

Electronic Supplementary Information

Chelation-directed remote *meta*-C–H functionalization of aromatic aldehydes and ketones

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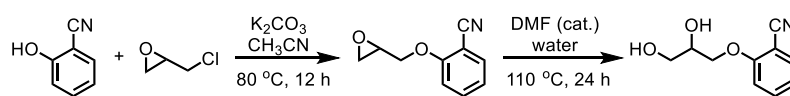
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1 General Information

All solvents and chemicals were commercially available and used directly without further purification. Analytical thin layer chromatography was performed on 0.25 mm silica gel 60-F254. Visualization was carried out with UV light. Preparative TLC was performed on 1.0 mm silica gel (Analtech). Columns for flash chromatography (FC) contained silica gel (32–63 μ , Dynamic Adsorbents, Inc.). The melting points were measured with Tektronix X4 microscopic melting point apparatus and are uncorrected. ^1H NMR spectra were recorded on Bruker AV-400 instrument (400 MHz). Chemical shifts were quoted in parts per million (ppm) referenced to 0.00 ppm for tetramethylsilane. The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad. Coupling constants, J , were reported in Hertz unit (Hz). ^{13}C NMR spectra were recorded on Bruker AV-400 instrument (100 MHz), and were fully decoupled by broad band proton decoupling. Chemical shifts were reported in ppm referenced to the center line of a triplet peak at 77.0 ppm of chloroform- d and the center line of a septet peak at 40.0 ppm of d_6 -DMSO. High-resolution mass spectra (HRMS) were recorded on an Agilent Mass spectrometer using ESI-TOF (electrospray ionization-time of flight).

2 Synthesis and Screening of Directing Templates

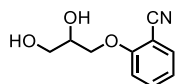
2.1 Synthesis of Template



General procedure for synthesis of template T₁-T₄: 2-cyanophenol (11.9 g, 100 mmol), K_2CO_3 (16.6g, 120 mmol) and epichlorohydrin (46 g, 500 mmol) in CH_3CN (150 ml) were stirred at $80\text{ }^\circ\text{C}$ for 12 h in air. The reaction mixture was then filtered and concentrated under reduced pressure. The resulting crude material (17.4 g, 100 mmol) was used for the next step without further purification.

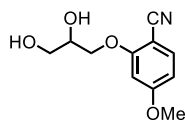
An efficient method for ring-opening reaction of epoxide described by Hua et al¹ was followed: The above crude material (100mmol), H_2O (5.4 g, 300 mmol) and DMF (730 mg, 10 mmol) were heated at $110\text{ }^\circ\text{C}$ for 24h. The reaction mixture was diluted with ethyl acetate (30 mL), and then concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: DCM/ CH_3OH = 25/1) to provide the template **T**₁ (15.9 g, 82.8 mmol).

In a similar manner, the directing templates **T**₂-**T**₄ were prepared in overall yields of >90%.



2-(2,3-dihydroxypropoxy)benzonitrile (**T**₁)

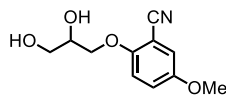
Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ = 7.56–7.44 (m, 2H), 6.97 (t, J = 7.7 Hz, 2H), 4.48–4.27 (m, 1H), 4.20–4.08 (m, 3H), 3.82 (dd, J = 16.8, 5.0 Hz, 2H), 3.16 (brs, 1H). ^{13}C -NMR (100 MHz, $CDCl_3$) δ = 160.29, 134.59, 133.45, 121.04, 116.66, 112.38, 101.52, 70.05, 69.89, 63.25. HR-MS (ESI) m/z calcd for $C_{10}H_{12}NO_3^+$ [$M+H^+$] 194.0812, found 194.0816.



2-(2,3-dihydroxypropoxy)-4-methoxybenzonitrile (**T**₂)

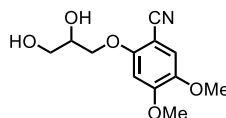
Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ = 7.35 (d, J = 9.2 Hz, 1H), 6.48–6.41 (m, 2H), 4.47 (brs, 1H), 4.13 (m, 1H), 4.08–4.03 (m, 2H), 3.83–3.74 (m, 5H), 3.26 (brs, 1H). ^{13}C -NMR (100 MHz, $CDCl_3$) δ = 164.63, 162.00, 134.46, 117.20, 106.58, 99.08, 93.40, 70.00, 69.91, 63.22, 55.69.

HR-MS (ESI) m/z calcd for $C_{11}H_{14}NO_4^+$ $[M+H]^+$ 224.0917, found 224.0916.



2-(2,3-dihydroxypropoxy)-5-methoxybenzonitrile (**T₃**)

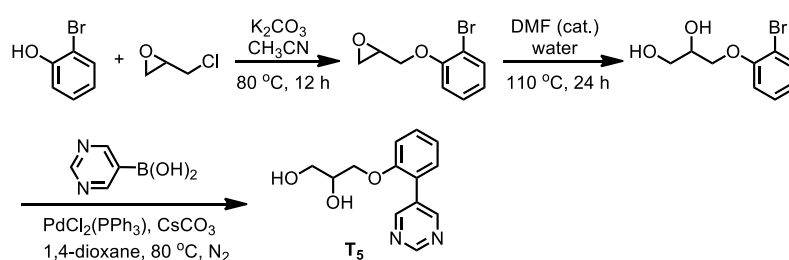
Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ = 7.06 (dd, J = 9.2, 3.1 Hz, 1H), 7.00 (d, J = 3.1 Hz, 1H), 6.93 (d, J = 9.2 Hz, 1H), 4.19–4.05 (m, 3H), 3.88–3.80 (m, 2H), 3.77 (s, 3H), 3.22 (brs, 1H), 2.48 (brs, 1H). ^{13}C -NMR (100 MHz, $CDCl_3$) δ = 154.69, 153.42, 120.91, 117.27, 116.43, 114.05, 101.94, 70.62, 70.13, 63.31, 55.87. HR-MS (ESI) m/z calcd for $C_{11}H_{14}NO_4^+$ $[M+H]^+$ 224.0917, found 224.0918.



2-(2,3-dihydroxypropoxy)-4,5-dimethoxybenzonitrile (**T₄**)

Yellow oil. 1H -NMR (400 MHz, $CDCl_3$) δ = 6.92 (s, 1H), 6.55 (s, 1H), 4.14 (m, 3H), 3.93 (s, 3H), 3.90–3.78 (m, 5H), 2.16 (brs, 2H). ^{13}C -NMR (100 MHz, $CDCl_3$) δ = 156.75, 154.26, 143.50, 117.16, 114.18, 97.85, 91.72, 71.03, 70.11, 63.28, 56.47, 56.25. HR-MS (ESI) m/z calcd for $C_{12}H_{16}NO_5^+$ $[M+H]^+$ 254.1023, found 254.1029.

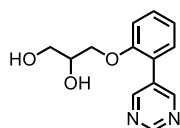
Preparation of template T₅:



2-bromophenol (3.4 g, 20 mmol), K_2CO_3 (3.3 g, 24 mmol) and epichlorohydrin (9.2 g, 100 mmol) in CH_3CN (50 ml) were stirred at 80 °C for 12 h. The reaction mixture was then filtered and concentrated under reduced pressure. The resulting crude material was used for the next step without further purification.

The above crude material (20 mmol), H₂O (1 g, 60 mmol) and DMF (146 mg, 2 mmol) were heated at 110 °C for 24 h. The reaction mixture was diluted with ethyl acetate (10 mL), and then concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: PE/EA = 1/1) to provide the pure diol product (4.4 g, 18 mmol).

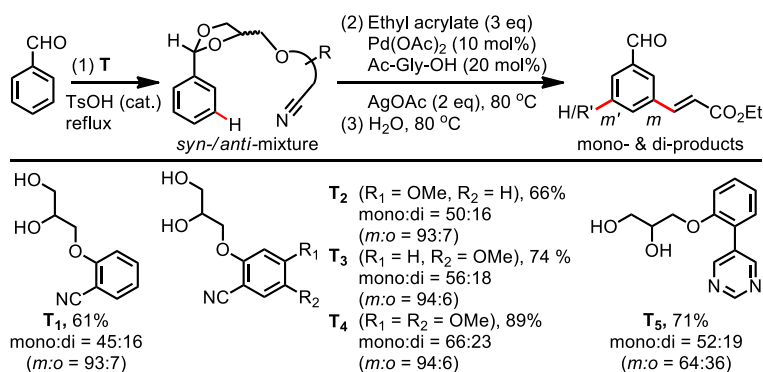
The above diol product (4.4 g, 18 mmol), 5-pyrimidinylboronic acid (3.4 g, 27 mmol), PdCl₂(PPh₃)₂ (364 mg, 1.8 mmol) and Cs₂CO₃ (11.7 g, 36 mmol) in 1,4-dioxane were stirred at 80 °C for 16 h under N₂. The reaction mixture was then filtered and concentrated under reduced pressure. The resulted residue was purified by silica gel column chromatography (eluent: DCM/CH₃OH = 20/1) to provide the template **T₅** (3.9 g, 16 mmol).



3-(2-(Pyrimidin-5-yl)phenoxy)propane-1,2-diol (T₅)

Yellow solid, m.p. 120-121 °C. ¹H-NMR (400 MHz, CDCl₃) δ = 9.02 (s, 1H), 8.93 (s, 2H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 8.4 Hz, 1H), 4.28 (brs, 1H), 4.09 (m, 3H), 3.84 (brs, 1H), 3.74 (m, 1H), 3.65 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ = 156.78, 156.35, 155.55, 132.11, 130.72, 130.19, 123.05, 121.73, 112.41, 70.33, 69.55, 63.57. HR-MS (ESI) *m/z* calcd for C₁₃H₁₅N₂O₃⁺ [M+H⁺] 247.1077, found 247.1083.

2.2 Screening of the Template



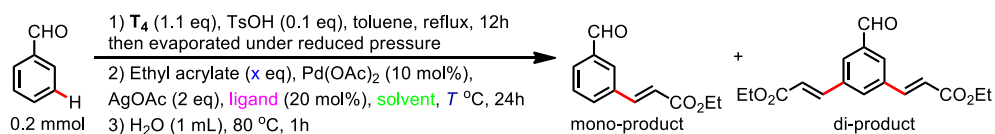
A mixture of benzaldehyde (0.4 mmol), template (0.44 mmol), 4 Å molecular sieves (200 mg) and TsOH (0.04 mmol) in toluene (5 ml) were heated at 120 °C for 24 h. Then, the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure to give the yellow oil. Yield of the crude acetal was estimated by ¹H NMR spectra with CH₂Br₂ as the internal standard.

In air, the acetal substrate (0.2 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), *N*-Acyl glycine (4.6 mg, 0.04 mmol) and silver acetate (67 mg, 0.4 mmol) were charged into a 10-mL reaction vial in turn. Then, olefin (0.6 mmol) and hexafluoroisopropanol (HFIP) (2 mL) were added by a syringe. The reaction vial was screwed by using a Teflon cap and stirred on a pre-heated plate (80 °C) for 24 h.

After cooling to the room temperature, the reaction system was added H₂O (1 ml) then heated at 80 °C for 1h. At that time, the reaction mixture was filtrated via a short pad of silica gel and washed with ethyl acetate exhaustively. The combined filtrates were concentrated to give a thick brown oil. Yield, regioselectivity and ratio of mono- versus di-products were evaluated by ¹H NMR spectra of the crude product with CH₂Br₂ as the internal standard.

Based on ¹H NMR analysis of the crude products, template T₄ was identified as the optimal directing group to give the desired product in 89% yield with 94:6 *meta:ortho* regioselectivity.

It was found that, without isolation of the intermediate acetal, direct C-H olefination of the crude acetal followed by in-situ hydrolysis also provides a comparable yield. Hence, subsequent surveys on the scope of substrates and olefins were performed by this sequential one-pot reaction, which facilitates installation of the directing template into aldehyde/ketone substrates and dissociation from the acetal/ketal products.

Table S1. Optimization of reaction conditions with template **T₄**

Entry	Equiv. (x)	Ligand	Solvent	T	Yield (%)	meta:ortho	mono:di
1	2.0	Ac-Gly-OH	HFIP	80	79	93:7	61:18
2	2.0	Ac-Ala-OH	HFIP	80	71	91:9	56:15
3	2.0	Ac-Val-OH	HFIP	80	62	89:11	51:11
4	2.0	Ac-Ile-OH	HFIP	80	51	91:9	42:9
5	2.0	Ac-Leu-OH	HFIP	80	56	91:9	47:9
6	2.0	Ac-Phe-OH	HFIP	80	44	90:10	38:6
7	1.5	Ac-Gly-OH	HFIP	80	71	92:8	53:18
8	2.5	Ac-Gly-OH	HFIP	80	83	93:7	64:19
9	3.0	Ac-Gly-OH	HFIP	80	89	94:6	66:23
10	3.0	Ac-Gly-OH	HFIP	60	64	94:6	53:11
11	3.0	Ac-Gly-OH	HFIP	65	71	94:6	56:15
12	3.0	Ac-Gly-OH	HFIP	70	79	93:7	62:17
13	3.0	Ac-Gly-OH	HFIP	75	85	94:6	64:19
14	3.0	Ac-Gly-OH	DCE	80	n.r.	-	-
15	3.0	Ac-Gly-OH	<i>i</i> PrOH	80	n.r.	-	-
16	3.0	Ac-Gly-OH	<i>t</i> BuOH	80	n.r.	-	-
17	3.0	Ac-Gly-OH	MeOtBu	80	n.r.	-	-
18	3.0	Ac-Gly-OH	DMF	80	21	n.d.	n.d.
19	3.0	Ac-Gly-OH	CHCl ₃	80	40	93:7	35:5
20	3.0	Ac-Gly-OH	CHCl ₃ /HFIP (1:1)	80	82	94:6	65:17
21	3.0	Ac-Gly-OH	CHCl ₃ /HFIP (3:1)	80	77	93:7	63:14
22	3.0	Ac-Gly-OH	CHCl ₃ /HFIP (5:1)	80	70	93:7	58:12
23	3.0	Ac-Gly-OH	CHCl ₃ /HFIP (10:1)	80	64	93:7	56:8

n.r.: no reaction. n.d.: not detected.

Figure S1. Regioselectivity comparison of templates **T₄** and **T₅** in C–H olefination

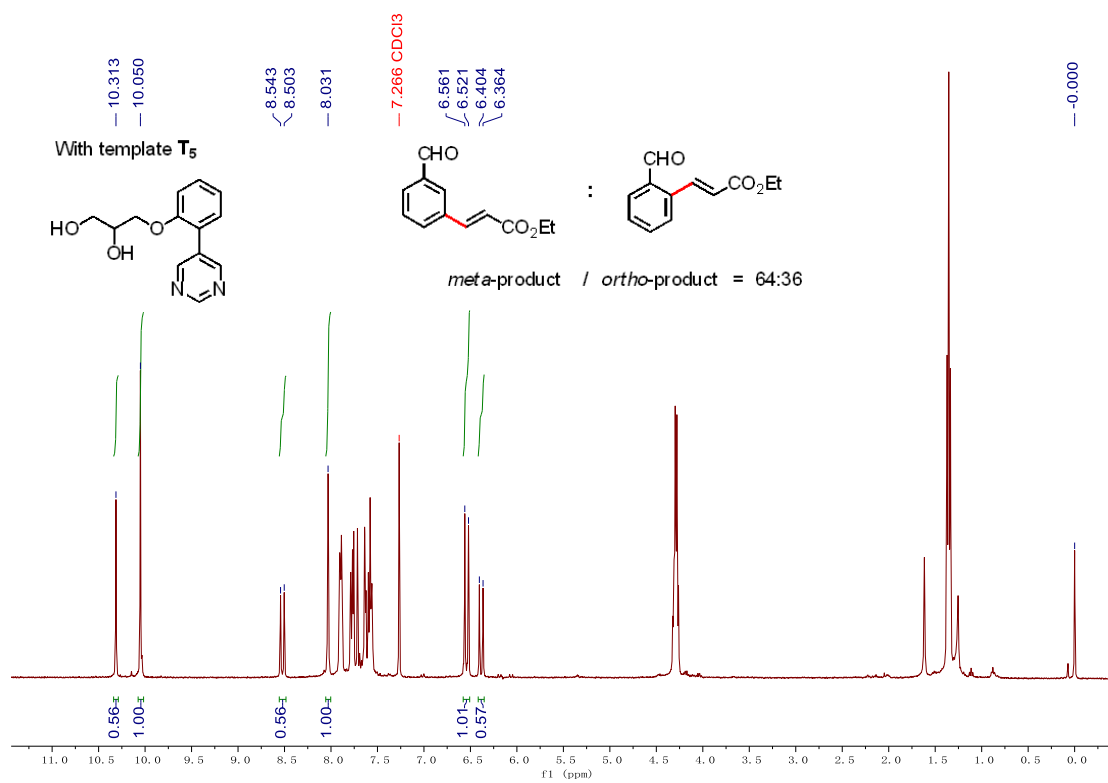
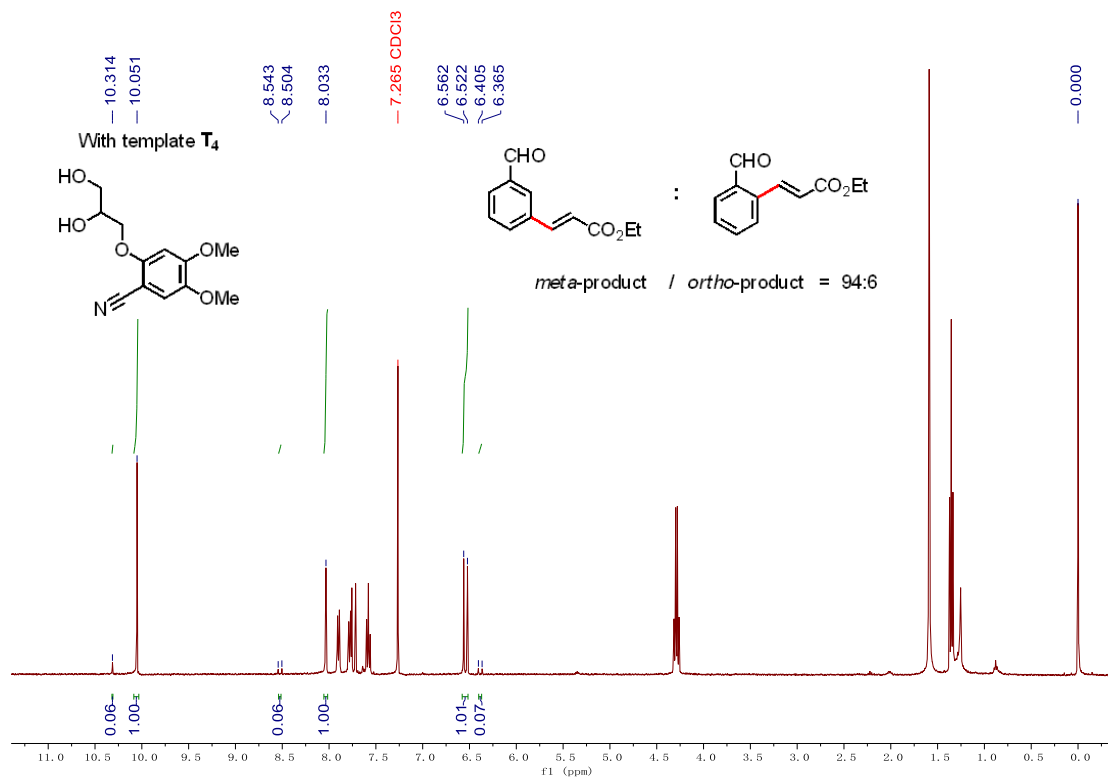
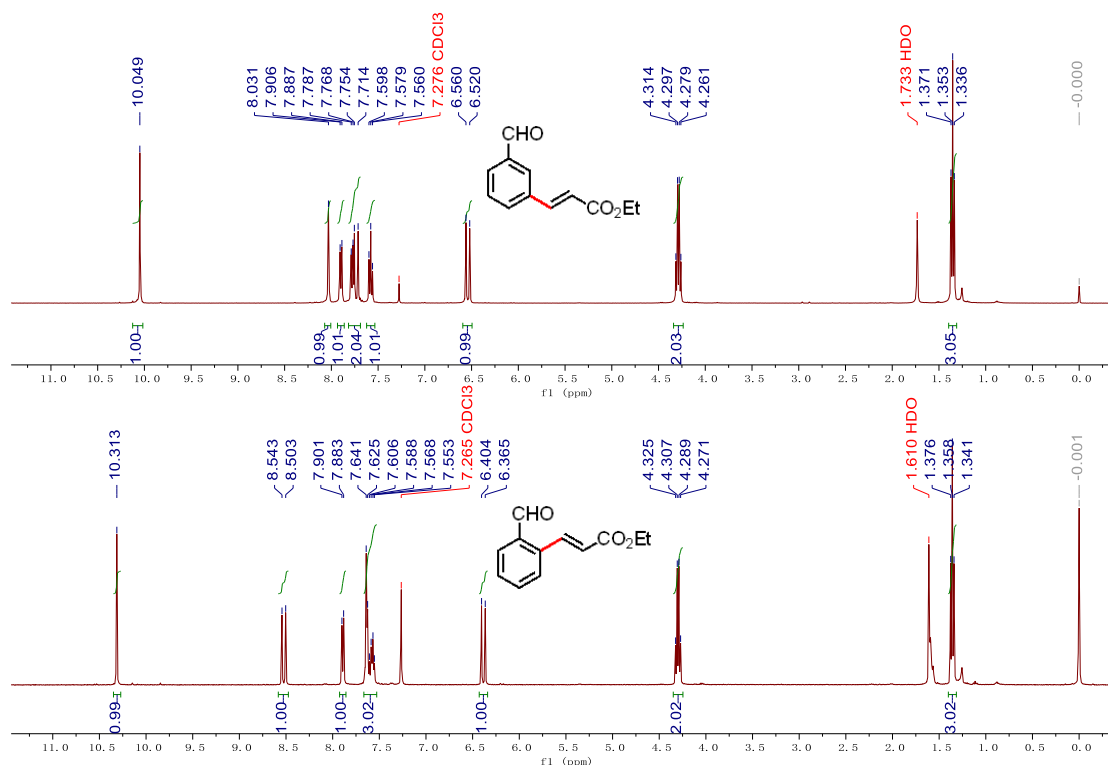


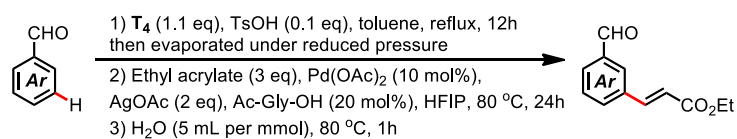
Figure S2. ^1H NMR spectra of pure *meta*- and *ortho*-olefinated benzaldehydes^a



^aPure *m*- or *o*-alkenylated benzaldehydes were prepared from the corresponding 3-bromo or 2-bromobenzaldehydes and ethyl acrylate via known Pd-catalyzed Heck coupling.^{2,3}

3 Template-Directed Remote *meta*-C–H Olefination

3.1 Palladium-Catalyzed *meta*-C–H Olefination of Aromatic Aldehydes

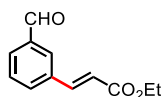


A mixture of aldehyde (0.4 mmol), template T_4 (0.44 mmol), 4 Å molecular sieves (200 mg) and TsOH (0.04 mmol) in toluene (5 ml) were heated at 120 °C for 24 h. Then, the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure to give the yellow oil. Yield of the crude acetal was estimated by ^1H NMR spectra with CH_2Br_2 as the internal standard.

In air, the acetal substrates (0.2 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), *N*-Acyl glycine (4.6 mg, 0.04mmol) and silver acetate (67 mg, 0.4 mmol) were charged into a 10-mL reaction vial in turn.

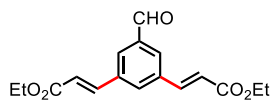
Then, olefin (0.6 mmol) and hexafluoroisopropanol (HFIP) (2 mL) were added by a syringe. The reaction vial was screwed by using a Teflon cap and stirred on a pre-heated plate (80 °C) for 24 h.

After cooling to the room temperature, the reaction system was added H₂O (1 ml) then heated at 80 °C for 1h. At that time, the reaction mixture was filtrated via a short pad of silica gel and washed with ethyl acetate exhaustively. The combined filtrates were concentrated and subjected to purification by silica gel column chromatography (eluent: hexane/ethyl acetate) or preparative thin-layer chromatography to provide the olefinated products. Isolated yield and ratio of mono- versus di-products were reported in the Table 1 of Main Text.



(E)-Ethyl 3-(3-formylphenyl)acrylate (1a_{mono})

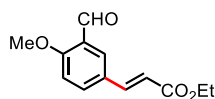
Yellow oil, $R_f = 0.56$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 94:6). The characterization data for major *m*-isomer : ¹H-NMR (400 MHz, CDCl₃) δ = 10.05 (s, 1H), 8.03 (s, 1H), 7.09 (d, $J = 7.6$ Hz, 1H), 7.79–7.72 (m, 2H), 7.58 (t, $J = 8.0$ Hz, 1H), 6.54 (d, $J = 16.0$ Hz, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 1.35 (t, $J = 7.2$ Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ = 191.63, 166.47, 142.81, 136.89, 135.47, 133.52, 130.99, 129.64, 128.81, 120.18, 60.74, 14.28. HR-MS (ESI) m/z calcd for C₁₂H₁₃O₃⁺ [M+H⁺] 205.0859, found 205.0863.



(2E,2'E)-Diethyl 3,3'-(5-formyl-1,3-phenylene)diacrylate (1a_{di})

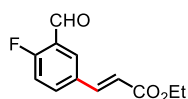
Yellow oil, $R_f = 0.42$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of two regioisomers (*m:others* = 94:6). The characterization data for major *m*-isomer : ¹H-NMR (400 MHz, CDCl₃) δ = 10.07 (s, 1H), 8.03 (d, $J = 1.6$ Hz, 2H), 7.87 (d, $J = 1.6$ Hz, 1H), 7.73 (d, $J = 16.0$ Hz, 2H), 6.57 (d, $J = 16.0$ Hz, 2H), 4.30 (q, $J = 7.2$ Hz, 4H), 1.36 (t, $J = 7.2$ Hz, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ = 190.98, 166.22, 142.04, 137.43, 136.27, 132.55, 129.66, 121.08, 60.87, 14.27. HR-MS (ESI) m/z calcd for C₁₇H₁₉O₅⁺ [M+H⁺]

303.1227, found 303.1231.



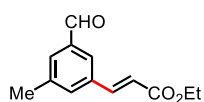
(E)-Ethyl 3-(3-formyl-4-methoxyphenyl)acrylate (1b)

Yellow solid, $R_f = 0.45$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 94–96 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 10.46$ (s, 1H), 8.01 (d, $J = 2.4$ Hz, 1H), 7.71 (dd, $J = 8.7, 2.4$ Hz, 1H), 7.64 (d, $J = 16.0$ Hz, 1H), 7.03 (d, $J = 8.7$ Hz, 1H), 6.39 (d, $J = 16.0$ Hz, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 3.98 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 189.11, 166.85, 162.84, 142.83, 135.27, 128.10, 127.28, 124.86, 117.63, 112.15, 60.49, 55.94, 14.29$. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4^+$ $[\text{M}+\text{H}^+]$ 235.0965, found 235.0961.



(E)-Ethyl 3-(4-fluoro-3-formylphenyl)acrylate (1c)

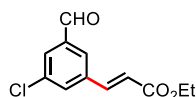
Yellow solid, $R_f = 0.58$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 88–90 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products ($m:o = 85:15$). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 10.39$ (d, $J = 16.8$ Hz, 1H), 8.04 (dd, $J = 6.5, 2.2$ Hz, 1H), 7.94–7.72 (m, 1H), 7.66 (d, $J = 16.0$ Hz, 1H), 7.36–7.18 (m, 1H), 6.45 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 1.34 (t, $J = 7.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 186.46$ (d, $J_{\text{C-F}} = 6$ Hz), 166.44 (d, $J_{\text{C-F}} = 16$ Hz), 163.91, 141.76, 135.30 (d, $J_{\text{C-F}} = 9$ Hz), 131.48 (d, $J_{\text{C-F}} = 4$ Hz), 128.07 (d, $J_{\text{C-F}} = 2$ Hz), 124.36 (d, $J_{\text{C-F}} = 9$ Hz), 119.97 (d, $J_{\text{C-F}} = 2$ Hz), 117.35 (d, $J_{\text{C-F}} = 11$ Hz), 60.75, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{FO}_3^+$ $[\text{M}+\text{H}^+]$ 223.0765, found 223.0762.



(E)-Ethyl 3-(3-formyl-5-methylphenyl)acrylate (1d)

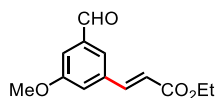
Yellow oil, $R_f = 0.60$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products ($m:o = 88:12$). The

characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 10.01 (s, 1H), 7.83 (s, 1H), 7.70 (s, 1H), 7.68 (d, J = 15.6 Hz, 1H), 7.58 (s, 1H), 6.52 (d, J = 16.1 Hz, 1H), 4.28 (q, J = 7.0 Hz, 2H), 2.46 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 191.83, 166.53, 142.99, 139.66, 136.94, 135.34, 134.29, 131.42, 126.43, 119.86, 60.66, 21.11, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3^+$ [$\text{M}+\text{H}^+$] 219.1016, found 219.1011.



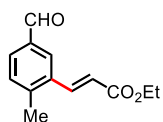
(E)-Ethyl 3-(3-chloro-5-formylphenyl)acrylate (1e)

Yellow solid, R_f = 0.53 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 96–98 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 98:2). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 10.00 (s, 1H), 7.87 (d, J = 17.0 Hz, 2H), 7.74 (d, J = 1.9 Hz, 1H), 7.66 (d, J = 16.0 Hz, 1H), 6.54 (d, J = 16.1 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 190.15, 166.05, 141.33, 138.13, 137.24, 136.10, 133.04, 130.29, 127.01, 121.55, 60.92, 14.25. HR-MS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{ClO}_3^+$ [$\text{M}+\text{H}^+$] 239.0469, found 239.0465.



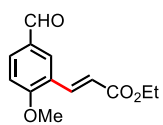
(E)-Ethyl 3-(3-formyl-5-methoxyphenyl)acrylate (1f)

Yellow oil, R_f = 0.55 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *o*-, *m*-, and *p*-isomers (*m:(o+p)* = 65:35). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 9.99 (s, 1H), 7.68 (d, J = 16.0 Hz, 1H), 7.61 (s, 1H), 7.41 (s, 1H), 7.30 (s, 1H), 6.51 (d, J = 16.0 Hz, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.90 (s, 3H), 1.35 (t, J = 7.1 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 191.46, 166.44, 160.50, 142.76, 139.59, 138.18, 122.63, 120.35, 120.11, 113.81, 60.75, 55.70, 14.28. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4^+$ [$\text{M}+\text{H}^+$] 235.0965, found 235.0969. A pure sample for compound **1f** has been synthesized from 3-bromo-5-methoxybenzaldehyde via known Heck coupling.²



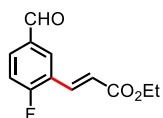
(E)-Ethyl 3-(5-formyl-2-methylphenyl)acrylate (1g)

Yellow oil, $R_f = 0.48$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 74:26). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 9.99$ (s, 1H), 8.04 (s, 1H), 7.96 (d, $J = 16.0$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 1H), 7.46–7.33 (m, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.29 (q, $J = 7.2$ Hz, 2H), 2.52 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 191.49, 166.57, 144.46, 140.74, 134.89, 134.44, 131.53, 130.46, 127.84, 121.25, 60.73, 20.30, 14.29$. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3^+$ [$\text{M}+\text{H}^+$] 219.1016, found 219.1022. A pure sample for compound **1g** has been synthesized from 3-bromo-4-methylbenzaldehyde via known Heck coupling.²



(E)-Ethyl 3-(5-formyl-2-methoxyphenyl)acrylate (1h)

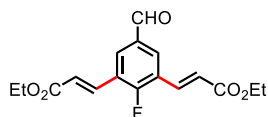
Yellow solid, $R_f = 0.33$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 110–112 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 9.91$ (s, 1H), 8.04 (s, 1H), 7.98 (d, $J = 16$ Hz, 1H), 7.90 (d, $J = 8.6$ Hz, 1H), 7.05 (d, $J = 8.4$ Hz, 1H), 6.61 (d, $J = 16$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 3.99 (s, 3H), 1.35 (td, $J = 7.2, 2.0$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 190.44, 166.98, 162.65, 138.42, 133.11, 130.46, 129.70, 124.22, 120.53, 111.27, 60.57, 56.03, 14.31$. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_4^+$ [$\text{M}+\text{H}^+$] 235.0965, found 235.0969.



(E)-Ethyl 3-(2-fluoro-5-formylphenyl)acrylate (1i_{mono})

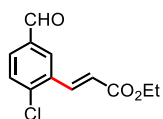
White solid, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 104–107 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 9.99$ (s, 1H), 8.10 (dd, $J = 7.1, 2.1$ Hz, 1H), 7.91 (m, 1H), 7.83 (d, $J = 16.2$ Hz, 1H), 7.28 (m, 1H), 6.64 (d, $J = 16.2$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 189.99, 166.23, 164.54$ (d, $J_{\text{C-F}}$

= 261 Hz), 135.48 (d, J_{C-F} = 3 Hz), 133.08, 132.65(d, J_{C-F} = 11 Hz), 130.83(d, J_{C-F} = 5 Hz), 123.63(d, J_{C-F} = 12 Hz), 122.68(d, J_{C-F} = 6 Hz), 117.26(d, J_{C-F} = 24 Hz), 60.86, 14.25. HR-MS (ESI) m/z calcd for $C_{12}H_{12}FO_3^+$ $[M+H^+]$ 223.0765, found 223.0771.



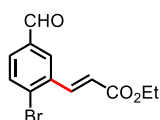
(2E,2'E)-Diethyl 3,3'-(2-fluoro-5-formyl-1,3-phenylene)diacrylate (1i_{dii})

White solid, R_f = 0.45 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V/V/V), m.p.: 113–115 °C. 1H -NMR (400 MHz, $CDCl_3$) δ = 10.00 (s, 1H), 8.10 (d, J = 6.5 Hz, 2H), 7.85 (d, J = 16.2 Hz, 2H), 6.65 (d, J = 16.2 Hz, 2H), 4.30 (q, J = 7.1 Hz, 4H), 1.36 (t, J = 7.1 Hz, 6H). ^{13}C -NMR (100 MHz, $CDCl_3$) δ = 189.59, 166.02, 162.34 (d, J_{C-F} = 267 Hz), 134.90 (d, J_{C-F} = 4 Hz), 132.86 (d, J_{C-F} = 4 Hz), 130.89 (d, J_{C-F} = 5 Hz), 124.54 (d, J_{C-F} = 13 Hz), 123.35 (d, J_{C-F} = 5 Hz), 60.98, 14.25. HR-MS (ESI) m/z calcd for $C_{17}H_{18}FO_5^+$ $[M+H^+]$ 321.1133, found 321.1138.



(E)-Ethyl 3-(2-chloro-5-formylphenyl)acrylate (1j)

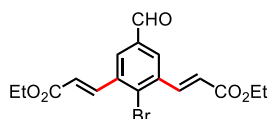
White solid, R_f = 0.45 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 110–112 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 95:5). The characterization data for major *m*-isomer: 1H -NMR (400 MHz, $CDCl_3$) δ = 10.01 (s, 1H), 8.12 (s, 1H), 8.08 (d, J = 16 Hz, 1H), 7.82 (dd, J = 8.2, 2.0 Hz, 1H), 7.61 (d, J = 8.2 Hz, 1H), 6.56 (d, J = 16.0 Hz, 1H), 4.30 (q, J = 7.0 Hz, 2H), 1.38–1.33 (t, 3H). ^{13}C -NMR (100 MHz, $CDCl_3$) δ = 190.41, 166.01, 140.85, 138.94, 135.07, 133.86, 131.06, 131.01, 128.75, 122.70, 60.92, 14.25. HR-MS (ESI) m/z calcd for $C_{12}H_{12}ClO_3^+$ $[M+H^+]$ 239.0469, found 239.0464.



(E)-Ethyl 3-(2-bromo-5-formylphenyl)acrylate (1k_{mono})

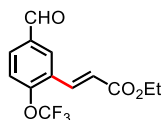
Yellow solid, R_f = 0.43 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 116–118 °C. This compound was obtained as a mixture of *meta*- and other isomers (*m:others*

= 95:5). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 10.01 (s, 1H), 8.08 (s, 1H), 8.05 (d, J = 16 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.72 (dd, J = 8.2, 2.0 Hz, 1H), 6.52 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 1.36 (t, J = 7.1 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 190.58, 165.93, 141.52, 135.75, 135.64, 134.36, 131.74, 130.96, 128.66, 122.86, 60.93, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{12}\text{H}_{12}\text{BrO}_3^+$ [$\text{M}+\text{H}^+$] 282.9964, found 282.9969.



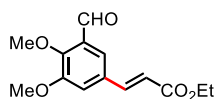
(2E,2'E)-Diethyl 3,3'-(2-bromo-5-formyl-1,3-phenylene)diacrylate (1k_{di})

Yellow solid, R_f = 0.35 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 126–128 °C. This compound was obtained as a mixture of *meta*- and other isomers (*m:others* = 95:5). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 10.03 (s, 1H), 8.12 (d, J = 15.9 Hz, 2H), 8.04 (s, 2H), 6.49 (d, J = 15.8 Hz, 2H), 4.30 (q, J = 7.1 Hz, 4H), 1.36 (t, J = 7.1 Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 190.16, 165.77, 141.97, 137.46, 135.38, 133.23, 128.88, 123.64, 61.01, 14.25. HR-MS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{18}\text{BrO}_5^+$ [$\text{M}+\text{H}^+$] 381.0332, found 381.0336.



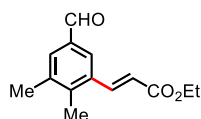
(E)-Ethyl 3-(5-formyl-2-(trifluoromethoxy)phenyl)acrylate (1l)

Yellow oil, R_f = 0.53 (petroleum ether / ethyl acetate / dichloromethane = 15 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 94:6). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 10.04 (s, 1H), 8.19 (s, 1H), 8.03–7.88 (m, 2H), 7.54–7.44 (m, 1H), 6.61 (d, J = 16.1 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.36 (t, J = 7.2 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 190.01, 165.93, 151.19, 135.76, 134.51, 131.95, 129.42, 128.37, 122.98, 120.95, 120.23 (q, $J_{\text{C-F}}$ = 262 Hz), 60.92, 14.19. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{12}\text{F}_3\text{O}_4^+$ [$\text{M}+\text{H}^+$] 289.0682, found 289.0687.



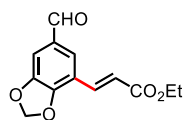
(E)-Ethyl 3-(3-formyl-4,5-dimethoxyphenyl)acrylate (1m)

Yellow solid, $R_f = 0.50$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 125–127 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 10.42$ (s, 1H), 7.63 (d, $J = 16$ Hz, 1H), 7.58 (s, 1H), 7.27 (d, $J = 2.1$ Hz, 1H), 6.41 (d, $J = 16.0$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 4.03 (s, 3H), 3.95 (s, 3H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 189.49, 166.60, 154.01, 153.19, 143.04, 130.46, 129.57, 119.49, 118.81, 116.04, 62.35, 60.60, 56.07, 14.26$. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_5^+$ [$\text{M}+\text{H}^+$] 265.1071, found 265.1076.



(E)-Ethyl 3-(5-formyl-2,3-dimethylphenyl)acrylate (1n)

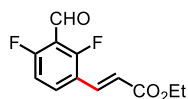
Yellow oil, $R_f = 0.53$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 50:50). The characterization data for both isomers: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 10.24$ (s, 1H), 9.95 (s, 1H), 8.49 (d, $J = 15.9$ Hz, 1H), 8.04 (d, $J = 15.8$ Hz, 1H), 7.86 (s, 1H), 7.68 (s, 1H), 7.63 (s, 1H), 7.41 (s, 1H), 6.39 (d, $J = 16$ Hz, 1H), 6.36 (d, $J = 16$ Hz, 1H), 4.31–4.25 (m, 4H), 2.39 (s, 6H), 2.35 (s, 6H), 1.35 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 191.77, 191.53, 166.60, 166.40, 143.64, 143.10, 141.92, 140.77, 139.06, 138.49, 134.77, 134.15, 133.22, 131.78, 131.43, 129.00, 126.26, 122.05, 121.50, 60.66, 20.59, 20.14, 19.51, 16.21, 14.28$. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3^+$ [$\text{M}+\text{H}^+$] 233.1172, found 233.1178.



(E)-Ethyl 3-(6-formylbenzo[d][1,3]dioxol-4-yl)acrylate (1o)

Yellow solid, $R_f = 0.50$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 114–116 °C. This compound was obtained as a mixture of *meta*- and other isomers (*m:others* = 87:13). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 9.83$ (s, 1H), 7.64 (d, $J = 16.1$ Hz, 1H), 7.49 (d, $J = 1.5$ Hz, 1H), 7.33 (d, $J = 1.5$ Hz, 1H), 6.70 (d, $J = 16.1$ Hz, 1H), 6.20 (s, 2H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 189.83, 166.66, 151.55, 149.23, 137.29, 131.86, 128.86, 122.40, 117.13, 107.30$.

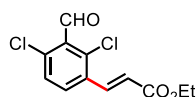
102.85, 60.72, 14.27. HR-MS (ESI) m/z calcd for $C_{13}H_{13}O_5^+$ $[M+H^+]$ 249.0757, found 249.0754.



(E)-Ethyl 3-(2,4-difluoro-3-formylphenyl)acrylate (1p)

Yellow oil, $R_f = 0.50$ (petroleum ether / ethyl acetate / dichloromethane = 15 : 1 : 2, V / V / V).

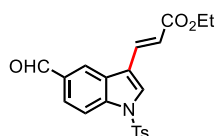
1H -NMR (400 MHz, $CDCl_3$) $\delta = 10.38$ (s, 1H), 7.83–7.72 (m, 2H), 7.05 (td, $J = 9.2, 1.4$ Hz, 1H), 6.52 (d, $J = 16.2$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (100 MHz, $CDCl_3$) $\delta = 184.50$ (dd, $J_{C-F} = 5.3, 4.0$ Hz), 166.16, 163.78 (dd, $J_{C-F} = 215.9, 5.9$ Hz), 161.10 (dd, $J_{C-F} = 218.1, 5.9$ Hz), 134.71 (dd, $J_{C-F} = 11.1, 5.9$ Hz), 134.57, 122.01 (dd, $J_{C-F} = 7, 1.9$ Hz), 120.02 (dd, $J_{C-F} = 11.4, 3.9$ Hz), 114.51 (d, $J_{C-F} = 11.7$ Hz), 113.07 (dd, $J_{C-F} = 21.6, 4.4$ Hz), 60.91, 14.25. HR-MS (ESI) m/z calcd for $C_{12}H_{11}F_2O_3^+$ $[M+H^+]$ 241.0671, found 241.0679.



(E)-Ethyl 3-(2,4-dichloro-3-formylphenyl)acrylate (1q)

Yellow oil, $R_f = 0.53$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V).

1H -NMR (400 MHz, $CDCl_3$) $\delta = 10.48$ (s, 1H), 8.08 (d, $J = 16.1$ Hz, 1H), 7.69 (d, $J = 8.5$ Hz, 1H), 7.42 (d, $J = 8.6$ Hz, 1H), 6.43 (d, $J = 16.0$ Hz, 1H), 4.30 (q, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (100 MHz, $CDCl_3$) $\delta = 188.68, 165.83, 138.32, 137.19, 136.35, 133.44, 131.82, 131.03, 129.72, 122.90, 60.99, 14.25$. HR-MS (ESI) m/z calcd for $C_{12}H_{11}Cl_2O_3^+$ $[M+H^+]$ 273.0080, found 273.0086.

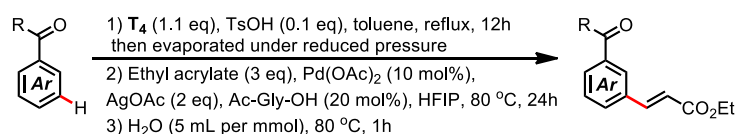


(E)-Ethyl 3-(5-formyl-1-tosyl-1H-indol-3-yl)acrylate (1r)

Yellow solid, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 5 : 1 : 2, V / V / V), m.p.: 130–132 °C. This compound was obtained as a mixture of *C3*- and *ortho*-olefinated products (*C3:others* = 83:17). The characterization data for major isomer: 1H -NMR (400 MHz, $CDCl_3$) $\delta =$

10.08 (s, 1H), 8.32 (d, $J = 1.4$ Hz, 1H), 8.14 (d, $J = 8.6$ Hz, 1H), 7.94–7.91 (m, 2H), 7.85–7.76 (m, 3H), 7.29 (d, $J = 8.1$ Hz, 2H), 6.58 (d, $J = 16.2$ Hz, 1H), 4.29 (t, $J = 7.1$ Hz, 2H), 2.37 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (100 MHz, CDCl_3) $\delta = 191.47, 166.70, 146.11, 138.69, 134.46, 132.60, 130.27, 129.47, 128.33, 127.01, 126.18, 123.64, 119.37, 118.47, 114.23, 60.89, 60.67, 21.61, 14.29$. HR-MS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{20}\text{NO}_5\text{S}^+$ $[\text{M}+\text{H}^+]$ 398.1057, found 398.1052.

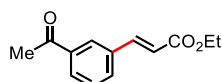
3.2 Palladium-Catalyzed *meta*-C–H Olefination of Aromatic Ketones



A mixture of aromatic ketone (0.4 mmol), template T_4 (0.44 mmol), 4 Å molecular sieves (200 mg) and TsOH (0.04 mmol) in toluene (5 ml) were heated at 120 °C for 24 h. Then, the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure to give the yellow oil. Yield of the crude ketal was estimated by ^1H NMR spectra with CH_2Br_2 as the internal standard.

In air, the ketal substrates (0.2 mmol), Pd(OAc) $_2$ (4.5 mg, 0.02 mmol), *N*-Acyl glycine (4.6 mg, 0.04mmol) and silver acetate (67 mg, 0.4 mmol) were charged into a 10-mL reaction vial in turn. Then, olefin (0.6 mmol) and hexafluoroisopropanol (HFIP) (2 mL) were added by a syringe. The reaction vial was screwed by using a Teflon cap and stirred on a pre-heated plate (80 °C) for 24 h.

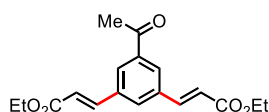
After cooling to the room temperature, the reaction system was added H_2O (1 ml) then heated at 80 °C for 1h. At that time, the reaction mixture was filtrated via a short pad of silica gel and washed with ethyl acetate exhaustively. The combined filtrates were concentrated and subjected to purification by silica gel column chromatography (eluent: hexane/ethyl acetate) or preparative thin-layer chromatography to provide the olefinated products. Isolated yield and ratio of mono-versus di-products were reported in the Table 2 of Main Text.



(E)-Ethyl 3-(3-acetylphenyl)acrylate (2a_{mono})

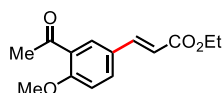
Yellow oil, $R_f = 0.60$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.11$ (s, 1H), 7.97 (d, $J = 7.8$ Hz, 1H), 7.77–7.68 (m, 2H), 7.50 (t, $J = 7.7$ Hz, 1H), 6.52 (d, $J = 16.1$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 2.64 (s, 3H), 1.35 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.43, 166.59, 143.34, 137.67, 134.98, 132.15, 129.75, 129.21, 127.69, 119.71, 60.68, 26.66, 14.29$. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 219.1016, found 219.1010.



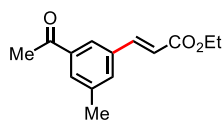
(2E,2'E)-Diethyl 3,3'-(5-acetyl-1,3-phenylene)diacrylate (2a_{di})

Yellow solid, $R_f = 0.48$ (petroleum ether / ethyl acetate / dichloromethane = 5 : 1 : 2, V / V / V), m.p.: 82–83 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.09$ (d, $J = 1.6$ Hz, 2H), 7.82 (s, 1H), 7.72 (d, $J = 16.0$ Hz, 2H), 6.55 (d, $J = 16.0$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 4H), 2.66 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 196.80, 166.33, 142.53, 138.25, 135.77, 131.18, 128.71, 120.62, 60.82, 26.72, 14.28$. HR-MS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{21}\text{O}_5^+$ $[\text{M}+\text{H}^+]$ 317.1384, found 317.1380.



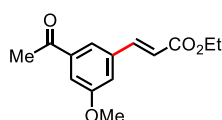
(E)-Ethyl 3-(3-acetyl-4-methoxyphenyl)acrylate (2b)

White solid, $R_f = 0.45$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 98–100 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.92$ (s, 1H), 7.68–7.59 (m, 2H), 6.99 (d, $J = 8.6$ Hz, 1H), 6.37 (d, $J = 16.0$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.96 (s, 3H), 2.62 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 199.06, 166.97, 160.13, 143.14, 133.13, 130.19, 128.44, 127.12, 117.17, 112.01, 60.42, 55.77, 31.76, 14.28$. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_4^+$ $[\text{M}+\text{H}^+]$ 249.1121, found 249.1129.



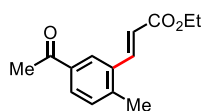
(E)-Ethyl 3-(3-acetyl-5-methylphenyl)acrylate (2c)

White solid, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 95–97 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.90$ (s, 1H), 7.78 (s, 1H), 7.69 (d, $J = 15.9$ Hz, 1H), 7.53 (s, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 2.62 (s, 3H), 2.44 (s, 3H), 1.35 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 97.68, 166.65, 143.52, 139.09, 137.67, 134.84, 132.87, 130.43, 125.13, 119.39, 60.61, 26.70, 21.24, 14.27$. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 233.1172, found 233.1168.



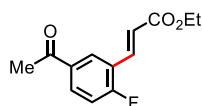
(E)-Ethyl 3-(3-acetyl-5-methoxyphenyl)acrylate (2d)

Yellow solid, $R_f = 0.50$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 90–92 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products ($m:o = 89:11$). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.73$ – 7.64 (m, 2H), 7.50 (d, $J = 2.3$ Hz, 1H), 7.24 (d, $J = 2.4$ Hz, 1H), 6.49 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.88 (s, 3H), 2.62 (s, 3H), 1.37–1.33 (m, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.27, 166.54, 160.13, 143.32, 138.90, 136.14, 120.68, 119.83, 118.01, 114.35, 60.69, 55.62, 26.72, 14.28$. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_4^+$ $[\text{M}+\text{H}^+]$ 249.1121, found 249.1126.



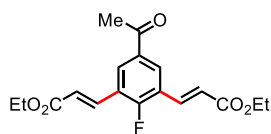
(E)-Ethyl 3-(5-acetyl-2-methylphenyl)acrylate (2e)

Yellow oil, $R_f = 0.60$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.14$ (s, 1H), 7.96 (d, $J = 15.9$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 6.47 (d, $J = 15.8$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 2.61 (s, 3H), 2.50 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.32, 166.69, 142.91, 141.24, 135.49, 133.86, 131.06, 129.42, 126.38, 120.80, 60.67, 26.55, 20.05, 14.30$. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 233.1172, found 233.1170.



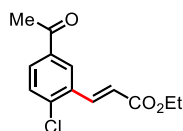
(E)-Ethyl 3-(5-acetyl-2-fluorophenyl)acrylate (2f_{mono})

White solid, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 9 : 1 : 2, V / V / V), m.p.: 79–81 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.21\text{--}8.14$ (m, 1H), 7.97 (ddd, $J = 7.8, 5.1, 2.1$ Hz, 1H), 7.81 (d, $J = 16.2$ Hz, 1H), 7.20 (t, $J = 9.3$ Hz, 1H), 6.63 (d, $J = 16.2$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 2.62 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 195.95, 166.38, 163.87$ (d, $J_{\text{C-F}} = 260$ Hz), 136.02 (d, $J_{\text{C-F}} = 3$ Hz), 133.77 (d, $J_{\text{C-F}} = 4$ Hz), 131.72 (d, $J_{\text{C-F}} = 10$ Hz), 129.67 (d, $J_{\text{C-F}} = 4$ Hz), 122.86 (d, $J_{\text{C-F}} = 8$ Hz), 122.27 (d, $J_{\text{C-F}} = 6$ Hz), 116.56 (d, $J_{\text{C-F}} = 22$ Hz), 60.80, 26.51, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{FO}_3^+$ $[\text{M}+\text{H}^+]$ 237.0921, found 237.0920.



(2E,2'E)-Diethyl 3,3'-(5-acetyl-2-fluoro-1,3-phenylene) diacrylate (2f_{di})

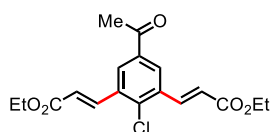
White solid, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 96–98 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.16$ (d, $J = 6.5$ Hz, 2H), 7.84 (d, $J = 16.1$ Hz, 2H), 6.64 (d, $J = 16.4$ Hz, 2H), 4.30 (q, $J = 7.2$ Hz, 4H), 2.64 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 195.54, 166.17, 160.05$ (d, $J_{\text{C-F}} = 280$ Hz) 135.41 (d, $J_{\text{C-F}} = 4$ Hz), 133.65, 130.08 (d, $J_{\text{C-F}} = 4$ Hz), 123.76 (d, $J_{\text{C-F}} = 14$ Hz), 122.94 (d, $J_{\text{C-F}} = 6$ Hz), 60.94, 26.51, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{FO}_5^+$ $[\text{M}+\text{H}^+]$ 335.1289, found 335.1283.



(E)-Ethyl 3-(5-acetyl-2-chlorophenyl)acrylate (2g_{mono})

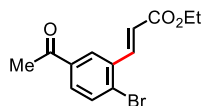
White solid, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 106–108 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated

products (*m:o* = 97:3). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.20 (d, J = 2.1 Hz, 1H), 8.08 (d, J = 16.0 Hz, 1H), 7.88 (dd, J = 8.3, 2.1 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 6.55 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.62 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 196.36, 166.14, 139.59, 139.39, 135.86, 133.22, 130.48, 130.23, 127.48, 122.30, 60.87, 26.57, 14.27. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{ClO}_3^+$ [$\text{M}+\text{H}^+$] 253.0626, found 253.0628.



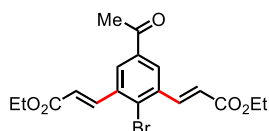
(2*E*,2'*E*)-Diethyl 3,3'-(5-acetyl-2-chloro-1,3-phenylene)diacrylate (2g_{ii})

White solid, R_f = 0.42 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 121–123 °C. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.17 (s, 2H), 8.12 (d, J = 16 Hz, 2H), 6.52 (d, J = 16.0 Hz, 2H), 4.31 (q, J = 7.1 Hz, 4H), 2.65 (s, 3H), 1.36 (t, J = 7.1 Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 195.95, 165.95, 139.56, 139.21, 135.59, 134.68, 128.07, 123.12, 60.98, 26.57, 14.27. HR-MS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{ClO}_5^+$ [$\text{M}+\text{H}^+$] 351.0994, found 351.0990.



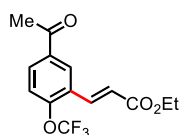
(*E*)-Ethyl 3-(5-acetyl-2-bromophenyl)acrylate (2h_{mono})

White solid, R_f = 0.47 (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 115–117 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 97:3). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ = 8.16 (d, J = 2.0 Hz, 1H), 8.04 (d, J = 15.9 Hz, 1H), 7.82–7.67 (m, 2H), 6.50 (d, J = 15.9 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 2.62 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ = 196.50, 166.05, 141.93, 136.44, 135.10, 133.79, 130.36, 130.21, 127.41, 122.44, 60.87, 26.55, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{14}\text{BrO}_3^+$ [$\text{M}+\text{H}^+$] 297.0121, found 297.0120.



