

Supporting Information for:

Acidic-functionalized ionic liquid as an efficient, green and reusable catalyst for hetero-Michael addition of nitrogen, sulfur and oxygen nucleophiles to α,β -unsaturated ketones

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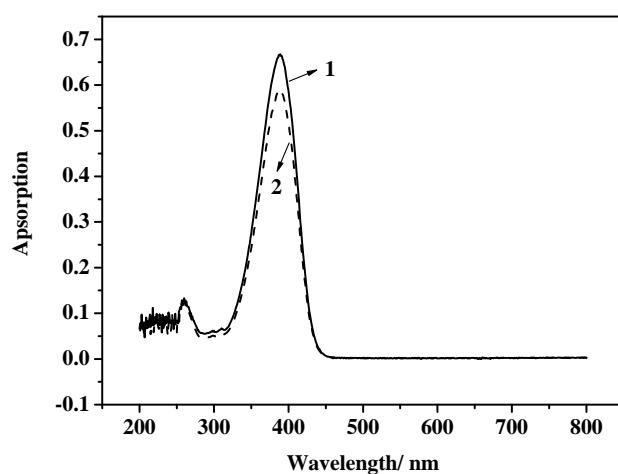
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1. UV-vis spectra of [Hmim]OTs



1: 4-nitroaniline; 2: 4-nitroaniline + [Hmim]OTs

Fig. S1 UV-vis spectra of [Hmim]OTs in DMSO.

According to the equation $H_o = pK(l)_{eq} + \log([l]_5/[l_{H^+}]_5)$, calculated pKa of [Hmim]OTs was 1.91.

pKa HCl 1.8

pKa H₂SO₄ 1.99

Ref.: *Acc. Chem. Res.* **1988**, *21*, 456, 463.

2. Hetero-Michael addition of 1-phenylbut-2-en-1-one with nitrogen nucleophiles catalyzed by [Hmim]OTs^a

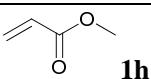
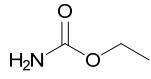
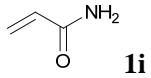
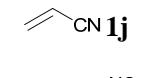
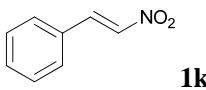
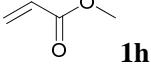
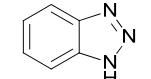
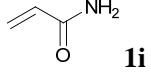
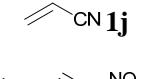
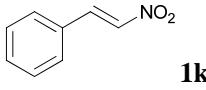
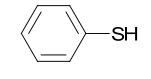
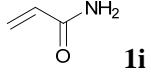
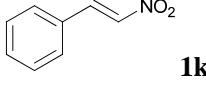
Table S1 Hetero-Michael addition of 1-phenylbut-2-en-1-one with nitrogen nucleophiles catalyzed by [Hmim]OTs^a

Entry	Enone	Nucleophile	Product	Time (h)	Yield ^b (%)
1				24	43
2 ^c				24	52
3 ^c				24	55
4 ^c				24	61
5 ^c				24	75
6 ^c				24	81
7 ^c				24	65
8 ^c				24	51

^a Reaction conditions: 1-phenylbut-2-en-1-one (0.5 mmol), carbamate or containing-nitrogen heterocycle (0.6 mmol), cat. [Hmim]OTs (30 mol%), rt. ^b Isolated yield. ^c 2 mL CH₂Cl₂ was added.

3. Hetero-Michael addition of other α,β -unsaturated electrophiles with nucleophiles catalyzed by [Hmim]OTs

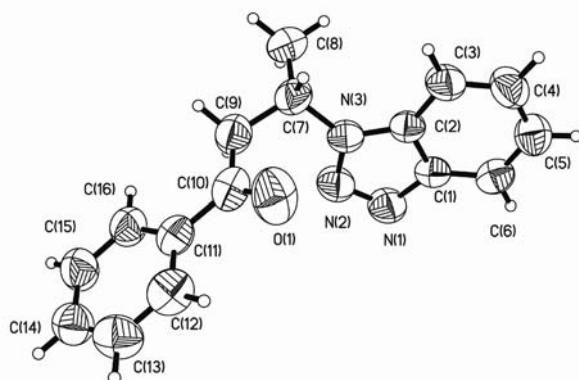
Table S2 Hetero-Michael addition of other α,β -unsaturated electrophiles with nucleophiles catalyzed by [Hmim]OTs^a

Entry	Nucleophile	α,β -unsaturated electrophiles	T (°C)	t (h)	Yield (%)
1		 1h	rt	24	NR
2	 2a	 1i	rt	24	NR
3		 1j	rt	24	NR
4		 1k	rt	24	NR
5		 1h	rt	24	NR
6	 2e	 1i	rt	24	NR
7		 1j	rt	24	NR
8		 1k	rt	24	NR
9	 3a	 1i	rt	24	trace
10		 1k	rt	24	NR

^a Reaction conditions: α,β -unsaturated electrophile (0.5 mmol), nucleophile (0.6 mmol), cat. [Hmim]OTs (30 mol%).

4. The crystal data of compounds 2ee and 2ef

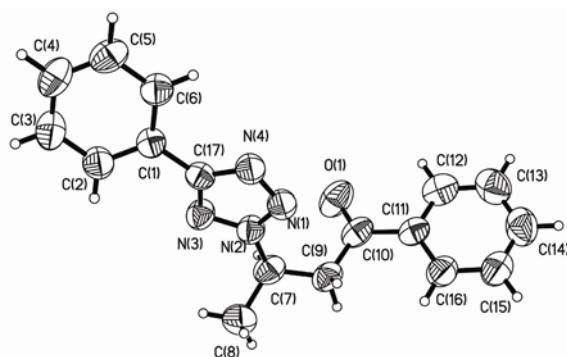
The structure of **2ee** and **2ef** were unambiguously confirmed by the X-ray crystallographic analysis. The product of compound **2ee** (Table S1, entry 5):



Bond precision 0.0031 \AA , Cell: $a = 9.912$, $b = 13.636$, $c = 10.633$, $\alpha = 90$, $\beta = 104.257$, $\gamma = 90$, $V = 1393.0 \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.265 \text{ g cm}^{-3}$, $T = 296 \text{ K}$, wavelength: 0.71073 . Final R indices [$I > 2\sigma(I)$], $RI = 0.0457$, $wR2 = 0.1423$; Reflections collected / unique: $1725 / 2442$; $(h,k,l)_{\text{max}} = 11, 16, 12$; $F_{(0,0,0)} = 560.0$, $T_{\min} = 0.976$, $T_{\max} = 0.980$; CCDC 836790.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The product of compound **2ef** (Table S1, entry 6):

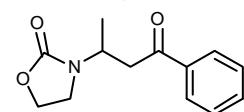


Bond precision 0.0044 \AA , Cell: $a = 6.203 (2)$, $b = 13.362 (5)$, $c = 18.973 (7)$, $\alpha = 90$, $\beta = 106.802 (10)$, $\gamma = 90$, $V = 1505.4 (9) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 1.290 \text{ g cm}^{-3}$, $T = 296 \text{ K}$, wavelength: 0.71073 . Final R indices [$I > 2\sigma(I)$], $RI = 0.0590$, $wR2 = 0.1850$; Reflections collected / unique: $1745 / 2599$; $(h,k,l)_{\text{max}} = 7, 15, 22$; $F_{(0,0,0)} = 616.0$, $T_{\min} = 0.975$, $T_{\max} = 0.979$; CCDC 836789.

These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

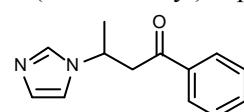
5. Characterization of the products in Table S1

3-(1-methyl-3-oxo-3-phenylpropyl) oxazolidin-2-one (**2ea**).



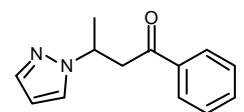
50.1 mg, 43% yield as white solid. mp: 75-76 °C . IR: 3352, 2980, 1687, 1532, 1255, 1065, 754, 692. ¹H NMR (400 MHz, CDCl₃) δ = 1.33 (d, *J* = 6.8 Hz, 3H), 3.14 (dd, *J* = 6.8, 6.4 Hz, 1H), 3.45 (dd, *J* = 7.2, 7.2 Hz, 1H), 3.58-3.67 (m, 1H), 4.28 (t, *J* = 8.0 Hz, 2H), 4.32-4.39 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.95 (t, *J* = 7.6 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 17.7, 42.3, 42.5, 62.0, 128.1, 128.7, 133.4, 136.4, 157.5, 197.7. HRMS-ESI: Calcd. For C₁₃H₁₅NNaO₃: 256.0944. Found: 256.0936.

3-(imidazol-1-yl)-1-phenylbutan-1-one (**2eb**).



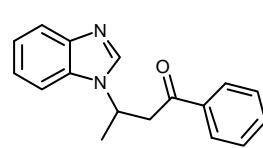
55.6 mg, 52% yield as white solid. mp: 68-69 °C. IR: 3353, 3215, 3111, 3062, 2979, 2935, 1684, 1598, 1480, 1451, 1409, 1367, 1286, 1220, 1081, 991, 911, 819, 758, 693, 666, 639. ¹H NMR (400 MHz, CDCl₃) δ = 3.20 (d, *J* = 6.8 Hz, 3H), 3.33 (dd, *J* = 6.8, 6.4 Hz, 1H), 3.48 (dd, *J* = 6.4, 6.4 Hz, 1H), 4.96-5.00 (m, 1H), 7.02 (d, *J* = 8.8 Hz, 2H), 7.45-7.47 (m, 2H), 7.55-7.57 (m, 1H), 7.61 (s, 1H), 7.88 (d, *J* = 7.2 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ = 21.7, 46.2, 48.9, 116.6, 127.8, 128.6, 129.2, 133.5, 135.8, 136.1, 196.1. HRMS-ESI: Calcd. For C₁₃H₁₅N₂O: 215.1179. Found: 215.1180.

1-phenyl-3-(1*H*-pyrazol-1-yl) butan-1-one (**2ec**).



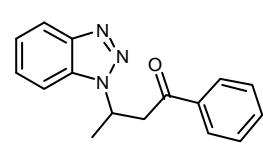
58.9 mg, 55% yield as white solid. mp: 47 °C. IR: 2981, 1685, 1446, 1398, 1287, 1214, 754, 691. ¹H NMR (400 MHz, CDCl₃) δ = 1.61 (d, *J* = 6.8 Hz, 1H), 3.32 (dd, *J* = 6.0, 6.4 Hz, 1H), 3.78 (dd, *J* = 6.8, 6.4 Hz, 1H), 5.01-5.10 (m, 1H), 6.17 (t, *J* = 2.0 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.48-7.50 (m, 2H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 21.3, 45.2, 53.4, 104.6, 128.0, 128.5, 133.3, 136.5, 139.3, 197.3. HRMS-ESI: Calcd. For C₁₃H₁₄N₂NaO: 237.0998. Found: 237.1007.

3-(1*H*-Benzo[d]imidazol-1-yl)-1-phenylbutan-1-one (**2ed**).



80.5 mg, 61% yield as white solid. mp: 94-95 °C. IR: 2980, 2936, 1685, 1491, 1455, 1363, 1287, 1208, 996, 893, 751, 692. ¹H NMR (400 MHz, CDCl₃) δ = 1.76 (d, *J* = 6.8 Hz, 3H), 3.52 (dd, *J* = 7.6, 7.6 Hz, 1H), 3.67 (dd, *J* = 5.6, 5.6 Hz, 1H), 5.24-5.32 (m, 1H), 7.28-7.32 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.51-7.58 (m, 2H), 7.81 (dd, *J* = 1.6, 2.4 Hz, 1H), 7.90 (d, *J* = 6.8 Hz, 2H), 8.07 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ = 20.7, 44.8, 47.9, 110.2, 120.6, 122.2, 122.9, 127.9, 128.8, 133.7, 136.2, 141.2, 144.0, 196.3. HRMS-ESI: Calcd. For C₁₇H₁₇N₂O: 265.1335. Found: 265.1340.

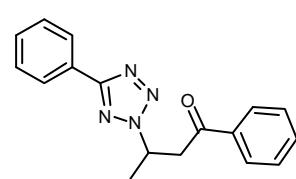
3-(1*H*-benzo[d][1,2,3]triazol-1-yl)-1-phenylbutan-1-one (**2ee**).



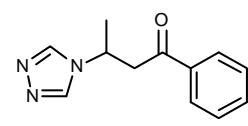
88.9 mg, 75% yield as white solid. mp: 96-97 °C. IR: 3449, 2985, 1683, 1640, 1271, 750, 690. ¹H NMR (400 MHz, CDCl₃) δ = 1.79 (d, *J* = 6.8 Hz, 3H), 3.66 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.11 (dd, *J* = 6.8, 7.2 Hz, 1H), 5.58-5.66 (m, 1H), 7.34-7.36 (m, 1H), 7.38-7.42 (m, 2H), 7.44-7.58 (m,

2H), 7.71 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.8 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ = 21.4, 44.7, 50.5, 109.7, 119.8, 123.9, 127.2, 128.0, 128.7, 132.6, 133.6, 136.2, 145.8, 196.6. HRMS-ESI: Calcd. For $\text{C}_{16}\text{H}_{15}\text{N}_3\text{NaO}$: 288.1107. Found: 288.1103.

1-phenyl-3-(5-phenyl-1*H*-tetrazol-1-yl) butan-1-one (**2ef**).

 118.2 mg, 81% yield as white solid. mp: 91-92 °C. IR: 3063, 2986, 1687, 1448, 1220, 999, 757, 691. ^1H NMR (400 MHz, CDCl_3) δ = 1.77 (d, J = 6.8 Hz, 3H), 3.59 (dd, J = 6.8, 7.2 Hz, 1H), 3.98 (dd, J = 6.4, 6.4 Hz, 1H), 5.66-5.74 (m, 1H), 7.44-7.48 (m, 5H), 7.56-7.59 (m, 1H), 7.96 (d, J = 7.6 Hz, 2H), 8.13 (d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ = 20.0, 43.0, 55.3, 125.8, 126.5, 127.1, 127.7, 127.8, 129.2, 132.7, 135.1, 163.8, 194.6. HRMS-ESI: Calcd. For $\text{C}_{17}\text{H}_{16}\text{N}_4\text{NaO}$: 315.1216. Found: 315.1201.

1-phenyl-3-(4*H*-1,2,4-triazol-4-yl)butan-1-one (**2eg**).

 69.9 mg, 65% yield as white solid. mp: 75-76 °C. IR: 3425, 3110, 2981, 2938, 1710, 1684, 1217, 759, 692, 667. ^1H NMR (400 MHz, CDCl_3) δ = 1.66 (d, J = 6.8 Hz, 2H), 3.33 (dd, J = 5.2, 5.2 Hz, 1H), 3.81 (dd, J = 7.6, 7.6 Hz, 1H), 5.16-5.24 (m, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.58 (t, J = 7.6 Hz, 1H), 7.90-7.92 (m, 3H), 8.21 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ = 21.0, 44.5, 51.6, 128.0, 128.7, 133.7, 136.2, 142.9, 151.9, 196.5. HRMS-ESI: Calcd. For $\text{C}_{12}\text{H}_{13}\text{N}_3\text{O}$: 216.1179. Found: 216.1175.

6. Characterization of the ionic liquids except [Hmim]OTs

[Bmim]BF₄

IR: 3639, 3563, 3162, 3122, 2965, 2939, 2875, 1627, 1572, 1466, 1384, 1286, 1171, 1061, 849, 758, 698, 652, 624, 522. ¹H NMR (400 MHz, D₂O) δ = 0.84 (t, *J* = 7.6 Hz, 3H), 1.19-1.28 (m, 2H), 1.73-1.80 (m, 2H), 3.81 (s, 1H), 4.11 (t, *J* = 7.2 Hz, 2H), 7.34 (s, 1H), 7.39 (s, 1H), 8.61 (s, 1H). ¹³C NMR (100 MHz, D₂O) δ = 12.6, 18.7, 31.2, 35.5, 49.2, 122.2, 123.4, 135.8. MS (ESI): [m/z]⁺ = 138.7, [m/z]⁻ = 86.6.

[Bmim]PF₆

IR: 3674, 3171, 3125, 2967, 2940, 2877, 1572, 1466, 1432, 1387, 1339, 1170, 1113, 1028, 823, 748, 699, 652, 624, 559, 409. ¹H NMR (400 MHz, (CD₃)₂SO) δ = 0.91 (t, *J* = 7.2 Hz, 3H), 1.22-1.32 (m, 2H), 1.74-1.81 (m, 2H), 3.85 (s, 3H), 4.16 (t, *J* = 7.2 Hz, 2H), 7.67 (t, *J* = 1.6 Hz, 1H), 7.73-7.74 (m, 1H), 9.08 (s, 1H). ¹³C NMR (100 MHz, (CD₃)₂SO) δ =13.1, 18.7, 31.3, 35.6, 48.5, 122.2, 123.5, 136.4. MS (ESI): [m/z]⁺ = 138.7, [m/z]⁻ = 144.6.

[Bmim]HSO₄

IR: 3151, 3108, 2963, 2874, 1645, 1570, 1464, 1170, 1047, 857, 756, 697, 621, 581, 438. ¹H NMR (400 MHz, D₂O) δ = 3.25 (t, *J* = 7.2 Hz, 3H), 3.60-3.70 (m, 2H), 4.15-4.22 (m, 2H), 6.23 (s, 3H), 6.53 (t, *J* = 6.8 Hz, 2H), 7.28 (s, 1H), 9.76-9.77 (m, 1H), 9.81-9.82 (m, 1H), 11.0 (s, 1H). ¹³C NMR (100 MHz, D₂O) δ = 15.1, 21.2, 33.7, 38.1, 51.7, 124.7, 126.0, 138.3. MS (ESI): [m/z]⁺ = 138.7, [m/z]⁻ = 96.5.

[Bsmim]HSO₄

IR: 3158, 3117, 2962, 1707, 1572, 1462, 1424, 1223, 1169, 1030, 836, 747, 651, 583, 561, 524. ¹H NMR (400 MHz, D₂O) δ = 1.33-1.41 (m, 2H), 1.61-1.69 (m, 2H), 2.55-2.59 (m, 2H), 3.52 (s, 3H), 3.86-3.89 (m, 2H), 7.07-7.08 (m, 1H), 7.12-7.13 (m, 1H), 8.35 (s, 1H). ¹³C NMR (100 MHz, D₂O) δ = 20.7, 27.9, 35.5, 48.7, 49.9, 121.1, 123.5, 135.7. MS (ESI): [m/z]⁺ = 218.7, [m/z]⁻ = 96.5.

PyHSO₄

IR: 3432, 2083, 1635, 1544, 1489, 1200, 1122, 1053, 750, 677, 617, 431. ¹H NMR (400 MHz, D₂O) δ = 7.80-7.84 (m, 2H), 8.34-8.39 (m, 1H), 8.53 (d, *J* = 5.2 Hz, 2H). ¹³C NMR (100 MHz, D₂O) δ = 127.3, 141.0, 147.1. MS (ESI): [m/z]⁺ = 79.7, [m/z]⁻ = 96.6.

[Hmim]HSO₄

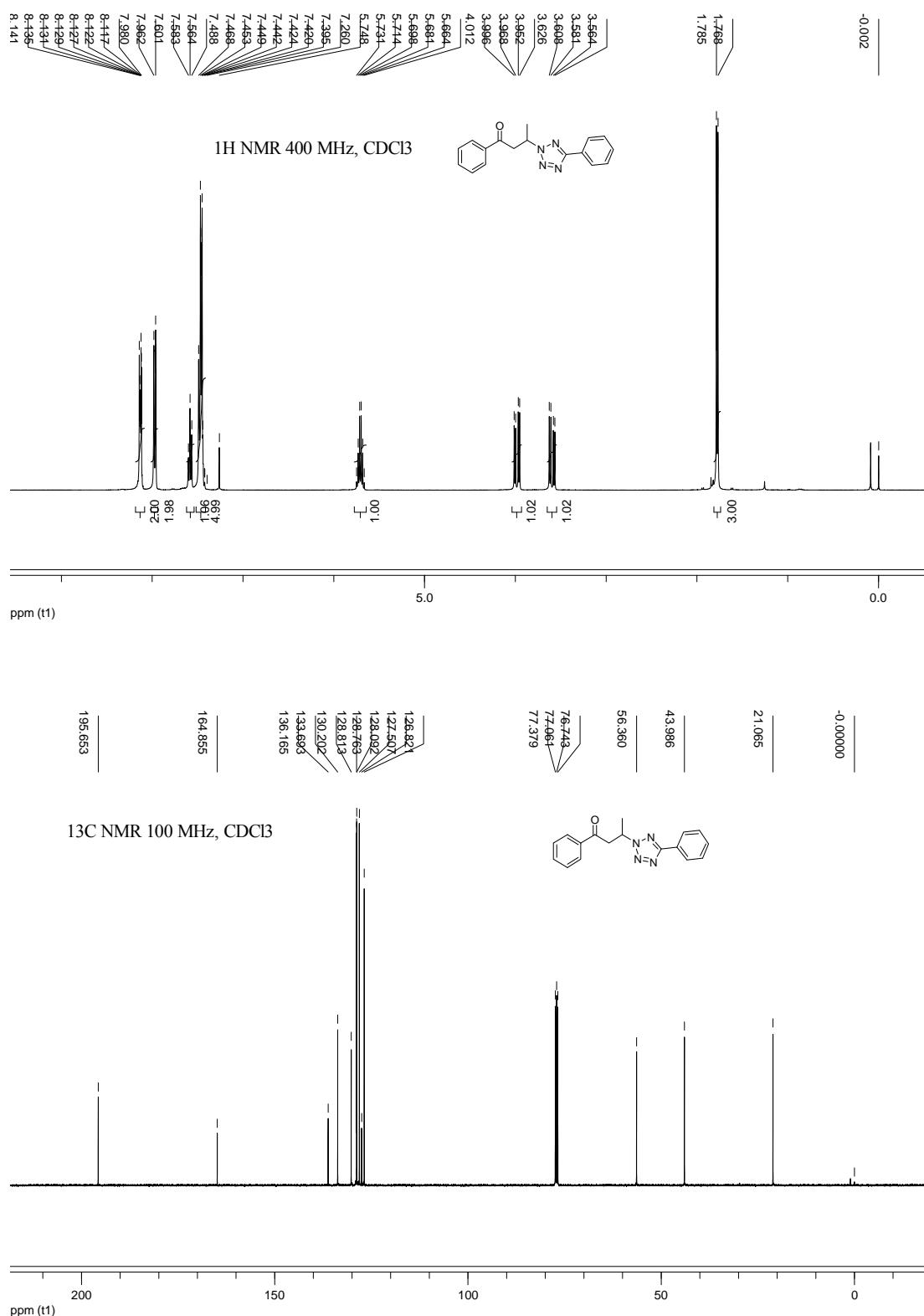
IR: 3148, 1642, 1587, 1552, 1453, 1377, 1280, 1192, 1086, 1049, 845, 761, 664, 624, 595, 439. ¹H NMR (400 MHz, D₂O) δ = 3.54 (s, 3H), 7.05 (d, *J* = 1.6 Hz, 2H), 8.27 (s, 1H). ¹³C NMR (100 MHz, D₂O) δ = 35.3, 119.2, 122.7, 134.7. MS (ESI): [m/z]⁺ = 82.8, [m/z]⁻ = 96.5.

