Electronic Supplementary Information

A Metal-free Catalytic System for the Oxidation of Benzylic Methylenes and Primary Amines under Solvent-Free Conditions

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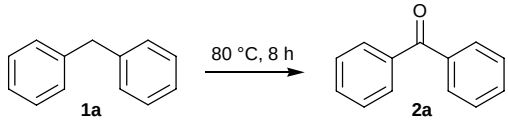
Further optimization of reaction conditions

Table ESI-1 **Further optimization of reaction conditions**



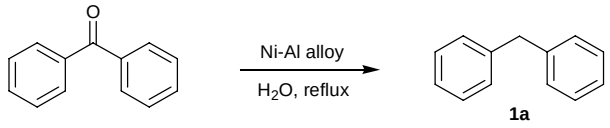
Entry	Cat. (mol %)	TBHP (equiv)	Solvent	Yield (%) [b]
1 [c]	I_2 (10 %)	-	Py	n.d.
2 [d]	I_2 (10 %)	-	Py	n.d.
3 [e]	I_2 (10 %)	-	Py	trace
4	I_2 / Py (10 % / 2.5 %)	3.0	MeCN	22
5	I_2 / Py (10 % / 5 %)	3.0	MeCN	70
6	I_2 / Py (10 % / 50 %)	3.0	MeCN	87
7	I_2 / Py (10 % / 100 %)	3.0	MeCN	84
8	I_2 / Py (10 % / 200 %)	3.0	MeCN	77
9 [f]	I_2 / Py (10 % / 10 %)	4.0	MeCN	94
10 [g]	I_2 / Py (10 % / 10 %)	4.0	MeCN	trace
11 [h]	I_2 / Py (10 % / 10 %)	4.0	MeCN	n.d.

[a] Reaction conditions: 0.2 mmol **1a** in 0.2 ml solvent was heated at 80 ˚C for 8 h with or with catalyst and TBHP. [b] GC yield with internal standard. [c] air (1 atm) was used as oxidant. n.d. = not detected. [d] O_2 (1 atm)was used as oxidant. [e] 3.0 equiv of H_2O_2 (30% aqueous) was used. [f] The reaction was carried out at 100 ˚C. [g] The reaction was carried out at 60 ˚C. [h] The reaction was carried out at 40 ˚C.

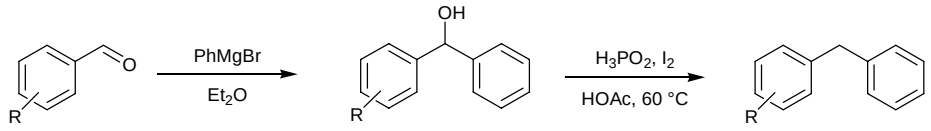
Synthesis of substances

1l, **1n**, **1p**, **1q, 5a, 5k, 5m** were purchased from commercial sources, others were prepared as following:

Scheme ESI-1 Synthesis of **1a** [1]

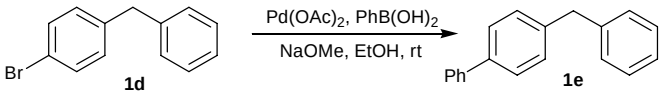


Scheme ESI-2 Synthesis of **1b-1d, 1g, 1h, 1j, 1k, 1m** [2]

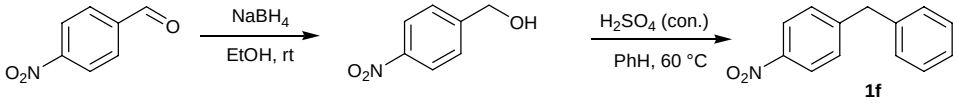


R= 4-F,	**1b**
R= 4-Cl,	**1c**
R= 4-Br,	**1d**
R= 4-Me,	**1g**
R= 4-OMe,	**1h**
R= 2-Cl,	**1j**
R= 3-Cl,	**1k**
R= naphthalen	**1m**

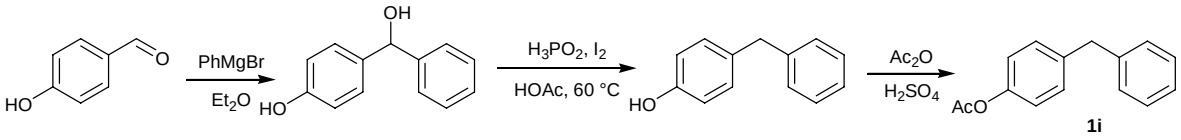
Scheme ESI-3 Synthesis of **1e** [3]



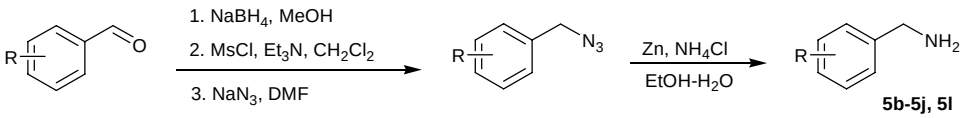
Scheme ESI-4 Synthesis of **1f**



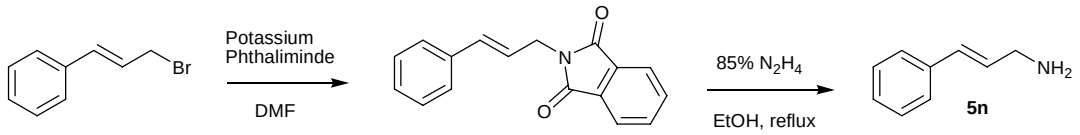
Scheme ESI-5 Synthesis of **1i** [2]



Scheme ESI-6 Synthesis of **5b-5j, 5l** [4]



Scheme ESI-7 Synthesis of **1n** [5]



References and Notes:

1 K. Ishimoto, Y. Mitoma, S. Nagashima, H. Tashiro, G. K. S. Prakash, G. A. Olah, M. Tashiro, *Chem. Commun.,* 2003, 514-515

2 The reduction of benzhydrols was consulted *Tetrahedron Lett.,* 2001, **42**, 831-833.

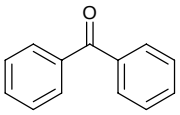
3 C. Deng, S. Guo, Y. Xie, J. Li, *Eur. J. Org. Chem.,* 2007, 1457-1462.

4 W. Q. Lin, X. M. Zhang, Z. He, Y. Jin, L. Z. Gong, A. Q. Mi, *Synth. Commun.* 2002, **32**, 3279-3284.

5 W. J. Gensler, J. C. Rockett, *J . Am. Chem. Soc.* 1955, **77**, 3262-3264.

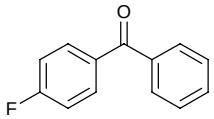
Characterization data for the products

benzophenone (2a) [6]



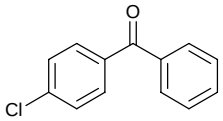
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.82-7.79 (4 H , m), 7.61-7.57 (2 H, m), 7.51-7.46 (4 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 196.5, 137.6, 132.4, 130.0 128.2; ν_{max}/cm^{-1} 1660, 1598, 1446, 1315, 1277, 919, 700, 638. HRMS calc. $C_{13}H_{10}O$: 182.0732, found: 182.0733.

(4-fluorophenyl)(phenyl)methanone (2b) [7]



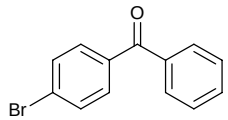
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.87-7.82 (2 H, m), 7.79-7.76 (2 H, m), 7.62-7.58 (1 H, m), 7.52-7.47 (2 H, m), 7.19-7.13 (2 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.1, 167.1, 163.7, 137.6, 133.1, 132.7, 132.6, 132.4, 129.8, 128.4, 115.6, 115.3; ν_{max}/cm^{-1} 3065, 1660, 1599, 1504, 1447, 1409, 1302, 1277, 1230, 1155, 924, 851, 738, 700, 600. HRMS calc. $C_{13}H_9FO$: 200.0637, found: 200.0634.

(4-chlorophenyl)(phenyl)methanone (2c) [6]



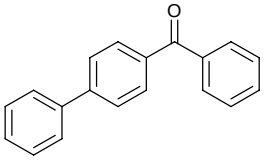
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.79-7.75 (4 H, m), 7.63-7.58 (1 H, m), 7.52-7.45 (4 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.3, 138.9, 137.4, 136.0, 132.6, 131.5, 129.9, 128.7, 128.5; ν_{max}/cm^{-1} 1651, 1582, 1284, 1089, 844, 788, 728, 695, 664. HRMS calc. $C_{13}H_9ClO$: 216.0342, found: 216.0340.

(4-bromophenyl)(phenyl)methanone (2d) [6]



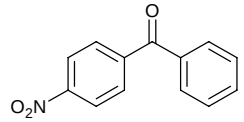
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.79-7.76 (2 H, m), 7.70-7.58 (5 H, m), 7.52-7.47 (2 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.5, 137.3, 136.5, 132.7, 131.7, 131.6, 130.0, 128.5, 127.5; ν_{max}/cm^{-1} 1736, 1650, 1585, 1284, 842, 788, 725, 696, 656, 468. HRMS calc. $C_{13}H_9BrO$: 259.9837, found: 259.9838.

biphenyl-4-yl(phenyl)methanone (2e) [8]



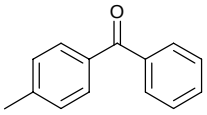
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.91-7.88 (2 H, m), 7.85-7.82 (2 H, m), 7.72-7.58 (5 H, m), 7.53-7.38 (5 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 196.2, 145.2, 140.0, 137.8, 136.2, 132.4, 130.7, 130.0, 129.0, 128.3, 128.2, 127.3, 126.9; ν_{max}/cm^{-1} 1646, 1600, 1446, 1402, 1293, 852, 763, 731, 694. HRMS calc. $C_{19}H_{14}O$: 258.1045, found: 258.1043.

(4-nitrophenyl)(phenyl)methanone (2f) [6]



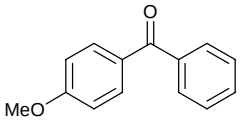
δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.34 (2 H, d, *J* 8.7 Hz), 7.94 (2 H, d, *J* 8.7 Hz), 7.82-7.79 (2 H, m), 7.68-7.63 (1 H, m), 7.55-7.50 (2 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 194.9, 150.0, 143.0, 136.4, 133.6, 130.8, 130.2, 128.8, 123.6; ν_{max}/cm^{-1} 1715, 1608, 1452, 1230, 1191, 1151, 1095, 917, 736, 670. HRMS calc. $C_{13}H_9NO_3$: 227.0582, found: 227.0584.

phenyl(p-tolyl)methanone (2g) [6]



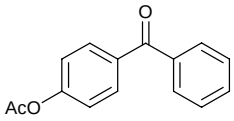
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.78 (2 H, d, *J* 7.5 Hz), 7.72 (2 H, d, *J* 7.8 Hz), 7.57 (1 H, t, *J* 7.5 Hz), 7.47 (2 H, t, *J* 7.5 Hz), 7.28 (2 H, d, *J* 7.8 Hz), 2.44 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 196.4, 143.2, 137.9, 134.9, 132.1, 130.3, 129.9, 129.0, 128.2, 21.6; ν_{max}/cm^{-1} 1657, 1604, 1447, 1409, 1311, 1278, 1178, 1149, 928, 838, 789, 731, 699. HRMS calc. $C_{14}H_{12}O$: 196.0888, found: 196.0887.

(4-methoxyphenyl)(phenyl)methanone (2h) [6]



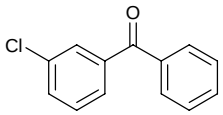
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.85-7.82 (2 H, m), 7.77-7.74 (2 H, m), 7.57-7.54 (1 H, m), 7.49-7.44 (2 H, m), 6.98-6.95 (2 H, m), 3.89 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.4, 163.2, 138.3, 132.5, 131.9, 130.1, 129.7, 128.2, 113.6, 55.5; ν_{max}/cm^{-1} 1652, 1600, 1507, 1451, 1312, 1257, 1175, 1028, 928, 846, 793, 742, 700, 604. HRMS calc. $C_{14}H_{12}O_2$: 212.0837, found: 212.0839.

4-benzoylphenyl acetate (2i) [9]



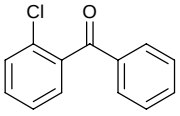
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.86 (2 H, d, *J* 8.7 Hz), 7.80 (2 H, d, *J* 8.7 Hz), 7.62-7.57 (1 H, m), 7.51-7.46 (2 H, m), 7.26-7.20 (2 H, m), 2.34 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.6, 169.0, 154.0, 137.6, 135.2, 132.6, 131.8, 130.0, 128.4, 121.6, 21.3; ν_{max}/cm^{-1} 3062, 1762, 1657, 1598, 1500, 1447, 1410, 1370, 1305, 1277, 1194, 1015, 939, 857, 747, 699; HRMS calc. $C_{15}H_{12}O_3$: 240.0786, found: 240.0783.

(3-chlorophenyl)(phenyl)methanone (2j) [6]



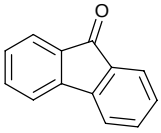
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.80-7.78 (3 H, m), 7.68-7.40 (6 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.0, 139.3, 137.0, 134.6, 132.8, 132.3, 130.0, 129.8, 129.6, 128.4, 128.1; ν_{max}/cm^{-1} 1662, 1568, 1420, 1272, 1077, 764, 717, 692, 605, 456. HRMS calc. $C_{13}H_9ClO$: 216.0342, found: 216.0344.

(2-chlorophenyl)(phenyl)methanone (2k) [6]



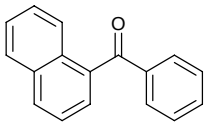
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.83-7.80 (2 H, m), 7.63 - 7.58 (1 H, m), 7.49-7.41 (4 H, m), 7.38-7.36 (2 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 195.2, 138.7, 136.6, 133.7, 131.3, 131.2, 130.1, 129.1, 128.7, 126.7; ν_{max}/cm^{-1} 3062, 1673, 1595, 1470, 1449, 1434, 1316, 1288, 1253, 1153, 1058, 929, 801, 764, 744, 730, 703, 688, 634. HRMS calc. $C_{13}H_9ClO$: 216.0342, found: 216.0341.

9*H*-fluoren-9-one (2l) [10]



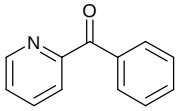
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.65 (2 H, d, *J* 7.5 Hz), 7.53-7.45 (4 H, m), 7.31-7.26 (2 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 193.7, 144.3, 134.5, 134.0, 128.9, 124.1, 120.2, 119.8; ν_{max}/cm^{-1} 1650, 1594, 1514, 1316, 1110, 871, 700, 617, 463. HRMS calc. $C_{13}H_8O$: 180.0575, found: 180.0576.

naphthalen-1-yl(phenyl)methanone (2m) [11]



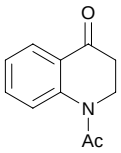
δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.10 - 8.07 (1 H, m), 8.01 (1 H, d, *J* 8.1 Hz), 7.94-7.85 (3 H, m), 7.62-7.43 (7 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 198.0, 138.5, 136.5, 133.8, 133.2, 131.3, 131.1, 130.4, 128.5, 127.8, 127.3, 126.5, 125.8, 124.4; ν_{max}/cm^{-1} 3059, 1660, 1596, 1448, 1313, 1282, 1250, 913, 799, 776, 713, 624. HRMS calc. $C_{17}H_{12}O$: 232.0888, found: 232.0886.

phenyl(pyridin-2-yl)methanone (2n) [10]



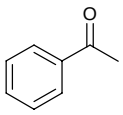
δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.74-8.72 (1 H, m), 8.09-8.03 (3 H, m), 7.93-7.87 (1 H, m), 7.62-7.57 (1 H, m), 7.51-7.49 (3 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 193.7, 154.9, 148.4, 136.9, 136.2, 132.8, 130.9, 128.0, 126.1, 124.4; ν_{max}/cm^{-1} 1665, 1597, 1579, 1447, 1433, 1319, 1304, 1282, 1245, 1162, 994, 940, 744, 696, 651. HRMS calc. $C_{12}H_9NO$: 138.0684, found: 138.0687.

1-acetyl-2,3-dihydroquinolin-4(1H)-one (2o) [12]



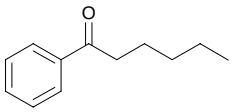
δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.03-8.00 (1 H, m), 7.59-7.53 (1 H, m), 7.46 (1 H, br), 7.31-7.26 (1 H, m), 4.25 (2 H, t, *J* 6.3 Hz), 2.80 (2 H, t, *J* 6.3 Hz), 2.35 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 194.0, 169.4, 144.0, 134.1, 127.8, 126.1, 125.6, 124.2, 44.0, 39.5, 23.1; ν_{max}/cm^{-1} 2933, 1665, 1601, 1479, 1385, 1303, 1268, 1213, 1161, 1121, 1035, 1001, 850, 771, 597, 562; HRMS calc. $C_{13}H_{10}O$: 189.0790, found: 189.0788.

acetophenone (2p) [10]



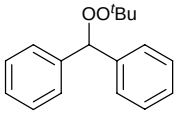
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.99-7.95 (2 H, m), 7.60-7.54 (1 H, m), 7.49-7.44 (2 H, m), 2.61 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 197.9, 137.0, 133.0, 128.4, 128.2, 26.4; ν_{max}/cm^{-1} 1686, 1599, 1449, 1360, 1266, 956, 761, 691, 590. HRMS calc. C_8H_8O: 120.0575, found: 120.0574.

1-phenylhexan-1-one (2q) [9]



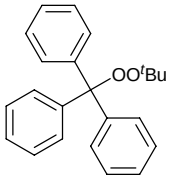
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.97-7.94 (2 H , m), 7.58-7.53 (1 H, m), 7.48-7.43 (2 H, m), 2.96 (2 H, t, *J* 7.5 Hz), 1.80-1.70 (2 H, m), 1.42-1.34 (4 H, m), 0.94-0.89 (3 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 200.7, 137.3, 133.0, 128.7 128.2, 38.7, 31.7, 24.2, 22.6, 14.1; ν_{max}/cm^{-1} 2957, 2931, 2872, 1687, 1598, 1449, 1205, 747, 691. HRMS calc. $C_{13}H_{10}O$: 176.1201, found: 176.1204.

(tert-butylperoxymethylene)dibenzene (3a) [13]



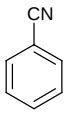
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.35-7.23 (10 H, m), 5.97 (1 H, s), 1.25 (9 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 140.5, 128.3, 127.8, 87.4, 80.6, 26.7; ν_{max}/cm^{-1} 3089, 3064, 3031, 2979, 2931, 1950, 1882, 1807, 1602, 1495, 1475, 1453, 1386, 1363, 1256, 1197, 1015, 883, 759, 741, 698, 657,623; Elemental Analysis: C, 79.68; H, 7.48; calc.: C, 79.65; H, 7.86.

(*tert*-butylperoxymethanetriyl)tribenzene (3b) [10]



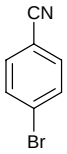
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.41-7.38 (6 H, m), 7.30-7.24 (9 H, m), 1.02 (9 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 143.7, 129.4, 127.4, 127.1, 90.8, 79.8, 26.5; ν_{max}/cm^{-1} 3089, 3060, 3025, 2979, 2930, 1598, 1492, 1449, 1363, 1196, 1000, 901, 878, 776, 758, 700, 646, 634.

benzonitrile (6a) [14]



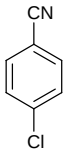
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.68-7.65 (2 H, m), 7.61-7.59 (1 H, m), 7.51-7.45 (2 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 132.7, 132.0, 129.1, 118.8, 112.2. GC-MS calc. C_7H_4BrN: 103, found: 103.

4-bromobenzonitrile (6b) [15]



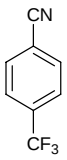
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.64 (2 H, d, *J* 8.7 Hz), 7.53 (2 H, d, *J* 8.7 Hz); δ_C (75 MHz; $CDCl_3$; Me_4Si) 133.3, 132.4, 127.8, 117.9, 111.1. GC-MS calc. C_7H_4BrN: 182, found: 182.

4-chlorobenzonitrile (6c) [14]



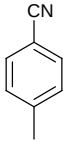
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.60 (2 H, d, *J* 8.4 Hz), 7.47 (2 H, d, *J* 8.4 Hz); δ_C (75 MHz; $CDCl_3$; Me_4Si) 139.6, 133.4, 129.7, 118.0, 110.9. GC-MS calc. C_7H_4ClN: 137, found: 137.

4-(trifluoromethyl)benzonitrile (6d) [16]



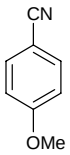
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.83-7.75 (4 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 134.5 (q, *J* 33.2 Hz), 132.8, 126.2 (q, *J* 3.8 Hz), 123.1 (q, *J* 271.3 Hz), 117.5, 116.1. GC-MS calc. C_8H_7N: 171, found: 171.

4-methylbenzonitrile (6e) [14]



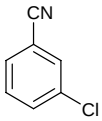
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.53 (2 H, d, *J* 8.1 Hz), 7.56 (2 H, d, *J* 8.1 Hz), 2.41 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 143.7, 132.0, 129.9, 119.2, 109.4, 21.8. GC-MS calc. C_8H_7N: 117, found: 117.

4-methoxybenzonitrile (6f) [14]



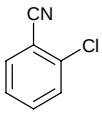
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.59 (2 H, d, *J* 8.7 Hz), 6.95 (2 H, d, *J* 8.7 Hz), 3.86 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 162.8, 133.8, 119.1, 114.7, 103.8, 55.5. GC-MS calc. C_8H_7NO: 133, found: 133.

3-chlorobenzonitrile (6g) [16]



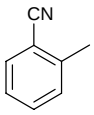
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.64-7.51 (3 H, m), 7.45-7.40 (1 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 135.2, 133.2, 131.9, 130.5, 130.3, 117.4, 114.0. GC-MS calc. C_7H_4ClN: 137, found: 137.

2-chlorobenzonitrile (6h) [17]



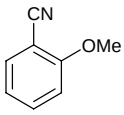
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.70-7.67 (1 H, m), 7.58-7.50 (2 H, m), 7.41-7.35 (1 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 136.8, 134.02, 133.96, 130.1, 116.0, 113.4. GC-MS calc. C_7H_4ClN: 137, found: 137.

2-methylbenzonitrile (6i) [18]



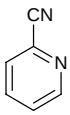
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.60-7.58 (1 H, m), 7.48-7.45 (1 H, m), 7.33-7.29 (2 H, m), 2.55 (3 H, s)); δ_C (75 MHz; $CDCl_3$; Me_4Si) 141.9, 132.7, 132.5, 130.3, 126.3, 118.1, 112.8, 20.5. GC-MS calc. C_8H_7N: 117, found: 117.

2-methoxybenzonitrile (6j) [19]



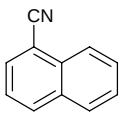
δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.57-7.51 (2 H, m), 7.03-6.96 (2 H, m), 3.93 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 161.1, 134.5, 133.6, 120.7, 116.5, 111.3, 101.5, 56.0. GC-MS calc. C_8H_7N: 133, found: 133.

picolinonitrile (6k) [16]



δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.74-8.73 (1 H, m), 7.88-7.83 (1 H, m), 7.73-7.70 (1 H, m), 7.56-7.52 (1 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 166.3, 155.6, 137.1, 128.6, 127.0. GC-MS calc. C_8H_7N: 104, found: 104.

1-naphthonitrile (6l) [20]

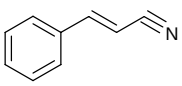


δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.24 (1 H, d, *J* 8.1 Hz), 8.08 (1 H, d, *J* 8.1 Hz), 7.94-7.89 (2 H, m), 7.72-7.59 (2 H, m), 7.55-7.49 (1 H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 133.1, 132.8, 132.5, 132.2, 128.6, 128.5, 127.4, 124.9, 124.8, 117.7, 110.0. GC-MS calc. $C_{11}H_7N$: 153, found: 153.

dodecanenitrile (6m) [19]

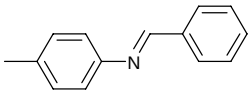
δ_H (300 MHz; $CDCl_3$; Me_4Si) 2.33 (2 H, t, *J* 6.9 Hz), 1.70-1.61 (2 H, m), 1.47-1.42 (2 H, m), 1.27 (16 H, m), 0.88 (2 H, t, *J* 6.6 Hz); δ_C (75 MHz; $CDCl_3$; Me_4Si) 119.9, 32.0, 29.62, 29.58, 29.4, 28.8, 28.7, 25.5, 22.7, 17.2, 14.2. GC-MS calc. $C_{12}H_{23}N$: 181, found: 181.

cinnamonitrile (6n) [13]



δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.46-7.37 (6 H, m), 5.88 (1 H, d, *J* 16.8 Hz)); δ_C (75 MHz; $CDCl_3$; Me_4Si) 150.7, 133.6, 131.3, 129.2, 127.5, 118.2, 96.5. GC-MS calc. C_9H_7N: 129, found: 129.

(E)-N-benzylidene-4-methylaniline [21]



δ_H (300 MHz; $CDCl_3$; Me_4Si) 8.46 (1 H, s), 7.91-7.88 (2 H, m), 7.47-7.45 (3 H, m), 7.21-7.12 (4 H, m), 2.37 (3 H, s); δ_C (75 MHz; $CDCl_3$; Me_4Si) 159.3, 149.3, 136.3, 135.6, 131.0, 129.7, 128.64, 128.59, 120.8, 20.9. GC-MS calc. C_9H_7N: 195, found: 195.

