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SUPPLEMENTARY MATERIAL TO

RuO_4-mediated oxidation of secondary amines. Part 1. Are hydroxylamines the main intermediates?

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NMR DATA OF SELECTED COMPOUNDS

The ^{1}H- and ^{13}C-NMR chemical shifts of the desired compounds are included in Table S-I. They are expressed with respect to internal $(CH_3)_4Si$ ($\delta_H = 0$) and $CDCl_3$ ($\delta_C = 77.16$ ppm, as suggested in H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **62** (1997) 7512).

Table S-I. NMR data of selected compounds

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
1a	Ph–CH_2–NH–CH_3
	δ_H: 1.65 (1H, *s*, NH),[b] 2.43 (3H, *s*, CH_3), 3.72 (2H, *s*, Bn), 7.17–7.35 (5H, *m*, *o*+*m*+*p*);
	δ_C: 36.0 (CH_3), 56.1 (Bn), 126.8 (*p*), 128.1 (*o*), 128.2 (*m*), *140.2*
1b	Ph–CH_2–NH–CH_2–CH_3
	δ_H: 1.12 (3H, *t*, J = 7.2, CH_3), 1.70 (1H, *s*, NH),[b] 2.67 (2H, *q*, J = 7.2, C**H**$_2$–CH_3), 3.78 (2H, *s*, Bn), 7.15–7.35 (5H, *m*, *o*+*m*+*p*);
	δ_C: 15.3 (CH_3), 43.6 (**C**H_2–CH_3), 54.0 (Bn), 126.8 (*p*), 128.0 (*o*), 128.3 (*m*), *140.6*
2a	Ph–CH=N–CH_3
	δ_H: 3.51 (3H, *d*, J = 1.7, CH_3), 7.36–7.45 (3H, *m*, *m*+*p*), 7.65–7.74 (2H, *m*, *o*), 8.27 (1H, *q*, J = 1.7, CH=N);
	δ_C: 48.3 (CH_3), 128.0 (*o*), 128.7 (*m*), 130.6 (*p*), *136.4*, 162.6 (CH=N)
2b	Ph–CH=N–CH_2–CH_3
	δ_H: 1.30 (3H, *t*, ^3J = 7.3, CH_3), 3.64 (2H, *qd*, ^3J = 7.3, ^4J = 1.3, CH_2), 7.37–7.44 (3H, *m*, *m*+*p*), 7.70–7.74 (2H, *m*, *o*), 8.28 (1H, *t*, ^4J = 1.3, CH=N);
	δ_C: 16.4 (CH_3), 56.0 (CH_2), 128.1 (*o*), 128.7 (*m*), 130.6 (*p*), *136.5*, 160.5 (CH=N)