[Hmim]BF₄

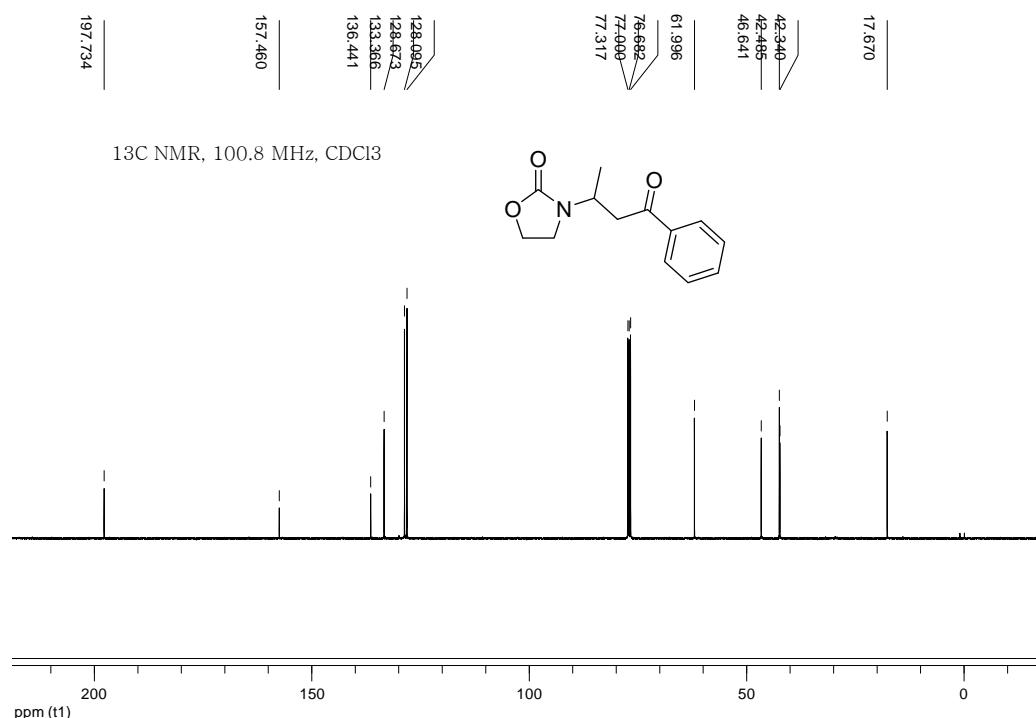
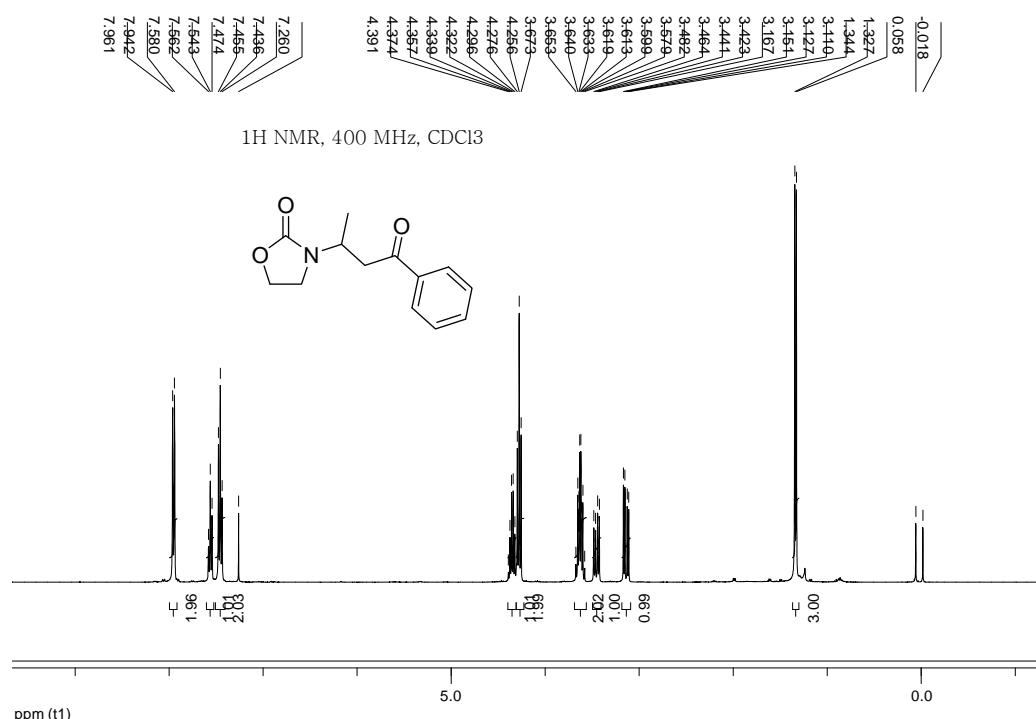
IR: 3610, 3332, 3169, 3033, 2980, 2887, 2765, 2647, 1632, 1589, 1553, 1449, 1382, 1332, 1309, 1285, 1059, 915, 852, 762, 666, 625, 580, 524. ¹H NMR (400 MHz, D₂O) δ = 3.23 (d, *J* = 2.0 Hz, 3H), 7.33 (s, 2H), 8.54 (s, 1H). ¹³C NMR (100 MHz, D₂O) δ = 35.4, 119.4, 122.9, 135.0. MS (ESI): [m/z]⁺ = 82.8, [m/z]⁻ = 86.6.6.

7. Typical ^1H NMR and ^{13}C NMR spectra of the products

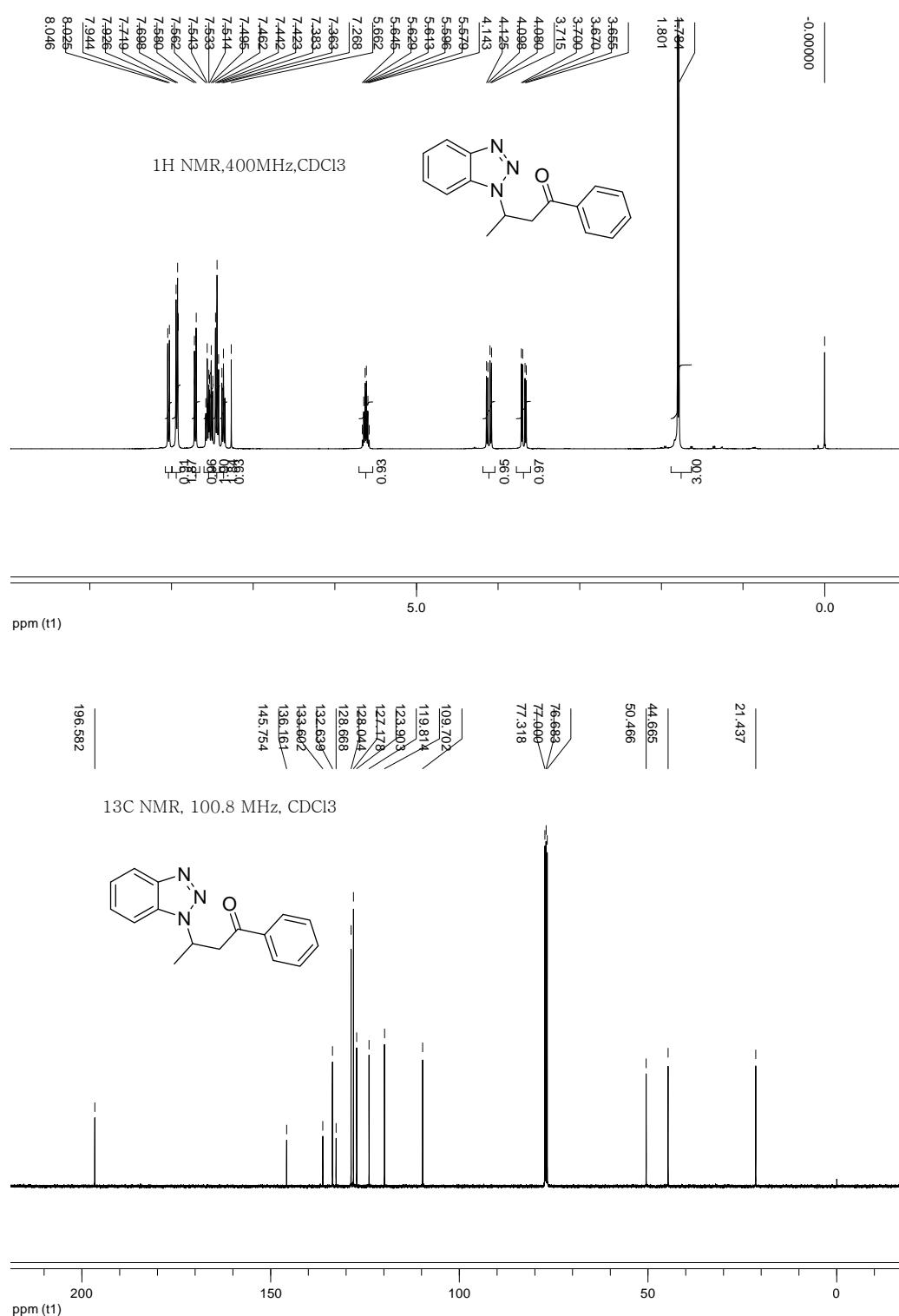
1-phenyl-3-(5-phenyl-2*H*-tetrazol-2-yl) butan-1-one



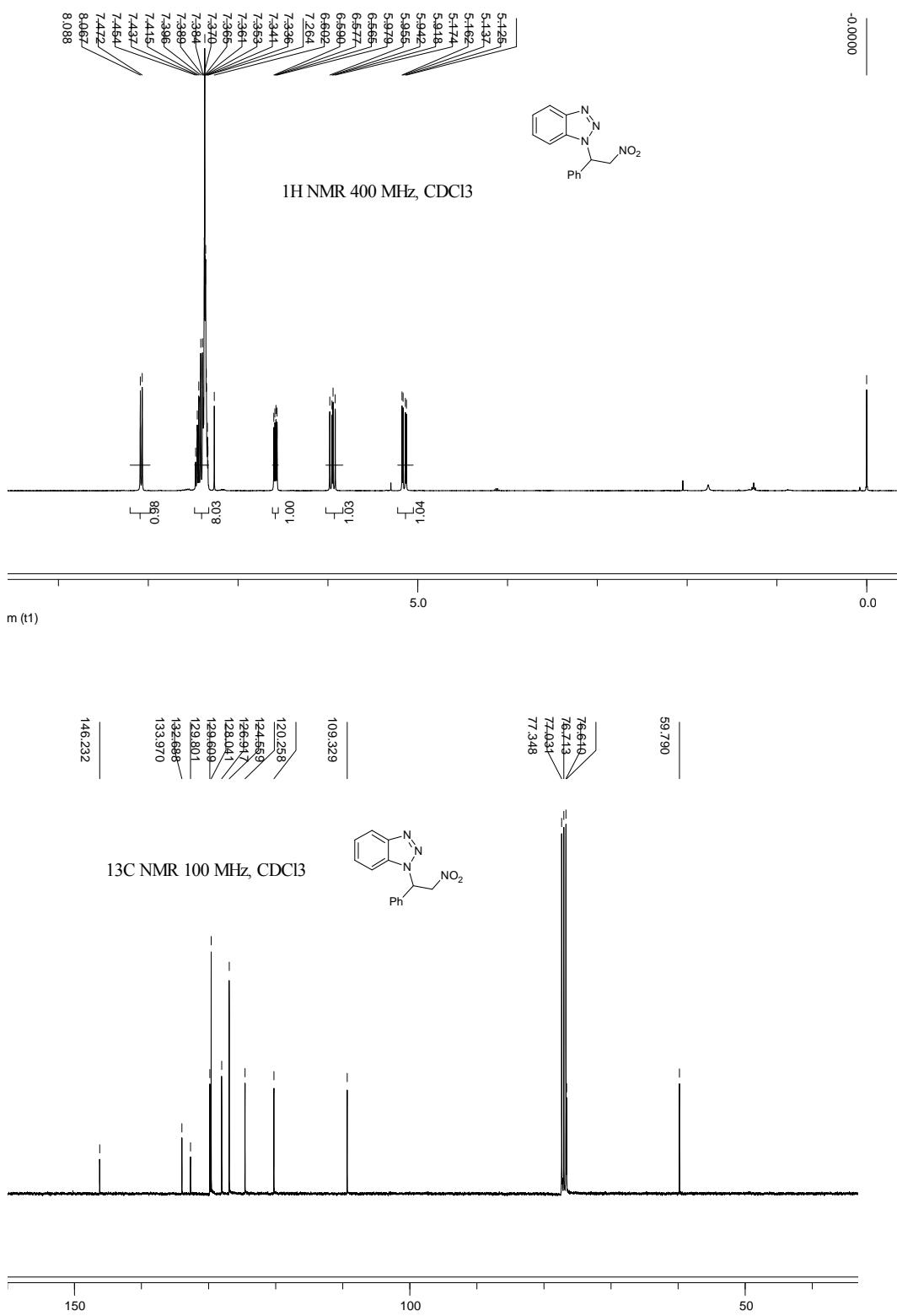
3-(1-Methyl-3-oxo-3-phenylpropyl) oxazolidin-2-one



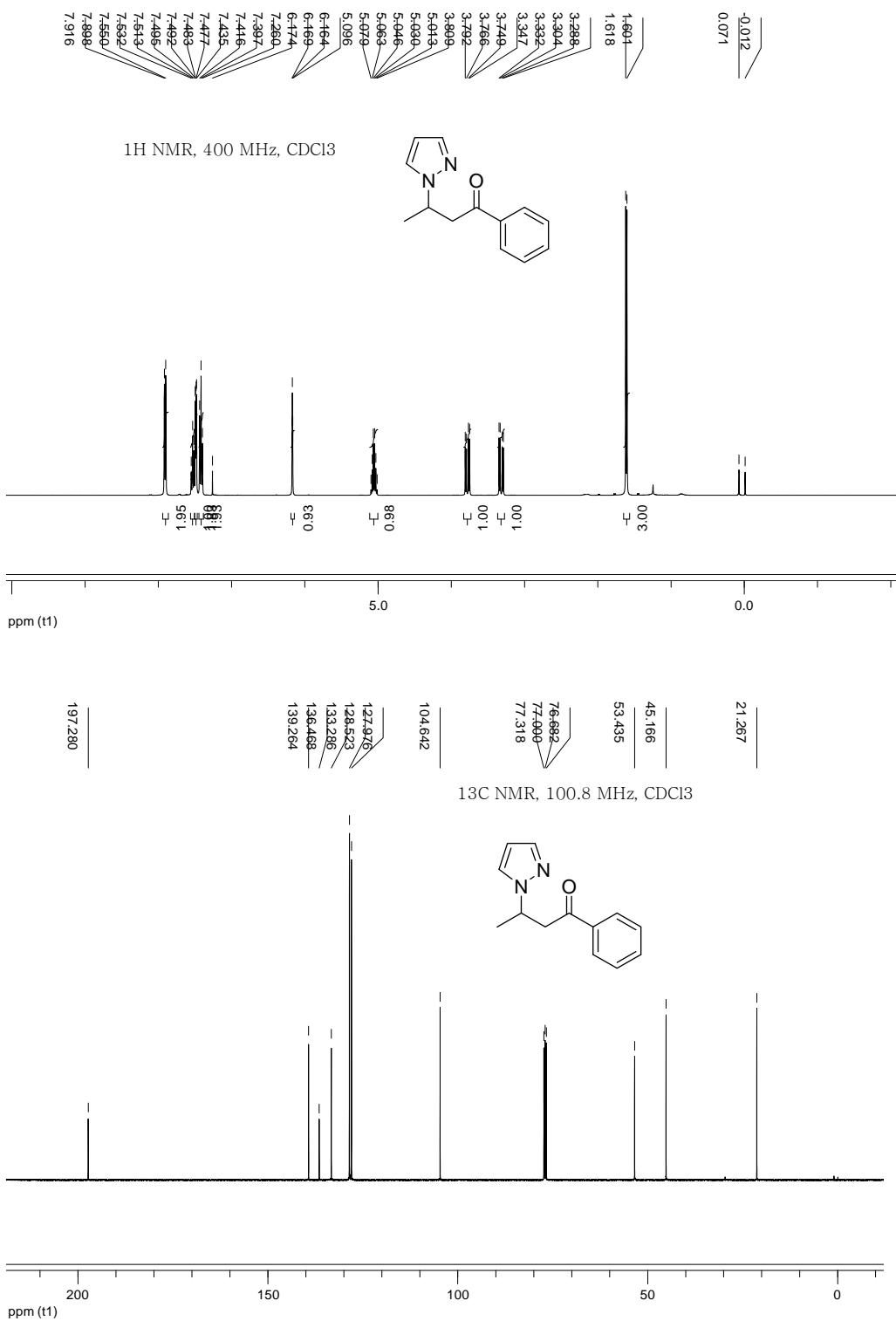
3-(1H-benzo[d][1,2,3]triazol-1-yl)-1-phenylbutan-1-one



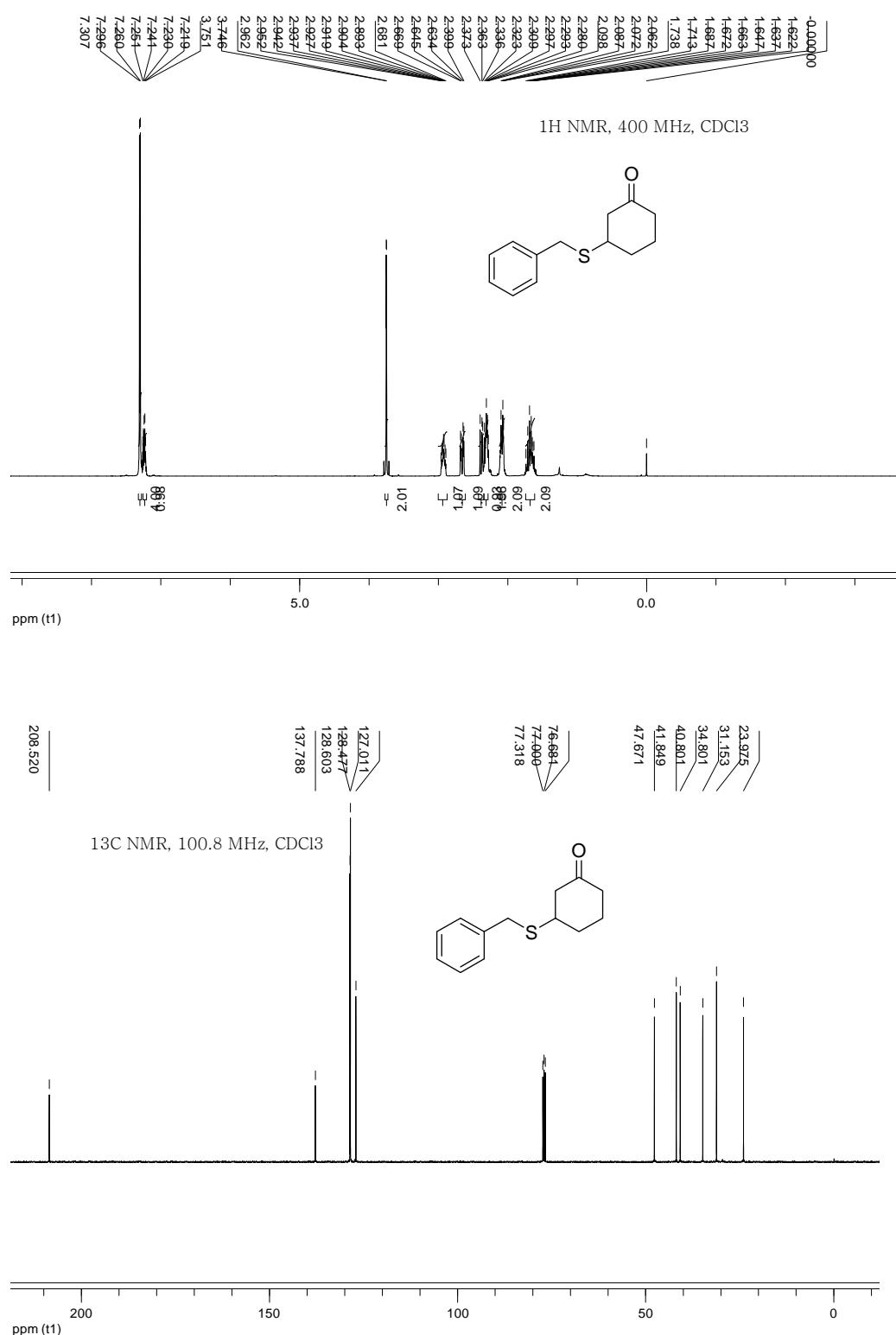
1-(2-Nitro-1-phenylethyl)-1*H*-benzo[1,2,3]triazole



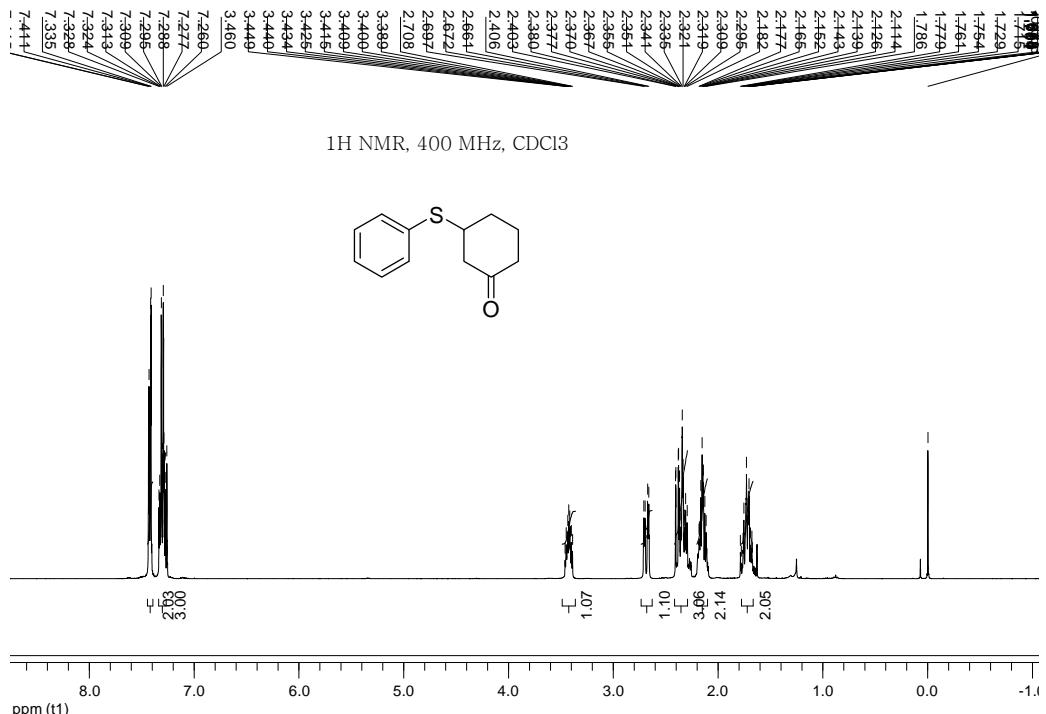
1-Phenyl-3-(1*H*-pyrazol-1-yl) butan-1-one