References and Notes:

6 M. Hirano, T. Morimoto, *Bull. Chem. Soc. Jpn.,* 1989, **62**, 4069-4071.

7 S. Sravber, Z. Planinšek, I. Košir, M. Zupan, *J. Fluorine Chem.,* 1992, **59**, 409-412.

8 G. V. M. Sharma, T. R Prasad, Rakesh, B. Srinivas, *Synthetic Commun.,* 2004, **35**, 941-950.

9 B. Zhao, X. Lu, *Org. Lett.,* 2006, **8**, 5987-5990.

10 M. Nakanishi, C.Bolm, *Adv. Synth. Catal.,* 2007, **349**, 861-864.

11 E. F. Pratt, S. P. Suskind, *J. Org. Chem.,* 1963, **28**, 638-642.

12 T. A. Crabb, S. L. Soilleux, *J. Chem. Soc., Perkin Trans. 1,* 1985, 1381-1385.

13 D. V. Avila, K. U. Ingold, A. A. D. Nardo, F. Zerbetto, M. Z. Zgierski, J. Lusztyk, *J. Am. Chem. Soc,.* 1995, **117**, 2711-2718.

14 T. Oishi,; K. Yamaguchi,; N. Mizuno, *Angew. Chem. Int. Ed.* 2009, DOI: 10.1002/anie.200900418.

15 S. Chiampanichayakul,; M. Pohmakotr,; V. Reutrakul,; T. Jaipetch,; C. Kuhakarn, *Synthesis* 2008, 2045.

16 C. Yang,; J. M. Williams, *Org. Lett.* 2004, **6**, 2837.

17 F. Drouet,; P. Fontaine,; G. Masson,; J. Zhu, *Synthesis* 2009, 1370.

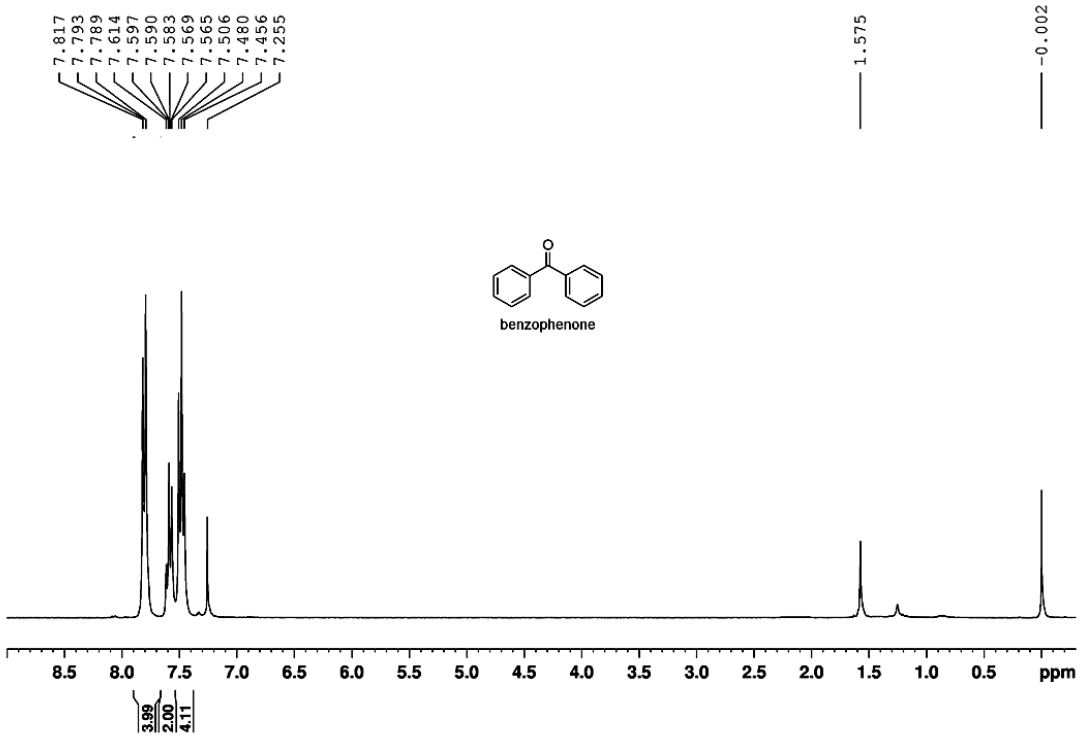
18 O. Grossman,; D. Gelman, *Org. Lett.* 2006, **8**, 1189.

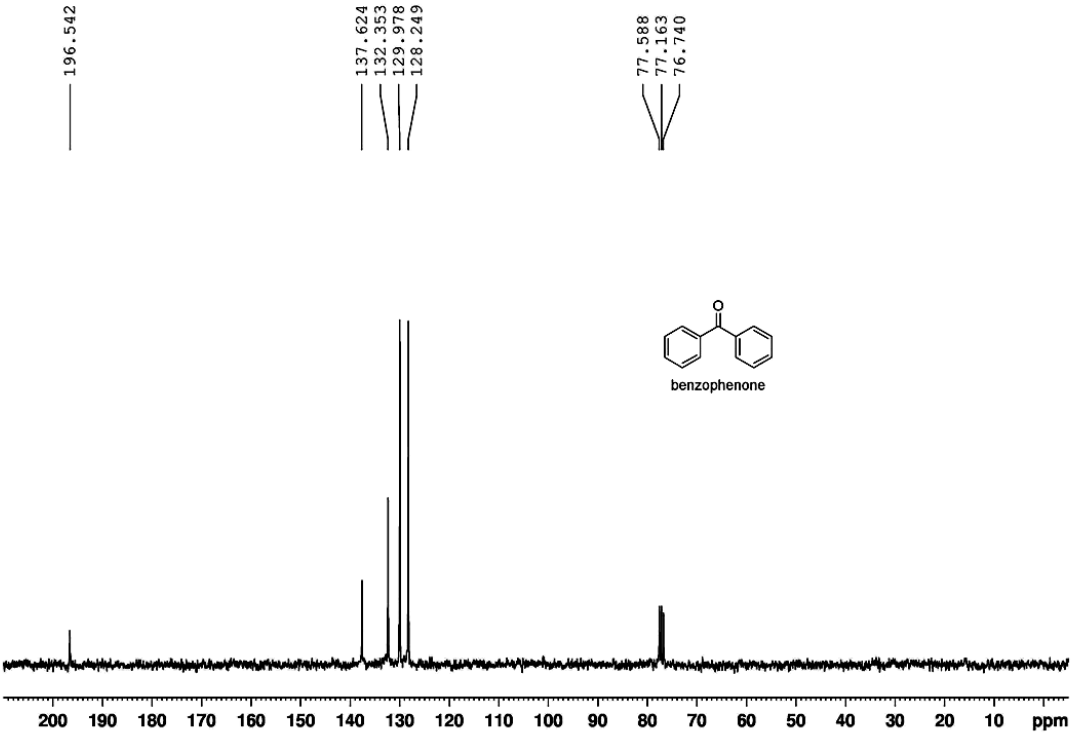
19 F. Li,; J. Chen,; Q. Zhang,; Y. Wang, *Green Chem.* 2008, **10**, 553.

20 S. Gao,; D. Herzig,; B. Wang, *Synthesis* 2001, 544.

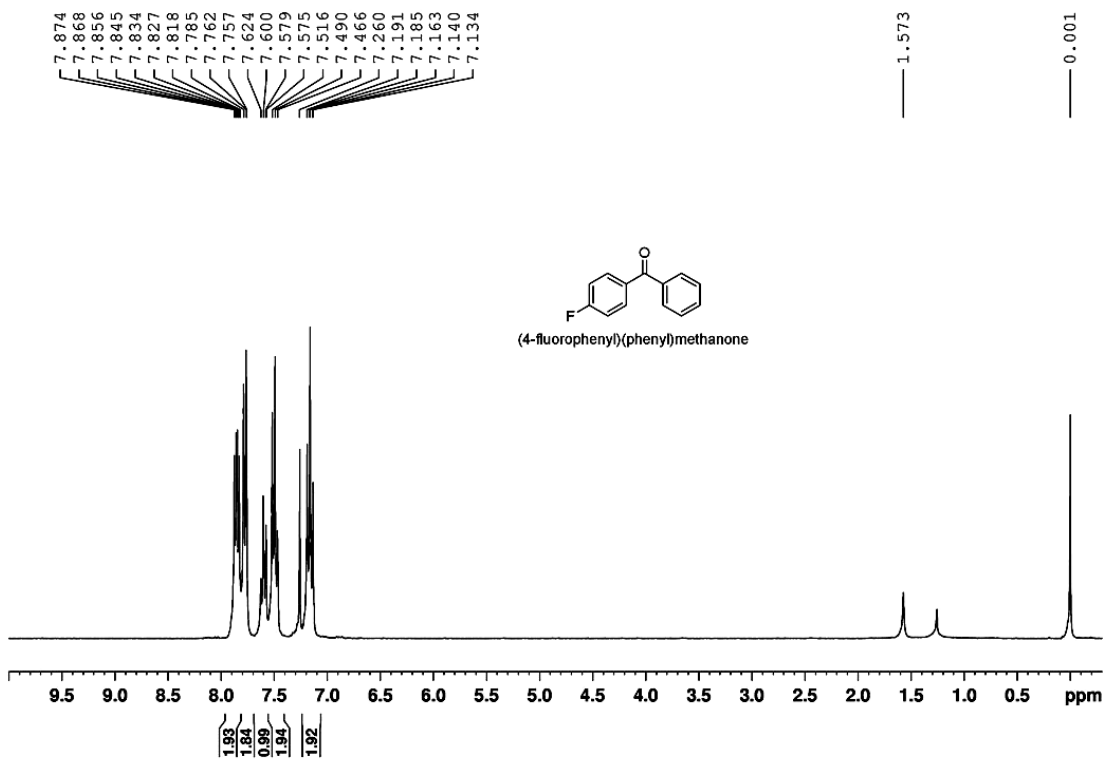
21 J. R. Wang,; Y. Fu,; B. B. Zhang,; X. Cui,; L. Liu,; Q. X. Guo, *Tetradedron Lett.* 2006, **47**, 8293.

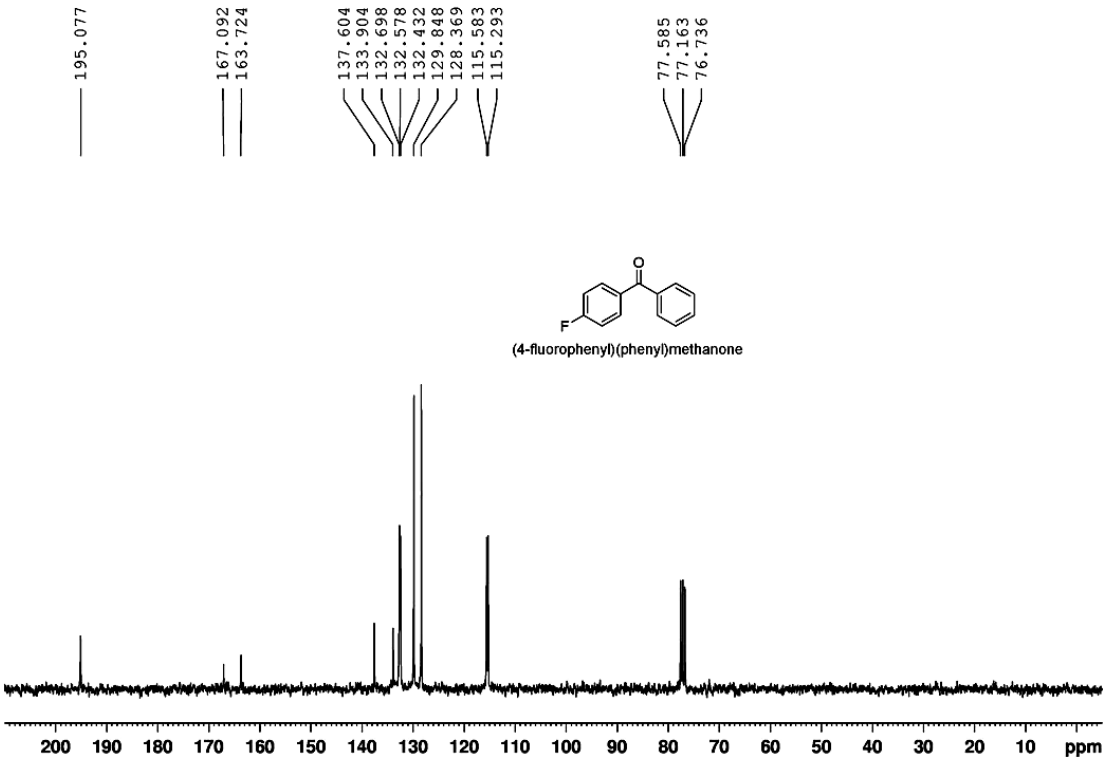
NMR spectra for the products
benzophenone (2a)



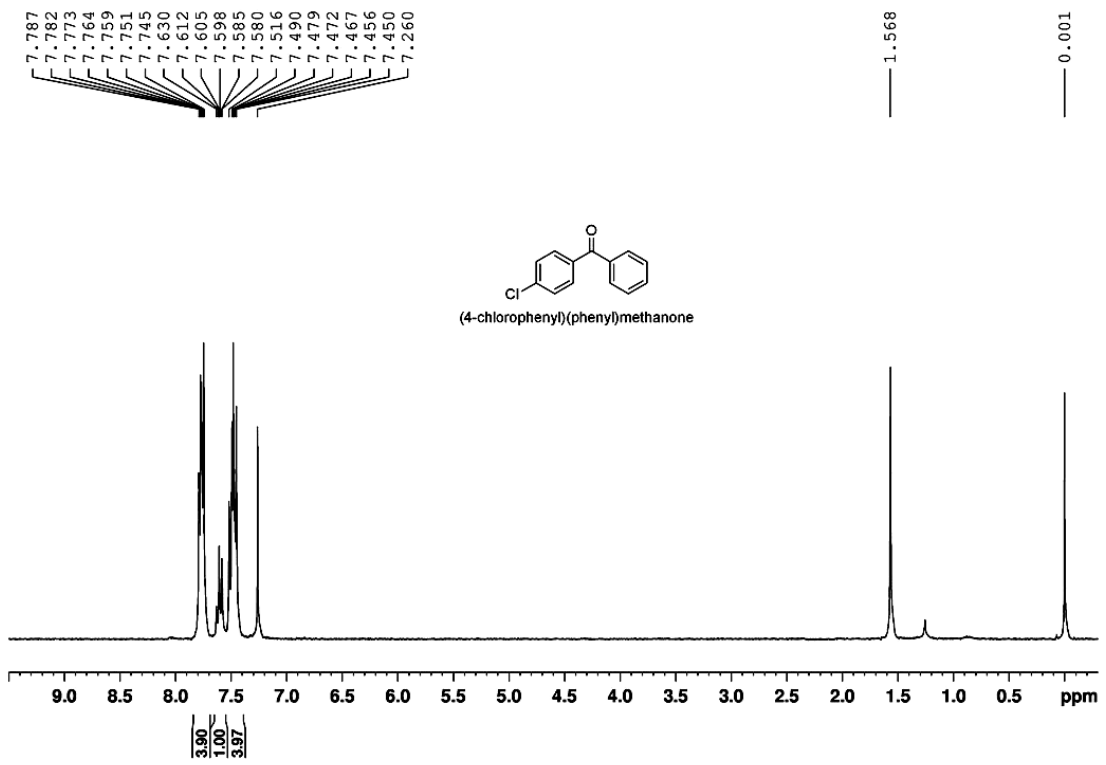


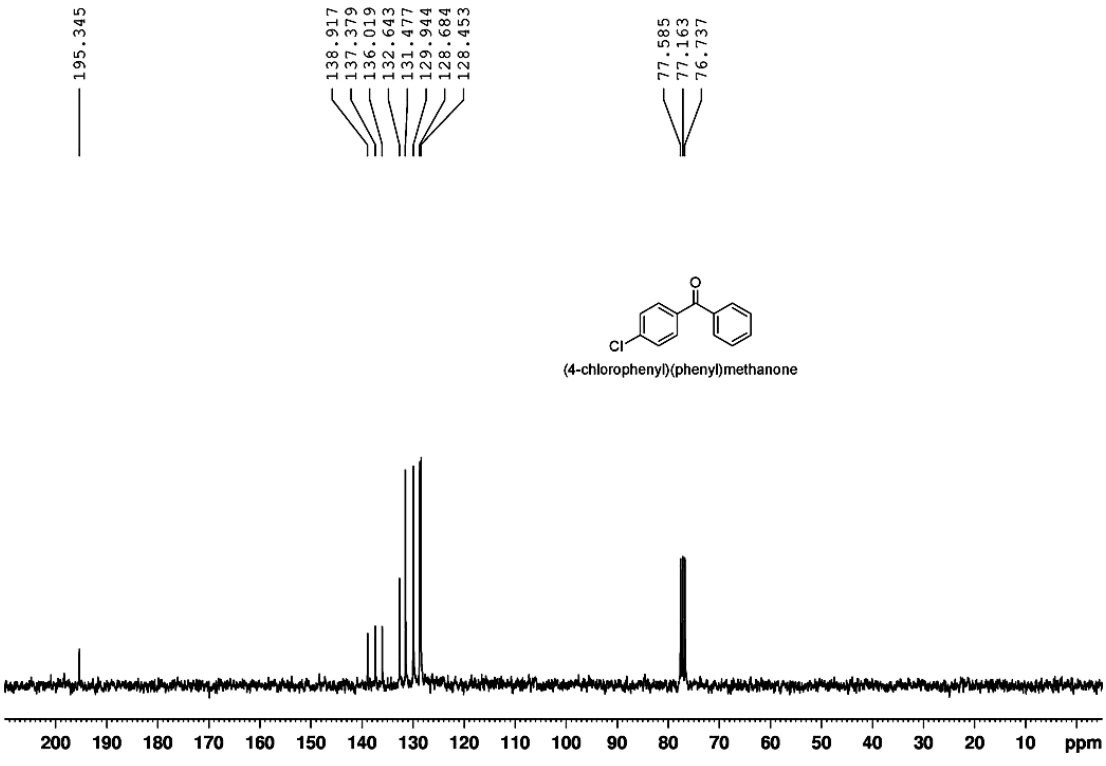
(4-fluorophenyl)(phenyl)methanone (2b)



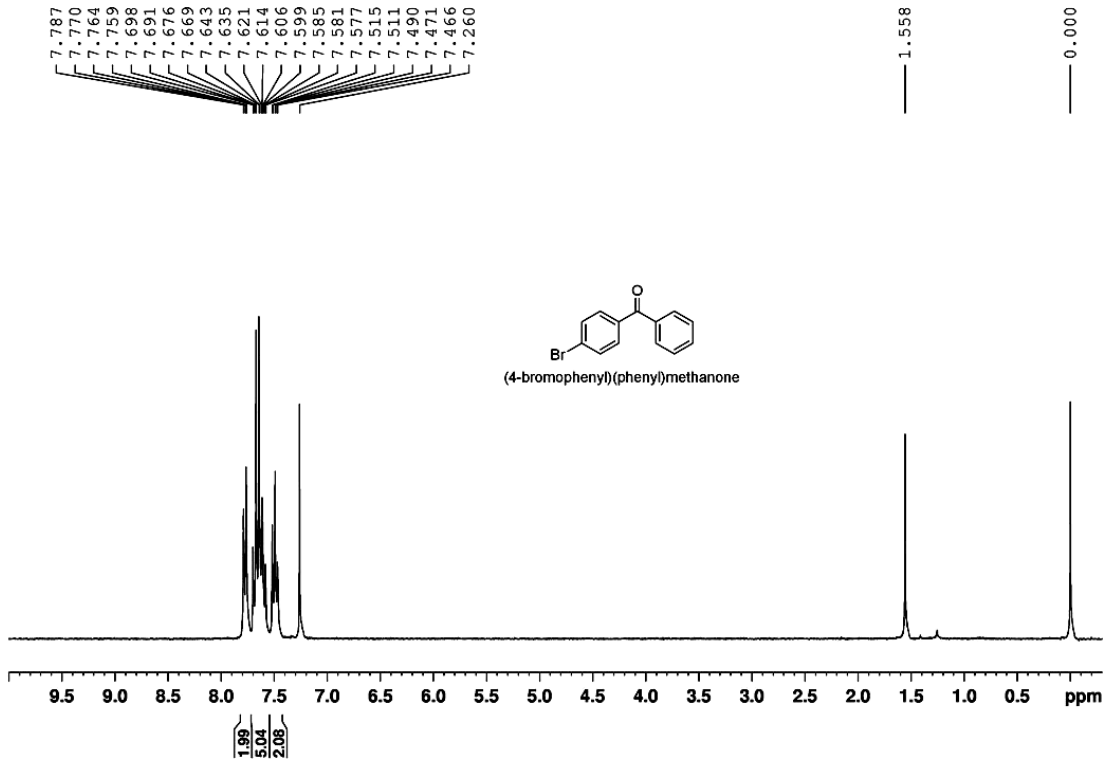


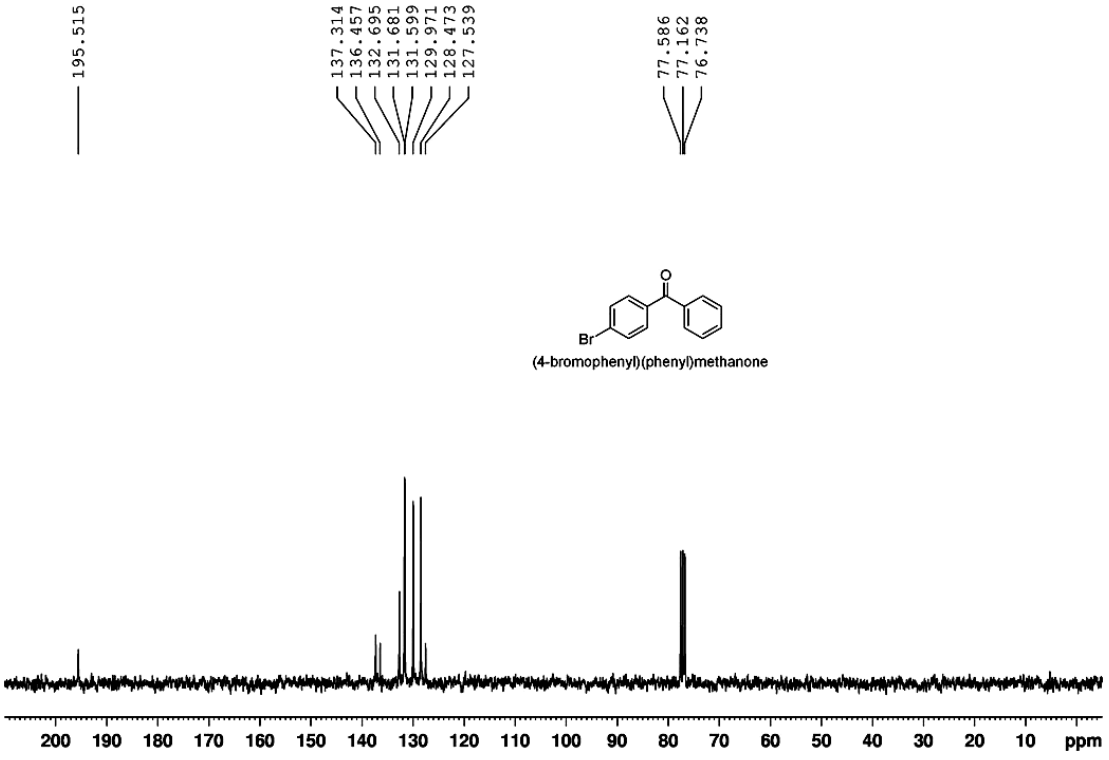
(4-chlorophenyl)(phenyl)methanone (2c)



