Supplementary Materials: High Catalytic Activity of Heterometallic (Fe_6Na_7 and Fe_6Na_6) Cage Silsesquioxanes in Oxidations with Peroxides

Alexey I. Yalymov, Alexey N. Bilyachenko, Mikhail M. Levitsky, Alexander A. Korlyukov, Victor N. Khrustalev, Lidia S. Shul'pina, Pavel V. Dorovatovskii, Marina A. Es'kova, Frédéric Lamaty, Xavier Bantreil, Benoît Villemejeanne, Jean Martinez, Elena S. Shubina, Yuriy N. Kozlov and Georgiy B. Shul'pin

X-ray Studies

All calculations were carried out using SHELX program suite [S1–S3] and OLEX2 program [S4]. In the case of **I**, we decided to treat the water molecule coordinated to Na as an oxonium cation H_3O^+, similar to the case reported earlier [S5].

References

S1 Sheldrick, G.M. *Acta Cryst.* **2008**, *A64*, 112–122.
S2 Sheldrick, G.M. *Acta Cryst* **2015**, *C71*, 3–8.
S3 Sheldrick, G.M. *Acta Cryst* **2015**, *A71*, 3–8.
S4 Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339–341.
S5 Starosta, W.; Leciejewicz, J. *Acta Crystallogr.* **2010**, *E66*, m1362–m1363.

*Oxidation of Methylcyclohexane with H_2O_2 Catalyzed by Compound **II***

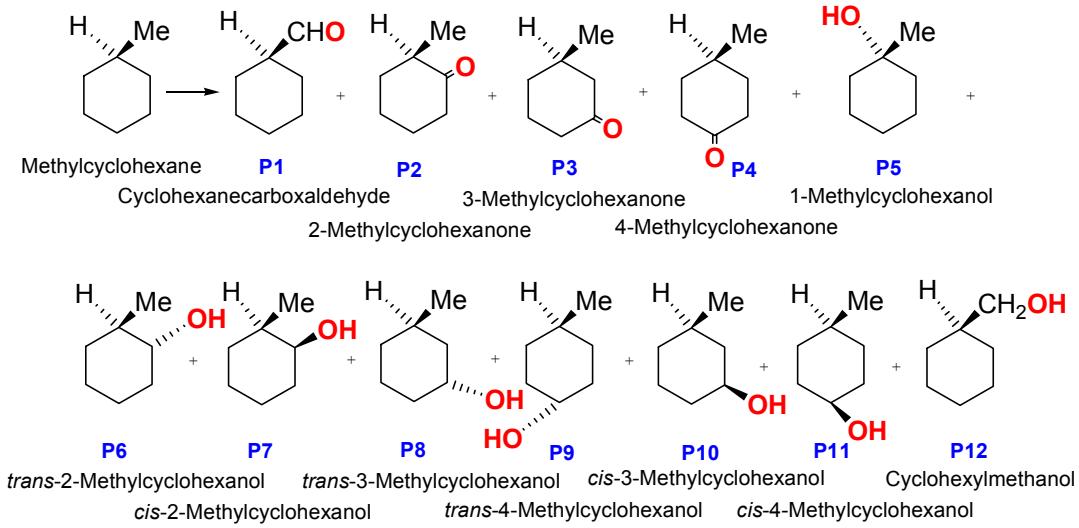


Figure S1. Isomeric products formed in the methylcyclohexane oxidation.

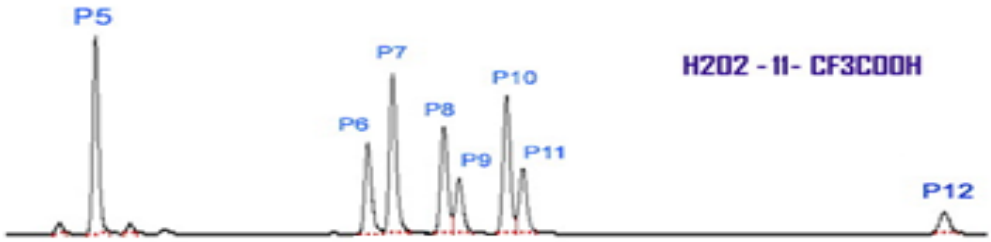


Figure S2. A chromatogram of products obtained in oxidations of methylcyclohexane by the "H_2O_2-**II**-CF_3COOH" system.

Kinetic Analysis of Cyclohexane Oxidation

It is reasonable to assume that the starting complex **II** is modified in an acidified TFA solution to produce particles with less iron atoms, including species containing only one iron. Taking this into account, we can accept the simplest assumption: the dimeric iron complexes generated in the system from monomers take part in the catalytic decomposition of hydrogen peroxide. In this case, the formation of catalytically active di-iron complexes can be presented by two equations (*L* are ligands):

$$\mathbf{II} \rightleftharpoons 6\ Fe^{3+}L \qquad \text{equilibrium constant } K_A \qquad (A)$$

$$2\ Fe^{3+}L \rightleftharpoons (Fe^{3+}L)_2 \qquad \text{equilibrium constant } K_B \qquad (B)$$

and the equation of material balance is

$$6\ [\mathbf{II}]_0 = 6\ [\mathbf{II}] + [Fe^{3+}L] + 2\ [(Fe^{3+}L)_2]$$

Here, $[\mathbf{II}]_0$ is the analytically measured concentration of catalyst introduced into the solution. All other parameters are equilibrium concentrations in the solution. If we assume that the equilibrium (A) is sufficiently shifted to the right; that is, the whole starting complex decomposes to produce species $Fe^{3+}L$; and the equilibrium constant K_B is low ($[(Fe^{3+}L)_2] \ll [Fe^{3+}L]$), it follows from the equation shown above that $[(Fe^{3+}L)_2] = K_B(6\ [\mathbf{II}]_0)^2$