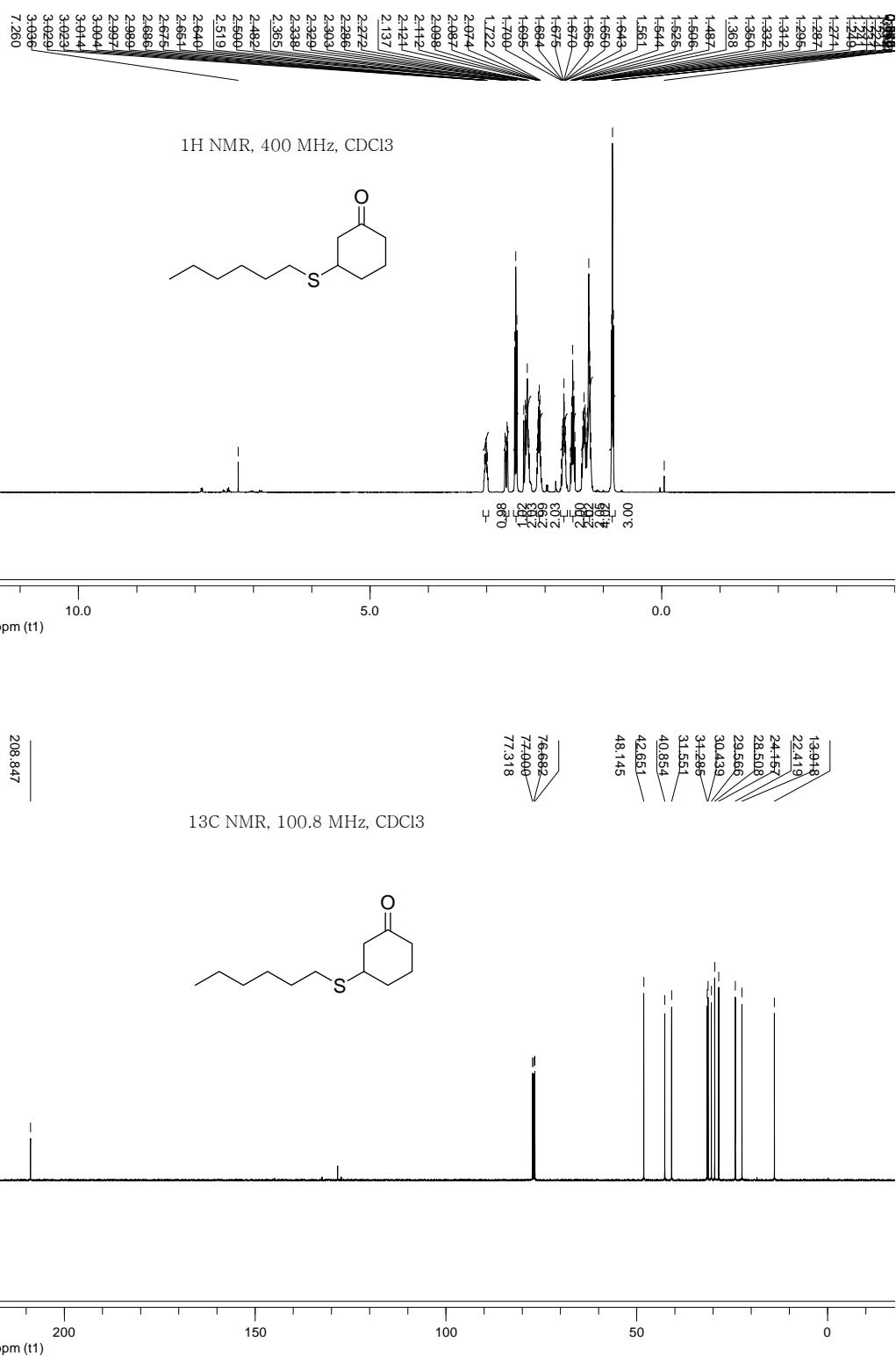
3-Benzylthio-cyclohexan-1-one



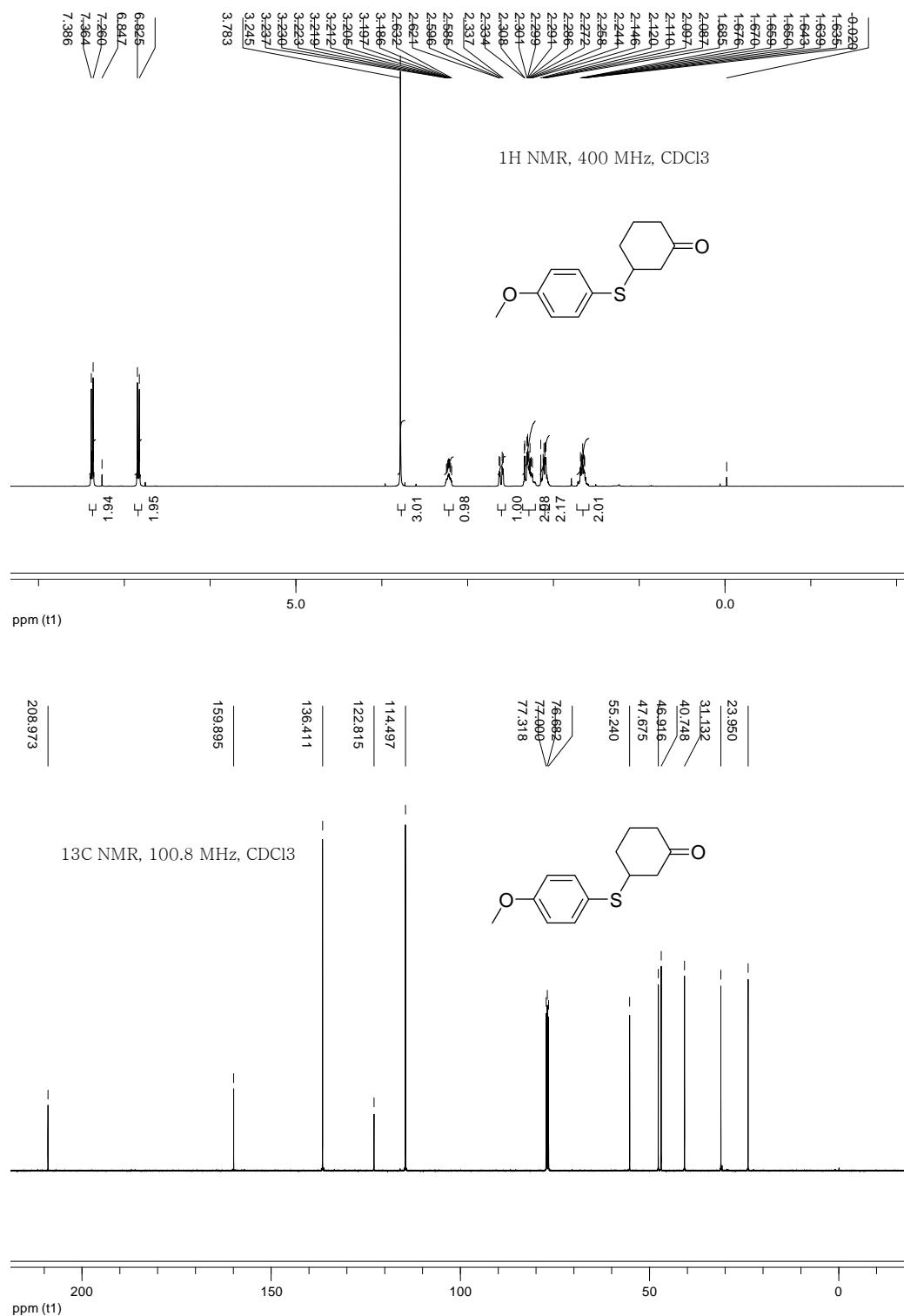
3-Phenylthiol-cyclohexan-1-one



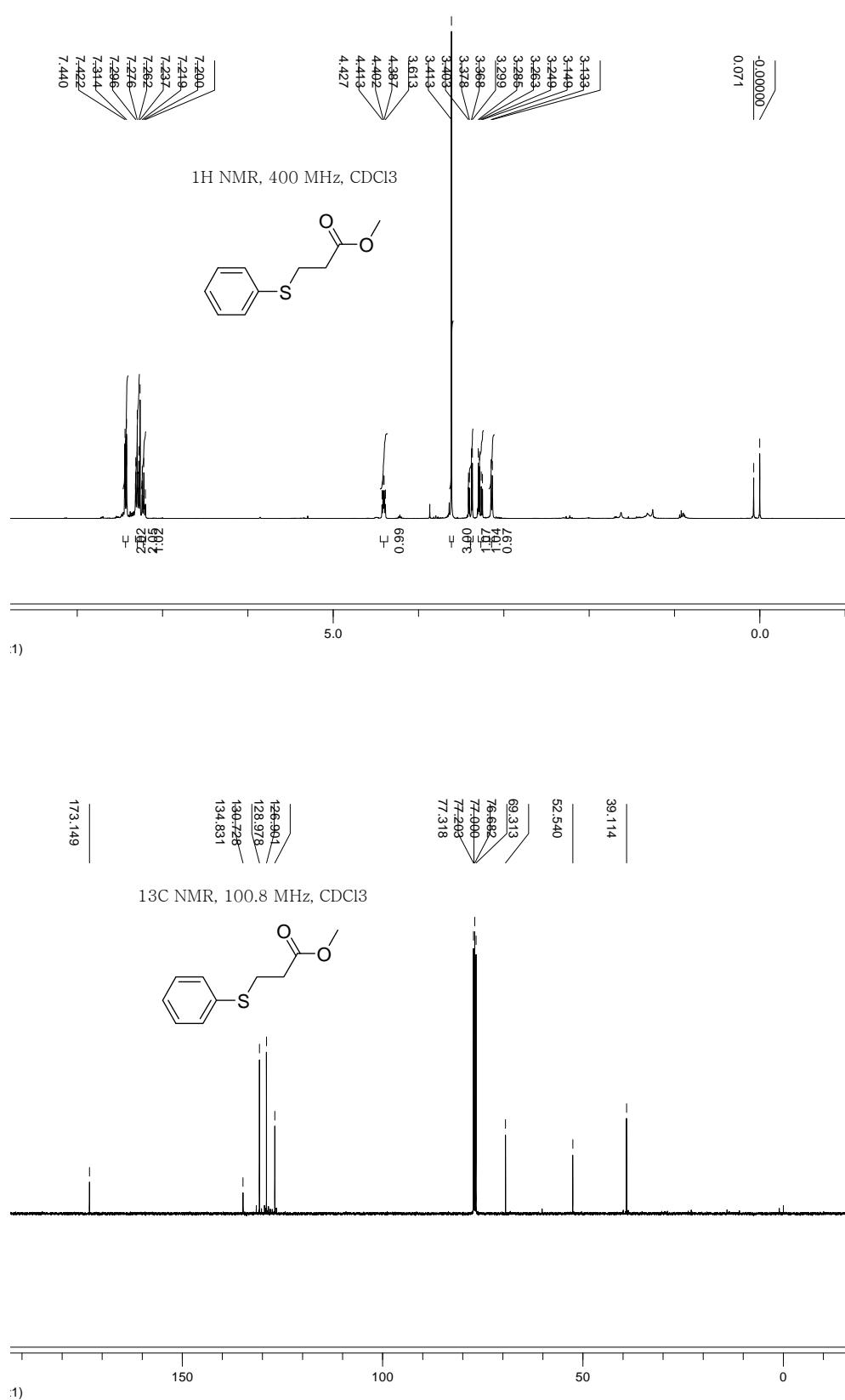
3-(Hexylsulfanyl)cyclohexanone



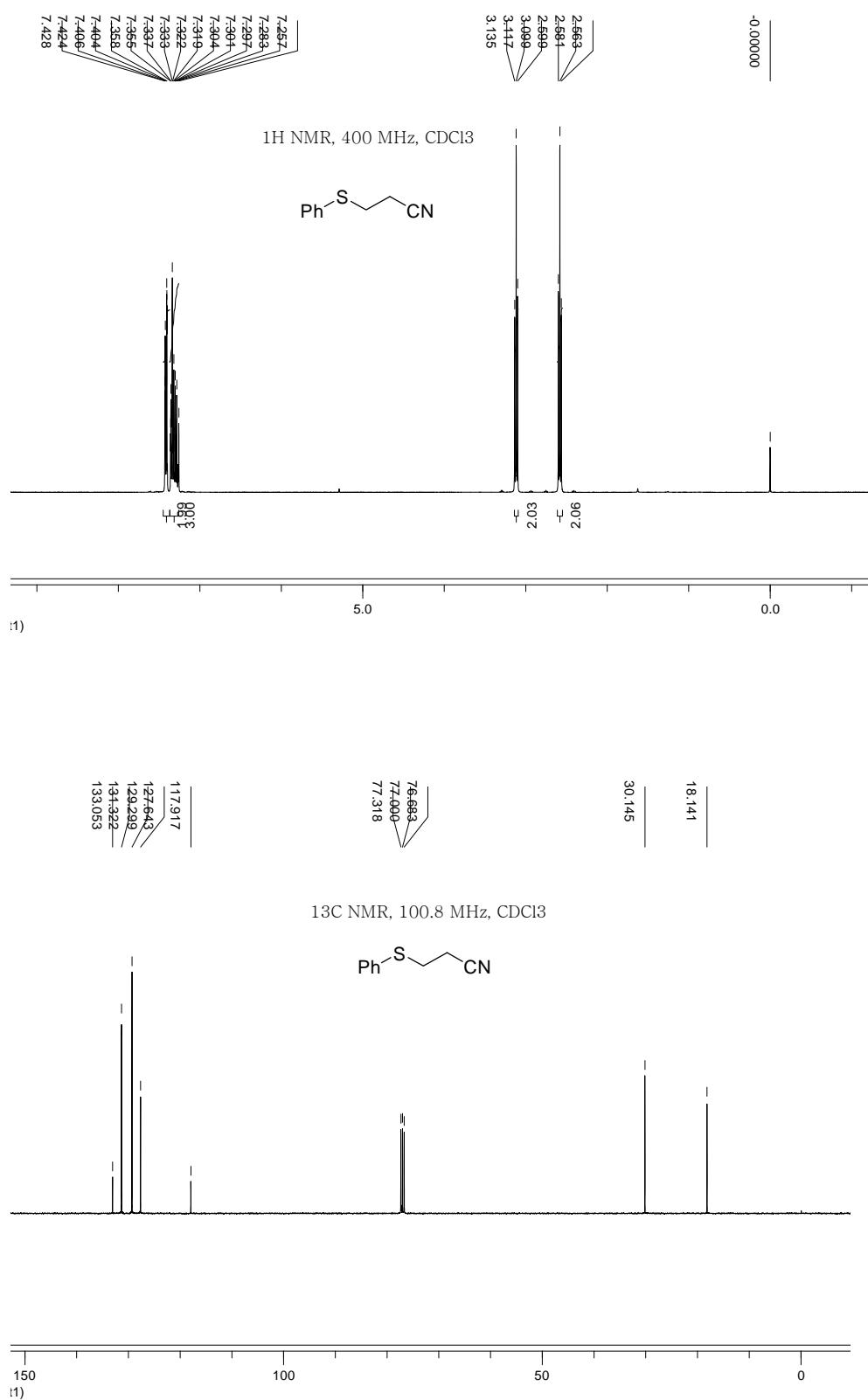
3-(4-Methoxyphenylthio)cyclohexanone



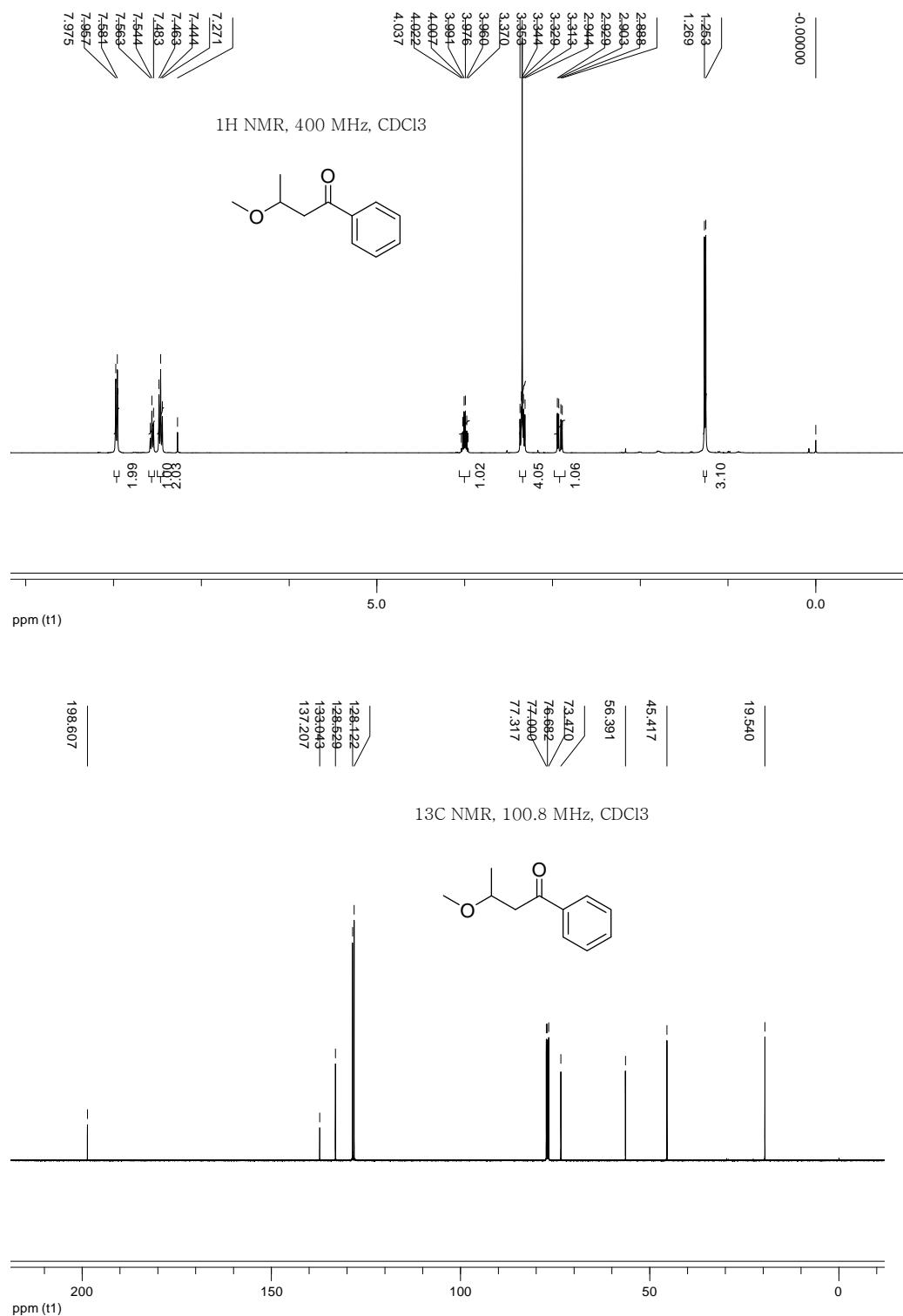
Methyl 3-(phenylthio)propanoate



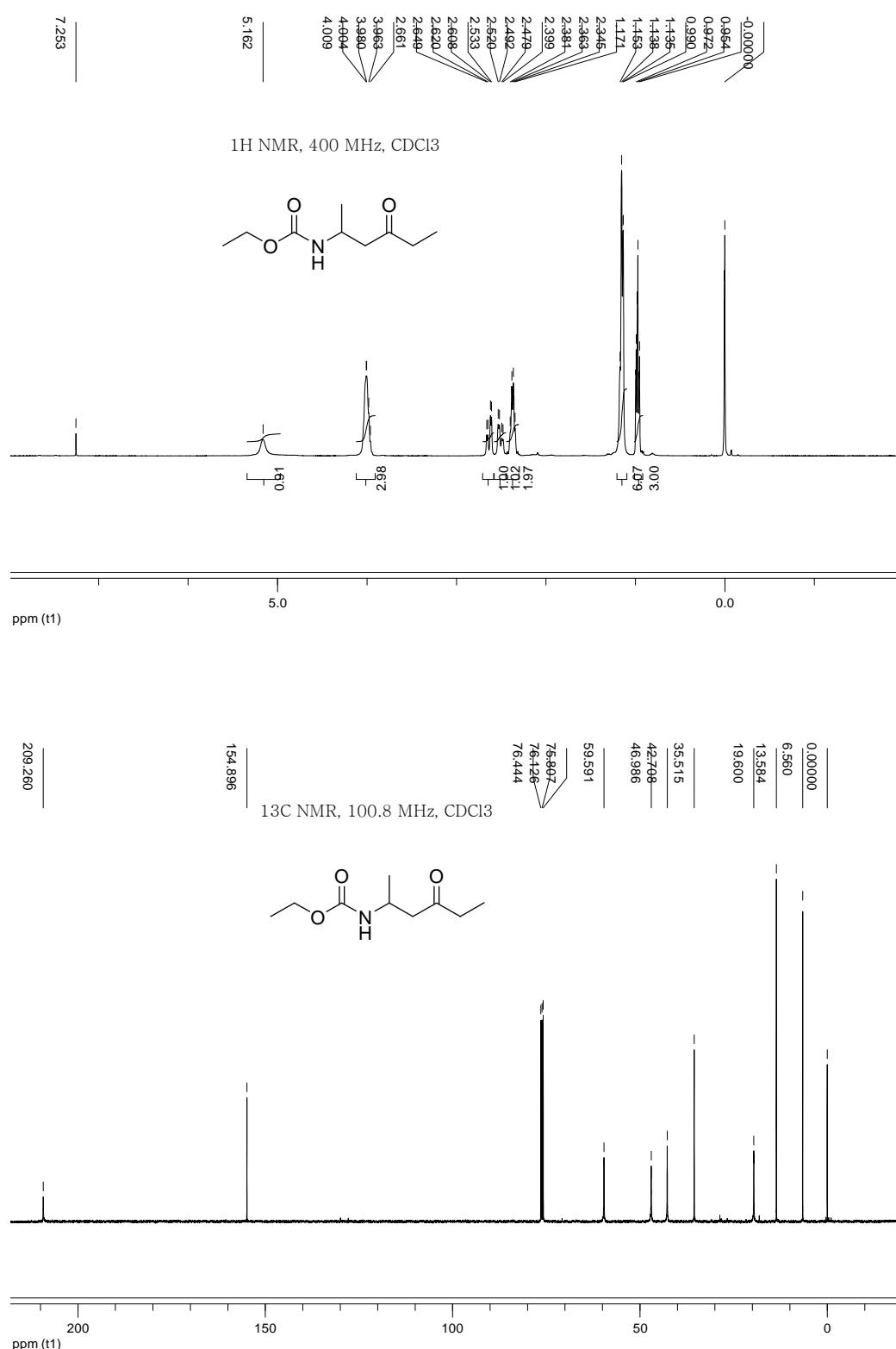
(Phenylthio)acetonitrile



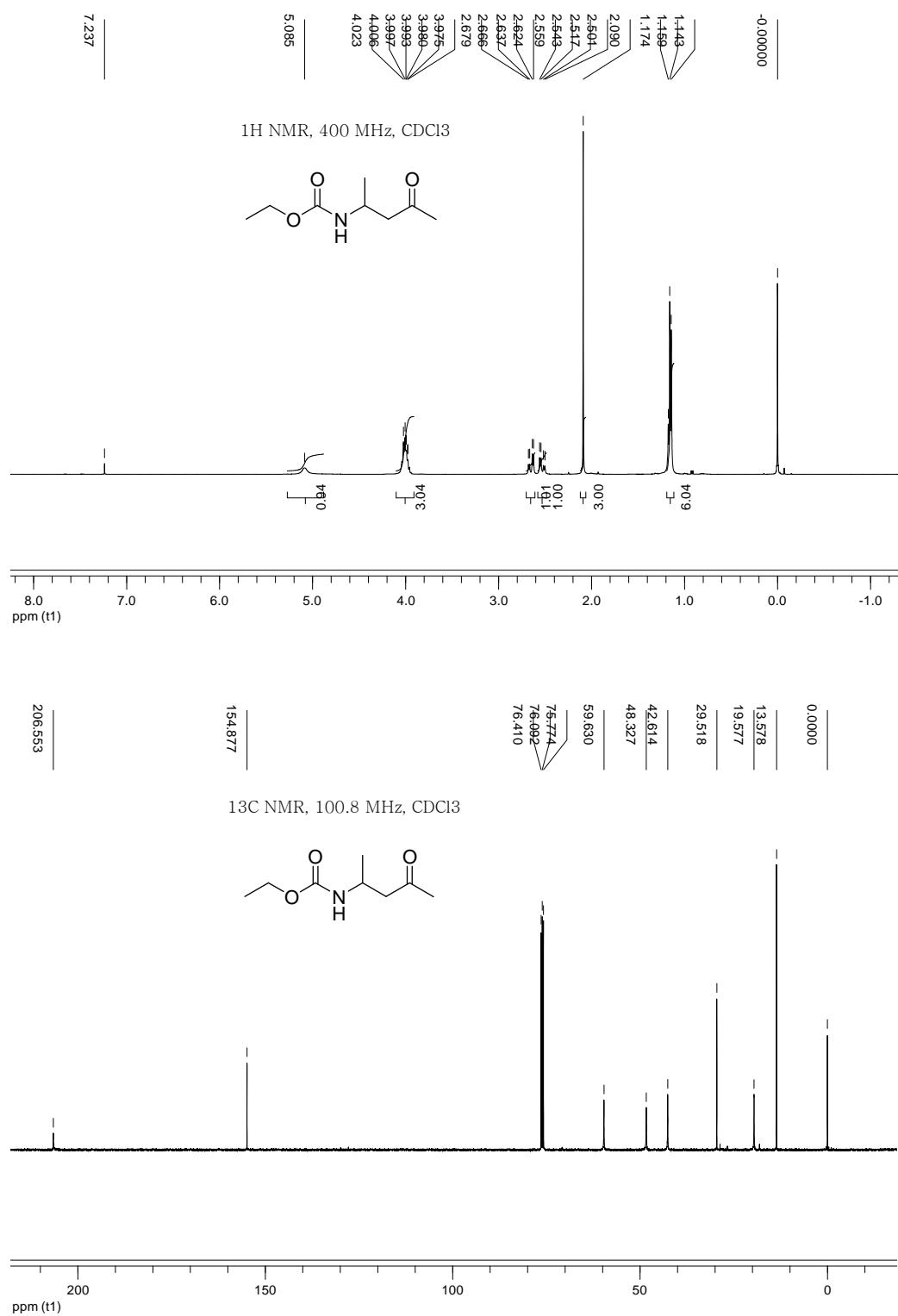