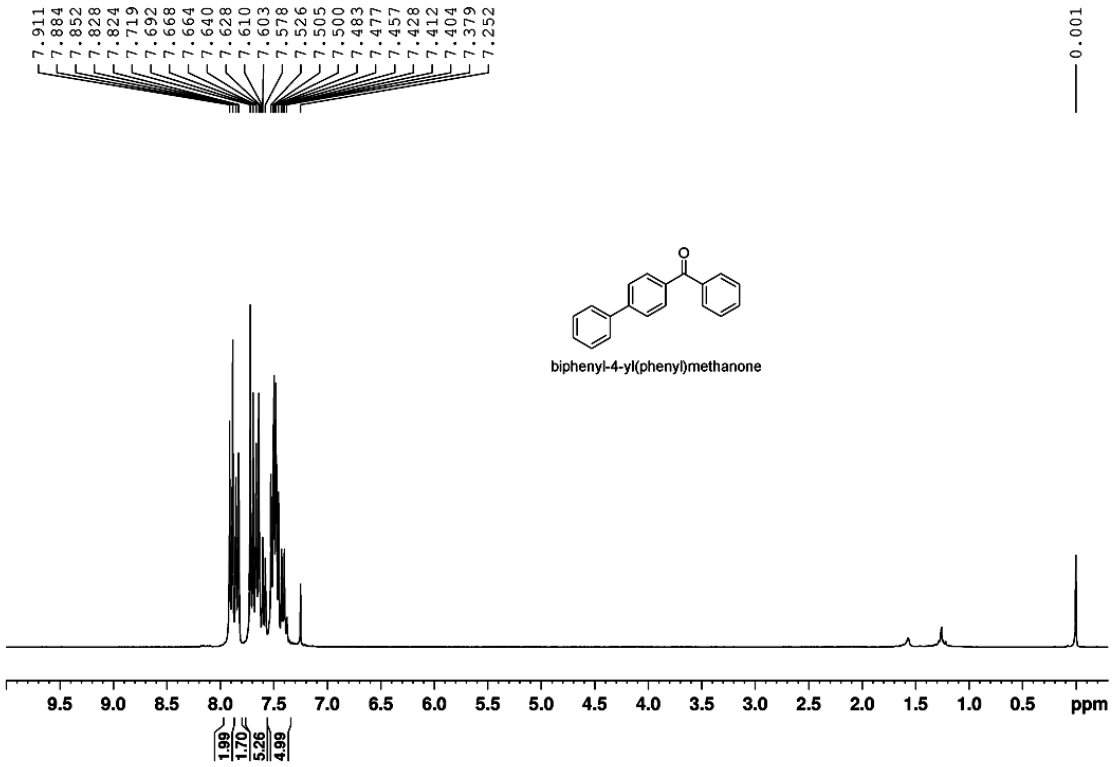


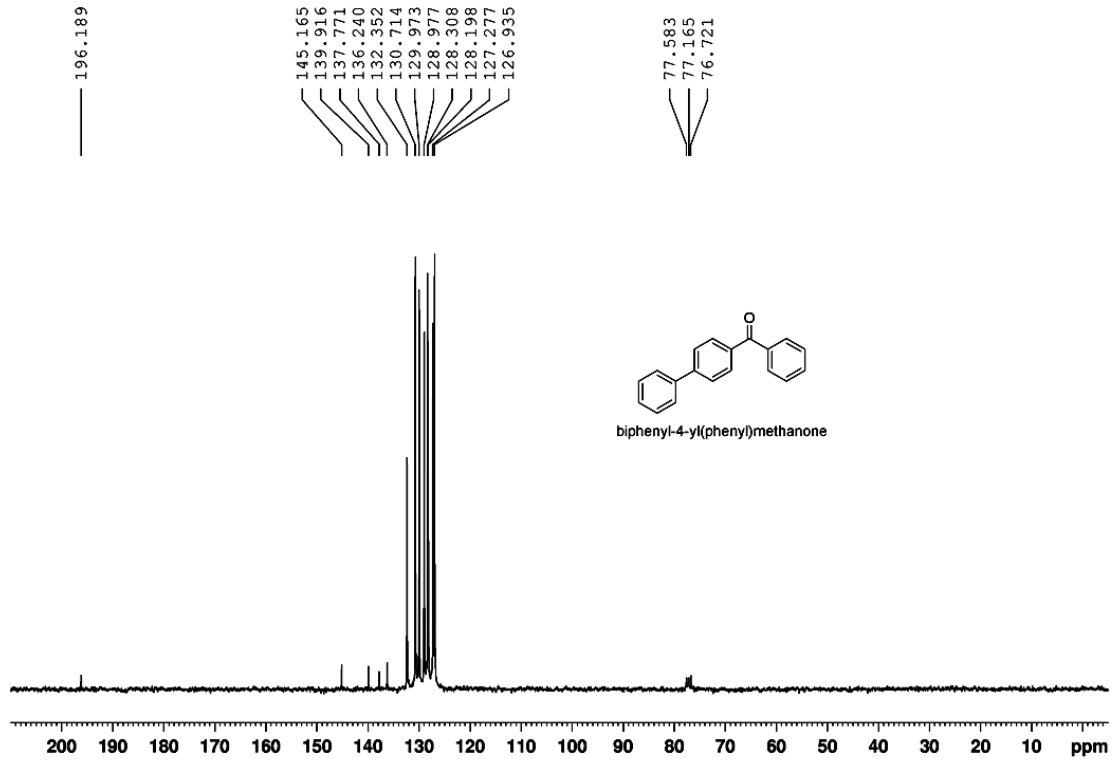
(4-bromophenyl)(phenyl)methanone (2d)



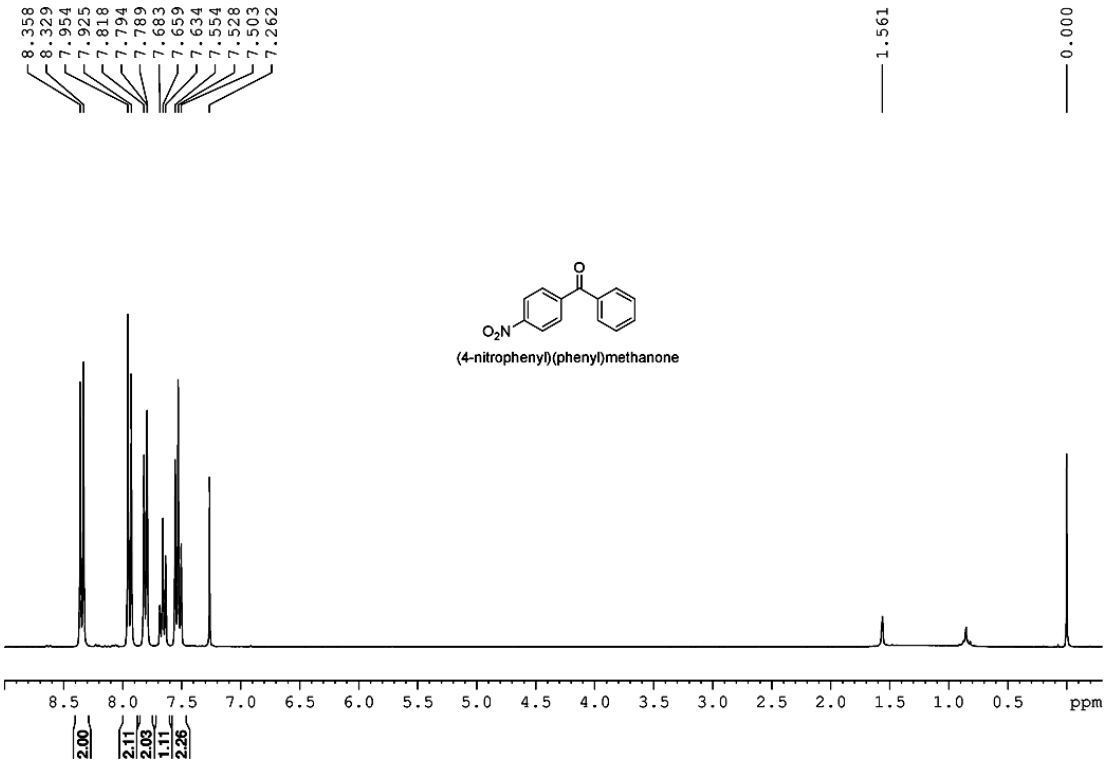


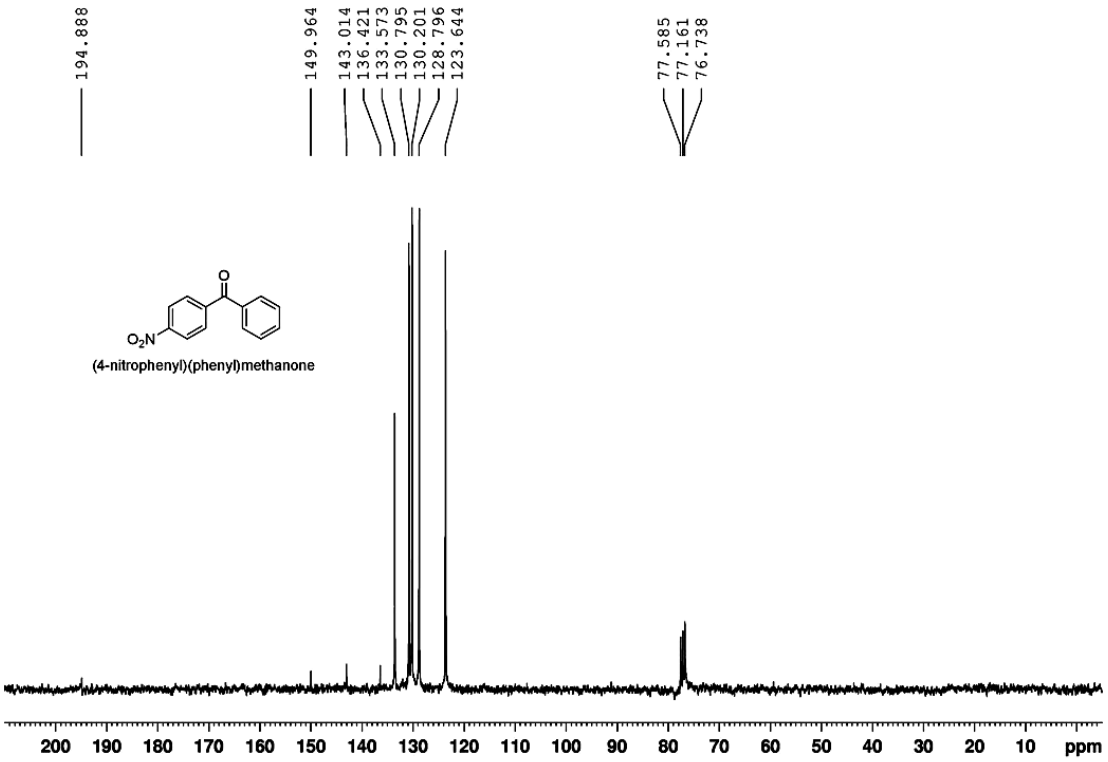
biphenyl-4-yl(phenyl)methanone (2e)



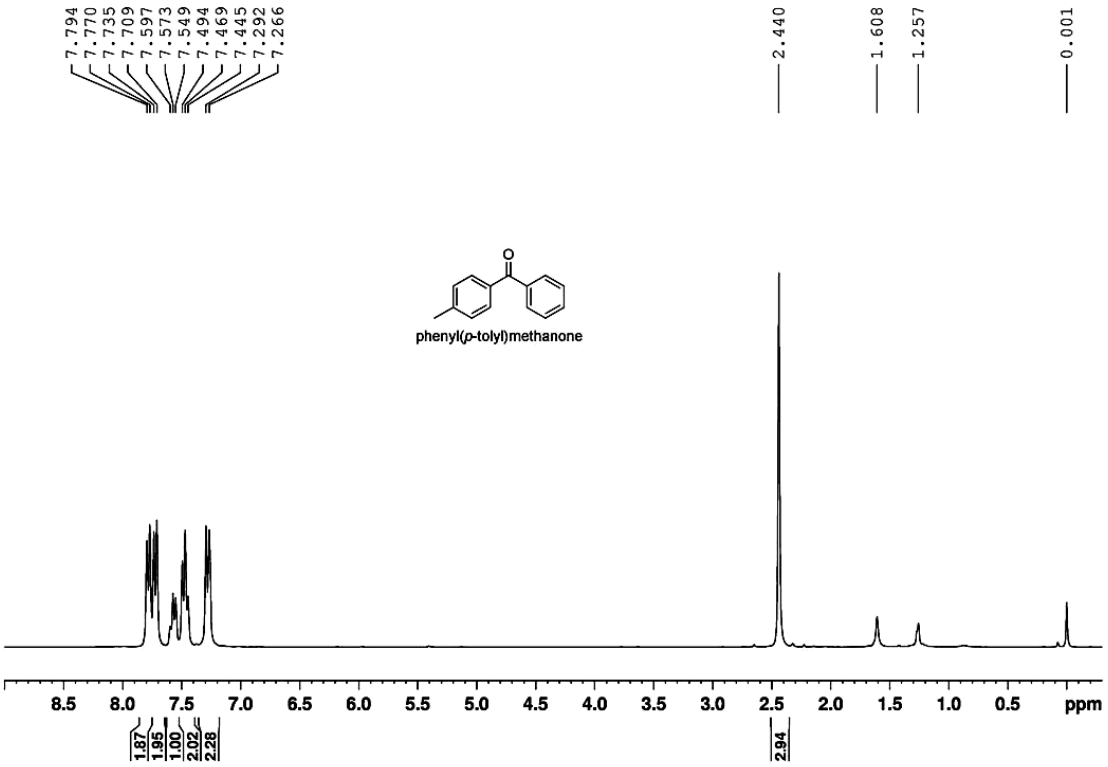


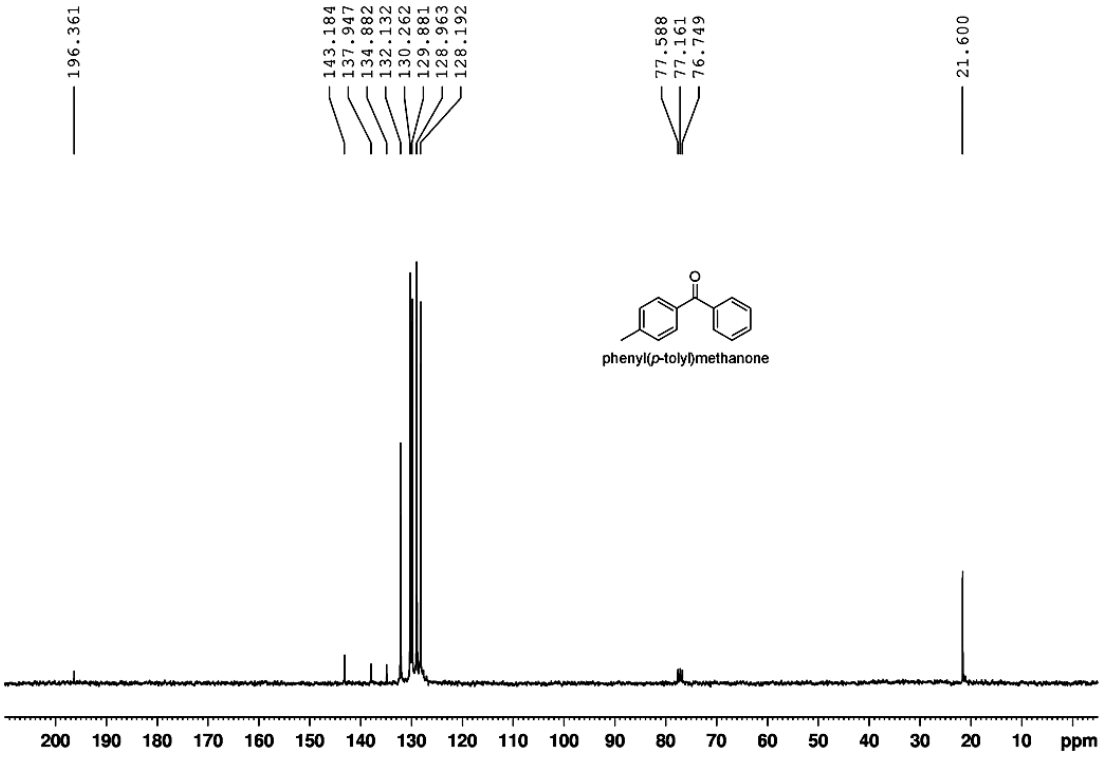
(4-nitrophenyl)(phenyl)methanone (2f)



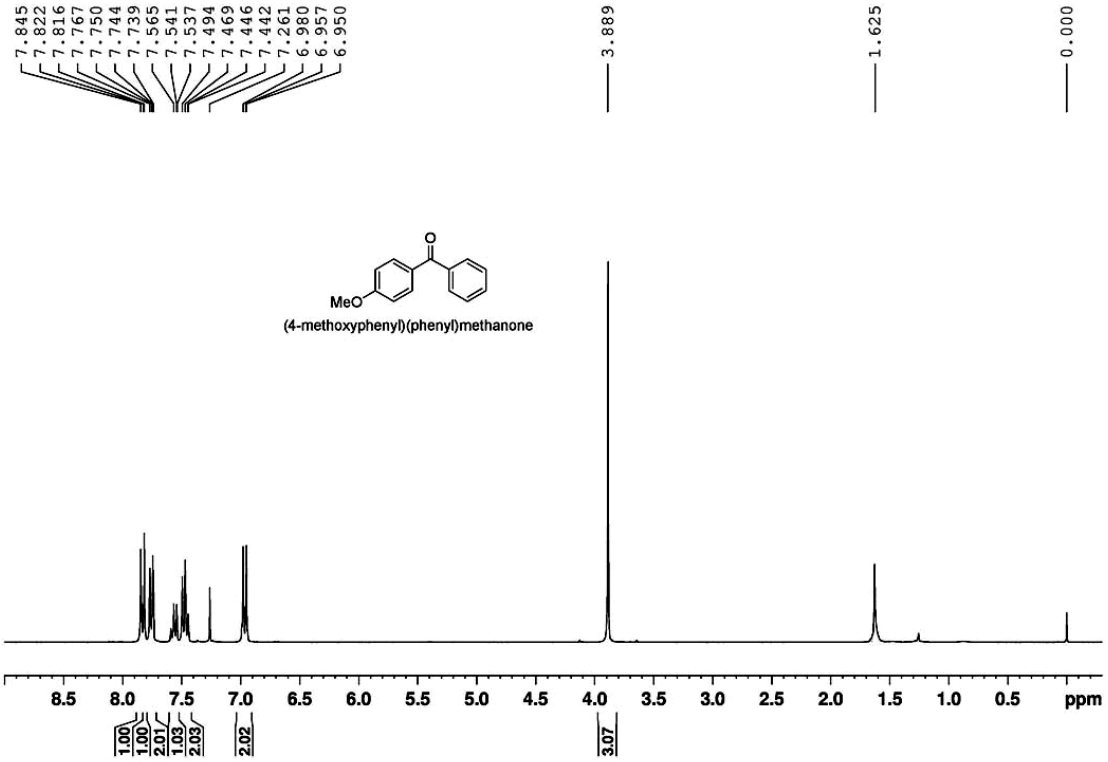


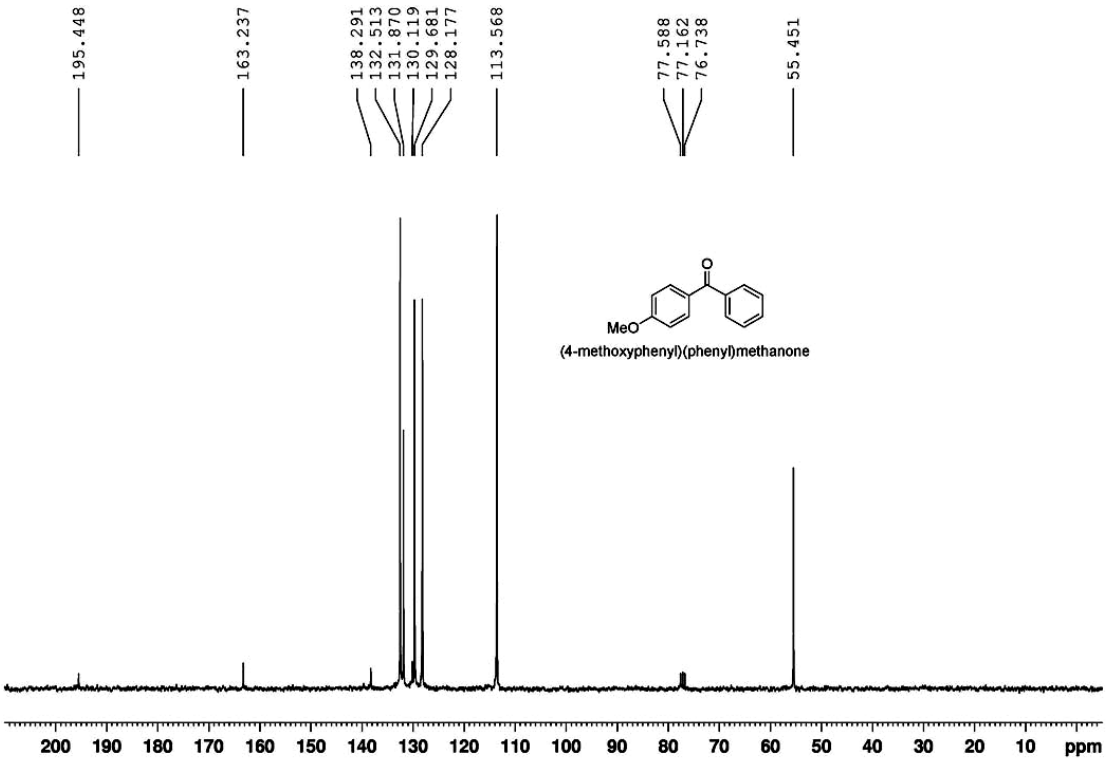
phenyl(p-tolyl)methanone (2g)



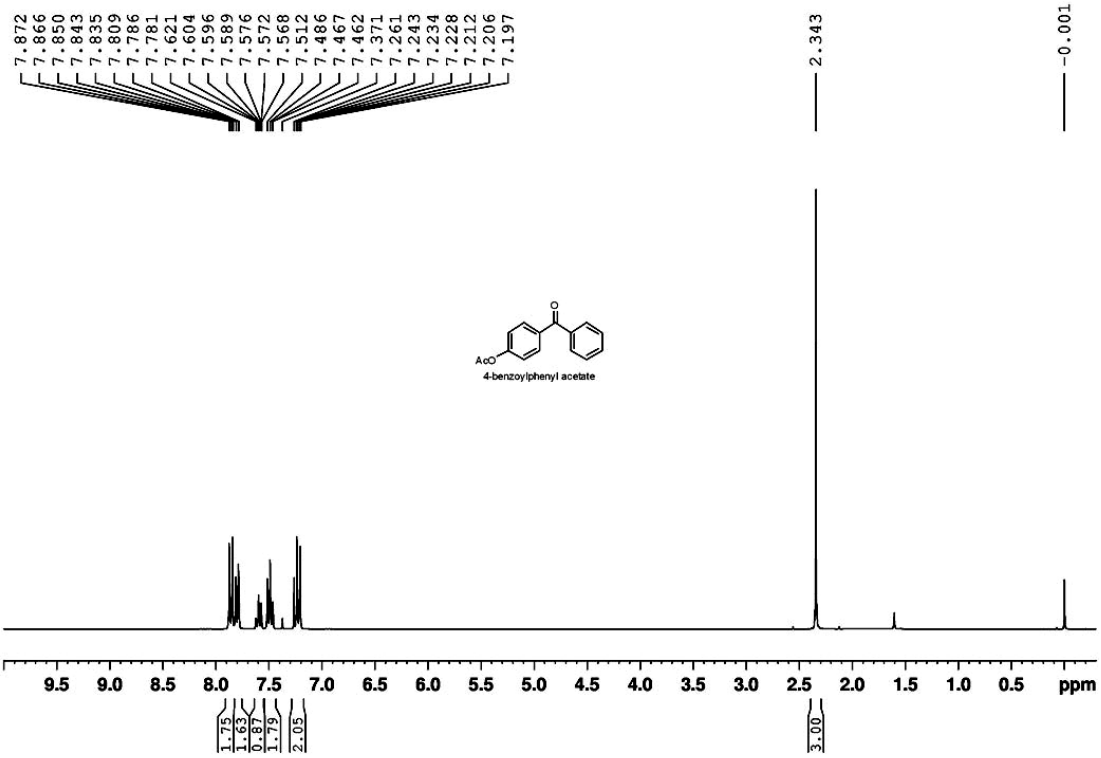


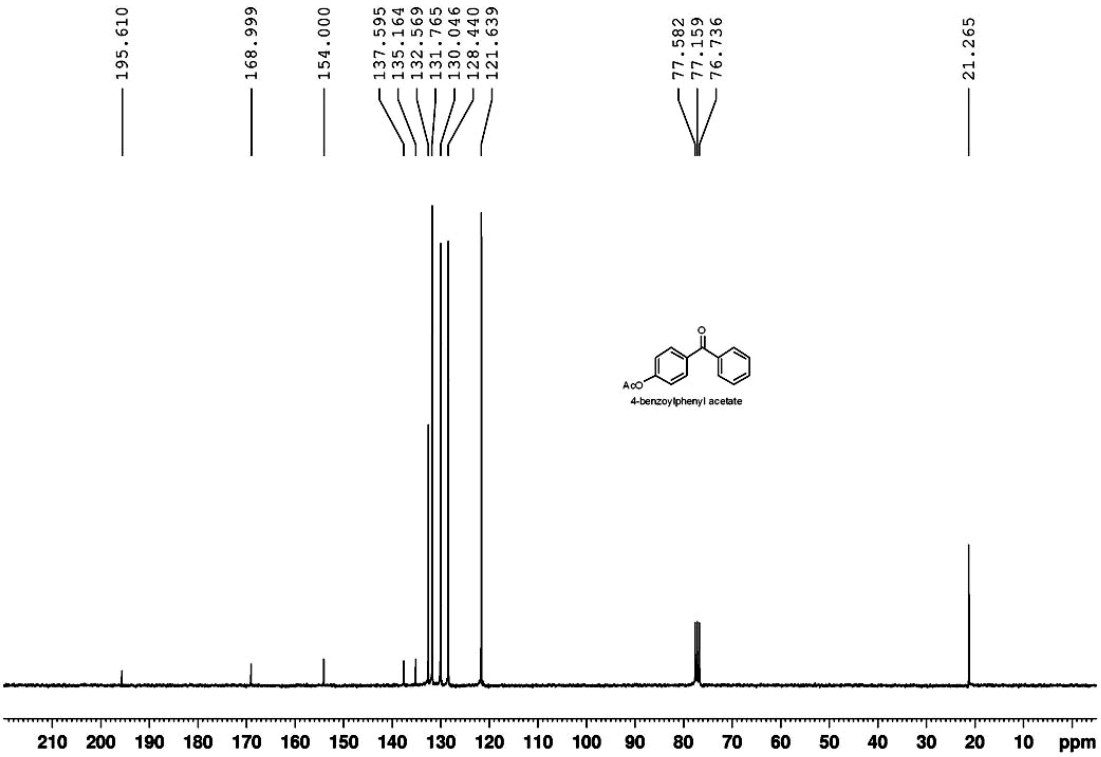
(4-methoxyphenyl)(phenyl)methanone (2h)



