Supplementary Data

"Green Organophotocatalysis. TiO_2-Induced Enantioselective α-Oxyamination of Aldehydes"

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Experimental Section

General. Dichloromethane was distilled from calcium hydride. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Varian Mercury plus (400 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) downfield from trimethylsilane. Coupling constants are reported in Hertz (Hz). Carbon-13 nuclear magnetic resonance (^{13}C NMR) spetra were recorded with a Varian Mercury plus (100 MHz) spectrometer. Chemical shifts are reported in delta (δ) units, part per million (ppm) relative to the center of the triplet at 77.00 ppm for deuteriochloroform. Degussa P25 titanium dioxide nanoparticles were purchased and used as photocatalysts. The mercury-lamp (50-500 W, Newport) was used as a UV light source. The enantiomeric excess (ee) of the products was determined by chiral stationary phase HPLC. Products **3a**,[1] **3b**,[1b] **3c**,[1b] **3d**,[1a] and **3e**[1a,c] exhibited spectral properties consistent with previous literature reports.

Representative procedure of α-oxyamination of aldehydes under photo-organocatalytic conditions

The mixture of the aldehyde (0.5 mmol), TEMPO (1 mmol), TiO_2 (35 mg) and a catalyst (0.1 mmol) in the solvent (0.1 M) was exposed to UV irradiation at ambient temperature until the aldehyde was consumed completely. The solvent was removed with a rotary evaporator to produce a residue which was purified by column chromatography on a silica gel eluting with hexane and ethyl acetate for the yield.

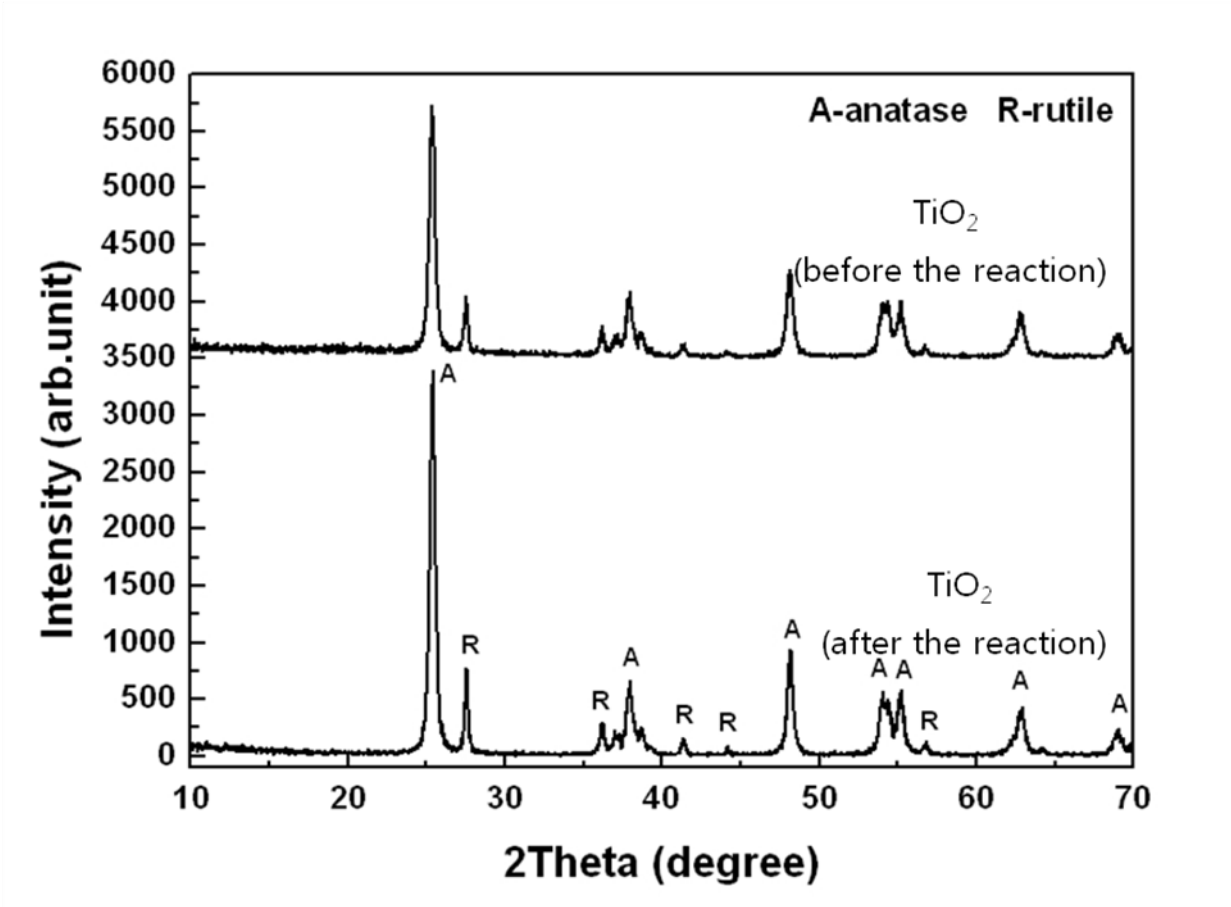
The Modification of the Aldehyde 3a-3h for the HPLC Analysis

The aldehyde (1eq) was exposed to the THF solution containing $NaBH_4$ (3eq) at 0^{o}C for 15 minutes, then the reaction mixture was stirred for 5 hours at room temperature, affording the alcohol (the reduced product). To measure the ee values for compounds **3a**, **3d**, **3e**, **3g**, and **3h**, the reduced compounds were analyzed by HPLC. The reduced compounds from **3b, 3c,** and **3f** were subjected to the pyridine solution containing benzoyl chloride (2eq with respect to the alcohol) for 18 hours at room temperature, forming the benzoylated compounds. The enatiomeric excess of these compounds was analyzed by HPLC.

The procedure for the coupling reaction of hydrocinnamaldehyde with TEMPO-derived oxoammonium ion

The mixture of hydrocinnamaldehyde (0.5 mmol), $TEMPO^+BF_4^-$ (1 mmol), TiO_2 (35 mg) and catalyst **A** (0.1 mmol) in acetonitrile (5 mL) was stirred at ambient temperature under N_2 for 18 h, to afford **3a** (2 mg) in 1% yield.

[1] (*a*) M. P. Sibi, M. Hasegawa, *J. Am. Chem. Soc.*, 2007, **129**, 395-405; (*b*) N.-N. Bui, X.-H. Ho, S.-i. Mho, H.-Y. Jang, *Eur. J. Org. Chem.*, 2009, 5309-5312; (*c*) K. Akagawa, T. Fujiwara, S. Sakamoto, K. Kudo, *Org. Lett.*, 2010, **12**, 1804-1807.



XRPD data of TiO_2

3-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanal (3a)

HPLC analysis (derivatized to the alcohol): Chiralcel OD-H, 99:1 (Hexane: IPA), flow rate 0.5mL/min, retention time 17.6 min and 21.3 min.

2-(2,2,6,6-tetramethylpiperidin-1-yloxy)octanal (3b)

HPLC analysis (derivatized to the benzoylated product): Chiralcel OD-H, 99:1 (Hexane: IPA), flow rate 0.5mL/min, retention time 15.2 and 18.4 min.

3-methyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)butanal (3c)

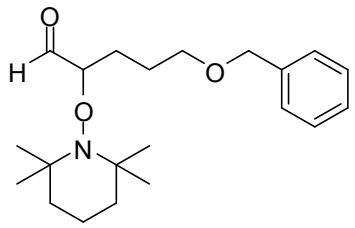
HPLC analysis (derivatized to the benzoylated product): Chiralcel AD-H, 100% Hexane, flow rate 0.5mL/min, retention time 21.0 and 25.0 min.

3-(4-methoxyphenyl)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanal (3d)

HPLC analysis (derivatized to the alcohol): Chiralcel AD-H, 98.5:1.5 (Hexane: IPA), flow rate 0.5mL/min, retention time 20.4 and 26.5 min.

4-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)butanal (3e)

HPLC analysis (derivatized to the alcohol): Chiralcel OD-H, 99:1 (Hexane: IPA), flow rate 0.5mL/min, retention time 22.0 and 25.5 min.



