

Supporting Information

Expedient Synthesis of Highly Functionalized 1,3-Dienes by Employing Cyclopropenes as C_4 Units

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General methods:

All reactions were carried out in flame or oven-dried glassware under nitrogen atmosphere with freshly distilled dry solvents under anhydrous conditions unless otherwise indicated. Flash column chromatography was performed with silica gel (200 - 300 mesh). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm or by staining with base solution of potassium permanganate and molybdate. NMR spectra were recorded at room temperature on 400 MHz Bruker spectrometers and 400 MHz JEOL spectrometers. The residual solvent signals were taken as the reference (0.00 ppm for ^1H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in CDCl_3). Chemical shift (δ) is reported in ppm, coupling constants (J) are given in Hz. The following abbreviations classify the multiplicity: s = singlet, d = doublet, t = triplet, m = multiplet, dd = doublet of doublet. HRMS (ESI) spectra were recorded on a Waters Q-ToF premier TM mass spectrometer.

Table S1 Optimization of reaction conditions^a

entry	catalyst	solvent	yield ^b (%)
1	AgNO ₃ ^c	DCM	10
2	Cu(OH) ₂ ^c	DCM	0
3	Rh ₂ (OAc) ₄	DCM	15
4	Rh ₂ (OAc) ₄	DCE	7
5	Rh ₂ (OAc) ₄	Tol.	10
6	Rh ₂ (OAc) ₄	THF	21
7	Rh ₂ (OAc) ₄	Et ₂ O	27
8	Rh ₂ (OAc) ₄	CF ₃ CH ₂ OH	29
9	Rh ₂ (OAc) ₄	HFIP	68
10	Rh₂(OAc)₄	HFIP:DCE = 9:1	84
11	Rh ₂ (TFA) ₄	HFIP:DCE = 9:1	8
12	Rh ₂ (Oct) ₄	HFIP:DCE = 9:1	27
13	Rh ₂ (esp) ₂	HFIP:DCE = 9:1	70

^a Reaction conditions are as follows if no otherwise noted: **1a** (0.20 mmol), **2a** (0.40 mmol) and catalyst (1.0 mol %) were stirred in 2.00 mL solution at room temperature under nitrogen atmosphere until **1a** was consumed completely. ^b Isolated yield. ^c 10 mol % DCM = dichloromethane, DCE = 1,2-dichloroethane, Tol. = toluene, THF = tetrahydrofuran, HFIP = hexafluoroisopropanol.

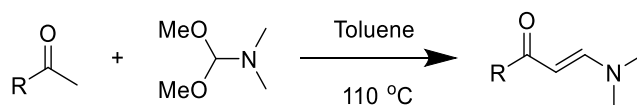
Table S2 Optimization of the leaving groups^a

2	product ^b	2	product ^b
	3aa, 84%		3aa, 65%
	no reaction		3aa, 32%
	decompose		 3aa', 61% (E/Z = 1 : 1)
	3aa, 53%		

^a Conditions: **1a** (0.20 mmol), **2** (0.40 mmol) and Rh₂(OAc)₄ (1.0 mol %) were stirred in 2.00 mL solution (HFIP:DCE = 9:1) under nitrogen atmosphere. ^b Isolated yields.

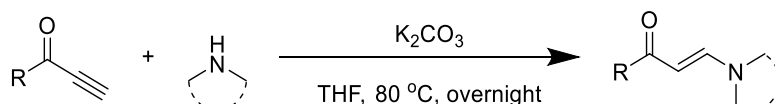
General procedure for enamines and their spectra data:

General procedure A¹:



To a stirred solution of ketone (5.0 mmol, 1.0 equiv.) in toluene (5.0 mL), 1,1-dimethoxy-*N,N*-dimethylmethanamine (7.0 mmol, 1.4 equiv.) was added and stirred at 110 °C. After completion of the reaction (monitored by TLC), it was quenched with water, extracted with ethyl acetate and dried with anhydrous Na₂SO₄. Then the reaction mixture was concentrated under reduced pressure and purified by column chromatography (hexane : ethyl acetate = 1 : 1) to give the desired product.

General procedure B²:



To a stirred solution of acetylenic ketone (3.0 mmol, 1.0 equiv.) and potassium carbonate (2.0 mmol, 2.0 equiv.) in 10 mL of THF, amine (3.0 mmol, 1.0 equiv.) was added dropwise and stirred at 80 °C. After completion of the reaction (monitored by TLC), the reaction mixture is concentrated under reduced pressure and purified by column chromatography to give the desired product.

The spectroscopic properties of these compounds were consistent with literature data: 1a, 1b, 1e-1g, 1i,1k,1m,1n,1p,1r-1t;³ 1c;⁴ 1h, 1j, 1q, 1u;⁵1v, 1w;⁶ 1d;⁷1l;⁸ 1o.⁹

¹ Y. Jiang, V. Y. K. Zhong, L. Emmanuvel and C.-M. Park, *Chem. Commun.*, 2012,**48**, 3133–3135.

² L. Šenica, U. Grošelj, M. Kasunič, D. Kočar, B. Stanovnik and J. Svete, *Eur. J. Org. Chem.*, 2014, **15**, 3067–3071.

³ M. Ni, J. Zhang, X. Liang, Y. Jiang and T.-P. Loh, *Chem. Commun.*, 2017,**53**, 12286–12289.

⁴ Y. Tang, Y. Chen, H. Liu and M. Guo, *Tetrahedron*, 2018,**59**, 3703-3705.

⁵ X. Liang, P. Guo, W. Yang, M. Li, C. Jiang, W. Sun, T.-P. Loh and Y. Jiang, *Chem. Commun.*, 2020,**56**, 2043–2046.

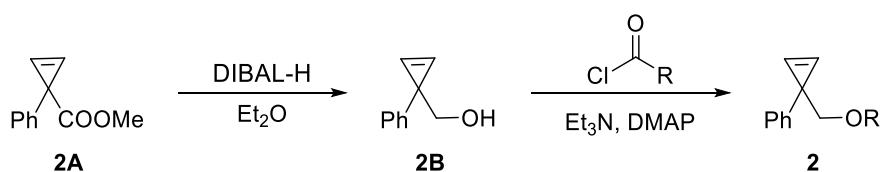
⁶ J. Chen, P. Guo, J. Zhang, J. Rong, W. Sun, Y. Jiang and T.-P. Loh, *Angew. Chem., Int. Ed.*, 2019,**58**, 12674–12679.

⁷ S. Zhou, J. Wang, L. Wang, C. Song, K. Chen and J. Zhu, *Angew. Chem., Int. Ed.*, 2016, **55**, 9384–9388.

⁸ G. Liang, J. Rong, W. Sun, G. Chen, Y. Jiang and T.-P. Loh, *Org. Lett.*, 2018, **20**, 7326–7331.

⁹ B. Qi, S. Guo, W. Zhang, X. Yu, C. Song and J. Zhu, *Org. Lett.*, 2018, **20**, 3996–3999.

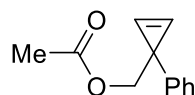
General procedure for the synthesis of cyclopropenes¹⁰:



Compounds **2A** were prepared according to literature procedures. To a stirred at $-78\text{ }^{\circ}\text{C}$ solution of ester **2A** (25 mmol, 1.0 equiv.) in dry ether, DIBAL-H (1.0 M solution in hexane, 50 mmol, 2.0 equiv.) was added dropwise. The mixture was stirred for 1 hour at $-78\text{ }^{\circ}\text{C}$, then additionally for 1 hour at room temperature. Then, the mixture was quenched (saturated NH_4Cl), acidified (aqueous HCl), and extracted (ether). Combined organic phases were washed (NaHCO_3 , brine), dried (MgSO_4), filtered, and concentrated. The residue was purified by preparative column chromatography on Silica gel, eluent hexane-EtOAc 3:1 to give alcohol **2B**.

To a stirred solution of alcohol **2B** (5.0 mmol, 1.0 equiv.), 4-(dimethylamino)pyridine (DMAP, 0.5 mmol, 10 mol %), and triethylamine (Et_3N , 7.5 mmol, 1.5 equiv.) in anhydrous CH_2Cl_2 (10 mL) was added acyl chloride (1.5 equiv.). The mixture was stirred at room temperature. After completion of the reaction (monitored by TLC), the solution was quenched (water) and extracted (CH_2Cl_2). Combined organic phases were washed (diluted aqueous HCl , saturated NaHCO_3 , brine), dried (MgSO_4), filtered, and concentrated in *vacuo*. The residue was purified by preparative column chromatography on silica gel, eluent Petroleum ether-EtOAc to give product **2**.

(1-Phenylcycloprop-2-en-1-yl)methyl acetate (**2a**):

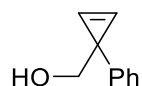


The title compound was prepared according to the general procedure (EA/PE = 1/20, $R_f = 0.28$). The product was obtained as colorless liquid in 86% yield (809.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.31 – 7.28 (m, 2H), 7.23 - 7.21 (m, 2H), 7.21 - 7.18 (m, 3H), 4.52 (s, 2H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 145.5, 128.1,

¹⁰ M. Rubina, M. Rubin and V. Gevorgyan, *J. Am. Chem. Soc.*, 2004, **126**, 3688–3689.

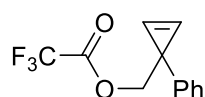
126.2, 125.8, 112.0, 71.2, 25.9, 21.0; HRMS (ESI) m/z $[M+H]$: Calcd for $C_{12}H_{13}O_2$: 189.0916. Found: 189.0913.

(1-Phenylcycloprop-2-en-1-yl)methanol (2aa):



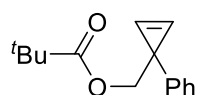
The title compound was prepared according to the general procedure (EA/PE = 1/5, R_f = 0.21). The product was obtained as white solid in 72% yield (2647.4 mg), Mp. 58 – 59°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 2H), 7.25 – 7.21 (t, J = 8.0 Hz, 2H), 7.17 – 7.15 (m, 2H), 7.13 – 7.10 (t, J = 7.2 Hz, 1H), 4.00 (s, 2H), 1.39 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.7, 128.1, 126.2, 125.7, 112.9, 67.8, 28.9; HRMS (ESI) m/z $[M+H]$: Calcd for $C_{10}H_{11}O$: 147.0810. Found: 147.0811.

(1-Phenylcycloprop-2-en-1-yl)methyl 2,2,2-trifluoroacetate (2ab):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.31). The product was obtained as colorless liquid in 78% yield (947.8 mg). 1H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.27 (s, 2H), 7.23 – 7.21 (m, 1H), 7.19 – 7.16 (m, 2H), 4.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6 (q, J = 41.9 Hz), 144.1, 128.4, 126.3, 126.1, 114.6 (q, J = 284.3 Hz), 111.7, 75.0, 25.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.86; HRMS (ESI) m/z $[M+H]$: Calcd for $C_{12}H_{10}F_3O_2$: 243.0633. Found: 243.0635.

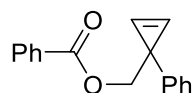
(1-Phenylcycloprop-2-en-1-yl)methyl pivalate (2ac):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.35). The product was obtained as colorless liquid in 86% yield (993.8 mg). 1H

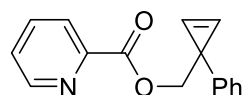
NMR (400 MHz, CDCl₃) δ 7.35 – 7.31 (m, 2H), 7.26 (m, 3H), 7.24 – 7.19 (m, 2H), 4.55 (s, 2H), 1.21 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 178.3, 145.5, 127.9, 126.1, 125.6, 111.9, 70.4, 38.7, 27.1, 25.9; HRMS (ESI) m/z [M+H]: Calcd for C₁₅H₁₉O₂: 231.1385. Found: 231.1382.

(1-Phenylcycloprop-2-en-1-yl)methyl benzoate (2ad):



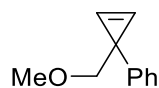
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.40). The product was obtained as colorless liquid in 75% yield (941.6 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.11 – 8.09 (m, 2H), 7.60 – 7.56 (m, 1H), 7.48 – 7.44 (m, 2H), 7.40 – 7.33 (m, 6H), 7.28 – 7.24 (m, 1H), 4.84 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 145.5, 132.8, 130.3, 129.5, 128.2, 128.1, 126.1, 125.7, 111.8, 71.6, 26.0; HRMS (ESI) m/z [M+H]: Calcd for C₁₇H₁₅O₂: 251.1072. Found: 251.1066.

(1-Phenylcycloprop-2-en-1-yl)methyl picolinate (2ae):



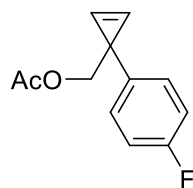
The title compound was prepared according to the general procedure (EA/PE = 1/4, R_f = 0.33). The product was obtained as white solid in 74% yield (932.7 mg), Mp. 47 – 48 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.72 – 8.70 (m, 1H), 8.03 – 8.01 (m, 1H), 7.76 – 7.72 (m, 1H), 7.40 – 7.37 (m, 1H), 7.29 – 7.27 (m, 1H), 7.26 – 7.24 (m, 5H), 7.17 – 7.13 (m, 1H), 4.85 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.7, 149.7, 147.8, 145.1, 136.7, 127.9, 126.5, 126.0, 125.6, 124.9, 111.5, 71.6, 25.8; HRMS (ESI) m/z [M+H]: Calcd for C₁₆H₁₄NO₂: 252.1025. Found: 252.1029.

(1-(Methoxymethyl)cycloprop-2-en-1-yl)benzene (2af):



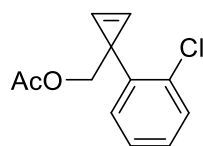
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.35). The product was obtained as colorless liquid in 80% yield (644.0 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.31 (m, 4H), 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 1H), 3.89 (s, 2H), 3.43 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 127.9, 126.2, 125.5, 112.5, 79.7, 58.4, 26.5; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{11}\text{H}_{13}\text{O}$: 161.0966. Found: 161.0969.

(1-(4-Fluorophenyl)cycloprop-2-en-1-yl)methyl acetate (2b):



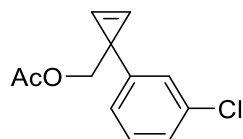
The title compound was prepared according to the general procedure (EA/PE = 1/19, R_f = 0.30). The product was obtained as yellow liquid in 83% yield (859.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.24 (s, 2H), 7.17 – 7.13 (m, 2H), 6.98 – 6.94 (m, 2H), 4.47 (s, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 161.0 (d, J = 242.1 Hz), 141.1 (d, J = 3.3 Hz), 127.6 (d, J = 7.9 Hz), 114.7 (d, J = 21.0 Hz), 112.2, 71.0, 25.3, 20.8; ^{19}F NMR (376 MHz, CDCl_3) δ -117.36; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{12}\text{H}_{12}\text{FO}_2$: 207.0821. Found: 207.0820.

(1-(2-Chlorophenyl)cycloprop-2-en-1-yl)methyl acetate (2c):



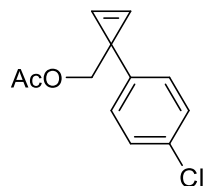
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.31). The product was obtained as yellow liquid in 71% yield (791.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.46 (s, 2H), 7.24 – 7.22 (m, 1H), 7.19 – 7.17 (m, 1H), 7.13 – 7.07 (m, 2H), 4.23 (s, 2H), 1.92 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 142.0, 134.1, 130.7, 129.6, 128.1, 127.0, 116.1, 70.7, 26.9, 20.9; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{12}\text{H}_{12}\text{ClO}_2$: 223.0526. Found: 223.0530.

(1-(3-Chlorophenyl)cycloprop-2-en-1-yl)methyl acetate (2d):



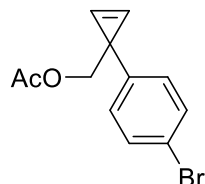
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.29). The product was obtained as yellow liquid in 73% yield (813.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.13 – 7.10 (m, 3H), 7.06 – 7.04 (m, 2H), 7.01 – 6.99 (m, 1H), 4.38 (s, 2H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 147.7, 134.0, 129.2, 126.4, 125.8, 124.3, 111.5, 70.7, 25.6, 20.8; HRMS (ESI) m/z [M+H]: Calcd for $\text{C}_{12}\text{H}_{12}\text{ClO}_2$: 223.0526. Found: 223.0536.

(1-(4-Chlorophenyl)cycloprop-2-en-1-yl)methyl acetate (2e):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.33). The product was obtained as yellow liquid in 82% yield (914.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.23 (m, 1H), 7.23 – 7.22 (m, 3H), 7.13 – 7.11 (m, 1H), 7.10 – 7.09 (m, 1H), 4.47 (s, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.0, 143.9, 131.4, 128.0, 127.5, 111.8, 70.9, 25.4, 20.9; HRMS (ESI) m/z [M+H]: Calcd for $\text{C}_{12}\text{H}_{12}\text{ClO}_2$: 223.0526. Found: 223.0525.

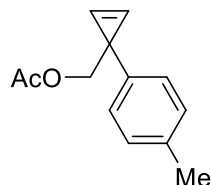
(1-(4-Bromophenyl)cycloprop-2-en-1-yl)methyl acetate (2f):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.31). The product was obtained as yellow liquid in 76% yield (1014.5 mg). ^1H

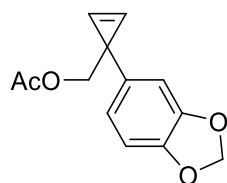
NMR (400 MHz, CDCl₃) δ 7.38 – 7.36 (m, 2H), 7.20 (s, 2H), 7.05 – 7.03 (m, 2H), 4.46 (s, 2H), 2.02 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.7, 144.4, 130.8, 127.8, 119.4, 111.6, 70.6, 25.3, 20.7; HRMS (ESI) m/z [M+H]: Calcd for C₁₂H₁₂BrO₂: 267.0021. Found: 267.0024.

(1-(*p*-Tolyl)cycloprop-2-en-1-yl)methyl acetate (2g):



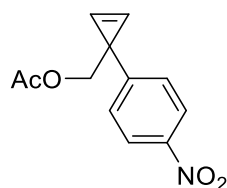
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.34). The product was obtained as yellow liquid in 79% yield (802.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.28 (s, 2H), 7.20 – 7.17 (m, 4H), 4.58 (s, 2H), 2.38 (s, 3H), 2.10 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.0, 142.3, 135.1, 128.7, 125.9, 112.0, 71.1, 25.4, 20.8, 20.7; HRMS (ESI) m/z [M+H]: Calcd for C₁₃H₁₅O₂: 203.1072. Found: 203.1075.

(1-(Benzo[*d*][1,3]dioxol-5-yl)cycloprop-2-en-1-yl)methyl acetate (2h):



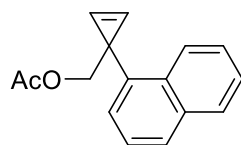
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.32). The product was obtained as yellow liquid in 82% yield (914.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.23 (s, 2H), 6.75 – 6.73 (m, 1H), 6.69 (m, 1H), 6.67 – 6.64 (m, 1H), 5.91 (s, 2H), 4.44 (s, 2H), 2.05 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 171.1, 147.5, 145.6, 139.7, 119.2, 112.5, 107.8, 106.9, 100.8, 71.3, 25.7, 20.9; HRMS (ESI) m/z [M+H]: Calcd for C₁₃H₁₃O₄: 233.0814. Found: 233.0813.

(1-(4-Nitrophenyl)cycloprop-2-en-1-yl)methyl acetate (2i):



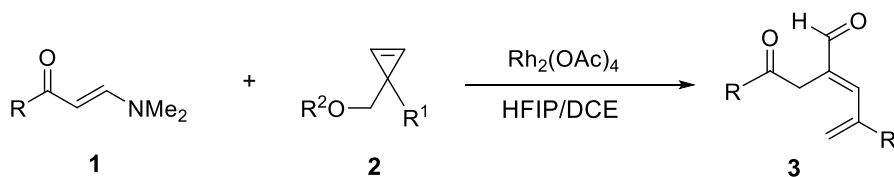
The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.23). The product was obtained as yellow liquid in 77% yield (900.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.13 – 8.11 (m, 2H), 7.36 – 7.34 (m, 2H), 7.27 – 7.26 (m, 2H), 4.53 (s, 2H), 2.06 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 153.5, 145.7, 126.8, 123.1, 110.8, 70.4, 26.0, 20.8; HRMS (ESI) m/z [$\text{M}+\text{H}$]: Calcd for $\text{C}_{12}\text{H}_{12}\text{NO}_4$: 234.0766. Found: 234.0767.

(1-(Naphthalen-1-yl)cycloprop-2-en-1-yl)methyl acetate (2j):



The title compound was prepared according to the general procedure (EA/PE = 1/20, R_f = 0.33). The product was obtained as yellow liquid in 85% yield (1015.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.43 – 8.41 (m, 1H), 7.90 – 7.88 (m, 1H), 7.78– 7.76 (m, 1H), 7.72 – 7.71 (m, 2H), 7.62 – 7.58 (m, 1H), 7.54 – 7.50 (m, 1H), 7.46 – 7.45 (m, 1H), 7.44 (d, J = 1.6 Hz, 1H), 4.46 (s, 2H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.9, 141.3, 133.9, 131.4, 128.8, 127.4, 126.0, 125.9, 125.8, 125.6, 124.3, 116.4, 70.7, 26.2, 20.9; HRMS (ESI) m/z [$\text{M}+\text{H}$]: Calcd for $\text{C}_{16}\text{H}_{15}\text{O}_2$: 239.1072. Found: 239.1066.

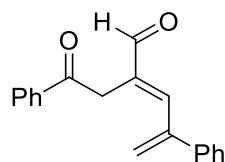
General procedure for 1,3-dienes and their spectra data:



A mixture of **1** (0.20 mmol, 1.0 equiv.), **2** (0.40 mmol, 2.0 equiv.) and $\text{Rh}_2(\text{OAc})_4$ (0.002 mmol, 1.0 mol %) was dissolved in 2.00 mL solution (HFIP:DCE = 9:1) under nitrogen atmosphere, and the reaction was stirred at room temperature until the starting material **1a** was consumed completely. Then the mixture was diluted with ethyl acetate, washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated to give the crude product, which was purified through a flash column chromatography (EA/PE = 1/20) to give the desired product **3**.

When the reaction was scaled up to 6.0 mmol, the Schlenk tube was replaced by Schlenk flask. A mixture of **1a** (6.0 mmol, 1.0 equiv.), **2a** (12.0 mmol, 2.0 equiv.) and $\text{Rh}_2(\text{OAc})_4$ (0.06 mmol, 1 mol %) was dissolved in 60 mL solution (HFIP:DCE = 9:1) under nitrogen atmosphere in a Schlenk flask and the mixture was stirred at room temperature until the starting material **1a** was consumed completely. Then the mixture was diluted with ethyl acetate, washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4 , filtered and concentrated to give the crude product, which was purified through a flash column chromatography (EA/PE = 1/20) to give the desired product **3aa** in 71% yield (1171.4 mg).

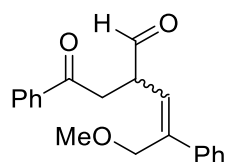
(*E*)-2-(2-Oxo-2-phenylethyl)-4-phenylpenta-2,4-dienal (**3aa**):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.31). The product was obtained as yellow oil in 84% yield (46.5 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.81 (m, 1H), 7.80 (m, 1H), 7.56 – 7.52 (m, 1H),

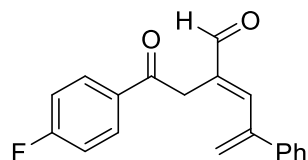
7.43 – 7.39 (m, 3H), 7.32 – 7.27 (m, 4H), 7.26 – 7.23 (m, 1H), 5.69 (d, $J = 1.2$ Hz, 1H), 5.53 – 5.52 (t, $J = 1.2$ Hz, 1H), 3.90 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.9, 194.2, 151.8, 144.0, 138.8, 138.3, 136.4, 133.1, 128.6, 128.4, 128.3, 128.1, 126.9, 121.0, 35.4; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2$: 277.1229. Found: 277.1231.

5-Methoxy-2-(2-oxo-2-phenylethyl)-4-phenylpent-3-enal (3aa'):



The title compound was prepared according to the general procedure (EA/PE = 1/9, $R_f = 0.33$). The product was obtained as yellow oil in 61% yield (37.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.80 & 9.53 (s, 1H), 8.00 – 7.98 & 7.96 – 7.93 (m, 2H), 7.61 – 7.55 (m, 2H), 7.50 (m, 2H), 7.48 – 7.45 (m, 2H), 7.43 – 7.41 (m, 1H), 7.40 – 7.39 (m, 1H), 7.36 – 7.35 (m, 1H), 7.34 – 7.33 (m, 1H), 7.32 – 7.30 (m, 2H), 7.30 – 7.28 (m, 2H), 7.24 (m, 1H), 7.22 – 7.21 (m, 1H), 7.02 – 7.00 (d, $J = 9.2$ Hz, 1H), 5.74 (d, $J = 10.0$ Hz, 1H), 4.51 – 4.42 (m, 2H), 4.32 – 4.26 (m, 1H), 4.08 – 4.00 (m, 2H), 3.93 – 3.89 (m, 1H), 3.76 – 3.70 (m, 3H), 3.41 & 3.34 (s, 3H), 3.29 – 3.24 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 199.6, 197.3, 195.6, 193.8, 156.6, 142.2, 140.7, 139.1, 138.0, 136.4, 136.3, 133.4, 133.2, 128.9, 128.7, 128.5, 128.4, 128.3, 128.1, 127.8, 127.8, 127.3, 126.3, 126.3, 75.8, 70.3, 59.0, 58.4, 47.7, 45.7, 39.0, 34.3; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{20}\text{H}_{21}\text{O}_3$: 309.1491. Found: 309.1490.

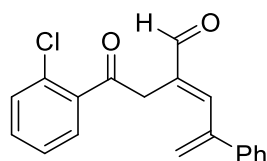
(E)-2-(2-(4-Fluorophenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ba):



The title compound was prepared according to the general procedure (EA/PE = 1/9, $R_f = 0.31$). The product was obtained as yellow oil in 79% yield (46.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.84 – 7.81 (m, 2H), 7.42 (d, $J = 1.2$ Hz, 1H), 7.29

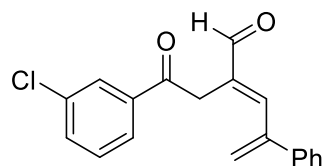
– 7.26 (m, 4H), 7.25 – 7.24 (m, 1H), 7.09 – 7.05 (m, 2H), 5.69 (d, $J = 1.2$ Hz, 1H), 5.54 (t, $J = 1.2$ Hz, 1H), 3.84 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.3, 194.2, 165.7 (d, $J = 253.7$ Hz), 151.9, 144.0, 138.7, 138.0, 132.8 (d, $J = 3.3$ Hz), 130.7 (d, $J = 9.3$ Hz), 128.6, 128.3, 127.0, 121.3, 115.5 (d, $J = 21.6$ Hz), 35.2; ^{19}F NMR (376 MHz, CDCl_3) δ -105.56; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{16}\text{FO}_2$: 295.1134. Found: 295.1135.

(E)-2-(2-(2-Chlorophenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ca):



The title compound was prepared according to the general procedure (EA/PE = 1/9, $R_f = 0.32$). The product was obtained as yellow oil in 36% yield (22.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 1H), 7.48 – 7.46 (m, 1H), 7.41 (s, 1H), 7.37 (m, 1H), 7.36 – 7.35 (m, 2H), 7.35 – 7.33 (m, 4H), 7.31 – 7.28 (m, 1H), 5.76 (d, $J = 1.2$ Hz, 1H), 5.61 (m, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.6, 194.0, 152.0, 143.8, 138.7, 138.0, 131.8, 130.9, 130.4, 129.5, 128.7, 128.4, 126.9, 126.8, 125.9, 121.1, 39.6; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{16}\text{ClO}_2$: 311.0839. Found: 311.0844.

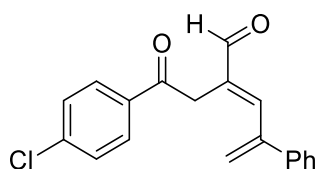
(E)-2-(2-(3-Chlorophenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3da):



The title compound was prepared according to the general procedure (EA/PE = 1/9, $R_f = 0.35$). The product was obtained as yellow oil in 45% yield (27.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.75 – 7.74 (t, $J = 2.0$ Hz, 1H), 7.68 – 7.66 (m, 1H), 7.52 – 7.50 (m, 1H), 7.43 (s, 1H), 7.37 – 7.33 (m, 1H), 7.30 – 7.27 (m, 4H), 7.26 – 7.25 (m, 1H), 5.70 (m, 1H), 5.54 (m, 1H), 3.83 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3)

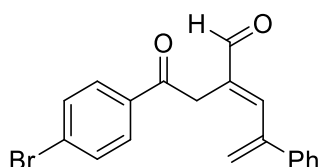
δ 194.7, 194.1, 151.9, 144.1, 138.7, 137.9, 137.7, 134.7, 133.0, 129.8, 128.7, 128.4, 128.2, 127.0, 126.1, 121.5, 35.4; HRMS (ESI) m/z [M+H]: Calcd for C₁₉H₁₆ClO₂: 311.0839. Found: 311.0842.

(E)-2-(2-(4-Chlorophenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ea):



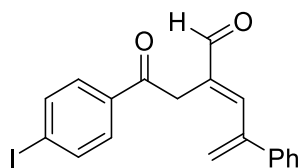
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.33). The product was obtained as yellow oil in 81% yield (50.2 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.65 (s, 1H), 7.74 – 7.72 (m, 2H), 7.42 – 7.41 (m, 1H), 7.39 – 7.36 (m, 2H), 7.28 – 7.26 (m, 4H), 7.25 (m, 1H), 5.69 (d, J = 1.2 Hz, 1H), 5.54 (t, J = 1.2 Hz, 1H), 3.82 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 194.7, 194.2, 151.9, 144.0, 139.5, 138.7, 137.8, 134.7, 129.4, 128.7, 128.6, 128.3, 127.0, 121.5, 35.2; HRMS (ESI) m/z [M+H]: Calcd for C₁₉H₁₆ClO₂: 311.0839. Found: 311.0838.

(E)-2-(2-(4-Bromophenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3fa):



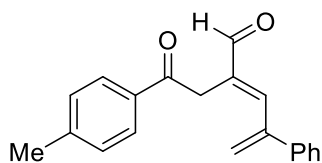
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.35). The product was obtained as yellow oil in 75% yield (53.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.65 (s, 1H), 7.69– 7.64 (m, 2H), 7.57– 7.53 (m, 2H), 7.44–7.42 (m, 1H), 7.31– 7.26 (m, 5H), 5.69 (d, J = 1.2 Hz, 1H), 5.54 (t, J = 1.2 Hz, 1H), 3.81 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 194.9, 194.1, 151.9, 144.1, 138.7, 137.8, 135.1, 131.7, 129.5, 128.6, 128.3, 128.3, 127.0, 121.5, 35.2; HRMS (ESI) m/z [M+H]: Calcd for C₁₉H₁₆BrO₂: 355.0334. Found: 355.0333.

(E)-2-(2-(4-Iodophenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ga):



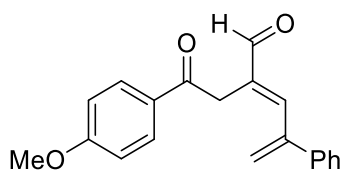
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.32). The product was obtained as yellow oil in 77% yield (61.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.65 (s, 1H), 7.78 – 7.75 (m, 2H), 7.51 – 7.48 (m, 2H), 7.41 (m, 1H), 7.30– 7.26 (m, 4H), 7.25 (m, 1H), 5.69 (d, J = 1.2 Hz, 1H), 5.54 – 5.53 (t, J = 1.2 Hz, 1H), 3.80 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.2, 194.1, 151.9, 144.0, 138.7, 137.8, 137.7, 135.7, 129.4, 128.6, 128.3, 127.0, 121.5, 101.1, 35.2; HRMS (ESI) m/z [$\text{M}+\text{H}$]: Calcd for $\text{C}_{19}\text{H}_{16}\text{IO}_2$: 403.0195. Found: 403.0201.

(E)-2-(2-Oxo-2-(*p*-tolyl)ethyl)-4-phenylpenta-2,4-dienal (3ha):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.33). The product was obtained as yellow oil in 80% yield (46.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.74–7.72 (m, 2H), 7.40 (m, 1H), 7.31 – 7.28 (m, 4H), 7.26 (m, 1H), 7.22 – 7.20 (d, J = 8.0 Hz, 2H), 5.69 (d, J = 1.2 Hz, 1H), 5.51 (t, J = 1.2 Hz, 1H), 3.88 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 194.3, 151.7, 143.9, 143.9, 138.8, 138.4, 134.0, 129.1, 128.6, 128.3, 128.2, 126.9, 120.7, 35.3, 21.6; HRMS (ESI) m/z [$\text{M}+\text{H}$]: Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2$: 291.1385. Found: 291.1389.

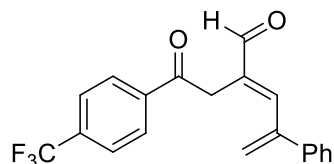
(E)-2-(2-(4-Methoxyphenyl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ia):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f

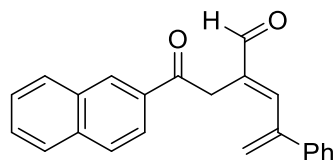
= 0.35). The product was obtained as yellow oil in 71% yield (43.5 mg). ¹H NMR (400 MHz, CDCl₃) δ9.66 (s, 1H), 7.83 – 7.79 (m, 2H), 7.40 (d, *J* = 1.2 Hz, 1H), 7.31 – 7.26 (m, 4H), 6.89 (m, 1H), 6.87 (m, 1H), 5.69 (d, *J* = 1.2 Hz, 1H), 5.52 (t, *J* = 1.2 Hz, 1H), 3.86 (s, 2H), 3.86, (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ194.4, 194.3, 163.5, 151.6, 143.9, 138.8, 138.5, 130.4, 129.5, 128.6, 128.3, 126.9, 120.7, 113.5, 55.4, 35.0; HRMS (ESI) *m/z* [M+H]: Calcd for C₂₀H₁₉O₃: 307.1334. Found: 307.1341.

(*E*)-2-(2-Oxo-2-(4-(trifluoromethyl)phenyl)ethyl)-4-phenylpenta-2,4-dienal (3ja):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.32). The product was obtained as colorless oil in 51% yield (35.1mg). ¹H NMR (400 MHz, CDCl₃) δ9.66 (s, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 1.2 Hz, 1H), 7.30 – 7.27 (m, 3H), 7.25– 7.22 (m, 2H), 5.70 (m, 1H), 5.56 (t, *J* = 1.2 Hz, 1H), 3.85 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ195.0, 194.1, 152.1, 144.1, 139.1, 138.7, 137.6, 128.7, 128.4, 128.3, 127.0, 125.5 (q, *J* = 3.8 Hz), 125.4, 124.7, 121.8, 35.6; ¹⁹F NMR (376 MHz, CDCl₃) δ-62.62; HRMS (ESI) *m/z* [M+H]: Calcd for C₂₀H₁₆F₃O₂: 345.1102. Found: 345.1108.

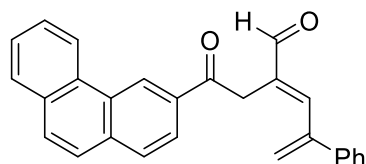
(*E*)-2-(2-(Naphthalen-2-yl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ka):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.28). The product was obtained as yellow oil in 65% yield (42.4 mg). ¹H NMR (400 MHz, CDCl₃) δ9.70 (s, 1H), 8.29 (s, 1H), 7.91– 7.89 (m, 2H), 7.87 – 7.84 (m, 2H), 7.62– 7.57 (m, 1H), 7.56– 7.52 (m, 1H), 7.44 (s, 1H), 7.35– 7.31 (m, 2H), 7.28–

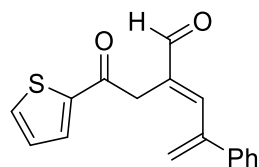
7.25 (m, 2H), 7.22– 7.17 (m, 1H), 5.70 (m, 1H), 5.56 (m, 1H), 4.04 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 194.3, 151.8, 144.0, 138.8, 138.3, 135.5, 133.7, 132.3, 129.7, 129.5, 128.6, 128.4, 128.3, 128.3, 127.7, 126.9, 126.7, 123.8, 121.1, 35.4; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{23}\text{H}_{19}\text{O}_2$: 327.1385. Found: 327.1389.

(E)-2-(2-Oxo-2-(phenanthren-3-yl)ethyl)-4-phenylpenta-2,4-dienal (3la):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.25). The product was obtained as yellow oil in 67% yield (50.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.71 (s, 1H), 9.13 (s, 1H), 8.68 (d, J = 8.0 Hz, 1H), 7.99–7.96 (m, 1H), 7.92–7.90 (m, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.75 – 7.70 (m, 1H), 7.68 (m, 1H), 7.66 – 7.64 (m, 1H), 7.45 (s, 1H), 7.34 (m, 1H), 7.33 – 7.32 (m, 1H), 7.25 – 7.22 (m, 2H), 7.17 – 7.15 (m, 1H), 5.71 (d, J = 0.8 Hz, 1H), 5.59 (m, 1H), 4.09 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.0, 194.3, 151.9, 144.1, 138.8, 138.3, 135.0, 134.1, 132.1, 130.6, 129.7, 129.6, 128.8, 128.7, 128.6, 128.3, 127.2, 127.2, 127.0, 126.2, 125.2, 123.6, 122.7, 121.4, 35.6; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{27}\text{H}_{21}\text{O}_2$: 377.1542. Found: 377.1543.

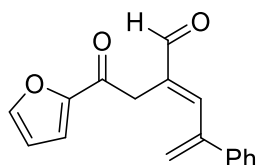
(E)-2-(2-Oxo-2-(thiophen-2-yl)ethyl)-4-phenylpenta-2,4-dienal (3ma):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.33). The product was obtained as yellow oil in 71% yield (40.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.65 (s, 1H), 7.61–7.60 (m, 1H), 7.58–7.56 (m, 1H), 7.41 (m, 1H), 7.33– 7.27 (m, 4H), 7.26– 7.25 (m, 1H), 7.08–7.06 (m, 1H), 5.71 (d, J = 1.2 Hz, 1H), 5.58 (t, J = 1.2 Hz, 1H), 3.86 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.1,

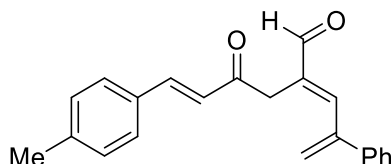
188.6, 152.1, 143.8, 143.3, 138.6, 137.5, 133.6, 132.0, 128.6, 128.3, 127.9, 126.9, 121.2, 35.7; HRMS (ESI) m/z [M+H]: Calcd for $C_{17}H_{15}O_2S$: 283.0793. Found: 283.0790.

(E)-2-(2-(Furan-2-yl)-2-oxoethyl)-4-phenylpenta-2,4-dienal (3na):



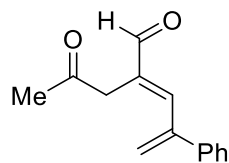
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.35). The product was obtained as yellow oil in 77% yield (40.9 mg). 1H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.53 (m, 1H), 7.41 (d, J = 1.2 Hz, 1H), 7.32–7.27 (m, 5H), 7.11–7.10 (m, 1H), 6.50–6.49 (m, 1H), 5.71 (m, 1H), 5.57 (t, J = 1.2 Hz, 1H), 3.78 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.1, 184.9, 152.2, 152.0, 146.2, 143.7, 138.6, 137.4, 128.6, 128.3, 126.9, 121.0, 117.1, 112.2, 34.9; HRMS (ESI) m/z [M+H]: Calcd for $C_{17}H_{15}O_3$: 267.1021. Found: 267.1020.

(2E,5E)-4-Oxo-2-(2-phenylallylidene)-6-(p-tolyl)hex-5-enal (2oa):



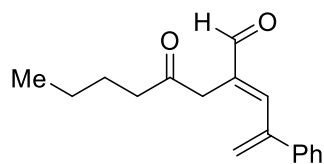
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.28). The product was obtained as yellow oil in 51% yield (32.2 mg). 1H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.44–7.40 (m, 2H), 7.38–7.37 (m, 2H), 7.33–7.31 (m, 4H), 7.25 (m, 1H), 7.20–7.18 (m, 2H), 6.62–6.57 (m, 1H), 5.72 (m, 1H), 5.56 (m, 1H), 3.60 (s, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 194.3, 151.8, 143.8, 143.1, 141.0, 138.8, 138.2, 131.6, 129.6, 128.7, 128.3, 126.9, 124.5, 121.0, 37.2, 21.5; HRMS (ESI) m/z [M+H]: Calcd for $C_{22}H_{21}O_2$: 317.1542. Found: 317.1537.

(E)-2-(2-Oxopropyl)-4-phenylpenta-2,4-dienal (3pa):



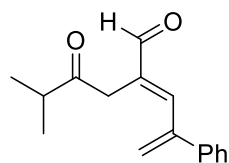
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.32). The product was obtained as yellow oil in 68% yield (29.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.57 (s, 1H), 7.37– 7.32 (m, 3H), 7.32 – 7.30 (m, 1H), 7.30– 7.28 (m, 2H), 5.70 (d, J = 1.2 Hz, 1H), 5.54– 5.53 (m, 1H), 3.30 (s, 2H), 2.01 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 204.4, 194.3, 151.8, 144.0, 138.8, 137.7, 128.6, 128.4, 127.0, 121.5, 39.7, 29.9; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_2$: 215.1072. Found: 215.1070.

(E)-4-oxo-2-(2-Phenylallylidene)octanal (3qa):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.34). The product was obtained as yellow oil in 65% yield (33.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.57 (s, 1H), 7.37– 7.33 (m, 3H), 7.32 – 7.26 (m, 3H), 5.69 (d, J = 1.2 Hz, 1H), 5.53 (t, J = 1.2 Hz, 1H), 3.29 (s, 2H), 2.30 – 2.23 (m, 2H), 1.51– 1.43 (m, 2H), 1.28– 1.23 (m, 2H), 0.87 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 206.6, 194.3, 151.6, 144.0, 138.9, 138.0, 128.6, 128.3, 127.0, 121.1, 42.5, 38.9, 25.7, 22.2, 13.8; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{17}\text{H}_{21}\text{O}_2$: 257.1542. Found: 257.1543.

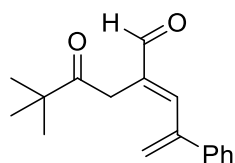
(E)-5-Methyl-4-oxo-2-(2-phenylallylidene)hexanal (3ra):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f

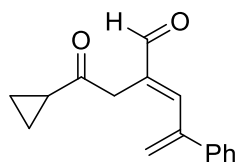
= 0.32). The product was obtained as yellow oil in 50% yield (24.2 mg). ¹H NMR (400 MHz, CDCl₃) δ9.56 (s, 1H), 7.36–7.29 (m, 6H), 5.68 (m, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 3.35 (s, 2H), 2.50–2.47 (m, 1H), 1.02 (d, *J* = 7.2 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ210.2, 194.3, 151.7, 143.9, 138.8, 138.2, 128.6, 128.3, 127.0, 120.9, 41.0, 36.8, 18.2; HRMS (ESI) *m/z* [M+H]: Calcd for C₁₆H₁₉O₂: 243.1385. Found: 243.1388.

(*E*)-5,5-Dimethyl-4-oxo-2-(2-phenylallylidene)hexanal (3sa):



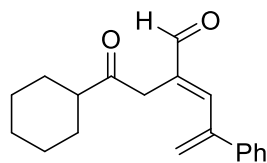
The title compound was prepared according to the general procedure (EA/PE = 1/9, *R_f* = 0.35). The product was obtained as yellow oil in 42% yield (21.5 mg). ¹H NMR (400 MHz, CDCl₃) δ9.55 (s, 1H), 7.35–7.30 (m, 6H), 5.67 (d, *J* = 1.2 Hz, 1H), 5.47 (t, *J* = 1.2 Hz, 1H), 3.39 (s, 2H), 1.06 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ211.5, 194.3, 151.6, 144.1, 138.9, 138.6, 128.6, 128.3, 127.0, 120.8, 44.3, 33.7, 26.6; HRMS (ESI) *m/z* [M+H]: Calcd for C₁₇H₂₁O₂: 257.1542. Found: 257.1546.

(*E*)-2-(2-Cyclopropyl-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ta):



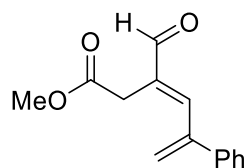
The title compound was prepared according to the general procedure (EA/PE = 1/9, *R_f* = 0.33). The product was obtained as yellow oil in 59% yield (28.3 mg). ¹H NMR (400 MHz, CDCl₃) δ9.58 (s, 1H), 7.38–7.29 (m, 6H), 5.71 (m, 1H), 5.51 (m, 1H), 3.47 (s, 2H), 1.83–1.77 (m, 1H), 0.98–0.97 (m, 2H), 0.85–0.80 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ206.3, 194.3, 151.7, 143.8, 138.9, 137.9, 128.6, 128.3, 126.9, 121.0, 39.5, 20.5, 11.0; HRMS (ESI) *m/z* [M+H]: Calcd for C₁₆H₁₇O₂: 241.1229. Found: 241.1233.

(E)-2-(2-Cyclohexyl-2-oxoethyl)-4-phenylpenta-2,4-dienal (3ua):



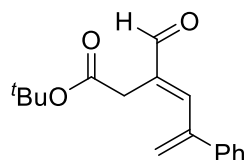
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.32). The product was obtained as yellow oil in 69% yield (38.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.49 (s, 1H), 7.29–7.26 (m, 3H), 7.25–7.22 (m, 3H), 5.61 (d, J = 1.2 Hz, 1H), 5.42 (t, J = 1.2 Hz, 1H), 3.28 (s, 2H), 2.19–2.12 (m, 1H), 1.72–1.68 (m, 2H), 1.67–1.64 (m, 2H), 1.23–1.08 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 209.5, 194.3, 151.6, 143.9, 138.8, 138.3, 128.6, 128.3, 127.0, 120.8, 50.8, 37.1, 28.4, 25.7, 25.5; HRMS (ESI) m/z [$\text{M}+\text{H}$]: Calcd for $\text{C}_{19}\text{H}_{23}\text{O}_2$: 283.1698. Found: 283.1702.

Methyl (E)-3-formyl-5-phenylhexa-3,5-dienoate (3va):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.30). The product was obtained as yellow oil in 52% yield (23.9 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.60 (s, 1H), 7.38–7.31 (m, 6H), 5.78 (m, 1H), 5.54 (t, J = 1.2 Hz, 1H), 3.62 (s, 3H), 3.26 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.1, 170.6, 151.6, 143.5, 138.5, 137.2, 128.6, 128.5, 126.8, 121.0, 52.1, 30.6; HRMS (ESI) m/z [$\text{M}+\text{H}$]: Calcd for $\text{C}_{14}\text{H}_{15}\text{O}_3$: 231.1021. Found: 231.1023.

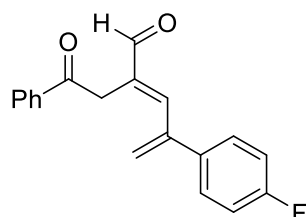
***tert*-Butyl (E)-3-formyl-5-phenylhexa-3,5-dienoate (3wa):**



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.31). The product was obtained as yellow oil in 41% yield (22.3 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.60 (s, 1H), 7.36–7.35 (m, 5H), 7.27–7.26 (m, 1H), 5.78 (m,

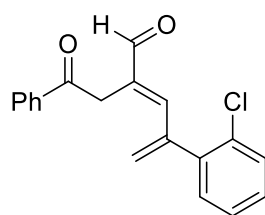
1H), 5.53 (m, 1H), 3.20 (s, 2H), 1.40 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 194.2, 169.3, 151.0, 143.5, 138.7, 138.0, 128.7, 128.4, 126.8, 120.4, 81.1, 32.1, 27.9; HRMS (ESI) m/z [M+H]: Calcd for C₁₇H₂₁O₃: 273.1491. Found: 273.1494.

(E)-4-(4-Fluorophenyl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3ab):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.34). The product was obtained as yellow oil in 72% yield (42.3 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.59 (s, 1H), 7.78 – 7.76 (m, 2H), 7.49–7.47 (m, 1H), 7.38 – 7.34 (m, 2H), 7.31 (s, 1H), 7.23 – 7.21 (m, 2H), 6.89 (t, *J* = 8.6 Hz, 2H), 5.58 (m, 1H), 5.44 (m, 1H), 3.84 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 195.8, 194.1, 162.7 (d, *J* = 246.9 Hz), 151.5, 142.9, 138.4, 136.3, 134.8 (d, *J* = 3.3 Hz), 133.3, 128.7 (d, *J* = 8.2 Hz), 128.3 (d, *J* = 47.0 Hz), 120.8, 115.6, 115.4, 35.3; ¹⁹F NMR (376 MHz, CDCl₃) δ -113.19; HRMS (ESI) m/z [M+H]: Calcd for C₁₉H₁₆FO₂: 295.1134. Found: 295.1143.

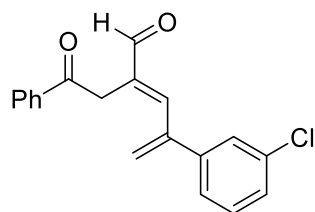
(E)-4-(2-Chlorophenyl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3ac):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.32). The product was obtained as yellow oil in 63% yield (39.1 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.60 (s, 1H), 7.68 – 7.66 (m, 2H), 7.51 – 7.49 (m, 1H), 7.38 – 7.33 (m, 3H), 7.28 – 7.26 (m, 1H), 7.12 (d, *J* = 7.6 Hz, 1H), 7.03 – 6.97 (m, 2H), 5.91 (m, 1H), 5.56 (m, 1H), 3.66 (s, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 195.3, 194.5, 151.2, 143.4, 138.3, 136.2, 136.1, 133.0, 132.5, 130.9, 129.4, 129.3, 128.4, 128.2,

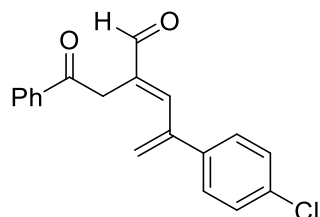
127.9, 127.0, 34.1; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{16}ClO_2$: 311.0839. Found: 311.0834.

