Supporting Information

In Situ Generation of Nitrile Oxides from Copper Carbene and *tert*-Butyl Nitrite: Synthesis of Fully Substituted Isoxazoles

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General information

All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz) and ^{19}F NMR (376 MHz) data were recorded with $CDCl_3$ as solvent at room temperature unless specified otherwise. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ= 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference. IR and HRMS were performed by the State-authorized Analytical Center in Soochow University.

General procedures for reactions

(a) The procedure for the synthesis of substituted ethyl benzoylacetates[1]

To a dried three-necked flask equipped with a dropping funnel, a condenser, and a magnetic stirrer was added NaH (60% dispersion in mineral oil, 40 mmol, 0.96 g), diethyl carbonate (20 mmol, 2.36 g), and anhydrous toluene (20 mL). The mixture was heated to reflux. A solution of ketone (20 mmol) in anhydrous toluene (10 mL) was added dropwise from the dropping funnel over 1-2 h. After the addition, the mixture was heated to reflux until the evolution of hydrogen ceased (15-20 min). When the reaction was cooled to room temperature, glacial acetic acid (5 mL) was added dropwise and a heavy, pasty solid appeared. Ice-water was added until the solid was dissolved completely. The toluene layer was separated, and the water layer was extracted with EtOAc (3×20 mL). The combined organic solution was washed with water (30 mL) and brine (30 mL), then dried over Na_2SO_4. After evaporation of the solvent, the mixture was distilled under reduced pressure or subjected chromatography to give corresponding the desired β-keto esters.

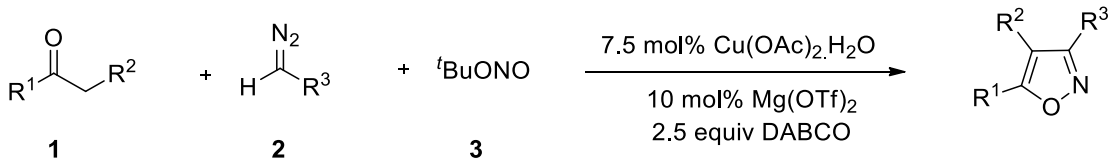
(b) The procedure for the synthesis of allyl benzoylacetate[2]

In a round-bottomed flask, 1N-NaOH (10 mL) was added to ethyl benzoylacetate (1.9 g, 10 mmol). After stirring for overnight at room temperature, the reaction mixture was washed with Et_2O (20 mL×3). The obtained aqueous layer was acidified with 3N-HCl to pH 1, and a precipitated white solid was filtered and dried under reduced pressure to give crude benzoylacetic acid (1.1 g, 64% yield) without purification. In a round-bottomed flask, a solution of N, N'-dicyclohexylcarbodiimide (1.44 g, 7.0 mmol) in MeCN (20 mL) was added dropwise to a solution of benzoylacetic acid and prop-2-en-1-ol (475 uL, 7.0 mmol) in MeCN (20 mL) at room temperature. After stirring for 6 h at room temperature, a precipitated white solid was removed by filtlation, and the obtained filtrate was concentrated under reduced pressure. Purification by column chromatography (ethyl acetate/petroleum ether = 1:30) gave desired product.

(c) The procedure for the synthesis of diazo compounds[3]

The corresponding alcohol (10 mmol) and $NaHCO_3$ (2.5 g, 30 mmol) were dissolved in acetonitrile (30 mL) and bromoacetyl bromide (1.3 mL, 15 mmol) was added slowly at 0 ℃. After stirring 30 min at this temperature, the reaction was quenched with H_2O. The solution was extracted with CH_2Cl_2 three times. The organic phase was washed with brine and dried over Na_2SO_4. The solvent was evaporated, and the residue was used in the next reaction without purification. The bromoacetate thus obtained and N, N'-ditosylhydrazine (6.8 g, 20 mmol) were dissolved in THF (50 mL) and cooled to 0 ℃. DBU (7.5 mL, 50 mmol) was added dropwise and stirred at the temperature for 30 minutes. After the quenching of the reaction by the addition of saturated $NaHCO_3$ solution, this was extracted with Et_2O three times. The organic phase was washed with brine, dried over Na_2SO_4 and evaporated to give the crude product. The crude product thus obtained was purified by chromatography over a column of silica gel using petroleum and EtOAc as eluent to afford the desired product.

(d) The procedure for the synthesis of isoxazoles

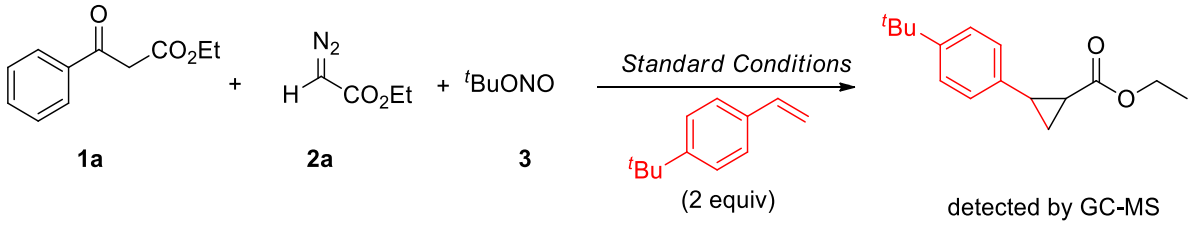


1 **2** **3**

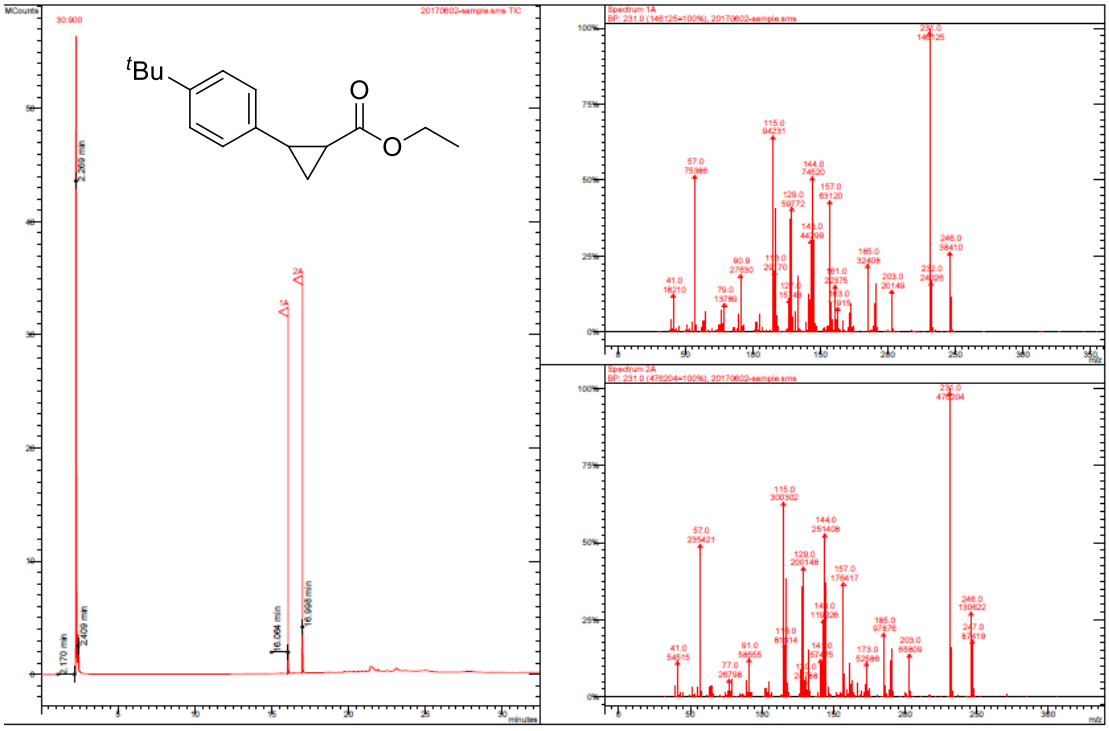
To a solution of $Cu(OAc)_2 \cdot H_2O$ (0.0375 mmol, 0.075 equiv), DABCO (1.25 mmol, 2.5 equiv), and $Mg(OTf)_2$ (0.05 mmol, 0.1 equiv) in cyclohexane (3.0 mL) were added β-keto esters **1** (0.5 mmol, 1.0 equiv), diazo compounds **2** (0.75 mmol, 1.5 equiv.) and ^{t}BuONO **3** (0.75 mmol, 1.5 equiv) successively. The mixture was stirred at 80 ^{o}C in a test tube (sealed with parafilm). After the reaction was complete (monitored by TLC), it was then poured in brine solution and extracted with EtOAc three times, then dried over anhydrous Na_2SO_4 and filtrated. After the solvent was removed under reduced pressure, the residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/30 to 1/10, v/v) to afford the desired product.

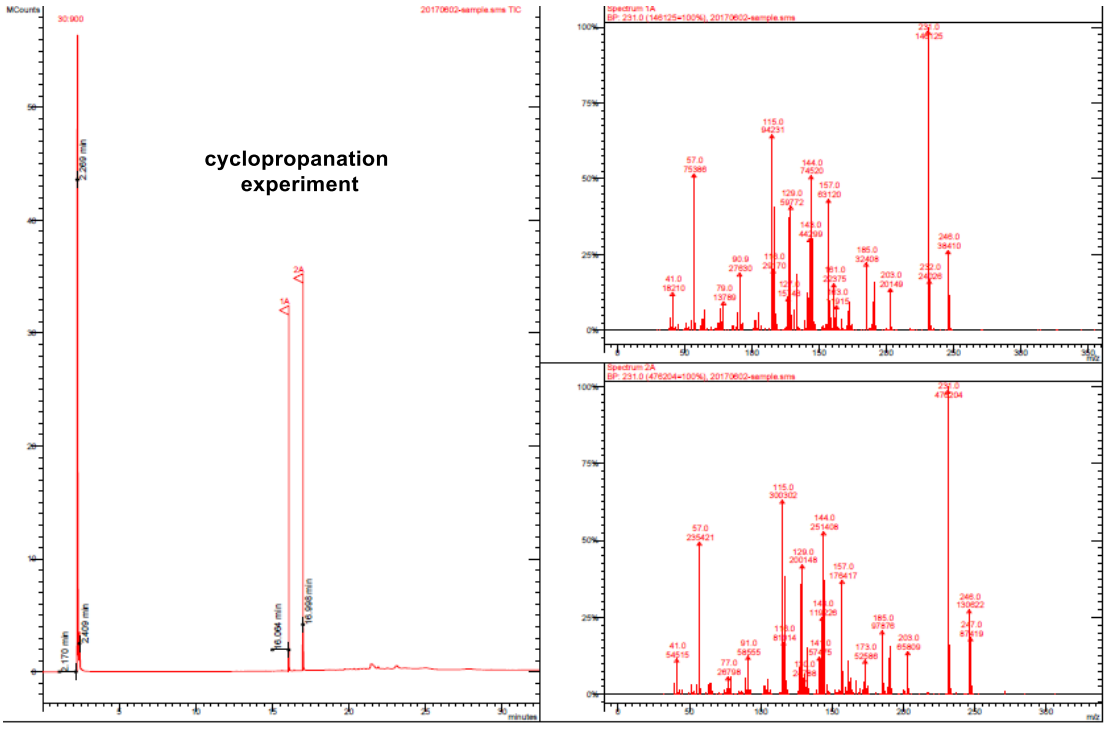
Mechanistic studies

(a) Cyclopropanation experiment



1a 2a 3





(b) DFT calculations

Computational methodology

DFT calculations were carried out using the Gaussian 09 software package.[4] The B3LYP density functional[5] was employed in this work, which has demonstrated to be effective for computations involving copper metal.[6] The LANL2DZ basis set combined with the LANL2DZ pseudo potential[7] was employed for the copper atom while the 6-31G(d) basis[8] set was utilized for other atoms. All stationary points were fully characterized by vibrational frequency analysis as either minima (all positive eigenvalues) or transition states (one negative eigenvalue). Intrinsic reaction coordinate calculations[9] were done to confirm that the optimized transition states link to their respective reactants and products. The Gibbs free energies of all optimized structures in gas phase were obtained at 298.15 K and 1 atm. To incorporate solvent effect, single point energy (SPE) calculations were performed on the optimized gas-phase geometries, employing the SMD solvation model[10] and cyclohexane as solvent. For such SPE calculations, LANL2DZ basis set for Cu atom and 6-311++G(d,p) for other atoms were utilized. The translational entropy correction in solution was done using the method proposed by Whitesides *et al.*[11] The enthalpy and Gibbs free energy of solvation were considered and their values were obtained from the addition of solvation single point energy and their respective gas-phase thermal correction to enthalpy and Gibbs free energy. The solvation Gibbs free energy was used in discussion.

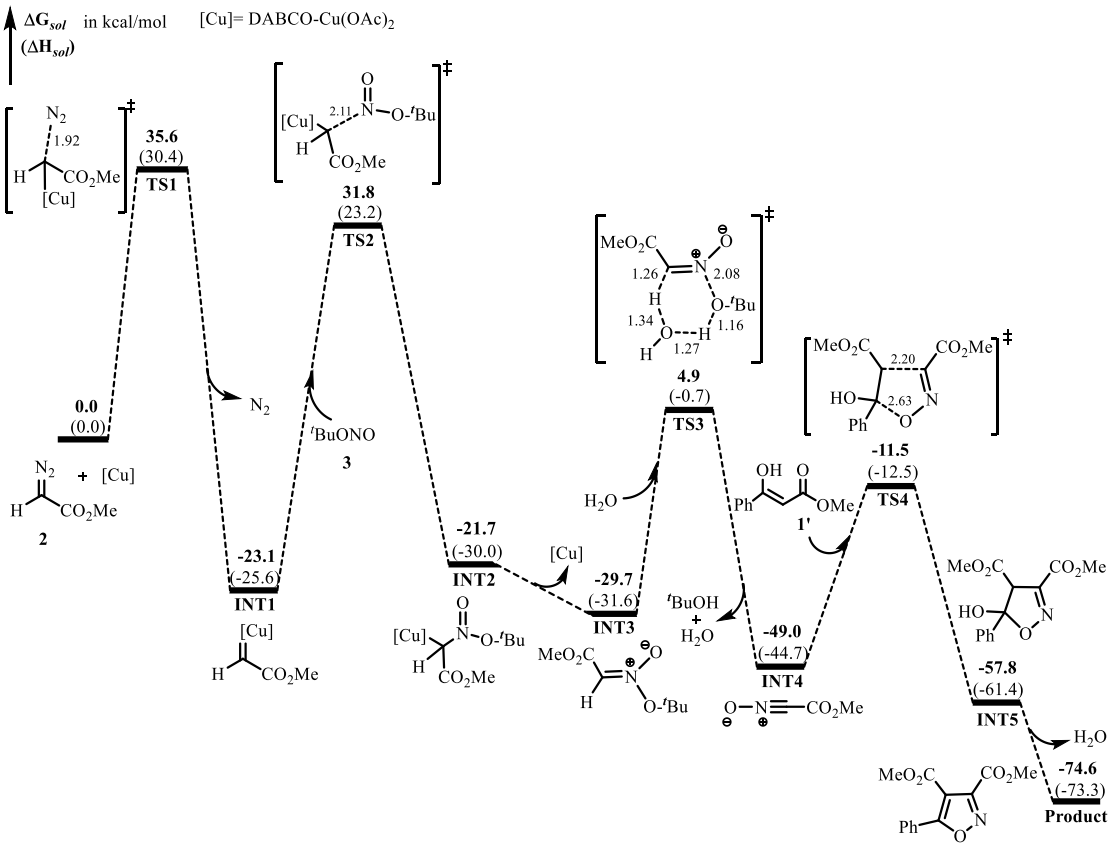
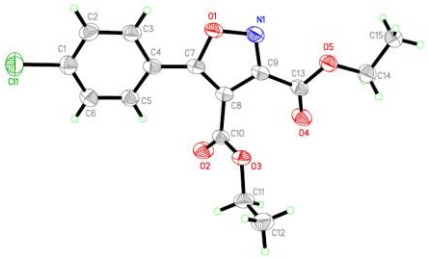


Figure S1. Energy profile (in kcal/mol) for the formation of isozaxoles. Bond lengths are shown in Å.

X-ray diffraction analysis of compound 4f and 5d



Structure of **4f** (CCDC 1546800)

Table S1. Crystal data and structure refinement for **4f**.

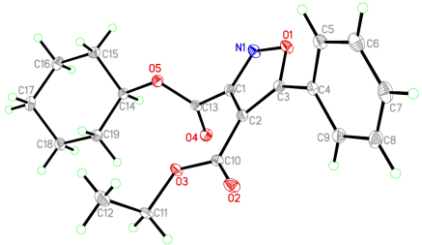
Empirical formula	$C_{15}H_{15}ClNO_5$
Formula weight	324.73
Temperature/K	213.50(10)
Crystal system	monoclinic

Space group	P21/c
a/Å	5.9532(3)
b/Å	26.9414(15)
c/Å	9.3953(5)
α/°	90
β/°	91.322(5)
γ/°	90
Volume/Å^3	1506.49(14)
Z	4
ρcalcg/cm^3	1.432
μ/mm-1	2.467
F(000)	676.0
Crystal size/mm^3	0.3 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.562 to 134.15
Index ranges	-5 ≤ h ≤ 7, -31 ≤ k ≤ 32, -11 ≤ l ≤ 11
Reflections collected	6750
Independent reflections	2680 [Rint = 0.0411, Rsigma = 0.0480]
Data/restraints/parameters	2680/0/201
Goodness-of-fit on F^2	0.942
Final R indexes [I>=2σ (I)]	R1 = 0.0495, wR2 = 0.1340
Final R indexes [all data]	R1 = 0.0723, wR2 = 0.1588
Largest diff. peak/hole / e Å^{-3}	0.23/-0.26

Table S2. Bond Lengths and Bond Angles for **4f**.

C1-C1	1.737(3)	C2-C3	1.376(4)
O1-N1	1.399(3)	C3-C4	1.399(4)
O1-C7	1.363(3)	C4-C5	1.396(4)
O2-C10	1.198(3)	C4-C7	1.460(4)
O3-C10	1.327(3)	C5-C6	1.376(4)
O3-C11	1.458(3)	C7-C8	1.365(4)
O4-C13	1.201(3)	C8-C9	1.419(4)
O5-C13	1.320(3)	C8-C10	1.489(3)
O5-C14	1.464(3)	C9-C13	1.490(4)
N1-C9	1.312(3)	C11-C12	1.485(4)
C1-C2	1.382(4)	C14-C15	1.504(4)
C1-C6	1.378(4)	O1-C7-C8	108.4(2)
C7-O1-N1	109.9(2)	C8-C7-C4	136.3(2)
C10-O3-C11	116.4(2)	C7-C8-C9	104.4(2)
C13-O5-C14	116.7(2)	C7-C8-C10	129.9(2)
C9-N1-O1	104.9(2)	C9-C8-C10	125.5(2)
C2-C1-Cl1	118.7(2)	N1-C9-C8	112.4(2)

C6-C1-Cl1	119.9(2)	N1-C9-C13	120.9(2)
C6-C1-C2	121.3(3)	C8-C9-C13	126.4(2)
C3-C2-C1	119.1(3)	O2-C10-O3	125.5(2)
C2-C3-C4	120.8(3)	O2-C10-C8	124.8(2)
C3-C4-C7	119.5(3)	O3-C10-C8	109.8(2)
C5-C4-C3	118.7(3)	O3-C11-C12	107.5(3)
C5-C4-C7	121.8(2)	O4-C13-O5	126.2(3)
C6-C5-C4	120.6(3)	O4-C13-C9	122.0(3)
C5-C6-C1	119.5(3)	O5-C13-C9	111.7(2)
O1-C7-C4	115.3(2)	O5-C14-C15	106.6(2)



Structure of **5d** (CCDC 1547520)

Table S3. Crystal data and structure refinement for **5d**.

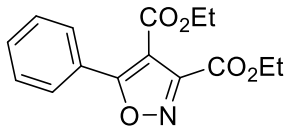
Empirical formula	$C_{19}H_{21}NO_5$
Formula weight	343.37
Temperature/K	120.05
Crystal system	triclinic
Space group	P-1
a/Å	9.2521(5)
b/Å	9.8028(5)
c/Å	9.9294(5)
α/°	75.6790(10)
β/°	88.544(2)
γ/°	79.757(2)
Volume/Å^3	858.51(8)
Z	2
ρcalcg/cm^3	1.328
μ/mm^{-1}	0.096
F(000)	364.0
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.36 to 55.1
Index ranges	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	27853

Independent reflections	3915 [Rint = 0.0468, Rsigma = 0.0272]
Data/restraints/parameters	3915/0/227
Goodness-of-fit on F^2	1.151
Final R indexes [I>=2σ (I)]	R1 = 0.0368, wR2 = 0.1098
Final R indexes [all data]	R1 = 0.0427, wR2 = 0.1212
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.30

Table S4. Bond Lengths and Bond Angles for **5d**.

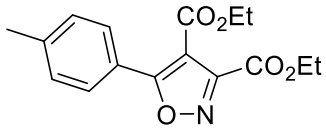
O5-C13	1.3241(14)	C5-C6	1.3860(17)
O5-C14	1.4721(13)	C19-C18	1.5288(16)
O3-C10	1.3374(14)	C15-C16	1.5289(17)
O3-C11	1.4615(13)	C9-C4	1.3956(17)
O4-C13	1.1998(15)	C9-C8	1.3855(17)
O2-C10	1.2020(14)	C2-C1	1.4220(15)
O1-N1	1.4164(12)	C2-C3	1.3653(16)
O1-C3	1.3488(14)	C4-C3	1.4672(15)
N1-C1	1.3030(15)	C17-C16	1.5240(19)
C10-C2	1.4762(15)	C17-C18	1.5261(18)
C13-C1	1.5052(15)	C11-C12	1.5034(18)
C14-C19	1.5178(16)	C6-C7	1.385(2)
C14-C15	1.5147(16)	C8-C7	1.388(2)
C5-C4	1.3957(17)	C6-C7-C8	120.16(12)
C13-O5-C14	116.91(9)	C3-C2-C10	127.81(10)
C10-O3-C11	116.55(9)	C3-C2-C1	103.82(10)
C3-O1-N1	109.22(9)	C5-C4-C3	119.82(11)
C1-N1-O1	104.84(9)	C9-C4-C5	120.27(11)
O3-C10C2	110.08(9)	C9-C4-C3	119.89(11)
O2-C10-O3	125.15(11)	C16-C17-C18	110.56(10)
O2-C10-C2	124.75(11)	N1-C1-C13	119.34(10)
O5-C13-C1	110.77(9)	N1-C1-C2	112.71(10)
O4-C13-O5	127.31(11)	C2-C1-C13	127.85(10)
O4-C13-C1	121.91(10)	C17-C16-C15	111.36(10)
O5-C14-C19	109.71(9)	C17-C18-C19	110.69(10)
O5-C14-C15	105.71(9)	O1-C3-C2	109.42(10)
C15-C14-C19	112.79(10)	O1-C3-C4	116.11(10)
C6-C5-C4	119.55(12)	C2-C3-C4	134.47(11)
C14-C19-C18	109.92(10)	O3-C11-C12	110.29(10)
C14-C15-C16	110.14(10)	C7-C6-C5	120.26(13)
C8-C9-C4	119.49(12)	C9-C8-C7	120.27(12)
C1-C2-C10	127.87(10)		

Compound characterizations



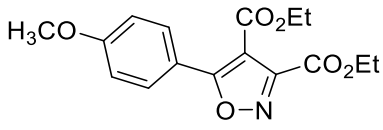
4a

diethyl 5-phenylisoxazole-3,4-dicarboxylate (**4a**) [12]. Light yellow liquid (116 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 2H), 7.58 – 7.45 (m, 3H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.8, 159.7, 156.2, 131.7, 128.6, 128.4, 125.6, 108.4, 62.6, 61.7, 13.9, 13.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{15}NO_5$: 312.0842, Found: 312.0836 ($M+Na^+$); IR (neat, cm^{-1}): υ 2984, 1730, 1473, 1218, 1069, 726, 690.



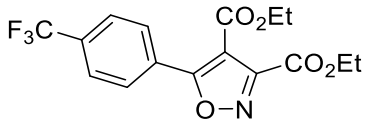
4b

diethyl 5-(p-tolyl)isoxazole-3,4-dicarboxylate (**4b**). White solid (83 mg, 55% yield), m.p. 44.6–45.3 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.43 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 161.0, 159.9, 156.3, 142.4, 129.4, 128.4, 122.9, 107.8, 62.6, 61.7, 21.5, 14.0, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_5$: 326.0999, Found: 326.0991 ($M+Na^+$); IR (neat, cm^{-1}): υ 2992, 1728, 1458, 1224, 1073, 827.



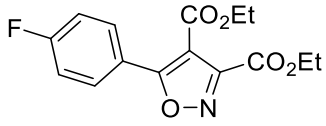
4c

diethyl 5-(4-methoxyphenyl)isoxazole-3,4-dicarboxylate (**4c**). Light yellow liquid (99 mg, 62% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 162.3, 161.0, 160.0, 156.4, 130.3, 118.1, 114.0, 106.9, 62.6, 61.6, 55.3, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_6$: 342.0948, Found: 342.0940 ($M+Na^+$); IR (neat, cm^{-1}): υ 2983, 1727, 1470, 1220, 1178, 1070, 836.



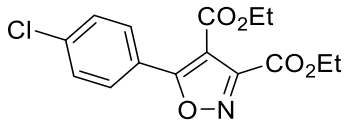
4d

diethyl 5-(4-(trifluoromethyl)phenyl)isoxazole-3,4-dicarboxylate (**4d**). Colorless liquid (102 mg, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.3 Hz, 2H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 160.5, 159.5, 156.4, 133.3 (q, *J* = 32.9 Hz), 128.9, 128.9, 125.7 (q, *J* = 3.7 Hz), 123.4 (q, *J* = 273.7 Hz), 109.6, 62.8, 62.1, 13.9, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.23; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{14}F_3NO_5$: 380.0716, Found: 380.0709 ($M+Na^+$); IR (neat, cm^{-1}): υ 2987, 1731, 1321, 1224, 1125, 1063, 847.



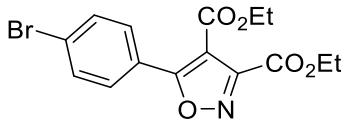
4e

diethyl 5-(4-fluorophenyl)isoxazole-3,4-dicarboxylate (**4e**). White solid (107 mg, 69% yield), m. p. 50.6–51.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 7.97 (m, 2H), 7.26 – 7.14 (m, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 164.6 (d, *J* = 254.0 Hz), 160.6, 159.7, 156.4, 130.9 (d, *J* = 9.0 Hz), 121.9 (d, *J* = 3.4 Hz), 115.9 (d, *J* = 22.1 Hz), 108.0, 62.7, 61.8, 13.9, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -106.39; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}FNO_5$: 330.0748, Found: 330.0744 ($M+Na^+$); IR (neat, cm^{-1}): υ 2985, 1728, 1473, 1220, 1070, 1014, 842.



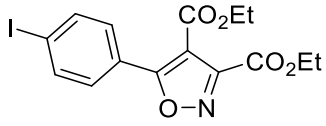
4f

diethyl 5-(4-chlorophenyl)isoxazole-3,4-dicarboxylate (**4f**). White solid (110 mg, 68% yield), m. p. 64.0–65.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 160.6, 159.6, 156.4, 138.1, 129.8, 129.0, 124.0, 108.5, 62.7, 61.9, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}{}^{35}ClNO_5$: 346.0453, Found: 346.0445 ($M+Na^+$); Anal. Calcd. For $C_{15}H_{14}{}^{37}ClNO_5$: 348.0423, Found: 348.0435 ($M+Na^+$); IR (neat, cm^{-1}): υ 2992, 1728, 1458, 1222, 1071, 1009, 839.



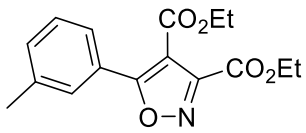
4g

diethyl 5-(4-bromophenyl)isoxazole-3,4-dicarboxylate (**4g**). Light yellow solid (136 mg, 74% yield), m. p. 55.6–57.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.65 (d, *J* = 8.5 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 160.6, 159.6, 156.4, 132.0, 129.9, 126.6, 124.4, 108.6, 62.7, 61.9, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}{}^{79}BrNO_5$: 389.9948, Found: 389.9948 ($M+Na^+$); Anal. Calcd. For $C_{15}H_{14}{}^{81}BrNO_5$: 391.9927, Found: 391.9943 ($M+Na^+$); IR (neat, cm^{-1}): υ 2981, 1726, 1464, 1219, 1066, 843, 725.



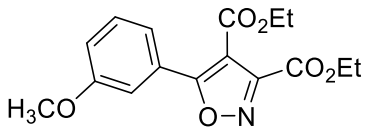
4h

diethyl 5-(4-iodophenyl)isoxazole-3,4-dicarboxylate (**4h**). Light yellow solid (147 mg, 71% yield), m. p. 42.4–44.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2H), 7.72 (d, *J* = 8.5 Hz, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 160.6, 159.6, 156.4, 137.9, 129.8, 125.0, 108.6, 99.0, 62.7, 61.9, 14.0, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}INO_5$: 415.9989, Found: 415.9978 ($M+H^+$); IR (neat, cm^{-1}): υ 2983, 1728, 1470, 1220, 1073, 1006, 828.



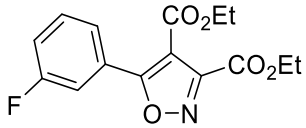
4i

diethyl 5-(m-tolyl)isoxazole-3,4-dicarboxylate (**4i**). Light yellow liquid (98 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.68 (m, 2H), 7.42 – 7.30 (m, 2H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.8, 159.7, 156.1, 138.4, 132.4, 128.8, 128.5, 125.5, 108.2, 62.5, 61.7, 21.2, 13.9, 13.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_5$: 326.0999, Found: 326.0984 ($M+Na^+$); IR (neat, cm^{-1}): υ 2984, 1731, 1471, 1220, 1090, 1072, 847, 781.



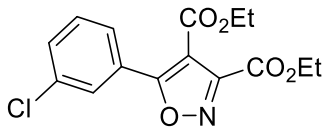
4j

diethyl 5-(3-methoxyphenyl)isoxazole-3,4-dicarboxylate (**4j**). Light yellow liquid (132 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.48 (m, 2H), 7.47 – 7.35 (m, 1H), 7.16 – 6.97 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 160.8, 159.6, 159.5, 156.2, 129.7, 126.6, 120.6, 117.8, 113.4, 108.6, 62.6, 61.8, 55.3, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_6$: 342.0948, Found: 342.0942 ($M+Na^+$); IR (neat, cm^{-1}): υ 2984, 1730, 1466, 1207, 1112, 1070, 848, 778.



4k

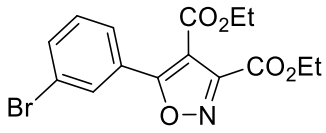
diethyl 5-(3-fluorophenyl)isoxazole-3,4-dicarboxylate (**4k**). Colorless liquid (84 mg, 55% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.69 (m, 2H), 7.54 – 7.43 (m, 1H), 7.30 – 7.21 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0 (d, *J* = 2.9 Hz), 162.4 (d, *J* = 247.5 Hz), 160.6, 159.6, 156.4, 130.5 (d, *J* = 8.2 Hz), 127.4 (d, *J* = 8.7 Hz), 124.2 (d, *J* = 3.2 Hz), 118.8 (d, *J* = 21.1 Hz), 115.6 (d, *J* = 24.5 Hz), 109.0, 62.8, 62.0, 14.0, 13.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.21; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}FNO_5$: 330.0748, Found: 330.0742 ($M+Na^+$); IR (neat, cm-1): υ 2984, 1730, 1473, 1218, 1069, 726, 690; IR (neat, cm^{-1}): υ 2985, 1730, 1580, 1454, 1224, 1190, 1109, 860, 784.



4l

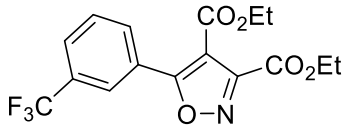
diethyl 5-(3-chlorophenyl)isoxazole-3,4-dicarboxylate (**4l**). Light yellow liquid (97 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 1H), 7.91 – 7.82 (m, 1H), 7.55 – 7.50 (m, 1H), 7.48 – 7.41 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 160.4, 159.5, 156.3, 134.7, 131.7, 130.0, 128.4, 127.1, 126.5, 109.0, 62.7, 62.0, 13.9, 13.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}{}^{35}ClNO_5$: 346.0453,

Found: 346.0441 ($M+Na^+$); Anal. Calcd. For $C_{15}H_{14}{}^{37}ClNO_5$: 348.0423, Found: 348.0435 ($M+Na^+$); IR (neat, cm^{-1}): υ 2984, 1729, 1466, 1220, 1070, 784.



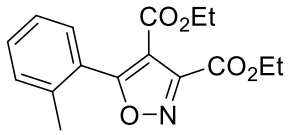
4m

diethyl 5-(3-bromophenyl)isoxazole-3,4-dicarboxylate (**4m**). Light yellow liquid (130 mg, 71% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 1.4 Hz, 1H), 7.91 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.68 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.45 – 7.34 (m, 1H), 4.48 (q, *J* = 7.1 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.35 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 160.4, 159.5, 156.4, 134.6, 131.3, 130.2, 127.4, 127.0, 122.6, 109.0, 62.8, 62.0, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}{}^{79}BrNO_5$: 389.9948, Found: 389.9956 ($M+Na^+$); Anal. Calcd. For $C_{15}H_{14}{}^{81}BrNO_5$: 391.9927, Found: 391.9936 ($M+Na^+$); IR (neat, cm^{-1}): υ 2983, 1729, 1465, 1220, 1119, 1068, 783, 735.



4n

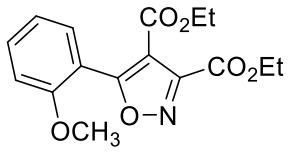
diethyl 5-(3-(trifluoromethyl)phenyl)isoxazole-3,4-dicarboxylate (**4n**). Light yellow liquid (125 mg, 70% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.19 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.62 (m, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 7.2 Hz, 3H), 1.34 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 160.4, 158.0 (d, *J* = 296.7 Hz), 131.7, 131.4, 131.1, 129.4, 128.3 (q, *J* = 3.5 Hz), 126.4, 125.6 (q, *J* = 3.9 Hz), 123.5 (q, *J* = 273.7 Hz), 109.3, 62.8, 62.1, 13.9, 13.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.99; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{14}F_3NO_5$: 380.0716, Found: 380.0726 ($M+Na^+$); IR (neat, cm^{-1}): υ 2987, 1730, 1306, 1227, 1119, 1070, 693.



4o

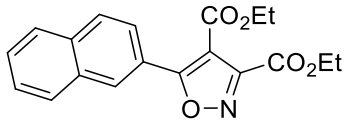
diethyl 5-(o-tolyl)isoxazole-3,4-dicarboxylate (**4o**). Colorless liquid (85 mg, 56% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.35 – 7.25 (m, 2H), 4.50 (q, *J* = 7.1 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.31 (s, 3H), 1.45 (t, *J* = 7.1 Hz, 3H),

1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 160.0, 159.8, 155.7, 137.8, 131.2, 130.5, 130.2, 125.5, 125.4, 110.1, 62.7, 61.4, 19.8, 13.9, 13.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_5$: 326.0999, Found: 326.0989 ($M+Na^+$); IR (neat, cm^{-1}): υ 2984, 1730, 1446, 1219, 1070, 757.



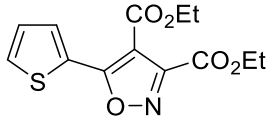
4p

diethyl 5-(2-methoxyphenyl)isoxazole-3,4-dicarboxylate (**4p**). Yellow liquid (54 mg, 34% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.54 – 7.45 (m, 1H), 7.11 – 7.04 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 161.0, 159.5, 156.6, 155.1, 132.9, 130.1, 120.5, 115.0, 111.1, 111.0, 62.4, 61.2, 55.2, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_6$: 342.0948, Found: 342.0947 ($M+Na^+$); IR (neat, cm^{-1}): υ 2983, 1732, 1466, 1213, 1047, 755.



4q

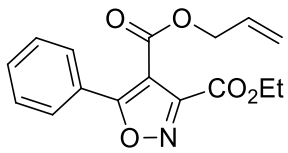
diethyl 5-(naphthalen-2-yl)isoxazole-3,4-dicarboxylate (**4q**). Light yellow liquid (115 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 7.97 – 7.88 (m, 3H), 7.85 (d, *J* = 7.8 Hz, 1H), 7.60 – 7.58 (m, 2H), 4.49 (q, *J* = 7.1 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.44 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.9, 159.8, 156.4, 134.4, 132.4, 129.4, 129.0, 128.4, 128.1, 127.7, 126.9, 124.2, 122.8, 108.5, 62.6, 61.8, 13.9, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{17}NO_5$: 362.0999, Found: 362.0994 ($M+Na^+$); IR (neat, cm^{-1}): υ 2983, 1729, 1315, 1216, 1104, 1069, 750.



4r

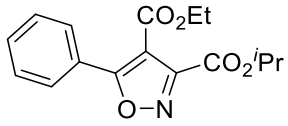
diethyl 5-(thiophen-2-yl)isoxazole-3,4-dicarboxylate (**4r**). Yellow liquid (71 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 3.8, 0.7 Hz, 1H), 7.67 (dd, *J* = 5.0, 0.7 Hz, 1H), 7.20 (dd, *J* = 4.8, 4.1 Hz, 1H), 4.47 (q, *J* = 7.1 Hz, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 160.4, 159.9, 156.5, 132.4, 132.0, 127.9, 126.4, 105.8, 62.7, 61.6,

13.9, 13.9; HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{13}NO_5S$: 318.0407, Found: 318.0410 ($M+Na^+$); IR (neat, cm^{-1}): υ 2983, 1720, 1586, 1474, 1212, 1101, 1045, 853, 715.



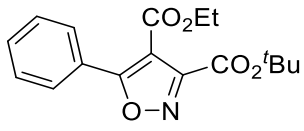
4s

4-allyl 3-ethyl 5-phenylisoxazole-3,4-dicarboxylate (**4s**). Colorless liquid (75 mg, 50% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.89 (m, 2H), 7.59 – 7.44 (m, 3H), 5.99 – 5.89 (m, 1H), 5.32 (ddd, *J* = 13.8, 11.4, 1.1 Hz, 2H), 4.78 (d, *J* = 5.8 Hz, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 160.5, 159.7, 156.2, 131.8, 131.0, 128.7, 128.5, 125.6, 119.2, 108.1, 66.4, 62.7, 13.9; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}NO_5$: 324.0842, Found: 324.0844 ($M+Na^+$); IR (neat, cm^{-1}): υ 2986, 1729, 1470, 1215, 1114, 1068, 762, 689.



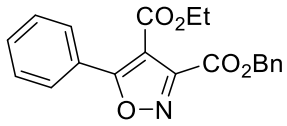
5a

4-ethyl 3-isopropyl 5-phenylisoxazole-3,4-dicarboxylate (**5a**). Colorless liquid (120 mg, 79% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.89 (m, 2H), 7.59 – 7.44 (m, 3H), 5.41 – 5.23 (m, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.43 (s, 3H), 1.42 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.9, 159.3, 156.4, 131.6, 128.6, 128.4, 125.7, 108.4, 70.8, 61.8, 21.6, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{17}NO_5$: 326.0999, Found: 326.0994 ($M+Na^+$); IR (neat, cm^{-1}): υ 2984, 1730, 1470, 1224, 1104, 1069, 762, 690.



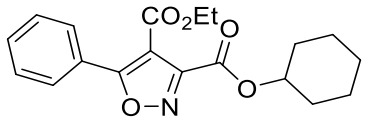
5b

3-(tert-butyl) 4-ethyl 5-phenylisoxazole-3,4-dicarboxylate (**5b**). Colorless liquid (106 mg, 67% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.92 (m, 2H), 7.72 – 7.31 (m, 3H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.64 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 161.0, 158.6, 157.0, 131.6, 128.6, 128.4, 125.8, 108.2, 84.4, 61.7, 27.8, 13.9; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{19}NO_5$: 340.1155, Found: 340.1153 ($M+Na^+$); IR (neat, cm^{-1}): υ 2981, 1729, 1273, 1154, 1070, 843, 766, 690.



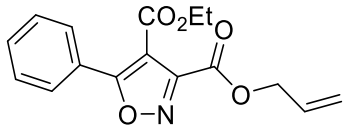
5c

3-benzyl 4-ethyl 5-phenylisoxazole-3,4-dicarboxylate (**5c**). Colorless liquid (95 mg, 54% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.90 (m, 2H), 7.55 – 7.43 (m, 5H), 7.42 – 7.28 (m, 4H), 5.43 (s, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 160.7, 159.6, 156.0, 134.5, 131.7, 128.6, 128.6, 128.5, 128.4, 125.6, 108.4, 68.1, 61.8, 13.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{17}NO_5$: 374.0999, Found: 374.1001 ($M+Na^+$); IR (neat, cm^{-1}): υ 2983, 1730, 1470, 1207, 1116, 1068, 692.



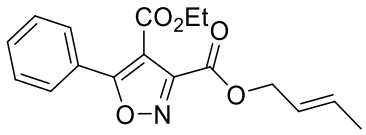
5d

3-cyclohexyl 4-ethyl 5-phenylisoxazole-3,4-dicarboxylate (**5d**). Light yellow solid (127 mg, 74% yield), m. p. 62.6–63.7 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.86 (m, 2H), 7.63 – 7.41 (m, 3H), 5.23 – 5.01 (m, 1H), 4.34 (qd, *J* = 7.1, 1.3 Hz, 2H), 2.11 – 1.93 (m, 2H), 1.87 – 1.74 (m, 2H), 1.68 – 1.53 (m, 3H), 1.50 – 1.37 (m, 2H), 1.37 – 1.22 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.9, 159.2, 156.5, 131.6, 128.6, 128.4, 125.7, 108.4, 75.6, 61.8, 31.3, 25.1, 23.5, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{21}NO_5$: 366.1312, Found: 366.1311 ($M+Na^+$); IR (neat, cm^{-1}): υ 2935, 1726, 1468, 1223, 1116, 1074, 755, 692.