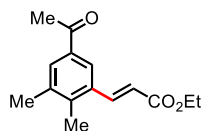
(2E,2'E)-Diethyl 3,3'-(5-acetyl-2-bromo-1,3-phenylene) diacrylate (2h_{di})

White solid, $R_f = 0.60$ (petroleum ether / ethyl acetate / dichloromethane = 5 : 1 : 2, V / V / V), m.p.: 126–128 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 97:3). The characterization data for *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.13$ (d, $J = 16$ Hz, 2H), 8.11 (s, 2H), 6.47 (d, $J = 15.9$ Hz, 2H), 4.31 (q, $J = 7.1$ Hz, 4H), 2.65 (s, 3H), 1.37 (t, $J = 7.1$ Hz, 6H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 196.06, 165.86, 142.35, 136.81, 136.24, 131.94, 128.00, 123.24, 60.96, 26.57, 14.26$. HR-MS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{20}\text{BrO}_5^+$ $[\text{M}+\text{H}^+]$ 395.0489, found 395.0483.



(E)-Ethyl 3-(5-acetyl-2-(trifluoromethoxy)phenyl)acrylate (2i)

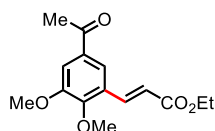
Yellow oil, $R_f = 0.50$ (petroleum ether / ethyl acetate / dichloromethane = 9 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 98:2). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.26$ (d, $J = 2.2$ Hz, 1H), 8.00 (dd, $J = 8.7, 2.2$ Hz, 1H), 7.91 (d, $J = 16.1$ Hz, 1H), 7.39 (dq, $J = 8.7, 1.8$ Hz, 1H), 6.59 (d, $J = 16.1$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 2.64 (s, 3H), 1.36 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 195.97, 166.09, 150.43, 136.25, 135.45, 130.99, 128.32, 127.81, 122.61, 121.08$ (q, $J_{\text{C-F}} = 229$ Hz), 120.57, 60.90, 26.58, 14.24. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{14}\text{F}_3\text{O}_4^+$ $[\text{M}+\text{H}^+]$ 303.0839, found 303.0835.



(E)-Ethyl 3-(5-acetyl-2,3-dimethylphenyl)acrylate (2j)

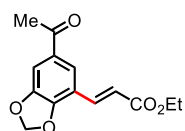
Yellow oil, $R_f = 0.60$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 72:28). The

characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.04$ (d, $J = 15.8$ Hz, 1H), 7.95 (d, $J = 1.8$ Hz, 1H), 7.76 (d, $J = 1.8$ Hz, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 4.32–4.23 (m, 2H), 2.59 (s, 3H), 2.34 (s, 6H), 1.40–1.32 (m, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.55$, 166.69, 142.40, 137.86, 134.81, 130.62, 129.51, 124.58, 121.13, 120.01, 60.59, 26.47, 20.62, 15.94, 14.28. HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3^+$ [$\text{M}+\text{H}^+$] 247.1329, found 247.1326.



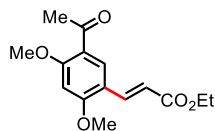
(*E*)-Ethyl 3-(5-acetyl-2,3-dimethoxyphenyl)acrylate (2k)

Yellow oil, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.18$ (d, $J = 15.8$ Hz, 1H), 7.21 (s, 1H), 7.04 (s, 1H), 6.24 (d, $J = 15.8$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.97 (s, 6H), 2.60 (s, 3H), 1.34 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 199.34$, 166.67, 151.65, 149.47, 143.84, 131.44, 129.05, 119.72, 112.00, 110.24, 60.54, 56.16, 56.10, 29.42, 14.33. HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{O}_5^+$ [$\text{M}+\text{H}^+$] 279.1227, found 279.1223.



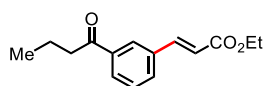
(*E*)-Ethyl 3-(6-acetylbenzo[*d*][1,3]dioxol-4-yl)acrylate (2l)

Yellow solid, $R_f = 0.54$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 84–86 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 95:5). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.61$ (s, 1H), 7.61 (d, $J = 16$ Hz, 1H), 7.42 (s, 1H), 6.68 (d, $J = 16.1$, 1H), 6.16 (s, 2H), 4.33–4.24 (q, 2H), 2.56 (s, 3H), 1.35 (t, $J = 6.8$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 195.70$, 166.74, 150.28, 148.67, 137.92, 132.08, 125.22, 122.04, 108.49, 102.57, 99.93, 60.62, 26.41, 14.26. HR-MS (ESI) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{O}_5^+$ [$\text{M}+\text{H}^+$] 263.0914, found 263.0918.



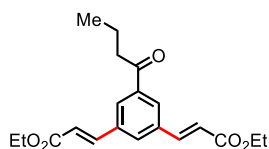
(E)-Ethyl 3-(5-acetyl-2,4-dimethoxyphenyl)acrylate (2m)

Yellow solid, $R_f = 0.50$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V), m.p.: 86–88 °C. This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 95:5). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.05$ (s, 1H), 7.87 (d, $J = 16.1$ Hz, 1H), 6.50 (d, $J = 16.1$ Hz, 1H), 6.43 (s, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.97 (s, 3H), 3.96 (s, 3H), 2.58 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.06$, 167.51, 162.82, 162.31, 138.73, 132.23, 120.78, 117.77, 116.47, 94.63, 60.25, 55.78, 55.72, 31.81, 14.35. HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{O}_5^+$ [$\text{M}+\text{H}^+$] 279.1227, found 279.1223.



(E)-Ethyl 3-(3-butylphenyl)acrylate (2n_{mono})

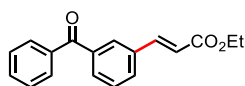
Colorless oil, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 94:6). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.10$ (s, 1H), 7.96 (d, $J = 7.7$ Hz, 1H), 7.83–7.64 (m, 2H), 7.49 (t, $J = 7.8$ Hz, 1H), 6.52 (d, $J = 16.0$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 3.01–2.89 (m, 2H), 1.84–1.73 (m, 2H), 1.35 (t, $J = 7.1$ Hz, 3H), 1.02 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 199.72$, 166.63, 143.45, 134.93, 131.93, 129.49, 129.17, 128.56, 127.47, 119.59, 60.66, 40.60, 17.67, 14.29, 13.84. HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{O}_3^+$ [$\text{M}+\text{H}^+$] 247.1329, found 247.1326.



(2E,2'E)-Diethyl 3,3'-(5-butyl-1,3-phenylene)diacrylate (2n_{di})

Colorless oil, $R_f = 0.45$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.09$ (d, $J = 1.6$ Hz, 2H), 7.81 (s, 1H), 7.72 (d, $J = 16.1$ Hz, 2H),

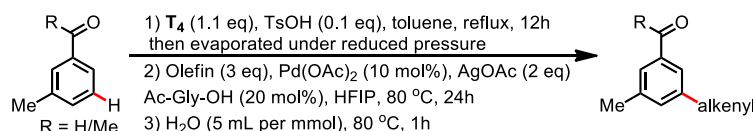
6.55 (d, $J = 16.0$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 4H), 2.98 (t, $J = 7.3$ Hz, 2H), 1.80 (q, $J = 7.4$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 6H), 1.03 (t, $J = 7.4$ Hz, 3H). ^{13}C -NMR (100 MHz, CDCl_3) $\delta = 199.09$, 166.36, 142.64, 138.27, 135.71, 130.97, 128.49, 120.50, 60.80, 40.68, 17.58, 14.28, 13.82. HR-MS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{25}\text{O}_5^+$ [$\text{M}+\text{H}^+$] 345.1697, found 345.1692.



(E)-Ethyl 3-(3-benzoylphenyl)acrylate (**2o**)

Colorless oil, $R_f = 0.45$ (petroleum ether / ethyl acetate / dichloromethane = 5 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products ($m:o = 68:32$). The characterization data for major *m*-isomer: ^1H -NMR (400 MHz, CDCl_3) $\delta = 7.95\text{--}7.41$ (m, 10H), 6.49 (d, $J = 16.0$ Hz, 1H), 4.23 (q, $J = 7.3$ Hz, 2H), 1.30 (t, $J = 7.0$ Hz, 3H). ^{13}C -NMR (100 MHz, CDCl_3) $\delta = 196.04$, 166.61, 143.35, 141.69, 132.73, 131.50, 131.45, 130.33, 130.00, 129.35, 128.93, 128.53, 128.43, 119.68, 60.67, 14.28. HR-MS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{17}\text{O}_3^+$ [$\text{M}+\text{H}^+$] 281.1172, found 281.1176. A pure sample for compound **2o** has been synthesized from 3-bromobenzophenone via known Heck coupling.²

3.3 Palladium-Catalyzed *meta*-C–H Functionalization with Various Olefins

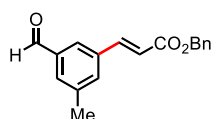


A mixture of *m*-methyl substituted benzaldehyde or acetophenone (0.4 mmol), template **T4** (0.44 mmol), 4 Å molecular sieves (200 mg) and TsOH (0.04 mmol) in toluene (5 ml) were heated at 120 °C for 24 h. Then, the reaction mixture was cooled to room temperature. Removal of solvent under reduced pressure to give the yellow oil. Yield of the crude ketal was estimated by ^1H NMR spectra with CH_2Br_2 as the internal standard.

In air, the *m*-methyl acetal or ketal substrates (0.2 mmol), $\text{Pd}(\text{OAc})_2$ (4.5 mg, 0.02 mmol), *N*-Acyl glycine (4.6 mg, 0.04 mmol) and silver acetate (67 mg, 0.4 mmol) were charged into a 10-mL reaction vial in turn. Then, olefin (0.6 mmol) and hexafluoroisopropanol (HFIP) (2 mL) were added by a syringe. The reaction vial was screwed by using a Teflon cap and stirred on a

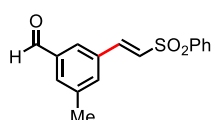
pre-heated plate (80 °C) for 24 h.

After cooling to the room temperature, the reaction system was added H₂O (1 ml) then heated at 80 °C for 1h. At that time, the reaction mixture was filtrated via a short pad of silica gel and washed with ethyl acetate exhaustively. The combined filtrates were concentrated and subjected to purification by silica gel column chromatography (eluent: hexane/ethyl acetate) or preparative thin-layer chromatography to provide the olefinated products. Isolated yield and ratio of mono- versus di-products were reported in the Table 3 of Main Text.



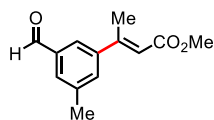
(E)-Benzyl 3-(3-formyl-5-methylphenyl)acrylate (3a)

Yellow oil, $R_f = 0.60$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 86:14). The characterization data for major *m*-isomer: ¹H-NMR (400 MHz, CDCl₃) $\delta = 10.00$ (s, 1H), 7.82 (s, 1H), 7.78–7.68 (m, 2H), 7.58 (s, 1H), 7.44–7.36 (m, 5H), 6.57 (d, $J = 16.0$ Hz, 1H), 5.26 (s, 2H), 2.45 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) $\delta = 191.82, 166.34, 143.61, 139.72, 136.97, 135.85, 135.25, 134.34, 131.55, 128.60, 128.31, 128.26, 126.54, 119.50, 66.52, 21.13$. HR-MS (ESI) m/z calcd for C₁₈H₁₇O₃⁺ [M+H⁺] 281.1172, found 281.1176.



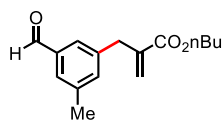
(E)-3-Methyl-5-(2-(phenylsulfonyl)vinyl)benzaldehyde (3b)

Yellow oil, $R_f = 0.70$ (petroleum ether / ethyl acetate / dichloromethane = 4 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and *ortho*-olefinated products (*m:o* = 80:20). The characterization data for major *m*-isomer: ¹H-NMR (400 MHz, CDCl₃) $\delta = 9.99$ (d, $J = 1.2$ Hz, 1H), 8.03–7.94 (m, 2H), 7.79 (s, 1H), 7.73 (s, 1H), 7.70–7.51 (m, 5H), 6.96 (d, $J = 15.4$ Hz, 1H), 2.46 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) $\delta = 191.48, 140.79, 140.03, 136.98, 134.75, 133.57, 132.47, 129.39, 129.30, 129.03, 127.85, 127.70, 126.56, 21.06$. HR-MS (ESI) m/z calcd for C₁₆H₁₅O₃S⁺ [M+H⁺] 287.0736, found 287.0730.



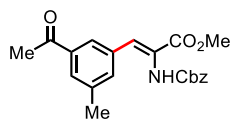
(E)-Methyl 3-(3-formyl-5-methylphenyl)but-2-enoate (3c)

Yellow oil, $R_f = 0.55$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 10.01$ (s, 1H), 7.78 (s, 1H), 7.69 (s, 1H), 7.54 (s, 1H), 6.18 (s, 1H), 3.77 (s, 3H), 2.60 (s, 3H), 2.47 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 192.08$, 166.90, 154.34, 143.03, 139.30, 136.65, 132.88, 130.59, 124.93, 117.73, 51.24, 21.23, 17.94. HR-MS (ESI) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 219.1016, found 219.1019.



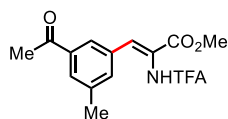
Butyl 2-(3-formyl-5-methylbenzyl)acrylate (3d)

Yellow oil, $R_f = 0.63$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). This compound was obtained as a mixture of *meta*- and other isomers (*m:others* = 90:10). The characterization data for major *m*-isomer: $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 9.96$ (s, 1H), 7.55 (s, 1H), 7.52 (s, 1H), 7.30 (s, 1H), 6.28 (s, 1H), 5.54 (d, $J = 1.4$ Hz, 1H), 4.12 (t, $J = 6.6$ Hz, 2H), 3.67 (s, 2H), 2.41 (s, 3H), 1.64–1.56 (m, 2H), 1.37–1.29 (m, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 192.54$, 166.65, 139.89, 139.54, 138.98, 136.65, 135.97, 128.33, 127.51, 126.67, 64.73, 37.82, 30.56, 21.11, 19.11, 13.67. HR-MS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 261.1485, found 261.1480.



(Z)-Methyl 3-(3-acetyl-5-methylphenyl)-2-(((benzyloxy)carbonyl)amino)acrylate (3e)

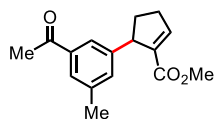
Yellow oil, $R_f = 0.59$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.88$ (s, 1H), 7.71 (s, 1H), 7.48 (s, 1H), 7.34 (m, 6H), 6.54 (brs, 1H), 5.10 (s, 2H), 3.84 (s, 3H), 2.49 (s, 3H), 2.35 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.69$, 165.49, 138.65, 137.24, 134.53, 134.21, 130.14, 129.52, 128.53, 128.36, 128.30, 128.21, 126.85, 124.59, 67.59, 52.82, 26.55, 21.29. HR-MS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{22}\text{NO}_5^+$ $[\text{M}+\text{H}^+]$ 368.1492, found 368.1486.



(Z)-Methyl 3-(3-acetyl-5-methylphenyl)-2-(2,2,2-trifluoroacetamido)acrylate (3f)

Yellow oil, $R_f = 0.52$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V).

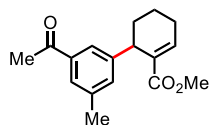
$^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 8.07$ (s, 1H), 7.79 (s, 1H), 7.76 (s, 1H), 7.63 (s, 1H), 7.40 (s, 1H), 3.91 (s, 3H), 2.56 (s, 3H), 2.40 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 197.44$, 164.24, 154.34, 139.00, 137.40, 134.43, 133.85, 133.24, 130.44, 126.54, 121.42, 115.47 (q, $J_{\text{C-F}} = 286$ Hz), 53.24, 26.49, 21.20. HR-MS (ESI) m/z calcd for $\text{C}_{15}\text{H}_{15}\text{F}_3\text{NO}_4^+$ $[\text{M}+\text{H}^+]$ 330.0948, found 330.0942.



Methyl 5-(3-acetyl-5-methylphenyl)cyclopent-1-ene-1-carboxylate (3g)

Yellow oil, $R_f = 0.52$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.59$ (s, 1H), 7.56 (s, 1H), 7.18 (s, 1H), 7.03 (s, 1H), 4.20–4.12 (m, 1H), 3.61 (s, 3H), 2.74–2.67 (m, 1H), 2.57 (m, 5H), 2.38 (s, 3H), 1.88 (td, $J = 8.6, 4.5$ Hz, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 198.56$, 165.01, 145.69, 145.48, 138.68, 138.38, 137.37, 132.56, 127.17, 124.10, 51.40, 49.95, 33.98, 32.24, 26.77, 21.38. HR-MS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 259.1329, found 259.1325.

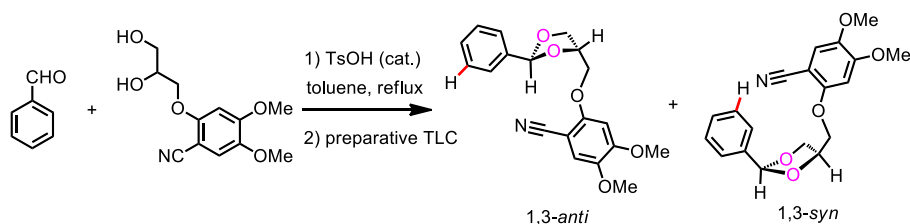


Methyl 3'-acetyl-5'-methyl-1,4,5,6-tetrahydro-[1,1'-biphenyl]-2-carboxylate (3h)

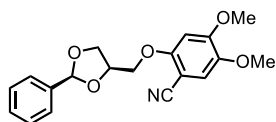
Yellow oil, $R_f = 0.52$ (petroleum ether / ethyl acetate / dichloromethane = 7 : 1 : 2, V / V / V).

$^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.59$ (s, 1H), 7.54 (s, 1H), 7.30 (s, 1H), 7.16 (s, 1H), 3.95 (s, 1H), 3.60 (s, 3H), 2.57 (s, 3H), 2.38 (s, 3H), 2.35–2.20 (m, 2H), 1.94 (dt, $J = 11.5, 6.4$ Hz, 1H), 1.77–1.71 (m, 1H), 1.53 (dd, $J = 8.9, 5.8$ Hz, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 198.61$, 167.35, 145.66, 142.28, 138.09, 137.16, 133.27, 131.32, 127.00, 124.75, 51.55, 39.40, 31.29, 26.75, 25.84, 21.38, 16.86. HR-MS (ESI) m/z calcd for $\text{C}_{17}\text{H}_{21}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 273.1485, found 273.1482.

4 Isolation and Characterization of *syn*- and *anti*-Diastereomers of Acetal

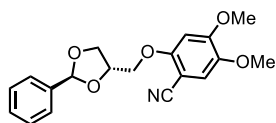


The *syn* and *anti*-diastereomers of acetal were separated successfully by preparative silica gel thin-layer chromatography (hexane/ethyl acetate = 3 : 2). Their structures were validated by 1D ^1H and ^{13}C NMR spectra and HRMS. The *syn*- and *anti*-diastereomers of acetal were tentatively assigned based on their 2D NOESY spectra, respectively.



4,5-Dimethoxy-2-(((2-phenyl-1,3-dioxolan-4-yl)methoxy)benzonitrile (***syn*-isomer**)

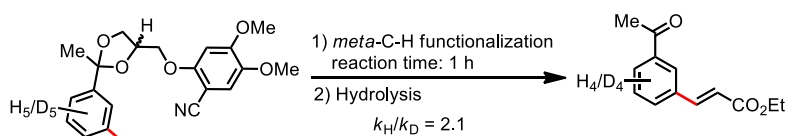
Yellow oil, $R_f = 0.70$ (petroleum ether / ethyl acetate = 3 : 2, V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.52\text{--}7.48$ (m, 2H), 7.43-7.36 (m, 3H), 6.97 (s, 1H), 6.61 (s, 1H), 6.06 (s, 1H), 4.68-4.60 (m, 1H), 4.41-4.36 (m, 1H), 4.30-4.22 (m, 2H), 4.15-4.09 (m, 1H), 3.93 (s, 3H), 3.86 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 156.53, 154.07, 143.78, 137.4, 129.34, 128.38, 126.43, 116.66, 114.47, 104.28, 98.32, 92.61, 73.92, 70.03, 67.44, 56.50, 56.22$. HR-MS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_5^+$ $[\text{M}+\text{H}^+]$ 342.1336, found 342.1331.



4,5-Dimethoxy-2-(((2-phenyl-1,3-dioxolan-4-yl)methoxy)benzonitrile (***anti*-isomer**)

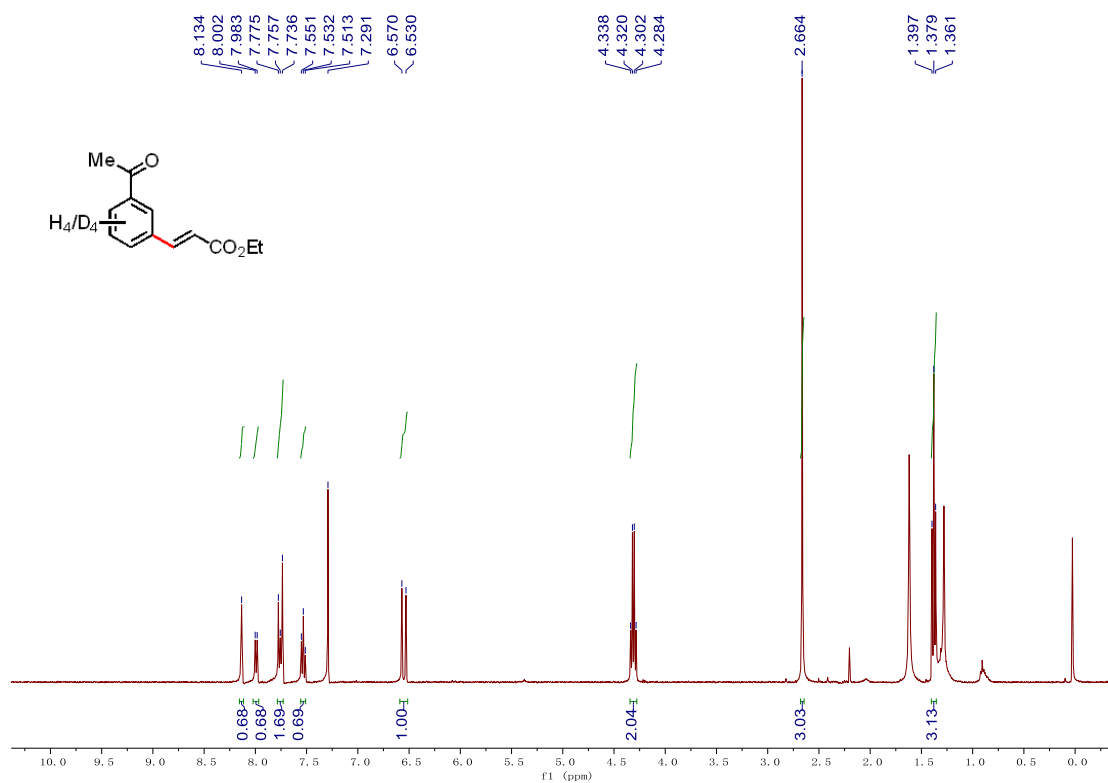
Yellow oil, $R_f = 0.68$ (petroleum ether / ethyl acetate = 3 : 2, V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.51\text{--}7.48$ (m, 2H), 7.40-7.36 (m, 3H), 6.95 (s, 1H), 6.56 (s, 1H), 5.86 (s, 1H), 4.67-4.60 (m, 1H), 4.28-4.23 (m, 3H), 4.13-4.09 (m, 1H), 3.84 (s, 3H), 3.82 (s, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 156.46, 154.02, 143.72, 136.78, 129.51, 128.37, 126.52, 116.66, 114.37, 104.46, 98.60, 92.50, 74.22, 70.48, 68.00, 56.47, 56.11$. HR-MS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{20}\text{NO}_5^+$ $[\text{M}+\text{H}^+]$ 342.1336, found 342.1331.

5 Kinetic Isotope Effect

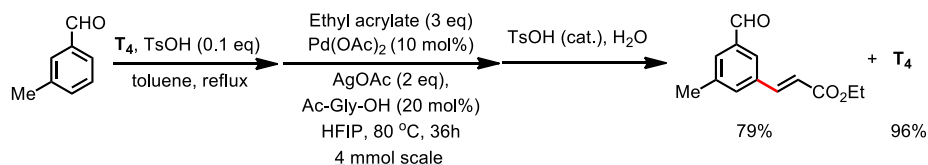


In air, ketal derived from acetophenone (0.1 mmol), [D₅]-ketal derived from [D₅]-acetophenone (0.1 mmol), Pd(OAc)₂ (4.5 mg, 0.02 mmol), *N*-acyl glycine (4.6 mg, 0.04 mmol) and silver acetate (67 mg, 0.4 mmol) were charged into a 10-mL reaction vial in turn. Then, olefin (0.2 mmol) and hexafluoroisopropanol (HFIP) (2 mL) were added by a syringe. The reaction vial was screwed by using a Teflon cap and stirred on a pre-heated plate (80 °C) for 60 min.

After cooling to the room temperature, H₂O (1 ml) and TsOH (3.4 mg, 0.02 mmol) were added to the reaction system, heated at 80 °C for 1h. At that time, the reaction mixture was filtrated via a short pad of silica gel and washed with ethyl acetate exhaustively. The combined filtrates were concentrated and subjected to purification by preparative thin-layer chromatography (hexane/ethyl acetate = 4 :1) to provide the olefinated products and analyzed for its isotopic distribution. The KIE value for this reaction was estimated to be $k_H/k_D \approx 2.1$ by ¹H NMR spectra.



6 Up-Scale Reaction and Recovery of Template

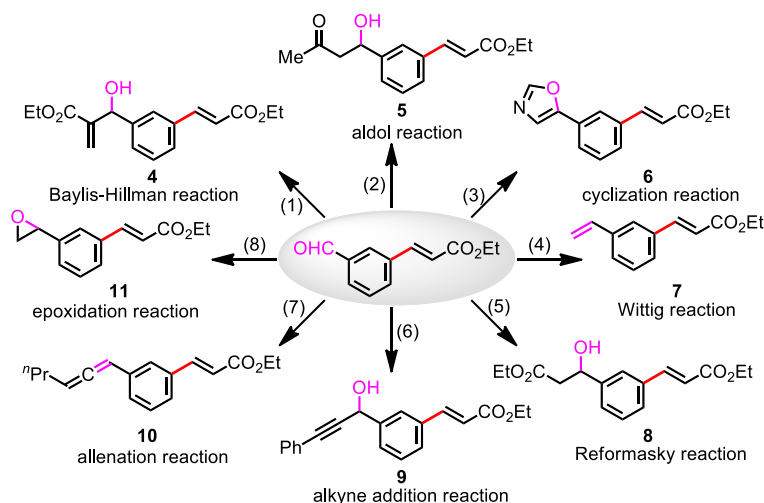


m-Tolualdehyde (24 mmol, 2.9 g), **T**₄ (20 mmol, 5.1 g), and TsOH (2 mmol, 344 mg) in toluene (100 ml) were heated to reflux on a hot oil-bath by using a Dean-Stark water-separated apparatus for 36 h. At that time, the reaction mixture was concentrated under reduced pressure. Yield of the crude acetal product was estimated by ¹H NMR using CH₂Br₂ as the internal standard.

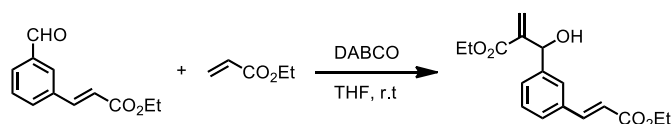
In air, the acetal substrates (1.4 g, 4 mmol), Pd(OAc)₂ (90 mg, 0.4 mmol), *N*-Acyl glycine (93 mg, 0.8 mmol) and silver acetate (1.33 g, 8 mmol) were charged into a 100-mL reaction vial in turn. To this mixture was added ethyl acrylate (1.2 g, 12 mmol) and hexafluoroisopropanol (HFIP) (40 mL) by a syringe. The resulting reaction mixture was then stirred at a heating plate of 80 °C for 36 h.

After cooling to the room temperature, the reaction system was added H₂O (10 ml) and then heated at 80 °C for 1 h. The reaction mixture were filtered and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography (eluent: PE/EA = 15/1) to provide the olefinated products (690 mg, 3.16 mmol), yield: 79%. In addition, the template **T**₄ was recovered from the reaction mixture in 96% yield (970 mg).

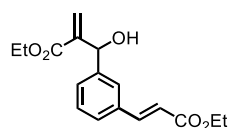
7 Diversification of *meta*-C–H Functionalized Benzaldehyde



(1) Baylis-Hillman reaction⁴



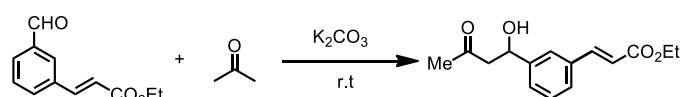
Benzaldehyde (0.2 mmol, 40.8 mg), ethyl acrylate (0.8 mmol, 80 mg) and DABCO (0.2 mmol, 22.4 mg) in THF (2 ml) were stirred at room temperature for 48 h. The mixture was filtered and concentrated under reduced pressure. The resulted residue was purified by silica gel column chromatography (eluent: PE/EA = 4/1). Isolated yield: 81%.



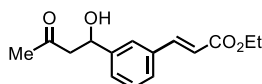
(*E*)-Ethyl 3-(3-(1-hydroxy-2-(methoxycarbonyl)allyl)phenyl)acrylate (4)

Colorless oil, $R_f = 0.40$ (petroleum ether / ethyl acetate = 4 : 1, V / V). ¹H-NMR (400 MHz, CDCl₃) $\delta = 7.67$ (d, $J = 16.0$ Hz, 1H), 7.54 (s, 1H), 7.48–7.34 (m, 3H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.36 (s, 1H), 5.85 (s, 1H), 5.57 (s, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 4.17 (q, $J = 7.1$ Hz, 2H), 3.29 (d, $J = 5.7$ Hz, 1H), 1.33 (t, $J = 7.1$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) $\delta = 166.92, 166.16, 144.34, 142.16, 141.82, 134.54, 128.90, 128.46, 127.39, 126.18, 126.15, 118.47, 72.99, 61.02, 60.50, 14.27, 14.00$. HR-MS (ESI) m/z calcd for C₁₇H₂₁O₅⁺ [M+H⁺] 305.1384, found 305.1389.

(2) Aldol reaction⁵



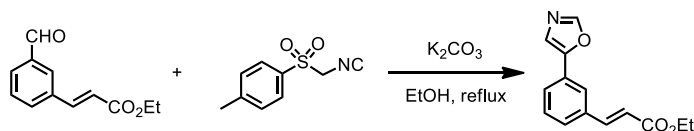
Benzaldehyde (0.3 mmol, 61 mg), K_2CO_3 (0.60 mmol, 83 mg) and acetone (2 ml) were stirred at room temperature for 12 h. The mixture was filtered and concentrated under reduced pressure. The resulted residue was purified by silica gel column chromatography (eluent: PE/EA = 4/1). Isolated yield: 72%.



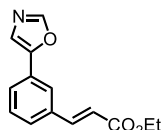
(E)-Ethyl 3-(3-(1-hydroxy-3-oxobutyl)phenyl)acrylate (5)

Colorless oil, $R_f = 0.42$ (petroleum ether / ethyl acetate = 4 : 1, V / V). 1H -NMR (400 MHz, $CDCl_3$) $\delta = 7.67$ (d, $J = 16.0$ Hz, 1H), 7.53 (d, $J = 1.7$ Hz, 1H), 7.43 (m, 1H), 7.39–7.33 (m, 2H), 6.45 (d, $J = 16.1$ Hz, 1H), 5.17 (dt, $J = 8.9, 3.2$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.56 (d, $J = 3.1$ Hz, 1H), 2.89 (ddd, $J = 17.6, 8.8, 3.6$ Hz, 1H), 2.82 (m, 1H), 2.20 (s, 3H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (100 MHz, $CDCl_3$) $\delta = 208.82, 166.87, 144.25, 143.53, 134.63, 129.00, 127.45, 127.25, 125.14, 118.49, 69.37, 60.47, 51.82, 30.71, 14.23$. HR-MS (ESI) m/z calcd for $C_{15}H_{19}O_4^+$ $[M+H]^+$ 263.1278, found 263.1276.

(3) Cyclization reaction⁶

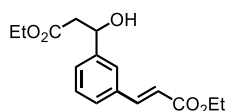


Benzaldehyde (0.3 mmol, 61.2 mg), tosylmethyl isocyanide (0.36 mmol, 70.3 mg) and K_2CO_3 (0.45 mmol, 62.1 mg) in EtOH (2 ml) were stirred at 80 °C for 12 h. The mixture was filtered and concentrated under reduced pressure. The resulted residue was purified by silica gel column chromatography (eluent: PE/EA = 4/1). Isolated yield: 83%.



(E)-Ethyl 3-(3-(oxazol-5-yl)phenyl)acrylate (6)

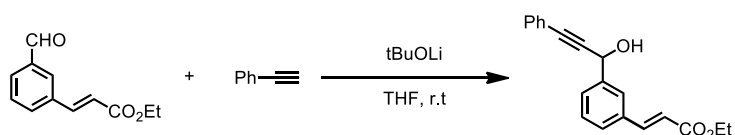
Colorless oil, $R_f = 0.48$ (petroleum ether / ethyl acetate = 4 : 1, V / V). 1H -NMR (400 MHz, $CDCl_3$) $\delta = 7.95$ (s, 1H), 7.81 (d, $J = 1.7$ Hz, 1H), 7.76–7.63 (m, 2H), 7.52–7.38 (m, 3H), 6.51 (d, $J = 16.0$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C -NMR (100 MHz, $CDCl_3$) $\delta =$



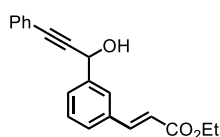
(E)-Ethyl 3-(3-(3-ethoxy-1-hydroxy-3-oxopropyl)phenyl)acrylate (8)

Colorless oil, $R_f = 0.42$ (petroleum ether / ethyl acetate = 4 : 1, V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.68$ (d, $J = 16.0$ Hz, 1H), 7.56 (d, $J = 1.8$ Hz, 1H), 7.48–7.35 (m, 3H), 6.45 (d, $J = 16.0$ Hz, 1H), 5.15 (m, 1H), 4.26 (q, $J = 7.1$ Hz, 2H), 4.19 (q, $J = 7.1$ Hz, 2H), 3.48 (d, $J = 3.5$ Hz, 1H), 2.77–2.69 (m, 2H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.27 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 172.27, 166.89, 144.26, 143.26, 134.72, 129.07, 127.51, 127.42, 125.24, 118.61, 69.90, 60.97, 60.51, 43.20, 14.28, 14.12$. HR-MS (ESI) m/z calcd for $\text{C}_{16}\text{H}_{21}\text{O}_5^+$ $[\text{M}+\text{H}^+]$ 293.1384, found 293.1389.

(6) Alkyne addition reaction⁹



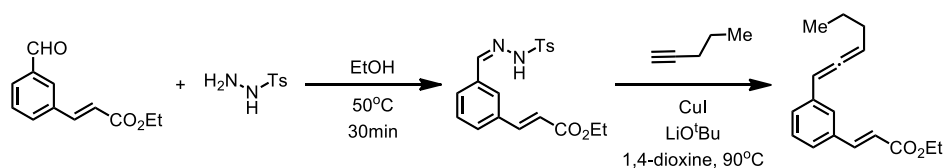
Benzaldehyde (0.2 mmol, 40.8 mg), phenylacetylene (0.3 mmol, 31 mg) and *t*BuOLi (0.4 mmol, 32 mg) in THF (2 ml) were stirred at room temperature for 1 h. The mixture was filtered and concentrated under reduced pressure. The resulted residue was purified by silica gel column chromatography (eluent: PE/EA = 4/1). Isolated yield: 70%.



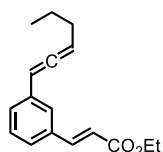
(E)-Ethyl 3-(3-(1-hydroxy-3-phenylprop-2-yn-1-yl)phenyl)acrylate (9)

Colorless oil, $R_f = 0.38$ (petroleum ether / ethyl acetate = 4 : 1, V / V). $^1\text{H-NMR}$ (400 MHz, CDCl_3) $\delta = 7.77$ (s, 1H), 7.71 (d, $J = 16.0$ Hz, 1H), 7.67–7.60 (m, 1H), 7.54–7.38 (m, 4H), 7.34 (m, 3H), 6.48 (d, $J = 16.1$ Hz, 1H), 5.72 (d, $J = 5.7$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 2.49 (d, $J = 6.0$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) $\delta = 166.92, 144.18, 141.38, 134.88, 131.76, 129.20, 128.75, 128.50, 128.34, 127.94, 126.30, 122.15, 118.80, 88.28, 86.96, 64.70, 60.57, 14.30$. HR-MS (ESI) m/z calcd for $\text{C}_{20}\text{H}_{19}\text{O}_3^+$ $[\text{M}+\text{H}^+]$ 307.1329, found 307.1325

(7) Allenation reaction¹⁰



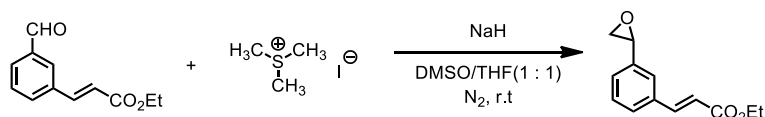
Under a nitrogen atmosphere, *p*-tosyl hydrazide (0.6 mmol, 112 mg) was added to a stirring solution of aromatic aldehyde (0.60 mmol, 121 mg) in MeOH (3 mL), and the resulting mixture was stirred at 50 °C for 30 minutes. The reaction mixture was concentrated and was used for the next step without further purification. The acetylene (1 equiv, 0.27 mmol) was added to a mixture of CuI (0.2 equiv, 0.06 mmol), Li^tOBu (3.5 equiv, 0.95 mmol), and the *N*-tosylhydrazone (2.2 equiv, 0.6 mmol) in 1,4-dioxane (10 mL), under a nitrogen atmosphere. The resulting solution was stirred at 90 °C, and the progress of the reaction was monitored by TLC. Upon completion of the reaction, the mixture was cooled to room temperature and was filtered through a short pad of silica gel eluting with EtOAc. The filtrate was concentrated under reduced pressure to yield a crude mixture, which was purified by silica gel flash column chromatography. Isolated yield: 52%.



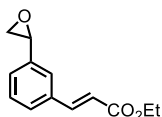
(*E*)-Ethyl 3-(3-(hexa-1,2-dien-1-yl)phenyl)acrylate (10)

Colorless oil, $R_f = 0.40$ (petroleum ether / ethyl acetate = 40 : 1, V / V). ¹H-NMR (400 MHz, CDCl₃) $\delta = 7.67$ (d, $J = 16.0$ Hz, 1H), 7.44 (s, 1H), 7.31 (m, 3H), 6.43 (d, $J = 16.0$ Hz, 1H), 6.12 (dd, $J = 6.3, 3.1$ Hz, 1H), 5.60 (dd, $J = 13.2, 6.8$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 2.13 (tt, $J = 7.1, 3.5$ Hz, 2H), 1.52 (m, 2H), 1.34 (t, $J = 7.1$ Hz, 3H), 0.98 (t, $J = 7.4$ Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) $\delta = 205.41, 167.01, 144.56, 135.93, 134.72, 129.03, 128.36, 126.21, 126.09, 118.33, 95.31, 94.00, 60.50, 30.72, 22.34, 14.32, 13.74$. HR-MS (ESI) m/z calcd for C₁₇H₂₁O₂⁺ [M+H⁺] 257.1536, found 257.1534.

(8) Epoxidation reaction¹¹



Trimethylsulfonium iodide (1.35 mmol, 276 mg), sodium hydride (60% dispersion in oil, 108 mg), DMSO (5 ml) and THF (3 ml) were stirred for 20 minutes at room temperature. The solution was then cooled to 0°C and aldehyde (0.9 mmol, 184 mg) in THF (2 ml) was added at 0°C and allowed to stir until consumption of aldehyde by TLC. The reaction system was diluted with water (20 ml) and extracted with EtOAc (30 ml × 3). The combined organic layers were washed with water (50 ml) and brine (30 ml × 2), dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: PE/EA = 8/1). Isolated yield: 72%.



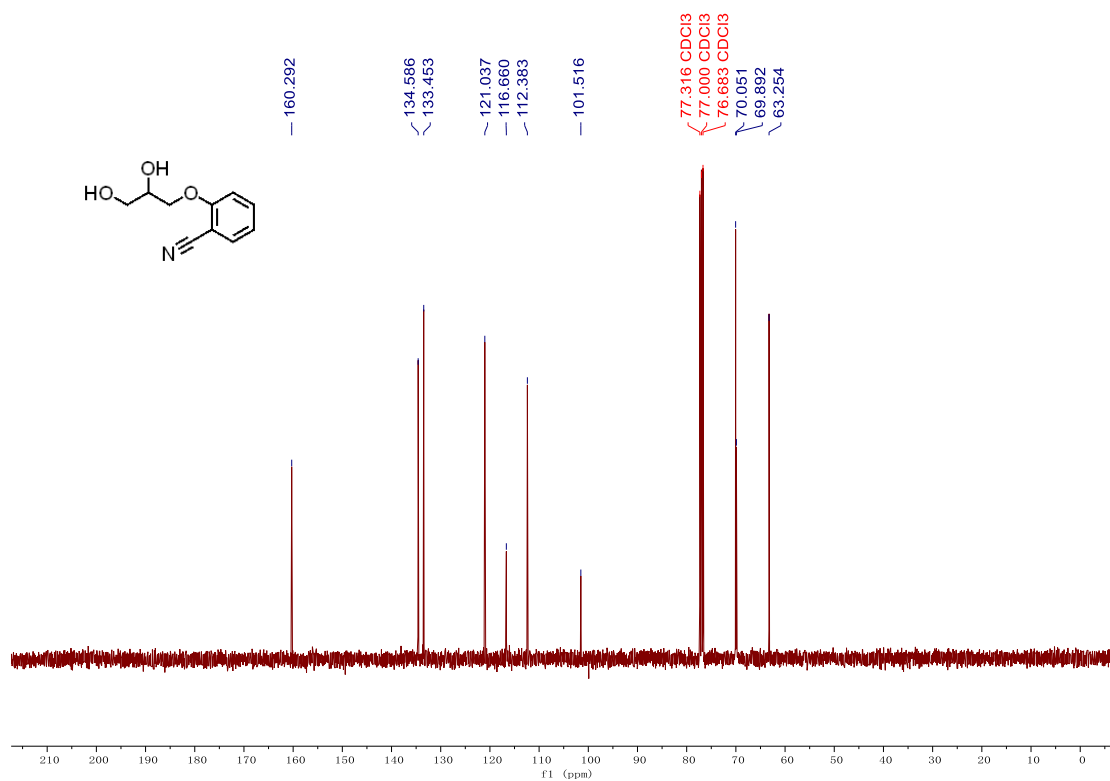
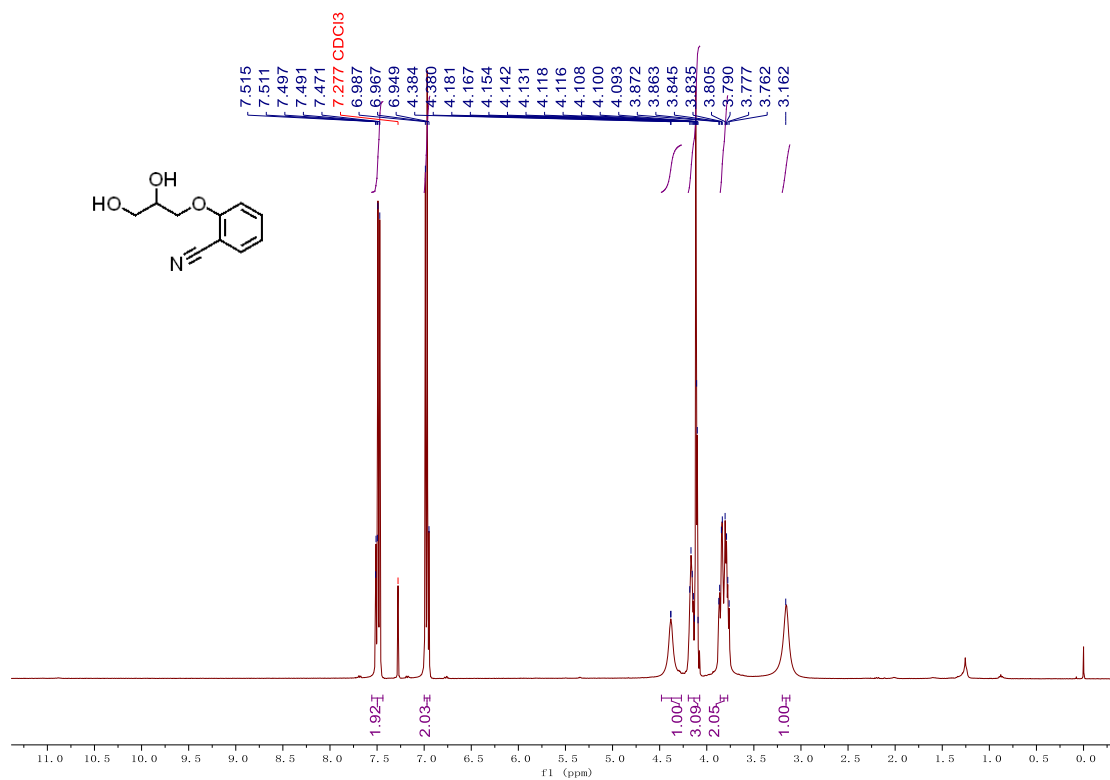
(E)-Ethyl 3-(3-(oxiran-2-yl)phenyl)acrylate (11)

Colorless oil, $R_f = 0.41$ (petroleum ether / ethyl acetate = 8 : 1, V / V). ¹H-NMR (400 MHz, CDCl₃) $\delta = 7.70$ (d, $J = 16.0$ Hz, 1H), 7.48 (m, 2H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.36–7.29 (m, 1H), 6.48 (d, $J = 16.0$ Hz, 1H), 4.29 (q, $J = 7.1$ Hz, 2H), 3.91 (dd, $J = 4.0, 2.5$ Hz, 1H), 3.20 (dd, $J = 5.5, 4.1$ Hz, 1H), 2.82 (dd, $J = 5.5, 2.5$ Hz, 1H), 1.37 (t, $J = 7.1$ Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) $\delta = 166.83, 144.01, 138.48, 134.78, 129.05, 127.84, 127.23, 124.87, 118.81, 60.54, 51.99, 51.21, 14.29$. HR-MS (ESI) m/z calcd for C₁₃H₁₅O₃⁺ [M+H⁺] 219.1016, found 219.1013.

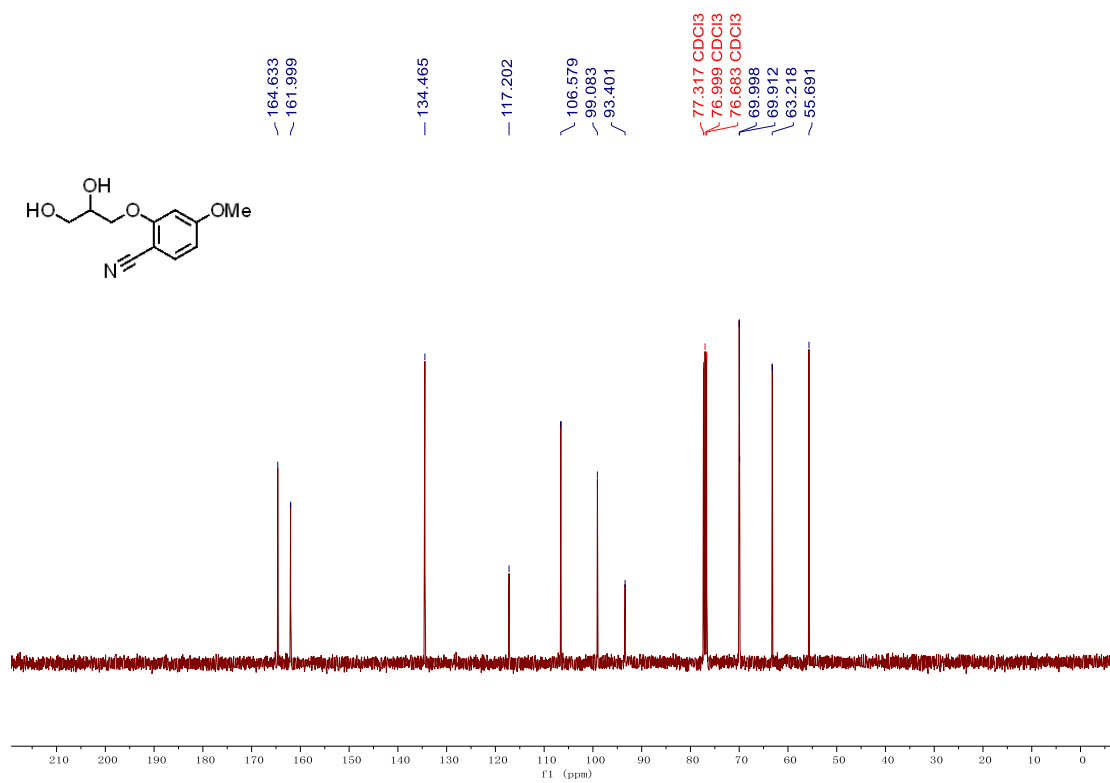
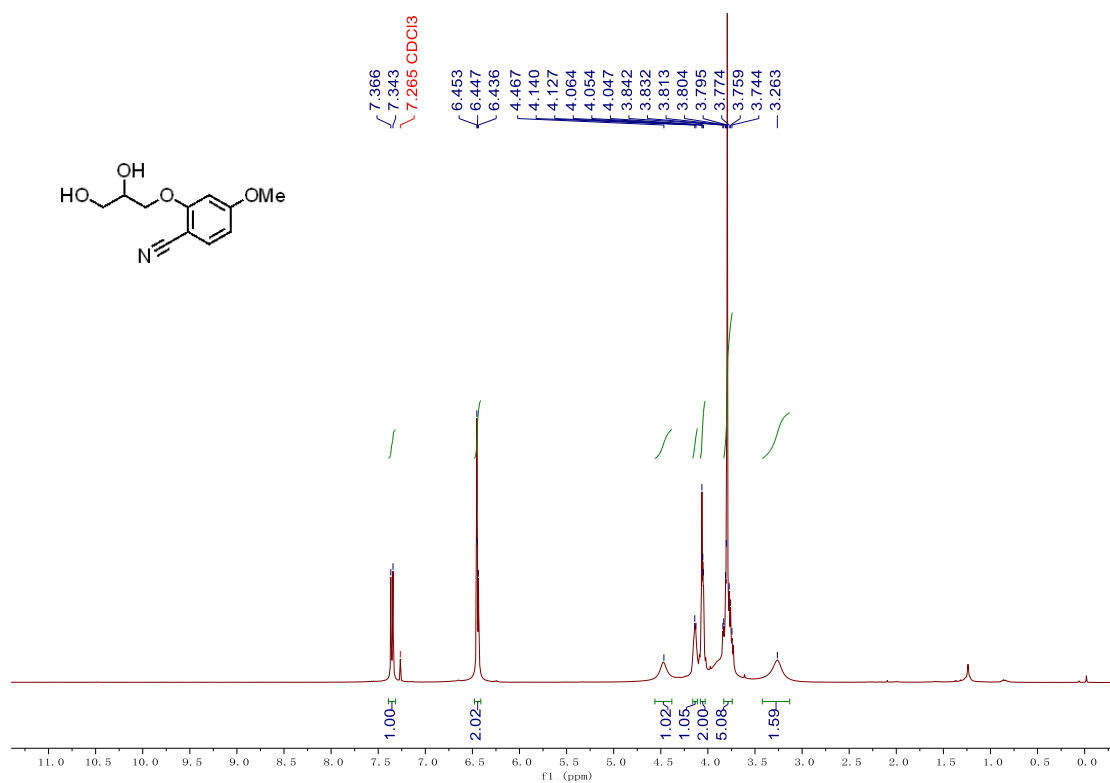
8 Reference

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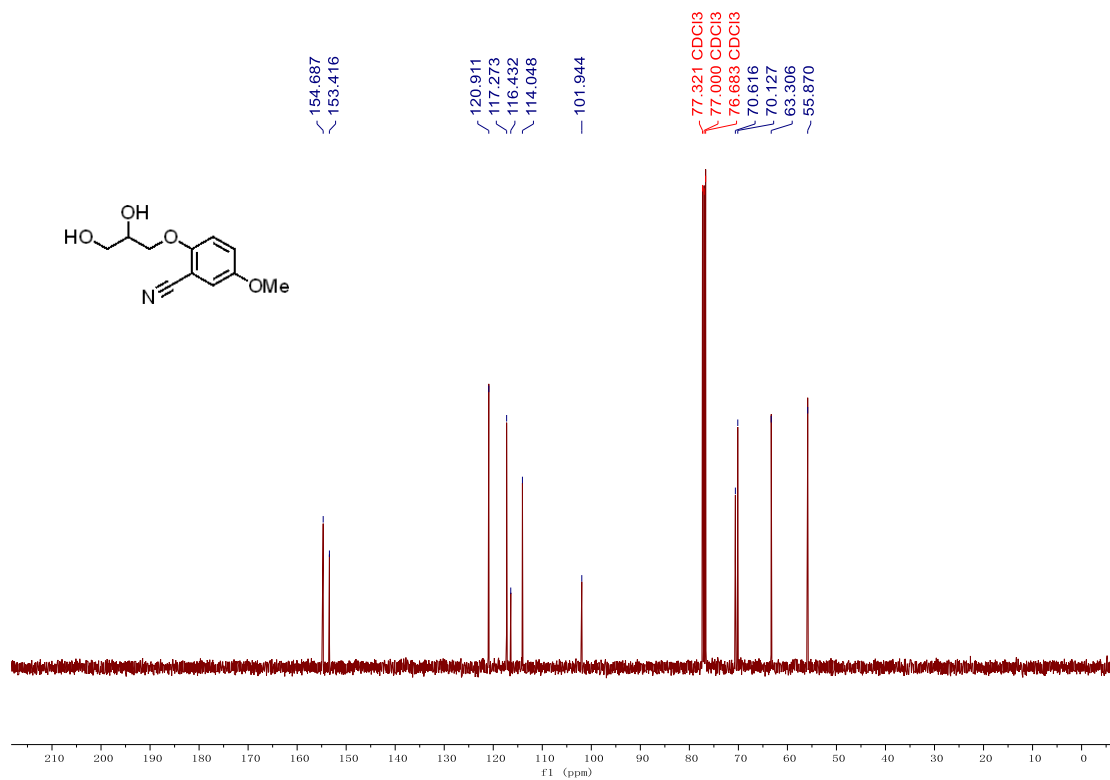
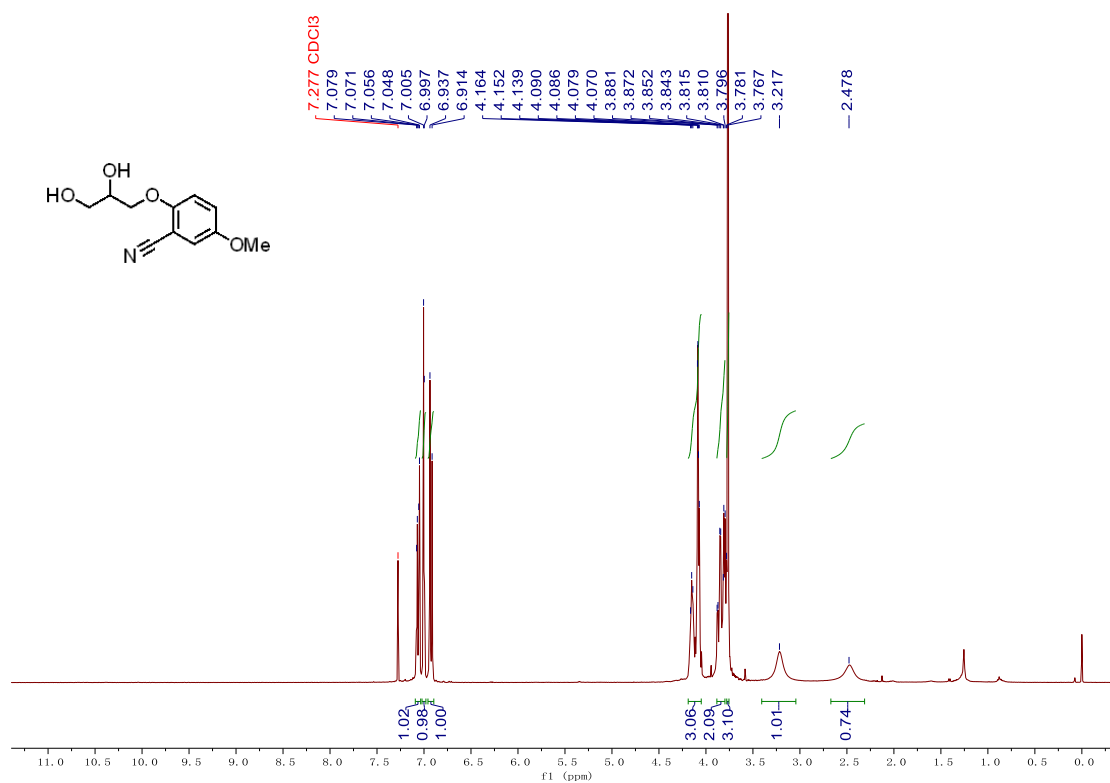
NMR Spectra of New Compounds