(E)-4-(3-Chlorophenyl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3ad):



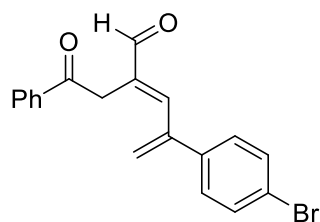
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.31). The product was obtained as yellow oil in 56% yield (34.7 mg). 1H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.56 (m, 1H), 7.42 (t, J = 7.6 Hz, 2H), 7.36 (s, 1H), 7.29 (s, 1H), 7.20 (s, 3H), 5.70 (m, 1H), 5.56 (m, 1H), 3.92 (s, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2SO$) δ 196.6, 195.5, 151.4, 142.2, 140.9, 139.2, 136.5, 134.0, 134.0, 131.0, 129.2, 128.7, 128.5, 126.9, 125.7, 121.7, 35.8; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{16}ClO_2$: 311.0839. Found: 311.0841.

(E)-4-(4-Chlorophenyl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3ae):



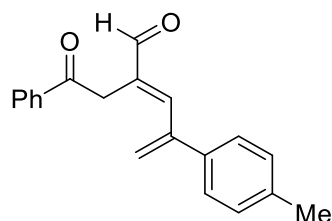
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.33). The product was obtained as yellow oil in 82% yield (50.8 mg). 1H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 7.84 – 7.81 (m, 2H), 7.56 – 7.54 (m, 1H), 7.45 – 7.41 (m, 2H), 7.37 – 7.26 (m, 1H), 7.23 (s, 4H), 5.67 (d, J = 1.2 Hz, 1H), 5.53 (t, J = 1.2 Hz, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 194.0, 151.0, 142.8, 138.5, 137.1, 136.3, 134.4, 133.3, 128.8, 128.5, 128.3, 128.0, 121.2, 35.3; HRMS (ESI) m/z $[M+H]^+$: Calcd for $C_{19}H_{16}ClO_2$: 311.0839. Found: 311.0840.

(E)-4-(4-Bromophenyl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3af):



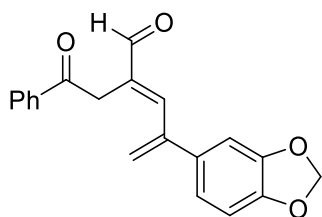
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.35). The product was obtained as yellow oil in 73% yield (51.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.83 – 7.81 (m, 2H), 7.56 – 7.54 (m, 1H), 7.45 – 7.43 (m, 2H), 7.41 – 7.36 (m, 3H), 7.18 – 7.16 (m, 2H), 5.68 (m, 1H), 5.54 (m, 1H), 3.90 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 194.0, 151.0, 142.9, 138.5, 137.6, 136.2, 133.3, 131.7, 128.6, 128.5, 128.0, 122.5, 121.3, 35.2; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{16}\text{BrO}_2$: 355.0334. Found: 355.0330.

(E)-2-(2-Oxo-2-phenylethyl)-4-(p-tolyl)penta-2,4-dienal (3ag):



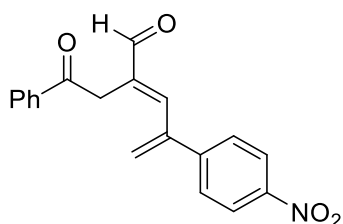
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.32). The product was obtained as yellow oil in 77% yield (44.7 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.82 – 7.80 (m, 2H), 7.54 – 7.52 (m, 1H), 7.43 – 7.39 (m, 3H), 7.19 – 7.17 (m, 2H), 7.07 – 7.05 (m, 2H), 5.65 (d, J = 1.2 Hz, 1H), 5.48 (t, J = 1.2 Hz, 1H), 3.89 (s, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.9, 194.3, 152.1, 143.8, 138.2, 138.1, 136.4, 135.8, 133.1, 129.3, 128.4, 128.0, 126.8, 120.4, 35.3, 21.0; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{20}\text{H}_{19}\text{O}_2$: 291.1385. Found: 291.1388.

(E)-4-(Benzo[d][1,3]dioxol-5-yl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3ah):



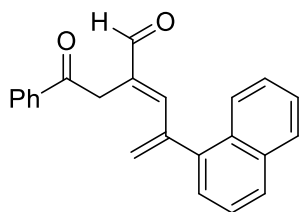
The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.31). The product was obtained as yellow oil in 70% yield (44.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.85 (d, J = 8.0 Hz, 2H), 7.57 – 7.54 (m, 1H), 7.45 – 7.41 (m, 2H), 7.36 (s, 1H), 6.77 – 6.75 (m, 2H), 6.72 – 6.69 (m, 1H), 5.81 (m, 2H), 5.60 (m, 1H), 5.45 (m, 1H), 3.91 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.8, 194.2, 151.8, 147.8, 147.6, 143.5, 138.1, 136.4, 133.1, 132.8, 128.4, 128.1, 120.8, 120.2, 108.2, 107.4, 101.1, 35.3; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{20}\text{H}_{17}\text{O}_4$: 321.1127. Found: 321.1132.

(E)-4-(4-Nitrophenyl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3ai):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.21). The product was obtained as red oil in 43% yield (27.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.69 – 9.67 (m, 1H), 8.13 – 8.09 (m, 2H), 7.81 – 7.80 (m, 2H), 7.55 – 7.54 (m, 1H), 7.50 – 7.45 (m, 2H), 7.42 – 7.37 (m, 3H), 5.80 (m, 1H), 5.69 (m, 1H), 3.92 – 3.90 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 193.7, 149.7, 147.5, 145.0, 142.2, 139.1, 136.0, 133.5, 128.6, 128.0, 127.9, 123.9, 123.4, 35.2; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{16}\text{NO}_4$: 322.1079. Found: 322.1085.

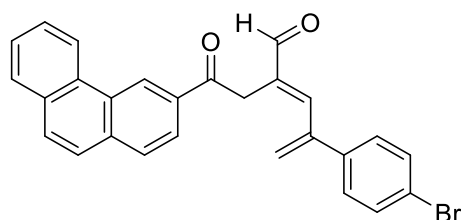
(E)-4-(Naphthalen-1-yl)-2-(2-oxo-2-phenylethyl)penta-2,4-dienal (3aj):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.28). The product was obtained as yellow oil in 62% yield (40.4 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.62 (s, 1H), 7.75 (m, 1H), 7.66 (m, 1H), 7.54 – 7.42 (m, 6H), 7.21 (m, 5H), 6.09 – 6.08 (m, 1H), 5.66 (m, 1H), 3.27 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.1, 194.7, 152.3, 144.5, 137.1, 136.2, 135.8, 133.3, 132.7, 131.0, 129.4, 128.3, 128.2, 127.9, 127.6, 126.6, 126.5, 126.2, 125.3, 99.9, 34.0; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{23}\text{H}_{19}\text{O}_2$: 327.1385. Found: 327.1389.

(E)-4-(4-Bromophenyl)-2-(2-oxo-2-(phenanthren-3-yl)ethyl)penta-2,4-dienal

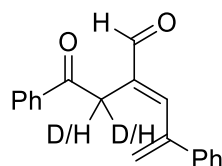
(3ak):



The title compound was prepared according to the general procedure (EA/PE = 1/9, R_f = 0.25). The product was obtained as yellow solid in 71% yield (64.5 mg), Mp. 163 – 164 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 9.72 (s, 1H), 9.18 (s, 1H), 8.71 (d, J = 8.4 Hz, 1H), 8.01 – 7.98 (m, 1H), 7.94 – 7.91 (m, 2H), 7.88 – 7.86 (m, 1H), 7.77 – 7.75 (m, 1H), 7.74 – 7.67 (m, 1H), 7.65 (t, J = 7.4 Hz, 1H), 7.41 (s, 1H), 7.36 (d, J = 8.4 Hz, 2H), 7.21 – 7.19 (m, 2H), 5.71 (s, 1H), 5.60 (s, 1H), 4.13 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.9, 194.1, 151.1, 142.9, 138.7, 137.6, 135.1, 134.0, 132.1, 131.8, 130.6, 129.8, 129.7, 128.9, 128.8, 128.6, 127.3, 127.2, 126.2, 125.1, 123.6, 122.7, 122.6, 121.4, 35.5; HRMS (ESI) m/z $[\text{M}+\text{Na}]$: Calcd for $\text{C}_{27}\text{H}_{19}\text{BrO}_2\text{Na}$: 477.0466. Found: 477.0457.

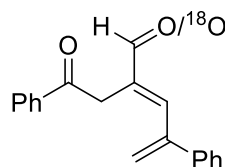
Spectral data of mechanistic investigations:

3aa-I:



The title compound was prepared under standard conditions with $(\text{CF}_3)_2\text{CDOD}$ instead of HFIP (EA/PE = 1/9, $R_f = 0.31$). The product was obtained as yellow oil in 81% yield (44.6 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.67 (s, 1H), 7.83 – 7.81 (m, 2H), 7.56 – 7.52 (m, 1H), 7.43 – 7.39 (m, 3H), 7.32 – 7.27 (m, 4H), 7.26 – 7.22 (m, 1H), 5.69 (m, 1H), 5.53 (s, 1H), 3.90 (s, 0.32H), 3.87 (s, 0.40H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.0, 195.9, 195.9, 194.3, 151.9, 143.8, 138.7, 138.2, 138.1, 138.1, 136.3, 133.1, 128.6, 128.4, 128.3, 128.0, 126.9, 121.0, 35.4, 35.3, 35.1, 34.9; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{15}\text{D}_2\text{O}_2$: 279.1354. Found: 279.1360.

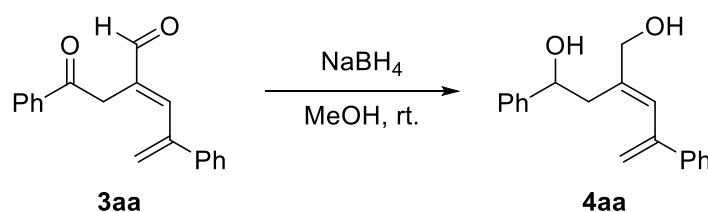
3aa-II:



The title compound was prepared under standard conditions with H_2^{18}O (2.0 equiv.) (EA/PE = 1/9, $R_f = 0.30$). The product was obtained as yellow oil in 72% yield (39.8 mg). ^1H NMR (400 MHz, CDCl_3) δ 9.66 (s, 1H), 7.83 – 7.82 (m, 1H), 7.80 (m, 1H), 7.56 – 7.52 (m, 1H), 7.43 – 7.39 (m, 3H), 7.32 – 7.26 (m, 4H), 7.26 – 7.23 (m, 1H), 5.69 (m, 1H), 5.53 – 5.52 (t, $J = 1.2$ Hz, 1H), 3.90 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.9, 194.3, 194.2, 151.8, 143.8, 138.7, 138.2, 136.3, 133.1, 128.6, 128.4, 128.3, 128.0, 126.9, 121.0, 35.3; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{17}\text{O}^{18}\text{O}$: 279.1271. Found: 279.1264.

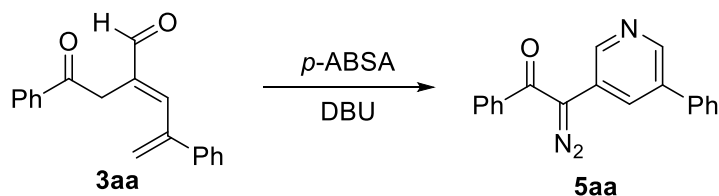
General procedure for applications and their spectral data:

(*E*)-1-Phenyl-3-(2-phenylallylidene)butane-1,4-diol (**4aa**)¹¹:



A mixture of **3aa** (0.10 mmol, 27.7 mg) in MeOH (2.00 mL) was cooled to 0 °C, NaBH₄ (0.4 mmol, 16 mg) was added and the reaction mixture was stirred at the same temperature for 30 min under nitrogen atmosphere. The mixture was poured into H₂O (5 mL) and extracted with EtOAc (10 mL). The organic layer was washed with brine (10 mL) and dried with Na₂SO₄. After removal of the solvent, the residue was subjected to column chromatography (EA/PE = 1/3, R_f = 0.24) to give **4aa** as white solid in 92% yield (25.8 mg), Mp. 106 – 107 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.39 – 7.33 (m, 3H), 7.32 – 7.31 (m, 1H), 7.30 – 7.26 (m, 3H), 7.25 (m, 1H), 7.23 – 7.19 (m, 3H), 6.36 (s, 1H), 5.58 (s, 1H), 5.17 (t, *J* = 1.2 Hz, 1H), 4.78 – 4.75 (m, 1H), 4.23 (s, 2H), 3.37 (s, 2H), 2.76 – 2.72 (m, 1H), 2.51 – 2.45 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 144.3, 144.3, 140.1, 139.9, 130.3, 128.4, 127.8, 127.5, 126.5, 125.5, 115.5, 74.0, 68.5, 40.1; HRMS (ESI) *m/z* [M+H]: Calcd for C₁₉H₂₁O₂: 281.1542. Found: 281.1538.

2-Diazo-1-phenyl-2-(5-phenylpyridin-3-yl)ethan-1-one (**5aa**)¹²:



To a solution of **3aa** (0.10 mmol, 27.7 mg) and *p*-acetamidobenzenesulfonyl azide (0.12 mmol, 57.7 mg) in CH₃CN at 0 °C was added DBU (0.15 mmol, 22.9 mg)

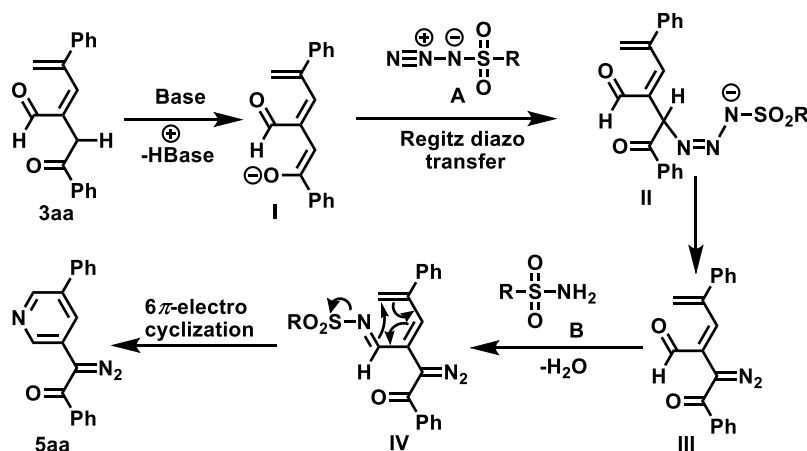
¹¹H. Suzuki, S. Yoshioka, A. Igesaka, H. Nishioka and Y. Takeuchi, *Tetrahedron*, 2013, **69**, 6399–6403.

¹²J. Sarabia, Q. Li and M. Ferreira, *Angew. Chem. Int. Ed.*, 2018, **57**, 11015–11019.

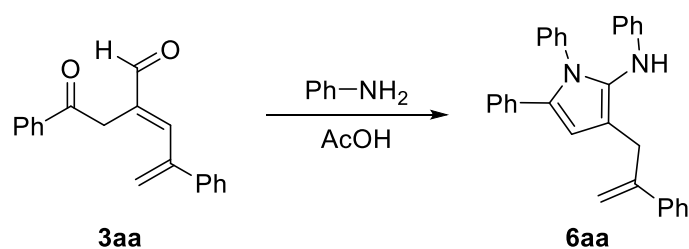
dropwise slowly. The reaction mixture was allowed to warm to room temperature and monitored by TLC. After completion of the reaction, the solvent was removed in *vacuo*. The crude residue was purified by flash chromatography (EA/PE = 1/20, R_f = 0.22) to afford product **5aa** as yellow oil in 67% yield (20.1 mg). ^1H NMR (400 MHz, CDCl_3) δ 8.97 (d, J = 2.4 Hz, 1H), 8.17 – 8.15 (m, 1H), 8.12 (m, 1H), 8.11 – 8.08 (m, 2H), 7.68 – 7.67 (m, 1H), 7.66 – 7.65 (m, 1H), 7.63 – 7.59 (m, 1H), 7.56 – 7.53 (m, 2H), 7.52 – 7.45 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 193.7, 153.4, 147.0, 139.0, 136.8, 136.4, 135.2, 132.9, 130.9, 129.3, 128.9, 128.2, 127.3, 124.9, 77.2; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{13}\text{N}_3\text{ONa}$: 322.0956. Found: 322.0958.

Possible reaction pathway for **5aa**¹³:

Under basic conditions, **3aa** was initially going through a well known diazo transfer process led to diazo **III**. The imine intermediate **IV** could be generated by condensation of **III** with tosyl amine **B**. Finally, the product **5aa** might be obtained by the tramolecular 6π -electrocyclization.



N,1,5-Triphenyl-3-(2-phenylallyl)-1H-pyrrol-2-amine (6aa)¹⁴:

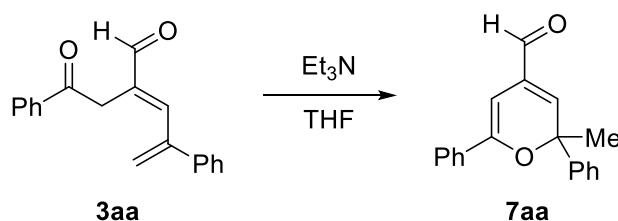


¹³Y. Jiang and C.-M Park, *Chem. Sci.*, 2014, **5**, 2347–2351.

¹⁴C. Zhu, R. Zhu, H. Zeng, F. Chen, C. Liu, W. Wu and H. Jiang, *Angew. Chem. Int. Ed.* 2017, **56**, 13324–13328.

Acetic acid (12.0 mg, 0.2 mmol) was added to the mixture of **3aa** (27.7 mg, 0.1 mmol), aniline (18.7 mg, 0.2 mmol) in MeOH (1 mL). Then the reaction mixture was stirred at room temperature and monitored by TLC. After completion of the reaction, brine (2 mL) was added, and extracted with DCM (5 ml \times 3). The combined organic layer were dried over Na₂SO₄, and concentrated in *vacuo*. The residue was purified by flash column chromatography (EA/PE = 1/20, R_f = 0.22) on silica gel give the desired product **6aa** as red solid in 72% yield (30.7 mg), Mp. 115 – 116 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.43 – 7.40 (m, 2H), 7.36 – 7.32 (m, 3H), 7.25 (m, 1H), 7.24 – 7.23 (m, 1H), 7.23 – 7.21 (m, 1H), 7.20 – 7.16 (m, 2H), 7.13 – 7.12 (m, 1H), 7.12 – 7.10 (m, 2H), 7.01 – 6.98 (m, 2H), 6.92 – 6.90 (m, 2H), 6.72 – 6.68 (m, 3H), 6.56, (s, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 5.72 (d, *J* = 2.0 Hz, 1H), 4.09 (s, 2H), 3.99 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 140.7, 139.9, 135.2, 133.5, 132.4, 129.2, 128.9, 128.8, 128.7, 128.1, 127.9, 127.4, 126.5, 126.3, 125.3, 124.5, 121.5, 120.1, 117.3, 113.1, 110.6, 52.2; HRMS (ESI) *m/z* [M+H]: Calcd for C₃₁H₂₇N₂: 427.2174. Found: 427.2167.

2-Methyl-2,6-diphenyl-2H-pyran-4-carbaldehyde (**7aa**)¹⁵:

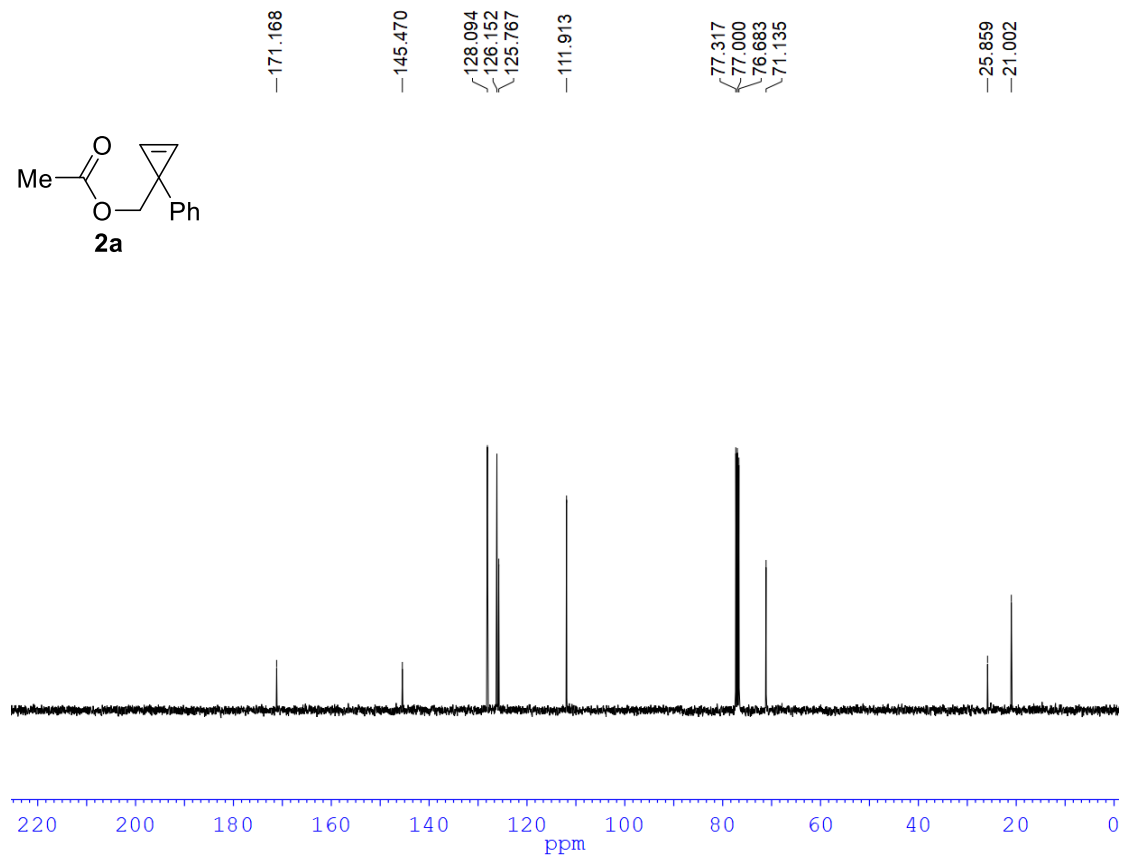
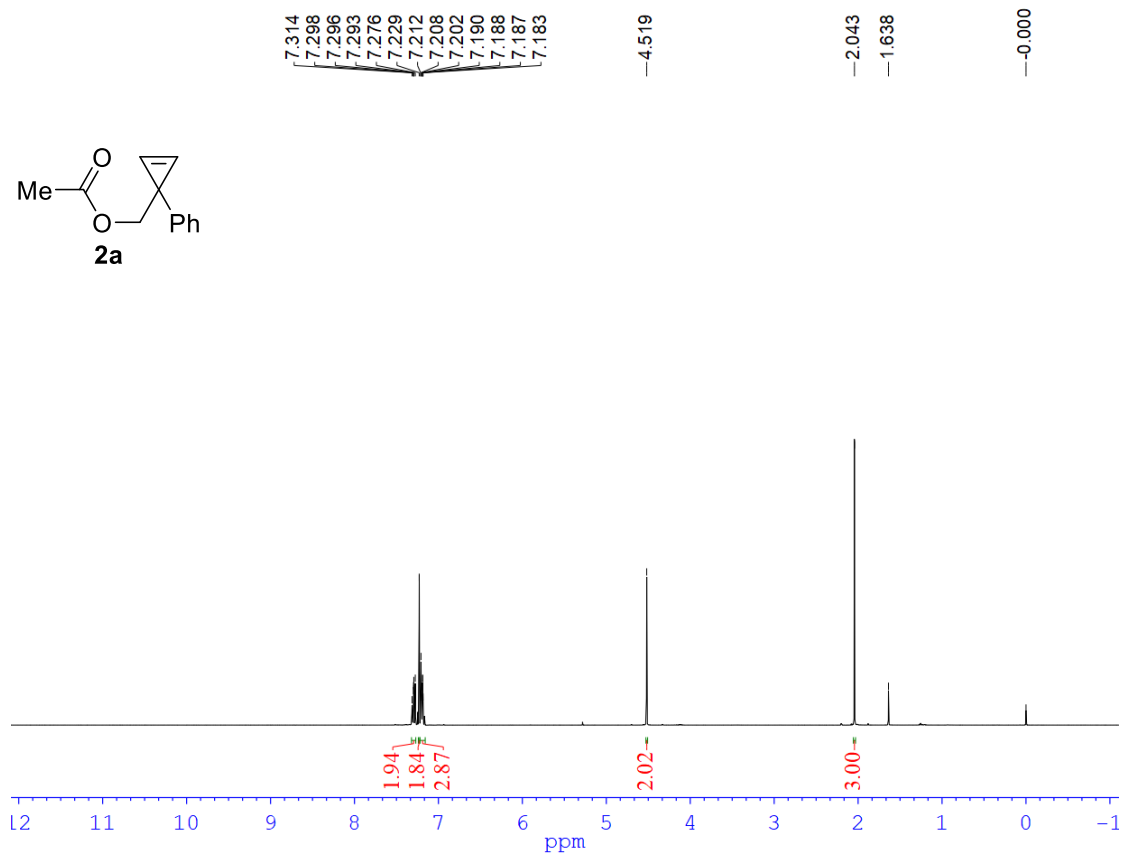


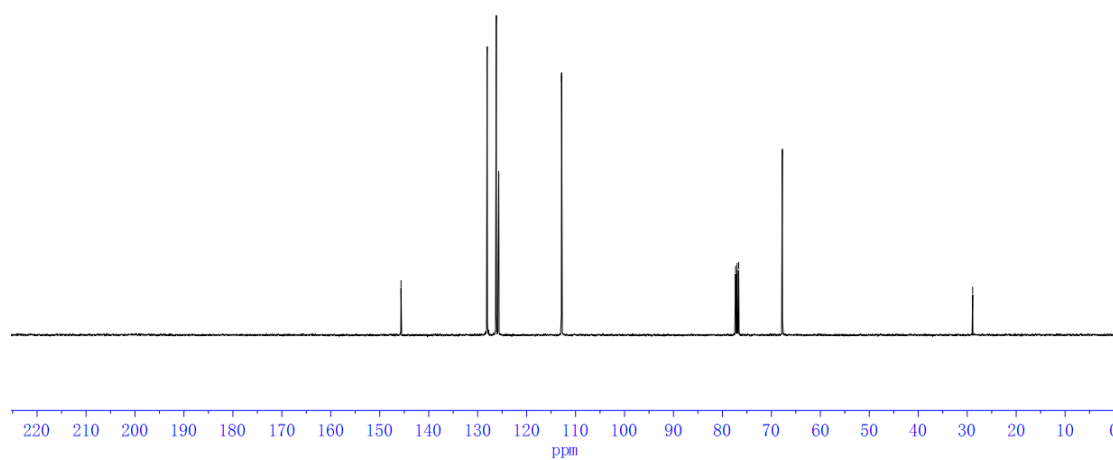
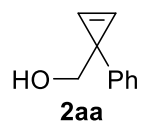
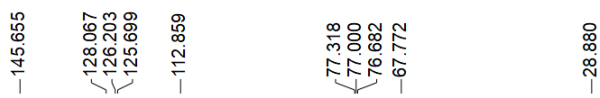
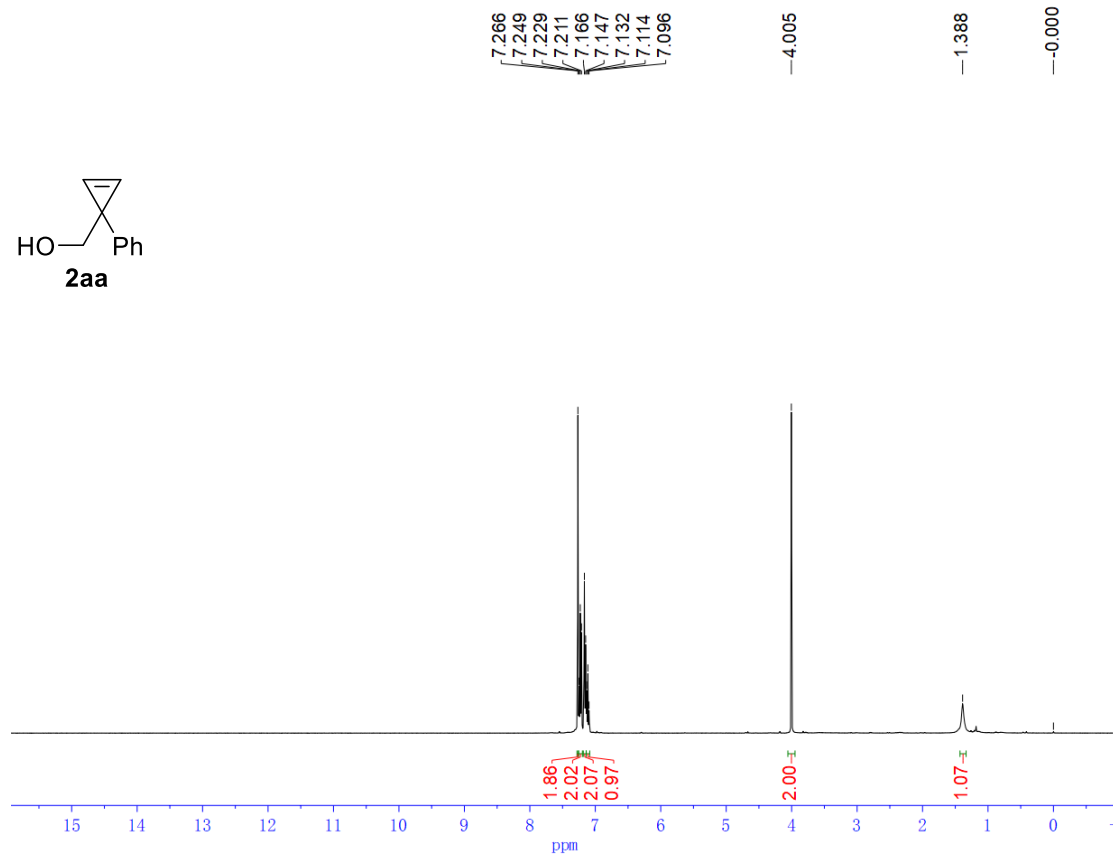
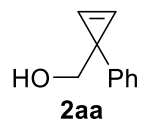
Triethylamine (20.3 mg, 0.2 mmol) was added to the mixture of **3aa** (27.7 mg, 0.1 mmol) in THF (1 mL). Then the reaction mixture was stirred at room temperature and monitored by TLC. After completion of the reaction, the combined organic layer were concentrated in *vacuo*. The residue was purified by flash column chromatography (EA/PE = 1/20, R_f = 0.21) on silica gel give the desired product **7aa** as yellow oil in 79% yield (21.8 mg). ¹H NMR (400 MHz, CDCl₃) δ 9.55 (s, 1H), 7.79 – 7.77 (m, 2H), 7.51 – 7.49 (m, 2H), 7.42 – 7.36 (m, 6H), 7.33 – 7.30 (m, 1H), 6.38 (d, *J* = 1.2 Hz,

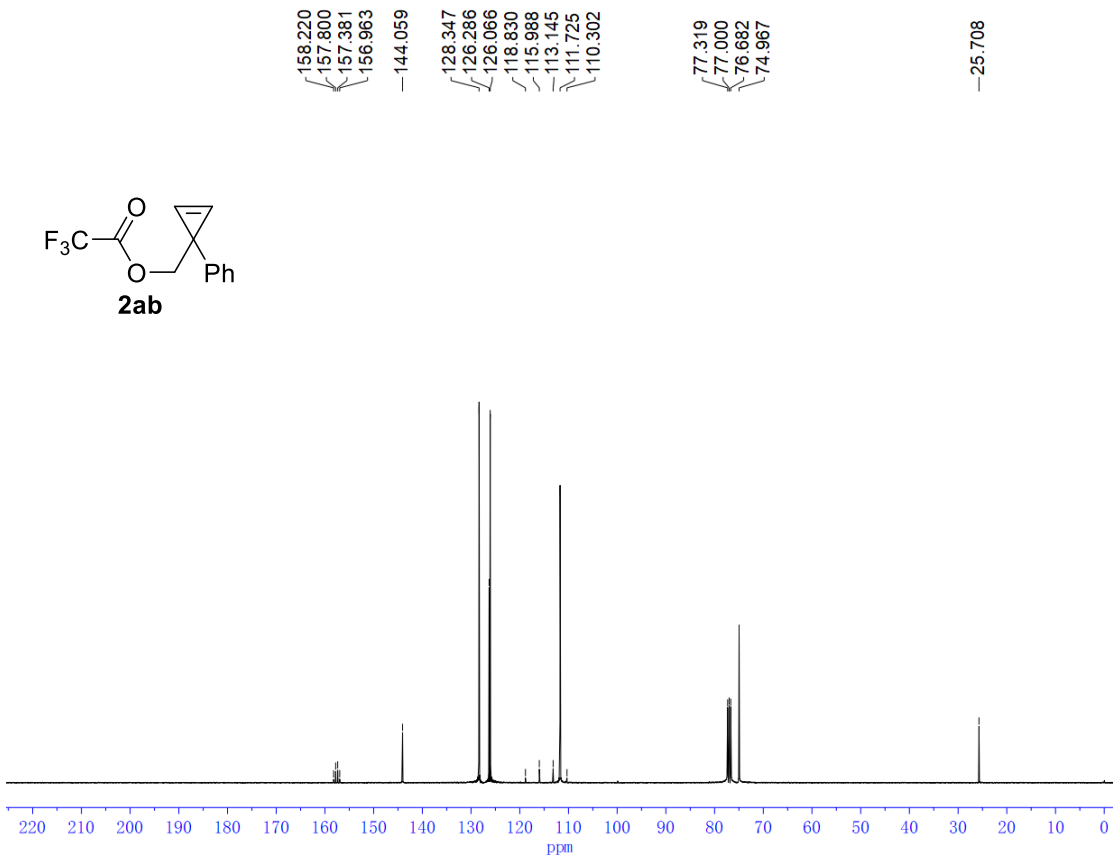
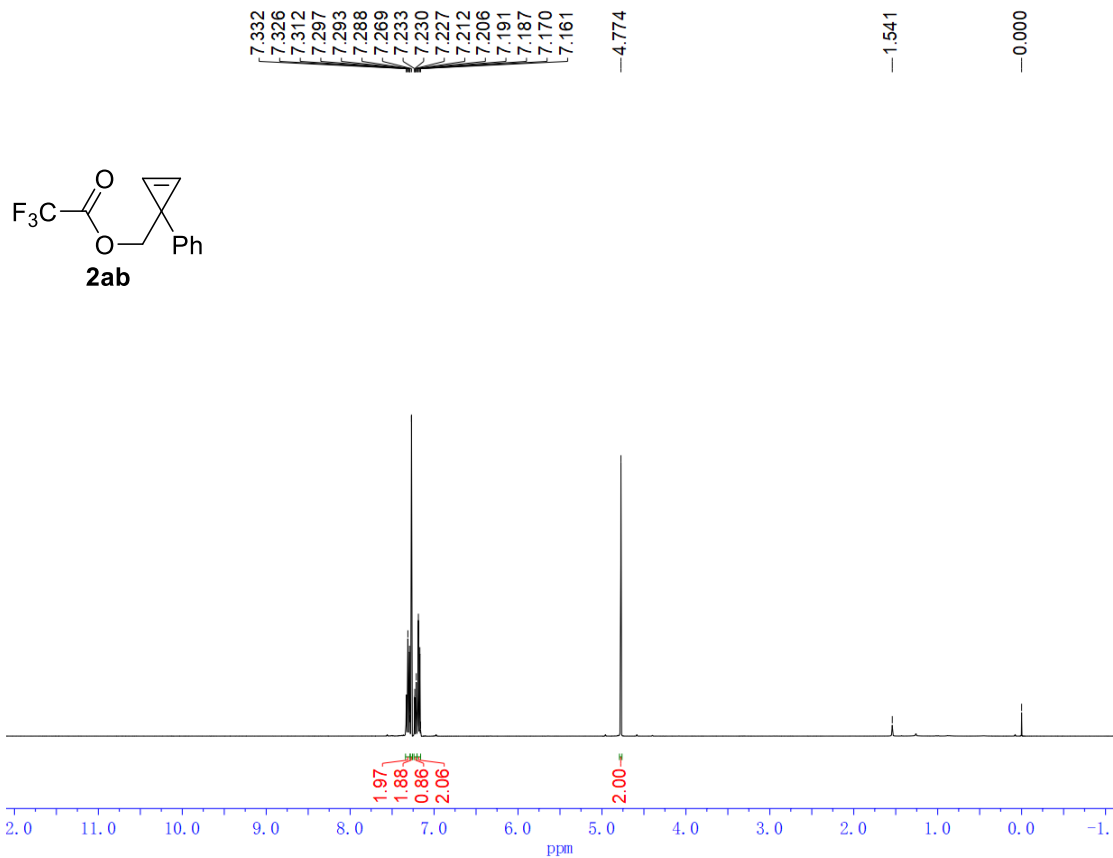
¹⁵T.-L. Shie, C.-H. Lin, S.-L. Lin and D.-Y. Yang, *Eur. J. Org. Chem.*, 2007, **29**, 4831–4836.

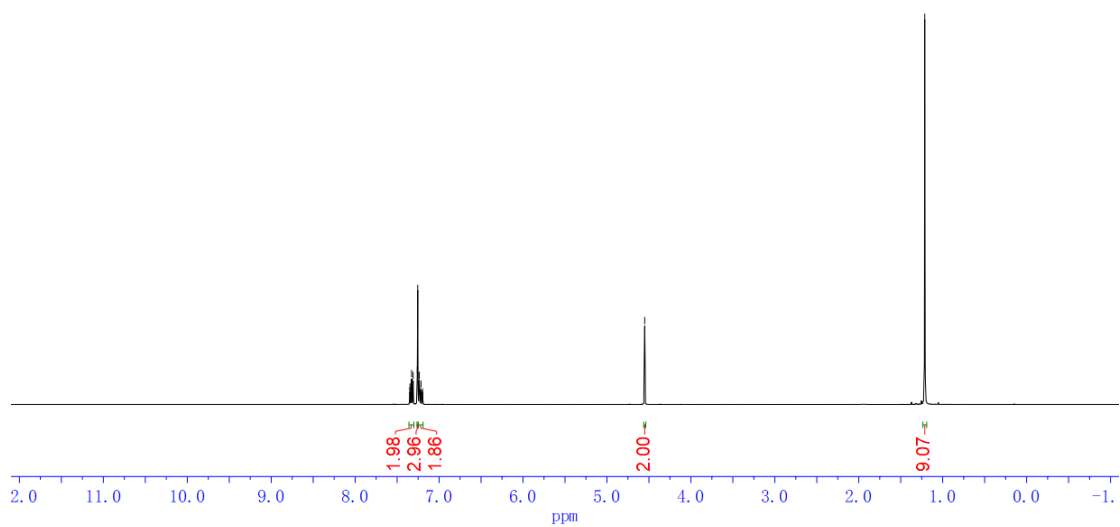
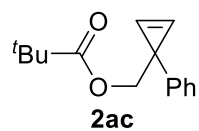
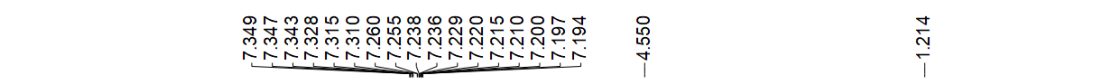
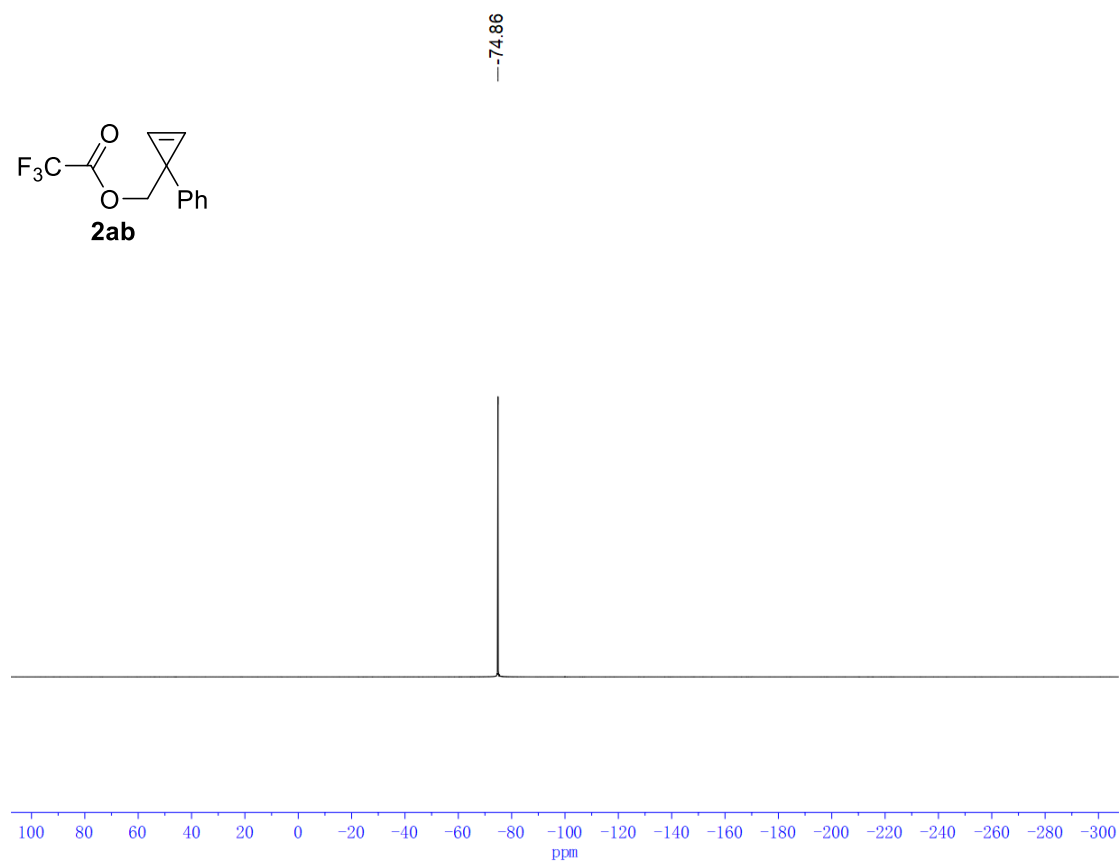
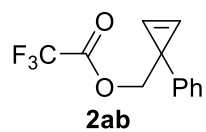
1H), 6.33 (d, $J = 1.2$ Hz, 1H), 1.89 (s, 3H); 13 C NMR (100 MHz, CDCl_3) δ 189.9, 153.1, 144.0, 138.9, 134.5, 133.7, 129.4, 128.5, 128.4, 127.9, 125.3, 124.8, 91.1, 79.9, 27.7; HRMS (ESI) m/z $[\text{M}+\text{H}]$: Calcd for $\text{C}_{19}\text{H}_{17}\text{O}_2$: 277.1229. Found: 277.1228.