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Table S-I. Continued

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
2c [c]	Ph–CH=N–CH_2–Ph δ_H: 4.80 (2H, *d*, ^4J = 1.6, Bn), 7.17–7.40 (8H, *m*, *o′*+*m′*+*p′*+*m*+*p*), 7.77 (2H, *d*, *J* = 7.8, *o*), 8.35 (1H, *t*, ^4J = 1.6, CH=N); δ_C: 65.0 (Bn), 126.9 (*p′*), 127.9 (*o′*), 128.2 (*o*), 128.4 (*m*), 128.5 (*m′*), 130.6 (*p*), *136.1* (*i*), *139.2* (*i′*), 161.8 (CH=N)
4a	Ph–CH_2–N(OH)–CH_3 δ_H: 2.54 (3H, *s*, CH_3), 3.71 (2H, *s*, Bn), 7.20–7.45 (5H, *m*, *o*+*m*+*p*); δ_C: 47.8 (CH_3), 66.6 (Bn), 127.6 (*p*), 128.4 (*m*), 129.9 (*o*), *137.1*
4b	Ph–CH_2–N(OH)–CH_2–CH_3 δ_H: 1.15 (3H, *t*, *J* = 7.2, CH_3), 2.75 (2H, *q*, *J* = 7.2, CH_2), 3.79 (2H, *s*, Bn), 7.20–7.45 (5H, *m*, *o*+*m*+*p*); δ_C: 12.3 (CH_3), 53.9 (CH_2), 64.8 (Bn), 127.5 (*p*), 128.4 (*m*), 129.9 (*o*), *137.3*
5c	Ph–CHO δ_H: 7.50 (2H, *t*, *J* = 7.6, *m*), 7.60 (1H, *t*, *J* = 7.6, *p*), 7.88 (2H, *d*, *J* = 7.2, *o*), 10.0 (1H, *s*, CHO); δ_C: 128.9 (*m*), 129.6 (*o*), 134.3 (*p*), *136.4*, 192.2 (CO)
Benzoic acid	Ph–CO_2H δ_H: 7.45 (2H, *t*, *J* = 7.7, *m*), 7.61 (1H, *t*, *J* = 7.4, *p*), 8.13 (2H, *d*, *J* = 7.5, *o*), 9.8–12.0 (1H, *brs*, OH);[b] δ_C: 128.6 (*m*), *129.5*, 130.4 (*o*), 133.9 (*p*), 172.5 (CO)
6a	Ph–CO–NH–CH_3 δ_H: 2.98 (3H, *d*, *J* = 4.9, CH_3),[d] 6.4–6.6 (1H, *brs*, NH),[b] 7.37–7.39 (2H, *m*, *m*), 7.47 (1H, *tt*, *J* = 7.3 & 1.5, *p*), 7.76 (2H, *dd*, *J* = 8.0 & 1.5, *o*); δ_C: 26.8 (CH_3), 126.8 (*o*), 128.5 (*m*), 131.3 (*p*), *134.5*, 168.3 (CO)
6b	Ph–CO–NH–CH_2–CH_3 δ_H: 1.23 (3H, *t*, *J* = 7.3, CH_3), 3.47 (2H, *qd*, *J* = 7.3 & 1.7, CH_2),[e] 6.4–6.6 (1H, *brs*, NH),[b] 7.37–7.39 (2H, *m*, *m*), 7.47 (1H, *tt*, *J* = 7.3 & 1.5, *p*), 7.77 (2H, *dd*, *J* = 8.0 & 1.5, *o*); δ_C: 14.8 (CH_3), 34.8 (CH_2), 126.8 (*o*), 128.4 (*m*), 131.2 (*p*), *134.7*, 167.5 (CO)
6c [c]	Ph–CO–NH–Bn δ_H: 4.56 (2H, *d*, *J* = 5.6, Bn),[d] 7.0–7.2 (1H, *brs*, NH),[b] 7.20–7.33 (5H, *m*, *o′*+*m′*+*p′*), 7.35 (2H, *t*, *J* = 7.6, *m*), 7.45 (1H, *t*, *J* = 7.4, *p*), 7.77 (2H, *d*, *J* = 7.8, *o*); δ_C: 43.9 (Bn), 127.0 (*o*+*p′*), 127.7 (*o′*), 128.4 (*m′*), 128.6 (*m*), 131.4 (*p*), 134.3 (*i*), 138.2 (*i′*), 167.4 (CO)
7a[f]	Ph–CH_2–NH–CHO δ_H: 4.38+4.45 (2H, *d*[d]+*d*,[d] *J* = 6.0, Bn), 6.10–6.14 (1H, *brs*, NH),[b] 7.15–7.40 (5H, *m*, *o*+*m*+*p*), 8.14+8.22 [1H, *d* (*J* = 12.0)[d] + *s*, CHO]; δ_C: 42.2+45.7 (Bn), 127.1+127.9 (*o*), 127.8+128.1 (*p*), 128.9+129.0 (*m*), *137.6*+*137.7*, 161.2+164.8 (CHO)
7b	Ph–CH_2–NH–CO–CH_3 δ_H: 1.89 (3H, *s*, CH_3), 4.29 (2H, *d*, *J* = 5.8, Bn),[d] 6.9–7.1 (1H, *brs*, NH),[b] 7.14–7.34 (5H, *m*, *o*+*m*+*p*); δ_C: 22.6 (CH_3), 43.2 (Bn), 127.0 (*o*), 127.4 (*p*), 128.3 (*m*), *138.2*, 170.3 (CO)