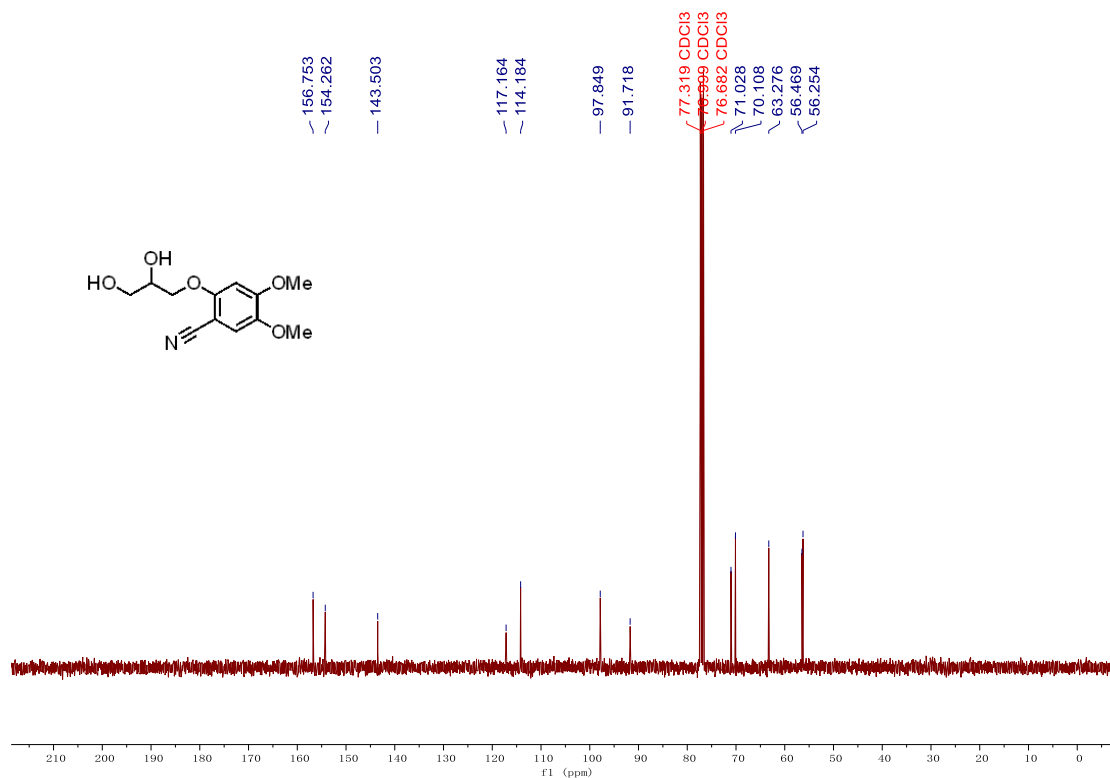
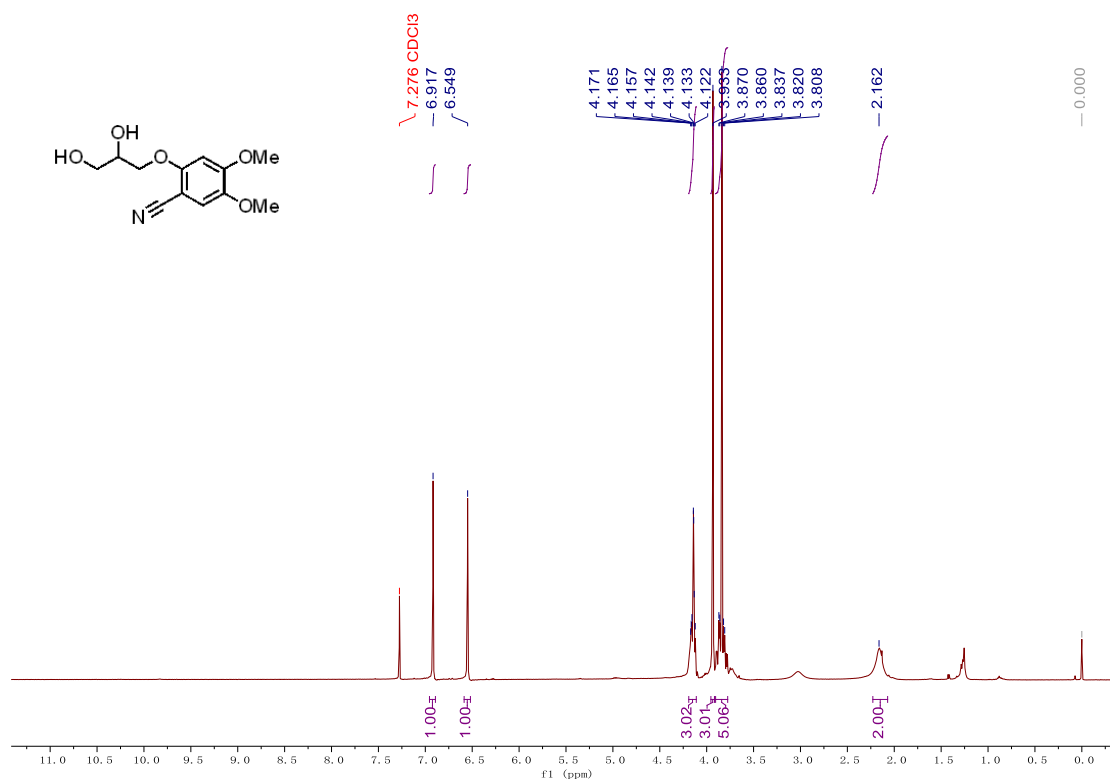
¹H and ¹³C NMR spectra of template T₁



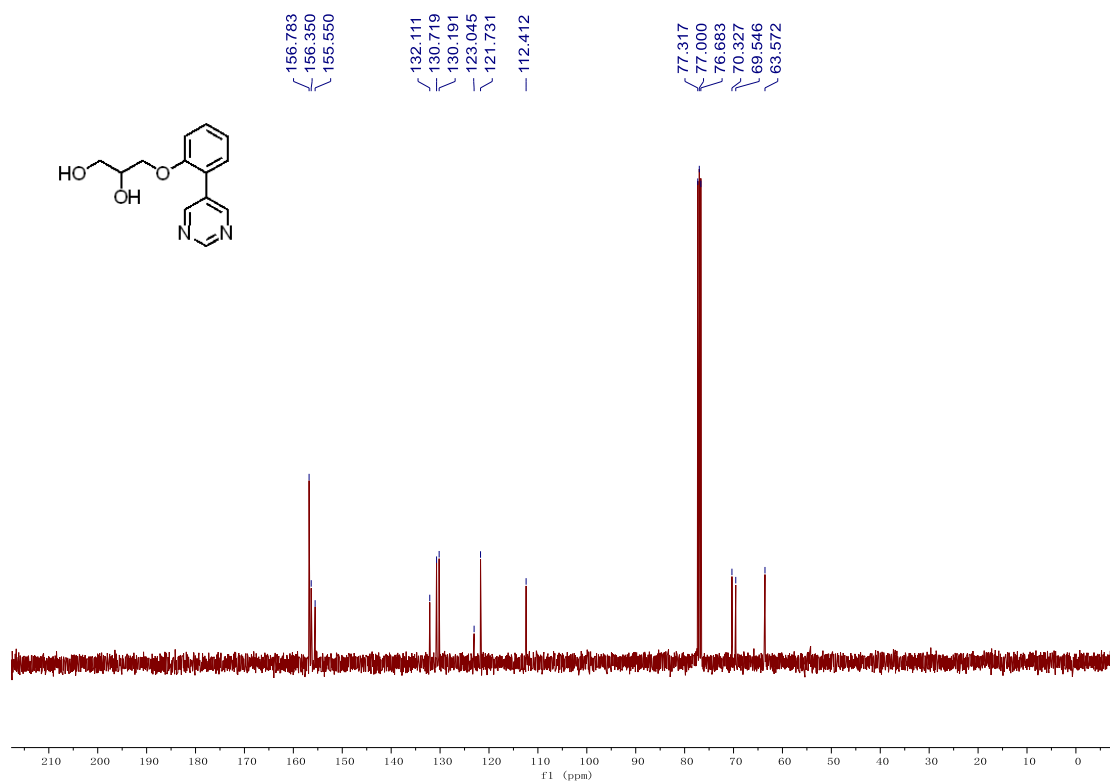
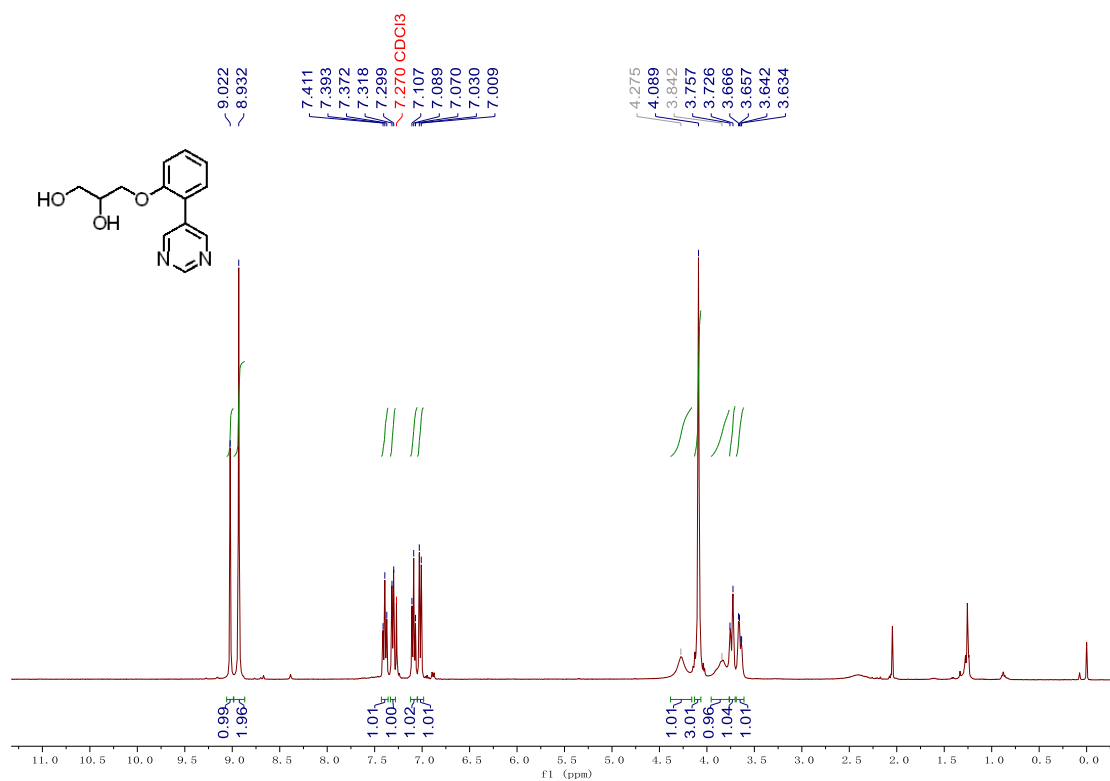
¹H and ¹³C NMR spectra of template **T₂**



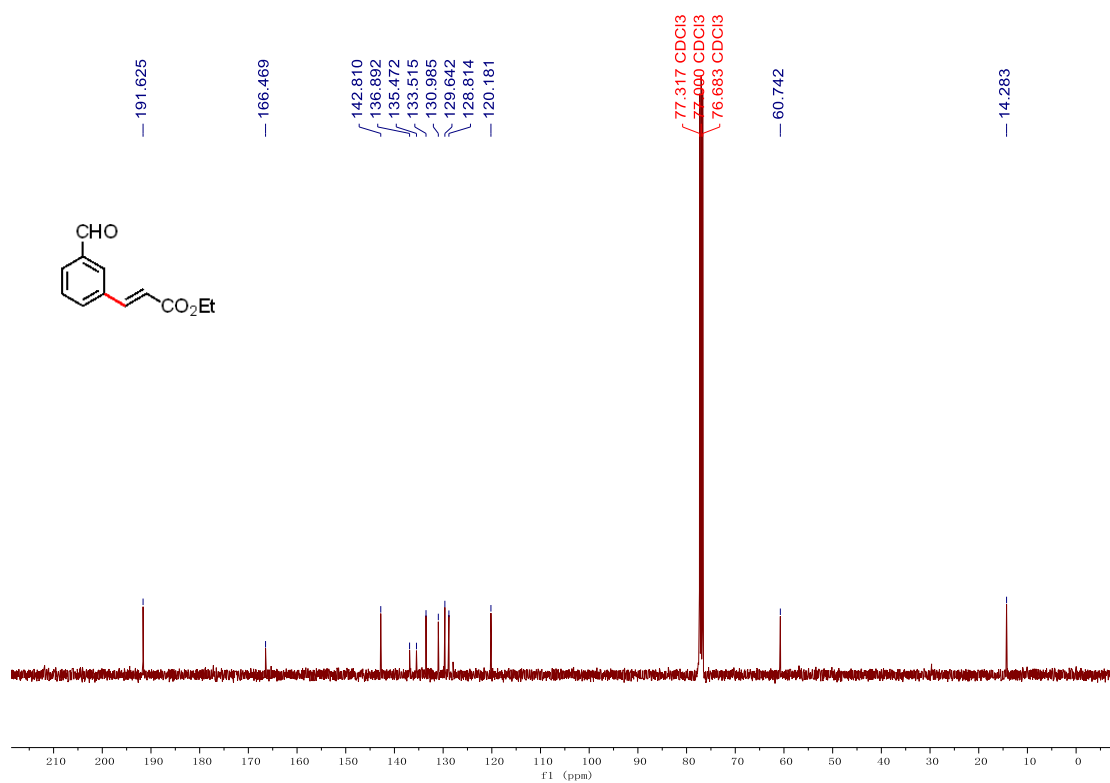
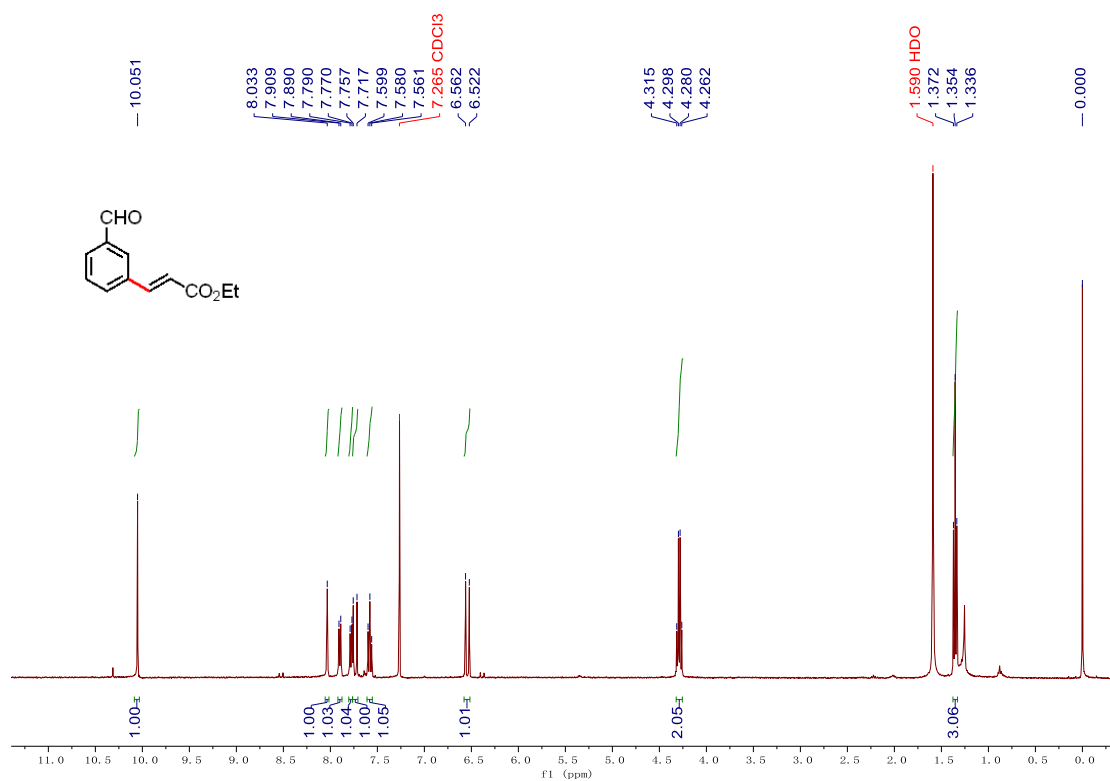
¹H and ¹³C NMR spectra of template T₃



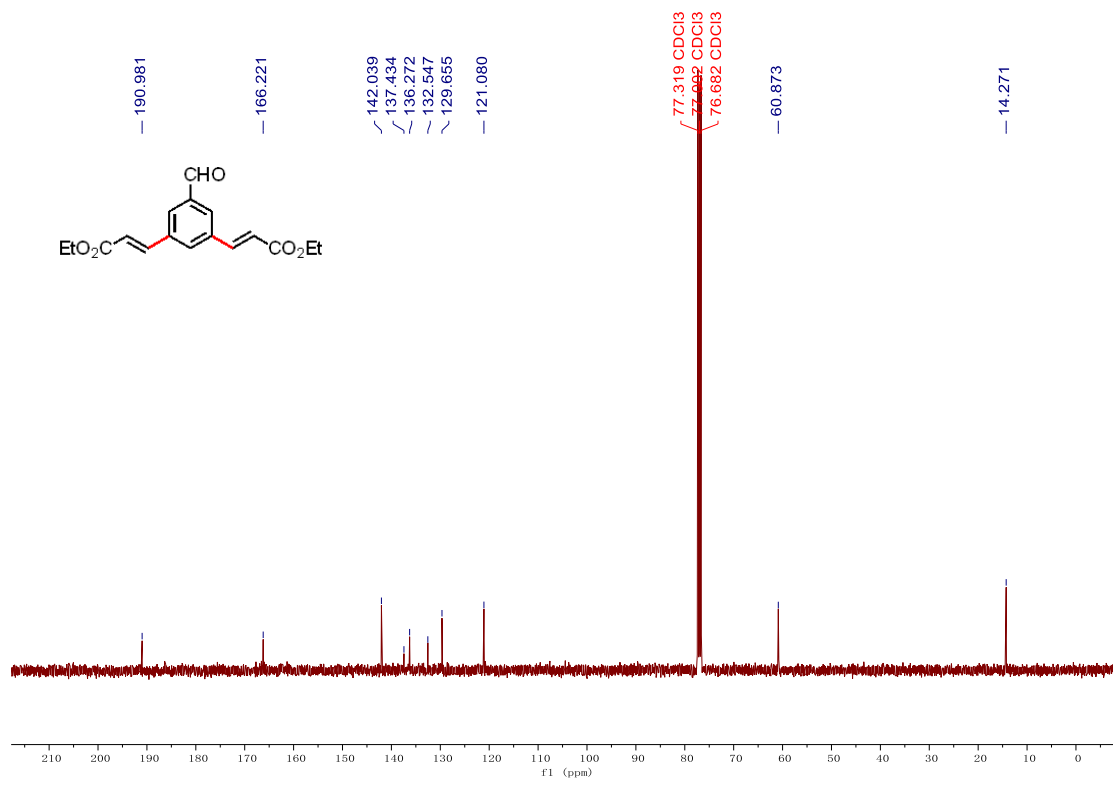
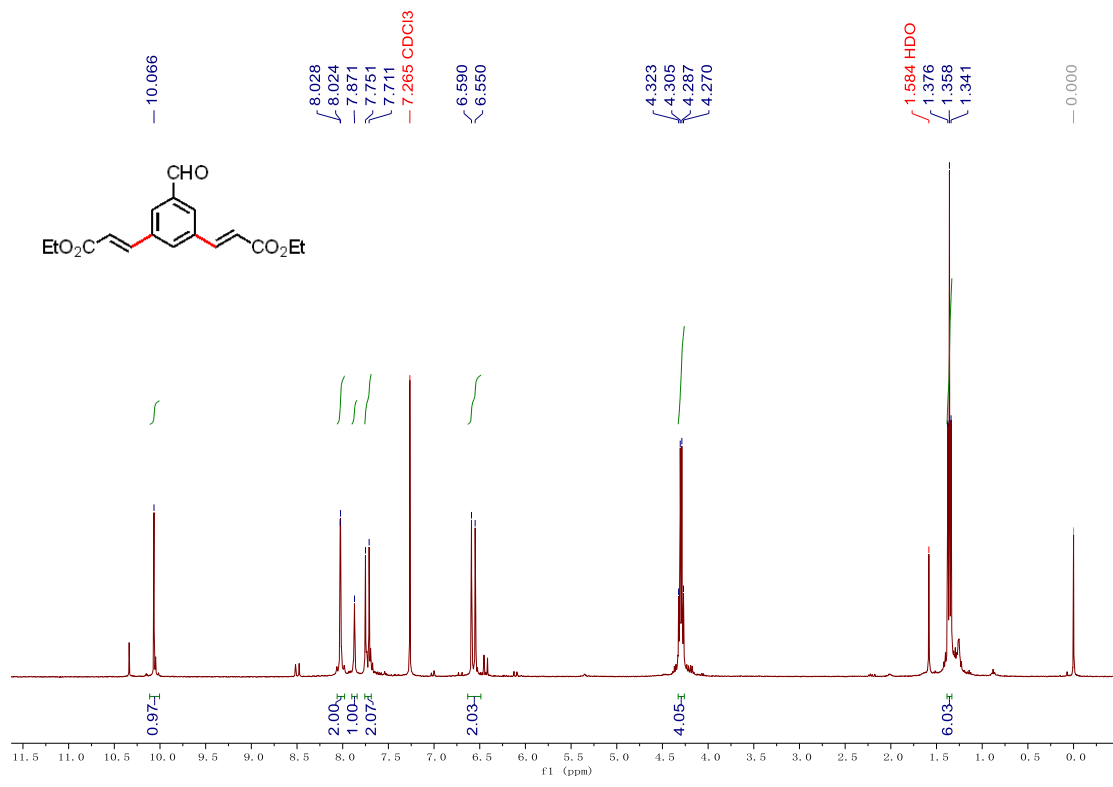
¹H and ¹³C NMR spectra of template **T₄**



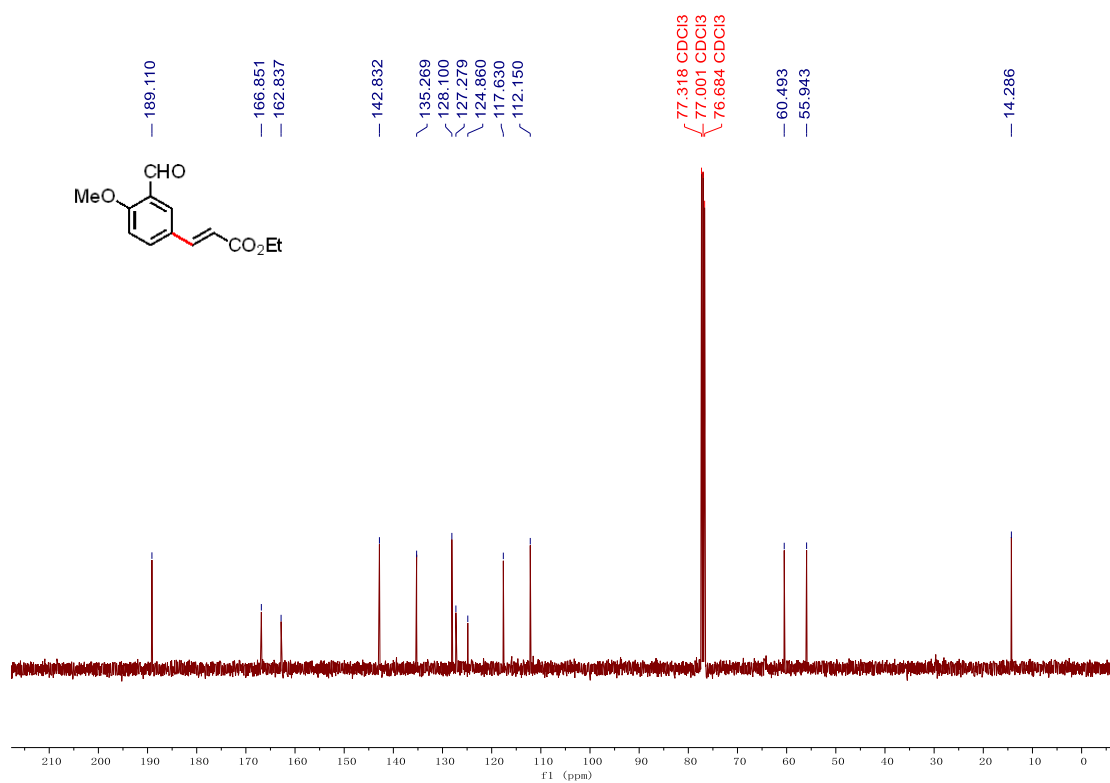
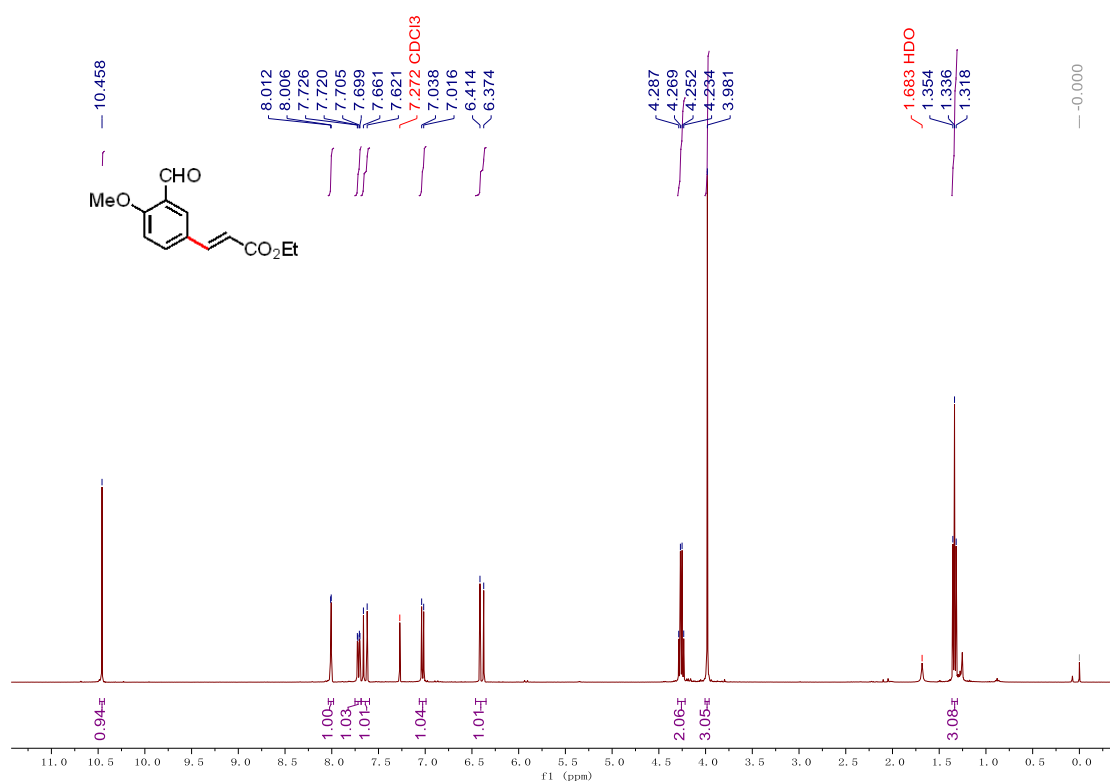
¹H and ¹³C NMR spectra of template T₅



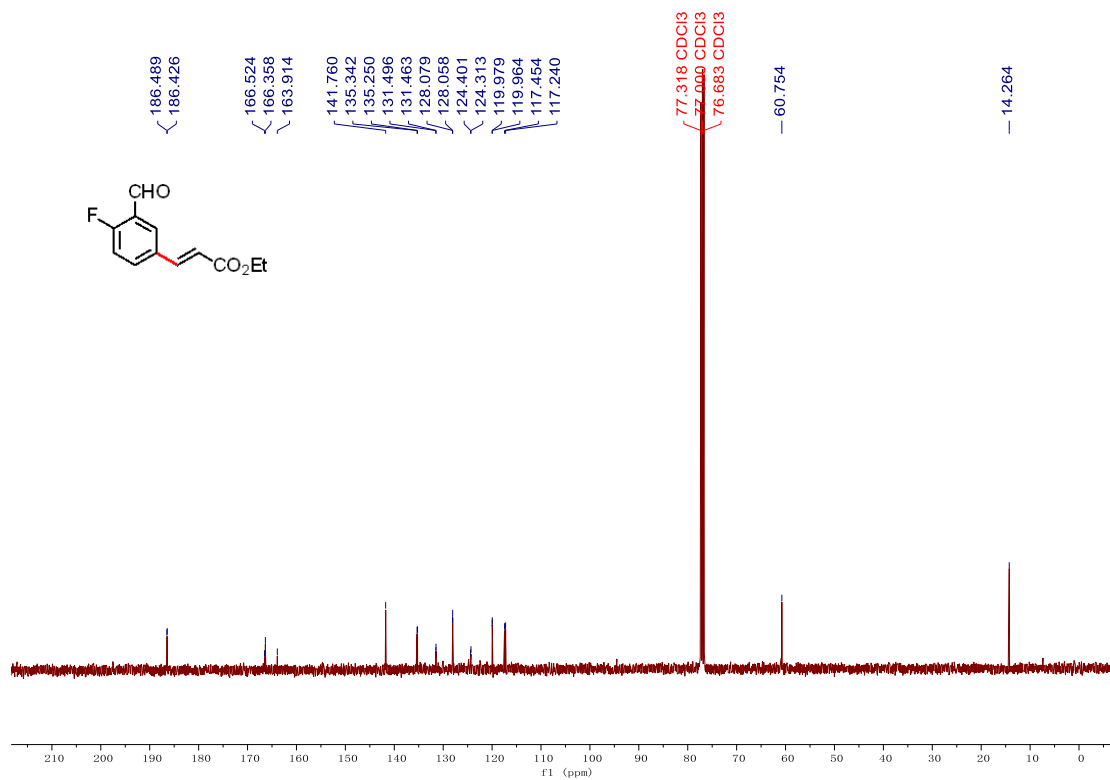
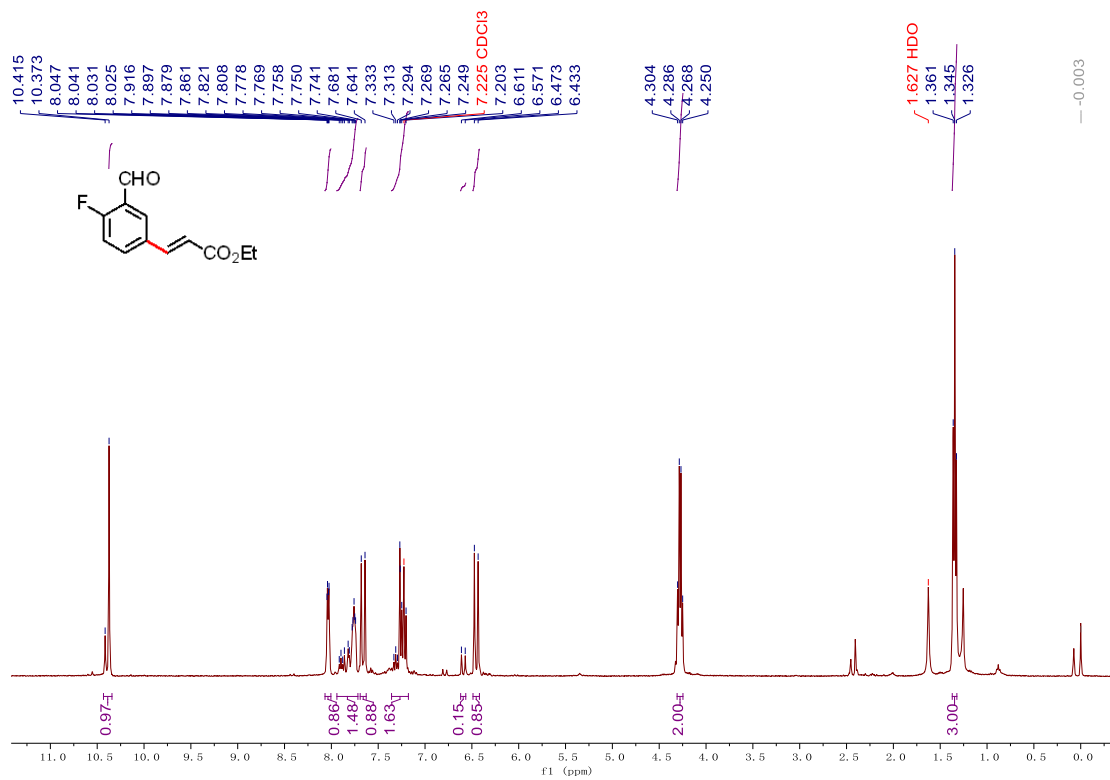
¹H and ¹³C NMR spectra of compound **1a_{mono}**



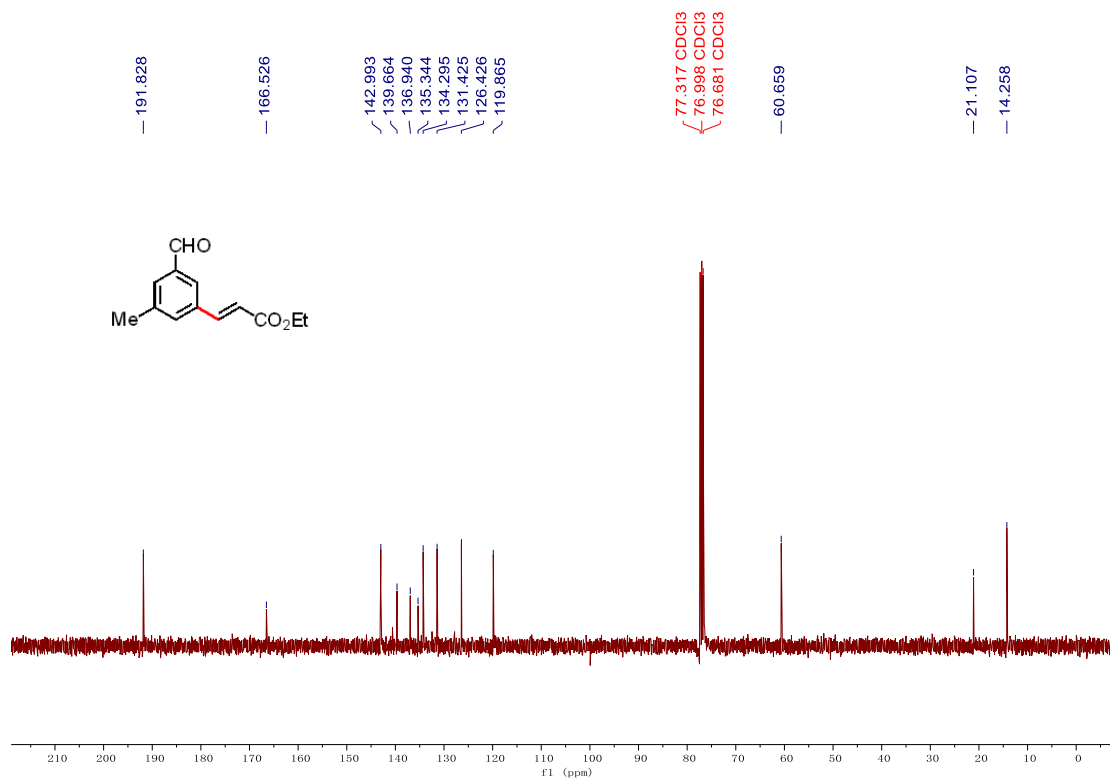
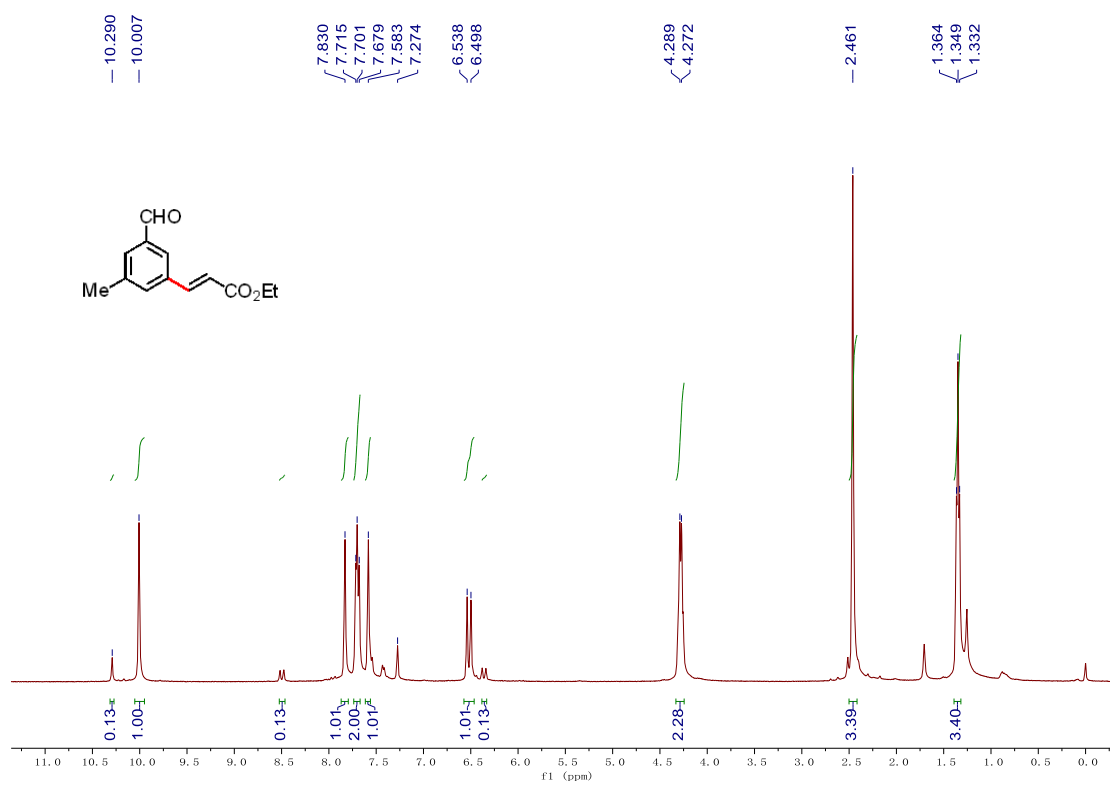
¹H and ¹³C NMR spectra of compound **1a_{ii}**



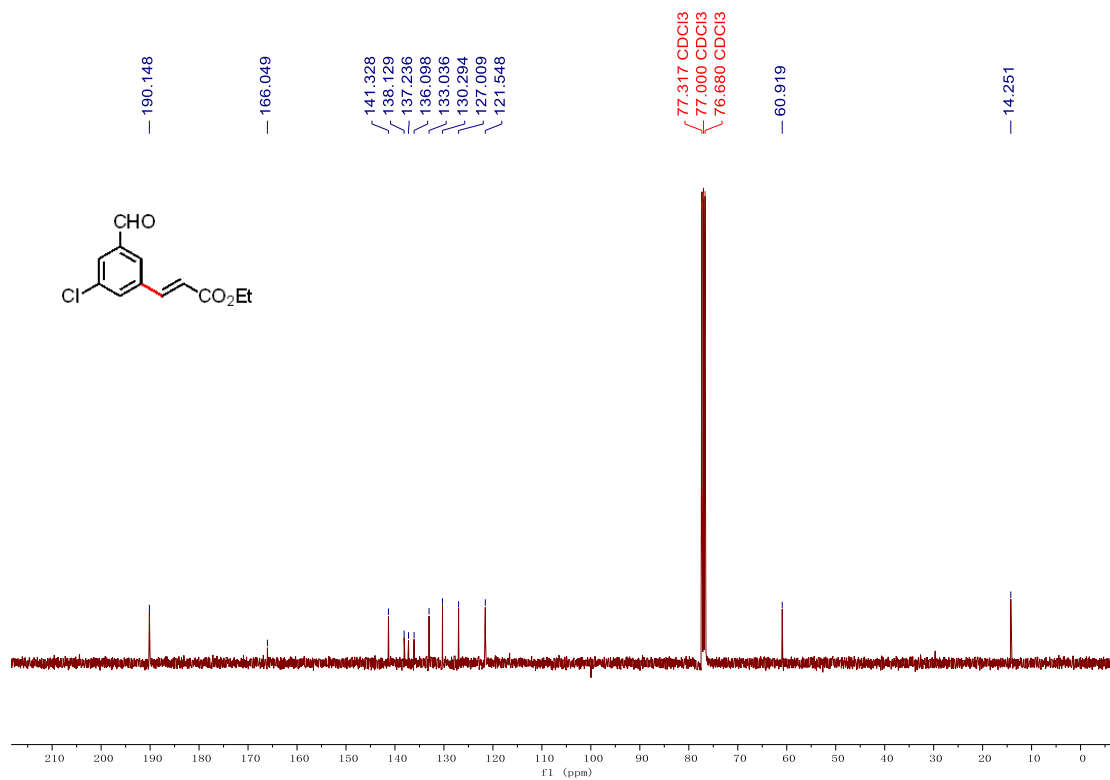
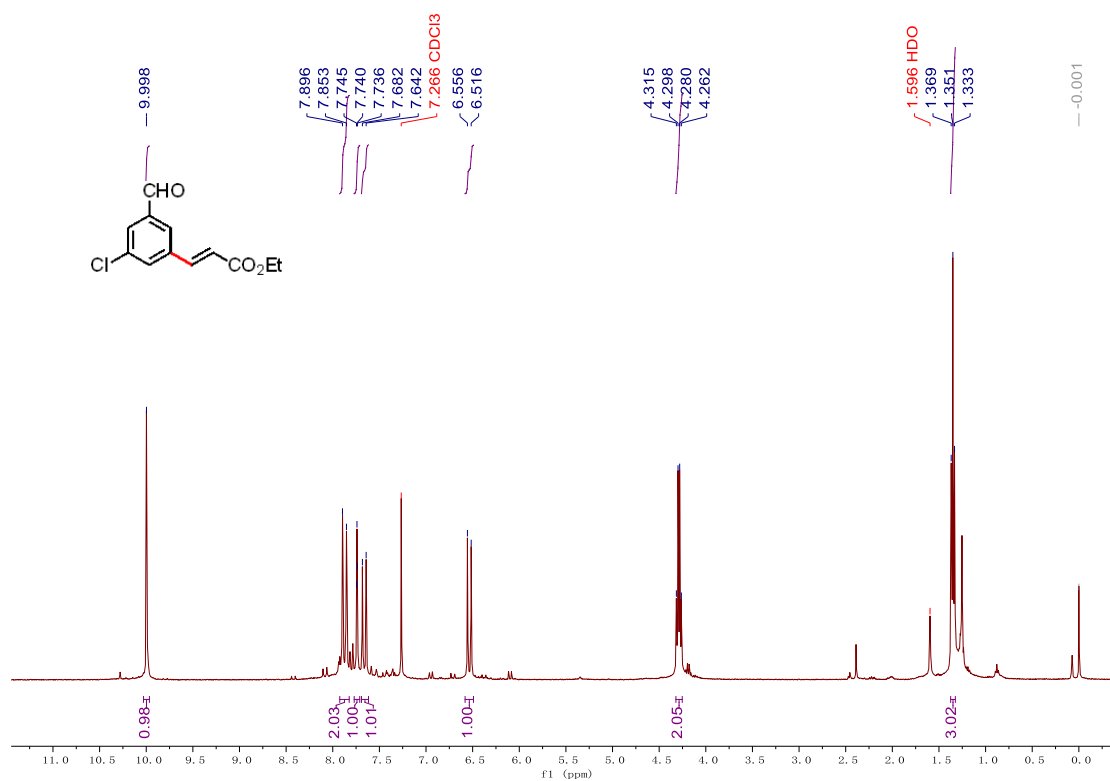
¹H and ¹³C NMR spectra of compound **1b**



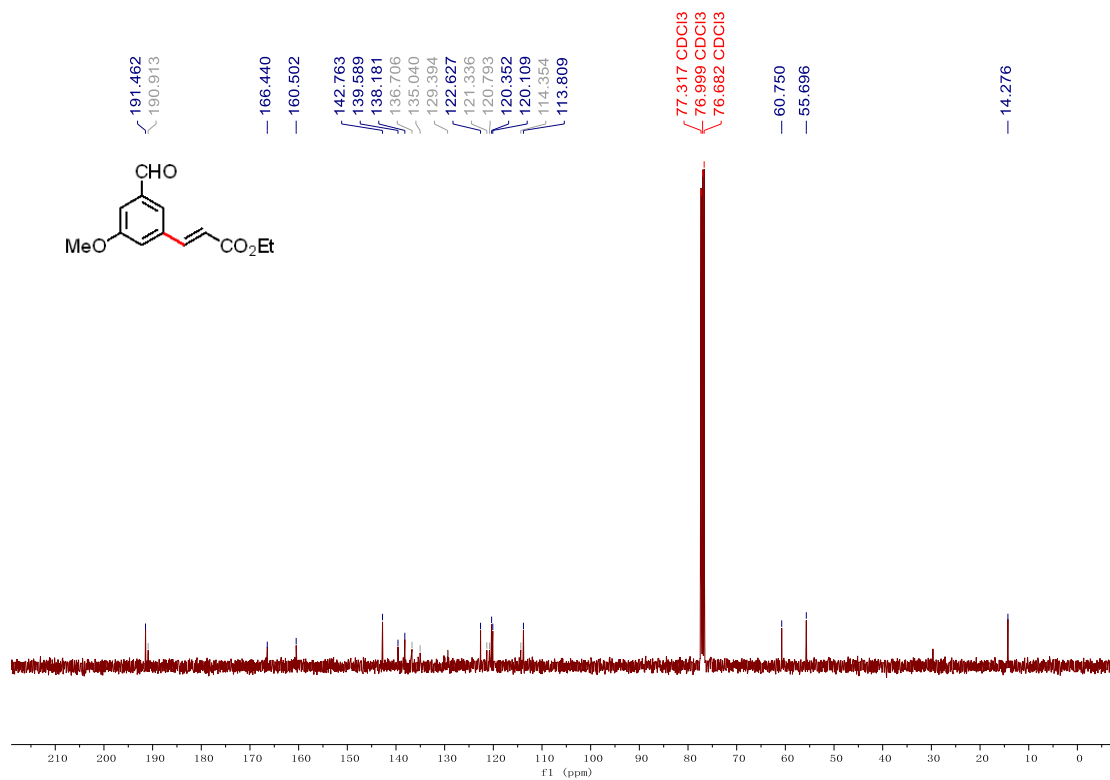
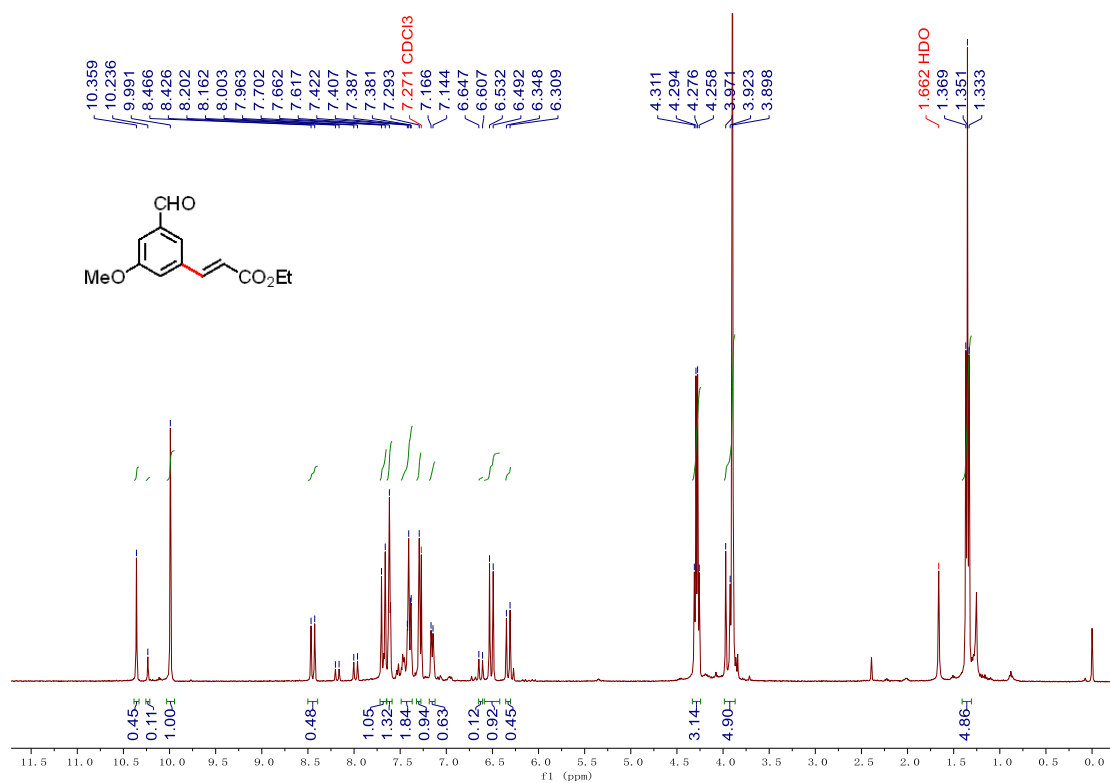
¹H and ¹³C NMR spectra of compound 1c



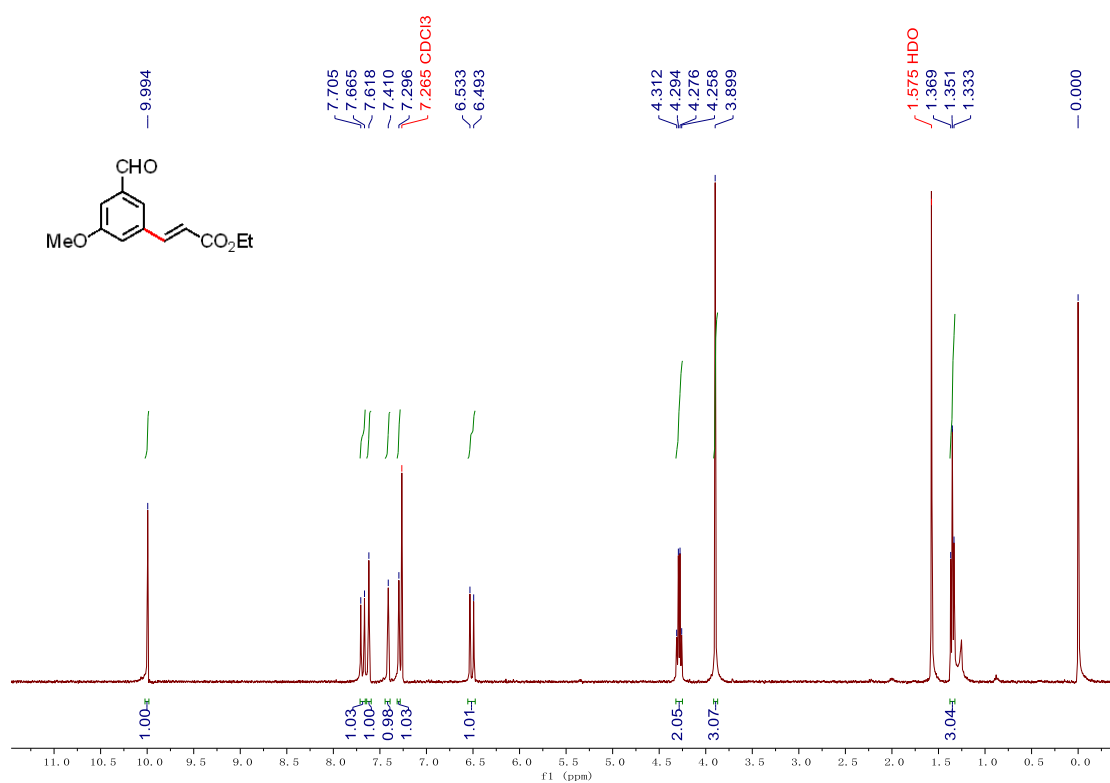
¹H and ¹³C NMR spectra of compound **1d**



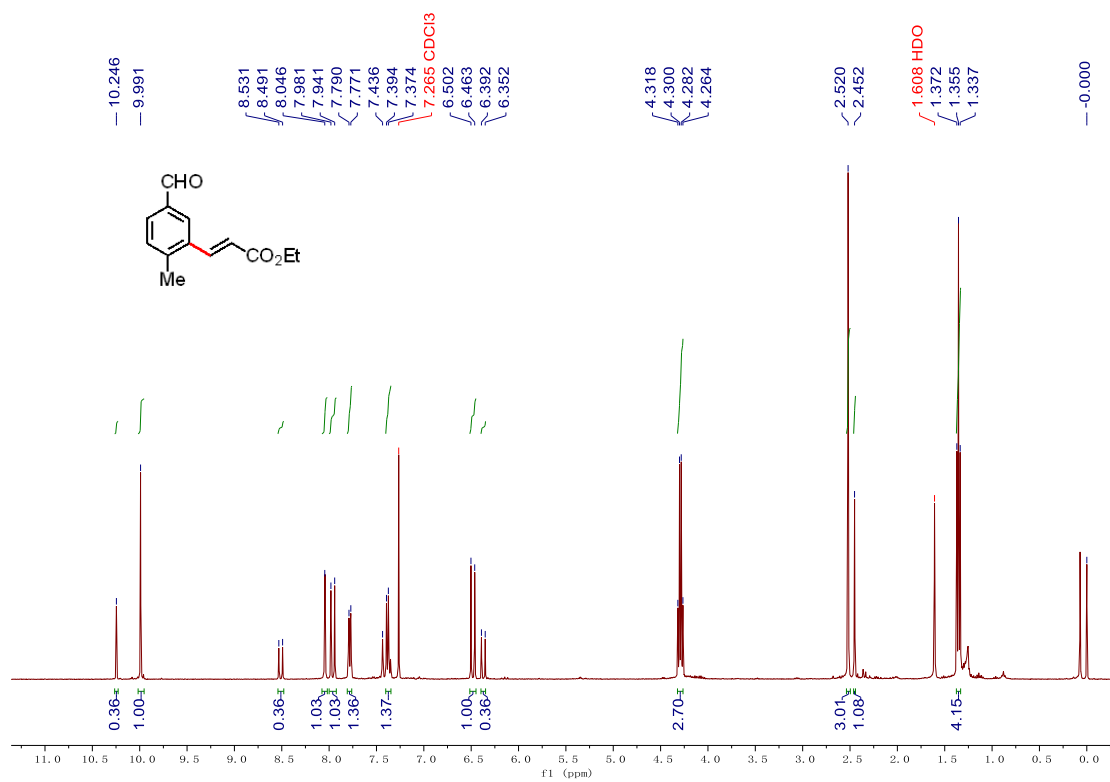
¹H and ¹³C NMR spectra of compound **1e**

