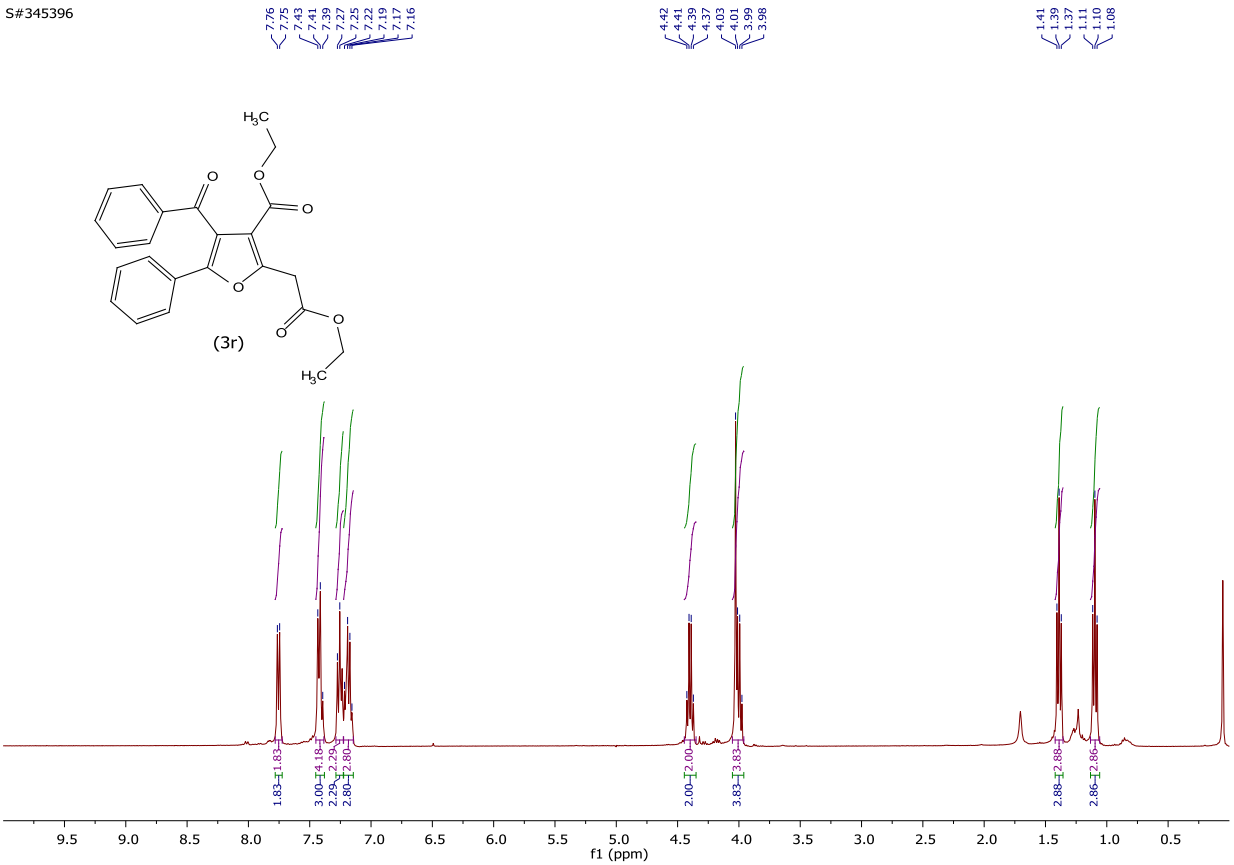
S#411444



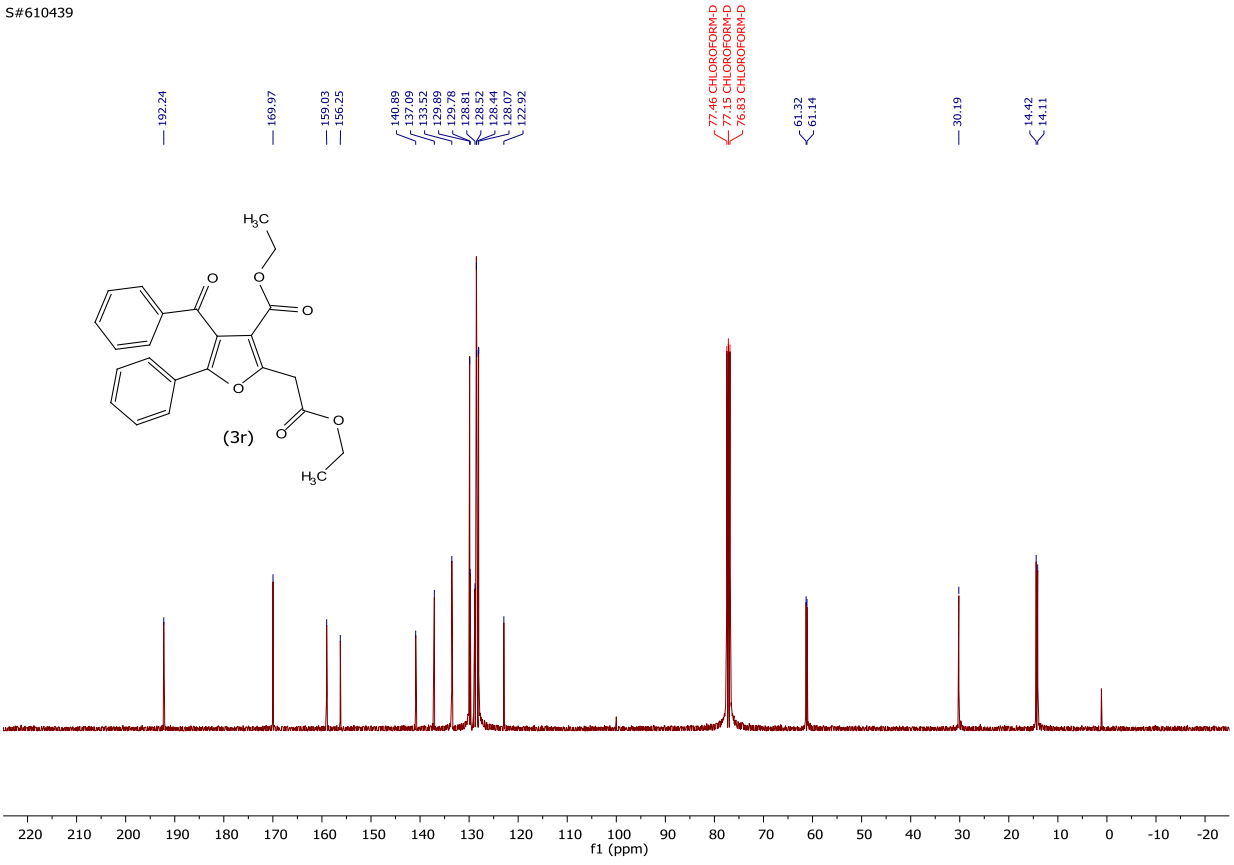
S#601590



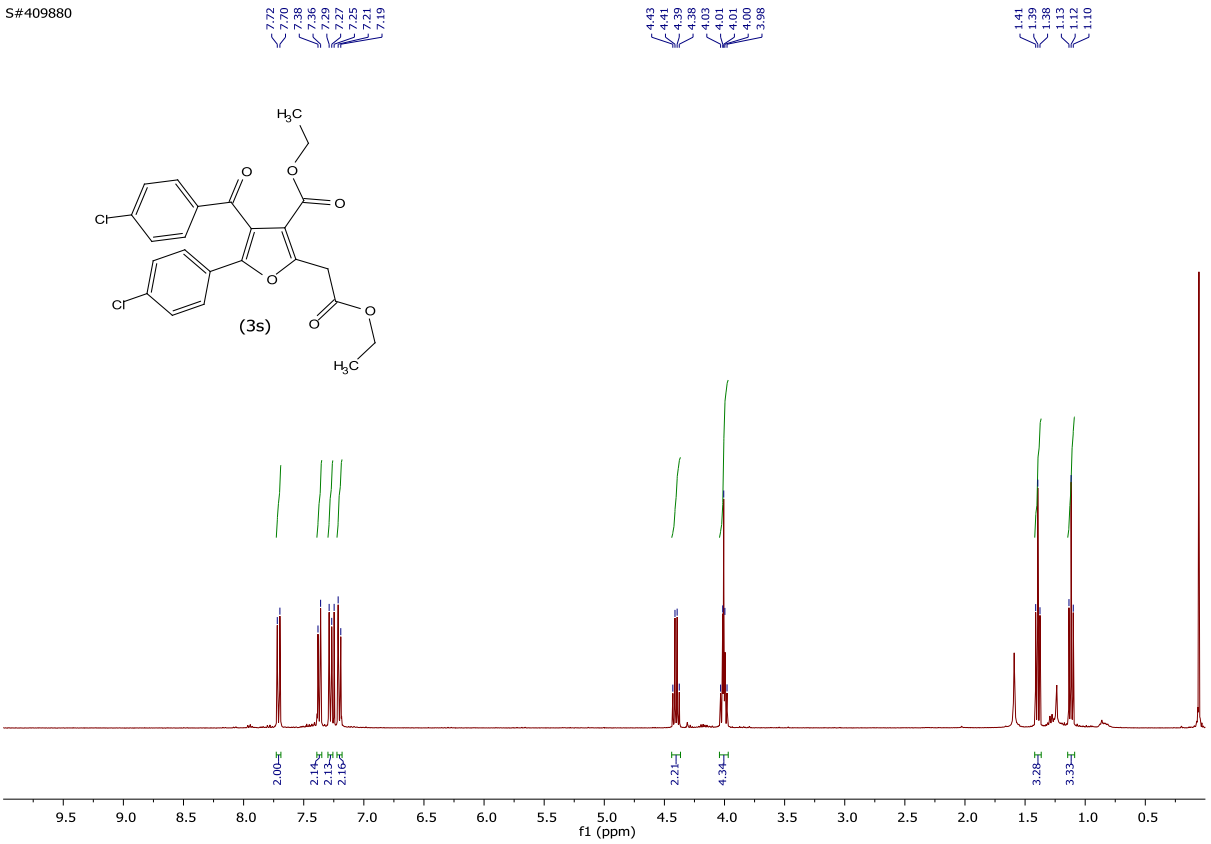
S#345396



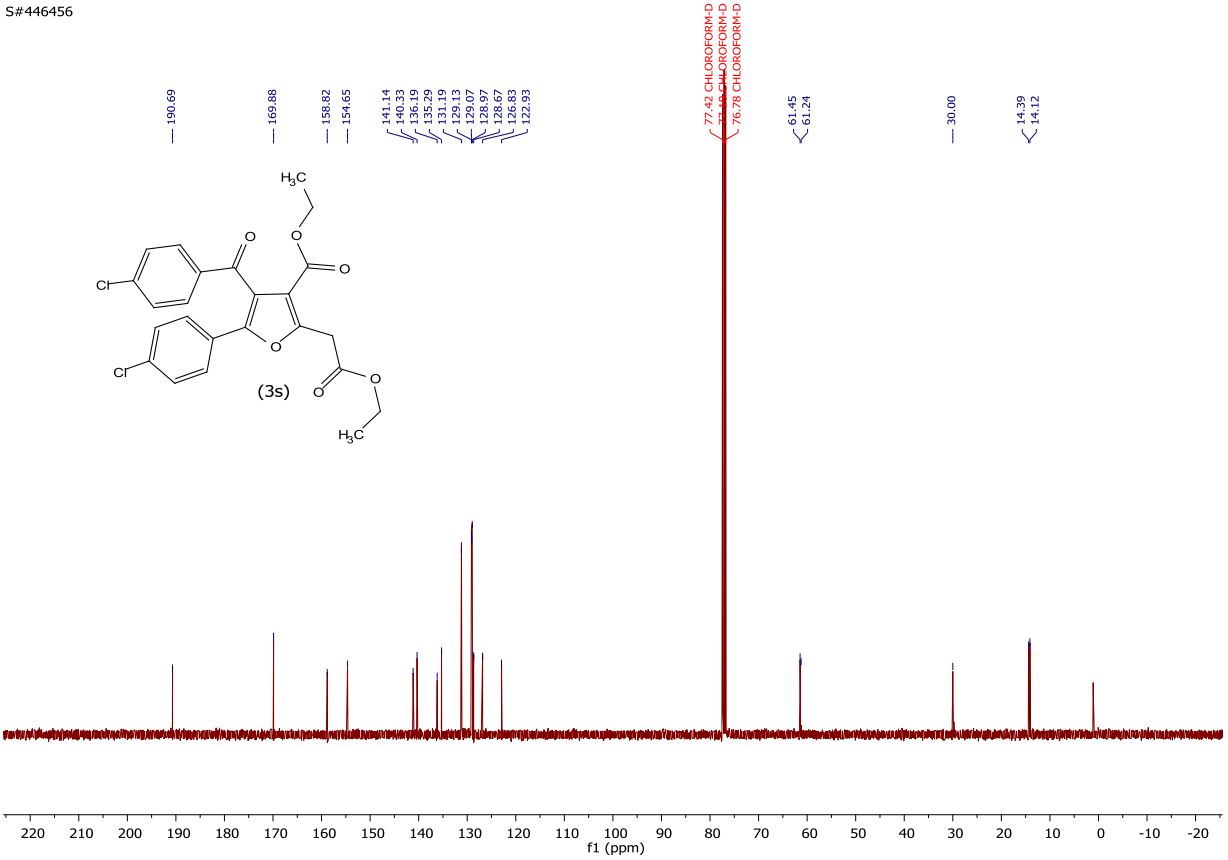
S#610439



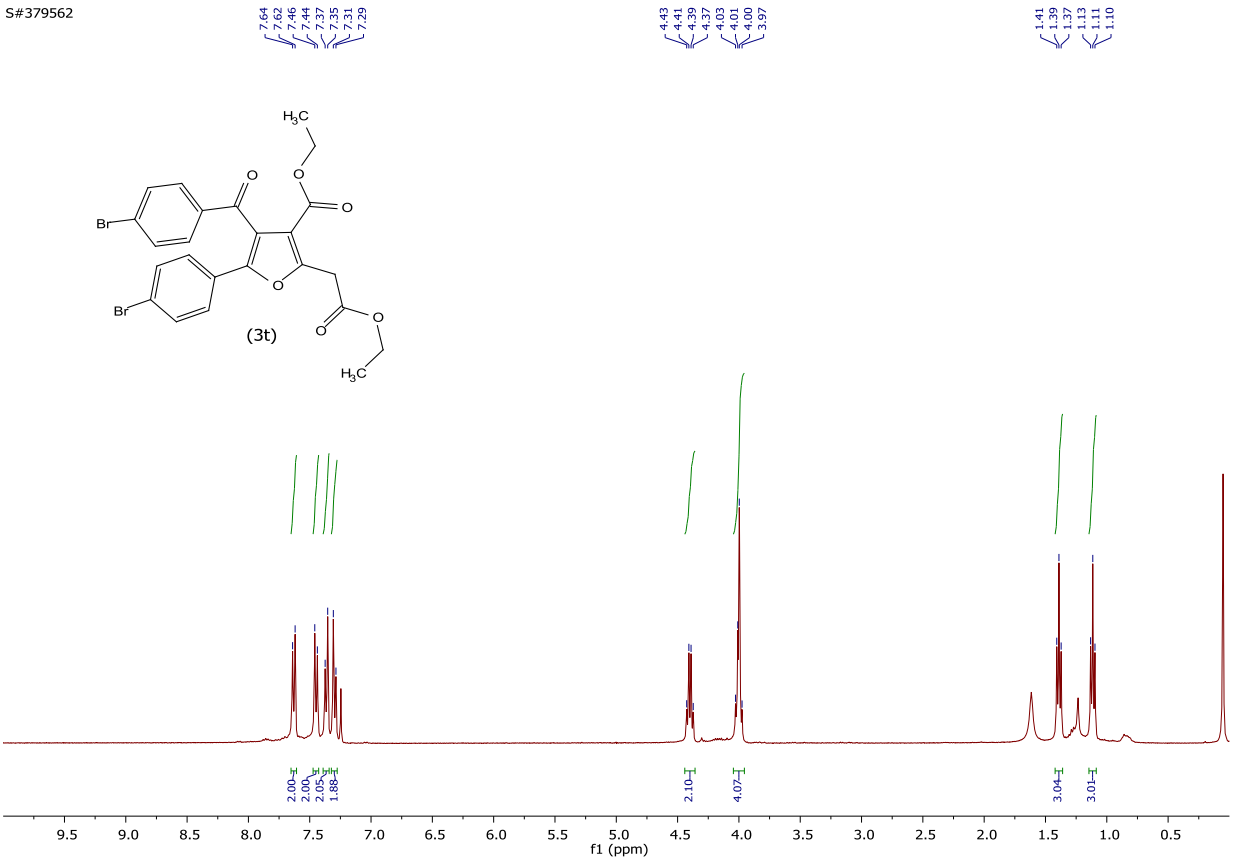