Table S-I. Continued

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
8a[f]	Ph–CH_2–N(CH_3)–CHO δ_H: 2.78+2.84 (3H, *s*+*s*, CH_3), 4.39+4.52 (2H, *s*+*s*, Bn), 7.20+7.25 (2H, *m*+*m*, *o*), 7.27–7.42 (3H, *m*, *m*+*p*), 8.16+8.28 (1H, *s*+*s*, CHO); δ_C: 29.5+34.1 (CH_3), 47.8+53.5 (Bn), 127.5+128.3 (*o*), 127.7+128.2 (*p*), 128.7+129.0 (*m*), 135.8+136.1, 162.6+162.8 (CHO)
8b[f]	Ph–CH_2–N(CH_2–CH_3)–CO–CH_3 δ_H: 1.11+1.13 (3H, *t*+*t*, *J* = 7.2, CH_2–C**H**$_3$), 2.10+2.18 (3H, *s*+*s*, CO–CH_3), 3.26+3.42 (2H, *q*+*q*, *J* = 7.2, C**H**$_2$–CH_3), 4.51+4.59 (2H, *s*+*s*, Bn), 7.15–7.40 (*m*, 5H, *o*+*m*+*p*); δ_C: 12.8+13.7 (CH_2–**C**H_3), 21.3+21.8 (CO–**C**H_3), 40.9+42.6 (**C**H_2–CH_3), 47.8+51.7 (Bn), 126.4+128.1 (*o*), 127.6+127.7 (*p*), 128.6+128.7 (*m*), 137.1+138.0, 170.5+170.9 (CO)
8c[g]	Ph–CH_2–N(CH_2–CH_3)–CHO δ_H: 1.05+1.17 (3H, *t*+*t*, *J* = 7.2, CH_2–C**H**$_3$), 3.20+3.28 (2H, *q*+*q*, *J* = 7.2, C**H**$_2$–CH_3), 4.38+4.54 (2H, *s*+*s*, Bn), 7.18–7.40 (5H, *m*, Ph), 8.22+8.24 (1H, *s*+*s*, CHO); δ_C: 12.0+14.1 (CH_3), 36.6+41.3 (C**H**$_2$–CH_3), 44.6+50.6 (Bn), 127.3+127.9 (*p*), 127.6+128.4 (*o*), 128.6+128.6 (*m*), 136.0+136.3, 162.4+162.4 (CHO)
8d[g]	Ph–CH_2–N(CH_3)–CO–Ph δ_H: 2.86+3.02 (3H, *s*+*s*, CH_3), 4.51+4.76 (2H, *s*+*s*, Bn), 7.17–7.48 (10H, *m*, 2×Ph); δ_C: 33.3+37.1 (CH_3), 50.9+55.3 (Bn), 127.0+127.7+128.3+128.5+128.9+129.7 (arom. CH), 136.8+137.2, 171.7+172.4 (CO)
8e[g,h]	Ph–CH_2–N(CH_2–CH_3)–CO–Ph δ_H: 0.95–1.30 (3H, *brs*, CH_3), 3.10–3.35 + 3.40–3.65 (2H, *brs*+*brs*, C**H**$_2$–CH_3), (4.40–4.65) + (4.65–4.90) (2H, *brs*+*brs*, Bn), 7.1–7.45 (10H, *m*, 2xPh); δ_C: 13.7 (weak, CH_3), 43.0 (weak, CH_2), 47.0 (weak, Bn), 126.6+127.6+128.6+128.8+129.5 (arom. CH), *134.6*+*136.8*, 172.1 (CO).
9a	Ph–CH=N^+(O^-)–CH_3 δ_H: 3.88 (3H, *s*, CH_3), 7.39–7.44 [4H, *m*, *m*+*p*+(CH=N^+ at ~7.41 ppm)[i]], 8.17–8.24 (2H, *m*, *o*); δ_C: 54.1 (CH_3), 128.4 (*o*), 129.5 (*m*), *130.1*, 130.5 (*p*), 135.8 (C=N^+)
9b	Ph–CH=N^+(O^-)–CH_2–CH_3 δ_H: 1.58 (3H, *t*, *J* = 7.3, CH_3), 4.00 (2H, *q*, *J* = 7.3, CH_2), 7.36–7.43 [4H, *m*, *m*+*p*+(CH=N at ~7.41 ppm)[i]], 8.17–8.29 (2H, *m*, *o*); δ_C: 13.7 (CH_3), 62.1 (CH_2), 128.6 (*o*), 129.4 (*m*), 130.4 (*p*), *130.7*, 133.7 (C=N^+)
9c[c]	Ph–CH=N^+(O^-)–CH_2–Ph δ_H: 4.96 (2H, *s*, Bn), 7.20–7.45 [9H, *m*, *o′*+*m′*+*p′*+*m*+*p*+(CH=N^+ at ≈7.33 ppm)[i]], 8.06–8.20 (2H, *m*, *o*); δ_C: 71.3 (Bn), 128.5 (*o*), 128.7 (*m*), 129.0 (*o′*+*p′*), 129.3 (*m′*), *130.50* (sh, *i*), 130.53 (*p*), 133.3 (*i′*), 134.3 (br, CH=N)
10a	Ph–CH_2–N^+(O^-)=CH_2 δ_H: 4.83 (2H, *s*, Bn), 6.15+6.45 (1+1H, *d*+*d*, ^2J = 7.3, N^+=CH_2), 7.28–7.38 (5H, *m*, *o*+*m*+*p*); δ_C: 69.8 (Bn), 123.8 (N^+=CH_2), 129.2 (*o*), 129.4 (*p*), 129.6 (*m*), *132.5*

