Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Phosphine-free Pd catalyst for the selective double carbonylation of aryl iodides.

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General Methods:

All reactions were carried out under an argon atmosphere using Standard Schlenk techniques. Solvents were distilled and degassed prior to use. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} and ^{19}F{^{1}H} NMR spectra were recorded on a Varian Gemini spectrometer at 300 and 400 MHz. Chemical shifts were reported relative to tetramethylsilane for ^{1}H and ^{13}C{^{1}H} as internal reference, H_3PO_4 85% for ^{31}P{^{1}H}, and trichlorofluoromethane for ^{19}F{^{1}H} as external references. Elemental analyses were carried out on a Carlo Erba Microanalyser EA 1108. VG-Autospect equipment was used for FAB mass spectral analyses with 3-nitrobenzylalcohol as matrix. EI mass spectra were obtained on an HP 5989 A spectrometer at an ionizing voltage of 70eV. Conversion and chemoselectivity was measured by NMR spectrometry and GC-MS spectra. HP-FFAP Column of polyethylene glycol (30 m x 0.25 mm x 0.25 μm). T^a= 250 ºC injector. Flow 1.5ml/min. Initial T^a= 50ºC, for 3 min. 10ºC/min until 230ºC, for 15 min, 15ºC/min until 240ºC, for 40 min. Analysis time 76.67 min. m/z acquisition range: 43-600.

General procedure for Pd-catalysed double carbonylation of aryl iodide:

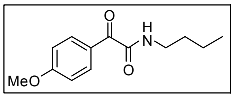
Primary amines:

A tube of multireactor was charged with the corresponding aryl iodide (0.5 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 mmol), DBU (1 mmol) and the primary amine desired (1.2 mmol) in toluene (5 mL). Then, the tube was pressurized with 1 bar of carbon monoxide. The reaction was stirred at 80ºC for 1 hour. After the reaction, the mixture was filtered over Celite, and washed with water (3x5 mL). The organic phase was dried over anhydrous $MgSO_4$. The drying agent was filtered off and the solvent was removed under reduced pressure. The conversion and chemoselectivity was determined by GC-MS chromatography.

Secondary amines:

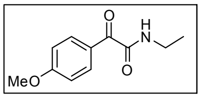
A tube of multireactor was charged with the corresponding aryl iodide (0.5 mmol), $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 mmol), DBU (1 mmol) and the secondary amine desired (1.2 mmol) in toluene (5 mL). Then, the tube was pressurized with 1 bar of carbon monoxide. The reaction was stirred at 60ºC for 14 hour. After the reaction, the mixture was filtered over Celite, and washed with water (3x5 mL). The organic phase was dried over anhydrous $MgSO_4$. The drying agent was filtered off and the solvent was removed under reduced pressure. The conversion and chemoselectivity was determined by GC-MS chromatography.

N-butyl-2-(4-methoxyphenyl)-2-oxoacetamide (3a)



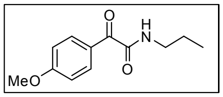
Following the general procedure for the synthesis of α-ketoamides using primary amines, compound **3a** was obtained in 87% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 8.40 (d, ^{3}J=9.2Hz, 2H, arom), 7.12 (br, 1H, NH), 6.93 (d, ^{3}J=9.2Hz, 2H, arom), 3.87 (s, 3H, CH_3), 3.37 (m, 2H, CH_2), 1.57 (m, 2H, CH_2), 1.39 (m, 2H, CH_2), 0.94 (t, ^{3}J=7.2Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 186.1 (C=O), 164.6 (C, arom), 162.5 (C=O), 134.2 (CH, arom), 126.5 (C, arom), 113.9 (CH, arom), 56.8 (CH_3), 39.4 (CH_2), 31.5 (CH_2), 20.2 (CH_2), 13.9 (CH_3). **HRMS** (ESI-TOF): *m/z*=197.1290, calcd for $[M]^+$: 197.1287.

N-ethyl-2-(4-methoxyphenyl)-2-oxoacetamide (3m)



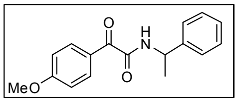
Following the general procedure for the synthesis of α-ketoamides using primary amines, compound **3m** was obtained in 78% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 8.39 (d, ^{3}J=8.8Hz, 2H, arom), 7.18 (br, 1H, NH), 6.92 (d, ^{3}J=8.8Hz, 2H, arom), 3.86 (s, 3H, CH_3), 3.40 (m, 2H, CH_2), 1.22 (t, ^{3}J=7.6Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 186.1 (C=O), 164.8 (C, arom), 162.4 (C=O), 134.1 (CH, arom), 126.6 (C, arom), 114.0 (CH, arom), 55.7 (CH_3), 34.4 (CH_2), 14.6 (CH_3).

2-(4-methoxyphenyl)-2-oxo-*N*-propylacetamide (3n)



Following the general procedure for the synthesis of α-ketoamides using primary amines, compound **3n** was obtained in 84% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 8.39 (d, ^{3}J=9.2Hz, 2H, arom), 7.19 (br, 1H, NH), 6.92 (d, ^{3}J=9.2Hz, 2H, arom), 3.87 (s, 3H, CH_3), 3.33 (m, 2H, CH_2), 1.60 (q, ^{3}J=7.2Hz, 2H, CH_2), 0.96 (t, ^{3}J=3.8Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 185.9 (C=O), 164.6 (C, arom), 162.3 (C=O), 133.9 (CH, arom), 126.4 (C, arom), 113.8 (CH, arom), 55.5 (CH_3), 41.0 (CH_2), 22.6(CH_2), 14.6 (CH_3).

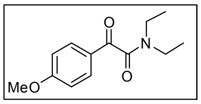
2-(4-methoxyphenyl)-2-oxo-*N*-(1-phenylethyl)acetamide (3p)



Following the general procedure for the synthesis of α-ketoamides using primary amines, compound **3p** was obtained in 81% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 8.42 (d, ^{3}J=9.2Hz, 2H, arom), 7.4 (br, 1H, NH), 7.37 (br, 2H, arom), 7.35 (br, 3H, arom), 6.93 (d, ^{3}J=9.2Hz, 2H, arom), 5.16 (m, 1H, CH), 3.88 (s, 3H, CH_3), 1.59 (d, ^{3}J=6.8Hz, 3H, CH_3). **^{13}C{^{1}H} NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 185.8 (C=O), 164.8 (C, arom), 161.5 (C=O), 142.6

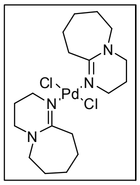
(C, arom), 134.1 (CH, arom), 131.8 (C, arom), 128.9 (CH, arom), 127.7 (CH, arom), 126.3 (CH, arom), 113.9 (CH, arom), 55.7 (CH_3), 49.2 (CH), 21.9 (CH_3).

***N*,*N*-diethyl-2-(4-methoxyphenyl)-2-oxoacetamide (3q)**



Following the general procedure for the synthesis of α-ketoamides using secondary amines, compound **3q** was obtained in 69% yield. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 7.9 (d, ^{3}J=8.8Hz, 2H, arom), 6.97 (d, ^{3}J=8.8Hz, 2H, arom), 3.87 (s, 3H, CH_3), 3.55 (q, ^{3}J=7.6Hz, 2H, CH_2), 3.23 (q, ^{3}J=7.6Hz, 2H, CH_2), 1.27 (t, ^{3}J=7.6Hz, 3H, CH_3), 1.14 (t, ^{3}J=7.6Hz, 3H, CH_3). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 190.5 (C=O), 167.2 (C, arom), 164.8 (C=O), 132.2 (CH, arom), 128.4 (C, arom), 114.4 (CH, arom), 55.7 (CH_3), 42.2 (CH_2), 38.8 (CH_2), 14.2 (CH_3), 12.9 (CH_3).

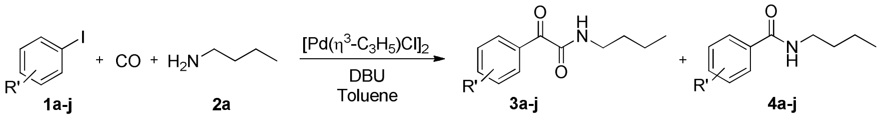
$PdCl_2(DBU)_2$ (5)

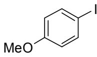
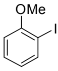
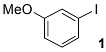
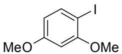
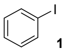
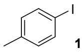
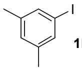
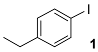
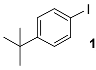


To a solution of $PdCl_2(PhCN)_2$ (300 mg, 0.79 mmol) in toluene was added 2,3,4,6,7,8,9,10-octahydropyrimido[1,2-a]azepine (DBU) (1.65 mmol). The solution was stirred overnight at room temperature. A yellow precipitate was formed which was filtered and washed with fresh toluene. The complex **5** was obtained in 71% yield (269 mg). **^{1}H NMR** ($CDCl_3$, 400 MHz, δ ppm): 3.57-3.56 (m, 4H, CH_2), 3.46-3.31 (m, 4H, CH_2), 3.20-3.18 (m, 4H, CH_2), 3.25-3.12 (m, 4 H, CH_2), 1.90 (br s, 4 H, CH_2), 1.78 (m, 4H, CH_2), 1.64 (br s, 4H, CH_2), 1.51 (br s, 4H, CH_2). **$^{13}C\{^1H\}$ NMR** ($CDCl_3$, 100.6 MHz, δ ppm): 163.5 (C=N), 53.8 (CH_2), 47.8 (CH_2), 38.9 (CH_2), 38.1 (CH_2), 29.6 (CH_2), 27.9 (CH_2), 24.4 (CH_2), 22.3 (CH_2). **HRMS** (ESI-TOF): *m/z*=486.1617, calcd for $[(M-Cl)+CH_3CN]^+$: 486.1611. Anal. Calcd for $C_{18}H_{32}Cl_2N_4Pd$: C, 44.87; H, 6.69; Cl, 14.72; N, 11.63; Pd, 22.09. Found: C, 44.76; H, 7.01; N, 11.69.

Table with the results obtained at 80ºC:

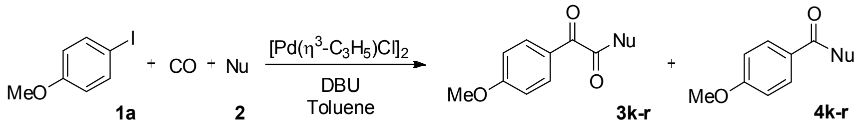
Table S1. Double carbonylation of different aryl iodies with *n*-butylamine.[a]

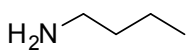
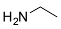
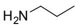
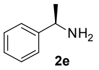
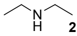
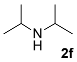
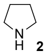
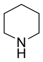
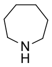


Entry	Aryl iodide	Conversion [%][b]	Selecitivity **3a-j** [%][c]
1	 **1a**	99	98
2	 **1b**	93	2
3	 **1c**	95	65
4	 **1d**	95	8
5	 **1e**	96	53
6	 **1f**	91	76
7	 **1h**	93	81
8	 **1i**	94	87
9	 **1j**	71	81

[a] [Pd(η^3-C$_3$H$_5$)Cl]$_2$ (0.005 mmol), aryl iodide (0.5 mmol), DBU (1 mmol), butylamine (1.2 mmol), toluene (5mL), CO (1 bar), 80ºC, 1h. [b] Determined by ^{1}H-NMR and GC-Mass spectroscopy.

Table S2. Double carbonylation of 1-iodo-*p*-methoxybenzene with different nucleophiles at 80ºC.[a]

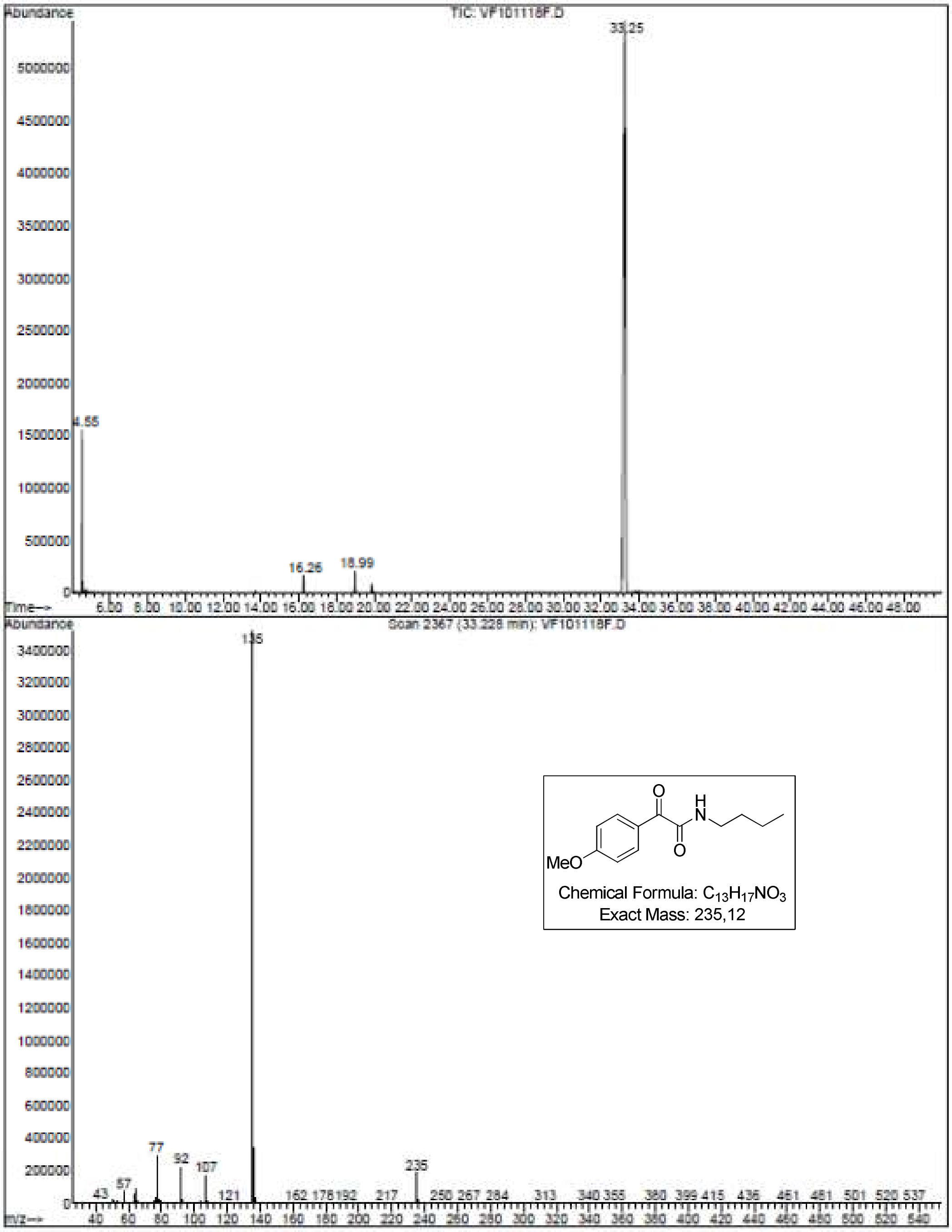


Entry	Nucleophile	Conversion [%][b]	Product **3a,k-r** Selecitivity [%][c]
1	 **2a**	99	**3a,** [98]
2	 **2b**	90	**3k,** [98]
3	 **2c**	93	**3l,** [94]
4	 **2e**	99	**3n,** [83]
5	 **2d**	81	**3o,** [60]
6	 **2f**	-	-
7	 **2g**	98	**3p,** [54]
8	 **2h**	98	**3q,** [80]
9	 **2i**	99	**3r,** [77]