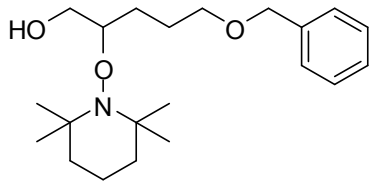
5-(benzyloxy)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)pentanal (3f)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.13 - 1.84 (m, 22H), 3.46 (t, J = 6 Hz, 6.4 Hz, 2H), 4.11 (m, 1H), 4.48 (s, 2H), 7.25 - 7.33 (m, 5H), 9.77 (d, J = 4.4 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.5, 20.6, 20.8, 25.0, 27.1, 31.3, 34.2, 34.7, 40.4, 60.1, 60.9, 70.1, 73.1, 88.3, 127.7 (2C), 127.9, 128.3, 128.5, 138.5, 204.4 ppm.

FTIR: 2932, 1729, 1454, 1374, 1101, 697 cm^{-1}.

HRMS : Calcd for $C_{21}H_{33}NO_3[M+H]^+$ 347.25, found 348.2539.



5-(benzyloxy)-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)pentan-1-ol

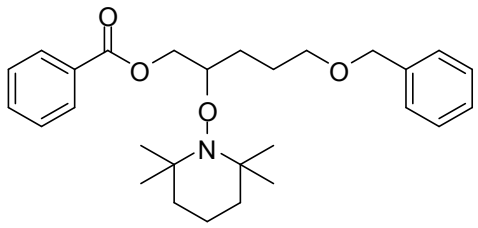
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.09 - 1.86 (22H), 3.43 (m, 2H), 3.54 (m, 1H), 3.94 (m, 1H), 4.25 (m, 1H), 4.49 (s, 2H), 6.00 (d, J = 9.6 Hz), 7.26 – 7.34 (m, 5H) ppm.

^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.5, 20.7, 20.8, 26.6, 28.2, 32.7, 35.0, 40.2, 40.6, 60.1, 61.8, 68.9, 70.6,

73.2, 80.0, 127.7, 127.8, 128.6, 138.5 ppm.

FTIR: 3426, 2930, 1454, 1362, 1099, 697 cm^{-1}.

HRMS : Calcd for $C_{21}H_{35}NO_3$ $[M+H]^+$ 349.26, found 350.2695.



5-(benzyloxy)-2-((2,2,6,6-tetramethylpiperidine-1-yloxy)pentyl benzoate

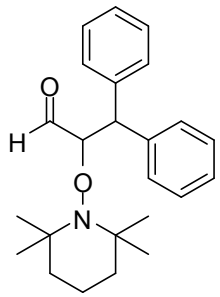
^{1}H NMR ($CDCl_3$, 400 MHz) δ: 1.10 - 1.86 (22H), 3.52 (t, *J* = 6, *J* = 4.8Hz, 2H), 4.16 (m, 2H), 4.45 (m, 1H), 4.50 (s, 2H), 4.57 (m, 1H), 7.23 - 7.59 (m, 8H), 8.04 - 8.13 (dd, *J* = 7.6, 8.4 Hz, 2H) ppm.

^{13}C NMR ($CDCl_3$, 100 Hz): 17.6, 20.8, 26.4, 28.2, 34.0, 34.8, 40.6, 59.9, 60.8, 65.3, 70.7, 73.1, 79.6, 127.6, 127.7, 128.4, 129.7, 130.5, 132.9, 138.6, 166.5 ppm.

HPLC analysis: Chiralcel AD-H, 99:1 (Hexane:IPA), flow rate 0.5mL/min, retention time 18.2 and 20.4 min for the racemic compound, t_m = 18.5 and T_M = 20.7 min for catalyst **A** as 59% ee, t_m = 19.4 and T_M = 21.9 min for catalyst **E** as 77% ee.

FTIR: 2932, 1789, 1723, 1278, 1213, 1039, 707 cm^{-1}.

HRMS : Calcd for $C_{28}H_{39}NO_4$ $[M+H]^+$ 453.29, found 454.2957.



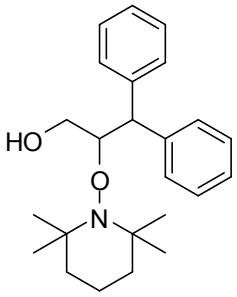
3,3-diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propanal (3g)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95-1.49 (18H), 4.39 (d, *J* = 6.8 Hz, 1H), 4.83 (m, 1H), 7.17 - 7.35 (m, 10H), 9.71 (d, *J* = 5.2 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.4, 34.3, 34.5, 40.4, 40.6, 53.4, 60.2, 61.8, 88.4, 126.9, 127.1, 128.4, 128.7, 129.1, 129.3, 139.7, 140. 3, 203.2 ppm.

FTIR: 2933, 1731, 1451, 1375 cm^{-1}.

HRMS : Calcd for $C_{24}H_{31}NO_2$ $[M+H]^+$ 365.24, found 366.2433.



3,3-diphenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)propan-1-ol

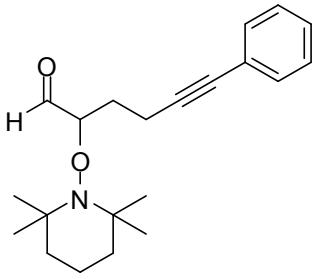
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25-1.50 (m, 18H), 3.64 (m, 1H), 3.83 (m, 1H), 3.97 (m, 1H), 5.02 (m, 1H), 6.22 (d, *J* = 6 Hz, 1H), 7.16-7.36 (m, 10H) ppm.

^{13}C NMR ($CDCl_3$, 100 Hz): δ 17.4, 20.4, 20.9, 32.6, 34.9, 40.3, 40.8, 54.7, 60.3, 62.1, 67.9, 81.8, 126.4, 126.8, 128.2, 128.4, 128.7, 128.8, 141.7, 142.0 ppm.

HPLC analysis: Chiralcel A D-H 98:2 (Hexane:IPA), flow rate 0.5mL/min, retention time 16.1 and 20.9 min for racemic, t_m = 20.8 and T_M = 16.1 min for catalyst **A** as 65% ee, t_m = 20.9 and T_M = 16.2 min for catalyst **E** as 35% ee.

FTIR: 3282, 2931, 1451, 1365, 1042cm^{-1}.

HRMS : Calcd for $C_{24}H_{33}NO_2$ $[M+H]^+$ 367.25, found 368.2590.



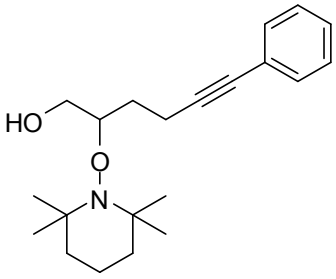
6-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-5-ynal (3h)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.16-1.55 (m, 18H), 1.98-2.08 (m, 2H), 2.50-2.56 (m, 2H), 4.31 (m, 1H), 7.25-7.27 (m, 3H), 7.36-7.37 (m, 2H), 9.93 (d, *J* = 4 Hz, 1H) ppm.

^{13}C NMR ($CDCl_3$, 100 Hz): 15.3, 17.5, 20.8, 29.9, 30.0, 34.4, 34.6, 40.5, 81.8, 87.1, 89.1, 123.7, 127.8, 128.3, 131.6, 204.3 ppm.

FTIR: 2972, 2932, 1728, 1490, 1374, 1133, 1061 cm^{-1}.

HRMS : Calcd for $C_{21}H_{29}NO_2$ $[M+H]^+$ 327.22, found 328.2277.



