Supporting Information

A Metal-Free, One-Pot Procedure for the Synthesis of α,β-Epoxy Ketones by Oxidative Coupling of Alkenes and Aldehydes with Base Catalysis

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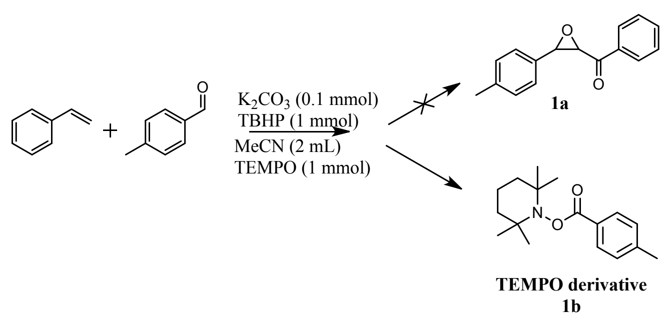
S1. Experimental Section

1. General. All the reagents were of analytical grade and used as received without further purification. N,N-dimethylformamide (DMF), acetonitrile (MeCN) and dimethyl sulfoxide (DMSO) were purchased from Amethyst Chemicals. Other reagents were obtained from Shanghai Chemical Reagents. Silica gel plates were used for thin-layer chromatography (TLC) and compounds were visualized using UV light. Solvents were distilled prior to use.

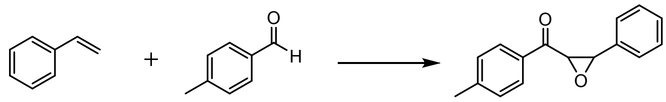
2. Reaction procedure. The catalyst (0.1 mmol), MeCN (2 mL), TBHP (70% in water, 1 mmol), styrene (0.5 mmol) and benzaldehyde (1 mmol) were all introduced into the reactor. A typical reaction mixture consisted of K_2CO_3 (13.8 mg), MeCN (2 mL), TBHP (70% in water, 95 μL), styrene (52 μL) and 4-methyl benzaldehyde (120 μL). The mixture was stirred at 100 °C for 12–24 h, after which H_2O (5 mL) and CH_2Cl_2 (5 mL) were added, the phases were separated and the organic layer was washed with water (2×5 mL). The organic phase was subsequently evaporated under reduced pressure to give the crude product. The GC yields were determined using an Agilent 7890 equipped with an HP-5 column (30 m × 0.25 mm). The product was purified by column chromatography on silica gel (50:1 petroleum ether/ethyl acetate).

3. Characterization. ^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded at 20 °C using $CDCl_3$ as the solvent. Chemical shifts are given in parts per million relative to TMS as the internal standard.



Scheme S1. Effect of adding TEMPO on the oxidative coupling reaction.

Table S1. Role of K_2CO_3 in the oxidative coupling reaction.



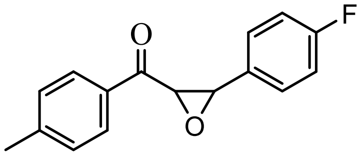
1a

Entry	Additive	Yield (%)
1	K_2CO_3	46
2	K_2CO_3, TBHP	90
3	TBHP	0
4[a]	-	0

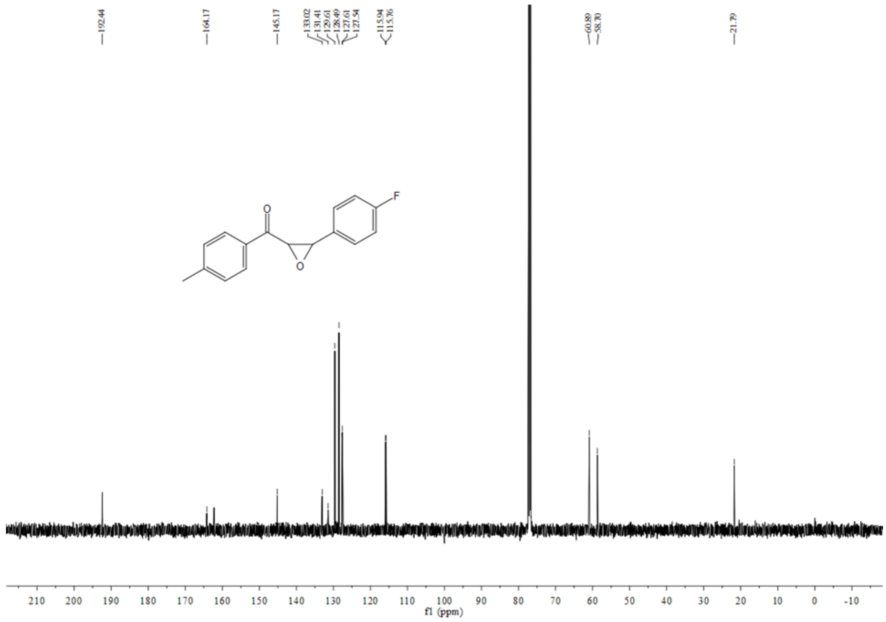
Reaction conditions: aldehyde substrate (1 mmol), styrene (0.5 mmol), TBHP (1 mmol), and MeCN (2 mL) under air at 100 °C for 12 h. Isolated yield. This coupling reaction was performed in MeCN solvent (N_2 degassed).

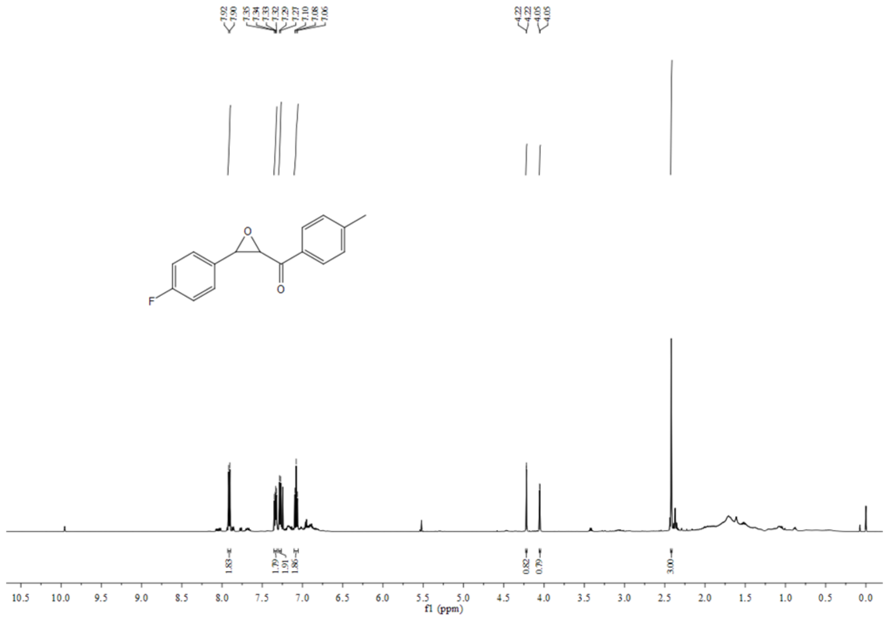
S2. NMR data

(1) **(3-(4-fluorophenyl)oxiran-2-yl)(p-tolyl)methanone**

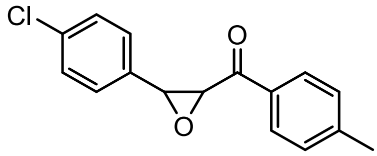


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.32 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.10 (t, *J* = 8.5 Hz, 2H), 4.24 (s, 1H), 4.06 (s, 1H), 2.43 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 192.44 (s), 164.17 (s), 145.17 (s), 133.02 (s), 131.41 (s), 129.61 (s), 128.49 (s), 127.58 (d, *J* = 8.4 Hz), 115.94 (s), 115.76 (s), 60.89 (s), 58.70 (s), 21.79 (s).

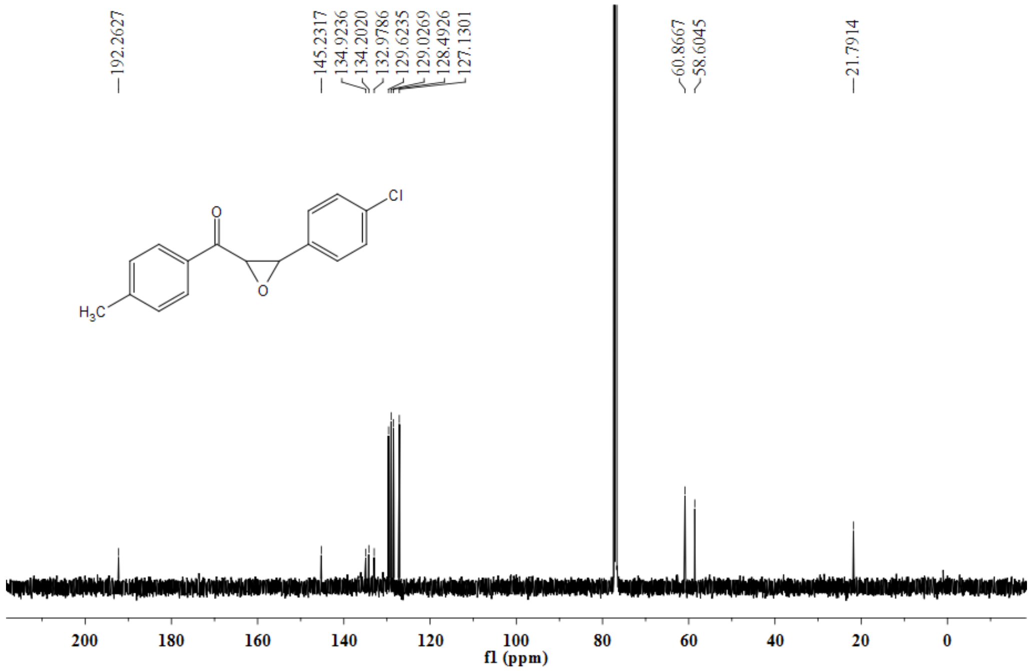


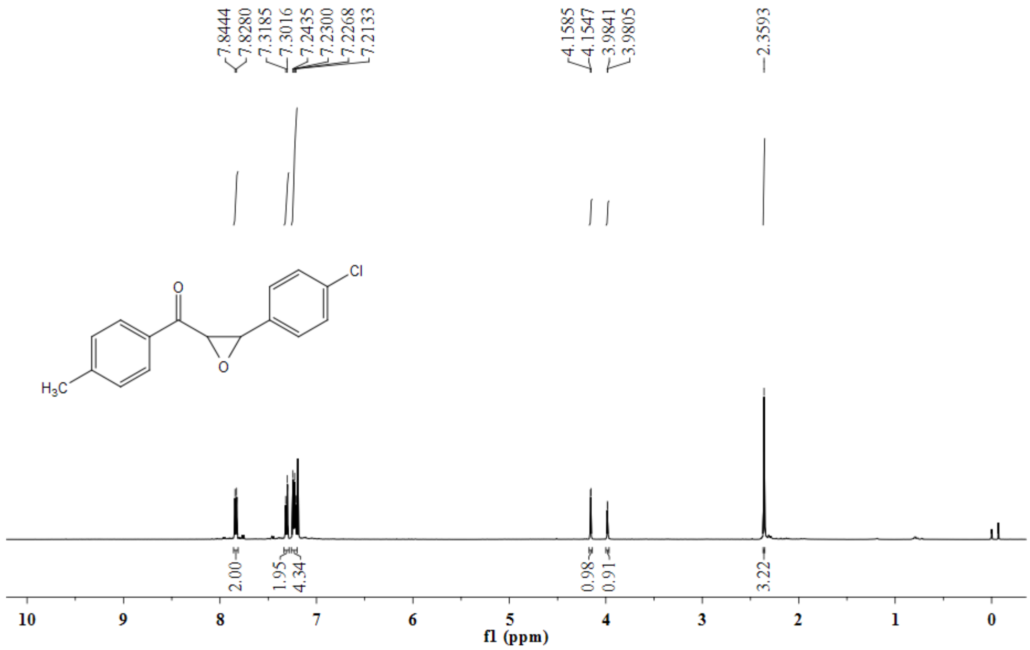


(2) **(3-(4-chlorophenyl)oxiran-2-yl)(p-tolyl)methanone**

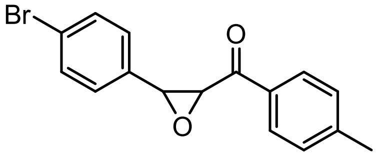


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.26 (s), 145.23 (s), 134.92 (s), 134.20 (s), 132.98 (s), 129.62 (s), 129.03 (s), 128.49 (s), 127.13 (s), 60.87 (s), 58.60 (s), 21.79 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (d, 2H), 7.31 (d, J = 8.5 Hz, 2H), 7.23 (dd, J = 8.4, 6.8 Hz, 4H), 4.16 (d, J = 1.9 Hz, 1H), 3.98 (d, J = 1.8 Hz, 1H), 2.36 (s, 3H).

