ELECTRONIC SUPPLEMENTARY INFORMATION

for

Reduction of Biginelli compounds by $LiAlH_4$: a rapid access to molecular diversity

Dragan B. Zlatković and Niko S. Radulović*

Department of Chemistry, Faculty of Science and Mathematics, University of Niš, Višegradska 33, 18000, Niš, Serbia. E-mail: nikoradulovic@yahoo.com; Fax: +381 18533014; Tel: +381 18533015

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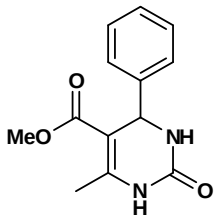
Table S1a. ^{1}H and ^{13}C chemical shifts (ppm) of compounds **1-10** in CD_3SOCD_3 at 400 and 100.6 MHz respectively)

Assignment	**1**		**2**		**3**		**4**		**5**		**6**		**7**		**8**		**9**		**10**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
C-2	152.6		152.6		152.0		151.1		152.6		152.1		152.1		152.4		152.5		151.5	
C-4	54.3	5.16	54.0	5.10	53.7	5.10	50.2	5.39	53.7	5.09	53.5	5.12	55.3	5.48	53.7	5.15	55.3	5.40	48.5	5.44
C-5	99.6		99.7		98.9		99.0		99.8		98.7		97.1		99.5		101.0		97.1	
C-6	149.0		148.8		148.4		148.5		148.7		148.6		149.1		149.2		146.6		149.1	
C-7	18.3	2.25	18.2	2.24	17.7	2.25	17.7	2.29	18.2	2.24	17.7	2.25	17.7	2.28	18.3	2.25	19.0	2.36	17.7	2.27
C-8	166.3		166.3		165.7		165.6		166.3		165.7		165.7		166.2		165.8		165.4	
C-1'	145.2		142.2		144.5		143.1		137.4		146.0		131.1		141.4		145.9		131.3	
C-2'	126.6	7.16-7.36 (5H)	126.5	7.11 (4H)	126.6	7.03	134.6		127.8	7.14	112.2	6.78	159.4		128.6	7.26	113.5	7.02	159.3	
C-3'	128.9		129.4		137.3		130.1	7.12	114.3	6.87	159.1		111.1	6.99	115.6	7.13	163.0		115.4	7.14
C-4'	127.7		136.8		127.8	7.06	127.1	7.12	158.9		112.0	6.83	120.0	6.87	161.8		115.0	6.97	129.3	7.30
C-5'					128.2	7.20	126.4	7.17			129.5	7.24	126.6	7.02			130.4	7.29	124.4	7.15
C-6'					123.2	7.01	126.4	7.17			118.0	6.81	128.6	7.23			122.1	7.10	128.6	7.24
C-1"			21.1	2.26	21.1	2.28	18.5	2.41	55.6	3.72	54.9	3.72	48.7	3.80						
CO_2Me	51.2	3.53	51.2	3.52	50.7	3.53	50.6	3.45	51.2	3.53	50.7	3.54	50.6	3.47	51.2	3.53	51.3	3.65	50.6	3.47
NH-1		9.14		9.10		9.17		9.17		9.10		9.21		/		9.17		7.32		9.27
NH-3		7.68		7.62		7.70		7.63		7.61		7.73		/		7.69		5.51		7.70

Table S1b. ^{1}H and ^{13}C chemical shifts (ppm) of compounds **12-15** in CD_3SOCD_3 at 400 and 100.6 MHz respectively)

Assignment	**12**		**13**		**14**		**15**	
	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H
C-2	153.0		152.8		153.2		153.0	
C-4	52.2	5.16	51.5	5.15	52.0	5.13	51.8	5.12
C-5	102.2		101.9		102.1		102.2	
C-6	150.7		151.0		151.0		150.6	
C-7	16.0	2.48	16.0	2.50	16.1	2.49	15.9	2.48
C-8	166.0		165.9		166.1		166.6	
C-1'	143.8		140.0 (*d*, J=3.0 Hz)		145.4		140.8	
C-2'	125.9	7.15-7.35 (5H)	127.9 (*d*, J=8.1 Hz)	7.25 (2H)	112.1	6.75	125.8	7.10 (4H)
C-3'	127.2		115.1 (*d*, J=21.2 Hz)	7.14 (2H)	159.3		128.9	
C-4'	128.4		161.3 (*d*, J=243.4 Hz)		112.1	6.82	136.4	
C-5'					129.7	7.24		
C-6'					118.0	6.78		
C-1"					55.0	3.72	20.5	2.25
CO_2Me	50.9	3.57	51.0	3.57	51.1	3.58	51.0	3.56
N-Me	29.6	3.10	29.7	3.10	29.8	3.09	29.6	3.08
NH-3		7.91		8.00		7.97		7.95

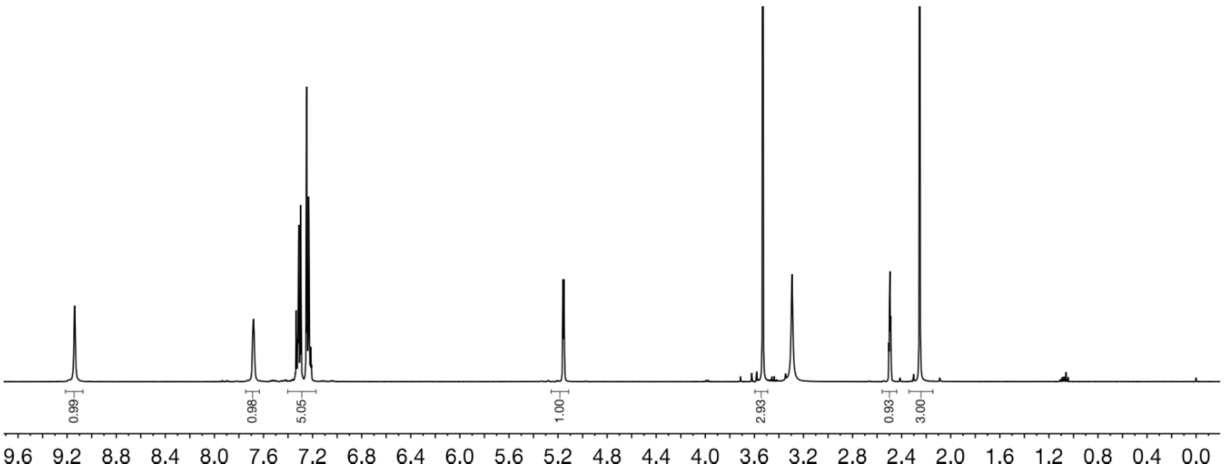
Methyl 6-methyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (1)



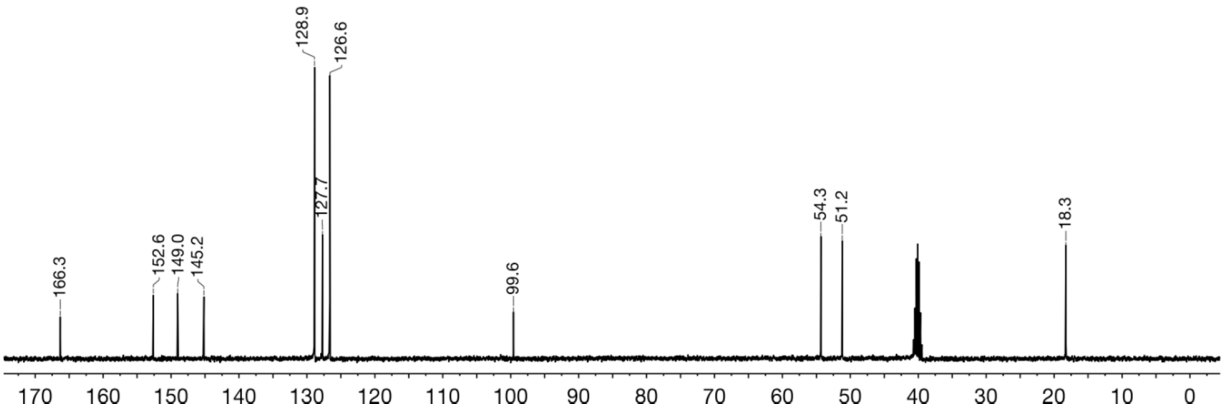
Yield: 85%

IR: 3230, 3100, 1700, 1650

EI-MS: EI-MS (*m/z*, rel. intensity): 246 (16, M^+), 231 (27), 187 (27), 169 (100), 137 (34)

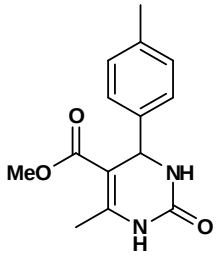


^{1}H NMR spectrum of compound **1** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **1** in CD_3SOCD_3 (100.6 MHz)

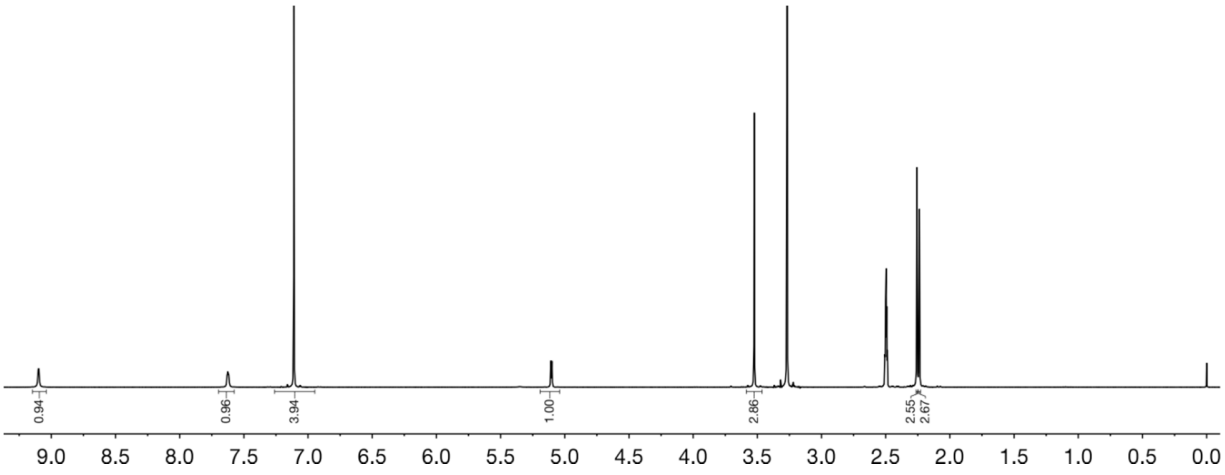
Methyl 6-methyl-2-oxo-4-(*p*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (2)



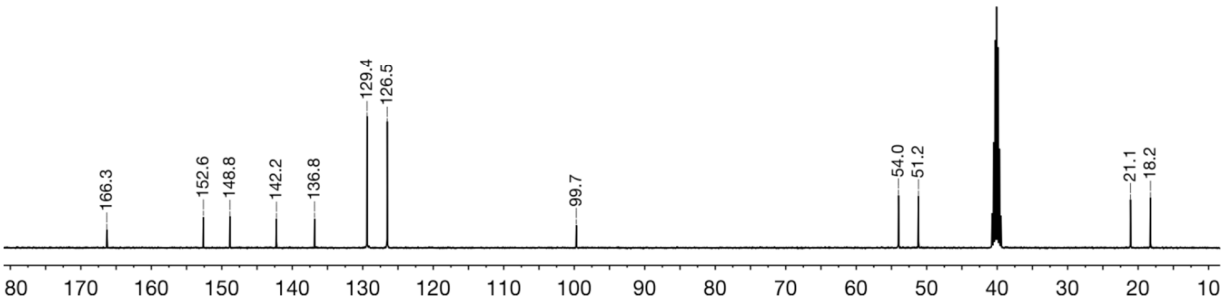
Yield: 82%

IR: 3225, 3100, 1695, 1655

EI-MS (*m/z*, rel. intensity): 260 (10, M^+), 245 (45), 201 (33), 183 (100).

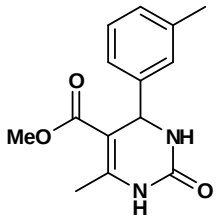


^{1}H NMR spectrum of compound **2** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **2** in CD_3SOCD_3 (100.6 MHz)

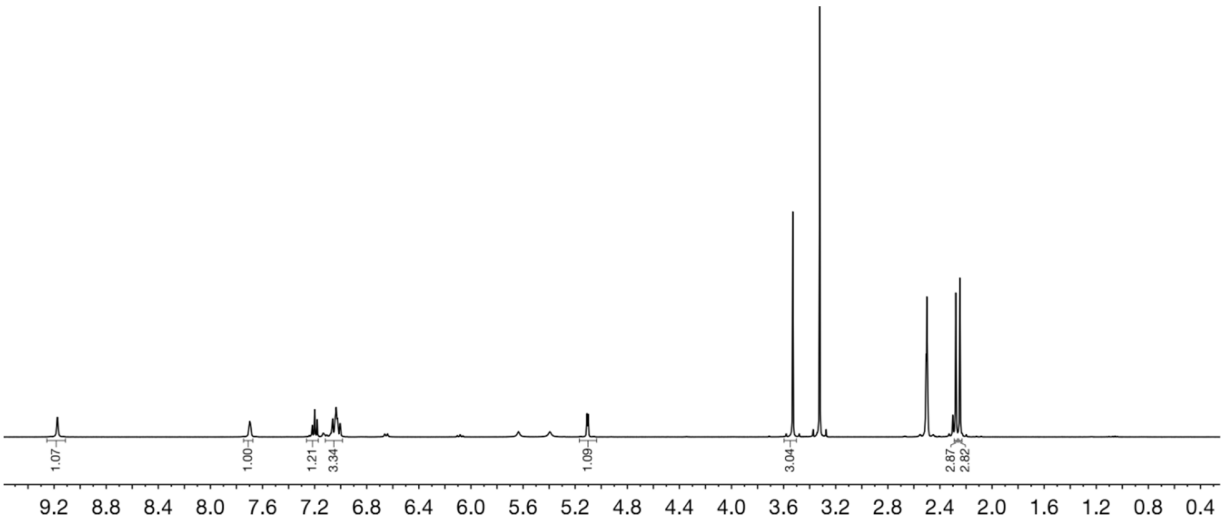
Methyl 6-methyl-2-oxo-4-(*m*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (3)



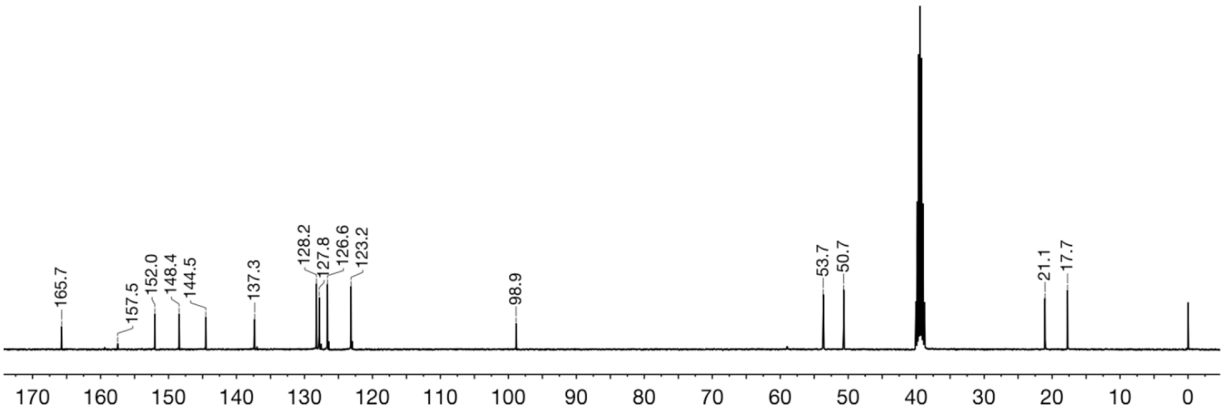
Yield: 90%

IR: 3220, 3100, 1720, 1675

EI-MS (*m/z*, rel. intensity): 260 (16, M^+), 245 (36), 201 (27), 183 (100).

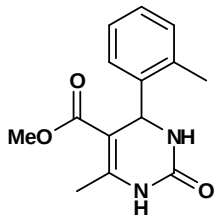


^{1}H NMR spectrum of compound **3** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **3** in CD_3SOCD_3 (100.6 MHz)

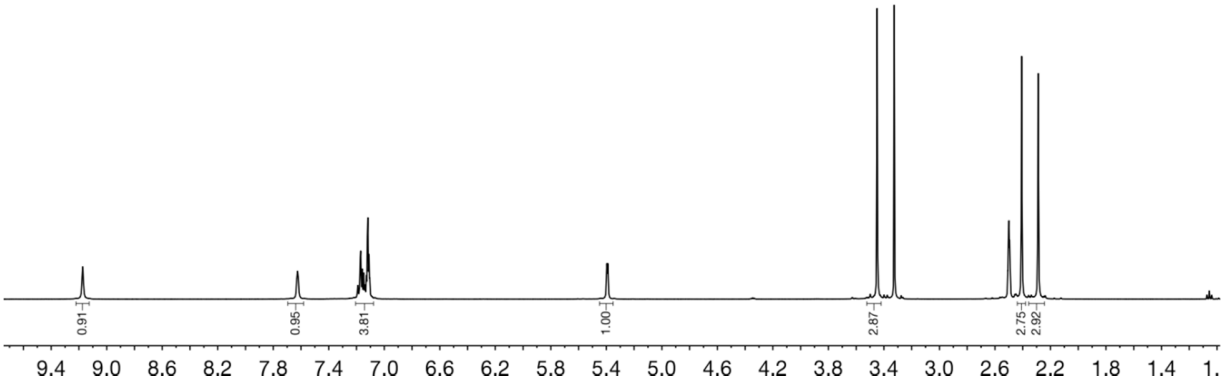
Methyl 6-methyl-2-oxo-4-(*o*-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (4)



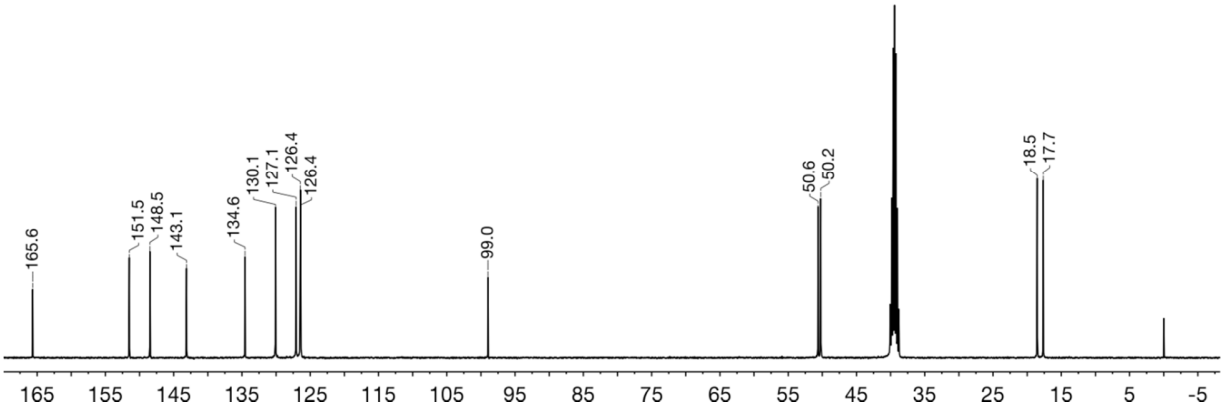
Yield: 80%

IR: 3210, 3100, 1700, 1675

EI-MS (*m/z*, rel. intensity): 260 (10, M^+), 245 (45), 201 (33), 183 (100).

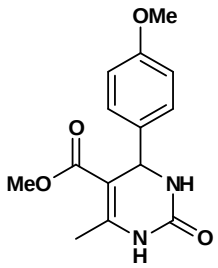


^{1}H NMR spectrum of compound **4** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **4** in CD_3SOCD_3 (100.6 MHz)

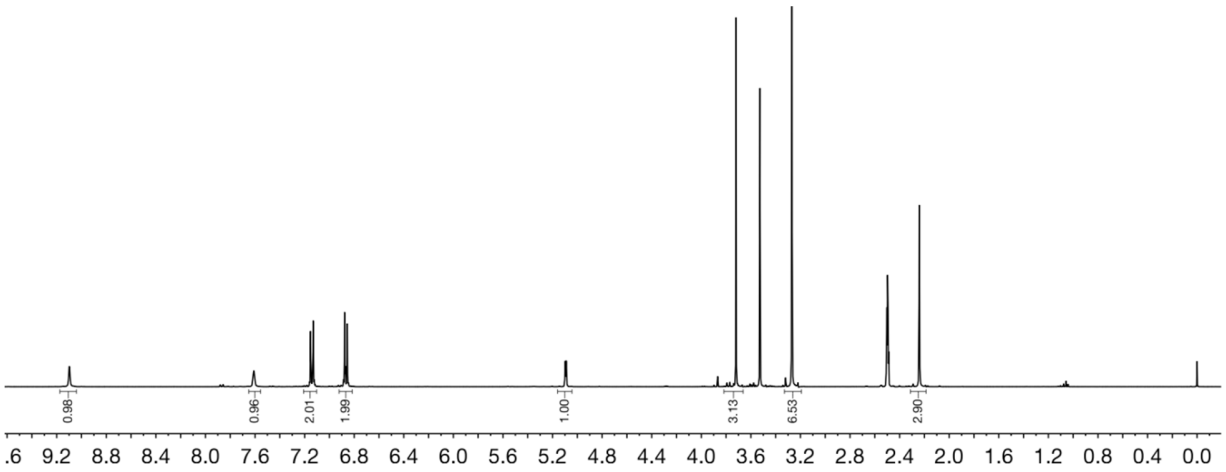
Methyl 4-(4-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (5)



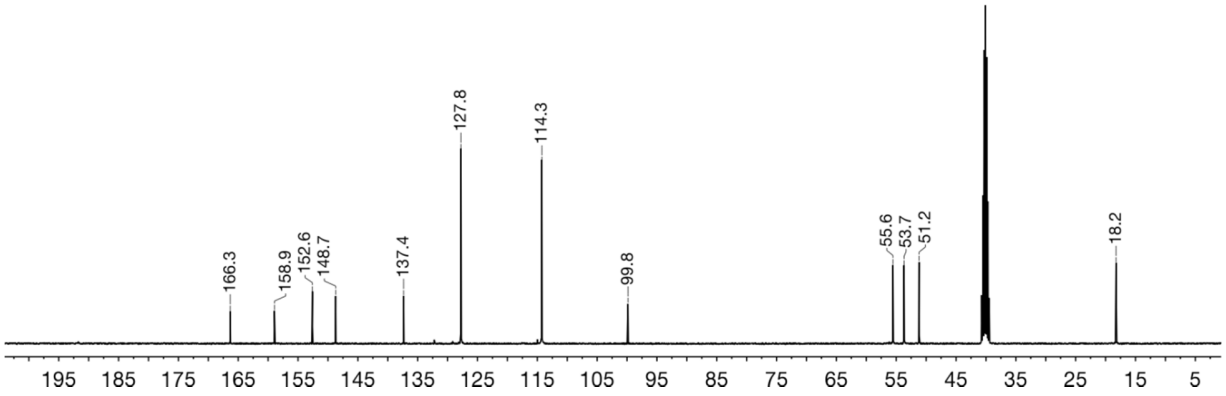
Yield: 82%

IR: 3220, 3100, 1700, 1665

EI-MS (*m/z*, rel. intensity): 276 (15, M^+), 217 (28), 169 (100).

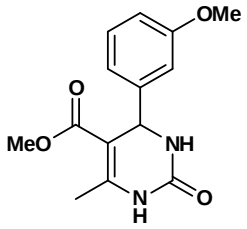


^{1}H NMR spectrum of compound **5** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **5** in CD_3SOCD_3 (100.6 MHz)

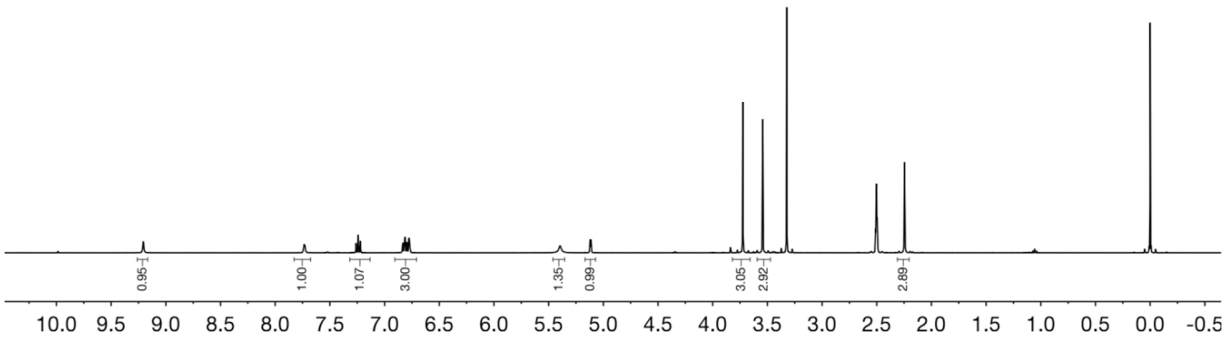
Methyl 4-(3-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (6)



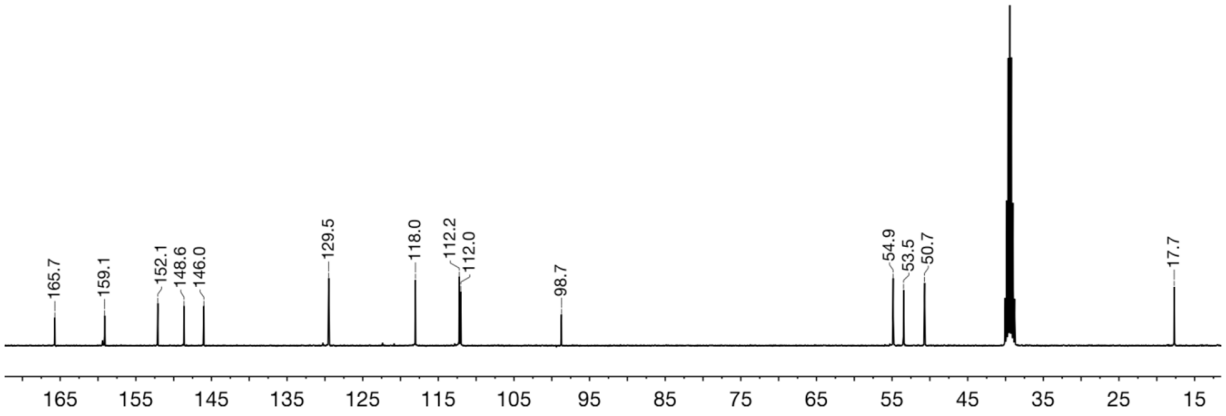
Yield: 85%

IR: 3215, 3100, 1690, 1640

EI-MS (*m/z*, rel. intensity): 276 (22, M^+), 217 (31), 169 (100).

