Supporting Information

Electrocatalytic Ring-opening Dihydroalkoxylation of *N*-Aryl Maleimides with Alcohols under Metal- and Oxidant-free Conditions

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General Methods.

Proton nuclear magnetic resonance spectra (^{1}H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 400 MHz and 100 MHz or 600 MHz and 150 MHz, respectively, using $CDCl_3$ as reference standard (δ 7.26 ppm) for ^{1}H NMR and (δ 77.04 ppm) for ^{13}C NMR. HRMS spectra were recorded with Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization. Melting points were uncorrected. Precoated silica gel plates GF-254 were used for thin-layer analytical chromatography. Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

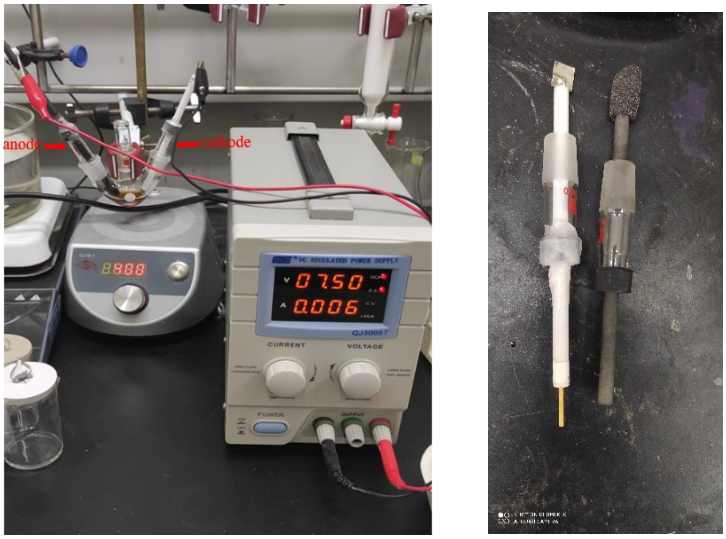
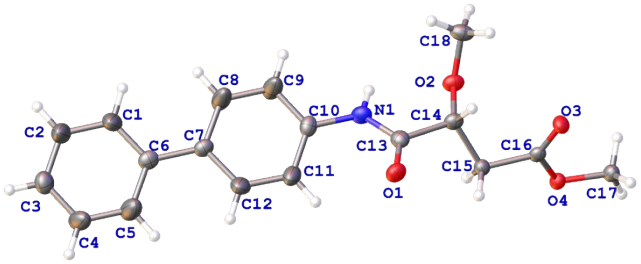


Figure S1. Electrolysis setup (undivided cell)

Crystallographic Data:

Table S1. Crystal data and structure refinement of **3n** (CCDC 2210698) (the crystal structure is with ellipsoids at 30% probability level)



Identification code	**3n**
Empirical formula	$C_{18}H_{19}NO_4$
Formula weight	313.34
Temperature/K	99.99(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	27.340(4)
b/Å	5.3646(6)
c/Å	10.6018(13)
α/°	90
β/°	94.192(12)
γ/°	90
Volume/Å^3	1550.8(3)
Z	4
ρ_{calc}g/cm^3	1.342
μ/mm^{-1}	0.779
F(000)	664.0
Crystal size/mm^3	0.12 × 0.11 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.484 to 133.182
Index ranges	$-32 \le h \le 32$, $-6 \le k \le 3$, $-12 \le l \le 11$
Reflections collected	5702
Independent reflections	2729 [R_{int} = 0.0558, R_{sigma} = 0.0859]
Data/restraints/parameters	2729/0/210
Goodness-of-fit on F^2	1.217
Final R indexes [I>=2σ (I)]	R_1 = 0.1125, wR_2 = 0.2955
Final R indexes [all data]	R_1 = 0.1369, wR_2 = 0.3212
Largest diff. peak/hole / e Å^{-3}	0.49/-0.38

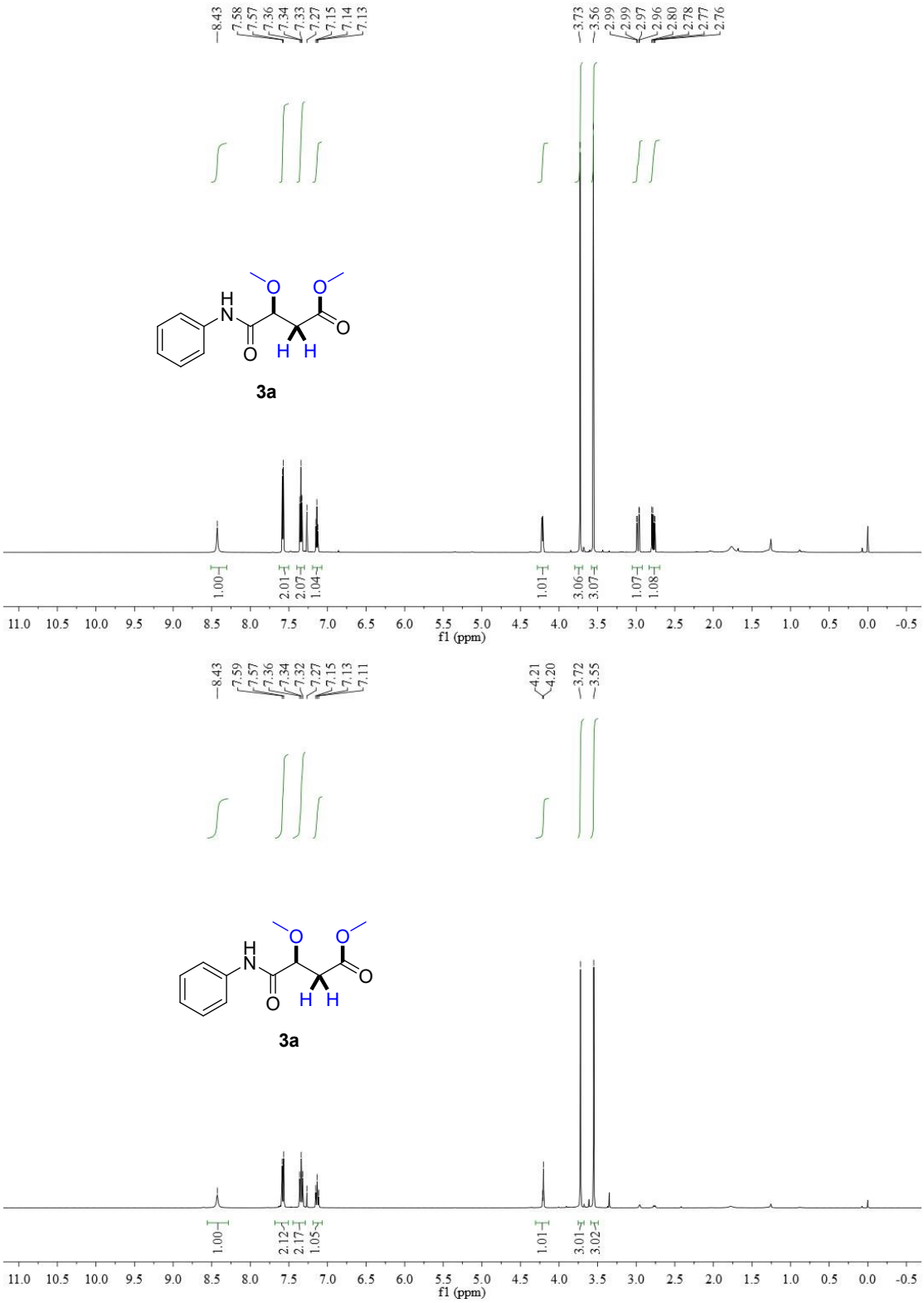


Figure S2. ^{1}H NMR spectra of product **3a** and *D*-labeled product **3a'**

Sample Name	zz-ddjc-1	**Position**	P1-A1	**Instrument Name**	Instrument 1
User Name		**Inj Vol**	0.2	**InjPosition**	
Sample Type	Sample	**IRM Calibration Status**	Success	**Data Filename**	ZZ-DDJC-1.d
ACQ Method	00-LHF.m	**Comment**		**Acquired Time**	11/2/2022 2:58:29 PM

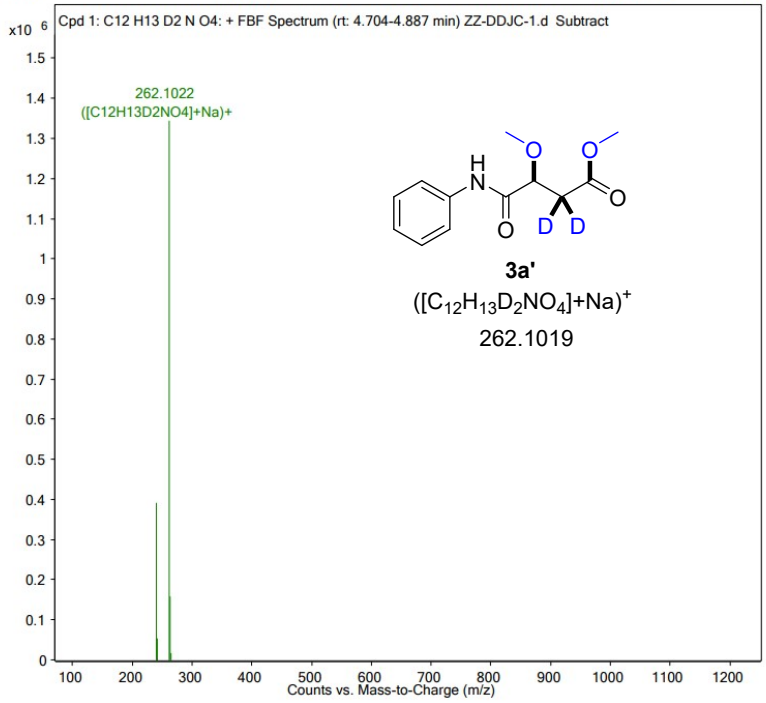


Figure S3. HRMS spectra of *D*-labeled product **3a'**

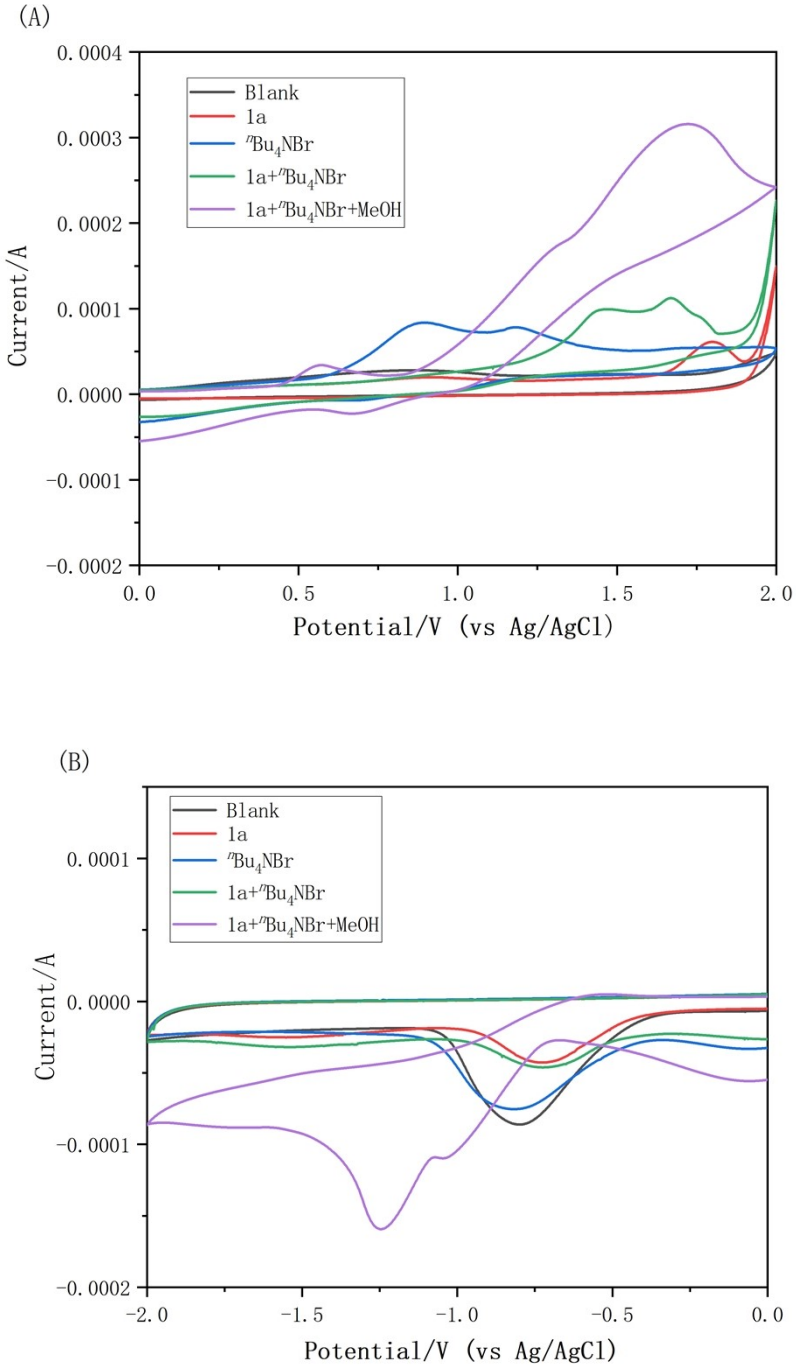


Figure S4. Cyclic voltammograms of related compounds in 0.1 M $ClLiO_4/CH_3CN$ using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. Scan rate: 0.1 V s-1. (a) Background ($LiClO_4$ (5 mM) + MeCN (5 mL)) (black curve); (b) **1a** (5 mM) (red curve); (c) $^{n}Bu_4NBr$ (5 mM) (blue curve); (d) **1a** (5 mM) + $^{n}Bu_4NBr$ (5 mM) (green curve); (e) **1a** (5 mM) + $^{n}Bu_4NBr$ (5 mM) + CH_3OH (50 mM) (purple curve)

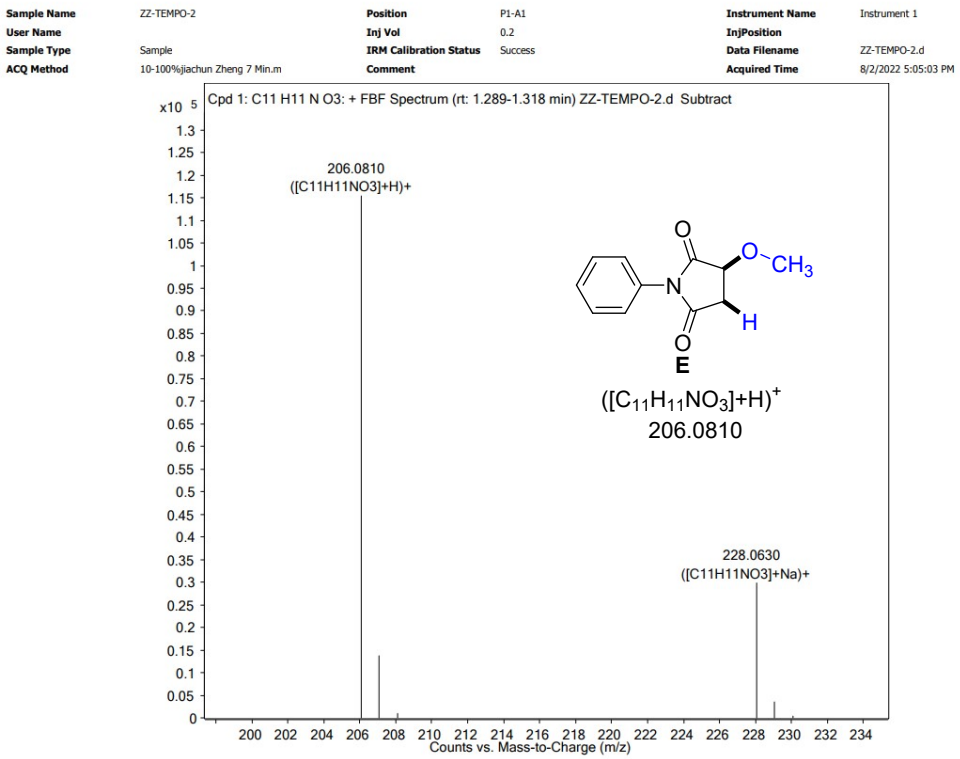
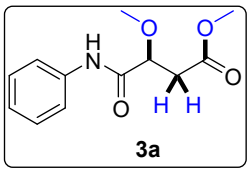
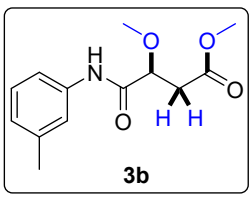


Figure S5. Intermediate **E** was detected by HRMS

Characterization Data for Products 3a-ah

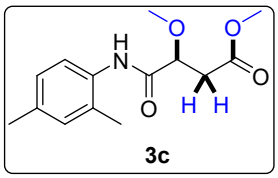


Methyl 3-methoxy-4-oxo-4-(phenylamino)butanoate ***(3a)***. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (39.9 mg, 84%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.42 (s, 1H), 7.58–7.56 (m, 2H), 7.35–7.32 (m, 2H), 7.15–7.12 (m, 1H), 4.21 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.55 (s, 3H), 2.97 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.77 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.2, 137.2, 129.2, 124.8, 119.9, 78.9, 59.3, 52.2, 37.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{15}NNaO_4$ 260.0893; Found 260.0890.



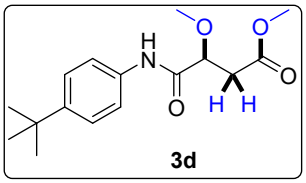
Methyl 3-methoxy-4-oxo-4-(m-tolylamino)butanoate ***(3b)***. Following the general procedure, eluted by petroleum

ether/ethyl acetate = 40/1 to 20/1. Brown oil (40.7 mg, 81%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.37 (s, 1H), 7.44–7.43 (m, 1H), 7.36–7.34 (m, 1H), 7.23–7.21 (m, 1H), 6.96–6.94 (m, 1H), 4.20 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 2.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.76 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.34 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.2, 139.2, 137.1, 129.0, 125.6, 120.5, 116.9, 79.0, 59.3, 52.2, 37.5, 21.6 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{17}NNaO_4$ 274.1050; Found 274.1051.



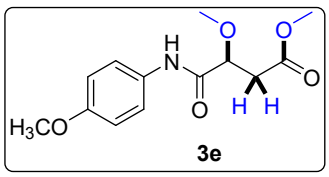
3c

*Methyl 4-((2,4-dimethylphenyl)amino)-3-methoxy-4-oxobutanoate (**3c**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (28.1mg, 53%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.30 (s, 1H), 7.77–7.76 (m, 1H), 7.03–7.00 (m, 2H), 4.23 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.73 (s, 3H), 3.57 (s, 3H), 2.99 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.77 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.29 (s, 3H), 2.24 (s, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.0, 169.1, 135.0, 132.4, 131.3, 128.7, 127.5, 122.4, 79.2, 59.4, 52.1, 37.7, 21.0, 17.6 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}NO_4$ 266.1387; Found 266.1391.



3d

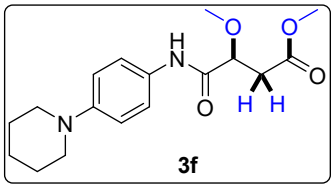
*Methyl 4-((4-isopropylphenyl)amino)-3-methoxy-4-oxobutanoate (**3d**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (48.7 mg, 83%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.37 (s, 1H), 7.507.48 (m, 2H), 7.37–7.34 (m, 2H), 4.21 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 2.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.76 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.30 (s, 9H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 169.1, 147.8, 134.5, 126.0, 119.7, 79.0, 59.3, 52.1, 37.6, 34.5, 31.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{23}NNaO_4$ 316.1519; Found 316.1524.



3e

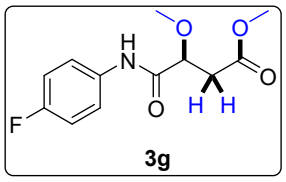
Methyl 3-methoxy-4-((4-methoxyphenyl)amino)-4-

*oxobutanoate (**3e**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (40.1 mg, 75%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.32 (s, 1H), 7.49–7.46 (m, 2H), 6.88–6.85 (m, 2H), 4.20 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.79 (s, 3H), 3.72 (s, 3H), 3.54 (s, 3H), 2.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.75 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 169.0, 156.7, 130.3, 121.6, 114.3, 78.9, 59.3, 55.6, 52.1, 37.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{17}NNaO_5$ 290.0999; Found 290.0997.



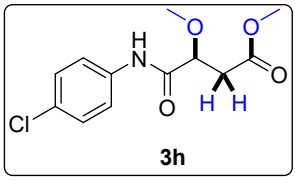
3f

*Methyl 3-methoxy-4-oxo-4-((4-(piperidin-1-yl)phenyl)amino)butanoate (**3f**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (49.3 mg, 77%). ^{1}H NMR ($CDCl_3$, 400MHz) δ 8.27 (s, 1H), 7.44–7.42 (m, 2H), 6.94–6.91 (m, 2H), 4.19 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 3.11 (t, *J* = 4.0 Hz, 4H), 2.97 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.74 (dd, *J* = 16.0, 8.0 Hz, 1H), 1.74–1.68 (m, 4H), 1.59–1.54 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.1, 168.8, 121.1, 117.3, 79.0, 59.3, 52.1, 51.3, 37.7, 25.9, 24.3 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{17}H_{25}N_2O_4$ 321.1809; Found 321.1810.



