

Supporting Information

Facile Access to Amides from Oxygenated or Unsaturated Organic Compounds by Metal Oxide Nanocatalysts Derived from Single-Source Molecular Precursors

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Table S1. Crystallographic parameters for SSMP-1 and SSMP-2.

Identification code	SSMP-1	SSMP-2
Empirical formula	C ₇ H ₁₇ NNiO ₉ S	C ₂₈ H ₂₆ Cu ₂ N ₂ O ₆
Formula weight	349.98	613.59
Temperature(K)	150(2)	150(2)
Wavelength(Å)	0.71073	0.71073
Crystal system space group	Monoclinic, P 21	Triclinic, P -1
<i>a</i> /Å	9.2823(2)	8.7223(4)
<i>b</i> /Å	6.9531(2)	10.0522(6)
<i>c</i> /Å	10.4772(3)	15.6671(8)
α /°	90	86.041(4)
β /°	92.237(2)	82.826(4)
γ /°	90	69.487(5)
<i>V</i> /Å ³	675.69(3)	1276.02(12)
<i>Z</i> , <i>d</i> _{calcd} (mg/m ³)	2, 1.720	2, 1.597
μ /mm ⁻¹	1.630	1.714
<i>F</i> (000)	364	628
Crystal size (mm ³)	0.34 x 0.28 x 0.22	0.33 x 0.26 x 0.22
θ range	3.518 to 32.513	3.428 to 30.507
Index ranges	-13 ≤ <i>h</i> ≤ 13, -10 ≤ <i>k</i> ≤ 10, -15 ≤ <i>l</i> ≤ 15	-12 ≤ <i>h</i> ≤ 12, -14 ≤ <i>k</i> ≤ 14, -21 ≤ <i>l</i> ≤ 22
Reflections collected / unique	6748 / 3834 [R(int) = 0.0142]	16337 / 7783 [R(int) = 0.0427]
Max. and min. transmission	1.00000 and 0.97274	1.00000 and 0.83202

Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3834 / 2 / 181	7783 / 0 / 343
GOF, F^2	1.058	1.051
R_1 , wR_2 [$I > 2\sigma(I)$]	$R_1 = 0.0291$, $wR_2 = 0.0726$	$R_1 = 0.0539$, $wR_2 = 0.1274$
R_1 , wR_2 (all data)	$R_1 = 0.0307$, $wR_2 = 0.0739$	$R_1 = 0.0936$, $wR_2 = 0.1496$
Absolute structure parameter	0.517(16)	---
Largest diff. peak and hole (e. $\text{\AA}^{-3}$)	0.667 and -0.588	0.807 and -0.657
CCDC No.	1048646	1511656

FT-IR analysis

FT-IR spectra were performed to determine the functional groups present in **SSMP-1** and **SSMP-2** (Figure S1 and S2). FT-IR band near 3200-3400 cm^{-1} was due to presence of $\nu(-\text{OH})$ and $\nu(-\text{SOH})$. Bands around 2800-2900 cm^{-1} were due to aliphatic C-H stretching. The symmetric and asymmetric vibrations of SO_4^{2-} yield sharp peaks in the 900-1500 cm^{-1} range (Figure S1). A similar FT-IR spectrum, with additional strong C=O stretching band in the range of 1600-1700, cm^{-1} was presented by **SSMP-2**, indicating the formation of the complex (Figure S2).

SSMP-1. FT-IR (KBr, cm^{-1}): 3280(br), 2905(w), 1615(m), 1489(m), 1434(m), 1371(m), 1114(s), 1028(m), 861(m), 766(w), 766(m), 623(m), 577(m).

SSMP-2. FT-IR (KBr, cm^{-1}): 3425(br), 2924(m), 2802(w), 1615(s), 1562(m), 1395(s), 1257(m), 1111(m), 1066(s), 1030(m), 769(m), 721(m), 682(m), 618(m).

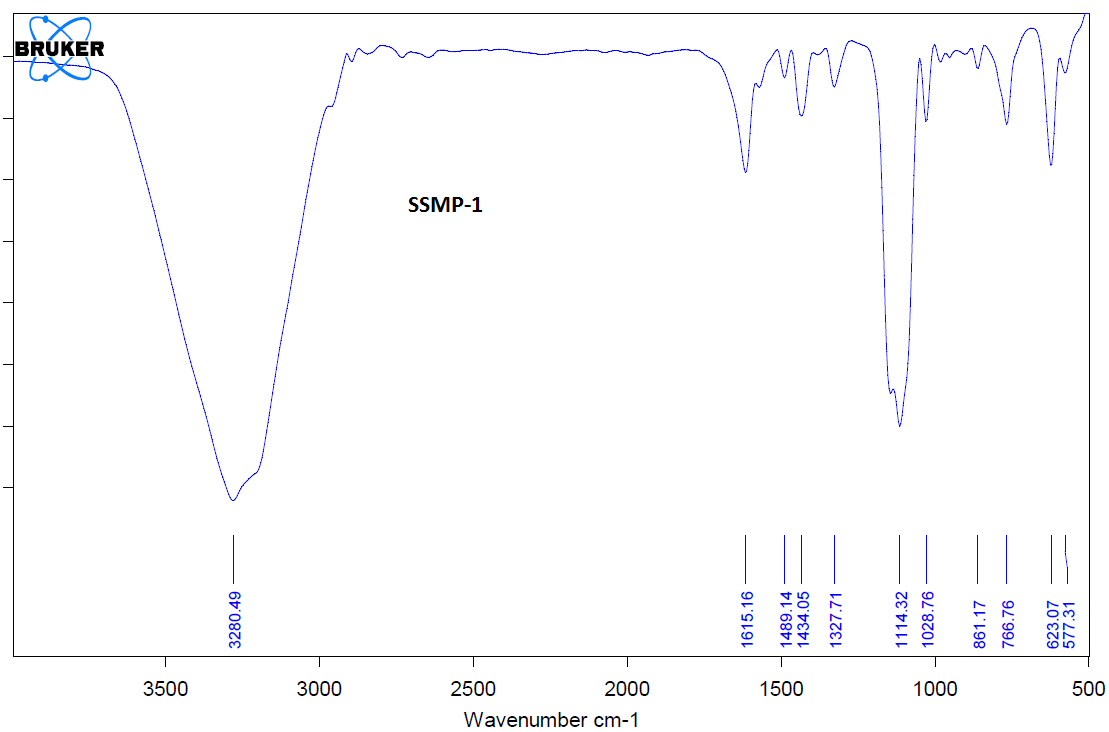


Figure S1. FT-IR analysis of SSMP-1.

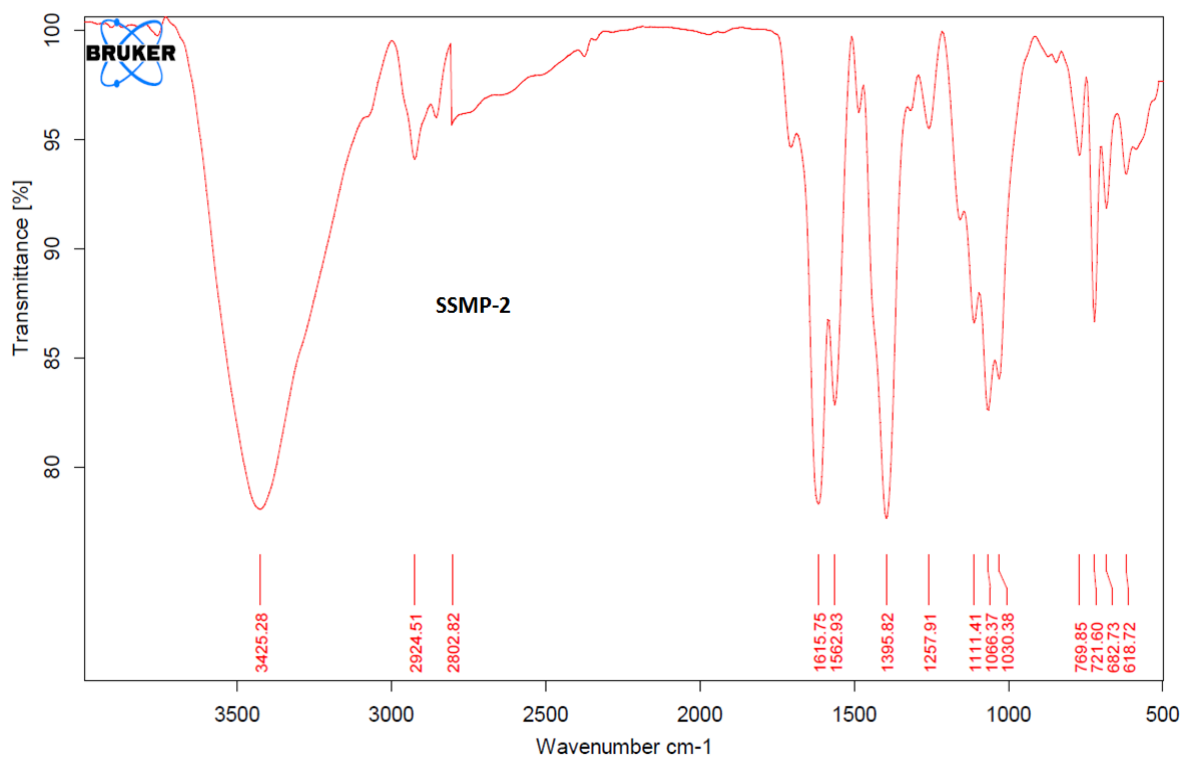


Figure S2. FT-IR analysis of SSMP-2.

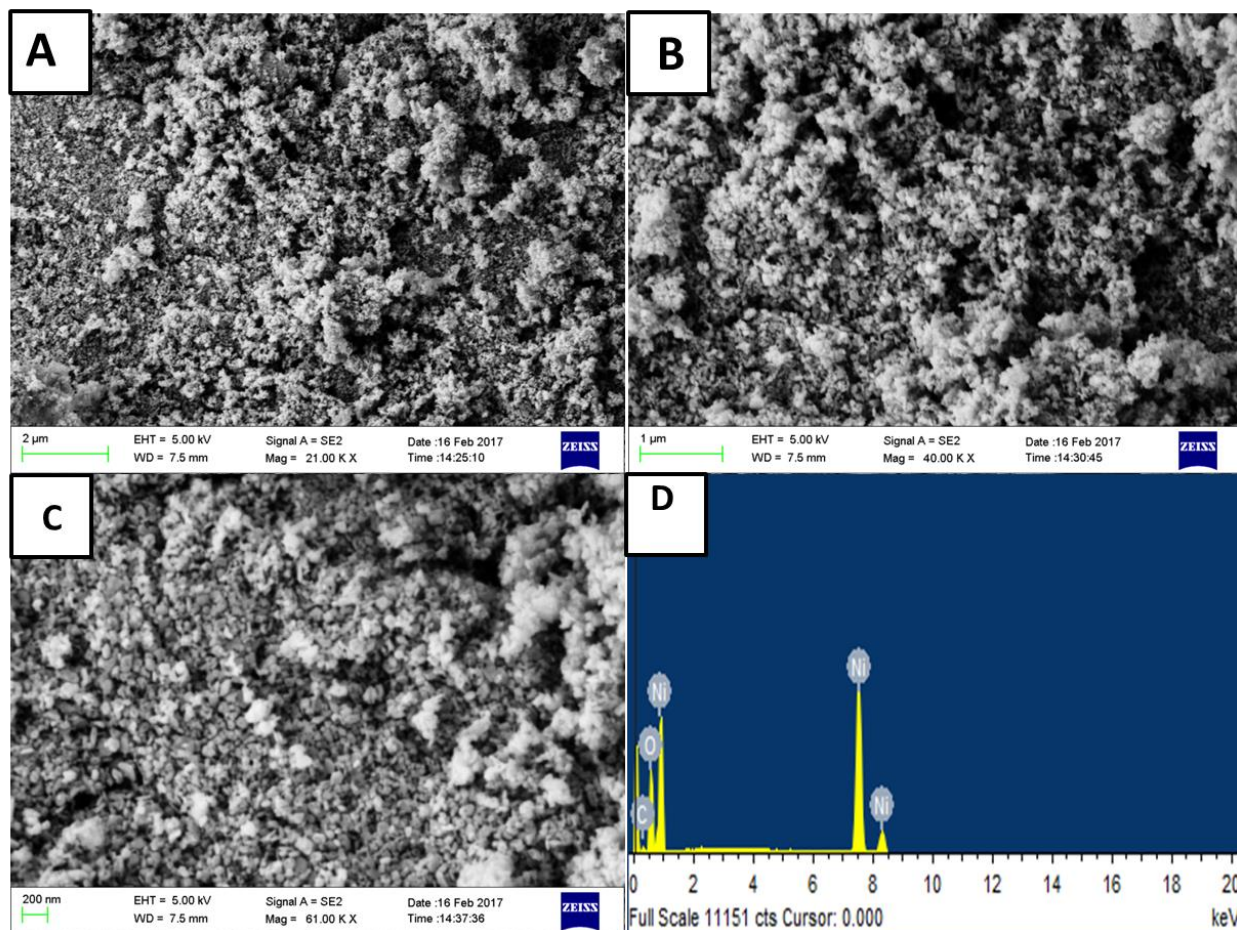


Figure S3. SEM image of fresh NiO nanoparticles at different magnifications (A-C) and EDAX pattern of fresh NiO (D).