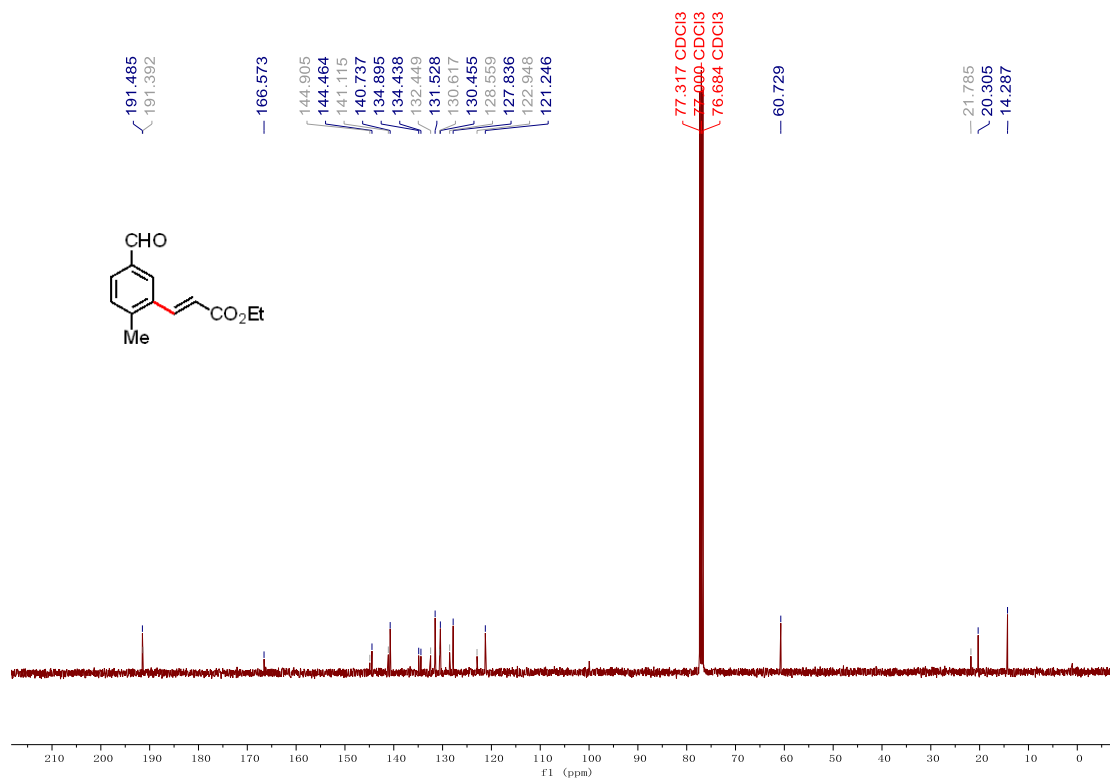


¹H and ¹³C NMR spectra of compound 1f

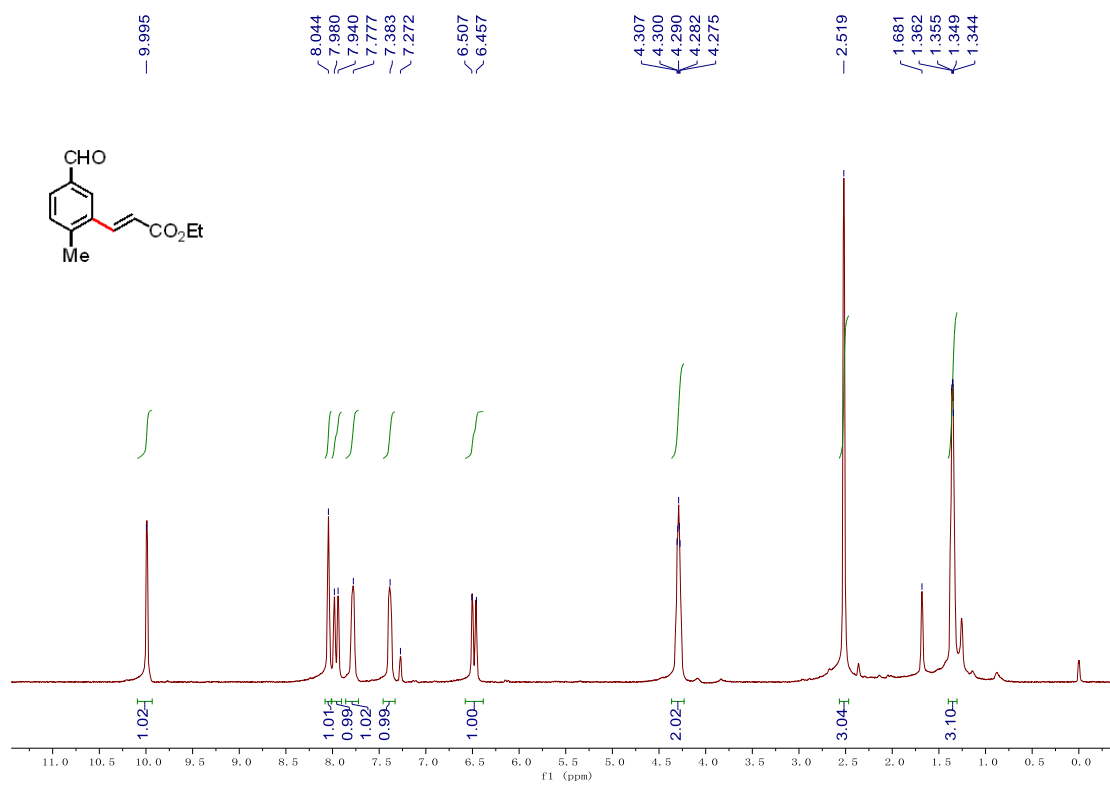


¹H NMR spectra of pure sample for compound **1f**

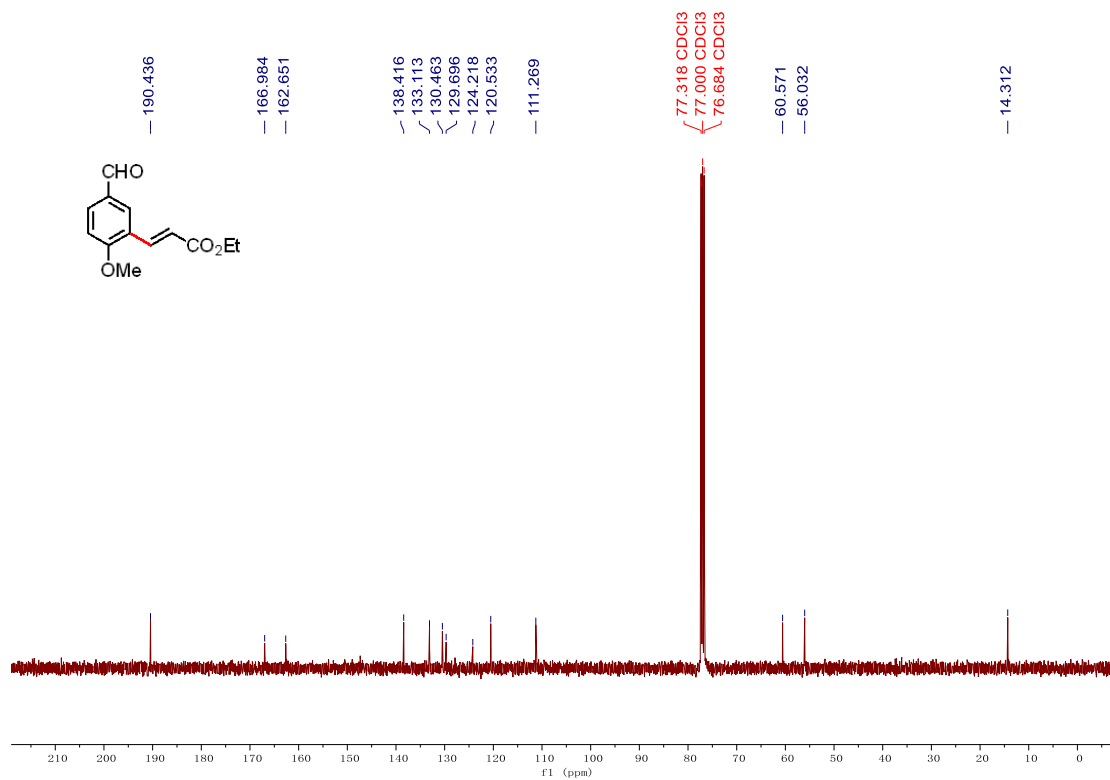
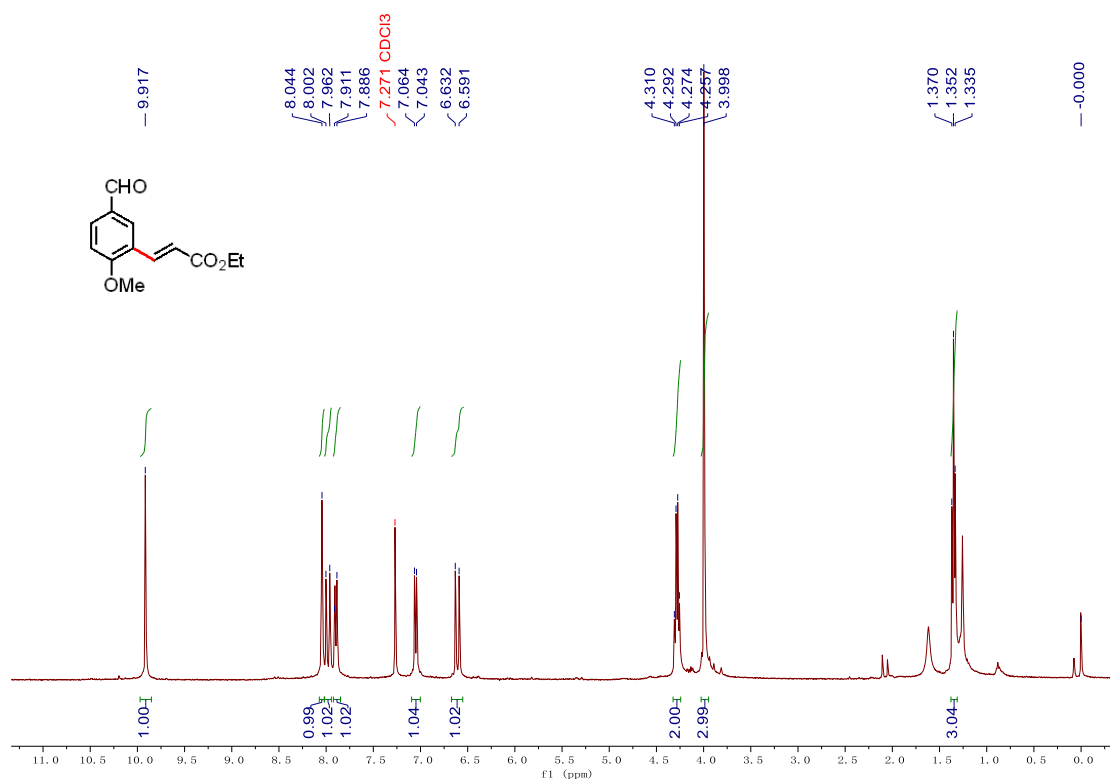




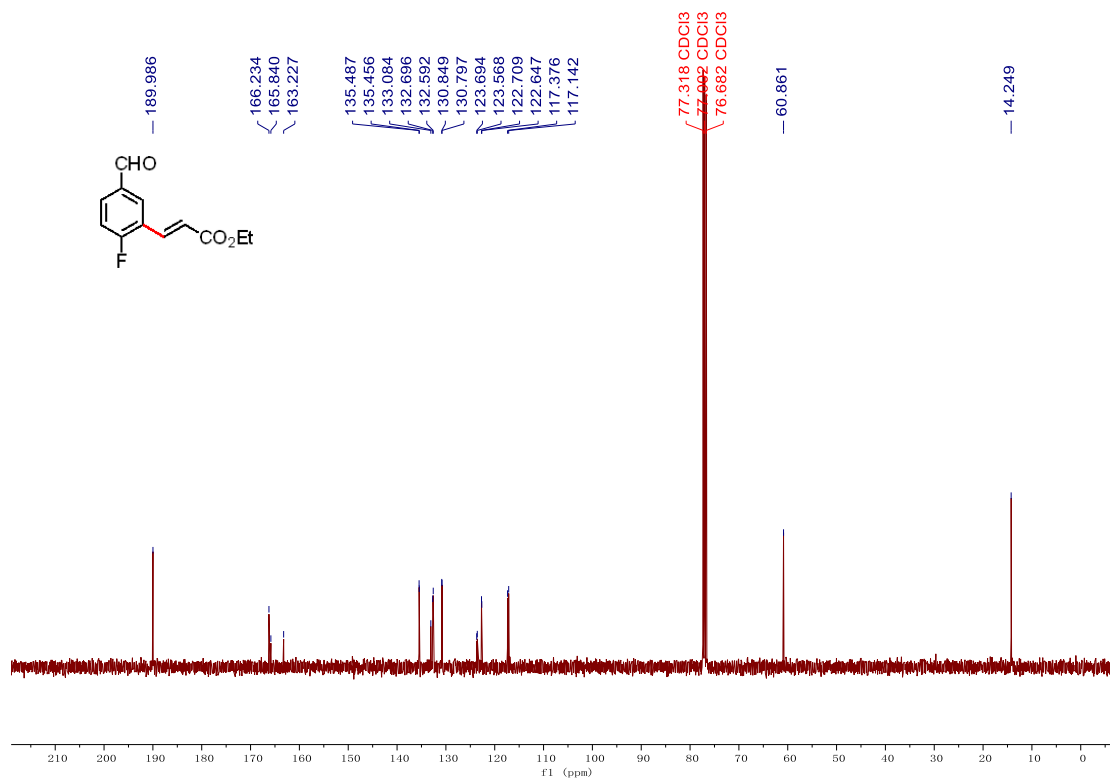
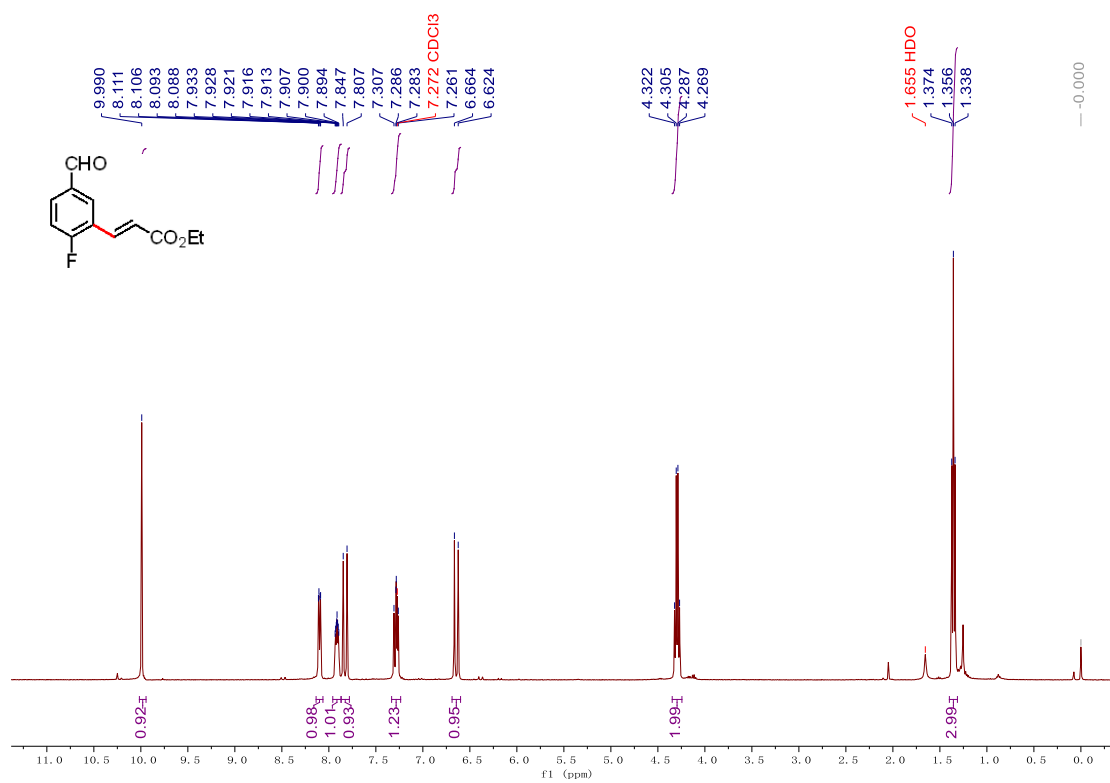
¹H and ¹³C NMR spectra of compound **1g**



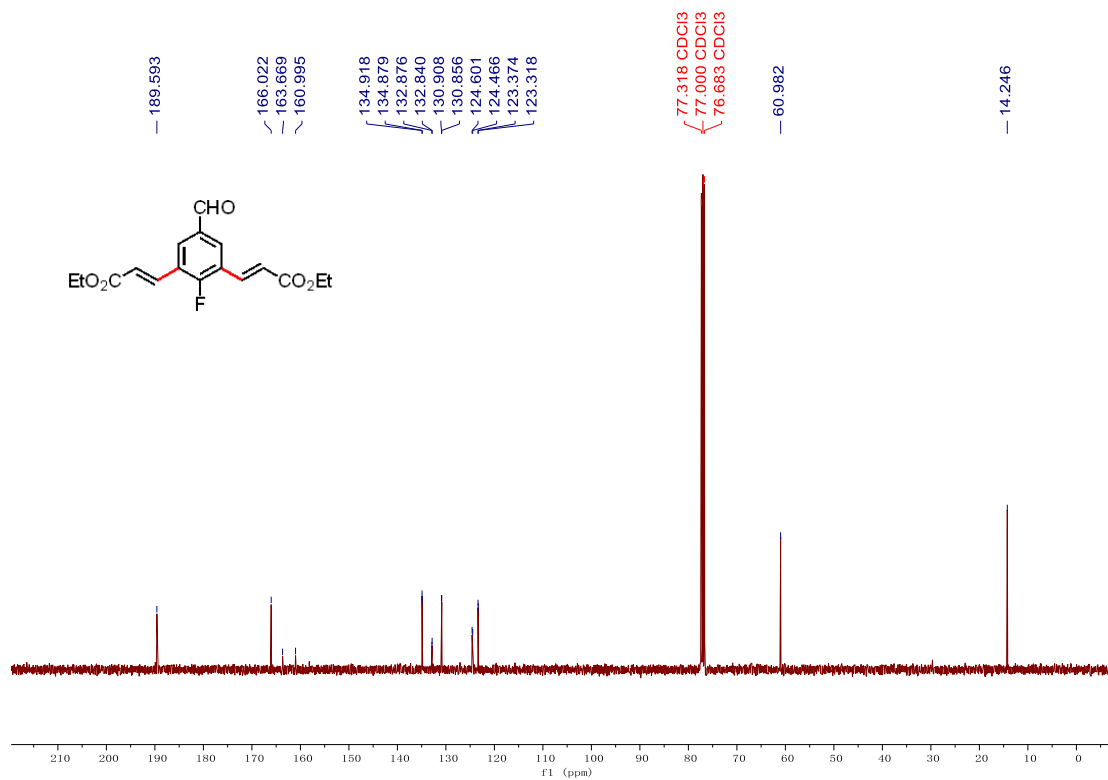
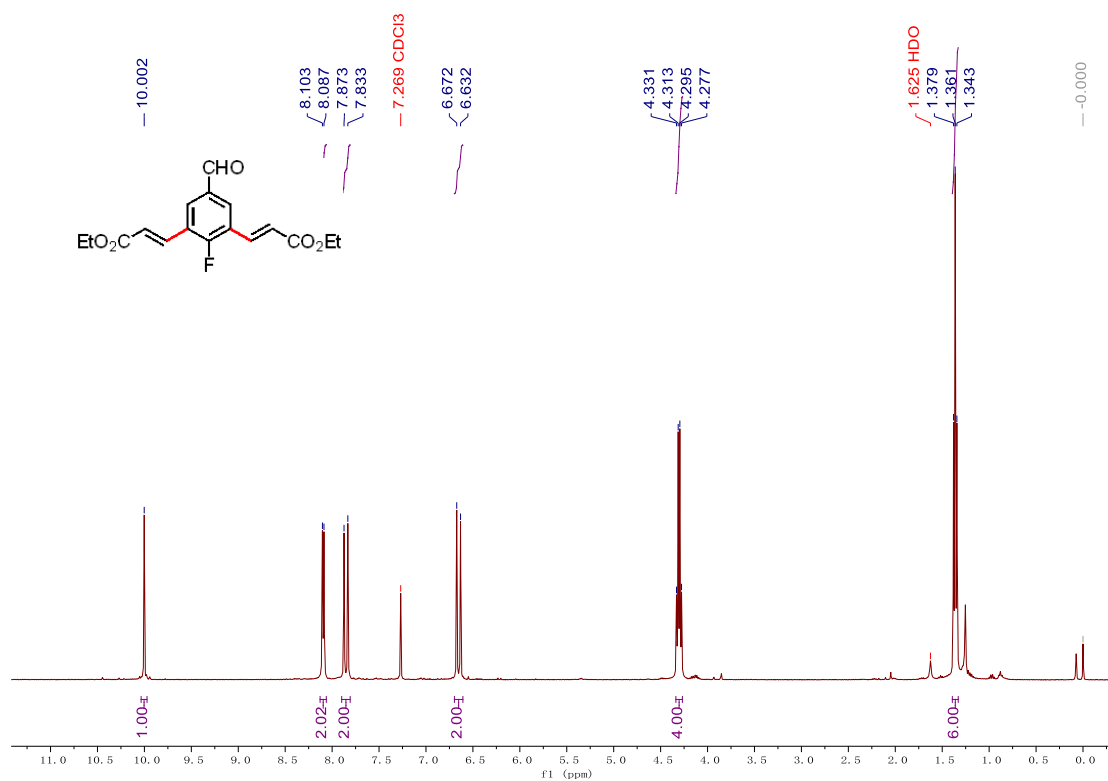
¹H NMR spectra of pure sample for compound **1g**



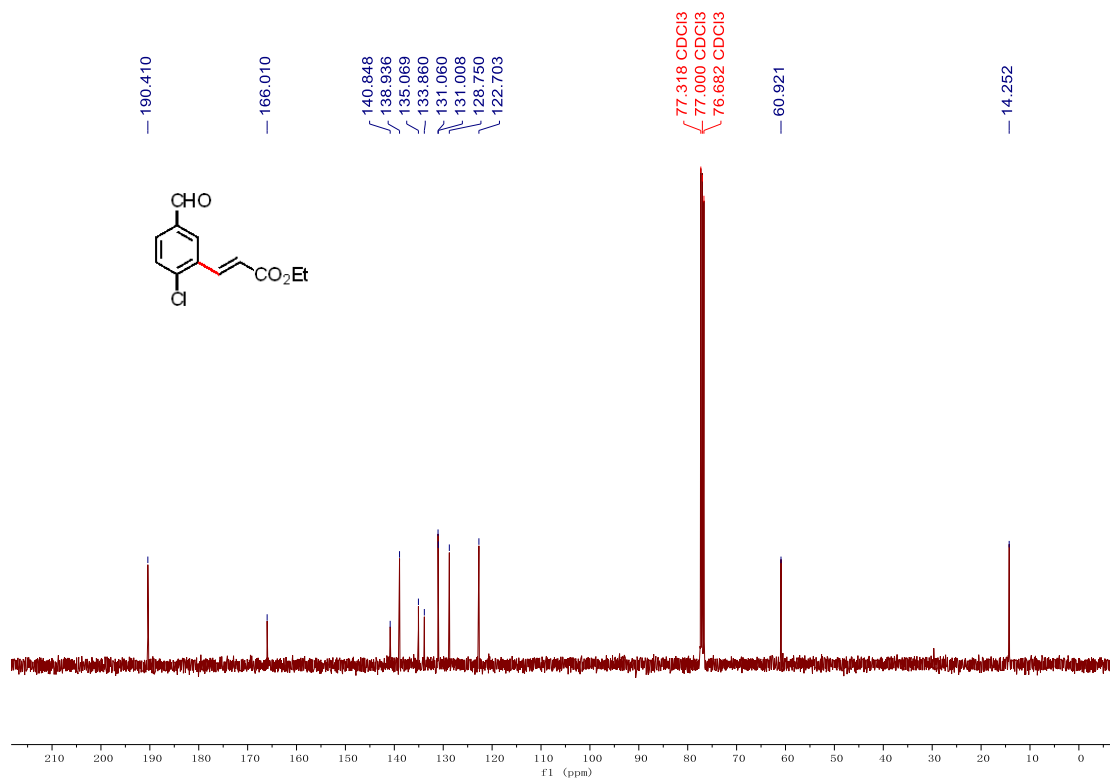
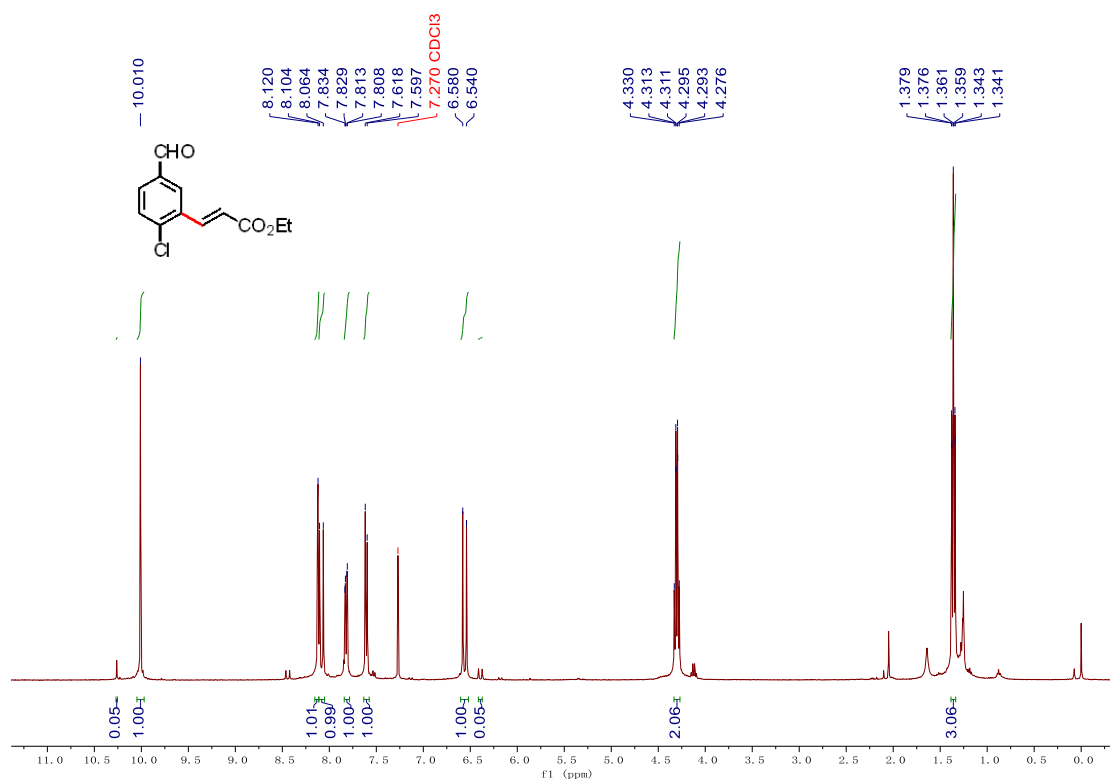
¹H and ¹³C NMR spectra of compound 1h



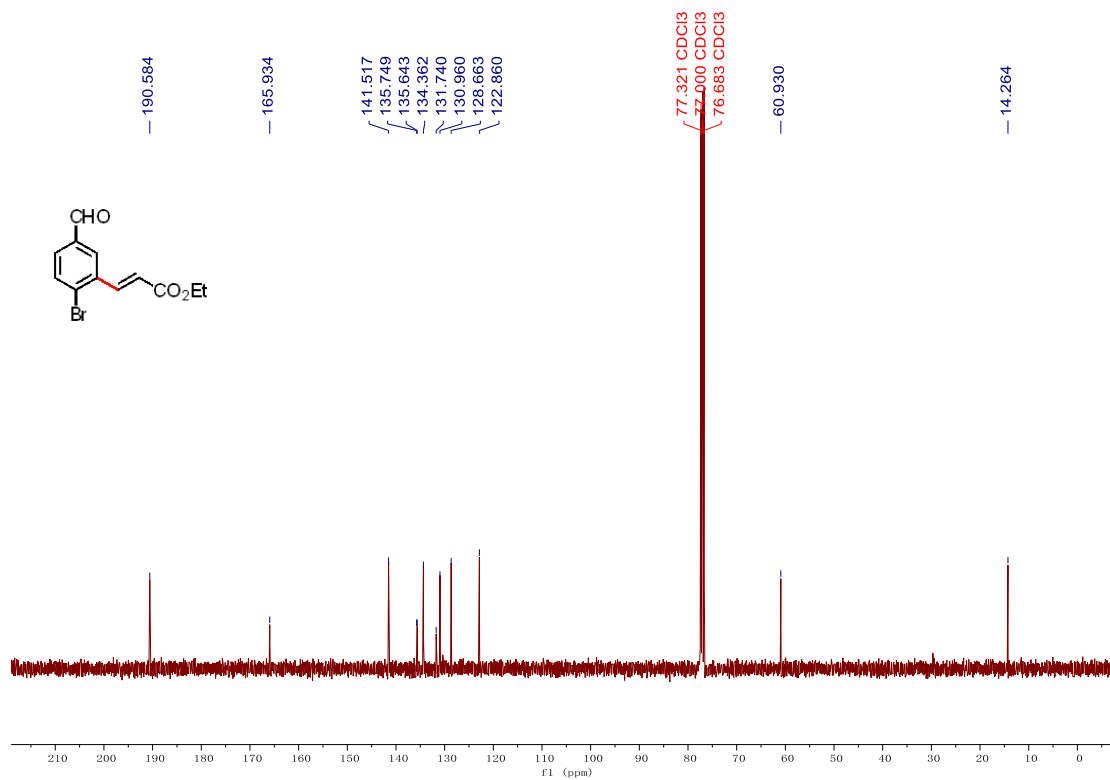
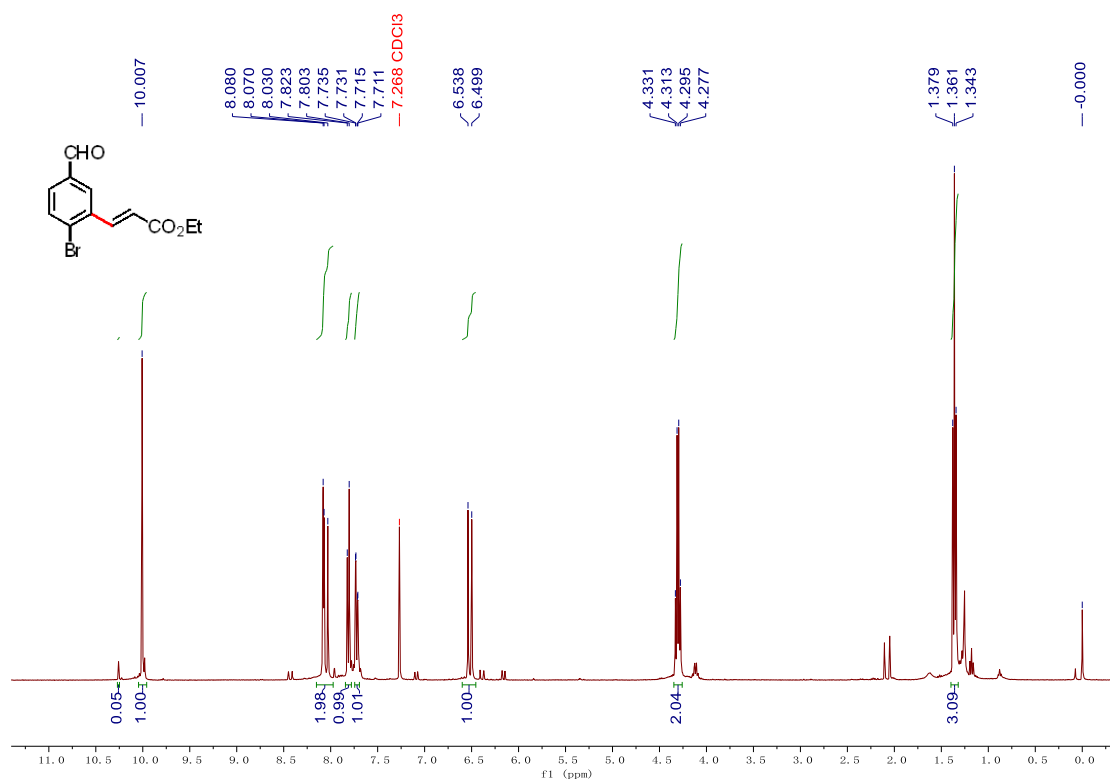
¹H and ¹³C NMR spectra of compound **1i_{mono}**



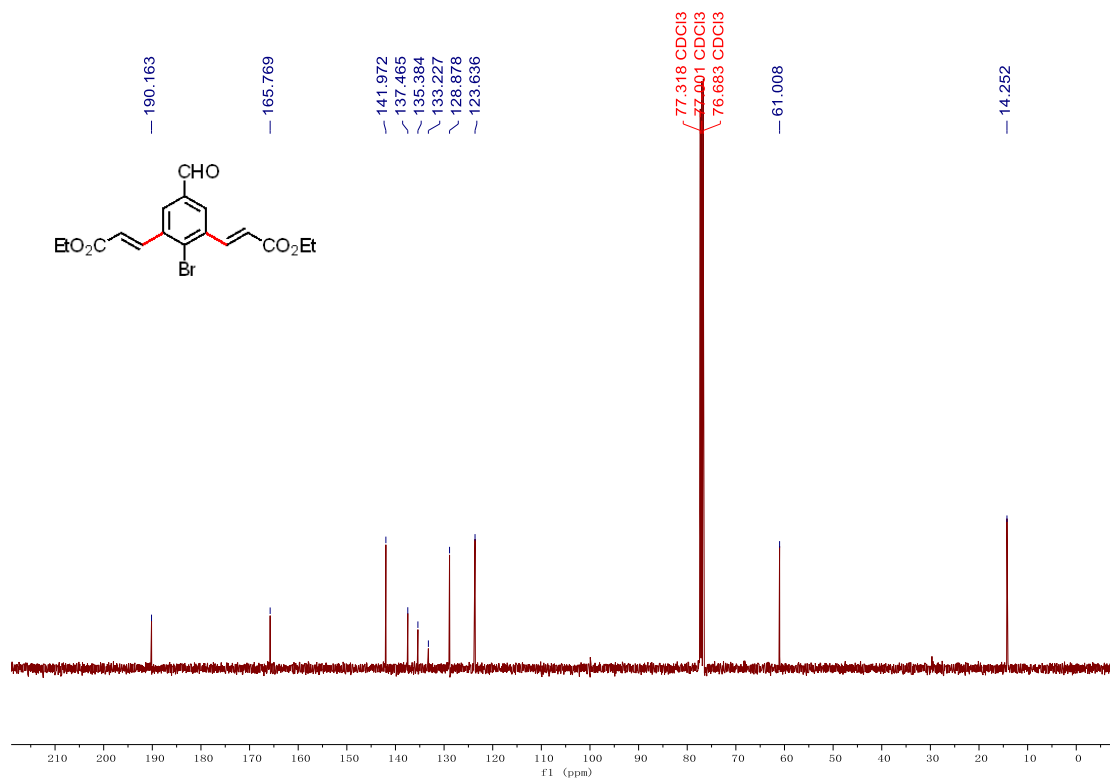
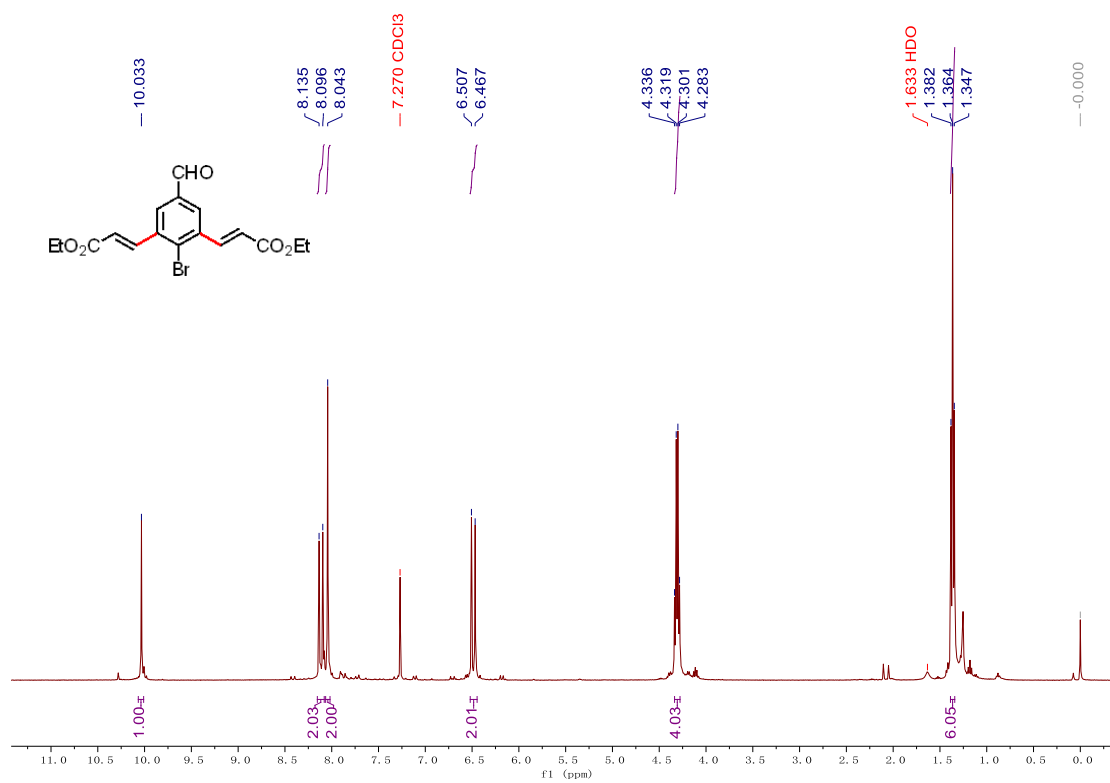
¹H and ¹³C NMR spectra of compound **1i**



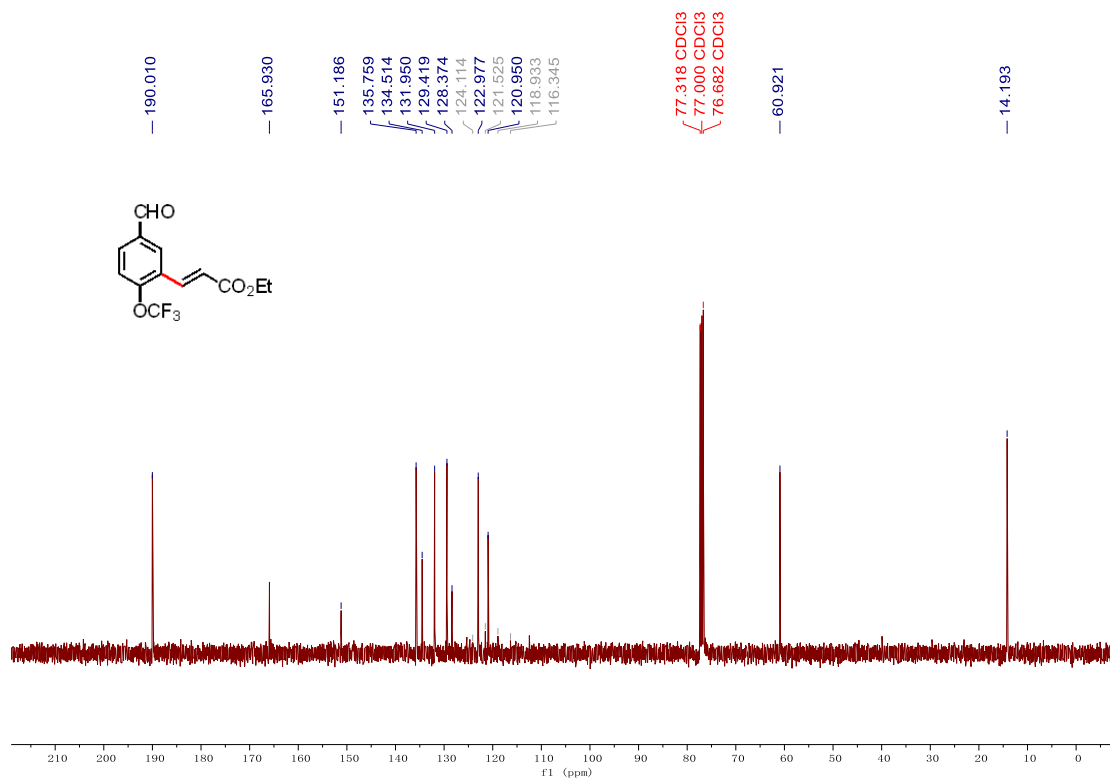
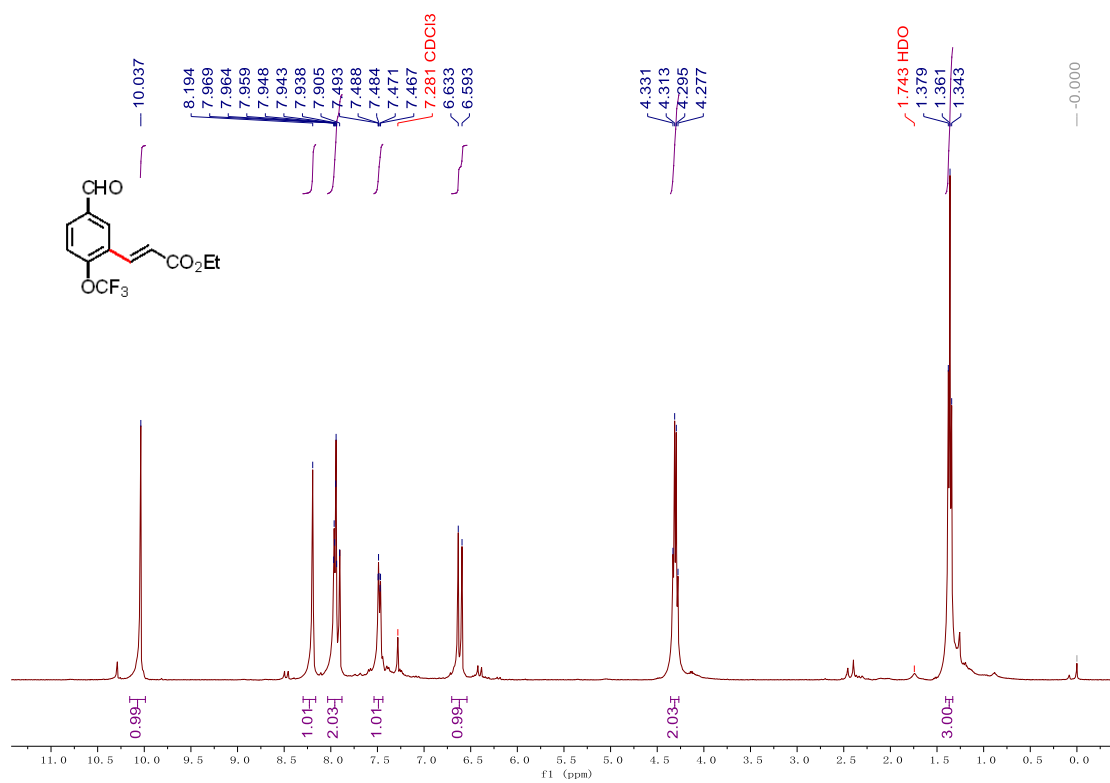
¹H and ¹³C NMR spectra of compound 1j



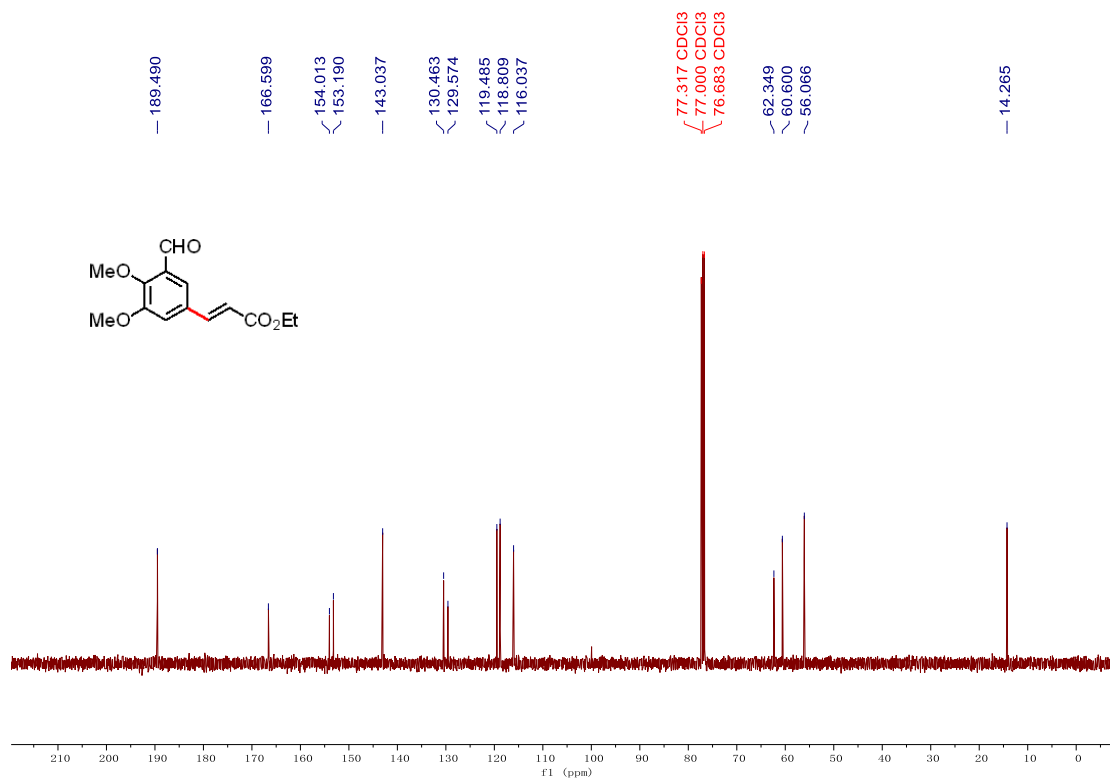
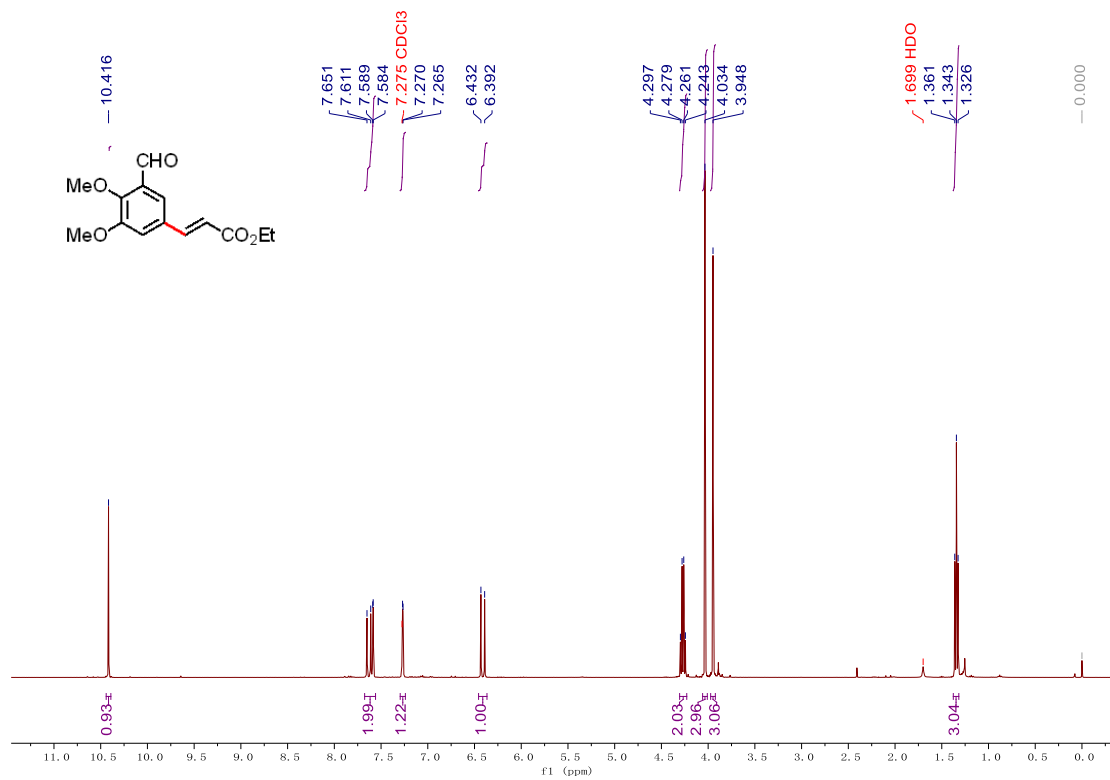
¹H and ¹³C NMR spectra of compound 1k_{mono}



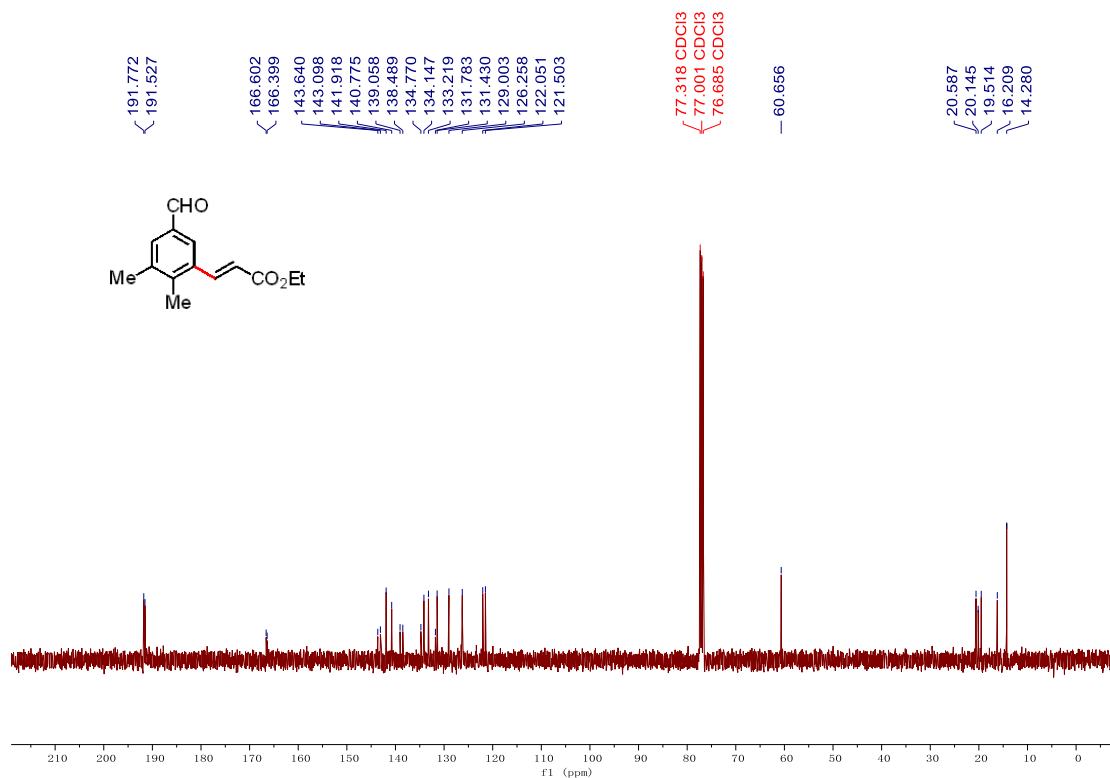
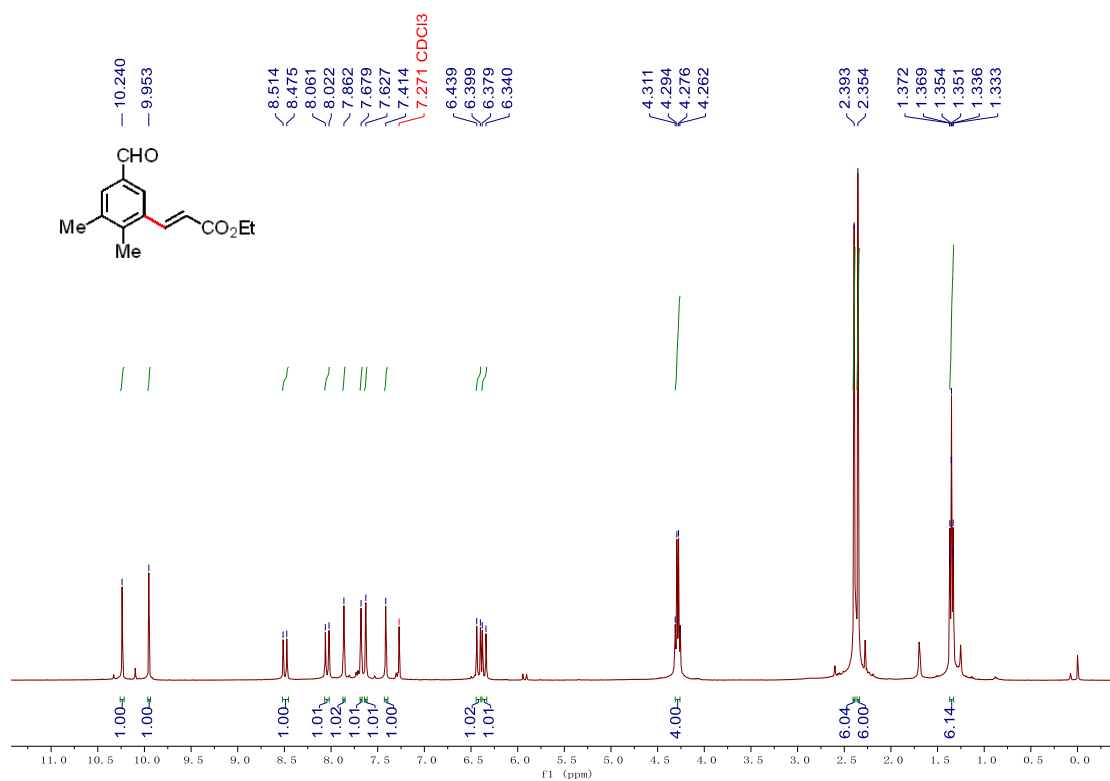
¹H and ¹³C NMR spectra of compound **1k_{di}**



