Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Visible light-driven carbamoyloxylation of α-C(sp^3)-H bond of arylacetones via radical-initiated hydrogen atom transfer

Xing He,‡ Xiangyang Yao,‡ Shuai-Fang Cai, Hong-Ru Li, Liang-Nian He*

E-mail: heln@nankai.edu.cn
Fax: (+86) 22-23503878; Tel: (+86) 22-23503878

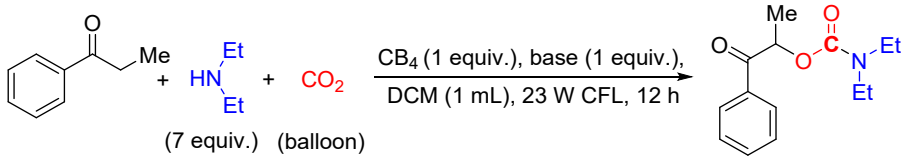
Table of Contents

I. General Information

Unless otherwise indicated, all reagents and carbon dioxide gas (purity 99.999%) were purchased from commercial sources and used without further treatment. Photoreactions were carried out using a 23 W household compact fluorescent lamp (CFL). The products were isolated by column chromatography on silica gel (200-300 mesh) using petroleum ether (60-90 ^{o}C) and ethyl acetate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer at 20 ^{o}C. All ^{1}H NMR spectra were reported in parts per million (ppm) downfield of TMS and measured relative to the signals for $CDCl_3$ (7.26 ppm) with ^{1}H decoupling. Coupling constants, *J*, were reported in hertz (Hz). Multiplets were assigned as singlet (s), doublet (d), triplet (t), doublet of doublet (dd), and multiplet (m). ^{13}C NMR were recorded at 100 MHz relative to $CDCl_3$ (77.16 ppm). GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-50 30 m × 0.25 μm) using a flame ionization detector. Mass spectra of GC-MS were recorded on a Shimadzu GCMS-QP2010 equipped with an RTX-5MS capillary column at an ionization voltage of 70 eV, the data were given as mass units per charge (m/z). FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer with KBr pellets. High-resolution mass spectra (HR-MS) were obtained with a Waters-Q-TOF-Premier (ESI).

II. Reaction Conditions Optimization, Scale-Up and Controlled Experiments

Table S1. Effect of the base[a]

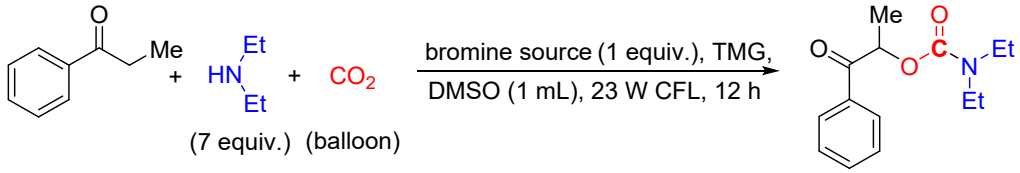


1a **2a** **3a**

Entry	Base	pK_a (in MeCN)	Yield (**3a**) (%)	Con. (**1a**) (%)
1	-	-	21	44
2	TMG	23.3	35	88
3	DBU	23.9	17	40
4	TBD	24.7	8	75
5	TEOA	15.9	3	40
6	*t*BuOK	-	23	82
7	Cs_2CO_3	-	14	46
8	Na_2CO_3	-	10	52
9	NaOH	-	23	73

[a] Unless otherwise noted, all the reactions were performed with **1a** (33.5 mg, 0.25 mmol), CBr_4 (82.9 mg, 0.25 mmol), base (0.25 mmol), **2a** (127.9 mg, 1.75 mmol), in 1 mL CH_2Cl_2 at room temperature under CO_2 (1 bar) with a 23 W CFL lamps for 12 h. The yield and conversion were determined by GC with 1,3,5-methoxybenzene as internal standard.

Table S2. Screening of the bromine source[a]



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

Entry	Bromine source	$BDE_{C/N-Br}$ (kcal/mol)	Yield (**3a**) (%)	Con. (**1a**) (%)
1	CBr_4	56.2	38	67
2	$CHBr_3$	64.8	trace	8
3	NBS	66	trace	31
4	CCl_3Br	55.7	33	59
5	Br_2	-	trace	2
6	PHP	-	26	82
7	DBDMH	-	3	50
8	NBSA	48	1	17
9[b]	CBr_4	56.2	28	53
10[c]	CBr_4	56.2	15	82
11[d]	CBr_4	56.2	14	87

[a] Unless otherwise noted, all the reactions were performed with **1a** (33.5 mg, 0.25 mmol), bromine source (0.25 mmol), TMG (28.8 mg, 0.25 mmol), **2a** (127.9 mg, 1.75 mmol) in 1 mL DMSO at room temperature under CO_2 (1 bar) with a 23 W CFL lamps for 12 h. The yield and conversion were determined by GC with 1,3,5-methoxybenzene as internal standard. NBS = *N*-bromosuccinimide, PHP = pyridine hydrobomide perbromide, DBDMH = 1,3-dibromo-5,5-dimethylhydantoin, NBSA = *N*-bromosaccharin. BDE data comes from ref S1-4. [b]CBr_4 (41.5 mg, 0.125 mmol). [c]CBr_4 (124.4 mg, 0.375 mmol). [d]CBr_4 (165.8 mg, 0.50 mmol).

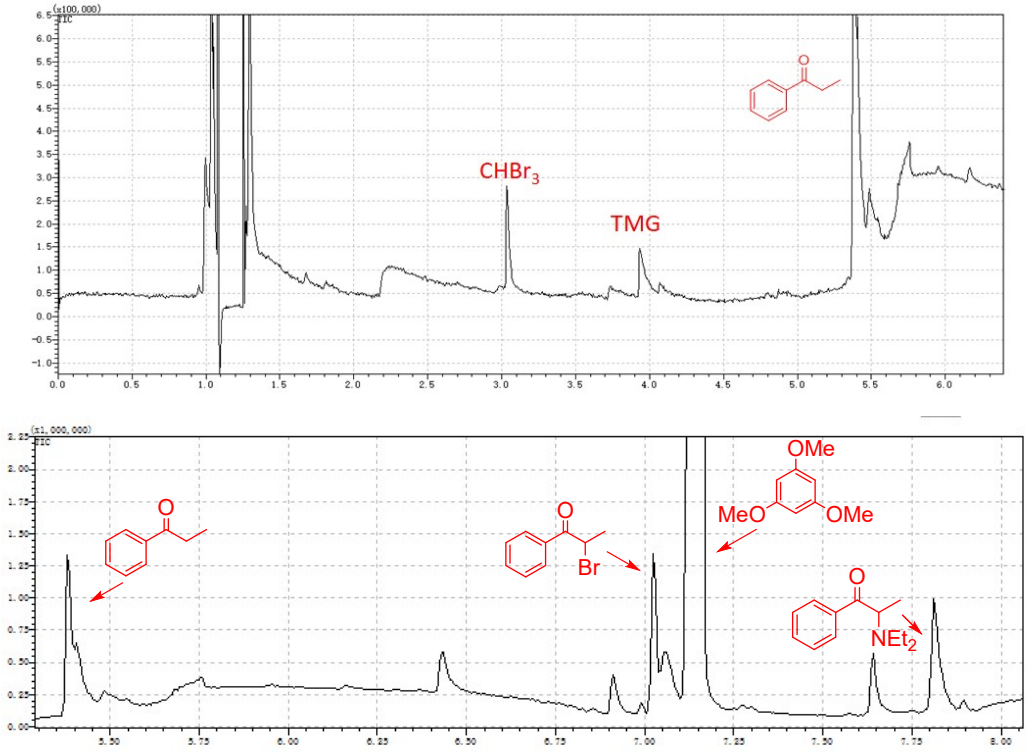
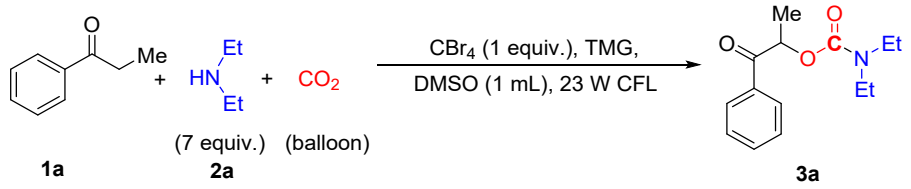


Figure S1. The detection of byproducts by GC-MS

Table S3. Effects of the loading of TMG and reaction time[a]

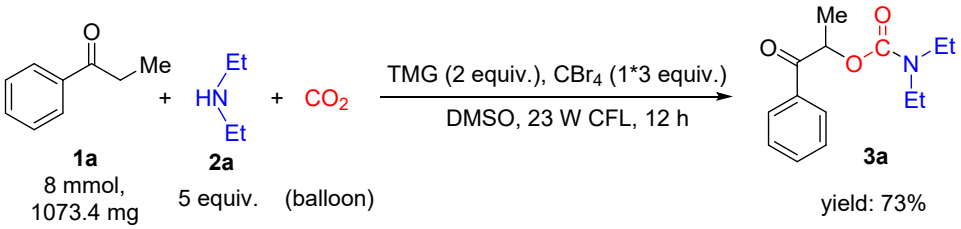


1a **2a** **3a**

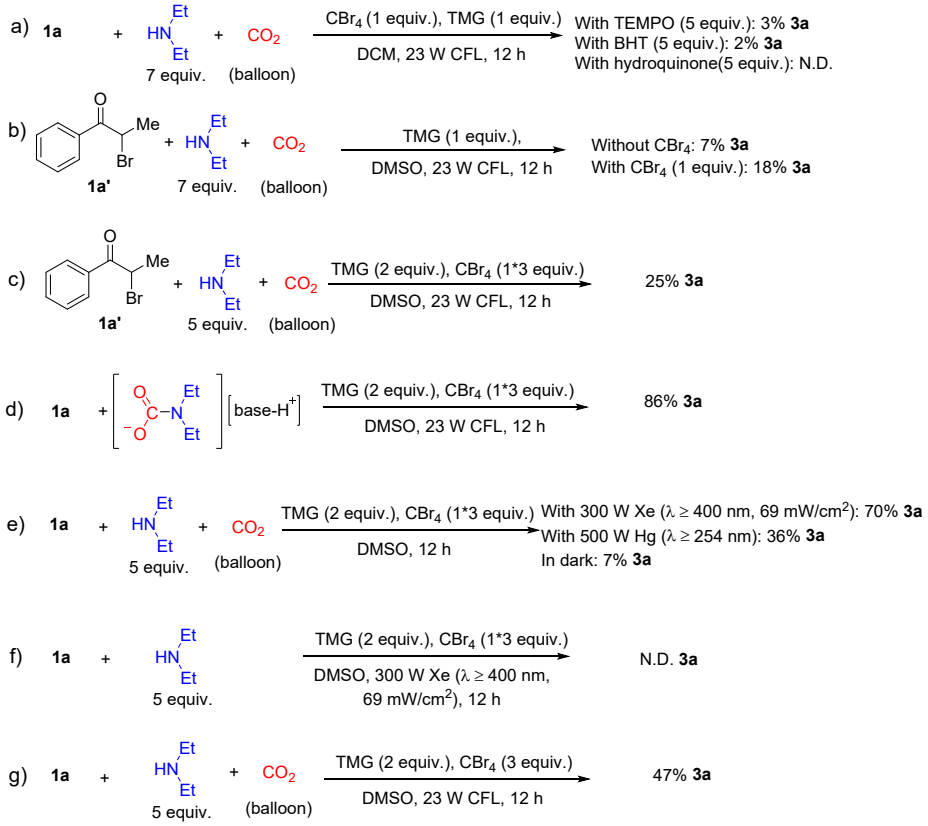
Entry	TMG (equiv.)	Time (h)	Yield (**3a**) (%)	Con. (1**a**) (%)
1	1	12	38	67
2	2	12	42	55
3	3	12	42	72
4	5	12	47	72
5	7	12	43	77
6	2	2	33	61
7	2	4	41	62
8	2	6	42	65
9	2	8	40	62
10	2	10	42	61

[a] Unless otherwise noted, all the reactions were performed with **1a** (33.5 mg, 0.25 mmol), bromine source (82.9 mg, 0.25 mmol), TMG (28.8 mg, 0.25 mmol), **2a** (127.9 mg, 1.75 mmol) in 1 mL DMSO at room temperature under CO_2 (1 bar) with a 23 W CFL lamps for 12 h. The yield and conversion were determined by GC with 1,3,5-methoxybenzene as the internal standard.

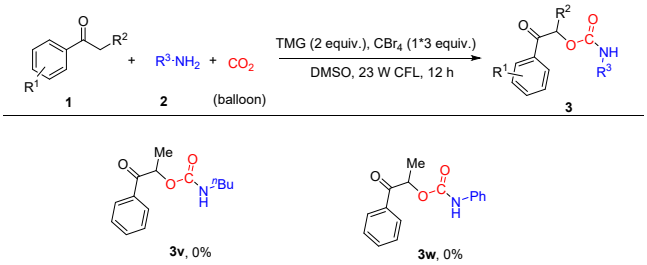
Scheme S1. A scale-up experiment



Scheme S2. Studies on the reaction intermediates



Scheme S3. Substrate scope of primary amines

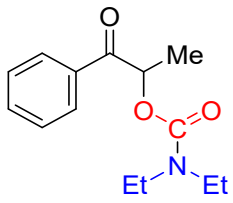


The reaction conditions with the stepwise addition procedure in equal amount for three times: **1** (0.25 mmol), **2** (1.25 mmol), TMG (57.6 mg, 0.5 mmol), and CBr_4 (248.7 mg, 0.25*3 mmol) in DMSO (1 mL) at r.t. under CO_2 (1 bar) with a 23 W CFL for 12 h.

III. General Procedure for the Synthesis of Organic Carbamates

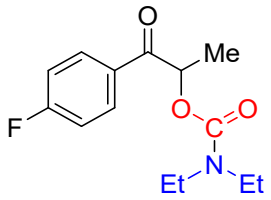
1 (33.5 mg, 0.25 mmol), **2** (91.4 mg, 1.25 mmol, 5 equiv.), TMG (28.8 mg, 0.5 mmol, 2 equiv.), and 1 mL DMSO were added successively in a 10 mL Schlenk tube, followed by bubbling CO_2 in an ice-water bath for 10 min. One single step was set to add CBr_4 (82.9 mg, 0.25 mmol, 1 equiv.) to the tube equipped with an extra CO_2 balloon vertically at 10 cm from 23 W CFL and stirred for 4 h. Such a single process was performed for three times in succession, which means 3 equiv. CBr_4 was added in total and illuminated for 12 h altogether. Upon completion, the mixture was quenched with distilled water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over anhydrous Mg_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to offer the product **3**. The scaled-up experiment was conducted with phenylacetone (1073.4 mg, 8 mmol), diethylamine (2925.6 mg, 40 mmol, 5 equiv.), TMG (1842.9 mg, 16 mmol, 2 equiv.), CBr_4 (2652.8mg, 8x3 mmol, 1 equiv.), and 20 mL DMSO in a 50 mL Schlenk flask with other operation unchanged.

IV. Characterization Data of Products



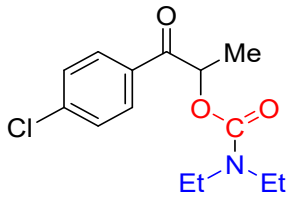
3a

1-oxo-1-phenylpropan-2-yl diethylcarbamate (compound 3a): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 8.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 2H), 5.94 (q, J = 7.0 Hz, 1H), 3.32-3.23 (m, 4H), 1.50 (d, J = 7.0 Hz, 3H), 1.16-1.08 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.9, 155.2, 134.9, 133.4, 128.2, 128.6, 71.7, 42.1, 41.6, 17.3, 14.1, 13.5; IR (KBr): 3064, 2979, 2935, 1695, 1597, 1429, 1275, 1173, 1098, 962, 778, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{20}NO_3$ 250.1443; Found 250.1436.



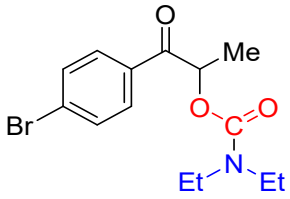
3b

1-(4-fluorophenyl)-1-oxopropan-2-yl diethylcarbamate (compound 3b): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 5.89 (d, *J* = 7.0 Hz, 1H), 3.32-3.22 (m, 4H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.15-1.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.8, 167.2, 164.7, 155.2, 131.3, 131.3, 116.1, 115.9, 71.5, 42.1, 41.6, 17.3, 14.1, 13.5; IR (KBr): 3074, 2977, 2935, 1697, 1599, 1429, 1273, 1230, 1174, 1098, 962, 848, 788, 702 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}FNO_3$ 268.1349; Found 268.1340.



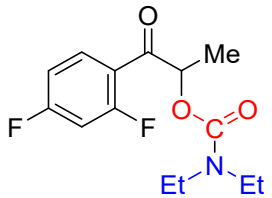
3c

1-(4-chlorophenyl)-1-oxopropan-2-yl diethylcarbamate (compound 3c): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 5.86 (q, *J* = 6.9 Hz, 1H), 3.31-3.24 (m, 4H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.11 (t, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.2, 155.1, 139.8, 133.3, 130.0, 129.1, 71.6, 42.1, 41.6, 17.2, 14.1, 13.5. IR (KBr): 3078, 2978, 2926, 1697, 1592, 1475, 1427, 1268, 1172, 1087, 964, 840, 763 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}ClNO_3$ 284.1053; Found 284.1045.



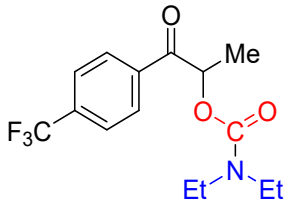
3d

1-(4-bromophenyl)-1-oxopropan-2-yl diethylcarbamate (compound 3d): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 5.86 (q, *J* = 6.9 Hz, 1H), 3.32-3.21 (m, 4H), 1.49 (d, *J* = 7.0 Hz, 3H), 1.12 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 155.1, 133.7, 132.1, 130.1, 128.6, 71.6, 42.1, 41.6, 17.2, 14.1, 13.5. IR (KBr): 2959, 2917, 1701, 1586, 1463, 1375, 1272, 1160, 1097, 1025, 825 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{19}BrNO_3$ 328.05483; Found 328.05435.



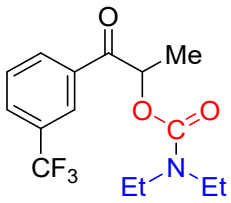
3e

1-(2,4-difluorophenyl)-1-oxopropan-2-yl diethylcarbamate (compound 3e): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (dd, *J* = 8.5, 6.6 Hz, 2H), 7.00-6.96 (t, *J* = 8.2 Hz 2H), 6.90-6.85 (m, 1H), 5.71 (q, *J* = 7.8, 6.9 Hz, 1H), 3.35-3.22 (m, 4H), 1.50 (t, *J* = 6.9 Hz, 3H), 1.14 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 195.5(d, *J* = 20Hz), 167.3 (d, *J* = 12 Hz), 164.8 (d, *J* = 13 Hz), 163.5 (d, *J* = 12 Hz), 161.0 (d, *J* = 12 Hz), 155.2, 133.3 (q, *J* = 5 Hz), 120.3 (dd, *J* = 4, 11 Hz), 112.5 (dd, *J* = 4, 18 Hz), 104.8 (dd, *J* = 25, 8 Hz), 74.7 (d, *J* = 8 Hz), 42.1, 41.6, 32.1, 16.4, 14.1, 13.5. IR (KBr): 3073, 2978, 2935, 1698, 1611, 1427, 1270, 1172, 1095, 975, 854, 778 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}F_2NO_3$ 286.1255; Found 286.1244.



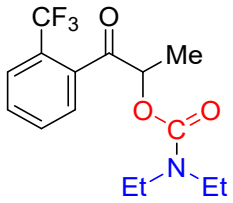
3f

1-oxo-1-(4-(trifluoromethyl)phenyl)propan-2-yl diethylcarbamate (compound 3f): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (d, J = 8.1 Hz, 2H), 7.72 (d, J = 8.1 Hz, 2H), 5.89 (q, J = 7.0 Hz, 1H), 3.32-3.21 (m, 4H), 1.51 (d, J = 7.0 Hz, 3H), 1.16-1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 155.1, 138.0, 134.6 (d, J = 32 Hz), 128.9, 125.6 (q, J = 4 Hz), 122.3, 71.9, 42.2, 41.7, 17.0, 14.1, 13.5. IR (KBr): cm^{-1}. IR (KBr): 3076, 2970, 1694, 1431, 1321, 1167, 1125, 1066, 961, 852, 770 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}F_3NO_3$ 318.1317; Found 318.1307.



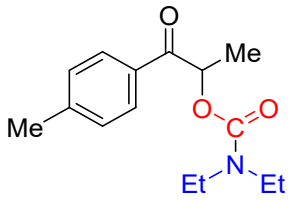
3g

1-oxo-1-(3-(trifluoromethyl)phenyl)propan-2-yl diethylcarbamate (compound 3g): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (s, 1H), 8.14 (d, J = 7.8 Hz, 1H), 7.81 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 5.88 (q, J = 7.0 Hz, 1H), 3.34-3.27 (m, 4H), 1.53 (d, J = 7.0 Hz, 3H), 1.16-1.07 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 155.1, 135.6, 131.8, 129.7(d, J = 3.6 Hz), 129.5, 125.5 (d, J = 5 Hz), 72.0, 42.2, 41.6, 17.1, 14.1, 13.5. IR (KBr): 3075, 2981, 1702, 1430, 1332, 1172, 1132, 970, 695 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}F_3NO_3$ 318.1317; Found 318.1308.



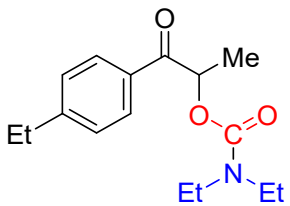
3h

1-oxo-1-(2-(trifluoromethyl)phenyl)propan-2-yl diethylcarbamate (compound 3h): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 7.4 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.58 (m, 2H), 5.73 (q, *J* = 7.0 Hz, 1H), 3.26-3.20 (m, 4H), 1.45 (d, *J* = 7.0 Hz, 3H), 1.09-1.01 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 155.0, 137.5, 131.8, 130.7, 128.2, 127.0 (q, *J* = 5 Hz), 123.5 (d, *J* = 272 Hz), 74.3, 42.1, 41.5, 16.3, 13.9, 13.5. IR (KBr): 3073, 2981, 1701, 1429, 1315, 1170, 1138, 956, 772 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{19}F_3NO_3$ 318.1317; Found 318.1307.



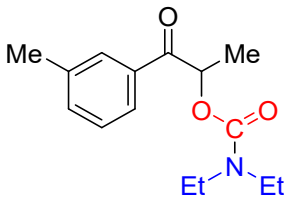
3i

1-oxo-1-(p-tolyl)propan-2-yl diethylcarbamate (compound 3i): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.87 (q, *J* = 7.0 Hz, 1H), 3.26-3.15 (m, 4H), 2.33 (s, 3H), 1.42 (d, *J* = 7.0 Hz, 3H), 1.10-1.02 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 155.2, 144.2, 132.3, 129.4, 128.7, 71.6, 42.0, 41.6, 21.8, 17.5, 14.1, 13.6. IR (KBr): 2977, 1697, 1428, 1273, 1172, 1096, 962, 771 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}NO_3$ 264.1600; Found 264.1591.



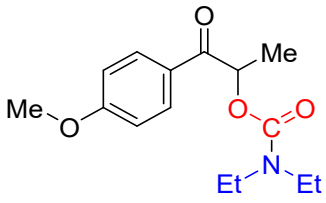
3j

1-(4-ethylphenyl)-1-oxopropan-2-yl diethylcarbamate (compound 3j): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 2H), 5.87 (q, *J* = 7.9, 7.0 Hz, 1H), 3.25-3.17 (m, 4H), 2.62 (d, *J* = 7.6 Hz, 2H), 1.42 (d, *J* = 8.0 Hz, 3H), 1.17 (t, *J* =8.1, 3H), 1.08-1.03 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 155.2, 150.4, 132.5, 128.8, 128.3, 71.5, 42.0, 41.6, 29.1, 17.4, 15.3, 14.0, 13.5. IR (KBr): 2971, 1697, 1607, 1427, 1273, 1172, 1097, 962, 770 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{24}NO_3$ 278.1756; Found 278.1747.



3k

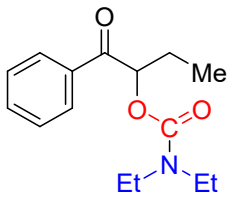
1-oxo-1-(m-tolyl)propan-2-yl diethylcarbamate (compound 3k): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (m, 2H), 7.34 (m, 2H), 5.93 (q, *J* = 6.9 Hz, 1H), 3.33-3.29 (m, 4H), 2.39 (s, 3H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.15-1.11 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 155.3, 138.6, 135.0, 134.2, 129.1, 128.7, 125.8, 71.8, 42.1, 41.6, 21.5, 17.4, 14.1, 13.6. IR (KBr): 2976, 1698, 1598, 1427, 1273, 1170, 1098, 970, 771 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{22}NO_3$ 264.1600; Found 264.1592.



3l

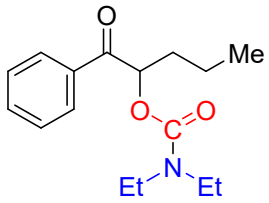
1-(4-methoxyphenyl)-1-oxopropan-2-yl diethylcarbamate (compound 3l): Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 5.91 (q, *J* = 7.0 Hz, 1H), 3.84 (s, 3H), 3.32-3.30 (m, 4H), 1.48 (d, *J* = 7.0 Hz, 3H), 1.14-1.09 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.5, 163.7, 155.2, 130.9, 127.7, 113.9, 71.3, 55.6, 42.0, 41.6, 17.4, 14.1, 13.5. IR (KBr): 2976, 1692, 1600, 1428,

1266, 1171, 1097, 962, 843, 773cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{15}H_{22}NO_4$ 280.1549; Found 280.1541.



3m

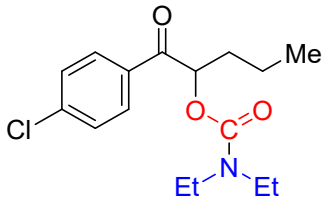
1-oxo-1-phenylbutan-2-yl diethylcarbamate (compound 3m): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 5.80 (dd, *J* = 8.1, 4.4 Hz, 1H), 3.34-3.28 (m, 4H), 1.94-1.81 (m, 2H), 1.19 (br, 3H), 1.10 (br, 3H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 155.5, 135.4, 133.3, 128.8, 128.5, 76.6, 42.1, 41.7, 25.0, 14.2, 13.6, 10.1. IR (KBr): 3063, 2976, 1698, 1428, 1277, 1173, 1096, 982, 699 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{15}H_{22}NO_3$ 264.1600; Found 264.1592.



3n, 79%

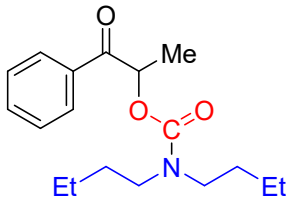
1-oxo-1-phenylpentan-2-yl diethylcarbamate (compound 3n): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.84 (t, *J* = 6.4 Hz, 1H), 3.35-3.26 (m, 4H), 1.84-1.78 (q, *J* = 7.1, 6.7 Hz, 2H), 1.53-1.46 (m, 2H), 1.19 (br, 3H), 1.10 (br, 3H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 155.5, 135.4, 133.3, 128.8, 128.5, 75.4, 42.1, 41.7, 33.7, 19.1, 14.2, 13.9, 13.6. IR (KBr): 3062, 2964, 2874, 1698, 1598, 1428, 1280, 1171, 1078, 970, 767, 699 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{16}H_{24}NO_3$

278.1756; Found 278.1746.



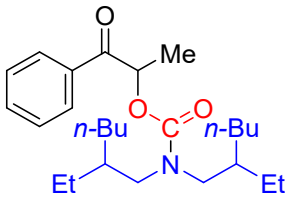
3o, 92%

1-(4-chlorophenyl)-1-oxopentan-2-yl diethylcarbamate (compound 3o): Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (d, *J* = 8.3 Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 5.76 (t, *J* = 6.4 Hz, 1H), 3.37-3.26 (m, 4H), 1.82-1.77 (q, *J* = 7.3 Hz, 2H), 1.53-1.43 (m, 2H), 1.19 (br, 3H), 1.10 (br, 3H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 155.4, 139.4, 133.8, 130.0, 129.1, 75.3, 42.2, 41.7, 33.6, 19.0, 14.2, 13.9, 13.6. IR (KBr): 3070, 2963, 1698, 1590, 1477, 1428, 1279, 1172, 1092, 970, 840, 768 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{16}H_{23}ClNO_3$ 312.1366; Found 312.1359.



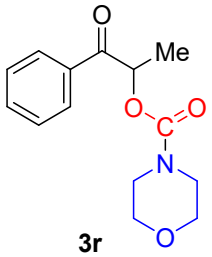
3p

1-oxo-1-phenylpropan-2-yl dibutylcarbamate (compound 3p): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 5.91 (q, *J* = 7.0 Hz, 1H), 3.28-3.13 (m, 4H), 1.53-1.44 (m, 7H), 1.30-1.22 (m, 4H), 0.91-0.86 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 155.5, 134.9, 133.3, 128.7, 128.6, 71.7, 47.4, 46.8, 31.6, 30.7, 30.2, 29.8, 20.1, 17.2, 13.9. IR (KBr): 3060, 2966, 2872, 1698, 1598, 1423, 1223, 1099, 970, 768, 700 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{28}NO_3$ 306.2069; Found 306.2060.



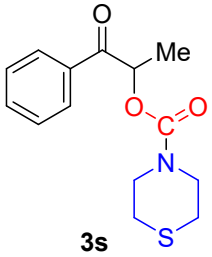
3q

1-oxo-1-phenylpropan-2-yl bis(2-ethylhexyl)carbamate (compound 3q): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 5.93 (q, *J* = 7.1 Hz, 1H), 3.26-3.05 (m, 4H), 1.50 (s, *J* = 6.9 Hz, 3H), 1.26-1.23 (m, 17H), 0.88-0.82 (m, 13H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 156.1, 135.0, 133.3, 128.7, 128.6, 71.8, 51.3, 50.3, 38.0, 37.3, 30.7, 30.5, 30.4, 28.9, 28.7, 23.8, 23.7, 23.2, 23.1, 17.1, 14.2, 10.8, 10.7. IR (KBr): 3065, 2960, 2862, 1698, 1598, 1468, 1228, 1158, 1100, 969, 767, 701 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{43}NO_3$ 418.3321; Found 418.3311.