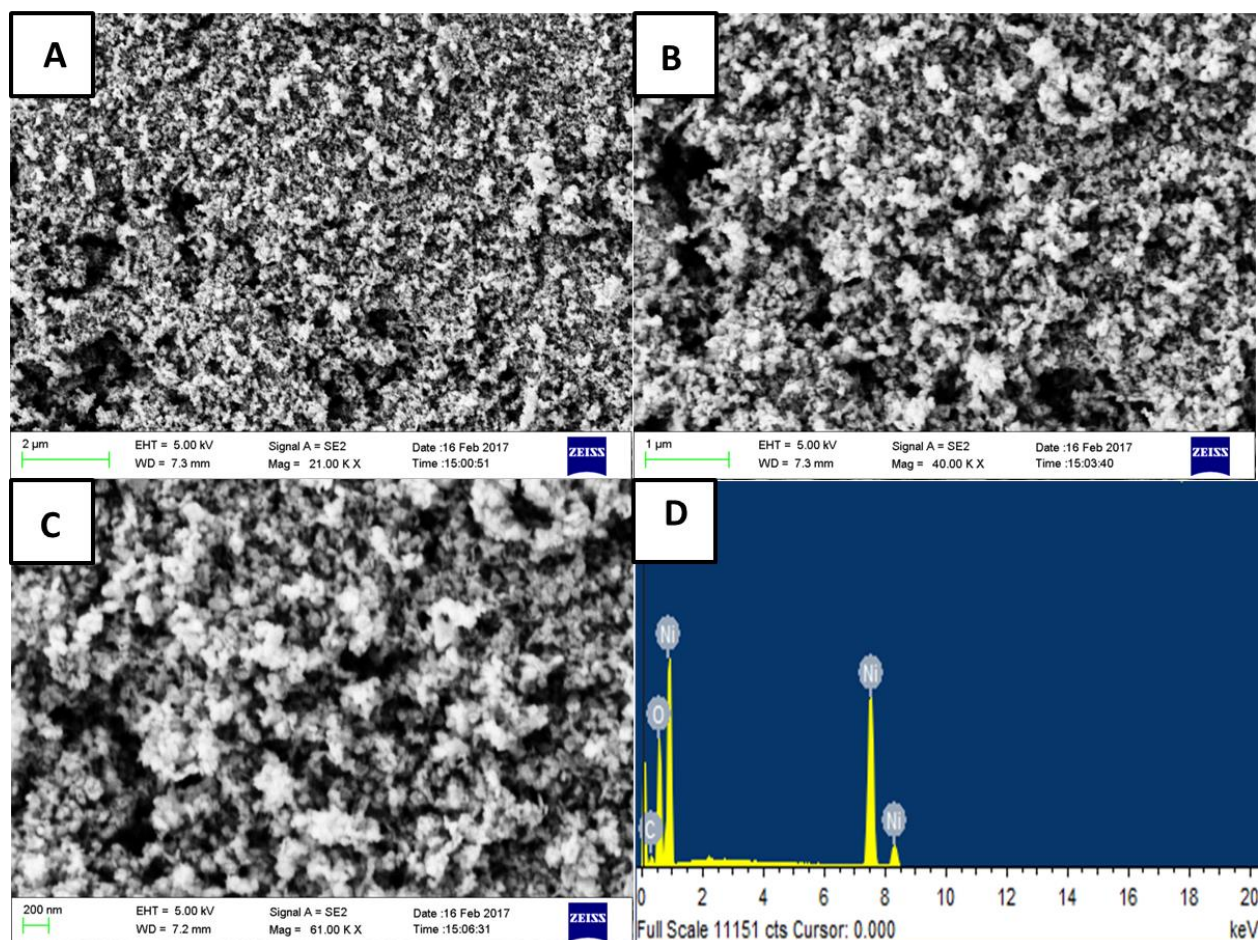


Figure S4. SEM image of used NiO nanoparticles at different magnifications (A-C) and EDAX pattern of used NiO (D).

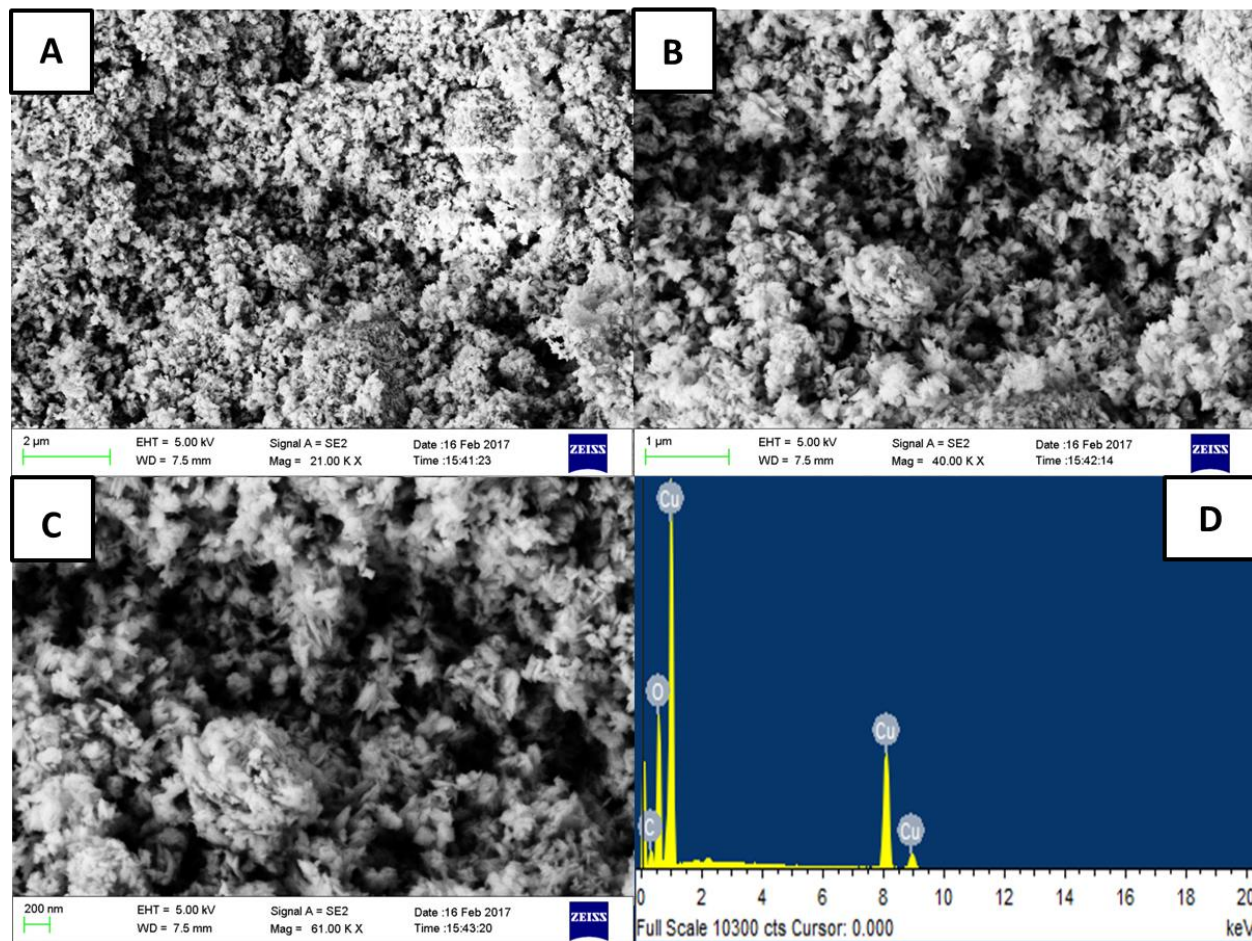


Figure S5. SEM image of fresh CuO nanoparticles at different magnifications (A-C) and EDAX pattern of fresh CuO (D).

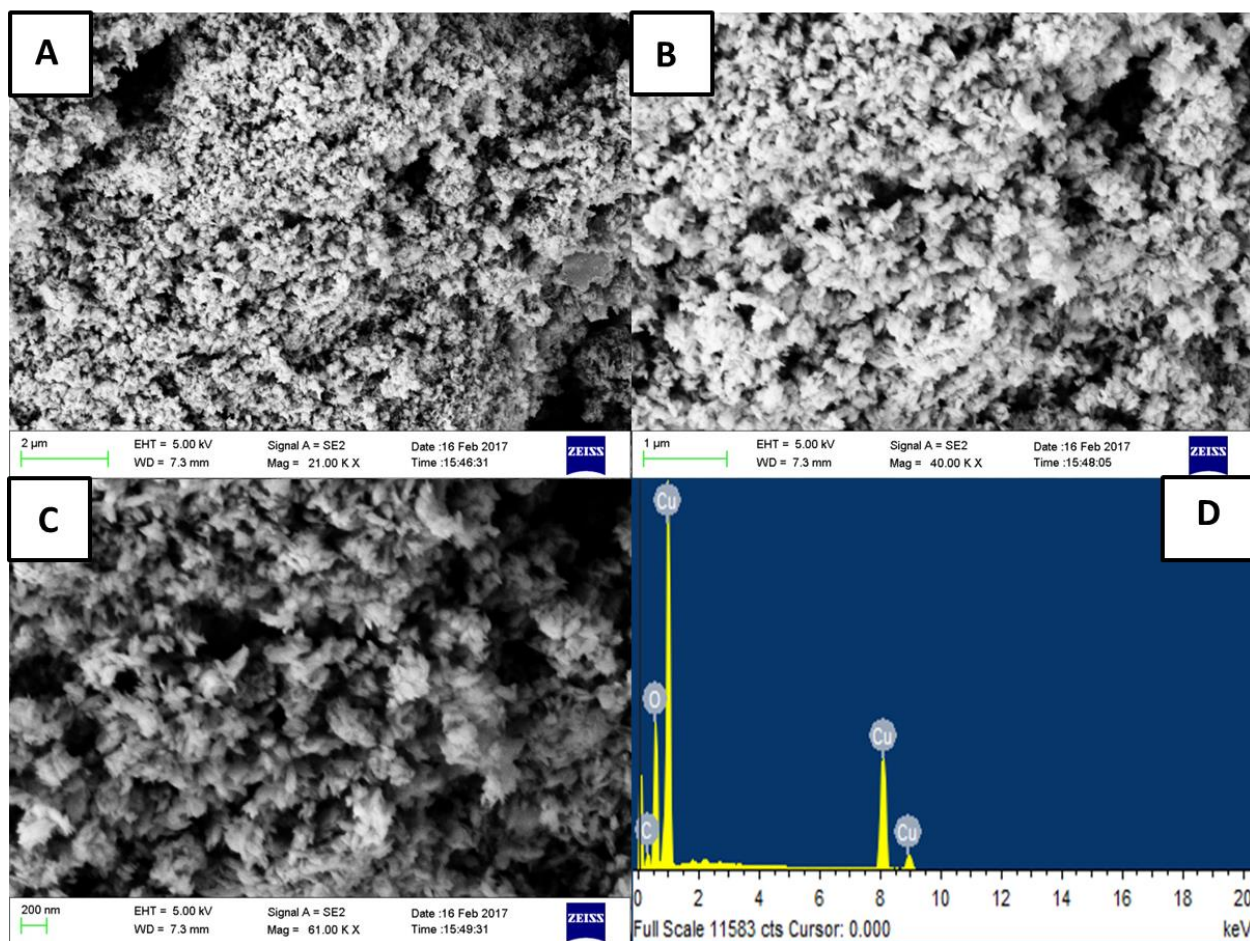


Figure S6. SEM image of used CuO nanoparticles at different magnifications (A-C) and EDAX pattern of used CuO (D).

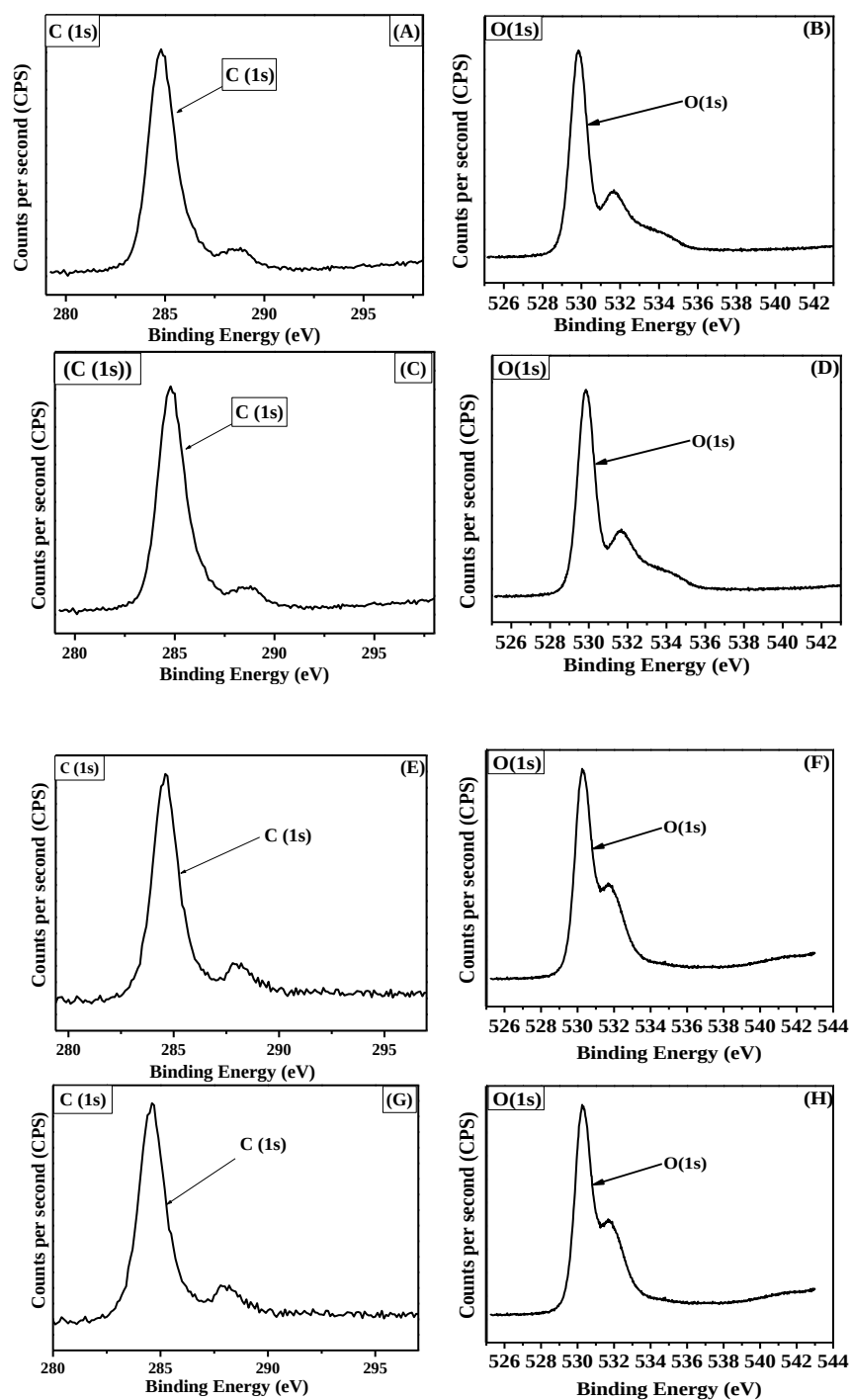
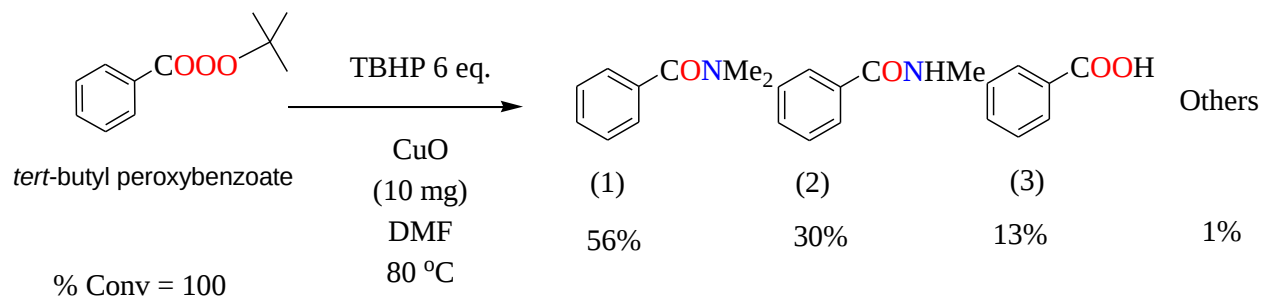


Figure S7. XPS spectra of fresh NiO (A) C (1s); (B) O (1s); spent NiO (C) C(1s); (D) O(1s); fresh CuO (E) C (1s); (F) O (1s); spent CuO (G) C (1s); (H) O (1s).