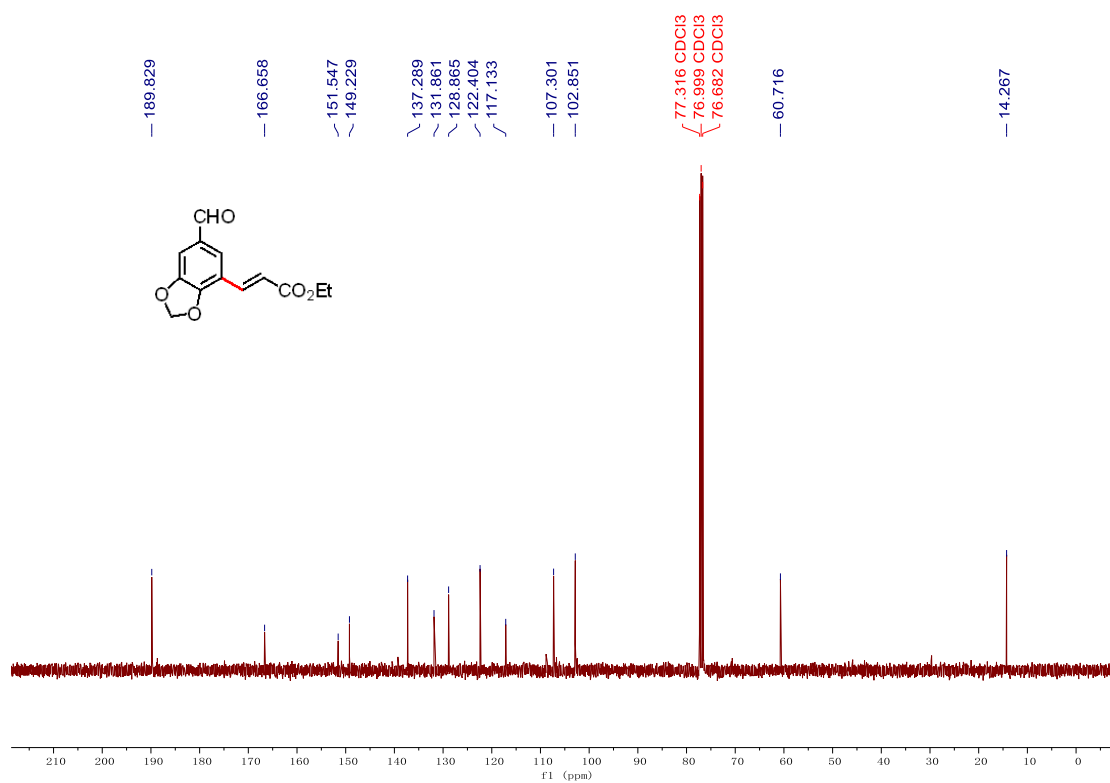
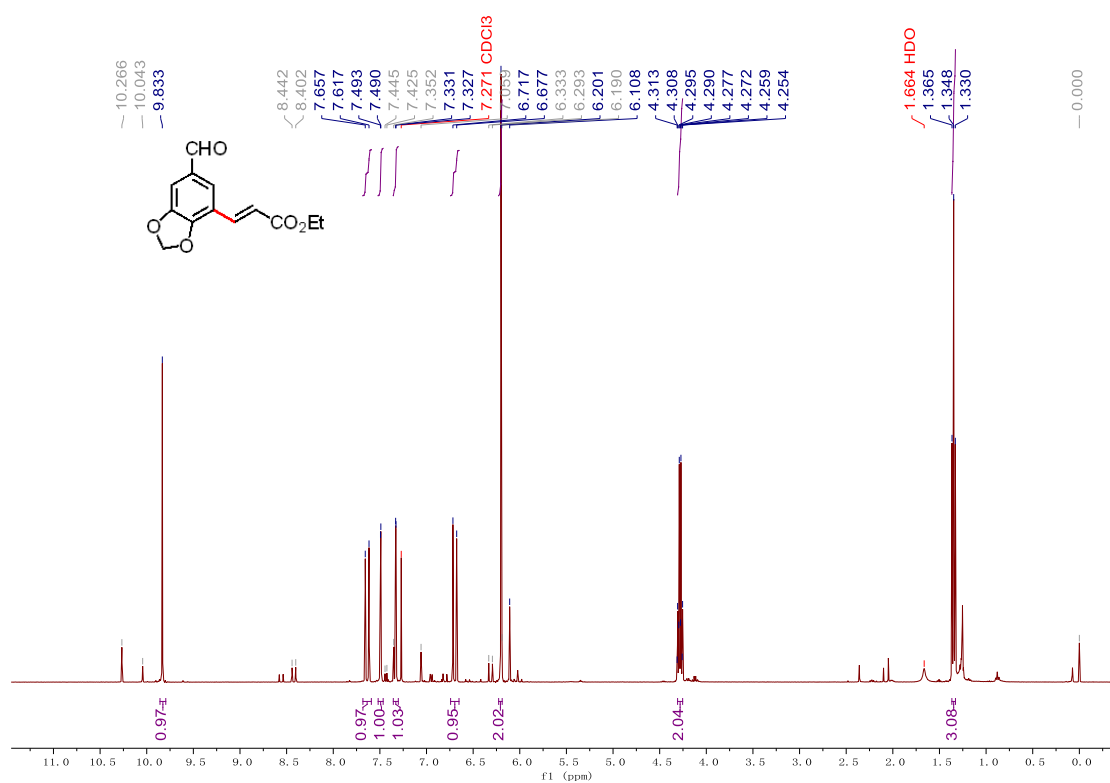
¹H and ¹³C NMR spectra of compound 11



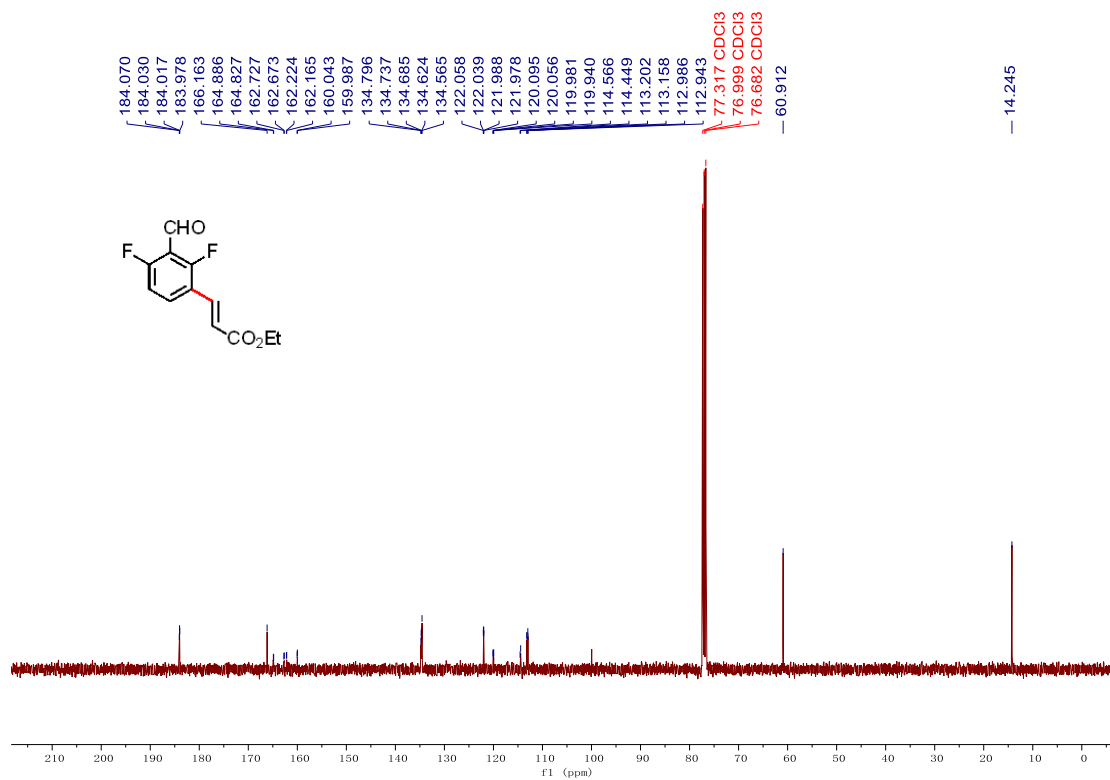
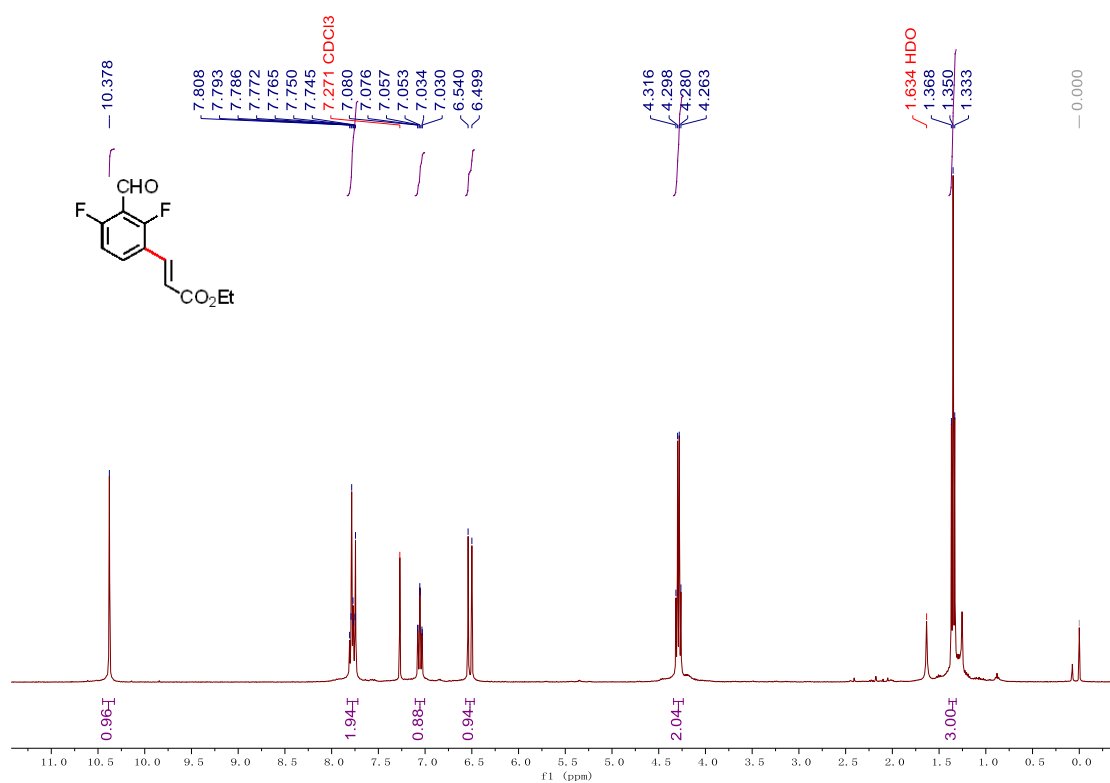
¹H and ¹³C NMR spectra of compound 1m



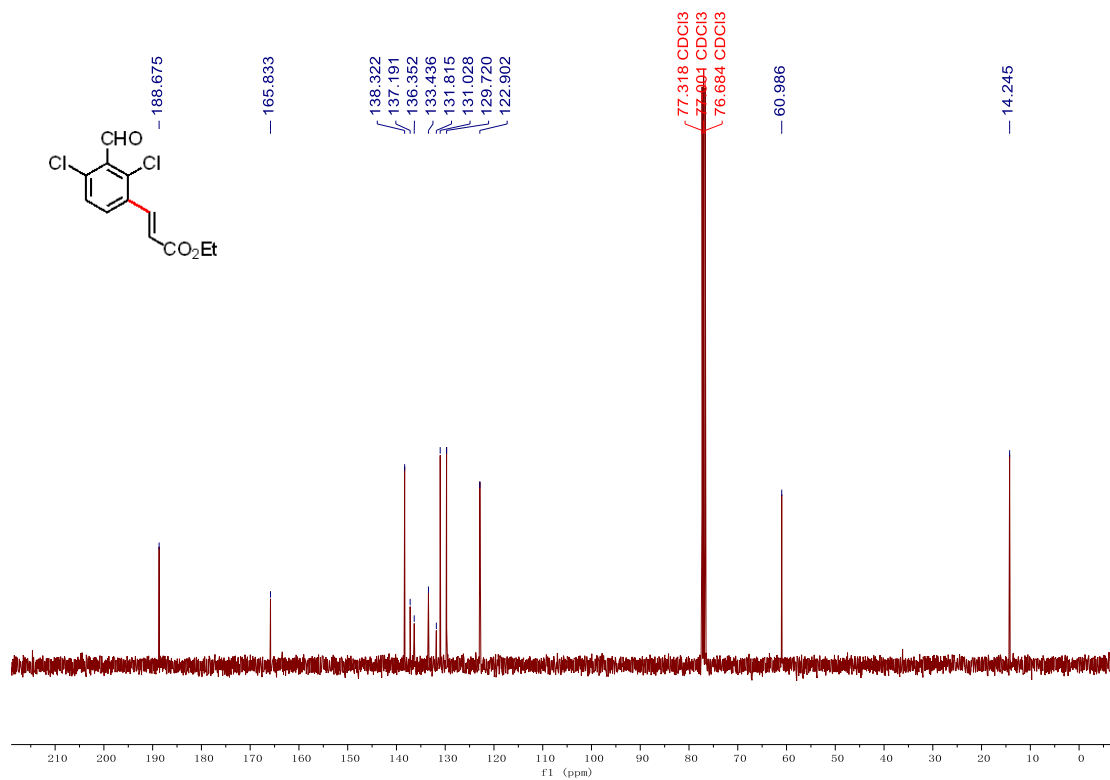
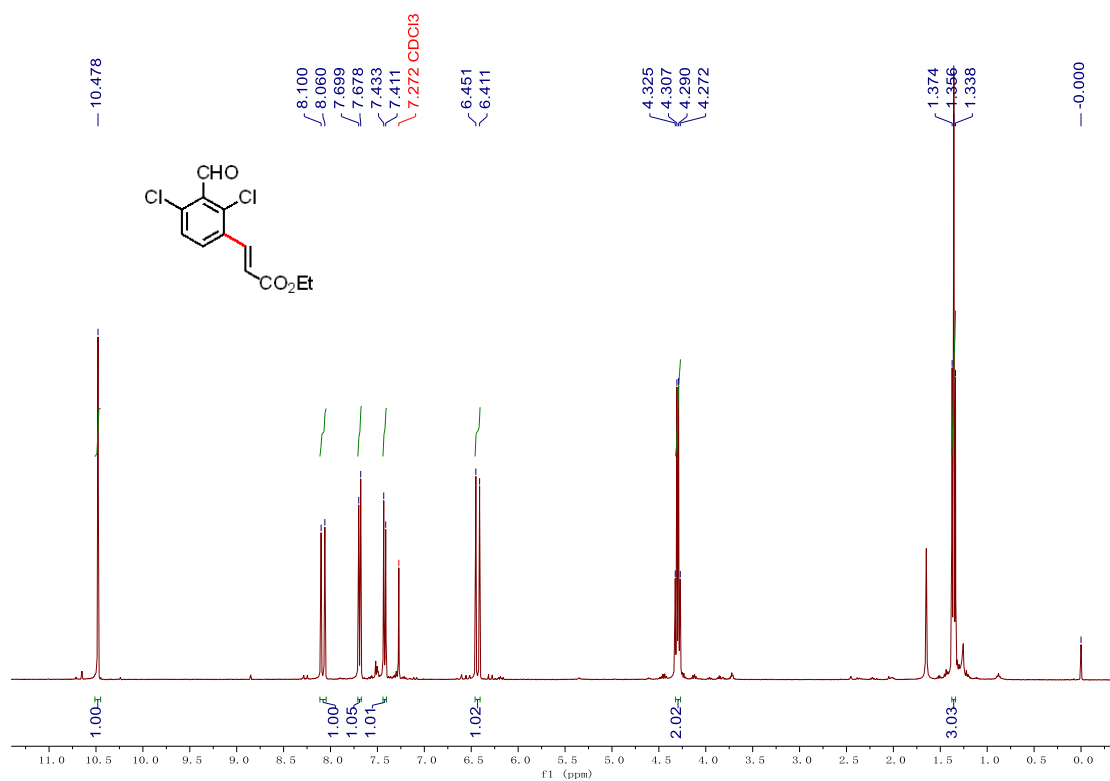
¹H and ¹³C NMR spectra of compound 1n



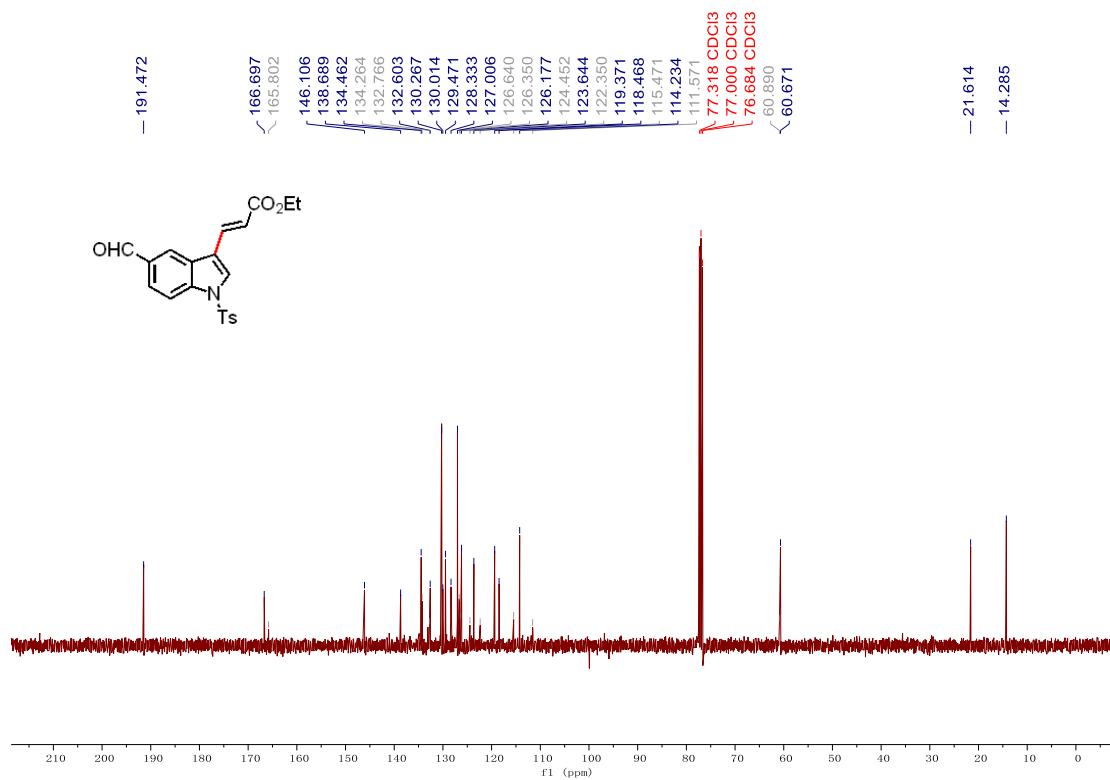
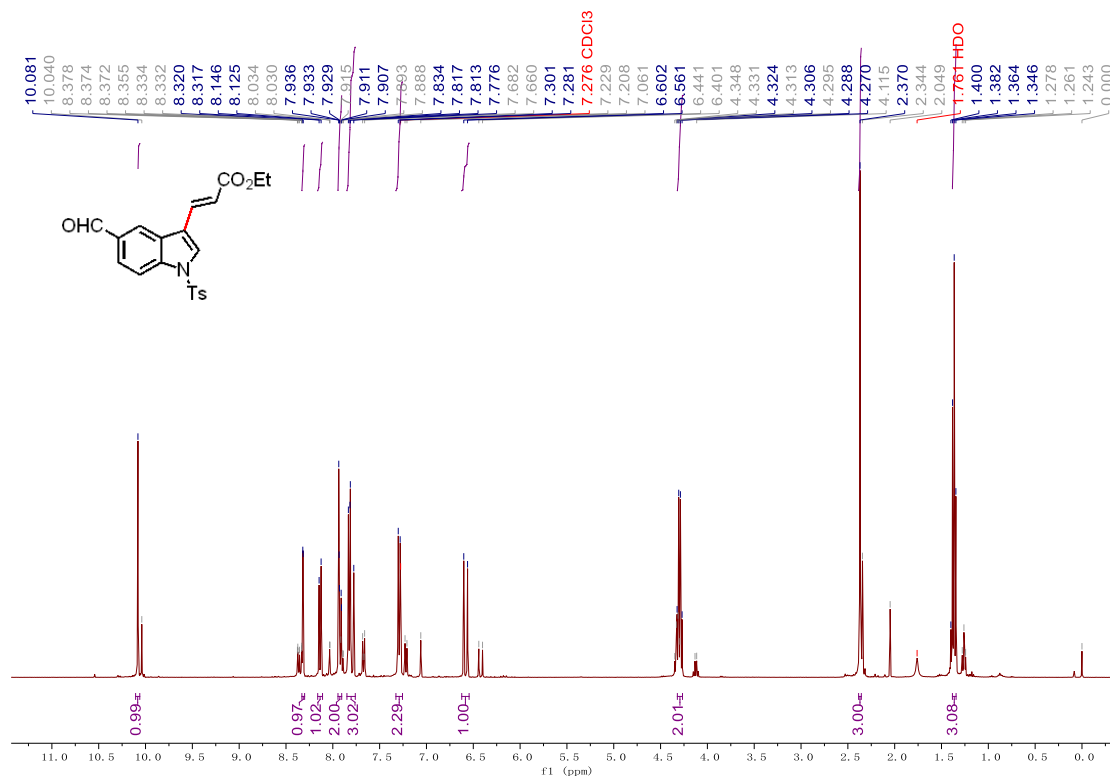
¹H and ¹³C NMR spectra of compound **1o**



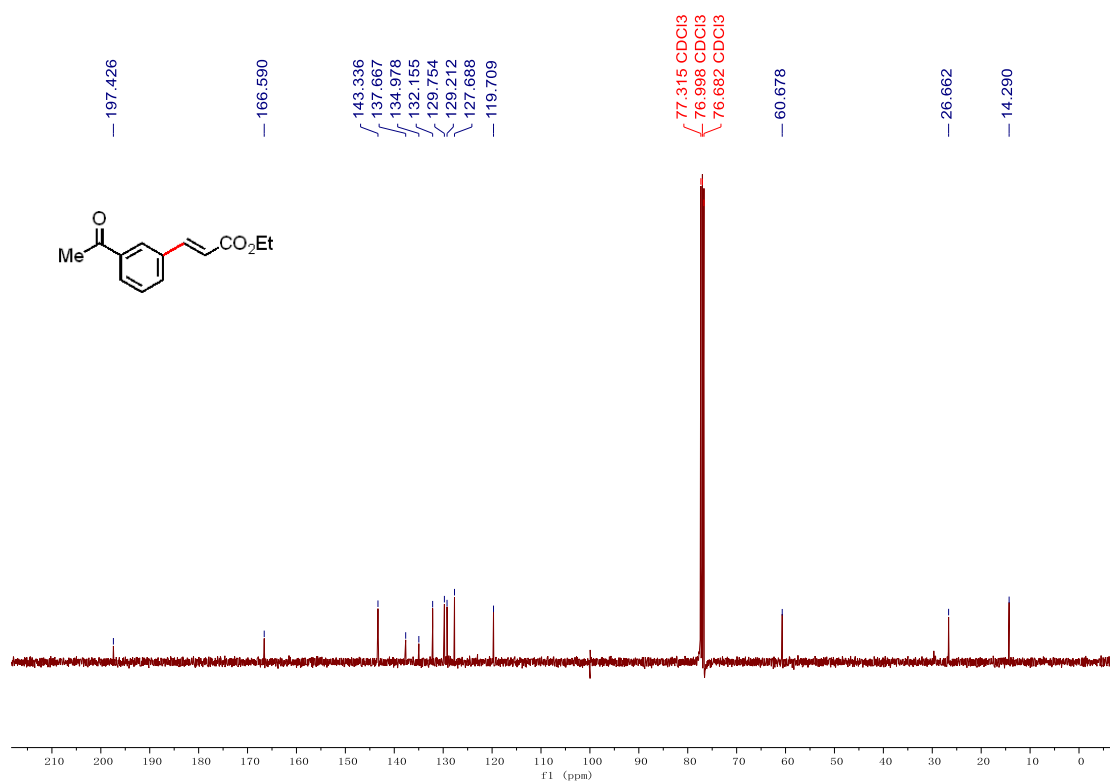
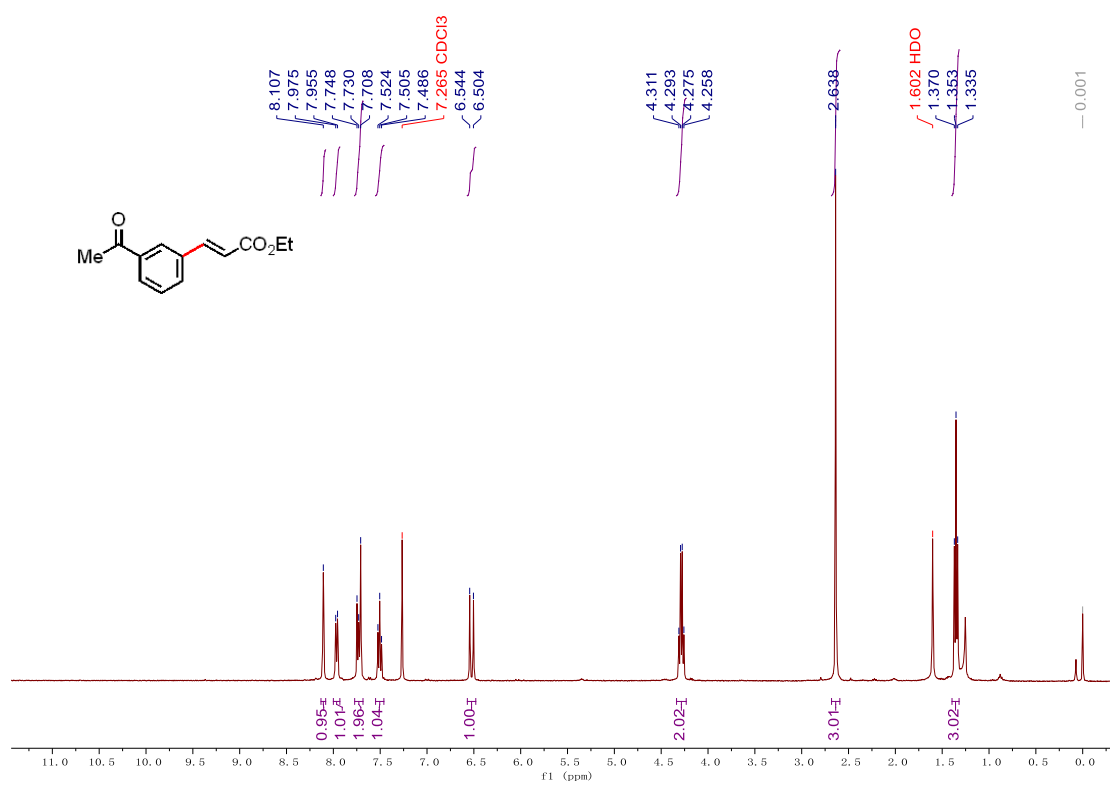
¹H and ¹³C NMR spectra of compound 1p



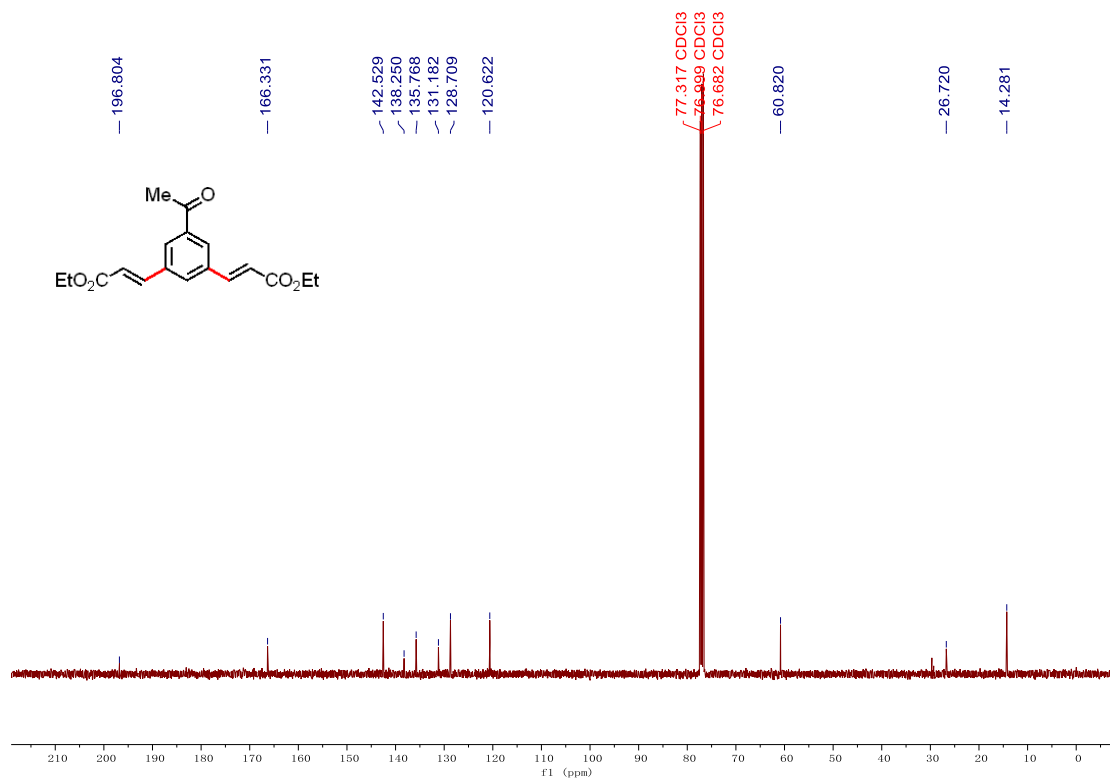
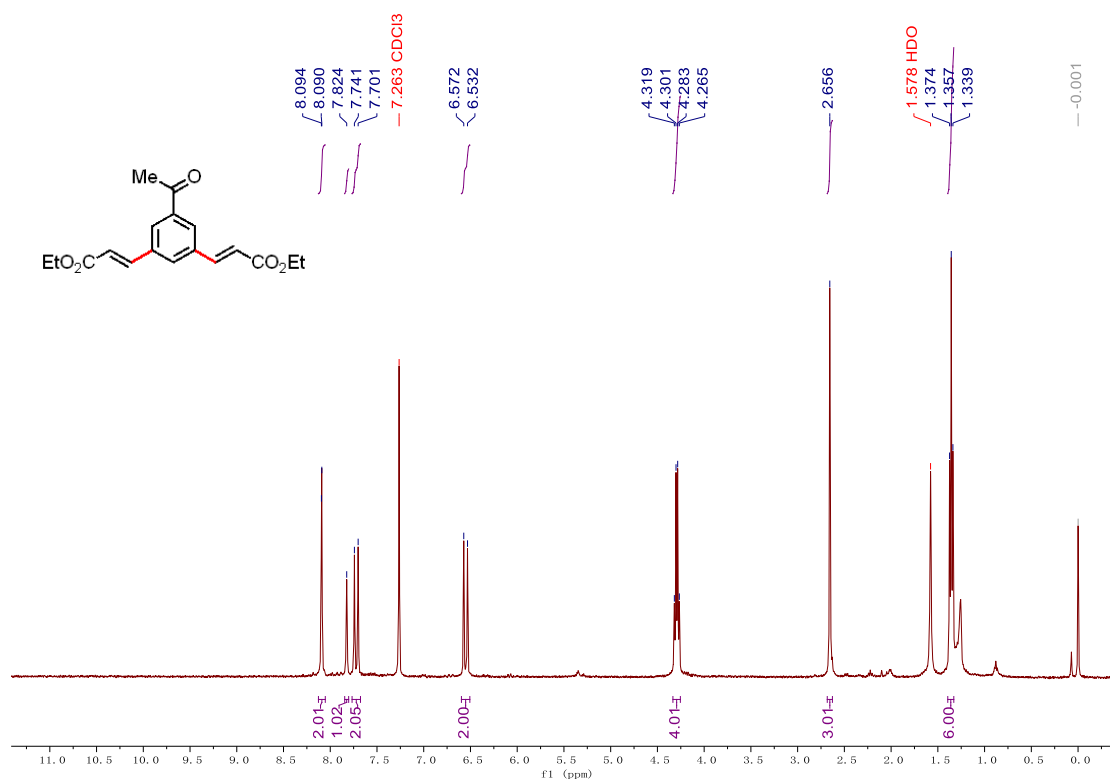
¹H and ¹³C NMR spectra of compound 1q



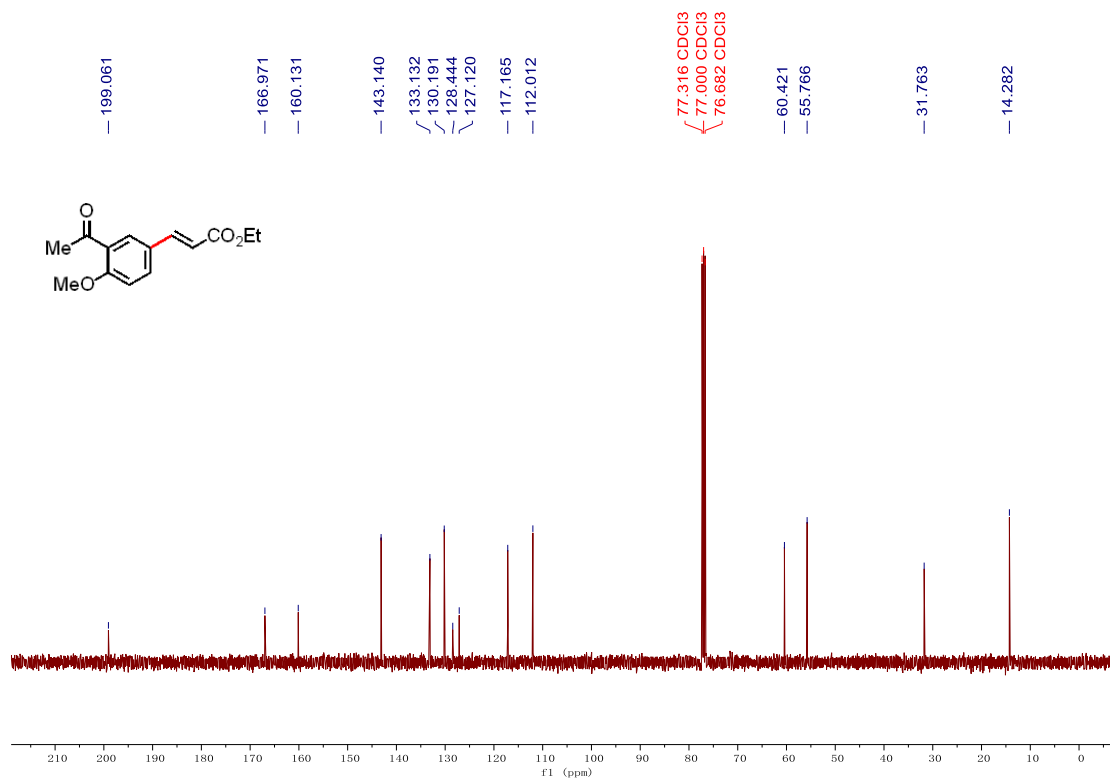
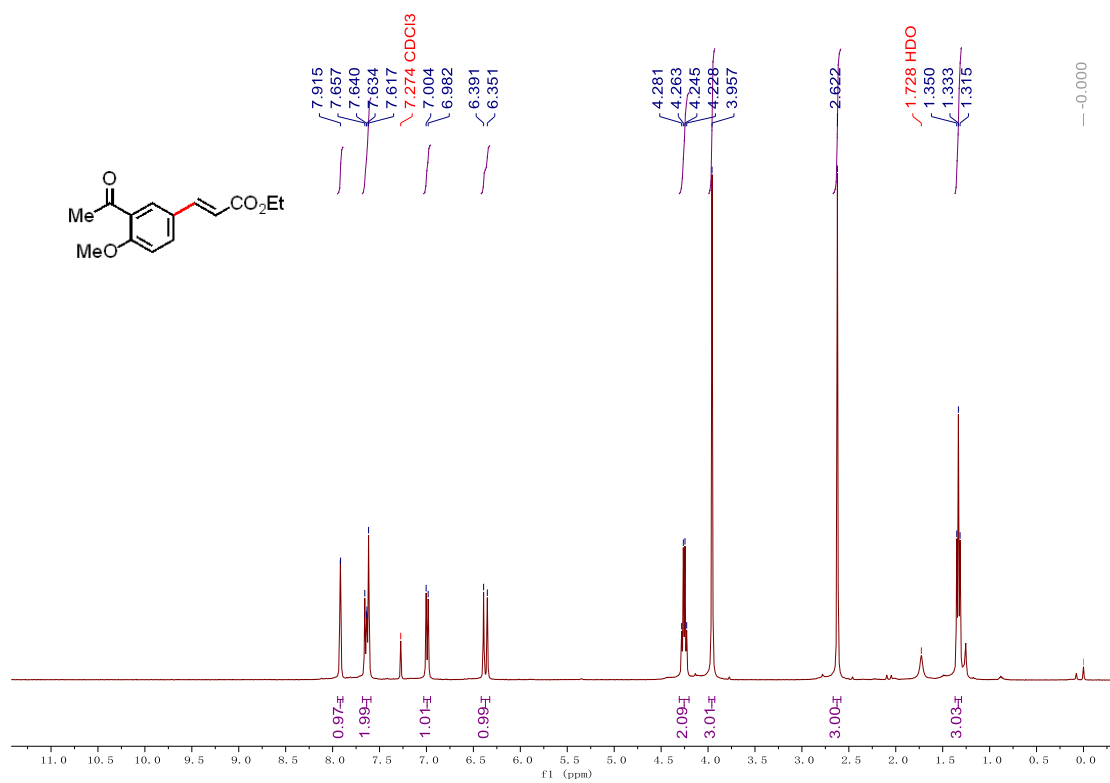
¹H and ¹³C NMR spectra of compound 1r



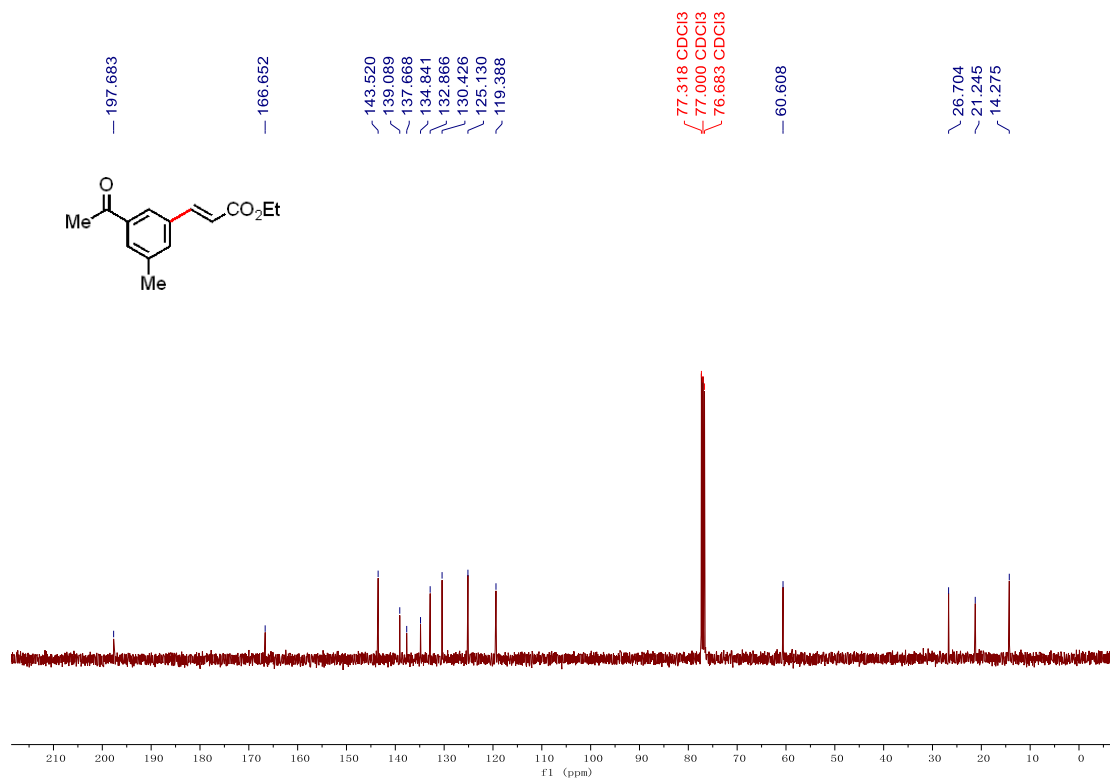
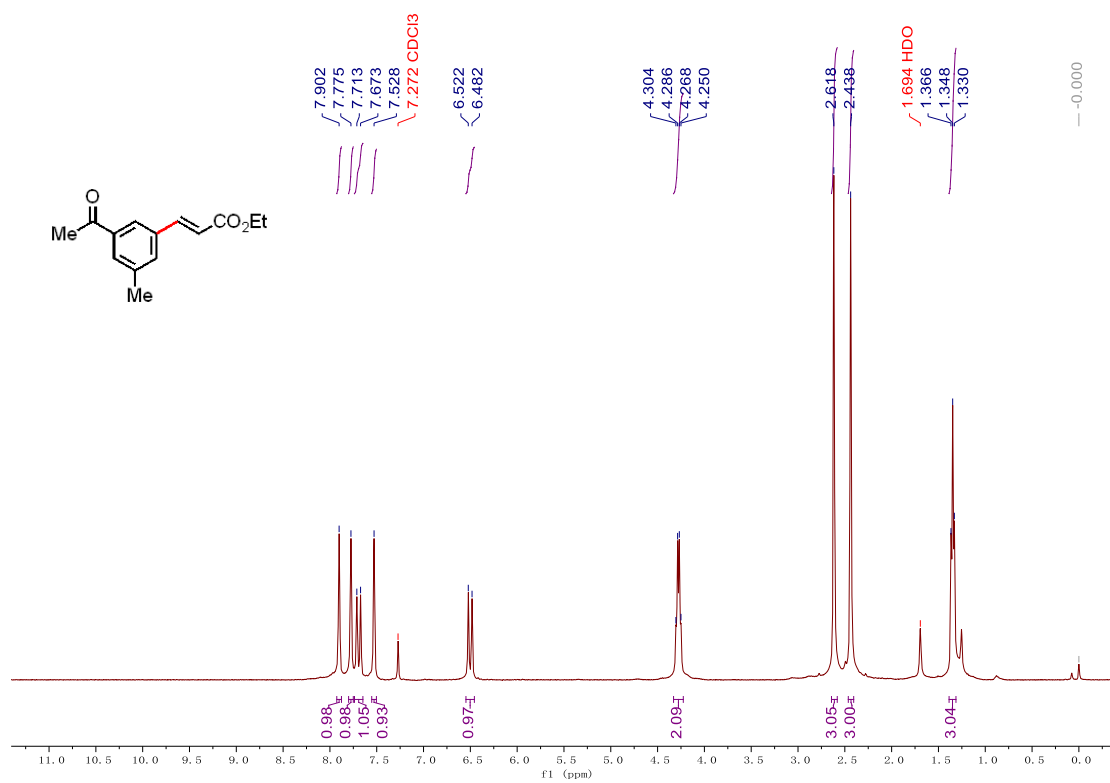
¹H and ¹³C NMR spectra of compound 2a_{mono}



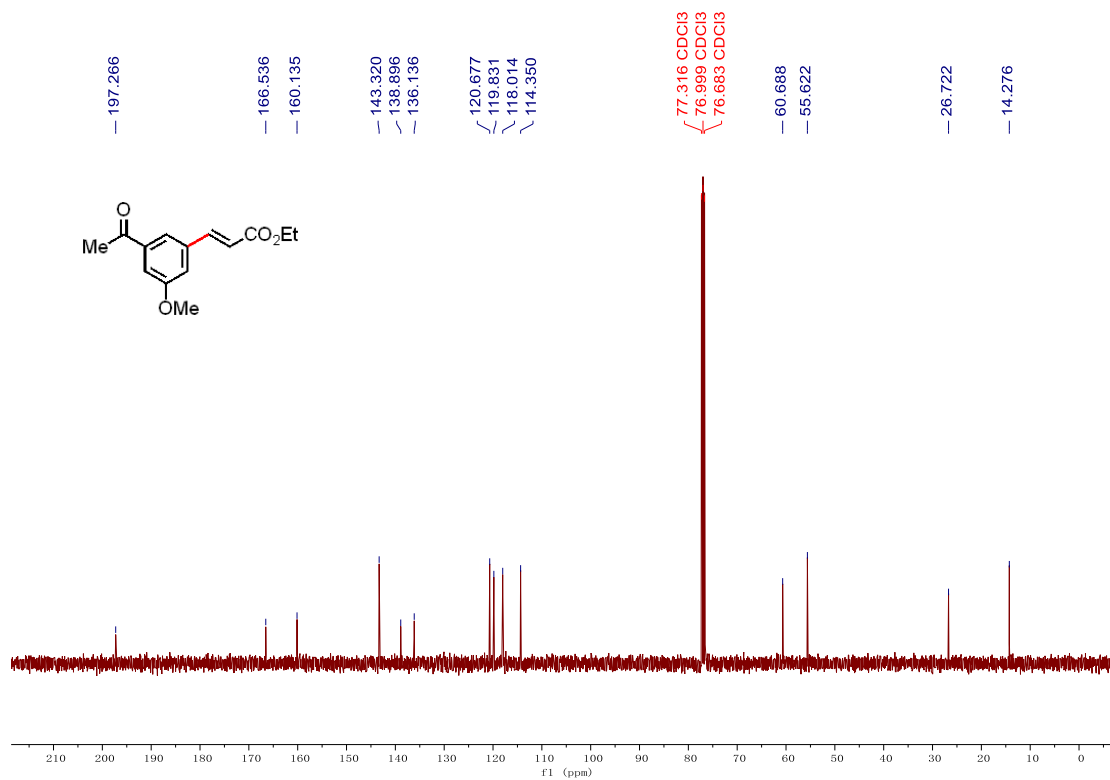
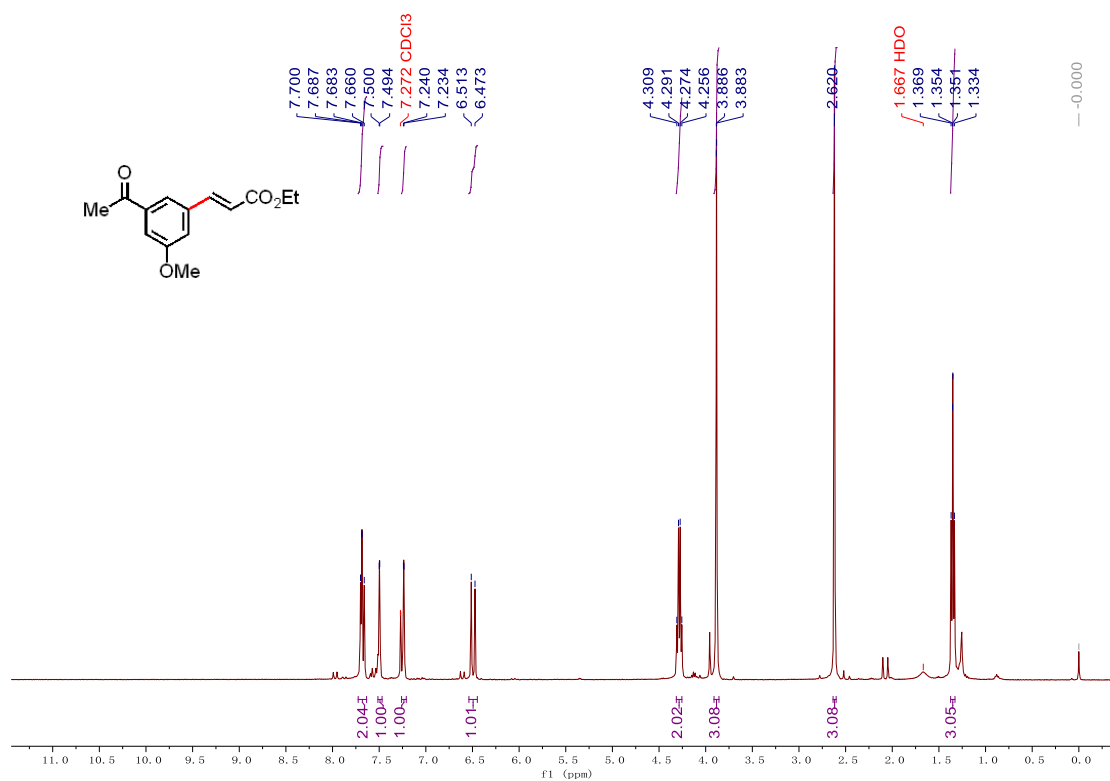
¹H and ¹³C NMR spectra of compound **2a_{di}**



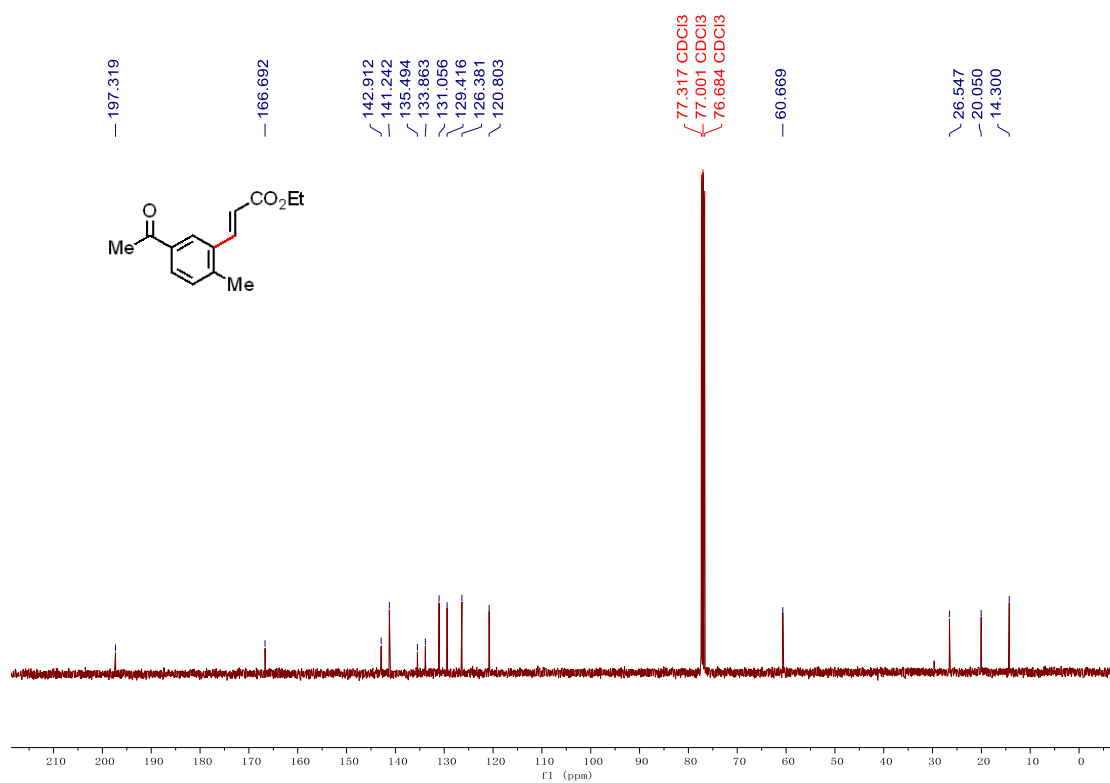
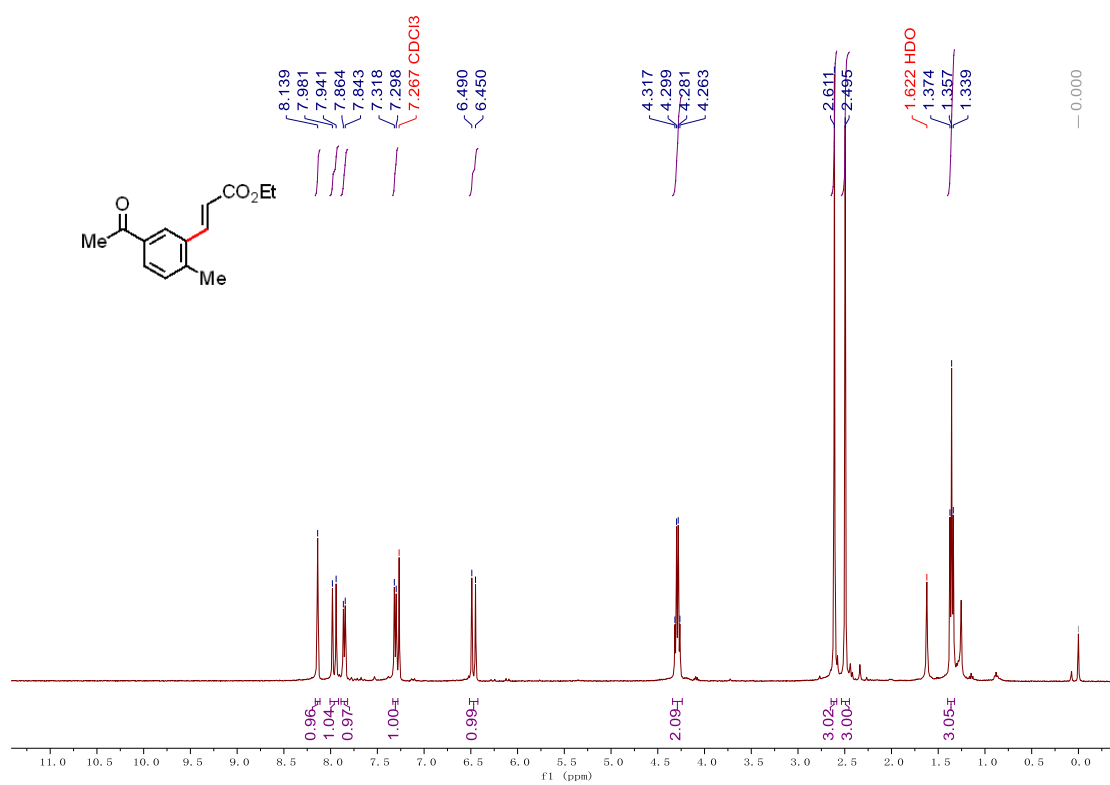
¹H and ¹³C NMR spectra of compound **2b**



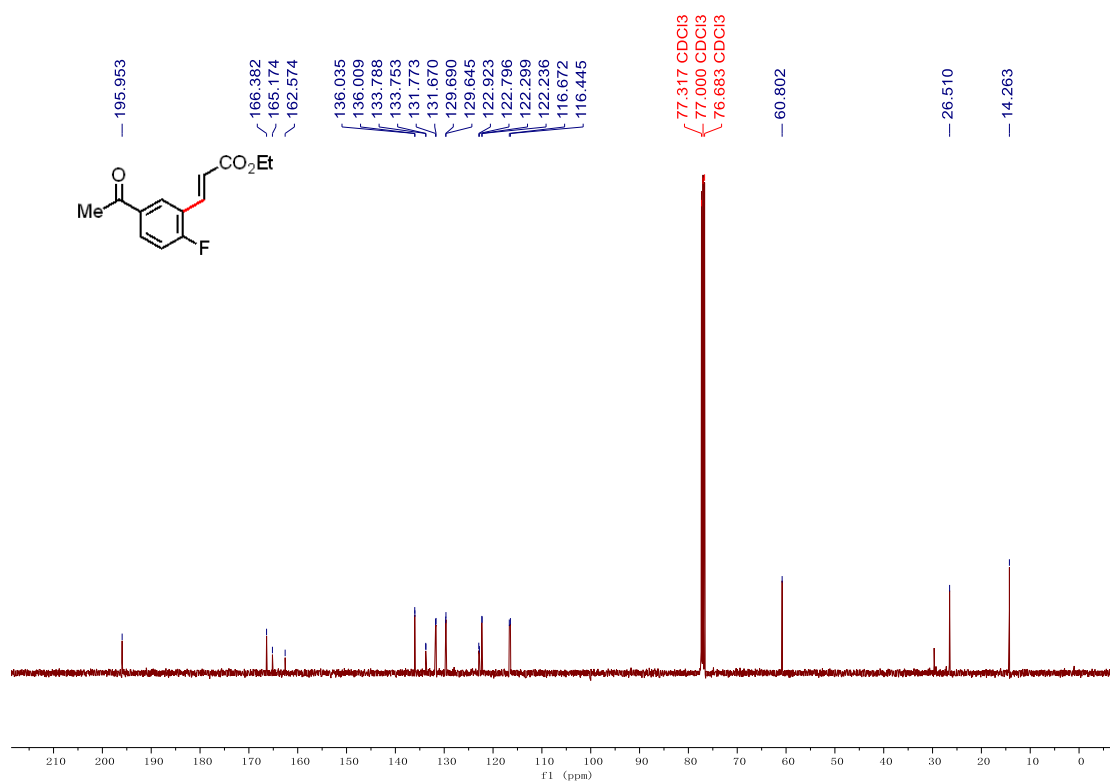
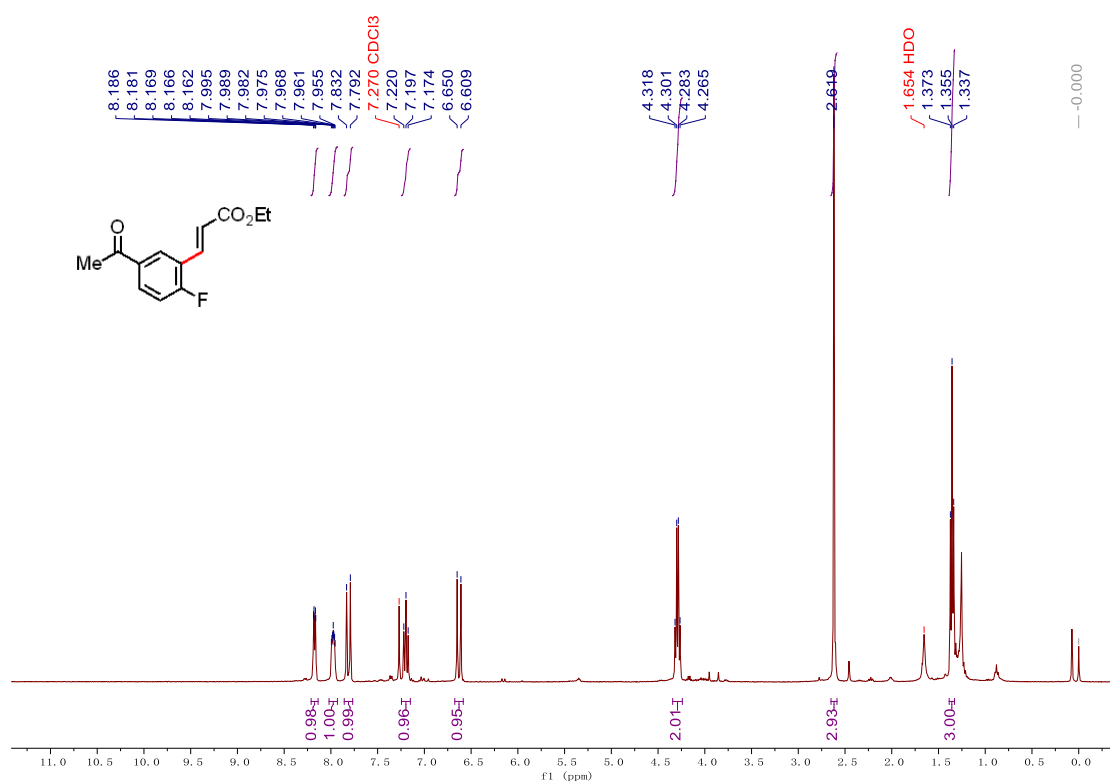
¹H and ¹³C NMR spectra of compound **2c**



