Facilitated Photochemical Cleavage of Benzylic C-O Bond. Application to photolabile Hydroxyl-Protecting Group Design.

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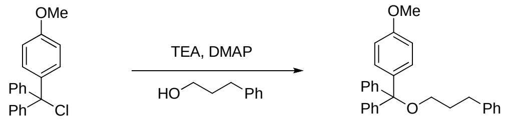
SUPPORTING MATERIALS

Contents

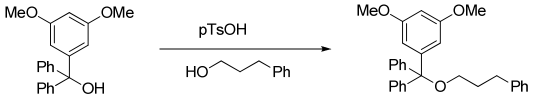
General Procedures. Organic solutions were concentrated by rotary evaporation at *ca*. 12 Torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Solvents were distilled from appropriate drying reagents under a nitrogen atmosphere at 760 torr. Other chemicals were obtained from commercial vendors and used without further purification.

Instrumentation. Infrared (IR) data are presented as frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^{1}H NMR or ^{13}C NMR) spectra were recorded on a 300 MHz and a 400 MHz NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration. UV absorpance was measured with 2x10^{-5} M solution in 1 cm cuvette.



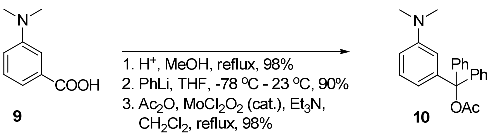
6

Preparation of **6**. 3-phenyl-1-propanol (67 μL, 0.5 mmol), triethylamine (348 μL, 2.5 mmol) and 4-dimethylaminopyridine (4 mg, 0.025 mmol) were added to 2.5 mL of dichloromethane and stirred for 10 min, followed by *p*-anisylchlorodiphenylmethane (191 mg, 0.6 mmol). The reaction mixture was stirred at room temperature under argon protection for 5 h. The solvent was removed and the residue was purified with column chromatography (eluted with hexane/ethyl acetate 6:1) to provide **6** (185.6 mg, 90%). Rf 0.5 (hexane/ethyl acetate 6:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.3 Hz, 4 H), 7.38-7.07 (m, 10 H), 6.82 (d, *J* = 8.8 Hz, 2 H), 3.78 (s, 1 H), 3.10 (t, *J* = 6.2 Hz, 2 H), 2.72 (t, *J* = 7.8 Hz, 2 H), 1.92 (m, *J* = 7.0 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 144.8, 142.2, 130.3, 128.4, 128.2, 127.7, 126.7, 125.6, 112.9, 86.0, 62.6, 55.2, 32.6, 31.8; FTIR (neat film) 3059, 3025, 2932, 2867, 2835, 1607, 1509, 1448, 1299, 1250, 1180, 1070, 1033, 830, 747, 727 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{29}H_{27}O_2$ (M-H) 407.2011, found 407.2021.



7

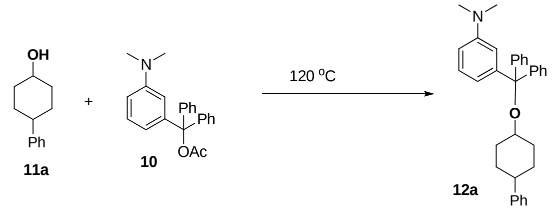
Preparation of **7**. (3,5-dimethoxyphenyl)diphenylmethanol (64 mg, 0.2 mmol), 3-phenyl-1-propanol (107 μL, 0.8 mmol) and a catalytic amount of *p*-toluenesulfonic acid (4 mg, 0.02 mmol) were stirred in 0.5 mL of benzene at room temperature for 40 h. The reaction solution was concentrated and purified with column chromatography (petroleum ether/ethyl acetate 5:1) to provide the desired ether **7** (55 mg, 62%). Rf 0.53 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.1 Hz, 4 H), 7.28 (t, *J* = 7.3 Hz, 4 H), 7.22 (t, *J* = 6.2 Hz, 4 H), 7.14 (t, *J* = 7.5 Hz, 3 H), 6.66 (d, *J* = 2.3 Hz, 2 H), 6.33 (t, *J* = 2.3 Hz, 1 H), 3.71 (s, 6 H), 3.12 (t, *J* = 6.3 Hz, 2 H), 2.73 (t, *J* = 7.9 Hz, 2 H), 1.92 (m, *J* = 7.1 Hz, 2 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.1, 147.1, 143.9, 142.1, 128.8, 128.4, 128.2, 127.6, 126.9, 125.6, 107.0, 98.3, 86.4, 62.9, 55.2, 32.6, 31.8; FTIR (neat film) 3059, 3025, 2936, 2870, 2834, 1595, 1455, 1423, 1308, 1289, 1204, 1155, 1067, 840, 745, 706 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{33}H_{40}NO_3Na$ (M+Na) 461.2093, found 461.2085.



Preparation of **10**. To a solution of 3-dimethylaminobenzoic acid (4.9557 g, 30 mmol) in methanol (50 mL), sulphuric acid (4.8 mL, 90mmol) was added dropwise. The reaction mixture was refluxed at 80 °C for 40 h. The solvent was then removed and the reaction mixture was neutralized with saturated sodium bicarbonate until pH = 7, followed by washing with brine. The product was extracted with dichloromethane and the organic layers were combined and dried over anhydrous sodium sulfate. The solvent was removed and methyl 3-(dimethylamino)benzoate (5.371 g, 99.9%) was obtained as a light yellow oil.

To a solution of 3-(dimethylamino)benzoate (3.5844g, 20 mmol) in freshly distilled tetrahydrofuran (10 mL), phenyllithium (30 mL, 60 mmol, 2.0M solution in dibutylether) was slowly added at -78 °C under argon protection. The reaction temperature was raised from -78 °C to room temperature over 5.5 h. The reaction was then quenched with saturated ammonium chloride until pH = 7. The aqueous layer was extracted with dichloromethane and the organic layers were combined and the solvent was removed. The residue was dissolved in ethyl acetate to crystallize and 3-dimethylaminotrityl alcohol (5.8872 g, 97%) was obtained as the white or pale yellow crystals.

3-Dimethylaminotrityl alcohol (0.825 g, 2.72 mmol) was dissolved in freshly distilled toluene (3 mL), followed by adding molybdenum(VI) dichloride dioxide (5.4 mg, 0.03 mmol), acetic anhydride (383 μL, 4.08 mmol) and triethylamine (379 μL, 2.72 mmol). The reaction mixture was heated at 120°C under argon protection for 6 h. Then solvent was removed and the residue was washed with petroleum ether. The organic layer was combined and the solvent was removed to afford light yellow oil. The oil was pumped dried by vacuum in a 75°C oil bath to obtain the light yellow solid **10** (0.922 g, 98%). ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.39 (d, J = 8.2 Hz, 4 H), 7.32-7.18 (m, 6 H), 7.14 (t, J = 8.0 Hz, 4 H), 6.76 (t, J = 2.0 Hz, 1 H), 6.65 (d, J = 7.9 Hz, 1 H), 6.62 (dd, J = 8.2, 2.5 Hz, 1 H), 2.86 (s, 6 H), 2.16 (s, 3 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 168.7, 150.0, 144.2, 143.5, 128.5, 128.3, 127.5, 127.1, 117.0, 113.2, 111.5, 90.3, 40.6, 22.6; FTIR (neat film) 3055, 2987, 2807, 2306, 1715, 1600, 1494, 1446, 1266, 1017, 744, 704 cm^{-1}; HRMS (FAB) m/z: calculated mass for $C_{23}H_{23}NO_2$ 345.1729, measured mass 345.1740.



Representative procedure of installing the PPG DMATr (Synthesis of **12a**): In a reaction vessel, 4-phenylcylcohexanol (**11a**) (18 mg, 0.1 mmol) and PPG reagent **10** (69 mg, 0.2 mmol) in 0.2 mL of toluene were heated in a 120 °C oil bath under argon protection. Toluene was evaporated under vacuum and the residue was sealed under argon and heated until the reaction completed (*ca*. 6.5 h). The reaction mixture was directly purified with column chromatography (eluted with petroleum ether/ethyl acetate 9:1) to provide **12a** (43 mg, 92%). Rf 0.6 (petroleum ether/ethyl acetate 9:1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.57 (d, J = 7.1 Hz, 4 H), 7.33-7.03 (m, 12 H), 7.00 (s, 1 H), 6.87 (d, J = 7.8 Hz, 1 H), 6.62 (dd, J = 8.2, 2.5Hz, 1 H), 3.51 (m, J = 4.8 Hz, 1 H), 2.88 (s, 6 H), 2.40 (tt, J = 11.9, 3.4 Hz, 1 H), 1.70 (d, J = 13.5 Hz, 2 H), 1.50-1.30 (m, 4 H), 1.21 (qd, J = 12.4, 4.2 Hz, 2 H); ^{13}C NMR (75 MHz, CDCl$_3$) δ 150.2, 146.9, 146.0, 145.9 ,129.1, 128.2, 128.1, 127.5, 126.72, 126.68, 125.8, 118.2, 113.9, 111.2, 86.9, 72.9, 43.6, 40.8, 34.4, 33.0; FTIR (neat film) 2932, 2360, 2341, 2254, 1601, 1493, 1384, 1061, 909, 735, 651 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{33}H_{36}NO$ (M+H) 462.2797, found 462.2784.

Experimental Details of PPG Installation

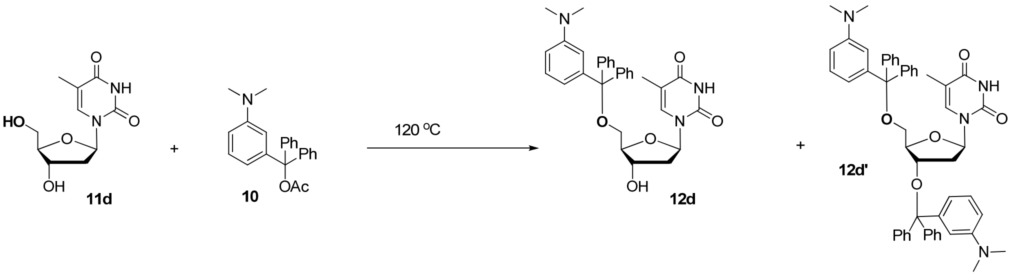
entry	Alcohol (mmol)	**10** (mmol)	Reaction conditions	product	Yield
1	3-phenyl-1-propanol (0.4)	0.6	2 h at 120 °C in neat	**8**	158 mg, 94%
2	**11a** (0.1)	0.2	6.5 h at 120 °C in 0.2 mL toluene (unsealed, solvent evaporated over heating)	**12a**	43 mg, 92%
3	**11b** (0.1)	0.15	5.5 h at 120 °C in 0.1 mL toluene	**12b**	70 mg, 93%
5	**11c** (0.2)	0.6	21 h at 120 °C in 0.2 mL toluene (unsealed, solvent evaporated over heating)	**12c**	83 mg, 83%
6	**11d** (0.1)	0.3	0.25 mL toluene, 120 °C The reaction was cooled as soon as a clear solution was obtained.	**12d**	42 mg, 79%[a]

[a] The di-protected product (*i.e.* both the primary and secondary hydroxyl groups were protected by the PPG) was isolated in 18% yield.