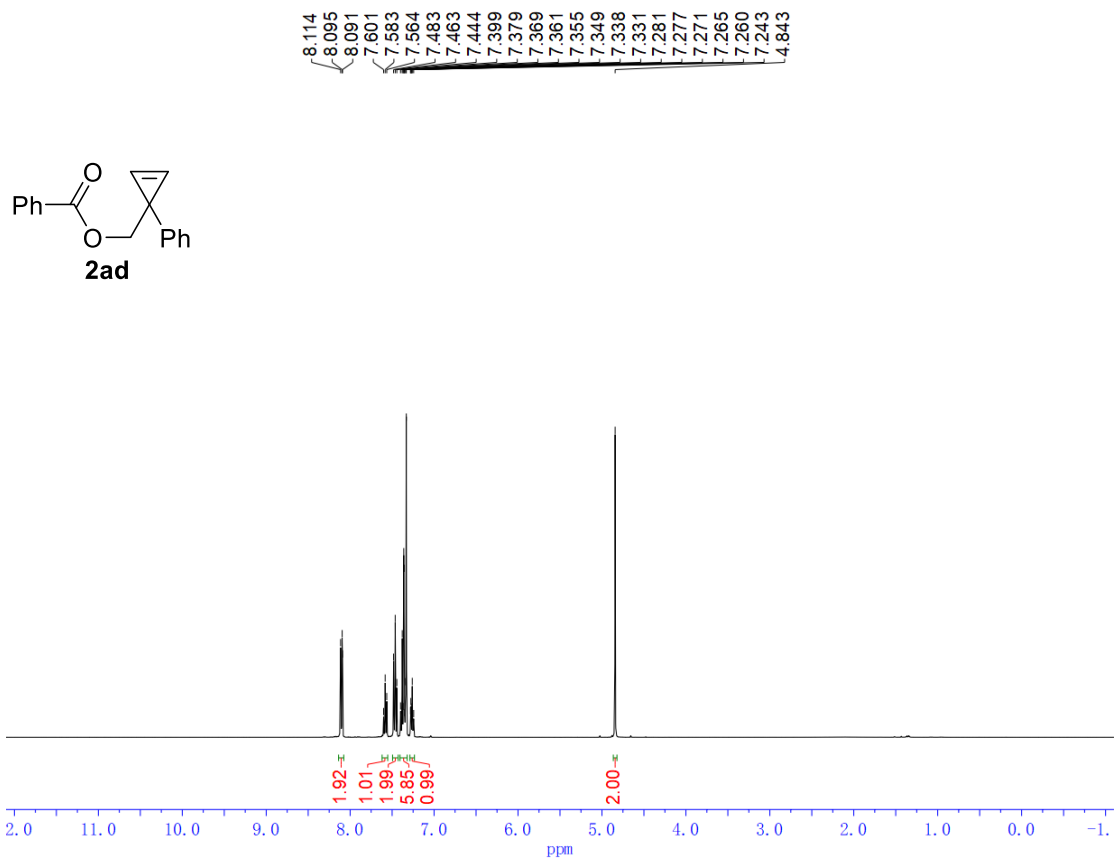
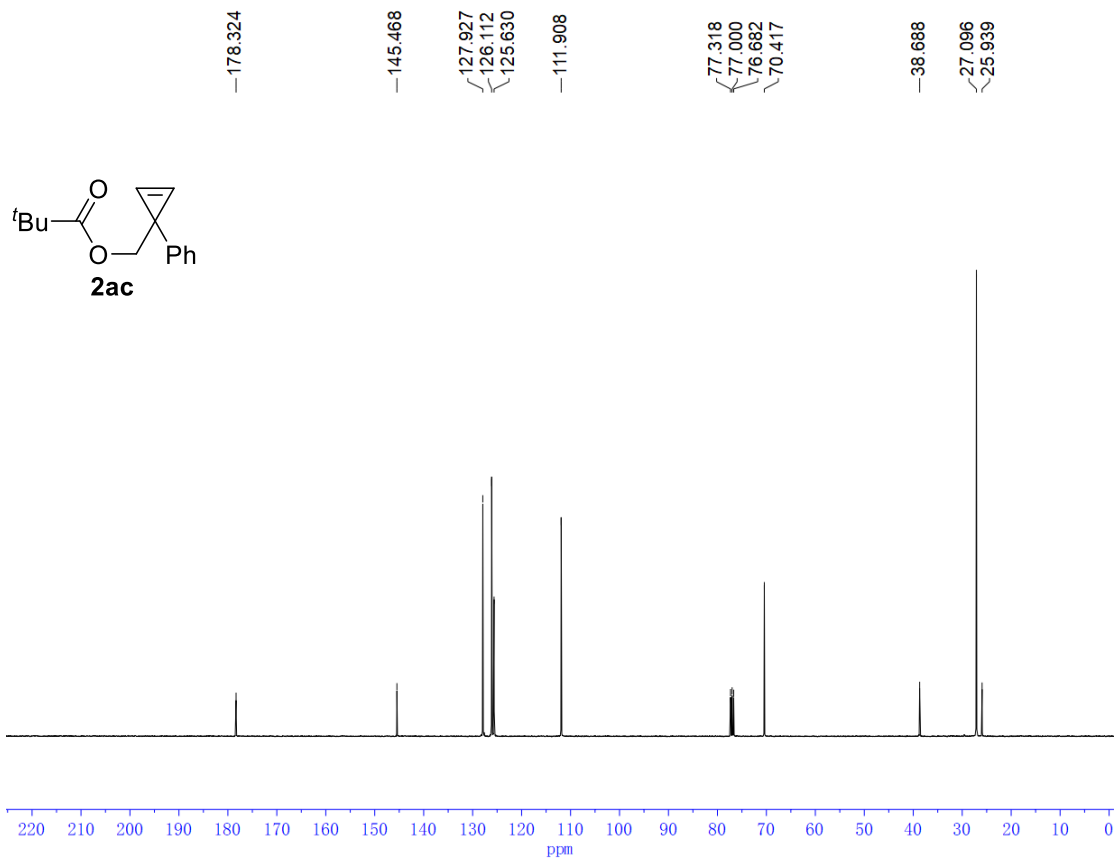
¹H and ¹³C NMR spectra of Cyclopropenes:

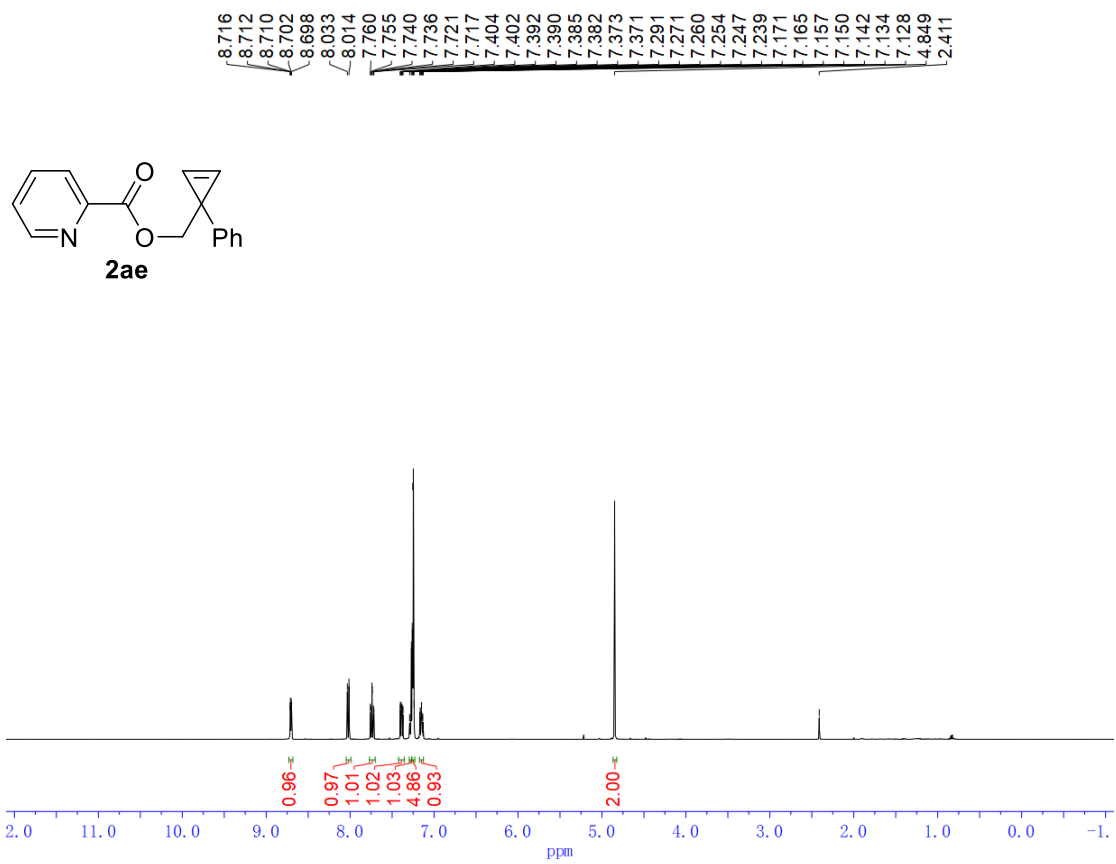
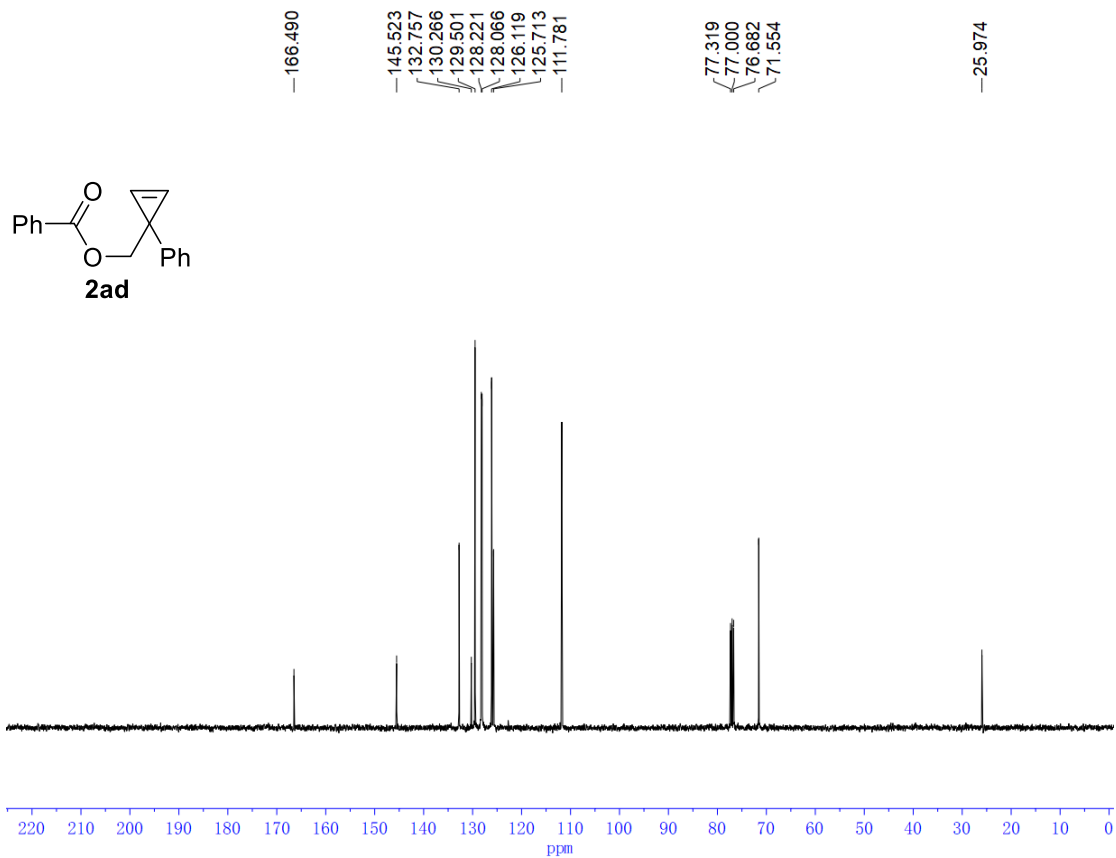


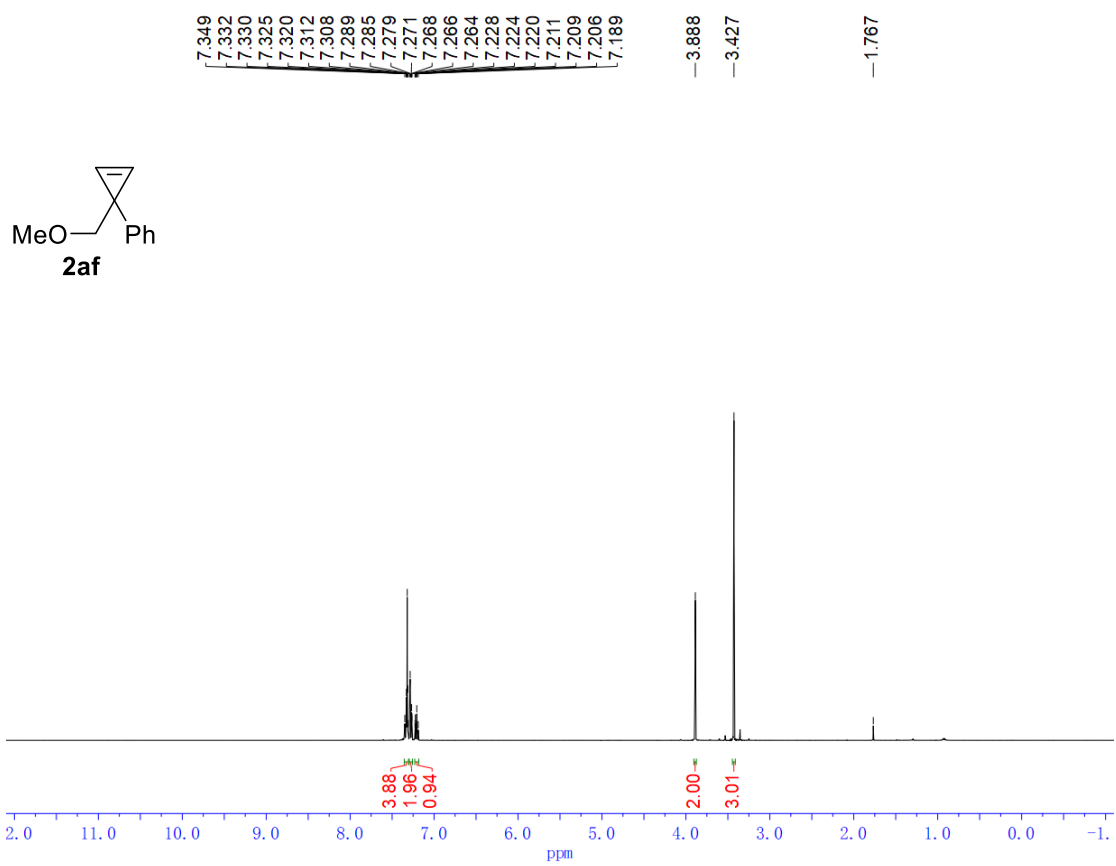
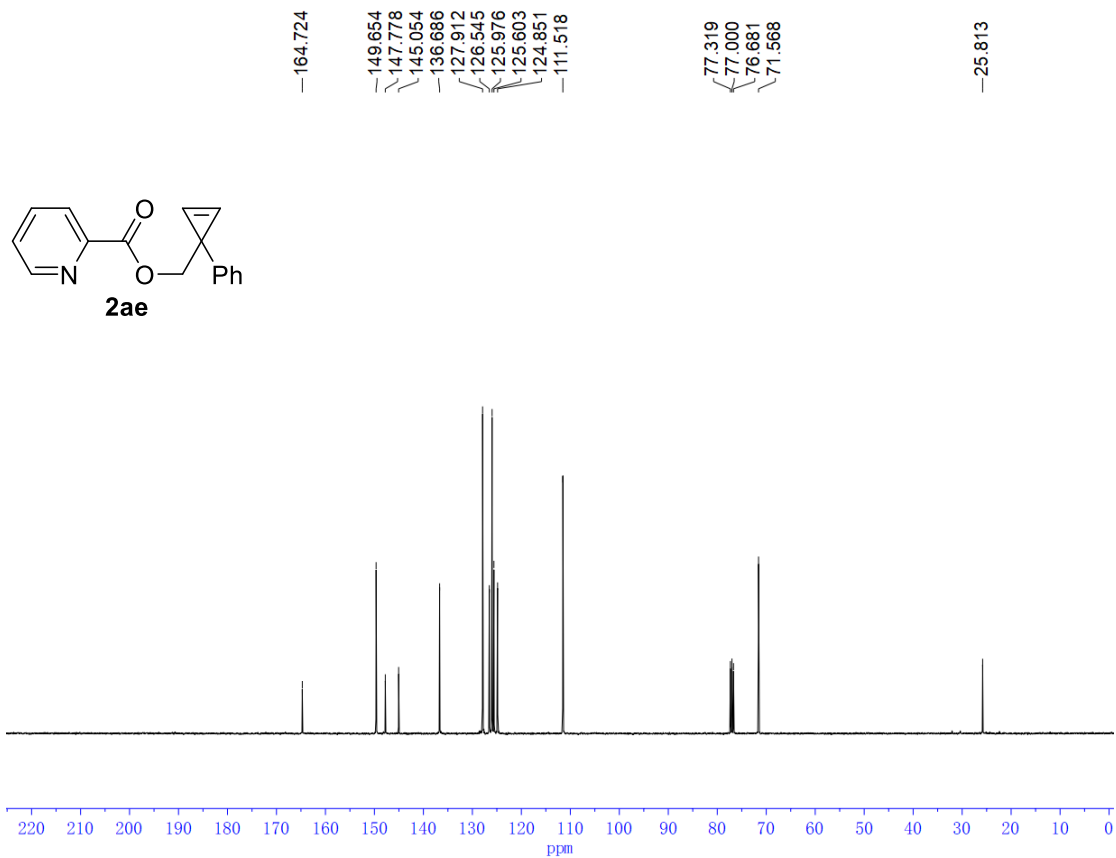


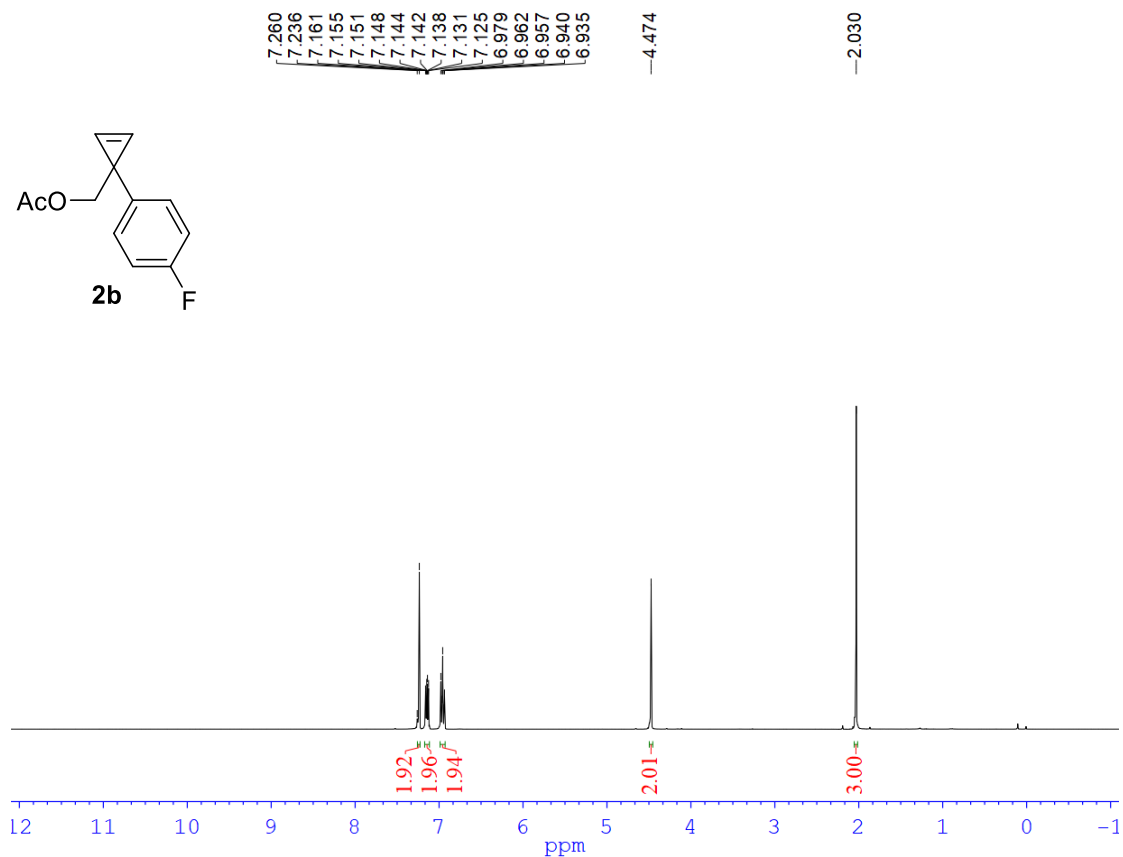
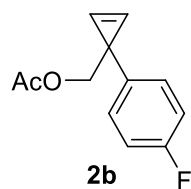
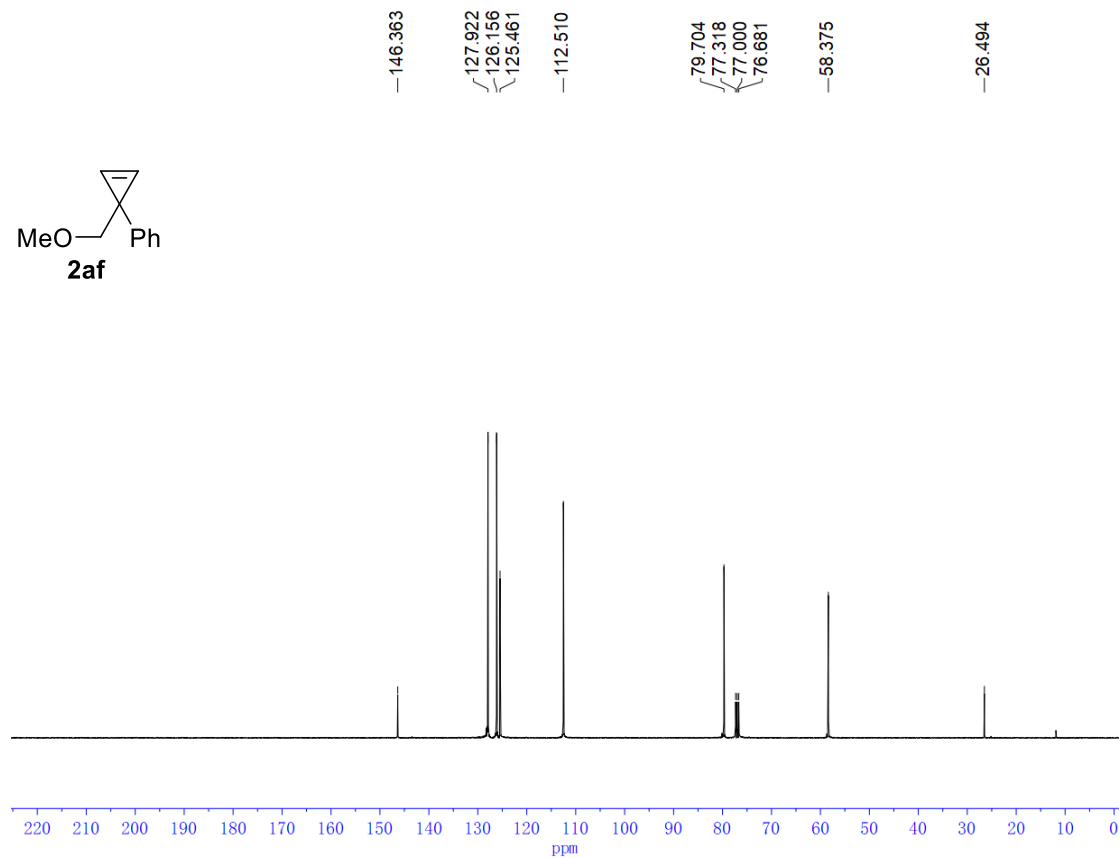
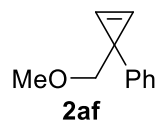


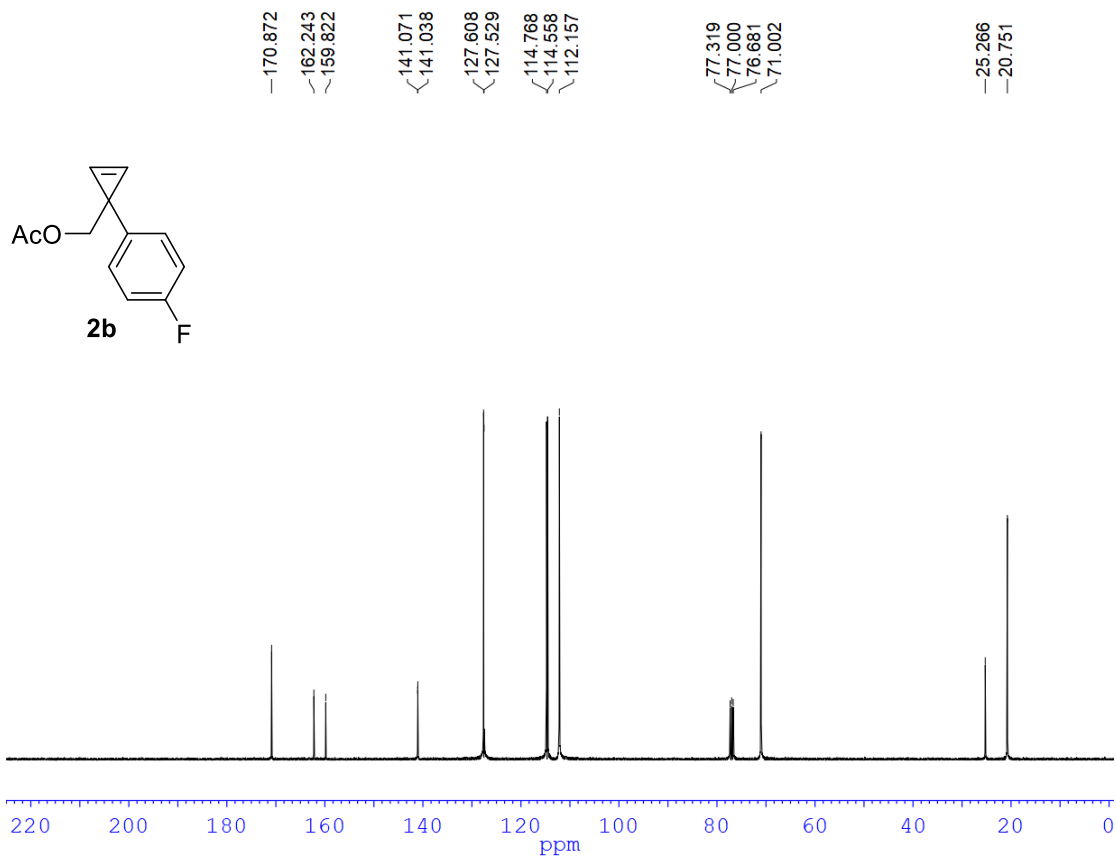


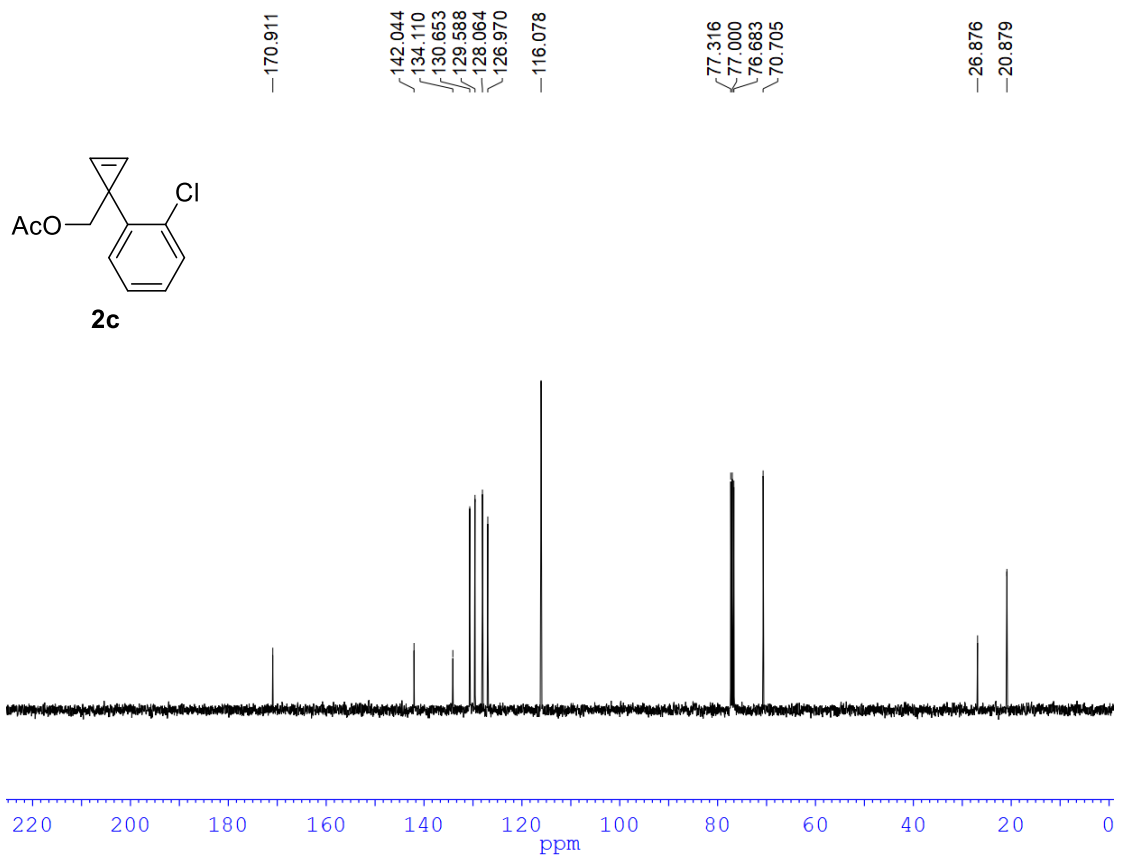
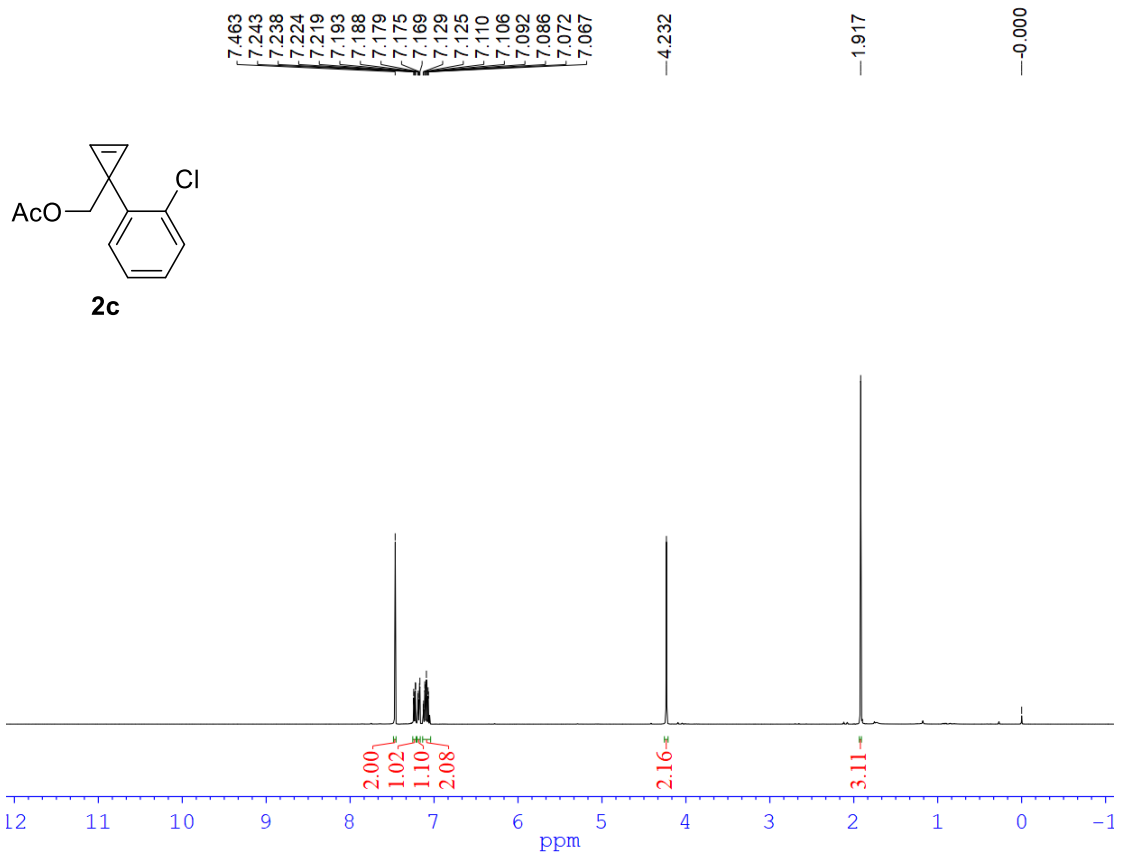


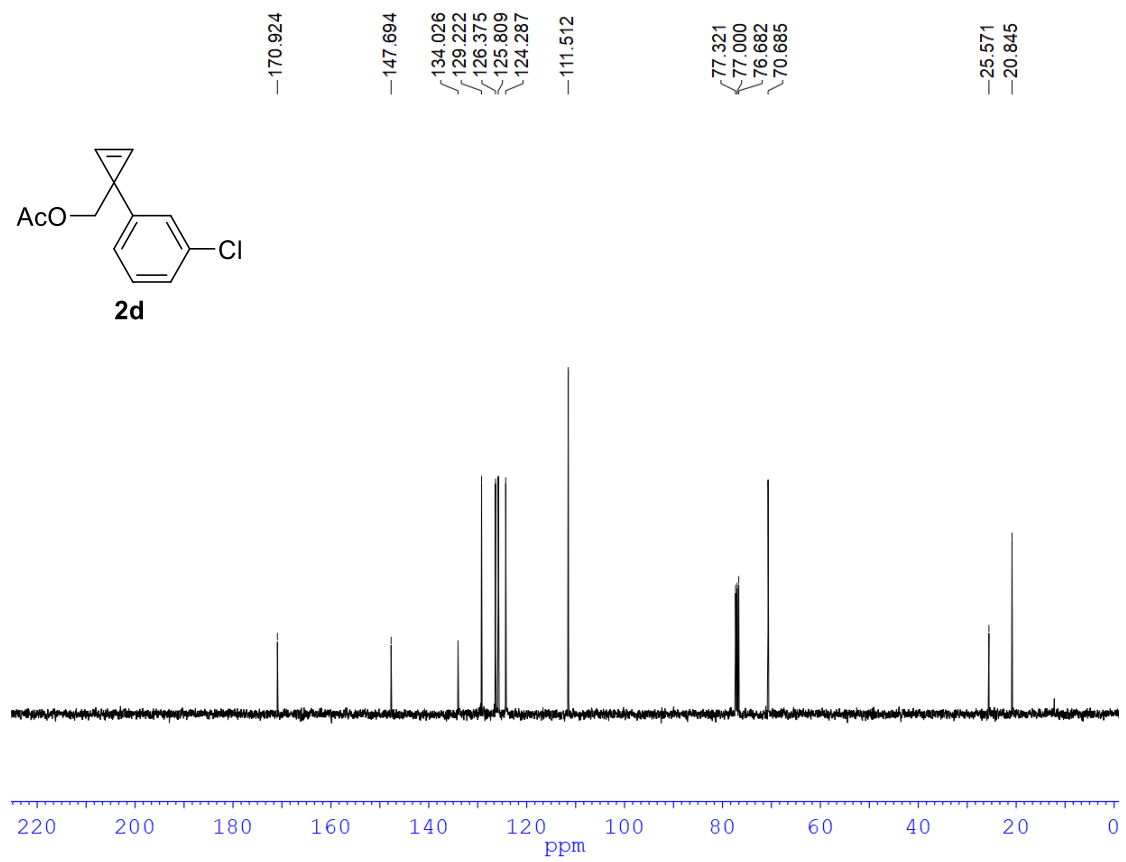
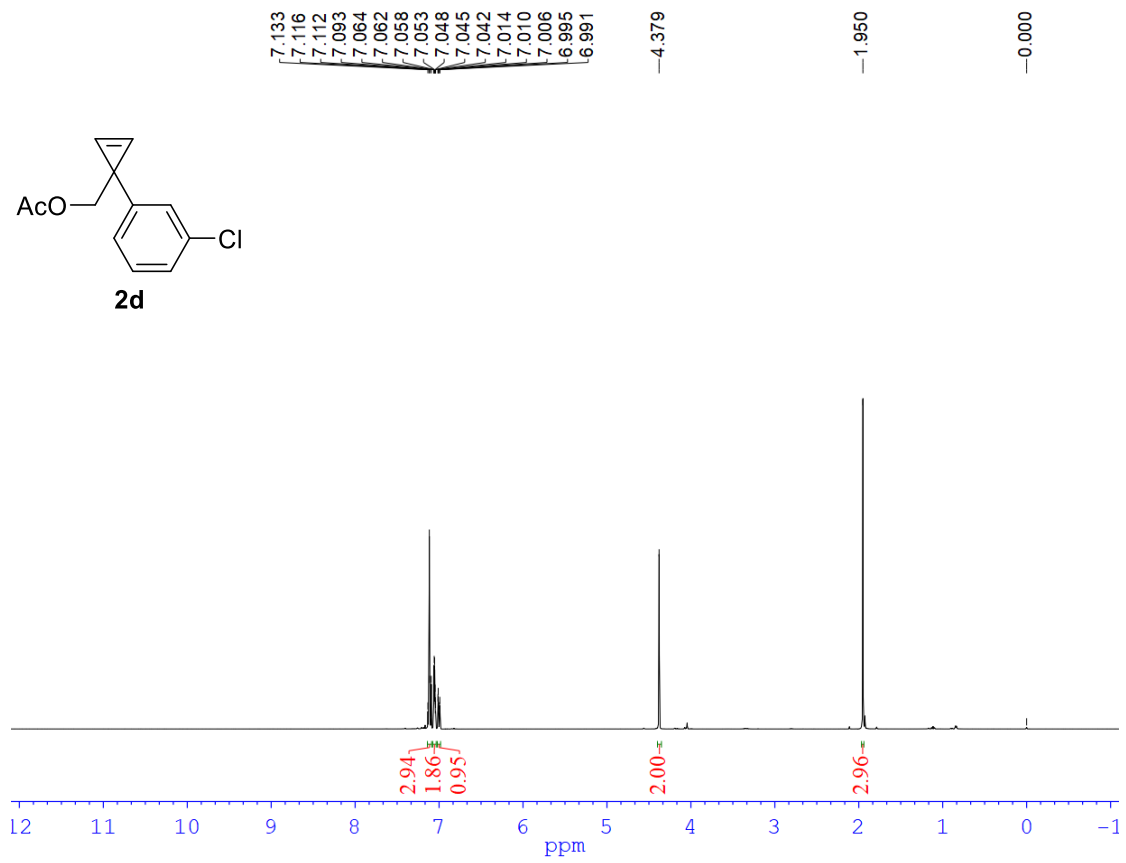


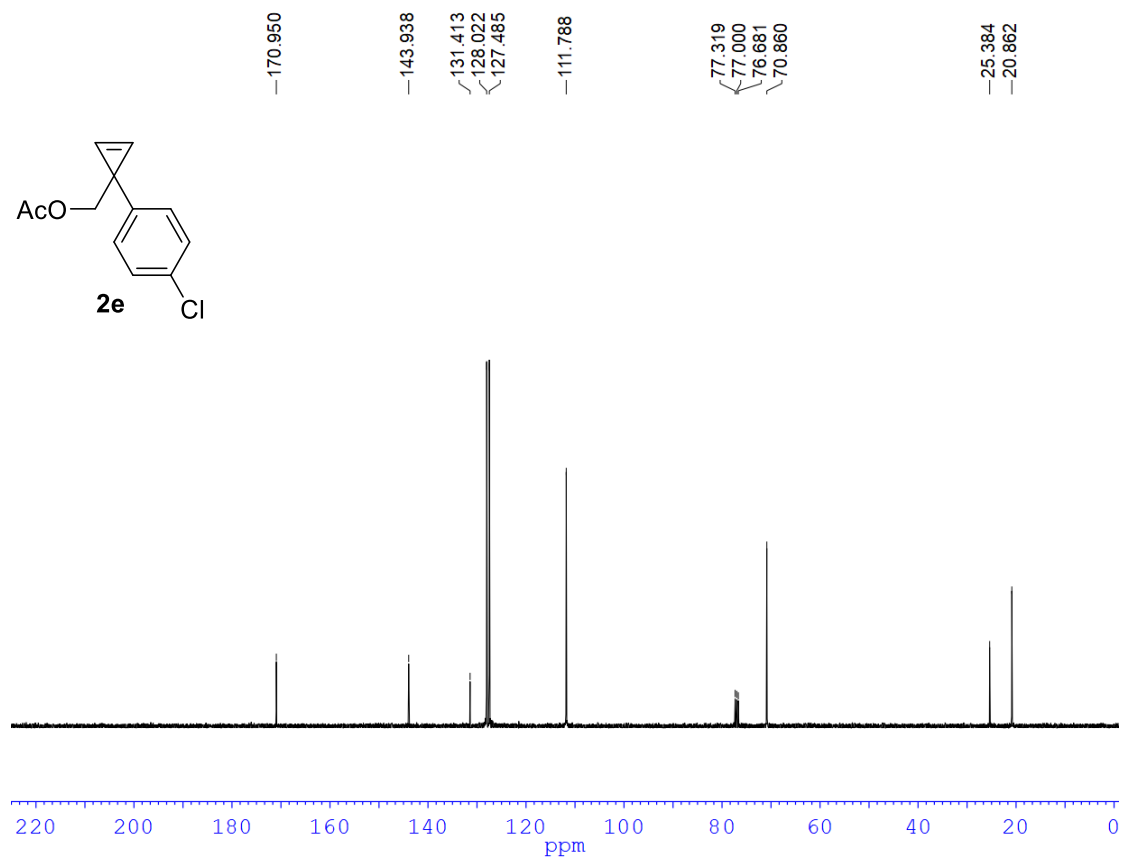
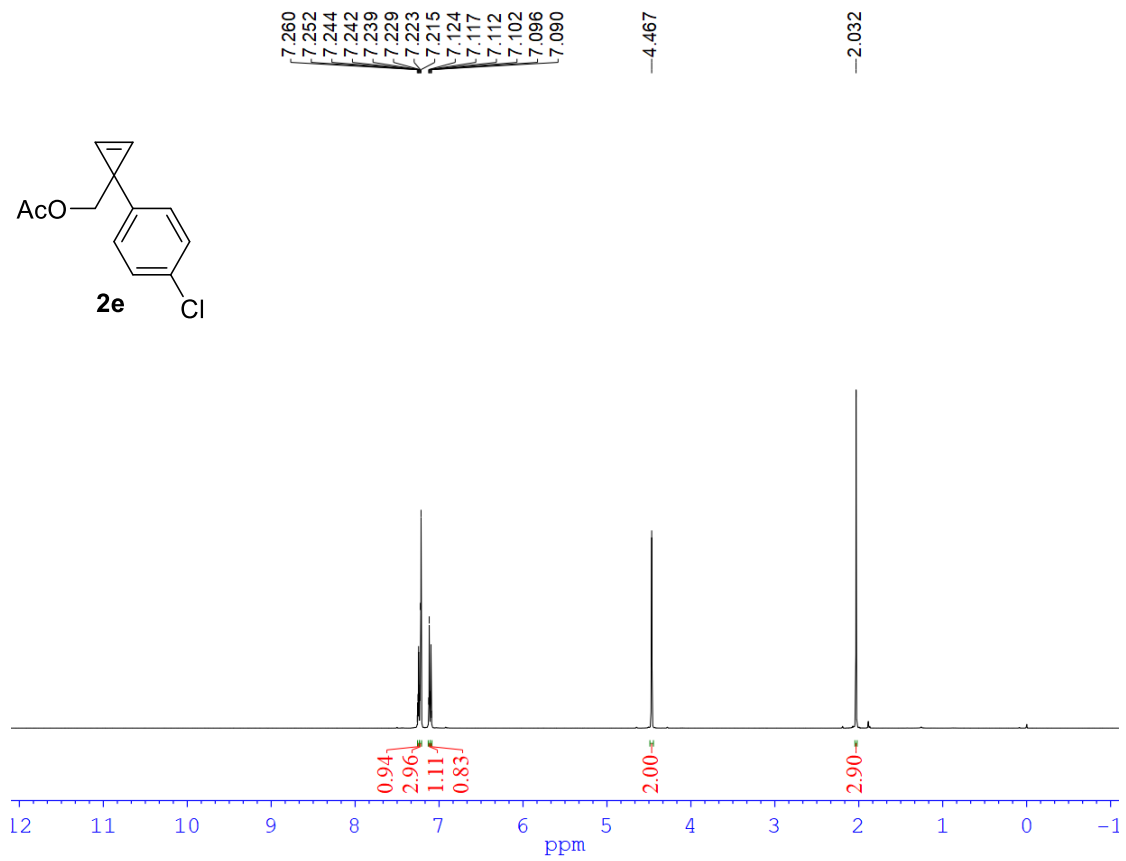


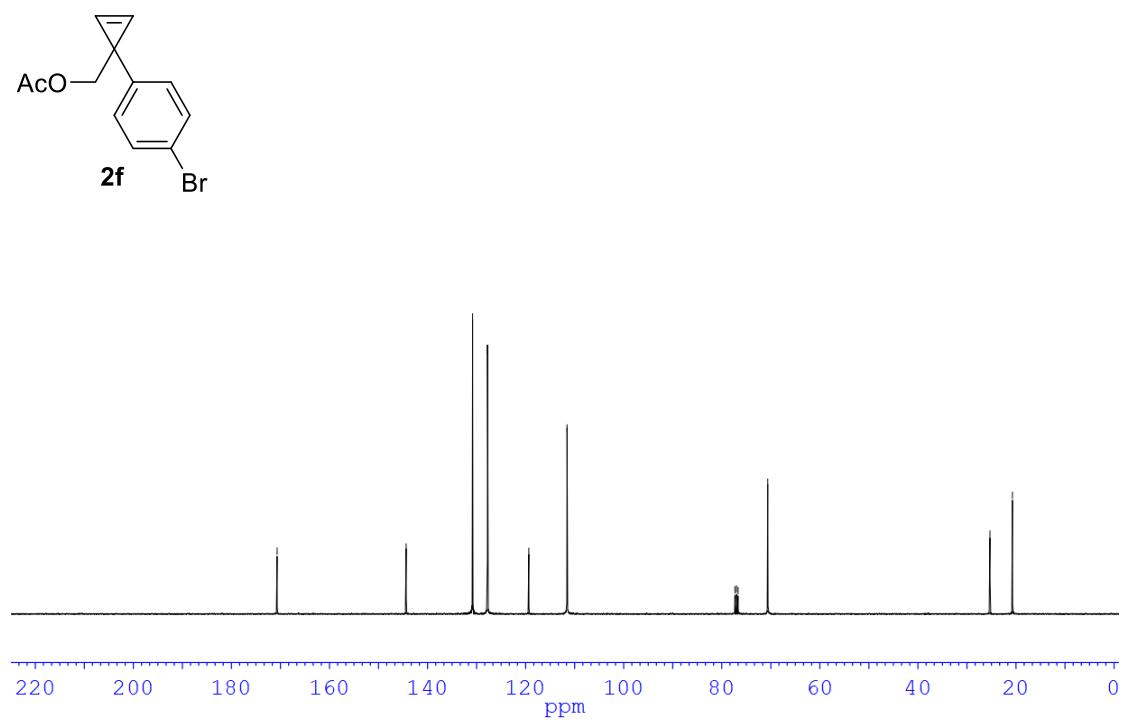
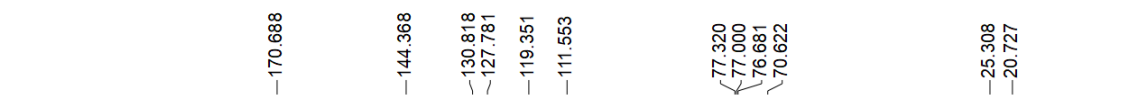
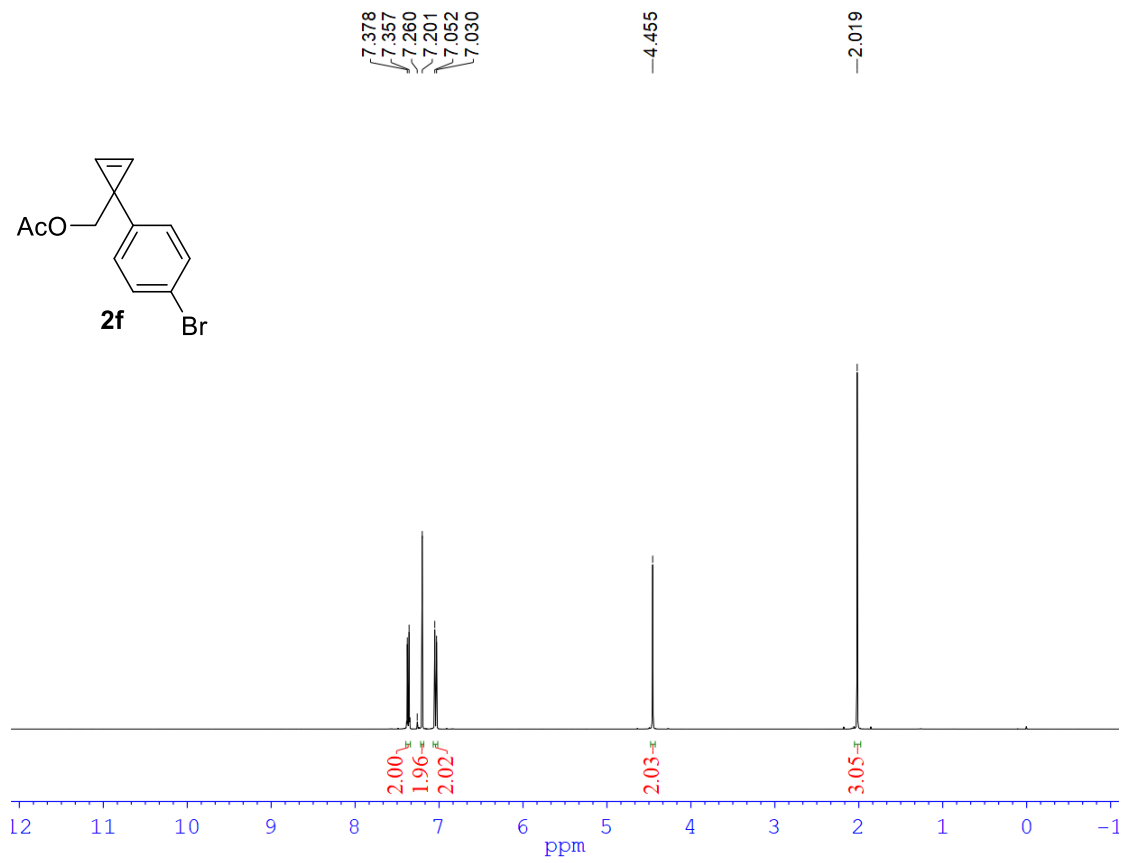


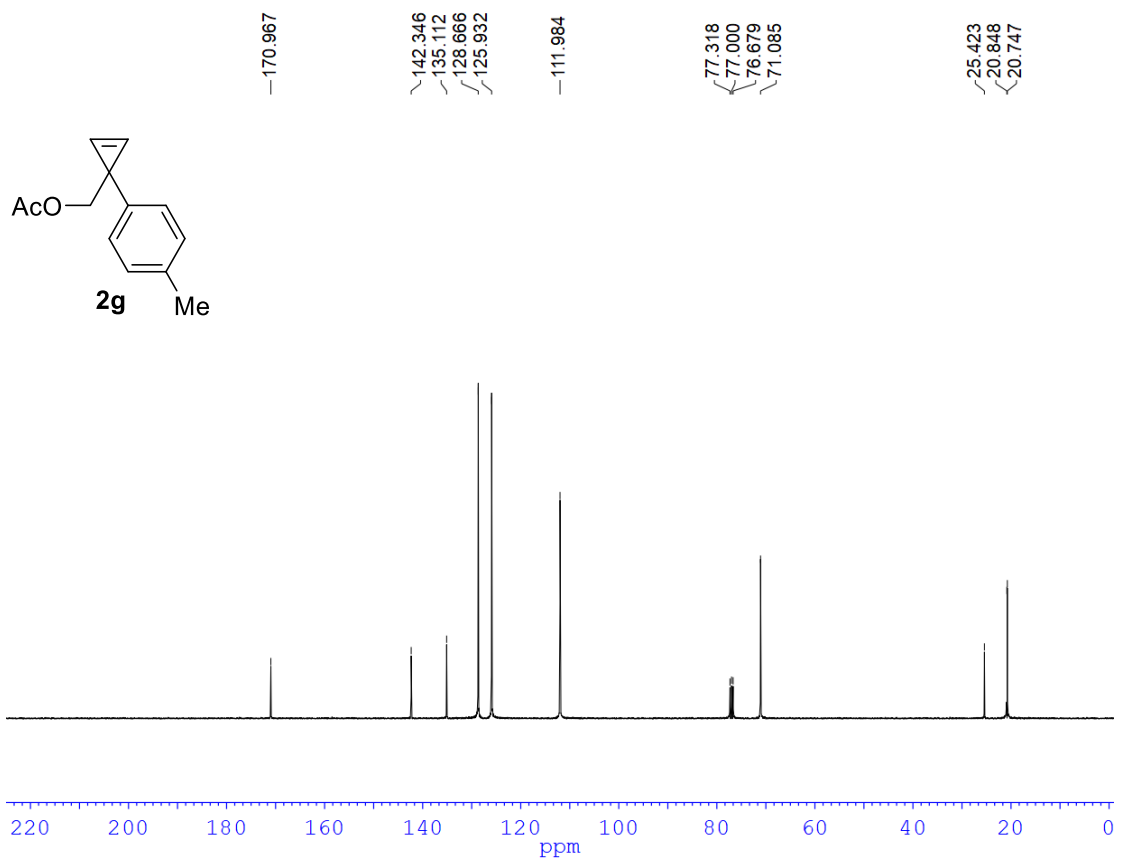
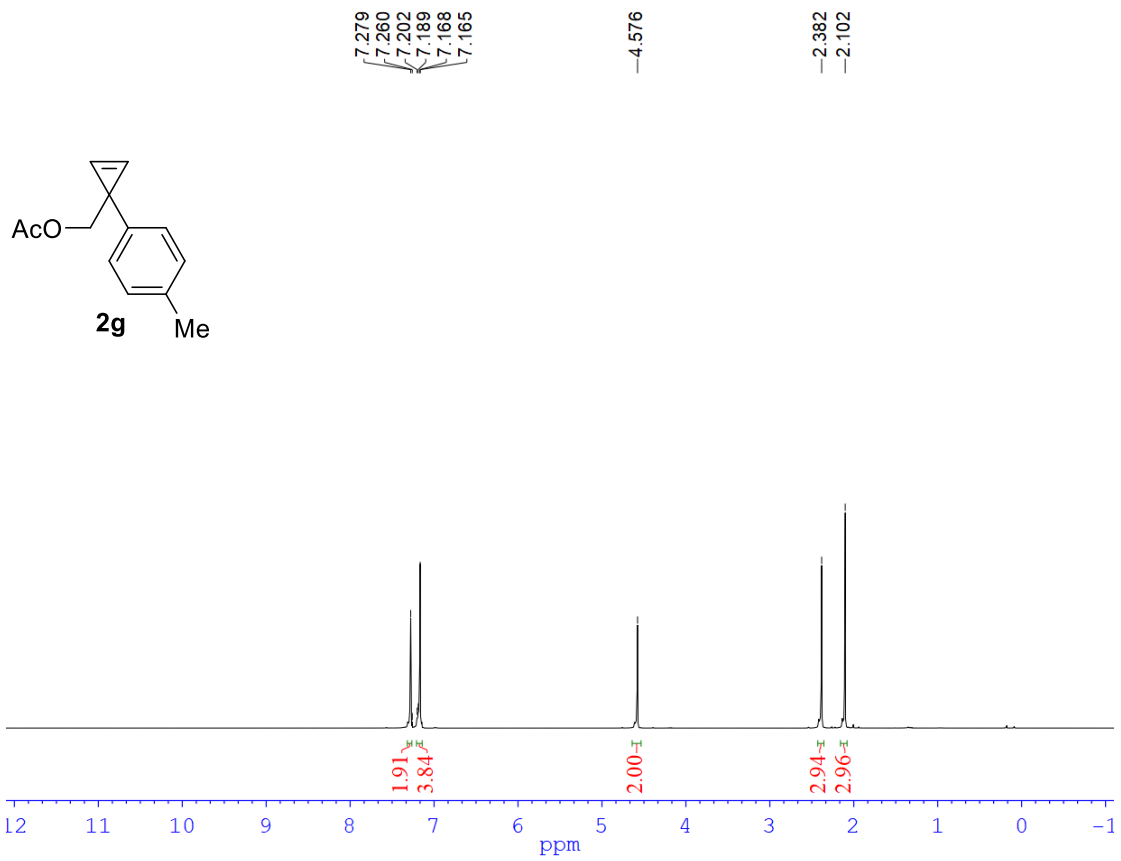