Chart S1. Reaction of *tert*-butyl benzoperoxoate with DMF in the Presence of CuO Nanocatalyst and TBHP as Oxidant^b



^a% conversion and % selectivity were determined by GC-MS analysis.

^bReaction condition: substrate = 1 mmol; TBHP = 6 equiv; catalyst = 10 mg; DMF = 2 g (2.12 mL); T = 80 °C; reaction time = 20 h.

Spectra for Chart S1.

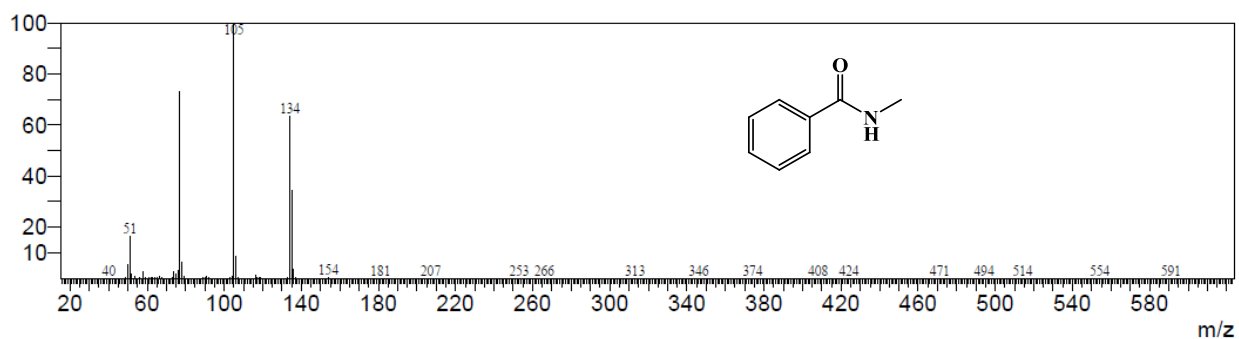
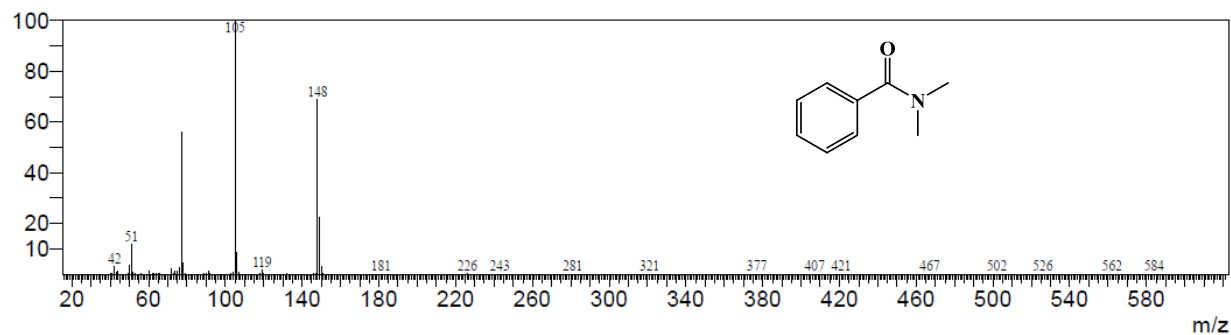
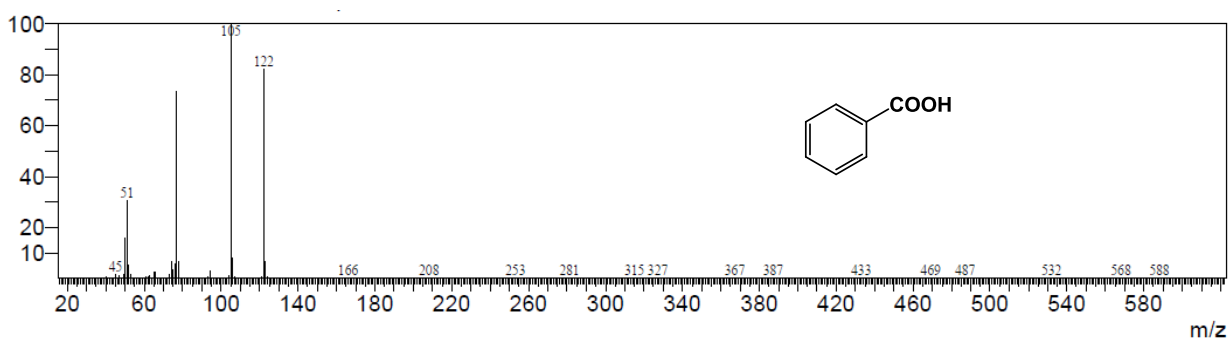
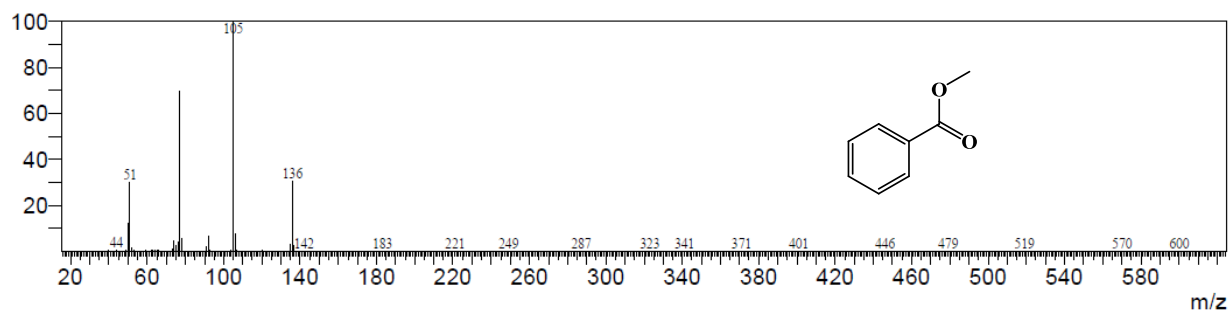
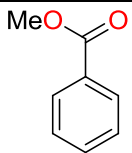
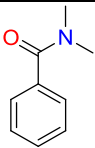
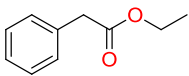
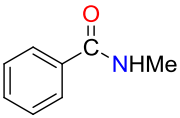
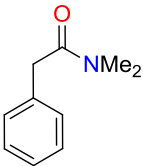
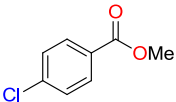
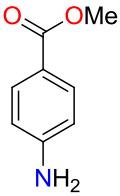
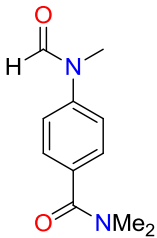


Table S2. Oxidative Amidation of Esters by Employing CuO Nanocatalyst^b

Entry	Compound Name	% Con. ^a	Product (D)	% Sel. ^a	Product (E)	% Sel. ^a
1		3		100		
2		6		35		30
3		0	NA		NA	
4		8		100		

^a% conversion and % selectivity were determined by GC-MS analysis.

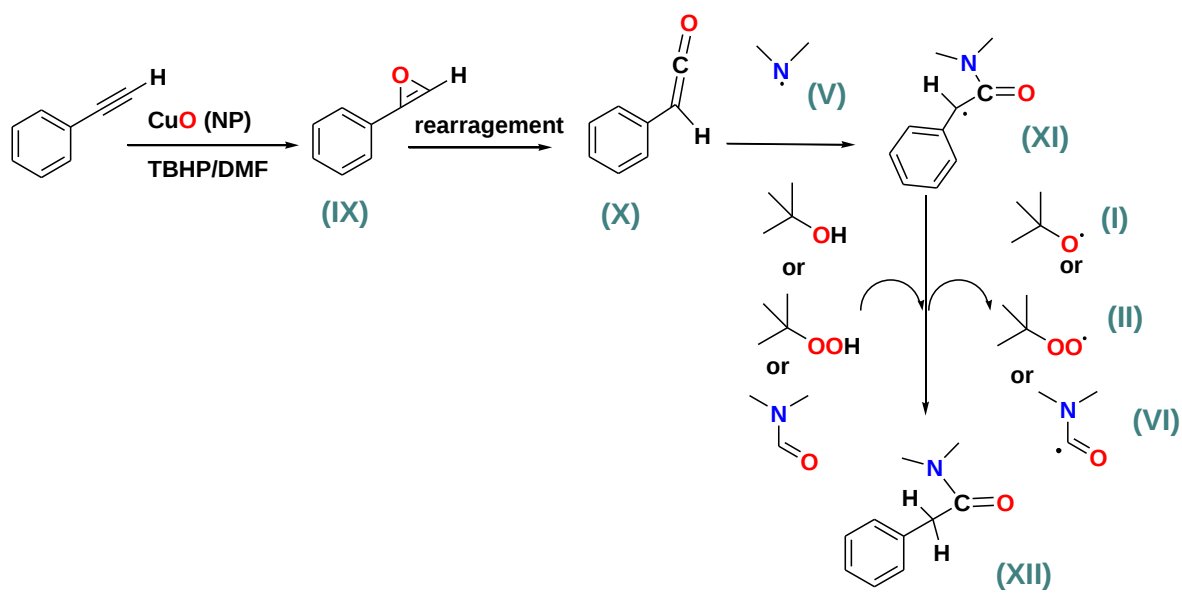
^bReaction condition: substrate = 1 mmol; TBHP = 6 equiv; catalyst = 10 mg; DMF = 2 g (2.12 mL); T = 80 °C; reaction time = 20 h.

Table S3. Comparative Study for Catalytic Performance of CuO with Previous Reported Catalyst

Catalyst	Substrate	Solvent	Oxidant	T (h)	T (°C)	TON	Yield (%)	Ref.
Cu(OTf) ₂ (1% mol)	Benzoic acid	DCE (1 mL) DMF (4 equiv)	DTBP (2 equiv)	12	130	100	71	1
Supported Cu(II)–acac (20 mg, 0.46% mol Cu)	Benzoic acid (1 mmol)	DMF (2 mL)	TBHP (1.5 equiv)	12	100	185	85	2
Cu(OAc) ₂ (5% mol)	Cinnamic acid (0.1 mmol)	TCE (1 mL) DMF (0.5 mmol)	TBHP (2 equiv)	12	90	17	86	3
CuSO ₄ 20% mol	Cinnamic acid (0.3 mmol)	DMF 20 mL (Ar)	DTBP (2 equiv)	12	100	4	83	4
Cu(bcmim) ₂ MOF (10% mol Cu)	Toluic acid (0.25 mmol)	DMF (0.5 mL, 25.8 equiv)	TBHP (1.6 equivs, in 5 portions)	6	100	10	31	5
Cu(ClO ₄) ₂ · 6H ₂ O 10% mol	Benzoic acid (1 mmol)	DMF (2 mL, 27 equiv)	TBHP (1.5 equivs)	15	100	9	90	6
CuO (10 mg, 13% mol Cu)	Benzoic acid (1 mmol)	DMF 2.12 mL	TBHP (6 equivs)	20	80	7.5	>99	This work
Cu ₂ O (10% mol) with 1,10- phenanthroline	Benzonitrile (1 mmol)	DMF 2 mL TsOH 1 mmol	O ₂ 1 atm	24	140	8.3	83	7
3 wt% Pd/γ- Al ₂ O ₃ 25 mg	Perfluorophenyl benzoate(0.2 mmol)	DMF (5equivs) PhCl 2 mL	TBHP (5 equivs)	24	120	5.2	85	8
Co@C-N (10% mol Co)	Benzaldehyde (0.5 mmol)	DMF (2.5 mmol) Toluene (1 mL)	TBHP (5 equiv)	24	100	9	91	9

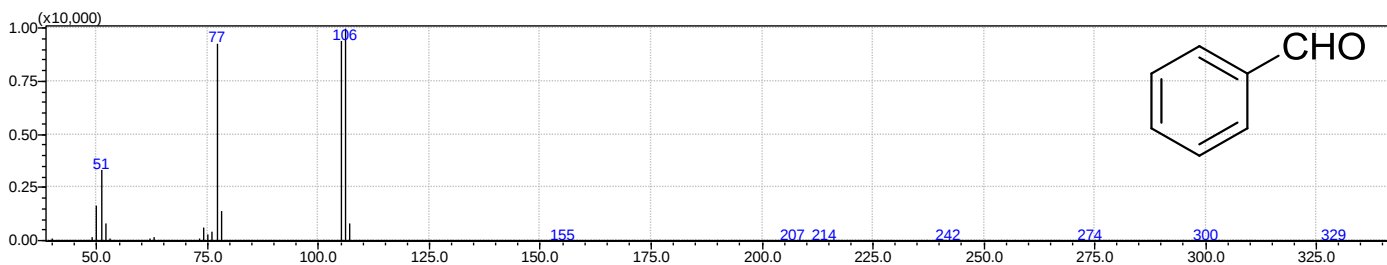
POPd (2.5% mol)	Benzaldehyde (1 mmol)	Si(NMe ₂) ₄ (1.3 equivs) CH ₃ CN 2 mL	-	24	25	36	90	10
-	Benzaldehyde (1 mmol)	B(NMe ₂) ₃ 1.2 equivs CH ₃ CN 2 mL	TBHP (1.2 equivs)	24	80	-	99	10
-	Substituted benzaldehydes (1 mmol)	pyrrolidine (1.2 equiv), CH ₃ CN 3 mL	TBHP (1.2 equivs)	5	80	-	<98	10
CuO (10 mg, 13% mol Cu)	Benzaldehyde (1 mmol)	DMF (2.12 mL)	TBHP (6 equivs)	20	80	6.8	80	This work

Scheme S1. Possible Mechanism for the Oxidative Amidation of Phenylacetylene

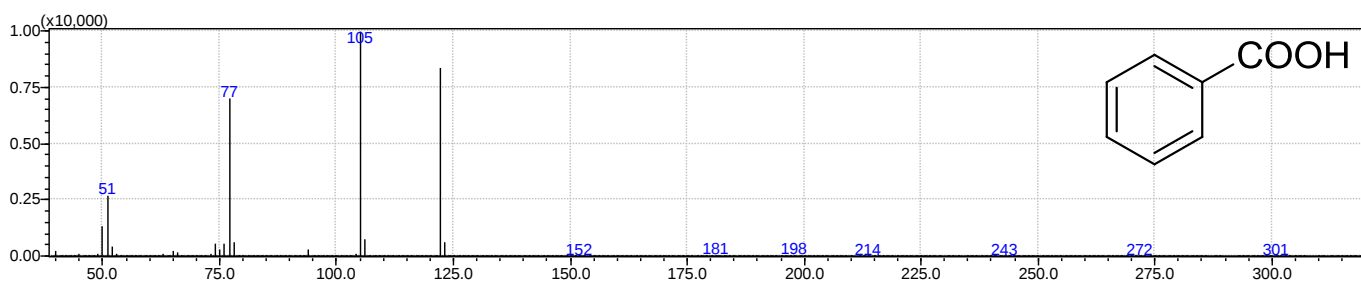


Spectra S1–S53. GC-MS Spectra of Catalytic Oxidative Amidation Reactions.