3g

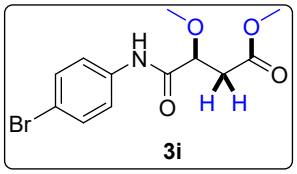
*Methyl 4-((4-fluorophenyl)amino)-3-methoxy-4-oxobutanoate (**3g**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (37.3 mg, 73%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.42 (s, 1H), 7.54–7.52 (m, 2H), 7.04–7.01 (m, 2H), 4.20 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.71 (s, 3H), 3.54 (s, 3H), 2.96 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.78 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 169.1, 159.4 (d, $^1J_{CF}$ = 243 Hz), 133.1 (d, ^4J = 3.0 Hz), 121.6 (d, $^3J_{CF}$ = 7.5 Hz), 115.7 (d, $^2J_{CF}$ = 22.5 Hz), 78.7, 59.2, 52.2, 37.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.9 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}FNNaO_4$ 278.0799; Found 278.0801.



3h

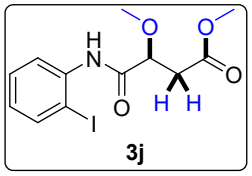
Methyl 4-((4-chlorophenyl)amino)-3-methoxy-4-

*oxobutanoate (**3h**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (38.6 mg, 71%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.44 (s, 1H), 7.54–7.52 (m, 2H), 7.31–7.26 (m, 2H), 4.20 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 2.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.78 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 169.3, 135.8, 129.7, 129.2, 121.1, 78.8, 59.3, 52.2, 37.2 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}ClNNaO_4$ 294.0504; Found 294.0508.



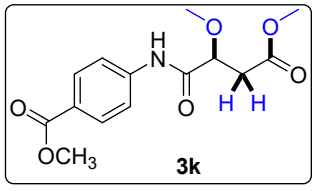
3i

*Methyl 4-((4-bromophenyl)amino)-3-methoxy-4-oxobutanoate (**3i**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (43.6 mg, 69%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.44 (s, 1H), 7.49–7.47 (m, 2H), 7.45–7.43 (m, 2H)，4.19 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.54 (s, 3H), 2.96 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.79 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 169.3, 136.3, 132.2, 121.4, 117.4, 78.8, 59.3, 52.2, 37.2 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{12}H_{15}BrNO_4$ 316.0179; Found 316.0174.



3j

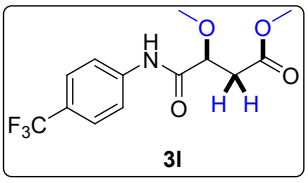
*Methyl 4-((2-iodophenyl)amino)-3-methoxy-4-oxobutanoate (**3j**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (36.3 mg, 50%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.95 (s, 1H), 8.30–8.28 (m, 1H), 7.81–7.78 (m, 1H), 7.38–7.33 (m, 1H), 6.88–6.84 (m, 1H), 4.23 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.74 (s, 3H), 3.63 (s, 3H), 2.98 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.78 (dd, *J* = 20.0, 12.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.9, 169.6, 139.1, 137.7, 129.4, 126.4, 121.6, 89.8, 79.2, 60.0, 52.2, 37.8 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{14}INNaO_4$ 385.9860; Found 385.9860.



3k

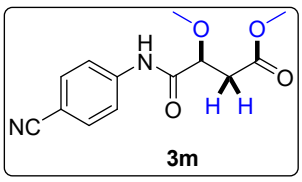
Methyl 4-(2,4-dimethoxy-4-oxobutanamido)benzoate

*(**3k**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (41.3 mg, 70%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.61 (s, 1H), 8.03–8.01 (m, 2H), 7.68–7.65 (m, 2H), 4.21 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.56 (s, 3H), 2.97 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.80 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 169.6, 166.7, 141.3, 131.0, 126.1, 119.0, 78.8, 59.3, 52.2, 52.1, 37.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{17}INNaO_6$ 318.0948; Found 318.0950.



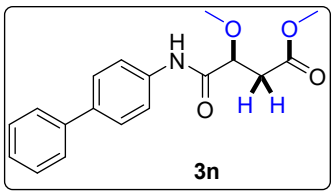
3l

*Methyl 3-methoxy-4-oxo-4-((4-(trifluoromethyl)phenyl)amino)butanoate (**3l**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (42.1 mg, 69%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.60 (s, 1H), 7.72–7.70 (m, 2H), 7.60–7.59 (m, 2H), 4.22 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.72 (s, 3H), 3.56 (s, 3H), 2.98 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.82 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.8, 169.7, 140.2, 126.5 (q, *J* = 3.0 Hz), 125.1, 124.0 (q, J_{CF} = 270.0 Hz), 119.4, 78.8, 59.3, 52.2, 37.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.2 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}F_3NNaO_4$ 328.0767; Found 328.0771.



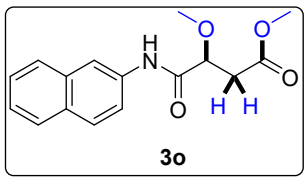
3m

*Methyl (S)-4-((4-cyanophenyl)amino)-3-methoxy-4-oxobutanoate (**3m**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (31.5 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.77–7.69 (m, 2H), 7.65 – 7.58 (m, 2H), 4.20 (dd, *J* = 6.8, 4.2 Hz, 1H), 3.72 (s, 3H), 3.56 (s, 3H), 2.97 (dd, *J* = 16.5, 4.2 Hz, 1H), 2.83 (dd, *J* = 16.5, 6.8 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.7, 141.1, 133.4, 119.7, 118.8, 107.6, 78.6, 59.1, 52.1, 36.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{15}N_2O_4$ 263.1026; Found 263.1029.



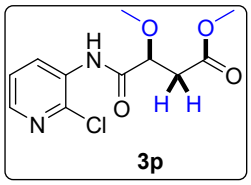
3n

*Methyl 4-([1,1'-biphenyl]-4-ylamino)-3-methoxy-4-oxobutanoate (**3n**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow solid (47.6 mg, 76%), m.p. 114.3-114.8 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.49 (s, 1H), 7.67–7.65 (m, 2H), 7.59–7.56 (m, 4H), 7.45–7.41 (m, 2H), 7.35–7.31 (m, 1H), 4.23 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.74 (s, 3H), 3.57 (s, 3H), 2.99 (dd, *J* = 8.0, 4.0 Hz, 1H), 2.80 (dd, *J* = 8.0, 4.0 Hz, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 169.3, 140.6, 137.7, 136.5, 128.9, 127.8, 127.3, 127.0, 120.2, 79.0, 59.3, 52.2, 37.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{19}NNaO_4$ 336.1206; Found 336.1208.



3o

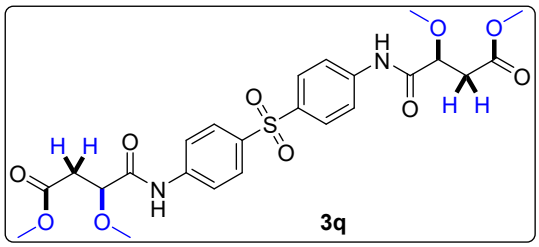
*Methyl 3-methoxy-4-(naphthalen-2-ylamino)-4-oxobutanoate (**3o**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow solid (41.9 mg, 73%), m.p. 134.8-135.2 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.59 (s, 1H), 8.28–8.27 (m, 1H), 7.82–7.78 (m, 3H), 7.53–7.51 (m, 1H), 7.48–7.40 (m, 2H), 4.27 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.74 (s, 3H), 3.59 (s, 3H), 3.02 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.83 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 171.1, 169.4, 134.6, 133.9, 130.9, 129.0, 127.8, 127.7, 126.7, 125.3, 119.8, 116.7, 79.0, 59.4, 52.2, 37.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}NNaO_4$ 310.1050; Found 310.1057.



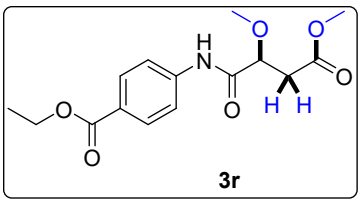
3p

*Methyl 4-((2-chloropyridin-3-yl)amino)-3-methoxy-4-oxobutanoate (**3p**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. White solid (37.1 mg, 68%), m.p. 89.4-89.6 °C. ^{1}H NMR ($CDCl_3$, 600 MHz) δ 9.04 (s, 1H), 8.69–8.67 (m, 1H), 8.08–8.06 (m, 1H), 7.23–7.20 (m, 1H), 4.19 (dd, *J* =

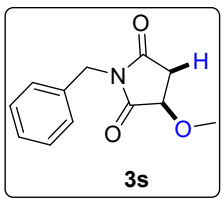
12.0, 6.0 Hz, 1H), 3.67 (s, 3H), 3.55 (s, 3H), 2.91 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.77 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.5, 170.1, 144.2, 140.3, 131.2, 128.6, 123.3, 78.7, 59.4, 52.1, 37.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{11}H_{14}ClN_2O_4$ 273.0637; Found 273.0641.



*Dimethyl 4,4'-((sulfonylbis(4,1-phenylene))bis(azanediyl))bis(3-methoxy-4-oxobutanoate) (**3q**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (69.8 mg, 65%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.67 (s, 2H), 7.87–7.85 (m, 4H), 7.72–7.70 (m, 4H), 4.18 (dd, *J* = 12.0, 6.0 Hz, 2H), 3.69 (s, 6H), 3.52 (s, 6H), 2.93 (dd, *J* = 18.0, 6.0 Hz, 2H), 2.79 (dd, *J* = 12.0, 6.0 Hz, 2H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.8, 141.5, 137.0, 129.0, 119.8, 78.6, 59.2, 52.2, 36.9 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{29}N_2O_{10}S$ 537.1537; Found 537.1541.

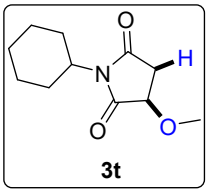


*Ethyl 4-(2,4-dimethoxy-4-oxobutanamido)benzoate (**3r**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (43.9 mg, 71%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.61 (s, 1H), 8.02–8.01 (m, 2H), 7.67–7.65 (m, 2H), 4.35 (d, *J* = 6.0 Hz, 2H), 4.21 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.71 (s, 3H), 3.55 (s, 3H), 2.96 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.80 (dd, *J* = 18.0, 6.0 Hz, 1H), 1.38 (t, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.9, 169.6, 166.2, 141.2, 130.9, 126.5, 119.0, 78.8, 61.0, 59.3, 52.2, 37.1, 14.5 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{20}NO_6$ 310.1285; Found 310.1292.

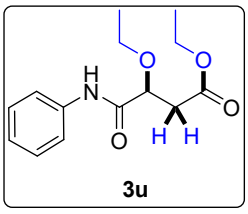


*1-Benzyl-3-methoxypyrrolidine-2,5-dione (**3s**)*. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Colourless oil (34.2 mg, 78%). ^{1}H NMR ($CDCl_3$, 600

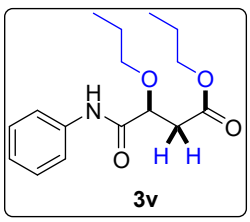
MHz) δ 7.37–7.36 (m, 2H), 7.32–7.27 (m, 3H), 4.65 (d, *J* = 6.0 Hz, 2H), 4.20 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.60 (s, 3H), 2.99 (dd, *J* = 18.0, 12.0 Hz, 1H), 2.62 (dd, *J* = 18.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 175.4, 173.9, 135.5, 128.9, 128.8, 128.2, 74.9, 59.0, 42.4, 36.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{12}H_{13}NNaO_3$ 242.0788; Found 242.0788.



1-Cyclohexyl-3-methoxypyrrolidine-2,5-dione ***(3t)***. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Colourless oil (39.5 mg, 72%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.11 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.99–3.89 (m, 1H), 3.58 (s, 3H), 2.92 (dd, *J* = 16.0, 8.0 Hz, 1H), 2.55 (dd, *J* = 20.0, 8.0 Hz, 1H), 2.15–2.05 (m, 2H), 1.83–1.79 (m, 2H), 1.66–1.55 (m, 3H), 1.34–1.17 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 175.9, 174.2, 74.5, 58.9, 51.8, 35.9, 28.9, 28.7, 25.9, 25.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{17}NNaO_3$ 234.1101; Found 234.1102.

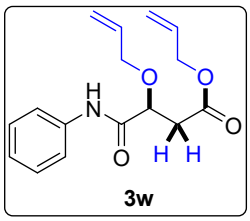


Ethyl 3-ethoxy-4-oxo-4-(phenylamino)butanoate ***(3u)***. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (36.1 mg, 68%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.48 (s, 1H), 7.58–7.55 (m, 2H), 7.36–7.31 (m, 2H), 7.15–7.11 (m, 1H), 4.29 (dd, *J* = 8.0, 4.0 Hz, 1H), 4.18 (q, *J* = 8.0 Hz, 2H), 3.77–3.67 (m, 2H), 2.95 (dd, *J* = 16.0, 4.0 Hz, 1H), 2.74 (dd, *J* = 16.0, 4.0 Hz, 1H), 1.29 (t, *J* = 8.0 Hz, 3H), 1.25 (t, *J* = 8.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.7, 137.2, 129.2, 124.7, 119.8, 77.3, 67.5, 61.0, 38.3, 15.5, 14.3 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{19}NNaO_4$ 288.1206; Found 288.1212.



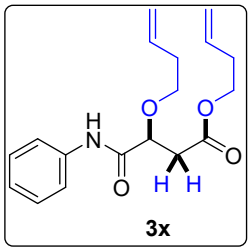
Propyl 4-oxo-4-(phenylamino)-3-propoxybutanoate ***(3v)***. Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (35.8 mg, 61%).

^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.48 (s, 1H), 7.57–7.56 (m, 2H), 7.36–7.33 (m, 2H), 7.14–7.12 (m, 1H), 4.29 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.11–4.04 (m, 2H), 3.67–3.56 (m, 2H), 2.96 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.75 (dd, *J* = 18.0, 6.0 Hz, 1H), 1.70–1.62 (m, 4H), 0.99 (t, *J* = 6.0 Hz, 3H), 0.93 (t, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.8, 137.3, 129.2, 124.7, 119.7, 77.5, 73.7, 66.6, 38.3, 23.1, 22.1, 10.8, 10.5 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{23}NNaO_4$ 316.1519; Found 316.1519.



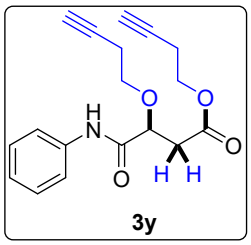
3w

*Allyl 3-(allyloxy)-4-oxo-4-(phenylamino)butanoate (**3w**).* Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Yellow oil (40.5 mg, 70%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.47 (s, 1H), 7.56–7.55 (m, 2H), 7.35–7.32 (m, 2H), 7.15–7.12 (m, 1H), 5.98–5.87 (m, 2H), 5.38–5.22 (m, 4H), 4.63–4.62 (m, 2H), 4.37 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.26–4.15 (m, 2H), 3.00 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.82 (dd, *J* = 18.0, 12.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 169.4, 137.2, 133.4, 131.9, 129.2, 124.8, 119.8, 118.9, 118.7, 76.6, 72.7, 65.7, 38.1 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{19}NNaO_4$ 312.1206; Found 312.1206.



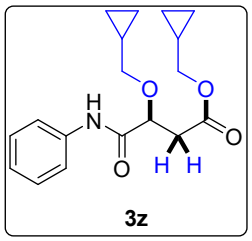
3x

*But-3-en-1-yl 3-(but-3-en-1-yloxy)-4-oxo-4-(phenylamino)butanoate (**3x**).* Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (37.5 mg, 59%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.54 (s, 1H), 7.56–7.55 (m, 2H), 7.35–7.32 (m, 2H), 7.14–7.11 (m, 1H), 5.90–5.74 (m, 2H), 5.23–5.05 (m, 4H), 4.30 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.20–4.16 (m, 2H), 3.85–3.81 (m, 1H), 3.65–3.62 (m, 1H), 2.98 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.74 (dd, *J* = 18.0, 12.0 Hz, 1H), 2.43–2.37 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.5, 137.3, 135.3, 134.0, 129.2, 124.7, 119.7, 118.0, 117.5, 71.2, 64.1, 38.2, 34.3, 33.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}NO_4$ 318.1700; Found 318.1698.



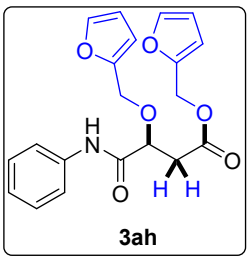
3y

*But-3-yn-1-yl 3-(but-3-yn-1-yloxy)-4-oxo-4-(phenylamino)butanoate (**3y**).* Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (40.1 mg, 64%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.72 (s, 1H), 7.52–7.51 (m, 2H), 7.28–7.26 (m, 2H), 7.08–7.05 (m, 1H), 4.30 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.18 (t, *J* = 12.0 Hz, 2H), 3.85–3.82 (m, 1H), 3.68–3.65 (m, 1H), 2.99 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.72 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.56–2.42 (m, 4H), 2.05 (t, *J* = 6.0 Hz, 1H), 1.93 (t, *J* = 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.2, 137.2, 129.2, 124.8, 120.0, 82.0, 80.1, 70.3, 70.2, 70.0, 62.7, 38.2, 20.3, 19.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{20}NO_4$ 314.1387; Found 314.1389.



3z

*Cyclopropylmethyl 3-(cyclopropylmethoxy)-4-oxo-4-(phenylamino)butanoate (**3z**).* Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (35.5 mg, 56%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.61 (s, 1H), 7.58–7.57 (m, 2H), 7.34–7.26 (m, 2H), 7.13–7.11 (m, 1H), 4.35–4.33 (m, 1H), 3.95 (d, *J* = 6.0 Hz, 2H), 3.60–3.57 (m, 1H), 3.45–3.42 (m, 1H), 2.99 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.76 (dd, *J* = 18.0, 6.0 Hz, 1H), 1.15–1.09 (m, 2H), 0.63–0.52 (m, 4H), 0.27–0.25 (m, 4H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.7, 169.8, 137.3, 129.2, 124.6, 119.6, 77.2, 77.0, 69.8, 38.4, 10.9, 9.8, 3.6, 3.4, 3.3, 3.01 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{24}NO_4$ 318.1700; Found 318.1702.



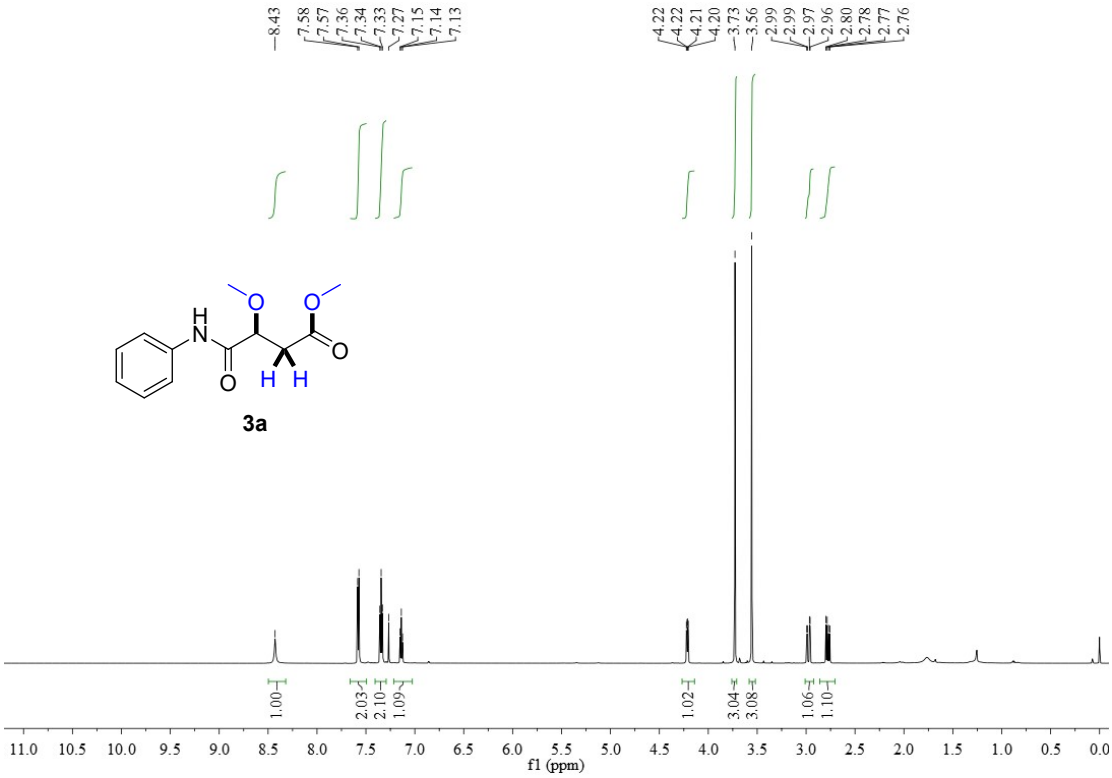
3ah

*Furan-2-ylmethyl 3-(furan-2-ylmethoxy)-4-oxo-4-(phenylamino)butanoate (**3ah**).* Following the general procedure, eluted by petroleum ether/ethyl acetate = 40/1 to 20/1. Brown oil (33.2 mg, 45%). ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.49 (s, 1H), 7.51–7.50 (m, 2H), 7.41–7.40 (m, 2H), 7.33–7.30 (m, 2H),

7.12–7.10 (m, 1H), 6.43–6.33 (m, 4H), 5.13 (q, *J* = 12.0 Hz, 2H), 4.75 (d, *J* = 12.0 Hz, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.44 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.05 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.78 (dd, *J* = 12.0, 6.0 Hz, 1H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.4, 169.1, 150.4, 149.2, 143.8, 143.45, 137.3, 129.1, 124.7, 119.8, 111.1, 110.9, 110.8, 110.7, 76.6, 65.8, 58.6, 38.2 ppm; HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{19}NNaO_6$ 392.1105; Found 392.1105.

Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for Products 3a-ah

Methyl 3-methoxy-4-oxo-4-(phenylamino)butanoate (**3a**)


8.43
7.58
7.57
7.36
7.34
7.33
7.27
7.15
7.14
7.13
4.22
4.22
4.21
4.20
3.73
3.56
2.99
2.99
2.97
2.96
2.80
2.78
2.77
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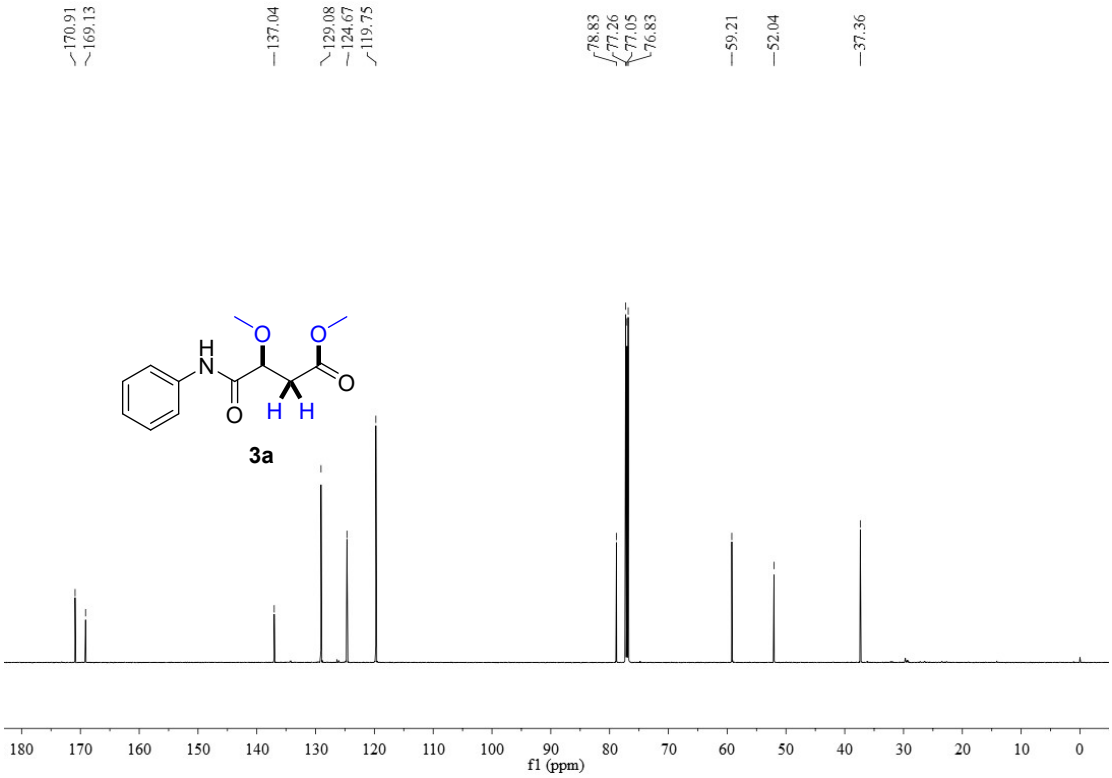
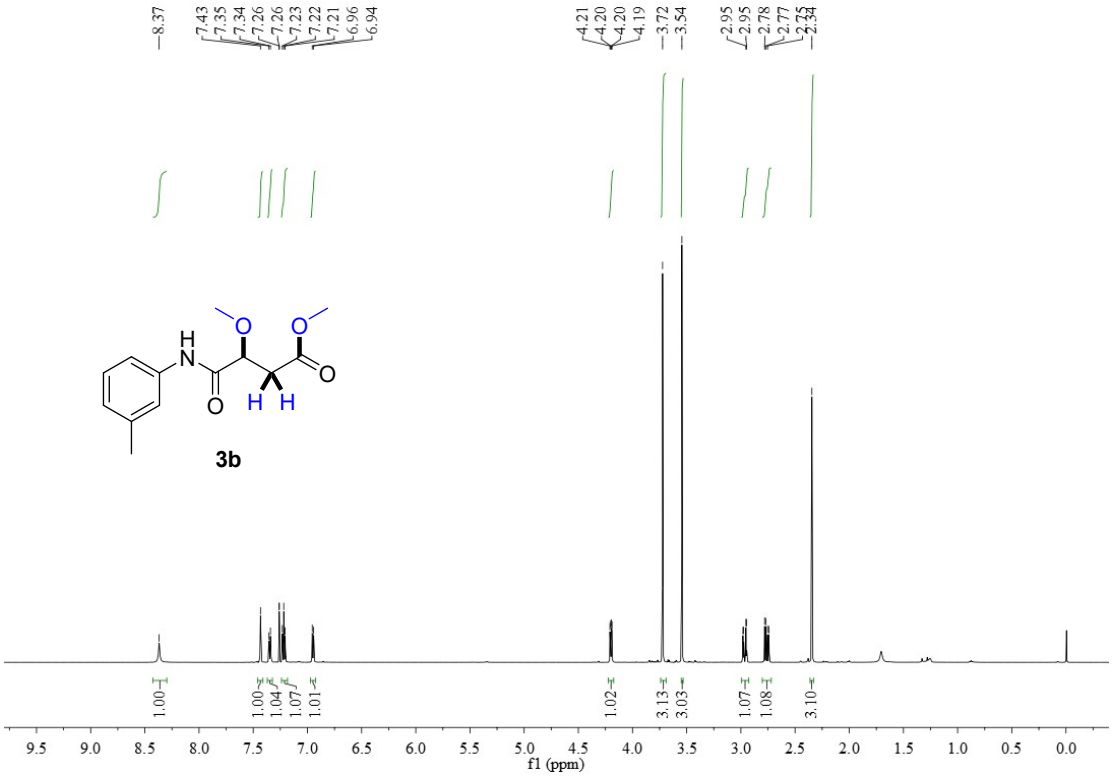
1.09
1.02
3.04
3.08
1.06
1.10
f1 (ppm)

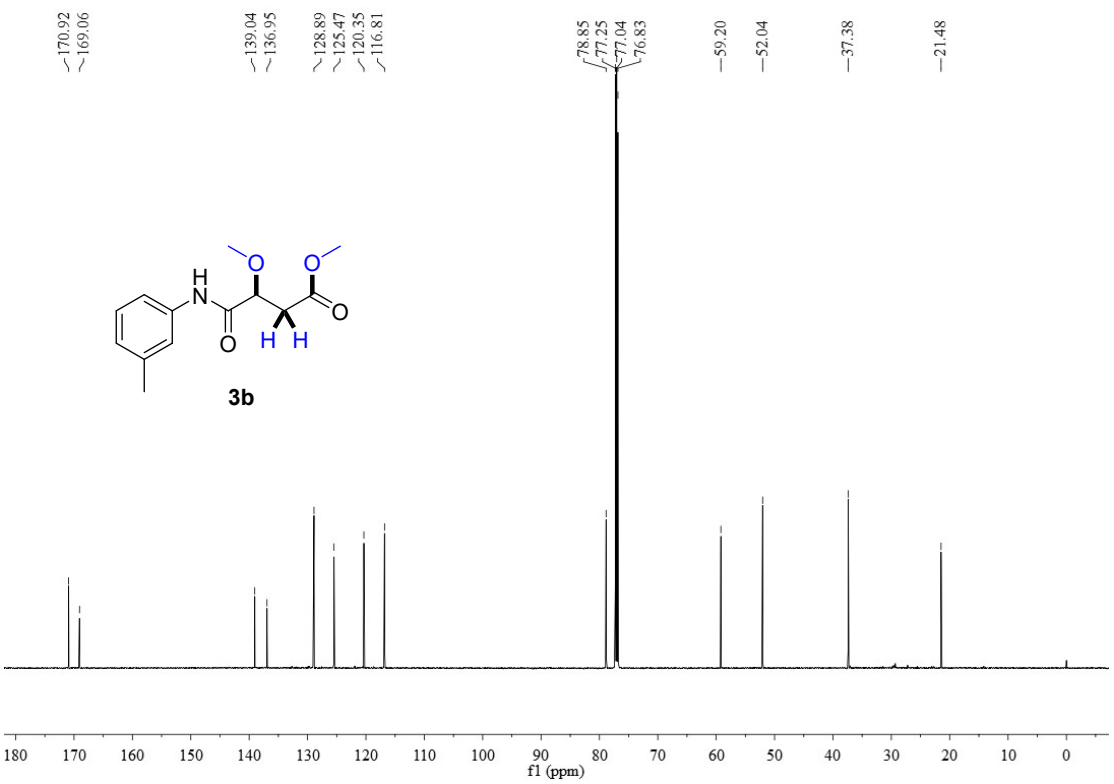
3a


170.91
169.13
137.04
129.08
124.67
119.75
78.83
77.26
77.05
76.83
59.21
52.04
37.36
f1 (ppm)

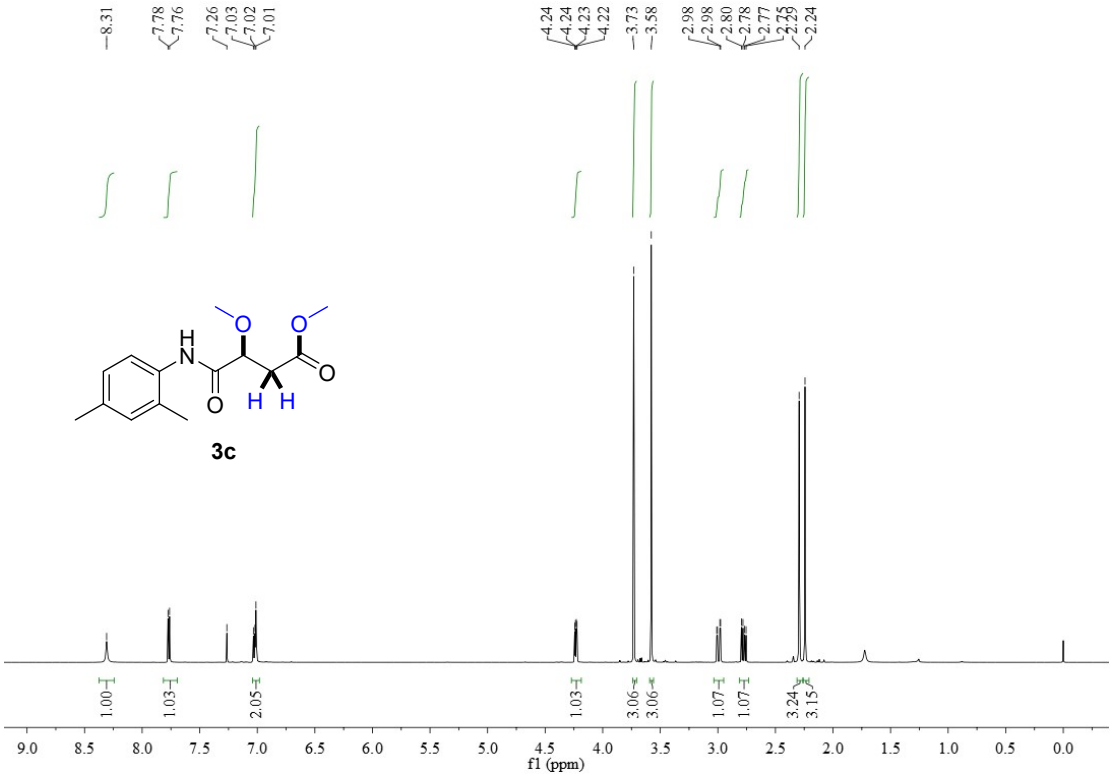
3a

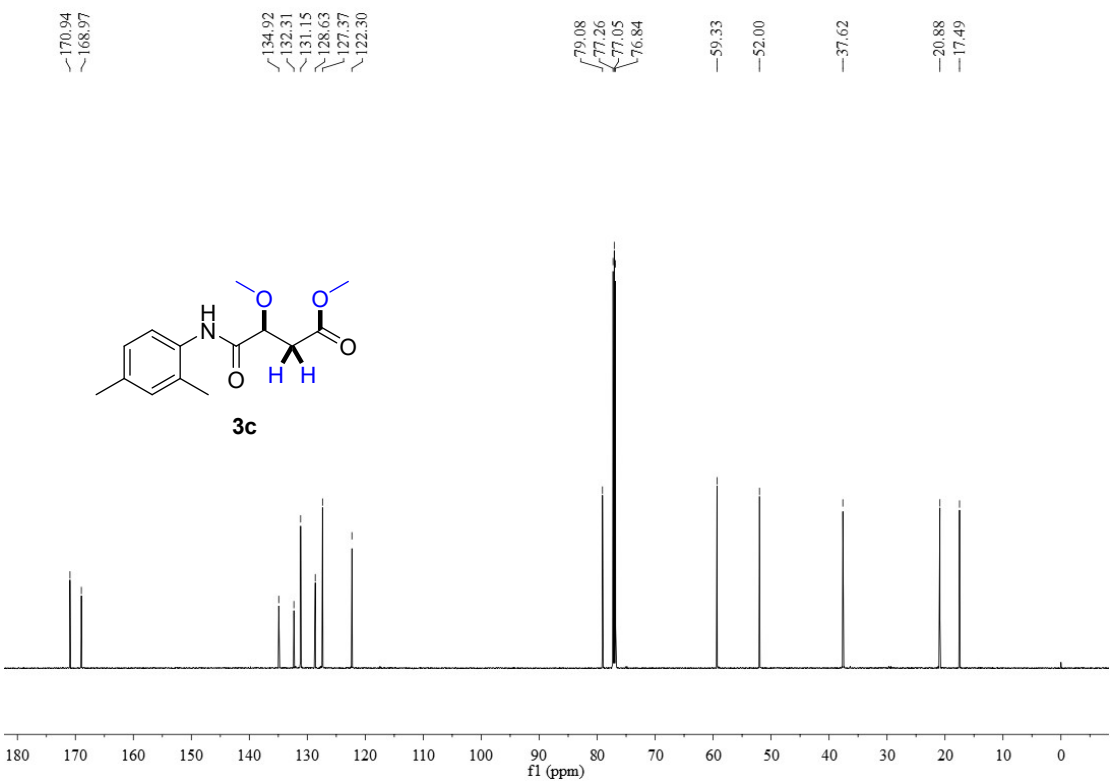
Methyl 3-methoxy-4-oxo-4-(m-tolylamino)butanoate (**3b**)



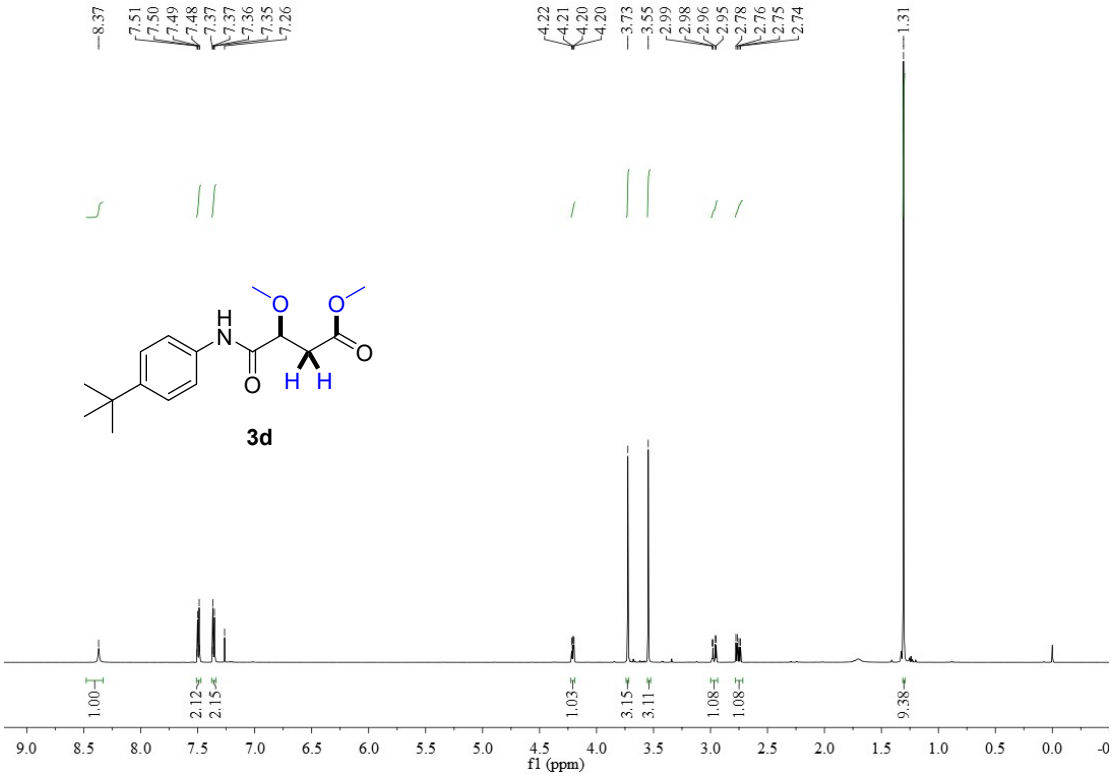


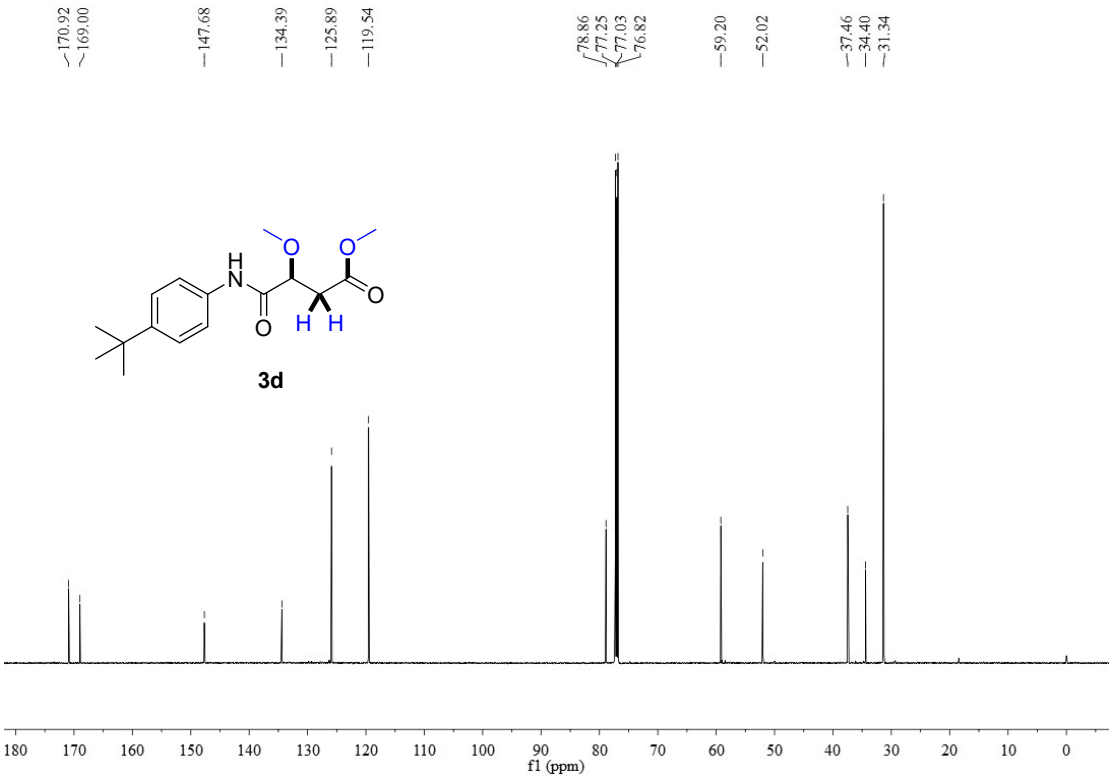
Methyl 4-((2,4-dimethylphenyl)amino)-3-methoxy-4-oxobutanoate (**3c**)