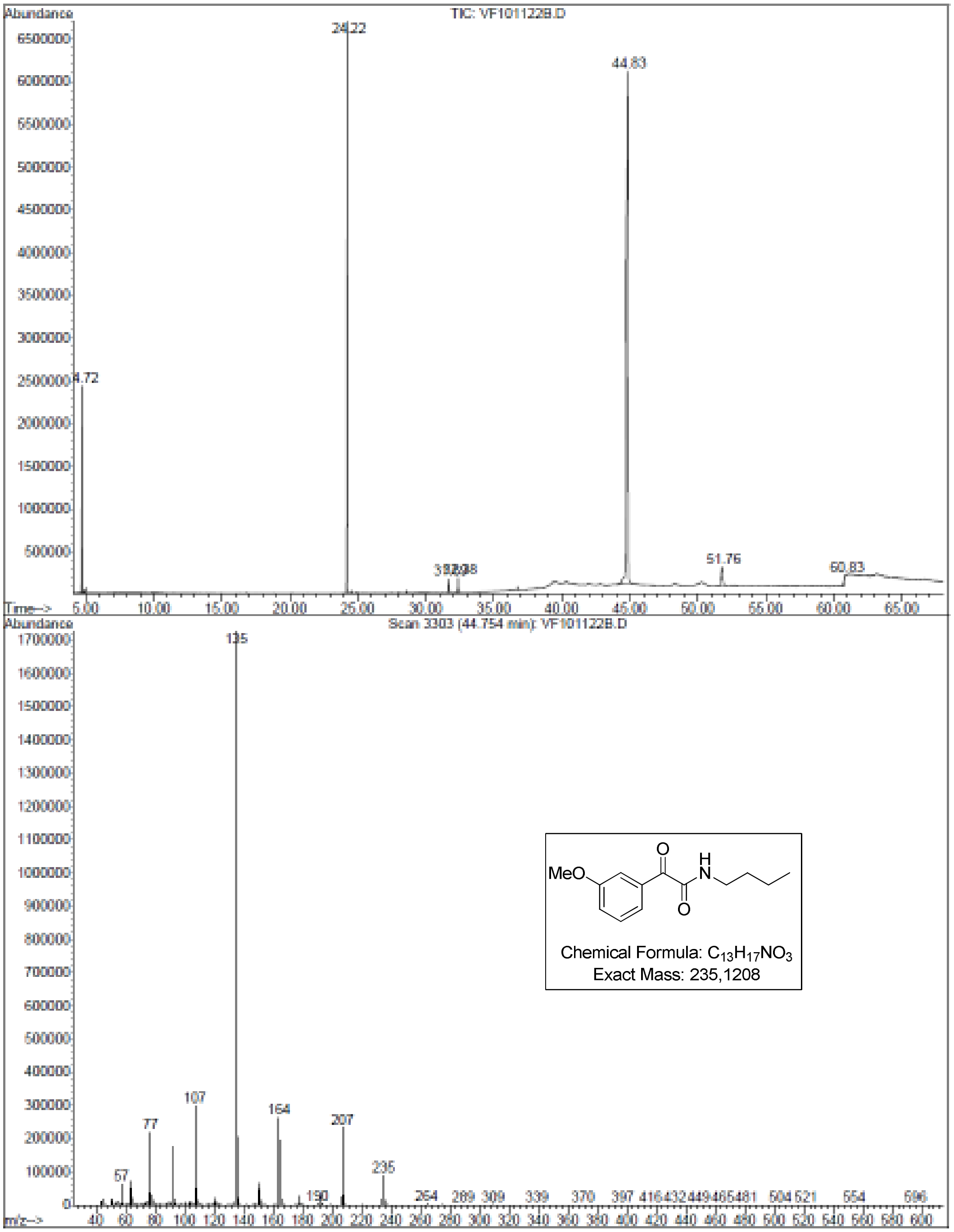
[a] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (0.005 mmol), 1-iodo-*p*-methoxybenzene (0.5 mmol), DBU (1 mmol), nucleophile (1.2 mmol), toluene (5mL), CO (1 bar), 80ºC, 1h. [b] Determined by ^{1}H-NMR and GC-Mass spectroscopy.

GC-MS chromatographs:

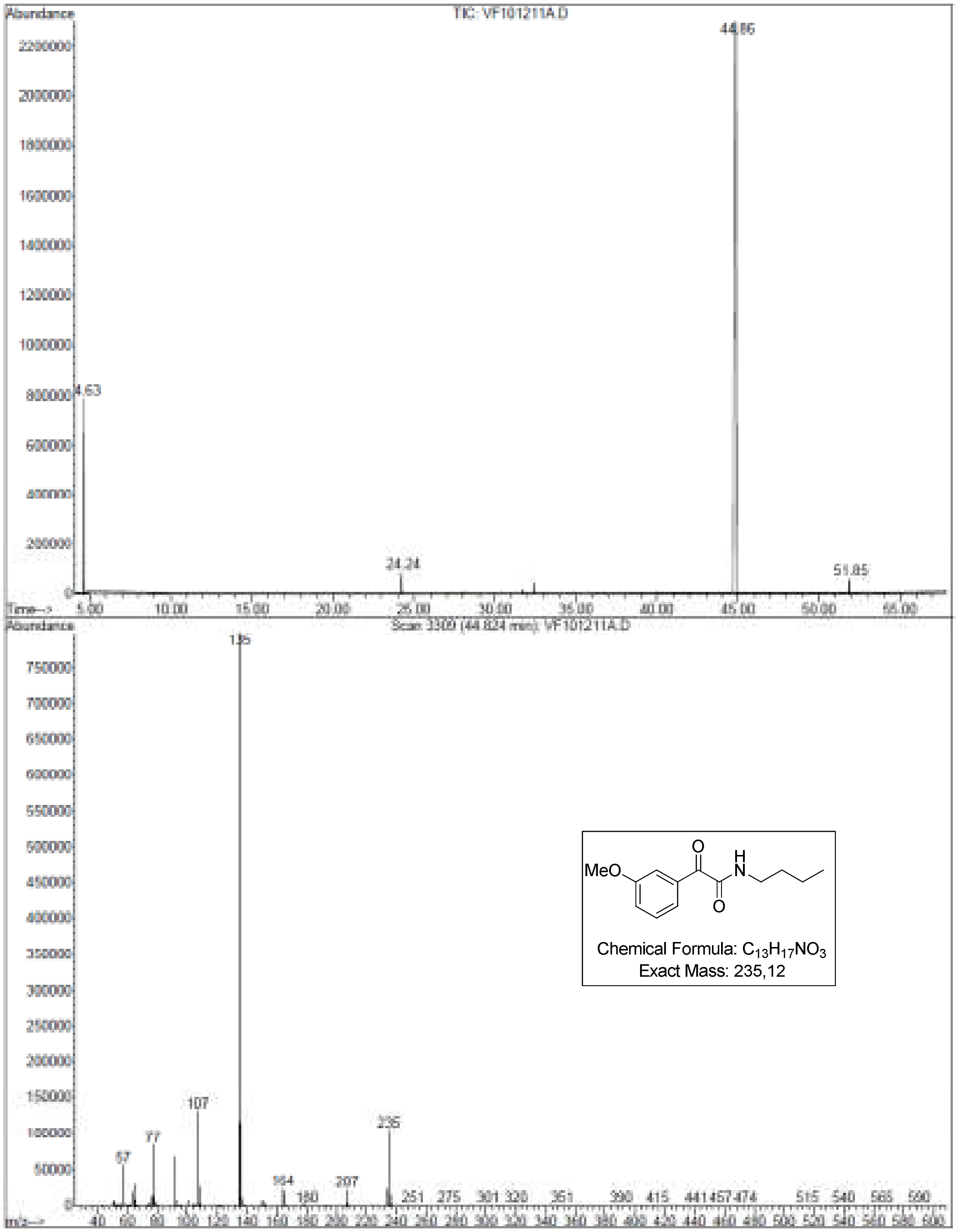
Compound 3a



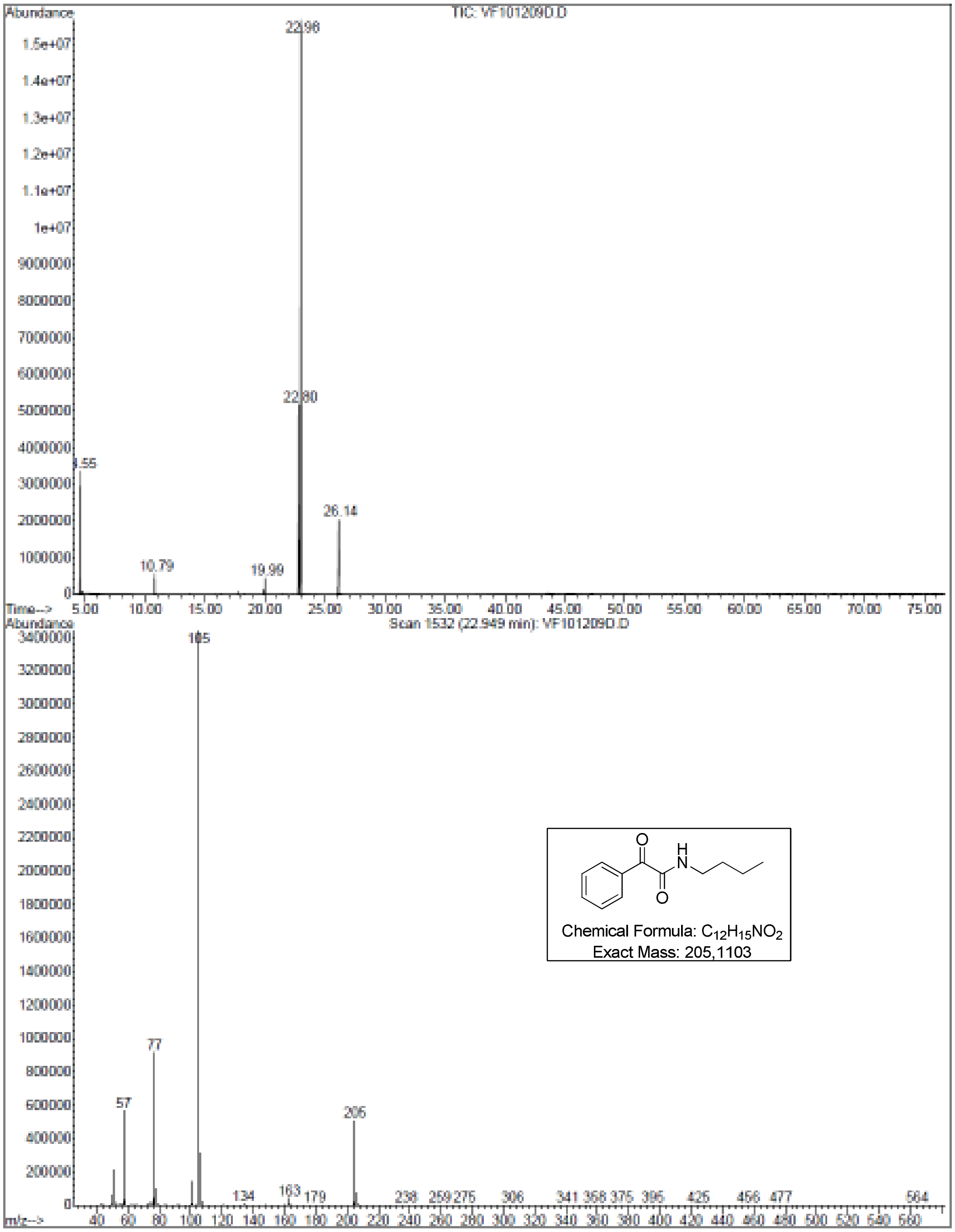
Compound 3c (Temperature=80ºC)



Compound 3c (Temperature=60ºC)



Compound 3e


Abundance
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1.3e+07
1.2e+07
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7000000
6000000
5000000
4000000
3000000
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4.55
26.14
10.79
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10.00
15.00
20.00
25.00
30.00
35.00
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45.00
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55.00
60.00
65.00
70.00
75.00
Abundance
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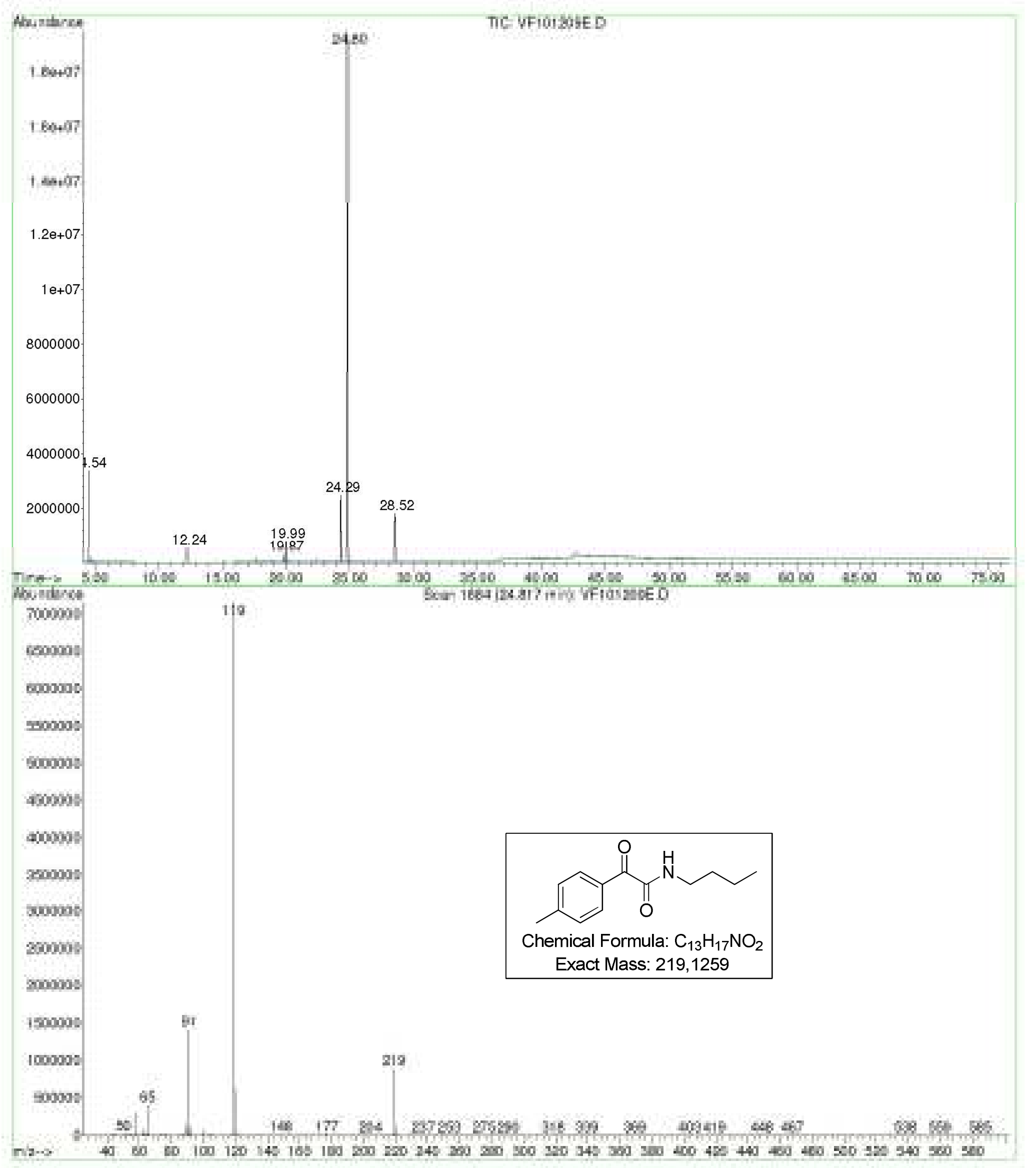
Exact Mass: 205,1103

