

Cleavage of 1,3-Dicarbonyls through Oxidative Amidation

Phillip Biallas^a, Andreas P. Häring^a and Stefan F. Kirsch^{a,b}

^a Organic Chemistry, Bergische Universität Wuppertal, Gaußstraße 20, 42119 Wuppertal

^b sfkirsch@uni-wuppertal.de

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1. General remarks

All reactions were operated under air and no measures were taken to exclude water. The commercially available compounds and solvents were used as received. TLC was conducted with aluminium sheets (TLC silica gel 60 F₂₅₄) and visualized by exposure to UV light (254 nm) or stained with ceric ammonium molybdate (CAM), basic potassium permanganate (KMnO₄) and subsequent heating or treatment with Cl₂ and staining with an aqueous KI/starch mixture. Flash column chromatography was performed on silica gel (40-60 µm), the eluent used is reported in the particular experiments. Abbreviations of solvents are as followed: PE: petroleum ether, EA: ethyl acetate, DCM: dichloromethane, MeOH: methanol, iPrOH: isopropanol. IR spectra were measured using ATR-technique in the range of 400-4000 cm⁻¹. ¹H NMR spectra were recorded at 400 MHz or 600 MHz spectrometers, ¹³C NMR at 101 MHz or 151 MHz. Chemical shifts are reported as δ-values in ppm, coupling constants *J* in Hz. Multiplicities were defined by standard abbreviations. Low-resolution mass spectra (LRMS) were recorded using a LC/MS-combination (ESI). High-resolution mass spectra (HRMS) were obtained using ESI ionization methods on a MicroTOF.

2. General procedures

General procedure for the synthesis of amides **3** from 1,3-diones **1**

The 1,3-dione **1** (1.0 eq.), tetrabutylammonium azide (4.0 eq.), 4-PPY (4.0 eq.), amine **2** (2.0 eq.) were dissolved in THF (0.15 M) and iodine (2.2 eq.) was added. The reaction mixture was stirred over night at room temperature. Concentration under reduced pressure and purification by flash-chromatography on silica gel furnished the corresponding amides **3**.

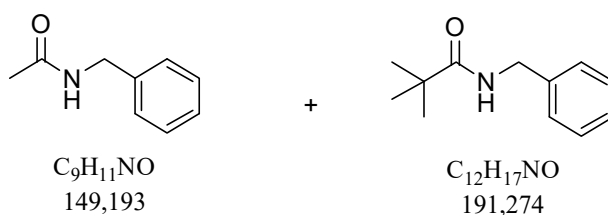
3. Experimental details

Synthesis of 2,2-diazido acylacetates **4** and **6**

The synthesis of 2,2-diazido acylacetates **4** and **6** was published recently.¹

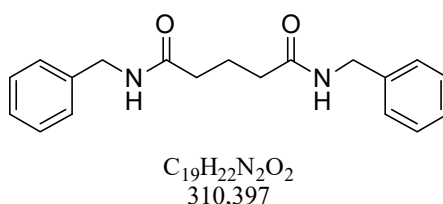
¹ H. Erhardt, A. P. Häring, A. Kotthaus, M. Roggel, M. L. Tong, P. Biallas, M. Jübermann, F. Mohr, S. F. Kirsch, *J. Org. Chem.*, **2015**, *80*, 12460

N-benzylacetamide (**3a**) and *N*-benzylpivalamide (**3b**)



3,3-Diazido-5,5-dimethylhexane-2,4-dione (50 mg, 0.22 mmol, 1.0 eq.) (**4**) was dissolved in 1.1 mL benzene and a solution of 53 mg (0.49 mmol, 2.2 eq.) benzylamine (**2a**) in 1.1 mL benzene was added. The reaction mixture was allowed to stir over night at room temperature. Evaporation of the solvent under reduced pressure and flash-chromatography on silica gel (EA:PE 1:9 → EA:*i*PrOH 8:2) gave 29 mg (0.19 mmol, 87%) *N*-benzylacetamide (**3a**) and 39 mg (0.20 mmol, 91%) *N*-benzylpivalamide (**3b**) as colorless solids. **3a**: **TLC**: R_f = 0.27 (DCM:MeOH 95:3) [Cl_2]. **^1H NMR** (400 MHz, CDCl_3) δ [ppm] = 7.42 - 7.27 (m, 5 H), 5.75 (br. s., 1 H), 4.43 (d, J = 5.6 Hz, 2 H), 2.02 (s, 3 H). **^{13}C NMR** (101 MHz, CDCl_3) δ [ppm] = 170.0, 138.4, 128.9, 128.0, 127.7, 44.0, 23.4. The analytical data are in agreement with previously reported ones.² **3b**: **TLC**: R_f = 0.73 (EA:PE 1:1) [Cl_2]. **^1H NMR** (400 MHz, CDCl_3) δ [ppm] = 7.38 - 7.23 (m, 5 H), 5.89 (br. s., 1 H), 4.44 (d, J = 5.8 Hz, 2 H), 1.23 (s, 9 H). **^{13}C NMR** (101 MHz, CDCl_3) δ [ppm] = 178.4, 138.8, 128.9, 127.8, 127.6, 43.8, 38.9, 27.8. The analytical data are in agreement with previously reported ones.³

*N*¹,*N*⁵-dibenzylglutaramide (**3c**)



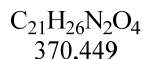
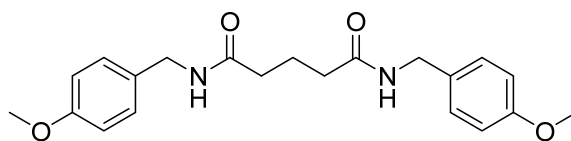
According to the general procedure using (25 mg, 0.22 mmol) cyclohexane-1,3-dione (**1a**), *N*¹,*N*⁵-dibenzylglutaramide (**3b**) was obtained as a colorless solid after chromatography (EA:PE 9:1 → EA). Yield: 42 mg, 0.14 mmol, 63%. **TLC**: R_f = 0.19 (EA:PE 9:1) [Cl_2]. **^1H NMR** (400 MHz, $\text{DMSO}-d_6$) δ [ppm] = 8.30 (t, J = 5.7 Hz, 2 H), 7.41 - 7.15 (m, 10 H), 4.27 (d, J = 6.1 Hz, 4 H), 2.17 (t, J = 7.6 Hz, 4 H), 1.79 (quin, J = 7.5 Hz, 2 H). **^{13}C NMR** (101 MHz, $\text{DMSO}-d_6$) δ [ppm] = 171.7, 139.6, 128.2, 127.1, 126.6, 41.9, 34.7, 21.6. The analytical data are in agreement with previously reported ones.⁴

² H. Morimoto, R. Fujiwara, Y. Shimizu, K. Morisaki, T. Ohshima, *Org. Lett.* **2014**, 16, 2018.

³ J. E. Taylor, M. D. Jones, J. M. J. Williams, S. D. Bull, *J. Org. Chem.* **2012**, 77, 2808.

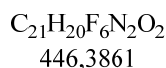
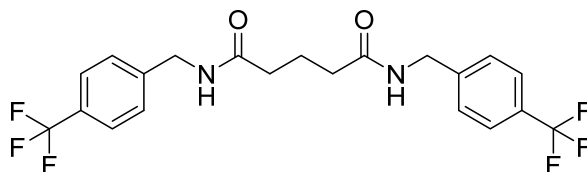
⁴ T. B. Nguyen, L. Ermolenko, M. T. H. Dau, A. Al-Mourabit, *Heterocycles* **2014**, 88, 403.

***N*¹,*N*⁵-bis(4-methoxybenzyl)glutaramide (3d)**



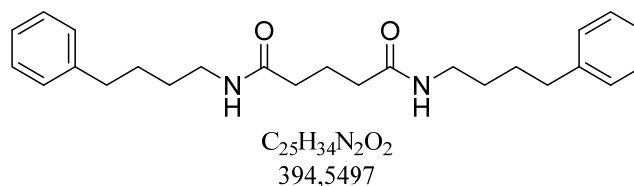
According to the general procedure using (10 mg, 0.09 mmol) cyclohexane-1,3-dione (**1a**), *N*¹,*N*⁵-bis(4-methoxybenzyl)glutaramide (**3b**) was obtained as a colorless solid after chromatography (EA). Yield: 27 mg, 0.07 mmol, 86%. **TLC**: R_f = 0.09 (DCM:MeOH 95:5) [Cl_2]. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3237, 3064, 3012, 2918, 2853, 1622, 1557, 1509, 1451, 1423, 1344, 1301, 1247, 1221, 1166, 1110, 1026, 815, 773, 586, 564, 525. **¹H NMR** (600 MHz, DMSO-*d*₆) δ [ppm] = 8.20 (t, J = 5.8 Hz, 2 H), 7.22 - 7.10 (m, 4 H), 6.93 - 6.81 (m, 4 H), 4.17 (d, J = 6.0 Hz, 4 H), 3.30 (s, 6 H), 2.12 (t, J = 7.5 Hz, 4 H), 1.75 (quin, J = 7.5 Hz, 2 H). **¹³C NMR** (151 MHz, DMSO-*d*₆) δ [ppm] = 171.5, 158.1, 131.6, 128.4, 113.6, 55.0, 41.4, 34.77, 21.6. **LRMS** (ESI): [m/z] 371.2 (100) [$M+H^+$]. **HRMS** (ESI): [m/z] 393.1784 (calcd. for $C_{21}H_{26}N_2O_4Na_1^+$: 393.1785).

***N*¹,*N*⁵-bis(4-(trifluoromethyl)benzyl)glutaramide (3e)**



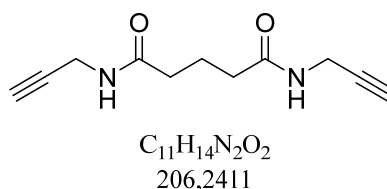
According to the general procedure using (15 mg, 0.13 mmol) cyclohexane-1,3-dione (**1a**), *N*¹,*N*⁵-bis(4-(trifluoromethyl)benzyl)glutaramide (**3e**) was obtained as a colorless solid after chromatography (EA). Yield: 33 mg, 0.07 mmol, 57%. **TLC**: R_f = 0.24 (DCM:MeOH 95:5) [Cl_2]. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3289, 3085, 2927, 2856, 1641, 1553, 1418, 1321, 1165, 1108, 1065, 1018, 846, 818, 638, 522. **¹H NMR** (600 MHz, DMSO-*d*₆) δ [ppm] = 8.42 (t, J = 5.8 Hz, 2 H), 7.67 (d, J = 8.3 Hz, 4 H), 7.46 (d, J = 7.9 Hz, 4 H), 4.35 (d, J = 6.0 Hz, 4 H), 2.19 (t, J = 7.5 Hz, 4 H), 1.80 (quin, J = 7.4 Hz, 2 H). **¹³C NMR** (151 MHz, DMSO-*d*₆) δ [ppm] = 171.9, 144.6, 127.7, 127.3 (q, J = 31.5 Hz), 125.1 (q, J = 4.1 Hz), 124.3 (q, J = 271.5 Hz), 41.6, 34.6, 21.4. **LRMS** (ESI): [m/z] 447.1 (100) [$M+H^+$]. **HRMS** (ESI): [m/z] 469.1322 (calcd. for $C_{21}H_{20}F_6N_2O_2Na_1^+$: 469.1321).