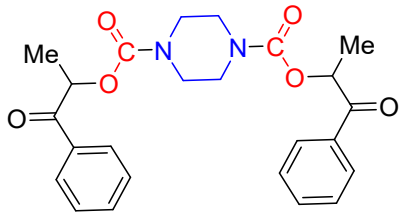
3r

1-oxo-1-phenylpropan-2-yl morpholine-4-carboxylate (compound 3r): Yellow soild. mp: 103-104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 6.3 Hz, 2H), 7.58 (m, 1H), 7.47 (t, *J* = 6.4 Hz, 2H), 5.95 (q, *J* = 6.9 Hz, 1H), 3.68-3.51 (m, 8H), 1.52 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 154.6, 134.6, 133.5, 128.8, 128.5, 72.2, 66.6, 44.6, 44.1, 17.3. IR (KBr): 3065, 2965, 2869, 1691, 1595, 1421, 1246, 1109, 968, 856, 775, 708 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}NO_4$ 264.1236 Found 264.1227.



3s

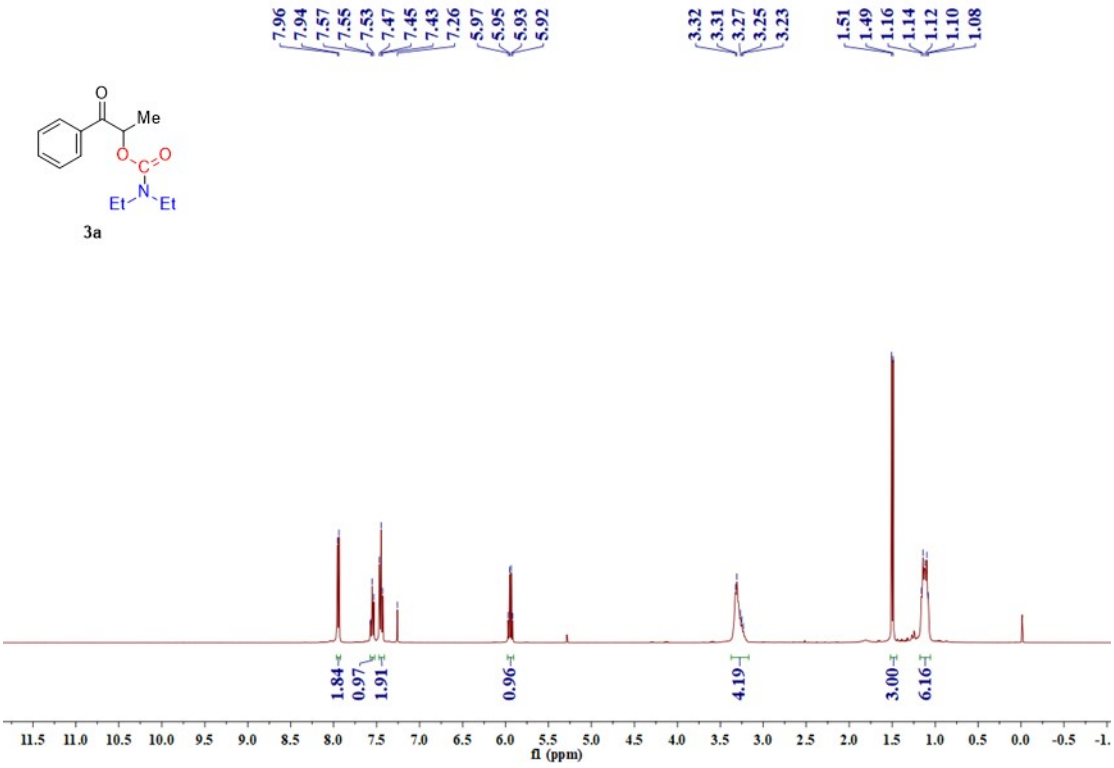
1-oxo-1-phenylpropan-2-yl thiomorpholine-4-carboxylate (compound 3s): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.57 (m, 1H), 7.51 – 7.41 (m, 2H), 5.94 (q, *J* = 7.0 Hz, 1H), 3.97 – 3.58 (m, 4H), 2.57 (br, 4H), 1.50 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 154.4, 134.7, 133.5, 128.8, 128.5, 72.3, 46.9, 46.6, 27.3, 17.3. IR (KBr): 3062, 2905, 1690, 1596, 1436, 1291, 1232, 1112, 964, 768, 703 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{18}NO_3S$ 280.1007; Found 280.0999.

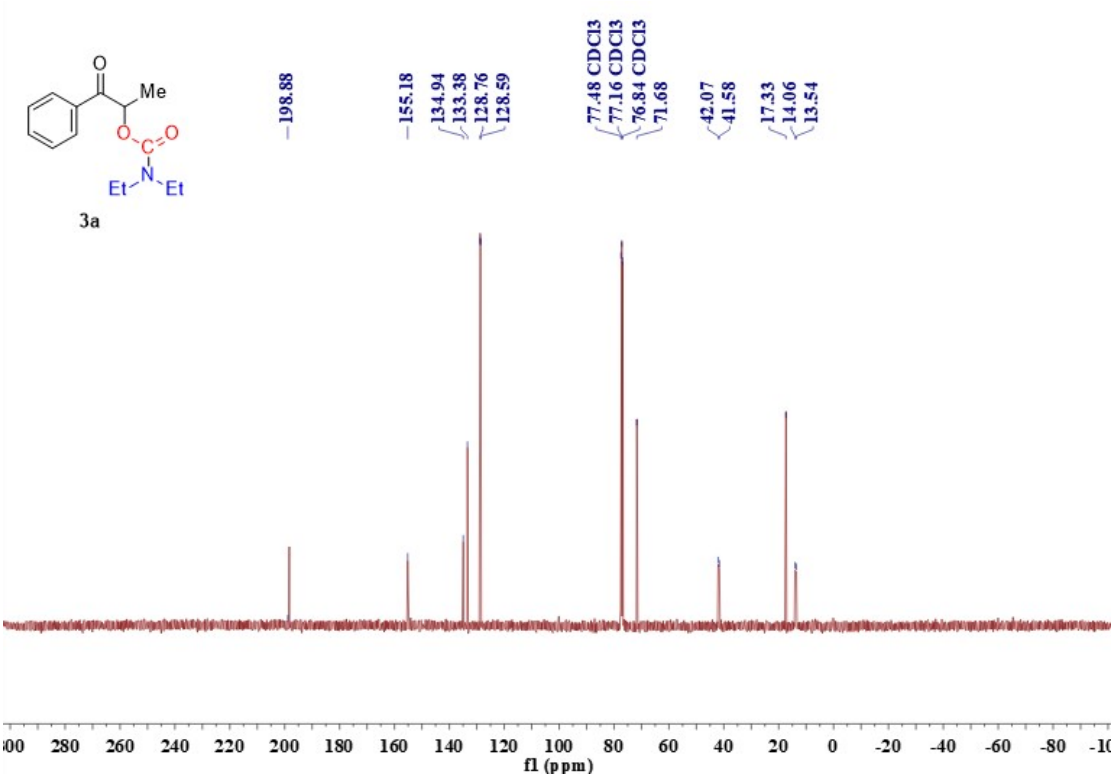


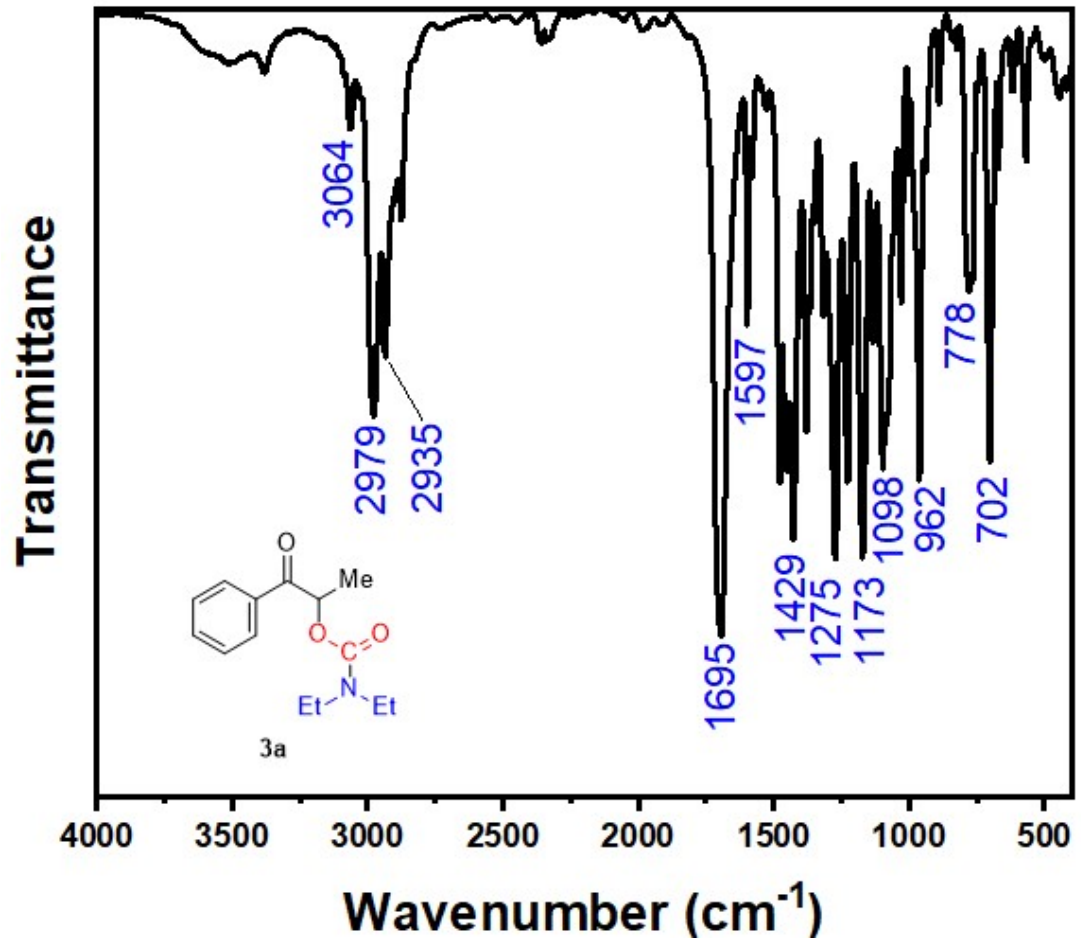
3t

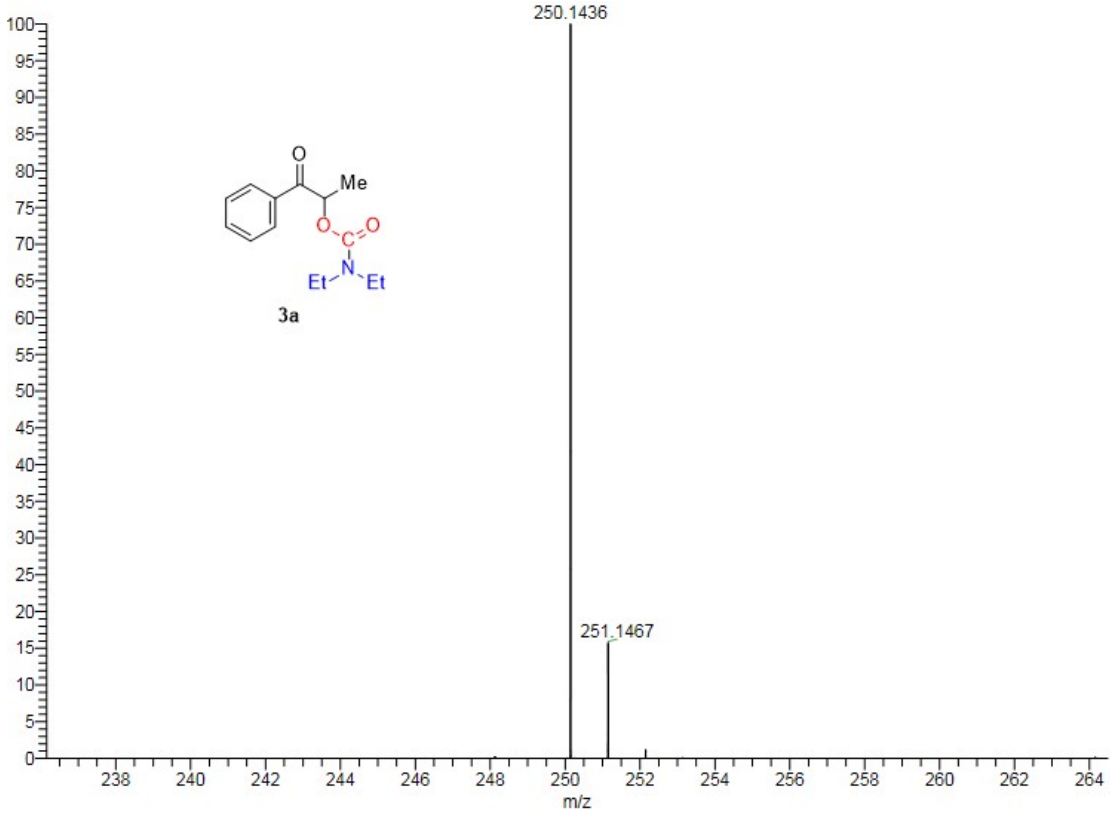
bis(1-oxo-1-phenylpropan-2-yl) piperazine-1,4-dicarboxylate (compound 3t): Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, *J* = 7.7 Hz, 4H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.4 Hz, 4H), 5.95 (q, *J* = 6.9 Hz, 2H), 3.55 (br s, 8H), 1.53 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 154.6, 134.6, 133.6, 128.9, 128.6, 72.4, 44.1, 43.7, 17.4. IR (KBr): 3063, 2987, 2936, 1689, 1596, 1425, 1241, 1102, 1001, 968, 757, 697 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{24}H_{27}N_2O_6$ 439.1869; Found 439.1862.

IV. ^{1}H NMR, ^{13}C NMR Spectra of the Products

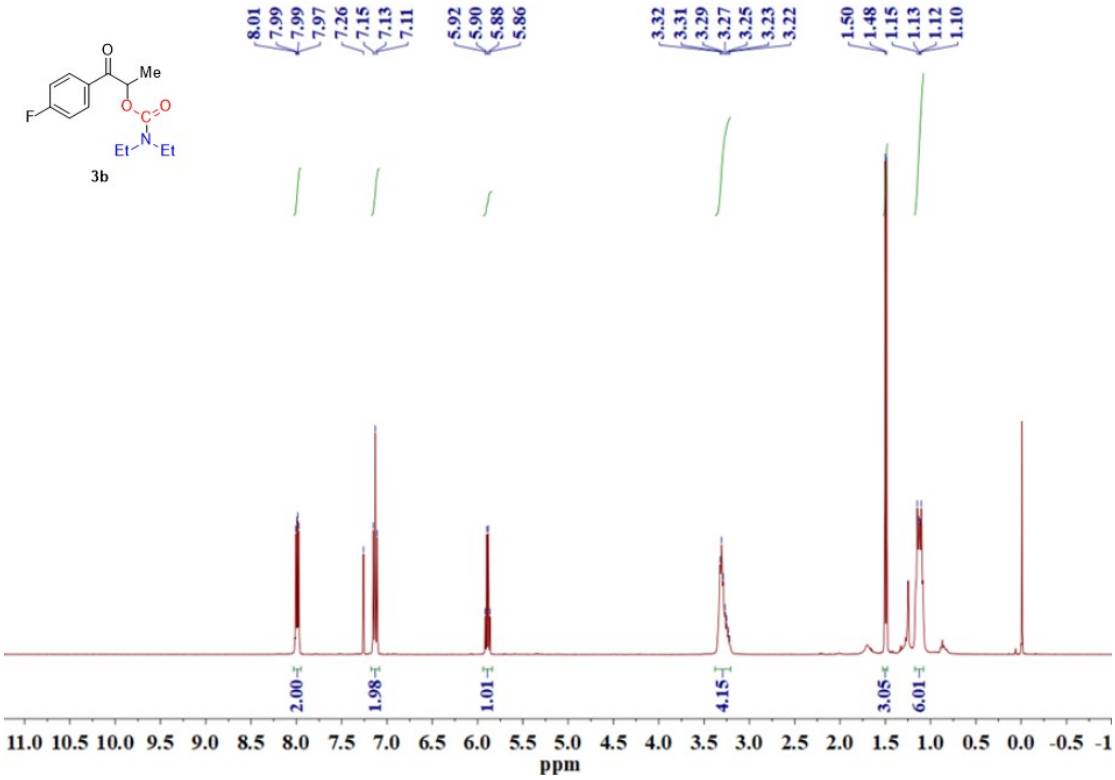


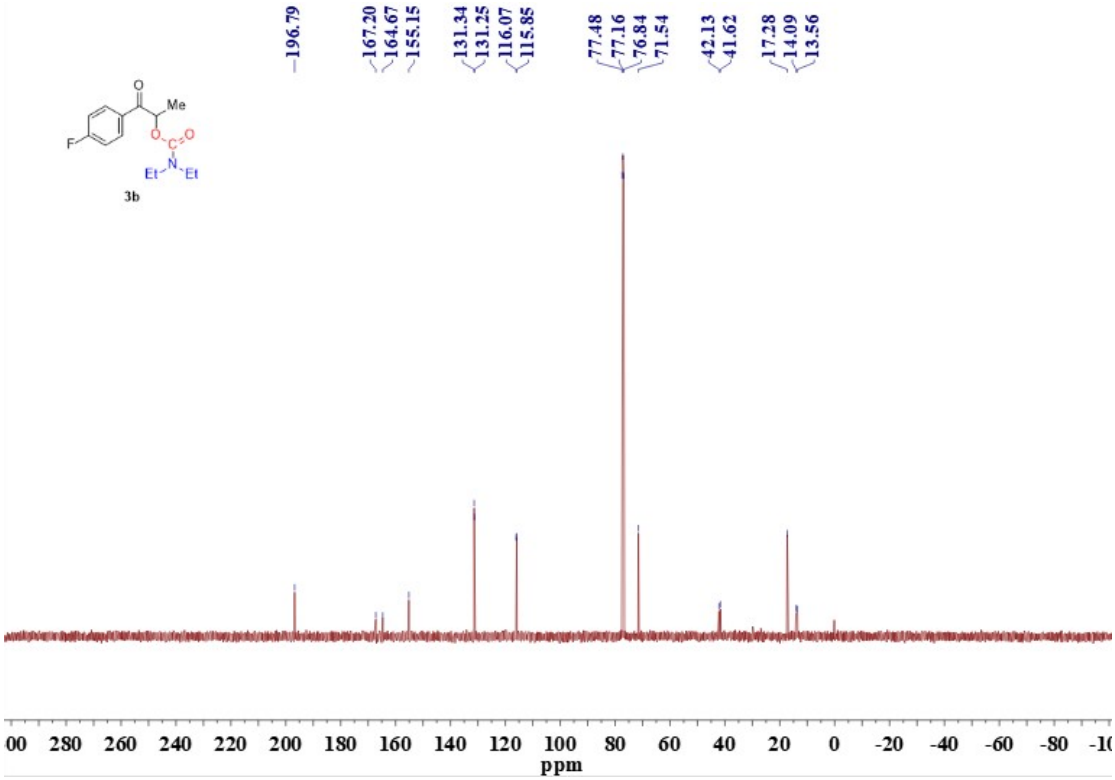


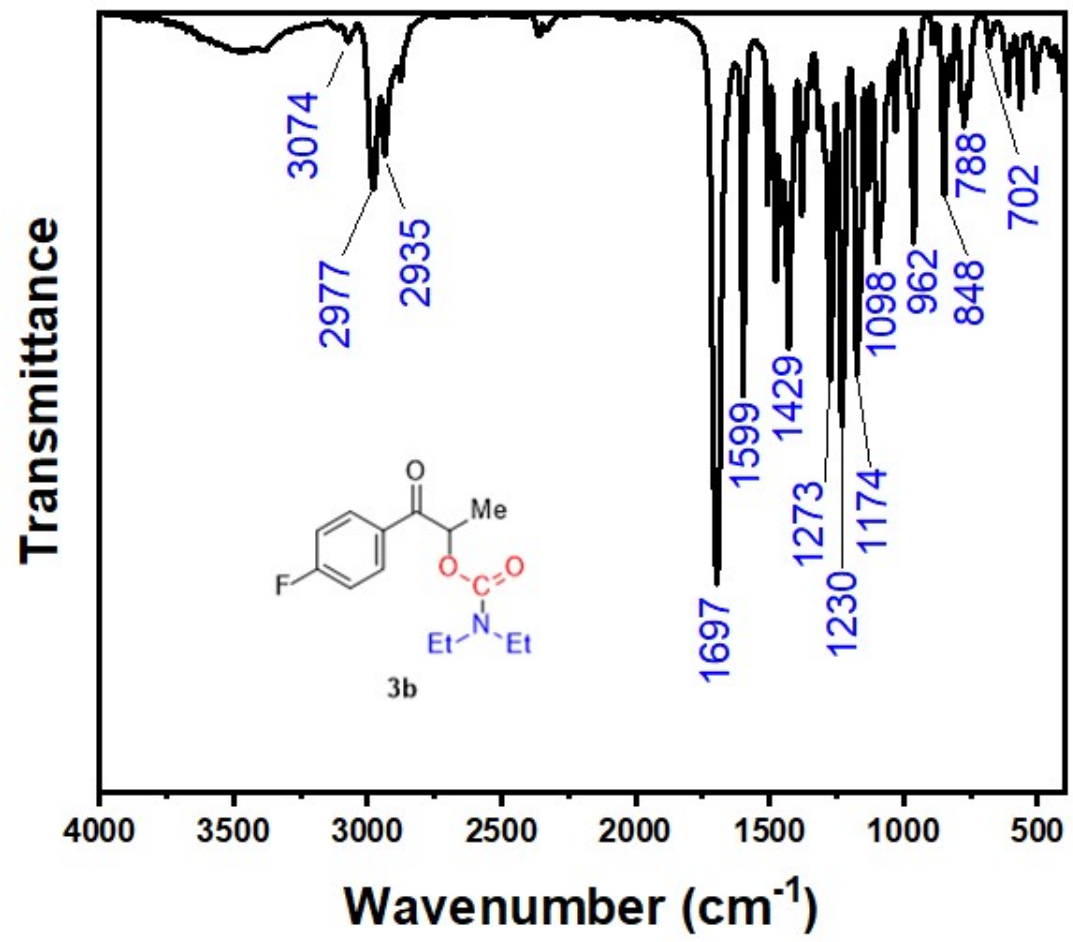


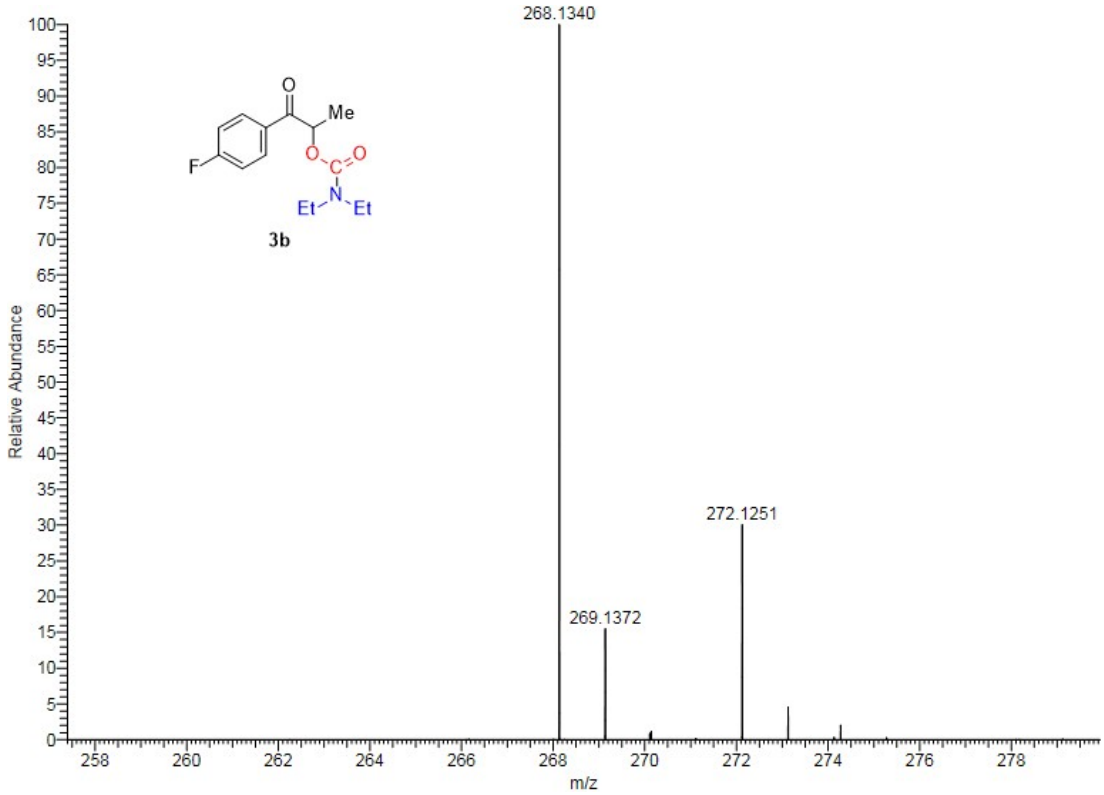


[1]H NMR, [13]C NMR, FT-IR, and HRMS spectra of compound 3a

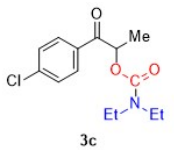

8.01
7.99
7.99
7.97
7.26
7.15
7.13
7.11
5.92
5.90
5.88
5.86
3.32
3.31
3.29
3.27
3.25
3.23
3.22
1.50
1.48
1.15
1.13
1.12
1.10
2.00
1.98
1.01
4.15
3.05
6.01
ppm


196.79
167.20
164.67
155.15
131.34
131.25
116.07
115.85
77.48
77.16
76.84
71.54
42.13
41.62
17.28
14.09
13.56
ppm



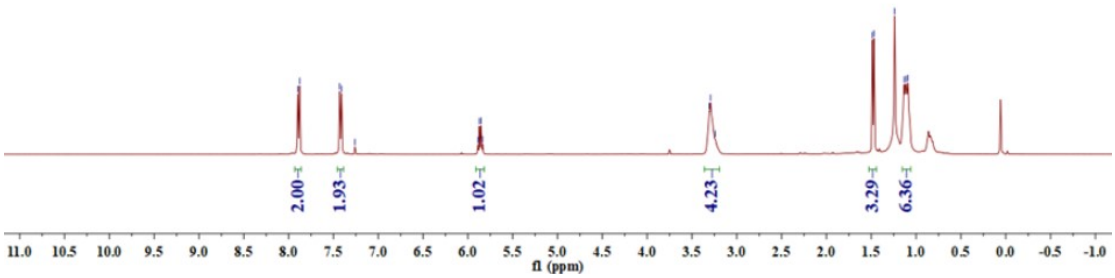


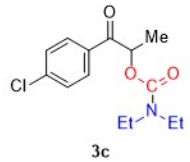
^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3b


O
Me
Cl
O
O
N
Et
Et

3c

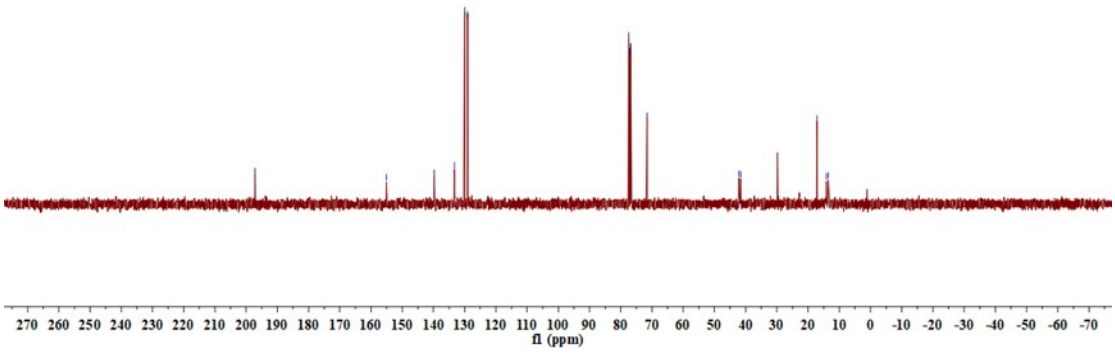

7.90
7.88
7.43
7.41
7.26
5.89
5.87
5.85
5.84
3.31
3.29
3.24
1.49
1.47
1.24
1.13
1.11
1.09

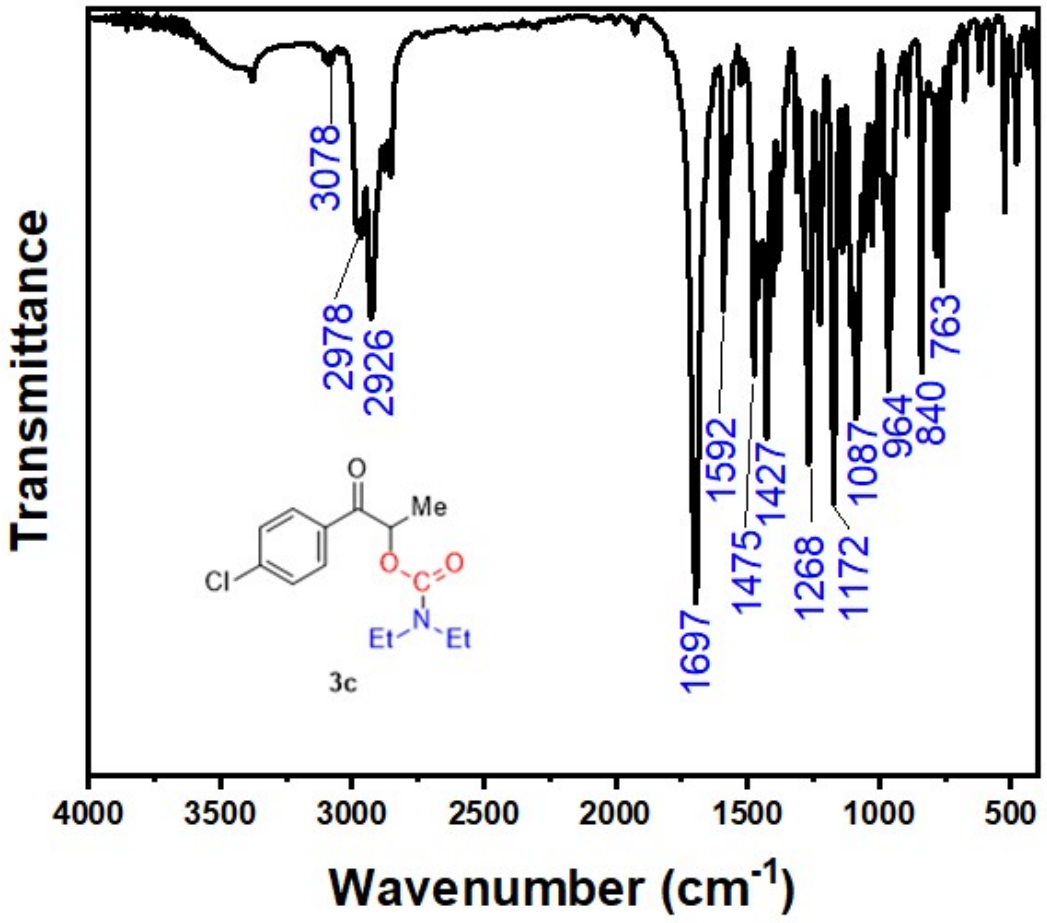

2.00
1.93
1.02
4.23
3.29
6.36
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