Compound 3f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446
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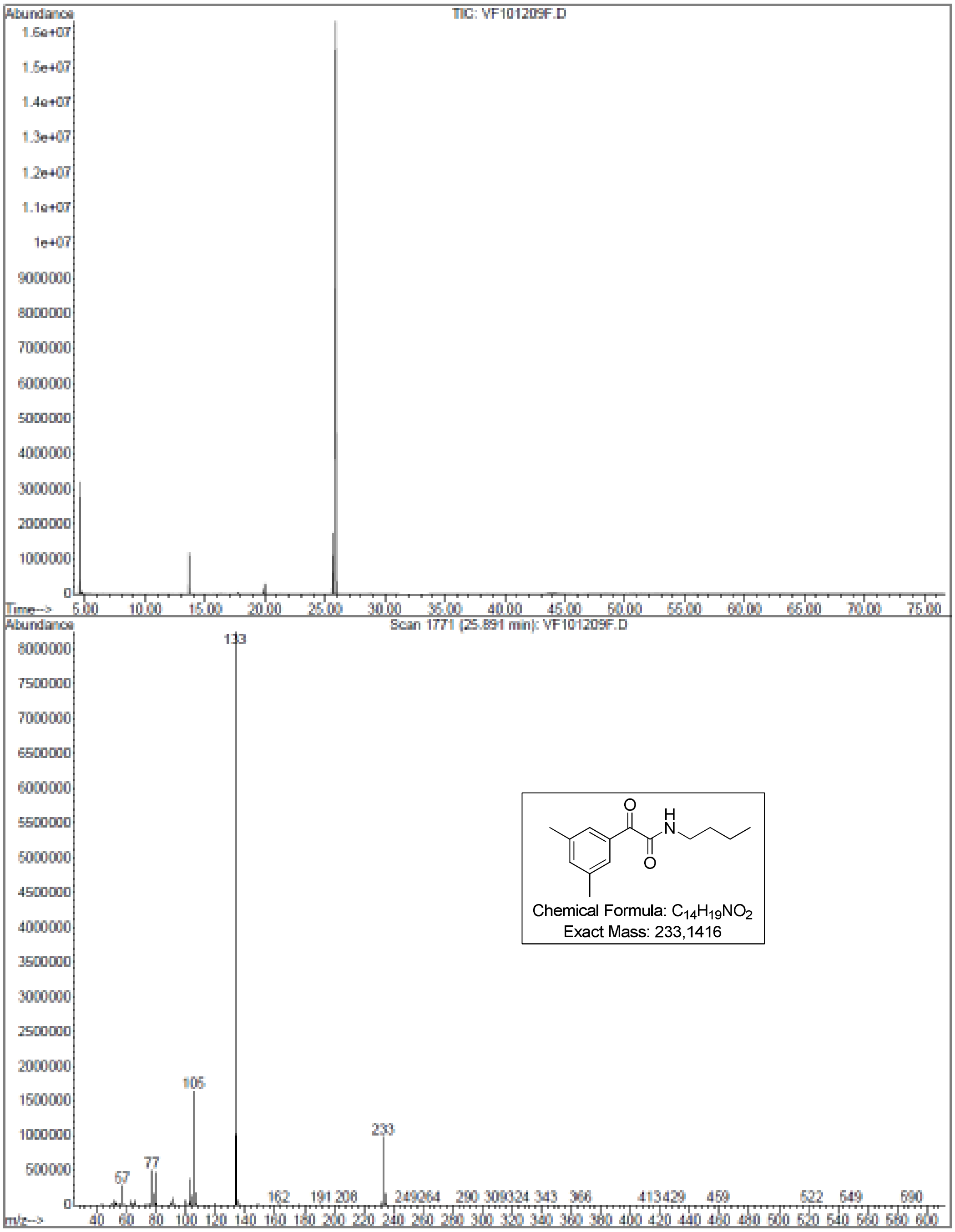
Exact Mass: 219,1259

Compound 3h


Abundance
TIC: VF101209F.D
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1e+07
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7000000
6000000
5000000
4000000
3000000
2000000
1000000
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15.00
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25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
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70.00
75.00
Abundance
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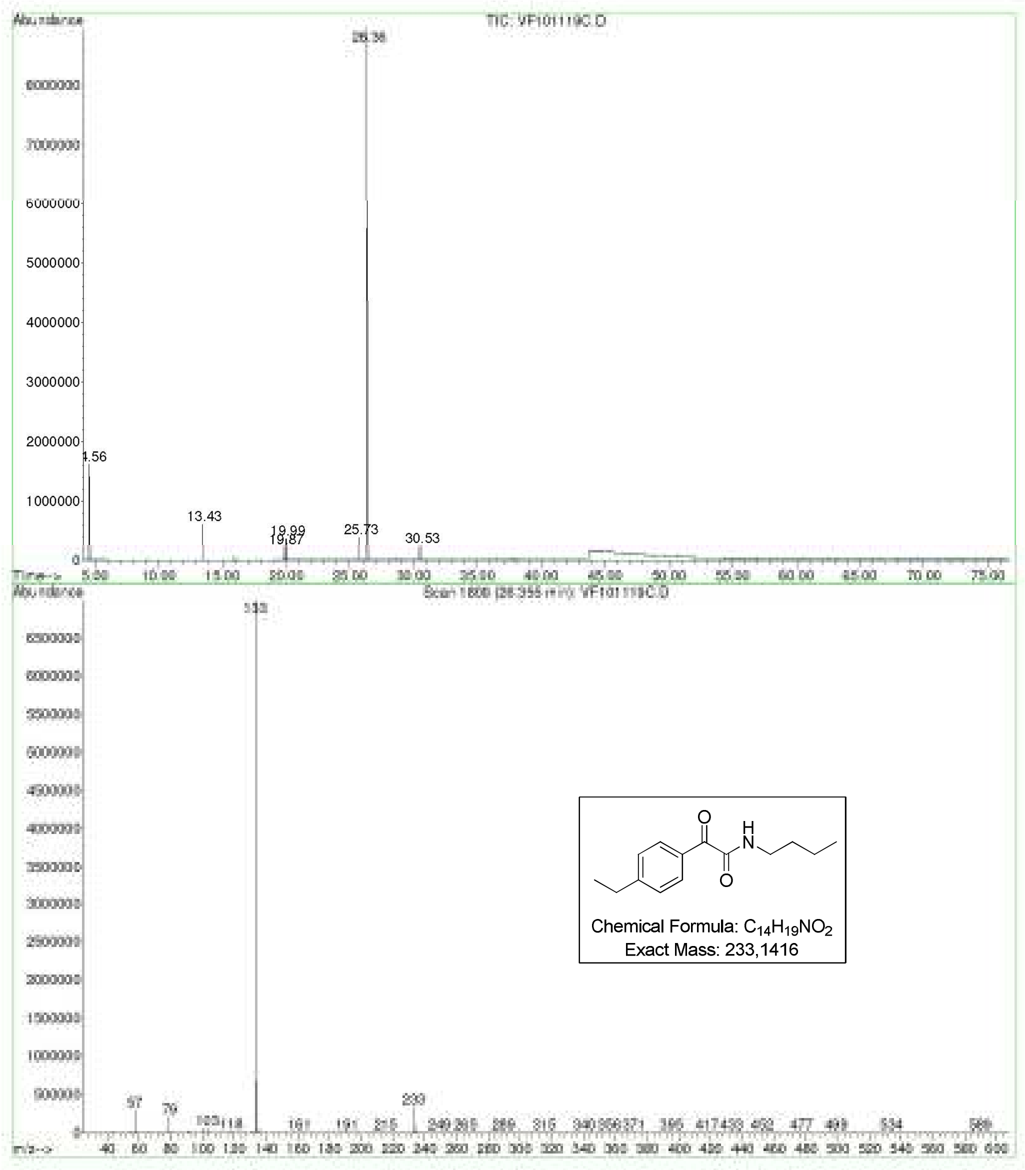
522
549
590
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
O
H
N
O
Chemical Formula: C14H19NO2
Exact Mass: 233,1416

Compound 3i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13.43
19.99
19.87
25.73
30.53
Time-->
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Abundance
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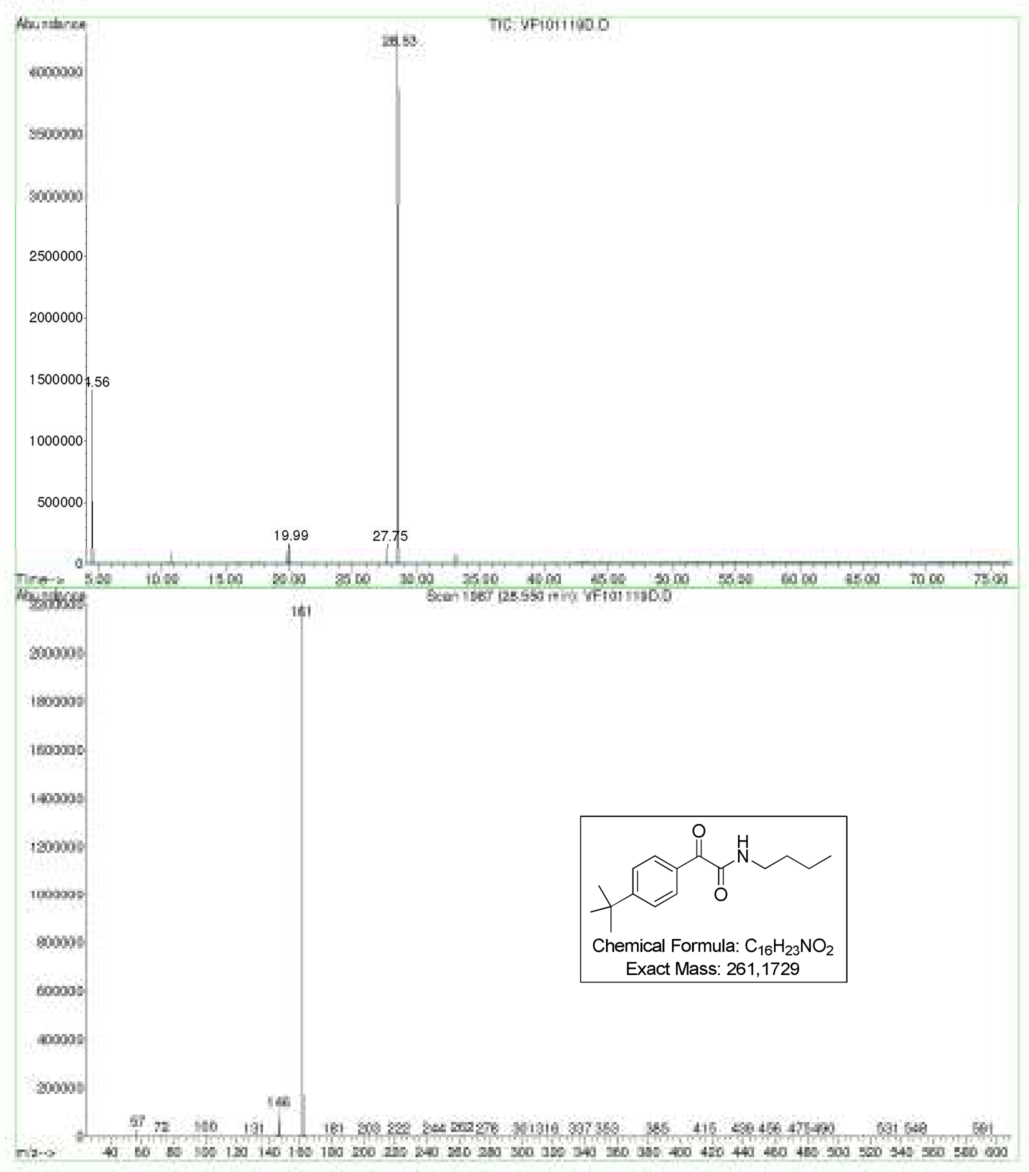
133
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
57
79
103
118
161
191
215
233
249
265
289
315
340
356
371
395
417
433
452
477
499
534
589
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600
O
H
N
O
Chemical Formula: C14H19NO2
Exact Mass: 233,1416

