Supporting Information (8 pages)

Covalently Linked Acceptor-Donor Systems Based on Isoquinoline *N*-oxide Acceptor: Photoinduced Electron Transfer Produces Dual-Channel Luminescent Systems that Evolve Chemically to Photohydroxylation of the Aromatic Donor

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Material. Isoquinoline Reissert was prepared using previously reported method.[S1] Benzyl chlorides were commercially available or prepared from the corresponding benzyl alcohols. All other reagents were used as received.

General procedure for the synthesis of 2a-f. In a 100 mL two-necked flask were placed the corresponding benzyl chloride (3.3 mmol), isoquinoline Reissert (2.8 mmol) and TEBA (200 mg) in 20 mL of benzene under an argon atmosphere. The resulting mixture was vigorously stirred and a

solution of 50% aqueous NaOH (10 mL) was added. After stirring h at room temperature for 24, the organic phase was decanted, washed with water, dried and concentrated to obtain a residue that was hydrolyzed as follows: the crude residue was dissolved in a mixture of 5 mL of methanol and 10 mL of 20 % aqueous NaOH, and the resulting solution refluxed for 3 h. The cooled solution was extracted with CH_2Cl_2 (3 x 100 mL). The organic extracts were dried with $MgSO_4$ and the solvent was removed *in vacuo*. The products were purified by column chromatography.

1-Benzylisoquinoline (2a).[S2]

1-(2-Methoxybenzyl)isoquinoline (2b). Brown liquid; yield 74%; R_f = 0.41 AcOEt/Hex (3:7); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.78 (s, 3H), 4.54 (s, 2H), 6.55 (t, 1H, *J* = 7.3 Hz), 6.16-6.83 (m, 2H), 7.05 (t, 1H, *J* = 7.9 Hz), 7.33-7.54 (m, 3H), 7.67 (d, 1H, *J* = 7.3 Hz), 8.05 (d, 1H, *J* = 8.5 Hz), 8.36 (d, 1H, *J* = 5.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 35.0, 55.4, 110.3, 119.5, 120.5, 126.0, 127.0, 127.1, 127.4, 127.9, 129.8, 129.8, 136.3, 141.9; MS *m/z* (%), 249 (2) $[M]^+$, 218 (100); Anal. Calcd. for $C_{17}H_{15}NO$: C 81,90; H 6.06; N 5.62. Found: C; 81.94; H 6.01; N 5.64.

1-(3-Methoxybenzyl)isoquinoline (2c). Brown liquid; yield 76%; R_f = 0.36 AcOEt/Hex (3:7); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.61 (s, 3H), 4.53 (s, 2H), 6.59 (d, 2H, *J* = 7.9 Hz), 6.74 (d, 1H, *J* = 7.3 Hz), 7.05 (t, 1H, *J* = 7.9 Hz), 7.14 (s, 1H), 7.37-7.65 (m, 3H), 7.69 (d, 1H, *J* = 7.3 Hz), 8.03 (d, 1H, *J* = 8.5 Hz), 8.37 (d, 1H, *J* = 6.7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.9, 54.9, 111.3, 114.4, 118.9, 119.7, 120.9, 122.7, 125.7, 127.1, 127.2, 129.3, 129.7, 136.4, 140.9, 141.8, 159.5; MS *m/z* (%), 249 (41) $[M]^+$, 248 (100); Anal. Calcd. for $C_{17}H_{15}NO$: C 81,90; H 6.06; N 5.62. Found: C 81.92; H 6.07; N 5.60.