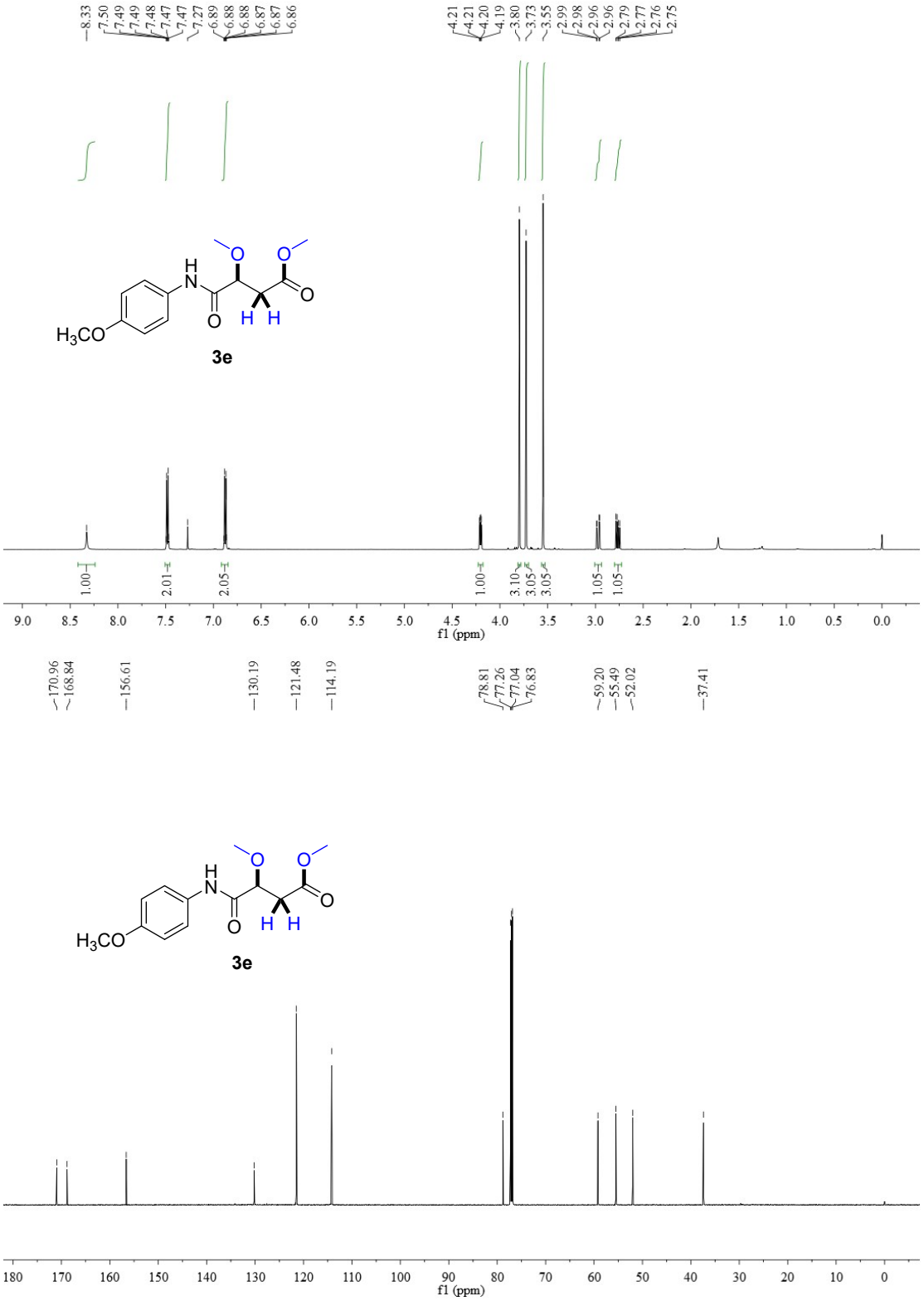


Methyl 4-((4-isopropylphenyl)amino)-3-methoxy-4-oxobutanoate (**3d**)

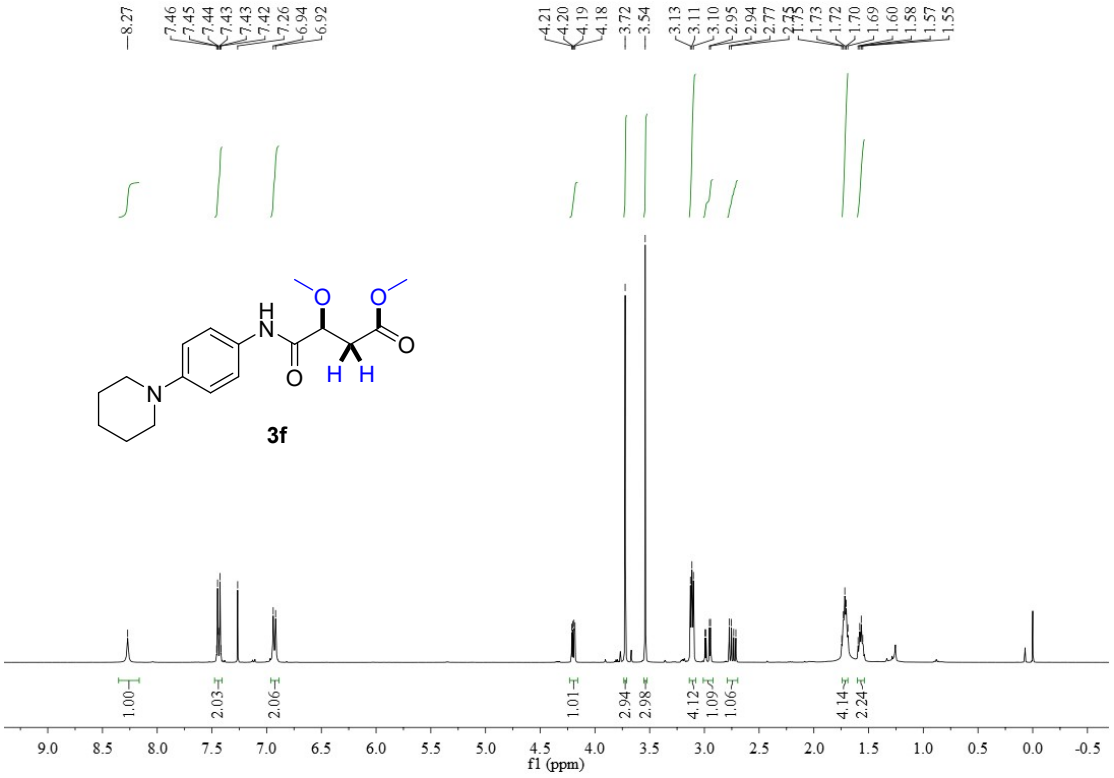


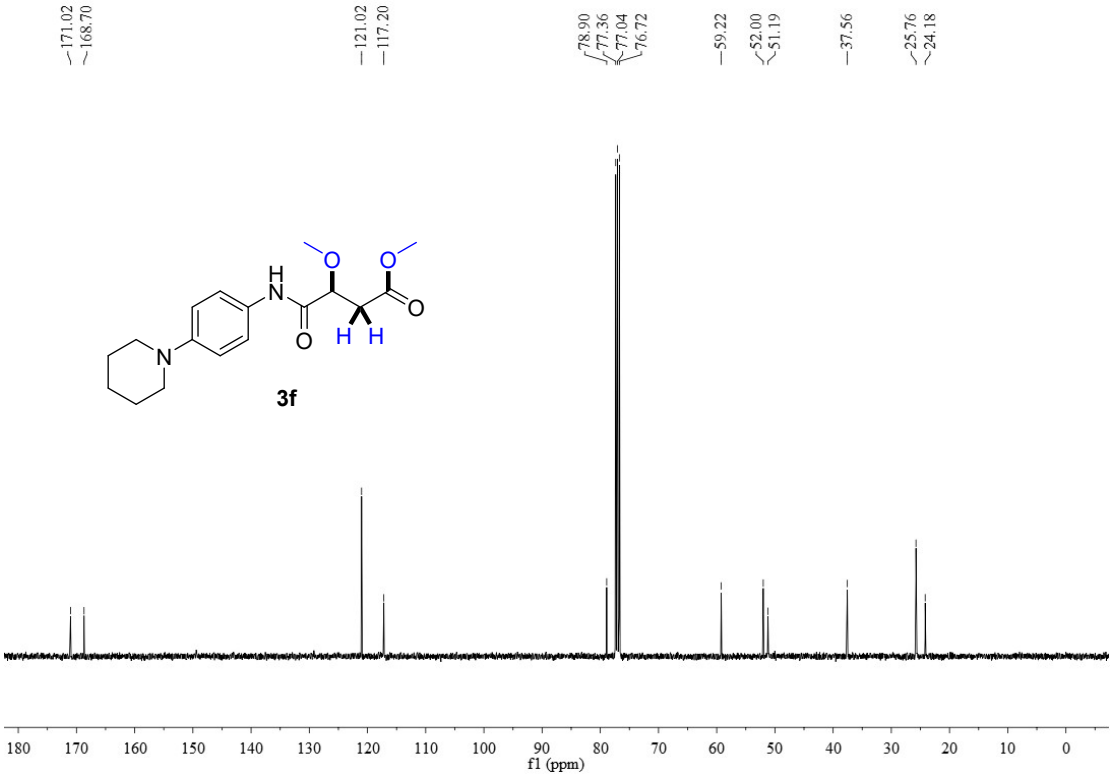


Methyl 3-methoxy-4-((4-methoxyphenyl)amino)-4-oxobutanoate (**3e**)

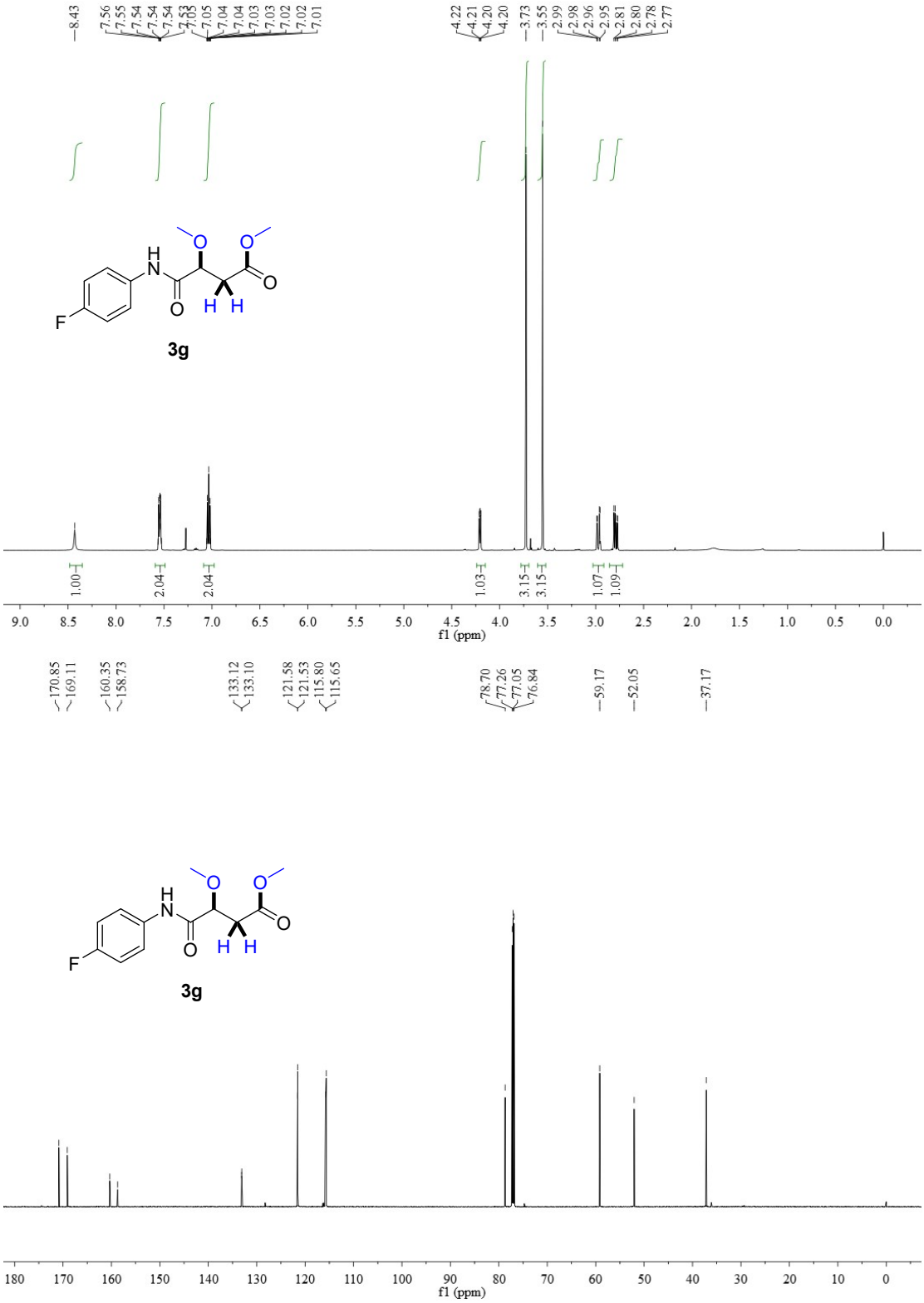


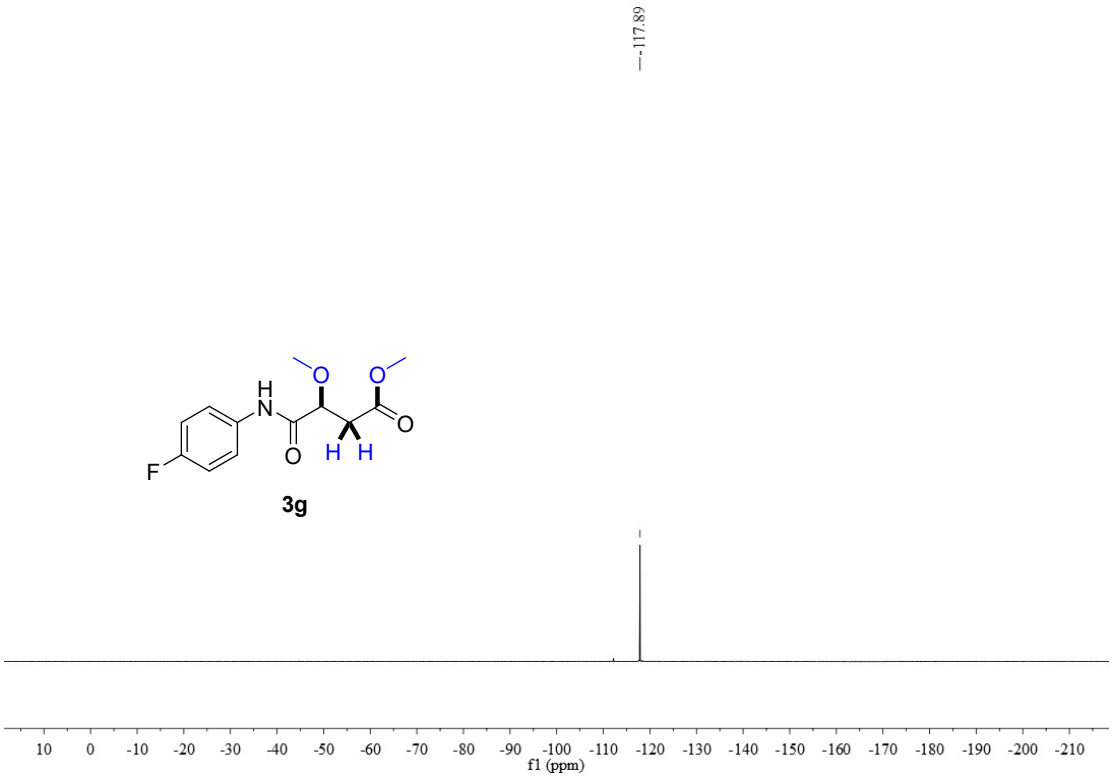
Methyl 3-methoxy-4-oxo-4-((4-(piperidin-1-yl)phenyl)amino)butanoate (**3f**)





Methyl 4-((4-fluorophenyl)amino)-3-methoxy-4-oxobutanoate (**3g**)

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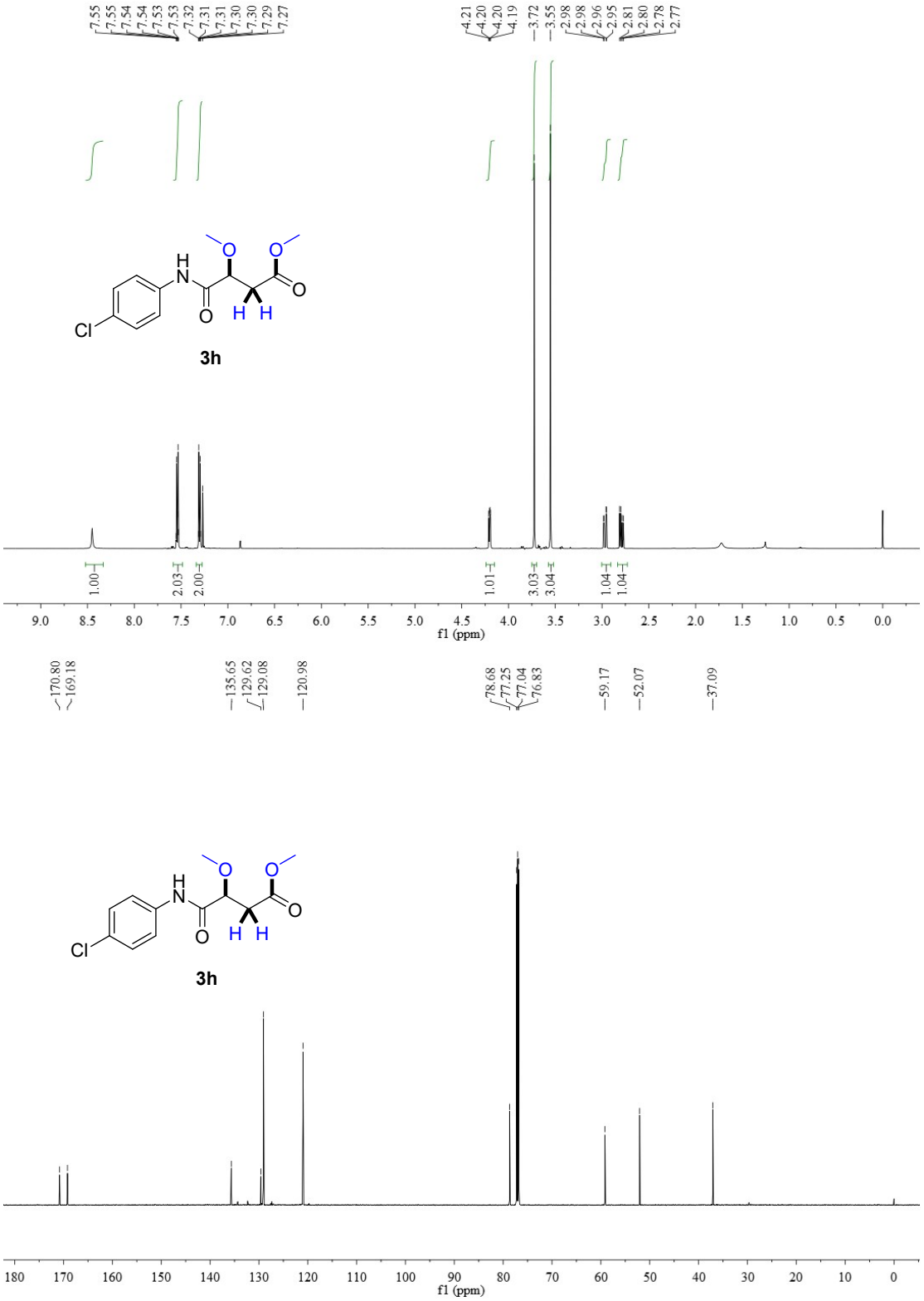
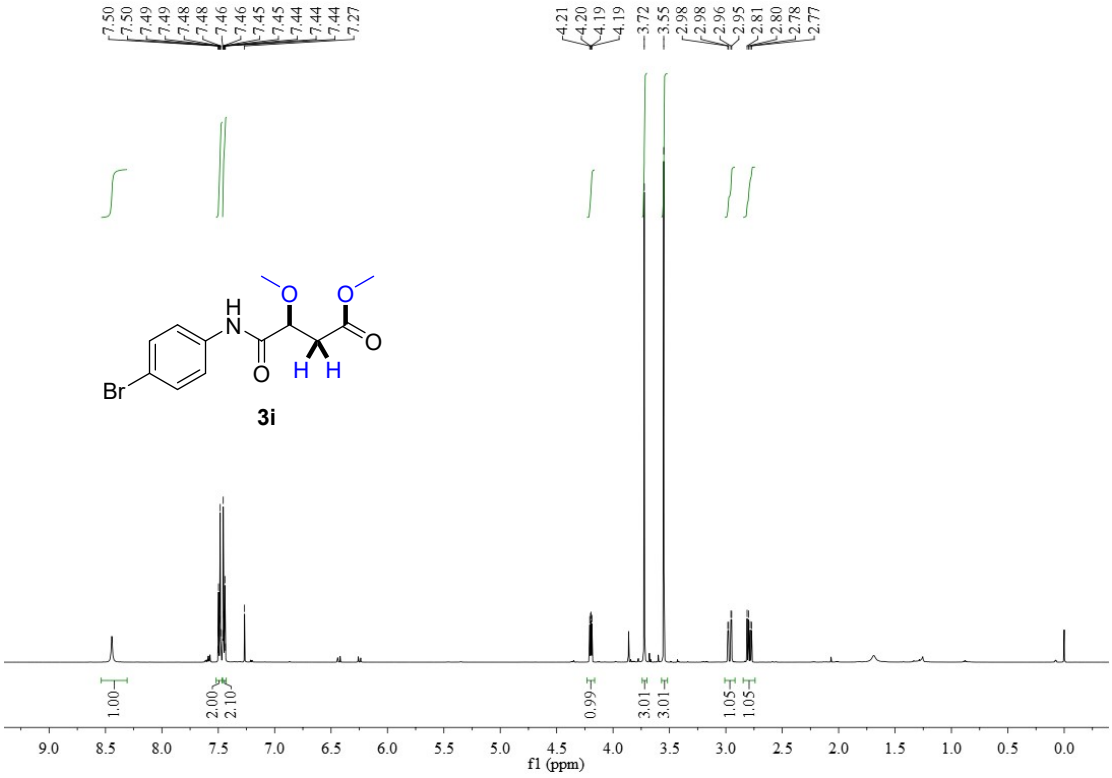
H
N
O
O
O
O
H H
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

