Supporting Information

One step selective deoxygenation of alcohols from acyloins

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1. Experimental Section

General Methods. Irradiation was conducted in a reactor equipped with two 400-W UV lamps emitting maximally at 350 nm (water-refrigerated). ^{1}H and ^{13}C-NMR spectra were recorded on a High Resolution Spectrometer Advance 400 (working frequency 400 MHz and 100 MHz, respectively), at ambient temperature in $CDCl_3$. The chemical shifts are quoted in parts per million (ppm), referenced to tetramethylsilane but calibrated on the solvent residual signal. Signal multiplicity is given by: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. The coupling constants are given in Hertz (Hz).

Materials. Benzoin, 2-hydroxyacetophenone, 1-hydroxycyclohexyl phenyl ketone, diethyl phosphite, 2-naphtol, potassium diphenylphosphide 0.5M in tetrahydrofuran and potassium *t*-butoxide were commercially available and used as received. DMSO was distilled under vacuum and stored under molecular sieves (4 Å).

Synthesis of α-methylbenzoin (2)

To 12 mL of dry and degassed DMSO under nitrogen were added *t*-BuOK (5 mmol), and cyclohexanone (5mmol). After 15 min benzoin (5 mmol) were added and the reaction was quenched with excess of ICH_3. The residue was dissolved with water and extracted with diethyl ether. The water phase was then extracted with diethyl ether. The desired product was purified by column chromatography employing diethyl ether:petroleum ether (5:95).

Photostimulated reactions of benzoin with EtO_2PO^- ions in DMSO. The following procedure is representative of reactions with this nucleophile. To 6 mL of dry and degassed DMSO under nitrogen were added *t*-BuOK (1 mmol), and EtO_2POH (1 mmol). After 5 min, KI (1mmol) and benzoin (1.0 mmol) were added and the reaction mixture was irradiated 90 min. The reaction was quenched with an excess of ammonium nitrate. The residue was dissolved with water and extracted with diethyl ether. Finally, HCl was added to the water phase up to pH= 5-6. The water phase was then extracted with diethyl ether. The products were isolated by column chromatography. In similar experiments the products were quantified by GC using the internal standard method.

Photostimulated reactions of benzoin with Ph_2P^- ions in DMSO. The following procedure is representative of reactions with this nucleophile. To 6 mL of dry and degassed DMSO under nitrogen were added 2 mL of Ph_2P^- solution (1 mmol). After 5 min, KI (1mmol) and benzoin (1.0 mmol) were added and the reaction mixture was irradiated 90 min. The reaction was quenched with an excess of NO_3NH_4. The residue was dissolved with water and extracted with diethyl ether. Finally, HCl was added to the water phase up to pH= 5-6. The water phase was then extracted with diethyl ether. The products were isolated by column chromatography. In similar experiments the products were quantified by GC using the internal standard method.

Photostimulated reactions of benzoin with 2-naphtoxide ions in DMSO. The following procedure is representative of reactions with this nucleophile. To 6 mL of dry and degassed DMSO under nitrogen were added *t*-BuOK (1 mmol), and 2-naphtol (1 mmol). After 5 min, KI (1mmol) and benzoin (1.0 mmol) were added and the reaction mixture was irradiated 180 min. The reaction was quenched with an excess of ammonium nitrate. The residue was dissolved with water and extracted with diethyl ether. Finally, HCl was added to the water phase up to pH= 5-6. The water phase was then extracted with diethyl ether. The products were isolated by column chromatography. In similar experiments the products were quantified by GC using the internal standard method.

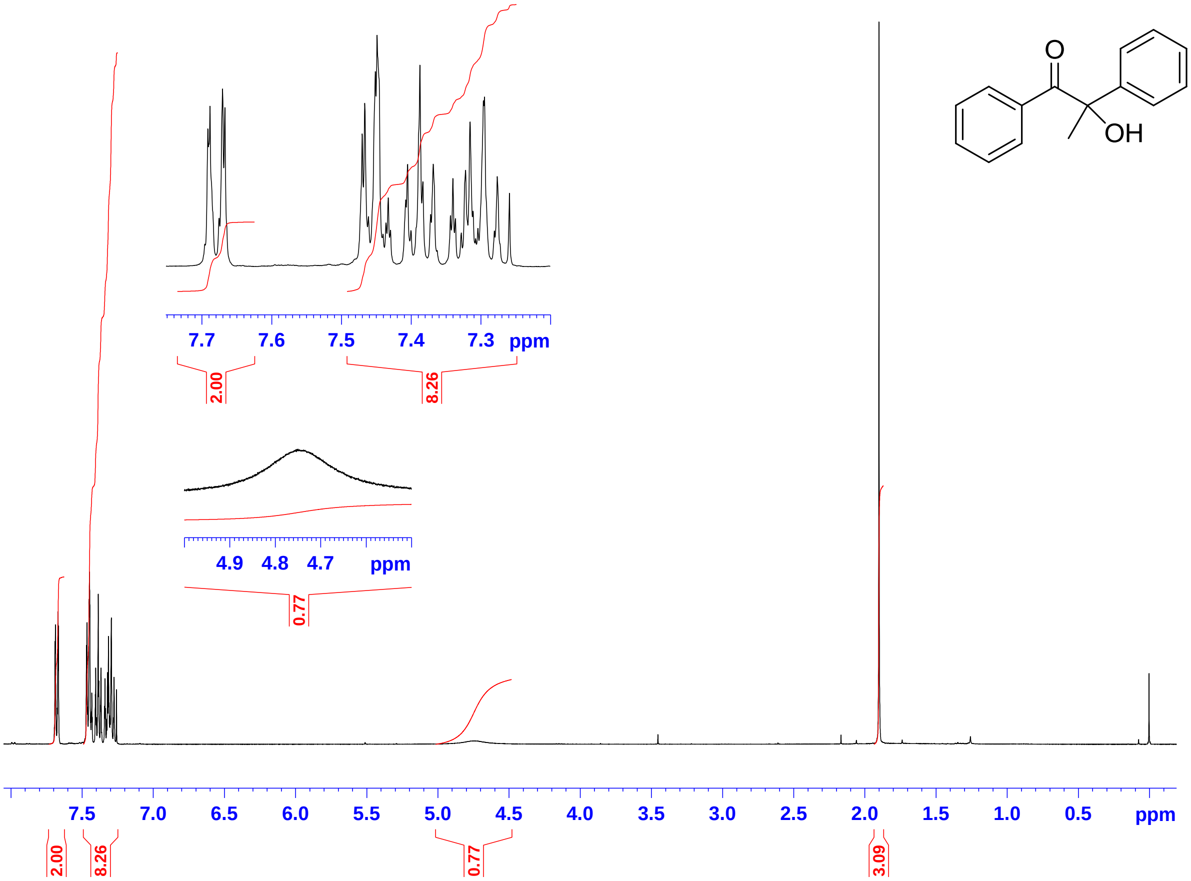
Reactions in the dark. The procedure was similar to that of the previous reaction, except that the reaction flask was wrapped with aluminum foil prior to substrate addition.