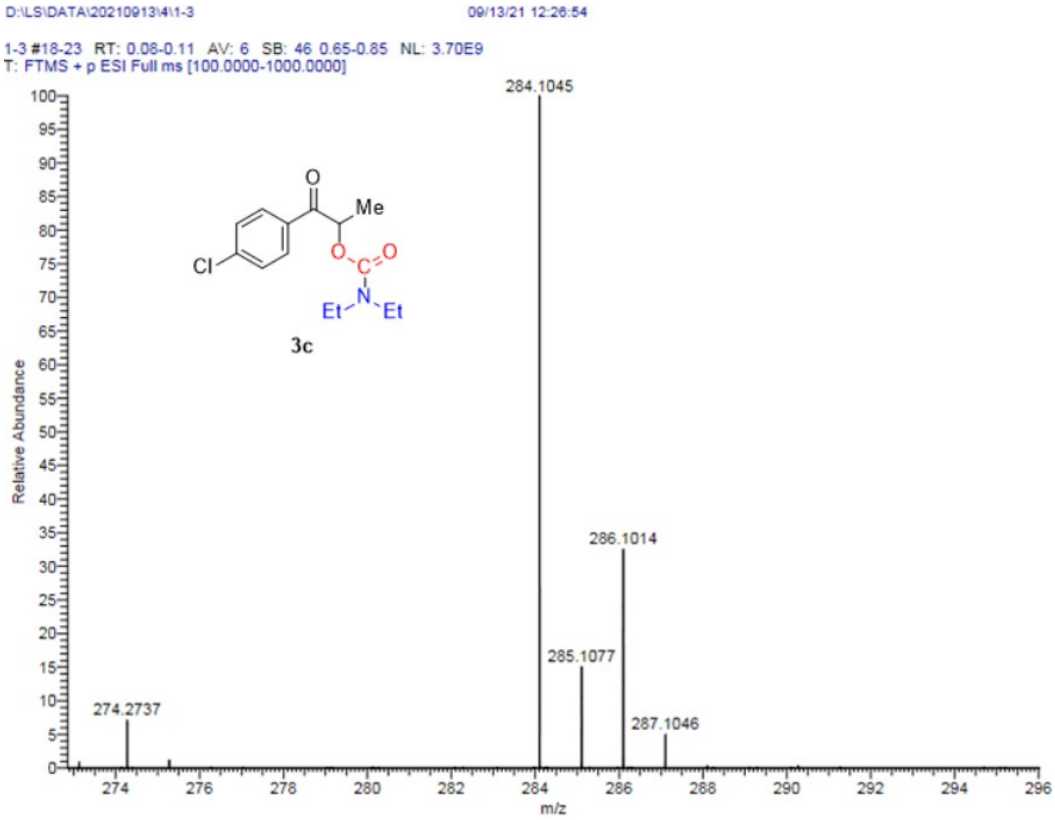

O
Me
Cl
O
O
N
Et
Et

3c

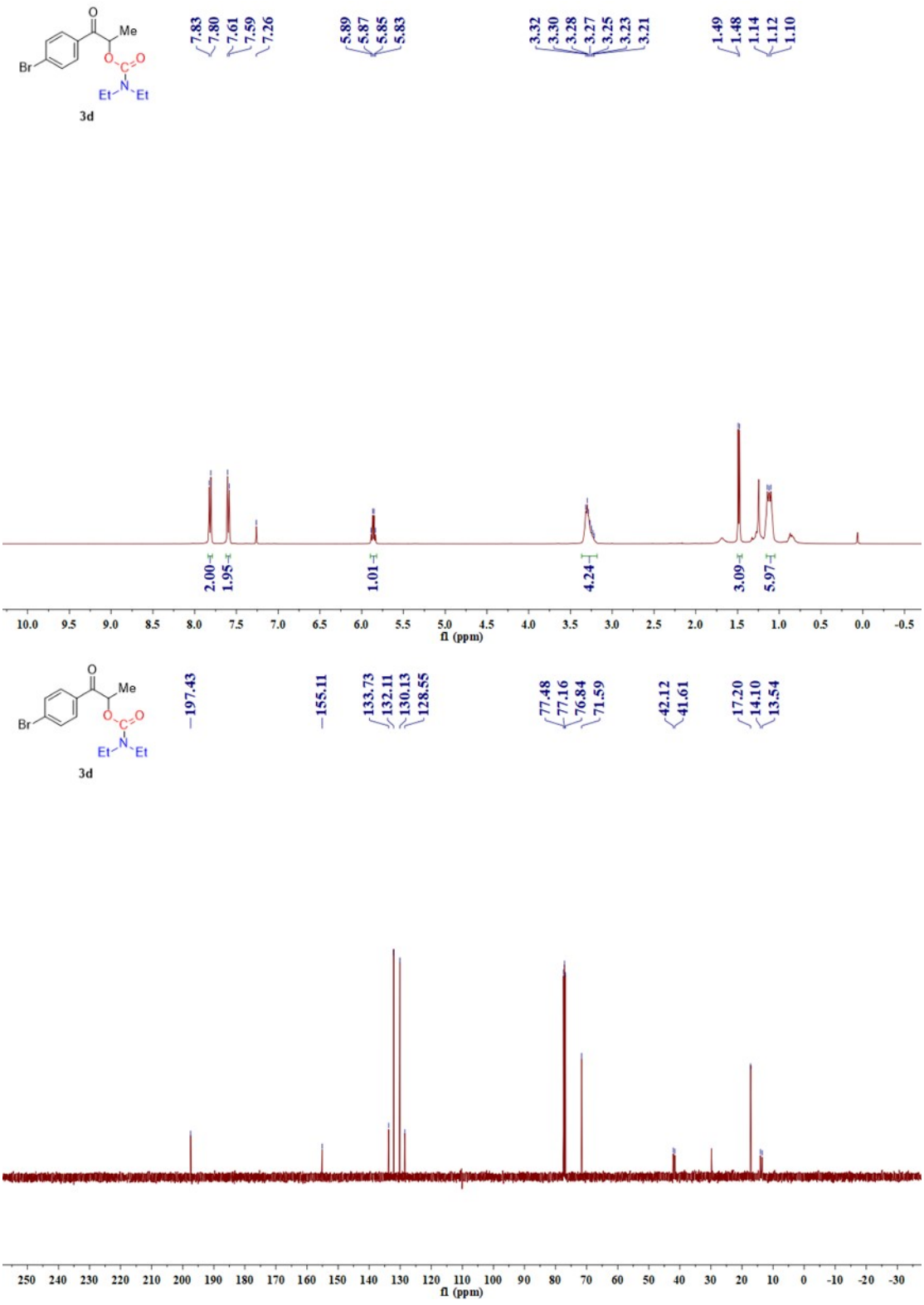

197.15
155.08
139.79
133.32
130.01
129.09
77.48
77.16
76.84
71.58
42.12
41.61
17.18
14.07
13.51

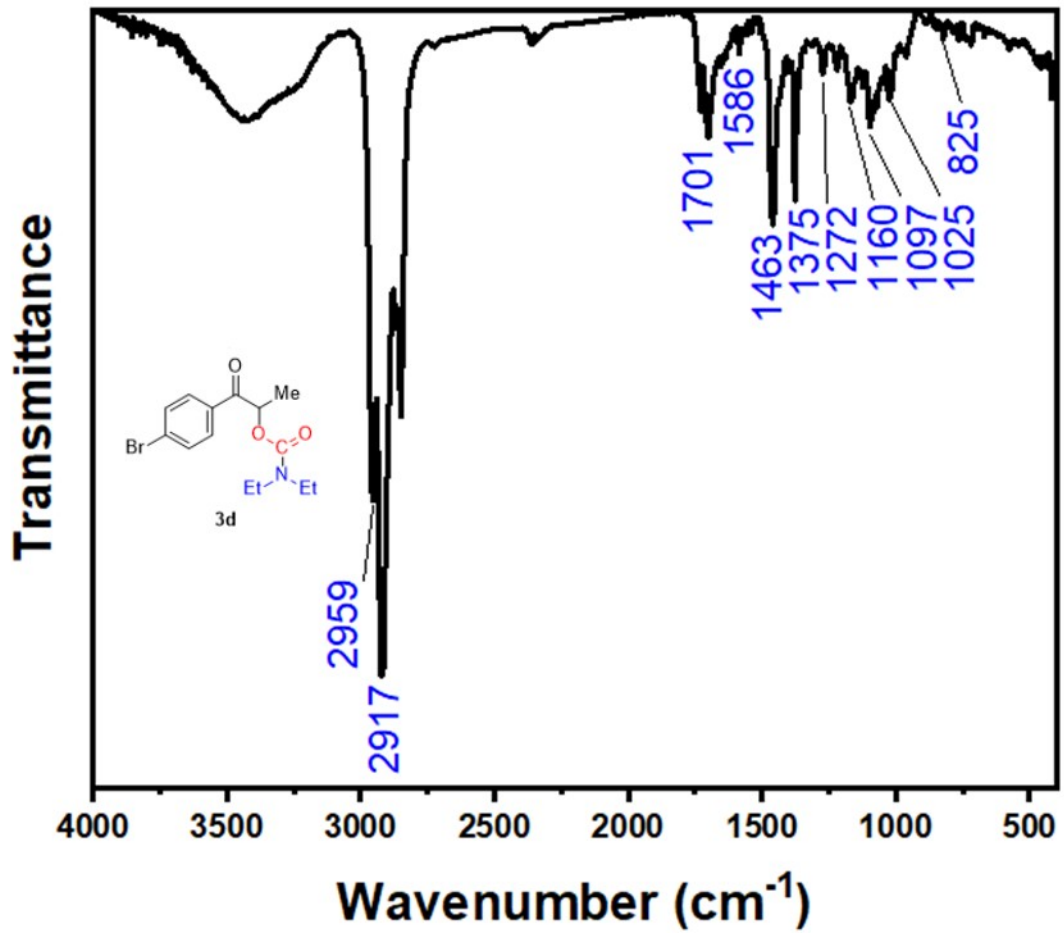

270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

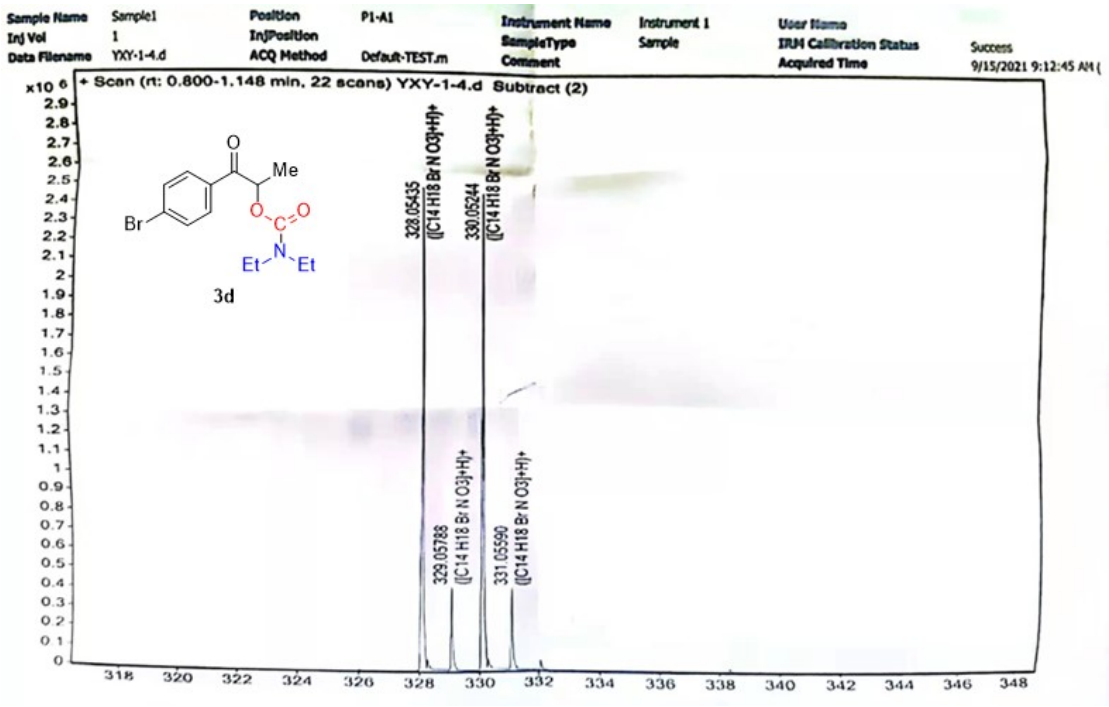




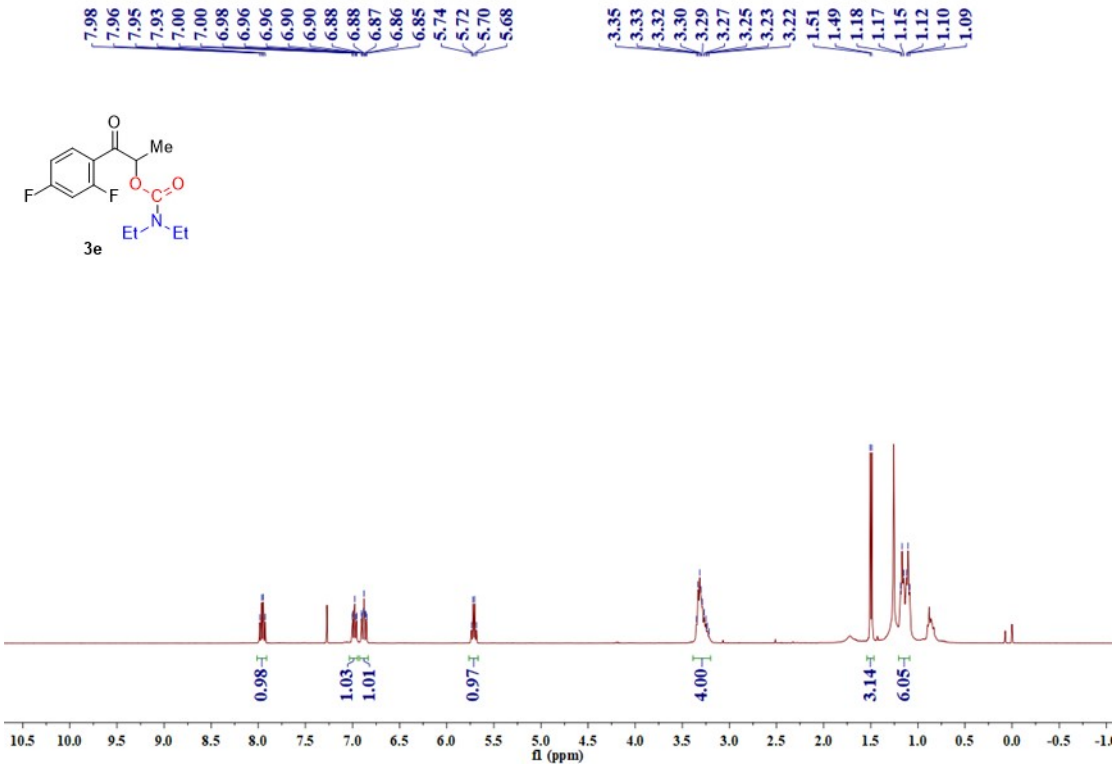
[1]H NMR, [13]C NMR, FT-IR, and HRMS spectra of compound 3c

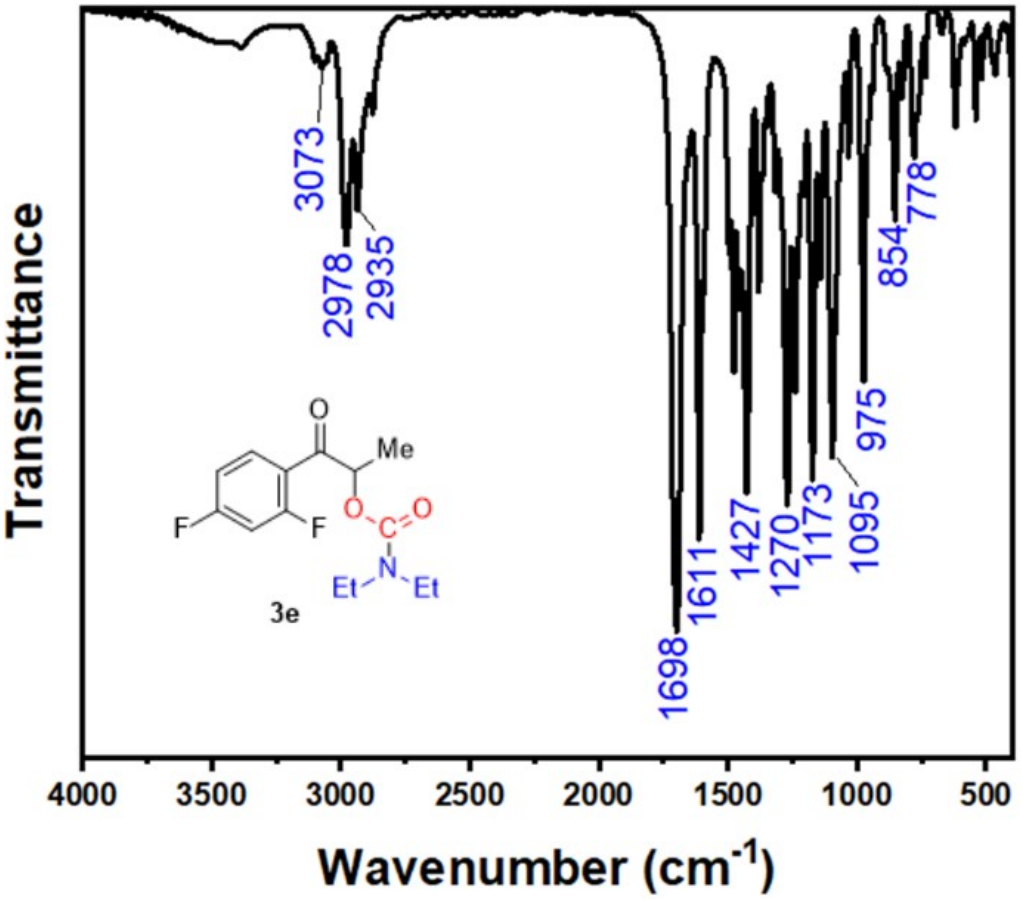

3d
7.83
7.80
7.61
7.59
7.26
5.89
5.87
5.85
5.83
3.32
3.30
3.28
3.27
3.25
3.23
3.21
1.49
1.48
1.14
1.12
1.10
2.00
1.95
1.01
4.24
3.09
5.97
f1 (ppm)
3d
197.43
155.11
133.73
132.11
130.13
128.55
77.48
77.16
76.84
71.59
42.12
41.61
17.20
14.10
13.54
f1 (ppm)

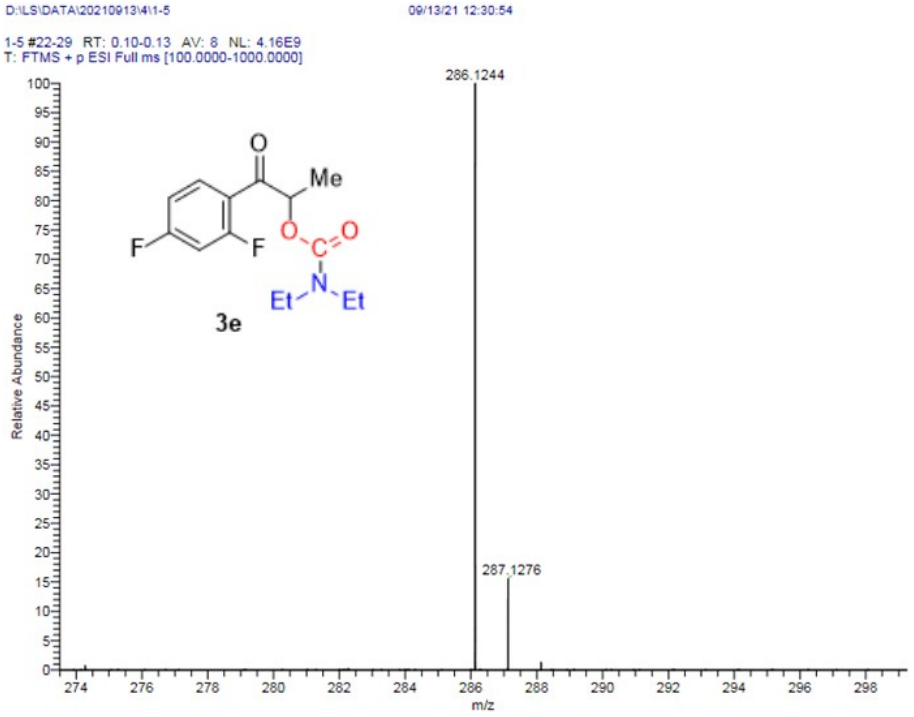




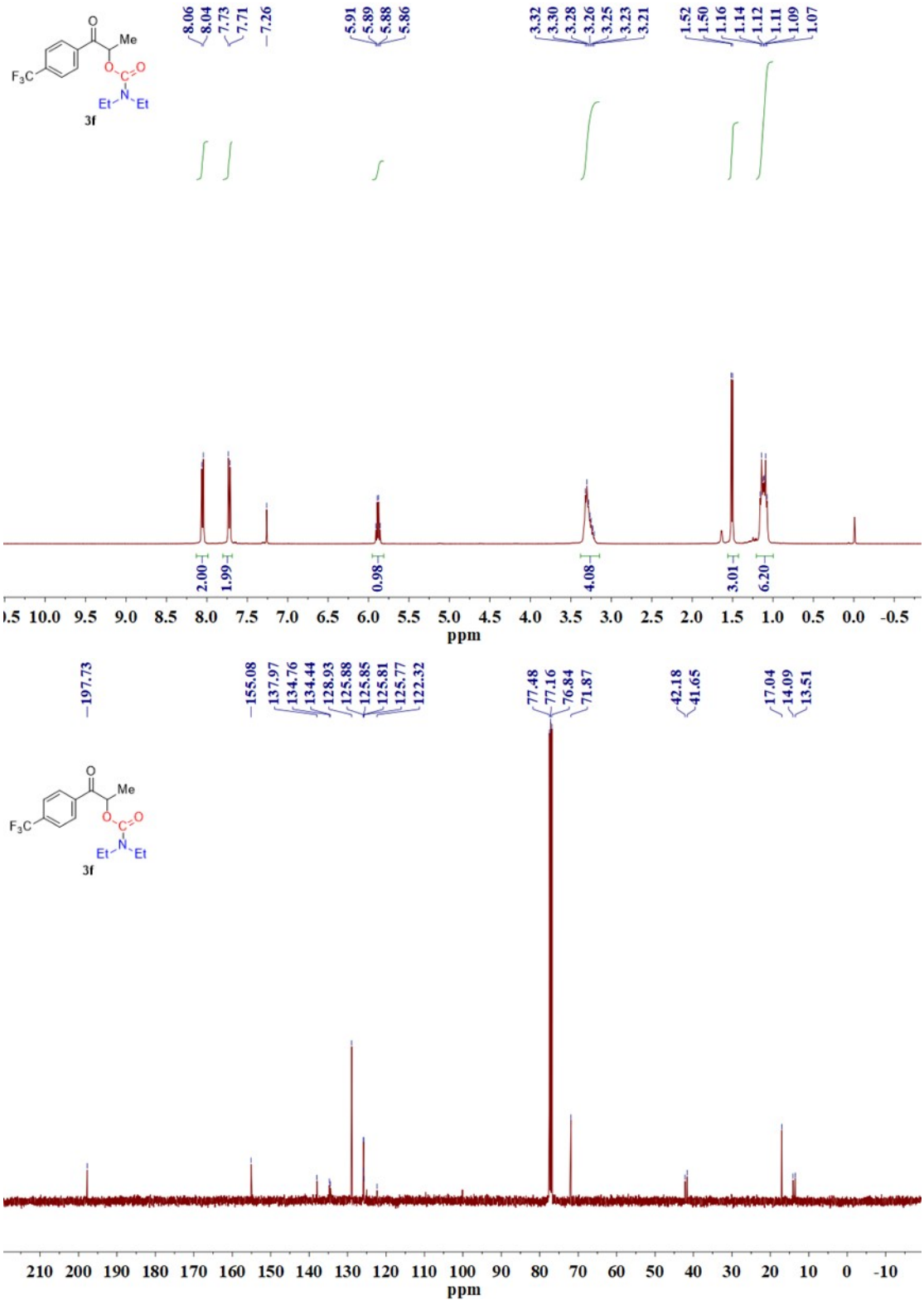
^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3d

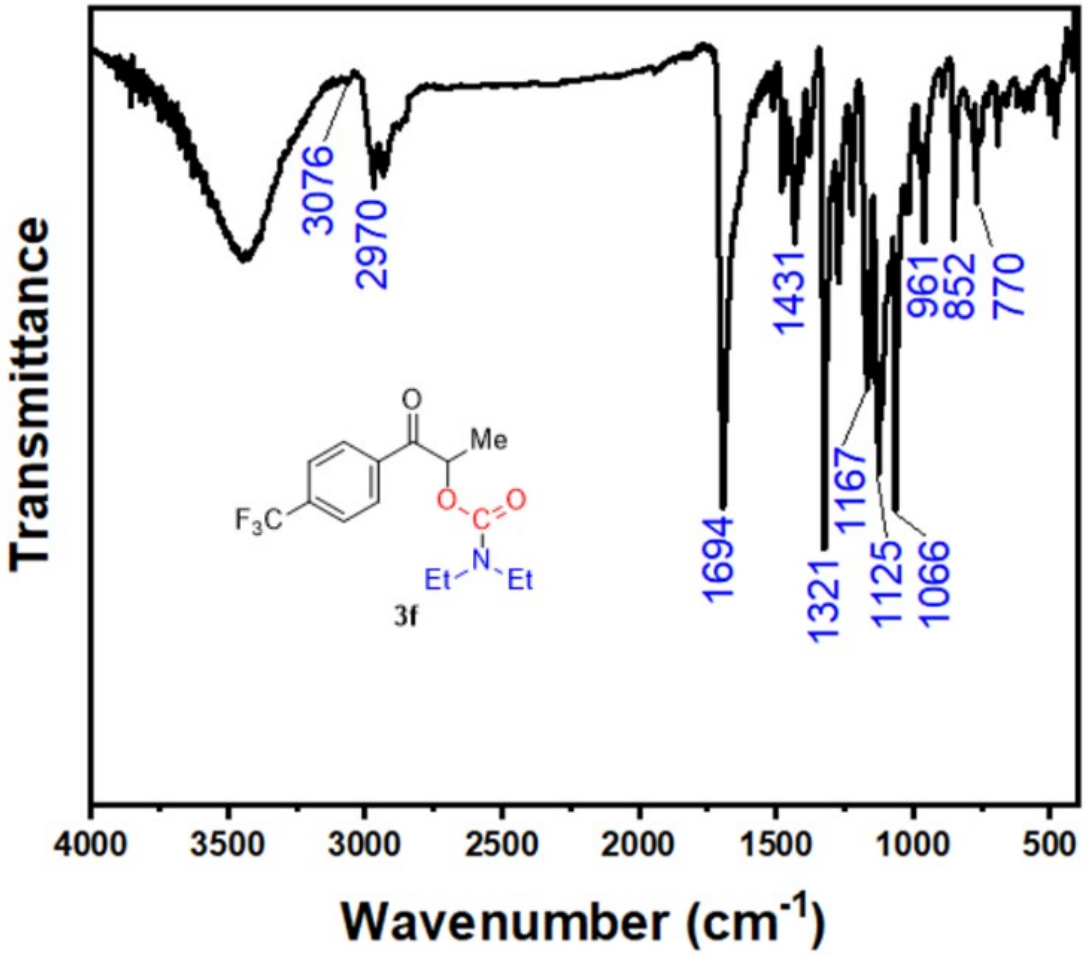

7.98
7.96
7.95
7.93
7.00
7.00
6.98
6.96
6.96
6.90
6.90
6.88
6.88
6.87
6.86
6.85
5.74
5.72
5.70
5.68
3.35
3.33
3.32
3.30
3.29
3.27
3.25
3.23
3.22
1.51
1.49
1.18
1.17
1.15
1.12
1.10
1.09
O
Me
F
F
O
C
O
N
Et
Et
3e
0.98
1.03
1.01
0.97
4.00
3.14
6.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
195.47
195.42
167.39
167.27
164.84
164.71
163.57
163.45
161.02
160.90
155.20
133.38
133.33
133.28
133.23
120.39
120.35
120.24
120.21
112.68
112.64
112.46
112.43
105.04
104.79
104.77
104.51
77.48
77.16
76.84
74.72
74.64
42.07
41.60
16.39
14.05
13.52
O
Me
F
F
O
C
O
N
Et
Et
3e
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