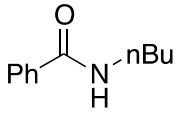
Thus, the concentration of dimeric species is proportional to a square of the starting complex concentration, and consequently the rate of active species generation should be proportional to $([\mathbf{II}]_0)^2$. In this case, the consequence of transformations leading to the generation of hydroxyl radicals can be presented by the following mechanism: dimeric complex $(Fe^{3+}L)_2$ is reduced with hydrogen peroxide to afford two ions Fe^{2+}. Each of these ions interact with H_2O_2 being oxidized to $Fe^{3+}$and to afford hydroxyl radical:

$$(Fe^{3+}L)_2 + H_2O_2 \rightarrow 2\ Fe^{2+}L + 2\ H^+ + O_2$$

$$Fe^{2+}L + H_2O_2 \rightarrow Fe^{3+}L + HO^- + HO^\bullet$$

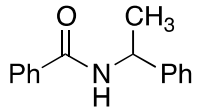
Description of Amides

N-*n*-Butylbenzamide **3a**[S6]



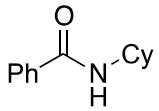
^{1}H NMR (400 MHz, $CDCl_3$) δ7.75 (dd, J = 8.3, 1.3 Hz, 2H), 7.47 – 7.40 (m, 1H), 7.36 (t, J = 7.4 Hz, 2H), 6.62 (s, 1H), 3.40 (dd, J = 13.1, 7.0 Hz, 2H), 1.64 – 1.48 (m, 2H), 1.44 – 1.29 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ167.7, 134.9, 131.3, 128.5, 127.0, 39.9, 31.7, 20.2, 13.8.

(±)-*N*-(α-Methylbenzyl)benzamide **3b**[S7]



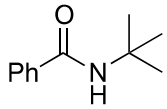
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.75 (m, 2H), 7.55 – 7.44 (m, 1H), 7.44 – 7.32 (m, 6H), 7.29 (dt, J = 4.9, 2.0 Hz, 1H), 6.48 (d, J = 6.4 Hz, 1H), 5.34 (p, J = 7.0 Hz, 1H), 1.59 (d, J = 6.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ166.7, 143.3, 134.7, 131.6, 128.8, 128.7, 127.6, 127.1, 126.4, 49.3, 21.8.

N-Cyclohexylbenzamide **3c**[S8]



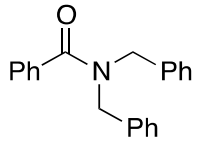
^{1}H NMR (400 MHz, $CDCl_3$) δ7.75 (d, J = 6.8 Hz, 2H), 7.45 (dq, J = 14.2, 7.0 Hz, 3H), 5.95 (s, 1H), 4.08 – 3.87 (m, 1H), 2.03 (d, J = 12.2 Hz, 2H), 1.81 – 1.59 (m, 4H), 1.52 – 1.35 (m, 2H), 1.31 – 1.15 (m, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ166.8, 135.2, 131.3, 128.6, 127.0, 48.8, 33.3, 25.7, 25.0.

N-*tert*-Butylbenzamide **3d**[S9]



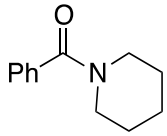
^{1}H NMR (400 MHz, $CDCl_3$) δ7.72 – 7.70 (m, 2H), 7.47 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 5.99 (s, 1H), 1.47 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ167.1, 136.0, 131.2, 128.6, 126.8, 51.7, 29.0.

N,*N*-Dibenzylbenzamide **3e**[S10]



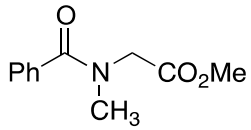
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.47 (m, 2H), 7.47 – 7.28 (m, 11H), 7.16 (s, 2H), 4.72 (s, 2H), 4.42 (s, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 137.1, 136.5, 136.3, 129.8, 129.0, 128.8, 128.7, 128.5, 127.8, 127.2, 126.8, 51.7, 47.0.

N-Benzoylpiperidine **3f**[S8]



^{1}H NMR (400 MHz, $CDCl_3$) δ7.37 (s, 8H), 3.70 (s, 3H), 3.33 (s, 3H), 1.66 (s, 6H), 1.51 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ170.4, 136.6, 129.5, 128.5, 126.9, 48.8, 43.2, 26.6, 25.7, 24.7.

N-Benzoylsarcosine methyl ester **3g**[S11]



Presence of rotamers 66:34
^{1}H NMR (400 MHz, $CDCl_3$) δ7.54 – 7.28 (m, 5H), 4.26 (s, 2H, 66%), 3.97 (s, 2H, 34%), 3.75 (s, 3H, 66%), 3.71 (s, 3H, 34%), 3.09 (s, 3H, 34%), 3.01 (s, 3H, 66%).
^{13}C NMR (101 MHz, $CDCl_3$) δ172.1, 169.6, 135.5, 129.9, 128.7, 128.6, 128.4, 127.2, 126.6, 53.2, 52.4, 52.2, 49.1, 38.7, 34.4.