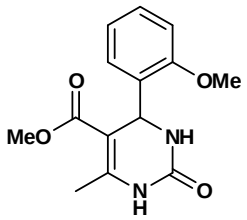


^{1}H NMR spectrum of compound **6** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **6** in CD_3SOCD_3 (100.6 MHz)

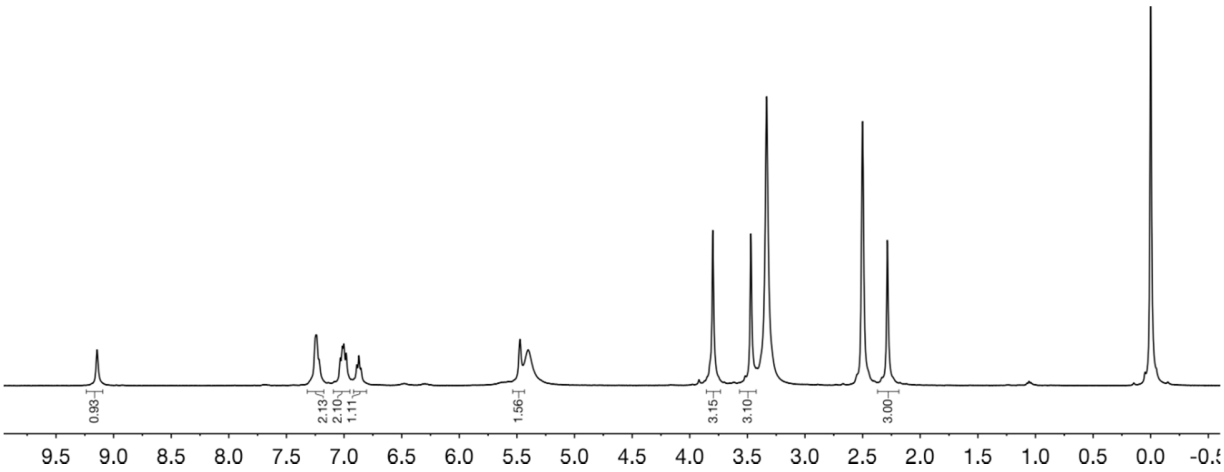
Methyl 4-(2-methoxyphenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (7)



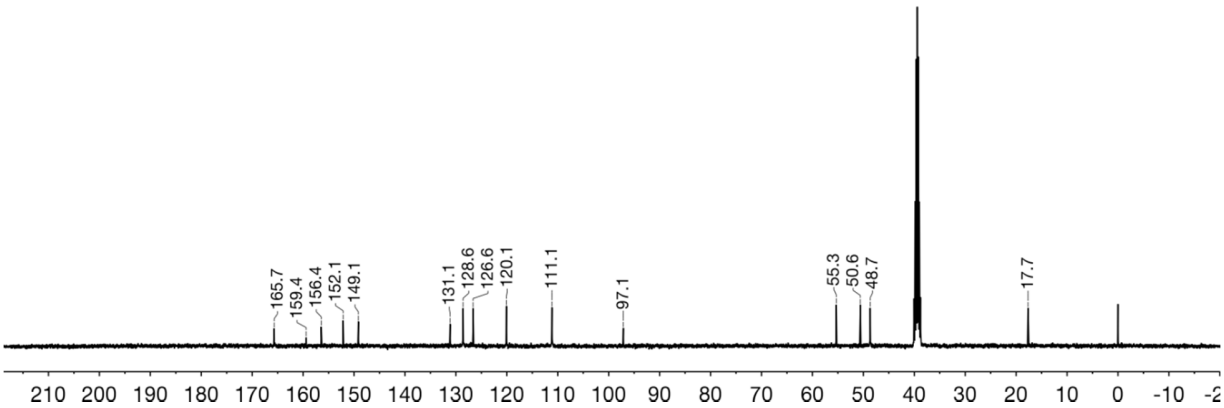
Yield: 80%

IR: 3225, 3100, 1710, 1630

EI-MS (*m/z*, rel. intensity): 276 (18, M^+), 217 (35), 169 (100).

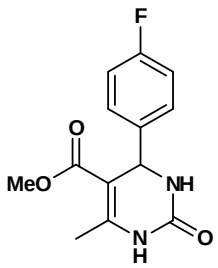


^{1}H NMR spectrum of compound **7** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **7** in CD_3SOCD_3 (100.6 MHz)

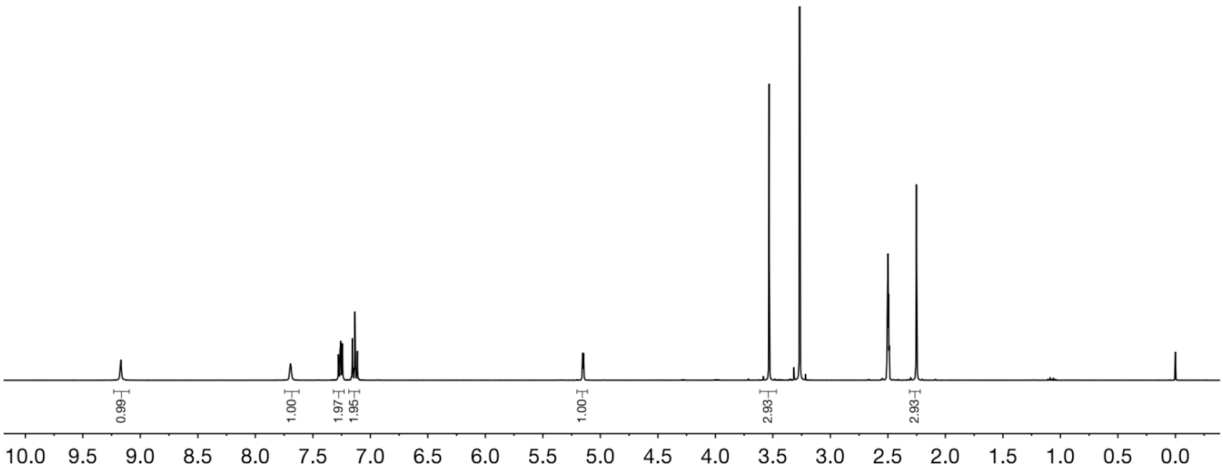
Methyl 4-(4-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (8)



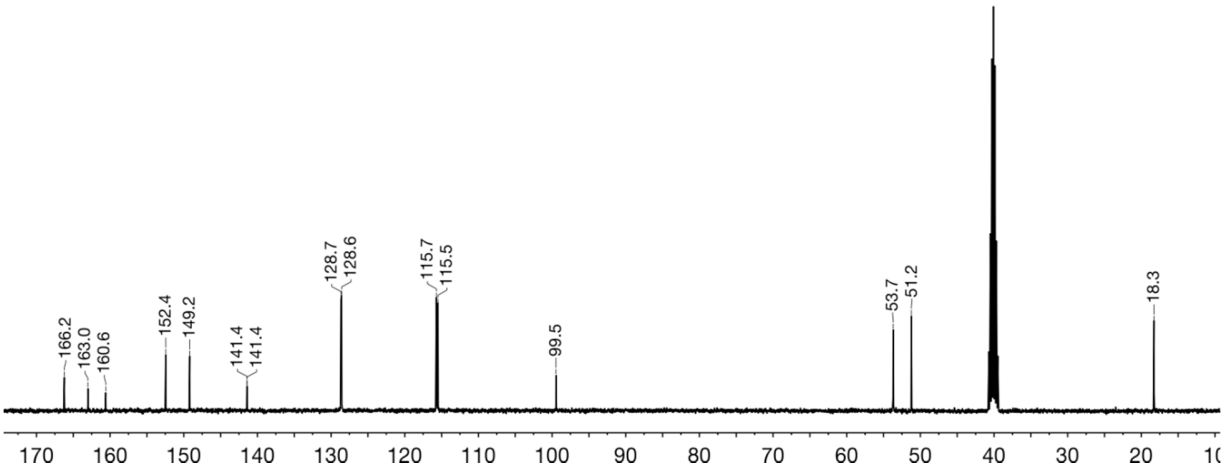
Yield: 85%

IR: 3220, 3100, 1700, 1650

EI-MS (*m/z*, rel. intensity): 264 (10, M^+), 249 (30), 205 (25), 169 (100), 137 (31)

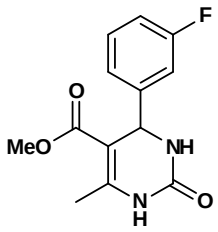


^{1}H NMR spectrum of compound **8** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **8** in CD_3SOCD_3 (100.6 MHz)

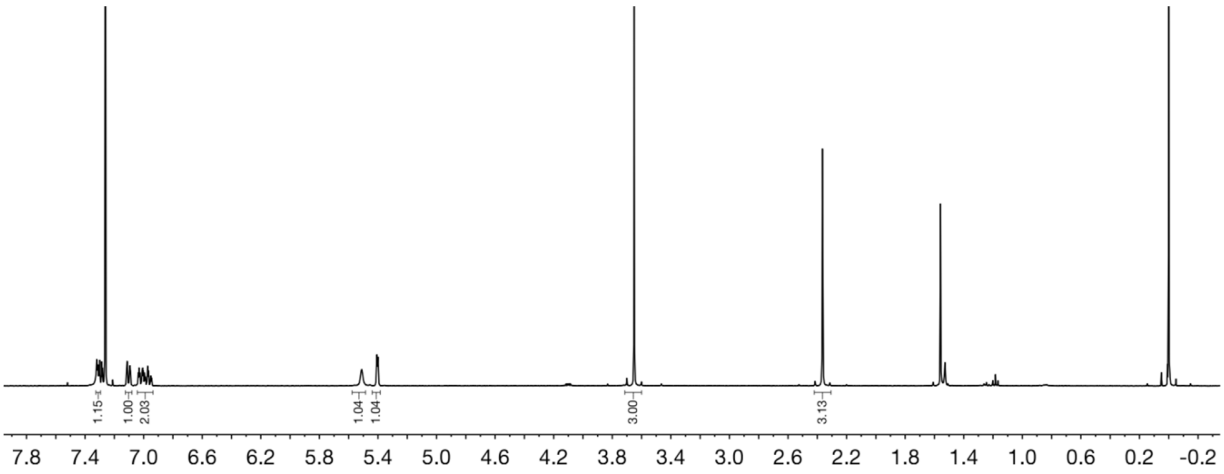
Methyl 4-(3-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (9)



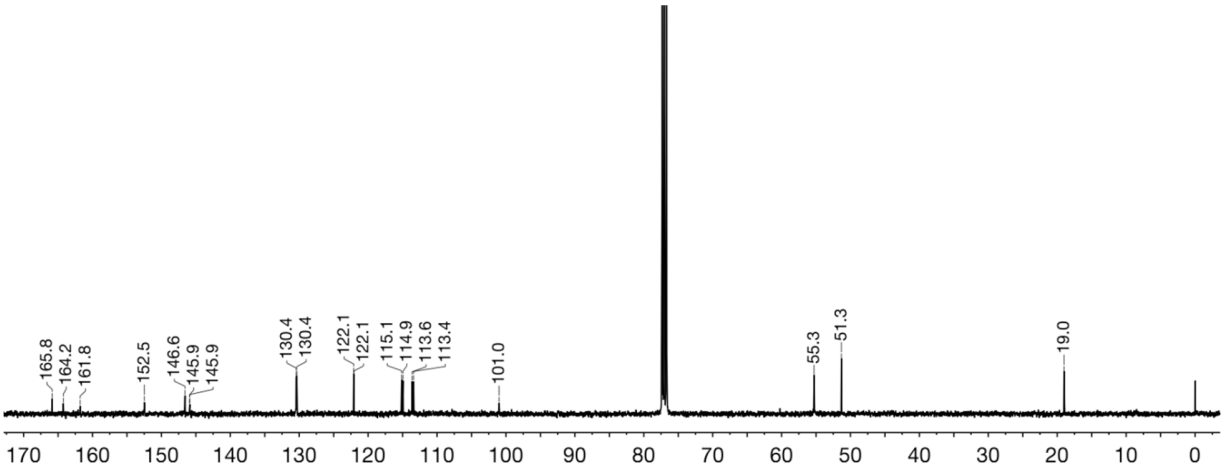
Yield: 85%

IR: 3210, 3100, 1680, 1650

EI-MS (*m/z*, rel. intensity): 264 (9, M^+), 249 (21), 205 (20), 169 (100), 137 (33)

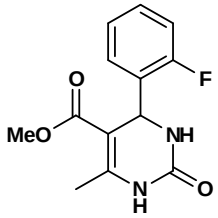


^{1}H NMR spectrum of compound **9** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **9** in $CDCl_3$ (100.6 MHz)

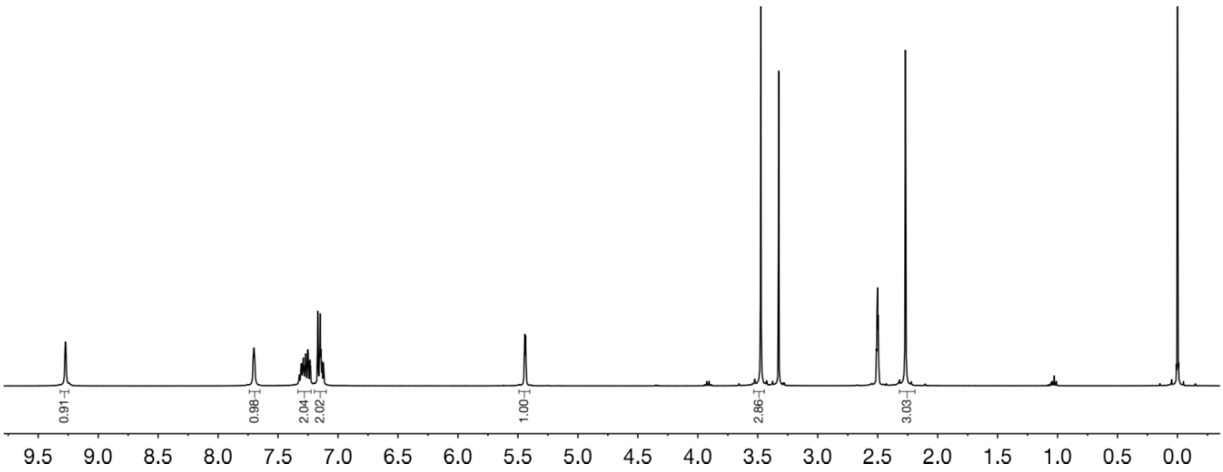
Methyl 4-(2-fluorophenyl)-6-methyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (10)



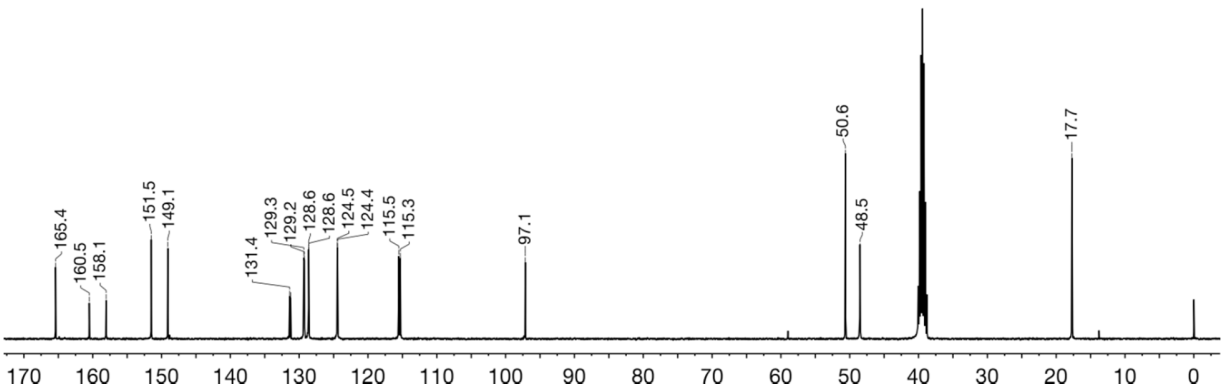
Yield: 80%

IR: 3210, 3100, 1705, 1665

EI-MS (*m/z*, rel. intensity): 264 (9, M^+), 249 (43), 205 (38), 169 (100), 137 (42)

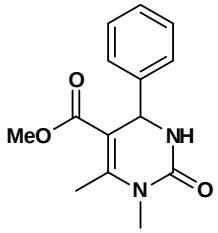


^{1}H NMR spectrum of compound **10** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **10** in CD_3SOCD_3 (100.6 MHz)

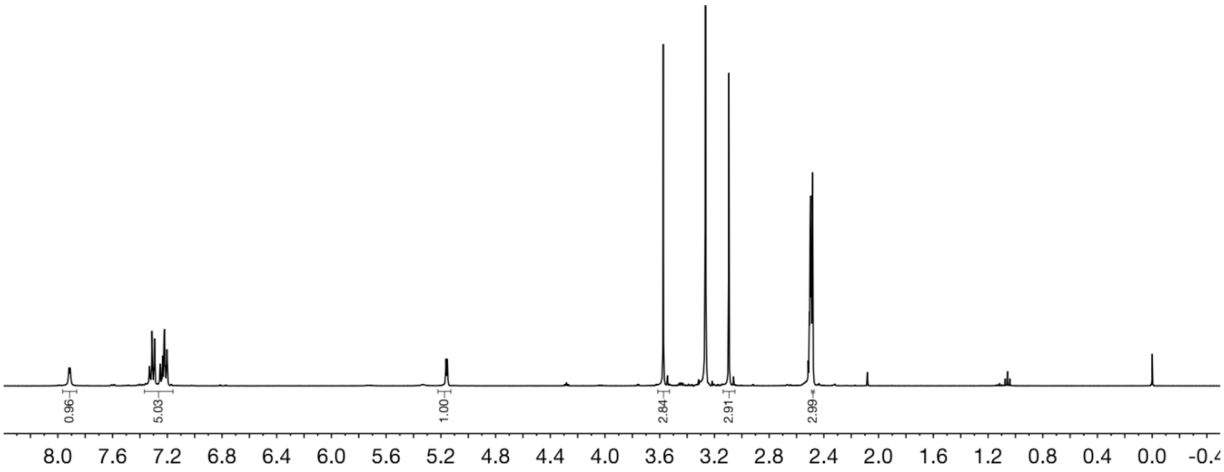
Methyl 1,6-dimethyl-2-oxo-4-phenyl-1,2,3,4-tetrahydropyrimidine-5-carboxylate (12)



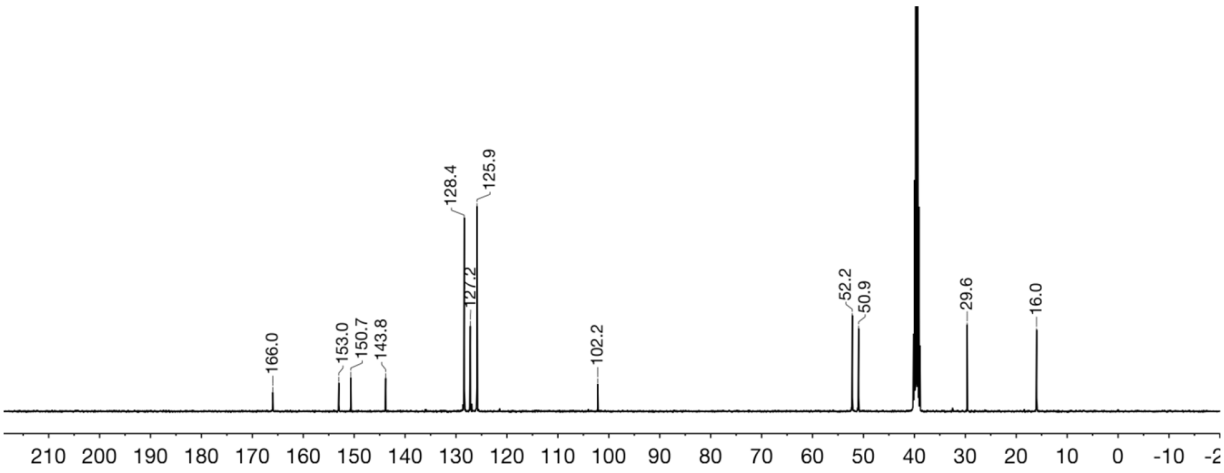
Yield: 85%

IR: 3225, 3100, 1695, 1655

EI-MS (*m/z*, rel. intensity): 260 (16, M^+), 245 (27), 201 (24), 183 (100), 151 (41)

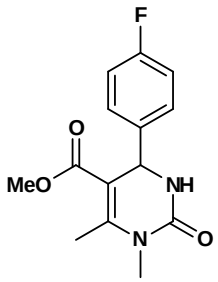


^{1}H NMR spectrum of compound **12** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **12** in CD_3SOCD_3 (100.6 MHz)

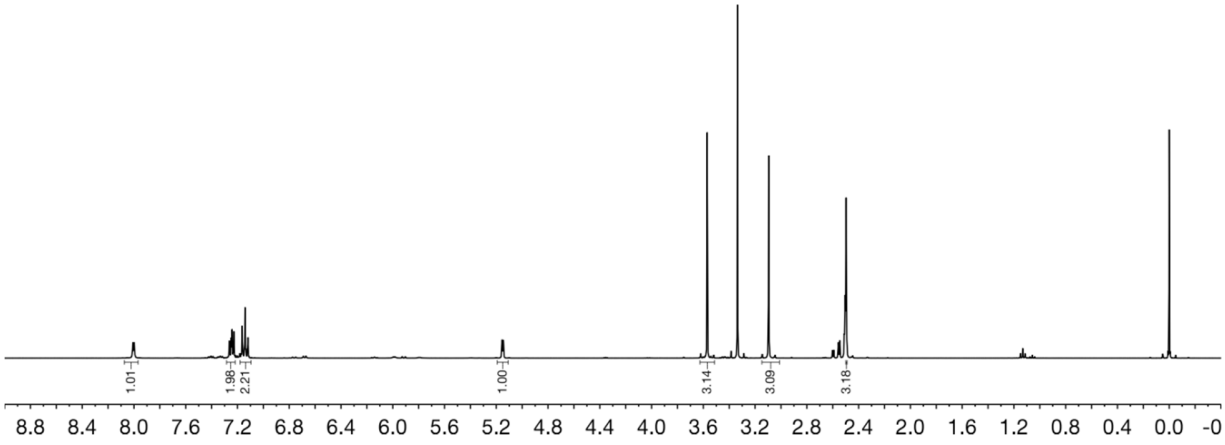
Methyl 4-(4-fluorophenyl)-1,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (13)



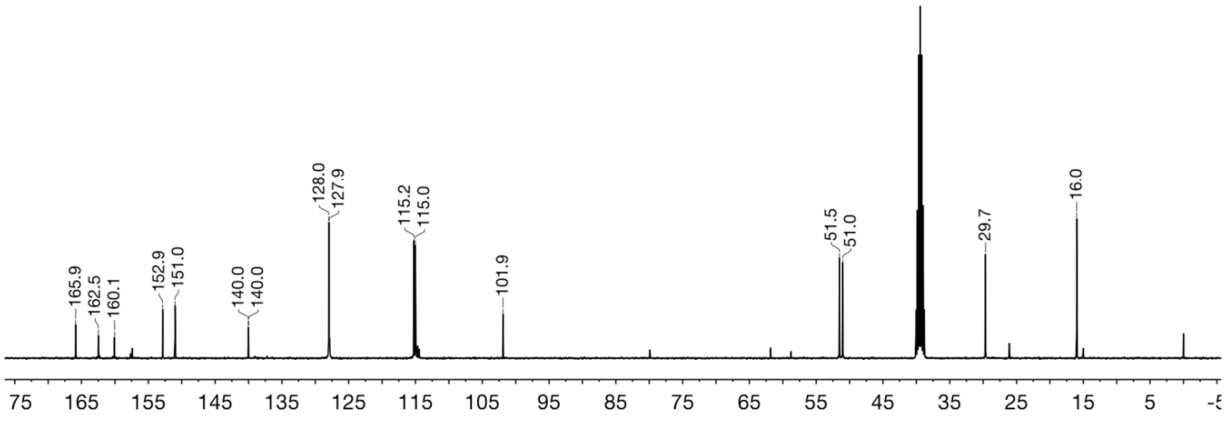
Yield: 82%

IR: 3220, 3100, 1700, 1660

EI-MS (*m/z*, rel. intensity): 278 (20, M^+), 263 (60), 219 (39), 183 (100), 151 (45).