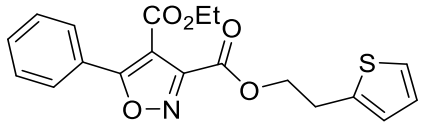
5e

3-allyl 4-ethyl 5-phenylisoxazole-3,4-dicarboxylate (**5e**). Colorless liquid (62 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 2H), 7.59 – 7.45 (m, 3H), 6.13 – 5.94 (m, 1H), 5.46 (ddd, *J* = 17.2, 2.8, 1.4 Hz, 1H), 5.35 (ddd, *J* = 10.4, 2.3, 1.1 Hz, 1H), 4.90 (dt, *J* = 5.9, 1.3 Hz, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 160.8, 159.4, 156.0, 131.8, 130.8, 128.7, 128.4, 125.6, 119.7, 108.4, 67.0, 61.8, 13.8; HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{15}NO_5$: 324.0842, Found: 324.0849 ($M+Na^+$); IR (neat, cm^{-1}): υ 2986, 1730, 1471, 1315, 1208, 1116, 1068, 763, 689.



5f

(E)-3-(but-2-en-1-yl) 4-ethyl 5-phenylisoxazole-3,4-dicarboxylate (**5f**). Colorless liquid (76 mg, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.88 (m, 2H), 7.59 – 7.44 (m, 3H), 6.00 – 5.85 (m, 1H), 5.77 – 5.64 (m, 1H), 4.83 (dd, *J* = 6.7, 0.7 Hz, 2H), 4.34 (qd, *J* = 7.1, 0.5 Hz, 2H), 1.76 (d, *J* = 6.5 Hz, 3H), 1.32 (td, *J* = 7.1, 0.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 160.8, 159.5, 156.1, 133.0, 131.7, 128.6, 128.4, 125.6, 123.8, 108.4, 67.2, 61.8, 17.7, 13.7; HRMS (ESI-TOF): Anal. Calcd. For $C_{17}H_{17}NO_5$: 338.0999, Found: 338.1004 ($M+Na^+$); IR (neat, cm^{-1}): υ 2982, 1730, 1471, 1206, 1116, 1067, 965, 763, 689.



5g

4-ethyl 3-(2-(thiophen-2-yl)ethyl) 5-phenylisoxazole-3,4-dicarboxylate (**5g**). Light yellow liquid (124 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.87 (m, 2H), 7.56 – 7.41 (m, 3H), 7.15 (dd, *J* = 4.9, 1.3 Hz, 1H), 6.97 – 6.86 (m, 2H), 4.60 (t, *J* = 6.9 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.30 (t, *J* = 6.9 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 160.5, 159.5, 155.9, 138.7, 131.6, 128.5, 128.3, 126.8, 125.7, 125.4, 124.0, 108.3, 66.4, 61.7, 28.7, 13.6; HRMS (ESI-TOF): Anal. Calcd. For $C_{19}H_{17}NO_5S$: 394.0720, Found: 394.0724 ($M+Na^+$); IR (neat, cm^{-1}): υ 2980, 2920, 1730, 1447, 1220, 1116, 1070, 763, 689.

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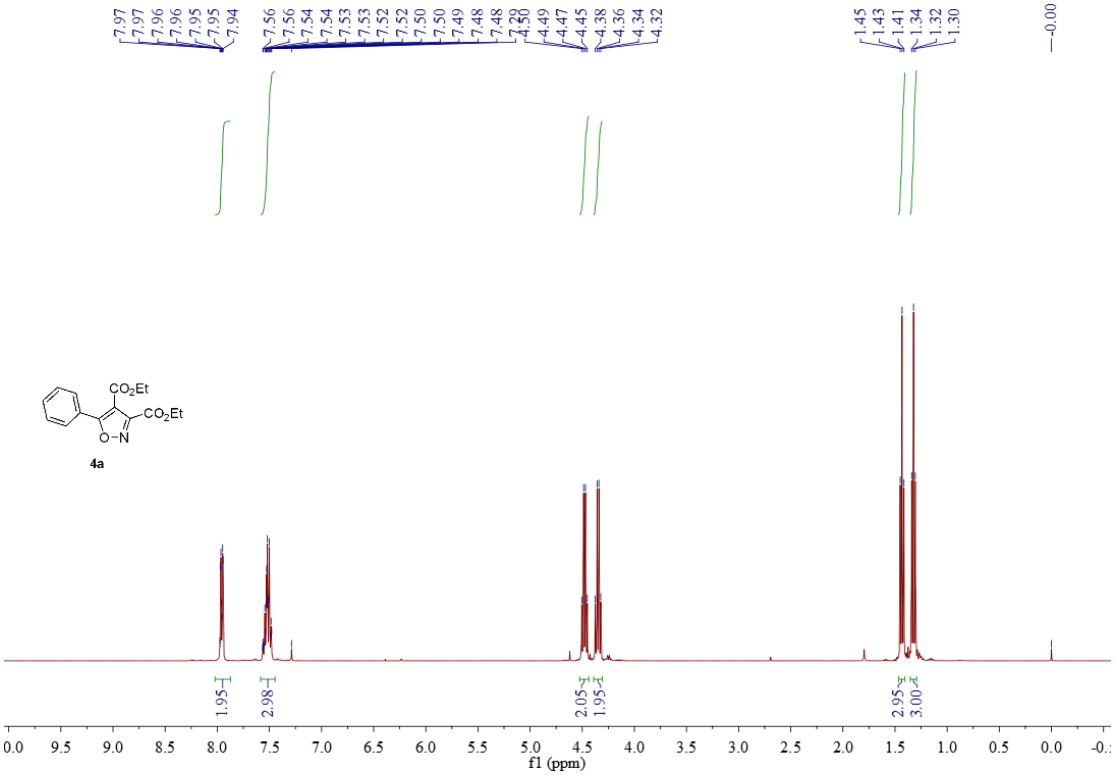
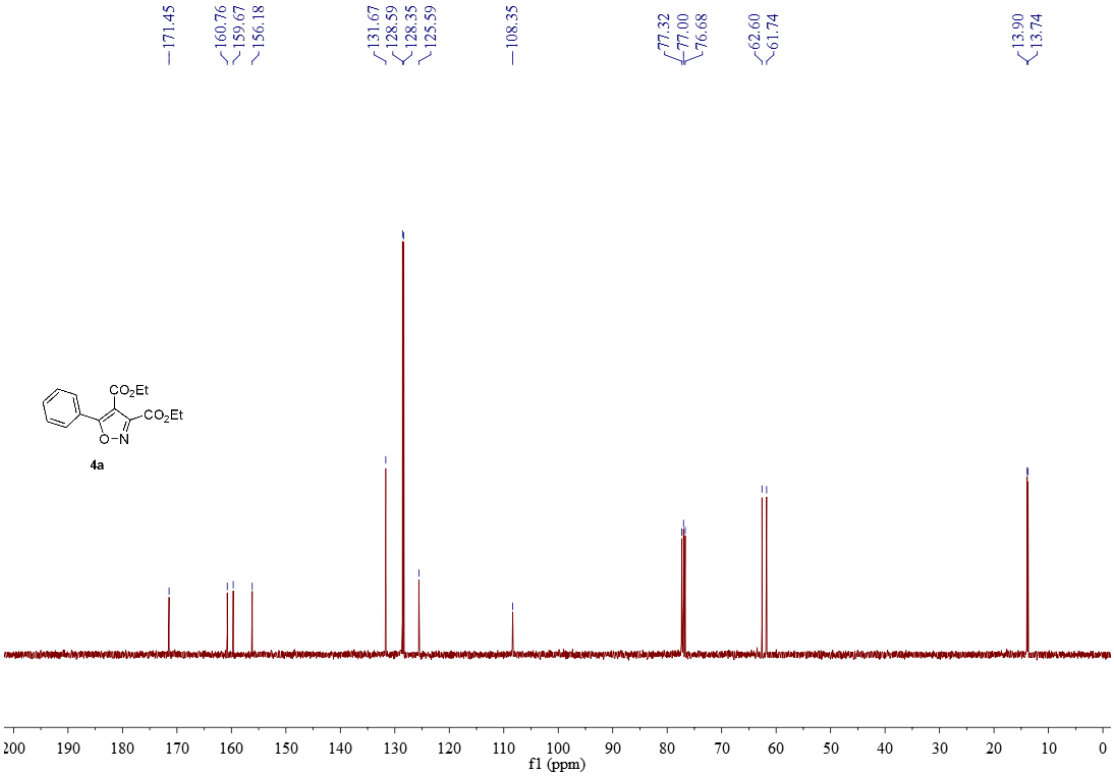
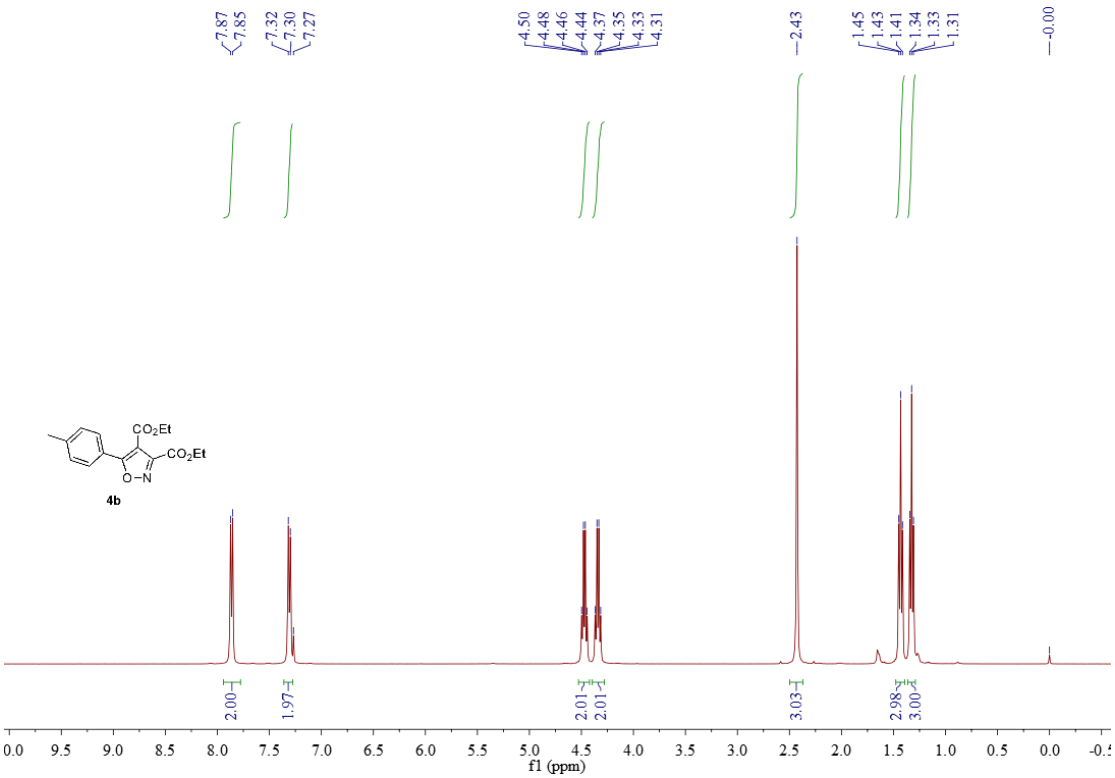
NMR spectroscopic data for products



