MgCl$_2$-Catalyzed $\alpha$-Amination of $\alpha$-Alkyl-$\beta$-ketoesters via Oxidative $N$-Acylnitroso Aldol Reaction with Hydroxamic Acids

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General experimental information

Dichloromethane and acetonitrile was distilled over CaH₂ under argon. Carbon tetrachloride was distilled over 4Å molecular sieves. Purification of the reaction products was carried out by flash column chromatography using 200–300 mesh silica gel. Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) or treatment with aqueous KMnO₄ followed by heating. High-resolution mass spectra (HRMS) were recorded on a Bruker BIO TOF Q mass spectrometer. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Varian Inova 400 MHz (¹H NMR at 400 MHz and ¹³C NMR at 100 MHz) spectrometer with solvent resonance as the internal standard (¹H NMR: CDCl₃ at 7.26 ppm; ¹³C NMR: CDCl₃ at 77.2 ppm). ¹H NMR data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m= multiplet), coupling constant(s) in Hz, integration. Hydroxycarbamates TrocNHOH (2c) and FmocNHOH (2d) were prepared according to literature precedent,¹ β-ketoesters 1b-i were prepared by alkylation of the corresponding acetoacetate with methyl iodide.² β-Ketoesters 1m and 1n were prepared by alkylation of the corresponding acetoacetate with bromoethane and BnBr.³ β-Ketoesters 1o and 1p were prepared by acylation of the corresponding ketone with diethylcarbomate.⁴ Other reagents such as BocNHOH (2a), CbzNHOH (2b), β-ketoesters 1a and 1q were used as received from commercial suppliers.

General procedure for the preparation of product 3

TBHP (5–6 M in decane, 0.48 mmol) was added dropwise to a mixture of β-ketoesters 1 (0.48 mmol), hydroxamic acids 2 (0.40 mmol) and MgCl₂ (3.8 mg, 0.040 mmol) in acetonitrile (2 mL). The reaction was stirred at 40 °C for the indicated time; reaction completion was confirmed based on the disappearance of hydroxamic acids (Table 2). Then the reaction mixture was cooled to room temperature, quenched with aqueous NaHSO₃ solution and extracted with DCM three times. The combined organic layers were dried over anhydrous Na₂SO₄, filtered and then concentrated in vacuo. The residue was purified by column chromatography to afford amination product 3.

Analytical data for all new compounds (α-quaternary α-amino-β-ketoesters 3b–3q)

(3a). General procedure was followed with 1a (69.2 mg, 0.48 mmol) and 2a (53.2 mg, 0.40 mmol). Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 94.3 mg (85%) of 3a as a colorless oil. The structure of 3a was identified by comparison with its ¹H NMR and ¹³C NMR spectra with the reported data.⁵

(3b). General procedure was followed with 99.0 mg (0.48 mmol) of 1b and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 113.0 mg (83%) of 3b as a colorless solid. Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.31 (m, 5H), 6.31 (br, 1H), 5.24 (s, 2H), 2.27 (s, 3H), 1.74 (s, 3H), 1.42 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ 199.8, 169.1, 158.1, 135.3, 128.8, 128.6, 128.4, 84.9, 78.7, 68.0, 28.1, 25.5, 19.4. HRMS (ESI) exact mass calculated for C₁₇H₂₃NNaO₆ [M+Na]⁺ requires m/z 360.1418, found m/z 360.1429.

(3c). General procedure was followed with 82.6 mg (0.48 mmol) of 1c and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 99.7 mg (82%) of 3c as a white solid. Analytical data: ¹H NMR (400 MHz, CDCl₃) δ 6.30 (br, 1H), 2.27 (s, 3H),

3H), 1.68 (s, 3H), 1.68 (s, 9H), 1.68 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.9, 168.2, 158.0, 84.4, 83.5, 78.9, 28.2, 28.0, 25.4, 19.2. HRMS (ESI) exact mass calculated for C$_{14}$H$_{25}$NNaO$_6$ [M+Na]$^+$ requires $m/z$ 326.1574, found $m/z$ 326.1572.

(3d). General procedure was followed with 75.9 mg (0.48 mmol) of 1d and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 93.1 mg (80%) of 3d as a colorless oil. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 6.18 (br, 1H), 4.31–4.22 (m, 2H), 2.70–2.62 (m, 2H), 1.74 (s, 3H), 1.47 (s, 9H), 1.31 (t, $J$=7.1 Hz, 3H), 1.11 (t, $J$=7.2 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 203.2, 169.4, 158.1, 84.7, 78.3, 62.4, 30.7, 28.2, 19.6, 14.2. HRMS (ESI) exact mass calculated for C$_{13}$H$_{23}$NNaO$_6$ [M+Na]$^+$ requires $m/z$ 312.1418, found $m/z$ 312.1418.