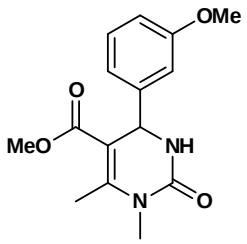


^{1}H NMR spectrum of compound **13** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **13** in CD_3SOCD_3 (100.6 MHz)

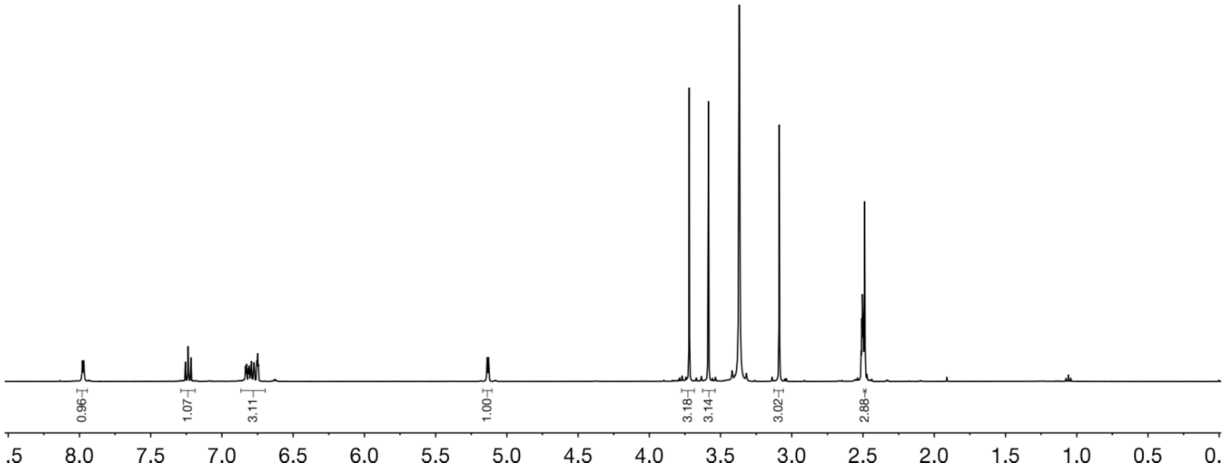
Methyl 4-(3-methoxyphenyl)-1,6-dimethyl-2-oxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (14)



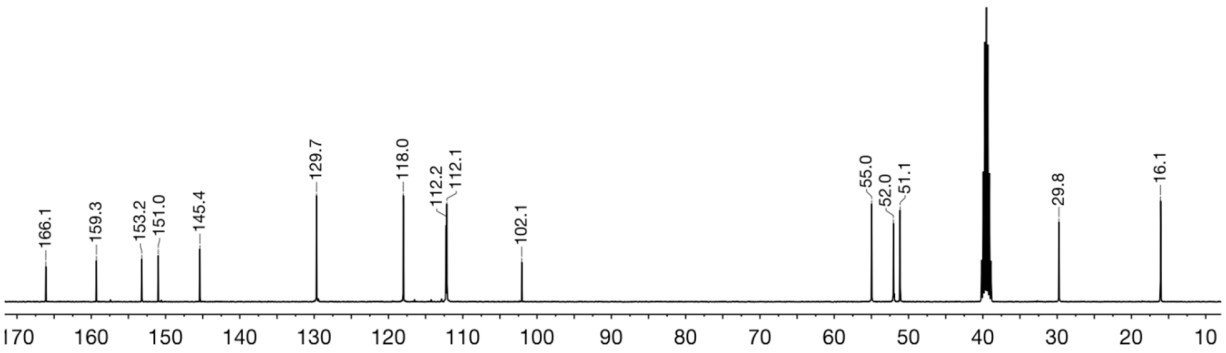
Yield: 80%

IR: 3220, 3100, 1695, 1655

EI-MS (*m/z*, rel. intensity): 290 (28, M^+), 275 (52), 231 (64), 183 (100), 151 (50)

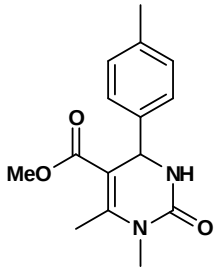


^{1}H NMR spectrum of compound **14** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **14** in CD_3SOCD_3 (100.6 MHz)

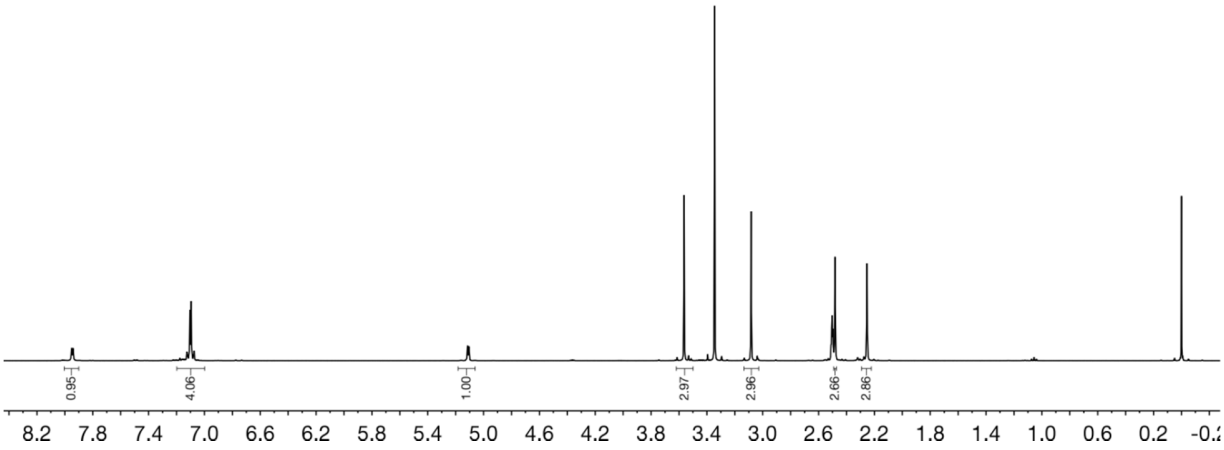
Methyl 1,6-dimethyl-2-oxo-4-(p-tolyl)-1,2,3,4-tetrahydropyrimidine-5-carboxylate (15)



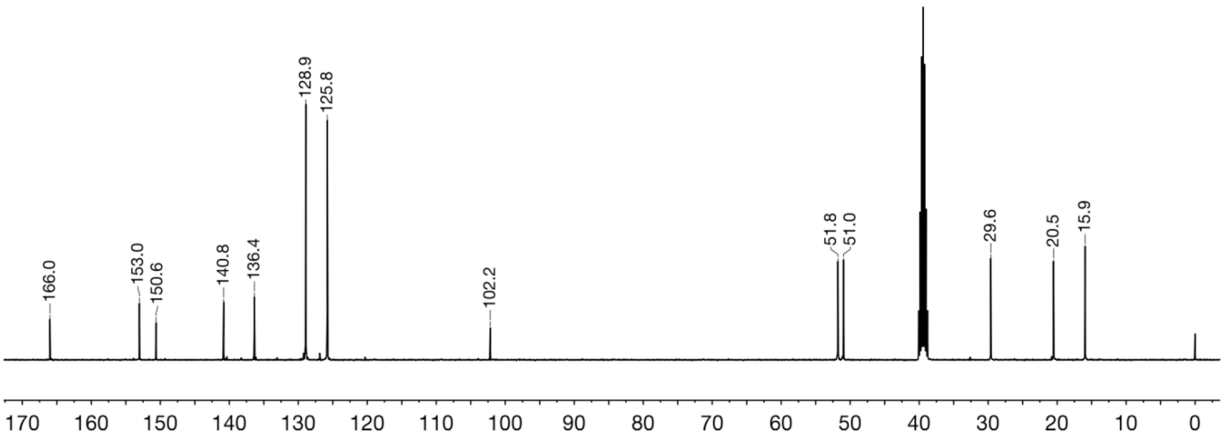
Yield: 90%

IR: 3225, 3100, 1720, 1655

EI-MS (*m/z*, rel. intensity): 274 (M^+, 9), 259 (22), 215 (21), 183 (100), 151 (33).

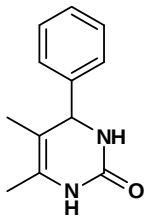


^{1}H NMR spectrum of compound **15** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **15** in CD_3SOCD_3 (100.6 MHz)

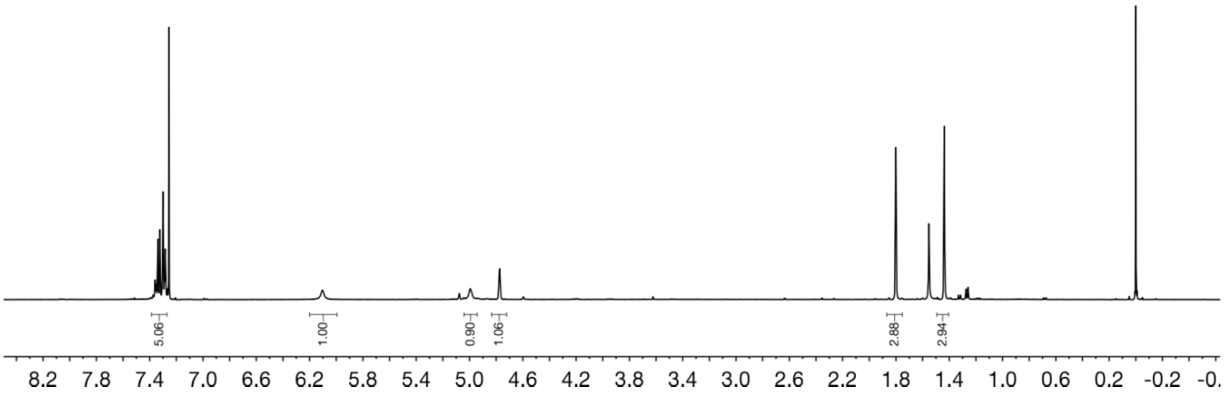
5,6-dimethyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (1a)



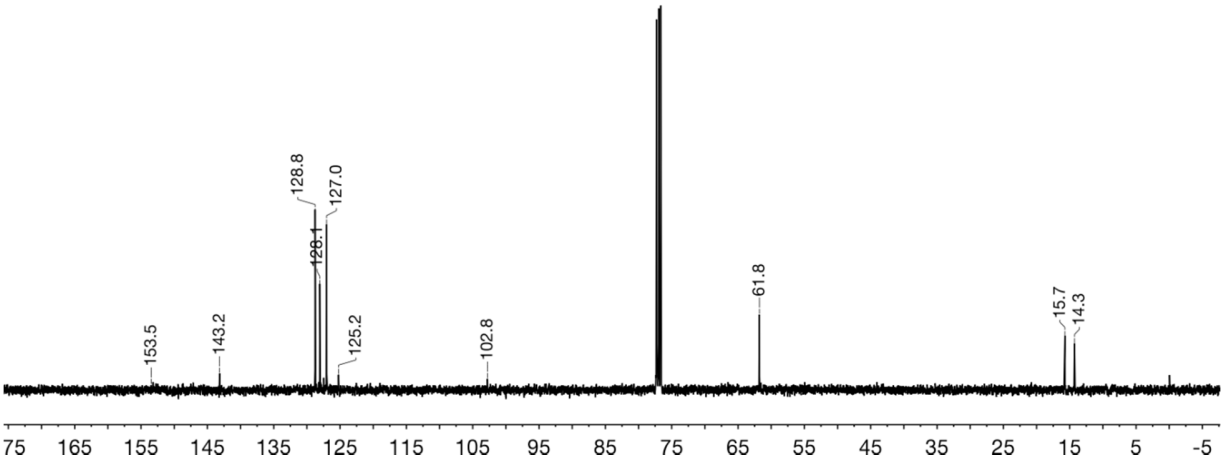
Yield: 95%

IR: 3210, 3100, 1650

EI-MS (*m/z*, rel. intensity): 202 (19, M^+), 187 (77), 125 (100).

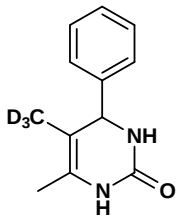


^{1}H NMR spectrum of compound **1a** in $CDCl_3$ (400 MHz)



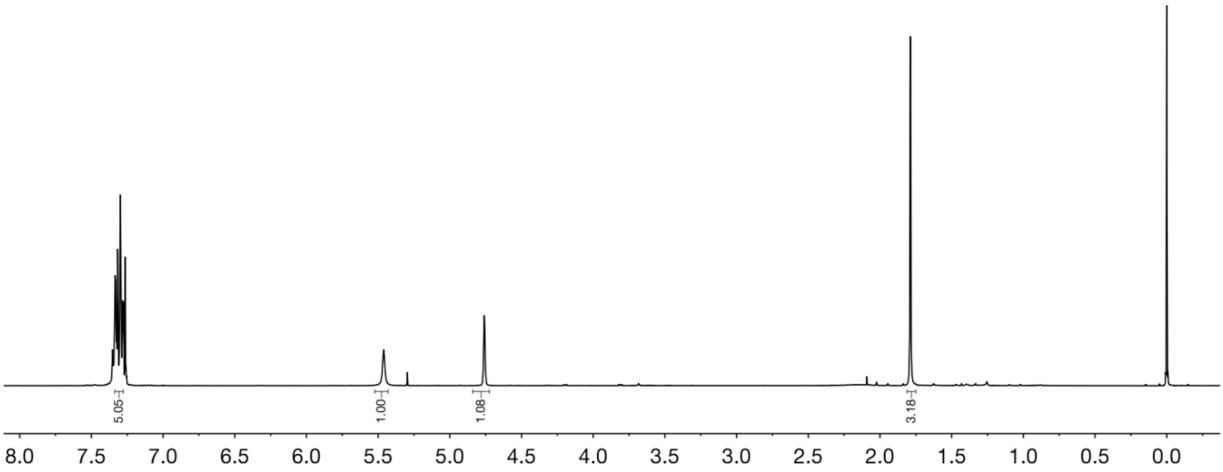
^{13}C NMR spectrum of compound **1a** in $CDCl_3$ (100.6 MHz)

(1a, deuterated at C-8)

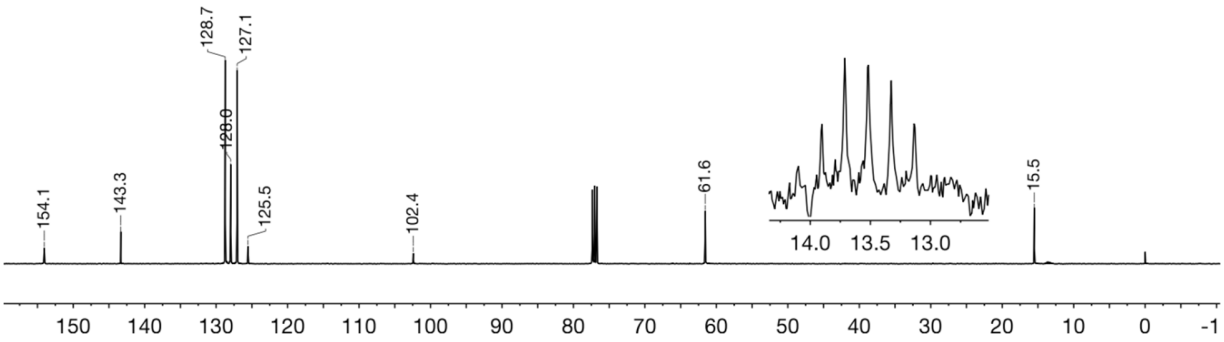


Yield: 95% EI-MS: EI-MS (*m/z*, rel. intensity): 205 (10, M^+), 187 (40), 161 (10), 128 (100).

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 13.5 (*heptet*, C-8), 15.5 (C-7), 61.6 (C-4), 102.4 (C-5), 125.5 (C-6), 127.1 (C-2'), 128.0 (C-4'), 128.7 (C-3'), 143.3 (C-1'), 154.1 (C-2'); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 1.79 (H-7), 4.76 (H-4), 7.28-7.34 (5H, ArH)

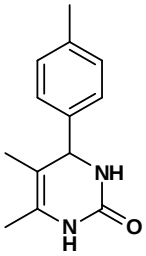


^{1}H NMR spectrum of compound **1a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **1a** in $CDCl_3$ (100.6 MHz)

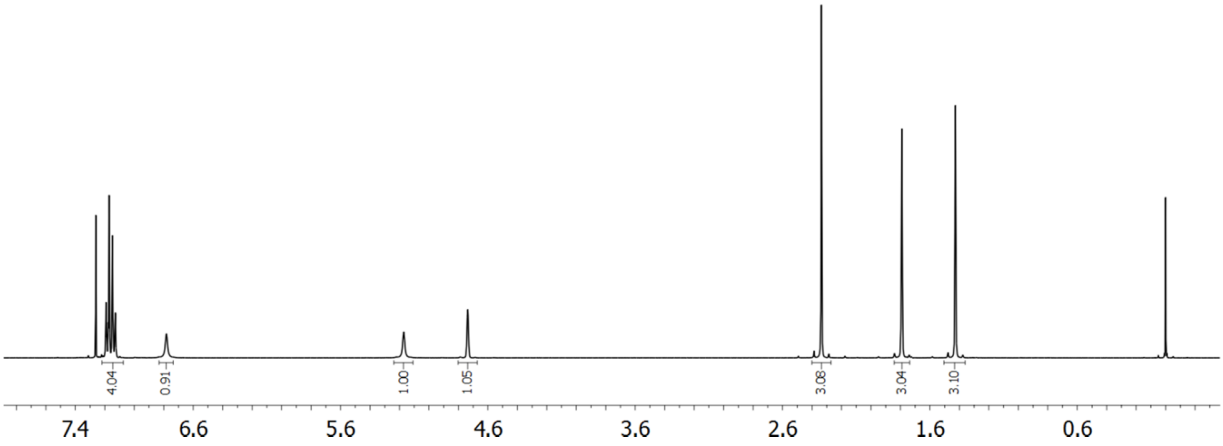
5,6-dimethyl-4-(*p*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (2a)



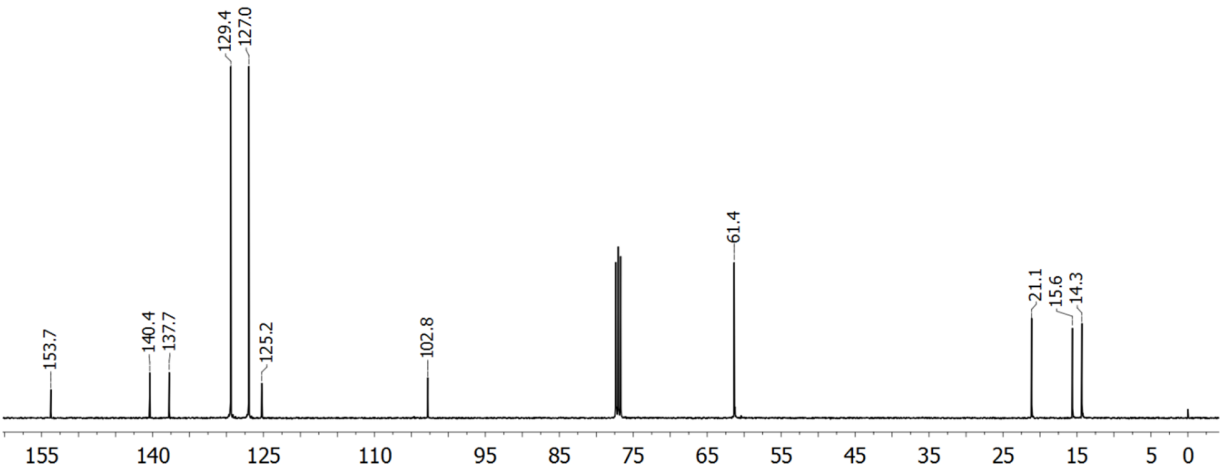
Yield: 92%

IR: 3250, 3100, 1655

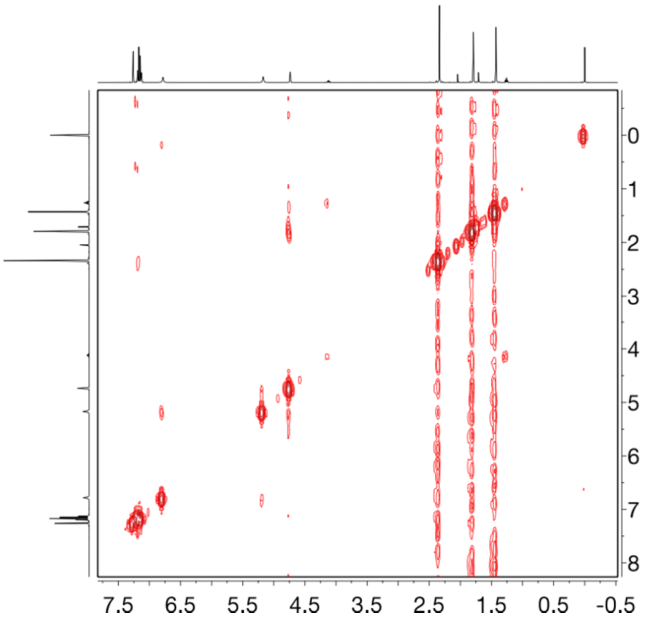
EI-MS: 216 (15, M^+), 201 (66), 125 (100).



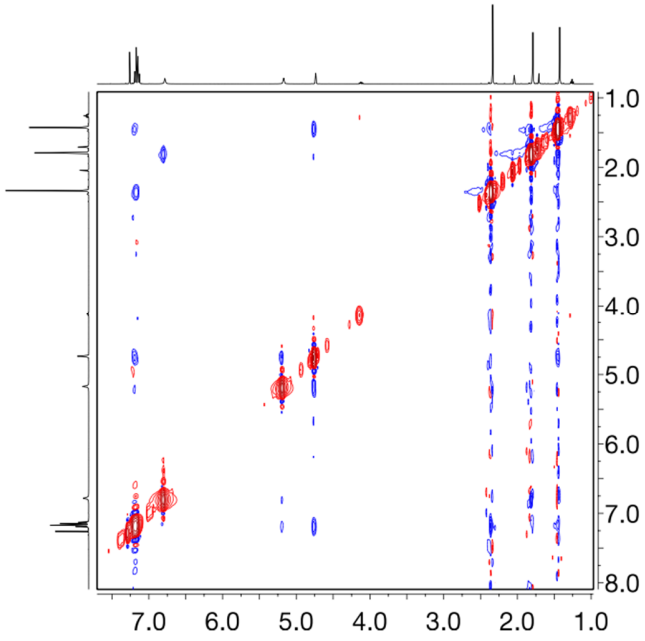
^{1}H NMR spectrum of compound **2a** in $CDCl_3$ (400 MHz)



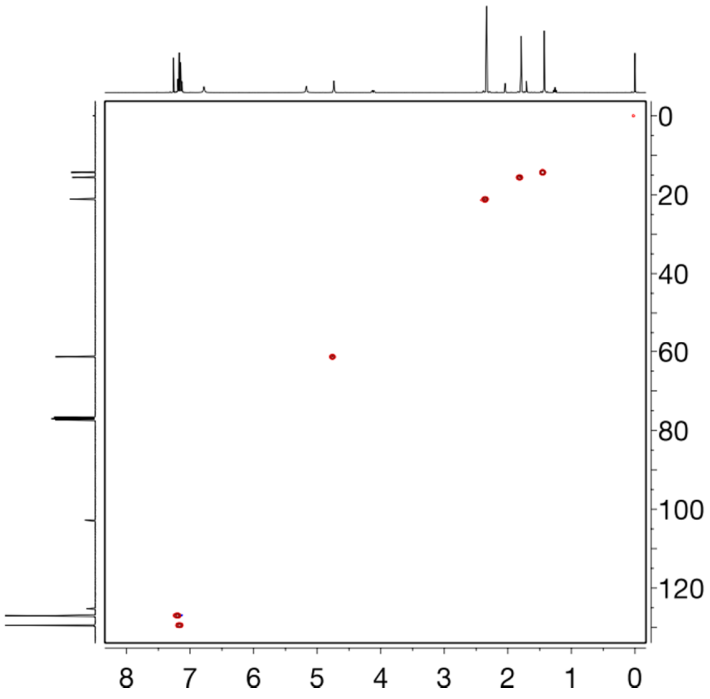
^{13}C NMR spectrum of compound **2a** in $CDCl_3$ (100.6 MHz)



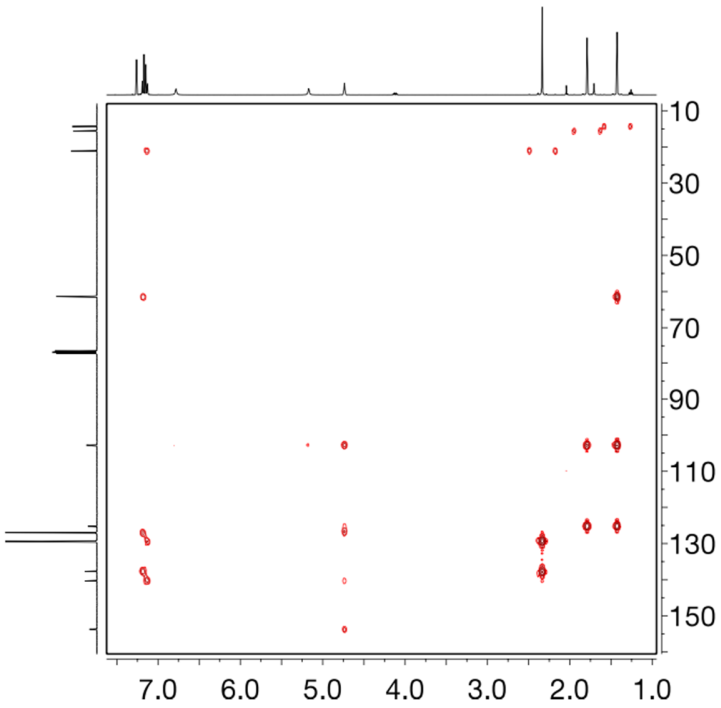
^{1}H-^{1}H COSY spectrum of compound **2a** in $CDCl_3$ (400 MHz)



NOESY spectrum of compound **2a** in $CDCl_3$ (400 MHz)

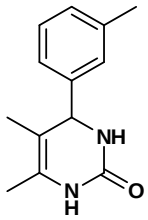


HSQC spectrum of compound **2a** in $CDCl_3$ (400 and 100.6 MHz)



HMBC spectrum of compound **2a** in $CDCl_3$ (400 and 100.6 MHz)

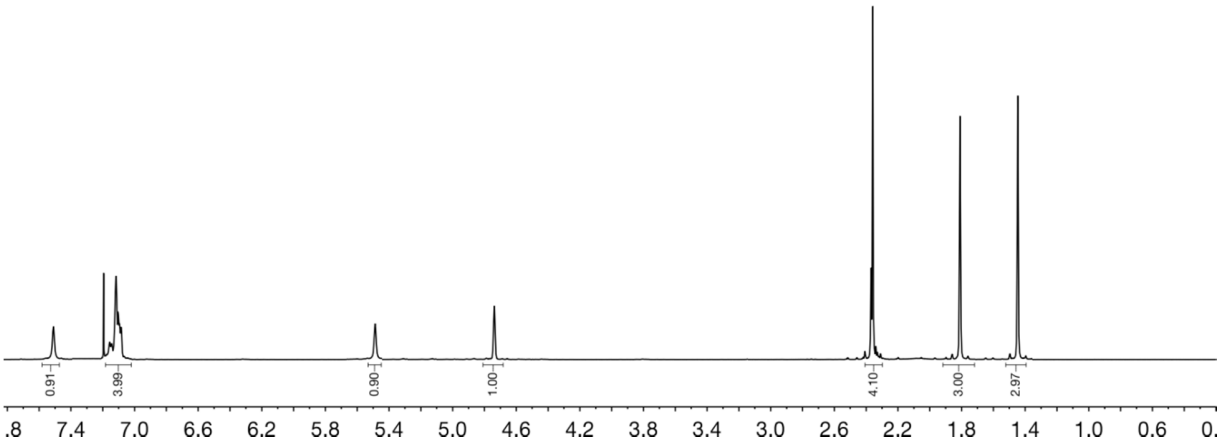
5,6-dimethyl-4-(*m*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (3a)



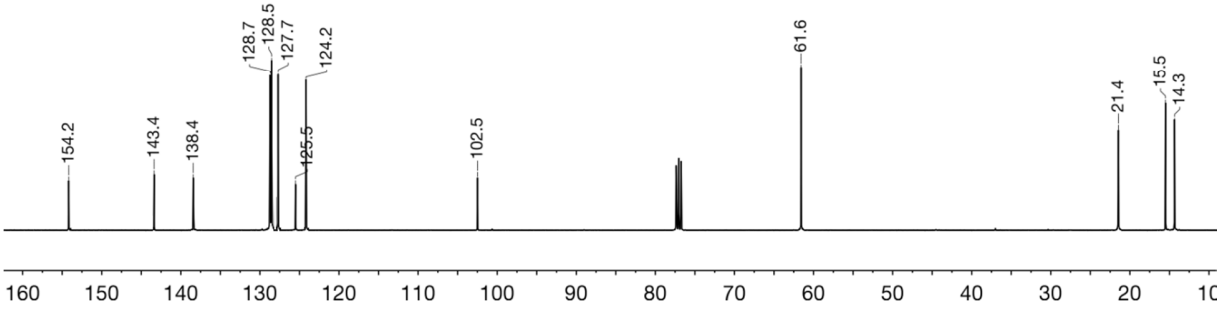
Yield: 88%

IR: 3225, 3100, 1695, 1655

EI-MS: 216 (13, M^+), 201 (55), 125 (100).