Compound 3j


Abundance
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2500000
2000000
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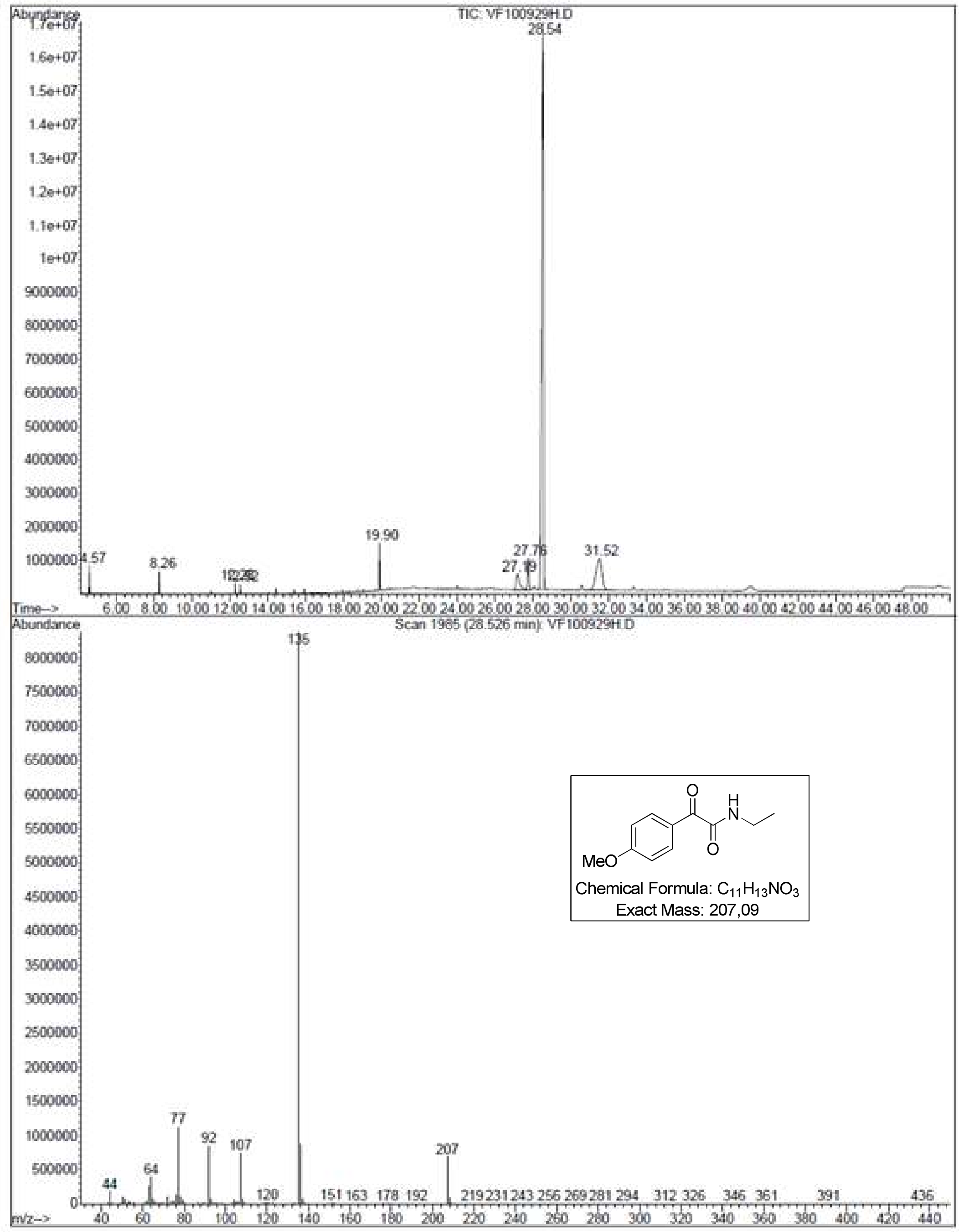
4.56
1000000
500000
19.99
27.75
0
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
Abundance
Scan 1987 (28.550 min): VF101119D.D
161
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
57
72
100
131
146
181
203
222
244
262
276
301
316
337
353
385
415
438
456
475
490
531
548
591
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
O
H
N
O
Chemical Formula: $C_{16}H_{23}NO_2$
Exact Mass: 261,1729

Compound 3m


Abundance
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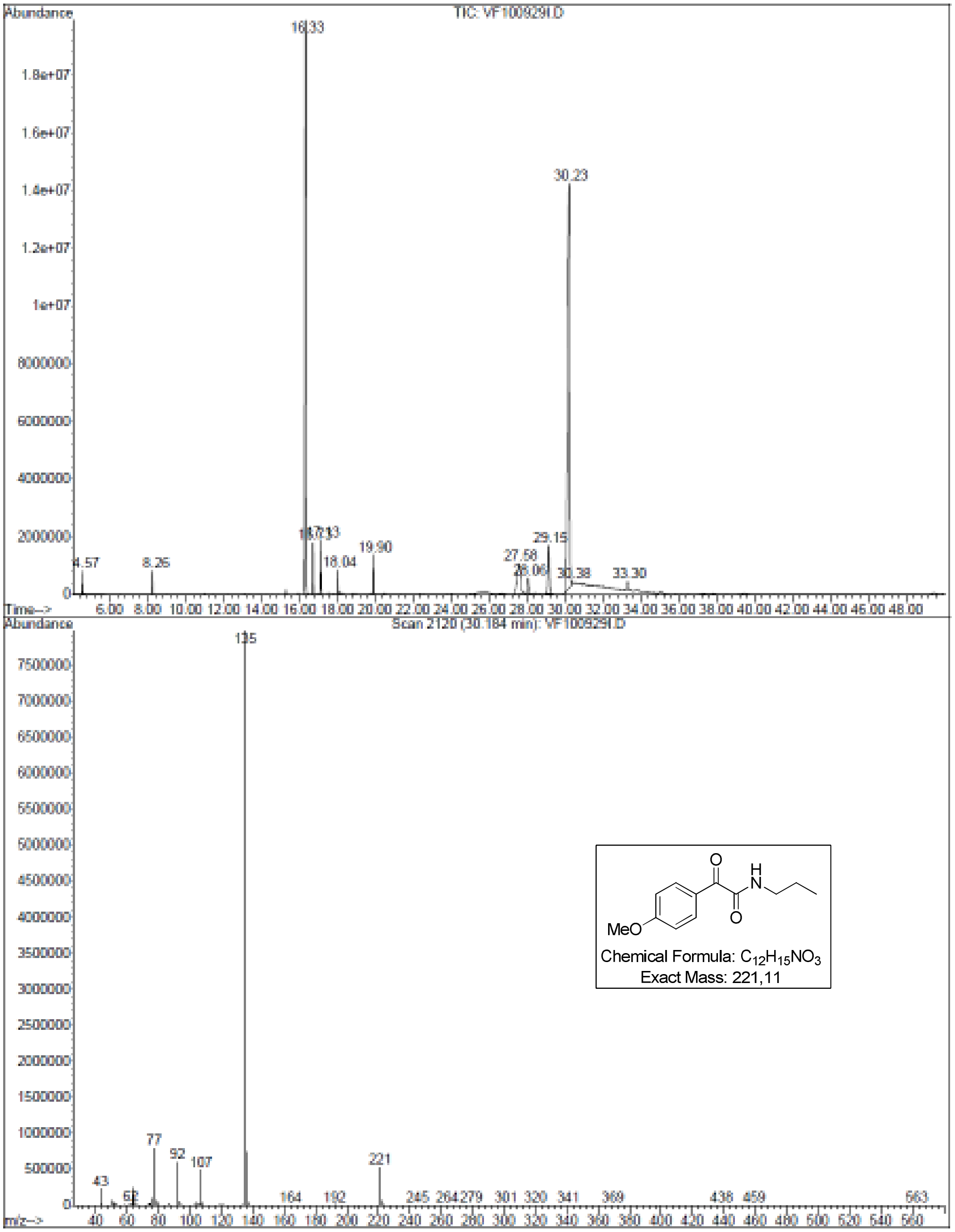
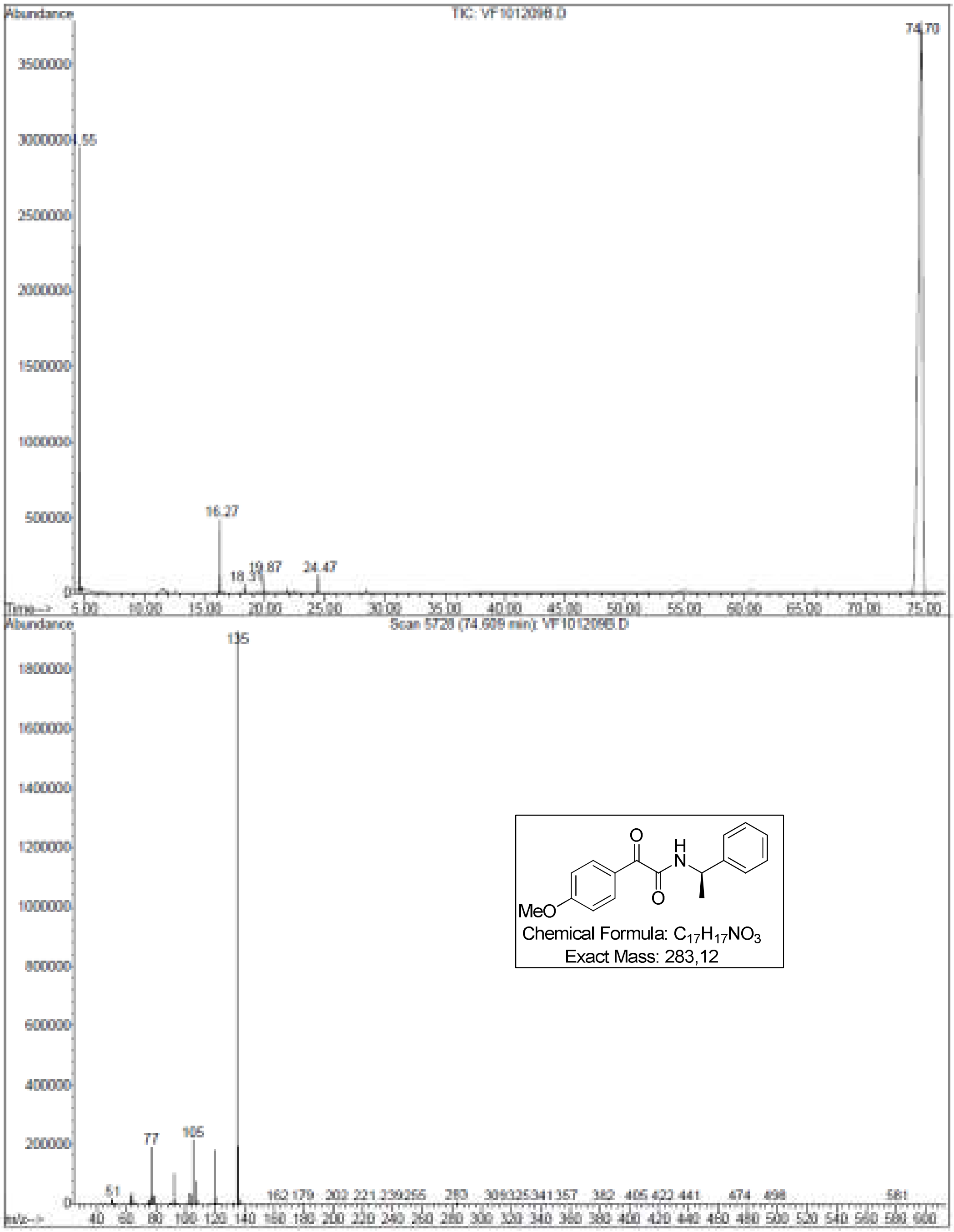
1.6e+07
1.5e+07
1.4e+07
1.3e+07
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
4.57
8.26
19.90
27.19
27.76
31.52
Time-->
6.00 8.00 10.00 12.00 14.00 16.00 18.00 20.00 22.00 24.00 26.00 28.00 30.00 32.00 34.00 36.00 38.00 40.00 42.00 44.00 46.00 48.00
Abundance
Scan 1985 (28.526 min): VF100929H.D
135
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
44
64
77
92
107
120
151 163 178 192
207
219 231 243 256 269 281 294 312 326 346 361 391 436
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440
MeO
O
H
N
O
Chemical Formula: C11H13NO3
Exact Mass: 207,09

Compound 3n


Abundance
TIC: VF100929I.D
16.33
30.23
4.57
8.26
18.04
19.90
27.58
28.06
29.15
30.38
33.30
Time-->
Abundance
Scan 2120 (30.184 min): VF100929I.D
135
43
77
92
107
221
164
192
245
264
279
301
320
341
369
438
459
563
m/z-->
MeO
O
H
N
O
Chemical Formula: $C_{12}H_{15}NO_3$
Exact Mass: 221,11