S#409880



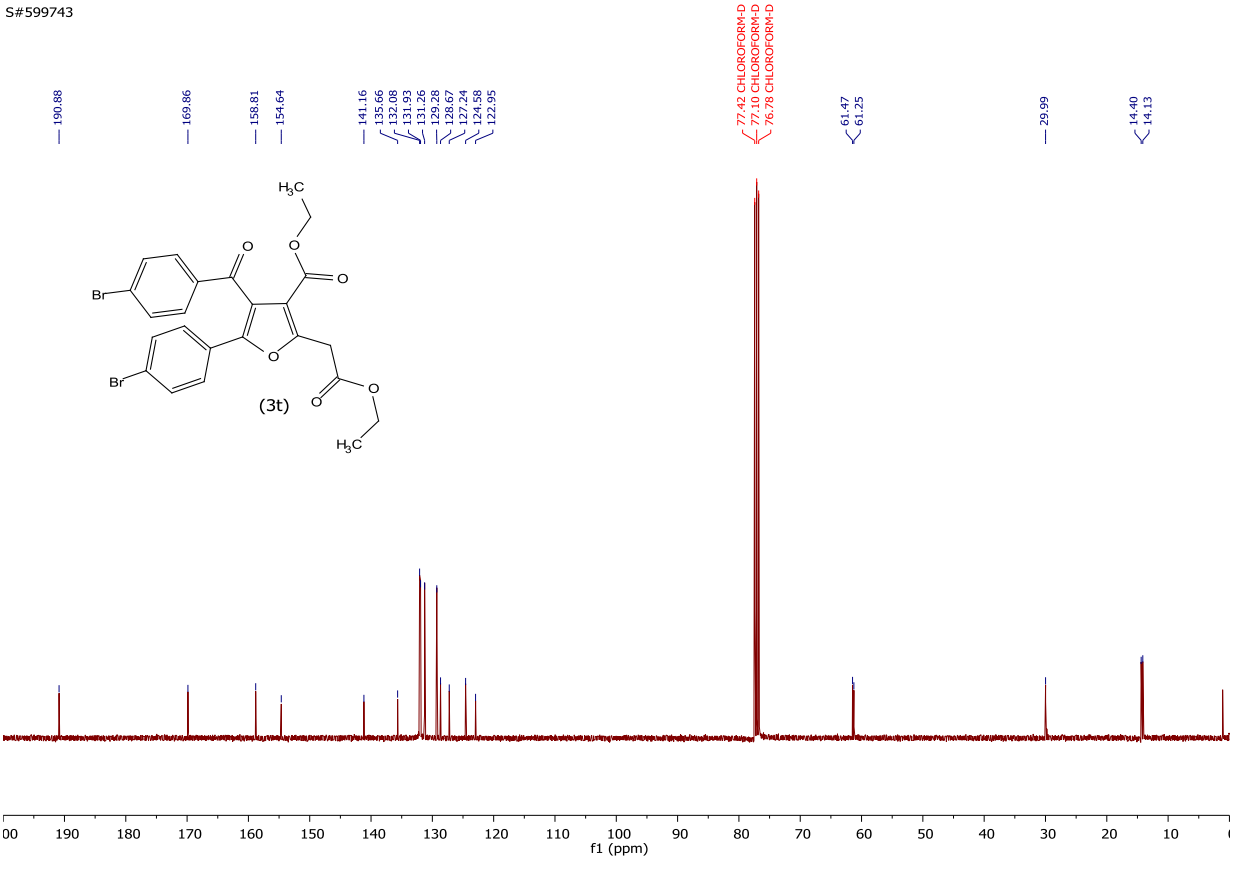
S#446456



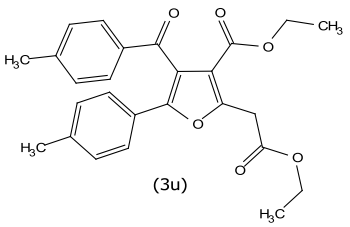
S#379562

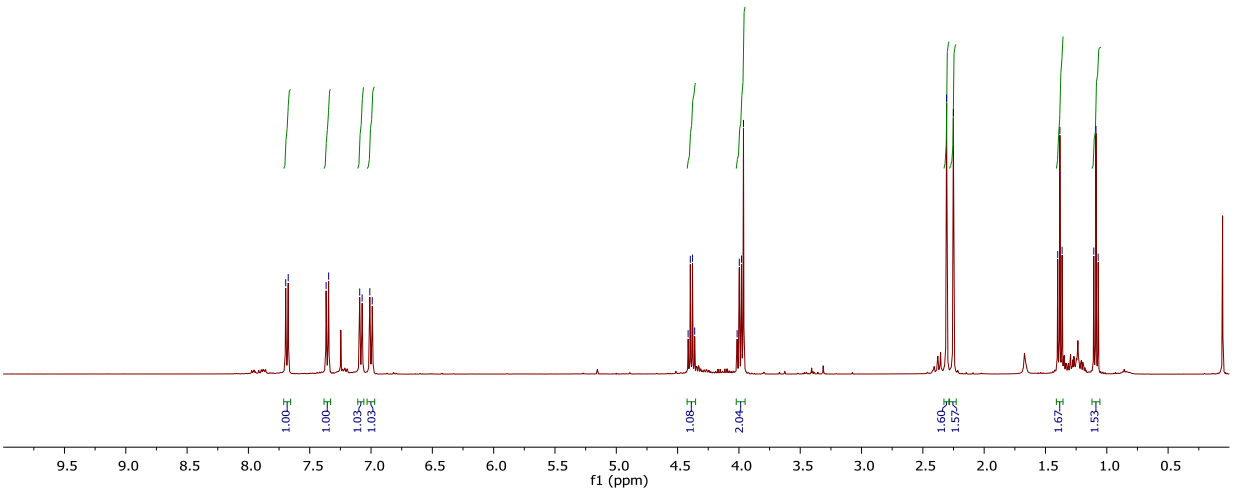


S#599743

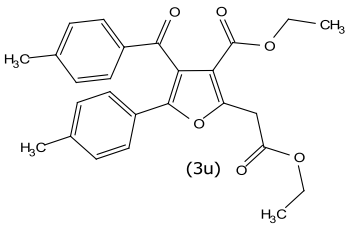