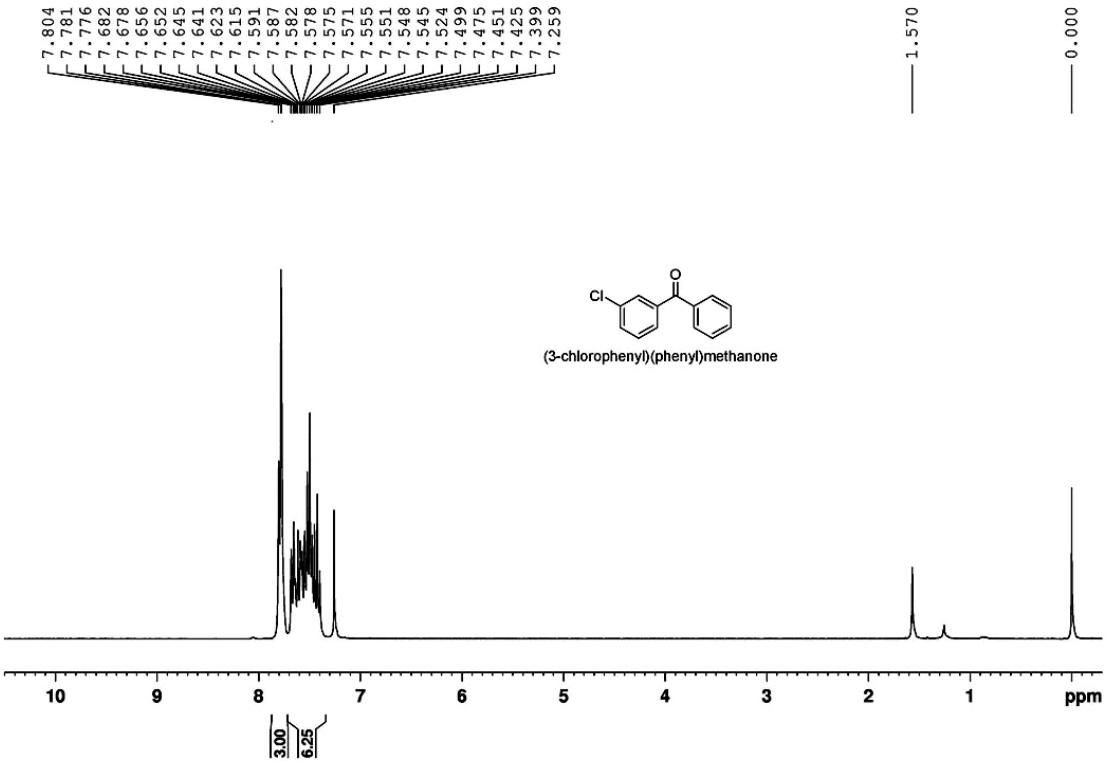


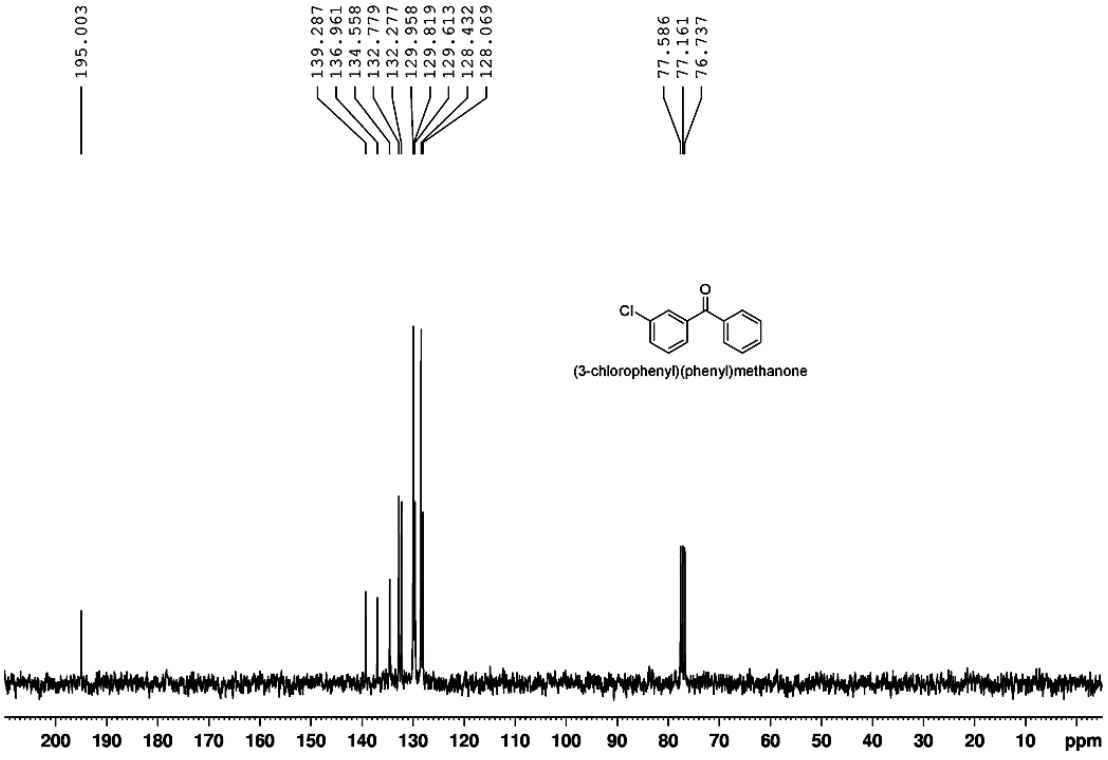
4-benzoylphenyl acetate (2i)



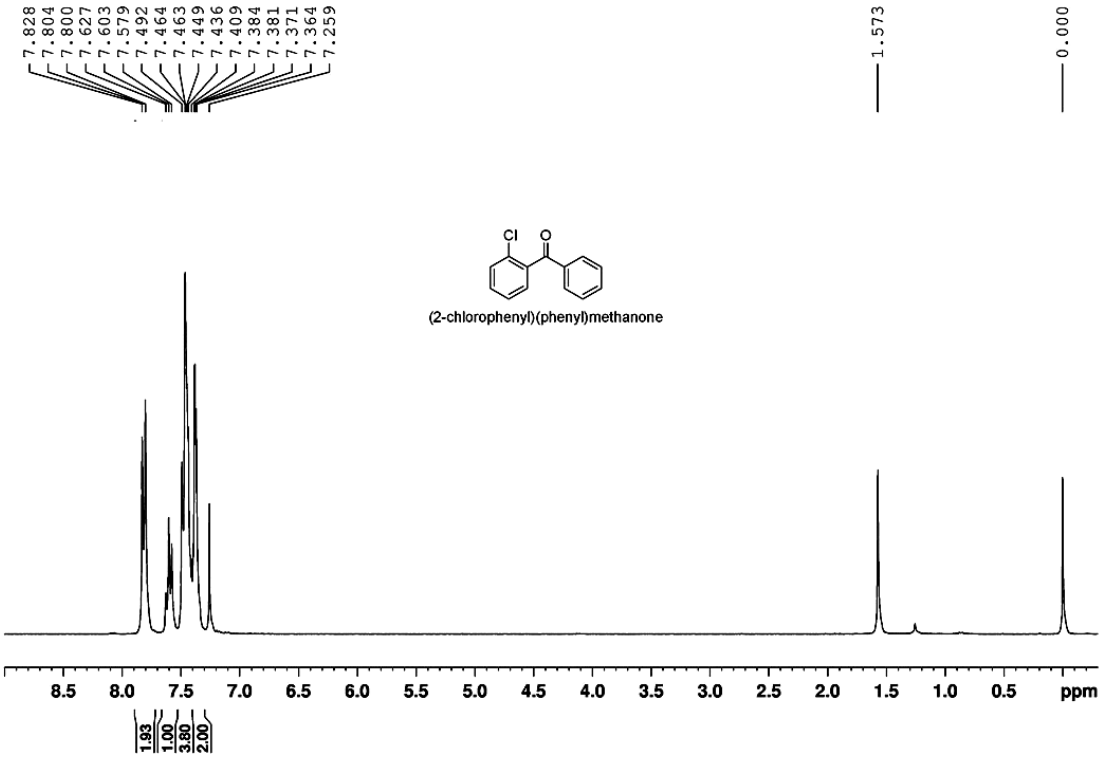


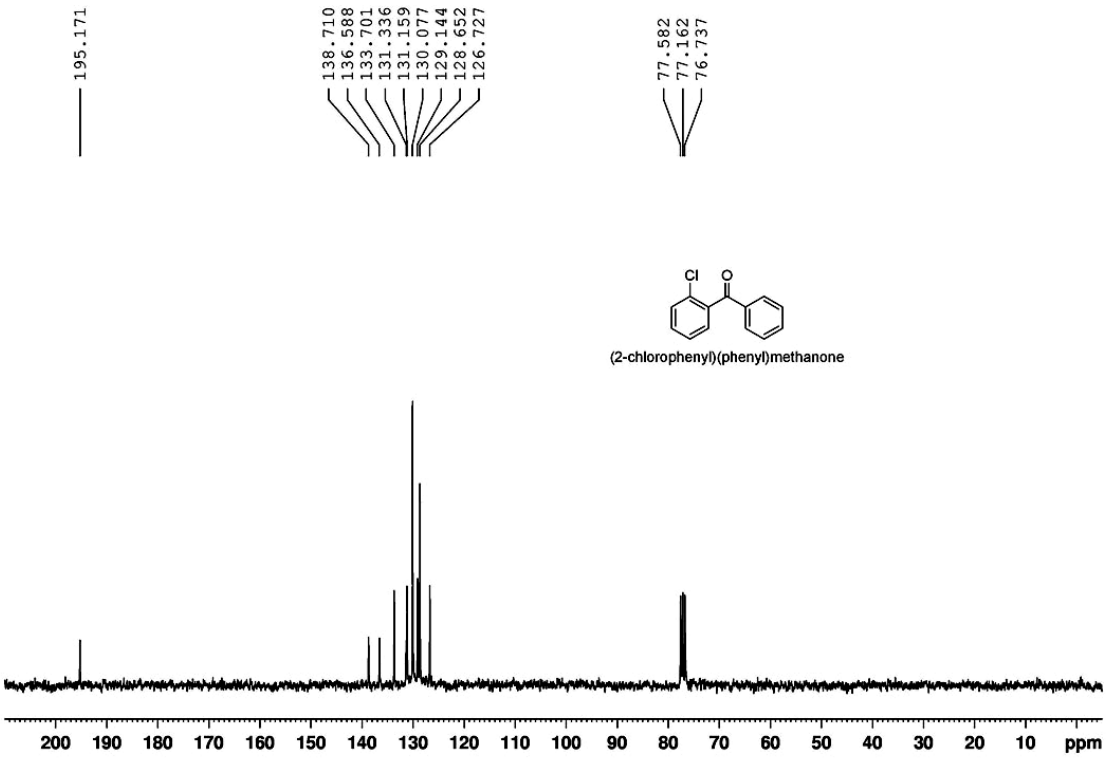
(3-chlorophenyl)(phenyl)methanone (2j)



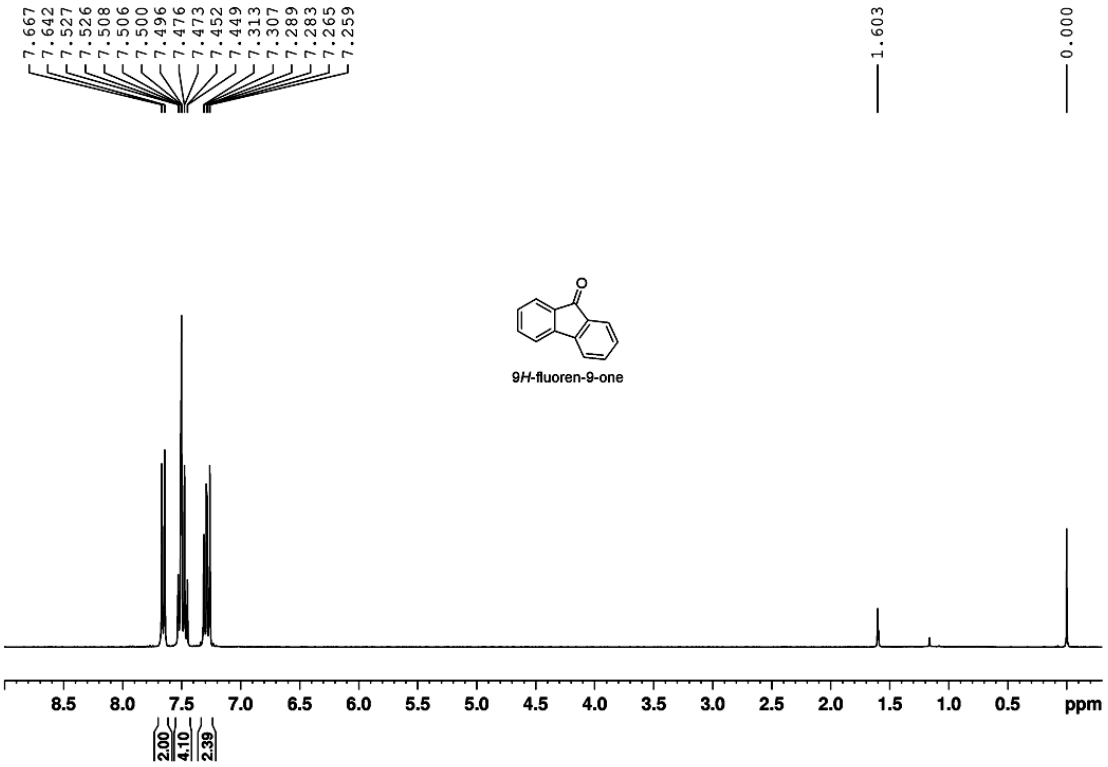


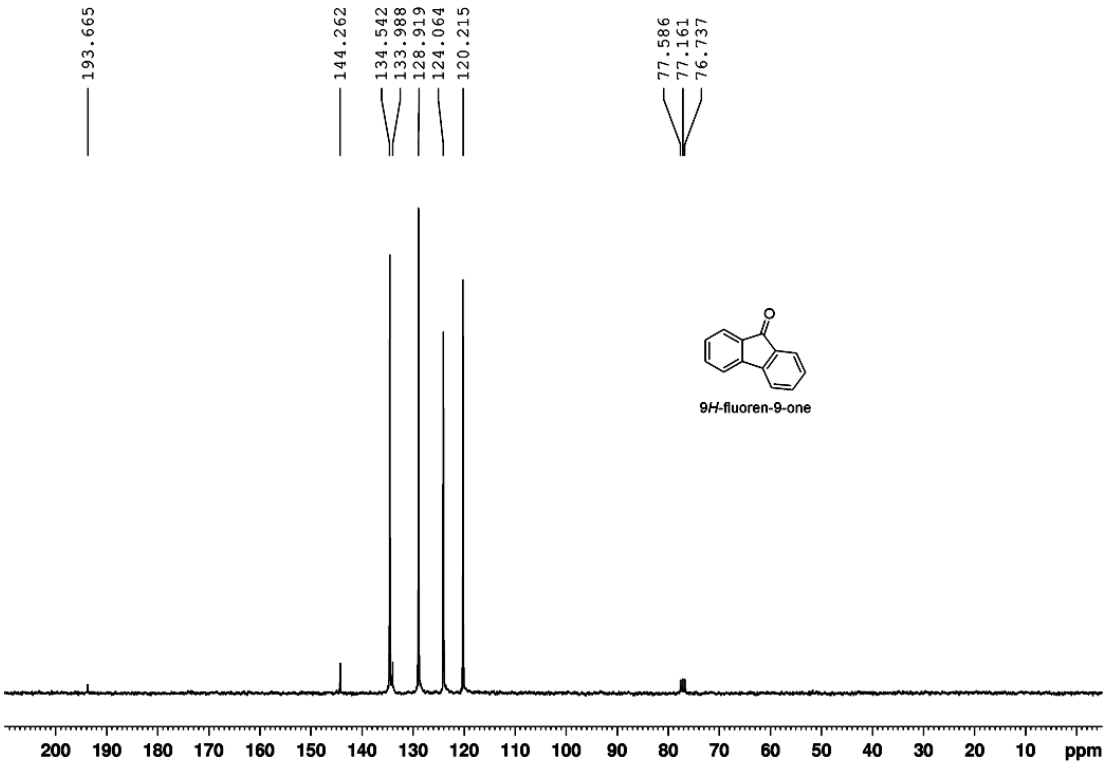
2-chlorophenyl)(phenyl)methanone (2k)



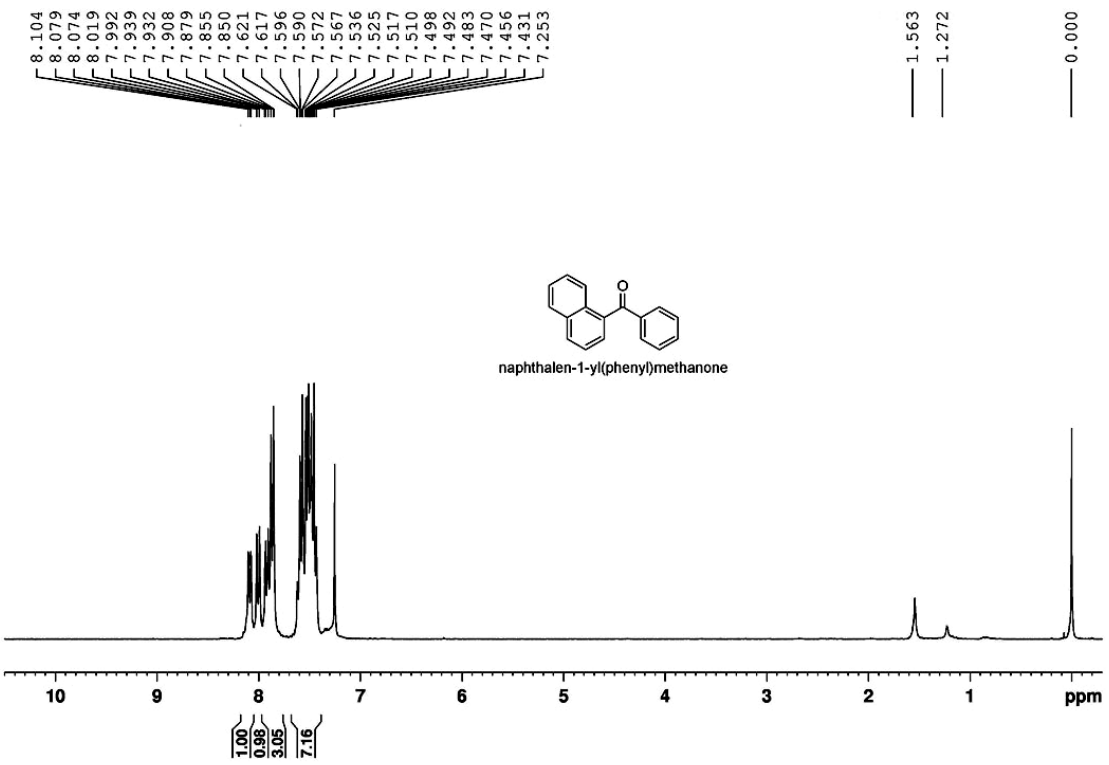


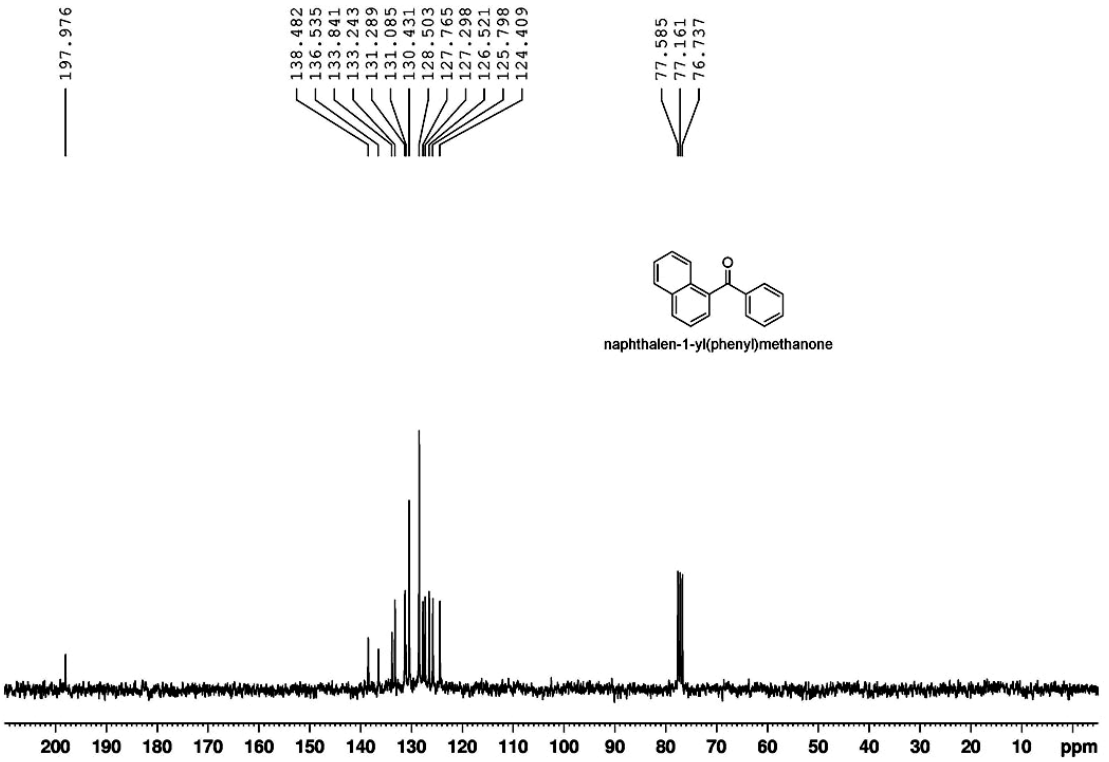
9*H*-fluoren-9-one (2l)



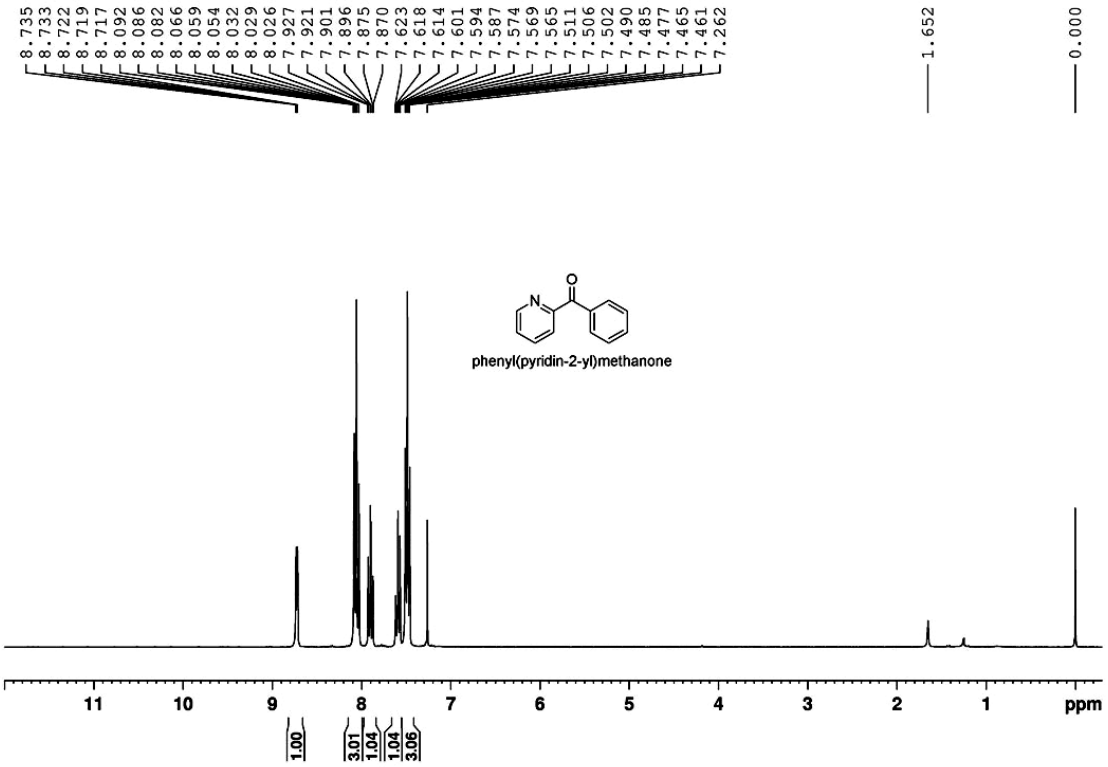


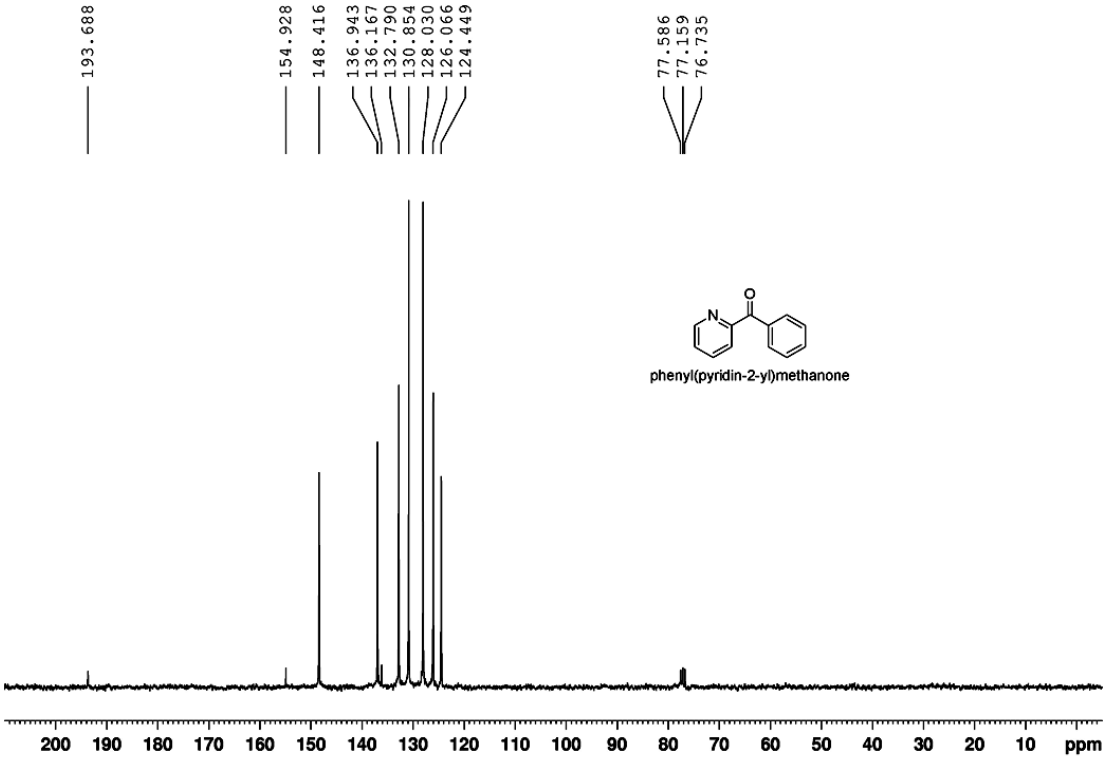
naphthalen-1-yl(phenyl)methanone (2m)