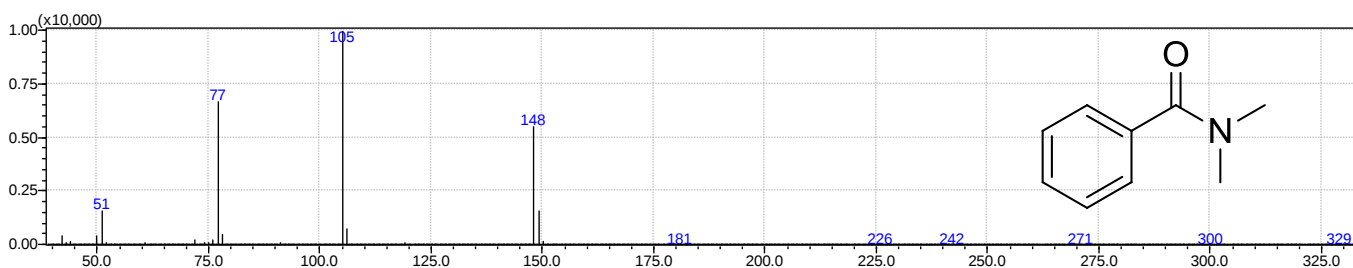
S1. Benzaldehyde



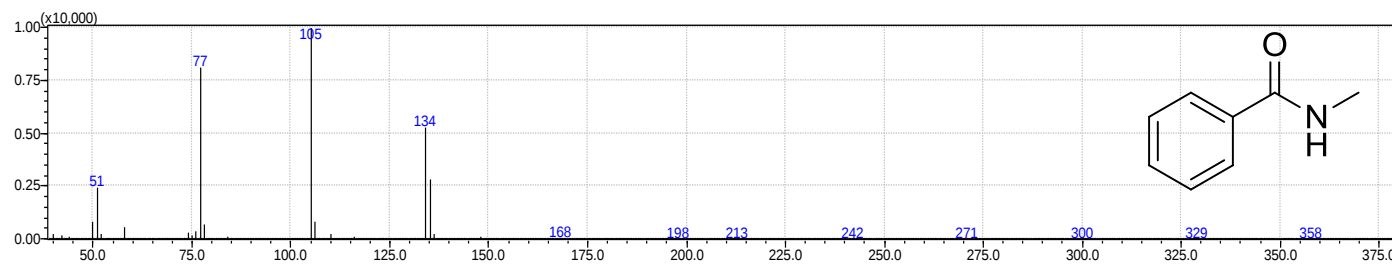
S2. Benzoic acid



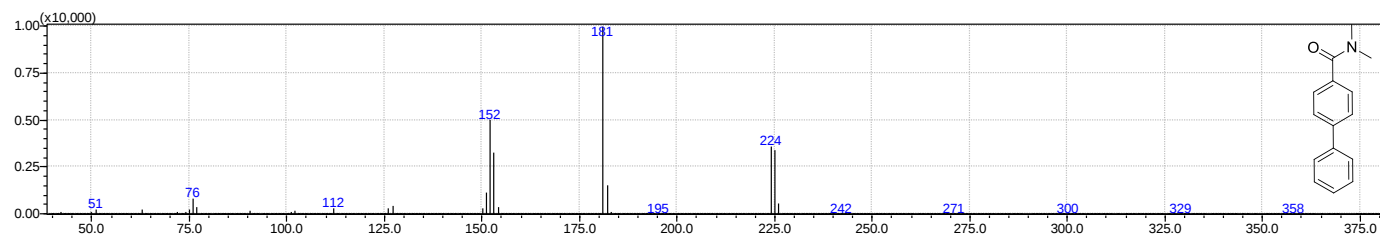
S3. N,N-dimethyl benzamide



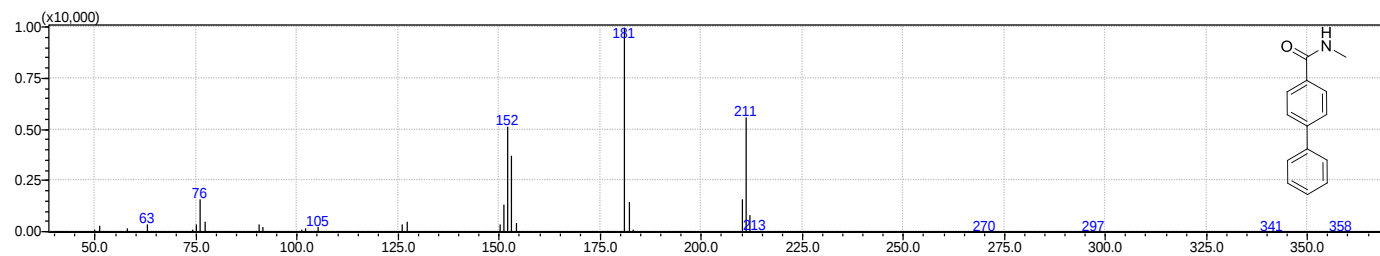
S4. N-methyl benzamide



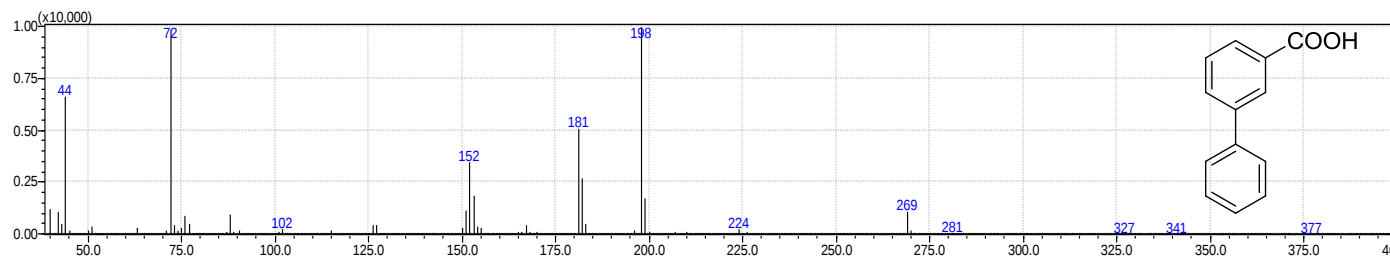
S5. N, N- dimethyl [1,1'-biphenyl]-4-carboxamide



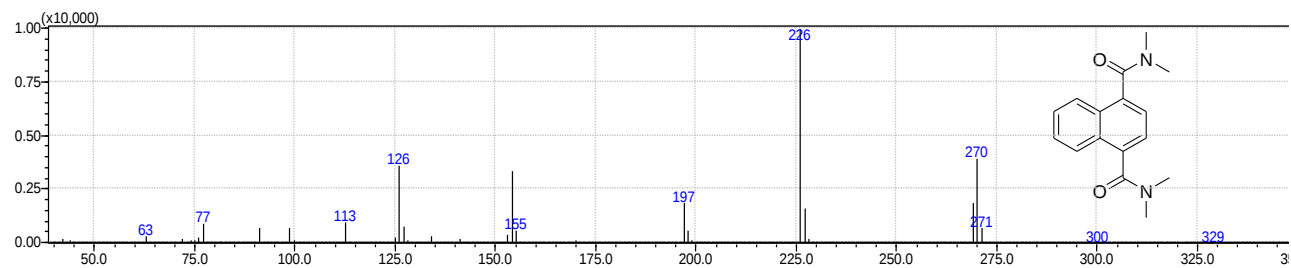
S6. N - methyl [1,1'-biphenyl]-4-carboxamide



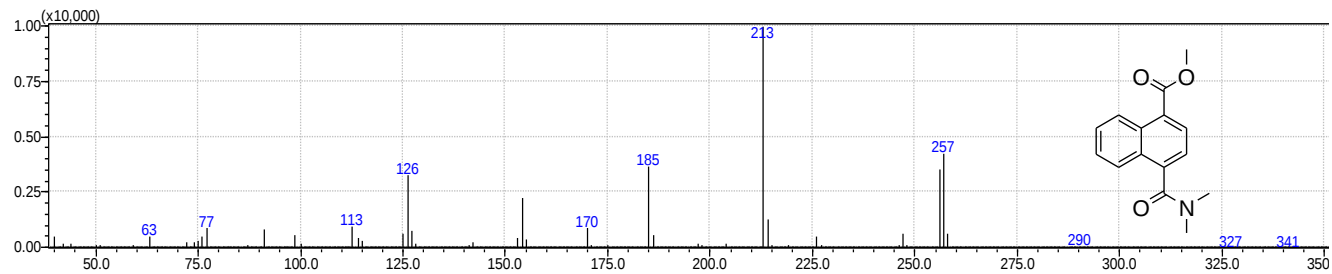
S7. [1,1'-biphenyl]-4-carboxylic acid



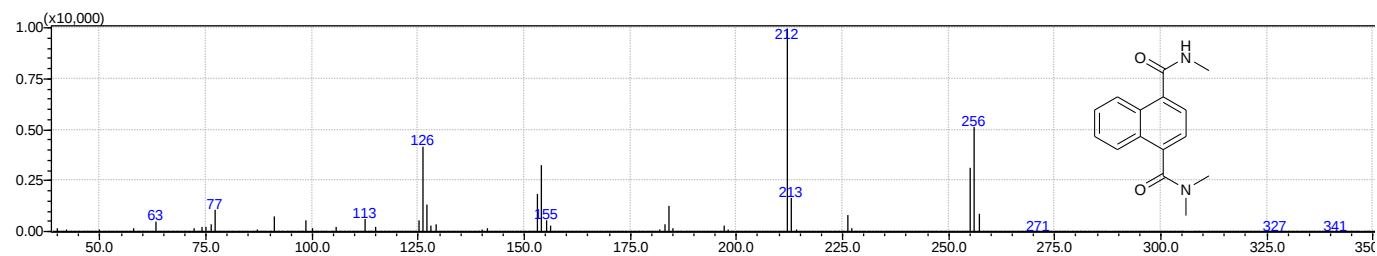
S8. N^1,N^1,N^4,N^4 -tetramethylnaphthalene-1,4-dicarboxamide



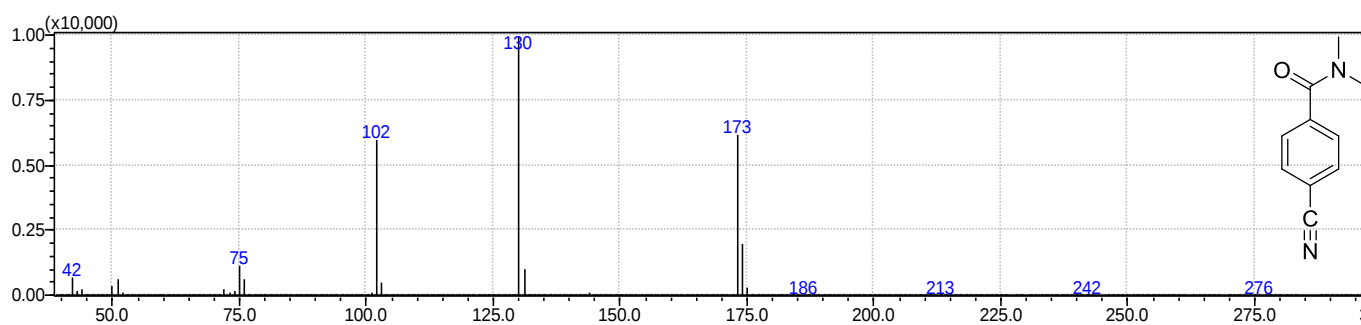
S9. methyl 4-(dimethylcarbamoyl)-1-naphthoate



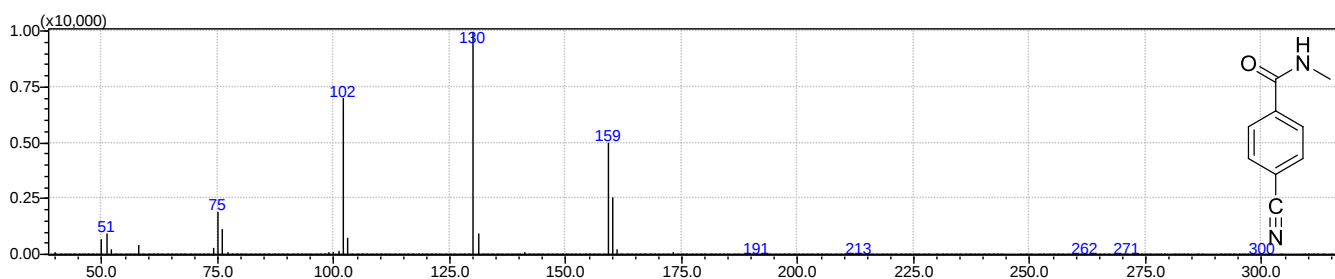
S10. N^1,N^1,N^4 -trimethylnaphthalene-1,4-dicarboxamide