1-(4-Methoxybenzyl)isoquinoline (2d). Brown solid; mp = 68-69 ºC; yield 68%; R_f = 0.28 AcOEt/Hex (2:8); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.71 (s, 3H), 4.60 (s, 2H), 6.55 (d, 2H, *J* = 8.5 Hz), 7.18 (d, 2H, *J* = 8,5 Hz), 7.46-7.55 (m, 2H), 7.61 (t, 1H, *J* = 6.7 Hz), 7.79 (d, 1H, *J* = 7.9 Hz), 8.14 (d, 1H, *J* = 8.5 Hz), 8.47 (d, 1H, *J* = 6.1 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.7, 54.6, 113.5, 119.4,

125.4, 126.7, 126.8, 126.9, 129.2, 129.4, 131.1, 136.1, 141.6, 157.7, 160.1; MS *m*/*z* (%), 249 (42) $[M]^+$, 248 (100), 234 (25); Anal. Calcd. for $C_{17}H_{15}NO$: C 81.90; H 6.06; N 5.62. Found: C 81.89; H 6.08; N 5.59.

1-(3,4-dimethoxybenzyl)isoquinoline (2e). White solid; mp = 118-120 ºC; yield 60%; R_f = 0.13 AcOEt/Hex (3:7); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.79 (s, 3H), 4.60 (s, 1H), 6.70-6.83 (m, 3H), 7.48-7.66 (m, 3H), 7.80 (d, 1H, *J* = 7.3 Hz), 8.17 (d, 1H, *J* = 8.5 Hz), 8,51 (d, 1H, *J* = 5.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 40.7, 54.6, 113.5, 119.4, 125.4, 126.7, 126.8, 126.9, 129.2, 129.4, 131.1, 136.1, 141.6, 157.7, 160.1; MS *m*/*z* (%), 279 (77) $[M]^+$, 278 (100), 264 (43); Anal. Calcd. for $C_{18}H_{17}NO_2$: C 77.40; H 6.13; N 5.01. Found: C 77.43; H 6.15; N 5.00.

1-(3,4,5-Trimethoxybenzyl)isoquinoline (2f). Colourless liquid; yield 81%; R_f = 0.14 AcOEt/Hex (3:7); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.74 (s, 9H), 4.59 (s, 2H), 6.49 (s, 2H), 7.52-7.68 (m, 3H), 7.78 (d, 1H, *J* = 9.1 Hz), 8.01 (d, 1H, *J* = 8.0 Hz), 8.23 (d, 1H, *J* = 6.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$): δ 41.9, 56.1, 60.8, 105.8, 120.1, 122.9, 125.8, 127.2, 127.4, 130.2, 134.8, 136.4, 141.4, 153.2, 159.9; MS *m*/*z* (%), 309 (100) $[M]^+$, 308 (78), 294 (62); Anal. Calcd. for $C_{19}H_{19}NO_3$: C 73.77; H 6.19; N 4.53. Found: C 73.75; H 6.21; N 4.56.

General *N*-oxidation Procedure. To a solution of the corresponding benzylisoquinoline **2a-f** (3.4 mmol), in 25 mL of chloroform, MCPBA (4.8 mmol) was added and the resulting solution stirred at room temperature for 24 h. The solution was washed with saturated aqueous $NaHCO_3$ and water, dried and concentrated, and the resulting solid recrystallized from AcOEt.

1-Benzylisoquinoline N-oxide (1a). White solid; mp = 102-104 ºC; yield 74%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.79 (s, 2H), 7.14-7.33 (m, 5H), 7.51-7.59 (m, 3H), 7.75 (d, 1H, *J* = 8.0 Hz), 7.97 (d, 1H, *J* = 7.9 Hz), 8.20 (d, 1H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.7, 122.5, 123.9, 126.5, 127.4,

128.1, 128.6, 128.8, 129.6, 136.8, 136.9, 146.8; MS *m*/*z* (%) 235 (7) $[M]^+$, 219 (25), 218 (100); Anal. Calcd. for $C_{16}H_{13}NO$: C 81.68; H 5.57; N 5.95. Found: C 81.80; H 5.60; N 6.00.