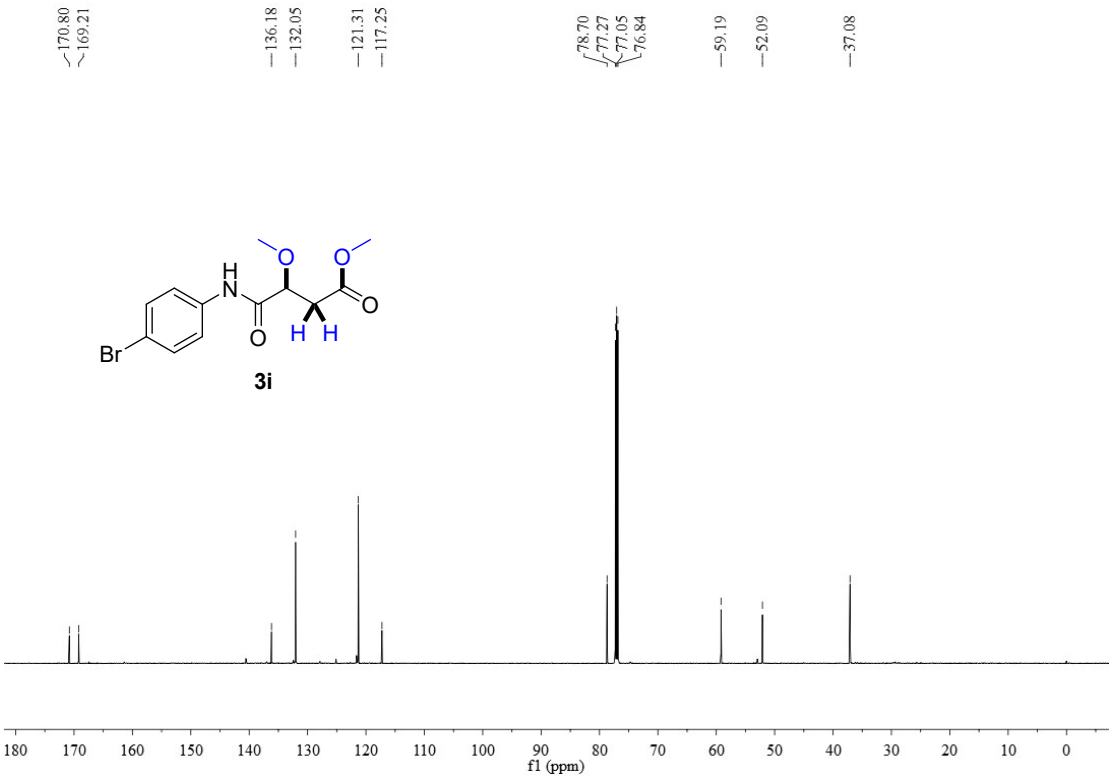
3g

Methyl 4-((4-chlorophenyl)amino)-3-methoxy-4-oxobutanoate (**3h**)

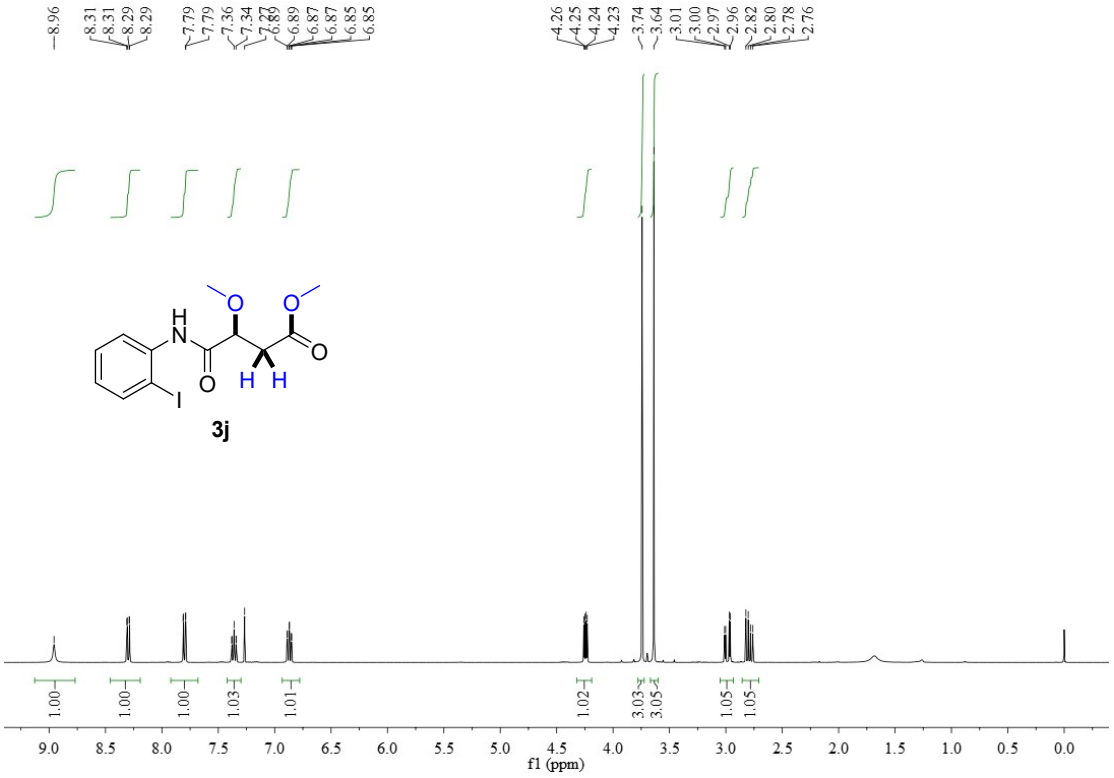


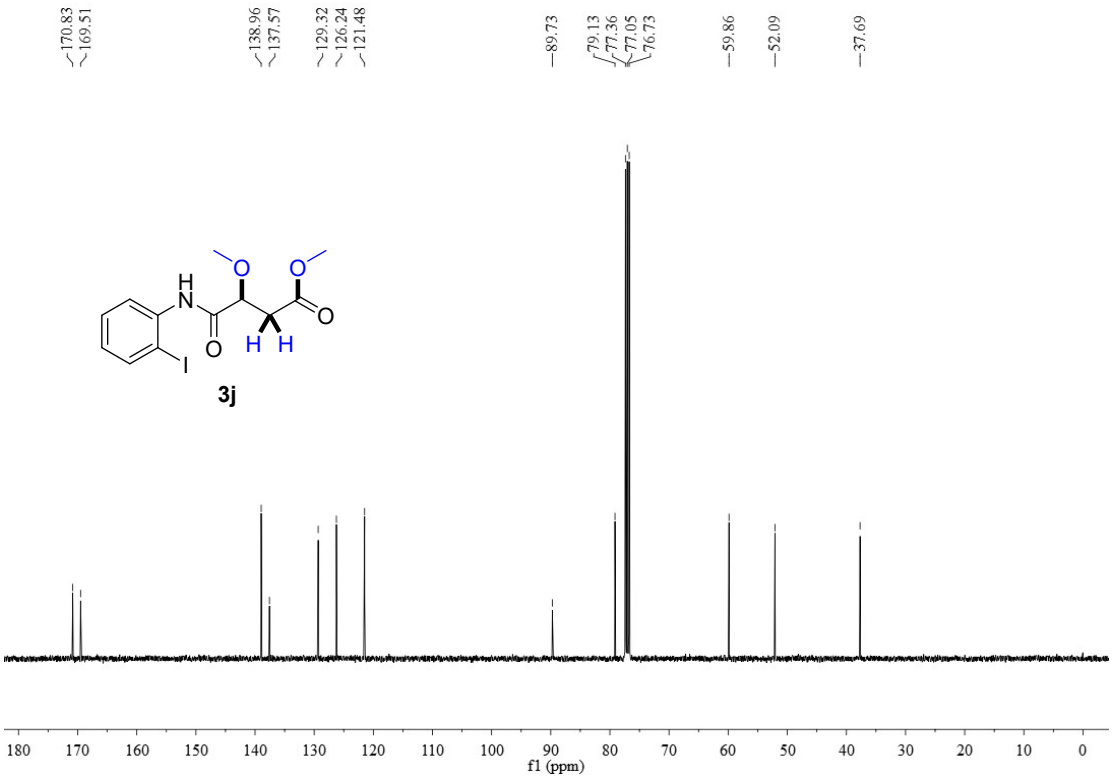
Methyl 4-((4-bromophenyl)amino)-3-methoxy-4-oxobutanoate (**3i**)



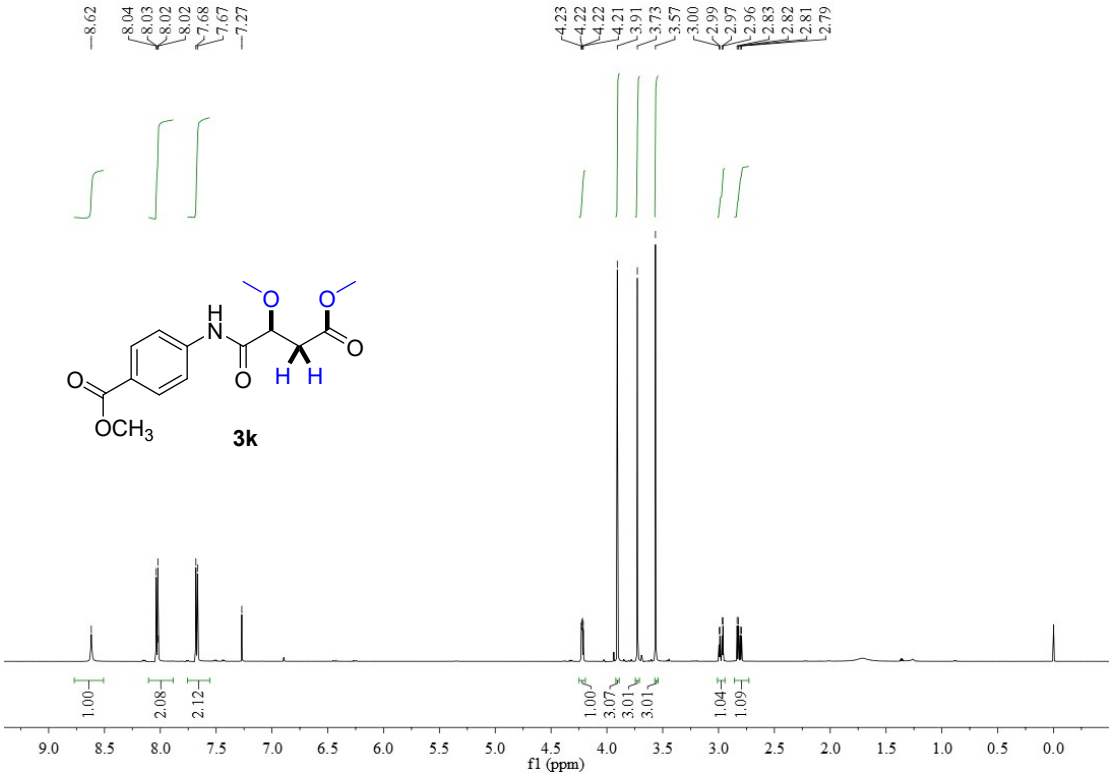


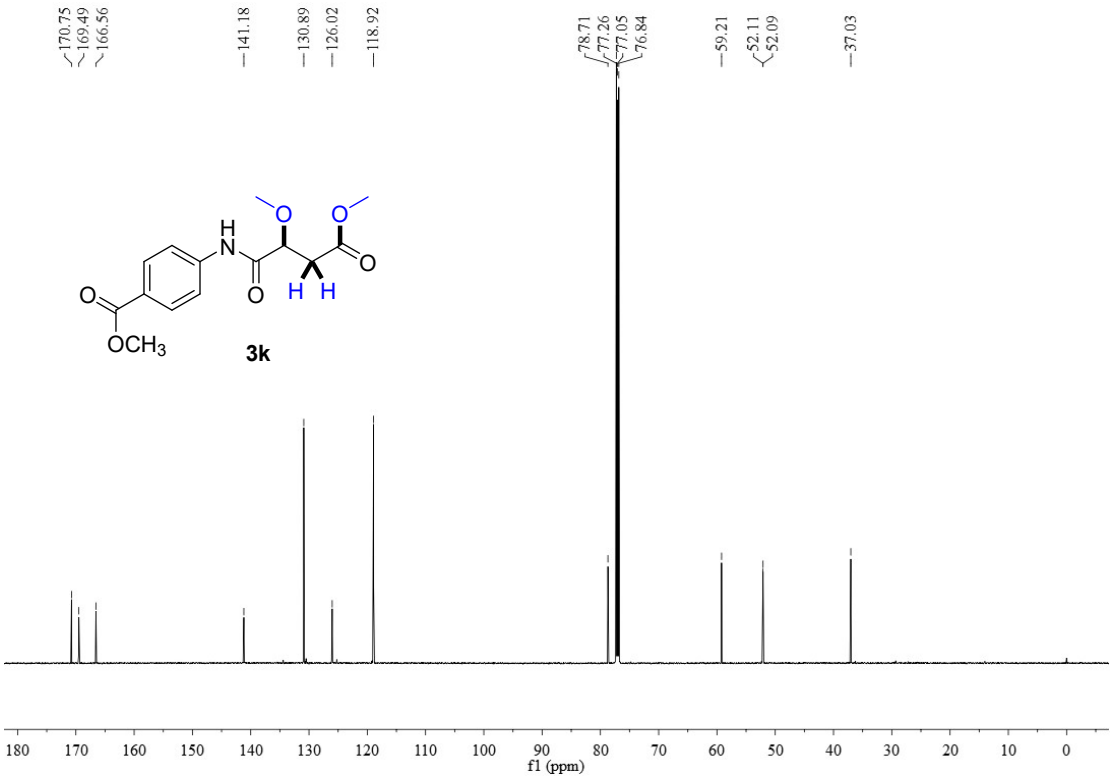
Methyl 4-((2-iodophenyl)amino)-3-methoxy-4-oxobutanoate (**3j**)



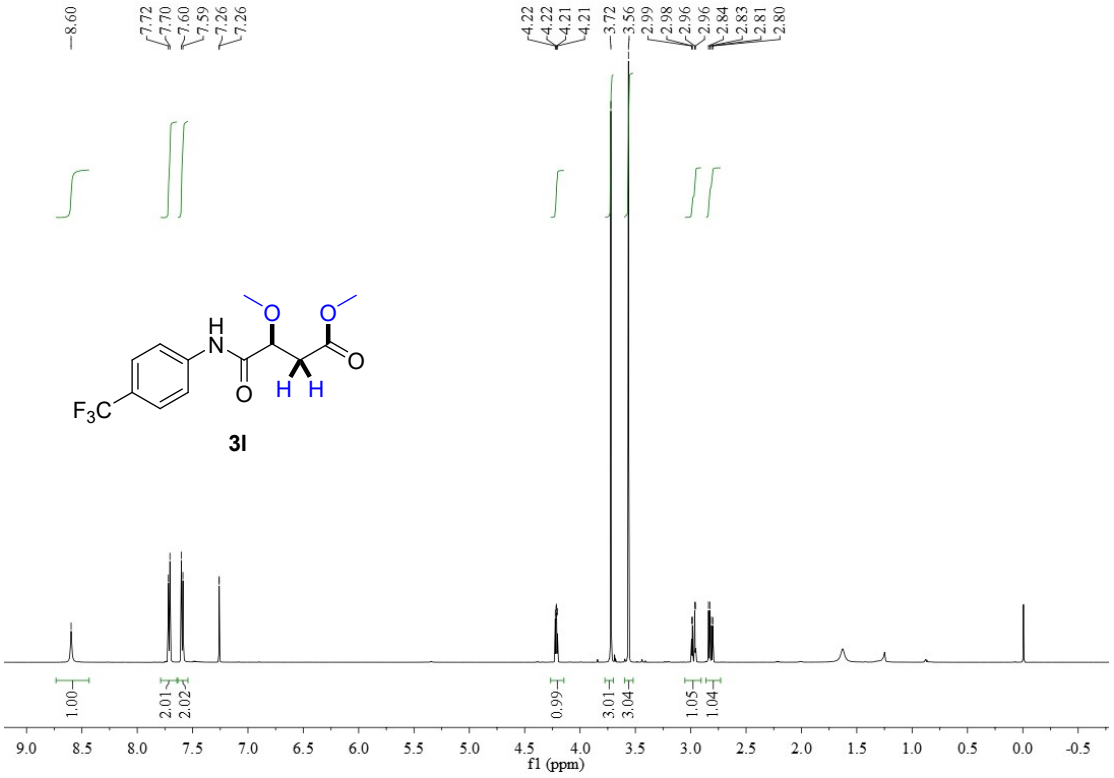


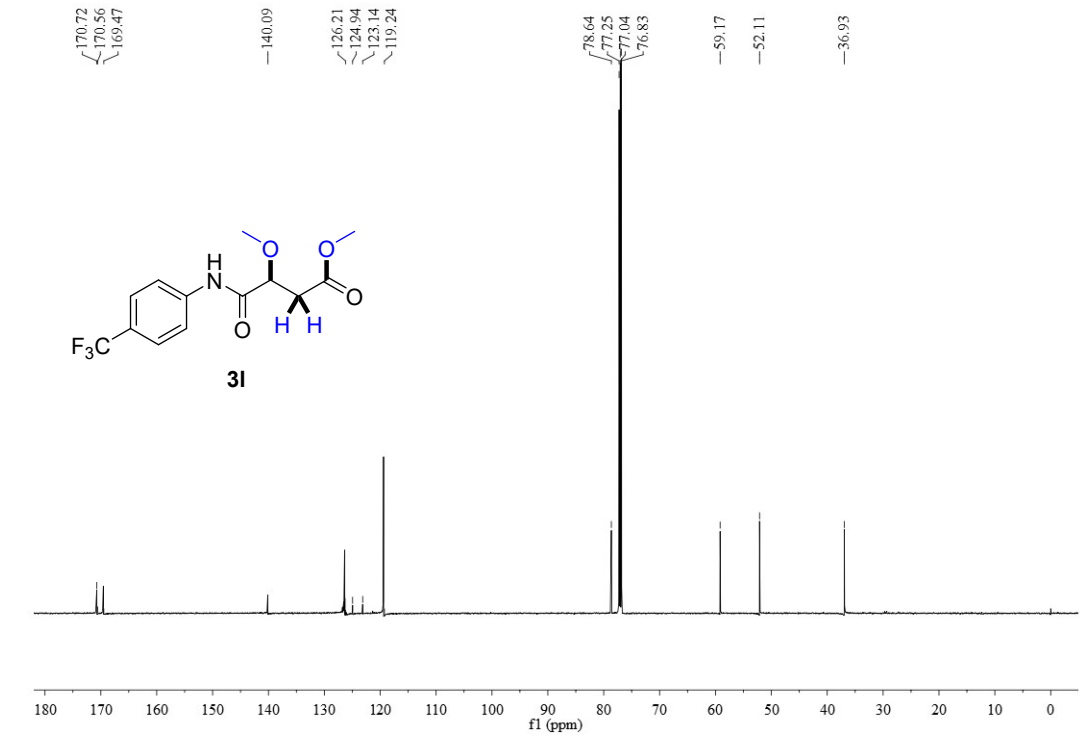
Methyl 4-(2,4-dimethoxy-4-oxobutanamido)benzoate (**3k**)

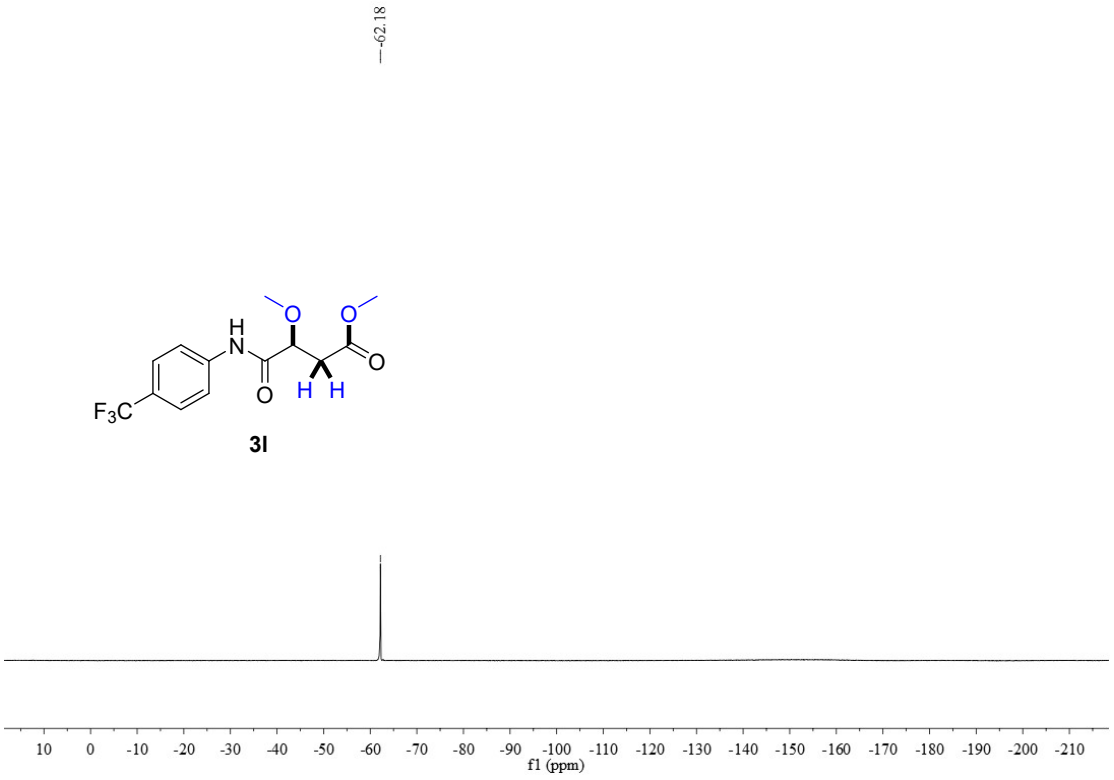




Methyl 3-methoxy-4-oxo-4-((4-(trifluoromethyl)phenyl)amino)butanoate (**3l**)