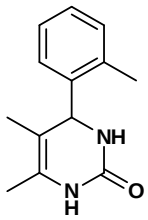


^{1}H NMR spectrum of compound **3a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **3a** in $CDCl_3$ (100.6 MHz)

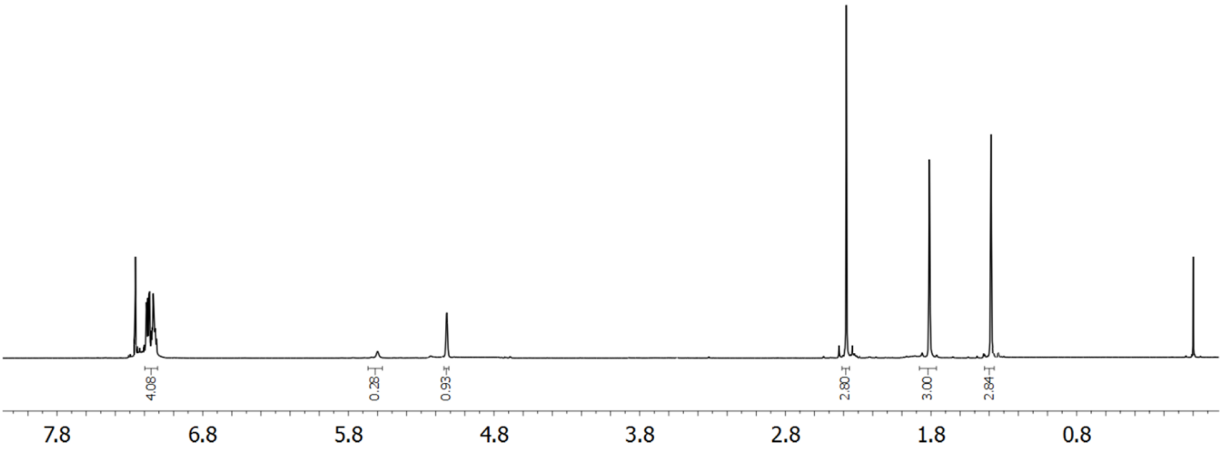
5,6-dimethyl-4-(*o*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (4a)



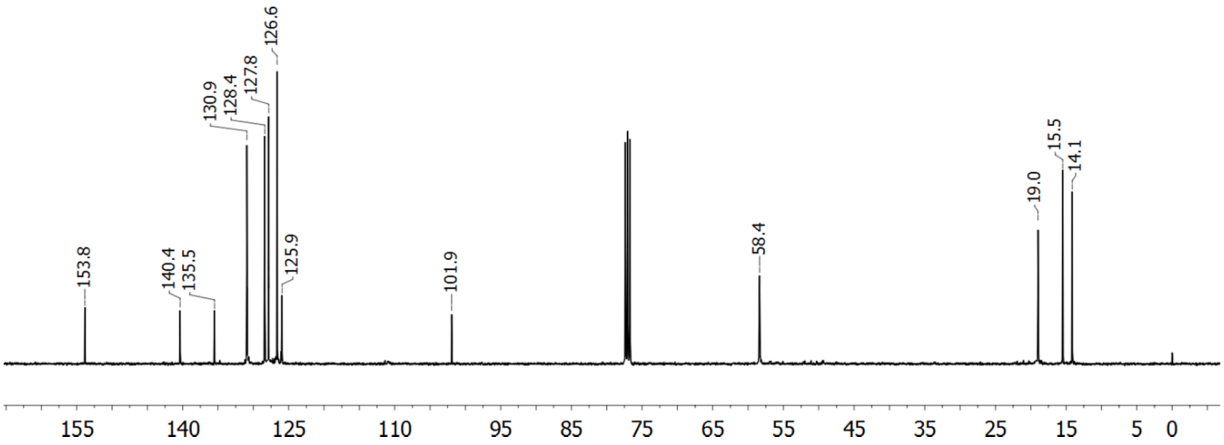
Yield: 81%

IR: 3225, 3100, 1655

EI-MS: 216 (9, M^+), 201 (65), 125 (100).

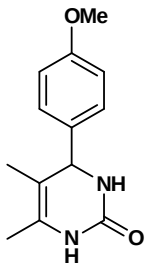


^{1}H NMR spectrum of compound **4a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **4a** in $CDCl_3$ (100.6 MHz)

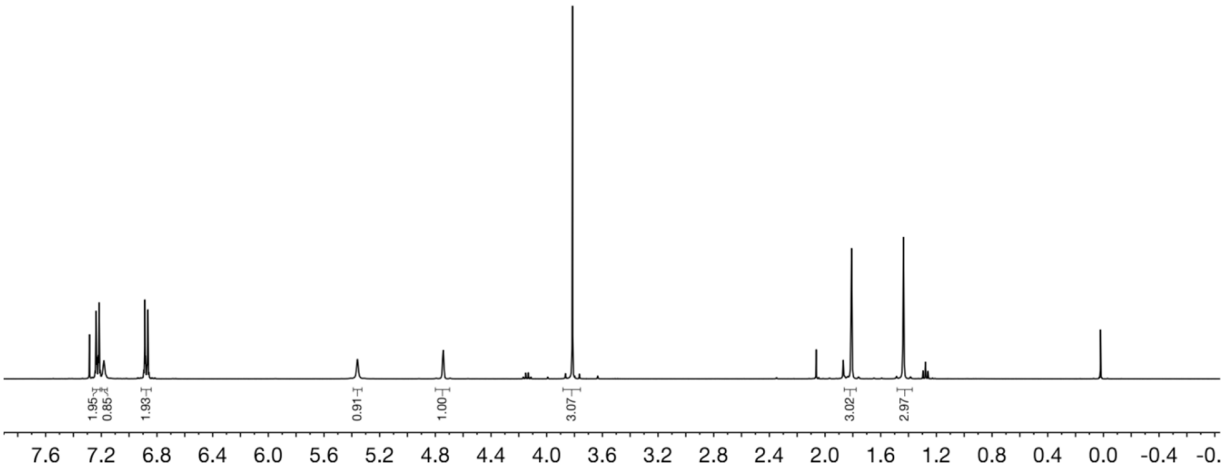
4-(4-methoxyphenyl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1H)-one (5a)



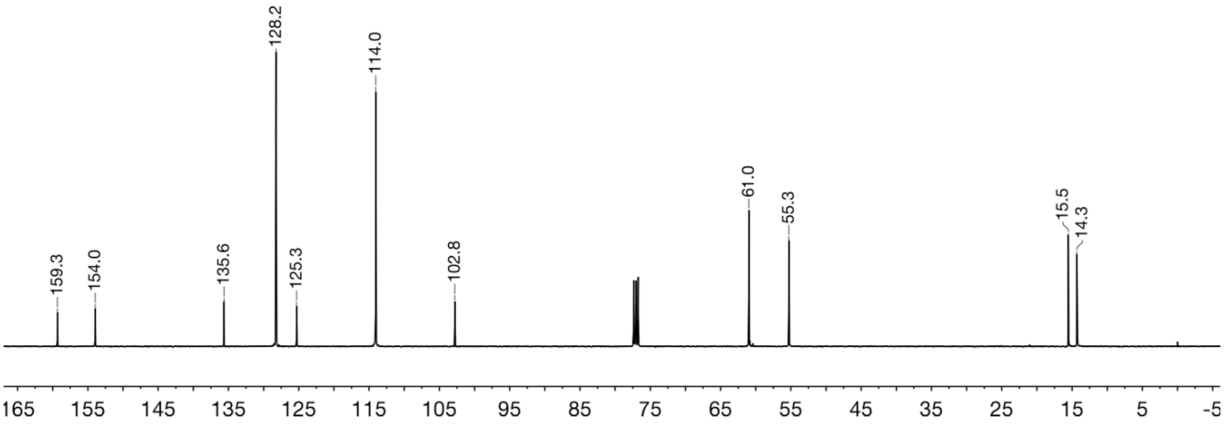
Yield: 92%

IR: 3235, 3100, 1670

EI-MS: 232 (17, M^+), 217 (61), 125 (100).

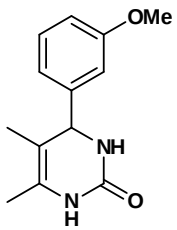


^{1}H NMR spectrum of compound **5a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **5a** in $CDCl_3$ (100.6 MHz)

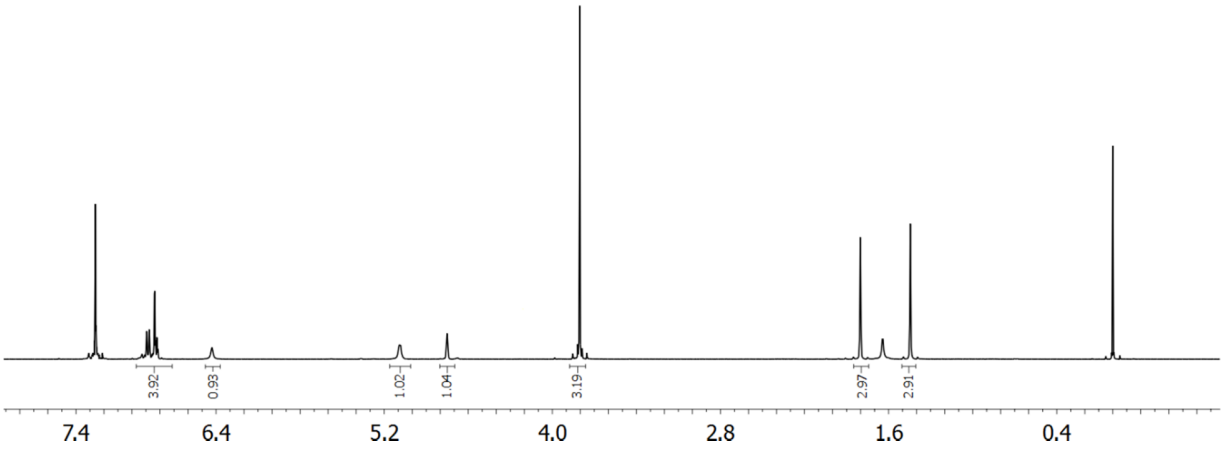
4-(3-methoxyphenyl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1*H*)-one (6a)



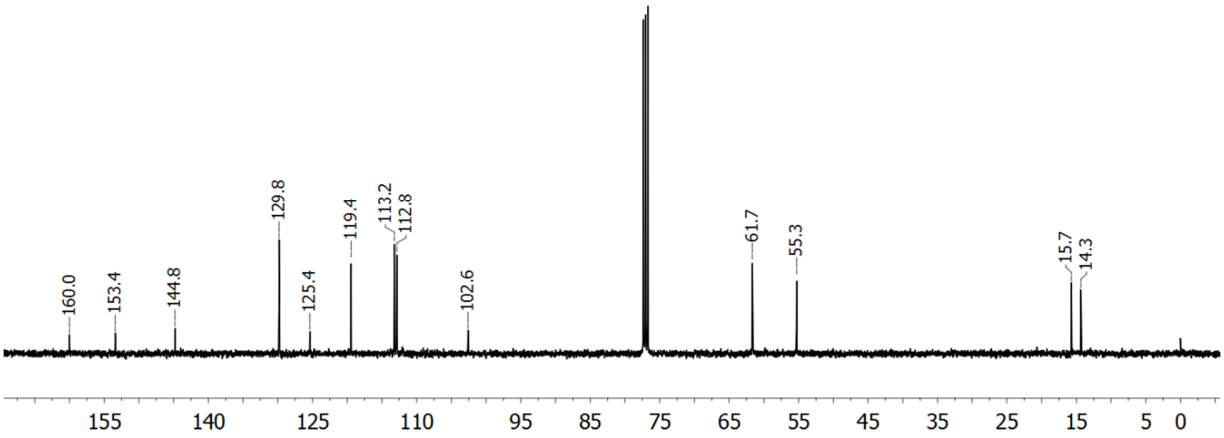
Yield: 87%

IR: 3225, 3100, 1660

EI-MS: 232 (10, M^+), 217 (52), 125 (100).

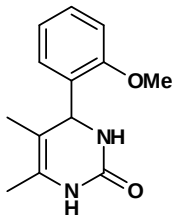


^{1}H NMR spectrum of compound **6a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **15** in $CDCl_3$ (100.6 MHz)

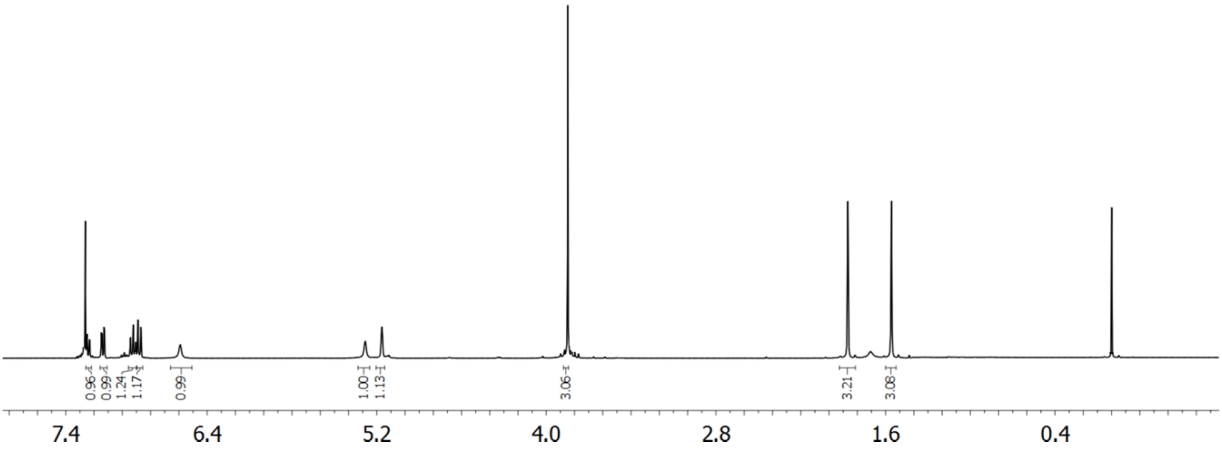
4-(2-methoxyphenyl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1*H*)-one (7a)



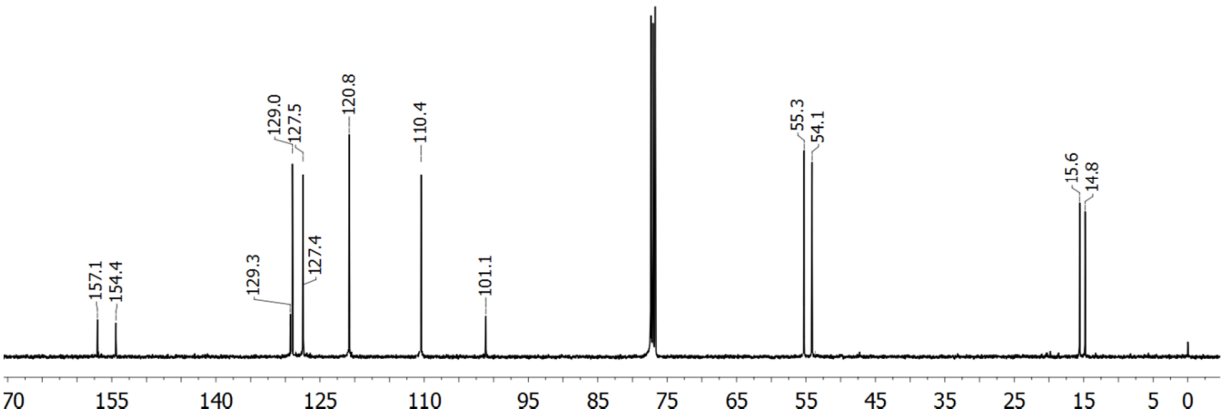
Yield: 82%

IR: 3230, 3100, 165

EI-MS (*m/z*, rel. intensity): 232 (17, M^+), 217 (61), 125 (100).

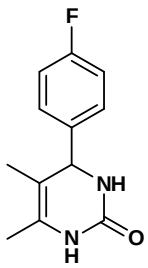


^{1}H NMR spectrum of compound **7a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **7a** in $CDCl_3$ (100.6 MHz)

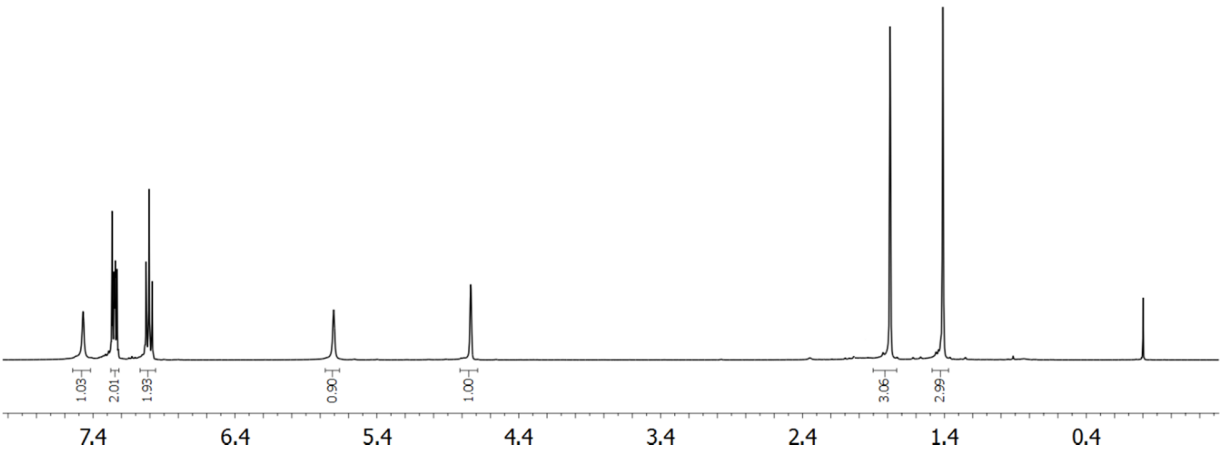
4-(4-fluorophenyl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1*H*)-one (8a)



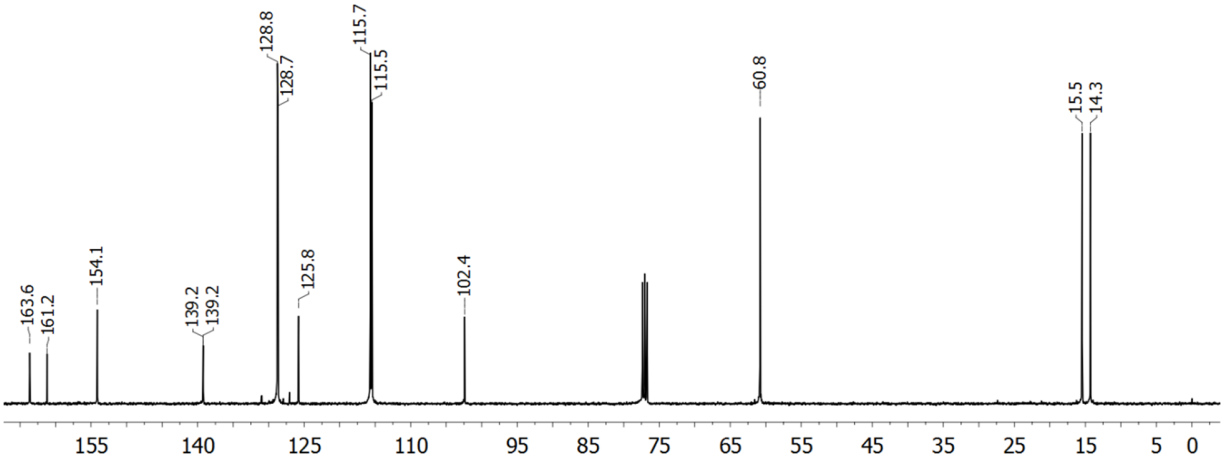
Yield: 90%

IR: 3230, 3100, 1670

EI-MS (*m/z*, rel. intensity): 220 (24, M^+), 205 (60), 125 (100).

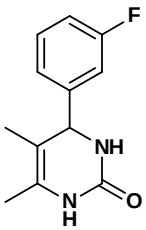


^{1}H NMR spectrum of compound **8a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **8a** in $CDCl_3$ (100.6 MHz)

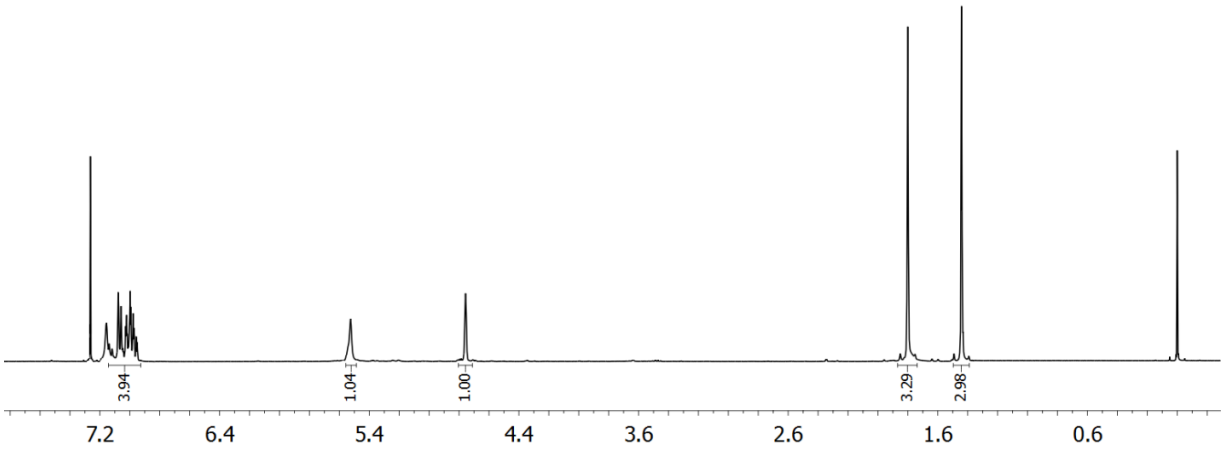
4-(3-fluorophenyl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1*H*)-one (9a)



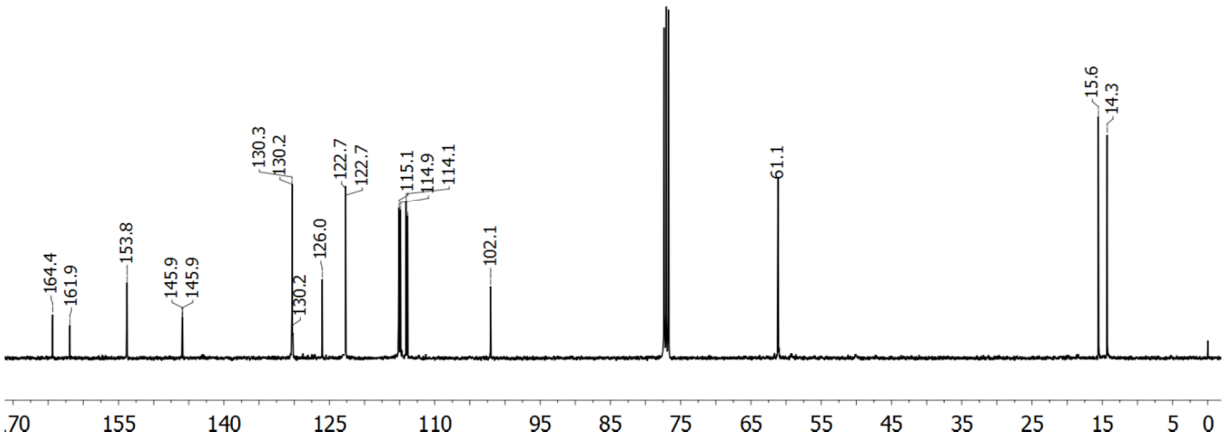
Yield: 85%

IR: 3240, 3100, 1655

EI-MS (*m/z*, rel. intensity): 220 (21, M^+), 205 (57), 125 (100).

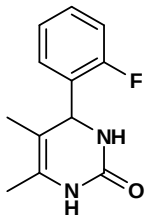


^{1}H NMR spectrum of compound **9a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **9a** in $CDCl_3$ (100.6 MHz)

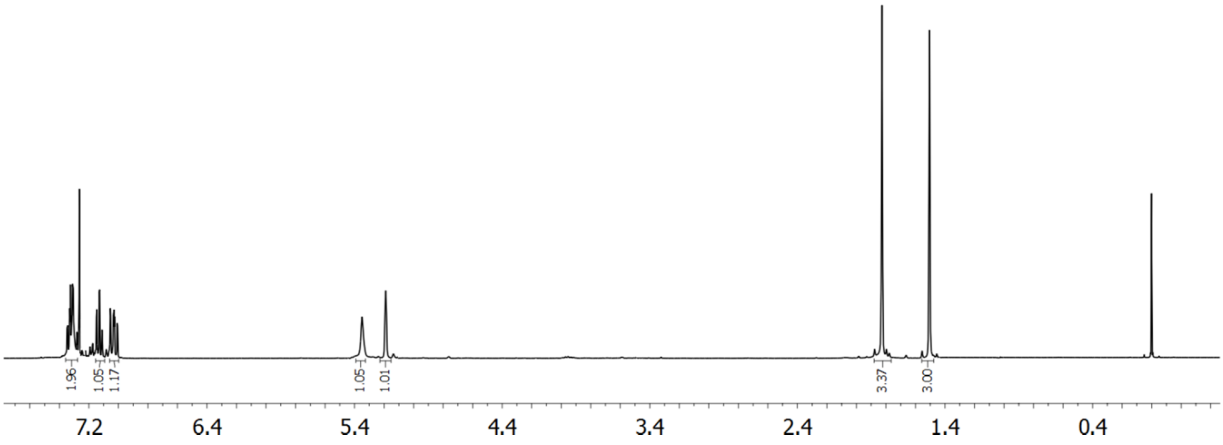
4-(2-fluorophenyl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1*H*)-one (10a)



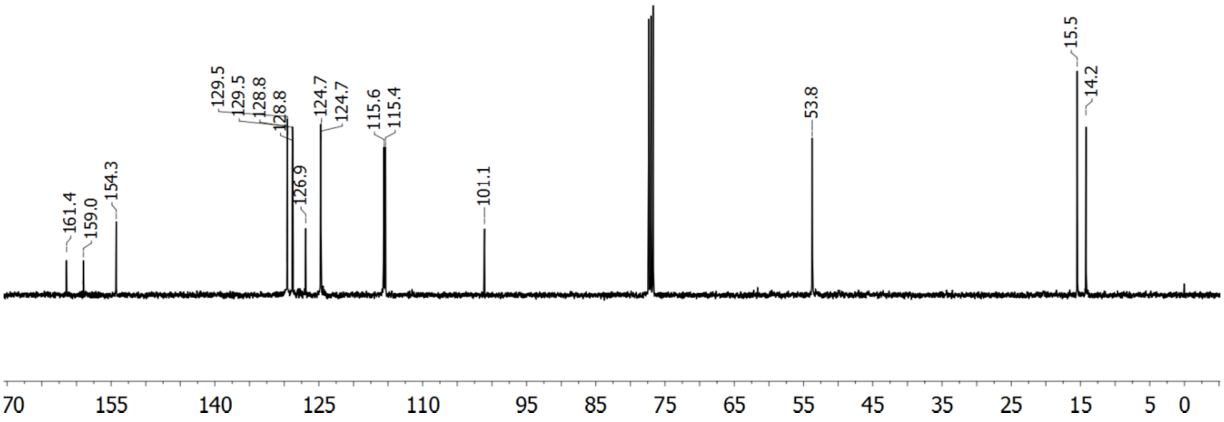
Yield: 82%

IR: 3230, 3100, 1680

EI-MS (*m/z*, rel. intensity): 220 (21, M^+), 205 (95), 125 (100)

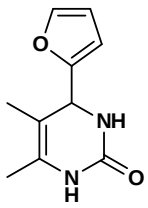


^{1}H NMR spectrum of compound **10a** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **10a** in $CDCl_3$ (100.6 MHz)