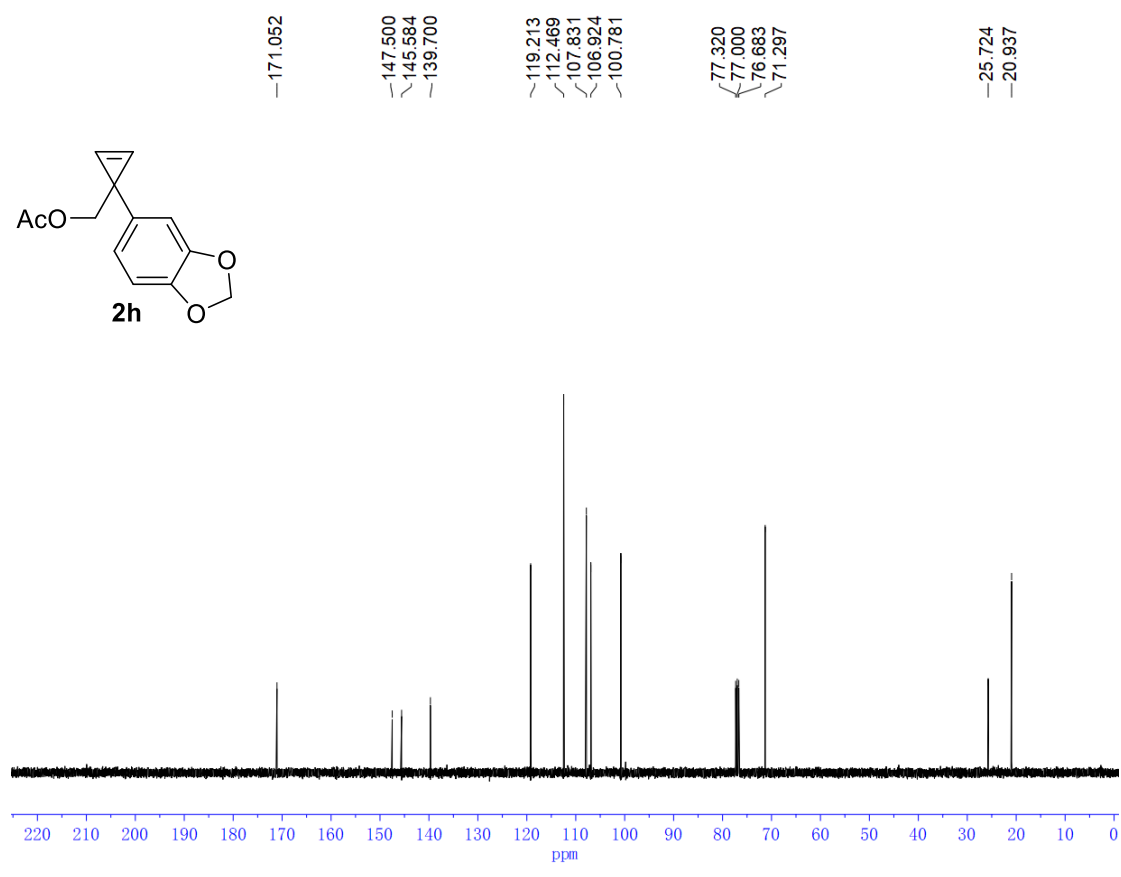
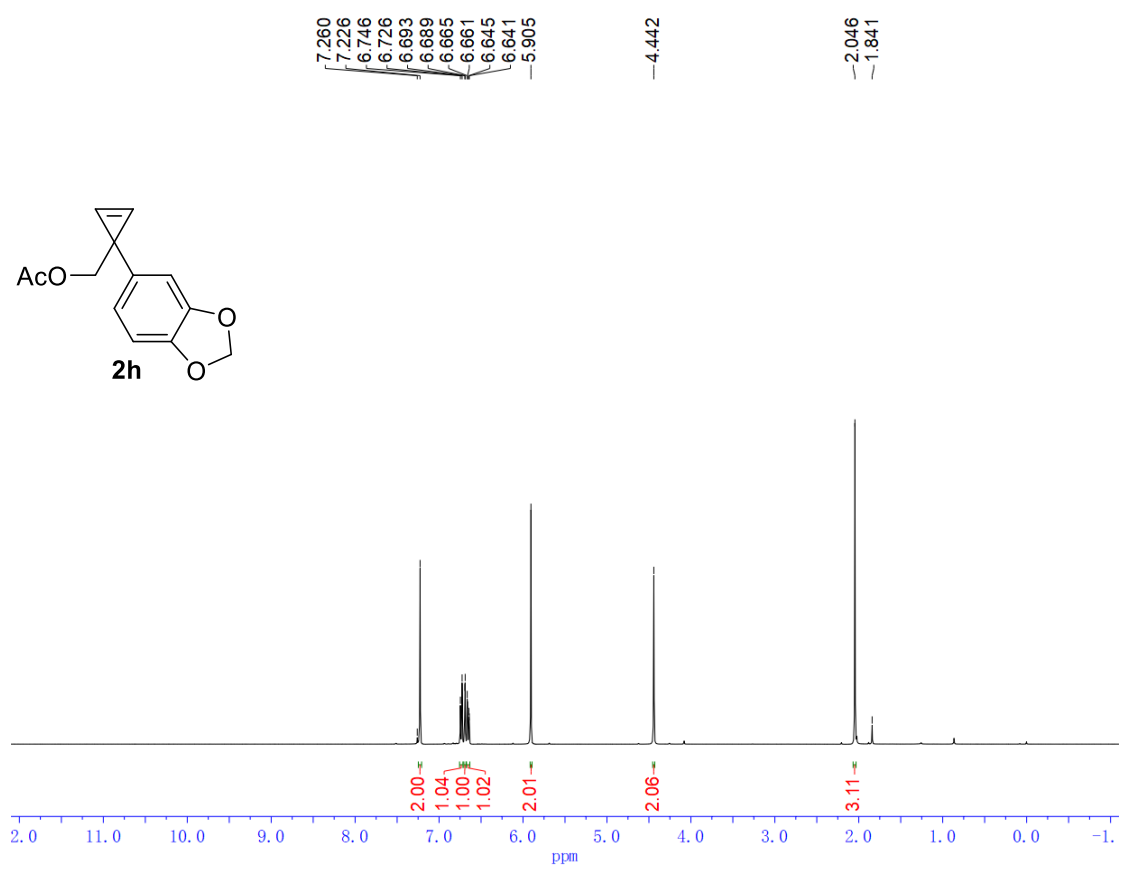


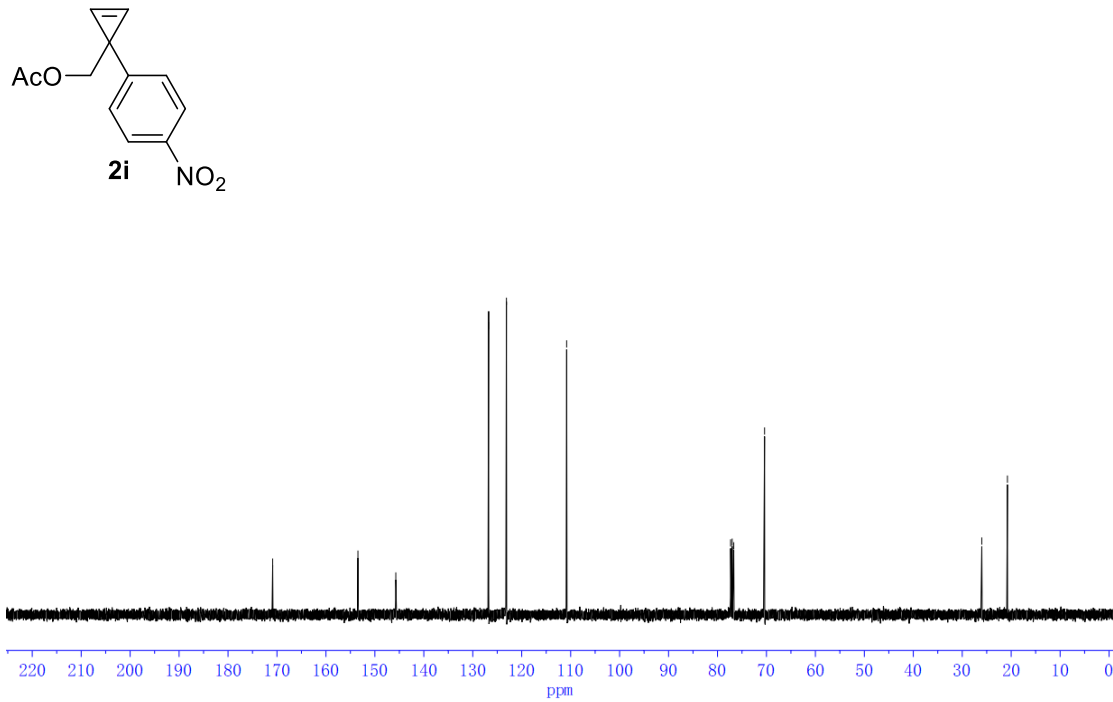
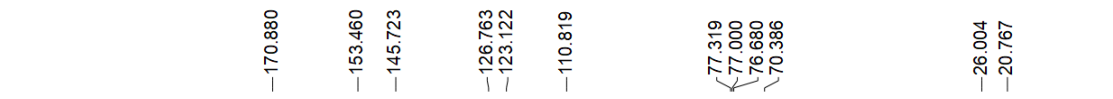
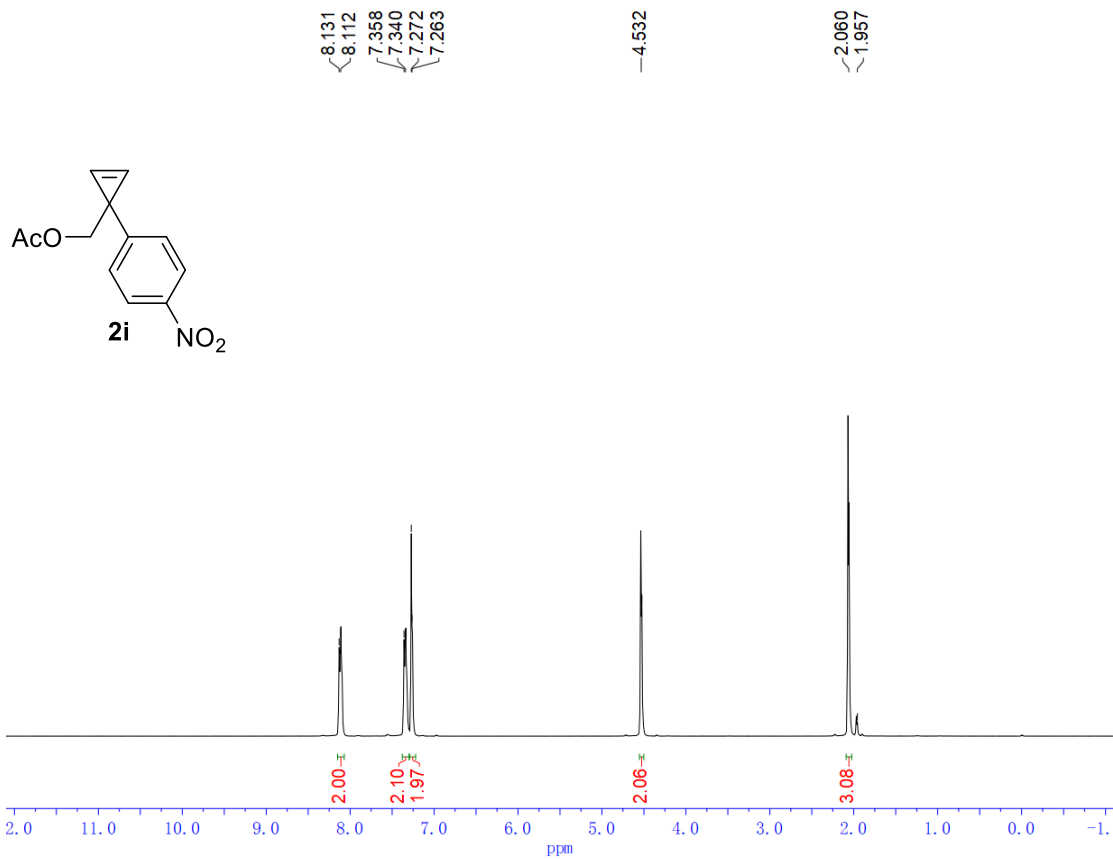


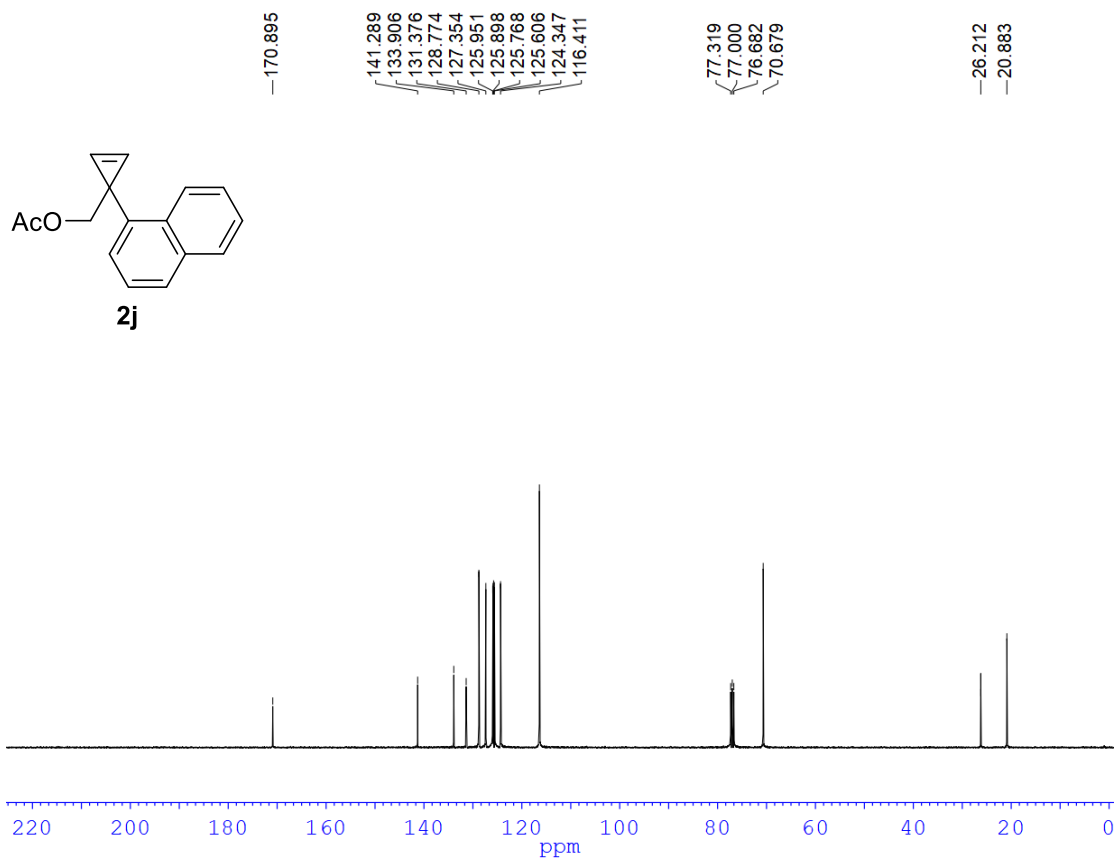
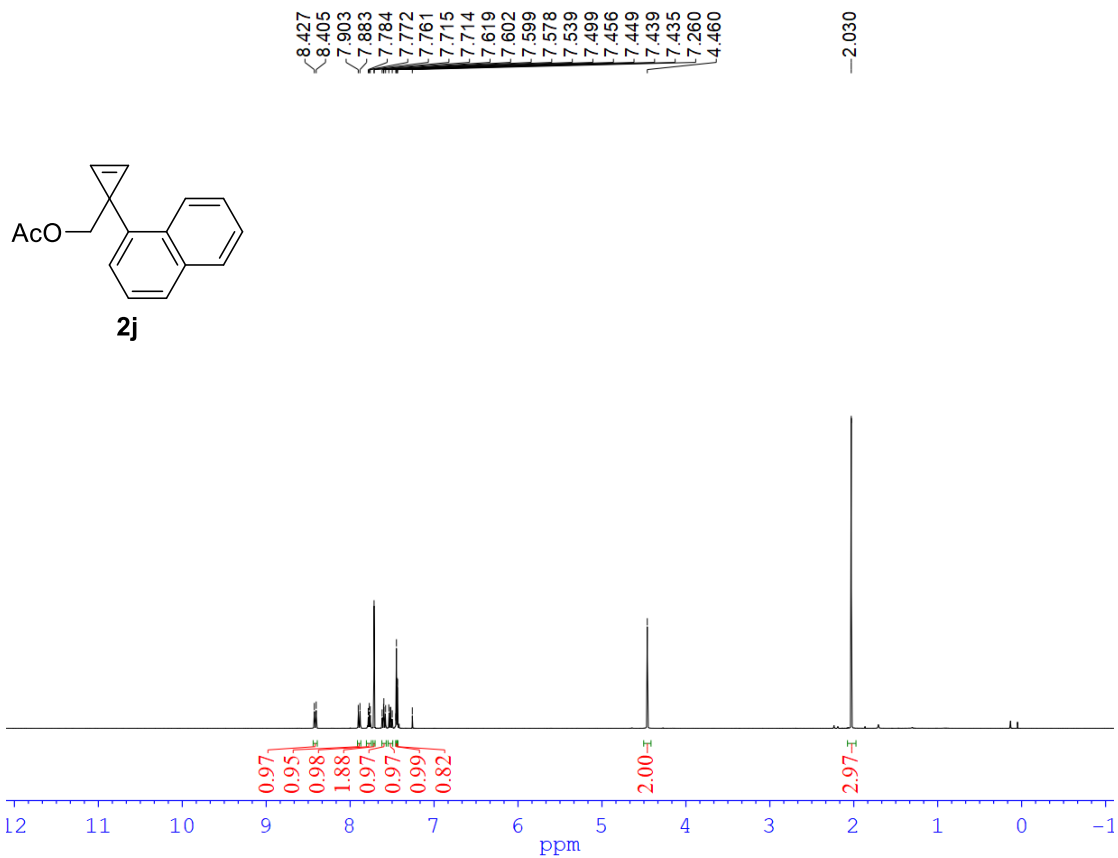




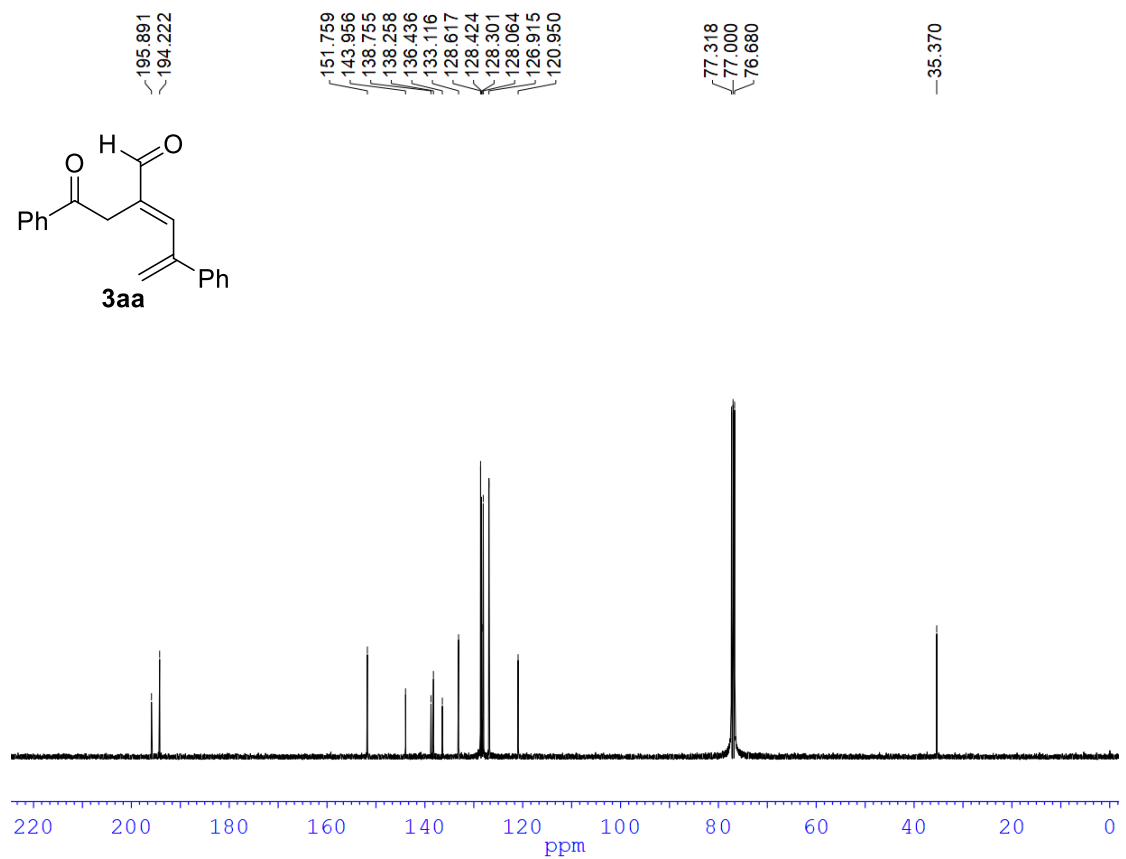
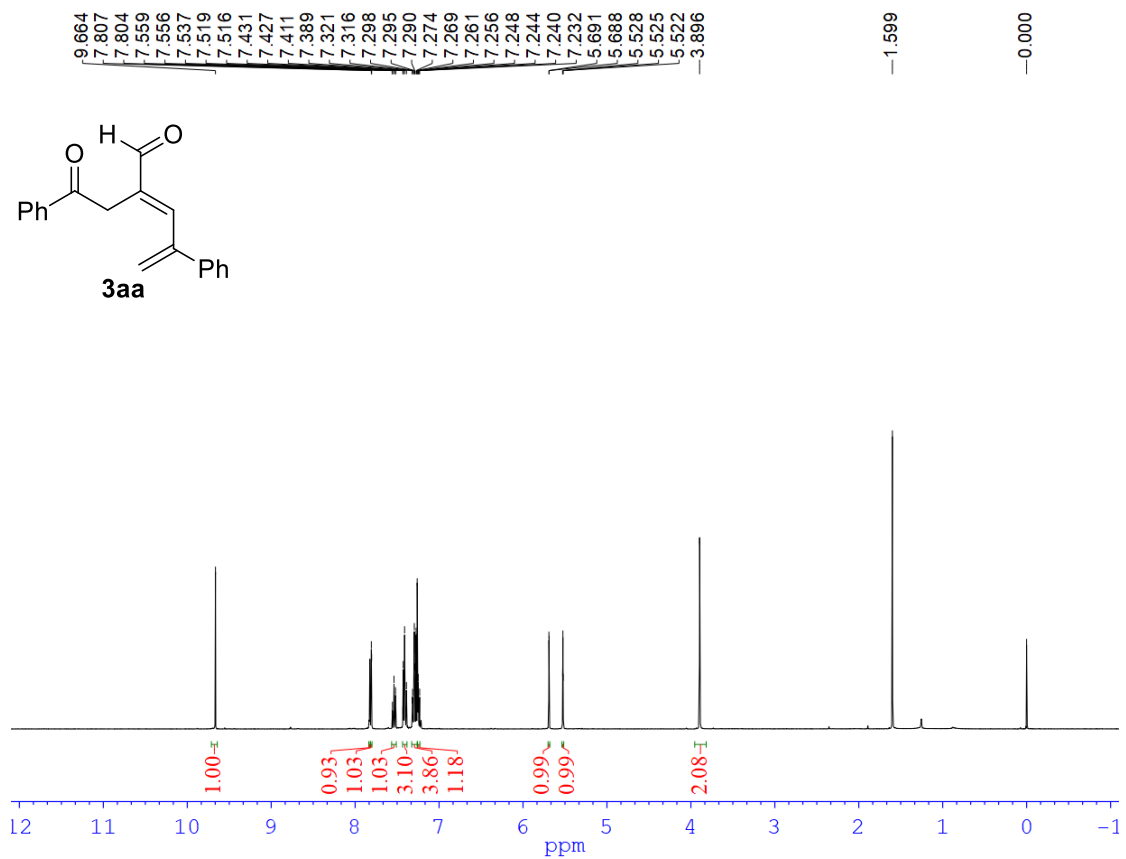




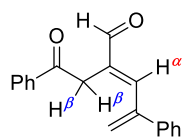
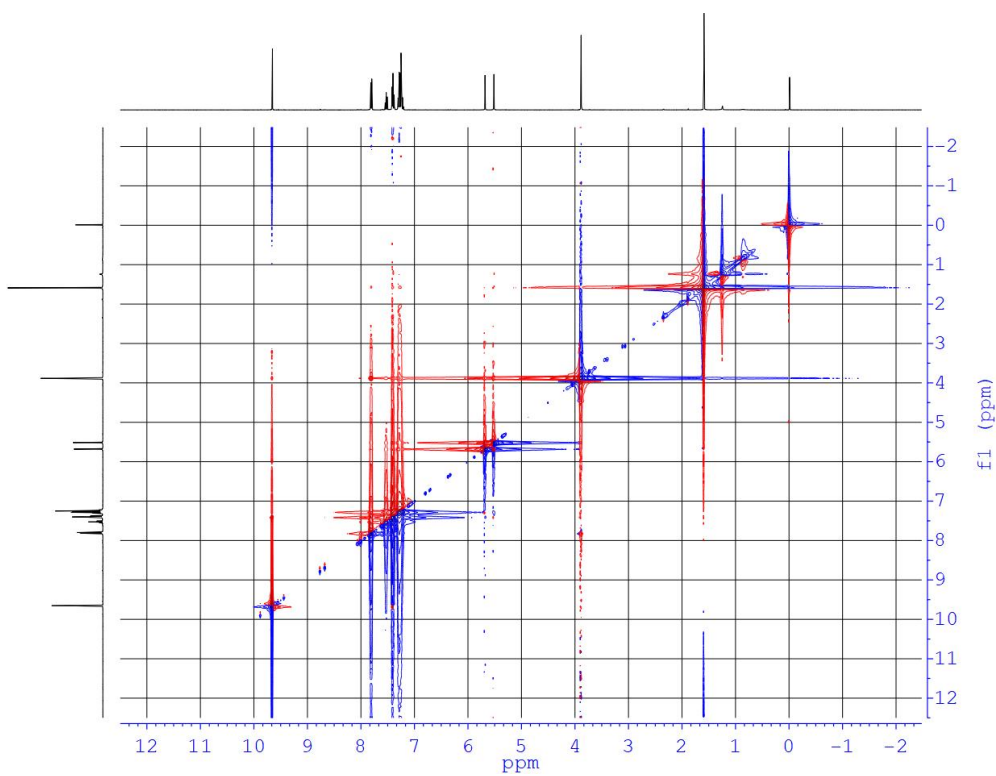




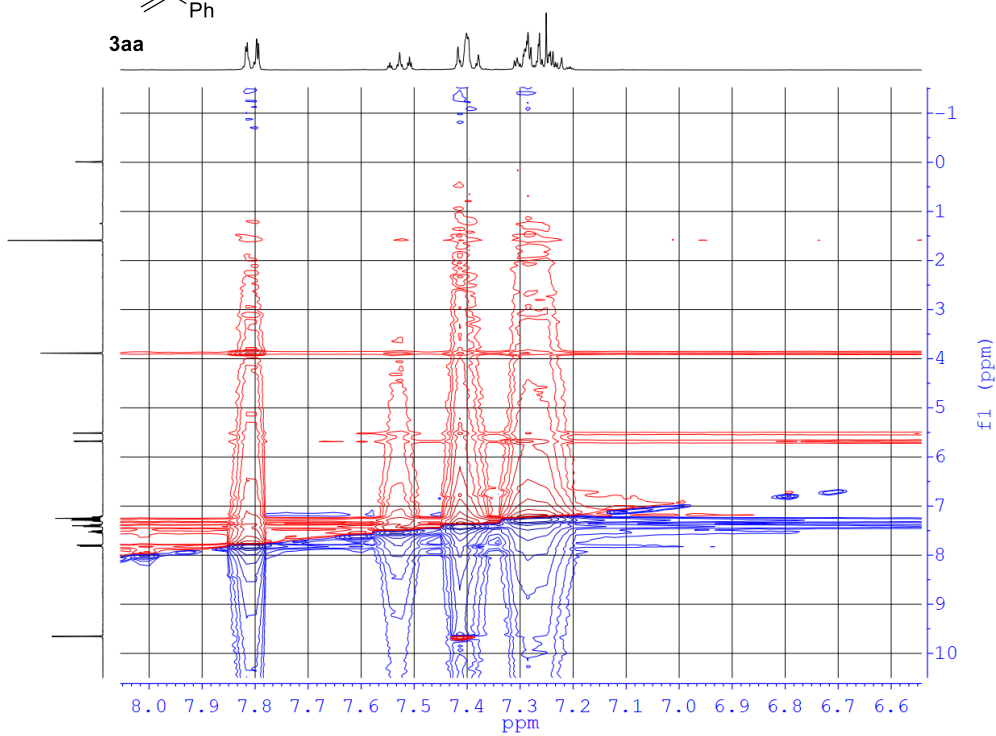
^1H and ^{13}C NMR spectra of 1,3-dienes:

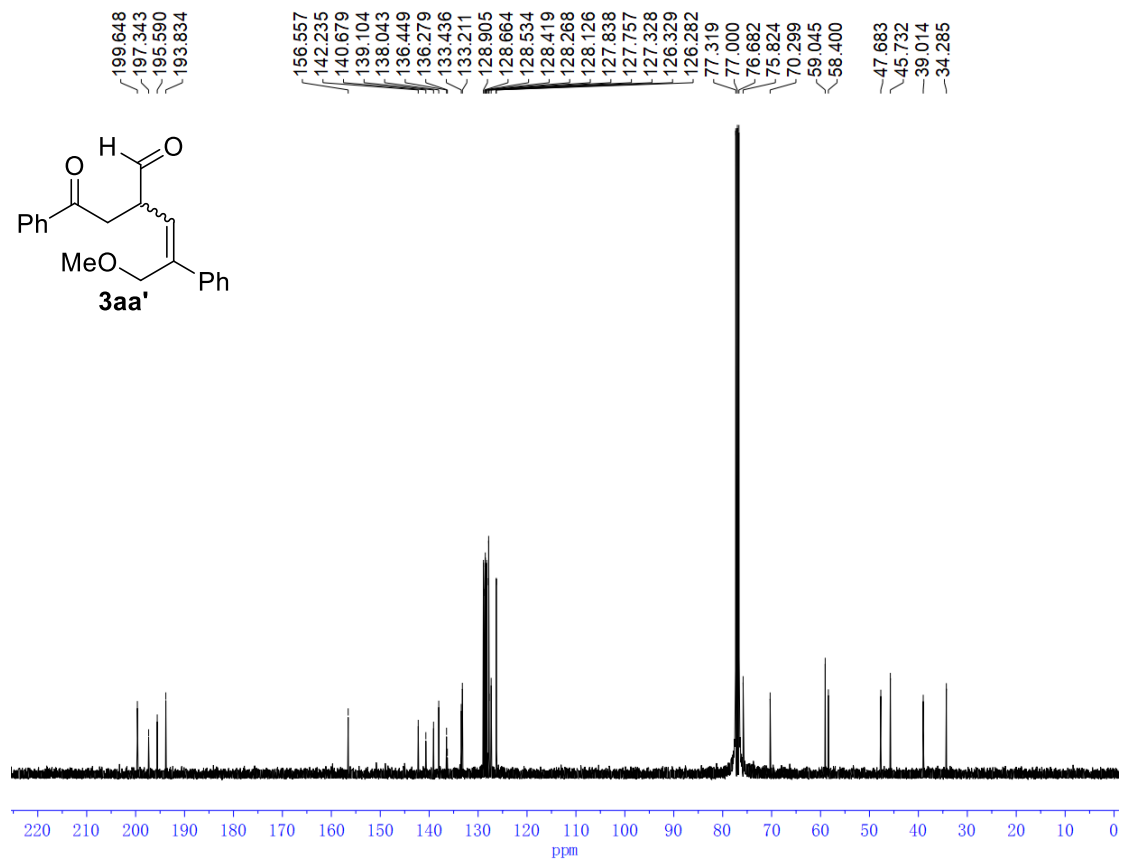
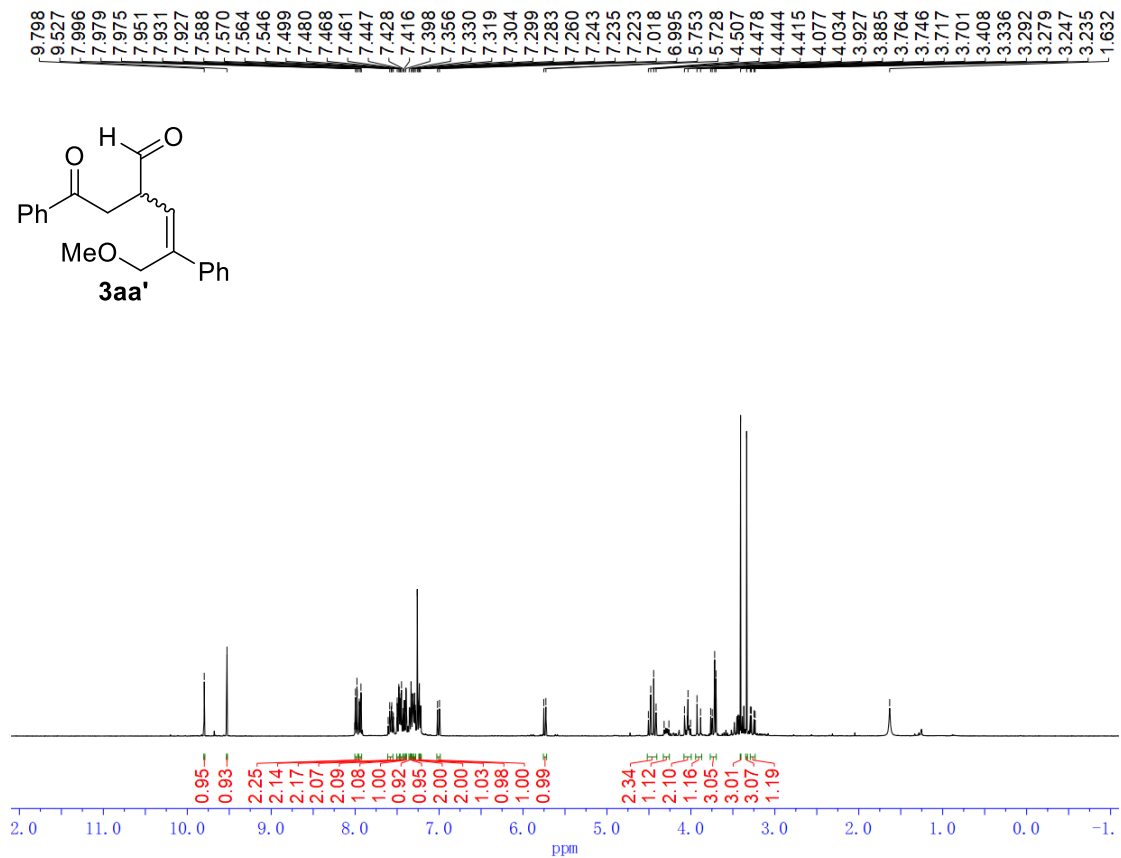


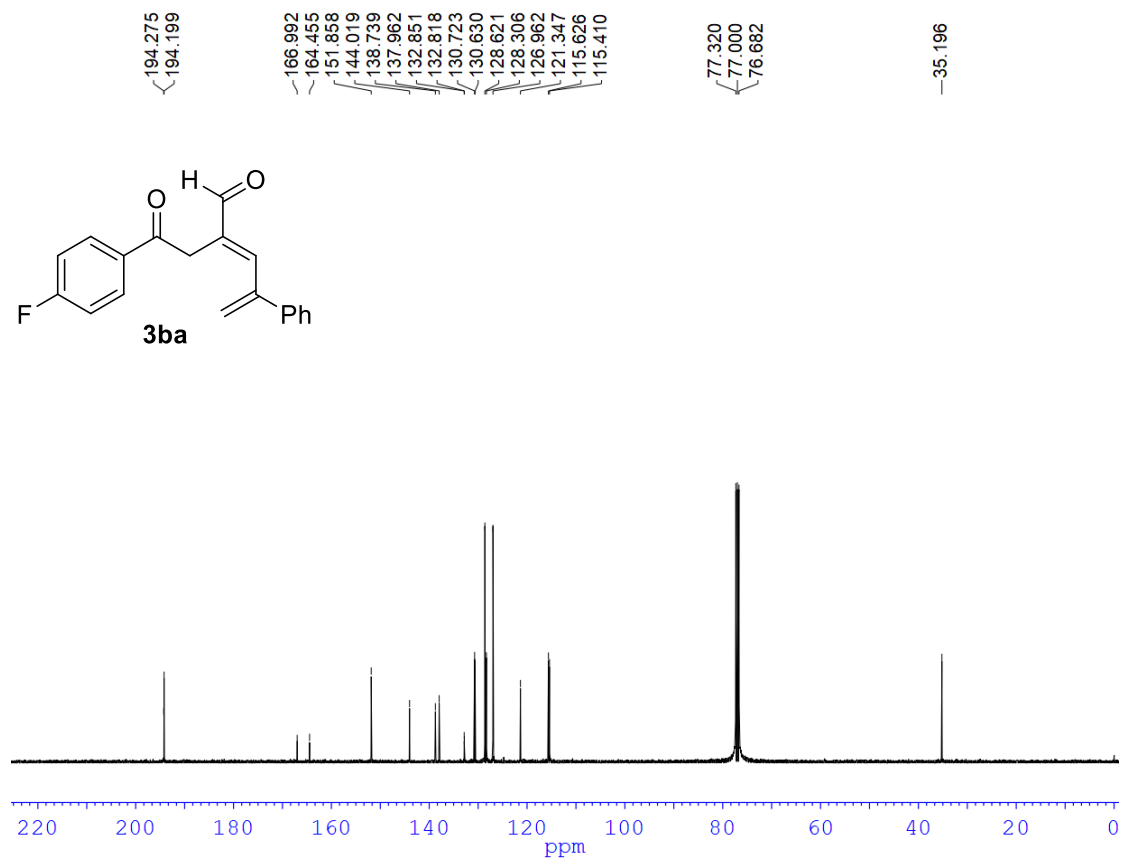
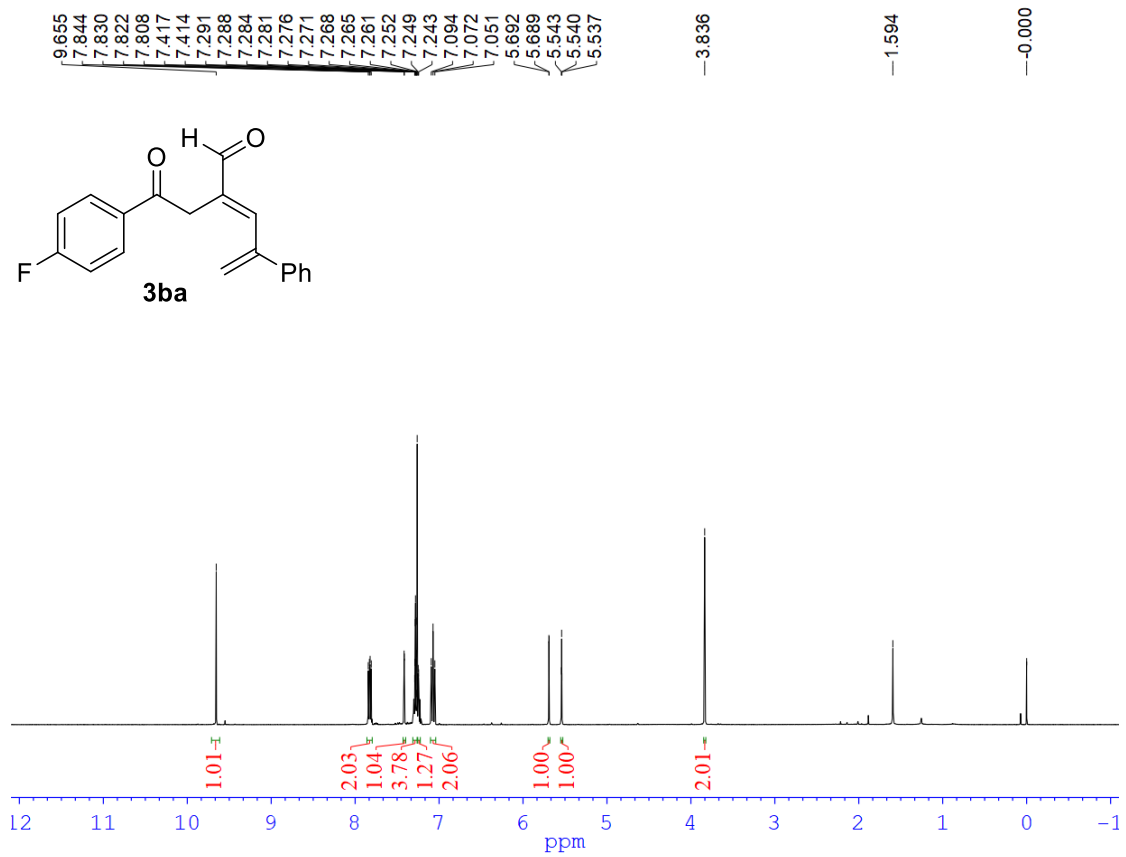
NOESY:

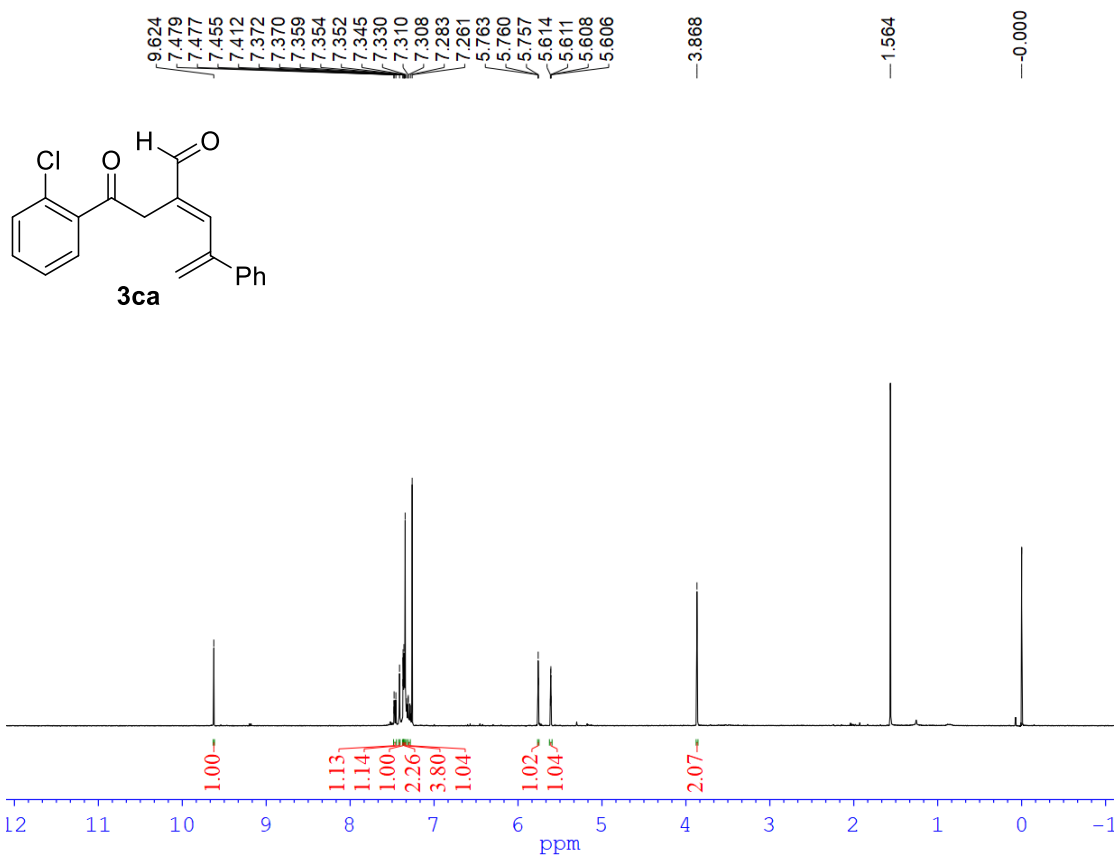
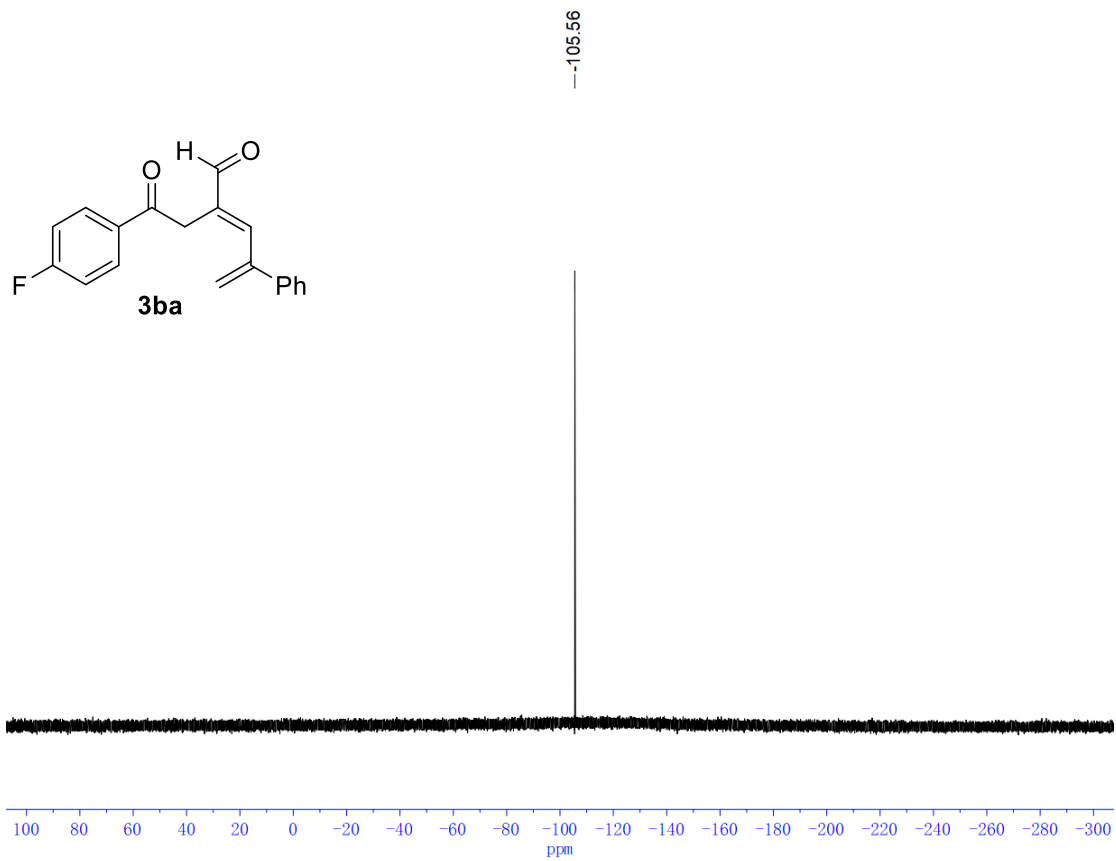