Compound 3p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4.55
16.37
18.31
19.87
24.47
Time-->
Abundance
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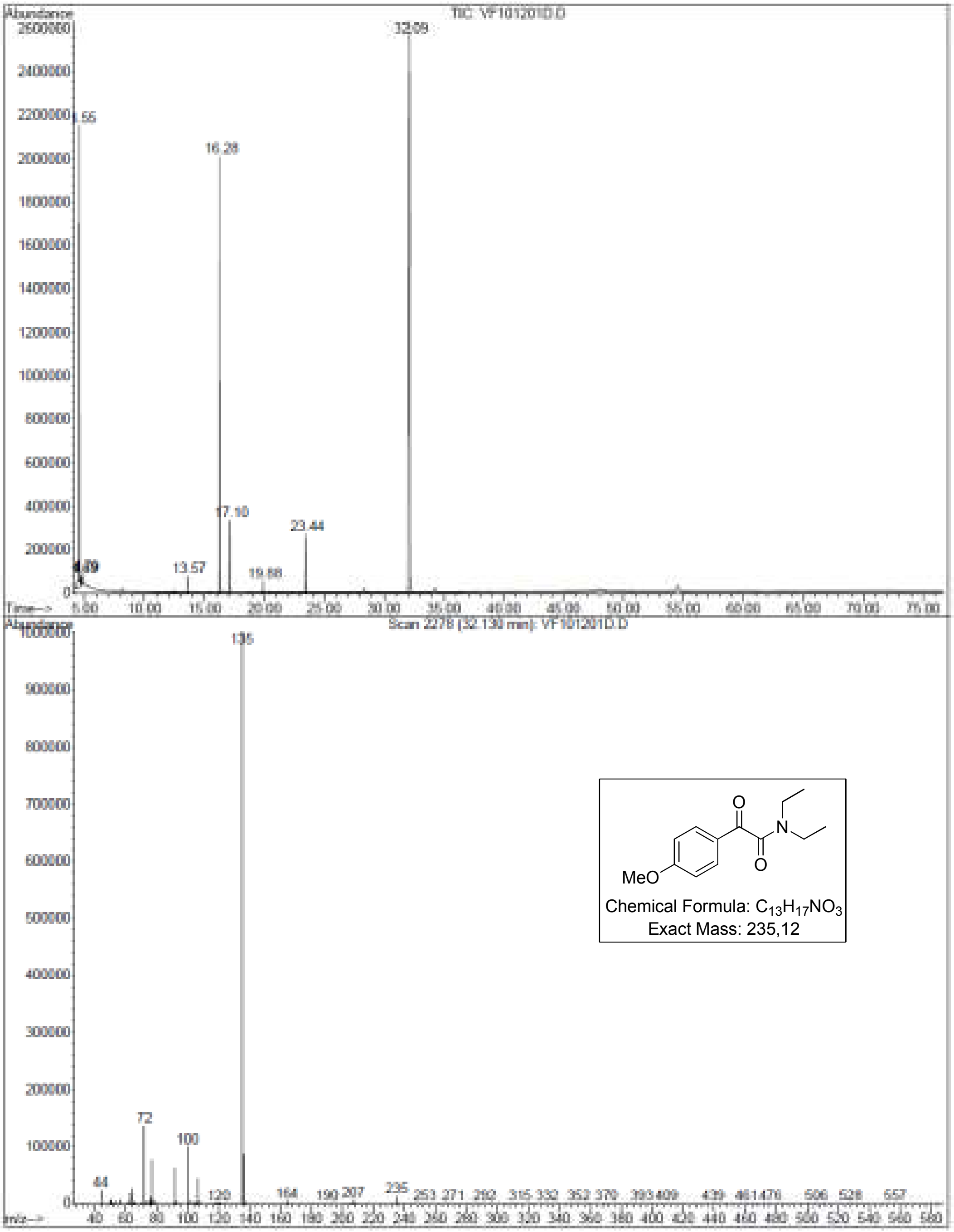
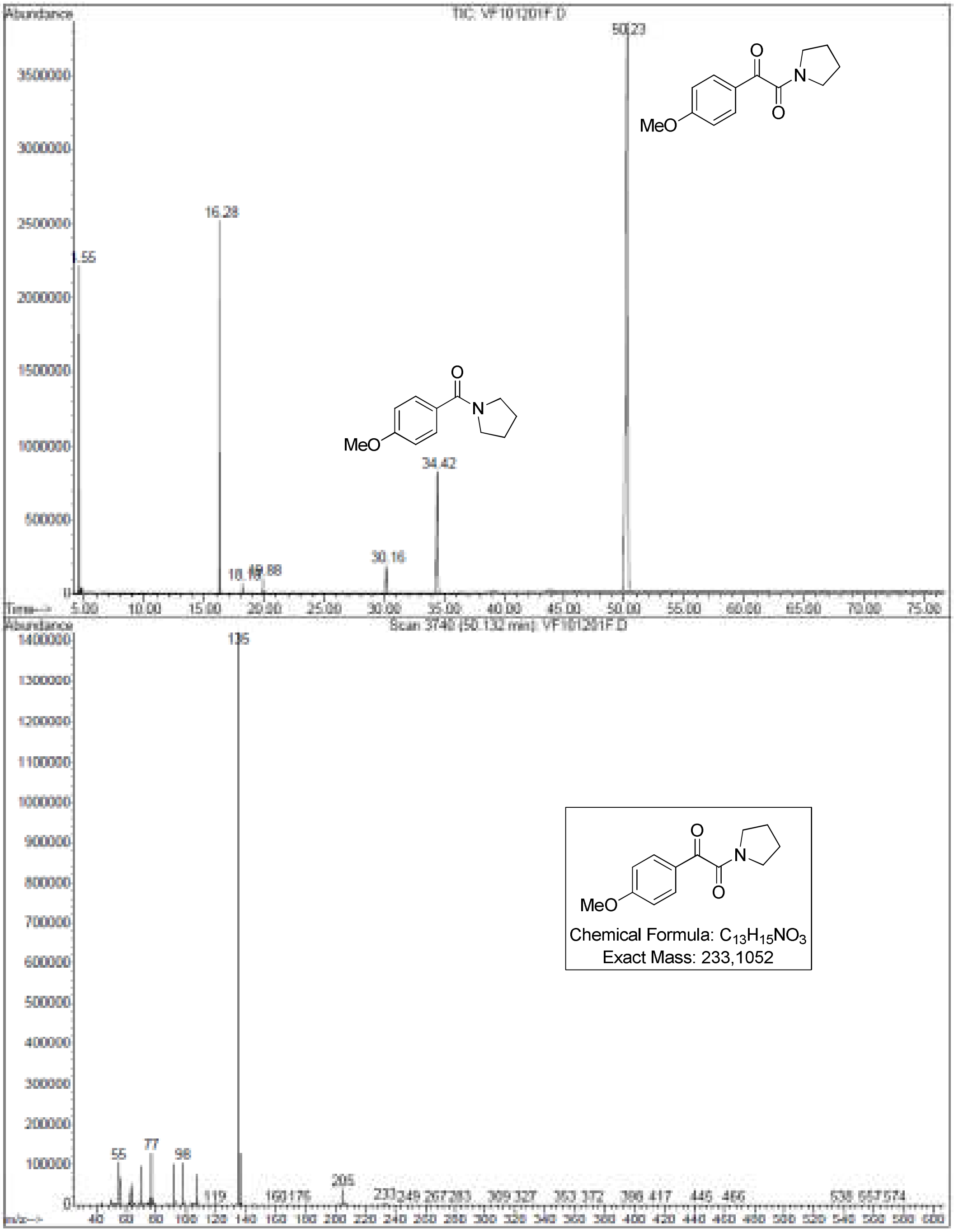
135
77
105
51
162 179 202 221 239 255 283 309 325 341 357 382 405 422 441 474 498 581
m/z-->
MeO
O
H
N
O
Chemical Formula: $C_{17}H_{17}NO_3$
Exact Mass: 283,12

Compound 3q


Abundance
TIC: VF101201D.D
32.09
4.55
16.28
17.10
23.44
13.57
19.88
Time-->
Abundance
Scan 2278 (32.130 min): VF101201D.D
135
72
100
44
120
164
190
207
235
m/z-->
MeO
O
N
O
Chemical Formula: $C_{13}H_{17}NO_3$
Exact Mass: 235,12

Compound 3r


Abundance
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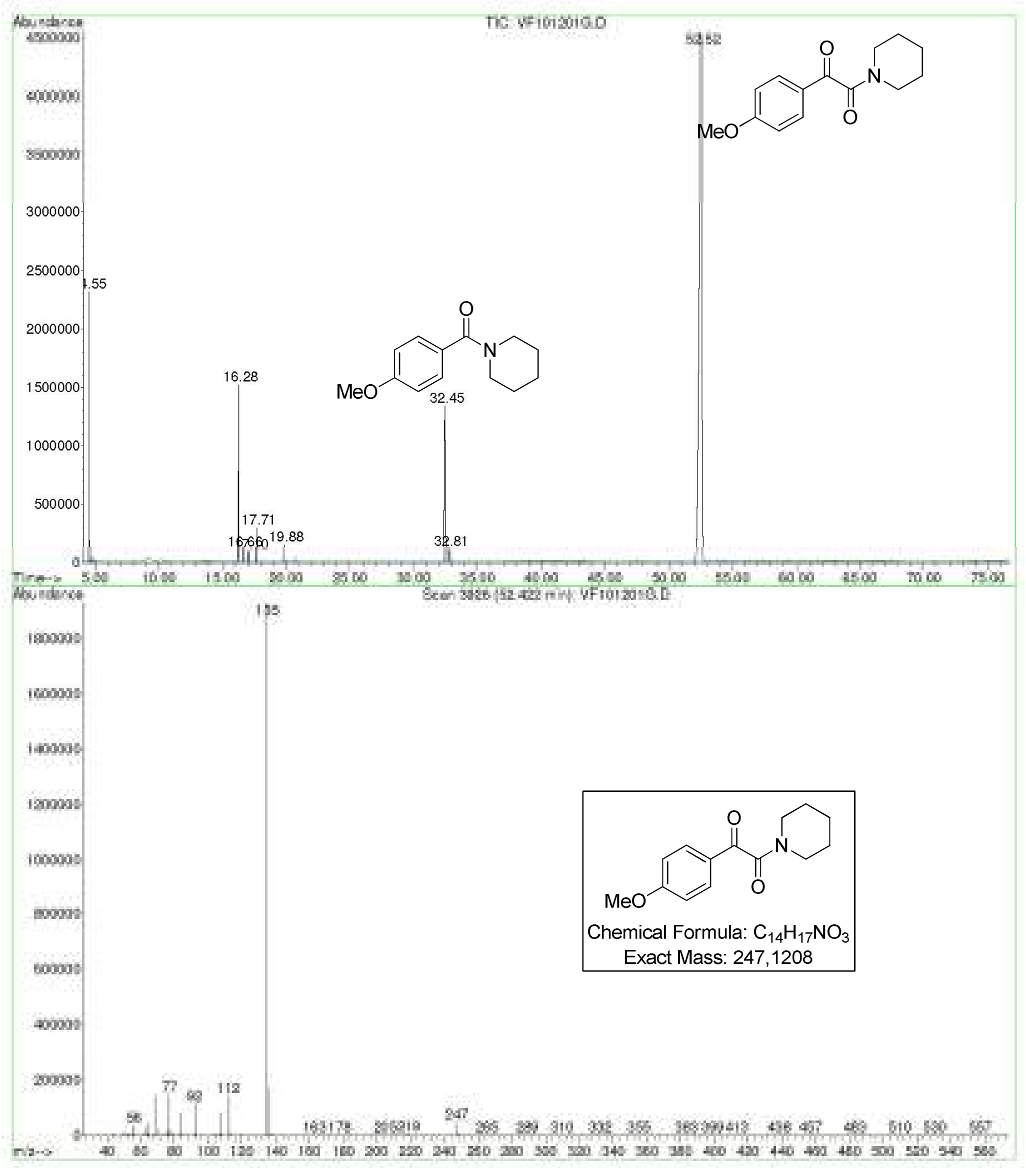
3000000
2500000
2000000
1500000
1000000
500000
0
16.28
1.55
18.18
19.88
30.16
34.42
O
N
MeO
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
Abundance
Scan 3740 (50.132 min): VF101201F.D
135
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
55
77
98
119
160 176
205
233 249 267 283
309 327
353 372
398 417
446 466
538 557 574
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560
580
600
Chemical Formula: $C_{13}H_{15}NO_3$
Exact Mass: 233,1052

Compound 3s


Abundance
TIC: VF101201G.D
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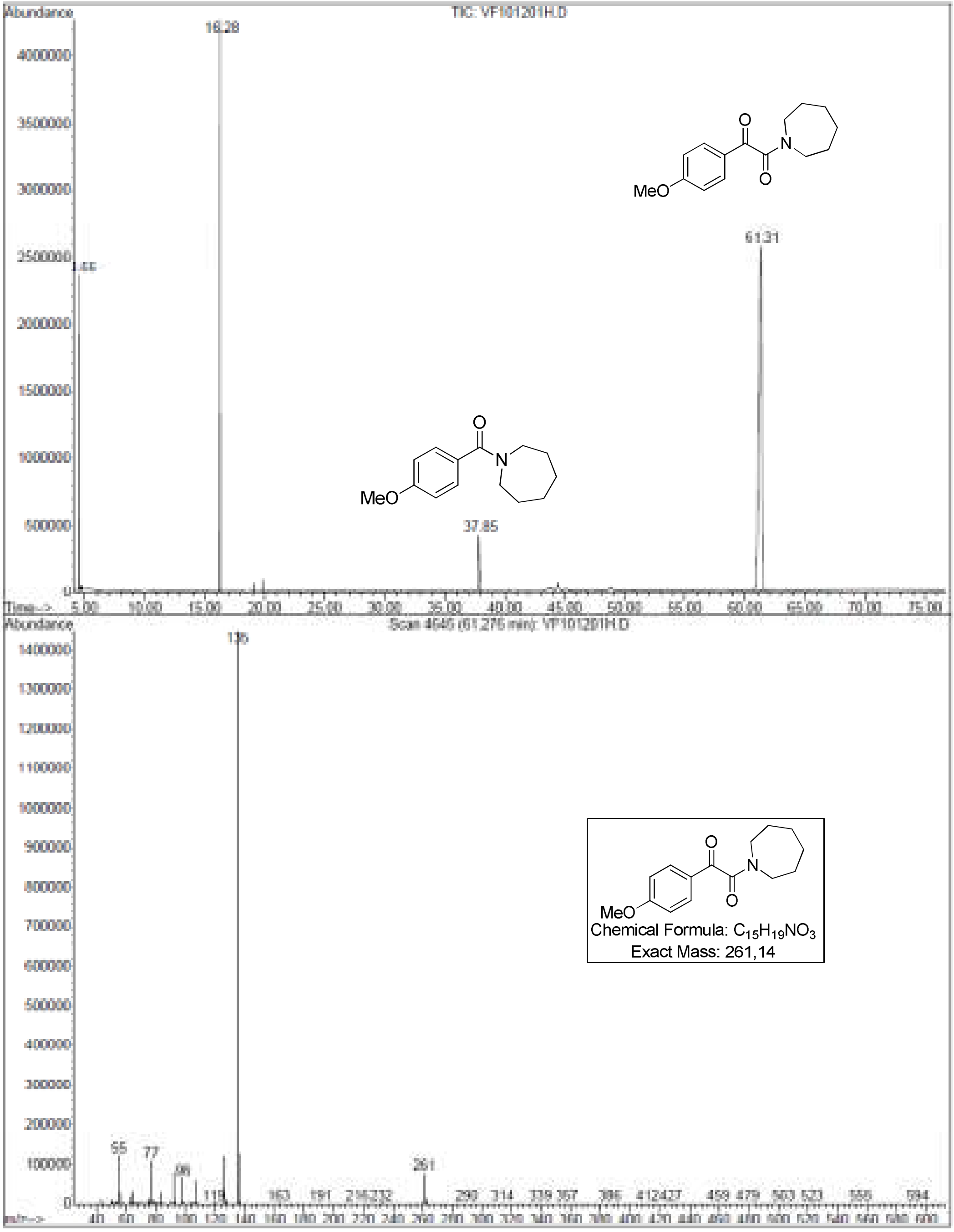
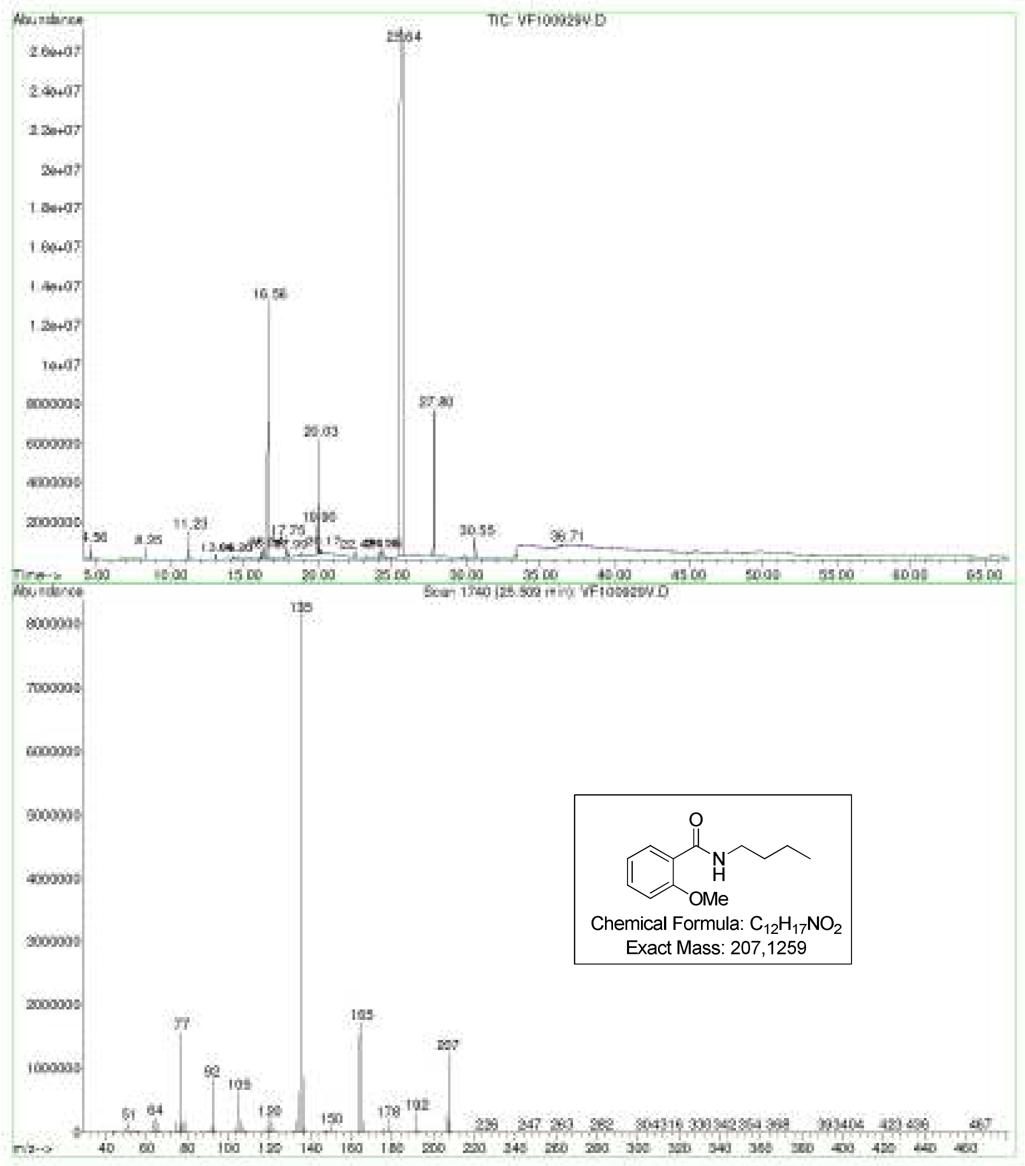
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.55
16.28
16.66
17.71
19.88
32.45
32.81
52.52
MeO
O
N
O
Time-->
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
50.00
55.00
60.00
65.00
70.00
75.00
Abundance
Scan 3826 (52.422 min): VF101201G.D
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
135
56
77
92
112
163
178
205
219
247
265
289
310
332
355
383
399
413
438
457
483
510
530
557
m/z-->
40
60
80
100
120
140
160
180
200
220
240
260
280
300
320
340
360
380
400
420
440
460
480
500
520
540
560
Chemical Formula: $C_{14}H_{17}NO_3$
Exact Mass: 247,1208