References

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[S7] N. Shangguan, S. Katukojvala, R. Greenberg, L. J. Williams, *J. Am. Chem. Soc.* **2003**, *125*, 7754-7755.
[S8] M. Kitamura, T. Suga, S. Chiba, K. Narasaka, *Org. Lett.* **2004**, *6*, 4619-4621.
[S9] S. C. Ghosh, J. S. Y. Ngiam, A. M. Seayad, D. T. Tuan, C. L. L. Chai, A. Chen, *J. Org. Chem.* **2012**, *77*, 8007-8015.
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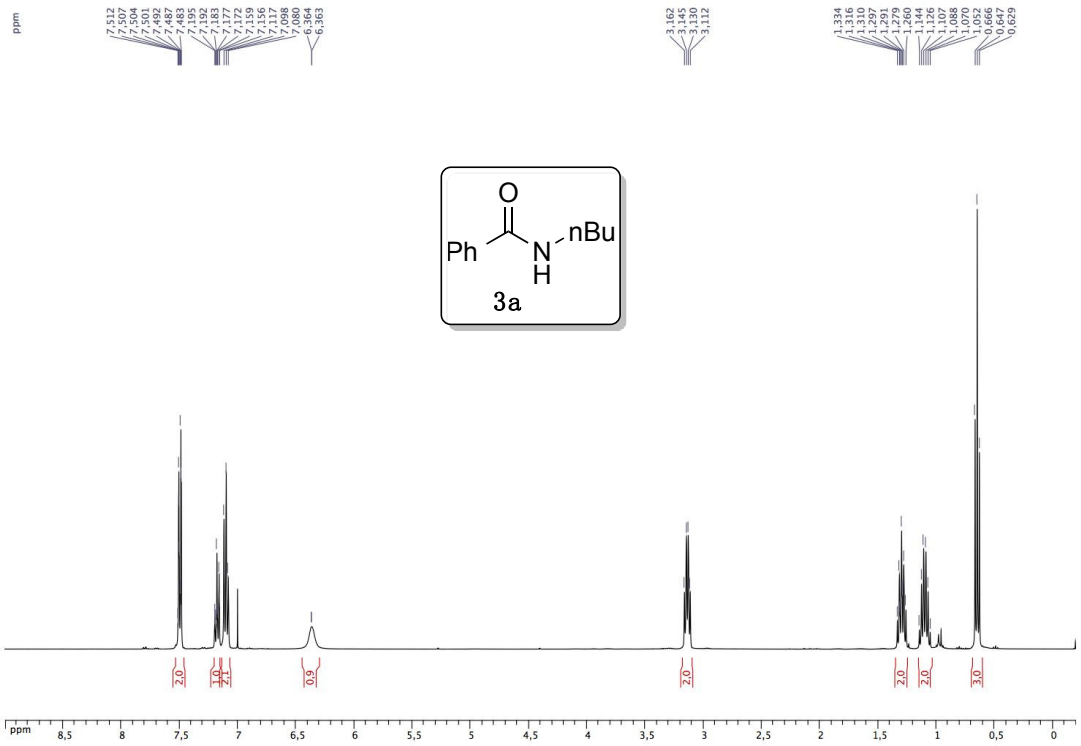
[S11] S. C. Ghosh, J. S. Y. Ngiam, C. L. L. Chai, A. M. Seayad, T. T. Dang, A. Chen, *Adv. Synth. Catal.* **2012**, *354*, 1407-

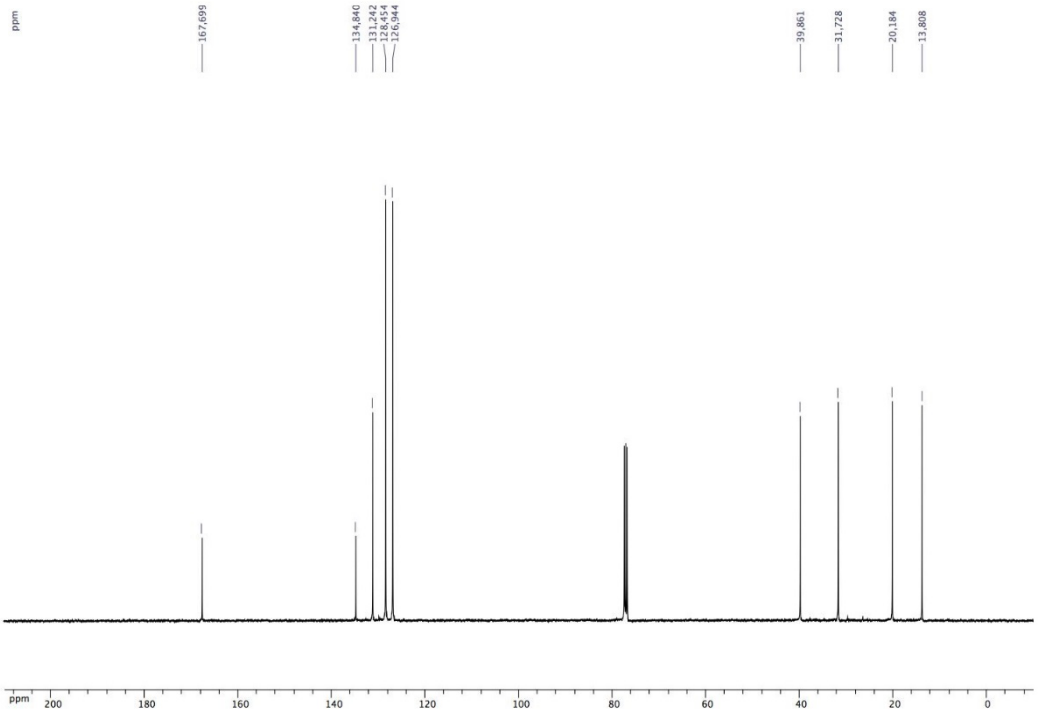
1412.

NMR of Amides (Pictures)

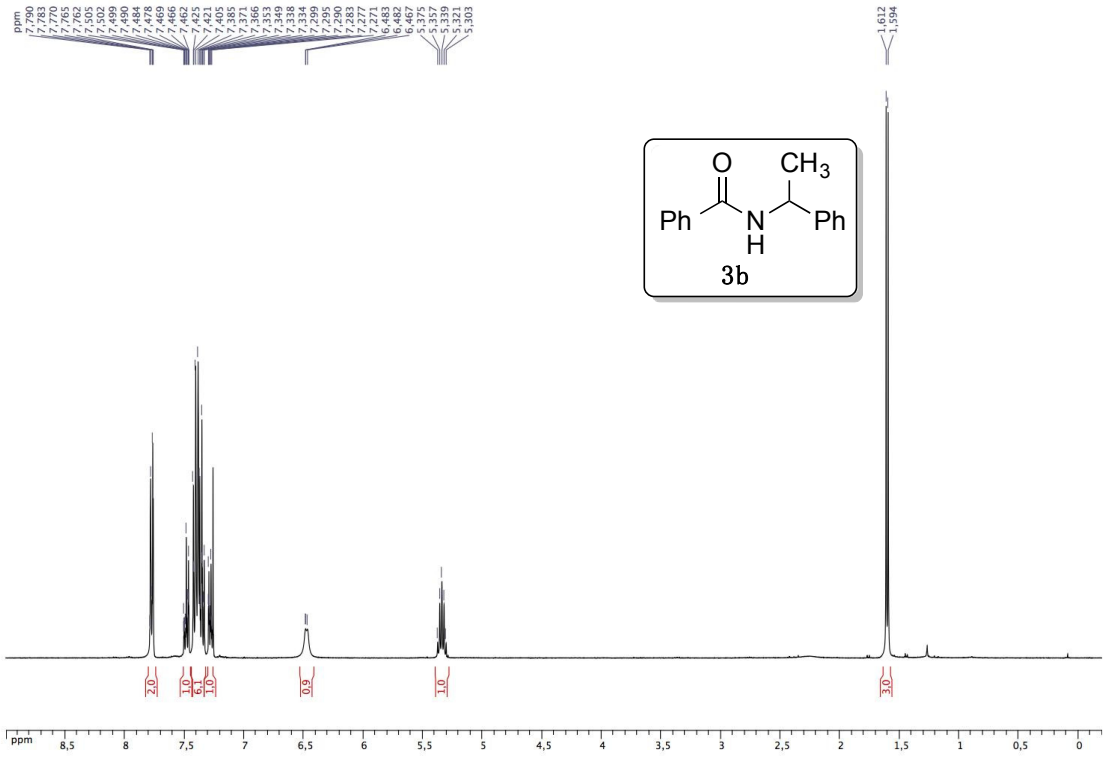
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-*n*-butylbenzamide **3a**



