

# Microwave-Assisted Organic Acid-Base-Co-Catalyzed Tandem Meinwald Rearrangement and Annulation of Styrylepoxides

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## Experimental details

**General Information.** Melting points were measured on a melting point apparatus and are uncorrected.  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were recorded on a 400 MHz NMR spectrometer. Chemical shifts are reported in ppm and referenced to tetramethylsilane (TMS) or residual solvent peaks as internal standards (for  $\text{CDCl}_3$ , tetramethylsilane 0 ppm for  $^1\text{H}$  and  $\text{CDCl}_3$  77.00 ppm for  $^{13}\text{C}$ ). IR spectra (KBr pellets,  $\nu$  ( $\text{cm}^{-1}$ )) were taken on an FT-IR spectrometer. The high-resolution mass spectra were obtained under ESI ionization using an LC/MSD TOF mass spectrometer. Microwave reactions were performed with CEM Discover. Column chromatography was carried out on silica gel (200–300 mesh) with a mixture of petroleum ether (PE, 60 °C –90 °C) and ethyl acetate (EA) as the eluent. All reactions were followed by thin-layer chromatography (TLC) where practical, using silica gel 60 F254 fluorescent treated silica gel plates, which were visualized under UV light (254 nm). Commercial-grade reagents and solvents were used without further purification unless otherwise noted, anhydrous solvent was purified with the standards process.

### General procedure for the synthesis of epoxides **1**<sup>1</sup>

Sodium hydride (0.9 g, 22.5 mmol, 60% mineral oil dispersion) was washed with petroleum ether (3 × 5 mL). The residual petroleum ether was removed under vacuum. Under atmosphere of nitrogen, dry THF (15 mL) and dry DMSO (15 mL) were added and the reaction mixture was cooled in an ice bath. A solution of trimethylsulfonium iodide (3.67 g, 18 mmol) in DMSO (4 mL) was added. After addition, cinnamyl aldehyde (15 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for an additional 12 h. The reaction mixture was slowly quenched with a mixture of water and ice (20 mL) and extracted with methylene chloride (3 × 10 mL). The combined organic extracts were washed with brine (2 × 30 mL), dried over sodium sulfate, filtered. The reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:25, v/v) to give (*E*)-2-styryloxirane (**1a**).

**(*E*)-2-Styryloxirane (1a)**<sup>1</sup> Yellow liquid, 1.23 g, 56% yield.  $R_f$  = 0.68, 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.44 – 7.40 (m, 2H), 7.36 (t,  $J$  = 7.4 Hz, 2H), 7.33 – 7.27 (m, 1H), 6.85 (d,  $J$  = 16.0 Hz, 1H), 5.92 (dd,  $J$  = 16.0, 8.0 Hz, 1H), 3.64 – 3.45 (m, 1H), 3.09 (dd,  $J$  = 5.0, 4.2 Hz, 1H), 2.81 (dd,  $J$  = 5.1, 2.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.1, 134.5, 128.6, 128.0, 126.9, 126.4, 52.5, 49.1.

**(*E*)-2-(2-Chlorostyryl)oxirane (1b)** Yellow oil. 786 mg, 44% yield.  $R_f$  = 0.65, 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (dd,  $J$  = 7.2, 2.2 Hz, 1H), 7.38–7.34 (m, 1H), 7.24–7.17 (m, 3H), 5.86 (dd,  $J$  = 16.0, 8.0 Hz, 1H), 3.57 (ddd,  $J$  = 7.6, 4.0, 2.8 Hz, 1H), 3.07 (dd,  $J$  = 5.1, 4.0 Hz, 1H), 2.78 (dd,  $J$  = 5.2, 2.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.2, 133.0, 130.6, 129.9, 129.8, 129.0, 126.9, 126.8, 52.5, 49.2. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{10}\text{H}_{10}\text{ClO}^+ [\text{M}+\text{H}]^+$ : 181.0415; found: 217.0419.

**(*E*)-2-(3-Chlorostyryl)oxirane (1c)** Yellow oil. 222 mg, 68% yield.  $R_f$  = 0.51, 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 – 7.34 (m, 1H), 7.29 – 7.20 (m, 3H), 6.75 (d,  $J$  = 16.0 Hz, 1H), 5.90 (dd,  $J$  = 16.0, 7.8 Hz, 1H), 3.50 (ddd,  $J$  = 7.8, 4.1, 2.6 Hz, 1H), 3.06 (dd,  $J$  = 5.2, 4.1 Hz, 1H), 2.76 (dd,  $J$  = 5.2, 2.6 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.0, 134.6, 133.0, 129.9, 128.6, 128.0, 126.4, 124.6, 52.3, 49.2. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{10}\text{H}_{10}\text{ClO}^+ [\text{M}+\text{H}]^+$ : 181.0415; found: 217.0421.

**(*E*)-2-(4-Chlorostyryl)oxirane (1d)**<sup>1</sup> Yellow liquid, 0.53 g, 59% yield.  $R_f$  = 0.65, 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.45 – 7.19 (m, 4H), 6.76 (d,  $J$  = 16.0 Hz, 1H), 5.86 (dd,  $J$  = 16.0, 7.9 Hz, 1H), 3.63 – 3.38 (m, 1H), 3.06 (dd,  $J$  = 4.8, 4.6 Hz, 1H), 2.77 (dd,  $J$  = 5.0, 2.4 Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  134.6, 133.7, 133.2, 128.8, 127.7, 127.6, 52.4, 49.2.

**(*E*)-2-(2,3-Dichlorostyryl)oxirane (1e)** Light yellow oil. 393 mg, 52% yield  $R_f$  = 0.50, 20% ethyl acetate in petroleum ether  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 (ddd,  $J$  = 12.8, 7.9, 1.4 Hz, 2H), 7.21 (d,  $J$  = 15.9 Hz, 1H),

7.18–7.13 (m, 1H), 5.86 (dd,  $J = 15.9, 7.9$  Hz, 1H), 3.61 – 3.53 (m, 1H), 3.08 (dd,  $J = 5.2, 4.1$  Hz, 1H), 2.78 (dd,  $J = 5.2, 2.6$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.6, 135.0, 133.5, 132.4, 131.3, 130.64, 129.6, 127.2, 125.0, 52.2, 49.2. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{10}\text{H}_9\text{Cl}_2\text{O}^+$   $[\text{M}+\text{H}]^+$ : 215.0025; found: 215.0032.

**(E)-2-(2-Fluorostyryl)oxirane (1f)** Yellow oil, 185 mg, 42% yield.  $R_f = 0.50$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (ddd,  $J = 7.7, 7.6, 1.7$  Hz, 1H), 7.25–7.19 (m, 1H), 7.07 (dddd,  $J = 11.9, 9.3, 7.9, 1.0$  Hz, 2H), 6.96 (d,  $J = 16.1$  Hz, 1H), 5.97 (dd,  $J = 16.1, 8.0$  Hz, 1H), 3.63–3.37 (m, 1H), 3.07 (dd,  $J = 5.2, 4.1$  Hz, 1H), 2.78 (dd,  $J = 5.2, 2.6$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.2 (d,  $J_{\text{C-F}} = 250.3$  Hz), 129.7 (d,  $J_{\text{C-F}} = 5.2$  Hz), 129.3 (d,  $J_{\text{C-F}} = 8.4$  Hz), 127.5 (d,  $J_{\text{C-F}} = 3.3$  Hz), 127.0 (d,  $J_{\text{C-F}} = 3.1$  Hz), 124.2 (d,  $J_{\text{C-F}} = 3.4$  Hz), 123.9 (d,  $J_{\text{C-F}} = 12.2$  Hz), 115.8 (d,  $J_{\text{C-F}} = 22.0$  Hz), 52.7, 49.2.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -117.67. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{10}\text{H}_{10}\text{FO}^+$   $[\text{M}+\text{H}]^+$ : 165.0710; found: 165.0713.

**(E)-2-(4-Fluorostyryl)oxirane (1g)** Light yellow oil, 344 mg, 42% yield.  $R_f = 0.55$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.34 (d,  $J = 8.6$  Hz, 1H), 7.32 (d,  $J = 8.6$  Hz, 1H), 7.01 (d,  $J = 8.6$  Hz, 1H), 6.99 (d,  $J = 8.6$  Hz, 1H), 6.76 (d,  $J = 16.0$  Hz, 1H), 5.79 (dd,  $J = 16.0, 7.9$  Hz, 1H), 3.54 – 3.45 (m, 1H), 3.04 (dd,  $J = 4.9, 4.4$  Hz, 1H), 2.75 (dd,  $J = 5.0, 2.6$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5 (d,  $J_{\text{C-F}} = 247.6$  Hz), 133.2, 132.3 (d,  $J_{\text{C-F}} = 3.3$  Hz), 127.9 (d,  $J_{\text{C-F}} = 8.1$  Hz), 126.7 (d,  $J_{\text{C-F}} = 2.2$  Hz), 115.5 (d,  $J_{\text{C-F}} = 21.7$  Hz), 52.4, 49.1.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -113.58. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{10}\text{H}_{10}\text{FO}^+$   $[\text{M}+\text{H}]^+$ : 165.0710; found: 165.0706.

**(E)-2-(3-(Trifluoromethyl)styryl)oxirane (1h)** Yellow liquid, 916 mg, 43% yield.  $R_f = 0.45$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.61 (s, 1H), 7.54 (d,  $J = 7.8$  Hz, 1H), 7.51 (d,  $J = 8.2$  Hz, 1H), 7.43 (dd,  $J = 8.0, 7.7$  Hz, 1H), 6.83 (d,  $J = 16.0$  Hz, 1H), 5.97 (dd,  $J = 16.0, 7.8$  Hz, 1H), 3.62–3.29 (m, 1H), 3.07 (dd,  $J = 4.9, 4.6$  Hz, 1H), 2.78 (dd,  $J = 5.1, 2.5$  Hz, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  136.9, 132.8, 131.1 (q,  $J_{\text{C-F}} = 32.2$  Hz), 129.5, 129.1, 124.5 (q,  $J_{\text{C-F}} = 3.8$  Hz), 124.0 (q,  $J_{\text{C-F}} = 272.3$  Hz), 123.1 (q,  $J_{\text{C-F}} = 3.8$  Hz), 52.2, 49.2.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.84. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}^+$   $[\text{M}+\text{H}]^+$ : 215.0678; found: 215.0676.

**(E)-2-(4-(Trifluoromethyl)styryl)oxirane (1i)** Yellow oil, 116 mg, 91% yield.  $R_f = 0.50$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (d,  $J = 8.2$  Hz, 2H), 7.46 (d,  $J = 8.1$  Hz, 2H), 6.83 (d,  $J = 16.0$  Hz, 1H), 5.99 (dd,  $J = 16.0, 7.8$  Hz, 1H), 3.57–3.48 (m, 1H), 3.08 (dd,  $J = 5.0, 4.6$  Hz, 1H), 2.78 (dd,  $J = 5.2, 2.5$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.5, 132.9, 130.0, 129.8, 129.7, 126.6, 125.6 (q,  $J_{\text{C-F}} = 3.8$  Hz), 124.2 (q,  $J_{\text{C-F}} = 253.5$  Hz), 52.3, 49.3.  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.60. HRMS (ESI-TOF)  $m/z$ : calcd. for  $\text{C}_{11}\text{H}_{10}\text{F}_3\text{O}^+$   $[\text{M}+\text{H}]^+$ : 215.0678; found: 215.0676.

**(E)-2-(2-Methoxystyryl)oxirane (1j)<sup>2</sup>** Yellow oil, 483 mg, 55% yield.  $R_f = 0.72$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.31 (d,  $J = 7.6$  Hz, 1H), 7.16–7.14 (m, 1H), 7.05 (d,  $J = 16.1$  Hz, 1H), 6.86 – 6.75 (m, 2H), 5.80 (dd,  $J = 16.1, 8.2$  Hz, 1H), 3.75 (s, 3H), 3.53–3.29 (m, 1H), 2.95 (dd,  $J = 5.1, 4.6$  Hz, 1H), 2.67 (dd,  $J = 5.1, 2.6$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 129.6, 129.0, 127.6, 127.0, 125.1, 120.6, 110.8, 55.3, 53.1, 49.1.

**(E)-2-(4-Methylstyryl)oxirane (1k)<sup>3</sup>** Colorless oil, 273 mg, 34% yield.  $R_f = 0.60$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (d,  $J = 8.0$  Hz, 1H), 7.11 (d,  $J = 7.9$  Hz, 1H), 6.76 (d,  $J = 16.0$  Hz, 1H), 5.80 (dd,  $J = 16.0, 8.0$  Hz, 1H), 3.58 – 3.40 (m, 1H), 3.02 (dd,  $J = 4.9, 4.6$  Hz, 1H), 2.74 (dd,  $J = 5.1, 2.6$  Hz, 1H), 2.32 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.9, 134.5, 133.3, 129.3, 126.3, 125.79, 52.7, 49.1, 21.1.

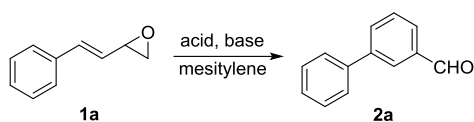
**(E)-2-(1-Phenylprop-1-en-2-yl)oxirane (1l)<sup>1</sup>** Colorless oil, 1.552 g, 97% yield.  $R_f = 0.5$ , 10% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 6.67 (s, 1H), 3.52 –

3.47 (m, 1H), 2.94 (dd,  $J = 5.0, 4.6$  Hz, 1H), 2.81 (dd,  $J = 5.0, 2.6$  Hz, 1H), 1.74 (s, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  137.1, 134.0, 128.9, 128.8, 128.2, 126.7, 56.1, 46.8, 11.8.

### Optimization of the conversion conditions

Styrylepoxide (**1a**) was selected as the model substrate to optimize the reaction conditions. Absolutely acid-free reaction conditions were hardly realized because both a trace amount of water and silica borate glassware's residue acidic sites were acids in the reaction system. To speed up screening of the efficient combination of acid and base co-catalysts, we first evaluated different organic bases. After preliminary screening of the reaction conditions with different organic bases (Table S1, entries 1-14) and their equivalents (data not shown), we found that TEA (triethylamine) was an efficient base catalyst for the conversion of styrylepoxide (**1a**) into 3-phenylbenzaldehyde (**2a**) in 59% yield when **1a** was heated and stirred in anhydrous meistylene at 165 °C for 24 h (Table S1, entry 2). Since the formation of **2a** would inevitably involve some sort of condensation between two molecules of the initial rearrangement intermediate from **1a**, calculation for the yield of **2a** was based on such stoichiometry. Next, TEA was applied as the base to optimize the combination of acid-base co-catalysts. Protonic acids HCl and  $\text{HCO}_2\text{H}$  were first tested, no desired product was observed (Table S1, entries 11 and 12). However, when  $\text{TsOH}\cdot\text{H}_2\text{O}$  was attempted under the same conditions, the desired product **2a** was obtained in 84% yield (Table S1, entry 13). Furthermore, several typical Lewis acids, including  $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ ,  $\text{AlCl}_3$ ,  $\text{CuCl}_2\cdot\text{H}_2\text{O}$ , and  $\text{BF}_3\cdot\text{OEt}_2$ , were further evaluated under the same conditions, affording the desired product **2a** in 71%, 38%, 27%, and 51%, respectively (Table S1, entries 14-17). The results indicated that the combination of  $\text{TsOH}\cdot\text{H}_2\text{O}$  (0.1 equiv.) and TEA (2 equiv.) was the best acid-base co-catalysts for the conversion (Table S1, entry 13). Thus, further optimizations were conducted with  $\text{TsOH}\cdot\text{H}_2\text{O}$  (0.1 equiv.) and TEA (2 equiv.) as the acid-base co-catalysts. Shortening the reaction time from 24 h to 12 h resulted in decreasing the yield from 84% to 58% (Table S1, entry 18). Considering that microwave irradiation could accelerate some organic reactions, the reaction under the co-catalysis of  $\text{TsOH}\cdot\text{H}_2\text{O}$  (0.1 equiv.) and TEA (2 equiv.) was carried out at 165 °C for 1 h under microwave irradiation, affording the desired product **2a** in 44% yield (Table S1, entry 19). The reaction temperature was raised to 200 °C under microwave irradiation, giving **2a** in 84% yield (Table S1, entry 20), the same yield as that under heating for 24 h. Further raising the reaction temperature to 235 °C resulted in decrease of the yield to 55% (Table S1, entry 21). Increasing and decreasing equivalents of  $\text{TsOH}\cdot\text{H}_2\text{O}$  and TEA showed negative effects (Table S1, entries 22-25). Prolonging and shortening reaction time did not further improve the yield (Table S1, entries 26 and 27). To further verify efficiency of the co-catalysts, reactions under the catalysis of  $\text{TsOH}\cdot\text{H}_2\text{O}$  and without any catalyst were performed. No desired product **2a** was observed in either of reactions (Table S1, entries 28 and 29). Finally, the optimal reaction conditions were identified as  $\text{TsOH}\cdot\text{H}_2\text{O}$  (0.1 equiv.) and TEA (2 equiv.) as the acid-base co-catalysts at 200 °C for 1 h under microwave irradiation (Table S1, entry 20).

**Table S1 Optimization of the conversion conditions<sup>a</sup>**



Entry	Acid <sup>b</sup> /equiv.	Base <sup>c</sup> /equiv.	Temp./°C	Time/h	Yield/%
1	-	TEA/2	130	24	0
2	-	TEA/2	165	24	59
3	-	DIEPA/2	165	24	0
4	-	MeMorp/2	165	24	0
5	-	MeIm/2	165	24	0
6	-	2-ClPy/2	165	24	0
7	-	4-MePy/2	165	24	0
8	-	2,6-Me <sub>2</sub> Py/2	165	24	7
9	-	DMAP/2	165	24	0
10	-	DBU/2	165	24	0
11	HCl/2.4 M, 0.1	TEA/2	165	24	0
12	HCO <sub>2</sub> H/0.1	TEA/2	165	24	0
13	TsOH/0.1	TEA/2	165	24	84
14	SnCl <sub>2</sub> /0.1	TEA/2	165	24	71
15	AlCl <sub>3</sub> /0.1	TEA/2	165	24	38
16	CuCl <sub>2</sub> /0.1	TEA/2	165	24	27
17	BF <sub>3</sub> OEt <sub>2</sub> /0.1	TEA/2	165	24	51
18	TsOH/0.1	TEA/2	165	12	58
19	TsOH/0.1	TEA/2	165	1	44 <sup>d</sup>
20	TsOH/0.1	TEA/2	200	1	84 <sup>d</sup>
21	TsOH/0.1	TEA/2	235	1	55 <sup>d</sup>
22	TsOH/0.1	TEA/1	200	1	70 <sup>d</sup>
23	TsOH/0.1	TEA/3	200	1	37 <sup>d</sup>
24	TsOH/0.2	TEA/2	200	1	73 <sup>d</sup>
25	TsOH/0.05	TEA/2	200	1	55 <sup>d</sup>
26	TsOH/0.1	TEA/2	200	1.5	77 <sup>d</sup>
27	TsOH/0.1	TEA/2	200	0.5	51 <sup>d</sup>
28	TsOH/0.1	-	165	24	0
29	-	-	165	24	0

<sup>a</sup>Reactions were conducted on a 0.3 mmol scale of **1a** in 2 mL of anhydrous mesitylene. All yields are the yields of the isolated product. <sup>b</sup>TsOH for TsOH·H<sub>2</sub>O, SnCl<sub>2</sub> for SnCl<sub>2</sub>·2H<sub>2</sub>O, CuCl<sub>2</sub> for CuCl<sub>2</sub>·H<sub>2</sub>O. <sup>c</sup>TEA (triethylamine), DIEPA (ethyl diisopropylamine), MeMorp (*N*-methylmorpholine), MeIm (*N*-methylimidazole), 2-ClPy (2-chloropyridine), 4-MePy (4-methylpyridine), 2,6-Me<sub>2</sub>Py (2,6-dimethylpyridine):

DMAP (4-dimethylaminopyridine), DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). <sup>d</sup>Reactions were conducted under microwave irradiation.

### General procedure for the conversion of styrylepoxydes **1** into [1,1'-biaryl]-3-carbaldehydes **2** and alkenals **3**.

Styrylepoxyde **1** (0.5 mmol) was dissolved in 2 mL of mesitylene in a 10 mL reaction tube. Et<sub>3</sub>N (101 mg, 1.0 mmol) and TsOH·H<sub>2</sub>O (9.5 mg, 0.05mmol) was added at room temperature, and then the reaction mixture was stirred and irradiated in a microwave reactor at 200 °C for 1 h. After cooling to room temperature, the reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:50, v/v) to afford product **2** or **3**.

**[1,1'-Biphenyl]-3-carbaldehyde (2a)**<sup>4</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as light yellow oil, 38 g, 84% yield. *R<sub>f</sub>* = 0.60, 20% ethyl acetate in petroleum ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.09 (s, 1H), 8.10 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.86 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.64–7.60 (m, 3H), 7.50–7.45 (m, 2H), 7.42–7.37 (m, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 192.3, 142.2, 139.7, 136.9, 133.1, 129.5, 129.0, 128.6, 128.2, 128.0, 127.1

**2'-Chloro-[1,1'-biphenyl]-3-carbaldehyde (2b)**<sup>5</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as colorless oil, 53 mg, 80% yield. *R<sub>f</sub>* = 0.60 20% ethyl acetate in petroleum ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.07 (s, 1H, CHO), 7.95 (dd, dd, *J* = 1.6, 1.6 Hz, 1H), 7.93–7.89 (m, 1H), 7.75–7.72 (m, 1H), 7.60 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.49–7.45 (m, 1H), 7.36–7.27 (m, 3H); <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 192.1, 140.3, 139.0, 136.3, 135.5, 131.2, 130.8, 130.1, 129.5, 129.2, 128.8, 127.1.

**3'-Chloro-[1,1'-biphenyl]-3-carbaldehyde (2c)**<sup>6</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 42 mg, 78% yield. *R<sub>f</sub>* = 0.58 20% ethyl acetate in petroleum ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.10 (s, 1H), 8.08 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.89 (ddd, *J* = 7.6, 1.5, 1.2 Hz, 1H), 7.84 (ddd, *J* = 7.6, 1.8, 1.2 Hz, 1H), 7.63 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.61 (dd, *J* = 2.0, 2.0 Hz, 1H), 7.51 (ddd, *J* = 7.6, 2.0, 1.6 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.38 (ddd, *J* = 7.6, 2.0, 1.6 Hz, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 192.0, 141.5, 137.0, 135.2, 135.1, 135.0, 132.9, 130.2, 129.7, 129.3, 128.0, 127.3, 125.3.

**4'-Chloro-[1,1'-biphenyl]-3-carbaldehyde (2d)**<sup>7</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as light yellow oil, 43 mg, 80% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.08 (s, 1H), 8.06 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.86 (ddd, *J* = 7.6, 1.6, 1.3 Hz, 1H), 7.82 (ddd, *J* = 7.7, 1.8, 1.2 Hz, 1H), 7.61 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.55 (dd, *J* = 8.6, 2.4 Hz, 2H), 7.44 (dd, *J* = 8.6, 2.4 Hz, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 192.1, 140.9, 138.1, 137.0, 134.2, 132.8, 129.6, 129.2, 129.0, 128.4, 127.8

**2',3'-Dichloro-[1,1'-biphenyl]-3-carbaldehyde (2e)** Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 26 mg, 41% yield. *R<sub>f</sub>* = 0.50 20% ethyl acetate in petroleum ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.08 (s, 1H), 7.97–7.88 (m, 2H), 7.70 (ddd, *J* = 7.7, 1.5, 1.5 Hz, 1H), 7.63 (ddd, *J* = 7.6, 7.6, 1.6 Hz, 1H), 7.52 (dd, *J* = 7.6, 2.0 Hz, 1H), 7.32–7.25(m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 191.9, 141.8, 140.2, 139.2, 138.7, 135.3, 130.6, 130.1, 129.3, 129.2, 128.9, 127.4, 123.9. HRMS (ESI-TOF) *m/z*: calcd. for C<sub>13</sub>H<sub>9</sub>Cl<sub>2</sub>O<sup>+</sup> [M+H]<sup>+</sup>:251.0025; found: 251.0026.

**2'-Fluoro-[1,1'-biphenyl]-3-carbaldehyde (2f)**<sup>8</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 44 mg, 88% yield. *R<sub>f</sub>* = 0.60 20% ethyl acetate in petroleum ether. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.08 (s, 1H), 8.06 (dd, *J* = 1.6, 1.6 Hz, 1H), 7.90 (ddd, *J* = 7.6, 1.5, 1.4 Hz, 1H), 7.83 (ddd, *J* = 7.7, 1.6, 1.6 Hz, 1H), 7.62 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.48 (ddd, *J* = 7.6, 7.6, 1.8 Hz, 1H), 7.41–7.34 (m, 1H), 7.24–7.15 (m, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, CDCl<sub>3</sub>) δ 192.2, 160.0 (d,

$J_{\text{C-F}} = 251.4$  Hz), 136.9, 136.7, 135.0, 130.4, 129.8 (d,  $J_{\text{C-F}} = 8.2$  Hz), 129.2, 128.8, 124.7, 124.6, 116.3 (d,  $J_{\text{C-F}} = 22.7$  Hz)  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -118.0.

**4'-Fluoro-[1,1'-biphenyl]-3-carbaldehyde (2g)**<sup>9</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 36 mg, 72% yield.  $R_f = 0.55$  20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.09 (s, 1H), 8.06 (s, 1H), 7.86 (d,  $J = 7.6$  Hz, 1H), 7.81 (d,  $J = 7.5$  Hz, 1H), 7.62 (d,  $J = 8.1$  Hz, 1H), 7.58 (d,  $J = 8.0$  Hz, 2H), 7.18 (d,  $J = 8.4$  Hz, 1H), 7.15 (d,  $J = 8.1$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.2, 162.9 (d,  $J_{\text{C-F}} = 247.5$  Hz), 141.2, 136.9, 135.8, 132.9, 129.6, 128.8, 128.8, 127.8, 115.9 (d,  $J_{\text{C-F}} = 21.6$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -114.5.

**3'-(Trifluoromethyl)-[1,1'-biphenyl]-3-carbaldehyde (2h)**<sup>10</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 33 mg, 66% yield.  $R_f = 0.50$  20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 8.11 (s, 1H), 7.92 (d,  $J = 7.6$  Hz, 1H), 7.89–7.85 (m, 2H), 7.81 (d,  $J = 7.6$  Hz, 1H), 7.69–7.59 (m, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.0, 140.7, 140.5, 137.1, 133.0, 131.6, 130.5, 129.8, 129.52, 129.49, 128.0, 126.2 (d,  $J_{\text{C-F}} = 207.8$  Hz), 124.7 (q,  $J_{\text{C-F}} = 3.8$  Hz), 123.95 (q,  $J_{\text{C-F}} = 3.7$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.6.