(3e). General procedure was followed with 105.7 mg (0.48 mmol) of 1e and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 118.8 mg (84%) of 3e as a white solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33–7.20 (m, 5H), 6.28 (br, 1H), 4.20 (q, $J$=7.1 Hz, 2H), 3.96 (s, 2H), 1.76 (s, 3H), 1.45 (s, 9H), 1.25 (t, $J$=7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 199.3, 169.1, 158.1, 134.2, 129.9, 128.5, 127.1, 84.7, 78.6, 62.5, 43.7, 28.1, 19.1, 14.2. HRMS (ESI) exact mass calculated for C$_{18}$H$_{25}$NNaO$_6$ [M+Na]$^+$ requires $m/z$ 374.1574, found $m/z$ 374.1588.

(3f). General procedure was followed with 82.7 mg (0.48 mmol) of 1f and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 7:1) afforded 98.1 mg (80%) of 3f as a white solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 6.35 (br, 1H), 4.25 (q, $J$=7.1 Hz, 2H), 3.21–3.14 (m, 1H), 1.78 (s, 3H), 1.47 (s, 9H), 1.30 (t, $J$=7.1 Hz, 3H), 1.17 (d, $J$=6.7 Hz, 3H), 1.11 (d, $J$=6.7 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 207.8, 169.6, 158.0, 83.8, 78.5, 62.3, 36.3, 28.2, 20.9, 20.8, 19.3, 14.2. HRMS (ESI) exact mass calculated for C$_{14}$H$_{25}$NNaO$_6$ [M+Na]$^+$ requires $m/z$ 326.1574, found $m/z$ 326.1578.

(3g). General procedure was followed with 99.0 mg (0.48 mmol) of 1g and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 4:1) afforded 130.0 mg (96%) of 3g as
a white solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.20 (d, $J=7.8$ Hz, 2H), 7.54 (t, $J=7.4$ Hz, 1H), 7.43 (t, $J=7.7$ Hz, 2H), 6.56 (br, 1H), 4.31 (q, $J=7.1$ Hz, 2H), 1.90 (s, 3H), 1.30 (t, $J=7.2$ Hz, 3H), 1.26 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 191.6, 169.6, 158.1, 134.7, 133.1, 129.8, 128.4, 85.1, 78.6, 62.5, 27.8, 20.6, 14.3. HRMS (ESI) exact mass calculated for C$_{17}$H$_{23}$NNaO$_6$ [M+Na]$^+$ requires m/z 360.1418, found m/z 360.1423.

**(3h).** General procedure was followed with 99.0 mg (0.48 mmol) of 1h and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 4:1) afforded 123.0 mg (91%) of 3h as a colorless solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, $J=8.1$ Hz, 2H), 7.22 (d, $J=8.0$ Hz, 2H), 6.57 (br, 1H), 3.84 (s, 3H), 2.40 (s, 3H), 1.89 (s, 3H), 1.27 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 191.5, 170.2, 158.2, 144.0, 132.0, 129.9, 129.1, 85.1, 78.9, 53.1, 27.8, 21.8, 20.9. HRMS (ESI) exact mass calculated for C$_{17}$H$_{23}$NNaO$_6$ [M+Na]$^+$ requires m/z 360.1418, found m/z 360.1419.

**(3i).** General procedure was followed with 106.6 mg (0.48 mmol) of 1i and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 3:1) afforded 107.0 mg (75%) of 3i as a colorless solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 (d, $J=8.7$ Hz, 2H), 6.90 (d, $J=8.7$ Hz, 2H), 6.52 (br, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 1.89 (s, 3H), 1.27 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 190.6, 170.3, 163.5, 158.2, 132.2, 127.5, 113.6, 85.0, 78.9, 55.6, 53.1, 27.8, 20.9. HRMS (ESI) exact mass calculated for C$_{17}$H$_{23}$NNaO$_7$ [M+Na]$^+$ requires m/z 376.1367, found m/z 376.1373.

**(3j).** General procedure was followed with 108.8 mg (0.48 mmol) of 1j and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 4:1) afforded 139.0 mg (97%) of 3j as a white solid. Analytical data: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.15 (d, $J=8.6$ Hz, 2H), 7.41 (d, $J=8.7$ Hz, 2H), 6.53 (br, 1H), 3.84 (s, 3H), 1.87 (s, 3H), 1.28 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 190.5, 169.9, 158.1, 139.6, 133.0, 131.2, 128.7, 85.5, 78.8, 53.3, 27.8, 20.6. HRMS (ESI) exact mass calculated for C$_{16}$H$_{20}$ClNNaO$_6$ [M+Na]$^+$ requires m/z 380.0871, found m/z 380.0877.