Table S-I. Continued

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
10b	Ph–CH_2–$N^+(O^-)$=CH–CH_3 δ_H: 2.01 (3H, *d*, *J* = 5.9, CH_3), 4.90 (2H, *s*, Bn), 6.72 (1H, *q*, *J* = 5.9, CH), 7.36–7.43 (5H, *m*, *o*+*m*+*p*); δ_C: 12.9 (CH_3), 69.2 (Bn), 129.0 (*o*), 129.3 (*p*), 129.5 (*m*), *132.9*, 134.9 (N^+=CH)
11	Ph-CH_2-NH_2 δ_H: 3.82 (2H, *s*, Bn), 7.2–7.4 (5H, *m*, *o*+*m*+*p*); δ_C: 46.5 (Bn), 126.7 (*p*), 127.0 (*o*), 128.4 (*m*), *143.30*
12	Ph–CN δ_H: 7.47 (2H, *t*, *J* = 7.7, *m*), 7.55–7.75 (3H, *m*, *o*+*p*); δ_C: 112.4, 118.8 (CN), 129.1 (*m*), 132.1 (*o*), 132.8 (*p*)
13[j]	Ph–CO–NH_2 δ_H: 7.28–7.50 (3H, *m*, *m*+*p*), 7.92 (2H, *d*, *J* = 7.8, *o*); δ_C: 127.4 (*o*), 127.9 (*m*), 131.0 (*p*), *134.1*, 168.5 (CO)
14	[Ph–CH_2–$N(CH_3)$–]$_2CH_2$ δ_H: 2.22 (6H, *s*, CH_3), 3.02 (2H, *s*, CH_2), 3.62 (4H, *s*, Bn), 7.20–7.35 (10H, *m*, *o*+*m*+*p*); δ_C: 40.5 (CH_3), 59.6 (Bn), 79.8 (N–CH_2–N), 126.7 (*p*), 128.2 (*o*), 128.9 (*m*), *139.8*
15a	Ph–CH(CN)–NH–CH_3 δ_H: 1.45–1.95 (1H, *brs*, NH),[b] 2.52 (3H, *s*, CH_3), 4.72 (1H, *s*, CH–CN), 7.30–7.44 (3H, *m*, *m*+*p*), 7.44–7.55 (2H, *m*, *o*); δ_C: 33.5 (CH_3), 55.9 (**C**H–CN), 118.6 (CN), 127.3 (*o*), 128.85 (*m*), 128.89 (*p*), *134.6*
15b	Ph–CH(CN)–NH–CH_2–CH_3 δ_H: 1.17 (3H, *t*, *J* = 7.1, CH_3), 1.45–1.95 (1H, *brs*, NH),[b] 2.72–2.97 (2H, AB*q* of *q*, *J* = 7.1, J_{AB} = 11.2, CH_2), 4.78 (1H, *s*, CH–CN), 7.36–7.45 (3H, *m*, *m*+*p*), 7.52 (2H, *m*, *o*); δ_C: 14.9 (CH_3), 42.0 (CH_2), 54.5 (**C**H–CN), 119.0 (CN), 127.4 (*o*), 129.1 (*m*+ *p*), *135.0*
15c[c]	Ph–CH(CN)–NH–CH_2–Ph δ_H: 1.7–1.9 (1H, *brs*, NH),[b] 3.96+4.06 [1+1H, *d*+*d* (ABq), J_{AB} = 12.8, Bn], 4.75 (1H, *s*, CH–CN), 7.29 (1H, *tt*, *J* = 7.2 & 1.6, *p*′), 7.33–7.44 (7H, *m*, *o*′+*m*+*m*′+*p*), 7.55 (2H, *dd*, *J* = 7.2 & 1.6, *o*); δ_C: 51.3 (Bn), 53.5 (**C**H–CN), 118.7 (CN), 127.3 (*o*), 127.6 (*p*′), 128.4 (*o*′), 128.6+128.96 (*m*+*m*′), 129.03 (*p*), 134.7 (*i*), 138.1 (*i*′)
16a	Ph–CH_2–NH–CH_2–CN δ_H: 1.63–1.65 (1H, *brs*, NH),[b] 3.56 (2H, *s*, CH_2–CN), 3.93 (2H, *s*, Bn), 7.26–7.38 (5H, *m*, *o*+*m*+*p*); δ_C: 36.4 (**C**H_2–CN), 52.5 (Bn), 117.8 (CN), 127.8 (*p*), 128.6 (*o*), 128.8 (*m*), *138.0*
16b	Ph–CH_2–NH–CH(CN)–CH_3 δ_H: 1.41 (3H, *d*, *J* = 7.1, CH_3), 3.51 (1H, *q*, *J* = 7.1, CH), 3.74+3.98 [1+1H, *d*+*d* (ABq), J_{AB} = 12.9, Bn], 7.18–7.33 (5H, *m*, *o*+*m*+*p*); δ_C: 19.8 (CH_3), 44.7 (CH), 51.8 (Bn), 120.7 (CN), 127.7 (*p*), 128.5 (*o*), 128.7 (*m*), *138.4*