S#406034

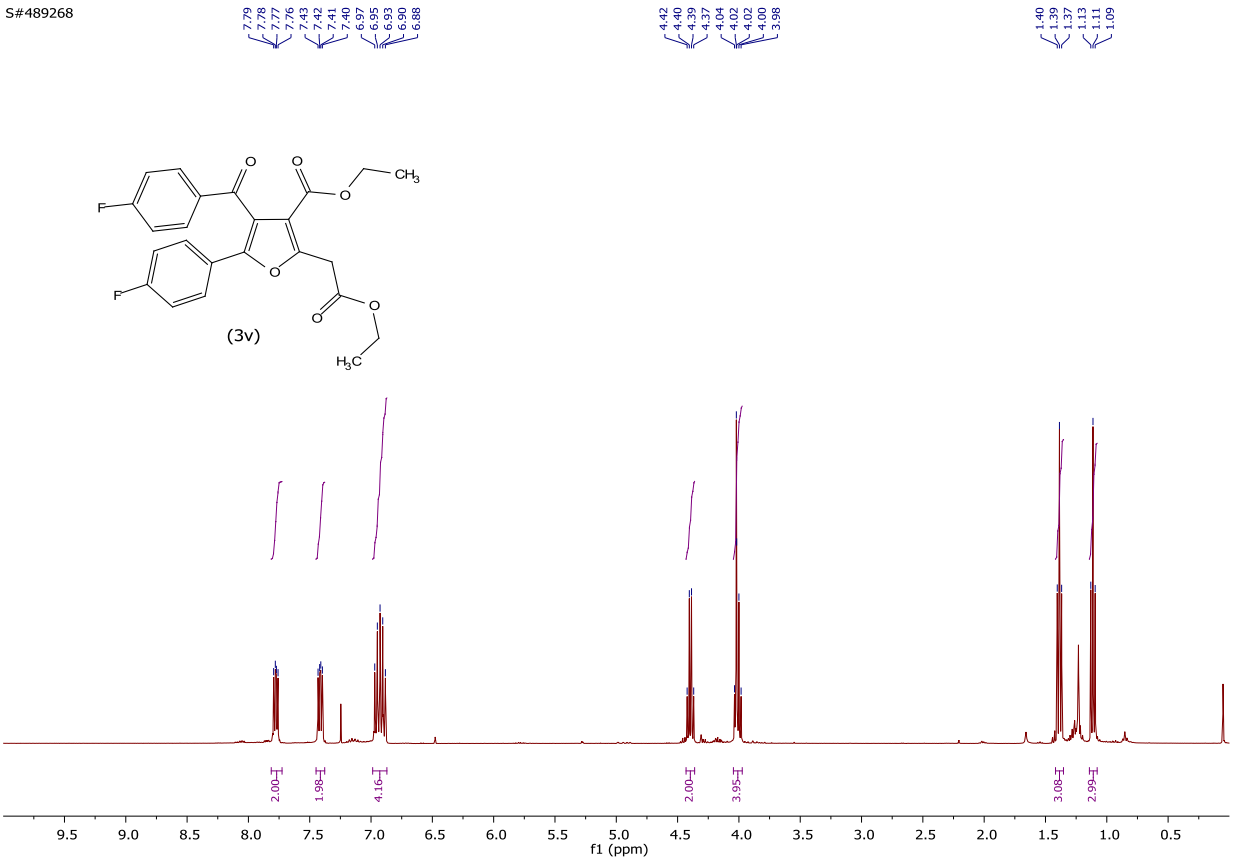




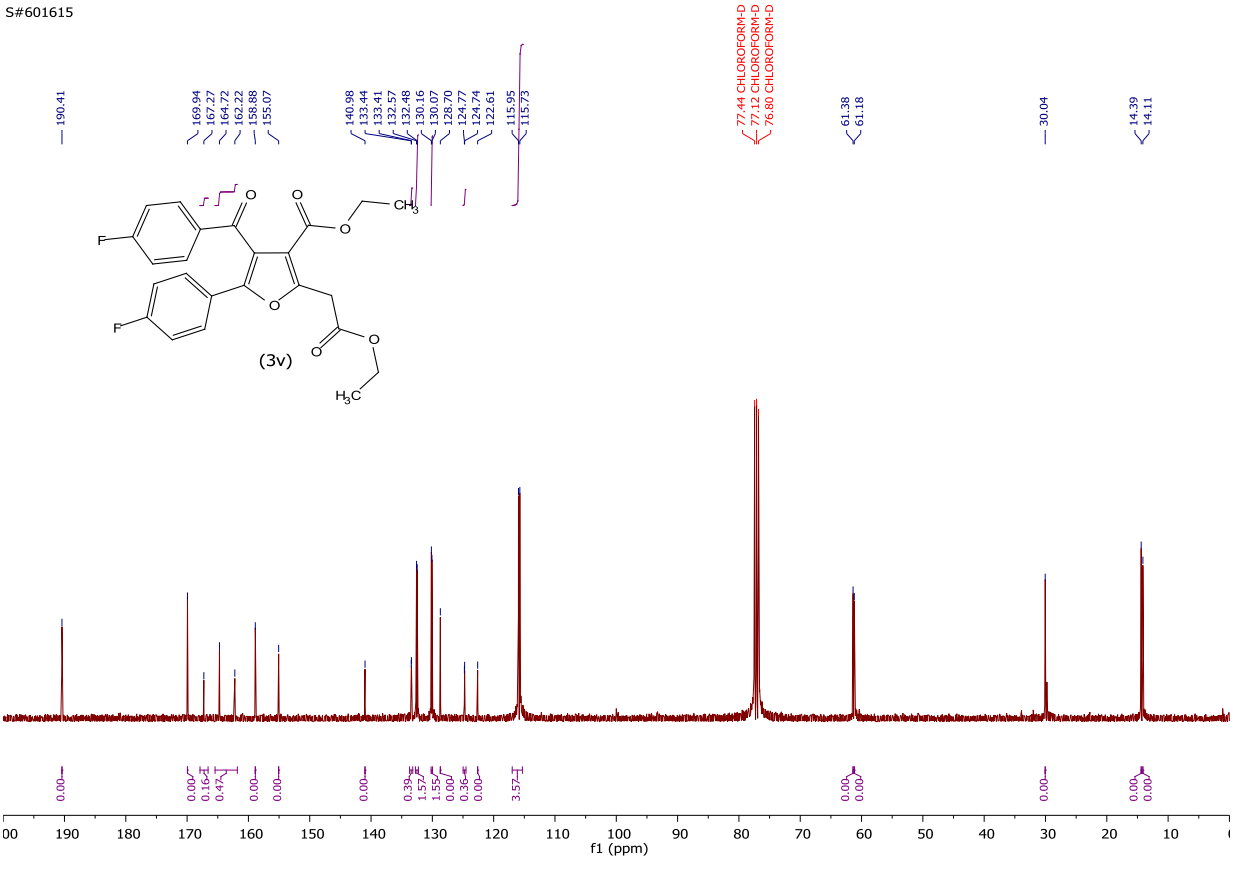
S#438051



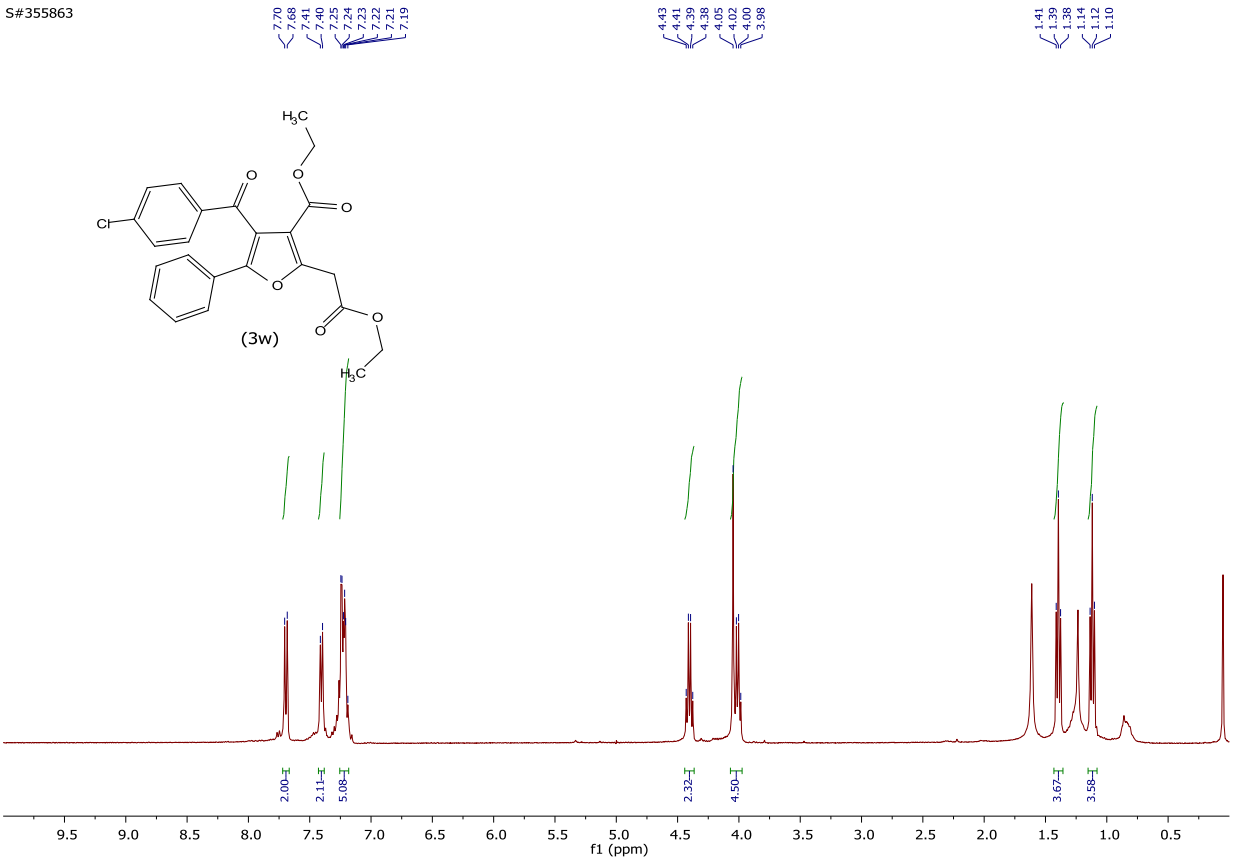
S#489268



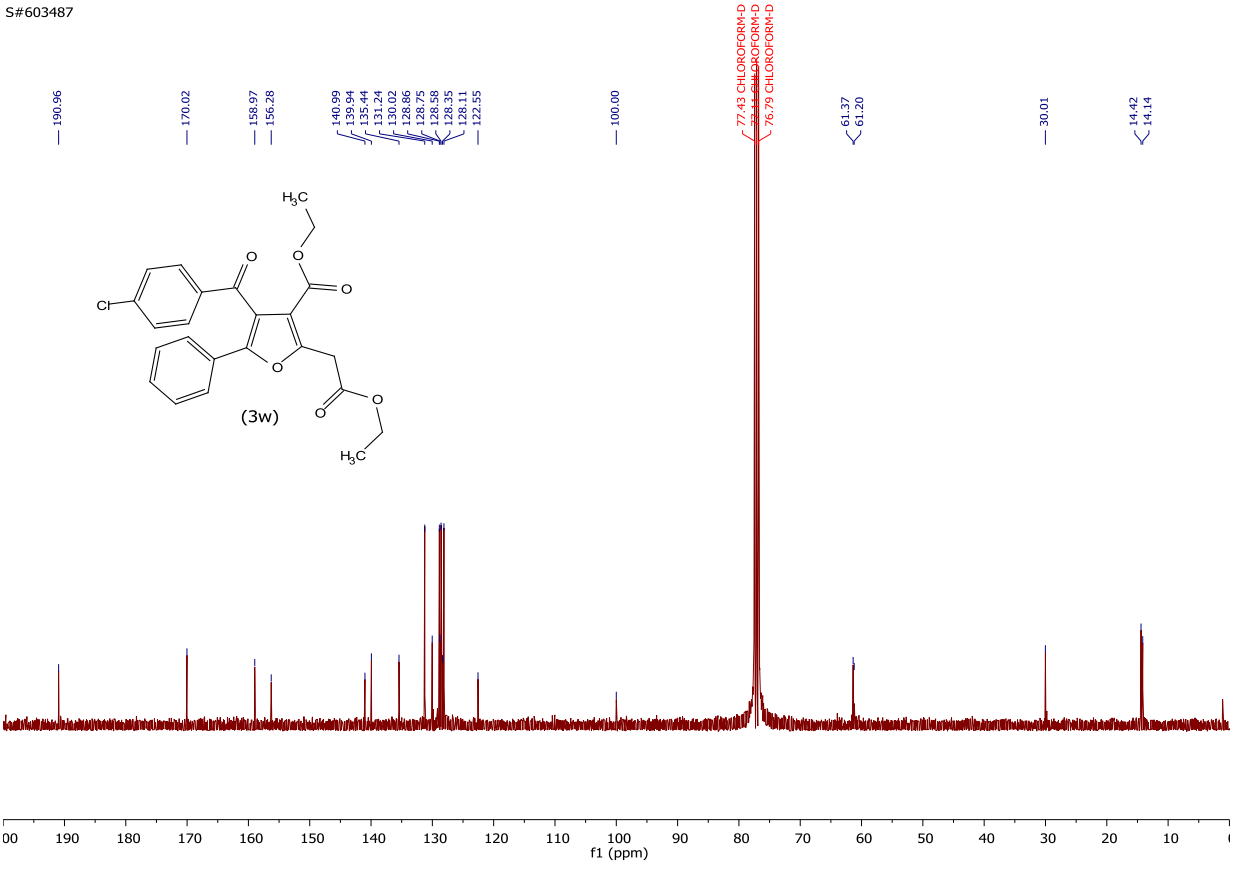
S#601615



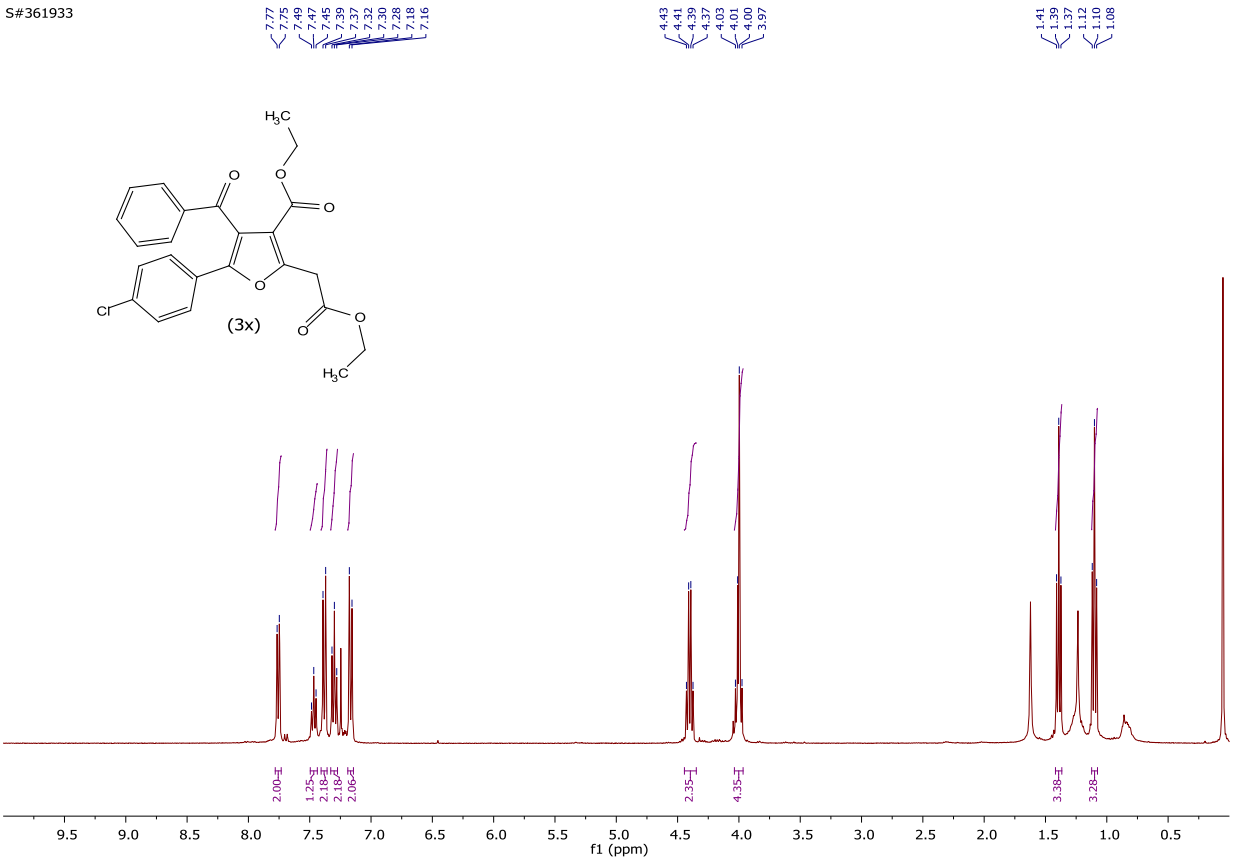