6-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)hex-5-yn-1-ol

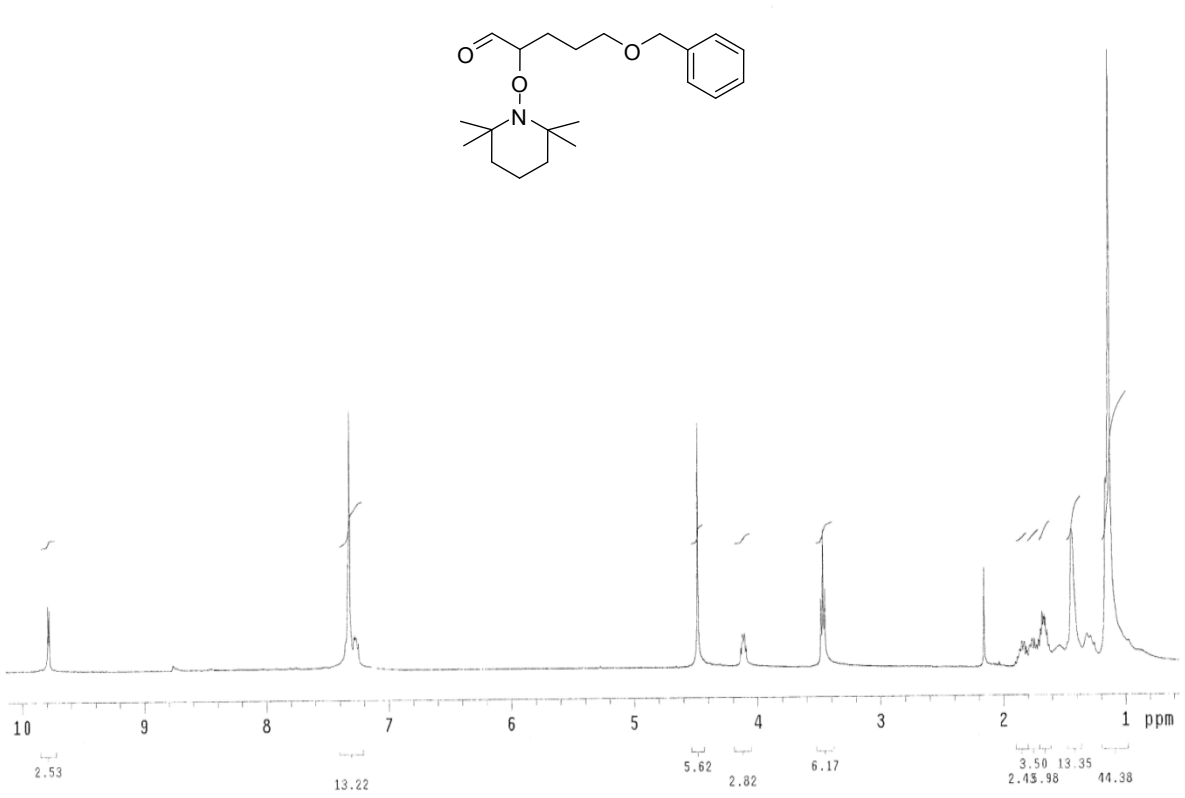
^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.25-1.50 (m, 20H), 2.51-2.60 (m, 2H), 3.60 (d, *J* = 11.6 Hz, 1H), 4.02 (t, *J* = 10 Hz, 11.6 Hz, 1H), 4.51-4.54 (m, 1H), 5.95 (br, 1H), 7.16-7.36 (m, 5H) ppm.

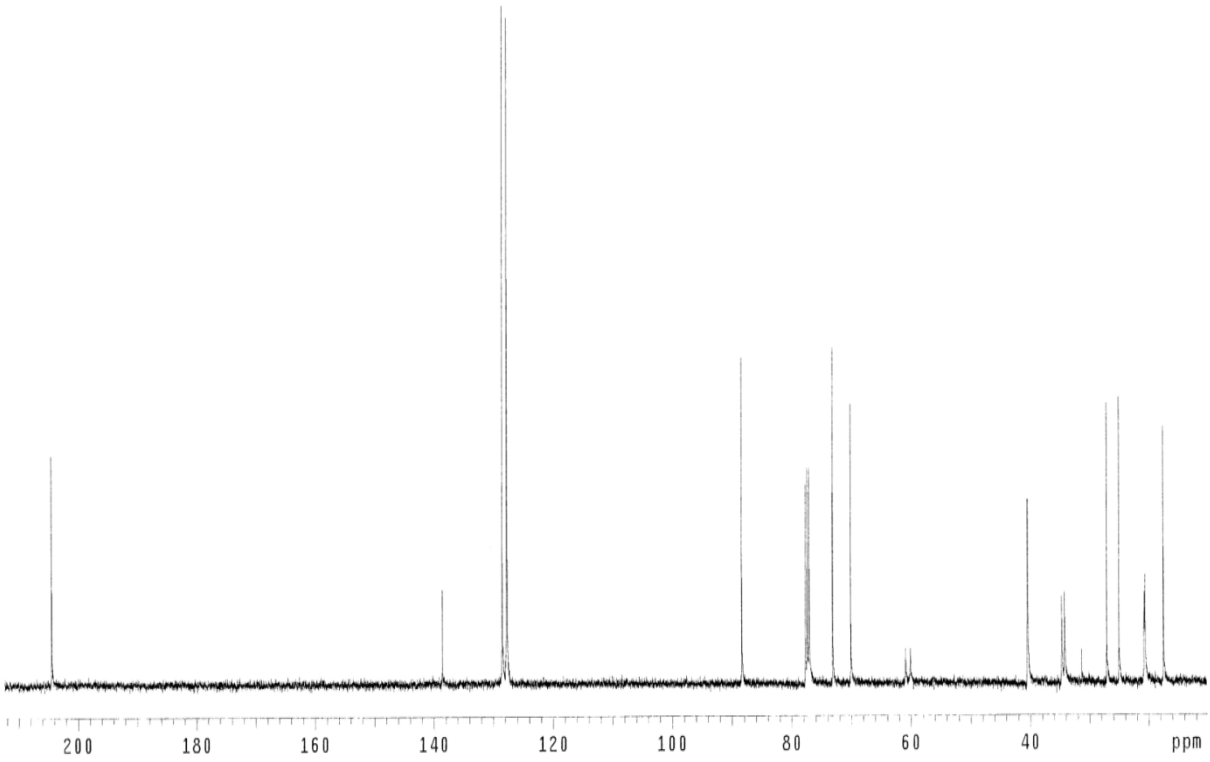
^{13}C NMR (CDCl3, 100 Hz): δ 16.4, 17.5, 20.7, 20.8, 30.6, 32.7, 34.9, 40.2, 40.8, 60.2, 62.0, 68.7, 78.5, 81.3, 89.8, 123.9, 127.7, 128.3, 131.6 ppm.

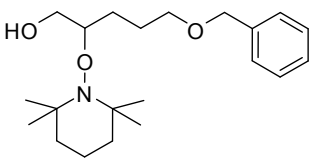
HPLC analysis: Chiralcel OD-H, 98:2 (Hexane:IPA), flow rate 1mL/min, retention time 10.4 and 14.8 min for the racemic compound, t_m = 15.3 and T_M = 10.4 min for catalyst **A** as 59% ee, t_m = 15.3 and T_M = 10.3 min for catalyst **E** as 69% ee..

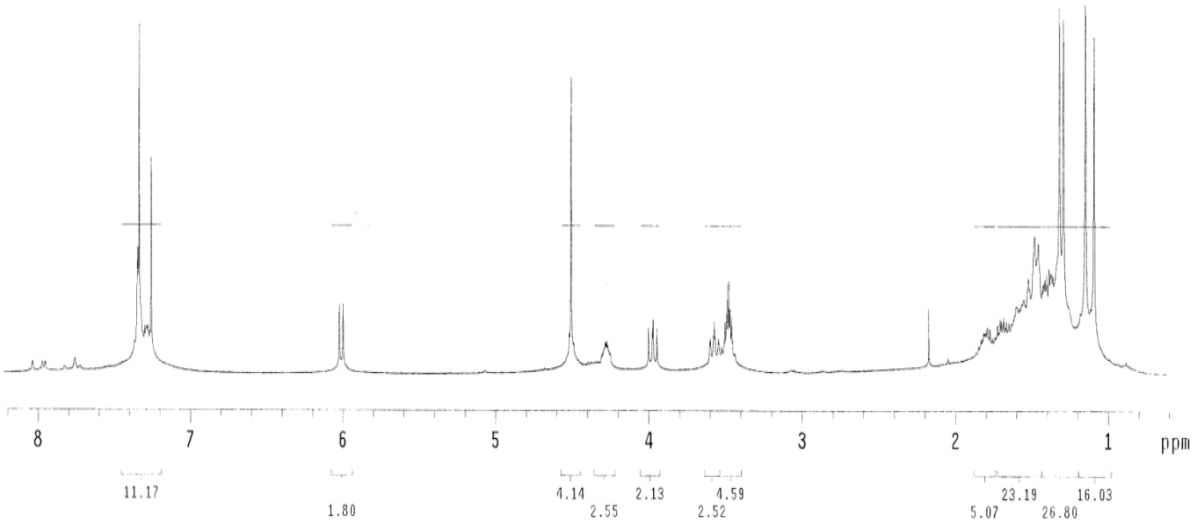
FTIR: 3441, 2930, 1489, 1380, 1131, 1047cm^{-1}.