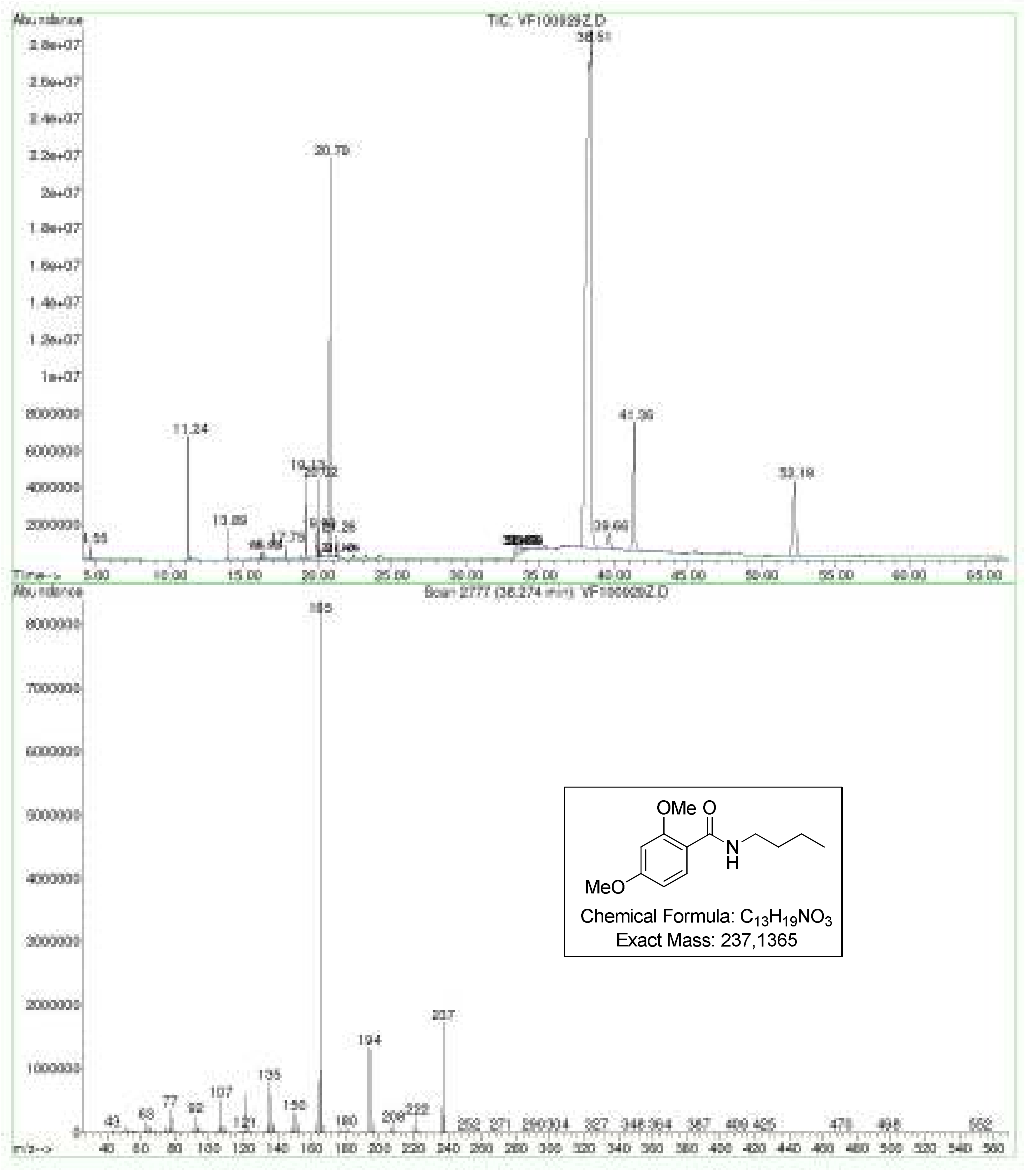
Compound 3t


Abundance
TIC: VF101201H.D
16.28
1.66
37.85
61.31
MeO
O
N
Time-->
5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00 65.00 70.00 75.00
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Abundance
Scan 4645 (61.276 min): VF101201H.D
135
55
77
98
119
163
191
216232
261
290
314
339 367
386
412427
459 479
503 523
556
594
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600
Chemical Formula: C15H19NO3
Exact Mass: 261,14

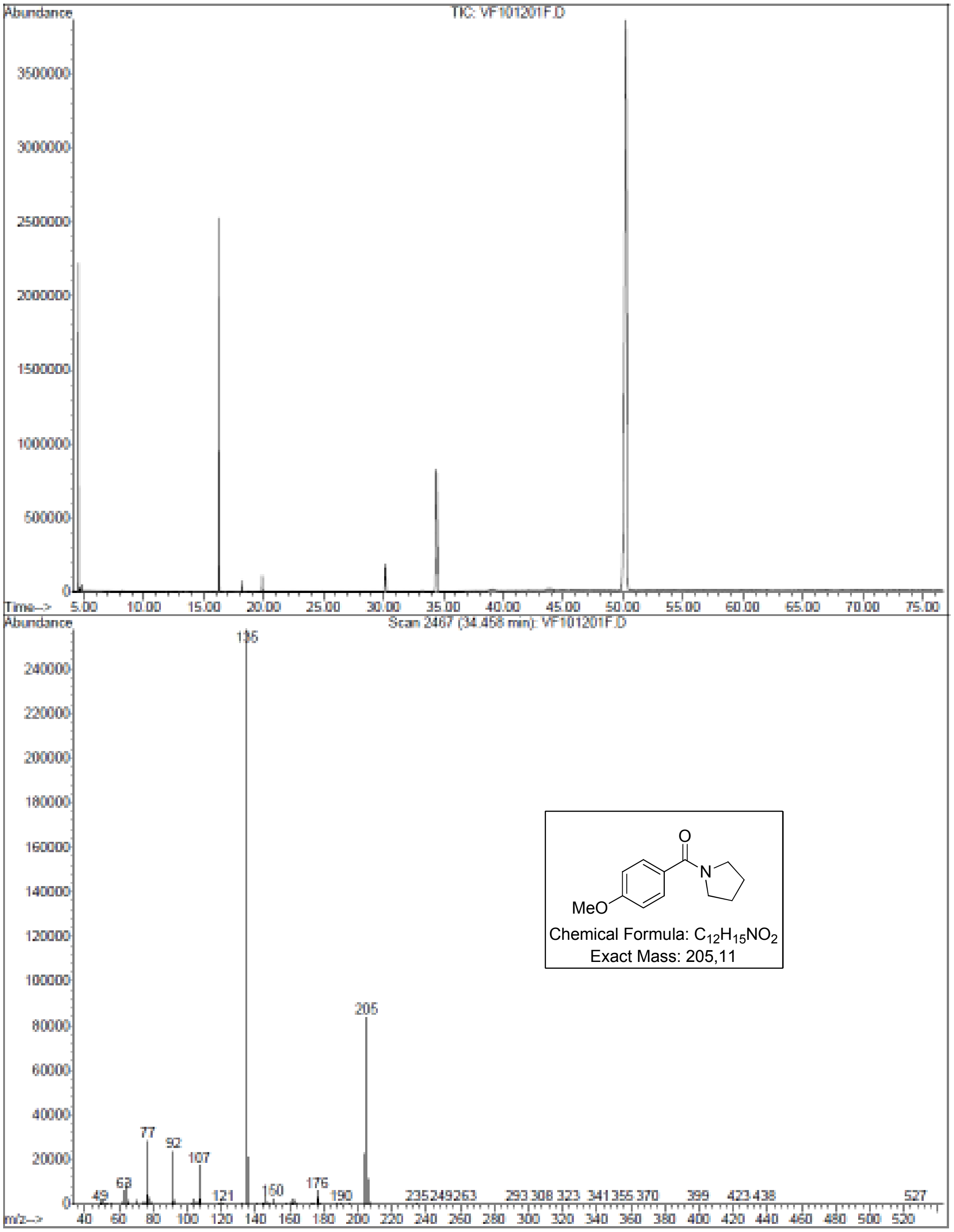
Compound 4b


Abundance
TIC: VF100929V.D
25.84
16.56
27.80
20.03
19.90
11.23
30.55
36.71
4.56
8.25
Time-->
Abundance
Scan 1740 (25.909 min): VF100929V.D
135
77
165
207
92
105
51
64
120
150
178
192
m/z-->
O
N
H
OMe
Chemical Formula: $C_{12}H_{17}NO_2$
Exact Mass: 207,1259

Compound 4d


Abundance
TIC: VF100929Z.D
38.51
20.79
11.24
41.36
52.19
19.13
20.72
13.89
17.75
21.26
39.60
4.55
Time-->
Scan 2777 (38.274 min): VF100929Z.D
165
237
194
135
107
77
92
63
43
121
150
180
208
223
252
271
290
304
327
348
364
387
408
425
470
498
552
m/z-->
OMe O
N
H
MeO
Chemical Formula: $C_{13}H_{19}NO_3$
Exact Mass: 237,1365

Compound 4r


Abundance
TIC: VF101201F.D
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3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
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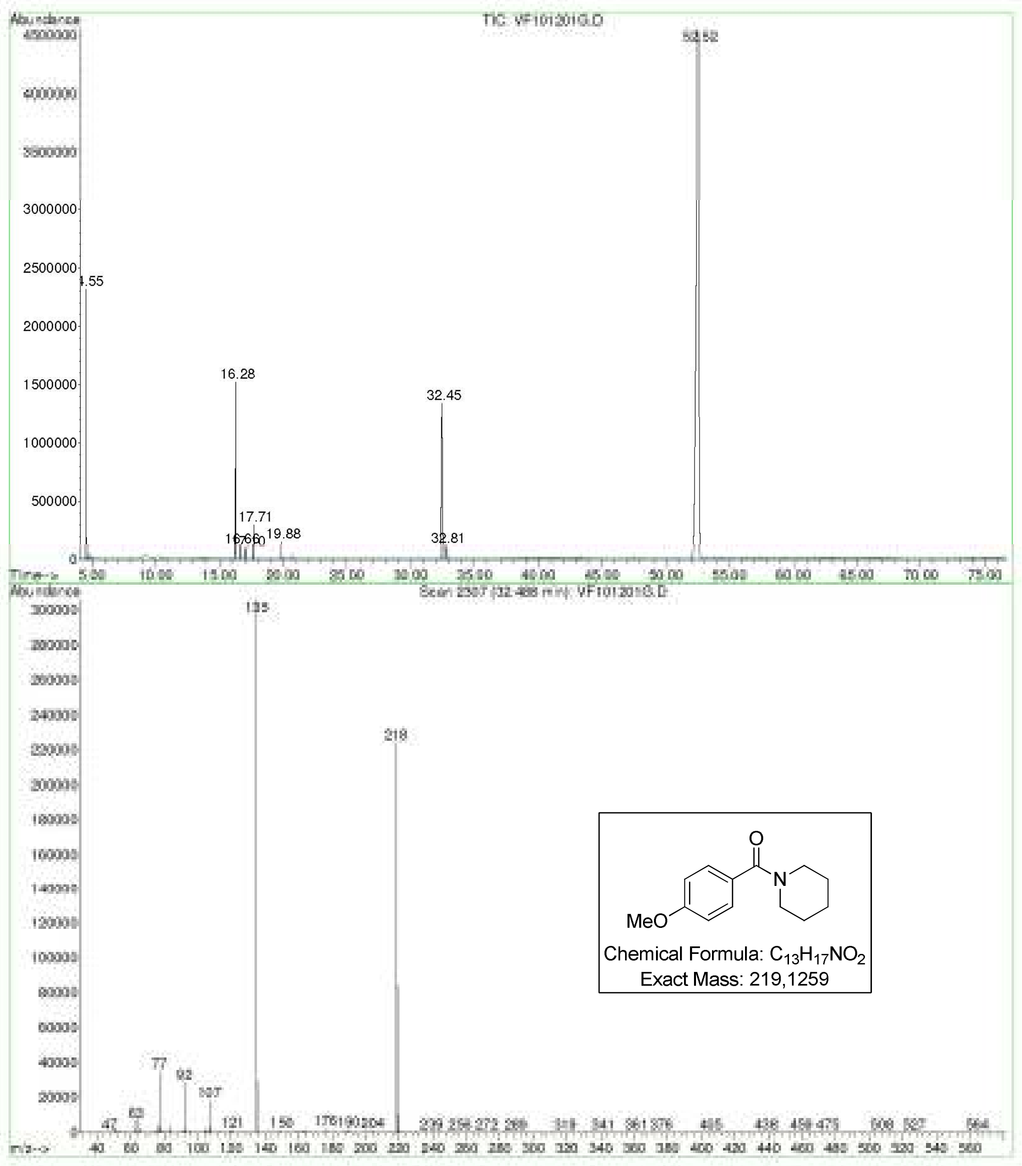
Abundance
Scan 2467 (34.458 min): VF101201F.D
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
135
205
77
92
107
63
49
121
150
176
190
235 249 263
293 308 323
341 355 370
399
423 438
527
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520
O
N
MeO
Chemical Formula: $C_{12}H_{15}NO_2$
Exact Mass: 205,11