Inhibited reactions. The procedure was similar to that of the previous reaction, except that the reaction flask was wrapped with aluminum foil and *m*-dinitrobenzene was added prior to substrate addition.

3. Isolation and Characterization (^{1}H and ^{13}C NMR spectrum)

All synthesized products are known and their spectroscopic data were compared with those available in literature.

α-Methyl benzoin (**2**).[1] The desired product was purified by column chromatography employing diethyl ether:petroleum ether (5:95) and isolated as a white solid (577 mg, 51%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.69 (m, 10H), 4.77 (s, 1H), 1.89 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 202.0, 142.4, 133.0, 130.2, 129.0, 128.3, 125.9, 79.1, 26.0. GC/MS (EI$^+$, 70eV) m/z (%):208(2), 183 (7), 121(100), 105 (39), 78 (7), 77 (38), 76(2), 51 (26).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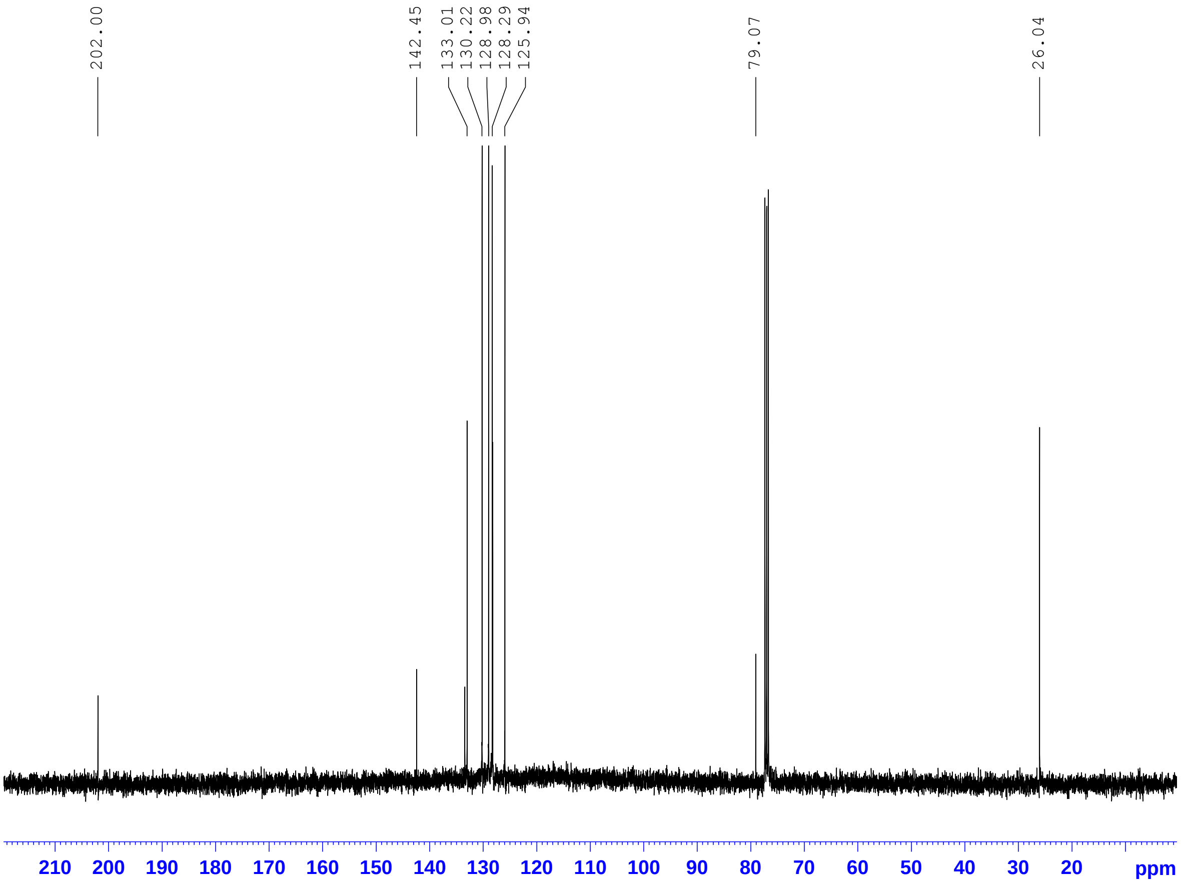
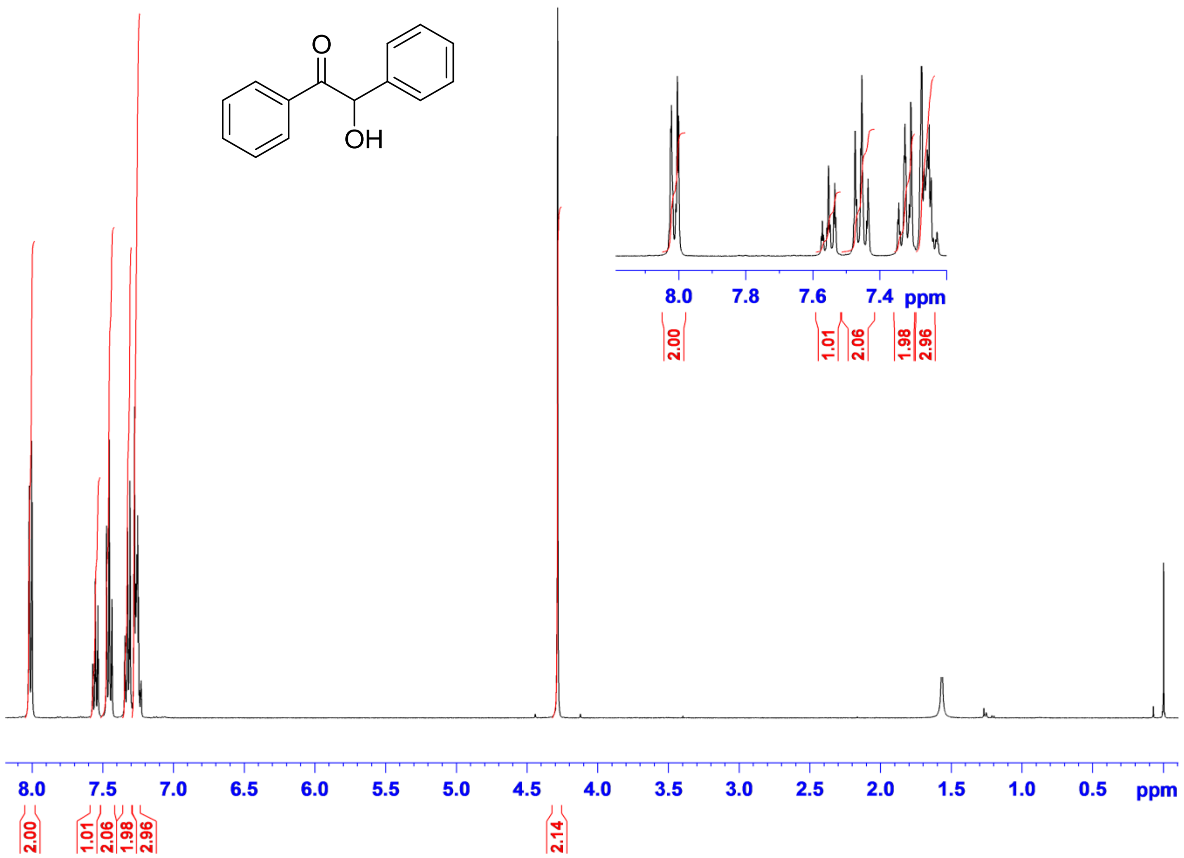