*N*¹,*N*⁵-bis(4-phenylbutyl)glutaramide (**3f**)



According to the general procedure using (15 mg, 0.13 mmol) cyclohexane-1,3-dione (**1a**), *N*¹,*N*⁵-bis(4-phenylbutyl)glutaramide (**3f**) was obtained as a yellow solid after chromatography (EA). Yield: 36 mg, 0.09 mmol, 70%. **TLC**: R_f = 0.16 (DCM:MeOH 95:5) [Cl_2]. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3271, 3061, 3029, 2941, 2877, 2859, 1652, 1629, 1547, 1476, 1422, 1356, 1248, 1168, 744, 697, 580, 525. **¹H NMR** (400 MHz, DMSO-*d*₆) δ [ppm] = 7.72 (t, J = 5.6 Hz, 2 H), 7.32 - 7.21 (m, 4 H), 7.21 - 7.10 (m, 6 H), 3.11 - 2.94 (m, 4 H), 2.56 (t, J = 7.6 Hz, 4 H), 2.02 (t, J = 7.5 Hz, 4 H), 1.68 (quin, J = 7.5 Hz, 2 H), 1.54 (quin, J = 7.6 Hz, 4 H), 1.39 (quin, J = 7.6 Hz, 4 H). **¹³C NMR** (101 MHz, DMSO-*d*₆) δ [ppm] = 171.5, 142.1, 128.2, 128.2, 125.6, 38.1, 34.8, 34.8, 28.8, 28.3, 21.6. **LRMS** (ESI): [m/z] 395.3 (100) [$\text{M}+\text{H}^+$]. **HRMS** (ESI): [m/z] 417.2514 (calcd. for $\text{C}_{25}\text{H}_{34}\text{N}_2\text{O}_2\text{Na}_1^+$: 417.2512).

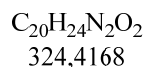
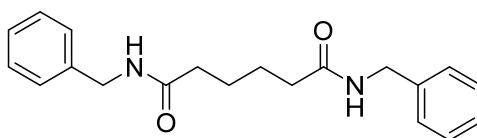
*N*¹,*N*⁵-di(prop-2-yn-1-yl)glutaramide (**3g**)



According to the general procedure using (15 mg, 0.13 mmol) cyclohexane-1,3-dione (**1a**), *N*¹,*N*⁵-di(prop-2-yn-1-yl)glutaramide (**3g**) was obtained as a colorless solid after chromatography (EA). Yield: 19 mg, 0.09 mmol, 72%. **TLC**: R_f = 0.48 (DCM:MeOH 95:5) [Cl_2]. **¹H NMR** (400 MHz, DMSO-*d*₆) δ [ppm] = 8.21 (t, J = 5.3 Hz, 2 H), 3.83 (dd, J = 2.5, 5.6 Hz, 4 H), 3.06 (t, J = 2.5 Hz, 2 H), 2.07 (t, J = 7.5 Hz, 4 H), 1.70 (quin, J = 7.5 Hz, 2 H). **¹³C NMR** (101 MHz, DMSO-*d*₆) δ [ppm] = 171.4, 81.3, 72.7, 34.3, 27.7, 21.1. The analytical data are in agreement with previously reported ones.⁵

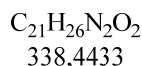
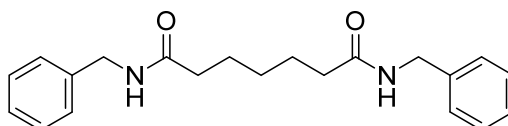
*N*¹,*N*⁶-dibenzyladipamide (**3h**)

⁵ V. Bretzler, M. Grübel, S. Meister, B. Rieger, *Macromol. Chem. Phys.* **2014**, 215, 1396.



According to the general procedure (3.0 eq. amine) using (25 mg, 0.19 mmol) cycloheptane-1,3-dione (**1b**), *N*¹,*N*⁶-dibenzyladipamide (**3h**) was obtained as a colorless solid after chromatography (EA:PE 9:1 → EA). Yield: 27 mg, 0.08 mmol, 43%. **TLC**: *R*_f = 0.21 (DCM:MeOH 95:5) [*Cl*₂]. **¹H NMR** (600 MHz, DMSO-*d*₆) δ [ppm] = 8.27 (t, *J* = 5.8 Hz, 2 H), 7.32 - 7.22 (m, 10 H), 4.26 (d, *J* = 6.0 Hz, 4 H), 2.14 (t, *J* = 6.4 Hz, 4 H), 1.53 (m, 4 H). **¹³C NMR** (151 MHz, DMSO-*d*₆) δ [ppm] = 171.9, 139.7, 128.2, 127.1, 126.6, 41.9, 35.2, 25.0. The analytical data are in agreement with previously reported ones.⁶

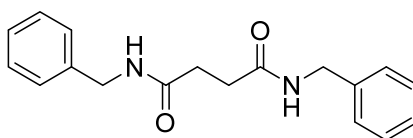
*N*¹,*N*⁷-dibenzylheptanediamide (**3i**)



According to the general procedure using (15 mg, 0.11 mmol) cyclooctane-1,3-dione (**1c**), *N*¹,*N*⁷-dibenzylheptanediamide (**3i**) was obtained as a colorless solid after chromatography (EA). Yield: 77 mg, 0.05 mmol, 51%. **TLC**: *R*_f = 0.35 (DCM:MeOH 95:5) [*Cl*₂]. **IR** (ATR): $\tilde{\nu}$ [cm⁻¹] = 3308, 3063, 3031, 2924, 2863, 1634, 1533, 1452, 1421, 1347, 1266, 1235, 1200, 1024, 692, 607, 570, 507. **¹H NMR** (600 MHz, DMSO-*d*₆) δ [ppm] = 8.26 (t, *J* = 5.6 Hz, 2 H), 7.35 - 7.19 (m, 10 H), 4.25 (d, *J* = 6.0 Hz, 4 H), 2.13 (t, *J* = 7.3 Hz, 4 H), 1.53 (quin, *J* = 7.5 Hz, 4 H), 1.31 - 1.21 (m, 2 H). **¹³C NMR** (151 MHz, DMSO-*d*₆) δ [ppm] = 172.0, 139.7, 128.2, 127.1, 126.6, 41.9, 35.2, 28.4, 25.1. **LRMS** (ESI): [*m/z*] 232.1 (6) [(*M*-C₇H₈N)⁺], 339.2 (100) [*M*+H⁺]. **HRMS** (ESI): [*m/z*] 361.1886 (calcd. for C₂₁H₂₆N₂O₂Na⁺: 361.1886).

*N*¹,*N*⁴-dibenzylsuccinamide (**3j**)

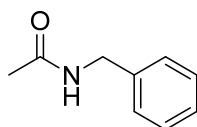
⁶ H. Zeng, Z. Guan, *J. Am. Chem. Soc.* **2011**, 133, 1159.



$C_{18}H_{20}N_2O_2$
296,3636

According to the general procedure using (25 mg, 0.25 mmol) cyclopentane-1,3-dione (**1d**), *N*¹,*N*⁴-dibenzylsuccinamide (**3j**) was obtained as a yellow solid after chromatography (EA:PE 9:1 → EA). Yield: 2 mg, 0.01 mmol, 3%. **TLC**: R_f = 0.33 (EA) [Cl_2]. **¹H NMR** (600 MHz, DMSO-*d*₆) δ [ppm] = 8.33 (t, J = 5.8 Hz, 2 H), 7.33 - 7.20 (m, 10 H), 4.26 (d, J = 6.0 Hz, 4 H), 2.42 (s, 4 H). **¹³C NMR** (151 MHz, DMSO-*d*₆) δ [ppm] = 171.3, 139.6, 128.2, 127.1, 126.6, 40.1, 30.1. The analytical data are in agreement with previously reported ones.⁴

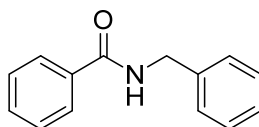
N-benzylacetamide (**3a**)



$C_9H_{11}NO$
149,1897

According to the general procedure using (10 mg, 0.10 mmol) acetylacetone (**1e**), *N*-benzylacetamide (**3a**) was obtained as a colorless solid after chromatography (EA:PE 9:1). Yield: 30 mg, 0.20 mmol, 99%. **TLC**: R_f = 0.16 (EA:PE 7:3) [Cl_2]. **¹H NMR** (400 MHz, CDCl₃) δ [ppm] = 7.42 - 7.27 (m, 5 H), 5.75 (br. s., 1 H), 4.43 (d, J = 5.6 Hz, 2 H), 2.02 (s, 3 H). **¹³C NMR** (101 MHz, CDCl₃) δ [ppm] = 170.0, 138.4, 128.9, 128.0, 127.7, 44.0, 23.4. The analytical data are in agreement with previously reported ones.²

N-benzylbenzamide (**3k**)

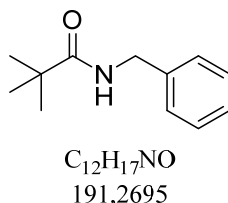


$C_{14}H_{13}NO$
211,2591

According to the general procedure using (20 mg, 0.09 mmol) 1,3-diphenylpropane-1,3-dione (**1f**), *N*-benzylbenzamide (**3k**) was obtained as a yellow solid after chromatography (EA:PE 3:7 → 1:1). Yield: 29 mg, 0.14 mmol, 80%. **TLC**: R_f = 0.22 (EA:PE 2:8) [Cl_2]. **¹H NMR** (400 MHz, CDCl₃) δ [ppm] = 7.86 - 7.65 (m, 2 H), 7.55 - 7.25 (m, 8 H), 6.52 (br. s., 1 H), 4.64 (d, J = 5.8 Hz, 2 H). **¹³C NMR** (101 MHz, CDCl₃) δ [ppm] = 167.5, 138.4, 134.5, 131.7,

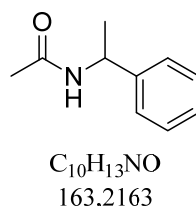
128.9, 128.7, 128.0, 127.7, 127.1, 44.3. The analytical data are in agreement with previously reported ones.⁷

***N*-benzylpivalamide (3b)**



According to the general procedure using (15 mg, 0.08 mmol) dipivaloylmethane (**1g**), *N*-benzylpivalamide (**3b**) was obtained as a colorless solid after chromatography (EA:PE 1:9 → 6:4). Yield: 21 mg, 0.11 mmol, 70%. **TLC**: R_f = 0.73 (EA:PE 1:1) [Cl_2]. **¹H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 7.38 - 7.23 (m, 5 H), 5.89 (br. s., 1 H), 4.44 (d, J = 5.8 Hz, 2 H), 1.23 (s, 9 H). **¹³C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 178.4, 138.8, 128.9, 127.8, 127.6, 43.8, 38.9, 27.8. The analytical data are in agreement with previously reported ones.³

***N*-(1-phenylethyl)acetamide (3l)**

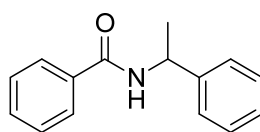


According to the general procedure using (10 mg, 0.10 mmol) acetylacetone (**1e**), *N*-(1-phenylethyl)acetamide (**3l**) was obtained as a pale yellow solid after chromatography (EA:PE 9:1). Yield: 28 mg, 0.17 mmol, 87%. **TLC**: R_f = 0.19 (EA:PE 7:3) [Cl_2]. **¹H NMR** (400 MHz, $CDCl_3$) δ [ppm] = 7.38 - 7.20 (m, 5 H), 6.02 (br. s., 1 H), 5.11 (dq, J = 2x 7.1 Hz, 1 H), 1.95 (s, 3 H), 1.47 (d, J = 7.1 Hz, 3 H). **¹³C NMR** (101 MHz, $CDCl_3$) δ [ppm] = 169.3, 143.4, 128.7, 127.4, 126.3, 48.9, 23.5, 21.8. The analytical data are in agreement with previously reported ones.⁸

⁷ H. Zeng, J. Huang, *Org. Lett.* **2015**, 17, 4276.