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1.33
1.31
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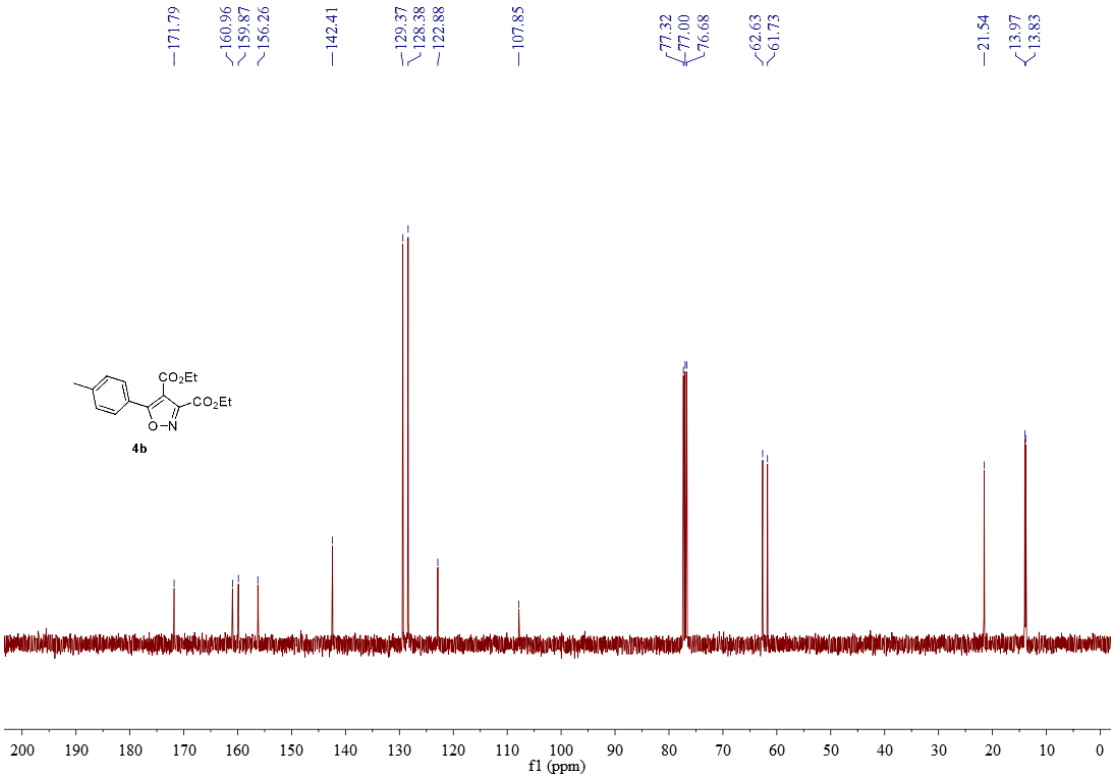
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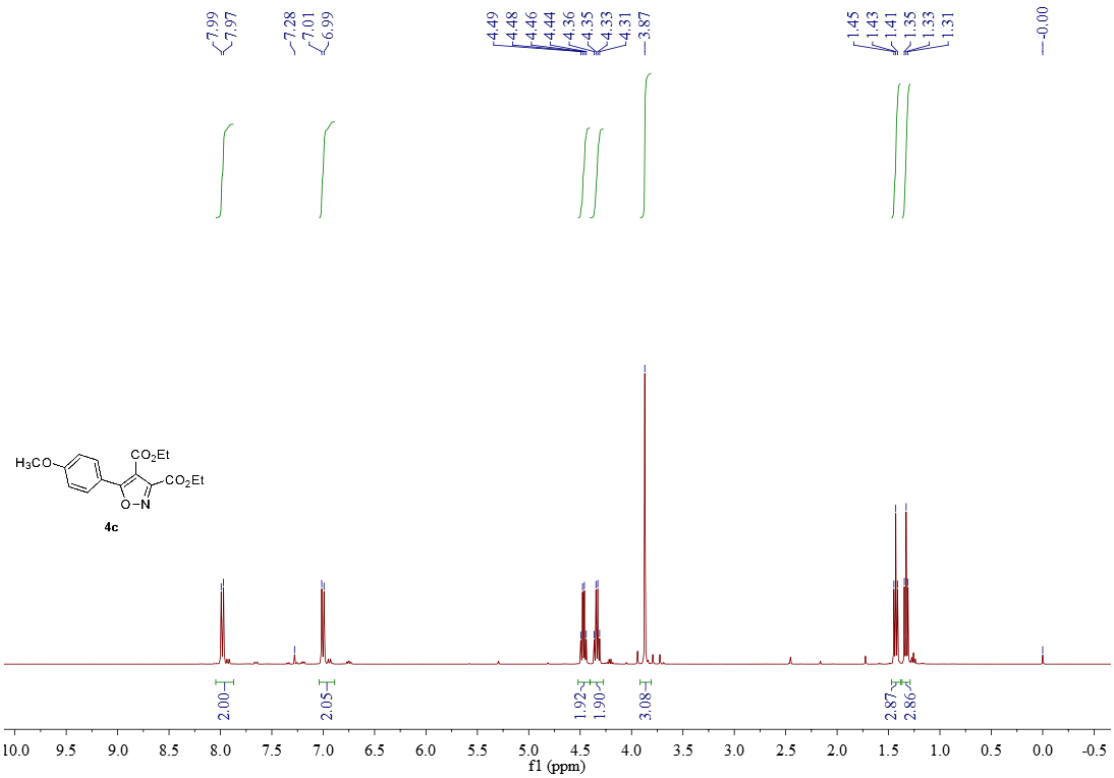
f1 (ppm)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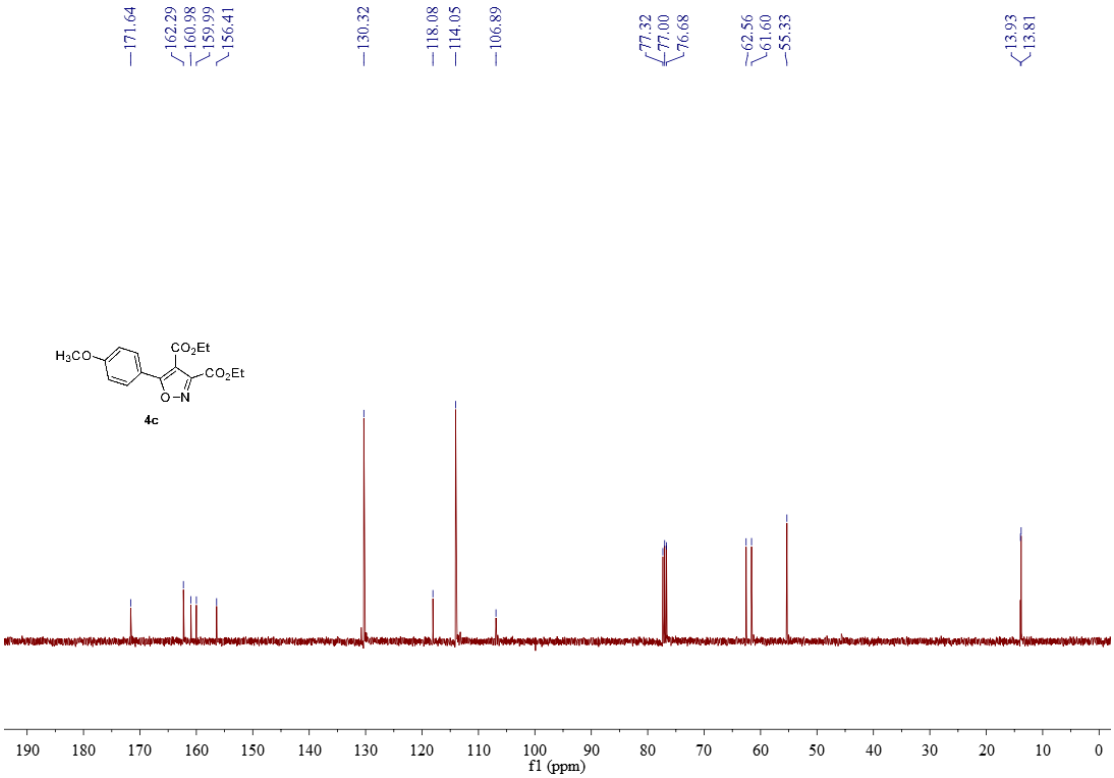
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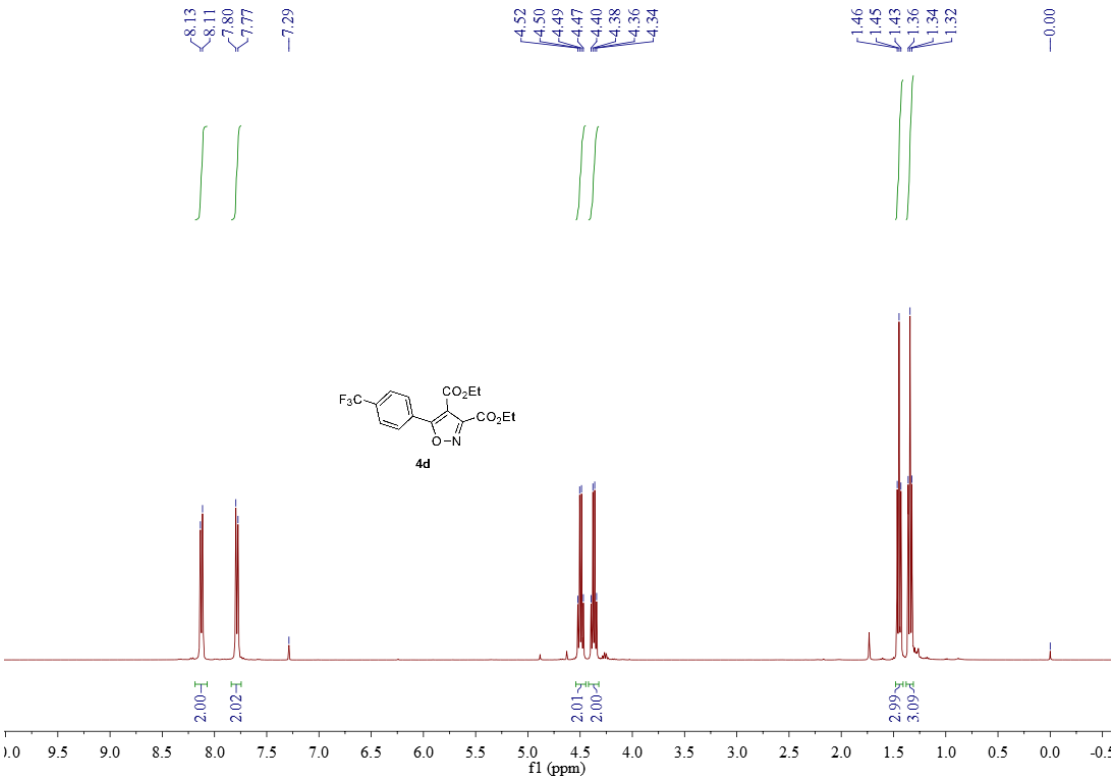
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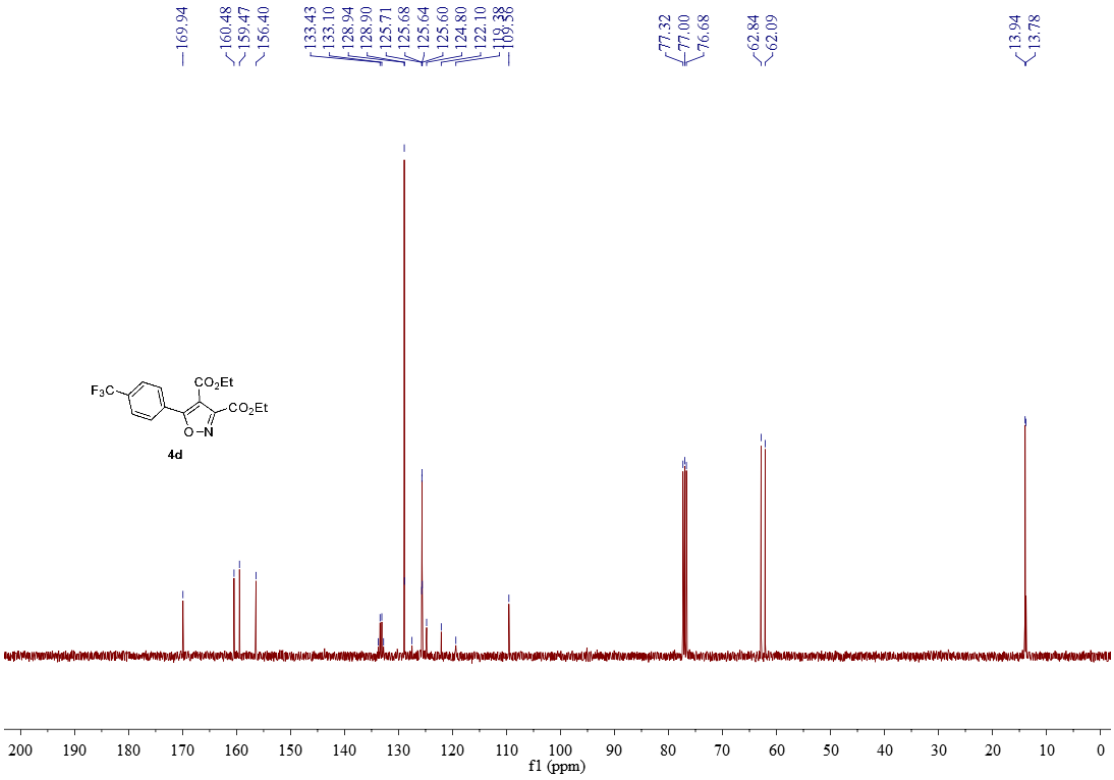
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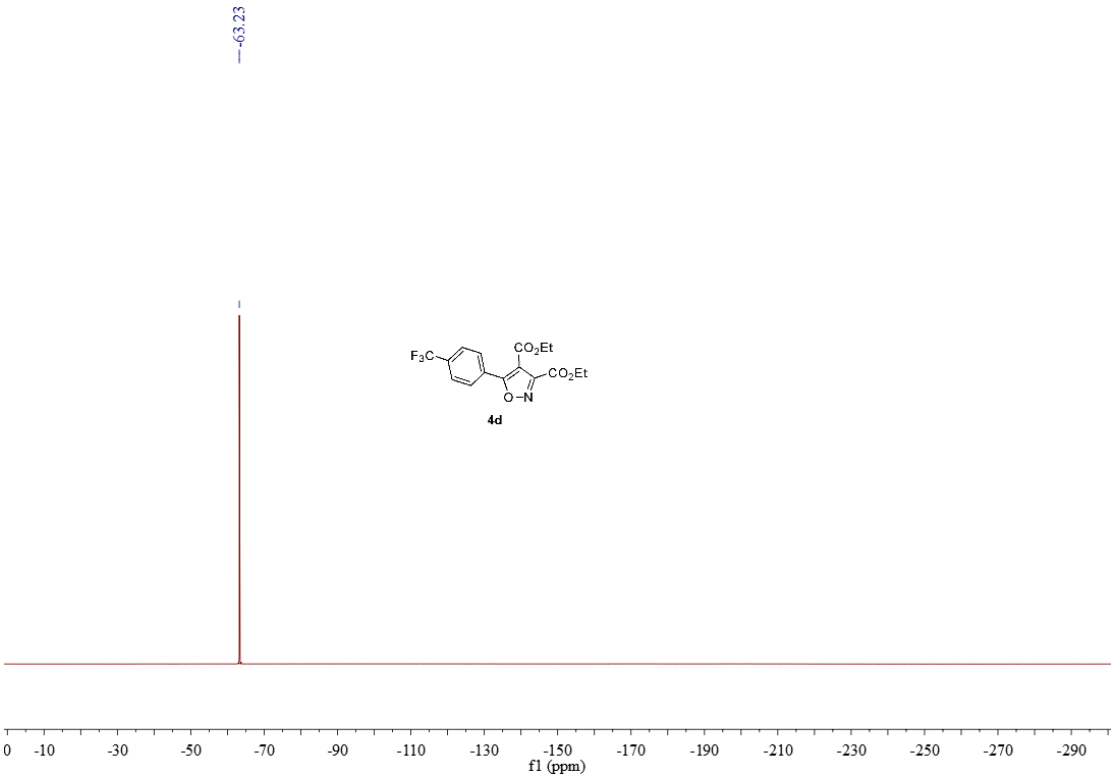
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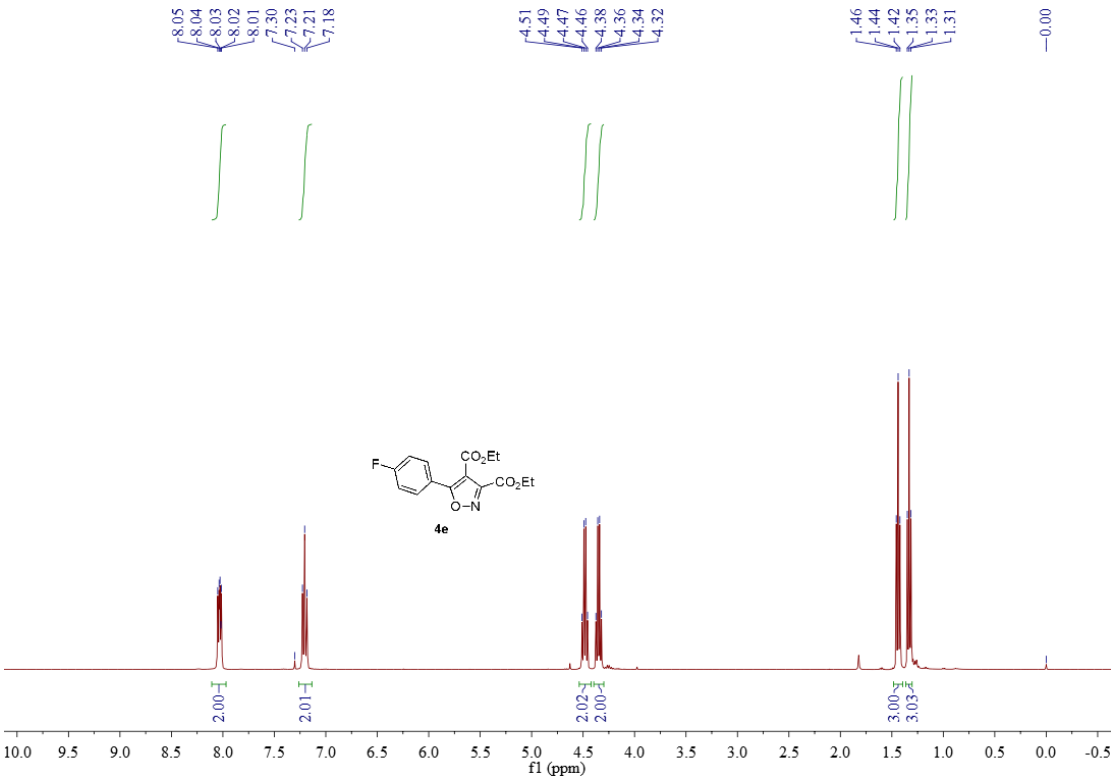
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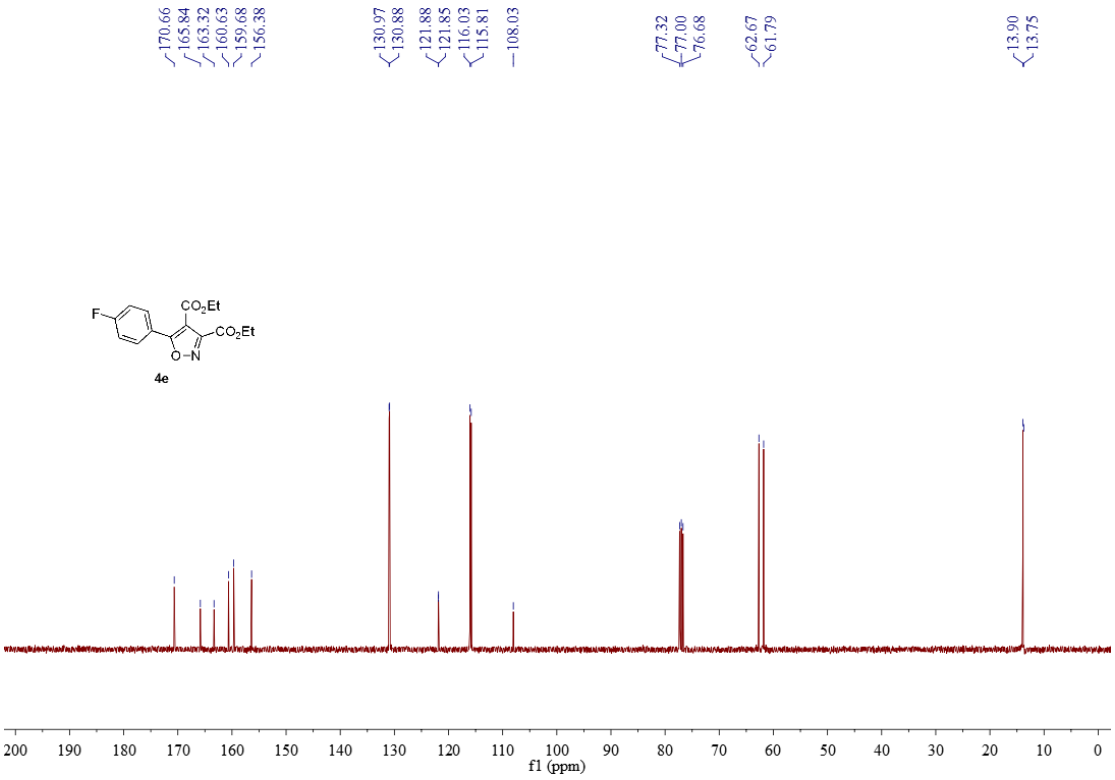
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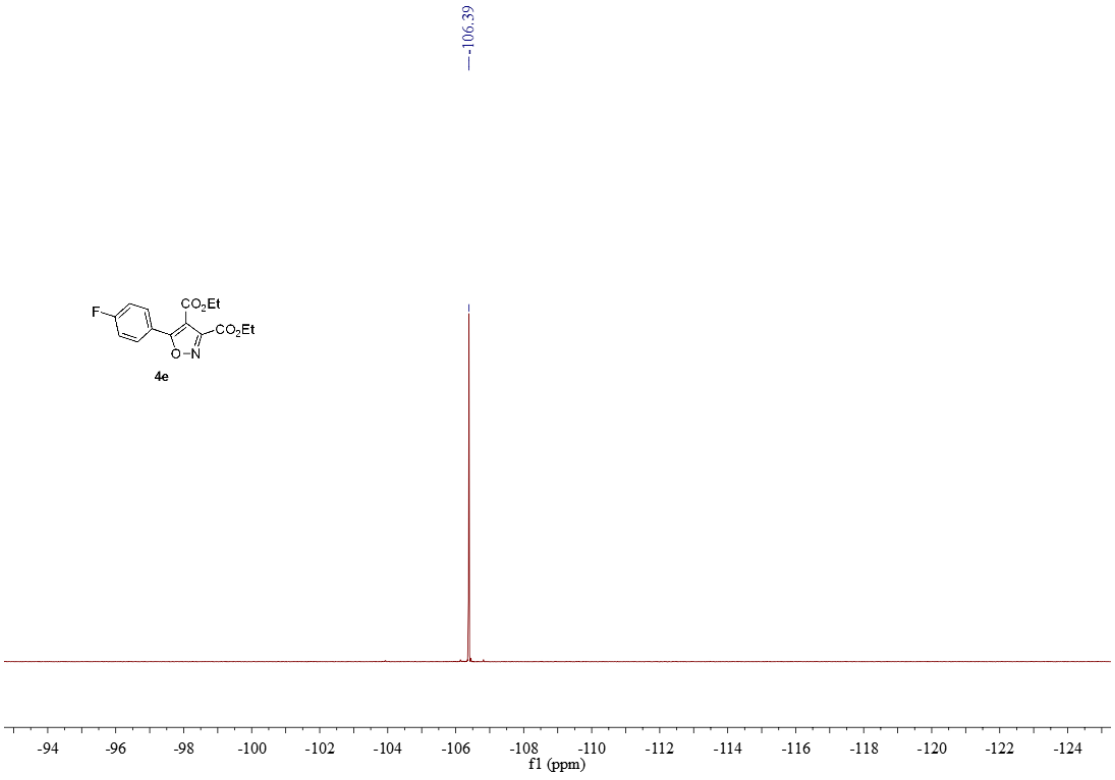
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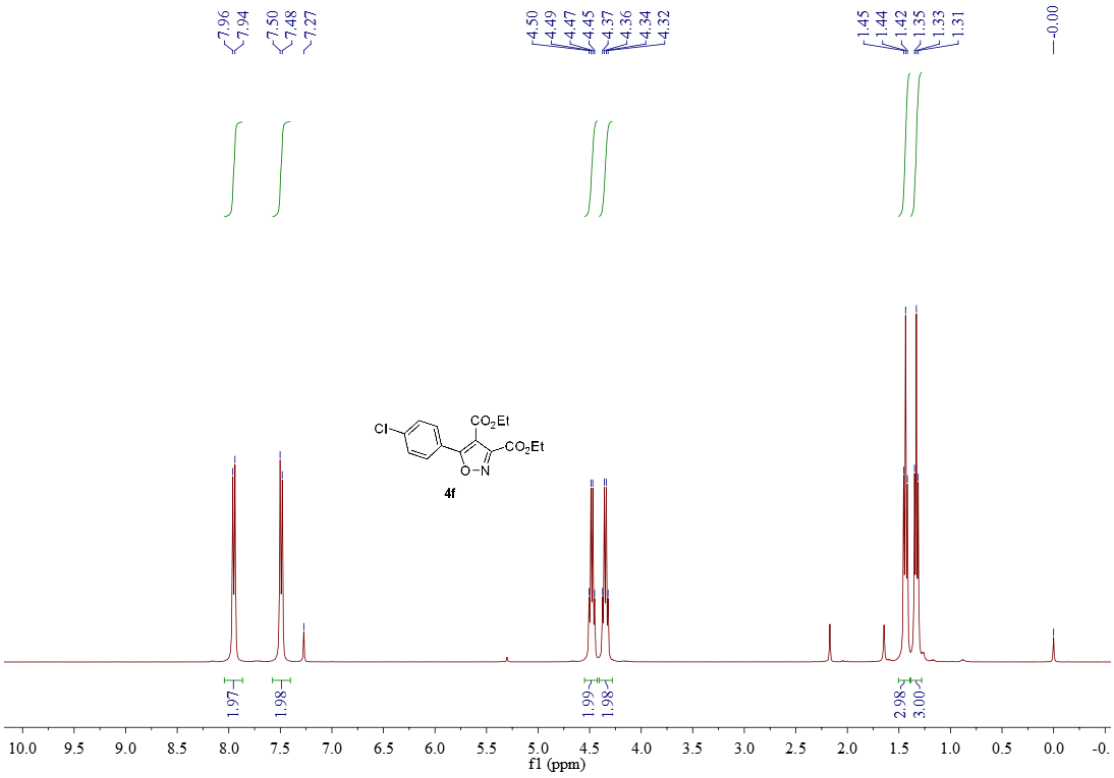
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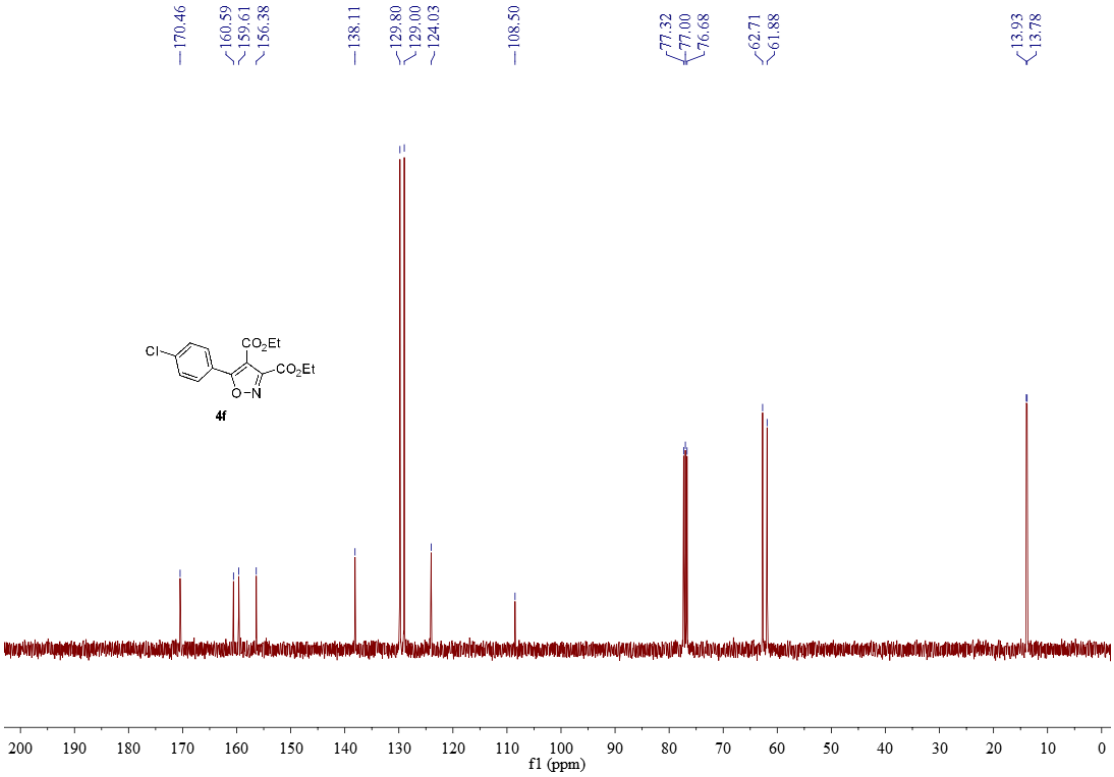
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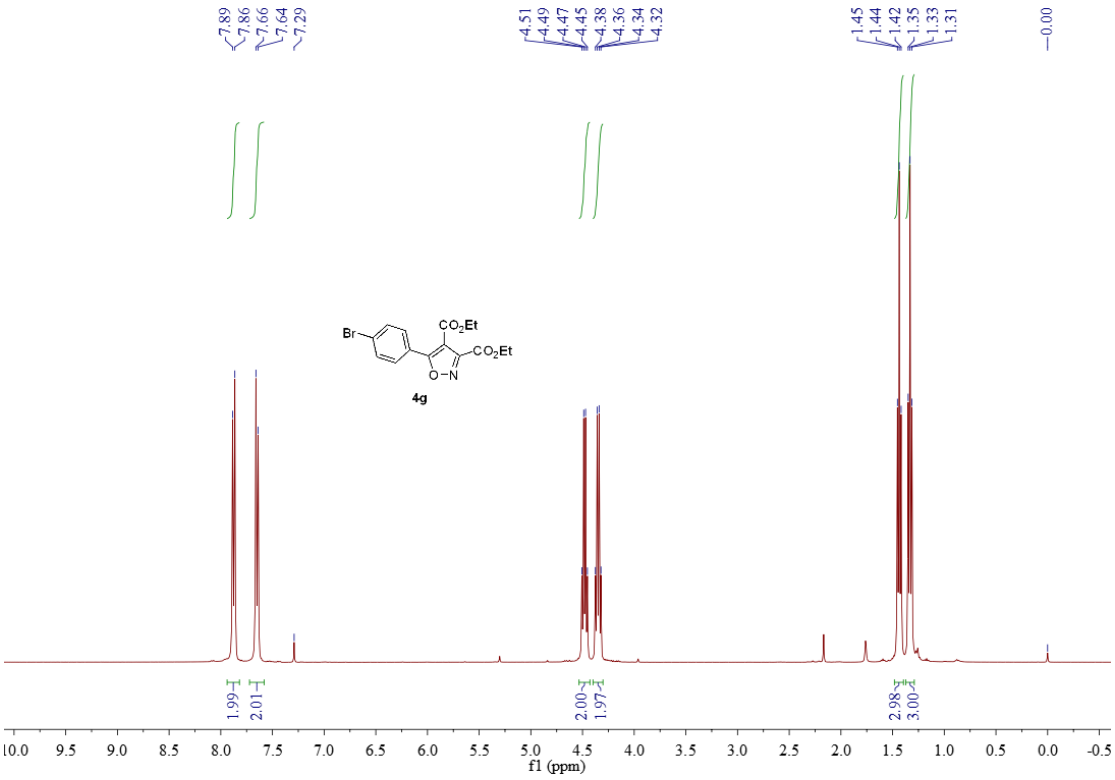
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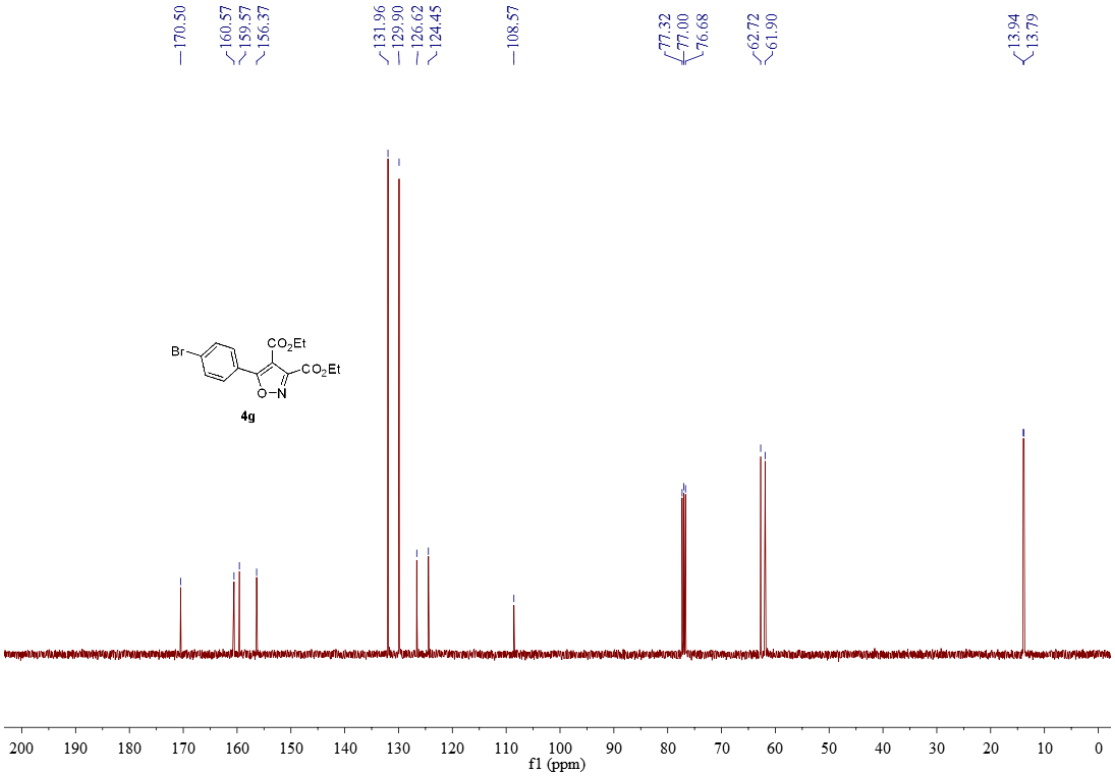
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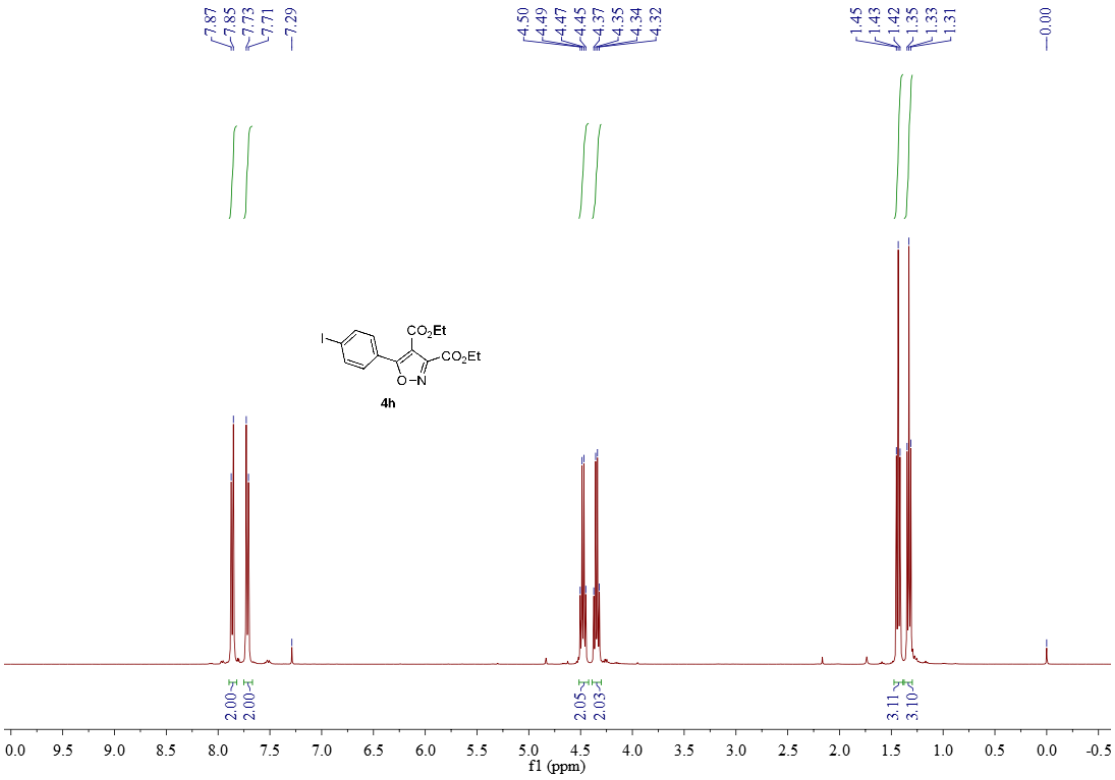
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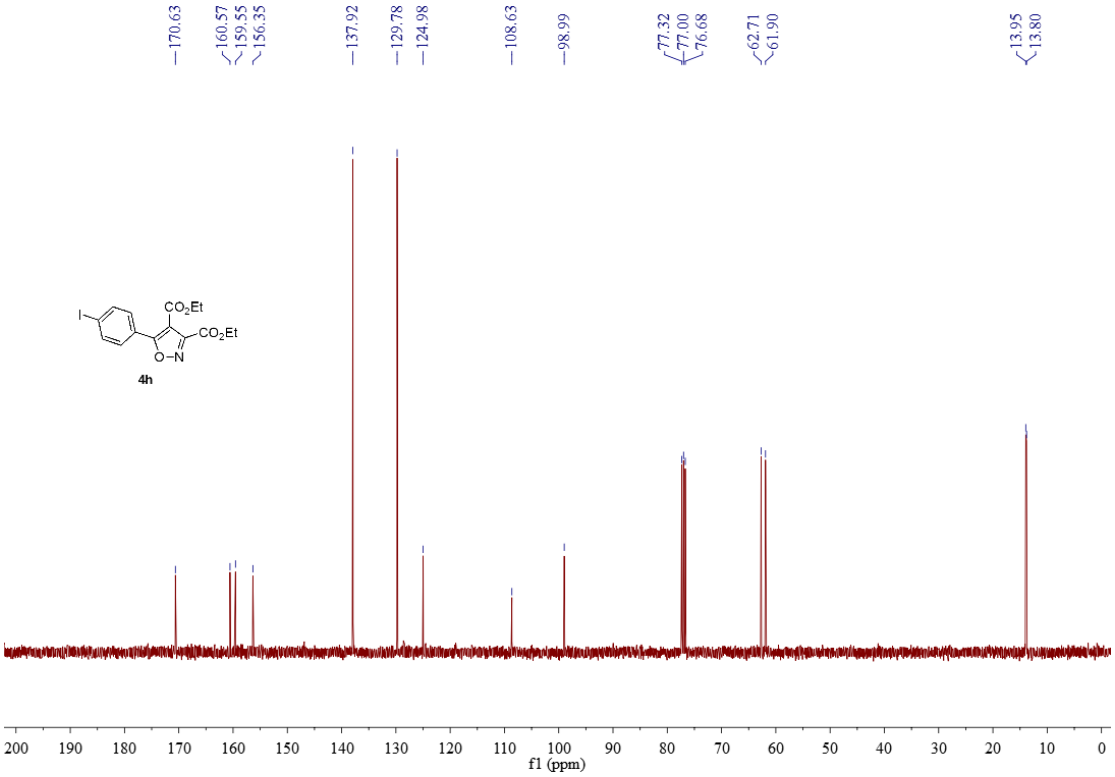
3.10
f1 (ppm)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159.55
156.35
137.92
129.78
124.98
108.63
98.99
77.32
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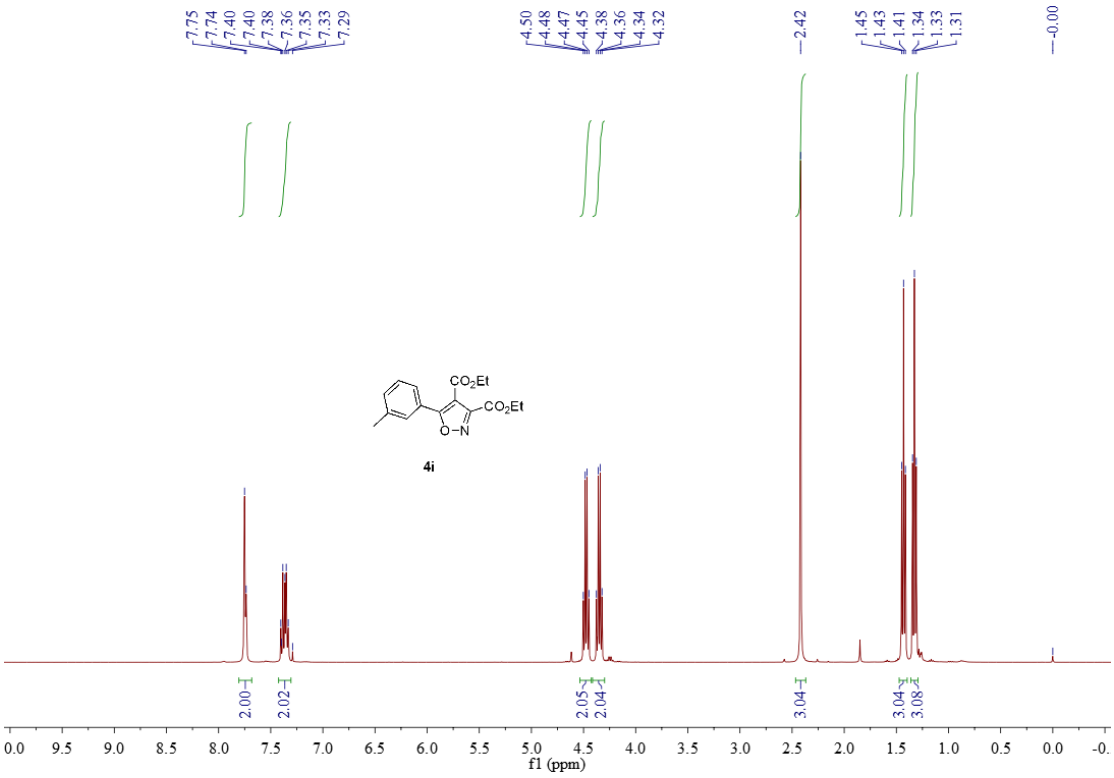
76.68
62.71
61.90
13.95
13.80
CO2Et
CO2Et
I
O–N
4h
f1 (ppm)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7.74
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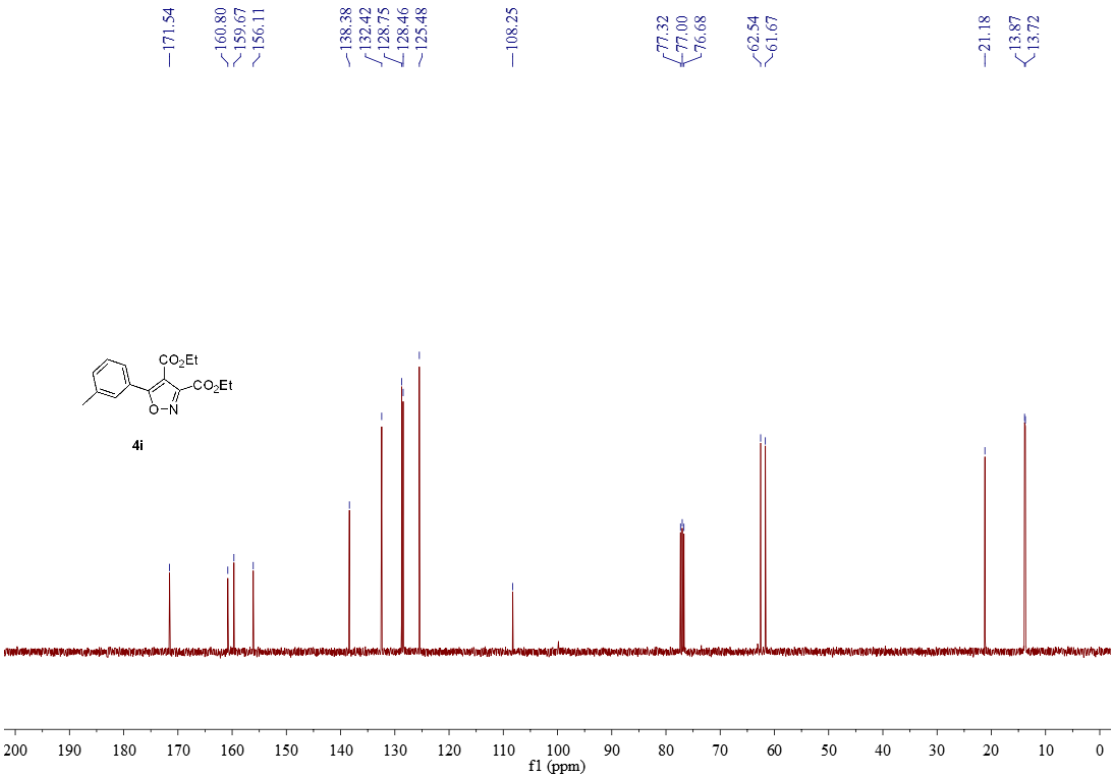
7.36
7.35
7.33
7.29
4.50
4.48
4.47
4.45
4.38
4.36
4.34
4.32
2.42
1.45
1.43
1.41
1.34
1.33
1.31
0.00
CO2Et
CO2Et
O–N
4i
2.00
2.02
2.05
2.04
3.04
3.04
3.08
f1 (ppm)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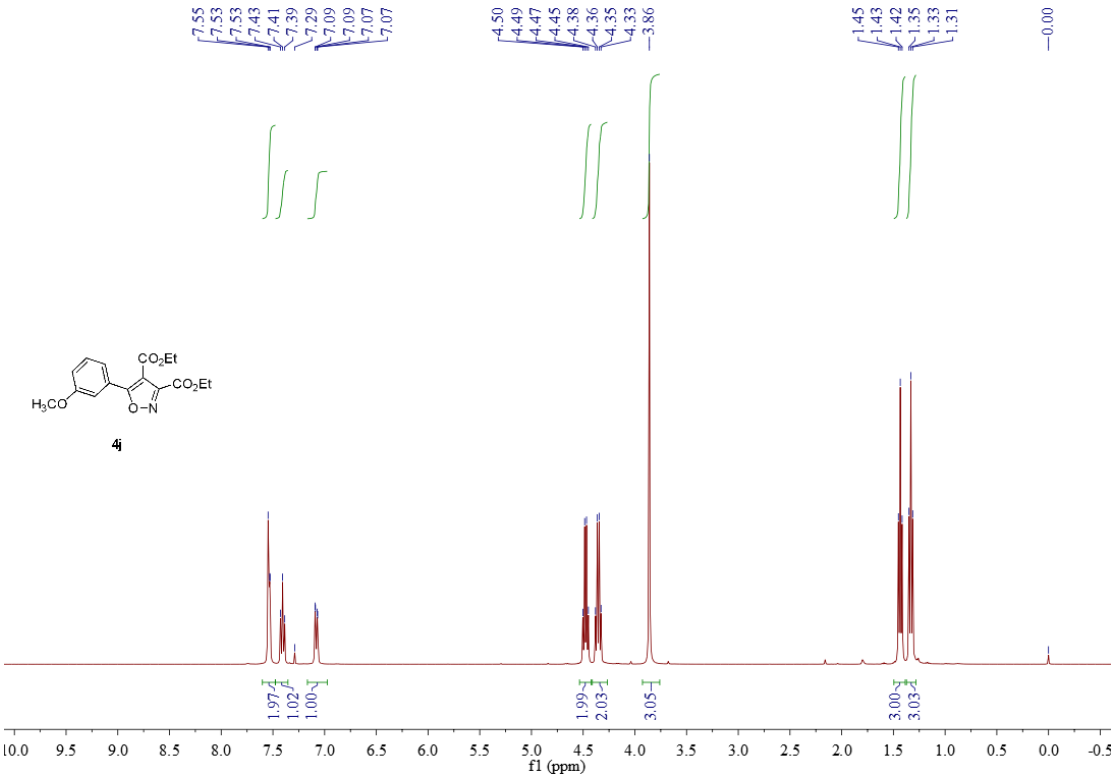
132.42
128.75
128.46
125.48
108.25
77.32
77.00
76.68
62.54
61.67
21.18
13.87
13.72
CO2Et
CO2Et
O–N
4i
f1 (ppm)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7.39
7.29
7.09
7.09
7.07
7.07
4.50
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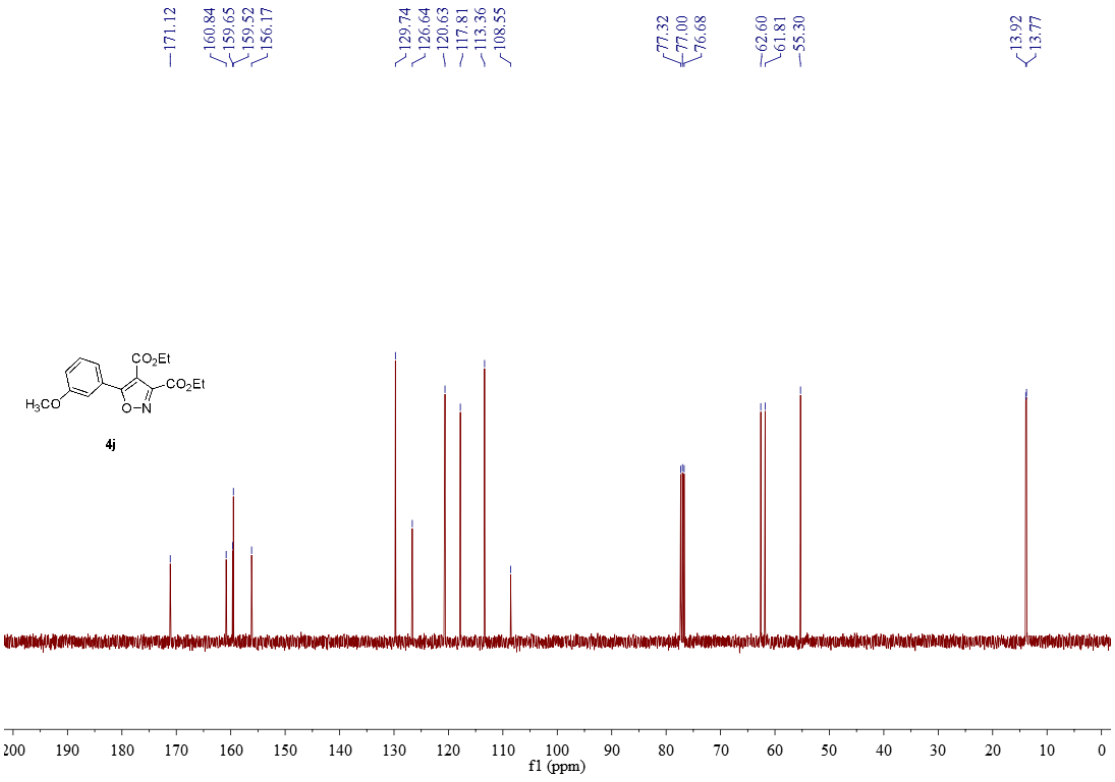
4.47
4.45
4.38
4.36
4.35
4.33
3.86
1.45
1.43
1.42
1.35
1.33
1.31
0.00
CO2Et
CO2Et
H3CO
O–N
4j
1.97
1.02
1.00
1.99
2.03
3.05
3.00
3.03
f1 (ppm)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120.63
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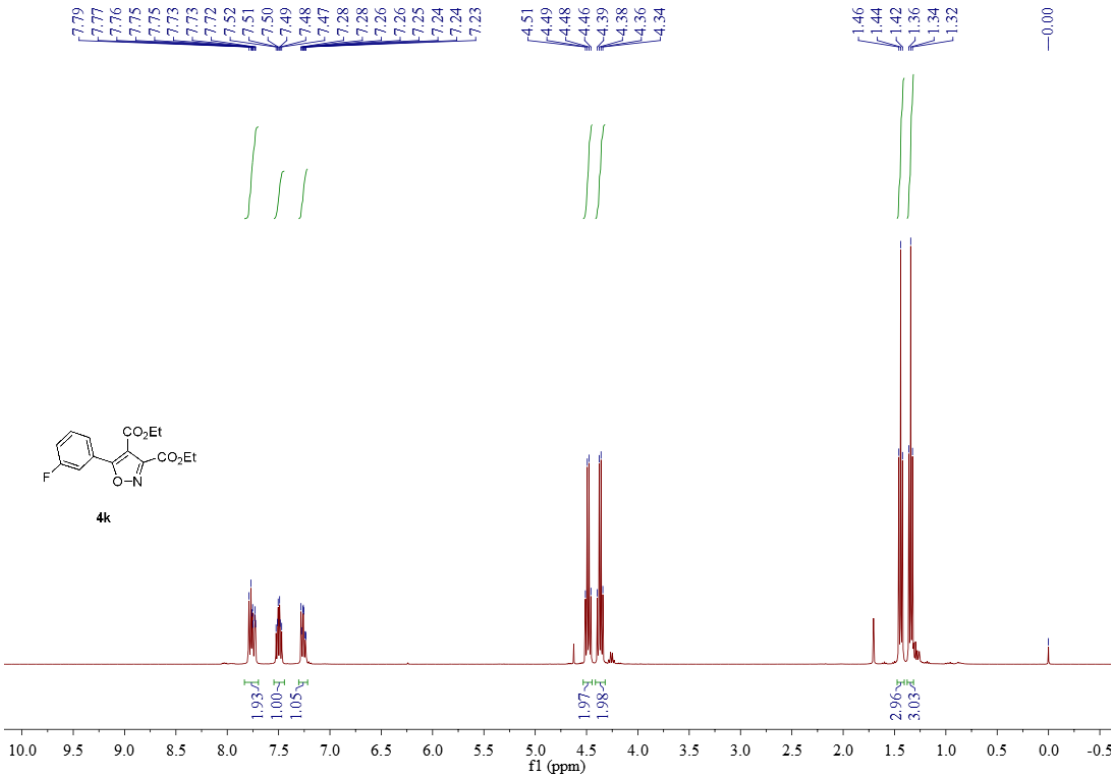
113.36
108.55
77.32
77.00
76.68
62.60
61.81
55.30
13.92
13.77
CO2Et
CO2Et
H3CO
O–N
4j
f1 (ppm)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7.77
7.76
7.75
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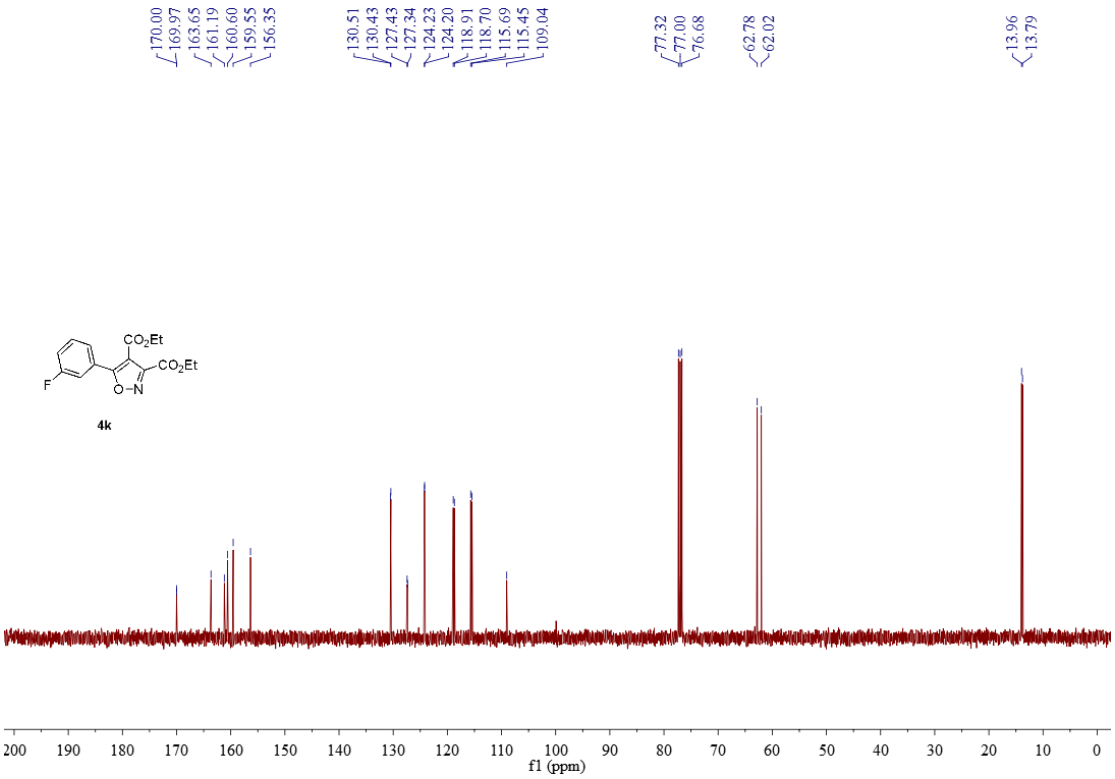
7.73
7.72
7.52
7.51
7.50
7.49
7.48
7.47
7.28
7.28
7.26
7.26
7.25
7.24
7.24
7.23
4.51
4.49
4.48
4.46
4.39
4.38
4.36
4.34
1.46
1.44
1.42
1.36
1.34
1.32
0.00
CO2Et
CO2Et
F
O
N
4k
1.93
1.00
1.05
1.97
1.98
2.96
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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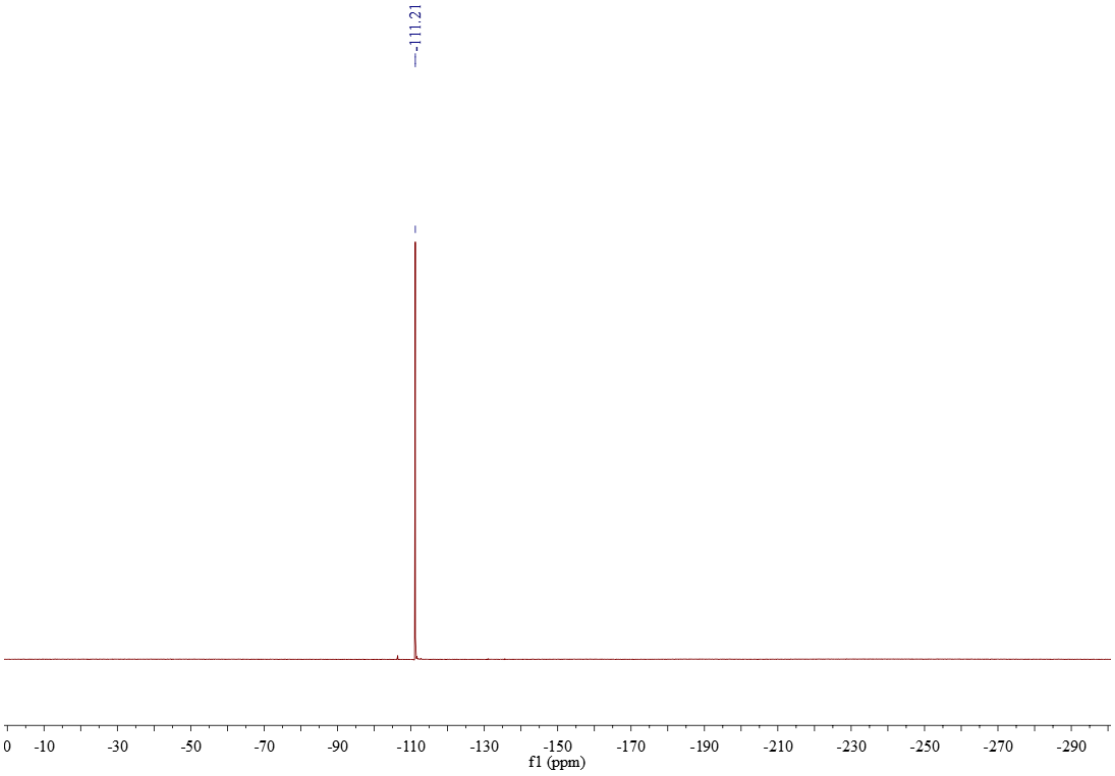
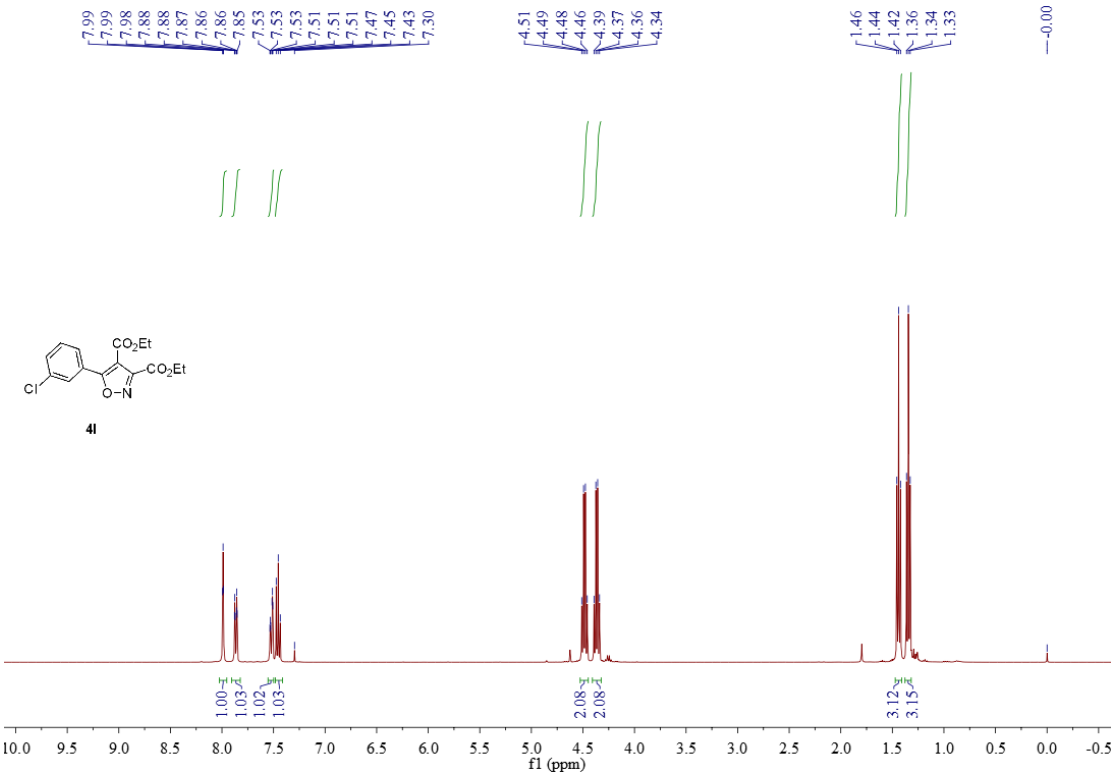
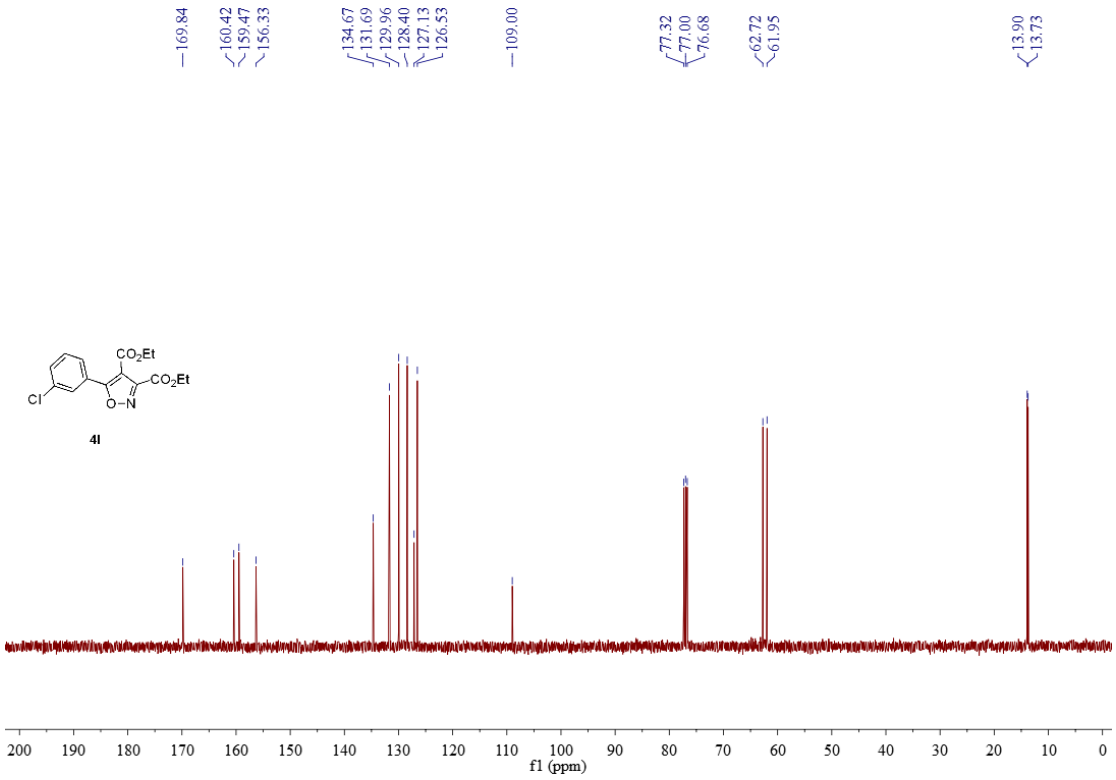
159.55
156.35
130.51
130.43
127.43
127.34
124.23
124.20
118.91
118.70
115.69
115.45
109.04
77.32
77.00
76.68
62.78
62.02
13.96
13.79
CO2Et
CO2Et
F
O
N
4k
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-111.21
0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)