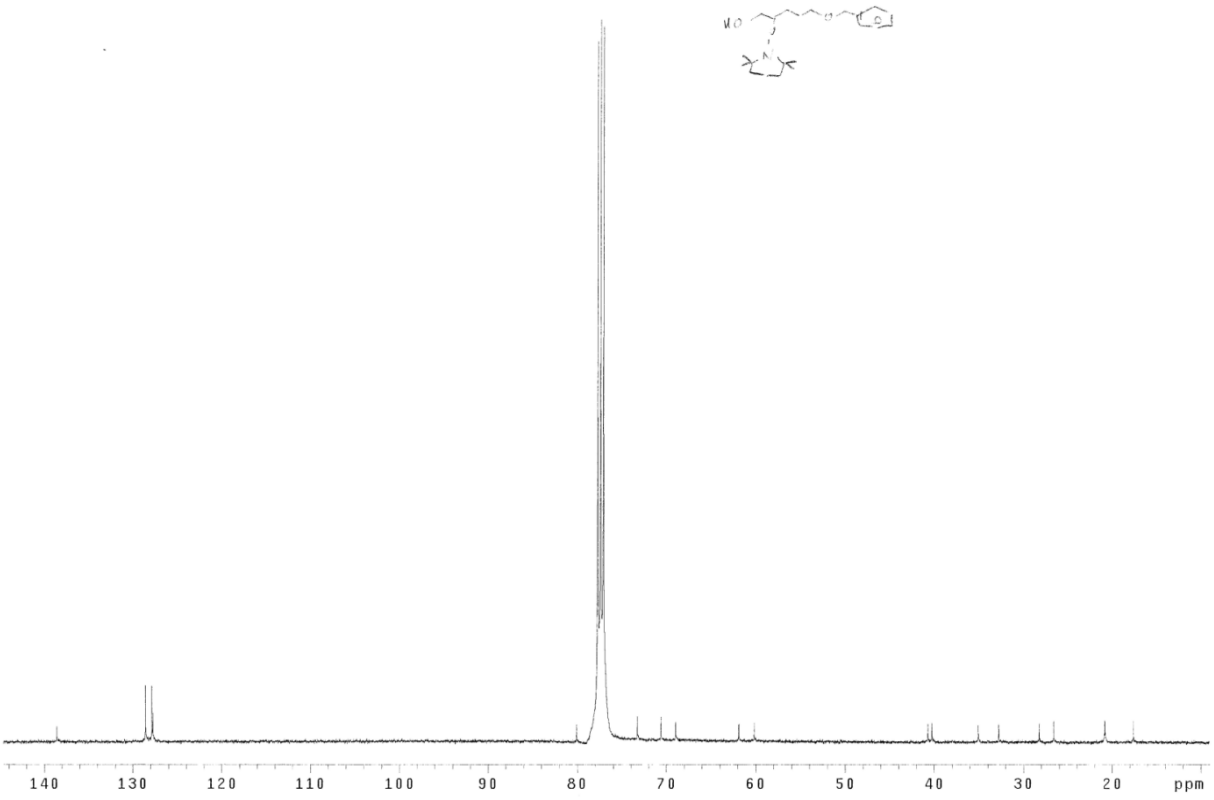
HRMS : Calcd for $C_{21}H_{31}NO_2$ $[M+H]^+$ 329.24, found 330.2433.