⁸ N. Hu, G. Zhao, Y. Zhang, X. Liu, G. Li, W. Tang, *J. Am. Chem. Soc.* **2015**, 137, 6746.

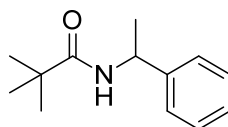
***N*-(1-phenylethyl)benzamide (3m)**



C₁₅H₁₅NO
225,2857

According to the general procedure using (20 mg, 0.09 mmol) 1,3-diphenylpropane-1,3-dione (**1f**), *N*-(1-phenylethyl)benzamide (**3m**) was obtained as a yellow solid after chromatography (EA:PE 3:7). Yield: 29 mg, 0.13 mmol, 75%. **TLC**: R_f = 0.24 (EA:PE 2:8) [Cl₂]. **¹H NMR** (400 MHz, CDCl₃) δ [ppm] = 7.86 - 7.72 (m, 2 H), 7.56 - 7.27 (m, 8 H), 6.42 (br. s., 1 H), 5.37 (quin, J = 7.1 Hz, 1 H), 1.63 (d, J = 7.1 Hz, 3 H). **¹³C NMR** (101 MHz, CDCl₃) δ [ppm] = 166.7, 143.3, 134.8, 131.6, 128.9, 128.7, 127.6, 127.1, 126.4, 49.4, 21.8. The analytical data are in agreement with previously reported ones.⁷

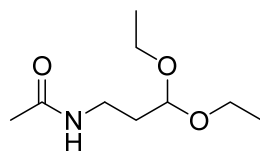
***N*-(1-phenylethyl)pivalamide (3n)**



C₁₃H₁₉NO
205,2961

According to the general procedure using (15 mg, 0.08 mmol) dipivaloylmethane (**1g**), *N*-(1-phenylethyl)pivalamide (**3n**) was obtained as a yellow solid after chromatography (EA:PE 3:7). Yield: 27 mg, 0.13 mmol, 82%. **TLC**: R_f = 0.81 (EA:PE 1:1) [Cl₂]. **¹H NMR** (600 MHz, CDCl₃) δ [ppm] = 7.38 - 7.21 (m, 5 H), 5.80 (br. s., 1 H), 5.11 (quin, J = 7.2 Hz, 1 H), 1.48 (d, J = 6.8 Hz, 3 H), 1.20 (s, 9 H). **¹³C NMR** (151 MHz, CDCl₃) δ [ppm] = 177.6, 143.7, 128.8, 127.37, 126.16, 48.6, 38.7, 27.7, 21.8. The analytical data are in agreement with previously reported ones.⁹

***N*-(3,3-diethoxypropyl)acetamide (3o)**



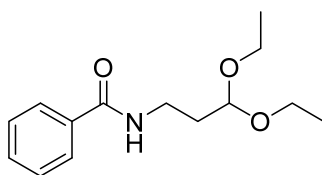
C₉H₁₉NO₃
189,2521

According to the general procedures using (10 mg, 0.10 mmol) acetylacetone (**1e**), *N*-(3,3-diethoxypropyl)acetamide (**3o**) was obtained as a yellow oil after chromatography (EA).

⁹ D. P. Iwaniuk, C. Wolf, *J. Org. Chem.* **2010**, 75, 6724.

Yield: 33 mg, 0.17 mmol, 86%. **TLC**: R_f = 0.13 (EA:PE 7:3) [Cl_2]. **IR** (ATR) : $\tilde{\nu}$ [cm^{-1}] = 3292, 3080, 2975, 2931, 2879, 1722, 1649, 1544, 1371, 1292, 1056, 600. **^1H NMR** (600 MHz, CDCl_3) δ [ppm] = 6.22 (br. s., 1 H), 4.52 (t, J = 5.3 Hz, 1 H), 3.64 (dq, J = 9.4 Hz, 7.0 Hz, 2 H), 3.47 (dq, J = 9.4 Hz, 7.0 Hz, 2 H), 3.36 - 3.26 (m, 2 H), 1.90 (s, 3 H), 1.82 - 1.73 (m, 2 H) 1.18 (t, J = 7.0 Hz, 6 H). **^{13}C NMR** (151 MHz, CDCl_3) δ [ppm] = 169.9, 102.6, 62.1, 35.7, 33.0, 23.4, 15.4. **LRMS** (ESI): [m/z] 144.1 (100) [$(\text{M}-\text{C}_2\text{H}_5)^+$], 212.1 (2) [$\text{M}+\text{Na}^+$]. **HRMS** (ESI): [m/z] 212.1256 (calcd. for $\text{C}_9\text{H}_{19}\text{N}_1\text{O}_3\text{Na}^+$: 212.1257).

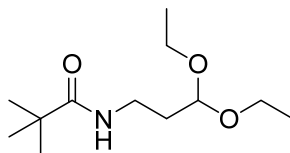
***N*-(3,3-diethoxypropyl)benzamide (3p)**



$\text{C}_{14}\text{H}_{21}\text{NO}_3$
251,3214

According to the general procedure using (20 mg, 0.09 mmol) 1,3-diphenylpropane-1,3-dione (**1f**), *N*-(3,3-diethoxypropyl)benzamide (**3p**) was obtained as a yellow oil after chromatography (EA:PE 4:6). Yield: 33 mg, 0.13 mmol, 75%. **TLC**: R_f = 0.10 (EA:PE 2:8) [Cl_2]. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3323, 2974, 2930, 2876, 1638, 1536, 1489, 1294, 1222, 1123, 1056, 973, 693, 508. **^1H NMR** (400 MHz, CDCl_3) δ [ppm] = 7.83 - 7.62 (m, 2 H), 7.62 - 7.34 (m, 3 H), 7.03 (br. s., 1 H), 4.64 (t, J = 4.9 Hz, 1 H), 3.71 (qd, J = 7.0, 9.3 Hz, 2 H), 3.63 - 3.48 (m, 4 H), 1.99 - 1.89 (m, 2 H), 1.23 (t, J = 7.1 Hz, 6 H). **^{13}C NMR** (101 MHz, CDCl_3) δ [ppm] = 167.2, 134.9, 131.4, 128.6, 126.9, 103.2, 62.4, 36.1, 32.9, 15.5. **LRMS** (ESI): [m/z] 105.0 (28) [$(\text{M}-\text{C}_7\text{H}_{16}\text{NO}_2)^+$], 206.1 (100) [$(\text{M}-\text{C}_2\text{H}_5\text{O})^+$], 274.1 (7) [$\text{M}+\text{Na}^+$]. **HRMS** (ESI): [m/z] 274.1412 (calcd. for $\text{C}_{14}\text{H}_{21}\text{N}_1\text{O}_3\text{Na}^+$: 274.1414).

***N*-(3,3-diethoxypropyl)pivalamide (3q)**

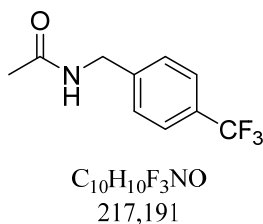


$\text{C}_{12}\text{H}_{25}\text{NO}_3$
231,3318

According to the general procedure using (15 mg, 0.08 mmol) dipivaloylmethane (**1g**), *N*-(3,3-diethoxypropyl)pivalamide (**3q**) was obtained as a yellow oil after chromatography (EA:PE 1:1). Yield: 21 mg, 0.09 mmol, 57%. **TLC**: R_f = 0.34 (EA:PE 1:1) [Cl_2]. **IR** (ATR): $\tilde{\nu}$

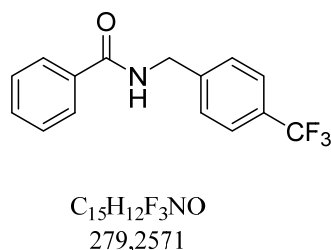
[cm^{-1}] = 3348, 2972, 2930, 2873, 1638, 1526, 1481, 1445, 1367, 1295, 1209, 1125, 1056, 979, 948, 648, 504. **^1H NMR** (600 MHz, CDCl_3) δ [ppm] = 6.43 (br. s., 1 H), 4.56 (t, J = 5.1 Hz, 1 H), 3.69 (qd, J = 7.1, 9.3 Hz, 2 H), 3.50 (qd, J = 7.0, 9.4 Hz, 2 H), 3.38 - 3.33 (m, 2 H), 1.81 (td, J = 4.8, 7.3 Hz, 2 H), 1.22 (t, J = 7.0 Hz, 6 H), 1.17 (s, 9 H). **^{13}C NMR** (151 MHz, CDCl_3) δ [ppm] = 178.3, 103.27, 62.3, 38.7, 35.6, 33.1, 27.7, 15.5. **LRMS** (ESI): [m/z] 186.2 (100) [(M-C₂H₅O)⁺], 254.2 (6) [M+Na⁺]. **HRMS** (ESI): [m/z] 254.1731 (calcd. for C₁₂H₂₅NiO₃Na⁺: 254.1727).