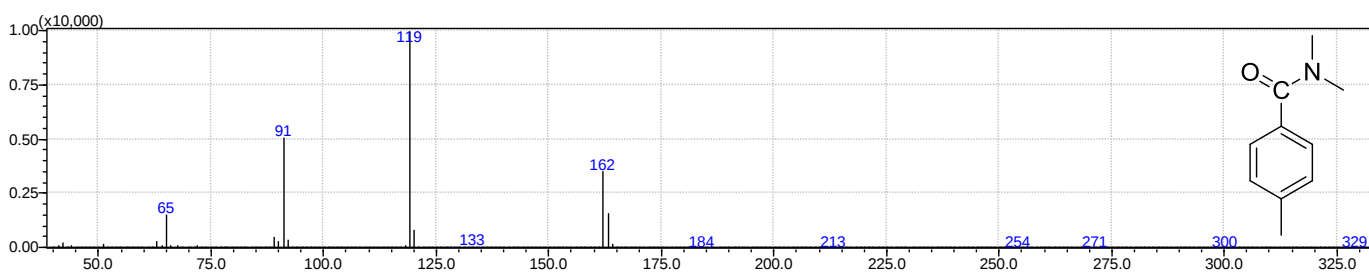
S 11. 4-cyano-N, N-dimethyl benzamide



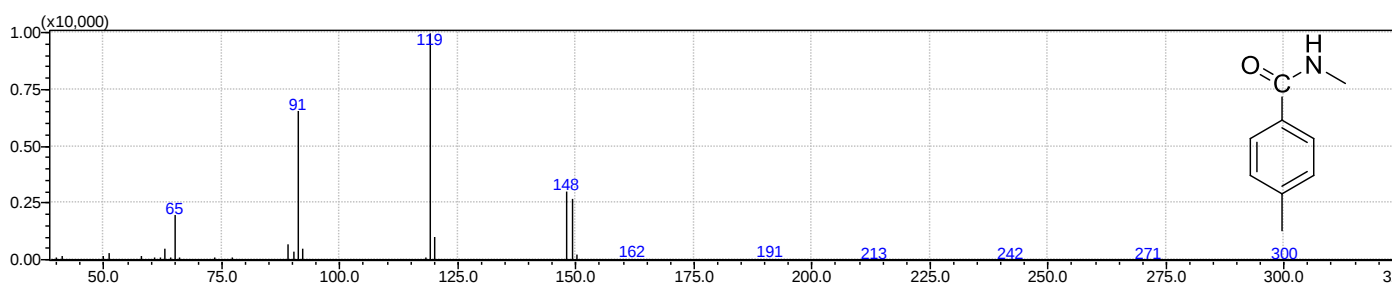
S 12. 4-cyano-N-methyl benzamide



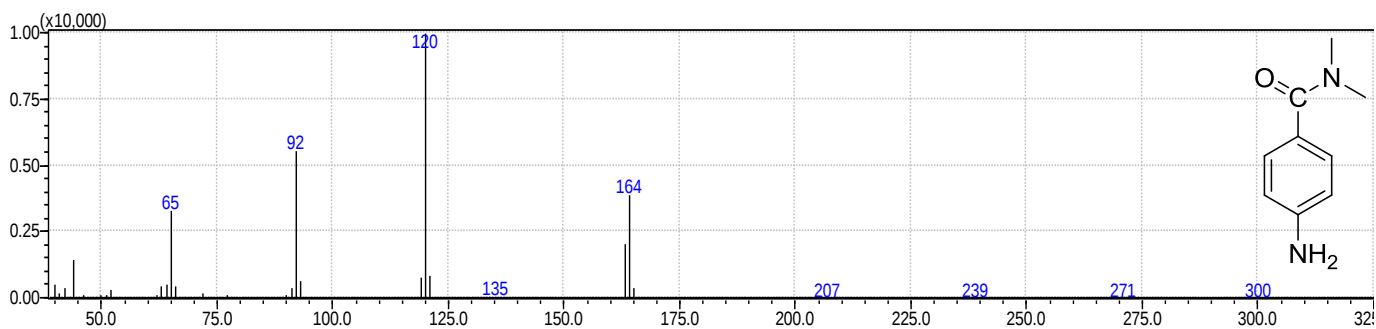
S 13. N,N,3-trimethyl- Benzamide



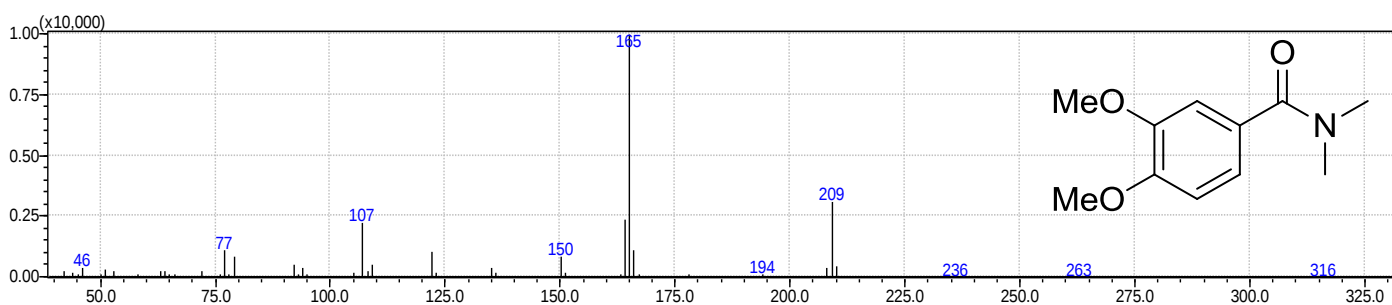
S 14. N-Methyl-p-toluamide



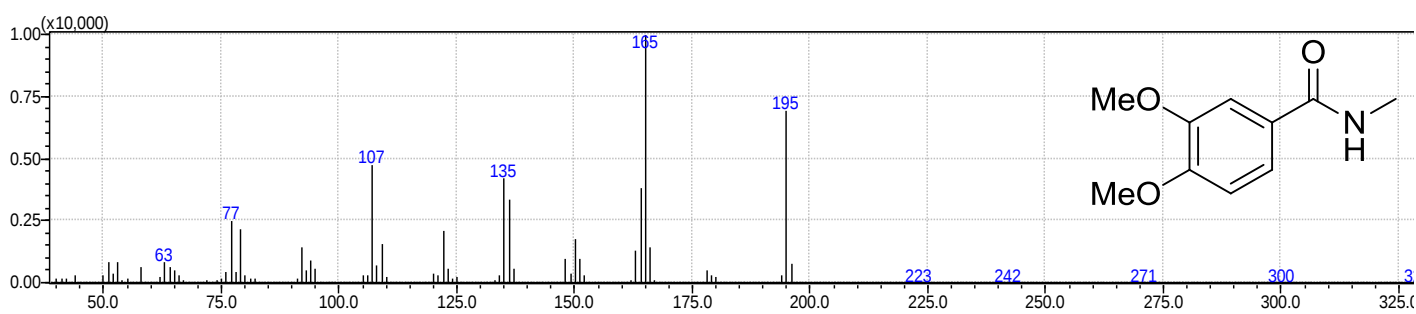
S 15. 4-amino-N-ethylbenzamide



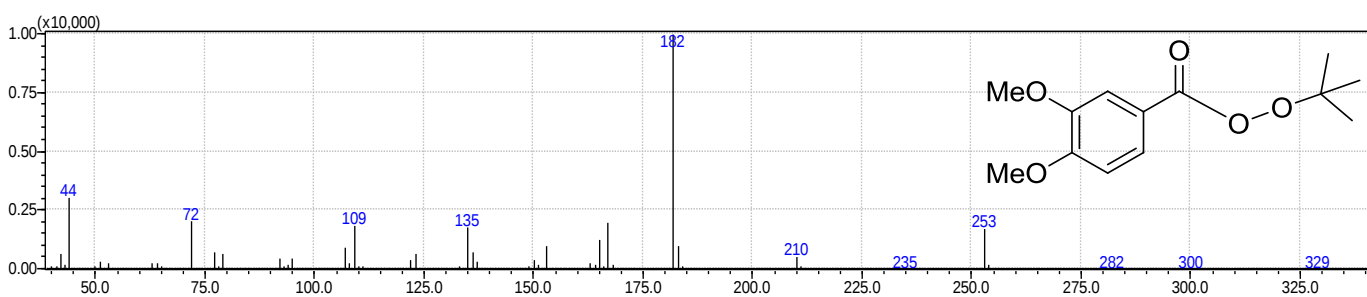
S 16. 3,4-dimethoxy-N-ethyl-benzamide



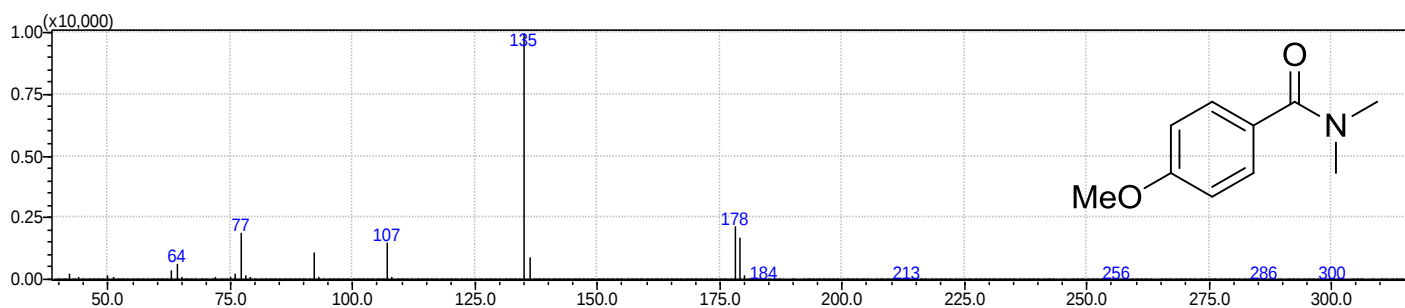
S 17. 3,4-dimethoxy-N-methyl- benzamide



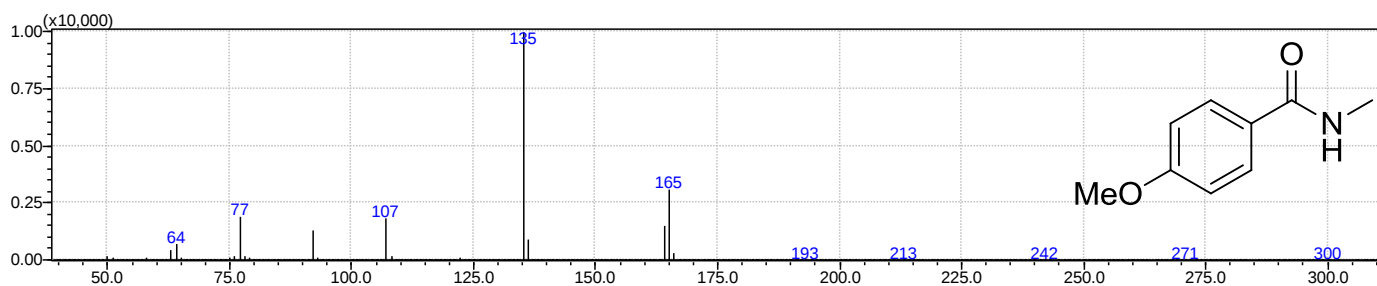
S 18. 3,4-dimethoxy-benzo tert-butyl benzoperoxide



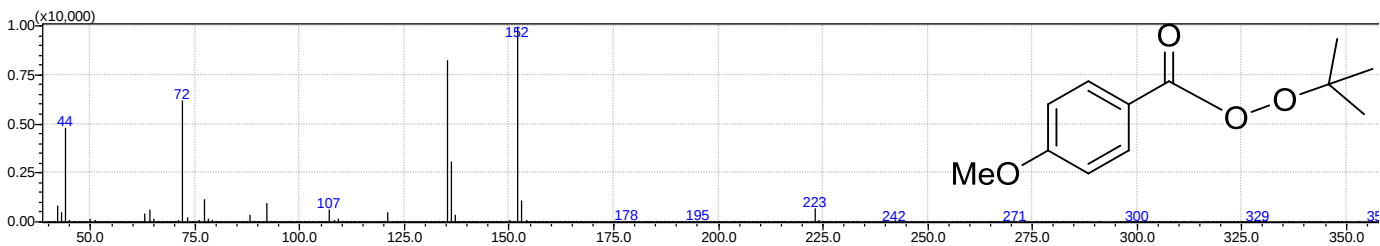
S 19. 4-methoxy-N-ethyl- benzamide



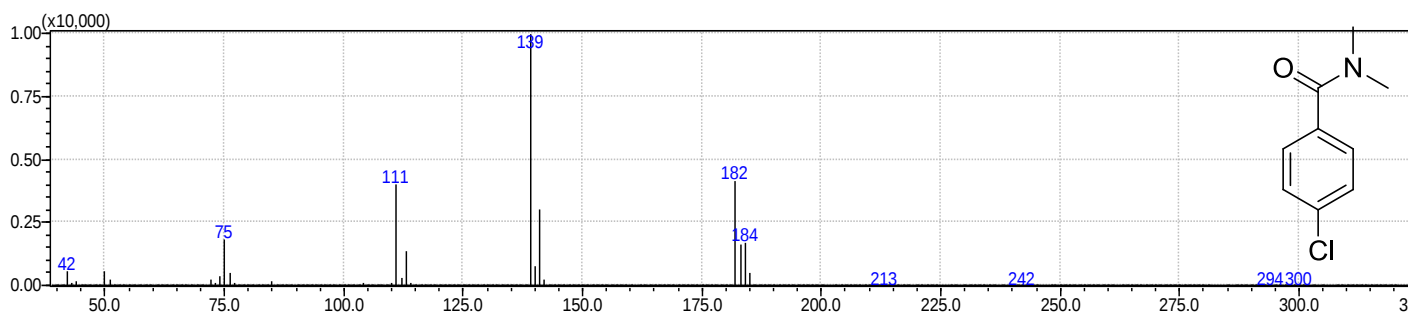
S 20. 4-methoxy-N-methyl- benzamide



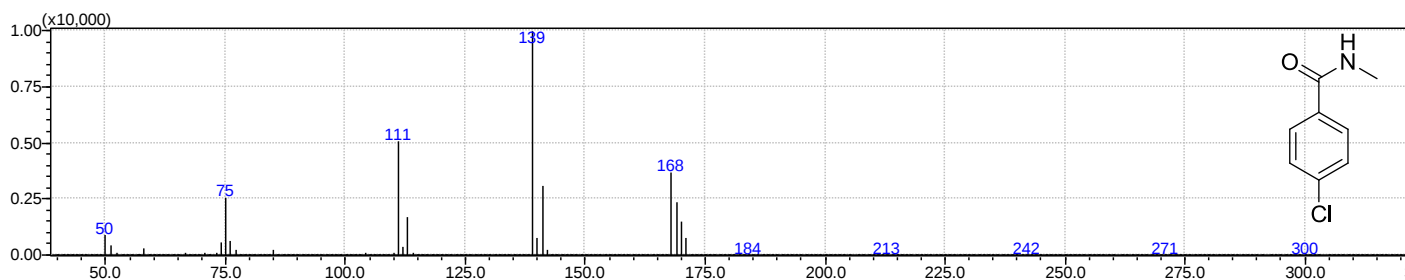
S 21. 4-methoxy benzoic acid tert-butyl peroxide