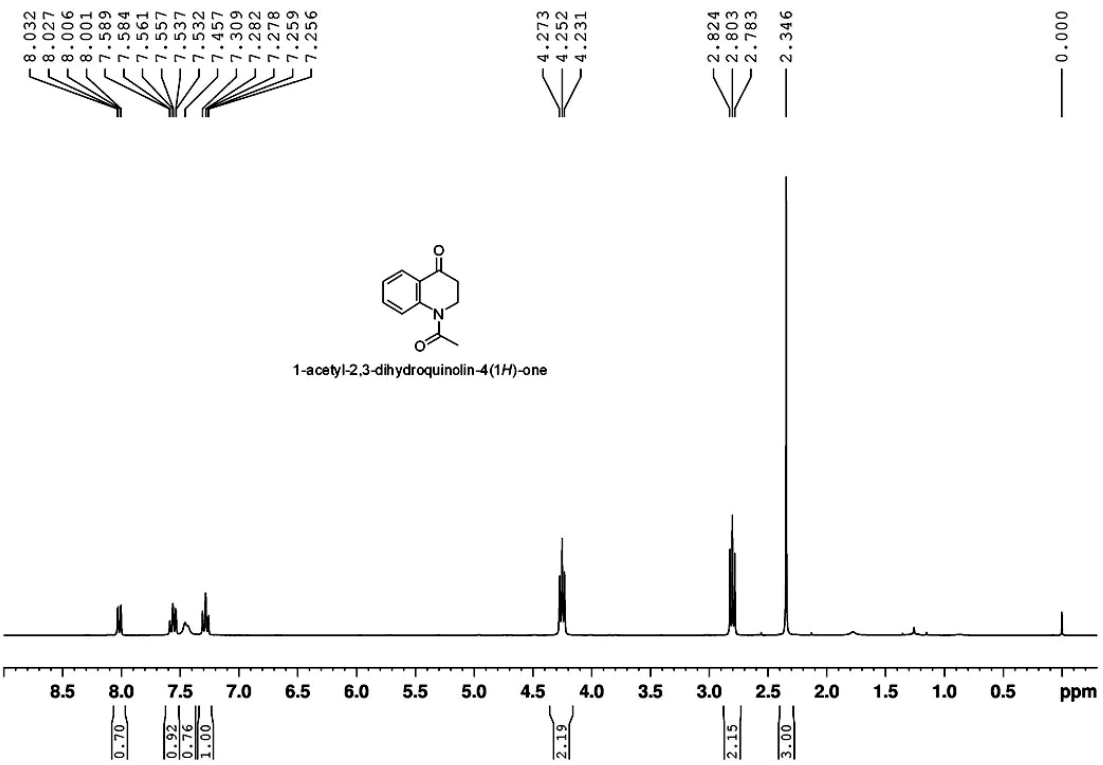


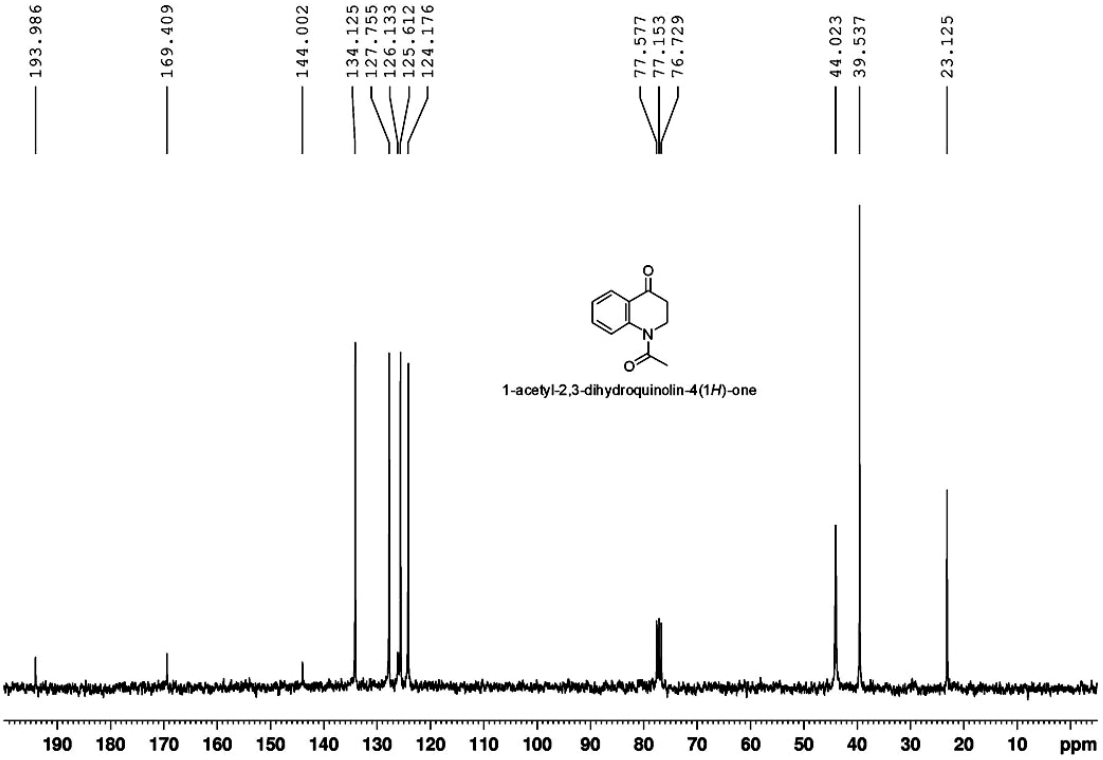
phenyl(pyridin-2-yl)methanone (2n)



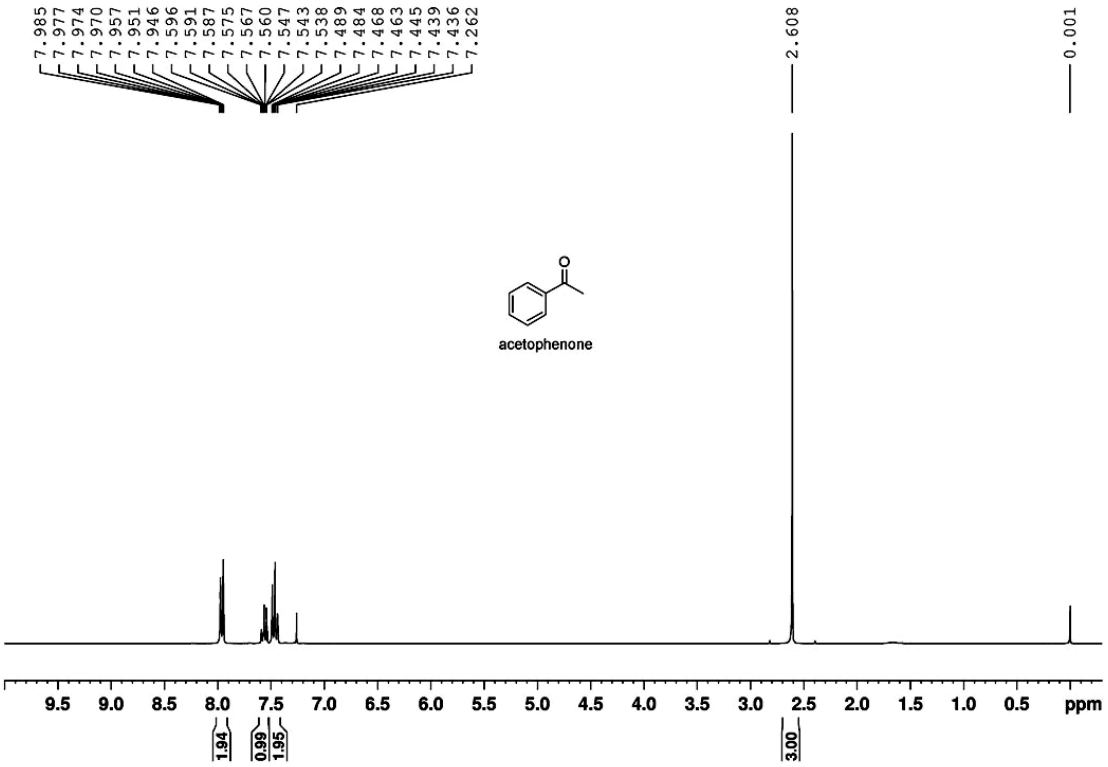


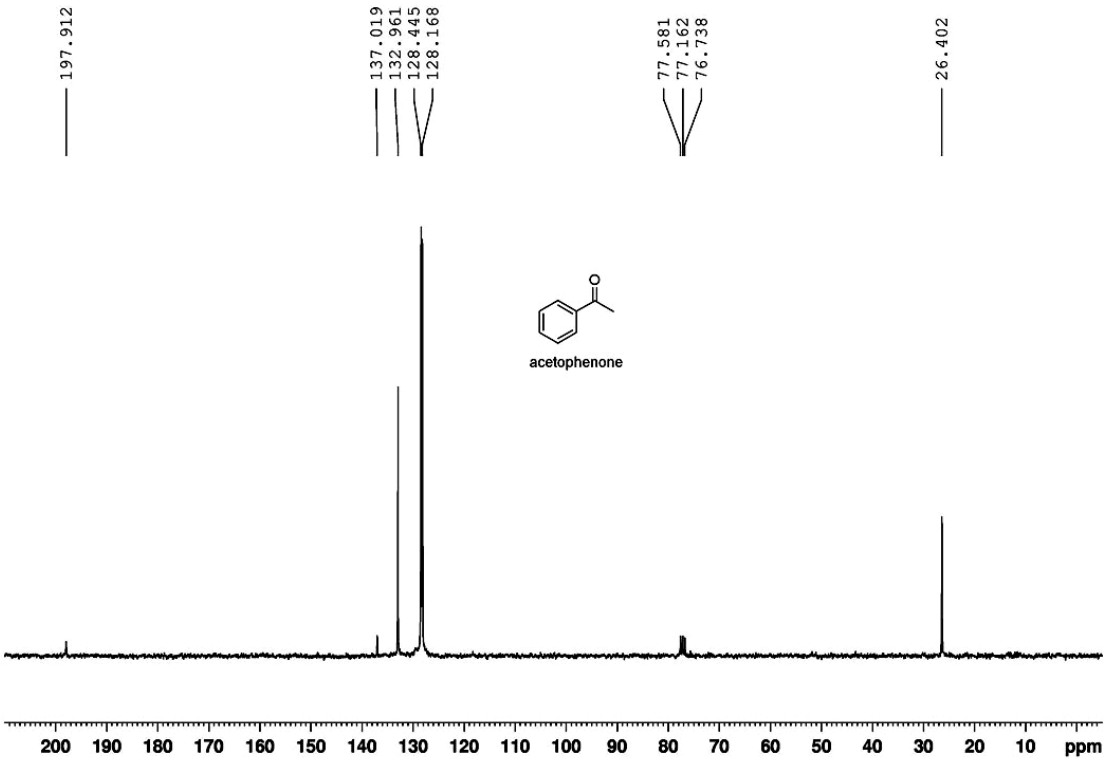
1-acetyl-2,3-dihydroquinolin-4(1H)-one (2o)



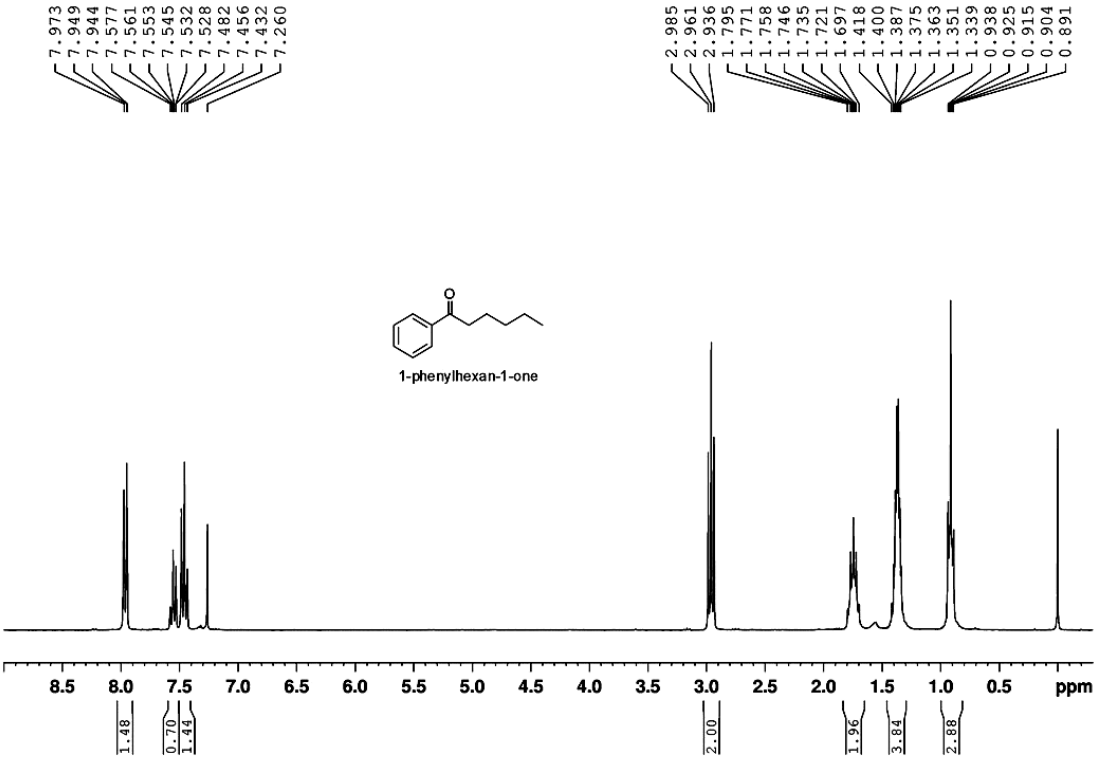


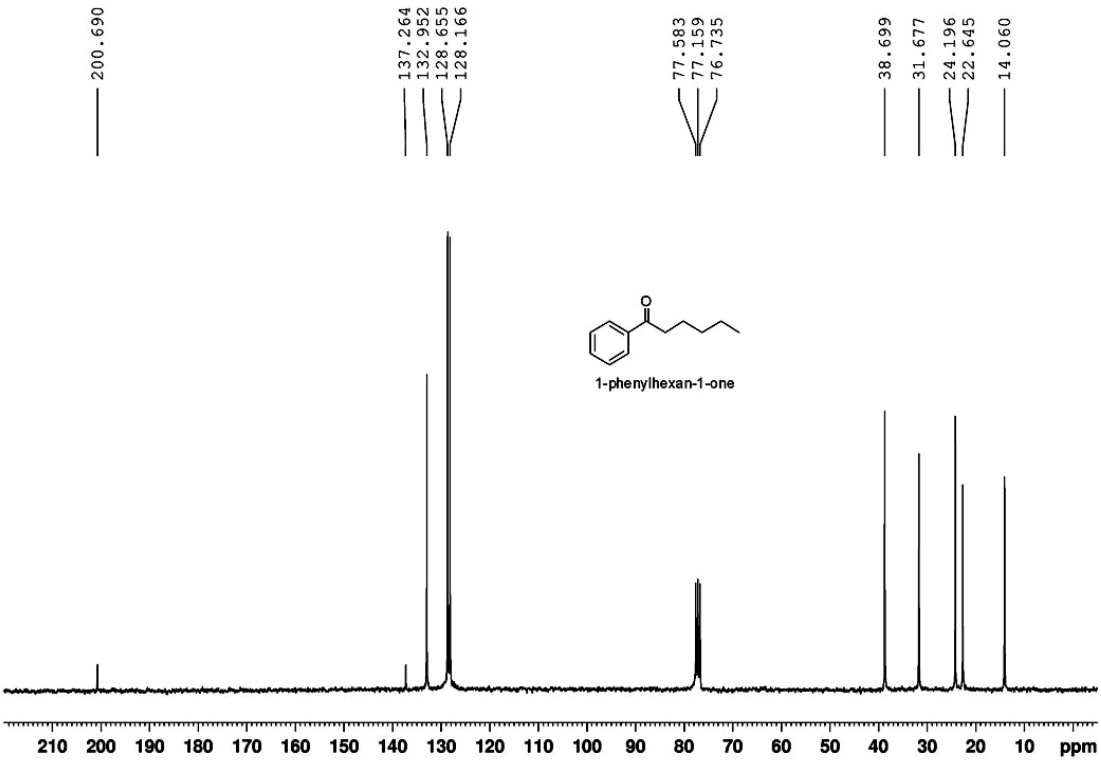
acetophenone (2p)



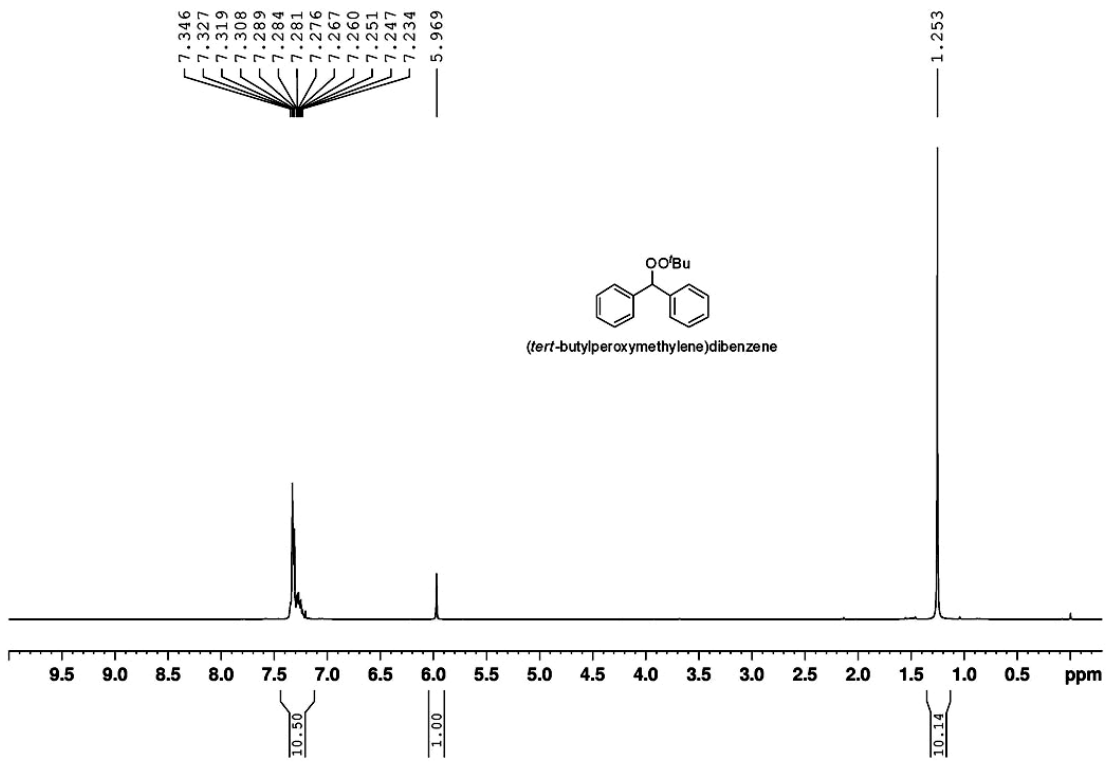


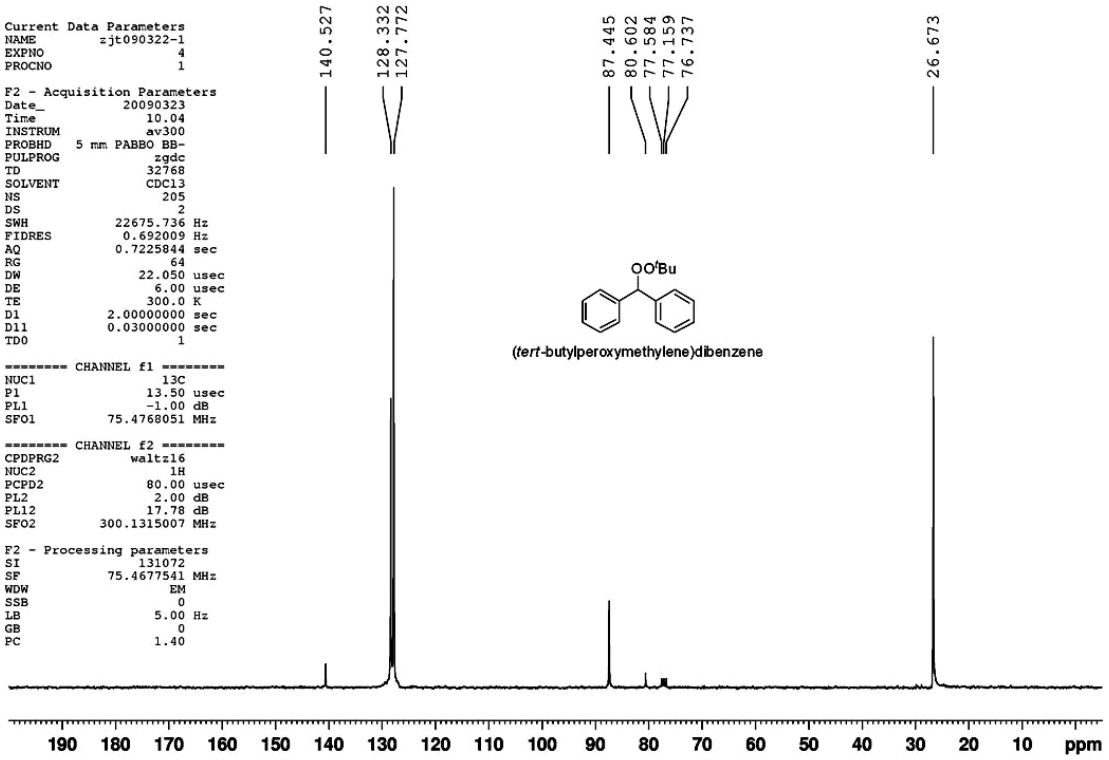
1-phenylhexan-1-one (2q)