***N*-(4-(trifluoromethyl)benzyl)acetamide (3r)**



According to the general procedure using (10 mg, 0.10 mmol) acetylacetone (**1e**), *N*-(4-(trifluoromethyl)benzyl)acetamide (**3r**) was obtained as a yellow solid after chromatography (EA). Yield: 28 mg, 0.13 mmol, 65%. **TLC**: R_f = 0.22 (EA:PE 8:2) [Cl_2]. **^1H NMR** (600 MHz, CDCl_3) δ [ppm] = 7.54 (d, J = 8.3 Hz, 2 H), 7.34 (d, J = 7.9 Hz, 2 H), 6.39 (br. s., 1 H), 4.42 (d, J = 6.0 Hz, 2 H), 1.99 (s, 3 H). **^{13}C NMR** (151 MHz, CDCl_3) δ [ppm] = 170.4, 142.6, 129.8 (q, J = 33.0 Hz), 127.9, 125.6 (q, J = 3.3 Hz), 124.2 (q, J = 271.8 Hz), 43.2, 23.1. The analytical data are in agreement with previously reported ones.¹⁰

***N*-(4-(trifluoromethyl)benzyl)benzamide (3s)**

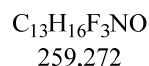
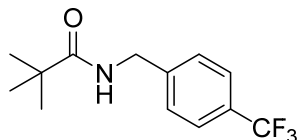


According to the general procedure using (20 mg, 0.09 mmol) 1,3-diphenylpropane-1,3-dione (**1f**), *N*-(4-(trifluoromethyl)benzyl)benzamide (**3s**) was obtained as a colorless solid after chromatography (EA:PE 3:7). Yield: 31 mg, 0.11 mmol, 65%. **TLC**: R_f = 0.22 (EA:PE 2:8) [Cl_2]. **^1H NMR** (400 MHz, CDCl_3) δ [ppm] = 7.85 - 7.69 (m, 2 H), 7.64 - 7.36 (m, 7 H), 6.70 (br. s., 1 H), 4.68 (d, J = 5.8 Hz, 2 H). **^{13}C NMR** (101 MHz, CDCl_3) δ [ppm] = 167.7, 142.5,

¹⁰ Y. Yamamoto, H. Hasegawa, H. Yamataka, *J. Org. Chem.* **2011**, 76, 4652.

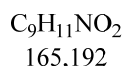
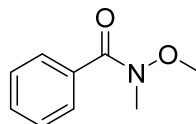
134.2, 131.9, 130.0 (q, $J = 32.2$ Hz), 128.8, 128.1, 127.1, 125.8 (q, $J = 3.7$ Hz), 121.5 (q, $J = 271.5$ Hz), 43.7. The analytical data are in agreement with previously reported ones.¹¹

***N*-(4-(trifluoromethyl)benzyl)pivalamide (3t)**



According to the general procedure using (15 mg, 0.08 mmol) dipivaloylmethane (**1g**), *N*-(4-(trifluoromethyl)benzyl)pivalamide (**3t**) was obtained as a colorless solid after chromatography (EA:PE 3:7). Yield: 30 mg, 0.11 mmol, 72%. **TLC:** $R_f = 0.64$ (EA:PE 1:1) [Cl_2]. **^1H NMR** (600 MHz, CDCl_3) δ [ppm] = 7.58 (d, $J = 8.3$ Hz, 2 H), 7.36 (d, $J = 7.9$ Hz, 2 H), 6.04 (br. s., 1 H), 4.48 (d, $J = 6.0$ Hz, 2 H), 1.23 (s, 9 H). **^{13}C NMR** (151 MHz, CDCl_3) δ [ppm] = 178.7, 143.0, 129.8 (q, $J = 33.0$ Hz), 127.9, 125.7 (q, $J = 4.4$ Hz), 124.3 (q, $J = 272.9$ Hz), 43.2, 38.9, 27.7. The analytical data are in agreement with previously reported ones.¹²

***N*-methoxy-*N*-methylbenzamide (3u)**



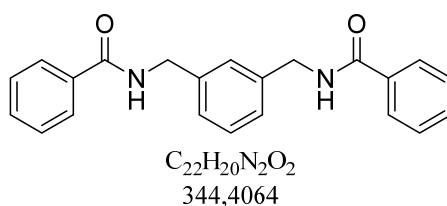
According to the general procedure using (30 mg, 0.13 mmol) 1,3-diphenylpropane-1,3-dione (**1f**), *N*-methoxy-*N*-methylbenzamide (**3u**) was obtained as a yellow oil after chromatography (EA:PE 3:7 $\rightarrow$ 1:1). Yield: 15 mg, 0.09 mmol, 35%. **TLC:** $R_f = 0.50$ (EA:PE 1:1) [UV]. **^1H NMR** (400 MHz, CDCl_3) δ [ppm] = 7.70 - 7.64 (m, 2 H), 7.49 - 7.36 (m, 3 H), 3.56 (s, 3 H), 3.36 (s, 3 H). **^{13}C NMR** (101 MHz, CDCl_3) δ [ppm] = 170.1, 134.3, 130.7, 128.3, 128.1, 61.2, 33.9. The analytical data are in agreement with previously reported ones.¹³

¹¹ D. P. Iwaniuk, C. Wolf, *J. Org. Chem.* **2010**, 75, 6724.

¹² L. Zhou, W. Lu, *Org. Lett.* **2014**, 16, 508.

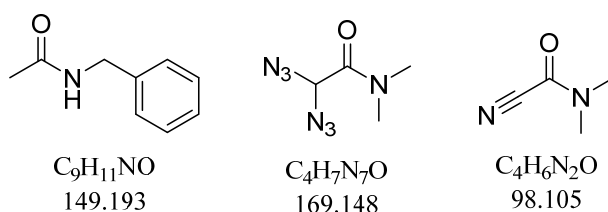
¹³ D. K. Friel, M. L. Snapper, A. H. Hoveyda, *J. Am. Chem. Soc.* **2008**, 130, 9942.

***N,N'*-(1,3-phenylenebis(methylene))dibenzamide (3v)**



According to the general procedure (1.0 eq. amine) using (20 mg, 0.09 mmol) 1,3-diphenylpropane-1,3-dione (**1f**), *N,N'*-(1,3-phenylenebis(methylene))dibenzamide (**3v**) was obtained as a yellow solid after chromatography (EA:PE 7:3). Yield: 18 mg, 0.05 mmol, 60%. **TLC**: R_f = 0.79 (EA:PE 7:3) [Cl_2]. **IR** (ATR): $\tilde{\nu}$ [cm^{-1}] = 3315, 3054, 3023, 2954, 2923, 2853, 1637, 1602, 1538, 1488, 1420, 1304, 1249, 991, 799, 753, 690, 519. **1H NMR** (600 MHz, DMSO- d_6) δ [ppm] = 9.02 (t, J = 6.0 Hz, 2 H), 7.98 - 7.78 (m, 4 H), 7.62 - 7.49 (m, 2 H), 7.49 - 7.38 (m, 4 H), 7.33 - 7.24 (m, 2 H), 7.24 - 7.15 (m, 2 H), 4.47 (d, J = 6.0 Hz, 4 H). **^{13}C NMR** (151 MHz, DMSO- d_6) δ [ppm] = 166.2, 139.8, 134.4, 131.1, 128.2, 128.2, 127.2, 125.8, 125.6, 42.5. **LRMS** (ESI): [m/z] 224.1 (15) [(M-C₇H₆NO)⁺], 345.2 (100) [M+H⁺], 367.1 (4) [M+Na⁺]. **HRMS** (ESI): [m/z] 367.1418 (calcd. for C₂₂H₂₀N₂O₂Na⁺: 367.1417).

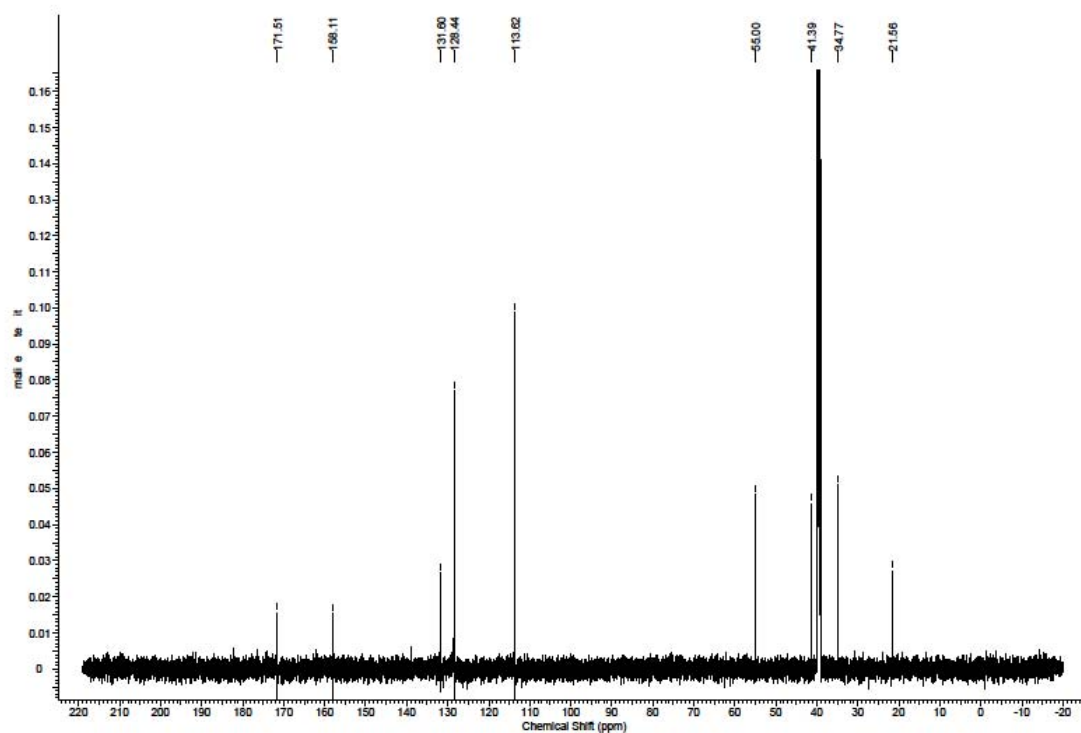
***N*-benzylacetamide (3a), dimethylcarbamoyl cyanide (7) and 2,2-diazido-*N,N*-dimethylacetamide (8)**



2,2-Diazido-*N,N*-dimethyl-3-oxobutanamide (50 mg, 0.24 mmol, 1.0 eq.) (**6**) was dissolved in benzene (1.2 mL, 0.1 M) under nitrogen. Benzylamine (56 mg, 0.52 mmol, 2.2 eq.) (**2a**) in benzene (1.2 mL) was added and the reaction mixture was stirred at room temperature for 20 h. Evaporation of the solvent under reduced pressure and flash-chromatography on silica gel (PE:EtOAc 9:1 → EA:*i*PrOH:MeOH 5:4:1) gave 13 mg of a 2:1 mixture containing dimethylcarbamoyl cyanide (7 mg, 0.07 mmol, 29%) (**7**) and 2,2-diazido-*N,N*-dimethylacetamide (6 mg, 0.04 mmol, 15%) (**8**) as colorless oil, and *N*-benzylacetamide (26 mg, 0.17 mmol, 74%) (**3a**) as white solid. **7**: R_f = 0.55 (PE:EtOAc 1:1) [$KMnO_4$]. **1H NMR** (400 MHz, CDCl₃) δ [ppm] = 3.29 (s, 3H), 3.01 (s, 3H). **^{13}C NMR** (101 MHz, CDCl₃) δ [ppm] = 144.9, 110.6, 38.0, 34.5. The analytical data are in agreement with previously