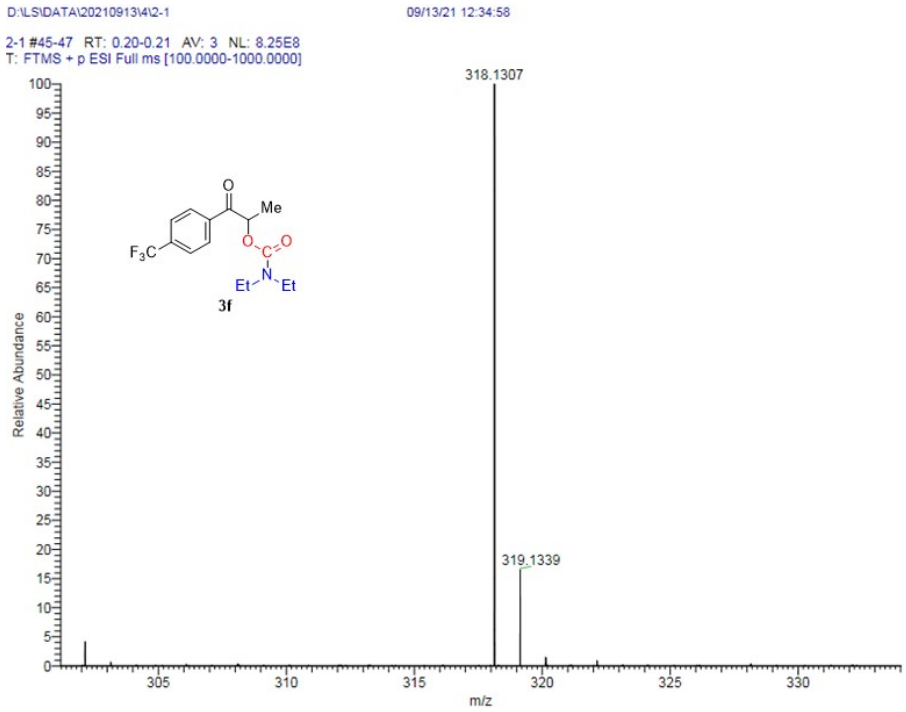




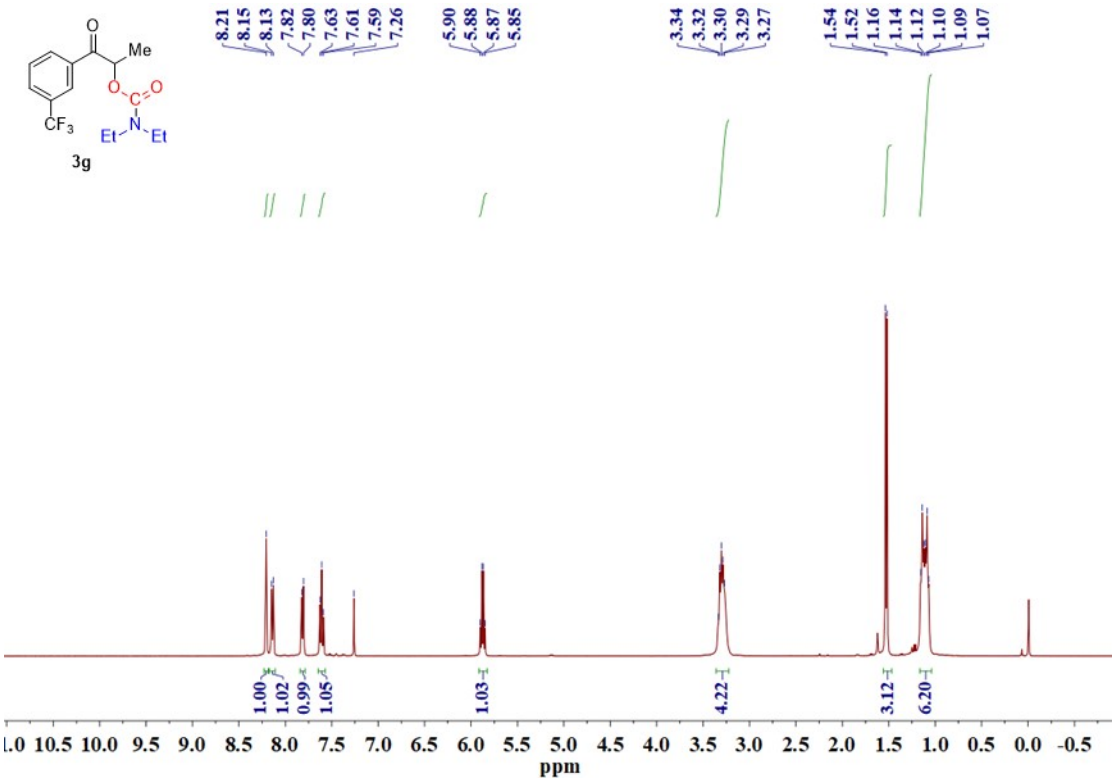
^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3e

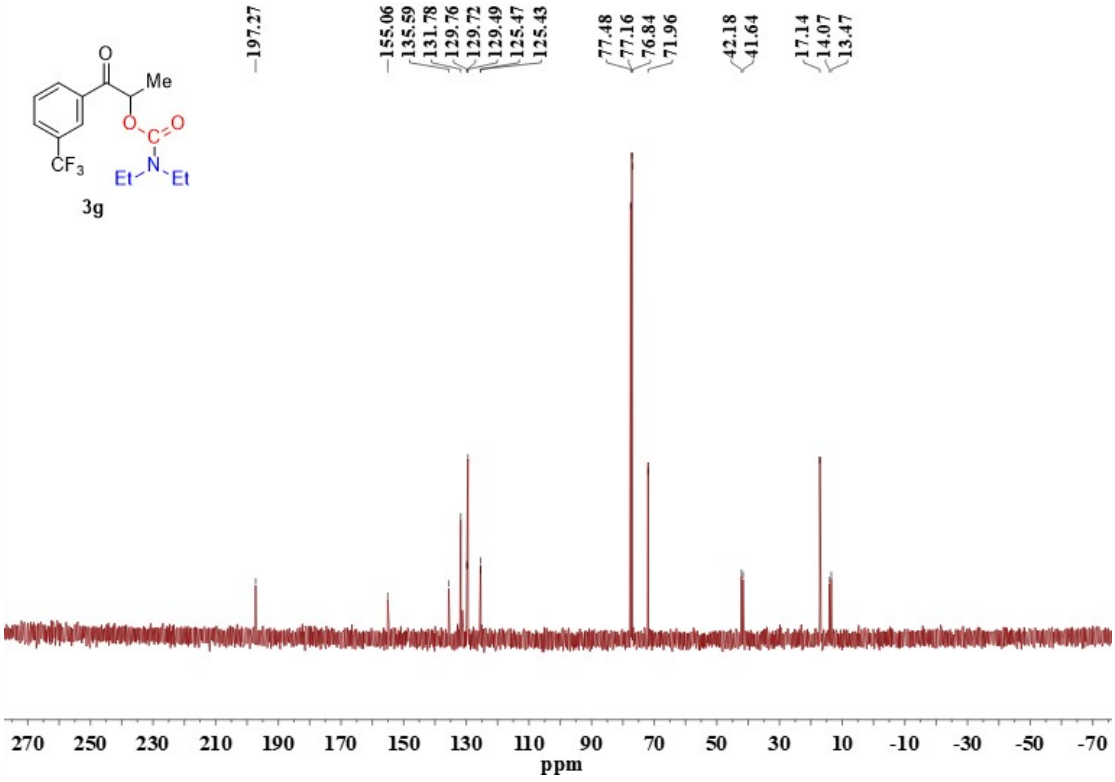

8.06
8.04
7.73
7.71
7.26
5.91
5.89
5.88
5.86
3.32
3.30
3.28
3.26
3.25
3.23
3.21
1.52
1.50
1.16
1.14
1.12
1.11
1.09
1.07
Me
O
F3C
Et
N
Et
3f
2.00
1.99
0.98
4.08
3.01
6.20
ppm
197.73
155.08
137.97
134.76
134.44
128.93
125.88
125.85
125.81
125.77
122.32
77.48
77.16
76.84
71.87
42.18
41.65
17.04
14.09
13.51
ppm

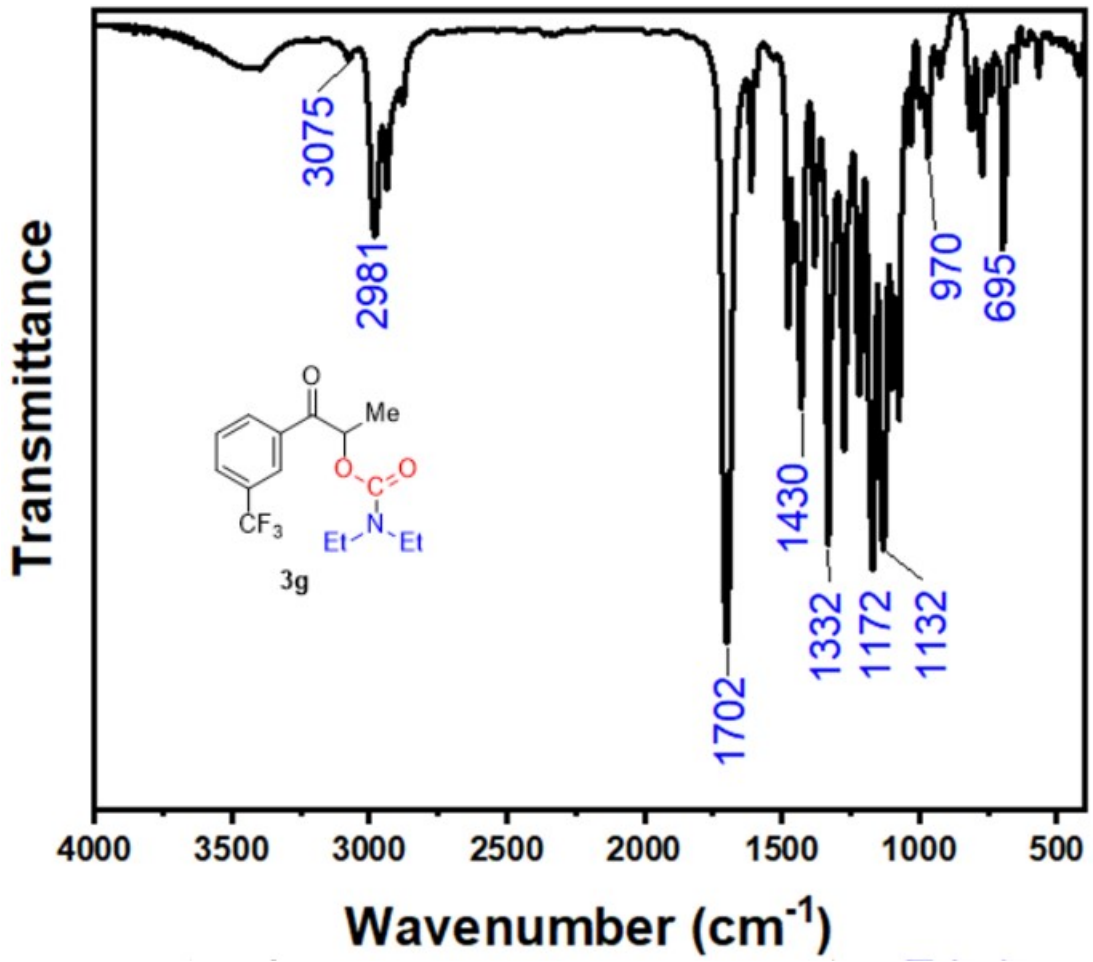


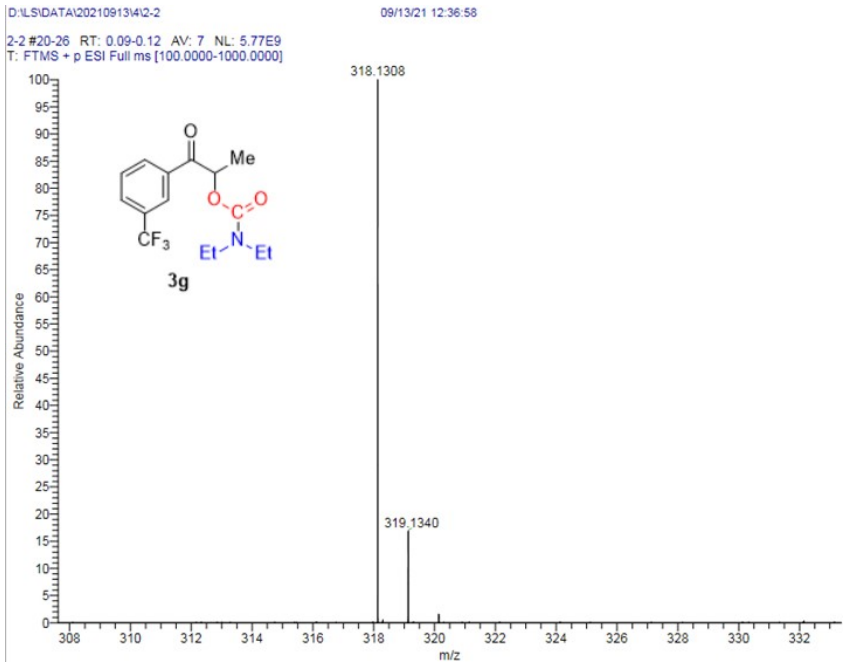


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3f

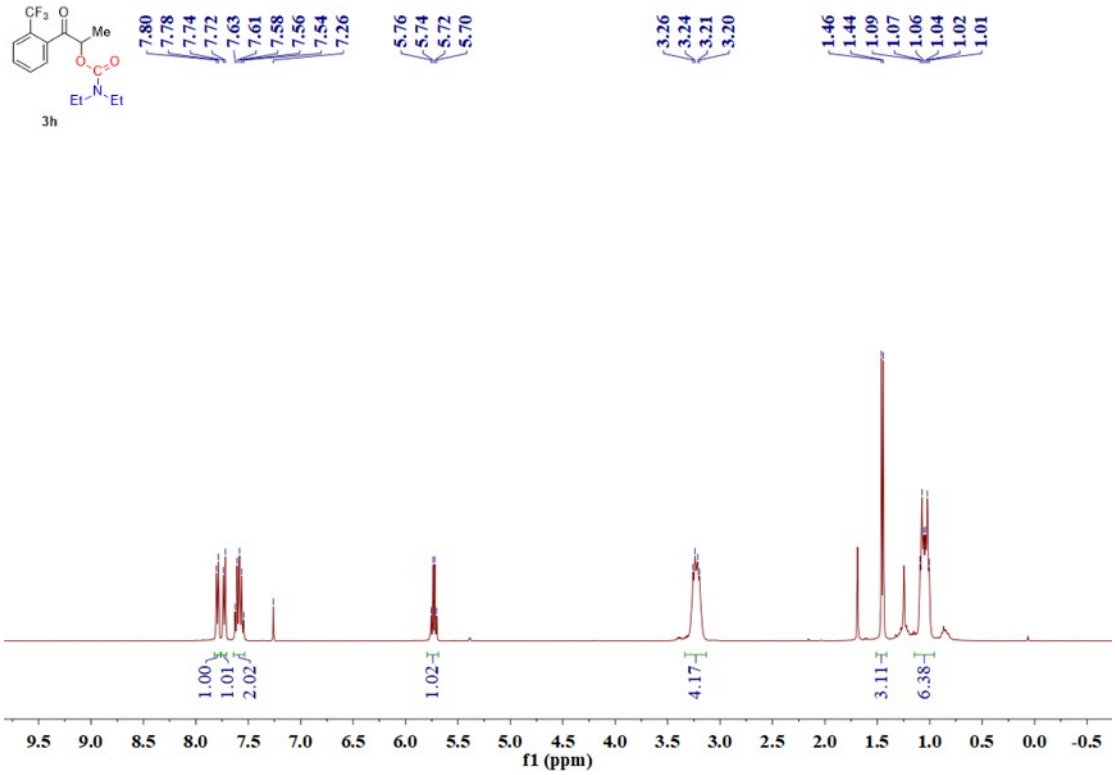

3g
8.21
8.15
8.13
7.82
7.80
7.63
7.61
7.59
7.26
5.90
5.88
5.87
5.85
3.34
3.32
3.30
3.29
3.27
1.54
1.52
1.16
1.14
1.12
1.10
1.09
1.07
1.00
1.02
0.99
1.05
1.03
4.22
3.12
6.20
ppm

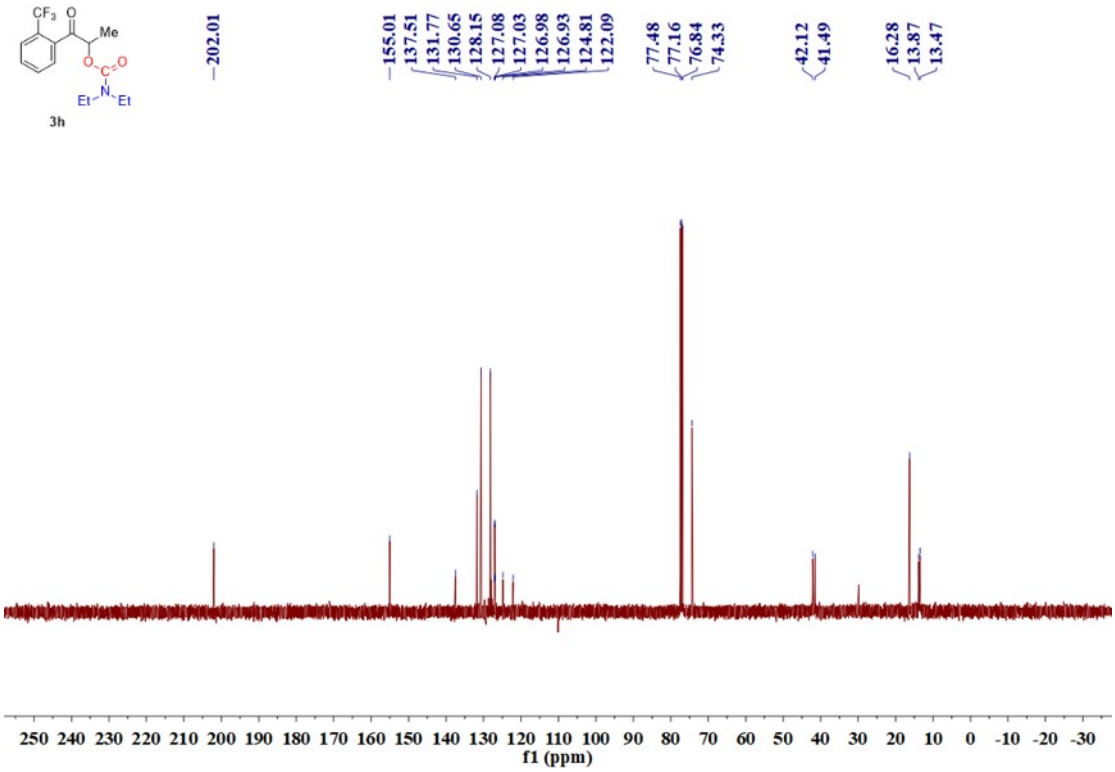

3g
197.27
155.06
135.59
131.78
129.76
129.72
129.49
125.47
125.43
77.48
77.16
76.84
71.96
42.18
41.64
17.14
14.07
13.47
ppm

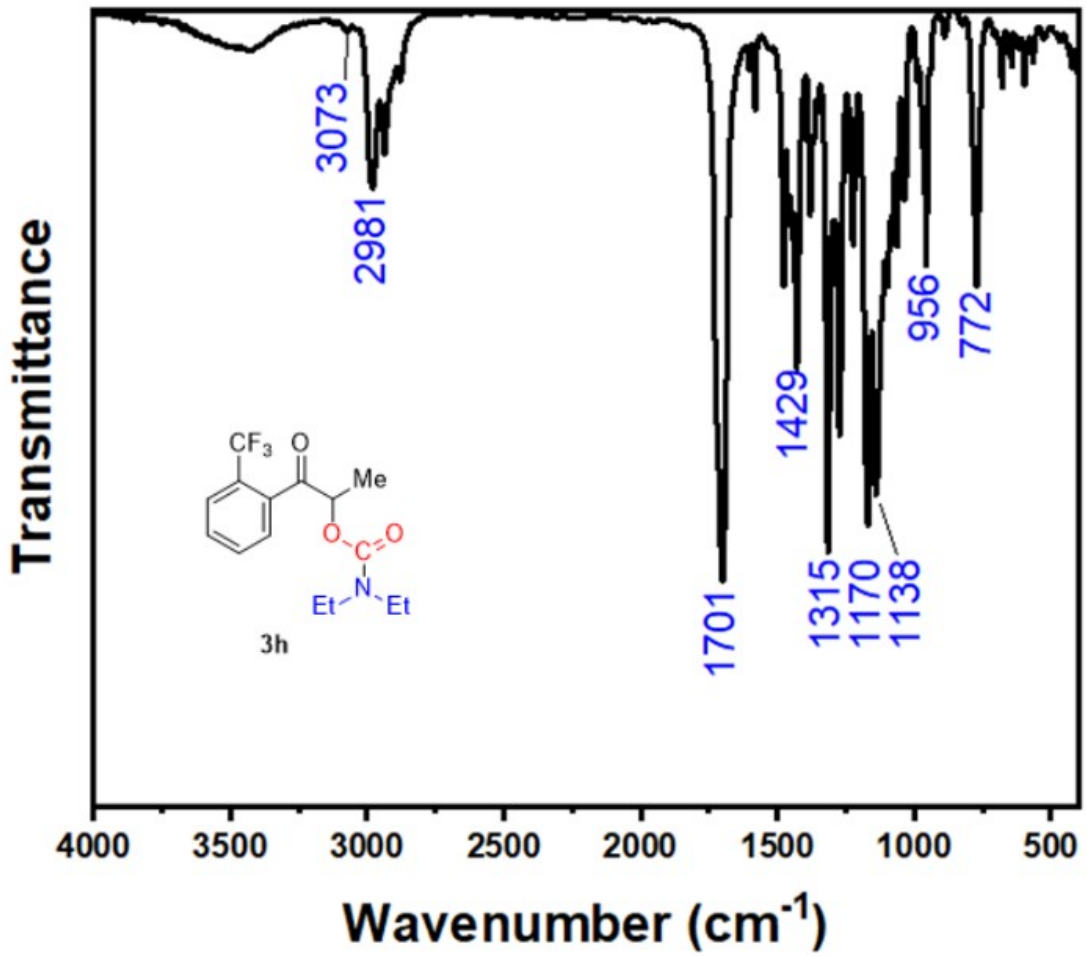


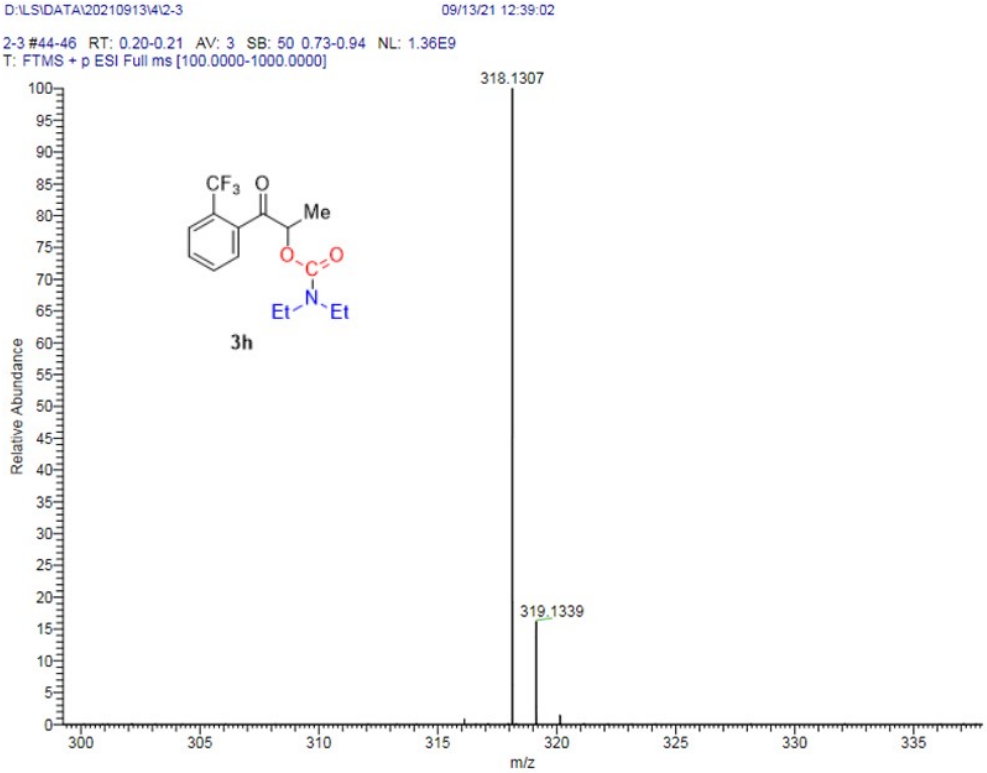


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3g

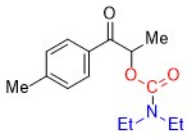

3h
7.80
7.78
7.74
7.72
7.63
7.61
7.58
7.56
7.54
7.26
5.76
5.74
5.72
5.70
3.26
3.24
3.21
3.20
1.46
1.44
1.09
1.07
1.06
1.04
1.02
1.01
1.00
1.01
2.02
1.02
4.17
3.11
6.38
f1 (ppm)


3h
202.01
155.01
137.51
131.77
130.65
128.15
127.08
127.03
126.98
126.93
124.81
122.09
77.48
77.16
76.84
74.33
42.12
41.49
16.28
13.87
13.47
f1 (ppm)

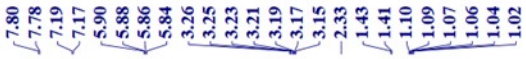


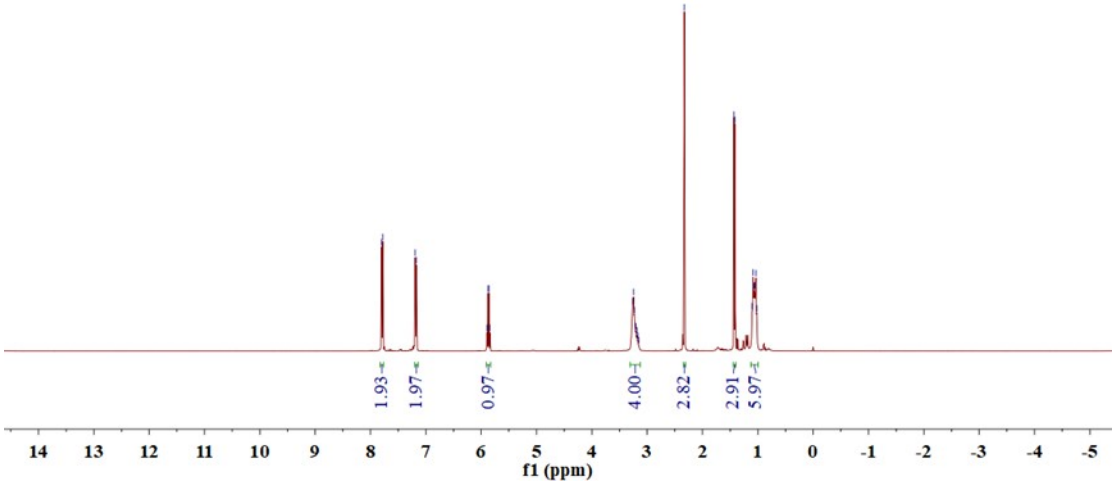


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3h


O
Me
Me
O
C
O
N
Et
Et

3i

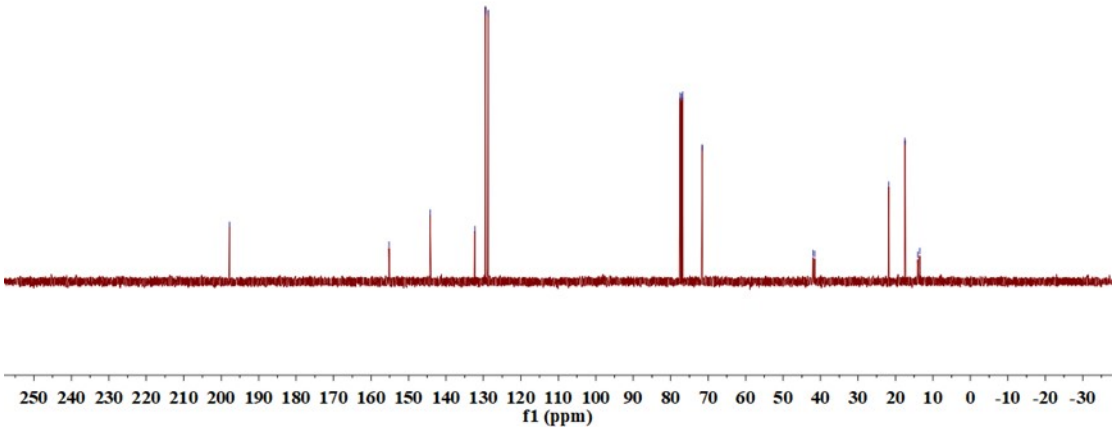

7.80
7.78
7.19
7.17
5.90
5.88
5.86
5.84
3.26
3.25
3.23
3.21
3.19
3.17
3.15
2.33
1.43
1.41
1.10
1.09
1.07
1.06
1.04
1.02

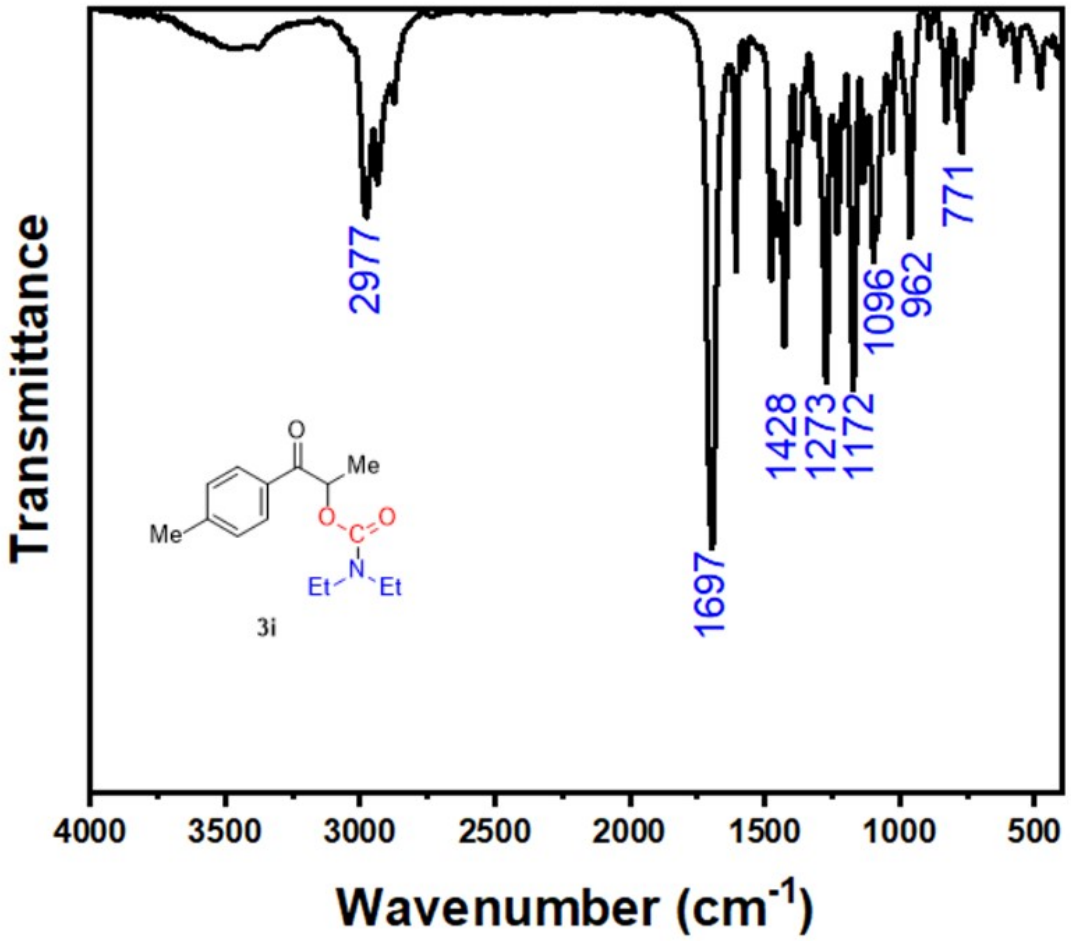

1.93
1.97
0.97
4.00
2.82
2.91
5.97
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)