1-(2-Methoxybenzyl)isoquinoline *N*-oxide (1b). White solid; mp = 80-82 ºC; yield 78%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.70 (s, 3H), 4.71 (s, 1H), 6.76 (d, 2H, *J* = 8.5 Hz), 7.25 (d, 2, *J* = 8.5 Hz), 7.48-7.63 (m, 3H), 7.73 (d, 1H, *J* = 7.3 Hz), 7.98 (d, 1H, *J* = 7.9 Hz), 8.19 (d, 1H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.6, 55.2, 110.1, 120.5, 122.4, 124.4, 124.9, 127.0, 127.6, 128.2, 128.8, 128.9, 129.2, 136.5, 147.3, 156.7; MS *m*/*z* (%), 235 (7) $[M]^+$, 219 (25), 218 (100); Anal. Calcd. for $C_{17}H_{15}NO_2$: C 76.96; H 5.70; N 5.28. Found: C 77.02; H 5.80; N 5.32.

1-(3-Methoxybenzyl)isoquinoline *N*-oxide (1c). White solid; mp = 73-75 ºC; yield 78%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.71 (s, 3H), 4.77 (s, 1H), 6.72 (d, 2H, *J* = 7.9 Hz), 6.85-6.89 (m, 2H), 7.14 (t, 1H, *J* = 7.9 Hz), 7.48-7.59 (m, 3H), 7.74 (d, 1H, *J* = 8.5 Hz), 7.95 (d, 1H, *J* = 7.3 Hz), 8.22 (d, 1H, *J* = 6.7 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.7, 55.1, 111.7, 114.5, 120.9, 122.6, 122.7, 123.9, 126.5, 127.4, 128.3, 128.6, 128.8, 128.9, 129.4, 129.5, 136.7, 138.4, 159.7; MS *m*/*z* (%), 265 (43) $[M]^+$, 248 (100), 217 (91); Anal. Calcd. for $C_{17}H_{15}NO_2$: C 76.96; H 5.70; N 5.28. Found: C 77.00; H 5.74; N 5.33.

1-(4-Methoxybenzyl)isoquinoline *N*-oxide (1d). White solid; mp = 67-69ºC; yield 78%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.70 (s, 3H), 4.71 (s, 1H), 6.76 (d, 2H, *J* = 8.5 Hz), 7.25 (d, 2, *J* = 8.5 Hz), 7.48-7.63 (m, 3H), 7.73 (d, 1H, *J* = 7.3 Hz), 7.98 (d, 1H, *J* = 7.9 Hz), 8.19 (d, 1H, *J* = 7.3 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 30.6, 54.9, 113.8, 122.3, 123.8, 127.2, 128.1, 128.4, 128.5, 128.8, 128.8, 129.2, 136.6, 147.1, 158.0; MS *m*/*z* (%), 235 (15) $[M]^+$, 219 (39), 218 (100); Anal. Calcd. for $C_{17}H_{15}NO_2$: C 76.96; H 5.70; N 5.28. Found: C 76.90; H 5.82; N 5.35.