Deoxybenzoin (**5**).[2] The ether layer was dried over $MgSO_4$ and evaporated under reduced pressure to afford a fine white powder (190 mg, 97%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.02-8.05 (m, 2H); 7.55-7.59 (m, 1H), 7.45-7.49 (m, 2H), 7.32-7.36 (m, 2H), 7.24-7.29 (m, 3H), 4.30 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.6, 136.7, 134.6, 133.1, 129.5, 128.64, 128.62, 126.9, 45.5. MS (EI$^+$, 70eV) m/z (%): 196 (3), 106 (8), 105 (100), 91 (5), 77(32), 78 (3), 65 (5), 51(7).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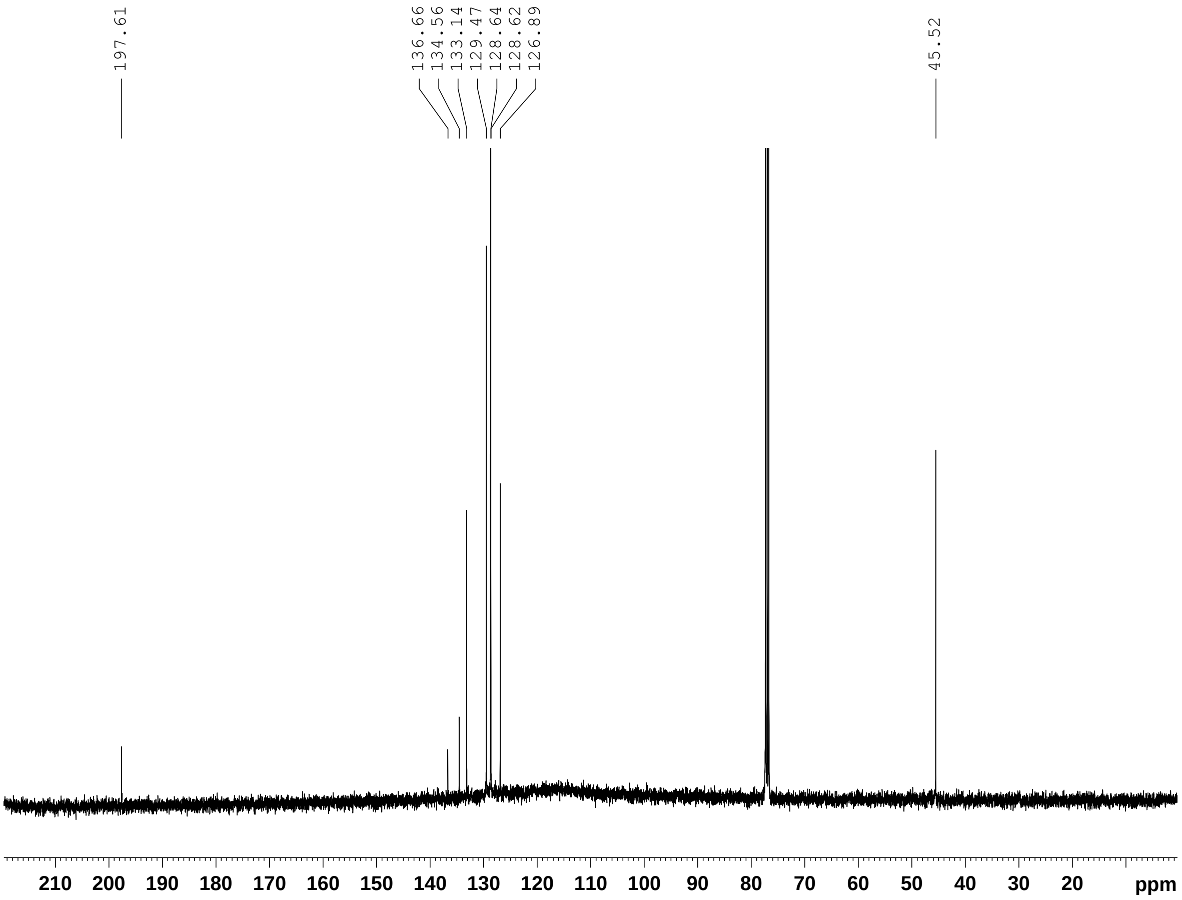
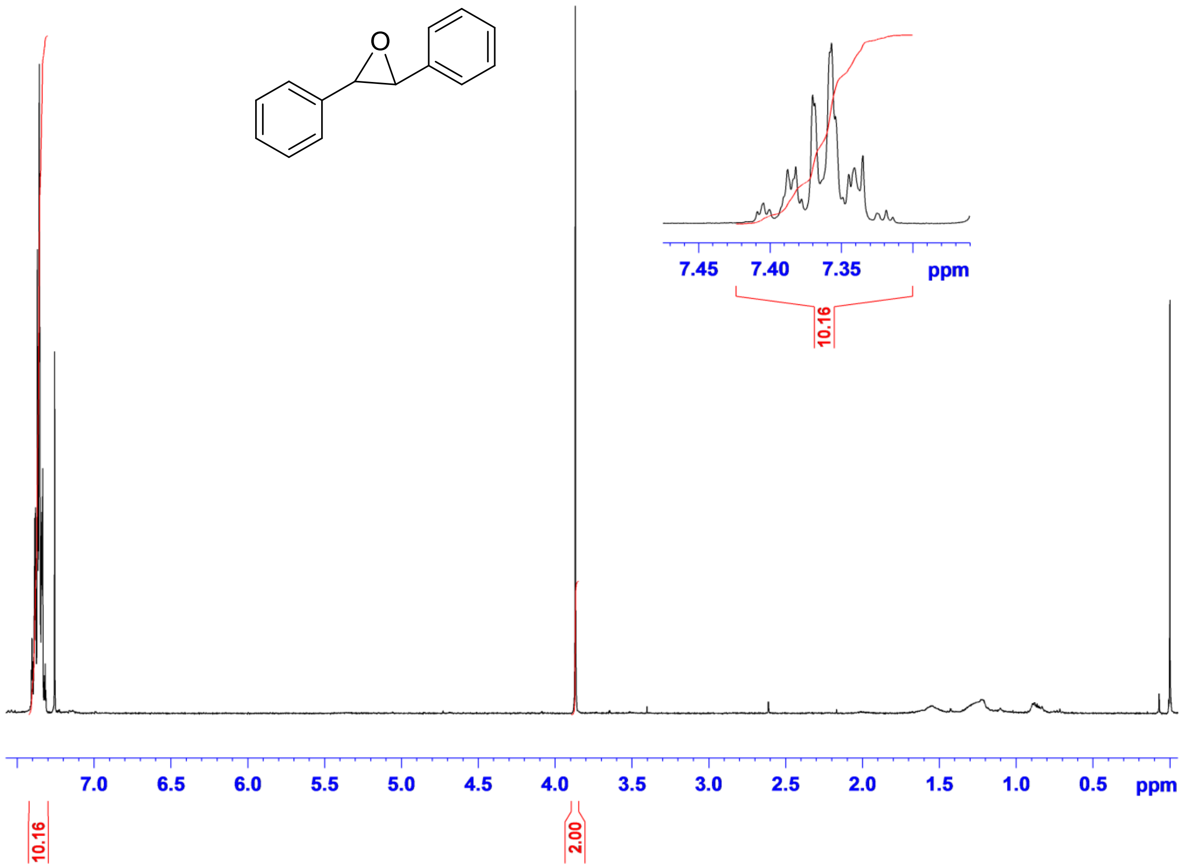