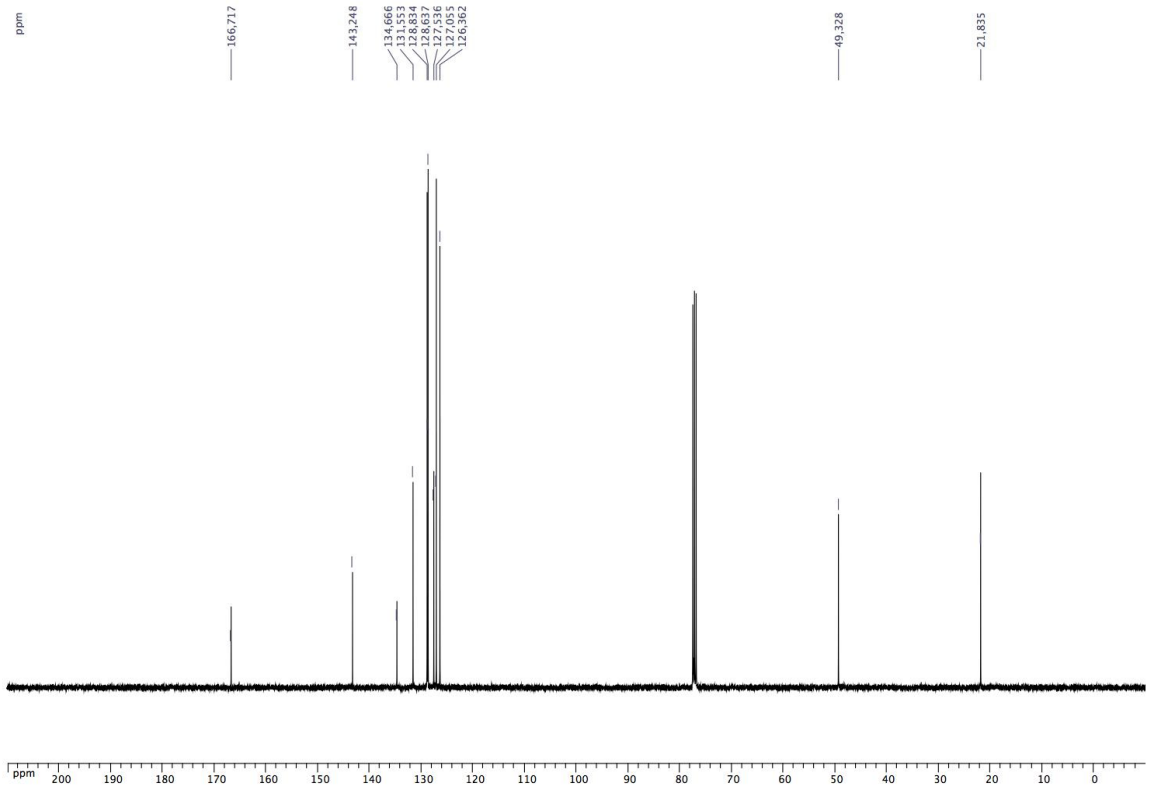
^{13}C NMR (101 MHz, $CDCl_3$) of *N*-*n*-butylbenzamide **3a**



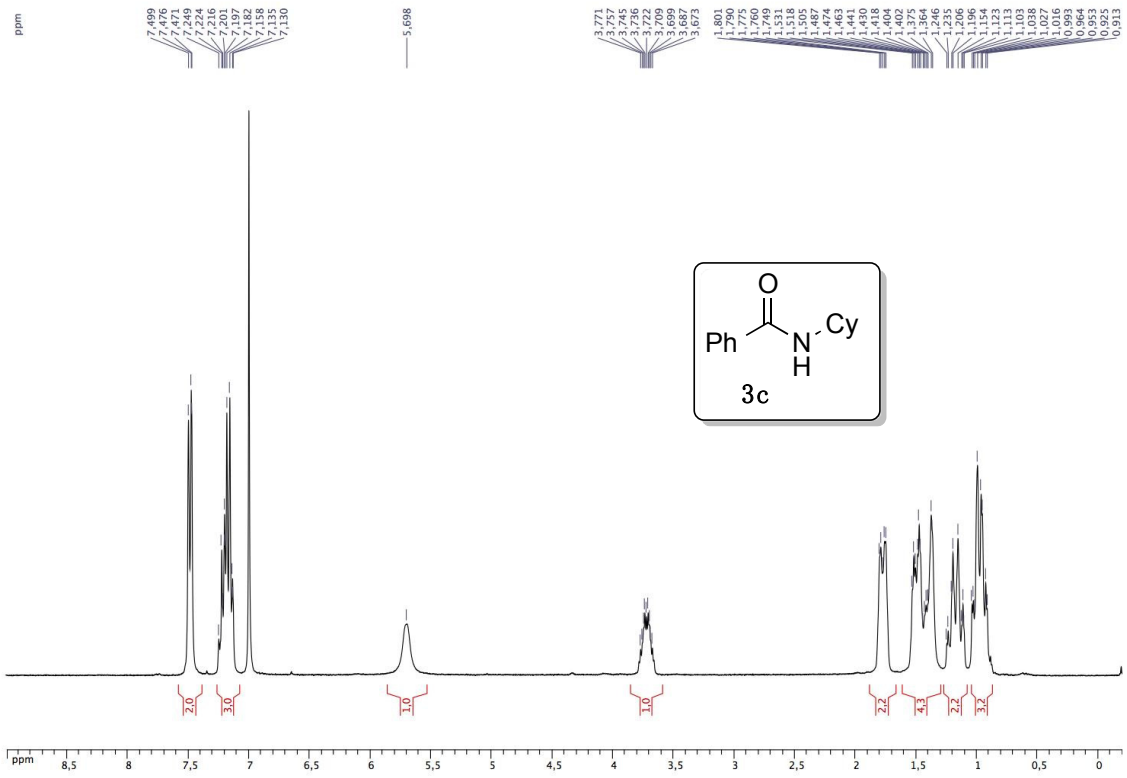
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-[(±)-1-phenylethyl]benzamide **3b**