Compound 4s


Abundance
TIC: VF101201G.D
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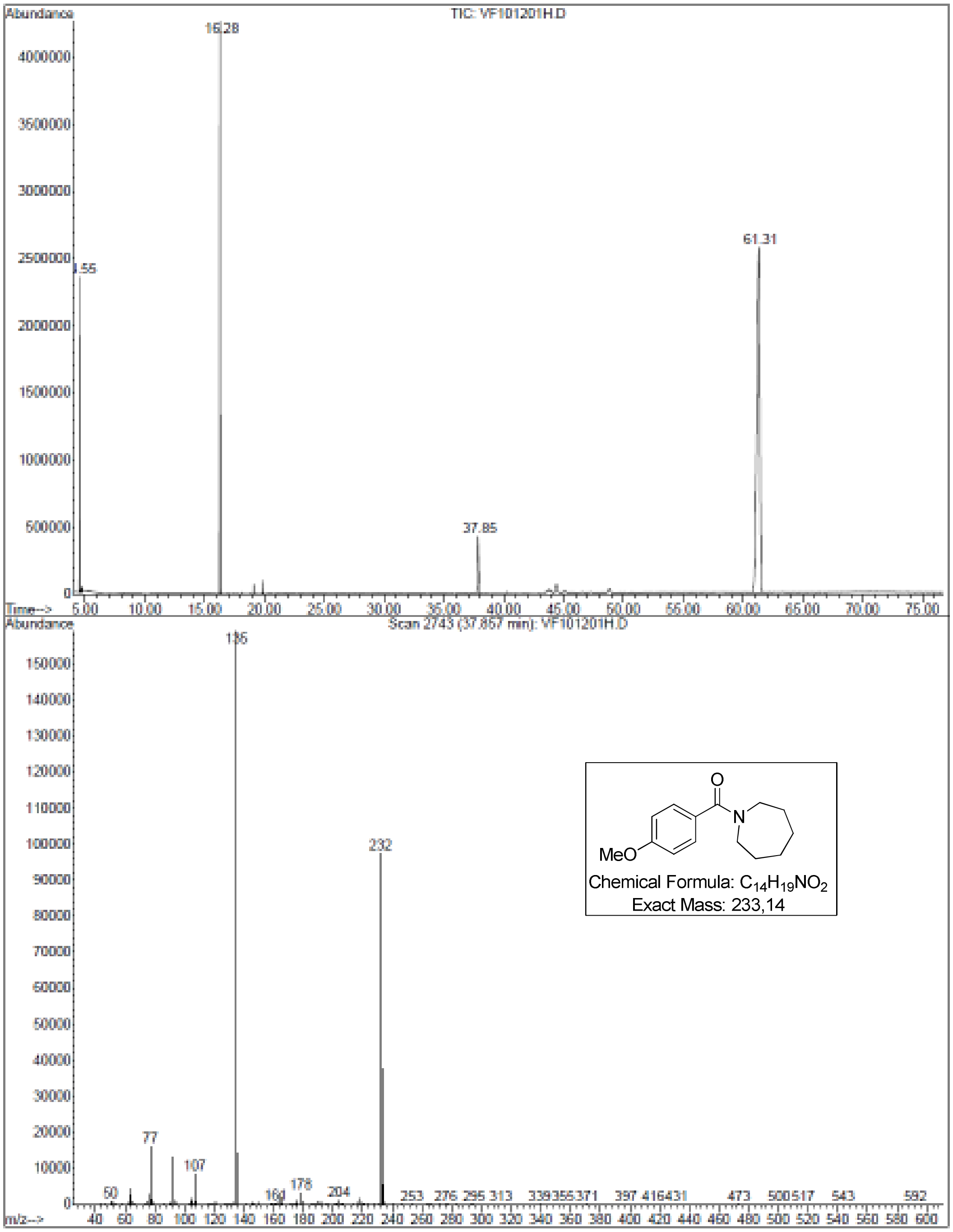
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
4.55
16.28
16.66
17.71
19.88
32.45
32.81
52.52
Time-->
5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00 65.00 70.00 75.00
Abundance
Scan 2507 (32.488 min): VF101201G.D
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
135
218
77
92
107
63
47
121
150
176
190
204
239 258 272 288 319 341 361 376 405 438 458 475 508 527 564
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560
O
N
MeO
Chemical Formula: $C_{13}H_{17}NO_2$
Exact Mass: 219,1259

Compound 4t


Abundance
TIC: VF101201H.D
16.28
4.55
61.31
37.85
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
5.00 10.00 15.00 20.00 25.00 30.00 35.00 40.00 45.00 50.00 55.00 60.00 65.00 70.00 75.00
Abundance
Scan 2743 (37.857 min): VF101201H.D
135
232
77
107
50
164
178
204
253 276 295 313 339 355 371 397 416 431 473 500 517 543 592
150000 140000 130000 120000 110000 100000 90000 80000 70000 60000 50000 40000 30000 20000 10000 0
m/z-->
40 60 80 100 120 140 160 180 200 220 240 260 280 300 320 340 360 380 400 420 440 460 480 500 520 540 560 580 600
O
N
MeO
Chemical Formula: $C_{14}H_{19}NO_2$
Exact Mass: 233,14

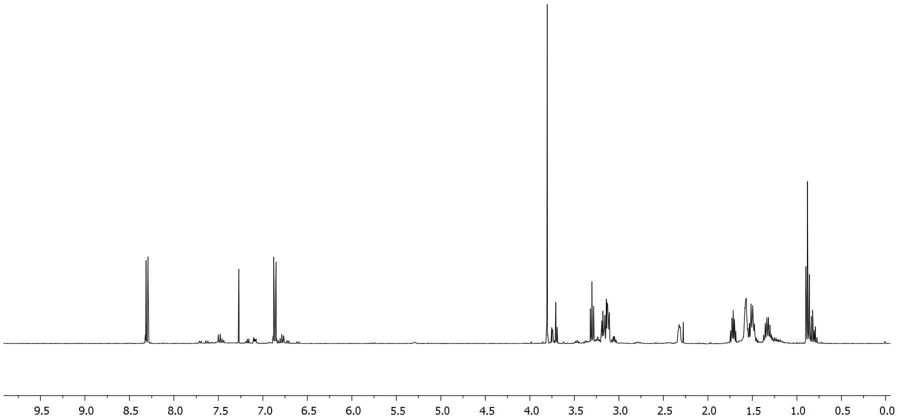


Figure 1. ^{1}H NMR of *N*-butyl-2-(4-methoxyphenyl)-2-oxoacetamide reaction crude (**3a**).

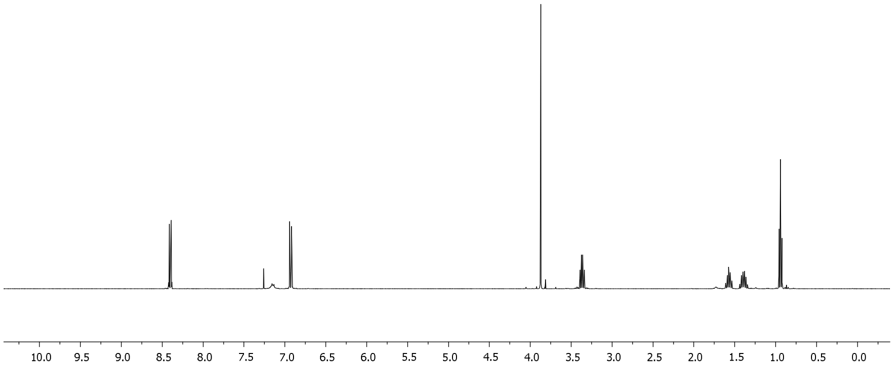


Figure 2. ^{1}H NMR of *N*-butyl-2-(4-methoxyphenyl)-2-oxoacetamide (**3a**).

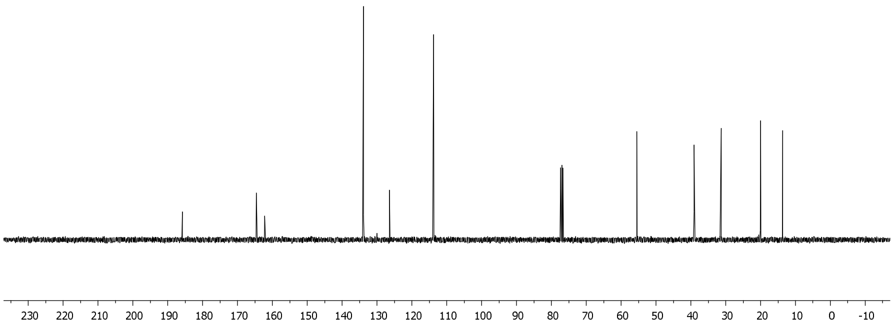


Figure 3. ^{13}C-{^{1}H} NMR of *N*-butyl-2-(4-methoxyphenyl)-2-oxoacetamide (**3a**).

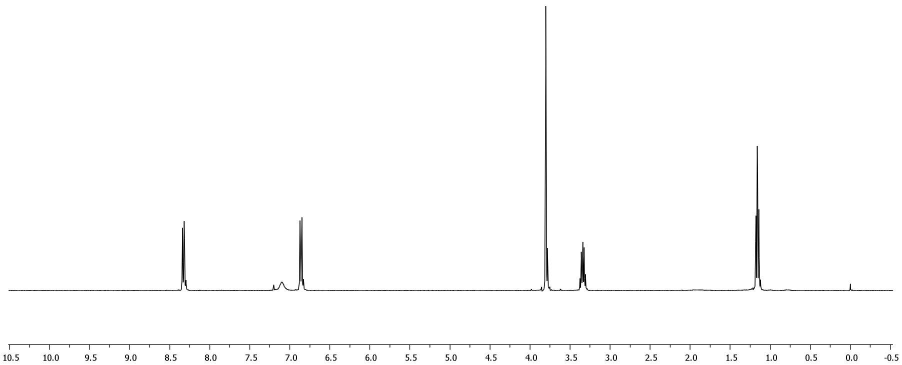


Figure 4. ^{1}H NMR of *N*-ethyl-2-(4-methoxyphenyl)-2-oxoacetamide (**3m**).

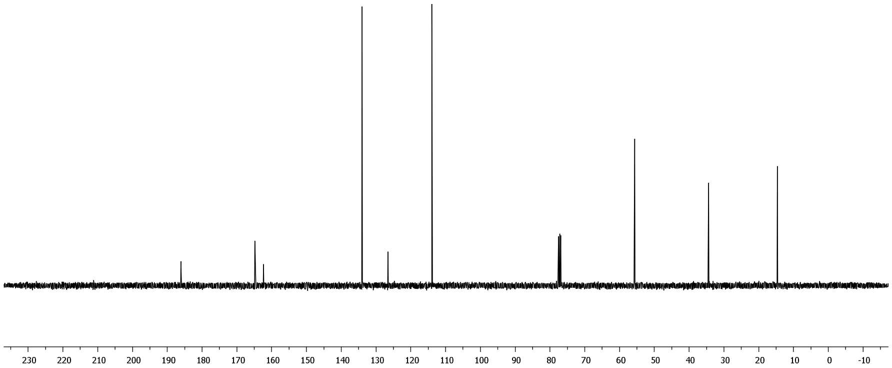


Figure 5. ^{13}C-{^{1}H} NMR of *N*-ethyl-2-(4-methoxyphenyl)-2-oxoacetamide (**3m**).

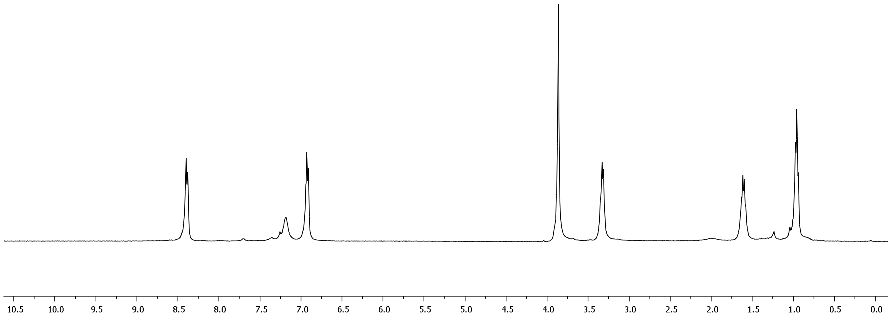


Figure 6. ^{1}H NMR of 2-(4-methoxyphenyl)-2-oxo-*N*-propylacetamide (**3n**).

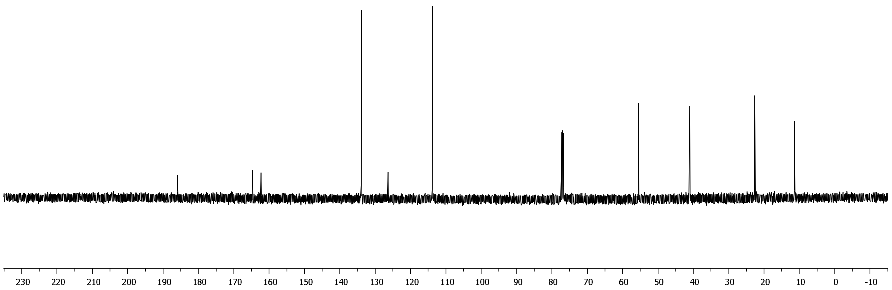


Figure 7. ^{13}C-{^{1}H} NMR of 2-(4-methoxyphenyl)-2-oxo-*N*-propylacetamide (**3n**).