7.99 7.99 7.98 7.88 7.88 7.87 7.86 7.86 7.85 7.53 7.53 7.53 7.51 7.51 7.51 7.47 7.45 7.43 7.30
4.51 4.49 4.48 4.46 4.39 4.37 4.36 4.34
1.46 1.44 1.42 1.36 1.34 1.33
0.00
CO2Et
CO2Et
Cl
O
N
4l
1.00 1.03 1.02 1.03
2.08 2.08
3.12 3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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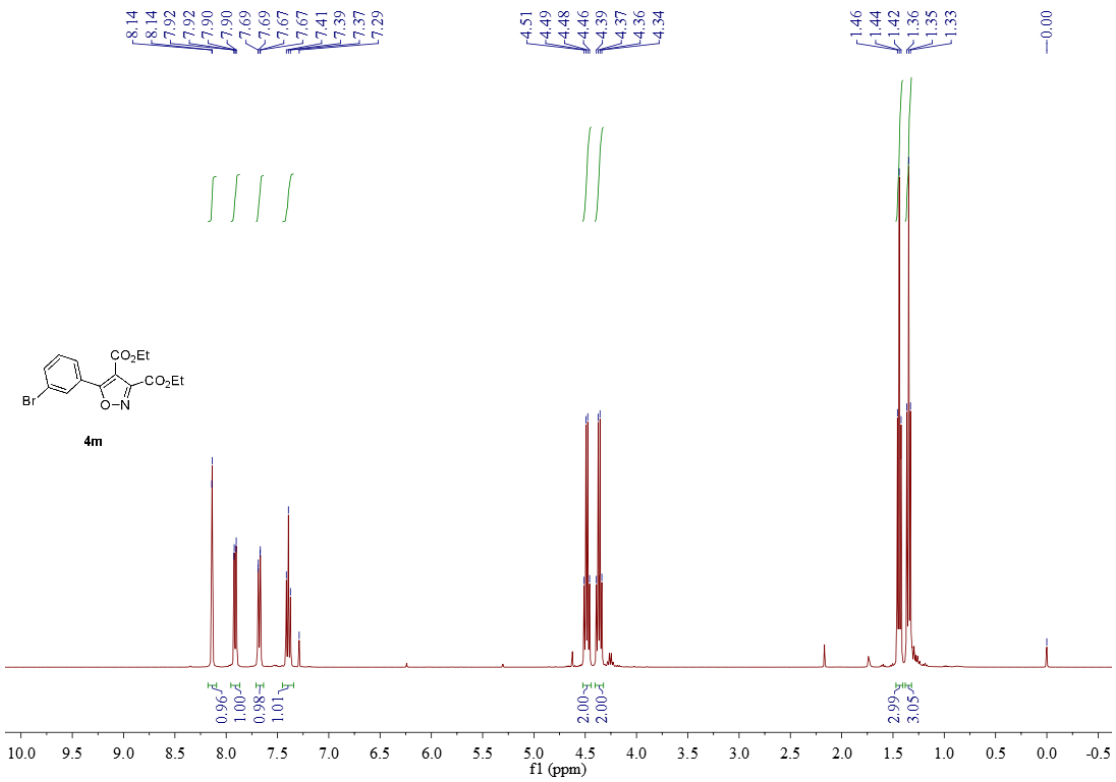
127.13
126.53
109.00
77.32
77.00
76.68
62.72
61.95
13.90
13.73
CO2Et
CO2Et
Cl
O–N
4l
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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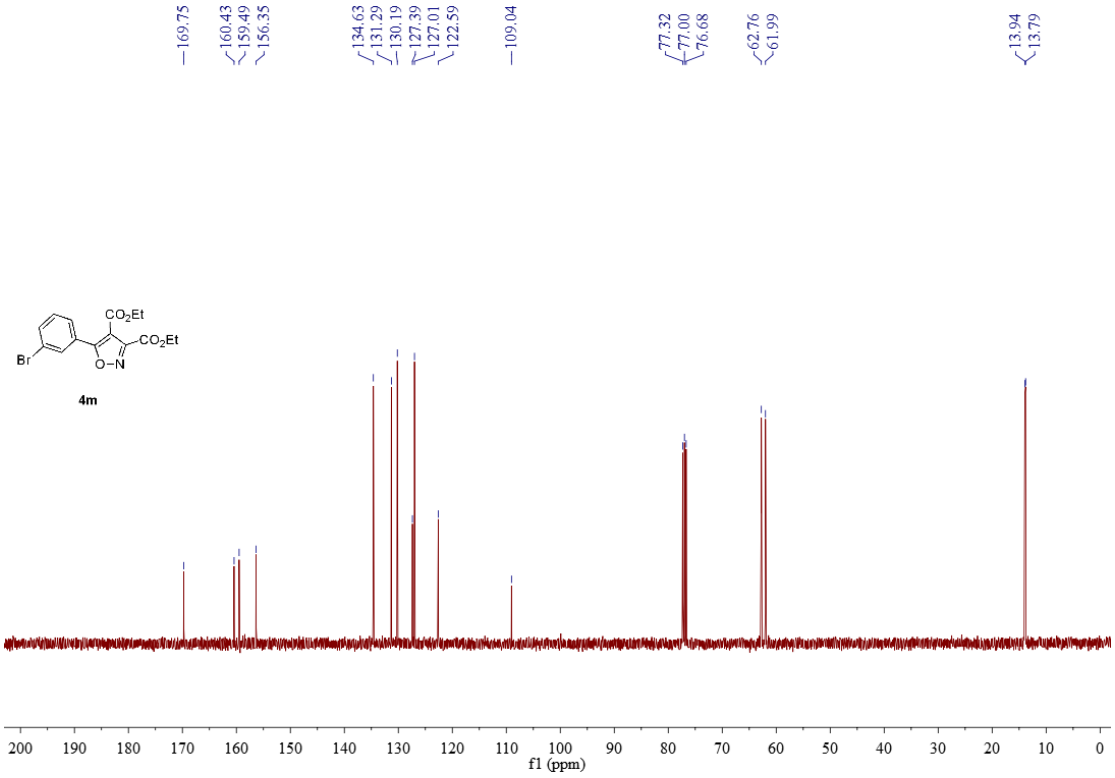
8.14
7.92
7.92
7.90
7.90
7.69
7.69
7.67
7.67
7.41
7.39
7.37
7.29
4.51
4.49
4.48
4.46
4.39
4.37
4.36
4.34
1.46
1.44
1.42
1.36
1.35
1.33
0.00
CO2Et
CO2Et
Br
O–N
4m
0.96
1.00
0.98
1.01
2.00
2.00
2.99
3.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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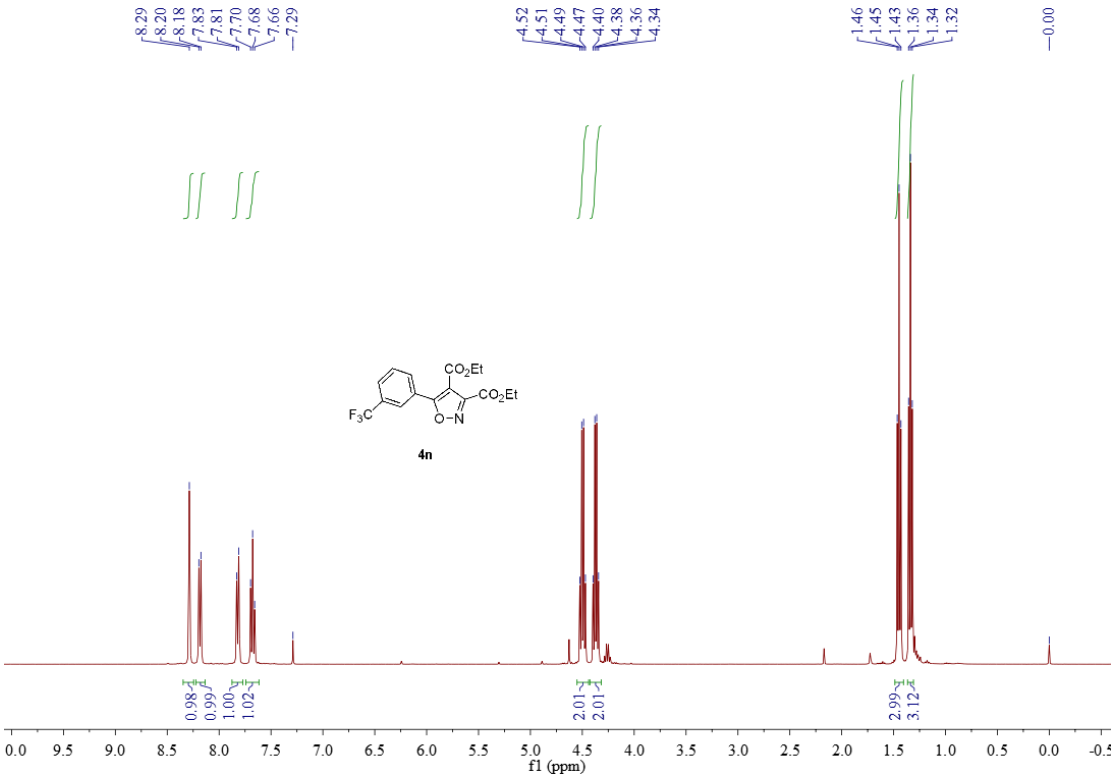
156.35
134.63
131.29
130.19
127.39
127.01
122.59
109.04
77.32
77.00
76.68
62.76
61.99
13.94
13.79
CO2Et
CO2Et
Br
O–N
4m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.81
7.70
7.68
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7.29
4.52
4.51
4.49
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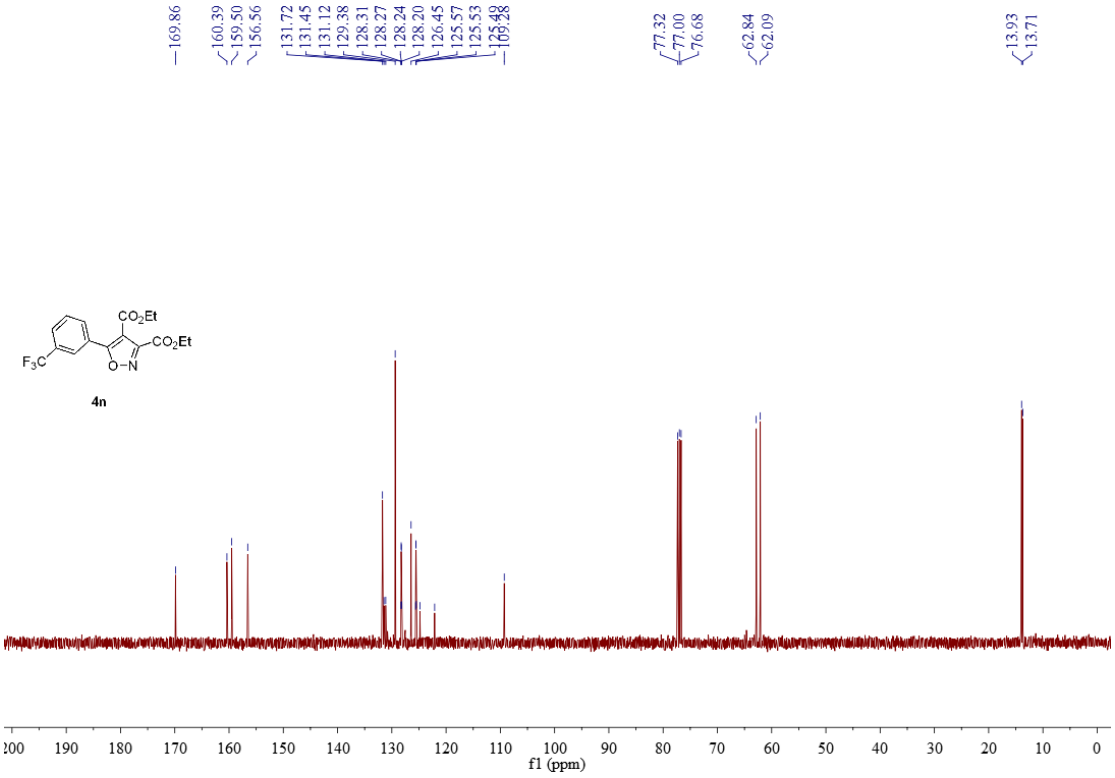
4.40
4.38
4.36
4.34
1.46
1.45
1.43
1.36
1.34
1.32
0.00
CO2Et
CO2Et
F3C
O–N
4n
0.98
0.99
1.00
1.02
2.01
2.01
2.99
3.12
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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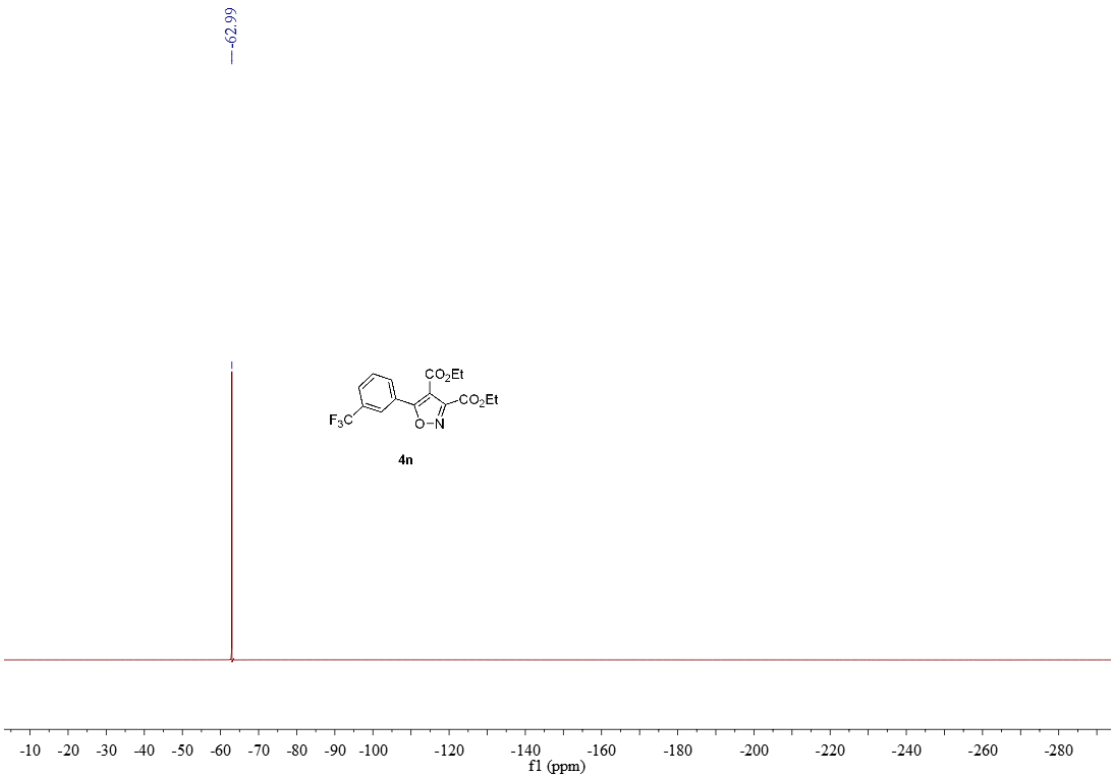
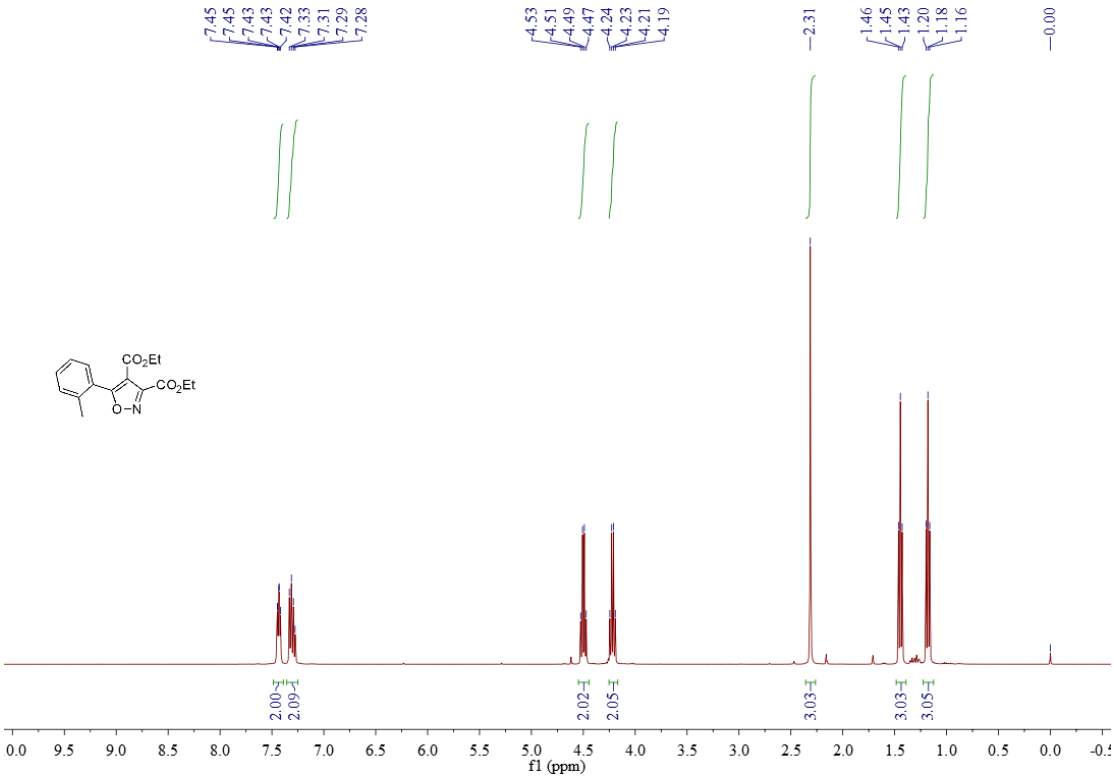
128.27
128.24
128.20
126.45
125.57
125.53
77.32
77.00
76.68
62.84
62.09
13.93
13.71
CO2Et
CO2Et
F3C
O–N
4n
f1 (ppm)


-62.99
CO2Et
CO2Et
F3C
O–N
4n
f1 (ppm)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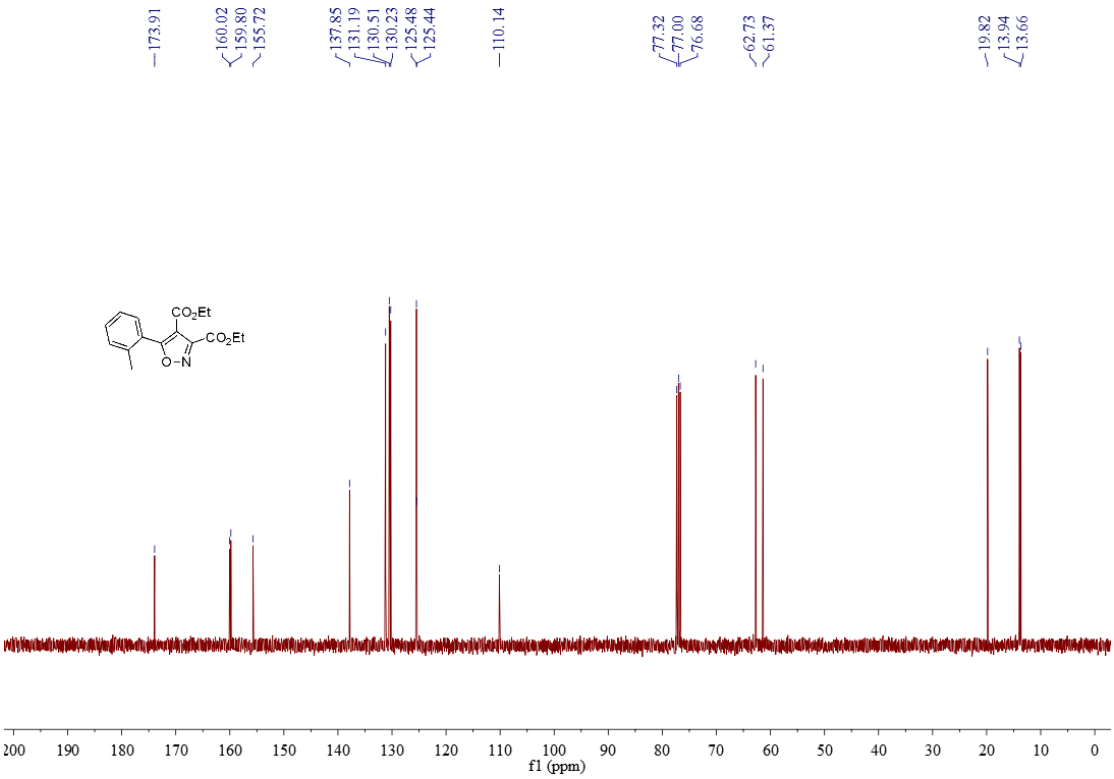
7.45
7.43
7.43
7.42
7.33
7.31
7.29
7.28
4.53
4.51
4.49
4.47
4.24
4.23
4.21
4.19
2.31
1.46
1.45
1.43
1.20
1.18
1.16
0.00
CO2Et
CO2Et
O–N
2.00
2.09
2.02
2.05
3.03
3.03
3.05
f1 (ppm)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125.44
110.14
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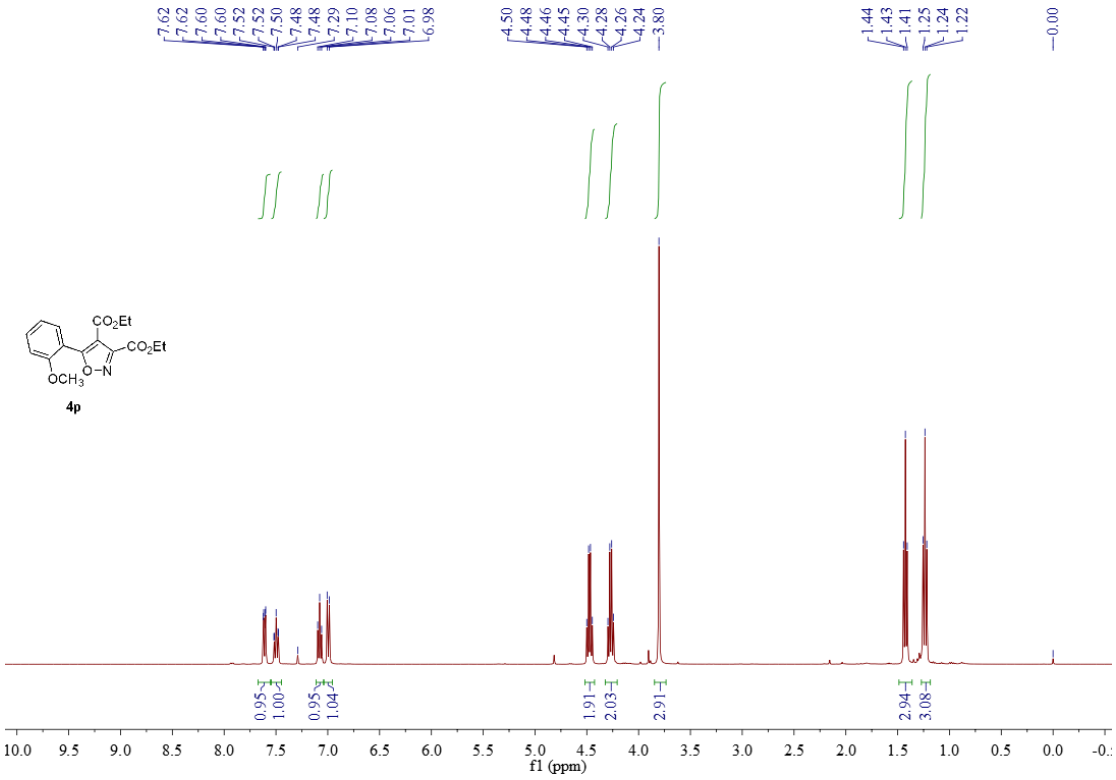
76.68
62.73
61.37
19.82
13.94
13.66
CO2Et
CO2Et
O–N
f1 (ppm)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7.50
7.48
7.48
7.29
7.10
7.08
7.06
7.01
6.98
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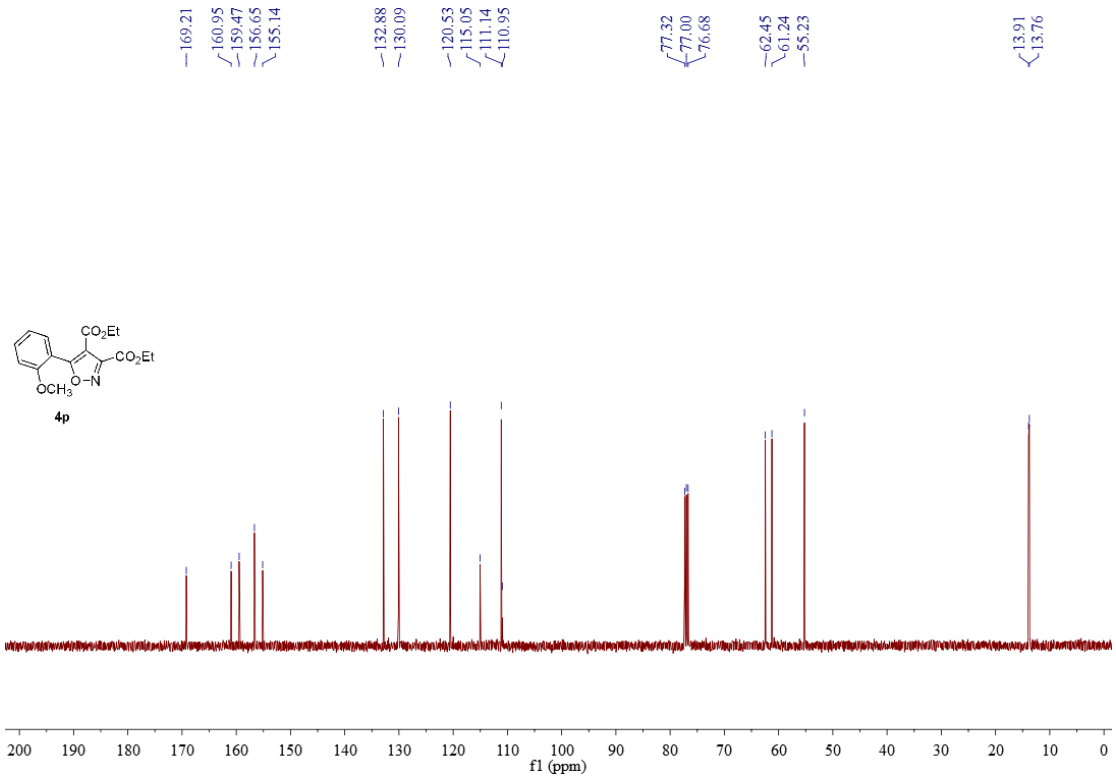
4.46
4.45
4.30
4.28
4.26
4.24
3.80
1.44
1.43
1.41
1.25
1.24
1.22
0.00
CO2Et
CO2Et
OCH3
O
N
4p
0.95
1.00
0.95
1.04
1.91
2.03
2.91
2.94
3.08
f1 (ppm)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111.14
110.95
77.32
77.00
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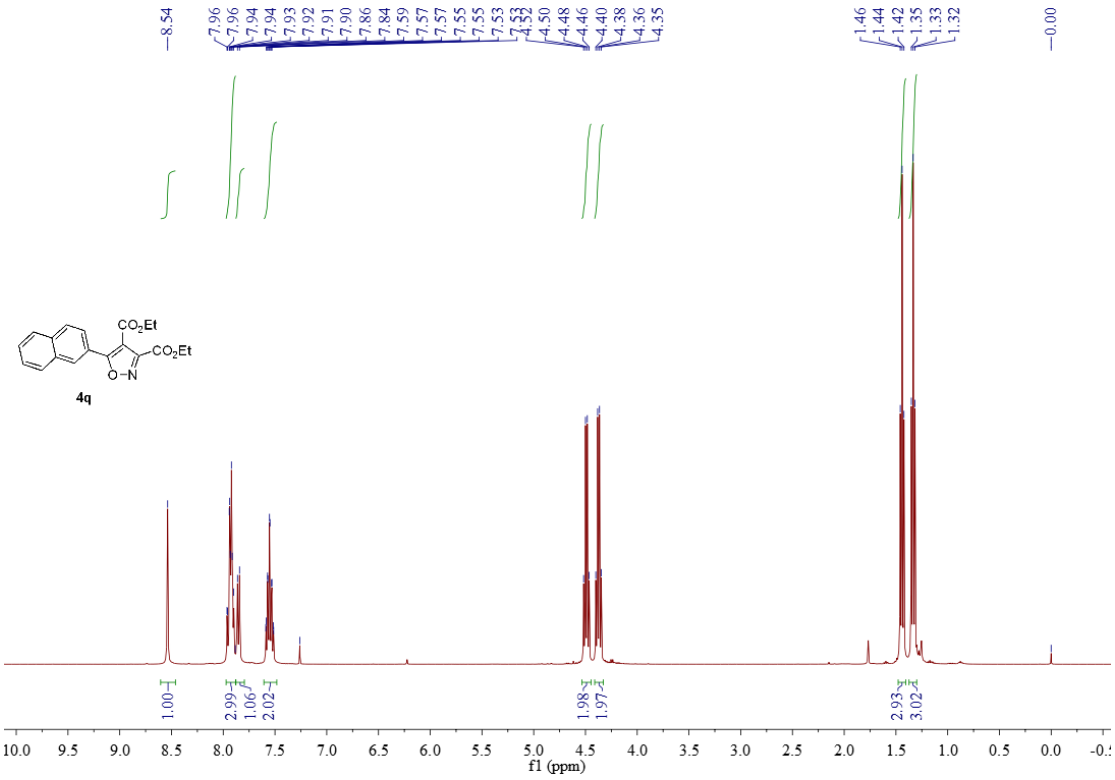
61.24
55.23
13.91
13.76
CO2Et
CO2Et
OCH3
O
N
4p
f1 (ppm)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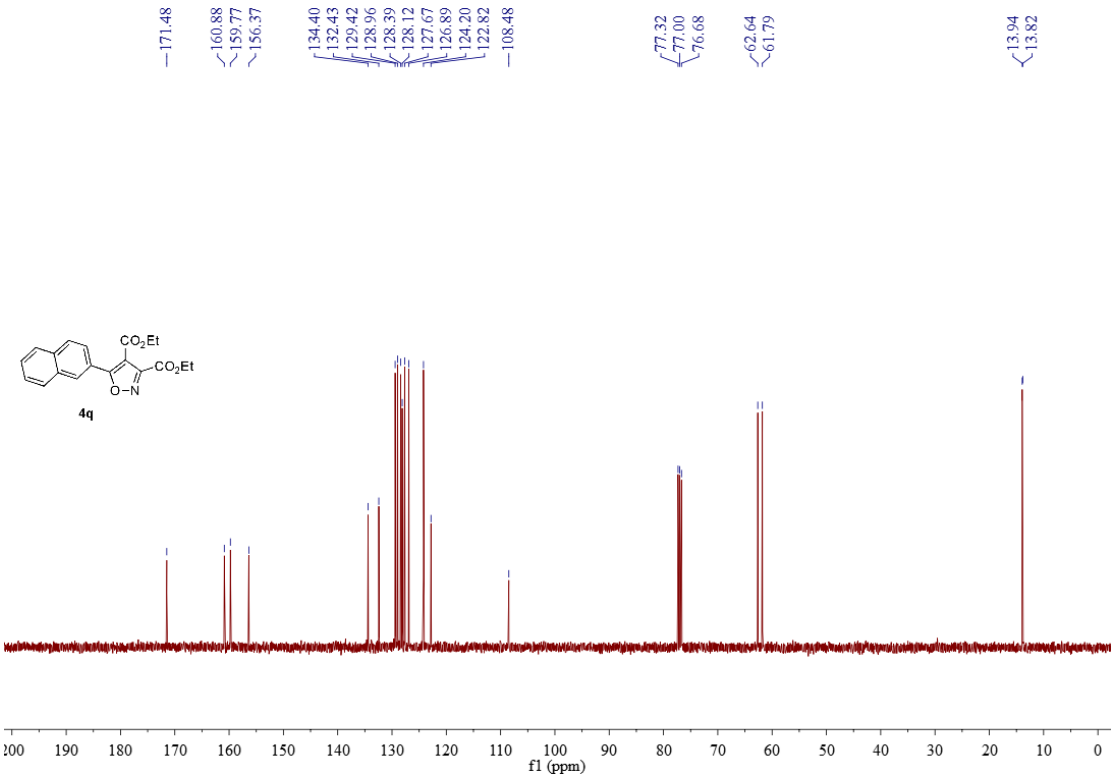
7.84
7.59
7.57
7.57
7.55
7.55
7.53
4.50
4.48
4.46
4.40
4.38
4.36
4.35
1.46
1.44
1.42
1.35
1.33
1.32
0.00
CO2Et
CO2Et
O–N
4q
1.00
2.99
1.06
2.02
1.98
1.97
2.93
3.02
f1 (ppm)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124.20
122.82
108.48
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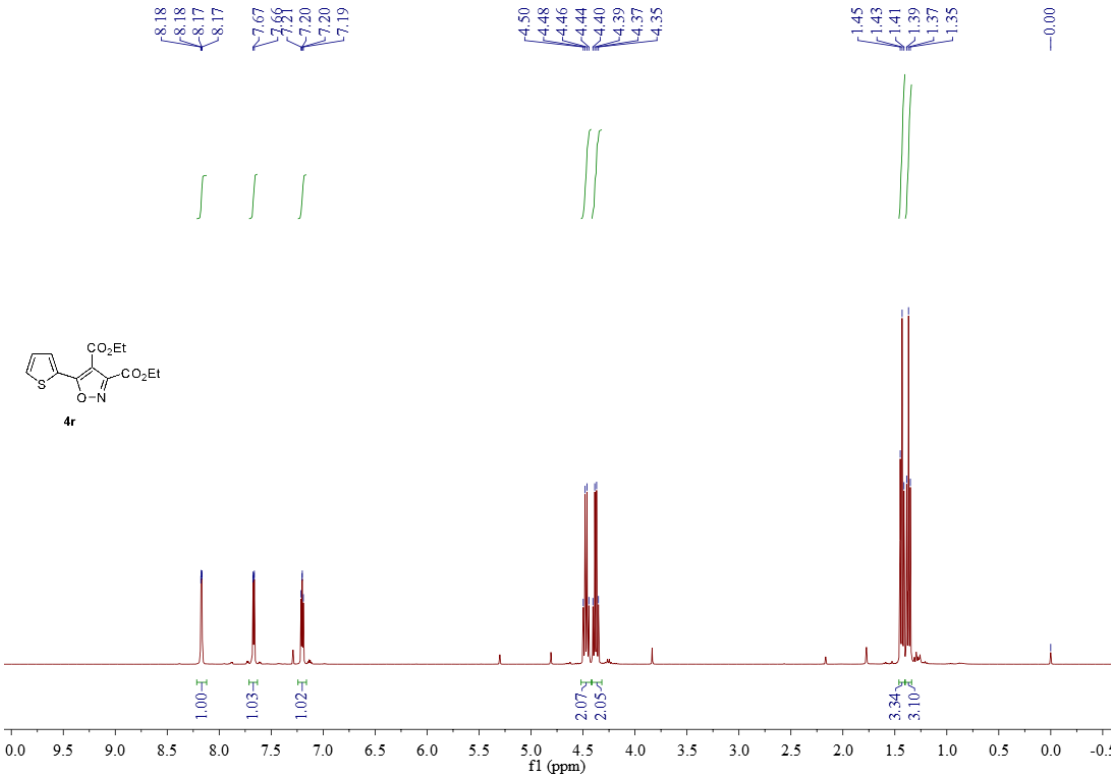
62.64
61.79
13.94
13.82
CO2Et
CO2Et
O–N
4q
f1 (ppm)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7.19
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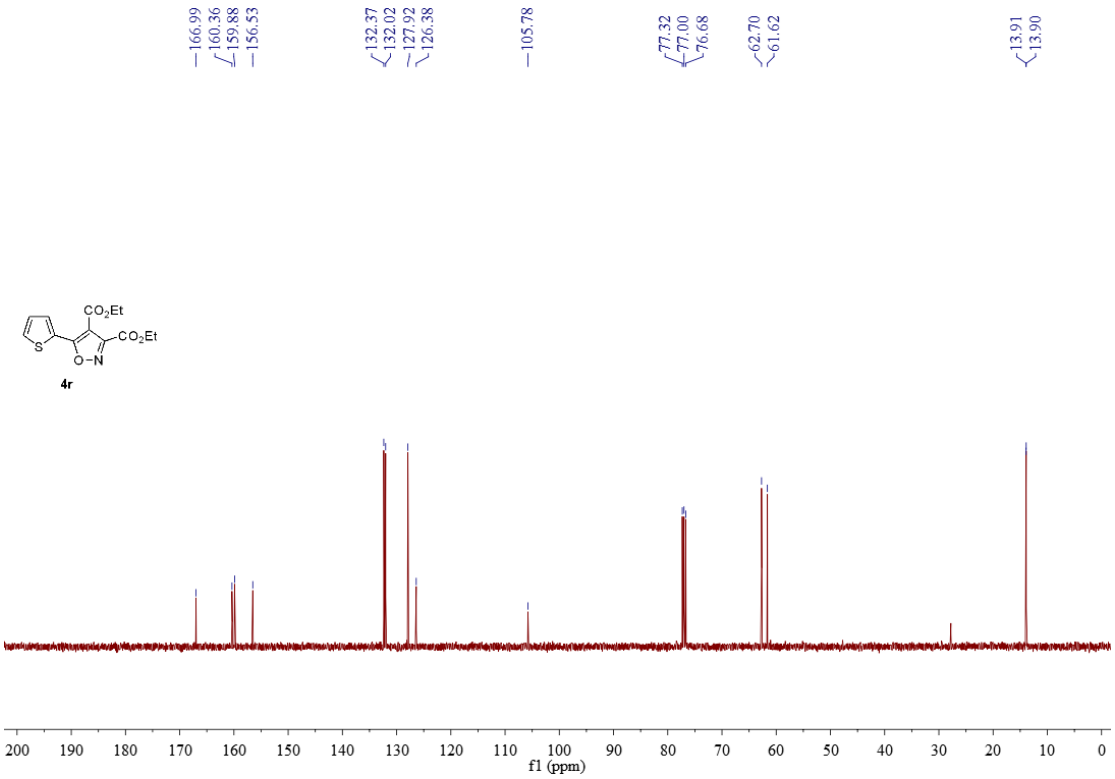
4.48
4.46
4.44
4.40
4.39
4.37
4.35
1.45
1.43
1.41
1.39
1.37
1.35
0.00
CO2Et
CO2Et
S
O–N
4r
1.00
1.03
1.02
2.07
2.05
3.34
3.10
f1 (ppm)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77.32
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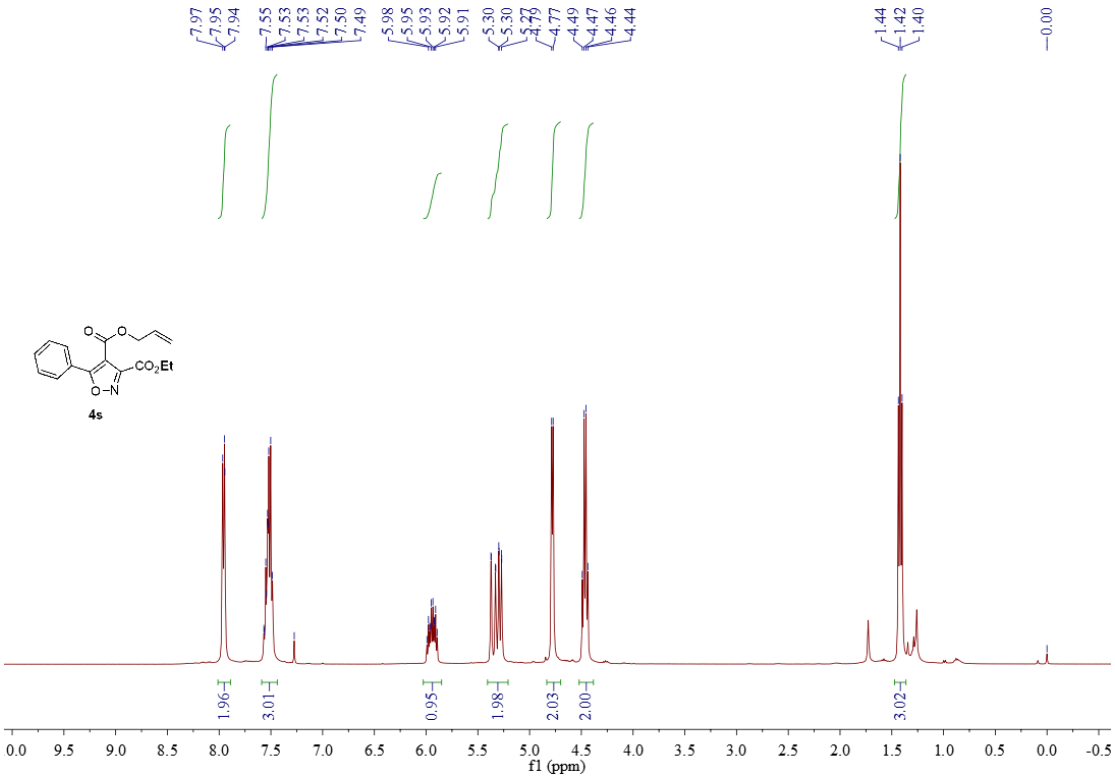
61.62
13.91
13.90
CO2Et
CO2Et
S
O–N
4r
f1 (ppm)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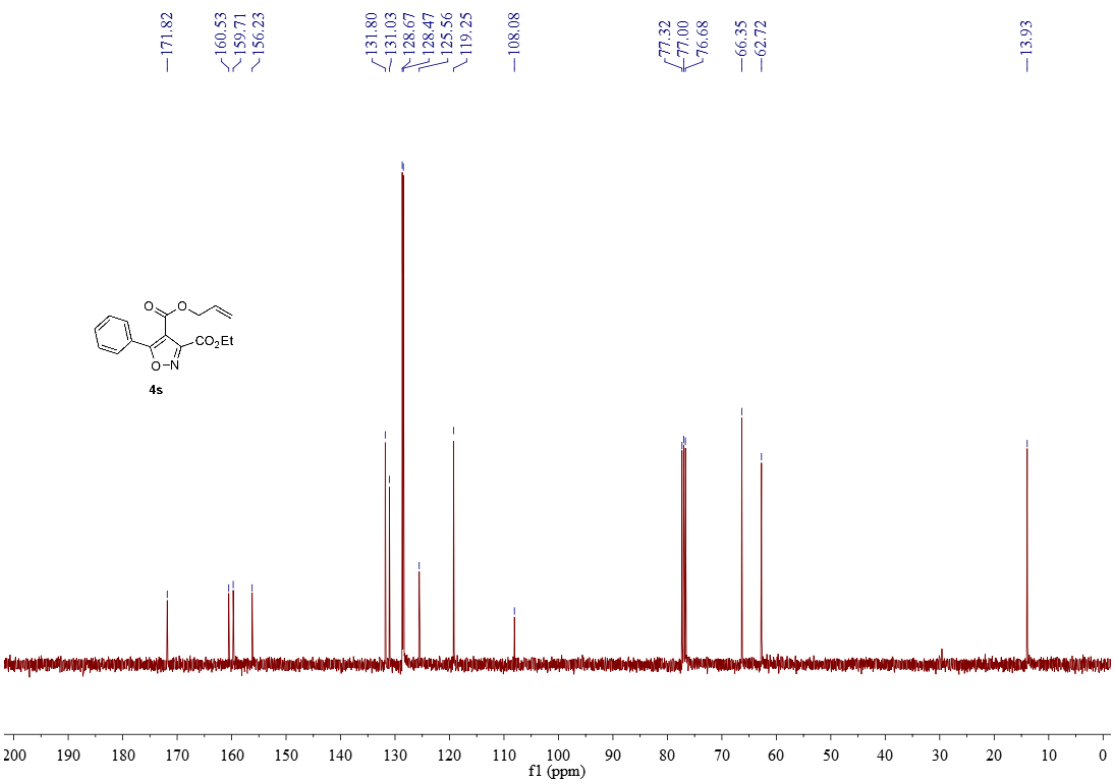
5.91
5.30
5.30
4.77
4.49
4.47
4.46
4.44
1.44
1.42
1.40
0.00
1.96
3.01
0.95
1.98
2.03
2.00
3.02
f1 (ppm)
4s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108.08
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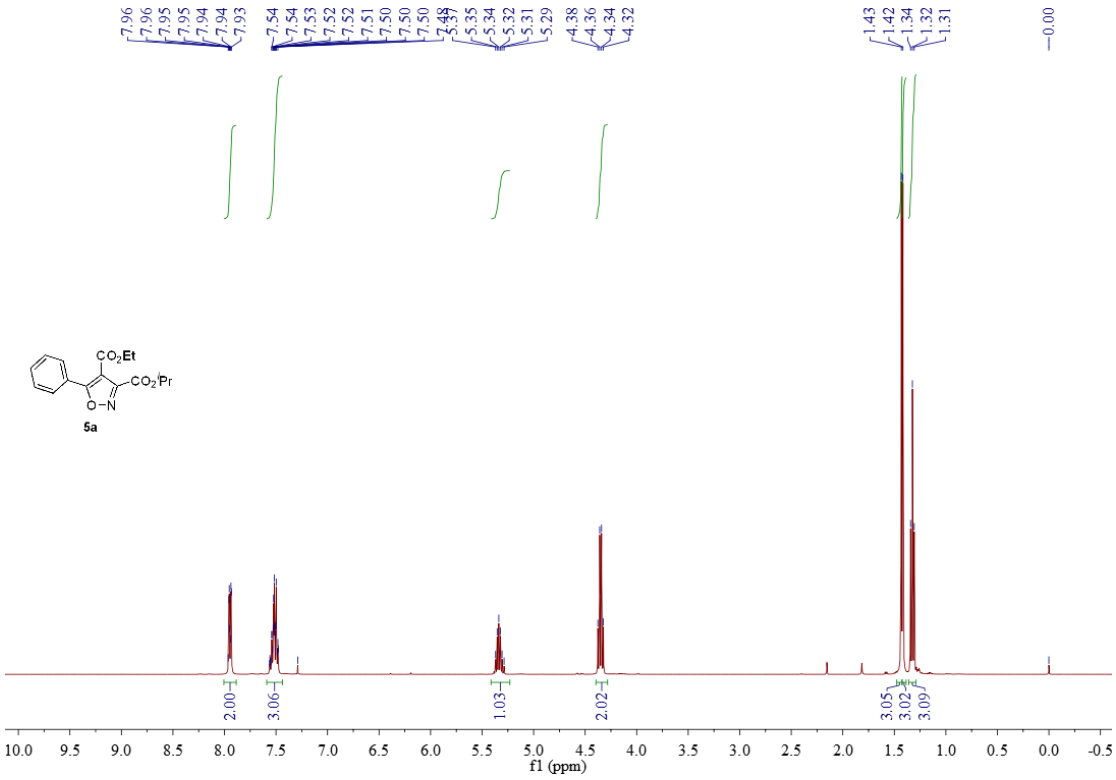
77.00
76.68
66.35
62.72
13.93
f1 (ppm)
4s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7.52
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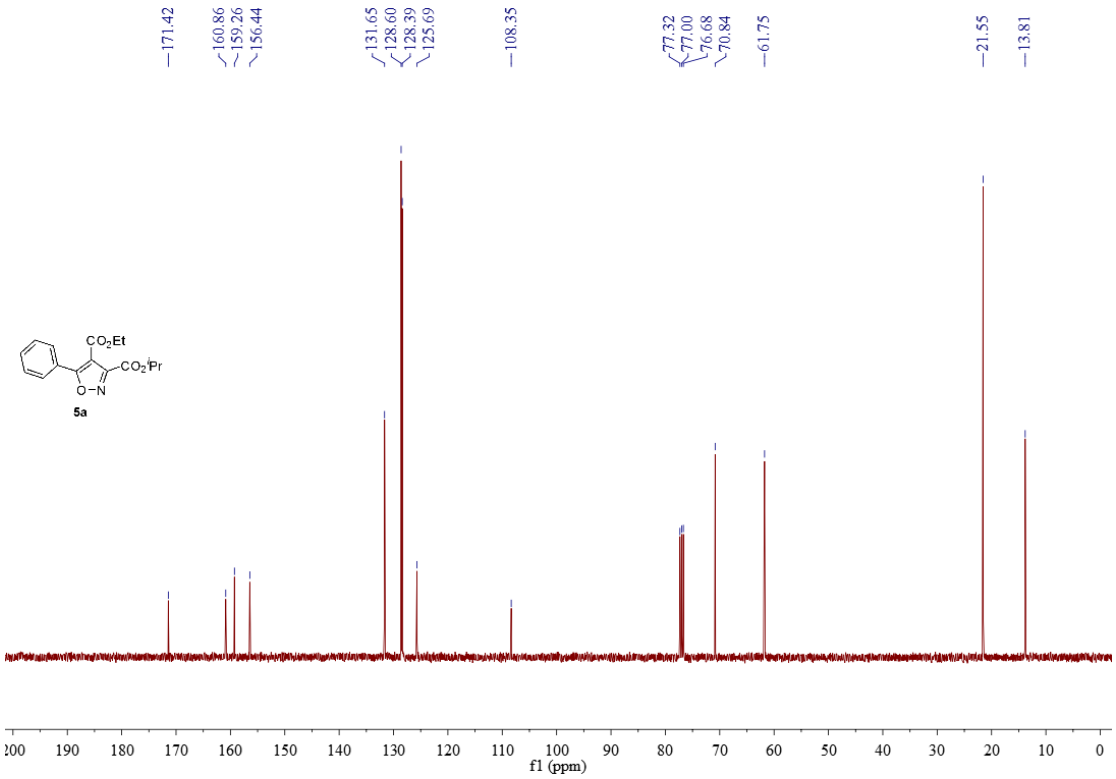
5.35
5.34
5.32
5.31
5.29
4.38
4.36
4.34
4.32
1.43
1.42
1.34
1.32
1.31
0.00
CO2Et
CO2iPr
O
N
5a
2.00
3.06
1.03
2.02
3.05
3.02
3.09
f1 (ppm)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125.69
108.35
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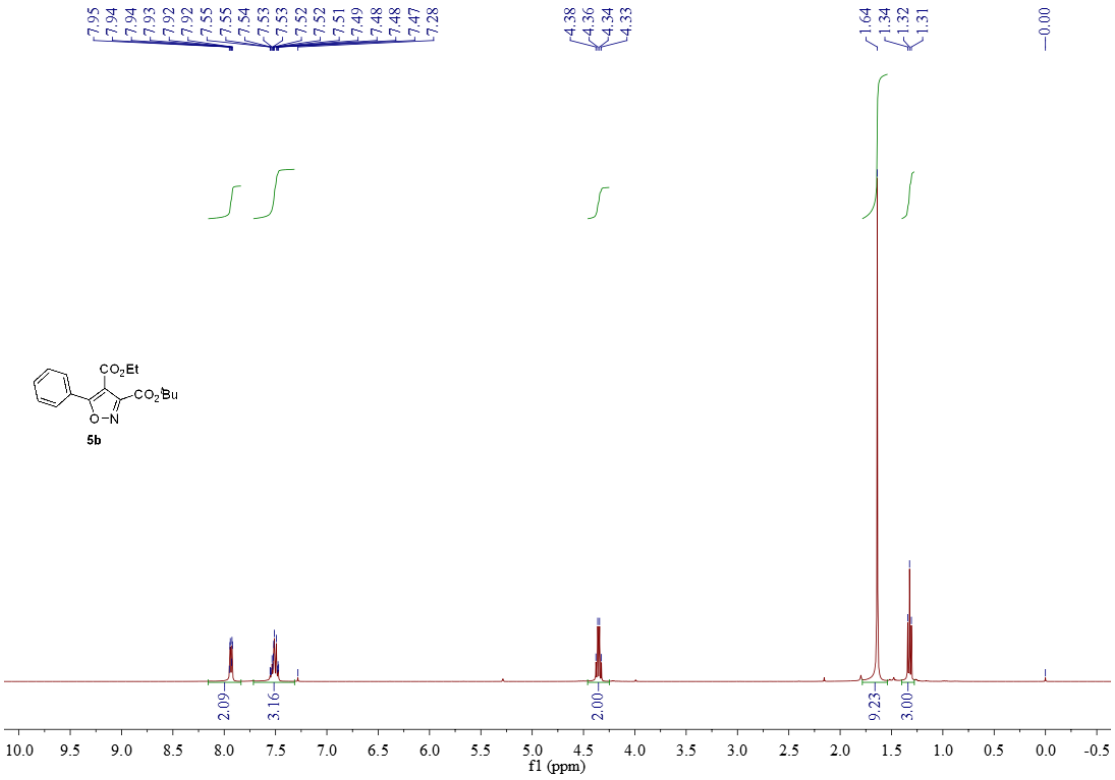
70.84
61.75
21.55
13.81
CO2Et
CO2iPr
O
N
5a
f1 (ppm)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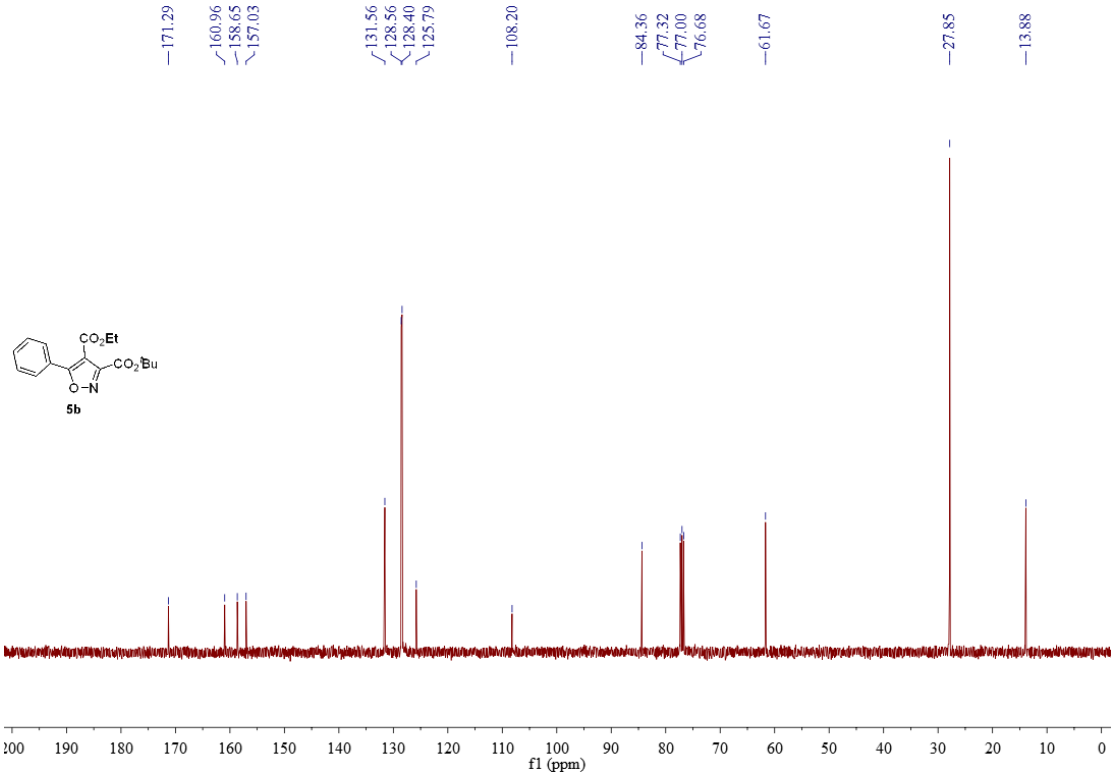
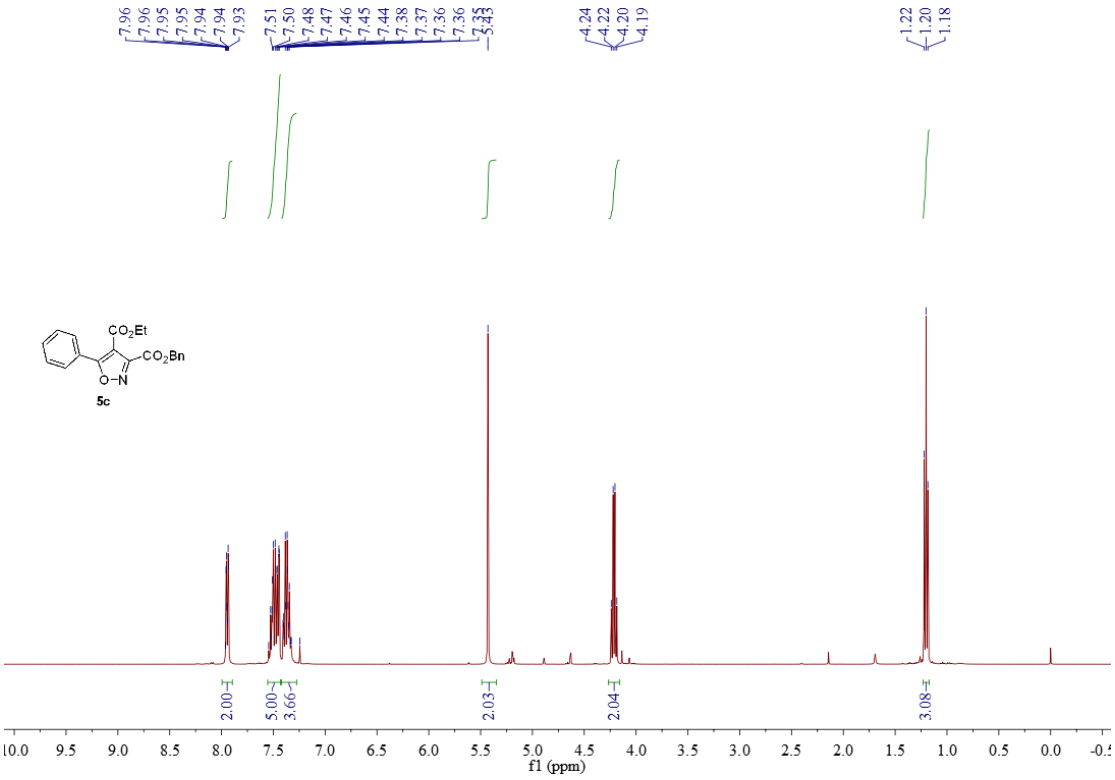
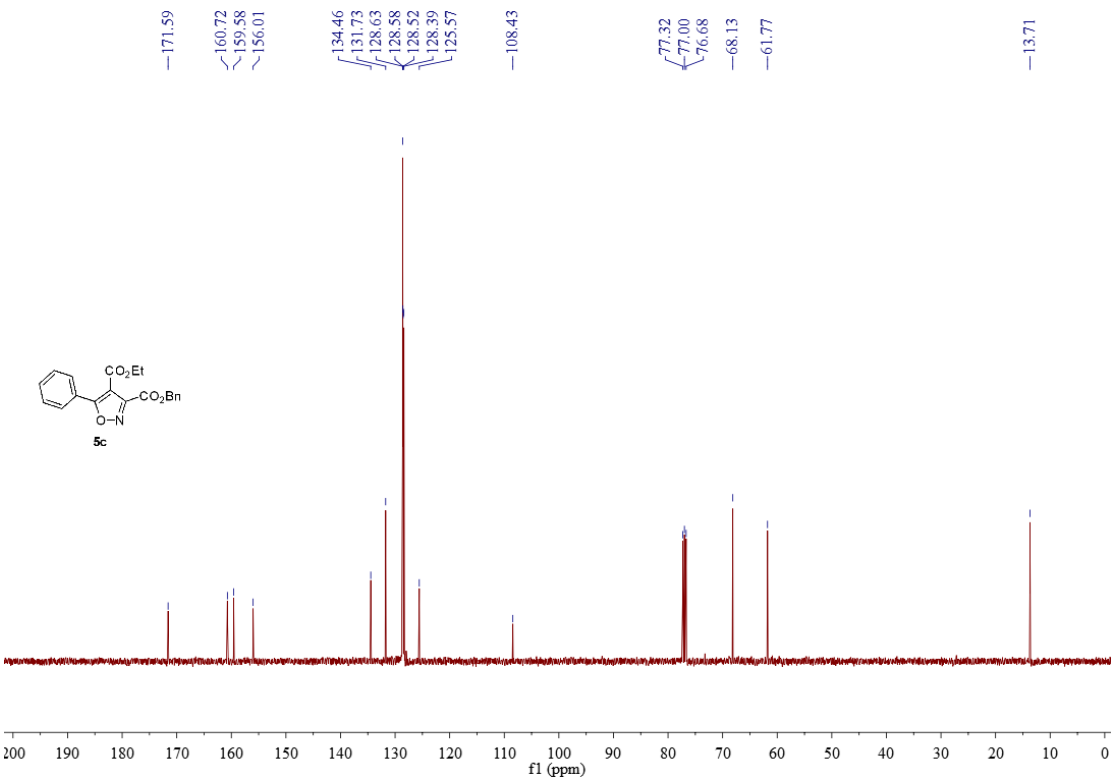
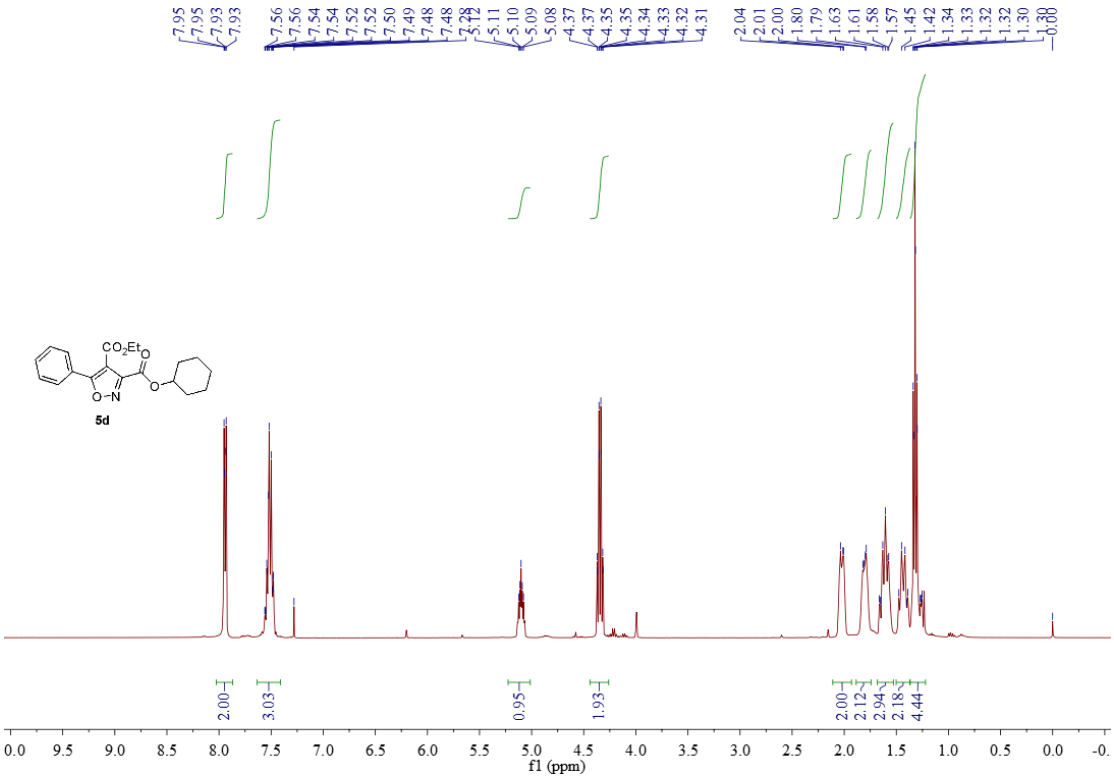
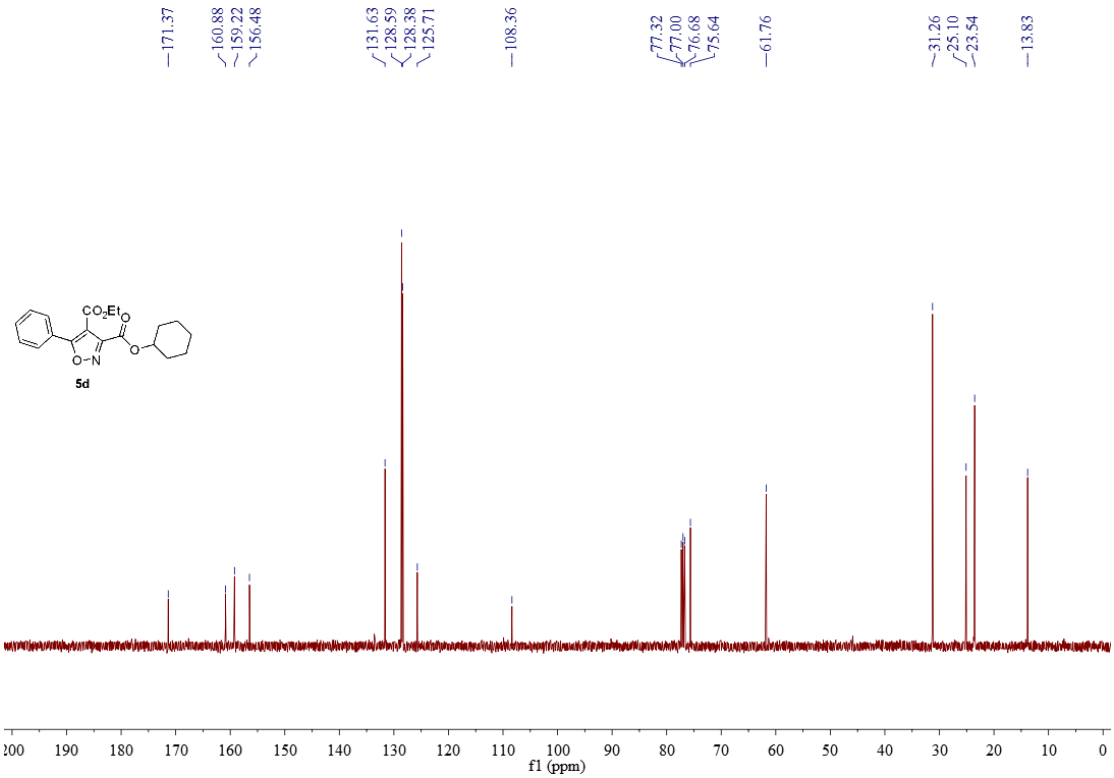
7.52
7.52
7.51
7.49
7.48
7.48
7.47
7.28
4.38
4.36
4.34
4.33
1.64
1.34
1.32
1.31
0.00
CO2Et
CO2tBu
O
N
5b
2.09
3.16
2.00
9.23
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