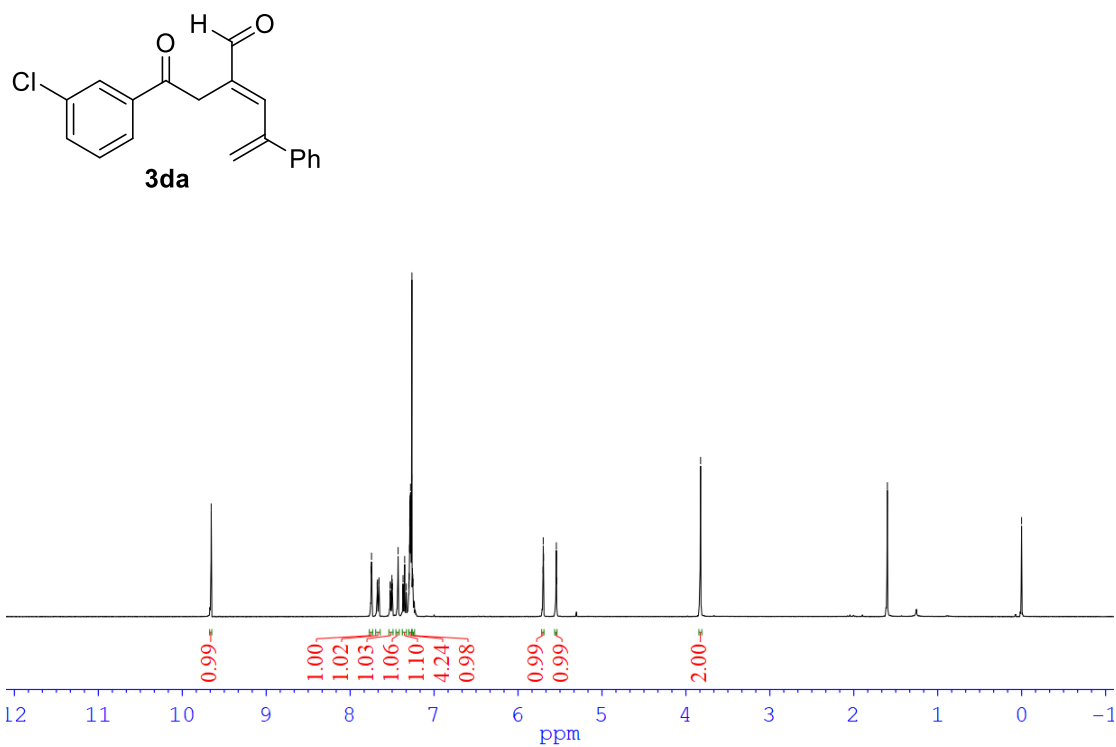
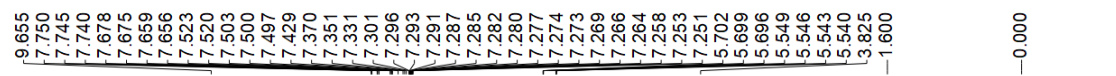
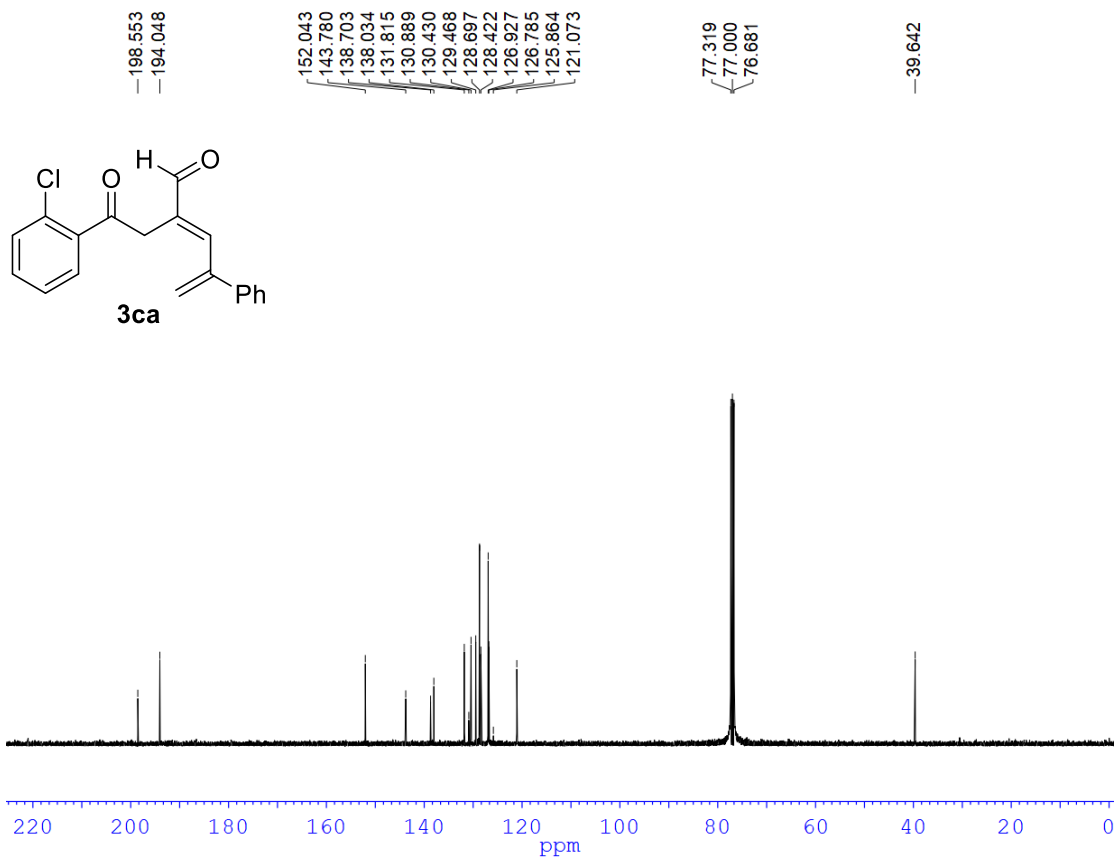
NO NOE was observed between H^α and H^β

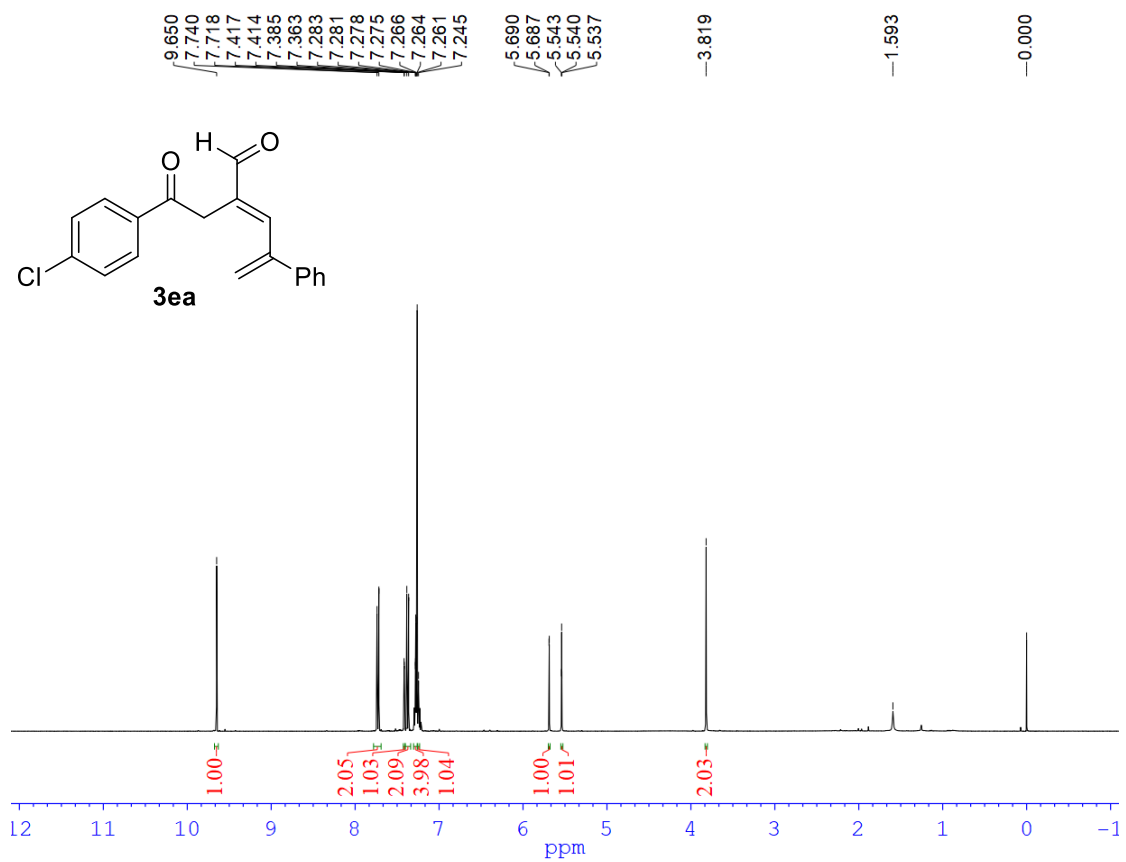
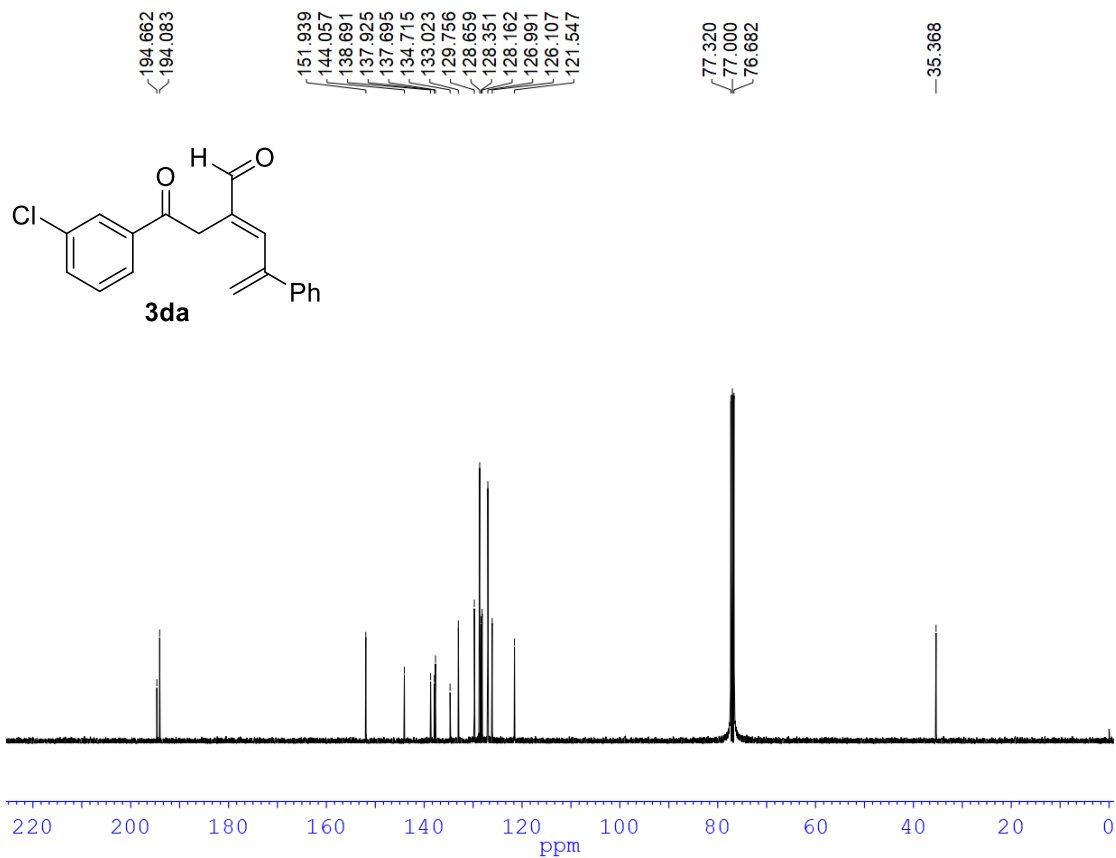


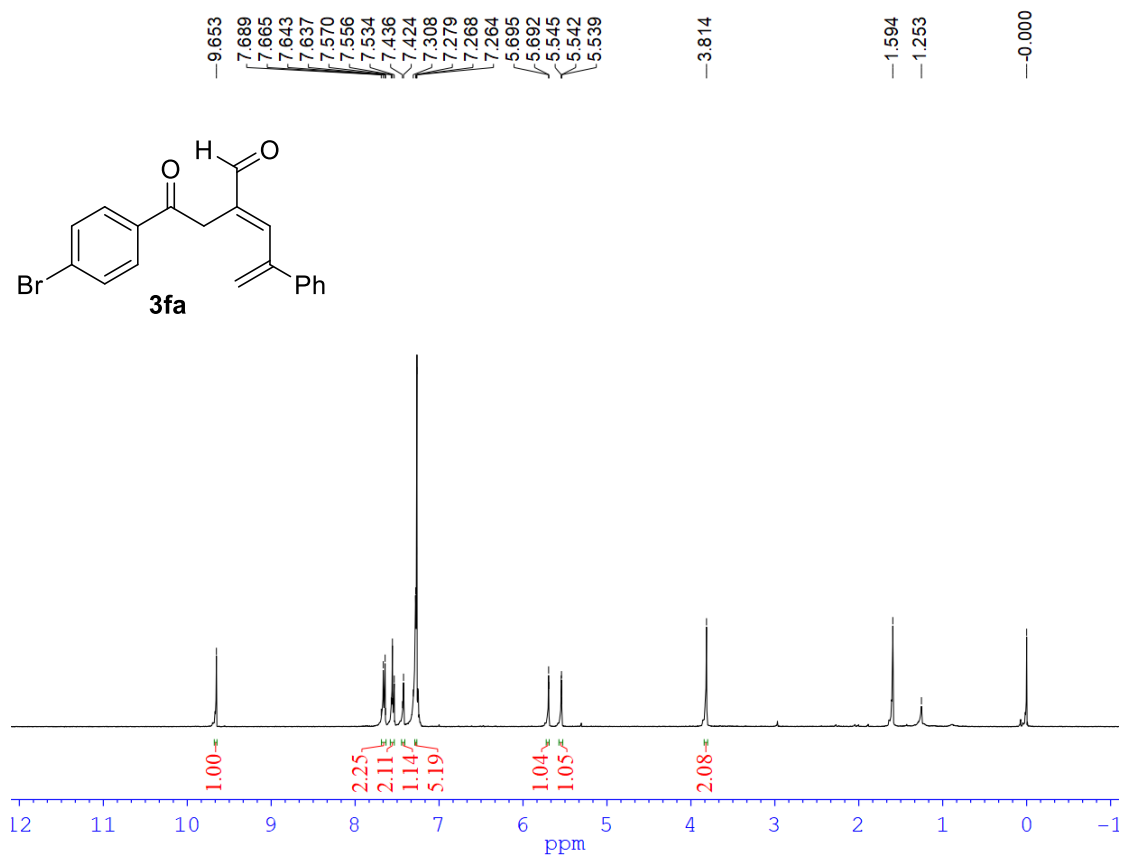
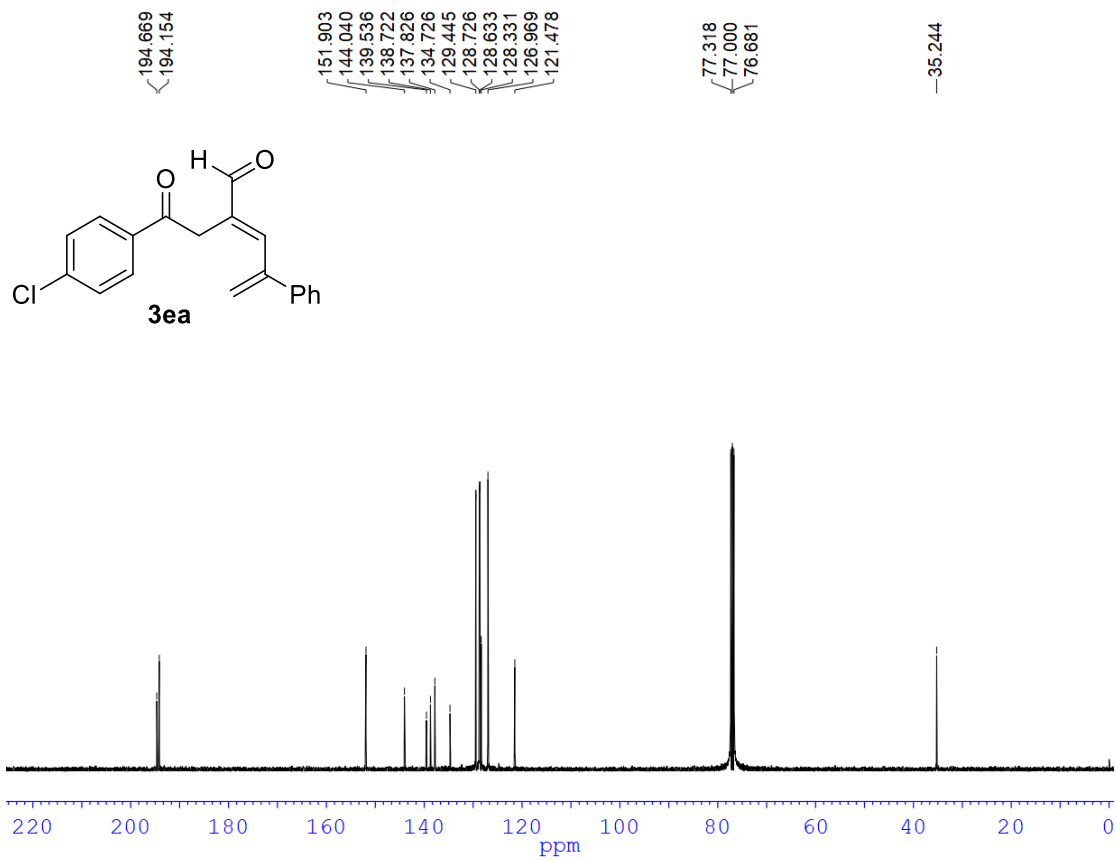


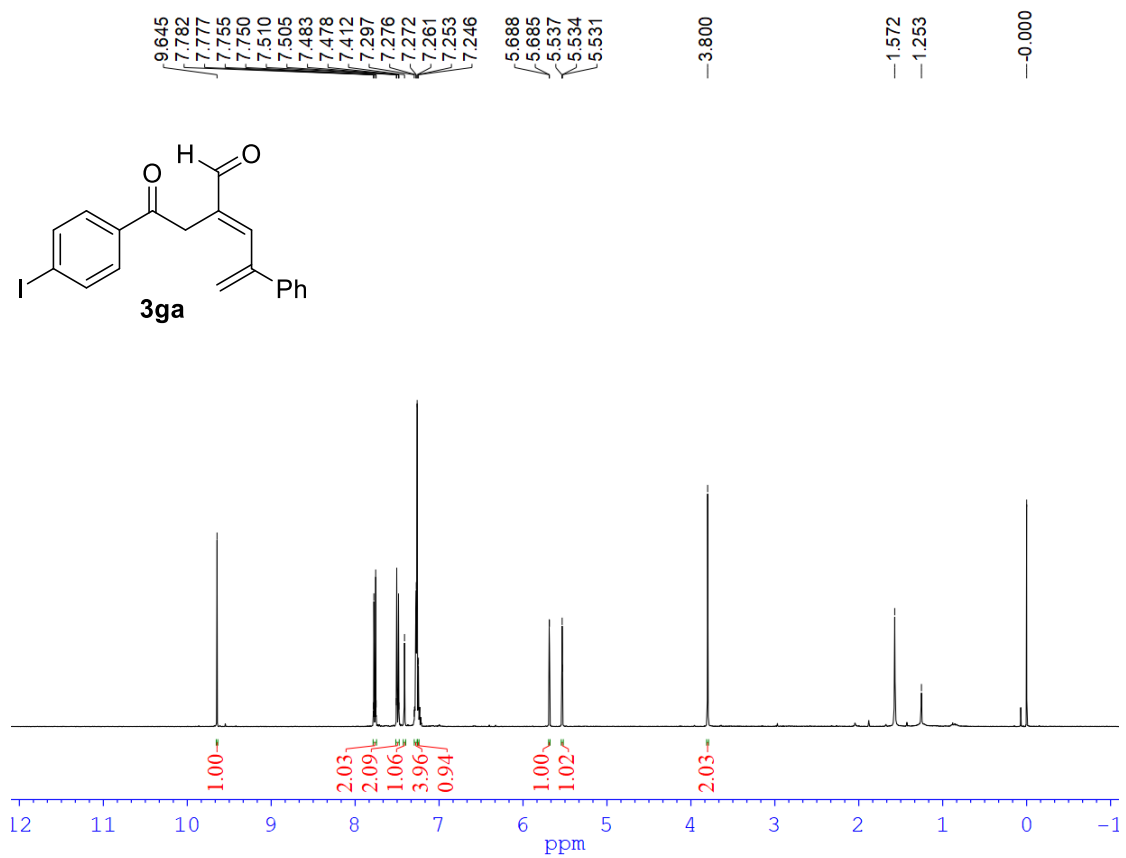
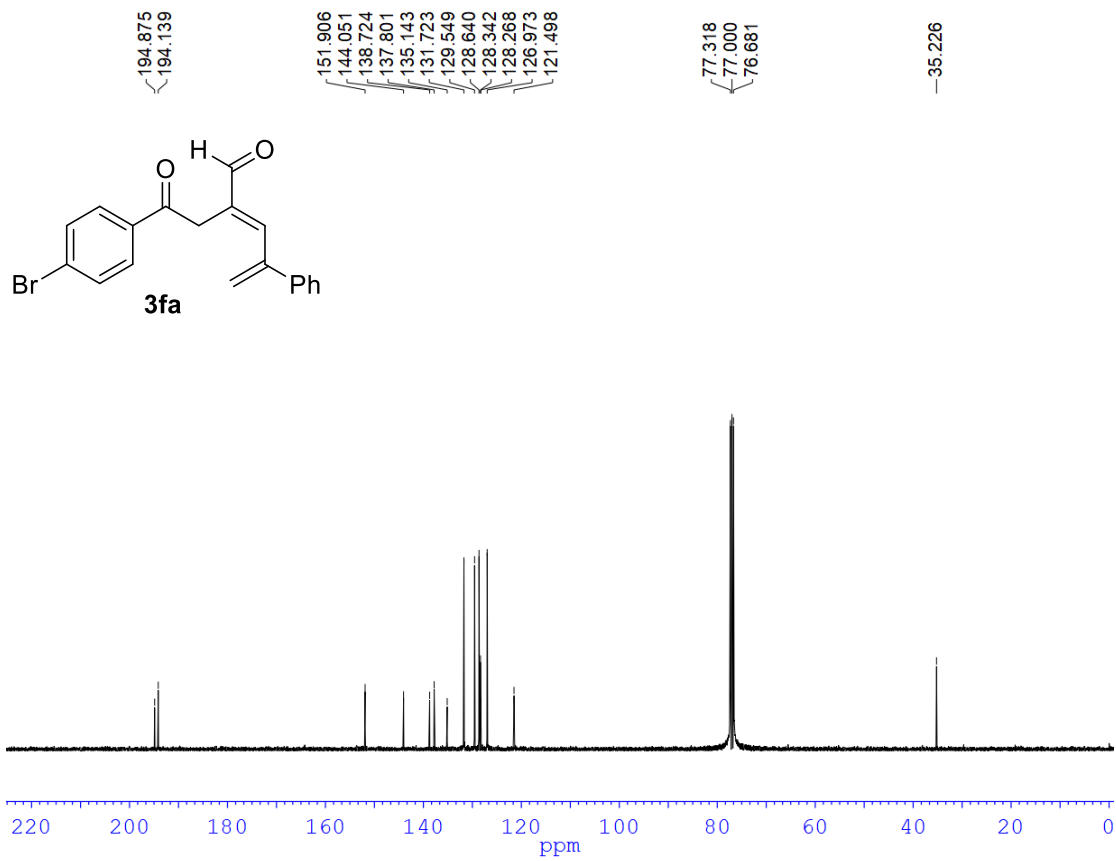


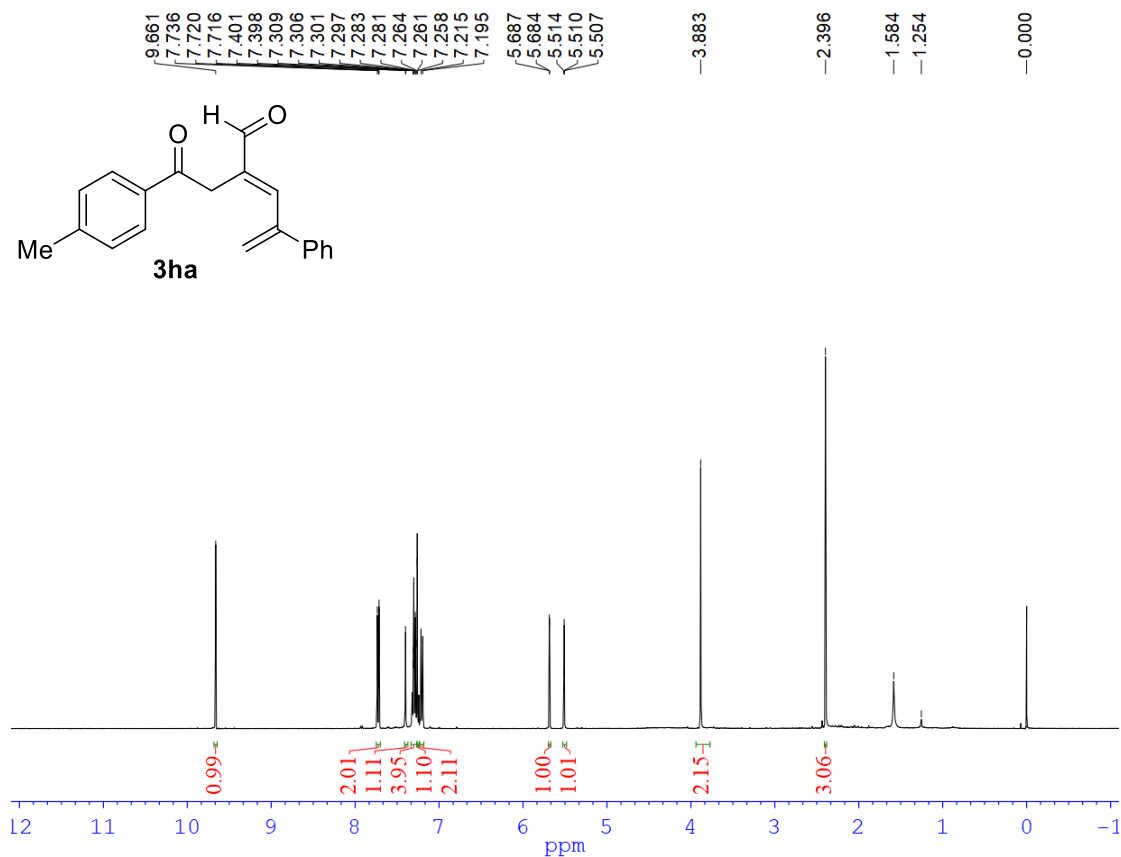
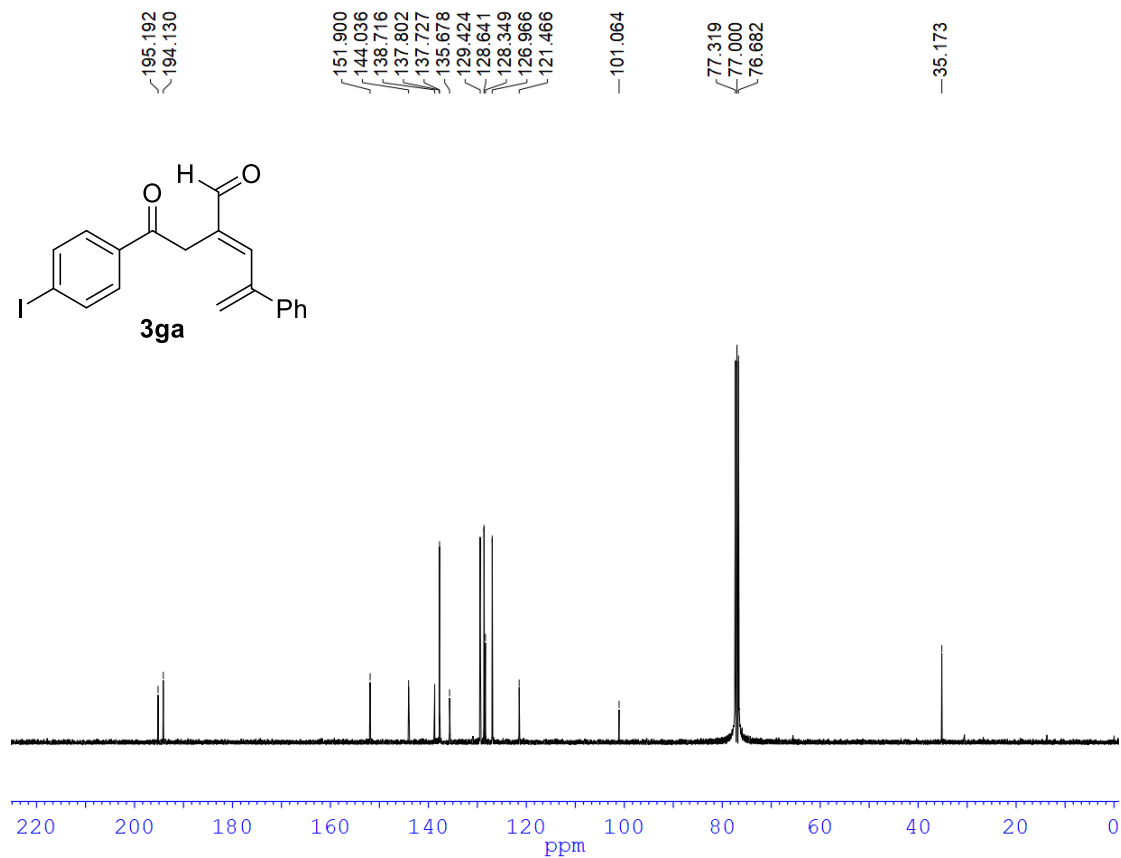


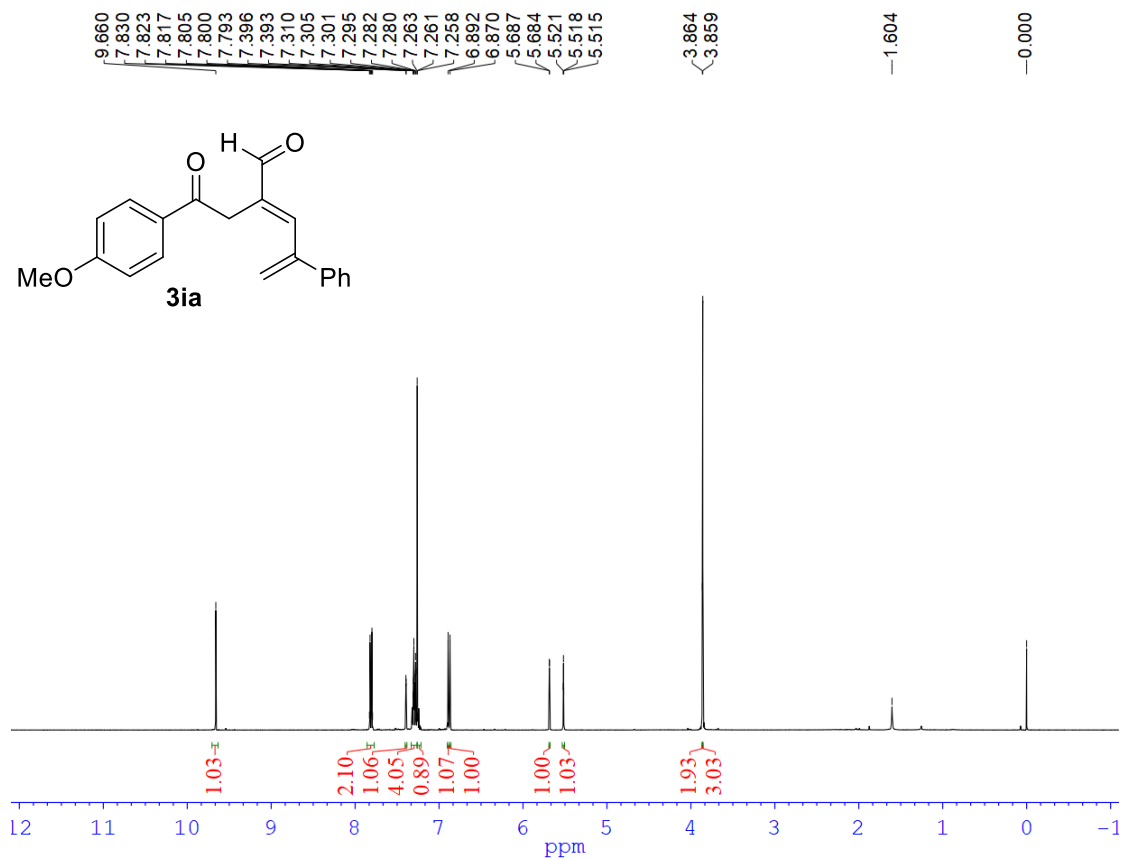
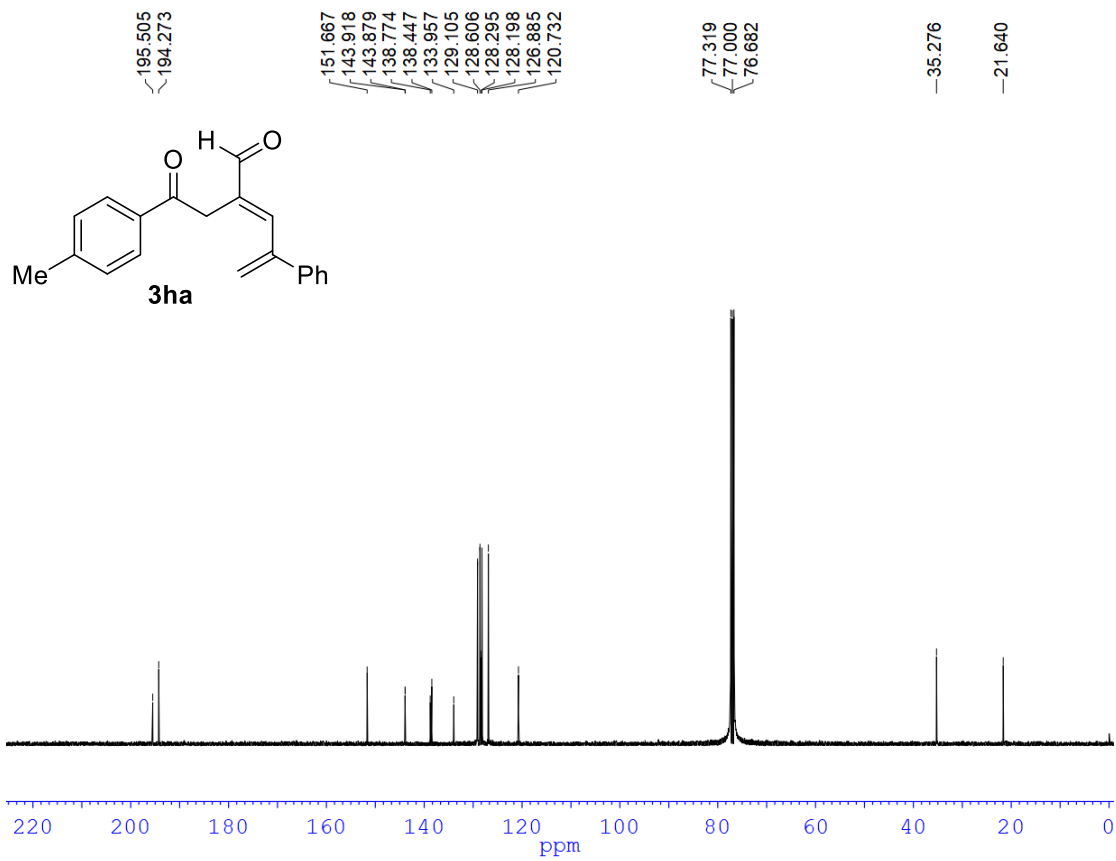


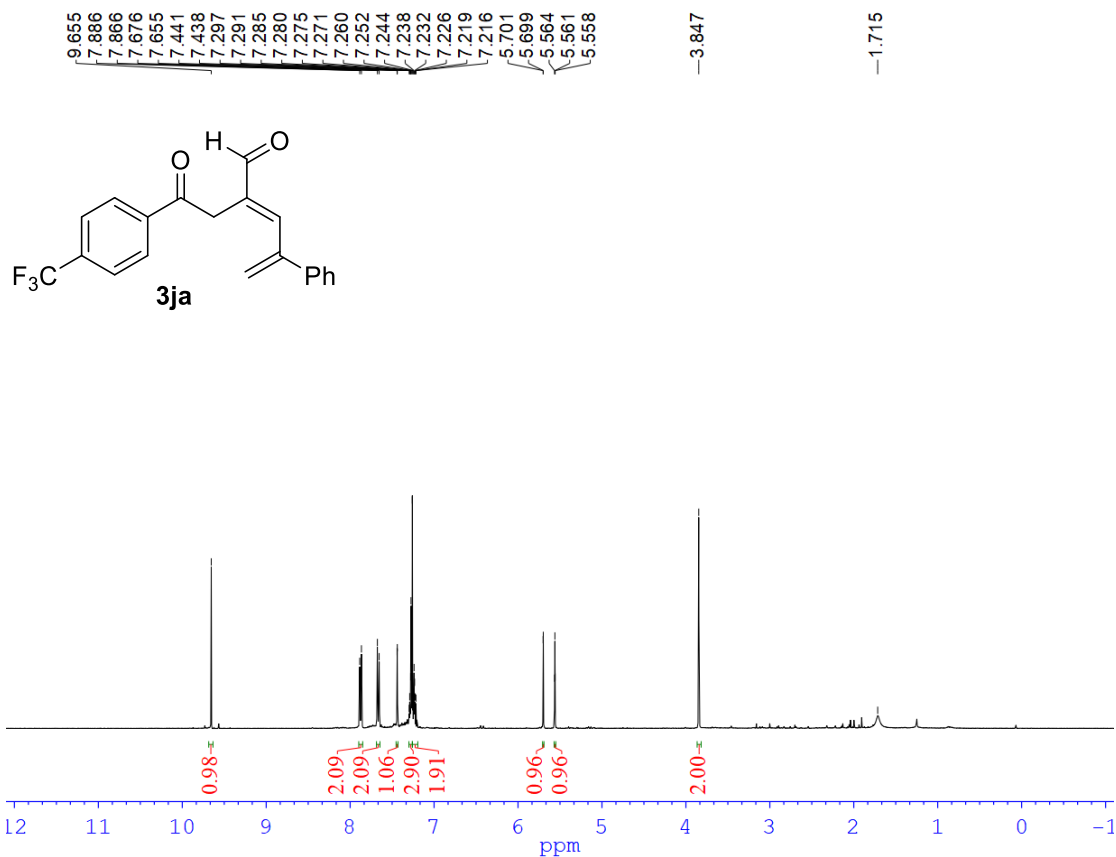
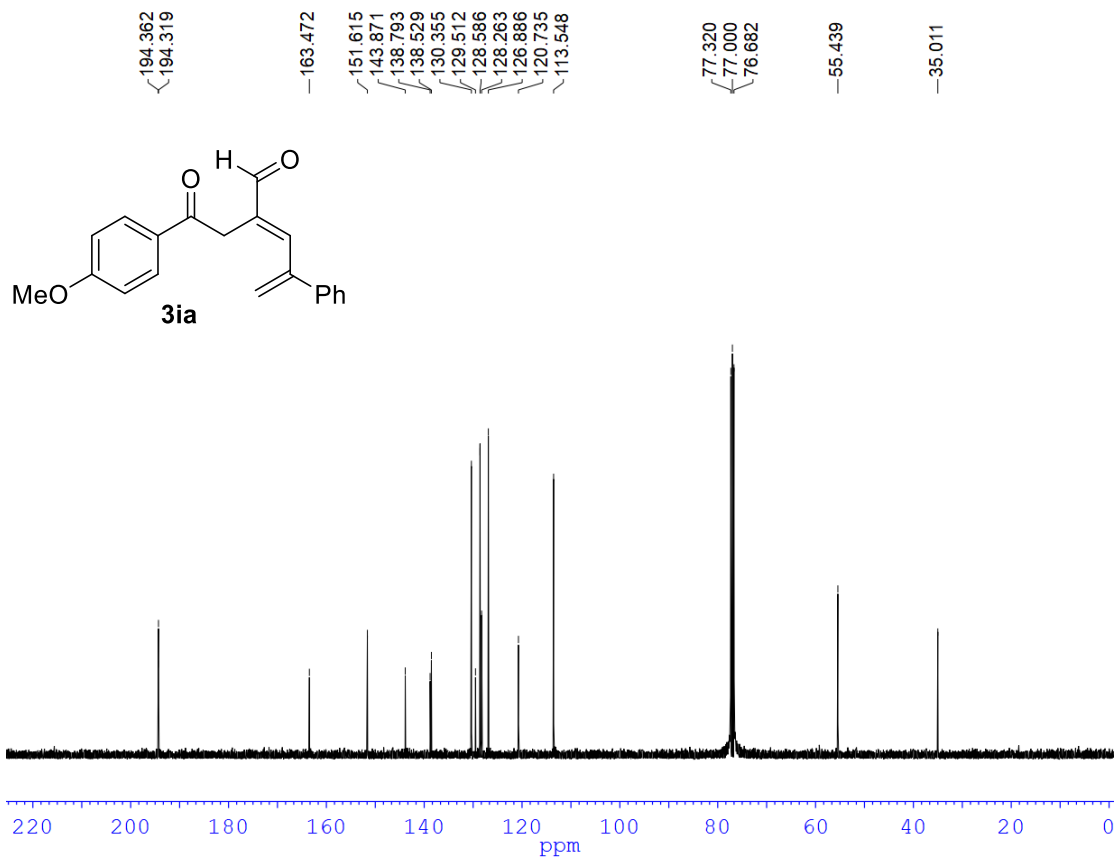


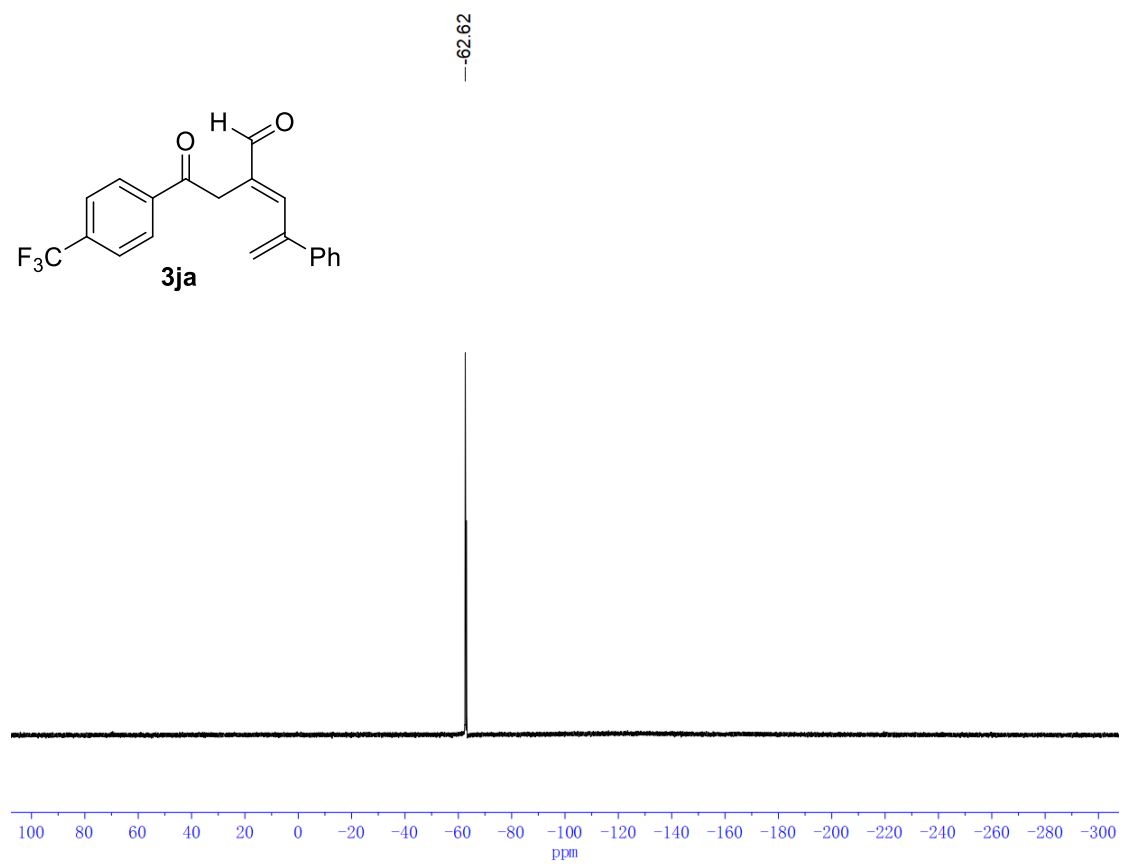
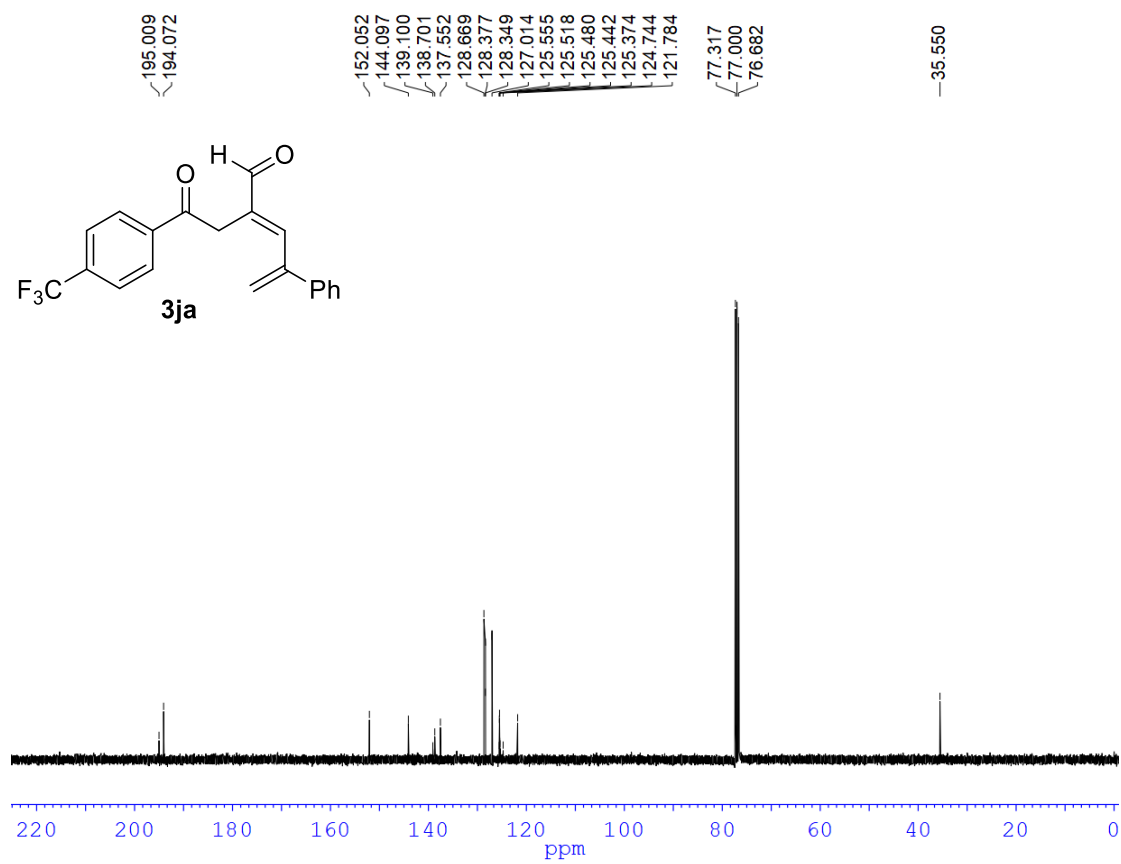


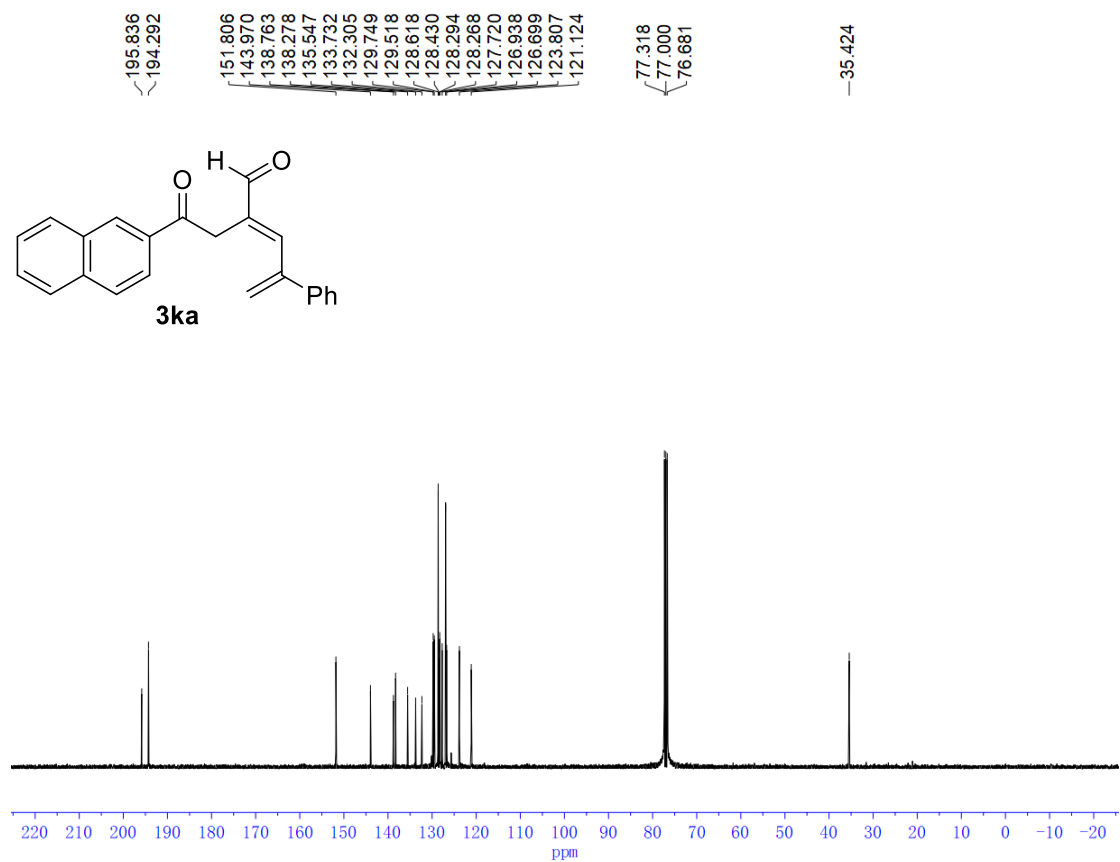
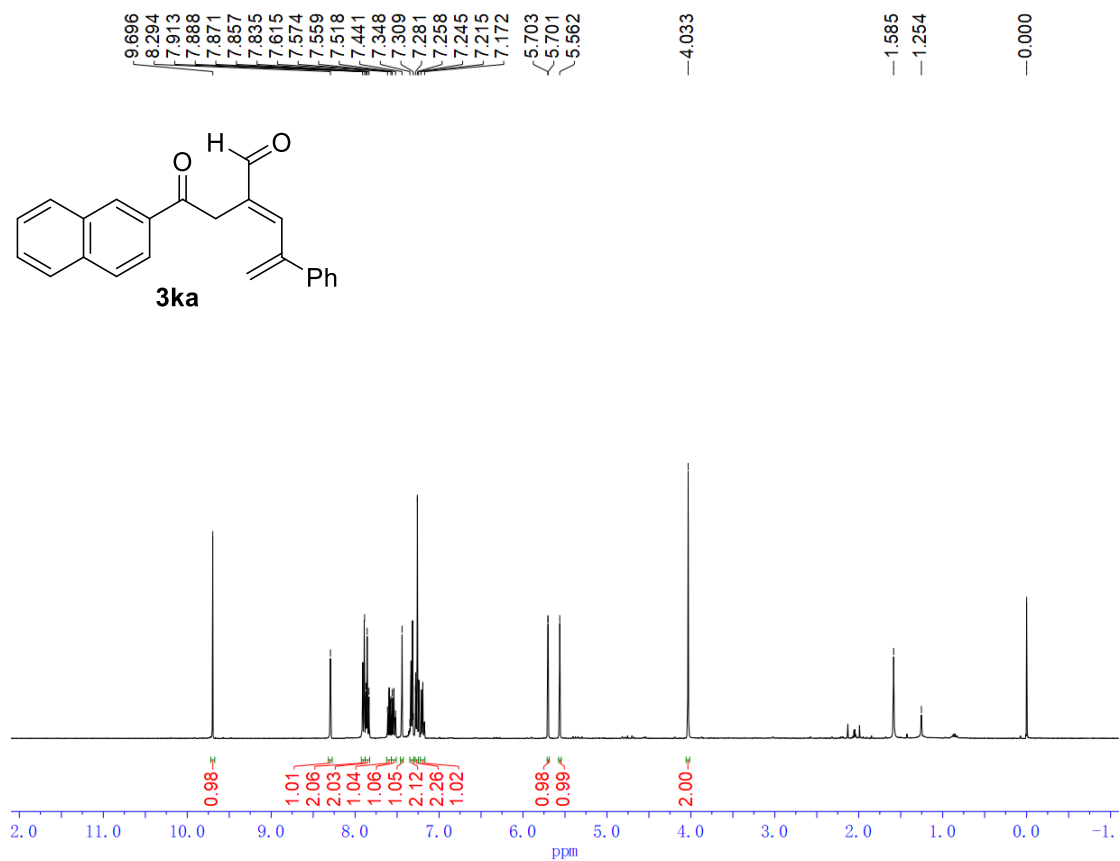