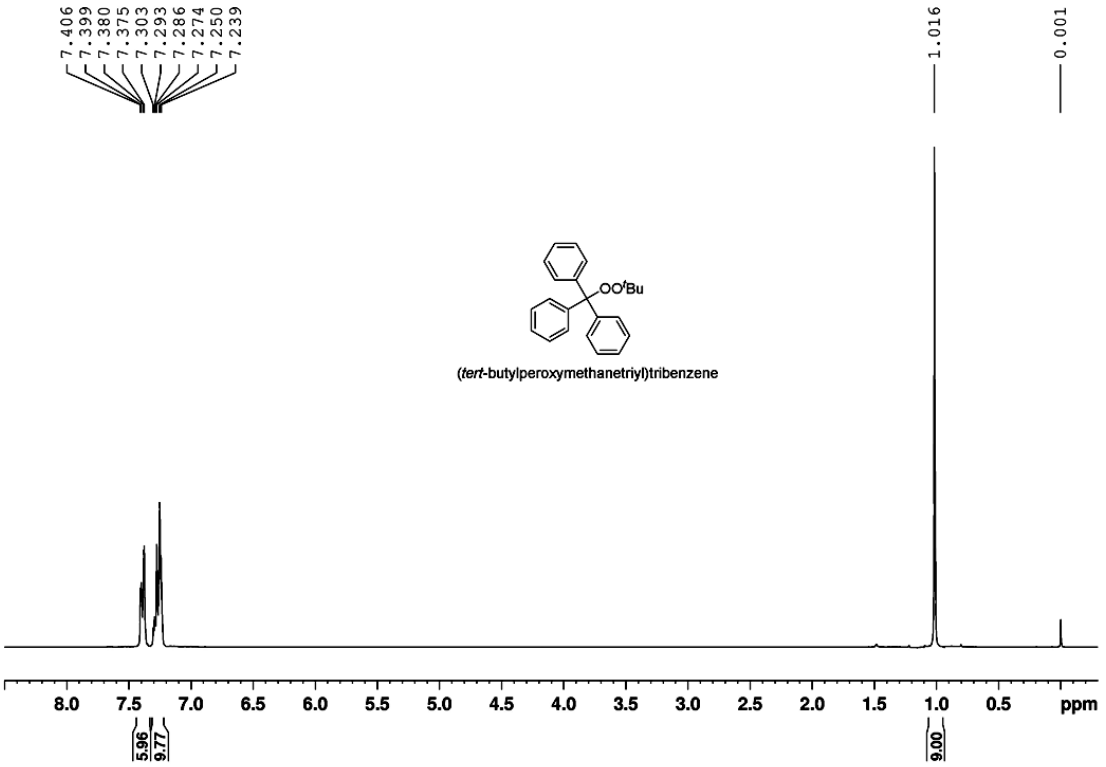


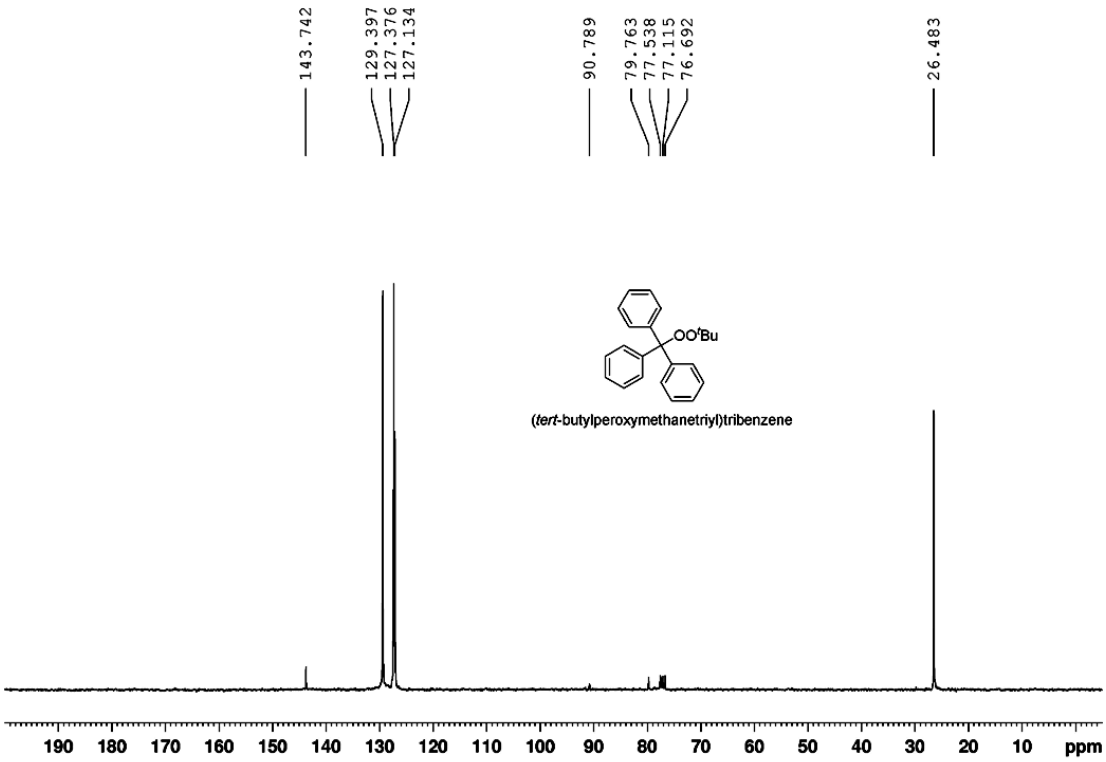
(tert-butylperoxymethylene)dibenzene (3a)



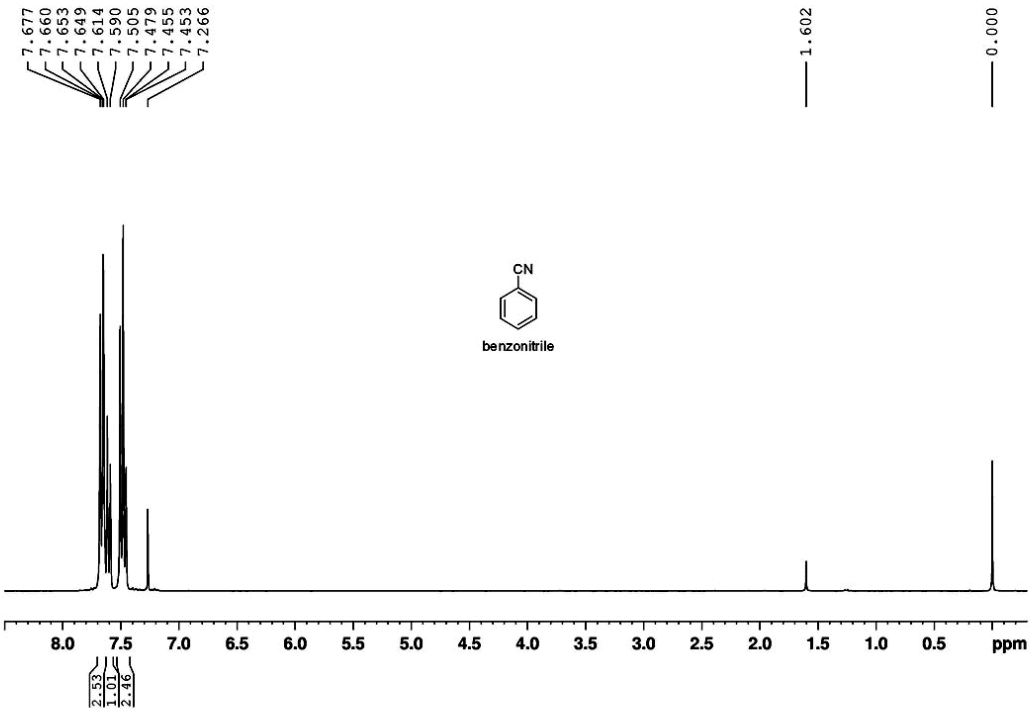


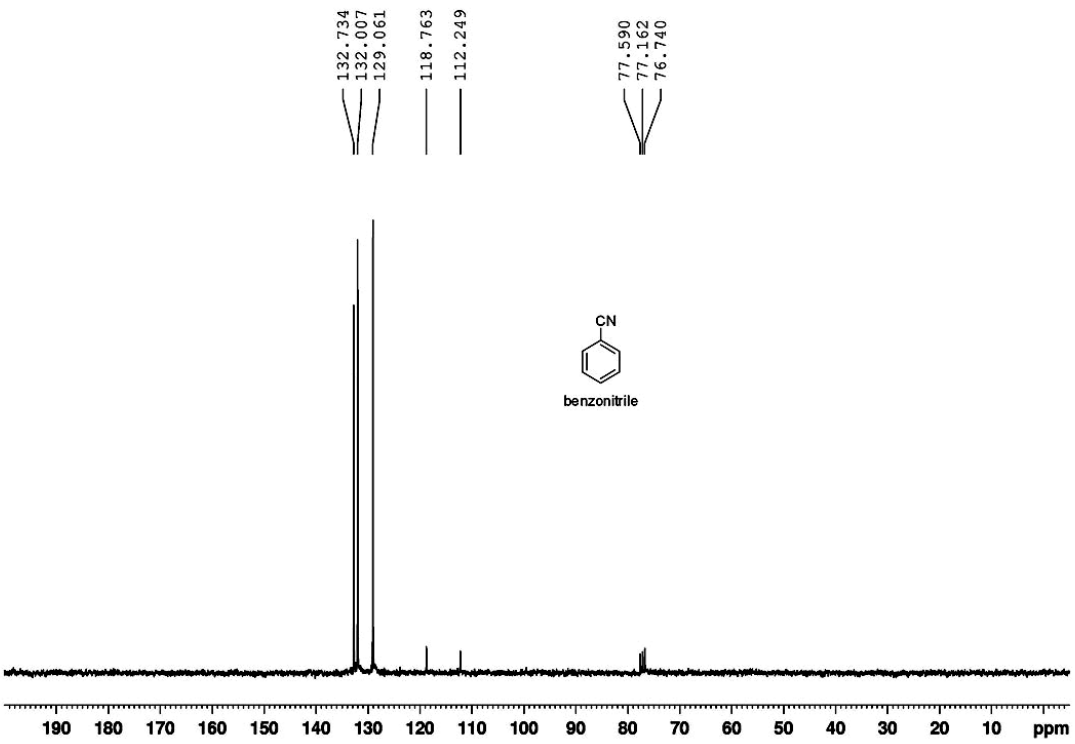
(*tert*-butylperoxymethanetriyl)tribenzene (3b)



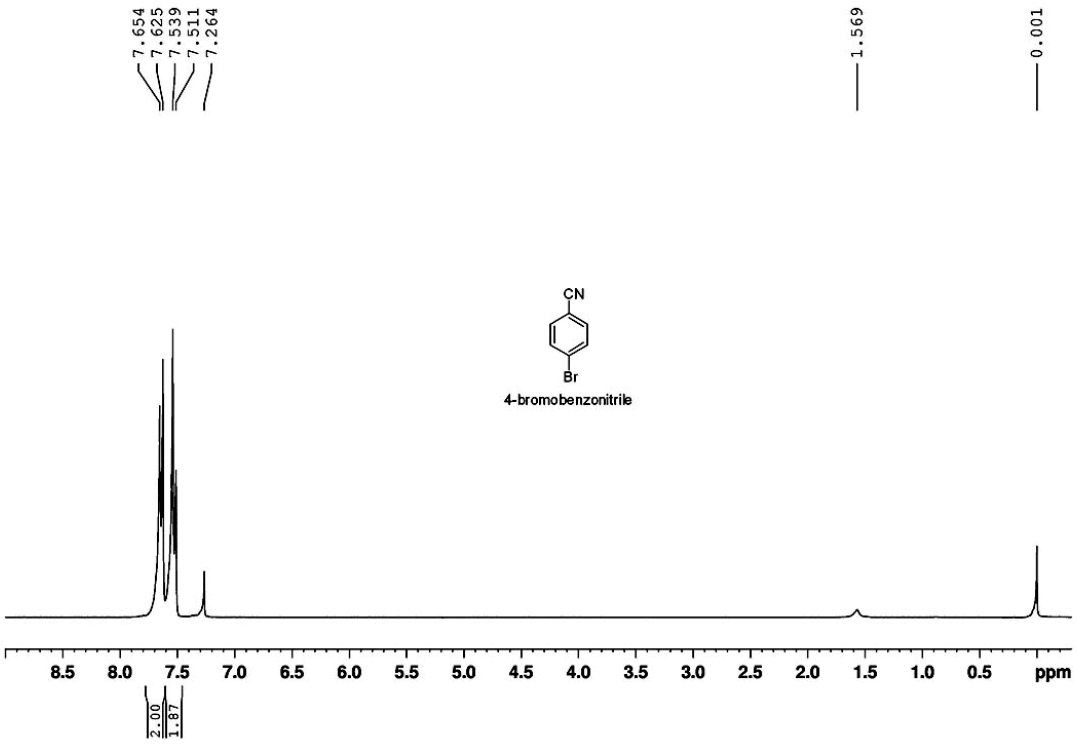


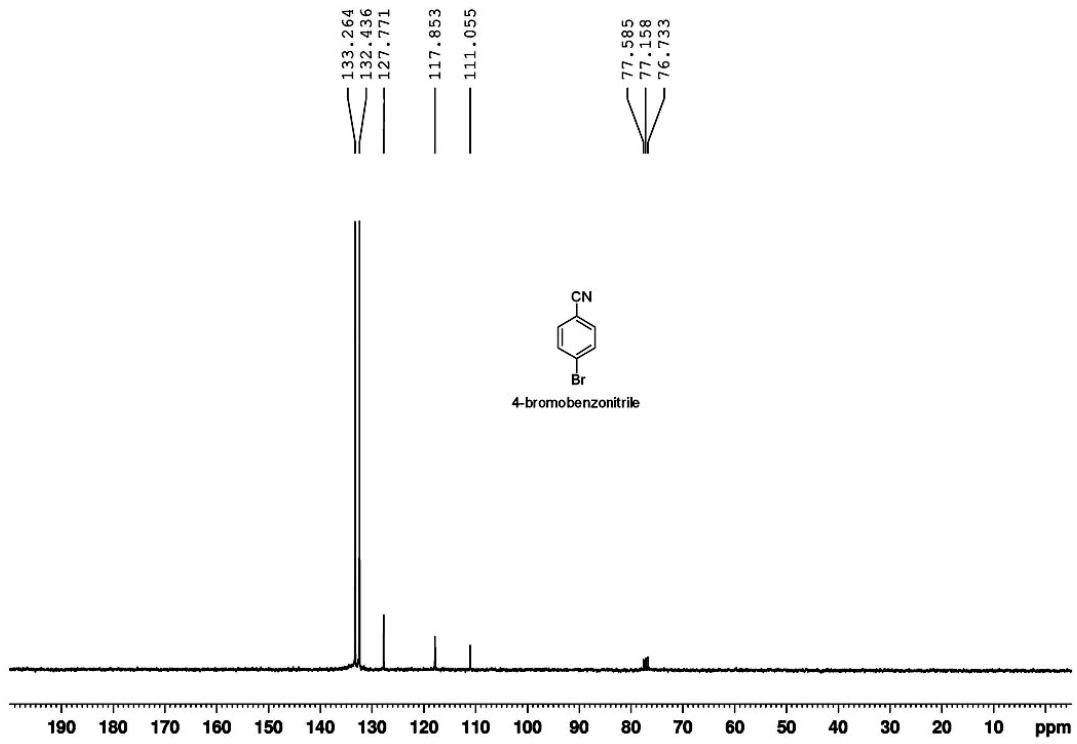
benzonitrile (6a)



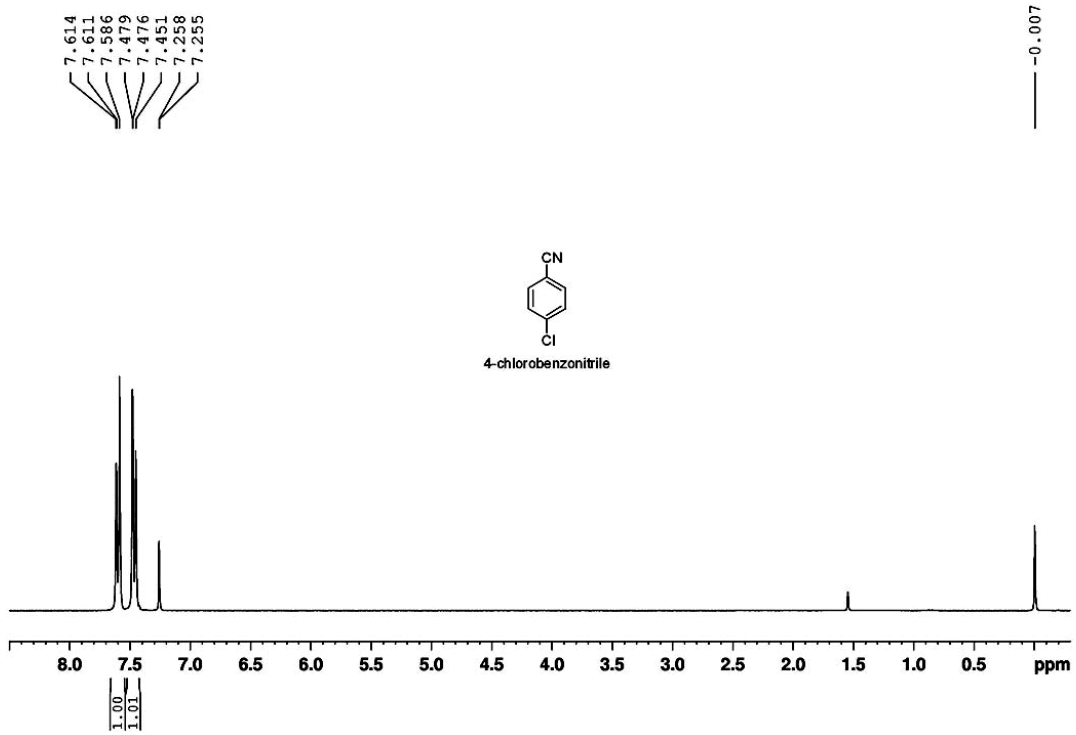


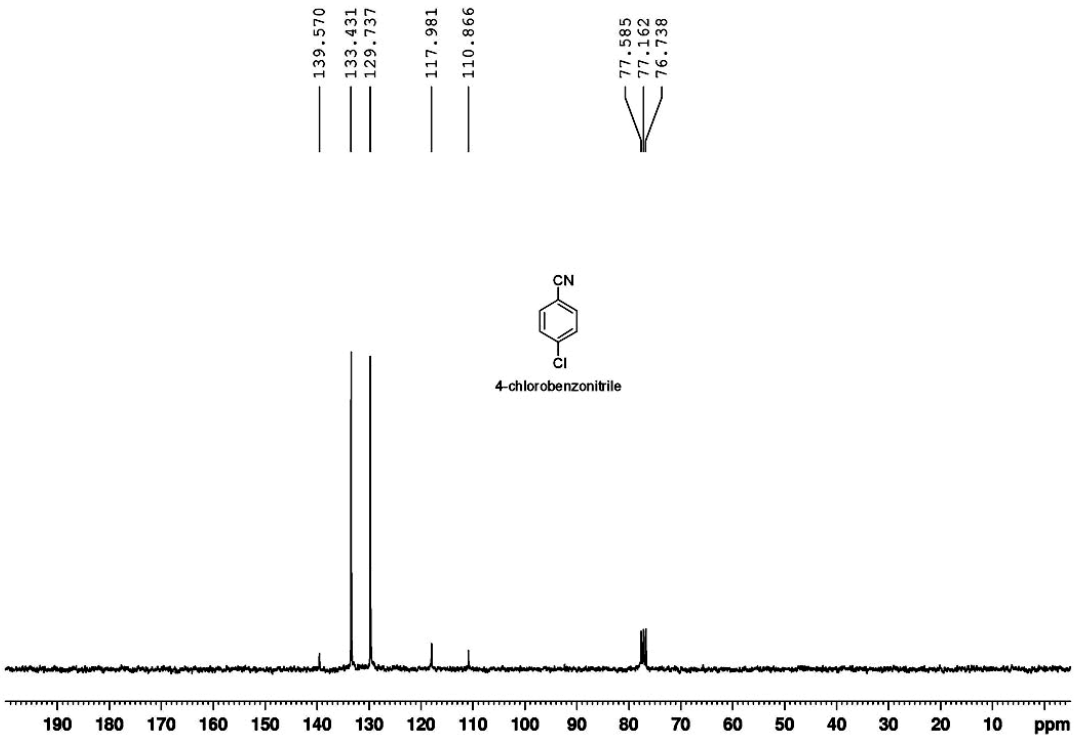
4-bromobenzonitrile (6b)



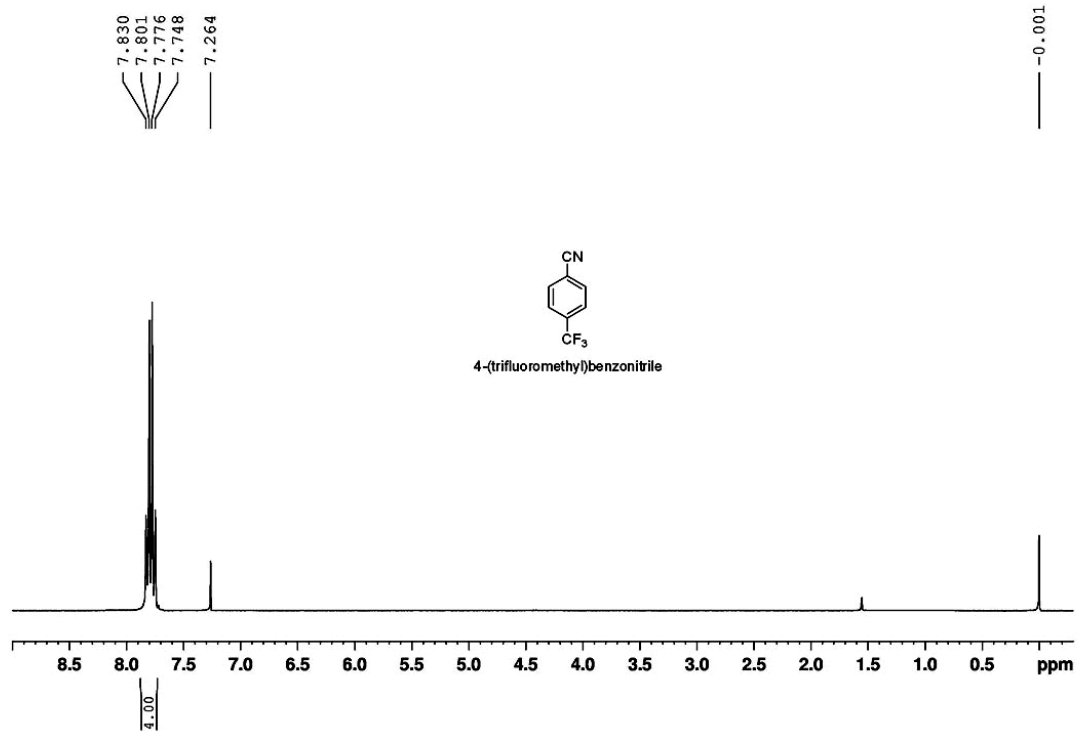


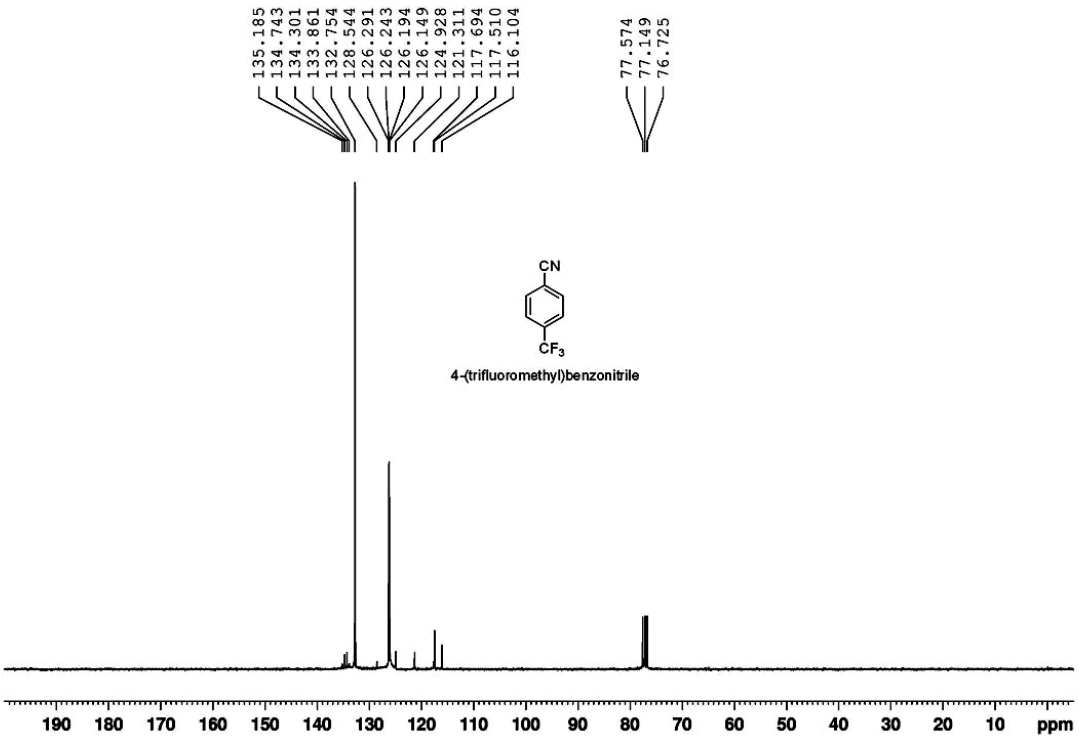
4-chlorobenzonitrile (6c)