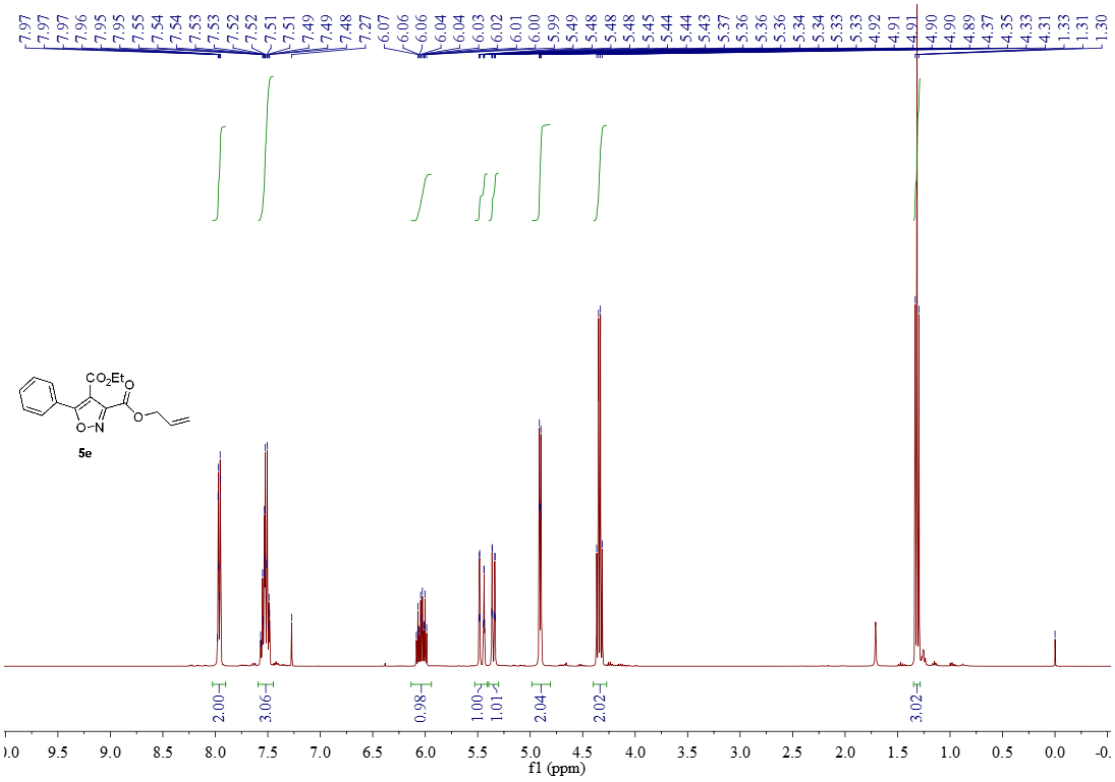

171.29
160.96
158.65
157.03
131.56
128.56
128.40
125.79
108.20
84.36
77.32
77.00
76.68
61.67
27.85
13.88
CO2Et
CO2tBu
O
N
5b
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

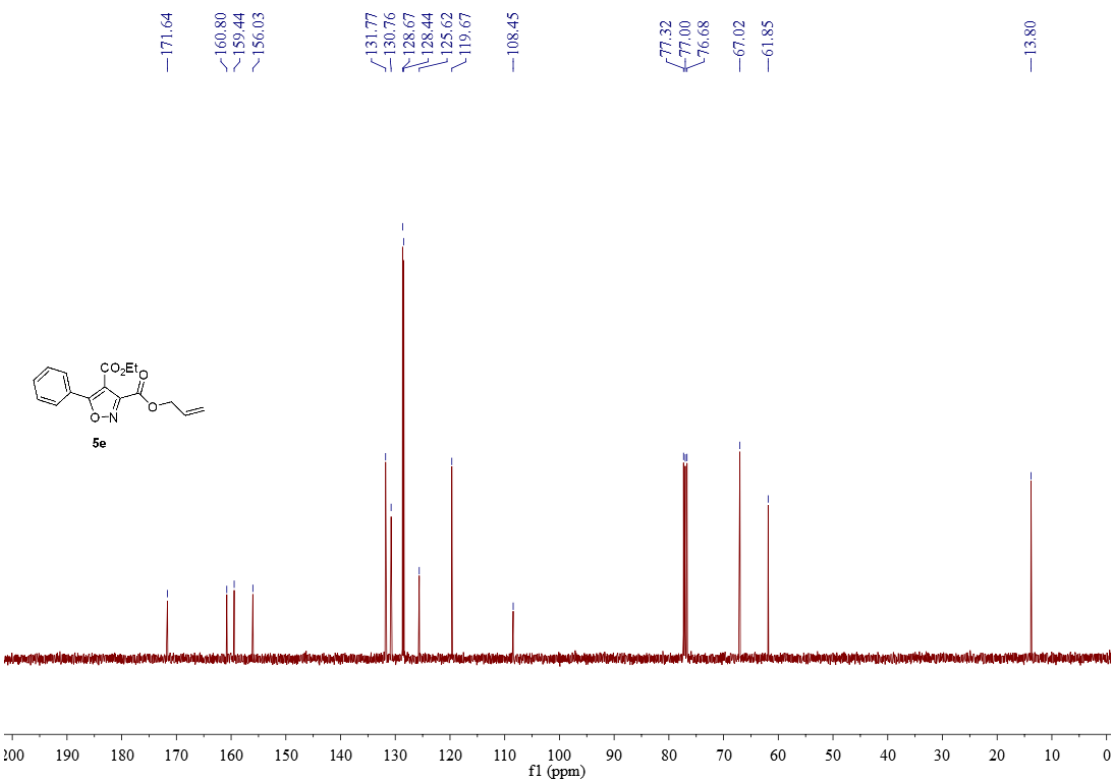

7.96
7.96
7.95
7.95
7.94
7.94
7.93
7.51
7.50
7.48
7.47
7.46
7.45
7.44
7.38
7.37
7.36
7.35
5.33
4.24
4.22
4.20
4.19
1.22
1.20
1.18
CO2Et
CO2Bn
O–N
5c
2.00
5.00
3.66
2.03
2.04
3.08
f1 (ppm)

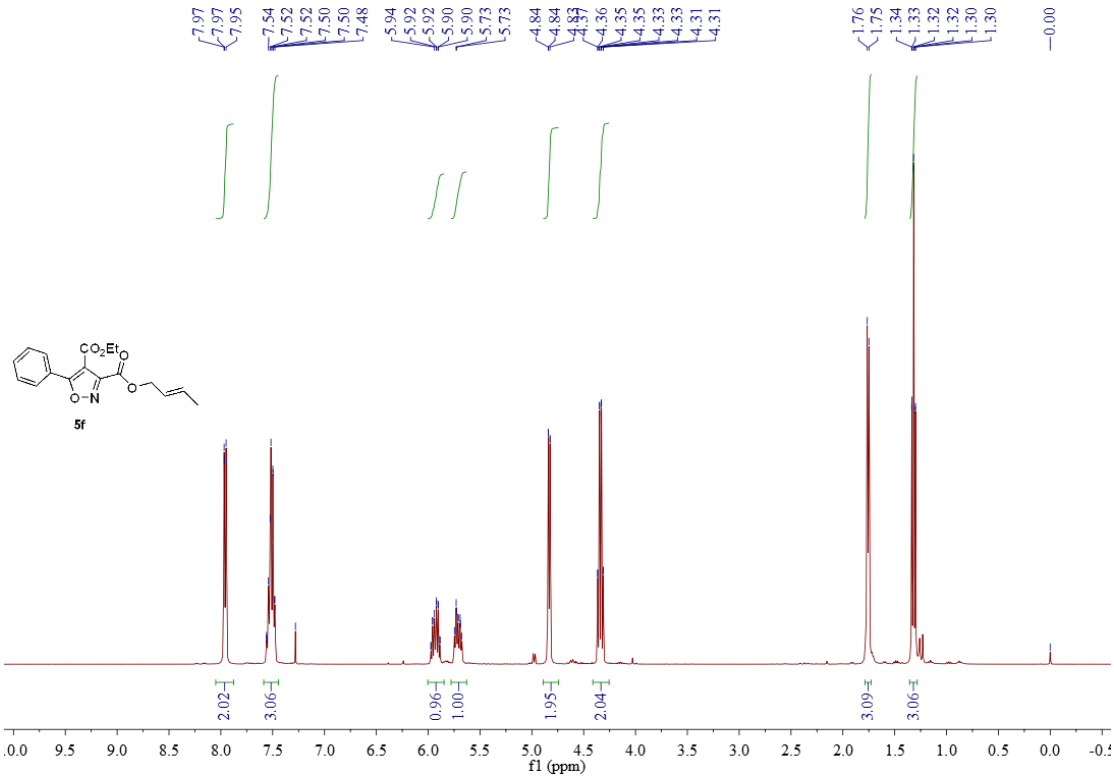

171.59
160.72
159.58
156.01
134.46
131.73
128.63
128.58
128.52
128.39
125.57
108.43
77.32
77.00
76.68
68.13
61.77
13.71
CO2Et
CO2Bn
O–N
5c
f1 (ppm)

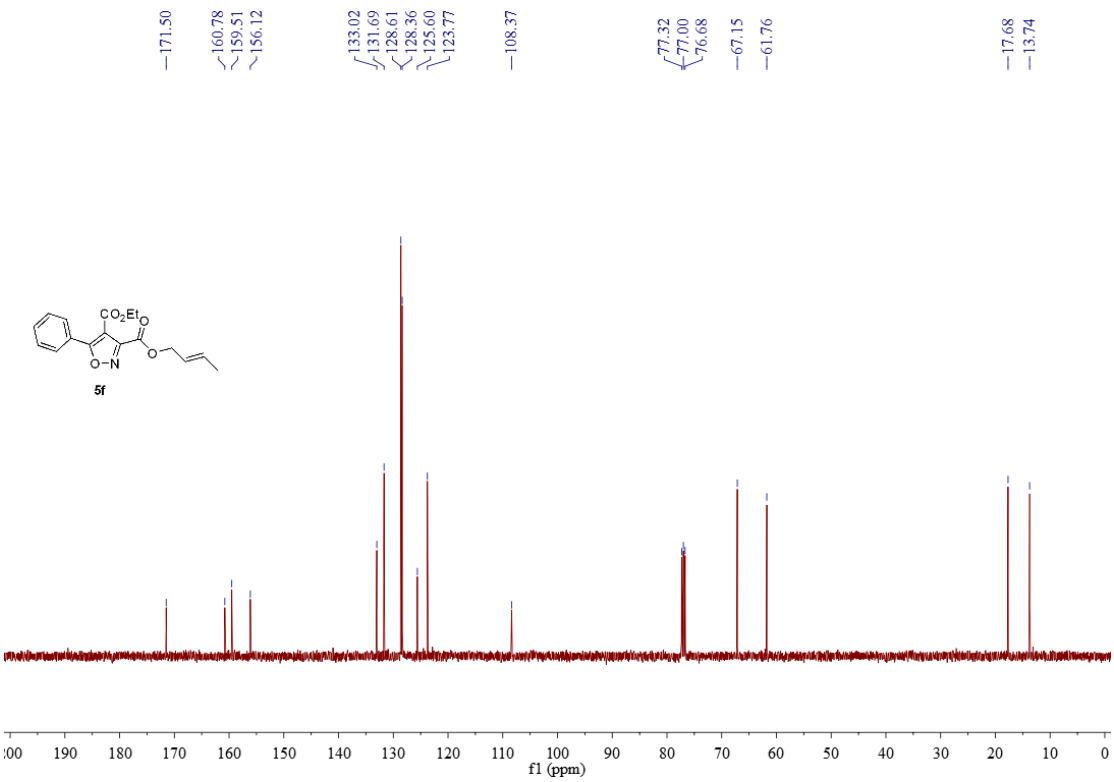

7.95
7.95
7.93
7.93
7.56
7.56
7.54
7.54
7.52
7.52
7.50
7.49
7.48
7.48
5.11
5.10
5.09
5.08
4.37
4.37
4.35
4.35
4.34
4.33
4.32
4.31
2.04
2.01
2.00
1.80
1.79
1.63
1.61
1.58
1.57
1.45
1.42
1.34
1.33
1.32
1.30
0.00
CO2Et
O
O-N
O
5d
2.00
3.03
0.95
1.93
2.00
2.12
2.94
2.18
4.44
f1 (ppm)

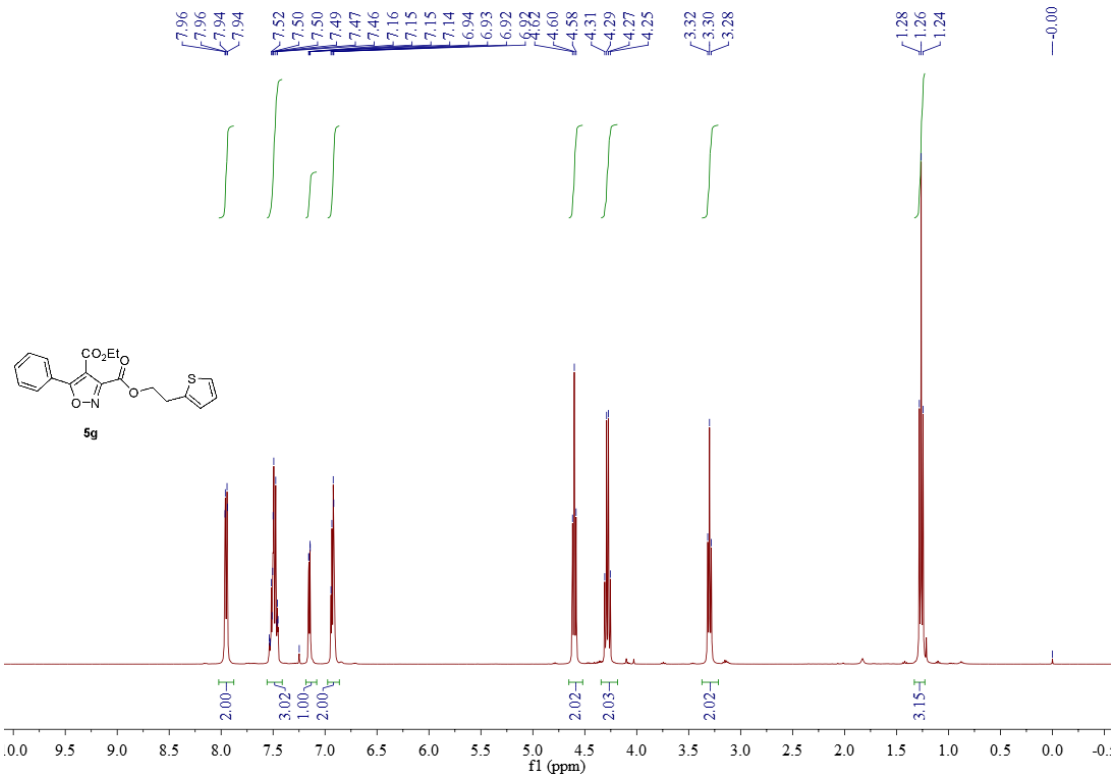

171.37
160.88
159.22
156.48
131.63
128.59
128.38
125.71
108.36
77.32
77.00
76.68
75.64
61.76
31.26
25.10
23.54
13.83
CO2Et
O
O-N
O
5d
f1 (ppm)

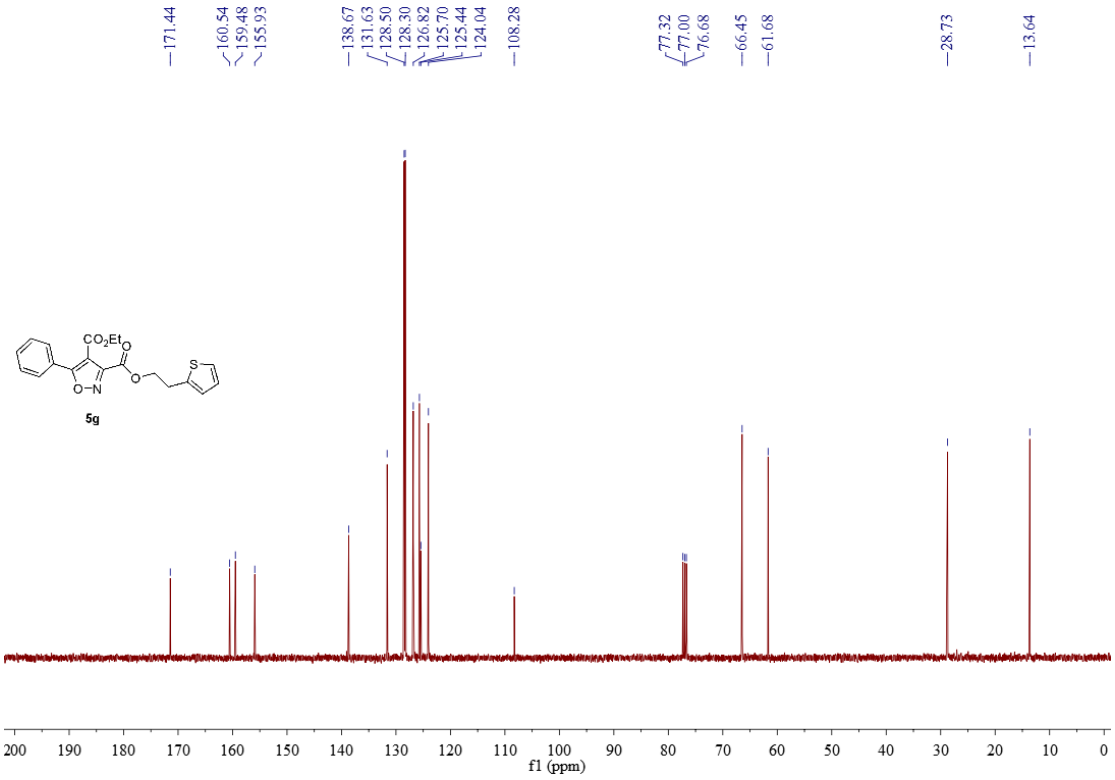

7.97
7.97
7.97
7.96
7.95
7.95
7.55
7.54
7.54
7.53
7.53
7.52
7.52
7.51
7.51
7.49
7.49
7.48
7.27
6.07
6.06
6.06
6.04
6.04
6.03
6.02
6.01
6.00
5.99
5.49
5.48
5.48
5.48
5.45
5.44
5.44
5.43
5.37
5.36
5.36
5.36
5.34
5.34
5.33
5.33
4.92
4.91
4.91
4.90
4.90
4.89
4.37
4.35
4.33
4.31
1.33
1.31
1.30
CO2Et
O
O-N
O
5e
2.00
3.06
0.98
1.00
1.01
2.04
2.02
3.02
f1 (ppm)


171.64
160.80
159.44
156.03
131.77
130.76
128.67
128.44
125.62
119.67
108.45
77.32
77.00
76.68
67.02
61.85
13.80
CO2Et
O
O-N
O
5e
f1 (ppm)

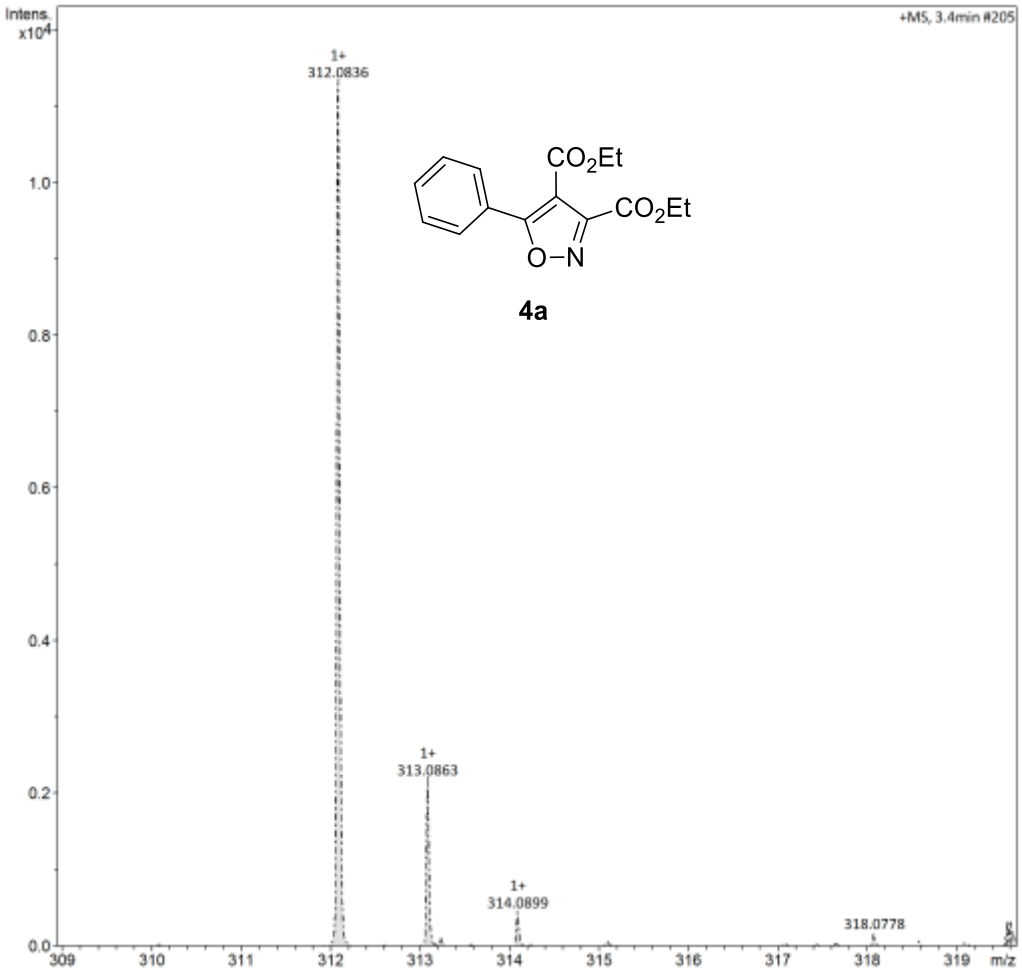

7.97
7.97
7.95
7.54
7.52
7.52
7.50
7.50
7.48
5.94
5.92
5.92
5.90
5.90
5.73
5.73
4.84
4.84
4.83
4.37
4.36
4.35
4.35
4.33
4.33
4.31
4.31
1.76
1.75
1.34
1.33
1.32
1.32
1.30
1.30
0.00
2.02
3.06
0.96
1.00
1.95
2.04
3.09
3.06
f1 (ppm)
5f