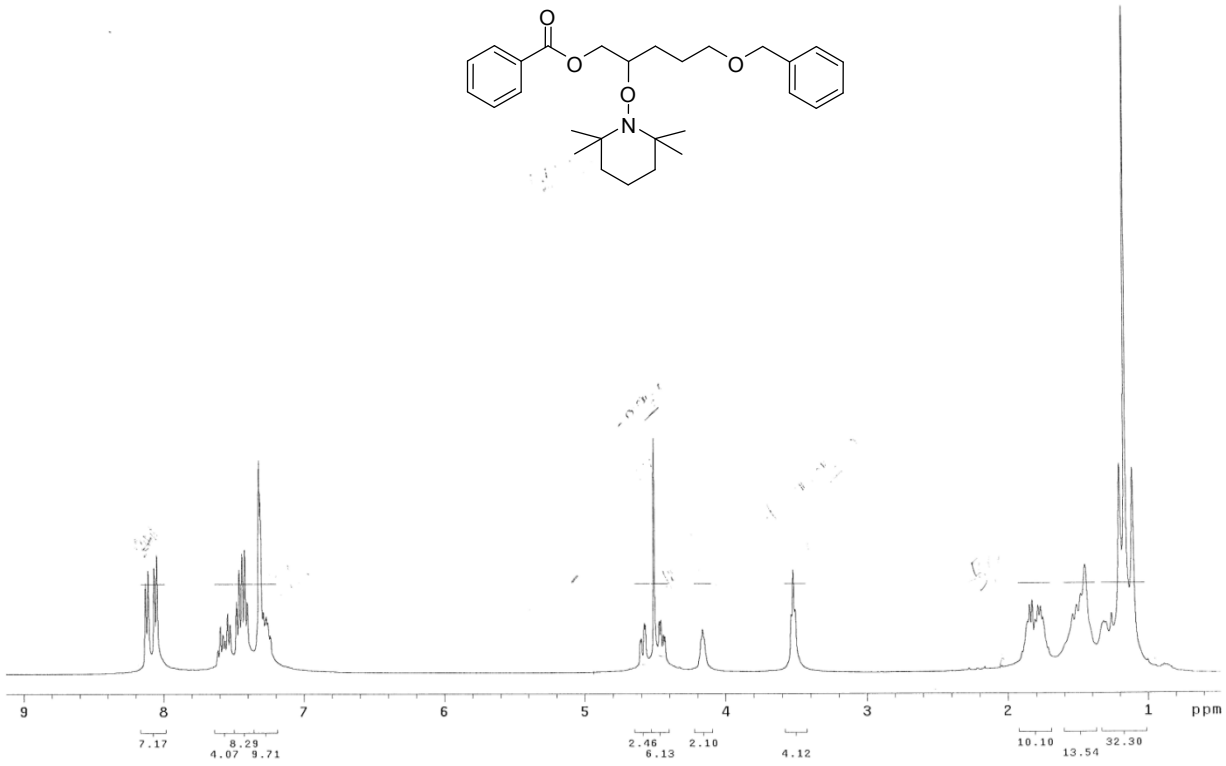


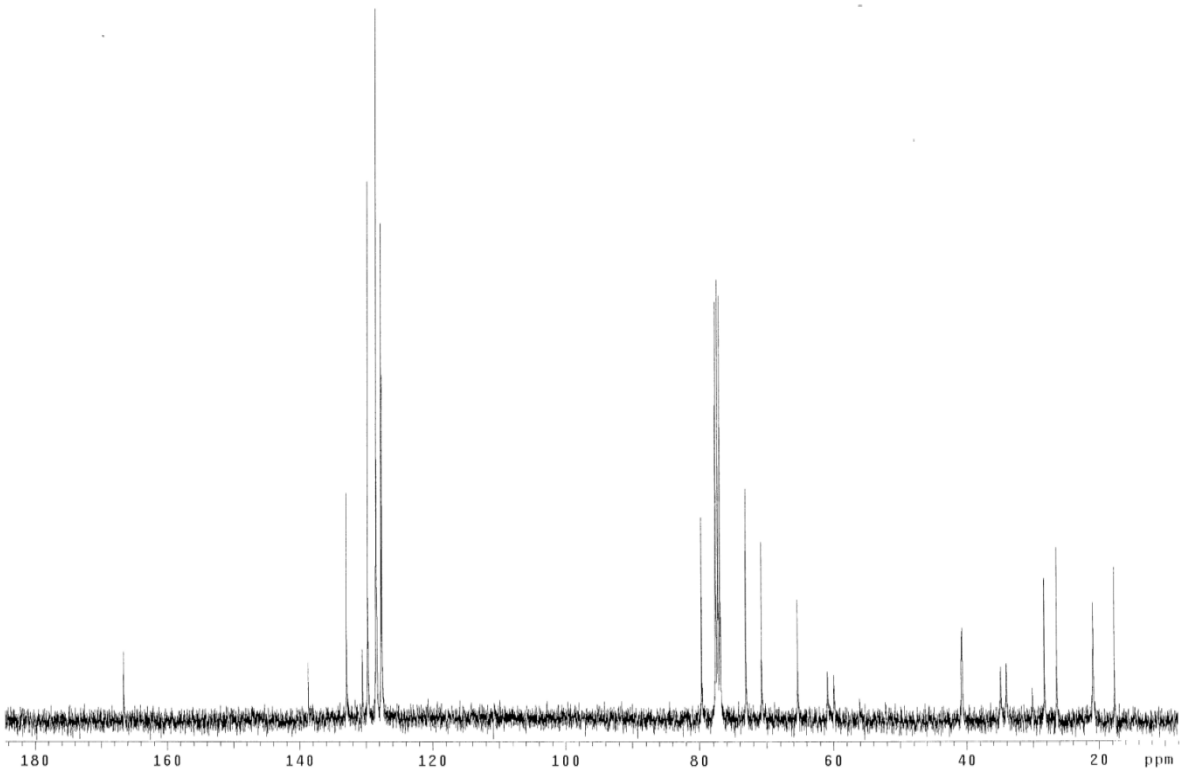


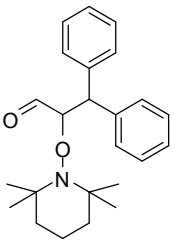


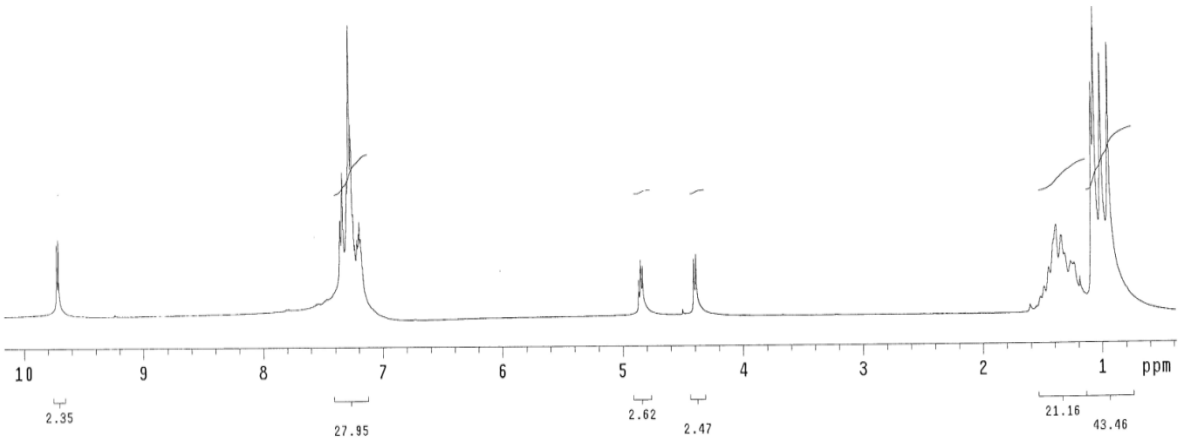


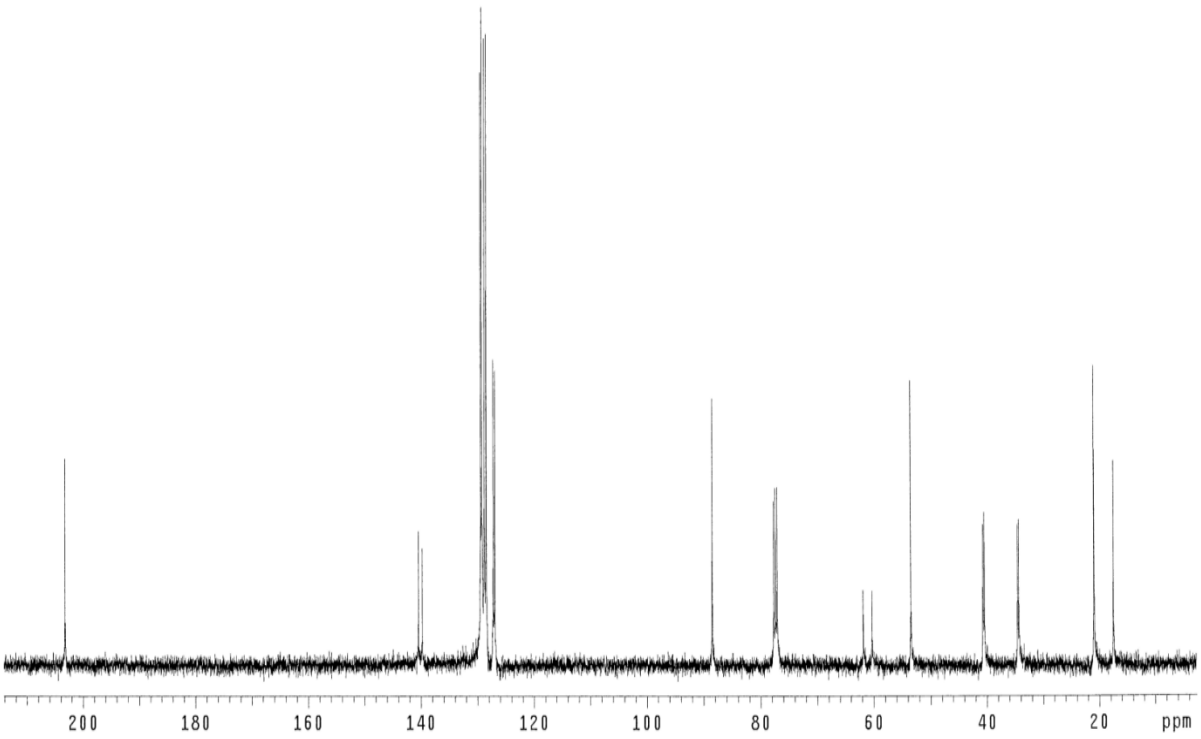