Table S-I. Continued

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
17a	Ph–CH_2–N(CH_3)–CH_2–CN δ_H: 2.42 (3H, *s*, CH_3), 3.43 (2H, *s*, CH_2–CN), 3.59 (2H, *s*, Bn), 7.27–7.46 (5H, *m*, *o*+*m*+*p*); δ_C: 42.2 (CH_3), 44.0 (**C**H_2–CN), 60.0 (Bn), 114.5 (CN), 127.7 (*p*), 128.5 (*m*), 128.8 (*o*), *136.9*
17b	Ph–CH_2–N(CH_2–CH_3)–CH(CN)–CH_3 δ_H: 1.13 (3H, *t*, *J* = 7.2, CH_2–C**H**$_3$), 1.43 (3H, *d*, *J* = 7.2, CH–C**H**$_3$), (2.40–2.52)+(2.68–2.81) (1+1H, AB*q* of *q*, *J* = 7.2, J_{AB} = 13, C**H**$_2$–CH_3), 3.72 (1H, *q*, *J* = 7.2, C**H**–CH_3), 3.37+3.95 [1+1H, *d*+*d* (ABq), J_{AB} = 14, Bn], 7.20–7.38 (5H, *m*, *o*+*m*+*p*) δ_C: 13.4 (CH_2–**C**H_3), 18.1 (CH–**C**H_3), 45.2 (CH_2), 48.3 (**C**H–CN), 55.5 (Bn), 118.6 (CN), 127.5 (*p*), 128.6 (*o*), 128.7 (*m*), *138.5*
17c	Ph–CH_2–N(CH_2–CH_3)–CH_2–CN δ_H: 1.16 (3H, *t*, *J* = 7.2, CH_3), 2.68 (2H, *q*, *J* = 7.2, CH_2), 3.46 (2H, *s*, CH_2–CN), 3.66 (2H, *s*, Bn), 7.25–7.38 (5H, *m*, *o*+*m*+*p*); δ_C: 12.9 (CH_3), 40.8 (**C**H_2–CN), 48.5 (**C**H_2–CH_3), 58.3 (Bn), 114.9 (CN), 127.8 (*p*), 128.7 (*m*), 129.1 (*o*), *137.5*
17d[c]	Ph–CH_2–N(CH_3)–CH(CN)–Ph δ_H: 2.26 (3H, *s*, CH_3), 3.55+3.82 [1+1H, *d*+*d* (ABq), J_{AB} = 13.1, Bn], 4.89 (1H, *s*, CH–CN), 7.29 (1H, *t*, *J* = 7.2, *p* or *p*′), 7.32–7.37 [3H, *m*, *m*′ (7.35 ppm, *t*, *J* = 7.2) & *p*′ (or *p*)], 7.37–7.44 (4H, *m*, *o*′+*m*), 7.54 (2H, *d*, *J* = 7.2, *o*); δ_C: 38.4 (CH_3), 59.4 (Bn), 60.3 (**C**H–CN), 115.3 (CN), 127.82 (*o*), 127.86 (*p*′), 128.77+128.87 (*m*+*m*′), 128.93 (*p*), 129.04 (*o*′), 133.9 (*i*′), 137.6 (*i*)
17e[c]	Ph–CH_2–N(CH_2–CH_3)–CH(CN)–Ph δ_H: 1.06 (3H, *t*, *J* = 7.1, CH_3), (2.39–2.51)+(2.52–2.65) (1+1H, AB*q* of *q*, J_{AB} = 13.2, *J* = 7.1, C**H**$_2$–CH_3), 3.36 + 3.91 [1+1H, *d*+*d* (ABq), J_{AB} = 13.6, Bn], 4.86 (1H, *s*, CH), 7.22–7.45 (8H, *m*, *m*+*p*+*o*′+*m*′+*p*′), 7.51 (2H, *d*, *J* = 7.2, *o*); δ_C: 13.0 (CH_3), 44.5 (**C**H_2–CH_3), 55.0 (Bn), 57.5 (CH), 115.7 (CN), 127.4+128.46 (*p*+*p*′), 127.9 (*o*), 128.40+128.50 (*m*′+*m*), 128.57 (*o*′), 134.1 (*i*′), 138.9 (*i*)
18a	Ph–C(CN)=N–CH_3 δ_H: 3.82 (3H, *s*, CH_3), 7.45 (2H, *t*, *J* = 7.2, *m*), 7.51 (1H, *t*, *J* = 7.2, *p*), 7.96 (2H, *dd*, *J* = 7.2 & 2.0, *o*); δ_C: 45.6 (CH_3), 109.3 (C≡N), 127.3 (*o*), 128.8 (*m*), 132.0 (*p*), *133.4*, 143.2 (C=N)
18b	Ph–C(CN)=N–CH_2–CH_3 δ_H: 1.40 (3H, *t*, *J* = 7.3, CH_3), 4.01 (2H, *q*, *J* = 7.3, CH_2), 7.38–7.56 (3H, *m*, *m*+*p*), 7.98 (2H, *dd*, *J* = 8.1 & 1.5, *o*); δ_C: 15.6 (CH_3), 53.5 (CH_2), 109.6 (C≡N), 127.6 (*o*), 129.0 (*m*), 132.2 (*p*), *133.6*, 141.4 (C=N)
19a[f]	Ph–CH_2–N=CH–CN δ_H: 4.87+5.02 (2H, *d*+*d*, ^4J = 2, Bn), 7.25–7.40 [6H, *m*, *o*+*m*+*p*+(CH=N)]; δ_C: 65.8+67.0 (Bn), 108.4+112.0 (C≡N), 127.3+127.5 (*p*), 128.1+128.2 (*o*), 128.7+128.9 (*m*), 133.1+134.4 (CH=N), *138.1+138.2*