S#355863



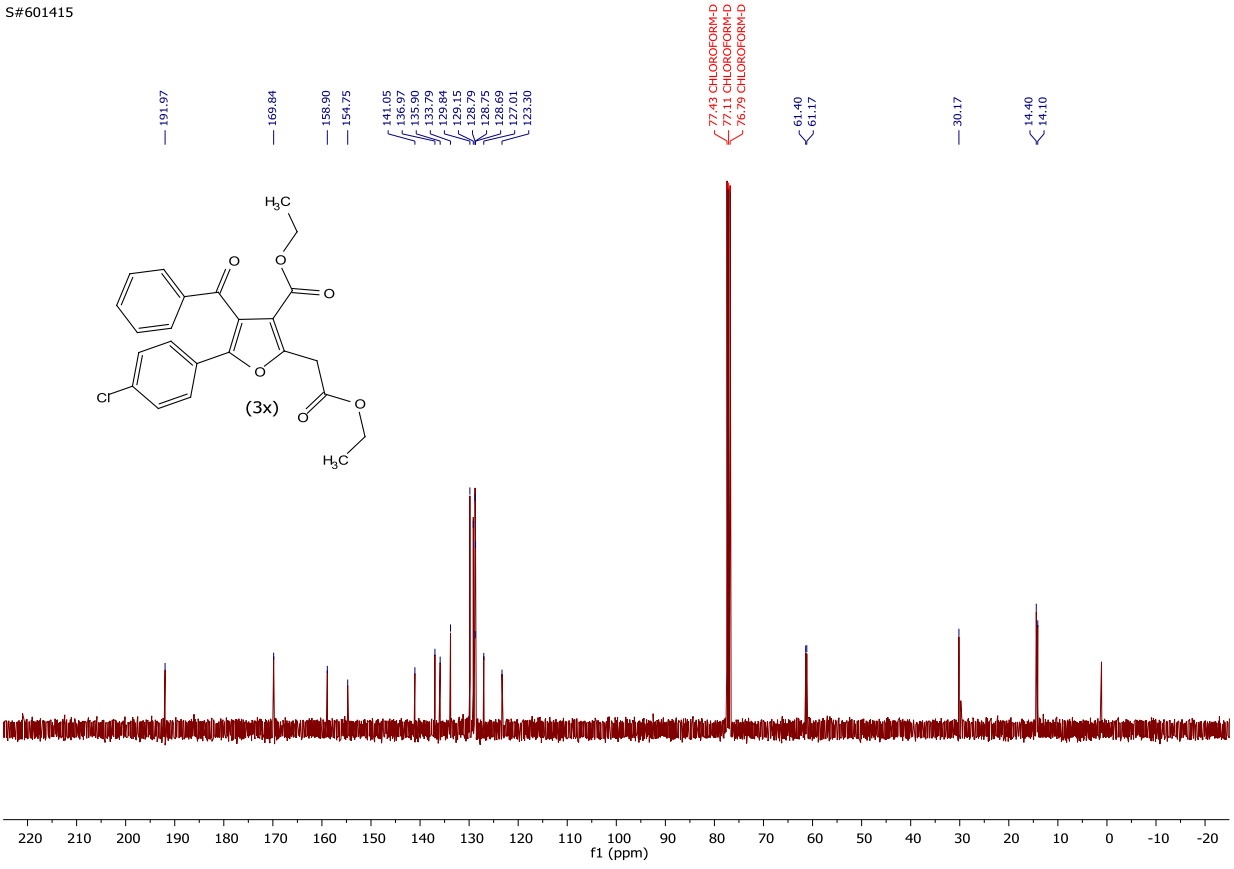
S#603487



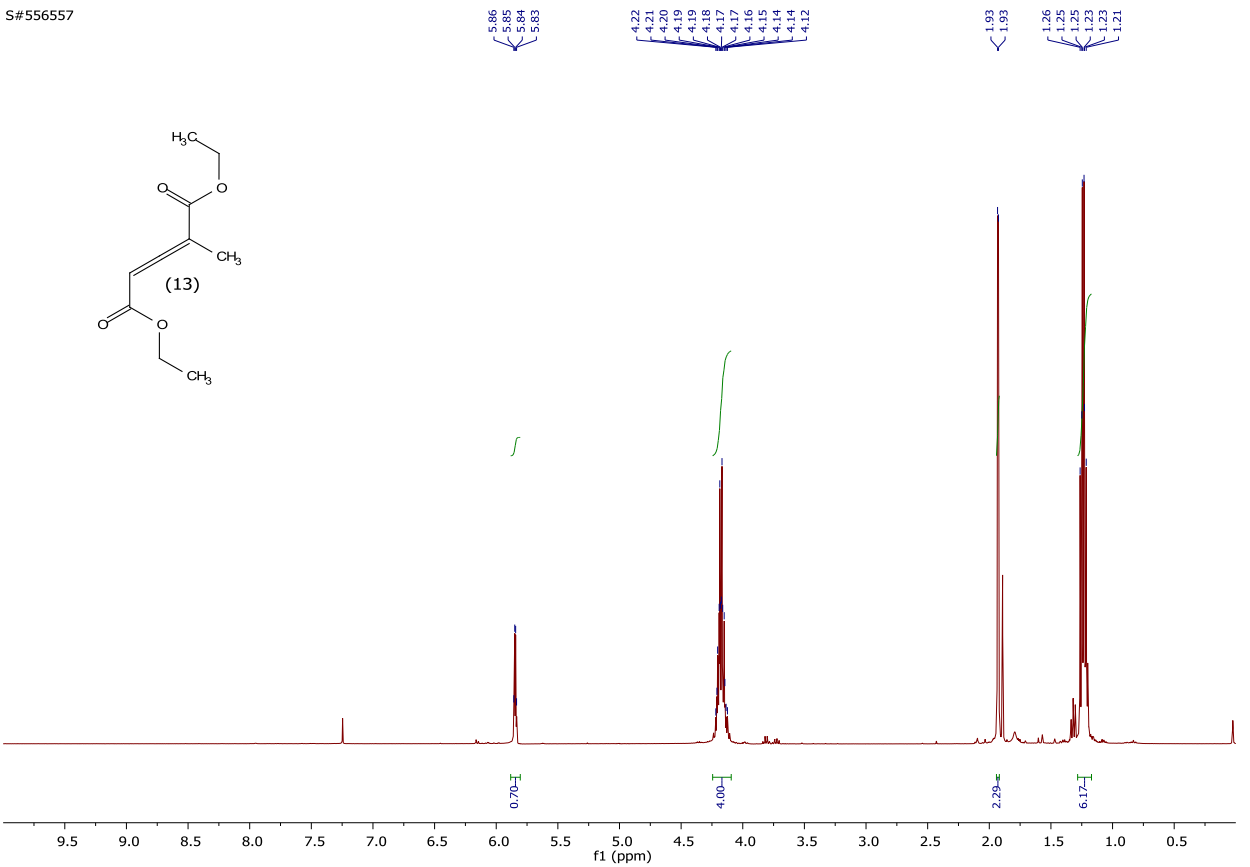
S#361933



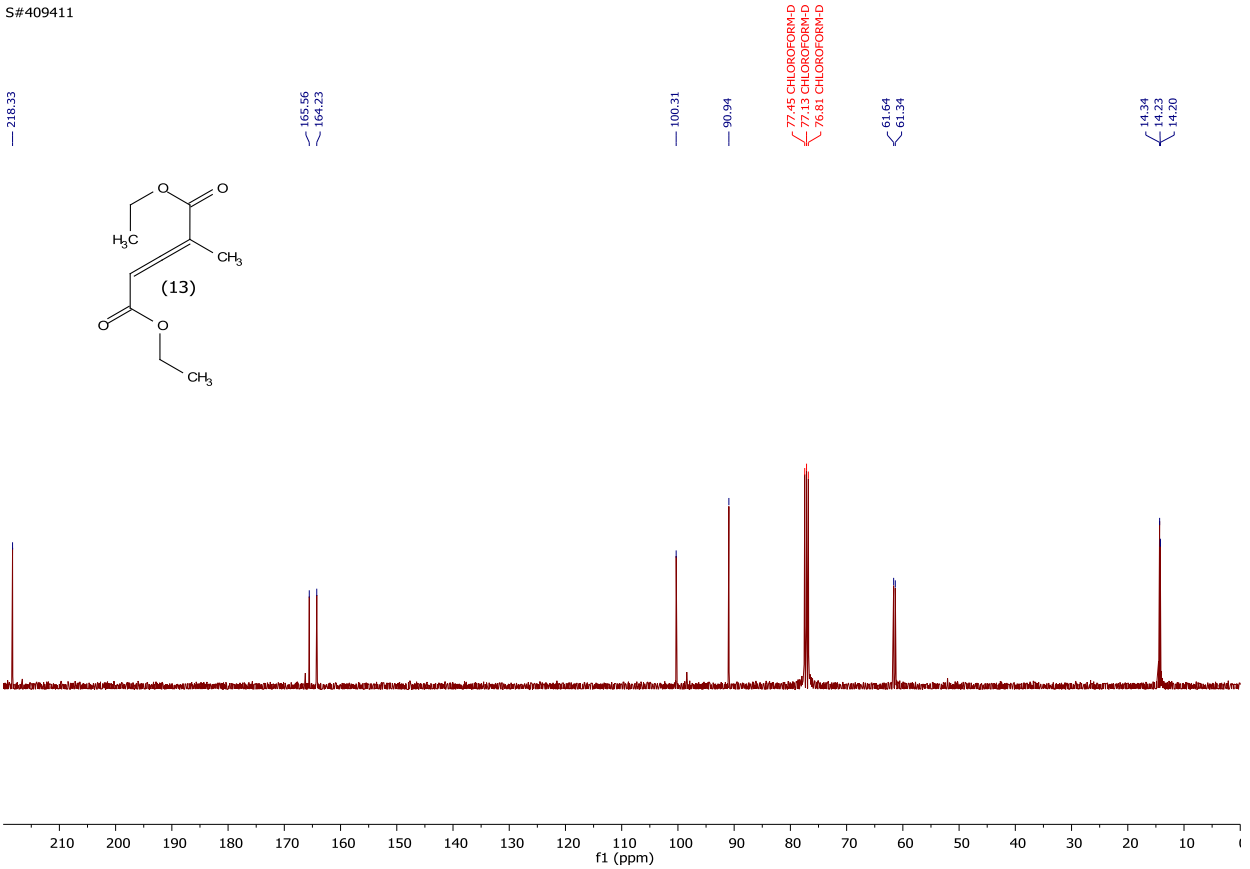
S#601415



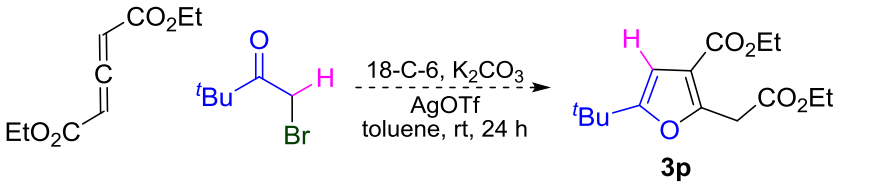