***trans*-Stilbene oxide (6)**.[3] The desired product was purified by column chromatography employing diethyl ether:petroleum ether (5:95) and isolated as a yellowish oil (43 mg, 22%) . ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.40-7.15 (m,10H), 3.88 (s, 2H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 137.1, 128.6, 128.5, 125.5, 62.8. MS (EI$^+$, 70eV) m/z (%): 196 (33), 195 (26), 180 (87), 179 (89), 178 (49), 167 (100), 165 (70), 152 (29), 105 (43), 90 (30), 89 (48), 77 (48), 63 (23); 51 (24).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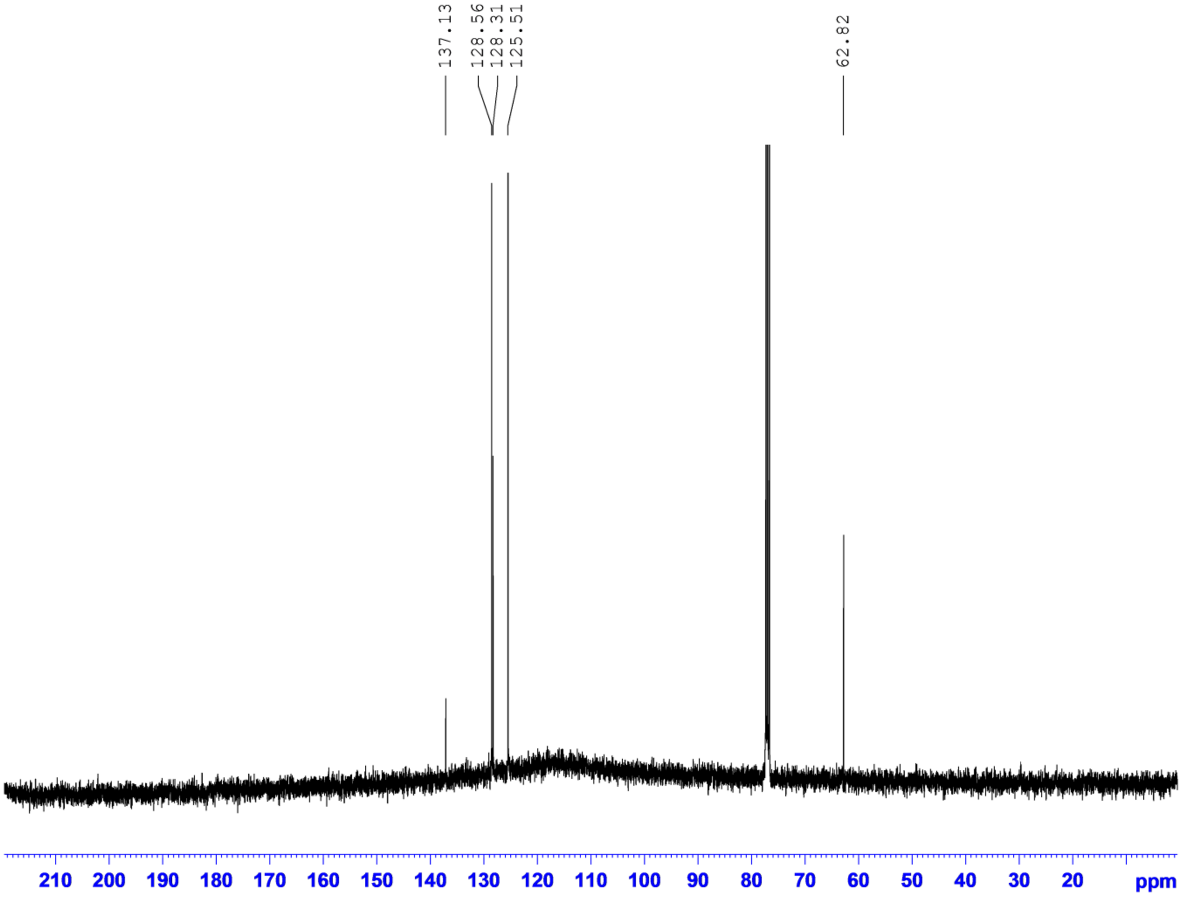
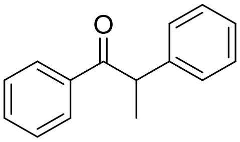
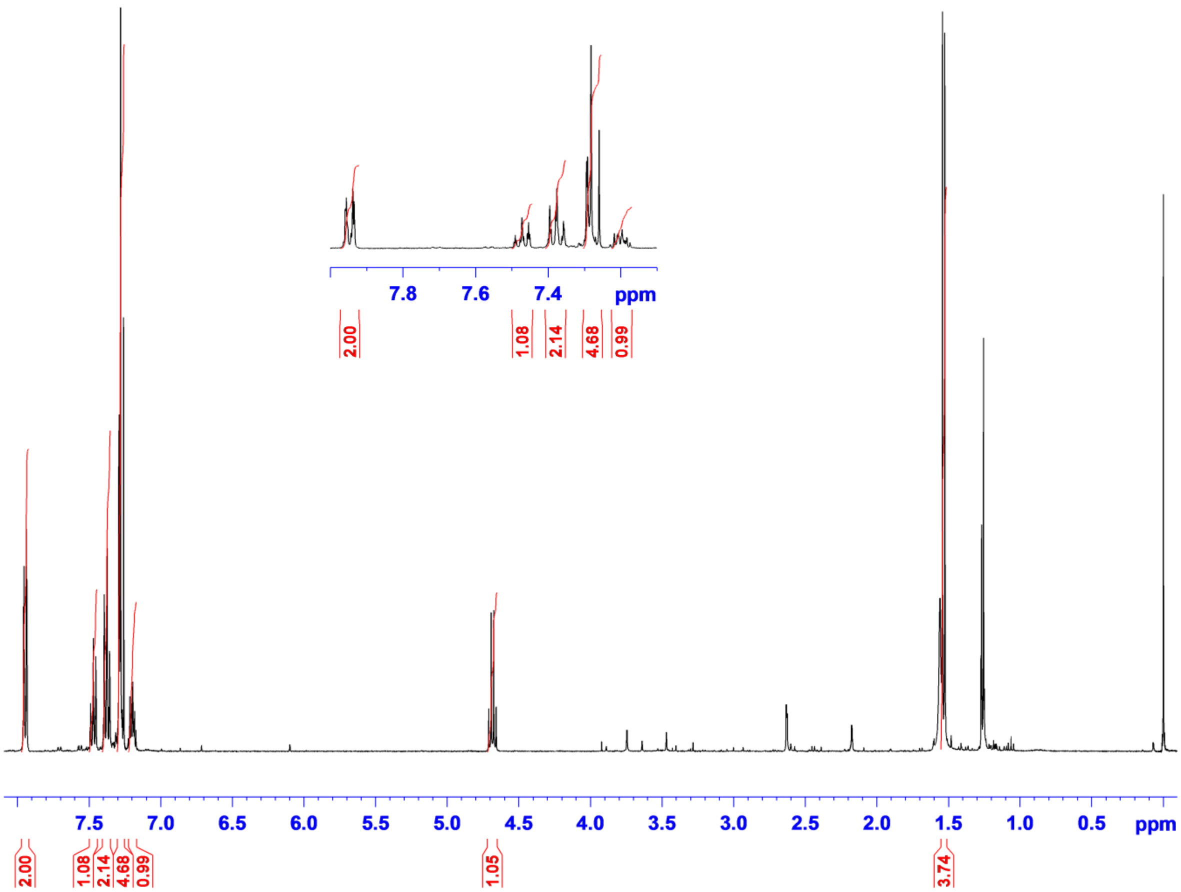