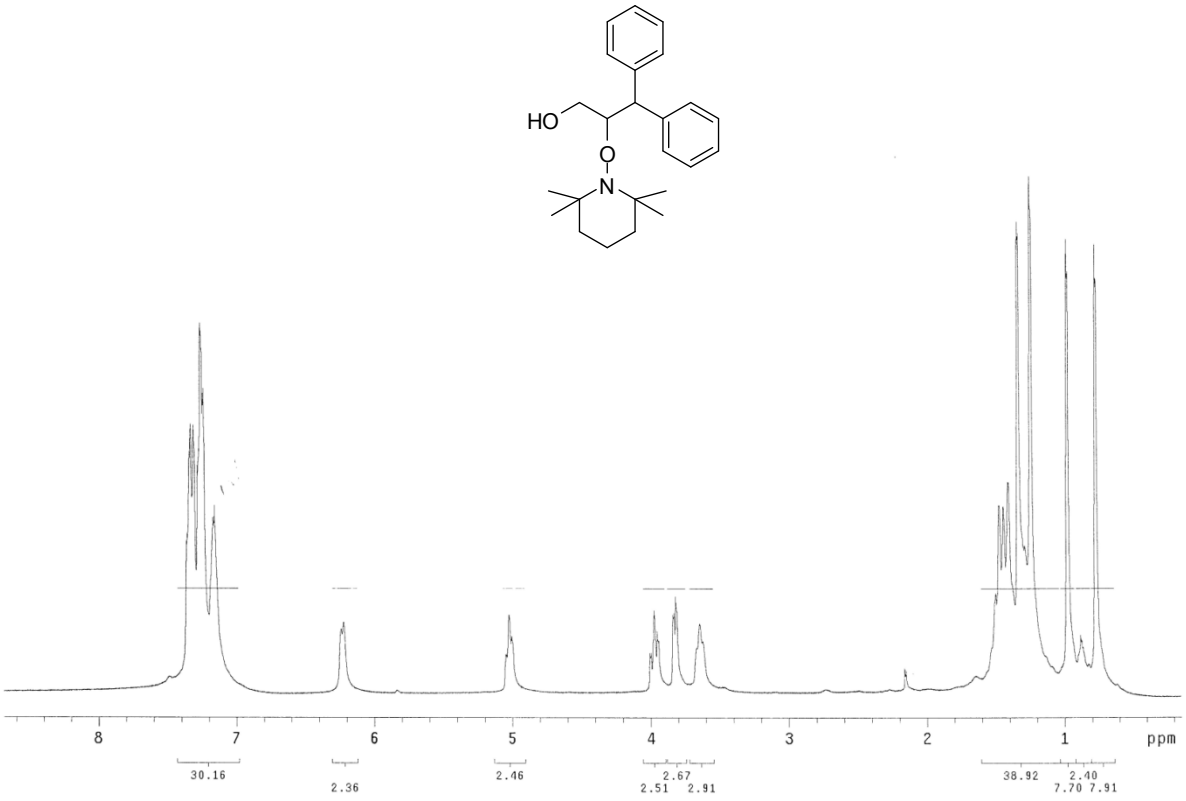


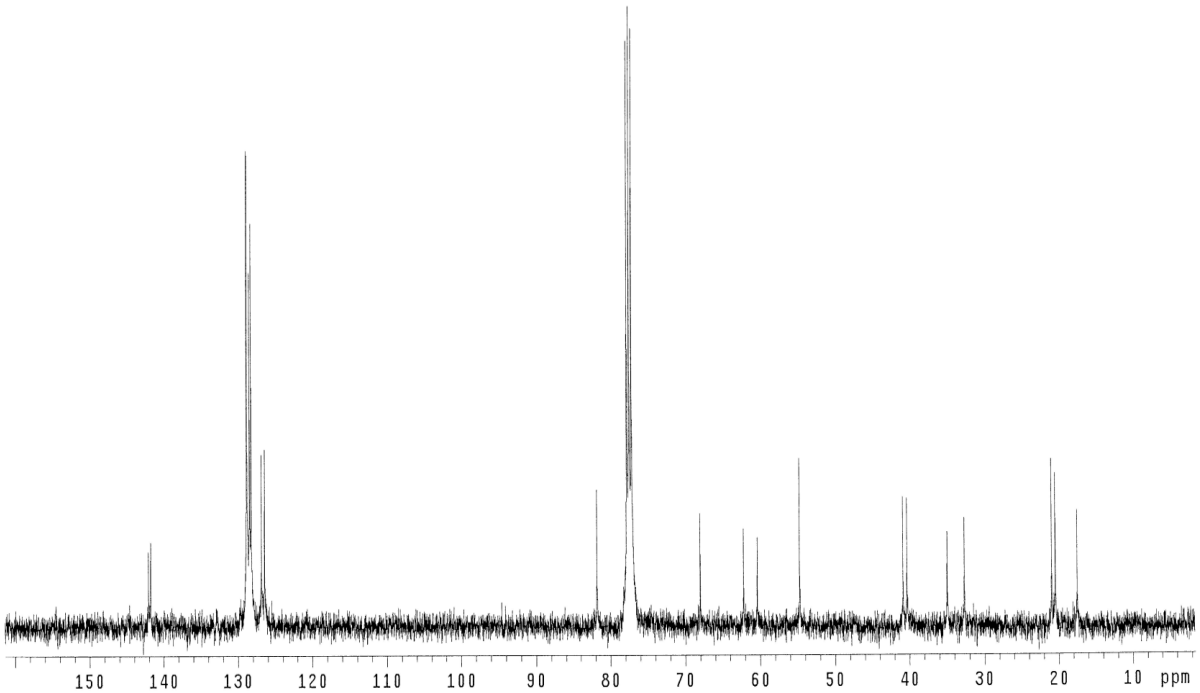


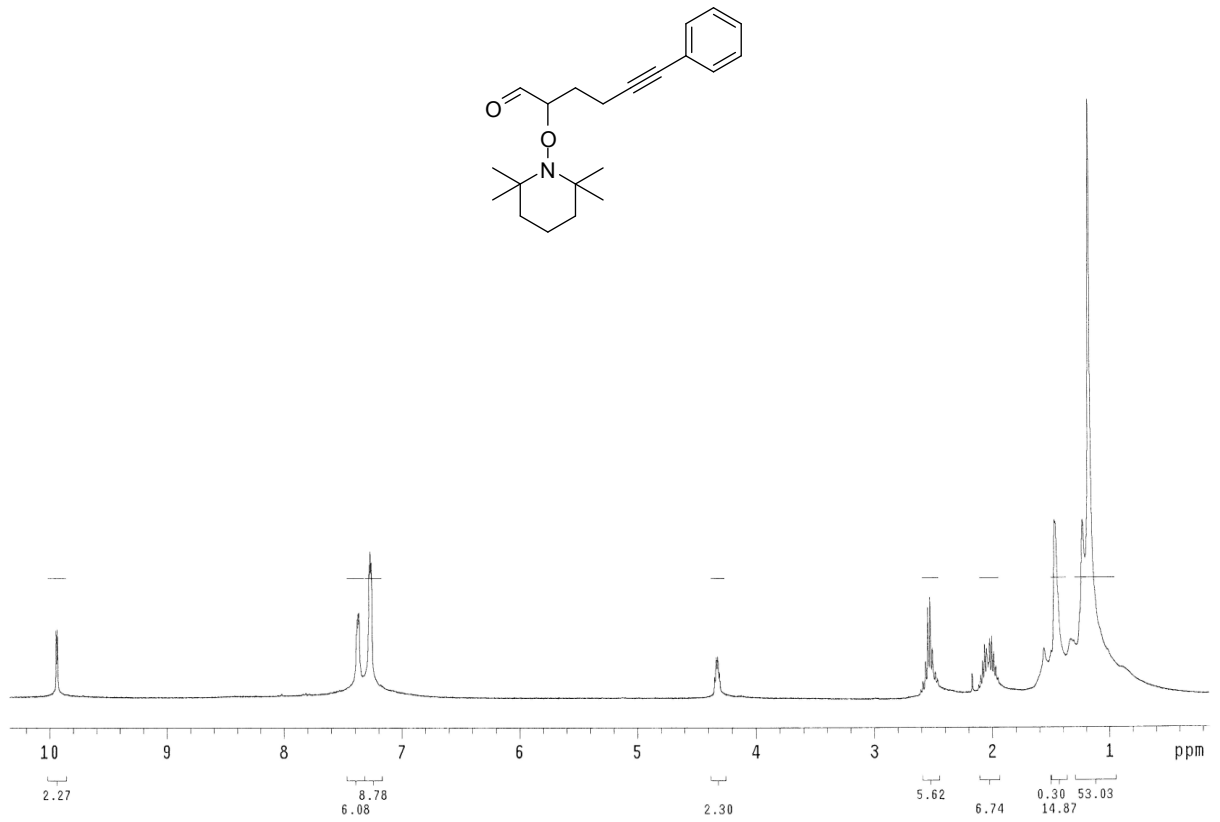


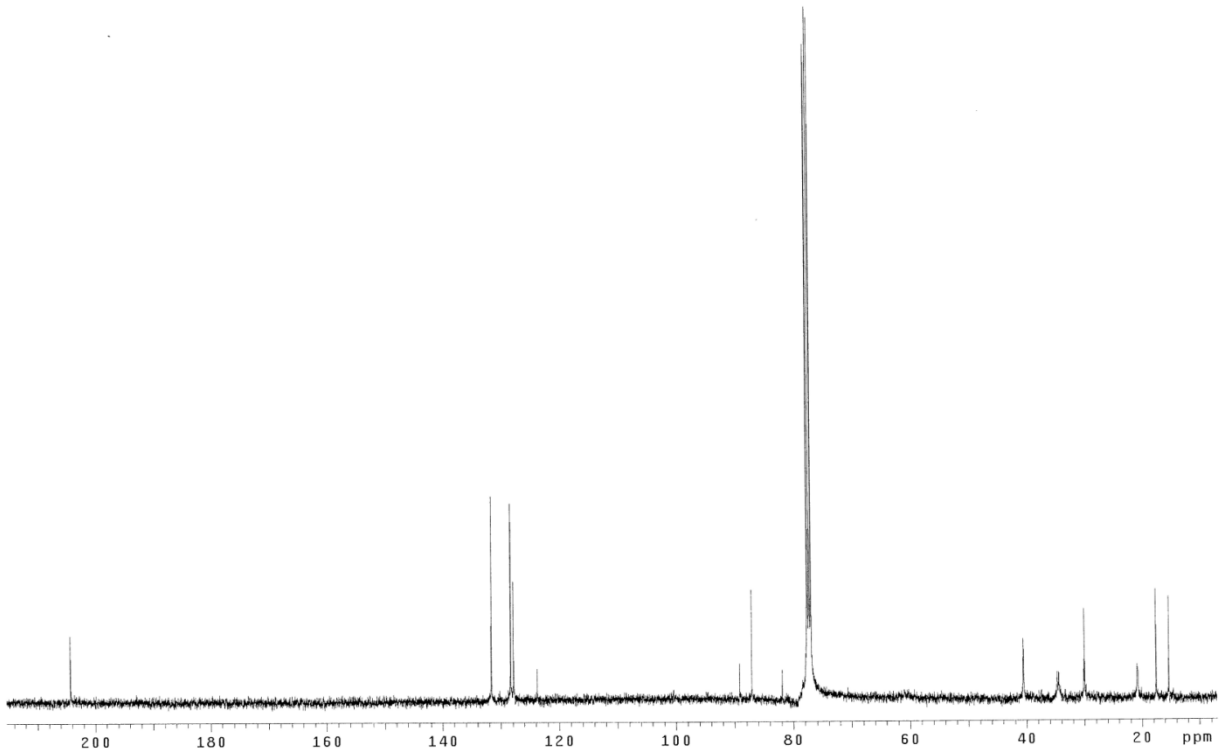


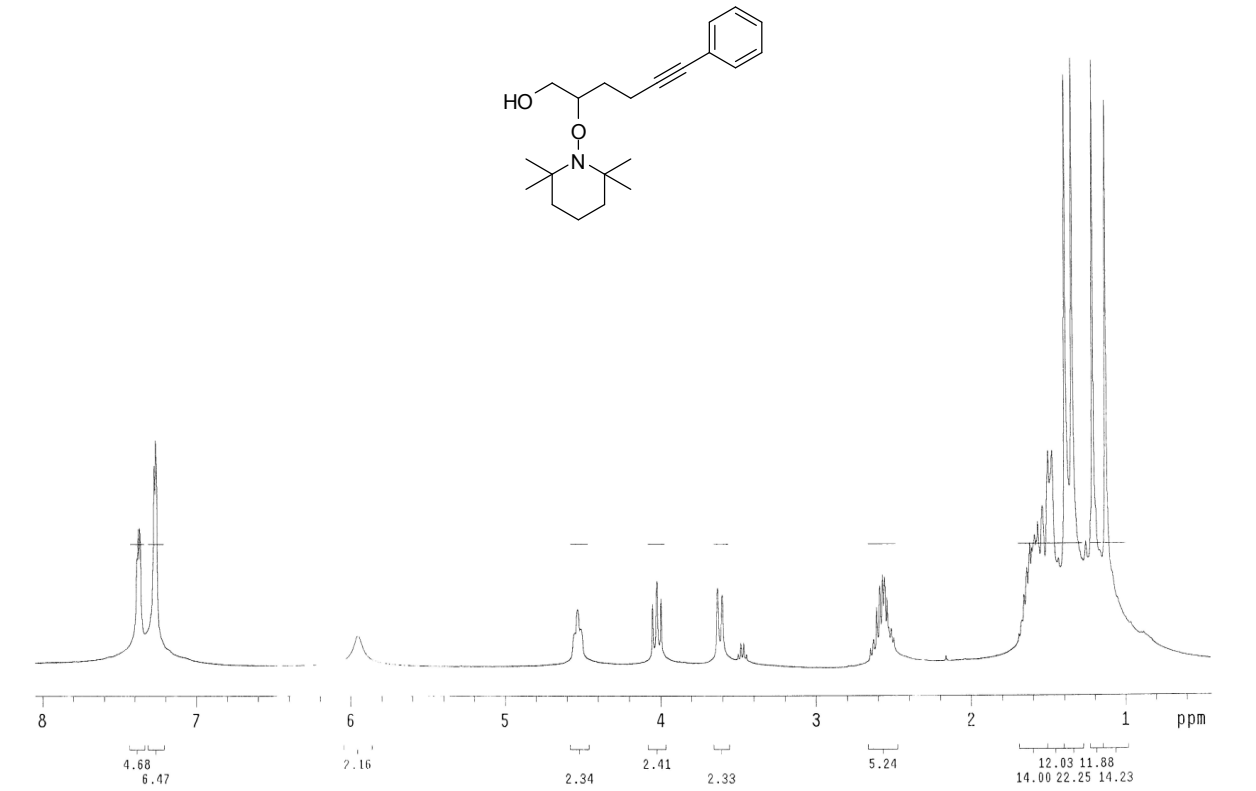


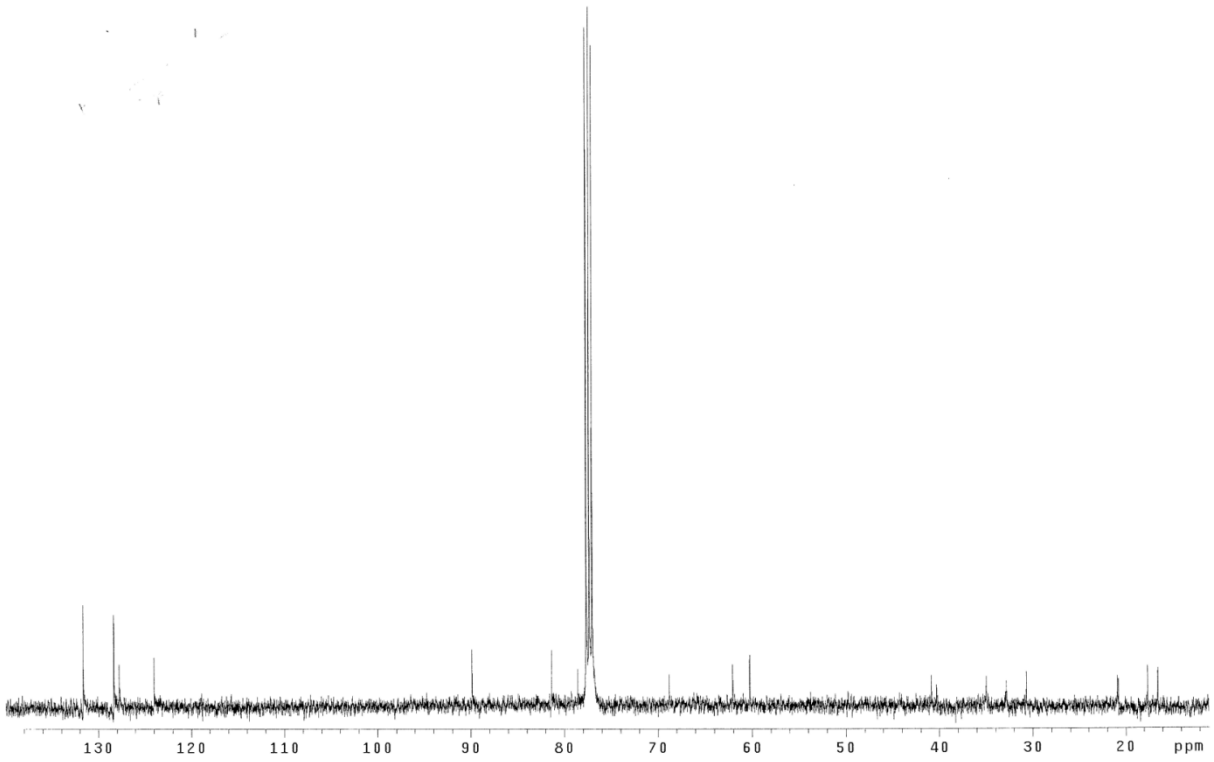