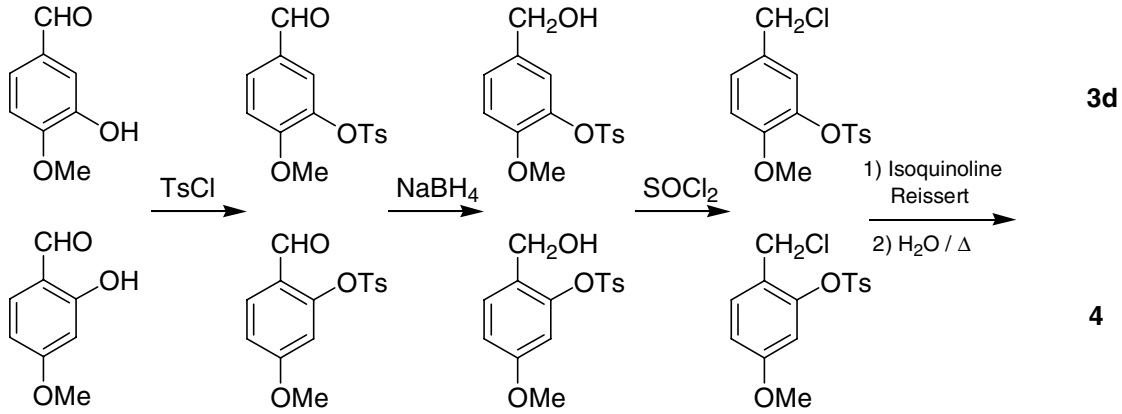
1-(3,4-Dimethoxybenzyl)isoquinoline *N*-oxide (1e). Pale yellow solid; mp = 128-130 ºC; yield 81%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.79 (s, 3H), 4.73 (s, 1H), 6.69 (d, 1H, *J* = 8.02 Hz), 6.77 (dd, 1H, *J* = 8.55, 1.6 Hz), 7.02 (d, 1H, *J* = 1.6 Hz), 7.5-7.64 (m, 3H), 7,98 (d, 1H, *J* = 8.5 Hz),

8.0 (d, 1H, *J* = 8.0 Hz), 8.21 (d, 1H, *J* = 7.48 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 31.7, 122,5, 123.9, 126.5, 127.4, 128.1, 128.6, 128.8, 129.6, 136.8, 136.9, 146.8. MS *m*/*z* (%), 295 (18) $[M]^+$, 279 (24), 278 (100), 262 (37), 247 (45); Anal. Calcd. for $C_{18}H_{17}NO_3$: C 73.20; H 5.80; N 4.74. Found: C 73.40; H 5.86; N 4.81.

1-(3,4,5-Trimethoxybenzyl)isoquinoline *N*-oxide (1f). Brown solid; mp = 72-74ºC; yield 60%; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.65 (s, 9H), 4.65 (s, 2H), 6.51 (s, 2H), 7.55-7.71 (m, 3H), 7.78 (d, 1H, *J* = 7.78 Hz), 8.00 (d, 1H, *J* = 8.0 Hz), 8.23 (d, 1H, *J* = 6.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 28.5, 57.4, 60.8, 61.1, 110.3, 116.5, 123.1, 124.7, 127. 8, 128.4, 129.8, 130.7, 133.1, 135.6, 145.2, 145.7, 147.7;; MS *m*/*z* (%), 325 (20) $[M]^+$, 308 (100); Anal. Calcd. for $C_{19}H_{19}NO4$: C 70.14; H 5.98; N 4.31. Found: C 71.01; H 6.02; N 4.29.

Synthesis of compounds 3d and 4

Compounds **3d** and **4** were synthesized according to the following scheme:



General Procedure for the Tosylation of Phenols

A mixture of 50 mL of dichloromethane and 20 mL of a 30% aqueous solution of NaOH was vigorously stirred, and the corresponding aldehyde (13 mmol) and TEBA (200 mg) added under a nitrogen atmosphere. A solution of tosyl chloride (21 mmol) in 50 mL of dichloromethane was added

dropwise and the reaction mixture stirred for 6 h. The organic phase was washed with water (2 x 50 mL), dried and concentrated. The crude product was pure enough to be used for in next step without further purification.

2-Formyl-5-methoxyphenyl 4-methylbenzenesulfonate. White solid; mp = 81-83 ºC; yield 94%; R_f = 0.42 AcOEt/:Hex (3:7); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.82 (s, 3H), 6.73 (d, 1H, *J* = 2.4 Hz), 6.87 (dd, 1H, *J* = 2.4, 8.5 Hz), 7.32 (d, 2H, *J* = 7.9 Hz), 7.75 (d, 2H, *J* = 8.5 Hz), 7.78 (d, 1H, *J* = 8.5 Hz), 9.76 (s, 1H); ^{3}C NMR (50 MHz, $CDCl_3$): δ 21.6, 55.8, 108.5, 113.7, 122.4, 128.3, 129.6, 129.9, 184.3, 130.0, 131.1, 146.2, 152.7, 164.9, 186.1; MS *m*/*z* (%), 306 (24) $[M]^+$, 155 (49), 91 (100), 65 (81); Anal. Calcd. for $C_{15}H_{14}O_5S$: C 58.81; H 4.61. Found: C 58.85; H 4.63.