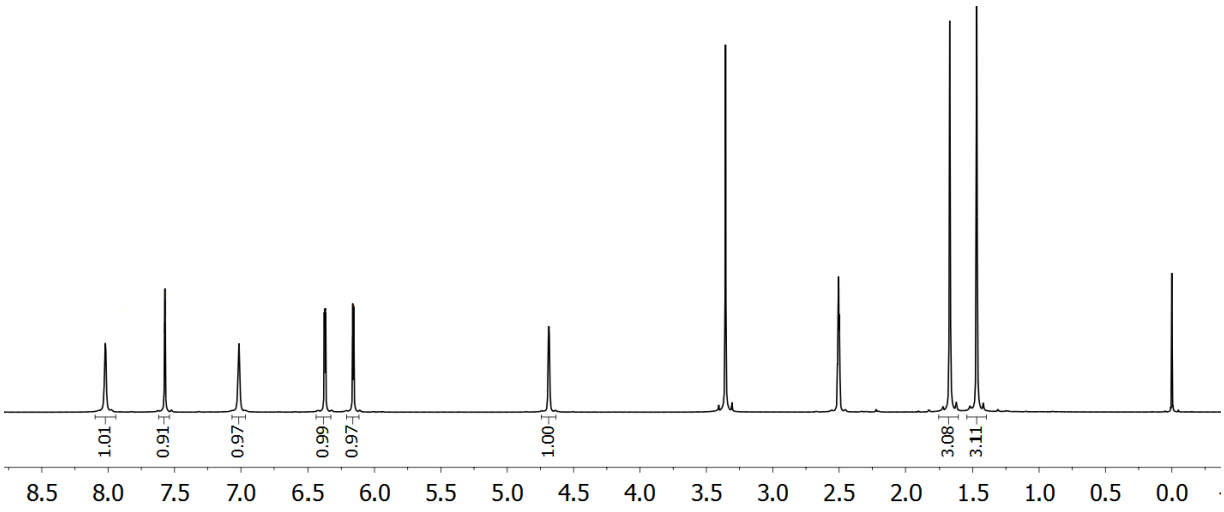
4-(furan-2-yl)-5,6-dimethyl-3,4-dihydropyrimidin-2(1H)-one (11a)



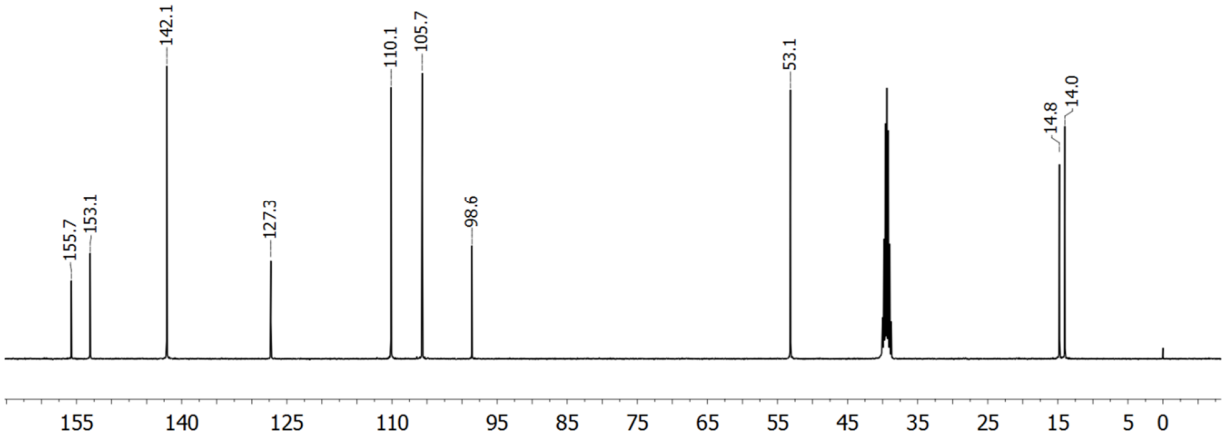
Yield: 95%

IR: 3210, 3100, 1650

EI-MS: 192 (39, M^+), 177 (100), 125 (22)

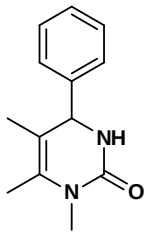


^{1}H NMR spectrum of compound **11a** in CD_3SOCD_3 (400 MHz)



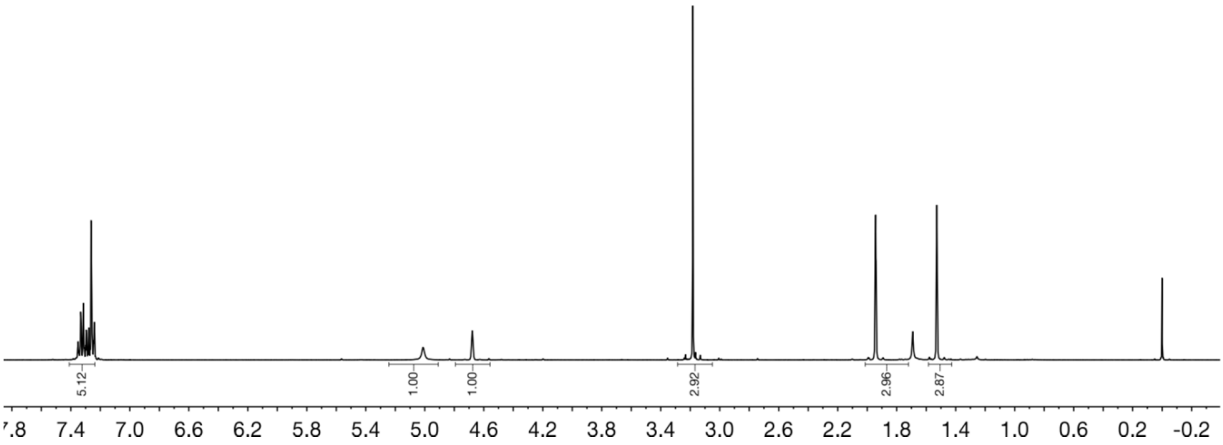
^{13}C NMR spectrum of compound **11a** in CD_3SOCD_3 (100.6 MHz)

1,5,6-trimethyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (12a)

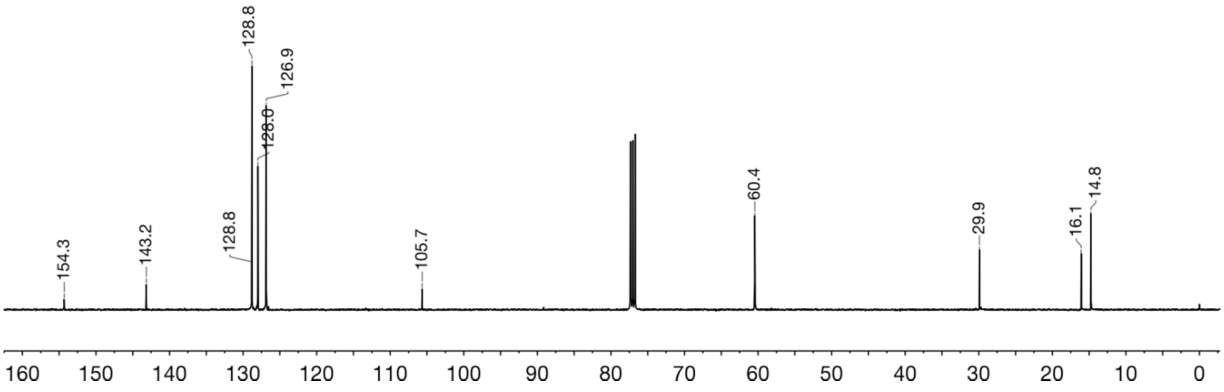


Yield: 14% IR: 3240, 3100, 1665 EI-MS (*m/z*, rel. intensity): 216 (16, M^+), 201 (48), 139 (100)

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 14.8 (C-8), 16.1 (C-7), 29.9 (NMe), 60.4 (C-4), 105.7 (C-5), 126.9 (C-2'), 128.0 (C-4'), 128.8 (C-3'), 128.8 (C-6), 143.2 (C-1'), 154.3 (C-2); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 1.53 (H-7), 1.94 (H-8), 3.18 (NMe), 4.68 (H-4), 5.01 (NH-3), 7.27-7.39 (5H, ArH).

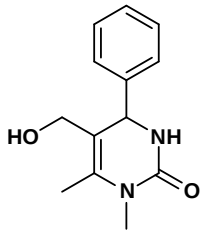


^{1}H NMR spectrum of compound **12b** in $CDCl_3$ (400 MHz)



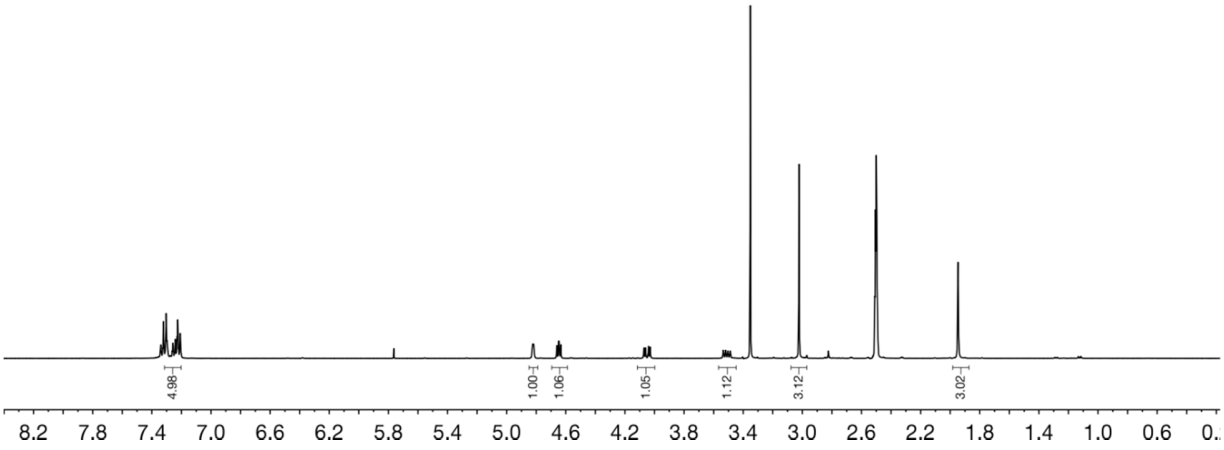
^{13}C NMR spectrum of compound **12b** in $CDCl_3$ (100.6 MHz)

5-(hydroxymethyl)-1,6-dimethyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (12b)

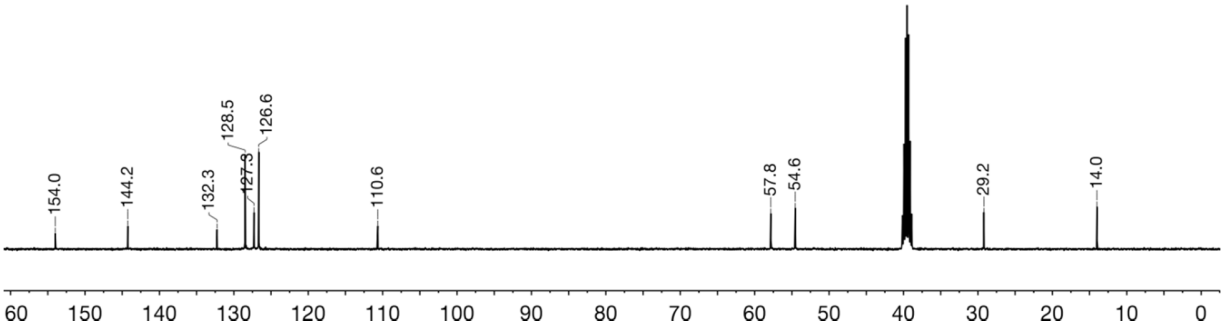


Yield: 74% IR: 3400-3200, 1670 EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ 14.0 (C-7), 29.2 (NMe), 54.6 (C-8), 57.8 (C-4), 110.6 (C-5), 126.6 (C-2'), 127.3 (C-4'), 128.5 (C-3'), 132.3 (C-6), 144.2 (C-1'), 154.0 (C-2); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ 1.95 (3H, H-7), 3.02 (3H, NMe), 3.51 (1H, *dd, J* = 12.5, 6.4 Hz, H-8), 4.05 (1H, *dd, J* = 12.5, 4.5 Hz, H-8), 4.65 (1H, OH, *dd, J*=6.4, 4.5 Hz), 4.82 (1H, H-4), 7.20-7.40 (5H).

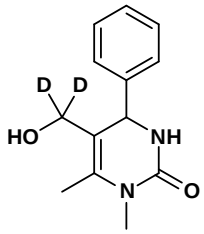


^{1}H NMR spectrum of compound **12b** in CD_3SOCD_3 (400 MHz)



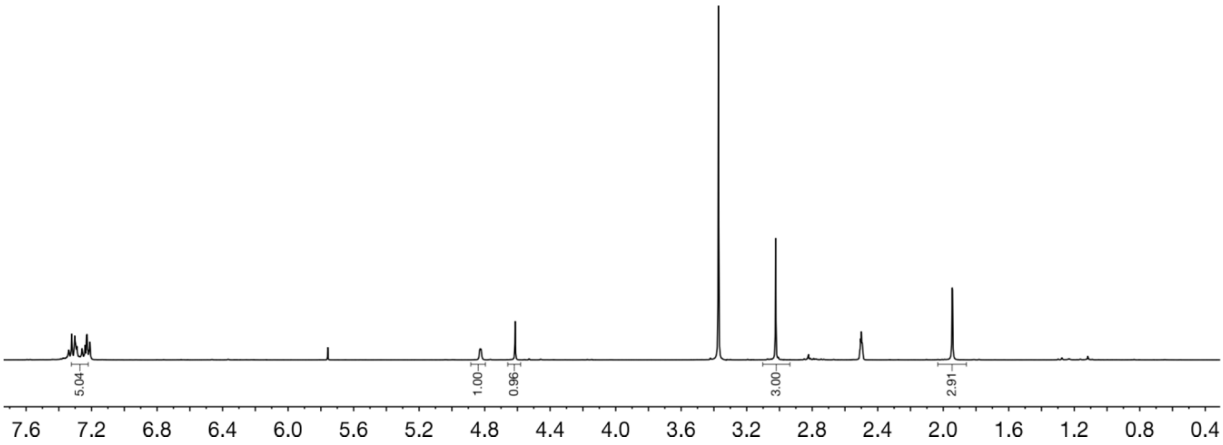
^{13}C NMR spectrum of compound **12b** in CD_3SOCD_3 (100.6 MHz)

(**12b, deuterated at C-8**)

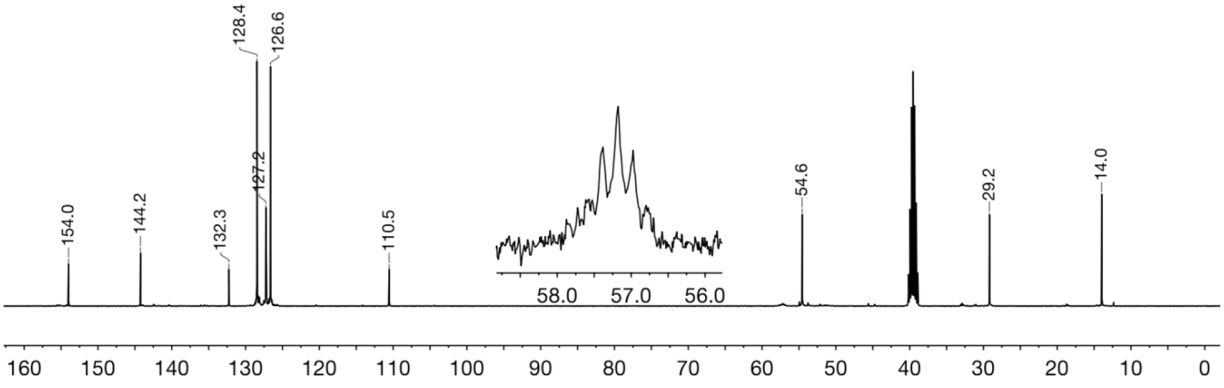


Yield: 70% EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ 14.0 (C-7), 29.2 (NMe), 54.6 (C-8), 57.2 (*q*, C-4), 110.5 (C-5), 126.6 (C-2'), 127.2 (C-4'), 128.4 (C-3'), 132.3 (C-6), 144.2 (C-1'), 154.0 (C-2); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ 1.94 (3H, H-7), 3.02 (3H, NMe), 4.61 (1H), 4.82 (1H, H-4), 7.20-7.40 (5H).

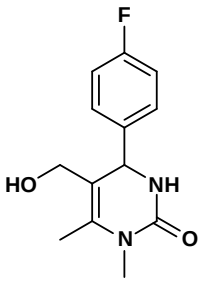


^{1}H NMR spectrum of compound **12b** in CD_3SOCD_3 (400 MHz)



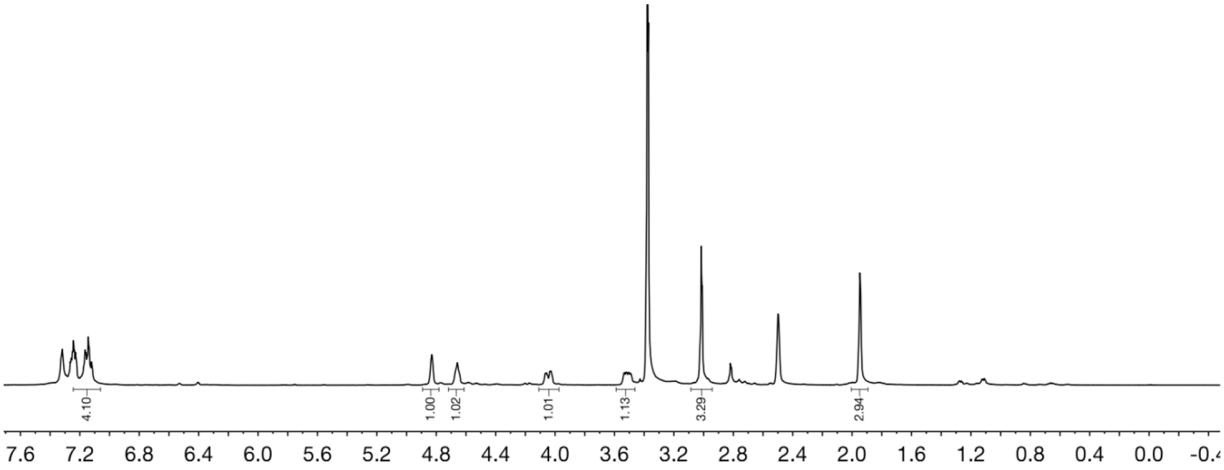
^{13}C NMR spectrum of compound **12b** in CD_3SOCD_3 (100.6 MHz)

4-(4-fluorophenyl)-5-(hydroxymethyl)-1,6-dimethyl-3,4-dihydropyrimidin-2(1H)-one (13b)

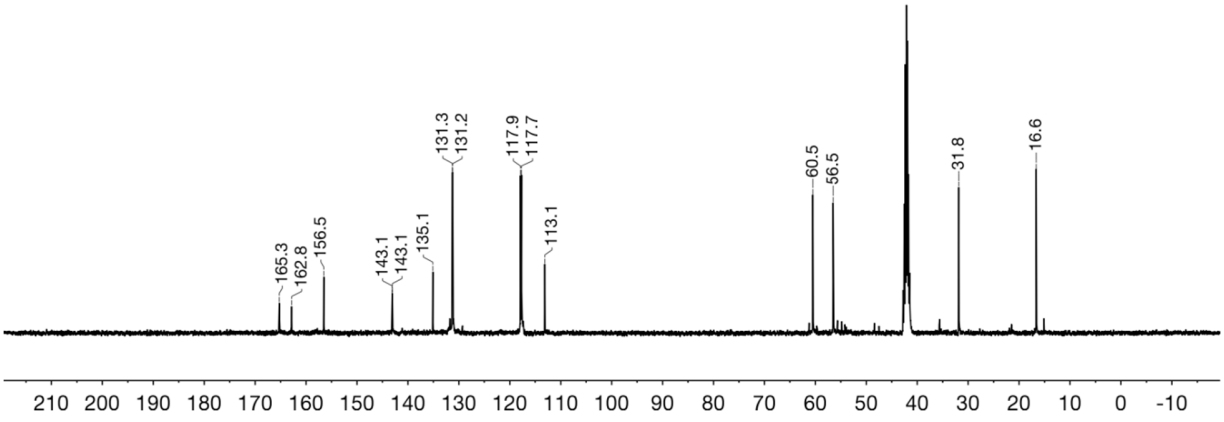


Yield: 75% IR: 3400-3200, 1660 EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ 16.6 (C-7), 31.8 (NMe), 56.5 (C-8), 60.5 (C-4), 113.1 (C-5), 117.8 (*d, J*= 21.2 Hz, C-3'), 131.2 (*d, J*=8.2 Hz, C-2'), 135.0 (C-6), 143.1 (C-1'), 156.0 (C-2) 164.0 (*d, J*= 242.7 Hz, C-4'); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ 1.95 (3H, H-7), 3.01 (3H, NMe), 3.51 (1H, *dd, J* = 12.5, 6.4 Hz, H-8), 4.04 (1H, *dd, J* = 12.5, 4.5 Hz, H-8), 4.66 (1H, OH, *dd, J*=6.4, 4.5 Hz), 4.83 (1H, H-4), 7.08-7.24 (5H, ArH).

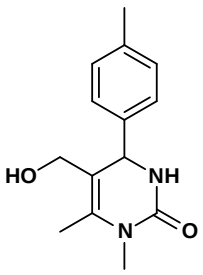


^{1}H NMR spectrum of compound **13b** in CD_3SOCD_3 (400 MHz)



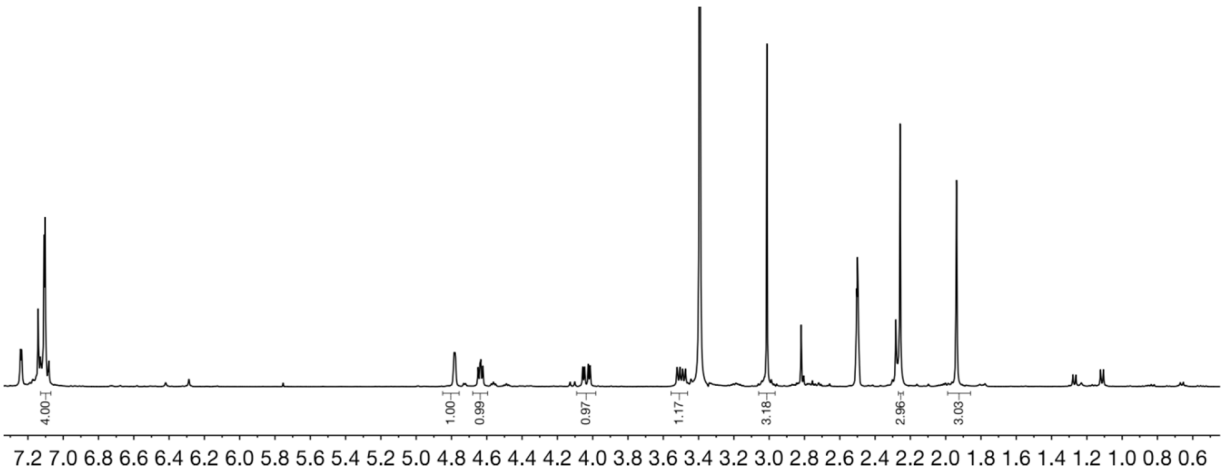
^{13}C NMR spectrum of compound **13b** in CD_3SOCD_3 (100.6 MHz)

5-(hydroxymethyl)-1,6-dimethyl-4-(*p*-tolyl)-3,4-dihydropyrimidin-2(1*H*)-one (15b)

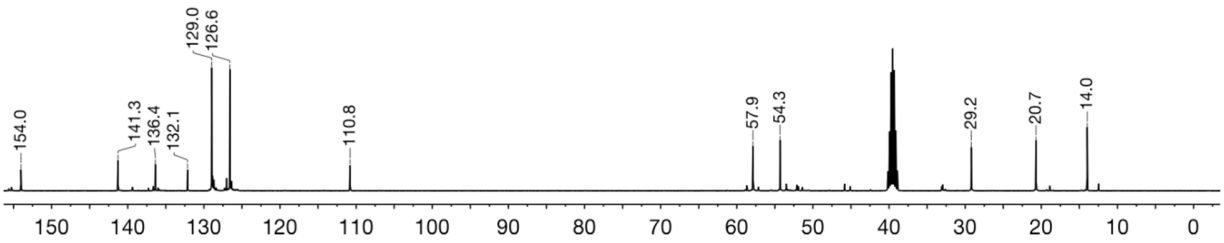


Yield: 80% IR: 3400-3200, 1650 EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ 14.0 (C-7), 20.7 (C-1"), 29.2 (NMe), 54.3 (C-8), 57.9 (C-4), 110.8 (C-5), 126.6 (C-2'), 129.0 (C-3'), 132.1 (C-6), 136.4 (C-4'), 141.3 (C-1'), 154.0 (C-2); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ 1.94 (3H, H-7), 2.26 (3H, H-1") 3.01 (3H, NMe), 3.50 (1H, *dd, J* = 12.5, 6.4 Hz, H-8), 4.04 (1H, *dd, J* = 12.5, 4.5 Hz, H-8), 4.64 (1H, OH, *dd, J*=6.4, 4.5 Hz), 4.76 (1H, H-4), 7.08-7.13 (4H).