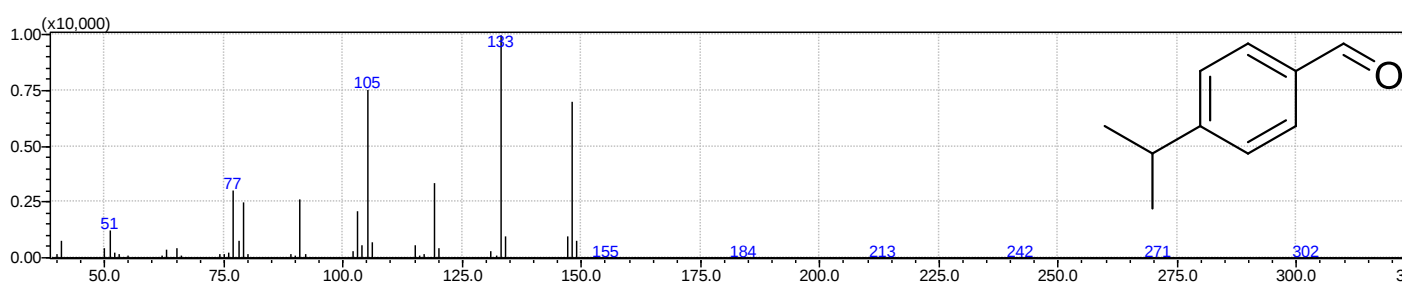
S 22. N-ethyl-4-Chlorobenzamide



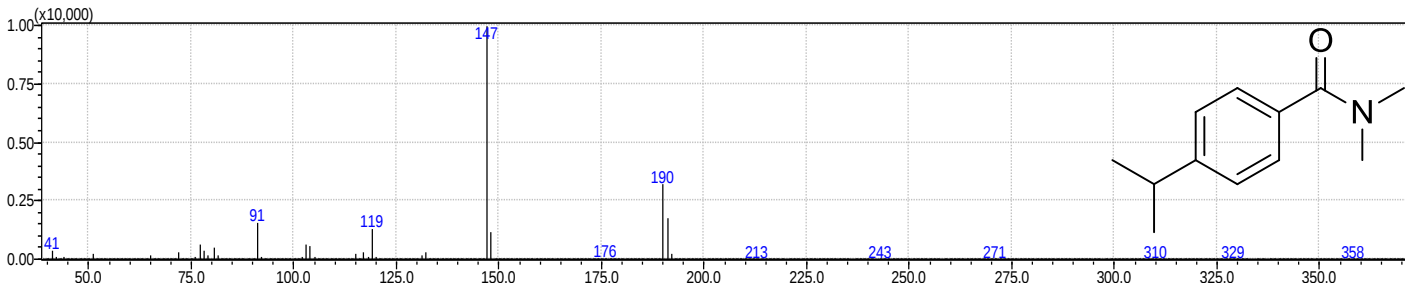
S 23. N-methyl-4-Chlorobenzamide



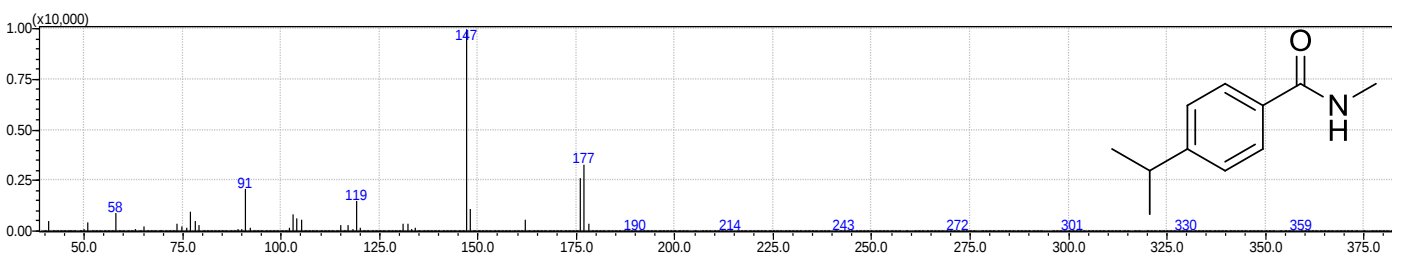
S 24. 4-(1-methylethyl)-Benzaldehyde



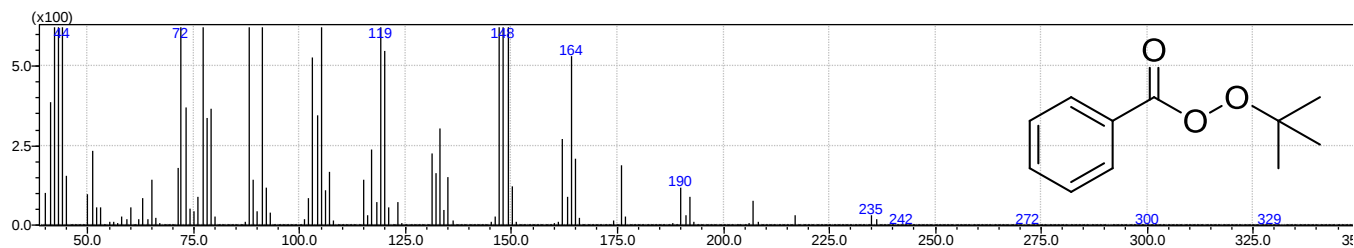
S 25. 4-*iso*-propyl-N, N-dimethylbenzamide



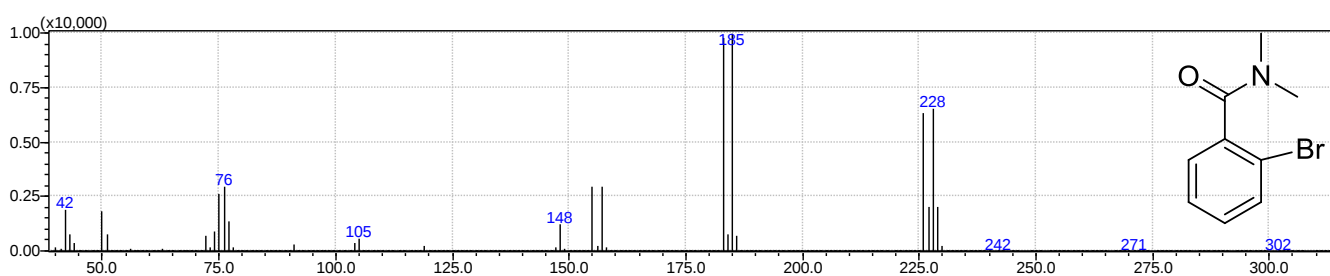
S 26. 4-*iso*-propyl-N-methylbenzamide



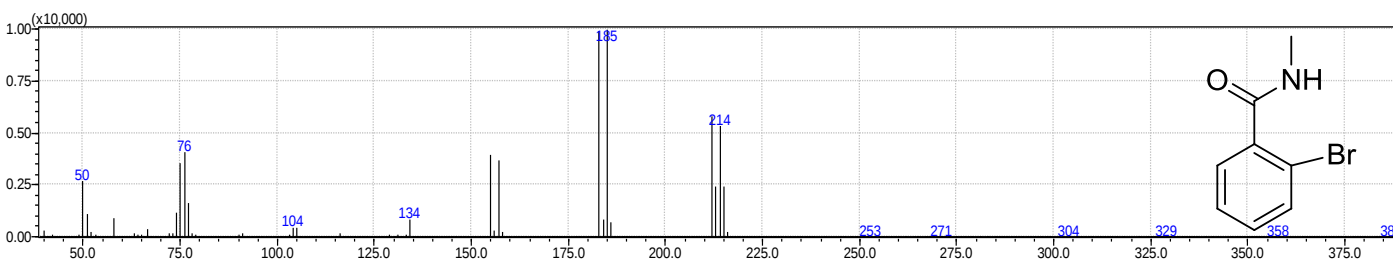
S 27. Tert-butyl 4-isopropylbenzoperoxoate



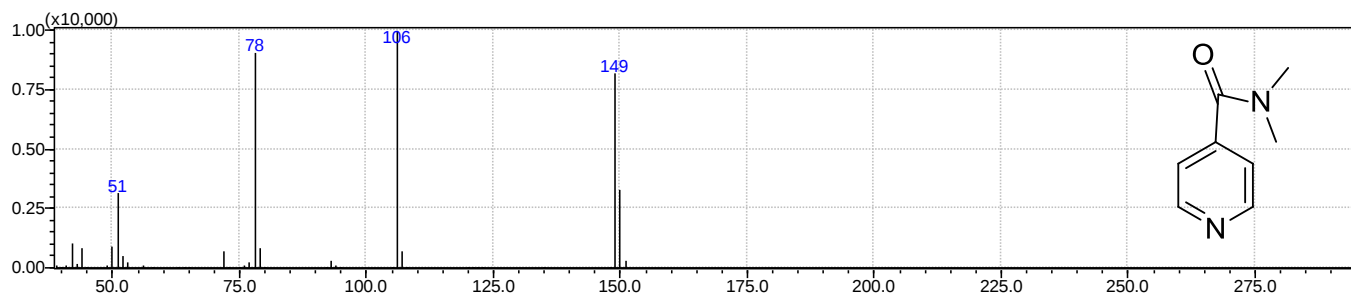
S 28. 2-bromo-N,N-dimethyl-Benzamide



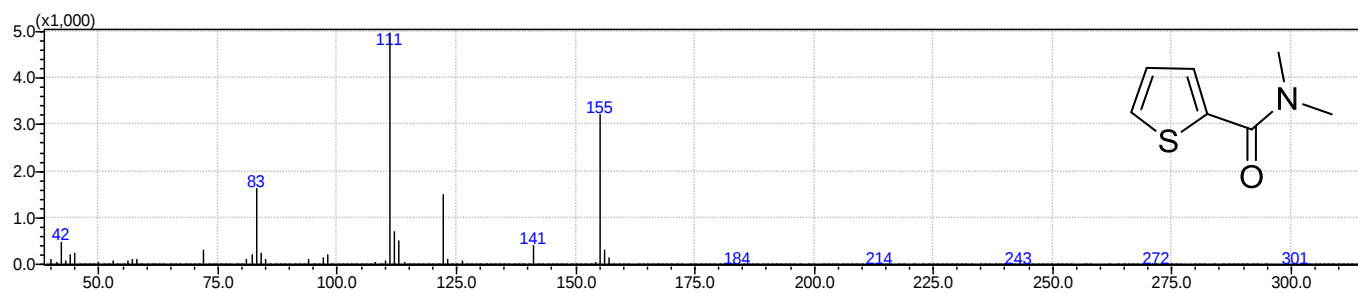
S 29. 2-bromo-N-methyl-benzamide



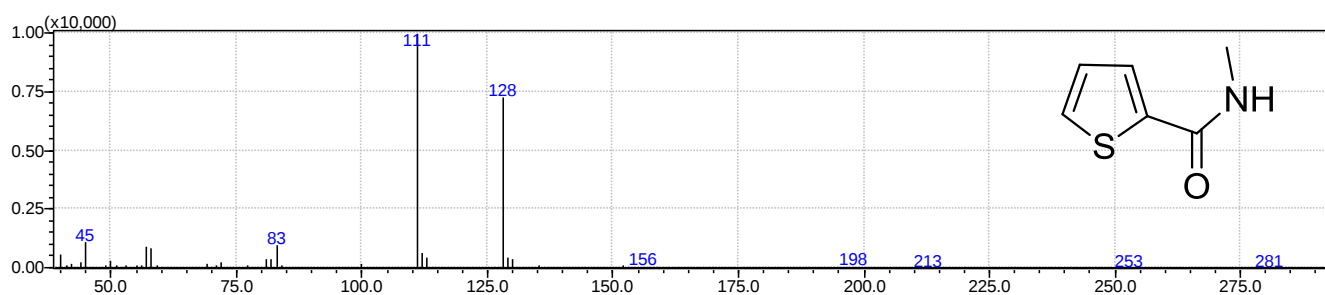
S 30. N,N-dimethylisonicotinamide



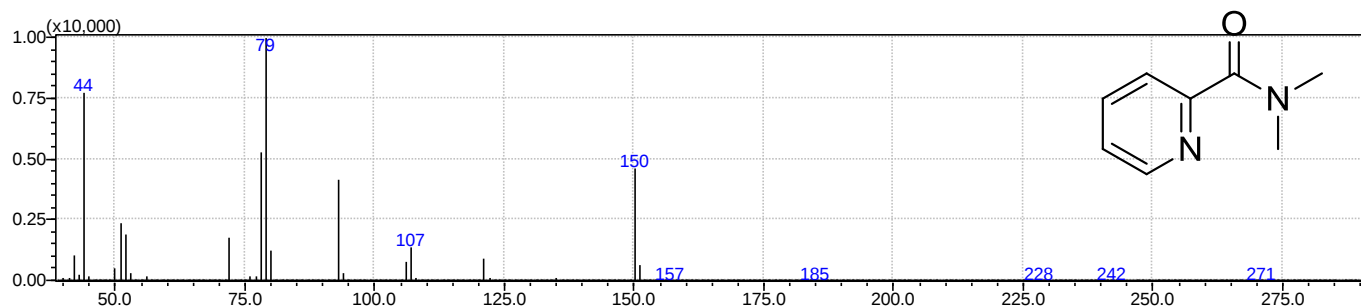
S 31. N, N-dimethylthiophene-2-carboxamide