**4'-(Trifluoromethyl)-[1,1'-biphenyl]-3-carbaldehyde (2i)**<sup>11</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 36 mg, 71% yield.  $R_f = 0.52$  20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.11 (s, 1H), 8.12 (s, 1H), 7.92 (d,  $J = 7.6$  Hz, 1H), 7.87 (d,  $J = 7.8$  Hz, 1H), 7.76–7.72 (m, 4H), 7.66 (dd,  $J = 7.7, 7.7$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.6, 140.4, 136.8, 132.8, 130.8, 129.6, 129.4, 129.3, 127.8, 127.2, 124.0 (q,  $J_{\text{C-F}} = 233.1$  Hz), 125.6 (q,  $J_{\text{C-F}} = 3.7$  Hz).  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.53.

**2'-Methoxy-[1,1'-biphenyl]-3-carbaldehyde (2j)**<sup>12</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as yellow oil, 33 mg, 66% yield.  $R_f = 0.50$  20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.09 (s, 1H), 8.07 (s, 1H), 7.86 (dd,  $J = 14.1, 7.7$  Hz, 2H), 7.60 (dd,  $J = 7.7, 7.6$  Hz, 1H), 7.39 (dd,  $J = 14.8, 8.0$  Hz, 2H), 7.14–7.01 (m, 1H), 3.86 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.5, 156.4, 139.5, 136.3, 135.6, 131.1, 130.7, 129.4, 129.1, 128.7, 128.0, 121.0, 111.3, 55.6.

**4'-Methyl-[1,1'-biphenyl]-3-carbaldehyde (2k)**<sup>6</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the desired product as colorless oil, 34 mg, 52% yield.  $R_f = 0.60$  20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.07 (s, 1H), 8.10–8.05 (m, 1H), 7.85–7.80 (m, 2H), 7.58 (dd,  $J = 8.0, 8.0$  Hz, 1H), 7.52 (d,  $J = 8.4$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 2.41 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.3, 142.0, 137.9, 136.9, 136.7, 132.8, 129.7, 129.4, 128.3, 127.9, 126.9, 21.1.

**(E)-4-Phenylbut-2-enal (3a)**<sup>13</sup> Purified by flash column chromatography (PE/EA 100:1, v/v) on silica gel to give the desired product as yellow oil, 7 mg, 16% yield.  $R_f = 0.40$  20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.54 (d,  $J = 7.9$  Hz, 1H), 7.36–7.31 (m, 2H), 7.27–7.24 (m, 1H), 7.19 (d,  $J = 6.9$  Hz, 1H), 6.97 (dt,  $J = 15.5, 6.7$  Hz, 1H), 6.11 (ddt,  $J = 15.5, 7.9, 1.5$  Hz, 1H), 3.65 (dt,  $J = 6.6, 1.2$  Hz, 1H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  193.7, 156.3, 133.5, 128.9, 128.8, 127.0, 39.0.

**(E)-3-Methyl-4-phenylbut-2-enal ((E)-3l)**<sup>14</sup> Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the first isomer of the desired product as colorless liquid, 46 mg, 57% yield.  $R_f = 0.48$ , 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.13 (d,  $J = 8.0$  Hz, 1H), 7.33 (dd,  $J = 7.3, 7.3$  Hz, 2H), 7.28–7.23 (m, 1H), 7.19 (d,  $J = 7.1$  Hz, 2H), 6.04 (d,  $J = 7.9$  Hz, 1H), 3.91 (s, 2H), 1.89 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  190.8, 161.6, 137.2, 129.3, 128.8, 128.6, 126.9, 38.3, 24.7.

**(Z)-3-Methyl-4-phenylbut-2-enal ((Z)-3l)**<sup>14</sup>

Purified by flash column chromatography (PE/EA 50:1, v/v) on silica gel to give the second isomer of the desired product as colorless liquid, 23 mg, 29% yield.  $R_f$  = 0.40, 20% ethyl acetate in petroleum ether.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.00 (d,  $J$  = 8.0 Hz, 1H), 7.32 (dd,  $J$  = 7.2, 7.2 Hz, 2H), 7.28 – 7.23 (m, 1H), 7.16 (d,  $J$  = 7.2 Hz, 2H), 5.89 (d,  $J$  = 7.9 Hz, 1H), 3.50 (s, 2H), 2.13 (s, 3H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.3, 162.2, 136.9, 129.1, 128.7, 128.5, 127.0, 46.9, 17.3.

#### General procedure for the preparation of 3-phenylbenzaldehydes 4 and 4'.

To a 100 mL flask fitted with a reflux condenser containing  $\text{Pd}(\text{PPh}_3)_4$  (174 mg, 0.15 mmol) with either 3-bromo-4-methylbenzaldehyde (1.00 g, 5.0 mmol) or 3-bromo-2-methylbenzaldehyde (1.00 g, 5.0 mmol) was added 20 mL of toluene, 20 mL of 1 N  $\text{Na}_2\text{CO}_3$  (aq) and  $\text{PhB}(\text{OH})_2$  (732 mg, 6.0 mmol) dissolved in 10 mL of ethanol. After heated at 110 °C for 6 hours, the reaction mixture was cooled to room temperature, diluted with 100 mL of water, extracted by 3×75 mL of  $\text{CH}_2\text{Cl}_2$ , and washed with 100 mL of brine. After drying over  $\text{Na}_2\text{SO}_4$ , flash column chromatography with 1:100 ethyl acetate/petroleum ether afforded the desired products.

**6-Methyl-[1,1'-biphenyl]-3-carbaldehyde (4)** 605 mg, light yellow oil, 62% yield,  $R_f$  = 0.40 (1:20 ethyl acetate/petroleum ether).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.99 (s, 1H, CHO), 7.79 – 7.69 (m, 2H, ArH), 7.47 – 7.40 (m, 3H, ArH), 7.40-7.35 (m, 1H, ArH), 7.35-7.30 (m, 2H, ArH), 2.34 (s, 1H,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  191.9, 143.0, 142.7, 140.4, 134.5, 131.3, 131.0, 129.0, 128.3, 128.2, 127.4, 20.9. HRMS  $m/z$ : calculated for  $[\text{M}+\text{H}^+](\text{C}_{14}\text{H}_{13}\text{O})$  197.0966, found 197.0963.

**2-Methyl-[1,1'-biphenyl]-3-carbaldehyde (4')** 501 mg, light yellow oil, 51% yield.  $R_f$  = 0.40 (1:20 ethyl acetate/petroleum ether).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.29 (s, 1H, CHO), 7.74 (dd,  $J$  = 1.2, 1.2 Hz, 1H, ArH), 7.40-7.28 (m, 5H, ArH), 7.22-7.15 (m, 2H, ArH), 2.55 (s, 3H,  $\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  192.9, 144.0, 140.7, 137.9, 135.3, 134.7, 131.0, 129.3, 128.3, 127.3, 125.8, 16.2. HRMS  $m/z$ : calculated for  $[\text{M}+\text{H}^+](\text{C}_{14}\text{H}_{13}\text{O})$  197.0966, found 197.0959.

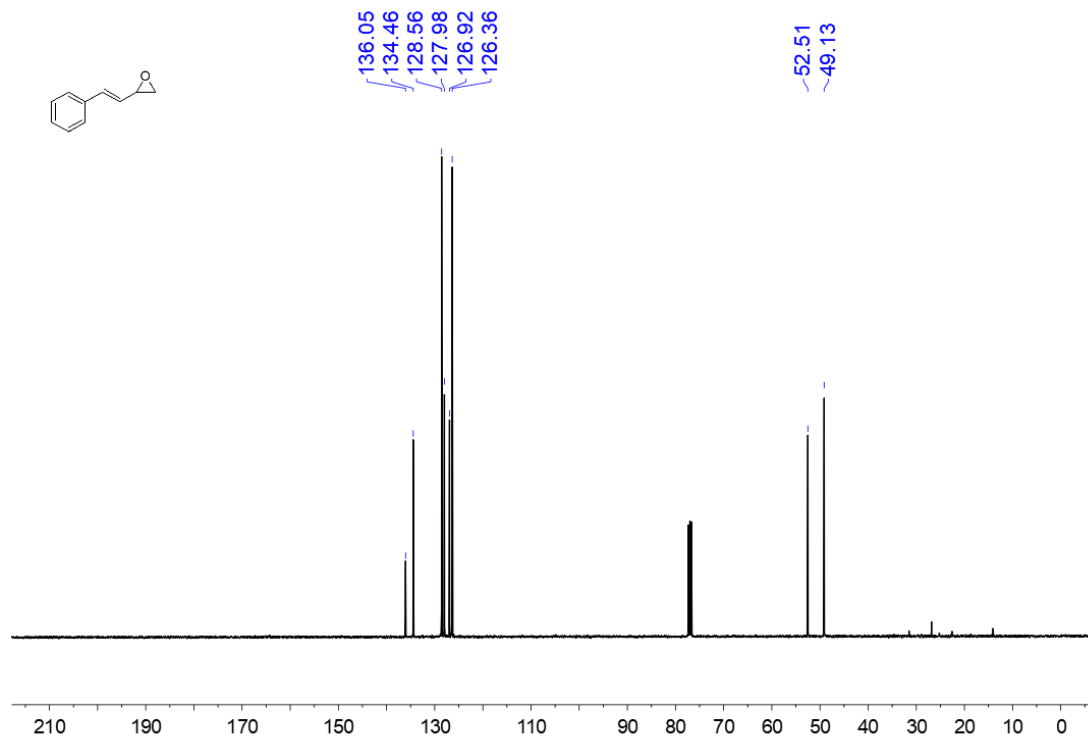
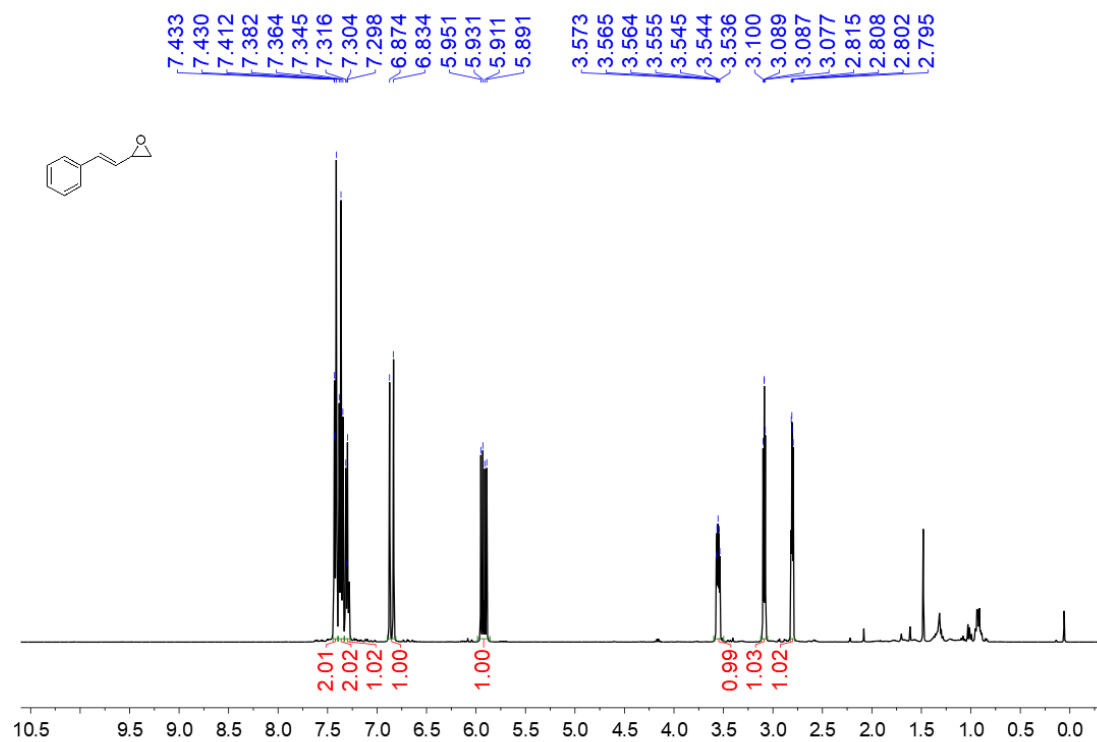
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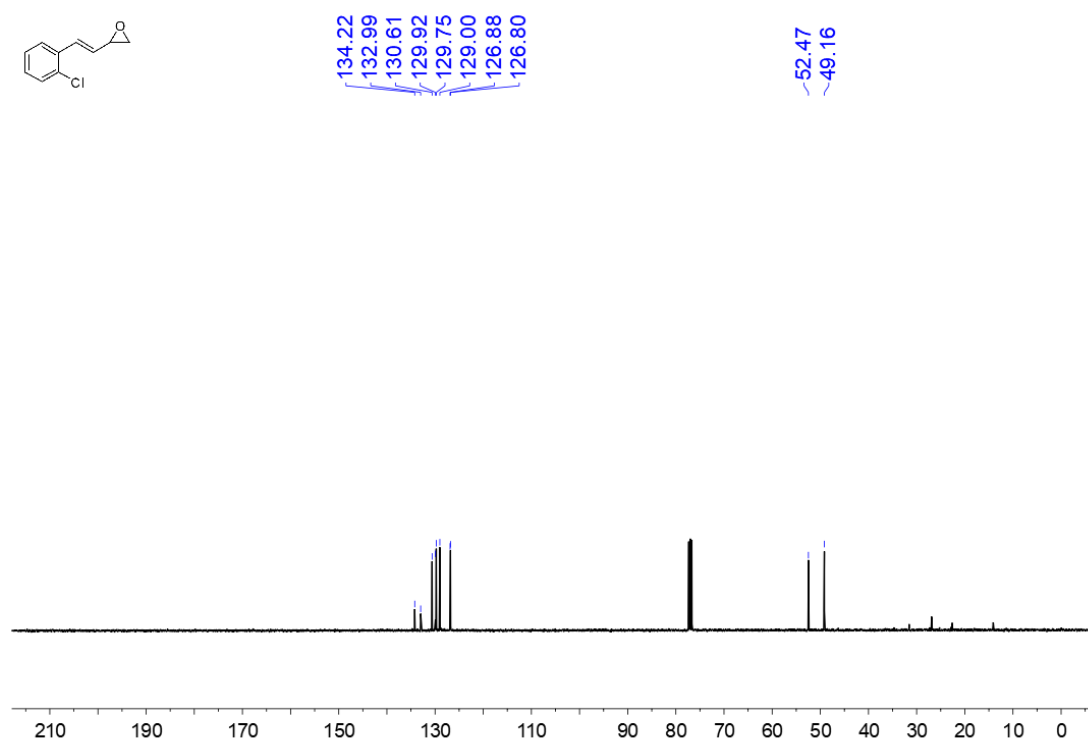
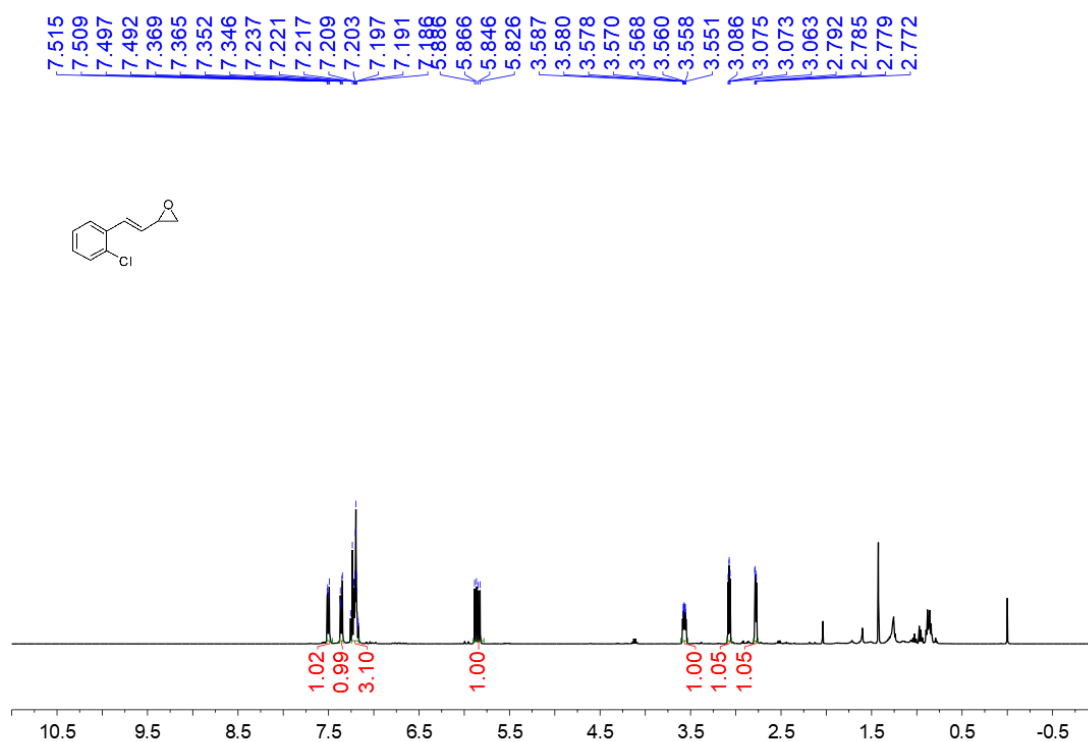


# Copies of $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra of styrylepoxydes **1**

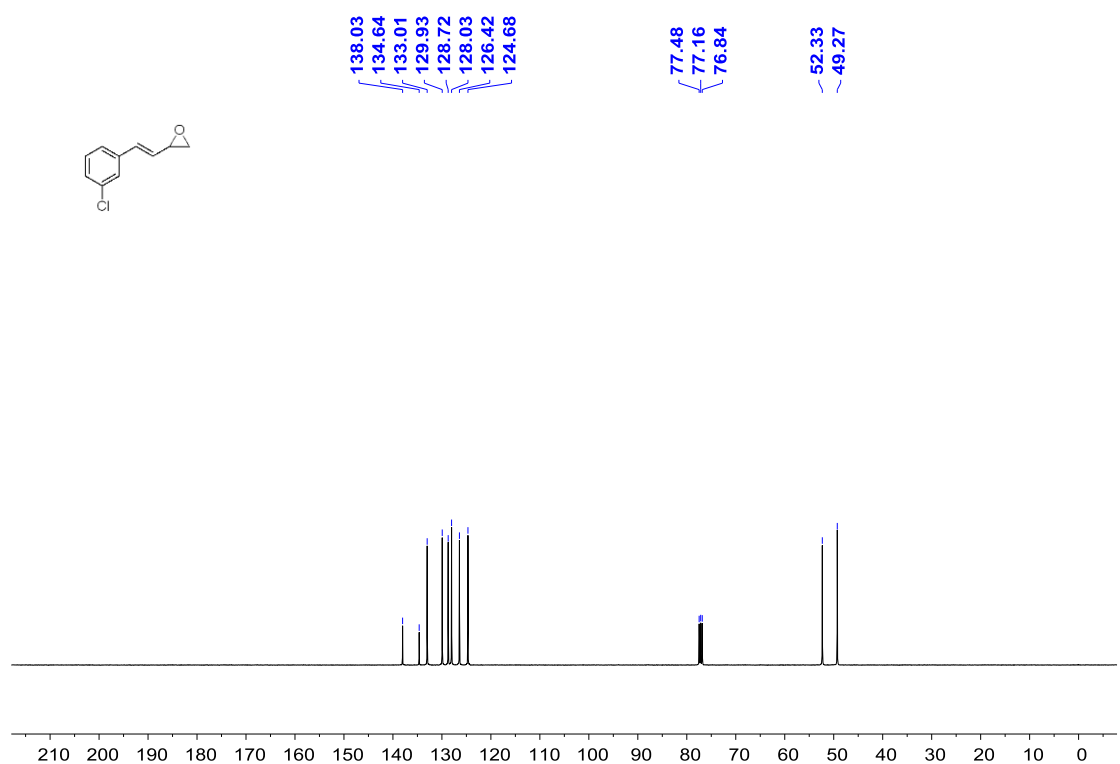
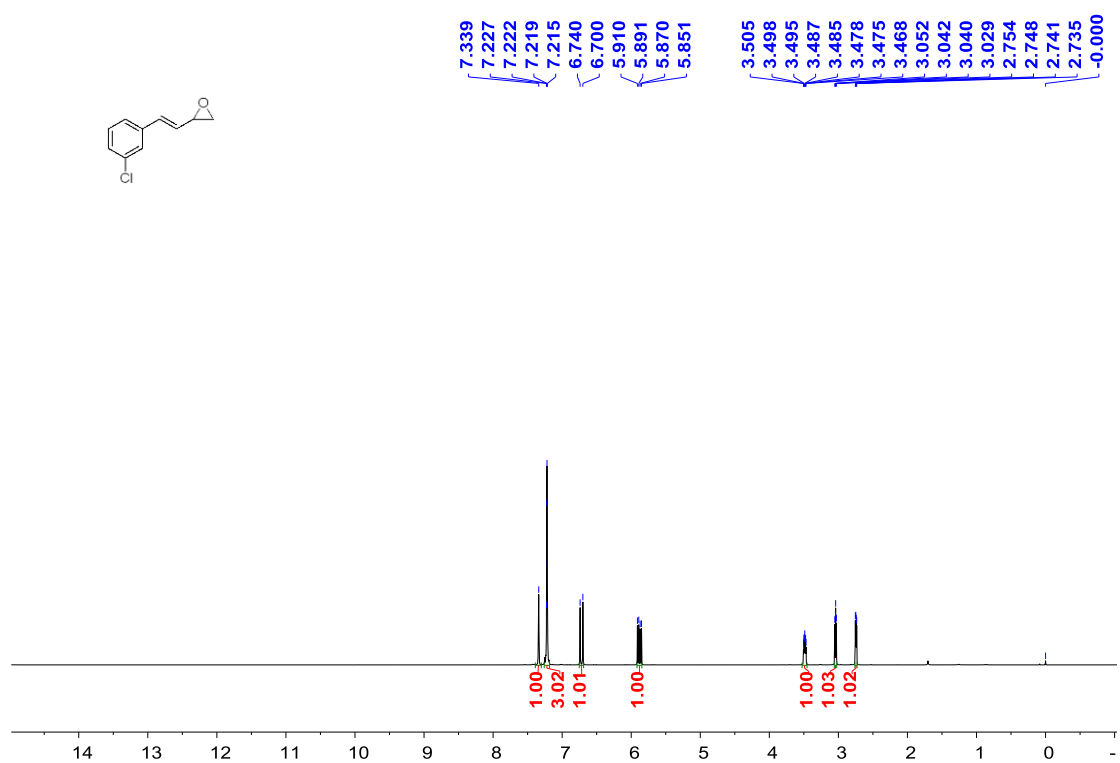
## (*E*)-2-Styryloxirane (**1a**)



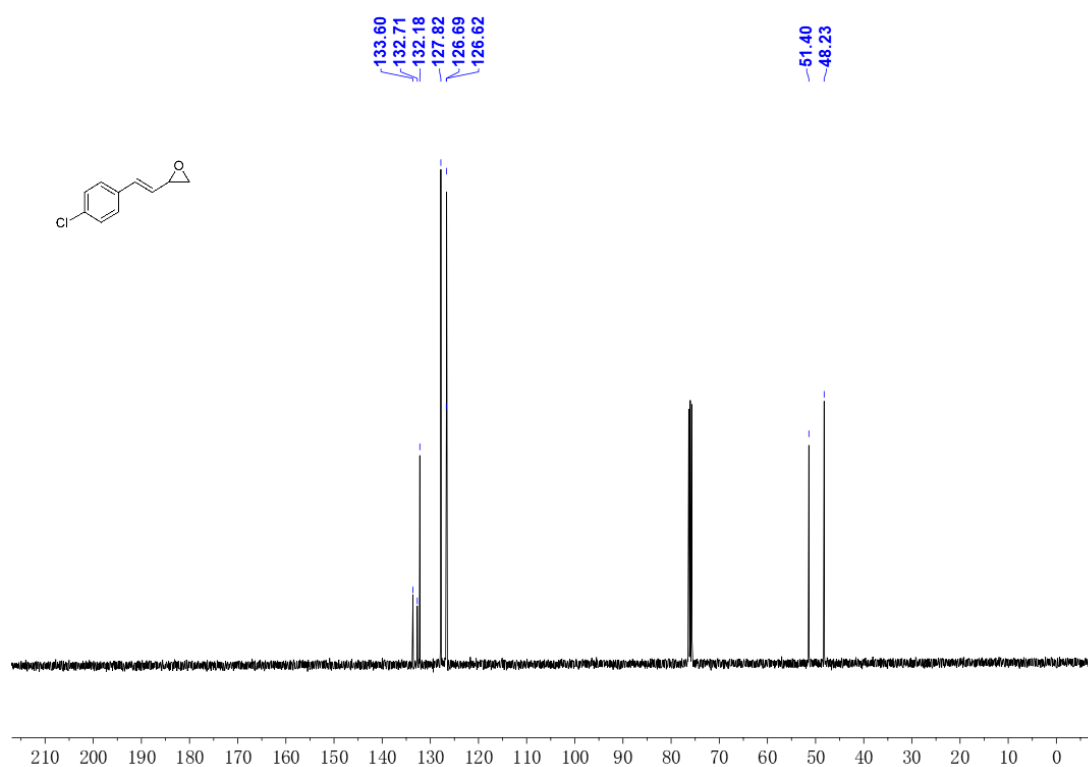
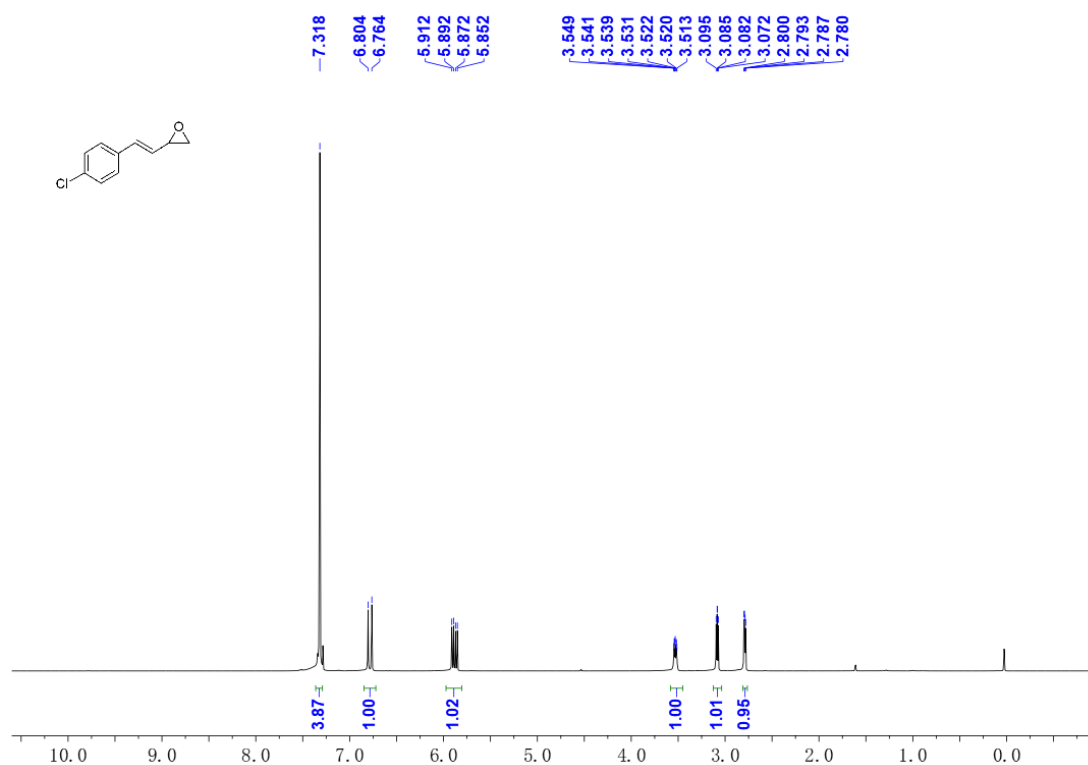
(*E*)-2-(2-Chlorostyryl)oxirane (**1b**)