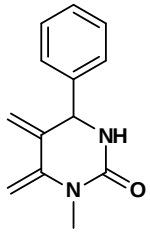


^{1}H NMR spectrum of compound **15b** in CD_3SOCD_3 (400 MHz)



^{13}C NMR spectrum of compound **15b** in CD_3SOCD_3 (100.6 MHz)

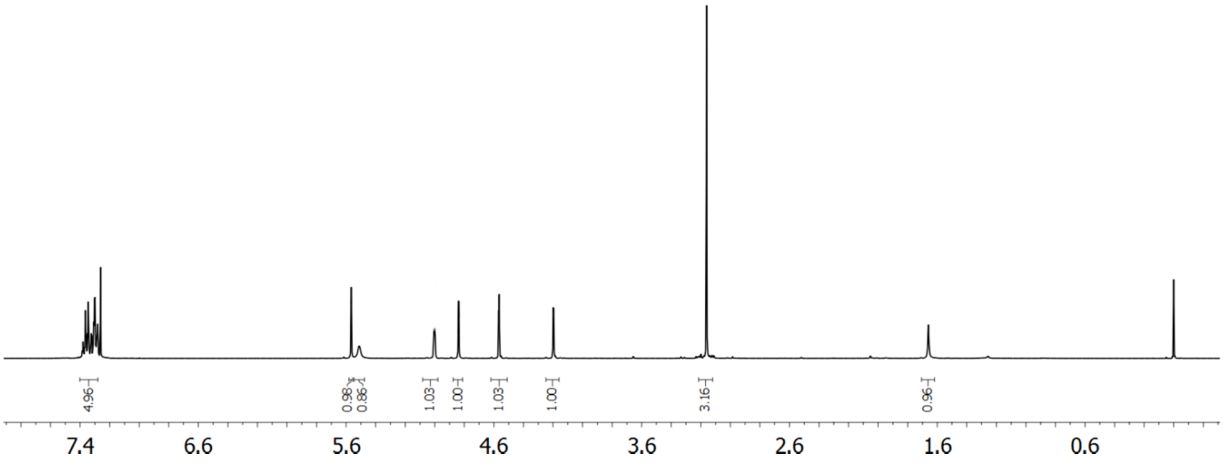
1-methyl-5,6-dimethylene-4-phenyltetrahydropyrimidin-2(1H)-one (12c)



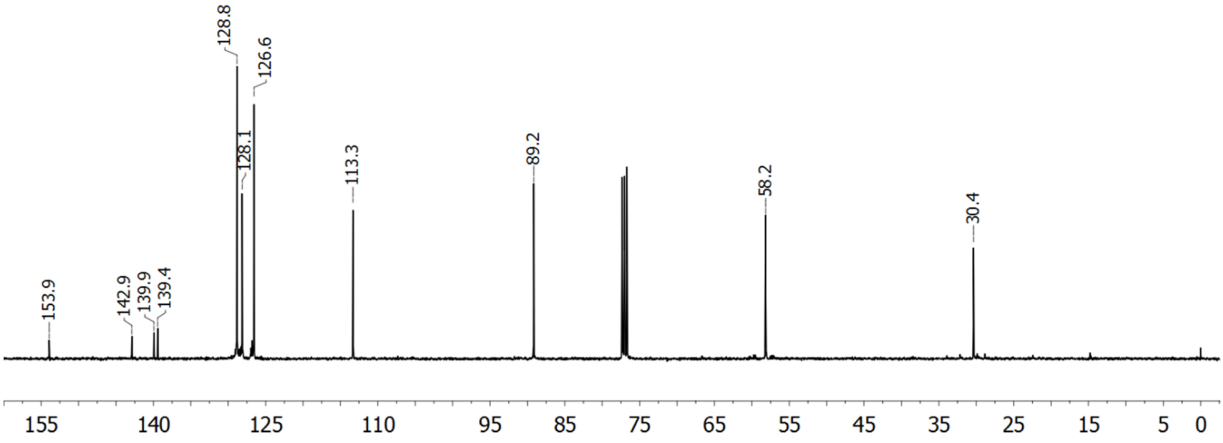
Yield: 55%

IR: 3240, 3100, 1700

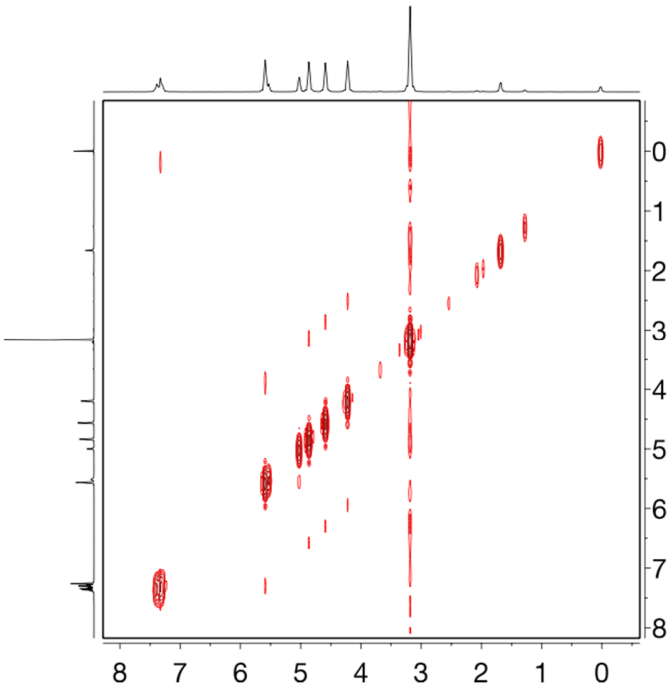
EI-MS (*m/z*, rel. intensity): 214 (100, M^+), 170 (57), 156 (24), 115 (33).



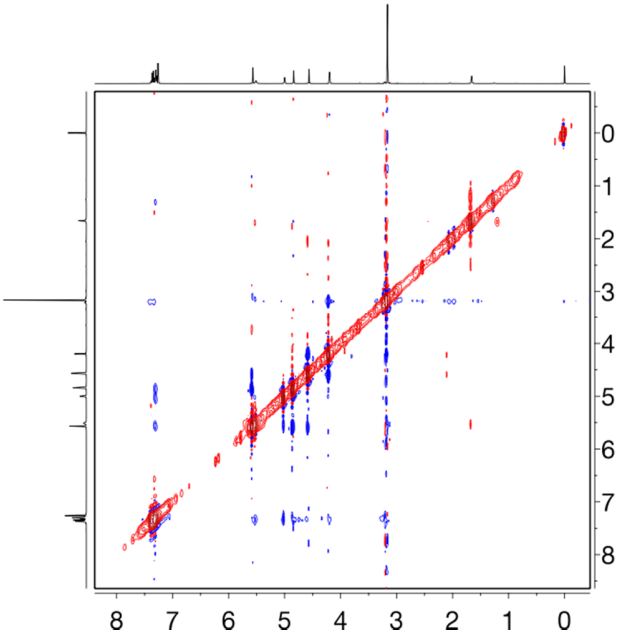
^{1}H NMR spectrum of compound **12c** in $CDCl_3$ (400 MHz)



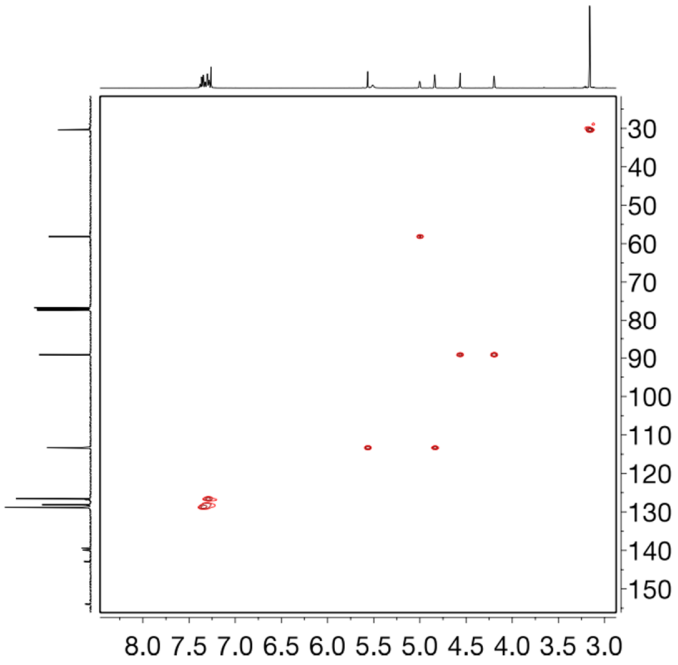
^{13}C NMR spectrum of compound **12c** in $CDCl_3$ (100.6 MHz)



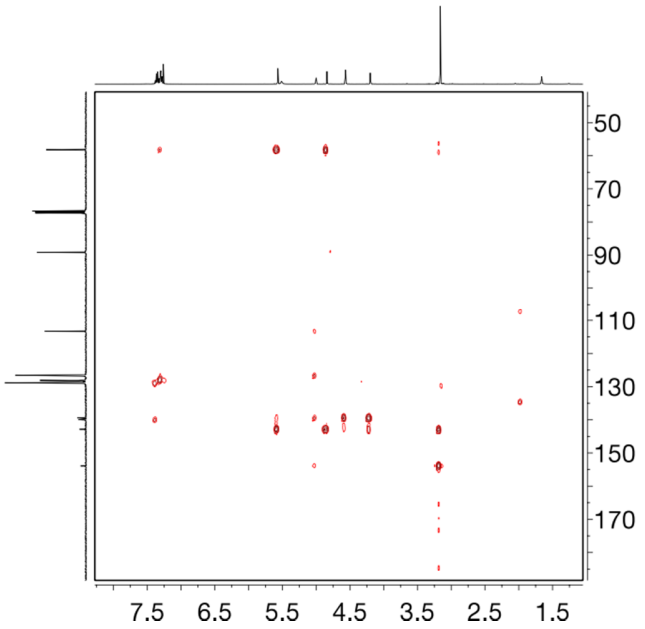
^{1}H-^{1}H COSY spectrum of compound **12c** in $CDCl_3$ (400 MHz)



NOESY spectrum of compound **12c** in $CDCl_3$ (400 MHz)

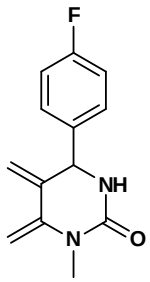


HSQC spectrum of compound **12c** in $CDCl_3$ (400 and 100.6 MHz)



HMBC spectrum of compound **12c** in $CDCl_3$ (400 and 100.6MHz)

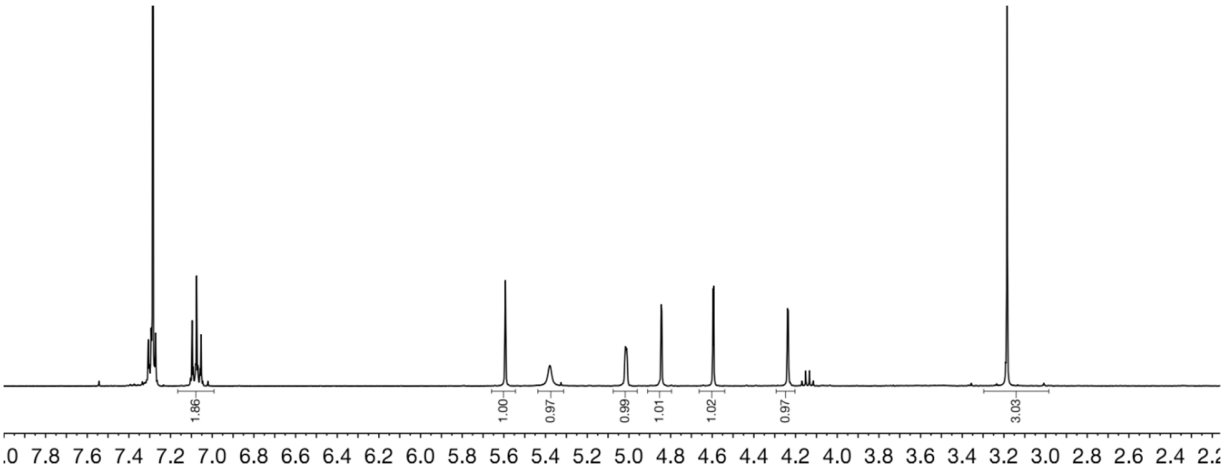
4-(4-fluorophenyl)-1-methyl-5,6-dimethylenetetrahydropyrimidin-2(1H)-one (13c)



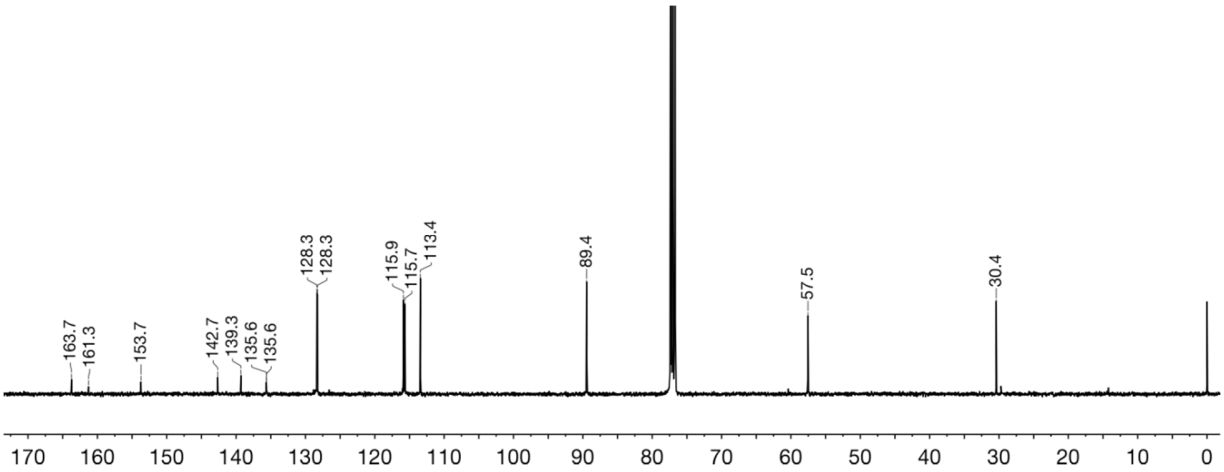
Yield: 52%

IR: 3230, 3100, 1680

EI-MS (*m/z*, rel. intensity): 232 (100, M^+), 188 (63), 174 (26), 133 (33).

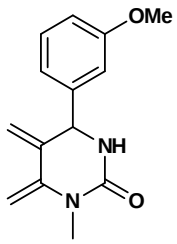


^{1}H NMR spectrum of compound **13c** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **13c** in $CDCl_3$ (100.6 MHz)

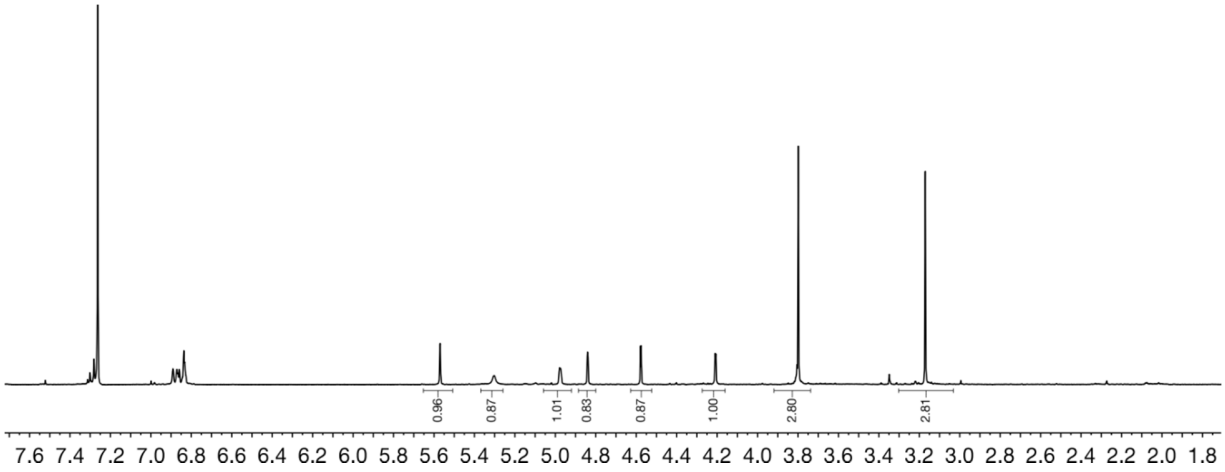
4-(3-methoxyphenyl)-1-methyl-5,6-dimethylenetetrahydropyrimidin-2(1H)-one (14c)



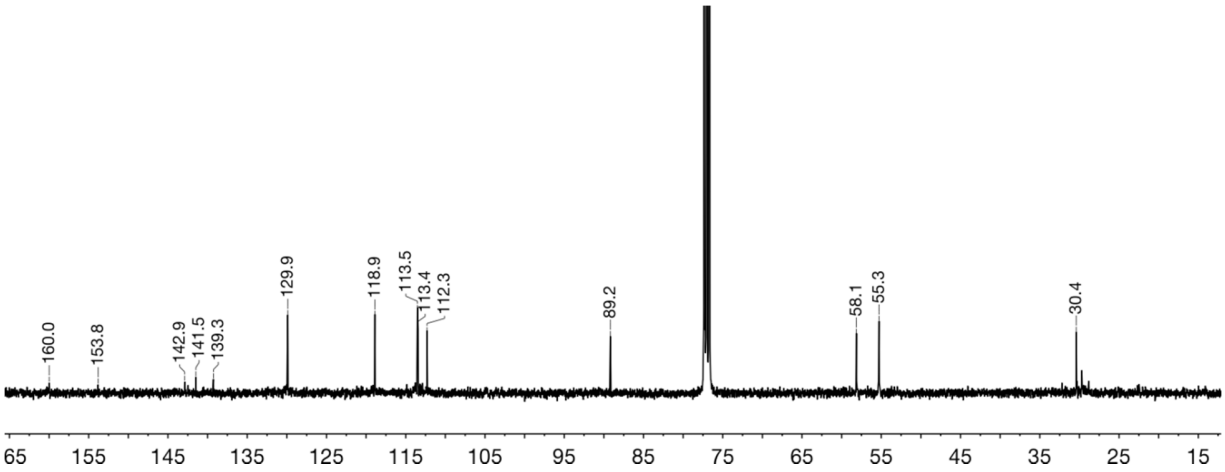
Yield: 52%

IR: 3230, 3100, 1670

EI-MS: EI-MS (*m/z*, rel. intensity): 244 (100, M^+), 229 (18), 200 (17), 186 (18), 121 (26).

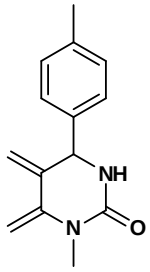


^{1}H NMR spectrum of compound **14c** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **14c** in $CDCl_3$ (100.6 MHz)

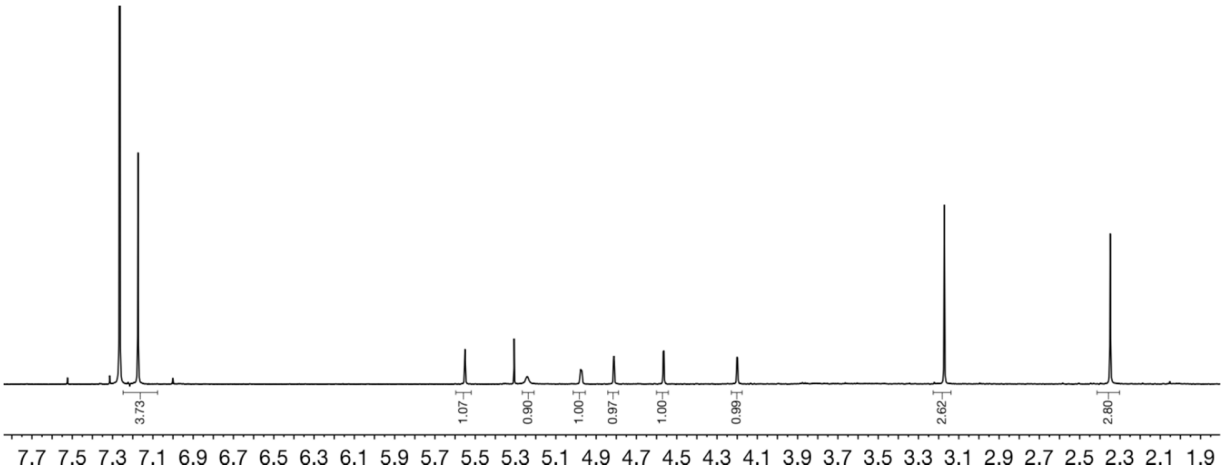
1-methyl-5,6-dimethylene-4-(p-tolyl)tetrahydropyrimidin-2(1H)-one (15c)



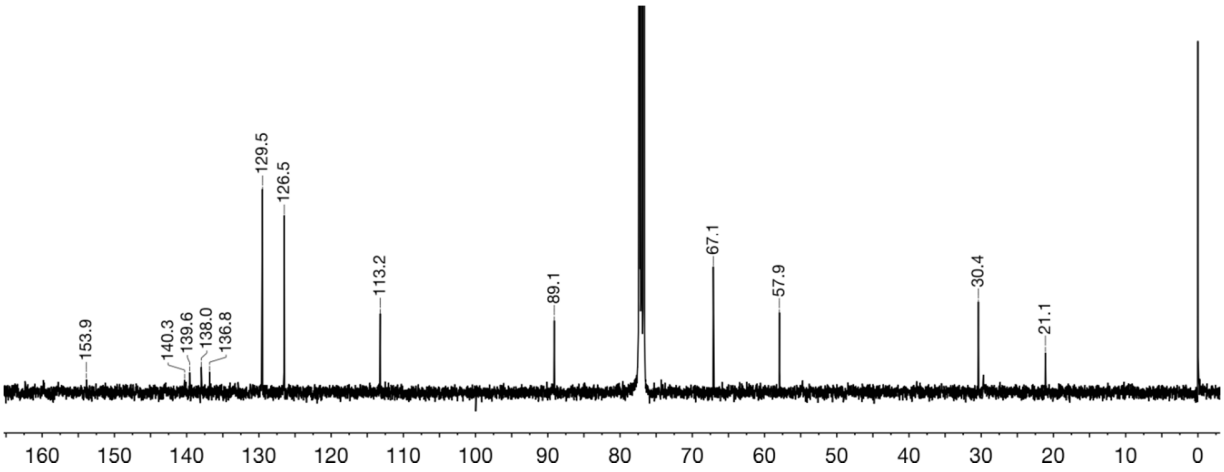
Yield: 60%

IR: 3220, 3100, 1660

EI-MS (*m/z*, rel. intensity): 228 (100, M^+), 213 (30), 184 (48), 170 (44), 129 (29).

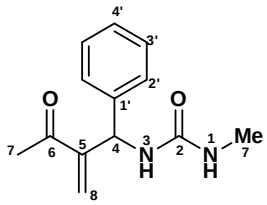


^{1}H NMR spectrum of compound **15c** in $CDCl_3$ (400 MHz)



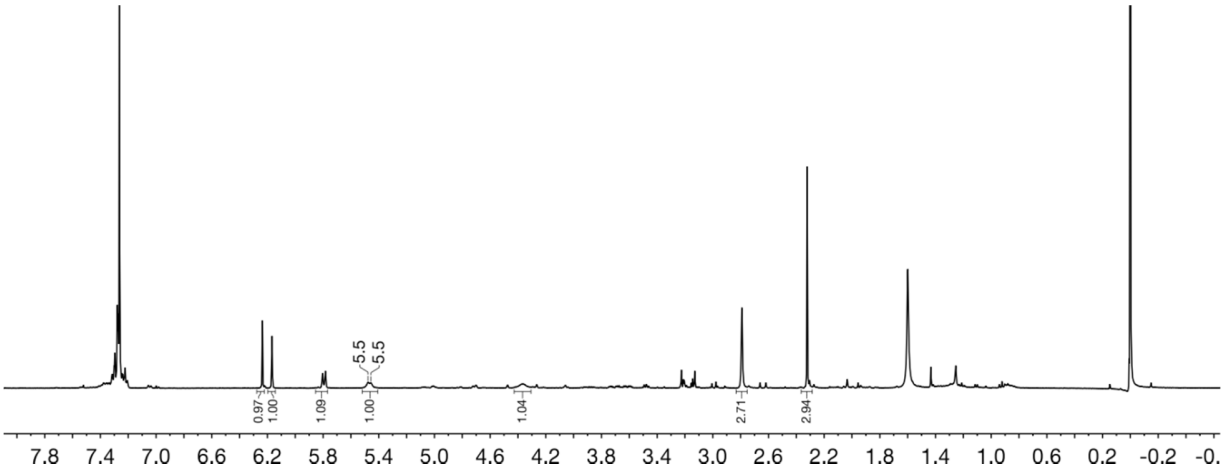
^{13}C NMR spectrum of compound **15c** in $CDCl_3$ (100.6 MHz)

1-methyl-3-(2-methylene-3-oxo-1-phenylbutyl)urea (12d)

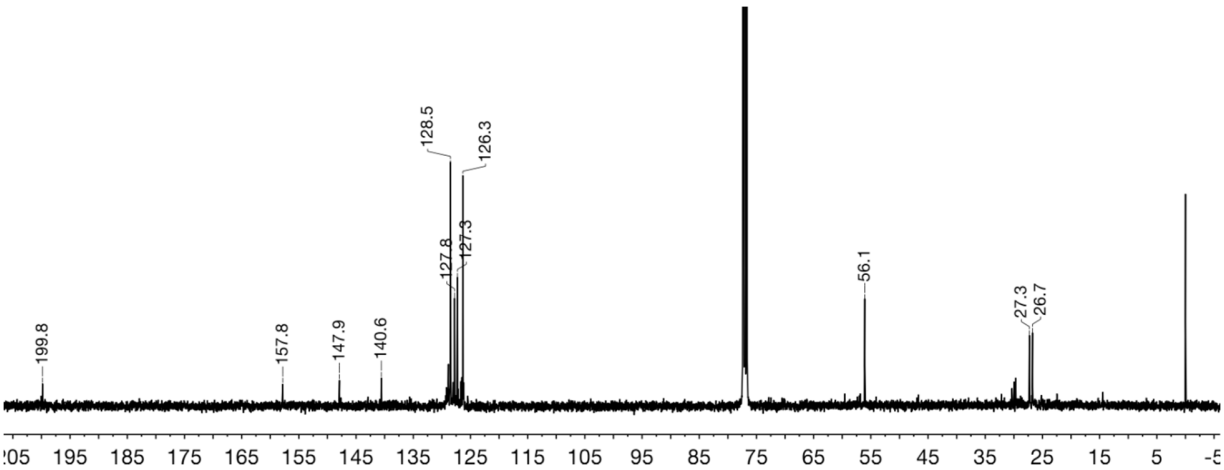


Yield: 60% IR: 3240, 3100, 1720, 1650 EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 26.7 (C-7), 27.3 (NMe), 56.1 (C-4), 126.3 (C-2'), 127.3 (C-4'), 127.8 (C-8), 128.5 (C-3'), 140.6 (C-4'), 147.9 (C-5), 157.8 (C-2), 199.8 (C-6);); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 2.37 (3H, H-7), 2.79 (3H, NMe), 4.37 (1H, NH-1), 5.47 (1H, d, J= 8.5 Hz, NH-3), 5.79 (1H, d, J=8.5 Hz, H-4), 6.17 (1H, H-8), 6.24 (1H, H-8), 7.25-7.29 (5H, ArH).