3-Methoxy-1-phenylbutan-1-one



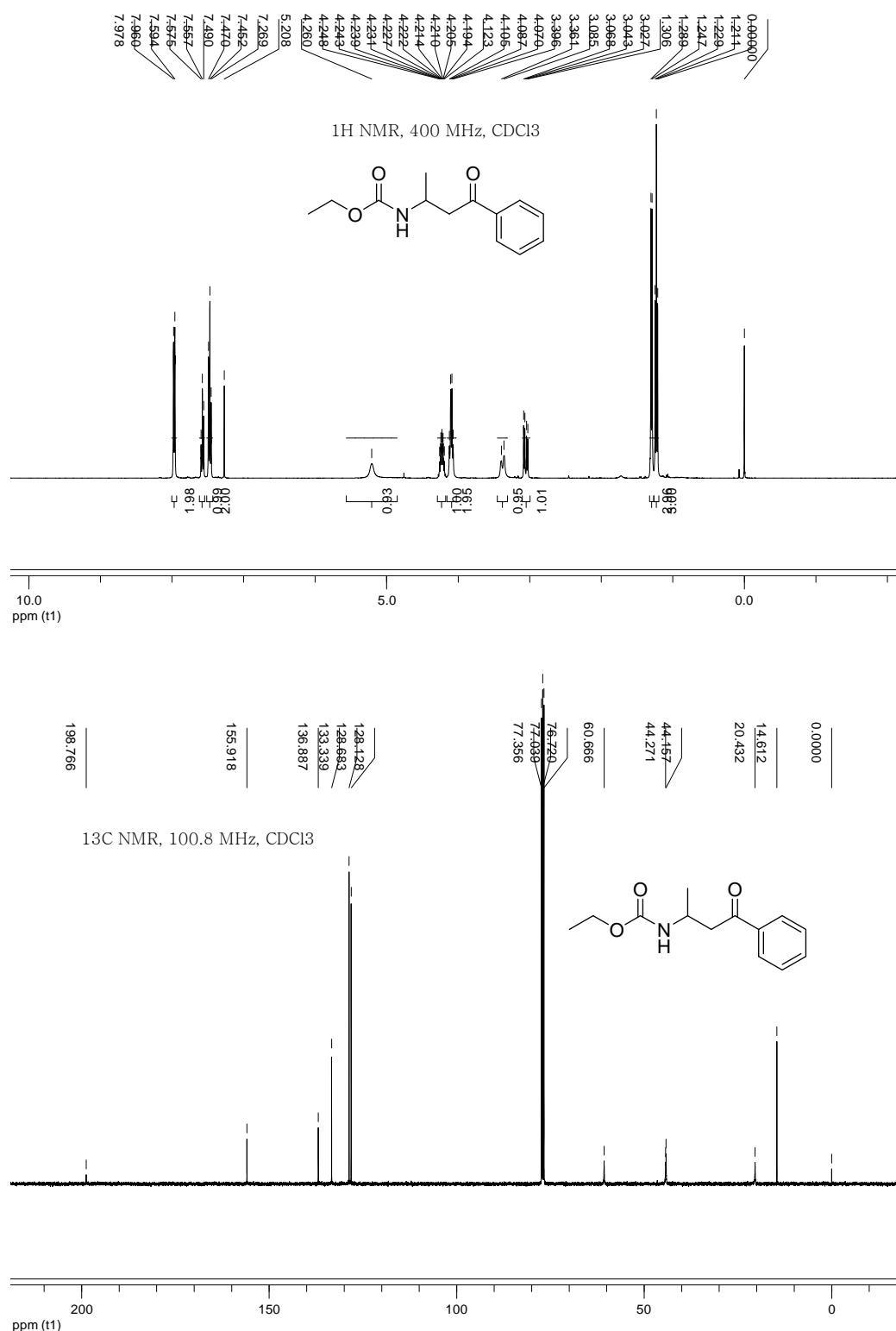
Ethyl 4-oxohexan-2-yl carbamate



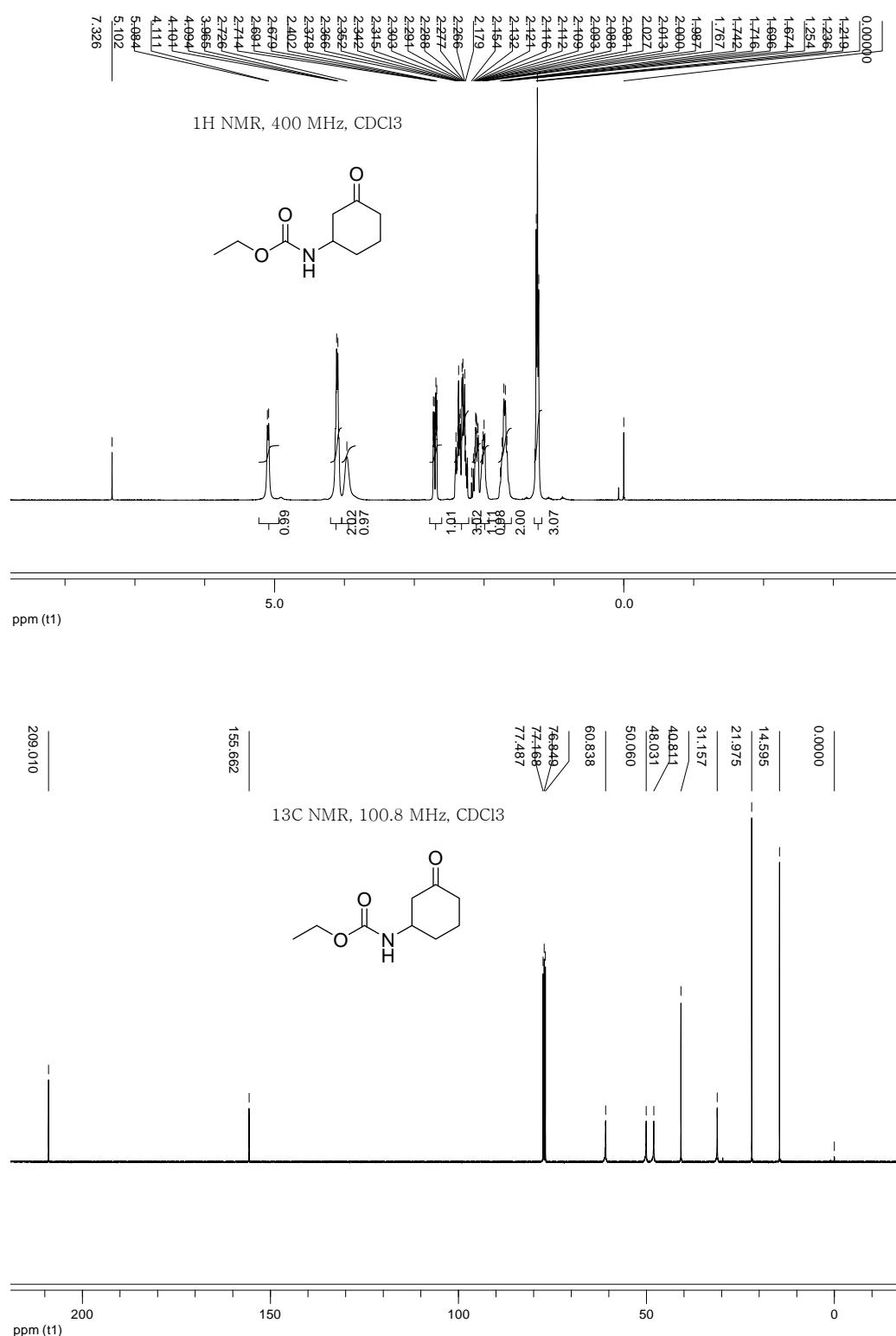
Ethyl 4-oxopentan-2-ylcarbamate



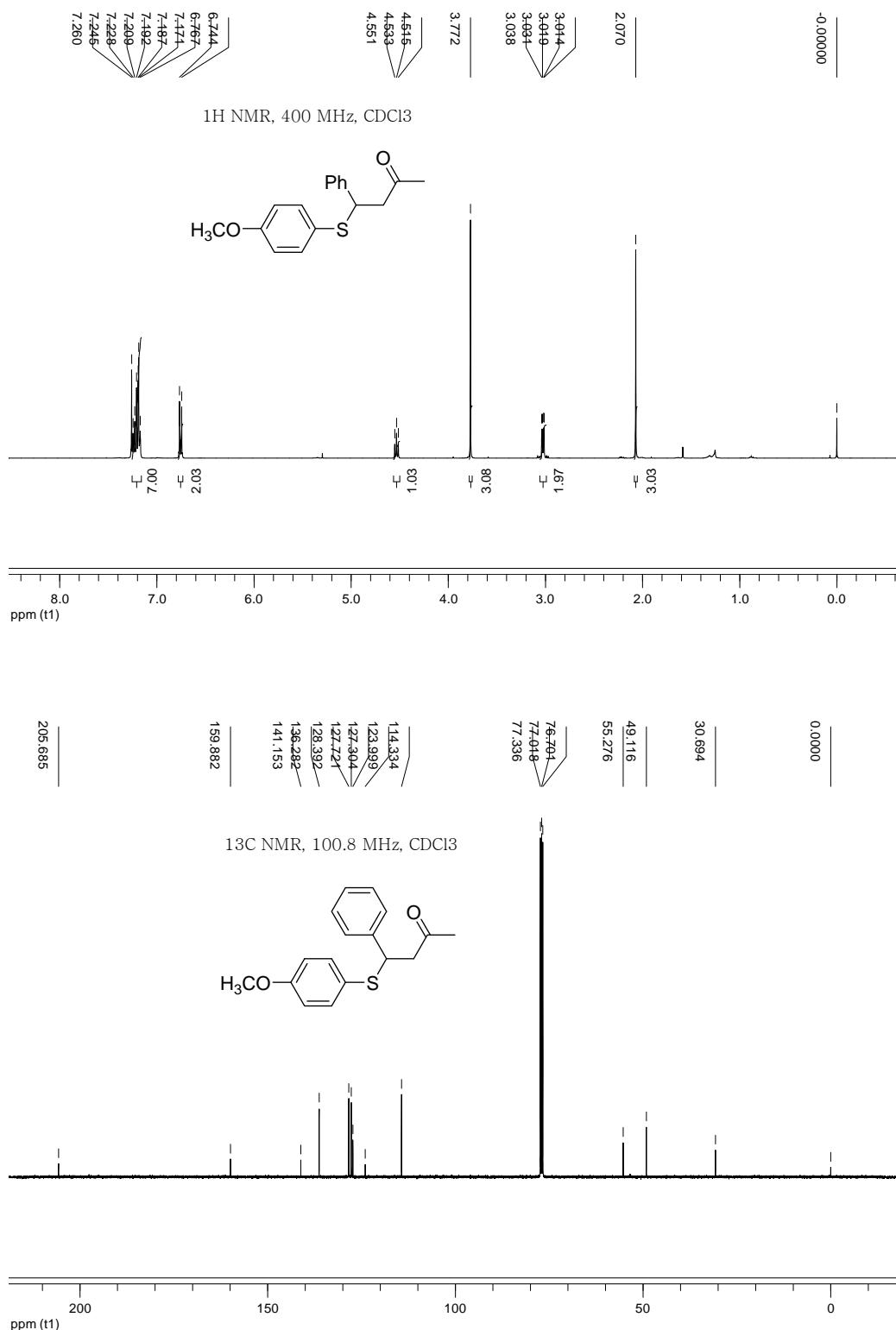
Ethyl (1-methyl-3-oxo-3-phenylpropyl)carbamate



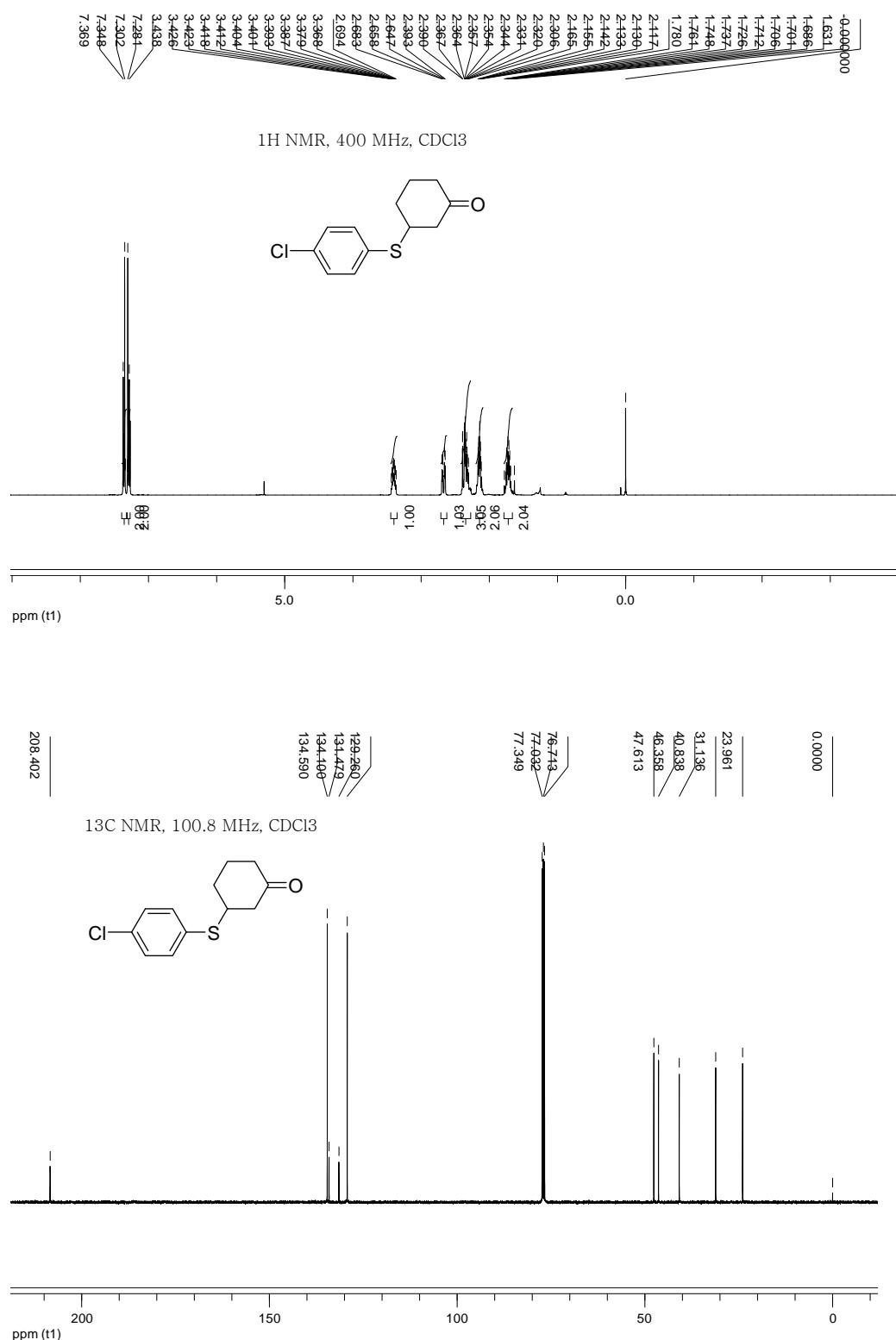
Ethyl 3-oxocyclohexylcarbamate



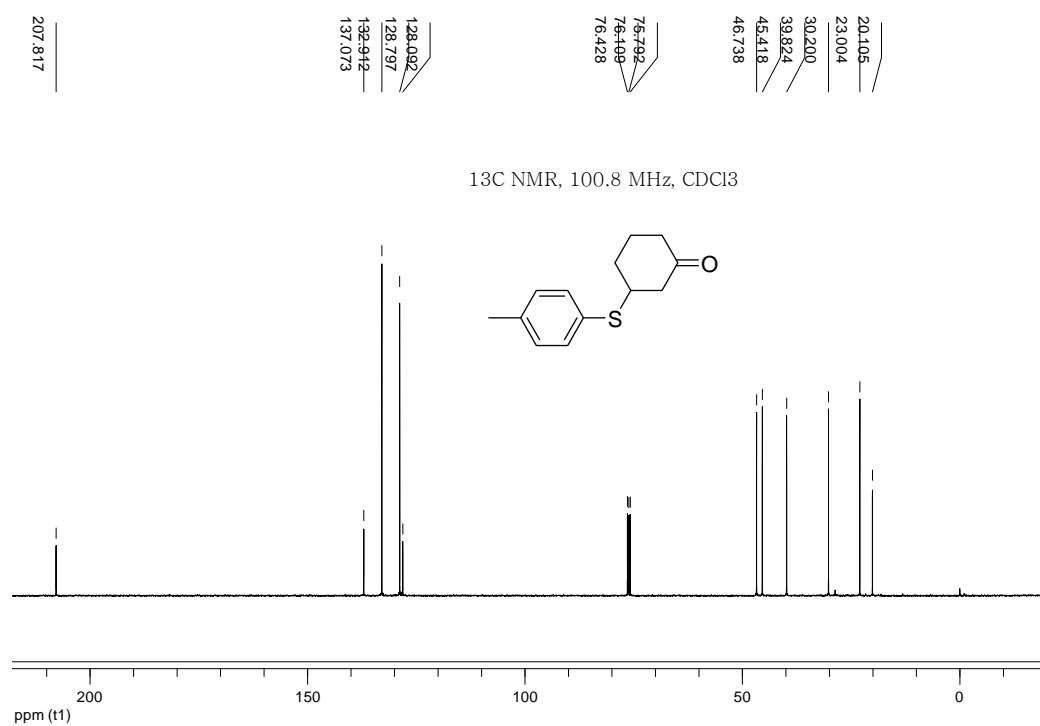
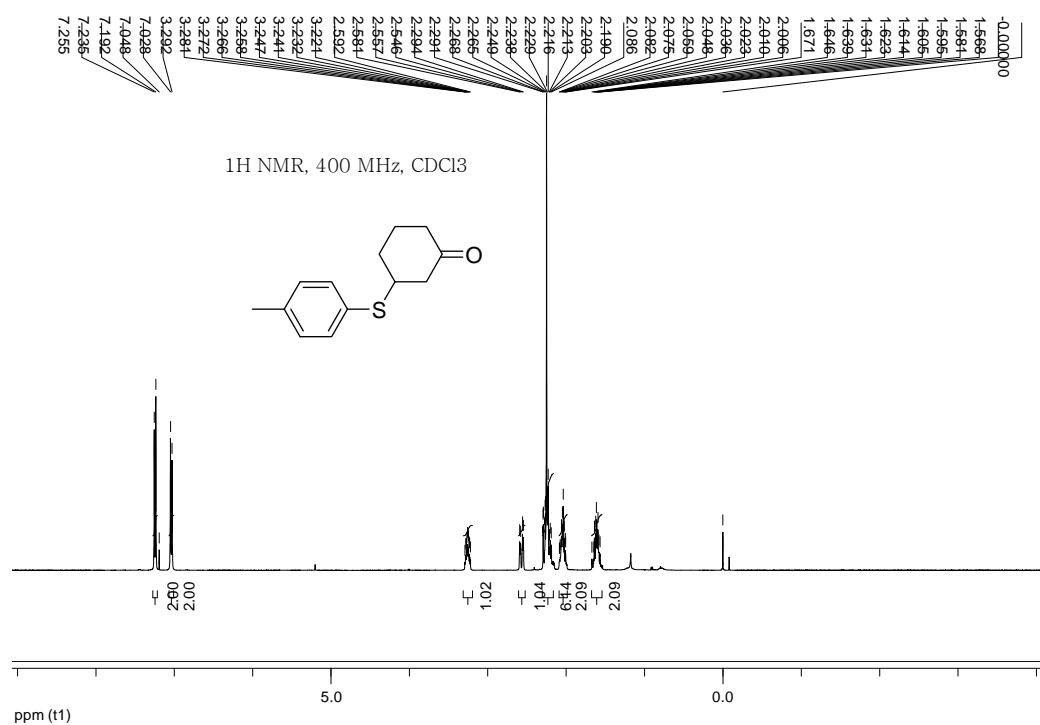
3-(4-methoxyphenylsulfanyl)-1,3-diphenylpropan-1-one