S#556557



S#409411

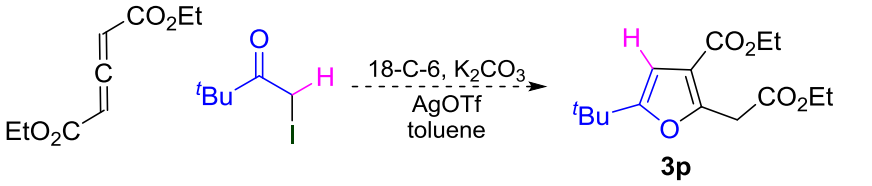


Attempted synthesis of derivative 3p: The synthesis of derivative 3o was attempted using general procedure B by employing both the bromo and iodo precursors. However, a complex mixture was obtained in all cases and no desired product could be obtained. The respective crude NMR's are appended below.



3p

complex mixture obtained;
no desired product

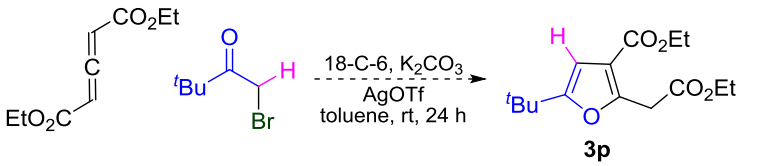


3p