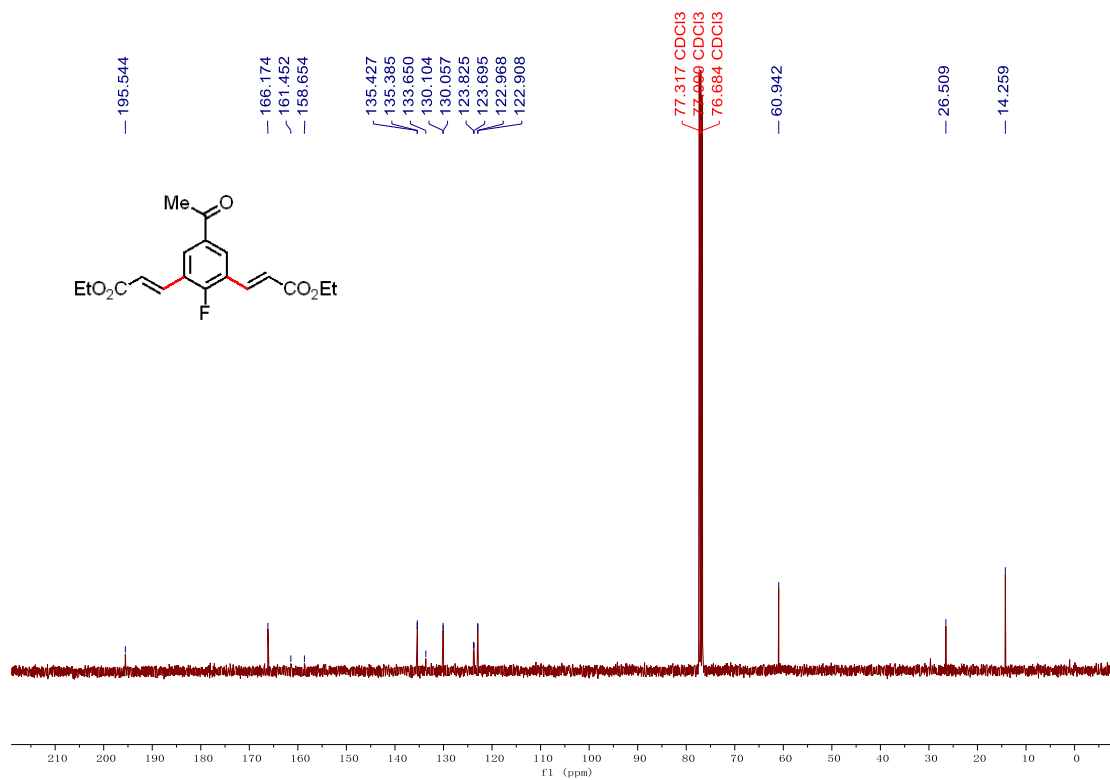
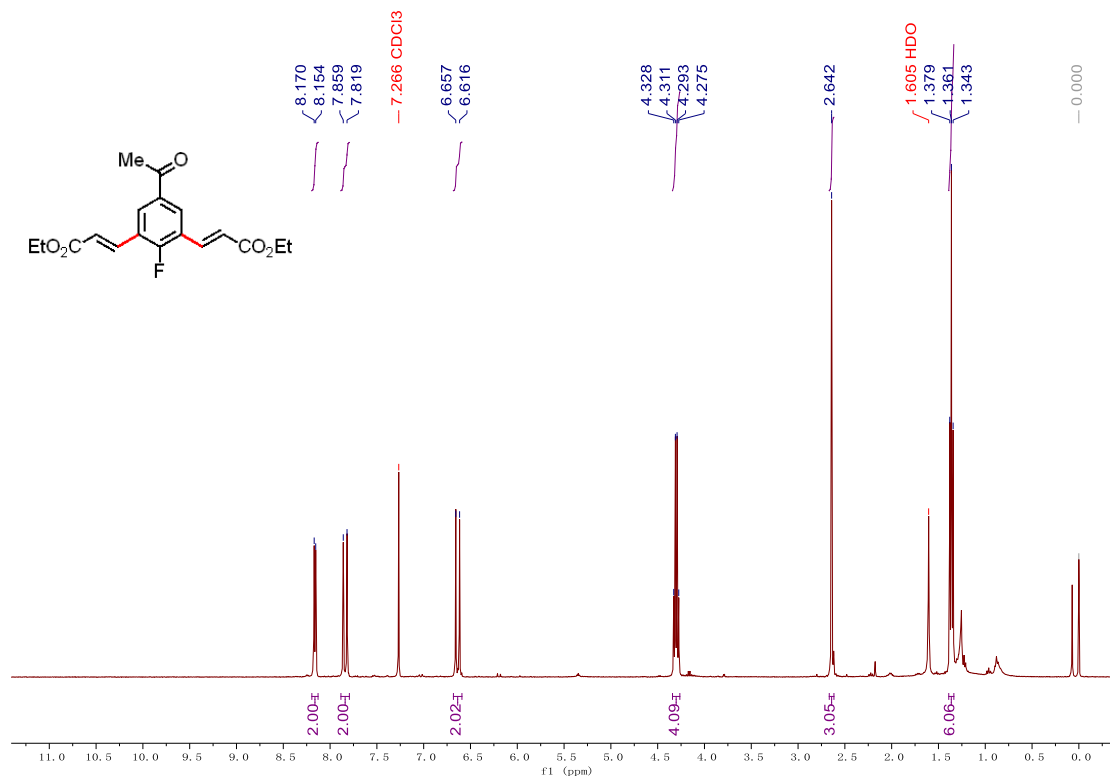
¹H and ¹³C NMR spectra of compound 2d



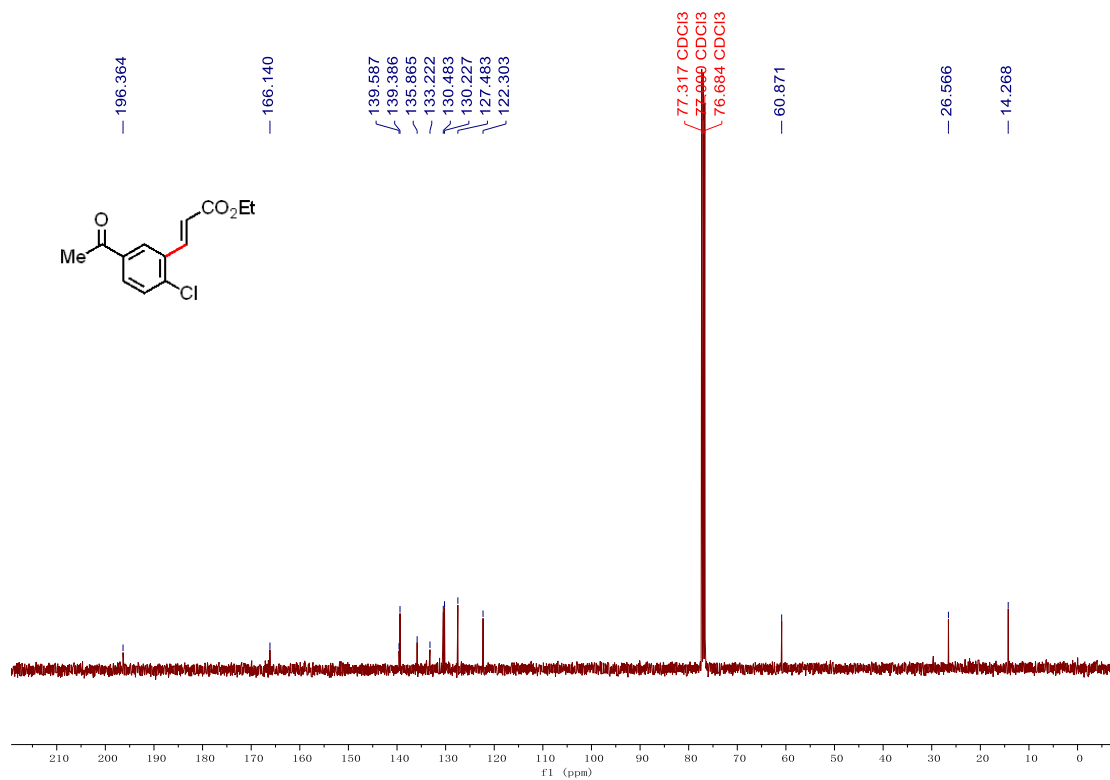
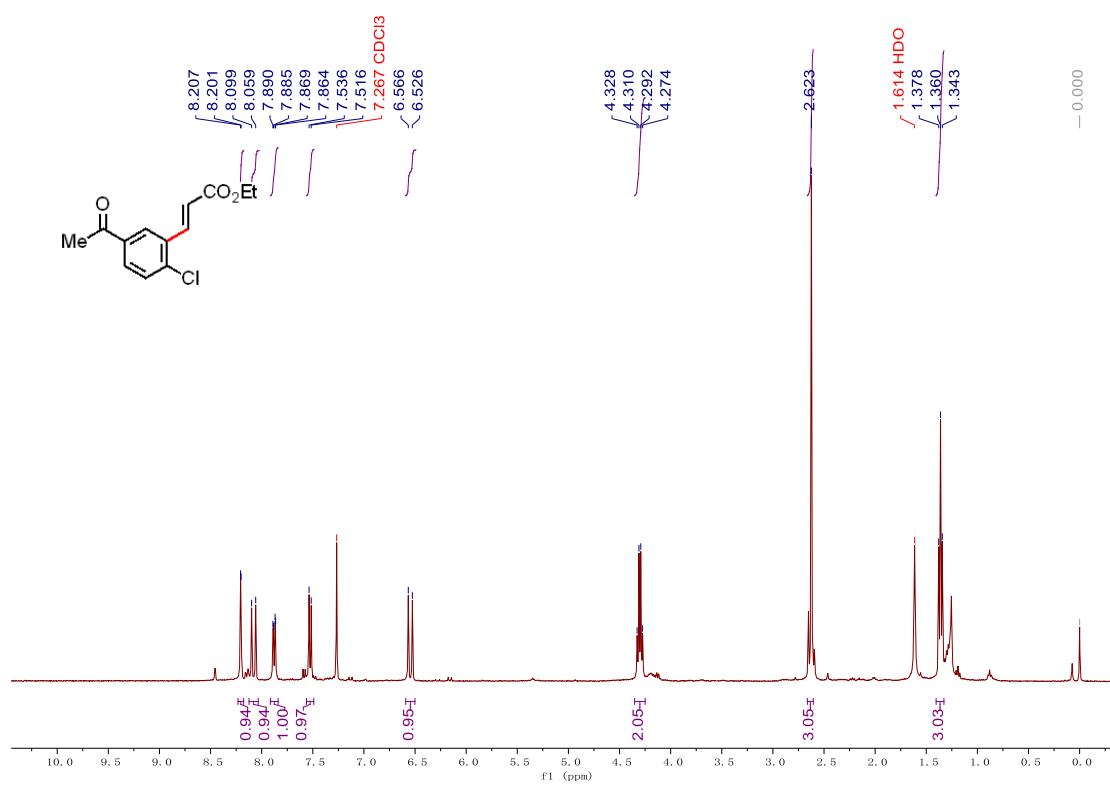
¹H and ¹³C NMR spectra of compound **2e**



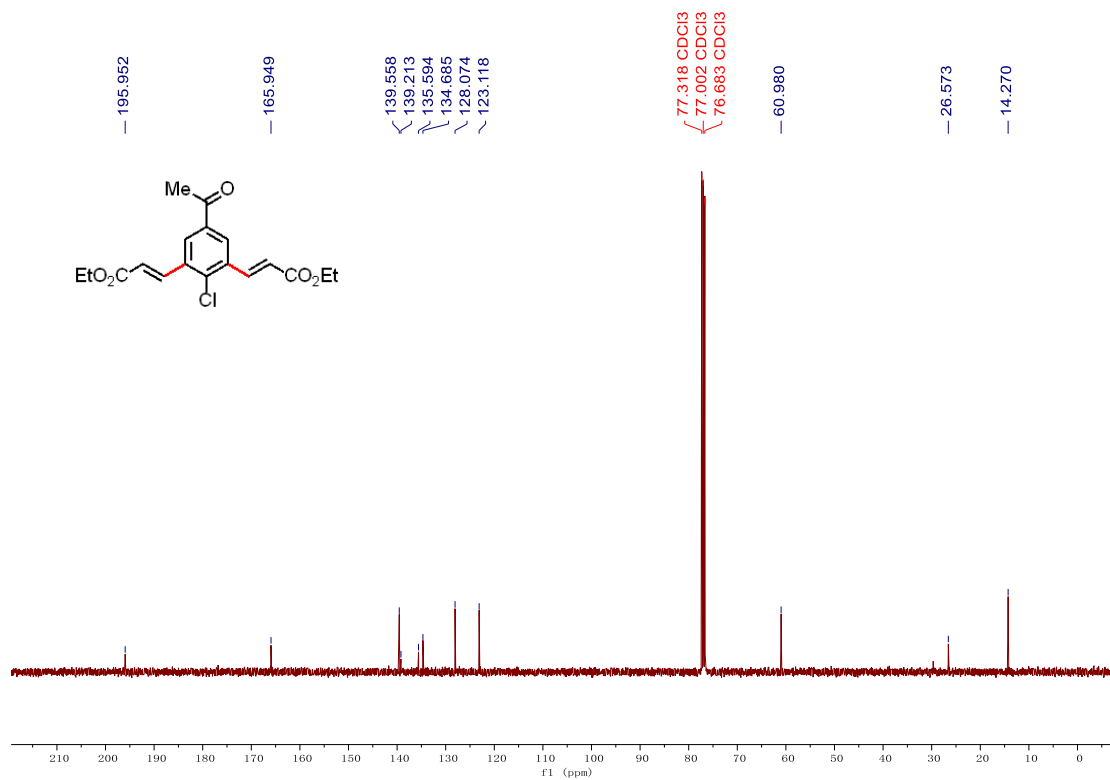
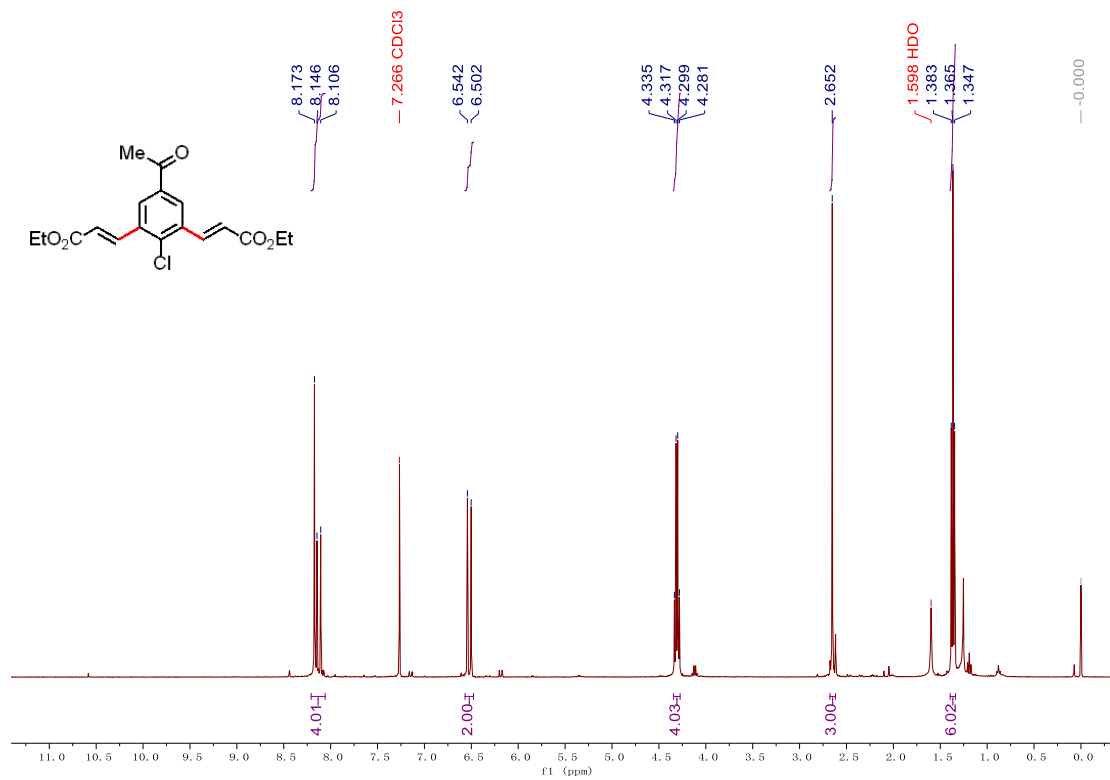
¹H and ¹³C NMR spectra of compound **2f_{mono}**



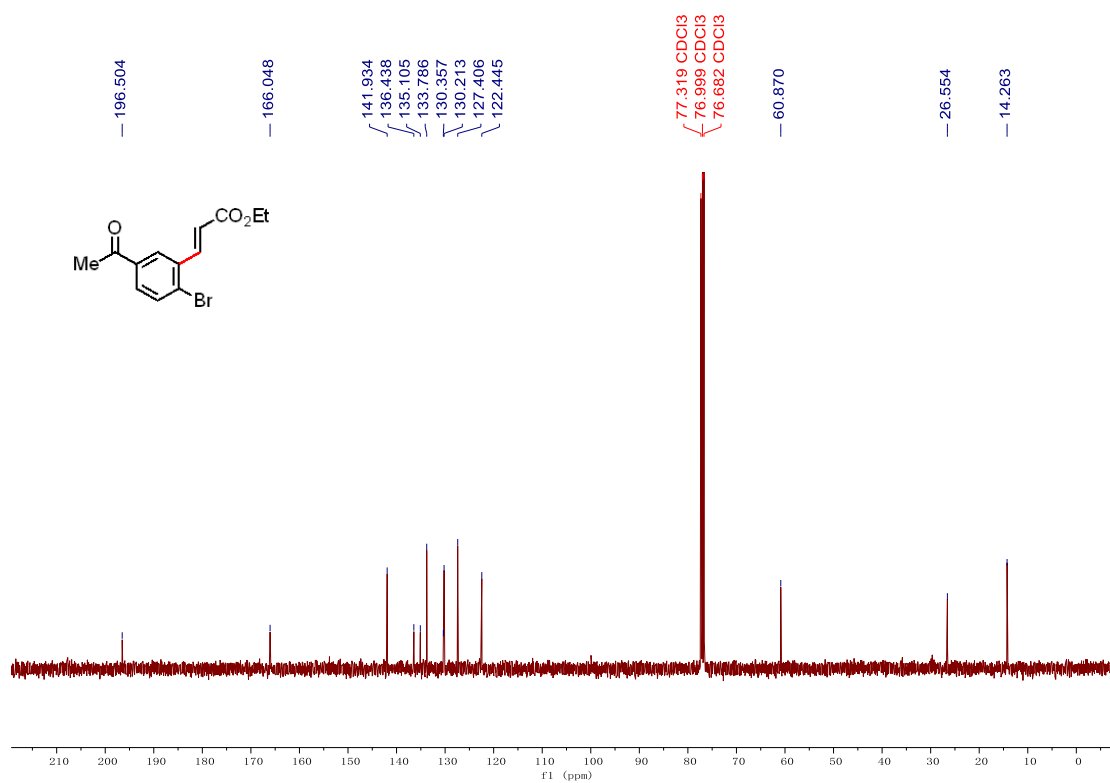
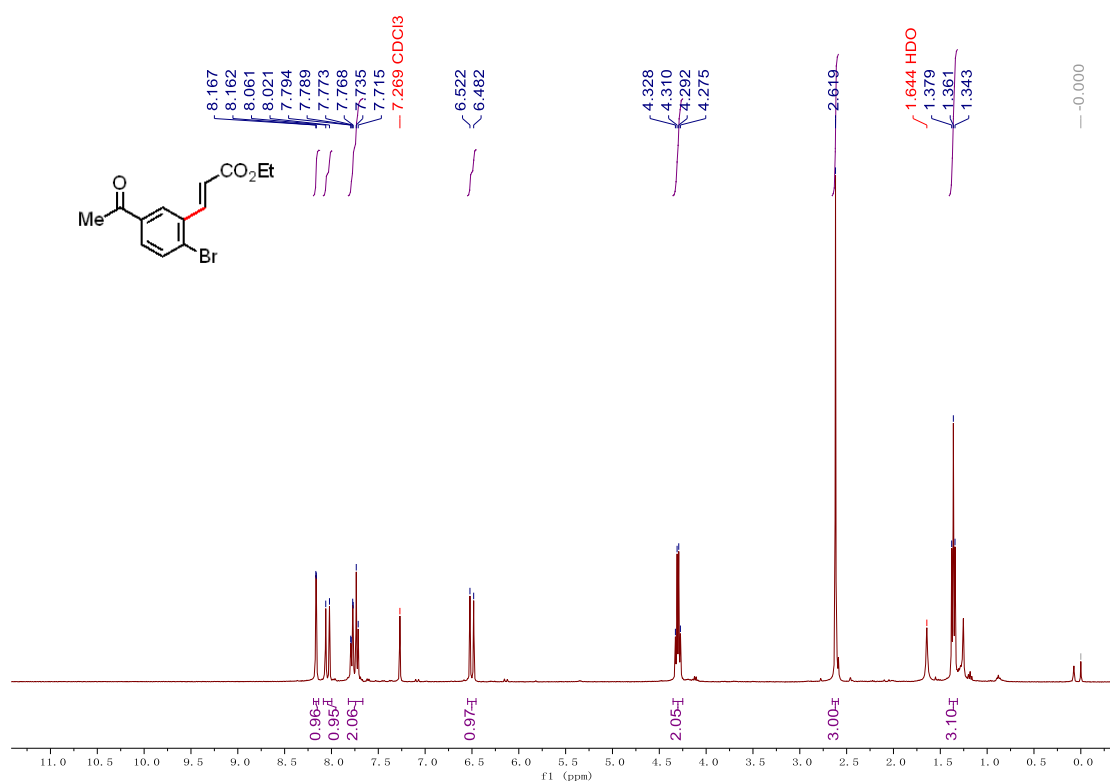
¹H and ¹³C NMR spectra of compound **2f_{di}**



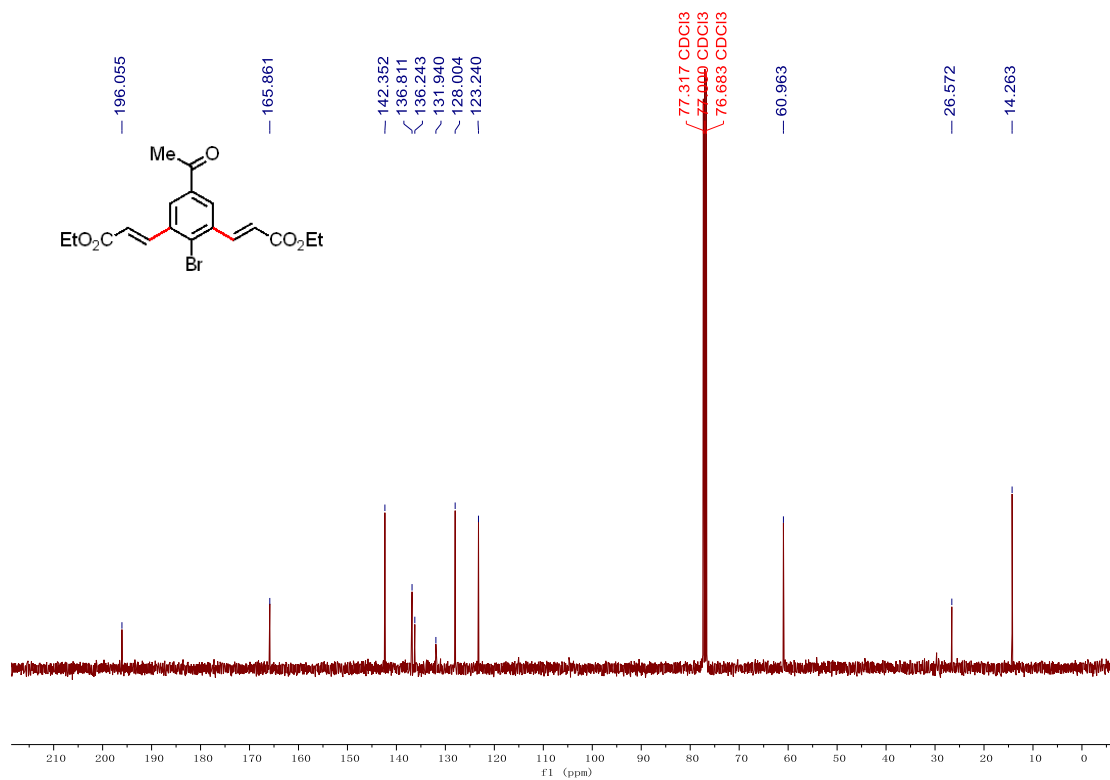
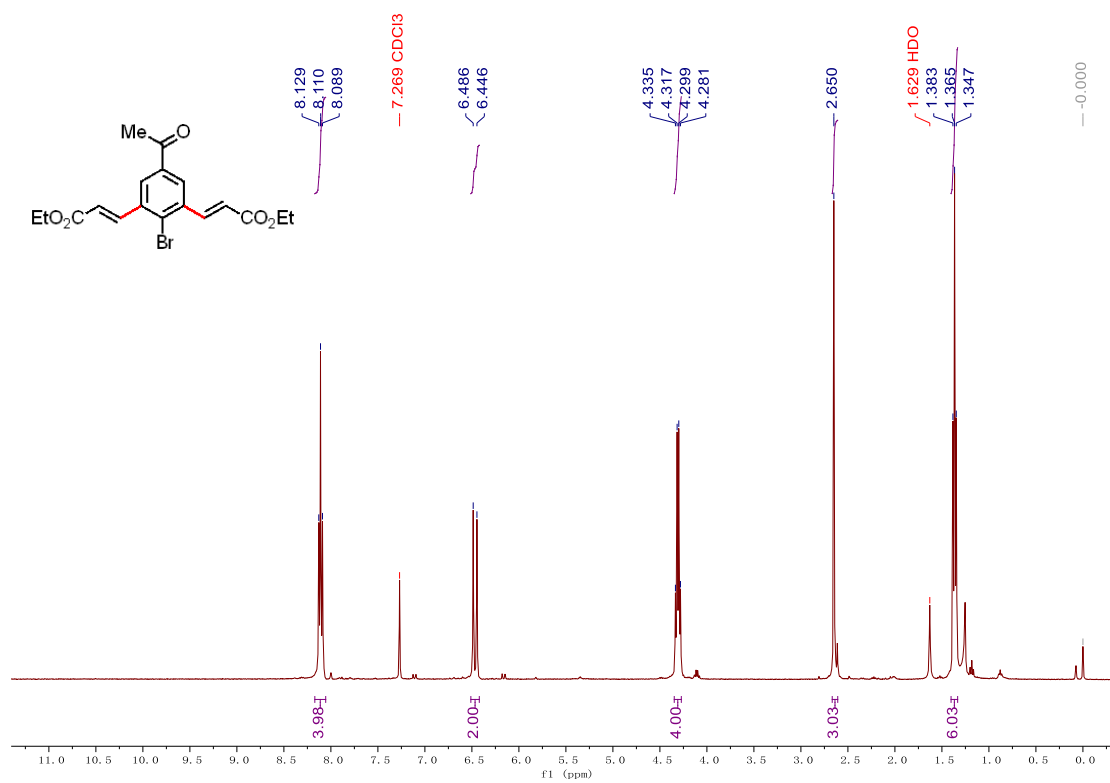
¹H and ¹³C NMR spectra of compound 2g_{mono}



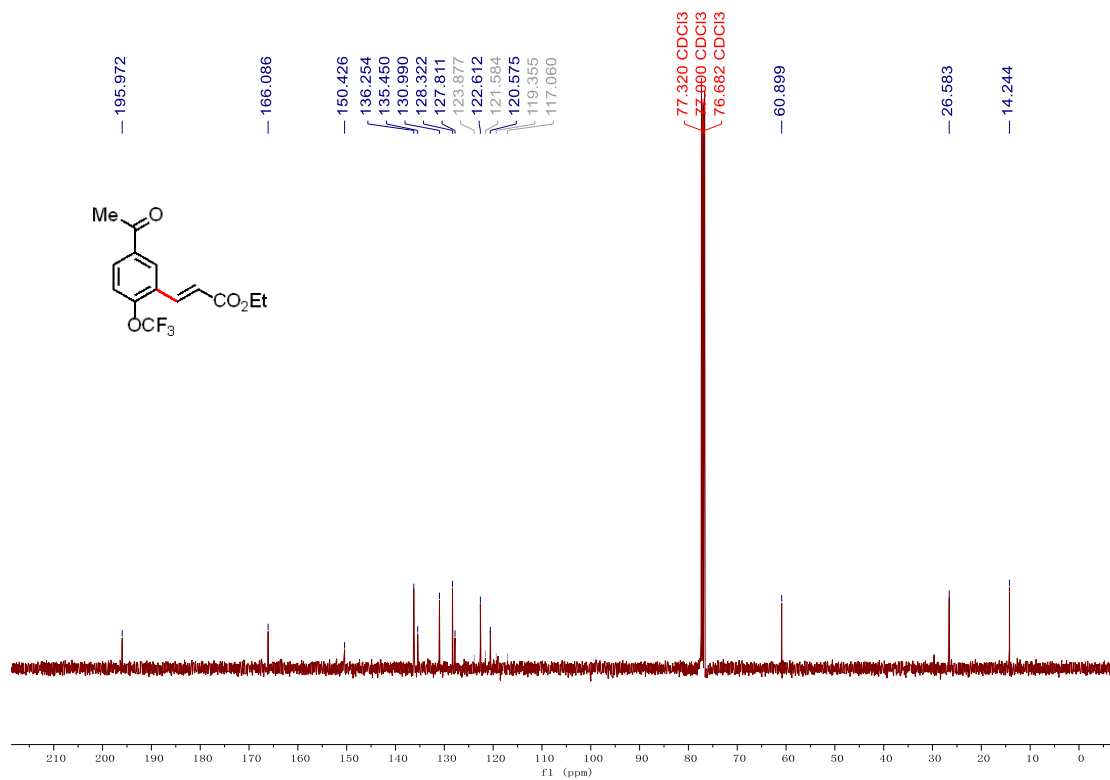
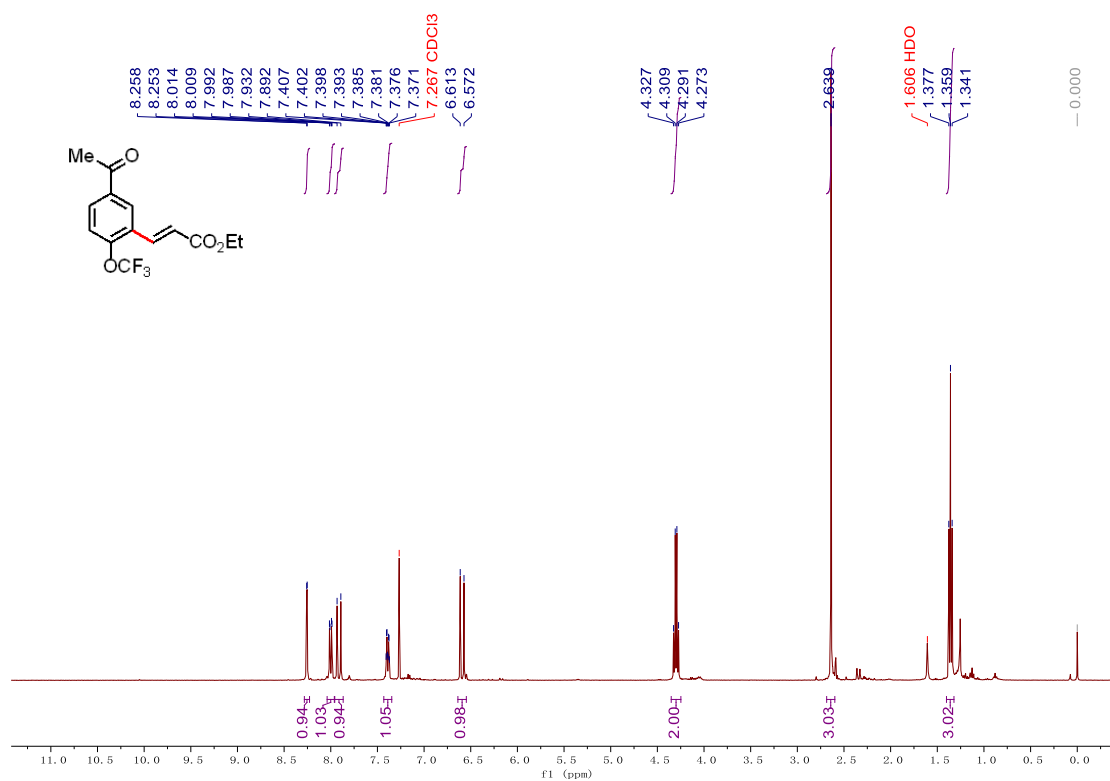
¹H and ¹³C NMR spectra of compound **2g_{di}**



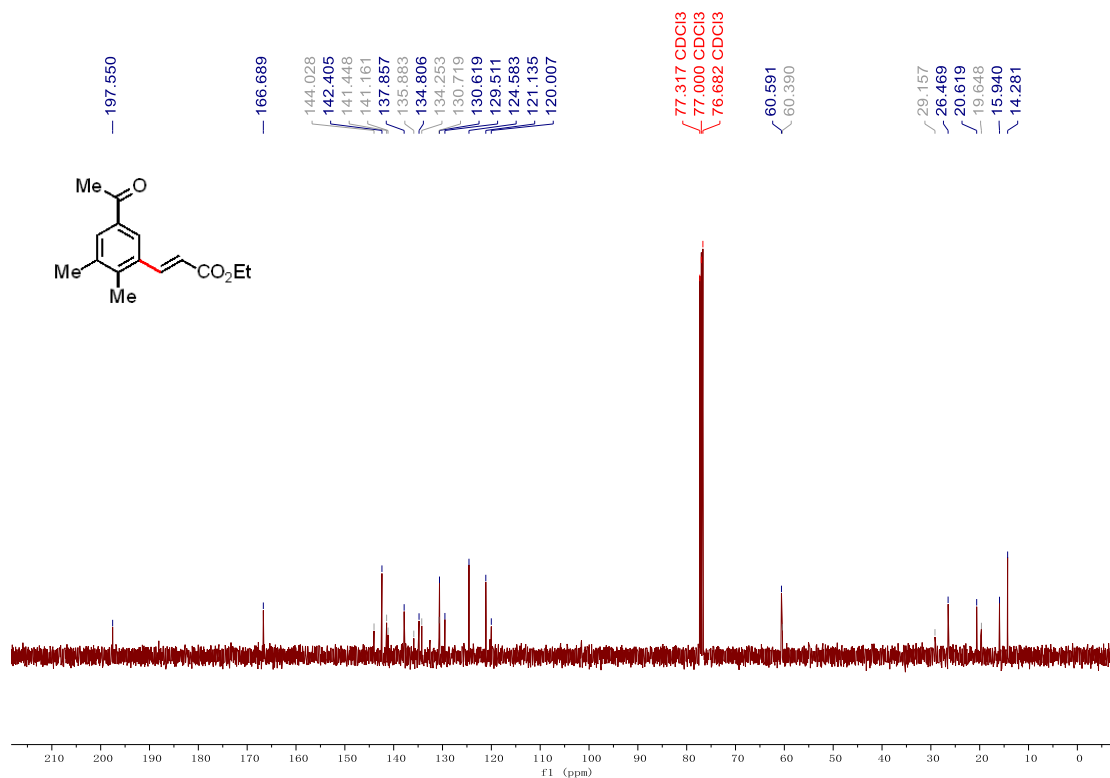
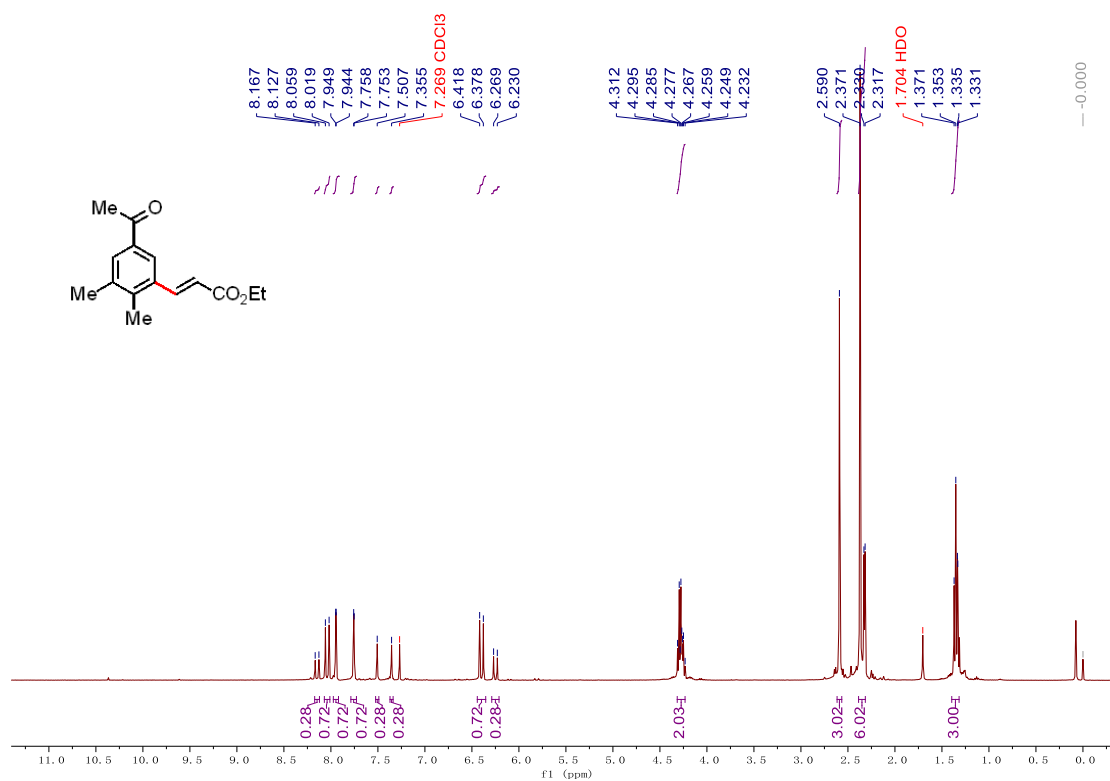
¹H and ¹³C NMR spectra of compound **2h_{mono}**



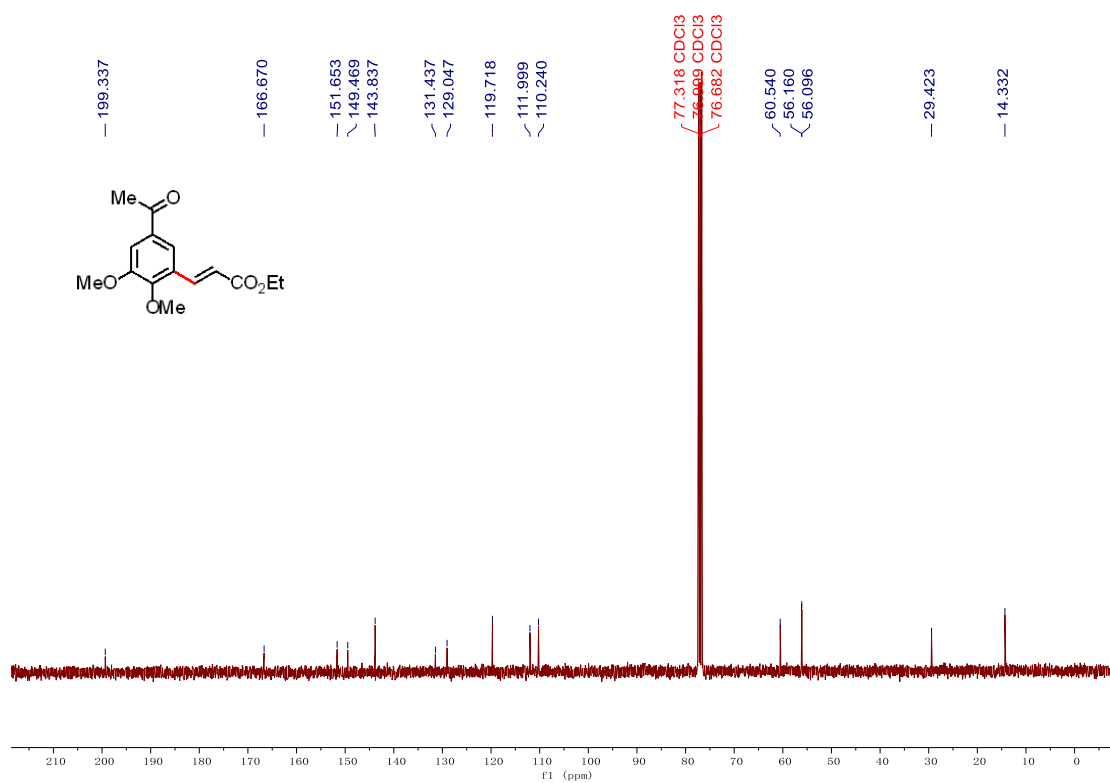
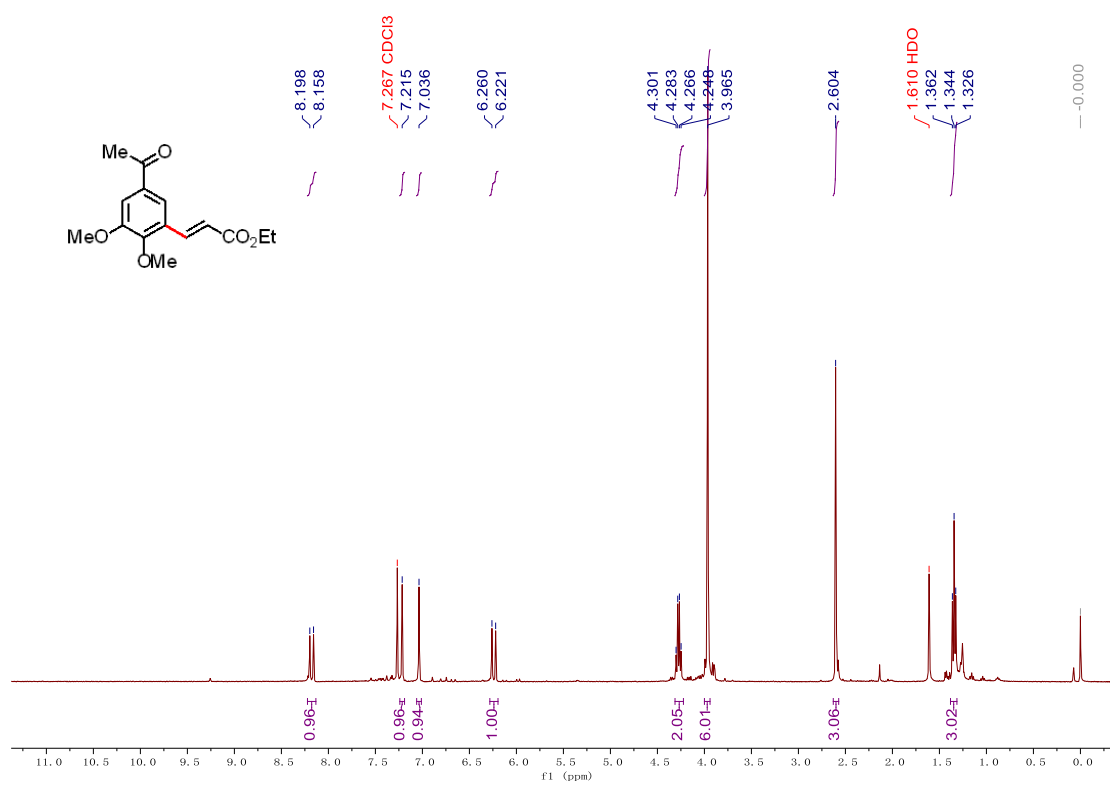
¹H and ¹³C NMR spectra of compound **2h_{di}**



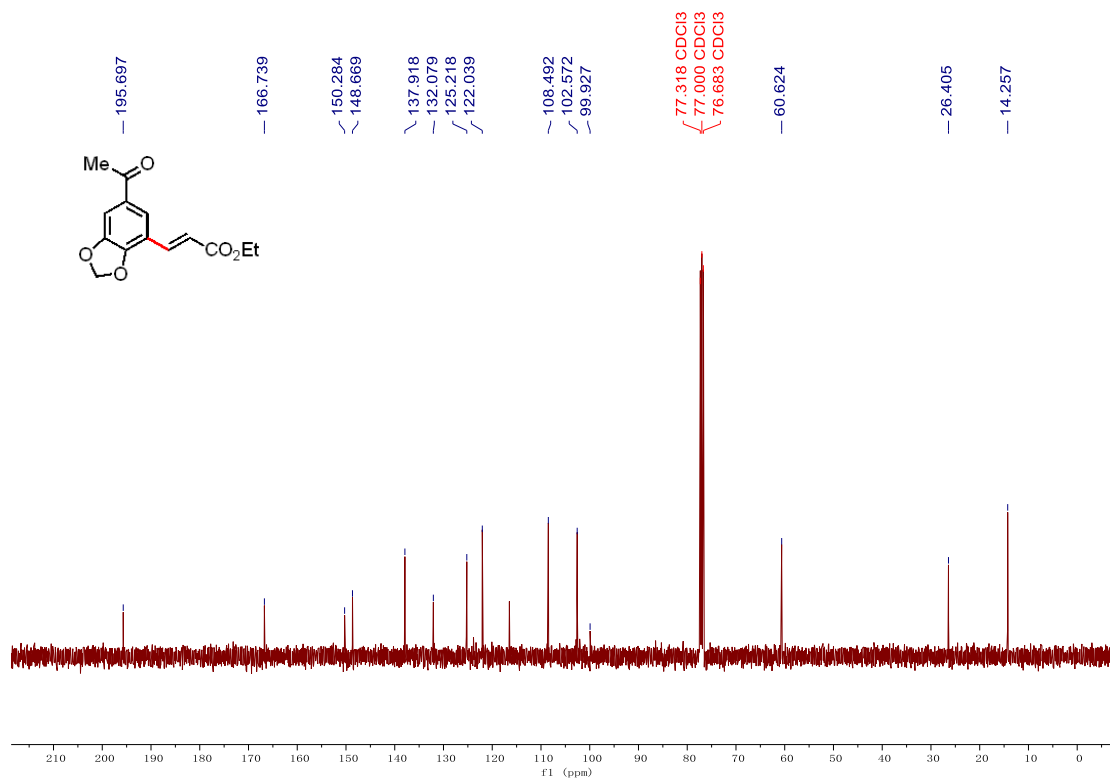
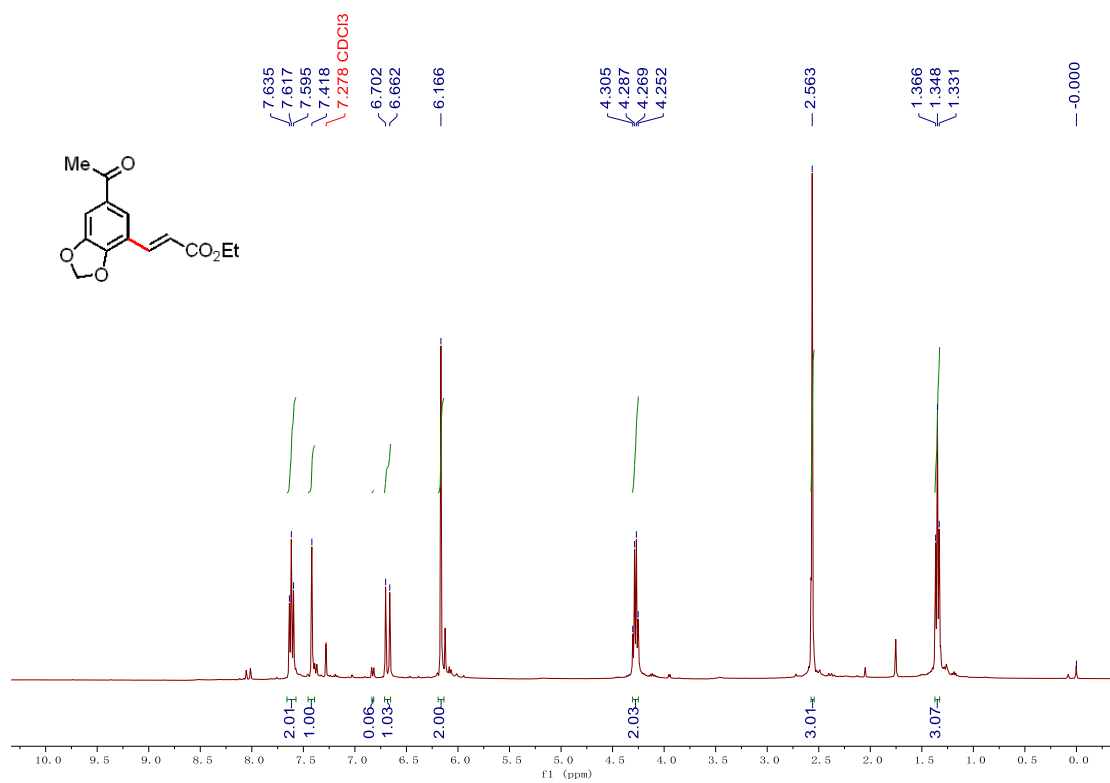
¹H and ¹³C NMR spectra of compound **2i**



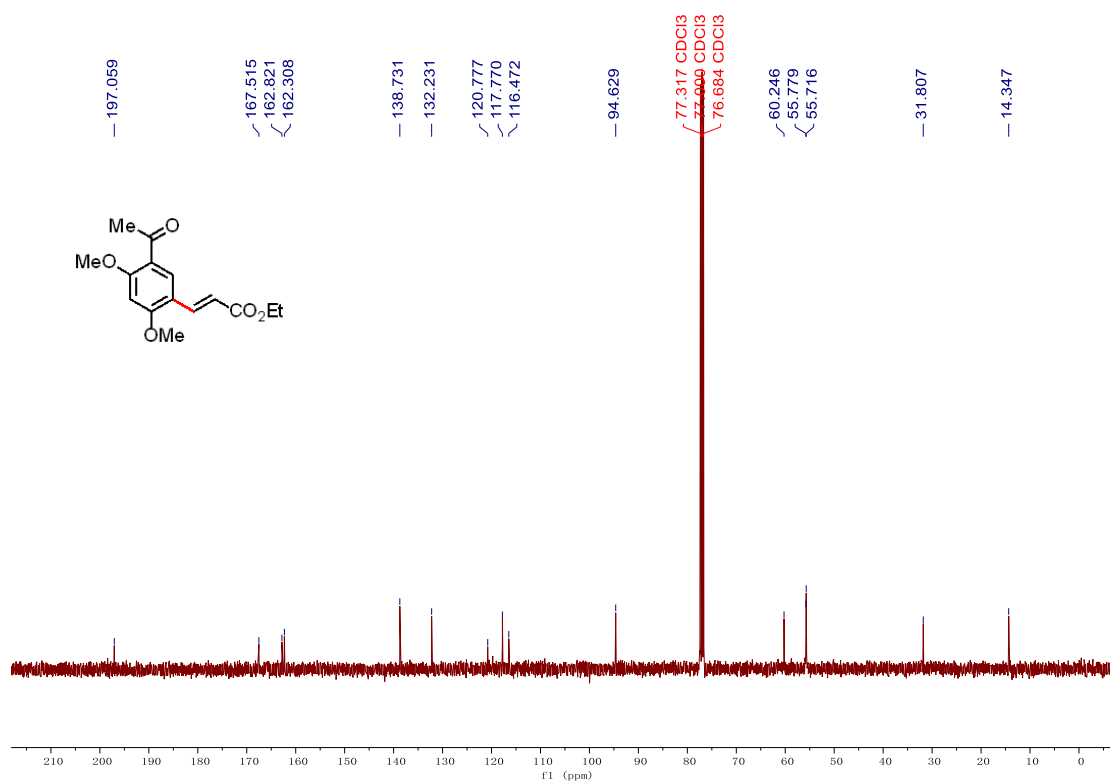
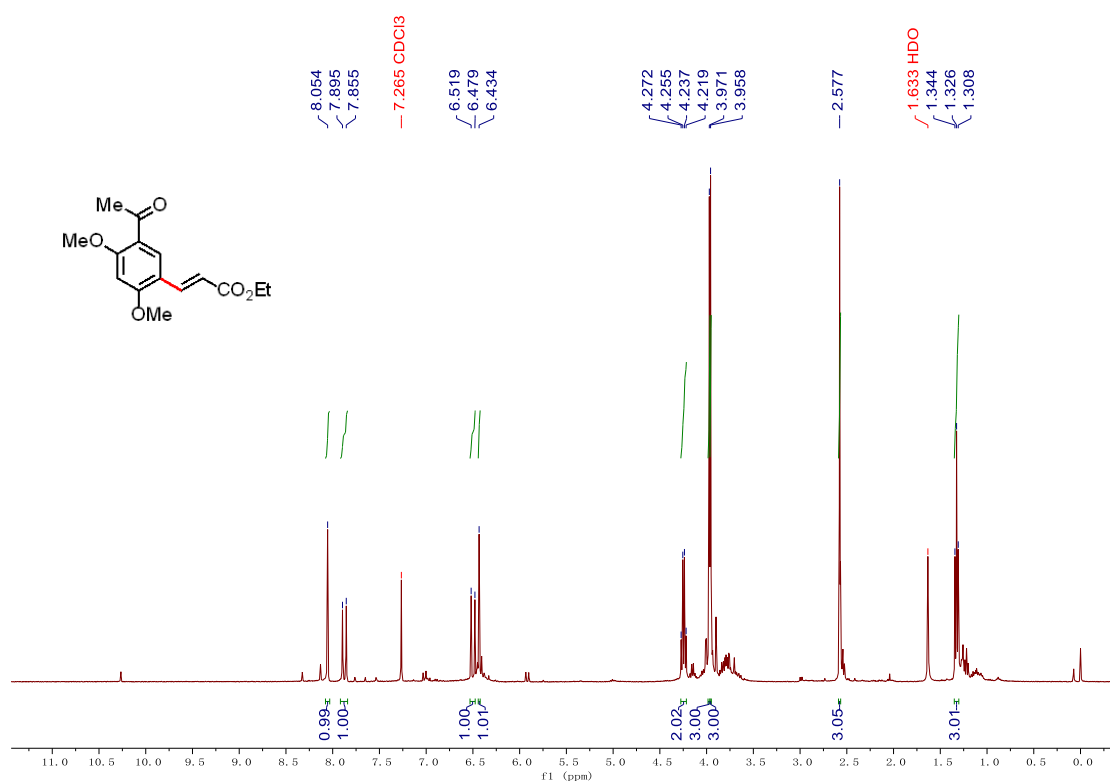
¹H and ¹³C NMR spectra of compound 2j