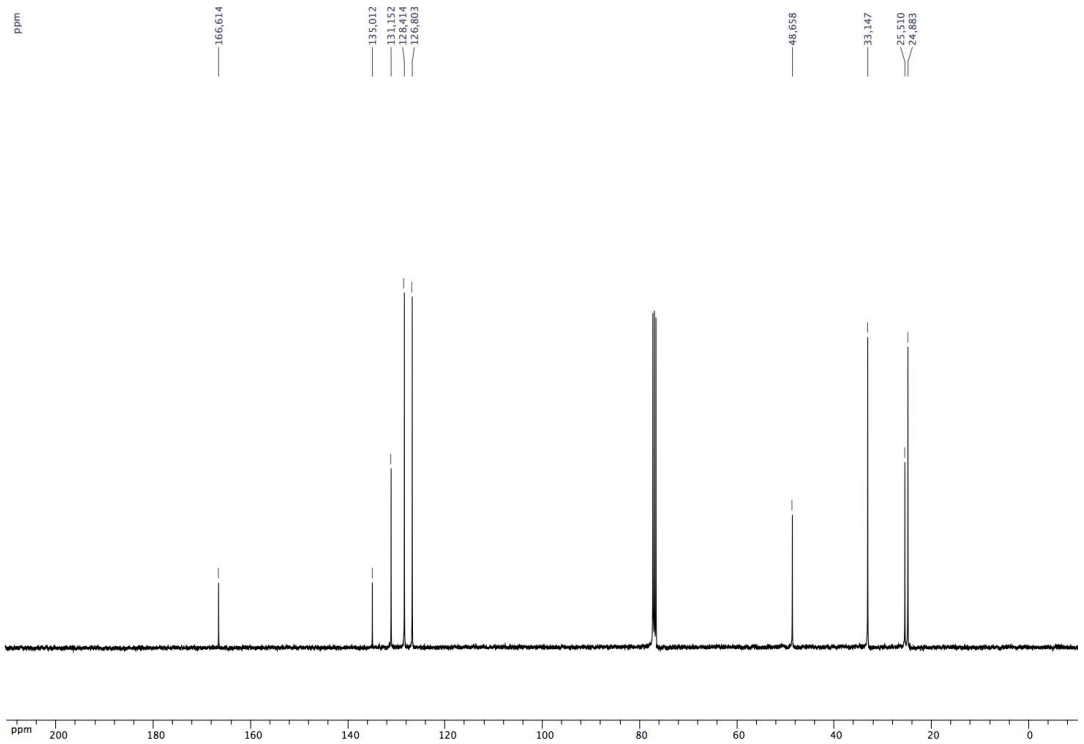
^{13}C NMR (101 MHz, $CDCl_3$) of *N*-[(±)-1-phenylethyl]benzamide **3b**



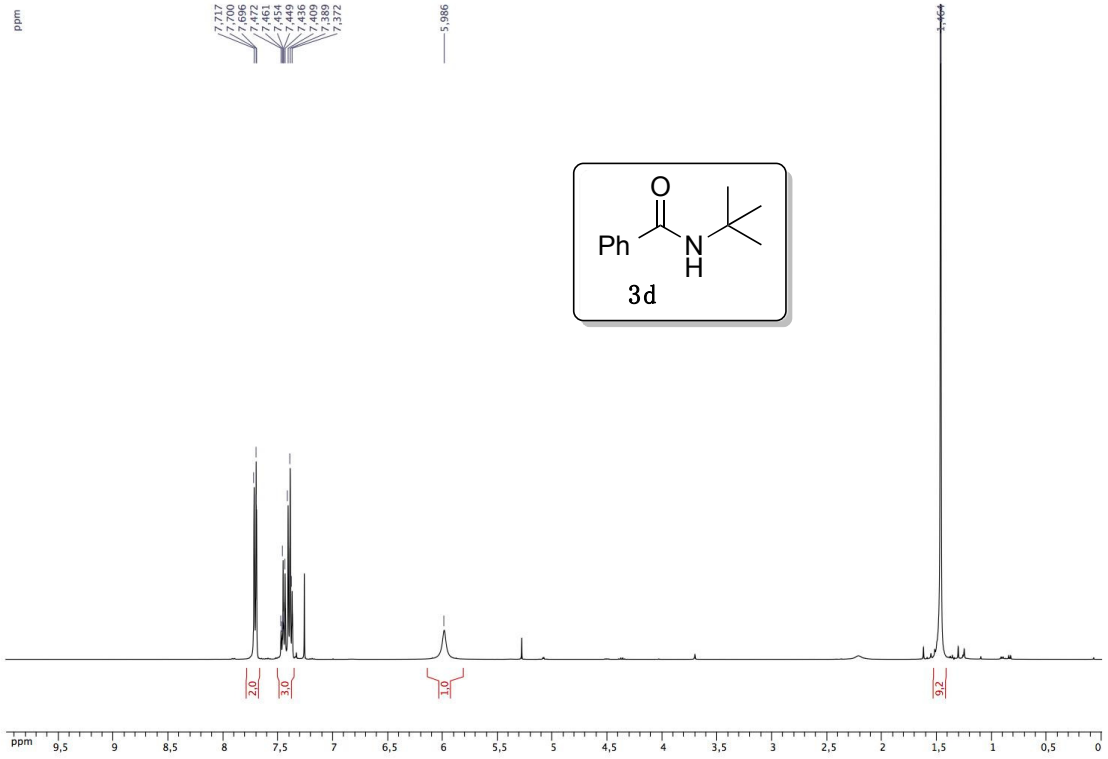
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-cyclohexylbenzamide **3c**