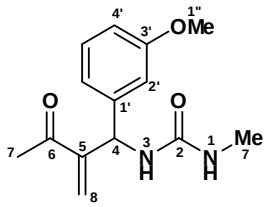


^{1}H NMR spectrum of compound **12d** in $CDCl_3$ (400 MHz)



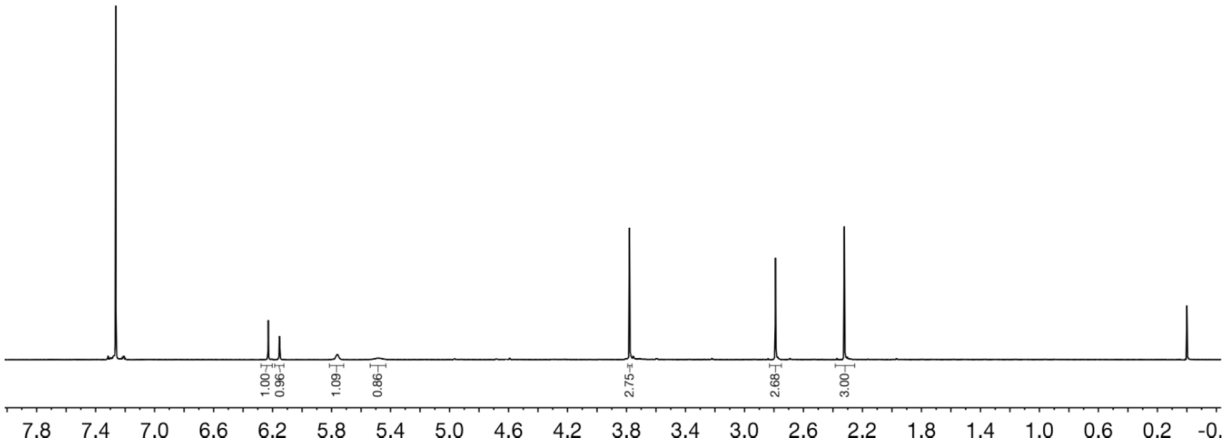
^{13}C NMR spectrum of compound **12d** in $CDCl_3$ (100.6 MHz)

1-(1-(3-methoxyphenyl)-2-methylene-3-oxobutyl)-3-methylurea (14d)

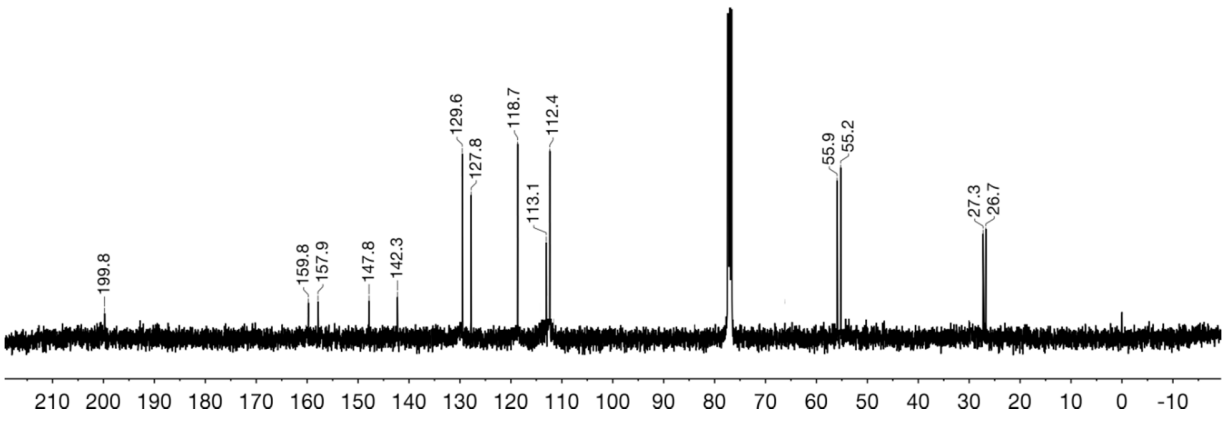


Yield: 60% IR: 3220, 3100, 1730, 1650 EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 26.7 (C-7), 27.3 (NMe), 55.2 (C-1"), 55.9 (C-4), 56.1 (C-4), 112.4 (C-4'), 113.1 (C-2'),118.7 (C-6'), 127.8 (C-8), 129.6 (C-5'), 142.3 (C-1'), 147.8 (C-5), 157.9 (C-2), 159.8 (C-3'), 199.8 (C-6); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 2.32 (3H, H-7), 2.79 (3H, NMe), 3.78 (3H, H-1"), 5.49 (1H, d, J= 8.5 Hz, NH-3), 5.76 (1H, d, J=8.5 Hz, H-4), 6.15 (1H, H-8), 6.23 (1H, H-8), 6.80-6.95 (4H, ArH).

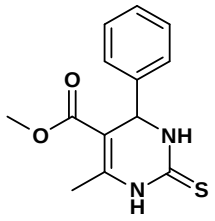


^{1}H NMR spectrum of compound **14d** in $CDCl_3$ (400 MHz)



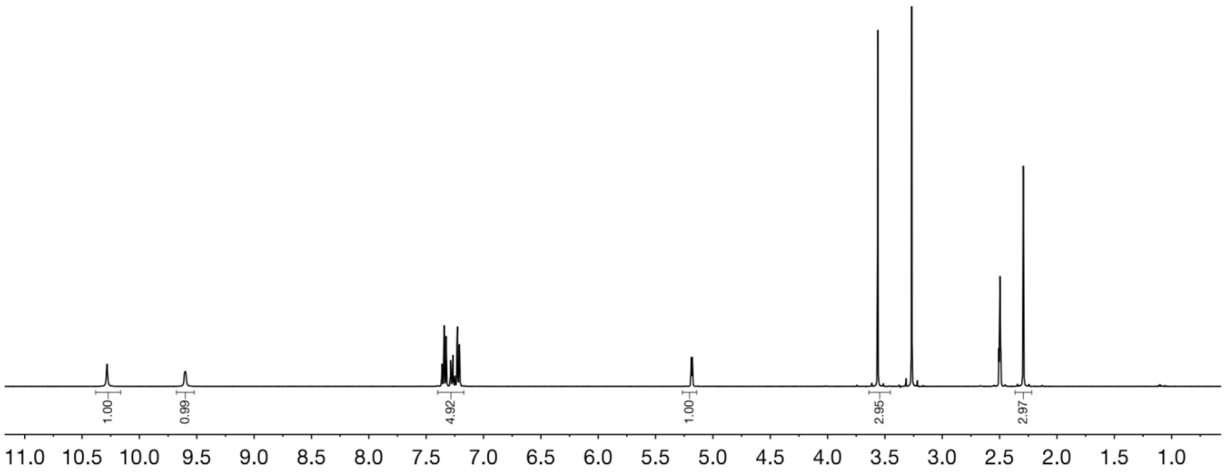
^{13}C NMR spectrum of compound **14d** in $CDCl_3$ (100.6 MHz)

Methyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate (16)

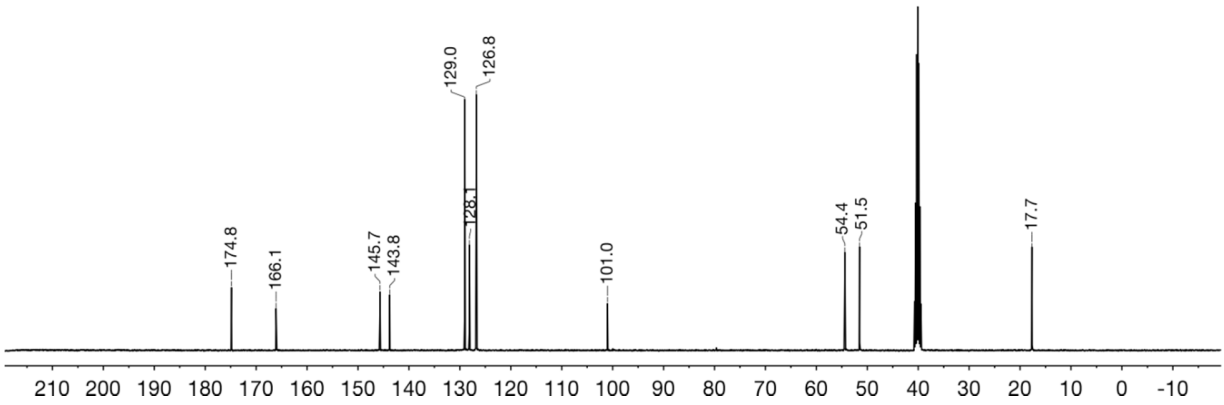


Yield: 90% IR: 3250, 3100, 1705, 1650

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ = 17,7 (C-7), 51.5 (C-9), 54.4 (C-4), 101.0 (C-5), 126.8 (C-2‘), 128.1 (C-4‘), 129.0 (C-3‘), 143.8 (C-1‘), 145.7 (C-6), 166.1 (C-8), 174.8 (C-2); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ = 2.29 (3H, H-7), 3.56 (3H, H-9), 5.18 (1H, H-4), 7.15-7.41 (5H, H-2’ – H-4’), 9.60 (1H, NH-3), 10.28 (1H, NH-1).

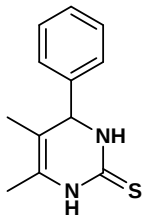


^{1}H NMR spectrum of compound **16** in CD_3SOCD_3 (400 MHz)



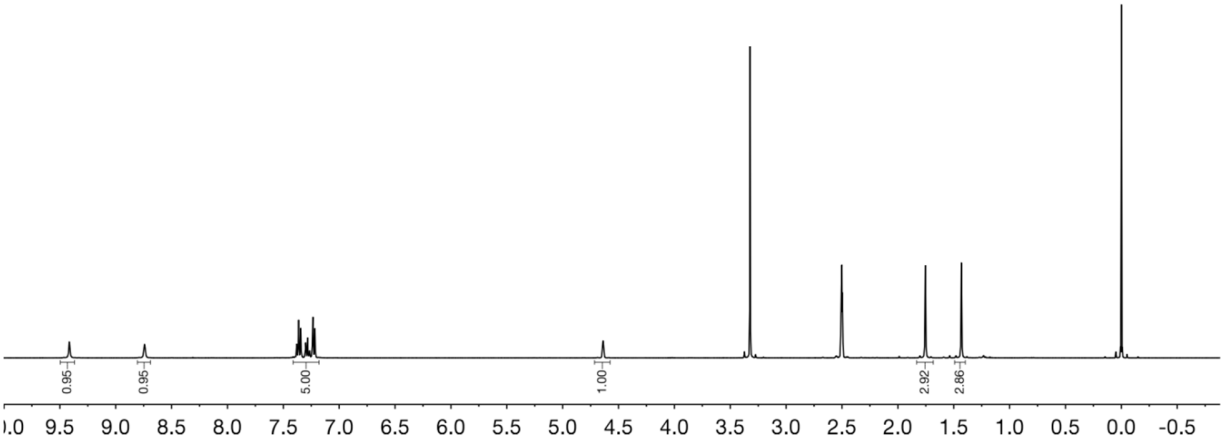
^{13}C NMR spectrum of compound **16** in CD_3SOCD_3 (100.6 MHz)

5,6-dimethyl-4-phenyl-3,4-dihydropyrimidine-2(1H)-thione (16a)

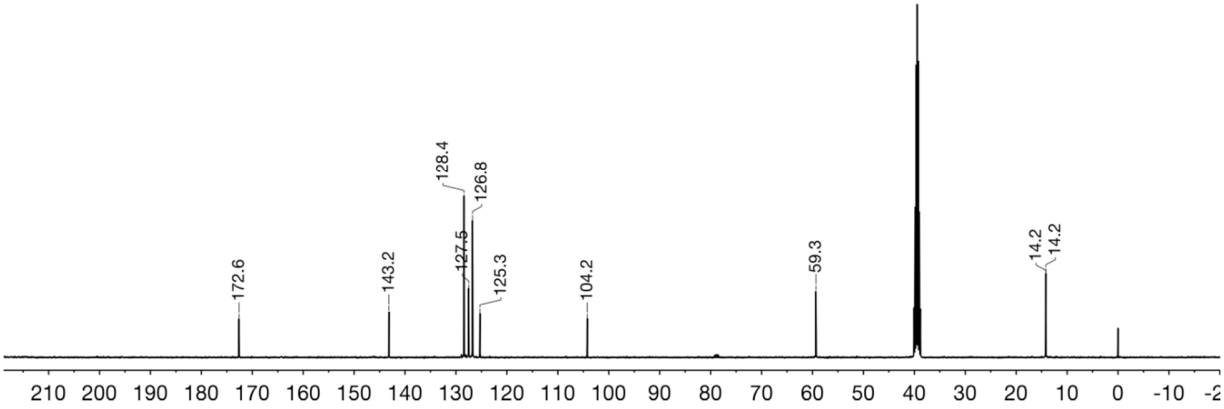


Yield: 22% IR: 3250, 3100, 1670 EI-MS (*m/z*): 218 (M^+, 63), 203 (38), 141 (100), 158 (16)

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ = 14.2 (C-7), 14.2 (C-7), 59.3 (C-4), 104.2 (C-5), 125.3 (C-6), 126.8 (C-2'), 127.5 (C-4'), 128.4 (C-3'), 143.2 (C-1'), 172.6 (C-2); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ = 1.43 (3H, H-8), 1.75 (3H, H-7), 4.64 (1H, H-4), 7.20-7.40 (5H, ArH), 8.74 (1H, NH-3), 9.41 (1H, NH-1).

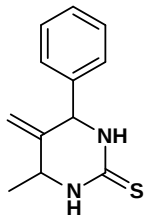


^{1}H NMR spectrum of compound **16a** in CD_3SOCD_3 (400 MHz)



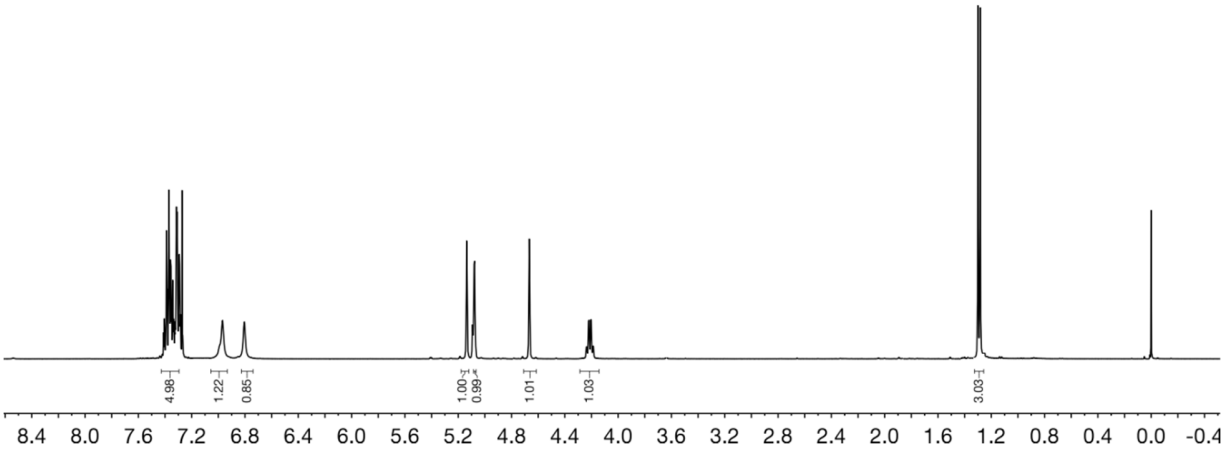
^{13}C NMR spectrum of compound **16a** in CD_3SOCD_3 (100.6 MHz)

4-methyl-5-methylene-6-phenyltetrahydropyrimidine-2(1*H*)-thione (16b)

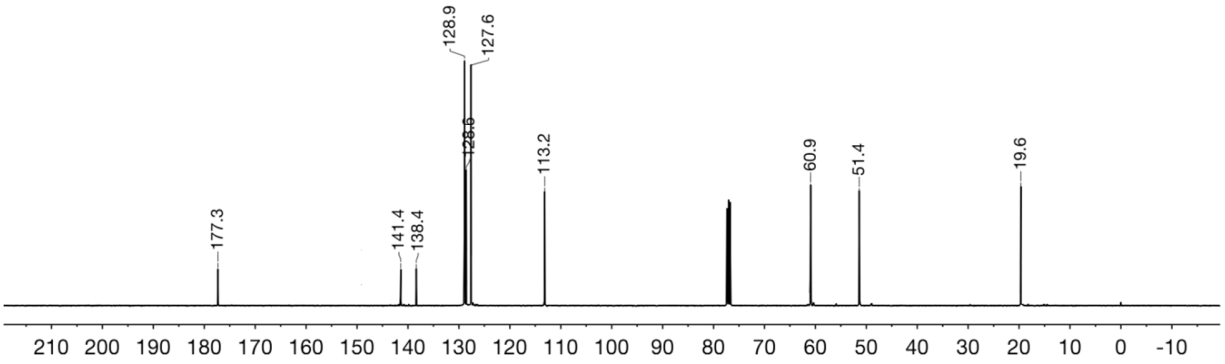


Yield: 57% IR: 3200, 3100, 1660 EI-MS (*m/z*): 218 (M^+, 44), 203 (45), 141 (100).

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ = 19.6 (C-7), 51.4 (C-6), 60.9 (C-4), 113.2 (C-8), 127.6 (C-2'), 128.6 (C-4'), 128.9 (C-3'), 138.4 (C-1'), 141.4 (C-5), 177.3 (C-2); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ = 1.29 (*d*, *J*=6.6 Hz, H-7), 4.21 (*qddd*, *J*=6.6, 1.5, 1.5, 1.5 Hz), 4.68 (*dd*, *J*=1.5, 1.5 Hz, H-8), 5.07 (H-4), 5.15 (*dd*, *J*=1.5, 1.5 Hz, H-8).

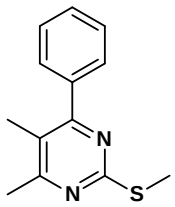


^{1}H NMR spectrum of compound **16b** in $CDCl_3$ (400 MHz)



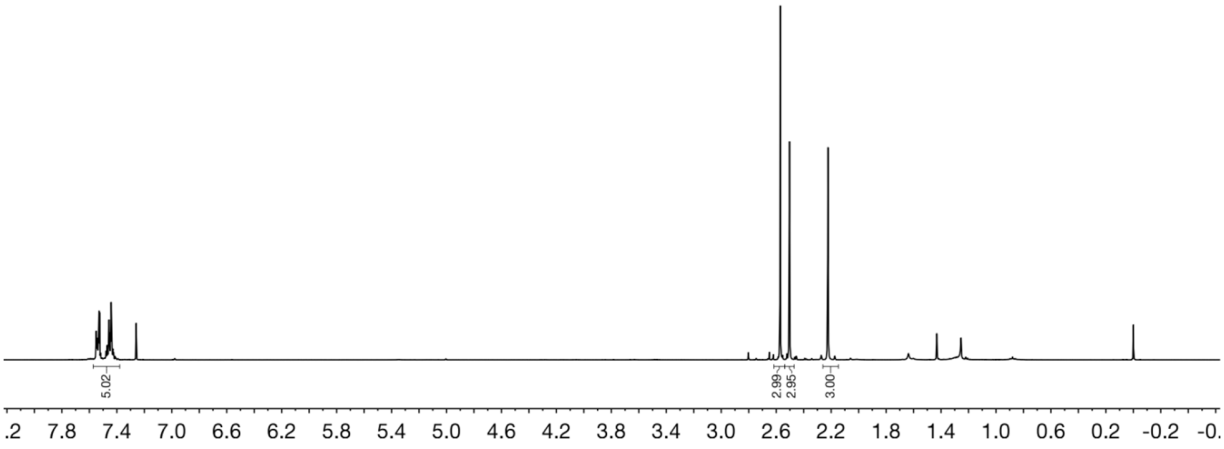
^{13}C NMR spectrum of compound **16a** in $CDCl_3$ (100.6 MHz)

4,5-dimethyl-2-(methylthio)-6-phenylpyrimidine (20)

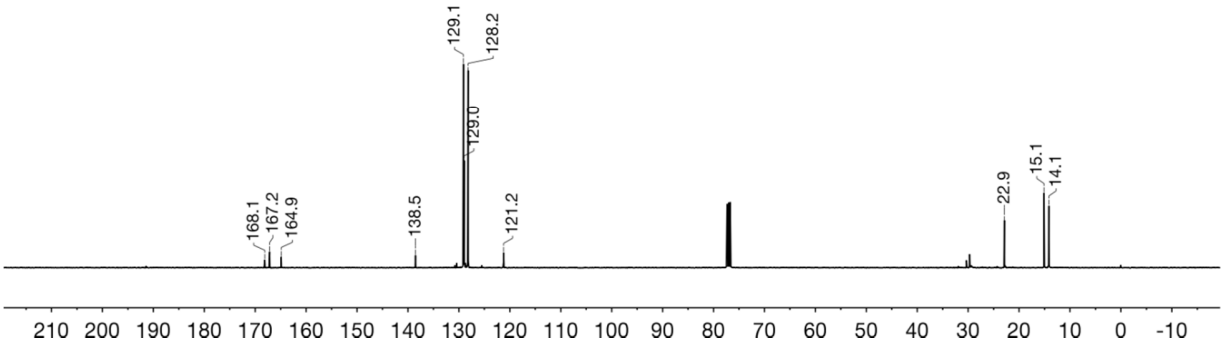


Yield: 10% IR: 3100,1400, 1250 EI-MS *(m/z*, rel. intensity*)*: 230 (100, M^+), 183 (43), 115 (27)

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 14.1 (-SMe), 15.1 (C-8), 22.9 (C-7), 121.2 (C-5), 128.2 (C-2'), 129.0 (C-4'), 129.1 (C-3'), 138.5 (C-1'), 164.9 (C-4), 167.2 (C-6), 168.1 (C-2); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 2.22 (3H, H-8), 2.50 (3H, H-7), 2.57 (3H, -SMe), 7.40-7.60 (5H, ArH).

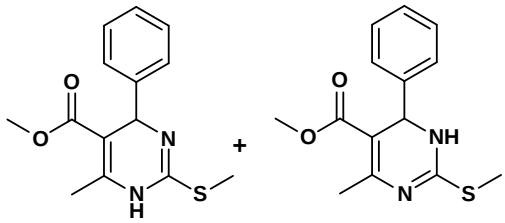


^{1}H NMR spectrum of compound **16b** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **16b** in $CDCl_3$ (106.6 MHz)

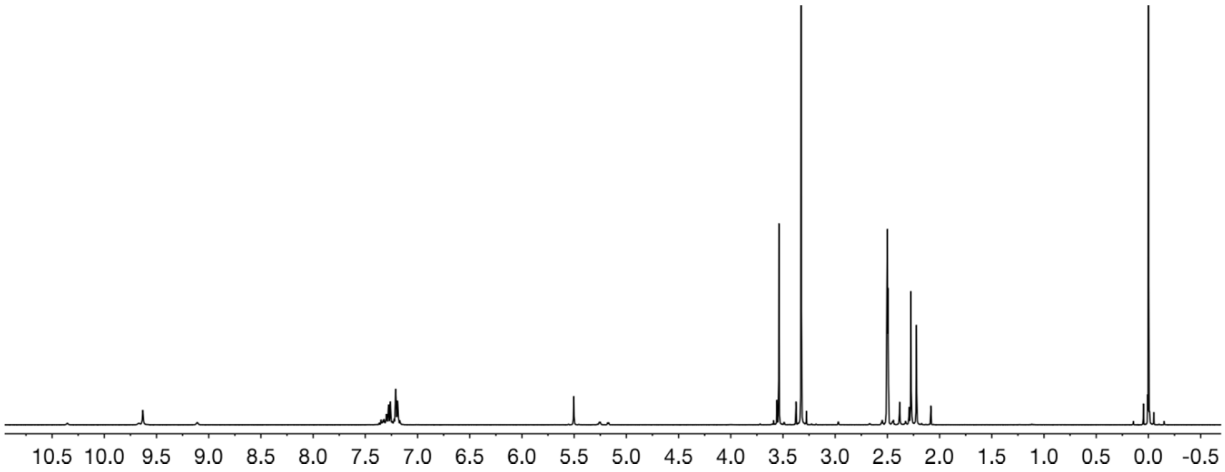
Methyl 6-methyl-2-(methylthio)-4-phenyl-1,4-dihydropyrimidine-5-carboxylate and methyl 4-methyl-2-(methylthio)-6-phenyl-1,6-dihydropyrimidine-5-carboxylate (mixture of tautomers, 17a and 17b)



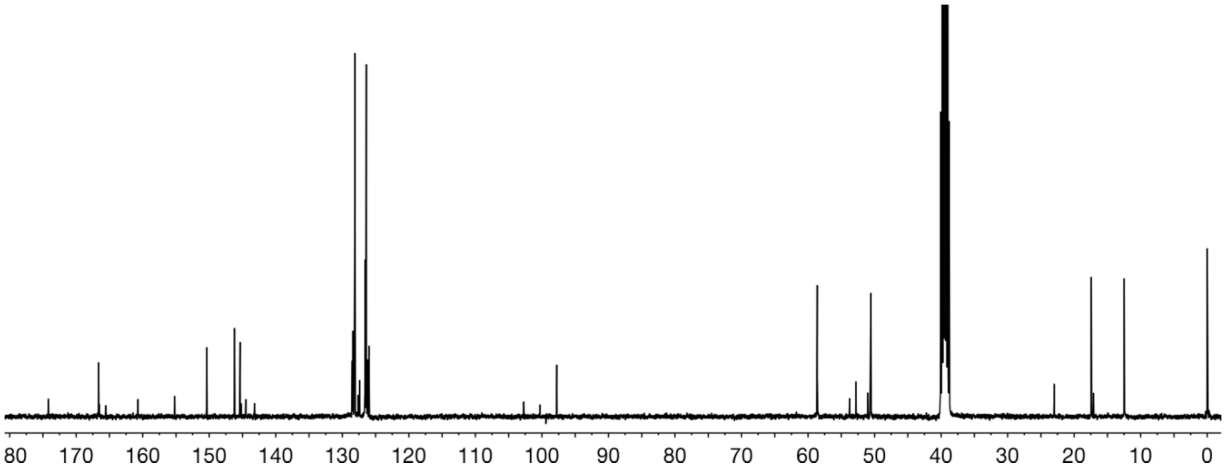
17a **17b**

Yield: 66% (both tautomers) IR: 3300, 3100, 1670 EI-MS *(m/z*, rel. intensity*)*: 276 (M^+, 8.6), 261 (29), 199 (100), 167 (13).

^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ = 2.22 (17a, H-7), 2.28 (17a, -SMe), 2.29 (17b, H-7), 2.38 (17b, -SMe), 3.54 (17a and b, CO_2Me), 5.24 (17b, H-4), 5.50 (17a, H-4), 7.15-7.35 (aromatic protons of both tautomers), 9.11 (17b, NH), 9.63 (17a, NH).