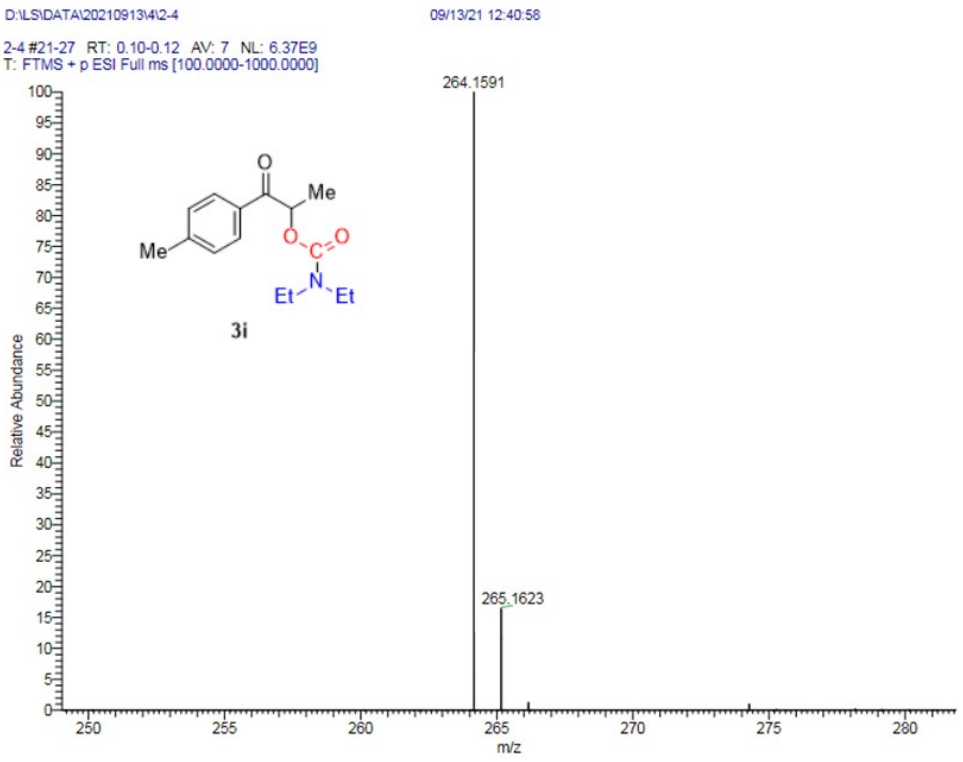

O
Me
Me
O
C
O
N
Et
Et

3i

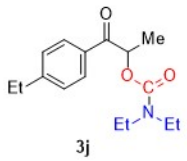

197.79
155.20
144.24
132.31
129.44
128.72
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.56
42.03
41.56
21.79
17.45
14.06
13.55


250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)



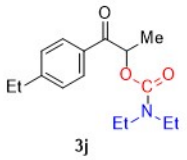


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3i


O
Me
Et
O
C
O
N
Et
Et

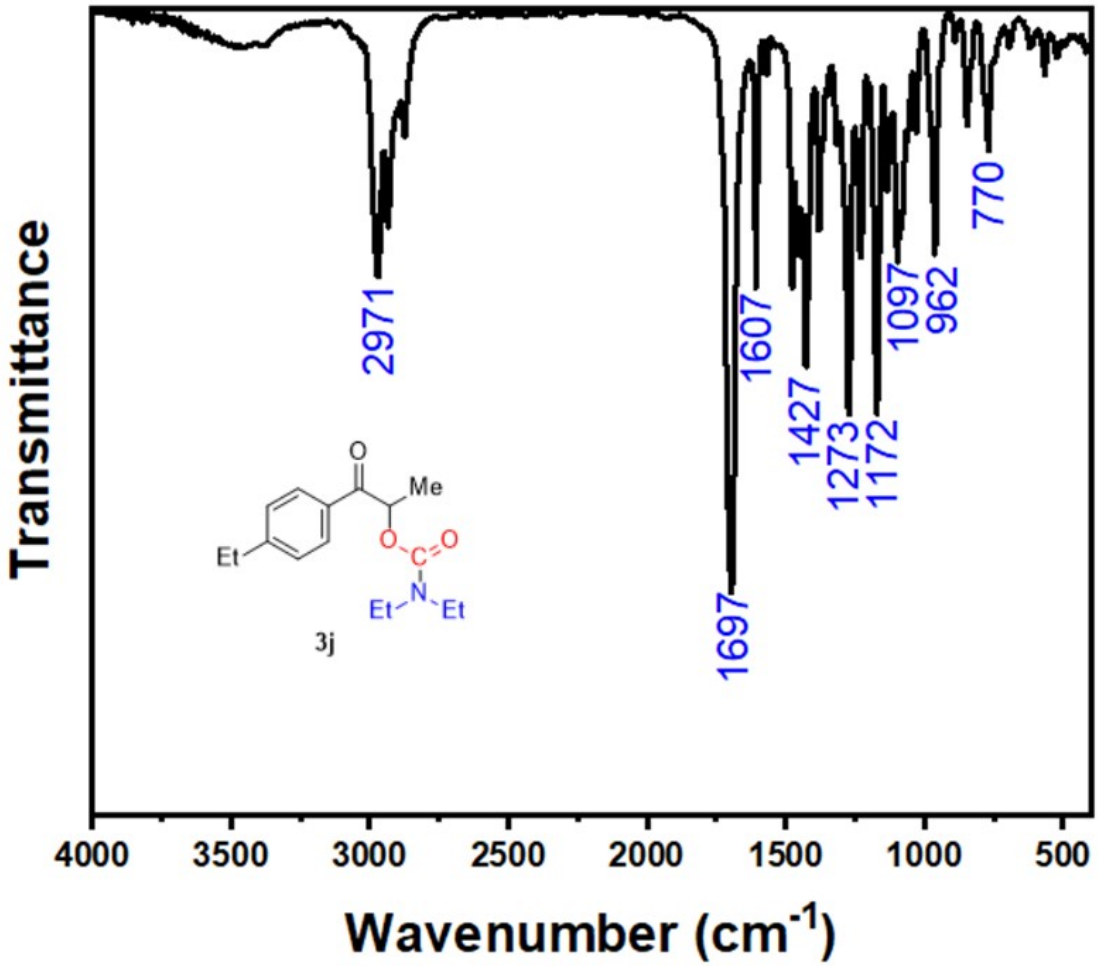
3j

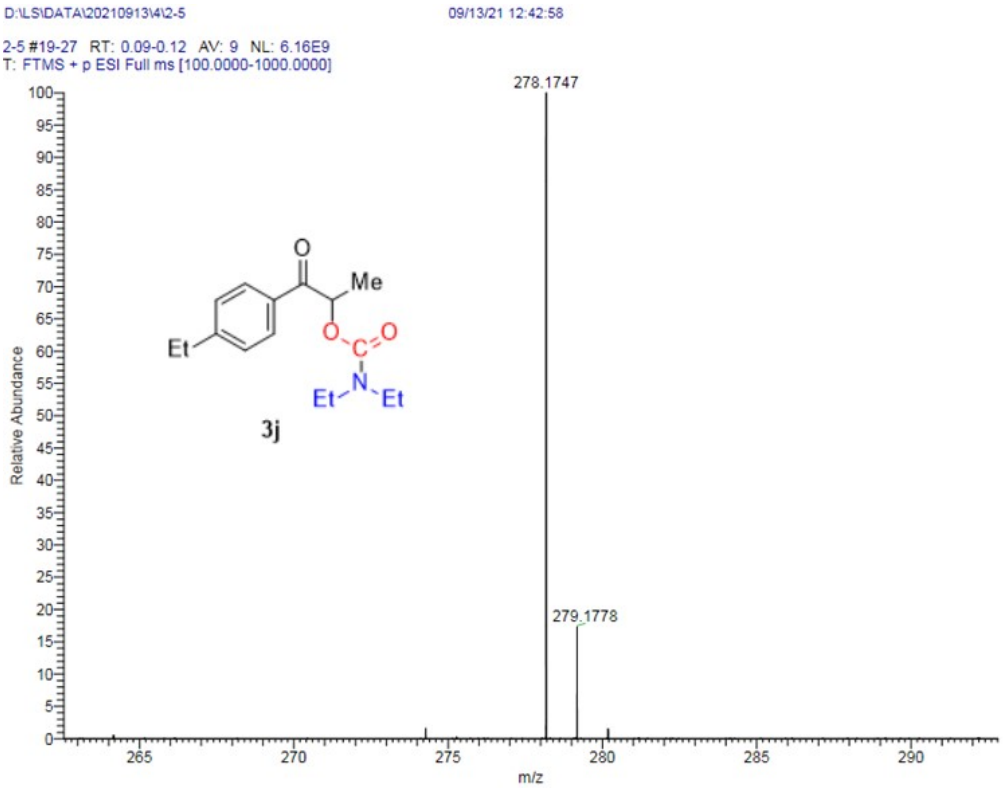
7.82
7.81
7.21
7.19
5.90
5.88
5.86
5.85
3.25
3.20
3.17
2.65
2.63
2.61
2.59
1.43
1.41
1.19
1.17
1.15
1.08
1.07
1.05
1.03
1.95
2.00
0.98
4.05
2.04
3.01
3.51
6.14
f1 (ppm)


O
Me
Et
O
C
O
N
Et
Et

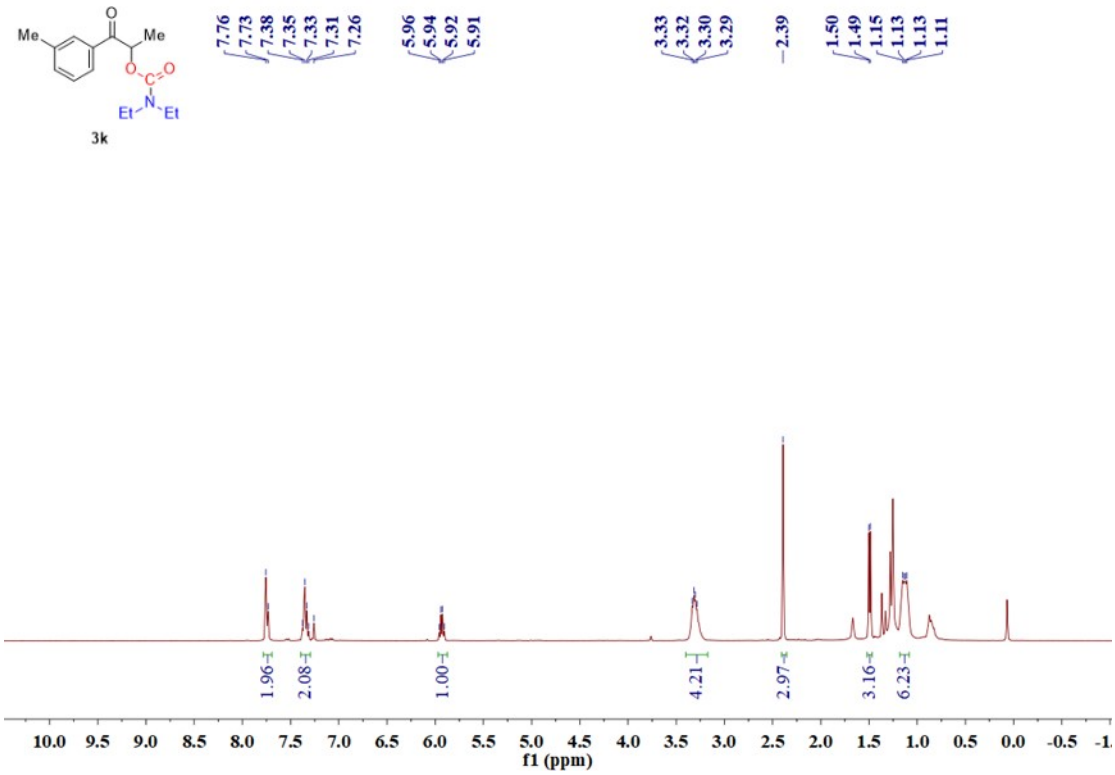
3j

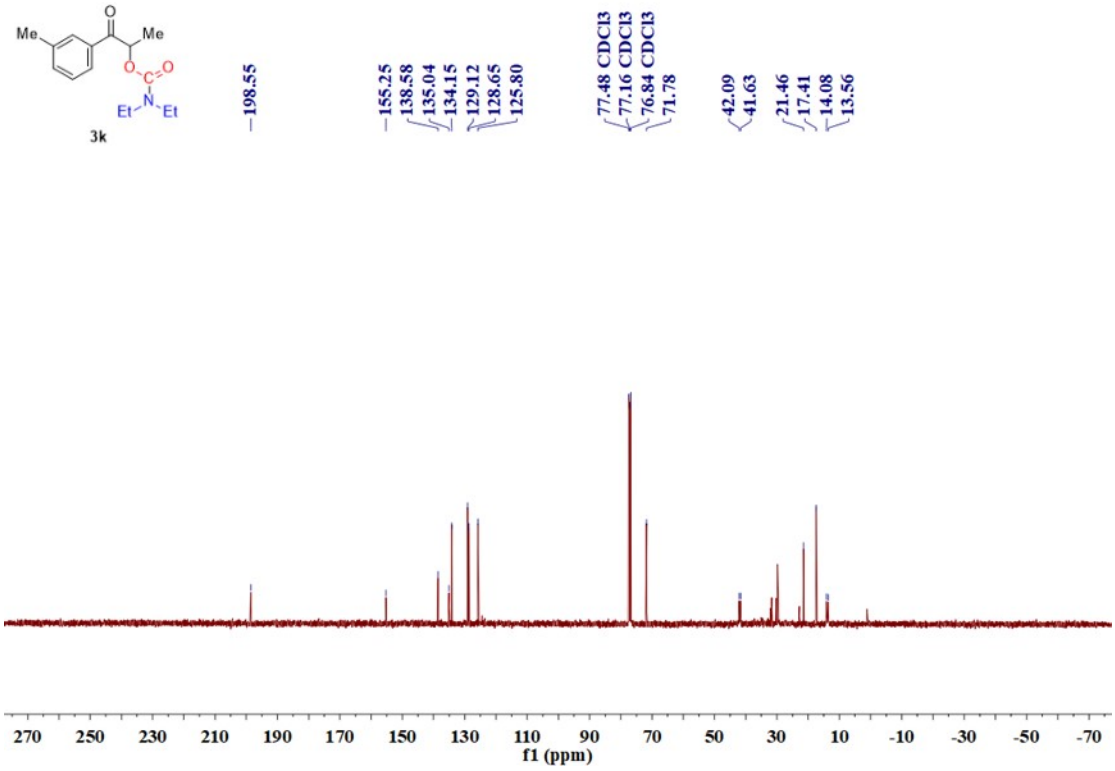
197.81
155.18
150.38
132.50
128.80
128.25
77.48
77.16
76.84
71.54
42.01
41.55
29.06
17.43
15.28
14.03
13.52
f1 (ppm)

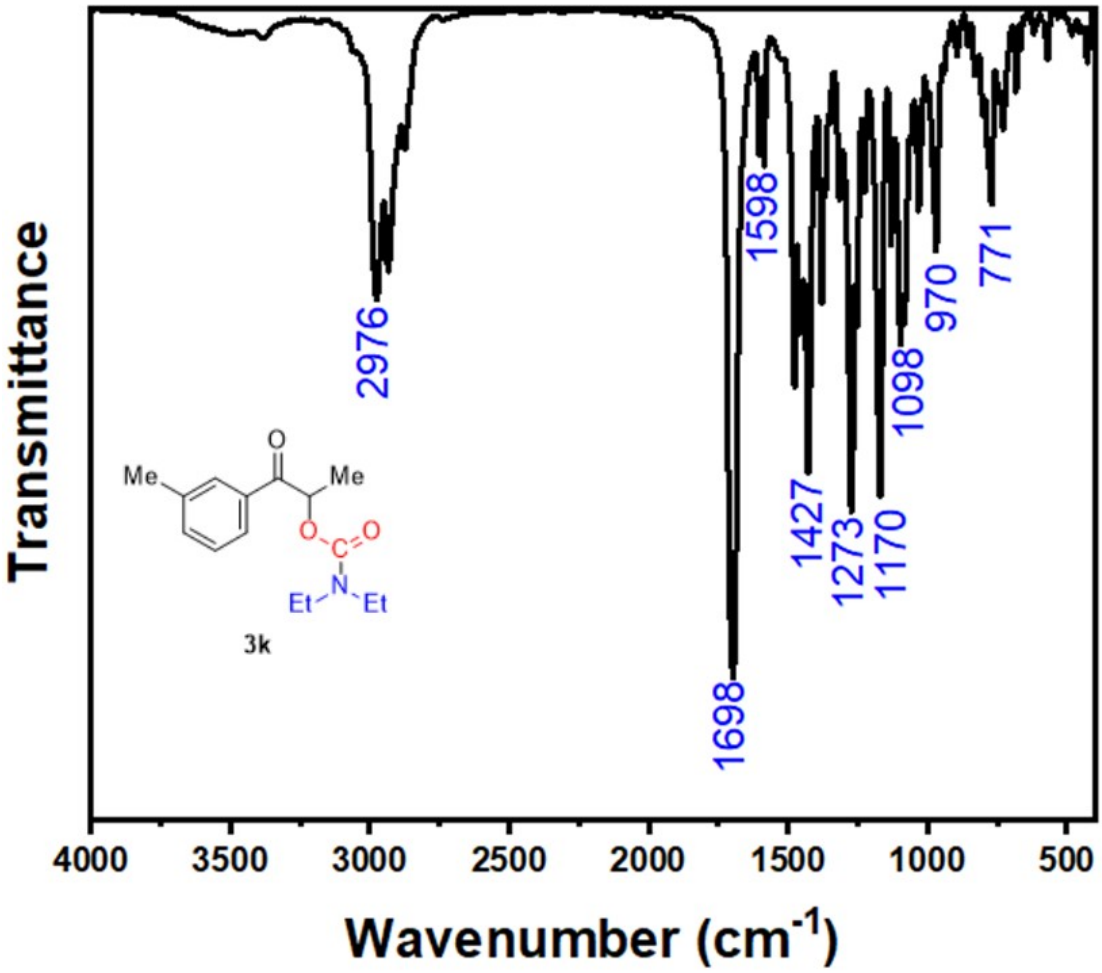


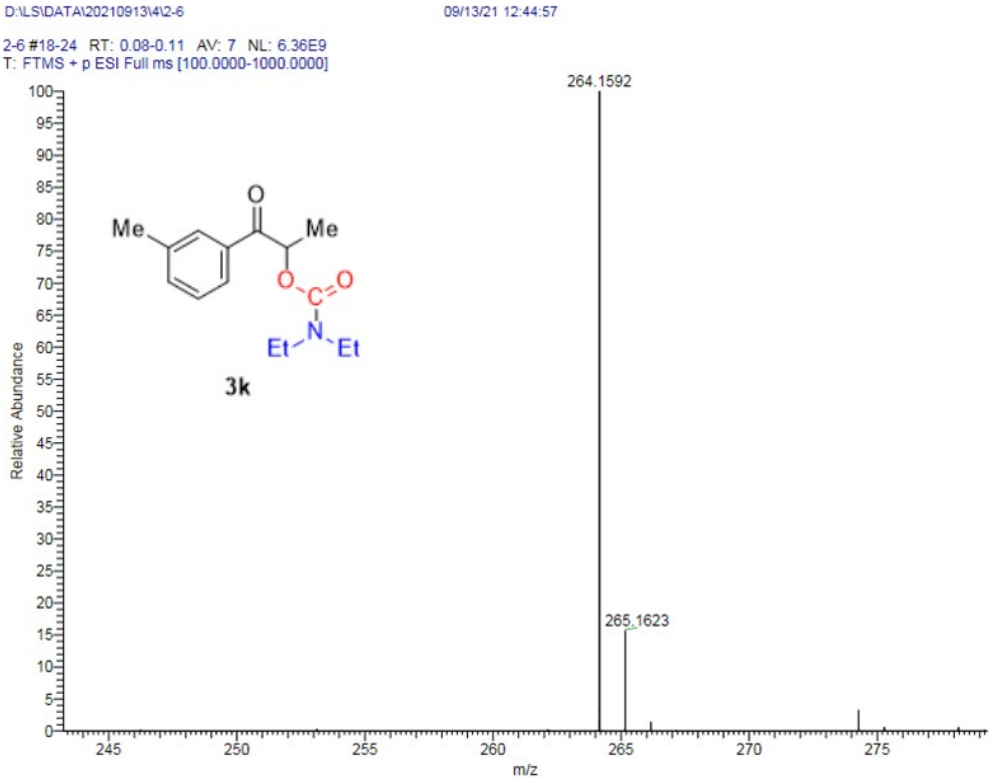


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3j

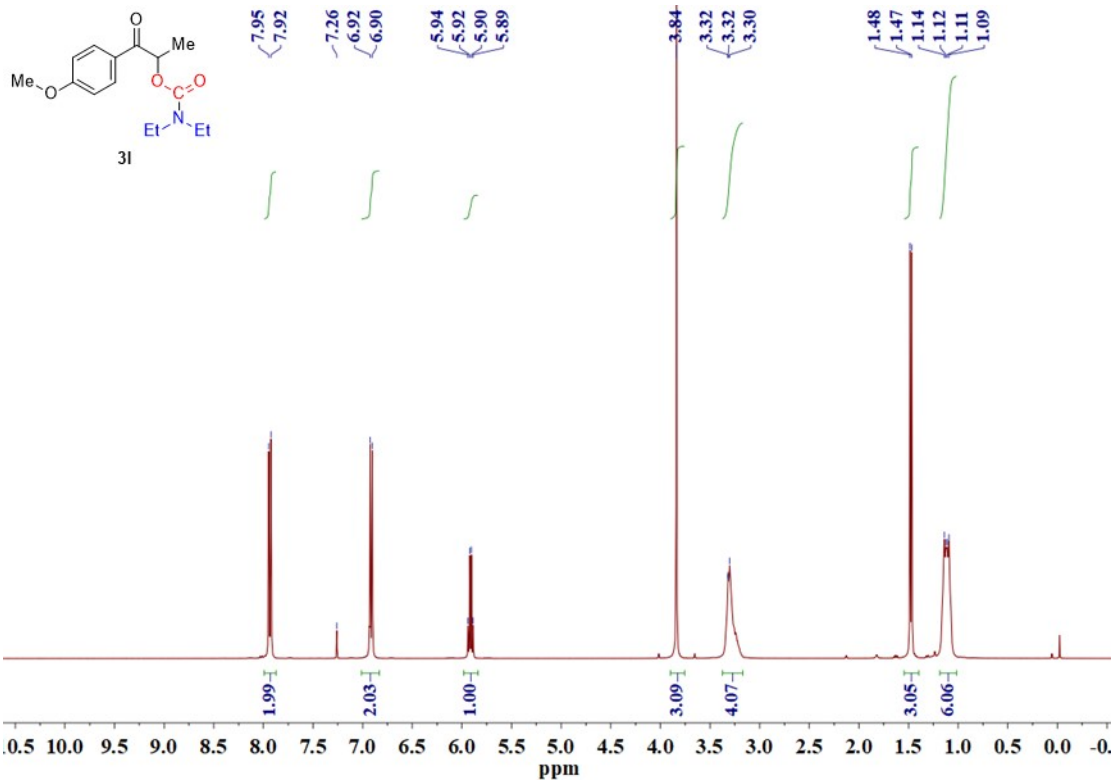

3k
7.76
7.73
7.38
7.35
7.33
7.31
7.26
5.96
5.94
5.92
5.91
3.33
3.32
3.30
3.29
2.39
1.50
1.49
1.15
1.13
1.13
1.11
1.96
2.08
1.00
4.21
2.97
3.16
6.23
f1 (ppm)

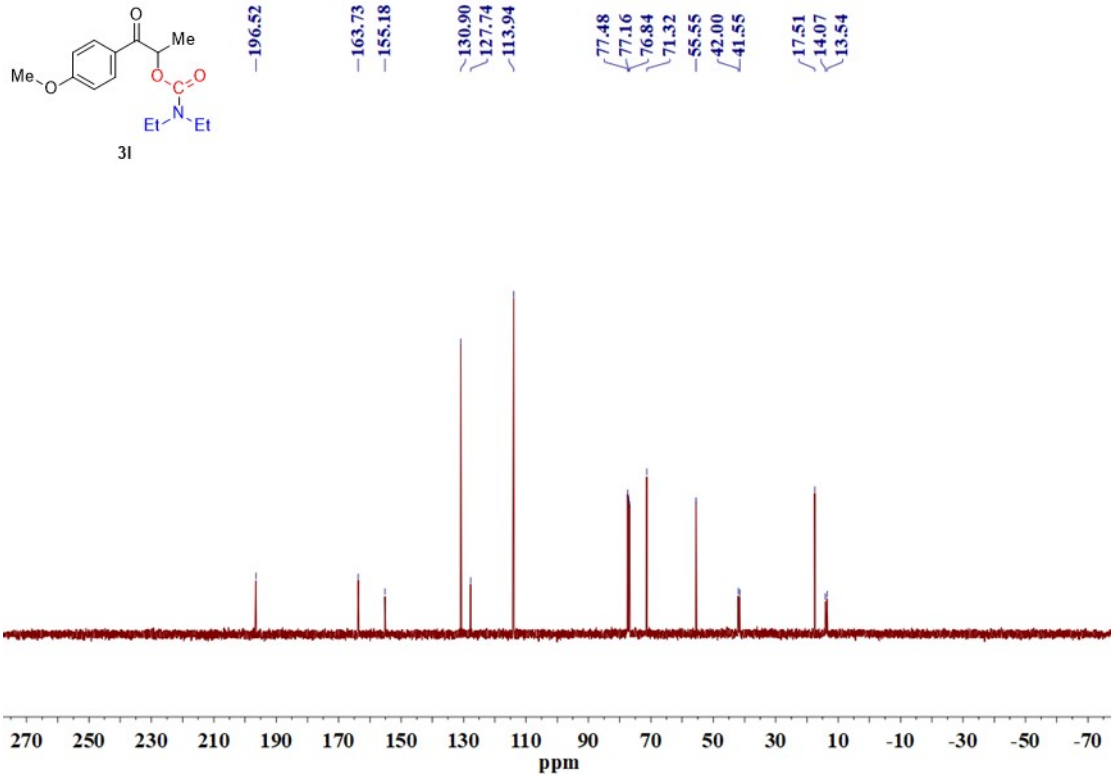

3k
198.55
155.25
138.58
135.04
134.15
129.12
128.65
125.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.78
42.09
41.63
21.46
17.41
14.08
13.56
f1 (ppm)