171.50
160.78
159.51
156.12
133.02
131.69
128.61
128.36
125.60
123.77
108.37
77.32
77.00
76.68
67.15
61.76
17.68
13.74
f1 (ppm)
5f

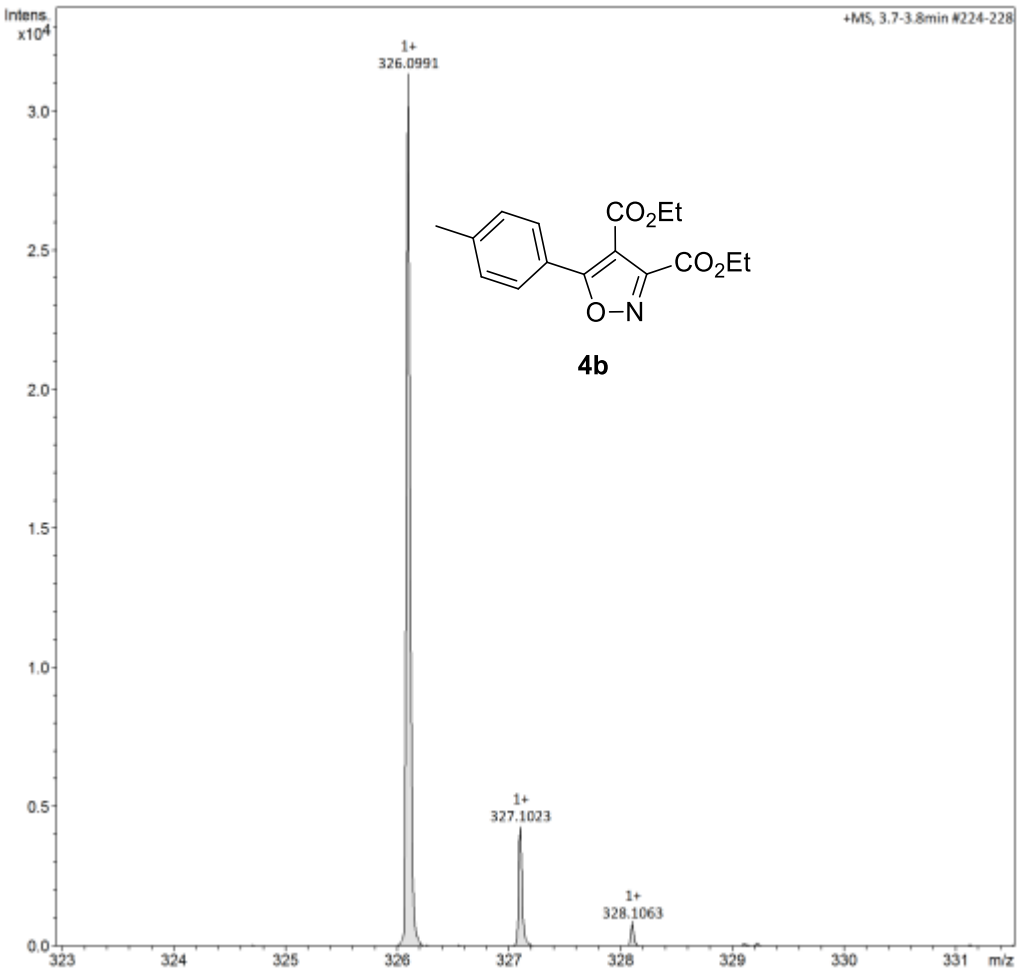

7.96
7.96
7.94
7.94
7.52
7.50
7.50
7.49
7.47
7.46
7.16
7.15
7.15
7.14
6.94
6.93
6.92
4.60
4.58
4.31
4.29
4.27
4.25
3.32
3.30
3.28
1.28
1.26
1.24
0.00
2.00
3.02
1.00
2.00
2.02
2.03
2.02
3.15
f1 (ppm)
5g


171.44
160.54
159.48
155.93
138.67
131.63
128.50
128.30
126.82
125.70
125.44
124.04
108.28
77.32
77.00
76.68
66.45
61.68
28.73
13.64
f1 (ppm)
5g

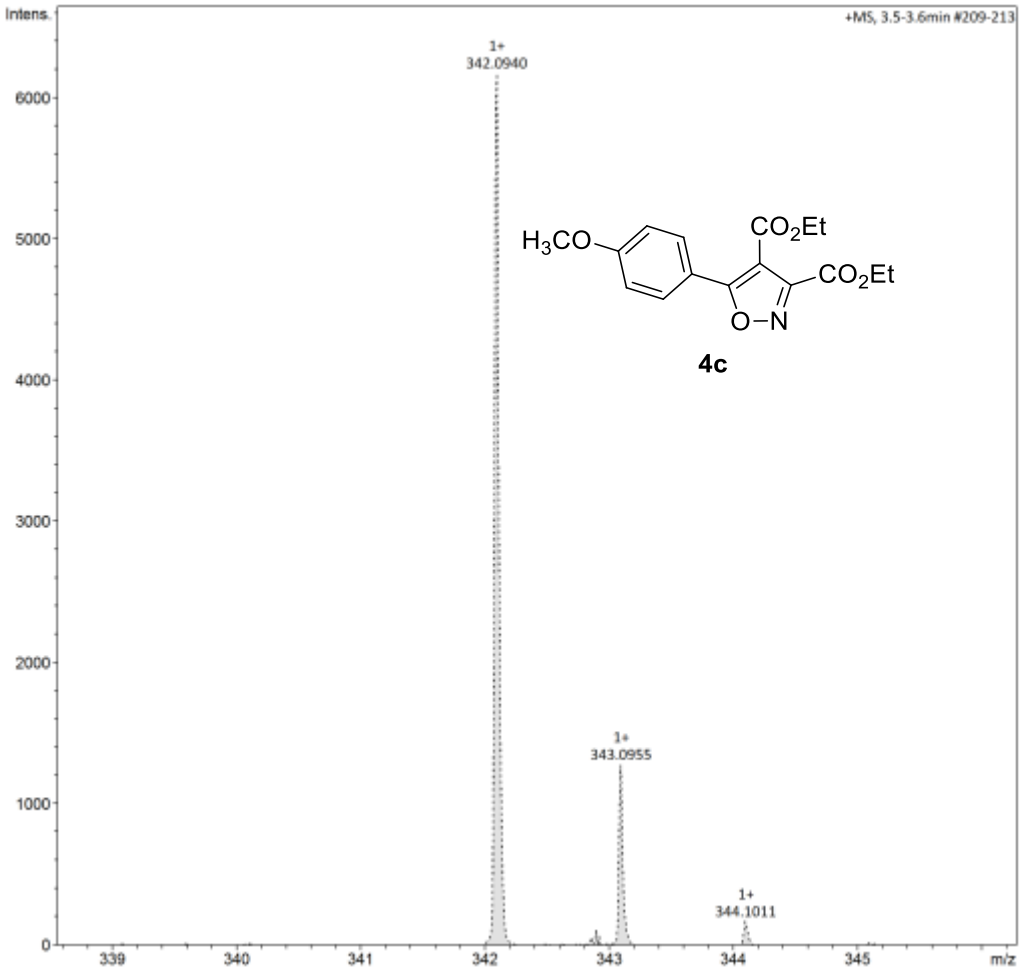
MS spectroscopic data for products



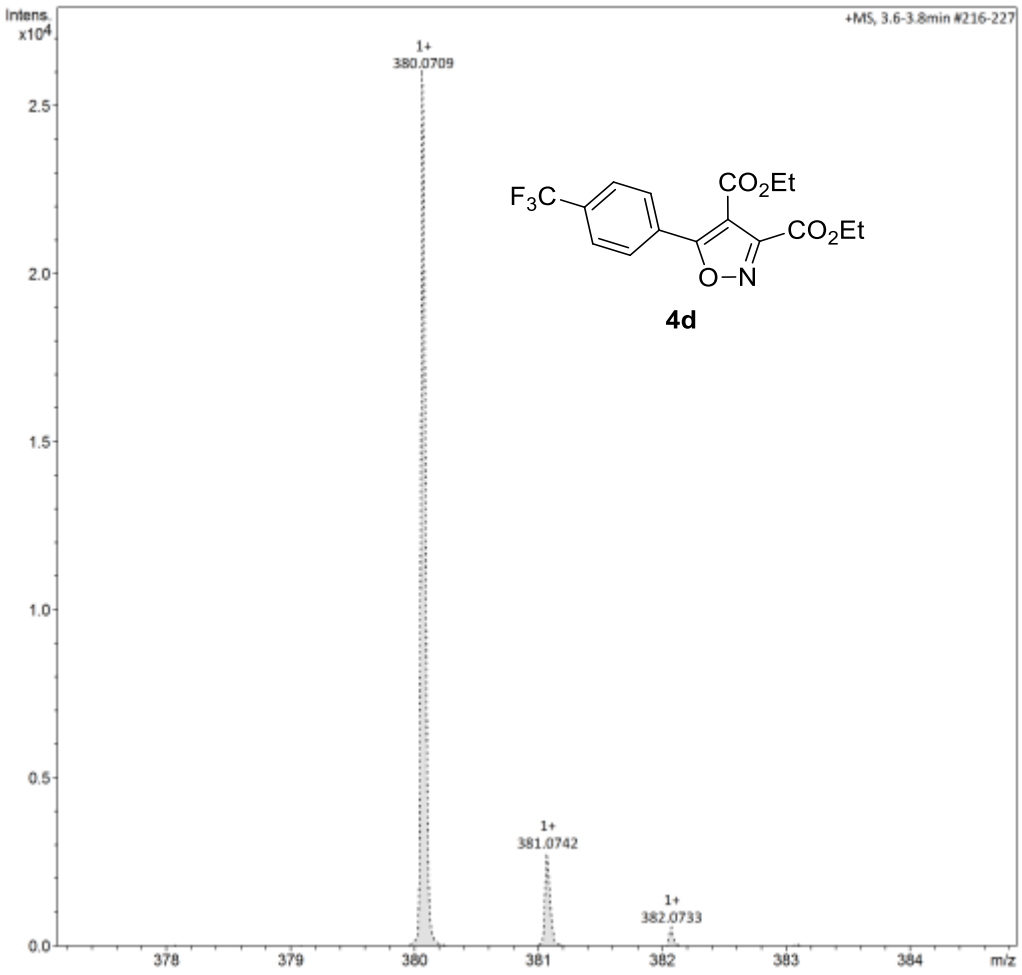
4a


Intens.
x10^4
+MS, 3.7-3.8min #224-228
1+
326.0991
1+
327.1023
1+
328.1063
3.0
2.5
2.0
1.5
1.0
0.5
0.0
323
324
325
326
327
328
329
330
331
m/z
CO2Et
CO2Et
O
N

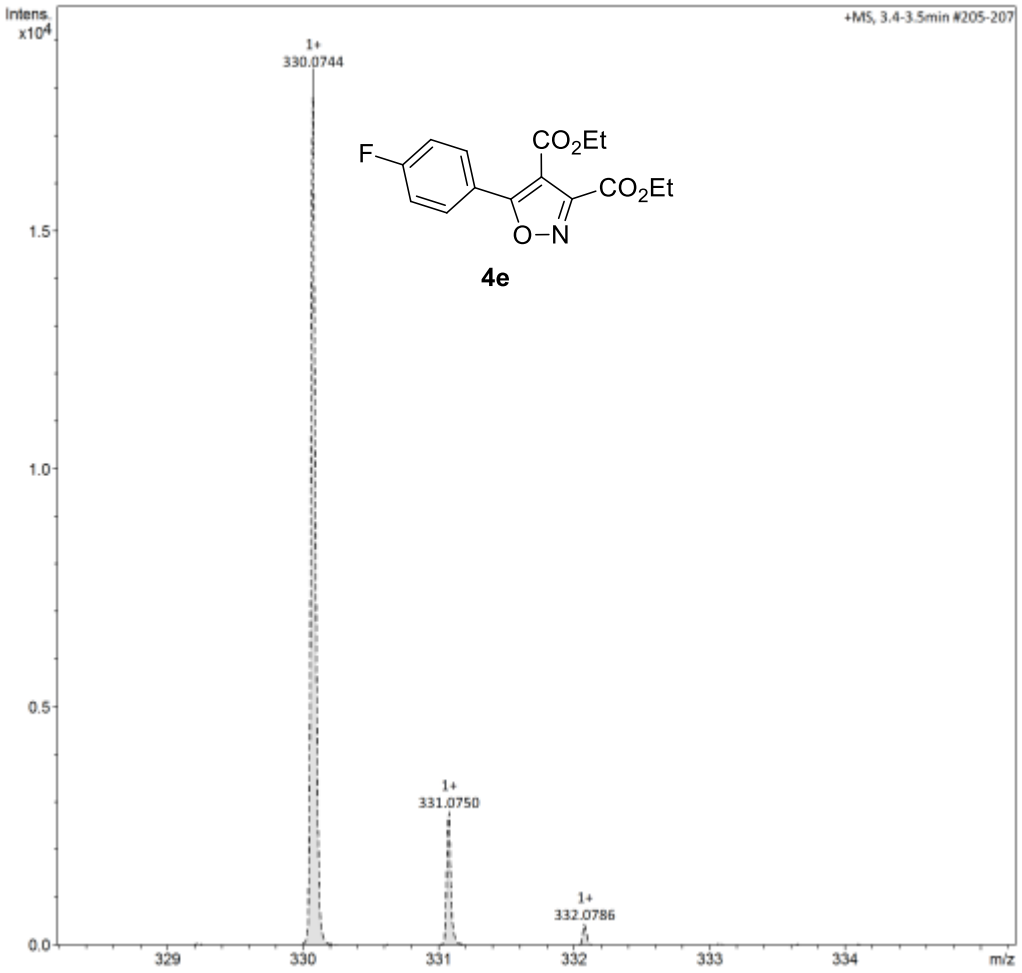
4b


Intens.
+MS, 3.5-3.6min #209-213
1+
342.0940
1+
343.0955
1+
344.1011
6000
5000
4000
3000
2000
1000
0
339
340
341
342
343
344
345
m/z
H3CO
CO2Et
CO2Et
O
N

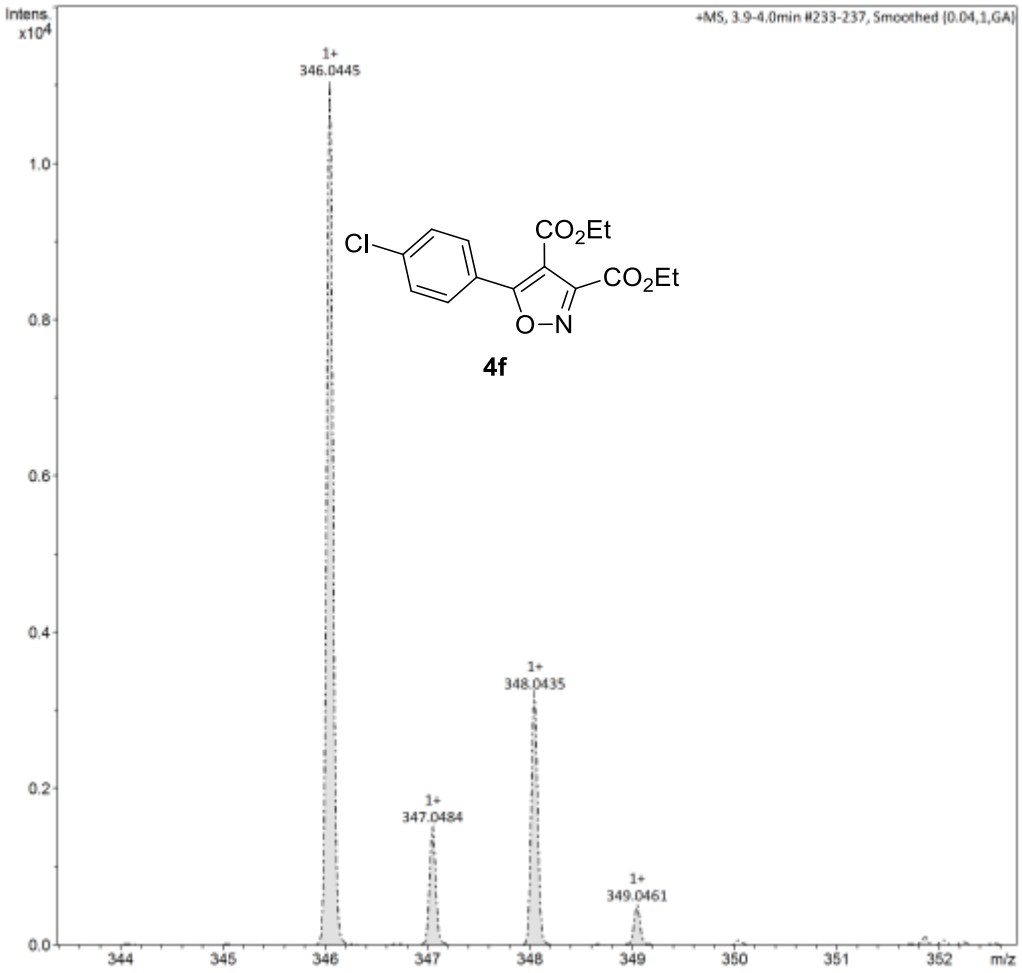
4c

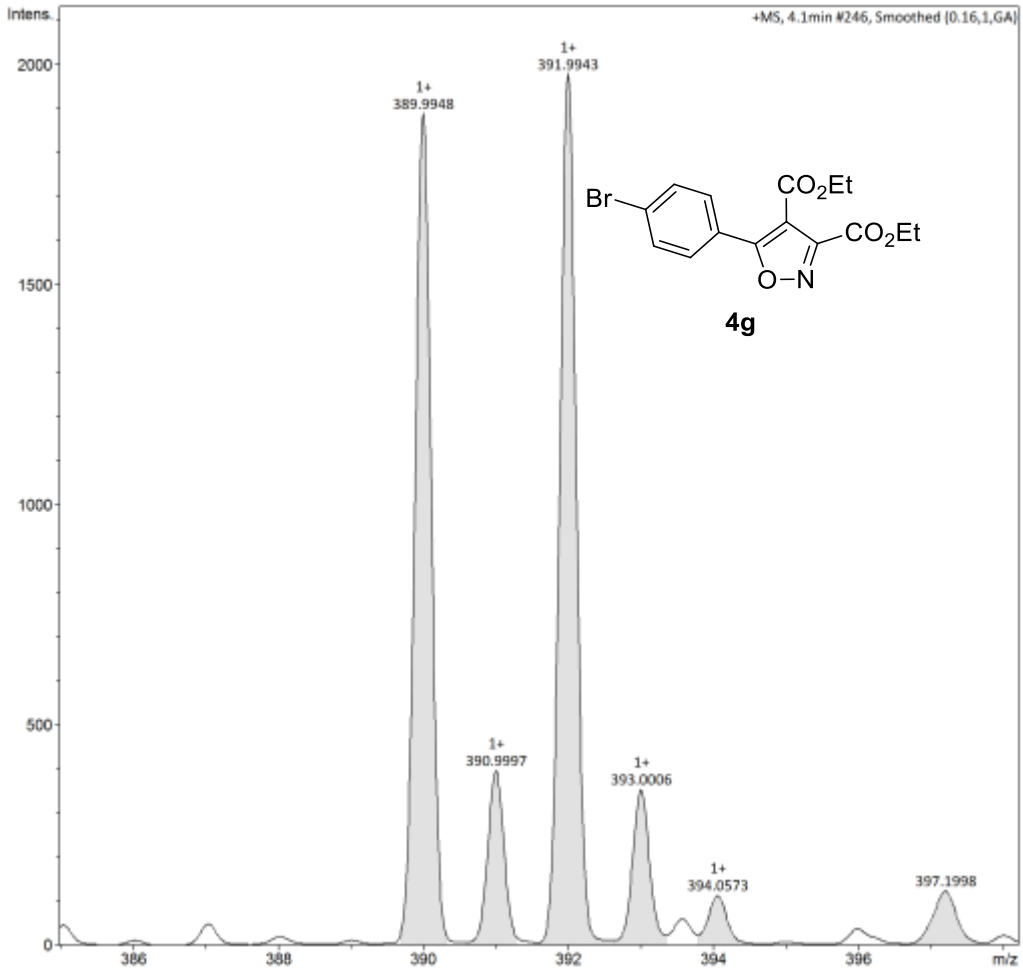

Intens.
x10^4
+MS, 3.6-3.8min #216-227
1+
380.0709
1+
381.0742
1+
382.0733
2.5
2.0
1.5
1.0
0.5
0.0
378
379
380
381
382
383
384
m/z
F3C
CO2Et
CO2Et
O
N

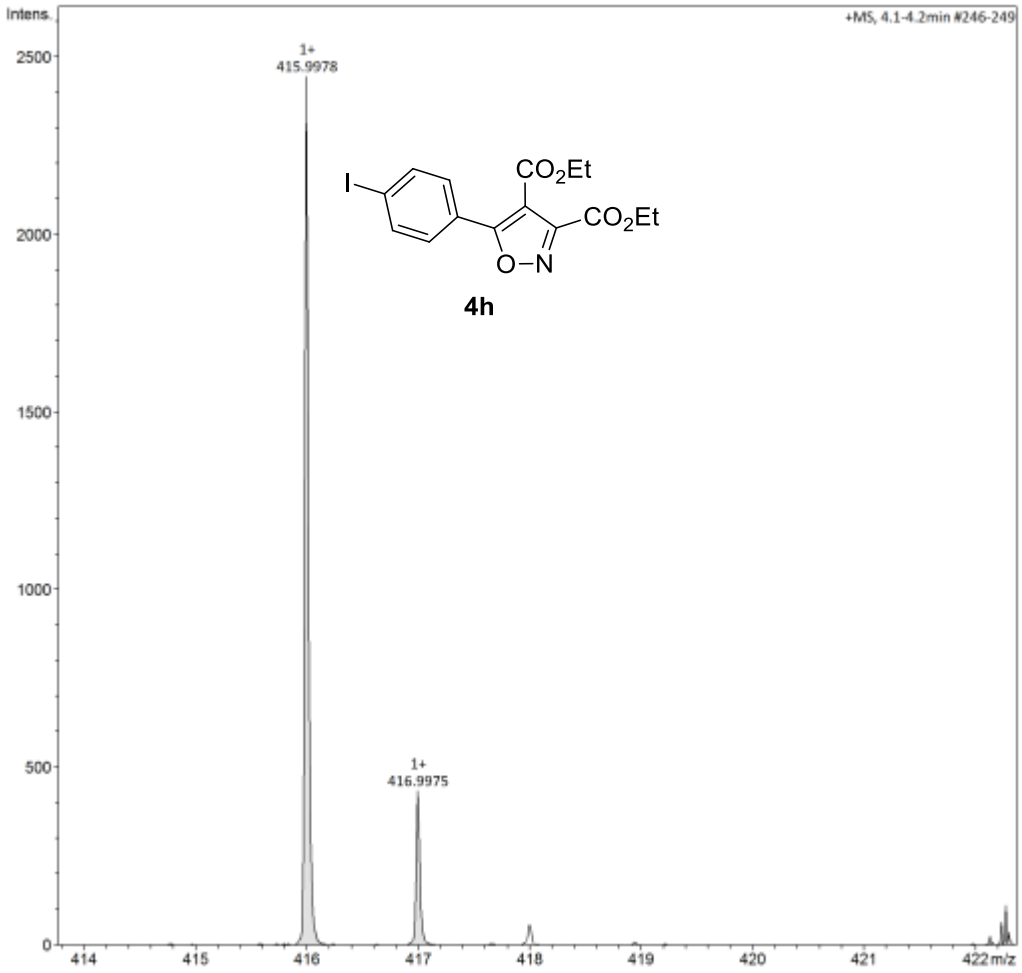
4d


Intens.
x10^4
+MS, 3.4-3.5min #205-207
1+
330.0744
1+
331.0750
1+
332.0786
1.5
1.0
0.5
0.0
329
330
331
332
333
334
m/z
F
CO2Et
CO2Et
O–N

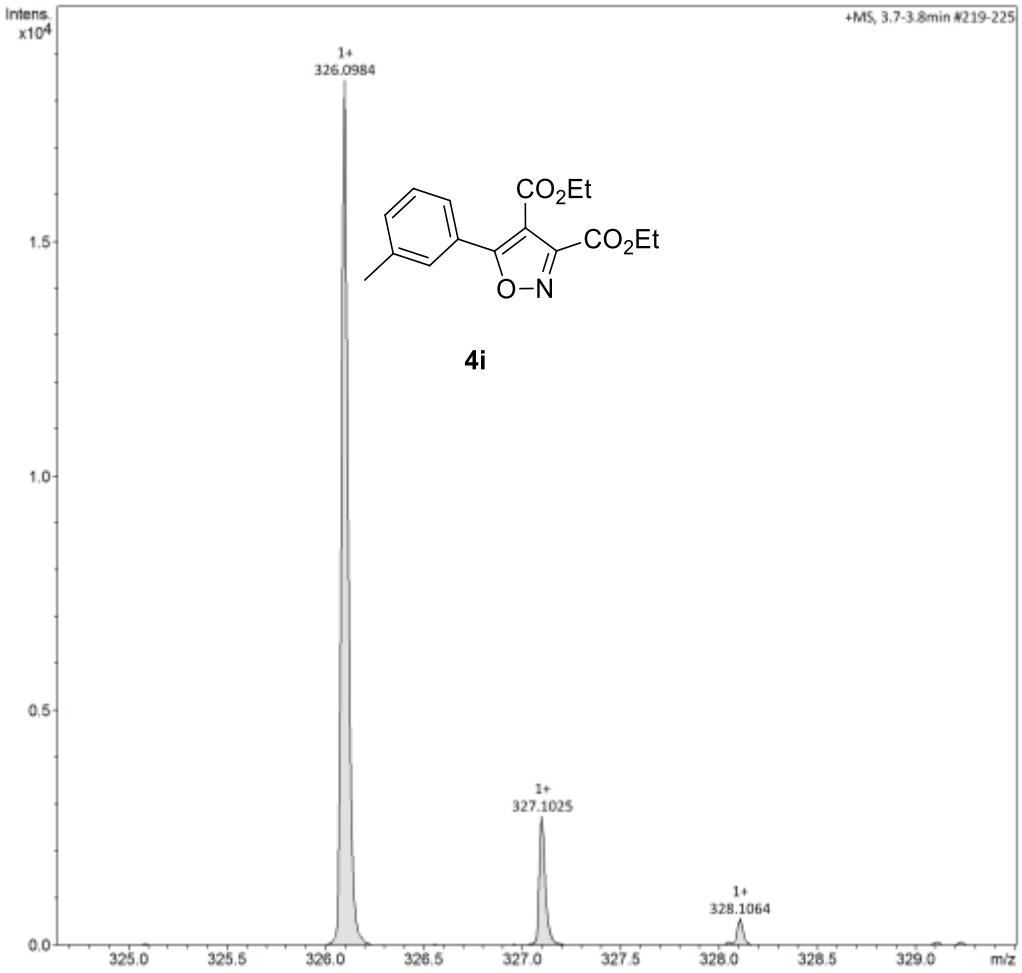
4e

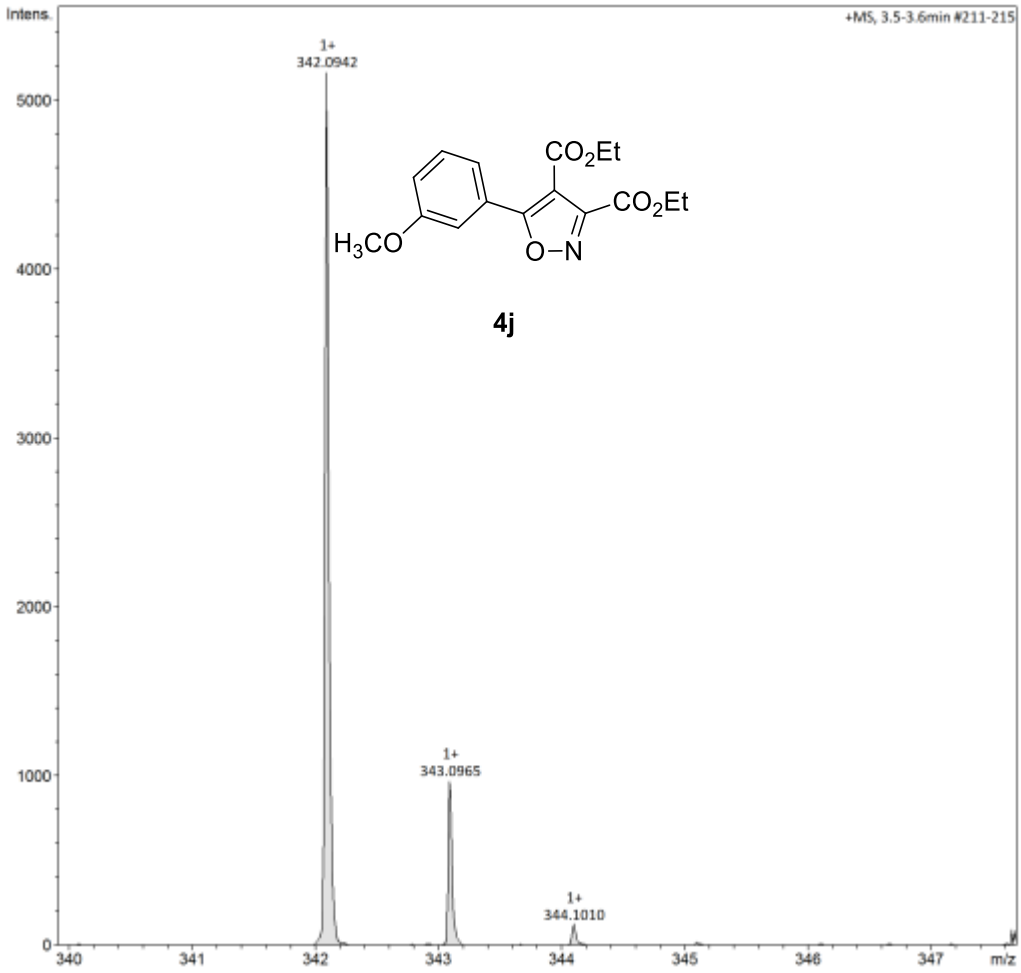

+MS, 3.9-4.0min #233-237, Smoothed (0.04,1,GA)
Intens.
x10^4
1+
346.0445
1+
348.0435
1+
347.0484
1+
349.0461
Cl
CO2Et
CO2Et
O–N
4f
m/z


Intens.
+MS, 4.1min #246, Smoothed (0.16,1,GA)
2000
1500
1000
500
0
1+
389.9948
1+
391.9943
1+
390.9997
1+
393.0006
1+
394.0573
397.1998
386
388
390
392
394
396
m/z
Br
CO2Et
CO2Et
O
N
4g

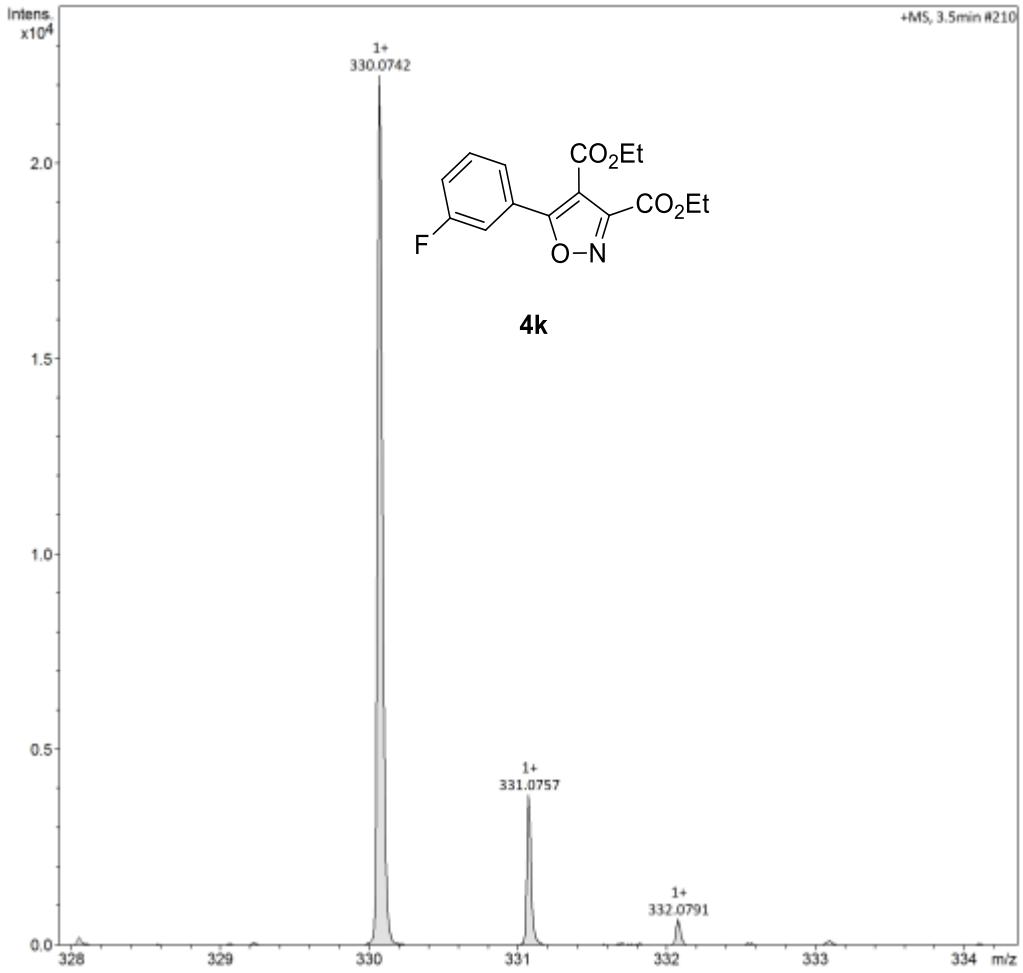

Intens.
+MS, 4.1-4.2min #246-249
2500
2000
1500
1000
500
0
1+
415.9978
1+
416.9975
414
415
416
417
418
419
420
421
422 m/z
I
CO2Et
CO2Et
O
N

4h

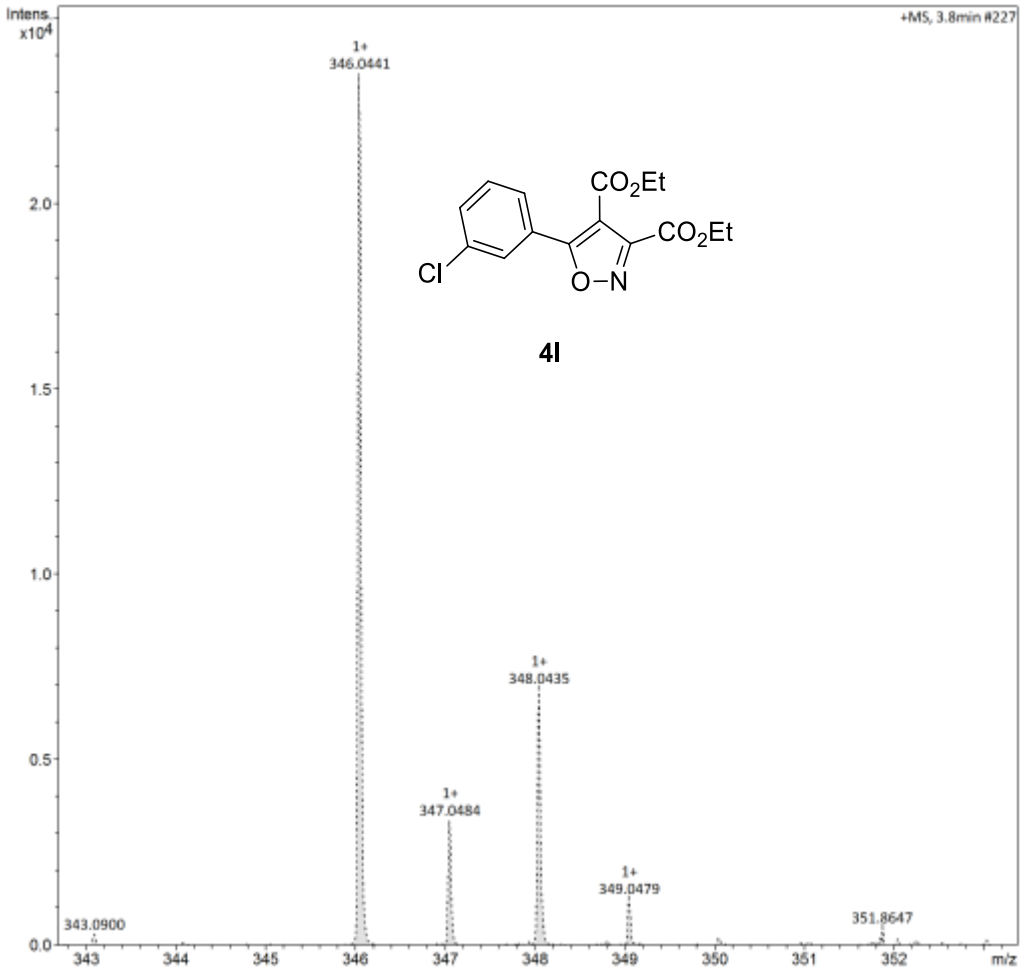

Intens.
x10^4
+MS, 3.7-3.8min #219-225
1+
326.0984
1+
327.1025
1+
328.1064
CO2Et
CO2Et
O–N
4i
1.5
1.0
0.5
0.0
325.0
325.5
326.0
326.5
327.0
327.5
328.0
328.5
329.0
m/z


Intens.
+MS, 3.5-3.6min #211-215
1+
342.0942
1+
343.0965
1+
344.1010
5000
4000
3000
2000
1000
0
340
341
342
343
344
345
346
347
m/z
CO2Et
CO2Et
H3CO
O–N

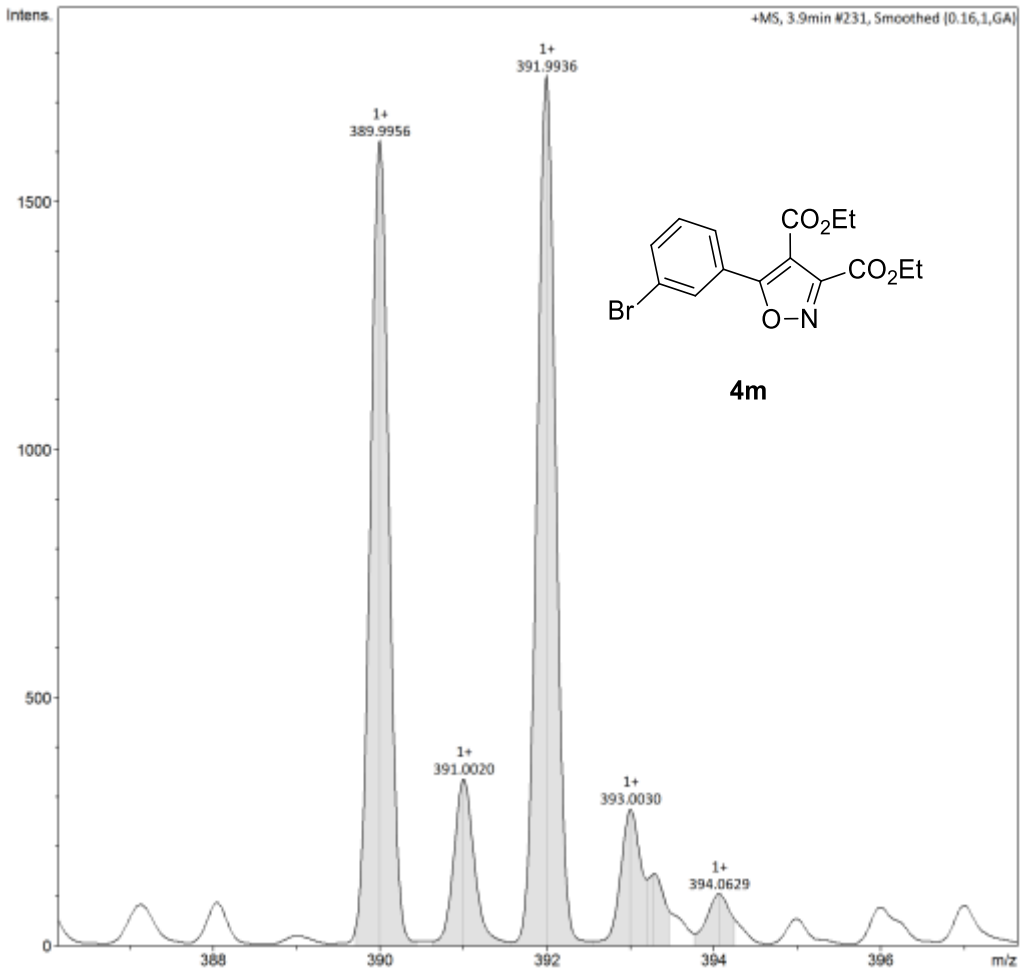
4j


Intens.
x10^4
+MS, 3.5min #210
1+
330.0742
1+
331.0757
1+
332.0791
2.0
1.5
1.0
0.5
0.0
328
329
330
331
332
333
334
m/z
CO2Et
CO2Et
F
O–N