Spectroscopic data of **8**. Rf 0.3 (petroleum ether/ethyl acetate 25:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.2 Hz, 4 H), 7.33-7.06 (m, 12 H), 6.93 (t, *J* = 2.0 Hz, 1 H), 6.77 (d, *J* = 7.8 Hz, 1 H), 6.61 (dd, *J* = 8.1, 2.5 Hz, 1 H), 3.14 (t, *J* = 6.3 Hz, 2 H), 2.87 (s, 6 H), 2.73 (t, *J* =7.9 Hz, 2 H), 1.92 (m, *J* =7.1 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.2, 145.0, 144.7, 142.3, 129.5, 128.8, 128.4, 128.2, 127.5, 126.7, 125.6, 117.8, 113.4, 111.1, 86.6, 62.9, 40.7, 32.7, 32.0; FTIR (neat film) 3025, 2928, 1600, 1495, 1447, 1350, 1276, 1218, 1068, 913, 748, 705 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{30}H_{32}NO$ (M+H) 422.2484, found 422.2475.

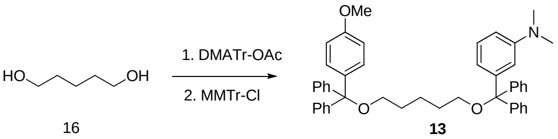
Spectroscopic data of **12b**. Rf 0.8 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.7 Hz, 2 H), 7.59-7.09 (m, 22 H), 7.05 (s, 1 H), 6.85 (dd, *J* = 7.7, 1.5 Hz, 2 H), 6.76 (d, *J* = 7.8Hz, 1 H), 6.59 (dd, *J* = 8.3, 2.0 Hz, 1 H), 4.94 ($\underline{A}B^1$, *J* = 10.7 Hz, 1 H), 4.85 ($\underline{A}B^2$, *J* = 12.1 Hz, 1 H), 4.81 ($A\underline{B}^1$, *J* = 10.7 Hz, 1 H), 4.72 ($A\underline{B}^2$, *J* = 12.1 Hz, 1 H), 4.67 (d, *J* = 3.6 Hz, 1 H), 4.66 ($\underline{A}B^3$, *J* = 10.2 Hz, 1 H), 4.72 ($A\underline{B}^3$, *J* = 10.3 Hz, 1 H), 3.96 (t, *J* = 9.3 Hz, 1 H), 3.80 (dd, *J* = 10.0 Hz, 1 H) 3.68 (t, *J* = 9.5 Hz, 1 H), 3.62 (dd, *J* = 9.6, 3.6 Hz, 1 H), 3.56 (dd, *J* = 10.1, 1.5 Hz, 1 H) 3.41 (s, 3 H), 3.23 (dd, *J* = 5.0, 4.4 Hz, 1 H), 2.83 (s, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.2, 144.8, 144.1, 143.8, 138.7, 138.3, 137.9, 129.2, 128.9, 128.43, 128.40, 128.2, 128.12, 128.09, 128.04, 127.8, 127.6, 126.9, 126.6, 117.9, 113.2, 111.0, 97.9, 86.4, 82.2, 80.2, 78.1, 75.9, 73.4, 70.3, 62.4, 54.9, 40.5, 29.7; FTIR (neat film) 3062, 3031, 2925, 1601, 1497, 1453, 1356, 1072, 738, 697 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{49}H_{52}NO_6$ (M+H) 750.3795, found 750.3807.

Spectroscopic data of **12c**. Rf 0.6 (petroleum ether/ethyl acetate 3:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (t, *J* = 6.1 Hz, 4 H), 7.36-7.17 (m, 6 H), 7.13 (t, *J* = 8.0 Hz, 1 H), 6.93 (s, 1 H), 6.77 (d, *J* = 7.8 Hz, 1 H), 6.61 (dd, *J* = 7.7, 2.3 Hz, 1 H), 5.97 (m, *J* = 5.7 Hz, 1 H), 5.35 (dd, *J* = 18.8, 1.6 Hz, 1 H), 5.23 (dd, *J* = 10.4, 1.7 Hz, 1 H), 4.75 (d, *J* = 1.3 Hz, 1 H), 4.24 (dd, *J* = 12.9, 5.2 Hz, 1 H), 4.13-3.98 (m, 3 H), 3.92 (m, *J* = 6.1 Hz, 1 H), 3.49 (dd, *J* = 3.8, 5.5 Hz, 1 H), 2.87 (s, 6 H), 1.22 (s, 3 H), 1.08 (s, 3 H), 1.01 (d, *J* = 6.7 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.1, 145.2, 144.8, 134.1, 129.4, 127.5, 126.9, 118.4, 117.5, 114.2, 111.3, 108.4, 96.8, 88.2, 74.6, 73.2, 68.5, 68.3, 40.7, 29.7, 27.1, 25.4, 19.0; FTIR (neat film) 3058, 2983, 1601, 1494, 1219, 1073, 1024, 748cm^{-1}; HRMS (ESI) m/z: calcd for $C_{33}H_{40}NO_5$ (M+H) 530.2906, found 530.2911.



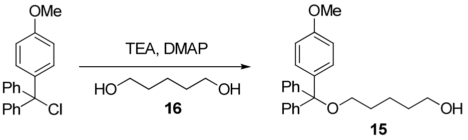
Spectroscopic data of **12d**. Rf 0.4 (petroleum ether/ethyl acetate 1:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1 H), 7.62 (s, 1 H), 7.43 (d, *J* = 13.4 Hz, 2 H), 7.42 (d, *J* = 13.3 Hz, 2 H), 7.34-7.22 (m, 6 H), 7.17 (t, *J* = 8.0 Hz, 1 H), 6.79 (s, 1 H), 6.72 (d, *J* = 7.8 Hz, 1 H), 6.65 (dd, *J* = 8.3, 2.5 Hz, 1 H), 6.42 (t, *J* = 6.8 Hz, 1 H), 4.60 (m, *J* = 2.3 Hz, 1 H), 4.04 (d, *J* = 2.8 Hz, 1 H), 3.53 ($\underline{A}B^1$, *J* = 10.6, 3.1 Hz, 1 H), 3.41 ($A\underline{B}^1$, *J* = 10.6, 2.7 Hz, 1 H), 2.84 (s, 6H), 2.40 ($\underline{A}B^2$, *J* = 13.7, 3.1 Hz, 1 H), 2.36 ($A\underline{B}^2$, *J* = 13.6, 6.7 Hz, 1 H), 1.44 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 150.6, 150.2, 143.8, 143.6, 143.4, 135.8, 128.7, 128.5, 127.8, 127.2, 117.6, 113.3, 111.6, 111.3, 87.7, 86.3, 84.6, 72.4, 63.7, 40.6, 11.7; FTIR (neat film) 3437, 2090, 1685, 1601, 1491, 1447, 1352, 1272, 1093, 1059, 1001, 961, 736, 703 cm^{-1}; HRMS (ESI) m/z: $C_{31}H_{34}N_3O_5$ (M+H) 528.2498, found 528.2484.

Spectroscopic data of **12d'**. Rf 0.5 (petroleum ether/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s, 1 H), 7.53 (s, 1 H), 7.40-7.28 (m, 4 H), 7.25-7.05 (m, 14 H), 7.00 (t, *J* = 8.0 Hz, 2 H), 6.72 (s, 1 H), 6.63 (d, *J* = 7.8 Hz, 1 H), 6.59 (s, 1 H), 6.53 (dd, *J* = 8.2, 1.8 Hz, 1 H), 6.49 (d, *J* = 8.0 Hz, 1 H), 6.44 (dd, *J* = 5.8, 9.0 Hz, 1 H), 4.45 (d, *J* = 4.9 Hz, 1 H), 3.77 (s, *J* = 2.8 Hz, 1 H), 3.16 ($\underline{A}B^1$, *J* = 10.5, 2.1 Hz, 1 H), 2.77 (A$\underline{\mathrm{B}}^1$, J = 2.0 Hz, 1 H), 2.75 (s, 6H), 2.70 (s, 6H), 2.00-1.85 (m, 2H), 1.22 (s, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.8, 150.3, 150.1, 144.6, 144.4, 144.1, 143.8, 143.1, 136.0, 128.9, 128.8, 128.5, 128.4, 127.85, 127.79, 127.77, 127.7, 127.2, 127.1, 127.0, 117.5, 113.2, 111.4, 111.1, 88.0, 87.6, 85.5, 84.8, 75.4, 63.8, 40.5, 39.7, 11.5; FTIR (neat film) 3059, 2806, 1689, 1600, 1495, 1433, 1353, 1271, 1031, 736, 708 cm^{-1}; HRMS (ESI) m/z: $C_{52}H_{53}N_4O_5$ (M+H) 813.4016, found 813.3996.



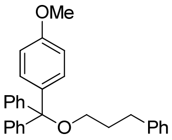
Preparation of **13**. The PPG reagent (**10**) (345.4 mg, 1.0 mmol), 1,5-pentanediol (0.44 mL, 4.0 mmol) were added to 0.2 mL of toluene. The reaction mixture was heated in a 120 °C oil bath under argon protection for 1.5 h. The reaction mixture was purified with column chromatography (eluted with petroleum ether/ethyl acetate 3:1) to provide the DMATr protected diol **14** (5-((3-(dimethylamino) phenyl)diphenylmethoxy)pentan-1-ol, 315 mg, 81%).

To the solution of **14** (195 mg, 0.5 mmol) in dichloromethane (2.5 mL), 4-dimethylaminopyridine (3 mg, 0.025 mmol) triethylamine (0.35 mL, 2.5 mmol) was added and the solution was stirred for 10 min, followed by *p*-anisylchlorodiphenylmethane (191 mg, 0.6 mmol). The reaction mixture was then stirred at room temperature with argon protection for 5 h. The solvent was removed and the residue was purified with column chromatography (eluted with petroleum ether/ethyl acetate 9:1) to provide **13** (285 mg, 86%). Rf 0.3 (petroleum ether/ethyl acetate 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (t, J = 7.9 Hz, 8 H), 7.34-7.09 (m, 15 H), 6.88 (s, 1 H), 6.80 (d, J = 7.0 Hz, 2 H), 6.76 (d, J = 7.4 Hz, 1 H), 6.60 (dd, J = 8.1, 2.2 Hz, 1 H), 3.77 (s, 3 H), 3.04 (m, J = 6.2 Hz, 4 H), 2.85 (s, 6 H), 1.70-1.38 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 150.1, 145.0, 144.8, 136.3, 130.3, 128.84, 128.77, 128.5, 128.3, 128.2, 127.9, 127.7, 127.5, 126.6, 117.8, 113.5, 113.0, 111.1, 86.6, 86.0, 63.6, 63.5, 55.2, 40.7, 30.1, 30.0, 23.3; FTIR (neat film) 3057, 2934, 2867, 1600, 1510, 1492, 1447, 1250, 1180, 1072, 1033, 706 cm^{-1}; HRMS (ESI) m/z: calcd for $C_{46}H_{48}NO_3$ (M+H) 622.3634, found 622.3630.