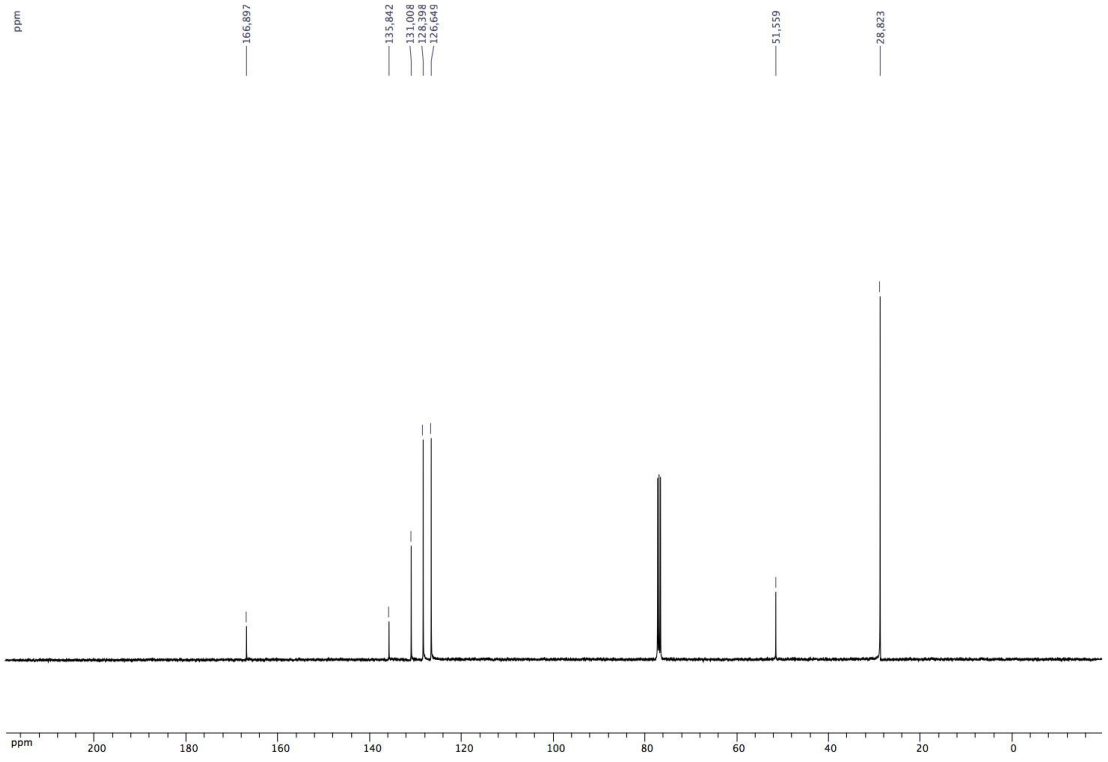
^{13}C NMR (101 MHz, $CDCl_3$) of *N*-cyclohexylbenzamide **3c**



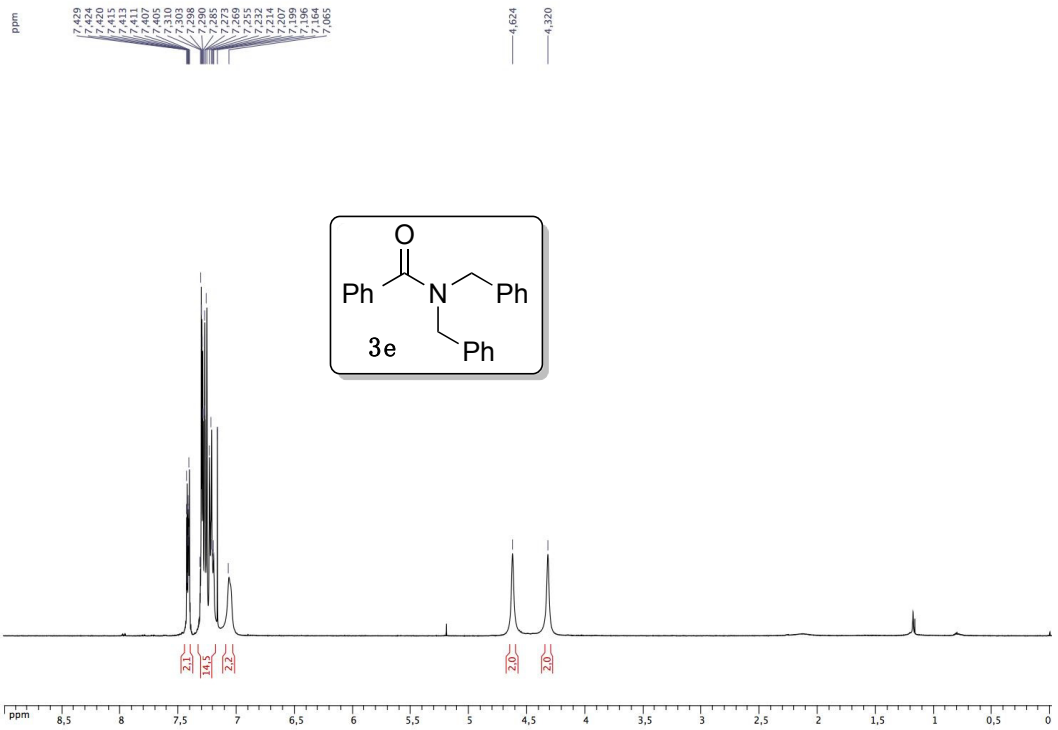
^{1}H NMR (400 MHz, $CDCl_3$) of *N-tert*-butylbenzamide **3d**