-62.18
H
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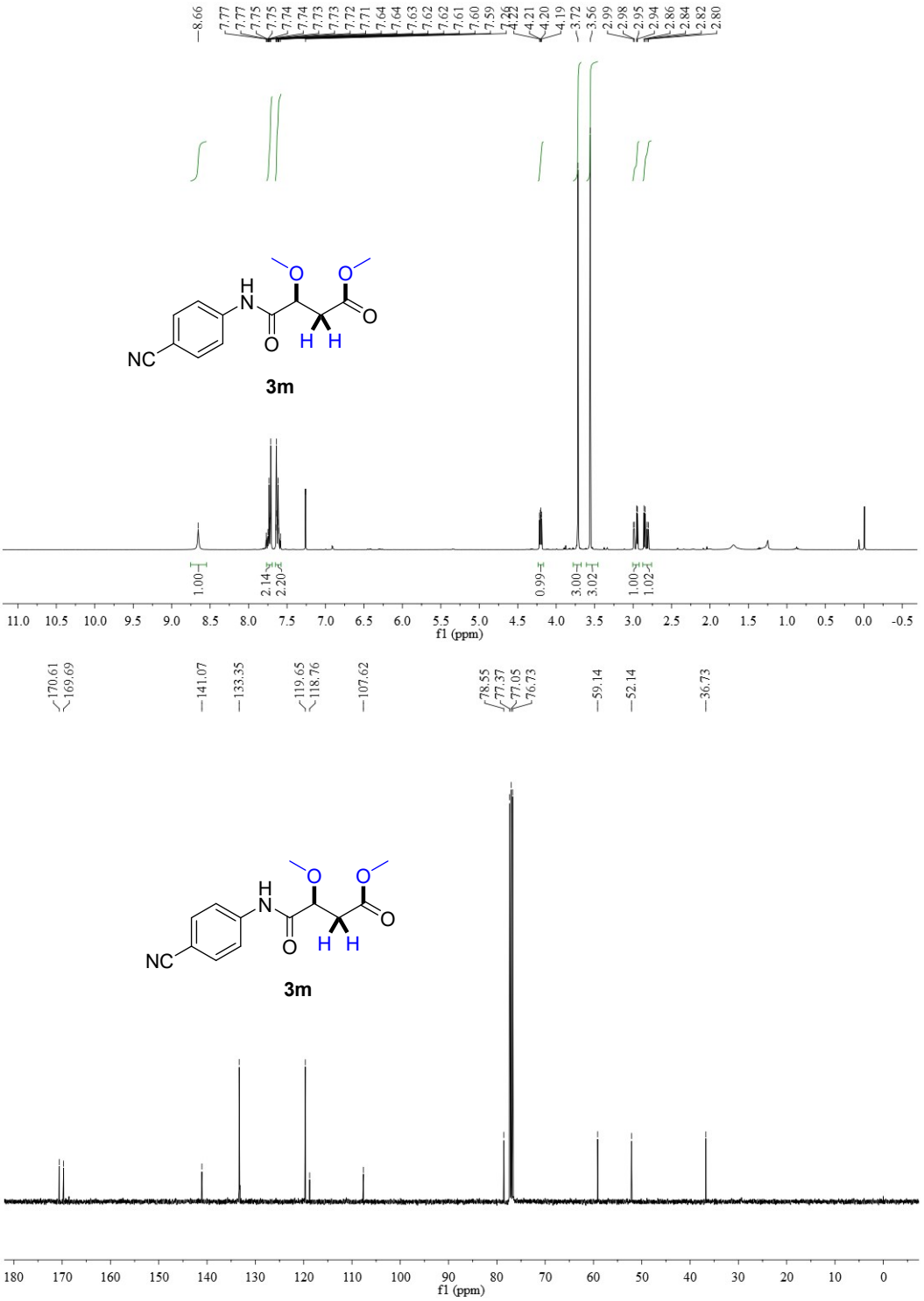
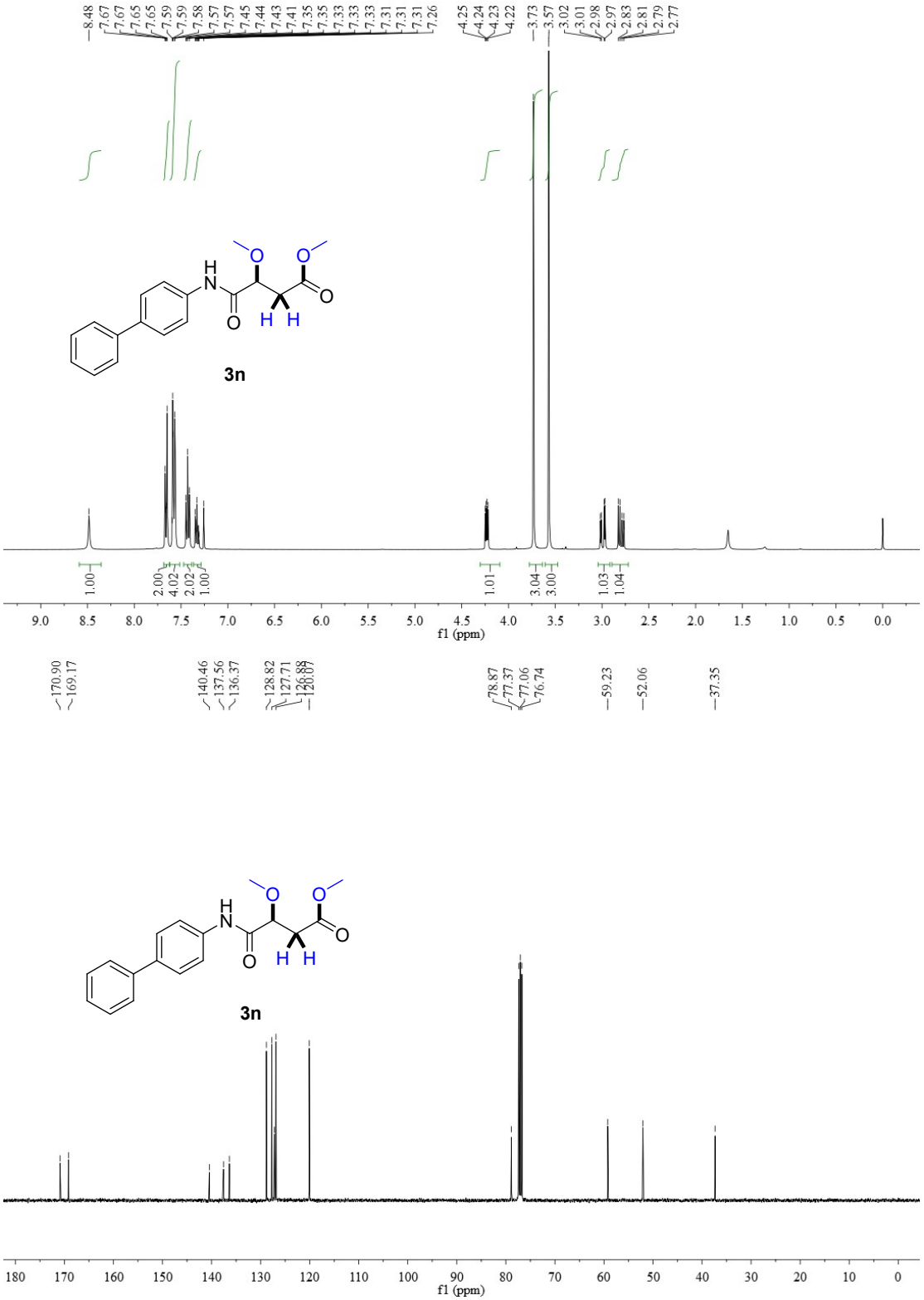
H H
F3C
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

3l

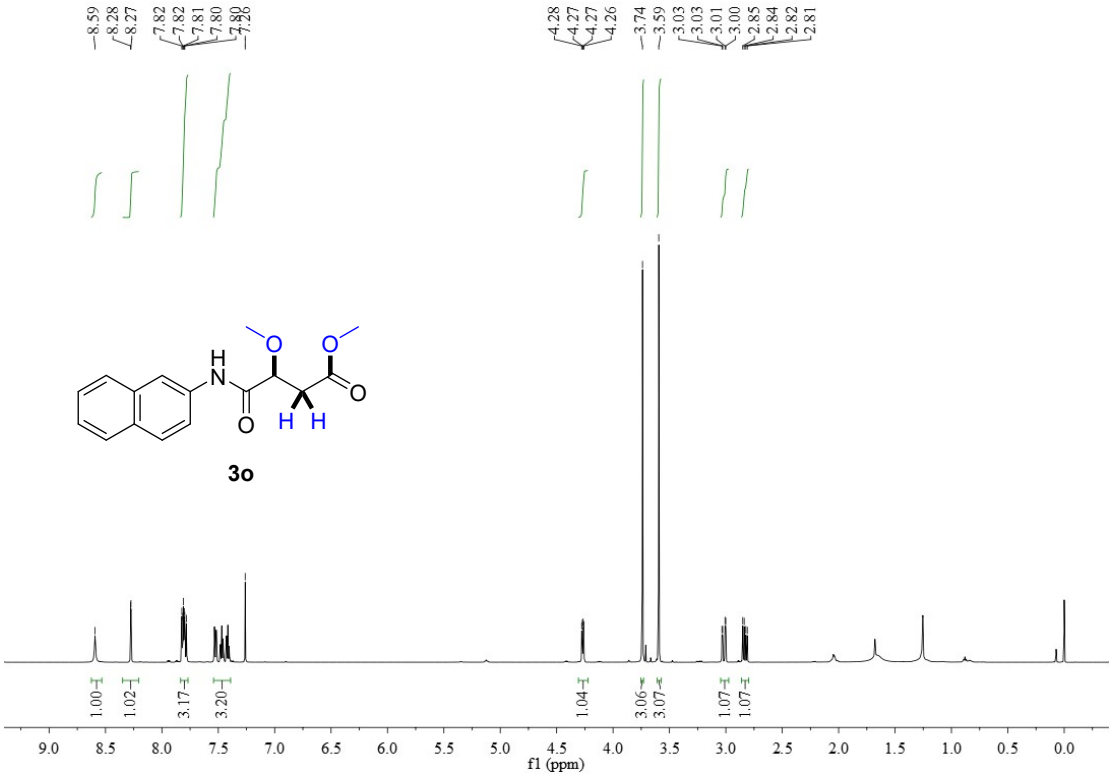
*Methyl (S)-4-((4-cyanophenyl)amino)-3-methoxy-4-oxobutanoate (**3m**)*



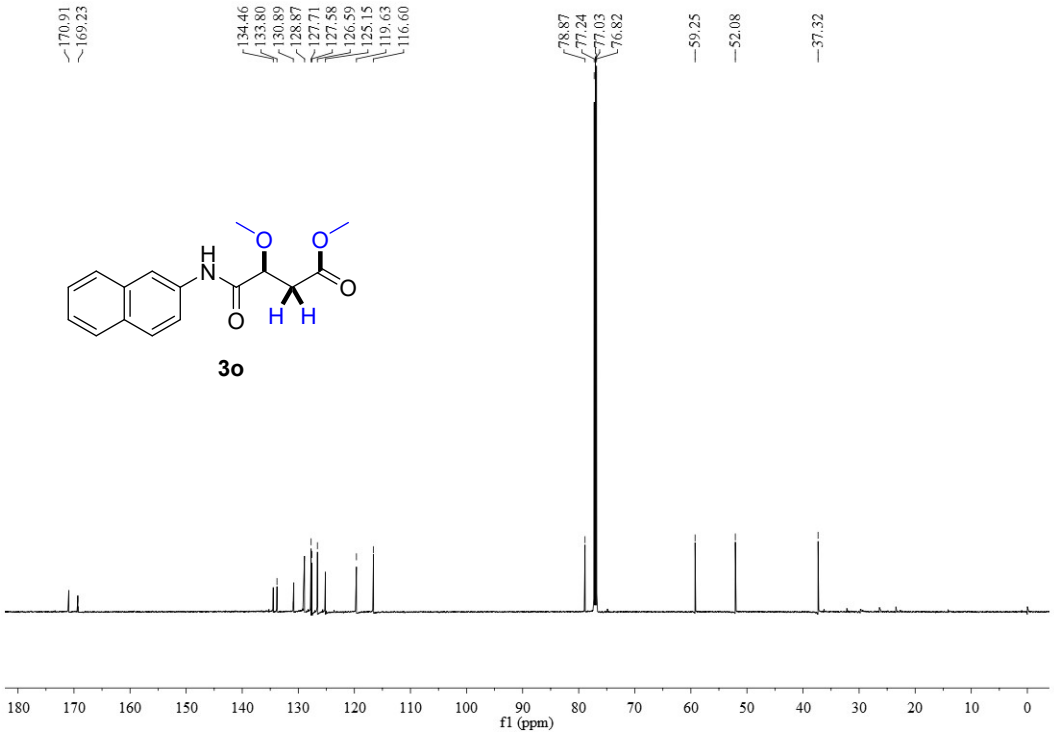
Methyl 4-([1,1'-biphenyl]-4-ylamino)-3-methoxy-4-oxobutanoate (**3n**)



Methyl 3-methoxy-4-(naphthalen-2-ylamino)-4-oxobutanoate (**3o**)

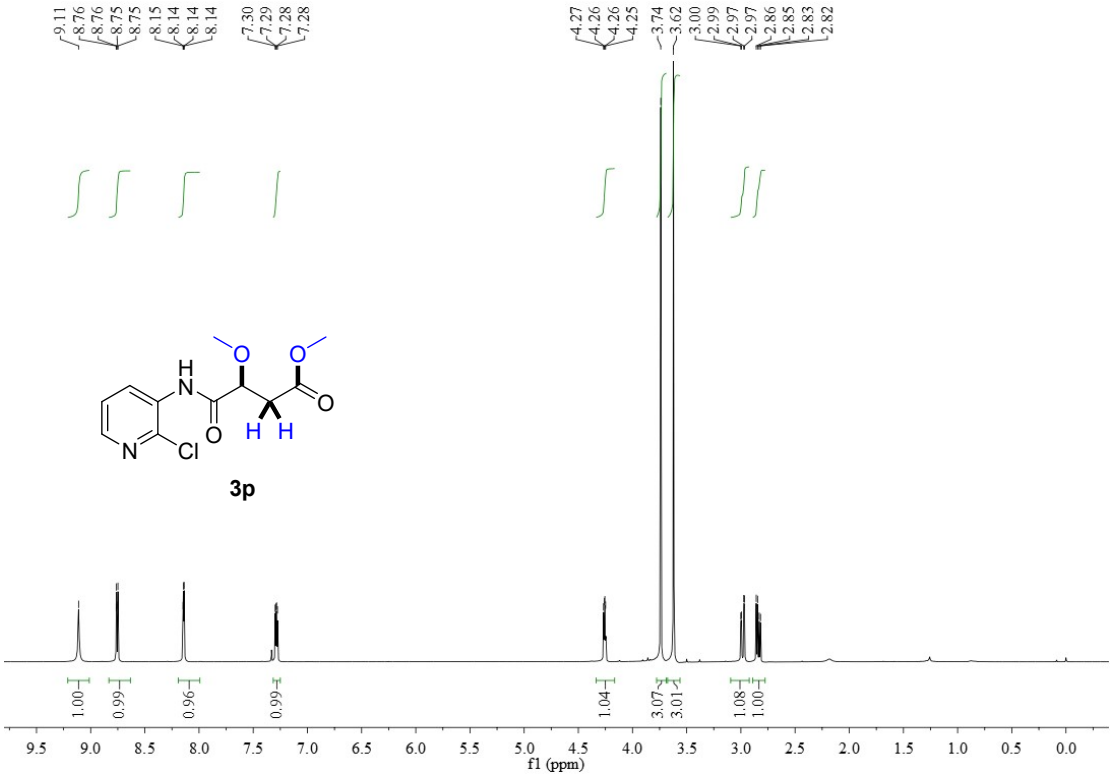


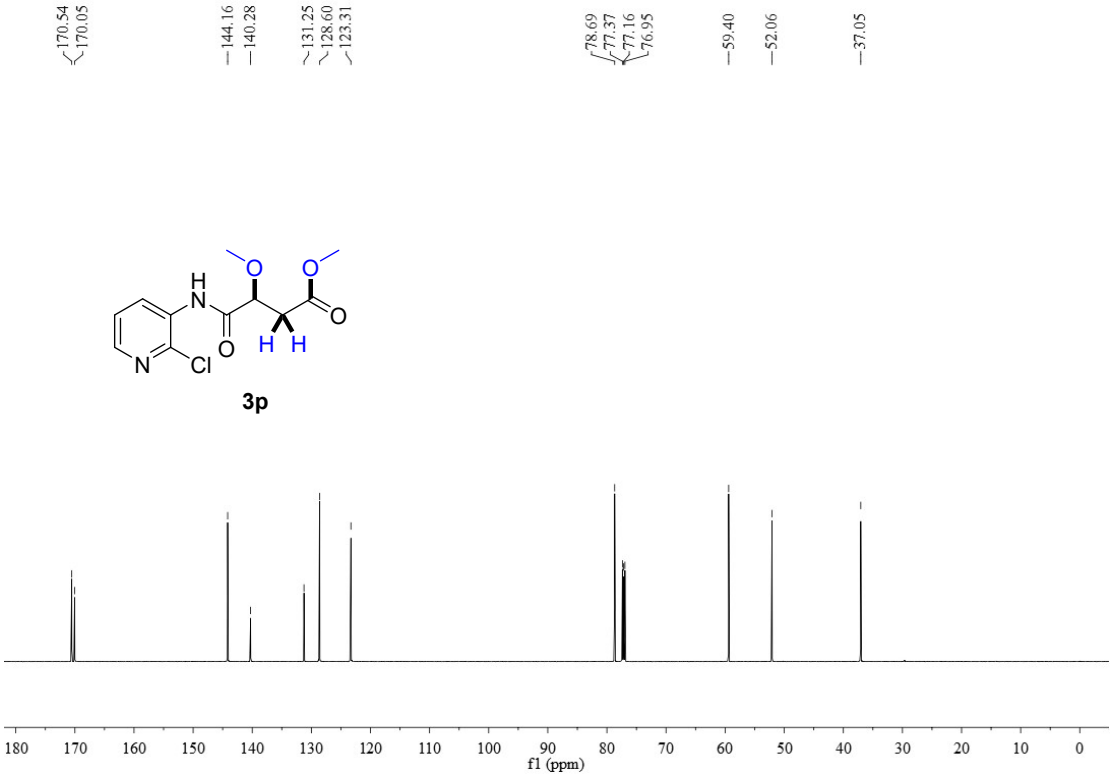
3o



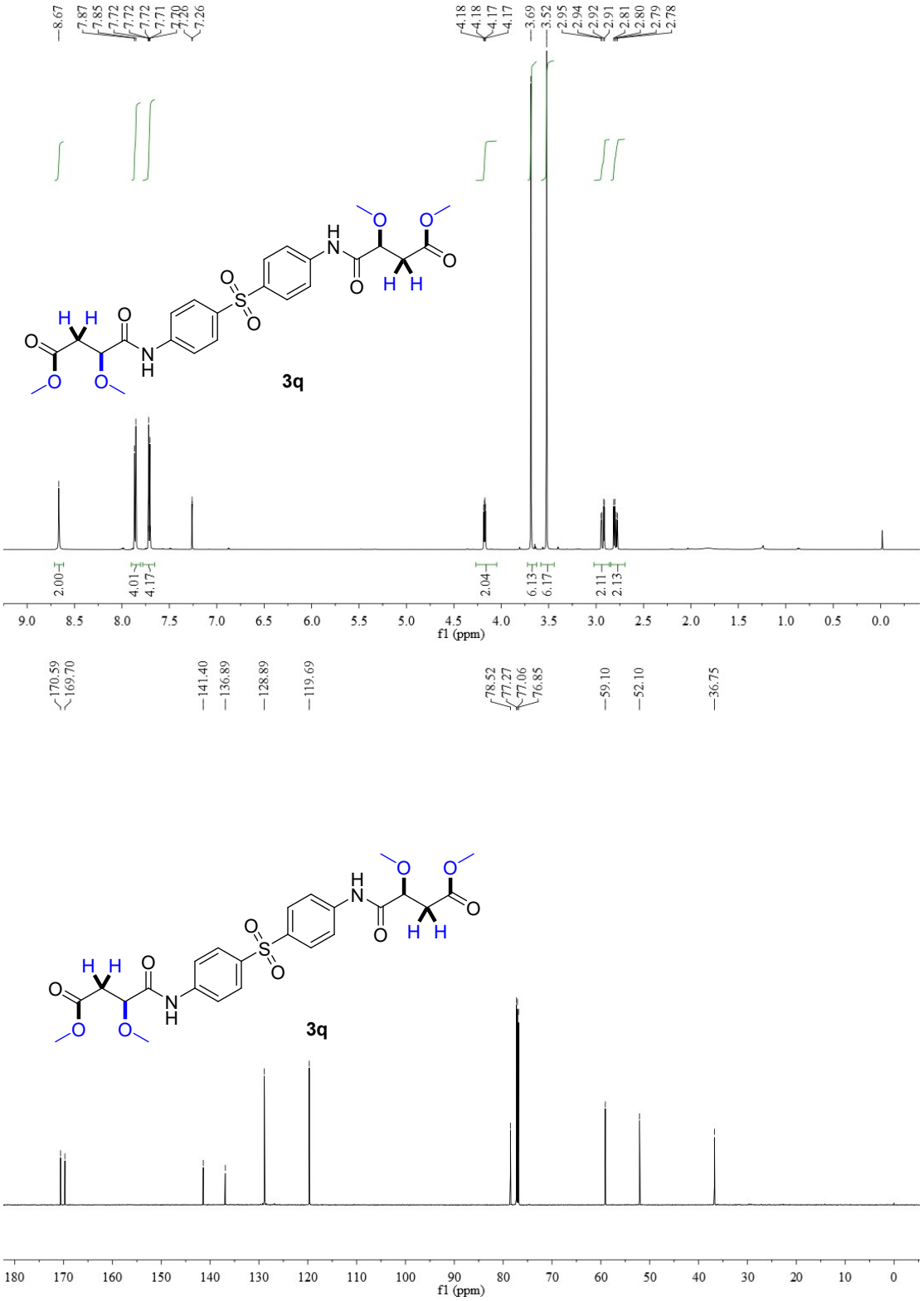
3o

Methyl 4-((2-chloropyridin-3-yl)amino)-3-methoxy-4-oxobutanoate (**3p**)