conditions: 1. rt, 24 h

2. 0 °C, 12 h

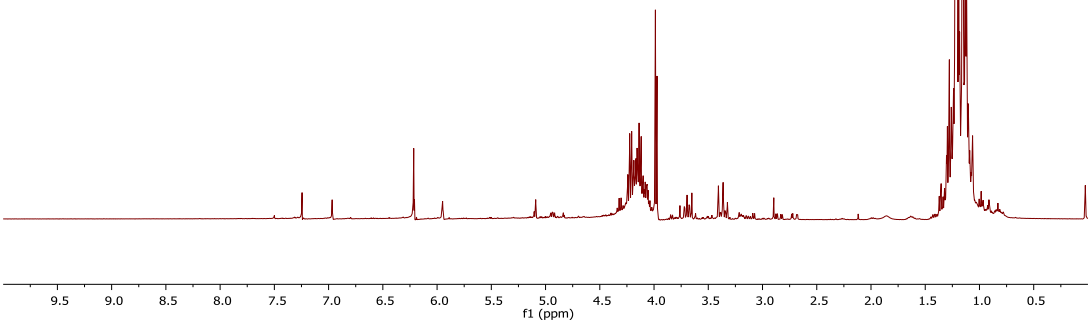
result: Under both conditions, complex mixture was obtained

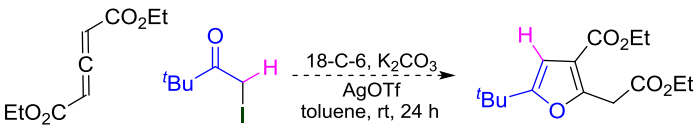


3p

complex mixture obtained;
no desired product