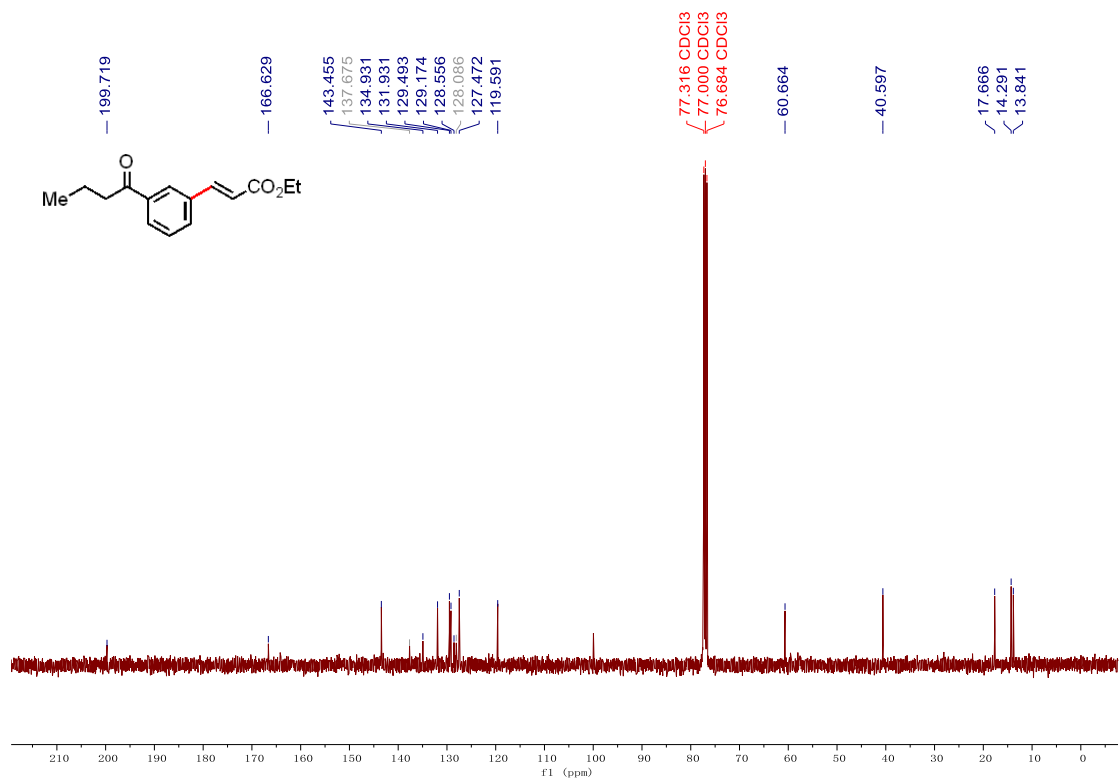
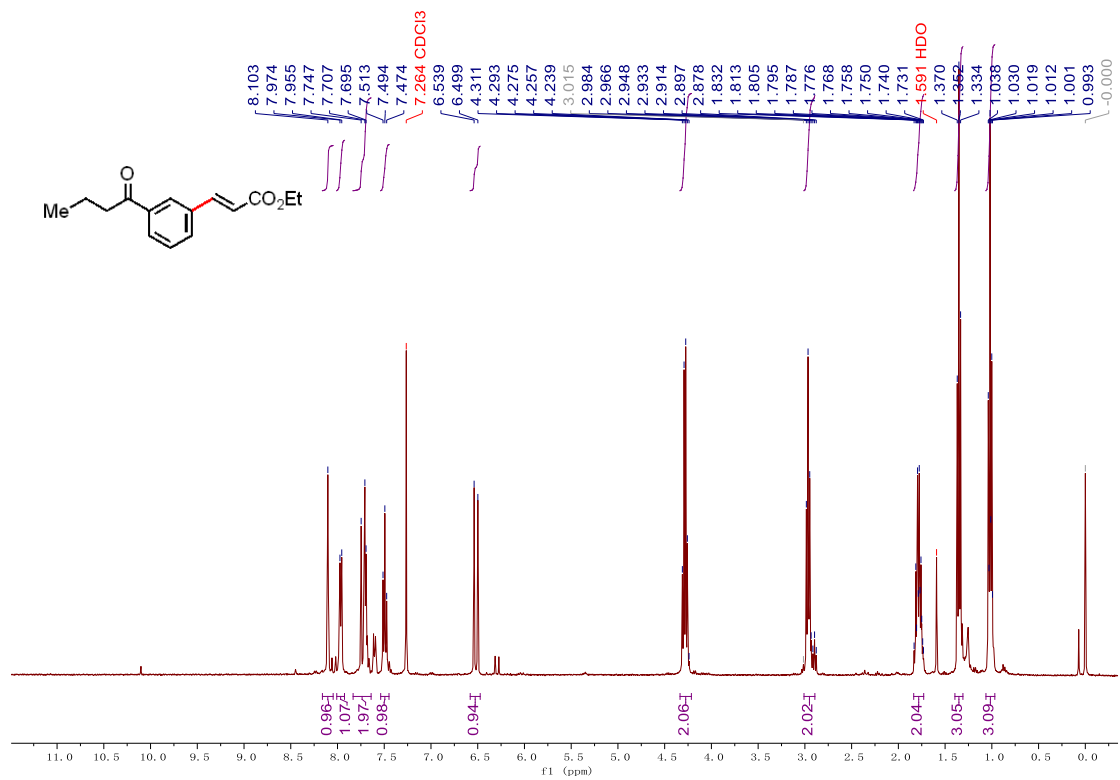
¹H and ¹³C NMR spectra of compound 2k



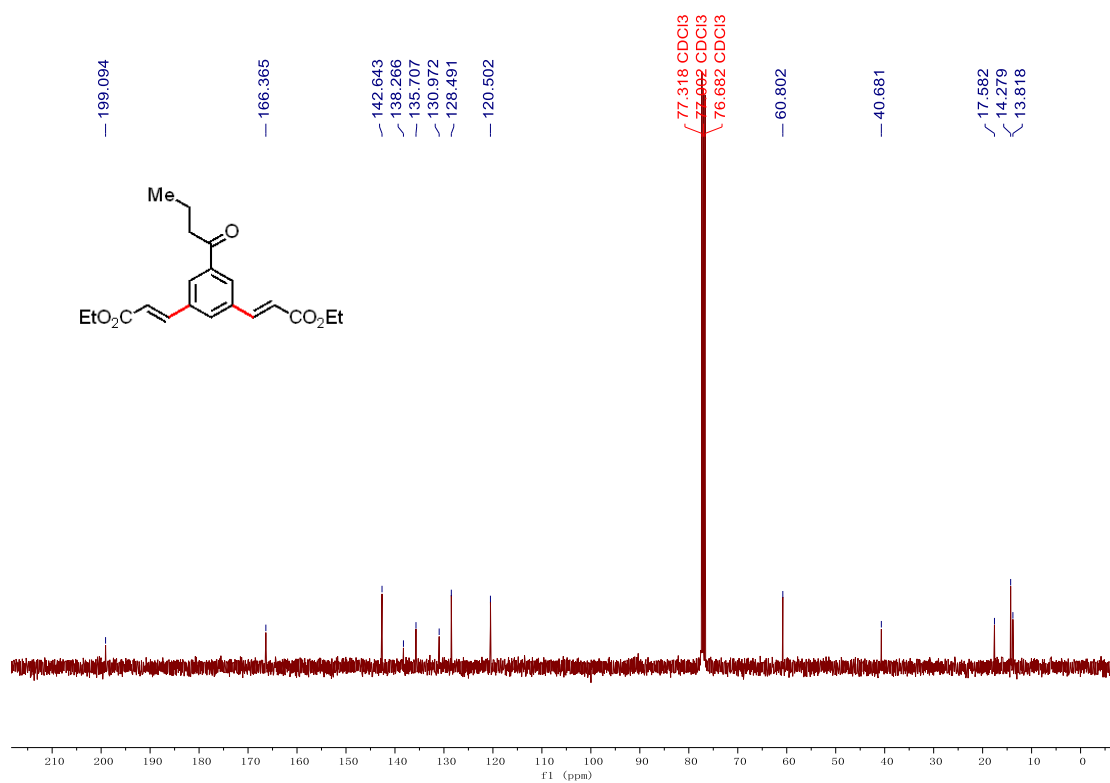
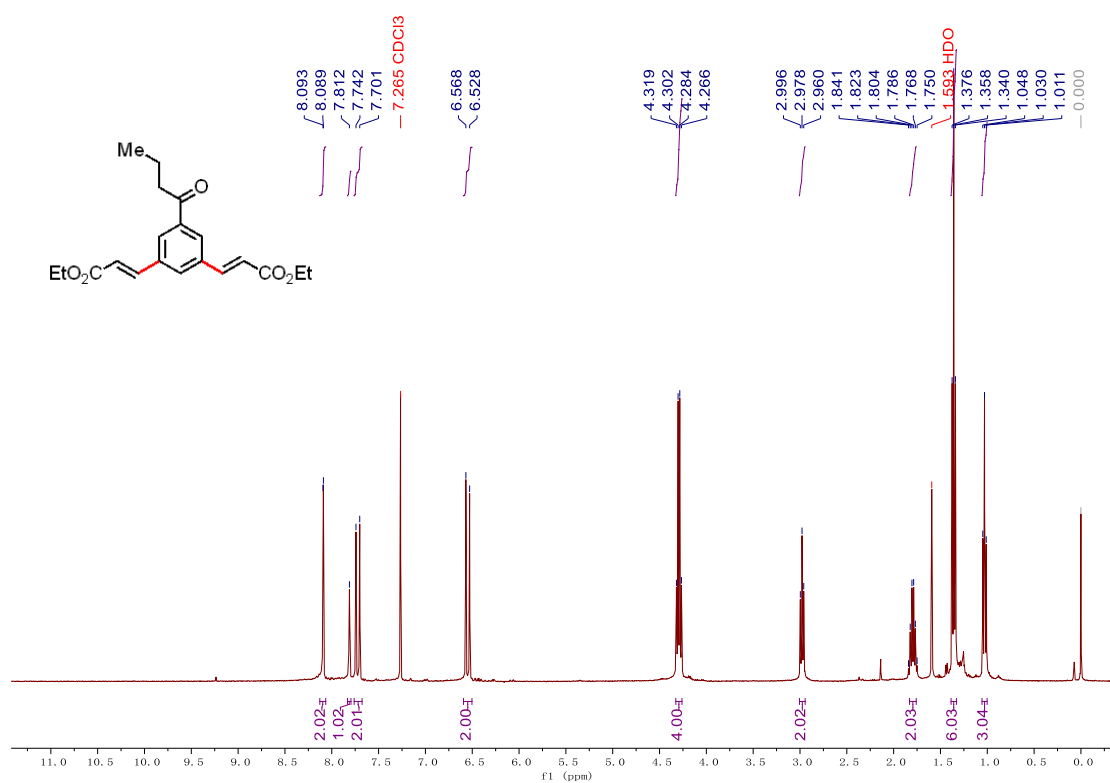
¹H and ¹³C NMR spectra of compound **21**



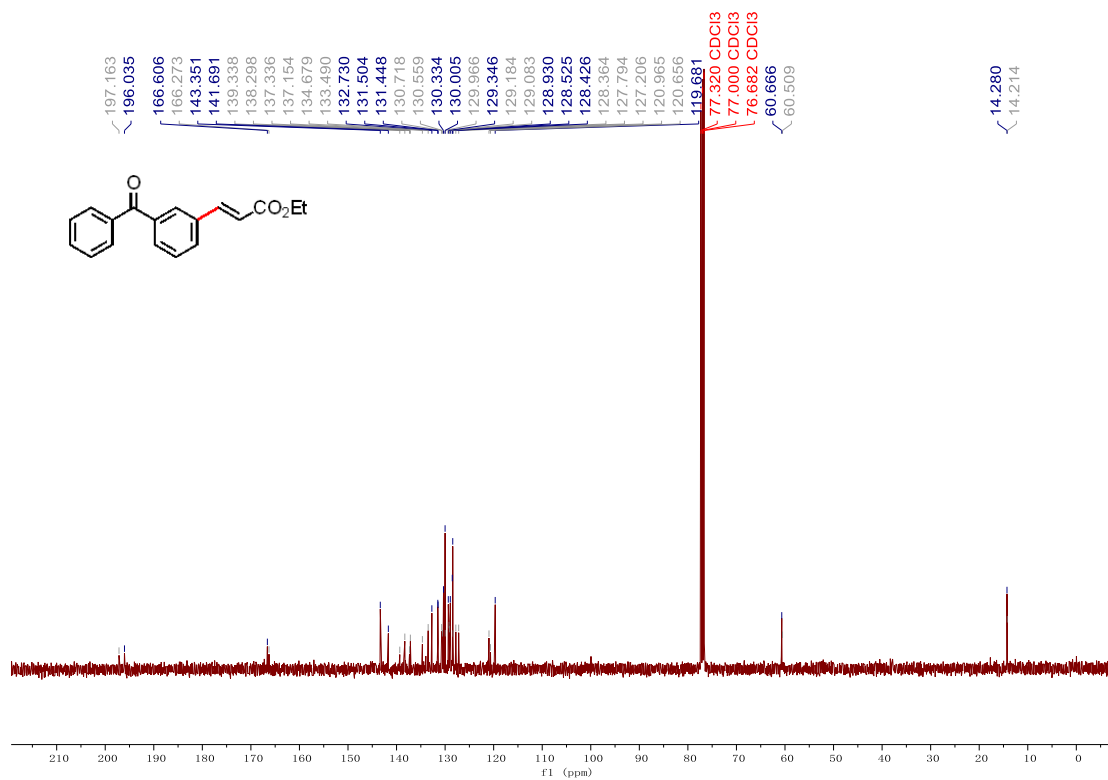
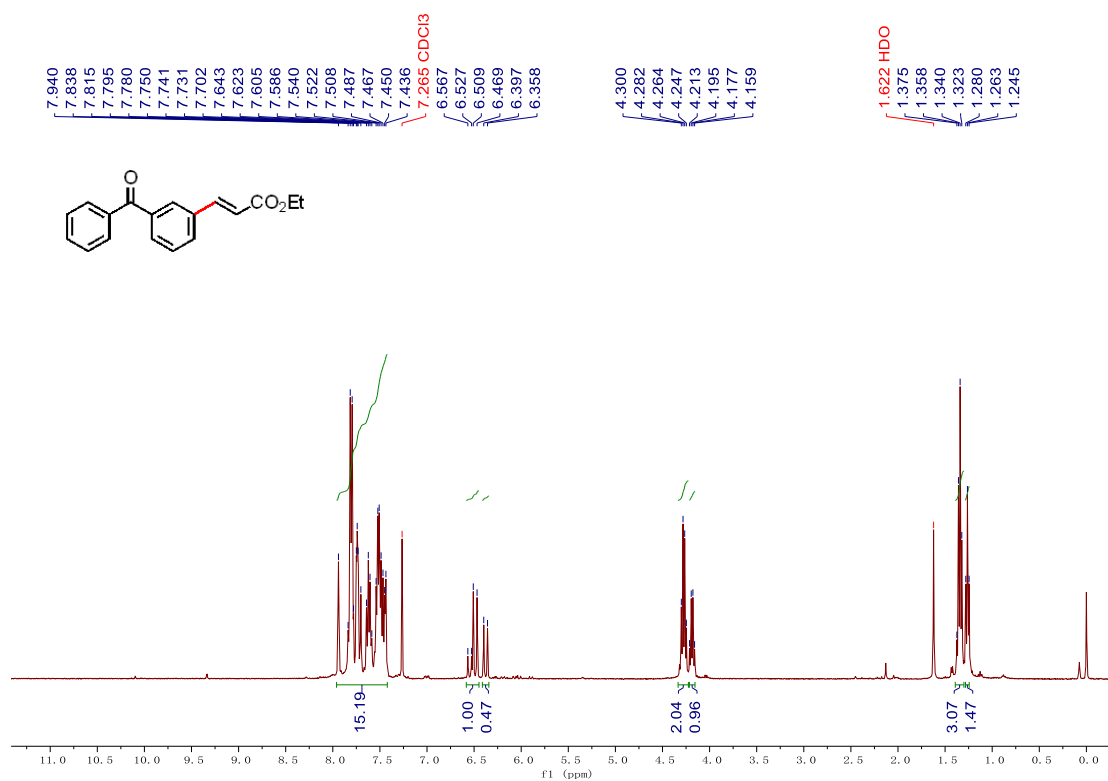
¹H and ¹³C NMR spectra of compound **2m**



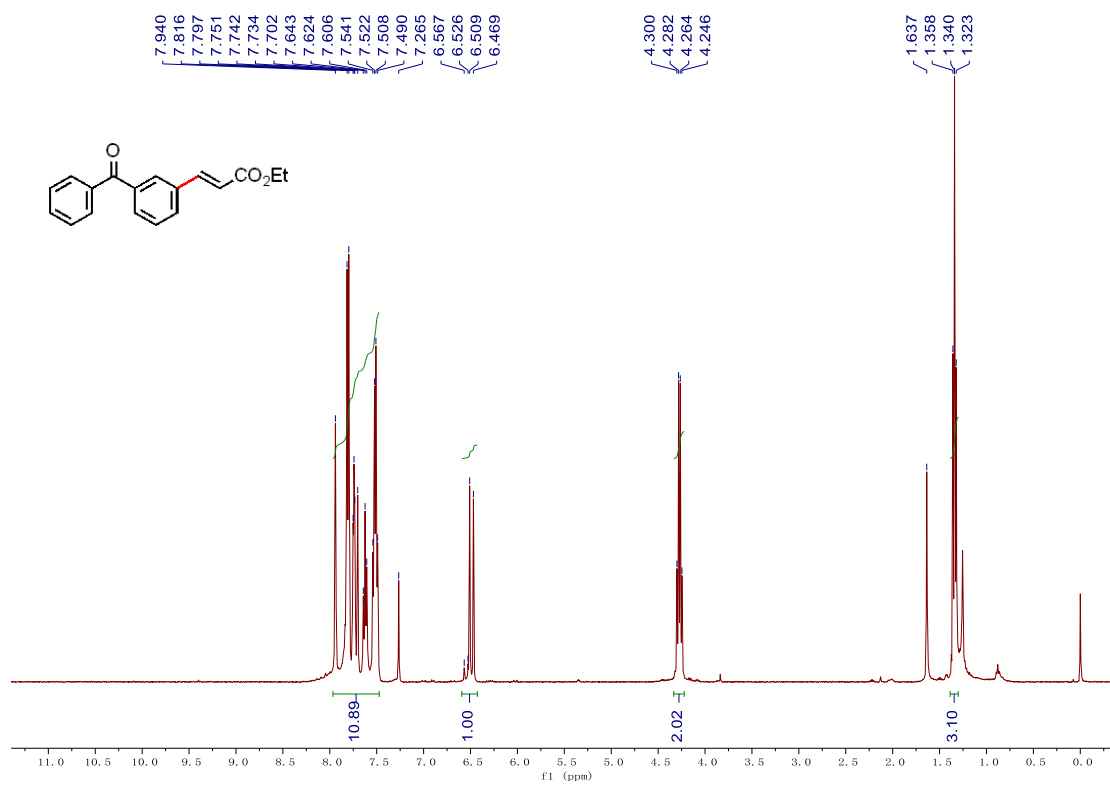
¹H and ¹³C NMR spectra of compound **2n_{mono}**



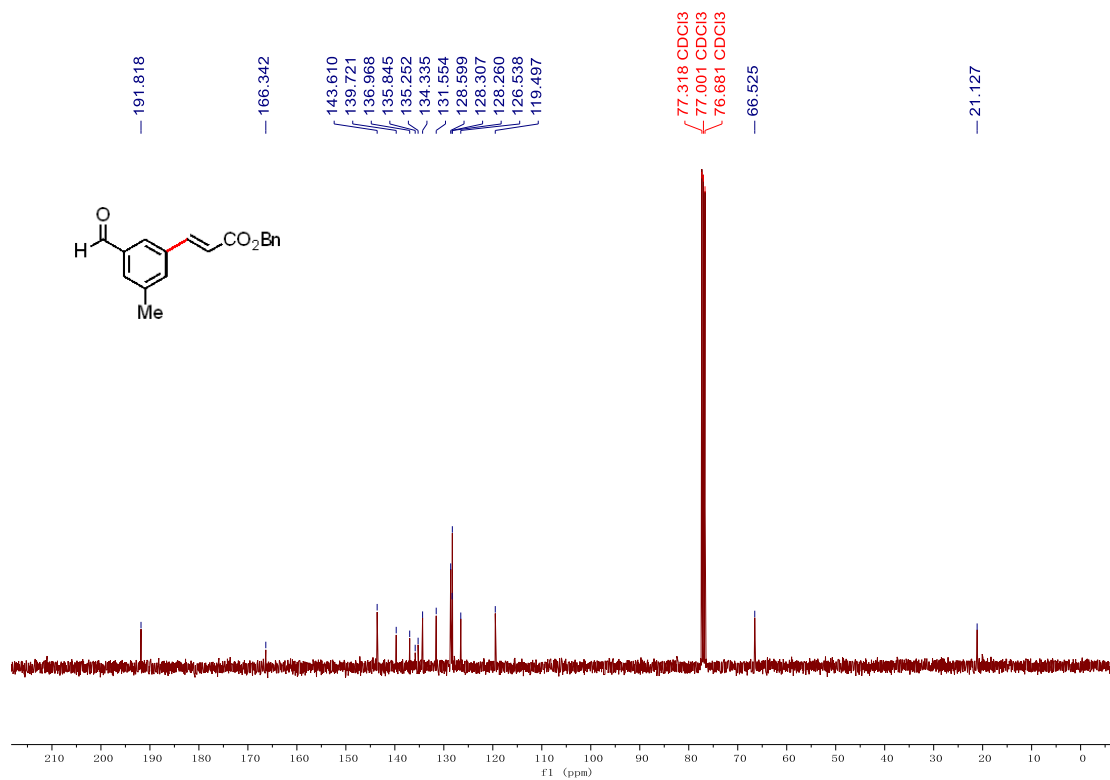
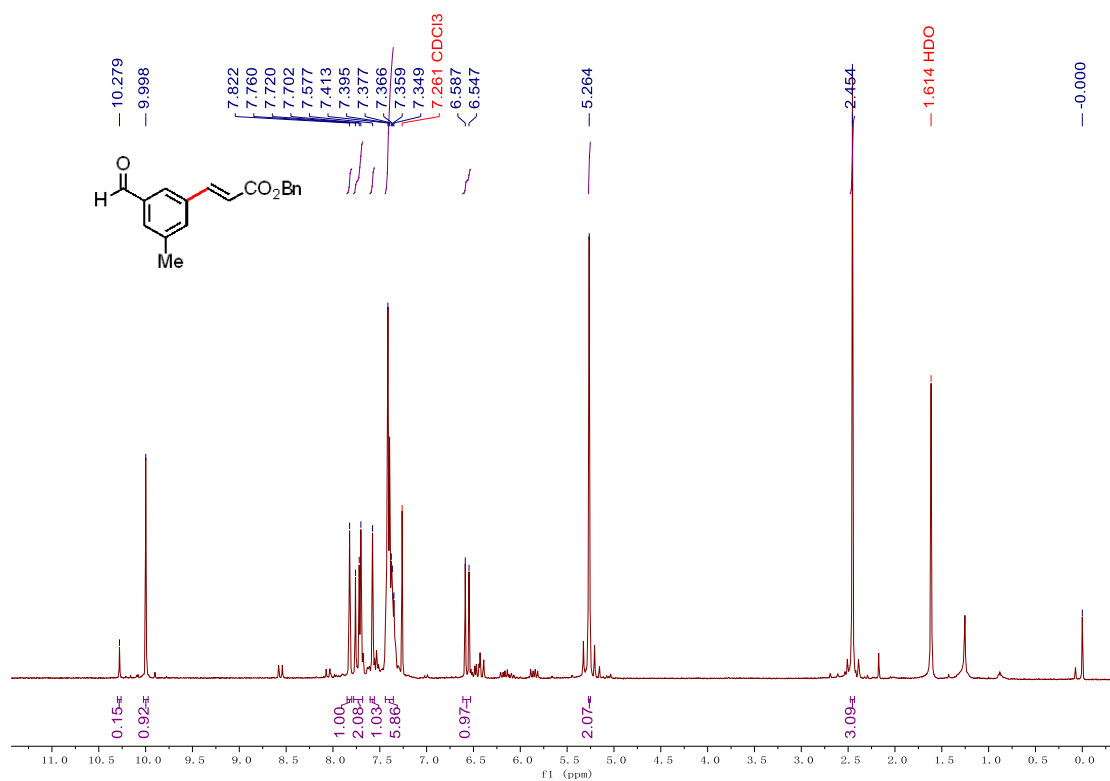
¹H and ¹³C NMR spectra of compound **2n_{di}**



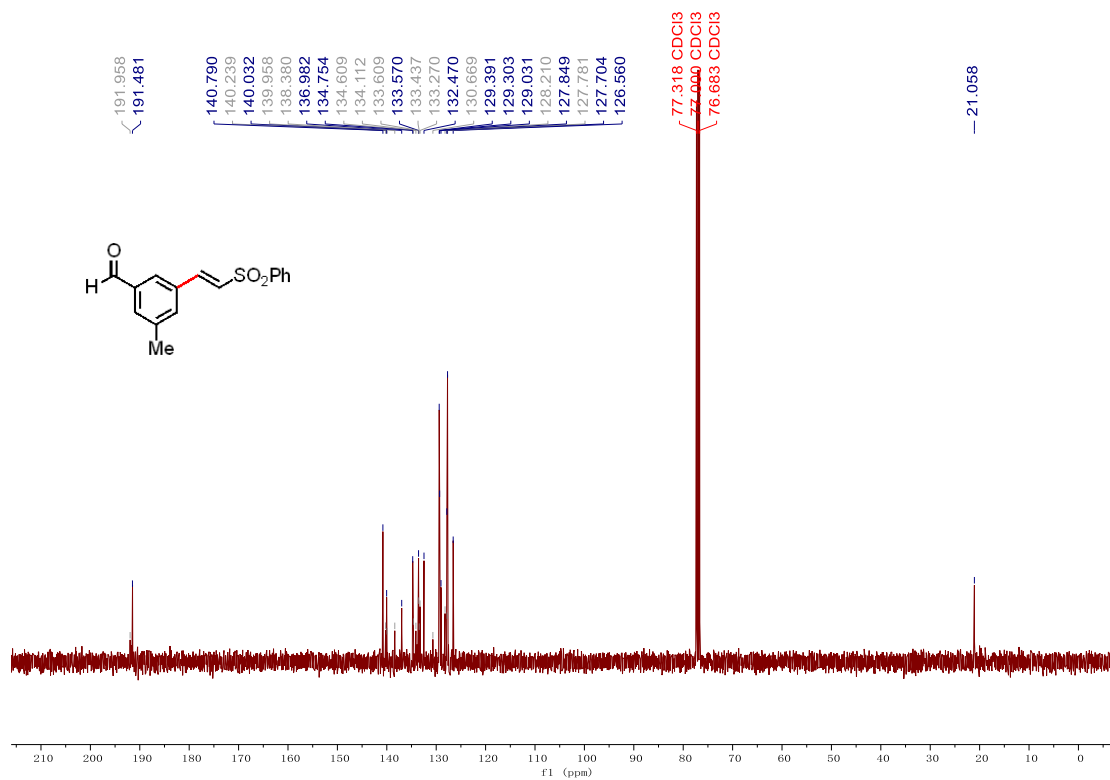
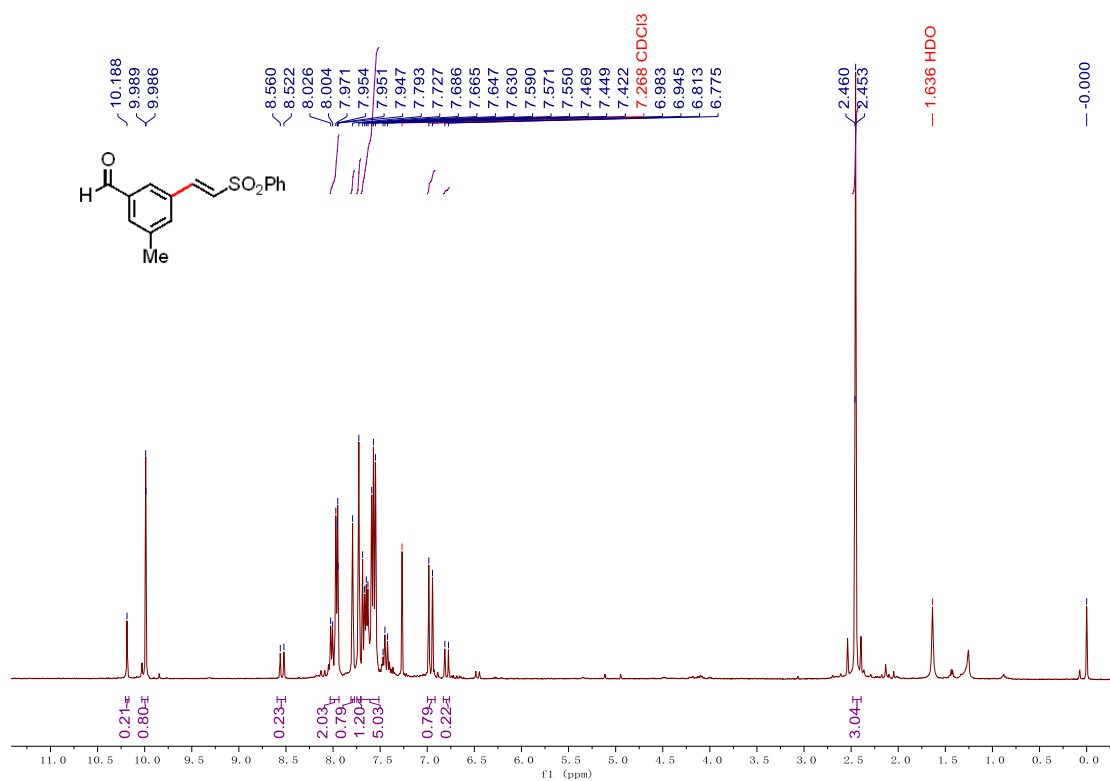
¹H and ¹³C NMR spectra of compound 2o



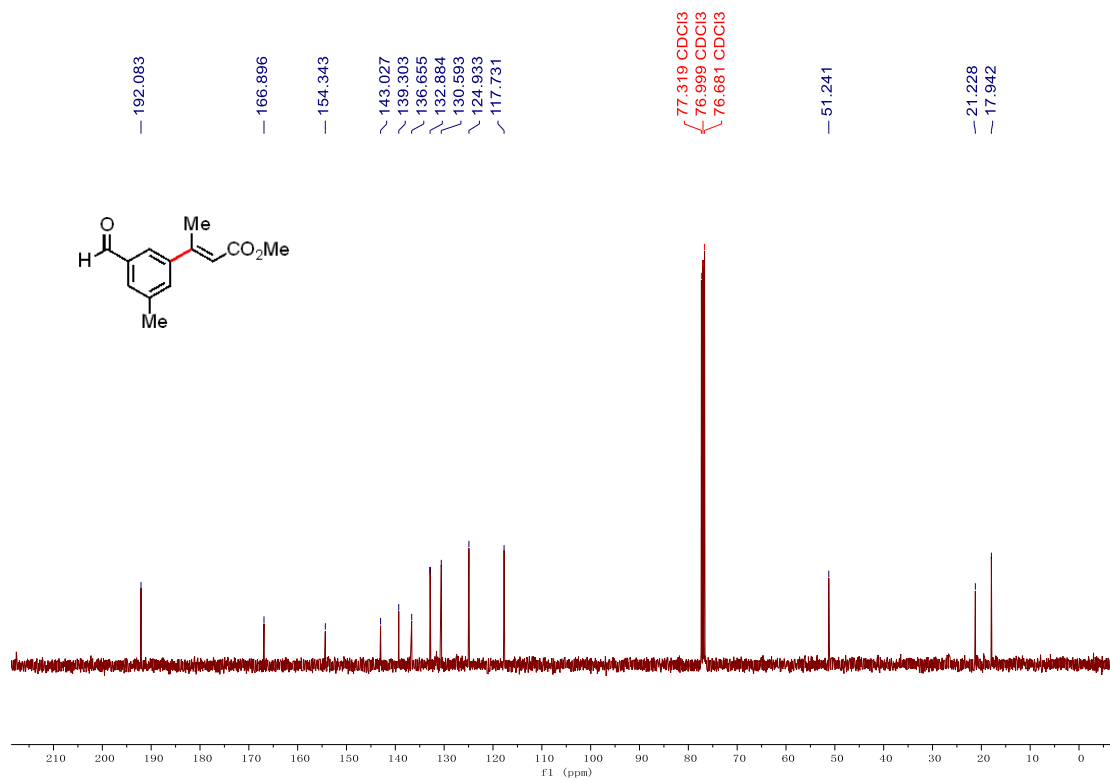
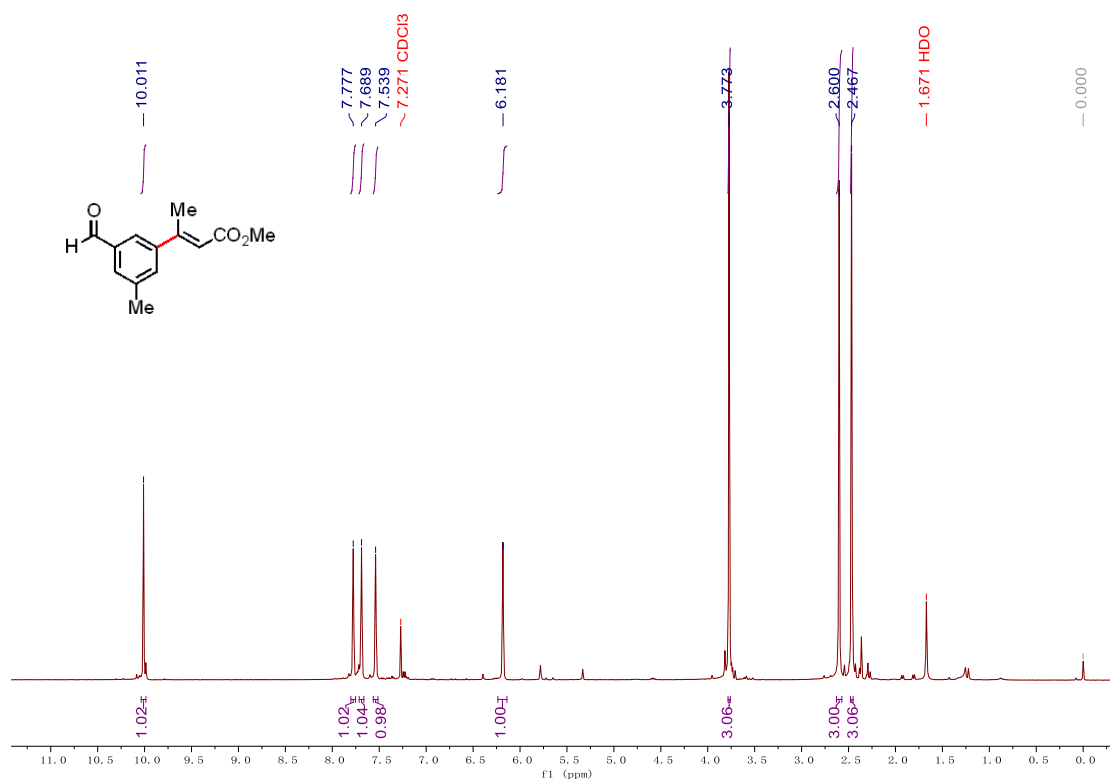
¹H NMR spectra of pure sample for compound **2o**



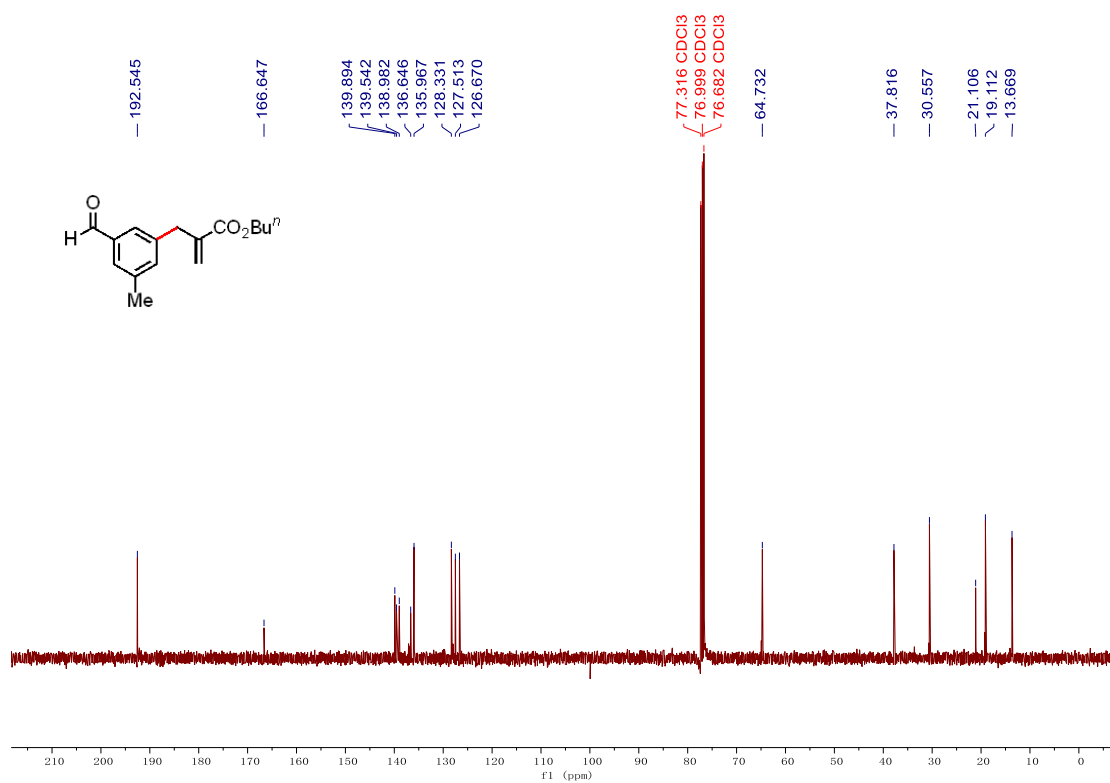
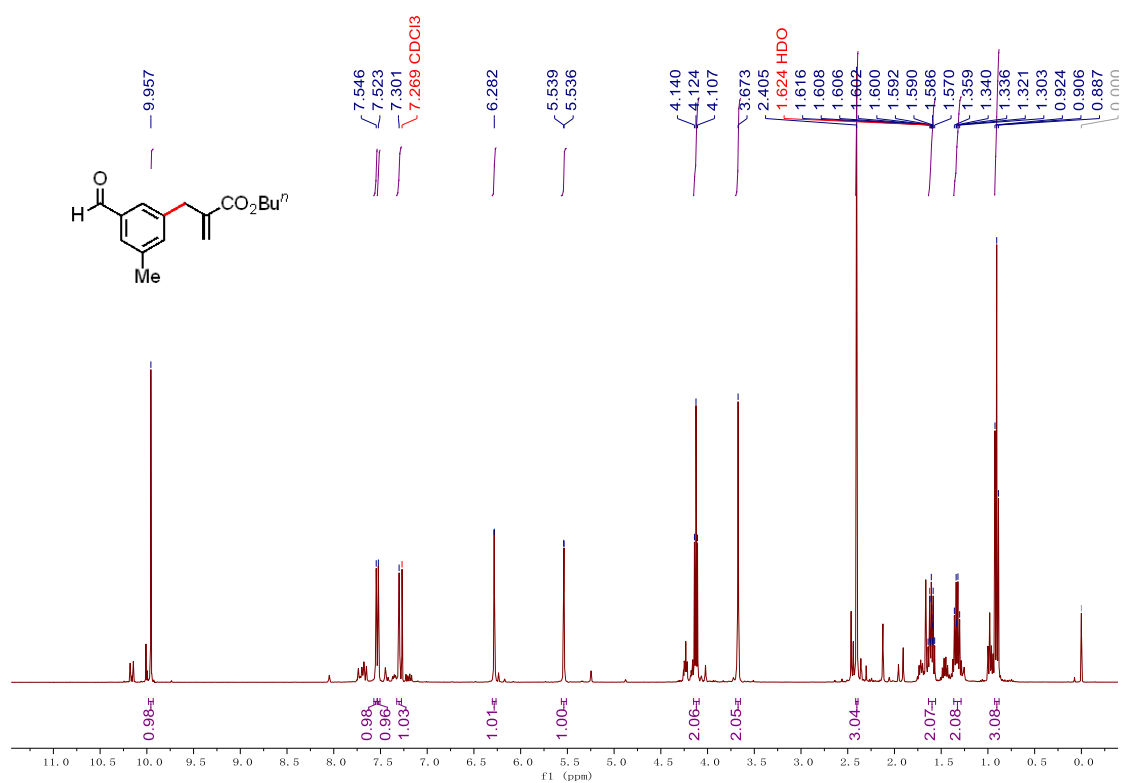
¹H and ¹³C NMR spectra of compound 3a



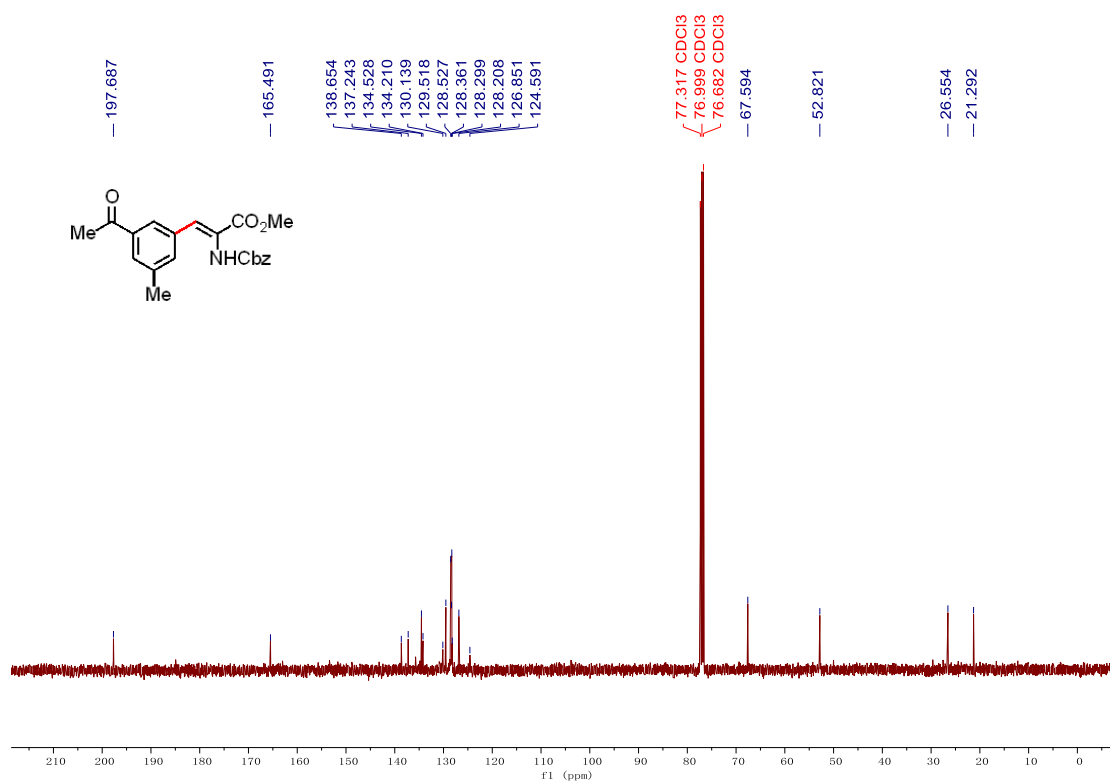
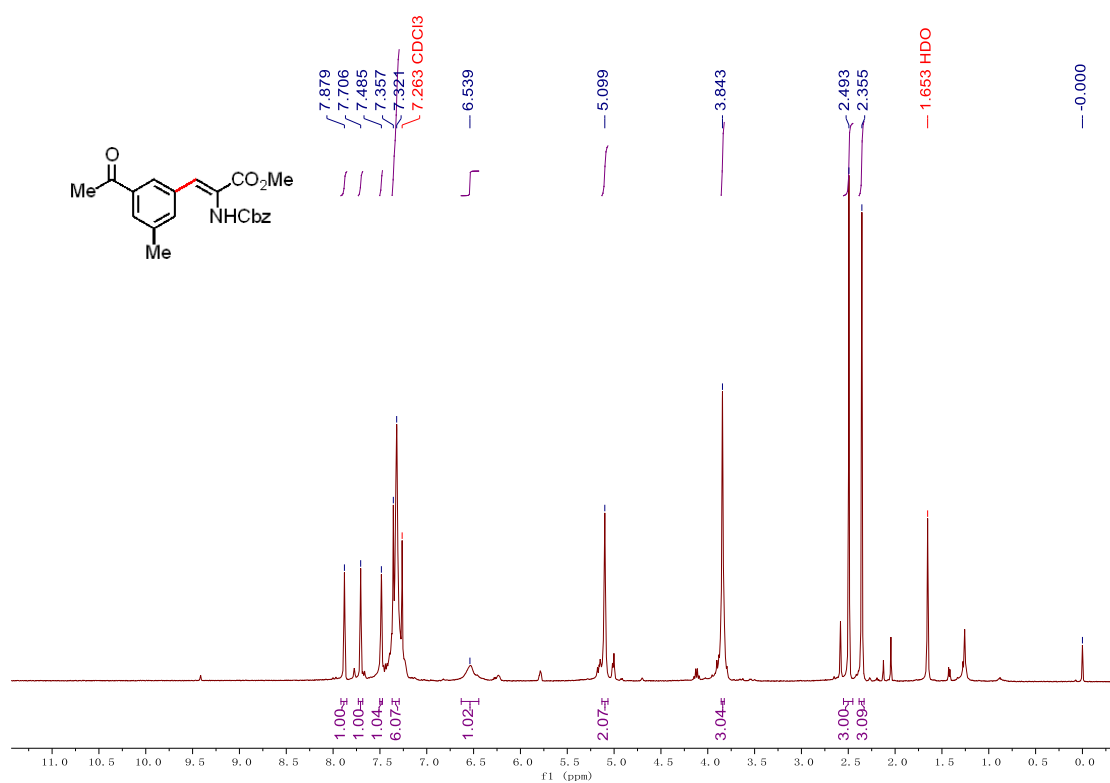
¹H and ¹³C NMR spectra of compound 3b



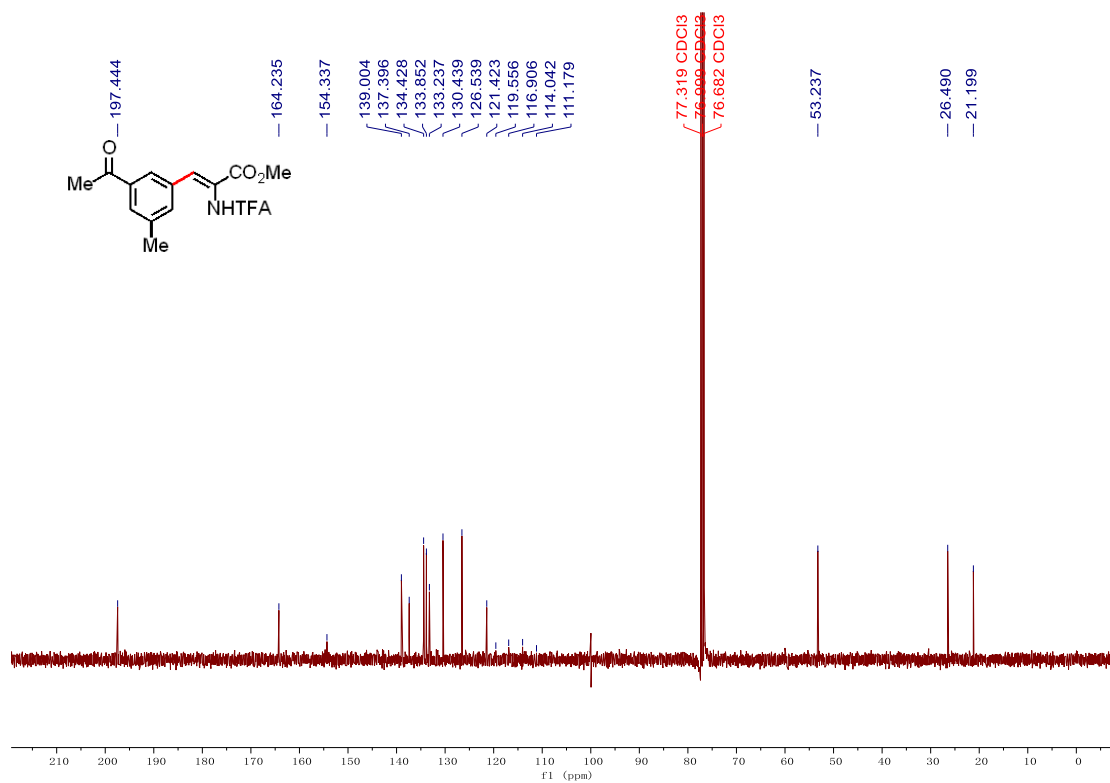
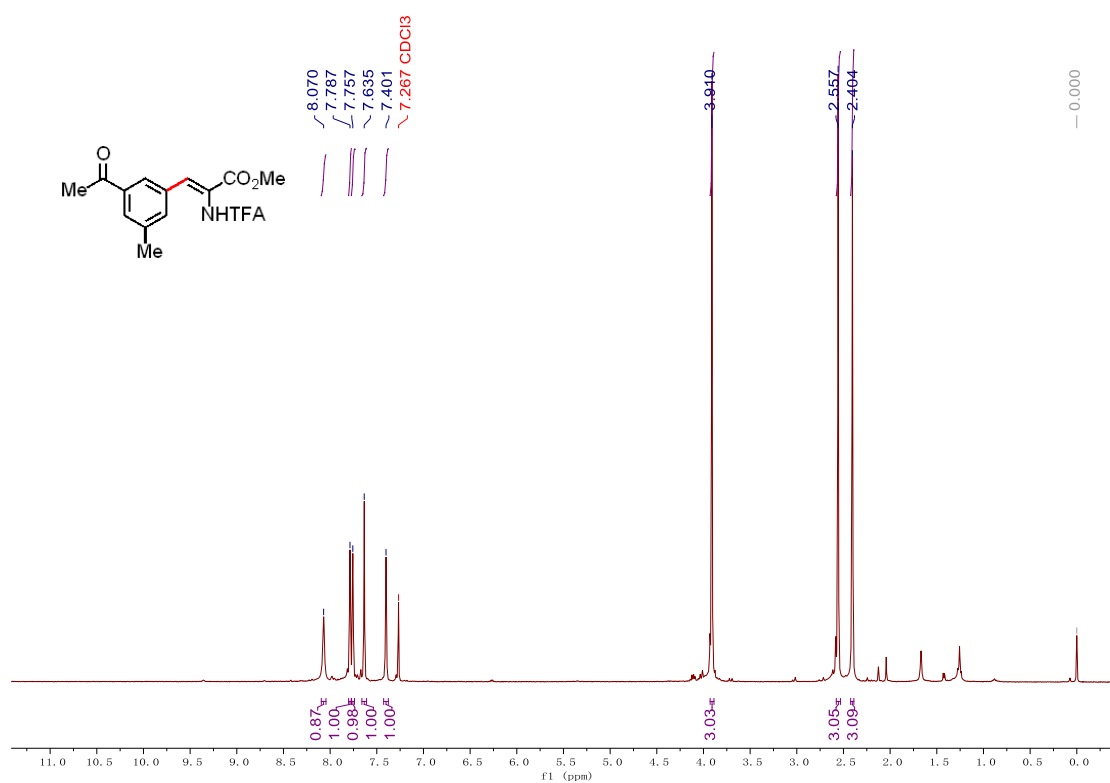
¹H and ¹³C NMR spectra of compound 3c



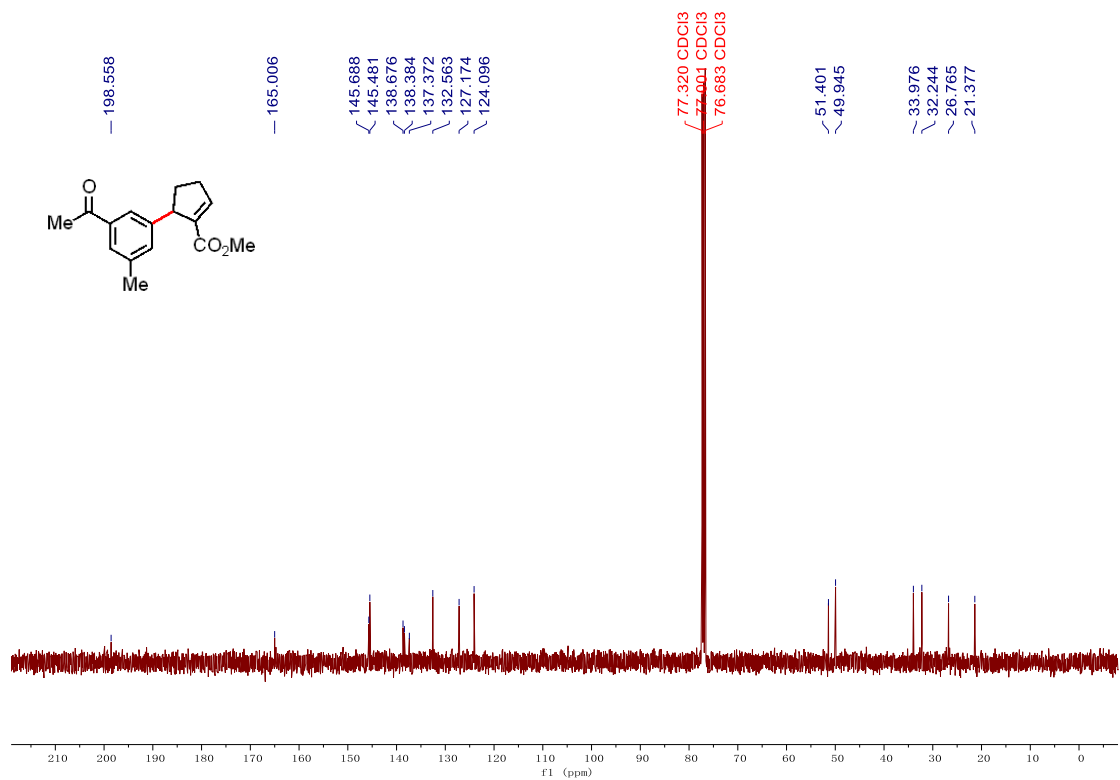
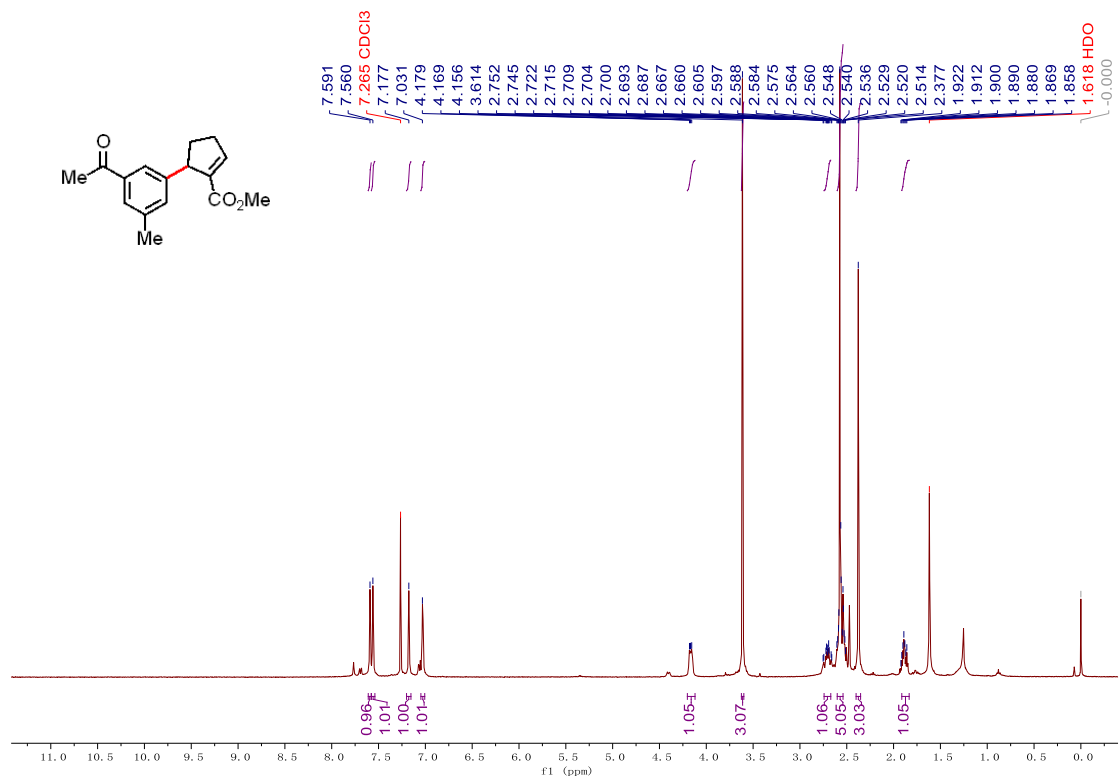
^1H and ^{13}C NMR spectra of compound **3d**