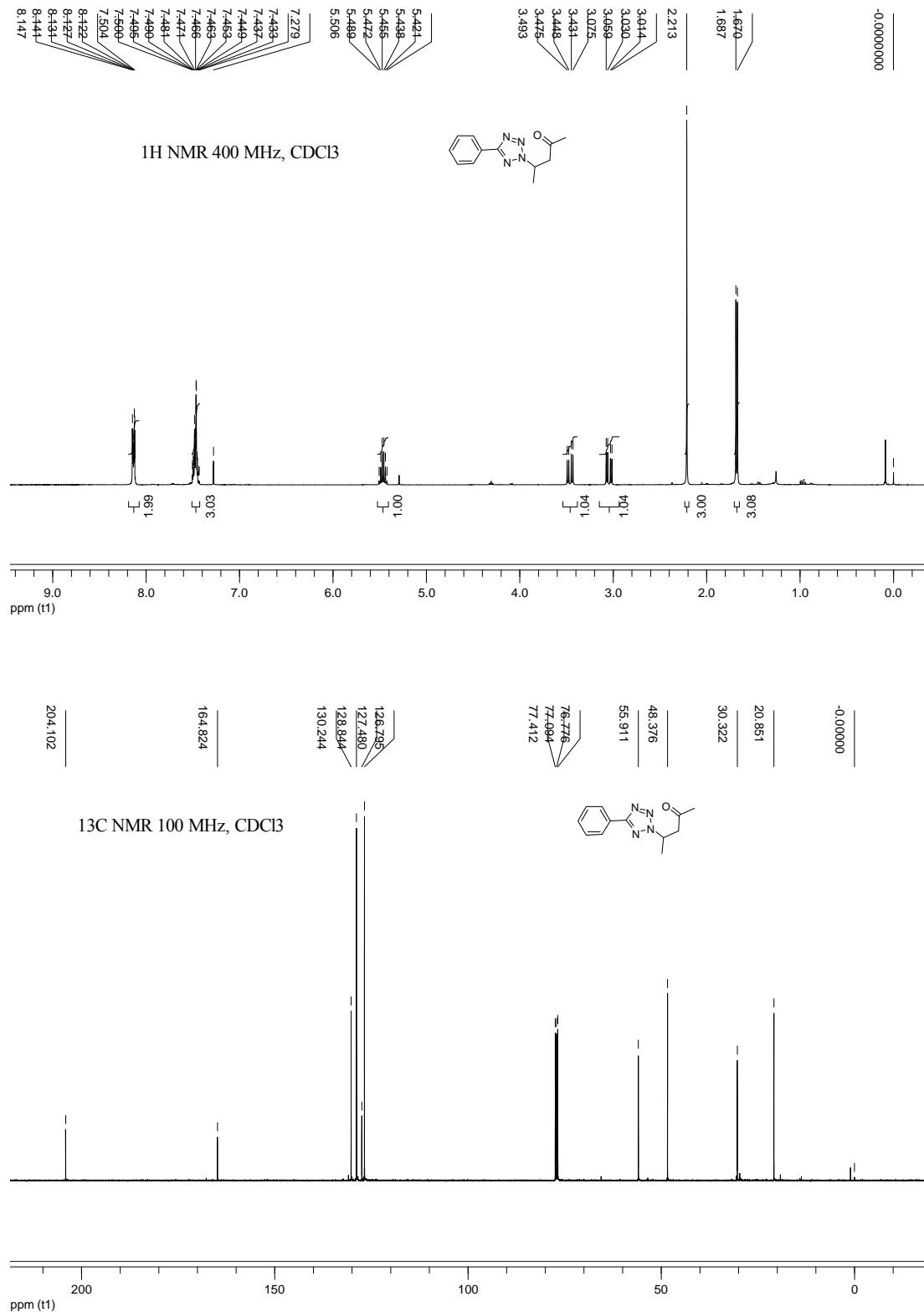
3-(4-Chlorophenylthio)cyclohexanone



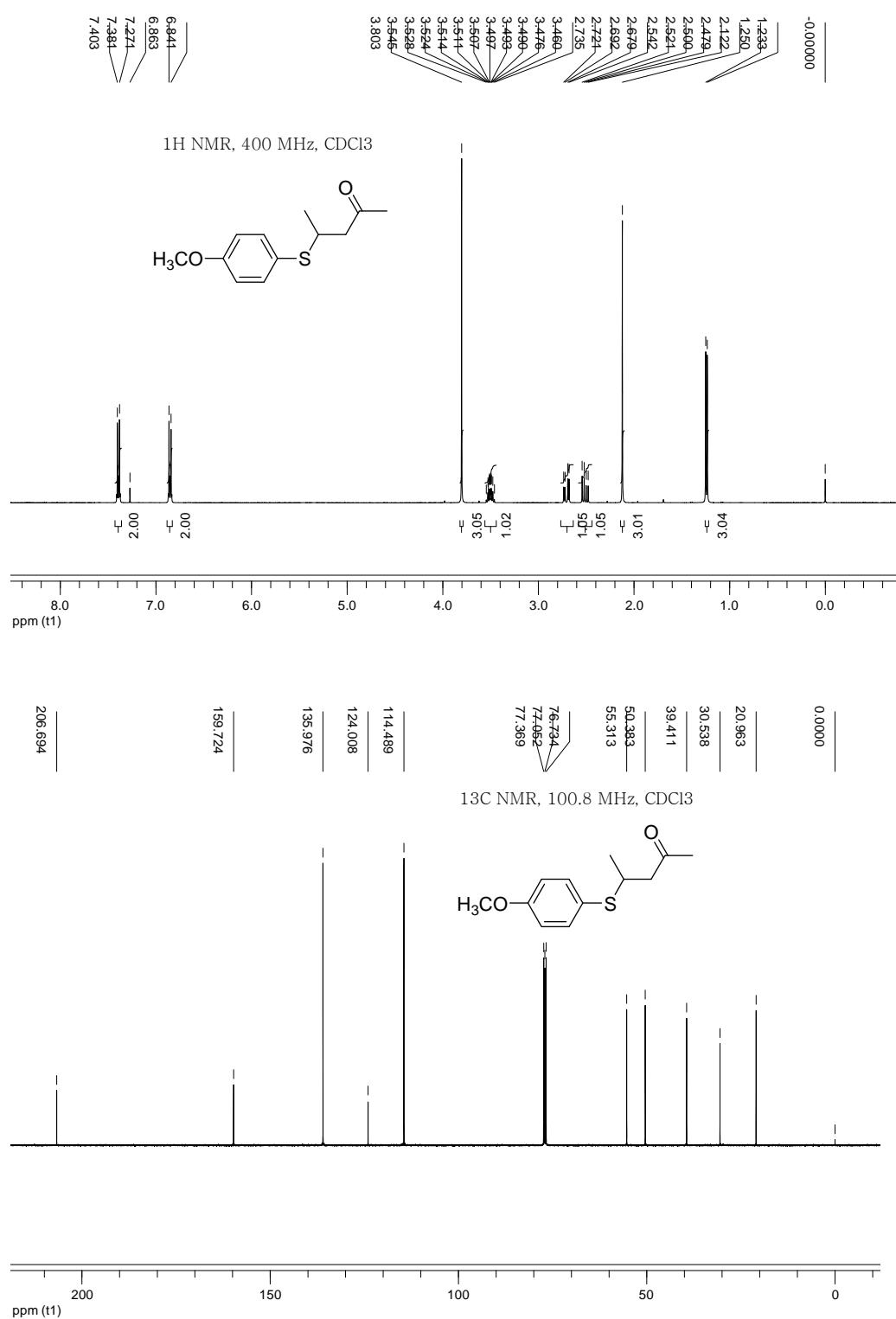
3-(4-Methylphenylthio) cyclohexan-1-one



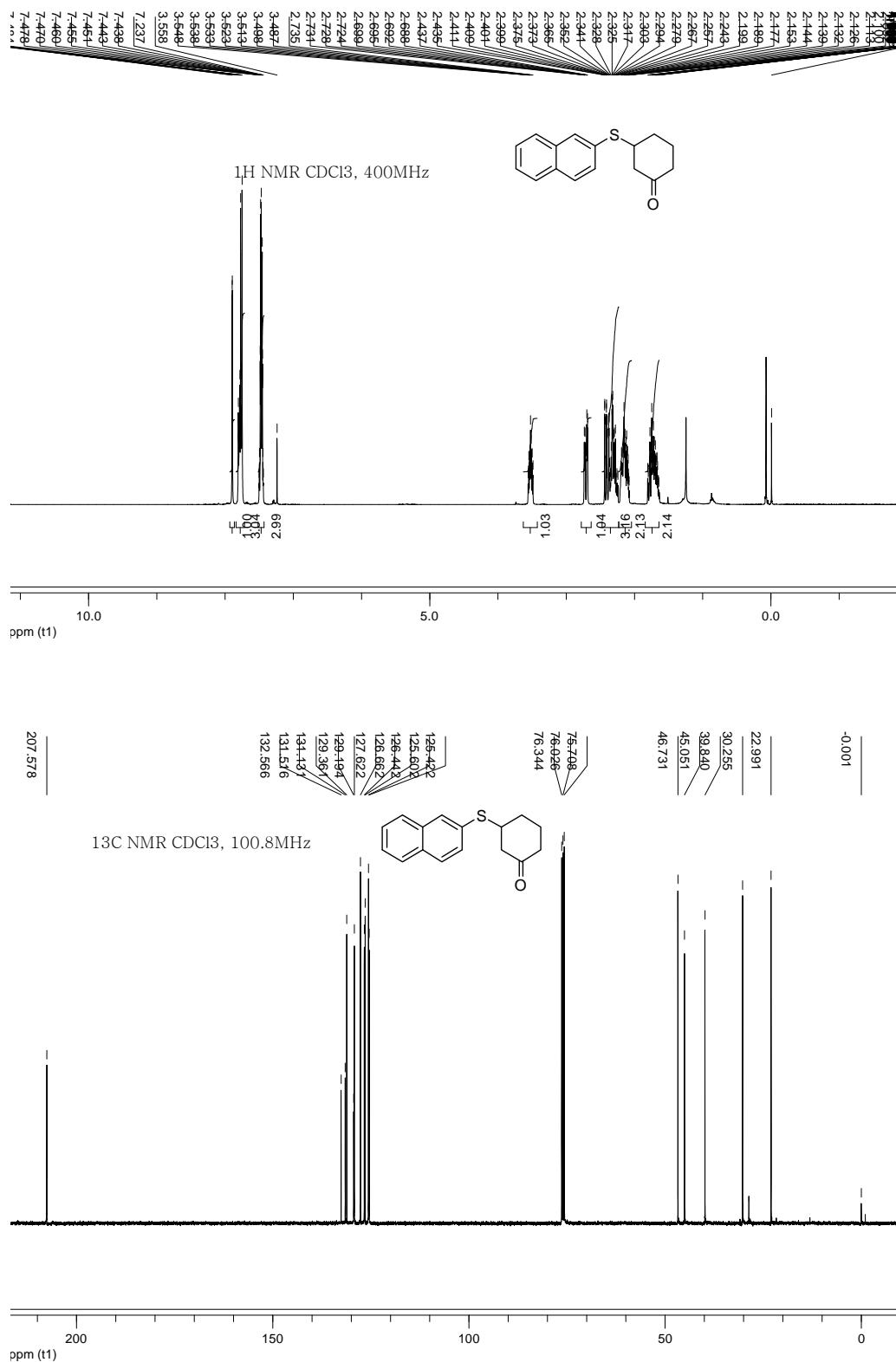
4-(5-phenyl-2*H*-tetrazol-2-yl) pentan-2-one



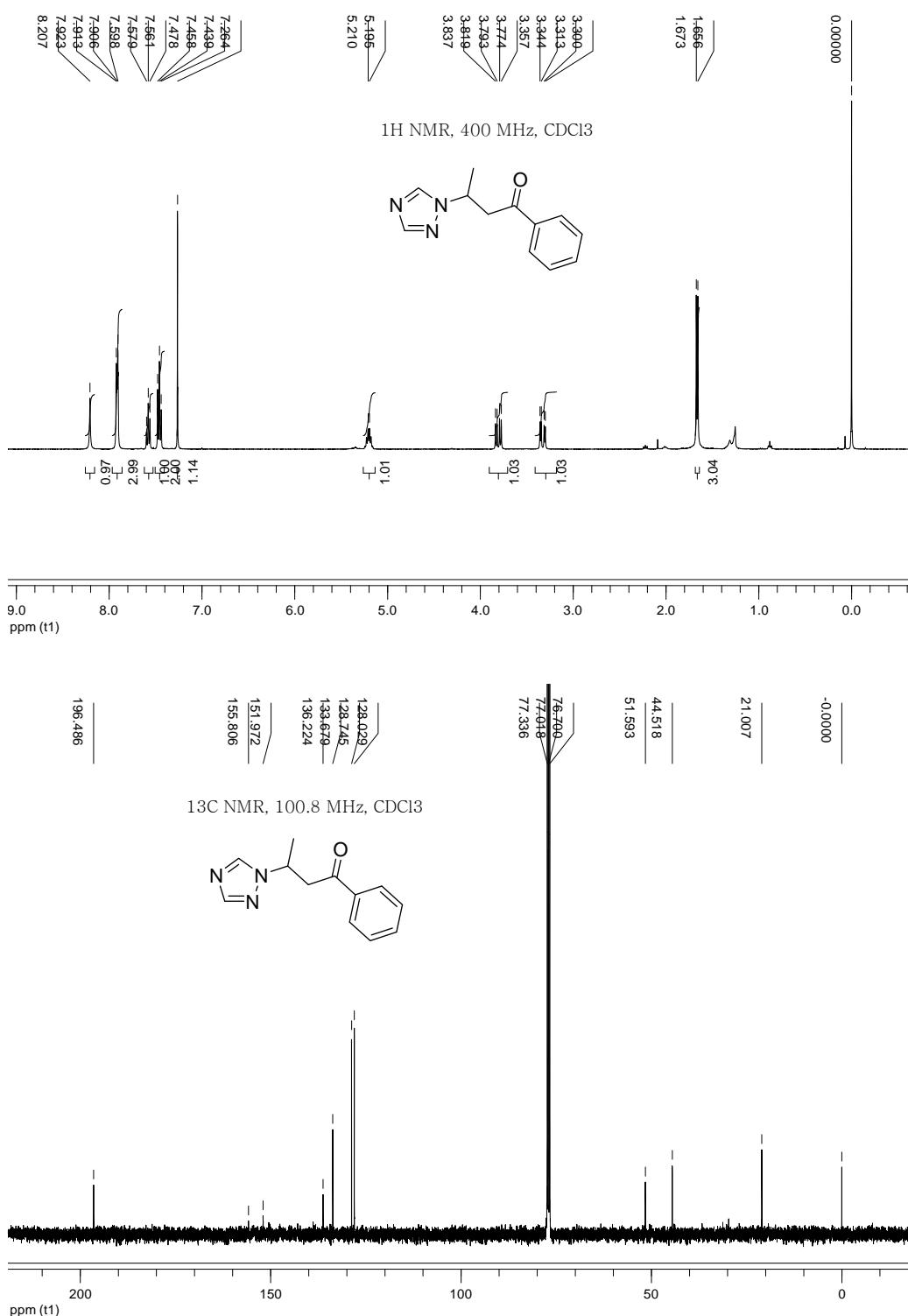
4-(4-Methoxyphenylthio) pentan-2-one



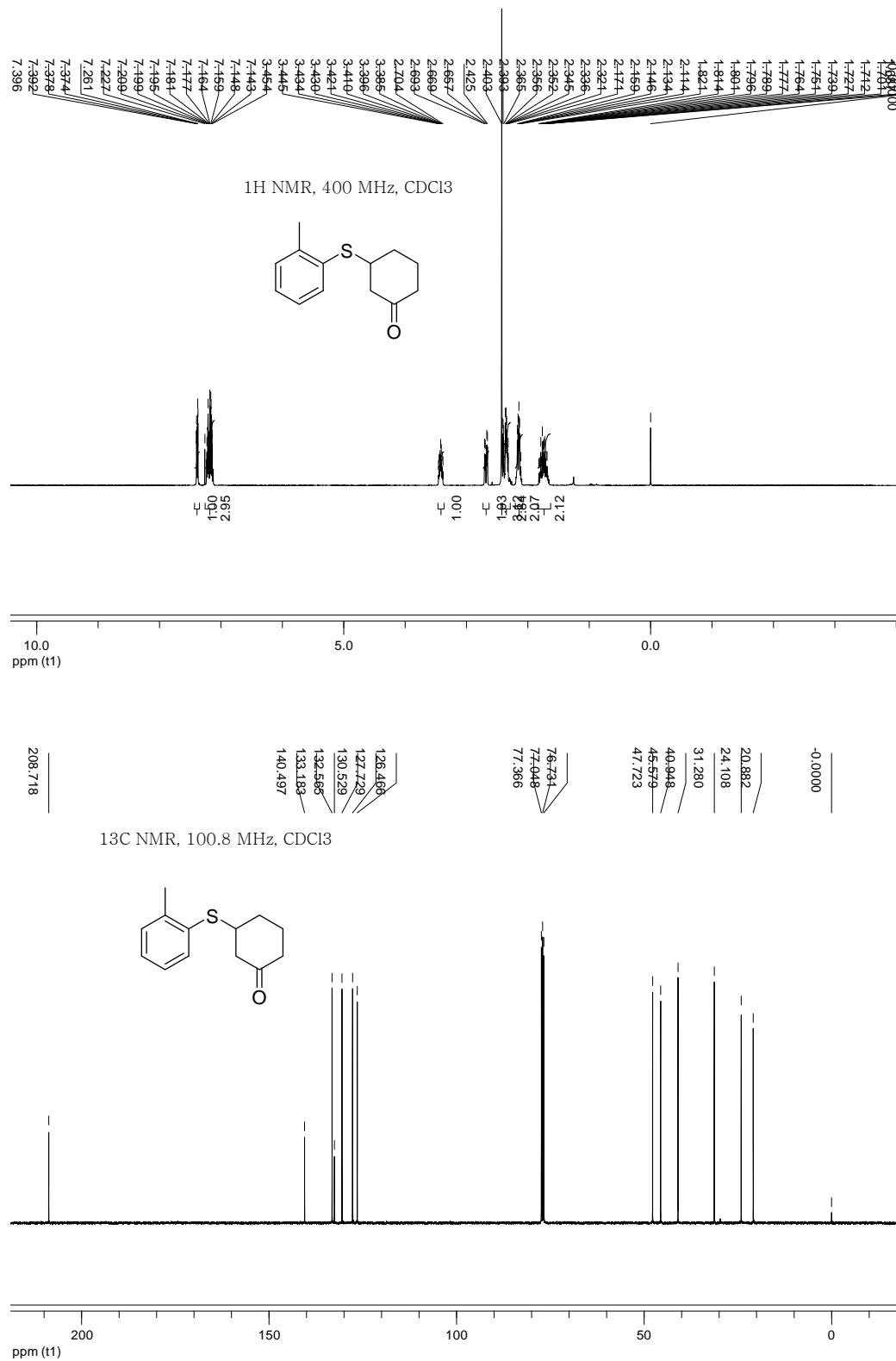
3-(naphthalen-2-ylthio)cyclohexanone



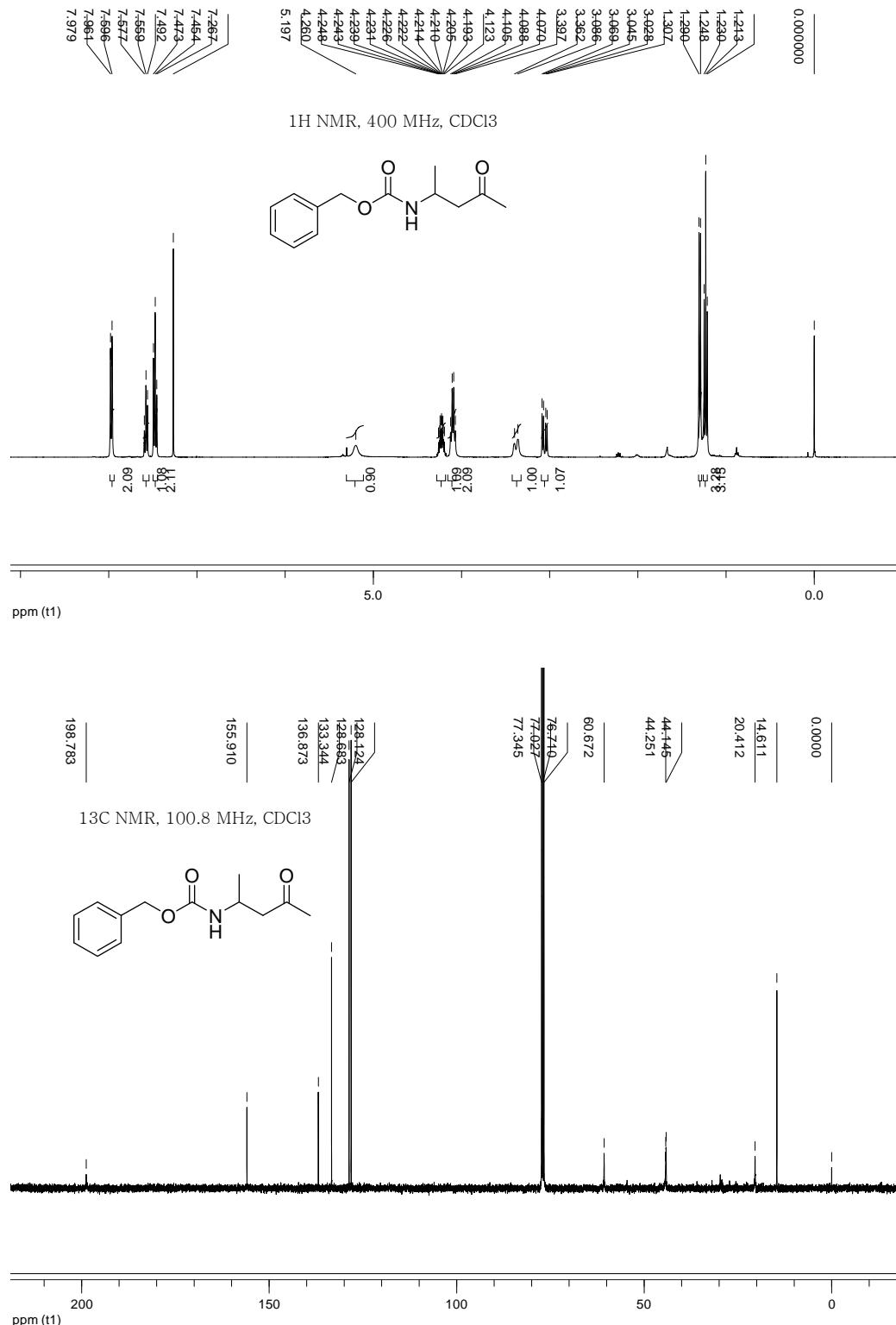
1-Phenyl-3-(1*H*-1,2,4-triazol-1-yl)butan-1-one



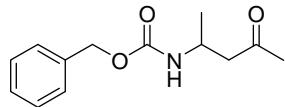
3-(*o*-Tolylthio)cyclohexanone



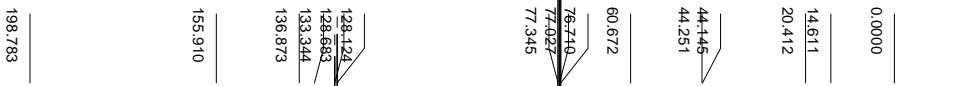
Benzyl 4-oxopentan-2-ylcarbamate



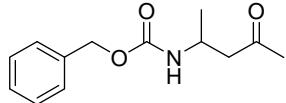
1H NMR, 400 MHz, CDCl₃



ppm (t1)

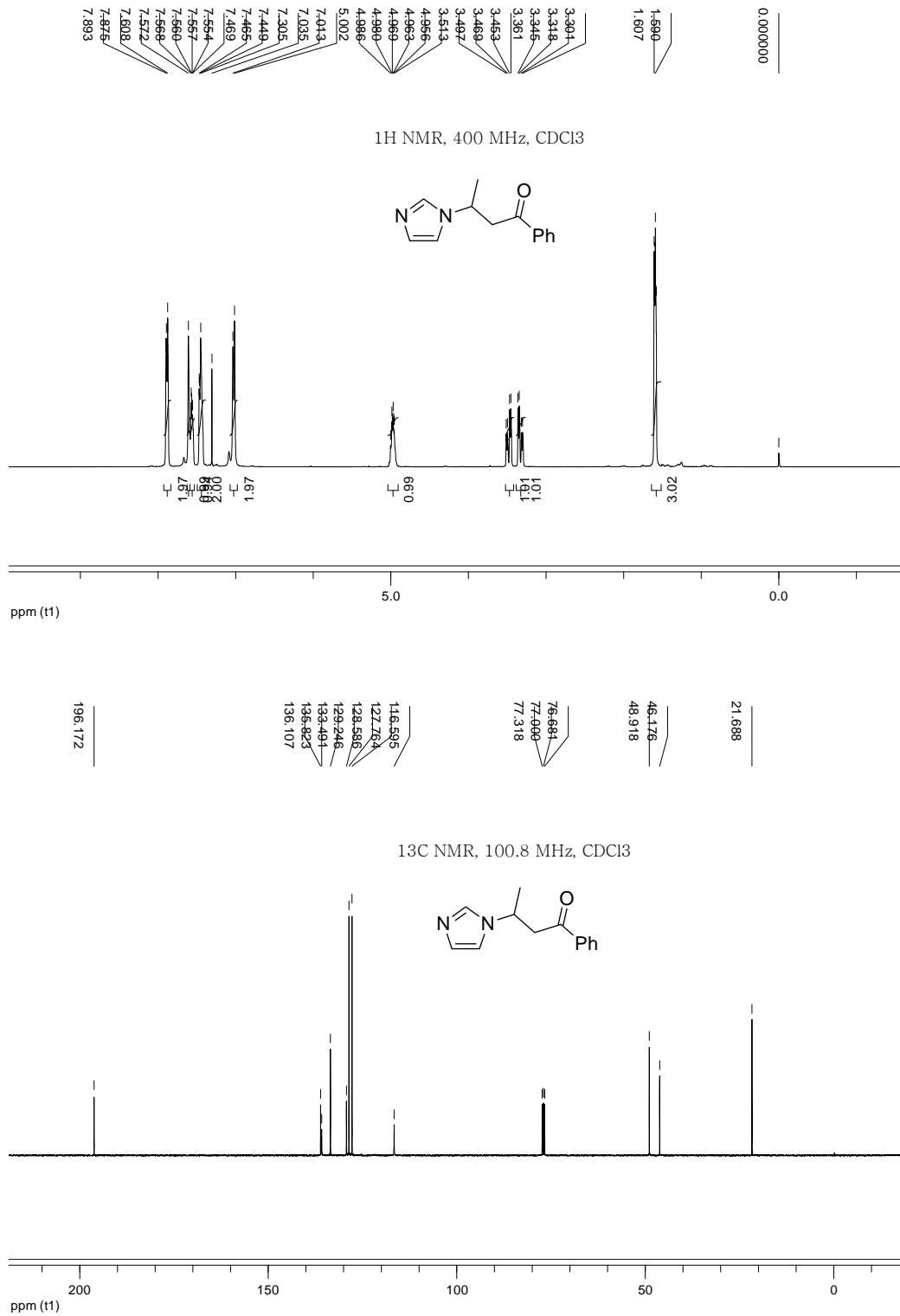


13C NMR, 100.8 MHz, CDCl₃

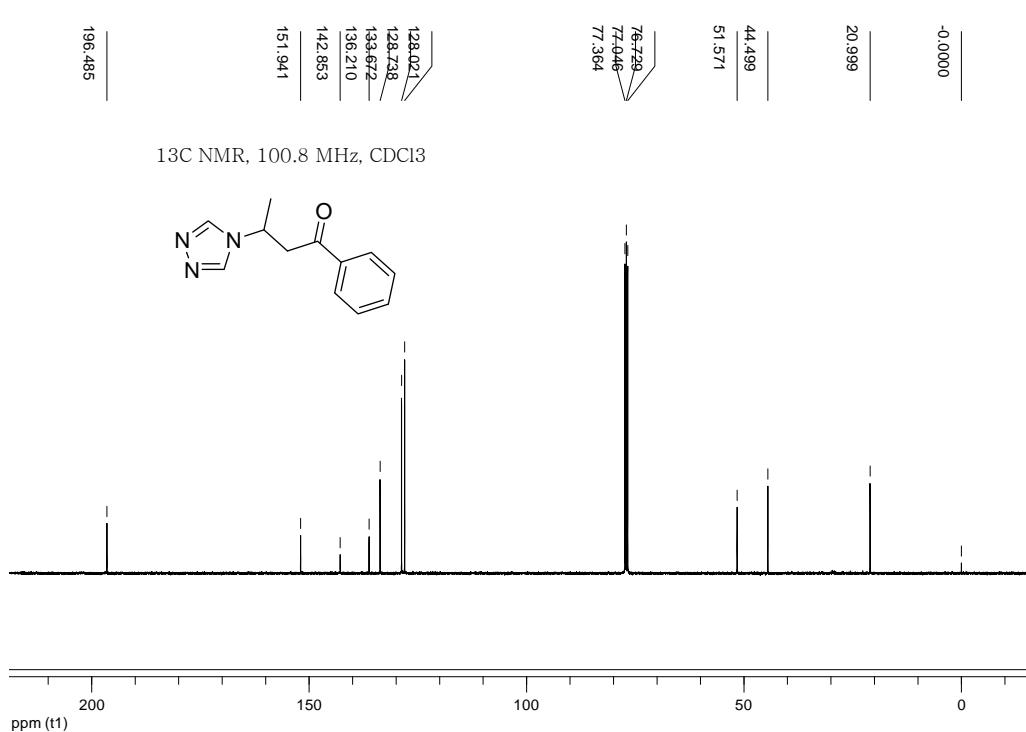
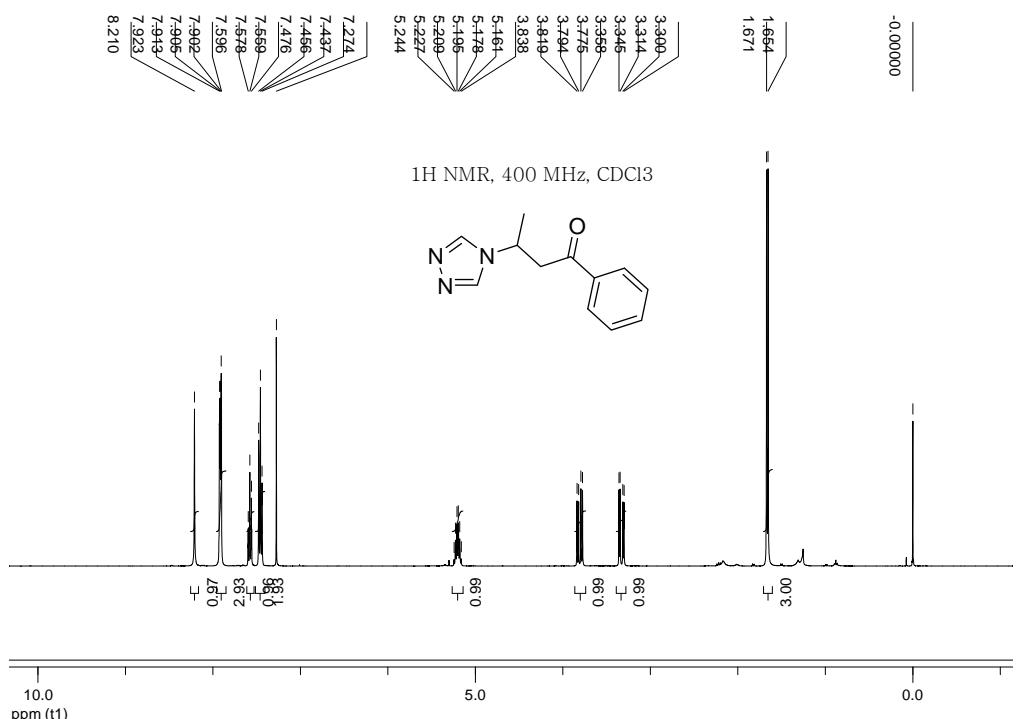


ppm (t1)