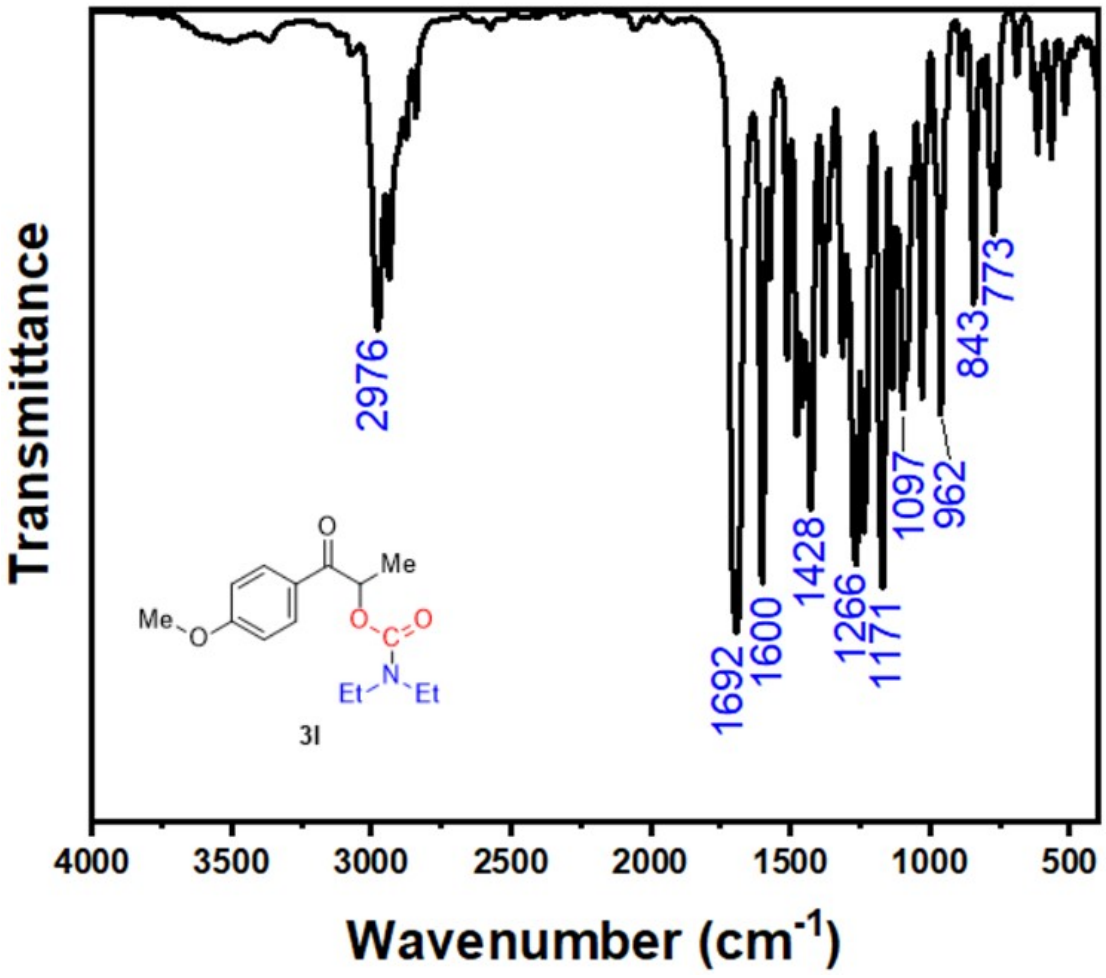


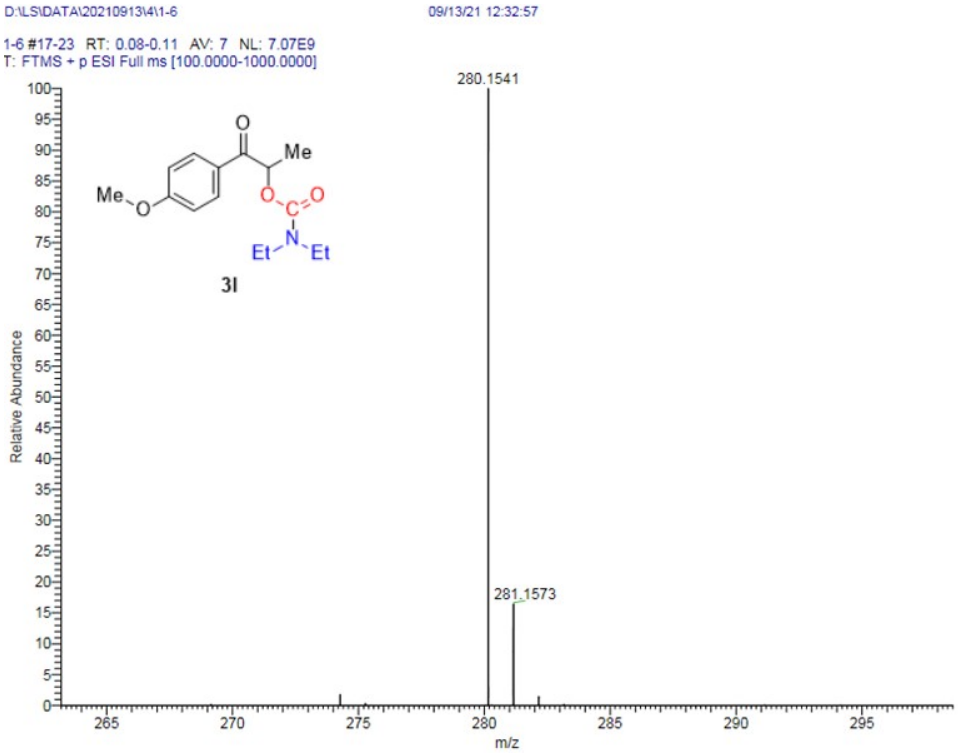


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3k

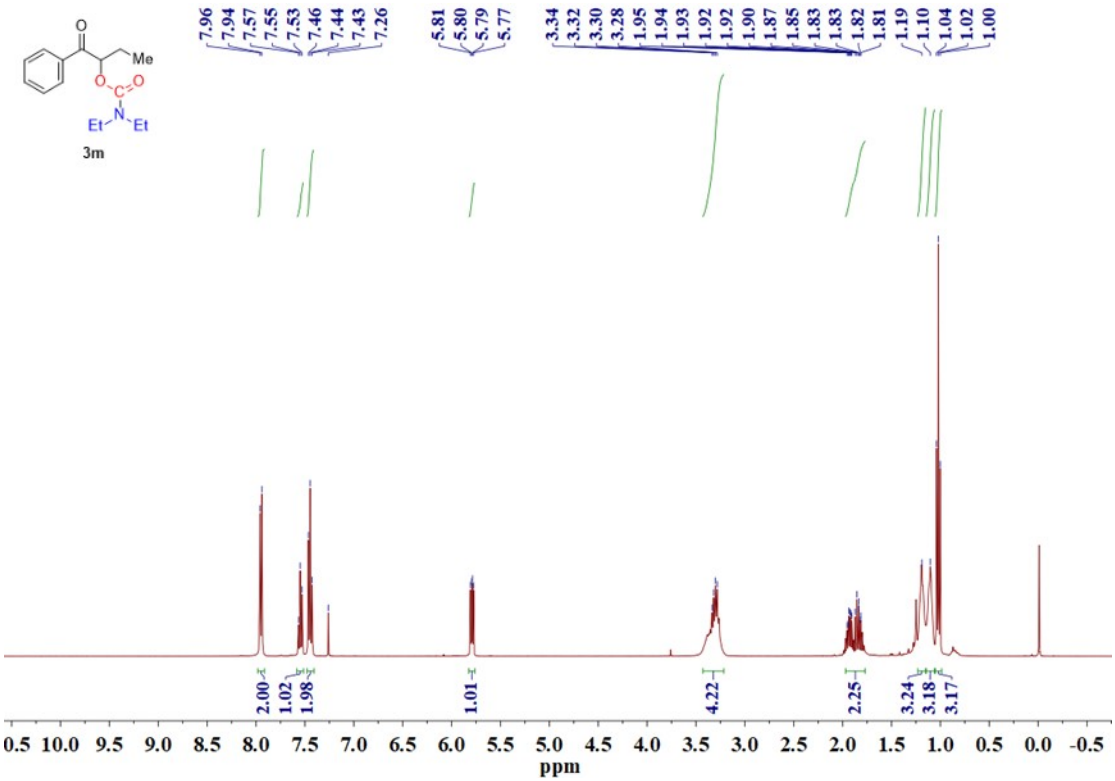

7.95
7.92
7.26
6.92
6.90
5.94
5.92
5.90
5.89
3.84
3.32
3.32
3.30
1.48
1.47
1.14
1.12
1.11
1.09
1.99
2.03
1.00
3.09
4.07
3.05
6.06
ppm

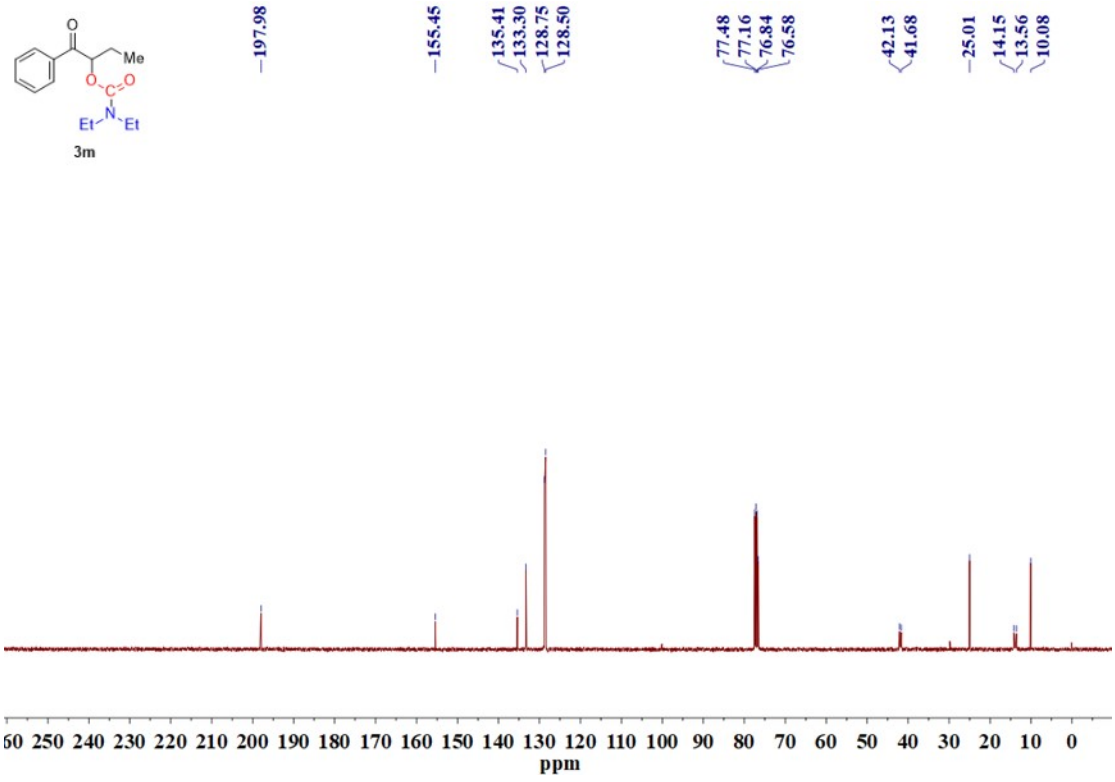

196.52
163.73
155.18
130.90
127.74
113.94
77.48
77.16
76.84
71.32
55.55
42.00
41.55
17.51
14.07
13.54
ppm

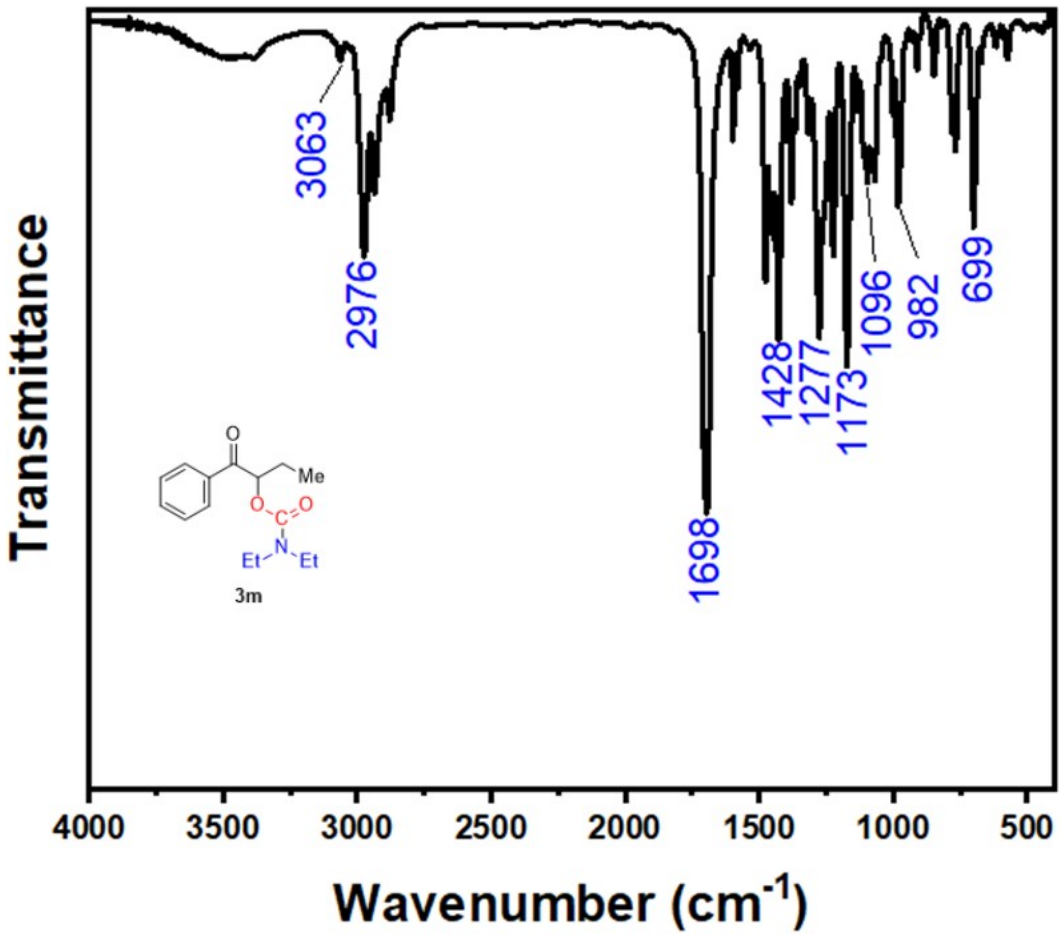


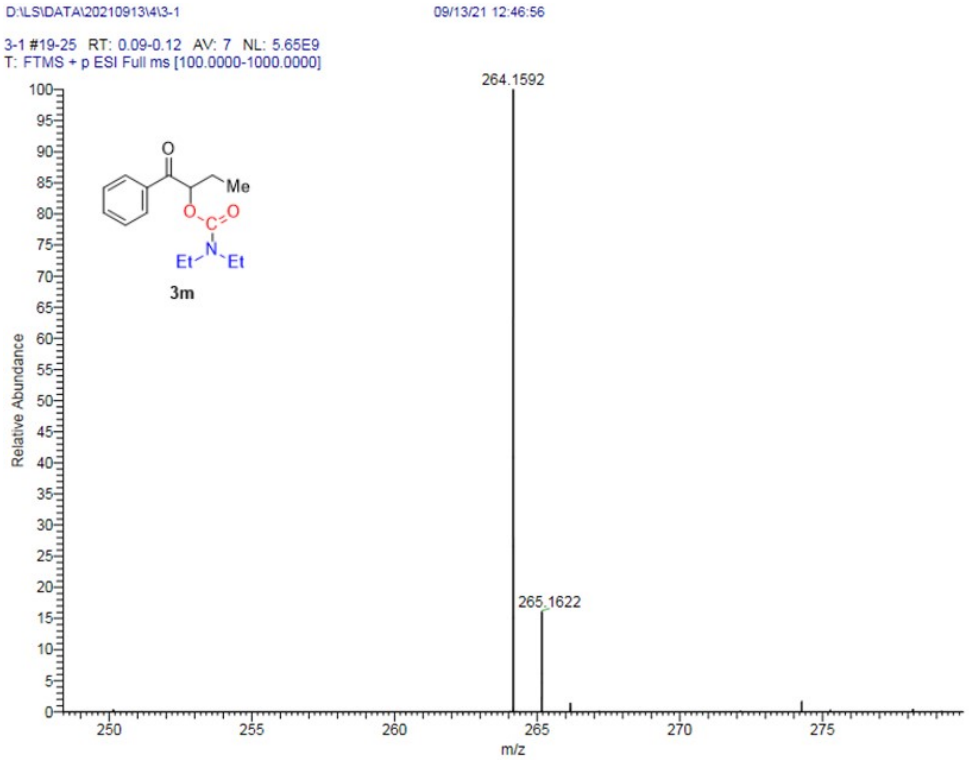


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3l

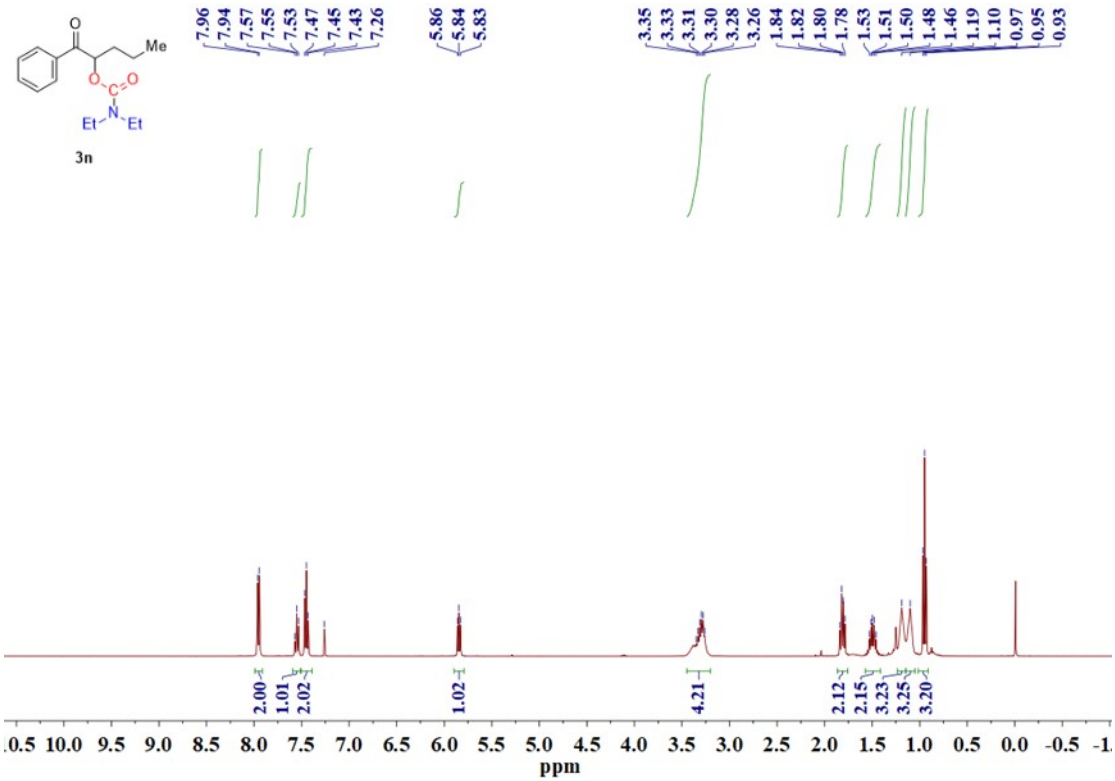

3m
7.96
7.94
7.57
7.55
7.53
7.46
7.44
7.43
7.26
5.81
5.80
5.79
5.77
3.34
3.32
3.30
3.28
1.95
1.94
1.93
1.92
1.92
1.90
1.87
1.85
1.83
1.83
1.82
1.81
1.19
1.10
1.04
1.02
1.00
2.00
1.02
1.98
1.01
4.22
2.25
3.24
3.18
3.17
ppm

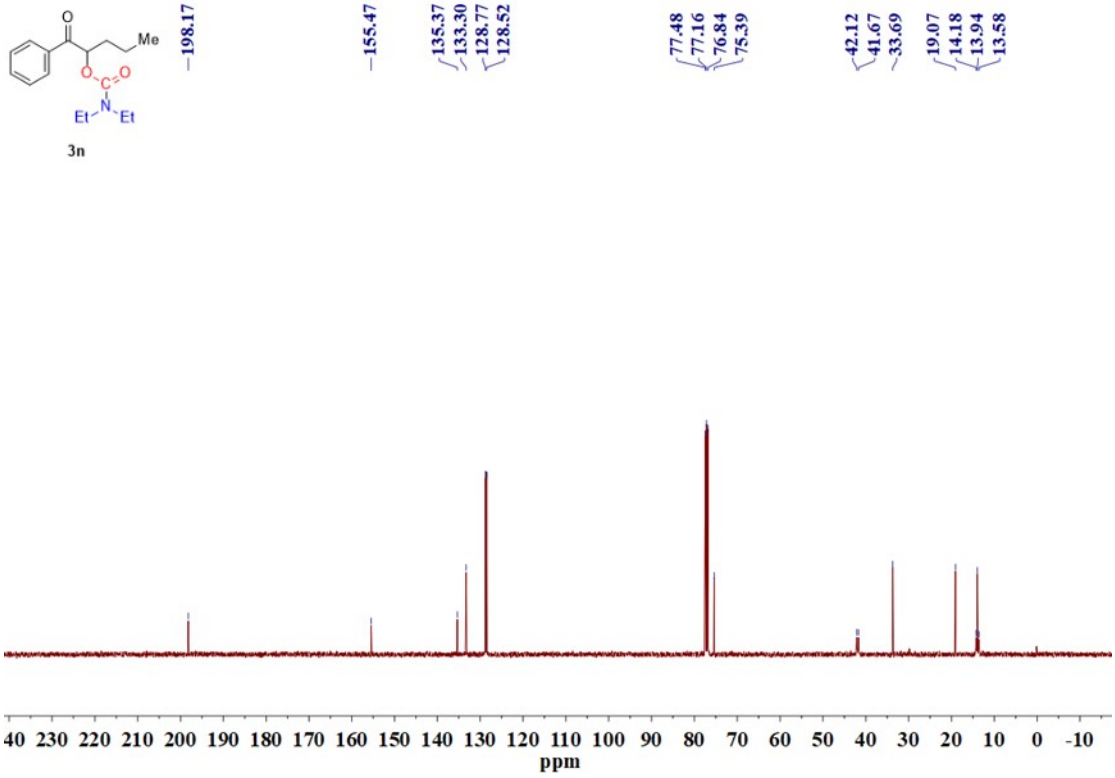

3m
197.98
155.45
135.41
133.30
128.75
128.50
77.48
77.16
76.84
76.58
42.13
41.68
25.01
14.15
13.56
10.08
ppm

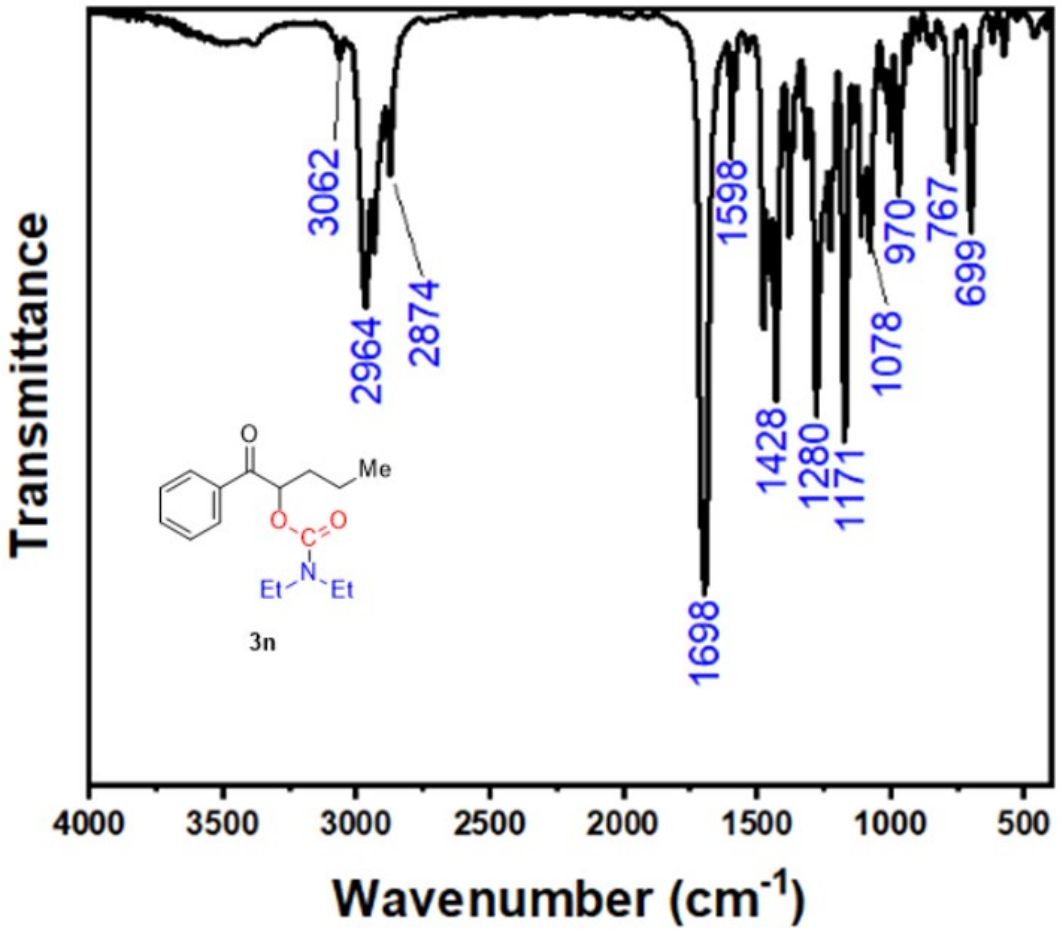


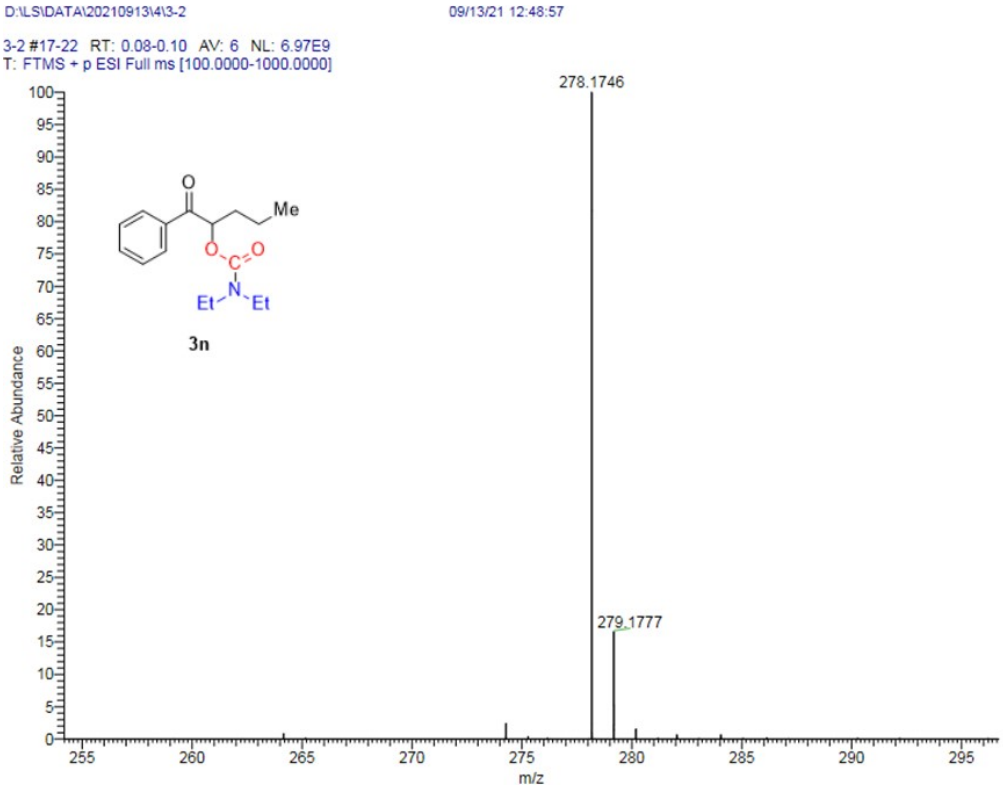


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3m

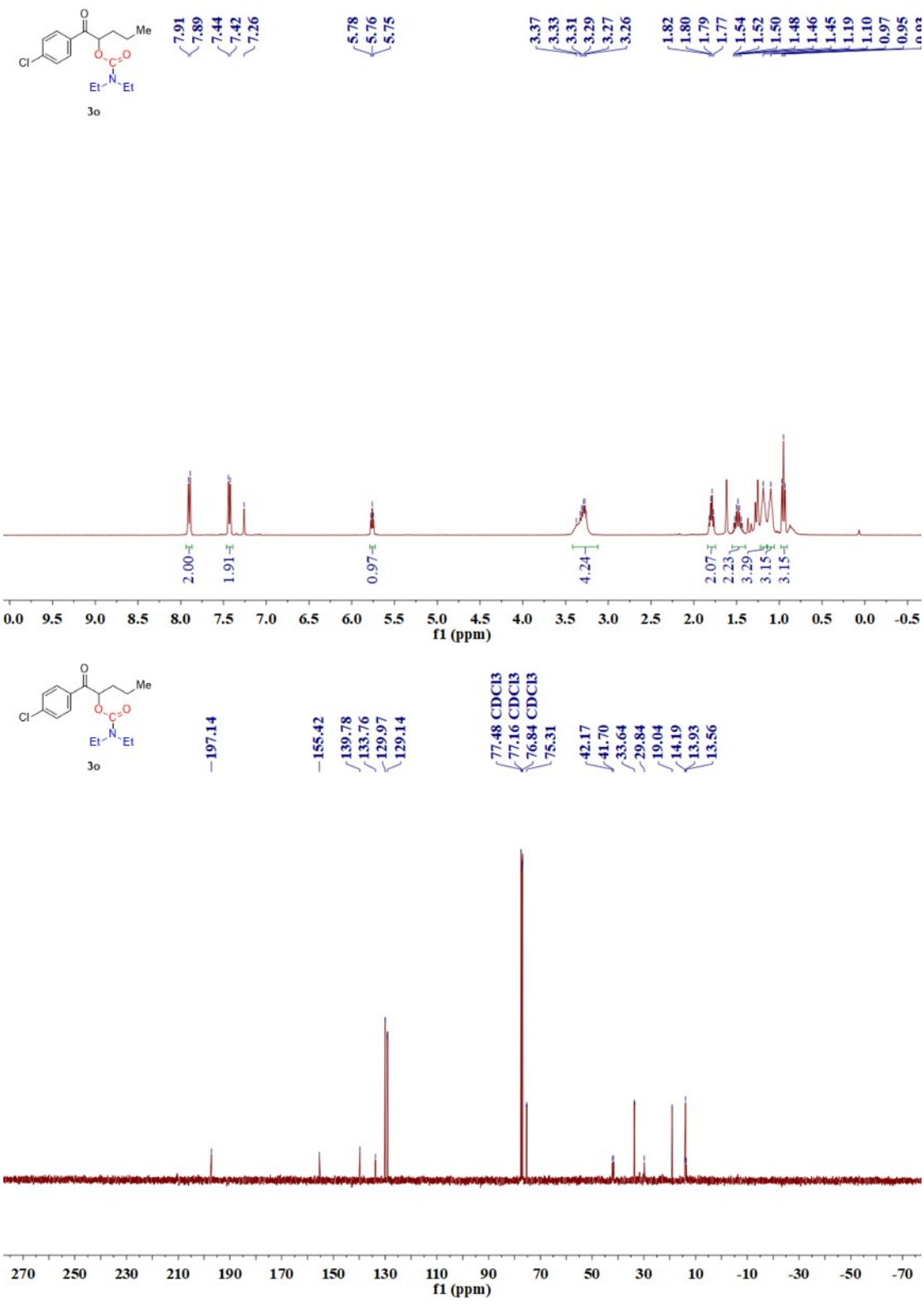

7.96
7.94
7.57
7.55
7.53
7.47
7.45
7.43
7.26
5.86
5.84
5.83
3.35
3.33
3.31
3.30
3.28
3.26
1.84
1.82
1.80
1.78
1.53
1.51
1.50
1.48
1.46
1.19
1.10
0.97
0.95
0.93
Me
Et
Et
3n
2.00
1.01
2.02
1.02
4.21
2.12
2.15
3.23
3.25
3.20
ppm