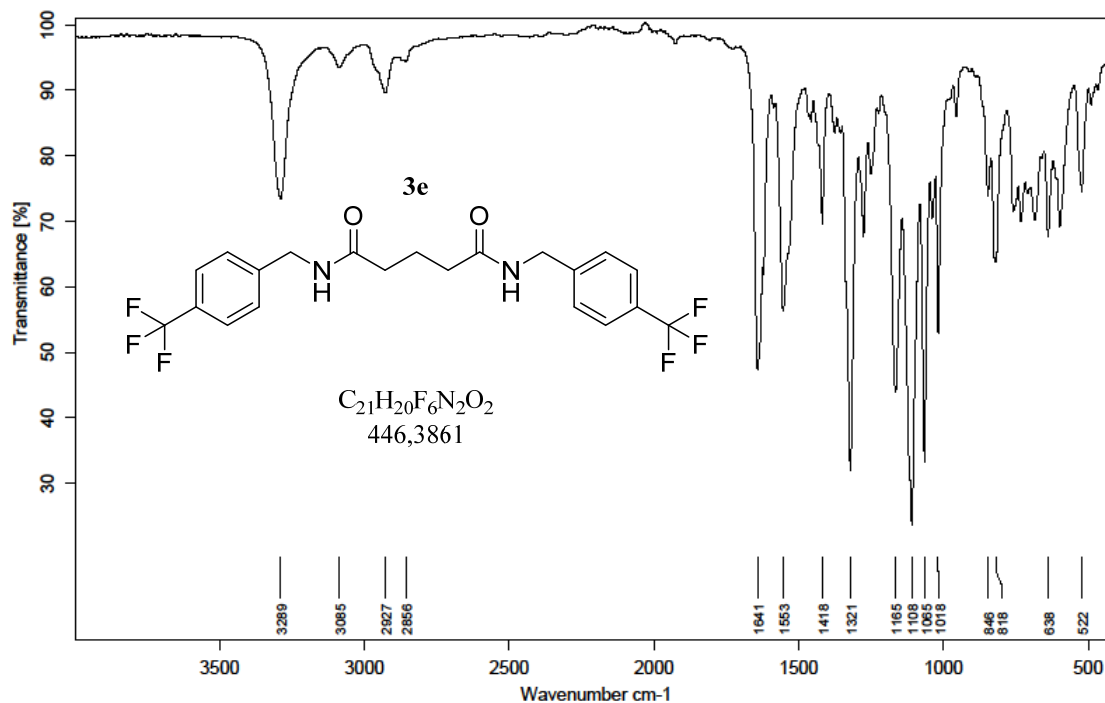
reported ones.¹⁴ **8**: $R_f = 0.55$ (PE:EtOAc 1:1) [KMnO₄]. ¹H NMR (400 MHz, CDCl₃) δ [ppm] = 5.01 (s, 1H), 3.06 (s, 3H), 3.02 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 164.5, 71.5, 37.0, 36.3. **3a**: $R_f = 0.27$ (DCM:MeOH 95:3) [Cl₂]. ¹H NMR (400 MHz, CDCl₃) δ [ppm] = 7.42 - 7.27 (m, 5 H), 5.75 (br. s., 1 H), 4.43 (d, $J = 5.6$ Hz, 2 H), 2.02 (s, 3 H). ¹³C NMR (101 MHz, CDCl₃) δ [ppm] = 170.0, 138.4, 128.9, 128.0, 127.7, 44.0, 23.4. The analytical data are in agreement with previously reported ones.²

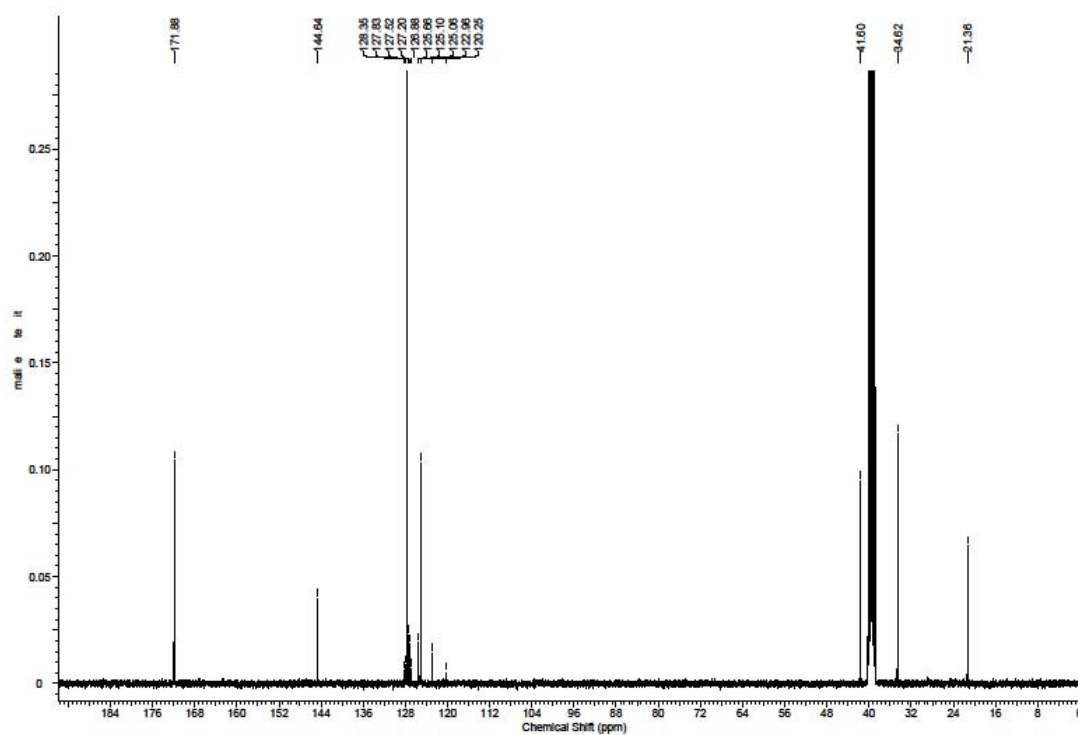
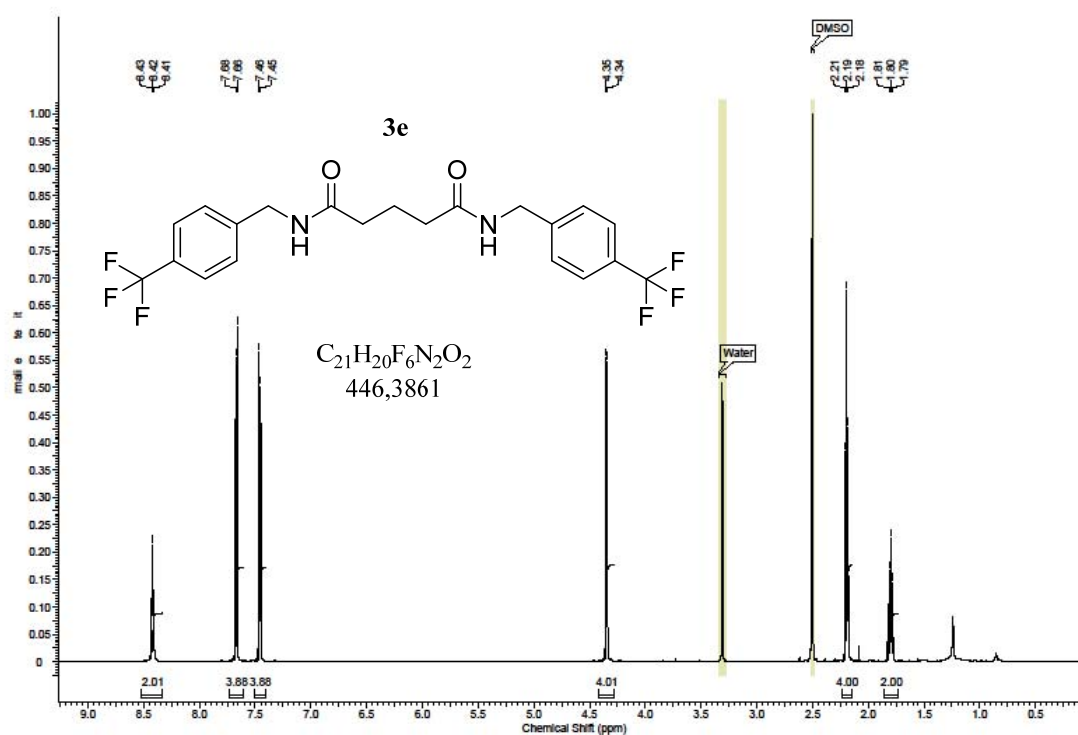
¹⁴ H. Kobler, K.-H. Schuster, G. Simchen, *Justus Liebigs Annalen der Chemie*, **1978**, 12, 1946.

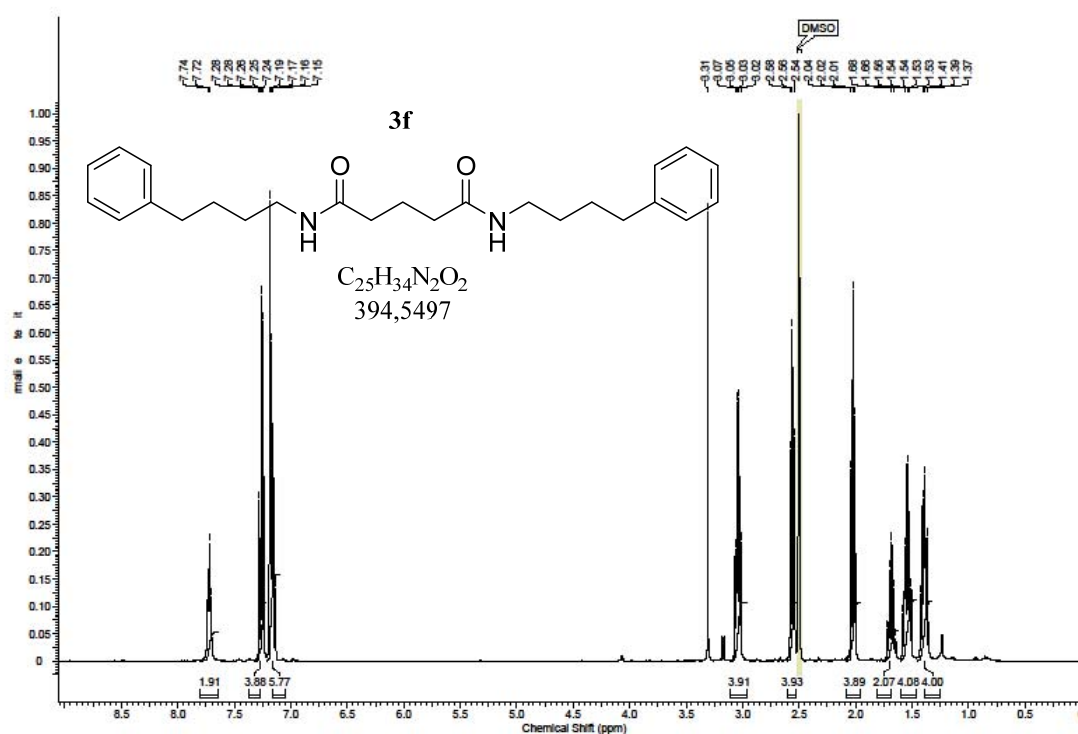
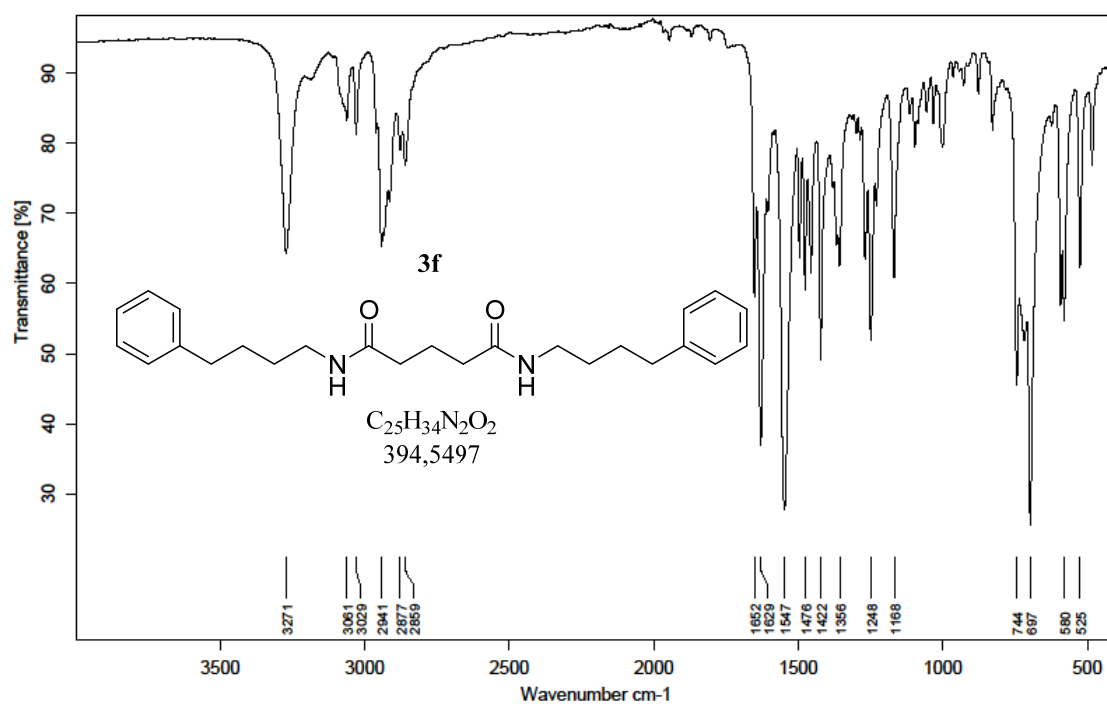