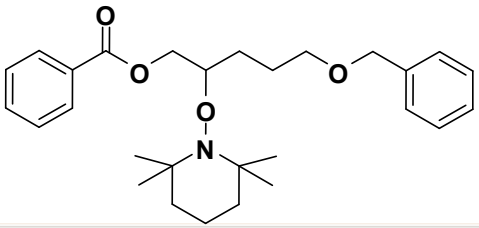


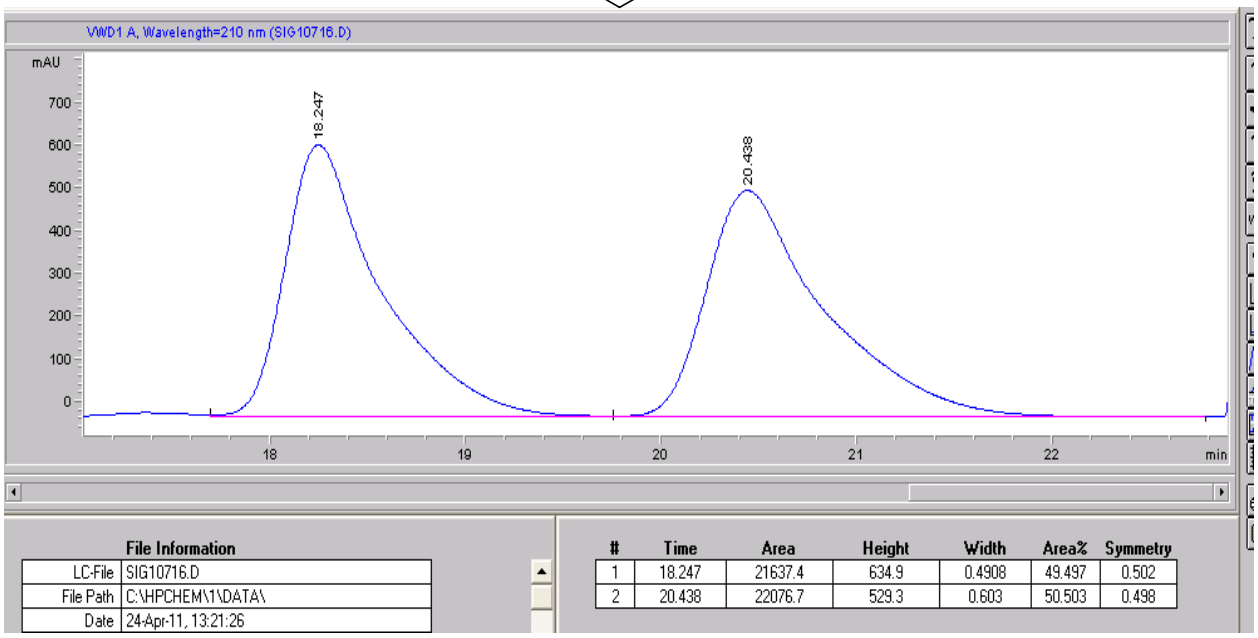






HPLC data





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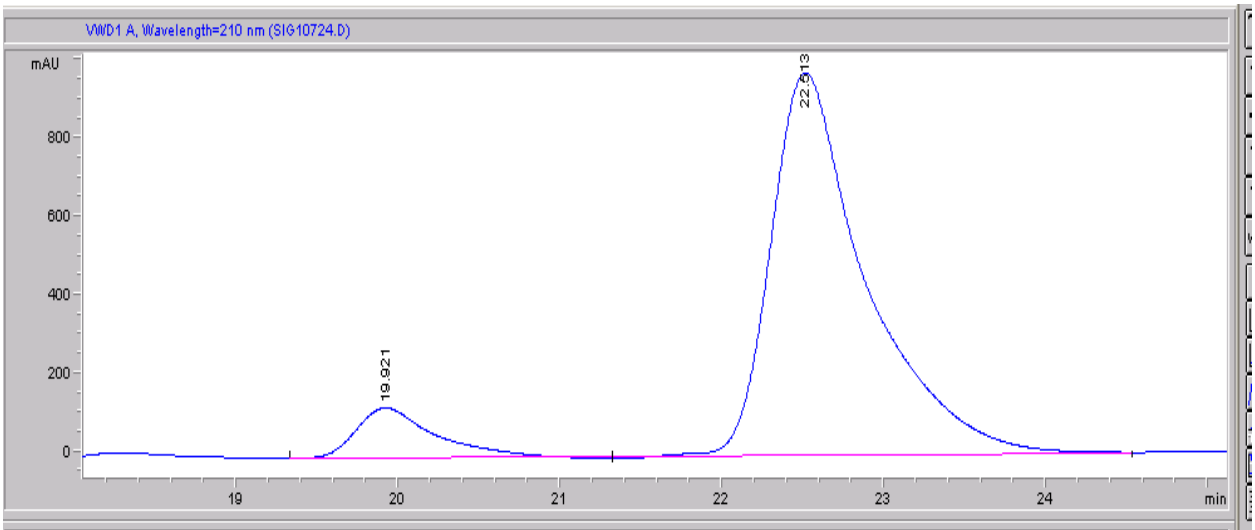