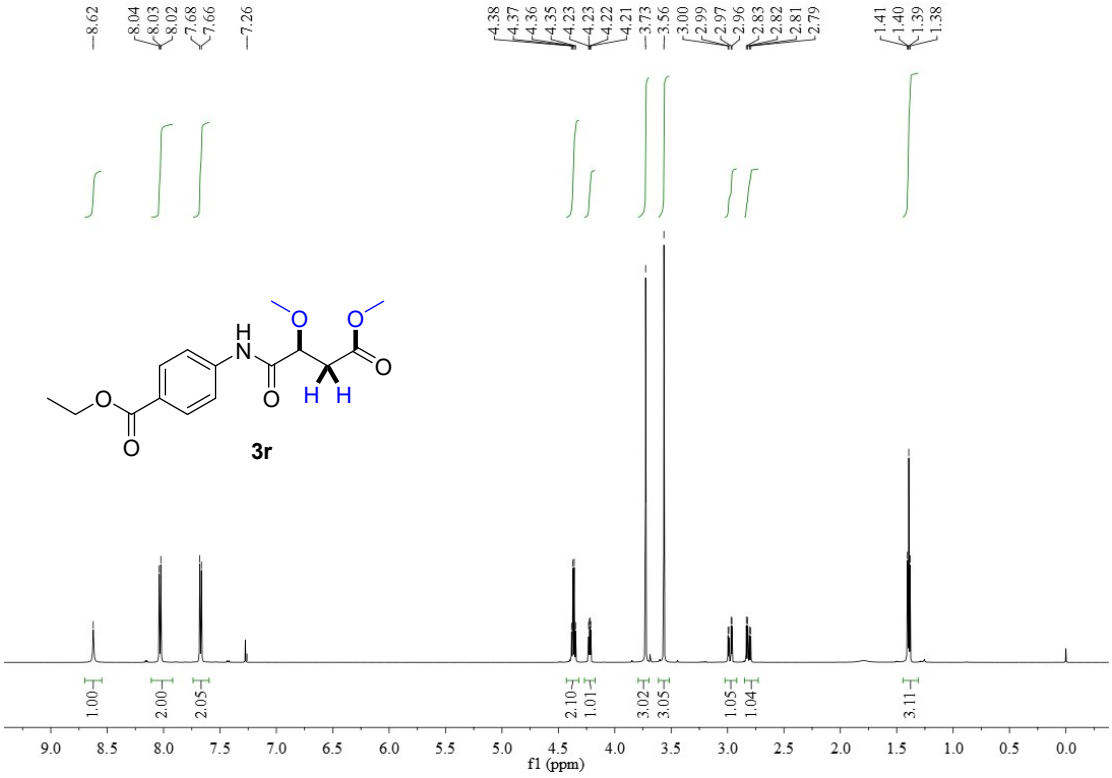


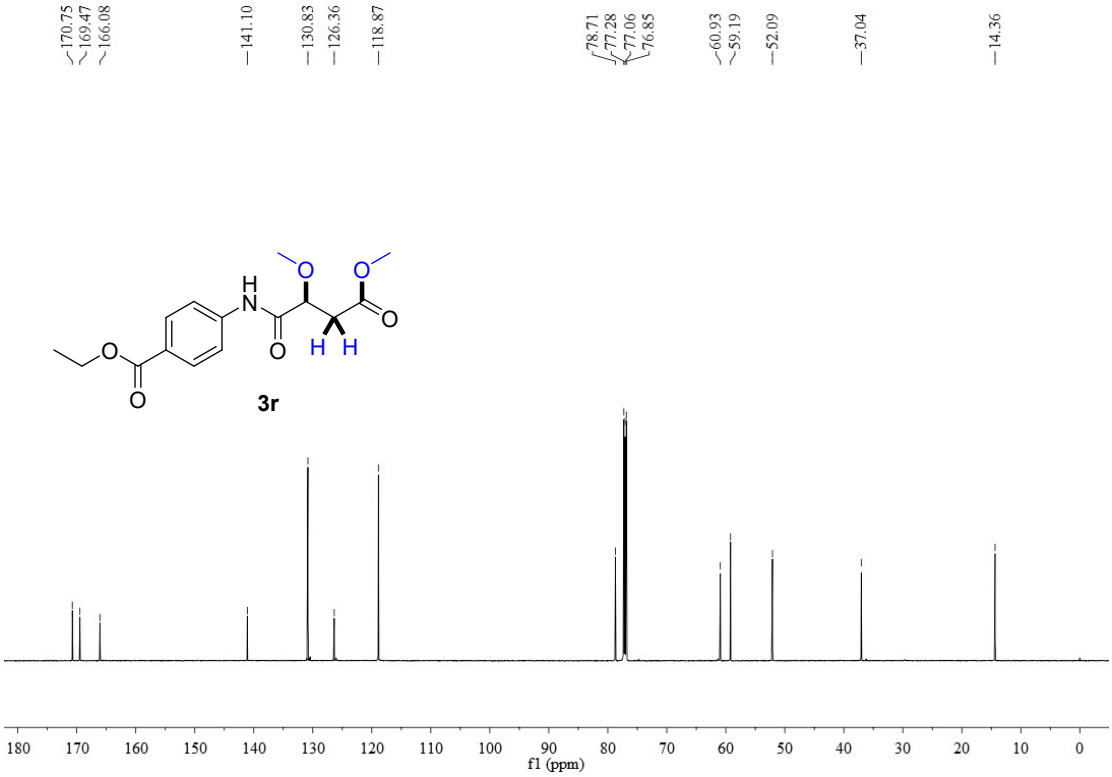


Dimethyl 4,4'-((sulfonylbis(4,1-phenylene))bis(azanediyl))bis(3-methoxy-4-oxobutanoate) (**3q**)

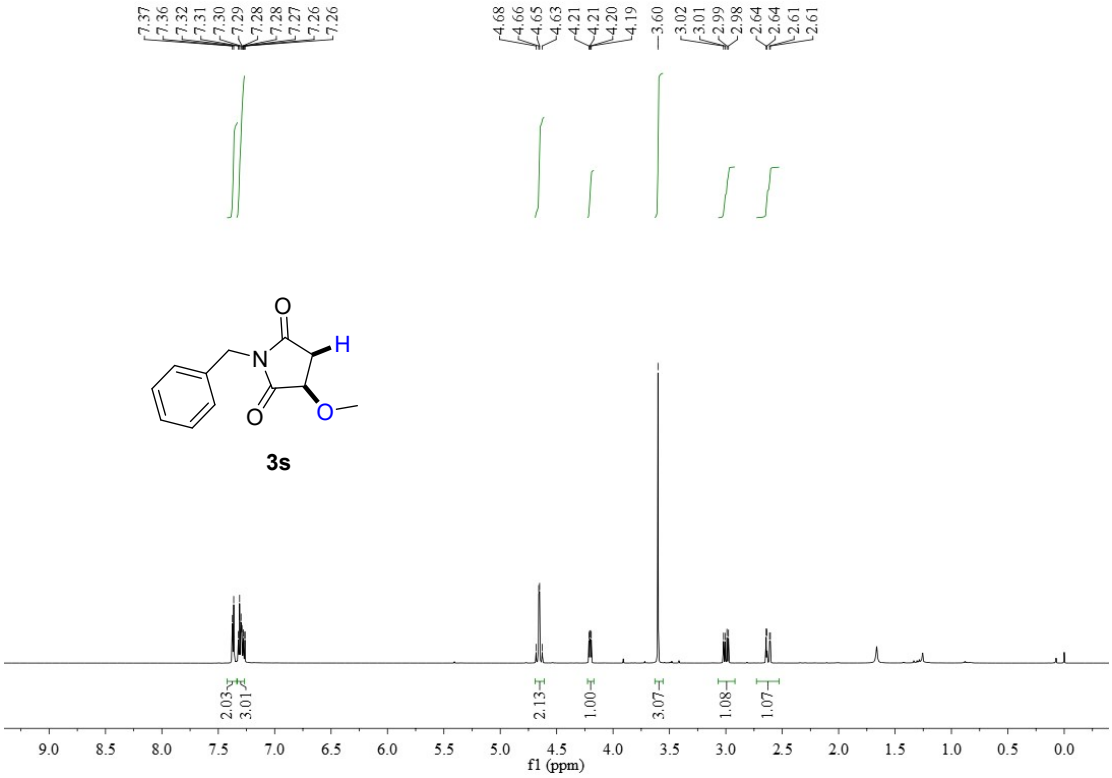


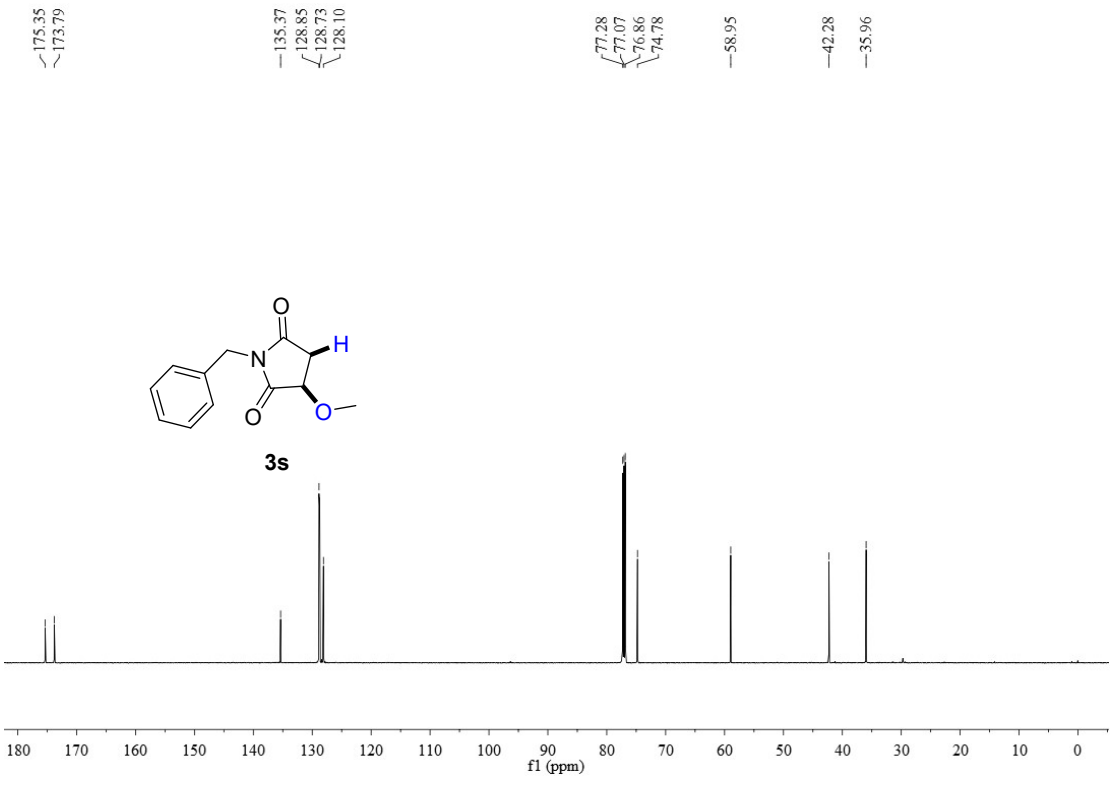
Ethyl 4-(2,4-dimethoxy-4-oxobutanamido)benzoate (**3r**)



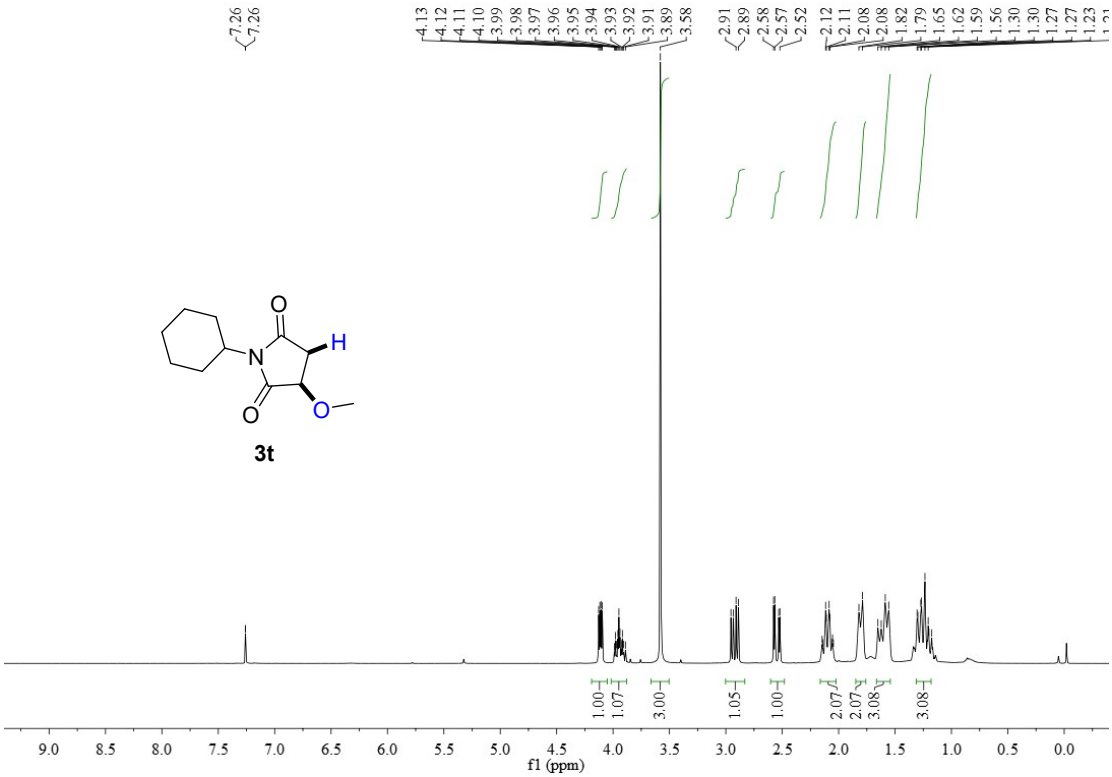


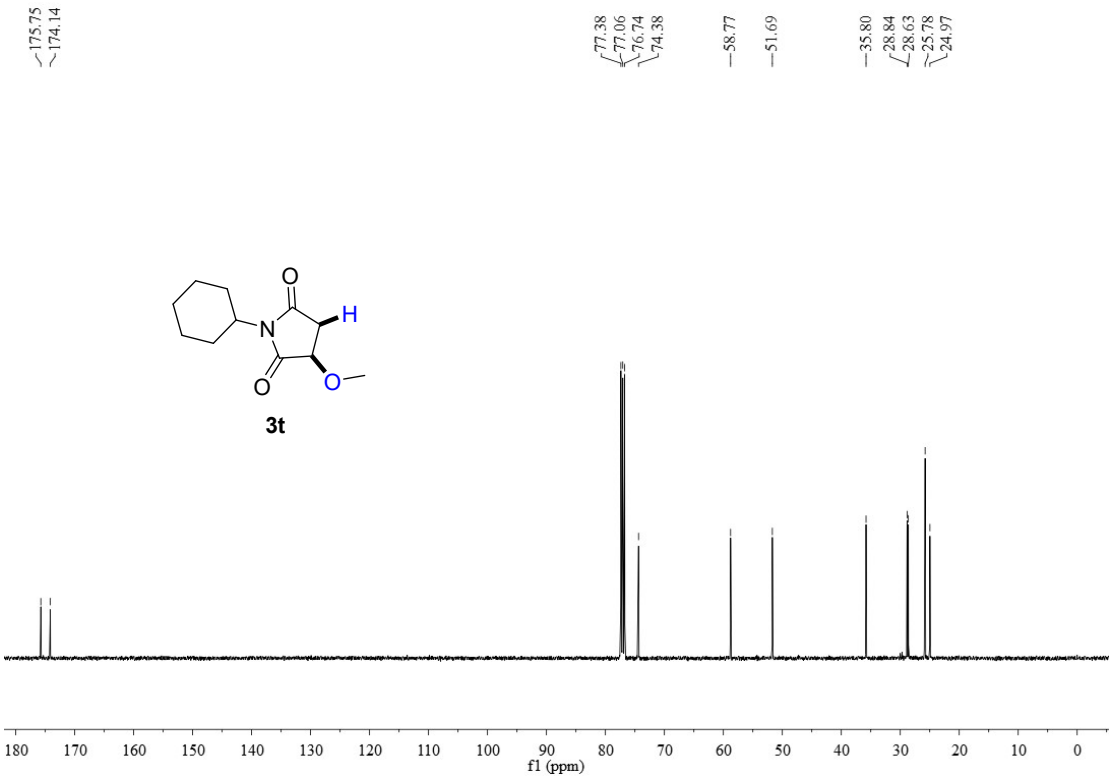
1-Benzyl-3-methoxypyrrolidine-2,5-dione (**3s**)



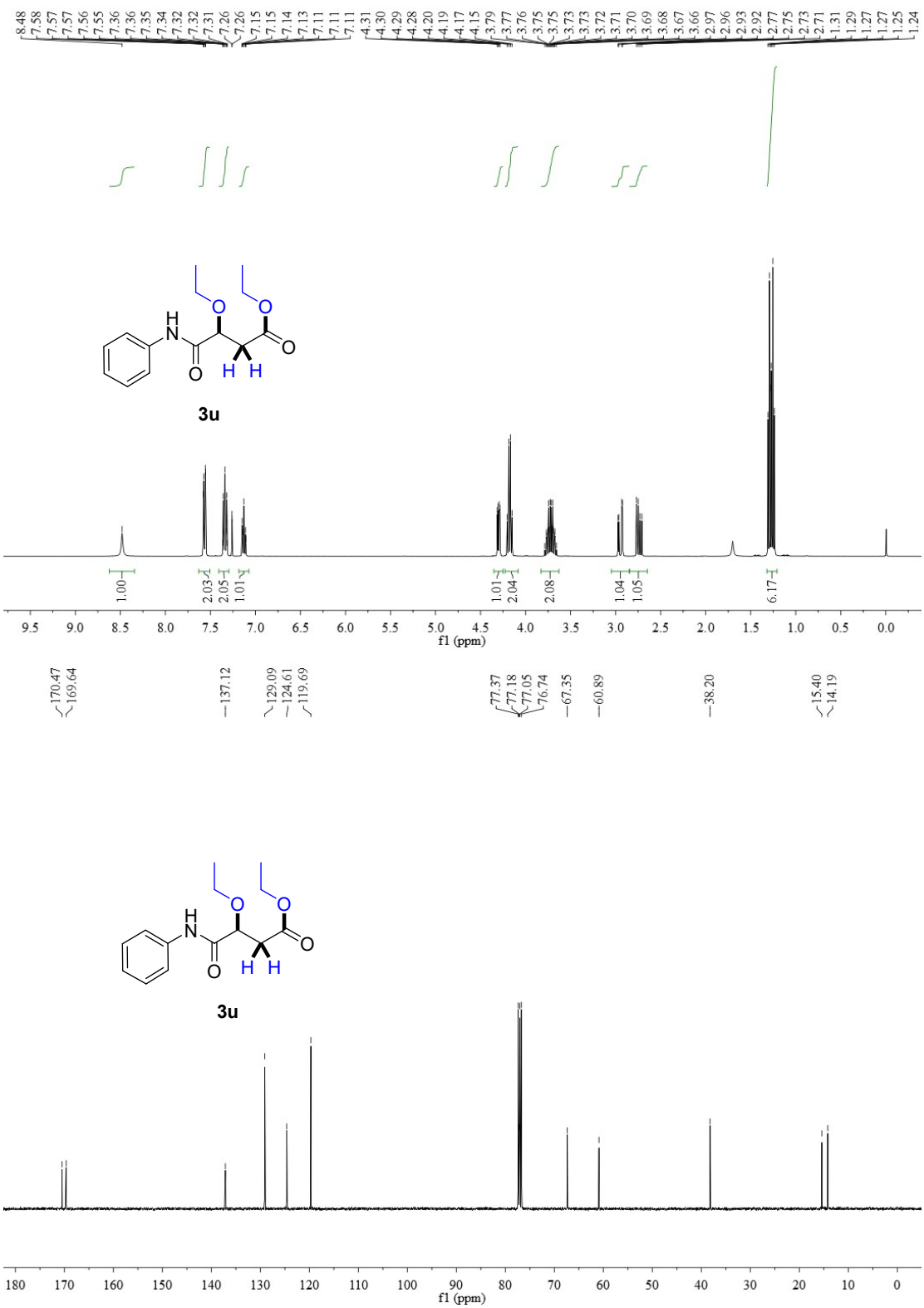


1-Cyclohexyl-3-methoxypyrrolidine-2,5-dione (**3t**)