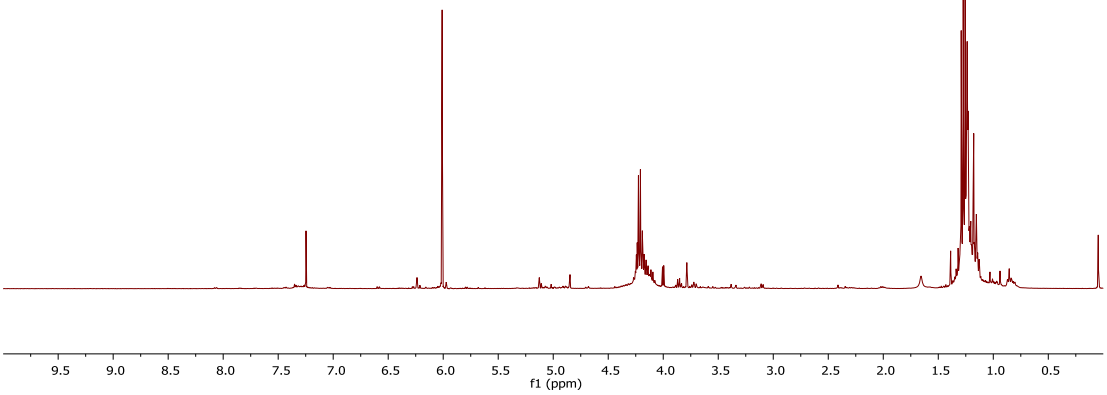
NMR of crude reaction mixture

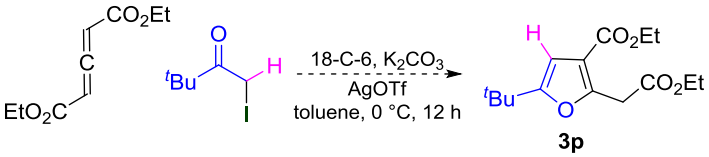




3p

NMR of crude reaction mixture





3p

NMR of crude reaction mixture

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