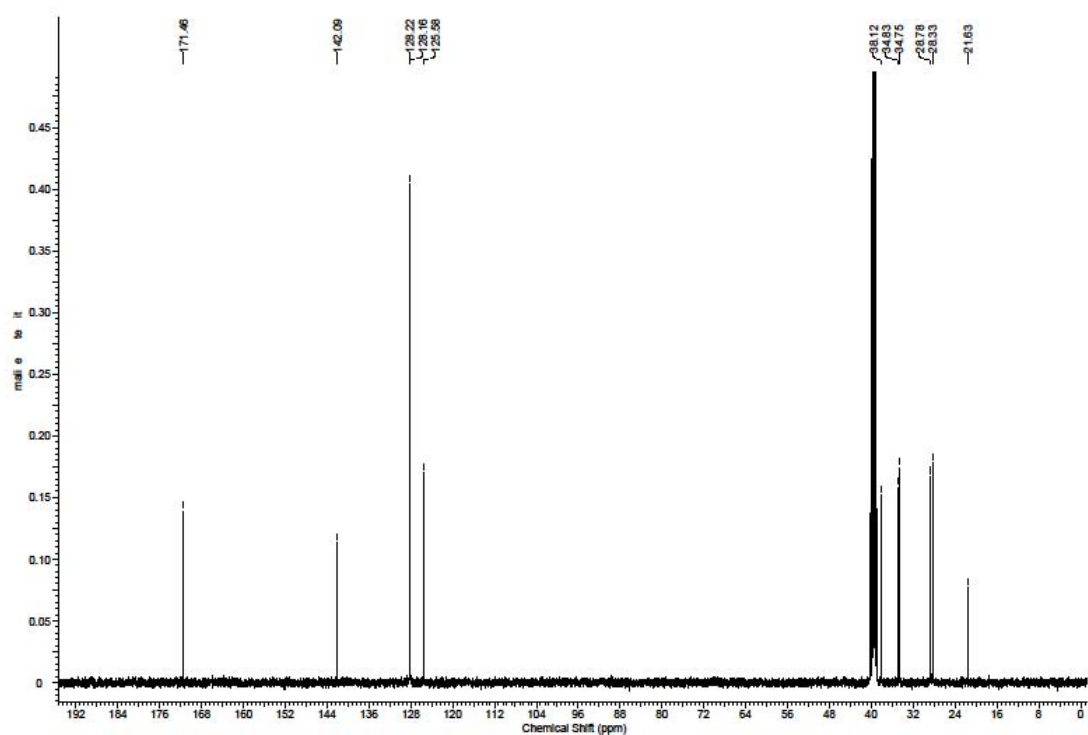
ocpb406.0

02.12.2015



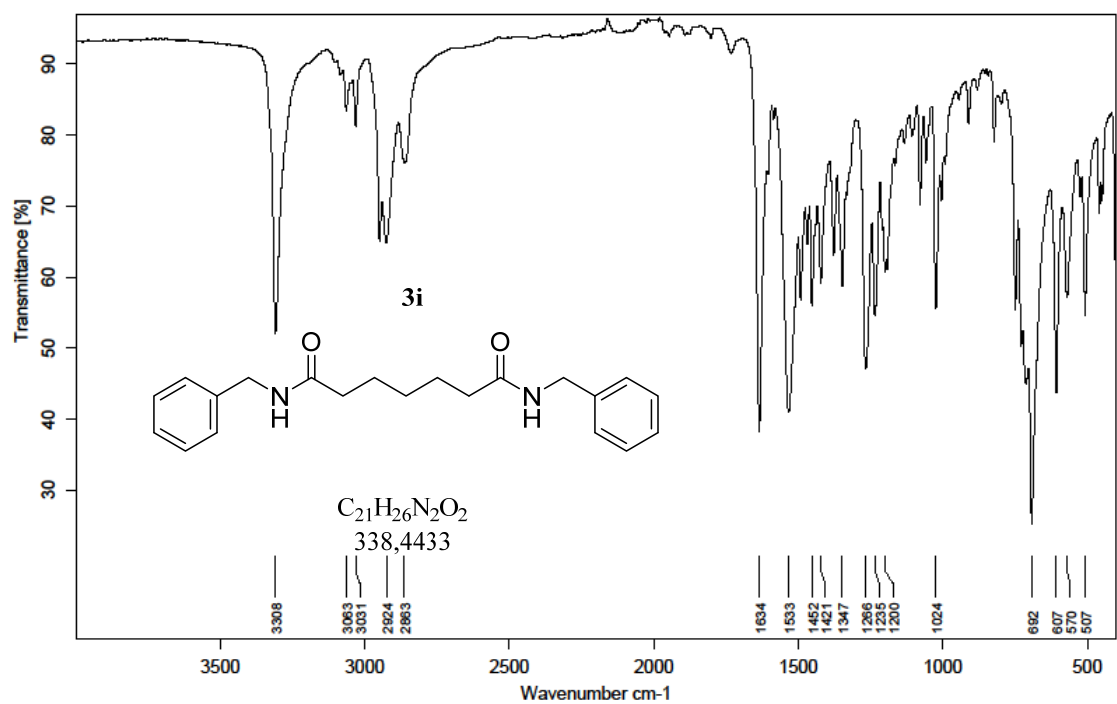


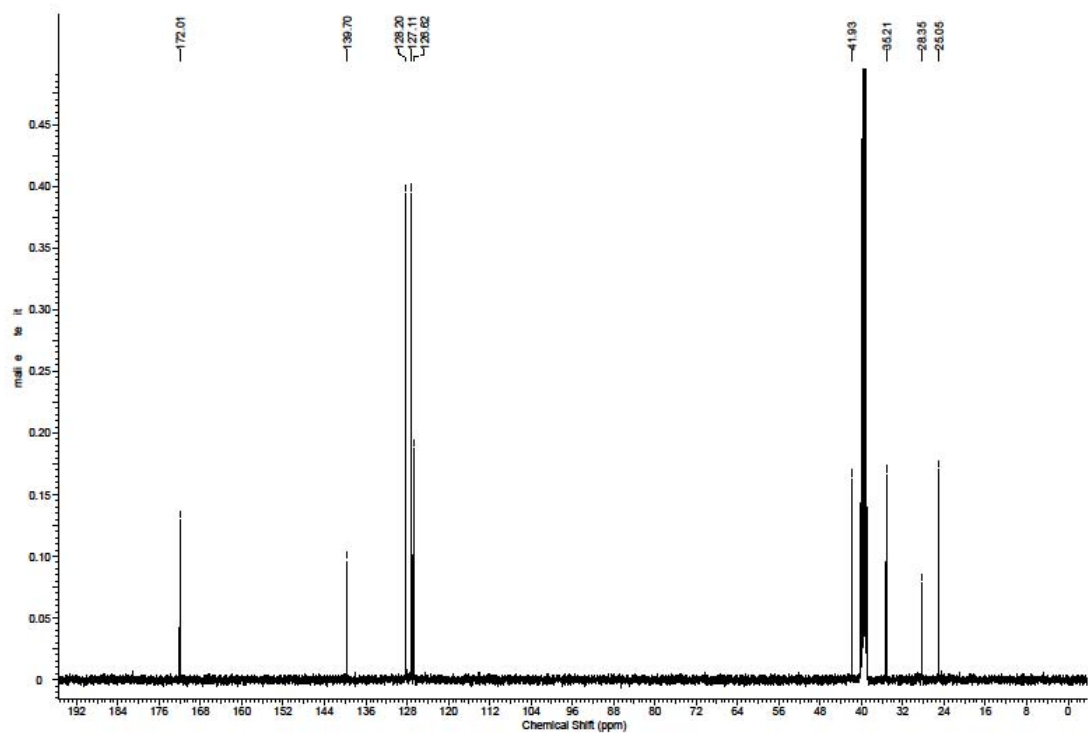