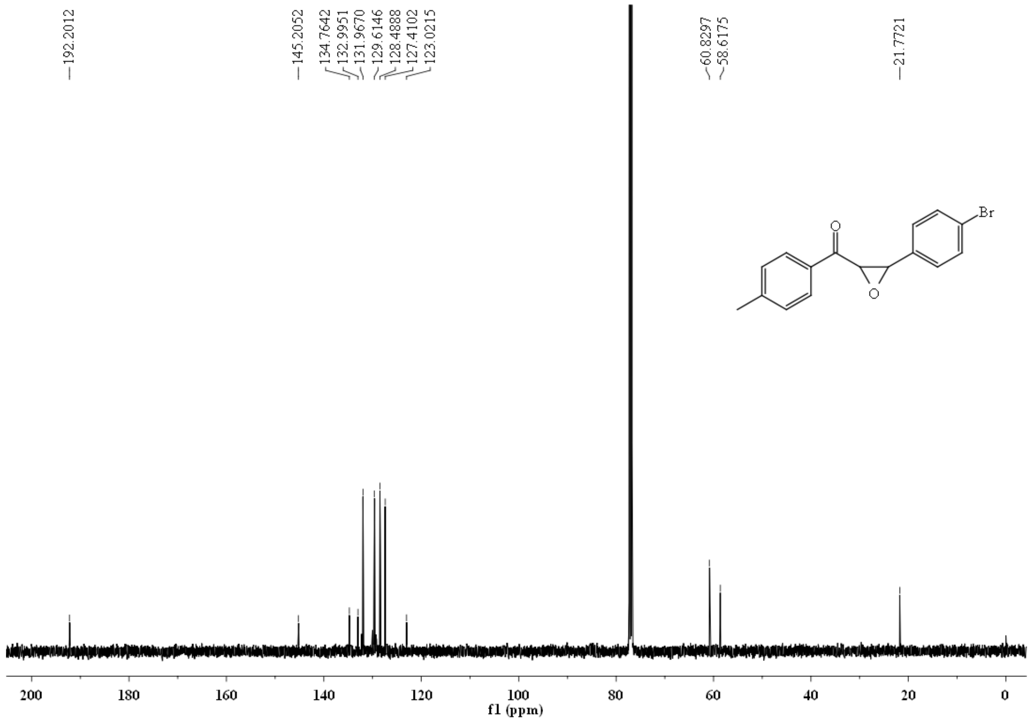


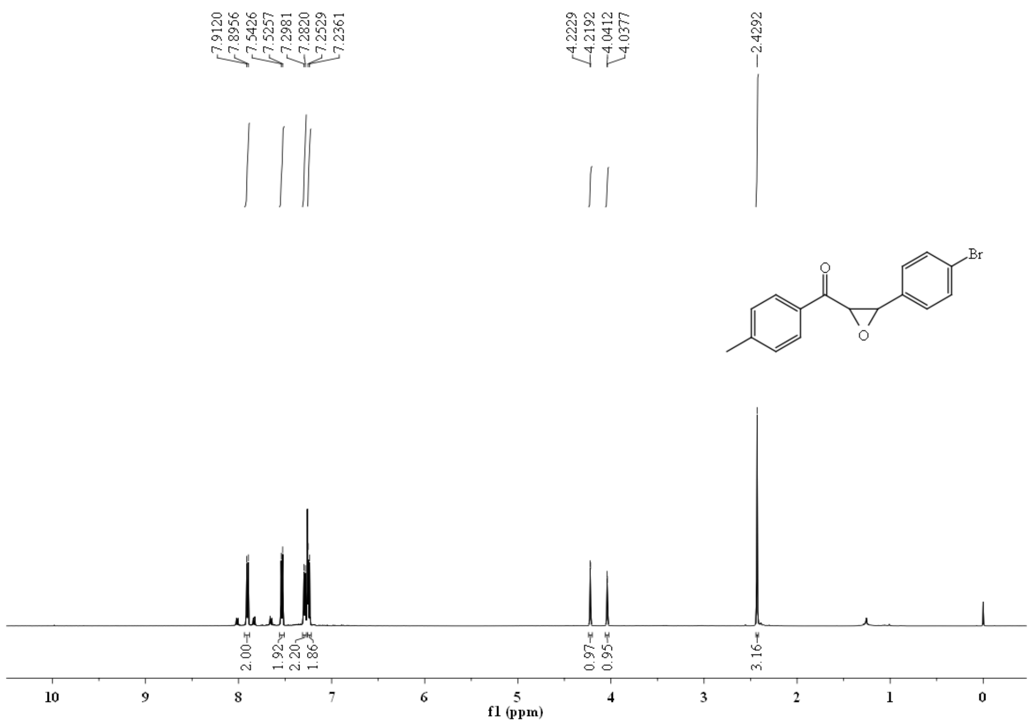


(3) **(3-(4-bromophenyl)oxiran-2-yl)(p-tolyl)methanone**

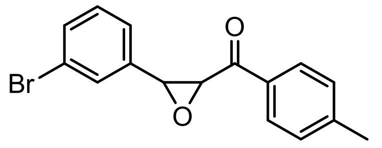


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.20 (s), 145.21 (s), 134.76 (s), 133.00 (s), 131.97 (s), 129.61 (s), 128.49 (s), 127.41 (s), 123.02 (s), 60.83 (s), 58.62 (s), 21.77 (s).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, J = 8.2 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 4.22 (d, J = 1.8 Hz, 1H), 4.04 (d, J = 1.7 Hz, 1H), 2.43 (s, 3H).

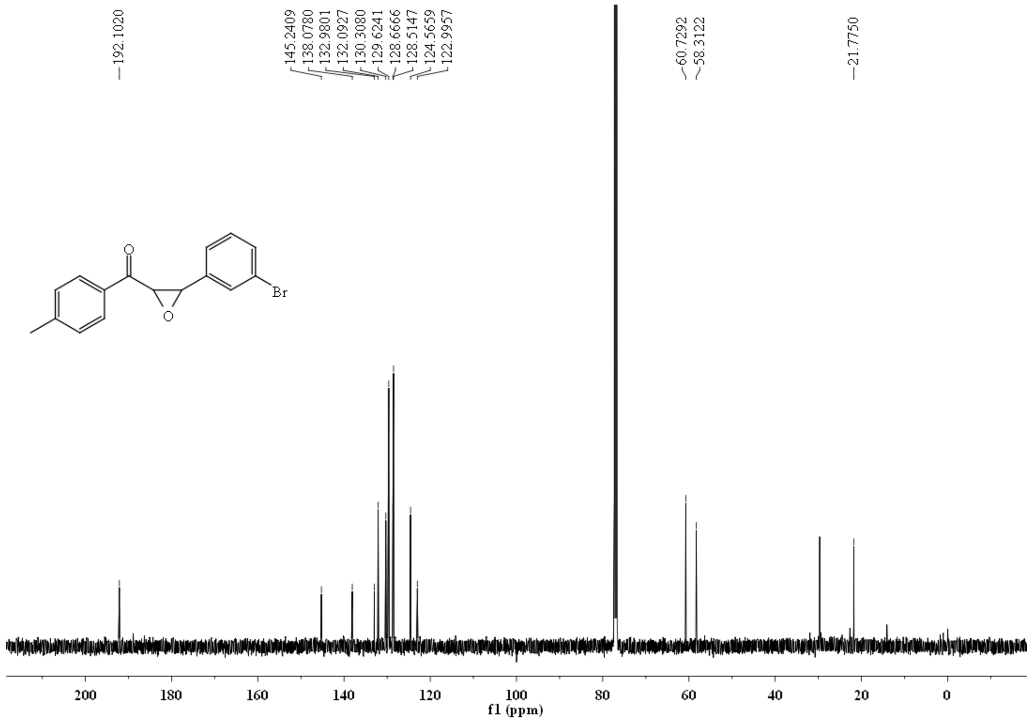


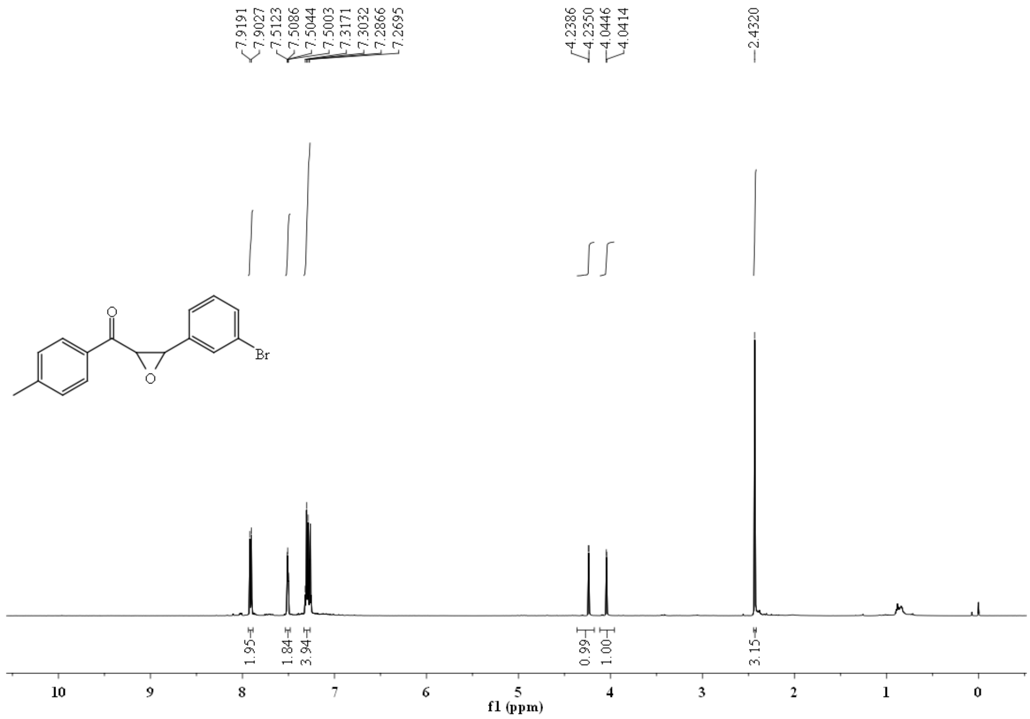


(4) **(3-(3-bromophenyl)oxiran-2-yl)(p-tolyl)methanone**

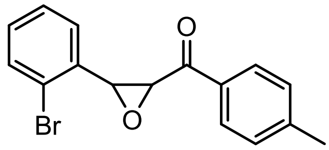


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.10 (s), 145.24 (s), 138.08 (s), 132.98 (s), 132.09 (s), 130.31 (s), 129.62 (s), 128.59 (d, J = 19.1 Hz), 124.57 (s), 123.00 (s), 60.73 (s), 58.31 (s), 21.78 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz, 2H), 7.51 (dd, J = 4.0, 1.9 Hz, 2H), 7.33 – 7.27 (m, 4H), 4.24 (d, J = 1.8 Hz, 1H), 4.04 (d, J = 1.6 Hz, 1H), 2.43 (s, 3H).

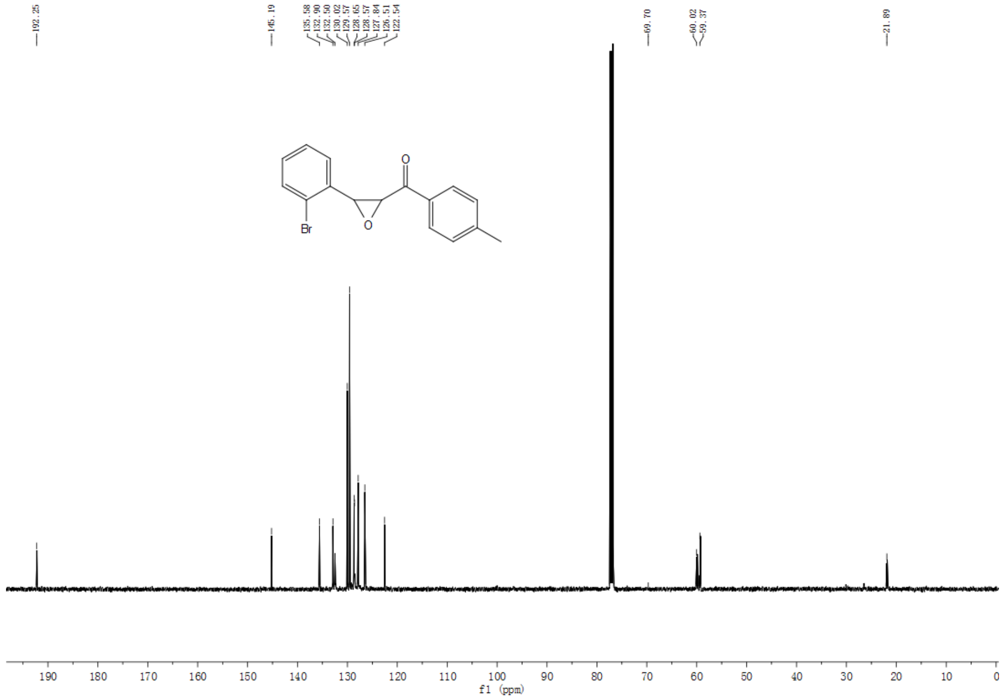


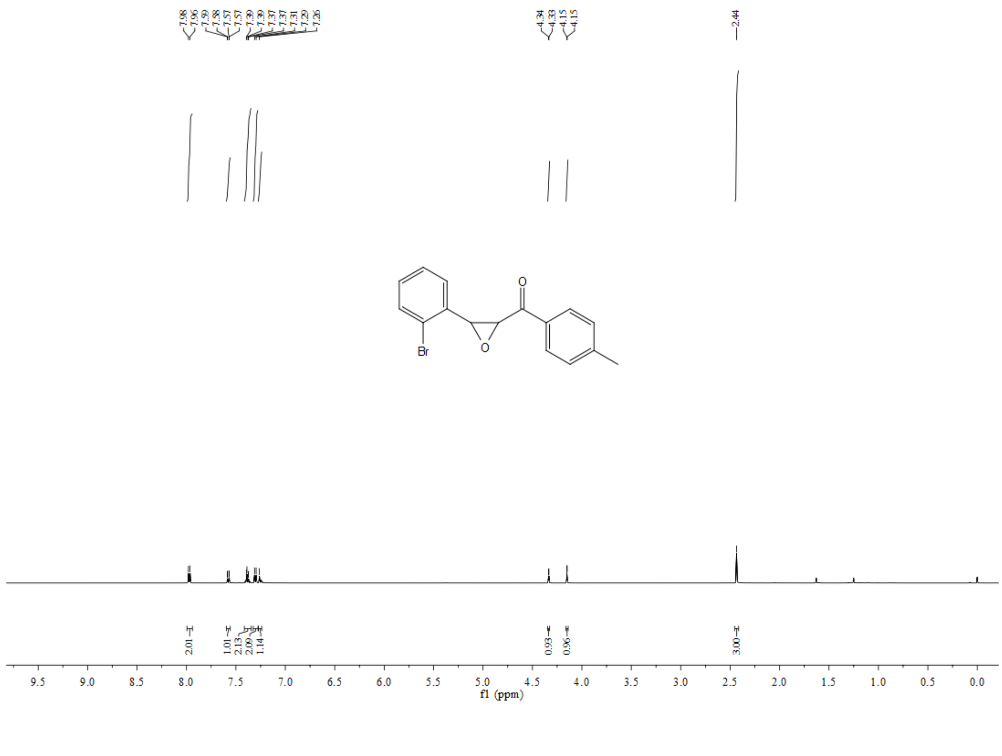


(5) **(3-(2-bromophenyl)oxiran-2-yl)(p-tolyl)methanone**

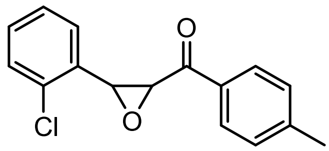


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.25 (s), 145.19 (s), 135.58 (s), 132.70 (d, J = 49.3 Hz), 130.02 (s), 129.57 (s), 128.61 (d, J = 10.2 Hz), 127.84 (s), 126.51 (s), 122.54 (s), 60.02 (s), 59.37 (s), 21.89 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, J = 8.2 Hz, 2H), 7.58 (dd, J = 8.0, 0.7 Hz, 1H), 7.38 (dd, J = 8.7, 1.5 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.26 (s, 1H), 4.34 (d, J = 1.9 Hz, 1H), 4.15 (d, J = 1.9 Hz, 1H), 2.44 (s, 3H).

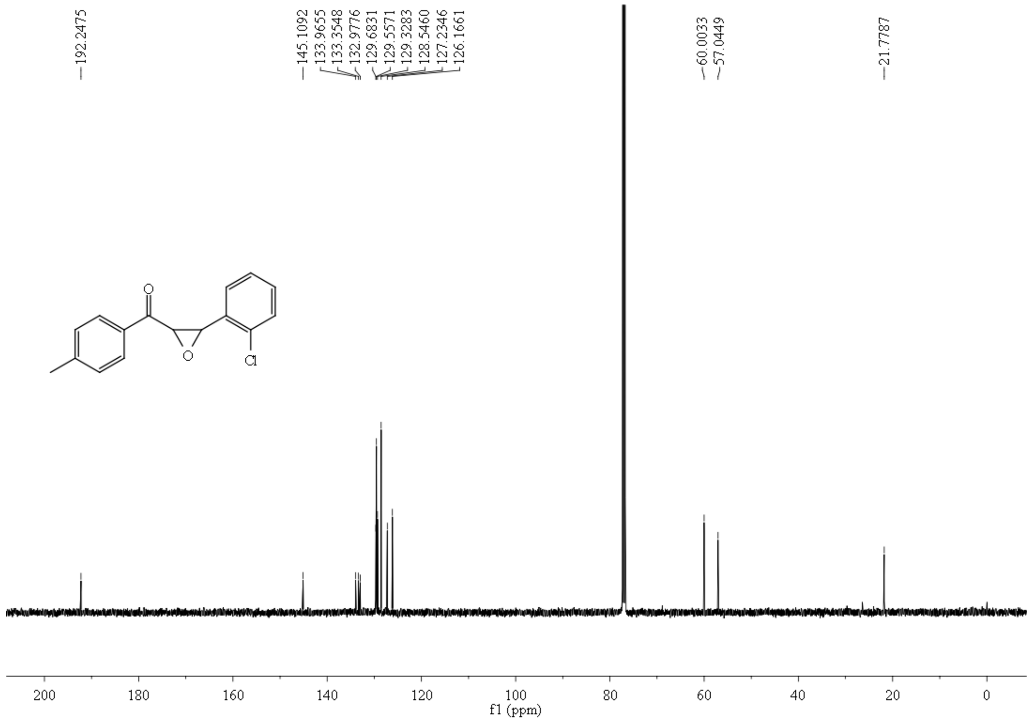


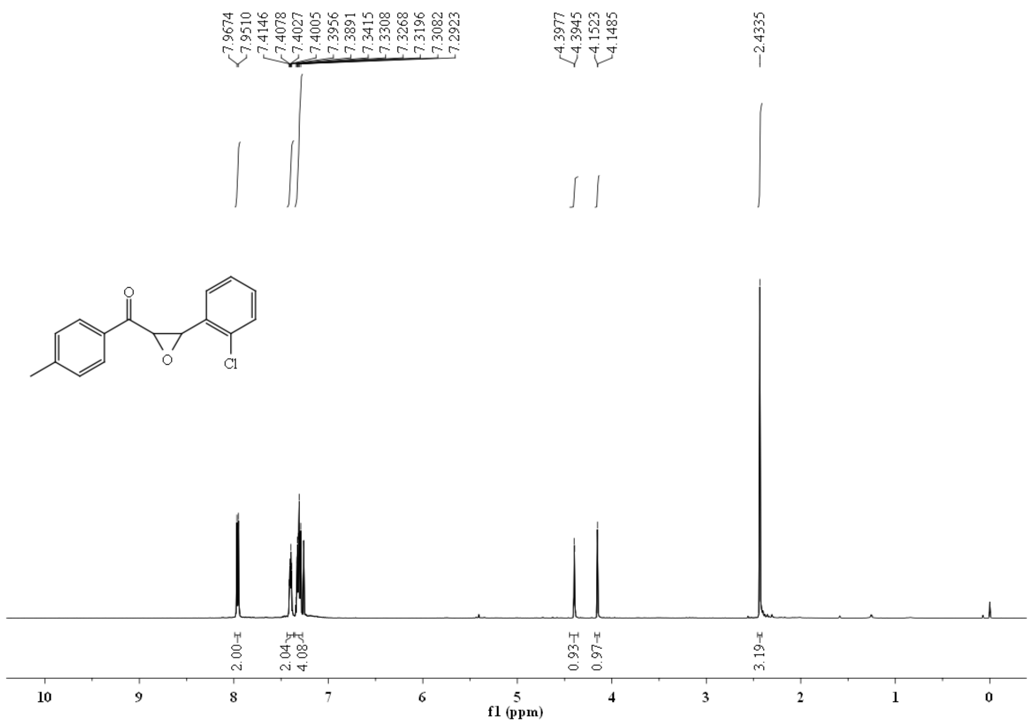


(6) **(3-(2-chlorophenyl)oxiran-2-yl)(p-tolyl)methanone**

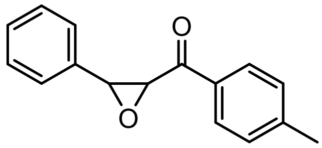


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.25 (s), 145.11 (s), 133.97 (s), 133.35 (s), 132.98 (s), 129.62 (d, J = 15.8 Hz), 129.33 (s), 128.55 (s), 127.23 (s), 126.17 (s), 60.00 (s), 57.04 (s), 21.78 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, 2H), 7.44 – 7.37 (m, 2H), 7.35 – 7.27 (m, 4H), 4.40 (d, J = 1.6 Hz, 1H), 4.15 (d, J = 1.9 Hz, 1H), 2.43 (s, 3H).

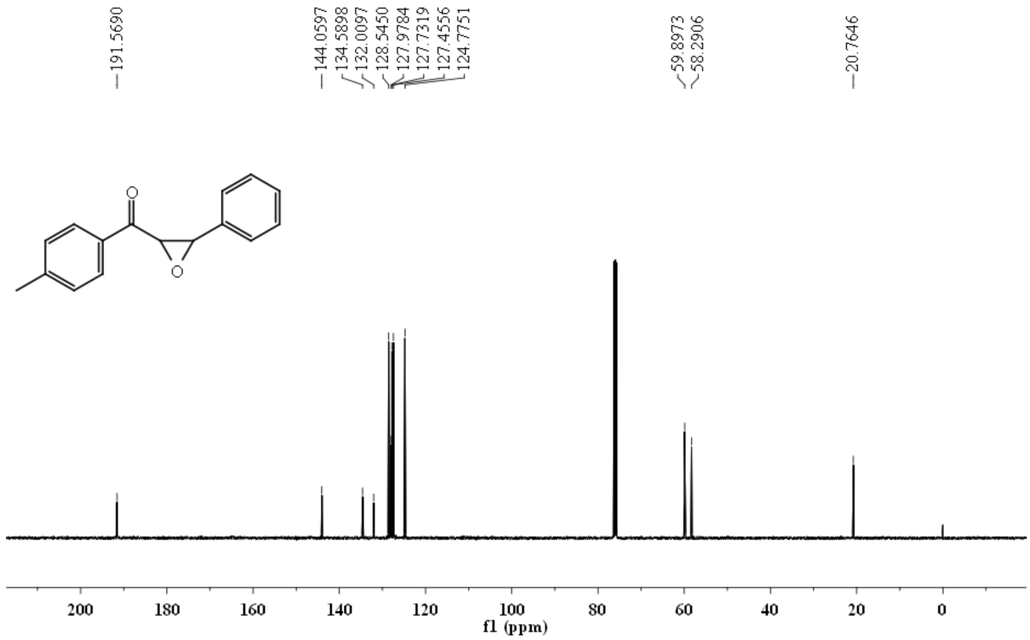


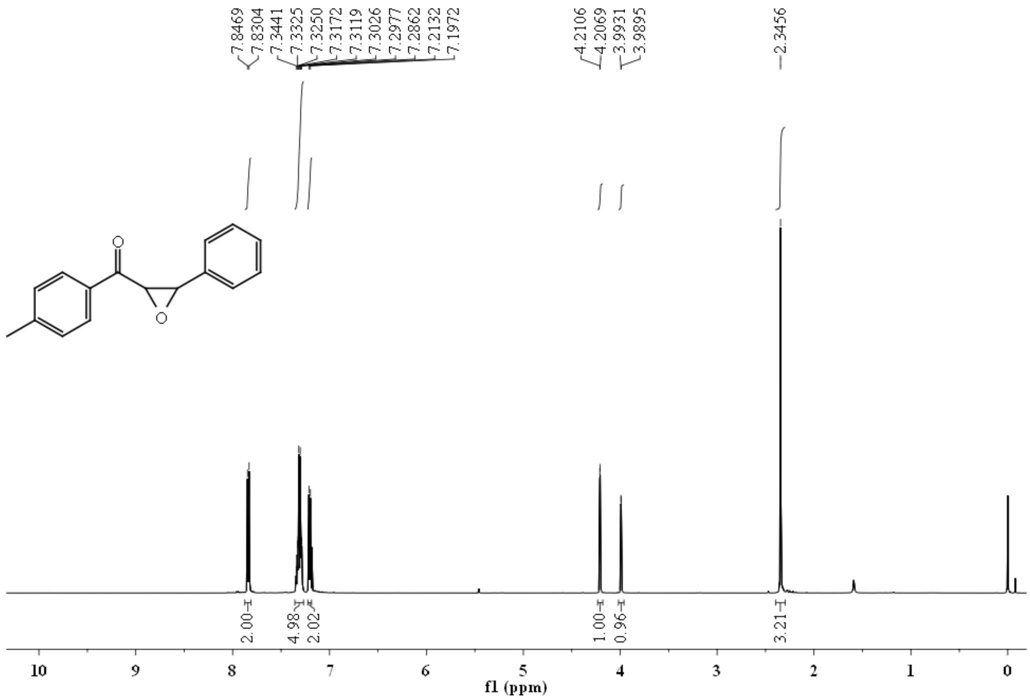


(7) **(3-phenyloxiran-2-yl)(p-tolyl)methanone**

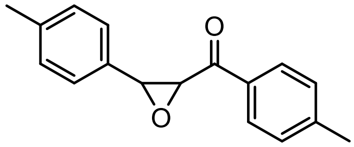


^{13}C NMR (125 MHz, $CDCl_3$) δ 191.57 (s), 144.06 (s), 134.59 (s), 132.01 (s), 128.55 (s), 127.98 (s), 127.73 (s), 127.46 (s), 124.78 (s), 59.90 (s), 58.29 (s), 20.76 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, J = 8.2 Hz, 2H), 7.36 – 7.27 (m, 5H), 7.21 (d, J = 8.0 Hz, 2H), 4.21 (d, J = 1.9 Hz, 1H), 3.99 (d, J = 1.8 Hz, 1H), 2.34 (d, J = 7.8 Hz, 3H).

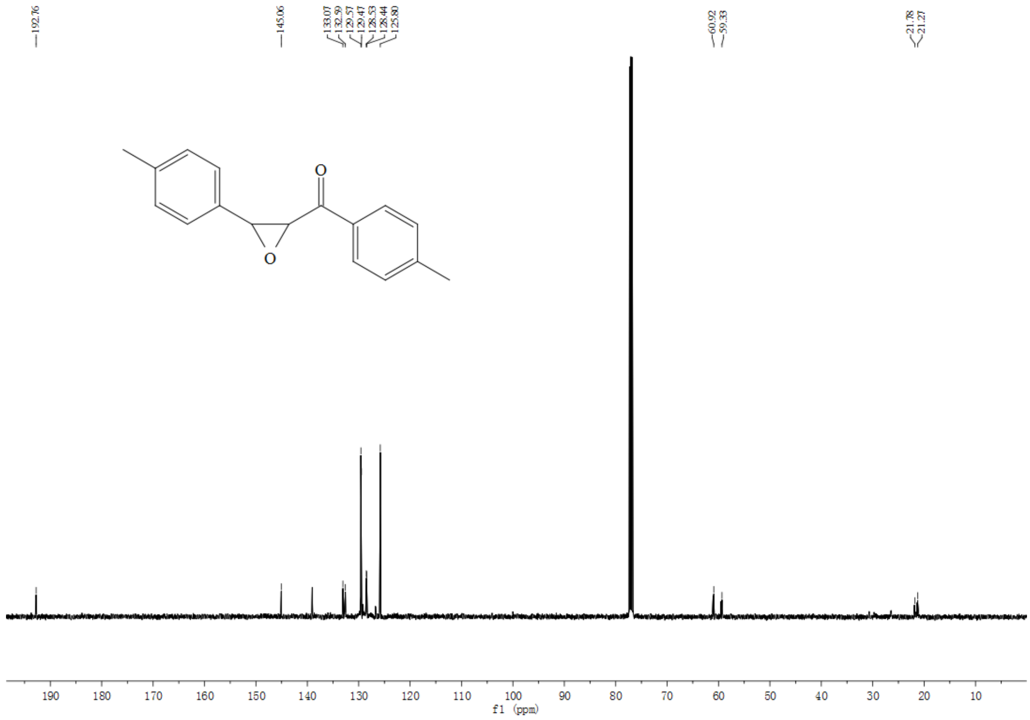


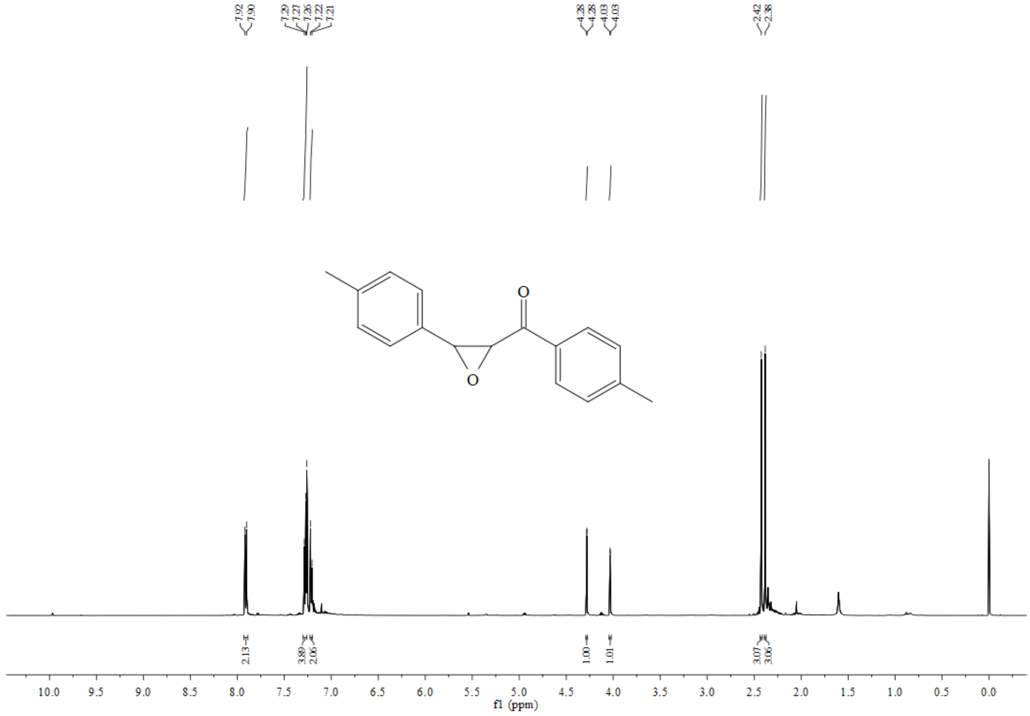


(8) p-tolyl(3-p-tolyloxiran-2-yl)methanone

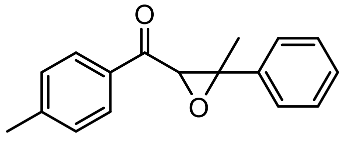


[13]C NMR (125 MHz, CDCl3) δ 192.76, 145.06, 133.07, 132.59, 129.57, 129.47, 128.53, 128.44, 125.80, 60.92, 59.33, 21.78, 21.27. **[1]H NMR** (500 MHz, CDCl3) δ 7.91 (d, J = 8.2 Hz, 2H), 7.30 – 7.26 (m, 4H), 7.21 (d, J = 8.0 Hz, 2H), 4.28 (d, J = 1.9 Hz, 1H), 4.03 (d, J = 1.8 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H).

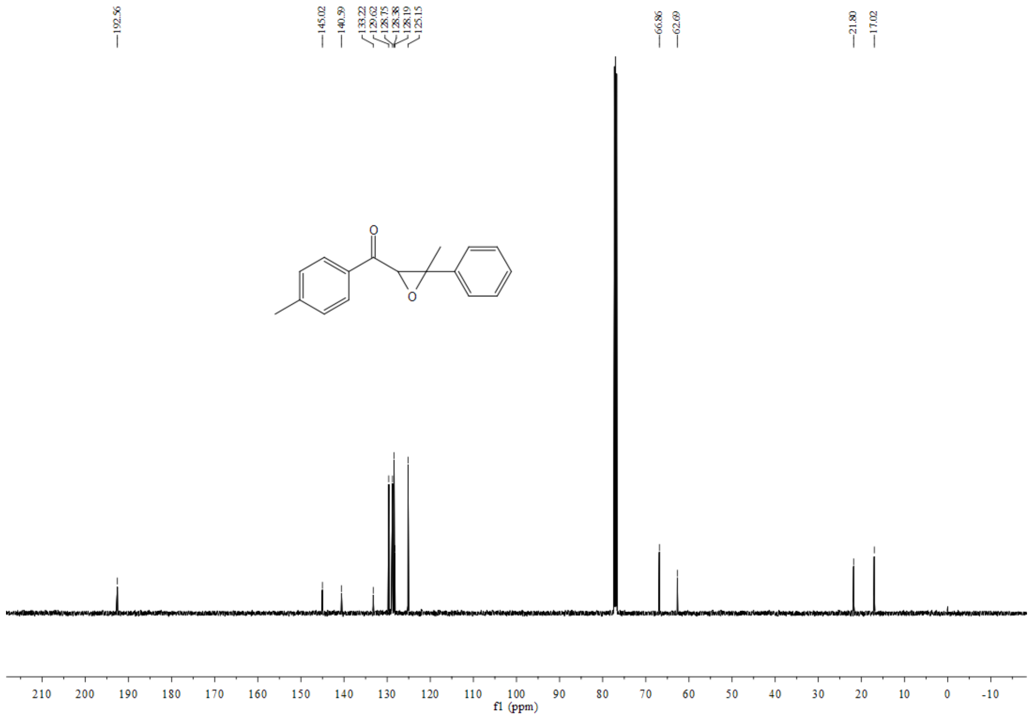


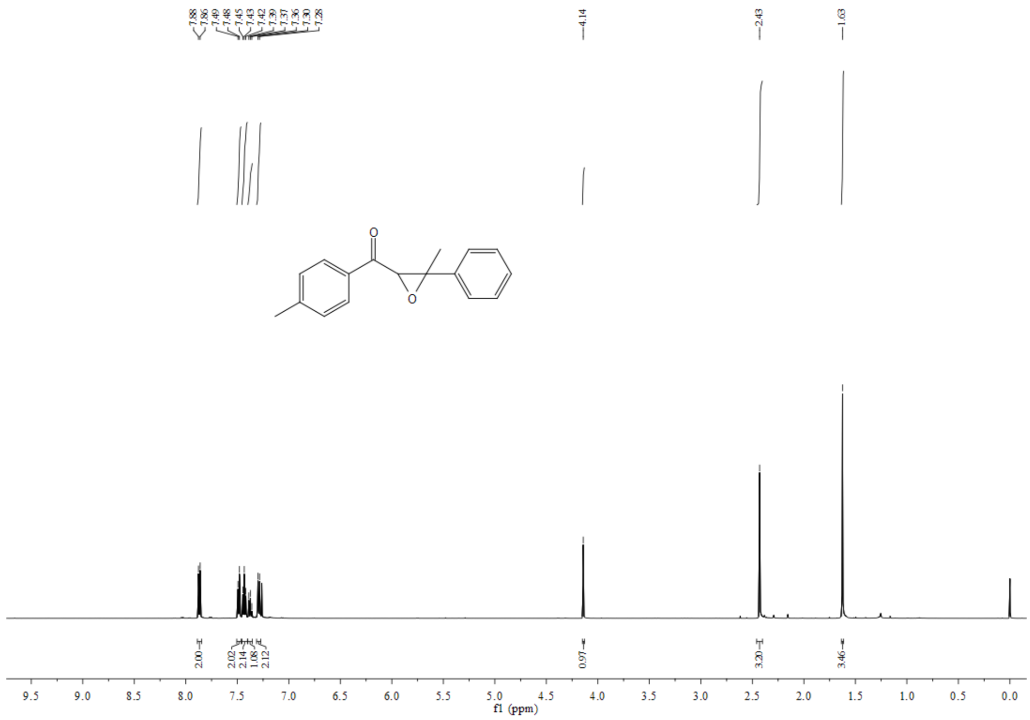


(9) (3-methyl-3-phenyloxiran-2-yl)(p-tolyl)methanone

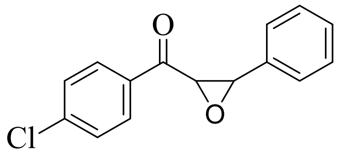


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.56 (s), 145.02 (s), 140.59 (s), 133.22 (s), 129.62 (s), 128.75 (s), 128.38 (s), 128.19 (s), 125.15 (s), 66.86 (s), 62.69 (s), 21.80 (s), 17.02 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, J = 8.2 Hz, 2H), 7.49 (d, J = 7.1 Hz, 2H), 7.43 (t, J = 7.4 Hz, 2H), 7.37 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 8.0 Hz, 2H), 4.14 (s, 1H), 2.43 (s, 3H), 1.63 (s, 3H).

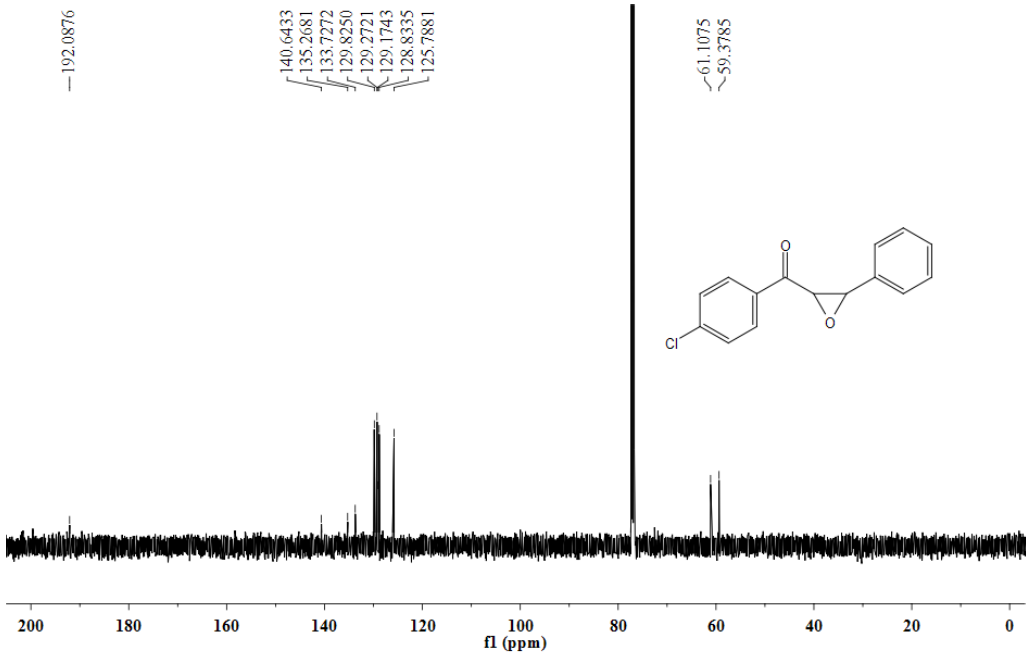


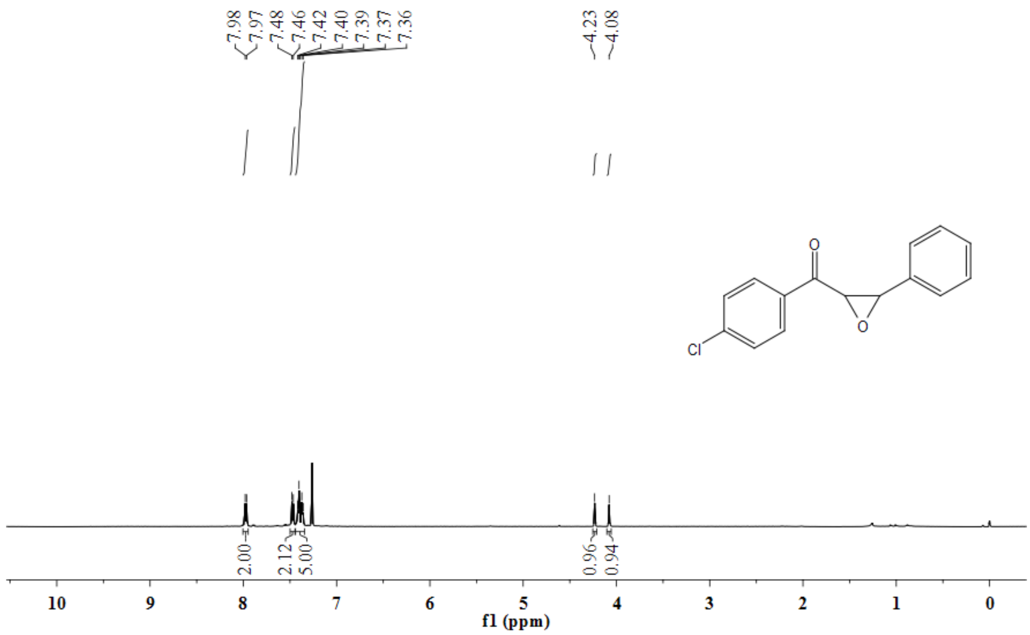


(10) (4-chlorophenyl)(3-phenyloxiran-2-yl)methanone

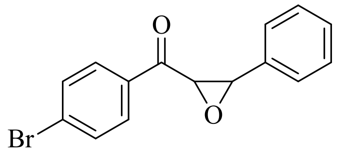


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.09 (s), 135.27 (s), 133.73 (s), 129.83 (s), 129.22 (d, J = 12.3 Hz), 128.83 (s), 125.79 (s), 61.11 (s), 59.38 (s).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.44 – 7.34 (m, 5H), 4.23 (d, 1H), 4.08 (d, 1H).

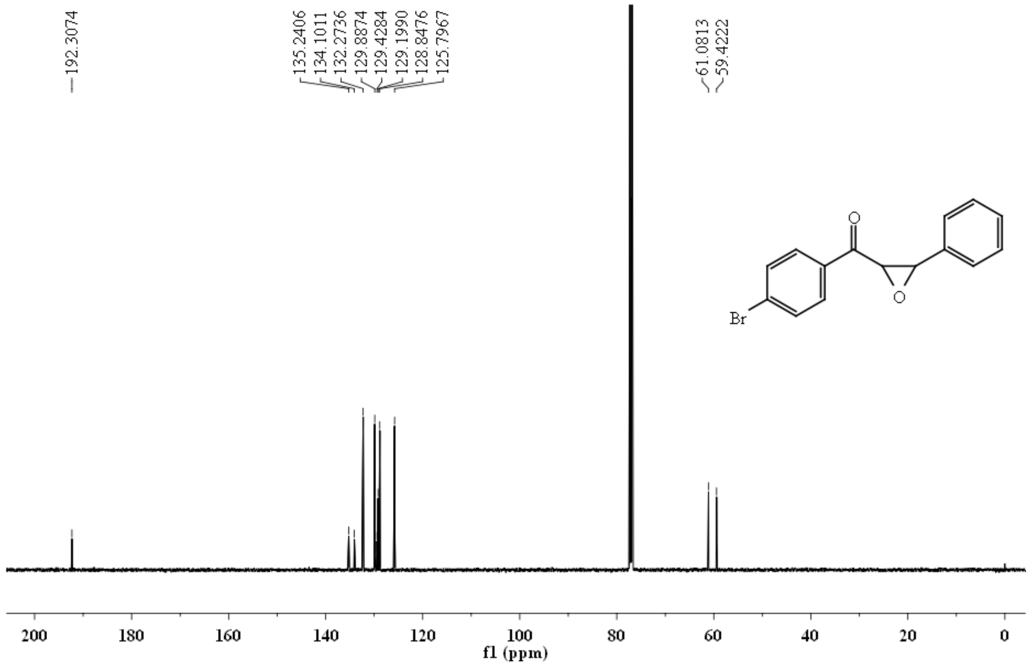


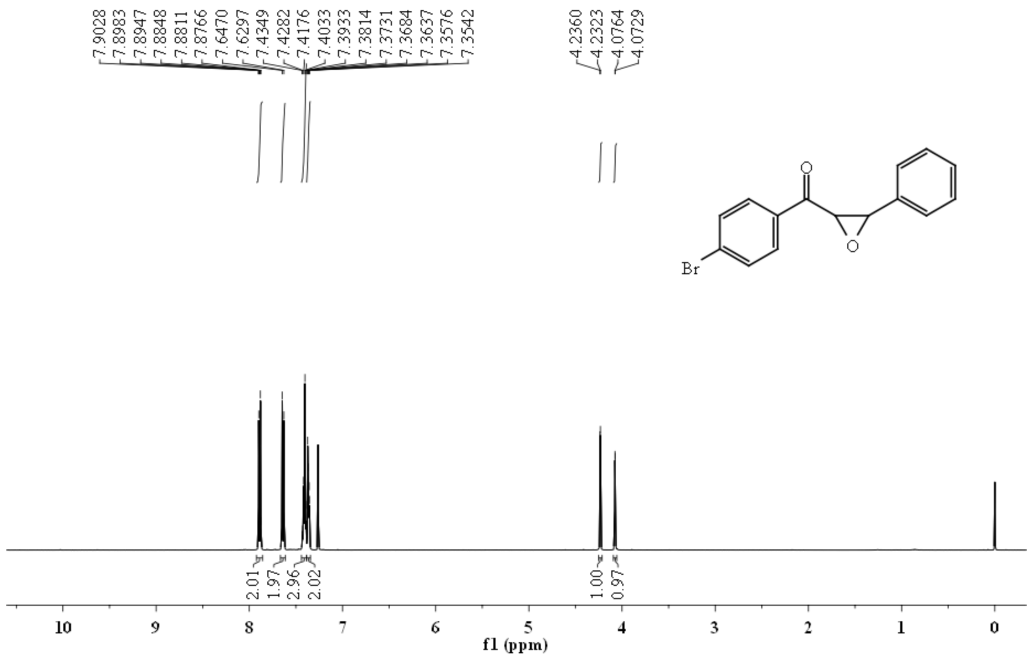


(11) (4-bromophenyl)(3-phenyloxiran-2-yl)methanone

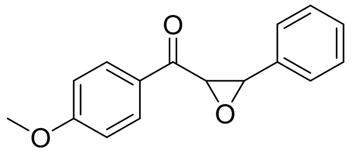


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.31 (s), 135.24 (s), 134.10 (s), 132.27 (s), 129.89 (s), 129.43 (s), 129.20 (s), 128.85 (s), 125.80 (s), 61.08 (s), 59.42 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.89 (d, 1H), 7.64 (d, 1H), 7.44 – 7.38 (m, 1H), 7.37 (dt, J = 4.8, 2.9 Hz, 1H), 4.23 (d, J = 1.8 Hz, 1H), 4.07 (d, J = 1.8 Hz, 1H).

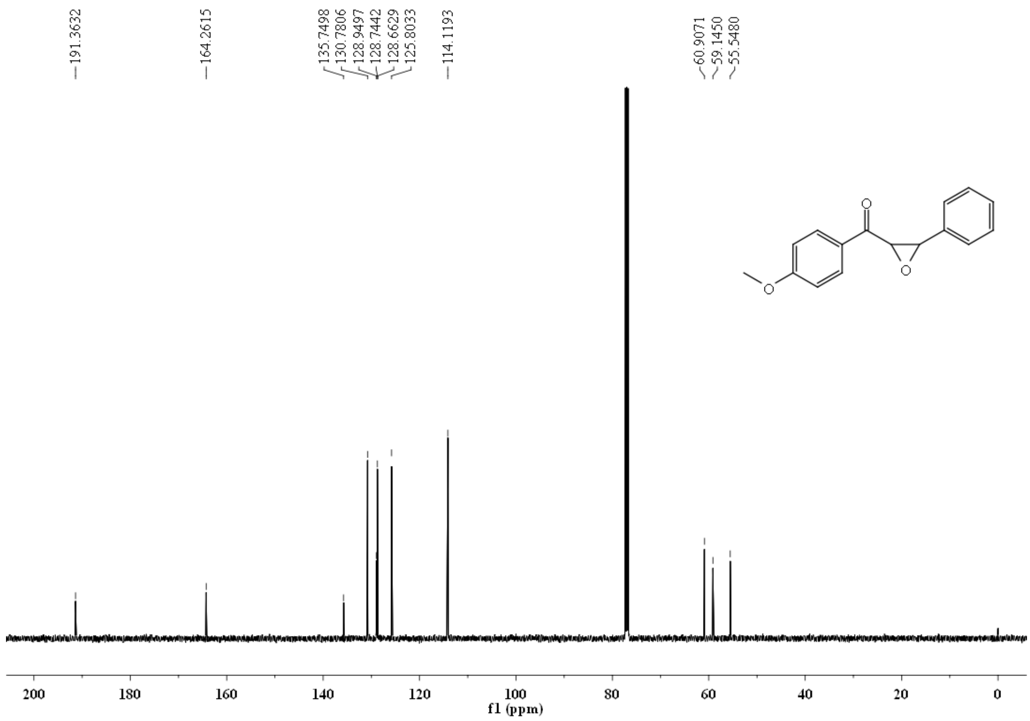


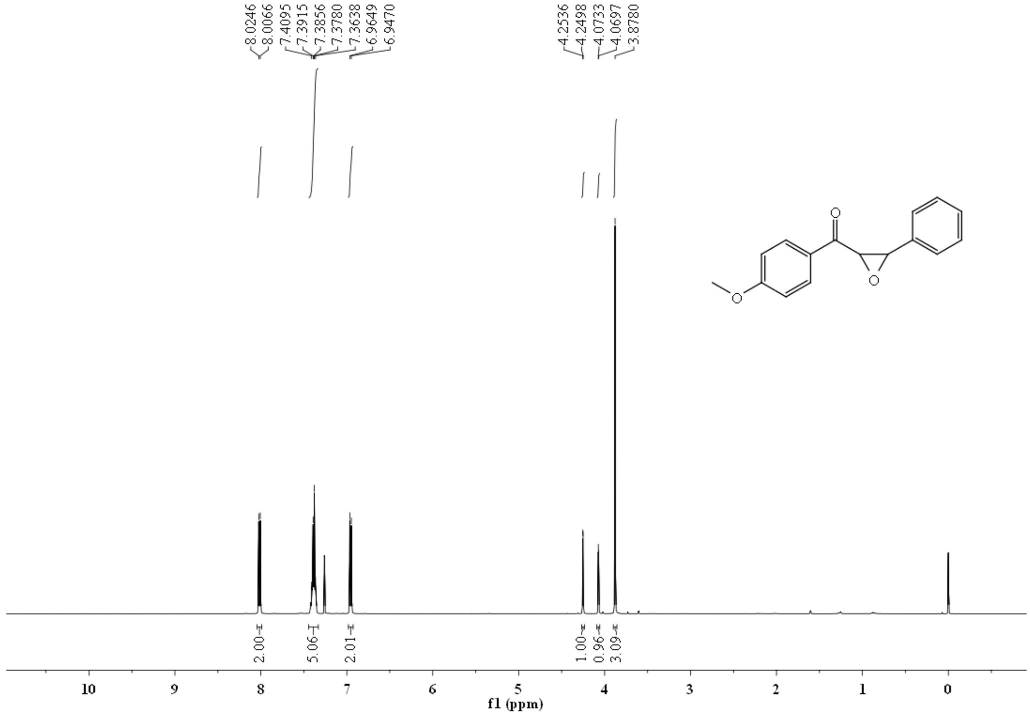


(12) (4-methoxyphenyl)(3-phenyloxiran-2-yl)methanone

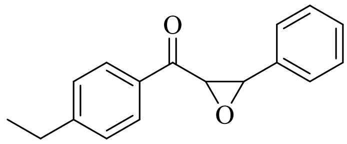


^{13}C NMR (125 MHz, $CDCl_3$) δ 191.36 (s), 164.26 (s), 135.75 (s), 130.78 (s), 128.95 (s), 128.70 (d, J = 10.2 Hz), 125.80 (s), 114.12 (s), 60.91 (s), 59.15 (s), 55.55 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, J = 9.0 Hz, 2H), 7.44 – 7.33 (m, 5H), 6.96 (d, J = 9.0 Hz, 2H), 4.25 (d, J = 1.9 Hz, 1H), 4.07 (d, J = 1.8 Hz, 1H), 3.88 (s, 3H).

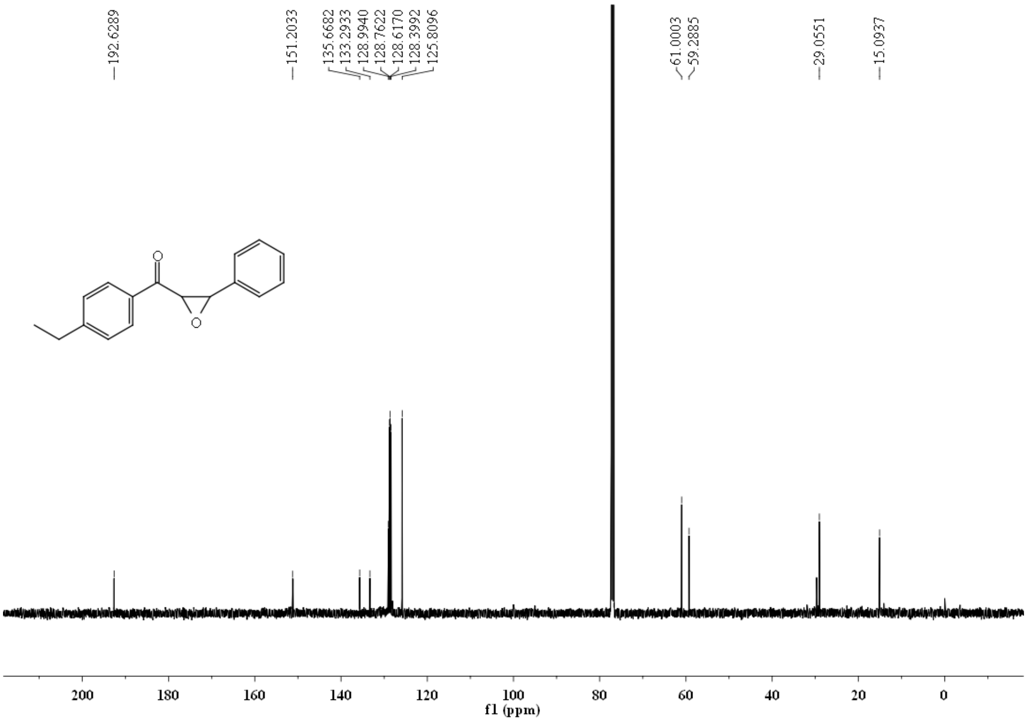


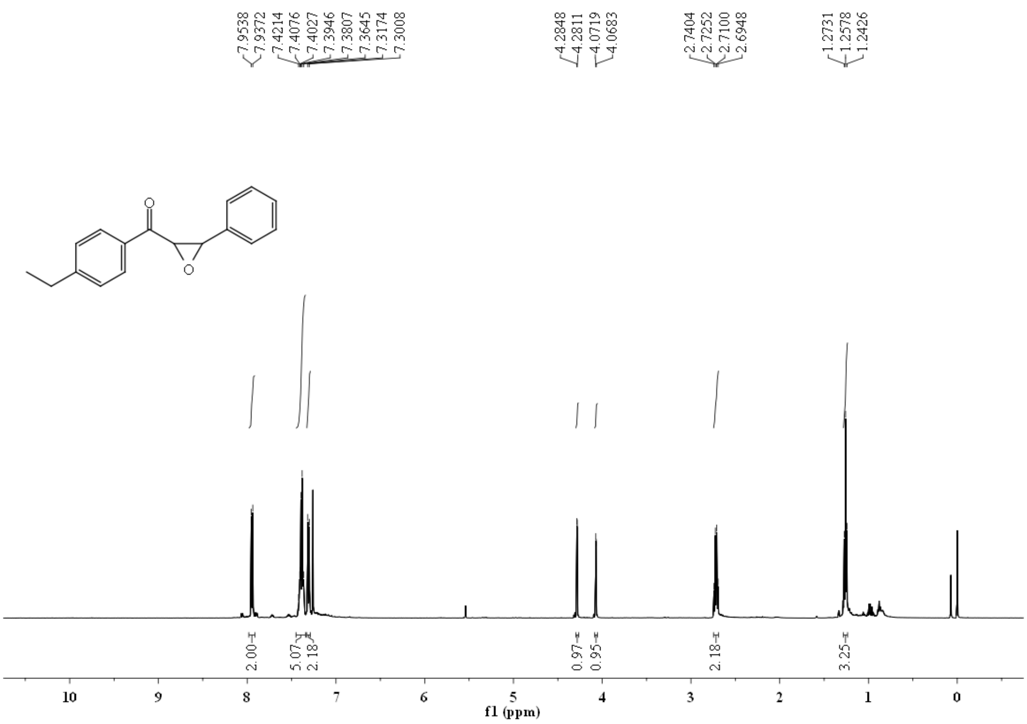


(13) (4-ethylphenyl)(3-phenyloxiran-2-yl)methanone

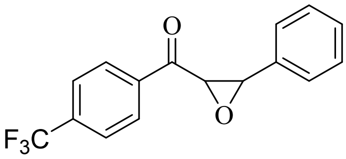


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.63 (s), 151.20 (s), 135.67 (s), 133.29 (s), 128.99 (s), 128.76 (s), 128.62 (s), 128.40 (s), 125.81 (s), 61.00 (s), 59.29 (s), 29.06 (s), 15.09 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.31 (d, J = 8.3 Hz, 2H), 4.28 (d, J = 1.9 Hz, 1H), 4.07 (d, J = 1.8 Hz, 1H), 2.72 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H).

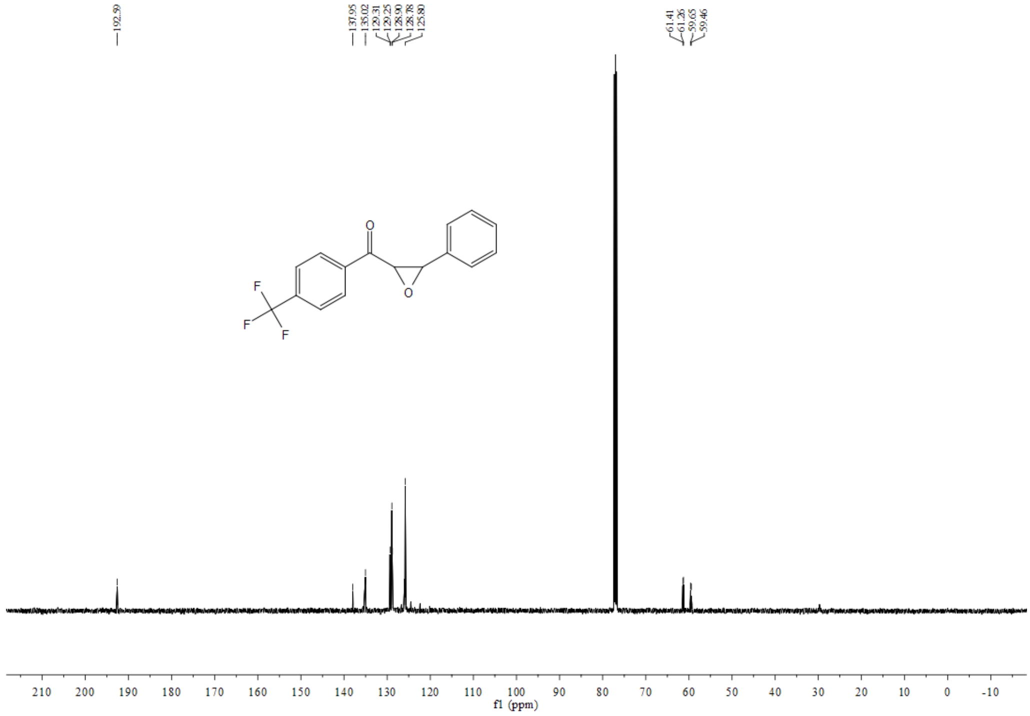


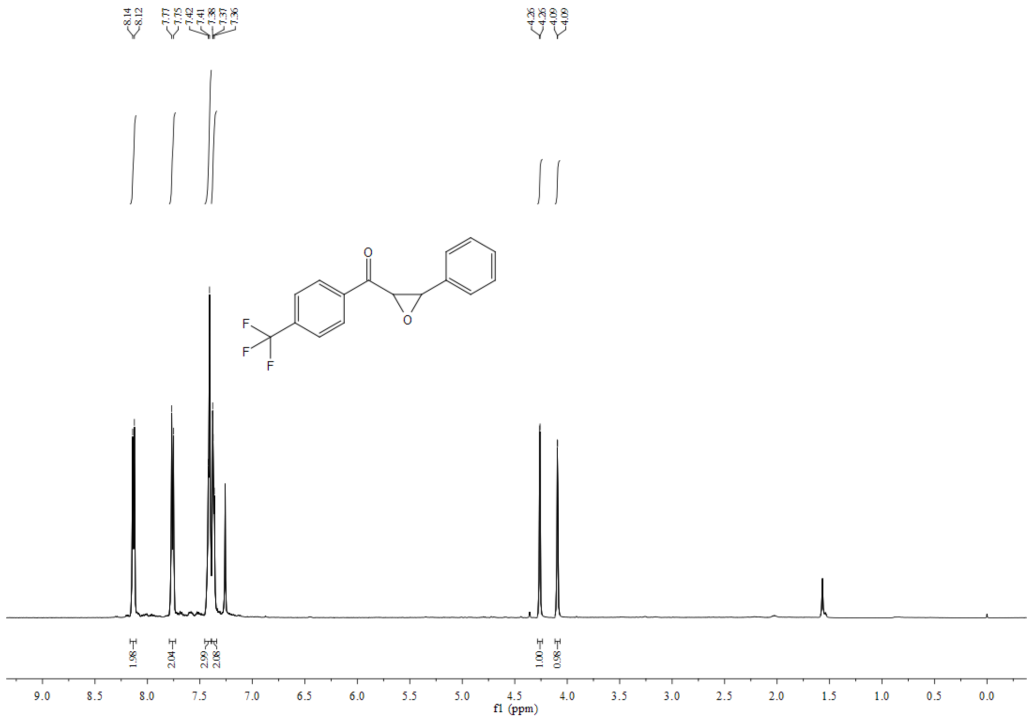


(14) (3-phenyloxiran-2-yl)(4-(trifluoromethyl)phenyl)methanone

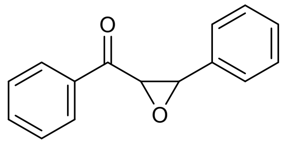


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.59 (s), 137.95 (s), 135.02 (s), 129.28 (d, J = 7.7 Hz), 128.84 (d, J = 14.7 Hz), 125.80 (s), 61.34 (d, J = 18.2 Hz), 59.65 (s), 59.46 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (d, J = 8.1 Hz, 2H), 7.76 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 6.1 Hz, 3H), 7.39 – 7.34 (m, 2H), 4.26 (d, J = 1.7 Hz, 1H), 4.09 (d, J = 1.3 Hz, 1H).

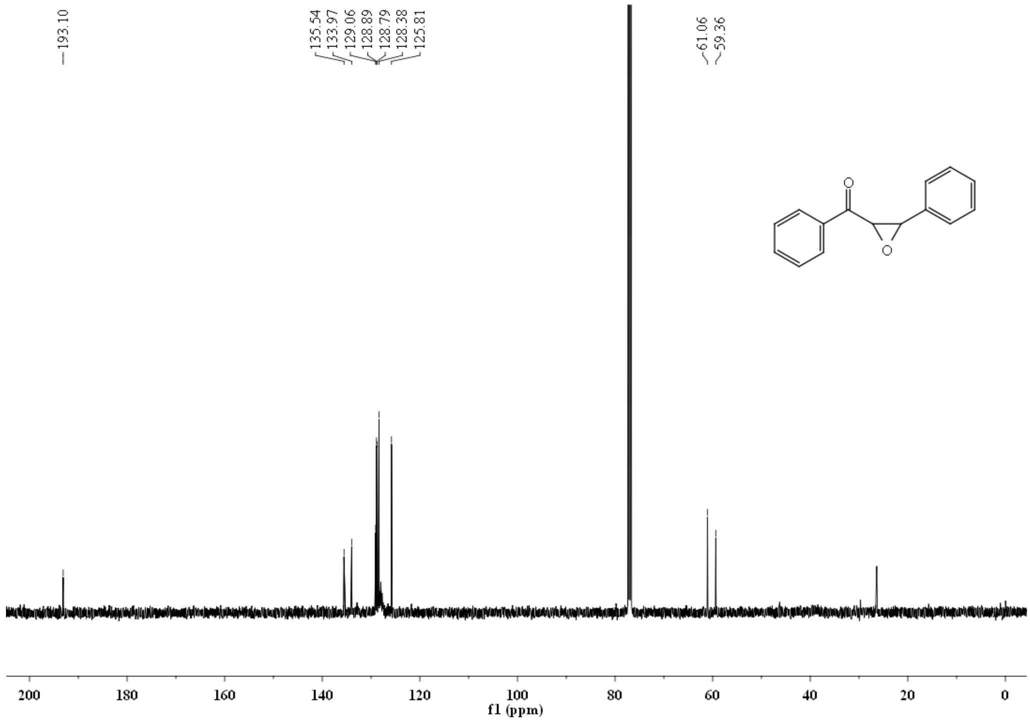


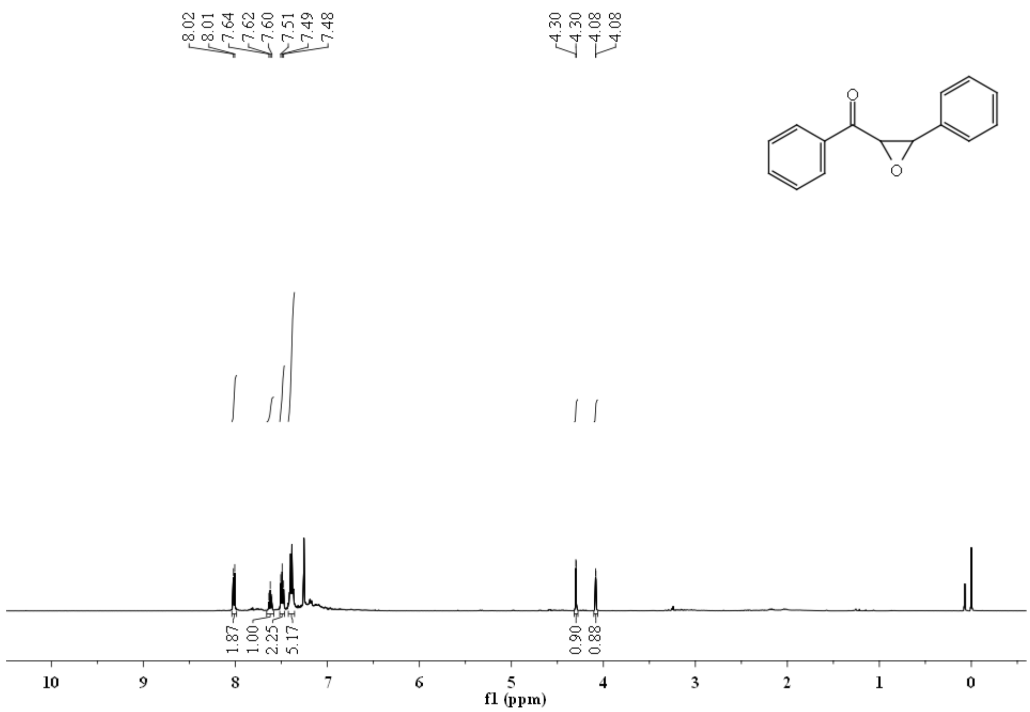


(15) phenyl(3-phenyloxiran-2-yl)methanone

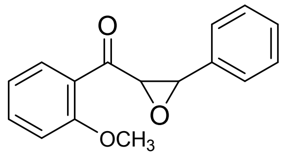


^{13}C NMR (125 MHz, $CDCl_3$) δ 193.10 (s), 135.54 (s), 133.97 (s), 129.06 (s), 128.84 (d, J = 12.5 Hz), 128.38 (s), 125.81 (s), 61.06 (s), 59.36 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, J = 7.2 Hz, 2H), 7.62 (t, J = 8.1 Hz, 1H), 7.49 (t, J = 7.8 Hz, 2H), 7.42 – 7.36 (m, 5H), 4.30 (d, J = 1.9 Hz, 1H), 4.08 (d, J = 1.8 Hz, 1H).

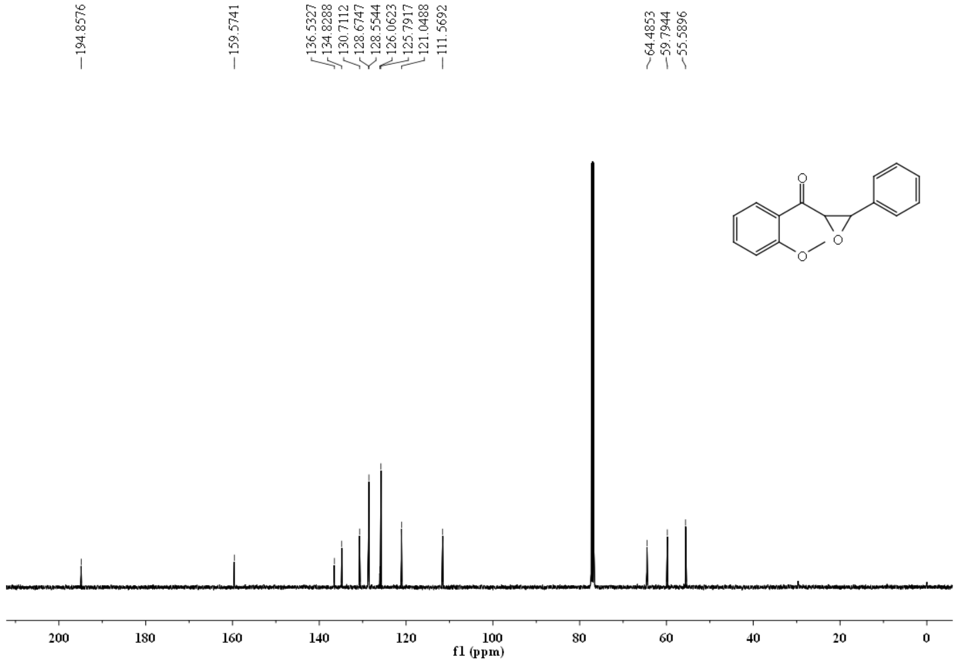


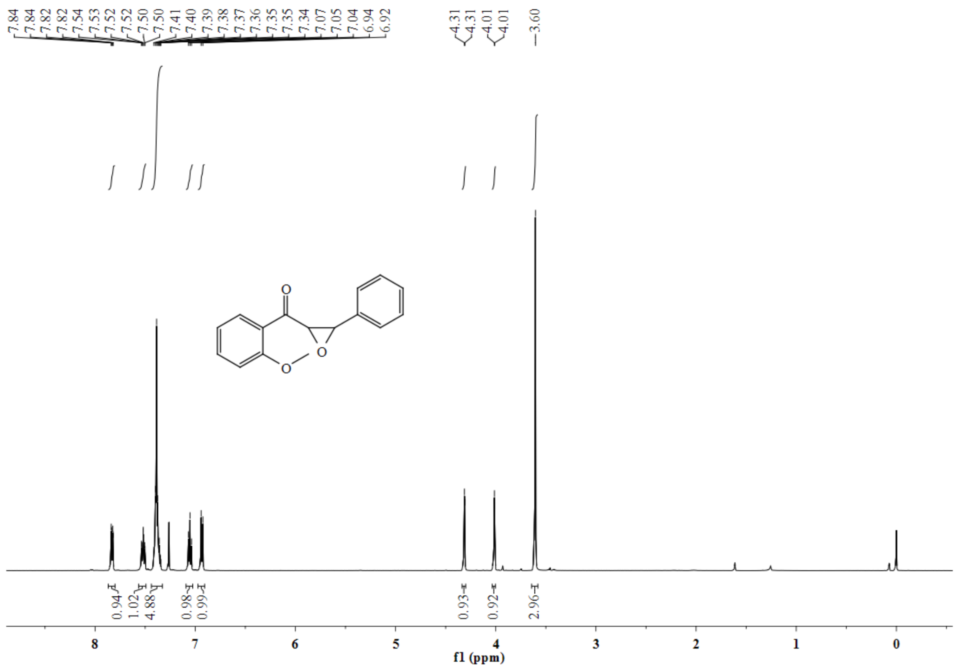


(16) (2-methoxyphenyl)(3-phenyloxiran-2-yl)methanone

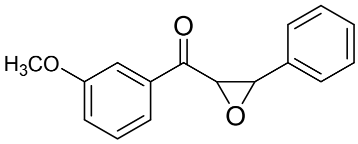


^{13}C NMR (125 MHz, $CDCl_3$) δ 194.86 (s), 159.57 (s), 136.53 (s), 134.83 (s), 130.71 (s), 128.61 (d, J = 15.1 Hz), 126.06 (s), 125.79 (s), 121.05 (s), 111.57 (s), 64.49 (s), 59.79 (s), 55.59 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, J = 7.7, 1.6 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.44 – 7.33 (m, 5H), 7.05 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 8.4 Hz, 1H), 4.31 (d, J = 1.8 Hz, 1H), 4.01 (d, J = 1.7 Hz, 1H), 3.60 (s, 3H).

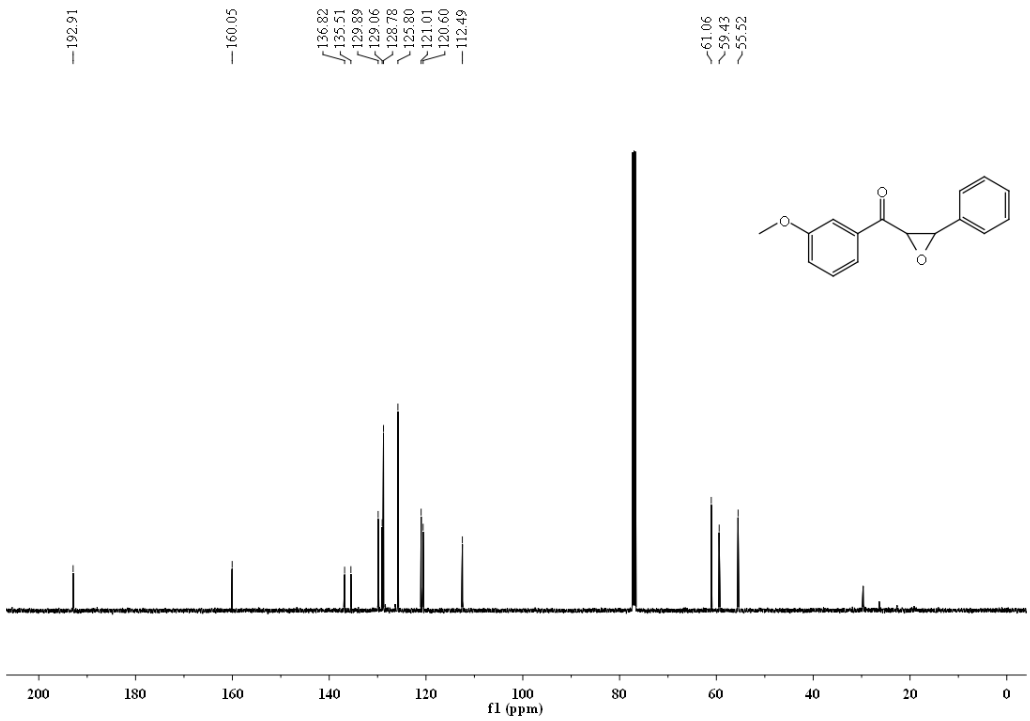


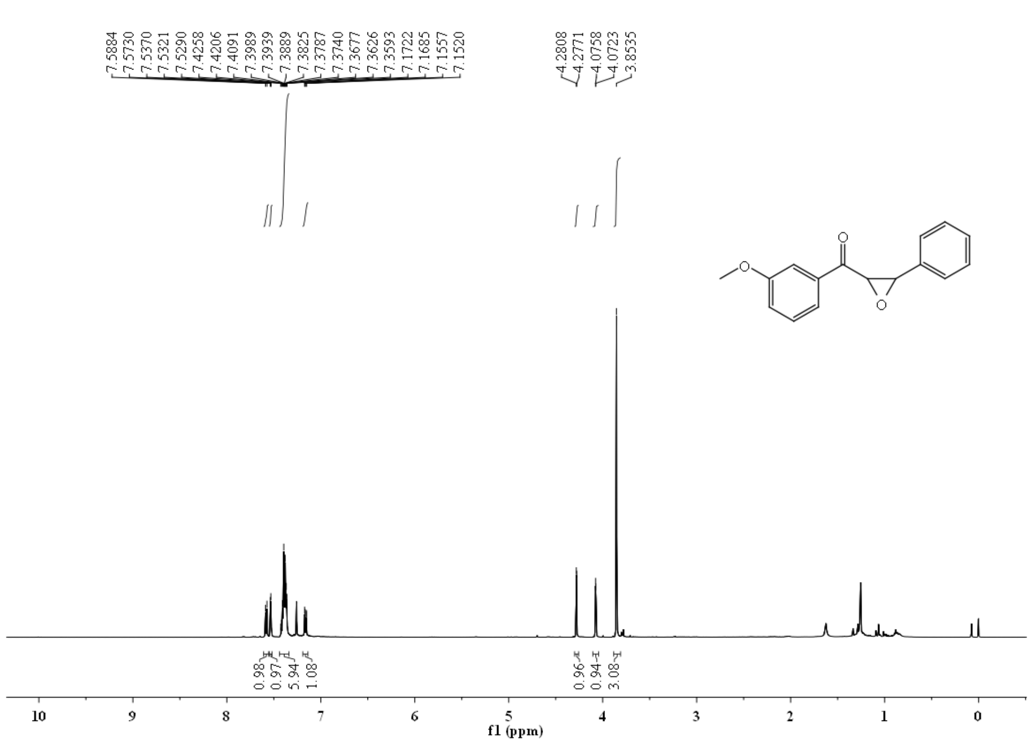


(17) (3-methoxyphenyl)(3-phenyloxiran-2-yl)methanone

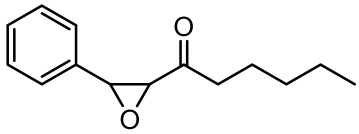


^{13}C NMR (125 MHz, $CDCl_3$) δ 192.91 (s), 160.05 (s), 136.82 (s), 135.51 (s), 129.89 (s), 129.06 (s), 128.78 (s), 125.80 (s), 121.01 (s), 120.60 (s), 112.49 (s), 61.06 (s), 59.43 (s), 55.52 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, J = 7.7 Hz, 1H), 7.53 (t, 1H), 7.44 – 7.34 (m, 6H), 7.16 (dd, J = 8.3, 1.9 Hz, 1H), 4.28 (d, J = 1.9 Hz, 1H), 4.07 (d, J = 1.8 Hz, 1H), 3.85 (s, 3H).

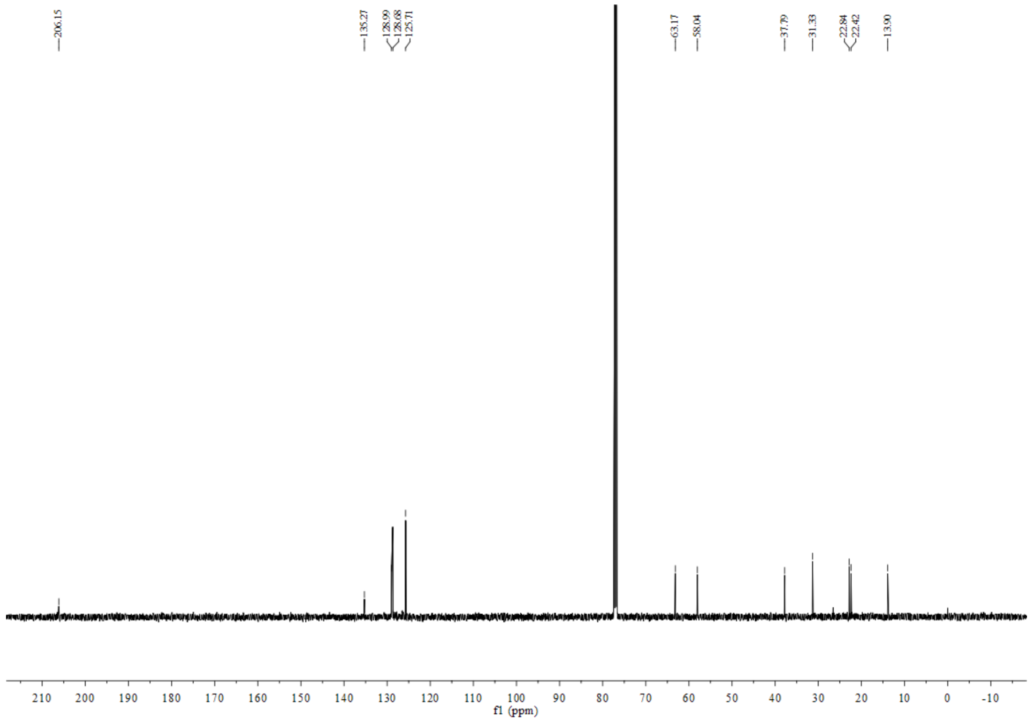


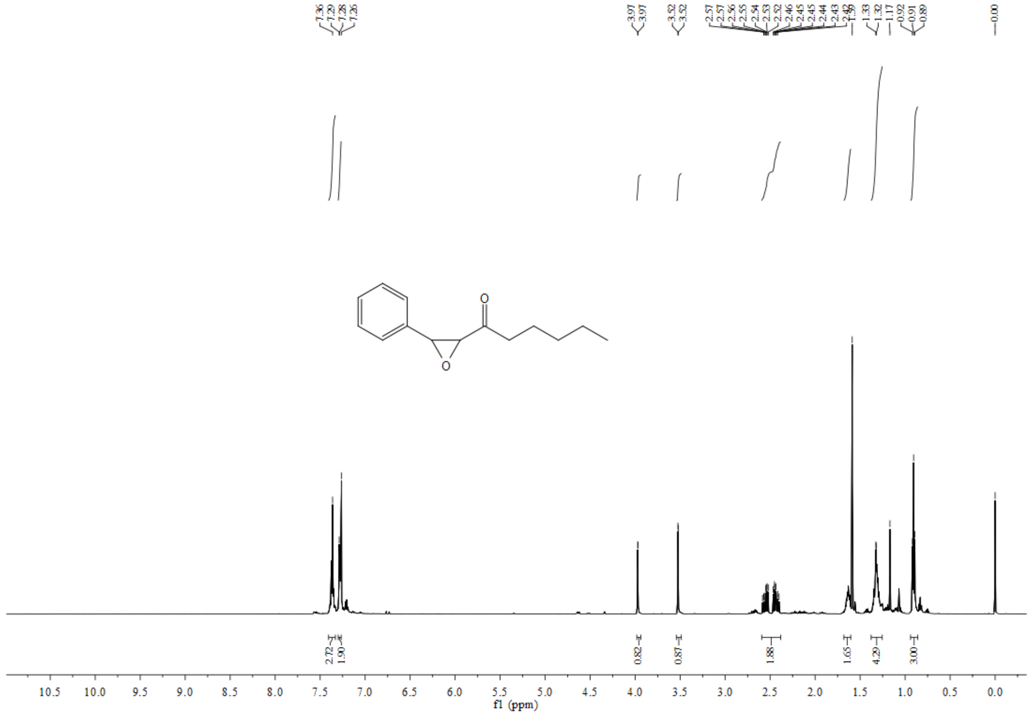


(18) 1-(3-phenyloxiran-2-yl)hexan-1-one

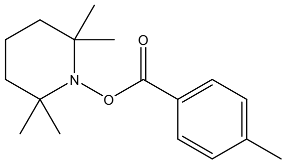


^{13}C NMR (125 MHz, $CDCl_3$) δ 206.15 (s), 135.27 (s), 128.99 (s), 128.76 – 128.60 (m), 125.71 (s), 63.17 (s), 58.04 (s), 37.79 (s), 31.33 (s), 22.84 (s), 22.42 (s), 13.90 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (s, 3H), 7.29 (d, *J* = 2.3 Hz, 2H), 3.97 (d, *J* = 1.8 Hz, 1H), 3.52 (d, *J* = 1.8 Hz, 1H), 2.59 – 2.38 (m, 2H), 1.68 – 1.60 (m, 2H), 1.32 (d, *J* = 3.8 Hz, 4H), 0.91 (t, *J* = 7.0 Hz, 3H).





(19) 2,2,6,6-tetramethylpiperidin-1-yl 4-methylbenzoate



^{13}C NMR (125 MHz, $CDCl_3$) δ 166.47 (s), 143.51 (s), 129.62 (s), 129.16 (s), 126.95 (s), 60.37 (s), 39.07 (s), 31.98 (s), 21.67 (s), 20.87 (s), 17.04 (s). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.75 (s, 2H), 1.57 (s, 4H), 1.27 (s, 6H), 1.11 (s, 6H).