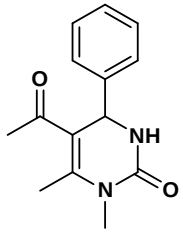


^{1}H NMR spectrum of compounds **17a** and **17b** in CD_3SOCD_3 (400 MHz)



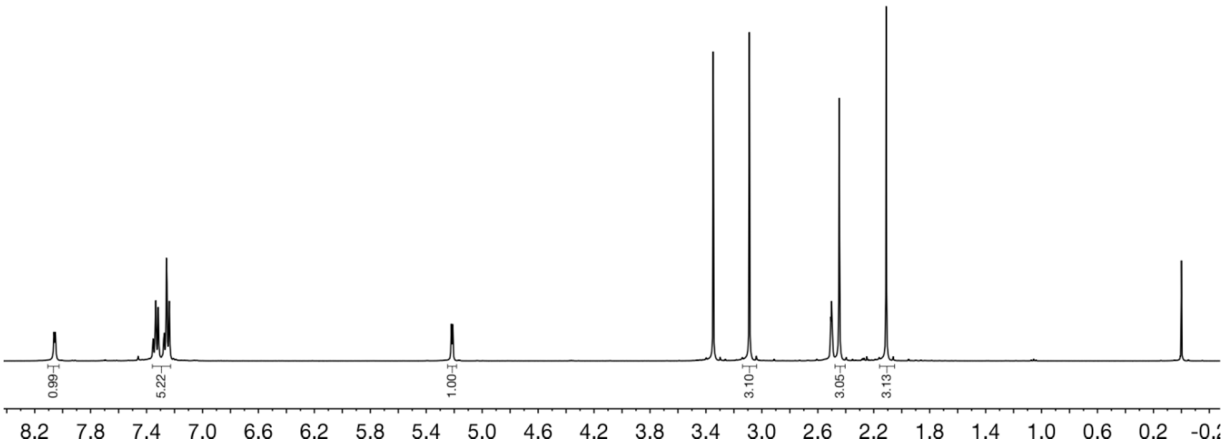
^{13}C NMR spectrum of compounds **17a** and **17b** in CD_3SOCD_3 (100.6 MHz)

5-acetyl-1,6-dimethyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (18)

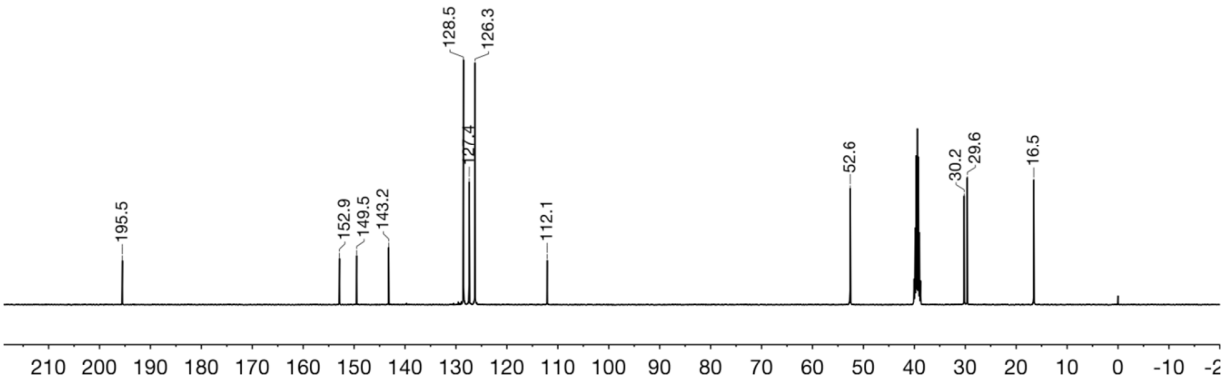


Yield: 86% IR: 3250, 3100, 1695, 1670

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ = 16.5 (C-7), 29.6 (C-9), 30.2 (NMe), 52.6 (C-4), 112.1 (C-5), 126.3 (C-2‘), 127.4 (C-4‘), 128.5 (C-3‘), 143.2 (C-1‘), 149.5 (C-6), 152.9 (C-2), 195.3 (C-8); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ = 2.11 (H9), 2.45 (3H, H-7), 3.09 (3H, NMe), 5.21 (1H, H-4), 7.22-7.36 (5H, H-2’ – H-4’), 8.05 (1H, NH-3).

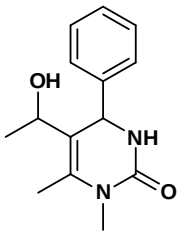


^{1}H NMR spectrum of compound **18** in CD_3SOCD_3 (400 MHz)



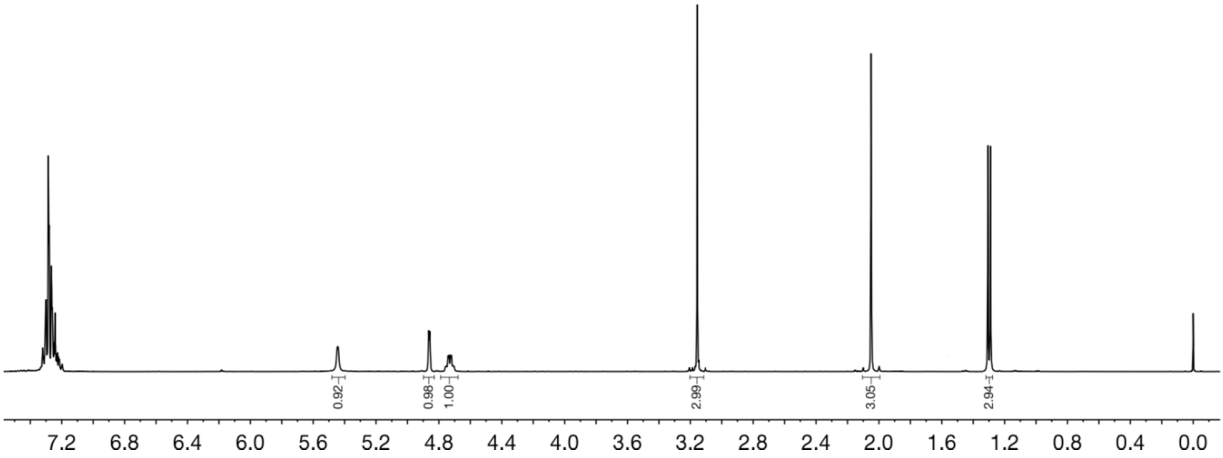
^{13}C NMR spectrum of compound **18** in CD_3SOCD_3 (100.6 MHz)

5-(1-hydroxyethyl)-1,6-dimethyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (18b)

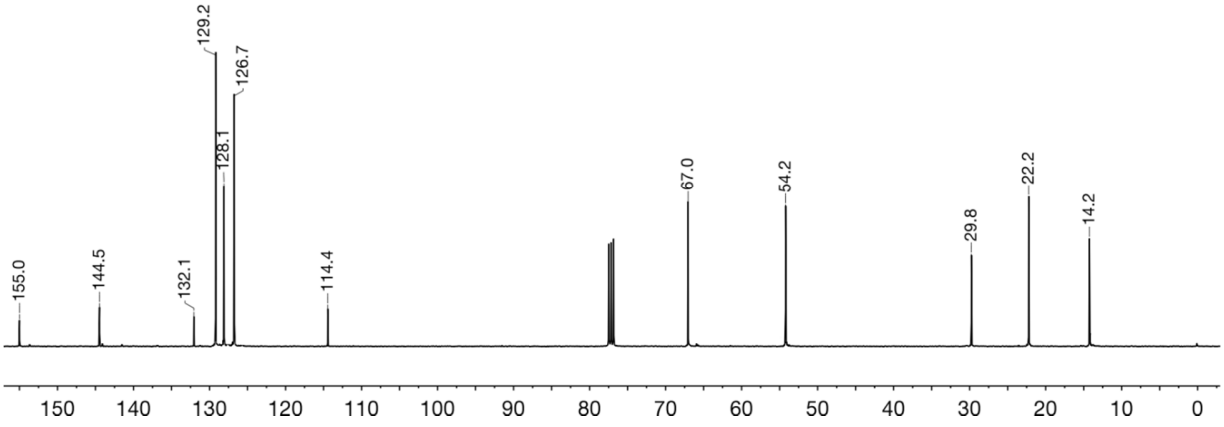


Yield: 66% IR: 3400-3200, 1650 EI-MS: Compound decomposes during GC/MS analysis

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 14.2 (C-7), 22.2 (C-9), 29.8 (NMe), 54.2 (C-4), 67.0 (C-8), 114.4 (C-5), 126.7 (C-2'), 128.1 (C-4'), 129.2 (C-3'), 132.1 (C-6), 144.5 (C-1'), 155.0 (C-2) ; ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 1.30 (3H, d, J= 6.5Hz), 2.05 (3H, H-7), 3.16 (3H, NMe), 4.73 (1H, qd, J= 6.5, 2.6 Hz), 4.87 (1H, H-4), 5.40 (1H, OH), 7.26-7.30 (5H, ArCH).

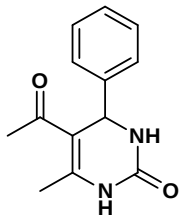


^{1}H NMR spectrum of compound **18b** in $CDCl_3$ (400 MHz)



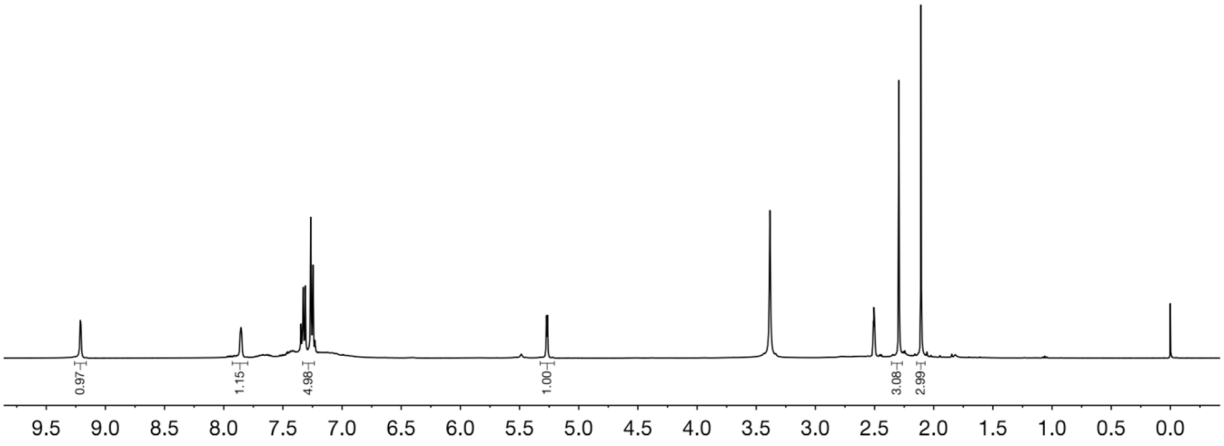
^{13}C NMR spectrum of compound **18b** in $CDCl_3$ (100.6 MHz)

5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (19)

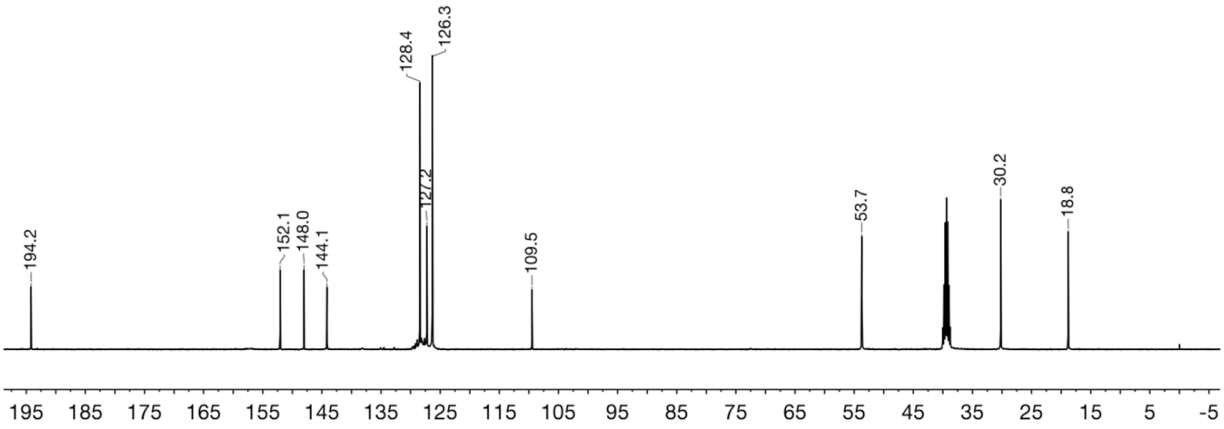


Yield: 90% IR: 3270, 3100, 1700, 1620

^{13}C-NMR spectrum (100.6 MHz, DMSO-d_6): δ = 18.8 (C-7), 30.2 (C-9), 53.7 (C-4), 109.5 (C-5), 126.3 (C-2‘), 127.2 (C-4‘), 128.4 (C-3‘), 144.1 (C-1‘), 148.1 (C-6), 152.1 (C-2), 194.2 (C-8); ^{1}H-NMR spectrum (400 MHz, DMSO-d_6): δ = 2.11 (H9), 2.30 (3H, H-7), 5.26 (1H, H-4), 7.24-7.34 (5H, H-2’ – H-4’), 7.85 (1H, NH-3), 9.21 (1H, NH-1).

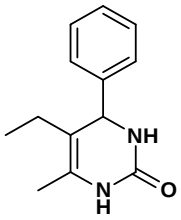


^{1}H NMR spectrum of compound **19** in CD_3SOCD_3 (400 MHz)



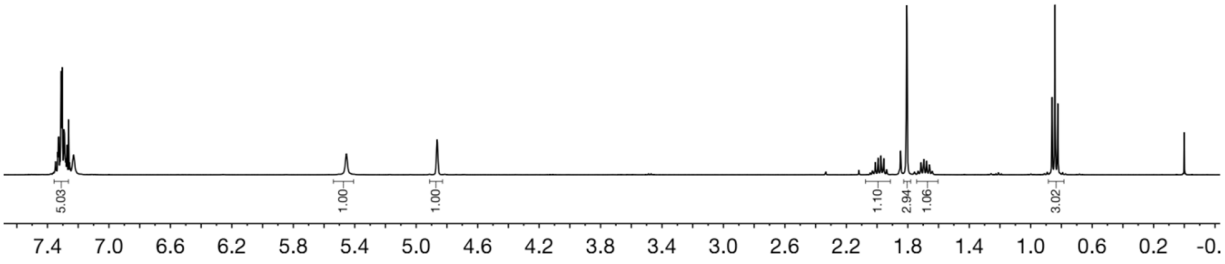
^{13}C NMR spectrum of compound **19** in CD_3SOCD_3 (100.6 MHz)

5-ethyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one (19a)

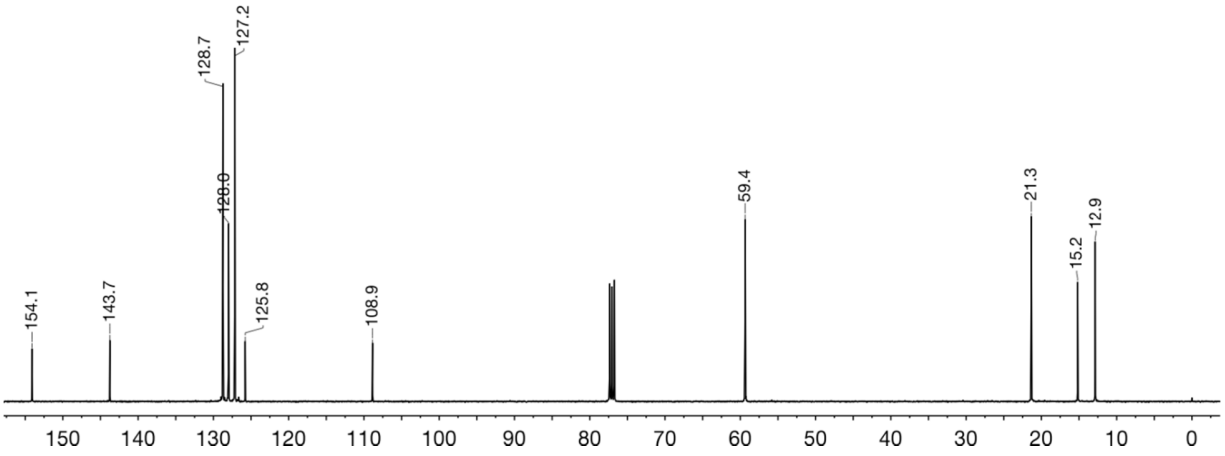


Yield: 87% IR: 3250, 3100, 1660 EI-MS *(m/z*, rel. intensity*)*: 216 (M^+, 13), 187 (29), 139 (100).

^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 12.9 (C-9), 15.2 (C-7), 21.3 (C-8), 59.4 (C-4), 108.9 (C-5), 125.8 (C-6), 127.2 (C-2'), 128.0 (C-4'), 128.7 (C-3'), 143.7 (C-1'), 154.1 (C-2); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 0.84 (3H, t, J= 7.5 Hz), 1.69 (1H,dq, J=15.0, 7.5 Hz, H-8), 1.80 (3H, H-7), 1.98 (1H,dq, J=15.0, 7.5 Hz, H-8), 4.86 (H-4), 5.45 (1H, NH-3), 7.28-7.34 (5H, ArH).

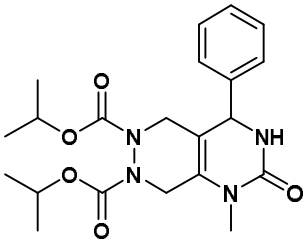


^{1}H NMR spectrum of compound **19a** in $CDCl_3$ (400 MHz)



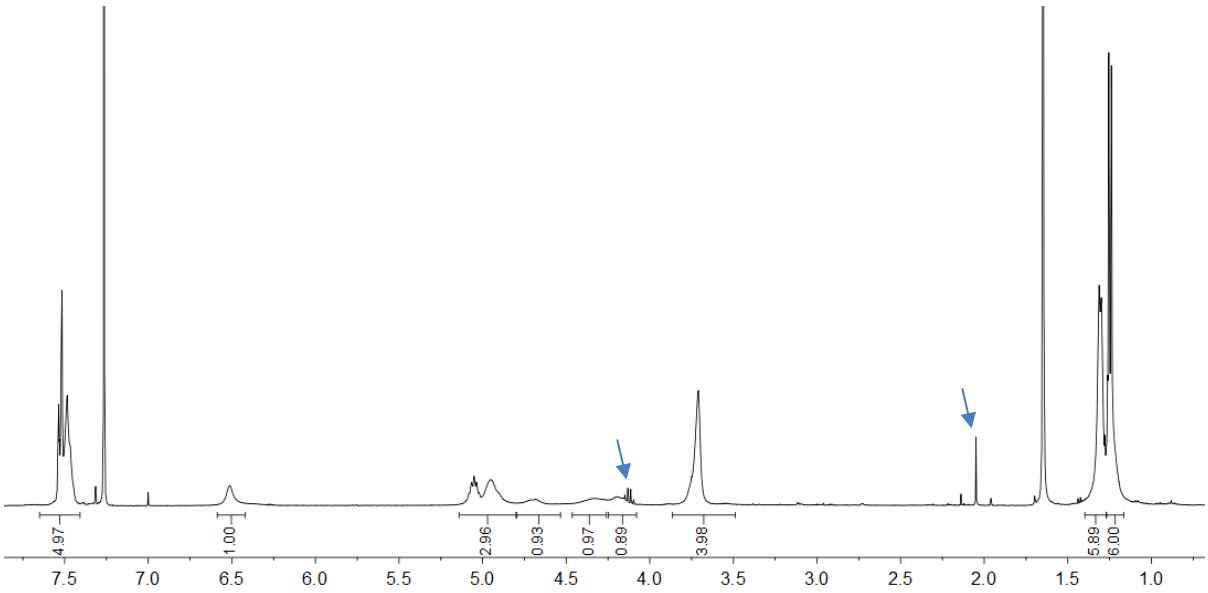
^{13}C NMR spectrum of compound **19a** in $CDCl_3$ (100.6 MHz)

Diisopropyl 1-methyl-2-oxo-4-phenyl-1,2,3,4,5,8-hexahydropyrimido[4,5-*d*]pyridazine-6,7-dicarboxylate (12e)

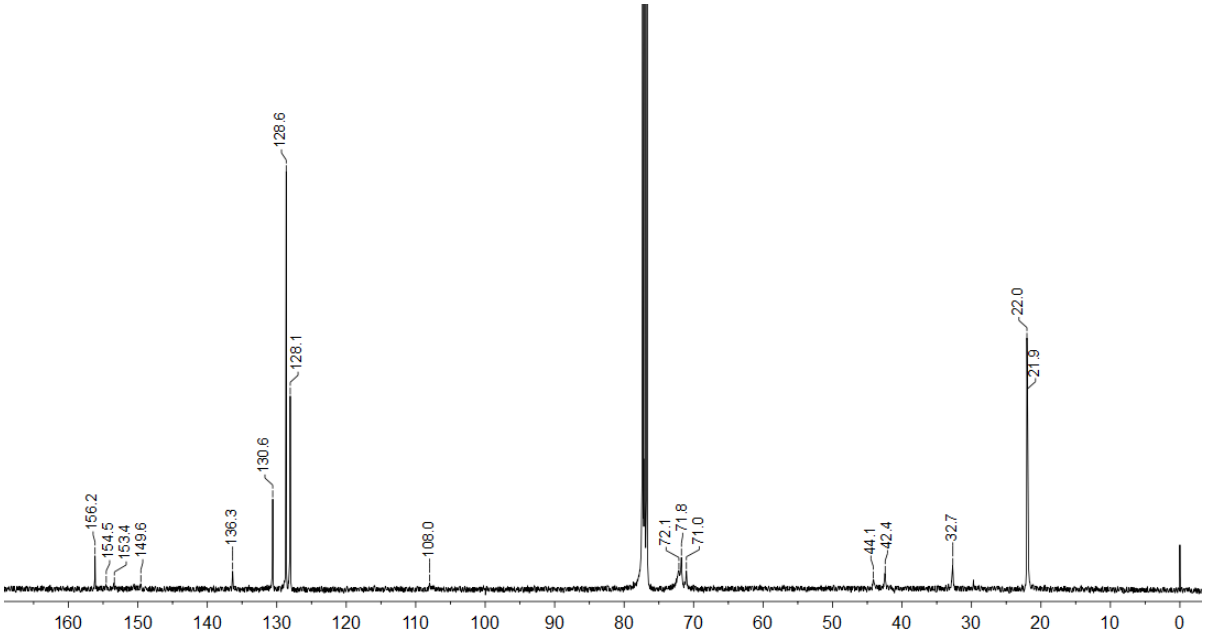


Yield: 97%

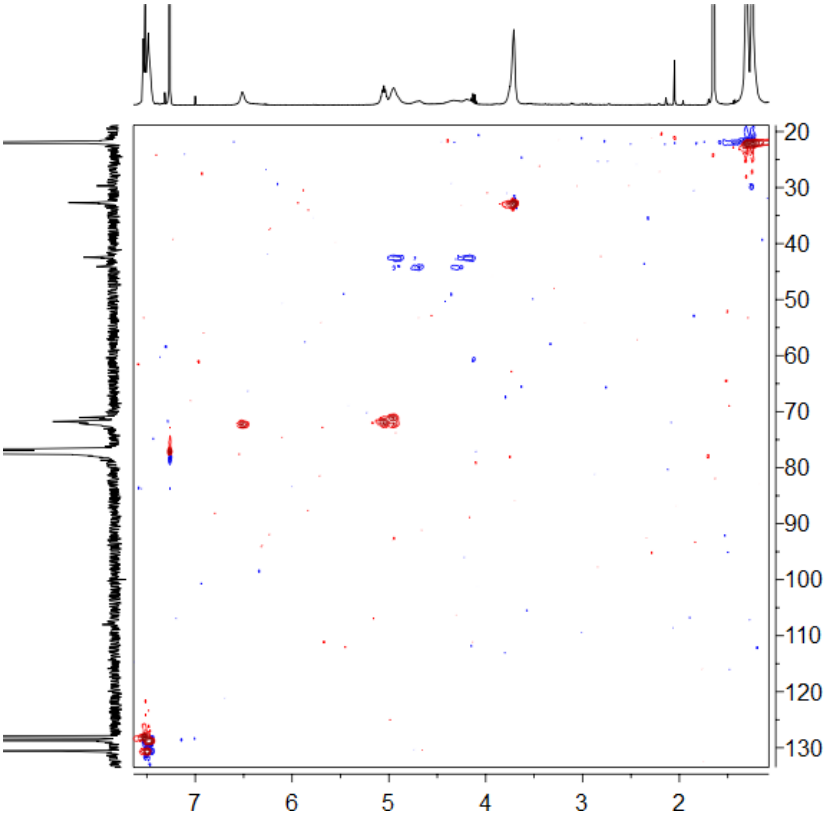
^{13}C-NMR spectrum (100.6 MHz, $CDCl_3$): δ = 21.9 (Me); 22.0 (Me), 32.7 (NMe), 42.4 (CH_2), 44.1 (CH_2), 71.0 (C$\underline{H}Me_2$), 71.8 (C$\underline{H}Me_2$), 72.3 (C4), 108.0, 128.1 (ArCH), 128.6 (ArCH), 130.6 (ArCH), 136.3 (C-1'), 149.6, 153.4 (ester carbonyl), 154.5 (ester carbonyl), 156.2 (C-2); ^{1}H-NMR spectrum (400 MHz, $CDCl_3$): δ = 1.25 (Me, d, J= 6.2 Hz, 6H), 1.31 (Me, brd, J= 5.4 Hz, 6H), 3.70 (NMe), 3.75 (NH), 4.19 and 4.93 (diastereotopic protons attached at carbon at δ 42.4), 4.30 and 4.70 (diastereotopic protons attached at carbon at δ 44.0), 4.95 (C$\underline{H}Me_2$), 5.05 (broad septuplet, J= 6.1, C$\underline{H}Me_2$), 6.51 (H-4), 7.40-7.60 (5H, ArH).



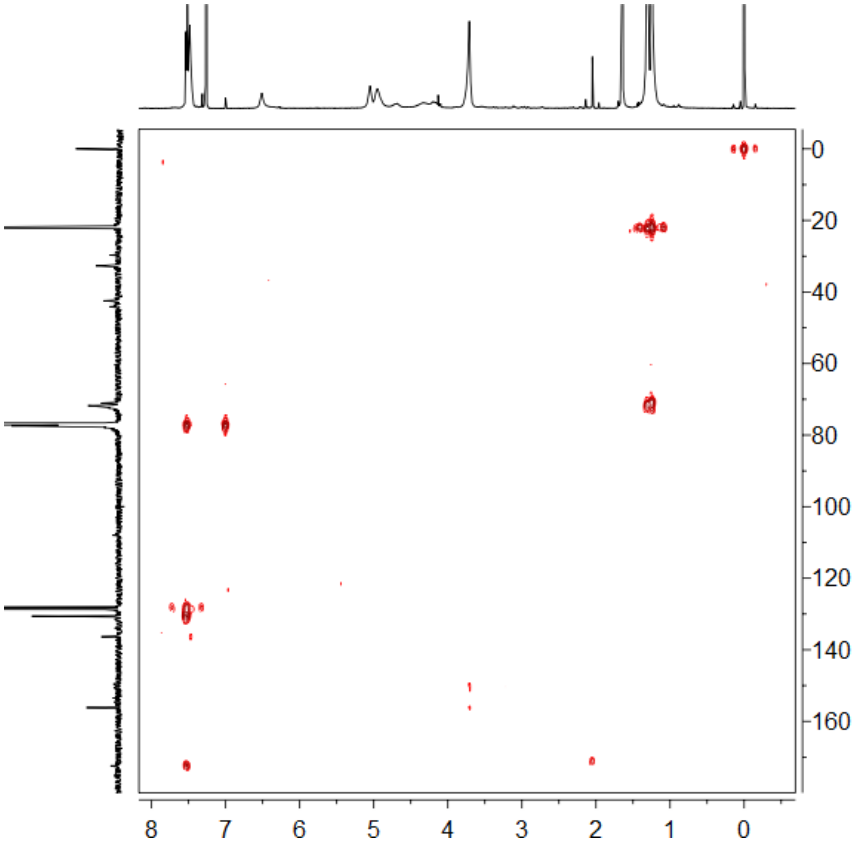
^{1}H NMR spectrum of compound **12e** in $CDCl_3$ (400 MHz). Signals marked with an arrow are due to traces of EtOAc in the recorded sample.



^{13}C NMR spectrum of compound **12e** in $CDCl_3$ (100.6 MHz)



Edited HSQC spectrum (blue cross-peaks correspond to CH_2 groups, while red ones correspond to CH and CH_3 groups) of compound **12e** in $CDCl_3$ (400 and 100.6 MHz)



HMBC spectrum of compound **12e** in $CDCl_3$ (400 and 100.6 MHz)