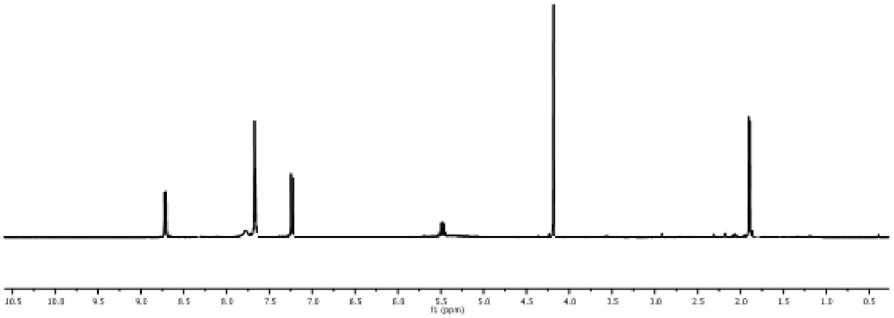


Figure 8. ^{1}H NMR of 2-(4-methoxyphenyl)-2-oxo-*N*-(1-phenylethyl)acetamide (**3p**).

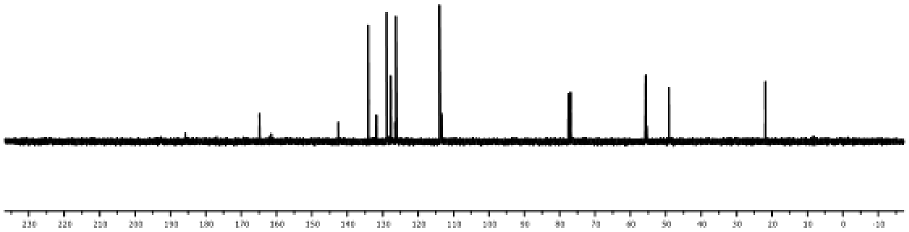


Figure 9. ^{13}C-{^{1}H} NMR of 2-(4-methoxyphenyl)-2-oxo-*N*-(1-phenylethyl)acetamide (**3p**).

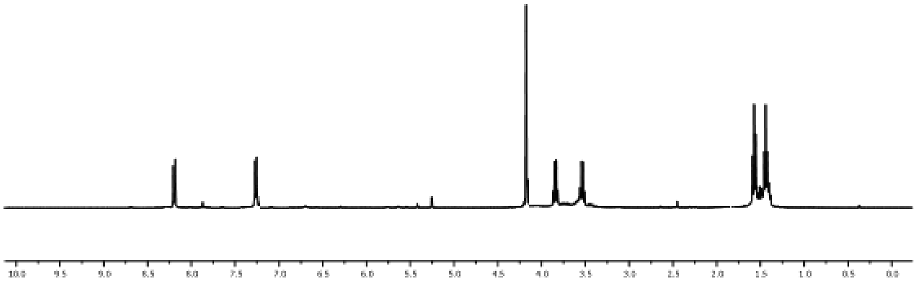


Figure 10. ^{1}H NMR of *N*,*N*-diethyl-2-(4-methoxyphenyl)-2-oxoacetamide (**3q**).

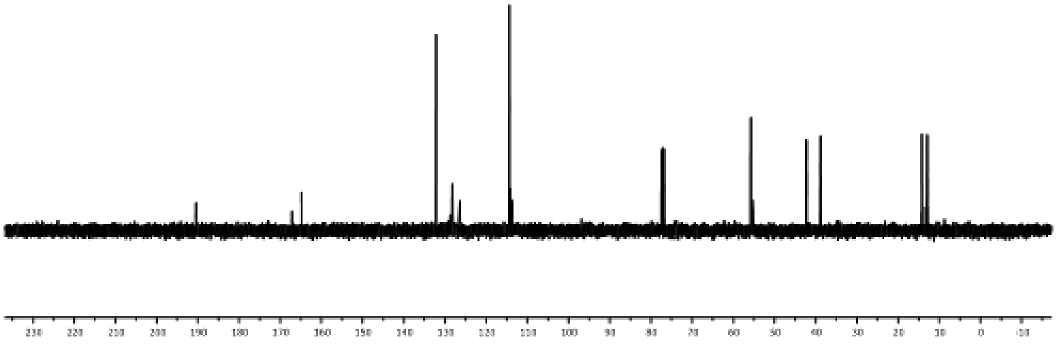


Figure 11. ^{13}C-{^{1}H} NMR of *N*,*N*-diethyl-2-(4-methoxyphenyl)-2-oxoacetamide (**3q**).

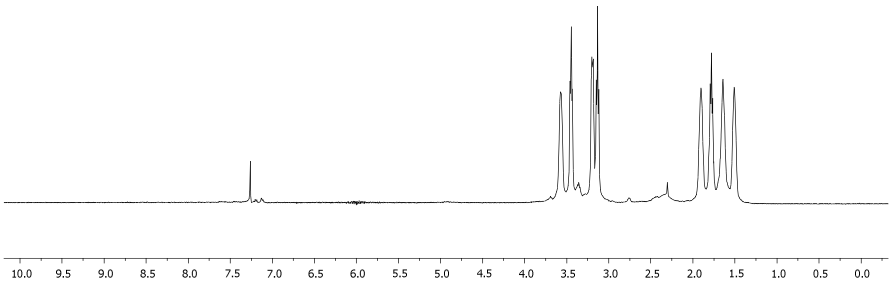


Figure 12. ^{1}H NMR of complex PdCl$_2$(DBU)$_2$ (**5**).

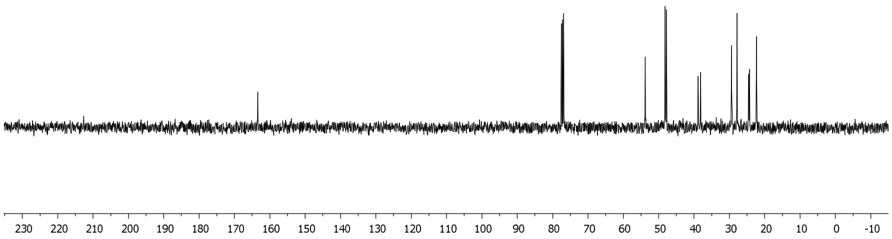


Figure 13. ^{13}C-{^{1}H} NMR of complex $PdCl_2(DBU)_2$ (**5**).

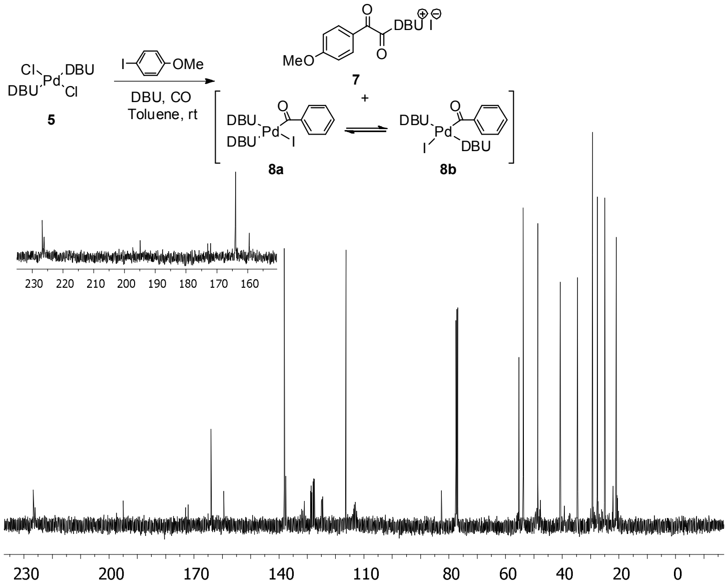


Figure 14. ^{13}C-{^{1}H} NMR spectrum of the reaction of $PdCl_2(DBU)_2$ with 1-iodo-4-methoxybenzene and DBU under atmospheric ^{13}CO pressure.

X-Ray Data:

Complex 6

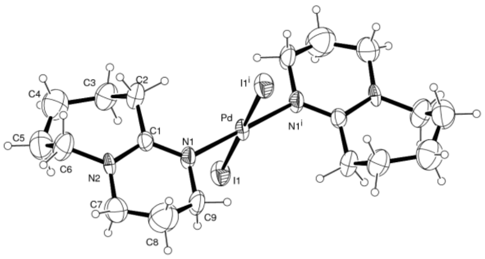


Table S3. Crystal data and structure refinement for structure **6**.

Empirical formula	$C_{18}H_{32}I_2N_4Pd$
Formula weight	664.68
Temperature	293(2) K
Wavelength	1.54180 A
Crystal system, space group	Monoclinic, P 21/c
Unit cell dimensions	a = 7.1690(9) A alpha = 90 deg.
	b = 11.1380(11) A beta = 100.49(2) deg.
	c = 14.9310(12) A gamma = 90 deg.
Volume	1172.3(2) A^3
Z, Calculated density	2, 1.883 Mg/m^3
Absorption coefficient	27.115 mm^-1
F(000)	640
Theta range for data collection	4.99 to 63.33 deg.
Limiting indices	-8<=h<=8, -12<=k<=12, -17<=l<=17
Reflections collected / unique	1745 / 2044 [R(int) = 0.0000]
Completeness to theta = 63.33	96.0 %
Absorption correction	Empirical (SHELXA)
Max. and min. transmission	0.0210 and 0.0060
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1745 / 30 / 118
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0768, wR2 = 0.2125
R indices (all data)	R1 = 0.0923, wR2 = 0.2320
Extinction coefficient	0.0034(7)
Largest diff. peak and hole	0.978 and -1.298 e.A^-3

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd	0	5000	0	59(1)
I(1)	1869(2)	3024(1)	478(1)	85(1)
N(1)	1730(15)	5914(9)	970(6)	66(3)
N(2)	2846(16)	6626(12)	2466(6)	76(3)
C(1)	1522(17)	6063(11)	1822(8)	60(3)
C(2)	-200(20)	5619(15)	2118(9)	85(4)
C(3)	80(30)	4567(17)	2760(11)	101(5)
C(4)	950(40)	4850(20)	3734(15)	133(7)
C(5)	2740(30)	5440(20)	3908(14)	126(6)
C(6)	2620(30)	6668(18)	3397(12)	109(6)
C(7)	4610(30)	7047(19)	2234(13)	110(6)
C(8)	4440(40)	7330(30)	1276(18)	155(9)
C(9)	3450(20)	6377(18)	701(9)	95(5)

Table S5. Bond lengths [A] and angles [deg].

Pd-N(1)#1	2.004(9)
Pd-N(1)	2.004(9)
Pd-I(1)	2.6077(10)
Pd-I(1)#1	2.6077(10)
N(1)-C(1)	1.318(14)
N(1)-C(9)	1.455(18)
N(2)-C(1)	1.374(15)
N(2)-C(6)	1.429(19)
N(2)-C(7)	1.45(2)
C(1)-C(2)	1.47(2)
C(2)-C(3)	1.50(2)
C(3)-C(4)	1.51(2)
C(4)-C(5)	1.42(3)
C(5)-C(6)	1.56(3)
C(7)-C(8)	1.45(3)
C(8)-C(9)	1.46(3)
N(1)#1-Pd-N(1)	180.0(6)
N(1)#1-Pd-I(1)	89.3(3)
N(1)-Pd-I(1)	90.7(3)

N(1)#1-Pd-I(1)#1	90.7(3)
N(1)-Pd-I(1)#1	89.3(3)
I(1)-Pd-I(1)#1	180.0
C(1)-N(1)-C(9)	118.1(10)
C(1)-N(1)-Pd	126.7(9)
C(9)-N(1)-Pd	115.1(7)
C(1)-N(2)-C(6)	120.6(13)
C(1)-N(2)-C(7)	120.1(11)
C(6)-N(2)-C(7)	118.8(13)
N(1)-C(1)-N(2)	123.3(11)
N(1)-C(1)-C(2)	119.8(11)
N(2)-C(1)-C(2)	116.9(11)
C(1)-C(2)-C(3)	115.7(14)
C(2)-C(3)-C(4)	115.8(16)
C(5)-C(4)-C(3)	118(2)
C(4)-C(5)-C(6)	110.3(18)
N(2)-C(6)-C(5)	116.2(15)
N(2)-C(7)-C(8)	112.8(16)
C(7)-C(8)-C(9)	112(2)
N(1)-C(9)-C(8)	116.1(14)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+1,-z

Table S6. Anisotropic displacement parameters (A^2 x 10^3) for vfm4. The anisotropic displacement factor exponent takes the form: -2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd	72(1)	67(1)	33(1)	-4(1)	-3(1)	-7(1)
I(1)	103(1)	81(1)	66(1)	2(1)	4(1)	13(1)
N(1)	82(7)	74(6)	39(5)	-14(4)	6(5)	-10(5)
N(2)	75(7)	112(8)	33(5)	-23(5)	-11(5)	-7(7)
C(1)	64(7)	69(7)	44(6)	5(5)	3(5)	12(6)
C(2)	120(13)	85(9)	53(7)	-6(7)	22(8)	-10(9)
C(3)	135(10)	85(8)	88(8)	6(7)	33(7)	-9(7)
C(4)	163(11)	117(10)	119(10)	21(8)	26(9)	14(8)
C(5)	143(10)	134(10)	95(9)	-3(8)	8(8)	28(9)
C(6)	150(17)	105(12)	78(11)	-34(9)	34(11)	-14(12)
C(7)	105(9)	122(10)	99(9)	-33(7)	9(7)	-10(7)
C(8)	156(12)	160(12)	154(12)	-10(9)	45(9)	-23(9)
C(9)	105(12)	135(14)	47(7)	-31(8)	17(8)	-40(11)

Table S7. Torsion angles [deg].

N(1)#1-Pd-N(1)-C(1)	83(77)
I(1)-Pd-N(1)-C(1)	-88.4(11)
I(1)#1-Pd-N(1)-C(1)	91.6(11)
N(1)#1-Pd-N(1)-C(9)	-102(77)
I(1)-Pd-N(1)-C(9)	87.0(11)
I(1)#1-Pd-N(1)-C(9)	-93.0(11)
C(9)-N(1)-C(1)-N(2)	0(2)
Pd-N(1)-C(1)-N(2)	174.9(9)
C(9)-N(1)-C(1)-C(2)	179.4(14)
Pd-N(1)-C(1)-C(2)	-5.3(18)
C(6)-N(2)-C(1)-N(1)	-174.5(14)
C(7)-N(2)-C(1)-N(1)	-3(2)
C(6)-N(2)-C(1)-C(2)	6(2)
C(7)-N(2)-C(1)-C(2)	177.7(14)
N(1)-C(1)-C(2)-C(3)	110.7(15)
N(2)-C(1)-C(2)-C(3)	-69.5(17)
C(1)-C(2)-C(3)-C(4)	76(2)
C(2)-C(3)-C(4)-C(5)	-56(3)
C(3)-C(4)-C(5)-C(6)	59(3)
C(1)-N(2)-C(6)-C(5)	66(2)
C(7)-N(2)-C(6)-C(5)	-106(2)
C(4)-C(5)-C(6)-N(2)	-84(2)
C(1)-N(2)-C(7)-C(8)	27(3)
C(6)-N(2)-C(7)-C(8)	-161(2)
N(2)-C(7)-C(8)-C(9)	-47(3)
C(1)-N(1)-C(9)-C(8)	-22(3)
Pd-N(1)-C(9)-C(8)	162.4(18)
C(7)-C(8)-C(9)-N(1)	45(3)