**(3k).** General procedure was followed with 130.0 mg (0.48 mmol) of 1k and 53.2
mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 160.3 mg (99%) of 3k as a white solid. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.08 (d, \(J=8.3\) Hz, 2H), 7.57 (d, \(J=8.5\) Hz, 2H), 6.65 (br, 1H), 3.84 (s, 3H), 1.87 (s, 3H), 1.28 (s, 9H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 190.7, 169.9, 158.1, 133.4, 131.8, 131.3, 128.4, 85.5, 78.8, 53.3, 27.8, 20.6. HRMS (ESI) exact mass calculated for C\(_{18}\)H\(_{20}\)BrNNaO\(_6\) [M+Na]\(^+\) requires \(m/z\) 424.0366, found \(m/z\) 424.0369.

(3l). General procedure was followed with 116.3 mg (0.48 mmol) of 1l and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 146.3 mg (97%) of 3l as a yellow oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.30 (d, \(J=8.4\) Hz, 1H), 8.20 (d, \(J=7.3\) Hz, 1H), 7.97 (d, \(J=8.2\) Hz, 1H), 7.87 (d, \(J=7.9\) Hz, 1H), 7.58–7.46 (m, 4H), 6.57 (br, 1H), 3.84 (s, 3H), 1.82 (s, 3H), 1.39 (s, 9H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 195.8, 170.4, 158.2, 134.0, 133.1, 132.4, 131.3, 128.7, 128.0, 127.5, 126.4, 125.5, 124.3, 84.8, 79.7, 53.2, 28.1, 21.0. HRMS (ESI) exact mass calculated for C\(_{20}\)H\(_{23}\)NNaO\(_6\) [M+Na]\(^+\) requires \(m/z\) 396.1418, found \(m/z\) 396.1424.

(3m). General procedure was followed with 75.9 mg (0.48 mmol) of 1m and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 93.2 mg (80%) of 3m as a colorless oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.32 (br, 1H), 4.26 (q, \(J=7.1\) Hz, 2H), 2.39–2.06 (m, 5H), 1.47 (s, 9H), 1.30 (t, \(J=7.1\) Hz, 3H), 1.08 (t, \(J=7.5\) Hz, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.6, 168.9, 157.9, 84.2, 81.2, 62.2, 28.1, 27.0, 26.8, 14.2, 9.5. HRMS (ESI) exact mass calculated for C\(_{13}\)H\(_{23}\)NNaO\(_6\) [M+Na]\(^+\) requires \(m/z\) 312.1418, found \(m/z\) 312.1406.

(3n). General procedure was followed with 105.6 mg (0.48 mmol) of 1n and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 6:1) afforded 129.2 mg (92%) of 3n as a colorless solid. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 (d, \(J=7.3\) Hz, 2H), 7.31–7.17 (m, 3H), 6.24 (s, 1H), 4.26 (q, \(J=7.1\) Hz, 2H), 3.58 (d, \(J=14.4\) Hz, 1H), 3.50 (d, \(J=14.4\) Hz, 1H), 2.10 (s, 3H), 1.35 (s, 9H), 1.28 (t, \(J=7.1\) Hz, 3H). \(^1^3\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 198.2, 168.0, 156.7, 135.5, 131.2, 128.4, 127.3, 84.0, 82.2, 62.8, 37.1, 28.1, 27.0, 14.1. HRMS (ESI) exact mass calculated for C\(_{18}\)H\(_{25}\)NNaO\(_6\) [M+Na]\(^+\) requires \(m/z\) 374.1574, found \(m/z\) 374.1563.
(3o). General procedure was followed with 81.6 mg (0.48 mmol) of 1o and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/ethyl acetate = 6:1) afforded 96.7 mg (80%) of 3o as a colorless oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.20 (br, 1H), 4.30–4.20 (m, 2H), 2.84 (td, \(J=12.7, 6.1\) Hz, 1H), 2.72–1.67 (m, 7H), 1.45 (s, 9H), 1.30 (t, \(J=7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 202.8, 168.9, 158.7, 84.9, 80.0, 62.2, 40.1, 35.2, 28.8, 28.1, 20.7, 14.3. HRMS (ESI) exact mass calculated for C\(_{14}\)H\(_{23}\)NNaO\(_6\) \([\text{M+Na}]^+\) requires \(m/\text{z}\) 324.1418, found \(m/\text{z}\) 324.1418.