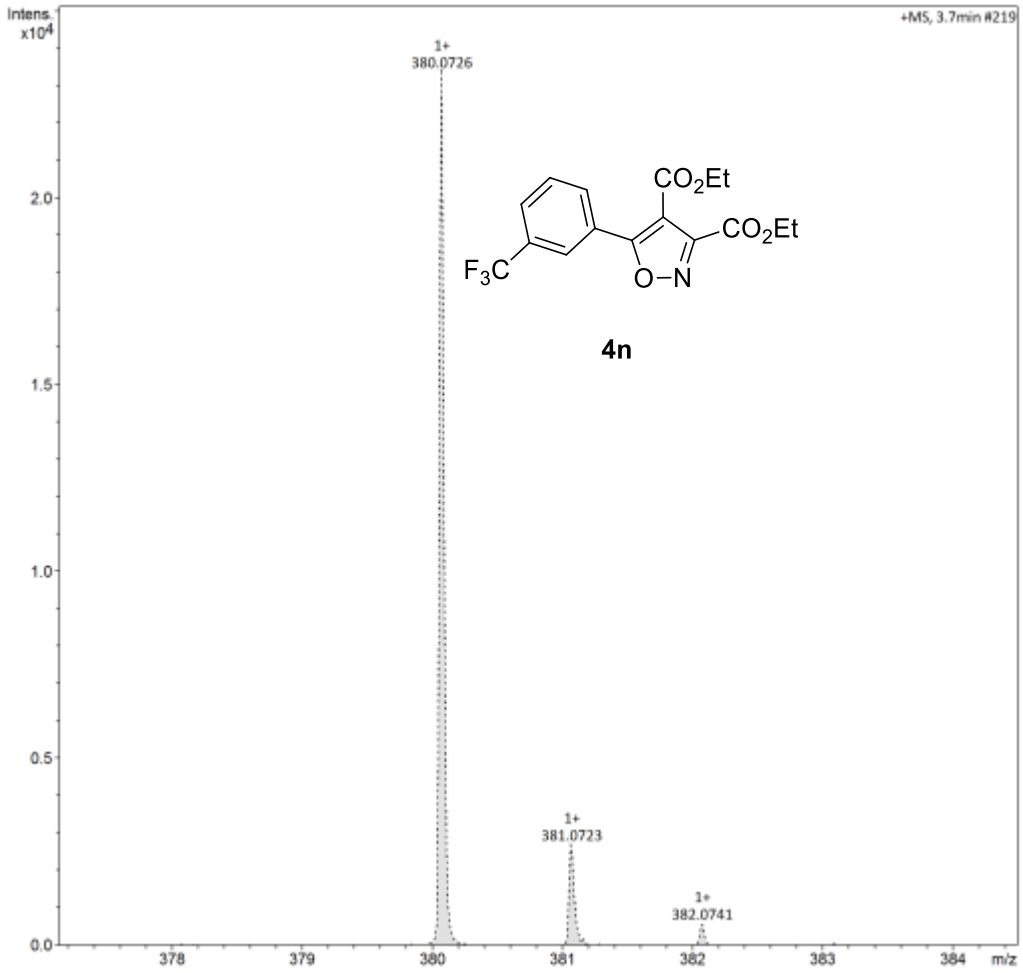
4k

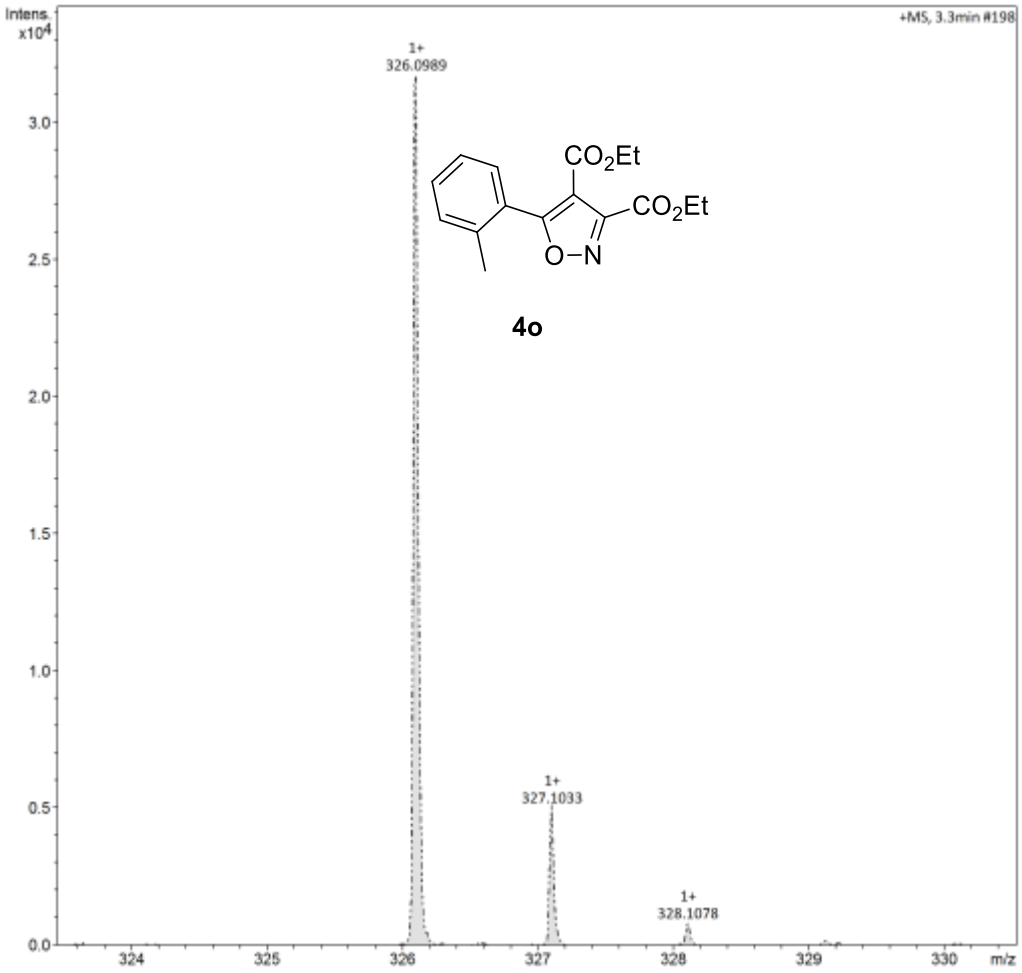

Intens.
x10^4
+MS, 3.8min #227
1+
346.0441
1+
348.0435
1+
347.0484
1+
349.0479
343.0900
351.8647
2.0
1.5
1.0
0.5
0.0
343
344
345
346
347
348
349
350
351
352
m/z
CO2Et
CO2Et
Cl
O–N

4l

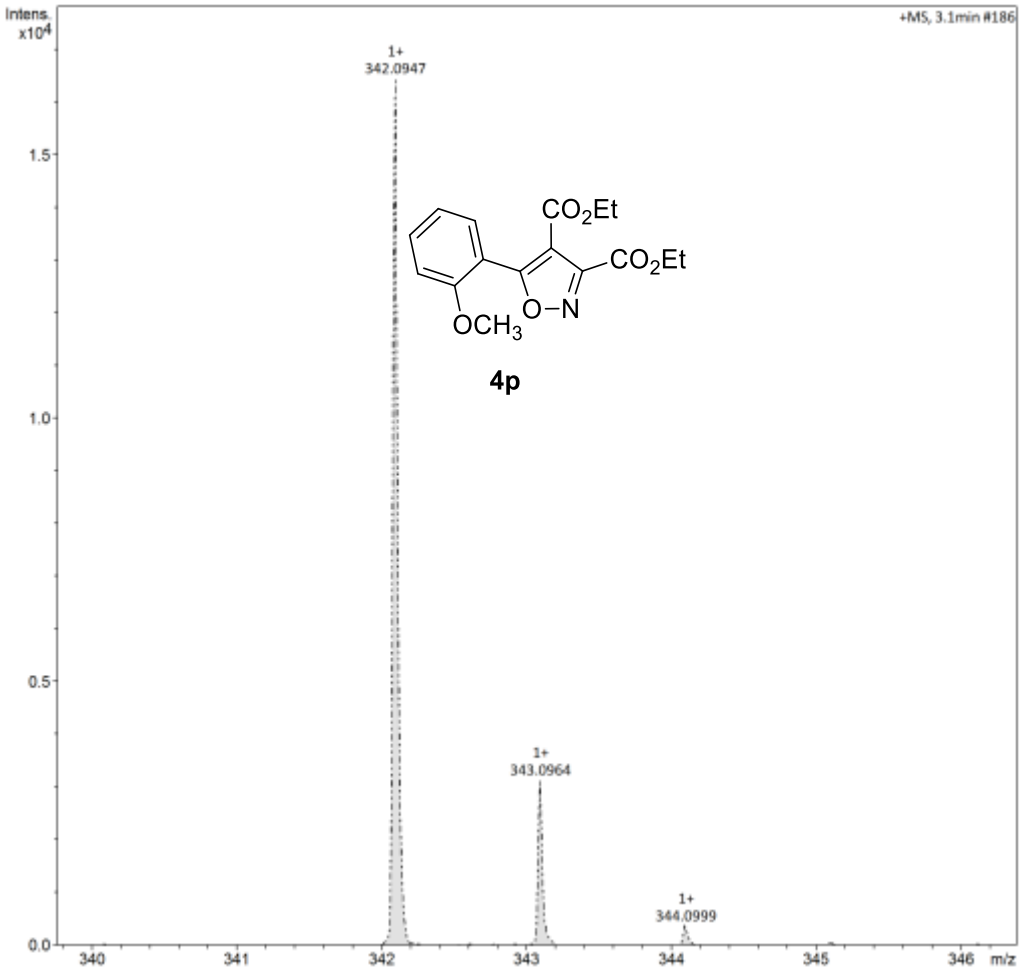

Intens.
+MS, 3.9min #231, Smoothed (0.16,1,GA)
1+
389.9956
1+
391.9936
1+
391.0020
1+
393.0030
1+
394.0629
1500
1000
500
0
388
390
392
394
396
m/z
CO2Et
CO2Et
Br
O–N

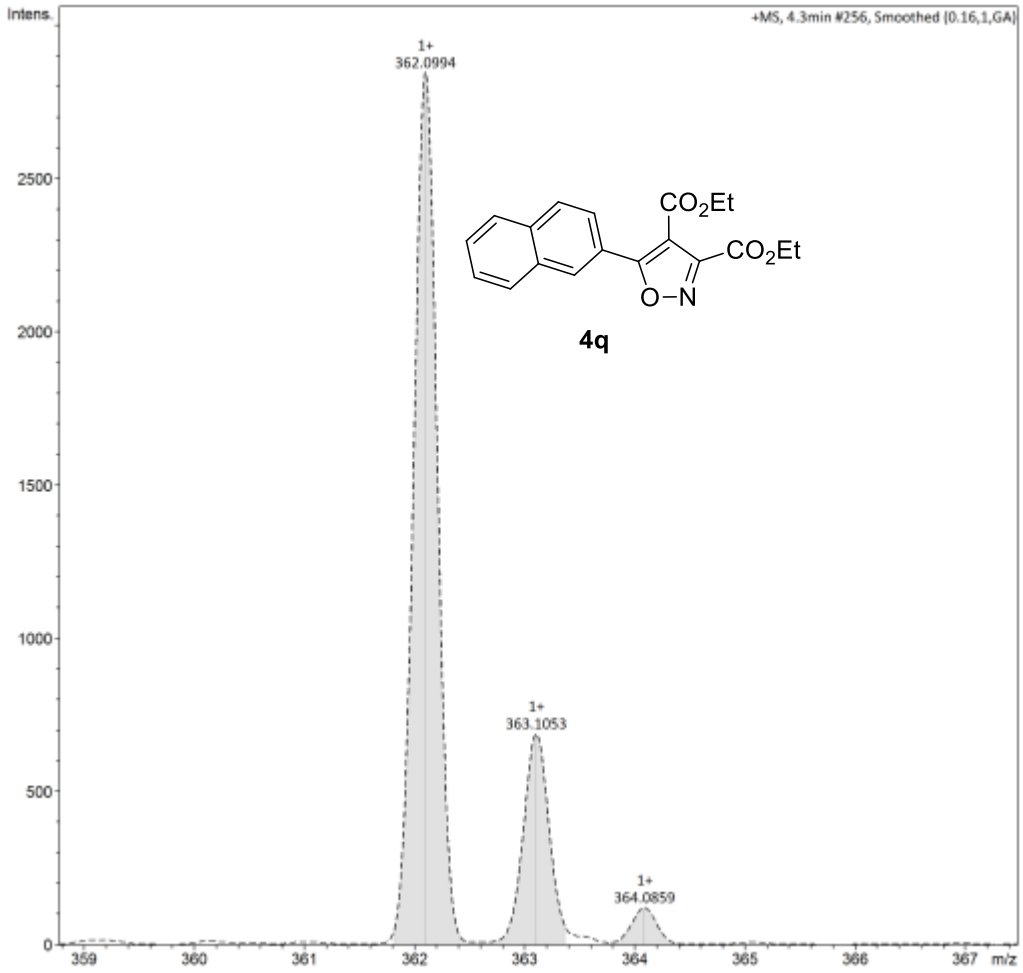
4m

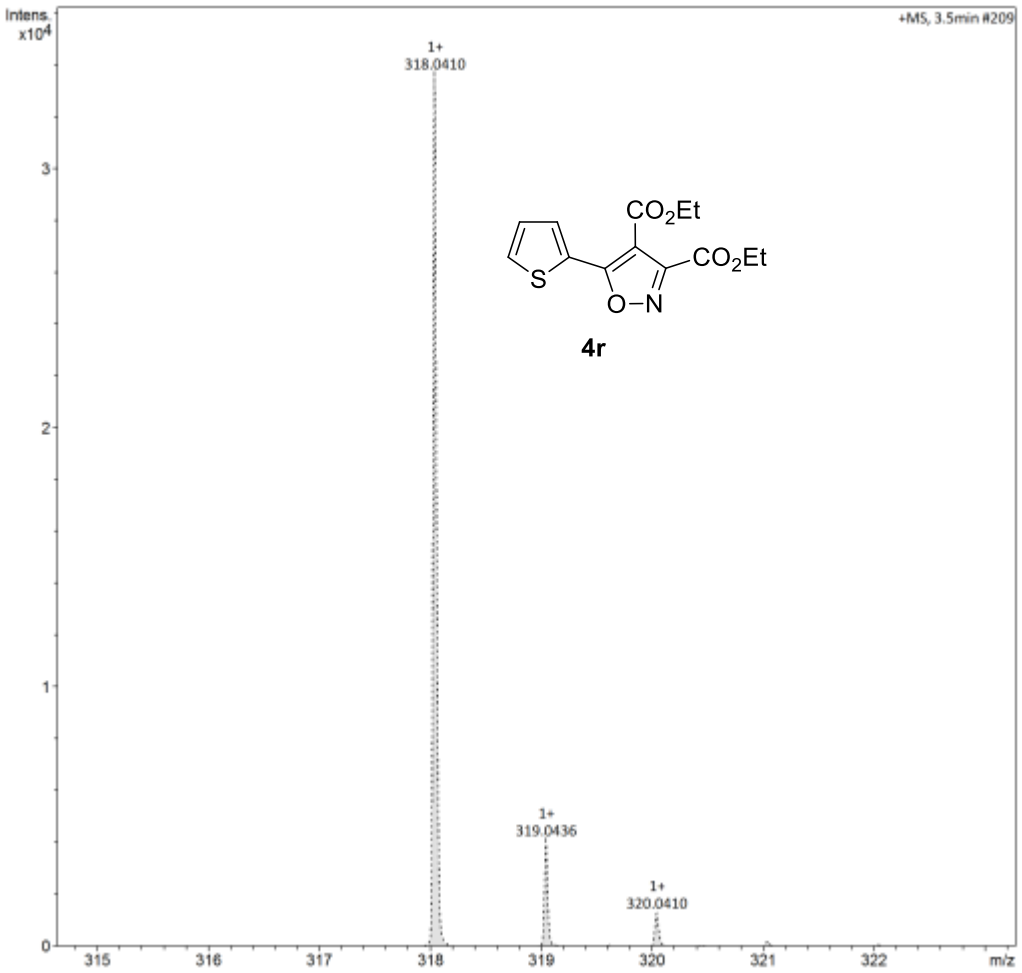

Intens.
x10^4
+MS, 3.7min #219
1+
380.0726
2.0
1.5
1.0
0.5
0.0
CO2Et
CO2Et
F3C
O–N
4n
1+
381.0723
1+
382.0741
378
379
380
381
382
383
384
m/z

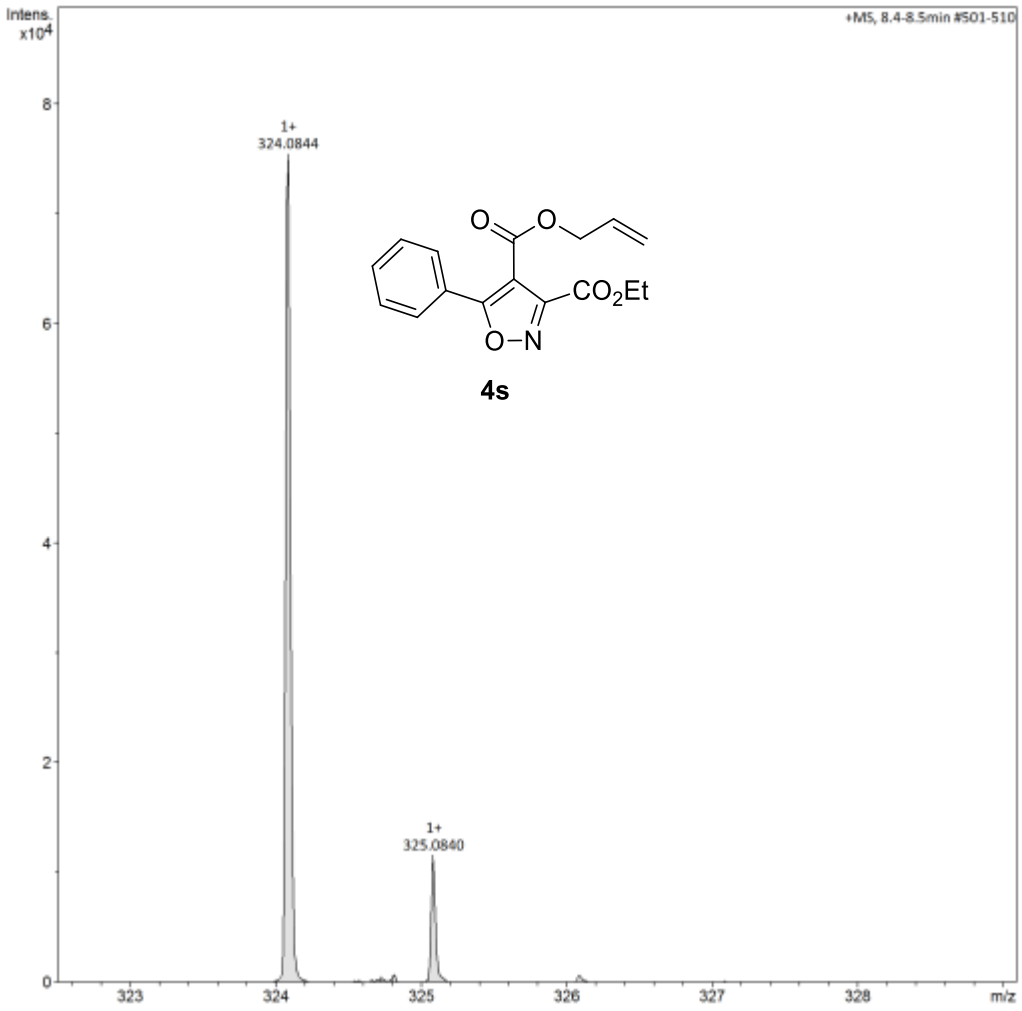

Intens.
x10^4
+MS, 3.3min #198
1+
326.0989
1+
327.1033
1+
328.1078
3.0
2.5
2.0
1.5
1.0
0.5
0.0
324
325
326
327
328
329
330
m/z
CO2Et
CO2Et
O–N

4o

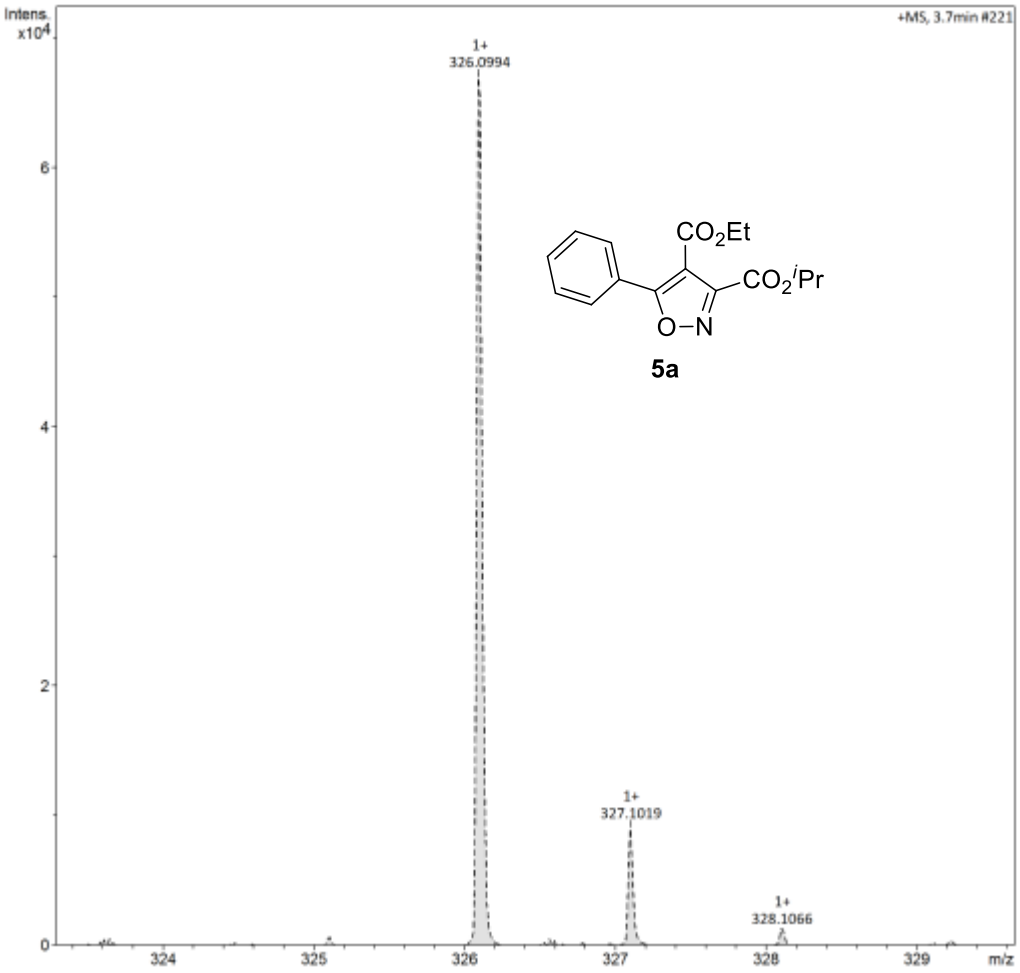

Intens.
x10^4
+MS, 3.1min #186
1+
342.0947
1.5
1.0
0.5
0.0
CO2Et
CO2Et
O–N
OCH3
4p
1+
343.0964
1+
344.0999
340
341
342
343
344
345
346
m/z


Intens.
+MS, 4.3min #256, Smoothed (0.16,1,GA)
1+
362.0994
1+
363.1053
1+
364.0859
2500
2000
1500
1000
500
0
359
360
361
362
363
364
365
366
367
m/z
CO2Et
CO2Et
O–N
4q

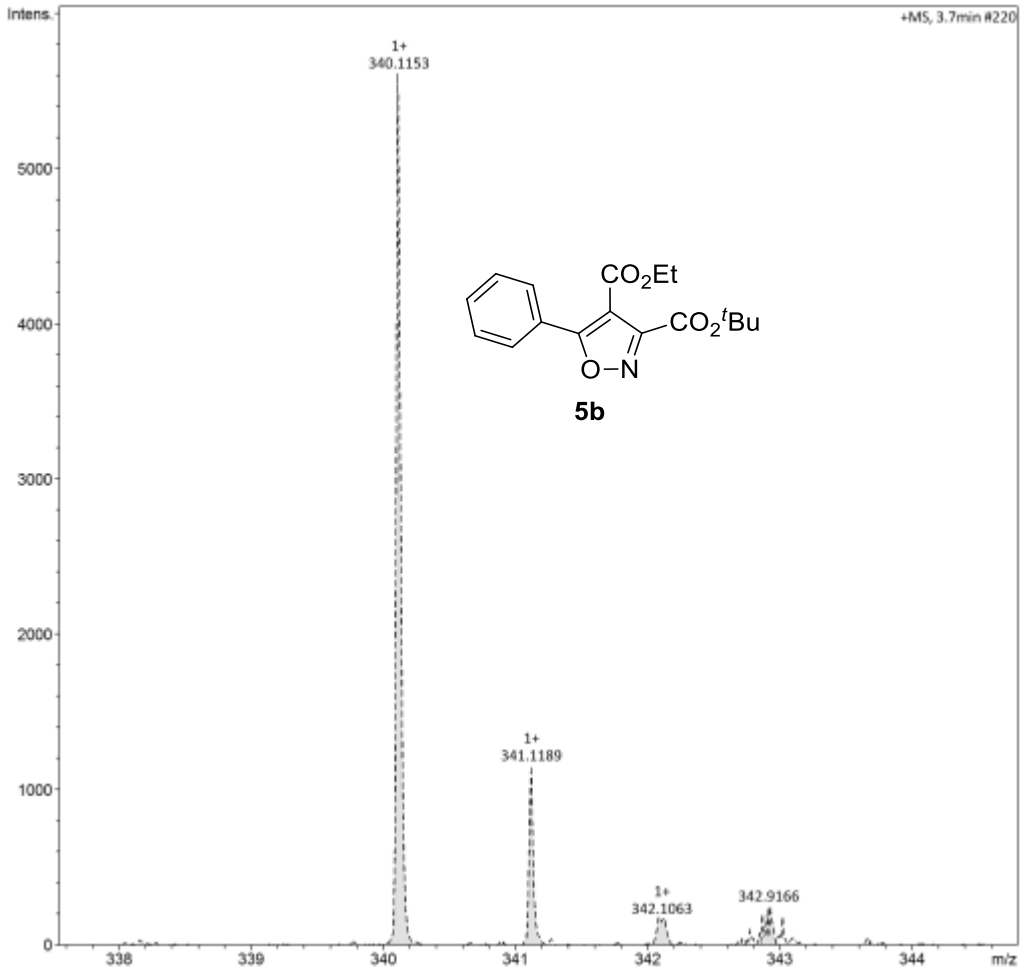

Intens.
x10^4
+MS, 3.5min #209
1+
318.0410
1+
319.0436
1+
320.0410
3
2
1
0
315
316
317
318
319
320
321
322
m/z
CO2Et
CO2Et
S
O–N
4r


Intens.
x10^4
+MS, 8.4-8.5min #501-510
8
6
4
2
0
1+
324.0844
1+
325.0840
323
324
325
326
327
328
m/z
O
O
CO2Et
O–N

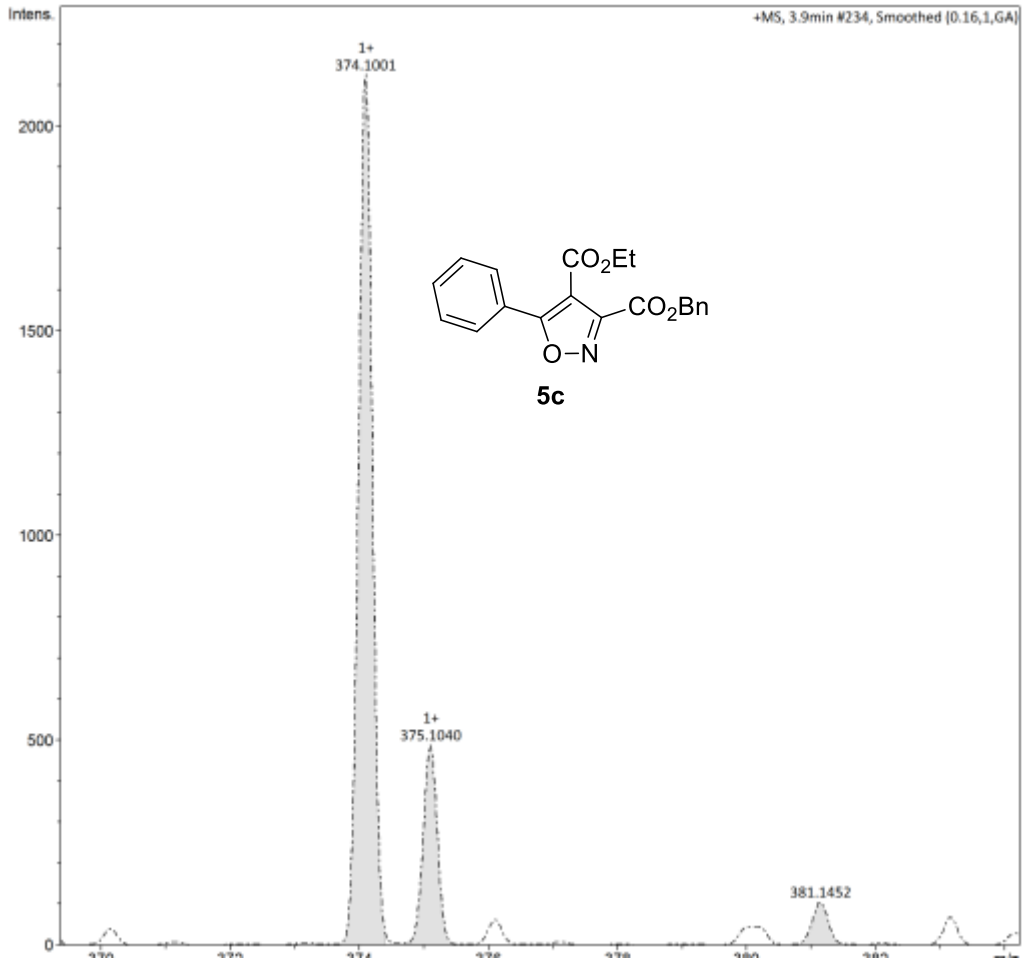
4s

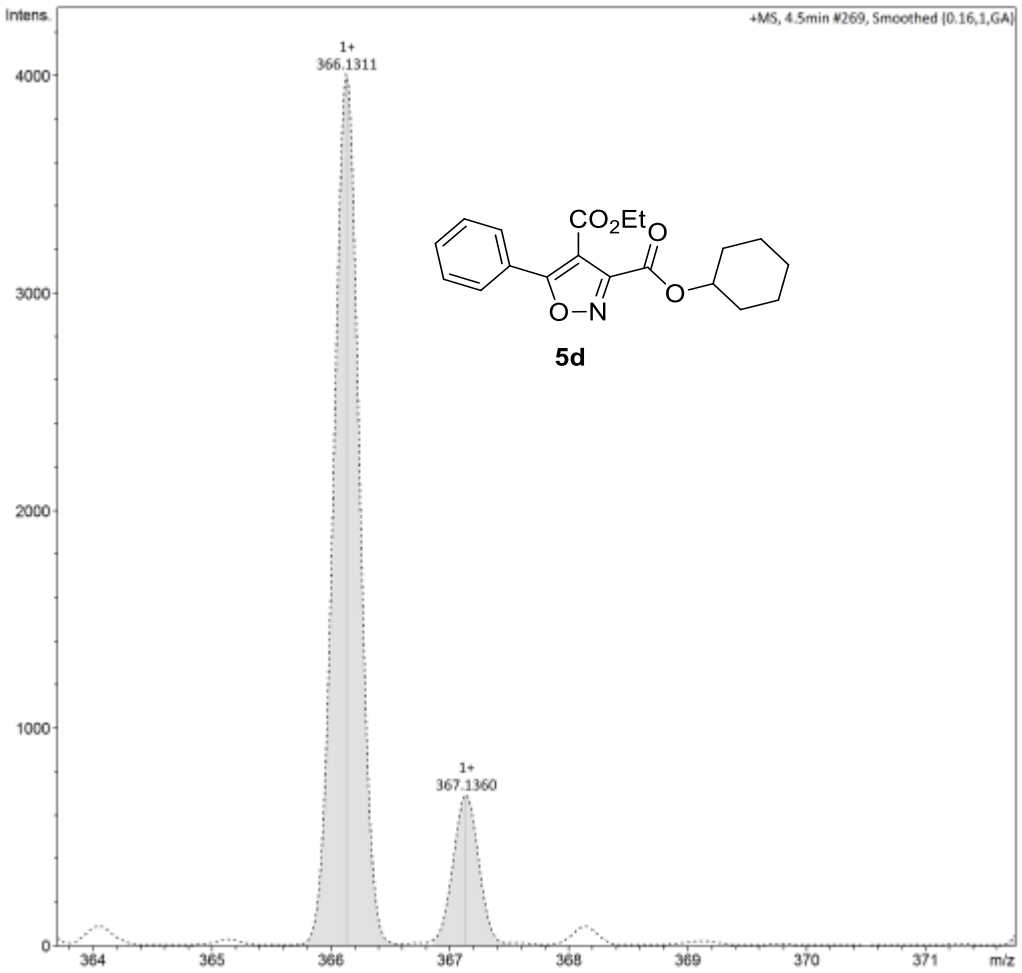

Intens.
x10^4
+MS, 3.7min #221
1+
326.0994
1+
327.1019
1+
328.1066
6
4
2
0
324
325
326
327
328
329
m/z
CO2Et
CO2iPr
O
N

5a

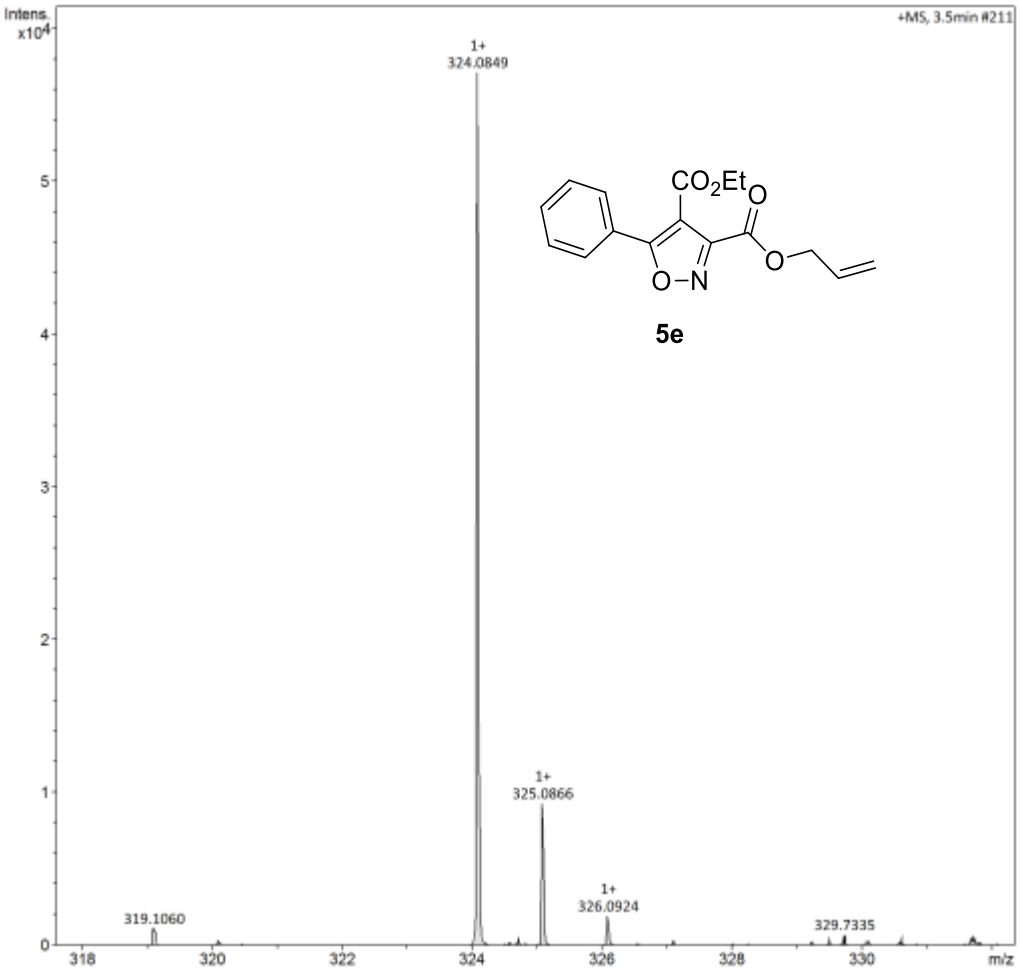

Intens.
+MS, 3.7min #220
1+
340.1153
5000
4000
3000
2000
1000
0
1+
341.1189
1+
342.1063
342.9166
338
339
340
341
342
343
344
m/z
CO2Et
CO2tBu
O–N

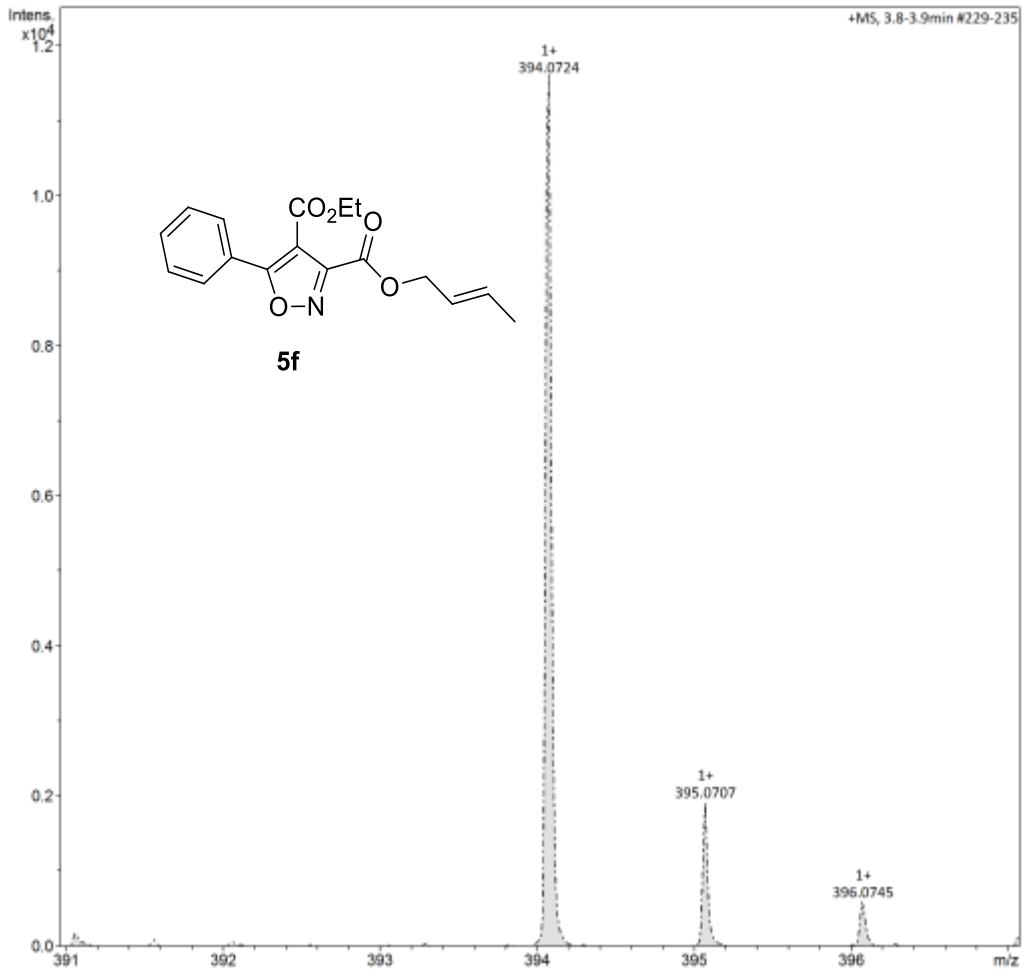
5b


Intens.
+MS, 3.9min #234, Smoothed (0.16,1,GA)
1+
374.1001
2000
1500
1000
500
0
1+
375.1040
381.1452
CO2Et
CO2Bn
O–N
5c