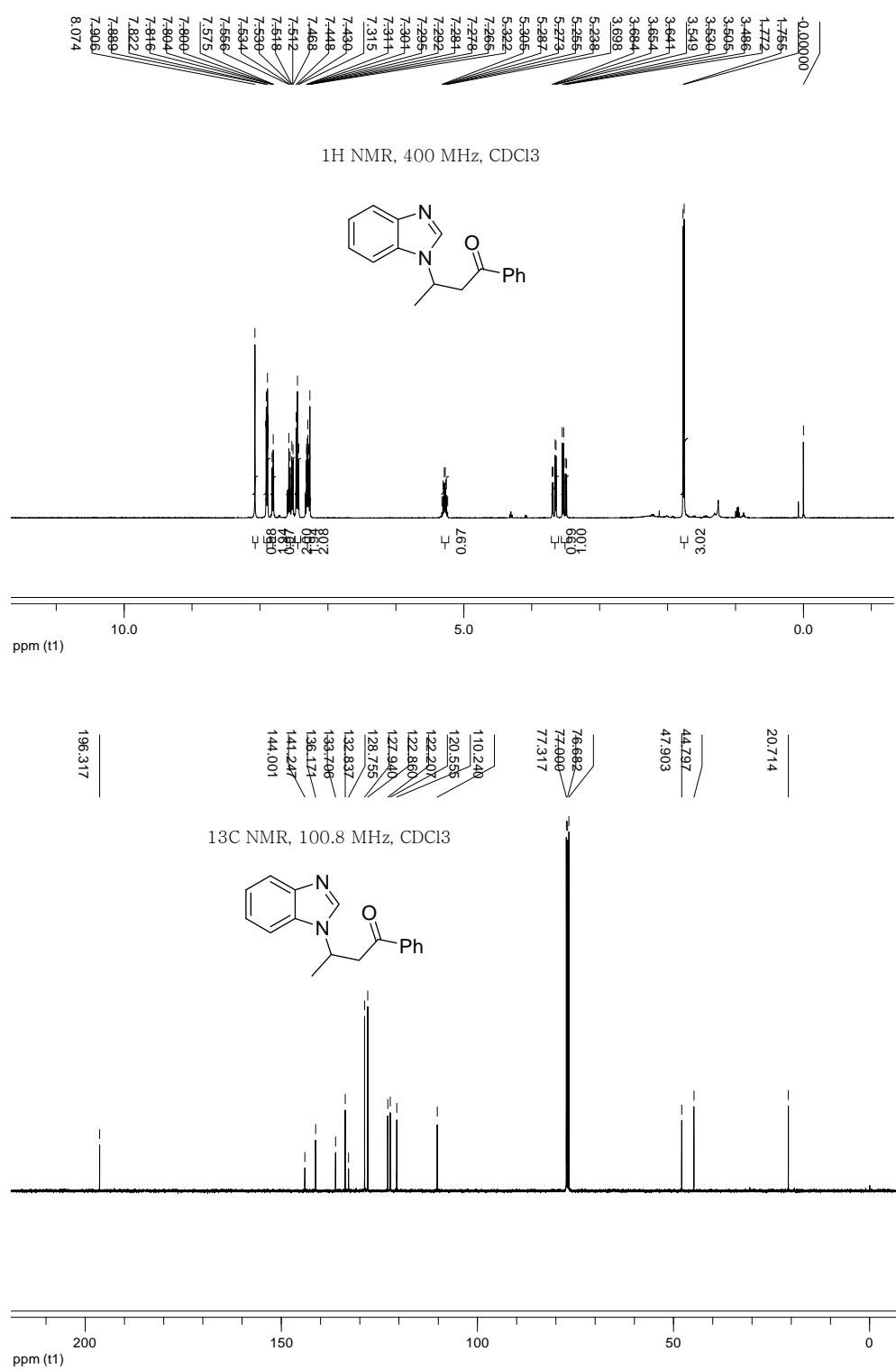
3-(imidazol-1-yl)-1-phenylbutan-1-one



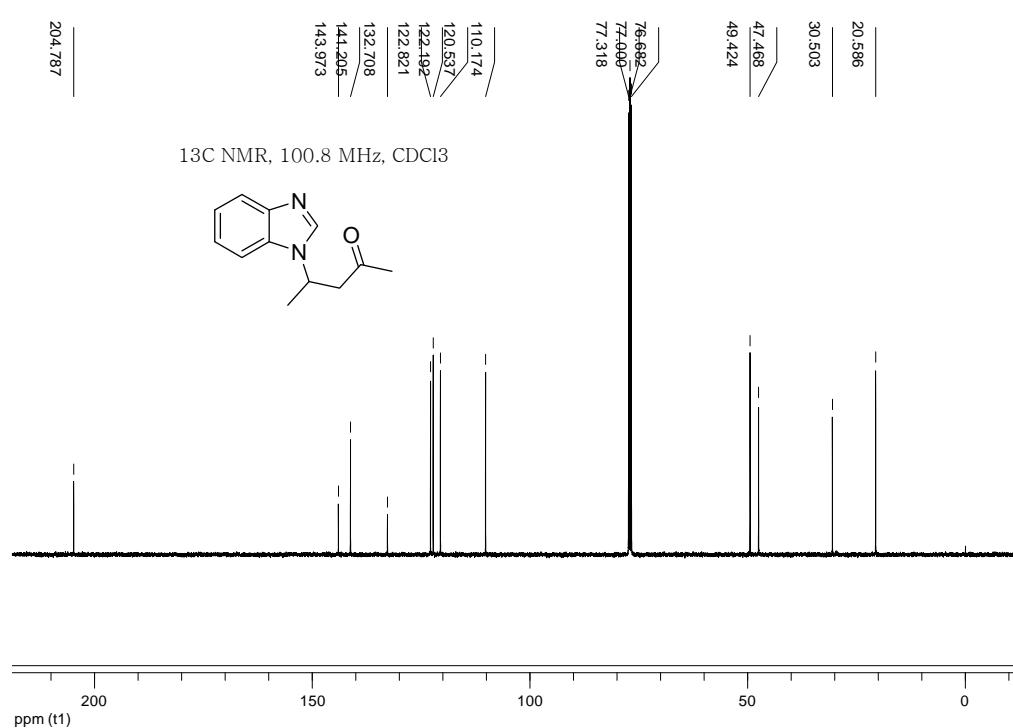
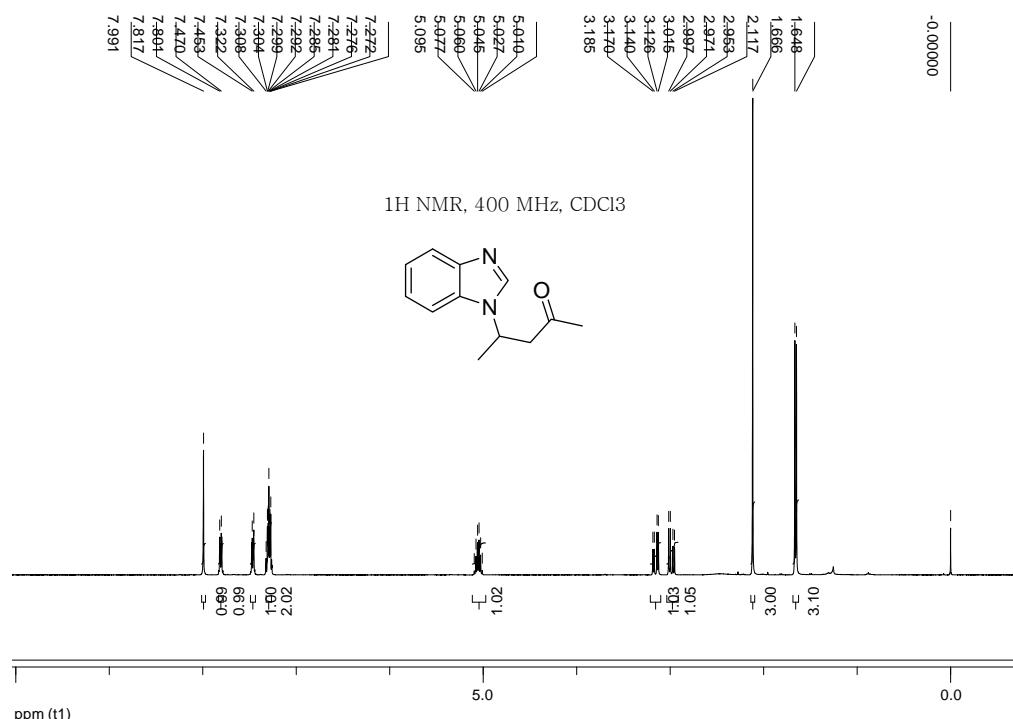
1-Phenyl-3-(4H-1,2,4-triazol-4-yl)butan-1-one



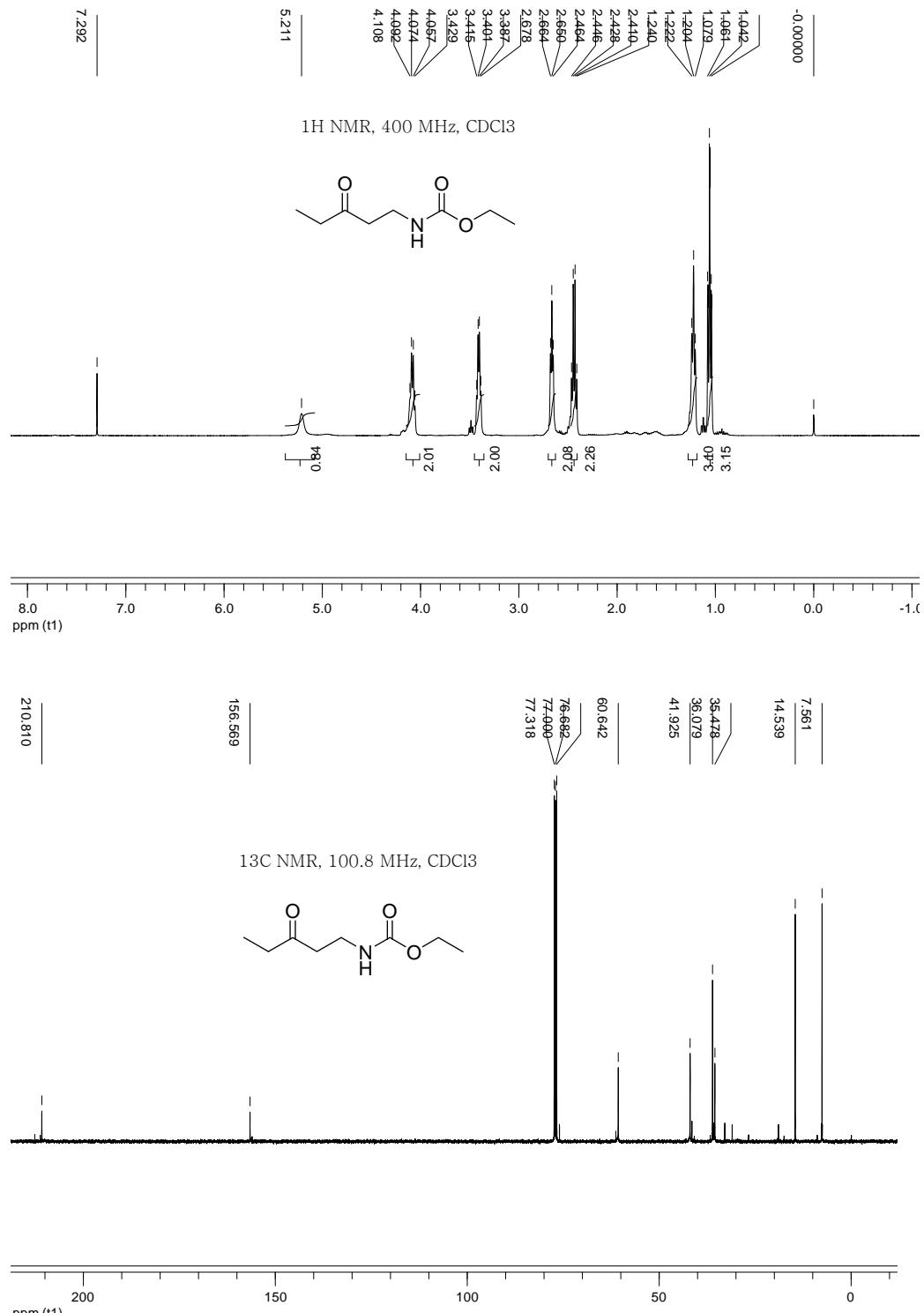
3-(1*H*-Benzo[d]imidazol-1-yl)-1-phenylbutan-1-one



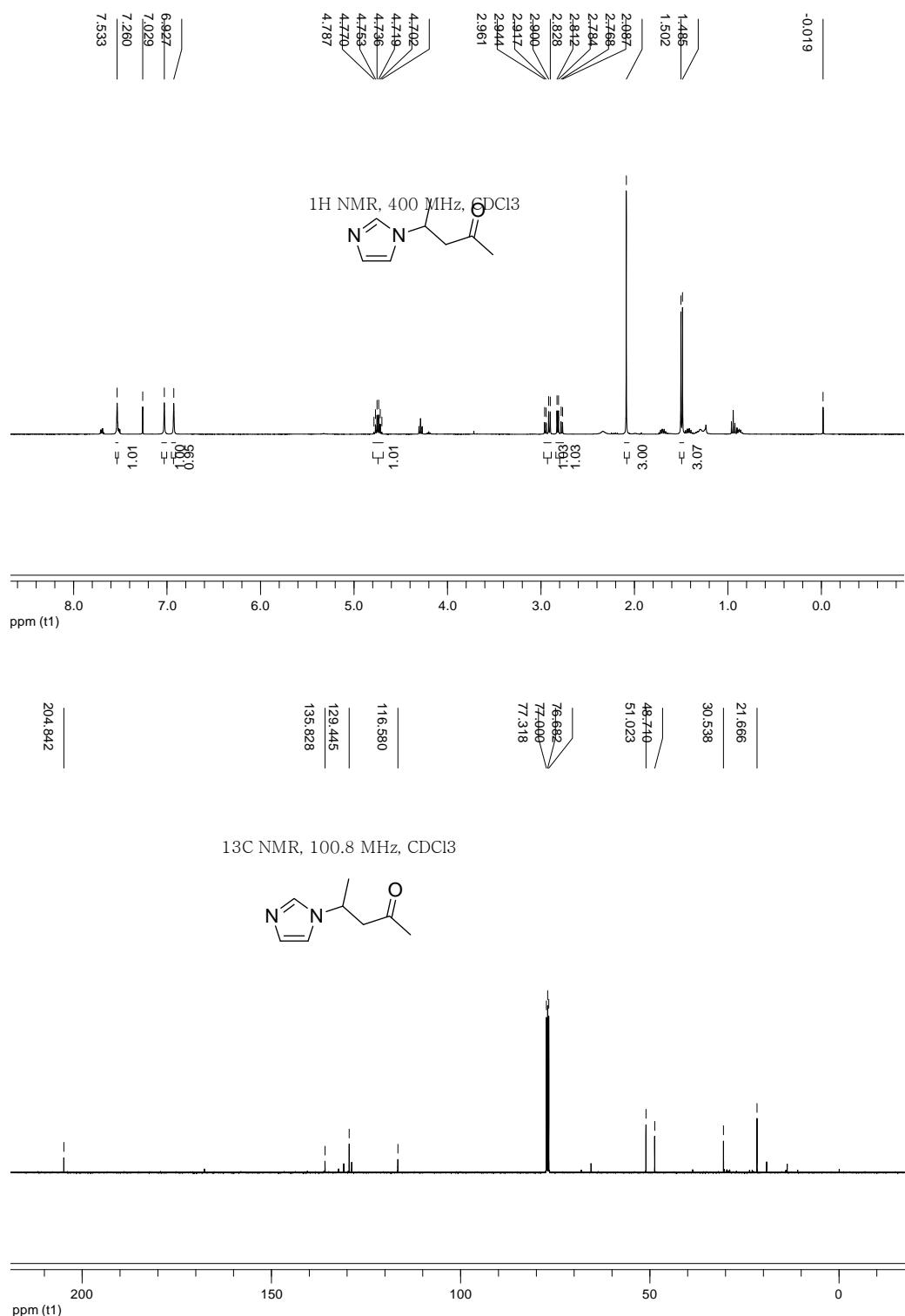
4-(1*H*-Benzo[d]imidazol-1-yl)pentan-2-one