(3p). General procedure was followed with 104.8 mg (0.48 mmol) of 1p and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 127.0 mg (90%) of 3p as a yellow oil. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.92 (d, \(J=7.8\) Hz, 1H), 7.48 (t, \(J=7.4\) Hz, 1H), 7.30 (t, \(J=7.5\) Hz, 1H), 7.23 (d, \(J=7.7\) Hz, 1H), 6.18 (s, 1H), 1.44 (s, 9H), 1.30 (t, \(J=7.1\) Hz, 2H), 3.30–3.16 (m, 1H), 2.95–2.85 (m, 2H), 2.74–2.62 (m, 1H), 1.44 (s, 9H), 1.29 (t, \(J=7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 191.2, 168.8, 158.7, 143.1, 133.6, 132.2, 128.7, 128.3, 126.8, 84.5, 76.5, 62.3, 31.6, 28.1, 25.8, 14.2. HRMS (ESI) exact mass calculated for C\(_{18}\)H\(_{23}\)NNaO\(_6\) \([\text{M+Na}]^+\) requires \(m/\text{z}\) 372.1418, found \(m/\text{z}\) 372.1424.

(3q). General procedure was followed with 80.0 mg (0.48 mmol) of 1q and 53.2 mg (0.40 mmol) of 2a. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 66.0 mg (57%) of 3q as a colorless solid. Analytical data: \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.45 (br, 1H), 4.25 (q, \(J=7.1\) Hz, 2H), 2.72–2.32 (m, 4H), 2.17–1.91 (m, 2H), 1.46 (s, 9H), 1.29 (t, \(J=7.1\) Hz, 3H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 206.4, 167.8, 157.3, 83.8, 77.4, 62.4, 36.3, 31.8, 28.2, 18.3, 14.2. HRMS (ESI) exact mass calculated for C\(_{13}\)H\(_{21}\)NNaO\(_6\) \([\text{M+Na}]^+\) requires \(m/\text{z}\) 310.1261, found \(m/\text{z}\) 310.1259.

(3r). General procedure was followed with 69.2 mg (0.48 mmol) of 1a and 66.9 mg (0.40 mmol) of 2b. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 4:1:0.75) afforded 108.2 mg (87%) of 3r as a colorless oil. The structure of 3r was identified by comparison with its \(^1\)H NMR and \(^{13}\)C NMR spectra with the reported data.\(^5\)
General procedure was followed with 69.2 mg (0.48 mmol) of 1a and 83.4 mg (0.40 mmol) of 2c. Column chromatography (petroleum ether/dichloromethane/ethyl acetate = 5:1:0.75) afforded 125.8 mg (89%) of 3s as a colorless oil. The structure of 3s was identified by comparison with its 1H NMR and 13C NMR spectra with the reported data.5

General procedure was followed with 69.2 mg (0.48 mmol) of 1a and 102.1 mg (0.40 mmol) of 2d. Column chromatography (petroleum ether/ethyl acetate = 4:1) afforded 65.0 mg (41%) of 3t as a colorless solid. The structure of 3t was identified by comparison with its 1H NMR and 13C NMR spectra with the reported data.5
$^1$H NMR and $^{13}$C NMR spectra for new compounds

$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3a

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3a
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3b

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3b
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3c

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3c

S11
$^{1}H$ NMR spectrum (CDCl$_3$, 400 MHz) of 3d

$^{13}C$ NMR spectrum (CDCl$_3$, 100 MHz) of 3d

S12
$^1$H NMR spectrum (CDCl₃, 400 MHz) of 3e

$^{13}$C NMR spectrum (CDCl₃, 100 MHz) of 3e
$^{1}$H NMR spectrum (CDCl$_3$, 400 MHz) of 3f

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3f
$^{1}H$ NMR spectrum (CDCl$_3$, 400 MHz) of 3g

$^{13}C$ NMR spectrum (CDCl$_3$, 100 MHz) of 3g
1H NMR spectrum (CDCl₃, 400 MHz) of 3h

13C NMR spectrum (CDCl₃, 100 MHz) of 3h
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3i

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3i

S17
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3j

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3j
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3k

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3k
$\text{H NMR spectrum (CDCl$_3$, 400 MHz) of 31}$

$\text{C NMR spectrum (CDCl$_3$, 100 MHz) of 31}$
S21

1H NMR spectrum (CDCl₃, 400 MHz) of 3m

13C NMR spectrum (CDCl₃, 100 MHz) of 3m

S21
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3n

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3n

S22
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3o

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3o

S23
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3p

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3p

S24
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3q

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3q
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3r

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3r
$^1$H NMR spectrum (CDCl$_3$, 400 MHz) of 3s

$^{13}$C NMR spectrum (CDCl$_3$, 100 MHz) of 3s

S27
$^{1}H$ NMR spectrum (CDCl$_3$, 400 MHz) of 3t

$^{13}C$ NMR spectrum (CDCl$_3$, 100 MHz) of 3t

S28