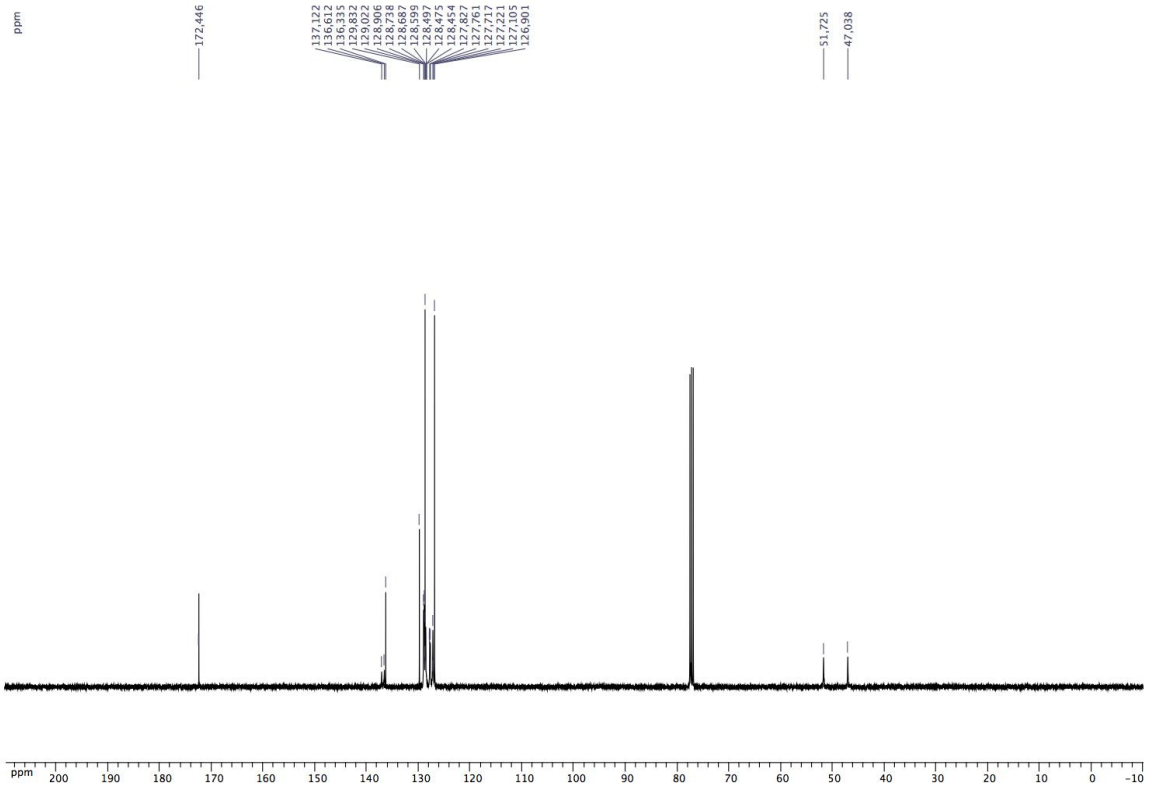
^{13}C NMR (101 MHz, $CDCl_3$) of *N-tert*-butylbenzamide **3d**



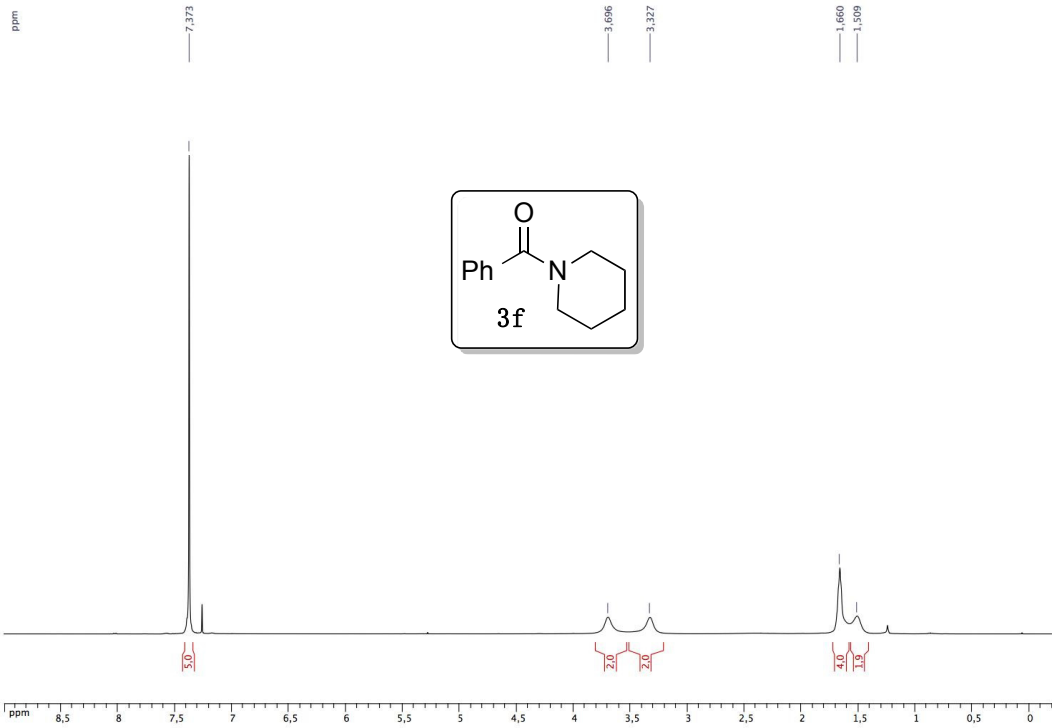
^{1}H NMR (400 MHz, $CDCl_3$) of *N*,*N*-dibenzylbenzamide **3e**