5-Formyl-2-methoxyphenyl 4-methylbenzenesulfonate. White solid; mp = 136-138 ºC; yield 85%; R_f = 0.30 AcOEt/:Hex (4:6); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.44 (s, 3H), 3.68 (s, 3H), 6.96 (d, 1H, *J* = 8.5 Hz), 7.51 (d, 1H, *J* = 7.9 Hz), 7.59 (d, 1H, *J* = 1.8 Hz), 7.74 (d, 3H, *J* = 7.9 Hz), 9.01 (s, 1H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.6, 55.9, 112.4, 124.8, 128.5, 129.4, 129.5, 129.7, 130.4, 132.8, 138.7, 145.4, 156.9, 189.6; MS *m*/*z* (%), 306 (2) $[M]^+$, 155 (34), 91 (100), 65 (69); Anal. Calcd. for $C_{15}H_{14}O_5S$: C 58.81; H 4.61. Found: C 58.83; H 4.64.

General Procedure for the Reduction of Aldehydes

To a solution of the corresponding aldehyde (11 mmol) in MeOH (50 mL) was added, in four portions, $NaBH_4$ (11 mmol) at 0 ºC. After stirring for 5 h, water was added and the resulting mixture extracted with CH_2Cl_2, dried and the solvent evaporated to obtain the alcohols.

2-Hydroxymethyl-5-methoxyphenyl 4-methylbenzenesulfonate. White solid; mp = 63-65 ºC; yield 70%; R_f = 0.28 AcOEt/:Hex (3:7); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.65 (s, 9H), 4.65 (s, 2H), 6.51 (s, 2H), 7.55-7.71 (m, 3H), 7.78 (d, 1H, *J* = 7.78 Hz), 8.00 (d, 1H, *J* = 8.0 Hz), 8.23 (d, 1H, *J* = 6.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.7, 55.4, 59.3, 108.1, 113.5, 122.8, 126.5, 128.6, 129.9, 131.3,

132.2, 145.9, 147.6; MS *m/z* (%), 308 (12) $[M]^+$ 155 (27), 95 (43), 91 (100), 65 (98); Anal. Calcd. for $C_{15}H_{16}O_5S$: C 58.43; H 5.23. Found: C 58.40; H 5.25.

5-Hydroxymethyl-2-methoxyphenyl 4-methylbenzenesulfonate. White solid; mp = 87-90 ºC; yield 90%; R_f = 0.18 AcOEt/Hex (4:6); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.51 (s, 3H), 4.54 (s, 2H), 6.78 (d, 1H, *J* = 8.5 Hz), 7.14-7.19 (m, 2H), 7.27 (d, 2H, *J* = 7.9 Hz), 7.71 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.6, 55.6, 64.2, 112.6, 122.8, 122.9, 126.6, 128.5, 129.3, 133.1, 133.6, 138.1, 145.0, 151.1; MS *m/z* (%), 308 (3) $[M]^+$, 155 (17), 91 (100), 65 (47); Anal. Calcd. for $C_{15}H_{16}O_5S$: C 58.43; H 5.23. Found: C 58.45; H 5.25.

General Procedure for Chlorination of Alcohols

A round-bottom flask containing the corresponding alcohol (6 mmol) was cooled in a water-ice mixture and $SOCl_2$ (7 mmol) was added by means of a dropping funnel. The reaction mixture was heated in a water bath for 6 h. Excess of $SOCl_2$ was removed *in vacuo* and the residue dissolved in CH_2Cl_2 (200 mL), washed with water (3 x 50 mL), dried and the solvent evaporated.