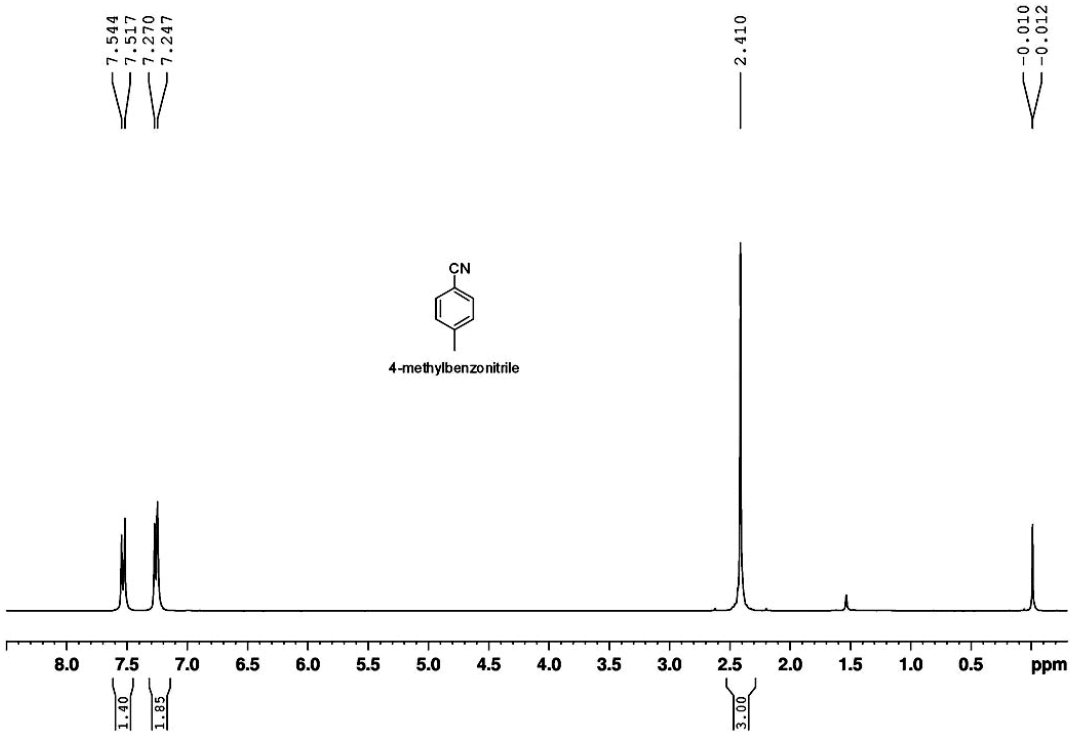


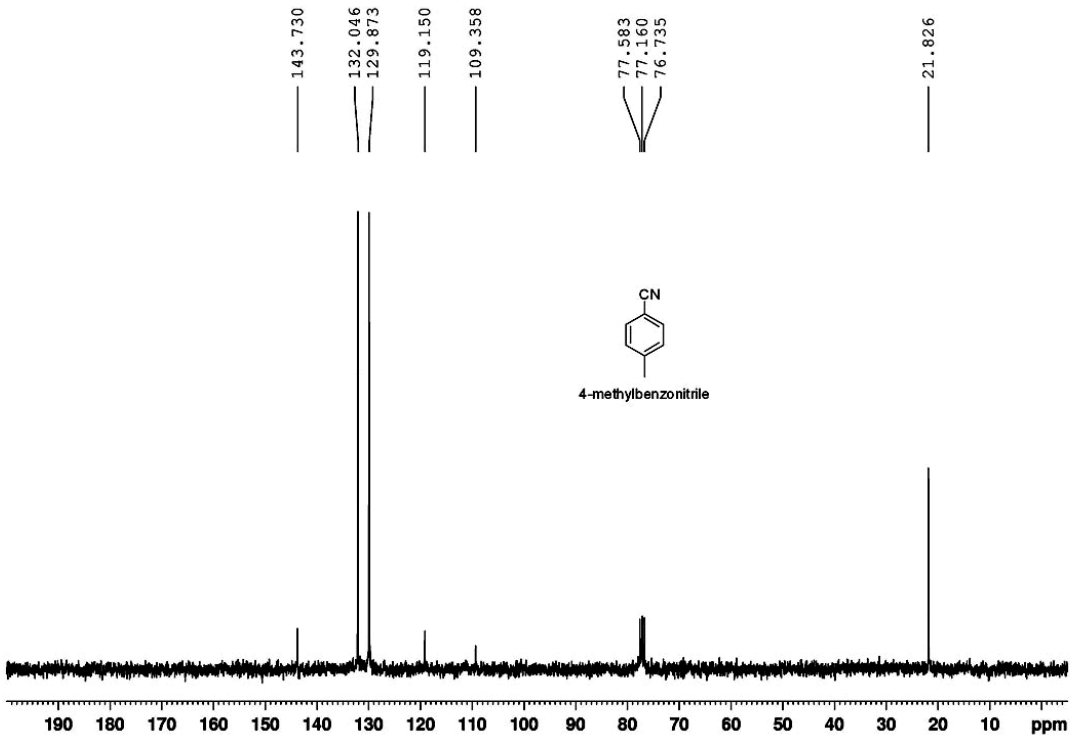
4-(trifluoromethyl)benzonitrile (6d)



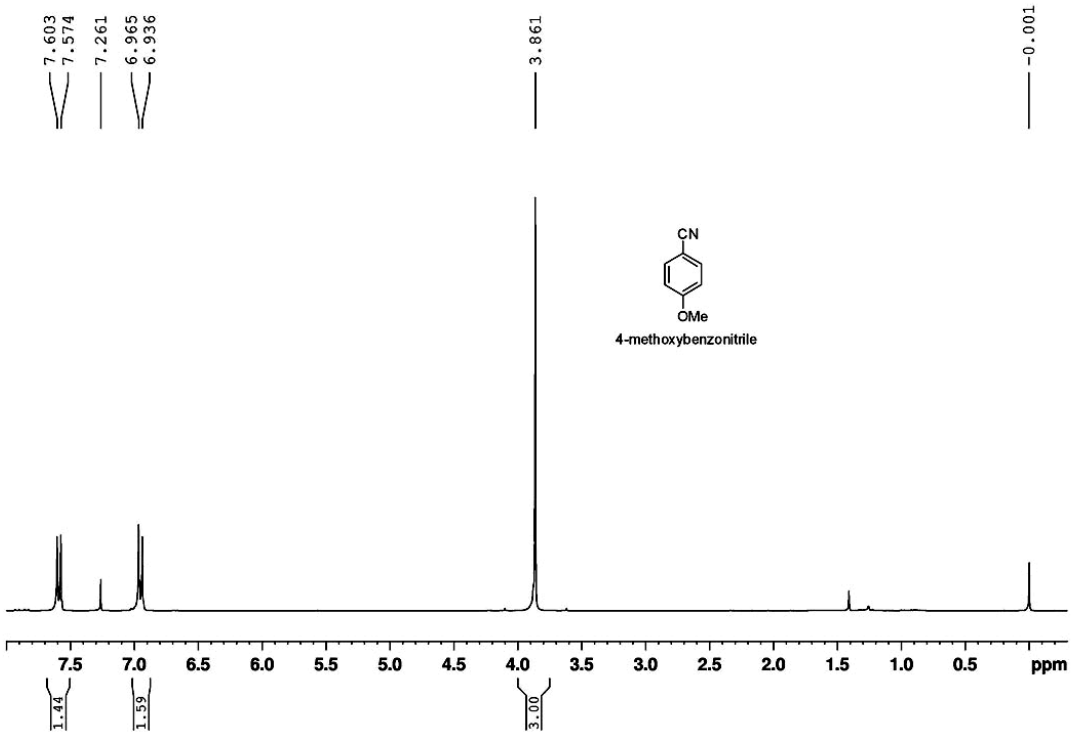


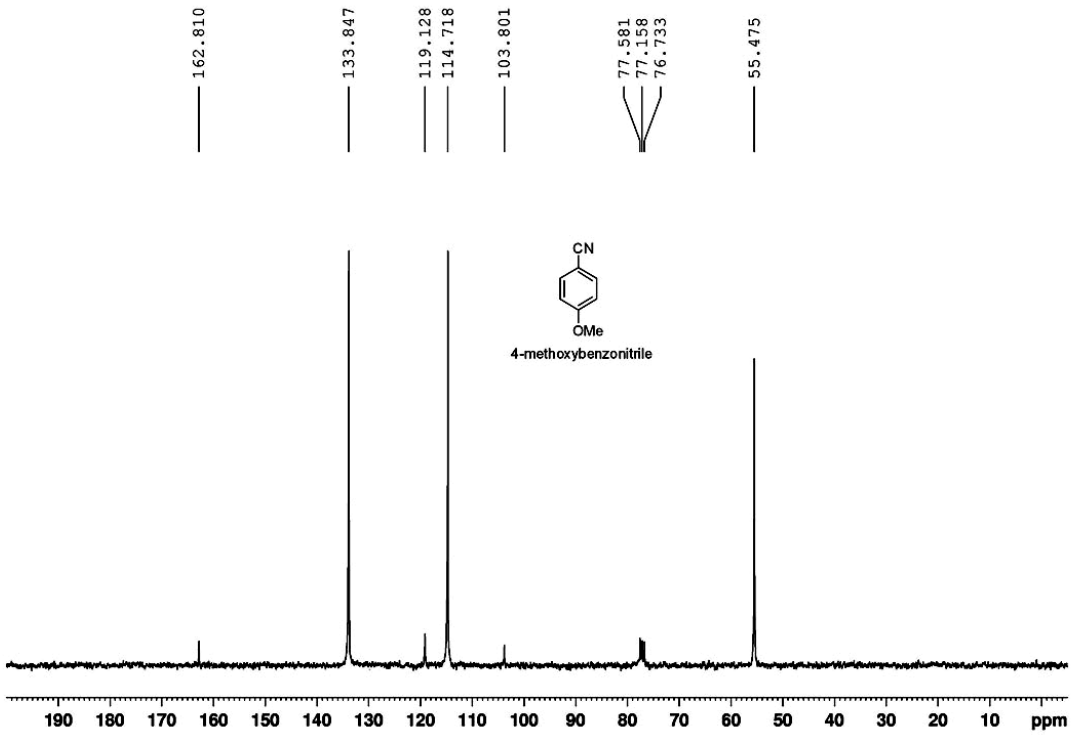
4-methylbenzonitrile (6e)



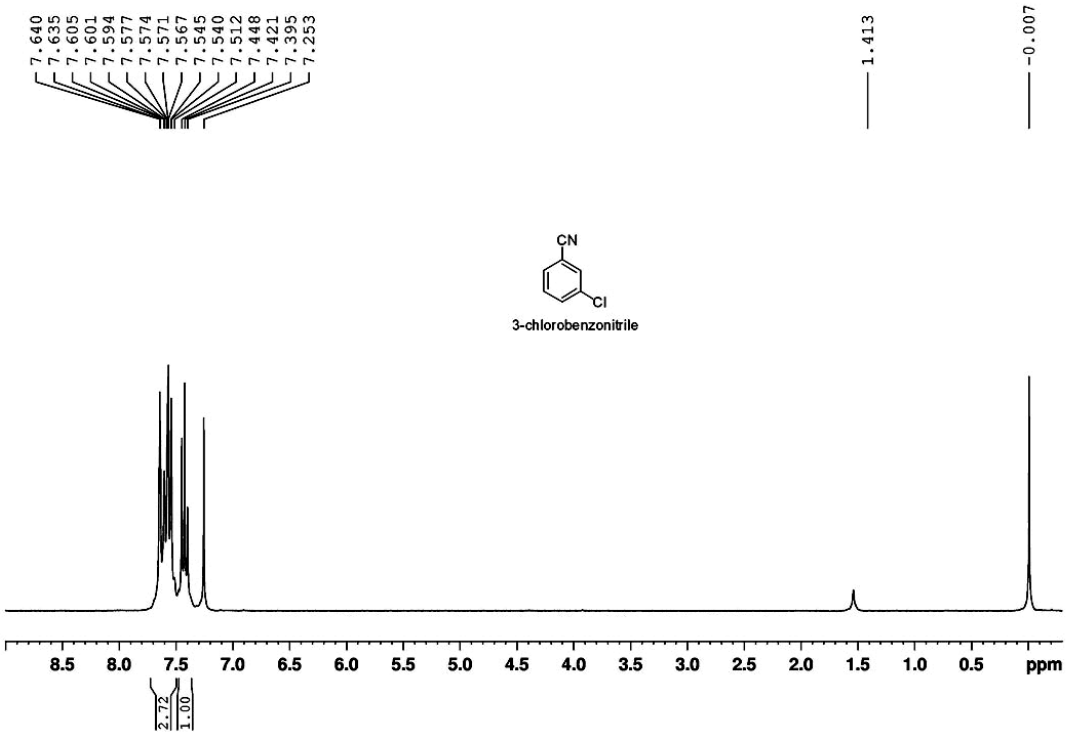


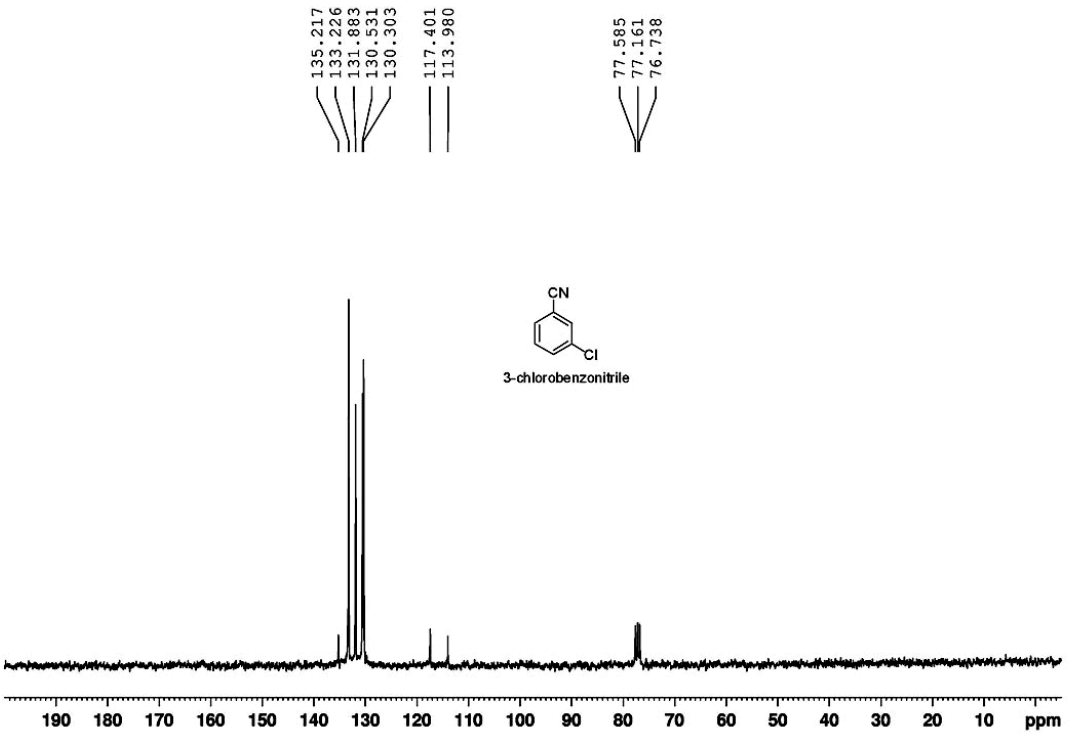
4-methoxybenzonitrile (6f)



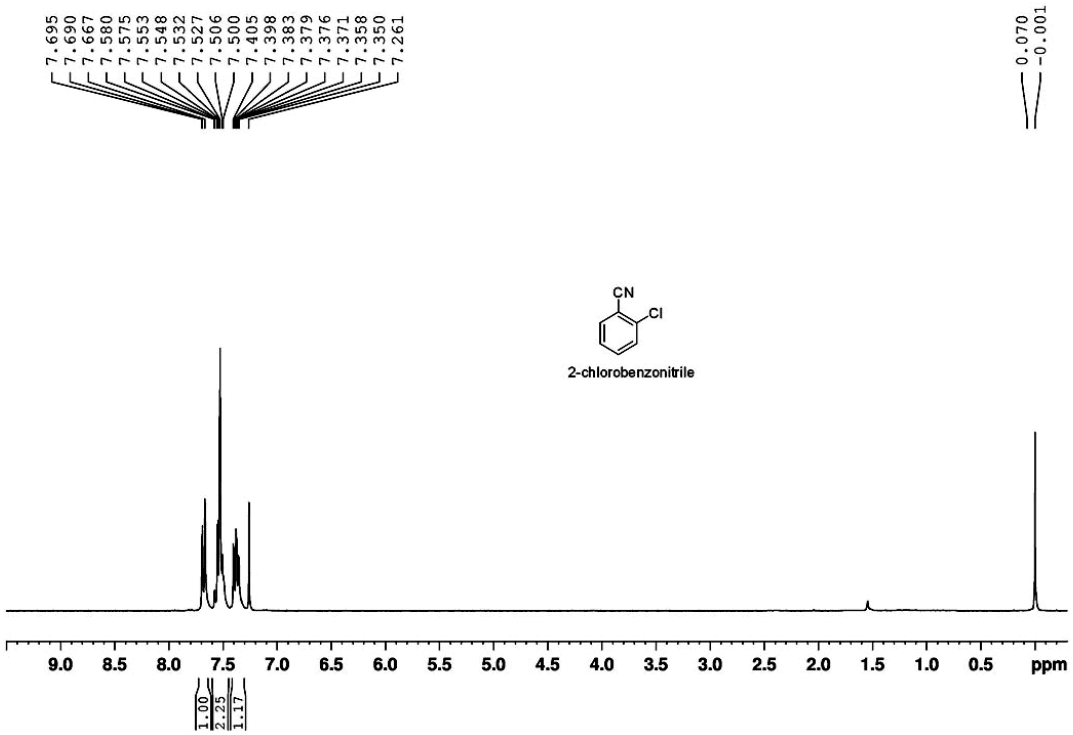


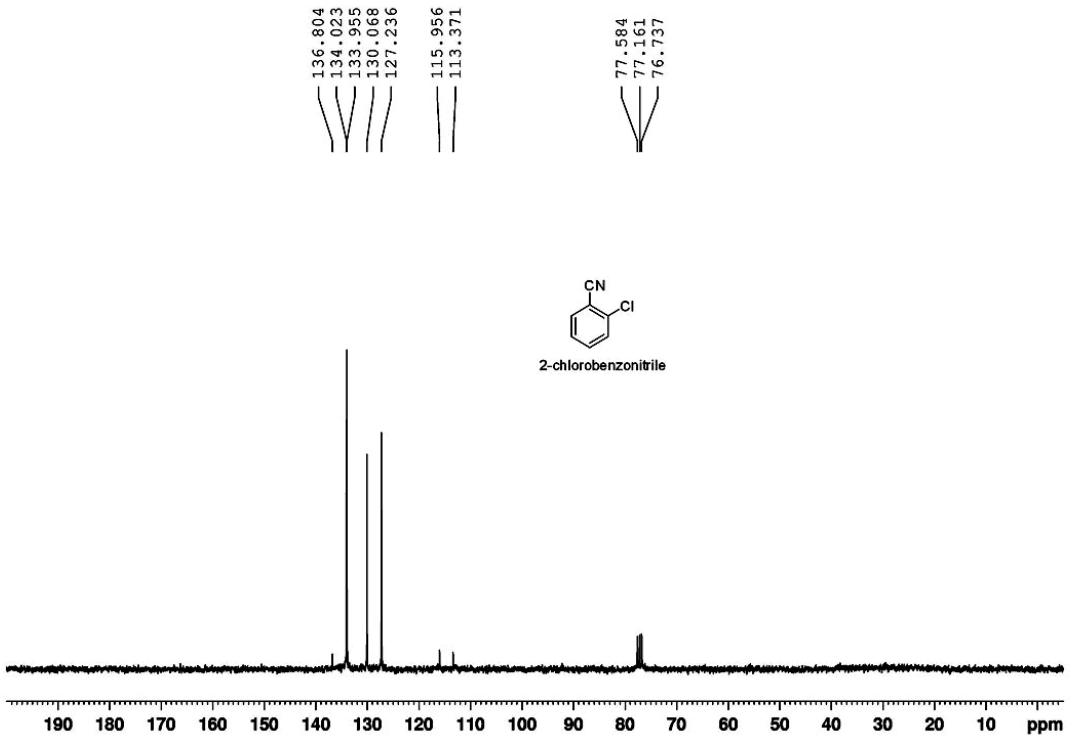
3-chlorobenzonitrile (6g)



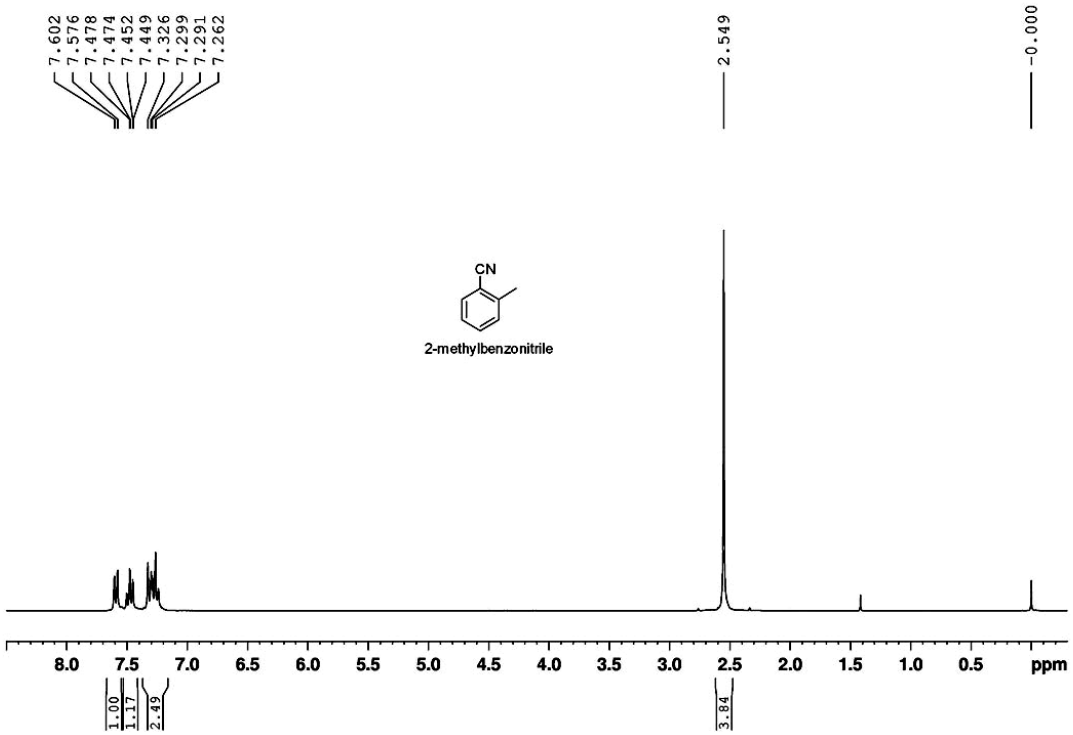


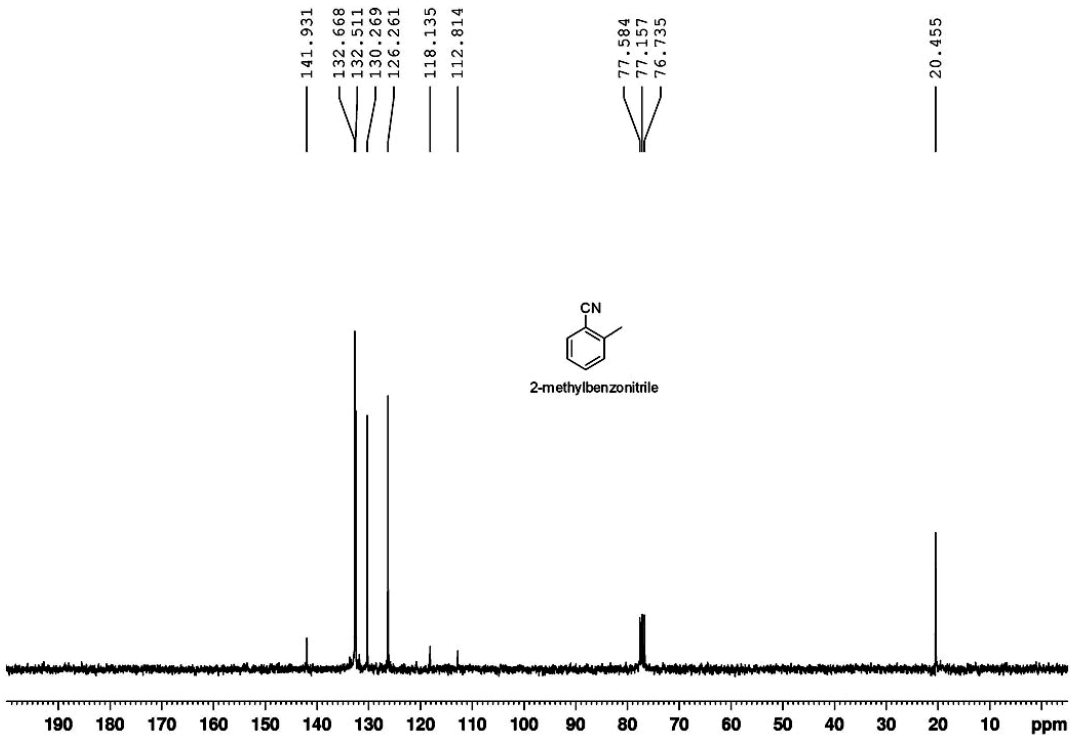
2-chlorobenzonitrile (6h)