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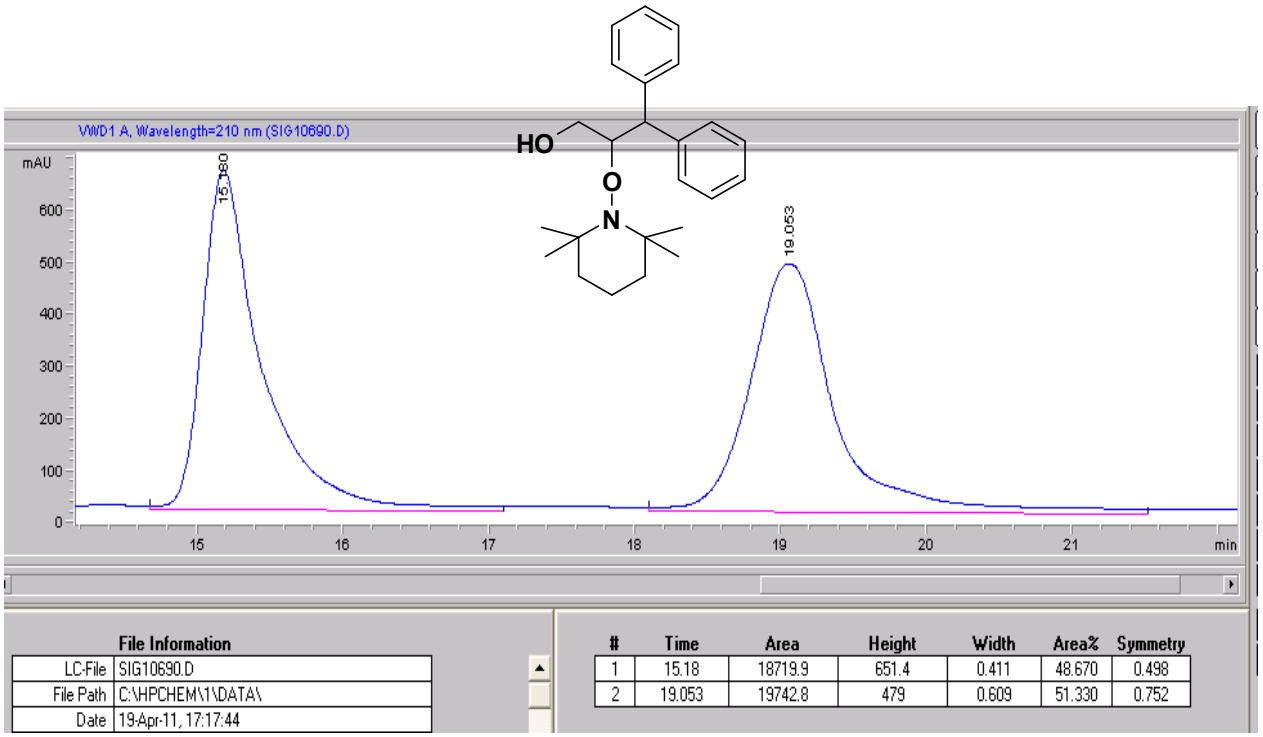

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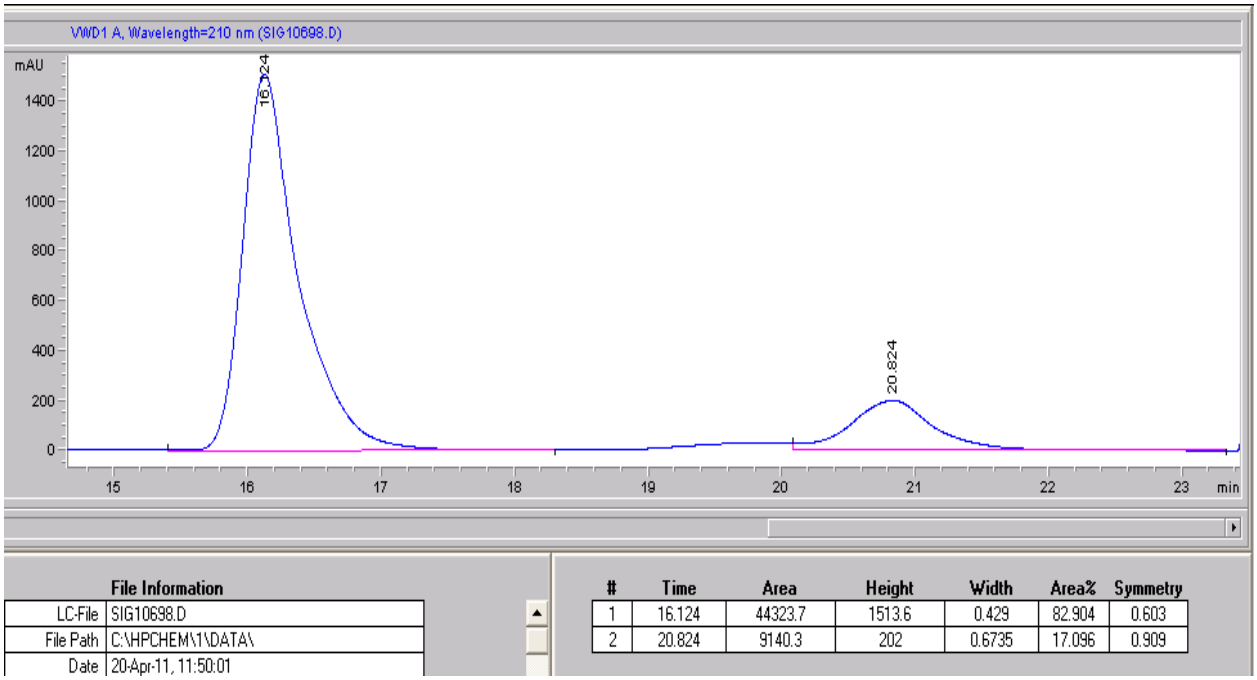

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