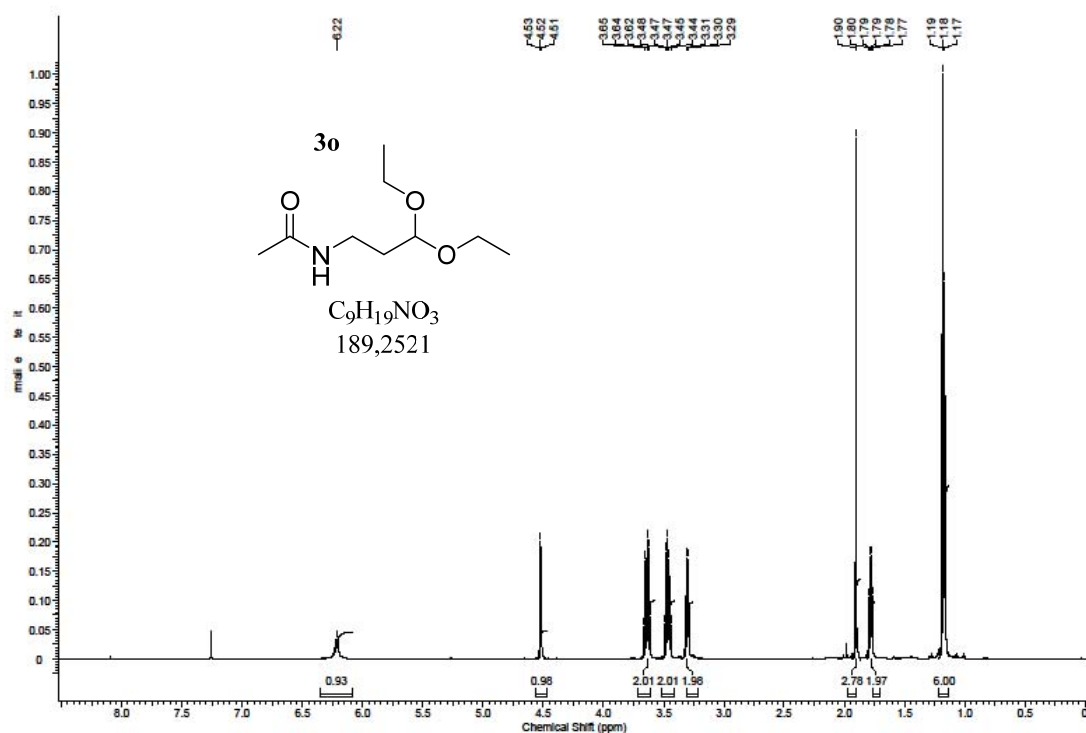
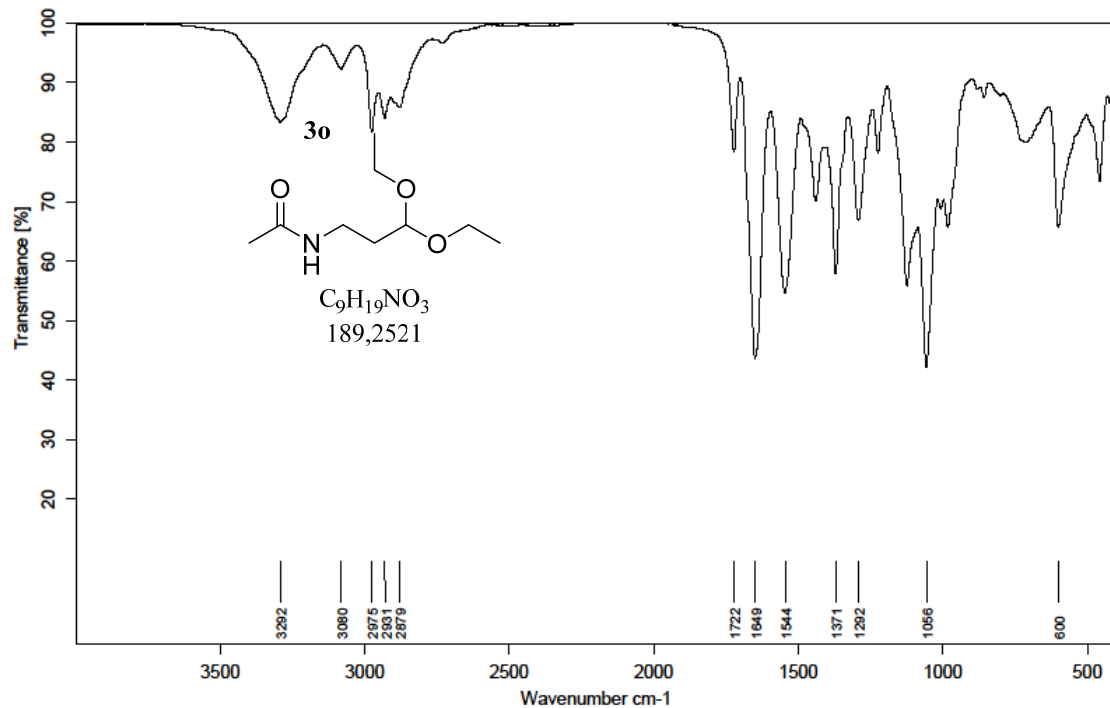


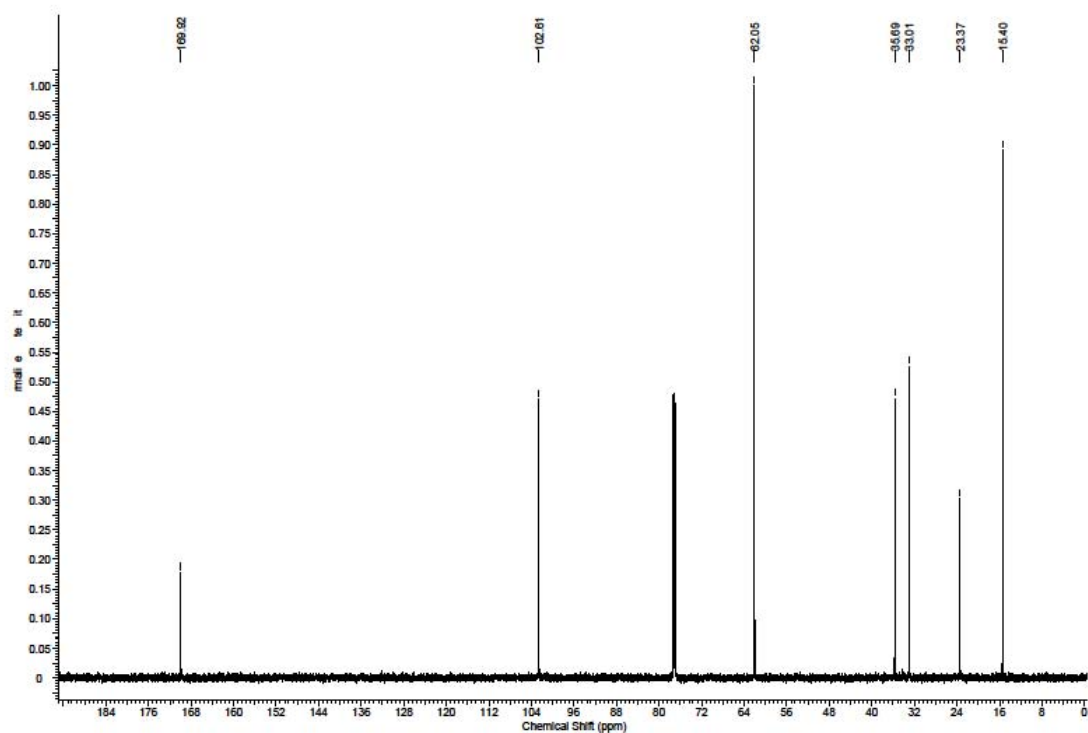
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11.12.2015



