Supporting information

In situ acidic carbon dioxide/ethylene glycol system for aerobic oxidative iodination of electron-rich aromatics catalyzed by $Fe(NO_3)_3 \cdot 9H_2O$

Ran Ma, Cheng-Bin Huang, An-Hua Liu, Xue-Dong Li, Liang-Nian He*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin, 300071, P. R. China. Fax: Fax +86-(22)-23503878; E-mail: heln@nankai.edu.cn

Contents Table

- 1. Analytic data of the products
- 2. ¹H NMR and ¹³C NMR spectra of the products
- 3. GC-MS spectra of the products
- 4. References

1. Analytic data of the products

1b 1-iodo-4-methoxybenzene¹: ¹H NMR (400 MHz, CDCl₃): δ 3.78 (s, 3 H), 6.61-6.74 (m, 2 H), 7.48-7.65 (m, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.3, 82.7, 116.3, 138.2, 159.4; GC-MS: m/z (%): 233.95 (100) [M]⁺.



2b 2-iodo-1-methoxy-4-methylbenzene²: ¹H NMR (400 MHz, CDCl₃): δ 2.26 (s, 3 H), 3.85 (s, 3 H), 6.72 (d, *J* = 8.3 Hz, 1 H), 7.10 (dd, *J* = 8.3, 1.5 Hz, 1 H), 7.60 (d, *J* = 1.7 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 19.9, 56.4, 85.7, 110.8, 129.9, 132.0, 139.8, 156.1; GC-MS: m/z (%): 248.00 (100) [M]⁺.



3b 4-(tert-butyl)-2-iodo-1-methoxybenzene¹: ¹H NMR (400 MHz, CDCl₃): δ 1.29 (s, 9 H), 3.86 (s, 3 H), 6.76 (d, *J* = 8.6 Hz, 1 H), 7.32 (dd, *J* = 8.6, 2.4 Hz, 1 H), 7.77 (d, *J* = 2.4 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 31.6, 34.1, 56.5, 86.0, 110.6, 126.5, 136.7, 145.7, 156.0; GC-MS: m/z (%): 275.15 (100) [M - CH₃]⁺, 290.20 (40) [M]⁺.



4b 4-bromo-2-iodo-1-methoxybenzene³: ¹H NMR (400 MHz, CDCl₃): δ 3.86 (s, 3 H), 6.67-6.70 (d, 1 H), 7.39-7.42 (dd, 1 H), 7.87-7.88 (d, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 57.0, 87.1, 112.4, 113.8, 132.6, 141.6, 157.9; GC-MS: m/z (%): 312.05 (100) [M]⁺, 314.05 (92.15) [M]⁺.



5b Methyl 3-iodo-4-methoxybenzoate²: ¹H NMR (400 MHz, CDCl₃): δ 3.88 (s, 3 H), 3.93 (s, 3 H), 6.82 (d, *J* = 8.6 Hz, 1 H), 8.01 (dd, *J* = 8.6, 2.1 Hz, 1 H), 8.45 (d, *J* = 2.1 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 52.3, 56.7, 85.4, 110.1, 124.4, 131.8, 141.1, 161.7, 165.7; GC-MS: m/z (%): 261.10 (100) [M - OMe]⁺, 292.15 (88) [M]⁺.



6b Methyl 4-iodo-3,5-dimethoxybenzoate: ¹H NMR (400 MHz, CDCl₃): δ 3.82 (s, 3 H), 3.87 (s, 3 H), 3.93 (s, 3 H), 6.52 (d, *J* = 2.7 Hz, 1 H), 6.80 (d, *J* = 2.7 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 52.7, 55.8, 56.9, 75.8, 101.4, 106.7, 139.1, 159.5, 161.1, 168.1; GC-MS: m/z (%): 322.00 (100) [M]⁺.



7b 1-iodo-4-methoxynaphthalene²: ¹H NMR (400 MHz, CDCl₃): δ 3.99 (s, 3 H), 6.59 (d, *J* = 8.1 Hz, 1 H), 7.55 (dt, *J* = 15.1, 7.3 Hz, 2 H), 7.95 (d, *J* = 8.1 Hz, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 8.24 (d, *J* = 8.3 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.8, 88.3, 105.7, 122.6, 126.1, 126.86, 128.3, 131.9, 134.8, 137.0, 156.4; GC-MS: m/z (%): 284.00 (100) [M]⁺.