1,2-Diphenylpropan-1-one (**7**).[4] The ether layer was dried over $MgSO_4$ and evaporated under reduced pressure to afford yellowish oil (181 mg, 86%). The desired product was purified by column chromatography employing diethyl ether:petroleum ether (5:95). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, J = 8.0 Hz, 2H), 7.45 (t, J = 8.0 Hz, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.27-7.25 (m, 4H), 7.19-7.17 (m, 1H), 4.67 (q, J = 7.0 Hz, 1H), 1.51 (d, J = 7.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 200.3, 141.5, 136.5, 132.7, 129.0, 128.8, 128.5, 127.8, 126.9, 47.9, 19.5. MS (EI^+, 70eV) m/z (%): 210 (M^+) (1), 208 (4), 183 (3), 165 (2), 122 (15), 121 (100), 106 (6), 105 (57), 103 (3), 78 (11), 77 (56), 51 (23).

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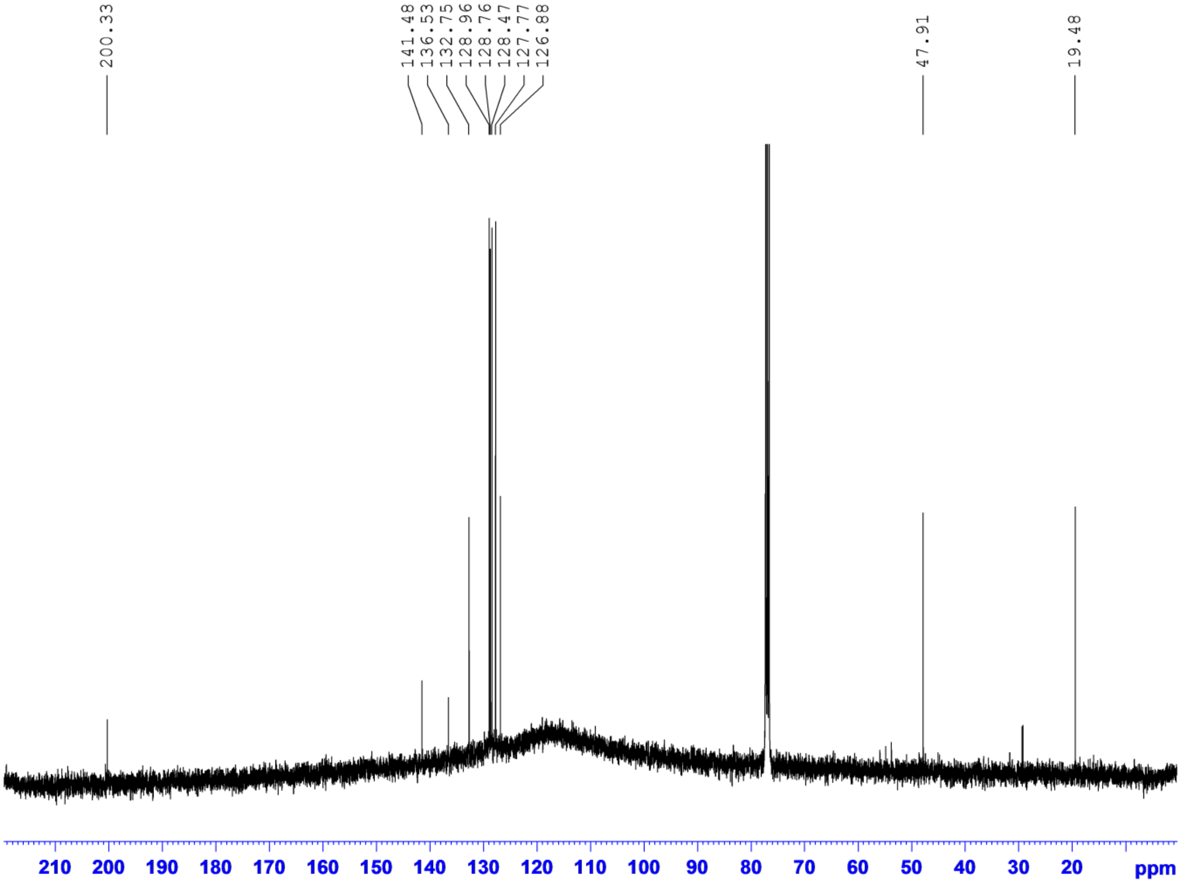
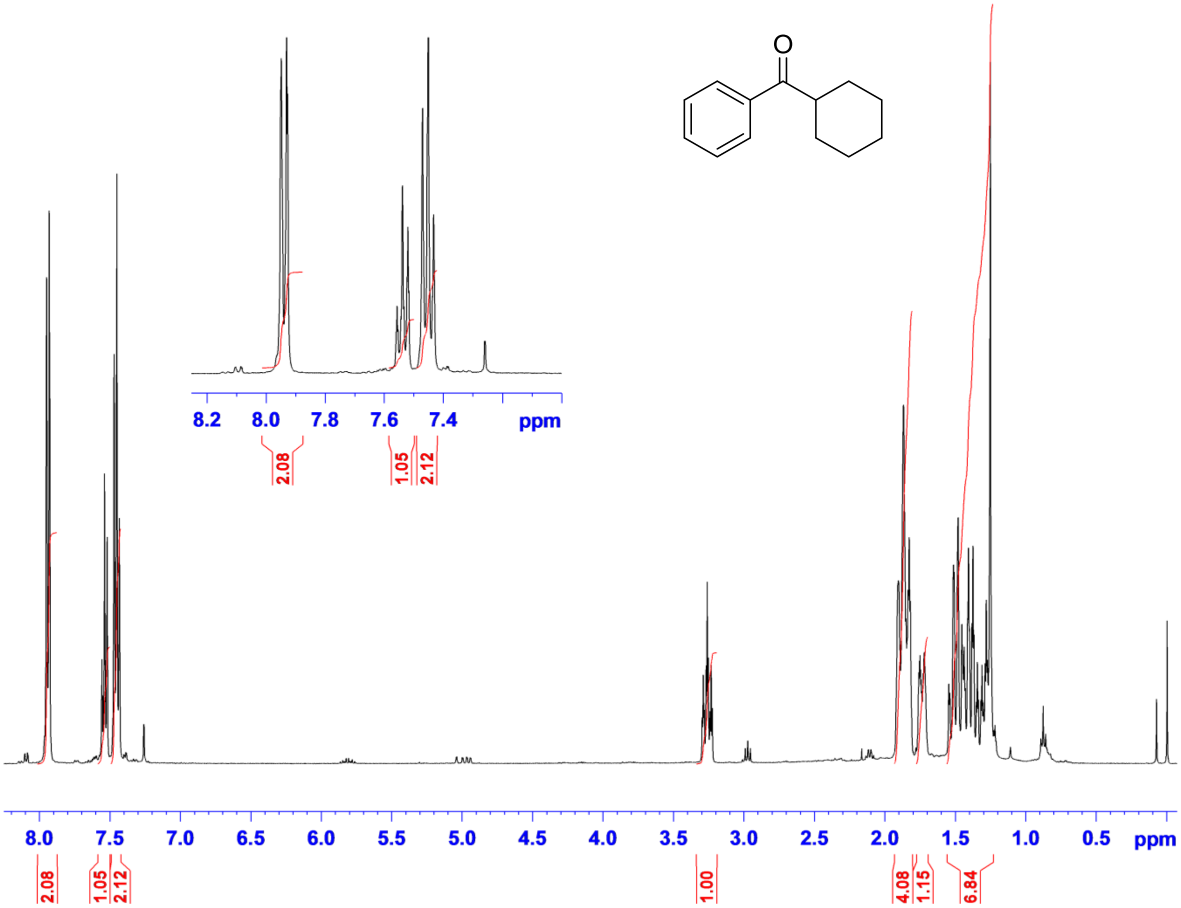


Cyclohexyl(phenyl)methanone (**8**).[5] The ether layer was dried over $MgSO_4$ and evaporated under reduced pressure to afford a yellowish oil (122 mg, 65%). The product was isolated from experiments with $(EtO)_2PO^-$ ions. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.94-7.96 (2H, m), 7.53-7.56 (1H, m), 7.45-7.48 (2H, m), 3.27 (1H, tt, *J* = 11.3, 3.3 Hz), 1.84-1.92 (4H, m), 1.47-1.55 (2H, m), 1.36-1.43 (2H, m), 1.22-1.34 (2H, m). ^{13}C NMR (100MHz, $CDCl_3$): 203.9, 136.4, 132.7, 128.6, 128.3, 45.6, 29.4, 26.0, 25.9. MS (EI^+, 70eV) m/z (%):189 (3), 188 (22), 133 (11), 120 (6), 107 (3), 106 (8), 105 (100), 78 (3), 77 (30), 55 (7), 51 (5).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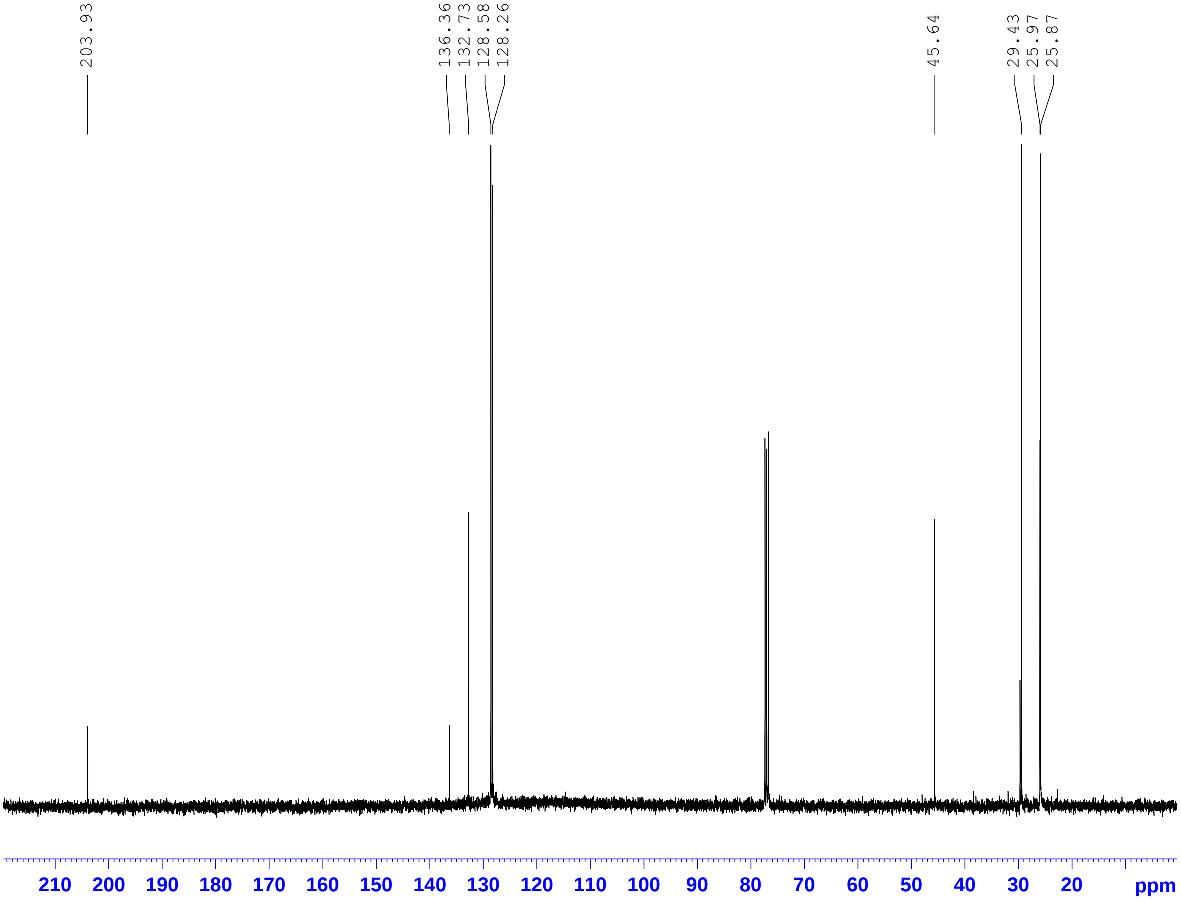
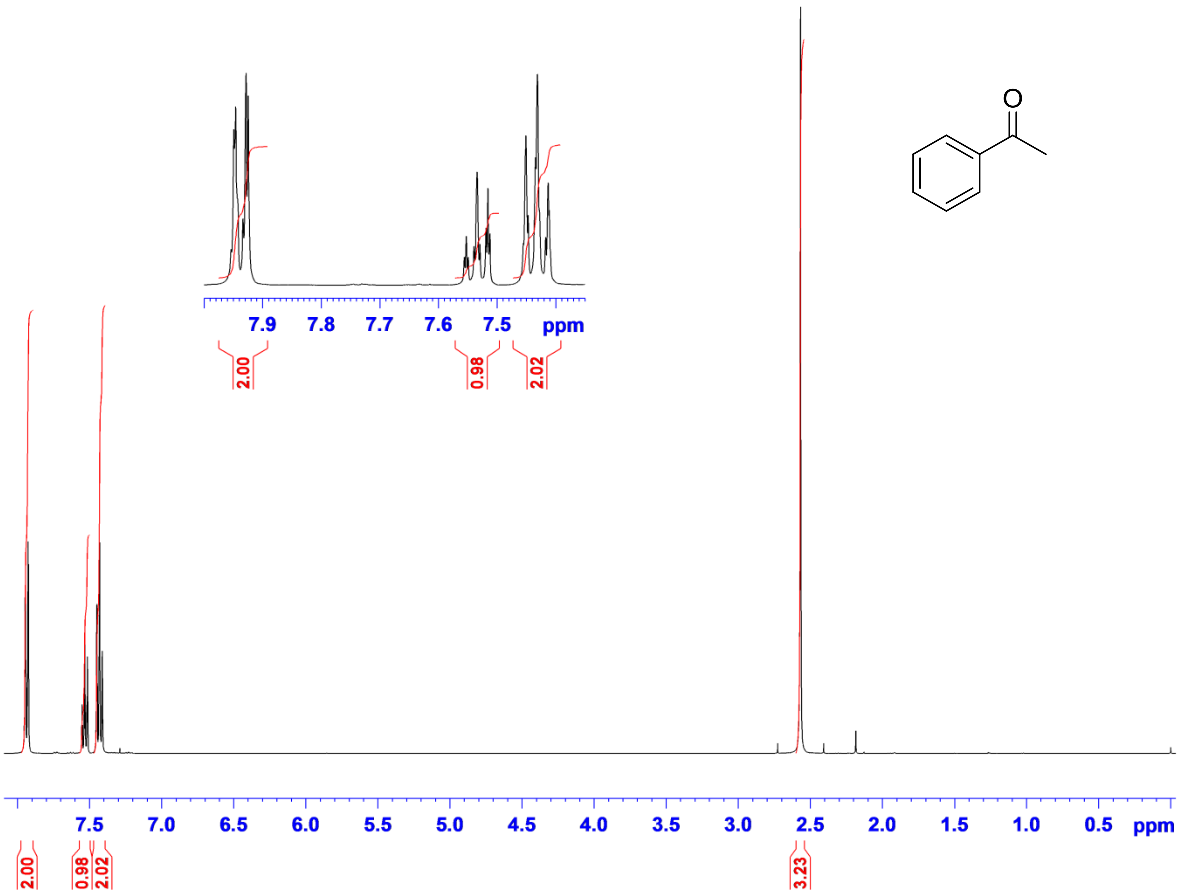


1,2-Epoxy-1-phenyl-cyclohexane (**9**).[6] The compound yield was less than 9% (GC). Consequently, it was identified by GC/MS. MS (EI$^+$, 70eV) m/z (%):188 (9), 129 (18), 117 (16), 115 (19), 105 (21), 104 (24), 91 (100), 81 (32), 79 (26), 77 (23), 67 (20), 65 (15).

Acetophenone (**10**).[7] The product was purified after chromatographic column employing diethyl ether:petroleum ether (2:98) and isolated as colorless oil (72 mg, 60%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.90-7.98 (m, 2 H), 7.51-7.57 (m, 1 H), 7.40-7.47 (m, 2 H), 2.57 (s, 3 H).^{13}C NMR (CDCl$_3$, 100 MHz) δ 198.0, 137.1, 133.0, 128.5, 128.3, 26.5. MS (EI$^+$, 70eV) m/z (%): 121 (3) 120 (35) 119 (5), 106 (8), 105 (100), 92 (5), 91 (13), 90 (6), 89 (8), 78 (10), 77 (84), 74 (5), 65 (5), 63 (5), 51 (23), 50 (10).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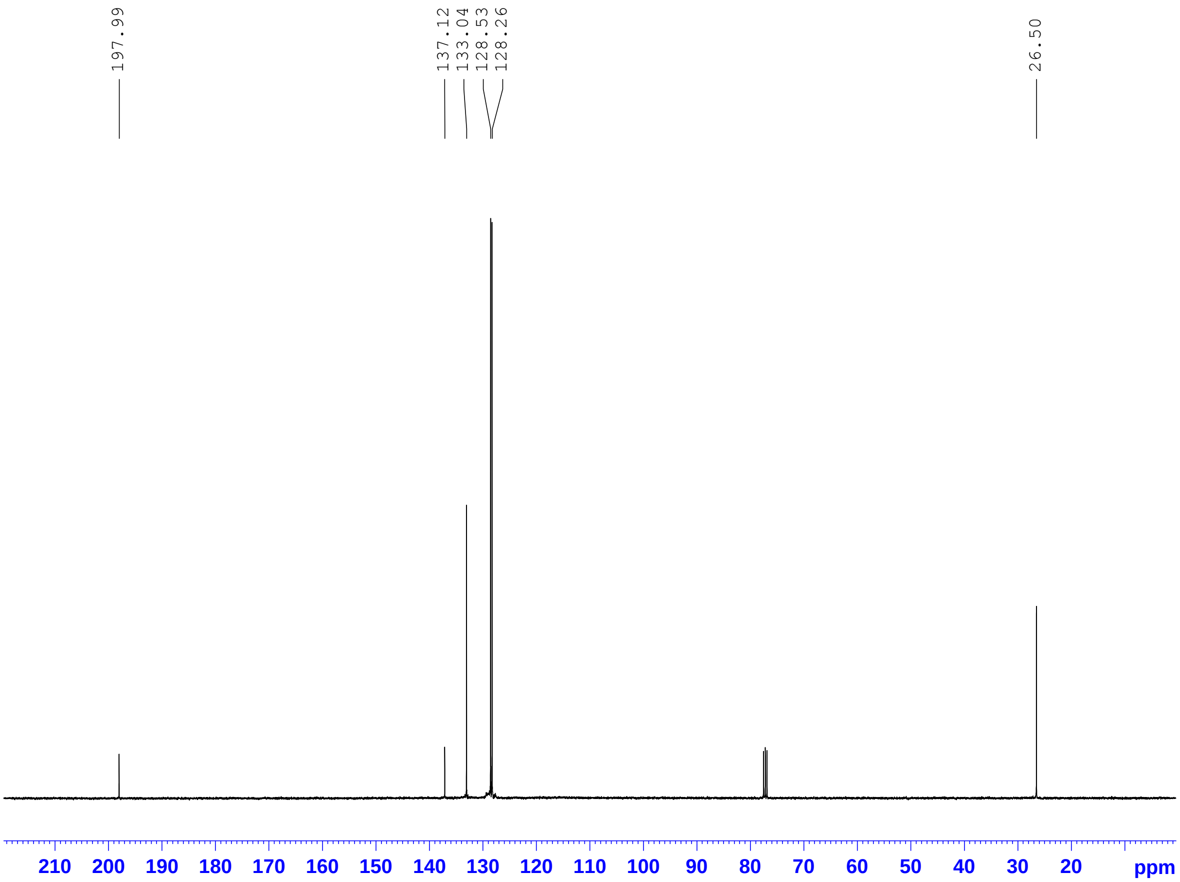
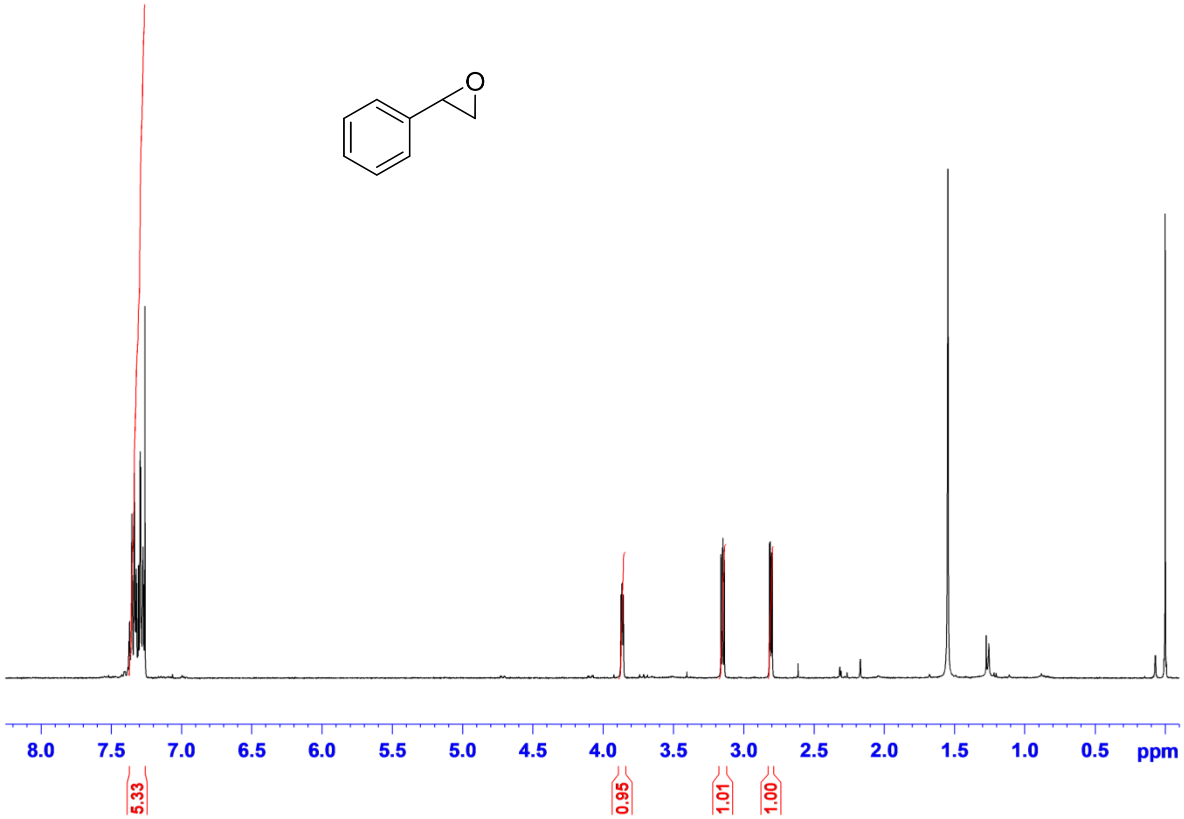


Phenyloxirane (**11**).[2] The product was purified after chromatographic column employing diethyl ether:petroleum ether (2:98) and isolated as colorless oil (12 mg, 10%). ^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.16-7.29 (m, 5 H); 3.78 (dd, *J* = 4.2, 2.6 Hz, 1 H), 3.06 (dd, *J* =5.6, 4.2 Hz, 1 H), 2.72 (dd, *J* =5.6, 2.6 Hz, 1 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ 51.3, 52.5, 125.6, 128.3, 128.6, 137.7. GC/MS (EI$^+$, 70eV) m/z (%): 120 (M$^+$, 41), 119 (65), 92 (37), 91 (100), 90 (64), 89 (79).



4. References

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[2] H. O. House, *J. Am. Chem. Soc.* 1955, ***77***, 3070.

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[7] B. Rickborn and R. M. Gerkin, *J. Am. Chem. Soc.* 1968, ***90***, 4193.