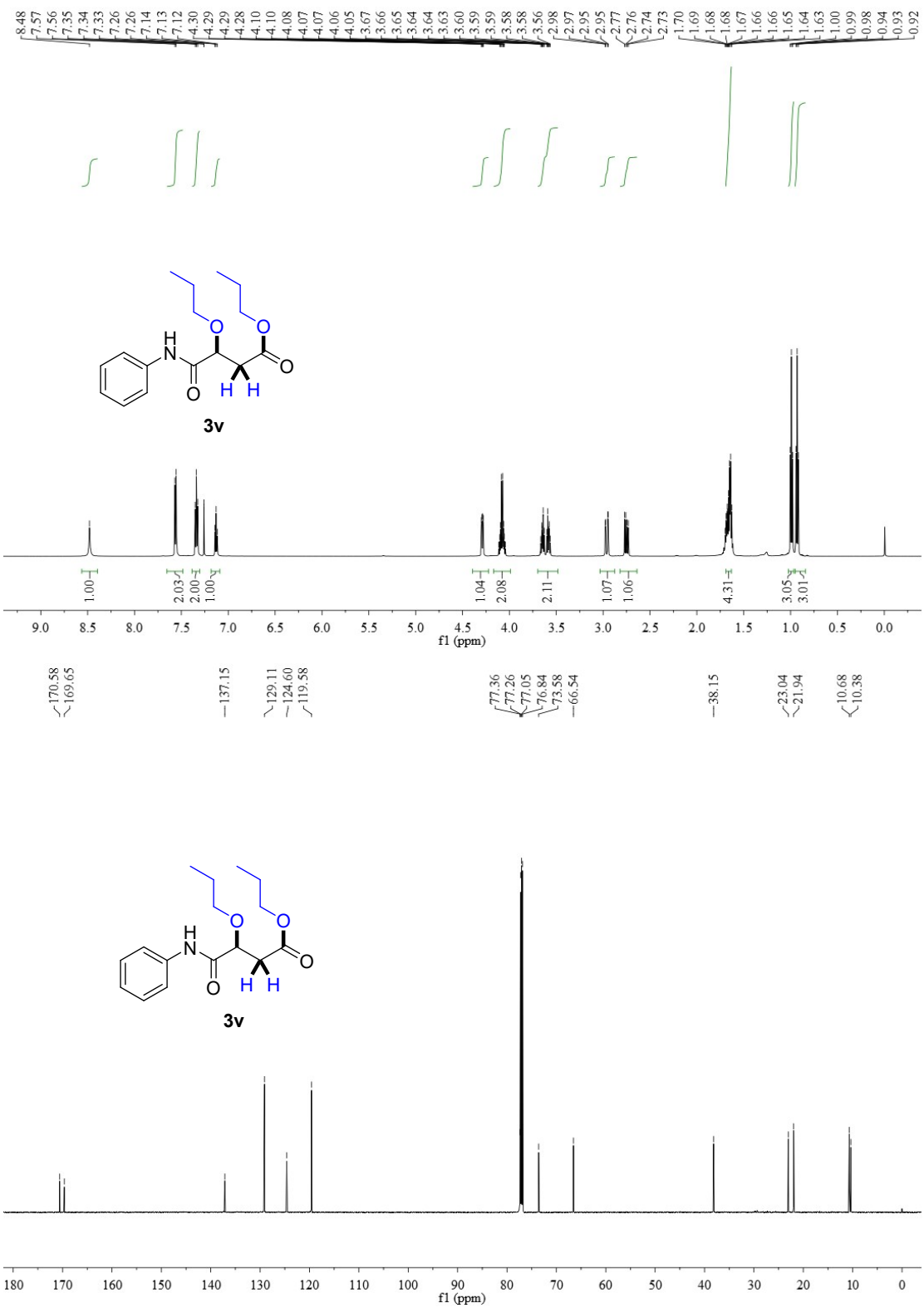




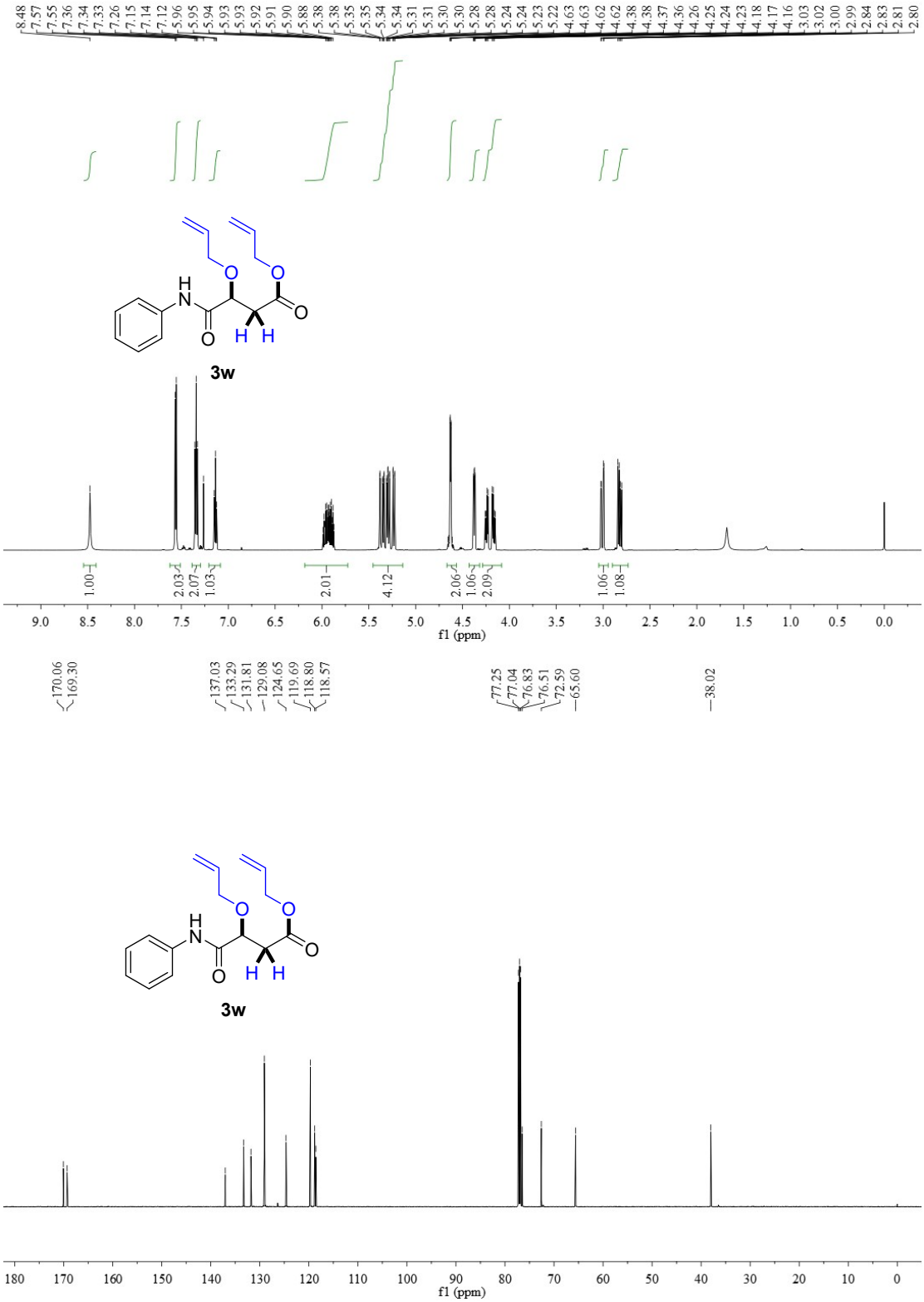
Ethyl 3-ethoxy-4-oxo-4-(phenylamino)butanoate (**3u**)



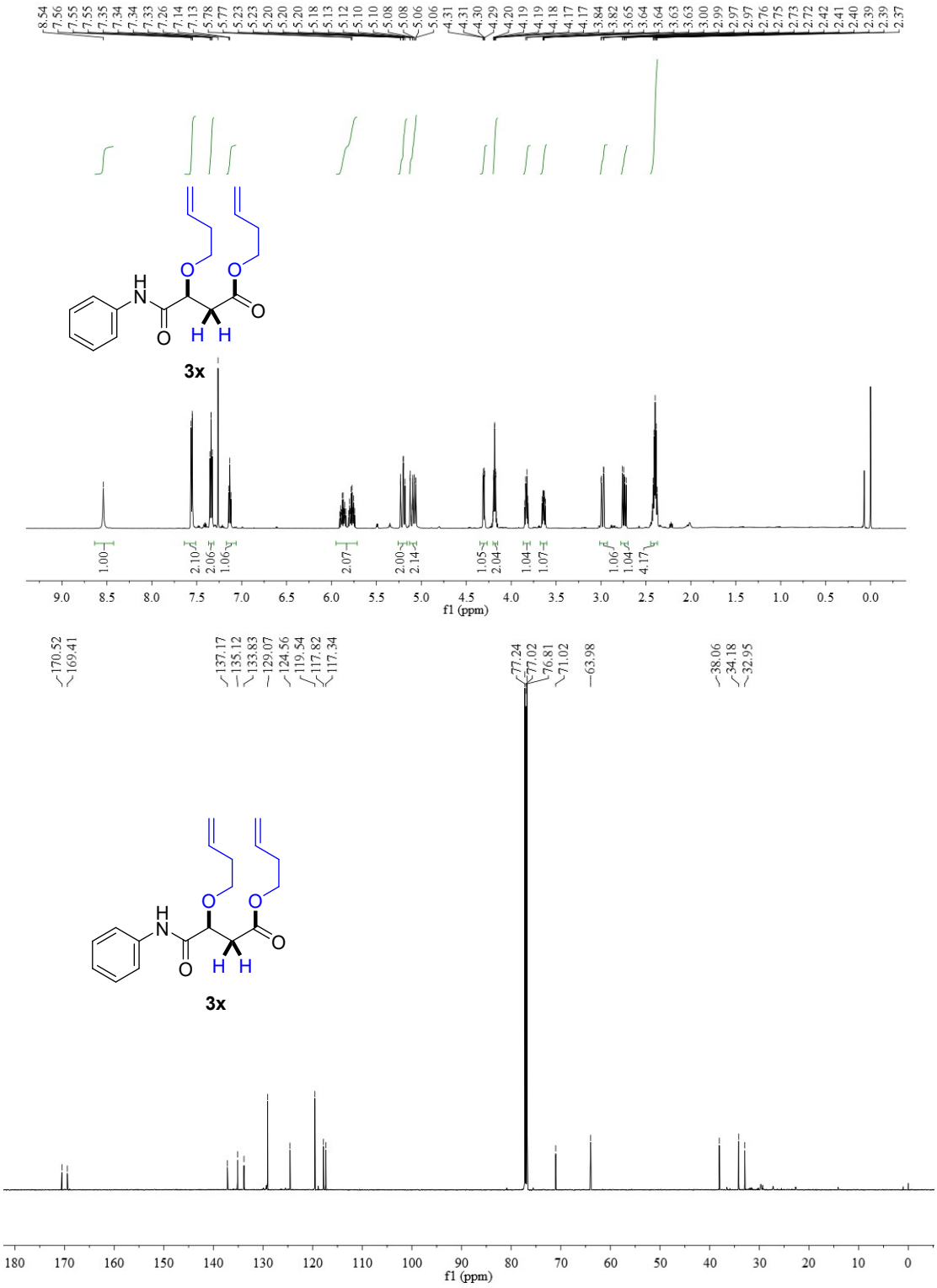
Propyl 4-oxo-4-(phenylamino)-3-propoxybutanoate (**3v**)



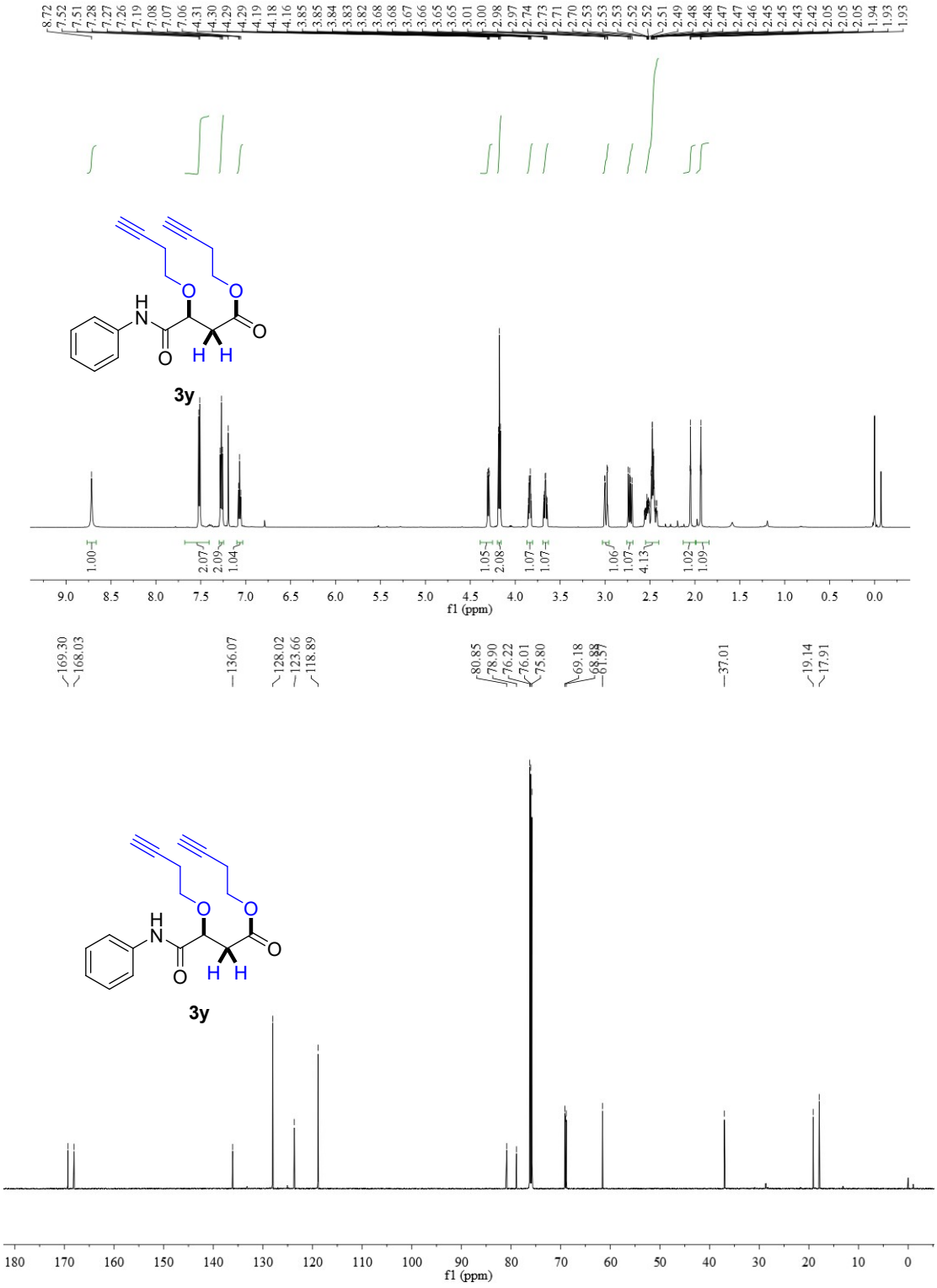
Allyl 3-(allyloxy)-4-oxo-4-(phenylamino)butanoate (**3w**)



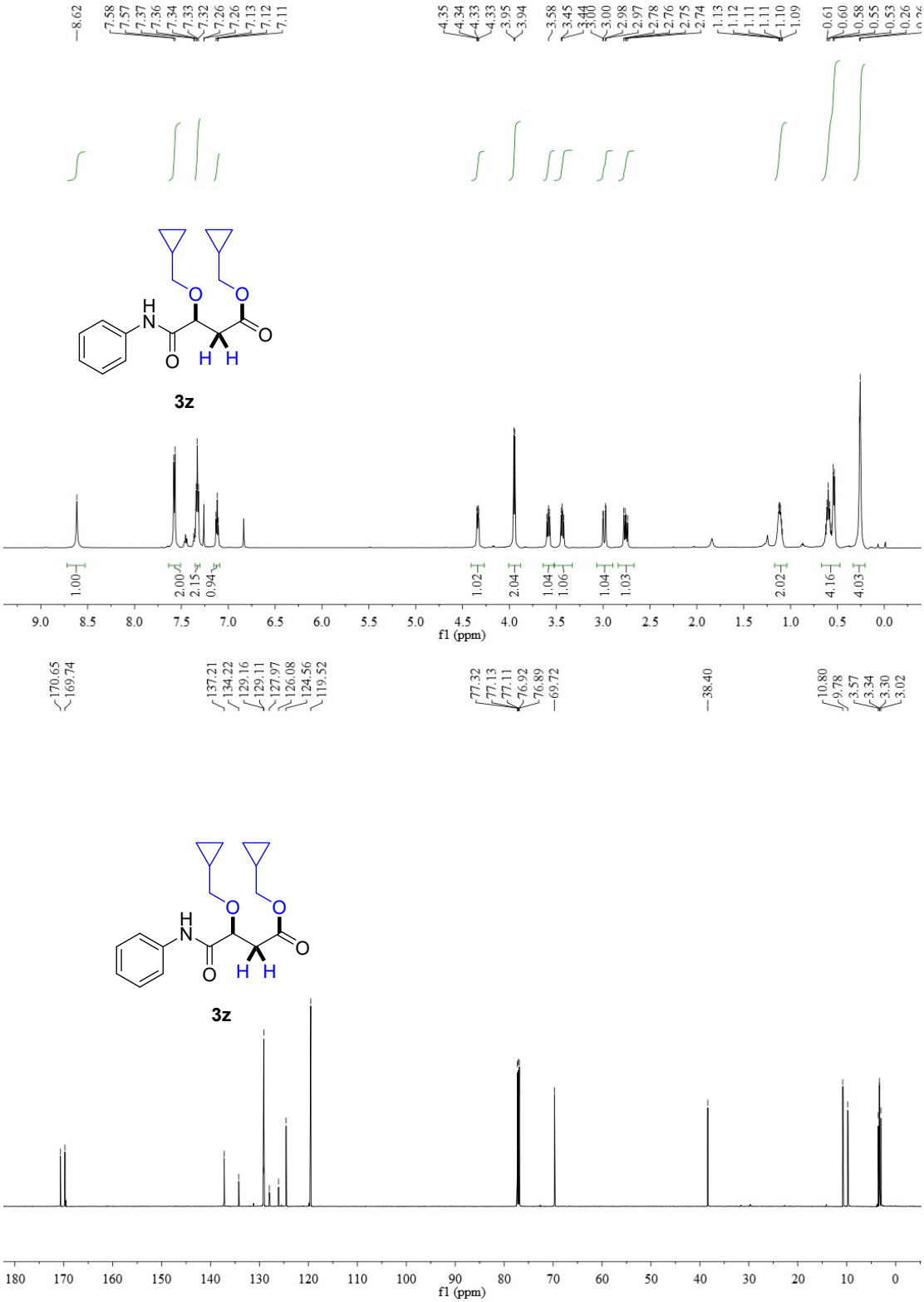
But-3-en-1-yl 3-(but-3-en-1-yloxy)-4-oxo-4-(phenylamino)butanoate (**3x**)



But-3-yn-1-yl 3-(but-3-yn-1-yloxy)-4-oxo-4-(phenylamino)butanoate (**3y**)



Cyclopropylmethyl 3-(cyclopropylmethoxy)-4-oxo-4-(phenylamino)butanoate (**3z**)



Furan-2-ylmethyl 3-(furan-2-ylmethoxy)-4-oxo-4-(phenylamino)butanoate (**3ah**)