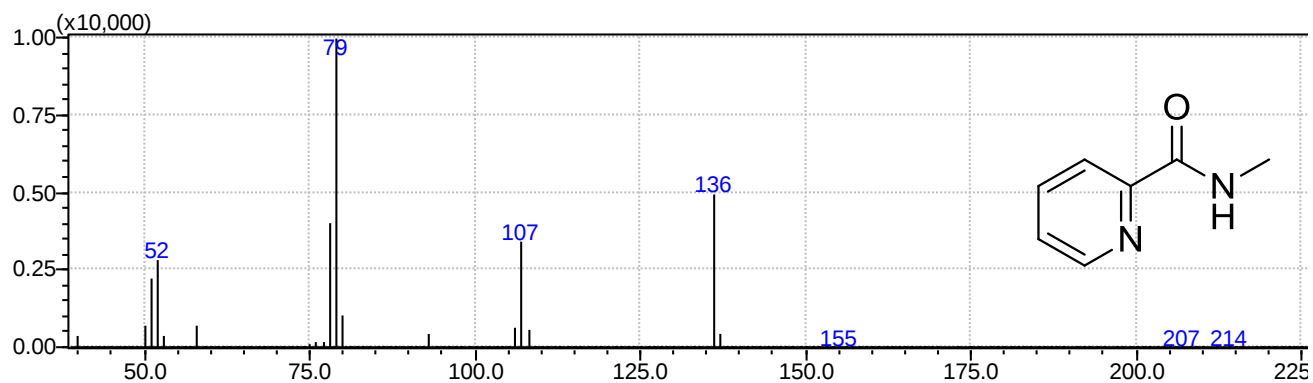
S 32. 2-Thiophenecarboxylic acid



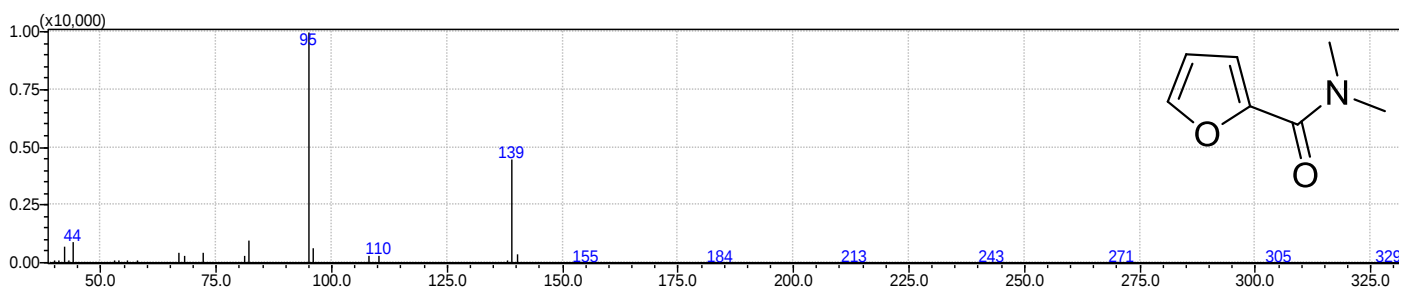
S 33. N, N-dimethylpicolinamide



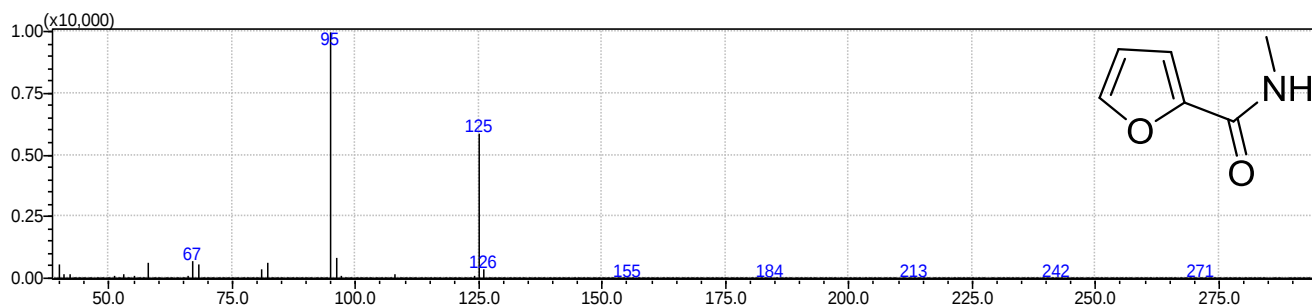
S 34. N-methylpicolinamide



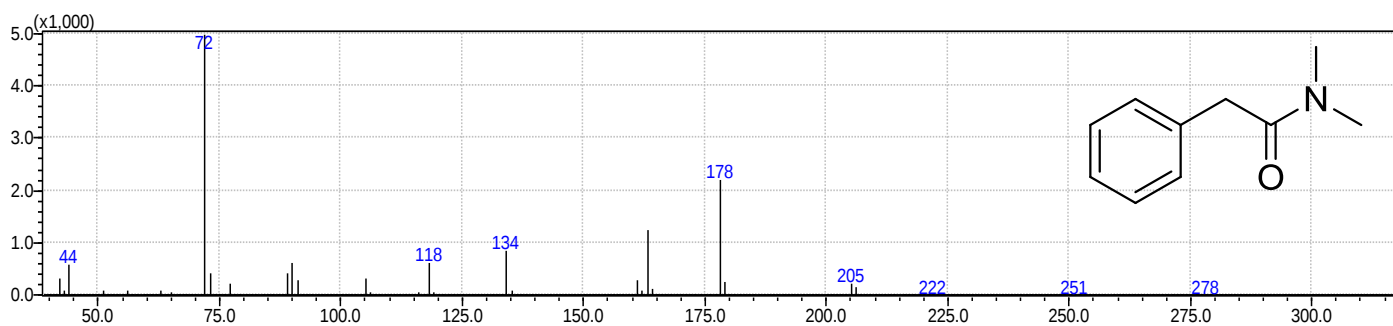
S 35. N-ethyl-2-furancarboxamide



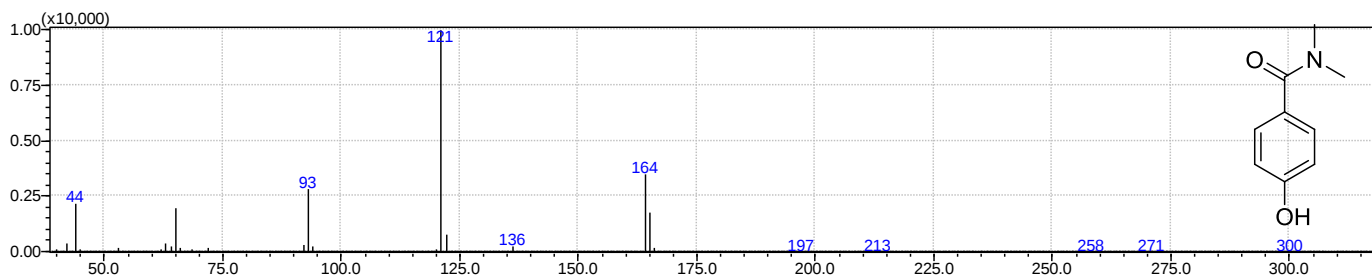
S 36. N-methyl 2-furancarboxamide



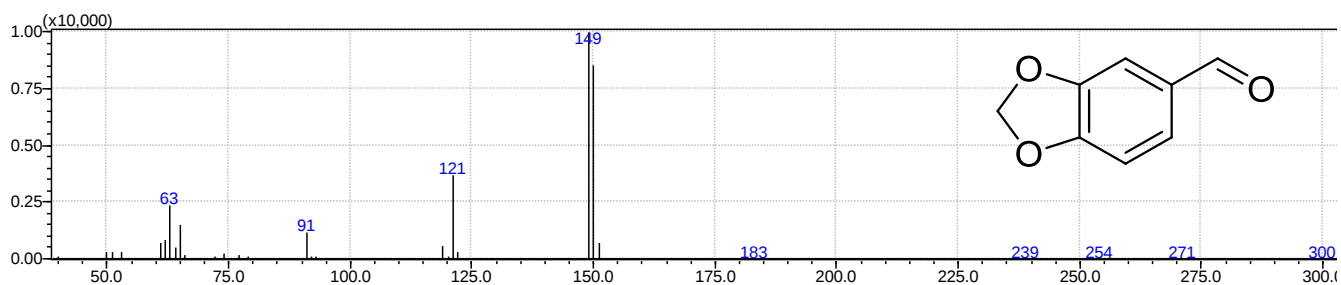
S 37. , N,N-dimethyl benzeneacetamide



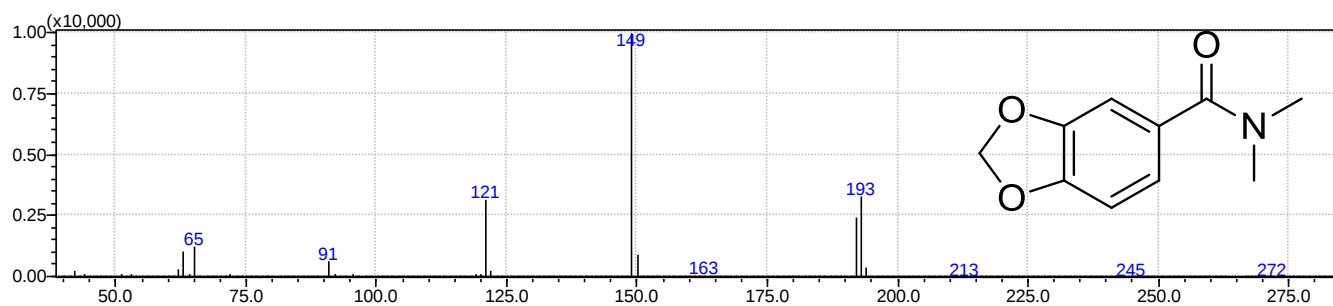
S 38. 4-hydroxy-N,N-dimethylbenzaldehyde



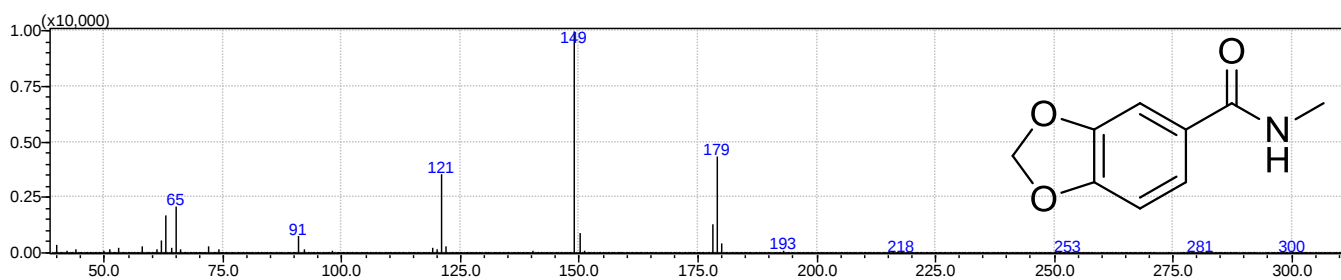
S 39. Piperonal



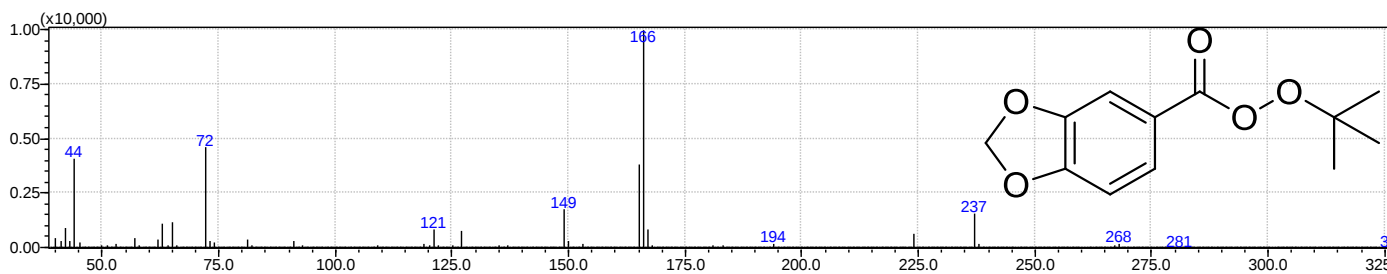
S 40. N, N-dimethylbenzo[d][1,3]dioxole-5-carboxamide



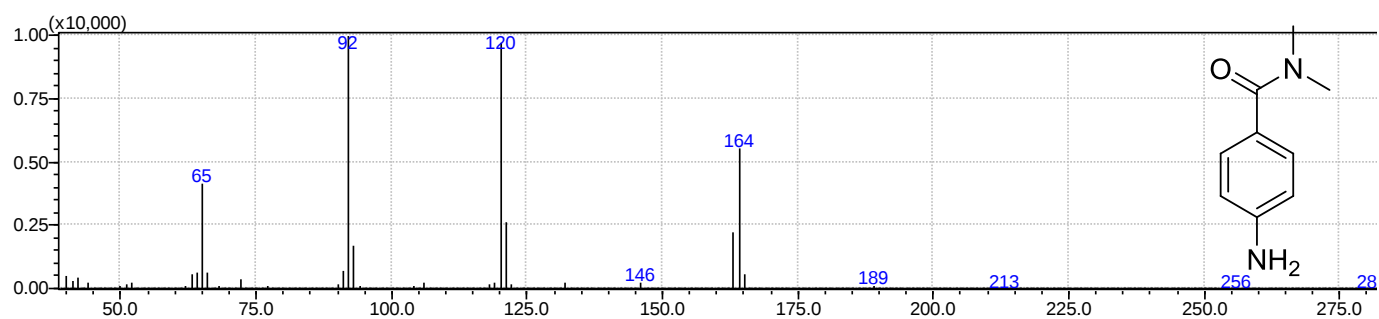
S 41. N-methylbenzo[d][1,3]dioxole-5-carboxamide



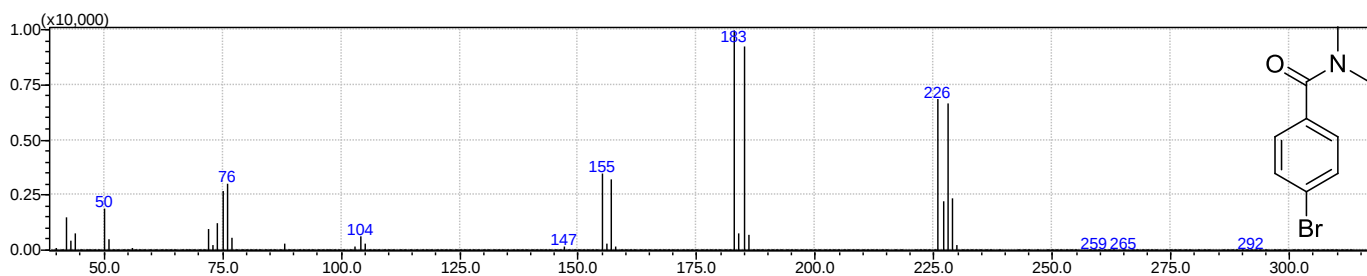
S 42. Tert-butyl benzo[d][1,3]dioxole-5-carboxylate