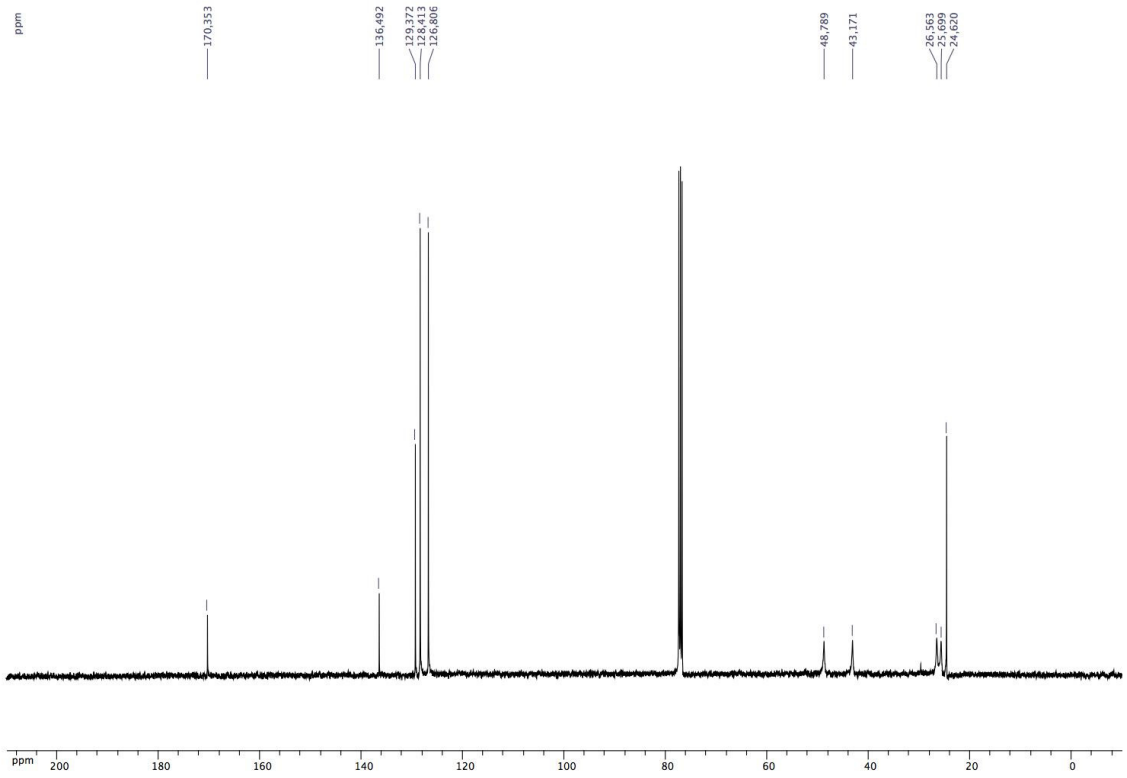
^{13}C NMR (101 MHz, $CDCl_3$) of *N*,*N*-dibenzylbenzamide **3e**



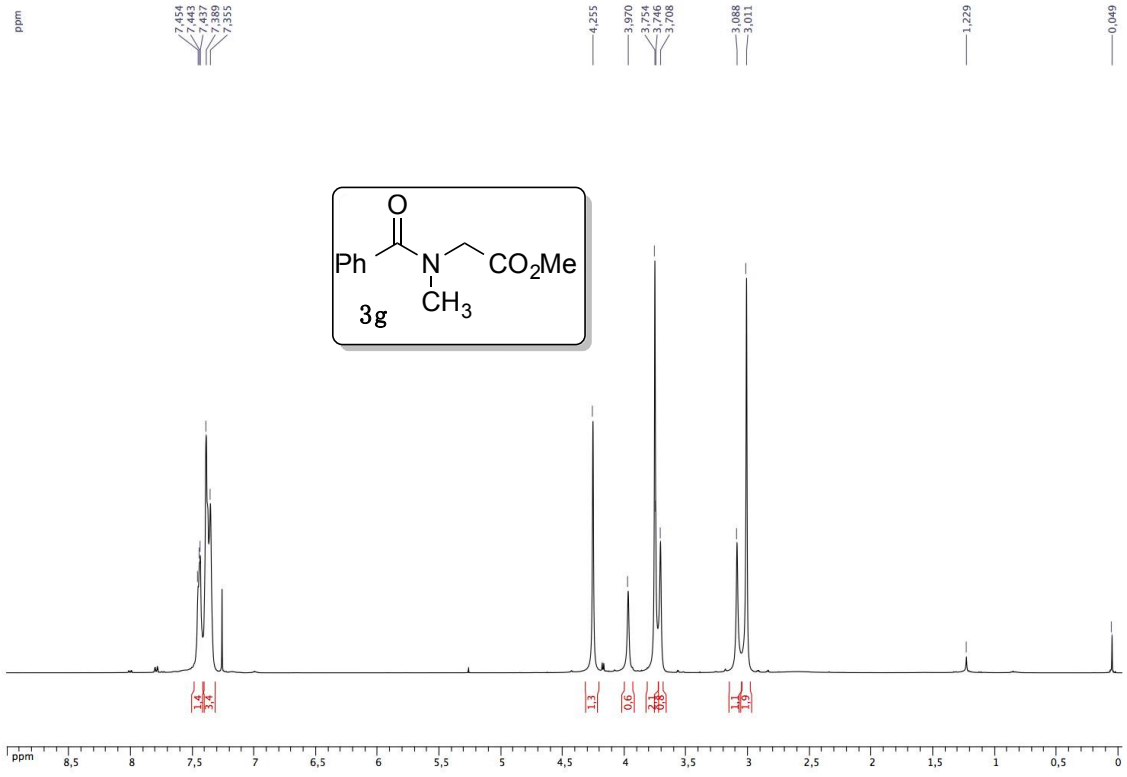
^{1}H NMR (400 MHz, $CDCl_3$) of *N*-benzoylpiperidine **3f**



^{13}C NMR (101 MHz, $CDCl_3$) of *N*-benzoylpiperidine **3f**



^{1}H NMR (400 MHz, $CDCl_3$) of *N*-benzoylsarcosine methyl ester **3g**



^{13}C NMR (101 MHz, $CDCl_3$) of *N*-benzoylsarcosine methyl ester **3g**