Table S-I. Continued

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
19b	Ph–CH_2–N=C(CH_3)–CN δ_H: 2.26 (3H, *t*, ^5J = 1.3, CH_3), 4.81 (2H, *q*, ^5J = 1.3, Bn), 7.25–7.40 (5H, *m*, *o*+*m*+*p*); δ_C: 25.5 (CH_3), 62.6 (Bn), 111.0 (C≡N), 127.3 (*p*), 128.1 (*o*), 128.7 (*m*), *137.1*, 140.3 (C=N)
20a	Ph–CH=N–CH_2–CN δ_H: 4.55 (2H, *d*, ^4J = 1.8, CH_2), 7.33–7.43 (3H, *m*, *m*+*p*), 7.70 (2H, *dd*, *J* = 1.6 & 7.8, *o*), 8.44 (1H, *t*, ^4J = 1.8, CH=N); δ_C: 45.8 (CH_2), 115.7 (C≡N), 128.1 (*o*), 128.3 (*m*), 131.3 (*p*), *134.5*, 164.6 (CH=N)
21a	Ph–C(CN)=N^+(O^-)–CH_3 δ_H: 4.28 (3H, *s*, CH_3), 7.33–7.47 (3H, *m*, *m*+*p*), 8.24–8.28 (2H, *m*, *o*); δ_C: 55.9 (CH_3), 114.6 (C≡N), 121.1 (C=N^+), 127.0 (*o*), *128.1*, 128.7 (*m*), 131.6 (*p*)
21b	Ph–C(CN)=N^+(O^-)–CH_2–CH_3 δ_H: 1.61 (3H, *t*, *J* = 7.3, CH_3), 4.51 (2H, *q*, *J* = 7.3, CH_2), 7.35–7.45 (3H, *m*, *m*+*p*), 8.25–8.35 (2H, *m*, *o*); δ_C: 13.3 (CH_3), 63.4 (CH_2), 114.5 (C≡N), 121.4 (C=N^+), 127.5 (*o*), *127.9*, 128.6 (*m*), 131.3 (*p*)
22a[f]	Ph–CH_2–N^+(O^-)=CH–CN δ_H: 4.99+5.28 (2H, *s*+*s*, Bn), 6.64+6.65 (1H, *sh*+*s*, CH=N), 7.32–7.48 (5H, *m*, *o*+*m*+*p*); δ_C: 70.0+71.5 (Bn), 107.5+108.4 (CH=N^+), 112.2+113.2 (C≡N), 129.2+129.8 (*o*), 130.3+130.3 (*m*), 130.5+130.7 (*p*), *130.8+131.5*
22b	Ph–CH_2–N^+(O^-)=C(CN)–CH_3 δ_H: 2.12 (3H, *s*, CH_3), 5.32 (2H, *s*, Bn), 7.33–7.45 (5H, *m*, *o*+*m*+*p*); δ_C: 15.9 (CH_3), 69.4 (Bn), 115.4 (C≡N), 118.9 (C=N^+), 129.4 (*o*), 130.3 (*m*), 130.7 (*p*), *132.0*
23a	Ph–CH_2–N(CH_3)–C(CN)=NH δ_H: 2.98 (3H, *s*, CH_3), 4.65 (2H, *s*, Bn), 7.22–7.26 (2H, *brd*, *J* = 7.8, *o*), 7.28–7.42 (3H, *m*, *m*+*p*), 7.56–7.76 (1H, *brs*, NH);[b] δ_C:[h] 32–36 (*v. br*, CH_3), 53–57 (*v. br*, Bn), 111.4 (C≡N), 127.6–127.8 (*br*, *o*), 128.2 (*p*), 129.0 (*m*), *135.9*, 142.6 (C=N)
23b	Ph–CH_2–N(CH_2–CH_3)–C(CN)=NH δ_H: 1.13 (3H, *t*, ^3J = 7.0, CH_3), 3.43 (2H, *q*, ^3J = 7.0, CH_2), 4.63 (2H, *s*, Bn), 7.24 (2H, *d*, *J* = 8.0, *o*), 7.26–7.50 (3H, *m*, *m*+*p*), 7.52–7.72 (1H, *brs*, NH);[b] δ_C:[h] 12.0–12.6 (*br*, CH_3), 41.5–42.5 (*v. br*, CH_2), 49.5–50.5 (*v. br*, Bn), 111.5 (C≡N), 127.6–127.8 (*br*, *o*), 128.0 (*p*), 128.9 (*m*), *136.35*, 142.1 (C=N)
24a	Ph–CH_2–N(CH_3)–CN δ_H: 2.78 (3H, *s*, CH_3), 4.16 (2H, *s*, Bn), 7.30–7.45 (5H, *m*, *o*+*m*+*p*); δ_C: 37.9 (CH_3), 57.3 (Bn), 119.0 (CN), 128.5 (*o*), 128.7 (*p*), 129.0 (*m*), *134.5*
24b	Ph–CH_2–N(CH_2–CH_3)–CN δ_H: 1.24 (3H, *t*, *J* = 7.2, CH_3), 2.92 (2H, *q*, *J* = 7.2, CH_2), 4.17 (2H, *s*, Bn), 7.30–7.40 (5H, *m*, *o*+*m*+*p*); δ_C: 12.5 (CH_3), 44.9 (CH_2), 55.4 (Bn), 117.6 (CN), 128.2 (*o*), 128.3 (*p*), 128.7 (*m*), *134.7*