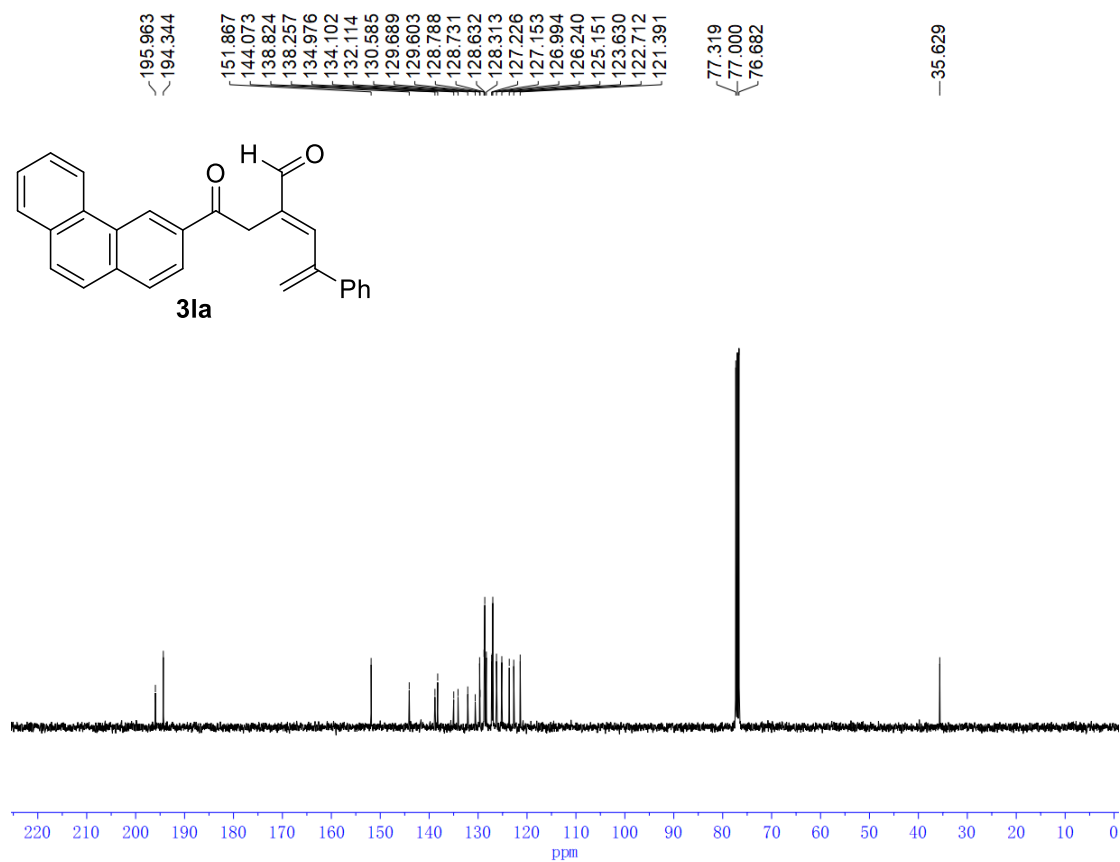
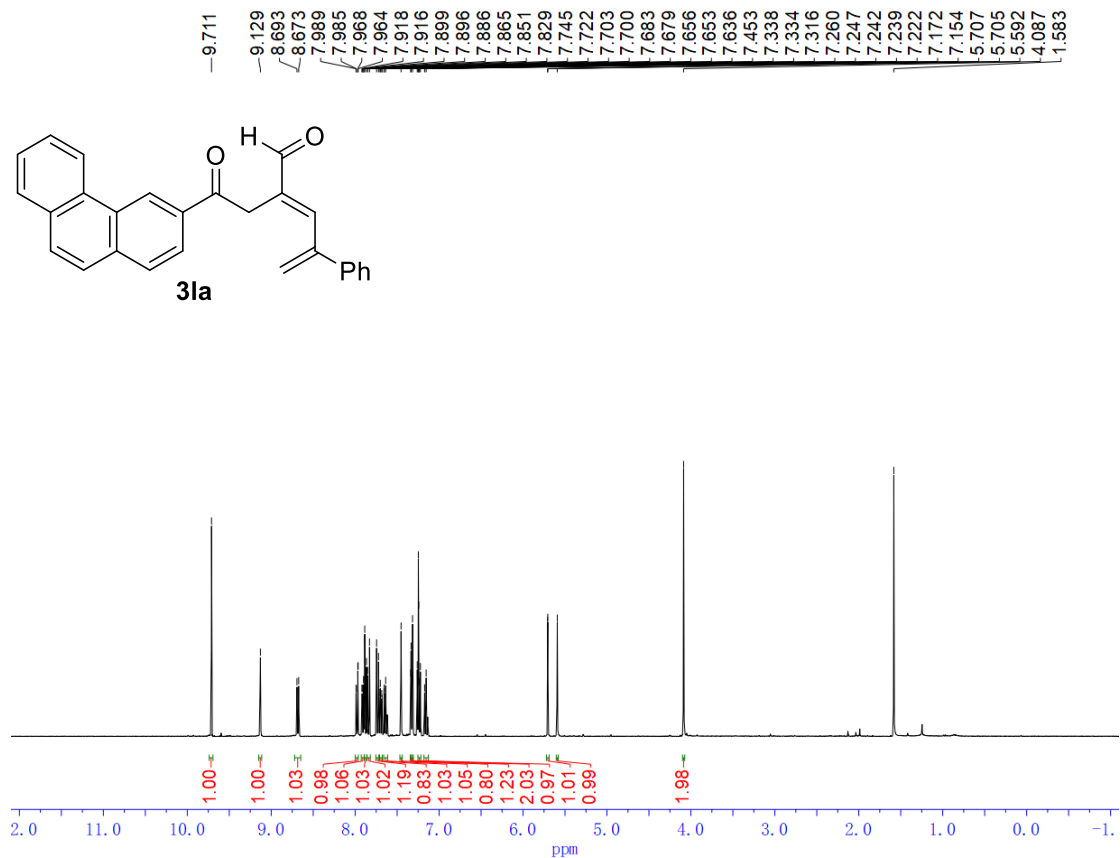


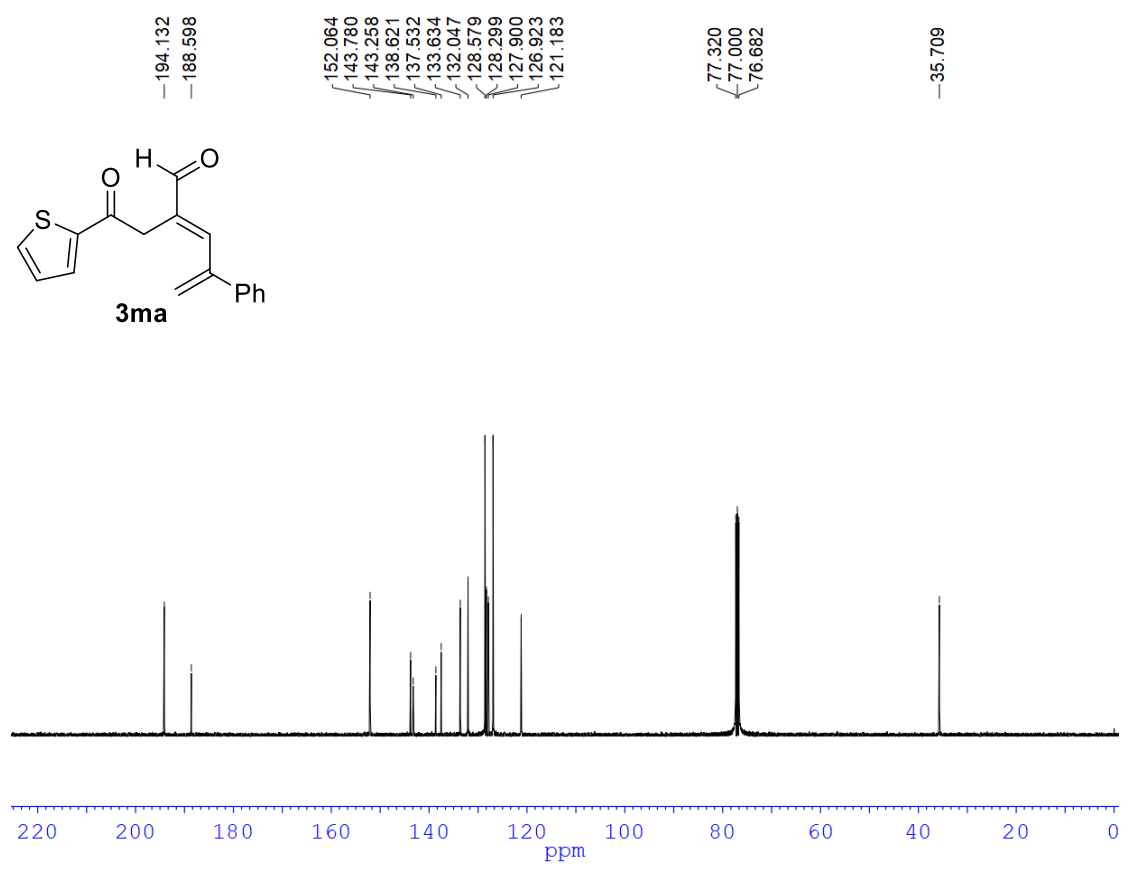
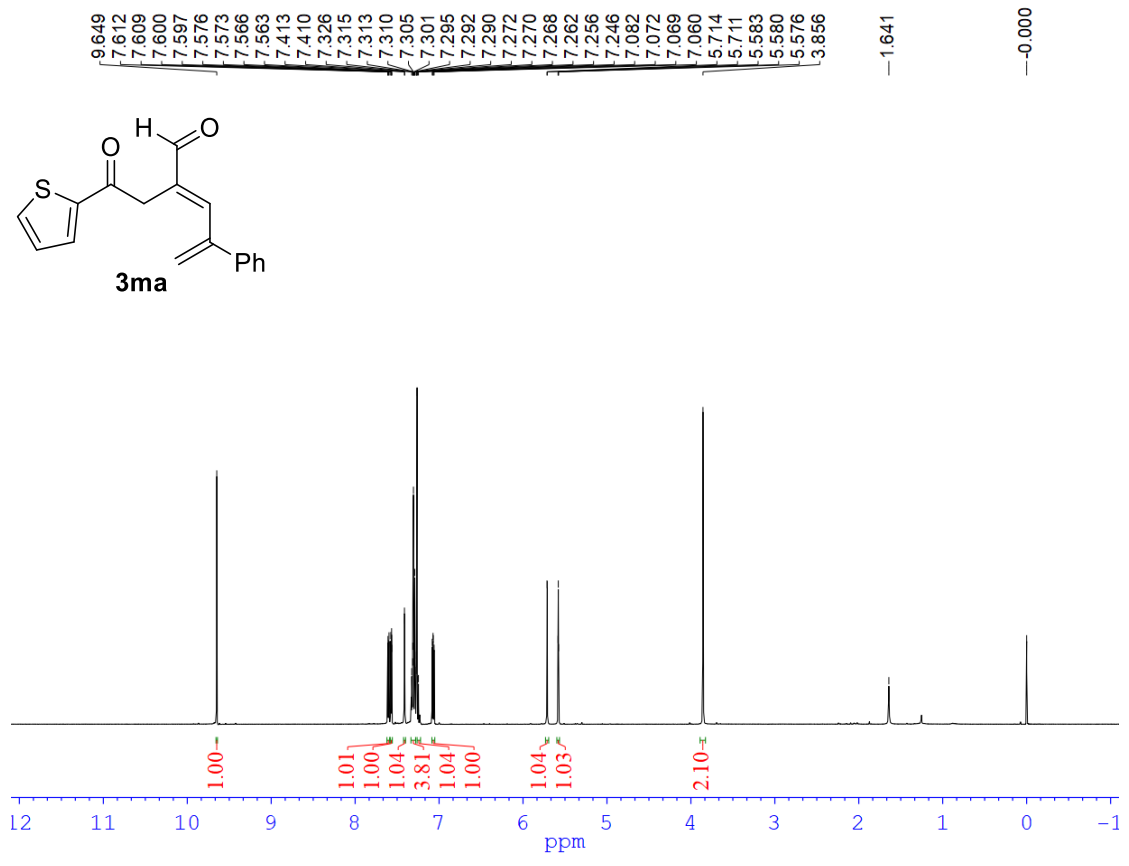


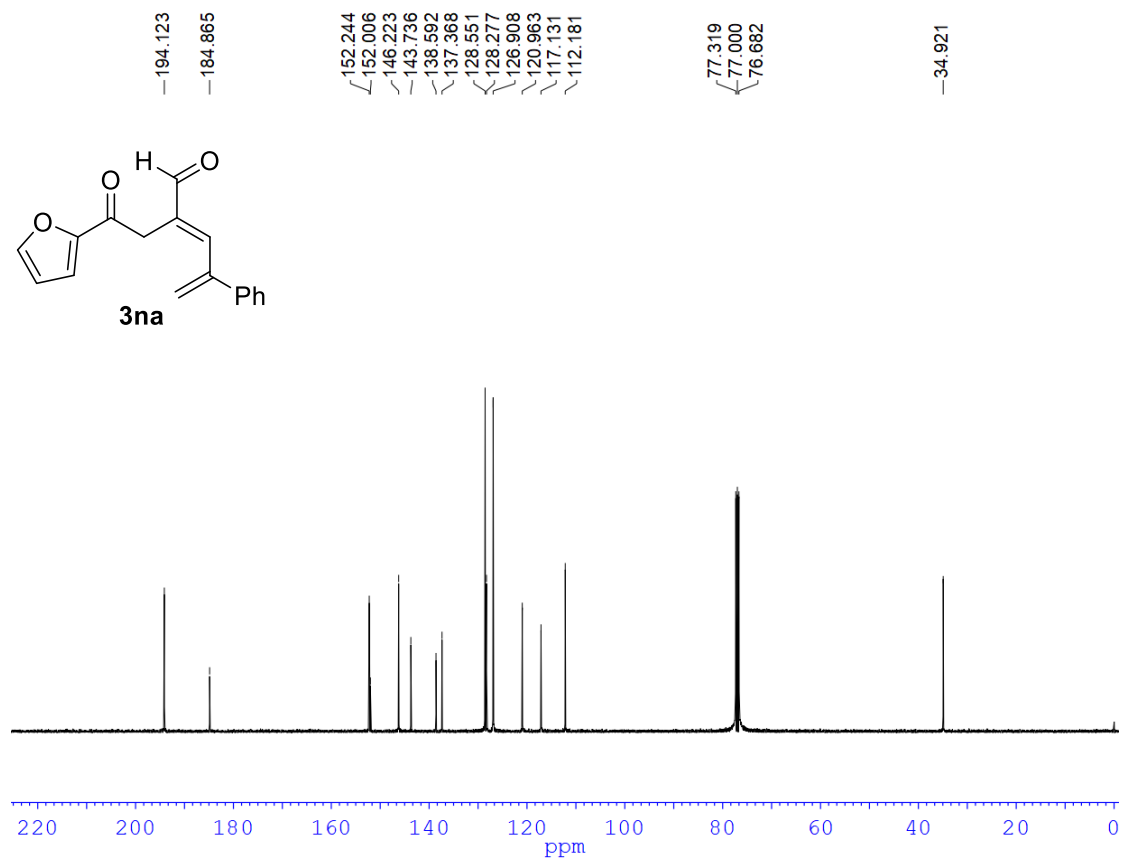
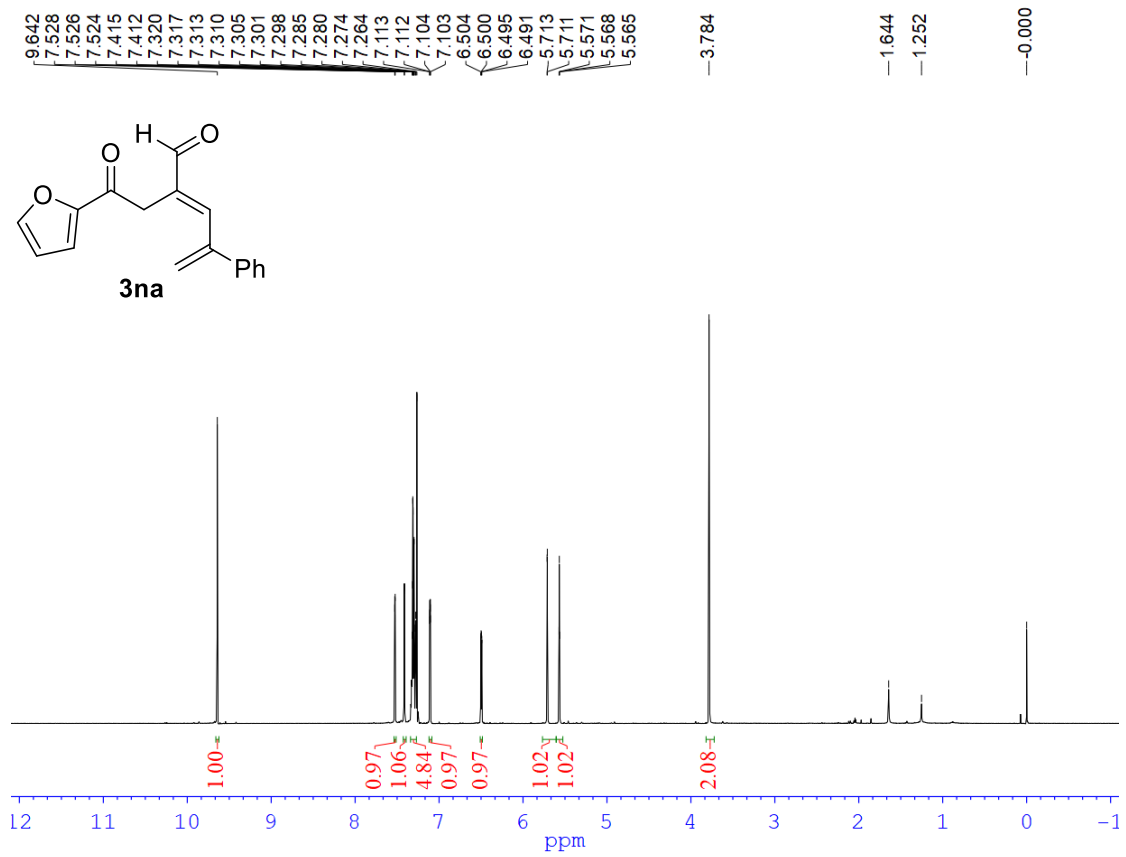


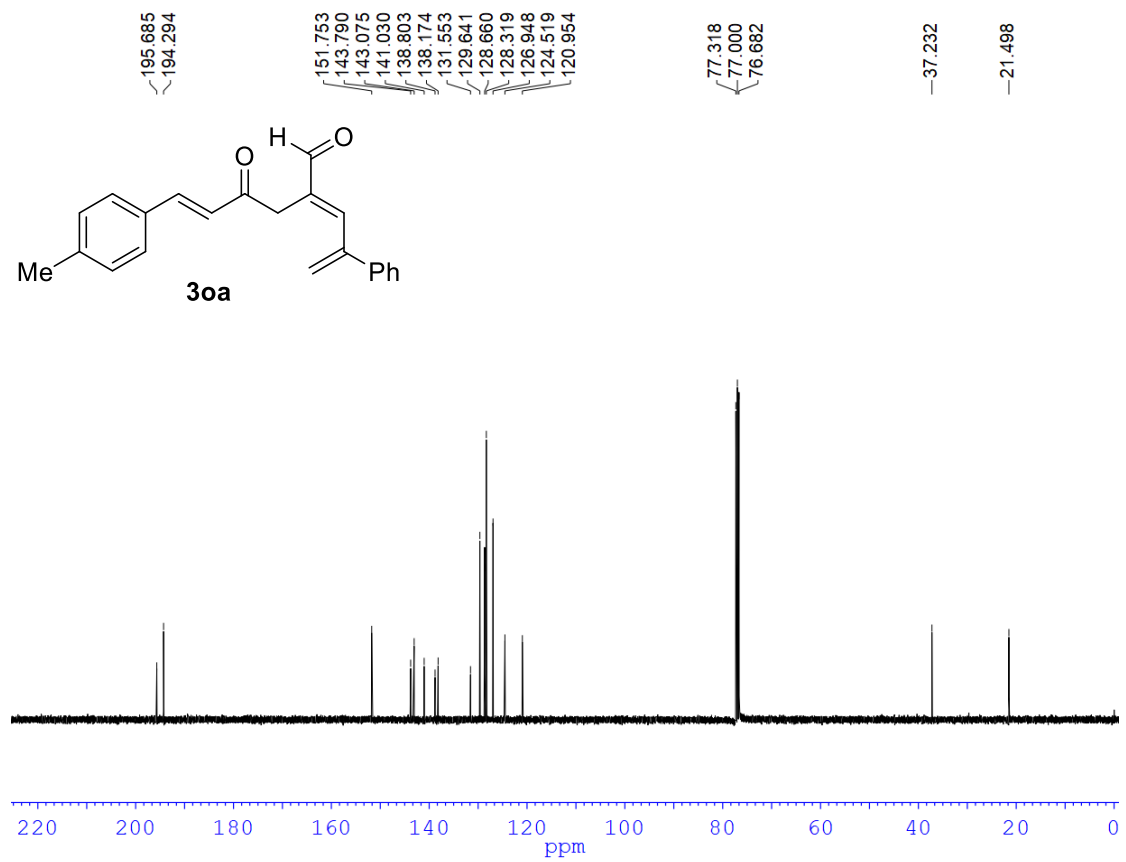
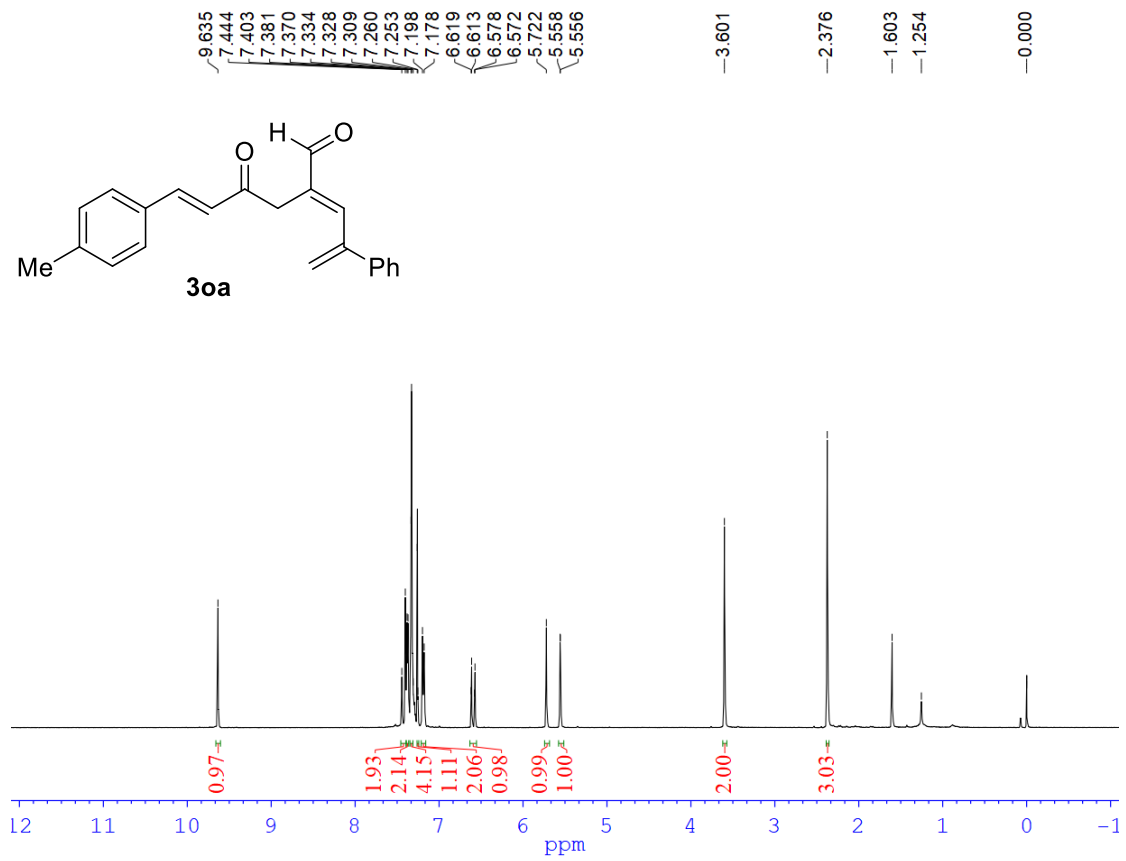


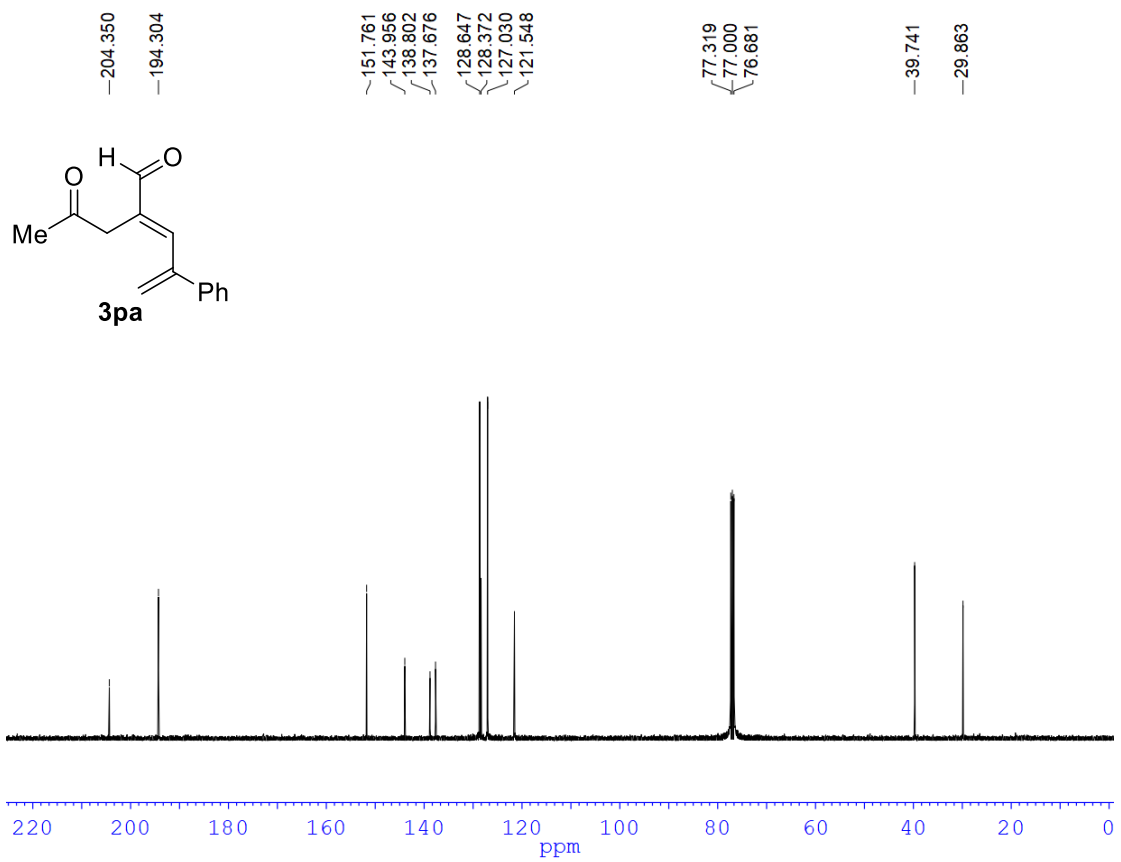
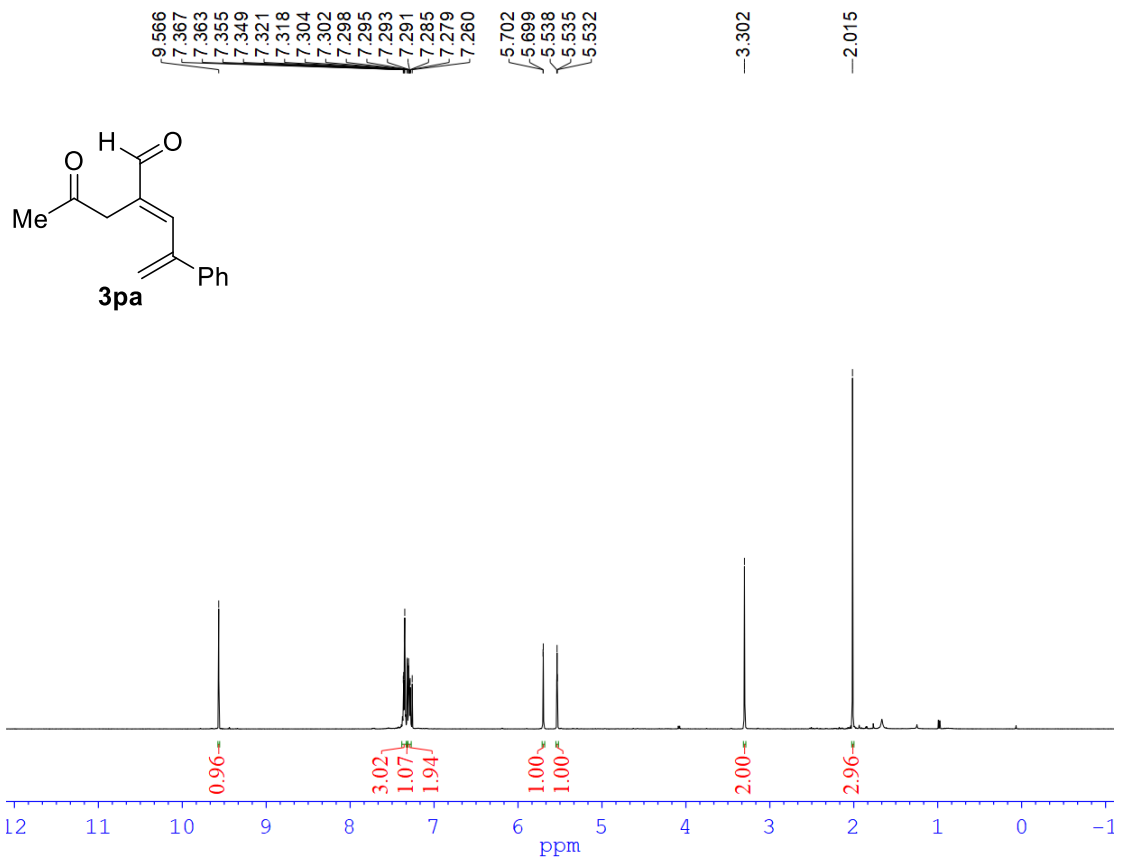


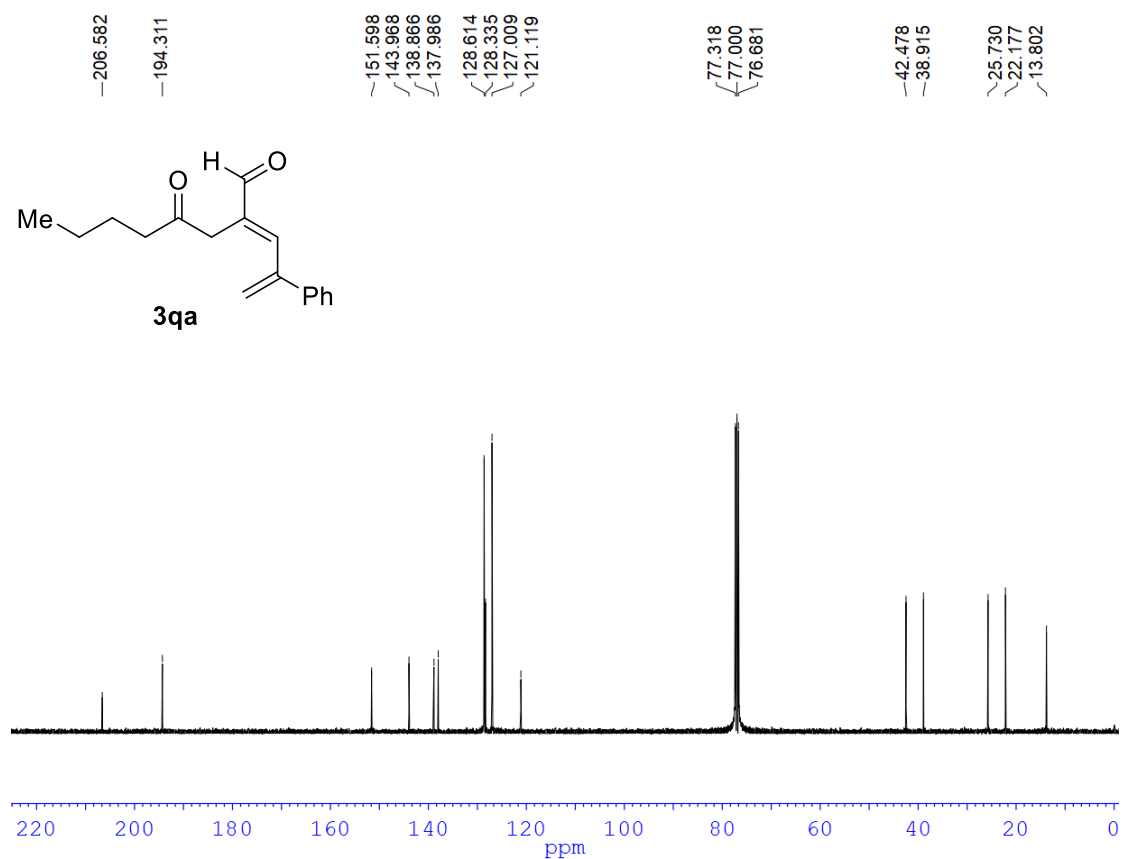
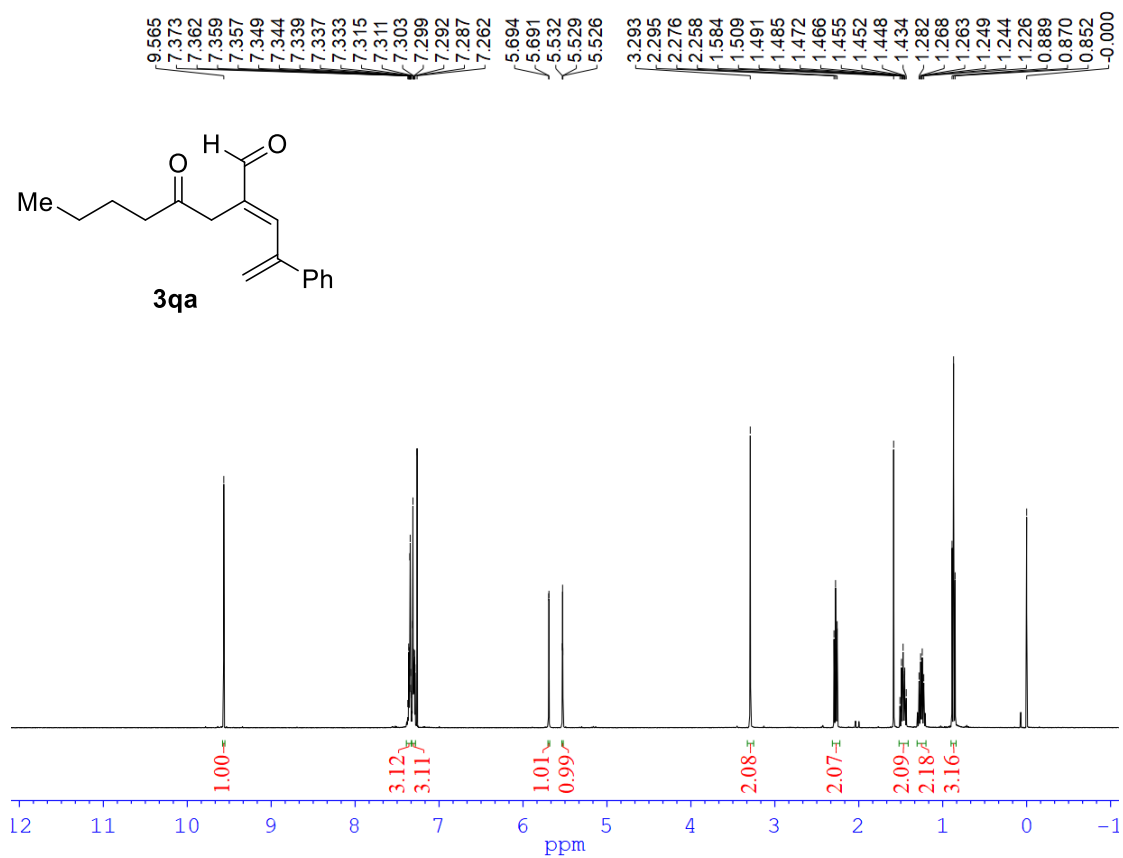


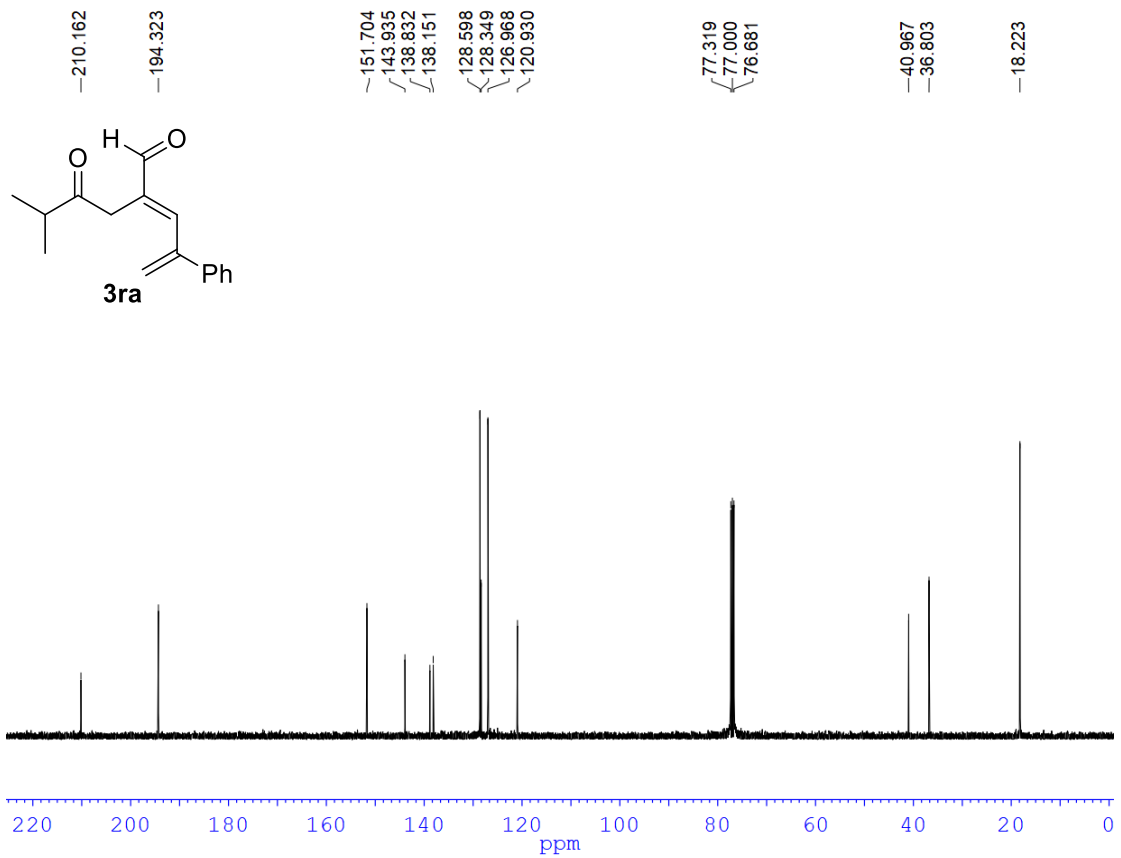
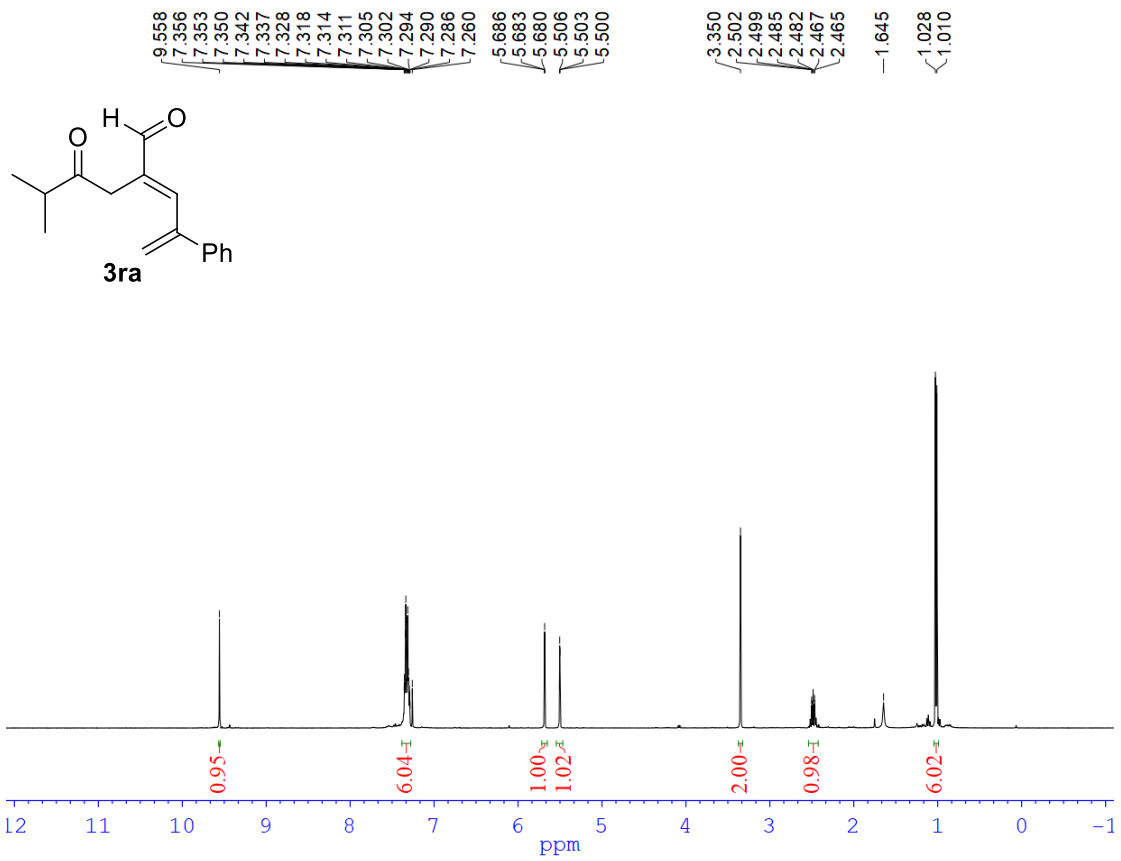


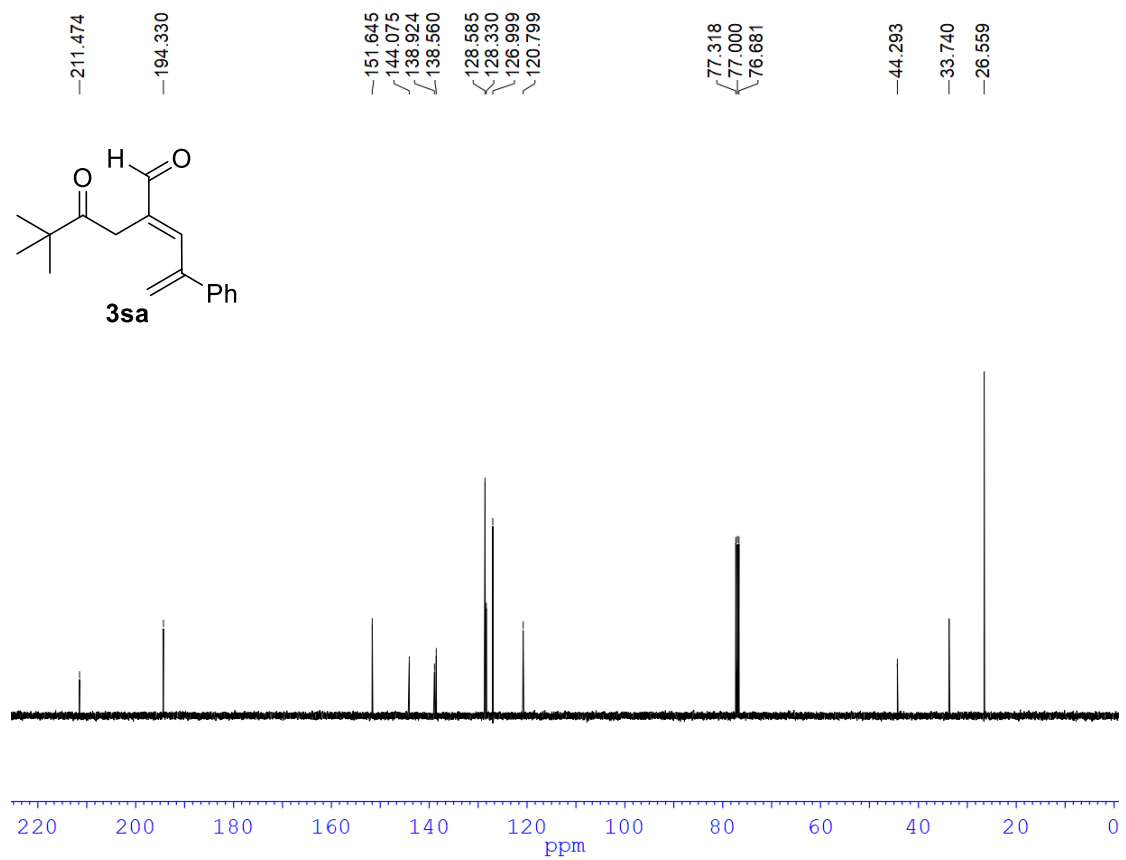
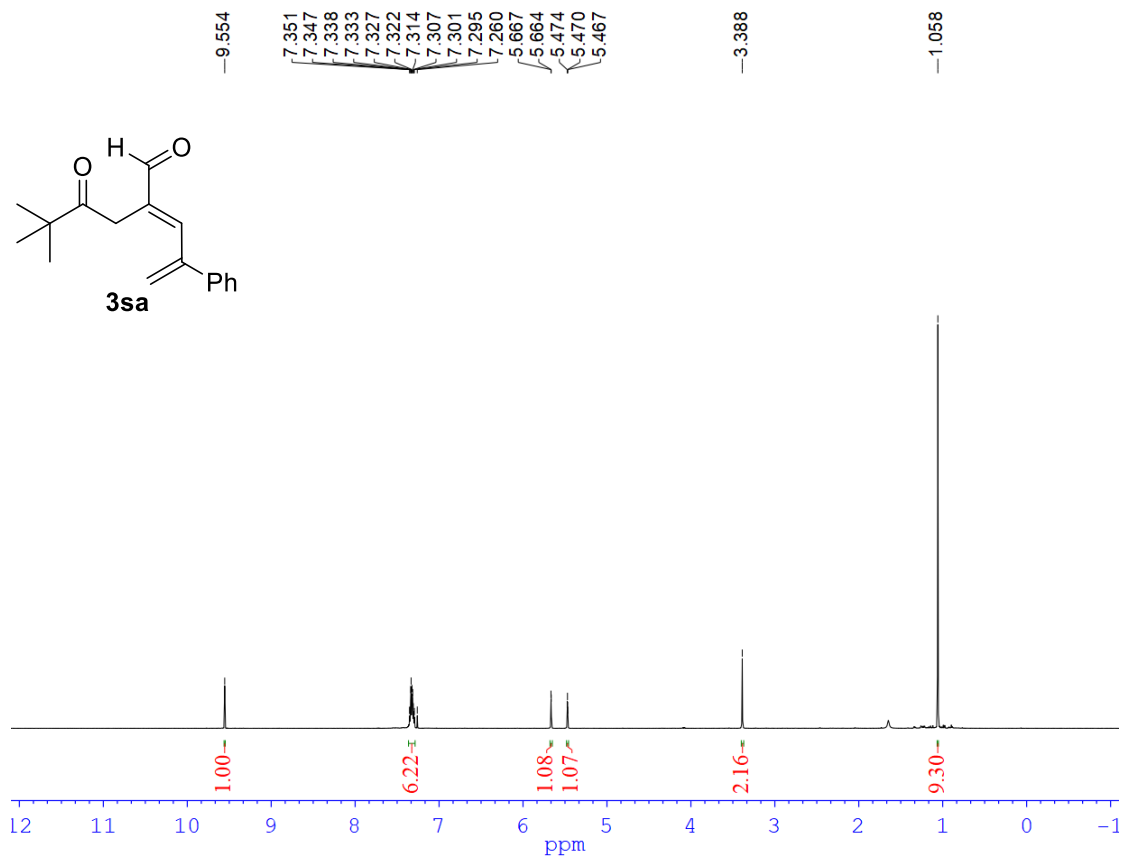