Preparation of **15**. 1,5-Pentanediol (0.65 mL, 6.0 mmol), triethylamine (0.94 mL, 6.75 mmol) and 4-dimethylaminopyridine (12.2 mg, 0.15 mmol) were added to 7.5 mL of dichloromethane and stirred for 15 min, followed by *p*-anisylchlorodiphenylmethane (477.5 mg, 1.5 mmol). The reaction mixture was stirred at room temperature under argon protection for 4.5 h. The solvent was then removed and the residue was purified with column chromatography (eluted with petroleum ether/ethyl acetate 2:1) to provide **15** (455 mg, 78%). Rf 0.4 (petroleum ether/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 10.4 Hz, 4 H), 7.35-7.16 (m, 8 H), 6.82 (d, J = 9.6 Hz, 2 H), 3.78 (s, 1 H), 3.60 (t, J = 6.5 Hz, 2 H), 3.05 (t, J = 6.6 Hz, 2 H), 1.64 (m, J = 7.0 Hz, 2 H), 1.53 (m, J = 6.8 Hz, 2 H), 1.49-1.37 (m, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 144.8, 136.1, 130.2, 128.3, 127.7, 126.6, 112.9, 85.9, 63.3, 62.8, 55.1, 32.5, 29.8, 22.4; FTIR (neat film) 3361, 3057, 2936, 2866, 1608, 1510, 1251, 1069, 1034, 707cm^{-1}; HRMS (ESI) m/z: calcd for $C_{25}H_{28}O_3Na$ (M+Na) 399.1936, found 399.1936.

Representative procedure of photochemical removal of the PPG DMATr: The DMATr protected 4-phenylcyclohexanol (**12a**) (58 mg, 0.125 mmol) in 500 mL of methanol was irradiated with a 450 W medium-pressure mercury lamp equipped with a Pyrex filter sleeve in a Honovia reactor for 15 min without deaeration. The reaction mixture was then concentrated and purified with column chromatography (eluted with petroleum ether/ethyl acetate 3:1) to provide **11a** (19.3 mg, 87%). Photoreactions were also carried out in 5 mM concentration in 10 mL Pyrex test tube(s).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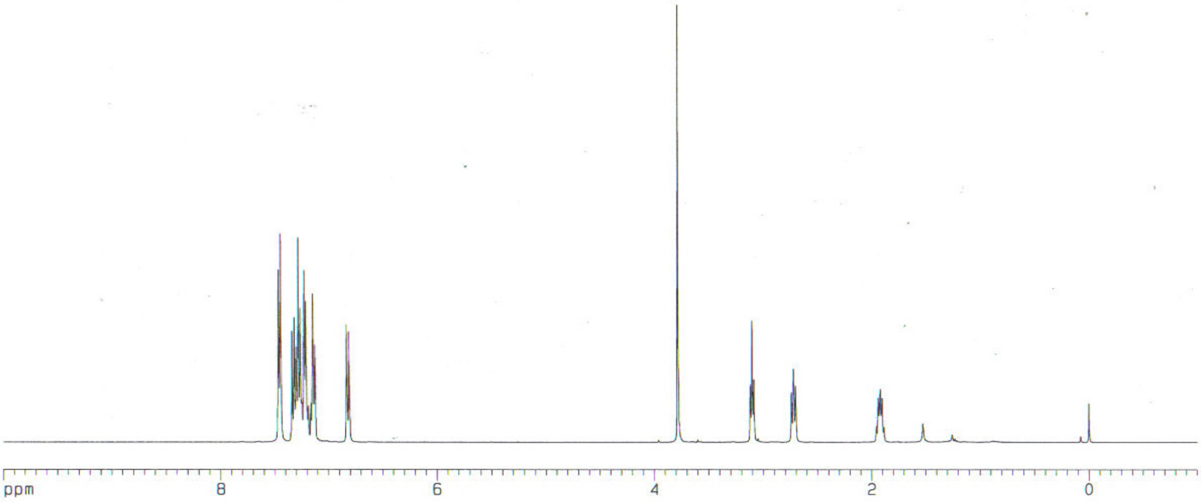
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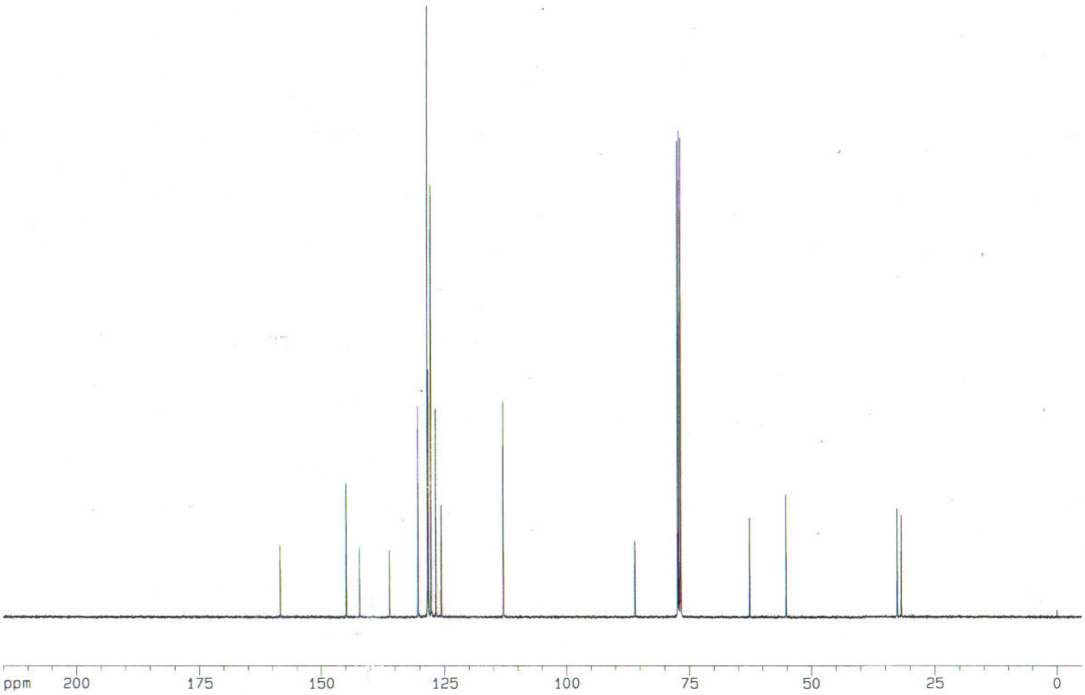
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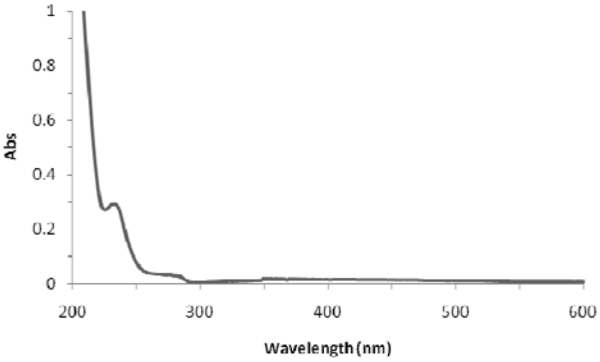
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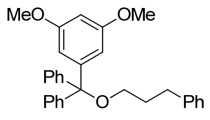
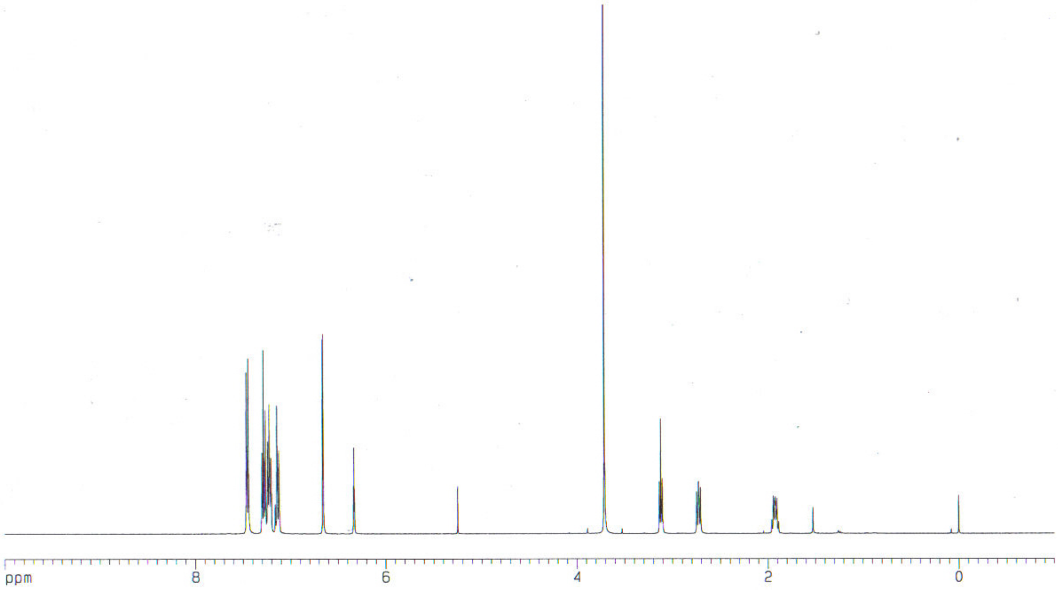
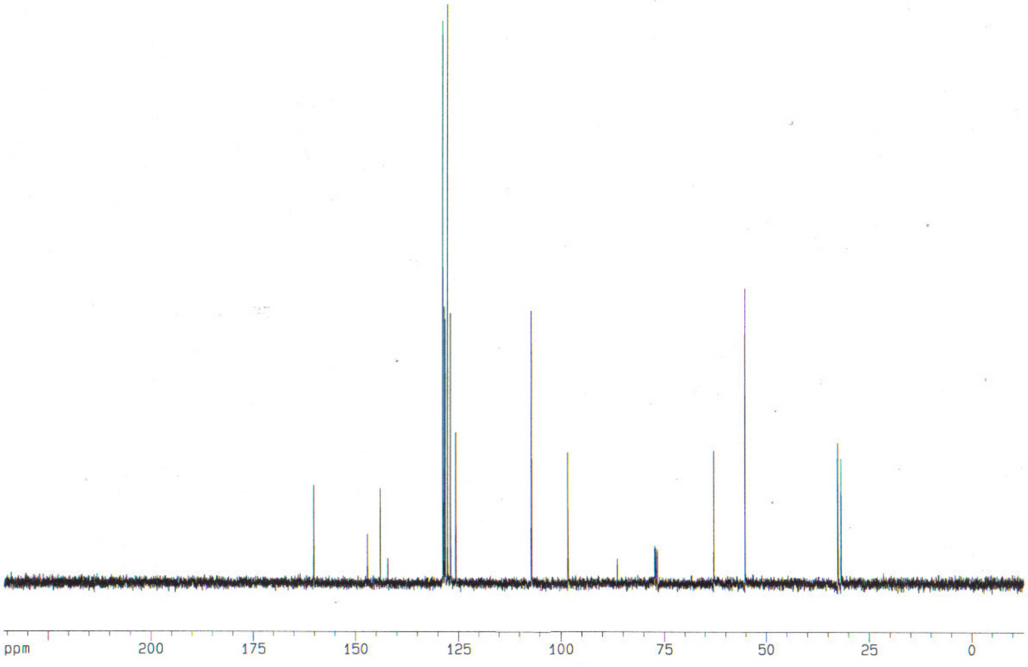
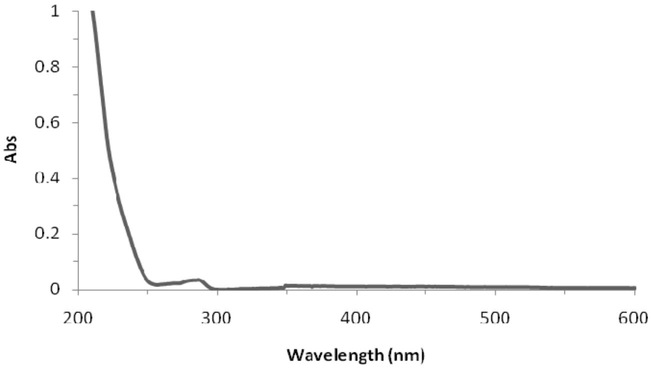
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength (nm)