Table S-I. Continued

Compd.	Chemical shifts ($CDCl_3$, δ / ppm, $J_{H,H}$ / Hz, 24 °C) and assignments[a]
25a	Ph–CH_2–N(CH_3)–CO–NH_2 δ_H: 2.91 (3H, *s*, CH_3), 4.49 (2H, *s*, Bn), 4.52–4.64 (2H, *brs*, NH_2),[b] 7.20–7.30 (3H, *m*, *o*+*p*), 7.34 (2H, *t*, ^3J = 7.2, *m*); δ_C: 34.9 (CH_3), 52.5 (Bn), 127.3 (*o*), 127.6 (*p*), 128.9 (*m*), *137.6*, 159.2 (CO)
25b	Ph–CH_2–N(CH_2–CH_3)–CO–NH_2 δ_H: 1.16 (3H, *t*, *J* = 7.1, CH_3), 3.33 (2H, *q*, *J* = 7.1, CH_2), 4.48 (2H, *s*, Bn), 7.20–7.37 (5H, *m*, *o*+*m*+*p*); δ_C: 13.3 (CH_3), 42.4 (CH_2), 50.3 (Bn), 127.1 (*o*), 127.6 (*p*), 128.9 (*m*), *137.8*, 158.9 (CO)
26	Ph–CH=N–OH δ_H: 7.30–7.42 (3H, *m*, *m*+*p*), 7.53–7.62 (2H, *m*, *o*), 8.17 (1H, *s*, CH=N); δ_C: 127.2 (*o*), 128.9 (*m*), 130.2 (*p*), *132.0*, 150.4 (C=N)
27[k]	Ph–CH_2–N=N^+(O^-)–CH_2–Ph δ_H: 4.58 (2H, *t*, ^5J = 0.8, Bn), 5.31 (2H, *t*, ^5J = 0.8, Bn′), 7.27–7.50 (10H, *m*, 2×Ph); δ_C: 56.6 (Bn), 74.0 (Bn′), 128.5 (*o*), 128.6 (*p*), 128.8 (*m*), 129.3 (*o′*), 129.46 (*p′*), 129.48 (*m′*), 132.1 (*i′*), 136.3 (*i*)
28	Ph–CH_2–NH–OH δ_H: 3.93 (2H, *s*, Bn), 7.19–7.32 (5H, *m*, *o*+*m*+*p*); δ_C: 58.4 (Bn), 127.8 (*p*), 128.7 (*m*), 129.3 (*o*), *137.2*

[a] Bn means benzyl protons or carbons. Aromatic protons or carbons are labeled as *o*, *m*, and *p*; the values of *ipso* carbons are lebeled as (*i*) or in *italics*; [b]vanishes with D_2O; [c]sign prime (′) refers to the aromatic atoms of Ph–CH_2; [d]singlet upon addition of D_2O; [e]quartet upon addition of D_2O; [f]mixture of unequally populated *E/Z* isomers; the underlined values belong to the main isomer; [g]mixture of equally populated *E/Z* isomers; the underlined isomer was chosen arbitrarily; [h]very broad signals due to the proximity of coalescence temperature; [i]deduced from two-dimension NMR experiment (HMBC); [j]in a $CDCl_3$/DMSO-d_6 mixture; [k]sign prime (′) refers to the Ph–**C**H_2–N^+(O^-) atoms

MS DATA OF SELECTED COMPOUNDS

The MS data of the desired compounds are presented in Table S-II, except those of **10a** and **b**, **14**, **15c** and **28**, which were too unstable in the adopted analytical conditions.

TABLE S-II. MS data for selected compounds

Compd.	Peaks (EI, 70 eV; *m*/*z* (relative intensities, %))
1a	121 (M^+, 54), 120 (100), 118 (11), 92 (12), 91 (62), 77 (13), 65 (18), 51 (12).
1b	135 (M^+, 12), 134 (13), 120 (32), 92 (10), 91 (100), 65 (11).
2a	119 (M^+, 59), 118 (100), 91 (14), 78 (17), 77 (27), 51 (13).
2b	133 (62, M^+), 132 (81), 118 (67), 105 (17), 104 (52), 92 (11), 91 (100), 89 (15), 78 (10), 77 (28), 51 (16).
4a[a]	137 (M^+, 22), 120 (6), 118 (6), 92 (9), 91 (100), 65 (11).
4b[a]	151 (M^+, 19), 136 (7), 92 (9), 91 (100), 65 (8).
5c	106 (M^+, 100), 105 (96), 78 (16), 77 (87), 51 (29), 50 (17).
Benzoic acid	122 (M^+; 89), 106 (8), 105 (100), 77 (61), 51 (22), 50 (14).
6a	135 (M^+, 35), 134 (52), 105 (100), 77 (72.6), 51 (20.5).

TABLE S-II. Continued

Compd.	Peaks (EI, 70 eV; *m*/*z* (relative intensities, %))
6b	149 (M^+, 34), 148 (39), 105 (100), 91 (10), 77 (50), 51 (15).
6c	211 (M^+, 45), 210 (17), 106 (23), 105 (100), 91 (15), 78 (10), 77 (77), 51 (28).
7a	135 (M^+, 100), 134 (47), 106 (32), 92 (9), 91 (38), 79 (27), 77 (21), 51 (11).
7b	149 (M^+, 89), 107 (18), 106 (100), 79 (9), 43 (20).
8a	149 (M^+, 100), 148 (32), 134 (11), 106 (24), 92 (12), 91 (58), 79 (22), 77 (9), 65 (16).
8b	177 (M^+, 65), 134 (11), 120 (15), 107 (10), 106 (100), 91 (80), 65 (15), 44 (11), 43 (19).
8c	163 (M^+, 87), 162 (9), 134 (33), 107 (9), 106 (41), 92 (14), 91 (100), 79 (27), 77 (11).
8d	225 (M^+, 56), 224 (71), 120 (10), 105 (100), 91 (17), 77 (49).
8e	239 (M^+, 38), 238 (29), 106 (9), 105 (100), 91 (15), 77 (37).
9a	135 (M^+, 66), 134 (100), 119 (33), 118 (62), 108 (21), 106 (10), 105 (16), 91 (11), 89 (22), 79 (11), 78 (14), 77 (45), 76 (5), 65 (17), 63 (15), 51 (18), 50 (9), 42 (29).
9b	149 (M^+, 96), 148 (60), 133 (79), 132 (100), 118 (76), 105 (40), 104 (55), 103 (10), 94 (10), 89 (22), 78 (28), 77 (42), 51 (14).
9c	211 (M^+, 14), 92 (10), 91 (100), 65 (12).
11	107 (M^+, 59), 106 (100), 91 (14), 79 (37), 78 (13), 77 (23), 51 (12).
12	103 (M^+, 100), 76 (31), 75 (8), 51 (7), 50 (11).
13	121 (M^+, 84), 105 (100), 78 (10), 77 (83), 51 (25), 50 (13).
15a[a]	146 (M^+, 5), 119 (50), 118 (100), 91 (16), 77 (21), 42 (13).
15b[a]	160 (M^+, 3), 145 (18), 133 (38), 132 (51), 118 (43), 117 (17), 116 (100), 104 (36), 91 (66), 89 (19), 77 (19), 51 (11).
16a	146 (M^+, 14), 145 (38), 119 (14), 92 (20), 91 (100), 65 (15).
16b[a]	160 (M^+, 6), 159 (20), 92 (33), 91 (100), 65 (11).
17a	160 (M^+, 24), 159 (15), 92 (29), 91 (100), 83 (36), 65 (15).
17b	188 (M^+, 4) 173 (13), 161 (25), 160 (23), 132 (13), 105 (9), 92 (12), 91 (100), 70 (11), 65 (12), 56 (9).
17c	174 (M^+, 9), 159 (19), 92 (12), 91 (100), 65 (9).
17d	236 (M^+, 23), 235 (9), 159 (26), 120 (27), 118 (22), 117 (13), 116 (62), 92 (35), 91 (100), 89 (14), 65 (16).
17e	250 (M^+, 13), 235 (41), 118 (60), 116 (34), 92 (13), 91 (100), 89 (10), 65 (12).
18a	144 (M^+, 59), 143 (44), 130 (10), 129 (100), 118 (30), 116 (11), 91 (13), 77 (20), 51 (11).
18b	158 (M^+, 91), 157 (82), 144 (9), 143 (93), 142 (12), 130 (23), 129 (33), 116 (25), 115 (16), 114 (13), 104 (46), 103 (23), 91 (100), 89 (13), 88 (12), 77 (32), 76 (14), 63 (9), 51 (19).
19a	144 (M^+, 15), 92 (10), 91 (100), 89 (9), 65 (13).
19b	158 (M^+, 11), 131 (8), 92 (8), 91 (100), 65 (9).
20a	144 (M^+; 81), 143 (100), 122 (9), 121 (84), 105 (78), 103 (11).
20b	158 (M^+, 68), 143 (65), 131 (22), 117 (100), 105 (24), 104 (45), 103 (15), 90 (15), 89 (35), 77 (81).
21a	161 (10), 160 (M^+, 100) 159 (84), 143 (22), 133 (16), 132 (28), 131 (29), 129 (11), 120 (10), 117 (11), 115 (34), 114 (31), 106 (13), 105 (25), 104 (22), 103 (12), 102 (9), 91 (10), 88 (31), 87 (9), 78 (11), 77 (27), 76 (15), 68 (18), 67 (35), 65 (15), 63 (17), 62 (16), 51 (15).

TABLE S-II. Continued

Compd.	Peaks (EI, 70 eV; *m*/*z* (relative intensities, %))
21b	174 (M^+, 100), 173 (61), 157 (17), 146 (11), 145 (53), 143 (10), 132 (13), 131 (12), 130 (10), 129 (17), 117 (14), 116 (43), 115 (30), 114 (22), 105 (15), 104 (24), 103 (14), 91 (22), 90 (10), 89 (71), 88 (22), 77 (21), 76 (11), 65 (13), 63 (17), 62 (12), 51 (14), 39 (9).
22a	92 (8), 91 (100), 65 (11).
22b	174 (M^+, 3), 92 (8), 91 (100), 65 (12).
23a	173 (M^+, 28), 172 (27), 158 (28), 120 (40), 106 (12), 92 (9), 91 (100), 77 (10), 65 (24).
23b	187 (27, M^+), 186 (23), 158 (60), 134 (18), 106 (12), 91 (100), 79 (16), 77 (11), 65 (22).
24a	146 (M^+, 16), 92 (8), 91 (100), 65 (12).
24b	160 (M^+, 16), 92 (8), 91 (100), 65 (9).
25a	164 (M^+, 98), 121 (15), 120 (71), 119 (24), 118 (35), 106 (64), 92 (13), 91 (100), 79 (17), 77 (17), 65 (25), 51 (12), 44 (41), 42 (28).
25b	178 (M^+, 25), 120 (18), 106 (40), 92 (11), 91 (100), 79 (11), 77 (10), 65 (14), 44 (11).
26	121 (M^+, 100), 120 (20), 104 (11), 103 (12), 94 (29), 78 (49), 77 (47), 76 (17), 66 (21), 65 (12), 51 (28), 50 (16).
27	226 (M^+, 5), 181 (18), 118 (5), 92 (9), 91 (100), 90 (16), 65 (15).

[a]Moderately stable compounds