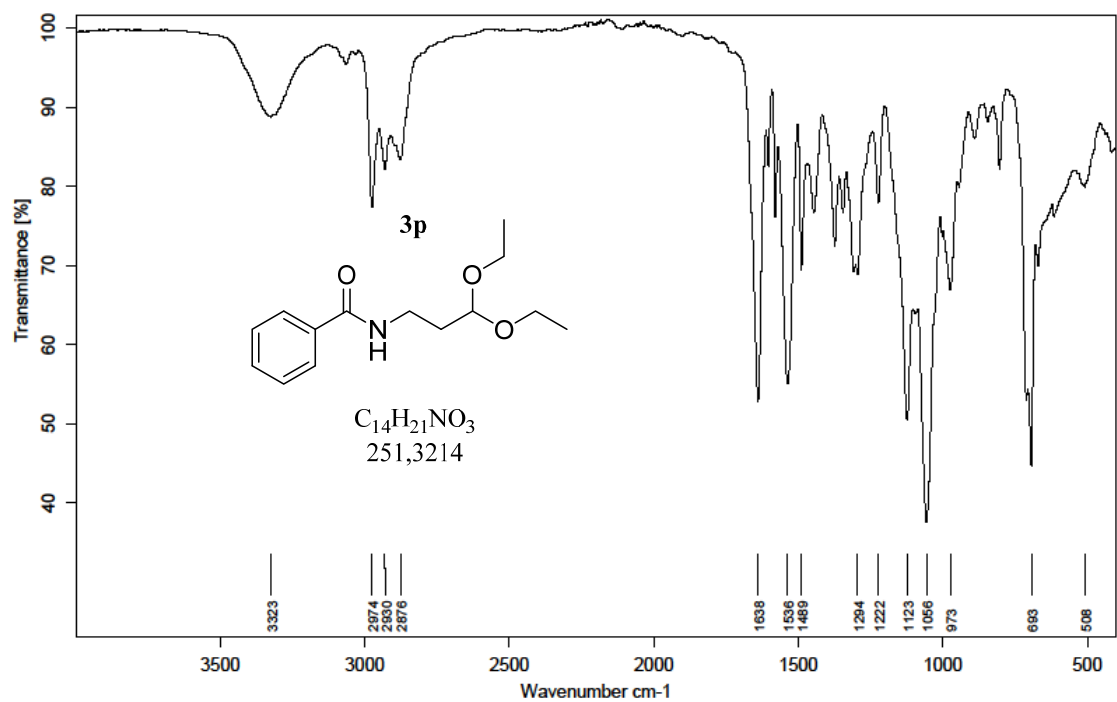


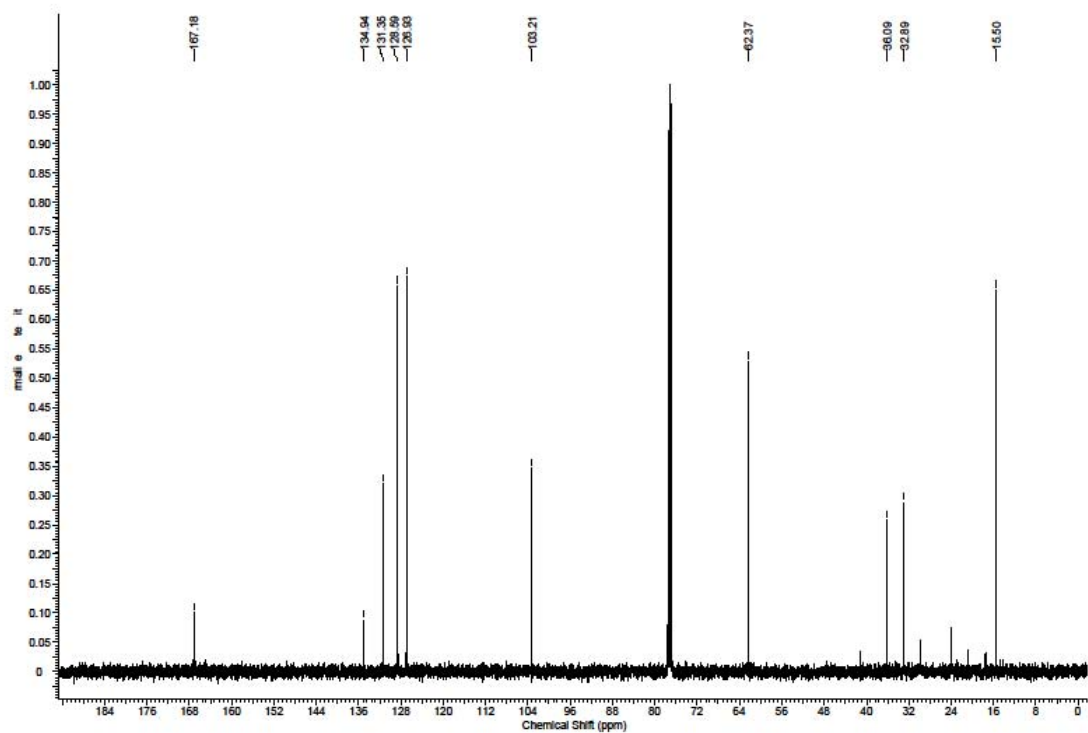
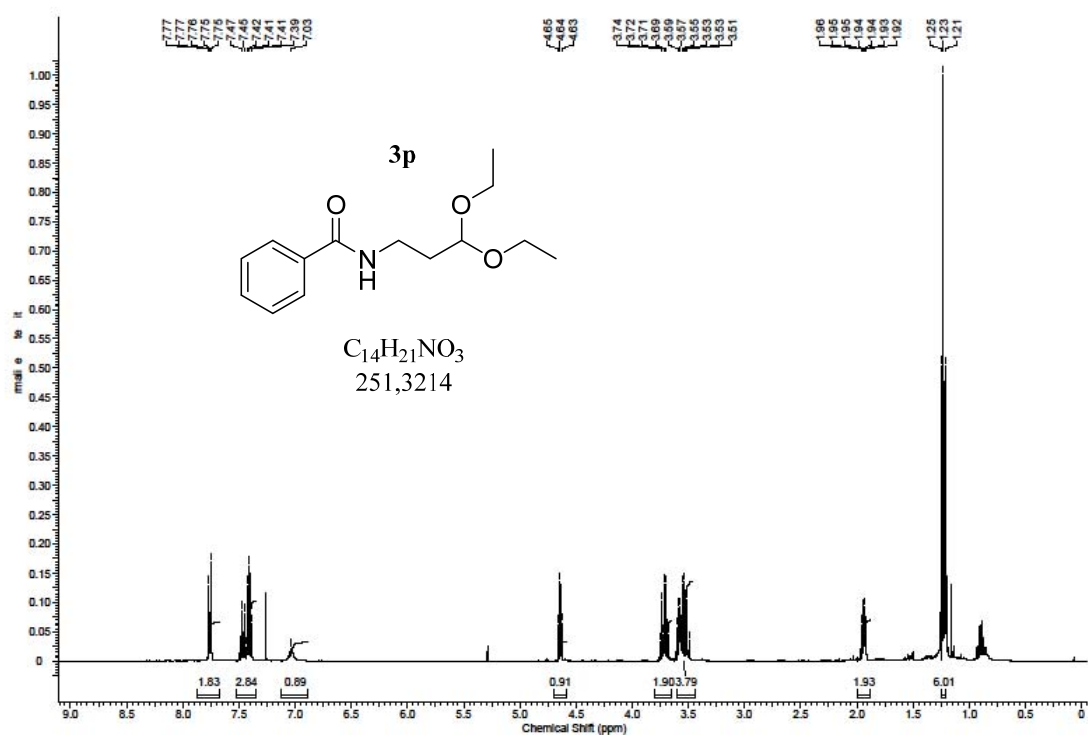


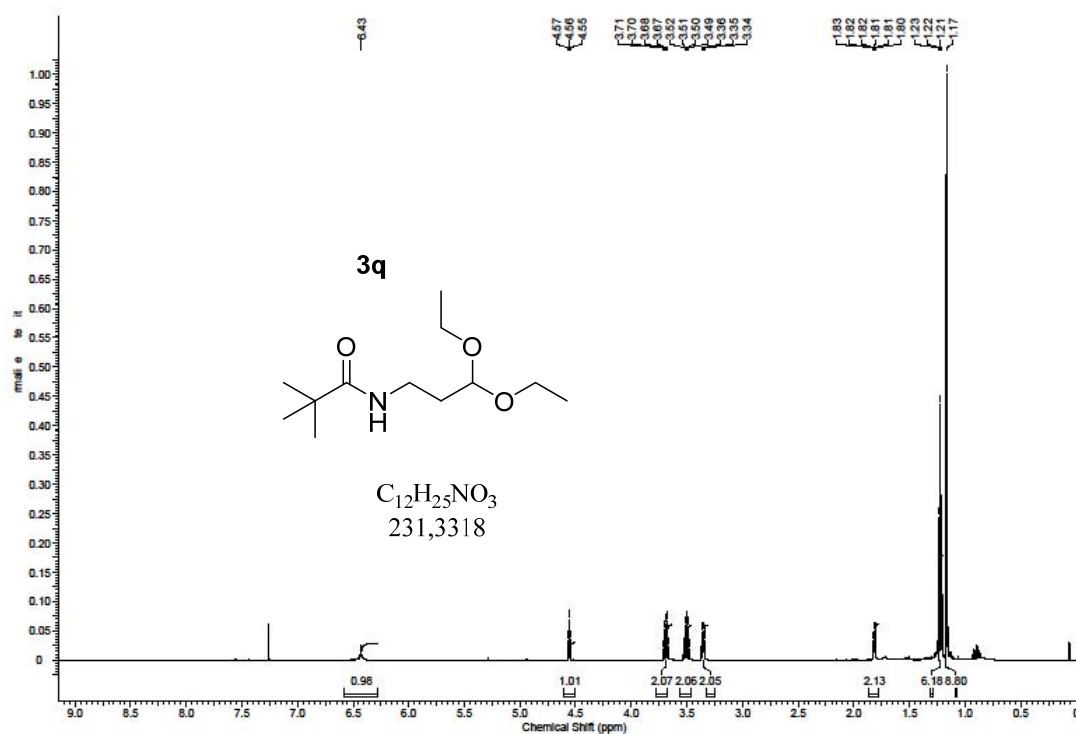
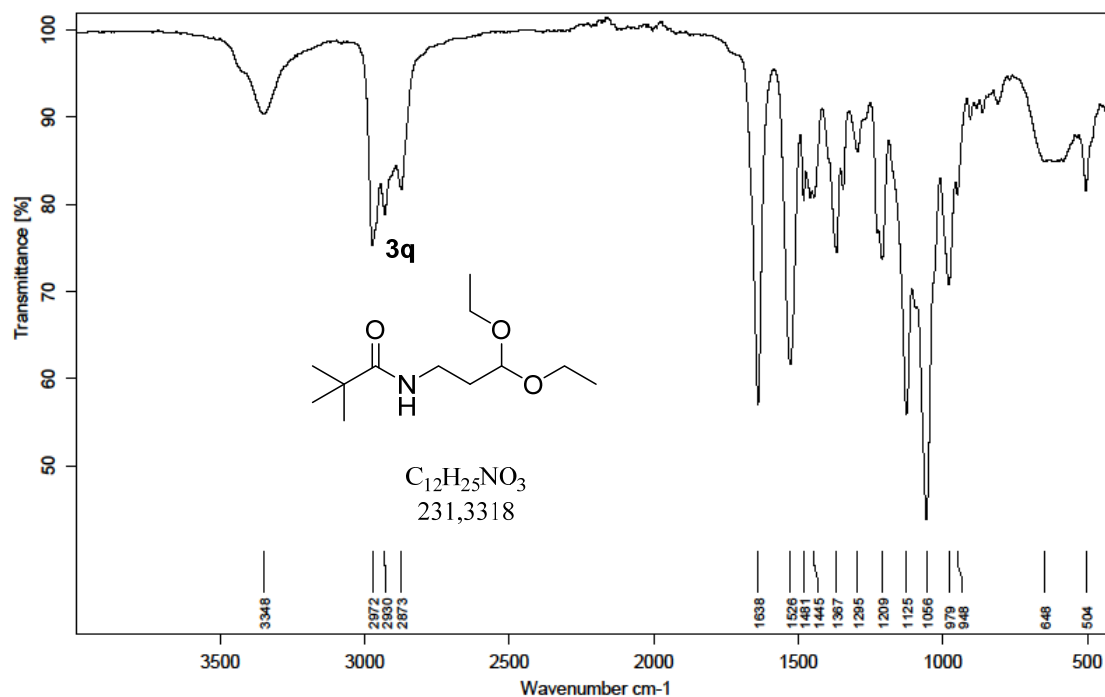


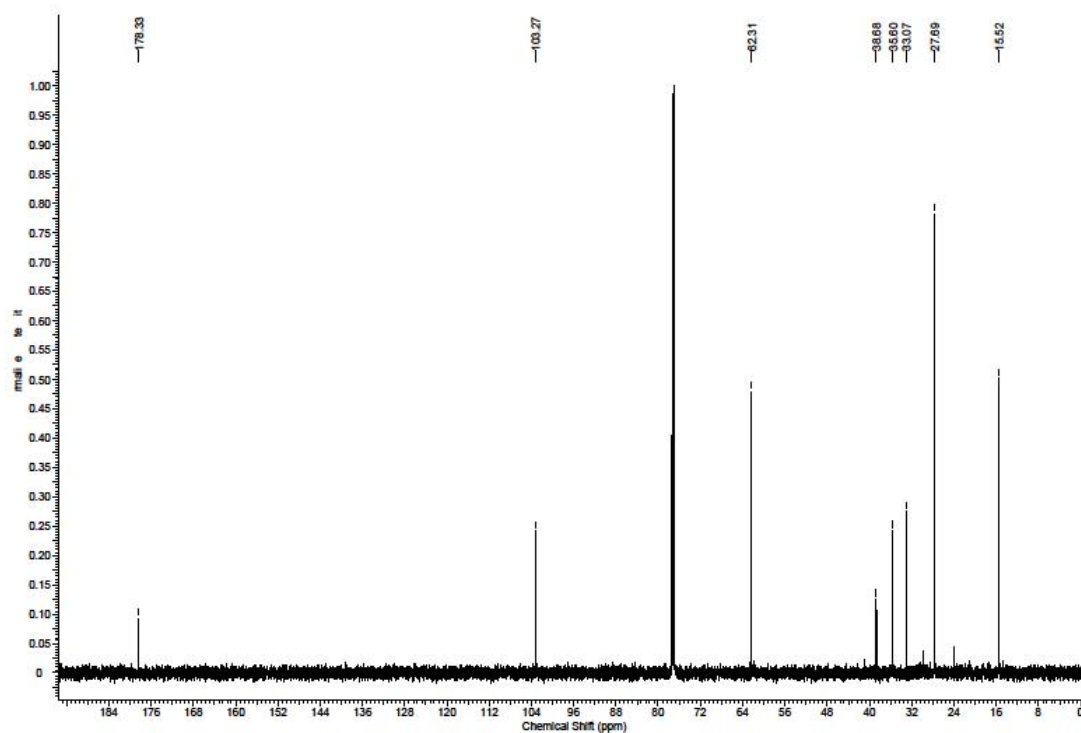
ocpb423.0

10.12.2015









ocpb429.0

16.12.2015