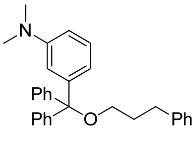

MeO
OMe
Ph
Ph
O
Ph

7

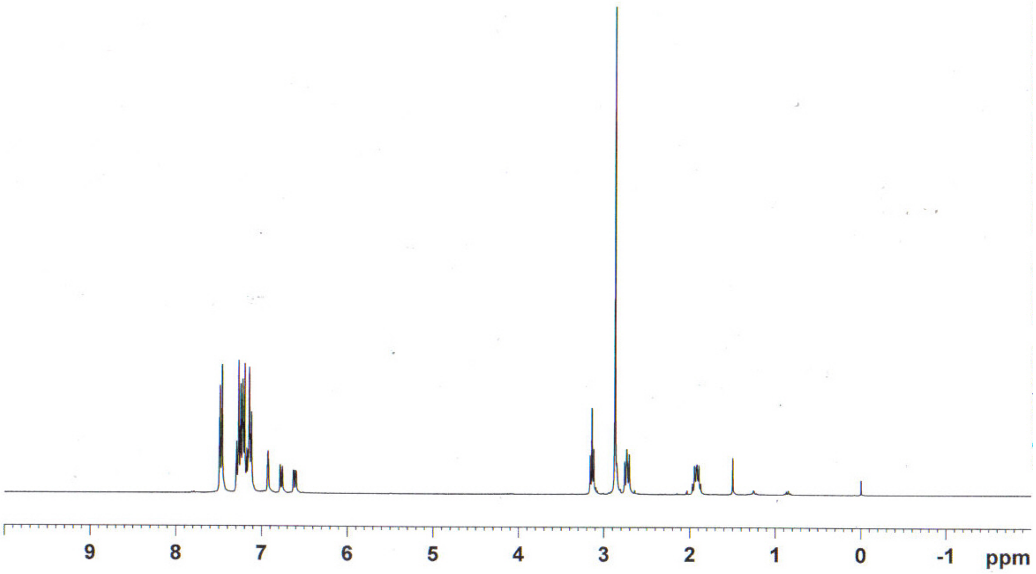

ppm
8
6
4
2
0

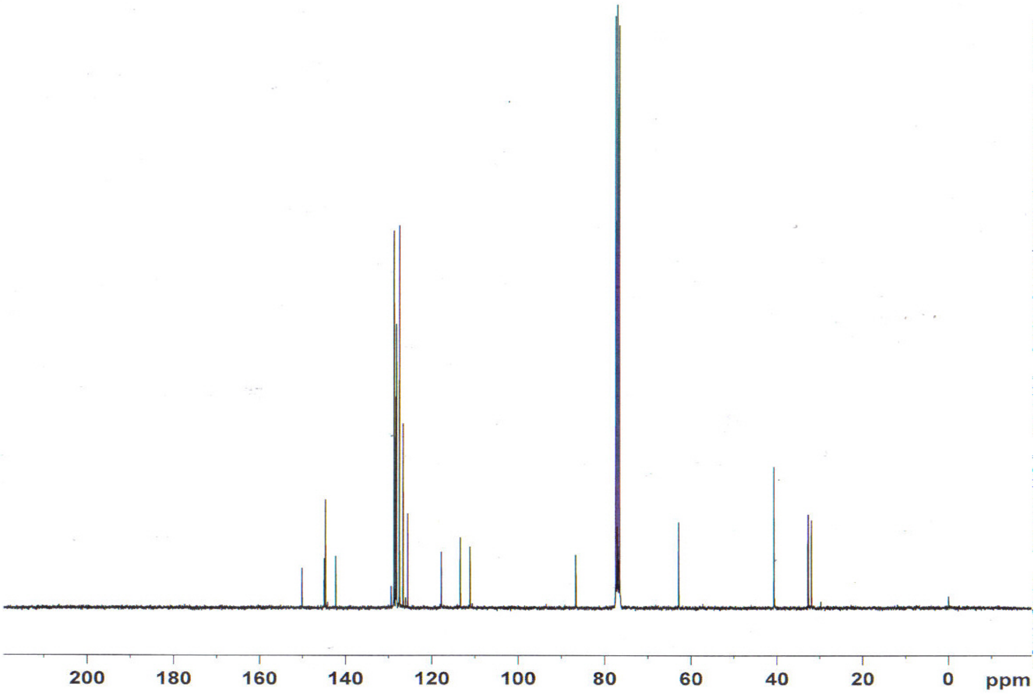

ppm
200
175
150
125
100
75
50
25
0

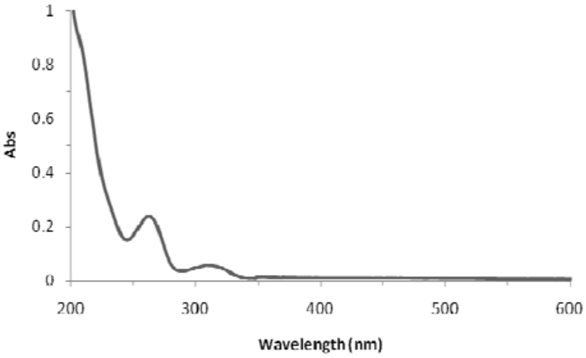

1
0.8
0.6
0.4
0.2
0
Abs
200
300
400
500
600
Wavelength (nm)

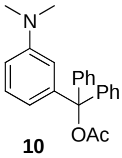

N
Ph
Ph
O
Ph

8

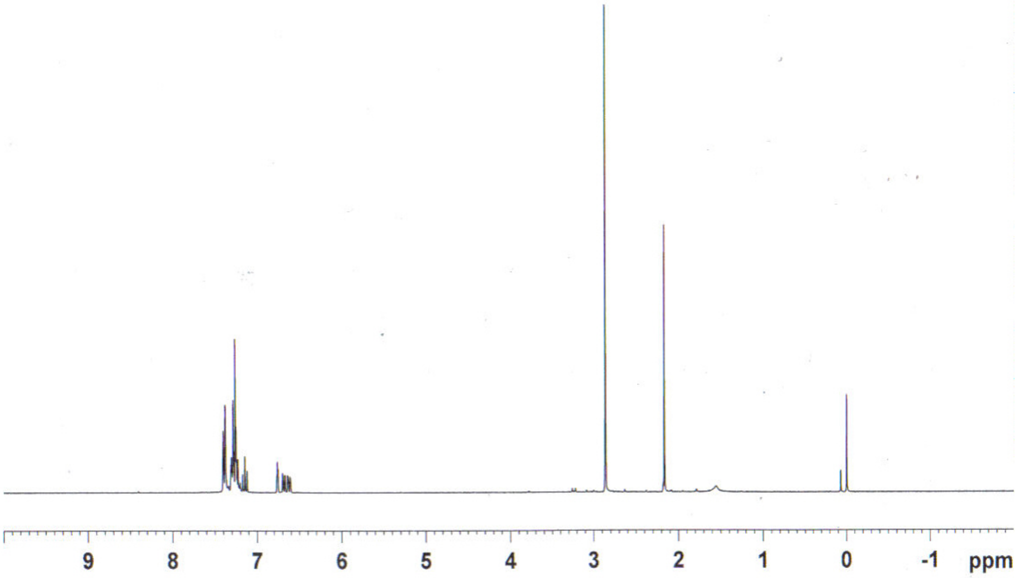

9
8
7
6
5
4
3
2
1
0
-1
ppm

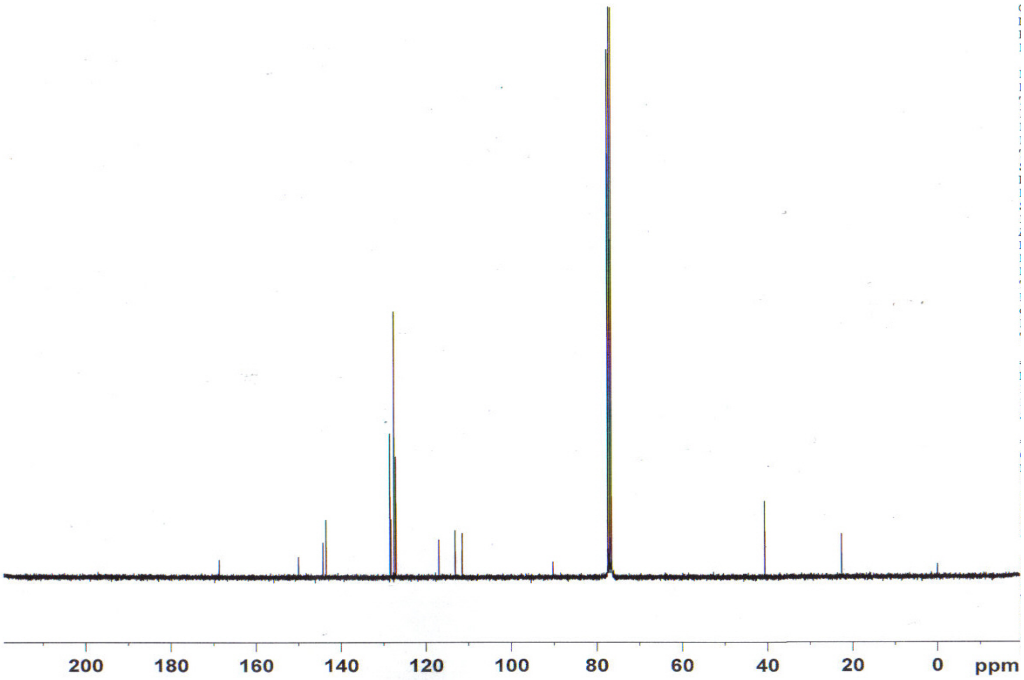

200
180
160
140
120
100
80
60
40
20
0
ppm

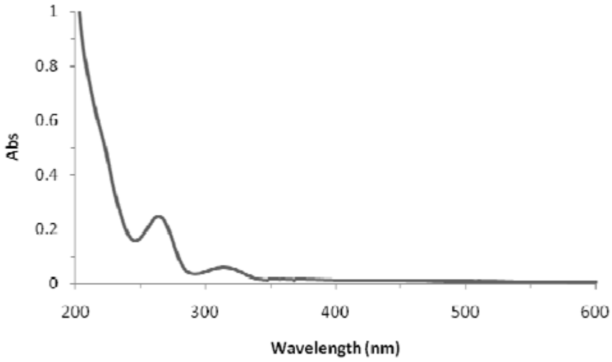

1
0.8
0.6
0.4
0.2
0
Abs
200
300
400
500
600
Wavelength (nm)

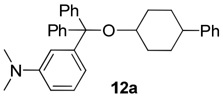

N
Ph
Ph
OAc

10

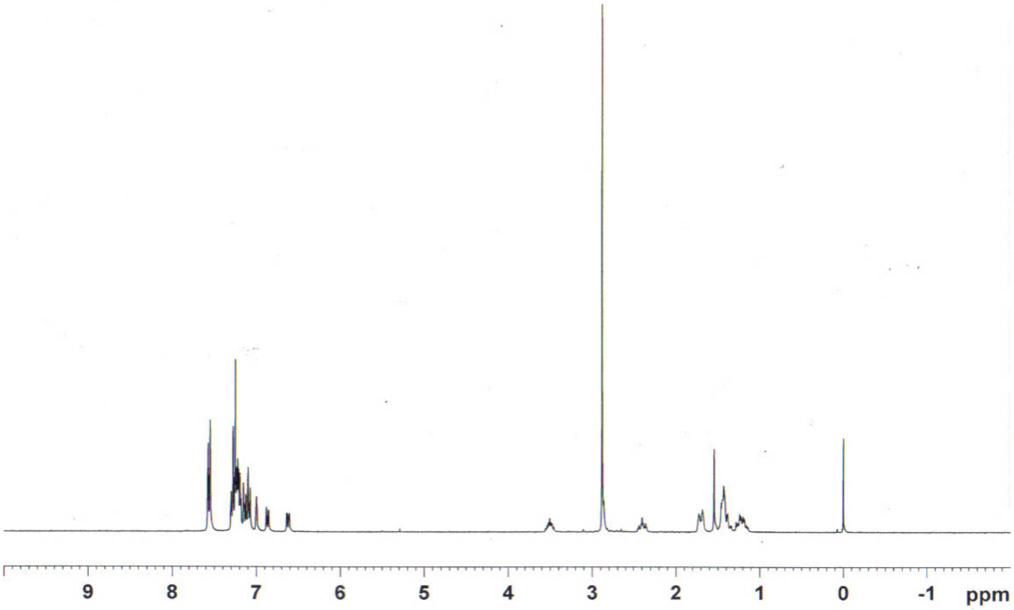

9
8
7
6
5
4
3
2
1
0
-1
ppm

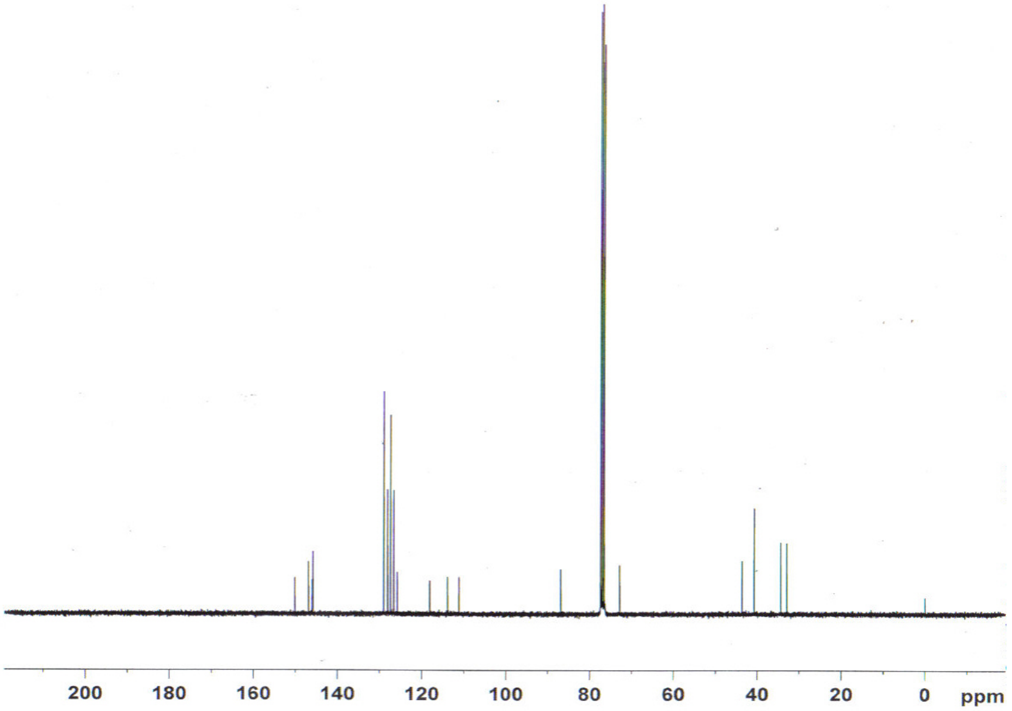

200
180
160
140
120
100
80
60
40
20
0
ppm

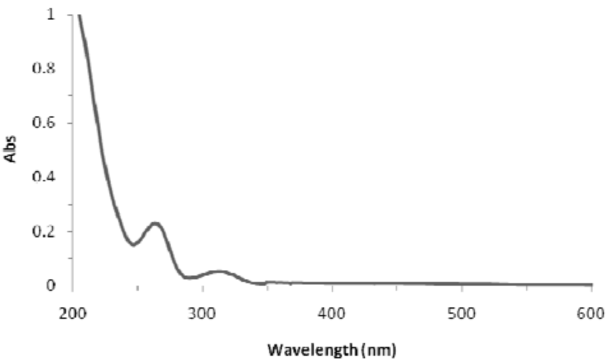

1
0.8
0.6
0.4
0.2
0
Abs
200
300
400
500
600
Wavelength (nm)

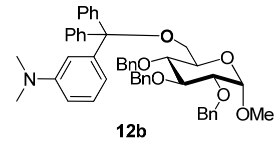

Ph
Ph
O
Ph
N

12a

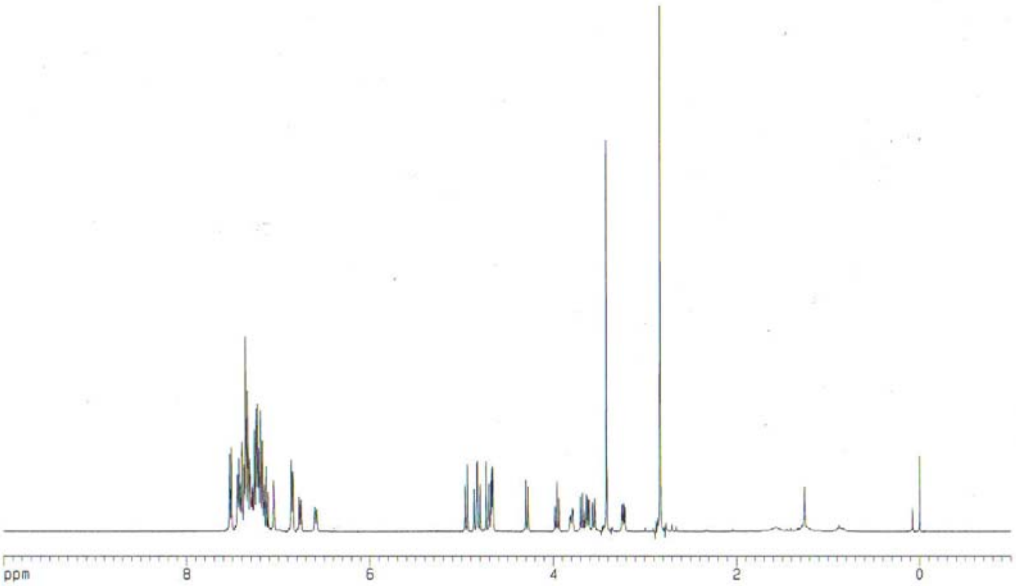

9
8
7
6
5
4
3
2
1
0
-1
ppm

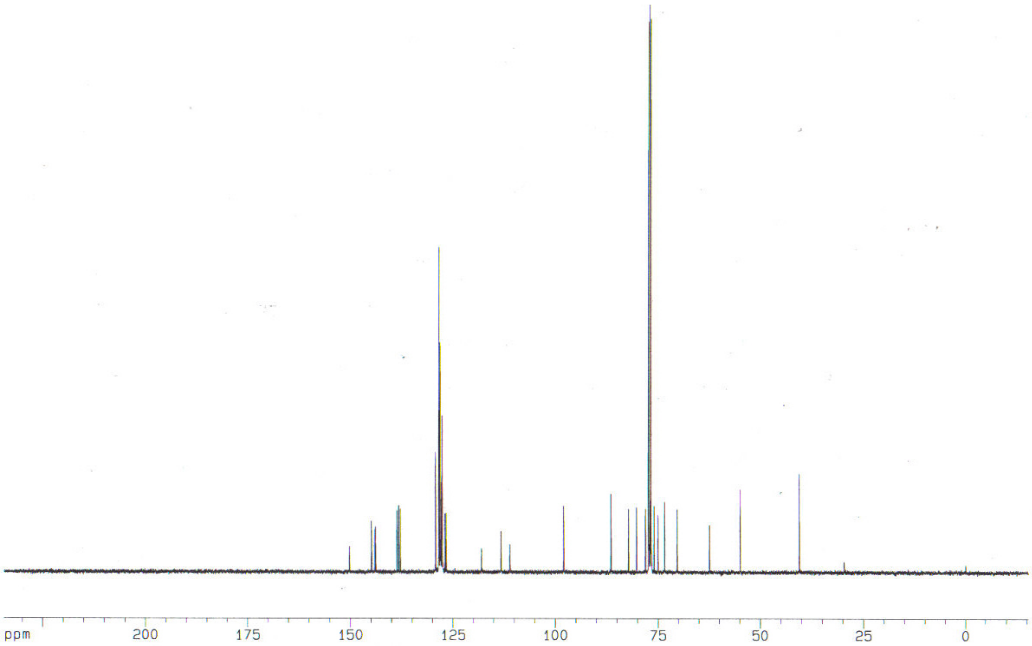

200
180
160
140
120
100
80
60
40
20
0
ppm

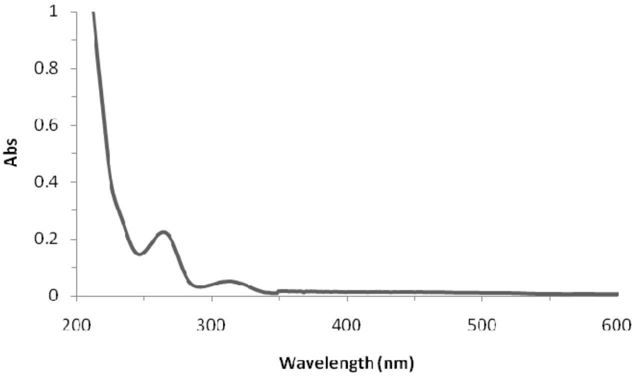

Abs
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength (nm)

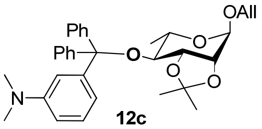

Ph
Ph
O
N
BnO
BnO
O
O
Bn
OMe

12b

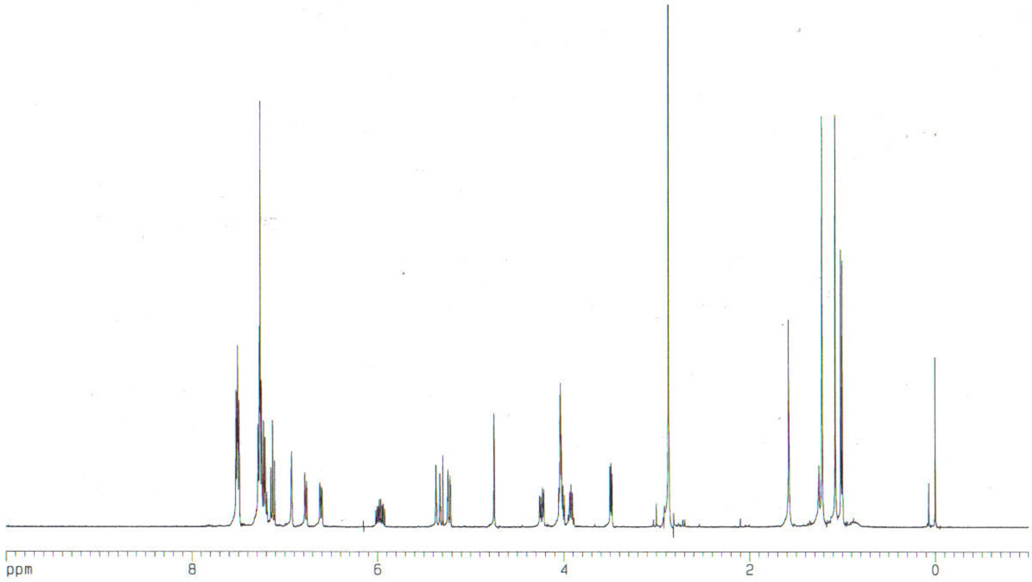

ppm
8
6
4
2
0

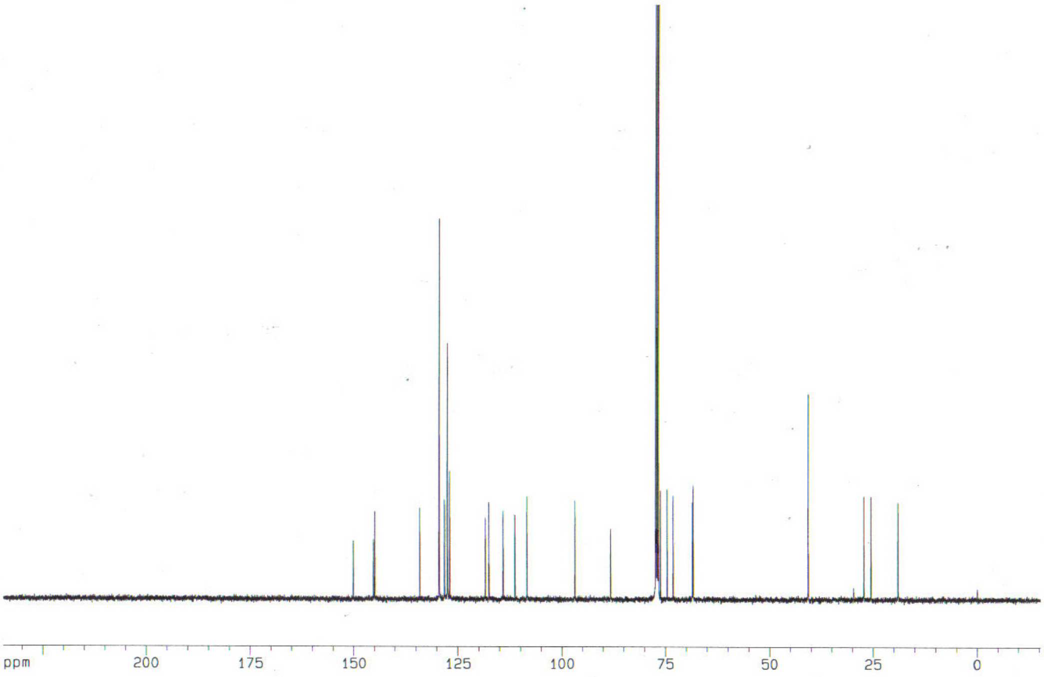

ppm
200
175
150
125
100
75
50
25
0

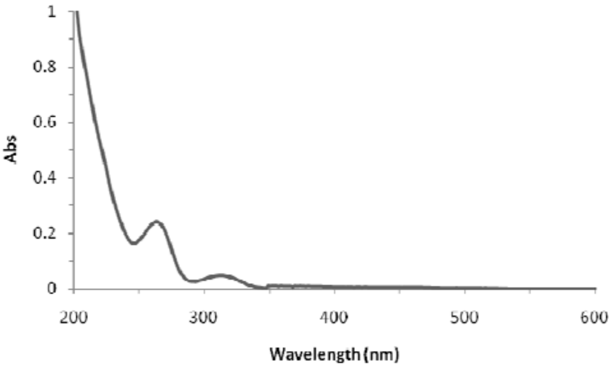

Abs
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength (nm)

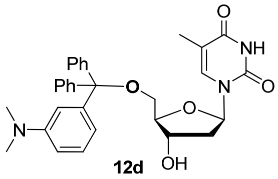

OAll
Ph
Ph
O
N
O
O
O

12c

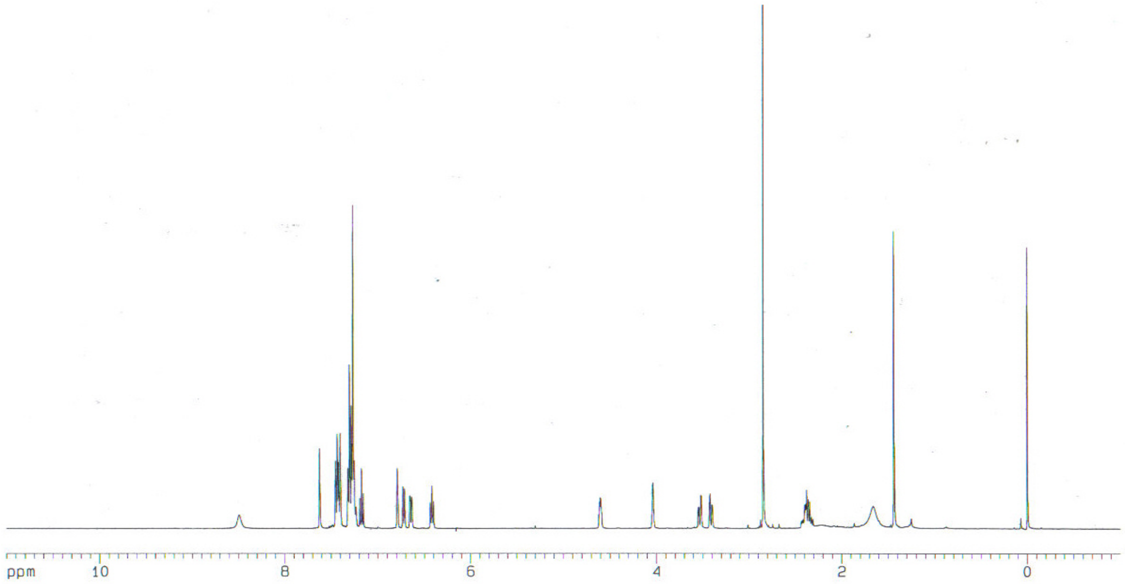

ppm
8
6
4
2
0

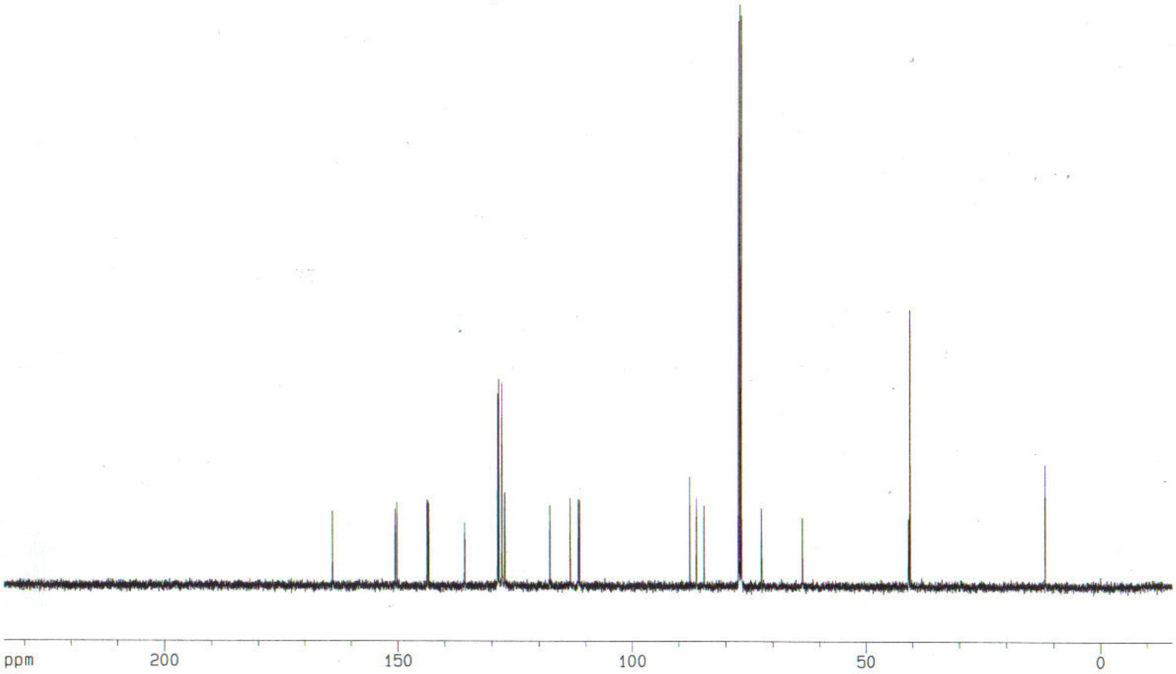

ppm
200
175
150
125
100
75
50
25
0

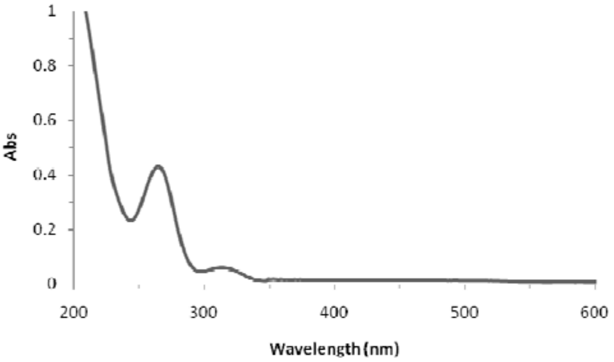

1
0.8
0.6
0.4
0.2
0
Abs
200
300
400
500
600
Wavelength (nm)

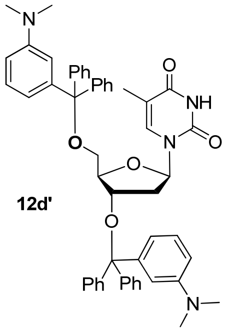

O
NH
O
N
Ph
Ph
O
O
N
OH

12d

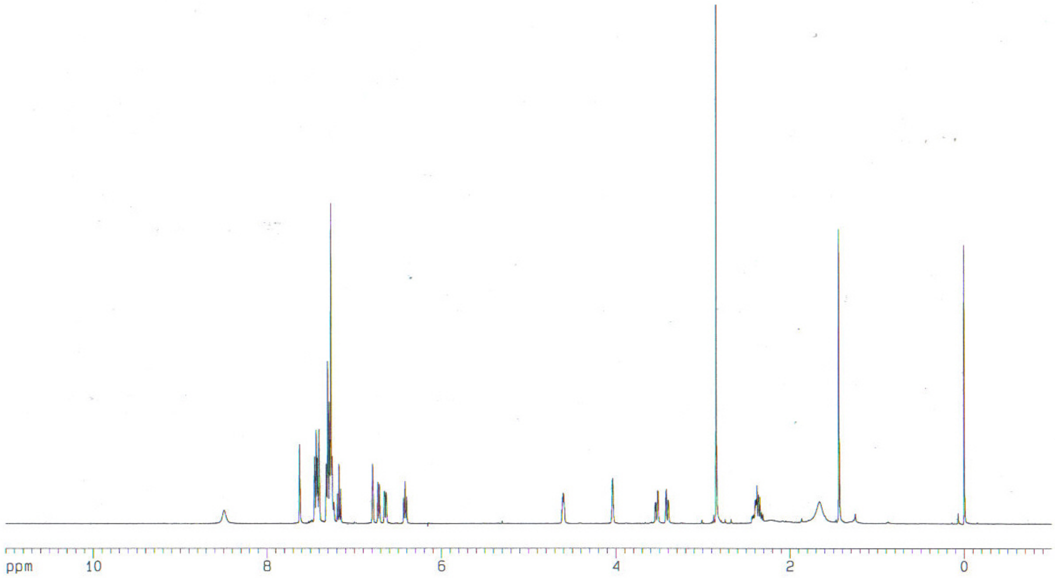

ppm
10
8
6
4
2
0

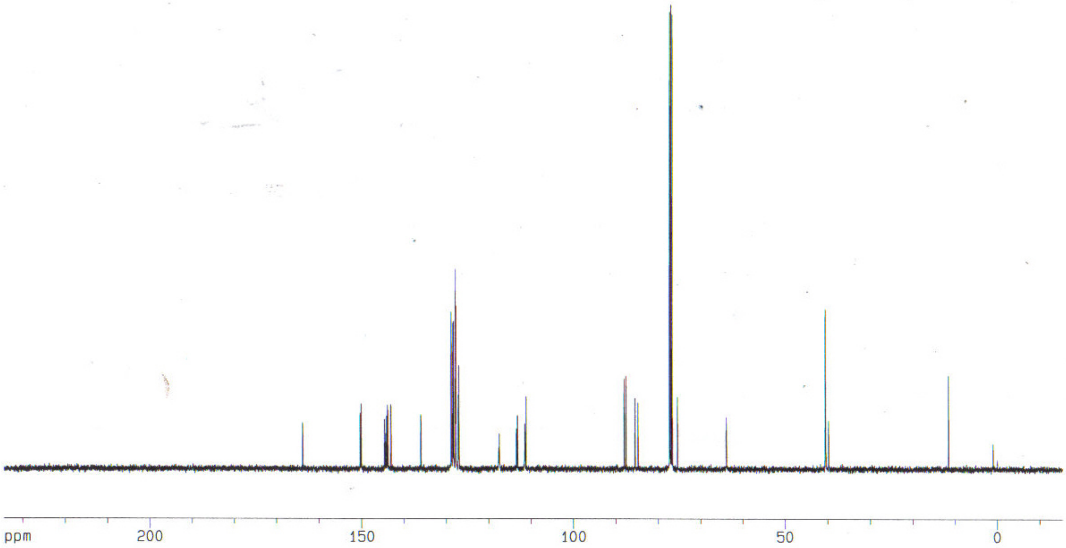

ppm
200
150
100
50
0

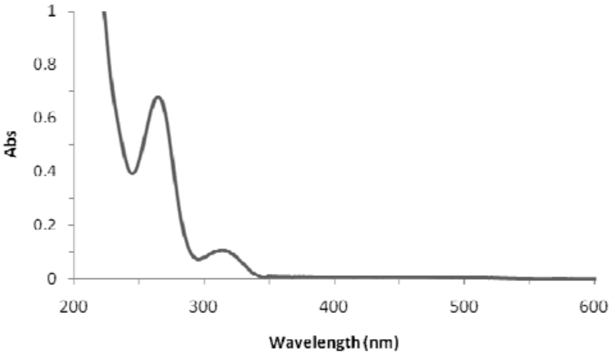

Abs
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength (nm)

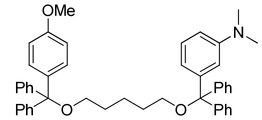

N
Ph
Ph
O
NH
O
N
O
O
O
Ph
Ph
N

12d'

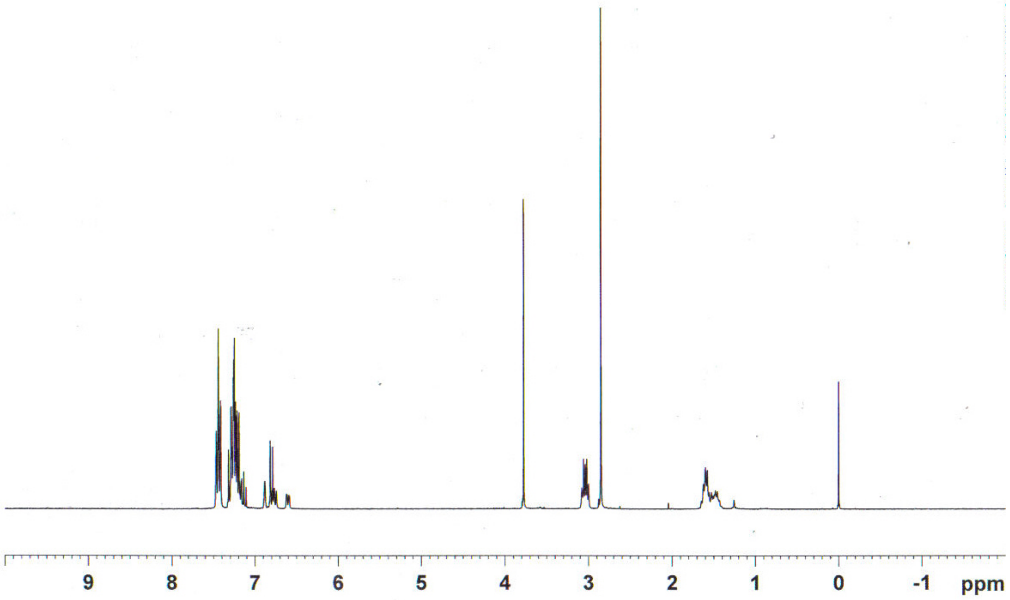

ppm
10
8
6
4
2
0

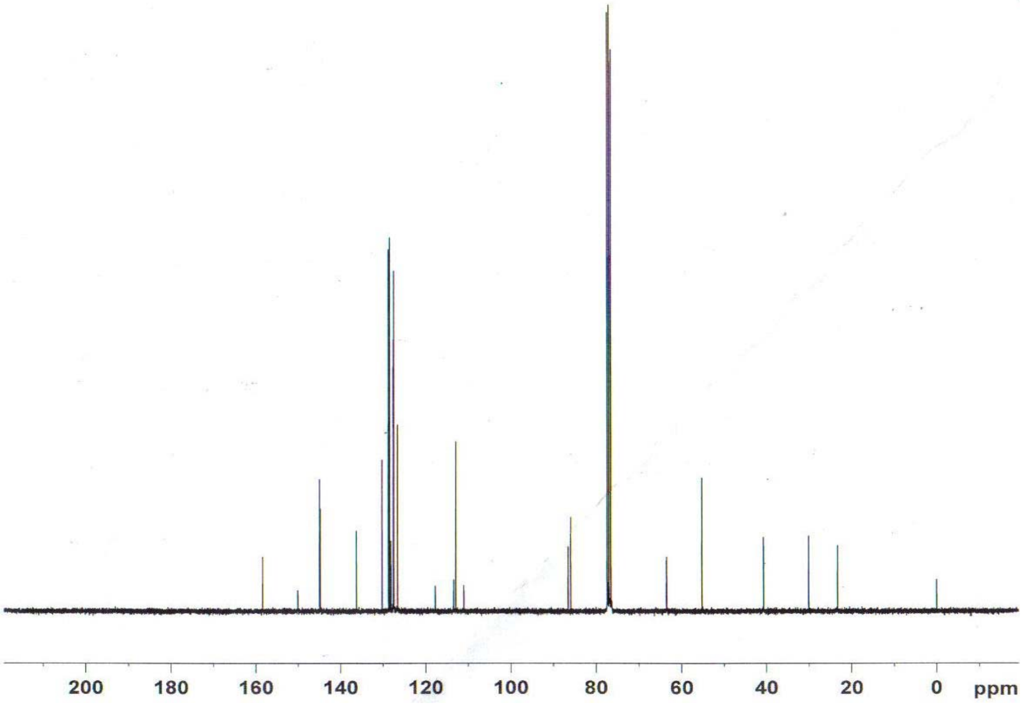

ppm
200
150
100
50
0

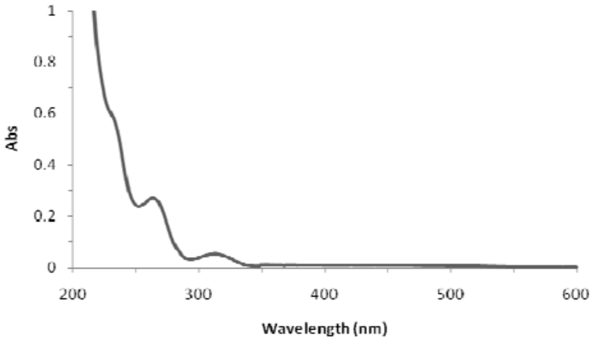

Abs
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength (nm)

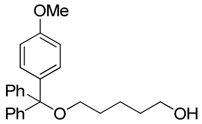

OMe
N
Ph
Ph
O
O
Ph
Ph

13

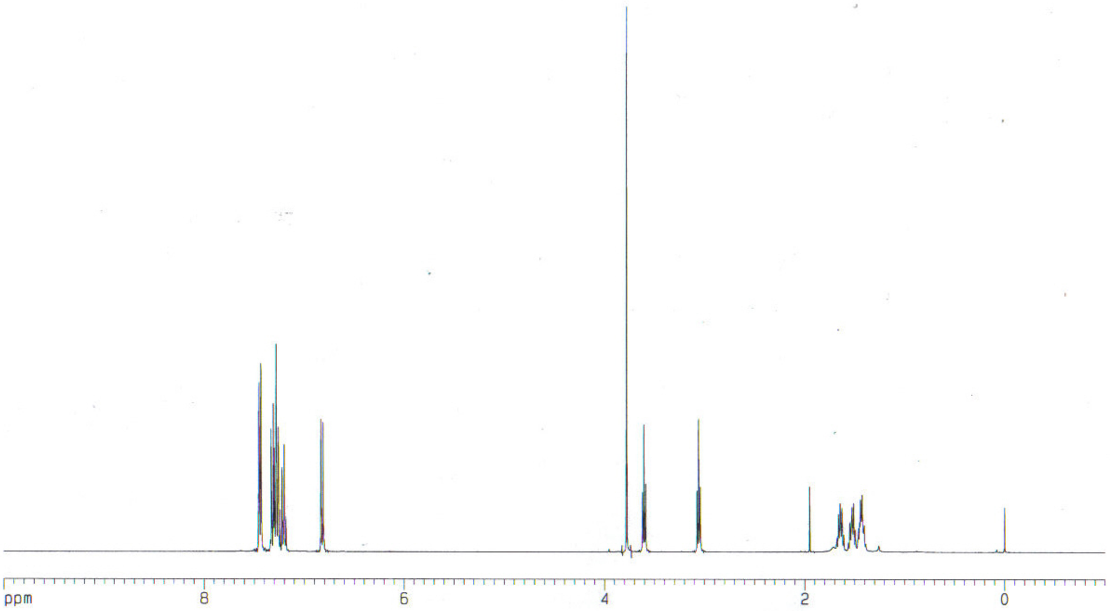

9
8
7
6
5
4
3
2
1
0
-1
ppm

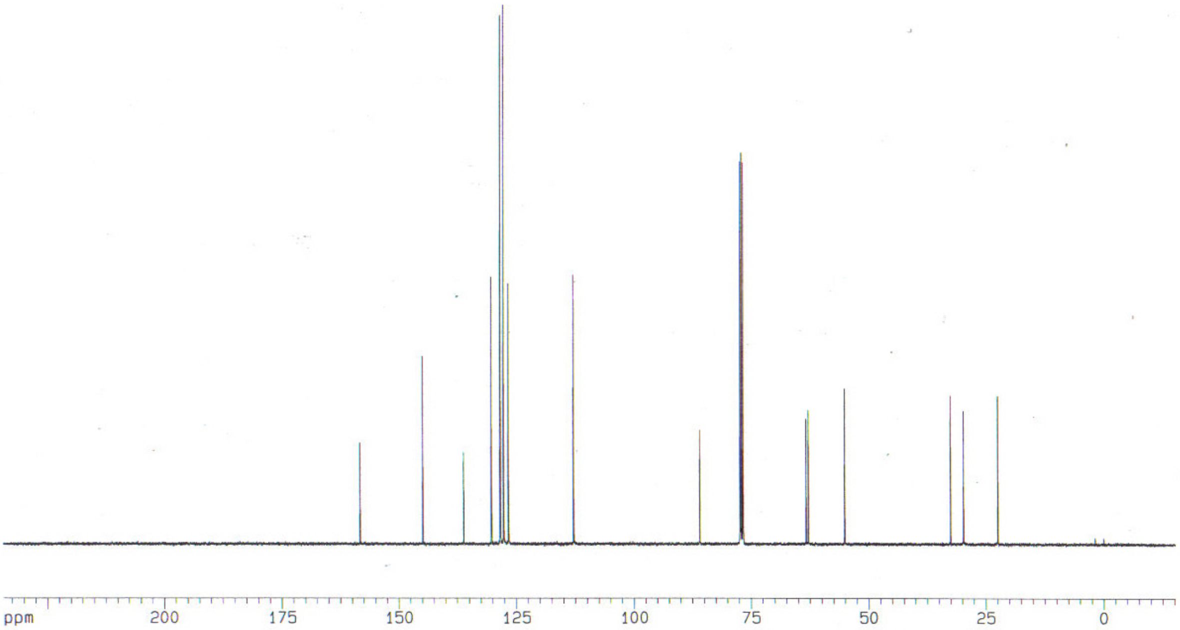

200
180
160
140
120
100
80
60
40
20
0
ppm

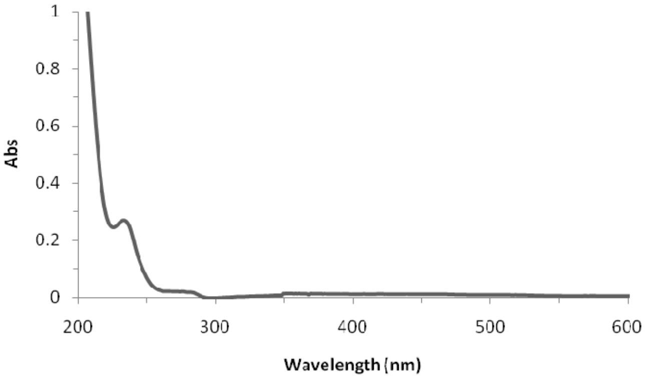

1
0.8
0.6
0.4
0.2
0
Abs
200
300
400
500
600
Wavelength (nm)

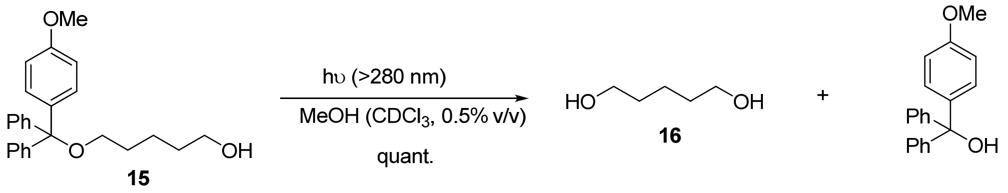

OMe
Ph
Ph
O
OH

15

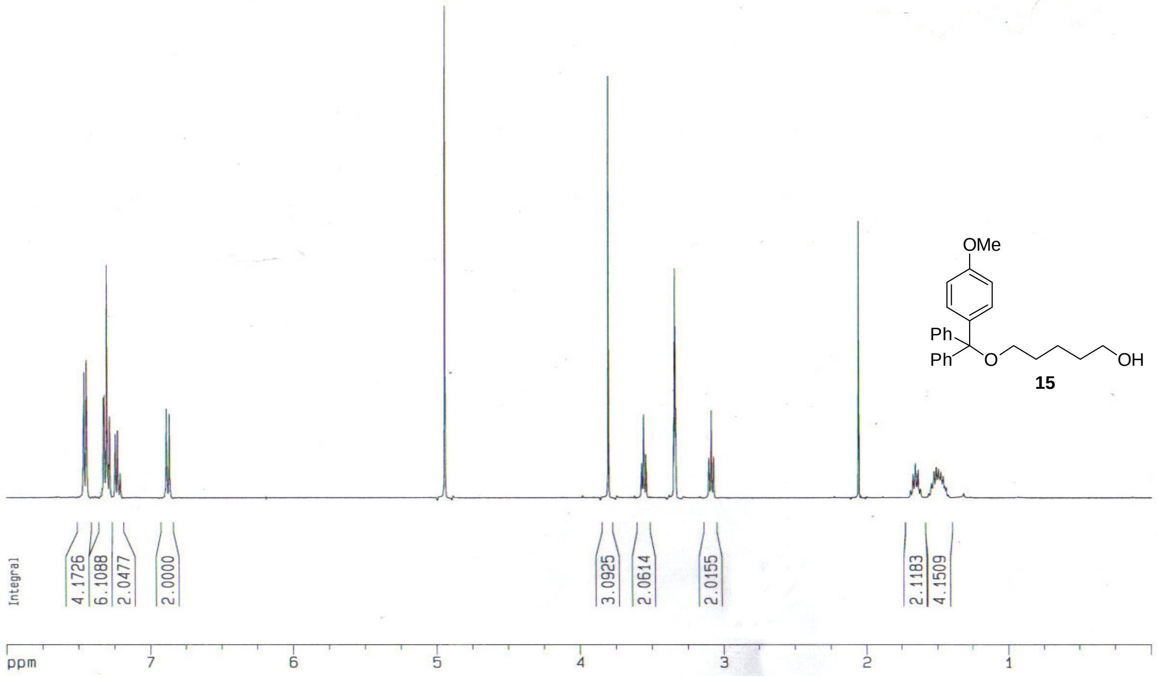

ppm
8
6
4
2
0


ppm
200
175
150
125
100
75
50
25
0


Abs
1
0.8
0.6
0.4
0.2
0
200
300
400
500
600
Wavelength (nm)



15 (5 mM) in CD$_3$OD (w/ 0.5% v/v CDCl$_3$) before irradiation



Crude reaction mixture after 15 min irradiation in a Pyrex NMR tube with Pyrex-filtered light