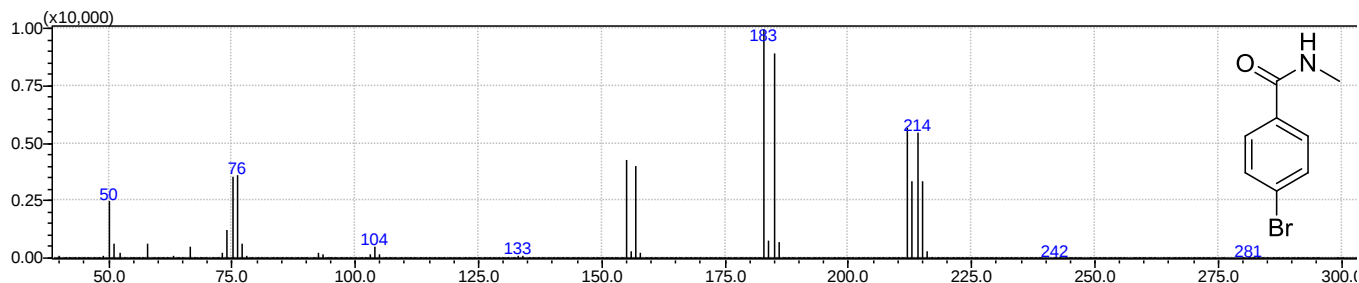
S 43. 4-amino-N, N-dimethylbenzamide



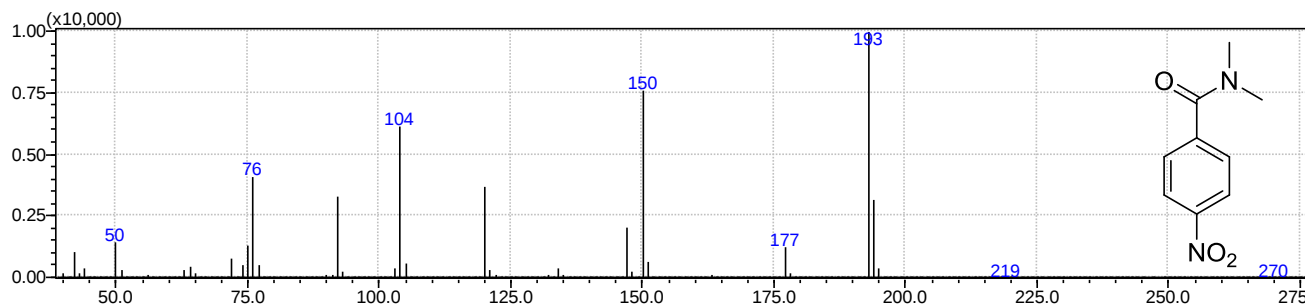
S 44. 4-bromo-N,N-dimethyl-Benzamide



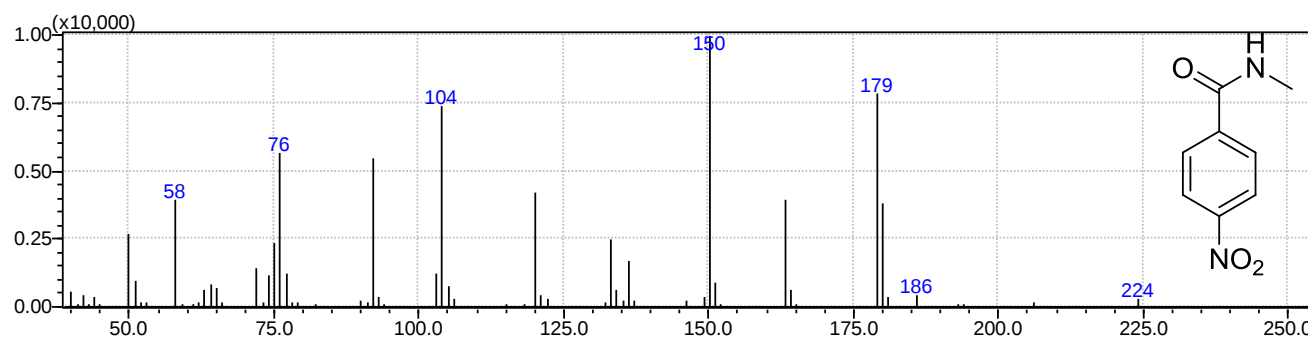
S 45. , 4-bromo-N-methyl-benzamide



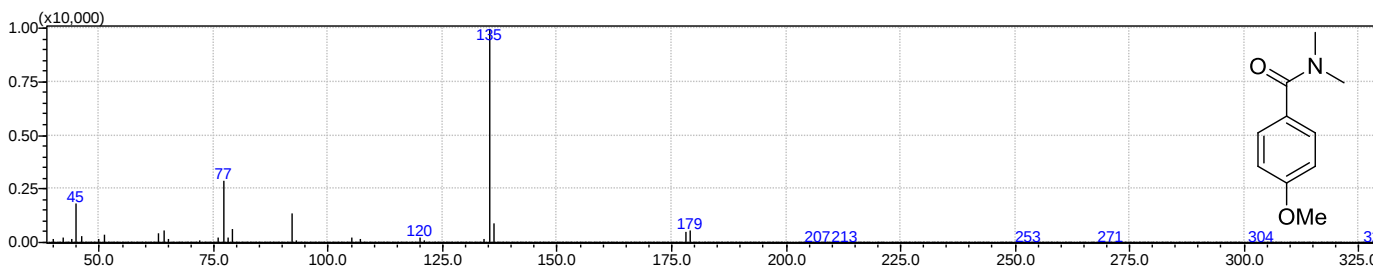
S 46. N,N-dimethyl-4-Nitrobenzamide



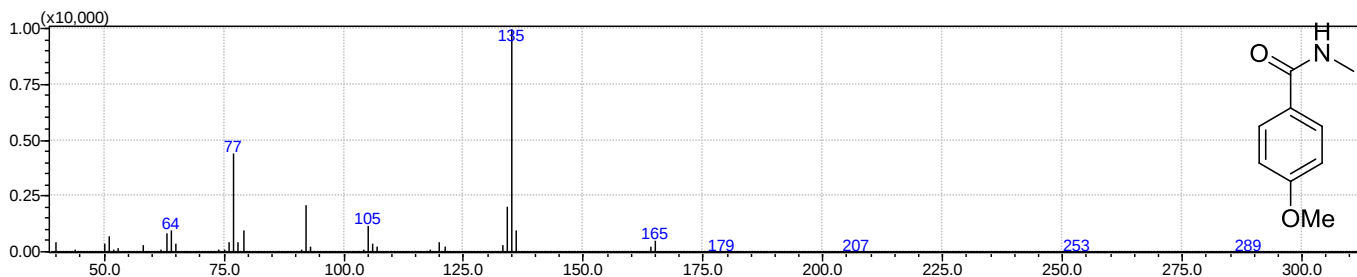
S 47. N-Methyl-p-nitrobenzamide



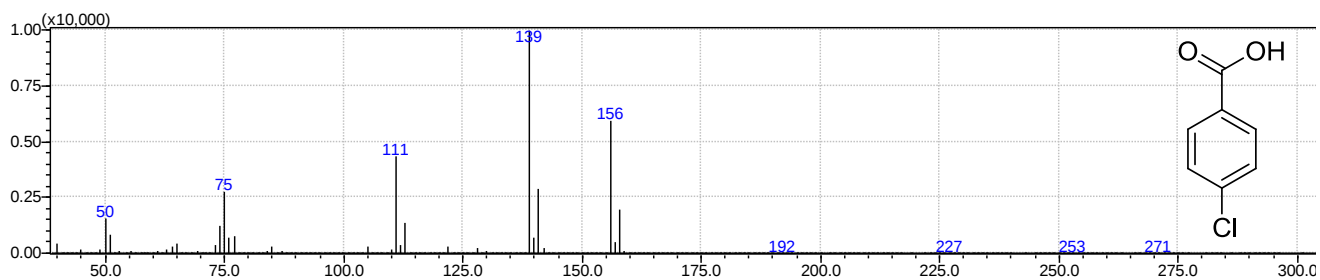
S 48. 2-methoxy-N,N-dimethyl-benzamide



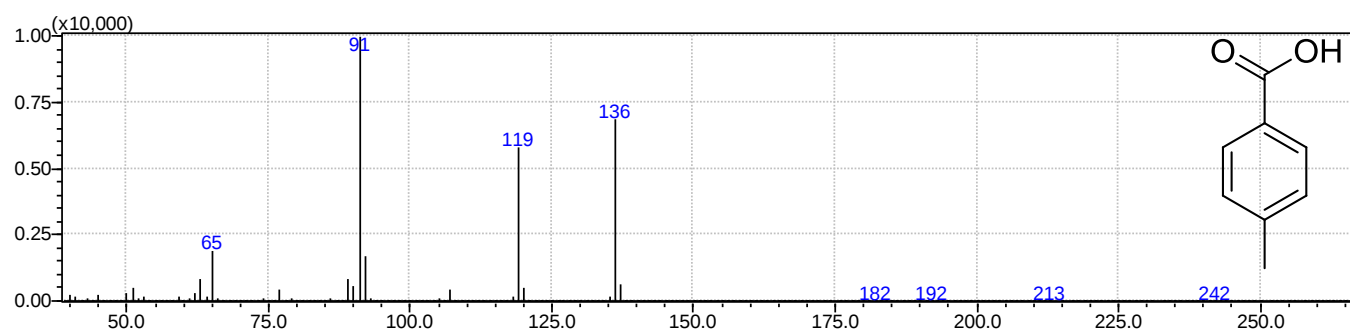
S 49. 2-methoxy-N-methyl-Benzamide



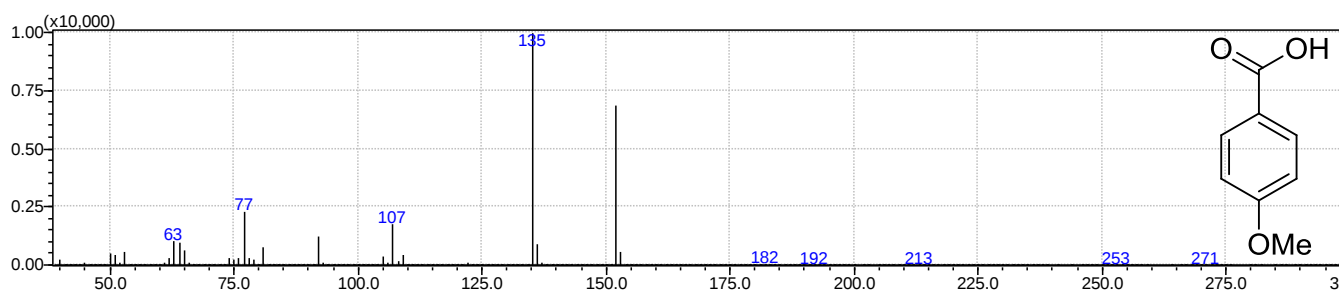
S 50. 4-chloro benzoic acid



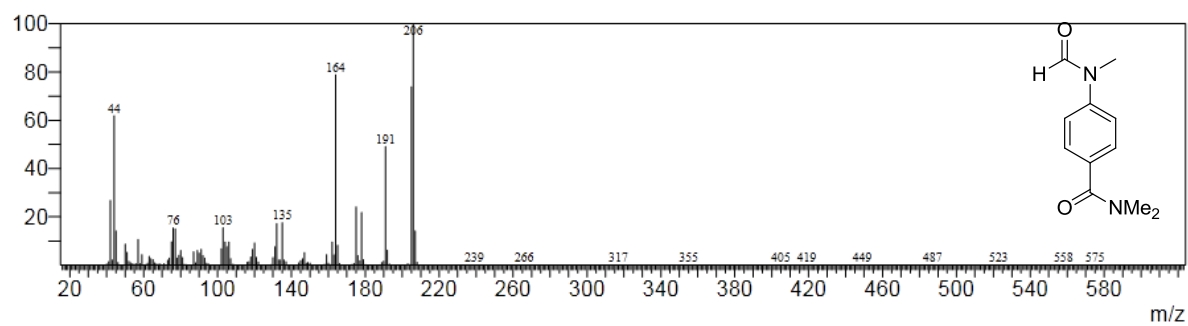
S 51. 4-methyl-benzoic acid



S 52. 4-methoxy-benzoic acid

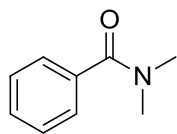


S 53. N,N-dimethyl-4-(N-methylformamido)benzamide

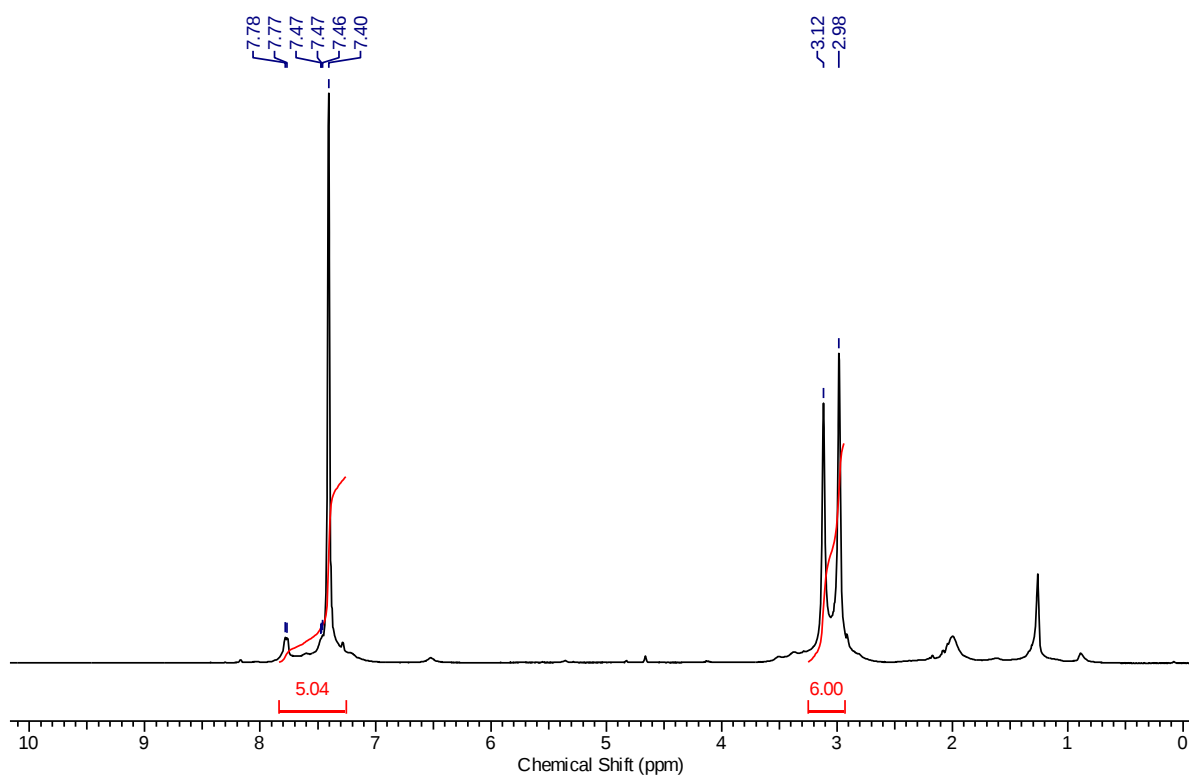


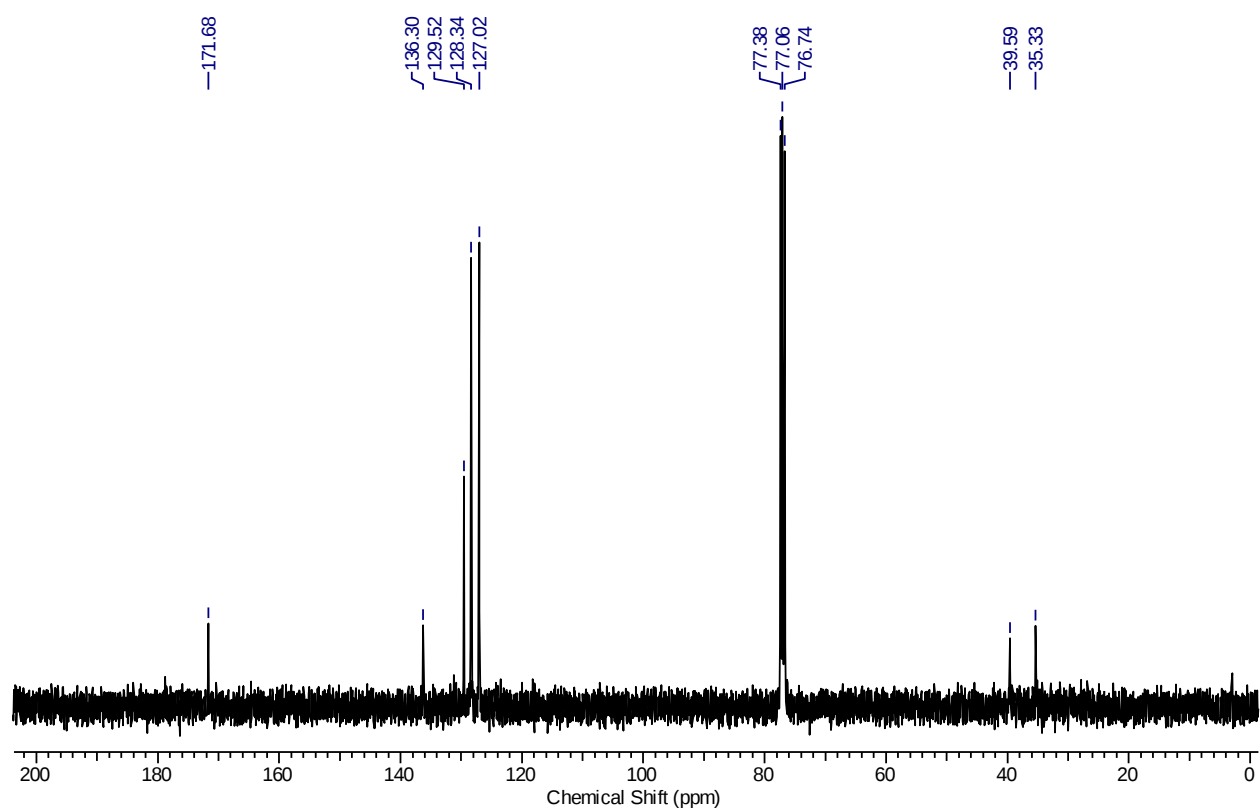
S54-S55- ^1H NMR and ^{13}C NMR Spectra of Product

N,N-dimethylbenzamide



^1H - NMR (400 MHz, CDCl_3) δ =7.78-7.40 (m, 5H), 3.12 (s, 3H), 2.98 (s, 3H). ^{13}C -NMR (100 MHz, CDCl_3) δ =171.68, 136.30, 129.52, 128.34, 127.02, 39.59, 35.33.





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