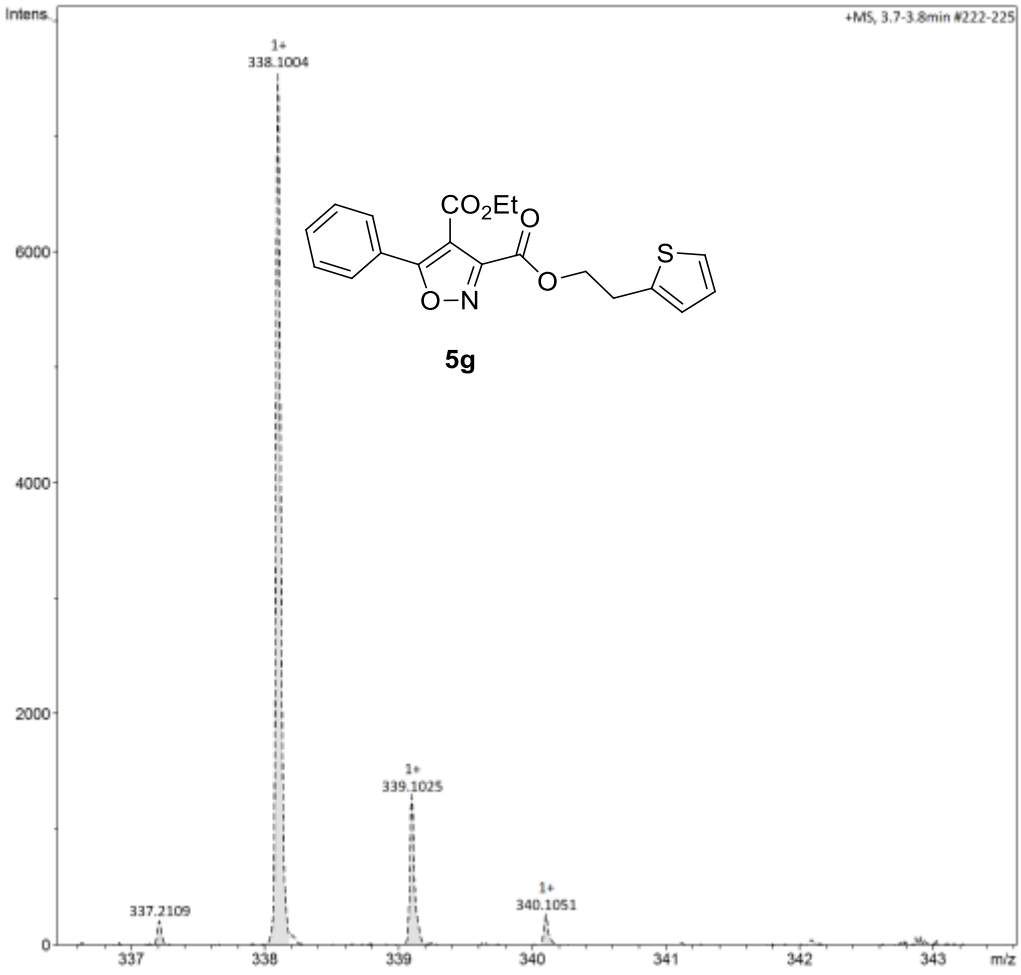

Intens.
+MS, 4.5min #269, Smoothed (0.16,1,GA)
1+
366.1311
1+
367.1360
4000
3000
2000
1000
0
364
365
366
367
368
369
370
371
m/z
CO2Et
O
O
O–N

5d


Intens.
x10^4
+MS, 3.5min #211
1+
324.0849
1+
325.0866
1+
326.0924
319.1060
329.7335
m/z
5e


Intens.
x10^4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
+MS, 3.8-3.9min #229-235
1+
394.0724
1+
395.0707
1+
396.0745
391
392
393
394
395
396
m/z
CO2Et
O
O
O–N

5f


Intens.
+MS, 3.7-3.8min #222-225
1+
338.1004
6000
4000
2000
0
337.2109
1+
339.1025
1+
340.1051
337
338
339
340
341
342
343
m/z
CO2Et
O
O
O–N
S

5g

Cartesian Coordinates and Energies

1'

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.019275	0.440200	-0.068790
2	6	0	-1.040911	-0.465644	0.059216
3	1	0	-0.845372	-1.515303	0.222982
4	6	0	1.415763	0.087552	-0.030341
5	6	0	1.857041	-1.236539	-0.191524
6	6	0	2.369323	1.099607	0.169308
7	6	0	3.214415	-1.540939	-0.140004
8	1	0	1.140881	-2.029972	-0.379463
9	6	0	3.726955	0.791110	0.222735
10	1	0	2.033274	2.123516	0.286155
11	6	0	4.154431	-0.528876	0.070323
12	1	0	3.540006	-2.569064	-0.271984
13	1	0	4.452309	1.583995	0.383383
14	1	0	5.213638	-0.768416	0.109271
15	6	0	-2.414118	-0.021773	0.011109
16	8	0	-2.774131	1.156668	-0.134023
17	8	0	-3.306195	-1.023965	0.144676
18	6	0	-4.687935	-0.636697	0.109833
19	1	0	-4.914328	0.062200	0.919568
20	1	0	-4.933192	-0.164094	-0.845109
21	1	0	-5.251138	-1.562158	0.234367
22	8	0	-0.250555	1.748109	-0.224595
23	1	0	-1.243173	1.864802	-0.218815

Zero-point correction= 0.182955 (Hartree/Particle)
Thermal correction to Energy= 0.194520
Thermal correction to Enthalpy= 0.195464
Thermal correction to Gibbs Free Energy= 0.144212
Sum of electronic and zero-point Energies= -612.583381
Sum of electronic and thermal Energies= -612.571816
Sum of electronic and thermal Enthalpies= -612.570871
Sum of electronic and thermal Free Energies= -612.622124
B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) energy in cyclohexane solvent = -612.95596231

2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.968584	0.907020	-0.000072
2	1	0	1.327798	1.925774	0.000510
3	7	0	1.862595	-0.046010	-0.000093
4	7	0	2.633108	-0.883583	0.000432
5	6	0	-0.457980	0.604442	-0.000362
6	8	0	-1.324968	1.455276	0.000237
7	8	0	-0.692250	-0.732509	-0.000298
8	6	0	-2.078953	-1.105917	0.000000
9	1	0	-2.582089	-0.718920	0.890084
10	1	0	-2.582477	-0.718870	-0.889843
11	1	0	-2.085315	-2.196237	-0.000026

Zero-point correction= 0.077023 (Hartree/Particle)
Thermal correction to Energy= 0.084255
Thermal correction to Enthalpy= 0.085199
Thermal correction to Gibbs Free Energy= 0.045283
Sum of electronic and zero-point Energies= -376.547375
Sum of electronic and thermal Energies= -376.540144
Sum of electronic and thermal Enthalpies= -376.539200
Sum of electronic and thermal Free Energies= -376.579116
B3LYP/6-311++G(d,p)//B3LYP/6-31G(d) energy in cyclohexane solvent = -376.74044834

3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.910905	-0.846890	1.272286
2	6	0	0.752741	-0.007975	-0.000001
3	1	0	0.741751	-0.229851	2.161025
4	1	0	0.202141	-1.679804	1.287417
5	1	0	1.924907	-1.258193	1.327637

6	6	0	0.910841	-0.848726	-1.271081
7	6	0	1.710085	1.185173	-0.000874
8	1	0	0.741576	-0.232991	-2.160702
9	1	0	1.924867	-1.260037	-1.325919
10	1	0	0.202130	-1.681702	-1.284932
11	1	0	2.747417	0.833494	-0.000600
12	1	0	1.553939	1.805453	-0.888983
13	1	0	1.553916	1.806759	0.886318
14	8	0	-0.571637	0.636763	-0.000405
15	7	0	-1.621954	-0.300799	0.000181
16	8	0	-2.671664	0.252358	-0.000159

Zero-point correction= 0.133001 (Hartree/Particle)
Thermal correction to Energy= 0.141432
Thermal correction to Enthalpy= 0.142376
Thermal correction to Gibbs Free Energy= 0.100848
Sum of electronic and zero-point Energies= -362.825316
Sum of electronic and thermal Energies= -362.816885
Sum of electronic and thermal Enthalpies= -362.815941
Sum of electronic and thermal Free Energies= -362.857469
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d,p) energy in cyclohexane solvent = -363.07402867

TS1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.124810	-0.573995	0.091109
2	8	0	-3.709840	-1.495053	-0.438179
3	8	0	-3.191028	-0.283587	1.399108
4	6	0	-2.168880	0.346629	-0.639329
5	6	0	-3.994133	-1.182664	2.187502
6	1	0	-5.017450	-1.219864	1.805053
7	1	0	-3.556595	-2.183223	2.160533
8	1	0	-2.465916	0.509711	-1.673327
9	29	0	-0.154126	0.337319	-0.326814
10	7	0	1.862622	-0.235796	0.055314
11	6	0	2.816836	0.887570	-0.192105
12	1	0	2.743779	1.155352	-1.249368
13	1	0	2.465150	1.734977	0.396304
14	6	0	2.300926	-1.417397	-0.746117
15	1	0	1.610354	-2.231460	-0.528853
16	1	0	2.204631	-1.156715	-1.803979
17	6	0	1.921307	-0.596757	1.506695
18	1	0	1.192965	-1.394750	1.669733
19	1	0	1.599366	0.285193	2.068280
20	8	0	-0.687587	-2.454836	0.450679
21	8	0	-0.798624	-1.219730	-1.424318
22	8	0	0.247565	2.429451	-1.626665
23	8	0	0.112767	2.104561	0.574284
24	6	0	4.257687	0.455884	0.221274
25	1	0	4.948565	0.526841	-0.626415
26	1	0	4.645996	1.103438	1.015633
27	6	0	3.375915	-1.031778	1.874781
28	1	0	3.782878	-0.403450	2.674972
29	1	0	3.394696	-2.068390	2.228953
30	6	0	3.763694	-1.801313	-0.358480
31	1	0	3.811793	-2.838984	-0.009686
32	1	0	4.436573	-1.711614	-1.218611
33	7	0	4.268699	-0.929388	0.710144
34	7	0	-2.799425	3.015010	0.436048
35	7	0	-2.891720	2.020560	-0.043900
36	6	0	0.267431	2.869295	-0.462018
37	6	0	-0.898196	-2.352873	-0.759371
38	6	0	0.516787	4.342674	-0.178488
39	1	0	-0.079888	4.685511	0.671006
40	1	0	1.573163	4.483702	0.082431
41	1	0	0.299015	4.941074	-1.065738
42	6	0	-1.318398	-3.533677	-1.614598
43	1	0	-0.739262	-3.565026	-2.542516
44	1	0	-1.200488	-4.466117	-1.059090
45	1	0	-2.371681	-3.399772	-1.884087
46	1	0	-3.972225	-0.777425	3.198740

Zero-point correction= 0.365707 (Hartree/Particle)
Thermal correction to Energy= 0.393904
Thermal correction to Enthalpy= 0.394848
Thermal correction to Gibbs Free Energy= 0.302560
Sum of electronic and zero-point Energies= -1374.720676
Sum of electronic and thermal Energies= -1374.692480

Sum of electronic and thermal Enthalpies= -1374.691536
Sum of electronic and thermal Free Energies= -1374.783823
B3LYP/6-311++G(d,p)-LANL2DZ/SMD//B3LYP /6-31G(d)-LANL2DZ energy in cyclohexane solvent = -1375.46764664

N_2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	0.552751
2	7	0	0.000000	0.000000	-0.552751

Zero-point correction= 0.005599 (Hartree/Particle)
Thermal correction to Energy= 0.007959
Thermal correction to Enthalpy= 0.008904
Thermal correction to Gibbs Free Energy= -0.012851
Sum of electronic and zero-point Energies= -109.518530
Sum of electronic and thermal Energies= -109.516170
Sum of electronic and thermal Enthalpies= -109.515225
Sum of electronic and thermal Free Energies= -109.536980
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -109.55390474

INT1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.847973	-0.122823	0.970810
2	8	0	-2.899850	-1.201992	1.540091
3	8	0	-3.139191	1.054685	1.572742
4	6	0	-2.394801	0.081312	-0.423473
5	6	0	-3.445030	0.969251	2.969932
6	1	0	-4.319512	0.334457	3.138202
7	1	0	-2.598204	0.558042	3.527959
8	1	0	-2.835148	0.934466	-0.931400
9	29	0	-0.352400	0.207319	-0.335922
10	7	0	1.668740	-0.216671	0.236671
11	6	0	2.385445	0.976809	0.770444
12	1	0	2.406831	1.721189	-0.027806
13	1	0	1.790393	1.391752	1.588023
14	6	0	2.414048	-0.717021	-0.958820
15	1	0	1.885695	-1.600941	-1.324151
16	1	0	2.342955	0.057932	-1.726351
17	6	0	1.664506	-1.281042	1.283486
18	1	0	1.079244	-2.121038	0.901083
19	1	0	1.142965	-0.879302	2.158973
20	8	0	-0.583167	-1.770491	-0.968540
21	8	0	-2.721167	-1.115774	-1.191845
22	8	0	0.367195	1.742185	-2.103821
23	8	0	-0.297995	2.183235	-0.022604
24	6	0	3.820485	0.563752	1.220553
25	1	0	4.578473	1.183855	0.728802
26	1	0	3.947316	0.687718	2.302066
27	6	0	3.133489	-1.690315	1.619881
28	1	0	3.332829	-1.591713	2.692937
29	1	0	3.322262	-2.734072	1.344888
30	6	0	3.886623	-1.037969	-0.556152
31	1	0	4.146060	-2.073488	-0.804217
32	1	0	4.591496	-0.387761	-1.086315
33	7	0	4.087803	-0.844518	0.889403
34	6	0	0.078785	2.556429	-1.200648
35	6	0	-1.752517	-1.992925	-1.317799
36	6	0	0.143195	4.056765	-1.438971
37	1	0	-0.873335	4.466512	-1.443286
38	1	0	0.685513	4.548272	-0.624922
39	1	0	0.622084	4.272143	-2.396122
40	6	0	-2.184044	-3.297671	-1.921933
41	1	0	-2.944774	-3.132613	-2.688695
42	1	0	-1.321666	-3.820205	-2.337973
43	1	0	-2.629911	-3.913797	-1.132384
44	1	0	-3.647625	1.992564	3.287863

Zero-point correction= 0.361053 (Hartree/Particle)
Thermal correction to Energy= 0.385994
Thermal correction to Enthalpy= 0.386938
Thermal correction to Gibbs Free Energy= 0.301626
Sum of electronic and zero-point Energies= -1265.295283
Sum of electronic and thermal Energies= -1265.270342
Sum of electronic and thermal Enthalpies= -1265.269398
Sum of electronic and thermal Free Energies= -1265.354710

B3LYP/6-311++G(d,p)-LANL2DZ/SMD//B3LYP/6-31G(d)-LANL2DZ energy in cyclohexane solvent = -1266.00408496

TS2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.773017	2.417821	0.383341
2	8	0	-2.227483	3.414516	-0.144893
3	8	0	-1.796237	2.185896	1.701226
4	6	0	-1.105932	1.287738	-0.362312
5	6	0	-2.389452	3.217381	2.503943
6	1	0	-1.846272	4.157494	2.375761
7	1	0	-3.435631	3.367474	2.222496
8	29	0	0.488508	0.246218	0.225190
9	7	0	2.474139	-0.482241	0.044976
10	6	0	2.580174	-1.158918	-1.285393
11	1	0	1.859344	-1.983259	-1.283600
12	1	0	2.274922	-0.435514	-2.044769
13	6	0	2.815944	-1.473770	1.107940
14	1	0	2.725154	-0.963342	2.069109
15	1	0	2.050489	-2.251498	1.073515
16	6	0	3.467205	0.631618	0.093351
17	1	0	3.337740	1.148882	1.048873
18	1	0	3.215199	1.326984	-0.708506
19	8	0	0.354103	-0.137356	2.640795
20	8	0	-0.309184	-1.454465	0.970622
21	8	0	1.309793	1.683968	-2.474292
22	8	0	0.627060	2.218345	-0.391578
23	6	0	4.042032	-1.665012	-1.496395
24	1	0	4.061522	-2.743462	-1.690787
25	1	0	4.506352	-1.167479	-2.355136
26	6	0	4.908084	0.056058	-0.077681
27	1	0	5.417295	0.527517	-0.925842
28	1	0	5.516016	0.241462	0.815028
29	6	0	4.247061	-2.038974	0.857440
30	1	0	4.893068	-1.871243	1.726745
31	1	0	4.217849	-3.119384	0.674956
32	7	0	4.868190	-1.395028	-0.309617
33	6	0	0.971045	2.518972	-1.645848
34	6	0	-0.231996	-1.156406	2.230932
35	6	0	0.890934	4.004204	-1.941568
36	1	0	-0.131750	4.348978	-1.752925
37	1	0	1.546989	4.555741	-1.259246
38	1	0	1.176543	4.203646	-2.975938
39	6	0	-0.910394	-2.119393	3.192348
40	1	0	-1.996699	-2.046923	3.065815
41	1	0	-0.623592	-3.152176	2.968792
42	1	0	-0.652675	-1.873094	4.224115
43	1	0	-1.284663	1.352811	-1.433374
44	1	0	-2.312106	2.864373	3.531871
45	6	0	-3.087973	-3.023595	-0.176616
46	6	0	-3.466659	-2.127948	-1.361003
47	1	0	-2.021967	-2.929645	0.049493
48	1	0	-3.653163	-2.777926	0.723980
49	1	0	-3.306543	-4.063775	-0.445238
50	6	0	-4.964771	-1.827872	-1.448918
51	6	0	-2.937418	-2.706295	-2.675734
52	1	0	-5.179190	-1.163732	-2.292595
53	1	0	-5.506348	-2.767119	-1.608331
54	1	0	-5.341897	-1.371207	-0.531665
55	1	0	-3.447727	-3.651577	-2.888940
56	1	0	-3.117767	-2.018584	-3.507655
57	1	0	-1.862253	-2.898952	-2.609125
58	8	0	-2.711788	-0.826497	-1.315912
59	7	0	-2.767583	-0.004468	-0.243844
60	8	0	-3.445937	-0.312817	0.687165

Zero-point correction= 0.493714 (Hartree/Particle)
Thermal correction to Energy= 0.528521
Thermal correction to Enthalpy= 0.529465
Thermal correction to Gibbs Free Energy= 0.422948
Sum of electronic and zero-point Energies= -1628.042754
Sum of electronic and thermal Energies= -1628.007947
Sum of electronic and thermal Enthalpies= -1628.007003
Sum of electronic and thermal Free Energies= -1628.113520

B3LYP/6-311++G(d,p)-LANL2DZ/SMD//B3LYP/6-31G(d)-LANL2DZ energy in cyclohexane solvent = -1629.00045900

INT2

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.897843	-1.828830	-0.506327
2	8	0	2.452516	-2.813142	-1.073081
3	8	0	3.704920	-1.885370	0.569204
4	6	0	2.569027	-0.479114	-0.972368
5	6	0	3.950459	-3.211272	1.063079
6	1	0	3.013978	-3.667788	1.394149
7	1	0	4.401831	-3.835818	0.287732
8	29	0	-1.106651	-0.939971	0.519119
9	7	0	-2.903217	0.080909	0.211346
10	6	0	-2.556274	1.429579	-0.333015
11	1	0	-1.891920	1.909107	0.390470
12	1	0	-1.992922	1.266597	-1.255464
13	6	0	-3.594615	0.249960	1.523701
14	1	0	-3.862835	-0.748758	1.884712
15	1	0	-2.873619	0.681870	2.222533
16	6	0	-3.825309	-0.597880	-0.743537
17	1	0	-4.000529	-1.613415	-0.380428
18	1	0	-3.298090	-0.674896	-1.696489
19	8	0	0.510714	-1.590878	1.630098
20	8	0	-0.342966	0.413060	1.830505
21	8	0	-0.435931	-0.868168	-1.810011
22	8	0	-1.414739	-2.481469	-0.641122
23	6	0	-3.869898	2.241614	-0.561552
24	1	0	-3.837647	3.196534	-0.025359
25	1	0	-4.012908	2.465157	-1.624294
26	6	0	-5.140288	0.236130	-0.862080
27	1	0	-5.346875	0.490035	-1.907536
28	1	0	-5.999859	-0.328854	-0.485019
29	6	0	-4.854922	1.153312	1.327363
30	1	0	-5.757339	0.646519	1.686495
31	1	0	-4.756249	2.088947	1.888456
32	7	0	-5.039405	1.484423	-0.091552
33	6	0	-0.815980	-2.058848	-1.707713
34	6	0	0.557963	-0.439417	2.161529
35	6	0	-0.547182	-3.065503	-2.802179
36	1	0	0.480194	-3.421542	-2.664213
37	1	0	-1.229648	-3.916006	-2.740794
38	1	0	-0.614433	-2.585386	-3.782163
39	6	0	1.661869	-0.075327	3.114200
40	1	0	2.588076	0.044124	2.539785
41	1	0	1.434267	0.854641	3.638758
42	1	0	1.816931	-0.888150	3.829629
43	1	0	1.809547	-0.383617	-1.733731
44	1	0	4.636125	-3.083584	1.901451
45	6	0	2.133032	3.129048	0.783577
46	6	0	2.705352	3.092316	-0.638664
47	1	0	1.176934	2.596593	0.830072
48	1	0	2.815931	2.680187	1.505737
49	1	0	1.960202	4.171961	1.073259
50	6	0	4.154860	3.586791	-0.713543
51	6	0	1.813492	3.897908	-1.593697
52	1	0	4.523196	3.522200	-1.743013
53	1	0	4.202396	4.636276	-0.399601
54	1	0	4.808152	2.997817	-0.069219
55	1	0	1.840376	4.956597	-1.314563
56	1	0	2.164488	3.802114	-2.625874
57	1	0	0.777546	3.547938	-1.546245
58	8	0	2.587636	1.753498	-1.243881
59	7	0	3.082527	0.639764	-0.502834
60	8	0	3.900560	0.829128	0.402654

Zero-point correction= 0.497226 (Hartree/Particle)
Thermal correction to Energy= 0.531844
Thermal correction to Enthalpy= 0.532788
Thermal correction to Gibbs Free Energy= 0.425728
Sum of electronic and zero-point Energies= -1628.129780
Sum of electronic and thermal Energies= -1628.095162
Sum of electronic and thermal Enthalpies= -1628.094217
Sum of electronic and thermal Free Energies= -1628.201278

B3LYP/6-311++G(d,p)-LANL2DZ/SMD//B3LYP/6-31G(d)-LANL2DZ energy in cyclohexane solvent = -1629.08850603

Copper catalyst- DABCO-Cu(OAc)$_2$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	0.967470	-0.006944	-0.247123
2	7	0	-1.111056	-0.172988	-0.123111

3	6	0	-1.561155	-1.273574	-1.025875
4	1	0	-1.346128	-0.962456	-2.053813
5	1	0	-0.952076	-2.152866	-0.802222
6	6	0	-1.848655	1.075800	-0.468603
7	1	0	-1.520946	1.843638	0.235180
8	1	0	-1.536780	1.386419	-1.468532
9	6	0	-1.429381	-0.540726	1.291792
10	1	0	-1.027837	0.253267	1.926821
11	1	0	-0.886840	-1.462159	1.516650
12	8	0	1.059221	1.899255	1.290347
13	8	0	1.086809	1.813990	-0.932109
14	8	0	2.925503	-0.672476	-0.442119
15	8	0	1.295562	-1.922793	0.312547
16	6	0	-3.086522	-1.528493	-0.803712
17	1	0	-3.636143	-1.453104	-1.748446
18	1	0	-3.260150	-2.532025	-0.400328
19	6	0	-2.974615	-0.707842	1.440183
20	1	0	-3.223870	-1.696675	1.840466
21	1	0	-3.385897	0.038906	2.127984
22	6	0	-3.383309	0.803594	-0.370029
23	1	0	-3.863633	1.524904	0.300146
24	1	0	-3.863288	0.896442	-1.350555
25	7	0	-3.643619	-0.550856	0.140029
26	6	0	2.539571	-1.781787	0.030256
27	6	0	1.192719	2.463413	0.185565
28	6	0	3.505671	-2.906491	0.288910
29	1	0	3.050109	-3.864214	0.022669
30	1	0	4.430526	-2.752804	-0.270239
31	1	0	3.740208	-2.934584	1.359505
32	6	0	1.507536	3.942904	0.076082
33	1	0	2.555961	4.062533	-0.220520
34	1	0	0.894166	4.410680	-0.699854
35	1	0	1.350793	4.437785	1.036491

Zero-point correction= 0.290176 (Hartree/Particle)
Thermal correction to Energy= 0.309309
Thermal correction to Enthalpy= 0.310254
Thermal correction to Gibbs Free Energy= 0.239015
Sum of electronic and zero-point Energies= -998.223266
Sum of electronic and thermal Energies= -998.204133
Sum of electronic and thermal Enthalpies= -998.203188
Sum of electronic and thermal Free Energies= -998.274427

B3LYP/6-311++G(d,p)-LANL2DZ /SMD//B3LYP/6-31G(d)-LANL2DZ energy in cyclohexane solvent = -998.77628370

INT3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.329370	-0.089807	-0.011758
2	8	0	-2.576641	-1.276602	0.029021
3	8	0	-3.281532	0.884973	-0.014692
4	6	0	-1.017871	0.554494	-0.063761
5	6	0	-4.631940	0.404748	0.034425
6	1	0	-4.849202	-0.227583	-0.831003
7	1	0	-4.803178	-0.174996	0.945826
8	1	0	-0.911508	1.626212	-0.102761
9	1	0	-5.259527	1.296593	0.024275
10	7	0	0.099516	-0.149746	-0.078091
11	8	0	0.258529	-1.363871	-0.028143
12	8	0	1.226356	0.718755	-0.188217
13	6	0	2.571176	0.142591	0.021434
14	6	0	2.690009	-0.486480	1.413557
15	6	0	2.938872	-0.822902	-1.111389
16	6	0	3.422791	1.415986	-0.067065
17	1	0	2.370321	0.226126	2.181478
18	1	0	2.091441	-1.393963	1.500571
19	1	0	3.738228	-0.742605	1.604245
20	1	0	2.763751	-0.348232	-2.082658
21	1	0	4.004297	-1.070670	-1.042007
22	1	0	2.361678	-1.745932	-1.061811
23	1	0	4.478662	1.156640	0.062265
24	1	0	3.301507	1.899208	-1.041499
25	1	0	3.141218	2.129600	0.713310

Zero-point correction= 0.205309 (Hartree/Particle)
Thermal correction to Energy= 0.219283
Thermal correction to Enthalpy= 0.220227
Thermal correction to Gibbs Free Energy= 0.163574
Sum of electronic and zero-point Energies= -629.909825

Sum of electronic and thermal Energies= -629.895851
Sum of electronic and thermal Enthalpies= -629.894907
Sum of electronic and thermal Free Energies= -629.951561
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -630.31247541

TS3

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.489828	-0.306383	-0.018127
2	8	0	-2.902271	-1.442573	0.026973
3	8	0	-3.237480	0.801363	0.101858
4	6	0	-1.058152	0.095288	-0.215245
5	6	0	-4.647593	0.568088	0.285509
6	1	0	-5.054056	0.013889	-0.564075
7	1	0	-4.822386	0.000312	1.202932
8	1	0	-0.610993	1.271732	-0.321947
9	1	0	-5.095913	1.558965	0.351516
10	7	0	-0.220395	-0.826649	-0.315138
11	8	0	0.068712	-1.978151	-0.331703
12	8	0	1.530562	0.213731	-0.733324
13	6	0	2.644798	-0.004541	0.148398
14	6	0	2.208623	0.097227	1.619801
15	6	0	3.236599	-1.387355	-0.158179
16	6	0	3.675203	1.094024	-0.183127
17	1	0	1.744595	1.069150	1.824005
18	1	0	1.487719	-0.688815	1.869687
19	1	0	3.068649	-0.012034	2.289764
20	1	0	3.498133	-1.453998	-1.219081
21	1	0	4.142513	-1.557831	0.434974
22	1	0	2.524079	-2.184421	0.068606
23	1	0	4.584408	0.958644	0.414592
24	1	0	3.944426	1.050807	-1.242865
25	1	0	3.269062	2.089781	0.025571
26	8	0	0.284193	2.252824	-0.506250
27	1	0	0.404491	2.676719	0.360199
28	1	0	1.090399	1.277985	-0.622529

Zero-point correction= 0.221745 (Hartree/Particle)
Thermal correction to Energy= 0.237959
Thermal correction to Enthalpy= 0.238903
Thermal correction to Gibbs Free Energy= 0.177297
Sum of electronic and zero-point Energies= -706.251492
Sum of electronic and thermal Energies= -706.235278
Sum of electronic and thermal Enthalpies= -706.234334
Sum of electronic and thermal Free Energies= -706.295940
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -706.7188488

H_2O

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.000000	0.000000	0.119720
2	1	0	0.000000	0.761560	-0.478879
3	1	0	0.000000	-0.761560	-0.478879

Zero-point correction= 0.021168 (Hartree/Particle)
Thermal correction to Energy= 0.024003
Thermal correction to Enthalpy= 0.024947
Thermal correction to Gibbs Free Energy= 0.003501
Sum of electronic and zero-point Energies= -76.387785
Sum of electronic and thermal Energies= -76.384950
Sum of electronic and thermal Enthalpies= -76.384006
Sum of electronic and thermal Free Energies= -76.405452
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -76.46193682

^{t}BuOH

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.490538	-0.000103	-0.357103
2	6	0	0.005445	-0.000001	0.013947
3	1	0	1.983788	0.886350	0.055034
4	1	0	1.983671	-0.886598	0.055083
5	1	0	1.622405	-0.000141	-1.444379
6	6	0	-0.690726	-1.265560	-0.509968

7	6	0	-0.690547	1.265661	-0.509958
8	1	0	-1.747860	-1.279772	-0.212570
9	1	0	-0.654445	-1.321229	-1.604253
10	1	0	-0.209714	-2.159617	-0.099735
11	1	0	-0.654226	1.321352	-1.604242
12	1	0	-1.747685	1.280013	-0.212588
13	1	0	-0.209419	2.159640	-0.099691
14	8	0	-0.013825	-0.000005	1.452172
15	1	0	-0.944171	0.000052	1.728456

Zero-point correction= 0.136162 (Hartree/Particle)
Thermal correction to Energy= 0.142897
Thermal correction to Enthalpy= 0.143842
Thermal correction to Gibbs Free Energy= 0.107152
Sum of electronic and zero-point Energies= -233.534796
Sum of electronic and thermal Energies= -233.528061
Sum of electronic and thermal Enthalpies= -233.527116
Sum of electronic and thermal Free Energies= -233.563806
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -233.75753536

INT4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.498459	0.295687	-0.001636
2	8	0	0.836165	1.457894	0.000555
3	8	0	1.321413	-0.763161	-0.001295
4	6	0	-0.888425	-0.140757	-0.005382
5	6	0	2.727842	-0.441399	0.002430
6	1	0	2.987208	0.135842	-0.888355
7	1	0	2.982710	0.135574	0.894670
8	1	0	3.239756	-1.402996	0.003531
9	7	0	-2.059553	-0.141169	-0.000347
10	8	0	-3.260085	-0.214911	0.003254

Zero-point correction= 0.065377 (Hartree/Particle)
Thermal correction to Energy= 0.072634
Thermal correction to Enthalpy= 0.073578
Thermal correction to Gibbs Free Energy= 0.032967
Sum of electronic and zero-point Energies= -396.380419
Sum of electronic and thermal Energies= -396.373161
Sum of electronic and thermal Enthalpies= -396.372217
Sum of electronic and thermal Free Energies= -396.412828
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -396.57298548

TS4

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.746824	-0.733819	-0.892625
2	6	0	0.385223	0.081792	-0.891034
3	6	0	-2.123158	-0.404424	-0.474238
4	6	0	-2.649919	0.880335	-0.679929
5	6	0	-2.958466	-1.411655	0.037131
6	6	0	-3.975997	1.158717	-0.354301
7	1	0	-2.032479	1.653749	-1.125460
8	6	0	-4.280926	-1.128840	0.363787
9	1	0	-2.549918	-2.402872	0.197835
10	6	0	-4.793319	0.157332	0.172051
11	1	0	-4.373104	2.155648	-0.523947
12	1	0	-4.913051	-1.911782	0.773375
13	1	0	-5.827068	0.375398	0.426422
14	6	0	0.463687	1.442173	-0.305401
15	8	0	1.030186	2.375881	-0.839684
16	8	0	-0.112987	1.518442	0.915717
17	6	0	-0.083870	2.815192	1.528995
18	1	0	0.946713	3.153680	1.664749
19	1	0	-0.618037	3.546310	0.915166
20	1	0	-0.578323	2.691574	2.492685
21	8	0	-0.685499	-1.925551	-1.534492
22	1	0	0.246943	-2.159563	-1.684068
23	6	0	3.217668	-0.682210	0.356534
24	8	0	4.049265	-1.047712	1.158541
25	8	0	3.474453	0.031996	-0.755718
26	6	0	1.781858	-0.956147	0.455170
27	6	0	4.850587	0.411922	-0.937166
28	1	0	4.864216	1.013649	-1.845317

29	1	0	5.199419	0.995712	-0.081969
30	1	0	5.479835	-0.475073	-1.048005
31	7	0	1.062157	-1.592761	1.213086
32	8	0	-0.115858	-1.855209	1.403800
33	1	0	1.084014	-0.052084	-1.712225

Zero-point correction= 0.247531 (Hartree/Particle)
Thermal correction to Energy= 0.267696
Thermal correction to Enthalpy= 0.268640
Thermal correction to Gibbs Free Energy= 0.195950
Sum of electronic and zero-point Energies= -1008.917063
Sum of electronic and thermal Energies= -1008.896897
Sum of electronic and thermal Enthalpies= -1008.895953
Sum of electronic and thermal Free Energies= -1008.968643
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -1009.47723827

INT5

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.623039	-1.271110	0.264507
2	6	0	-0.575286	-0.357334	0.658019
3	6	0	1.984106	-0.625694	0.069568
4	6	0	2.842343	-0.496556	1.169069
5	6	0	2.382869	-0.131455	-1.178859
6	6	0	4.087100	0.114770	1.020760
7	1	0	2.528727	-0.872999	2.137424
8	6	0	3.630439	0.476301	-1.323349
9	1	0	1.721099	-0.237119	-2.030996
10	6	0	4.484687	0.600554	-0.225937
11	1	0	4.744773	0.211757	1.880118
12	1	0	3.937275	0.846819	-2.297745
13	1	0	5.456071	1.073674	-0.342097
14	6	0	-0.297386	1.140699	0.566317
15	8	0	0.036330	1.823108	1.506172
16	8	0	-0.442466	1.594887	-0.693260
17	6	0	-0.132775	2.987111	-0.886179
18	1	0	-0.757314	3.609165	-0.240626
19	1	0	0.919840	3.172248	-0.657991
20	1	0	-0.340917	3.188008	-1.937037
21	8	0	0.641007	-2.286858	1.231516
22	6	0	-3.050998	-0.498679	-0.320887
23	8	0	-3.887662	-0.902113	-1.094453
24	8	0	-3.294536	0.372006	0.687721
25	6	0	-1.609464	-0.865427	-0.314072
26	6	0	-4.657615	0.816238	0.797223
27	1	0	-4.673637	1.499827	1.645981
28	1	0	-4.966724	1.327105	-0.118370
29	1	0	-5.321534	-0.034262	0.971992
30	7	0	-1.152441	-1.669756	-1.205557
31	8	0	0.205278	-1.843769	-1.014596
32	1	0	-0.836420	-0.564540	1.697141
33	1	0	1.325888	-2.925985	0.969223

Zero-point correction= 0.251957 (Hartree/Particle)
Thermal correction to Energy= 0.270768
Thermal correction to Enthalpy= 0.271712
Thermal correction to Gibbs Free Energy= 0.203275
Sum of electronic and zero-point Energies= -1008.998922
Sum of electronic and thermal Energies= -1008.980110
Sum of electronic and thermal Enthalpies= -1008.979166
Sum of electronic and thermal Free Energies= -1009.047603
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -1009.55830896

Product

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.843487	-0.677940	-0.106863
2	6	0	-0.295447	0.104698	-0.128219
3	6	0	2.288836	-0.451378	-0.041215
4	6	0	2.871066	0.741843	-0.503187
5	6	0	3.114646	-1.465460	0.481902
6	6	0	4.252099	0.913645	-0.429179
7	1	0	2.240517	1.518261	-0.918937
8	6	0	4.492003	-1.282813	0.548889
9	1	0	2.669477	-2.388094	0.838253
10	6	0	5.065407	-0.092033	0.095341
11	1	0	4.693471	1.838035	-0.791091

12	1	0	5.118667	-2.070048	0.958462
13	1	0	6.141585	0.048850	0.148806
14	6	0	-0.429416	1.576610	-0.056971
15	8	0	0.288273	2.386512	-0.611783
16	8	0	-1.464570	1.919279	0.731698
17	6	0	-1.767463	3.323826	0.779373
18	1	0	-0.914279	3.886656	1.166091
19	1	0	-2.020421	3.690019	-0.218741
20	1	0	-2.623470	3.411713	1.448297
21	6	0	-2.824813	-0.581986	-0.289232
22	8	0	-3.263186	0.344798	-0.934312
23	8	0	-3.568989	-1.505188	0.336580
24	6	0	-1.362170	-0.849989	-0.127028
25	6	0	-4.990614	-1.364682	0.162794
26	1	0	-5.431808	-2.190588	0.720220
27	1	0	-5.329618	-0.404346	0.559760
28	1	0	-5.253547	-1.427884	-0.896193
29	7	0	-0.923109	-2.086924	-0.111265
30	8	0	0.461655	-1.979172	-0.091495

Zero-point correction= 0.225500 (Hartree/Particle)
Thermal correction to Energy= 0.242755
Thermal correction to Enthalpy= 0.243699
Thermal correction to Gibbs Free Energy= 0.178234
Sum of electronic and zero-point Energies= -932.617480
Sum of electronic and thermal Energies= -932.600225
Sum of electronic and thermal Enthalpies= -932.599281
Sum of electronic and thermal Free Energies= -932.664746
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -933.11226316

NO-radical

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	7	0	0.000000	0.000000	-0.617977
2	8	0	0.000000	0.000000	0.540730

Zero-point correction= 0.004536 (Hartree/Particle)
Thermal correction to Energy= 0.006897
Thermal correction to Enthalpy= 0.007841
Thermal correction to Gibbs Free Energy= -0.015469
Sum of electronic and zero-point Energies= -129.883620
Sum of electronic and thermal Energies= -129.881259
Sum of electronic and thermal Enthalpies= -129.880315
Sum of electronic and thermal Free Energies= -129.903626
B3LYP/6-311++G(d,p)/SMD//B3LYP/6-31G(d) energy in cyclohexane solvent = -129.92927171

$Cu(OAc)_2(O^tBu)$

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-0.408857	0.049397	-0.232608
2	8	0	-0.909317	-2.716026	0.809434
3	8	0	-0.223975	-1.647479	-1.050857
4	8	0	-0.017387	2.171846	-1.756714
5	8	0	-0.608985	1.830988	0.376147
6	6	0	-0.426387	2.597935	-0.675097
7	6	0	-0.686264	-2.687706	-0.399055
8	6	0	-0.764391	4.060152	-0.442803
9	1	0	-0.451940	4.385030	0.553654
10	1	0	-0.292743	4.674752	-1.212244
11	1	0	-1.851318	4.186129	-0.507488
12	6	0	-0.926530	-3.892594	-1.299117
13	1	0	-0.123885	-4.006753	-2.033397
14	1	0	-1.021268	-4.795787	-0.692805
15	1	0	-1.858025	-3.730581	-1.853846
16	6	0	-3.836336	1.495138	0.371881
17	6	0	-3.191530	0.106922	0.523816
18	1	0	-3.102440	2.278205	0.576100
19	1	0	-4.212801	1.624344	-0.648915
20	1	0	-4.675613	1.617972	1.067535
21	6	0	-4.240914	-1.008343	0.269011
22	6	0	-2.611491	-0.078176	1.943813
23	1	0	-3.778403	-1.990148	0.401879
24	1	0	-5.074920	-0.904224	0.973926
25	1	0	-4.632766	-0.934349	-0.750371
26	1	0	-3.416440	-0.028500	2.686206
27	1	0	-2.115057	-1.049235	2.021071

28	1	0	-1.896733	0.720927	2.165836
29	8	0	-2.233093	-0.112769	-0.491534
30	7	0	4.210646	-0.155924	0.509376
31	6	0	3.494503	-1.152015	1.311012
32	1	0	3.807697	-2.148601	0.982766
33	1	0	3.789414	-1.040509	2.359934
34	6	0	3.905418	-0.377022	-0.909284
35	1	0	4.422307	0.390075	-1.495654
36	1	0	4.312079	-1.349713	-1.205725
37	6	0	3.740945	1.177337	0.892641
38	1	0	4.328008	1.927792	0.352374
39	1	0	3.930973	1.315607	1.962411
40	6	0	1.945921	-0.984174	1.155399
41	1	0	1.456137	-1.914110	0.873411
42	1	0	1.479762	-0.634854	2.081525
43	6	0	2.216743	1.348770	0.571562
44	1	0	1.642341	1.670680	1.441638
45	1	0	2.057150	2.069602	-0.230526
46	6	0	2.362195	-0.326978	-1.166386
47	1	0	2.086695	0.424230	-1.910387
48	1	0	1.959909	-1.287023	-1.487775
49	7	0	1.666424	0.042865	0.104673

Zero-point correction= 0.417119 (Hartree/Particle)
Thermal correction to Energy= 0.443230
Thermal correction to Enthalpy= 0.444174
Thermal correction to Gibbs Free Energy= 0.359846
Sum of electronic and zero-point Energies= -1231.101172
Sum of electronic and thermal Energies= -1231.075060
Sum of electronic and thermal Enthalpies= -1231.074116
Sum of electronic and thermal Free Energies= -1231.158445

B3LYP/6-311++G(d,p)-LANL2DZ/SMD//B3LYP/6-31G(d)-LANL2DZ energy in cyclohexane solvent = -1231.85431077