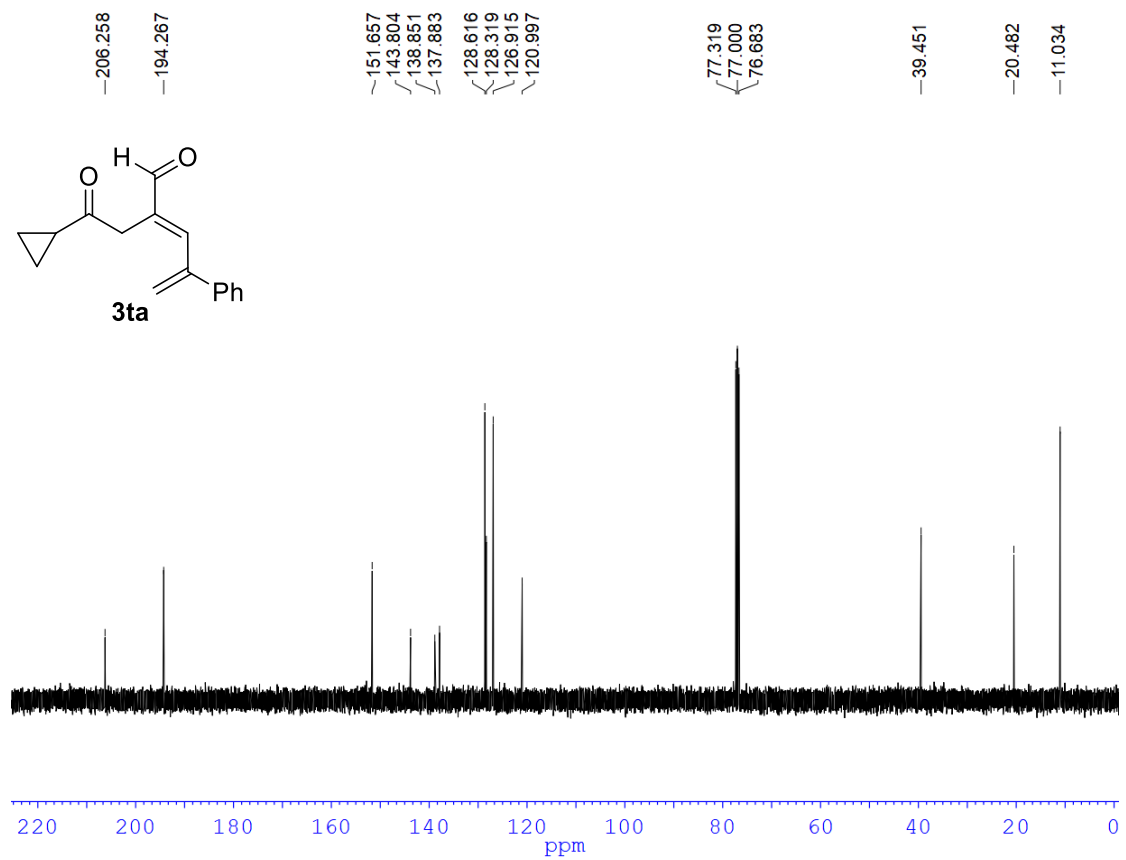
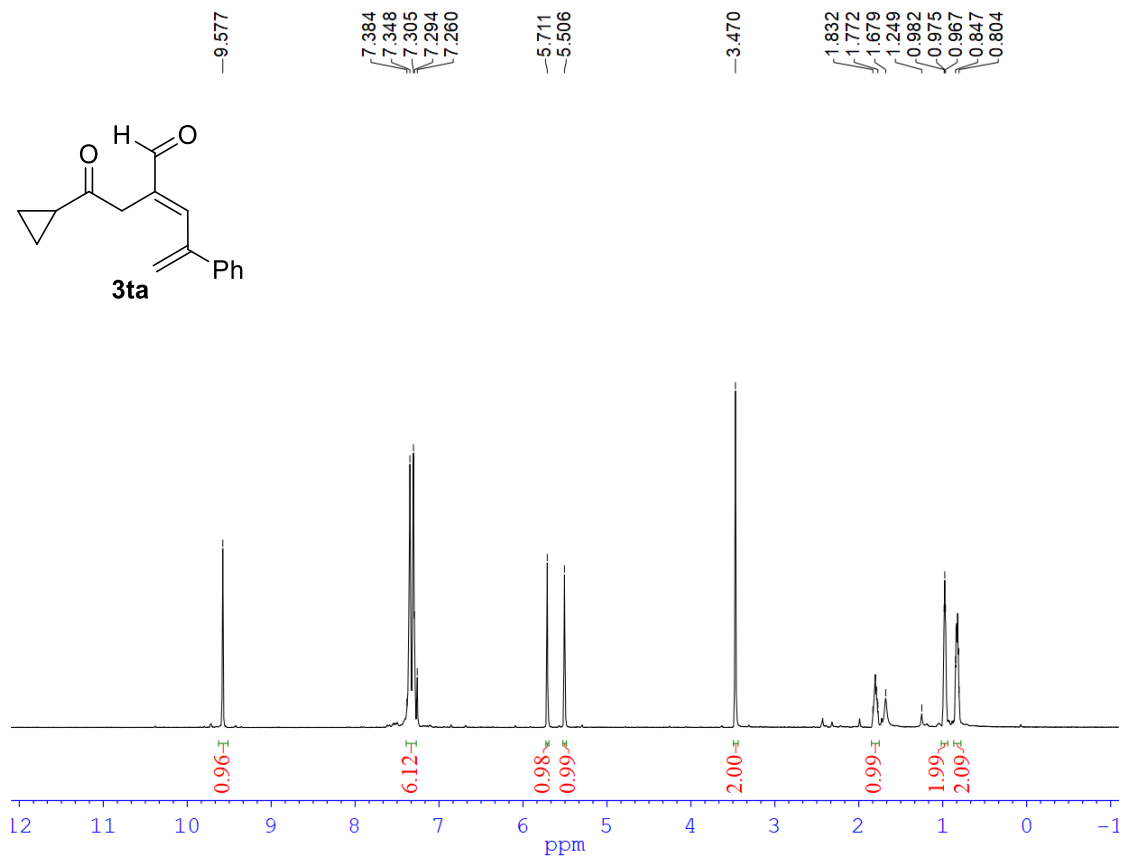


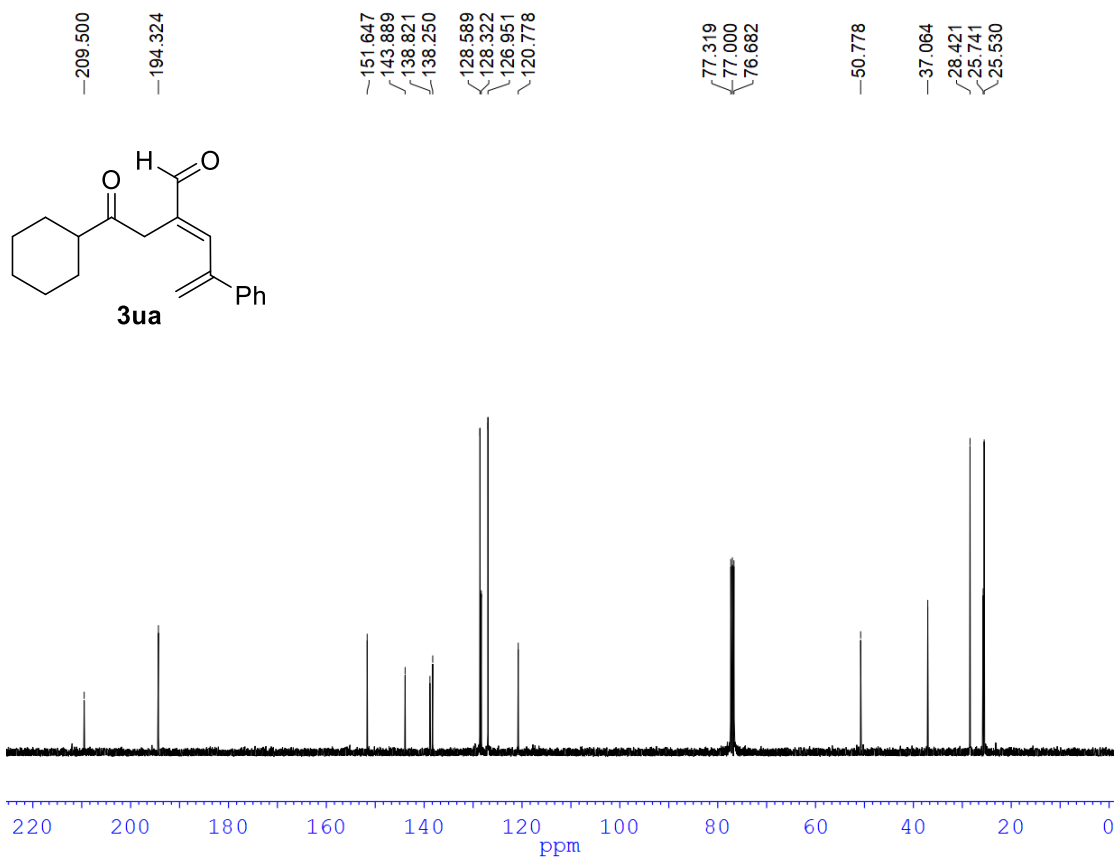
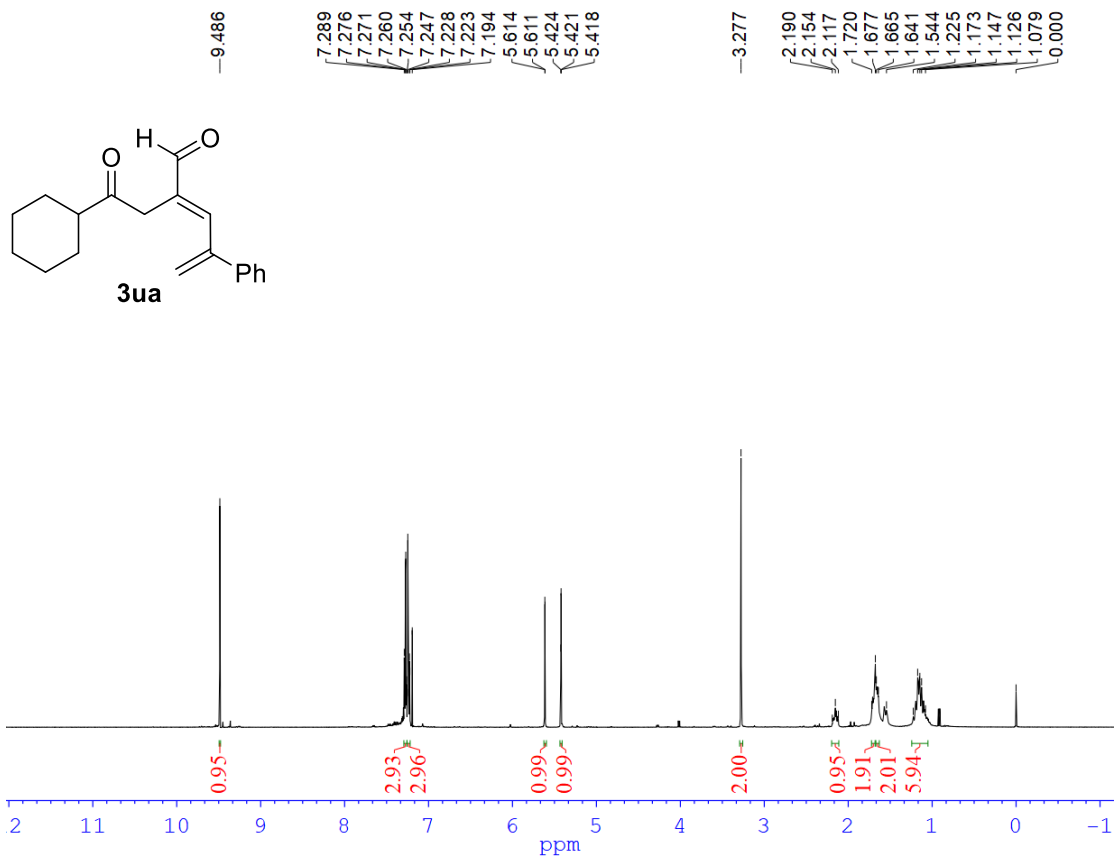


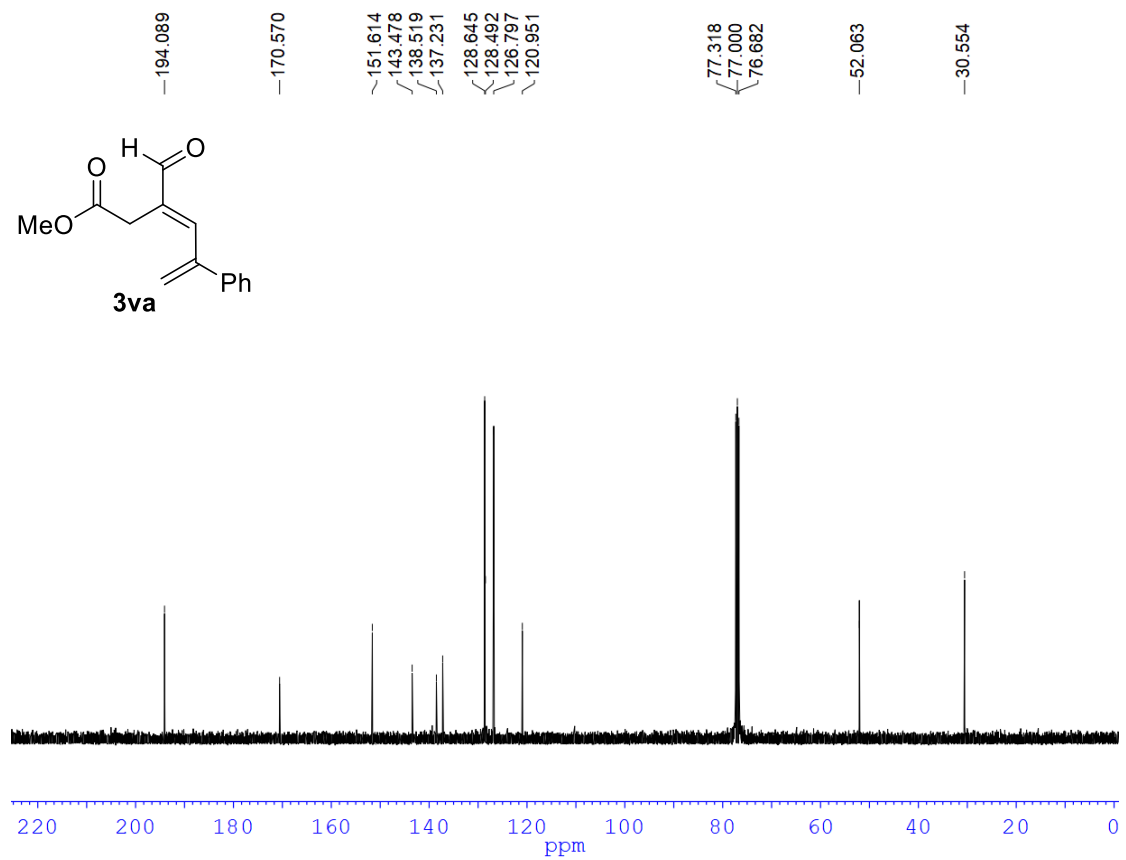
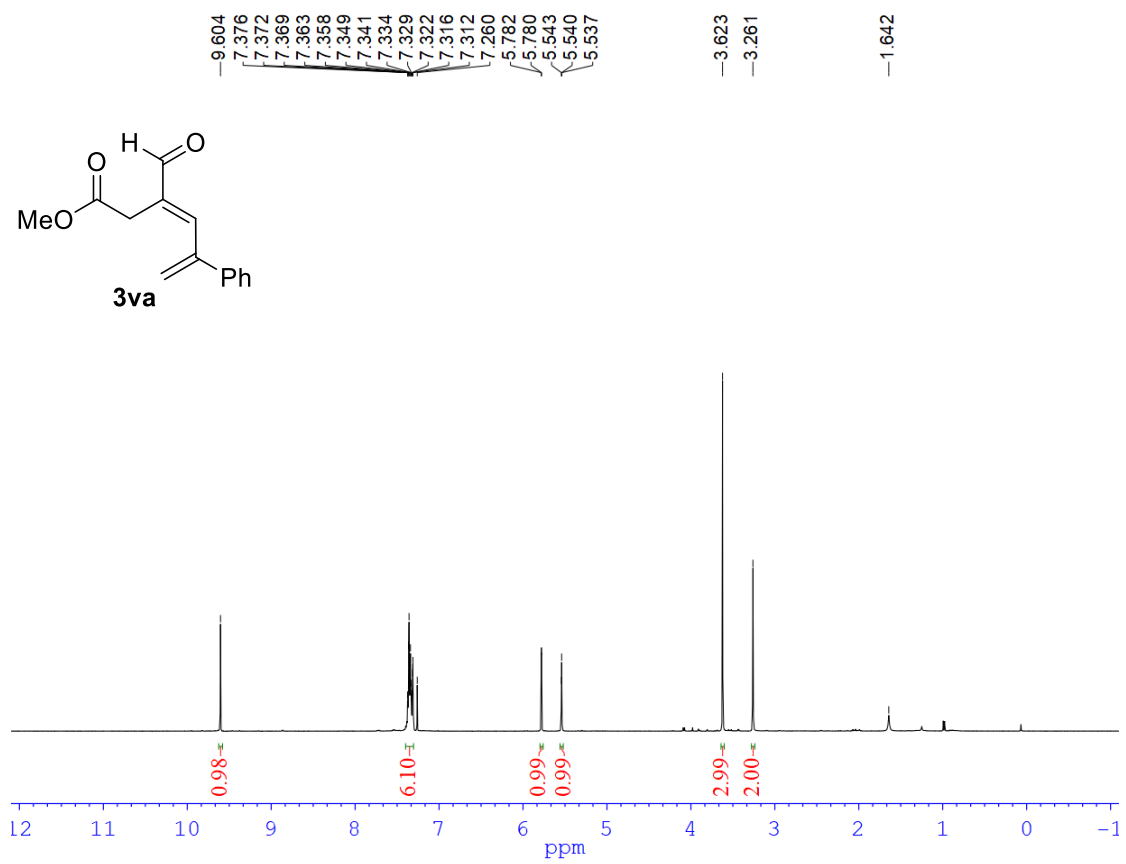


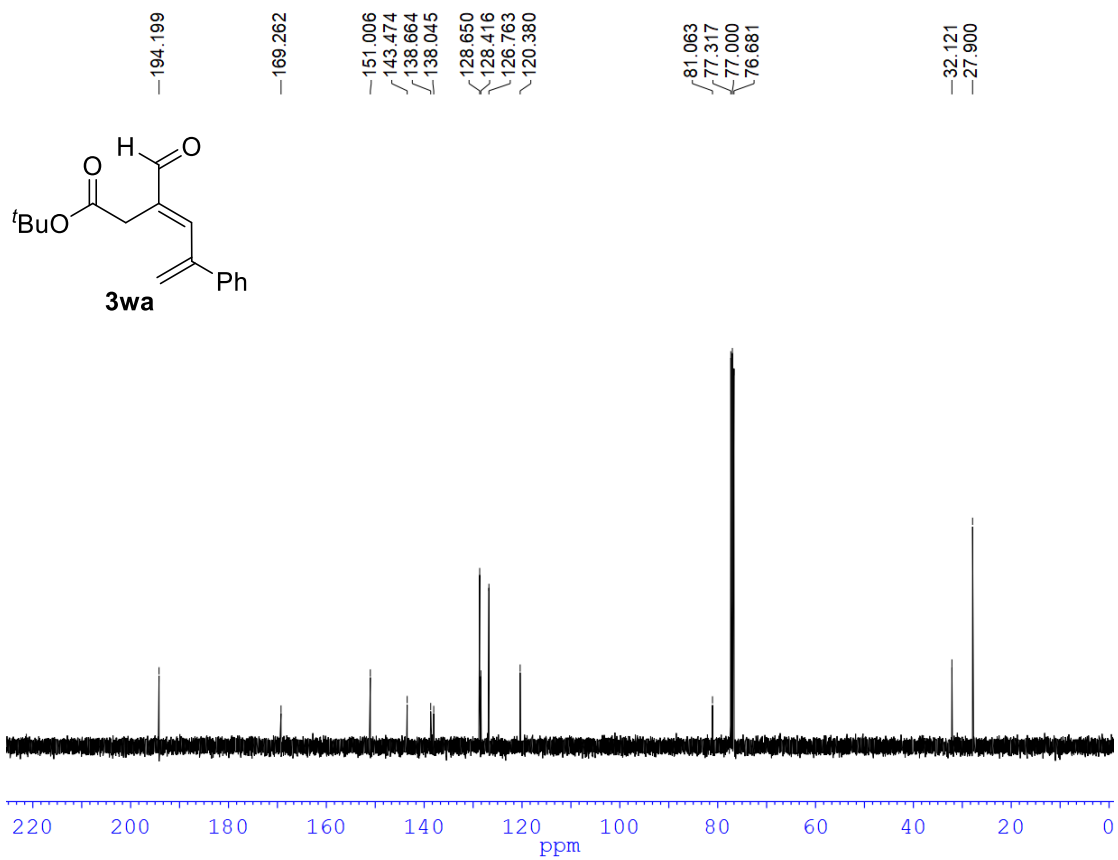
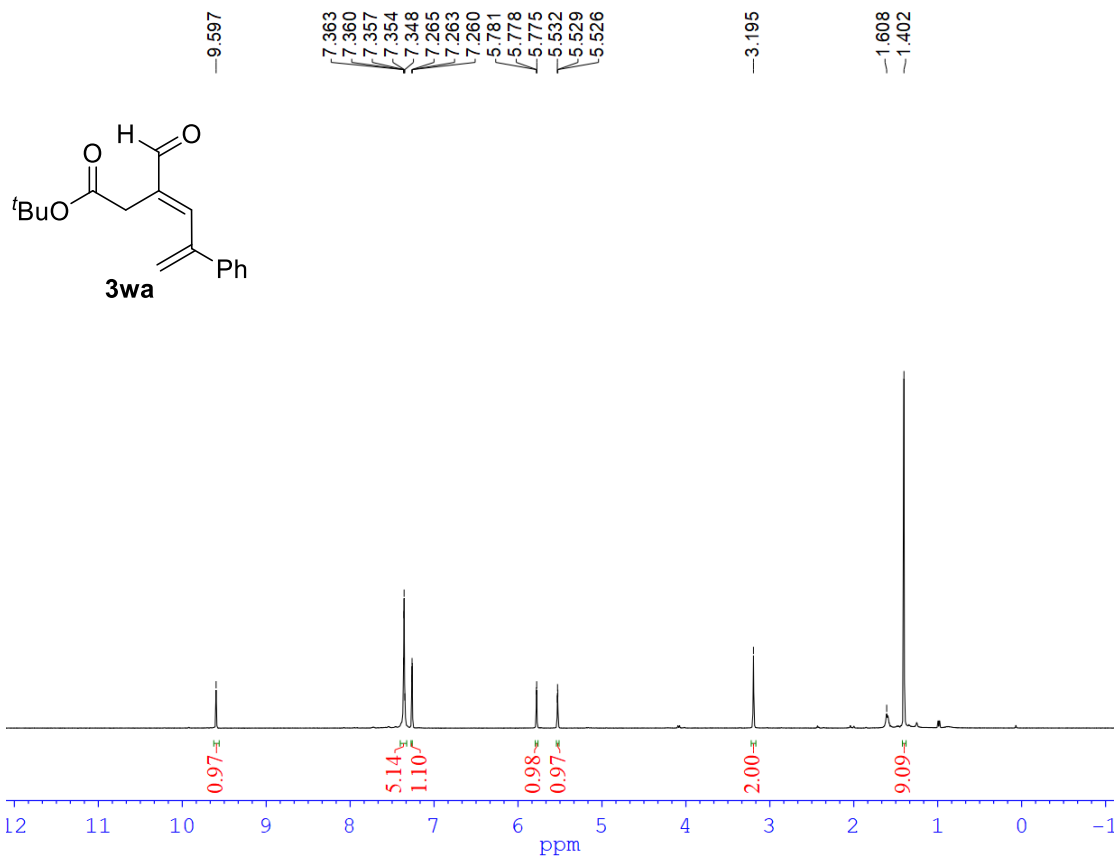


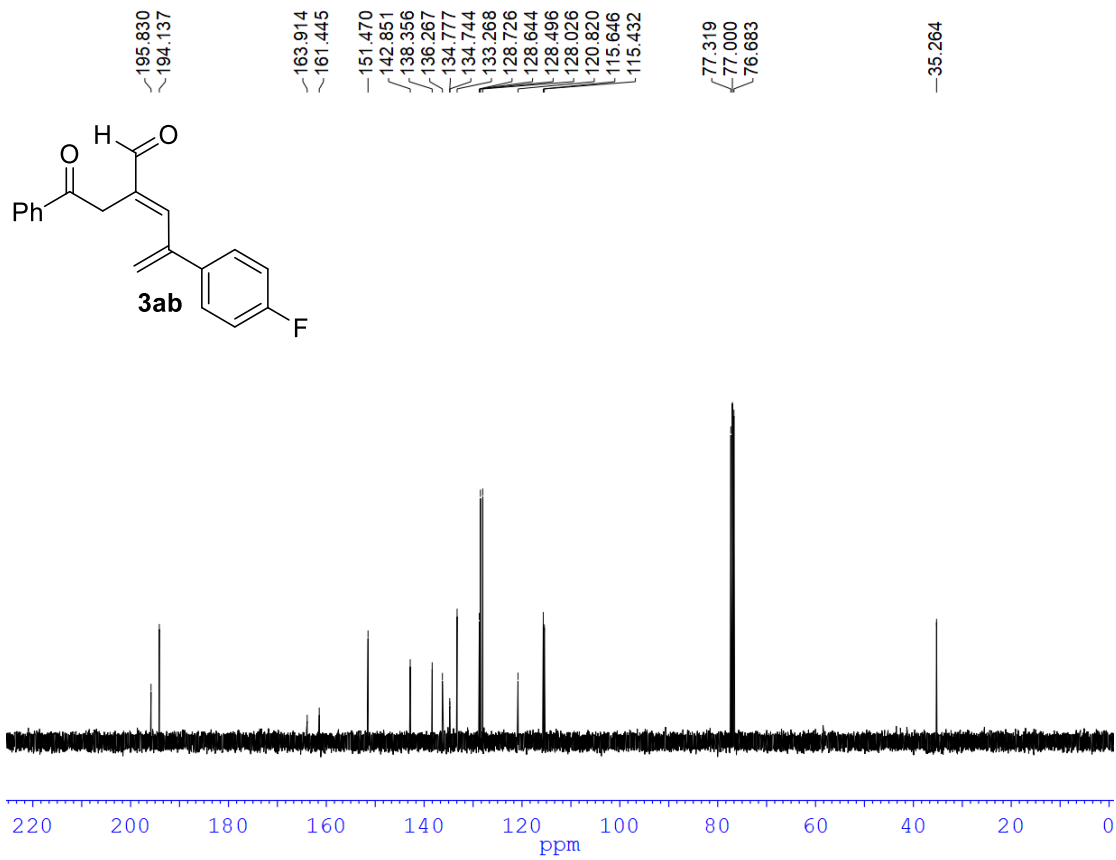
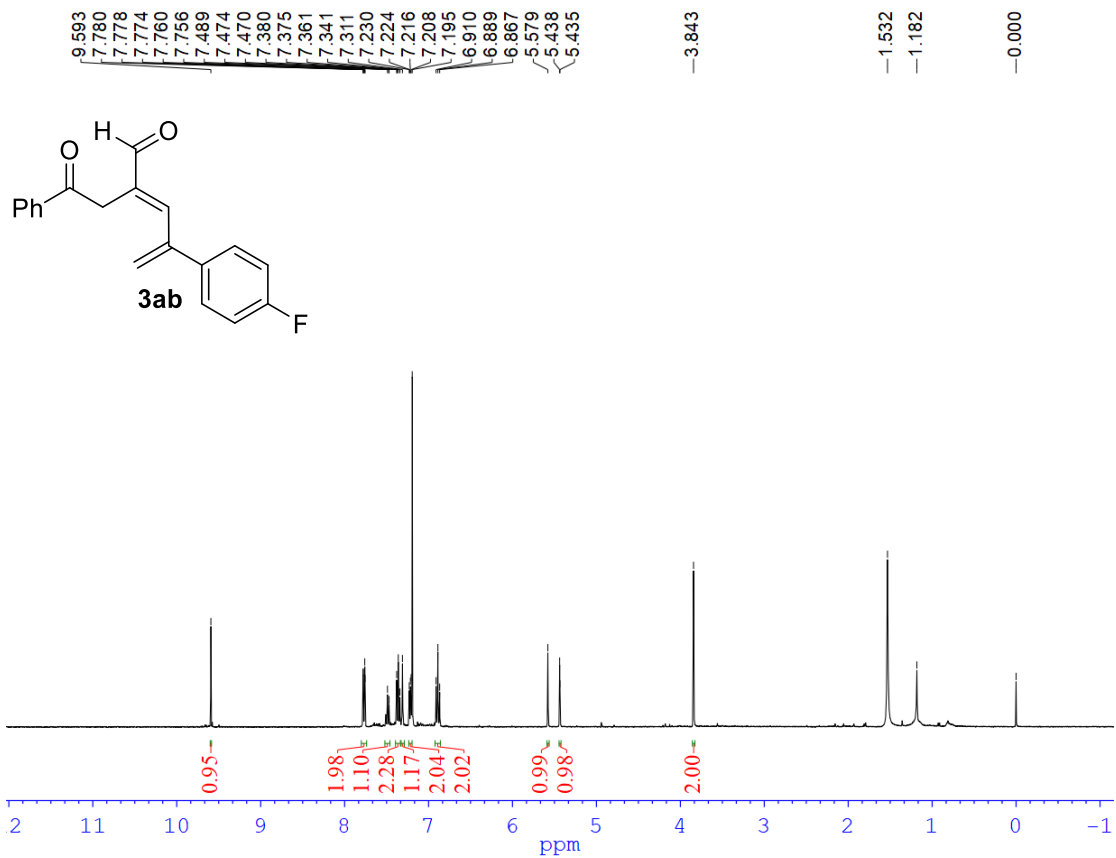


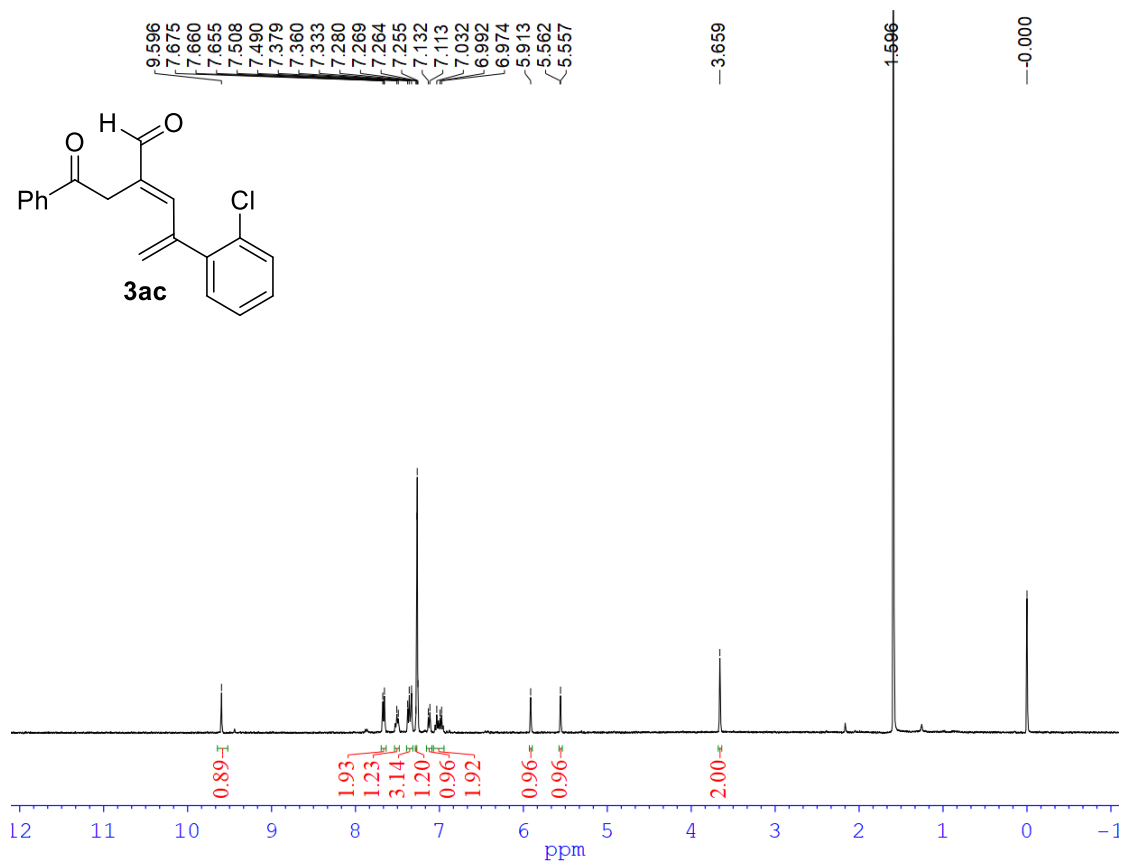
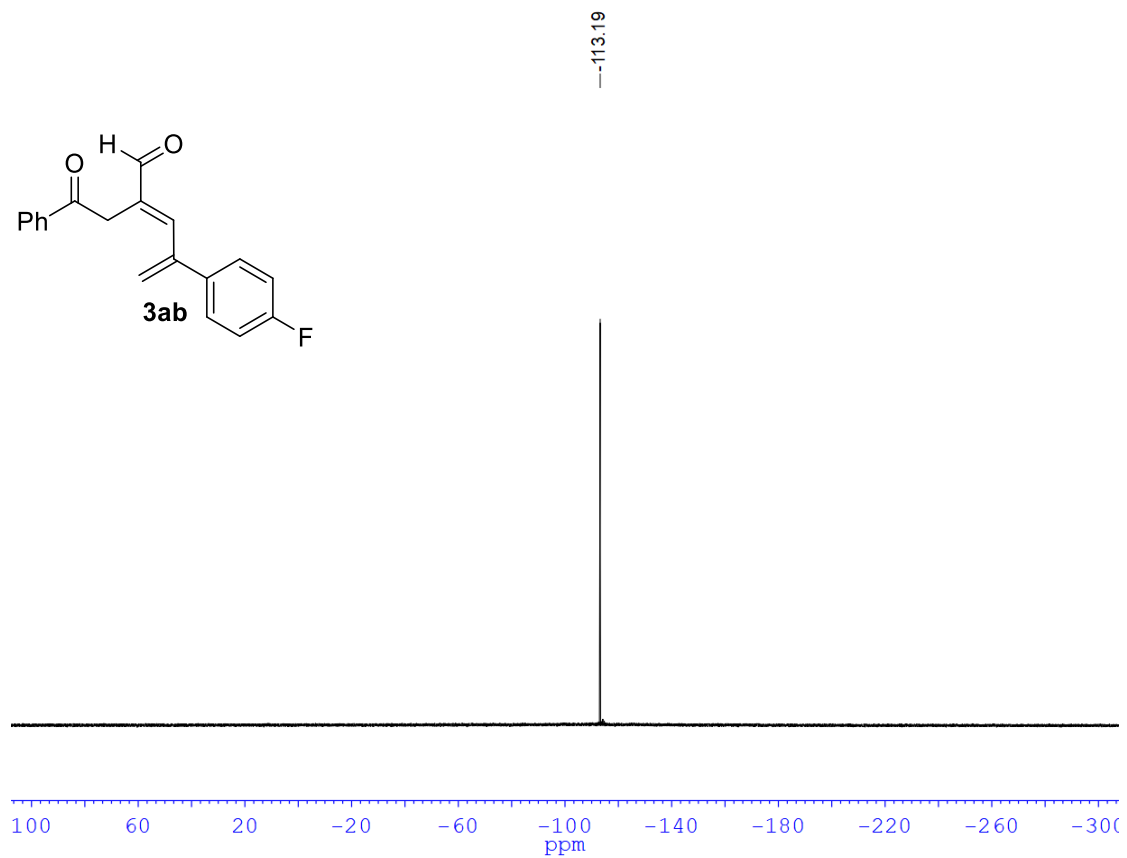


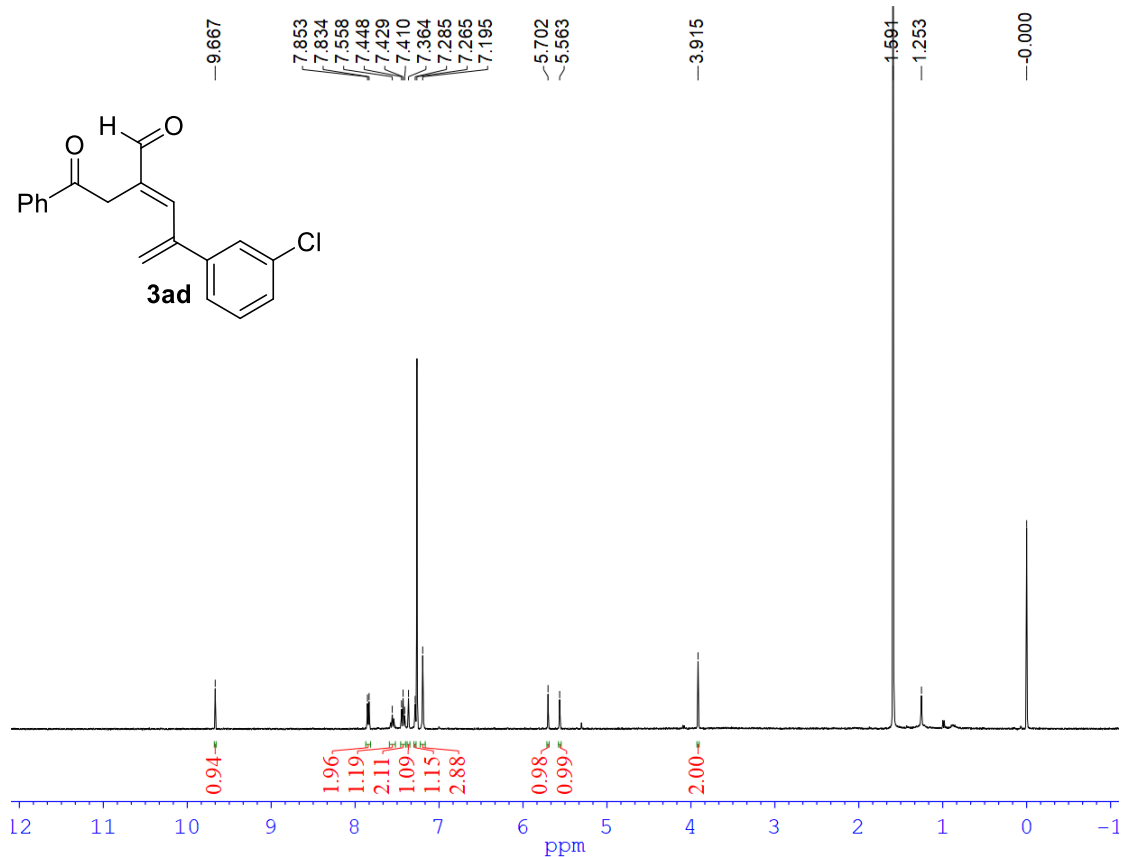
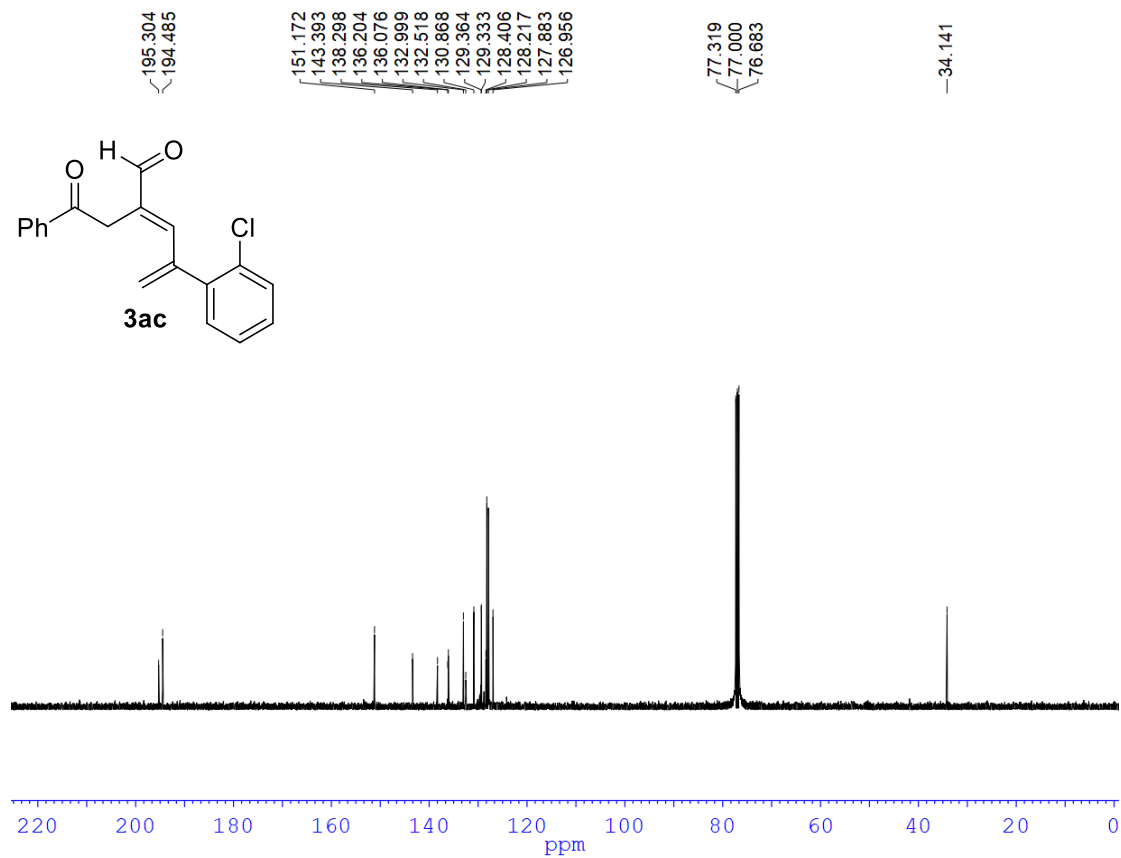


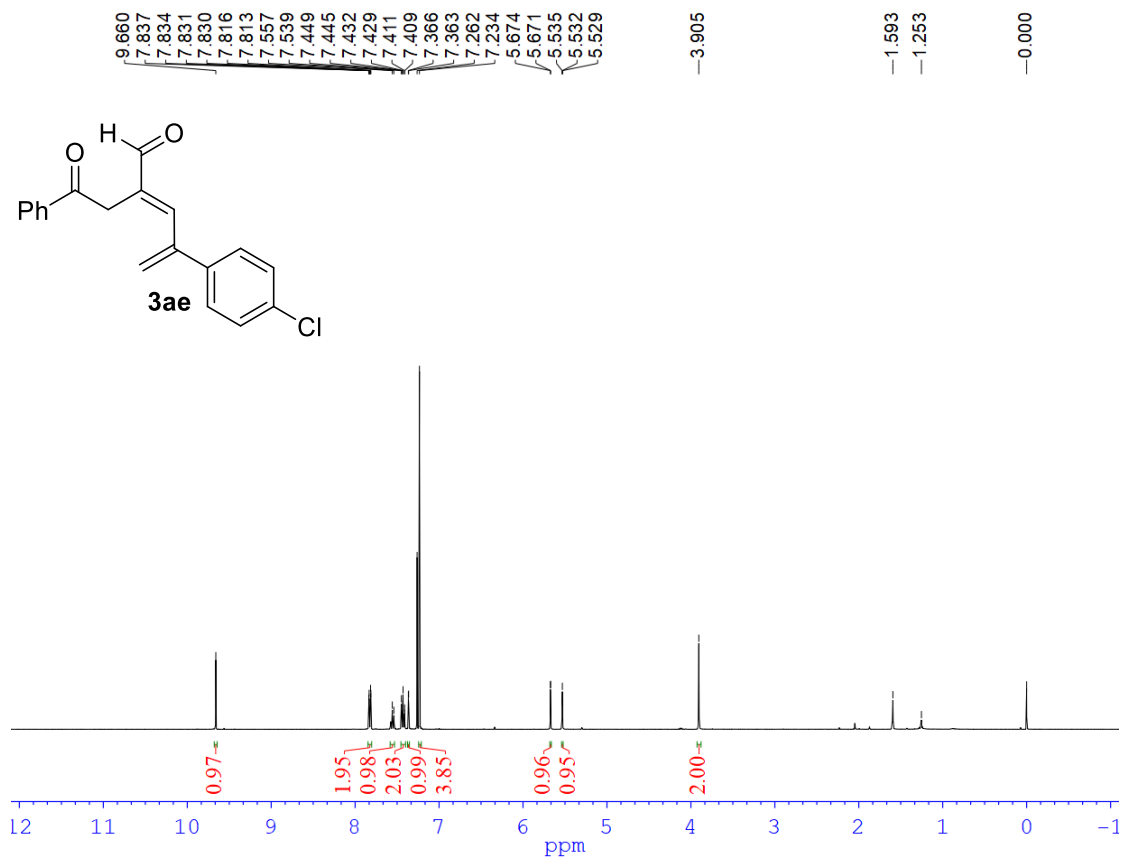
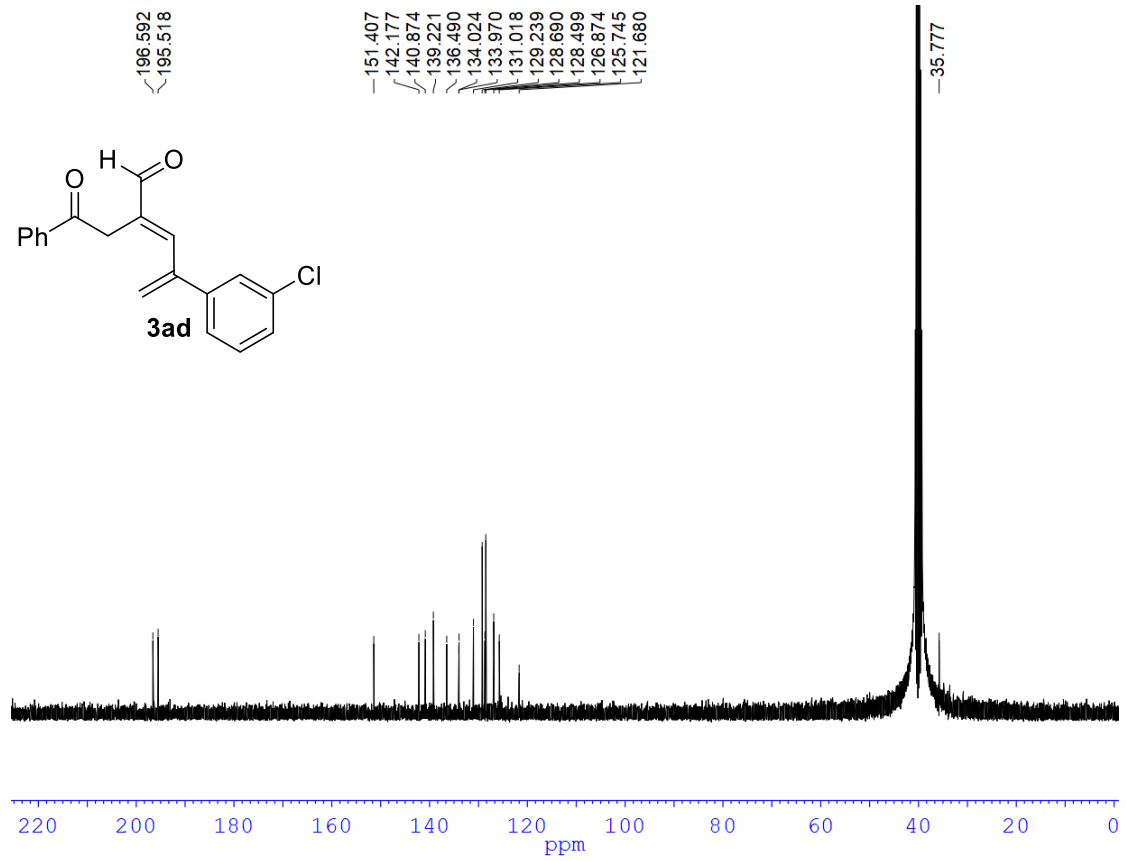


