Advanced Synthesis & Catalysis

Supporting Information

Photoredox Removal of *p*-Methoxybenzyl Ether Protecting Group with Hydrogen Peroxide as Terminal Oxidant

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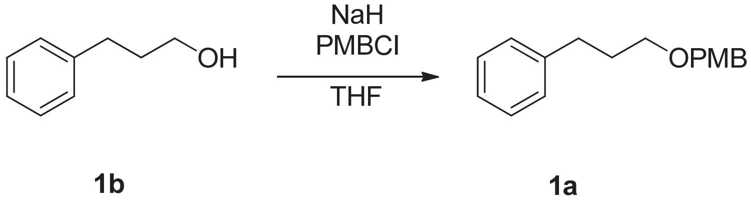
Supporting Information

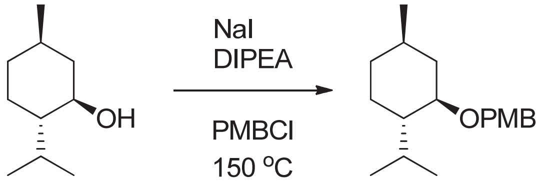
General: ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance II 400 spectrometer and resolved with MestreNova software. IR spectra were recorded on ThermoFisher Nicolet iS5. Column chromatography was performed on silica gel from Qingdao Marine Chemical Industry. Fluorescence quenching experiments were performed on HITACHI F-7000FL 5J1-0004. Solvents used for chromatography were AR grade, as appropriate. Acetonitrile, ethyl acetate, 1,4-Dioxane, EtOH and DCE were distilled from commercial available source.

Procedures for Preparation of Starting Materials



A flame dried round bottom flask equipped with a magnetic stir bar was charged with compound **1b** (680 mg, 5 mmol), dry THF (20 mL) and cooled to 0 °C. The mixture was then treated with 60% dispersion of NaH (240 mg, 6 mmol) in mineral oil and stirred at room temperature for 30 minutes. PMBCl (936 mg, 6 mmol) and Bu_4NBr (166 mg, 0.5 mmol) were then added consequently. The mixture was stirred at room temperature for 12 hours, and then water and ethyl acetate was added. The mixture was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. Then it was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **1a** as colorless oil (980 mg, 78%).

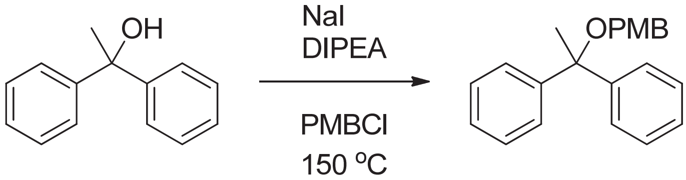
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, J = 7.6, 5.6 Hz, 4H), 7.21 (dd, J = 7.2, 4.1 Hz, 3H), 6.91 (d, J = 8.4 Hz, 2H), 4.46 (s, 2H), 3.83 (s, 3H), 3.49 (t, J = 6.4 Hz, 2H), 2.78 – 2.67 (m, 2H), 1.97 – 1.90 (m, 2H).



2b **2a**

DL-menthanol **2b** (156 mg, 1 mmol), PMBCl (234 mg, 1.5 mmol), NaI (15 mg, 0.1 mmol) and DIPEA (208 mg, 1.6 mmol) were charged in a reaction vessel equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 $^{\circ}$C for 2 hours. The resulting mixture was typically a biphasic mixture. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 7:1) as eluent to give the product **2a** as colorless oil (237 mg, 86%).

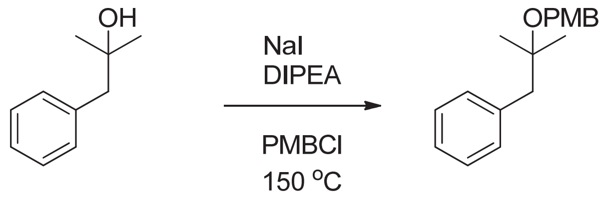
^{1}H NMR (400 MHz, $CDCl_3$) δ7.27 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.59 (d, J = 11.0 Hz, 1H), 4.33 (d, J = 11.0 Hz, 1H), 3.80 (s, 3H), 3.18 – 3.11 (m, 1H), 2.32 – 2.15 (m, 2H), 1.69 – 1.58 (m, 2H), 1.41 – 1.23 (m, 2H), 1.04 – 0.79 (m, 9H), 0.69 (d, J = 6.9 Hz, 3H).



3b **3a**

Alcohol **3b** (198 mg, 1 mmol), PMBCl (234 mg, 1.5 mmol), NaI (15 mg, 0.1 mmol) and DIPEA (208 mg, 1.6 mmol) were charged in reaction vessel equipped with magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 $^{\circ}$C for 2 hours. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 19:1) as eluent to give the product **3a** as colorless oil (216 mg, 68%).

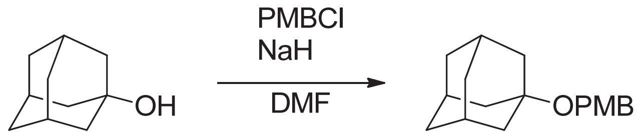
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.47 (m, 4H), 7.37 – 7.33 (m, 6H), 7.28 (d, J = 7.2 Hz, 2H), 6.93 (d, J = 8.6 Hz, 2H), 4.32 (s, 2H), 3.84 (s, 3H), 2.01 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 158.87, 146.76, 131.64, 128.72, 128.04, 126.87, 126.85, 113.73, 80.96, 64.50, 55.32, 26.06.
IR (thin film cm^{-1}): 756, 823, 900, 1032, 1123, 1172, 1247, 1301, 1380, 1444, 1492, 1512, 1585, 1612, 2834, 2906, 2979, 3023, 3058.
EI (M^+): calc. for 318, found: 318.
HRMS, ESI ($M+Na^+$), calc. for ($C_{22}H_{22}NaO_2^+$) 341.1512, found: 341.1517



4b **4a**

Alcohol **4b** (150 mg, 1 mmol), PMBCl (234 mg, 1.5 mmol), NaI (15 mg, 0.1 mmol) and DIPEA (208 mg, 1.6 mmol,) were charged in a reaction vessel equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 °C for 2 hours. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture and the mixture was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **4a** as colorless oil (205 mg, 76%).

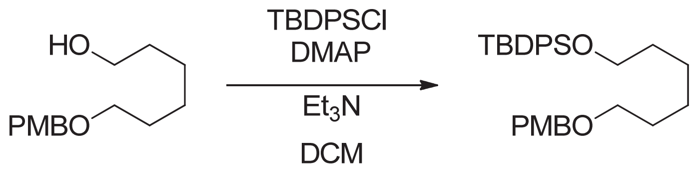
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 7H), 6.88 (d, J = 8.7 Hz, 2H), 4.47 (s, 2H), 3.81 (s, 3H), 2.88 (s, 2H), 1.24 (s, 6H).



5b **5a**

To a mixture of adamantan-1-ol (304 mg, 2 mmol) in DMF (5 mL) was added NaH (100 mg, 60% in mineral oil, 100 mg, 2.5 mmol,) at 0 °C. After 10 minutes, PMBCl (374 mg, 2.4 mmol) was added dropwise. The reaction was stirred for 1 hour and then quenched with Sat. NH_4Cl (1 mL). The mixture was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layer was dried over $MgSO_4$, filtered and concentrated under reduced pressure. The mixture was then purified by silica gel flash column chromatography with PE/EA (v/v = 9:1) as eluent to give the compound **5a** as white solid (400 mg, 73%).

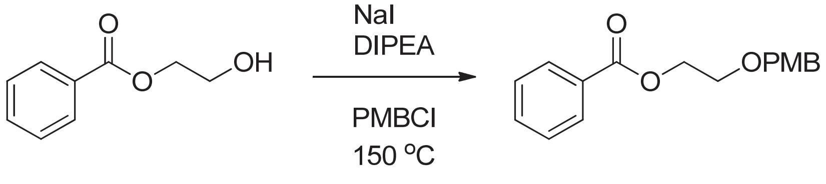
^{1}H NMR (400 MHz, $CDCl_3$) δ7.27 (d, J = 8.5 Hz, 2H), 6.86 (d, J = 8.5 Hz, 2H), 4.44 (s, 2H), 3.79 (s, 3H), 2.17 (s, 3H), 1.84 (d, J = 2.1 Hz, 6H), 1.72 – 1.58 (m, 6H).



6b **6a**

A flask equipped with a magnetic stir bar was charged with compound **6b** (643 mg, 2.7 mmol), Et_3N (810 mg, 8 mmol), DMAP (33 mg, 0.27 mmol) and DCM (16 mL) under nitrogen atmosphere. The TBDPSCl (890 mg, 3.22 mmol,) was added to the mixture after 5 minutes. Then the mixture was stirred at room temperature for 12 hours. The mixture was added water and DCM. The aqueous layer was extracted with DCM three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 19:1) as eluent to give the product **6a** as colorless oil (964 mg, 75%).

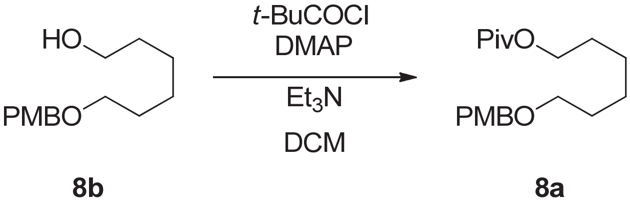
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 – 7.69 (m, 4H), 7.47 – 7.38 (m, 6H), 7.29 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 4.46 (s, 2H), 3.82 (s, 3H), 3.69 (t, *J* = 6.5 Hz, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 1.66 – 1.57 (m, 4H), 1.41 – 1.36 (m, 4H), 1.09 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.14, 135.60, 134.20, 130.84, 129.51, 129.23, 127.60, 113.79, 72.56, 70.17, 63.96, 55.28, 32.58, 29.80, 26.93, 26.01, 25.71, 19.26.
IR (thin film cm^{-1}): 1037, 1112, 1172, 1247, 1301, 1360, 1427, 1452, 1461, 1512, 1612, 2857, 2934.
MS, ESI ($M+Na^+$), calc. for 499, found: 499.
HRMS, ESI ($M+Na^+$), calc. for ($C_{30}H_{40}NaO_3Si^+$) 499.2639, found: 499.2639.



7b **7a**

Alcohol **7b** (166 mg, 1 mmol), PMBCl (234 mg, 1.5 mmol), NaI (15 mg, 0.1 mmol) and DIPEA (208 mg, 1.6 mmol) were charged in a reaction vessel equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 °C for 2 hours. The resulting mixture typically showed 2 phases. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 19:1) as eluent to give the product **7a** as colorless oil (160 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 4.54 (s, 2H), 4.51 – 4.47 (m, 2H), 3.83 – 3.75 (m, 5H).

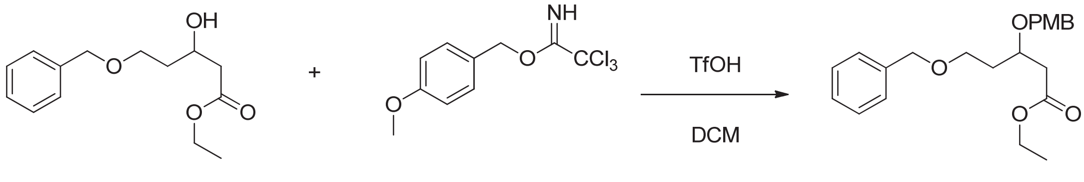


8b **8a**

A flask equipped with a magnetic stir bar was charged with compound **8b** (640 mg, 2.7 mmol), Et_3N (810 mg, 8 mmol), DMAP (33mg, 0.27 mmol) and DCM (16 mL) under nitrogen atmosphere. The *t*-BuCOCl (390 mg, 3.22 mmol,) was added to the mixture after 5 minutes. Then the mixture was stirred at room temperature for 12 hours. The mixture was added water and DCM. The aqueous layer was extracted with

DCM three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **8a** as colorless oil (608 mg, 70%).

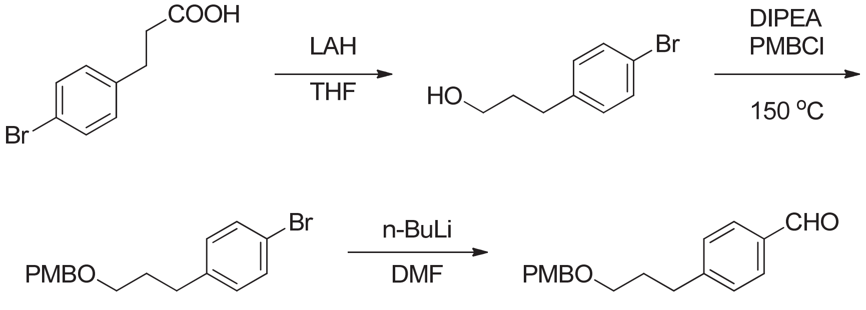
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.2 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 4.43 (s, 2H), 4.04 (t, *J* = 6.5 Hz, 2H), 3.81 (s, 3H), 3.44 (t, *J* = 6.5 Hz, 2H), 1.65 – 1.57 (m, 4H), 1.43 – 1.31 (m, 4H), 1.19 (s, 9H).



9b **9a**

A flask equipped with a magnetic stir bar was charged with compound **9b** (250 mg, 1 mmol), 4-methoxybenzyl 2,2,2-trichloroacetimidateand(565 mg, 2 mmol) and DCM (10 mL) under nitrogen atmosphere. Then TfOH (14 μL, 0.1 mmol) was added to the mixture. The mixture was stirred at room temperature for 24 hours and concentrated. The residue was suspended on hexanes and filtered through filter paper. The filtrate was concentrated and purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **9a** as colorless oil (112 mg, 30%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 5H), 7.23 (d, *J* = 8.6 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 4.54 – 4.43 (m, 4H), 4.19 – 4.06 (m, 3H), 3.79 (s, 3H), 3.62 – 3.56 (m, 2H), 2.58 (ddd, *J* = 20.5, 15.1, 6.3 Hz, 2H), 1.91 (q, *J* = 6.2 Hz, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.59, 159.22, 138.47, 130.62, 129.44, 128.39, 127.69, 127.58, 113.77, 73.22, 72.98, 71.53, 66.55, 60.45, 55.26, 40.29, 34.82, 14.25.
IR (thin film cm^{-1}): 1034, 1096, 1173, 1248, 1302, 1367, 1453, 1462, 1513, 1612, 1729, 1737, 2860, 2933.
MS, ESI (M+Na$^+$), calc. for 395, found: 395.
HRMS, ESI (M+Na$^+$), calc. for ($C_{22}H_{28}NaO_5^+$) 395.1829, found: 395.1835.



s-1a **10a**

A flask equipped with a magnetic stir bar was charged with 3-(4-bromophenyl)propionic acid (1.2 g, 5.3 mmol) and dry THF (20 mL), and then cooled to 0 °C. The mixture was then added LAH (608 mg, 16 mmol) slowly. Then the mixture was stirred at room temperature for 12 hours. After the completion of the reaction, water was added to the mixture and the organic layer was separated. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was used for next step without purification.

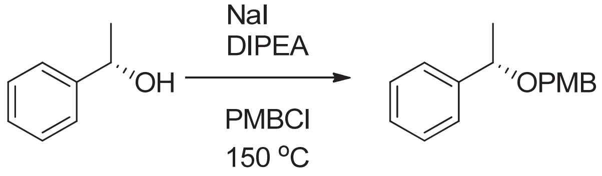
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 3.66 (t, *J* = 6.4 Hz, 2H), 2.70 – 2.62 (m, 2H), 1.91 – 1.81 (m, 2H).
Alcohol 3-(4-Bromophenyl)propan-1-ol (639 mg, 3 mmol), PMBCl (702 mg, 4.5 mmol), NaI (45 mg, 0.3 mmol) and DIPEA (624 mg, 4.8 mmol) were charged into a reaction vessel equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 °C for 2 hours. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture and the aqueous layer was extracted by ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 19:1) as eluent to give the product **s-1a** as colorless oil (872 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 4.45 (s, 2H), 3.83 (s, 3H), 3.46 (t, *J* = 6.3 Hz, 2H), 2.70 – 2.66 (m, 2H), 1.95 – 1.88 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.16, 142.04, 130.71, 129.29, 128.49, 128.30, 125.74, 113.79, 72.59, 69.23, 55.30, 32.42, 31.39.
IR (thin film cm-1): 1011, 1041, 1073, 1100, 1171, 1247, 1302, 1377, 1452, 1461, 1488, 1513, 2850.
EI (M^+): calc. for 334, found: 334.
HRMS, ESI ($M+Na^+$), calc. for ($C_{17}H_{19}BrNaO_2^+$) 357.0461, found: 357.0462.

To a solution of **s-1a** (334 mg, 1 mmol) in anhydrous THF (5mL) at -78 °C under nitrogen atmosphere, *n*-BuLi (0.5 mL, 2 mol/L in *n*-hexane, 1 mmol) was added. The solution was stirred for 15 minutes at -78 °C. Then DMF (88 mg, 1.2 mmol) was added dropwise. The reaction was stirred for another 2 hours at -78 °C and then warmed to room temperature. The reaction was quenched with NH_4Cl aqueous solution. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel column chromatography with PE/EA (v/v = 19:1) to give the product **10a** as colorless oil (142 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.42 (s, 2H), 3.77 (s, 3H), 3.44 (t, *J* = 6.2 Hz, 2H), 2.79 – 2.75 (m, 2H), 1.96 – 1.89 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 191.98, 159.22, 149.59, 134.51, 130.49, 129.92, 129.30, 129.17, 113.80, 72.65, 68.78, 55.29, 32.68, 30.97.
IR (thin film cm^{-1}): 827, 1034, 1098, 1169, 1213, 1247, 1303, 1364, 1462, 1512, 1576, 1585, 1606, 1692, 1703, 2856, 2934.

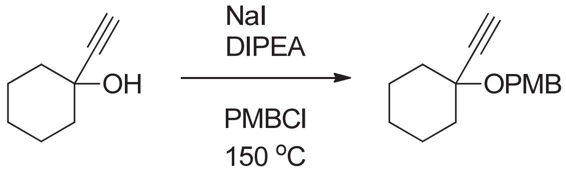
EI (M^+): calc. for 284, found: 284.
HRMS, ESI ($M+Na^+$), calc. for ($C_{18}H_{20}NaO_3^+$) 307.1305, found: 307.1308



11b **11a**

Alcohol **11b** (122 mg, 1 mmol), PMBCl (234 mg, 1.5 mmol), NaI (15 mg, 0.1 mmol) and DIPEA (208 mg, 1.6 mmol) were charged into a reaction vessel equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 °C for 2 hours. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture and the aqueous layer extracted by ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **11a** as colorless oil (193 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 4H), 7.32 – 7.27 (m, 1H), 7.24 (d, J = 8.6 Hz, 2H), 6.87 (d, J = 8.6 Hz, 2H), 4.48 (q, J = 6.5 Hz, 1H), 4.38 (d, J = 11.4 Hz, 1H), 4.22 (d, J = 11.4 Hz, 1H), 3.80 (s, 3H), 1.46 (d, J = 6.5 Hz, 3H).
HPLC, AD-H, 220nm, IPA/*n*-hexane = 19:1(v/v), 0.5mL/min, t_{minor} = 10.12 min, t_{major} = 11.22 min, ee = 99.5%.



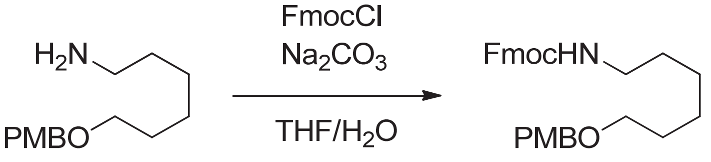
12b **12a**

Alcohol **12b** (124 mg, 1 mmol), PMBCl (234 mg, 1.5 mmol), NaI (15 mg, 0.1 mmol) and DIPEA (208 mg, 1.6 mmol) were charged into a reaction vessel equipped with a magnetic stir bar under nitrogen atmosphere. The mixture was refluxed at 150 °C for 2 hours. Ethyl acetate and 10% aqueous sodium bisulfate were added to the mixture and the aqueous layer extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 19:1) as eluent to give the product **12a** as colorless oil (195 mg, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.5 Hz, 2H), 6.89 (d, J = 8.6 Hz, 2H), 4.60 (s, 2H), 3.80 (s, 3H), 2.54 (s, 1H), 1.99 – 1.96 (m, 2H), 1.74 – 1.54 (m, 7H), 1.37 – 1.26 (m, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.00, 131.29, 129.28, 113.75, 85.54, 73.78, 65.18, 55.29, 37.25, 25.44, 22.71.
IR (thin film cm^{-1}): 821, 1036, 1076, 1172, 1248, 1301, 1378, 1450, 1462, 1513, 1612, 2858, 2935, 3289.

EI (M^+): calc. for 244, found: 244

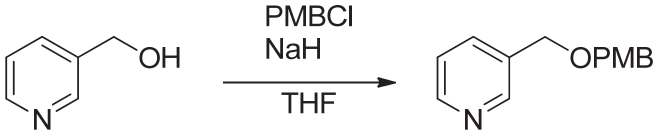
HRMS, ESI ($M+Na^+$), calc. for ($C_{16}H_{20}NaO_2^+$) 267.1356, found: 267.1358



13b **13a**

A 50 mL round bottom flask equipped with a magnetic stir bar was charged with compound **13b** (711 mg, 3.0 mmol), Na_2CO_3 (318 mg, 3.0 mmol), THF (12 mL) and H_2O (3 mL) and treated with FmocCl (775 mg, 3 mmol). The mixture was stirred at room temperature for 12 hours. The mixture was poured into a separator funnel containing 50 mL of ethyl acetate and 50 mL of H_2O. The layers were separated and the aqueous layer was extracted with ethyl acetate (50 mL x 2). The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 4:1) as eluent to afford the product **13a** as a white solid (1.02 g, 74%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.0 Hz, 2H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 2H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2 H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.73 (s, 1H), 4.43(s, 3H), 4.40 (d, *J* = 6.8 Hz, 2H), 4.22 (t, *J* = 6.8 Hz, 1H), 3.80 (s, 3H), 3.43 (t, *J* = 6.5 Hz, 2H), 3.18 (q, *J* = 6.5 Hz, 2H), 1.63 – 1.57 (m, 2H), 1.53 – 1.46 (m, 2H), 1.41 – 1.30 (m, 4H).



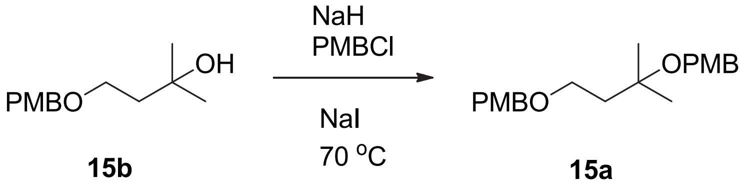
14b **14a**

A flame dried 50 mL round bottom flask equipped with a magnetic stir bar was charged with compound **14b** (218 mg, 2 mmol) and dry THF (10 mL) and cooled to 0 °C. To the mixture was added with NaH (60% in mineral oil, 120 mg, 3 mmol). After the reaction was stirred for at room temperature for 30 minutes, PMBCl (312 mg, 2 mmol) was added. The reaction was stirred at room temperature for 12 hours, followed by addition of water and ethyl acetate. The layers were separated and the aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 3:1) as eluent to give the product **14a** as colorless oil (265 mg, 58%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.54 (d, *J* = 3.9 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.26 (m, 3H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.52 (d, *J* = 6.6 Hz, 4H), 3.80 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.41, 149.09, 148.90, 135.65, 133.91, 129.81, 129.47, 123.46, 113.93, 72.23, 69.19, 55.30.

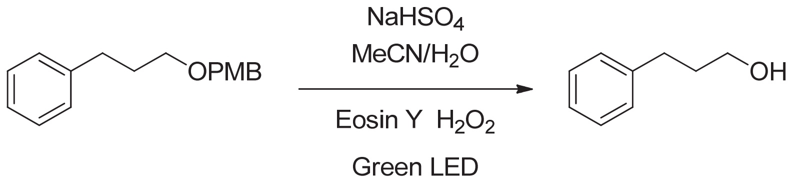
IR (thin film cm^{-1}): 819, 1031, 1174, 1248, 1302, 1359, 1426, 1462, 1513, 1585, 1612, 2857, 2934.
EI (M$^+$): calc. For 229, found: 229.
HRMS, ESI (M+H$^+$), calc. for ($C_{14}H_{16}NO_2^+$) 230.1176, found: 230.1178.



A flame dried round bottom flask equipped with a magnetic stir bar was charged with compound **15b** (224 mg, 1 mmol) dry THF (10mL) and cooled to 0 °C. The mixture was then treated with NaH (60% in mineral oil, 60 mg, 1.5 mmol) and stirred at room temperature for 30 minutes. PMBCl (234 mg, 1.5 mmol) and NaI (15 mg, 0.1 mmol) were then added. The mixture was stirred at 70 °C for 12 hours. The mixture was cooled to room temperature, and then water and ethyl acetate were added. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **15a** as colorless oil (120 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 6.89 – 6.84 (m, 4H), 4.44 (s, 2H), 4.33 (s, 2H), 3.80 (d, *J* = 3.6 Hz, 6H), 3.61 (t, *J* = 7.3 Hz, 2H), 1.93 (t, *J* = 7.3 Hz, 2H), 1.27 (s, 6H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.14, 158.86, 131.75, 130.67, 129.31, 128.85, 113.79, 113.75, 74.26, 72.69, 66.41, 63.37, 55.29, 55.28, 39.80, 26.19.
IR (thin film cm^{-1}): 820, 1035, 1093, 1171, 1247, 1301, 1364, 1462, 1513, 1612, 2853, 2928.
MS, ESI (M+Na$^+$), calc. for 367, found: 367.
HRMS, ESI (M+Na$^+$), calc. for ($C_{21}H_{28}NaO_4^+$) 367.1880, found: 367.1882

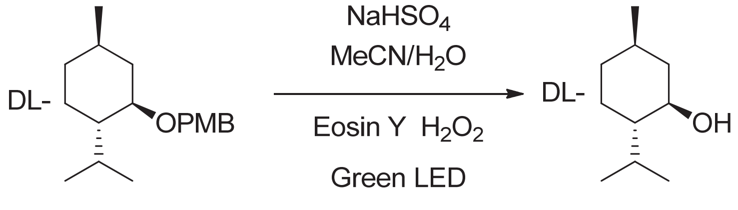
General Procedure A:



1a **1b**

A flask equipped with a rubber septum and magnetic stir bar was charged with PMB ether **1a** (25.6 mg, 0.1 mmol), $NaHSO_4$ (12 mg, 0.1 mmol), H_2O_2 (30 mg, 30%, 0.26 mmol,), $MeCN/H_2O$ (v/v = 1:1, 1 mL), and Eosin Y (3.2 mg, 0.005 mmol). The mixture was then irradiated with green LED under ambient atmosphere. After 15 hours, more 30 mg H_2O_2 was added to the mixture. When the reaction was completed after 10 hours (monitored by TLC analysis), the mixture was poured into a mixture of Sat. $NaHCO_3$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **1b** as colorless oil (11.5 mg, 85%).

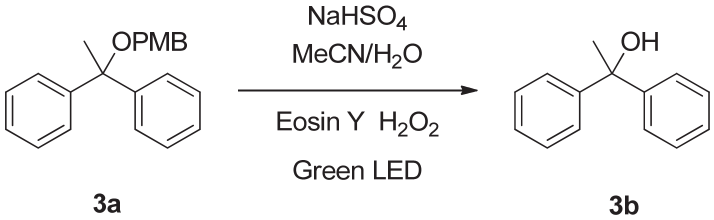
^1H NMR (400 MHz, $CDCl_3$) δ7.31 – 7.18 (m, 5H), 3.69 (t, *J* = 6.4 Hz, 2H), 2.78 – 2.66 (m, 2H), 1.95 – 1.86 (m, 2H).



2a **2b**

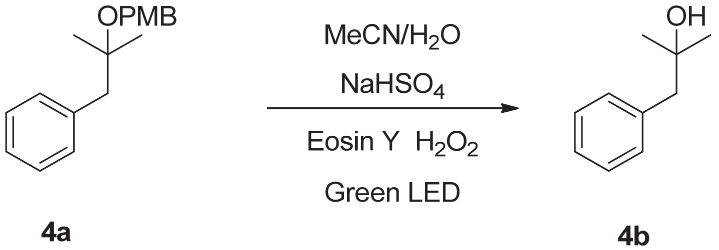
Compound **2b** was prepared from **2a** according to the general procedure A in the yield of 83%.

^1H NMR (400 MHz, $CDCl_3$) δ3.44 – 3.38 (m, 1H), 2.22 – 2.13 (m, 1H), 1.96 (d, *J* = 11.6 Hz, 1H), 1.70 – 1.57 (m, 2H), 1.48 – 1.35 (m, 2H), 1.16 – 1.07 (m, 1H), 0.98 (dd, *J* = 12.4, 3.4 Hz, 2H), 0.92 (d, *J* = 6.5 Hz, 6H), 0.81 (d, *J* = 7.0 Hz, 3H).



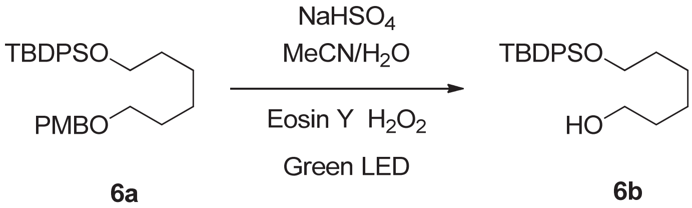
Compound **3b** was prepared from **3a** according to the general procedure A in the yield of 68%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.37 – 7.29 (m, 10H), 2.05 (s, 3H).



Compound **4b** was prepared from **4a** according to the general procedure A in the yield of 72%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.35 – 7.19 (m, 5H), 2.77 (s, 2H), 1.23 (s, 6H).

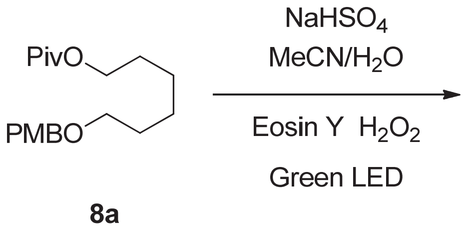


Compound **6b** was prepared from **6a** according to the general procedure A in the yield of 65%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (d, *J* = 7.3 Hz, 4H), 7.45 – 7.34 (m, 6H), 3.70 – 3.58 (m, 4H), 1.68 – 1.55 (m, 4H), 1.44 – 1.35 (m, 4H). 1.05 (s, 9H).

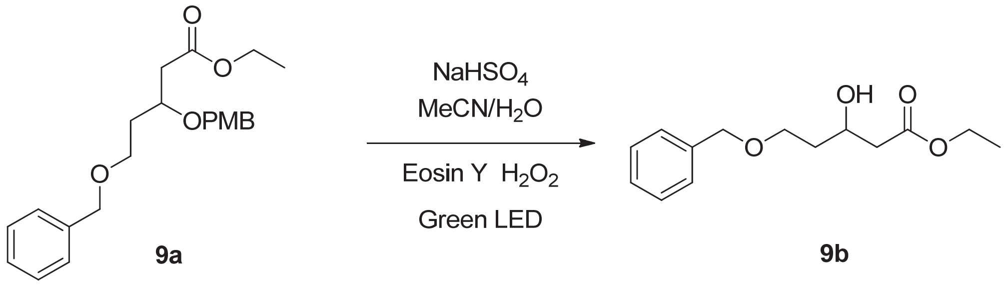
Compound **7b** was prepared from **7a** according to the general procedure A in the yield of 73%.

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, *J* = 7.3 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 4.50 – 4.44 (m, 2H), 4.00 – 3.94 (m, 2H).



Compound **8b** was prepared from **8a** according to the general procedure A in the yield of 78%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (t, *J* = 6.4 Hz, 2H), 3.64 (t, *J* = 6.4 Hz, 2H), 1.67 –1.61 (m, 3 H), 1.59 – 1.55 (m, 2 H), 1.41 – 1.37 (m, 4 H), 1.19 (s, 9 H).

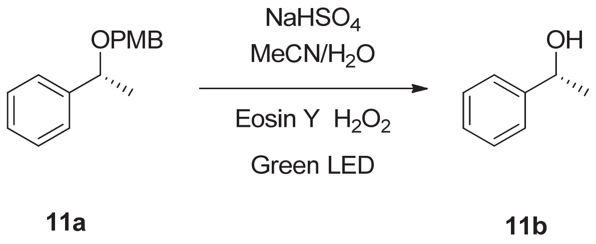


Compound was **9b** prepared from **9a** according to the general procedure A in the yield of 65%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 5H), 4.52 (s, 2H), 4.29 – 4.20 (m, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.75 – 3.61 (m, 2H), 2.49 (d, *J* = 6.3 Hz, 2H), 1.81 (dd, *J* = 11.5, 6.1 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 3H).

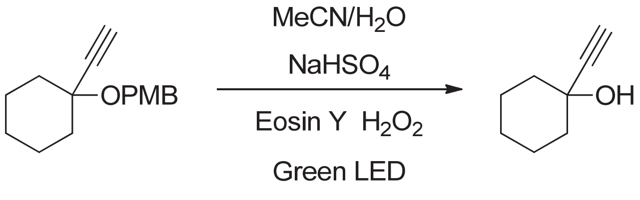
Compound **10b** was prepared from **10a** according to the general procedure A in the yield of 89% (80% purity).

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.81 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 3.70 (t, *J* = 6.3 Hz, 2H), 2.87 – 2.72 (m, 2H), 1.98 – 1.88 (m, 2H).



Compound **11b** was prepared from **11a** according to the general procedure A in the yield of 71% and 94% ee.

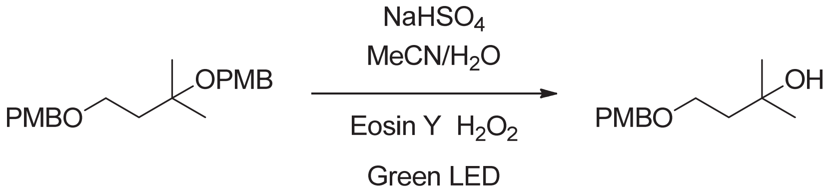
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 5H), 4.91 (q, *J* = 6.5 Hz, 1H), 1.51 (d, *J* = 6.5 Hz, 3H).
HPLC, CJ of Venusil, 220nm, IPA/hexane = 9:1(v/v), 0.5mL/min, t_{minor} =17.7 min, t_{major} = 19.9 min, ee = 94%.



12a **12b**

Compound **12b** was prepared from **12a** according to the general procedure A in the yield of 56%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 (s, 1H), 1.96 – 1.87 (m, 2H), 1.73 – 1.53 (m, 8H).

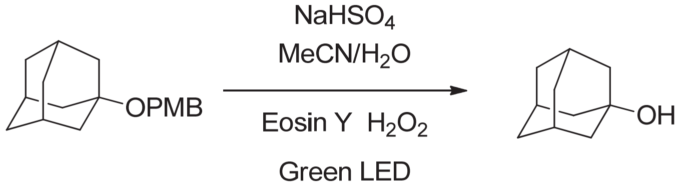


15a **15b**

Compound **15b** was prepared from **15a** according to the general procedure A in the yield of 67%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 2H), 4.38 (s, 2H), 3.73 (s, 3H), 3.61 (t, *J* = 5.9 Hz, 2H), 1.71 (t, *J* = 5.9 Hz, 2H), 1.15 (s, 6H).

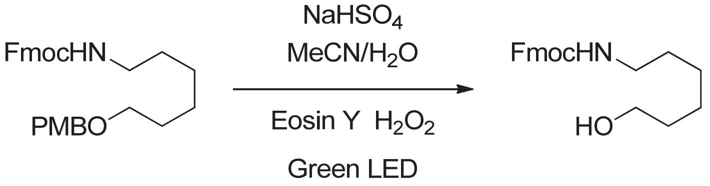
General Procedure B:



5a **5b**

A flask equipped with a rubber septum and a magnetic stir bar was charged with PMB ether **5a** (27.2 mg, 0.1 mmol), $NaHSO_4$ (12 mg, 0.1 mmol), H_2O_2 (30 mg, 30%, 0.26 mmol), MeCN (1 mL), H_2O (0.5 mL) and Eosin Y (3.2 mg, 0.005 mmol). The mixture was then irradiated with green LED under ambient atmosphere. After 24 hours, H_2O_2 (30 mg, 30%, 0.26 mmol) was added to the mixture. Upon the completion of reaction after another 24 hours, the mixture was poured into a mixture of Sat. $NaHCO_3$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **5b** as white solid (11mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (s, 3H), 1.71 (d, *J* = 2.3 Hz, 6H), 1.66 – 1.57 (m, 6H).

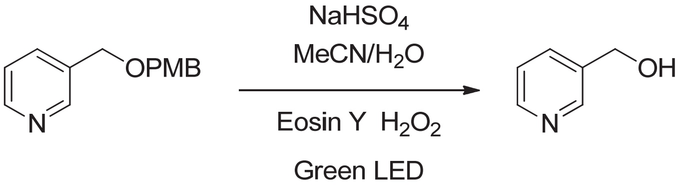


13a **13b**

Compound **13b** was prepared from **13a** according to the general procedure B in the yield of 77%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 4.78 (s, 1H), 4.41 (d, *J* = 6.7 Hz, 2H), 4.22 (t, *J* = 6.6 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 3.19 (d, *J* = 4.7 Hz, 2H), 1.60 – 1.50 (m, 4H), 1.37 – 1.24 (m, 4H).

General Procedure C:

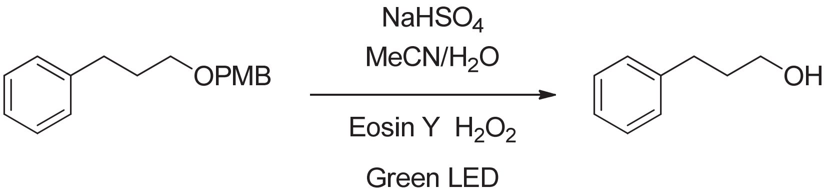


14a **14b**

A flask equipped with a rubber septum and a magnetic stir bar was charged with PMB ether **14a** (23 mg, 0.1 mmol), $NaHSO_4$ (12 mg, 0.1 mmol), H_2O_2 (30 mg, 30%, 0.26 mmol,), Eosin Y (3.2 mg, 0.005 mmol), MeCN (1 mL) and H_2O (0.5 mL). The mixture was then irradiated with green LED under ambient atmosphere. After 24 hours, H_2O_2 (30 mg, 30%, 0.26 mmol,) was added to the mixture. Upon the completion after another 24 hours (monitored by TLC analysis), the reaction mixture was poured into a mixture of Conc. HCl and ethyl acetate. The organic layer was extracted with water three times. Then the combined aqueous layer was brought to pH = 8 with sat. $NaHCO_3$, and extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 1:3) as eluent to give the product **14b** as colorless oil (6.2 mg, 57%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 8.40 – 8.32 (m, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.23 (dd, *J* = 7.6, 4.9 Hz, 1H), 4.65 (s, 2H).

Photoredox cleavage of PMB ether 1a at gram scale



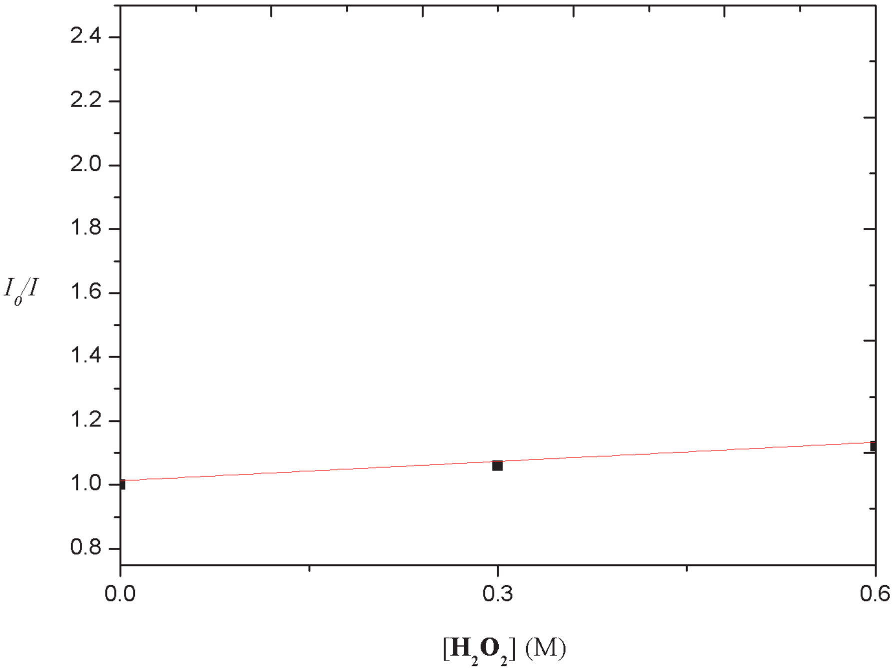
1a **1b**

A flask equipped with a rubber septum and magnetic stir bar was charged with PMB ether **1a** (1.53 g, 6 mmol), $NaHSO_4$ (720 mg, 6 mmol), H_2O_2 (1.8 g, 30%, 15.6mmol), MeCN/H_2O (v/v, 1:1, 60 mL), and Eosin Y (192 mg, 0.3 mmol). The mixture was then irradiated with 24W green LED under ambient atmosphere. After 24 hours, H_2O_2 (1.8 g, 30%, 15.6mmol) was added to the mixture. Upon the full conversion monitored by TLC analysis after another 24 hours, the mixture was poured into a mixture of Sat. $NaHCO_3$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **1b** as colorless oil (700 mg, 81%).

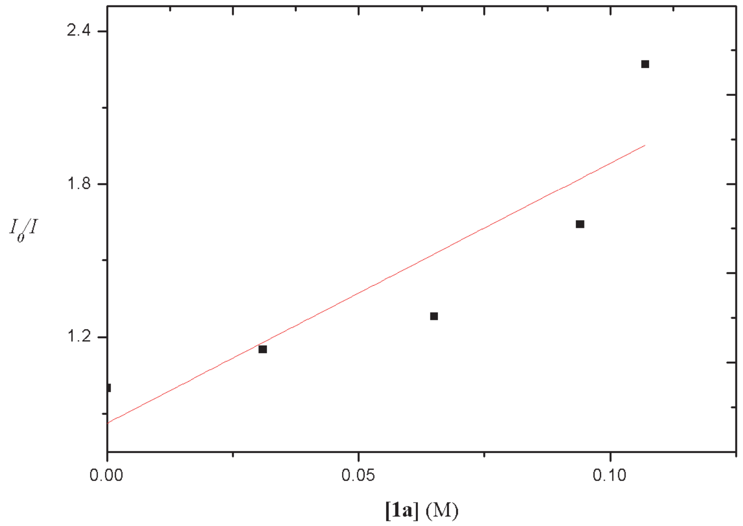
Fluorescence quenching experiments:

All Eosin Y solutions were irradiated at 530 nm and the emission intensity at 555 nm was observed. In a typical experiment, a 5 mM solution of Eosin Y in MeCN/H_2O was added to appropriate amount of quencher. Then the emission spectrum of the sample was collected.

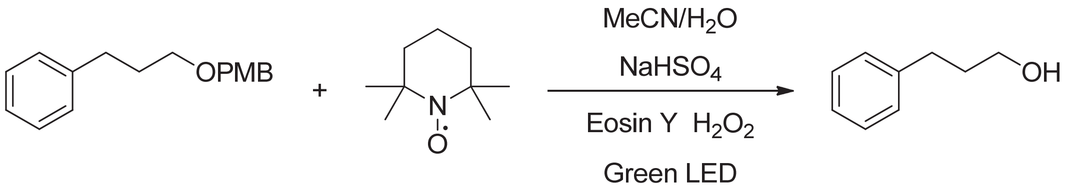
Eosin Y Emission Quenching by H_2O_2



Eosin Y Emission Quenching by PMB ether

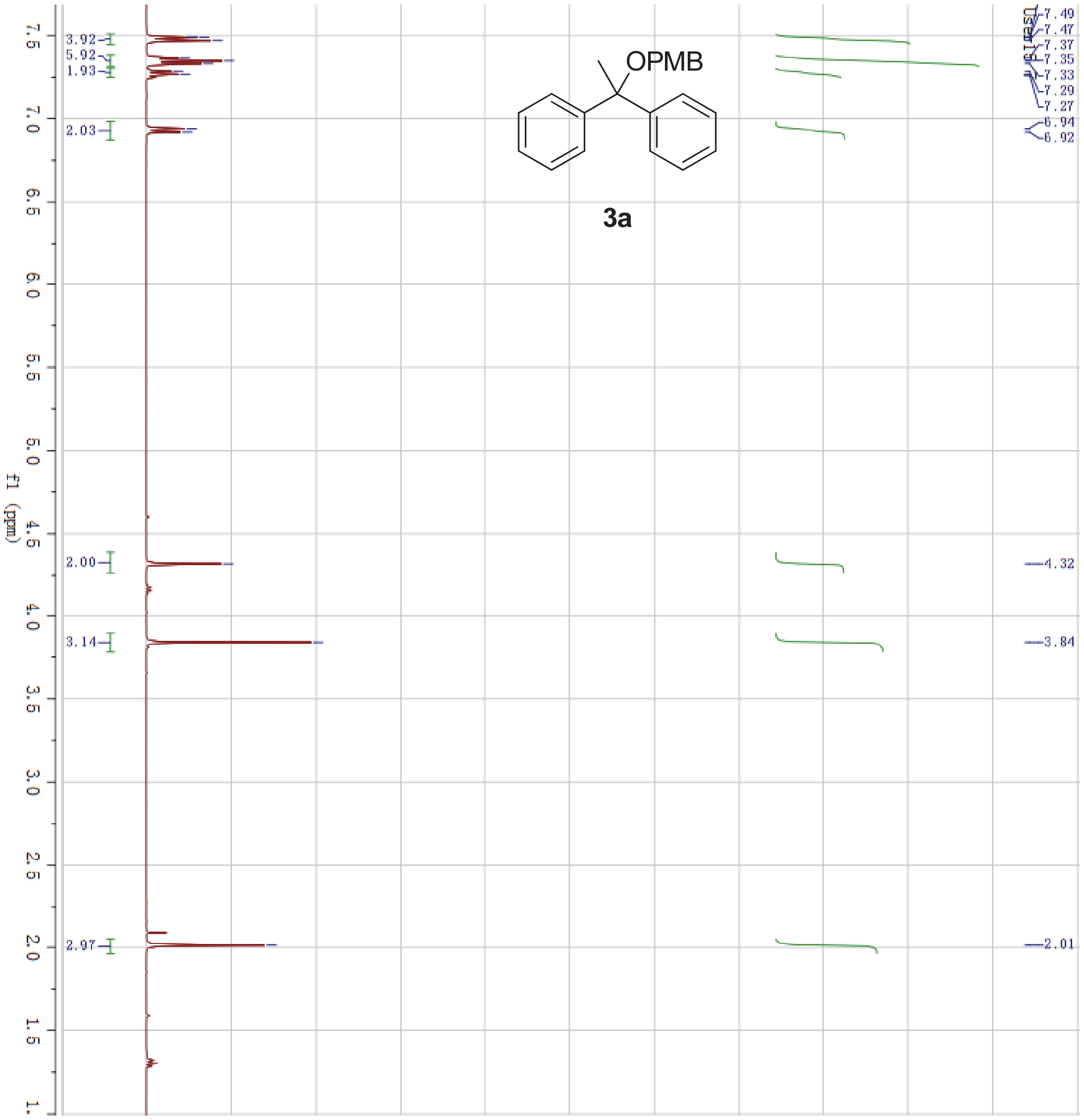


TEMPO additive experiment:



1a **1b**

A flask equipped with a rubber septum and magnetic stir bar was added PMB ether **1a** (25.6 mg, 0.1 mmol), TEMPO (15.6 mg, 0.1 mmol), $NaHSO_4$ (12 mg, 0.1 mmol), H_2O_2 (30 mg, 30%, 0.26 mmol), MeCN/H_2O (v/v = 1:1, 1 mL), and Eosin Y (3.2 mg, 0.005 mmol). The mixture was then irradiated with green LED under ambient atmosphere. After 15 hours, H_2O_2 (30 mg, 30%, 0.26 mmol) was added. Upon the full conversion with additional 10 hours (monitored by TLC analysis), the mixture was poured into a mixture of Sat. $NaHCO_3$ and ethyl acetate. The aqueous layer was extracted with ethyl acetate three times. The combined organic layer was dried (Na_2SO_4) and concentrated. The residue was purified by silica gel chromatography with PE/EA (v/v = 9:1) as eluent to give the product **1b** as colorless oil (11 mg, 81%).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7.33
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6.92
4.32
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3.92
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1.93
2.03
2.00
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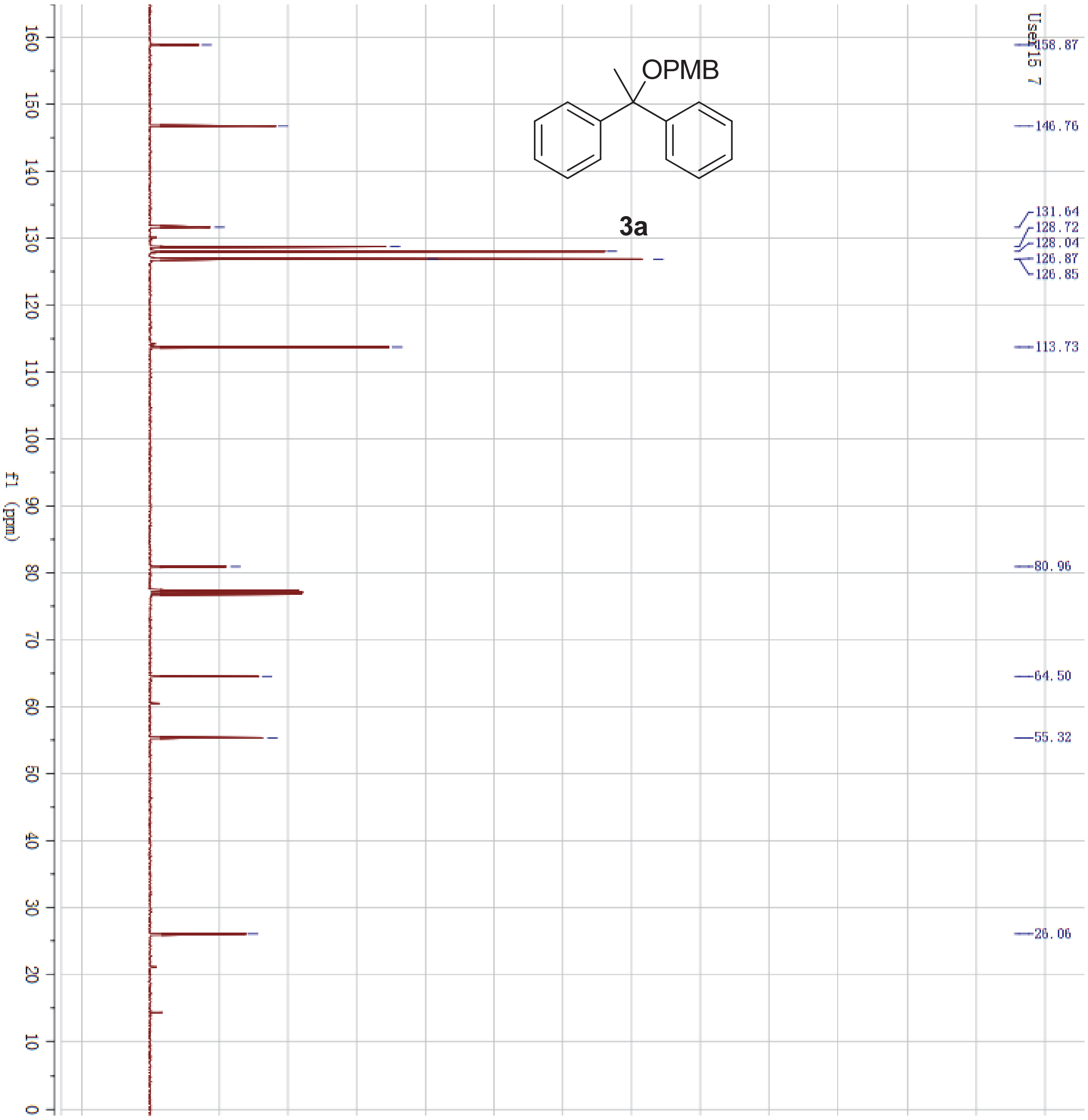
1.5
1.
f1 (ppm)

3a


3a

OPMB
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128.04
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113.73
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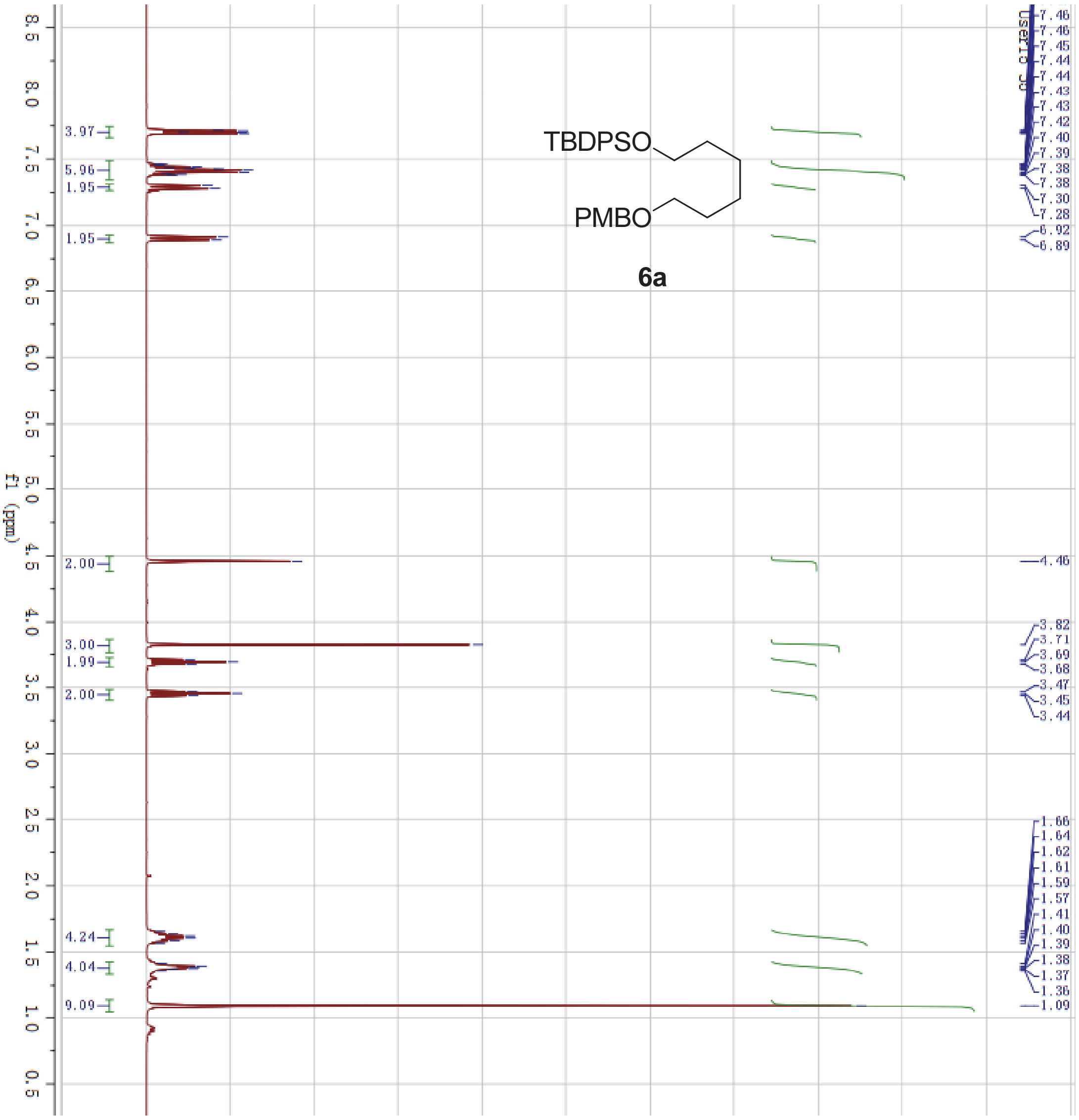
55.32
26.06
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
User 15 7



6a

TBDPSO
PMBO
f1 (ppm)
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7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
3.97
5.96
1.95
1.95
2.00
3.00
1.99
2.00
4.24
4.04
9.09
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.40
7.39
7.38
7.38
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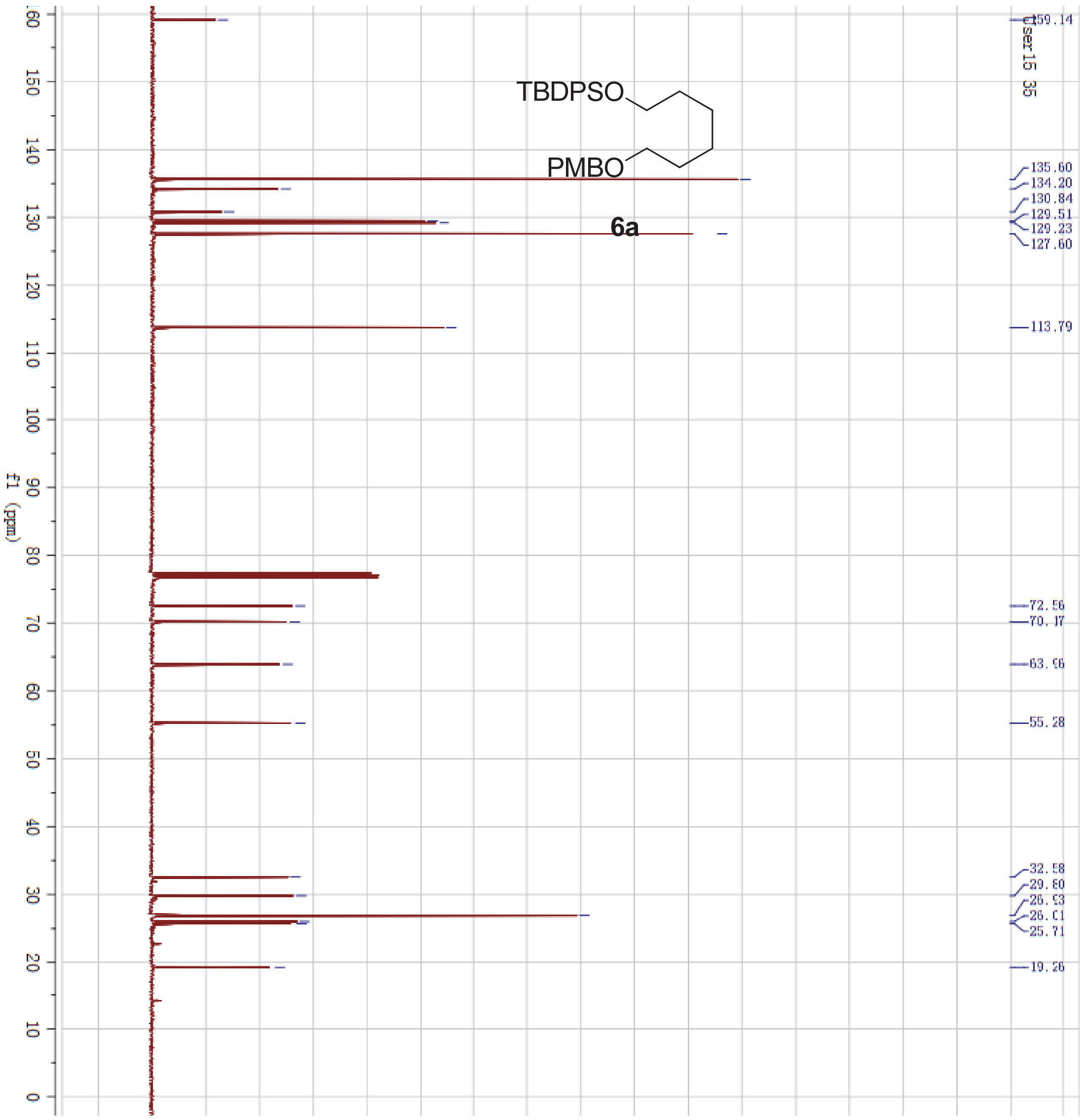
1.36
1.09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PMBO
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150
140
130
120
110
100
90
80
70
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50
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30
20
10
0
159.14
User15 35
135.60
134.20
130.84
129.51
129.23
127.60
113.79
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70.17
63.96
55.28
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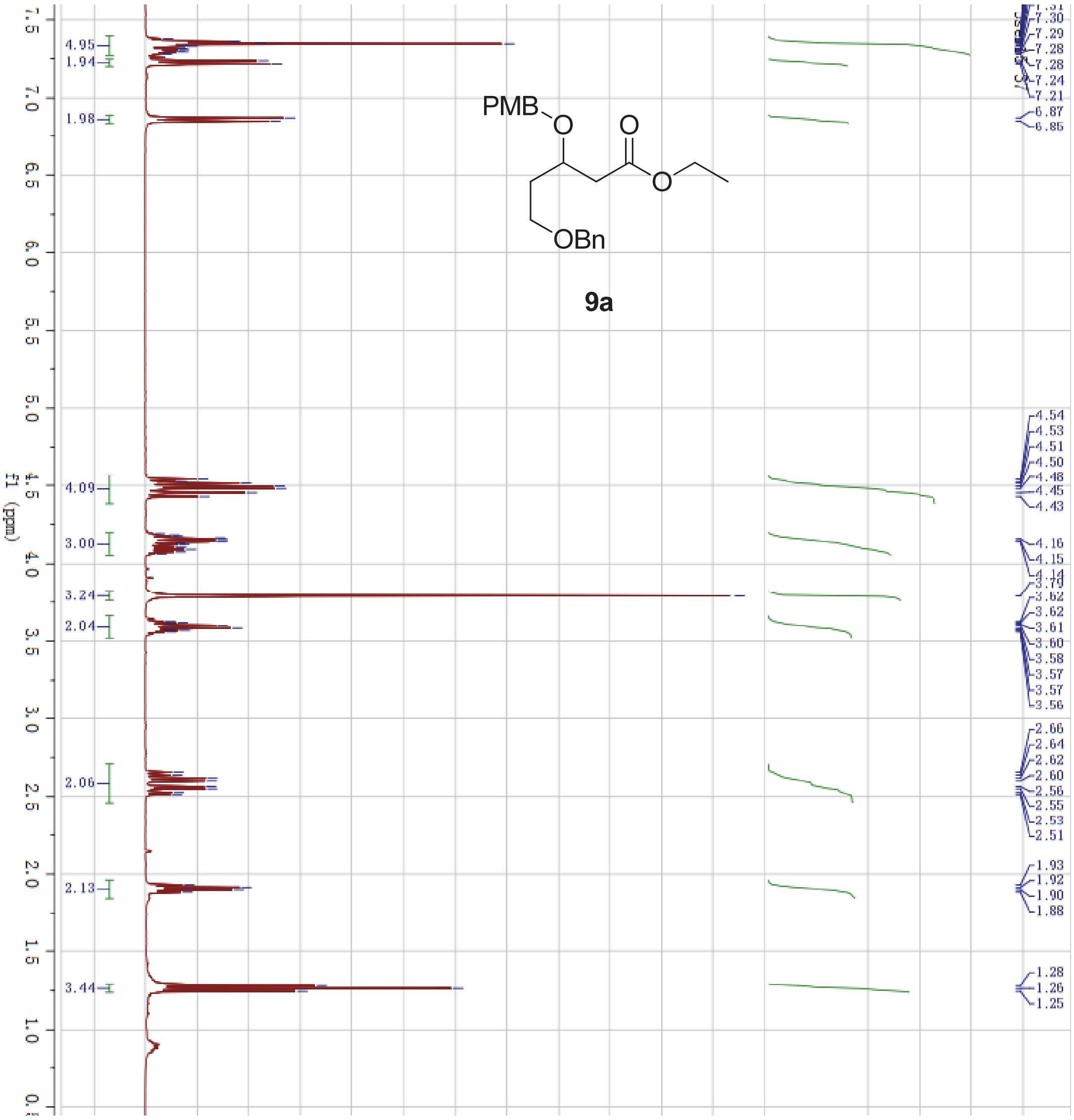
26.93
26.01
25.71
19.26

6a


PMB
O
O
O
OBn
4.95
1.94
1.98
4.09
3.00
3.24
2.04
2.06
2.13
3.44
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
7.30
7.29
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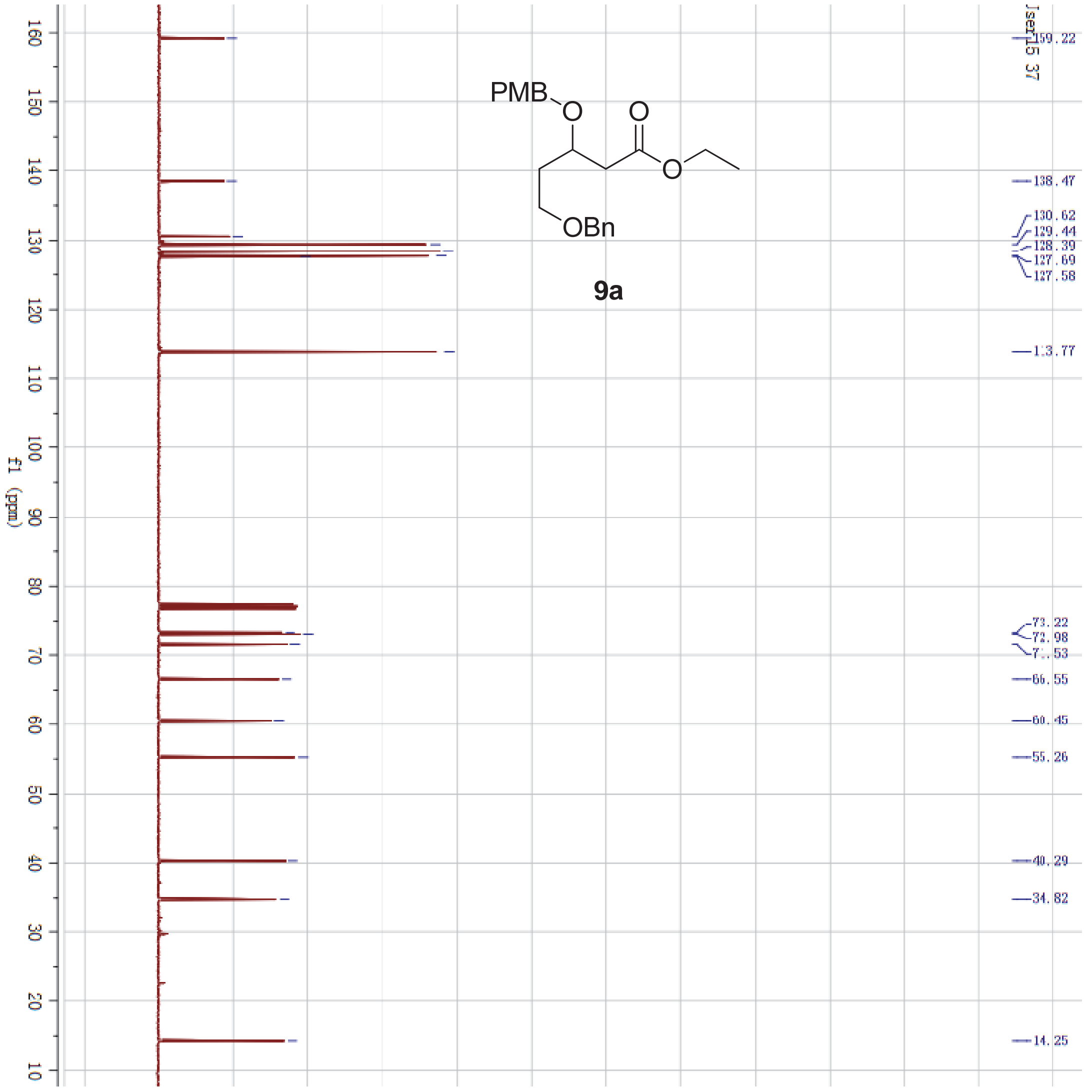
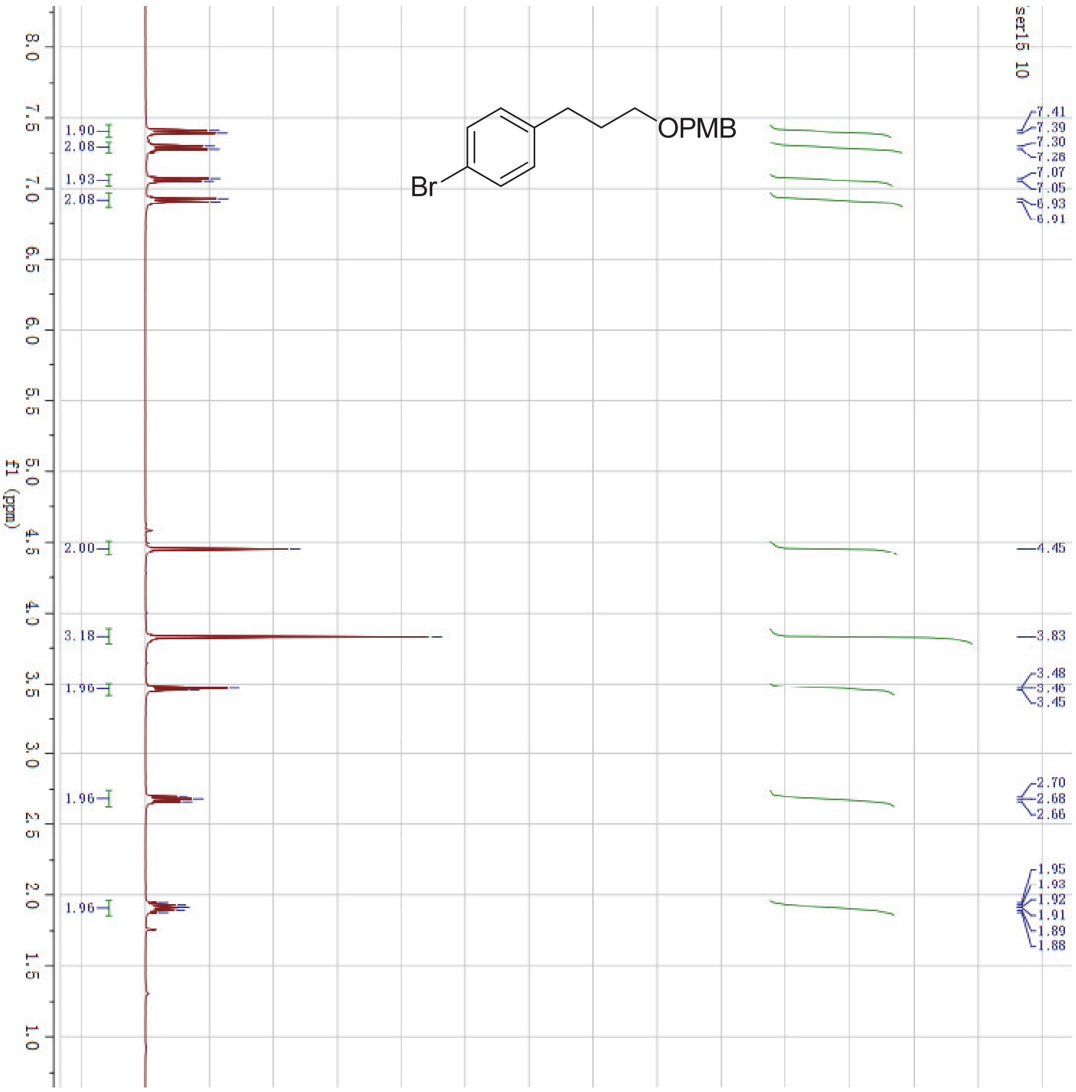
1.28
1.26
1.25

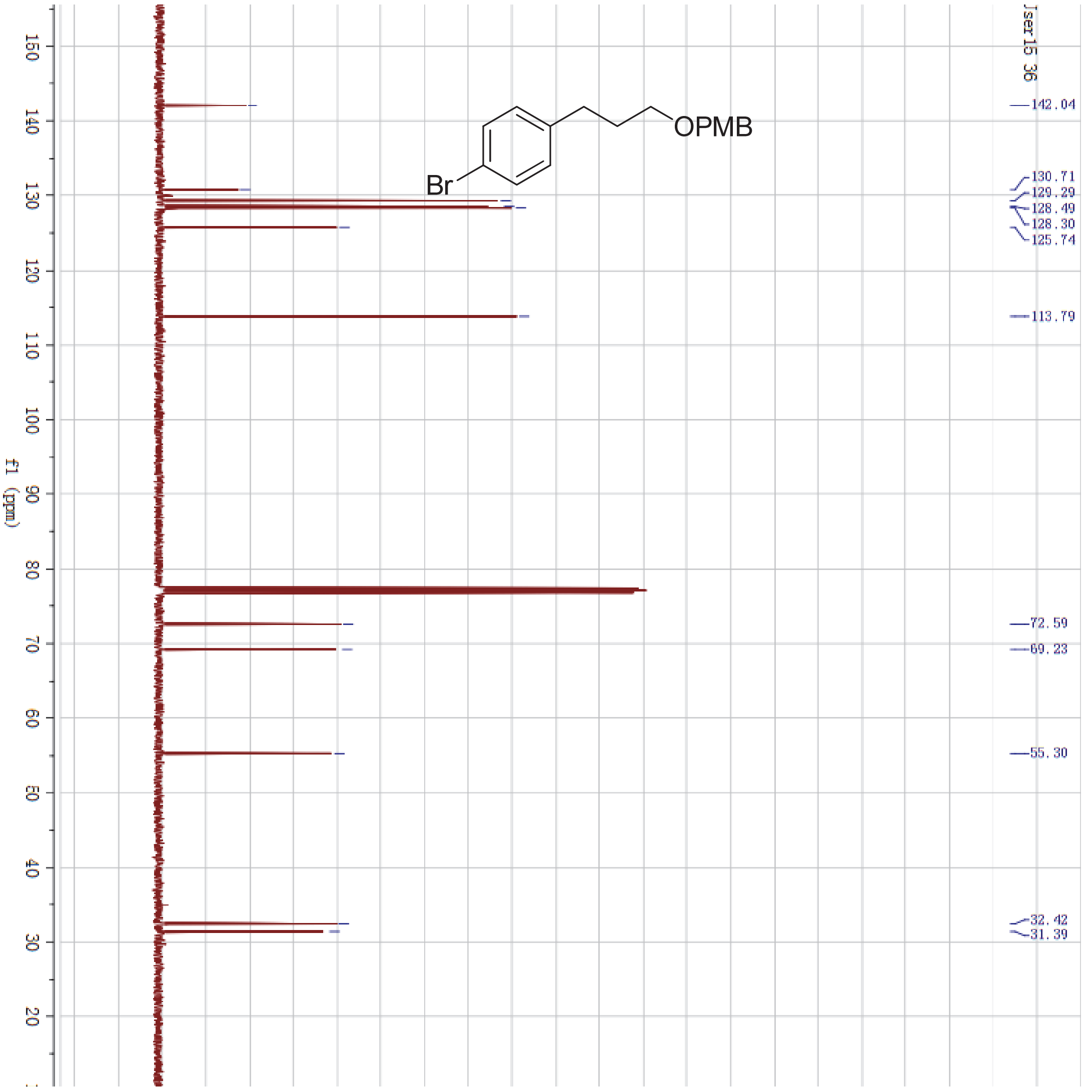
9a



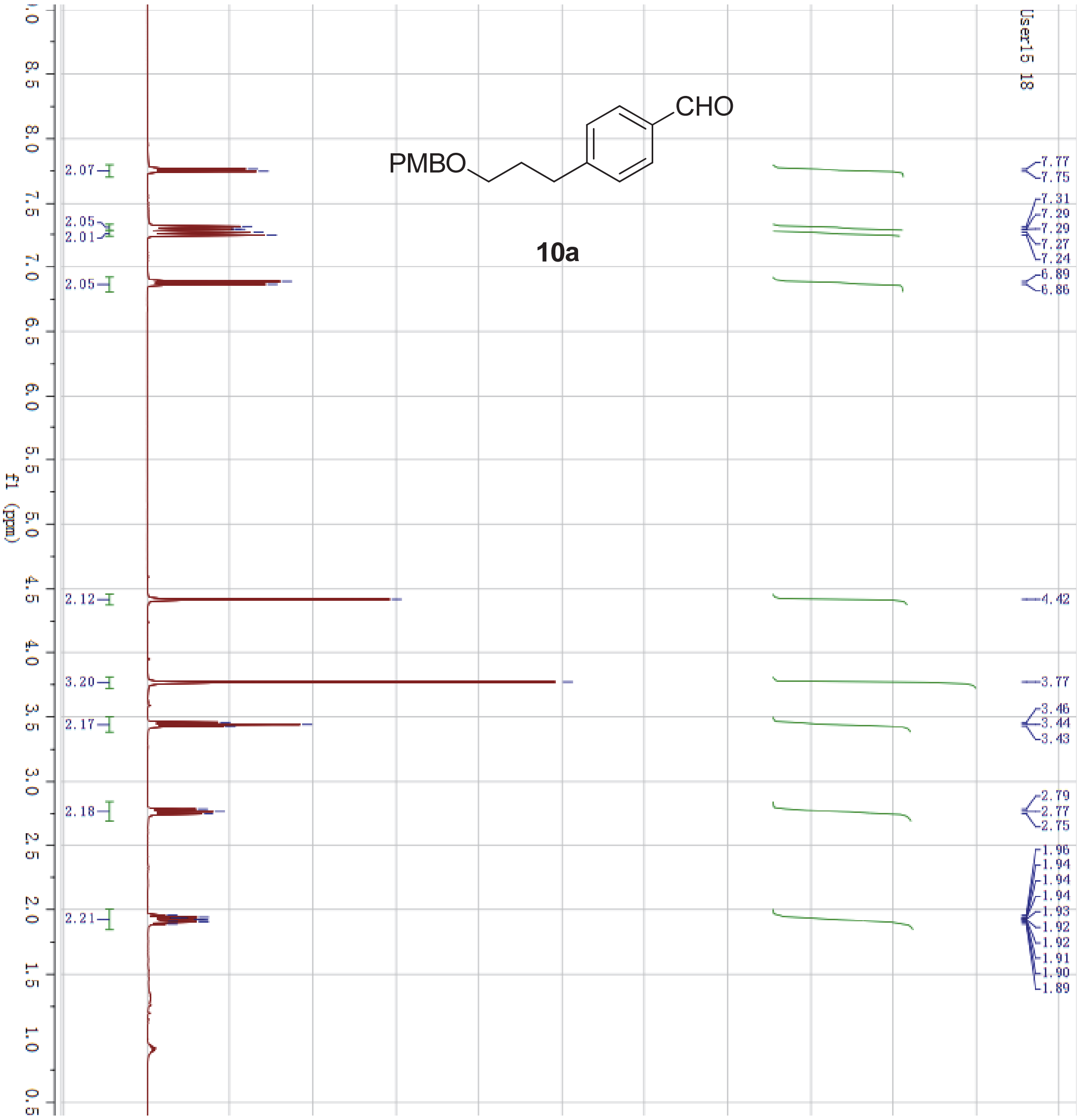
9a

PMB
O
O
O
OBn
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Jser15 37
159.22
138.47
130.62
129.44
128.39
127.69
127.58
113.77
73.22
72.98
71.53
66.55
60.45
55.26
40.29
34.82
14.25

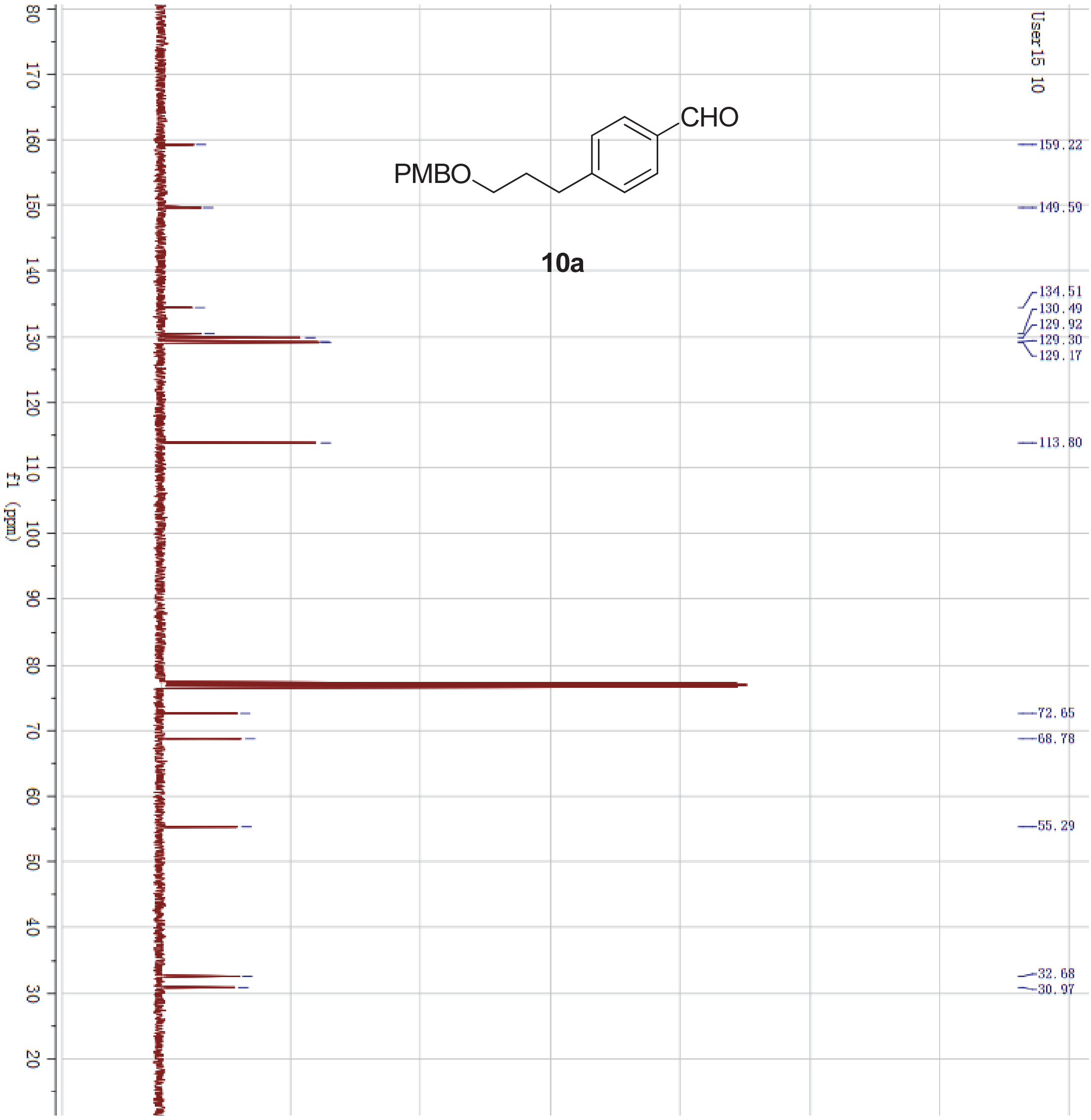

ser15 10
Br
OPMB
7.41
7.39
7.30
7.28
7.07
7.05
6.93
6.91
4.45
3.83
3.48
3.46
3.45
2.70
2.68
2.66
1.95
1.93
1.92
1.91
1.89
1.88
1.90
2.08
1.93
2.08
2.00
3.18
1.96
1.96
1.96
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)



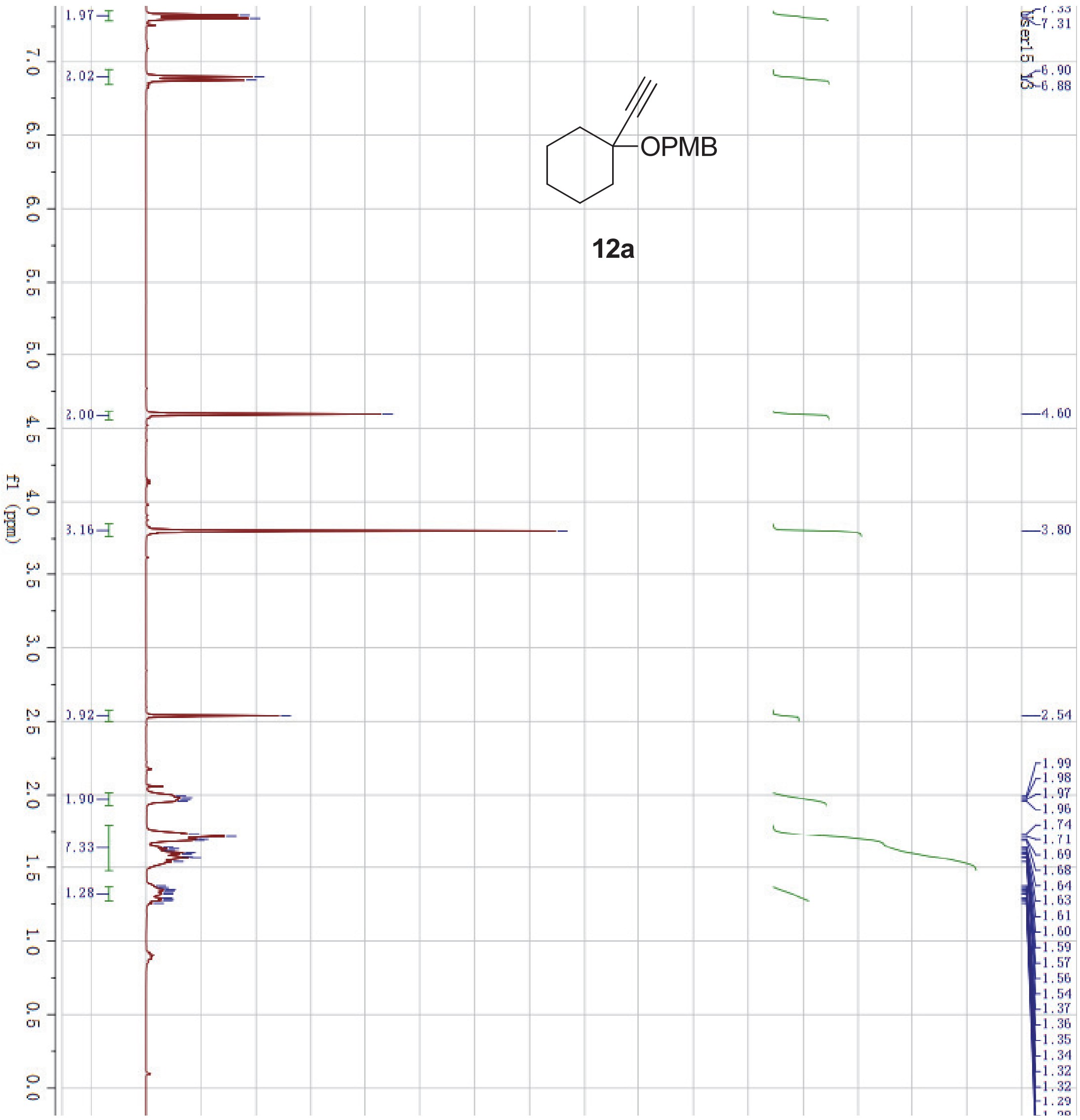
Br
OPMB
Jser15 36
142.04
130.71
129.29
128.49
128.30
125.74
113.79
72.59
69.23
55.30
32.42
31.39
f1 (ppm)
150
140
130
120
110
100
90
80
70
60
50
40
30
20



PMBO
CHO
10a
User15 18
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
2.07
2.05
2.01
2.05
2.12
3.20
2.17
2.18
2.21
7.77
7.75
7.31
7.29
7.29
7.27
7.24
6.89
6.86
4.42
3.77
3.46
3.44
3.43
2.79
2.77
2.75
1.96
1.94
1.94
1.94
1.93
1.92
1.92
1.91
1.90
1.89


10a

CHO
PMBO
User15 10
159.22
149.59
134.51
130.49
129.92
129.30
129.17
113.80
72.65
68.78
55.29
32.68
30.97
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


OPMB
12a
f1 (ppm)
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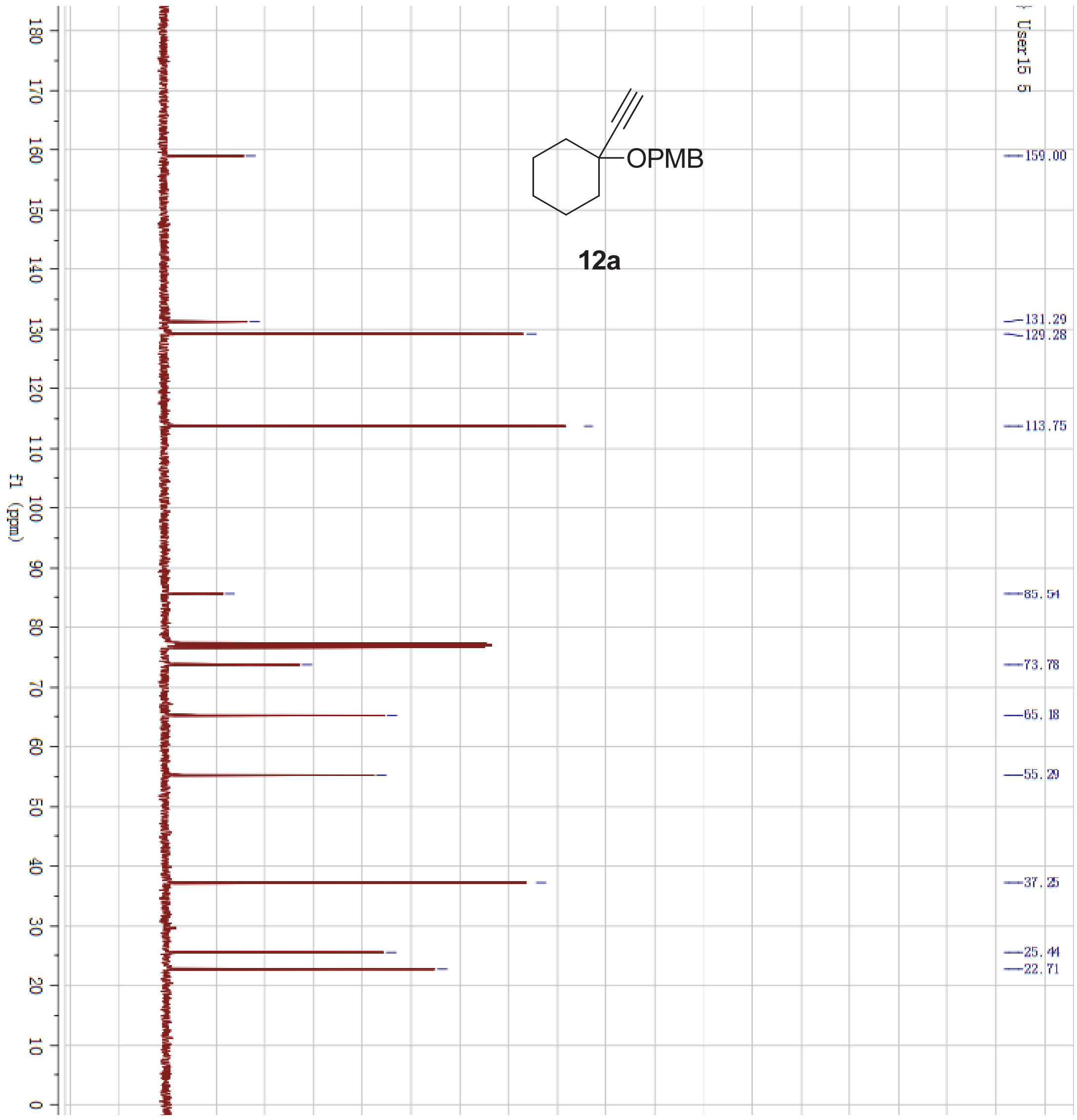
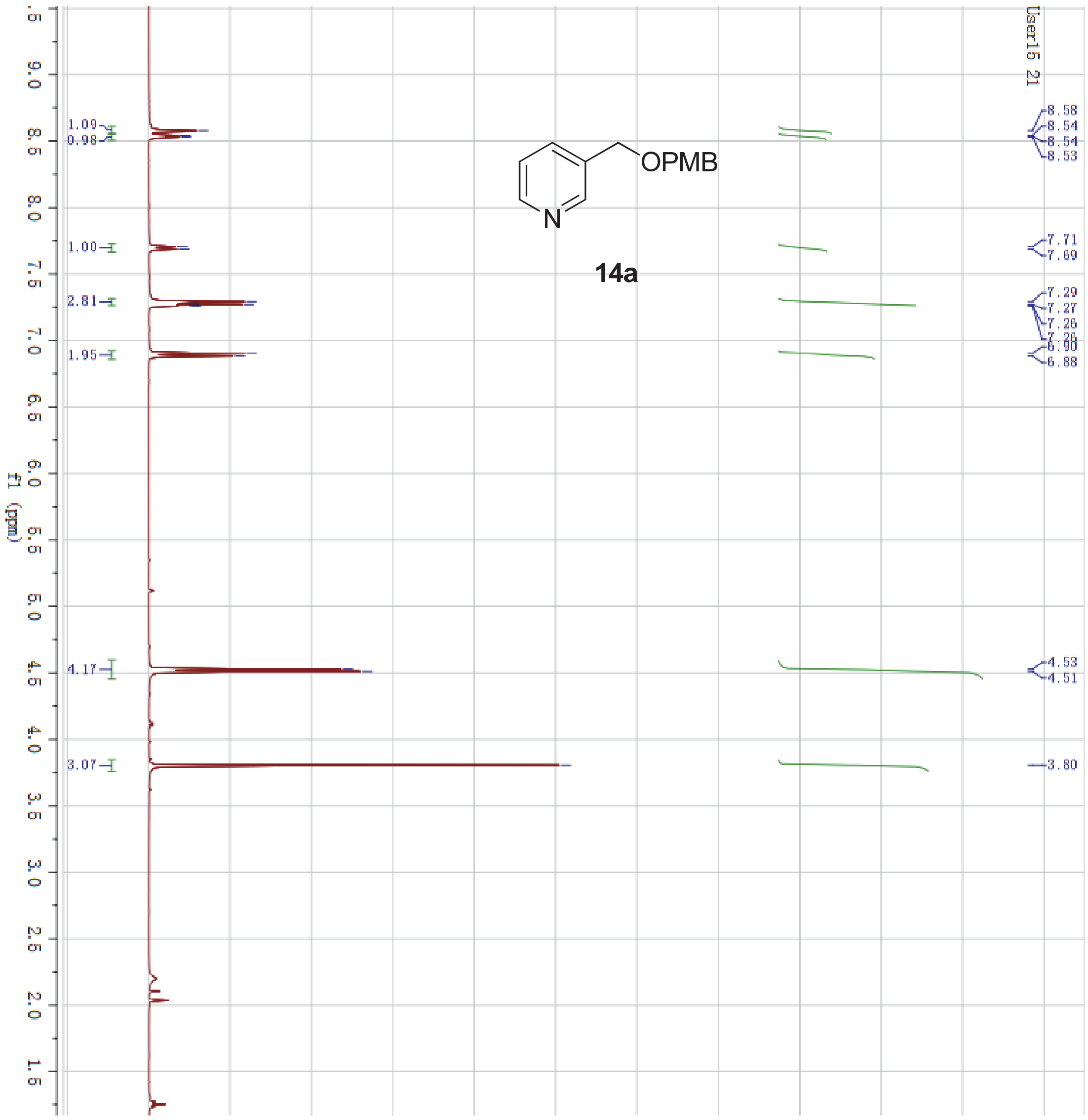
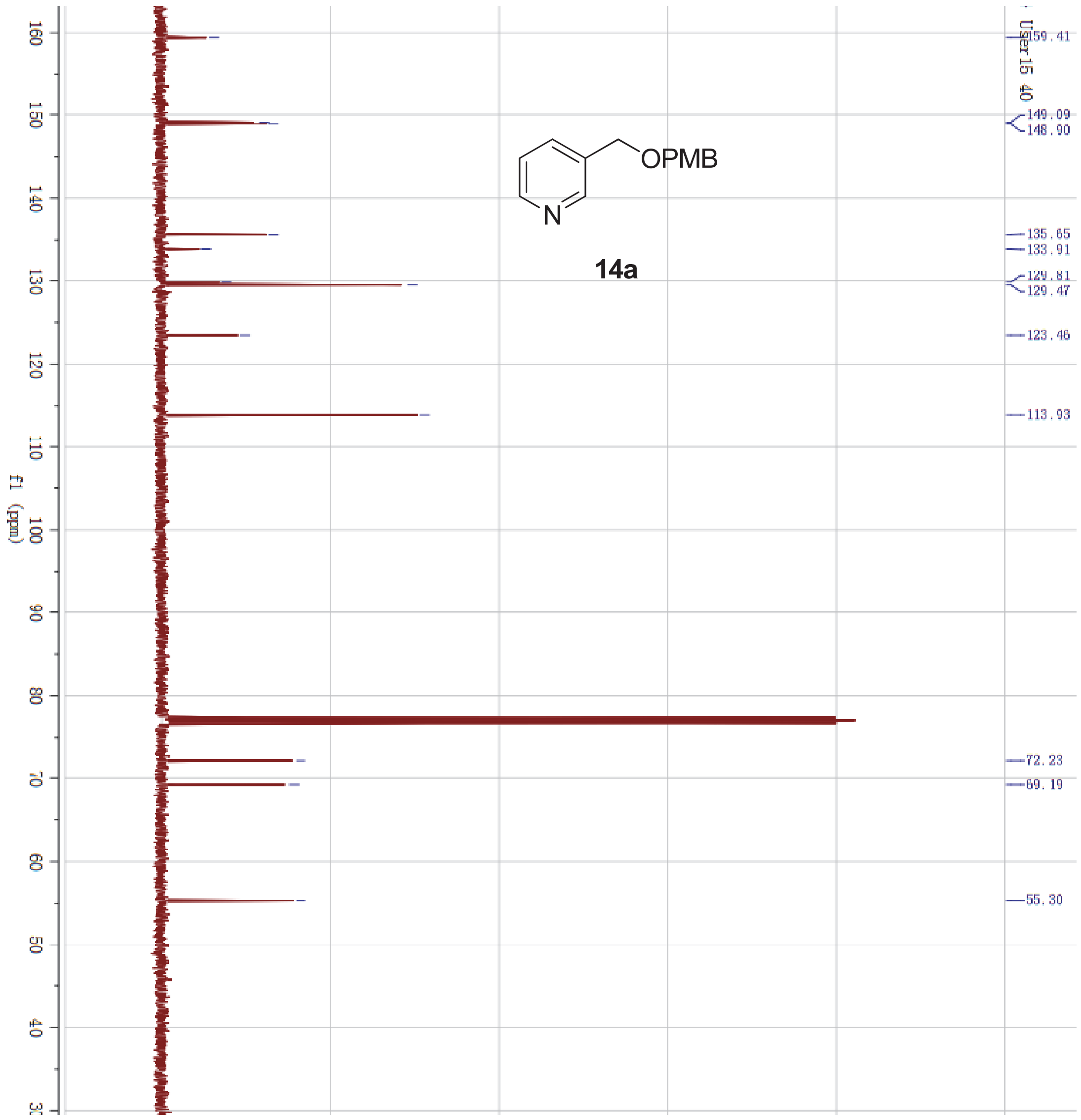
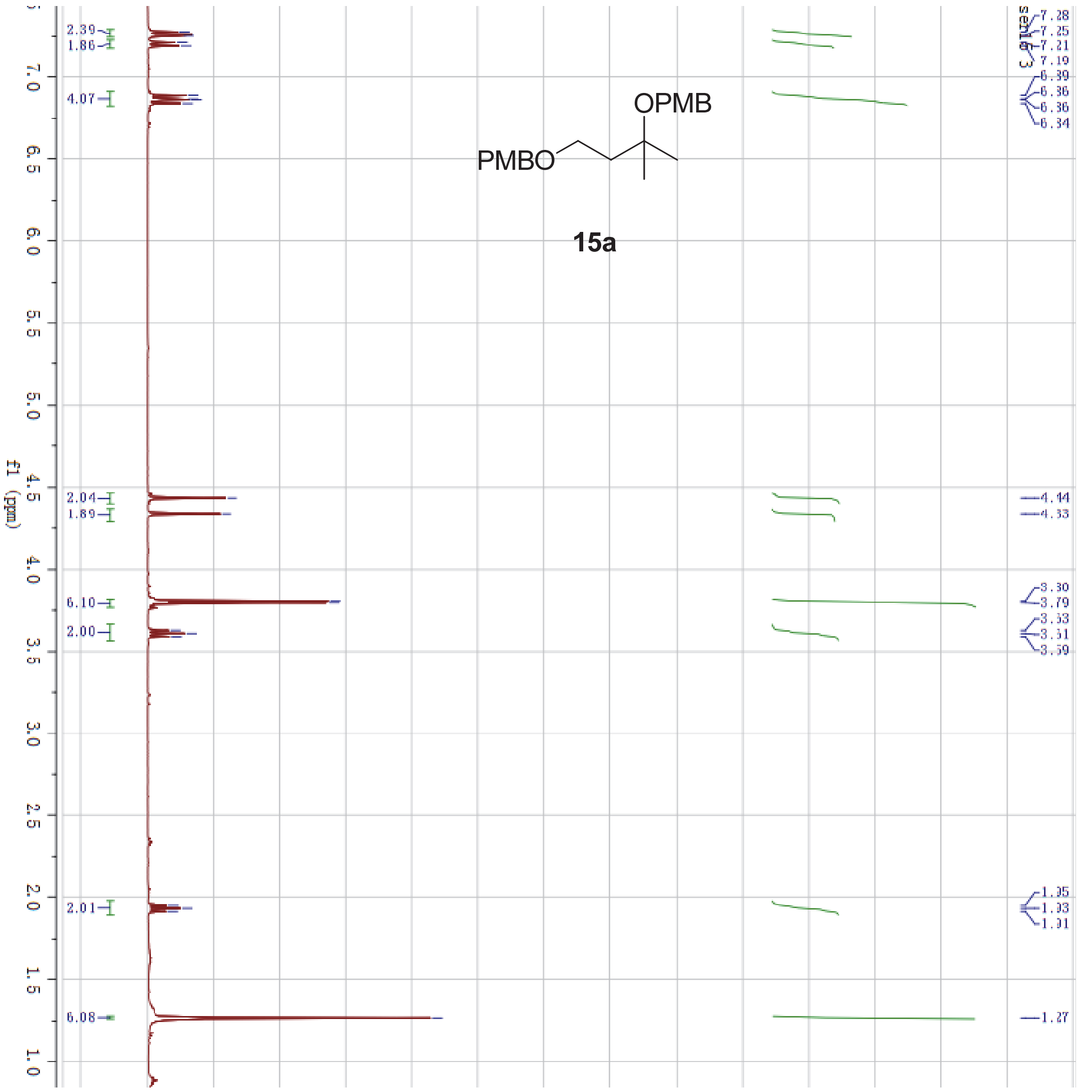
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1.97
2.02
2.00
3.16
0.92
1.90
7.33
1.28
7.31
6.90
6.88
4.60
3.80
2.54
1.99
1.98
1.97
1.96
1.74
1.71
1.69
1.68
1.64
1.63
1.61
1.60
1.59
1.57
1.56
1.54
1.37
1.36
1.35
1.34
1.32
1.32
1.29


User15 5
OPMB
12a
159.00
131.29
129.28
113.75
85.54
73.78
65.18
55.29
37.25
25.44
22.71
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OPMB
N
14a
User15 21
f1 (ppm)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.09
0.98
1.00
2.81
1.95
4.17
3.07
8.58
8.54
8.54
8.53
7.71
7.69
7.29
7.27
7.26
7.26
6.90
6.88
4.53
4.51
3.80

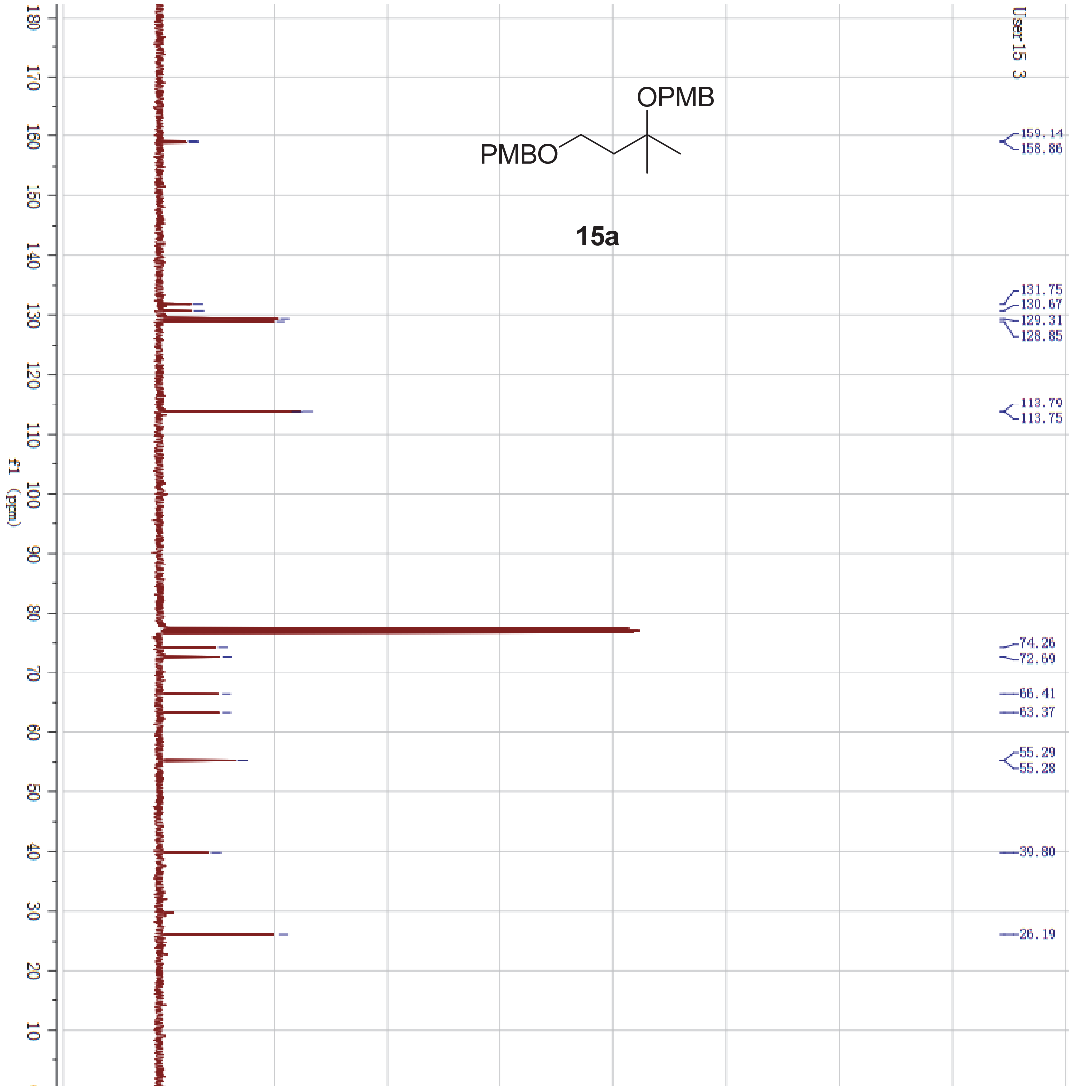

OPMB
N
User15 40
159.41
149.09
148.90
135.65
133.91
129.81
129.47
123.46
113.93
72.23
69.19
55.30
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

14a



15a

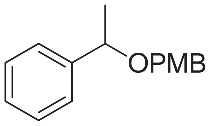
PMBO
OPMB
f1 (ppm)
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
2.39
1.86
4.07
2.04
1.89
6.10
2.00
2.01
6.08
7.28
7.25
7.21
7.19
6.89
6.86
6.86
6.84
4.44
4.33
3.80
3.79
3.53
3.51
3.49
1.35
1.33
1.31
1.27



15a

User15 3
PMBO
OPMB
159.14
158.86
131.75
130.67
129.31
128.85
113.79
113.75
74.26
72.69
66.41
63.37
55.29
55.28
39.80
26.19
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

SHIMADZU LabSolutions 分析报告



racemic **11a**

<样品信息>

样品名 : 1-benyichu-ceshi-adh
样品ID : 1-benyichu-ceshi-adh
数据文件名 : 1-benyichu-ceshi-adh004.lcd
方法文件名 : 50to50.lcm
批处理文件名 :
样品瓶号 : 1-1 样品类型 : 未知
进样体积 : 10 uL
分析日期 : 2014/5/16 12:22:50 分析者 : 张翼
处理日期 : 2014/5/16 13:10:09 处理者 : 张翼

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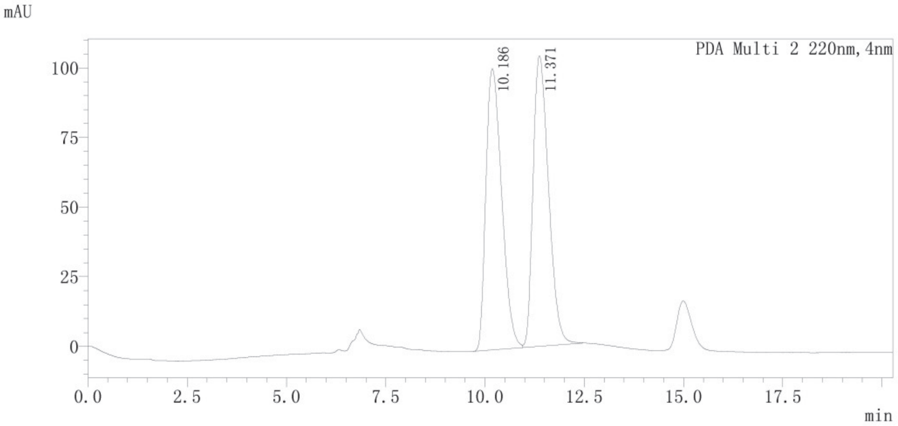
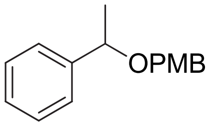


<峰表>

PDA Ch2 220nm

峰号	保留时间	面积	标记	面积%
1	10.186	2797764		49.710
2	11.371	2830360	V	50.290
总计		5628124		100.000

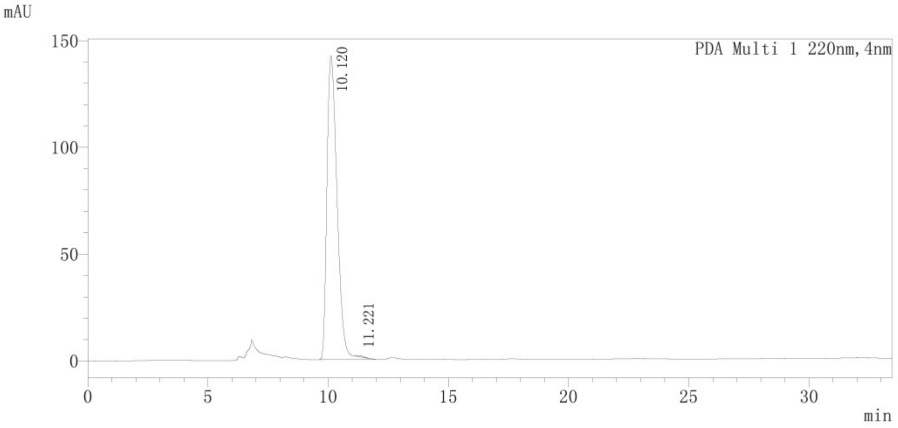
SHIMADZU LabSolutions 分析报告



<样品信息>

样品名	: 1-benyichu-ceshi-adh		
样品ID	: 1-benyichu-ceshi-adh		
数据文件名	: 1-benyichu-ceshi-adh005.lcd		
方法文件名	: 50to50.lcm		
批处理文件名	:		
样品瓶号	: 1-1	样品类型	: 未知
进样体积	: 10 uL		
分析日期	: 2014/5/16 12:44:35	分析者	: 张翼
处理日期	: 2014/5/16 13:23:24	处理者	: 张翼

<色谱图>



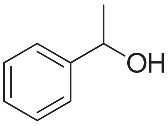
<峰表>

PDA Ch1 220nm

峰号	保留时间	面积	面积%
1	10.120	4159934	99.778
2	11.221	9270	0.222
总计		4169204	100.000

SHIMADZU LabSolutions

分析报告

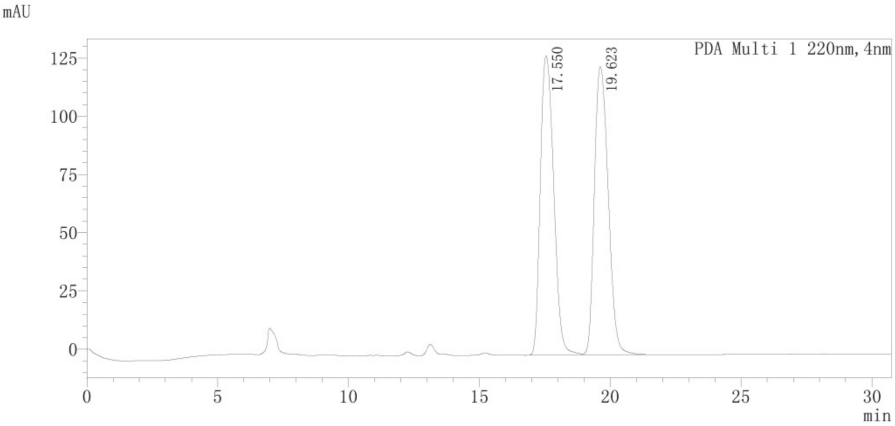


racemic **11b**

〈样品信息〉

样品名 : lz-04-05-xiaoxuan
样品ID :
数据文件名 : lz-04-05-xiaoxuan.lcd
方法文件名 : 50to50.lcm
批处理文件名 :
样品瓶号 : 1-1 样品类型 : 未知
进样体积 : 10 uL
分析日期 : 2014/6/7 14:30:22 分析者 : 张翼
处理日期 : 2014/6/7 15:01:09 处理者 : 张翼

〈色谱图〉



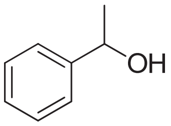
〈峰表〉

PDA Ch1 220nm

峰号	保留时间	面积	面积%
1	17.550	4565873	50.084
2	19.623	4550556	49.916
总计		9116429	100.000

SHIMADZU LabSolutions

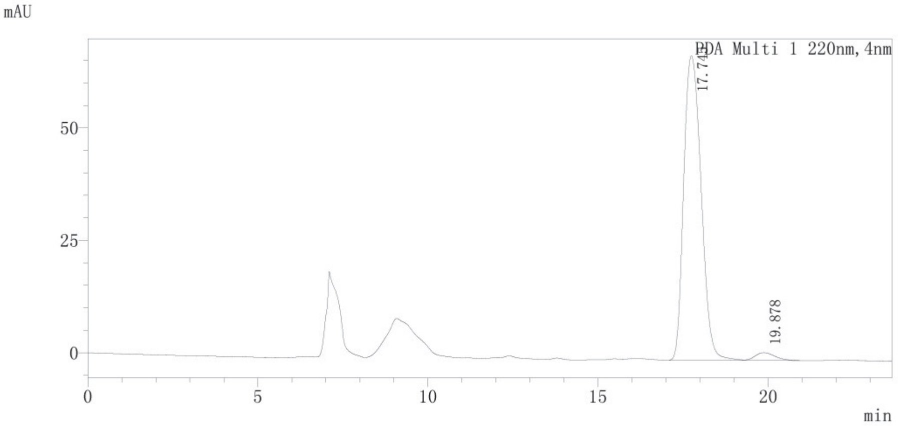
分析报告



〈样品信息〉

样品名 : lz-04-05-GUANGXUE
样品ID :
数据文件名 : lz-04-05-GUANGXUE001.lcd
方法文件名 : 50to50.lcm
批处理文件名 :
样品瓶号 : 1-1 样品类型 : 未知
进样体积 : 10 uL
分析日期 : 2014/6/7 15:31:54 分析者 : 张翼
处理日期 : 2014/6/7 15:55:35 处理者 : 张翼

〈色谱图〉



〈峰表〉

PDA Ch1 220nm

峰号	保留时间	面积	面积%
1	17.745	2411724	97.144
2	19.878	70898	2.856
总计		2482622	100.000