2-Chloromethyl-5-methoxyphenyl 4-methylbenzenesulfonate. White solid; mp = 86-88 ºC; yield 80%; R_f = 0.66 AcOEt/:Hex (4:6); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.41 (s, 3H), 3.51 (s, 3H), 4.54 (s, 2H), 6.78 (d, 1H, *J* = 8.5 Hz), 7.14-7.19 (m, 2H), 7.27 (d, 2H, *J* = 7.9 Hz), 7.71 (d, 2H, *J* = 8.5 Hz), 8.23 (d, 1H, *J* = 6.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.7, 40.2, 55.5, 108.1, 113.3, 113.8, 122.6, 128.4, 128.6, 129.9, 130.0, 131.6, 132.4, 145.8, 147.9, 160.3; MS *m/z* (%), 326 (4) $[M]^+$, 91 (100), 65 (90); Anal. Calcd. for $C_{15}H_{15}O_4ClS$: C 55.13; H 4.63. Found: C 55.15; H 4.65.

5-Chloromethyl-2-methoxyphenyl 4-methylbenzenesulfonate. White solid; mp = 110-112 ºC; yield 86%; R_f = 0.60 AcOEt/:Hex (4:6); ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H), 3.55 (s, 3H), 4.47 (s, 2H), 6.79 (d, 1H, *J* = 8.5 Hz), 7.12 (d, 1H, *J* = 1.8 Hz), 7.25 (dd, 1H, *J* = 2.4, 8.5 Hz), 7.33 (d, 2H, *J* = 8.5 Hz), 7.73 (d, 2H, *J* = 8.5 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 21.7, 45.3, 55.7, 112.6, 124.4,

128.2, 128.6, 129.4, 129.9, 133.0, 138.2, 145.1, 151.9; MS *m/z* (%), 326 (6) $[M]^+$, 91 (100), 65 (66); Anal. Calcd. for $C_{15}H_{15}O_4ClS$: C 55.13; H 4.63. Found: C 55.16; H 4.65.

General procedure for the synthesis 3d and 4. Both compounds were prepared by using the above described general method for benzyl isoquinolines **2a**-**f**. The protecting tosyl group was removed during the hydrolysis.

1-(2-Hydroxy-4-methoxybenzyl)isoquinoline (4). White solid; mp = 184-186 ºC; yield 70%; R_f = 0.27 AcOEt/:Hex (4:6); ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.72 (s, 3H), 4.51 (s, 2H), 6.37 (dd, 1H, *J* = 3.0, 8.5 Hz), 6.54 (d, 1H, *J* = 2.4 Hz), 7.18 (d, 1H, *J* = 8.5 Hz), 7.54 (d, 1H, *J* = 5.5 Hz), 7.63-7.75 (m, 2H), 7.82 (d, 1H, *J* = 7.9 Hz), 8.33 (d, 1H, *J* = 6.0 Hz), 8.41 (d, 1H, *J* = 7.9 Hz); ^{13}C NMR (50 MHz, $CDCl_3$): δ 36.0, 55.2, 103.7, 105.8, 117.3, 118.7, 120.1, 122.8, 125.2, 126.1, 127.6, 127.8, 130.473, 130.8, 136.9, 139.7, 158.2, 160.1, 161.3; MS *m/z* (%), 265 (100) $[M]^+$, 248 (86); Anal. Calcd. for $C_{17}H_{15}NO_2$: C 76.96; H 5.70; N 5.28. Found: C 76.99; H 5.73; N 5.27.

Additional References

(S1) Koizumi, T.; Tekeda, K.; Yoshisa, K.; Yoshii, E. *Synthesis* **1977**, 497-498.

(S2) Boekeheide, V.; Weinstock, J. *J. Am. Chem. Soc.* **1952**, *74*, 660-663.