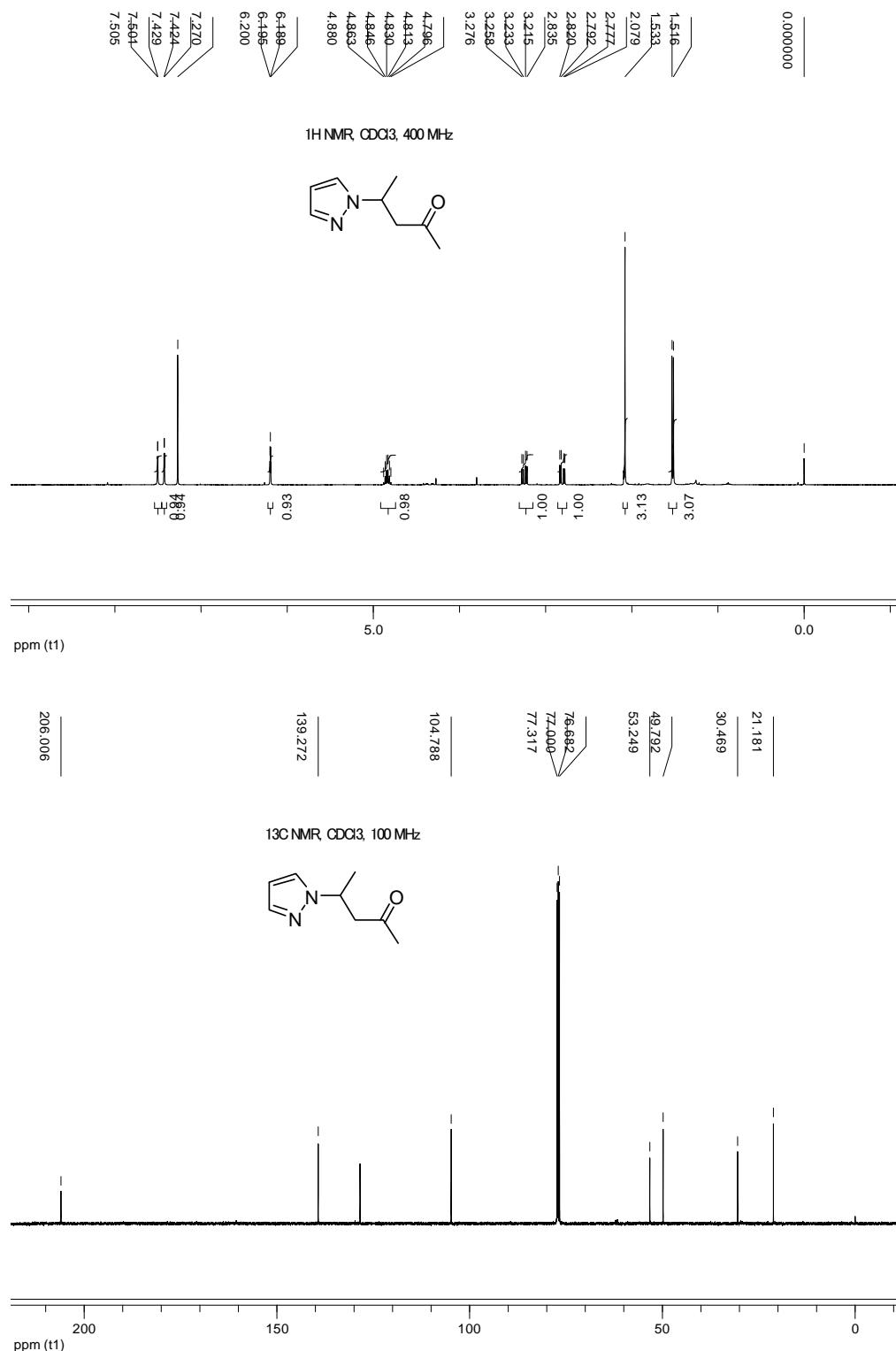
Ethyl 3-oxopentylcarbamate



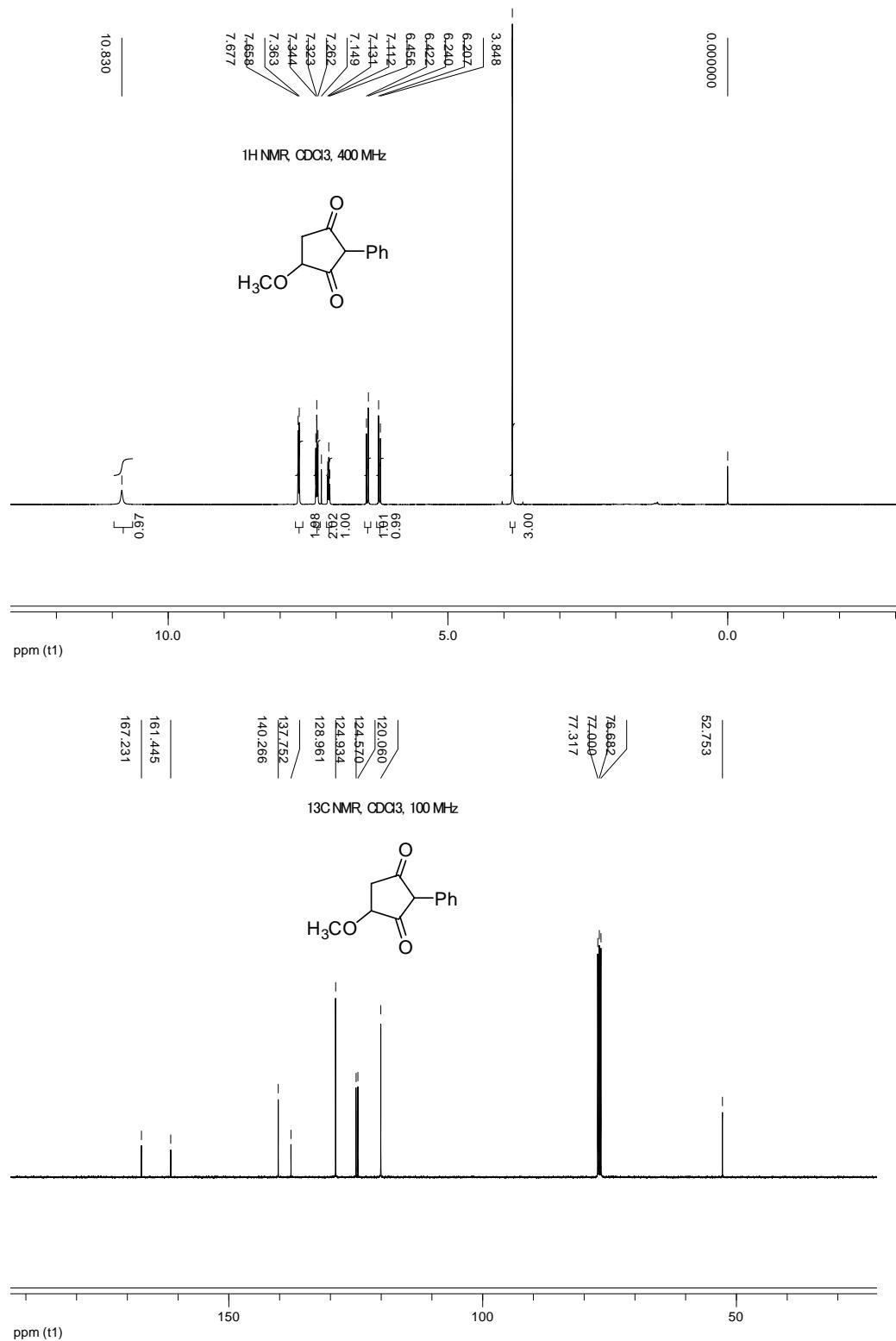
4-(1*H*-imidazol-1-yl)pentan-2-one



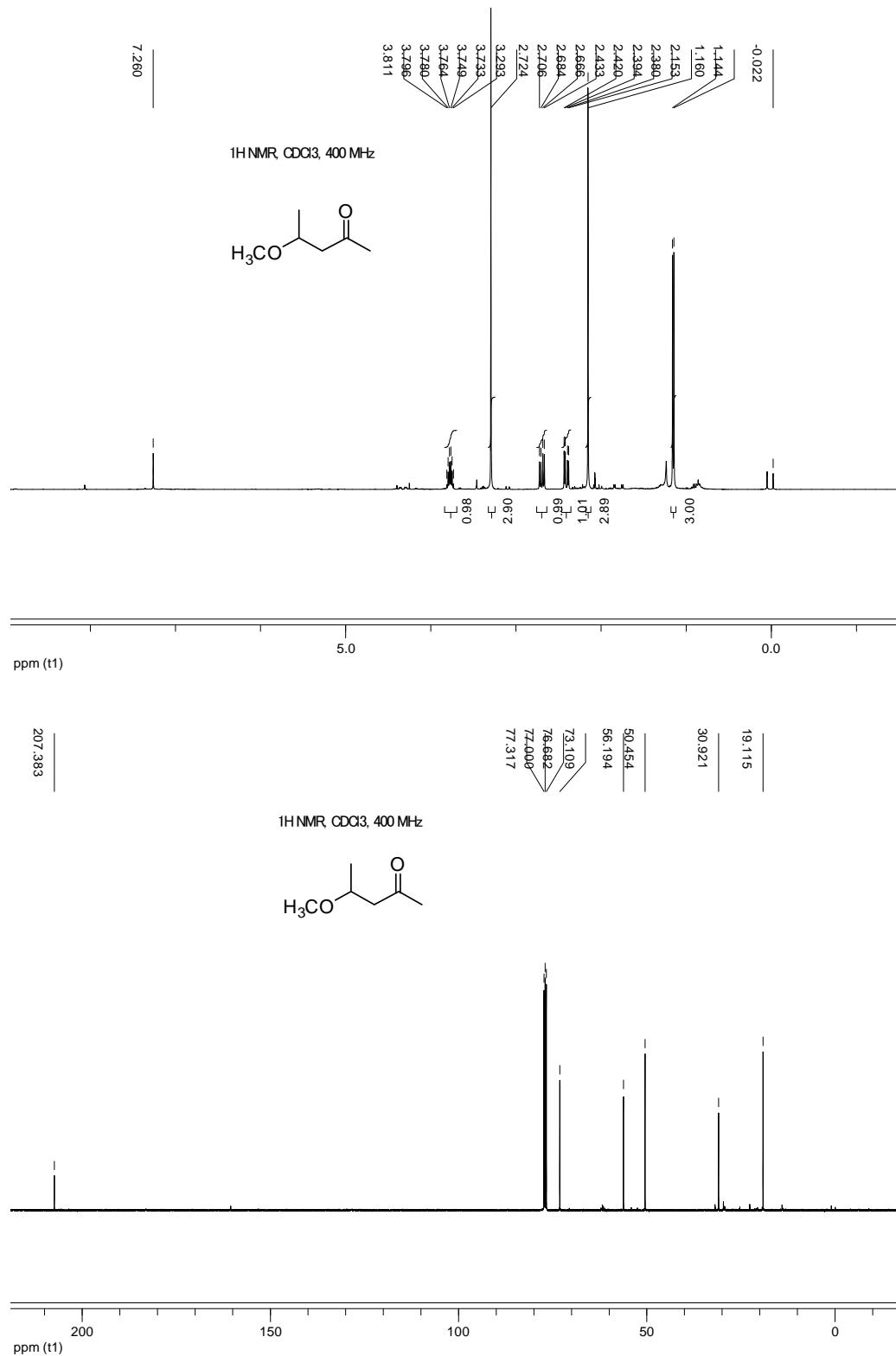
4-(1*H*-pyrazol-1-yl)pentan-2-one



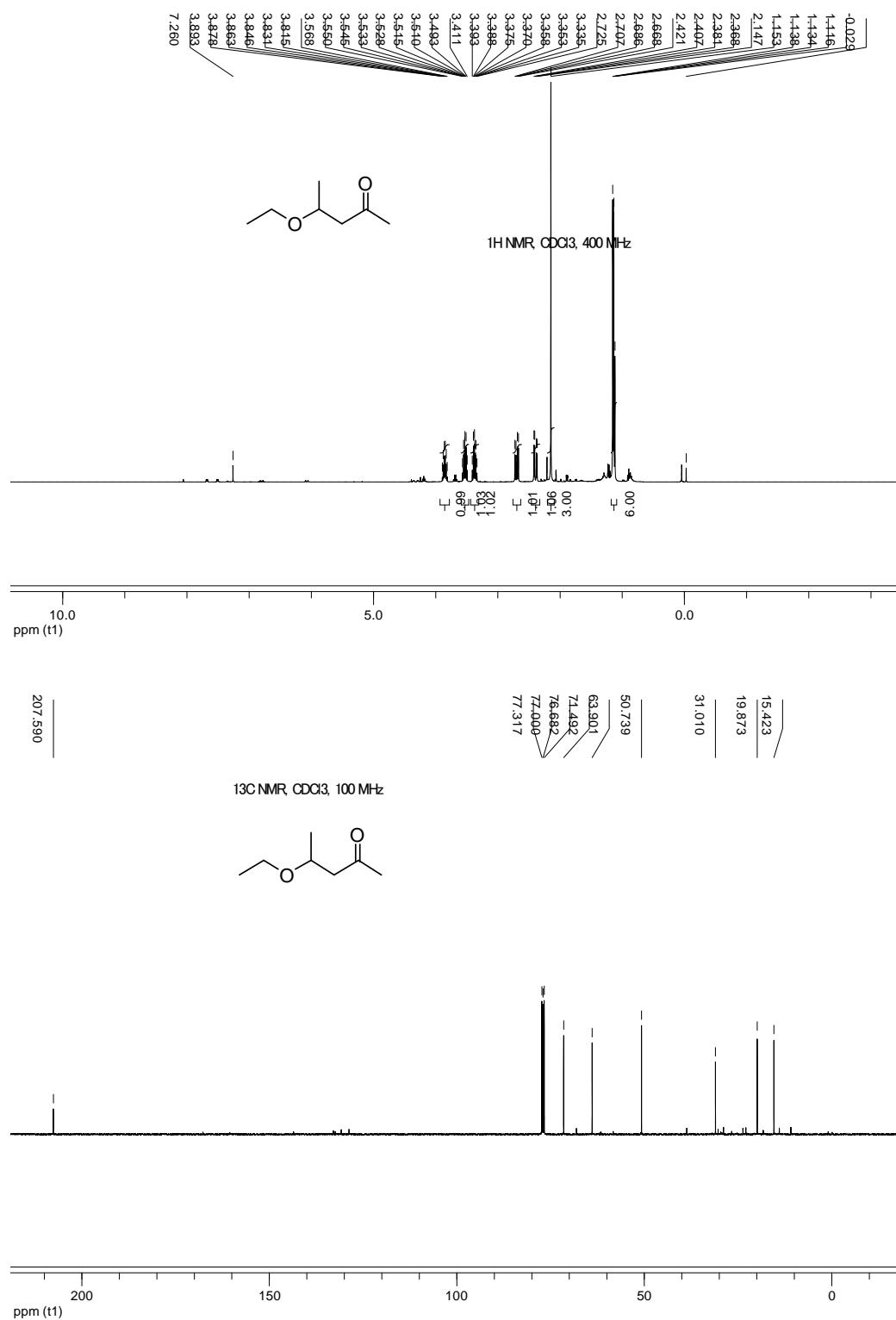
3-methoxy-1-phenylpyrrolidine-2,5-dione



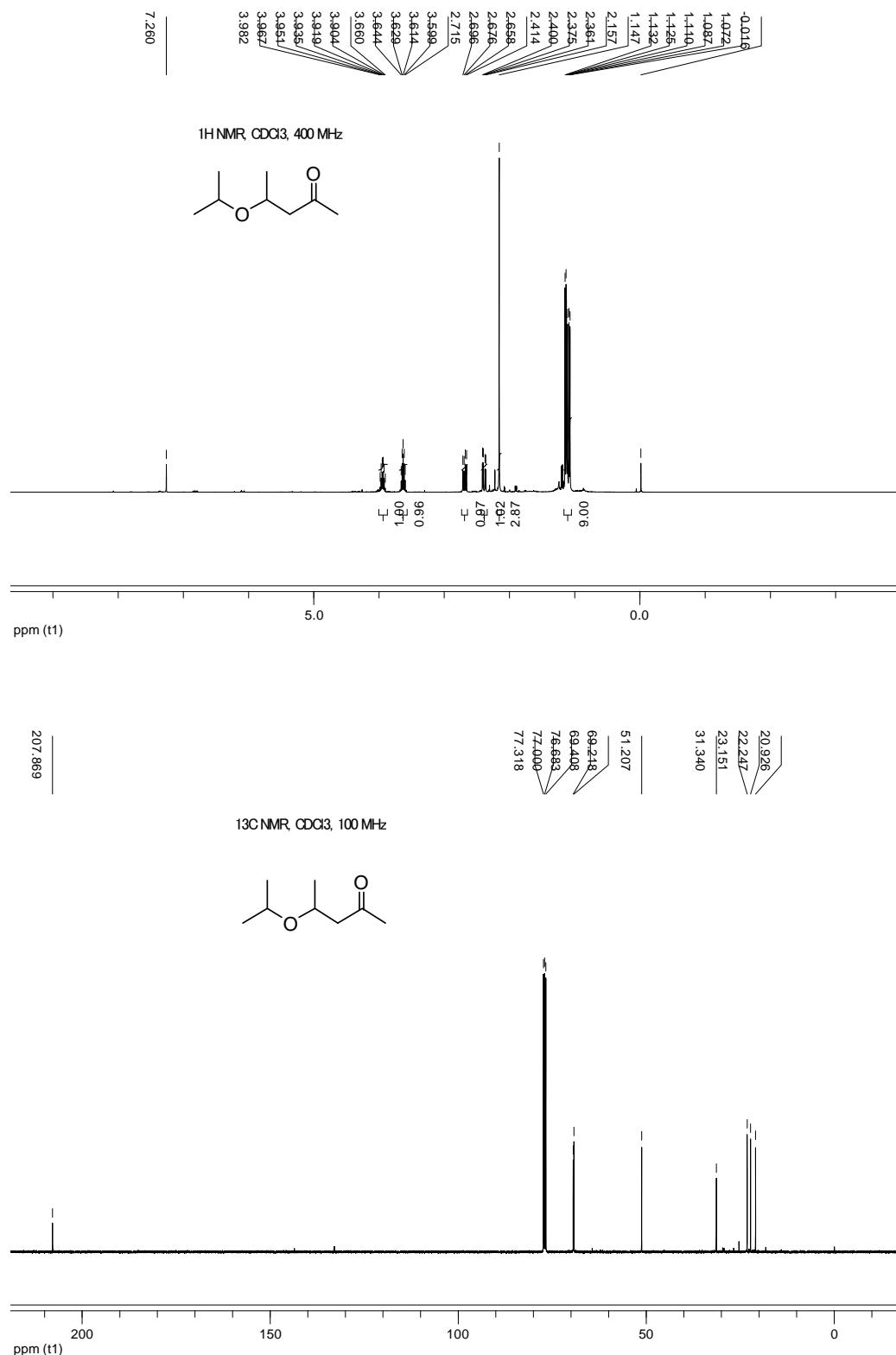
4-methoxypentan-2-one



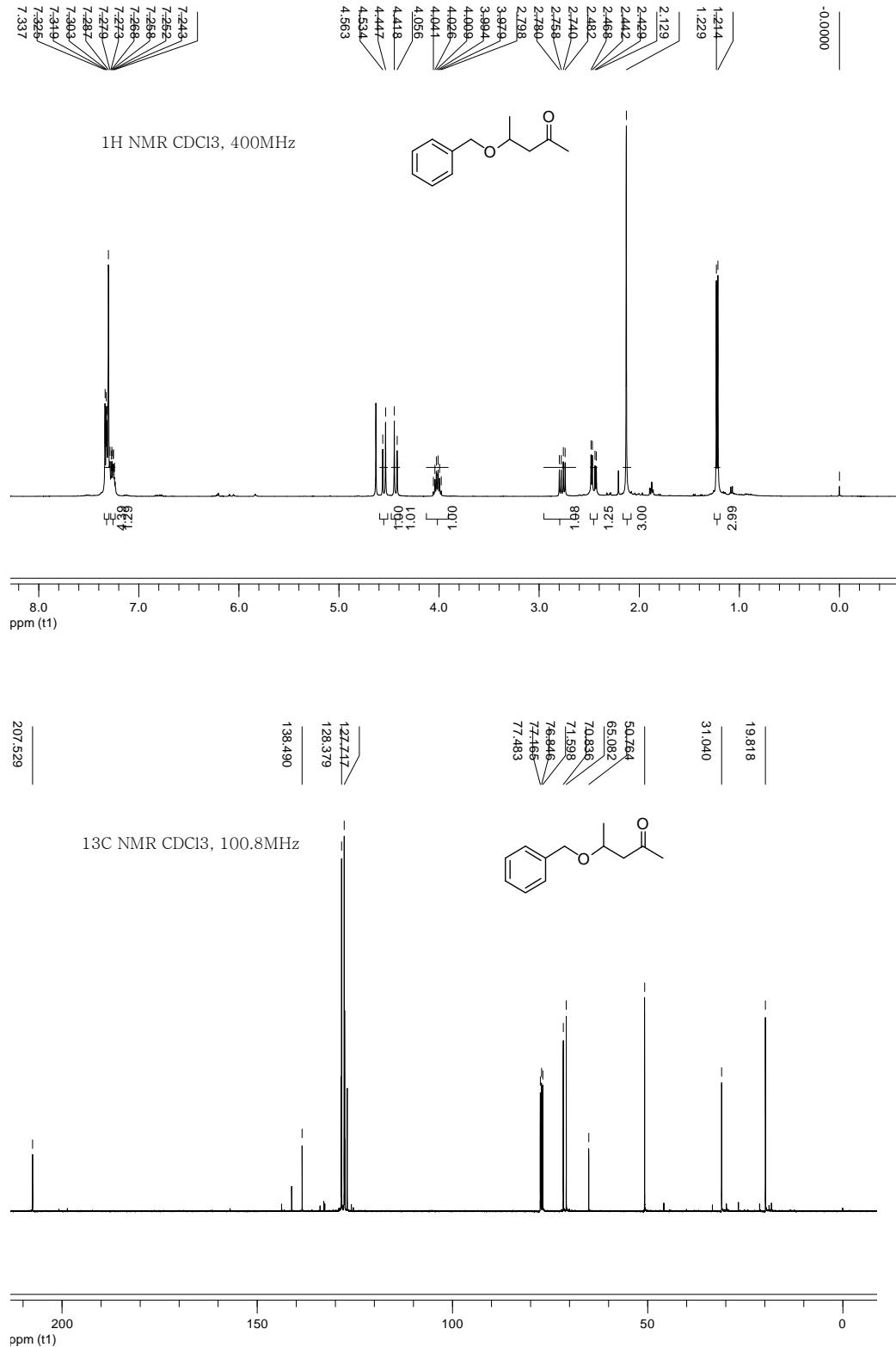
4-ethoxypentan-2-one



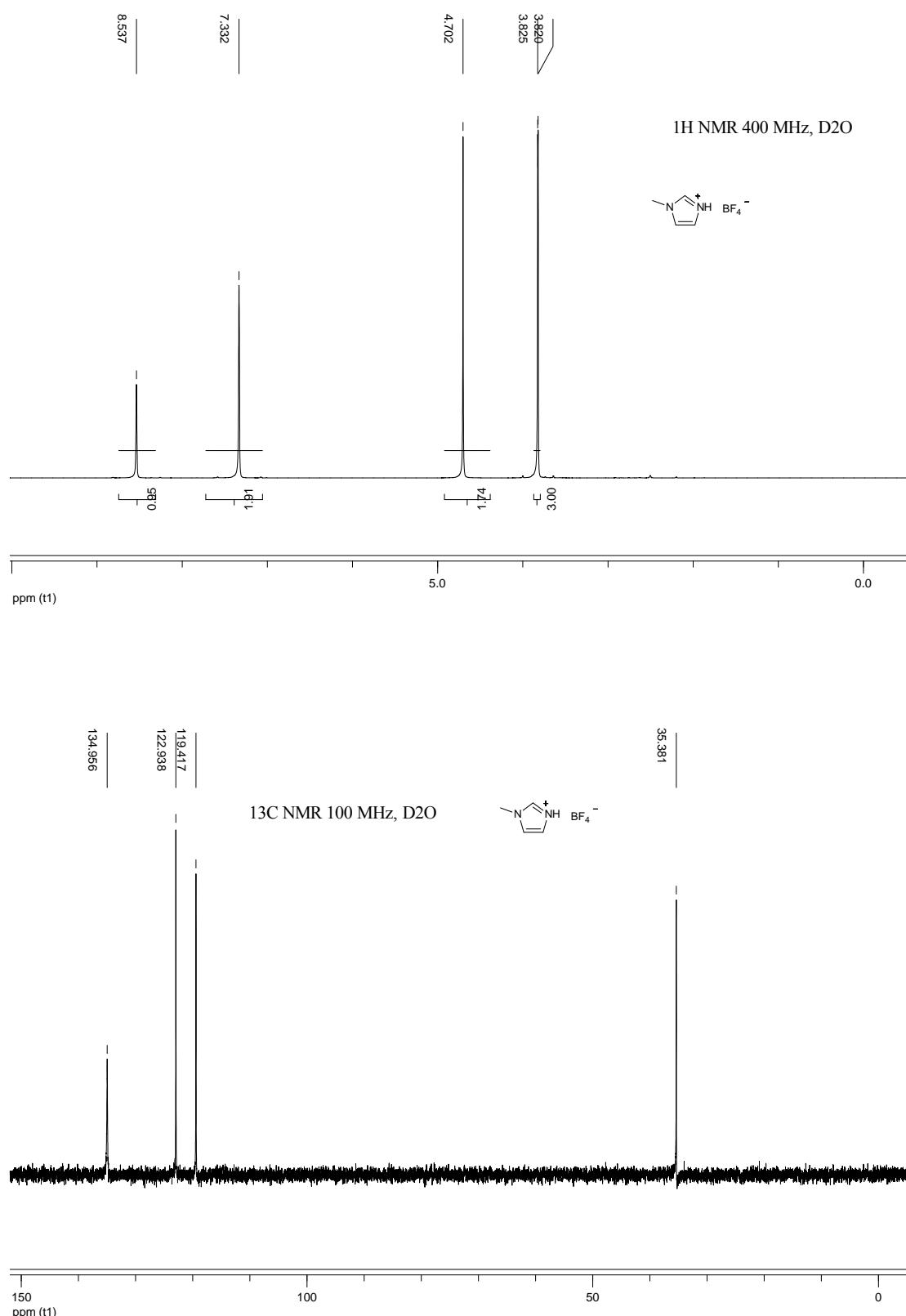
4-isopropoxypentan-2-one



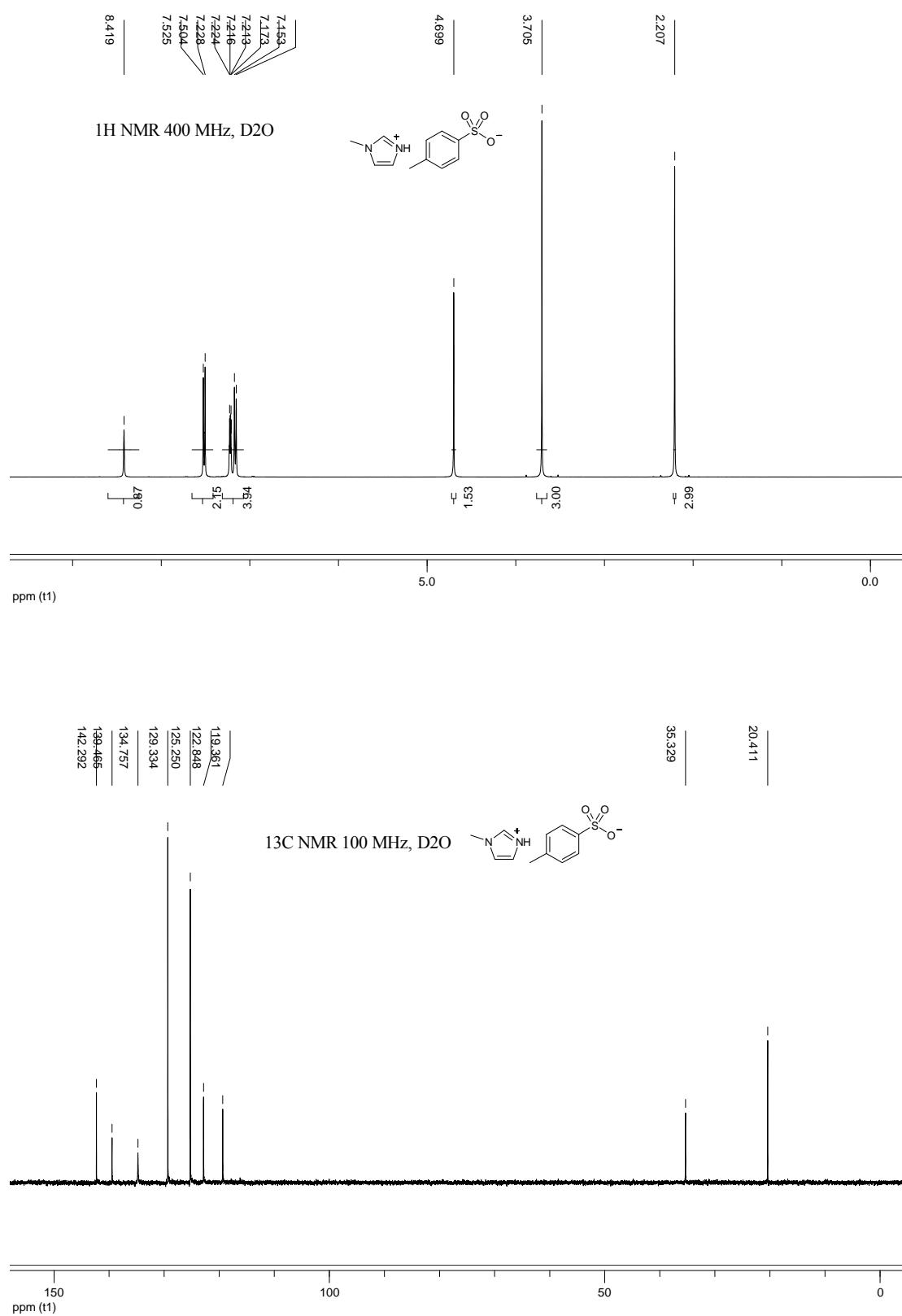
4-(benzyloxy)pentan-2-one



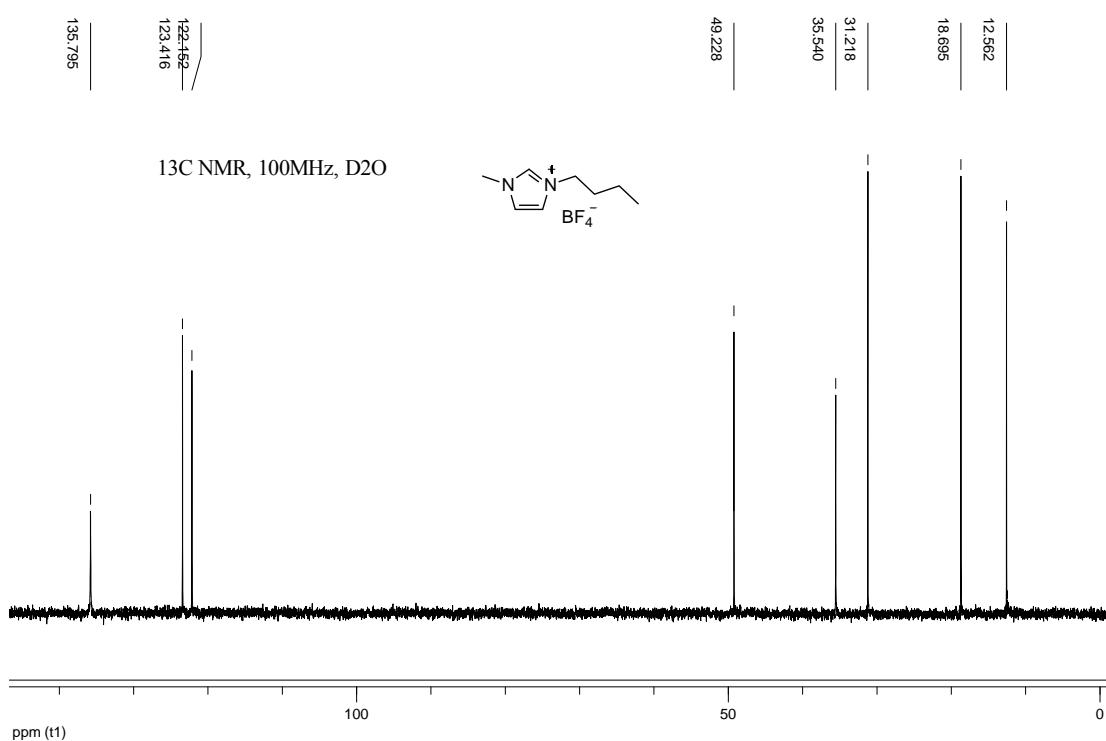
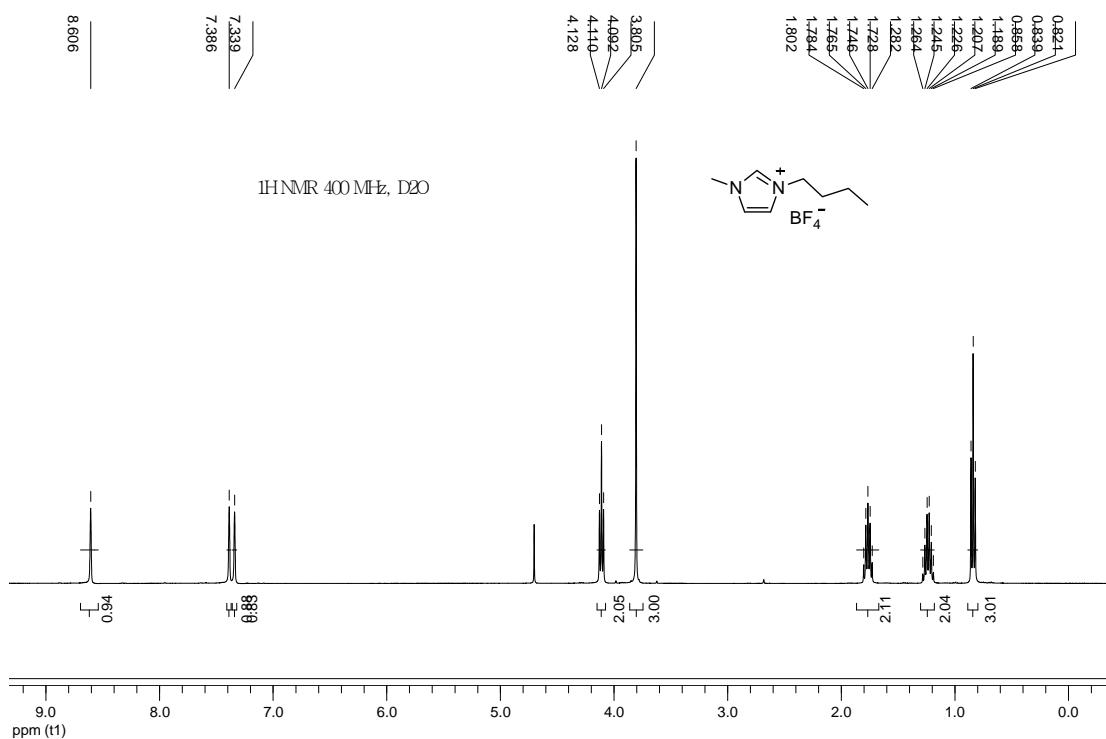
**8. ^1H NMR and ^{13}C NMR spectra of the ionic liquids
[Hmim]BF₄**



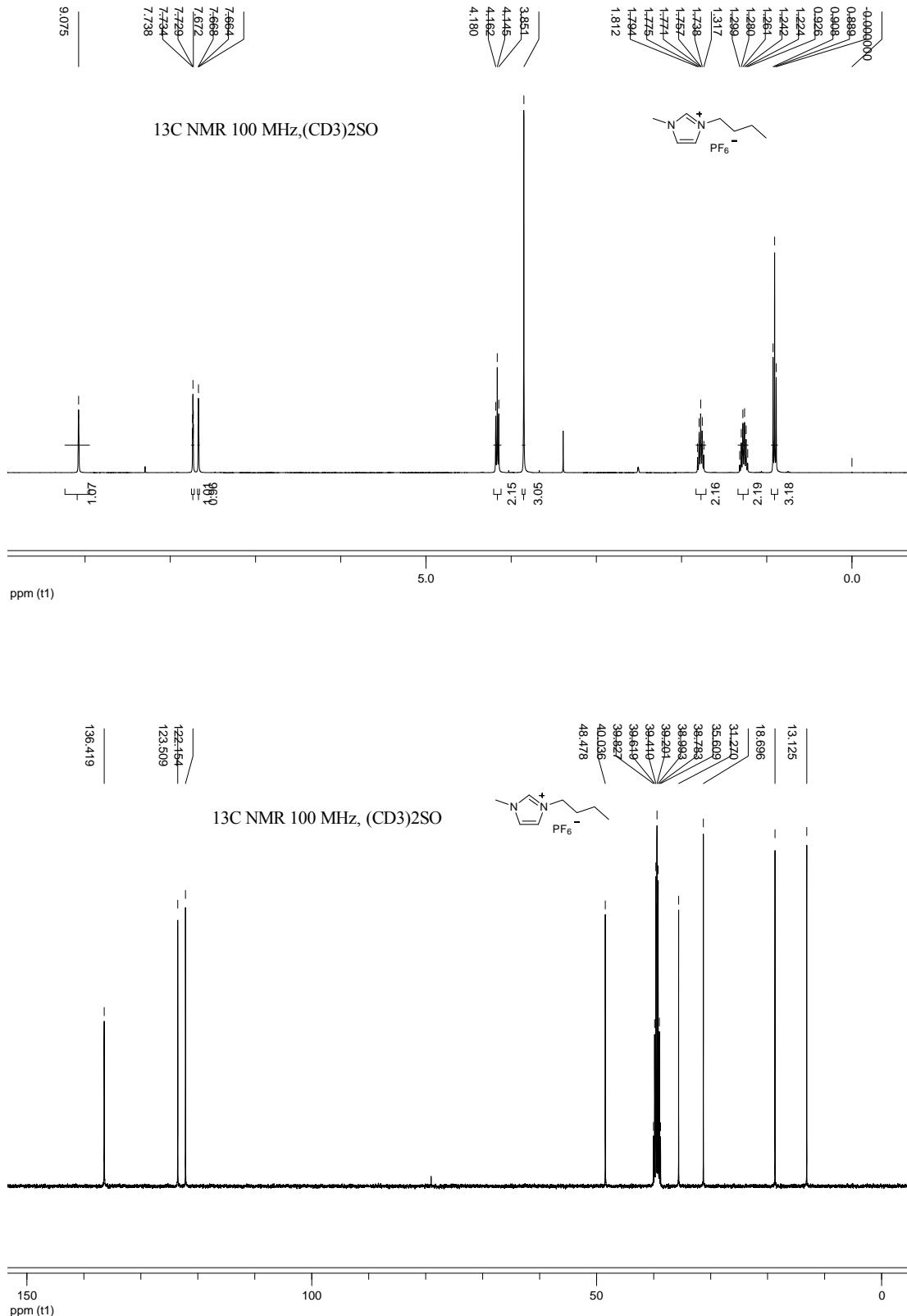
[Hmim]OTs



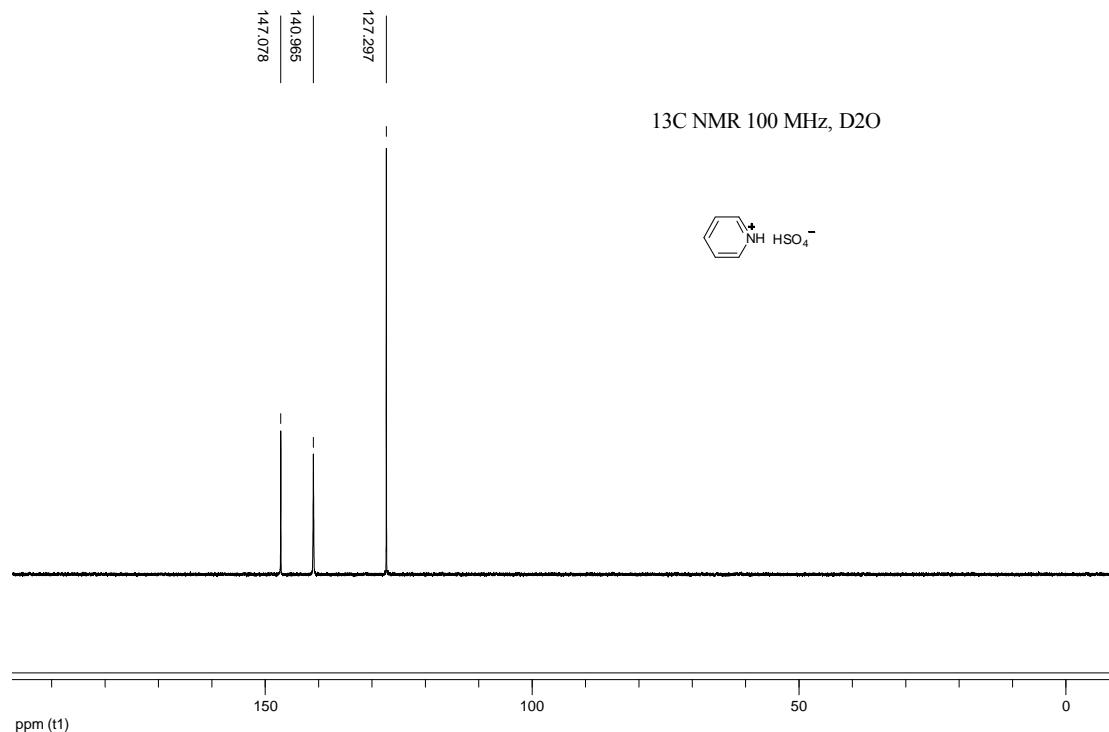
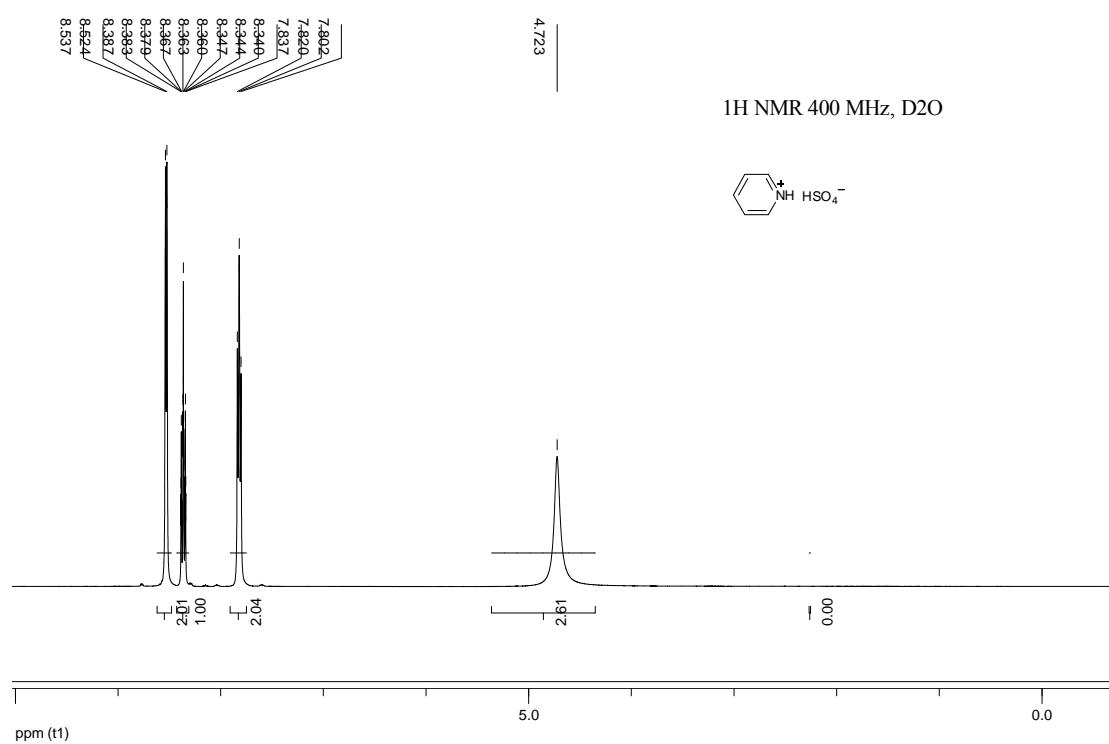
[Bmim]BF₄



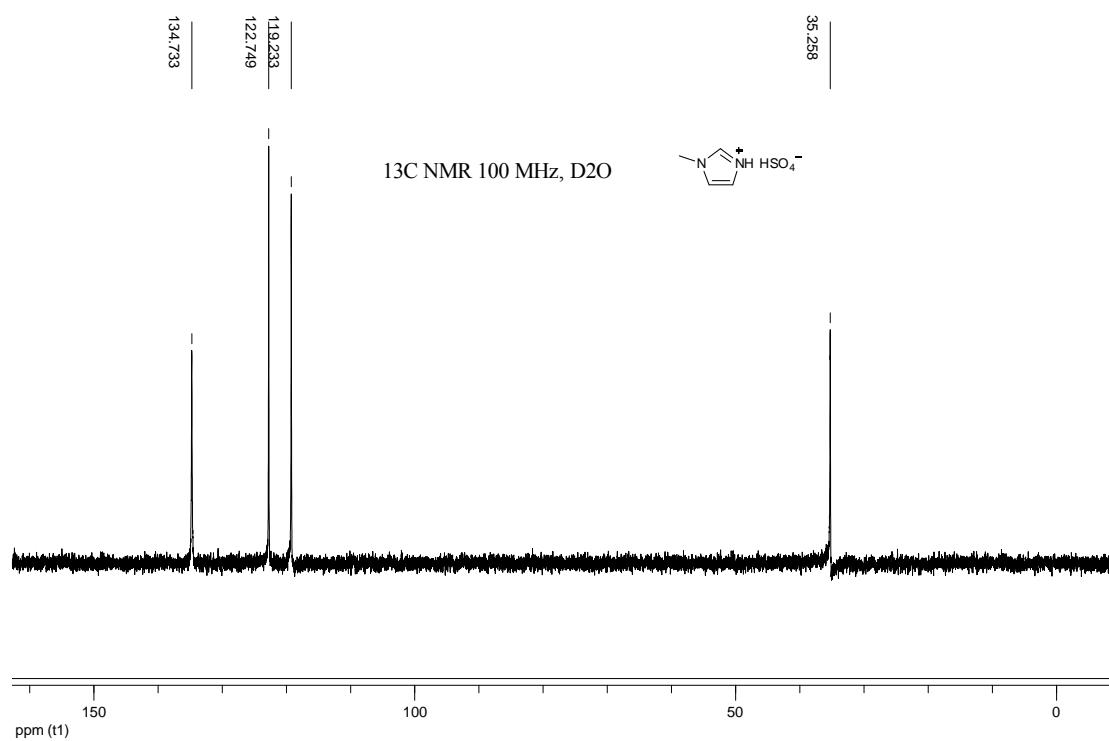
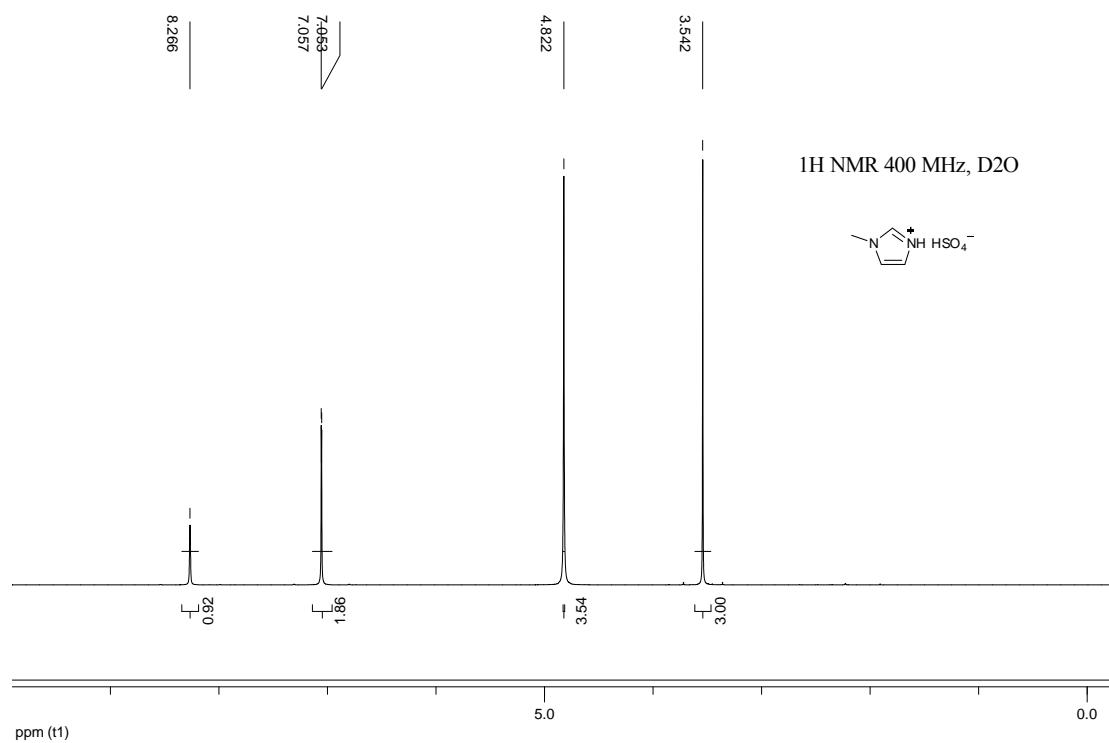
[Bmim]PF₆



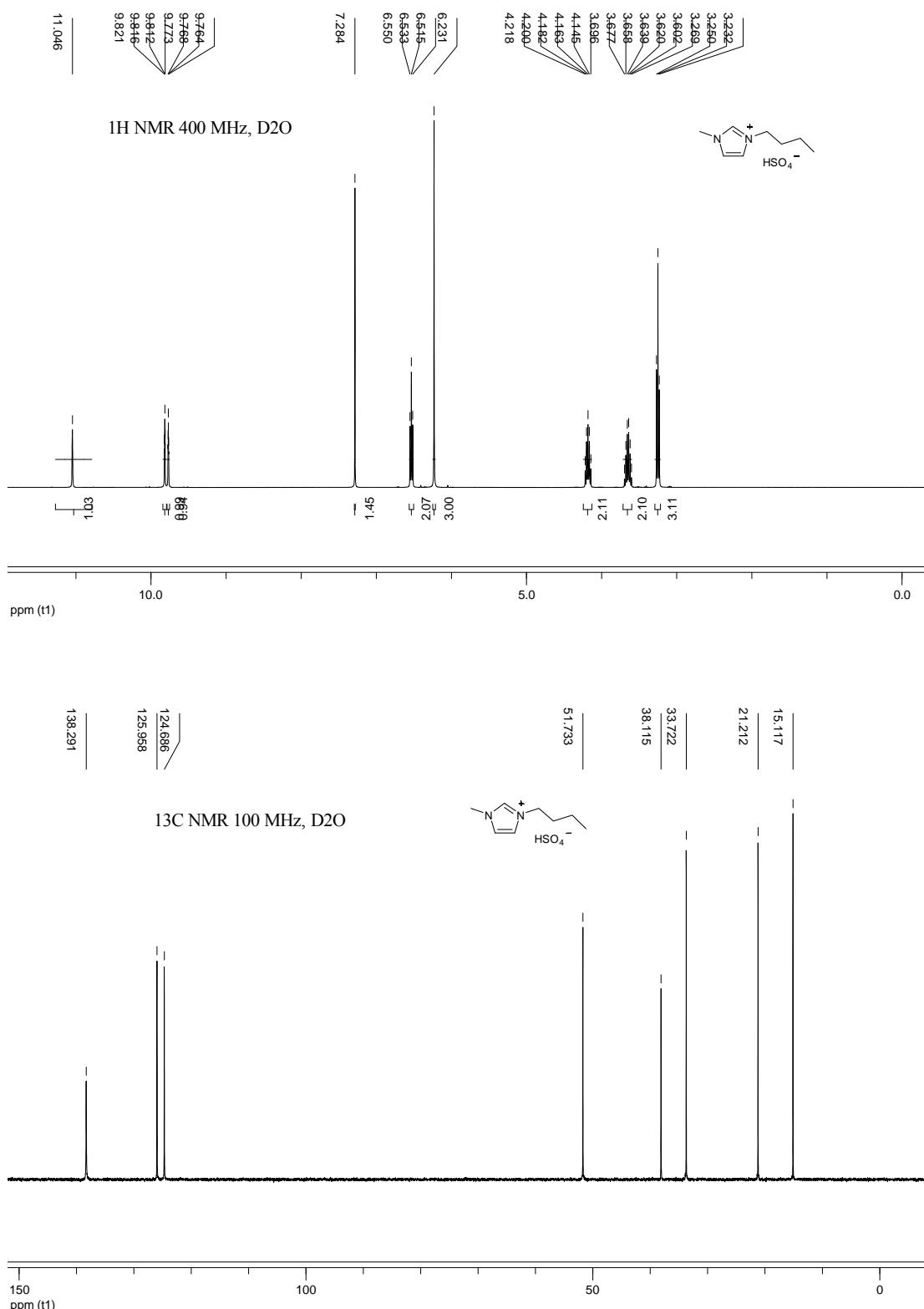
PyHSO₄



[Hmim]HSO₄



[Bmim]HSO₄



[Bsmim]HSO₄