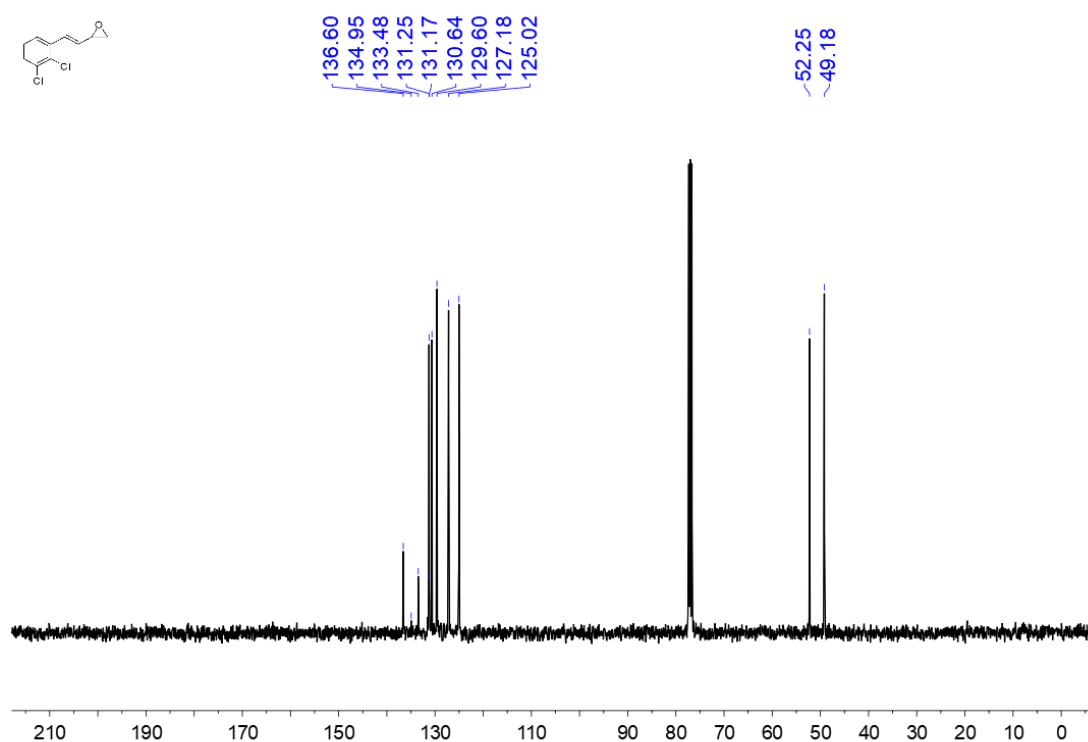
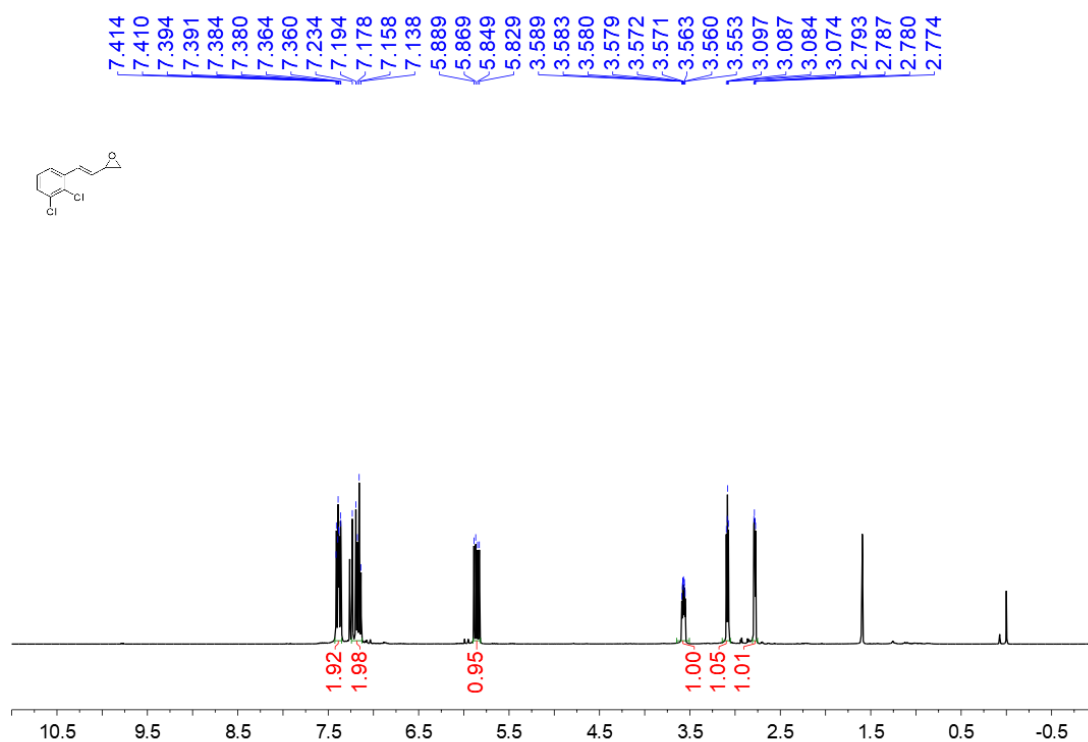
(*E*)-2-(3-Chlorostyryl)oxirane (**1c**)



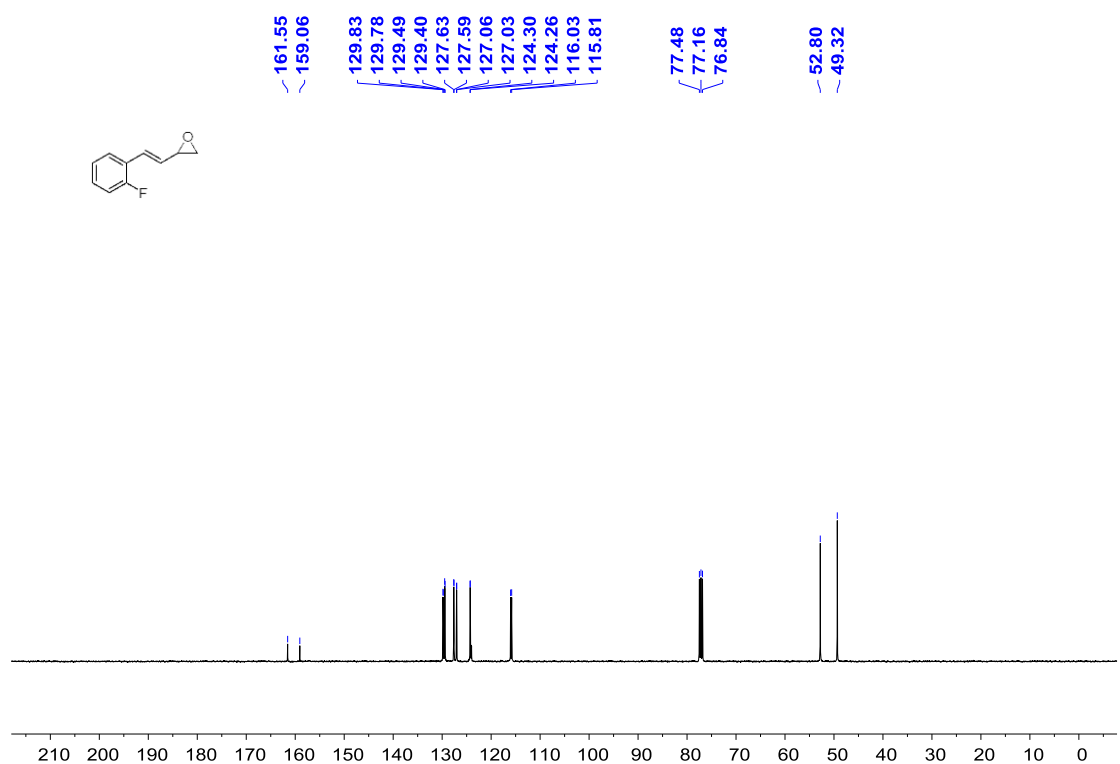
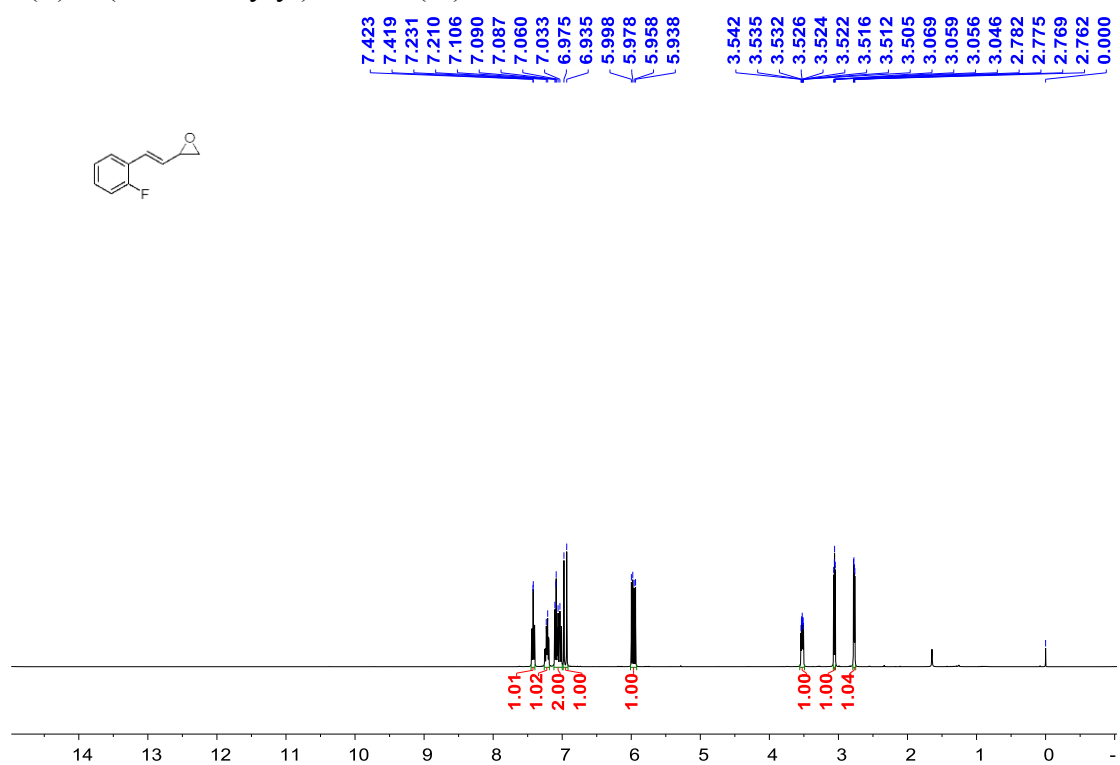
(*E*)-2-(4-Chlorostyryl)oxirane (**1d**)

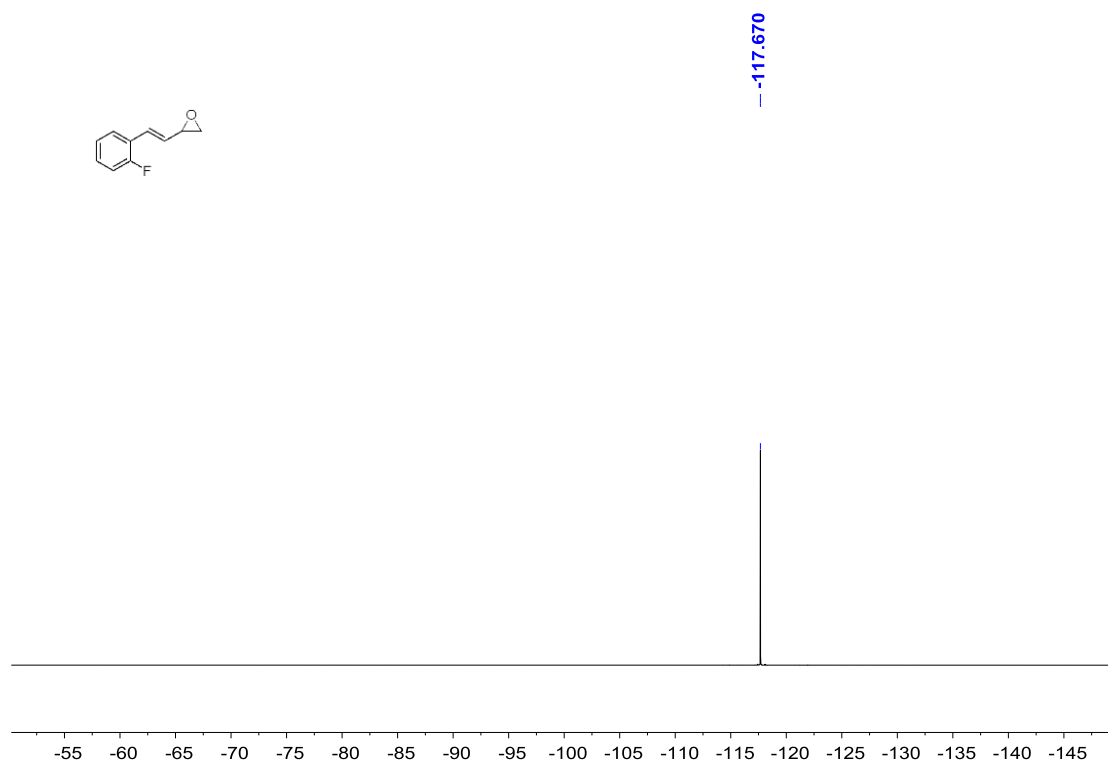


(*E*)-2-(2,3-Dichlorostyryl)oxirane (**1e**)

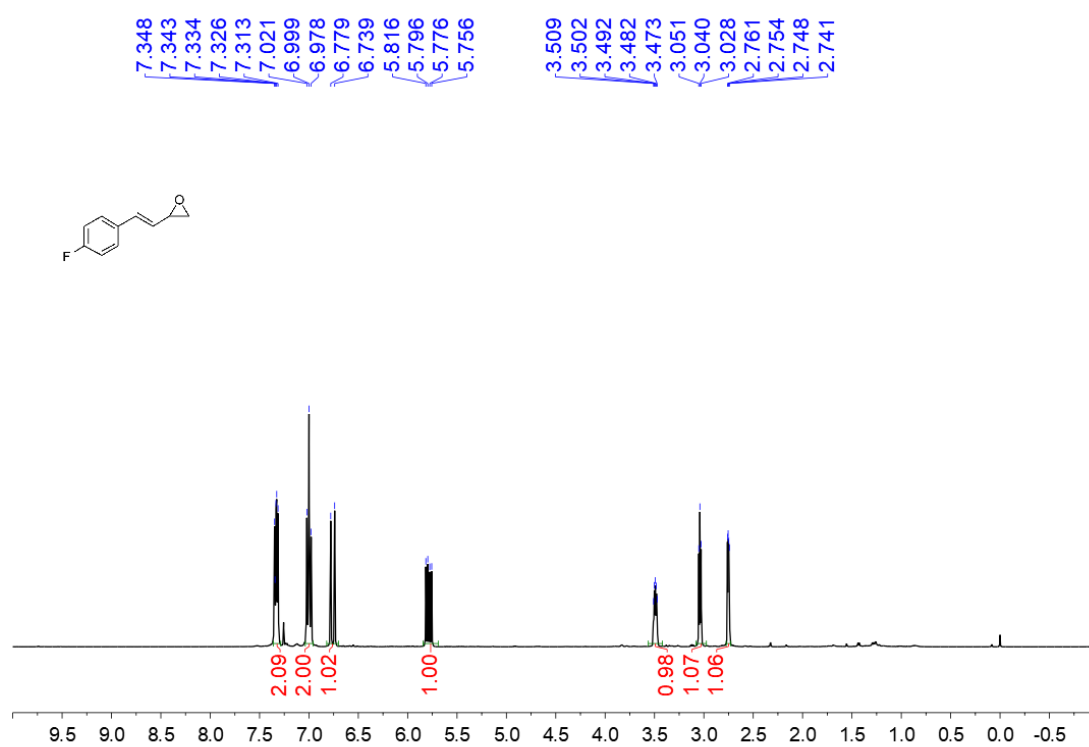


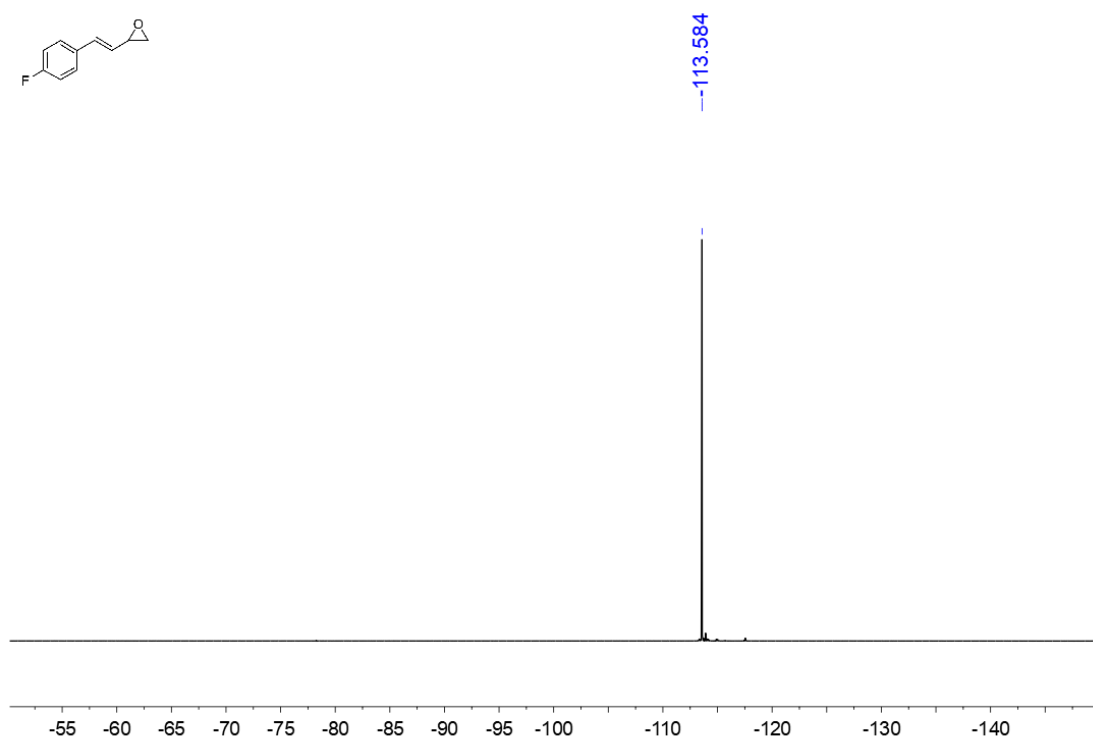
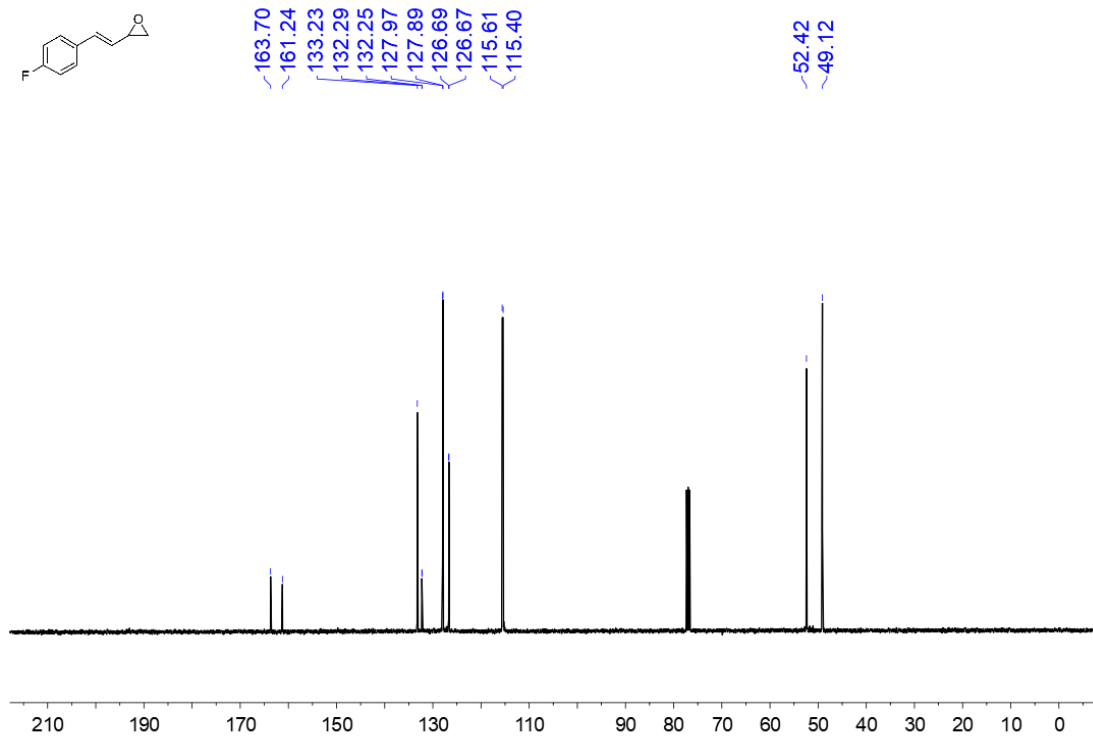
(*E*)-2-(2-Fluorostyryl)oxirane (**1f**)





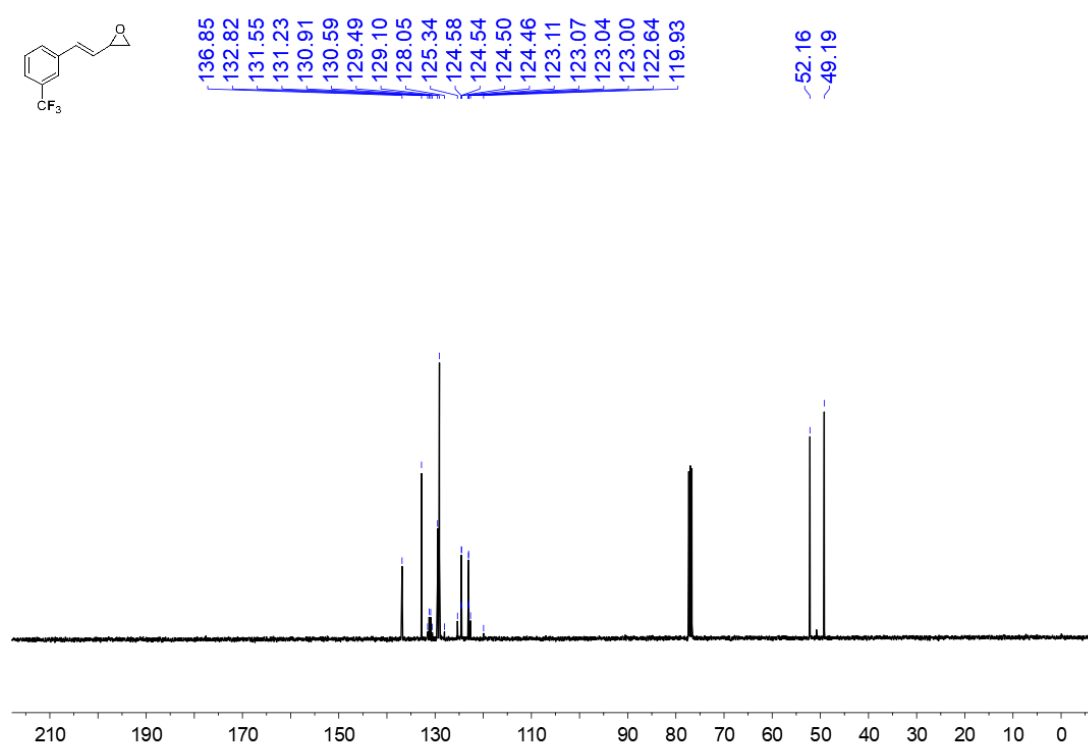
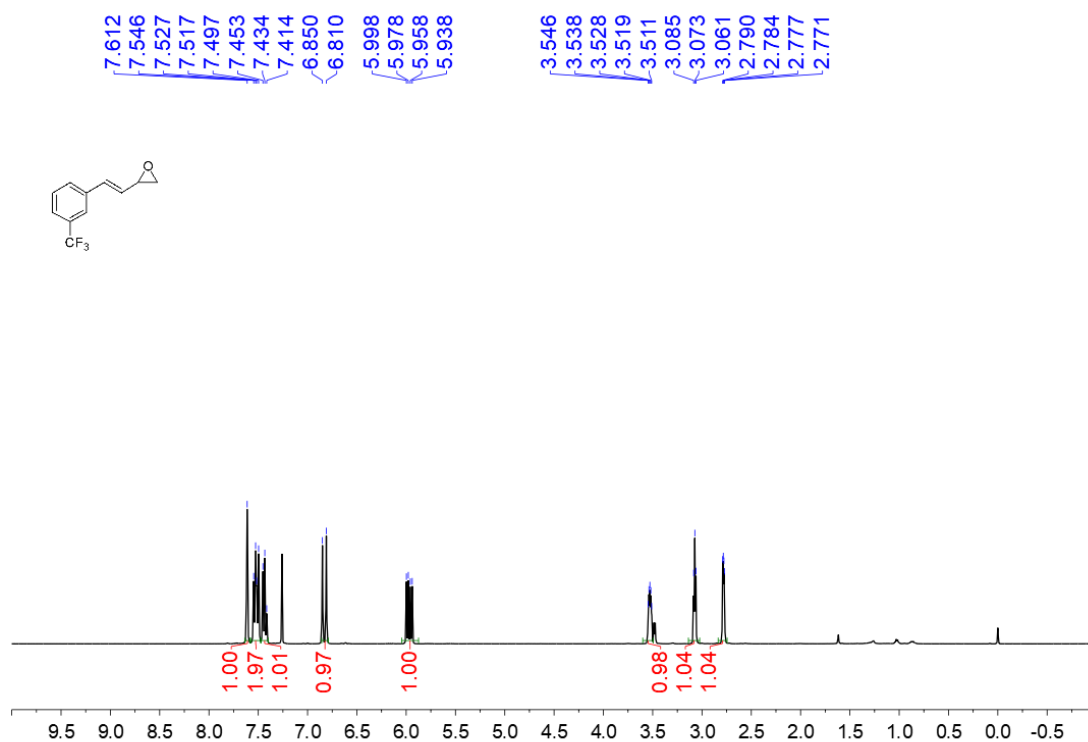
(*E*)-2-(4-Fluorostyryl)oxirane (**1g**)

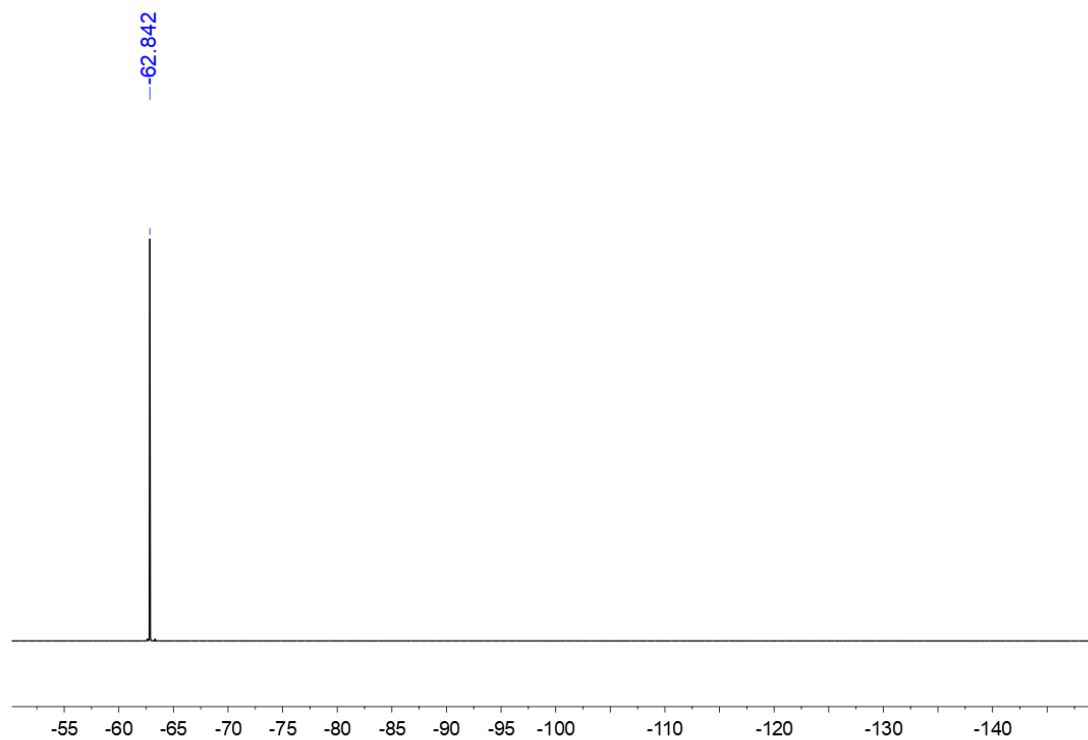




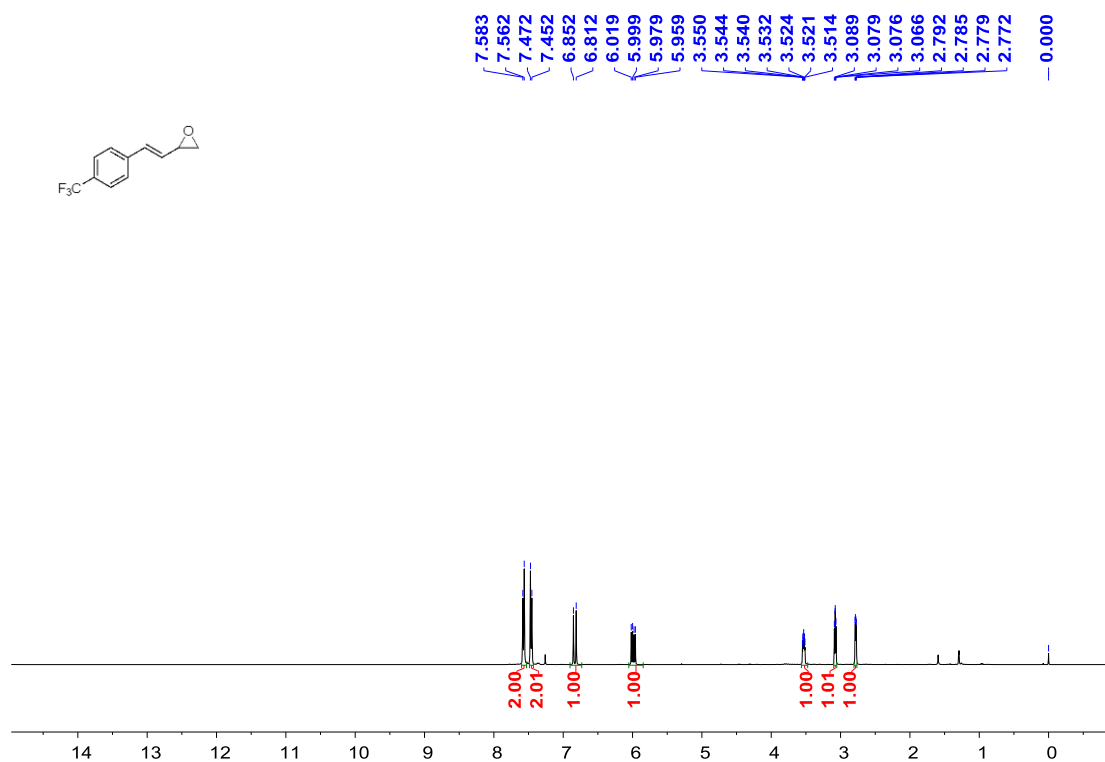
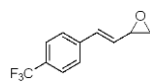


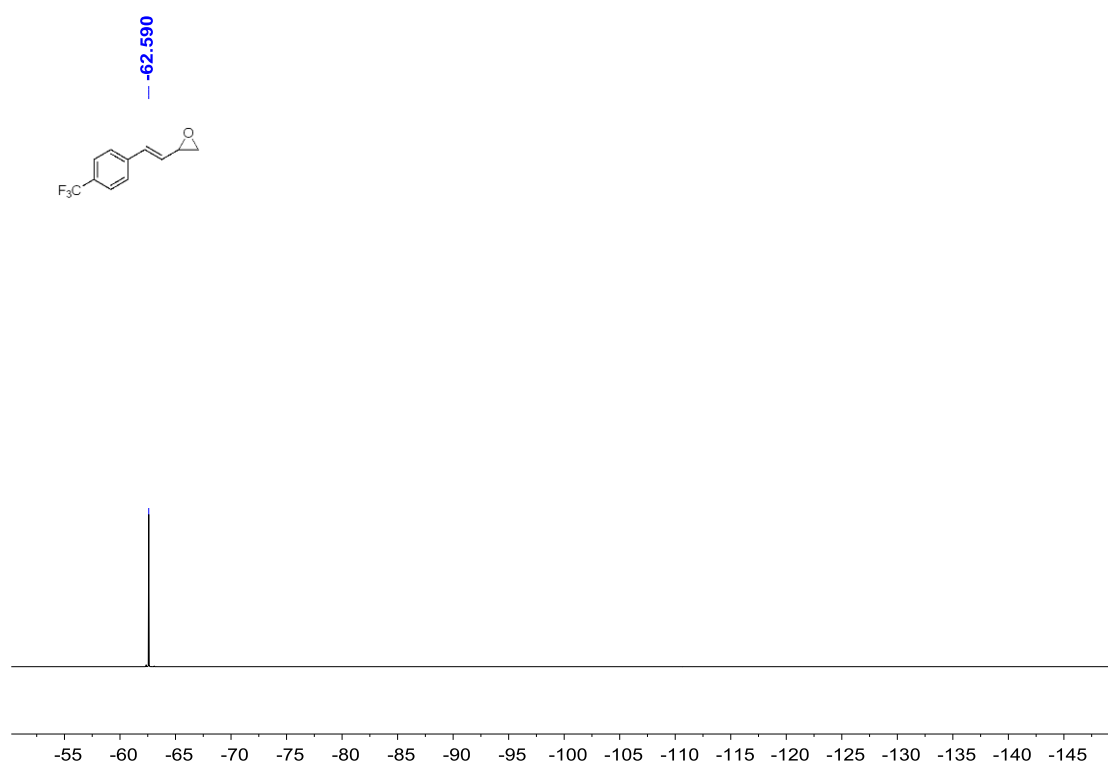
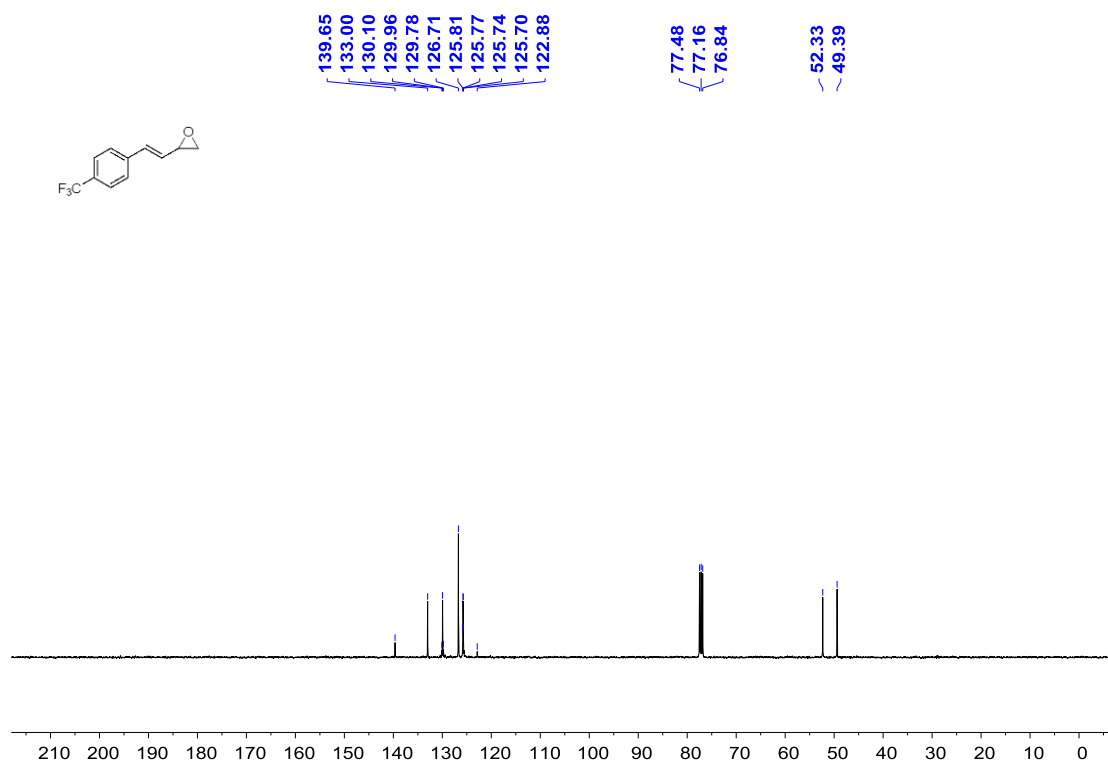
(*E*)-2-(3-(Trifluoromethyl)styryl)oxirane (**1h**)



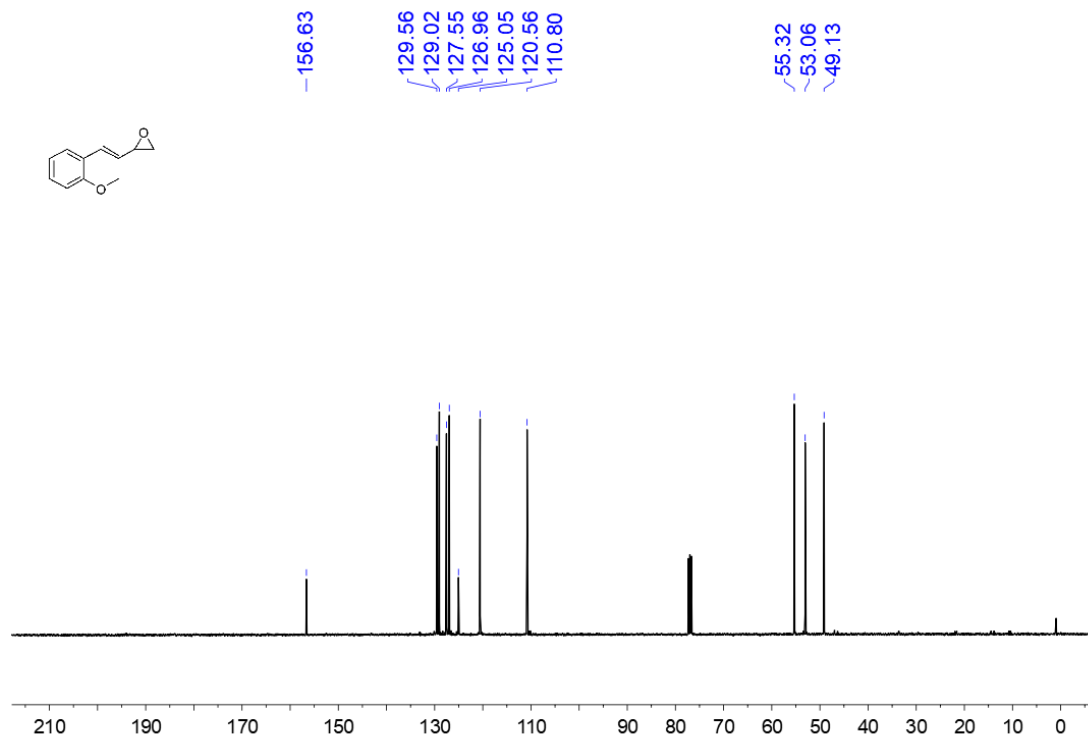
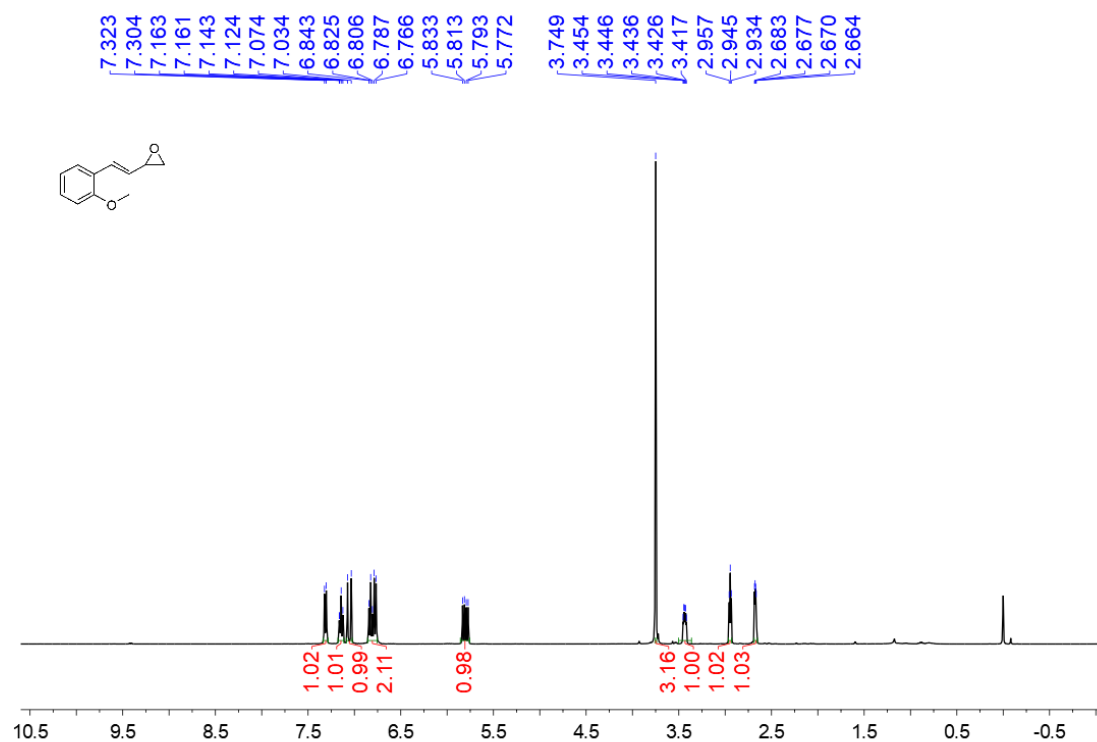


(*E*)-2-(4-(Trifluoromethyl)styryl)oxirane (**1i**)

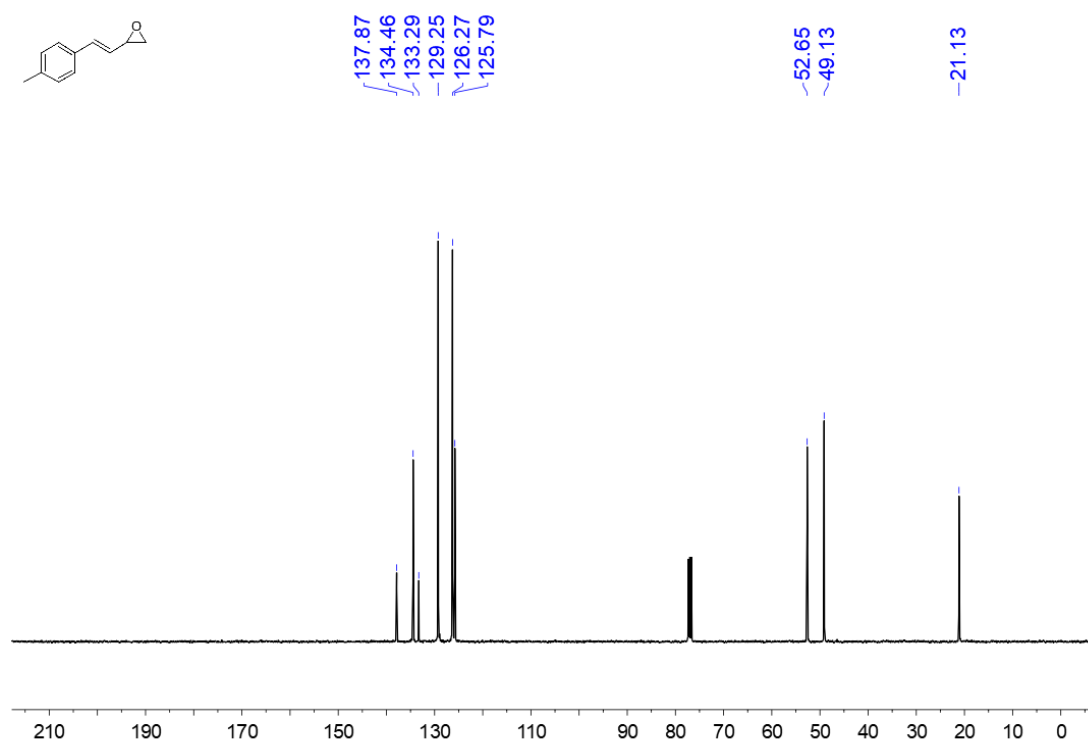
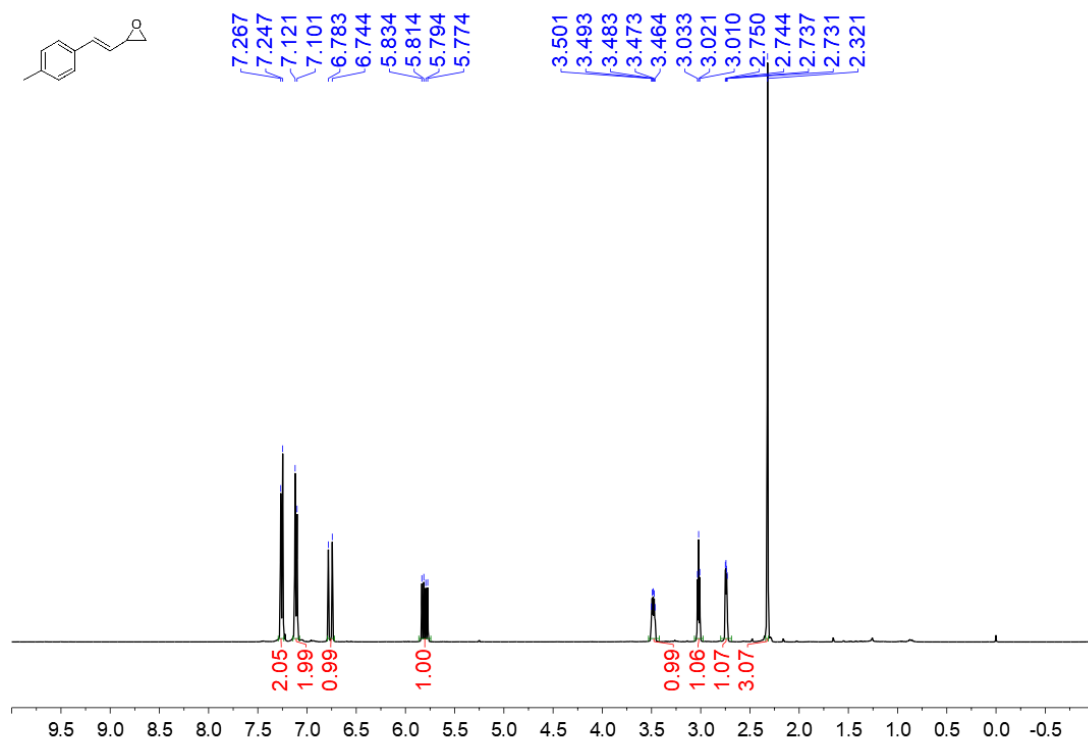




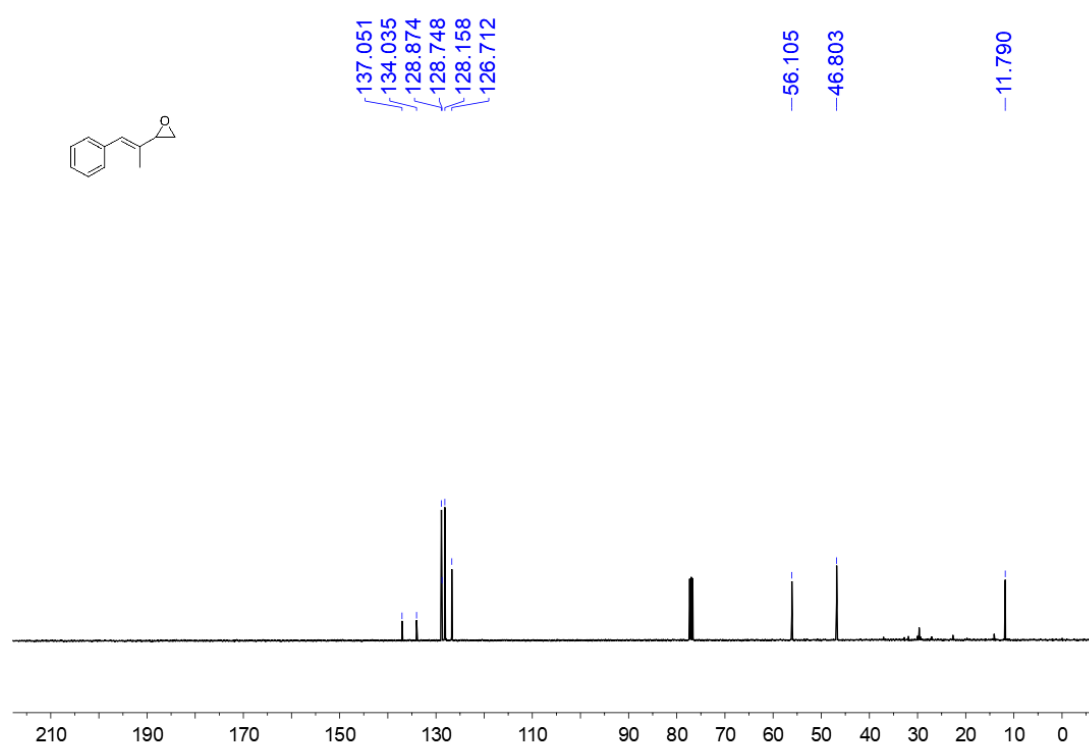
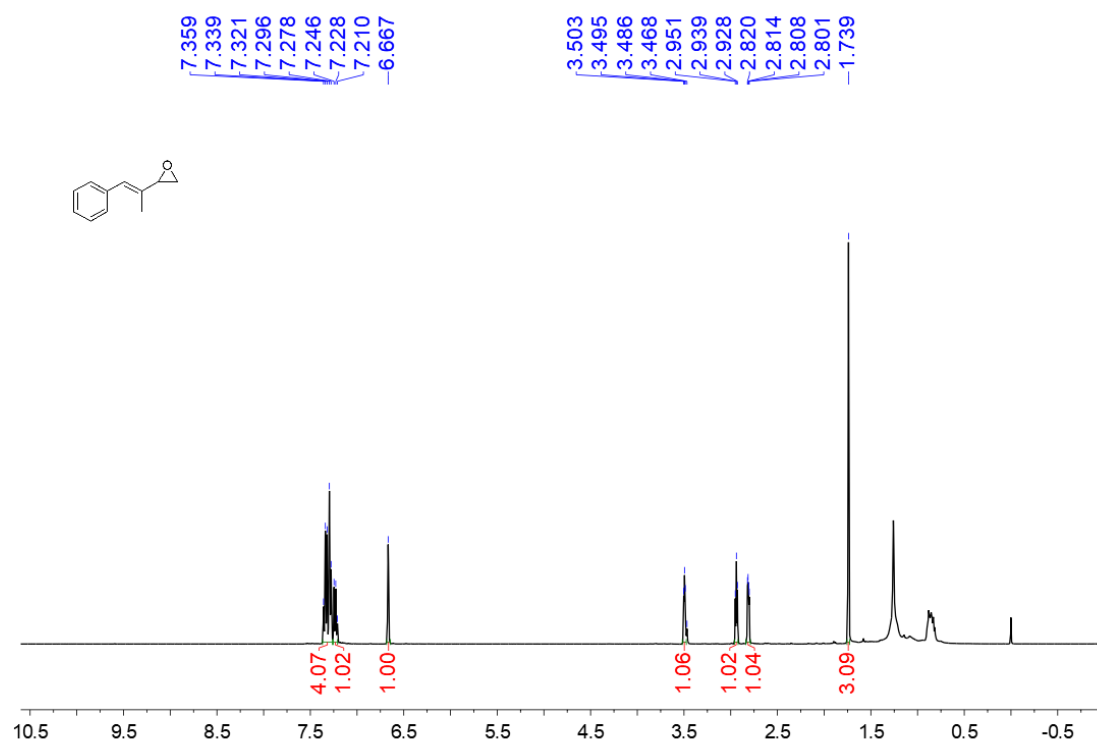
(*E*)-2-(2-Methoxystyryl)oxirane (**1j**)



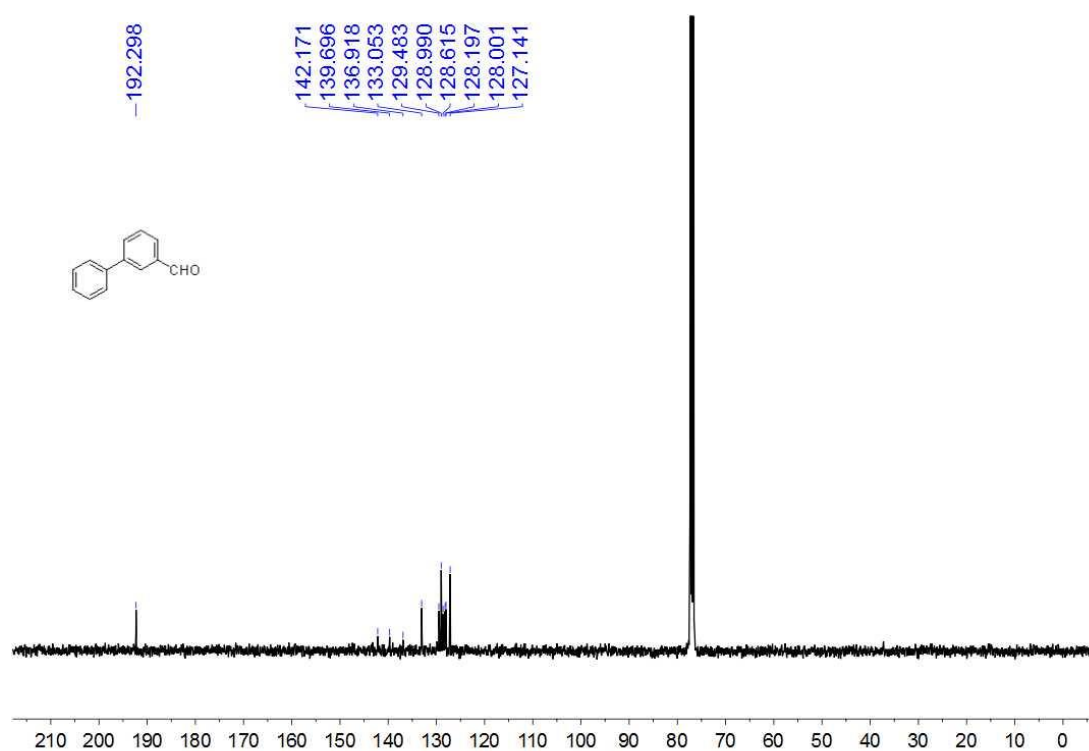
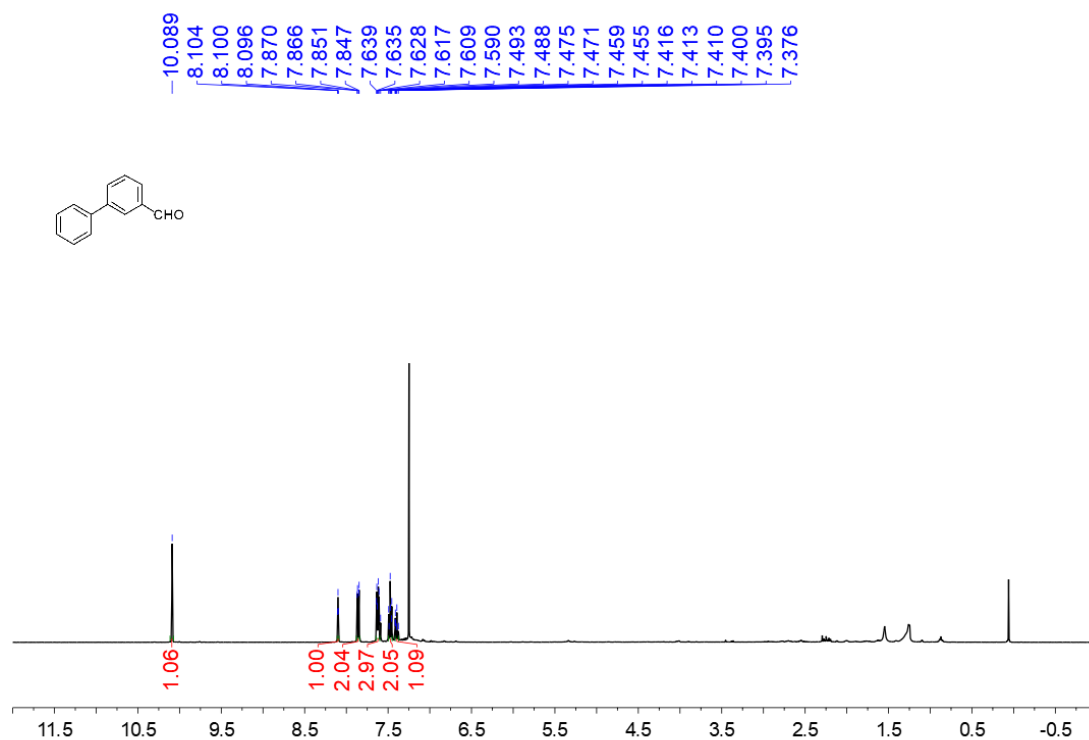
(*E*)-2-(4-Methylstyryl)oxirane (**1k**)



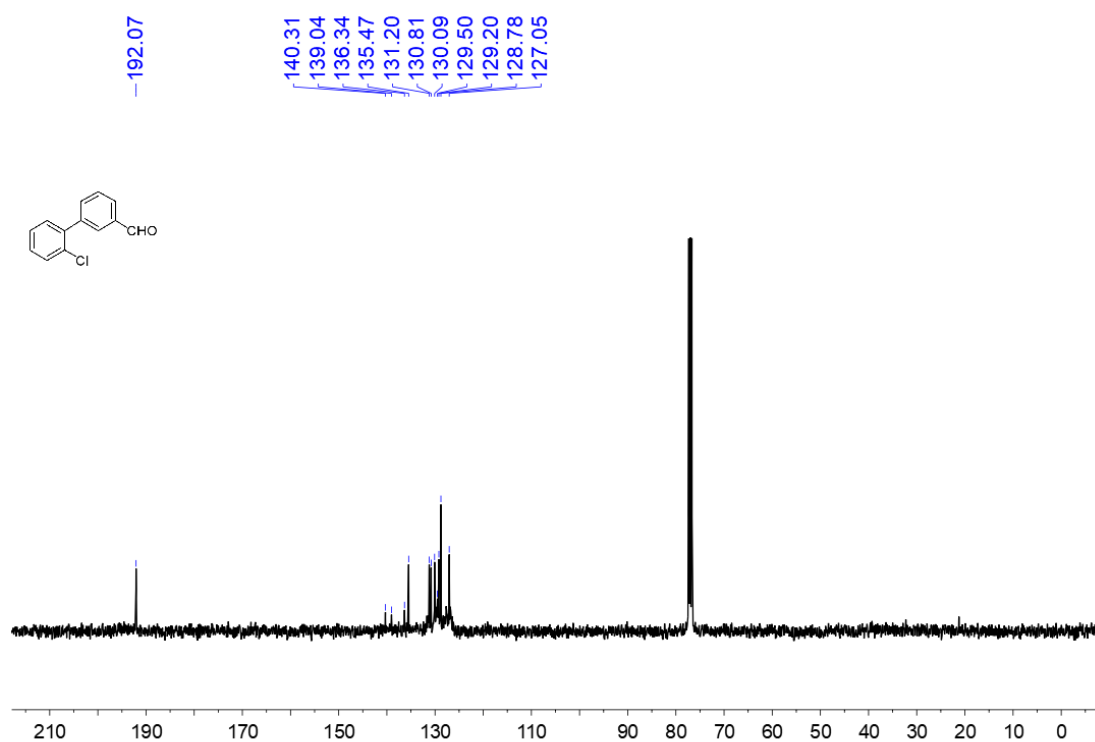
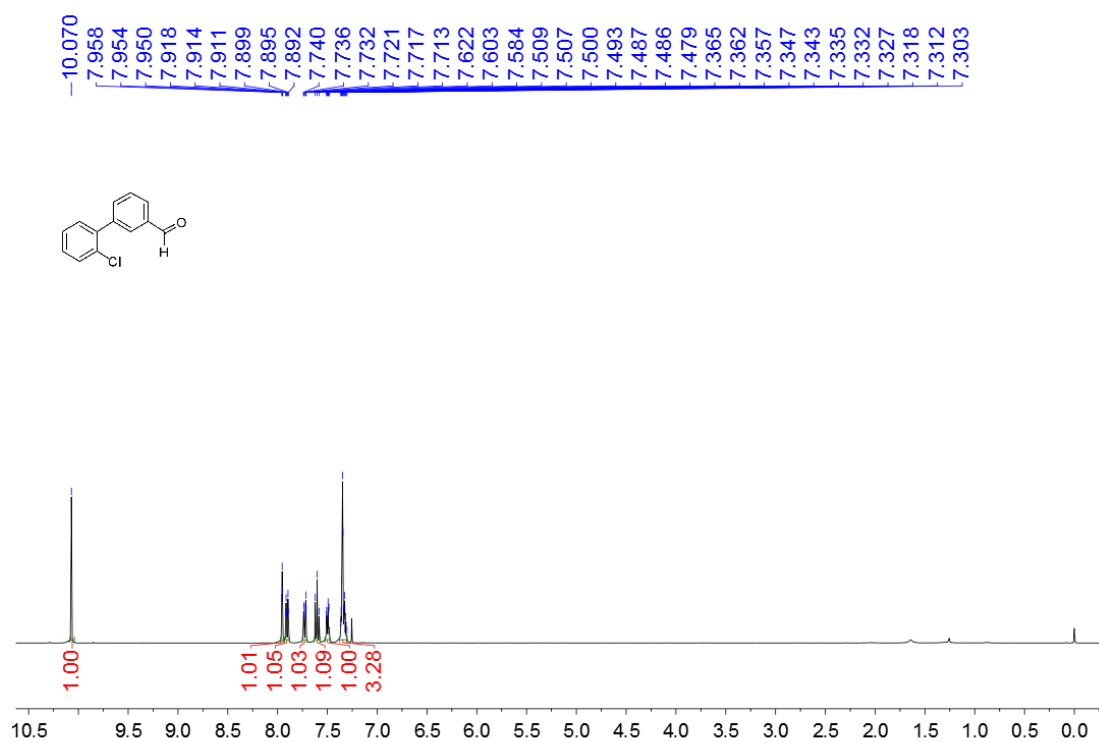
(*E*)-2-(1-Phenylprop-1-en-2-yl)oxirane (**11**)



Copies of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra of [1,1'-biaryl]-3-carbaldehydes **2**  
[1,1'-Biphenyl]-3-carbaldehyde (**2a**)

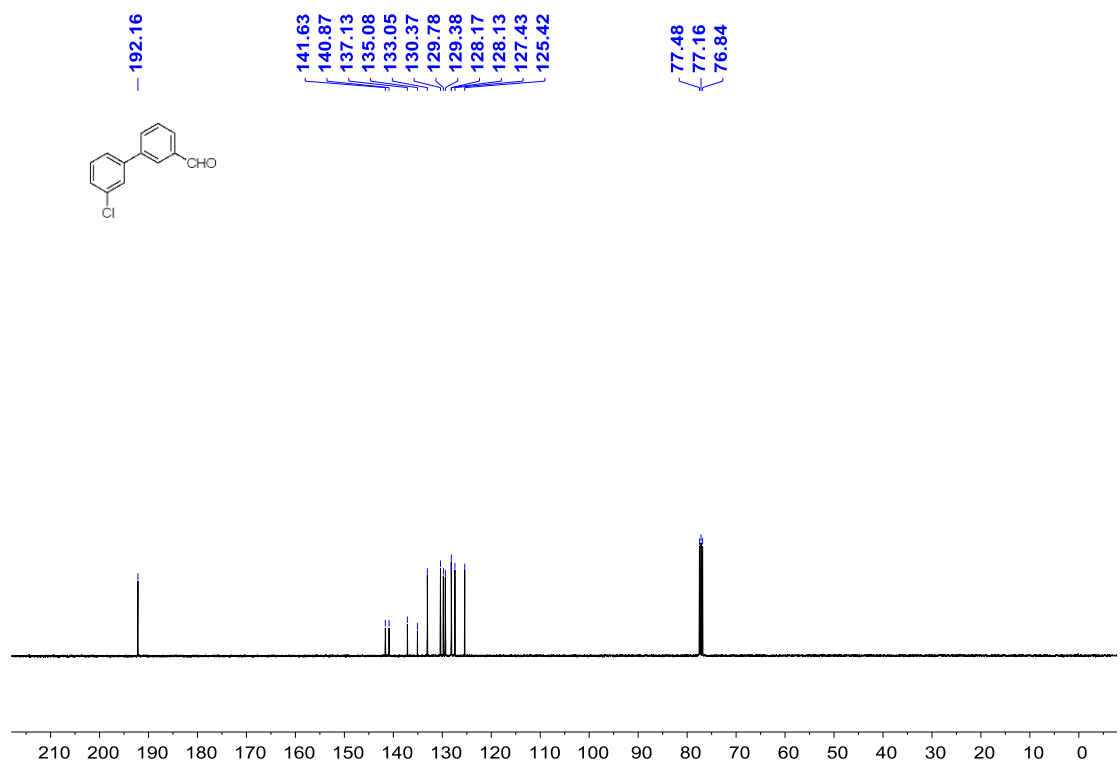
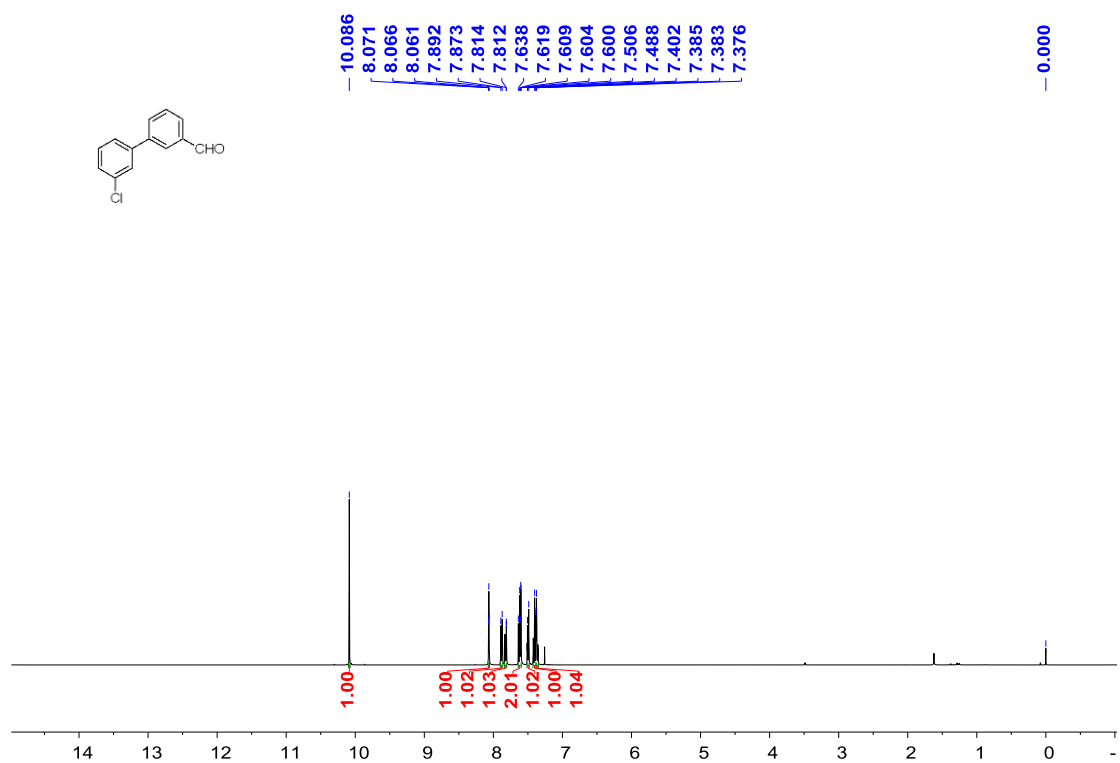


2'-Chloro-[1,1'-biphenyl]-3-carbaldehyde (**2b**)

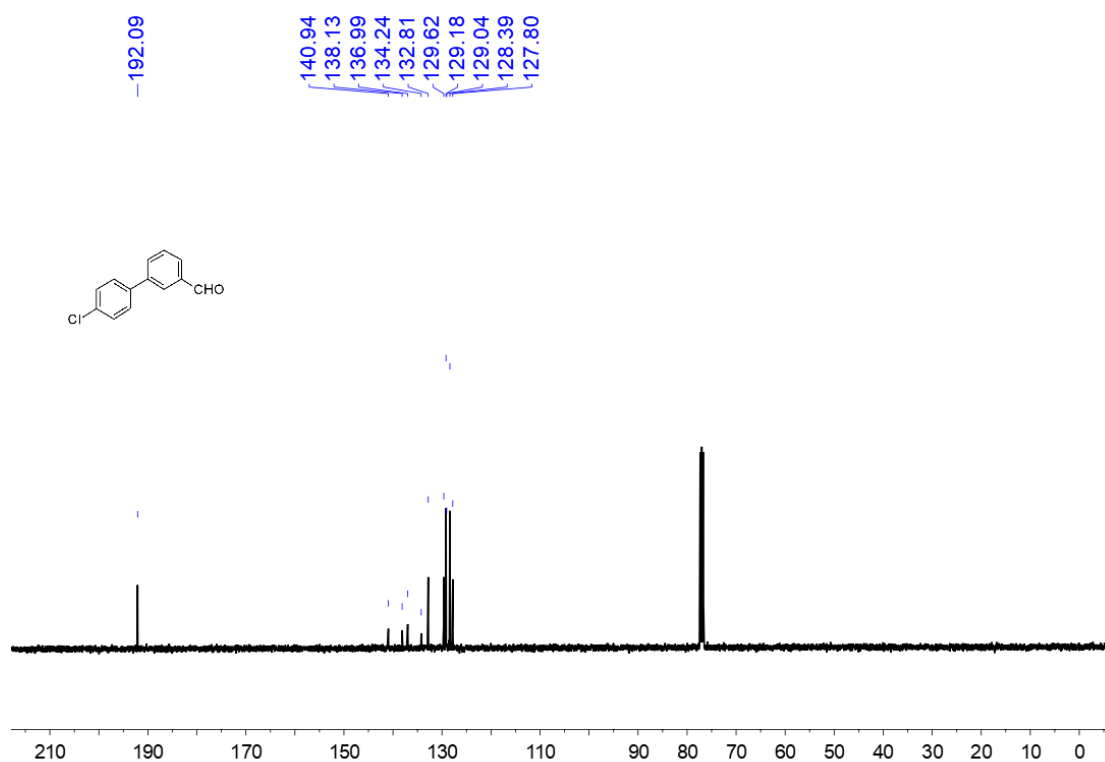
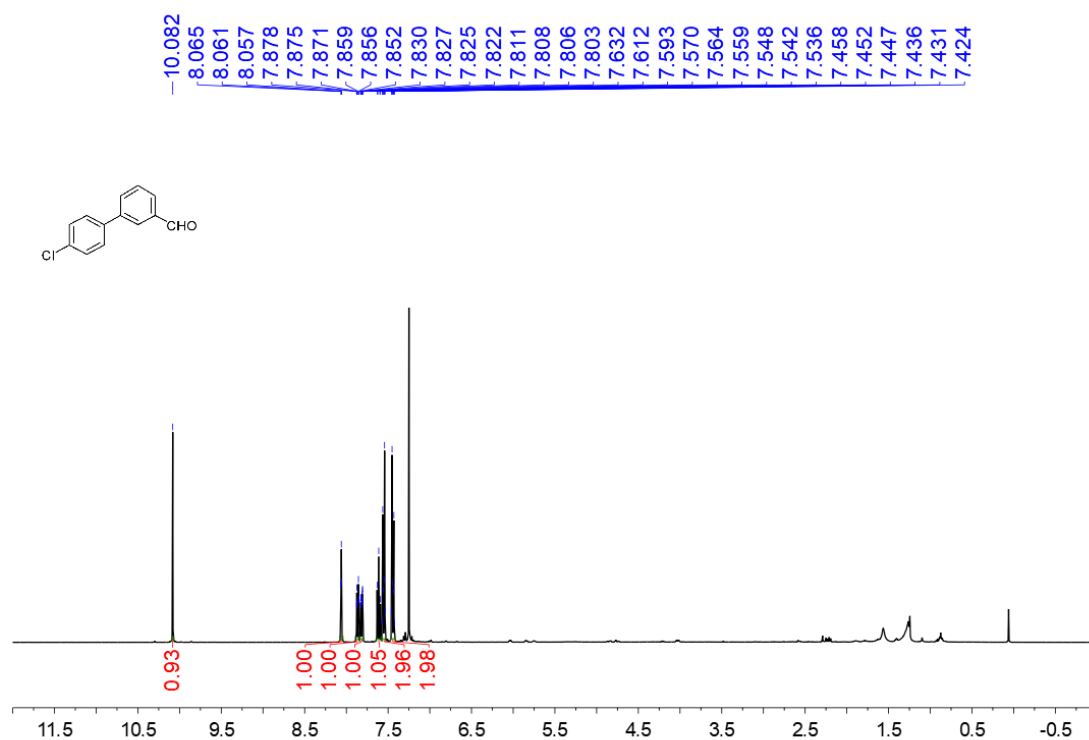




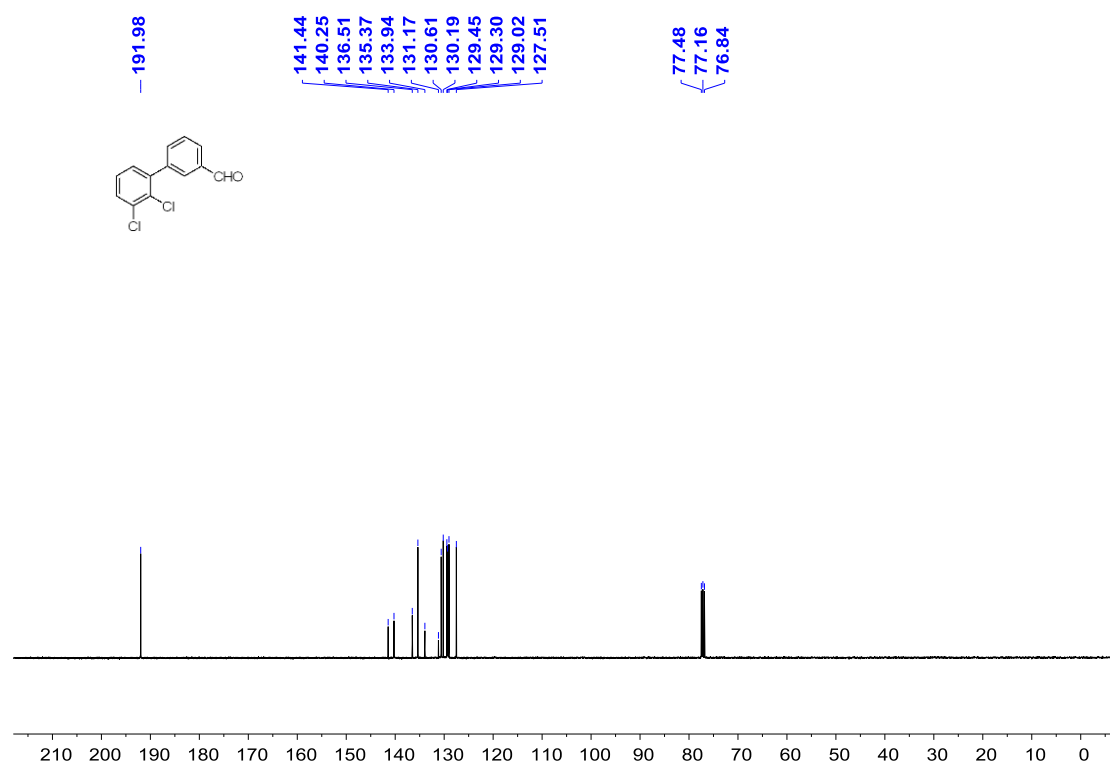
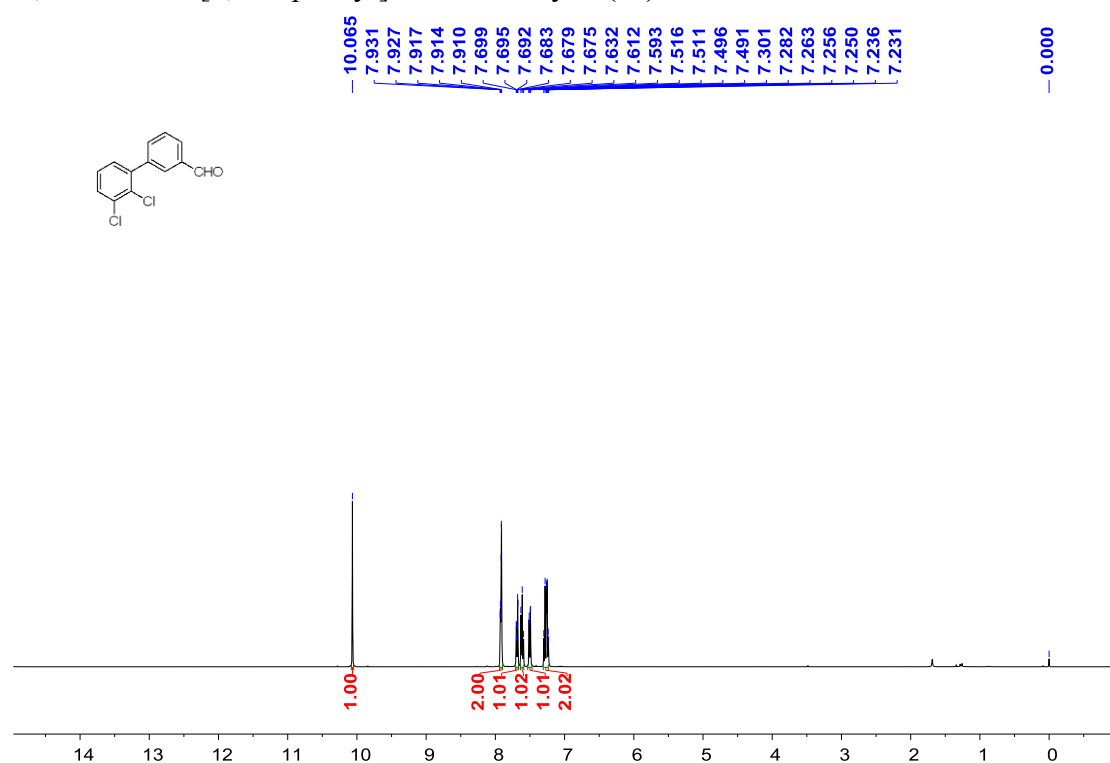
# 3'-Chloro-[1,1'-biphenyl]-3-carbaldehyde (**2c**)



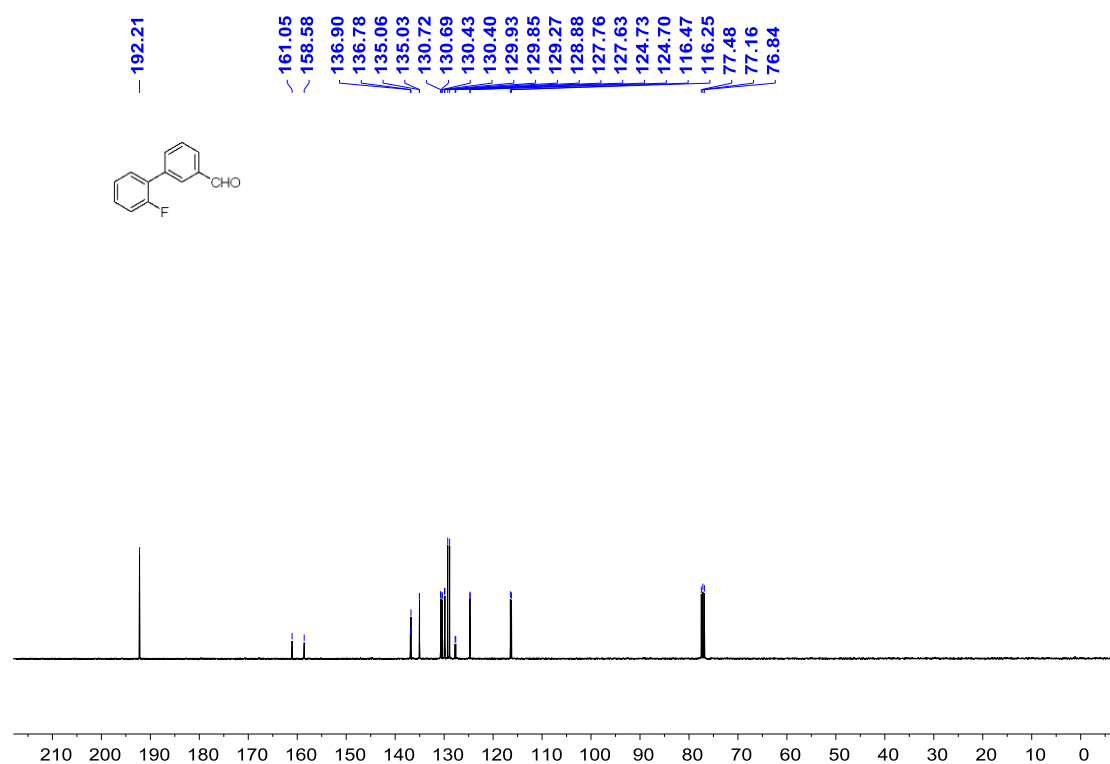
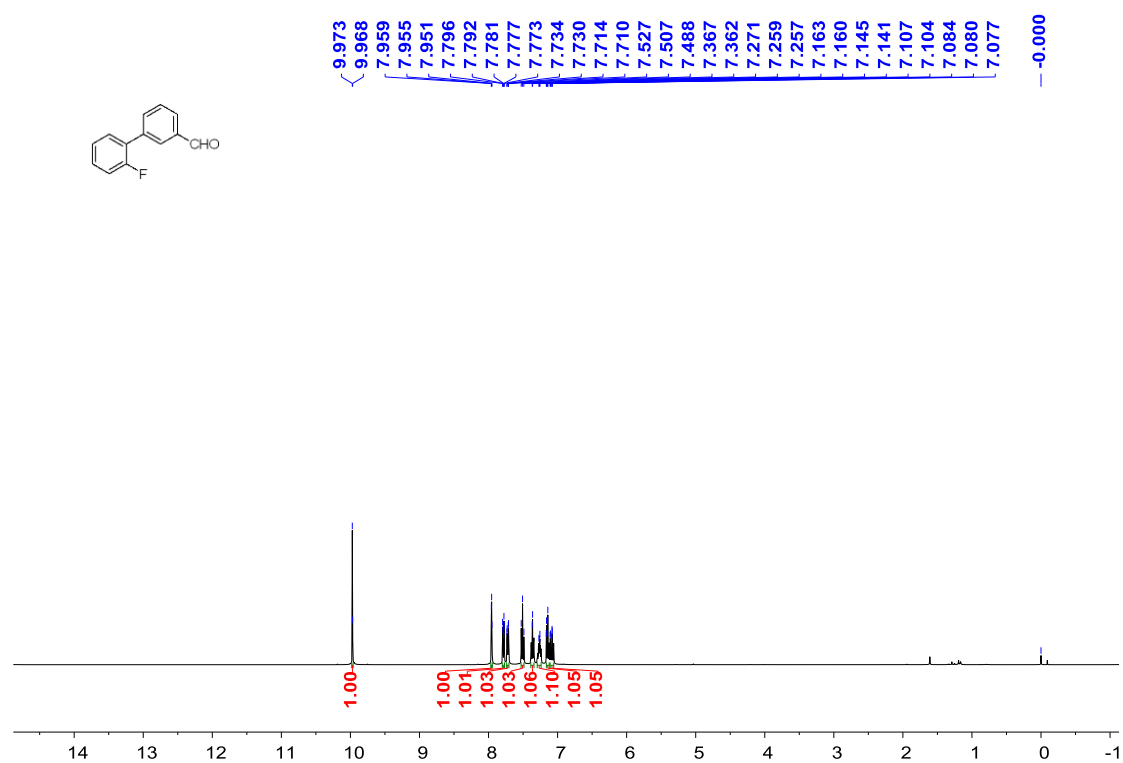
4'-Chloro-[1,1'-biphenyl]-3-carbaldehyde (**2d**)

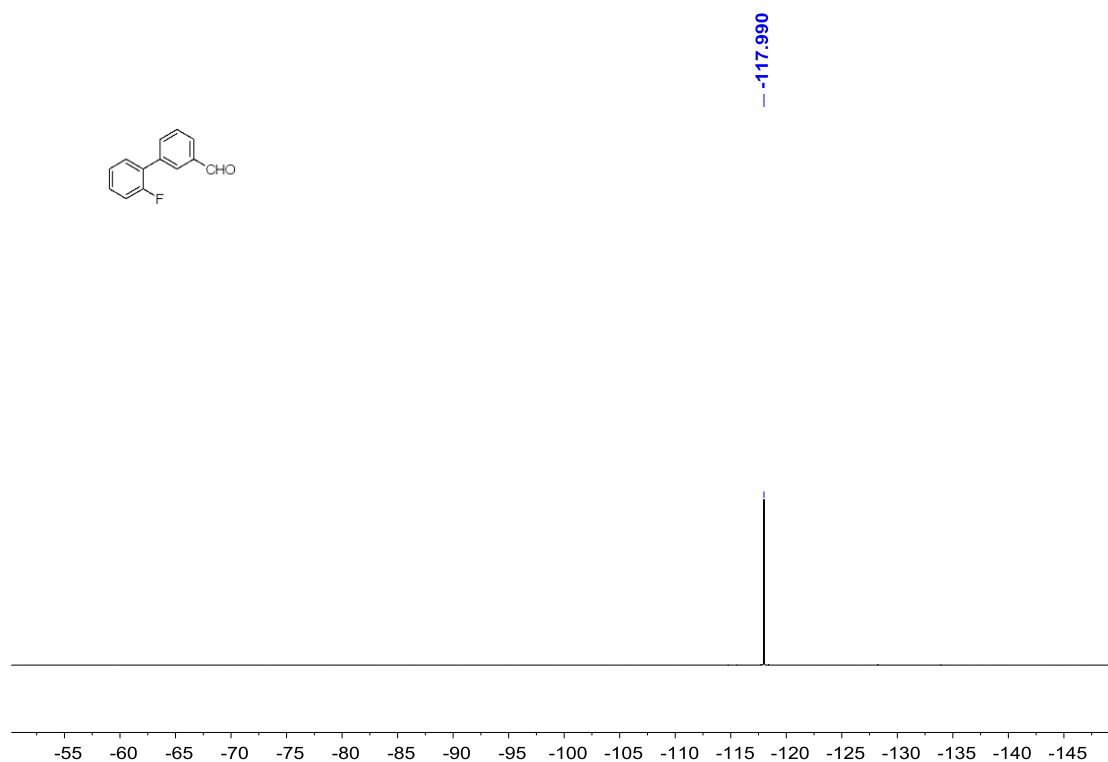


# 2',3'-Dichloro-[1,1'-biphenyl]-3-carbaldehyde (**2e**)

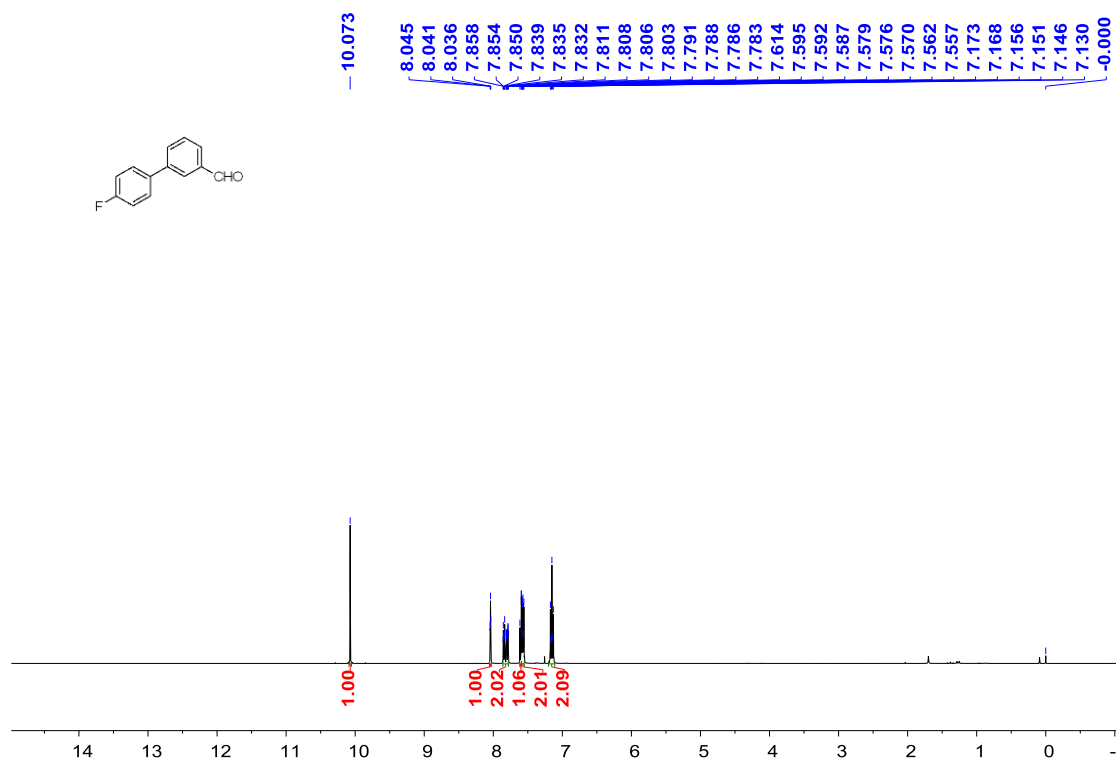


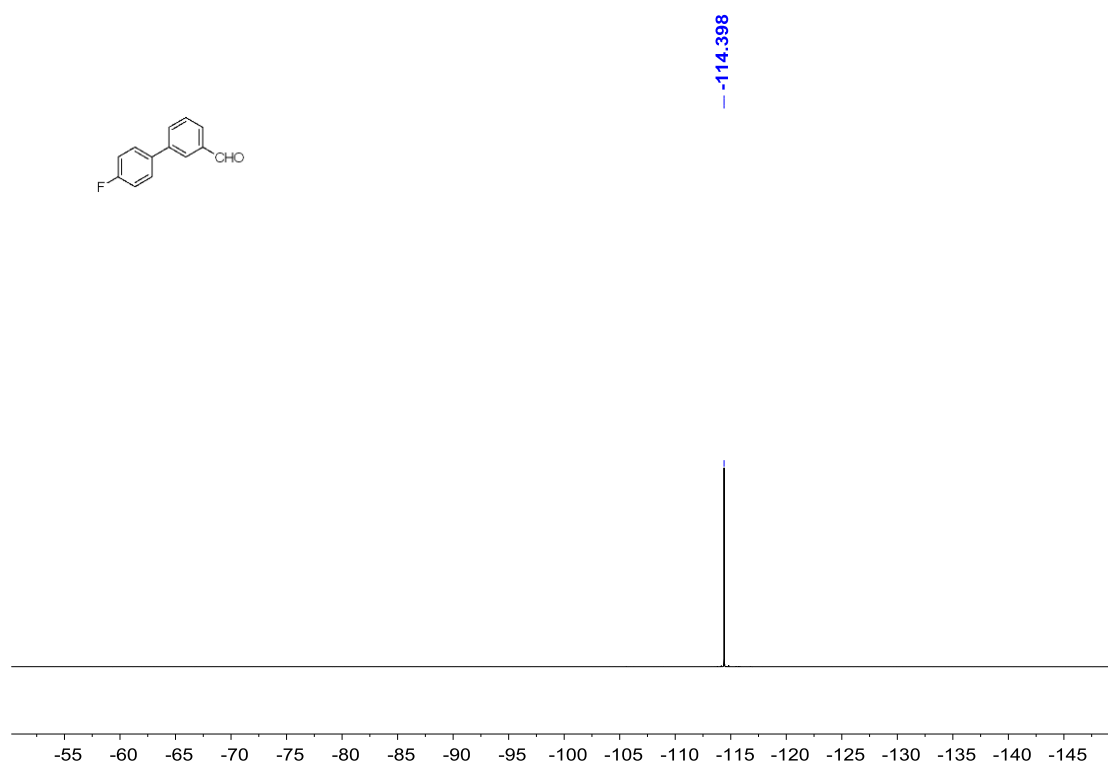
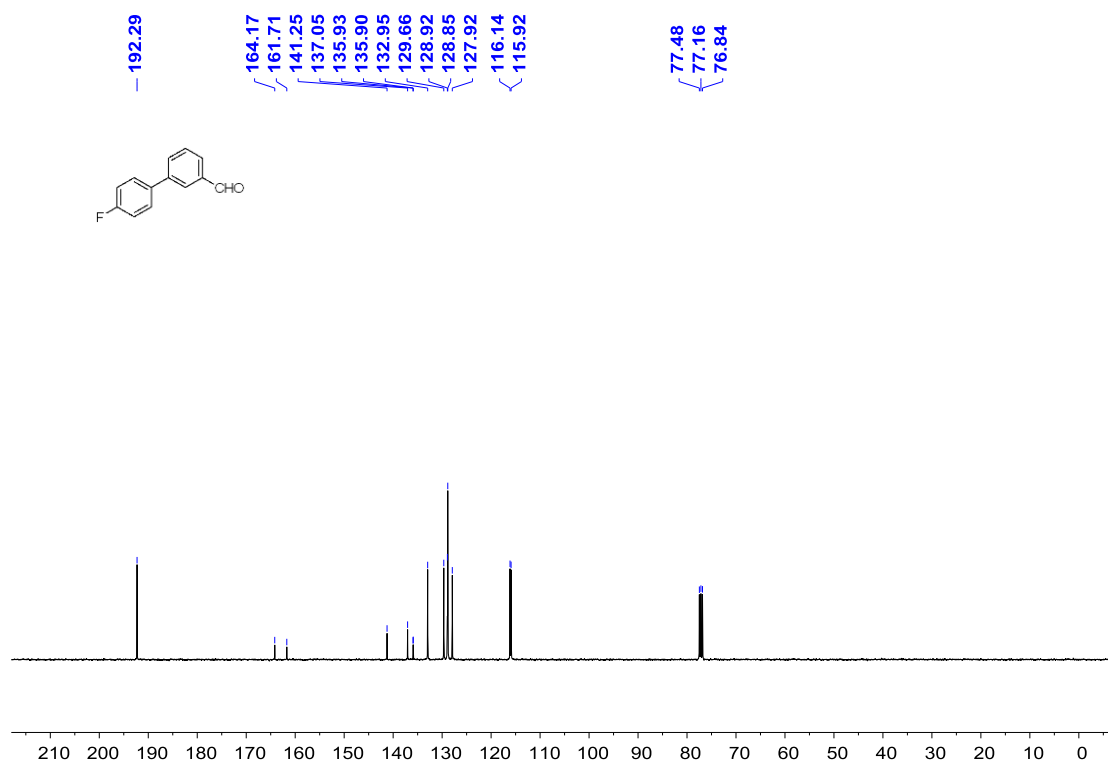
# 2'-Fluoro-[1,1'-biphenyl]-3-carbaldehyde (**2f**)



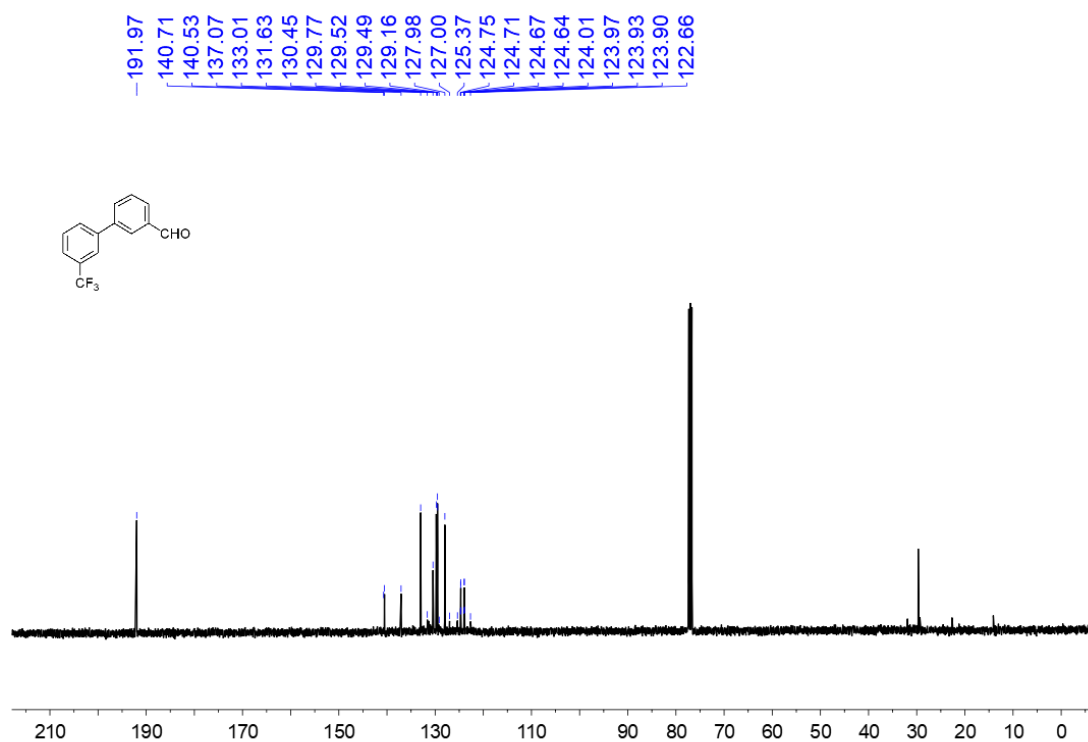
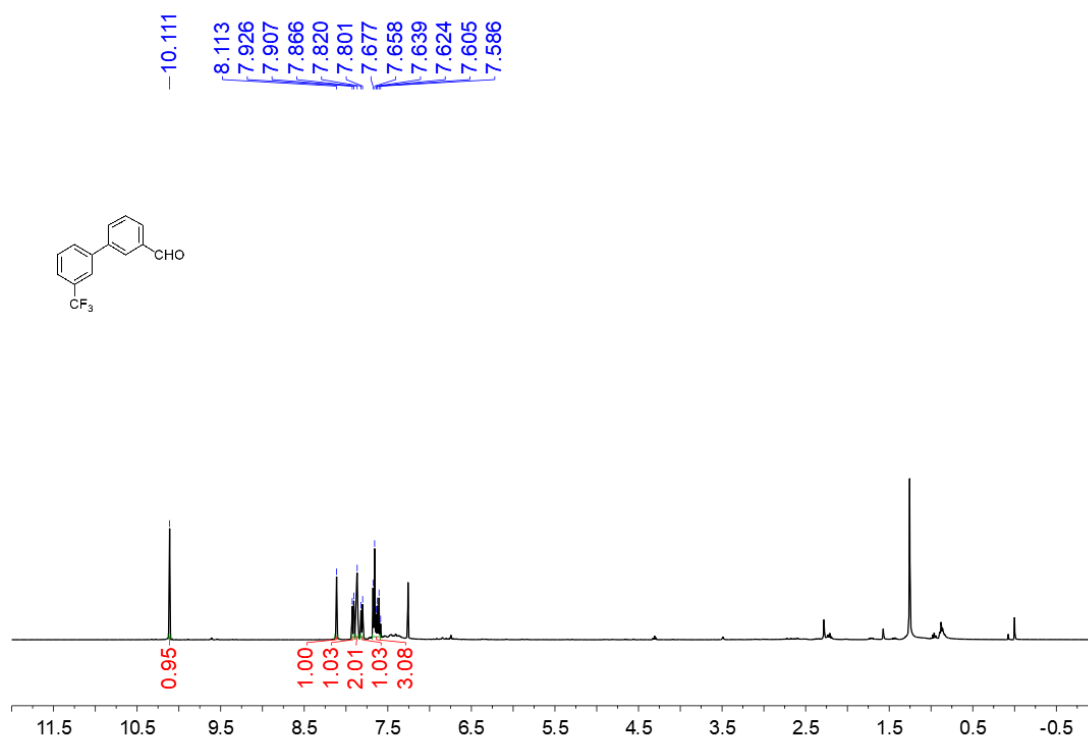


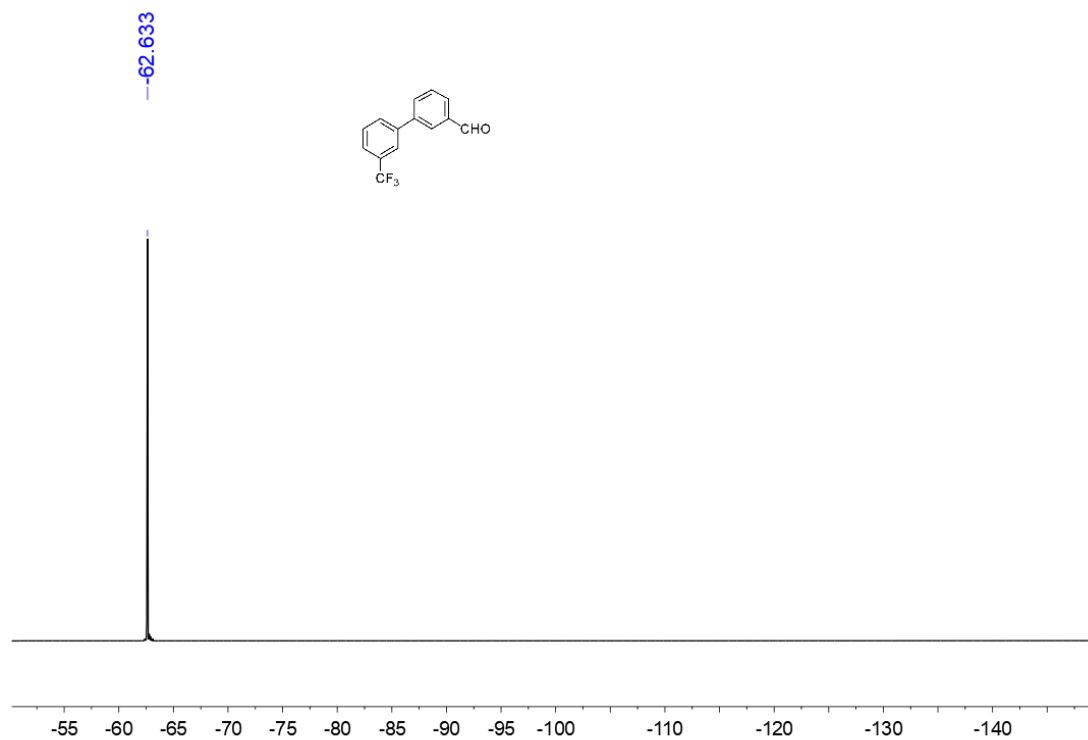
4'-Fluoro-[1,1'-biphenyl]-3-carbaldehyde (**2g**)



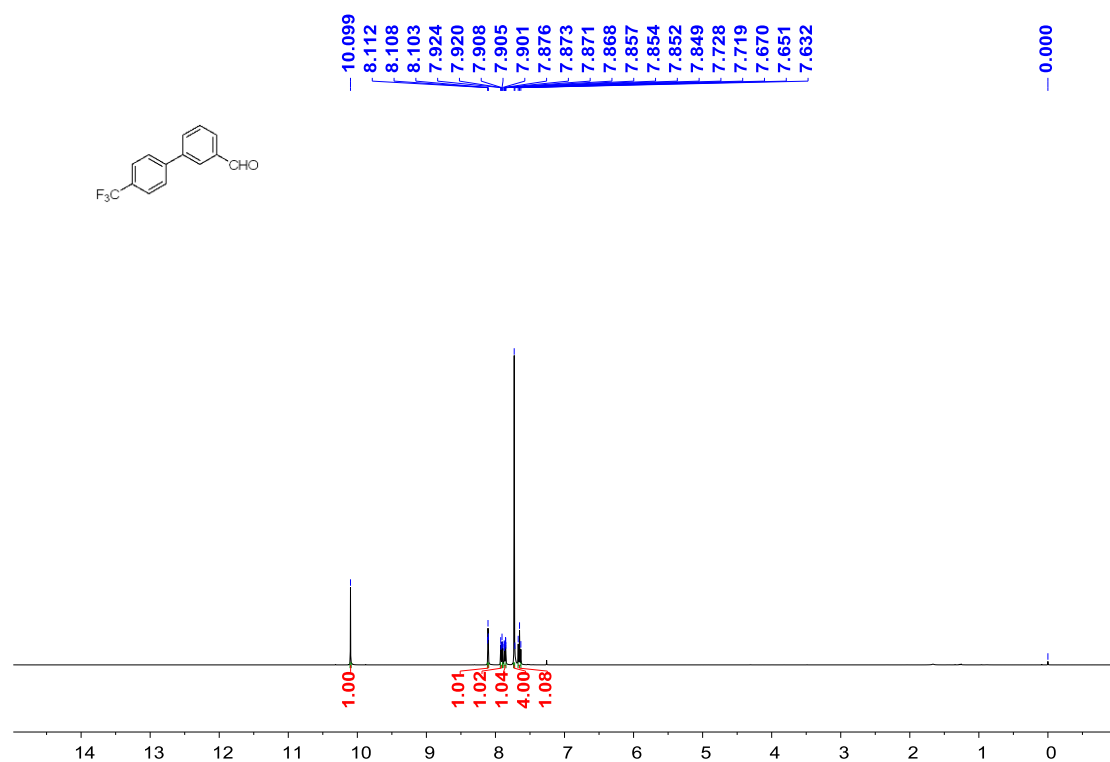


3'-(Trifluoromethyl)-[1,1'-biphenyl]-3-carbaldehyde (**2h**)

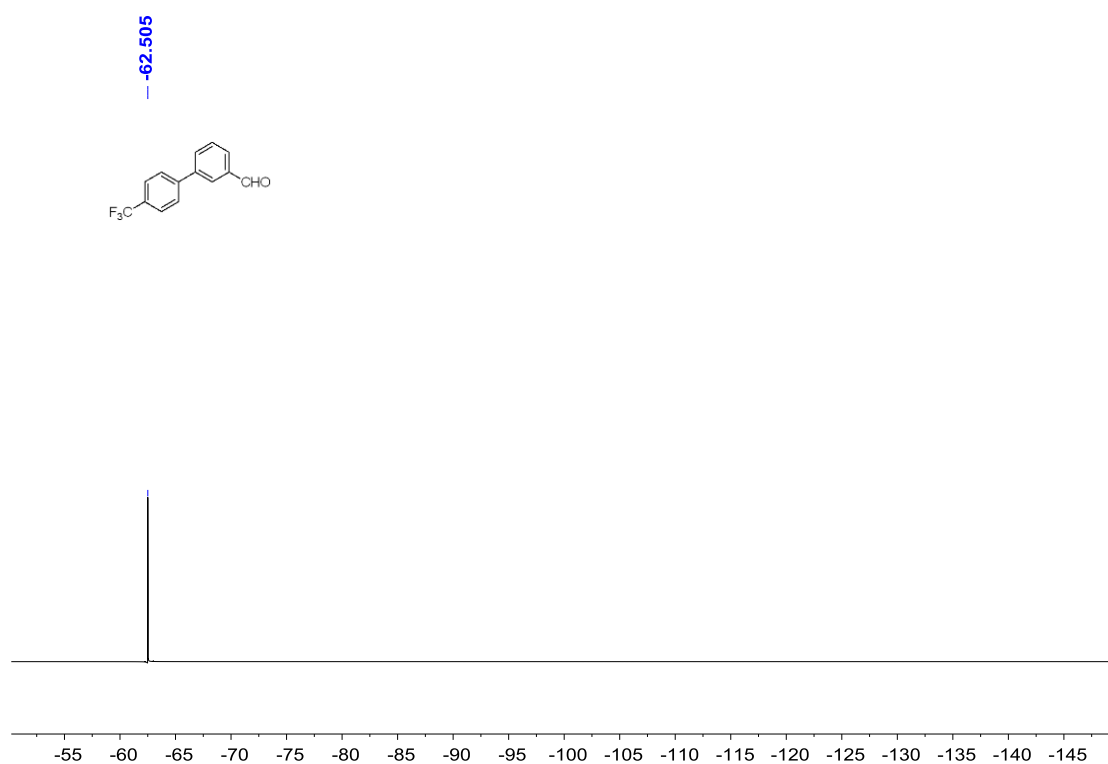
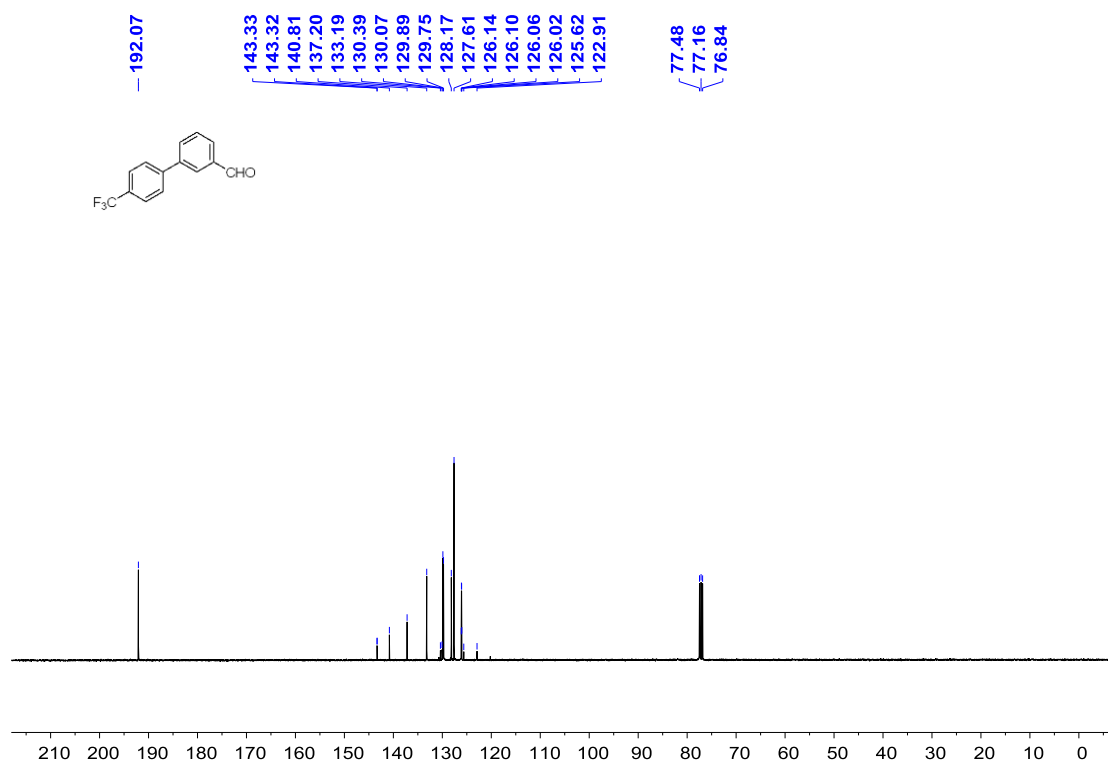




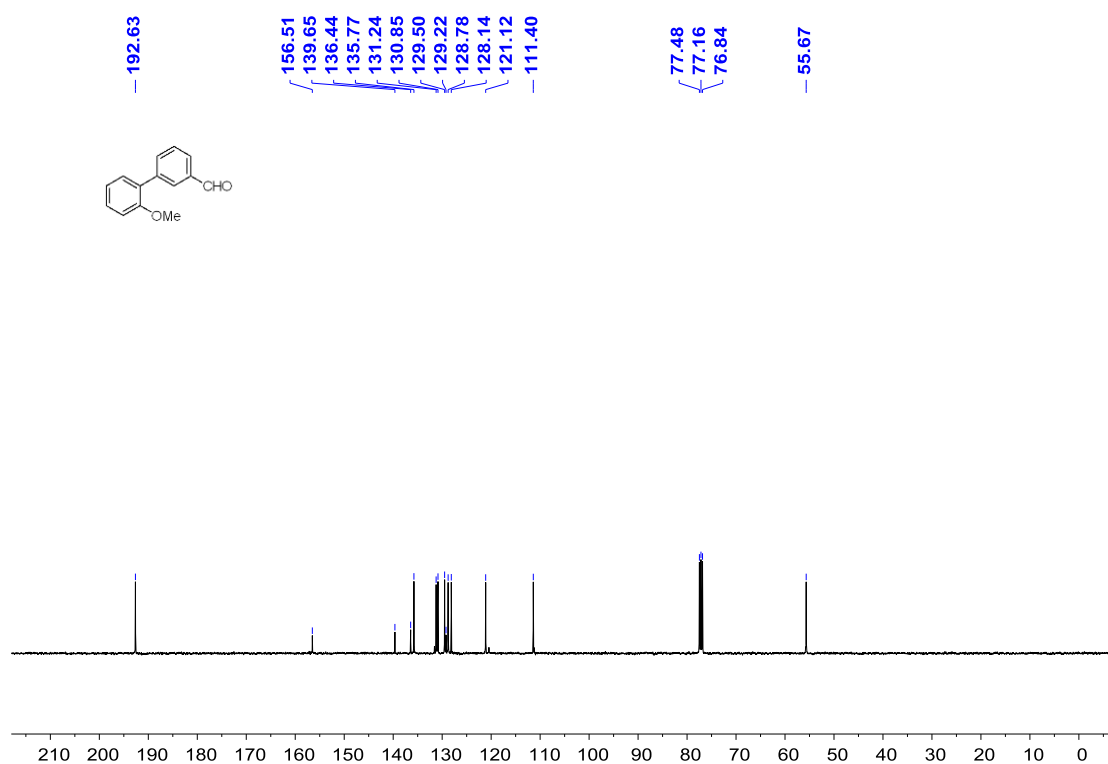
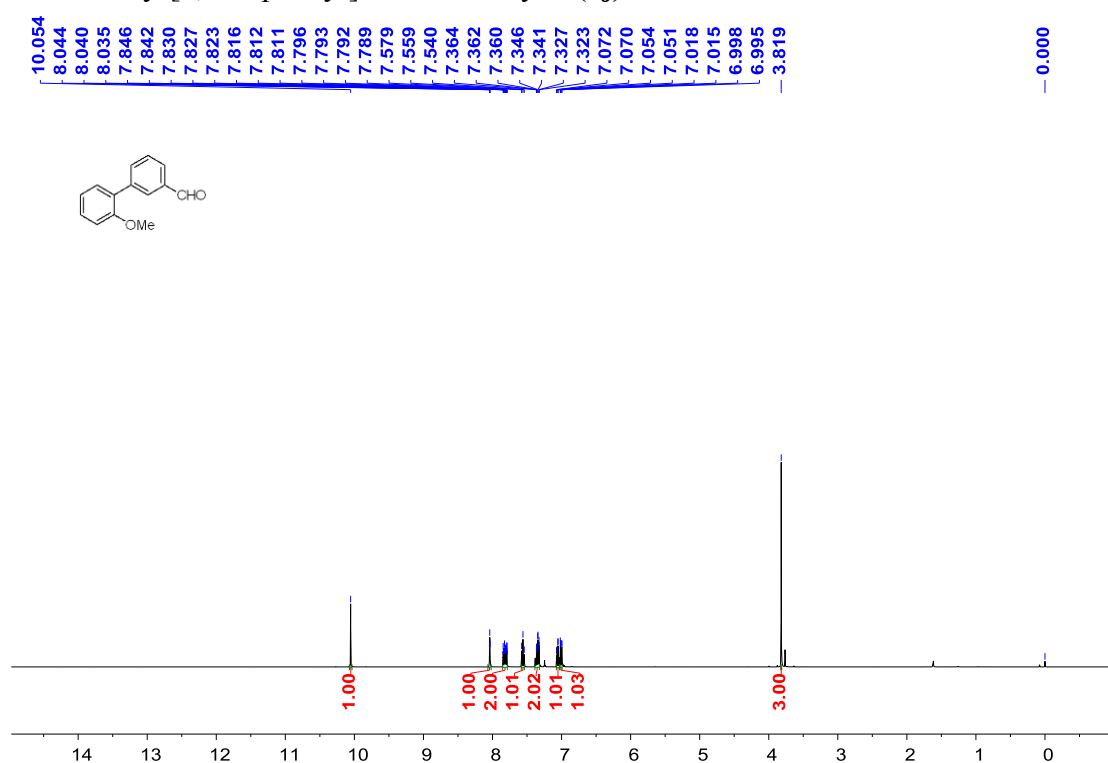
4'-(Trifluoromethyl)-[1,1'-biphenyl]-3-carbaldehyde (**2i**)



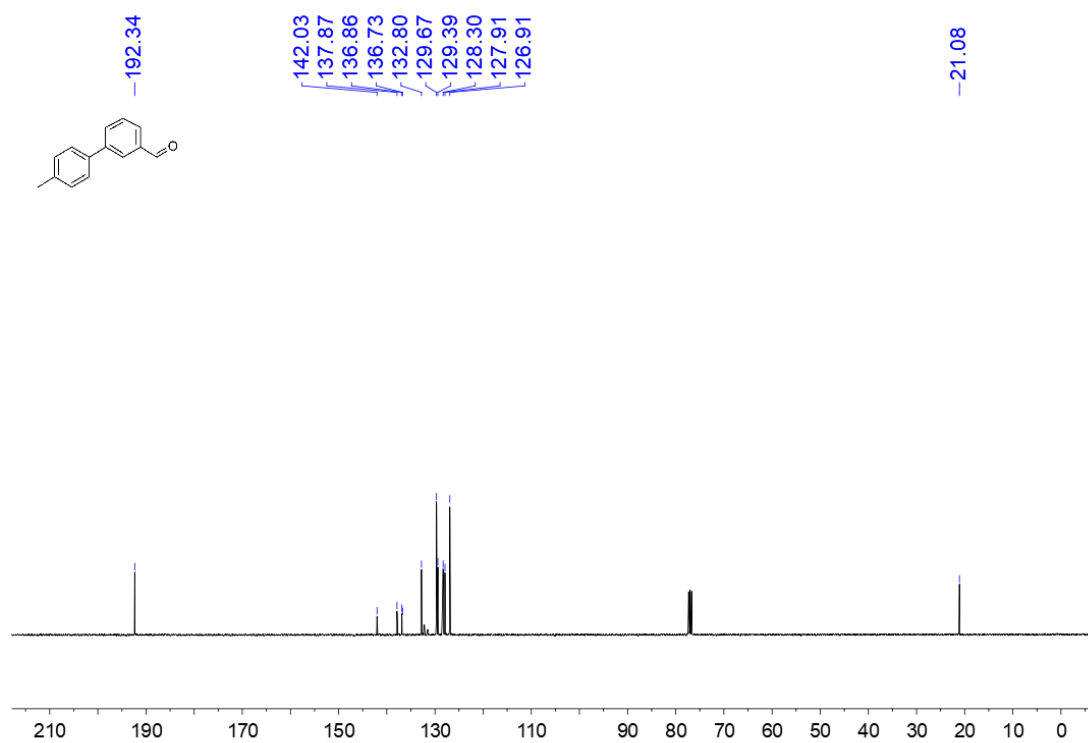
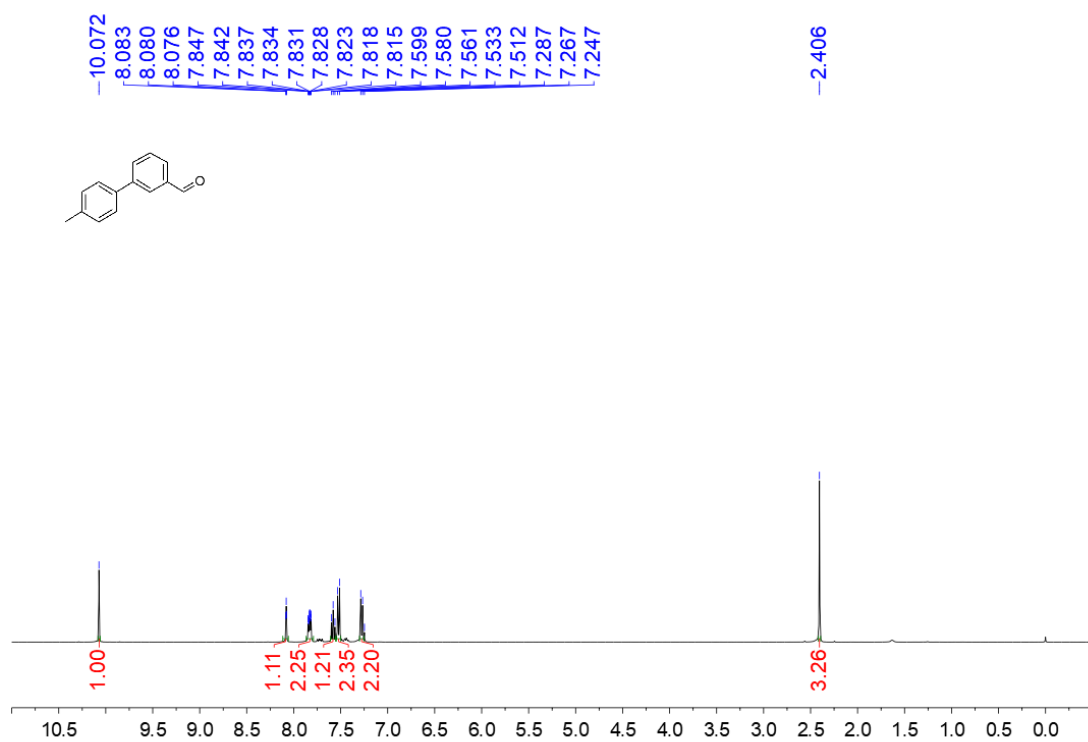




2'-Methoxy-[1,1'-biphenyl]-3-carbaldehyde (**2j**)

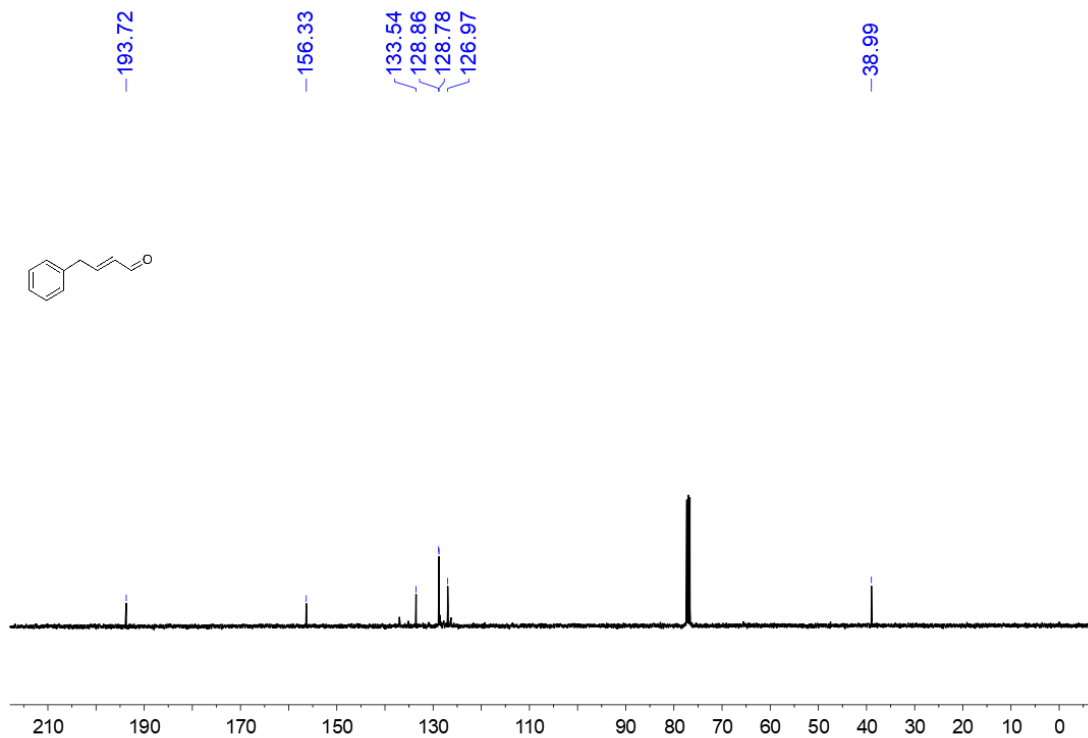
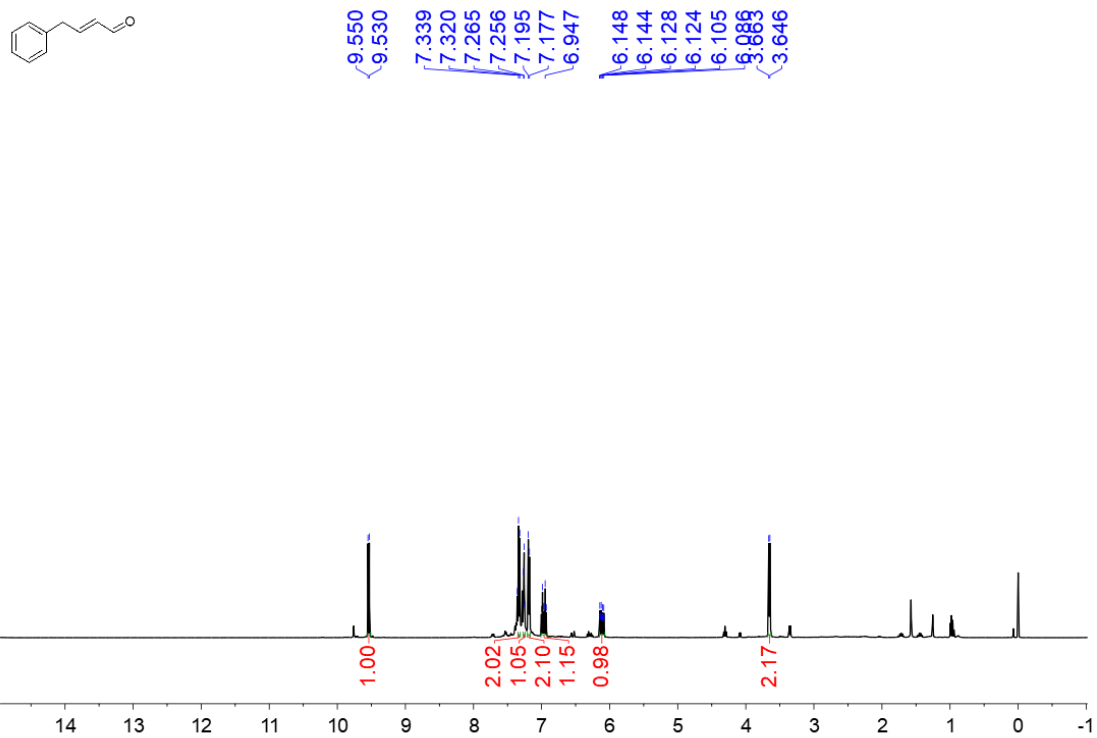


4'-Methyl-[1,1'-biphenyl]-3-carbaldehyde (**2k**)

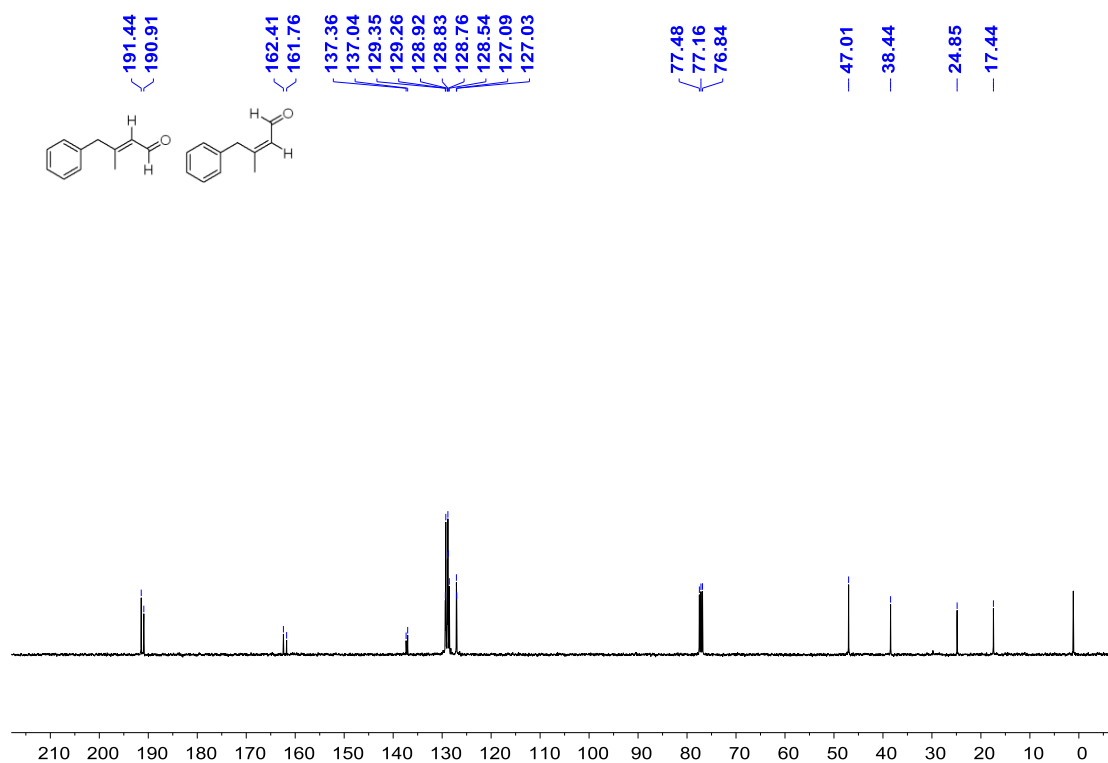
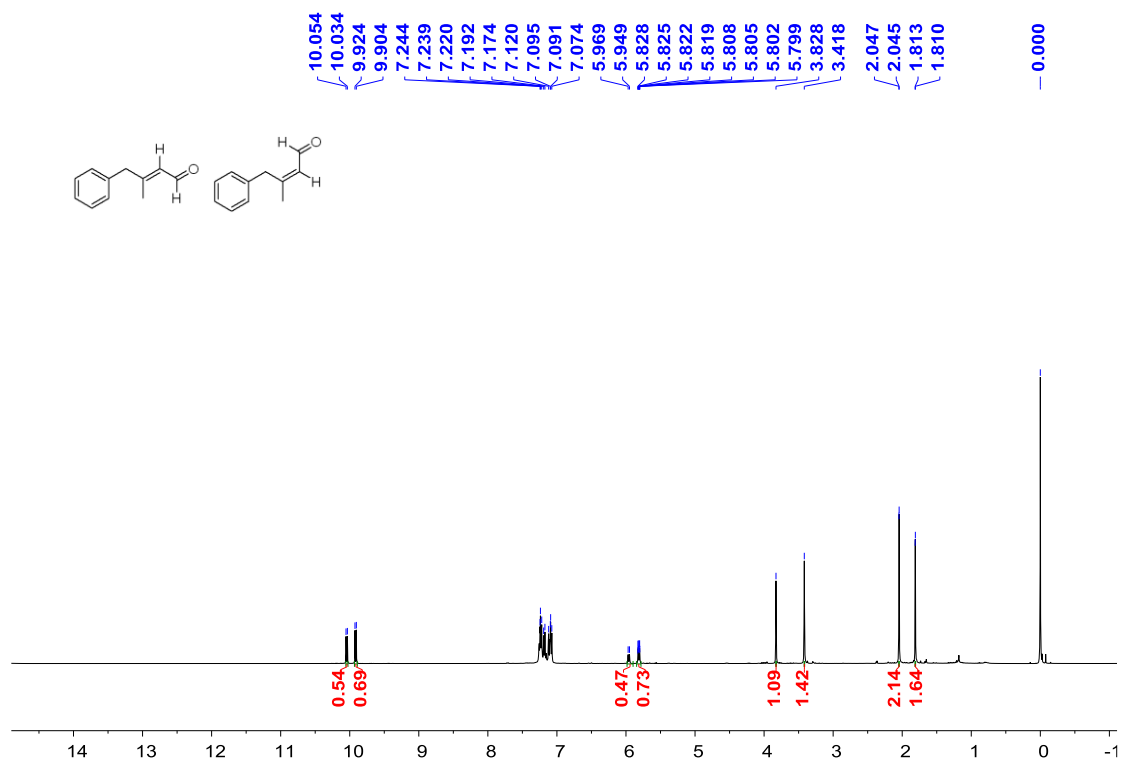


# Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of 4-phenylbut-2-enals **3**

## (*E*)-4-Phenylbut-2-enal (**3a**)

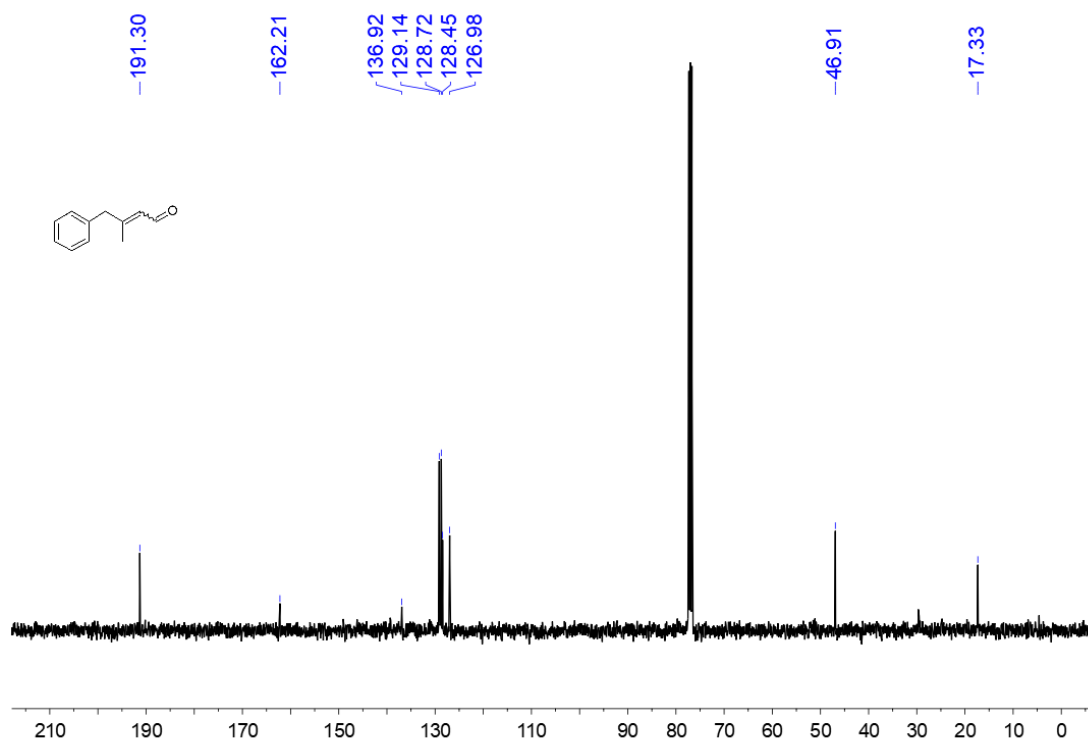
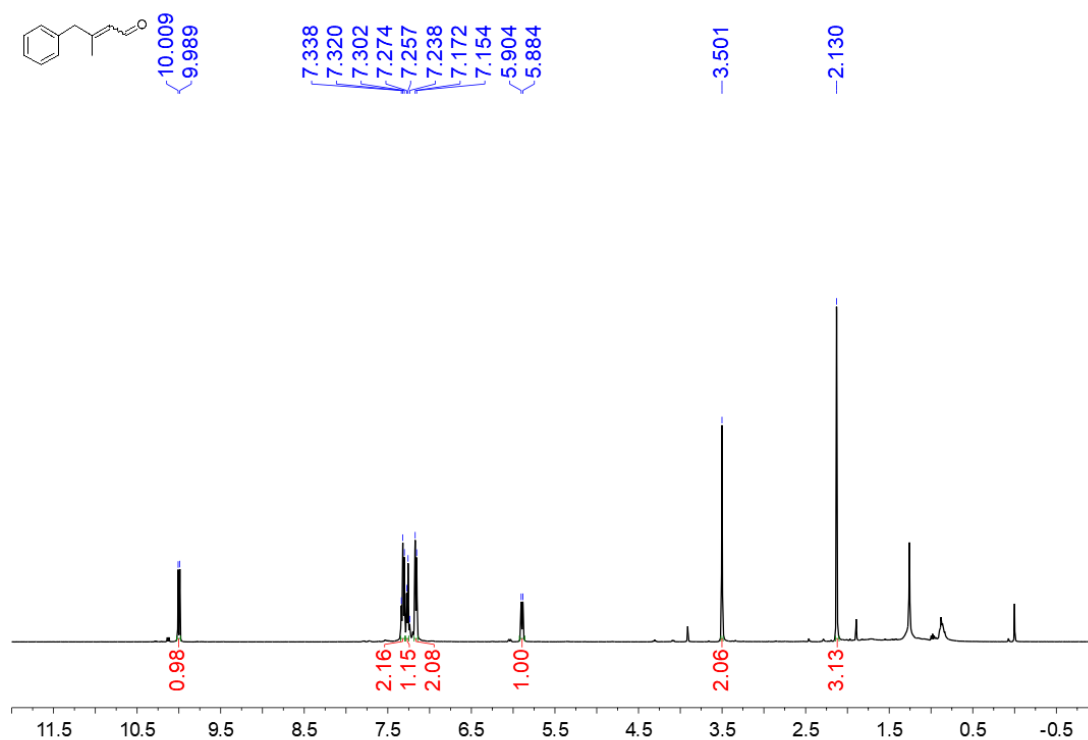


3-Methyl-4-phenylbut-2-enal (**3I**) as an E/Z mixture in 57:43 ratio

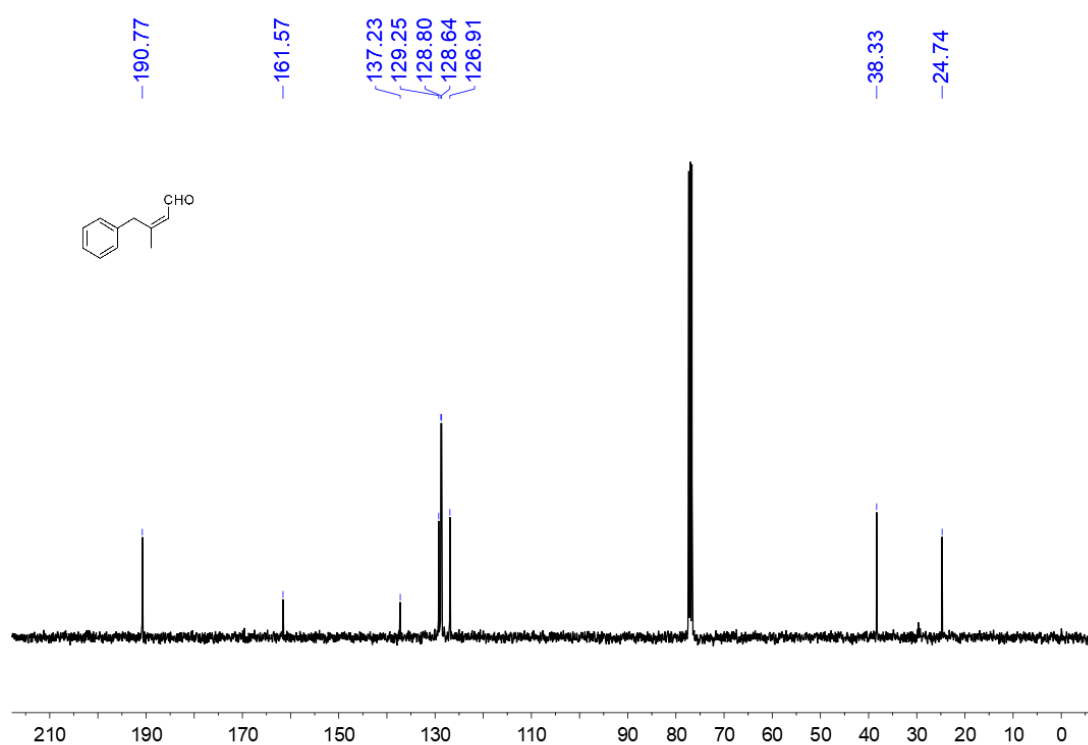
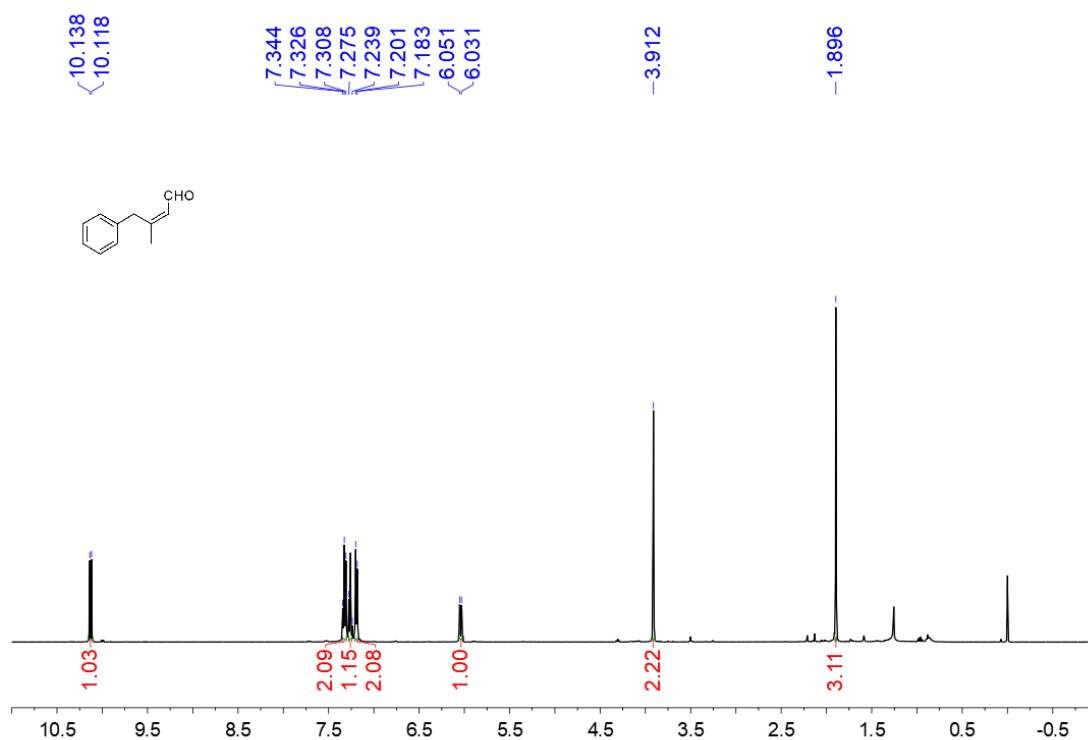


E and Z Isomers were separated on preparative TLC.

(*E*)-3-Methyl-4-phenylbut-2-enal ((*E*)-**3l**)

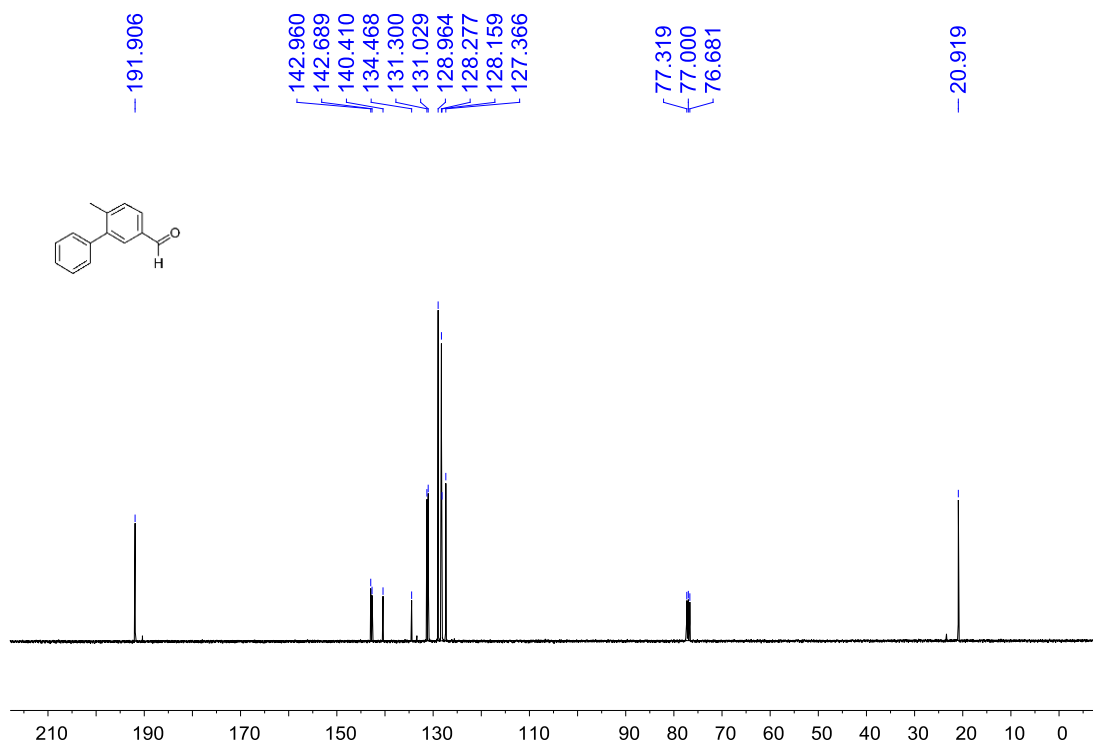
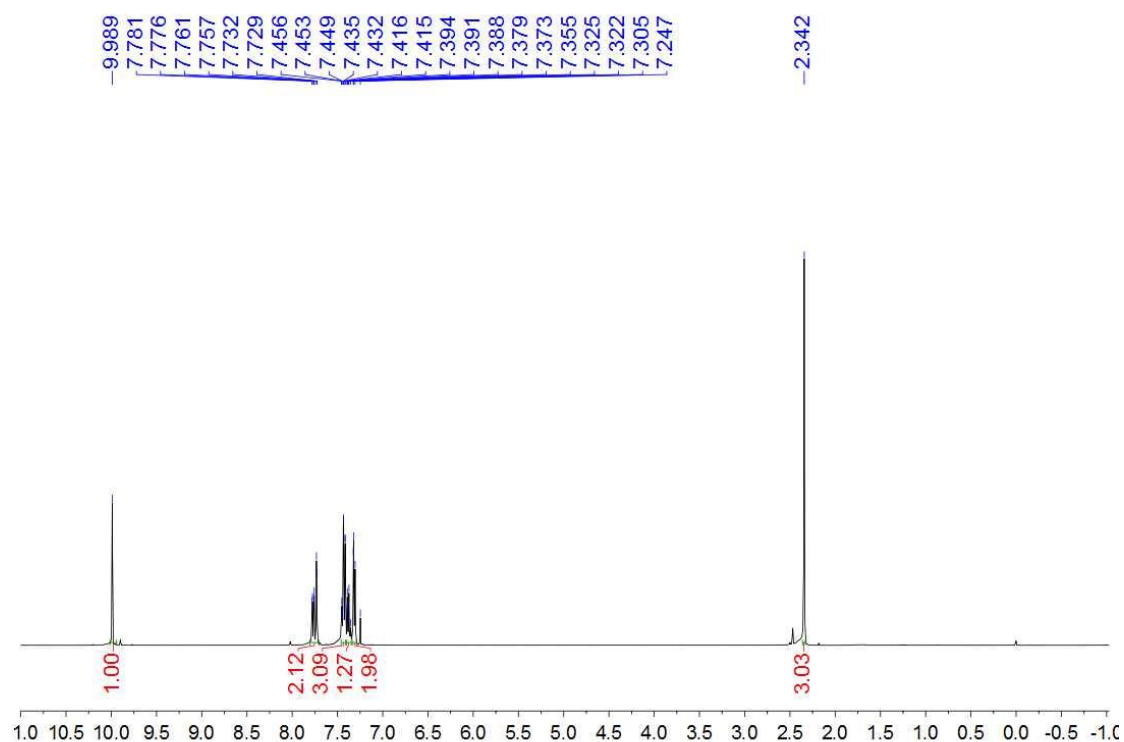


(Z)-3-Methyl-4-phenylbut-2-enal ((Z)-3I)



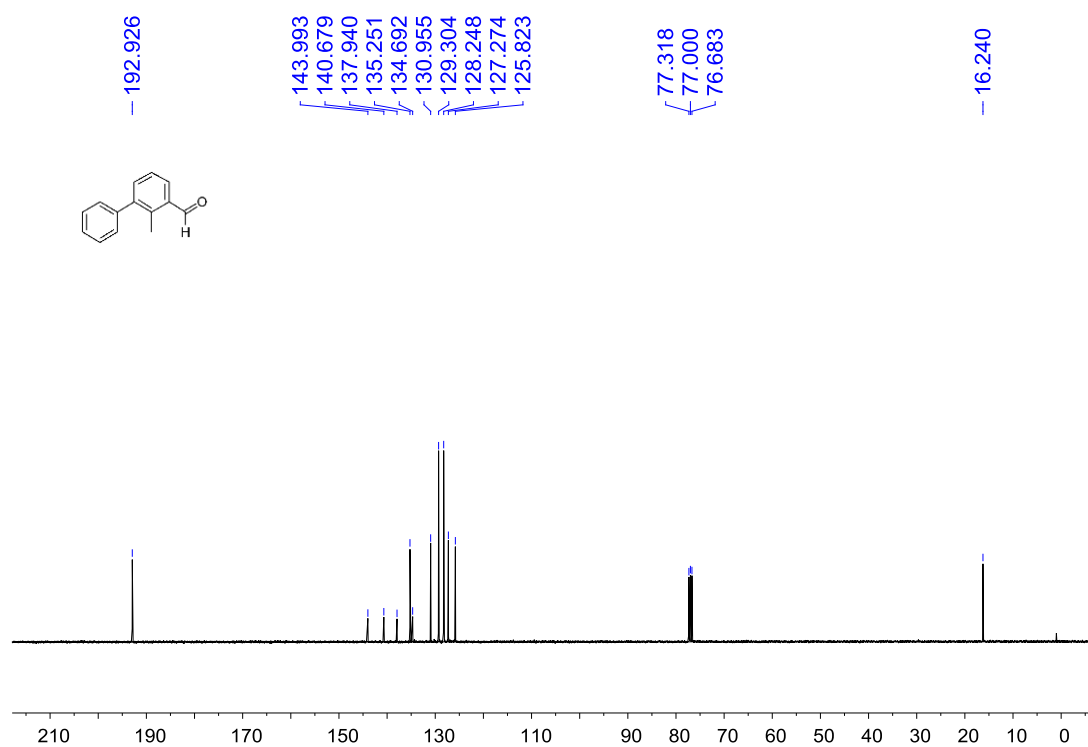
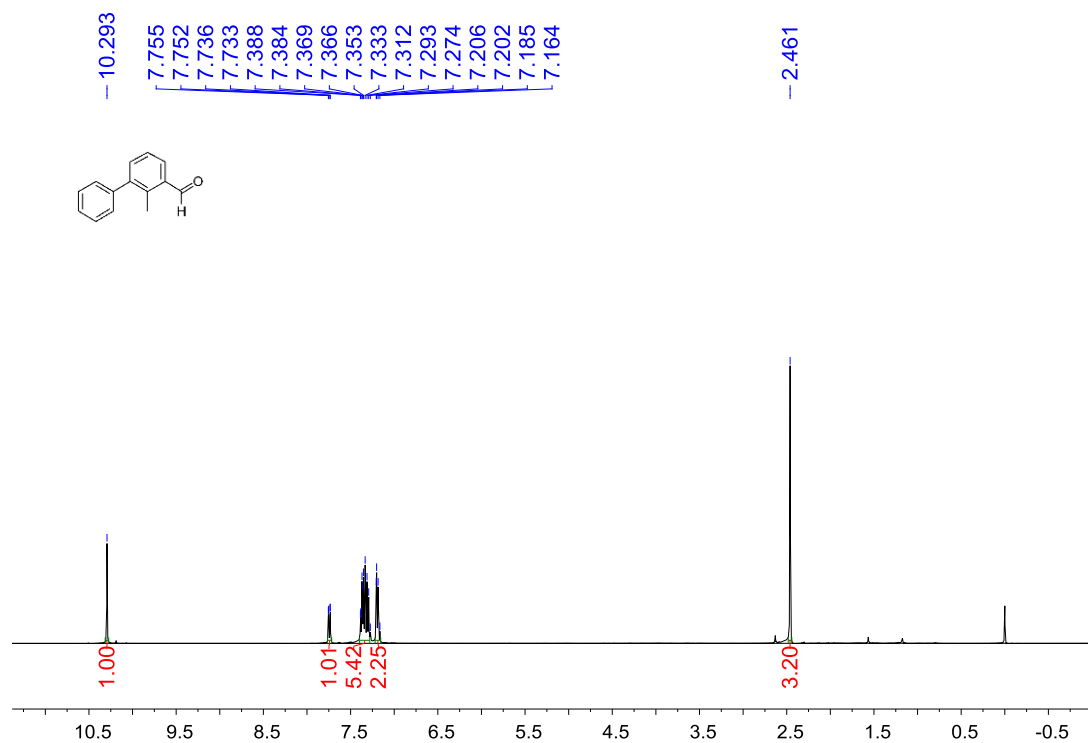
Copies of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of [1,1'-biaryl]-3-carbaldehydes 4 and 4'

6-Methy-[1,1'-biphenyl]-3-carbaldehyde (4)



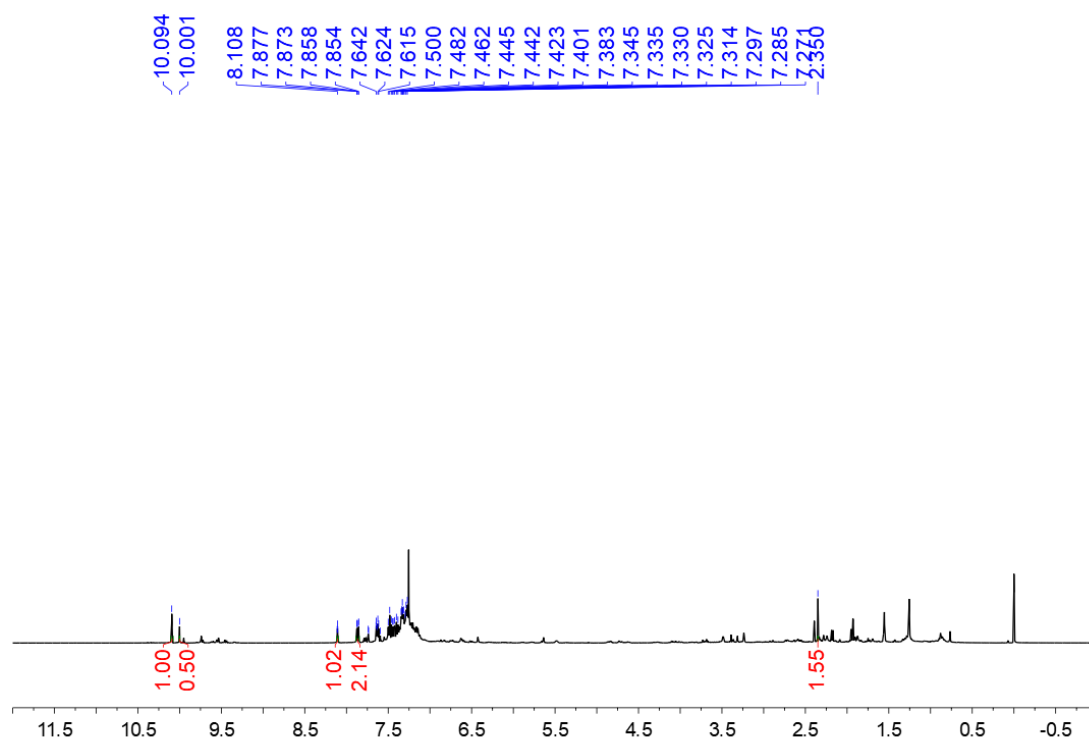


# 2-Methy-[1,1'-biphenyl]-3-carbaldehyde (**4'**)



## Copy of $^1\text{H}$ NMR spectrum of product mixture of cross-condensation reaction

Copy of  $^1\text{H}$  NMR spectrum of the product mixture



Product mixture from cross-condensation reaction shown in Scheme 2 indicates the