8b 1-iodo-2-methoxynaphthalene²: ¹H NMR (400 MHz, CDCl₃): δ 4.03 (s, 3 H), 7.21 (d, J = 8.9 Hz, 1 H), 7.34-7.42 (m, 1 H), 7.55 (ddd, J = 8.4, 6.9, 1.1 Hz, 1 H), 7.74 (d, J = 8.1 Hz, 1 H), 7.83 (d, J = 8.9 Hz, 1 H), 8.15 (d, J = 8.6 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 57.2, 87.7, 112.9, 124.3, 128.10, 128.2, 129.9, 130.4, 131.2, 135.6, 156.6; GC-MS: m/z (%): 284.00 (100) [M]⁺.



9b 1-iodo-2,4-dimethoxybenzene¹: ¹H NMR (400 MHz, CDCl₃): δ 3.80 (s, 3 H), 3.85 (s, 3 H), 6.32 (dd, *J* = 8.6, 2.7 Hz, 1 H), 6.43 (d, *J* = 2.6 Hz, 1 H), 7.62 (d, *J* = 8.6 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.5, 56.3, 74.8, 99.3, 107.0, 139.2, 158.9, 161.4; GC-MS: m/z (%): 264.00 (100) [M]⁺.



10b 4-iodo-1,2-dimethoxybenzene¹: ¹H NMR (400 MHz, CDCl₃): δ 3.74-3.92 (m, 6 H), 6.54-6.65 (m, 1 H), 7.04-7.14 (m, 1 H), 7.17-7.25 (m, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.9, 56.1, 82.3, 113.1, 120.3, 129.7, 149.1, 149.8; GC-MS: m/z (%): 264.15 (100) [M]⁺.



11b 2-iodo-1,3,5-trimethoxybenzene⁴: ¹H NMR (400 MHz, CDCl₃): δ 3.82 (s, 3 H), 3.86 (s, 6 H), 6.14 (s, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 55.7, 56.6, 91.3, 159.9, 162.3; GC-MS: m/z (%): 294.20 (100) [M]⁺.



12b 5-iodobenzo[d][1,3]dioxole⁵: ¹H NMR (400 MHz, CDCl₃): δ 5.96 (s, 2 H), 6.59 (d, *J* = 8.0 Hz, 1 H), 7.07-7.20 (m, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 82.3, 101.6, 110.6, 117.8, 130.8, 148.0, 148.8; GC-MS: m/z (%): 247.95 (100) [M]⁺.



13b 6-iodo-2,3-dihydrobenzo[b][1,4]dioxine⁶: ¹H NMR (400 MHz, CDCl₃): δ 4.18-4.28 (m, 4 H), 6.61 (d, *J* = 8.5 Hz, 1 H), 7.12 (dd, *J* = 8.5, 2.1 Hz, 1 H), 7.19 (d, *J* = 2.1 Hz, 1 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 64.3, 82.5, 119.1, 126.1, 130.3, 143.7, 144.6; GC-MS: m/z (%): 261.95 (100) [M]⁺.



14b 1-ethoxy-4-iodobenzene⁷: ¹H NMR (400 MHz, CDCl₃): δ 1.40 (t, *J* = 7.0 Hz, 3 H), 3.99 (q, *J* = 7.0 Hz, 2 H), 6.67 (d, *J* = 8.8 Hz, 2 H), 7.54 (d, *J* = 8.8 Hz, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 14.7, 63.5, 82.5, 116.9, 138.2, 158.8; GC-MS: m/z (%): 219.95 (89) [M - CH₂CH₂]⁺; 248.00 (100) [M]⁺.



15b 2-(4-iodophenoxy)ethanol⁸: ¹H NMR (400 MHz, CDCl₃): δ 2.27 (s, 1 H), 3.86-3.97 (m, 2 H), 4.00-4.08 (m, 2 H), 6.68 (d, *J* = 8.8 Hz, 2 H), 7.47-7.68 (m, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 61.3, 69.3, 83.2, 116.9, 138.3, 158.5; GC-MS: m/z (%): 219.95 (100) [M - OCH₂CH₂]⁺, 264.00 (52) [M]⁺.

16b 1-(benzyloxy)-4-iodobenzene⁹: ¹H NMR (400 MHz, CDCl₃): δ 5.04 (s, 2 H), 6.69-6.84 (m, 2 H), 7.29-7.48 (m, 5 H), 7.51-7.63 (m, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 70.1, 83.1, 83.2, 117.3, 127.5, 128.2, 128.7, 136.6, 138.3, 158.7; GC-MS: m/z (%): 310.15 (100) [M]⁺.



17b 1-iodo-4-phenoxybenzene¹⁰: ¹H NMR (400 MHz, CDCl₃): δ 6.72-6.82 (m, 2 H), 6.95-7.05 (m, 2 H), 7.13 (t, J = 7.4 Hz, 1 H), 7.29-7.41 (m, 2 H), 7.53-7.70 (m, 2 H); ¹³C NMR (100.6 MHz, CDCl₃): δ 86.0, 119.3, 121.0, 121.2, 123.9, 130.0, 138.8, 139.0, 156.7, 157.6; GC-MS: m/z (%): 296.00 (100) [M]⁺.



18b 2-iodo-1,3,5-trimethylbenzene²: ¹H NMR (400 MHz, CDCl₃): δ 2.24 (s, 3 H), 2.44 (s, 6 H), 6.89 (s, 2 H). ¹³C NMR (100.6 MHz, CDCl₃): δ 20.8, 29.6, 104.4, 128.1, 137.4, 141.9; GC-MS: m/z (%): 246.05 (100) [M]⁺.



19b 1-iodo-2,4,5-trimethylbenzene: ¹H NMR (400 MHz, CDCl₃): δ 2.19 (s, 3 H), 2.37 (s, 3H), 7.58 (s, 1H), 7.01 (s, 1H); ¹³C NMR (100.6 MHz, CDCl₃): δ 18.69, 19.24, 27.28, 97.21, 130.98, 136.00,136.67,138.41,139.42; GC-MS: m/z (%): 246.20 (100) [M]⁺.

2 ¹H NMR and ¹³C NMR spectra of the products.



























 $\left\{\begin{array}{c} 7.15\\ 7.15\\ 7.13\\ 7.13\\ 7.12\\ 7.12\\ 7.12\\ 6.60\\ 6.58\end{array}\right\}$





























3 GC-MS Spectral of the Products.













4. References

- 1. L. Bedrač and J. Iskra, Adv. Synth. Catal., 2013, 355, 1243.
- 2. C.-Y. Zhou, J. Li, S. Peddibhotla, D. Romo, Org. Lett., 2010, 12, 2104.
- M. S. Yusubov, R. Y. Yusubova, V. N. Nemykin, A. V. Maskaev, M. R. Geraskina, A. Kirschning, V. V. Zhdankin, *Eur. J. Org. Chem.*, 2012, 5935.
- 4. Q. Wen, J. Jin, Y. Mei, P. Lu, Y. Wang, *Eur. J. Org. Chem.*, 2013, 4032.
- 5. H. He, D. Zatorska, J. Kim, J. Aguirre, L. Llauger, Y. She, N. Wu, R. M. Immormino, D. T. Gewirth, G. Chiosis, *J. Med. Chem.*, 2005, **49**, 381.
- H. Togo, T. Muraki, Y. Hoshina, K. Yamaguchi, M. Yokoyama, J. Chem. Soc, Perkin Trans. 1, 1997, 787.
- 7. M. Yoshida, T. Doi, S. Kang, J. Watanabe, T. Takahashi, Chem. Commun., 2009, 2756.
- 8. J.-d. A. K. Twibanire, H. Al-Mughaid, T. B. Grindley, *Tetrahedron*, 2010, 66, 9602.
- 9. T. Furuyama, M. Yonehara, S. Arimoto, M. Kobayashi, Y. Matsumoto, M. Uchiyama, *Chem. Eur. J.*, 2008, **14**, 10348.
- 10. X. Qu, T. Li, Y. Zhu, P. Sun, H. Yang, J. Mao, Org. Biomol. Chem., 2011, 9, 5043.