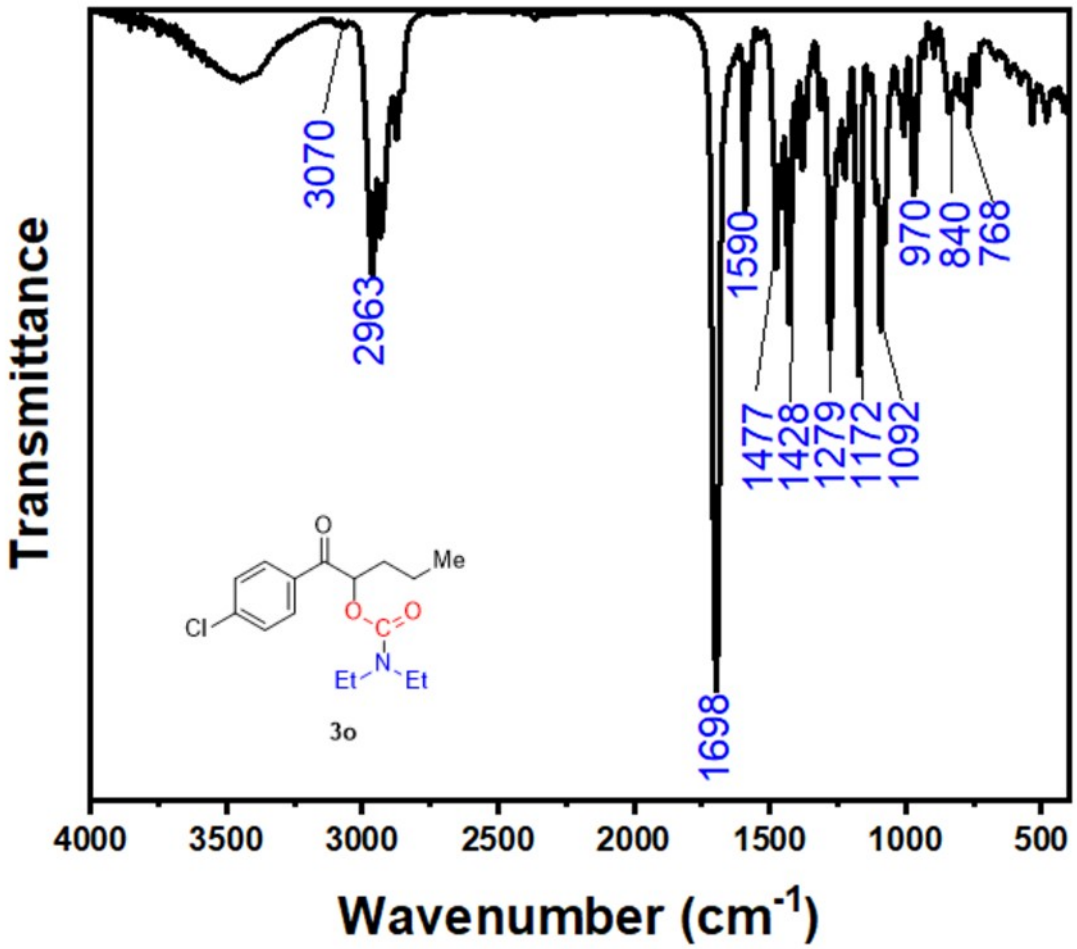

198.17
155.47
135.37
133.30
128.77
128.52
77.48
77.16
76.84
75.39
42.12
41.67
33.69
19.07
14.18
13.94
13.58
Me
Et
Et
3n
ppm

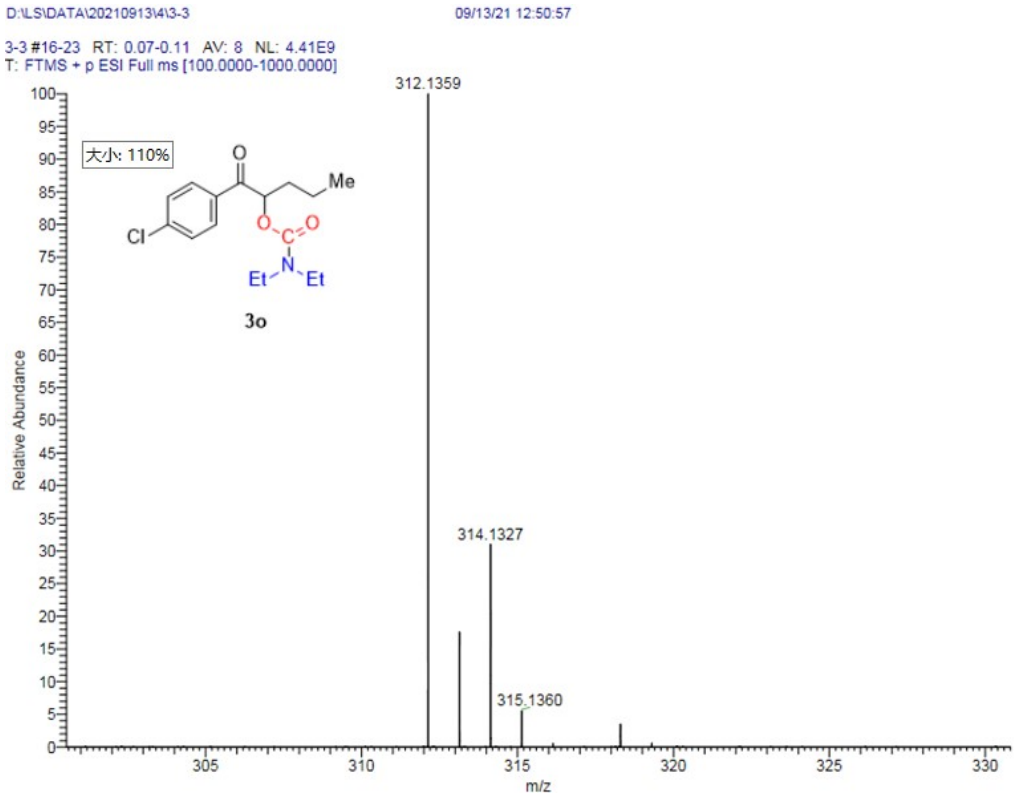




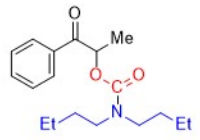
^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3n


3o
7.91
7.89
7.44
7.42
7.26
5.78
5.76
5.75
3.37
3.33
3.31
3.29
3.27
3.26
1.82
1.80
1.79
1.77
1.54
1.52
1.50
1.48
1.46
1.45
1.19
1.10
0.97
0.95
2.00
1.91
0.97
4.24
2.07
2.23
3.29
3.15
3.15
f1 (ppm)
3o
197.14
155.42
139.78
133.76
129.97
129.14
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
75.31
42.17
41.70
33.64
29.84
19.04
14.19
13.93
13.56
f1 (ppm)

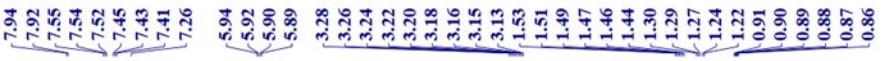


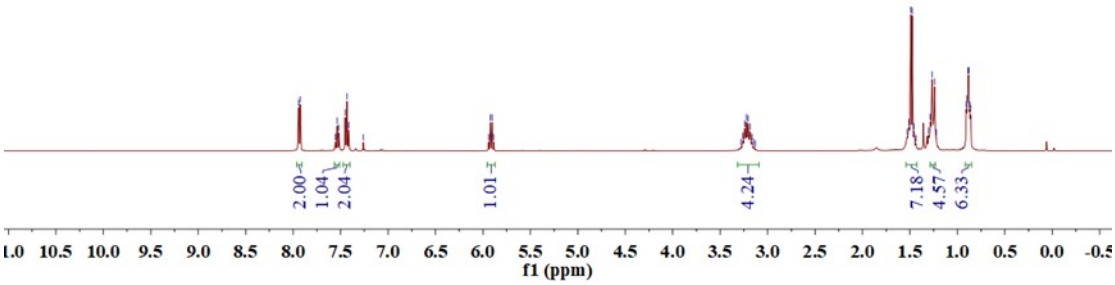


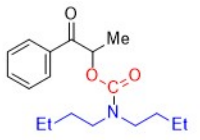
^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3o


O
Me
O
C
O
N
Et
Et

3p

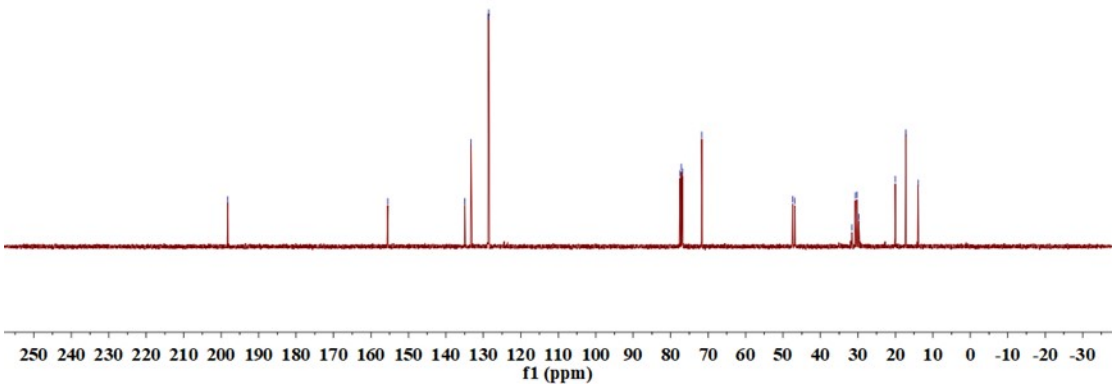

7.94
7.92
7.55
7.54
7.52
7.45
7.43
7.41
7.26
5.94
5.92
5.90
5.89
3.28
3.26
3.24
3.22
3.20
3.18
3.16
3.15
3.13
1.53
1.51
1.49
1.47
1.46
1.44
1.30
1.29
1.27
1.24
1.22
0.91
0.90
0.89
0.88
0.87
0.86

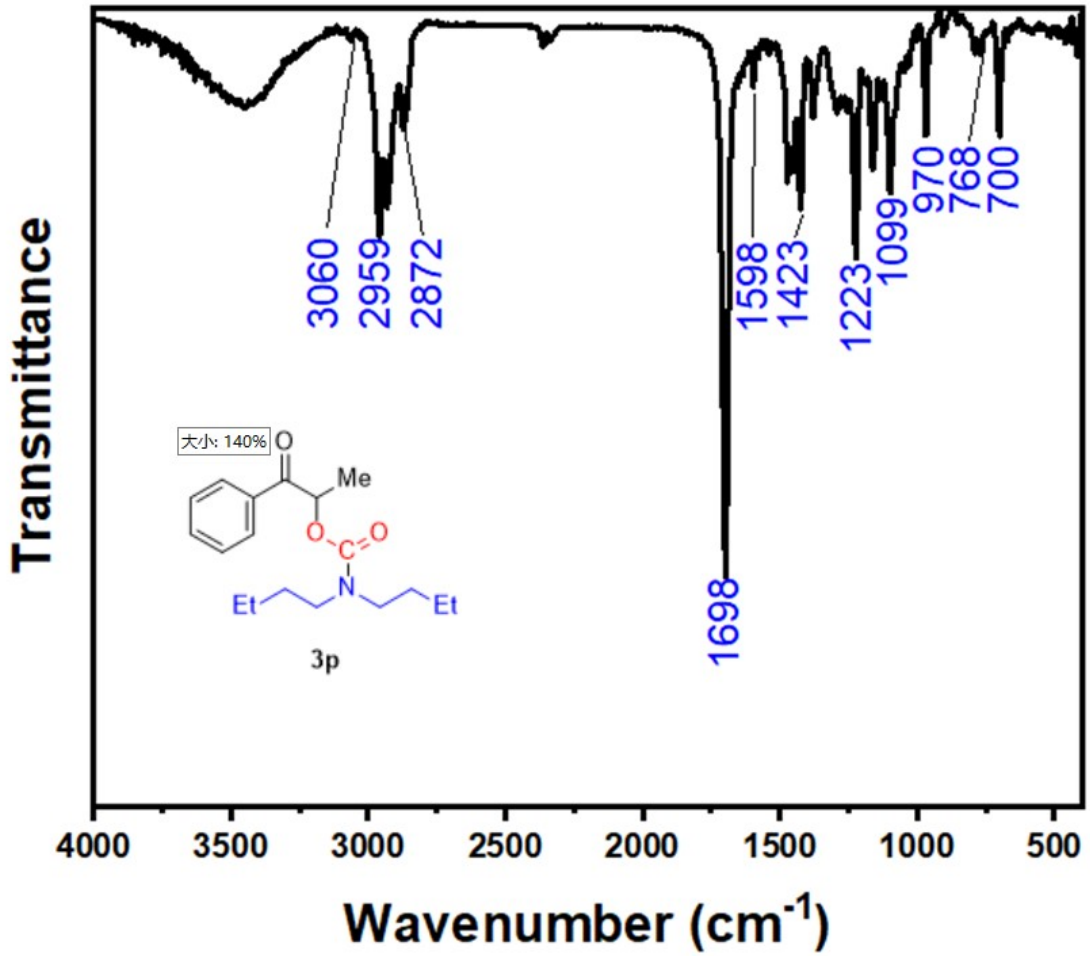

2.00
1.04
2.04
1.01
4.24
7.18
4.57
6.33
f1 (ppm)

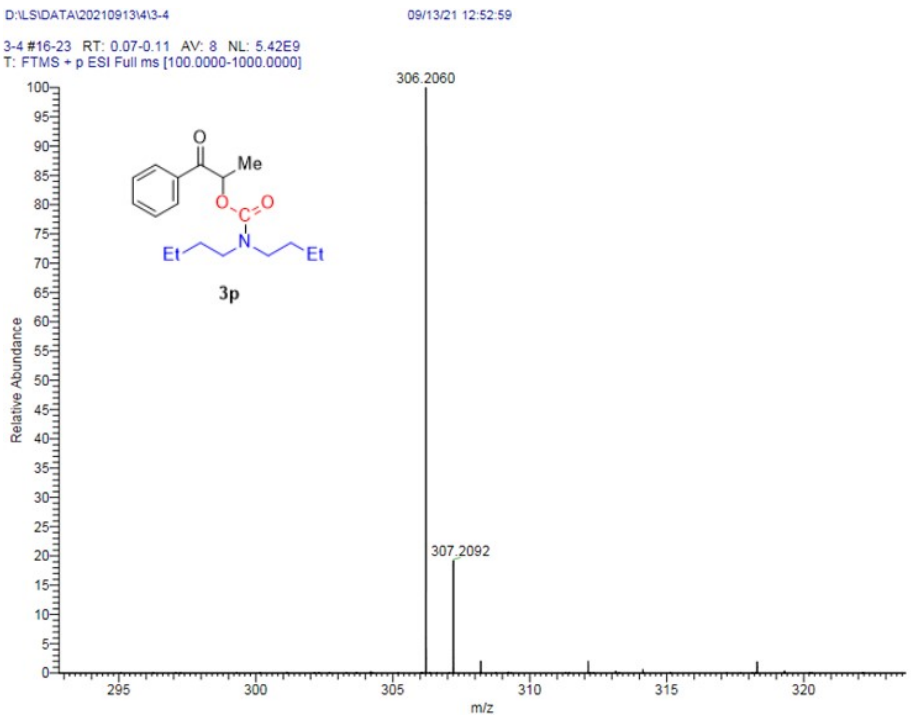

O
Me
O
C
O
N
Et
Et

3p

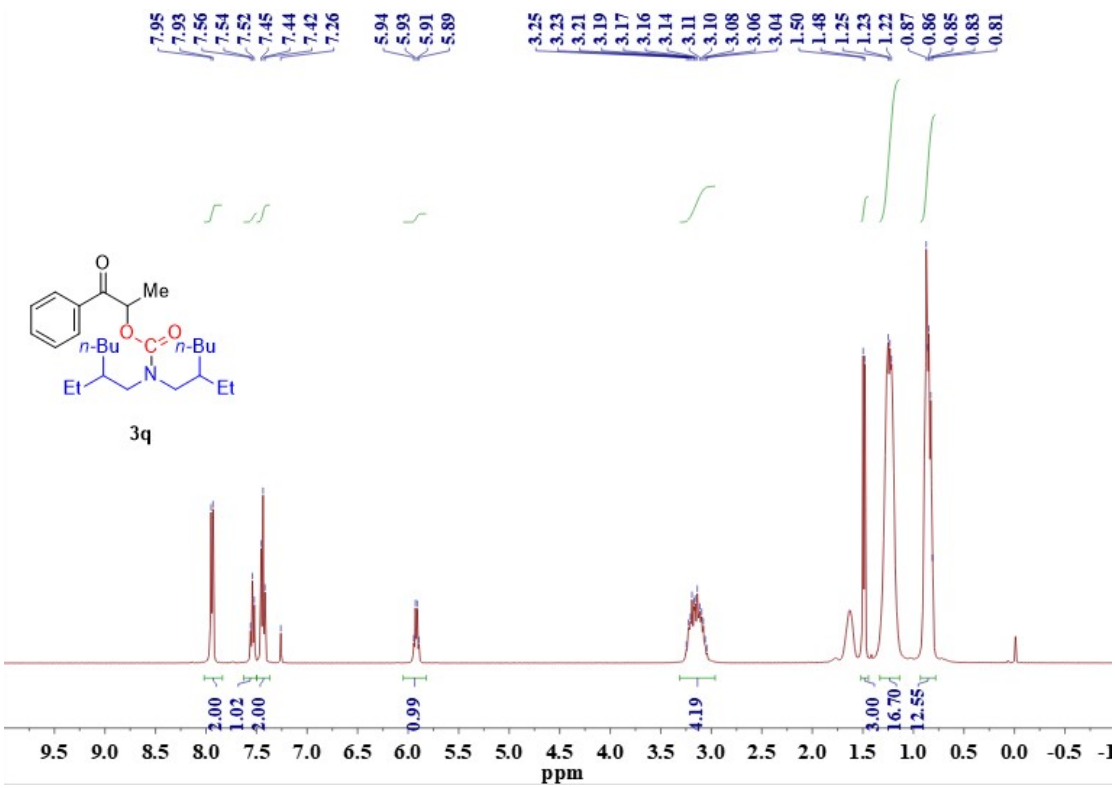

198.22
155.49
134.93
133.30
128.70
128.55
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
71.71
47.42
46.81
31.57
30.70
30.21
29.77
20.05
17.19
13.90

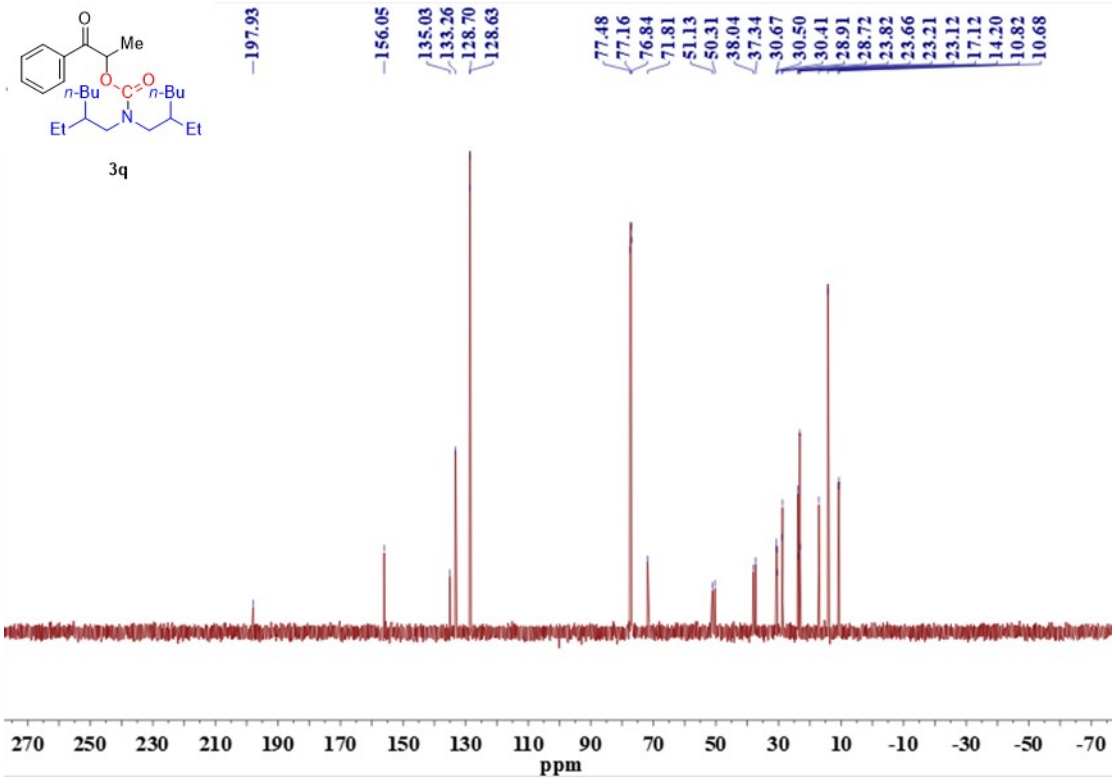

f1 (ppm)

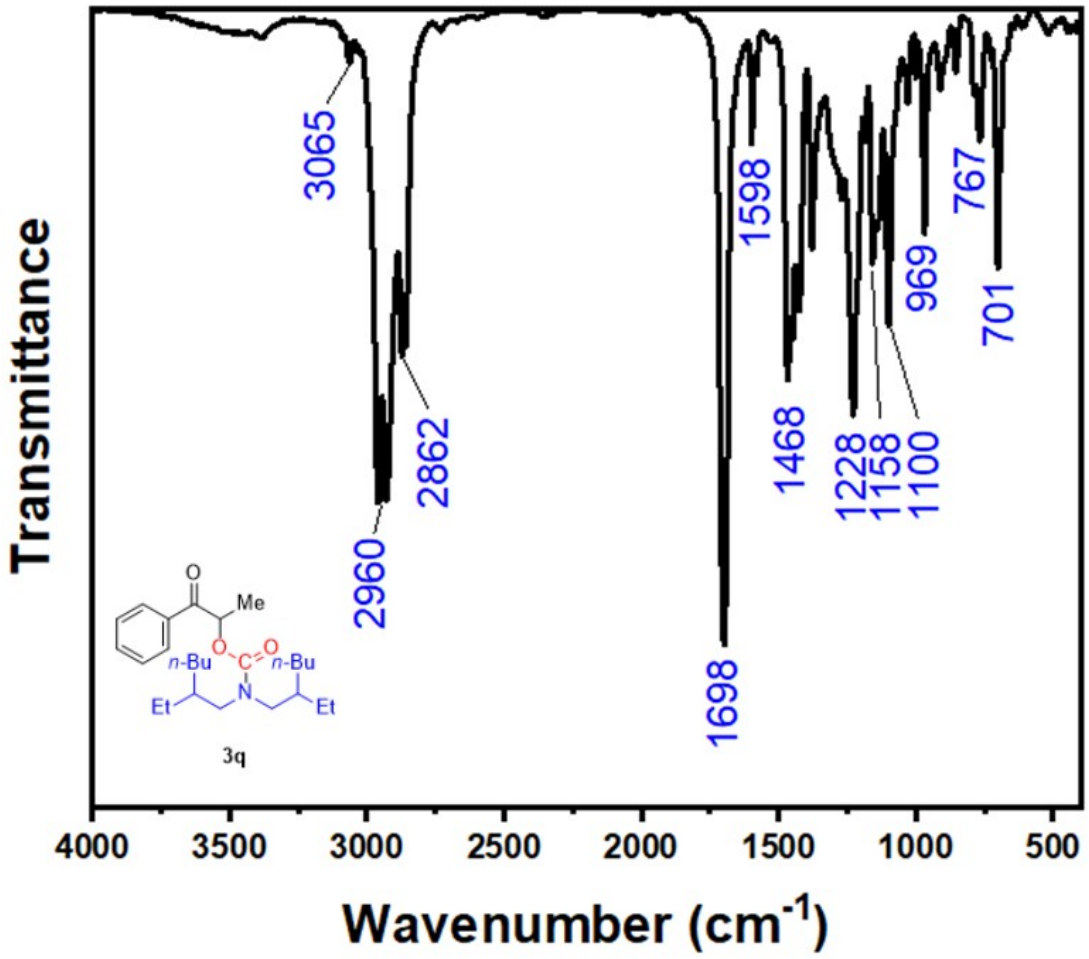


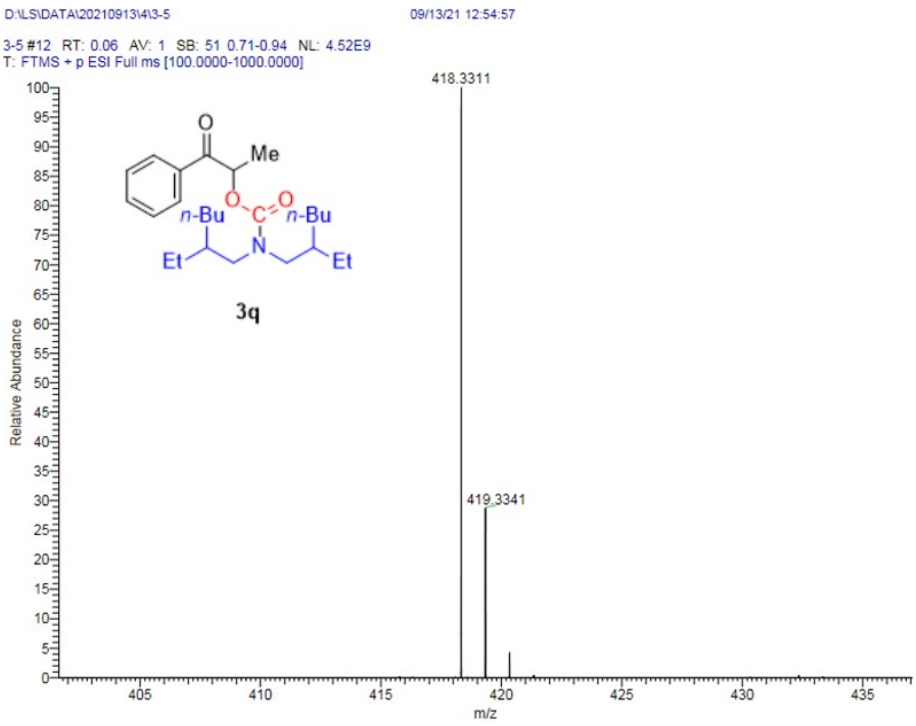


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3p

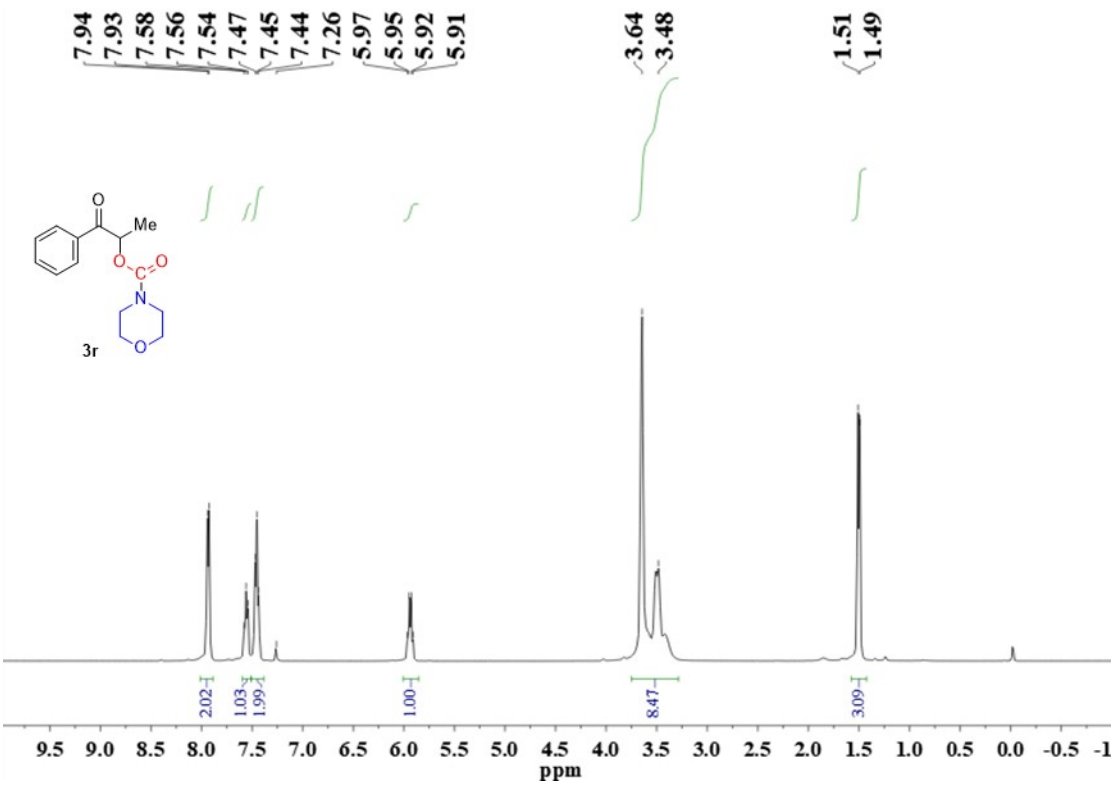

7.95
7.93
7.56
7.54
7.52
7.45
7.44
7.42
7.26
5.94
5.93
5.91
5.89
3.25
3.23
3.21
3.19
3.17
3.16
3.14
3.11
3.10
3.08
3.06
3.04
1.50
1.48
1.25
1.23
1.22
0.87
0.86
0.85
0.83
0.81
Me
n-Bu
n-Bu
Et
Et
3q
2.00
1.02
2.00
0.99
4.19
3.00
16.70
12.55
ppm

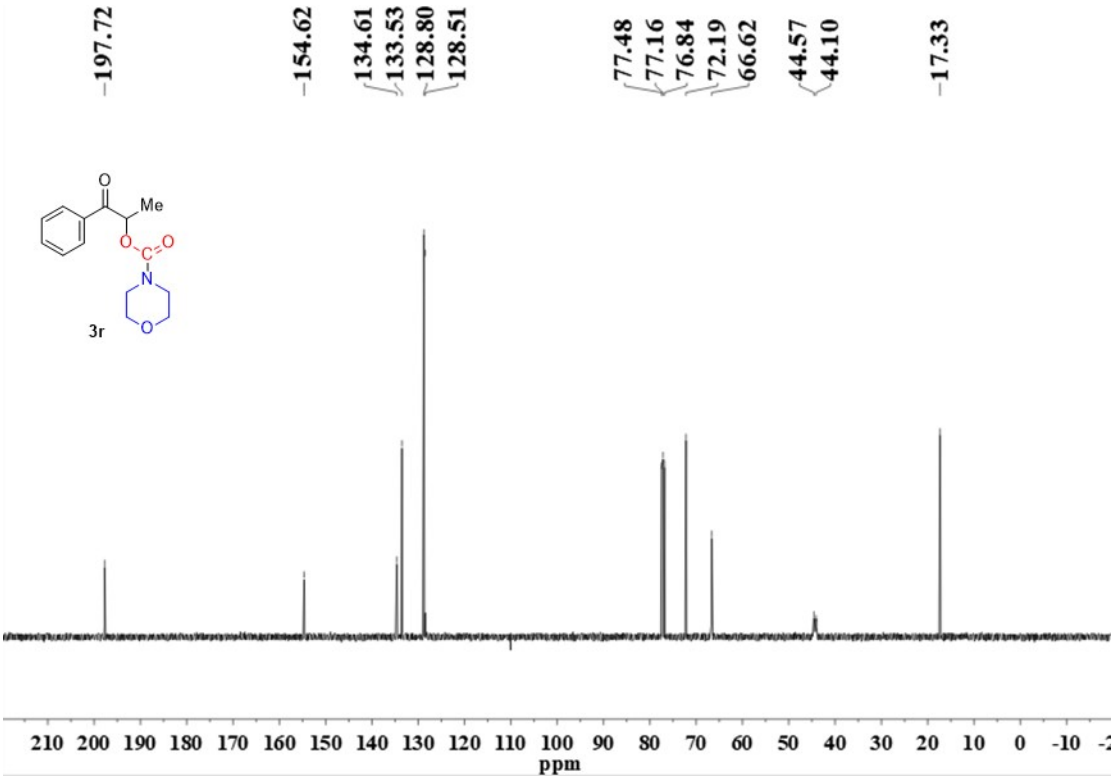

Me
n-Bu
n-Bu
Et
Et
3q
197.93
156.05
135.03
133.26
128.70
128.63
77.48
77.16
76.84
71.81
51.13
50.31
38.04
37.34
30.67
30.50
30.41
28.91
28.72
23.82
23.66
23.21
23.12
17.12
14.20
10.82
10.68
ppm