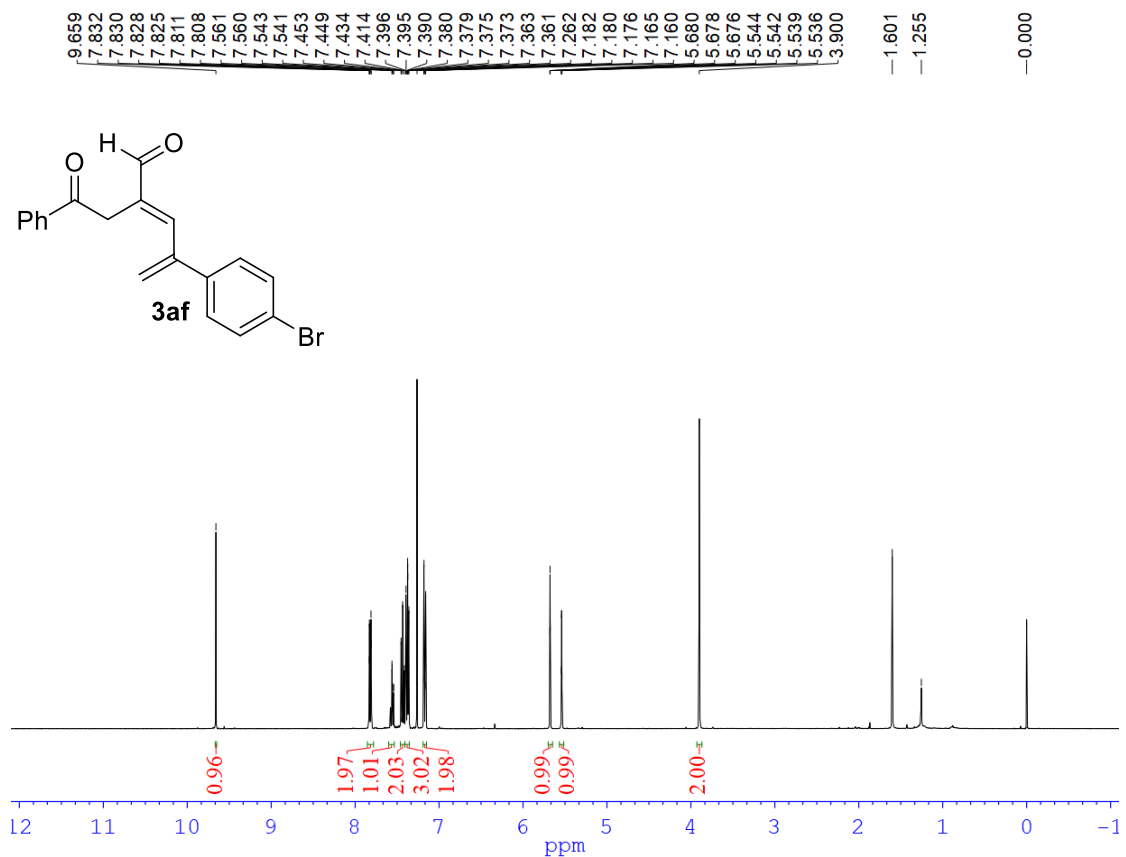
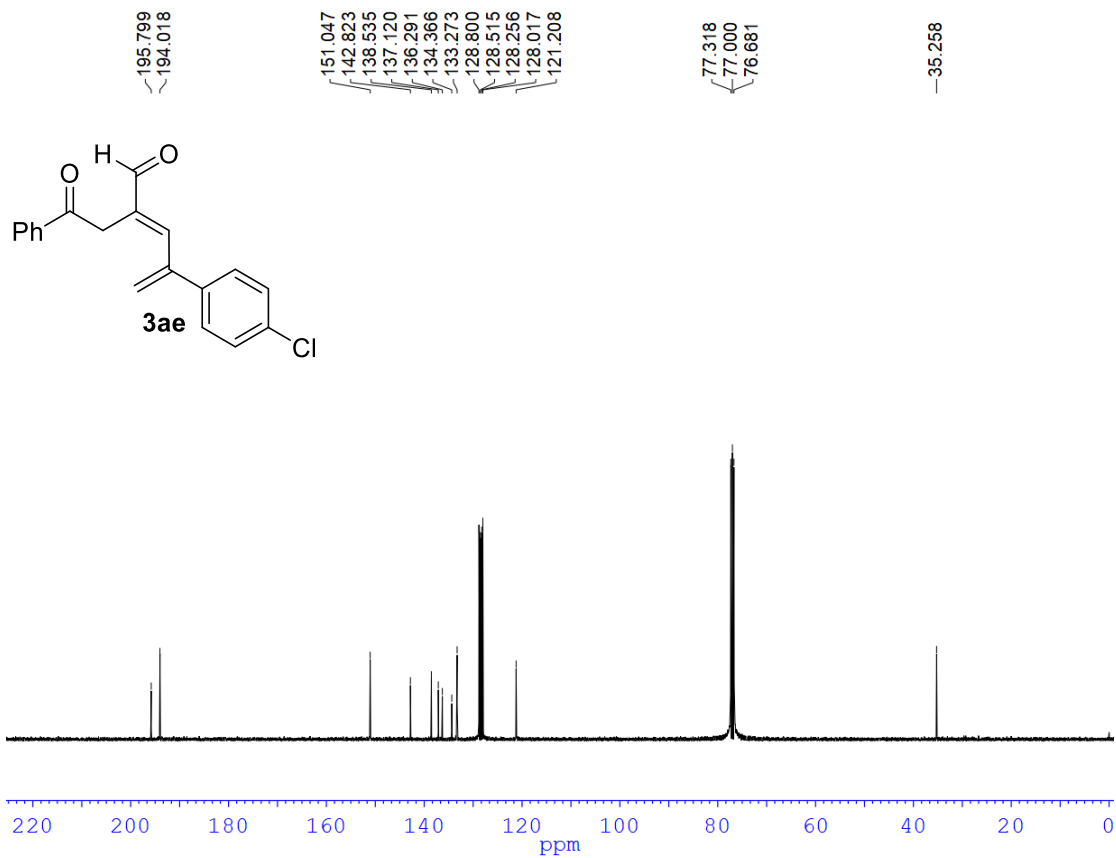


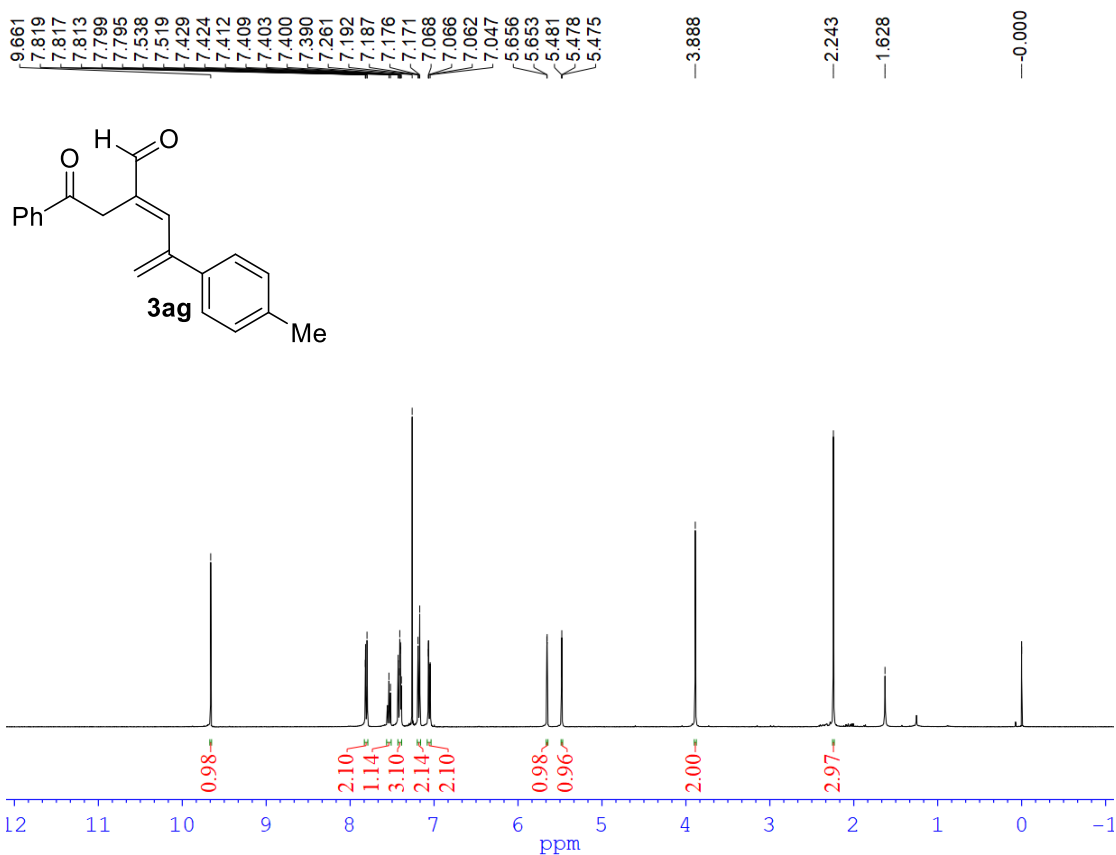
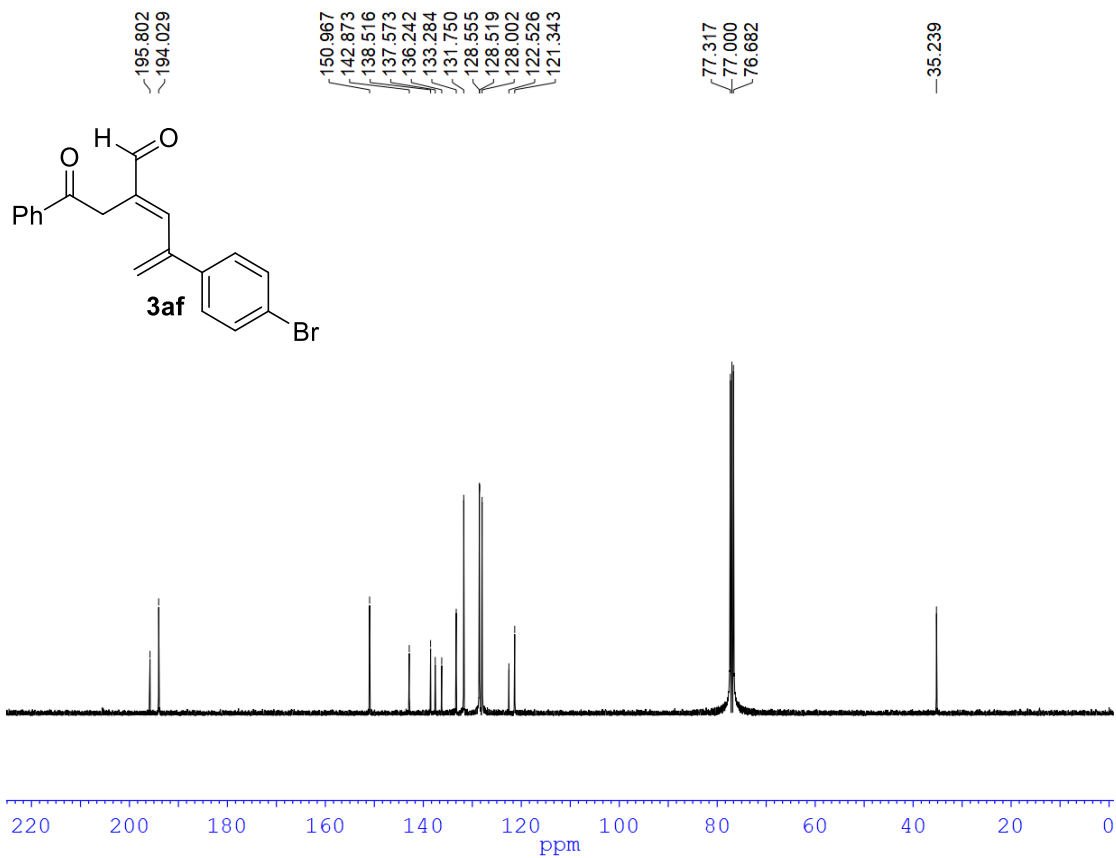


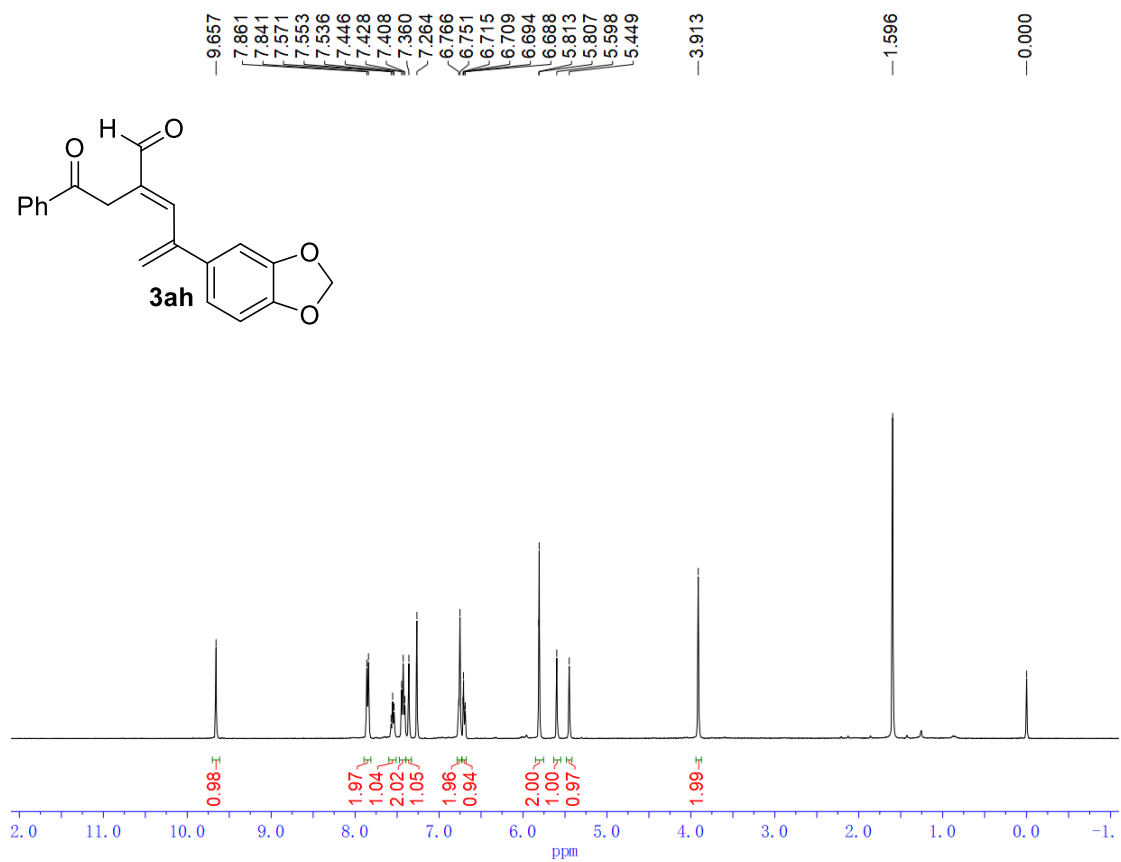
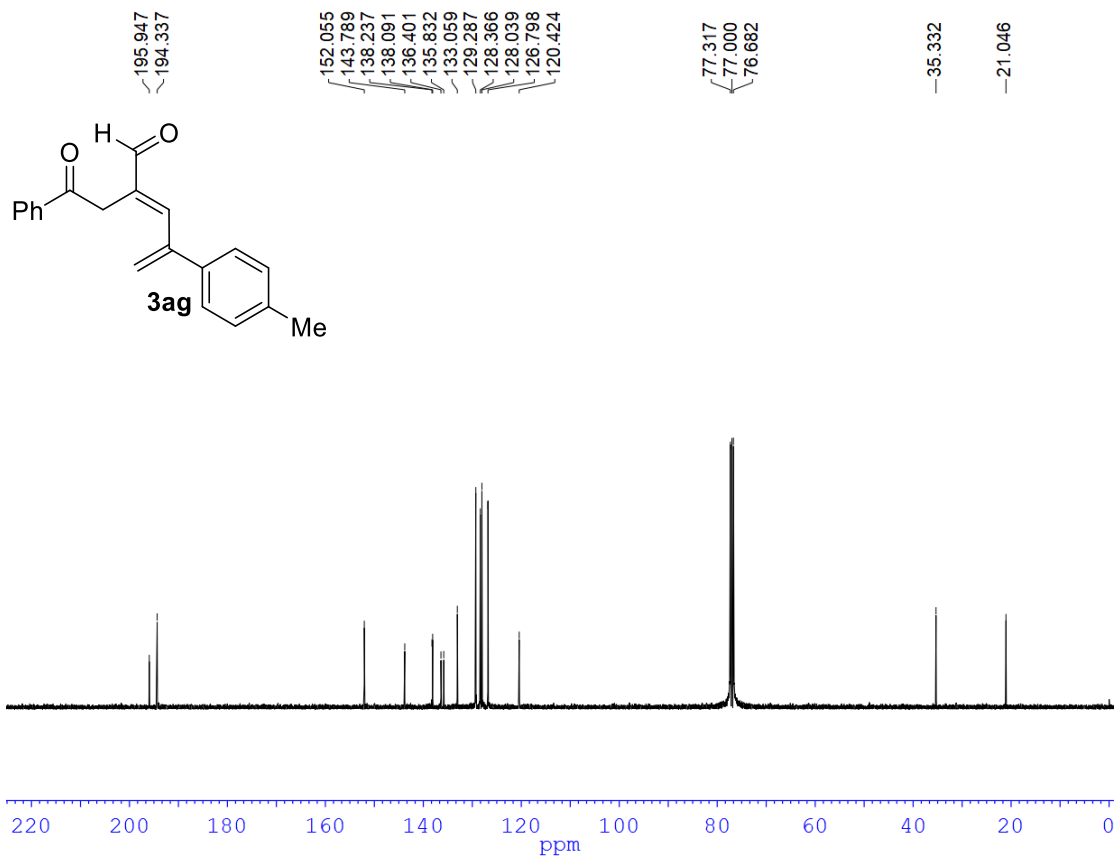


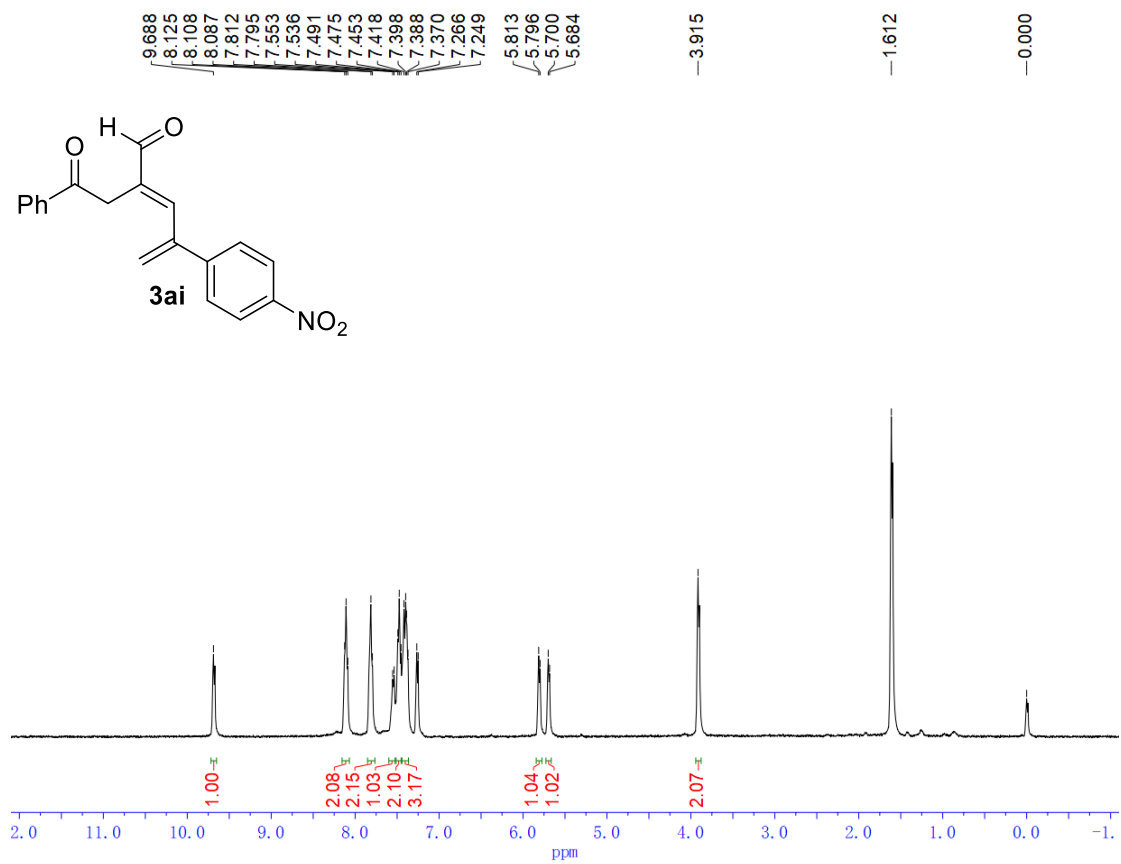
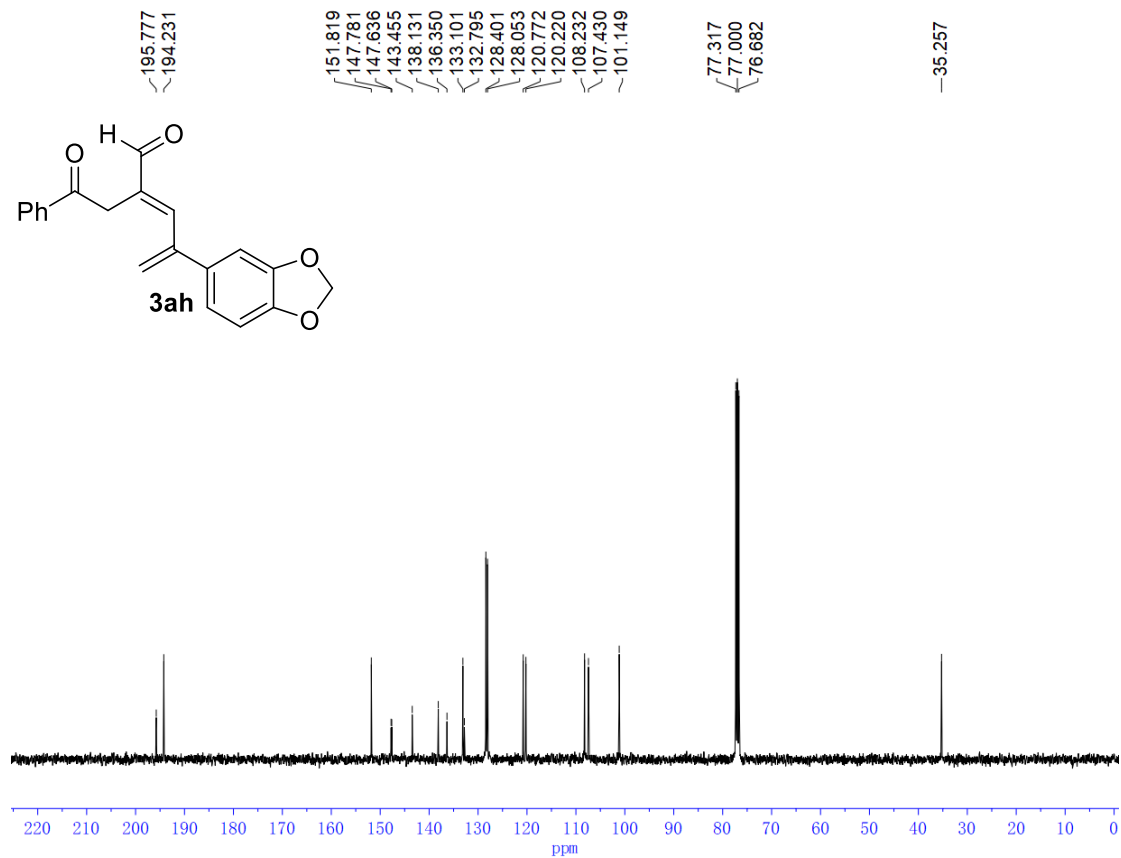


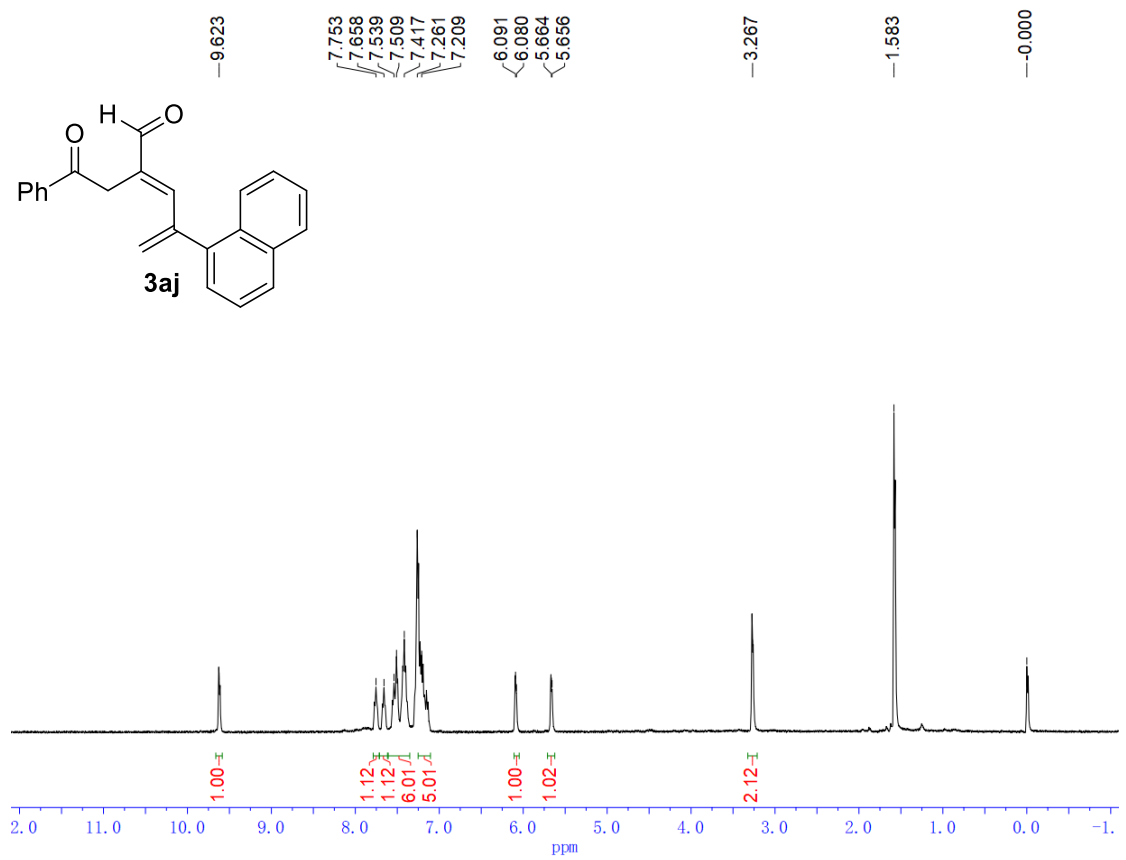
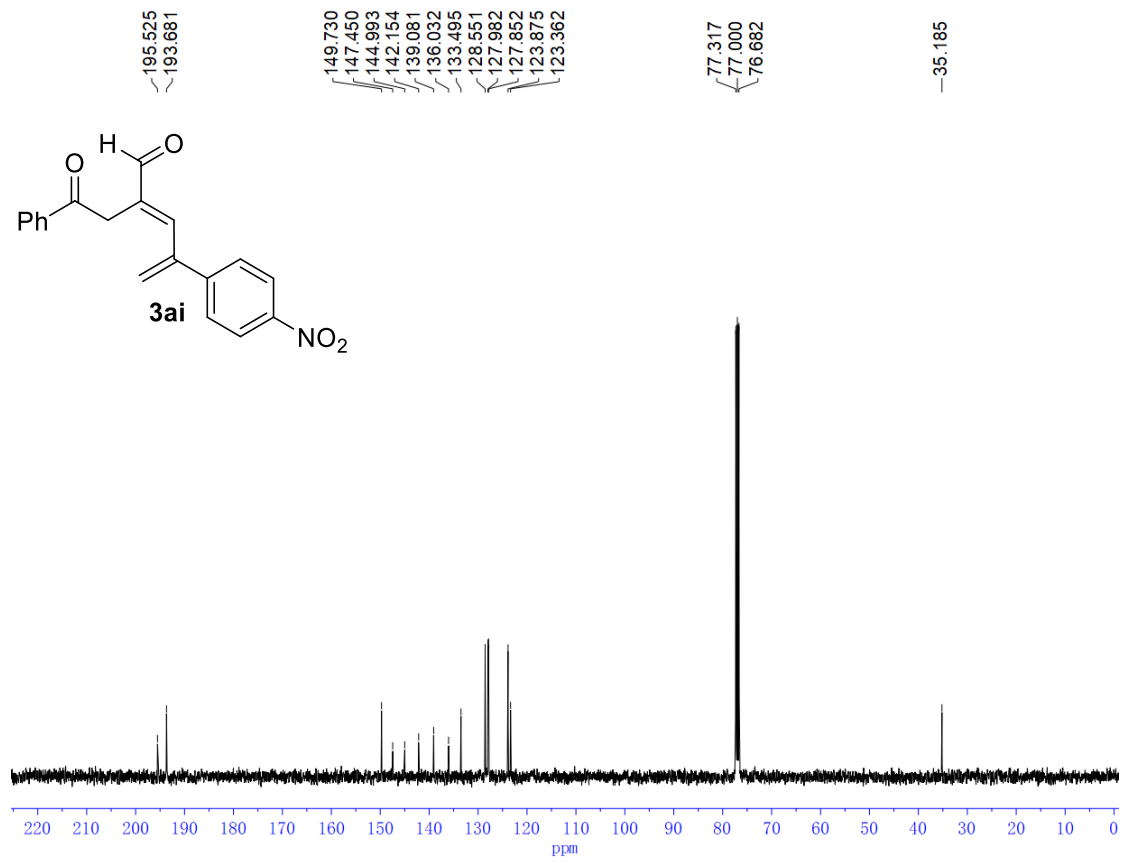


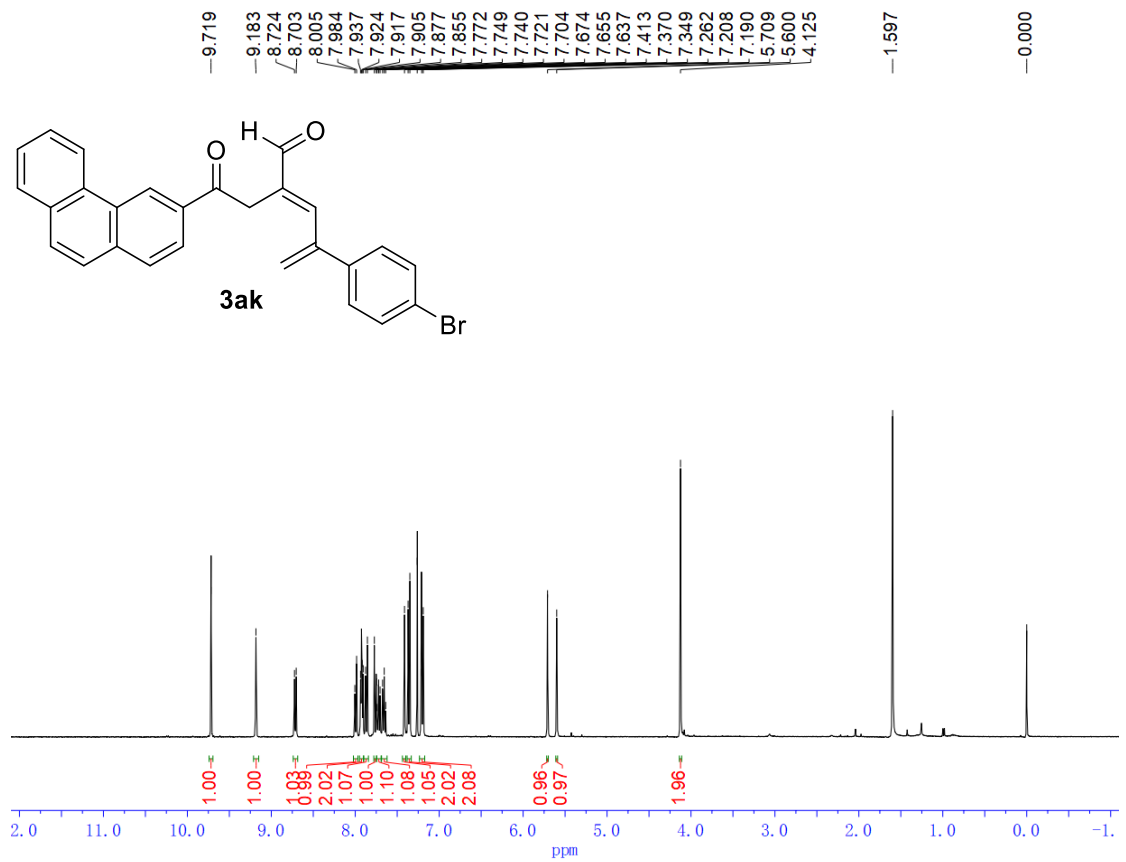
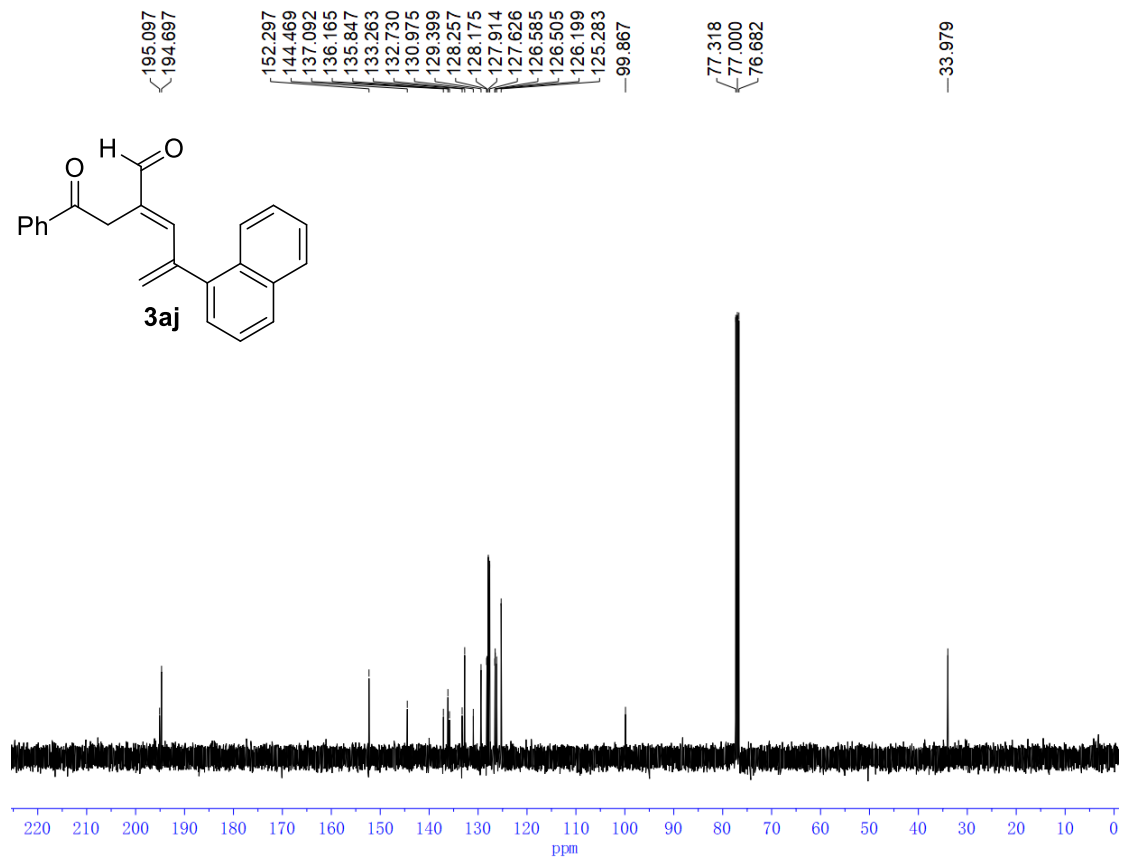


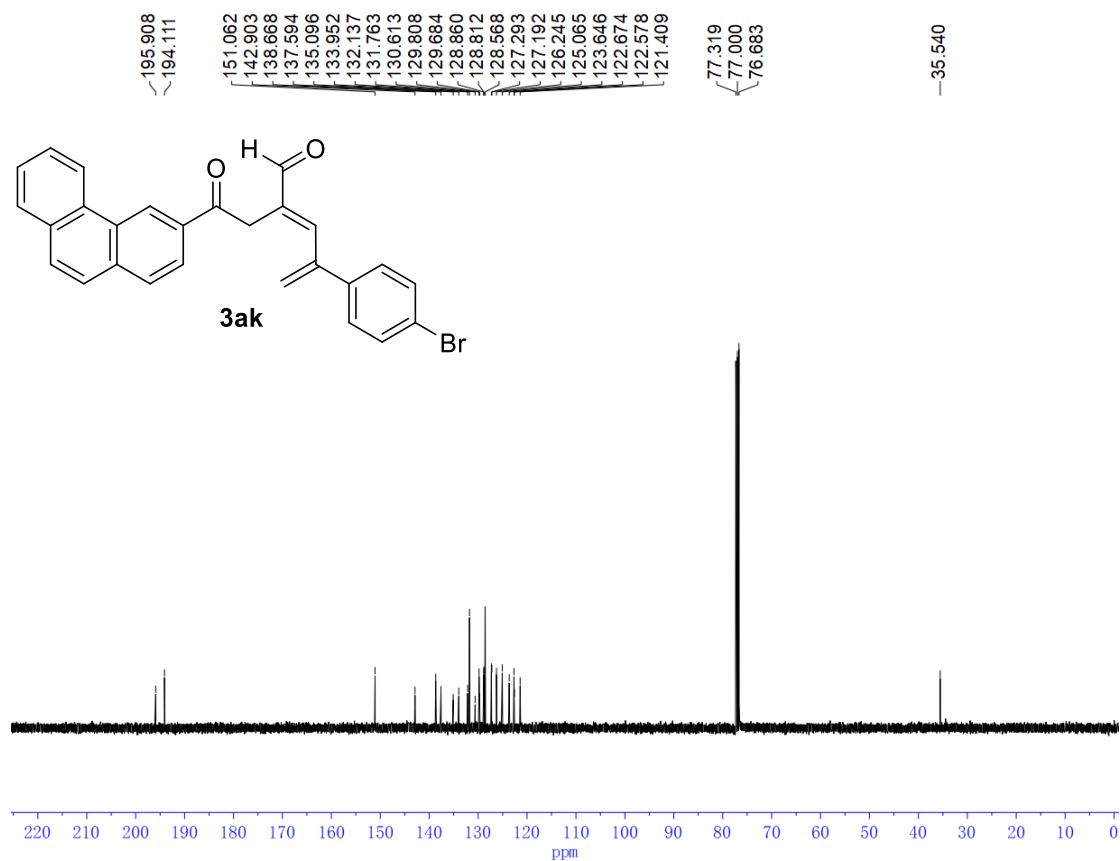




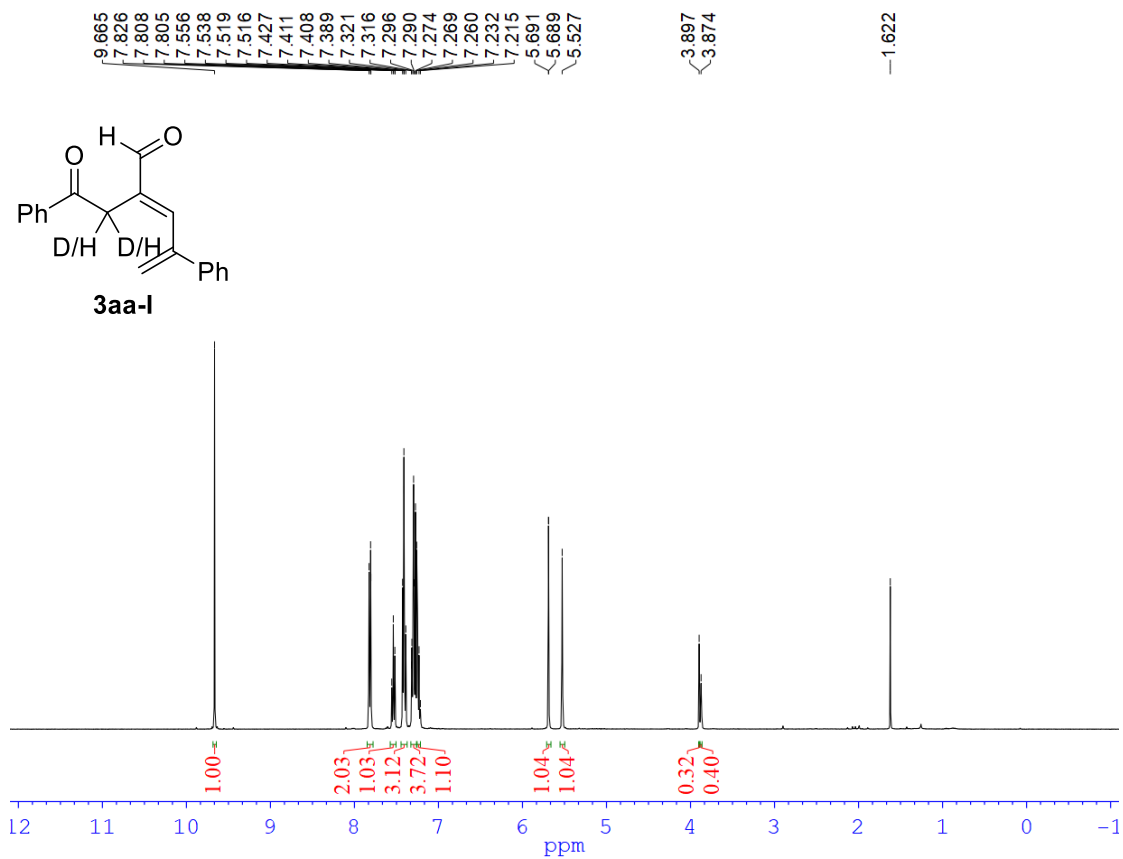


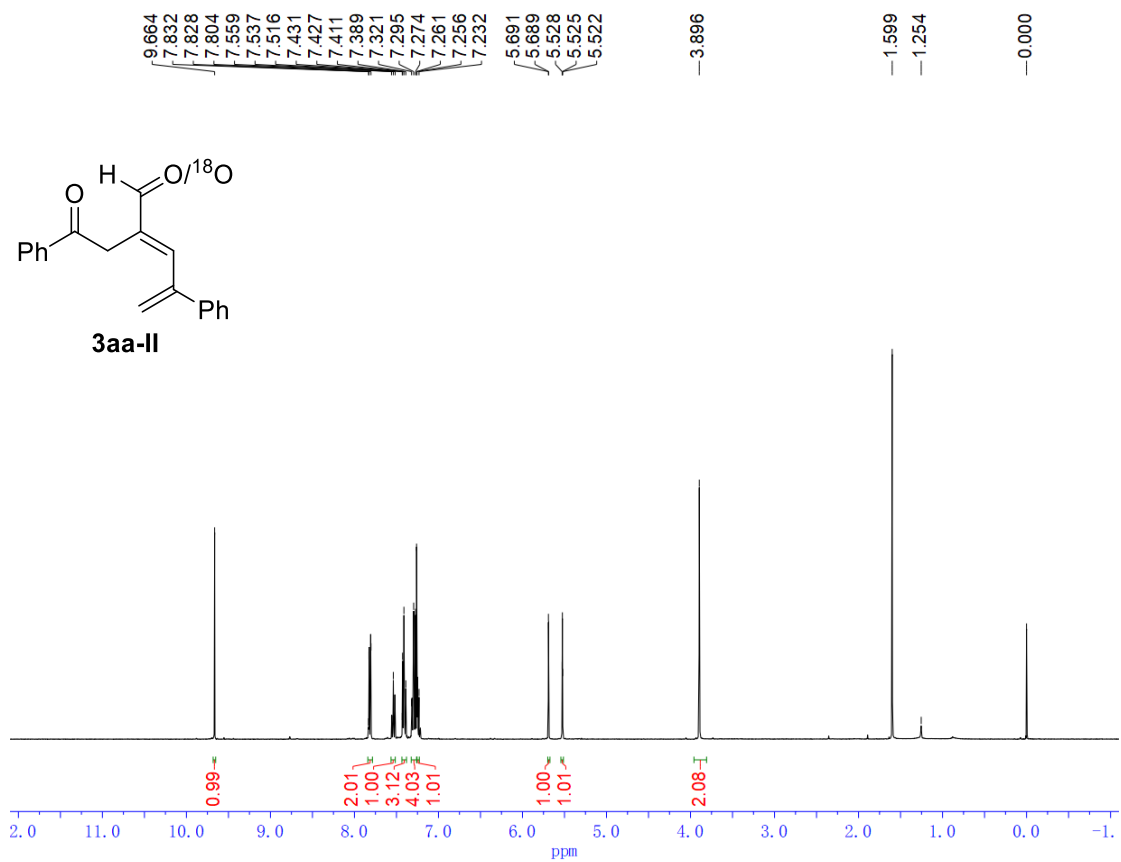
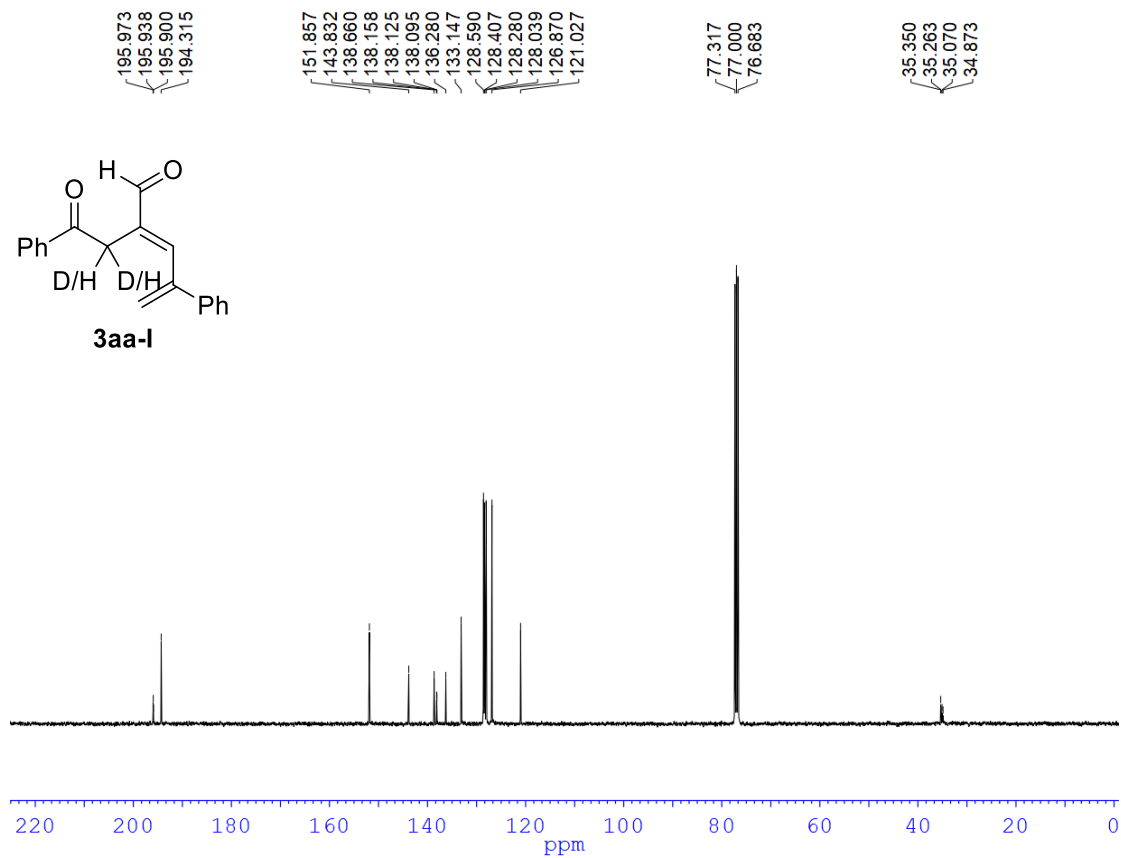


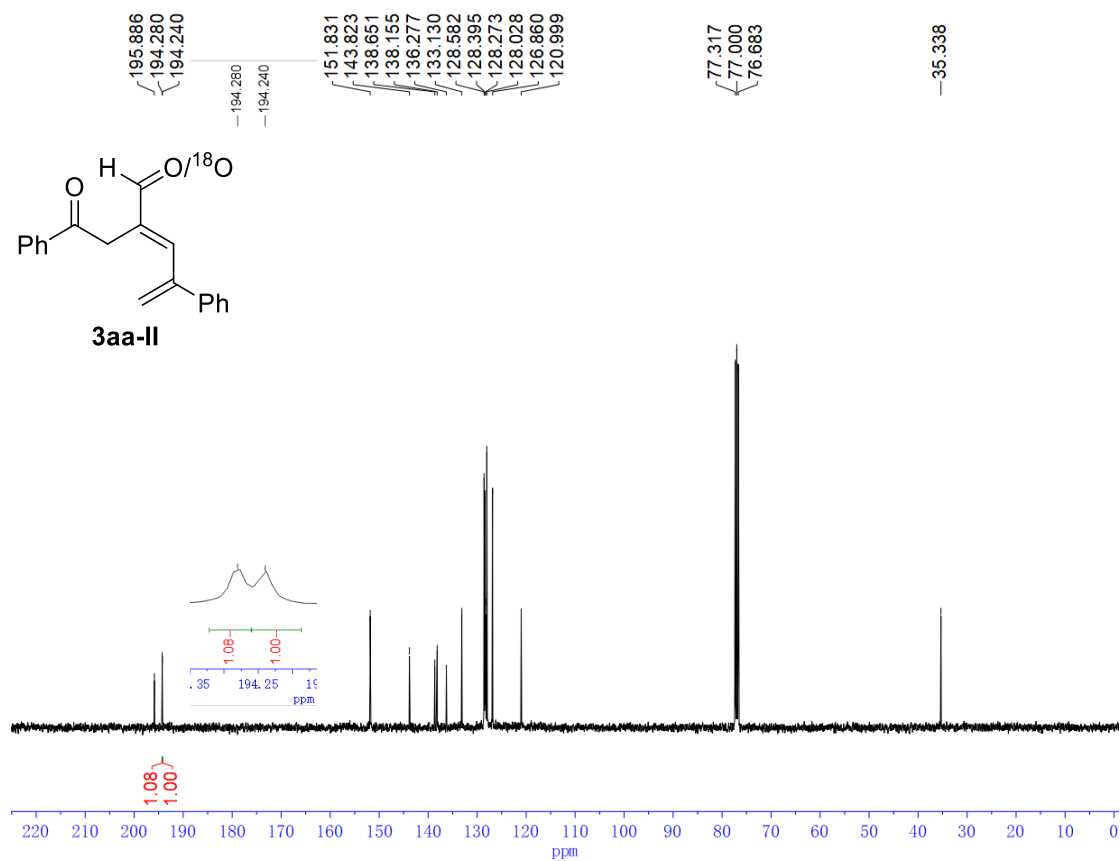




¹H and ¹³C NMR spectra of mechanistic investigations:







¹H and ¹³C NMR spectra of applications:

