

Supporting Information

Palladium-Catalyzed Decarboxylative *O*-Allylation of Phenols with γ -Methylidene- δ -valerolactone

Ran Song,[‡] Zhendong Lian,[‡] Wei Feng, Tianyi Guan, Wen Si,* Daoshan Yang, and Jian Lv*

Key Laboratory of Optic-electric Sensing and Analytic Chemistry for Life Science, MOE, College of Chemistry and Molecular Engineering, Qingdao University of Science & Technology, Qingdao 266042, China

*Email: lvjian@iccas.ac.cn (for J. Lv); siwen@qust.edu.cn (for W. Si)

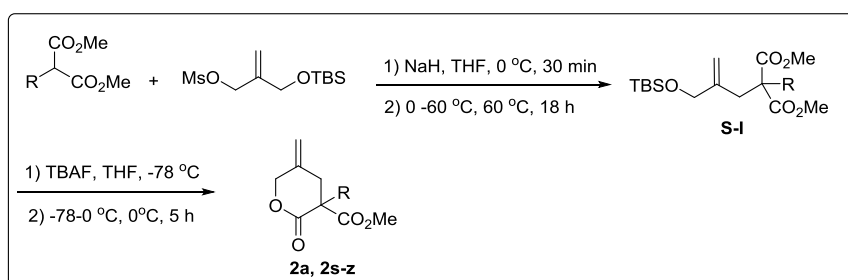
TABLE OF CONTENTS		PAGE
I	General Experiment Information and Materials	S1
II	Experimental Procedures and Characterization Data	S2
III	Control Experiments	S38
IV	X-ray crystal Data	S41
V	NMR Spectrum	S42
VI	References	S95

I. General Experiment Information and Materials

All commercial reagents were used without further purification unless otherwise noted. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using. All of γ -Methylidene- δ -valerolactones **2**, **6** and *ortho*-hydroxy benzylic alcohols **4a-s** were prepared according to literature procedure,¹⁻⁶ *ortho*-hydroxy benzylic alcohol **4t** is commercial reagent and was used without further purification. Proton and carbon magnetic resonance spectra (¹H NMR and ¹³C NMR) were recorded on a Bruker Avance 500 MHz spectrometer. Tetramethylsilane (TMS) served as the internal standard for ¹H NMR, and CDCl₃ served as the internal standard for ¹³C NMR. ¹H NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, td = triplet of doublet, dt = doublet of triplet, dd = doublet of doublet), coupling constants (Hz), and integration. Infrared Spectroscopy was conducted on Thermo Fisher Nicolet is 10. The X-ray single-crystal diffraction was performed on Saturn 724+ instrument. High resolution mass spectra were obtained on an Ultima Global spectrometer with an ESI source.

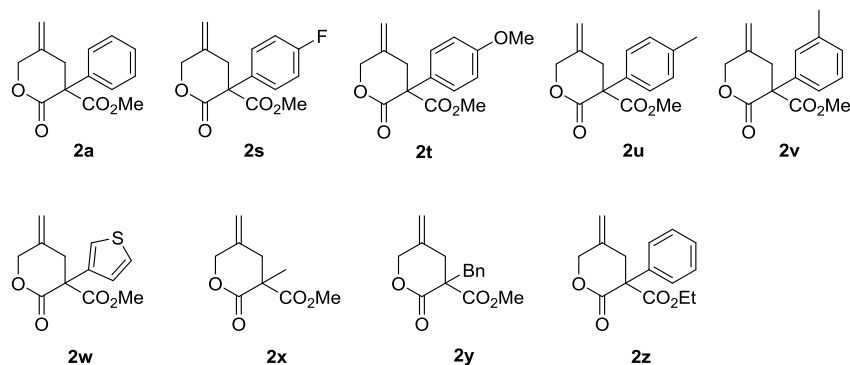
II. Experimental Procedure and Characterization Data

A) Preparation of γ -Methylidene- δ -valerolactones **2a**, **2s-2z**¹⁻³

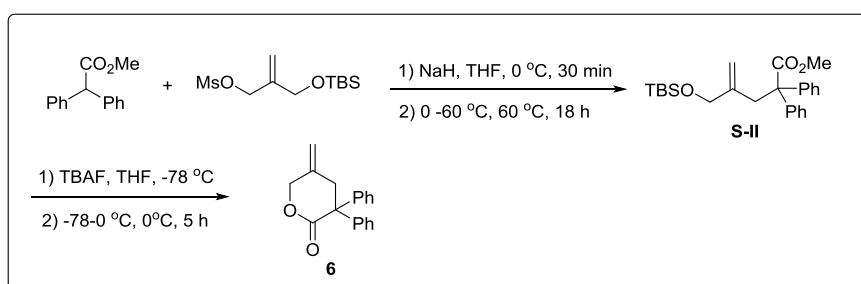


A solution of dimethyl phenylmalonate (2.08 g, 10.0 mmol) in THF (15 mL) was added to a suspension of NaH (420 mg, 10.5 mmol; 60 wt% in mineral oil) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and a solution of 2-(tert-butyldimethylsiloxy)methyl-2-propen-1-yl methanesulfonate (3.23 g, 11.5 mmol) in THF (12 mL) was added to it. The resulting mixture was stirred for 18 h at 60 °C and was quenched with water. After extraction with EtOAc, the organic layer was washed with NaCl (saturated aqueous), dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (20:1, v/v) to afford the product **S-I**.

TBAF (1.1 equiv; 1.0 M solution in THF) was added to a solution of **S-I** in THF at -78 °C. The mixture was stirred for 5 h while gradually raising the temperature to 0 °C and the reaction was quenched with water. After extraction with EtOAc, the organic layer was washed with NaCl (saturated aqueous), dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1, v/v) to afford the products **2a**, **2s-2z**.



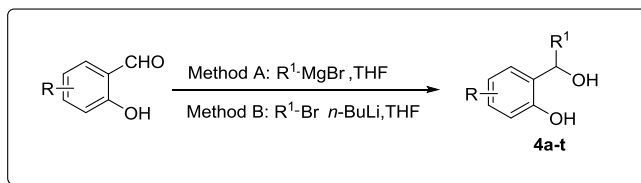
B) Preparation of γ -Methylidene- δ -valerolactones **6**⁴



A solution of methyl diphenylacetate (2.26 g, 10.0 mmol) in THF (15 mL) was added to a suspension of NaH (420 mg, 10.5 mmol; 60 wt% in mineral oil) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C and a solution of 2-(tert-butyldimethylsiloxy)methyl-2-propen-1-yl methanesulfonate (3.23 g, 11.5 mmol) in THF (12 mL) was added to it. The resulting mixture was stirred for 36 h at 60 °C and was quenched with water. After extraction with EtOAc, the organic layer was washed with NaCl (saturated aqueous), dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (30:1, v/v) to afford the product **S-II**.

TBAF (1.1 equiv; 1.0 M solution in THF) was added to a solution of **S-II** in THF at -78 °C. The mixture was stirred for 5 h while gradually raising the temperature to 0 °C and the reaction was quenched with water. After extraction with EtOAc, the organic layer was washed with NaCl (saturated aqueous), dried over Na₂SO₄, filtered, and concentrated under vacuum. The crude product was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (10:1, v/v) to afford the products **6**.

C) Preparation of ortho-hydroxy benzylic alcohols **4**

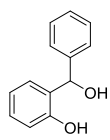


Method A⁵:

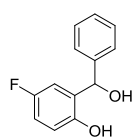
Under a nitrogen atmosphere, a solution of substituted salicylaldehyde (5.0 mmol) in tetrahydrofuran (10 mL) was added dropwise to a solution of the phenyl Grignard reagent (10.0 mmol, 1.0 M in THF, 10 mL), and the mixture was stirred at room temperature. After complete conversion (monitored by TLC), the reaction mixture was quenched by saturated ammonium chloride (10 mL) and extracted with EtOAc (30 mL \times 3). The combined organic layer was dried by anhydrous Na₂SO₄ and concentrated. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (5:1, v/v) to give the products **4a-4l**.

Method B⁶:

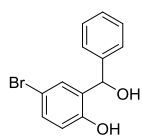
Under a nitrogen atmosphere, to an oven-dried flask charged with a solution of the R¹Br (12.5 mmol) in dry THF (12.5 mL) was added n-BuLi (12.5 mmol, 2.5 M in hexane, 5 mL) dropwise at -78 °C. The resulting mixture was stirred at the same temperature for 1 h, and then a solution of substituted salicylaldehyde (5 mmol) in dry THF (2.5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. Upon completion of the reaction (monitored by TLC), the reaction mixture was cooled to 0 °C and treated with saturated aqueous NH₄Cl solution (20 mL). The mixture was extracted with EtOAc (3 \times 30 mL). The combined organic layers were dried over Na₂SO₄, filtered, and concentrated. The residue was chromatographed on silica gel eluting with petroleum ether/EtOAc (5:1, v/v) to give the pure products **4m-4s**.



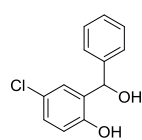
4a



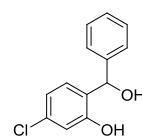
4b



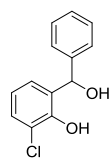
4c



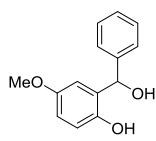
4d



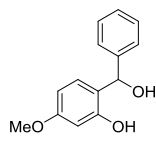
4e



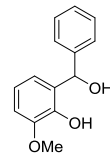
4f



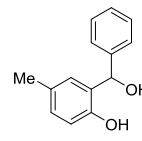
4g



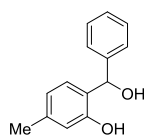
4h



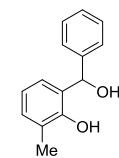
4i



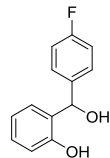
4j



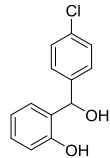
4k



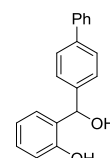
4l



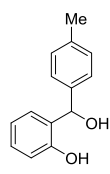
4m



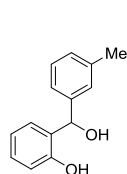
4n



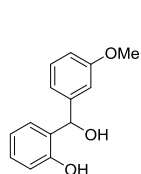
4o



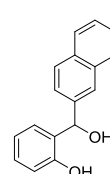
4p



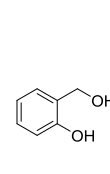
4q



4r

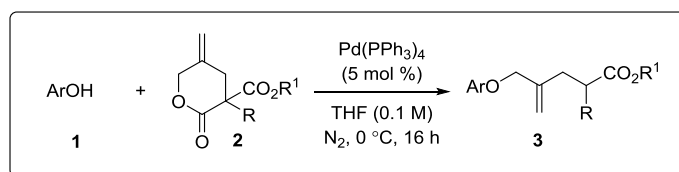


4s

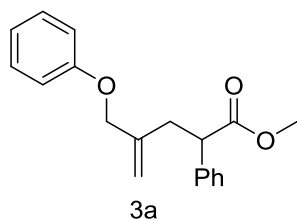


4t

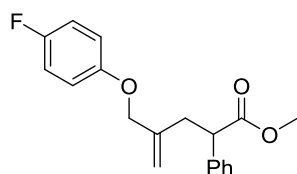
D) Synthesis of decarboxylative *O*-allylation products **3**



General Procedure: Under a nitrogen atmosphere, to an oven dried 10 mL Schlenk flask equipped with a stirring bar was added Phenols **1** (0.1 mmol), GMDVs **2** (0.15 mmol), Pd(PPh₃)₄ (5 mol %) and dry THF (1.0 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred at 0 °C for the indicated time. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15;1), giving the corresponding product **3**.

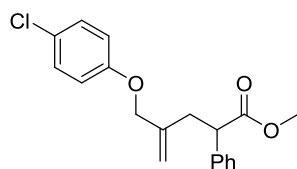


3a: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (25.5 mg, 86% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.29 (m, 4H), 7.28-7.23 (m, 3H), 6.97-6.91 (m, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.16 (s, 1H), 5.01 (s, 1H), 4.46-4.38 (m, 2H), 3.91 (dd, *J* = 9.0, 6.5 Hz, 1H), 3.64 (s, 3H), 2.96 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.61 (dd, *J* = 15.0, 6.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.8, 158.5, 141.9, 138.5, 129.4, 128.7, 127.9, 127.4, 120.9, 114.7, 114.5, 70.7, 52.0, 50.0, 36.7 ppm. IR (KBr, cm⁻¹): 3060, 2962, 2920, 1733, 1653, 1492, 1450, 1344, 1260, 1028, 905, 753, 693. HRMS (ESI) [M+Na]⁺ calcd for C₁₉H₂₀O₃Na: 319.1305, found: 319.1321.



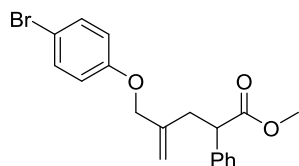
3b

3b: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (28.6 mg, 91% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.23 (m, 5H), 7.00-6.87 (m, 2H), 6.85-6.73 (m, 2H), 5.15 (s, 1H), 5.01 (s, 1H), 4.4-4.31 (m, 2H), 3.89 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.64 (s, 3H), 2.95 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.60 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 157.3 (d, $J = 238.9$ Hz), 154.7, 141.8, 138.5, 128.7, 127.9, 127.5, 115.8 (d, $J = 10.1$ Hz), 115.6 (d, $J = 4.9$ Hz), 114.6, 71.5, 52.1, 50.0, 36.6 ppm. IR (KBr, cm^{-1}): 3029, 2954, 2920, 2851, 1734, 1655, 1600, 1503, 1435, 1349, 1204, 1020, 909, 827, 731, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{FO}_3\text{Na}$: 337.1210, found: 337.1215



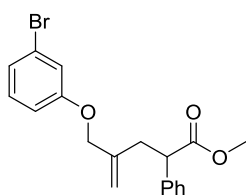
3c

3c: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (28.4 mg, 86% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.35-7.23 (m, 5H), 7.20 (d, $J = 9.0$ Hz, 2H), 6.78 (d, $J = 9.0$ Hz, 2H), 5.14 (s, 1H), 5.02 (s, 1H), 4.42-4.32 (m, 2H), 3.88 (dd, $J = 8.5, 6.5$ Hz, 1H), 3.63 (s, 3H), 2.94 (dd, $J = 15.0, 6.5$ Hz, 1H), 2.59 (dd, $J = 14.5, 6.6$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 157.1, 141.6, 138.4, 129.2, 128.7, 127.9, 127.5, 125.7, 116.0, 114.7, 71.1, 52.1, 50.0, 36.6 ppm. IR (KBr, cm^{-1}): 3029, 2920, 2850, 1735, 1656, 1490, 1453, 1238, 1161, 1066, 911, 823, 732, 699, 672. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{ClO}_3\text{Na}$: 353.0915, found: 353.0913.



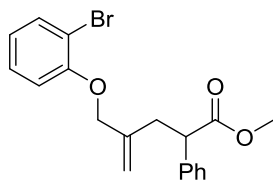
3d

3d: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (34.5 mg, 92% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.29 (m, 6H), 7.27 (td, $J = 8.5, 4.0$ Hz, 1H), 6.73 (d, $J = 8.5$ Hz, 2H), 5.14 (s, 1H), 5.02 (s, 1H), 4.42-4.32 (m, 2H), 3.88 (dd, $J = 8.5, 6.5$ Hz, 1H), 3.63 (s, 3H), 2.94 (dd, $J = 14.5, 9.0$ Hz, 1H), 2.58 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 157.6, 141.5, 138.4, 132.2, 128.7, 127.9, 127.5, 116.5, 114.7, 113.0, 71.0, 52.1, 50.0, 36.6 ppm. IR (KBr, cm^{-1}): 3029, 2950, 2920, 2850, 1735, 1655, 1465, 1349, 1237, 1003, 910, 821, 732, 698, 646. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{19}\text{H}_{20}\text{BrO}_3$: 375.0590, found: 375.0592.



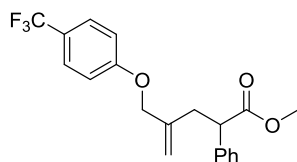
3e

3e: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (33.4 mg, 89% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.37-7.22 (m, 5H), 7.09 (dt, $J = 16.0, 8.0$ Hz, 2H), 7.03 (d, $J = 1.5$ Hz, 1H), 6.79 (dd, $J = 8.0, 1.0$ Hz, 1H), 5.15 (s, 1H), 5.02 (s, 1H), 4.45-4.33 (m, 2H), 3.88 (dd, $J = 8.5, 7.0$ Hz, 1H), 3.64 (s, 3H), 2.94 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.59 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 159.3, 141.4, 138.4, 130.5, 128.7, 127.8, 127.5, 124.0, 122.7, 118.0, 114.9, 113.7, 71.0, 52.1, 50.0, 36.6 ppm. IR (KBr, cm^{-1}): 3028, 2920, 2850, 1735, 1658, 1589, 1475, 1433, 1223, 1158, 1016, 910, 769, 732, 699, 679. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{BrO}_3\text{Na}$: 397.0410, found: 397.0414.



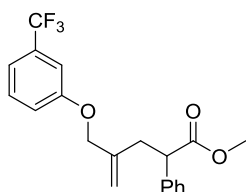
3f

3f: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (33.8 mg, 90% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.54 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.38-7.28 (m, 4H), 7.28-7.19 (m, 2H), 6.89-6.72 (m, 2H), 5.22 (s, 1H), 5.03 (s, 1H), 4.56-4.40 (m, 2H), 3.99 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.64 (s, 3H), 2.98 (dd, $J = 14.5, 9.0$ Hz, 1H), 2.65 (dd, $J = 14.5, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.9, 154.8, 141.2, 138.5, 133.3, 128.7, 128.3, 127.9, 127.4, 122.0, 115.0, 113.3, 112.2, 71.7, 52.1, 50.0, 36.7 ppm. IR (KBr, cm^{-1}): 2960, 2920, 2850, 1734, 1656, 1585, 1477, 1440, 1261, 1159, 1030, 799, 748, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{BrO}_3\text{Na}$: 397.0410, found: 397.0414.



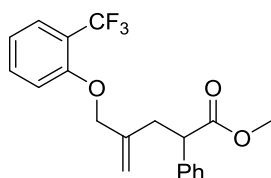
3g

3g: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (29.9 mg, 82% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.51 (d, $J = 9.0$ Hz, 2H), 7.35-7.23 (m, 5H), 6.91 (d, $J = 8.5$ Hz, 2H), 5.17 (s, 1H), 5.05 (s, 1H), 4.50-4.39 (m, 2H), 3.89 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.64 (s, 3H), 2.95 (dd, $J = 14.5, 8.5$ Hz, 1H), 2.60 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 160.9, 141.3, 138.4, 128.7, 127.9, 127.5, 126.8 (q, $J = 3.5$ Hz), 124.3 (q, $J = 271.7$ Hz), 123.1 (d, $J = 32.6$ Hz), 114.9, 114.7, 71.0, 52.1, 50.1, 36.5 ppm. IR (KBr, cm^{-1}): 2921, 1736, 1614, 1435, 1328, 1254, 1160, 1112, 1068, 1009, 912, 836, 733, 699. HRMS (ESI) $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{O}_3$: 365.1359, found: 365.1367.



3h

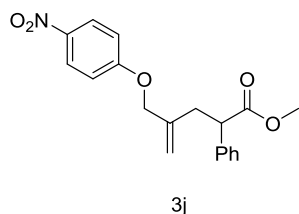
3h: Prepared according to the general procedure above, and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (30.2 mg, 83% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.29 (m, 5H), 7.28-7.24 (m, 1H), 7.20 (d, $J = 7.5$ Hz, 1H), 7.10 (s, 1H), 7.02 (dd, $J = 8.5, 2.0$ Hz, 1H), 5.18 (s, 1H), 5.05 (s, 1H), 4.48-4.38 (m, 2H), 3.89 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.64 (s, 3H), 2.96 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.61 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 158.7, 141.4, 131.9, 131.6, 129.9, 128.7, 127.8, 127.5, 123.9 (q, $J = 273.3$ Hz), 118.2, 117.6 (q, $J = 3.4$ Hz), 115.0, 111.5 (q, $J = 3.7$ Hz), 71.1, 52.1, 50.1, 36.6 ppm. IR (KBr, cm^{-1}): 2965, 2921, 1736, 1657, 1451, 1329, 1262, 1164, 1124, 1065, 1046, 880, 796, 733, 698. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{19}\text{F}_3\text{O}_3\text{Na}$: 387.1179, found: 387.1178.



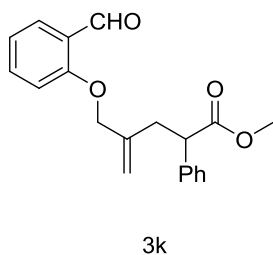
3i

3i: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (28.8mg, 79% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.56 (d, $J = 7.5$ Hz, 1H), 7.43 (t, $J = 7.5$ Hz, 1H), 7.36-7.22 (m, 5H), 6.99 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 5.21 (s, 1H), 5.03 (s, 1H), 4.50 (q, $J = 12.6$ Hz, 2H), 3.91 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.63 (s, 3H), 2.95 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.63 (dd, $J = 15.0, 7.0$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 156.3, 141.0, 138.4, 133.1, 128.7, 127.9, 127.4, 127.1 (q, $J = 5.0$ Hz), 123.7 (q, $J = 272.9$ Hz), 120.1, 118.8 (q, $J = 31.4$ Hz), 114.7, 112.8, 71.0,

52.0, 49.8, 36.4 ppm. IR (KBr, cm^{-1}): 2956, 1735, 1608, 1495, 1458, 1323, 1275, 1258, 1162, 1118, 1058, 1037, 913, 756, 699. HRMS (ESI) $\text{C}_{20}\text{H}_{19}\text{F}_3\text{O}_3\text{Na}^+$ calcd for $[\text{M}+\text{Na}]^+$: 387.1179, found: 387.1188.

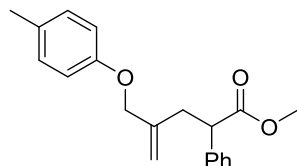


3j: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (27.3 mg, 80% yield). ^1H NMR (500 MHz, CDCl_3) δ 8.17 (d, $J = 9.0$ Hz, 2H), 7.36 – 7.26 (m, 5H), 6.90 (d, $J = 9.5$ Hz, 2H), 5.18 (s, 1H), 5.08 (s, 1H), 4.55 – 4.41 (m, 2H), 3.88 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.65 (s, 3H), 2.95 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.61 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.6, 163.5, 141.6, 140.7, 138.2, 133.6, 128.8, 127.8, 127.6, 115.3, 114.7, 71.5, 52.2, 50.1, 36.4 ppm. IR (KBr, cm^{-1}): 2962, 2921, 1729, 1654, 1588, 1493, 1433, 1336, 1259, 1106, 1027, 907, 842, 800, 732, 695. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{NO}_5\text{Na}$: 364.1155, found: 364.1169.



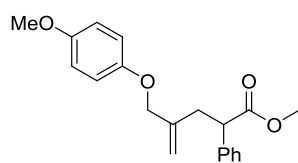
3k: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (26.0 mg, 80% yield). ^1H NMR (500 MHz, CDCl_3) δ 10.52 (s, 1H), 7.84 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.54-7.45 (m, 1H), 7.36-7.23 (m, 5H), 7.02 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 8.5$ Hz, 1H), 5.22 (s, 1H), 5.09 (s, 1H), 4.56 – 4.47 (m, 2H), 3.90 (dd, $J = 9.0, 6.6$ Hz, 1H), 3.63 (s, 3H), 2.99 (dd, $J = 15.0, 9.5$ Hz, 1H), 2.62 (dd, $J = 15.0, 7.0$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 189.51, 173.6, 160.8, 141.1, 138.2, 135.8, 128.8, 128.4,

127.8, 127.6, 125.0, 120.9, 114.9, 112.7, 71.1, 52.1, 50.1, 36.6 ppm. IR (KBr, cm^{-1}): 3030, 2953, 2859, 2759, 1734, 1688, 1598, 1482, 1454, 1394, 1235, 1160, 1011, 912, 760, 733, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{20}\text{O}_3\text{Na}$: 347.1254, found: 347.1258.



3l

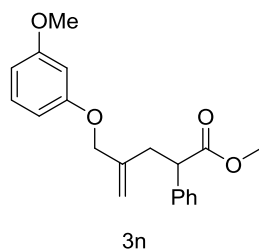
3l: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (23.0 mg, 74% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.22 (m, 5H), 7.05 (d, $J = 8.0$ Hz, 2H), 6.77 (d, $J = 8.5$ Hz, 2H), 5.15 (s, 1H), 5.00 (s, 1H), 4.45-4.33 (m, 2H), 3.90 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.63 (s, 3H), 2.95 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.60 (dd, $J = 15.0, 6.5$ Hz, 1H), 2.28 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 156.4, 142.1, 138.5, 130.1, 129.8, 128.7, 127.9, 127.4, 114.5, 114.4, 70.9, 52.0, 50.0, 36.8, 20.0 ppm. IR (KBr, cm^{-1}): 3029, 2950, 2922, 1736, 1654, 1510, 1453, 1349, 1236, 1028, 909, 816, 732, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{Na}$: 333.1461, found: 333.1469.



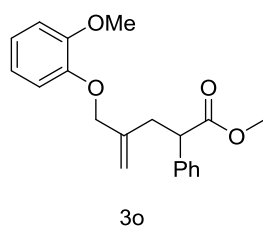
3m

3m: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (29.0 mg, 89% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36-7.28 (m, 4H), 7.27-7.22 (m, 1H), 6.80 (s, 4H), 5.14 (s, 1H), 4.99 (s, 1H), 4.41-4.31 (m, 2H), 3.90 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.75 (s, 3H), 3.63 (s, 3H), 2.95 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.60 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 153.9, 152.7, 142.2, 138.5, 128.6, 127.9, 127.4, 115.6, 114.5, 114.3, 71.5, 55.6, 52.0, 50.0, 36.7 ppm. IR (KBr, cm^{-1}):

2951, 1735, 1658, 1507, 1437, 1228, 1159, 1038, 825, 731, 699. HRMS (ESI) $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$: 349.1410, found: 319.1421.

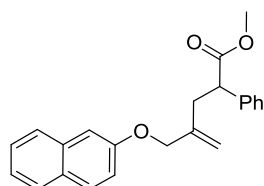


3n: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (29.4 mg, 90% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.28-7.22 (m, 1H), 7.15 (t, $J = 8.0$ Hz, 1H), 6.48 (dd, $J = 17.5, 8.0$ Hz, 3H), 5.16 (s, 1H), 5.01 (s, 1H), 4.46-4.34 (m, 2H), 3.90 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 2.96 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.60 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 160.8, 159.8, 141.9, 138.5, 129.8, 128.7, 127.9, 127.4, 114.5, 106.9, 106.4, 101.2, 70.8, 55.2, 52.0, 50.0, 36.7 ppm. IR (KBr, cm^{-1}): 2920, 2849, 1735, 1453, 1334, 1150, 1042, 912, 764, 732, 699. HRMS (ESI) $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$: 349.1410, found: 319.1413.



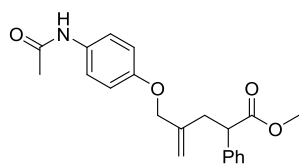
3o: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (29.4 mg, 90% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.27-7.22 (m, 1H), 6.94-6.82 (m, 3H), 6.79 (d, $J = 8.0$ Hz, 1H), 5.15 (s, 1H), 4.99 (s, 1H), 4.57-4.39 (m, 2H), 4.03-3.91 (m, 1H), 3.86 (d, $J = 10.5$ Hz, 3H), 3.63 (s, 3H), 2.95 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.62 (dd, $J = 14.5, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.9, 149.6, 148.0, 141.7, 138.6, 128.6, 127.9, 127.3, 121.3, 120.7, 114.4, 113.9, 111.8, 71.9,

55.8, 52.0, 49.9, 36.7 ppm. IR (KBr, cm^{-1}): 3061, 3027, 2923, 2851, 1733, 1657, 1501, 1452, 1327, 1250, 1026, 906, 740, 698. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4\text{Na}$: 349.1410, found: 319.1414.



3p

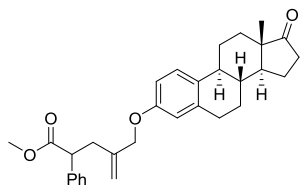
3p: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (29.4 mg, 85% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.78-7.66 (m, 3H), 7.42 (t, $J = 7.0$ Hz, 1H), 7.37-7.29(m, 5H), 7.28-7.20(m, 1H), 7.15 (dd, $J = 9.0, 2.5$ Hz, 1H), 7.08 (d, $J = 2.0$ Hz, 1H), 5.22 (s, 1H), 5.05 (s, 1H), 4.57-4.47 (m, 2H), 3.94 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.63 (s, 3H), 3.01 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.66 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 156.5, 141.8, 138.5, 134.4, 129.4, 129.0, 128.7, 127.9, 127.6, 127.4, 126.7, 126.3, 123.6, 118.9, 114.7, 107.0, 70.9, 52.0, 50.1, 36.8 ppm. IR (KBr, cm^{-1}): 3056, 3024, 2919, 2850, 1732, 1653, 1627, 1597, 1507, 1451, 1390, 1213, 1158, 1012, 908, 835, 809, 769, 743, 697. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{23}\text{H}_{22}\text{O}_3\text{Na}$: 369.1461, found: 369.1469.



3q

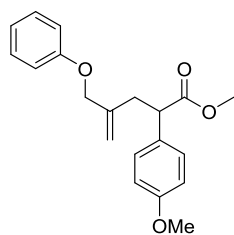
3q: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (30.0 mg, 85% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 9.0$ Hz, 3H), 7.32 (d, $J = 4.0$ Hz, 4H), 7.29-7.23 (m, 1H), 6.81 (d, $J = 9.0$ Hz, 2H), 5.14 (s, 1H), 5.00 (s, 1H), 4.43-4.33 (m, 2H), 3.89 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.64 (s, 3H), 2.94 (dd, $J = 14.5, 9.0$

Hz, 1H), 2.59 (dd, $J = 15.0, 7.0$ Hz, 1H), 2.13 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 168.3, 155.3, 141.8, 138.4, 131.2, 128.7, 127.9, 127.4, 121.8, 115.0, 114.5, 71.1, 52.1, 50.0, 36.6, 24.3 ppm. IR (KBr, cm^{-1}): 3295, 3059, 2962, 2922, 2853, 1734, 1662, 1509, 1436, 1370, 1260, 1021, 908, 800, 723, 696. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{Na}$: 376.1519, found: 376.1524.



3r

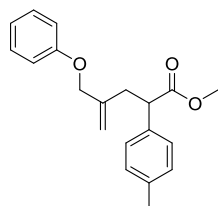
3r: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (35.9 mg, 76% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 9.0$ Hz, 2H), 7.33- 7.23 (m, 6H), 6.80 (d, $J = 9.0$ Hz, 2H), 5.14 (s, 1H), 5.00 (s, 1H), 4.43-4.33 (m, 2H), 3.89 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.63 (s, 3H), 2.94 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.59 (dd, $J = 15.0, 6.5$ Hz, 1H), 2.12 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 156.6, 142.0, 138.5, 137.7, 132.2, 128.7, 127.9, 127.4, 126.3, 114.7, 114.4, 112.3, 70.8, 52.1, 50.4, 50.0, 48.0, 44.0, 38.3, 36.7, 35.9, 31.6, 29.6, 26.5, 25.9, 21.6, 13.8 ppm. IR (KBr, cm^{-1}): 3027, 2921, 2855, 1733, 1654, 1495, 1257, 1155, 1024, 908, 805, 731, 697. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{31}\text{H}_{36}\text{O}_4\text{Na}$: 495.2506, found: 495.2507.



3s

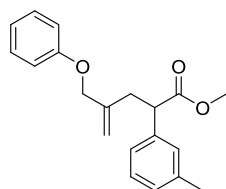
3s: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (20.9 mg, 64% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.29-7.21 (m, 4H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.90-6.81 (m, 4H), 5.16 (s, 1H), 5.00 (s, 1H), 4.45-4.35 (m, 2H), 3.89-3.80 (m, 1H),

3.77 (s, 3H), 3.63 (s, 3H), 2.93 (dd, $J = 14.5, 8.5$ Hz, 1H), 2.59 (dd, $J = 15.0, 7.0$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 174.1, 158.9, 158.5, 141.2, 130.5, 129.4, 128.9, 120.8, 114.7, 114.5, 114.0, 70.7, 55.2, 52.0, 49.1, 36.8 ppm. IR (KBr, cm^{-1}): 2925, 1733, 1597, 1510, 1493, 1243, 1031, 906, 793, 795, 690. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}_4\text{Na}$: 349.1410, found: 349.1408.



3t

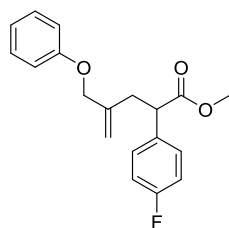
3t: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (23.0mg, 74% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.28 (s, 1H), 7.25 (s, 1H), 7.22 (d, $J = 7.0$ Hz, 2H), 7.13 (d, $J = 7.0$ Hz, 2H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 8.0$ Hz, 2H), 5.16 (s, 1H), 5.01 (s, 1H), 4.46-4.35 (m, 2H), 3.87 (t, $J = 7.5$ Hz, 1H), 3.63 (s, 3H), 2.94 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.59 (dd, $J = 15.0, 6.5$ Hz, 1H), 2.32 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 174.0, 158.5, 142.0, 137.1, 135.5, 129.4, 127.8, 120.8, 114.7, 114.4, 70.7, 52.0, 50.0, 36.7, 21.1 ppm. IR (KBr, cm^{-1}): 2962, 1735, 1597, 1197, 1054, 879, 800, 754, 691. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{Na}$: 333.1461, found: 333.1455.



3u

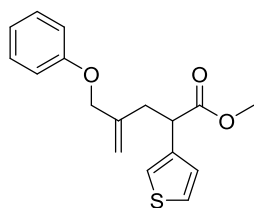
3u: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (25.8mg, 83% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.27 (d, $J = 7.0$ Hz, 1H), 7.24 (s, 1H), 7.20

(t, $J = 7.5$ Hz, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 7.5$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.87 (d, $J = 7.5$ Hz, 2H), 5.16 (s, 1H), 5.02 (s, 1H), 4.51-4.27 (m, 2H), 3.86 (t, $J = 7.0$ Hz, 1H), 3.63 (s, 3H), 2.95 (dd, $J = 15.0, 9.5$ Hz, 1H), 2.59 (dd, $J = 15.0, 6.5$ Hz, 1H), 2.32 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.9, 158.5, 142.0, 138.4, 138.3, 129.4, 128.5, 128.2, 124.9, 120.8, 114.7, 114.4, 70.7, 52.0, 49.9, 36.7, 21.4 ppm. IR (KBr, cm^{-1}): 3027, 2950, 1736, 1654, 1598, 1494, 1240, 1032, 909, 780, 754, 692. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{20}\text{H}_{22}\text{O}_3\text{Na}$: 333.1461, found: 333.1466.



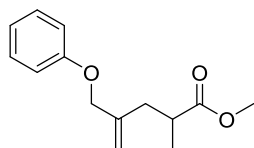
3v

3v: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (25.8mg, 82% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.32-7.23 (m, 4H), 6.99 (t, $J = 8.5$ Hz, 2H), 6.94 (t, $J = 7.0$ Hz, 1H), 6.87 (d, $J = 8.5$ Hz, 2H), 5.16 (s, 1H), 4.99 (s, 1H), 4.49-4.35 (m, 2H), 3.95 – 3.83 (m, 1H), 3.63 (s, 3H), 2.93 (dd, $J = 14.8, 8.9$ Hz, 1H), 2.59 (dd, $J = 14.9, 6.8$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 162.1 (d, $J = 246.5$ Hz), 158.6, 141.7, 134.2 (d, $J = 2.9$ Hz), 129.4 (d, $J = 8.2$ Hz), 129.4, 120.9, 115.5 (d, $J = 21.5$ Hz), 114.8, 114.6, 70.7, 52.1, 49.2, 36.8 ppm. IR (KBr, cm^{-1}): 3039, 2951, 1736, 1653, 1598, 1495, 1224, 1031, 911, 835, 754, 691. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{19}\text{FO}_3\text{Na}$: 333.1461, found: 333.1455.



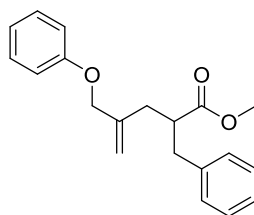
3w

3w: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (26.3mg, 87% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.30-7.23 (m, 3H), 7.15 (d, $J = 1.5$ Hz, 1H), 7.07 (d, $J = 5.0$ Hz, 1H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 2H), 5.18 (s, 1H), 5.02 (s, 1H), 4.48-4.35 (m, 2H), 4.05 (dd, $J = 9.0, 7.0$ Hz, 1H), 3.65 (s, 3H), 2.91 (dd, $J = 15.0, 9.0$ Hz, 1H), 2.63 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.5, 158.5, 141.8, 138.6, 129.4, 127.0, 125.8, 122.0, 120.9, 114.7, 114.6, 70.6, 52.0, 45.5, 36.7 ppm. IR (KBr, cm^{-1}): 2960, 2923, 1735, 1596, 1493, 1214, 1051, 1030, 907, 799, 754, 690. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{18}\text{O}_3\text{SNa}$: 325.0869, found: 325.0869.



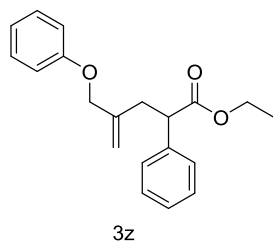
3x

3x: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (19.2mg, 82% yield). ^1H NMR (500 MHz, CDCl_3) δ 7.27 (dd, $J = 15.5, 7.5$ Hz, 2H), 6.98-6.86 (m, 3H), 5.19 (s, 1H), 5.02 (s, 1H), 4.51-4.40 (m, 2H), 3.65 (s, 3H), 2.82-2.68 (m, 1H), 2.55 (dd, $J = 14.5, 8.0$ Hz, 1H), 2.25 (dd, $J = 14.5, 6.5$ Hz, 1H), 1.19 (d, $J = 7.0$ Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 176.6, 158.6, 142.2, 129.4, 120.8, 114.7, 114.3, 70.4, 51.6, 37.9, 37.2, 17.2 ppm. IR (KBr, cm^{-1}): 2923, 1736, 1598, 1494, 1195, 1055, 754, 691. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{Na}$: 257.1148, found: 257.1154.



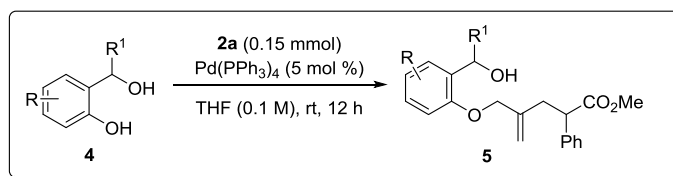
3y

3y: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (25.5mg, 82% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.27 (t, *J* = 7.0 Hz, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 2H), 5.18 (s, 1H), 5.04 (s, 1H), 4.52-4.37 (m, 2H), 3.55 (s, 3H), 3.05-2.88 (m, 2H), 2.81 (t, *J* = 10.0 Hz, 1H), 2.50 (dd, *J* = 14.5, 9.0 Hz, 1H), 2.38 (d, *J* = 14.0 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 175.4, 158.5, 142.1, 138.9, 129.4, 128.8, 128.4, 126.5, 120.9, 114.7, 114.4, 70.4, 51.5, 46.1, 38.6, 35.6 ppm. IR (KBr, cm⁻¹): 3028, 2950, 1735, 1598, 1370, 1216, 1032, 910, 754, 693. HRMS (ESI) [M+Na]⁺ calcd for C₂₀H₂₂O₃Na: 333.1461, found: 333.1458.



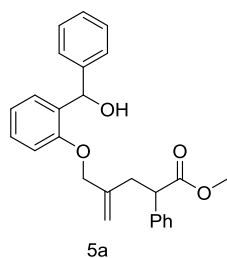
3z: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (15:1, v/v) as the eluent. Colorless oil (22.0mg, 71% yield). ¹H NMR (500 MHz, CDCl₃) δ 7.32 (q, *J* = 7.0 Hz, 4H), 7.29-7.22 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 5.17 (s, 1H), 5.02 (s, 1H), 4.48-4.37 (m, 2H), 4.24-3.99 (m, 2H), 3.88 (dd, *J* = 9.0, 6.5 Hz, 1H), 2.96 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.60 (dd, *J* = 14.5, 6.0 Hz, 1H), 1.18 (t, *J* = 7.0 Hz, 3H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.3, 158.5, 142.0, 138.7, 129.4, 128.6, 127.9, 127.3, 120.8, 114.7, 114.3, 70.7, 60.8, 50.1, 36.7, 14.1 ppm. IR (KBr, cm⁻¹): 3030, 2981, 2932, 1731, 1652, 1598, 1494, 1369, 1239, 1032, 910, 754, 694. HRMS (ESI) [M+Na]⁺ calcd for C₂₀H₂₂O₃Na: 333.1461, found: 333.1464.

E) Synthesis of decarboxylative *O*-allylation products **5**



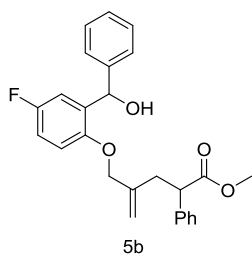
General procedure: Under a nitrogen atmosphere, to an oven dried 10 mL Schlenk flask equipped with a stirring bar was added γ -methylidene- δ -valerolactones **2a** (0.15 mmol), *ortho*-hydroxy benzylic alcohols **4** (0.1 mmol), Pd(PPh₃)₄ (5 mol%), and dry THF (1.0 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred room temperature for the indicated time. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1, v/v), giving the corresponding product **5**.

Large-scale Reaction: Under a nitrogen atmosphere, to an oven dried 100 mL Schlenk flask equipped with a stirring bar was added γ -methylidene- δ -valerolactones **2a** (1.4 g, 5.7 mmol), *ortho*-hydroxy benzylic alcohols **4a** (760.9 mg, 3.8 mmol), Pd(PPh₃)₄ (5 mol%), and dry THF (38 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred room temperature for the indicated time. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (5:1, v/v), giving the corresponding product **5a** (1.53 g, 78% yield).

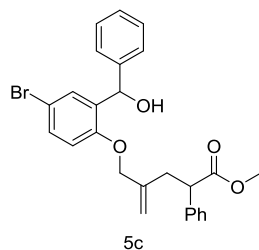


5a: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (33 mg, 82% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.40-7.33 (m, 2H), 7.33 – 7.22 (m, 8H),

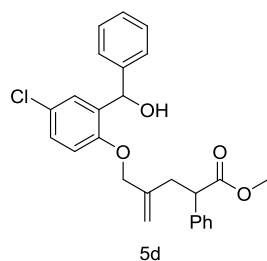
7.21-7.14 (m, 2H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.12-6.03 (m, 1H), 5.06 (s, 1H), 4.98 (s, 1H), 4.46-4.29 (m, 2H), 3.89-3.75 (m, 1H), 3.61 (d, $J = 4.0$ Hz, 3H), 3.02 (dd, $J = 10.5, 5.5$ Hz, 1H), 2.91-2.79 (m, 1H), 2.50-2.39 (m, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 155.6, 155.5, 143.3, 141.7, 141.6, 138.3, 132.1, 128.7, 128.6, 128.1, 128.0, 127.9, 127.8, 127.5, 127.1, 126.5, 126.4, 121.0, 114.6, 111.7, 72.0, 70.9, 52.1, 50.0, 36.4 ppm. IR (KBr, cm^{-1}): 3511, 3030, 2950, 1733, 1654, 1598, 1489, 1452, 1397, 1231, 1017, 913, 754, 732, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{26}\text{O}_4\text{Na}$: 425.1723, found: 425.1725.



Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil 5b (32.4 mg, 77% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.22 (m, 9H), 7.19 (t, $J = 7.0$ Hz, 1H), 7.09 (dd, $J = 9.0, 2.5$ Hz, 1H), 6.90-6.81 (m, 1H), 6.66 (dd, $J = 8.5, 4.0$ Hz, 1H), 6.05 (d, $J = 9.5$ Hz, 1H), 5.05 (s, 1H), 4.99 (s, 1H), 4.38-4.26 (m, 2H), 3.84-3.75 (m, 1H), 3.61 (d, $J = 2.5$ Hz, 3H), 3.01-2.77 (m, 2H), 2.44 (dd, $J = 15.0, 6.0$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 173.7, 157.2 (d, $J = 239.7$ Hz), 151.4, 142.7, 141.6, 138.2, 134.1 (d, $J = 6.5$ Hz), 134.0 (d, $J = 6.3$ Hz), 128.7, 127.3, 127.8, 127.5 (d, $J = 8.7$ Hz), 126.5 (d, $J = 2.0$ Hz), 114.7, 114.5 (d, $J = 14.0$ Hz), 114.2 (d, $J = 23.1$ Hz), 112.7 (d, $J = 2.2$ Hz), 112.6 (d, $J = 2.4$ Hz), 71.5, 71.2, 71.1, 52.1, 49.9, 36.3, 36.3 ppm. IR (KBr, cm^{-1}): 3398, 2964, 2922, 1733, 1652, 1491, 1432, 1261, 1191, 1021, 881, 801, 731, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{FO}_4\text{Na}$: 443.1629, found: 443.1633

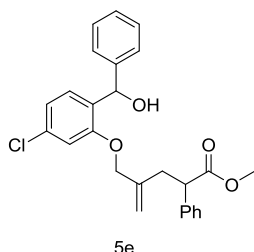


5c: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (37.5 mg, 78% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, $J = 2.5$ Hz, 1H), 7.36-7.22 (m, 10H), 7.19 (t, $J = 7.5$ Hz, 1H), 6.61 (d, $J = 9.0$ Hz, 1H), 6.04 (dd, $J = 9.5, 4.5$ Hz, 1H), 5.03 (s, 1H), 4.99 (s, 1H), 4.37-4.28 (m, 2H), 3.82-3.74 (m, 1H), 3.62 (d, $J = 2.5$ Hz, 3H), 2.89-2.74 (m, 2H), 2.47-2.36 (m, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 154.5, 154.4, 142.6, 141.3, 138.2, 134.4, 134.3, 131.1, 130.5, 128.7, 128.3, 127.8, 127.6, 127.5, 126.5, 114.9, 114.8, 113.4, 71.3, 71.2, 71.1, 52.1, 50.0, 36.3 ppm. IR (KBr, cm^{-1}): 3358, 3062, 3029, 2920, 2850, 1734, 1657, 1453, 1236, 1021, 914, 879, 803, 766, 731, 698, 594. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{BrO}_4\text{Na}$: 503.0834, found: 503.0834.

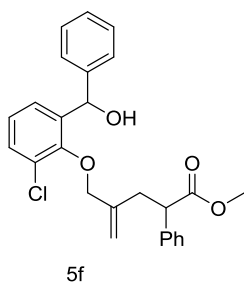


5d: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (31.5 mg, 72% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.29 (m, 5H), 7.29-7.26 (m, 2H), 7.26-7.26 (m, 1H), 7.26-7.24 (m, 2H), 7.19 (t, $J = 7.0$ Hz, 1H), 7.15 (dd, $J = 9.0, 2.5$ Hz, 1H), 6.66 (dd, $J = 8.5, 1.0$ Hz, 1H), 6.05 (dd, $J = 9.5, 5.0$ Hz, 1H), 5.04 (s, 1H), 4.99 (s, 1H), 4.39-4.28 (m, 2H), 3.85-3.75 (m, 1H), 3.62 (d, $J = 3.0$ Hz, 3H), 2.90-2.75 (m, 2H), 2.43 (dd, $J = 15.5, 6.0$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 154.0, 142.6, 141.4, 138.2, 134.0, 133.9, 128.7, 128.3, 128.1, 127.8, 127.6, 127.5, 126.5, 126.1, 114.9, 114.8, 112.9, 71.3, 71.2, 52.1, 50.0, 36.3 ppm. IR (KBr,

cm⁻¹): 3359, 3029, 2919, 2850, 1734, 1658, 1484, 1454, 1238, 1018, 901, 802, 767, 729, 699. HRMS (ESI) [M+Na]⁺ calcd for C₂₆H₂₅ClO₄Na: 459.1334, found: 459.1338.

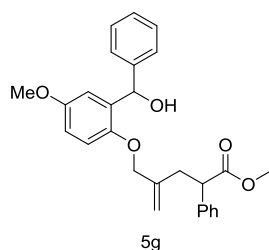


5e: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (29.3 mg, 67% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.32 (dd, *J* = 12.0, 6.5 Hz, 4H), 7.29-7.22 (m, 6H), 7.18 (t, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.77 (s, 1H), 6.04 (d, *J* = 8.5 Hz, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.40-4.30 (m, 2H), 3.84-3.76 (m, 1H), 3.62 (d, *J* = 3.5 Hz, 3H), 2.91-2.77 (m, 2H), 2.43 (dd, *J* = 15.0, 6.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 156.0, 142.9, 141.2, 141.1, 138.2, 133.9, 130.9, 130.8, 128.7, 128.6, 128.3, 127.8, 127.6, 127.4, 126.4, 121.0, 115.1, 115.0, 112.4, 71.3, 71.2, 71.1, 52.1, 50.0, 36.4, 36.3 ppm. IR (KBr, cm⁻¹): 3360, 2974, 2896, 1732, 1654, 1486, 1453, 1381, 1238, 1088, 1048, 880, 801, 699. HRMS (ESI) [M+Na]⁺ calcd for C₂₆H₂₅ClO₄Na: 459.1334, found: 459.1334.

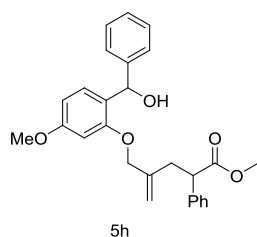


5f: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (31.0 mg, 71% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.38-7.31 (m, 4H), 7.31-7.26 (m, 4H), 7.26-7.23 (m, 2H), 7.03 (t, *J* = 6.0 Hz, 1H),

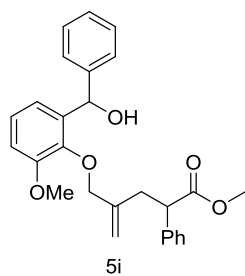
6.80 (td, $J = 8.0, 3.5$ Hz, 1H), 5.62 (s, 1H), 5.08 (s, 1H), 4.99 (d, $J = 3.5$ Hz, 1H), 4.00-3.87 (m, 2H), 3.85-3.75 (m, 1H), 3.62 (s, 3H), 2.97-2.84 (m, 1H), 2.53 (dd, $J = 14.5, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 150.2, 150.1, 142.0, 140.0, 138.4, 129.0, 128.7, 128.6, 128.1, 127.8, 127.7, 127.4, 127.2, 127.1, 126.8, 121.2, 120.5, 115.1, 115.0, 81.0, 72.0, 71.9, 52.0, 50.0, 36.8 ppm. IR (KBr, cm^{-1}): 3358, 3029, 2920, 2850, 1734, 1658, 1453, 1243, 1071, 913, 773, 734, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{26}\text{H}_{25}\text{ClO}_4\text{Na}$: 459.1334, found: 459.1342.



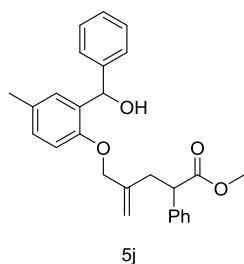
5g: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (31.1 mg, 72% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.36 (d, $J = 4.0$ Hz, 2H), 7.33-7.21 (m, 7H), 7.17 (dd, $J = 8.0, 6.5$ Hz, 1H), 6.91 (s, 1H), 6.77-6.64 (m, 2H), 6.04 (d, $J = 5.0$ Hz, 1H), 5.05 (s, 1H), 4.96 (s, 1H), 4.37-4.21 (m, 2H), 3.81 (dd, $J = 8.5, 3.5$ Hz, 1H), 3.73 (s, 3H), 3.61 (d, $J = 2.5$ Hz, 3H), 3.01 (dd, $J = 14.5, 4.5$ Hz, 1H), 2.85 (dd, $J = 24.5, 10.0$ Hz, 1H), 2.44 (dd, $J = 15.0, 6.0$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 173.7, 153.8, 149.7, 143.2, 143.1, 141.9, 141.9, 138.3, 133.4, 133.3, 128.7, 128.2, 127.9, 127.5, 127.2, 126.5, 126.4, 114.4, 114.0, 112.9, 112.8, 72.0, 71.9, 71.6, 55.6, 52.1, 50.0, 36.5, 36.4 ppm. IR (KBr, cm^{-1}): 3489, 3029, 2949, 1733, 1600, 1494, 1453, 1432, 1208, 1038, 913, 731, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{Na}$: 455.1829, found: 455.1829.



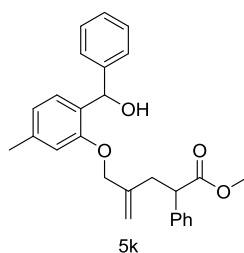
5h: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (30.3 mg, 70% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.40-7.33 (m, 2H), 7.33-7.22 (m, 7H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.13 (d, $J = 8.5$ Hz, 1H), 6.46 (dd, $J = 8.5, 2.0$ Hz, 1H), 6.40 (d, $J = 1.5$ Hz, 1H), 6.03 (t, $J = 6.0$ Hz, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.42-4.30 (m, 2H), 3.84-3.74 (m, 4H), 3.62 (d, $J = 4.0$ Hz, 3H), 2.94-2.80 (m, 2H), 2.51-2.39 (m, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 160.2, 156.6, 143.6, 141.6, 138.3, 128.8, 128.7, 128.1, 127.8, 127.5, 127.0, 126.4, 124.9, 124.8, 114.8, 104.5, 99.7, 71.7, 71.6, 71.0, 55.4, 52.1, 50.0, 49.9, 36.5, 36.4 ppm. IR (KBr, cm^{-1}): 3361, 2921, 2851, 1733, 1609, 1501, 1451, 1260, 1160, 1044, 881, 798, 731, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{Na}$: 455.1829, found: 455.1835.



5i: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (30.7 mg, 71% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.38-7.32 (m, 2H), 7.32-7.19 (m, 8H), 7.05 (td, $J = 8.0, 2.0$ Hz, 1H), 6.97-6.91 (m, 1H), 6.86 (d, $J = 8.5$ Hz, 1H), 6.02 (dd, $J = 14.0, 6.0$ Hz, 1H), 4.98 (d, $J = 10.5$ Hz, 1H), 4.91 (d, $J = 4.5$ Hz, 1H), 4.26 (dd, $J = 24.0, 11.5$ Hz, 1H), 4.06 (dd, $J = 11.5, 5.5$ Hz, 1H), 3.97 (dt, $J = 8.5, 6.5$ Hz, 1H), 3.83 (s, 3H), 3.63 (d, $J = 1.5$ Hz, 3H), 3.07-2.91 (m, 2H), 2.57 (dd, $J = 15.0, 6.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 174.0, 152.6, 145.1, 145.0, 143.8, 142.5, 138.7, 138.6, 128.6, 128.2, 127.9, 127.3, 127.1, 126.4, 126.3, 124.2, 119.9, 114.6, 111.8, 75.0, 74.9, 72.1, 72.0, 55.7, 52.0, 49.8, 49.7, 37.0 ppm. IR (KBr, cm^{-1}): 3359, 3029, 2920, 2849, 1734, 1658, 1480, 1440, 1351, 1270, 1064, 907, 792, 732, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{25}\text{O}_4\text{Na}^+$: 455.1829, found: 455.1834.

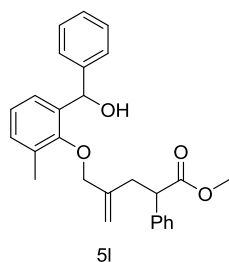


5j: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (20.4 mg, 49% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.36 (dd, $J = 8.0, 3.0$ Hz, 2H), 7.33 – 7.21 (m, 7H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.10 (s, 1H), 7.00 (dd, $J = 8.3, 1.1$ Hz, 1H), 6.67 (d, $J = 8.3$ Hz, 1H), 6.07-6.00 (m, 1H), 5.05 (s, 1H), 4.97 (s, 1H), 4.40-4.28 (m, 2H), 3.84-3.76 (m, 1H), 3.62 (d, $J = 3.5$ Hz, 3H), 2.99 (dd, $J = 11.5, 5.5$ Hz, 1H), 2.90-2.79 (m, 1H), 2.53-2.37 (m, 1H), 2.26 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 173.7, 153.5, 143.5, 143.4, 141.8, 138.3, 131.8, 130.3, 130.2, 128.8, 128.7, 128.6, 128.1, 127.9, 127.5, 127.1, 127.0, 126.4, 114.5, 114.4, 111.7, 72.1, 72.0, 71.0, 52.2, 50.0, 49.9, 36.4, 20.6 ppm. IR (KBr, cm^{-1}): 3360, 2960, 2919, 2850, 1733, 1655, 1496, 1452, 1240, 1158, 1021, 911, 802, 732, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{O}_4\text{Na}^+$: 439.1880, found: 439.1885.

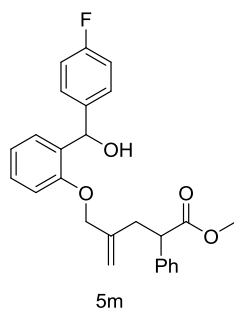


5k: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (21.7 mg, 52% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.39-7.20 (m, 9H), 7.20 -7.09 (m, 2H), 6.76 (d, $J = 7.5$ Hz, 1H), 6.62 (s, 1H), 6.04 (t, $J = 6.0$ Hz, 1H), 5.07 (s, 1H), 4.98 (s, 1H), 4.43-4.32 (m, 2H), 3.86-3.77 (m, 1H), 3.62 (d, $J = 3.5$ Hz, 3H), 2.96 (dd, $J = 9.5, 6.0$ Hz, 1H), 2.90-2.81 (m, 1H), 2.46 (dt, $J = 12.5, 6.0$ Hz, 1H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 173.7, 155.6, 143.5, 141.7, 138.7, 138.3, 129.3,

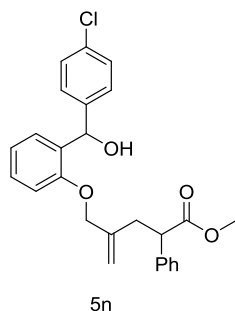
129.2, 128.7, 128.1, 127.9, 127.5, 127.0, 126.4, 121.6, 114.6, 112.7, 72.0, 71.9, 70.9, 52.1, 50.0, 36.5, 36.5, 21.5 ppm. IR (KBr, cm^{-1}): 3365, 2965, 2922, 1734, 1659, 1452, 1261, 1090, 1042, 880, 801, 731, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{O}_4\text{Na}$: 439.1880, found: 439.1887.



5l: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (20.8 mg, 50% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.37 (t, J = 6.7 Hz, 2H), 7.34-7.29 (m, 6H), 7.29-7.22 (m, 3H), 7.19-7.08 (m, 2H), 7.06-6.99 (m, 1H), 6.07-6.00 (m, 1H), 5.15 (d, J = 8.0 Hz, 1H), 4.97 (s, 1H), 4.12-3.95 (m, 2H), 3.90-3.81 (m, 1H), 3.65 (s, 3H), 3.00-2.83 (m, 2H), 2.54-2.47 (m, 1H), 2.25 (d, J = 2.5 Hz, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.9, 154.8, 143.8, 142.3, 138.5, 138.4, 136.9, 131.3, 131.0, 128.7, 128.3, 127.9, 127.4, 127.2, 126.5, (126.2, 126.1, dr=1:1), 124.3, 113.7, 75.4, 75.3, 71.8, 71.7, 52.1, 50.3, 36.9, 16.3 ppm. IR (KBr, cm^{-1}): 3453, 3029, 2950, 2923, 2853, 1735, 1658, 1452, 1351, 1257, 1189, 1028, 914, 772, 730, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{O}_4\text{Na}$: 439.1880, found: 439.1888.



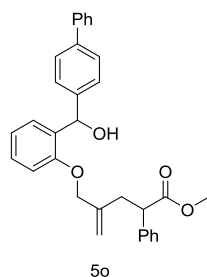
5m: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (30.7 mg, 73% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.28 (m, 4H), 7.27 (d, *J* = 5.5 Hz, 2H), 7.26-7.19 (m, 3H), 6.99-6.89 (m, 3H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.04 (t, *J* = 6.0 Hz, 1H), 5.06 (s, 1H), 4.99 (s, 1H), 4.45-4.31 (m, 2H), 3.80 (dt, *J* = 9.0, 6.0 Hz, 1H), 3.62 (d, *J* = 4.5 Hz, 3H), 3.02 (dd, *J* = 17.5, 5.5 Hz, 1H), 2.85 (dt, *J* = 15.0, 9.5 Hz, 1H), 2.50-2.40 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 173.7, 162.9 (d, *J* = 245.8 Hz), 155.5, 141.6, 139.1, 138.2, 131.9 (d, *J* = 10.6 Hz), 128.7, 128.2 (d, *J* = 4.9 Hz), 128.1 (d, *J* = 4.9 Hz), 127.8, 127.7, 127.5, 121.0, 114.9 (d, *J* = 21.3 Hz), 114.7 (d, *J* = 10.7 Hz), 111.7, 71.5, 71.4, 70.9, 52.1, 49.9, 36.4, 36.4 ppm. IR (KBr, cm⁻¹): 3455, 3063, 3031, 2950, 2924, 1733, 1656, 1601, 1506, 1452, 1222, 1016, 911, 754, 732, 699. HRMS (ESI) [M+Na]⁺ calcd for C₂₆H₂₅FO₄Na: 443.1629, found: 443.1630.



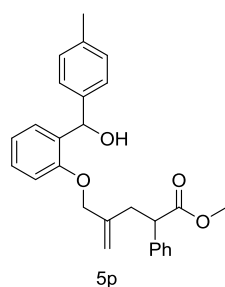
5n: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (32.3 mg, 74% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.28 (m, 5H), 7.27 (s, 2H), 7.23 (dd, *J* = 13.5, 5.0 Hz, 2H), 7.02-6.88 (m, 3H), 6.78 (d, *J* = 8.5 Hz, 1H), 6.05 (t, *J* = 6.0 Hz, 1H), 5.06 (s, 1H), 4.99 (s, 1H), 4.44-4.33 (m, 2H), 3.80 (dt, *J* = 9.5, 6.5 Hz, 1H), 3.62 (d, *J* = 4.5 Hz, 3H), 3.03 (dd, *J* = 17.5, 5.5 Hz, 1H), 2.86 (dt, *J* = 15.0, 9.5 Hz, 1H), 2.52-2.40 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 155.5, 141.9, 141.6, 138.2, 132.8, 131.7, 131.6, 130.3, 128.8, 128.7, 128.2, 127.9, 127.8, 127.5, 121.1, 114.7, 111.7, 71.4, 71.3, 70.9, 52.1, 50.0, 36.5, 36.4 ppm. IR (KBr, cm⁻¹): 3455,

3064, 3031, 2949, 1733, 1654, 1488, 1451, 1349, 1230, 1014, 911, 833, 754, 698.

HRMS (ESI) $[M+Na]^+$ calcd for $C_{26}H_{25}ClO_4Na$: 459.1334, found: 459.1342.

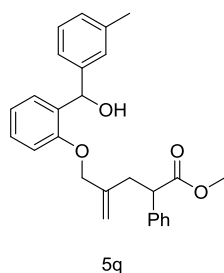


5o: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (34.9 mg, 73% yield, dr = 1:1). 1H NMR (500 MHz, $CDCl_3$) δ 7.58-7.52 (m, 2H), 7.50 (dd, J = 8.5, 2.0 Hz, 2H), 7.47-7.39 (m, 4H), 7.33 (dd, J = 16.0, 8.0 Hz, 2H), 7.29-7.20 (m, 6H), 6.98 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.14 (dd, J = 7.5, 5.0 Hz, 1H), 5.09 (s, 1H), 5.01 (s, 1H), 4.46-4.35 (m, 2H), 3.84 (dt, J = 9.0, 6.0 Hz, 1H), 3.59 (d, J = 5.0 Hz, 3H), 3.03 (dd, J = 14.5, 5.5 Hz, 1H), 2.91 (td, J = 14.5, 9.5 Hz, 1H), 2.56-2.47 (m, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.7, 155.6, 142.4, 141.7, 140.9, 140.0, 138.3, 132.1, 132.0, 128.7, 127.9, 127.8, 127.5, 127.2, 127.1, 126.9, 126.91, 121.1, 121.0, 114.7, 111.7, 71.8, 71.7, 71.0, 52.1, 50.0, 36.5 ppm. IR (KBr, cm^{-1}): 3361, 3028, 2920, 2851, 1733, 1656, 1597, 1487, 1451, 1230, 1034, 911, 757, 698. HRMS (ESI) $[M+Na]^+$ calcd for $C_{32}H_{30}O_4Na$: 501.2036, found: 501.2041.

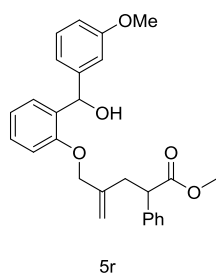


5p: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (21.2 mg, 51% yield, dr = 1:1). 1H NMR (500 MHz, $CDCl_3$) δ 7.35-7.23 (m, 8H), 7.22 -7.18 (m, 1H), 7.07 (dd, J = 8.0, 1.5 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.77 (d, J = 8.0 Hz, 1H),

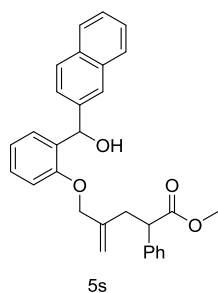
6.07 (dd, $J = 8.0, 4.0$ Hz, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.44-4.33 (m, 2H), 3.83 (dt, $J = 9.5, 6.0$ Hz, 1H), 3.72-3.55 (m, 3H), 2.98-2.81 (m, 2H), 2.56-2.43 (m, 1H), 2.29 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.8, 173.7, 155.6, 141.7, 140.3, 138.3, 136.7, 132.4, 132.3, 128.9, 128.7, 128.5, 127.9, 127.5, 126.5, 121.0, 114.6, 111.7, 71.8, 71.7, 70.9, 52.1, 50.0, 36.5, 21.1 ppm. IR (KBr, cm^{-1}): 3359, 2963, 2920, 1733, 1655, 1488, 1452, 1260, 1020, 800, 754, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{O}_4\text{Na}$: 439.1880, found: 439.1887.



5q: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (20.8 mg, 50% yield, dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.33-7.26 (m, 5H), 7.25 (s, 1H), 7.23-7.17 (m, 2H), 7.13 (d, $J = 2.5$ Hz, 2H), 7.04-6.91 (m, 2H), 6.78 (d, $J = 8.0$ Hz, 1H), 6.05 (d, $J = 5.5$ Hz, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.44-4.34 (m, 2H), 3.85-3.78 (m, 1H), 3.62 (d, $J = 3.5$ Hz, 3H), 2.98-2.81 (m, 2H), 2.47 (dd, $J = 14.5, 5.5$ Hz, 1H), 2.28 (s, 3H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 173.7, 155.6, 143.2, 141.7, 138.3, 137.7, 132.3, 130.3, 128.7, 128.5, 128.0, 127.9, 127.8, 127.5, 127.2, 127.1, 123.6, 121.0, 114.7, 111.7, 72.0, 71.9, 70.9, 52.1, 50.0, 36.5, 21.4 ppm. IR (KBr, cm^{-1}): 3359, 2965, 2921, 1734, 1657, 1487, 1452, 1261, 1046, 880, 799, 754, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{27}\text{H}_{28}\text{O}_4\text{Na}$: 439.1880, found: 439.1882.

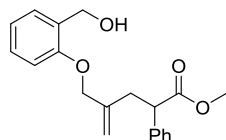


5r: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (30.3mg, 70% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.23 (m, 6H), 7.23 -7.13 (m, 3H), 6.94 (td, *J* = 7.5, 3.5 Hz, 1H), 6.90-6.73 (m, 3H), 6.43 (t, *J* = 5.0 Hz, 1H), 5.09 (d, *J* = 3.0 Hz, 1H), 4.97 (d, *J* = 5.5 Hz, 1H), 4.50-4.32 (m, 2H), 3.89-3.78 (m, 1H), 3.75 (d, *J* = 12.0 Hz, 3H), 3.61 (s, 3H), 3.36 (dd, *J* = 8.0, 5.0 Hz, 1H), 2.96-2.77 (m, 1H), 2.49 (dd, *J* = 15.0, 6.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 156.8, 155.6, 141.8, 138.4, 138.3, 131.2, 131.1, 131.0, 128.6, 128.4, 128.2, 127.9, 127.7, 127.4, 120.7, 120.5, 114.4, 114.3, 111.4, 111.3, 110.3, 70.9, 70.7, , 66.7, 55.3, 55.2, 52.0, 49.9, 36.4 ppm. IR (KBr, cm⁻¹): 3532, 3031, 2949, 2838, 1733, 1489, 1453, 1240, 1160, 1026, 911, 753, 699. HRMS (ESI) [M+Na]⁺ calcd for C₂₇H₂₅O₄Na: 455.1829, found: 455.1825.



5s: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (33.5, 74% yield, dr = 1:1). ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.82-7.69 (m, 3H), 7.49-7.39 (m, 3H), 7.33-7.18 (m, 7H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 6.28 (dd, *J* = 9.5, 4.5 Hz, 1H), 5.09 (s, 1H), 5.00 (s, 1H), 4.49-4.26 (m, 2H), 3.95-3.70 (m, 1H), 3.59 (d, *J* = 4.0 Hz, 3H), 3.14 (dd, *J* = 22.5, 5.0 Hz, 1H), 3.03-2.81 (m, 1H), 2.58-2.36 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.7, 155.7, 141.7, 141.6, 140.7, 140.6, 138.3, 133.2, 132.7, 132.1, 132.0, 128.7, 128.1, 128.0, 127.8, 127.6, 127.5, 125.9, 125.6, 125.0, 125.0, 121.1, 114.8, 114.7, 111.8, 71.9, 71.7, 71.0, 52.1, 50.0, 36.6, 36.5 ppm. IR (KBr, cm⁻¹): 3507, 3057, 2949, 1733, 1654, 1599, 1489,

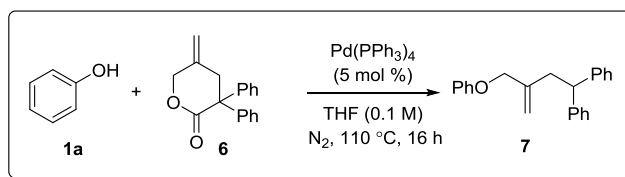
1452, 1358, 1230, 1160, 1027, 909, 820, 753, 699. HRMS (ESI) $[M+Na]^+$ calcd for $C_{32}H_{28}O_4Na$: 475.1880, found: 475.1883.



5t

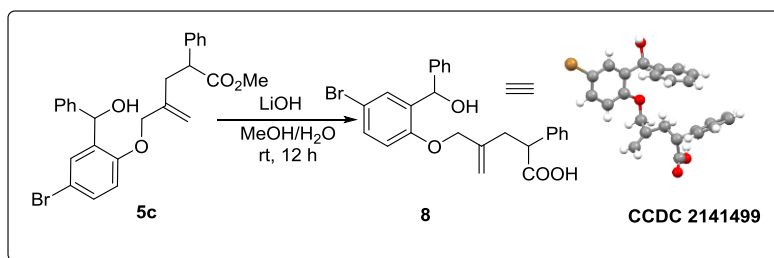
5t: Prepared according to the general procedure above and purified by a flash chromatography column with PE/EA (5:1, v/v) as the eluent. Colorless oil (18.6mg, 57% yield). 1H NMR (500 MHz, $CDCl_3$) δ 7.37-7.20 (m, 7H), 6.95 (t, $J = 7.5$ Hz, 1H), 6.79 (d, $J = 8.5$ Hz, 1H), 5.18 (s, 1H), 5.05 (s, 1H), 4.72 (s, 2H), 4.58-4.40 (m, 2H), 3.91 (dd, $J = 9.0, 6.5$ Hz, 1H), 3.63 (s, 3H), 3.00 (dd, $J = 14.5, 9.0$ Hz, 1H), 2.58 (dd, $J = 15.0, 6.5$ Hz, 1H), 2.47 (s, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 156.3, 141.7, 138.3, 129.3, 128.9, 128.8, 128.7, 127.8, 127.5, 120.9, 114.7, 111.3, 70.7, 61.9, 52.1, 50.1, 36.8 ppm. IR (KBr, cm^{-1}): 3360, 3030, 2919, 2850, 1732, 1658, 1601, 1491, 1453, 1359, 1233, 1012, 910, 754, 699. HRMS (ESI) $[M+Na]^+$ calcd for $C_{20}H_{22}O_4Na$: 349.1410, found: 349.1410.

F) Synthesis of decarboxylative *O*-allylation product **7**



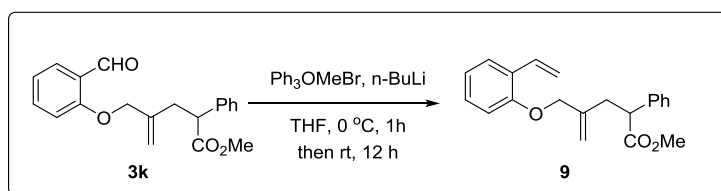
Under a nitrogen atmosphere, to an oven dried 10 mL Schlenck flask equipped with a stirring bar was added GMDVs **6** (0.15 mmol), Phenoles **1a** (0.1 mmol), Pd(PPh₃)₄ (5 mol %) and dry THF (1.0 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred at 110 °C for the indicated time. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15:1, v/v), giving the corresponding colorless oil **7** in 50% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.30-7.21 (m, 10H), 7.17 (t, *J* = 7.0 Hz, 2H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.0 Hz, 2H), 5.10 (s, 1H), 4.92 (s, 1H), 4.35 (s, 2H), 4.25 (t, *J* = 8.0 Hz, 1H), 2.93 (d, *J* = 8.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 158.6, 144.3, 142.6, 129.4, 128.4, 127.9, 126.3, 120.8, 114.8, 114.7, 70.8, 49.5, 39.2 ppm. IR (KBr, cm⁻¹): 3026, 2922, 1651, 1597, 1493, 1239, 1031, 905, 751, 697. HRMS (ESI) [M+H]⁺ calcd for C₂₃H₂₃O: 315.1743, found: 315.1754.

G) Synthesis of hydrolysis product **8** (CCDC 2141499)



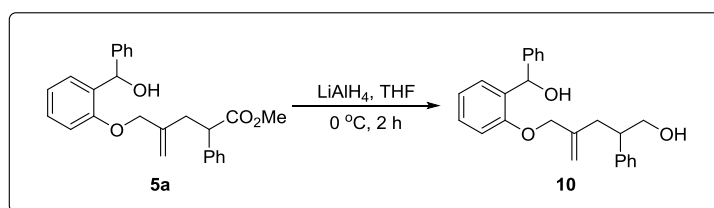
To a flame dried round bottom flask was added compound **5c** (0.1 mmol) and LiOH (0.2 mmol). Then 1.1ml CH₃OH-H₂O (0.09M, 10:1) was added at room temperature and the reaction mixture was then stirred overnight. The mixture was acidified with hydrochloric acid after the completion of the reaction. Then the reaction mixture was extracted with EtOAc, dried over anhydrous sodium sulfate, concentrated the mixture under vacuum and then purified by flash column chromatography with DCM/CH₃OH (20:1, v/v) to afford the corresponding product **8** in 83% yield and 1:1 dr as a white solid. Melting point: 89.8-90.1 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.51 (s, 1H), 7.30 (d, *J* = 6.0 Hz, 6H), 7.26-7.21 (m, 4H), 7.15 (t, *J* = 7.0 Hz, 1H), 6.59 (d, *J* = 9.0 Hz, 1H), 6.01 (d, *J* = 9.0 Hz, 1H), 5.03 (s, 1H), 5.00 (s, 1H), 4.39-4.23 (m, 2H), 3.77 (t, *J* = 11.5 Hz, 1H), 2.79 (td, *J* = 16.0, 9.0 Hz, 1H), 2.41 (dd, *J* = 15.0, 6.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 178.8, (154.4, 154.3, dr=1:1), 142.6, 141.1, 137.5, 134.2, 134.1, 131.1, 130.4, 128.8, 128.3, 128.0, 127.8, 127.5, 126.5, 115.2, 113.5, 113.4, 71.3, 71.2, 49.8, 35.7 ppm. IR (KBr, cm⁻¹): 3029, 2927, 2855, 1707, 1483, 1453, 1238, 1016, 914, 803, 161, 727, 698, 595. HRMS (ESI) [M+Na]⁺ calcd for C₂₅H₂₃BrO₄Na: 489.0672, found: 489.0671.

H) Synthesis of Wittig reaction product **9**



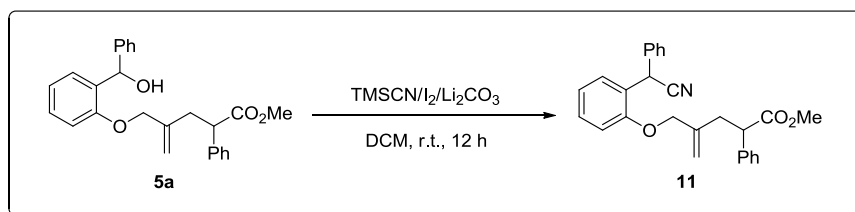
To a flame-dried round-bottom flask, Ph₃PCH₂Br (1.2 equiv) was added. Under nitrogen atmosphere, THF (0.25M) and *n*-BuLi (1.2 equiv) were added at 0 °C. After 1 h, **3k** (1.0 equiv) was added at room temperature and the reaction mixture was then stirred overnight. The reaction mixture was quenched with NH₄Cl, extracted with EtOAc, dried over anhydrous sodium sulfate, concentrated the mixture under vacuum and then purified by flash column chromatography with PE/EA (10:1, v/v) to afford the colorless oil **9** in 56% yield. ¹H NMR (500 MHz, CDCl₃) δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.36-7.28 (m, 4H), 7.27 (dd, *J* = 6.5, 3.0 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.09 (dd, *J* = 17.5, 11.0 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 1H), 5.73 (d, *J* = 18.0 Hz, 1H), 5.25 (d, *J* = 11.0 Hz, 1H), 5.19 (s, 1H), 5.03 (s, 1H), 4.52-4.35 (m, 2H), 3.91 (dd, *J* = 9.0, 7.0 Hz, 1H), 3.64 (s, 3H), 2.98 (dd, *J* = 15.0, 9.0 Hz, 1H), 2.62 (dd, *J* = 15.0, 6.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.8, 155.6, 141.9, 138.5, 131.6, 128.7, 127.9, 127.4, 127.1, 126.4, 120.9, 114.4, 112.2, 71.1, 52.0, 50.0, 36.9 ppm. IR (KBr, cm⁻¹): 3358, 3195, 2920, 2850, 1738, 1658, 1469, 1383, 721. HRMS (ESI) [M+Na]⁺ calcd for C₂₁H₂₂O₃Na: 345.1461, found: 345.1466

I) Synthesis of reduction product **10**



The compound **5a** was dissolved in THF (0.25 M), and the resulting solution was cooled to $0\text{ }^\circ\text{C}$. LiAlH_4 (1.5 equiv) was added portion wise, and the resulting mixture was allowed to stir for 2h. The reaction was quenched using the Fieser method, filtered through celite, and concentrated in vacuo. The residue was purified by column chromatography with PE/EA (2:1, v/v) to afford the colorless oil **10** in 70% yield (dr = 1:1). ^1H NMR (500 MHz, CDCl_3) δ 7.37 (dd, $J = 7.5, 3.5$ Hz, 2H), 7.30 (t, $J = 7.5$ Hz, 5H), 7.25-7.17 (m, 3H), 7.13 (t, $J = 7.0$ Hz, 2H), 6.94 (t, $J = 7.5$ Hz, 1H), 6.72 (t, $J = 8.0$ Hz, 1H), 6.08 (d, $J = 10.0$ Hz, 1H), 5.00 (s, 1H), 4.90 (s, 1H), 4.43-4.23 (m, 2H), 3.64 (t, $J = 10.0$ Hz, 2H), 3.15 (d, $J = 30.0$ Hz, 1H), 3.04-2.88 (m, 1H), 2.52 (ddd, $J = 20.5, 15.0, 6.0$ Hz, 1H), 2.31 (dt, $J = 14.5, 10.0$ Hz, 1H), 1.52 (d, $J = 28.5$ Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3) δ 155.7, 155.6, 143.5, 143.4, 142.1, 141.4, 131.9, 128.6, 128.1, 128.0, 127.1, 126.9, 126.5, 120.9, 114.9, 111.7, 72.0, 70.9, 67.3, 67.2, 46.7, 46.6, 35.3 ppm. IR (KBr, cm^{-1}): 3358, 3028, 2920, 2850, 1657, 1489, 1452, 1235, 1020, 906, 754, 699. HRMS (ESI) $[\text{M}+\text{Na}]^+$ calcd for $\text{C}_{25}\text{H}_{26}\text{O}_3\text{Na}$: 397.1774, found: 397.1776

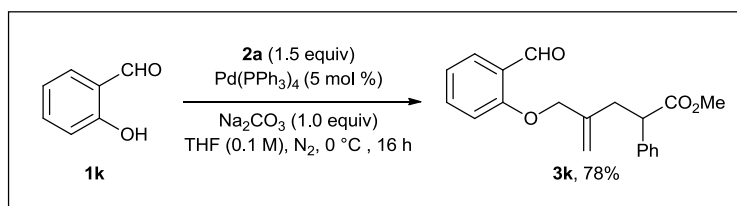
J) General Procedure for the Synthesis of **11**



To a round-bottom flask was charged with compounds **5a** (0.1 mmol) in DCM (2 mL), Li₂CO₃ (0.02 mmol), TMSCN (0.45 mmol), and I₂ (0.18 mmol) in sequence successively. Then the resulting mixture was stirred overnight under closed conditions at room temperature. The reaction was quenched with saturated solution of Na₂S₂O₃. The organic phase was separated, and the aqueous layer was extracted with DCM. The combined organic solution was dried with Na₂SO₄ and concentrated in vacuo. The resulting residue was purified by a column chromatography with PE/EA (6:1, v/v) to give the corresponding colorless oil **11** in 83% yield and 1:1 dr. ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.30 (m, 4H), 7.30-7.27 (m, 4H), 7.26-7.19 (m, 4H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H), 5.55 (s, 1H), 5.10 (s, 1H), 5.02 (s, 1H), 4.48-4.35 (m, 2H), 3.89-3.79 (m, 1H), 3.62 (d, *J* = 2.0 Hz, 3H), 2.90 (dt, *J* = 15.0, 9.0 Hz, 1H), 2.58-2.44 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃) δ 173.6, 155.0, 141.3, 138.2, 135.5, 129.6, 129.0, 128.8, 128.7, 127.8, 127.6, 127.5, 124.5, 124.4, 121.2, 119.9, 114.7, 114.6, 111.9, 71.1, 52.1, 50.0, 49.9, 36.4, 36.3 ppm. IR (KBr, cm⁻¹): 3029, 2945, 2360, 1734, 1653, 1491, 1451, 1241, 1159, 1010, 911, 752, 732, 697. HRMS (ESI) [M+Na]⁺ calcd for C₂₇H₂₅NO₃Na: 434.1727, found: 434.1731.

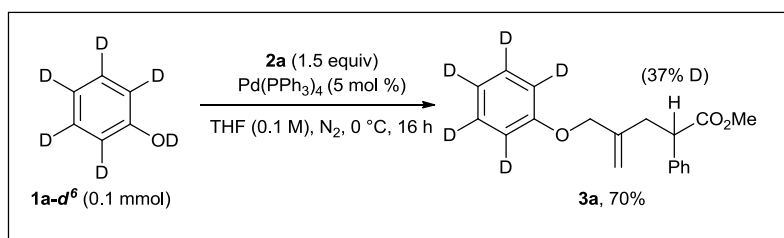
III. Control Experiments

A) Base Effect

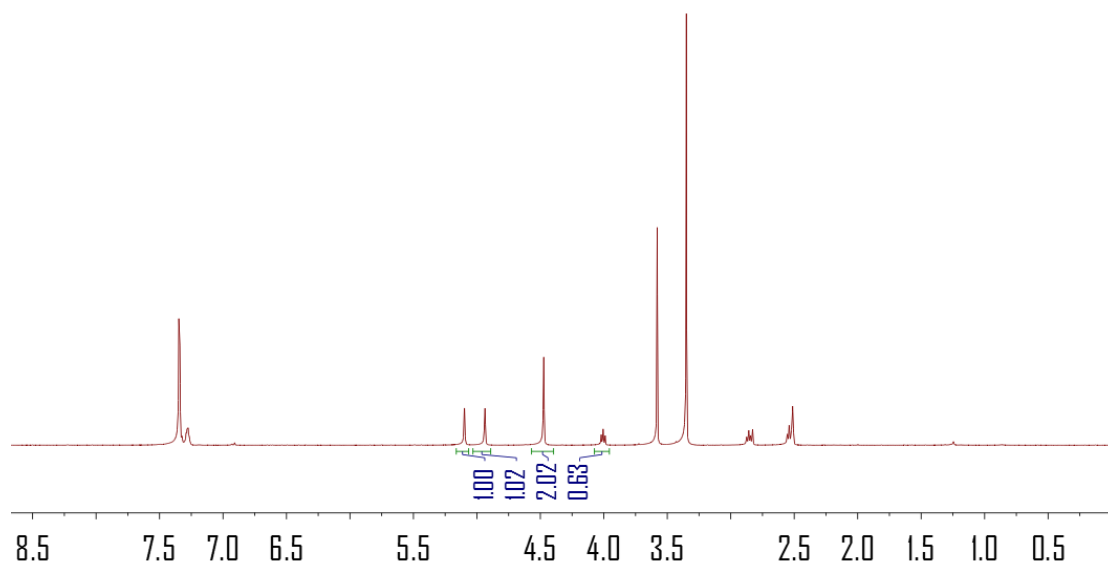


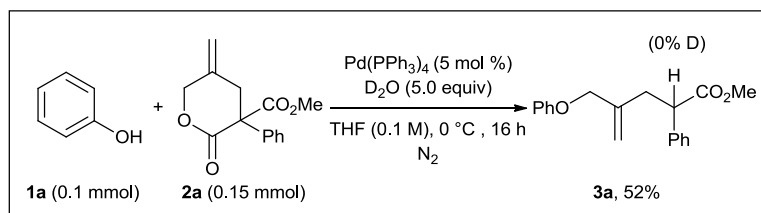
Reaction procedure A: Under a nitrogen atmosphere, to an oven dried 10 mL Schlenk flask equipped with a stirring bar was added phenol **1k** (0.1 mmol), GMDVs **2a** (0.15 mmol), Na₂CO₃ (0.1 mmol), Pd(PPh₃)₄ (5 mol %) and dry THF (1.0 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred at 0 °C for 16 h. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15;1), giving the corresponding product **3k** (25.3 mg, 78%).

B) Deuterium-labelling Experiments

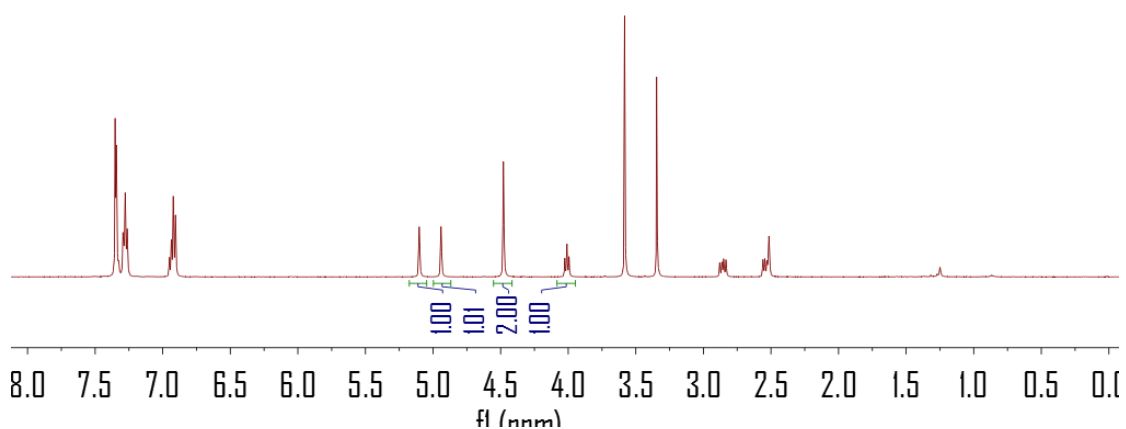


Reaction procedure A: Under a nitrogen atmosphere, to an oven dried 10 mL Schlenk flask equipped with a stirring bar was added phenol **1a-d⁶** (0.1 mmol), GMDVs **2a** (0.15 mmol), Pd(PPh₃)₄ (5 mol %) and dry THF (1.0 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred at 0 °C for 16 h. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15;1), giving the corresponding product **3a** (37% D, determined by ¹H NMR) in 78% yield.





Reaction procedure B: Under a nitrogen atmosphere, to an oven dried 10 mL Schlenk flask equipped with a stirring bar was added phenol **1a** (0.1 mmol), GMDVs **2a** (0.15 mmol), Pd(PPh₃)₄ (5 mol %), D₂O (0.5 mmol) and dry THF (1.0 mL). The resultant mixture was degassed three times by freeze-pump-thaw cycles. The reaction mixture was stirred at 0 °C for 16 h. And then the reaction mixture was purified by flash column chromatography on silica gel eluting with petroleum ether/ethyl acetate (15;1), giving the corresponding product **3a** (0% D, determined by ¹H NMR) in 52% yield.



IV. X-ray Crystal Data

A) X-Ray Structure of product 8 (CCDC 2141499)

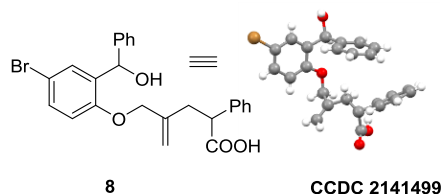
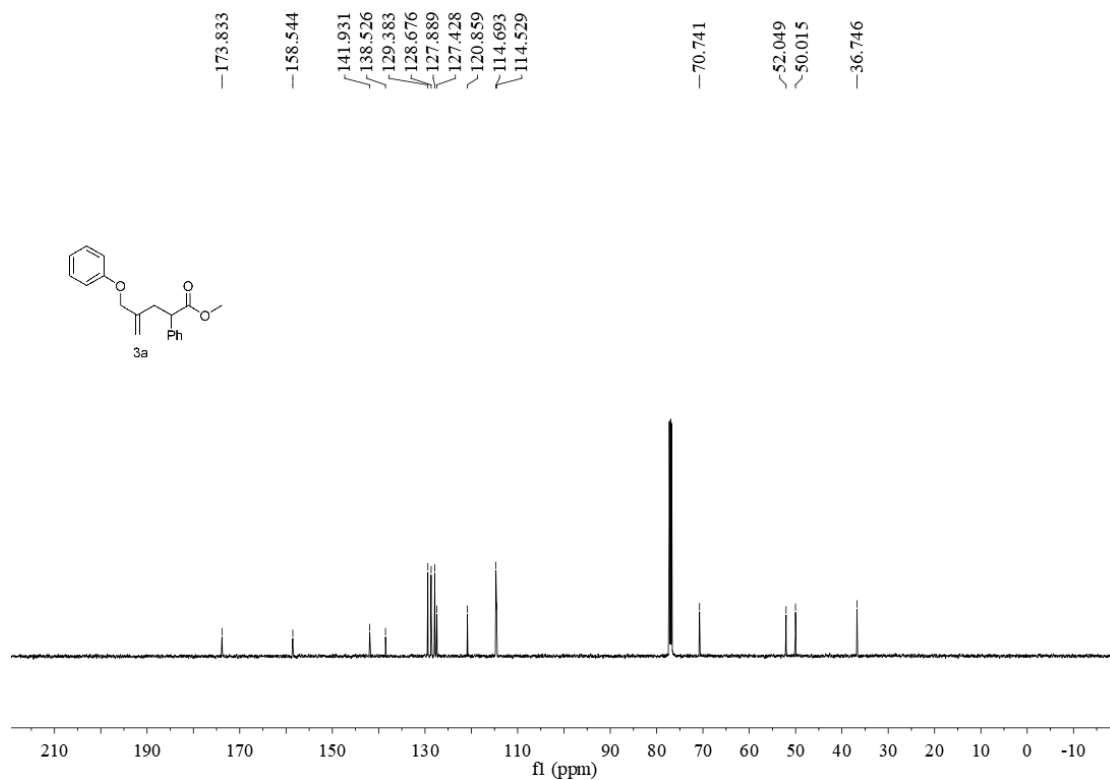
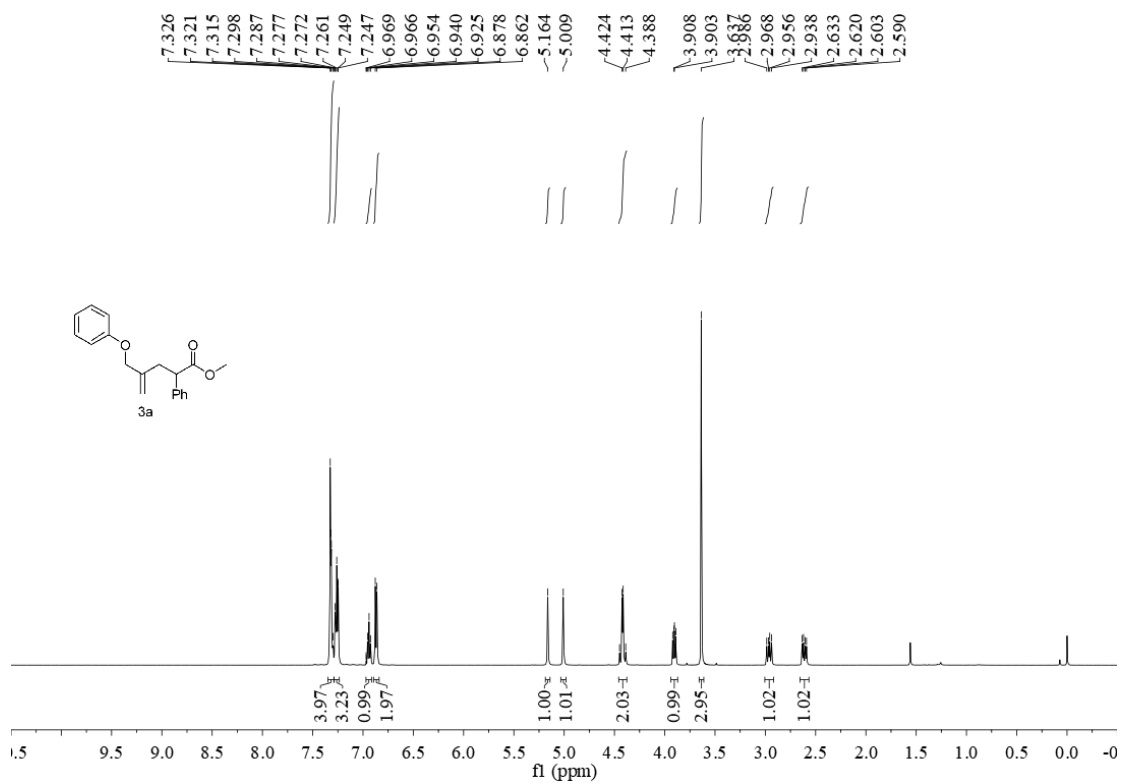


Table S1 Crystal data and structure refinement for **8**

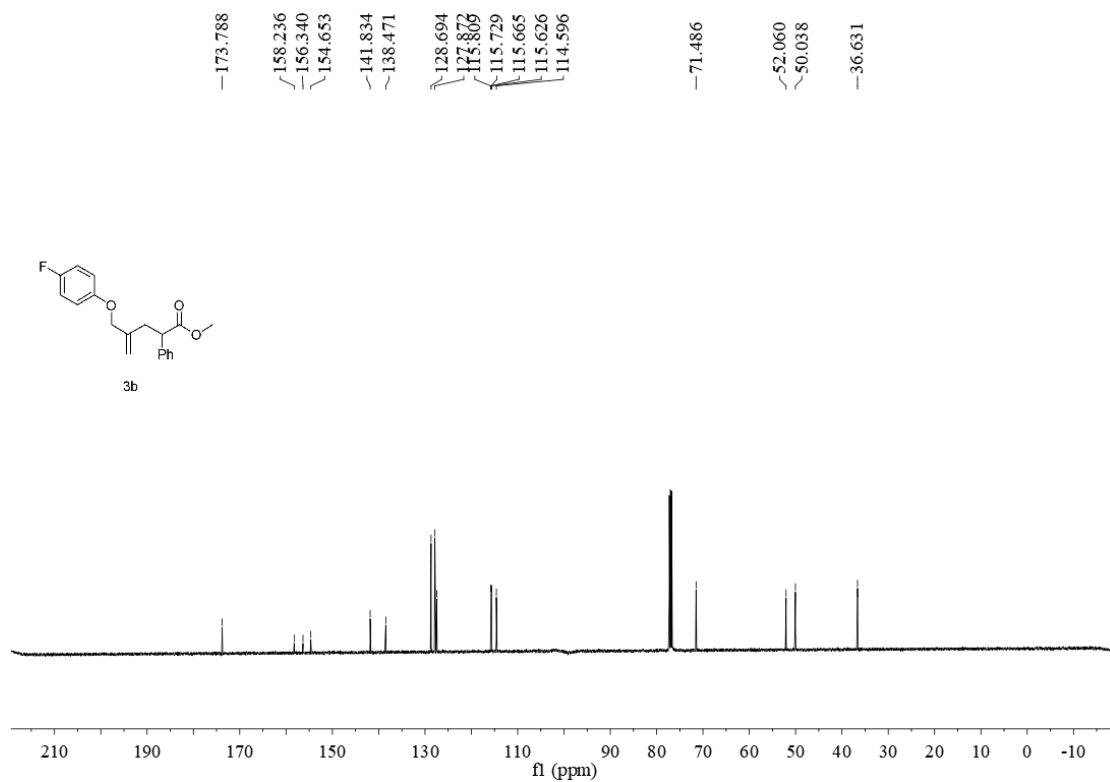
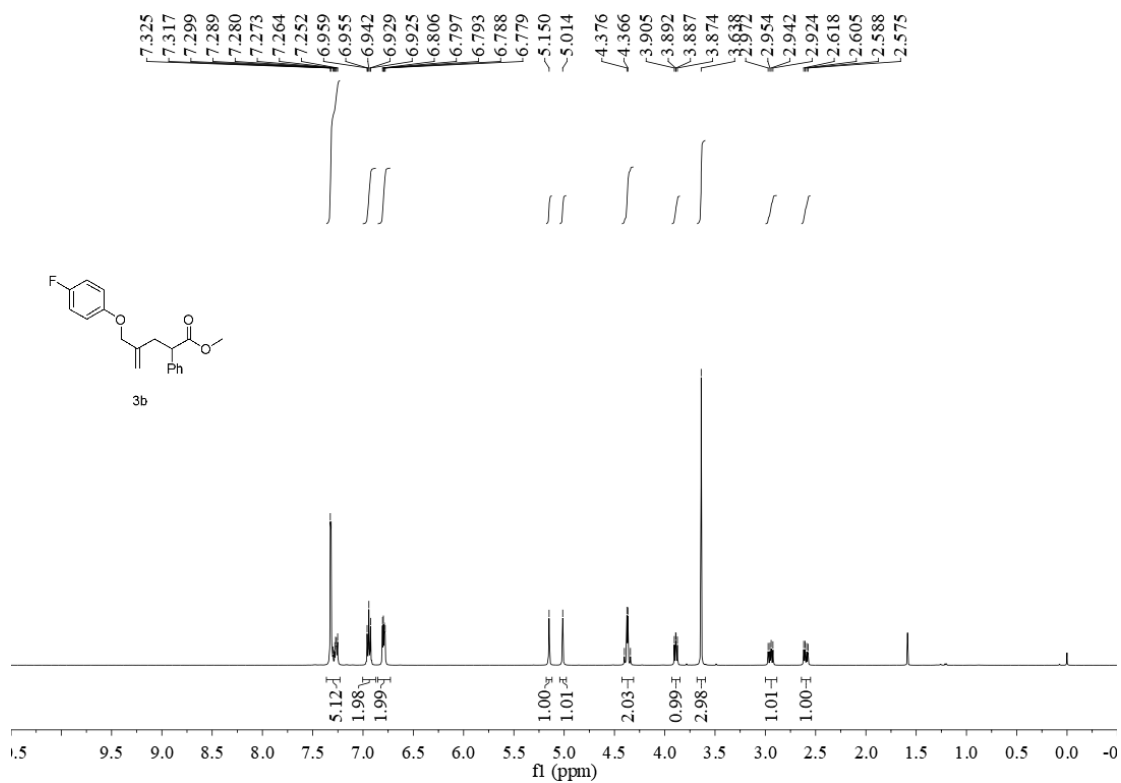
Empirical formula	C ₂₅ H ₂₂ BrNO ₄
Formula weight	466.33
Temperature/K	170(2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	5.772(3)
b/Å	17.482(10)
c/Å	21.743(12)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	2194(2)
Z	4
ρ _{calc} /cm ³	1.412
μ/mm ⁻¹	1.902
F(000)	956.0
Crystal size/mm ³	0.18 × 0.12 × 0.06
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.412 to 50.236
Index ranges	-6 ≤ h ≤ 6, -18 ≤ k ≤ 20, -23 ≤ l ≤ 25
Reflections collected	9178
Independent reflections	3787 [R _{int} = 0.1828, R _{sigma} = 0.2797]
Data/restraints/parameters	3787/21/273
Goodness-of-fit on F ²	0.985
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0919, wR ₂ = 0.1836
Final R indexes [all data]	R ₁ = 0.2435, wR ₂ = 0.2669
Largest diff. peak/hole / e Å ⁻³	0.61/-0.57
Flack parameter	0.47(2)

VI. NMR Spectrum

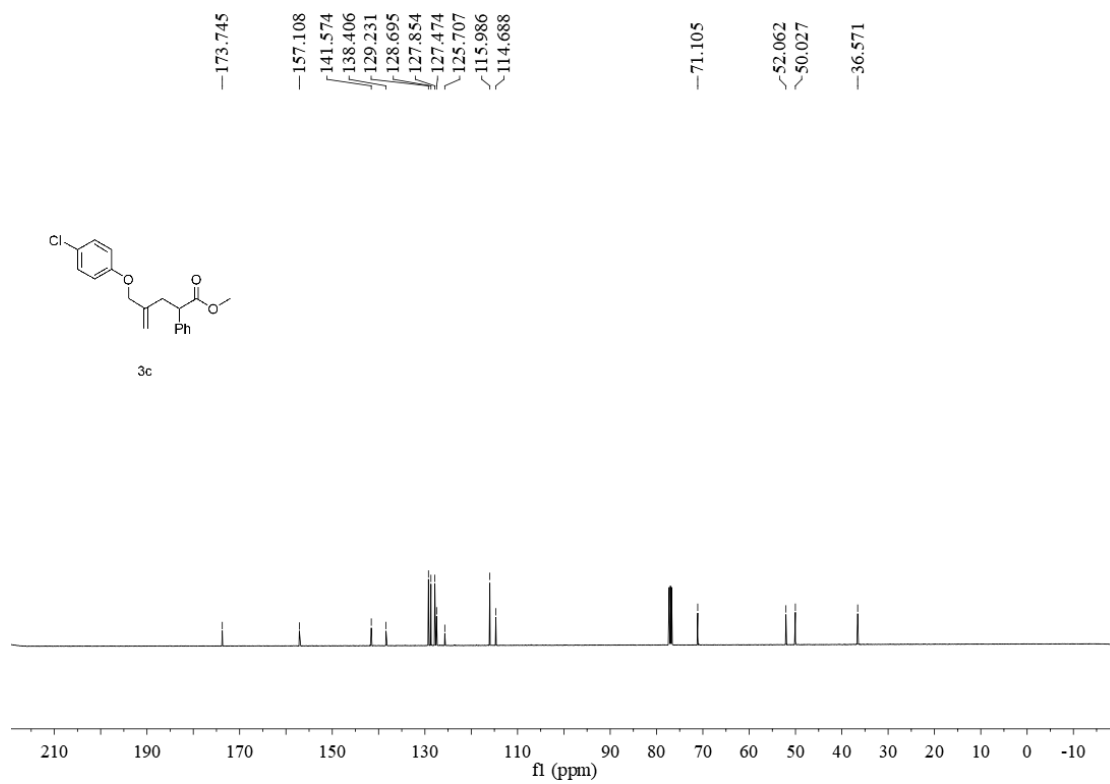
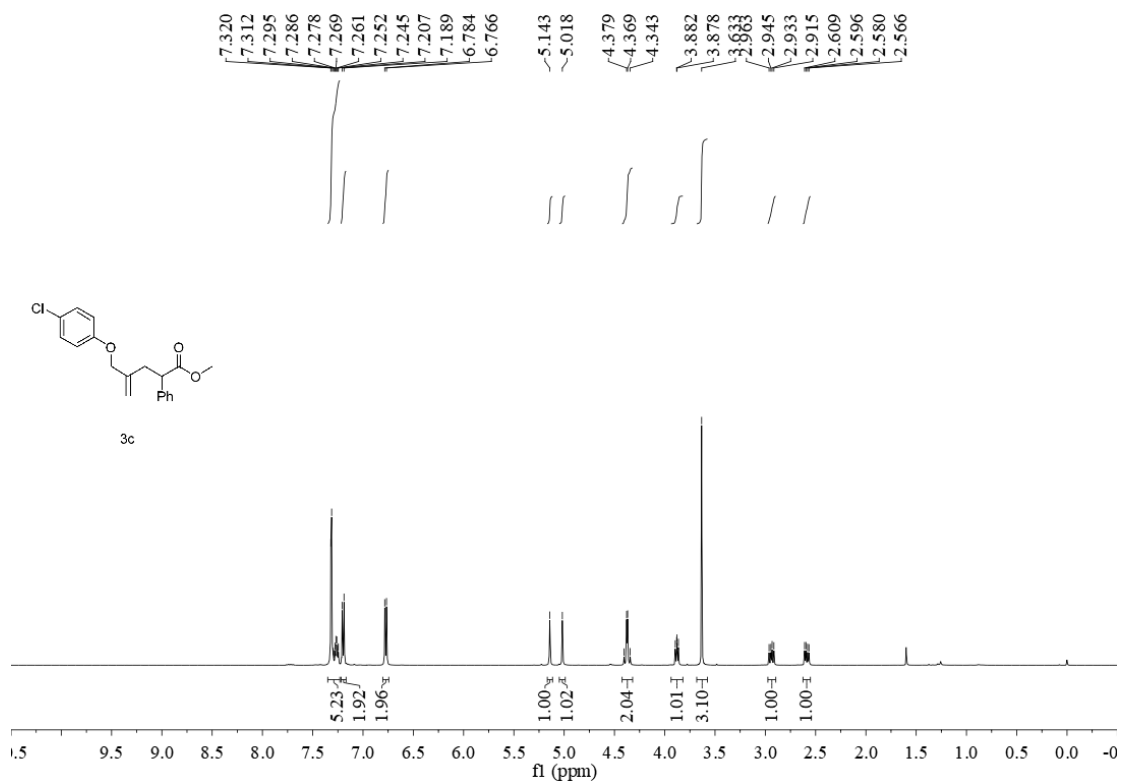
3a:



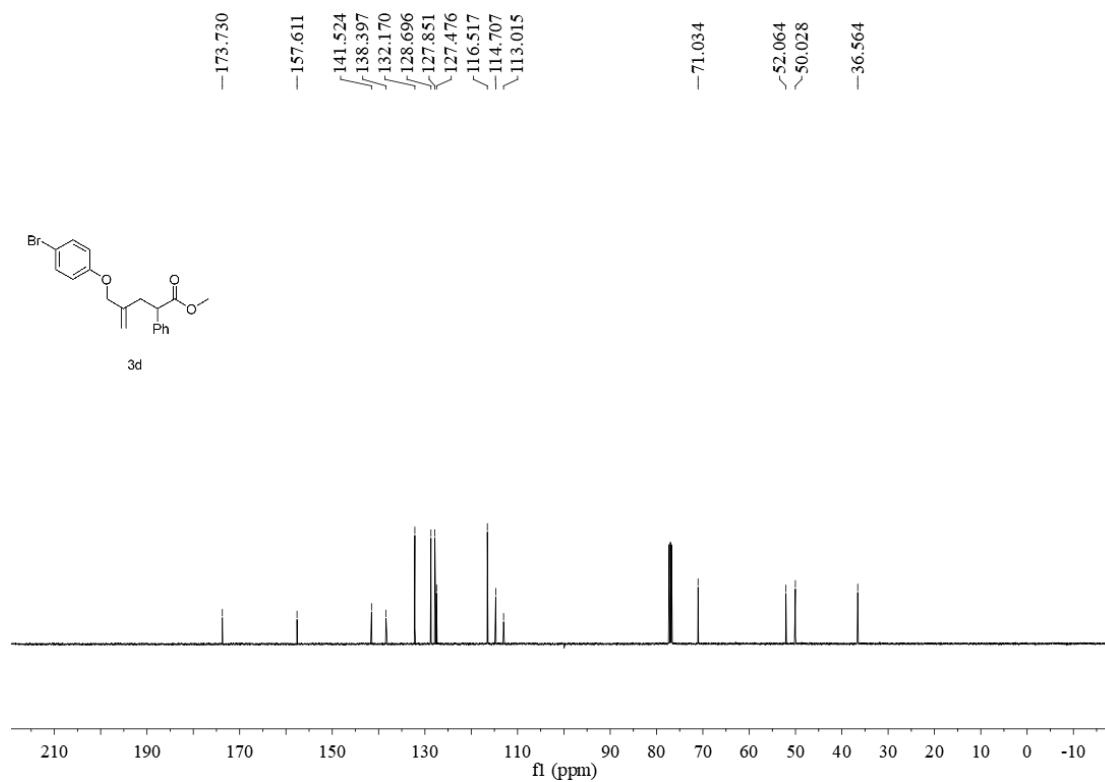
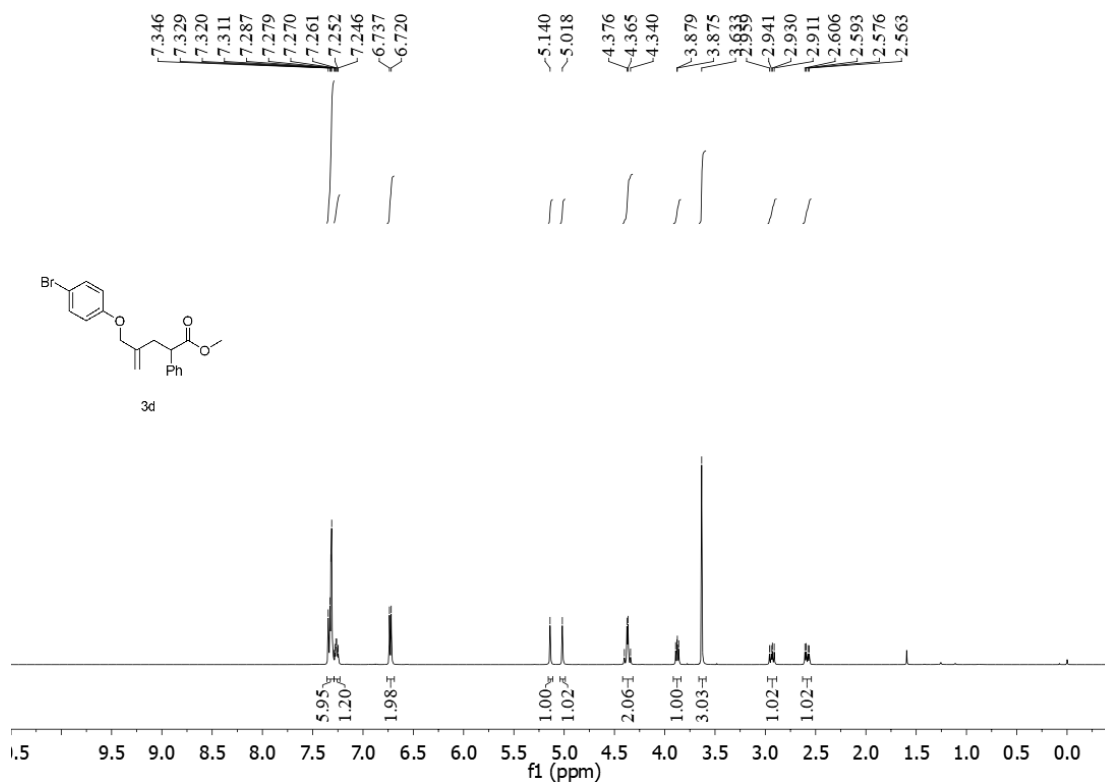
3b:



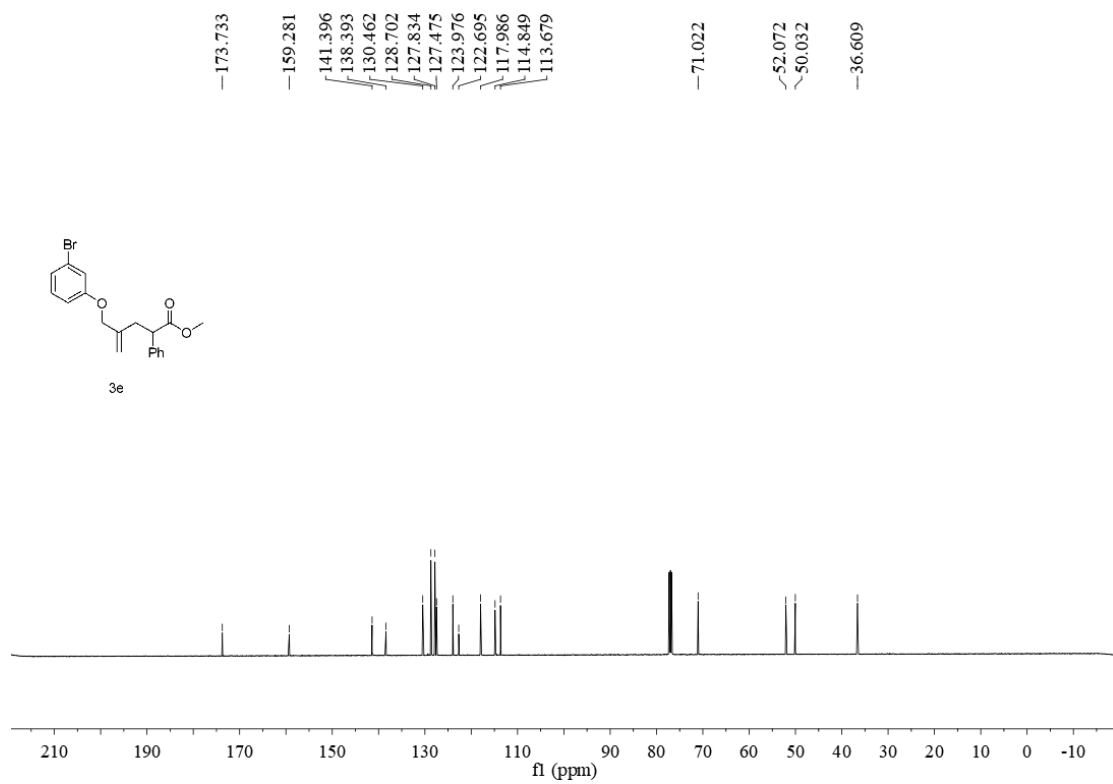
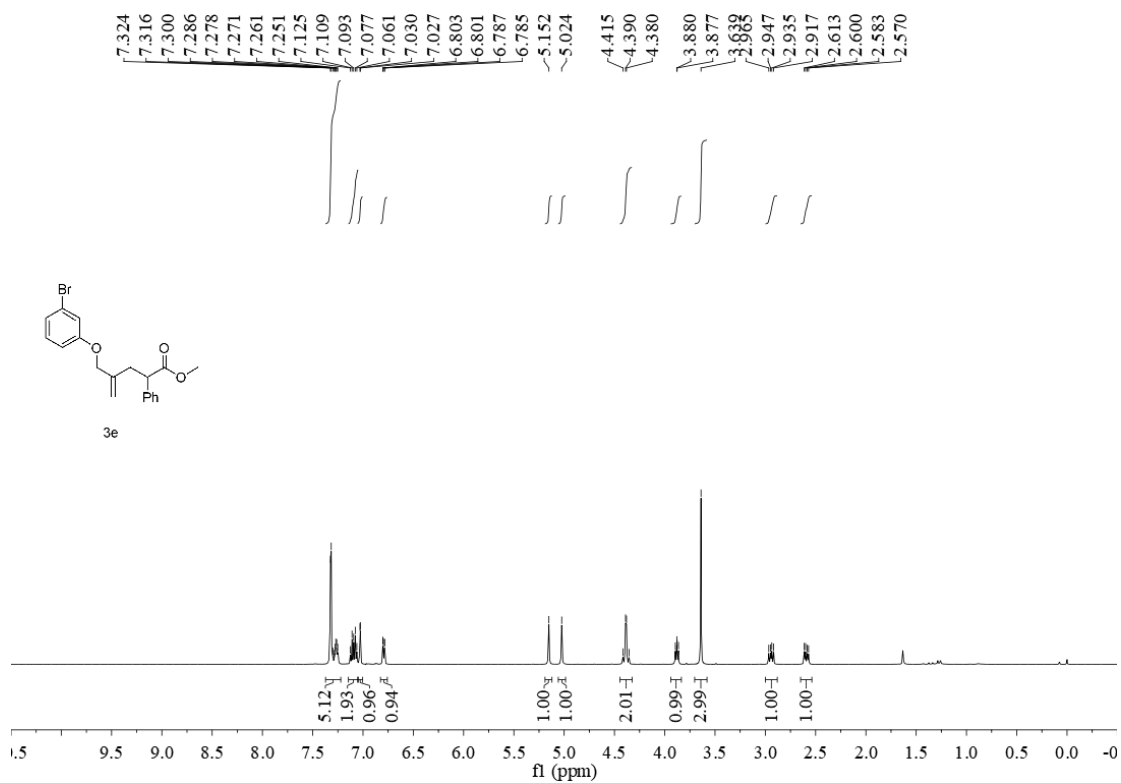
3c:



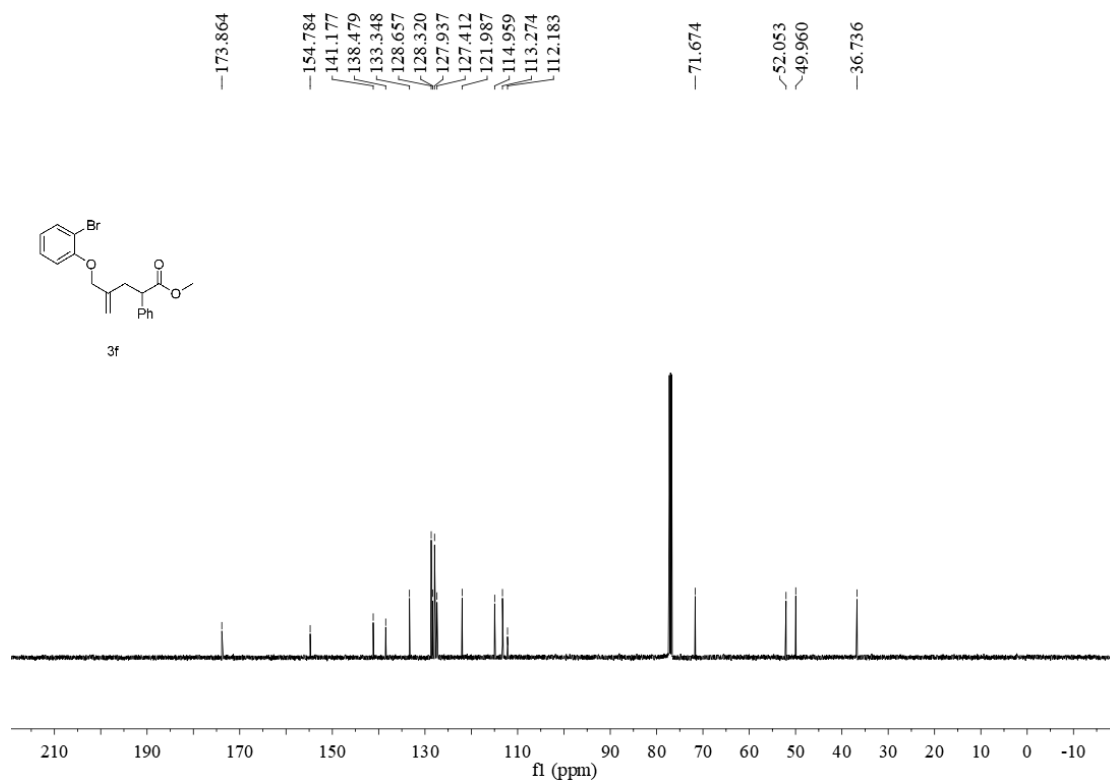
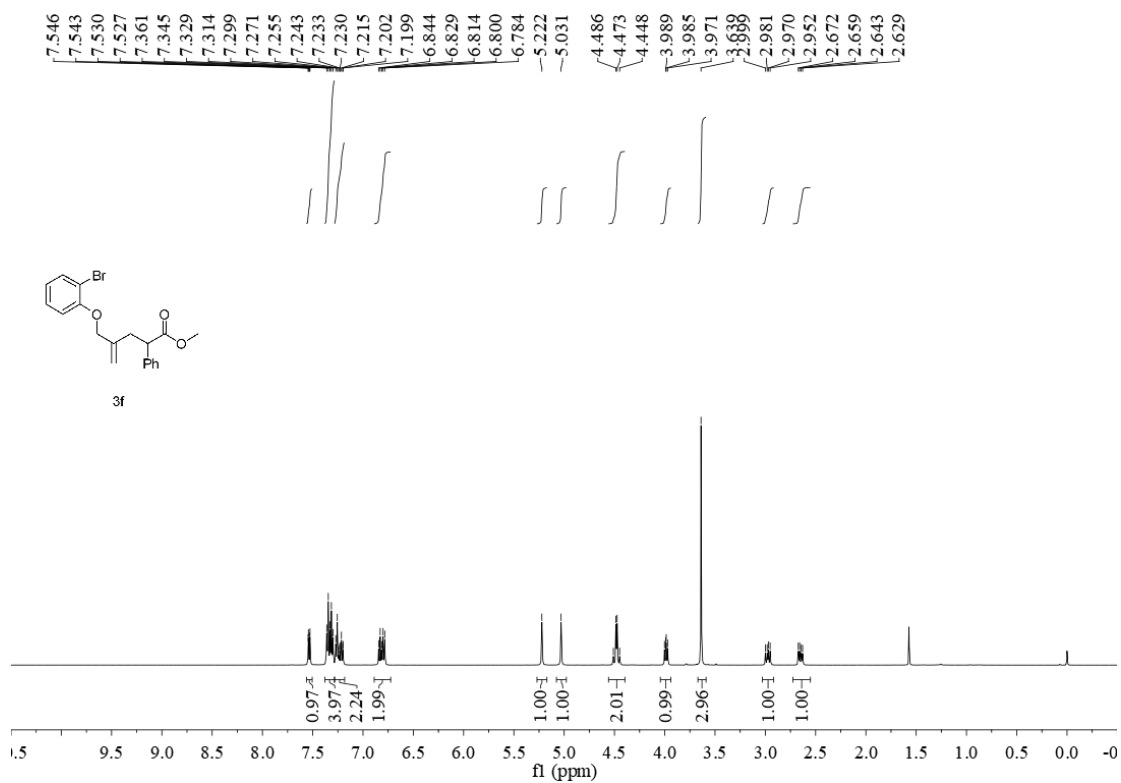
3d:



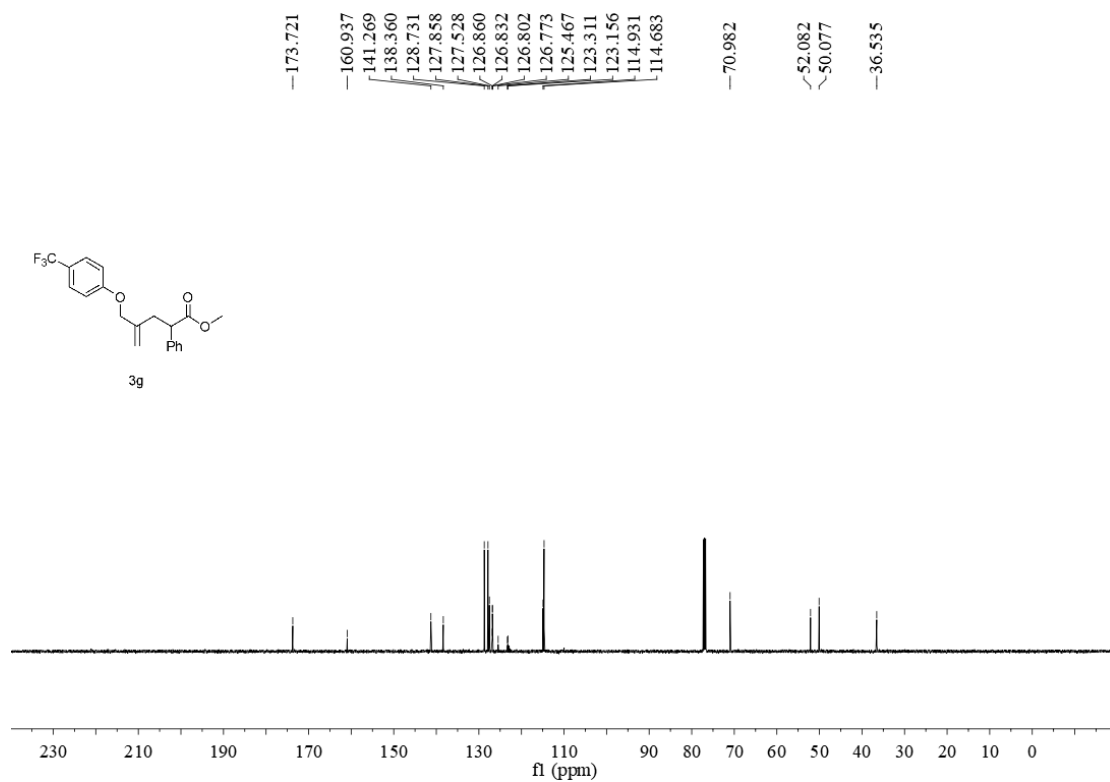
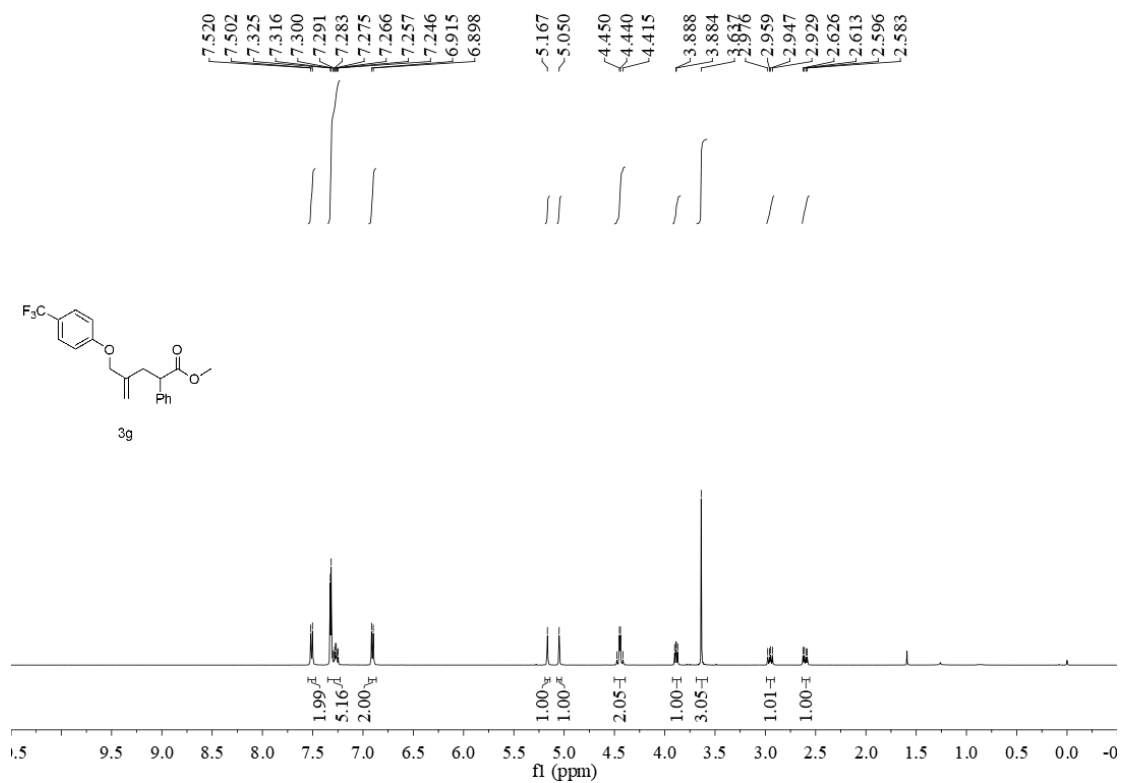
3e:



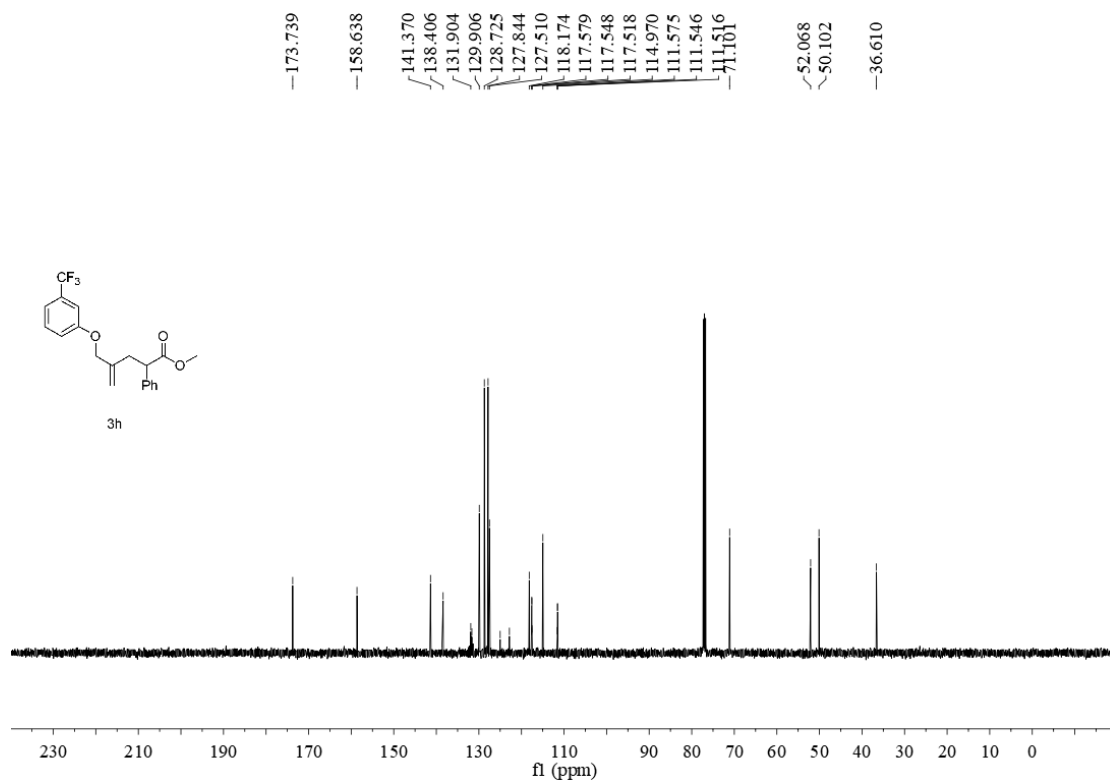
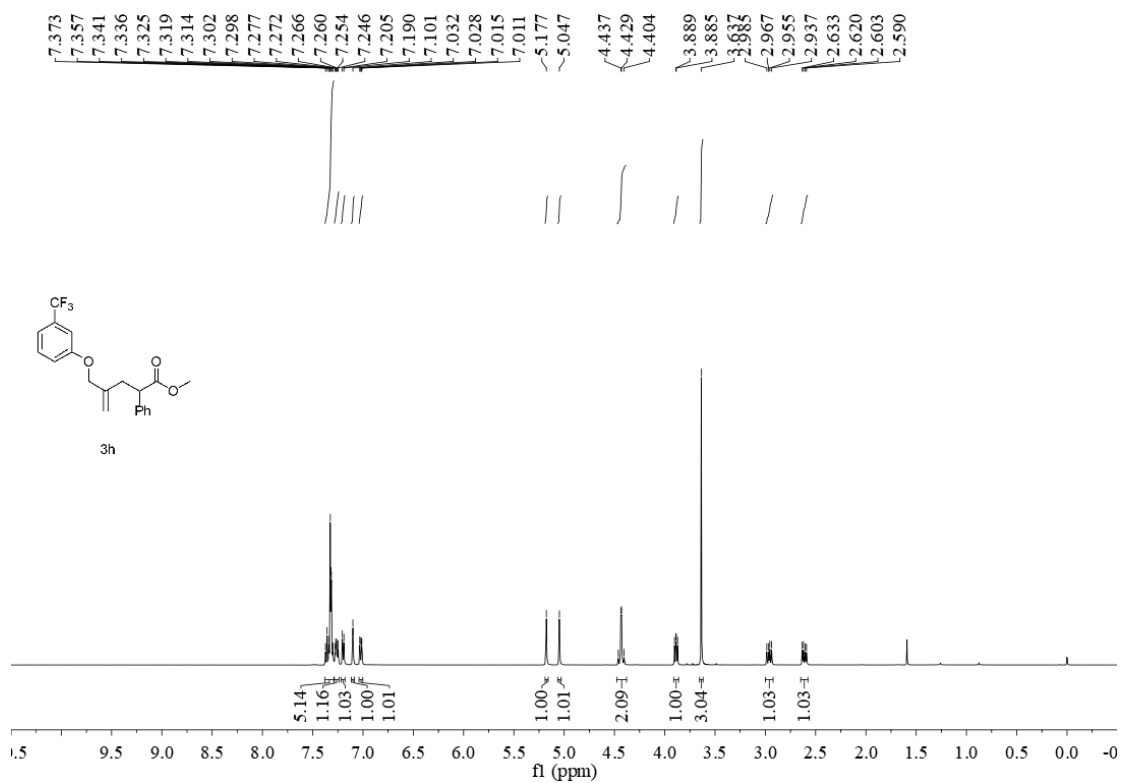
3f:



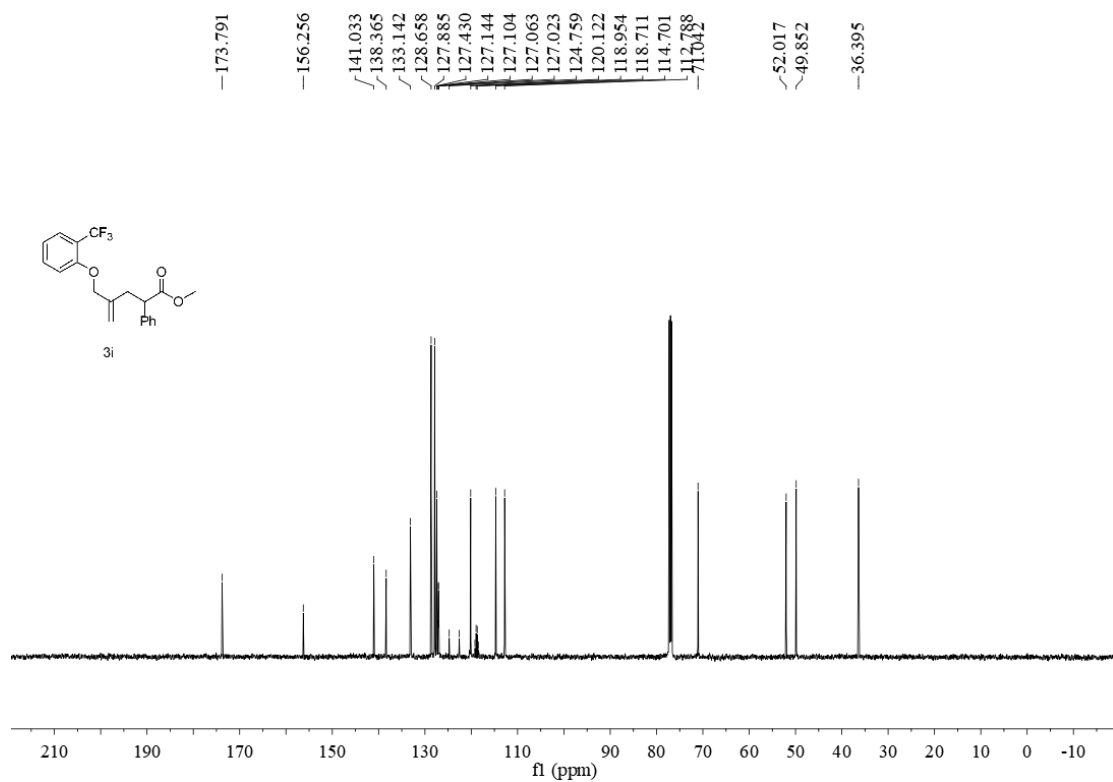
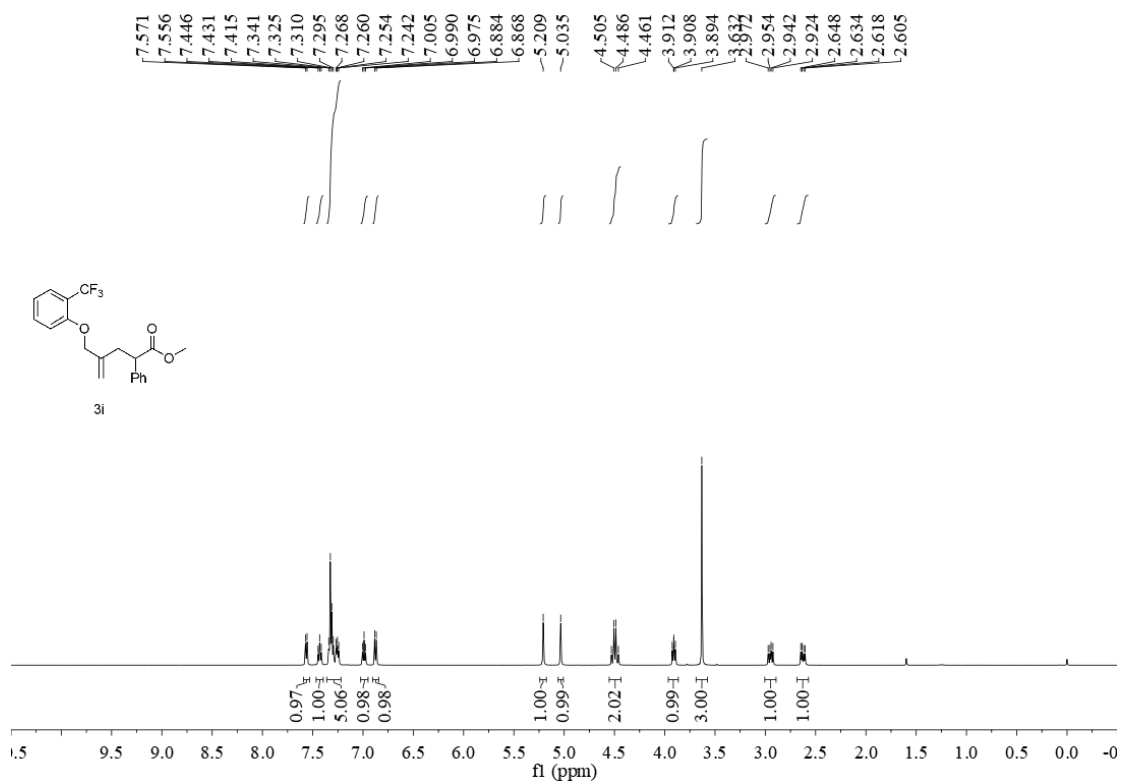
3g:



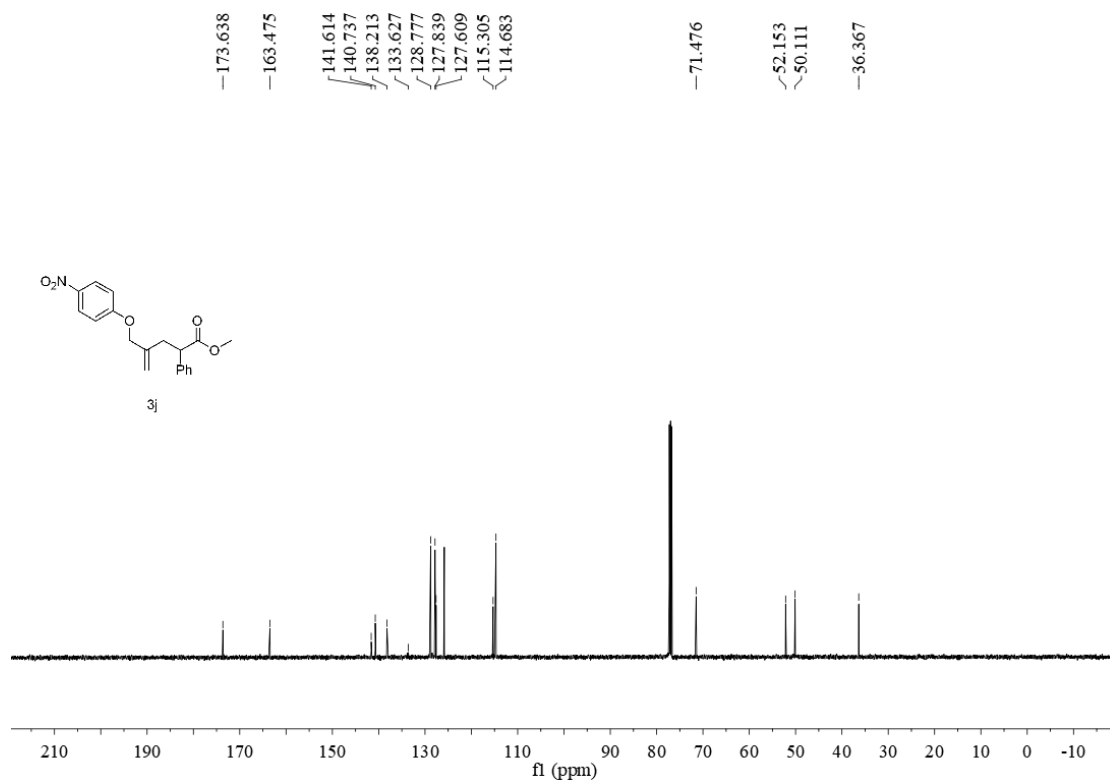
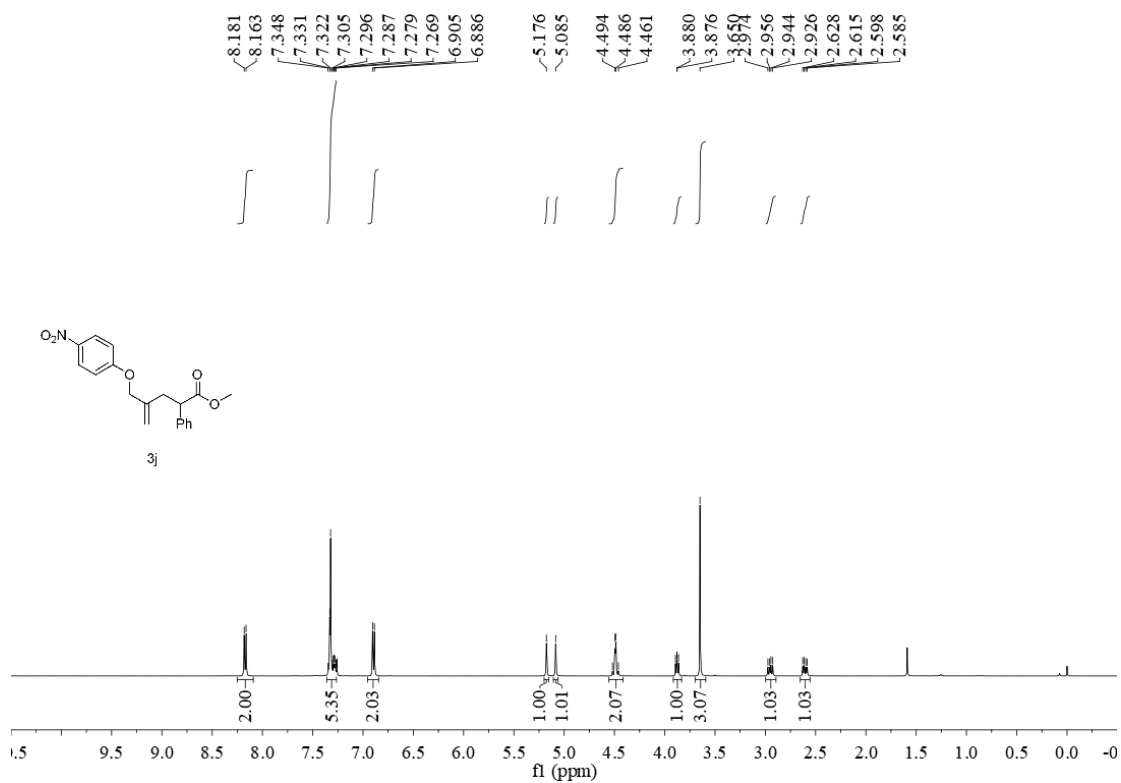
3h:



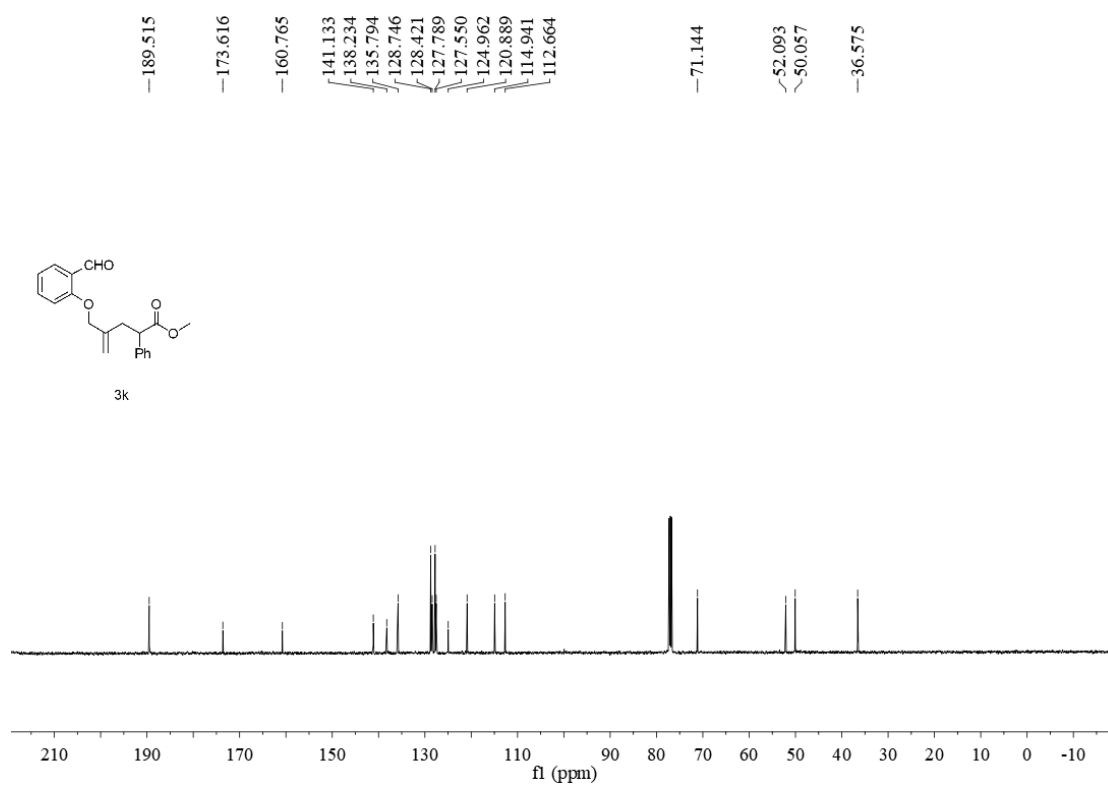
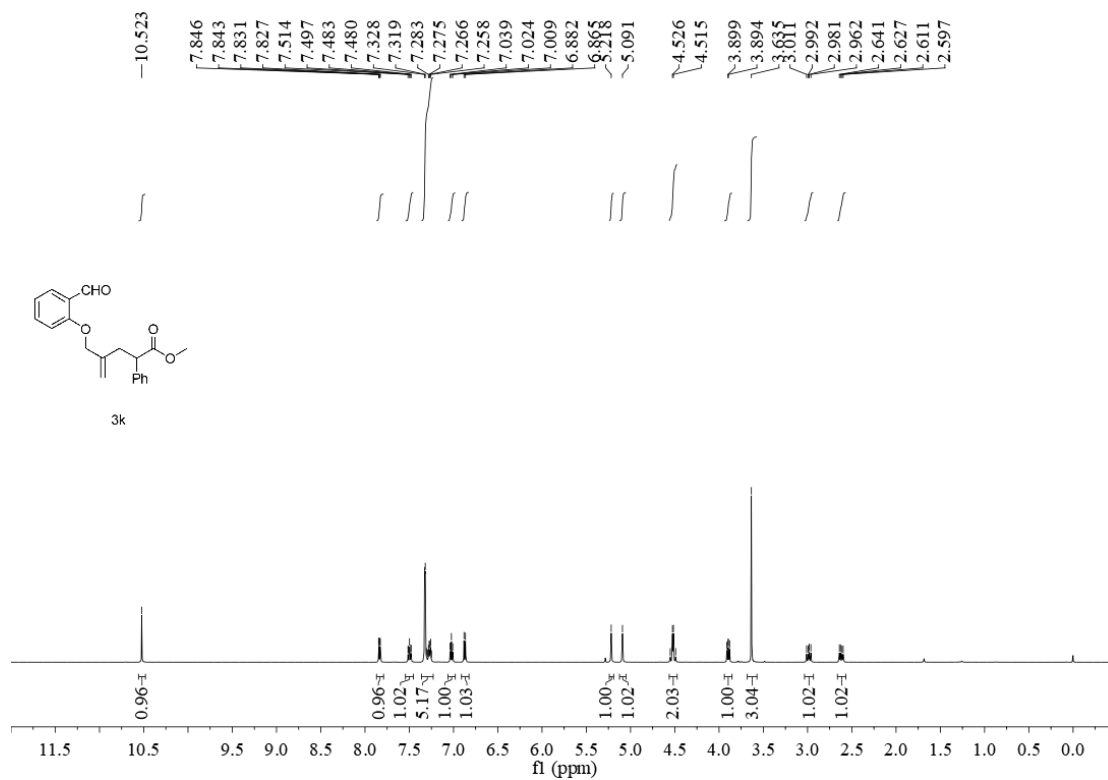
3i:



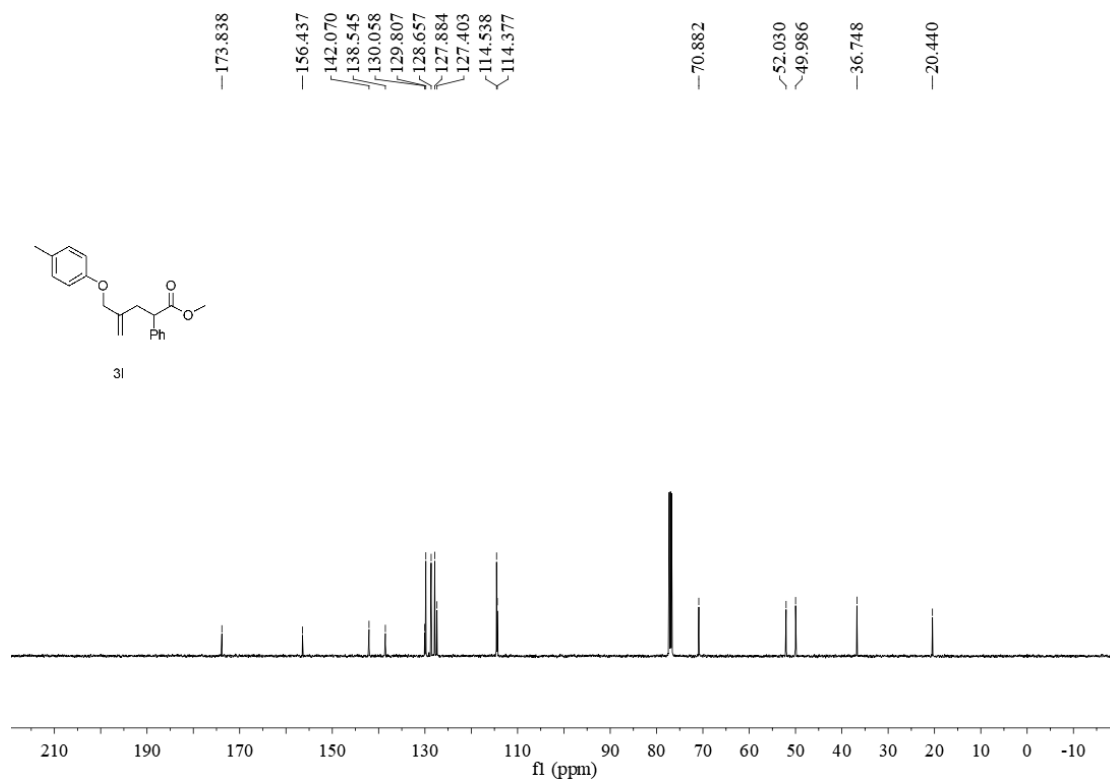
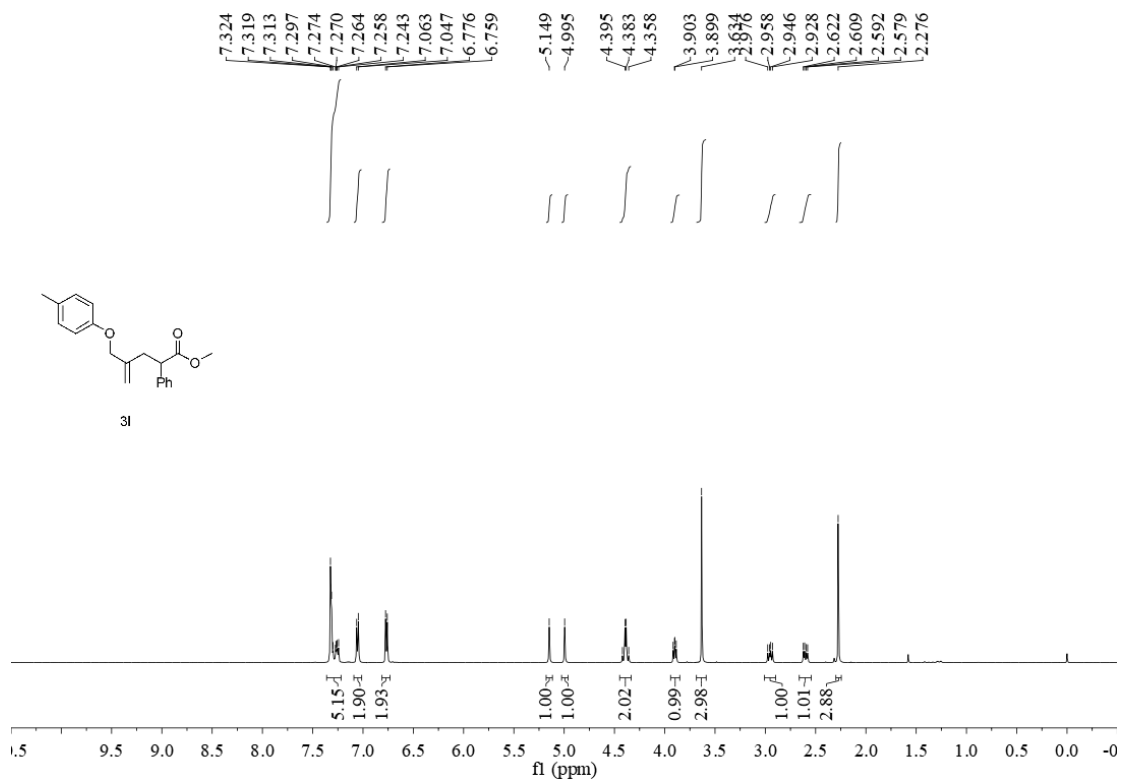
3j:



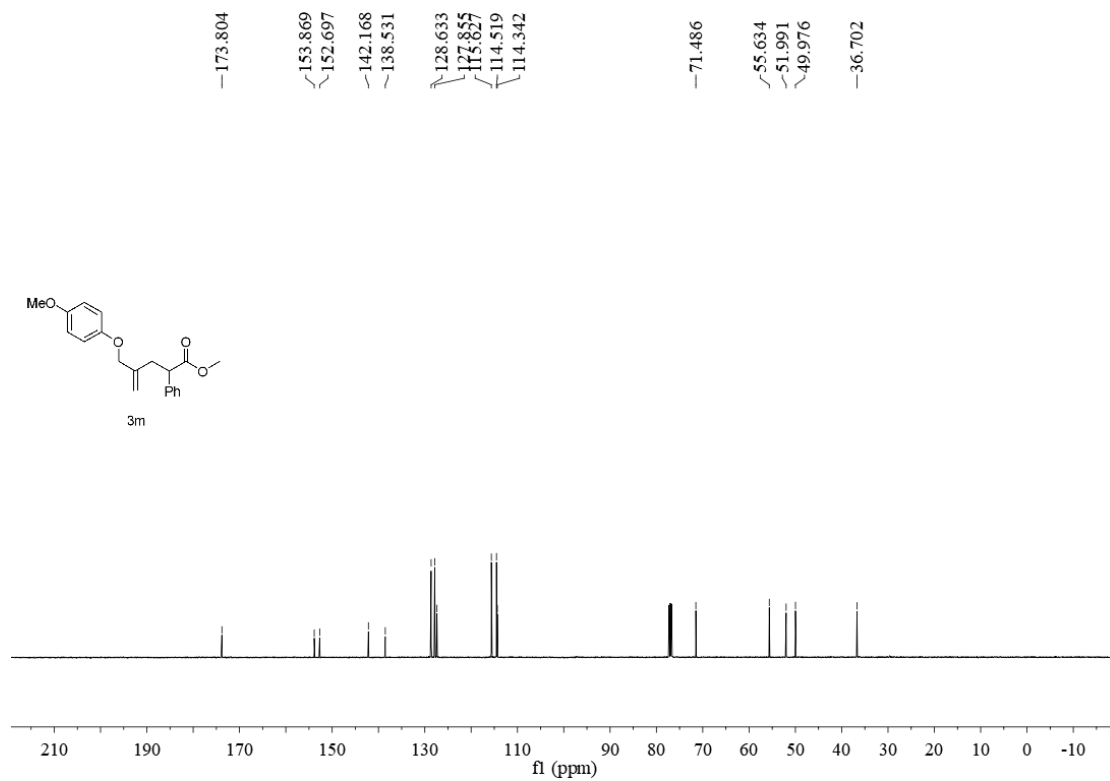
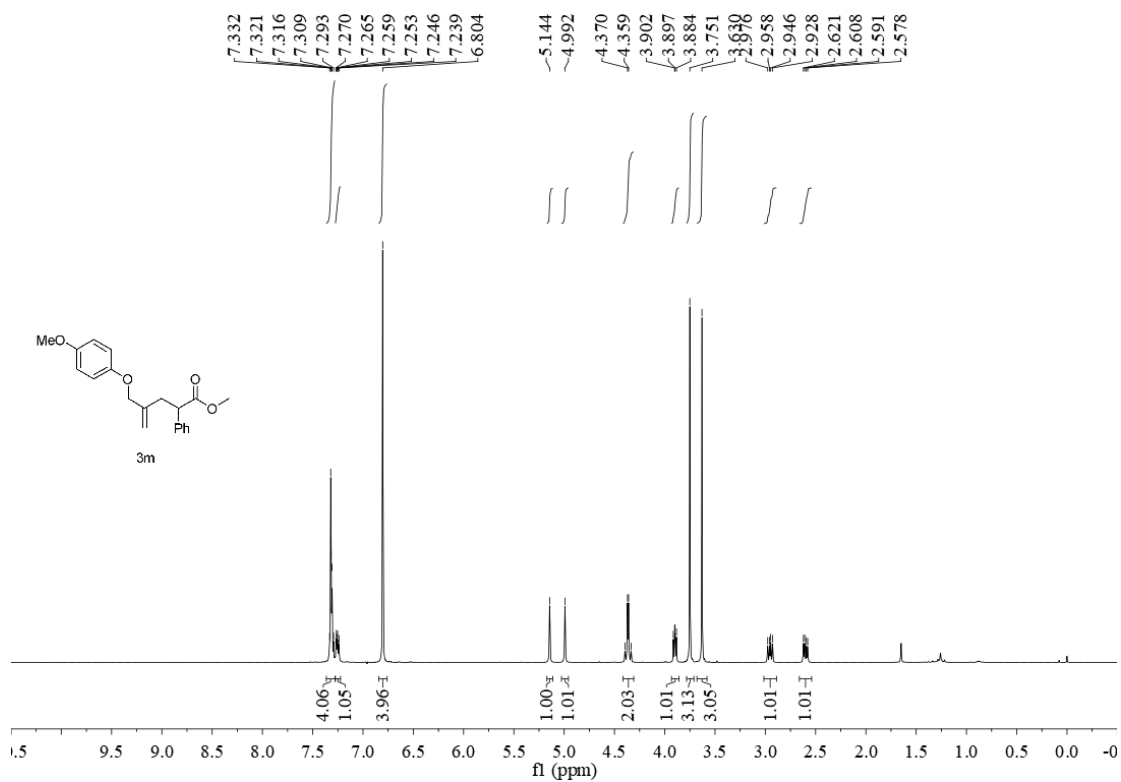
3k:



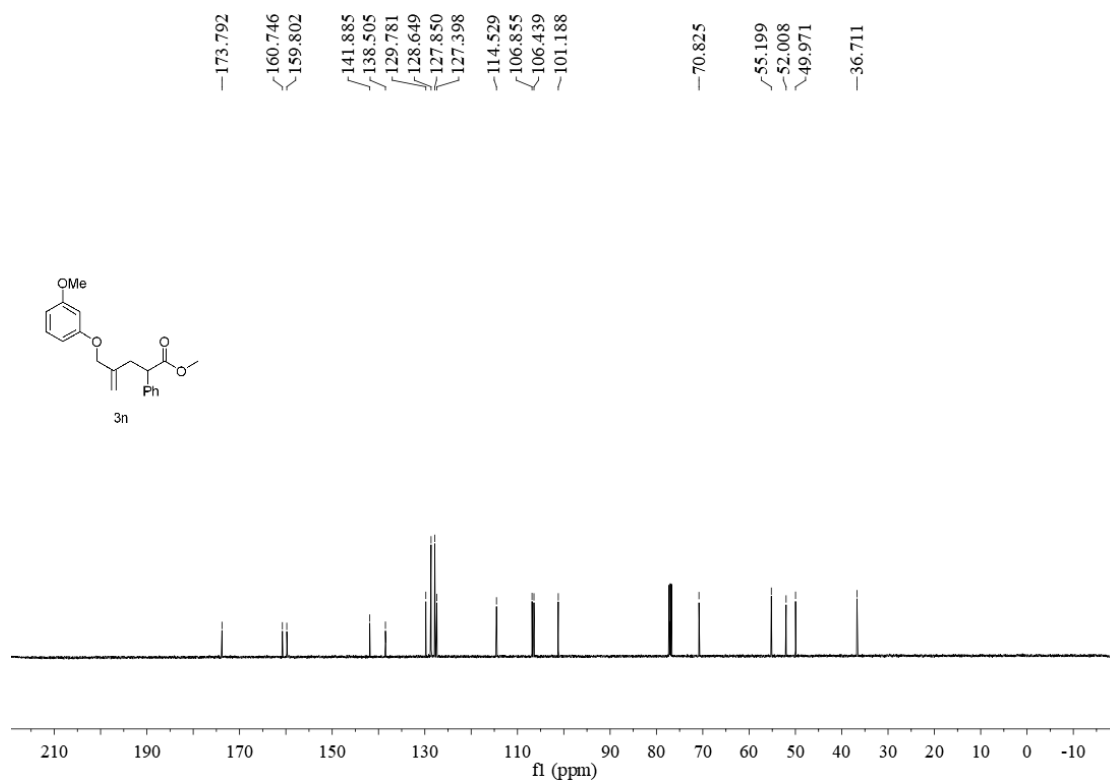
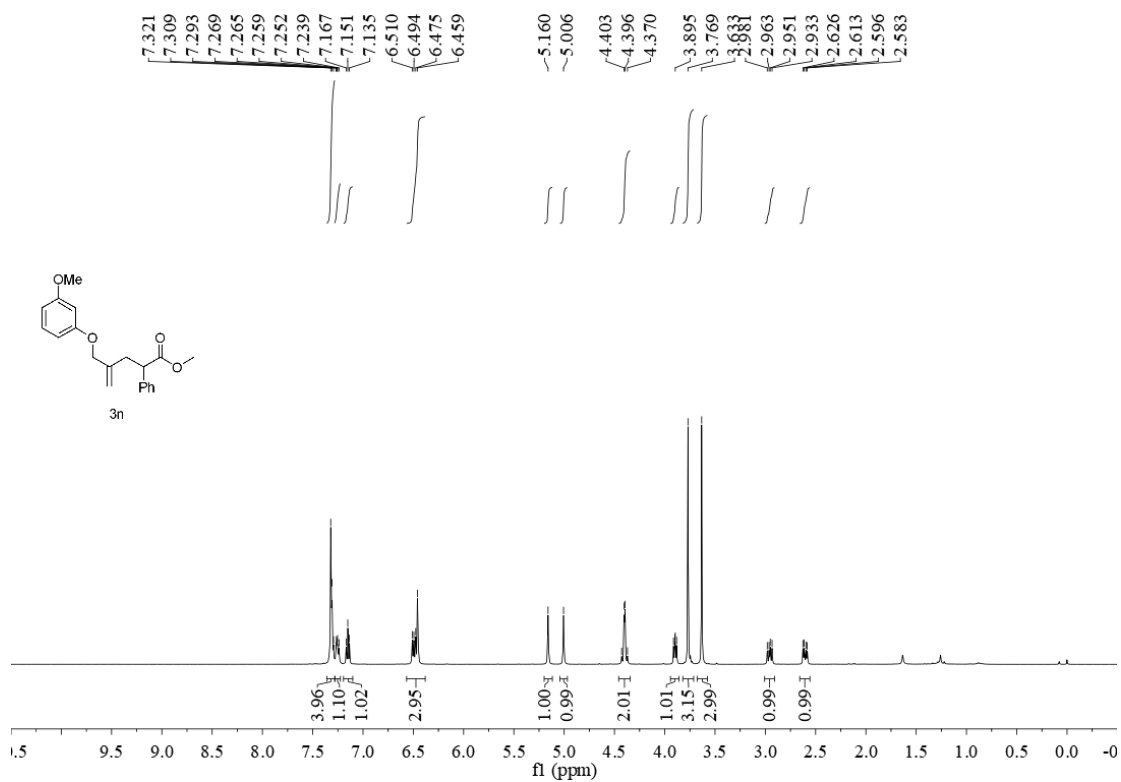
3l:



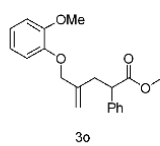
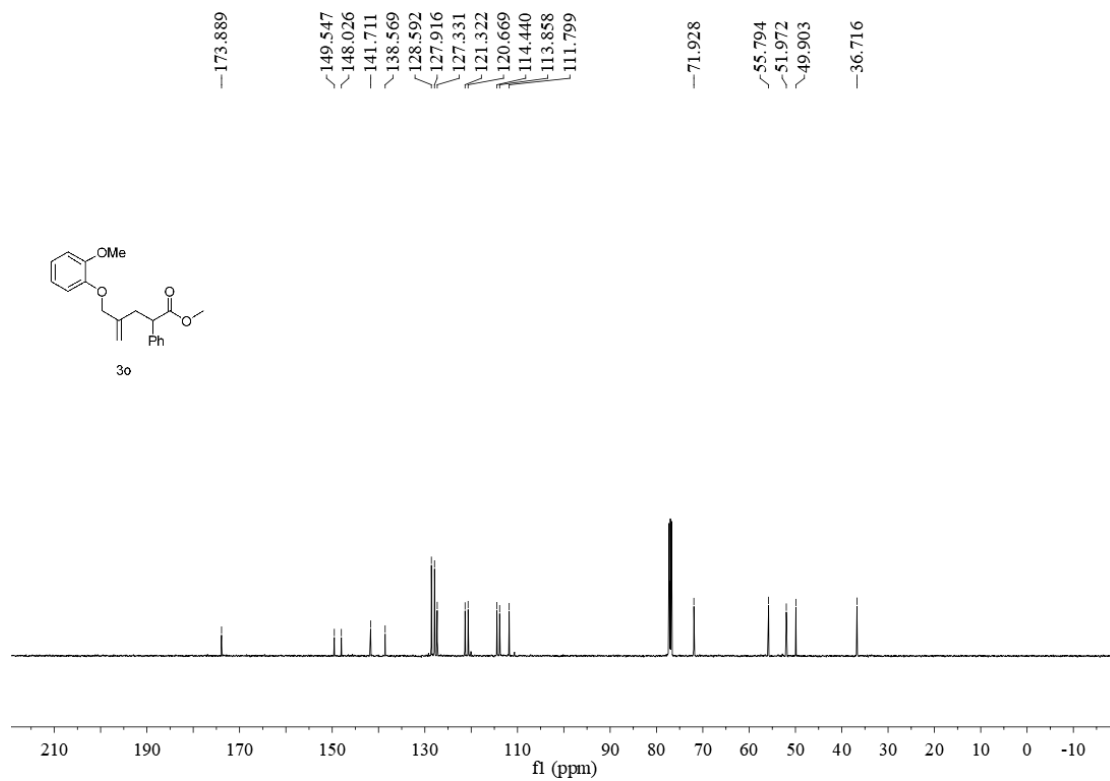
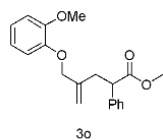
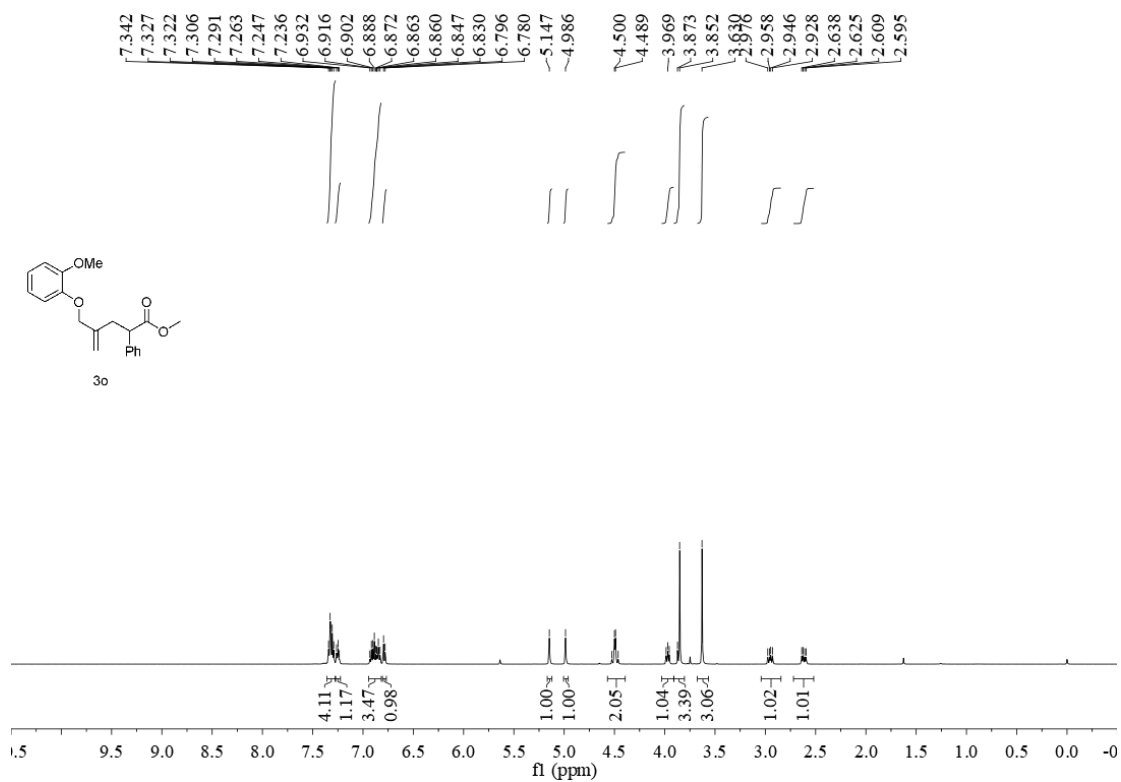
3m:



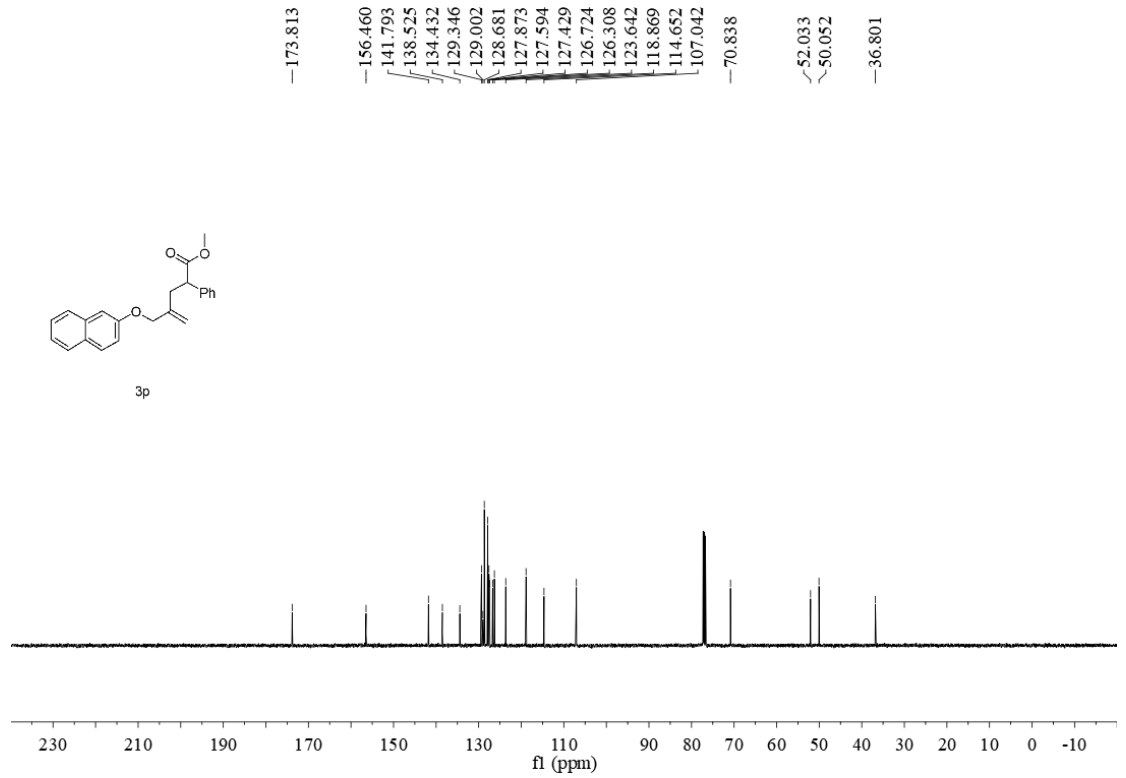
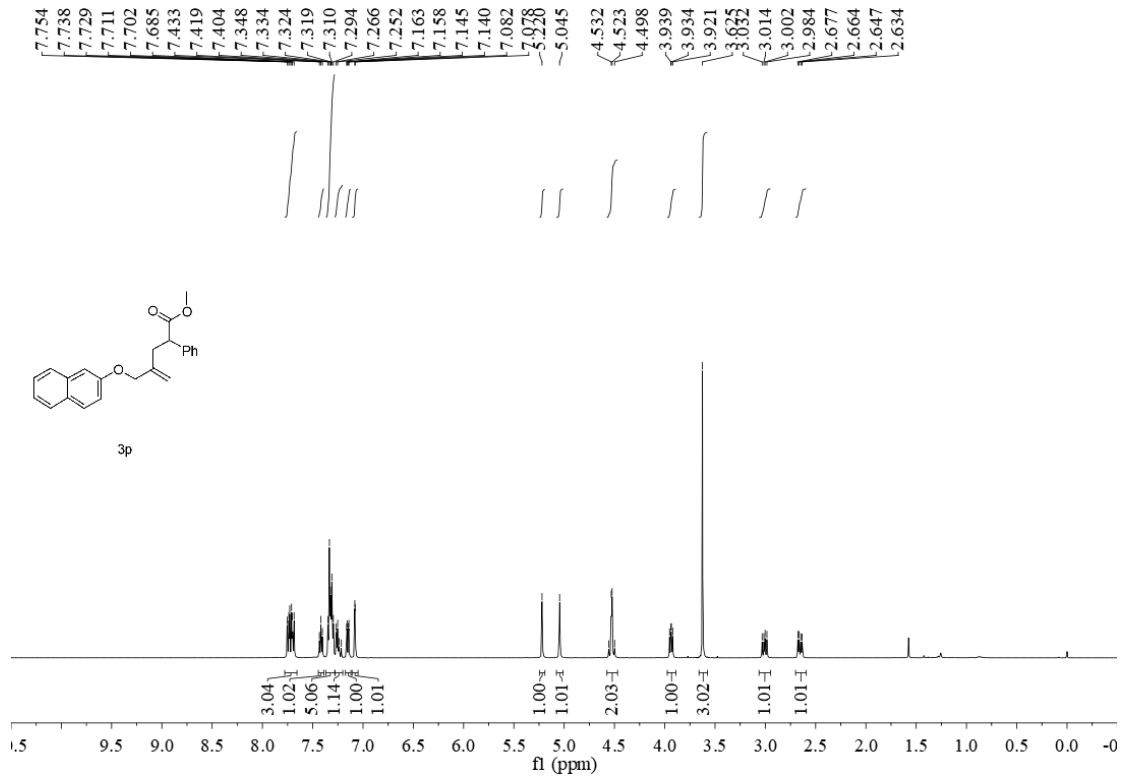
3n:



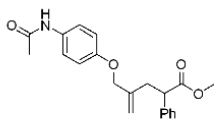
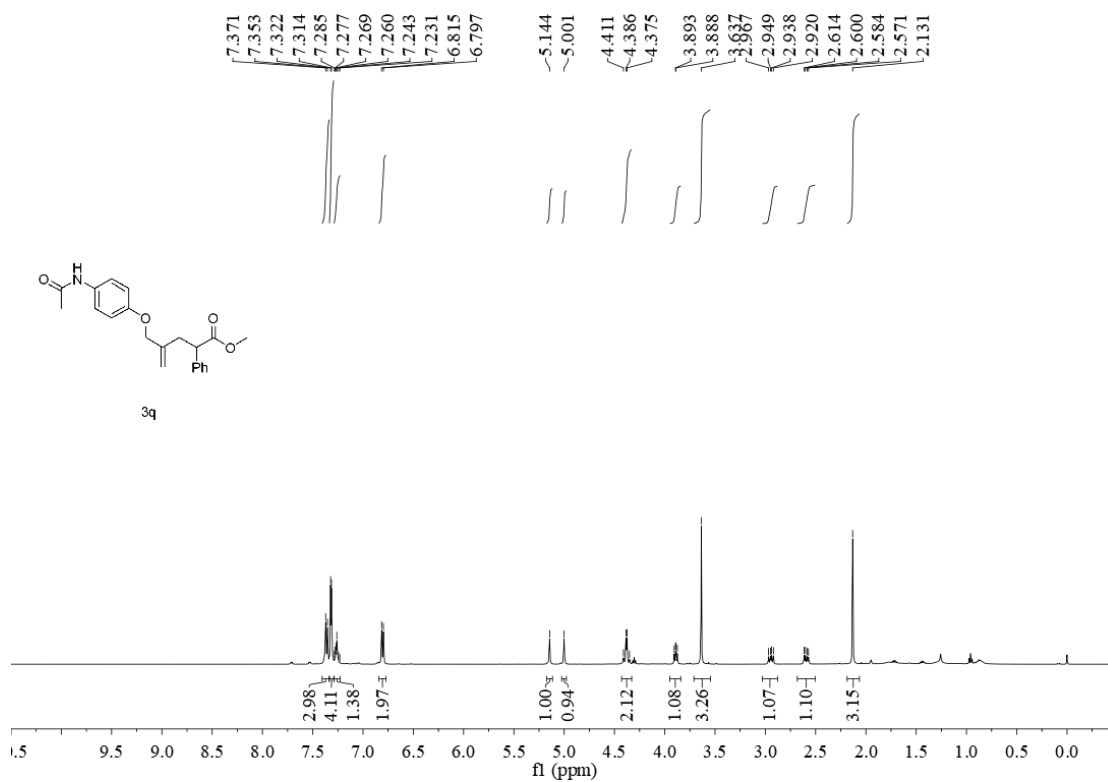
30:



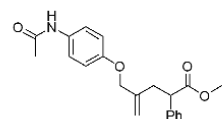
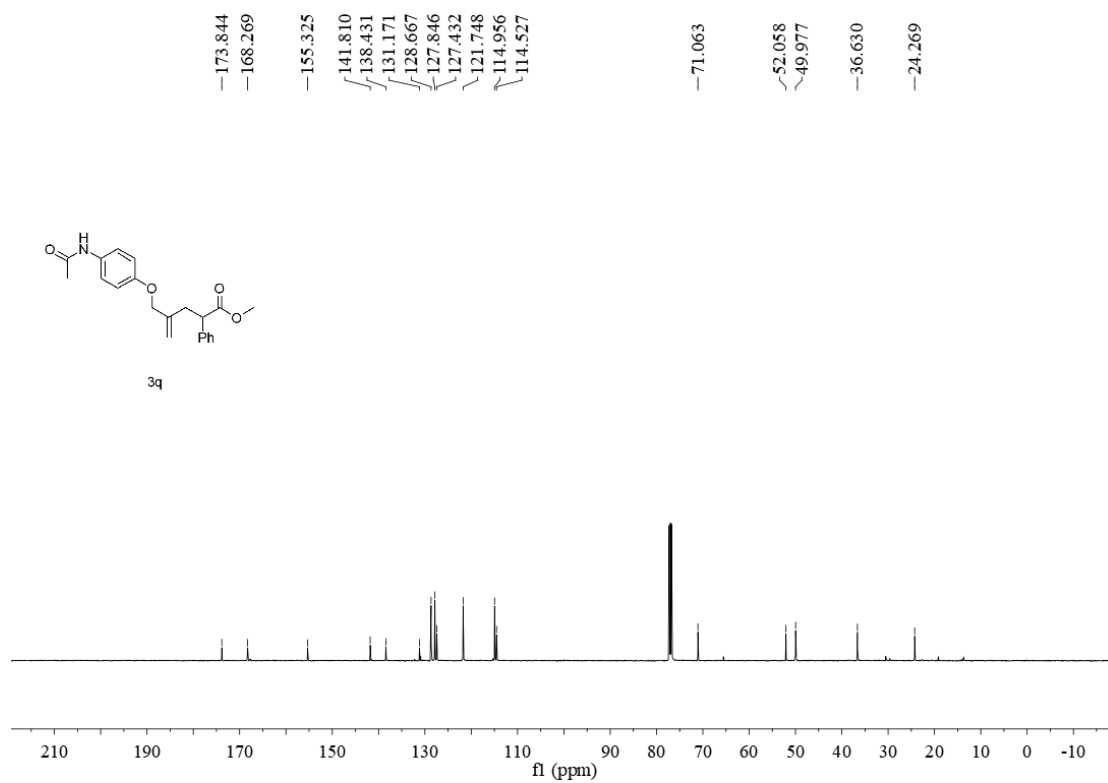
3p:



3q:

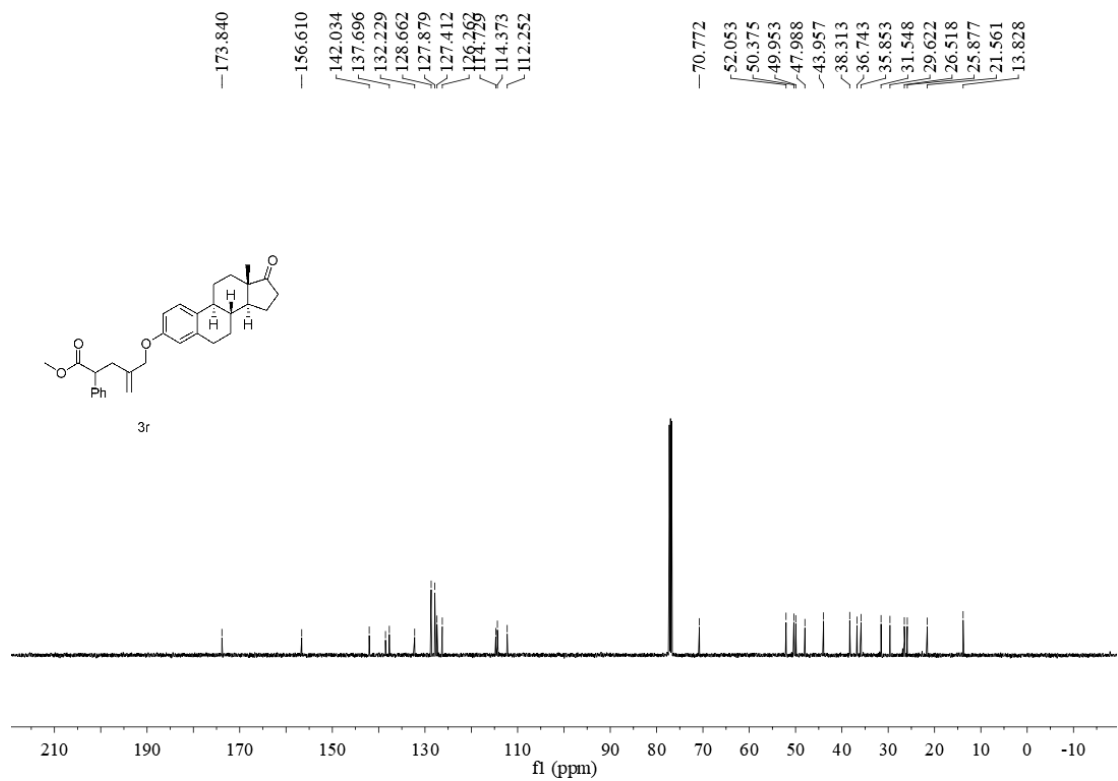
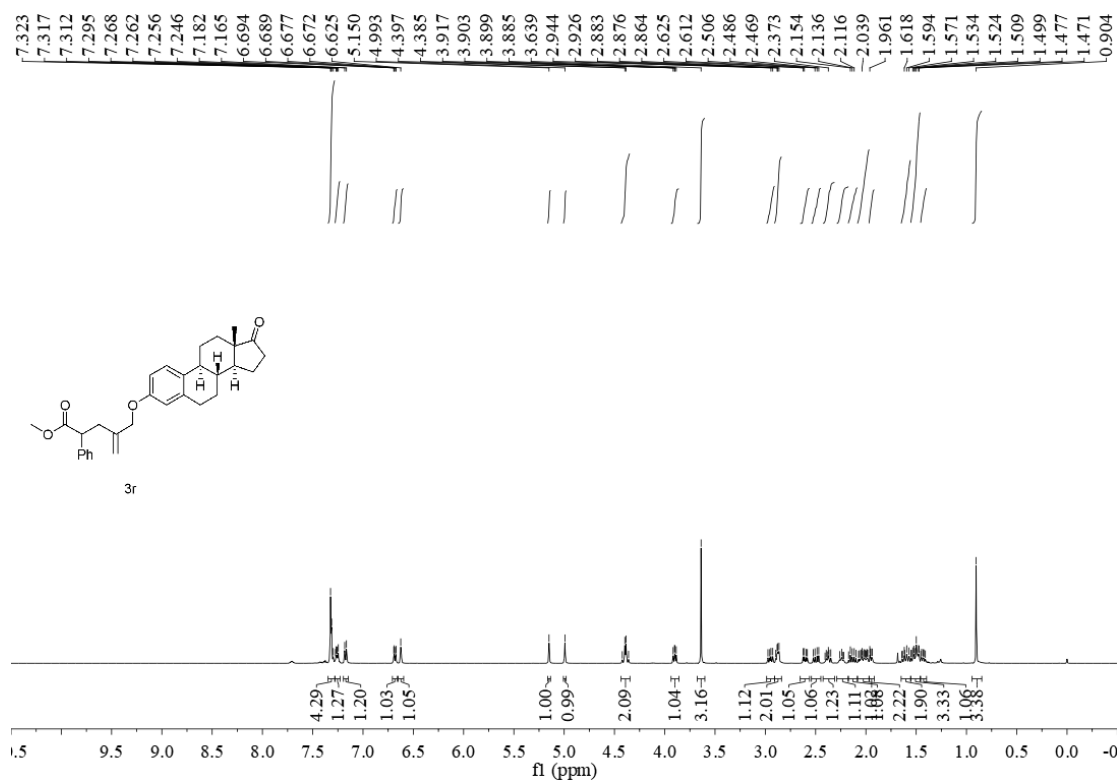


3q

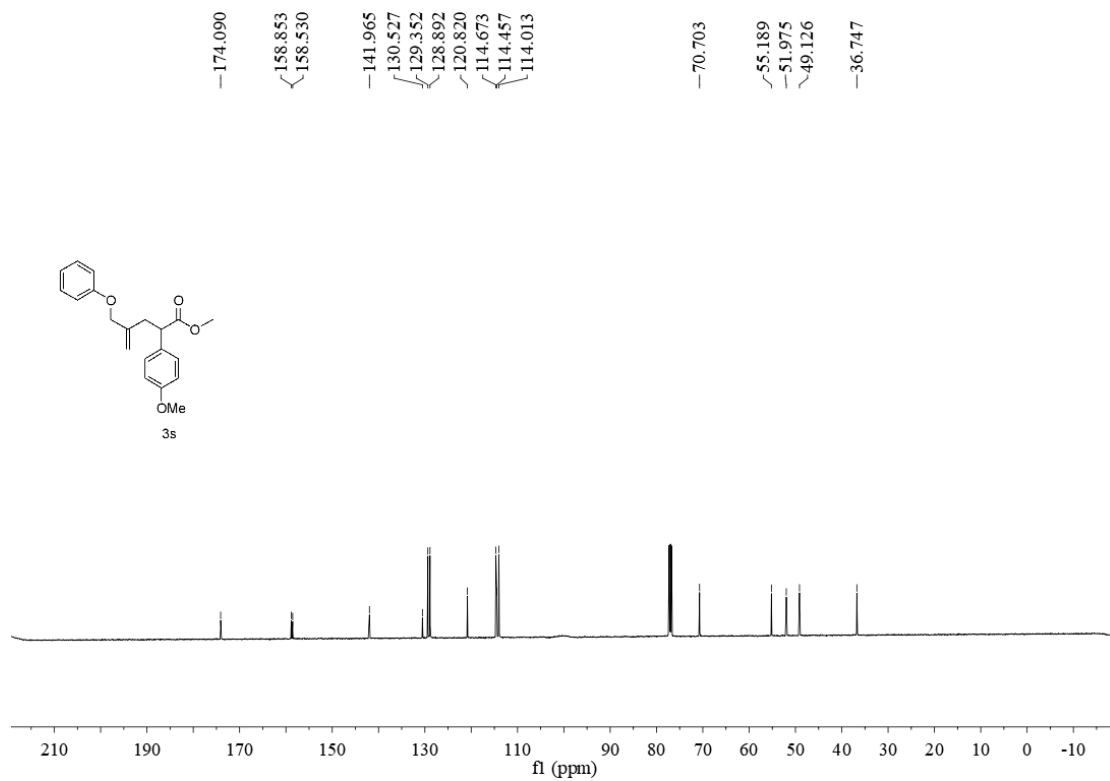
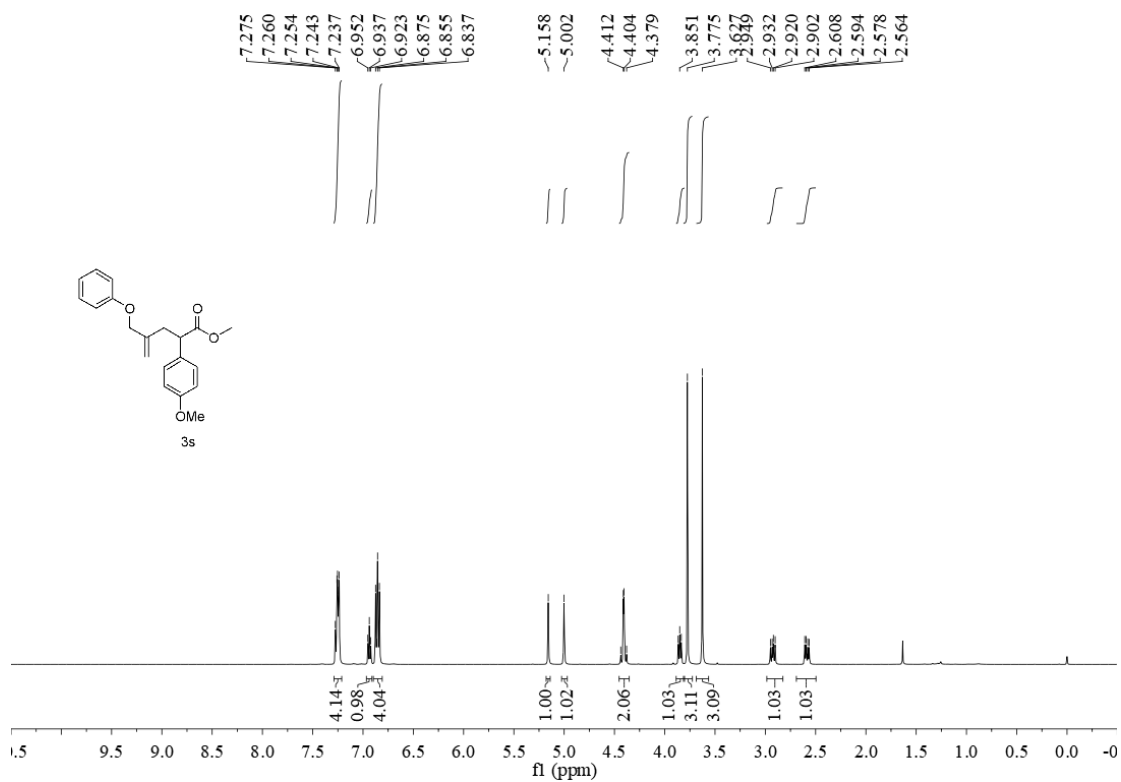


3q

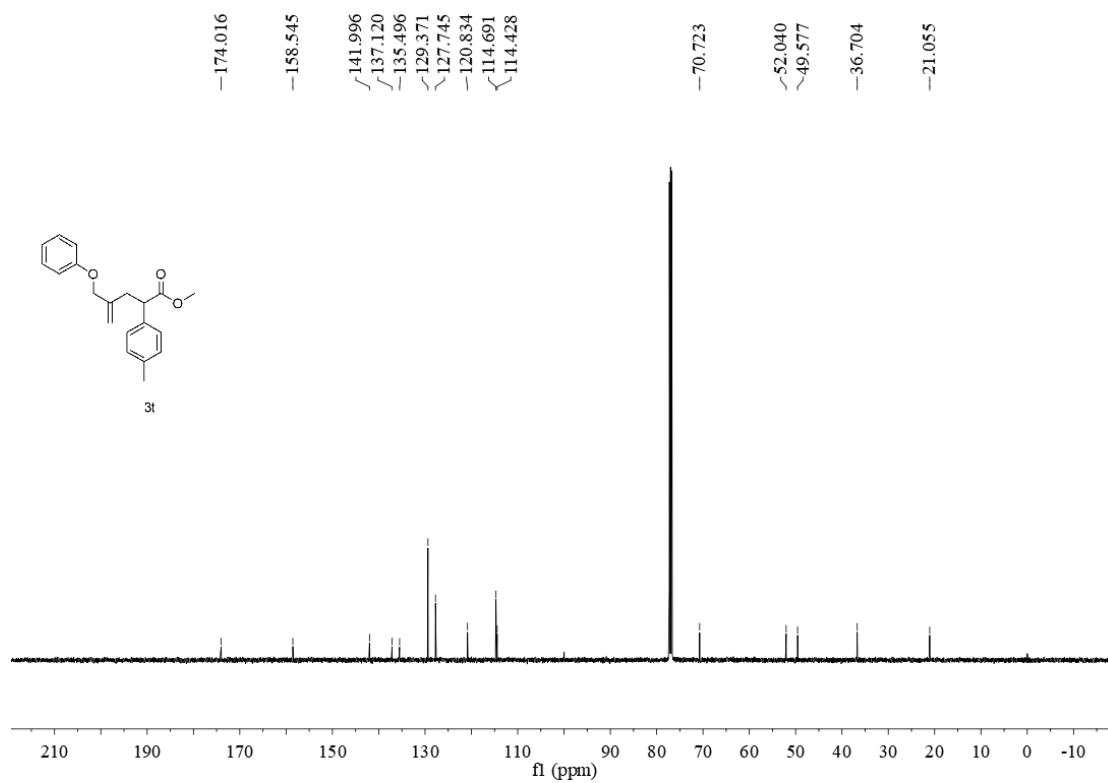
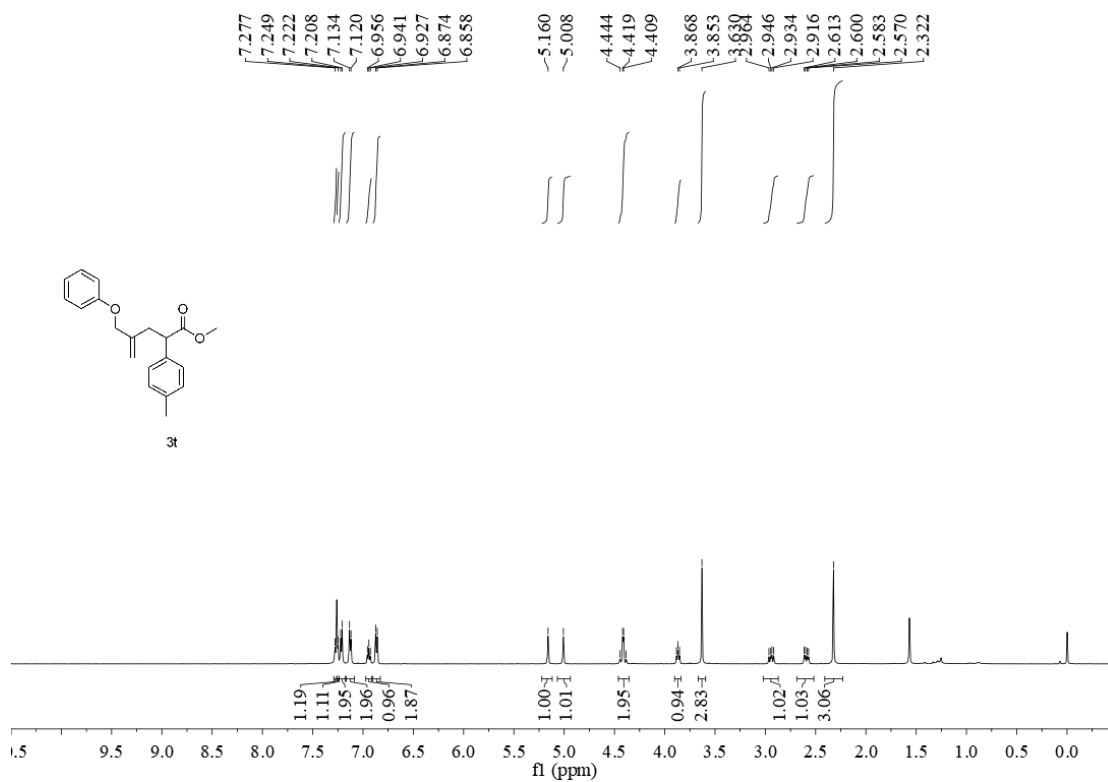
3r:



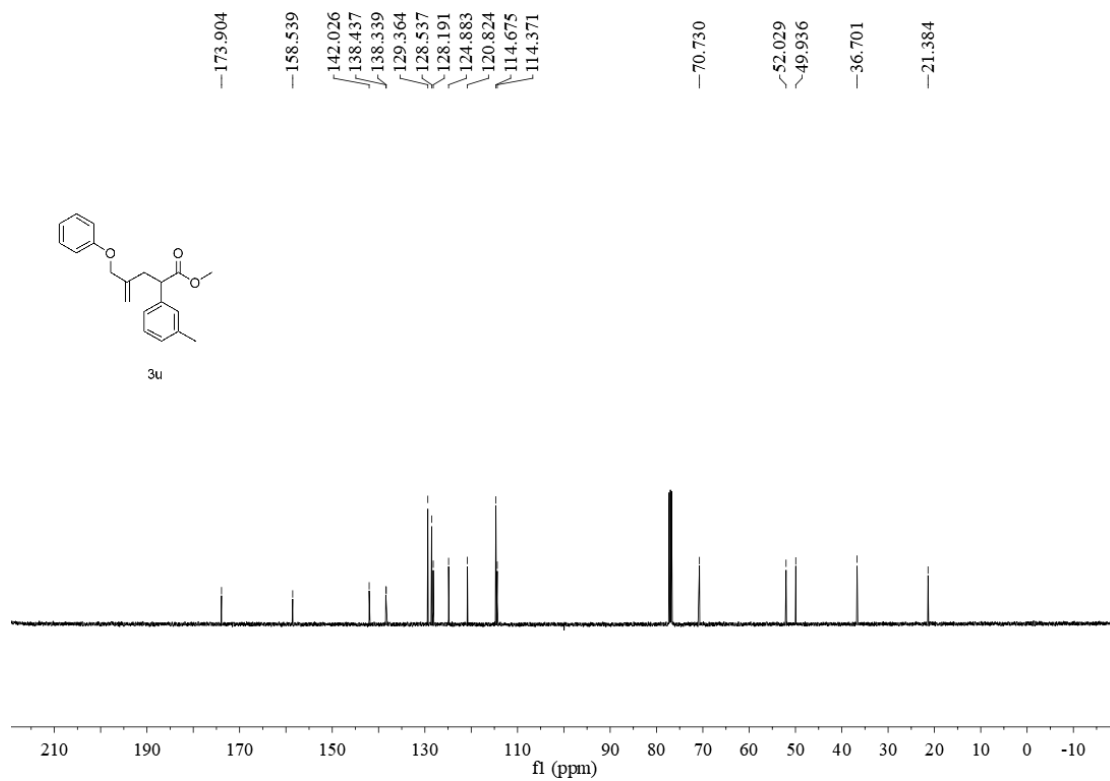
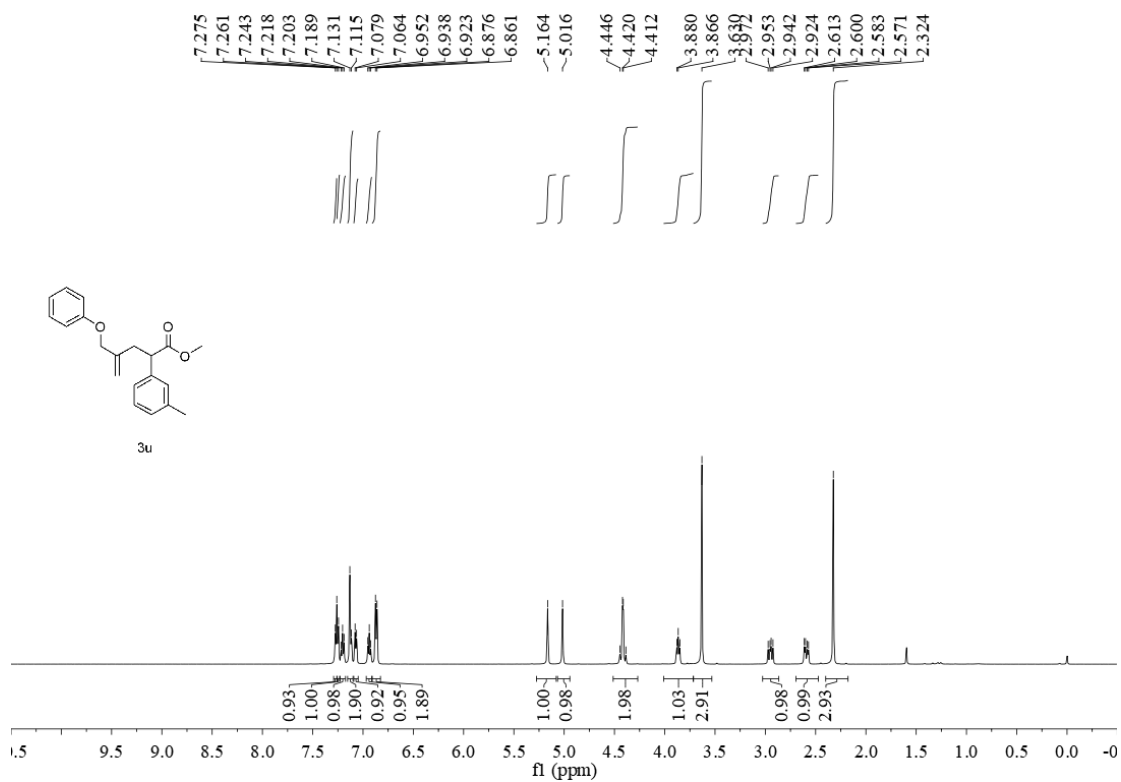
3s:



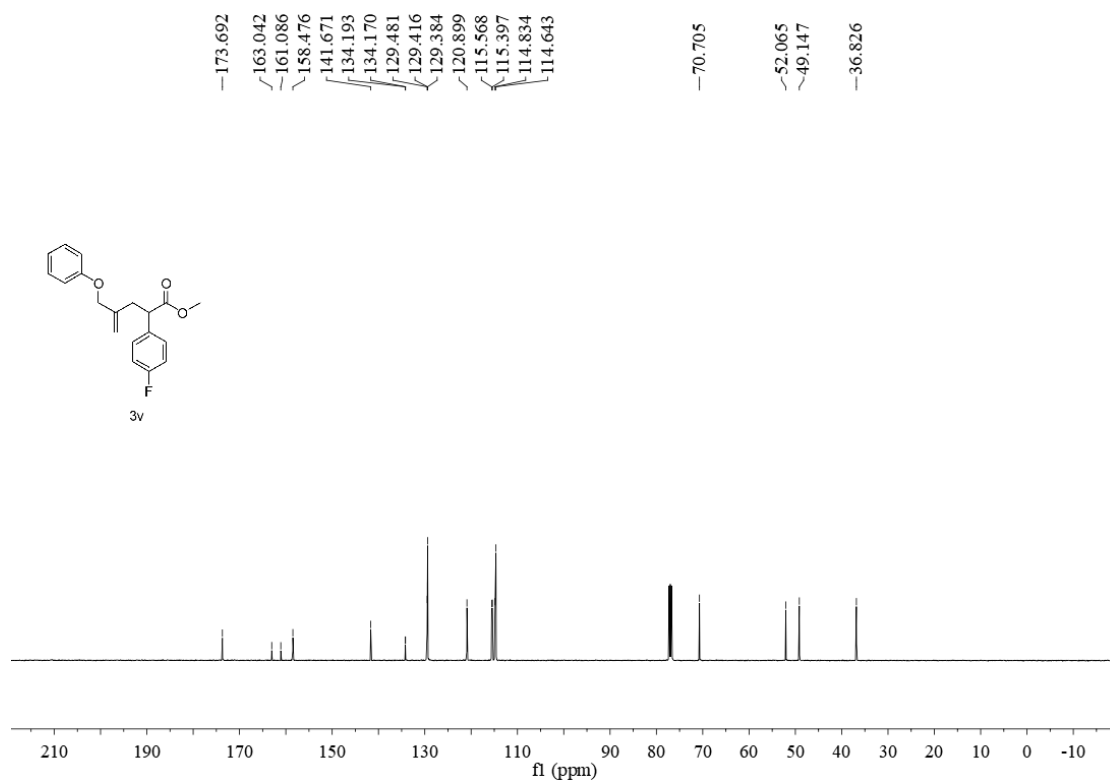
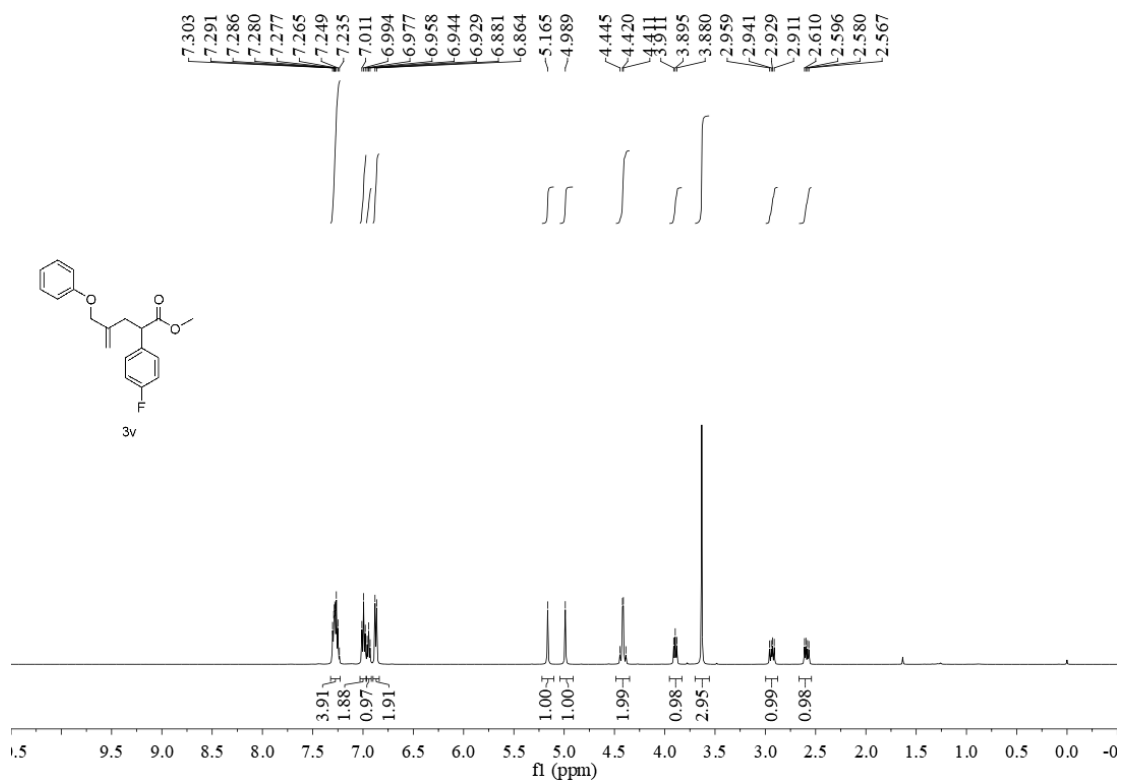
3t:



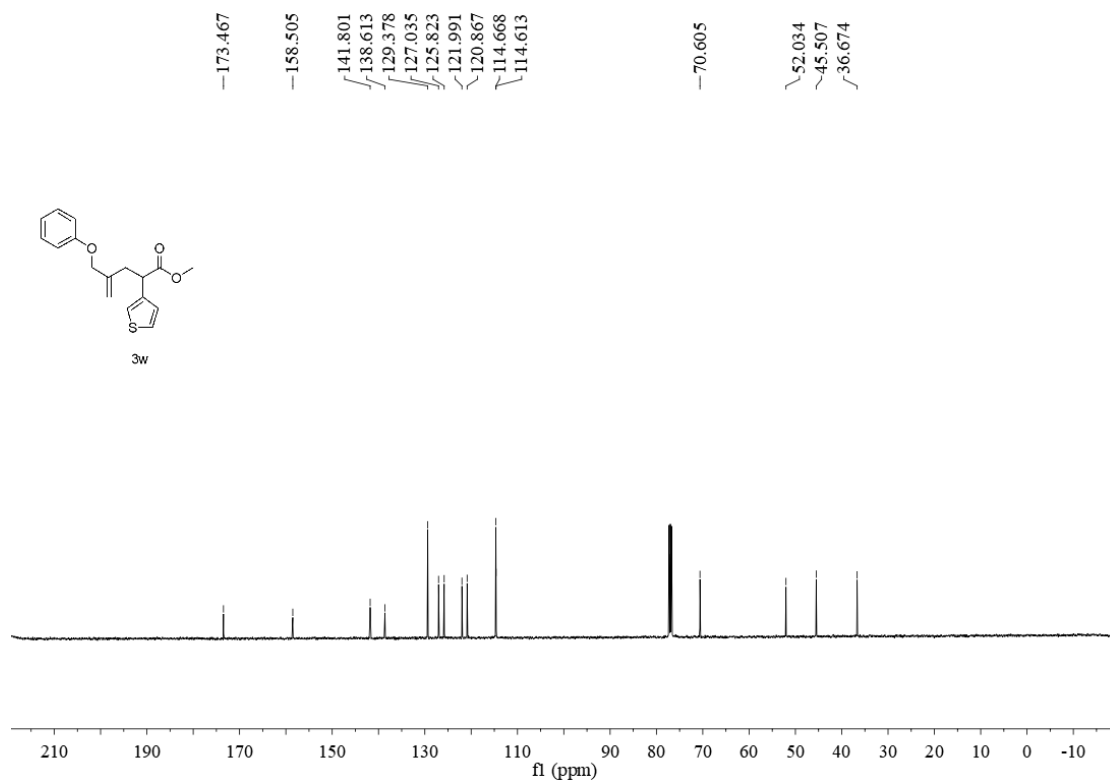
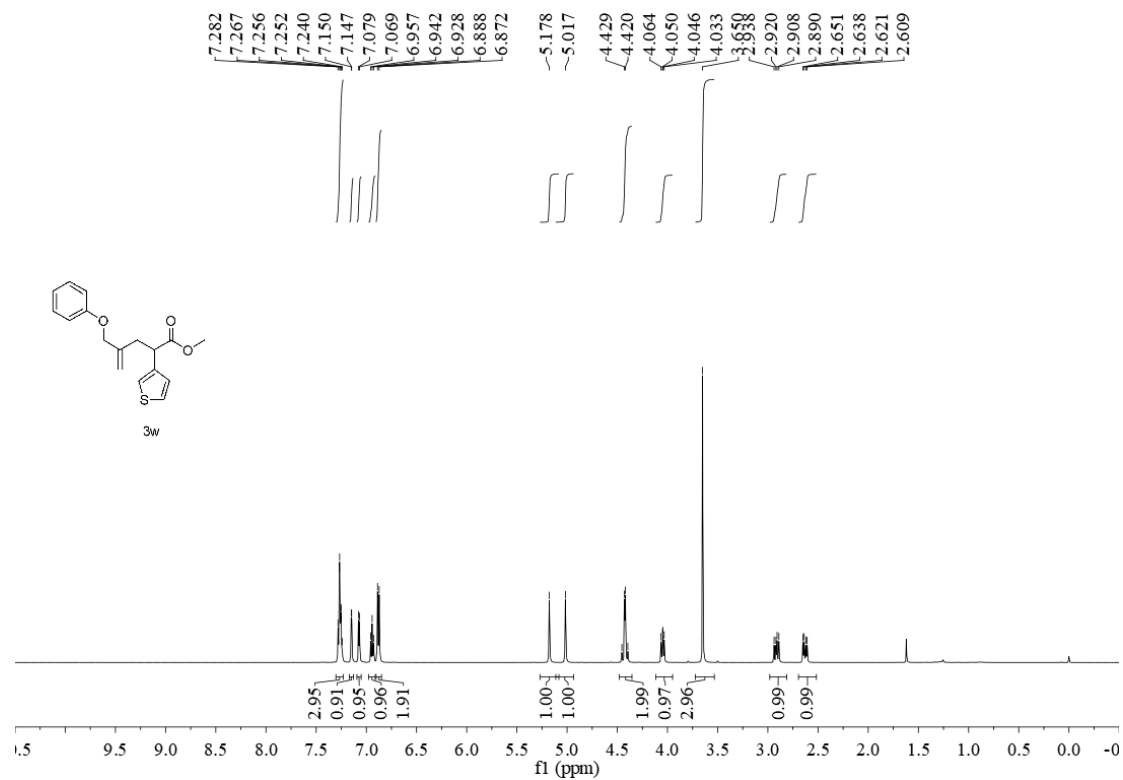
3u:



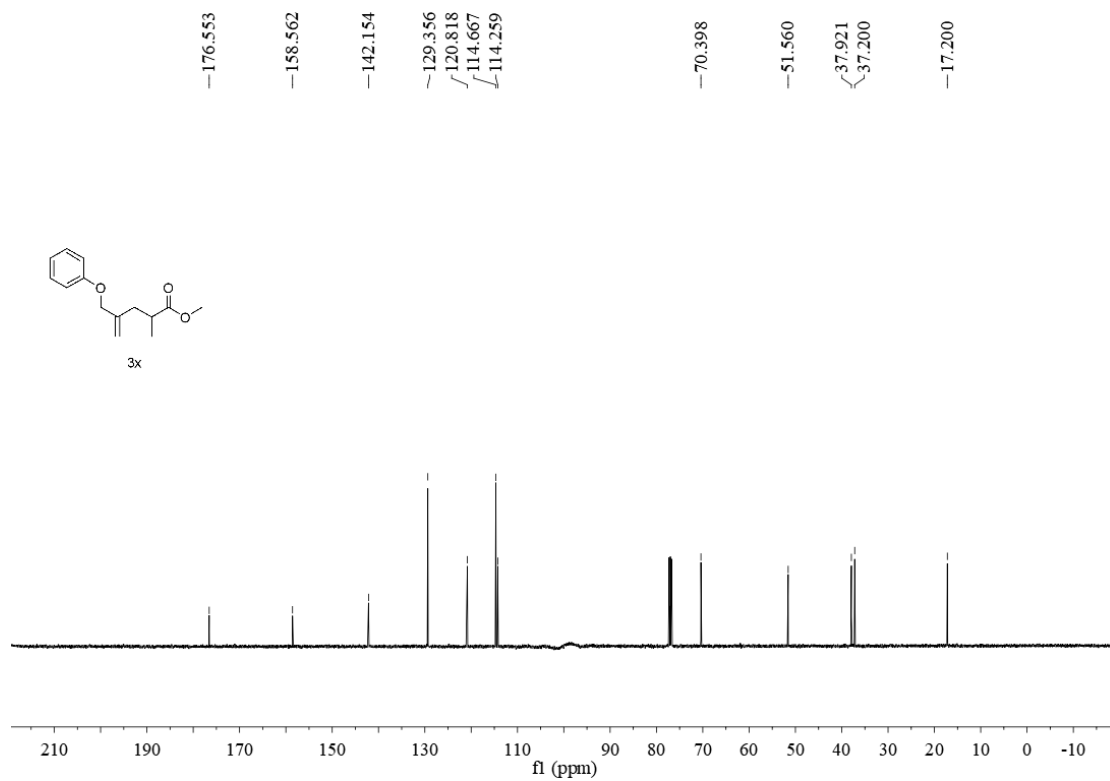
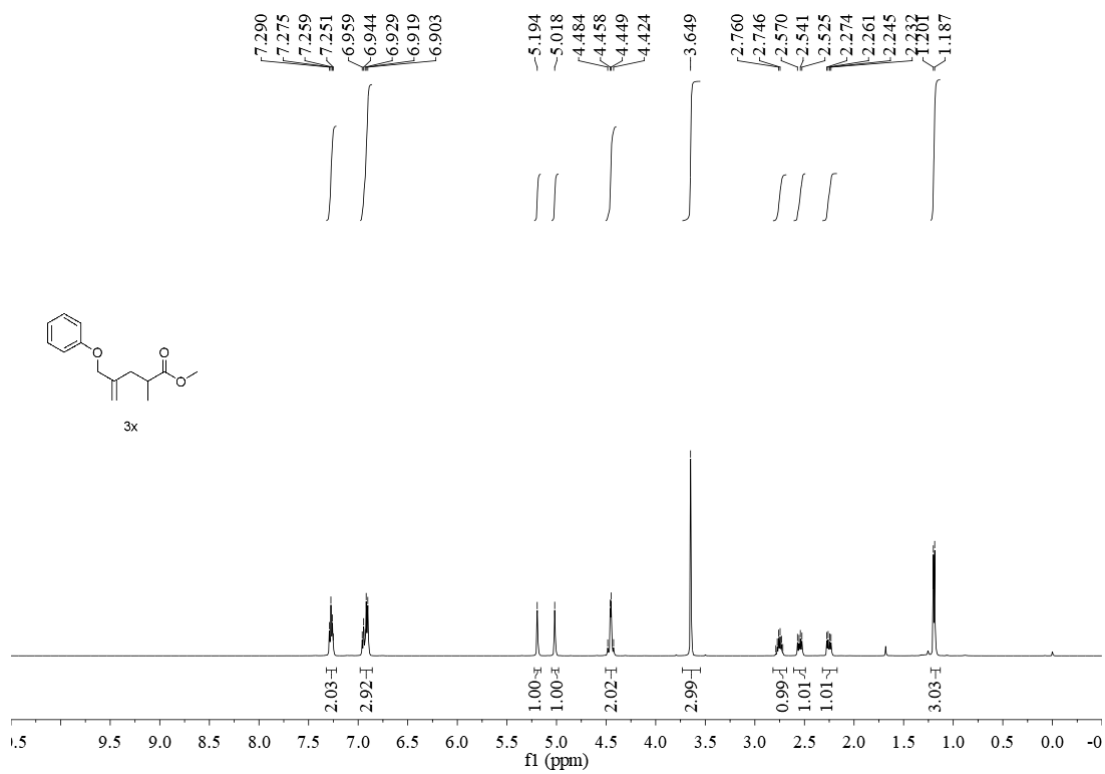
3v:



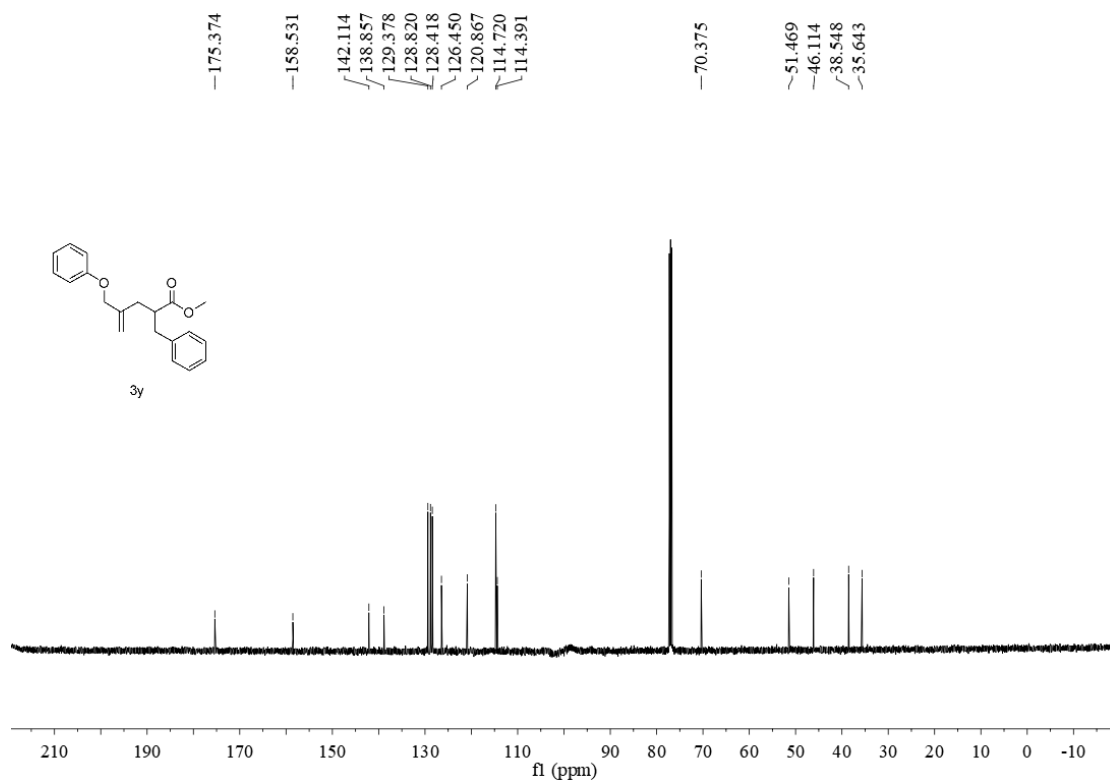
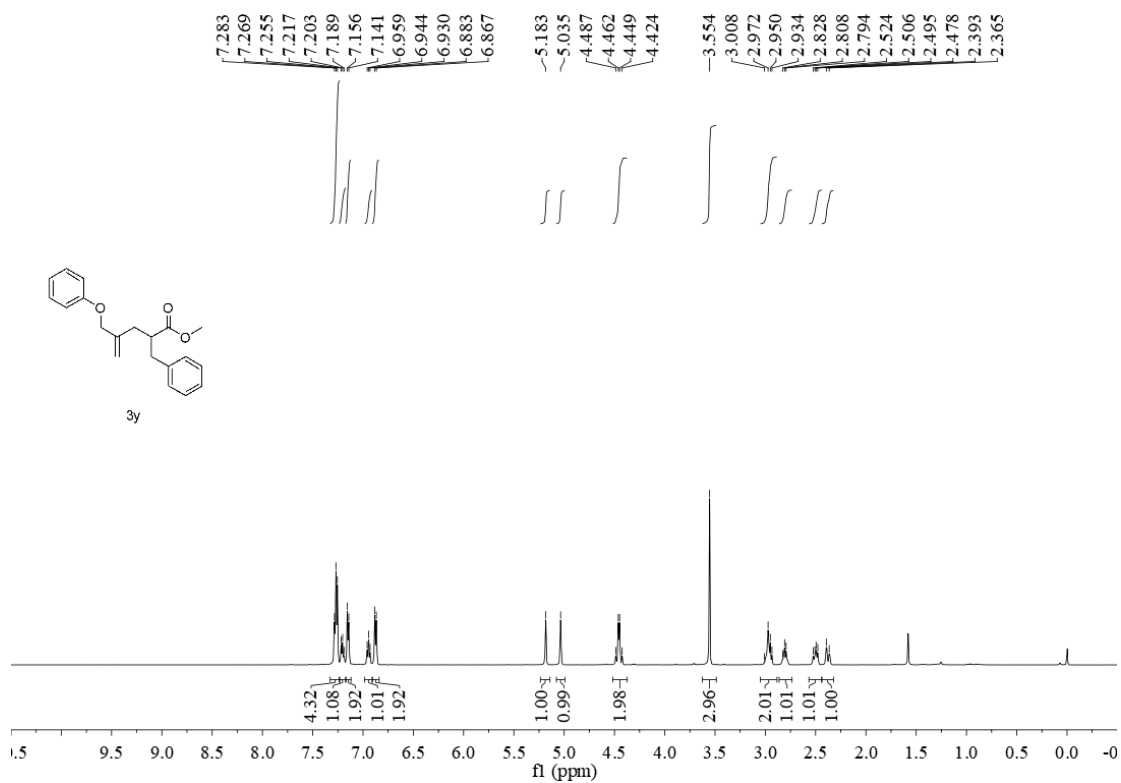
3w:



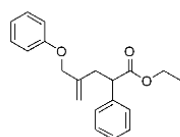
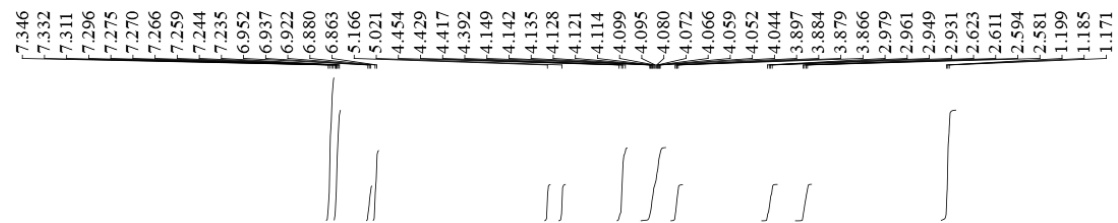
3x:



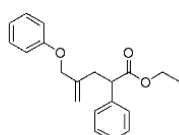
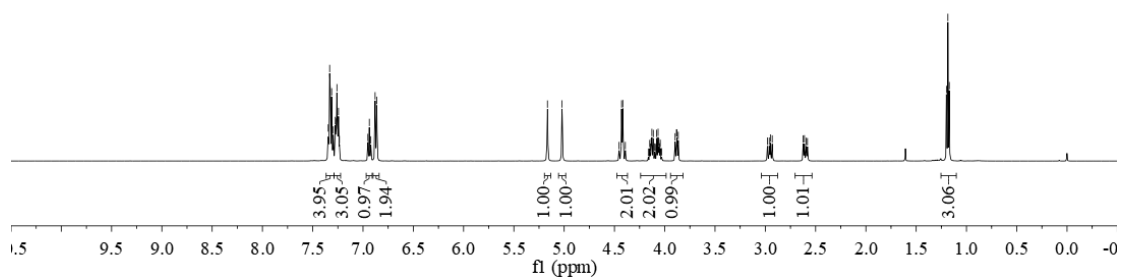
3y:



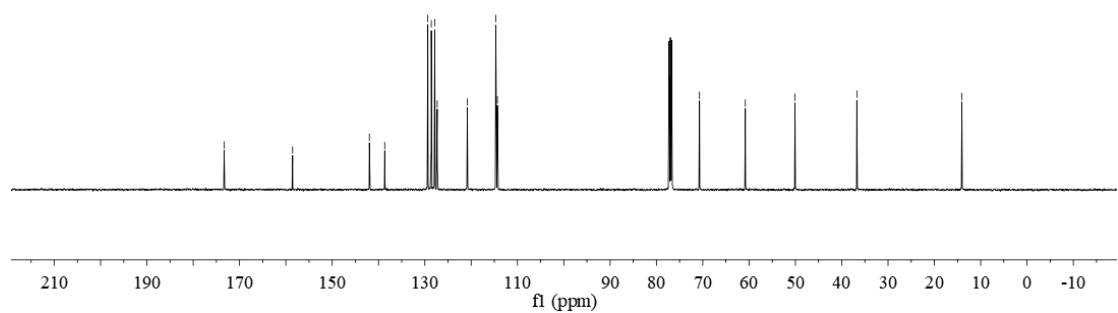
3z:



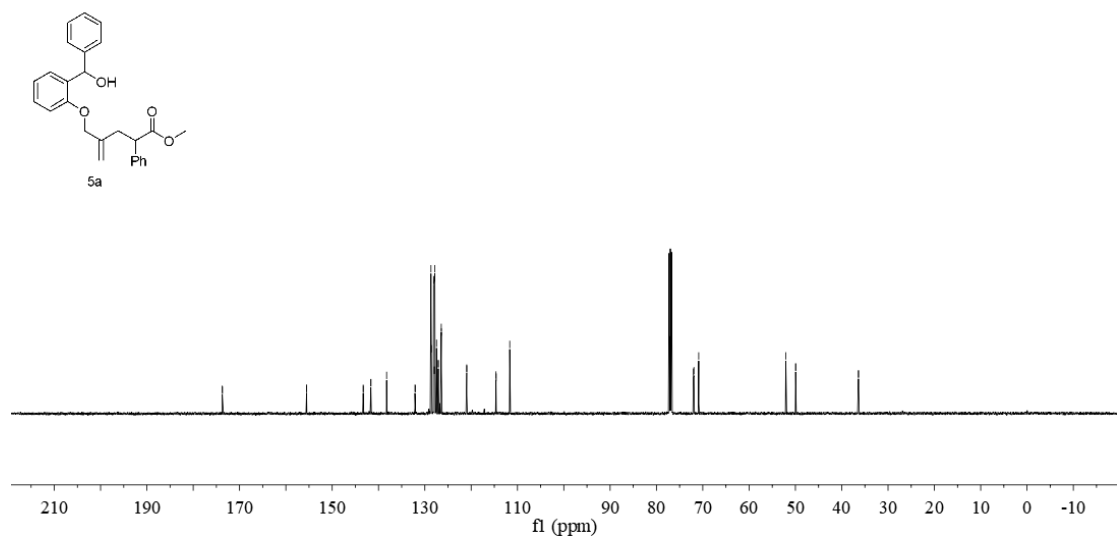
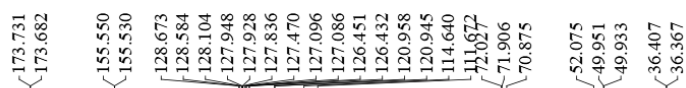
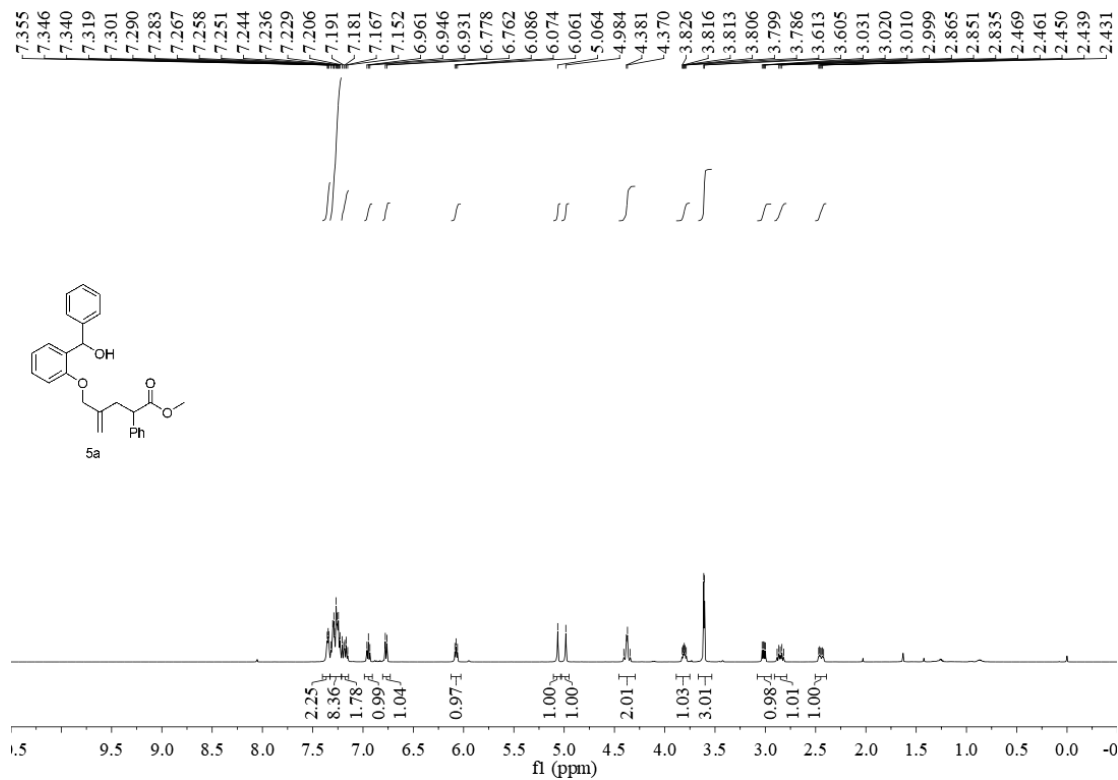
3z



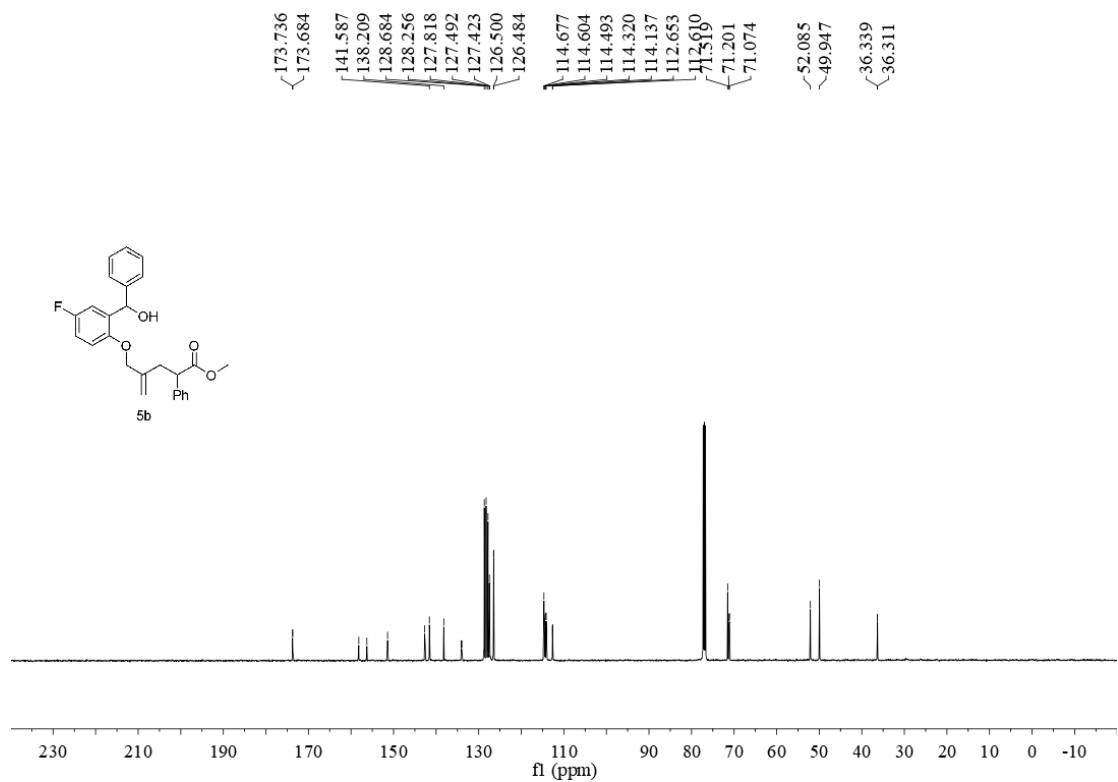
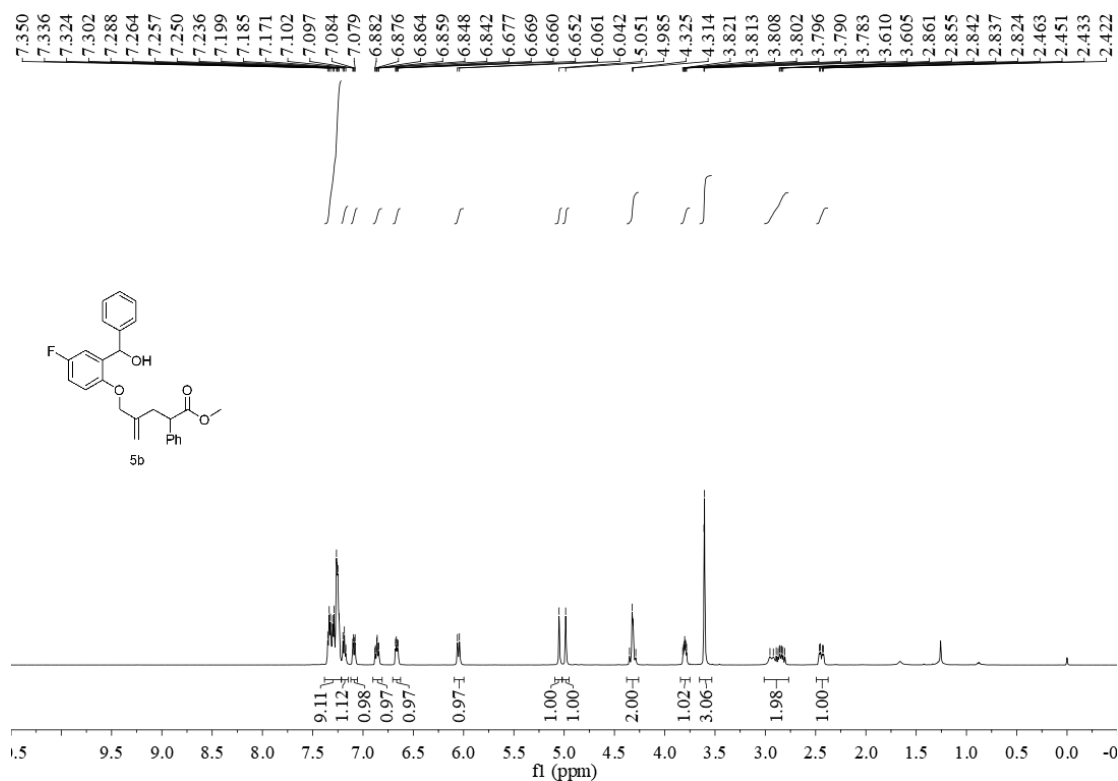
3z



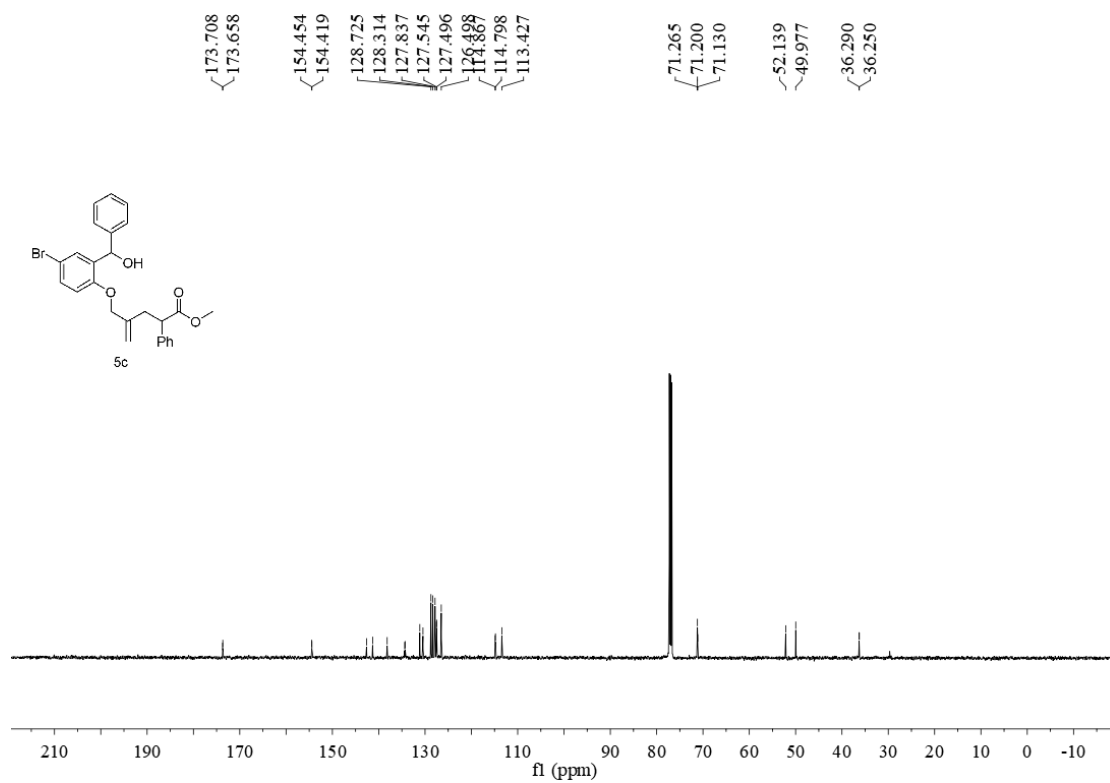
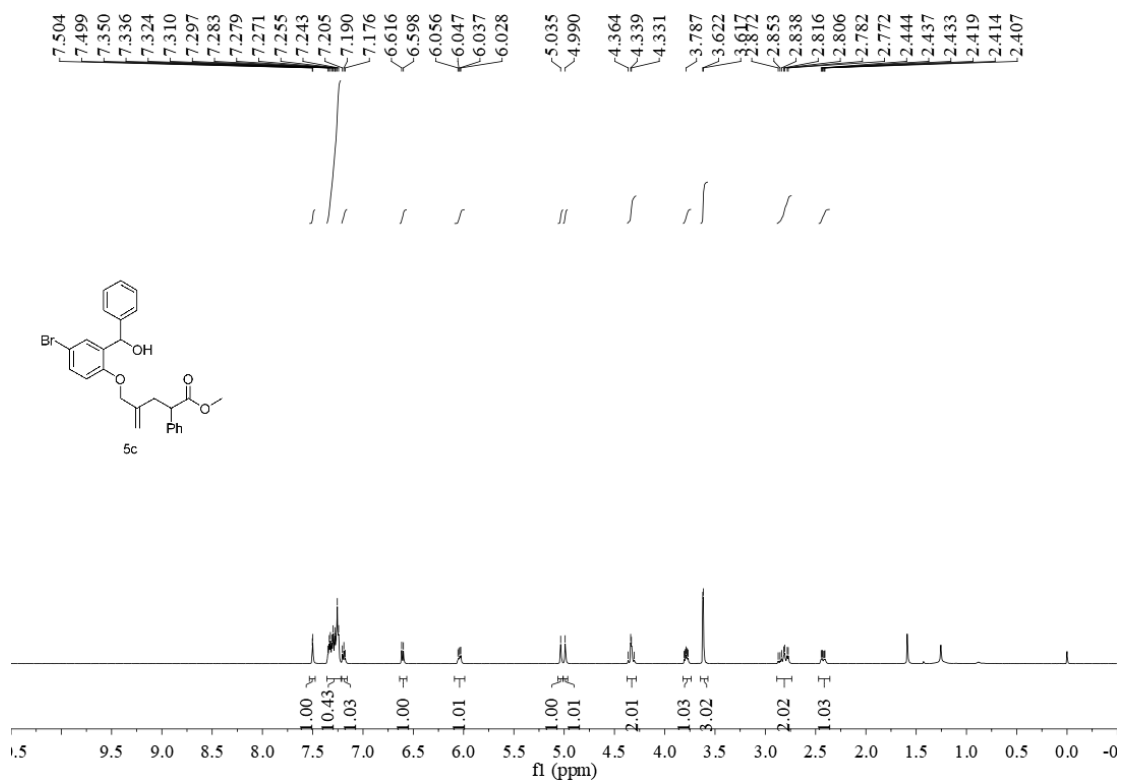
5a:



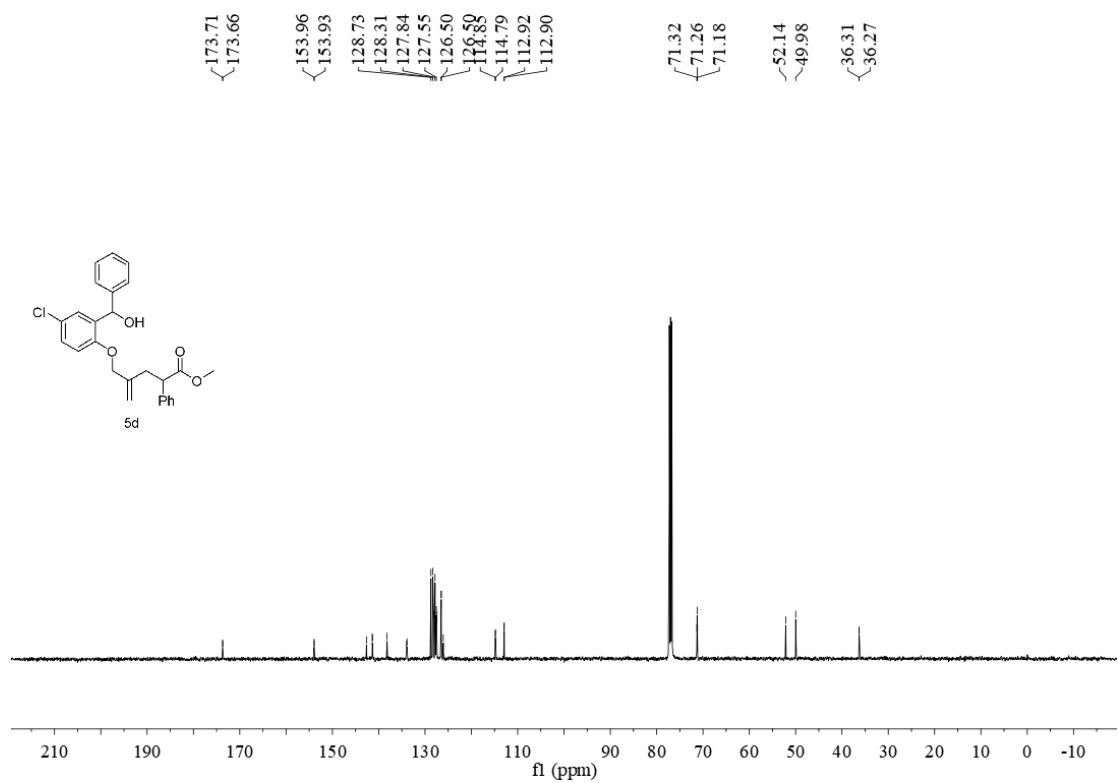
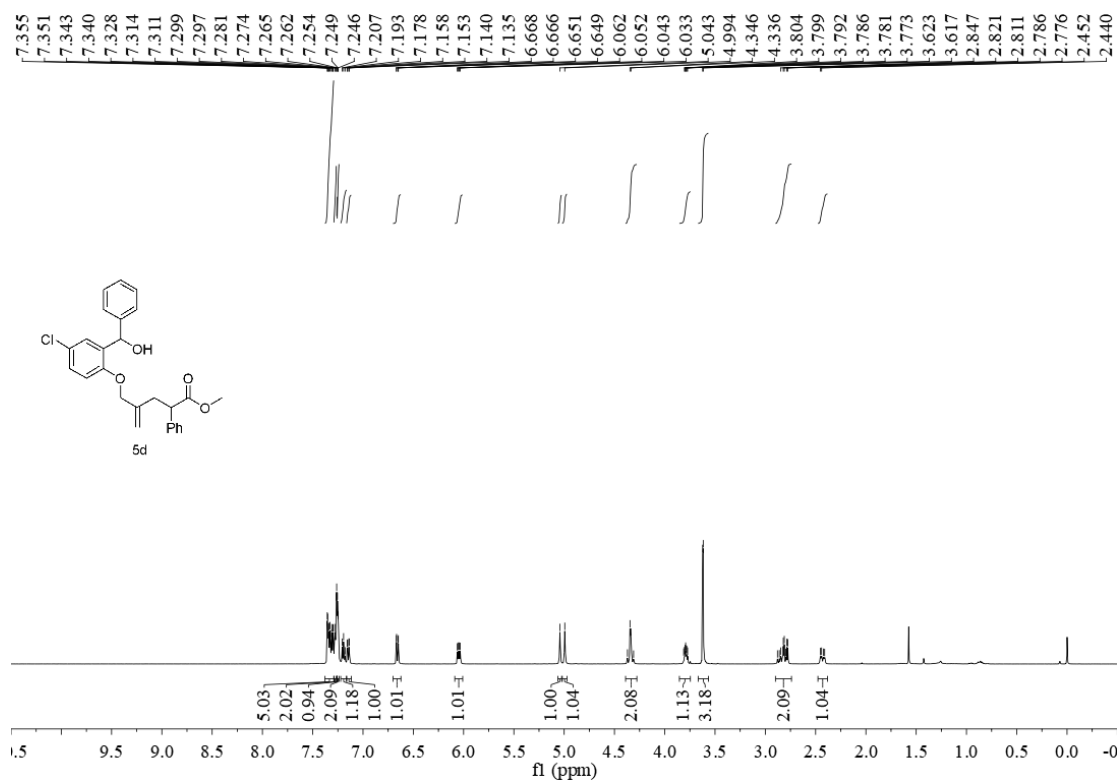
5b:



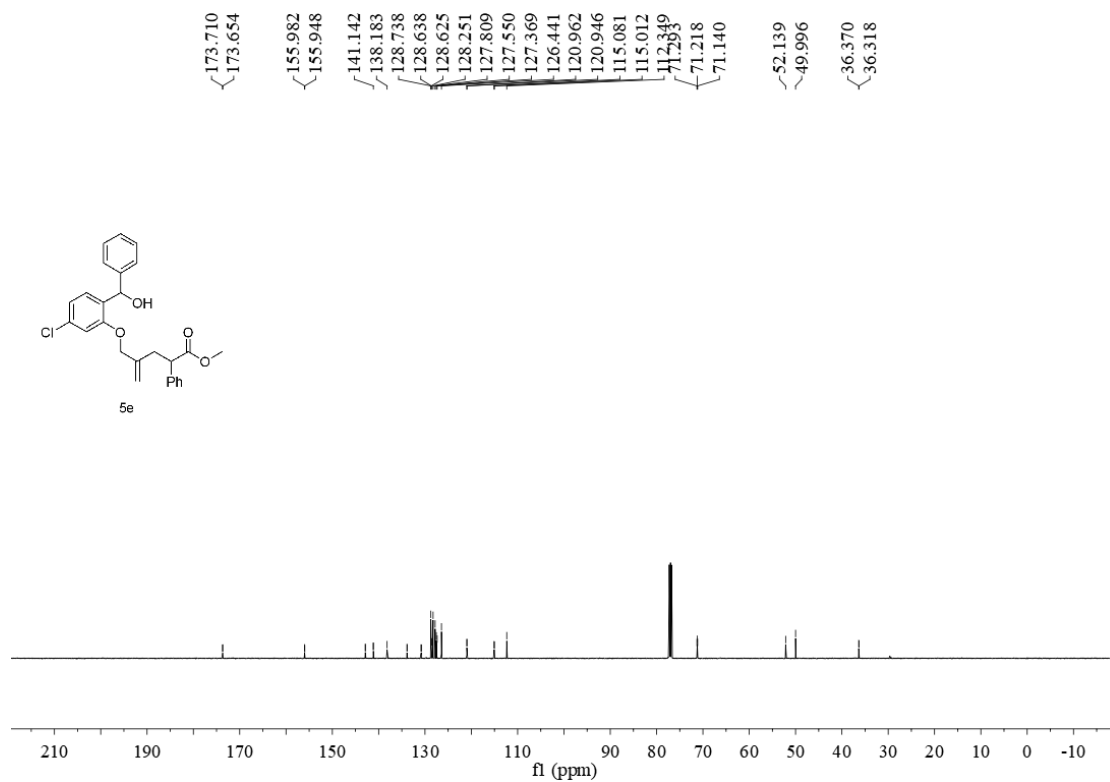
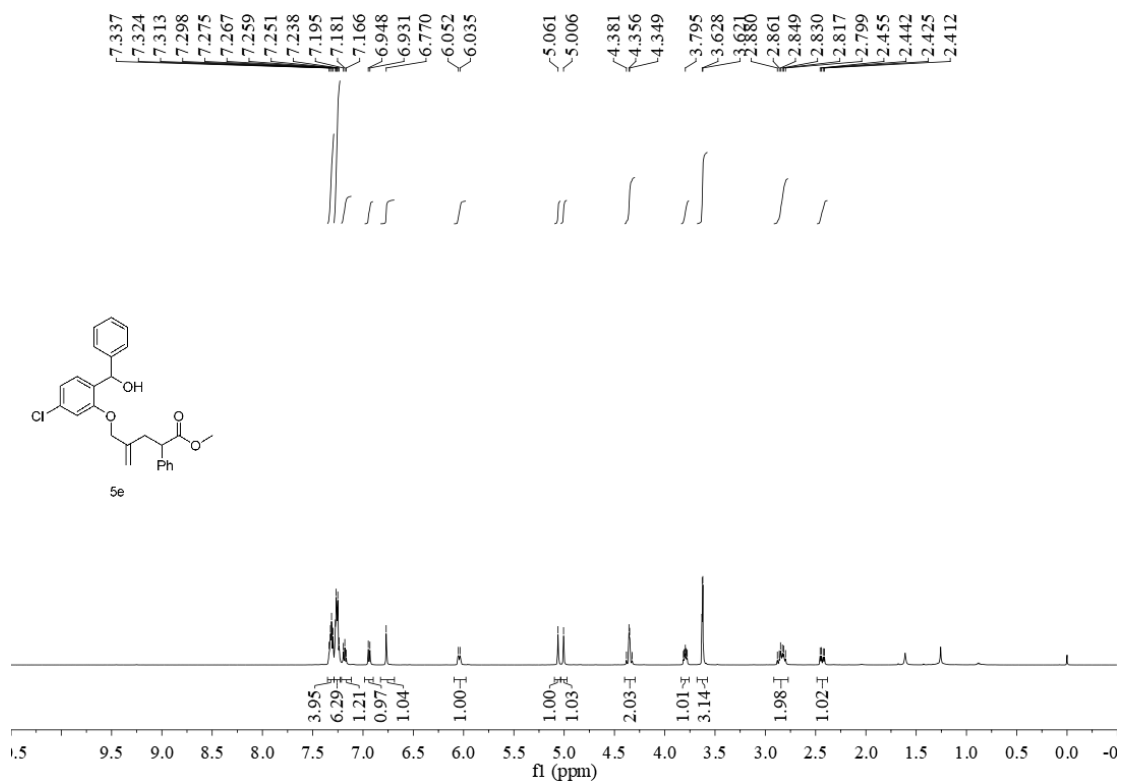
5c:



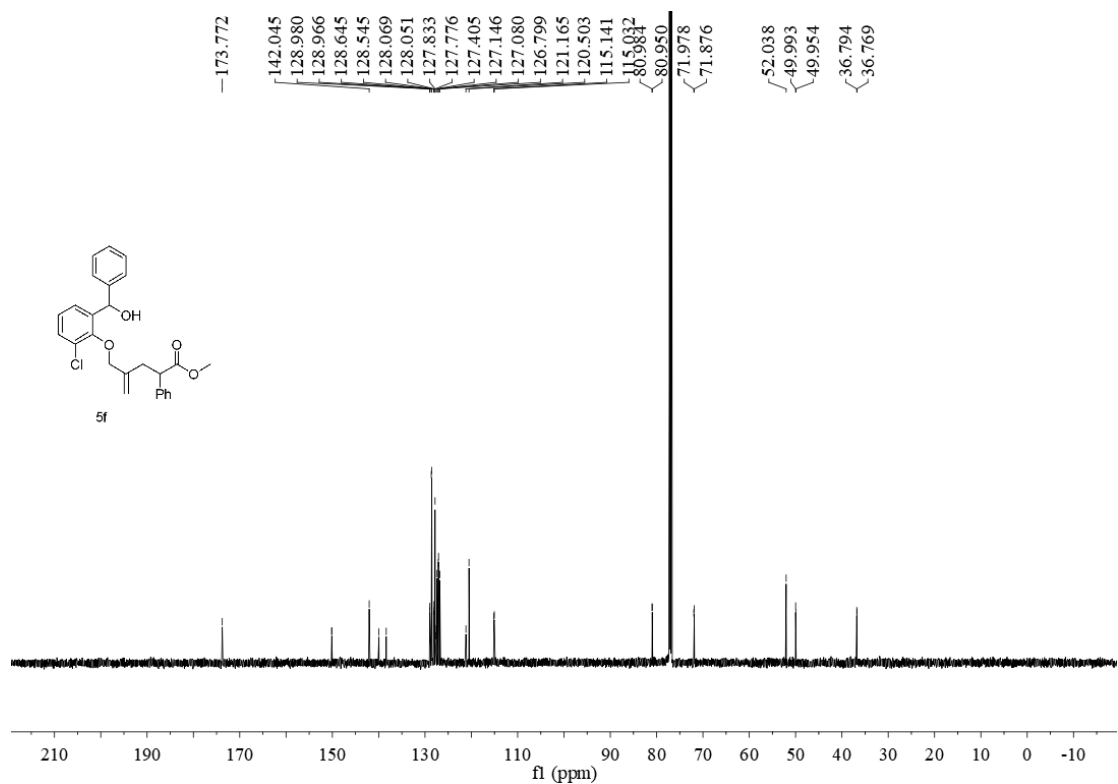
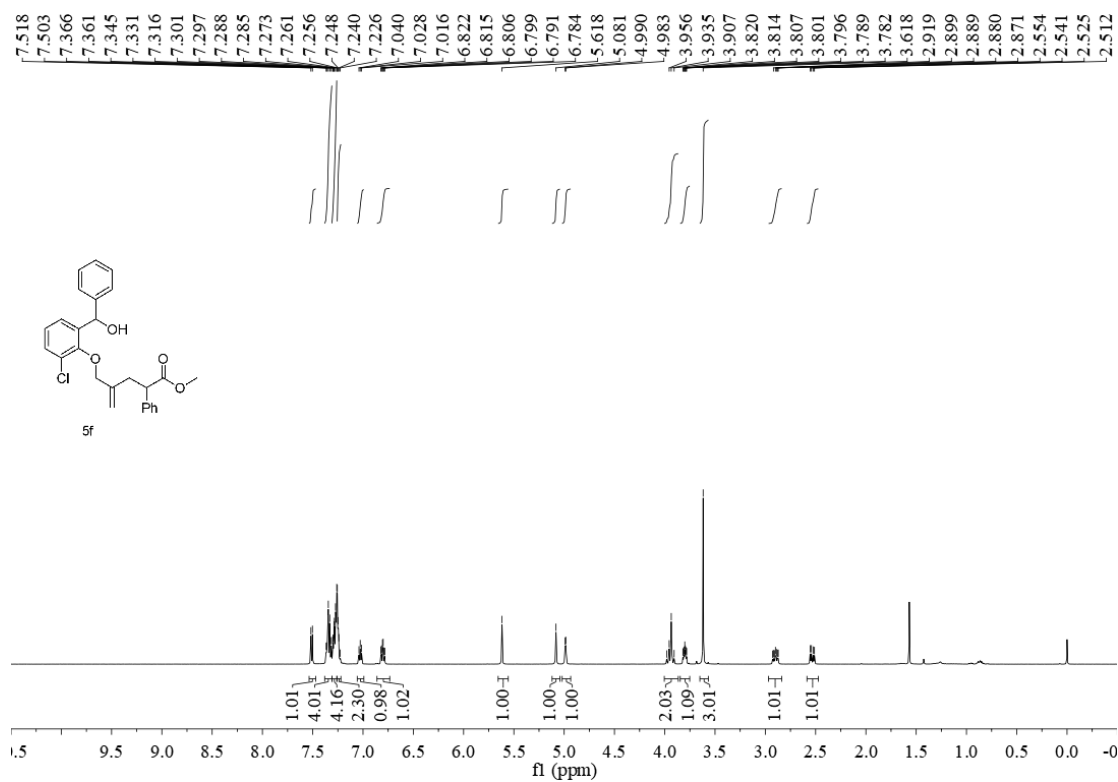
5d:



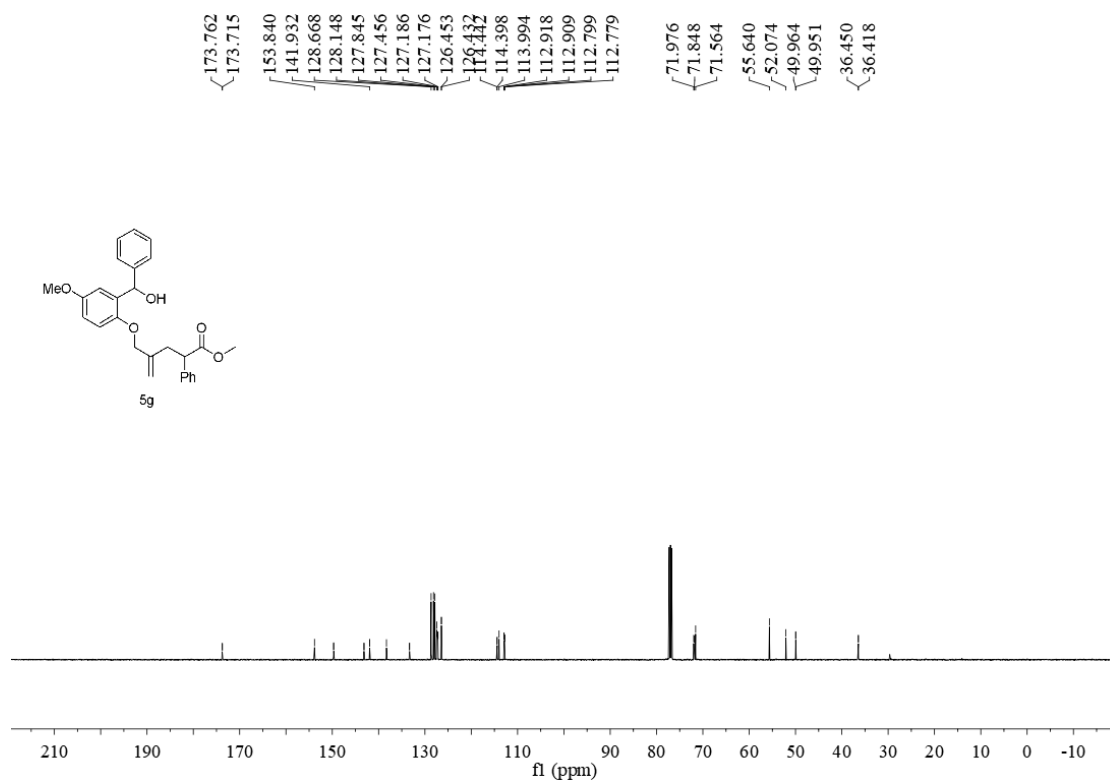
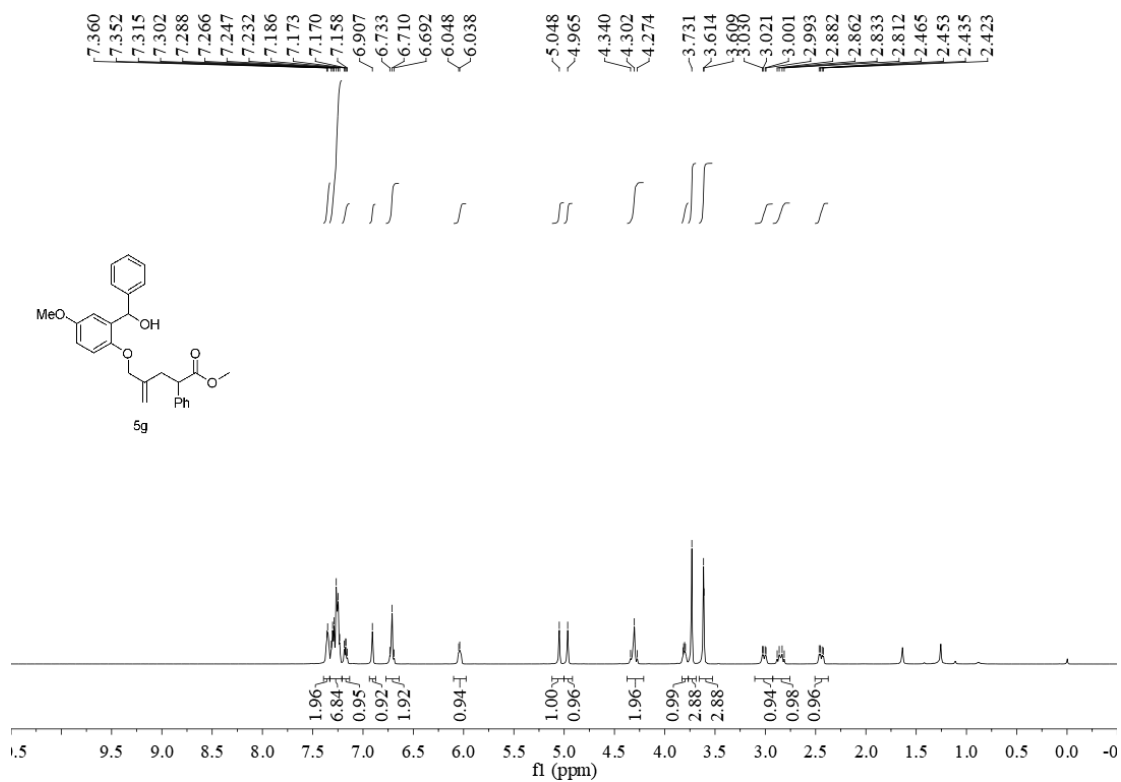
5e:



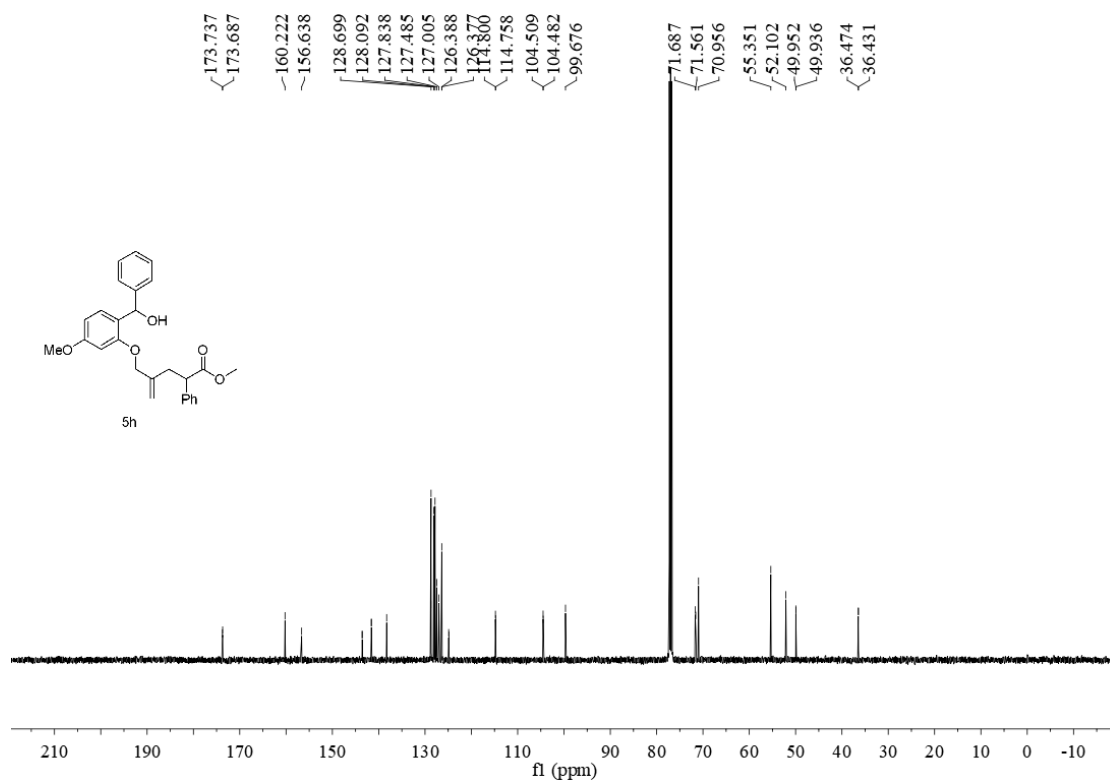
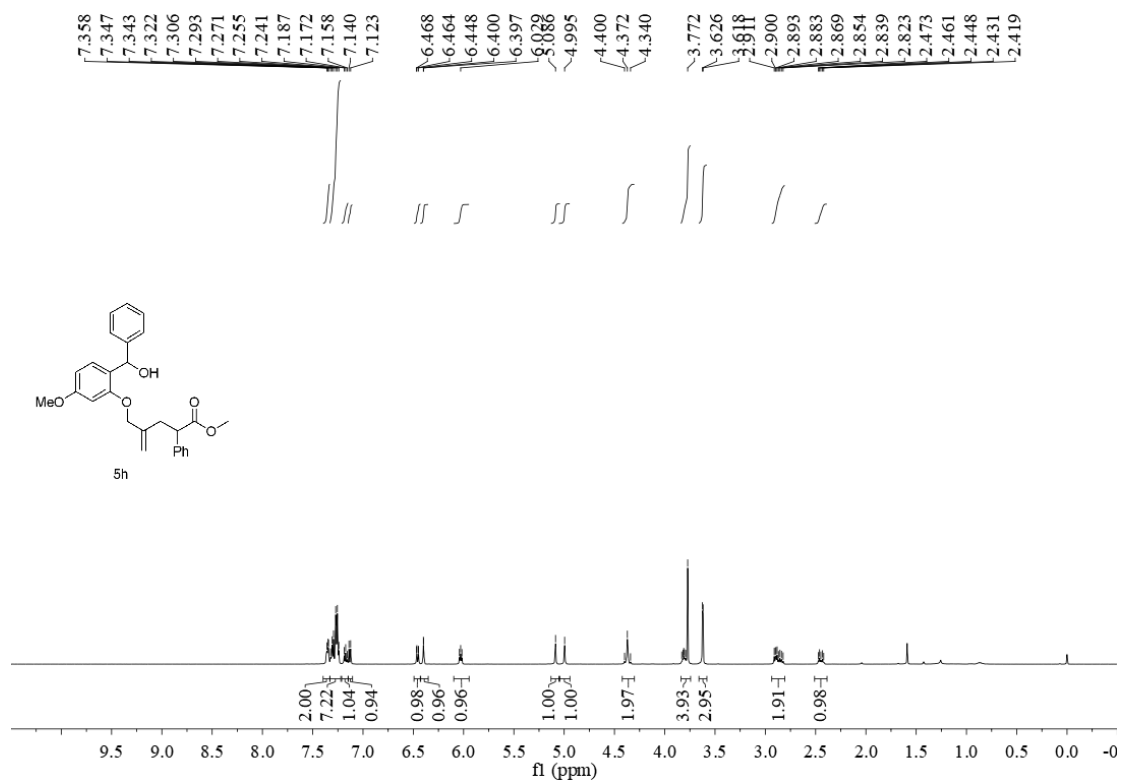
5f:



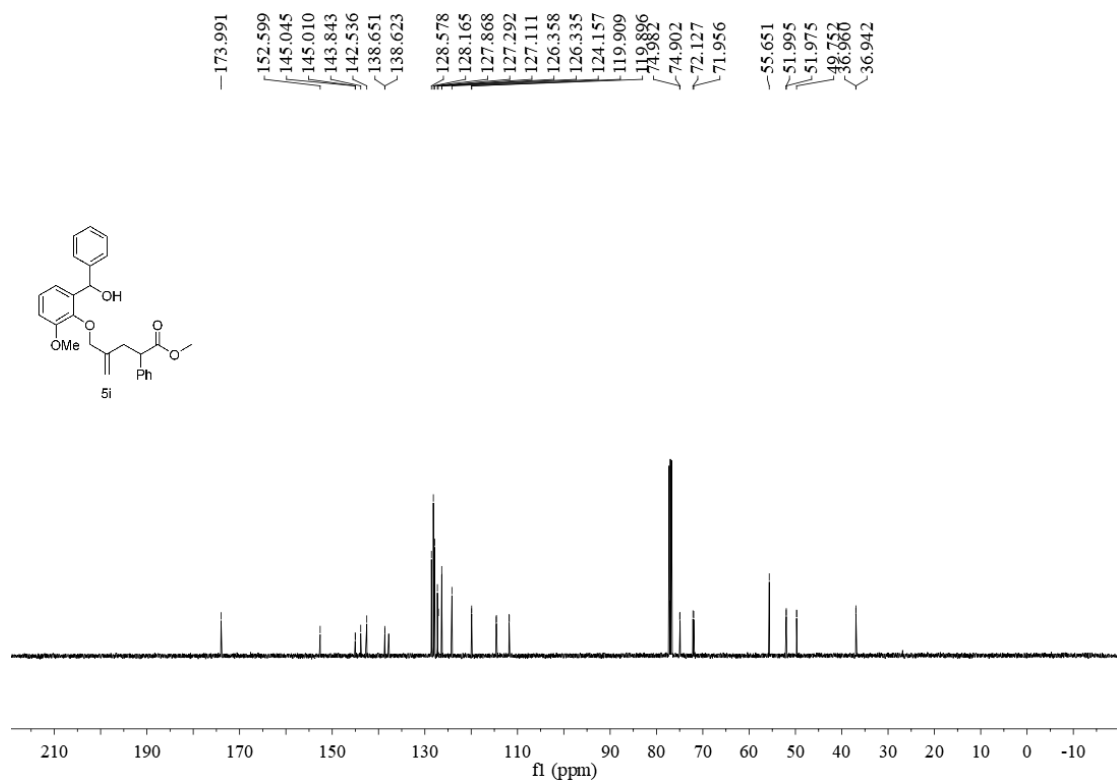
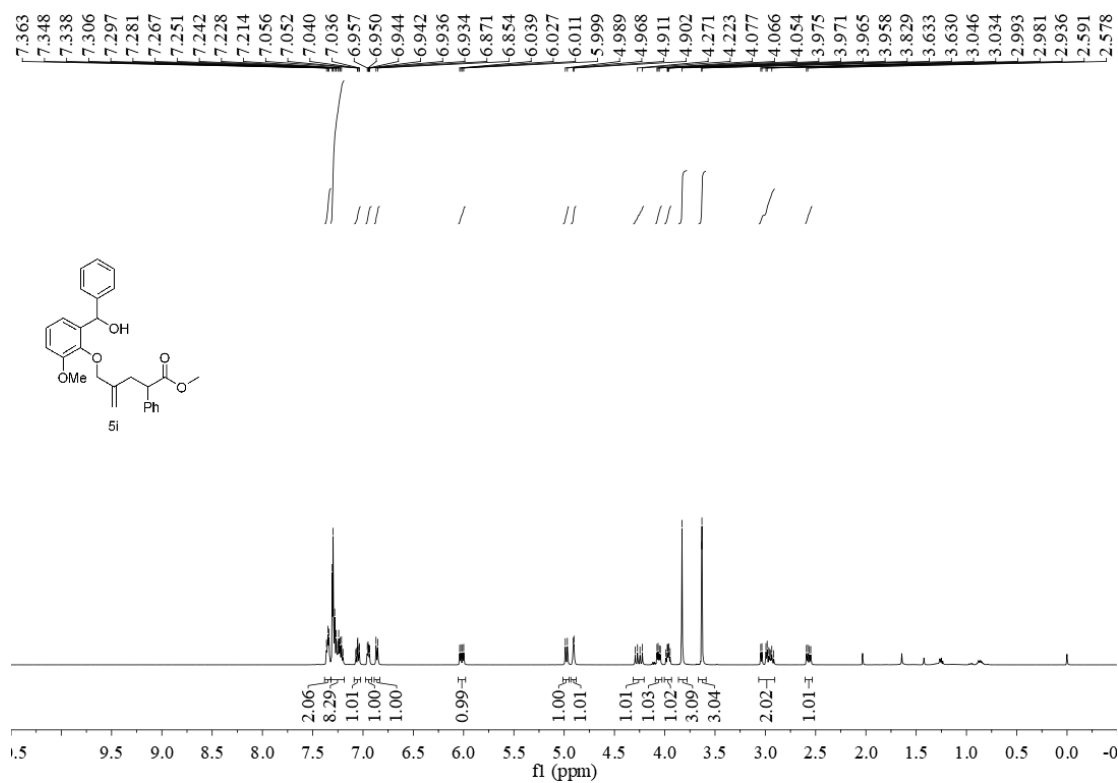
5g:



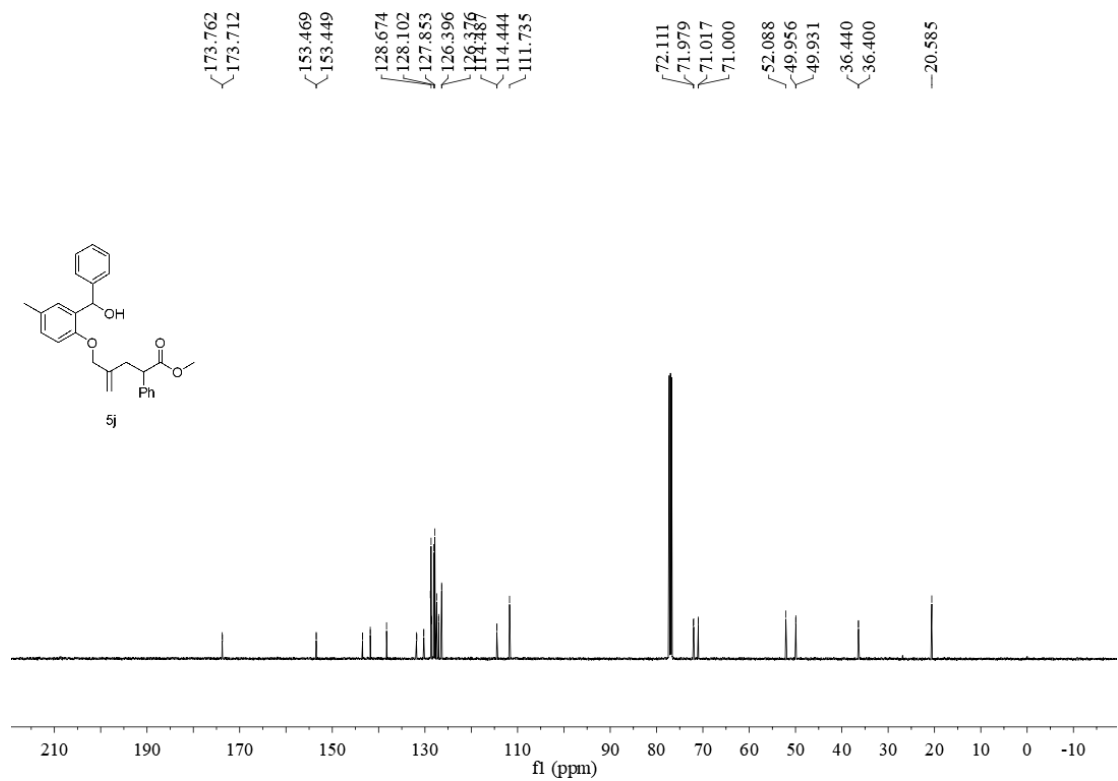
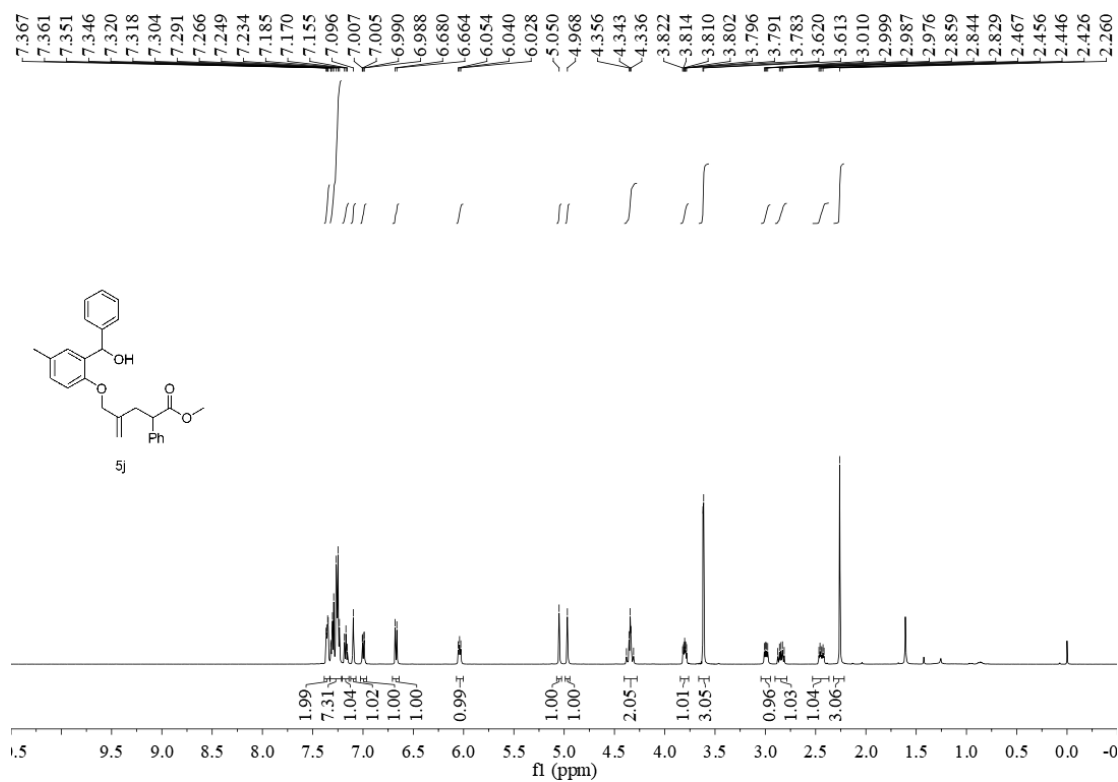
5h:



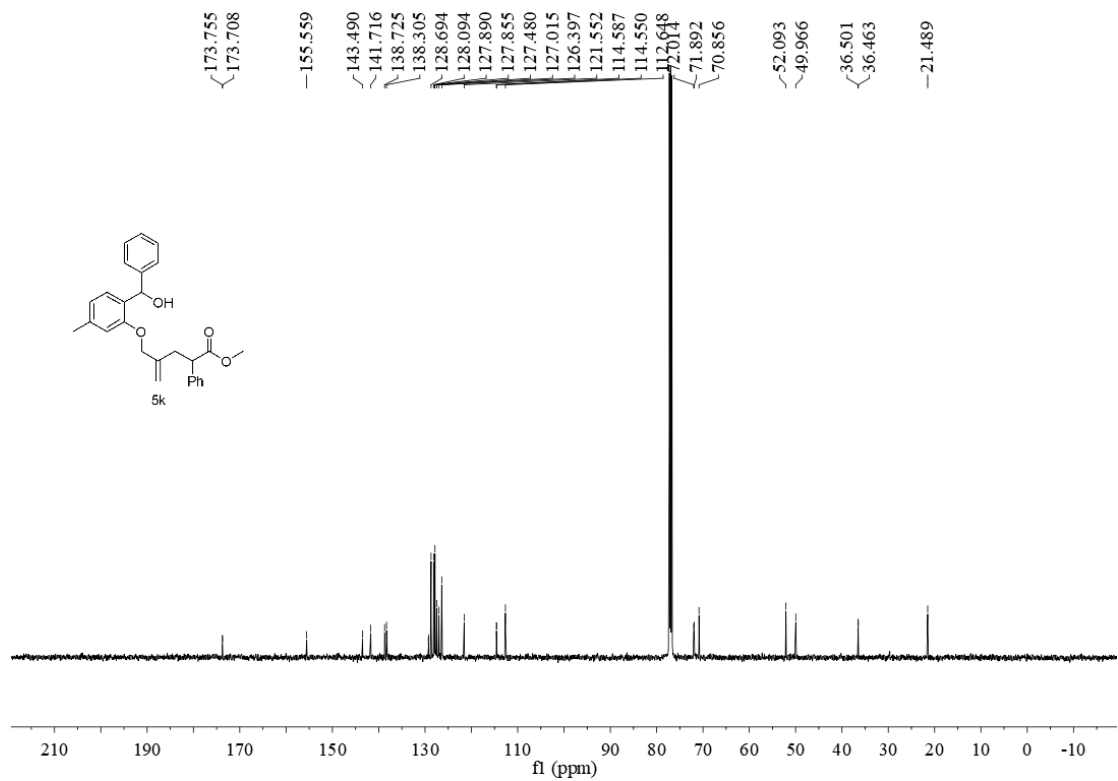
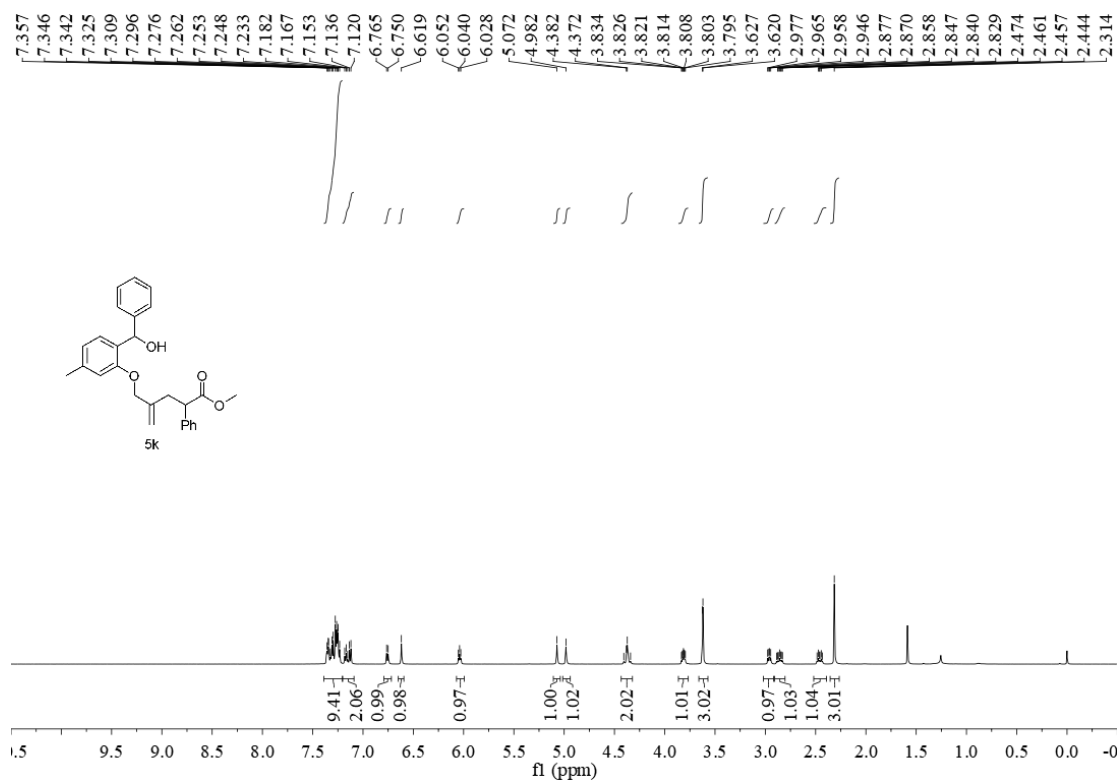
5i:



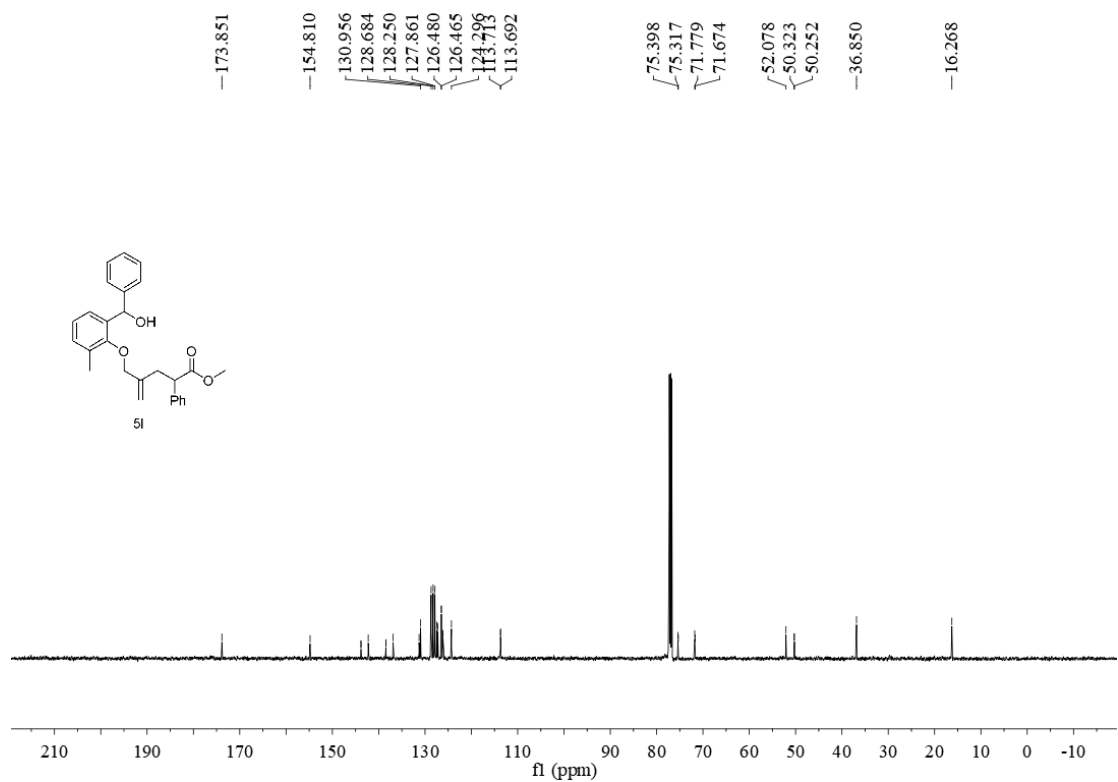
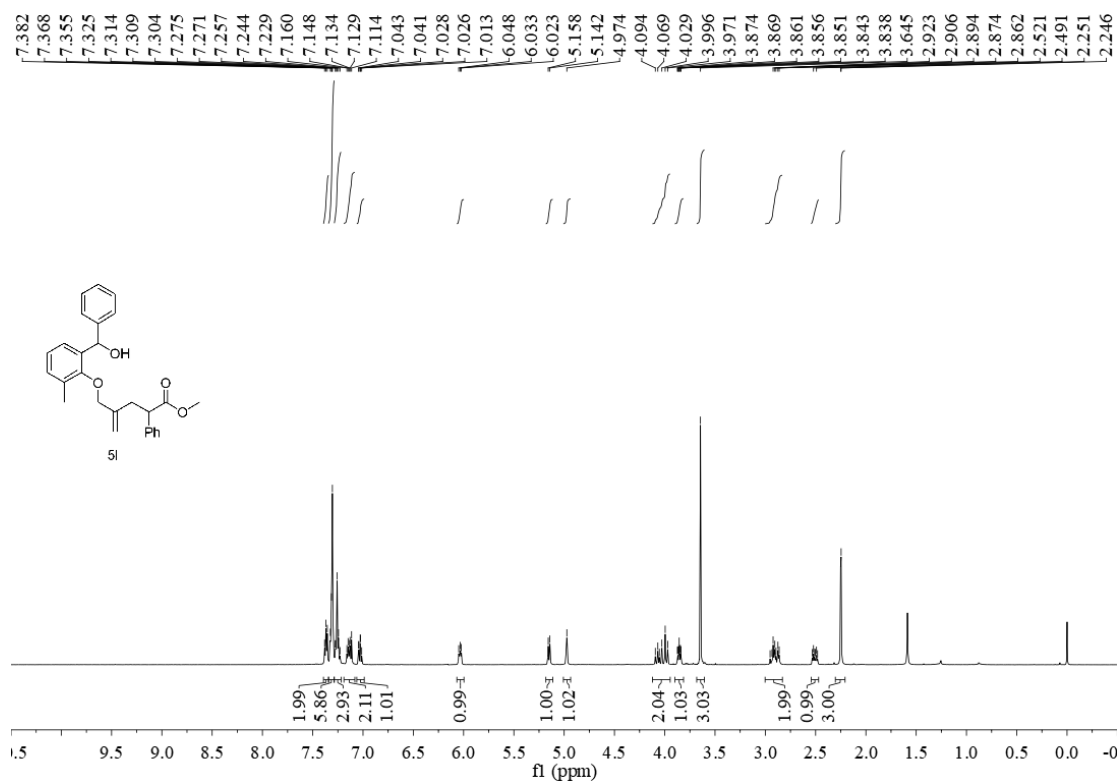
5j:



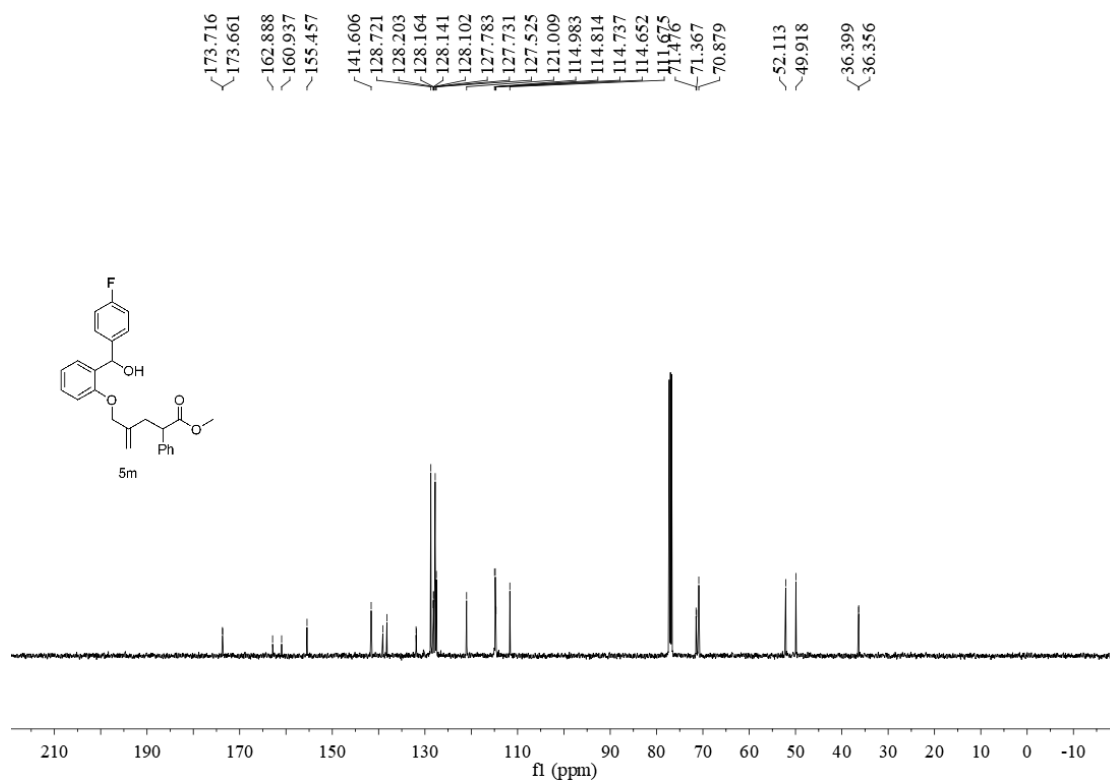
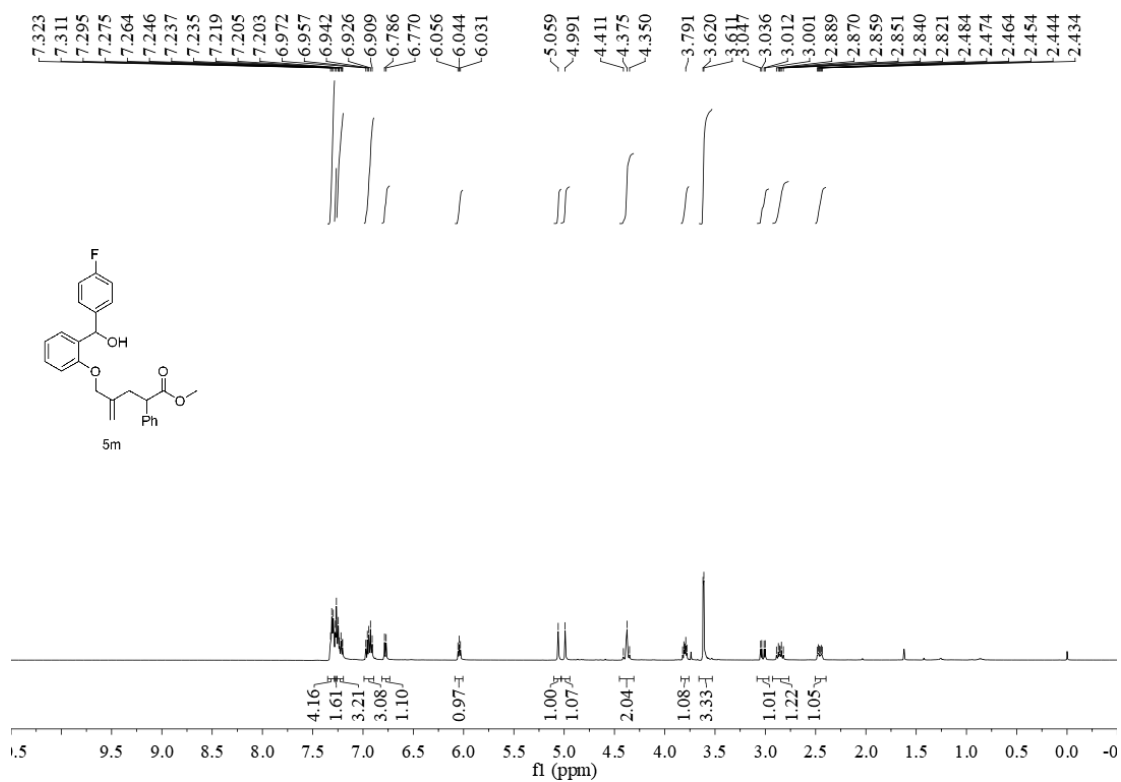
5k:



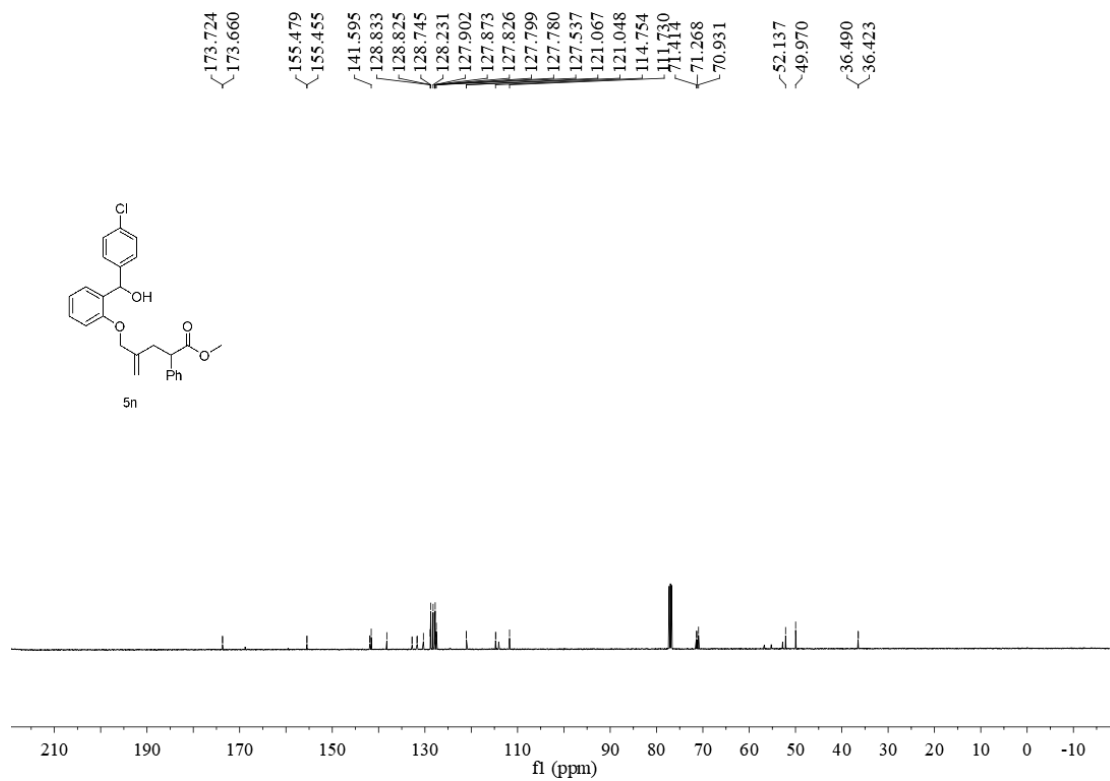
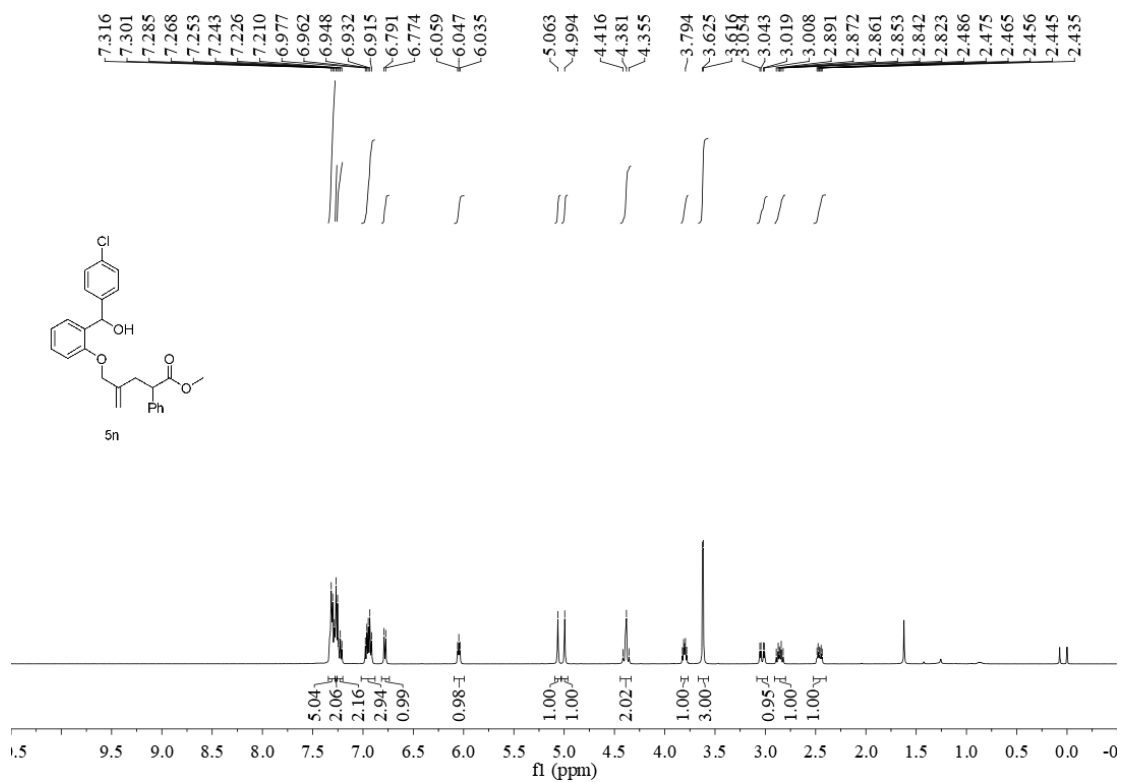
5l:



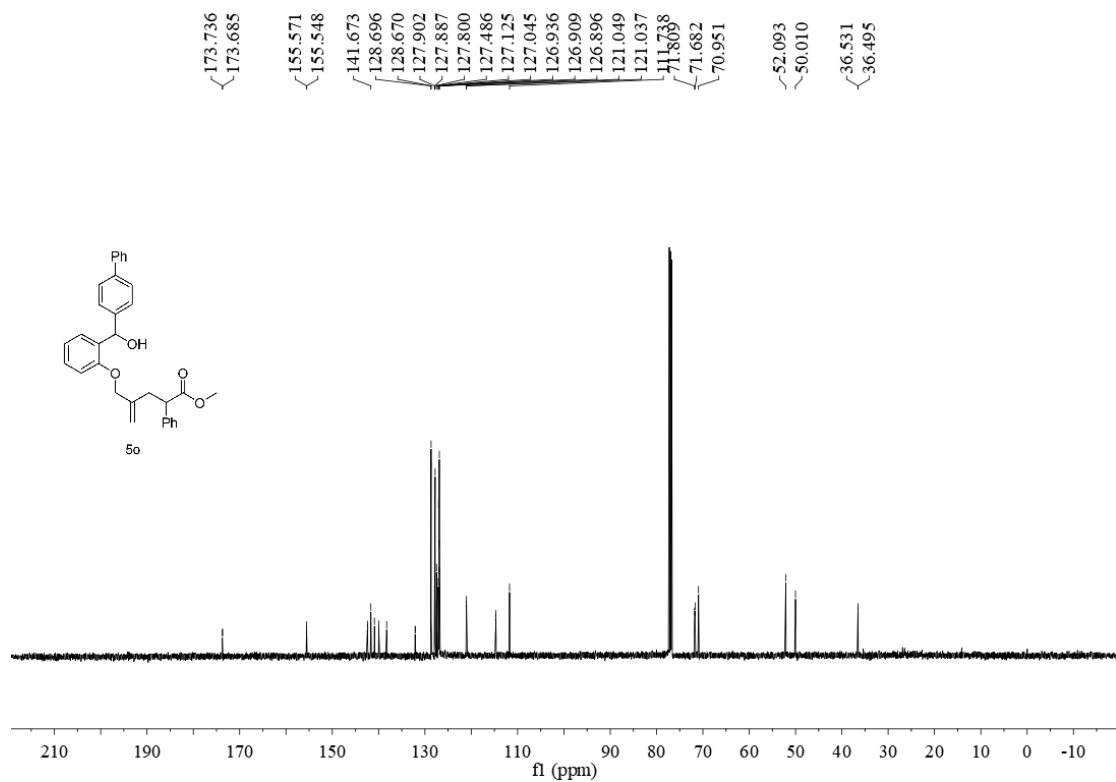
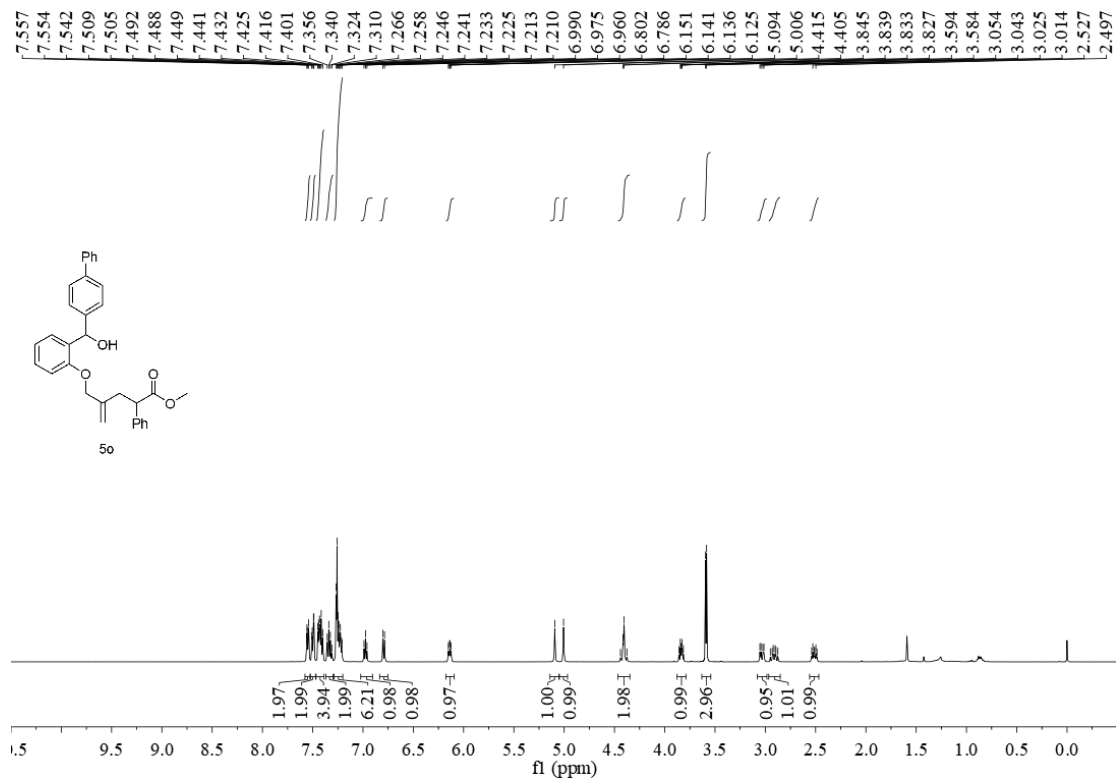
5m:



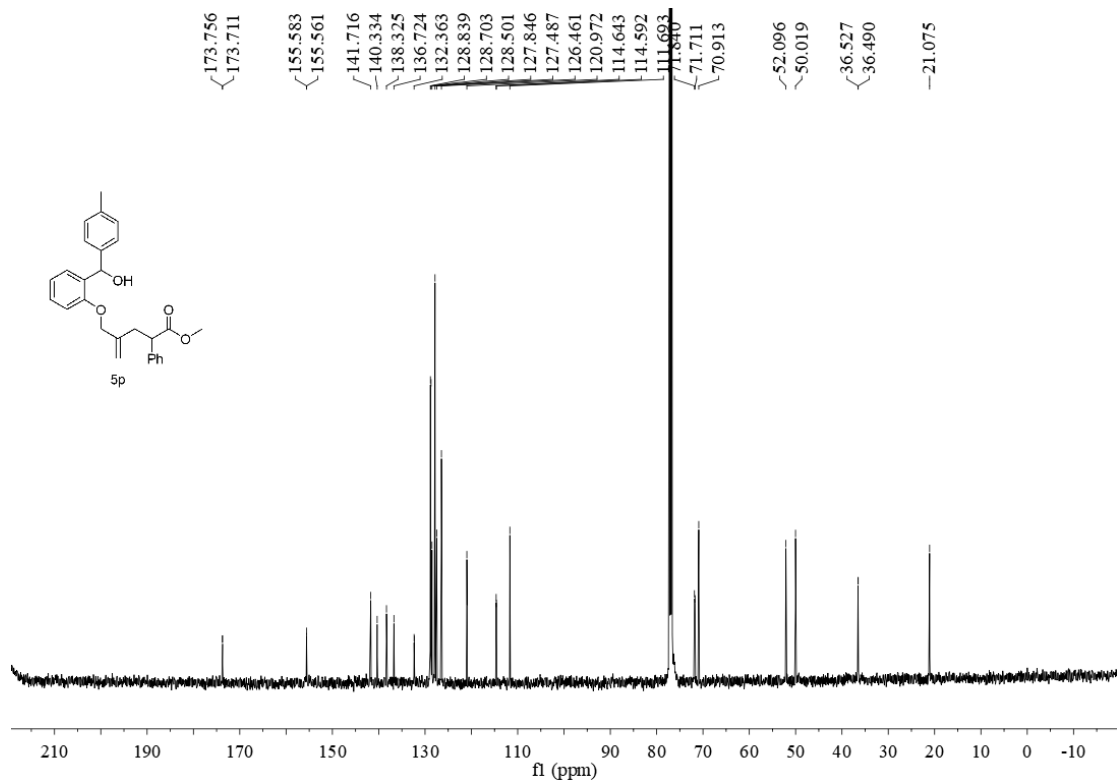
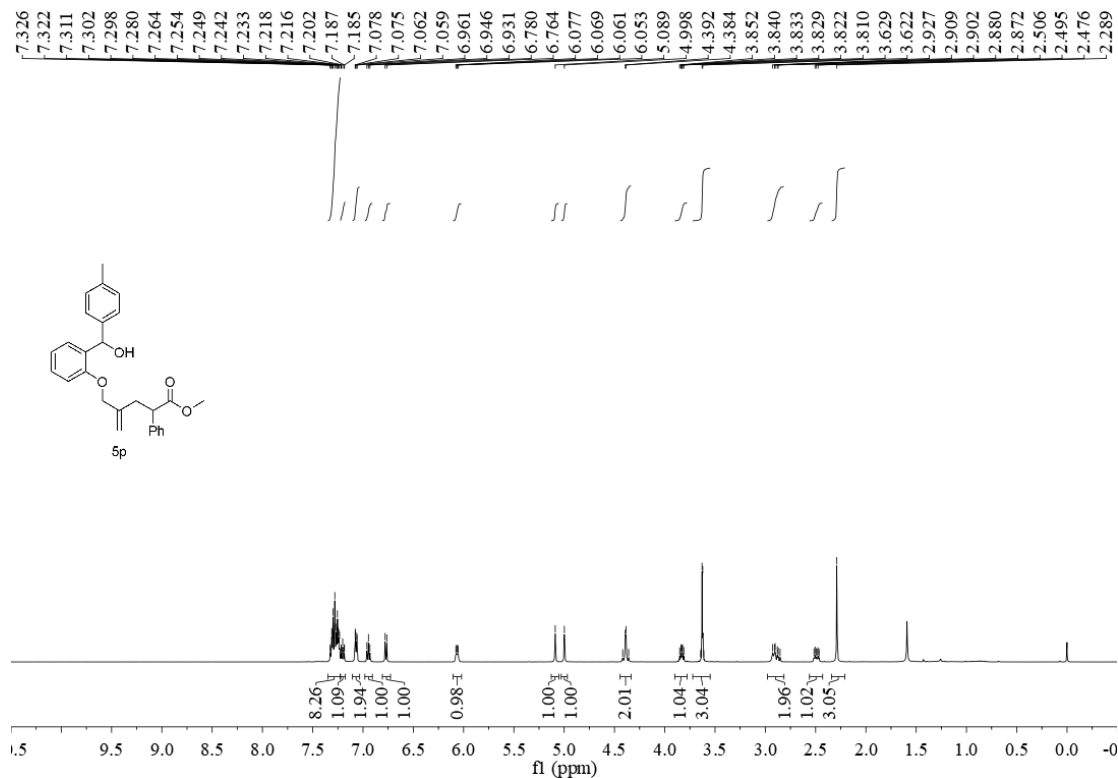
5n:



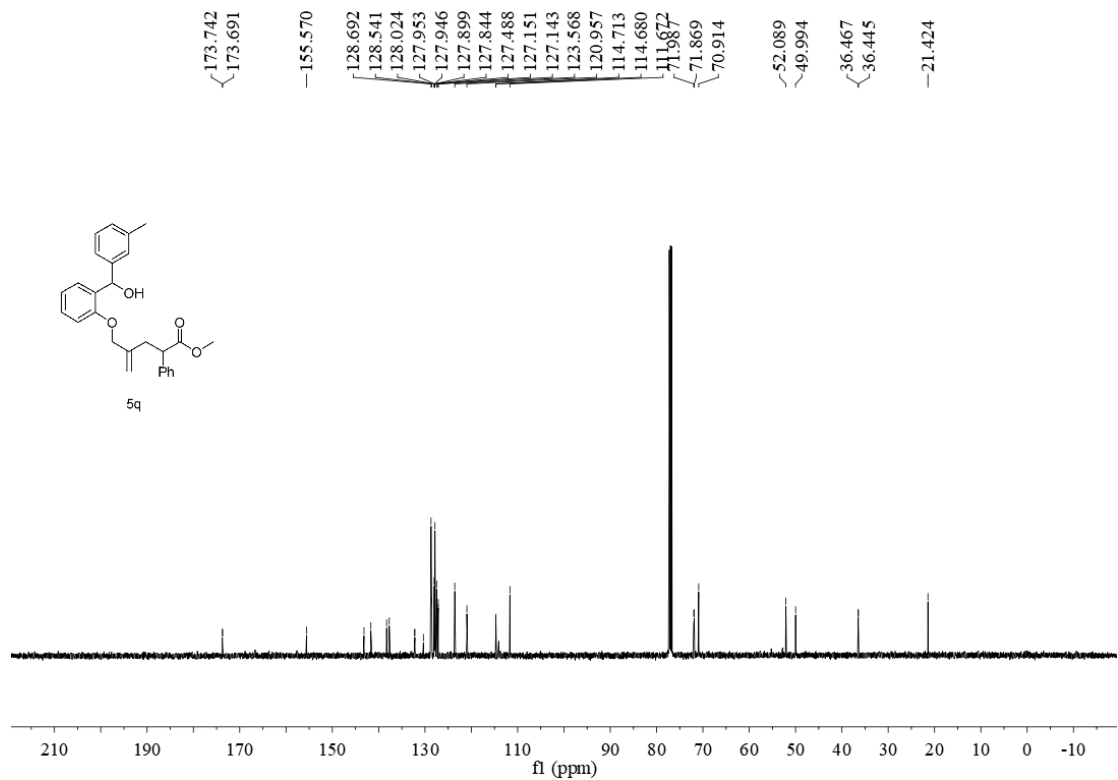
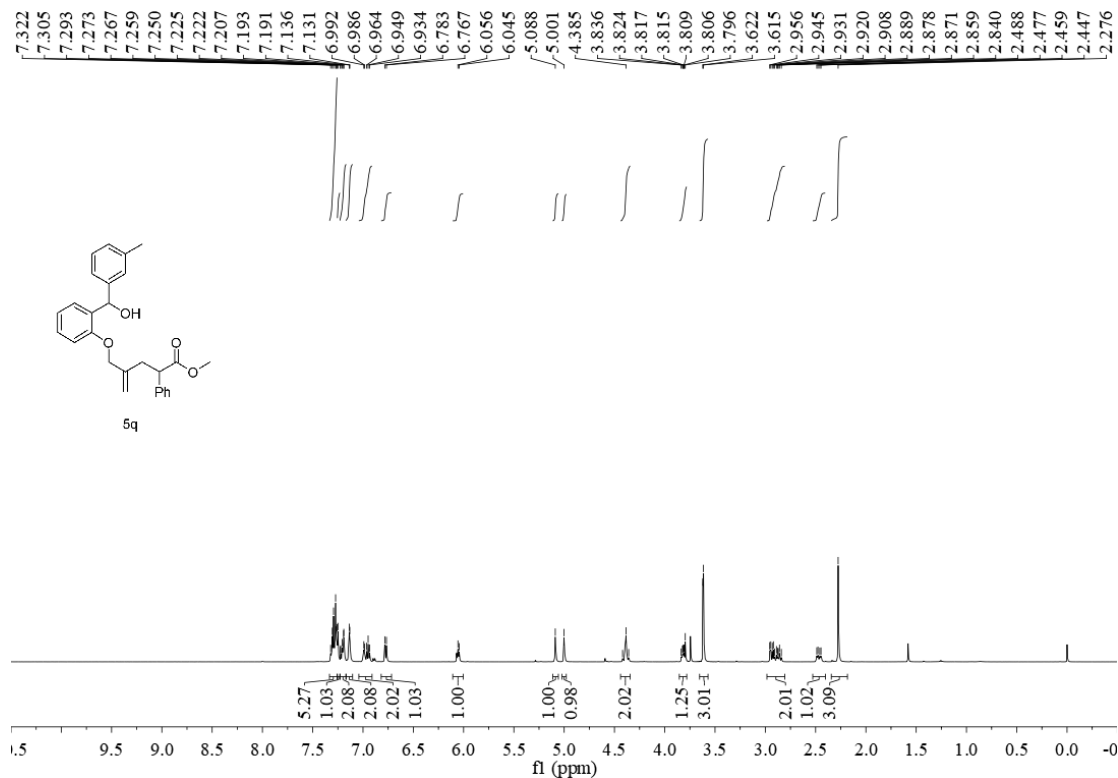
50:



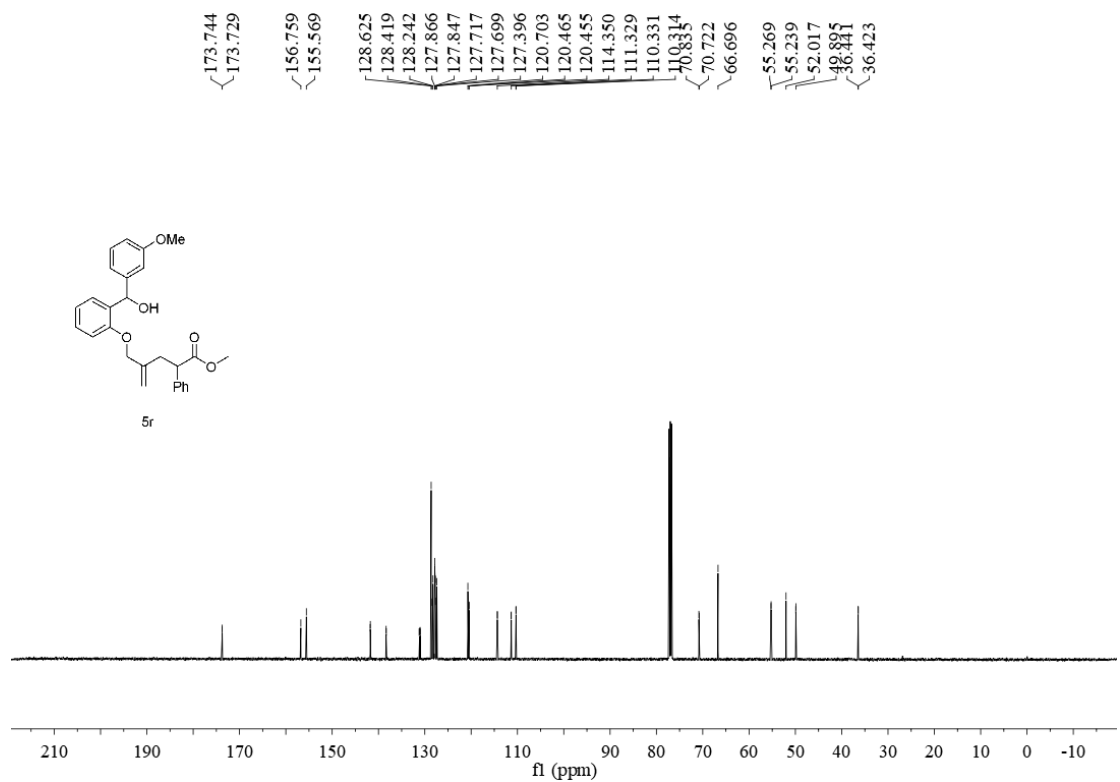
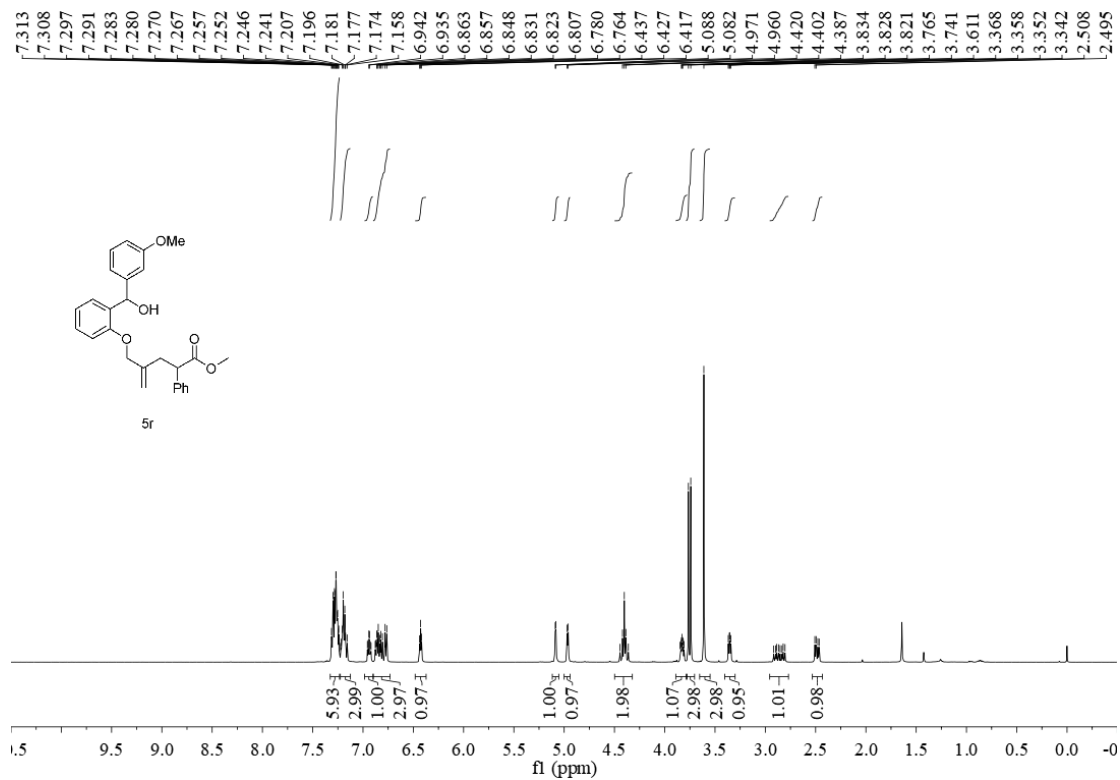
5p:



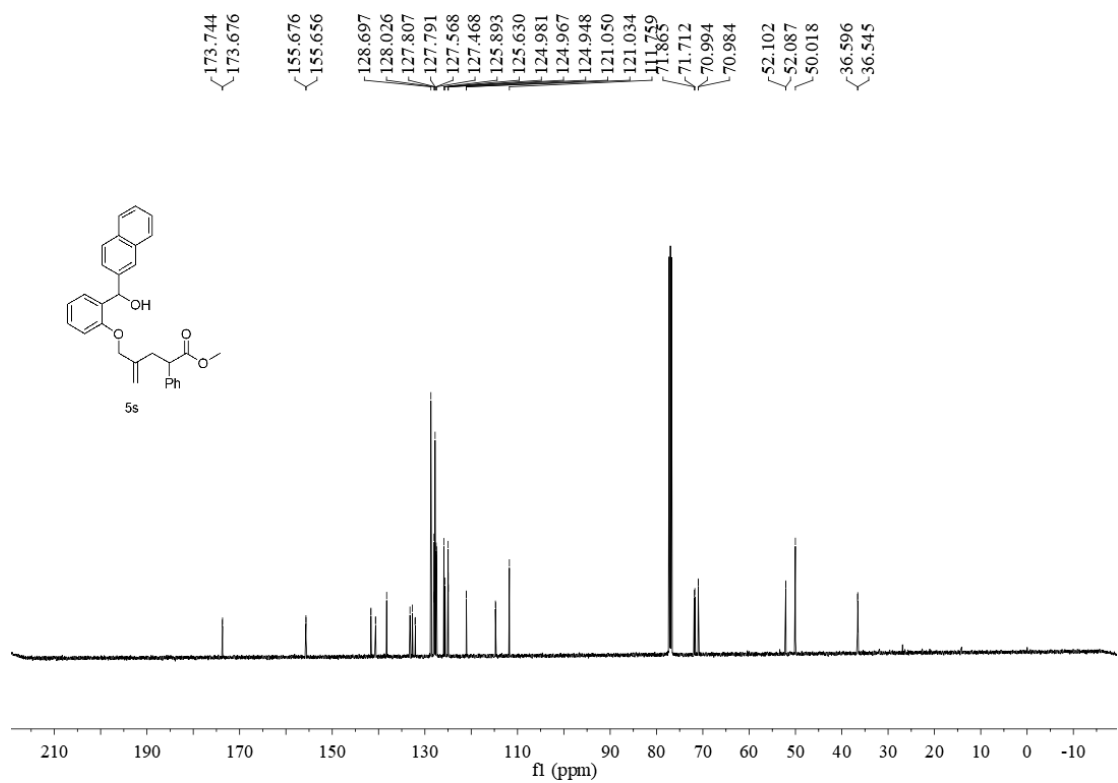
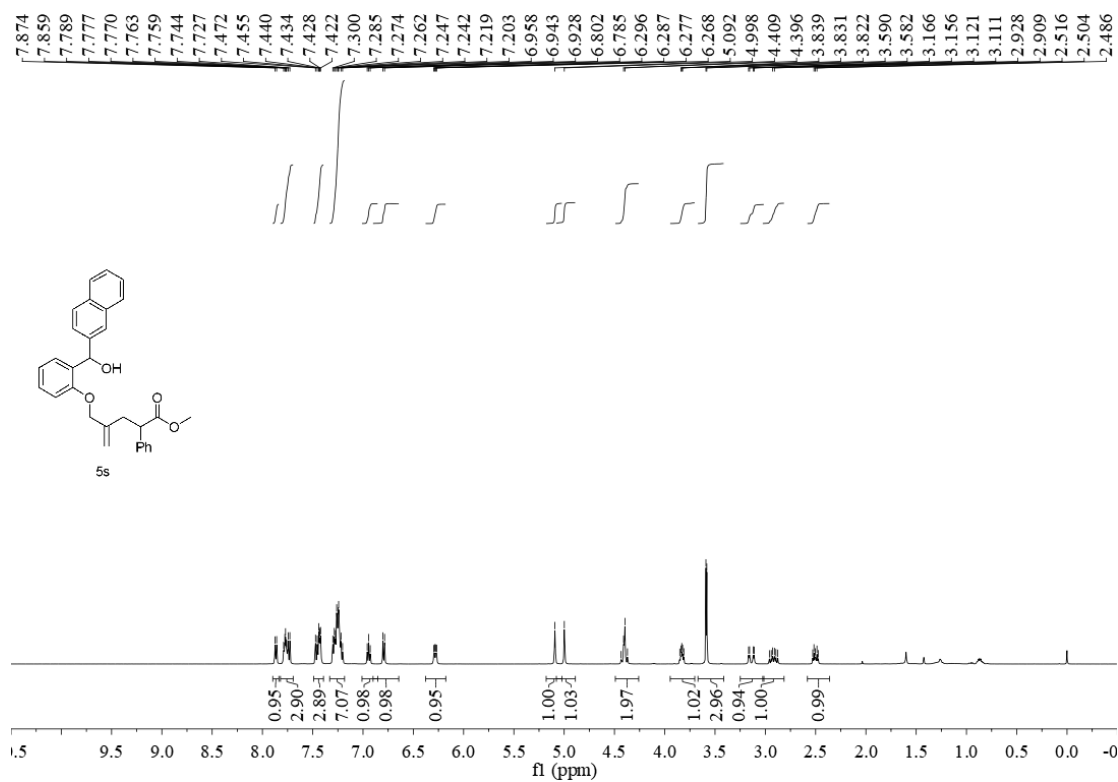
5q:



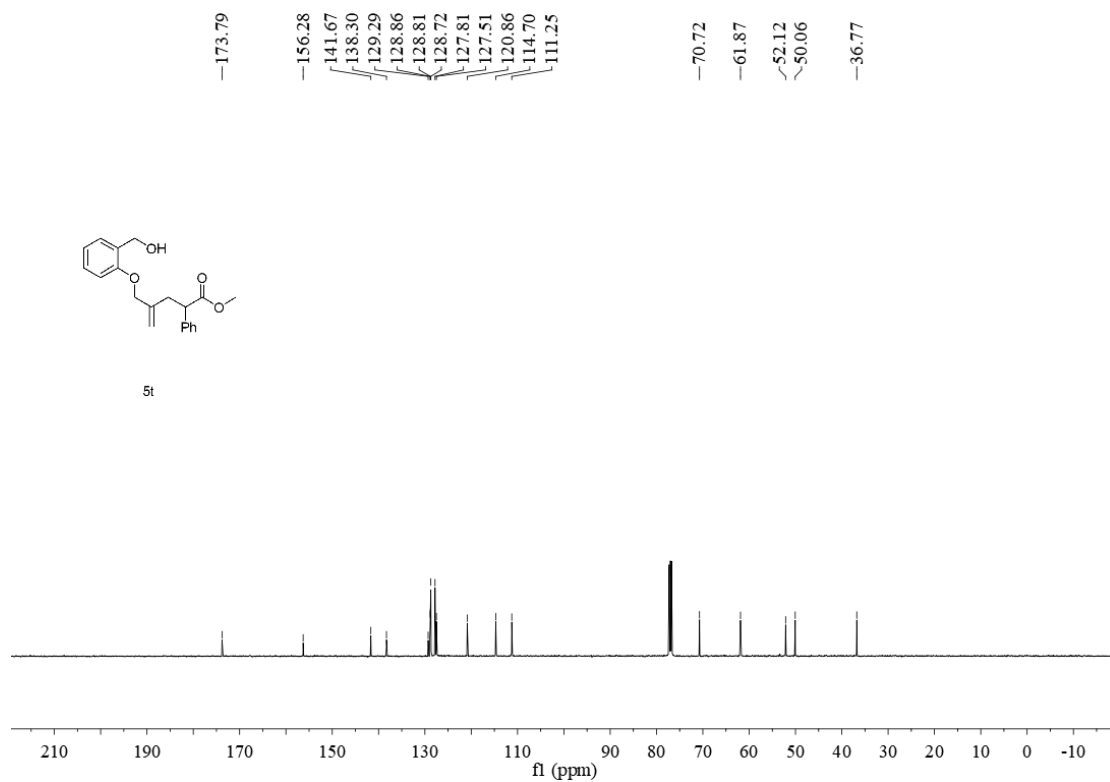
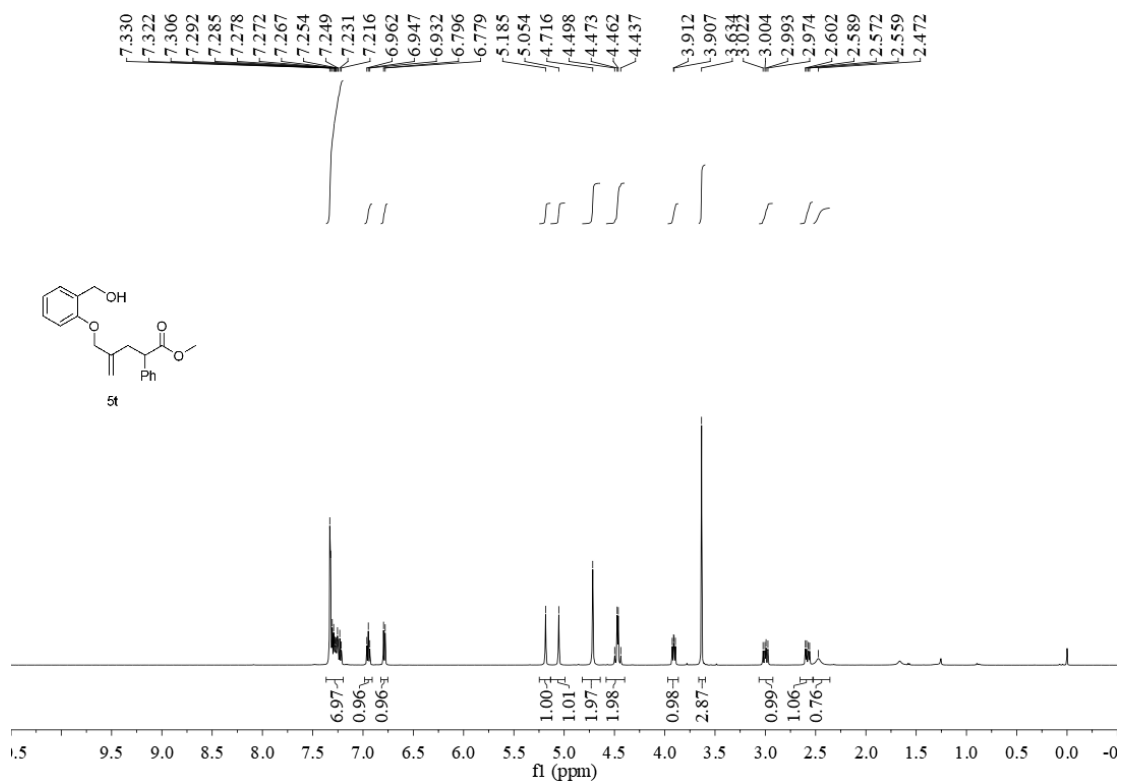
5r:



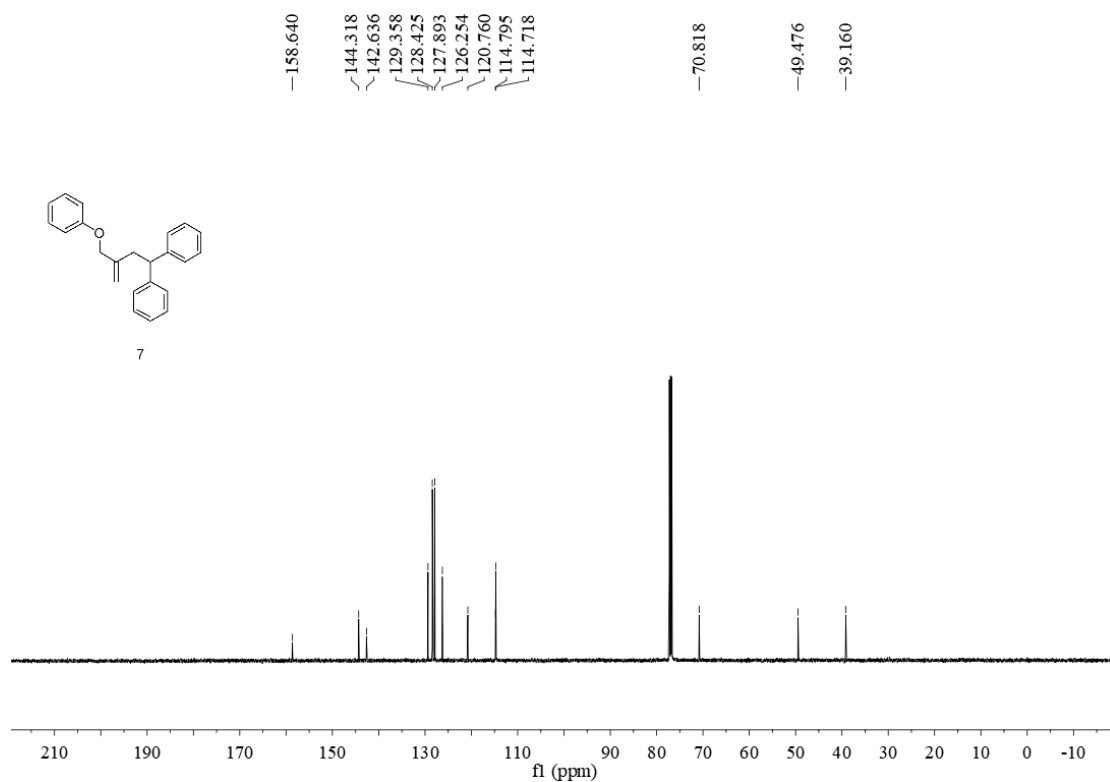
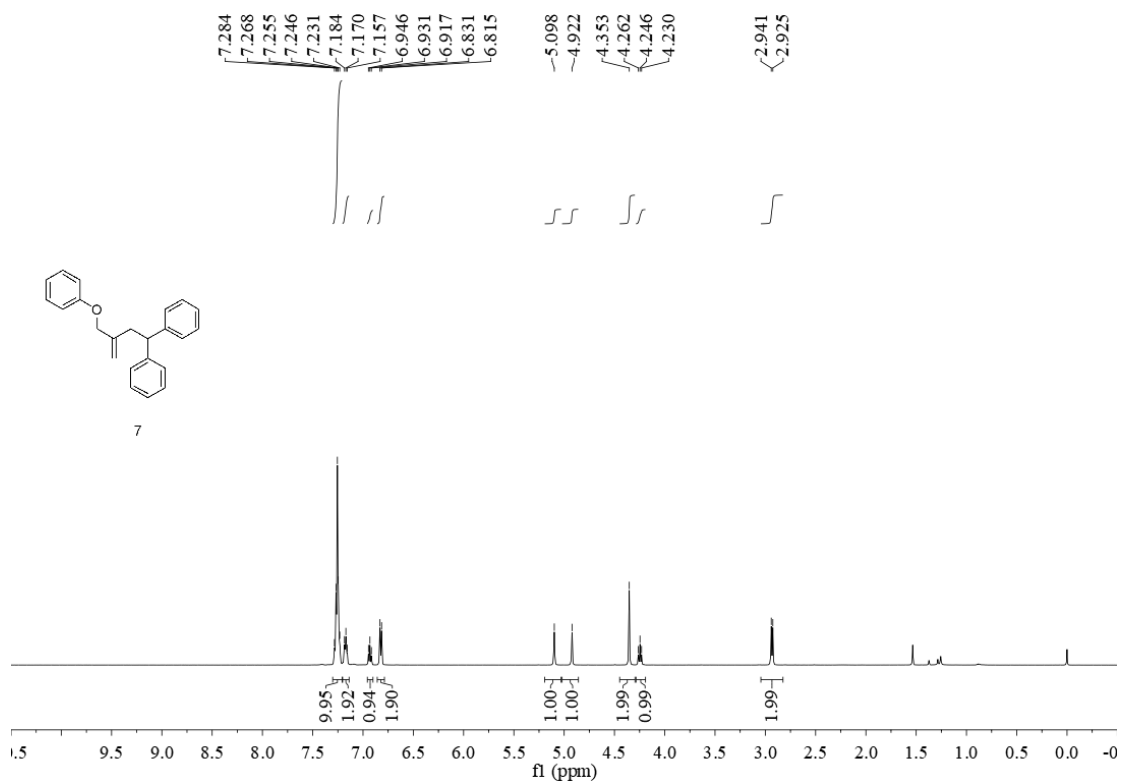
5s:



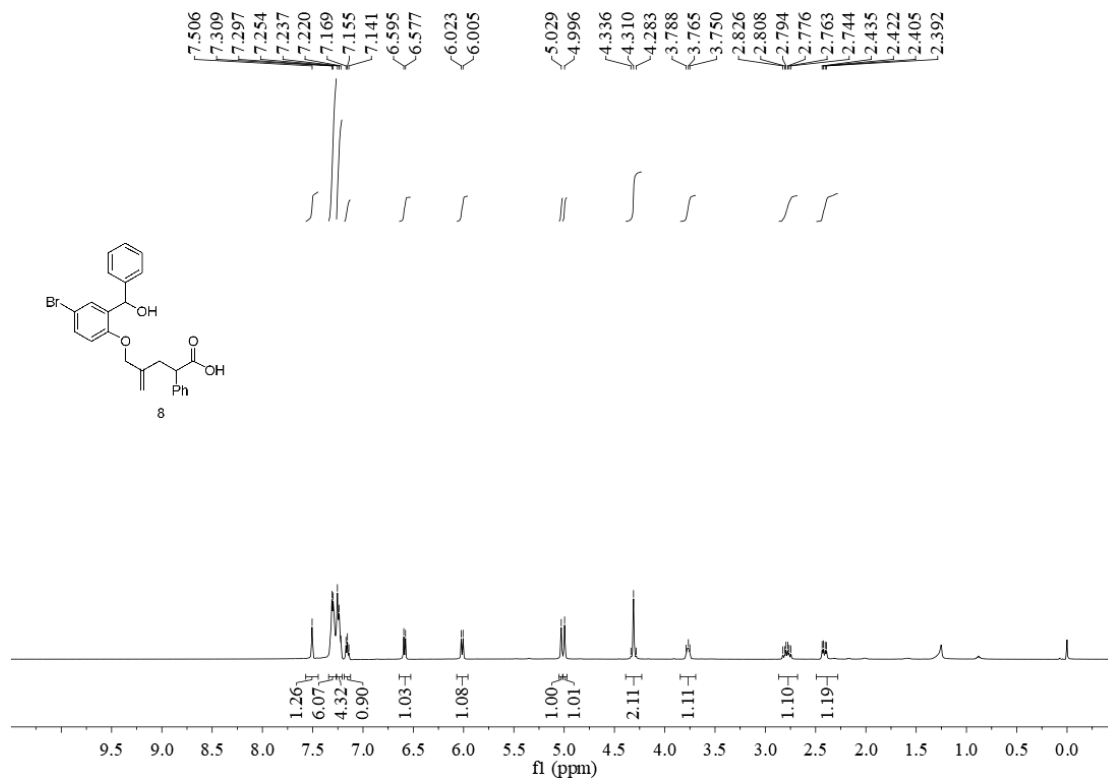
5t:

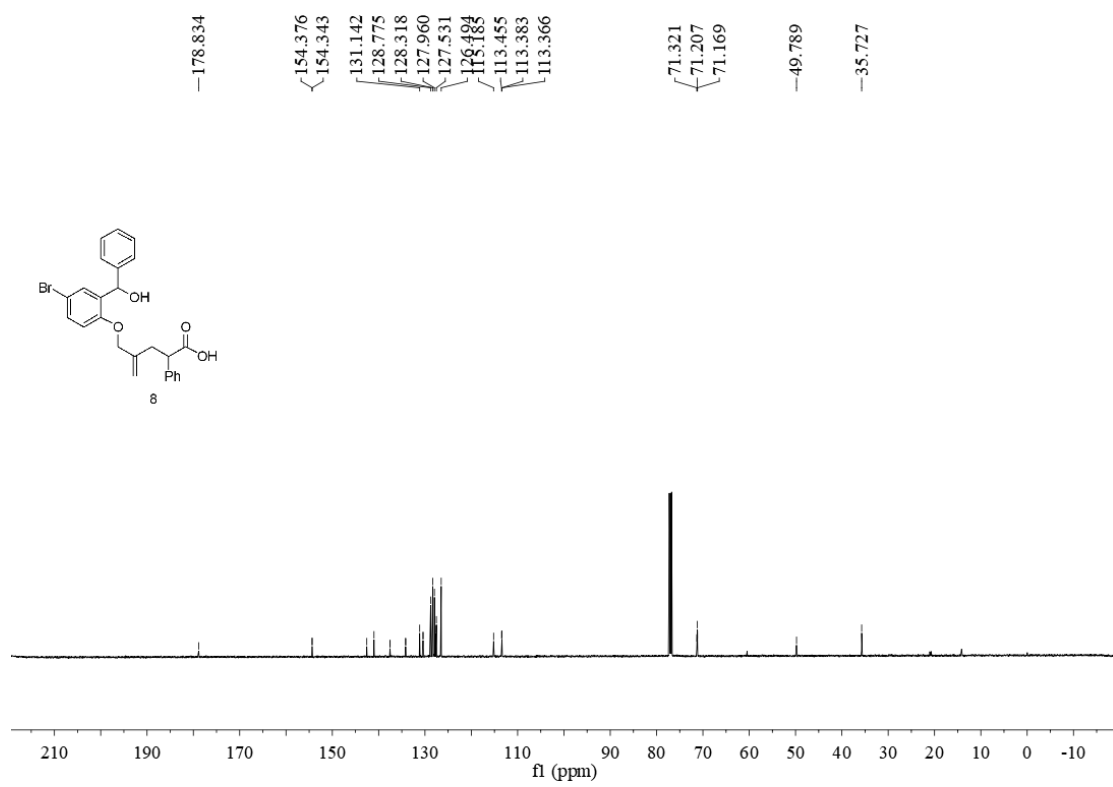


7:

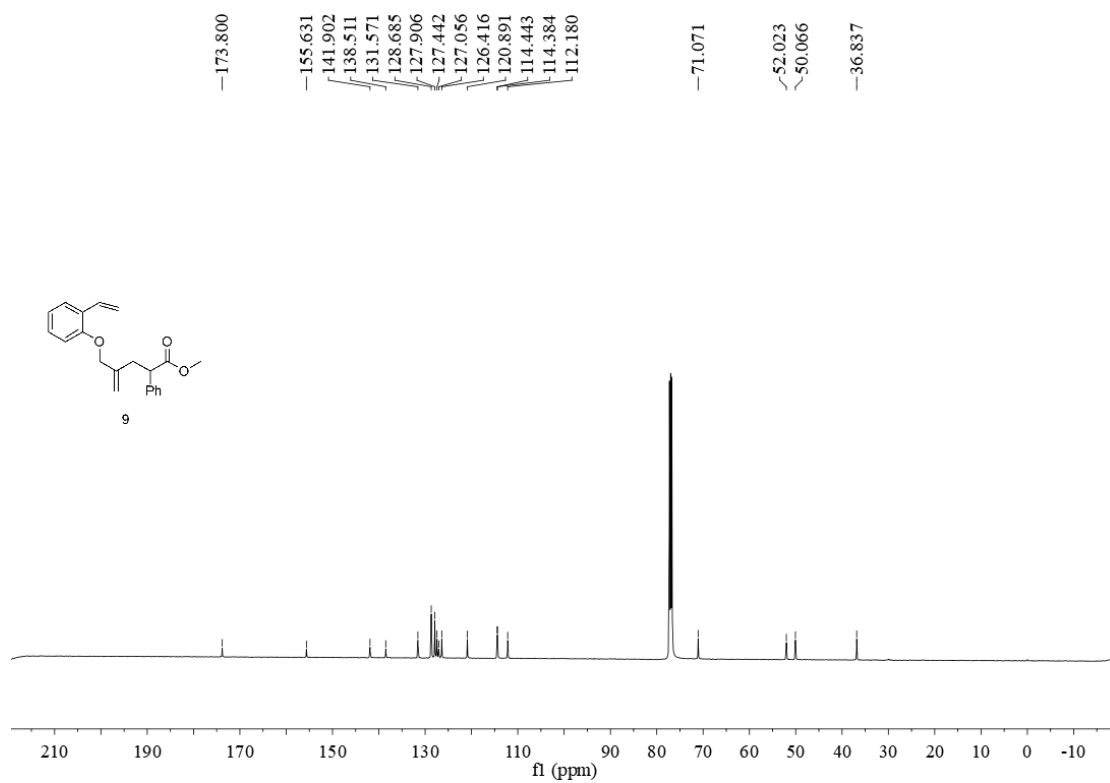
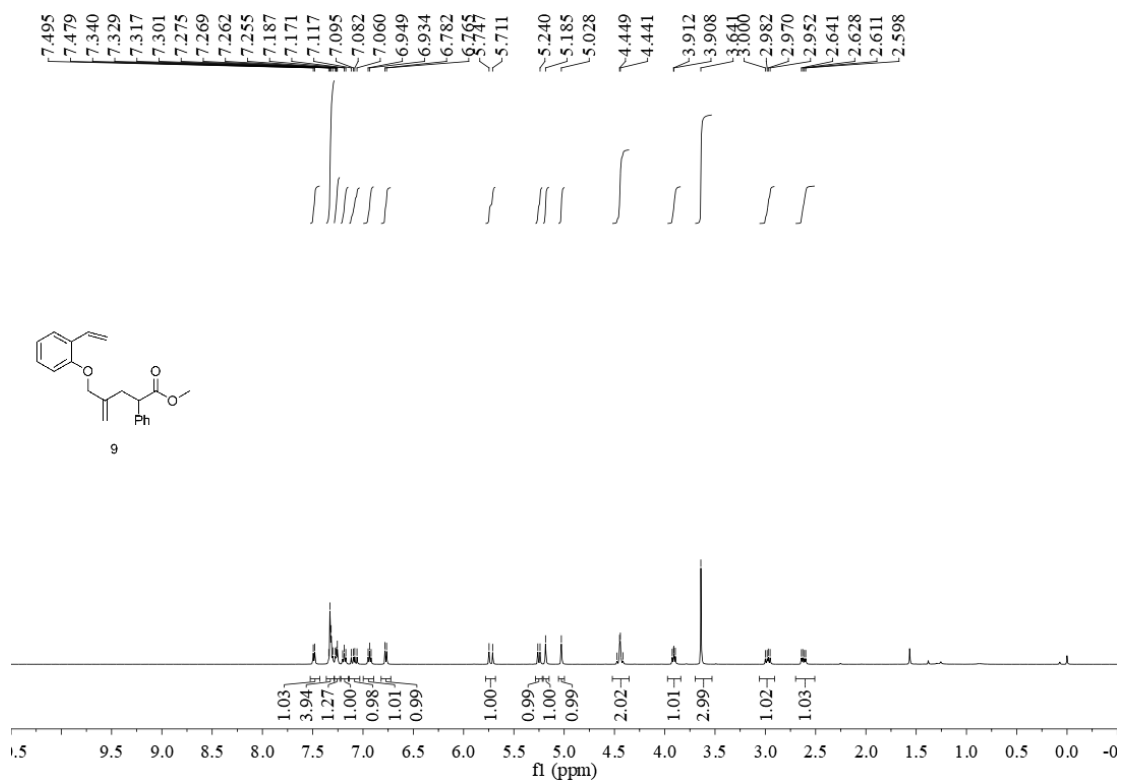


8:

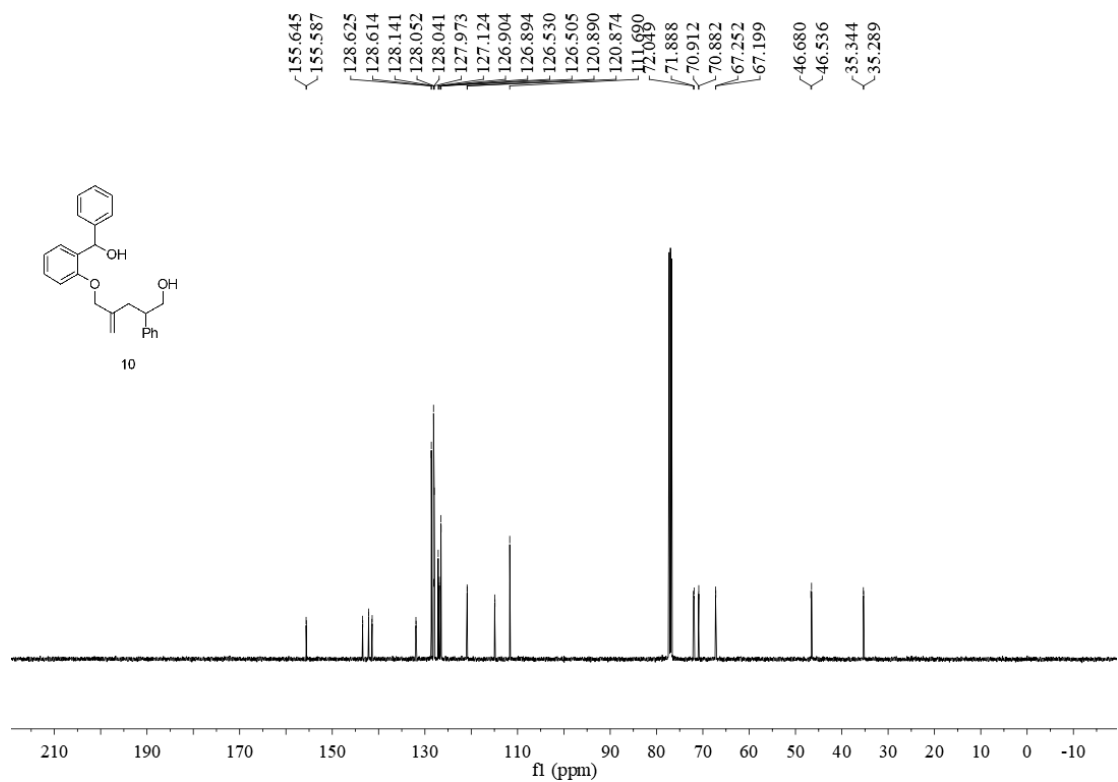
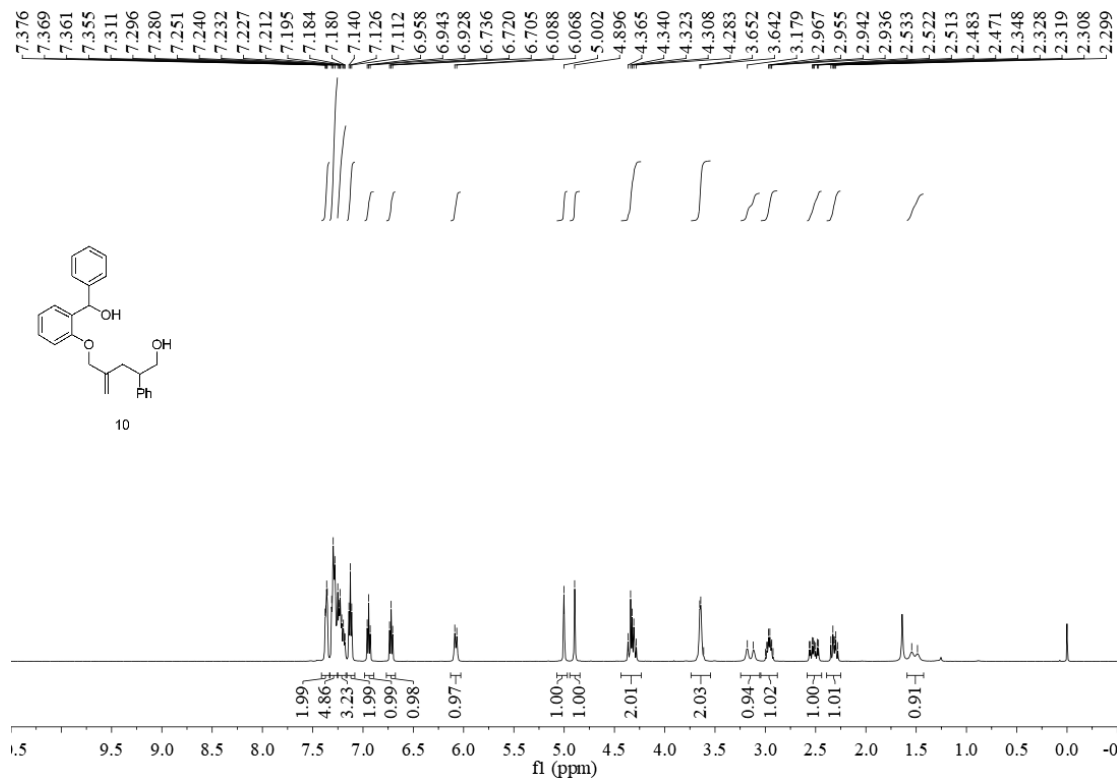




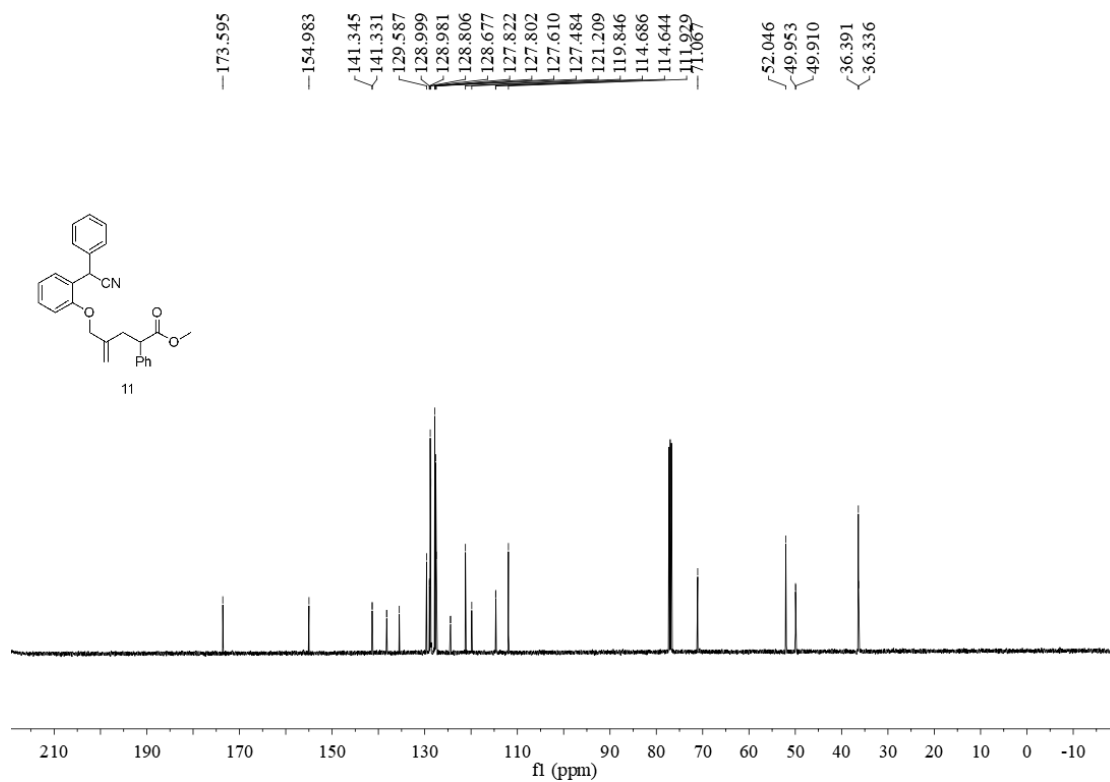
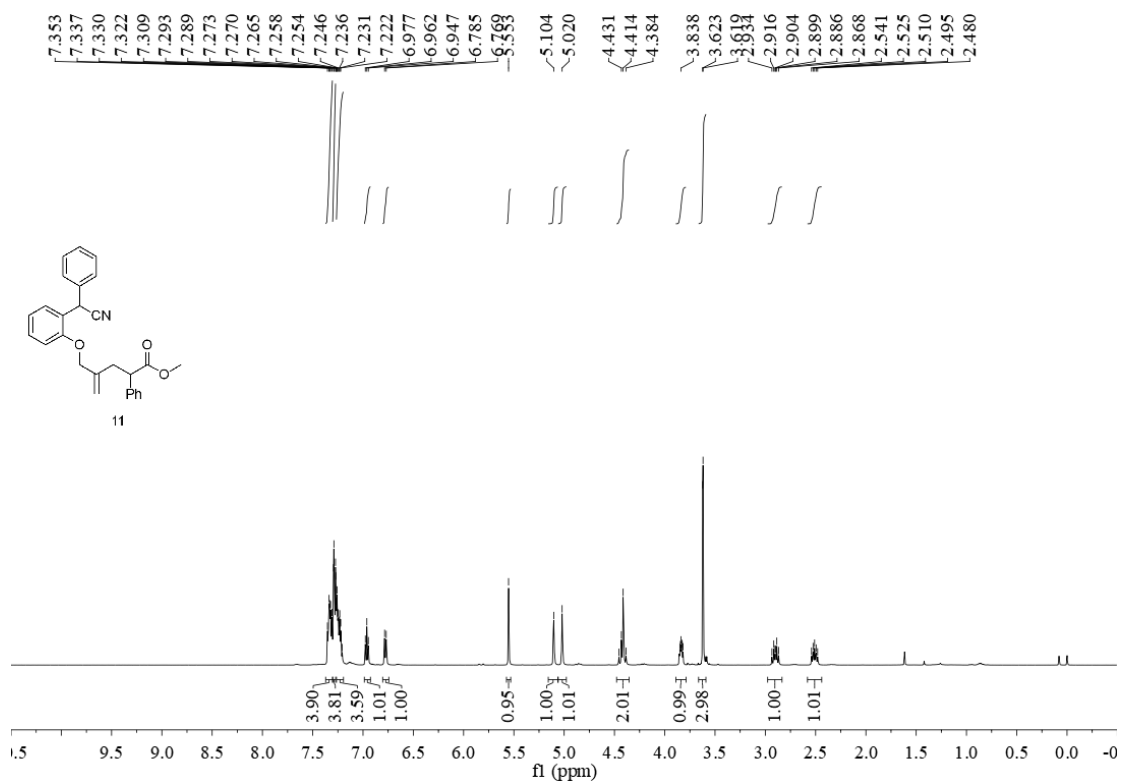
9:



10:



11:



VII. Reference

1. R. Shintani, M. Murakami, T. Hayashi, γ -Methylidene- δ -valerolactones as a Coupling Partner for Cycloaddition: Palladium-Catalyzed [4 + 3] Cycloaddition with Nitrones. *J. Am. Chem. Soc.* 2007, **129**, 12356.
2. R. Shintani, M. Murakami, T. Hayashi, Stereoselective Synthesis of Nipecotnic Acid Derivatives via Palladium-Catalyzed Decarboxylative Cyclization of γ -Methylidene- δ -valerolactones with Imines. *Org. Lett.* 2009, **11**, 457.
3. S. Park, R. Shintani, T. Hayashi, Palladium-catalyzed Decarboxylative [4+1] Cyclization of γ -Methylidene- δ -valerolactones with Isocyanides. *Chem. Lett.* 2009, **38**, 204.
4. R. Shintani, K. Ikehata, T. Hayashi, Synthesis of Nine-Membered Azlactones by Palladium-Catalyzed Ring-Expansion of γ -Methylidene- δ -valerolactones with Aziridines. *J. Org. Chem.* 2011, **76**, 4776.
5. J. Zhou, W.-J. Huang, G.-F. Jiang, Synthesis of Chiral Pyrazolone and Spiropyrazolone Derivatives through Squaramide-Catalyzed Reaction of Pyrazolin-5-ones with *o*-Quinone Methides. *Org. Lett.* 2018, **20**, 1158.
6. W. Zhao, Z. Wang, B. Chu, J. Sun, Enantioselective Formation of All-Carbon Quaternary Stereocenters from Indoles and Tertiary Alcohols Bearing a Directing Group. *Angew. Chem., Int. Ed.* 2015, **54**, 1910.