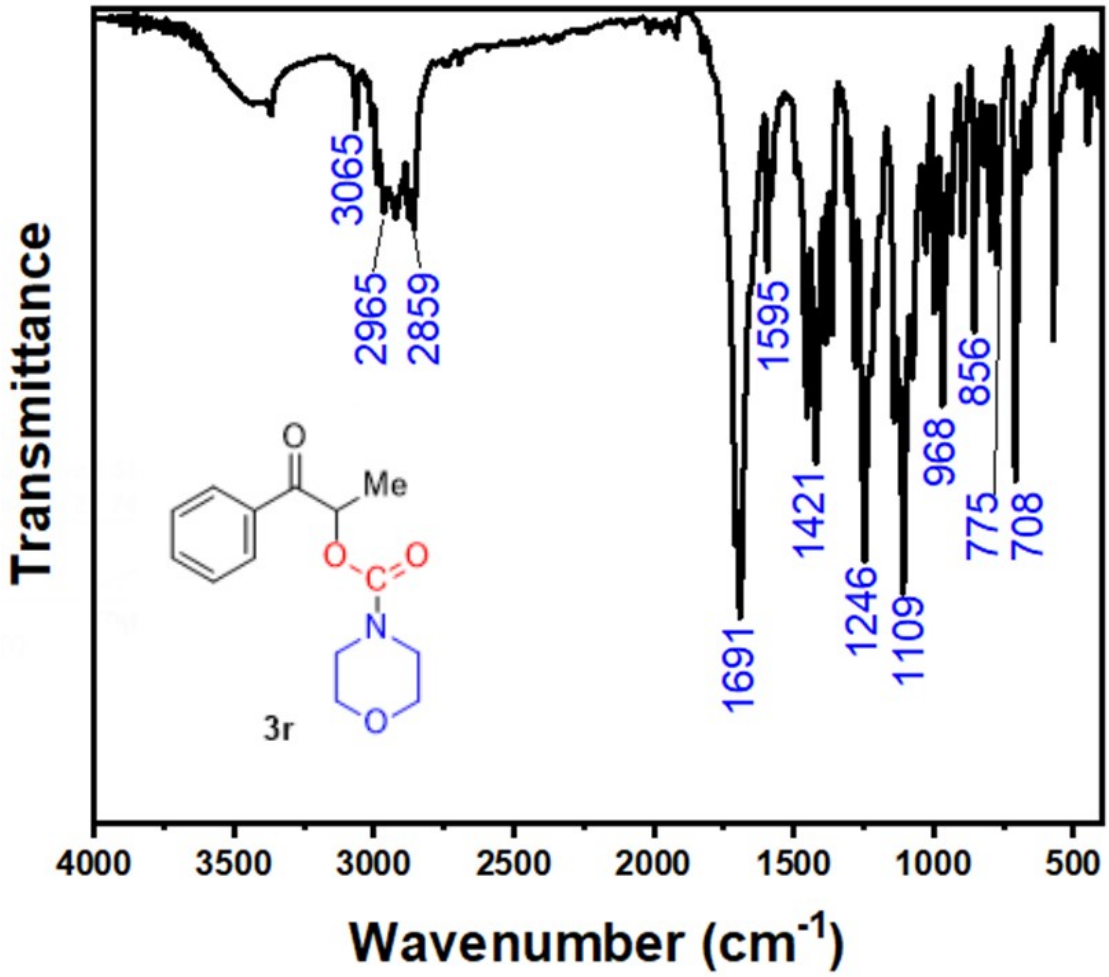


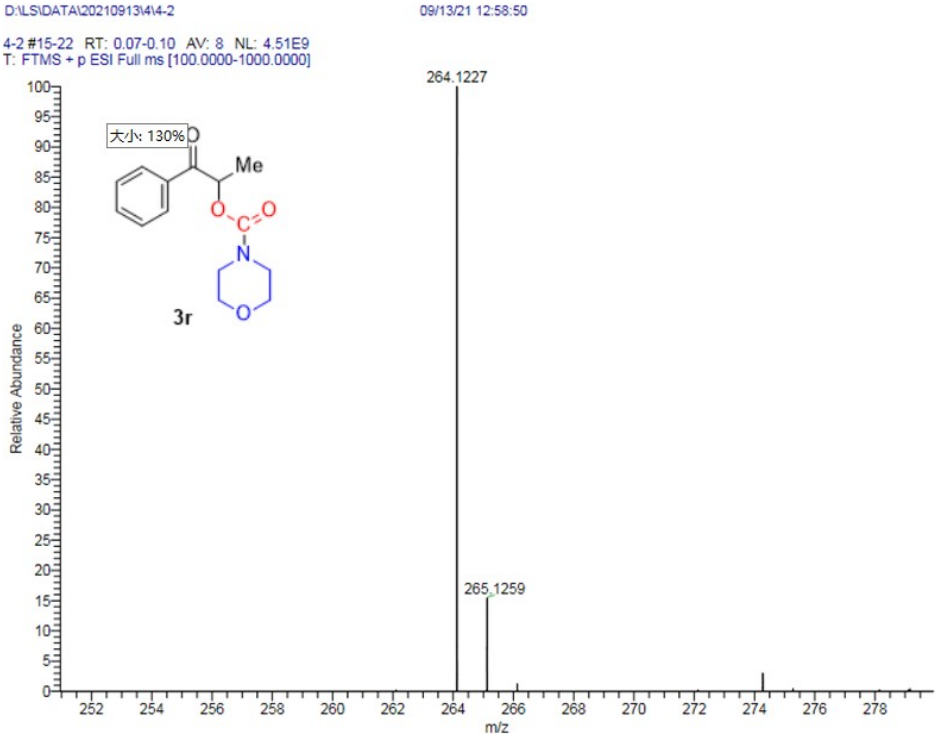


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3q

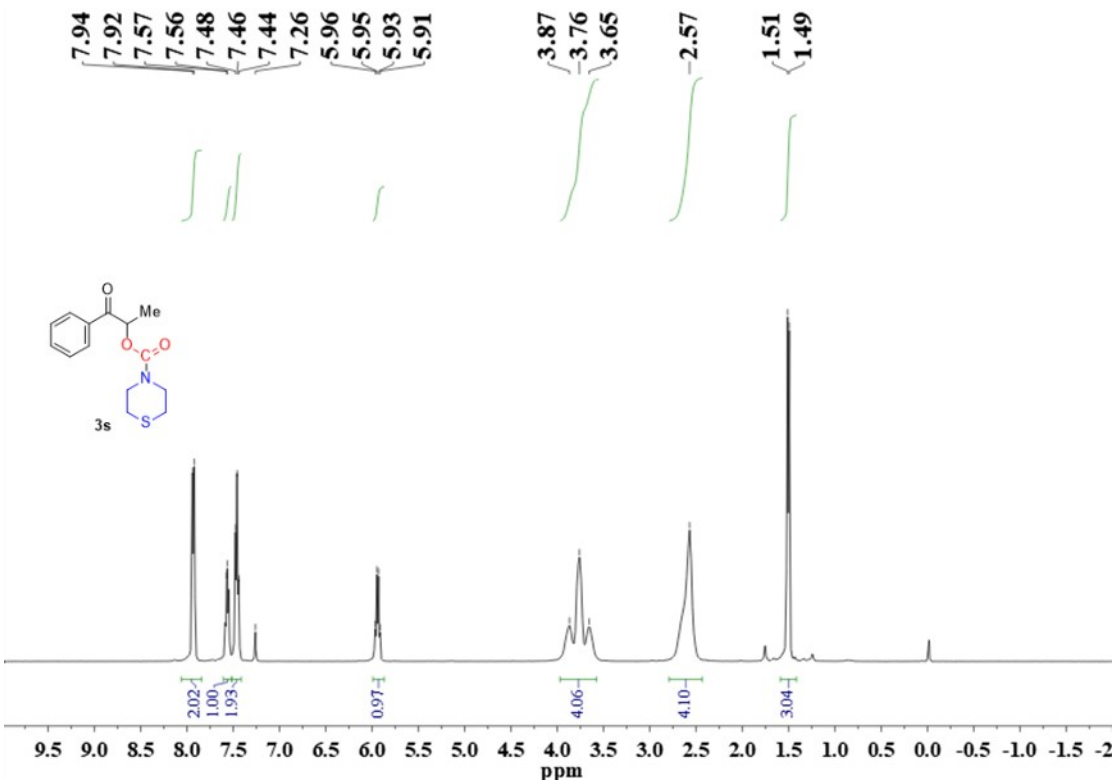

7.94
7.93
7.58
7.56
7.54
7.47
7.45
7.44
7.26
5.97
5.95
5.92
5.91
3.64
3.48
1.51
1.49
Me
O
O
C
O
N
O
3r
2.02
1.03
1.99
1.00
8.47
3.09
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
ppm

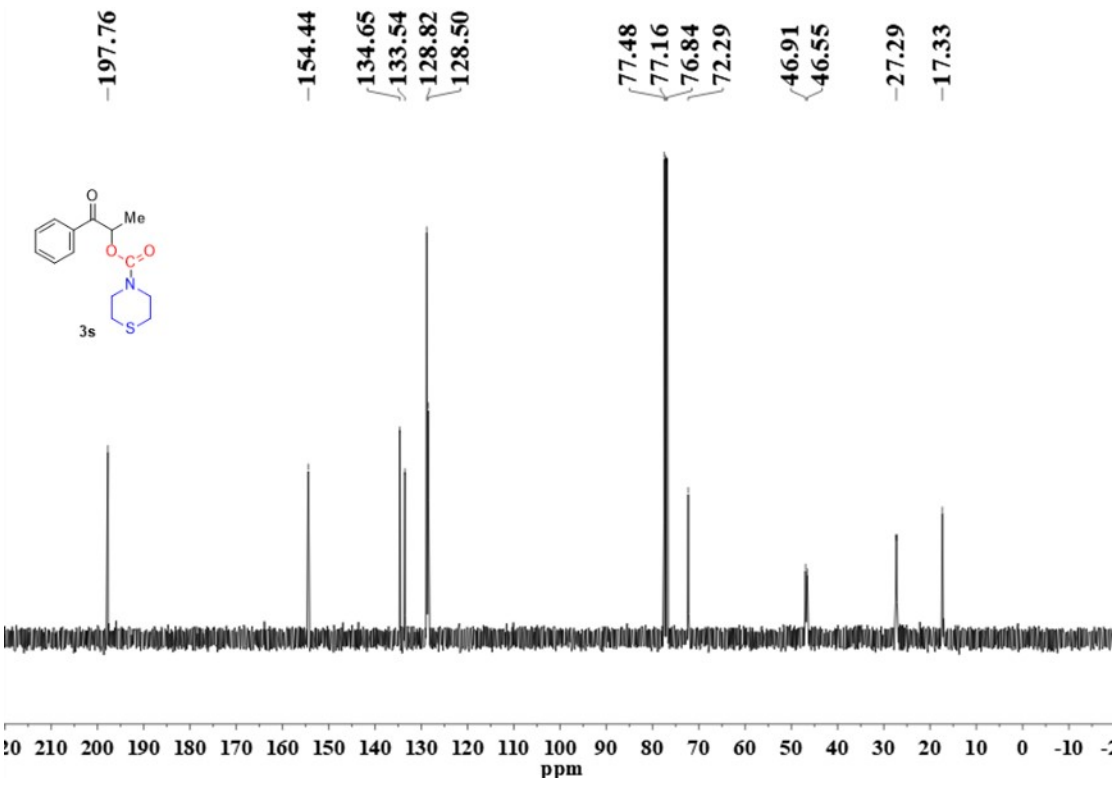

197.72
154.62
134.61
133.53
128.80
128.51
77.48
77.16
76.84
72.19
66.62
44.57
44.10
17.33
Me
O
O
C
O
N
O
3r
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
ppm

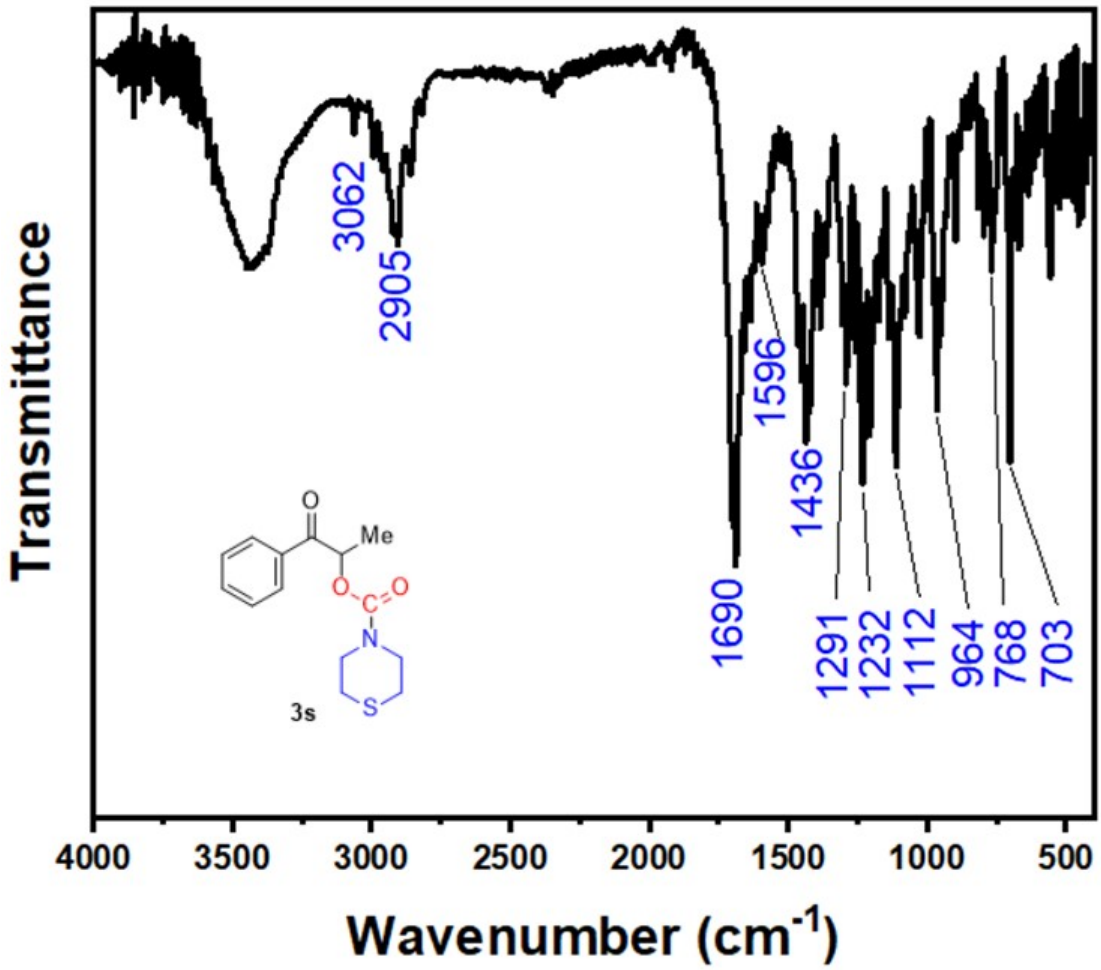


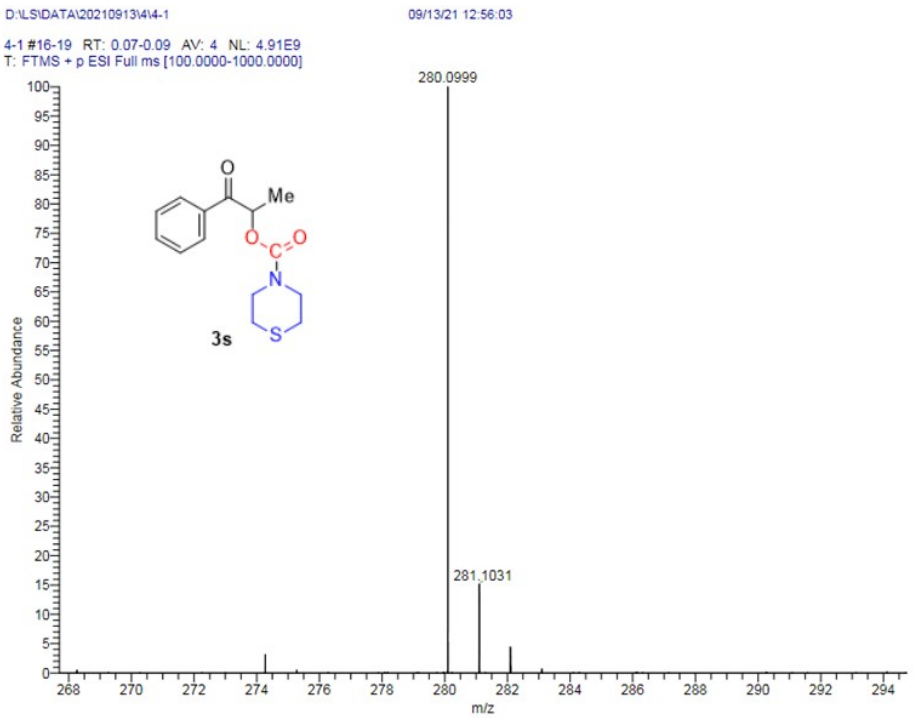


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3r

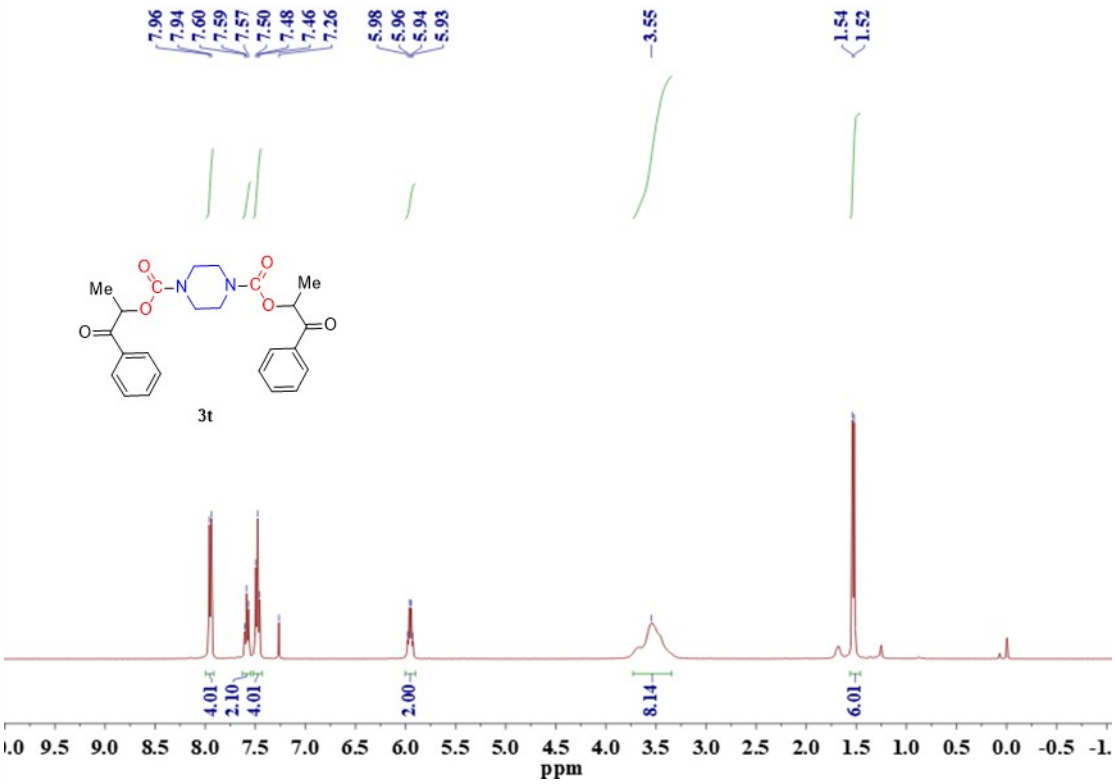

7.94
7.92
7.57
7.56
7.48
7.46
7.44
7.26
5.96
5.95
5.93
5.91
3.87
3.76
3.65
2.57
1.51
1.49
Me
3s
2.02
1.00
1.93
0.97
4.06
4.10
3.04
ppm

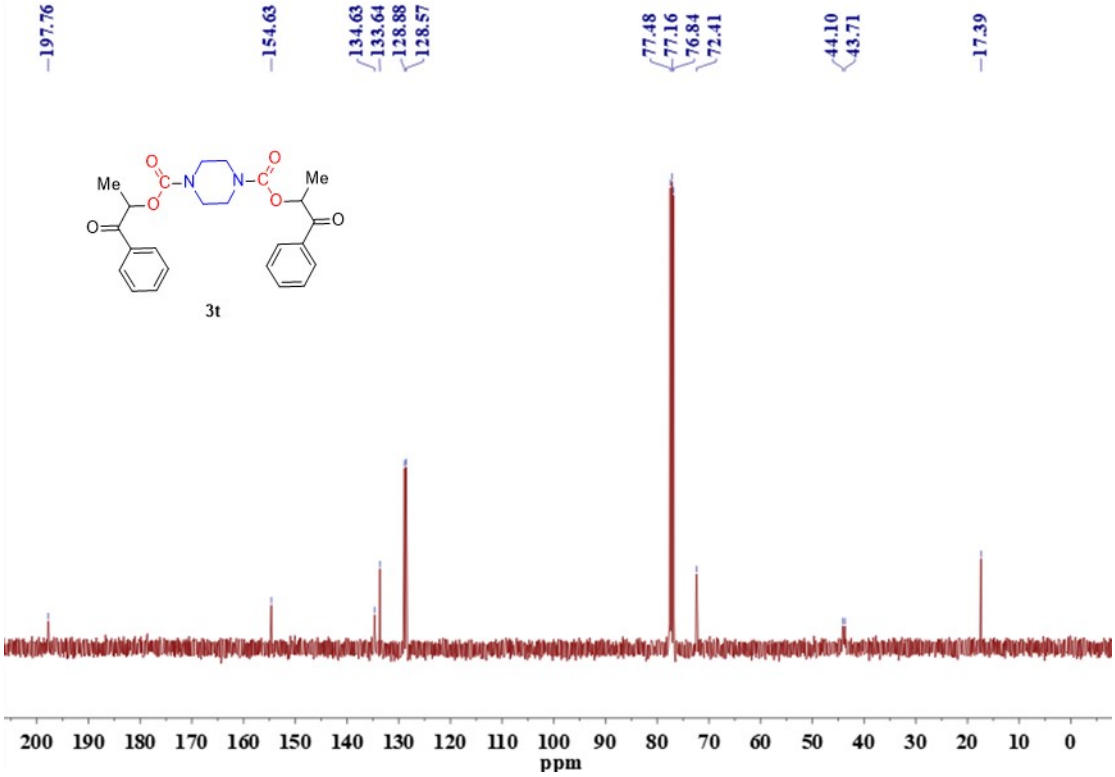

197.76
154.44
134.65
133.54
128.82
128.50
77.48
77.16
76.84
72.29
46.91
46.55
27.29
17.33
Me
3s
ppm

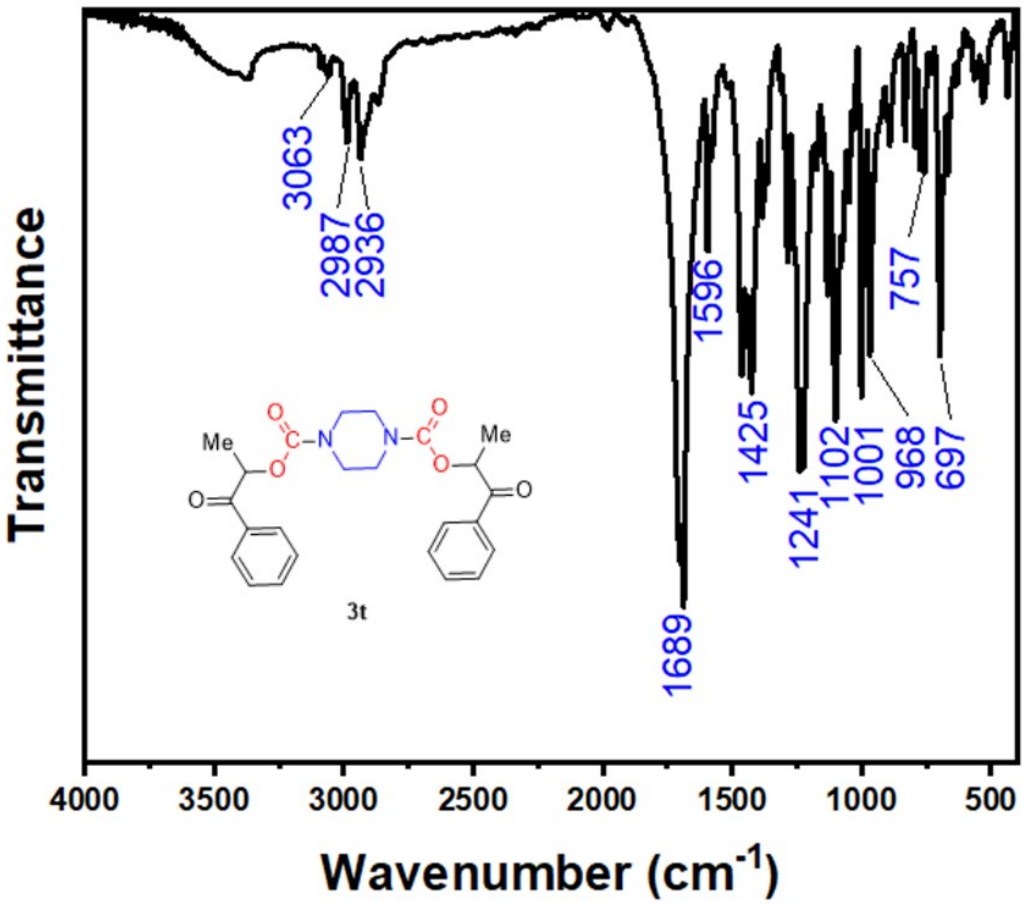


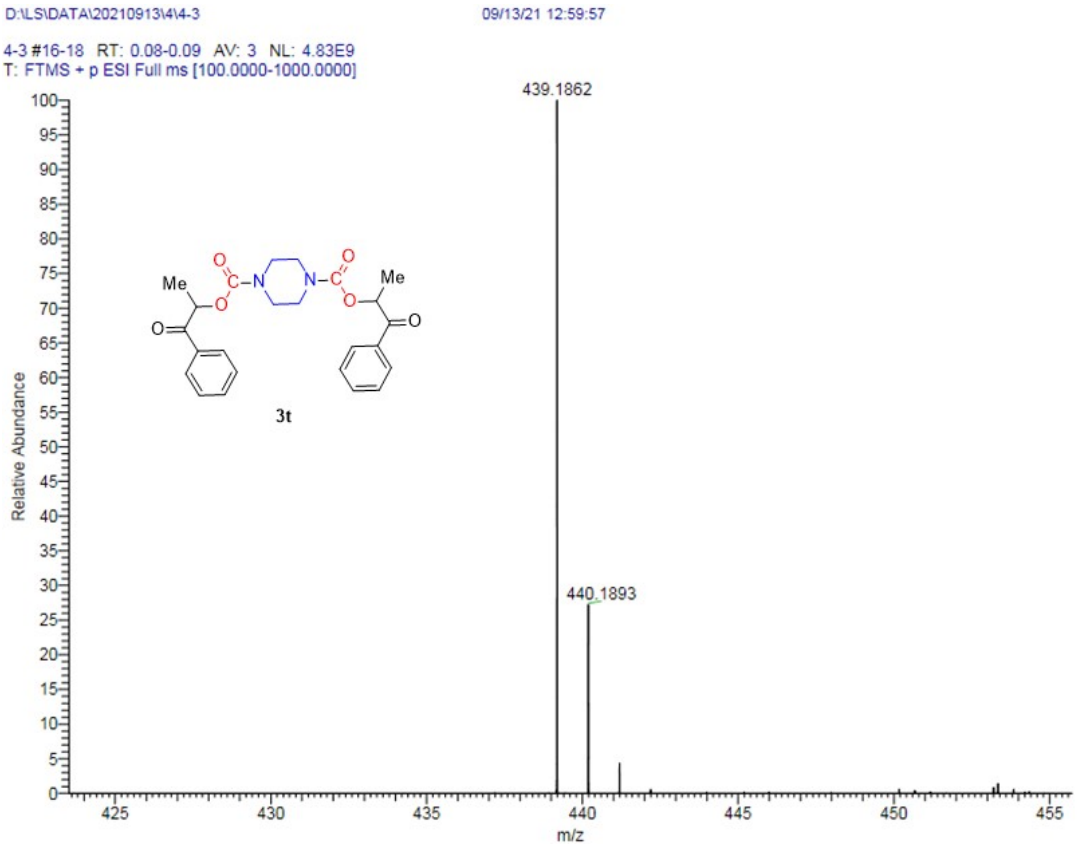


^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3s


7.96
7.94
7.60
7.59
7.57
7.50
7.48
7.46
7.26
5.98
5.96
5.94
5.93
3.55
1.54
1.52
Me
Me
3t
4.01
2.10
4.01
2.00
8.14
6.01
ppm


197.76
154.63
134.63
133.64
128.88
128.57
77.48
77.16
76.84
72.41
44.10
43.71
17.39
Me
Me
3t
ppm





^{1}H NMR, ^{13}C NMR, FT-IR, and HRMS spectra of compound 3t

V. References

[S1] E. C. M. Chen, K. Albyn, L. Dussack, *J. Phys. Chem.*, **1989**, *93*, 6827-6832.

[S2] G. D. Mendenhall, D. M. Golden, S. W. Benson, *J. Phys. Chem.*, **1973**, *77*, 2707-2709.

[S3] L. Song, L. Zhang, S. Z. Luo, J. P. Cheng, *Chem. Eur. J.*, **2014**, *20*, 14231-14234.

[S4] http://ibond.nankai.edu.cn