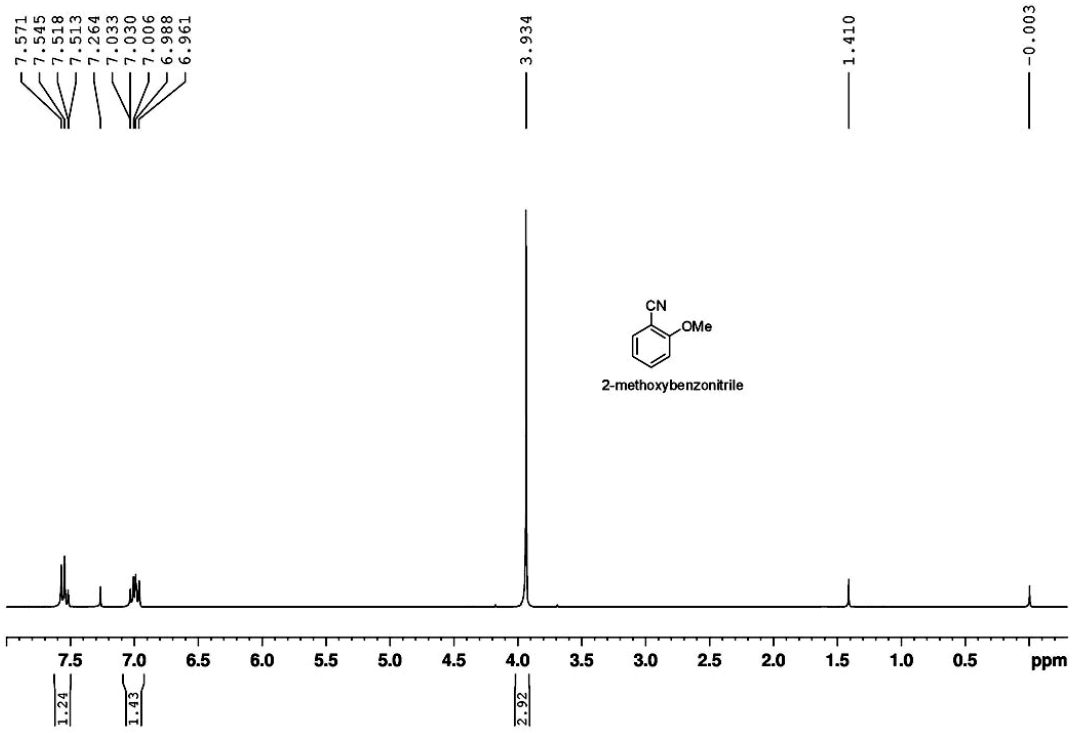


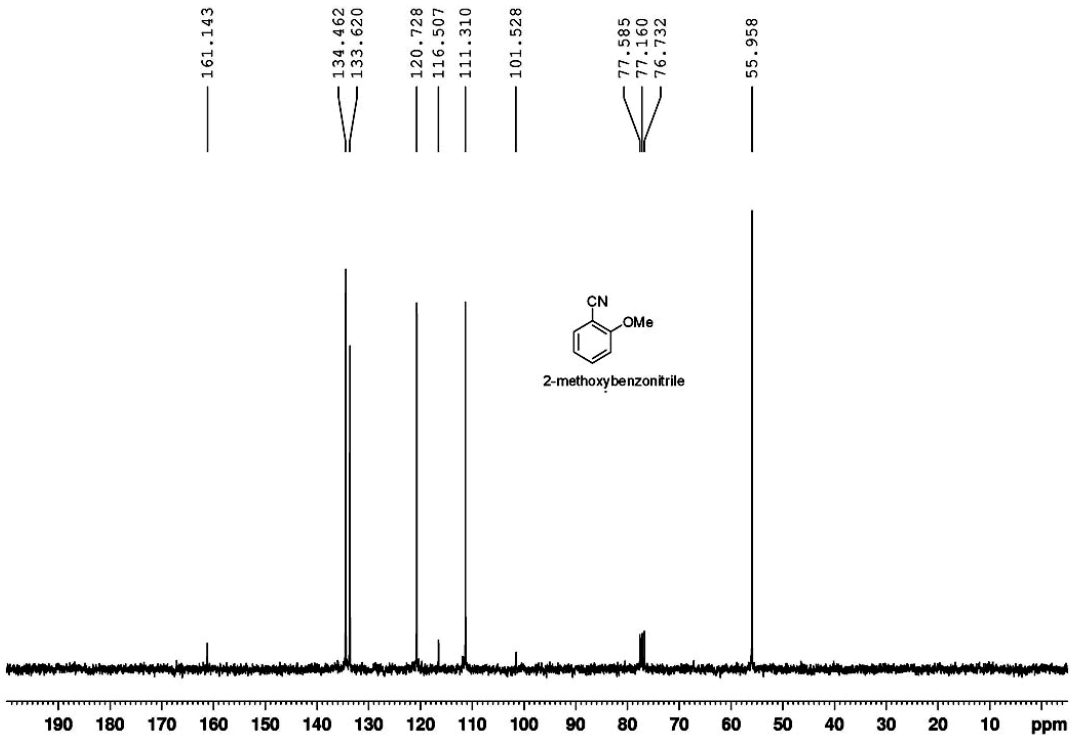
2-methylbenzonitrile (6i)



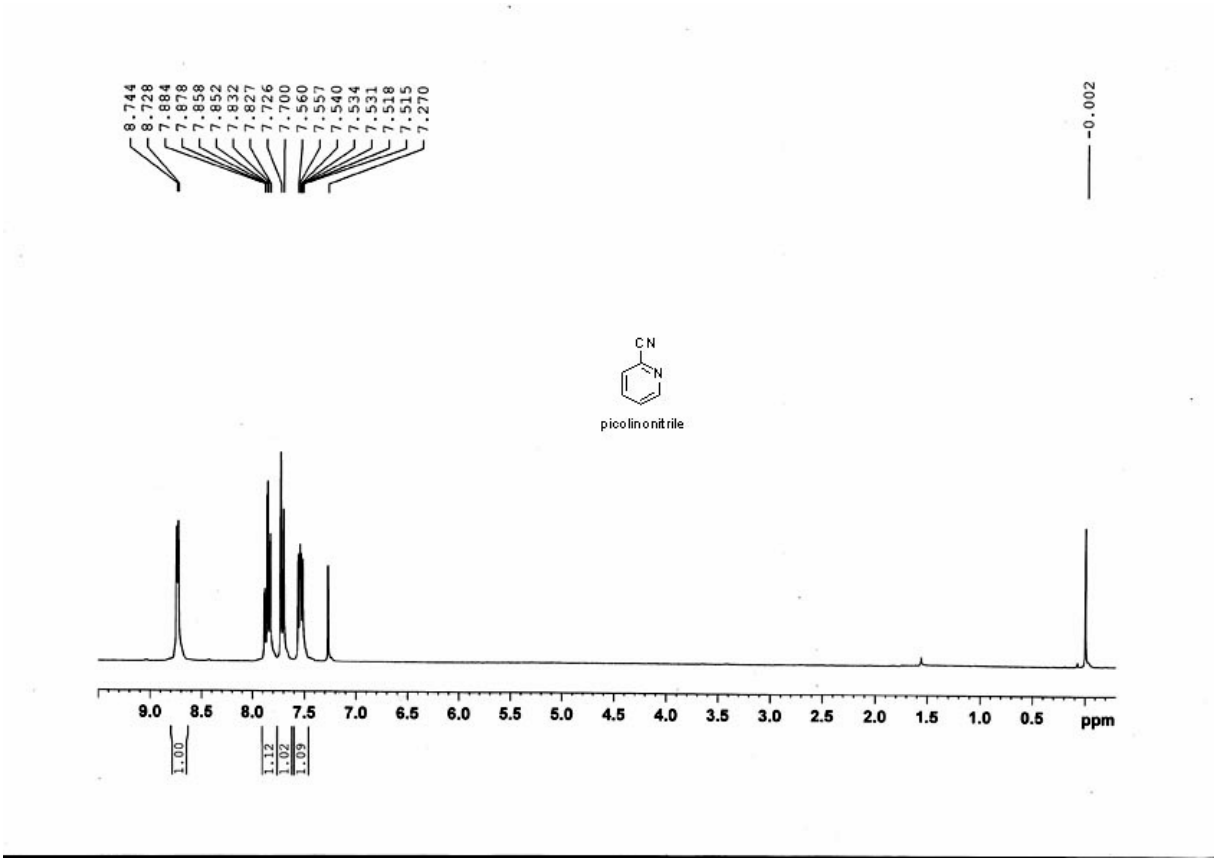


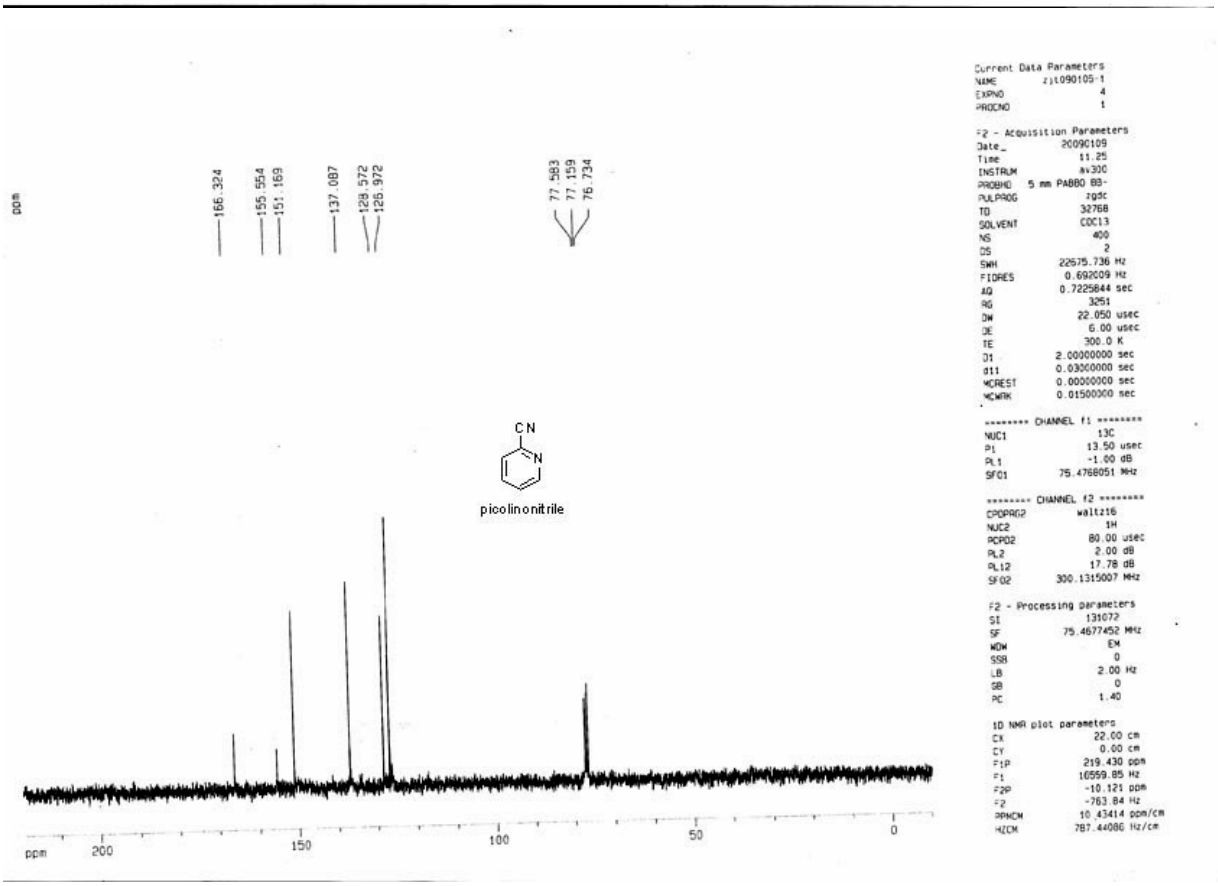
2-methoxybenzonitrile (6j)



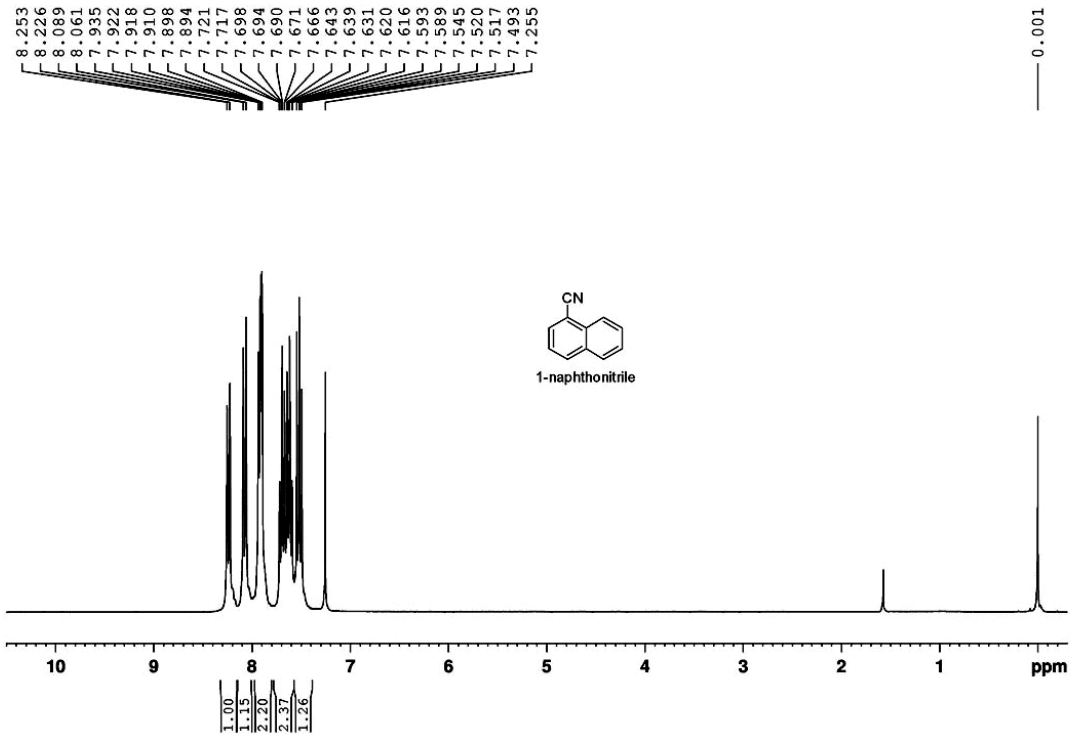


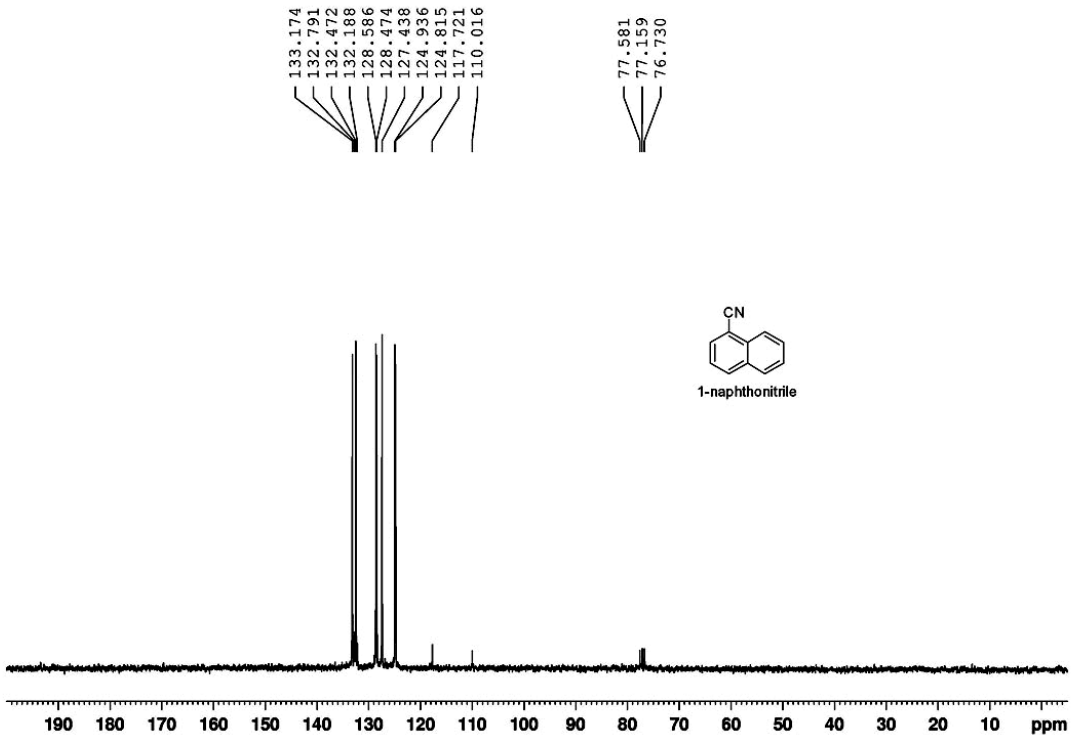
picolinonitrile (6k)



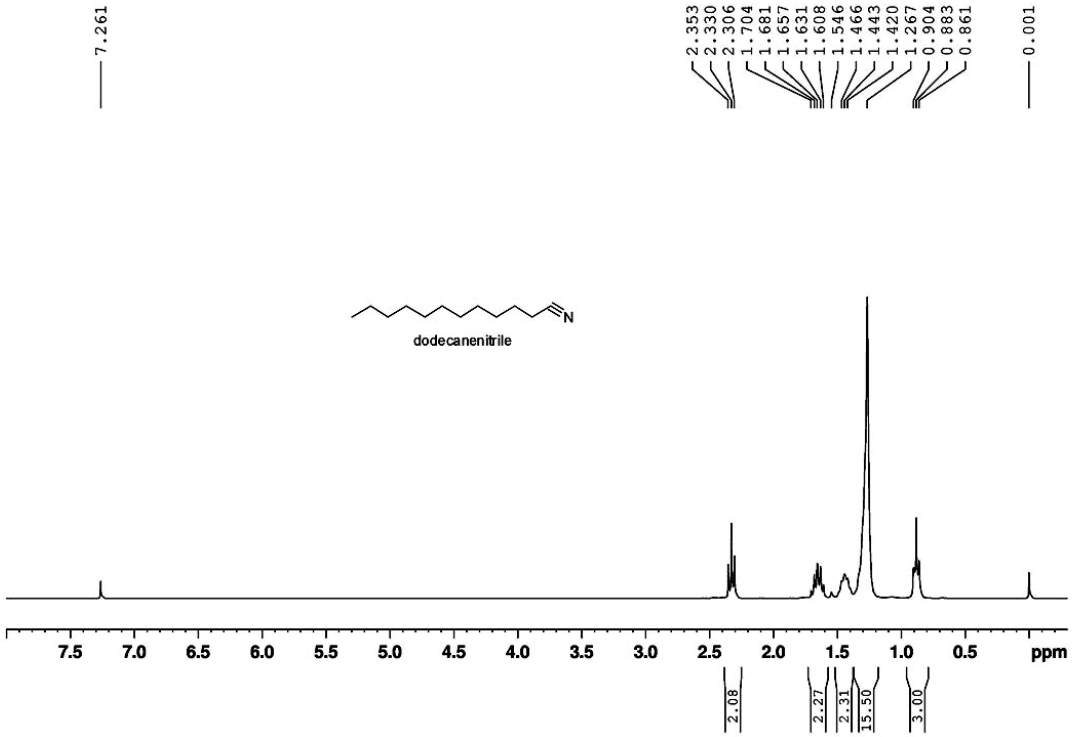


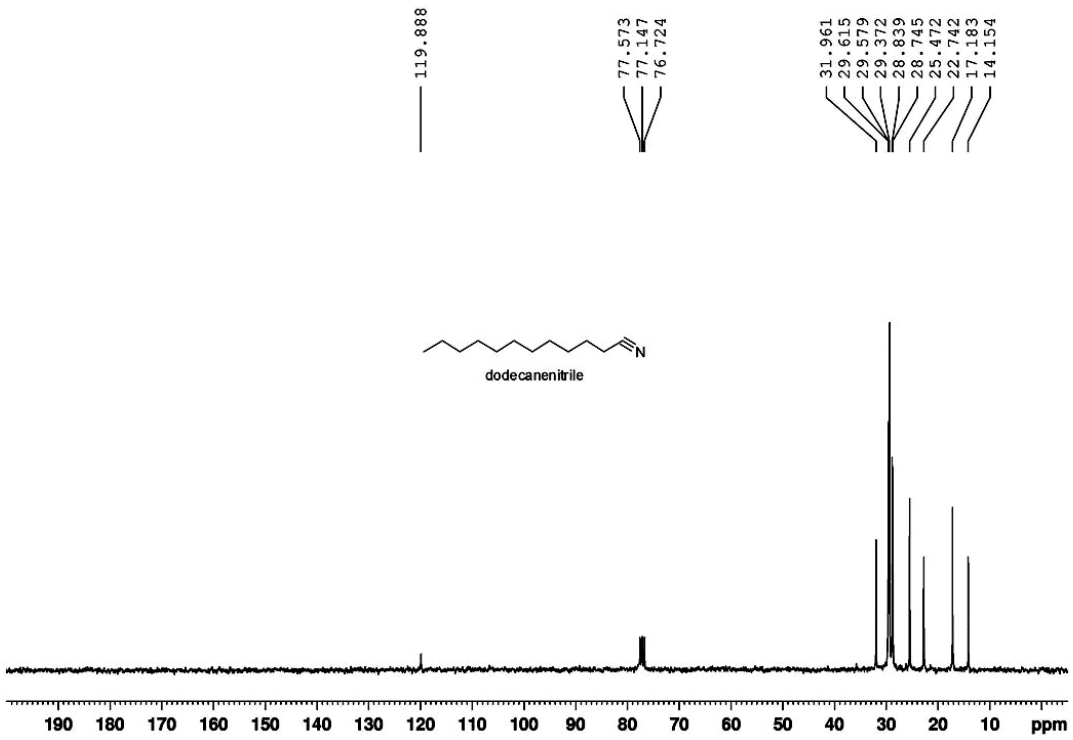
1-naphthonitrile (6l)



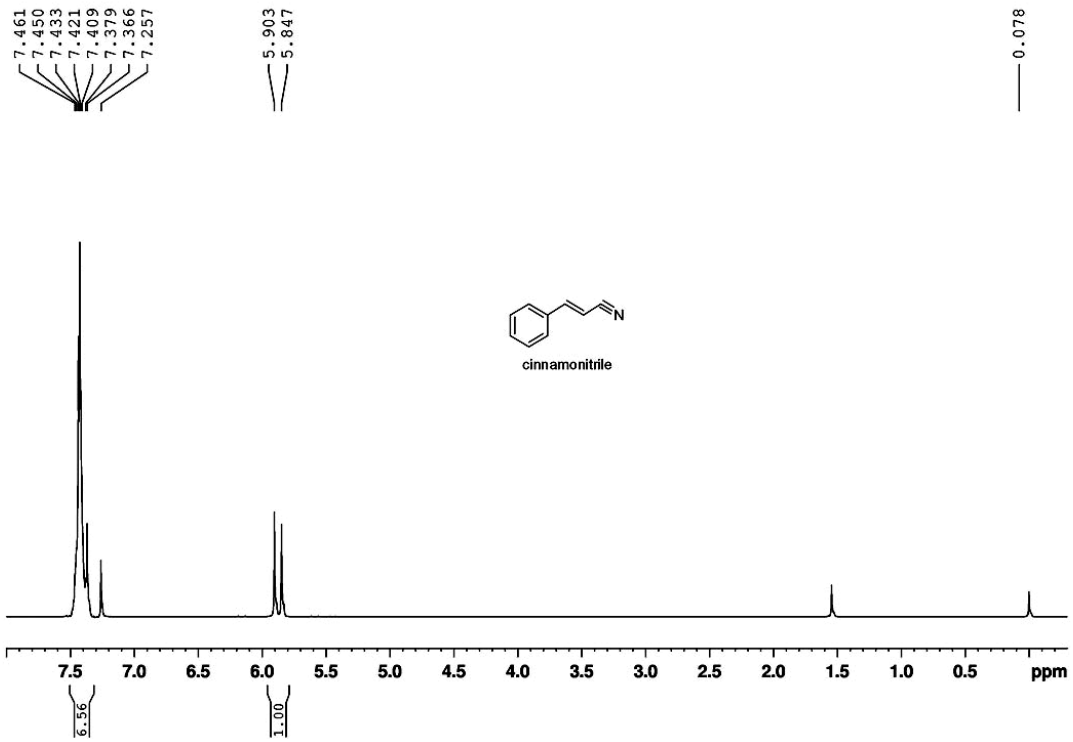


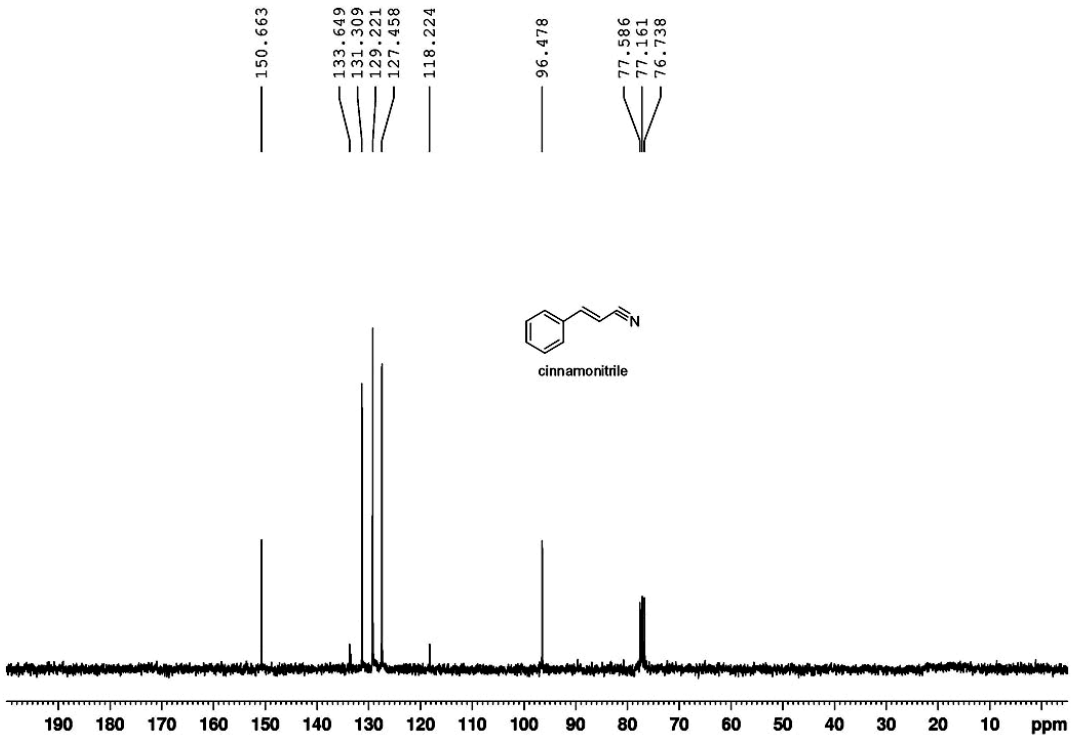
dodecanenitrile (6m)





cinnamonitrile (6n)





(E)-N-benzylidene-4-methylaniline