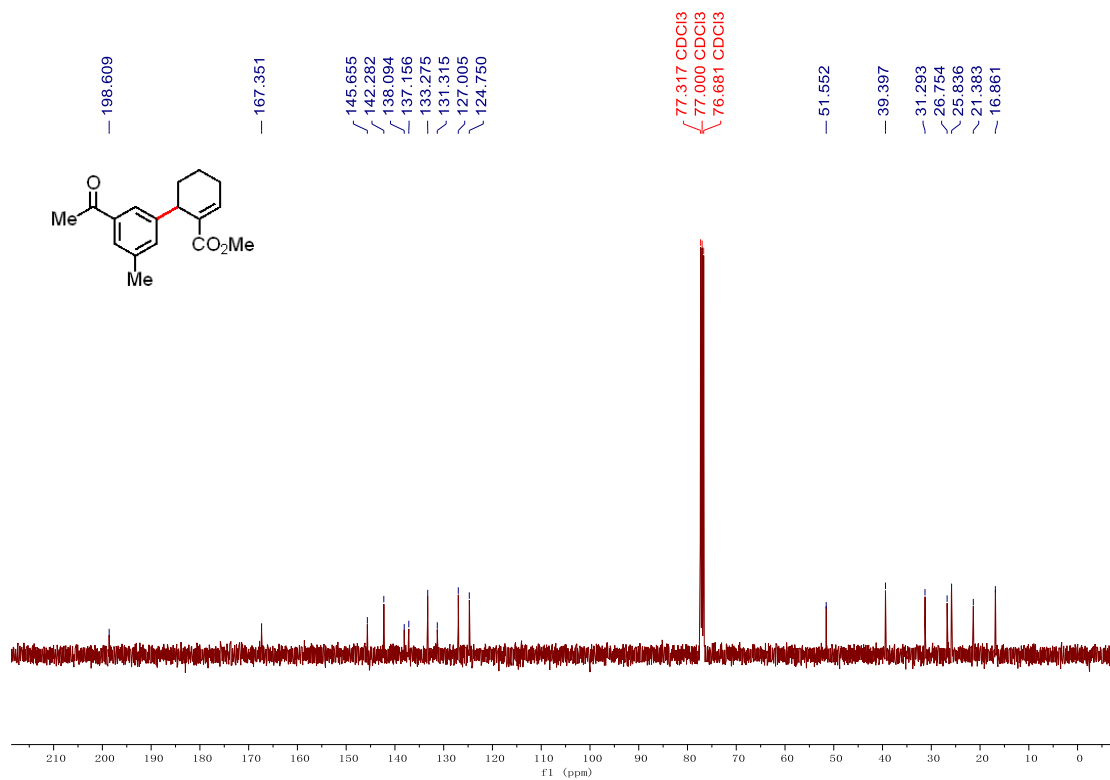
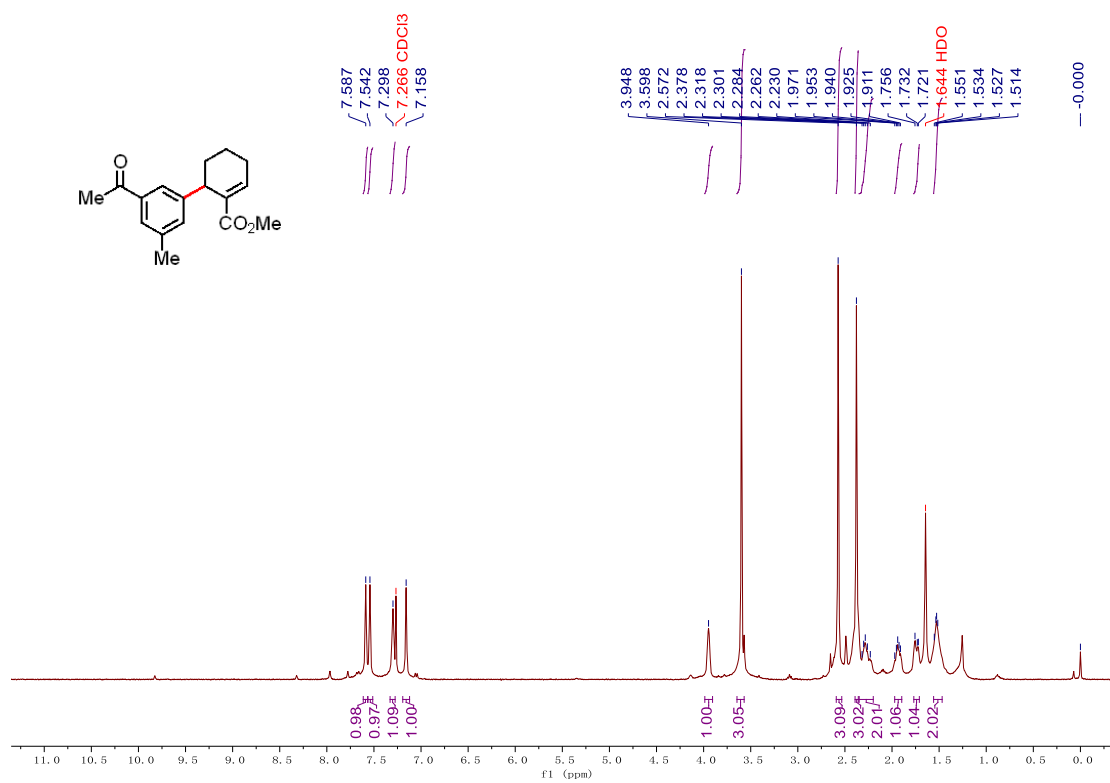
^1H and ^{13}C NMR spectra of compound **3e**



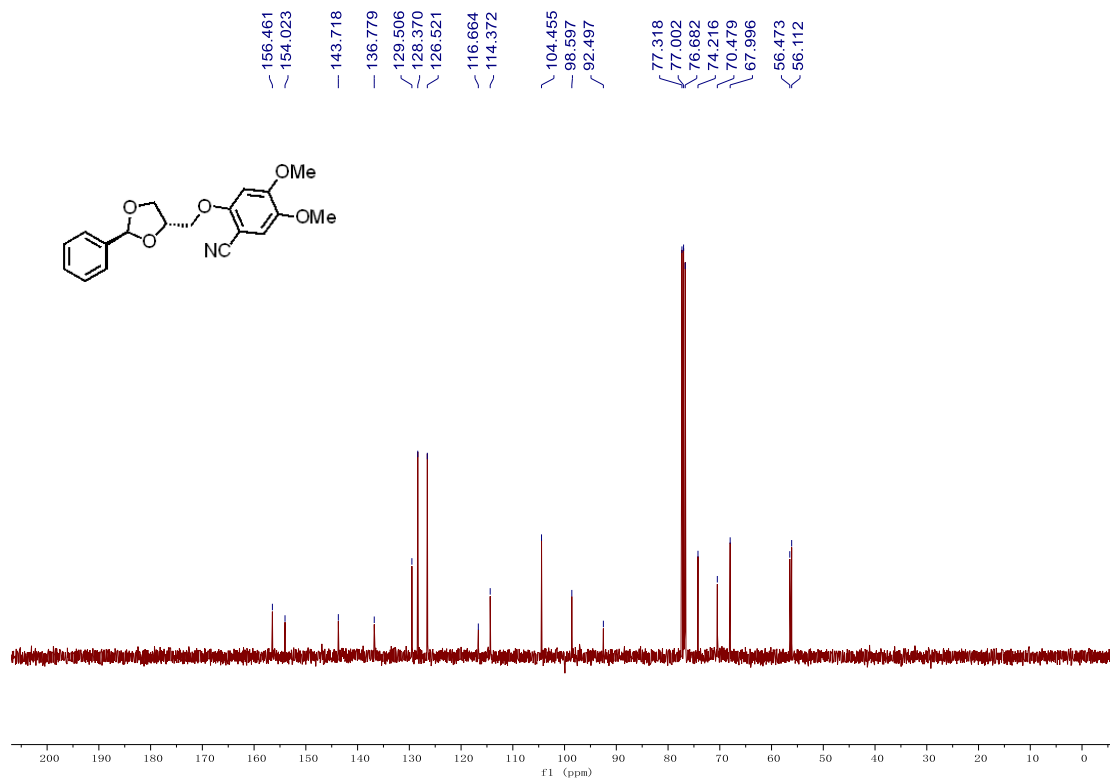
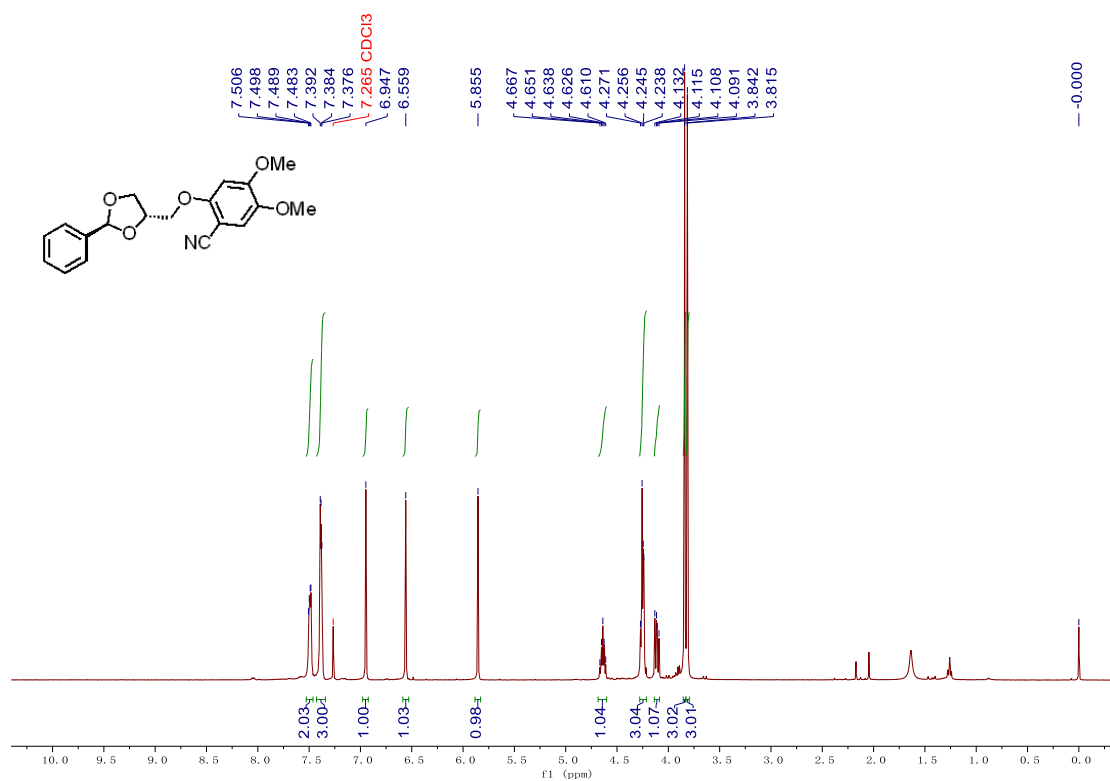
^1H and ^{13}C NMR spectra of compound **3f**



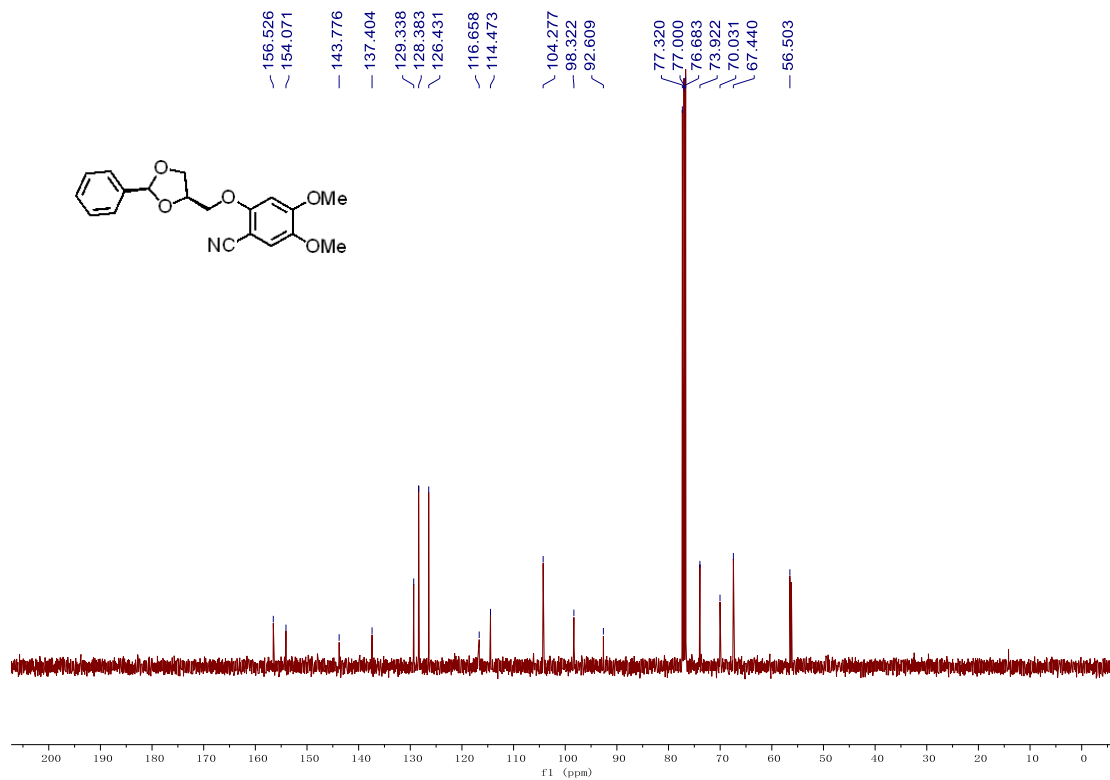
¹H and ¹³C NMR spectra of compound 3g



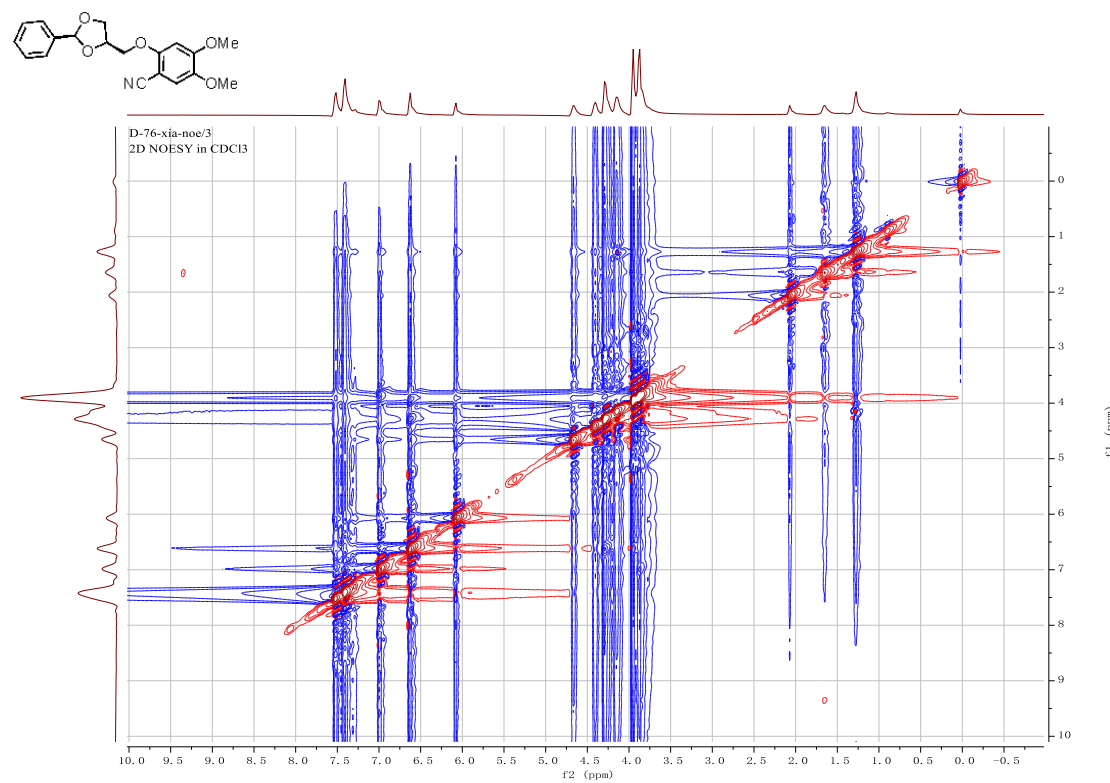
¹H and ¹³C NMR spectra of compound 3h



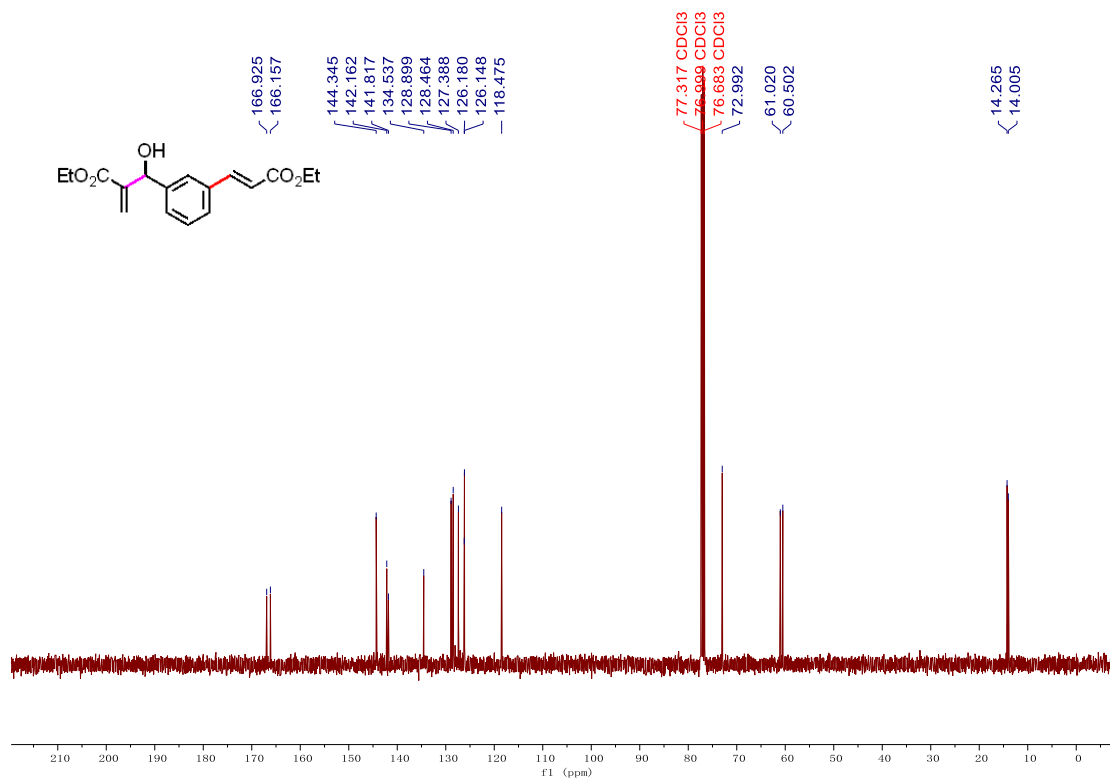
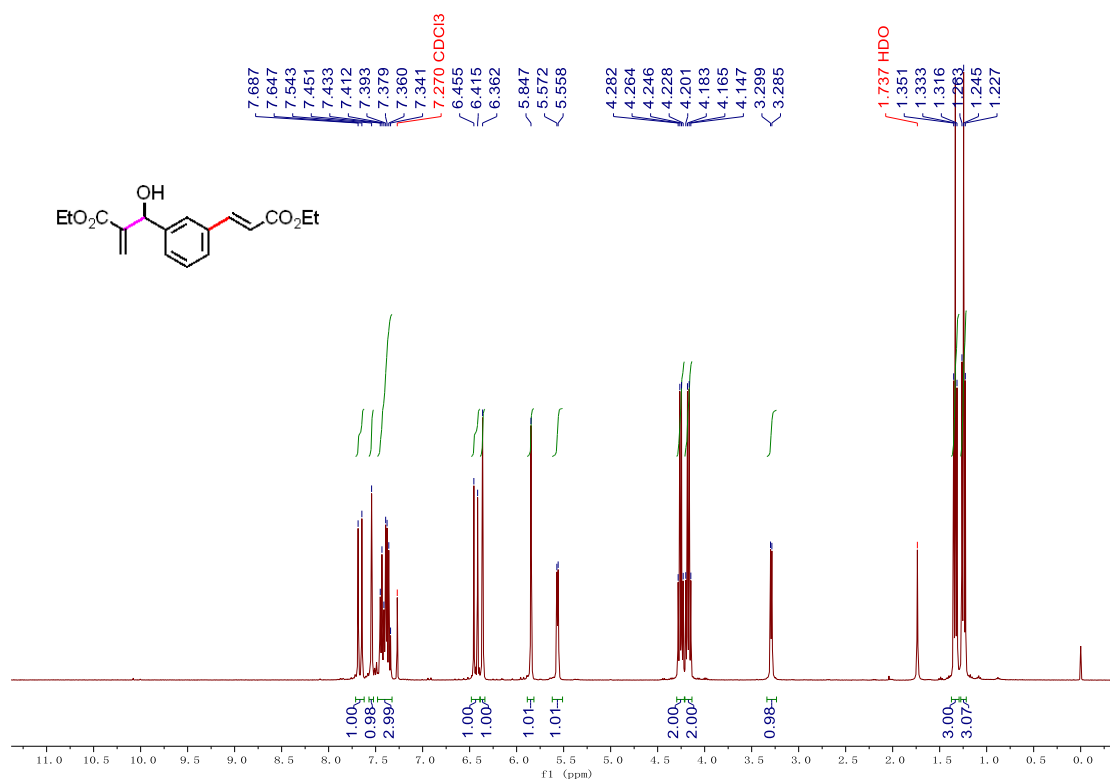
¹H and ¹³C NMR spectra of *anti*-diastereomer of acetal



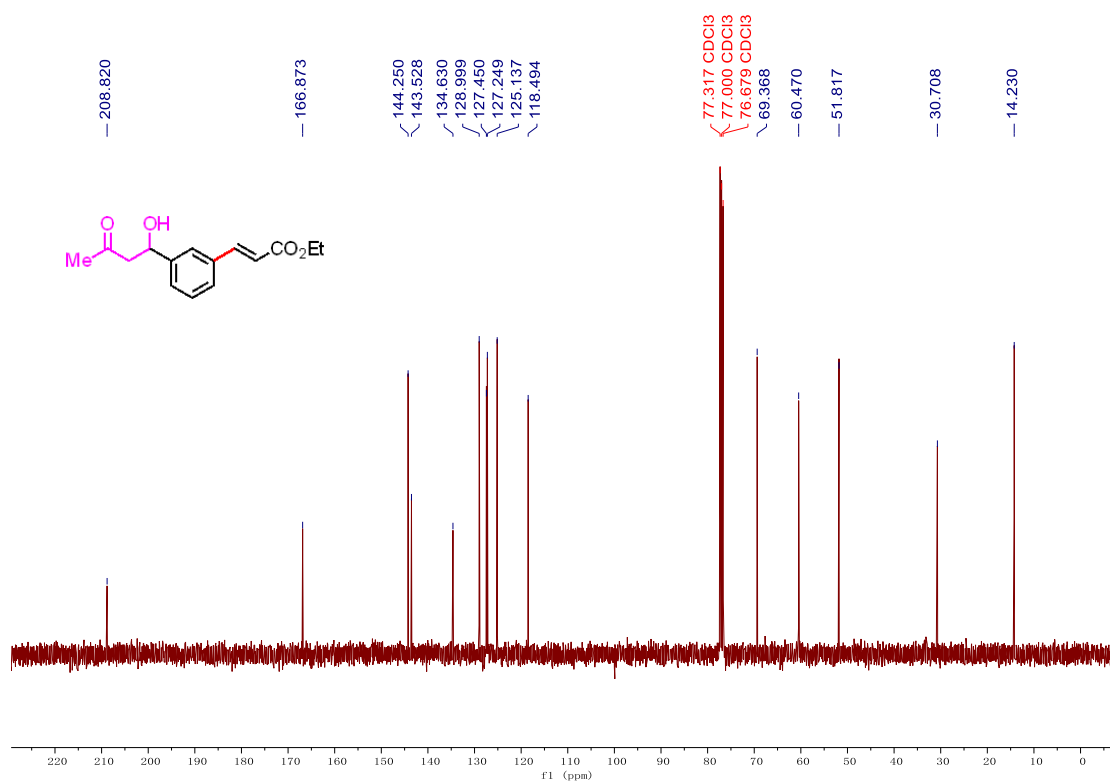
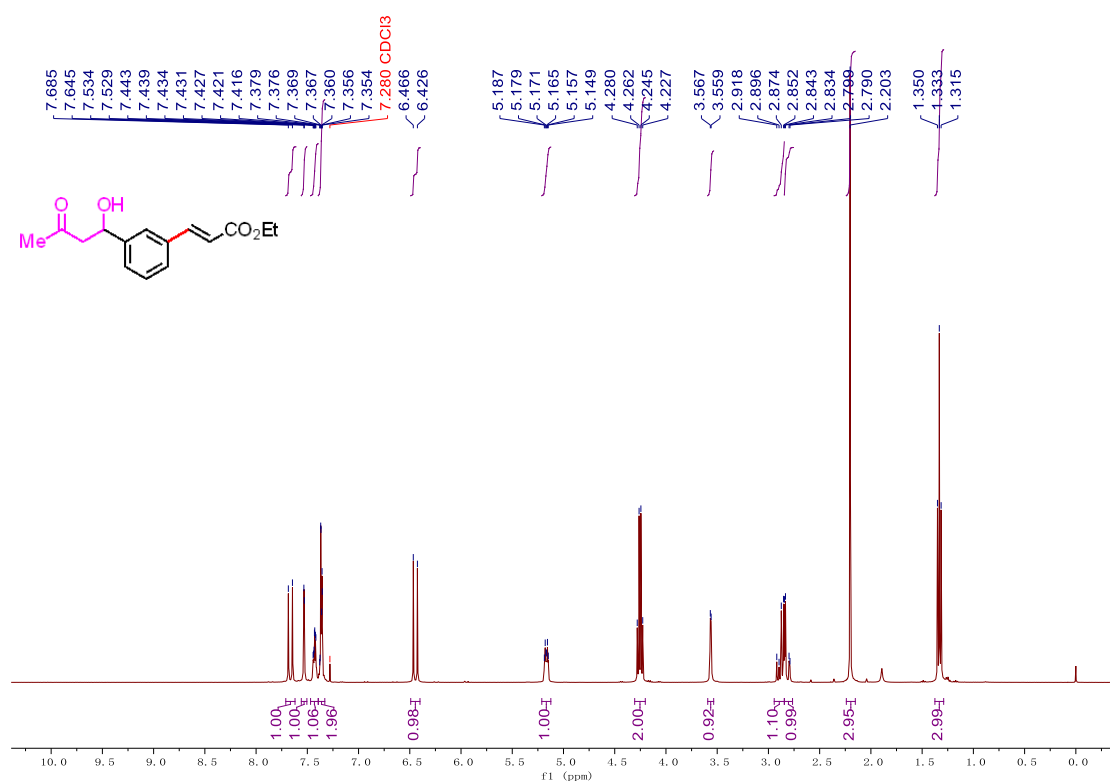
¹H and ¹³C NMR spectra of *anti*-diastereomer of acetal



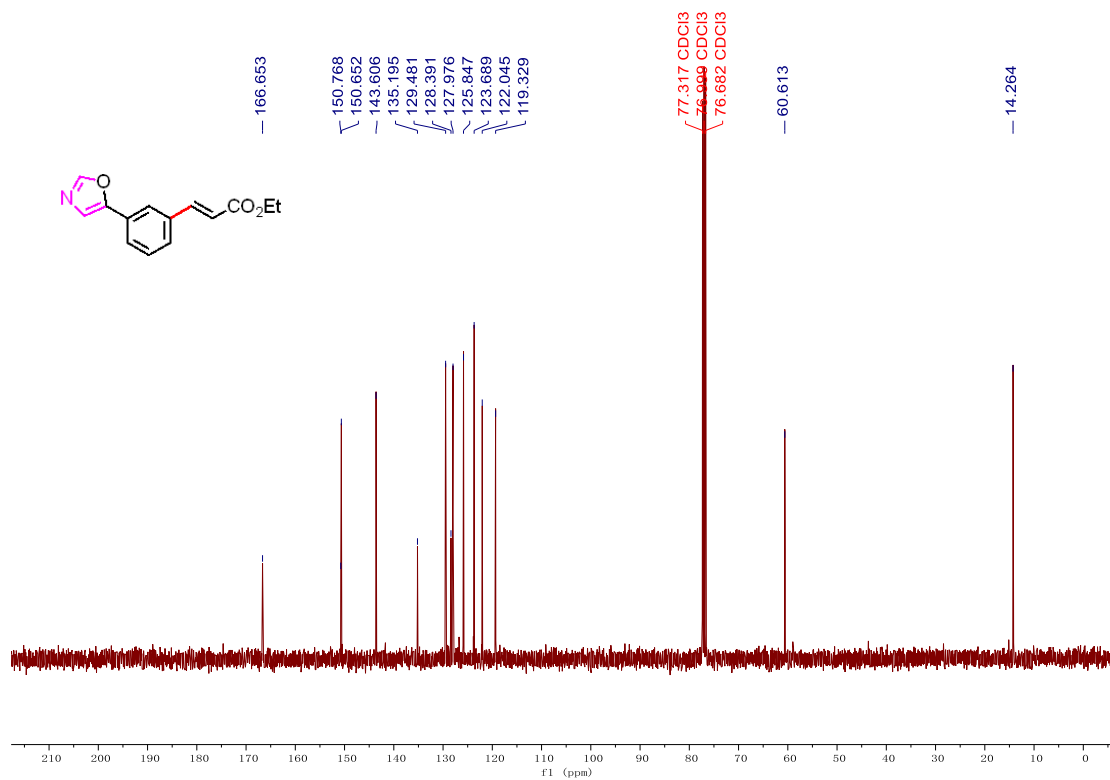
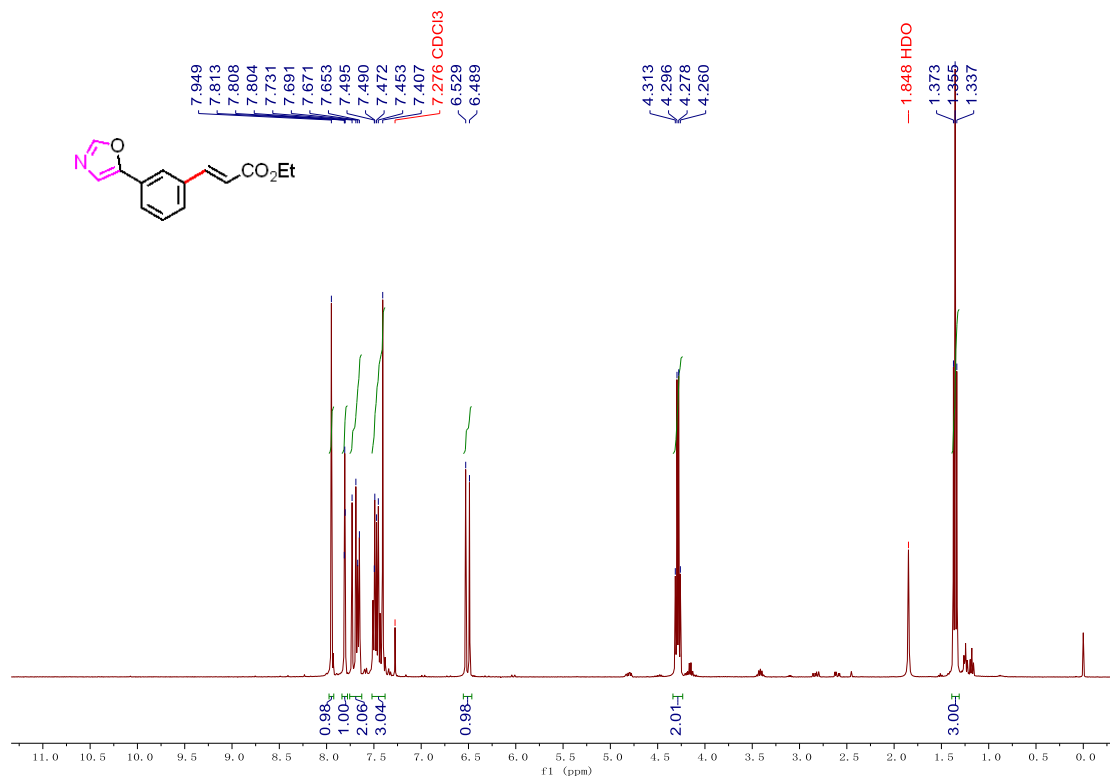
¹H-¹H NOESY spectra of *syn*-diastereomer of acetal



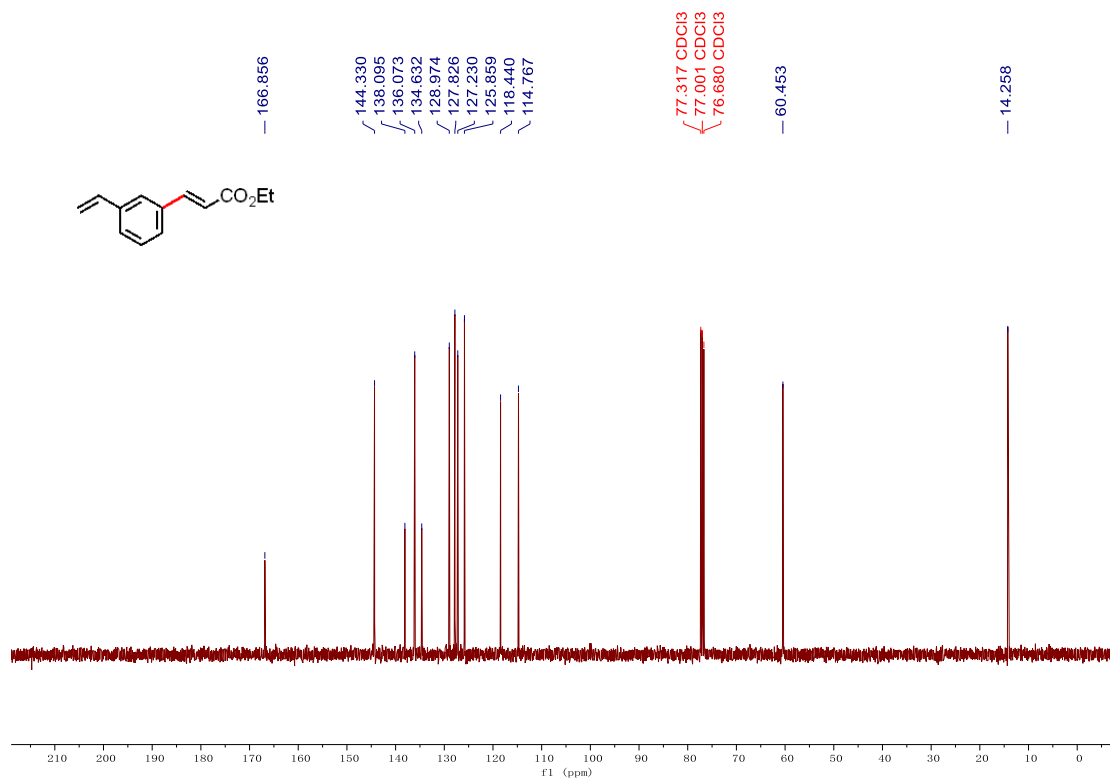
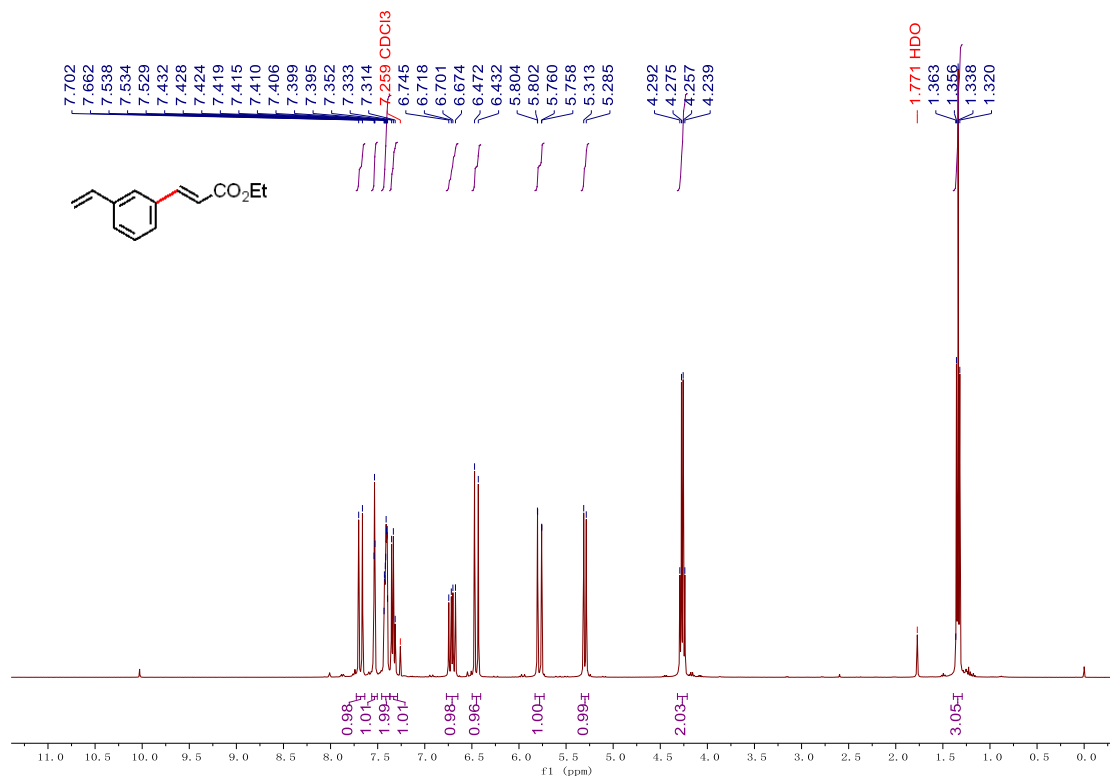
¹H and ¹³C NMR spectra of compound 4



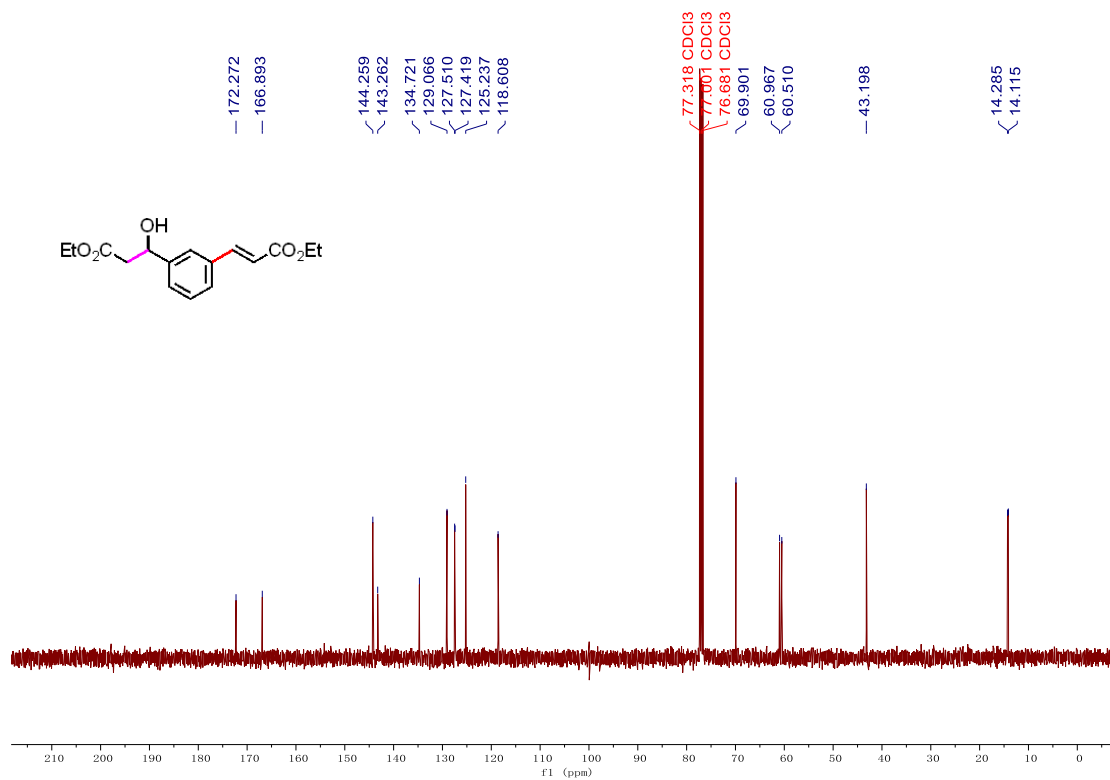
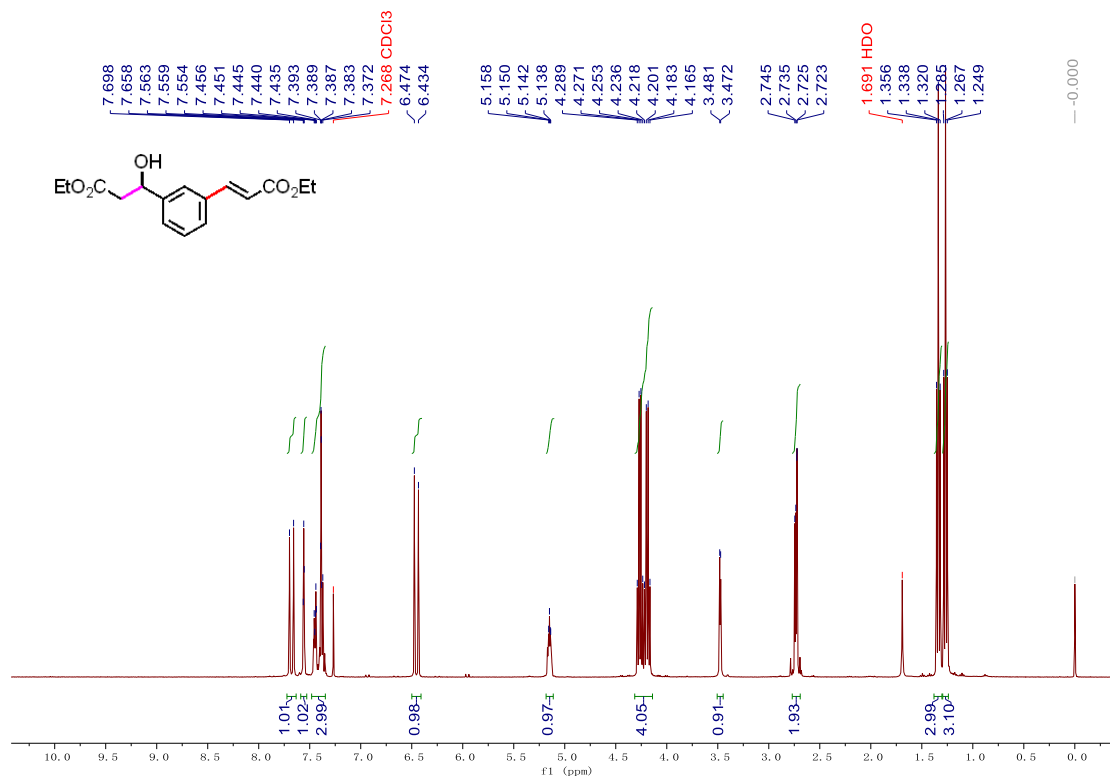
¹H and ¹³C NMR spectra of compound 5



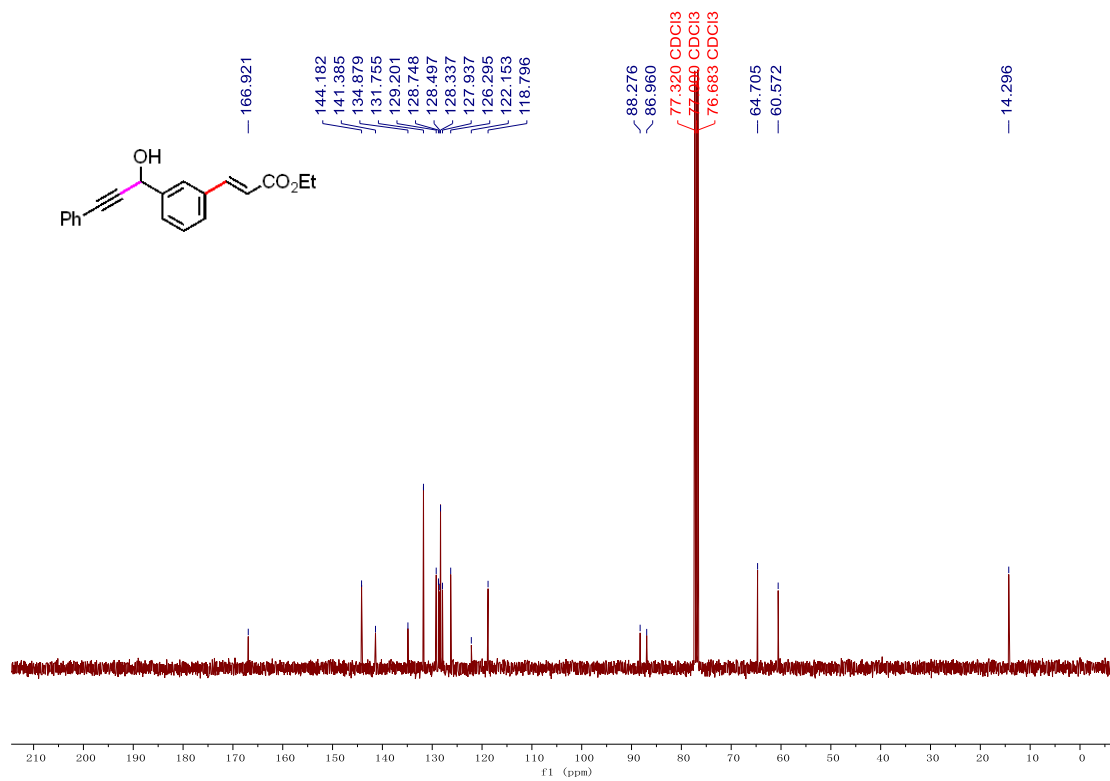
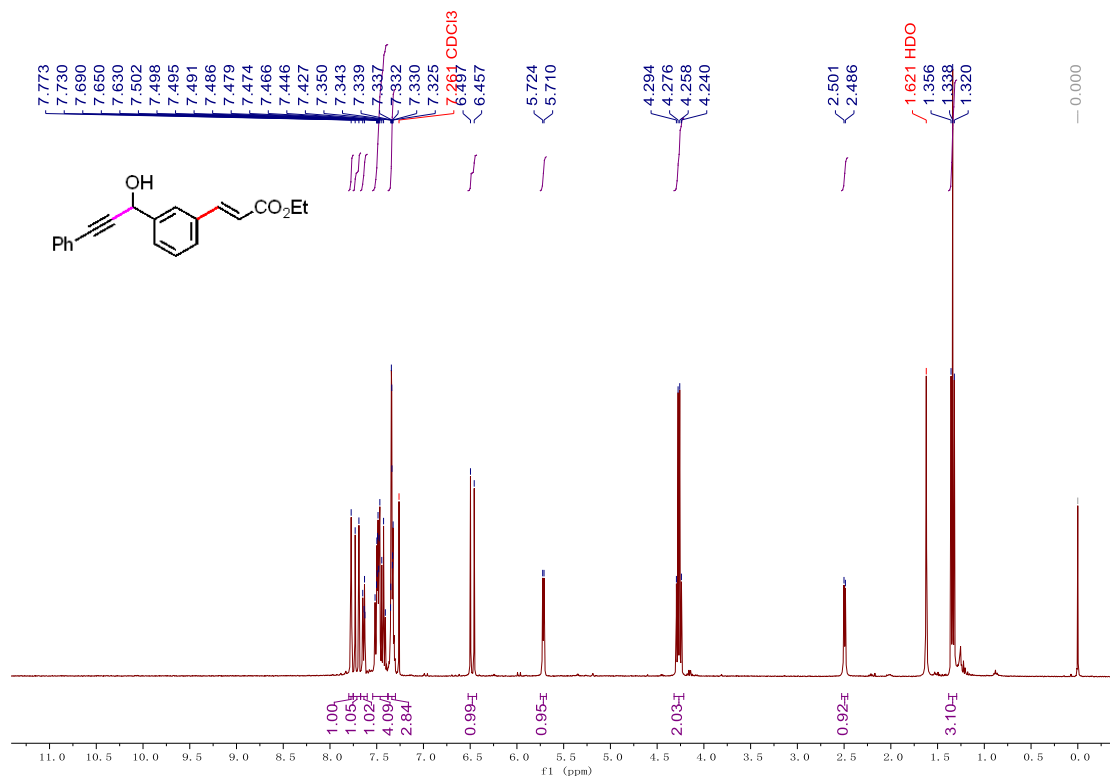
¹H and ¹³C NMR spectra of compound 6



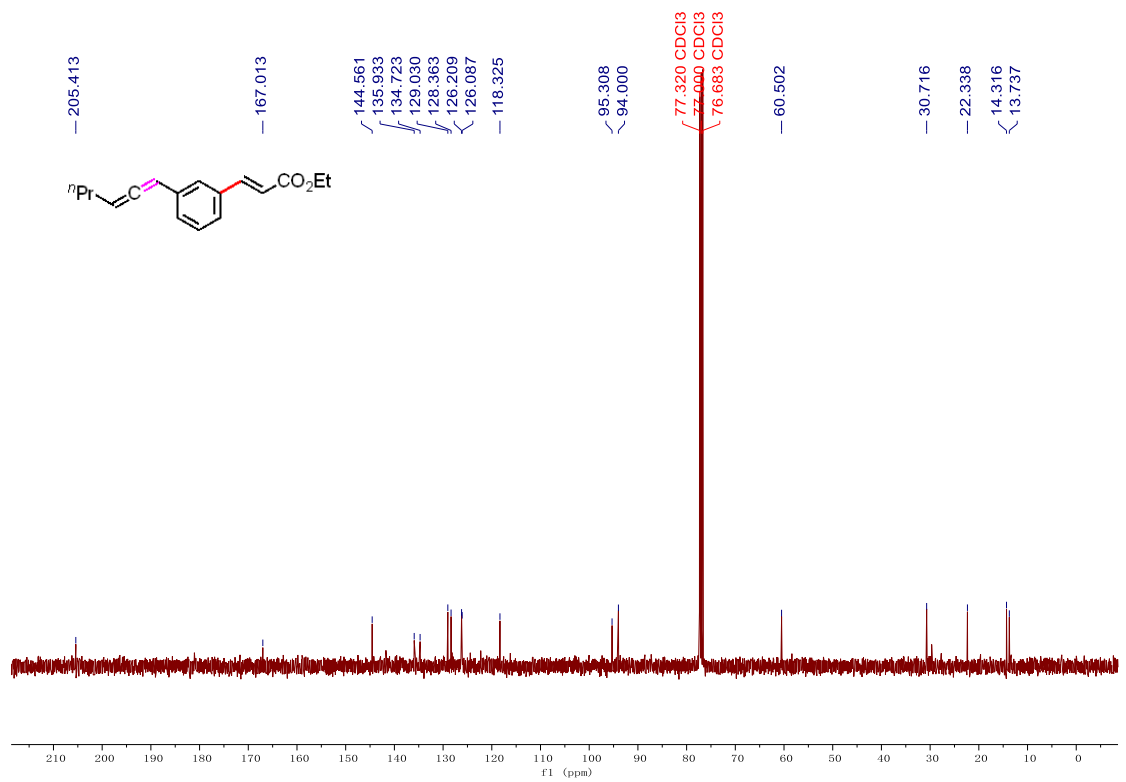
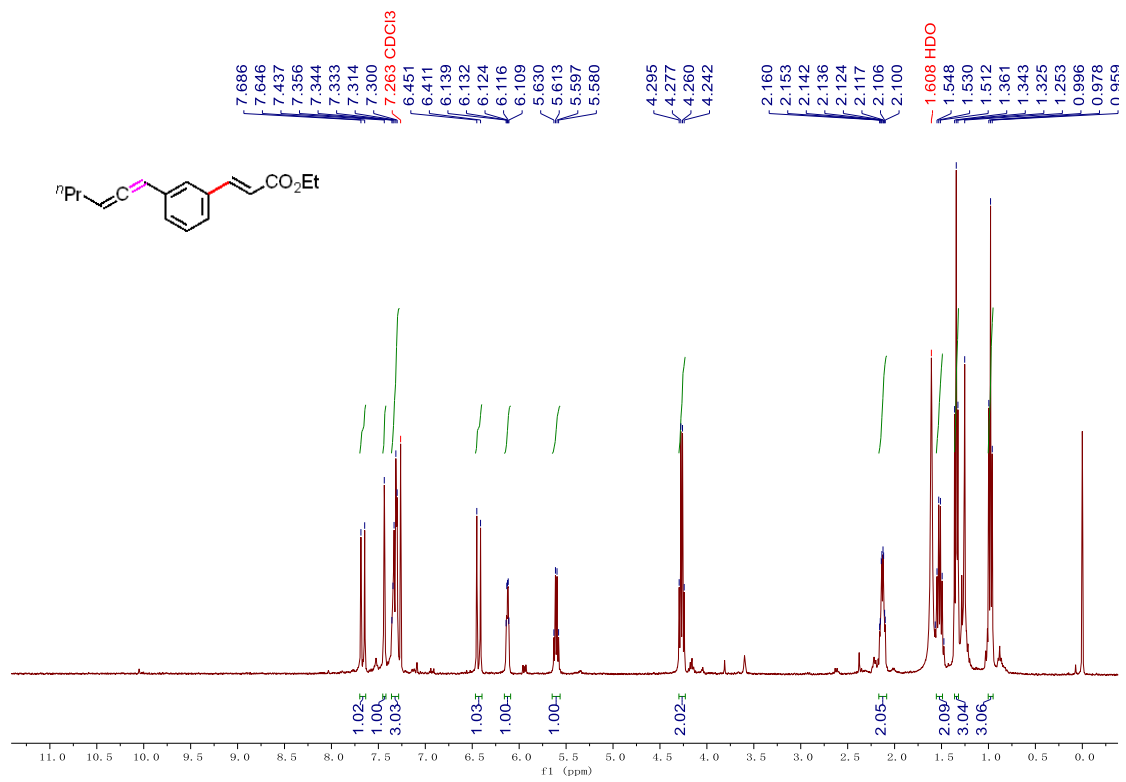
¹H and ¹³C NMR spectra of compound 7



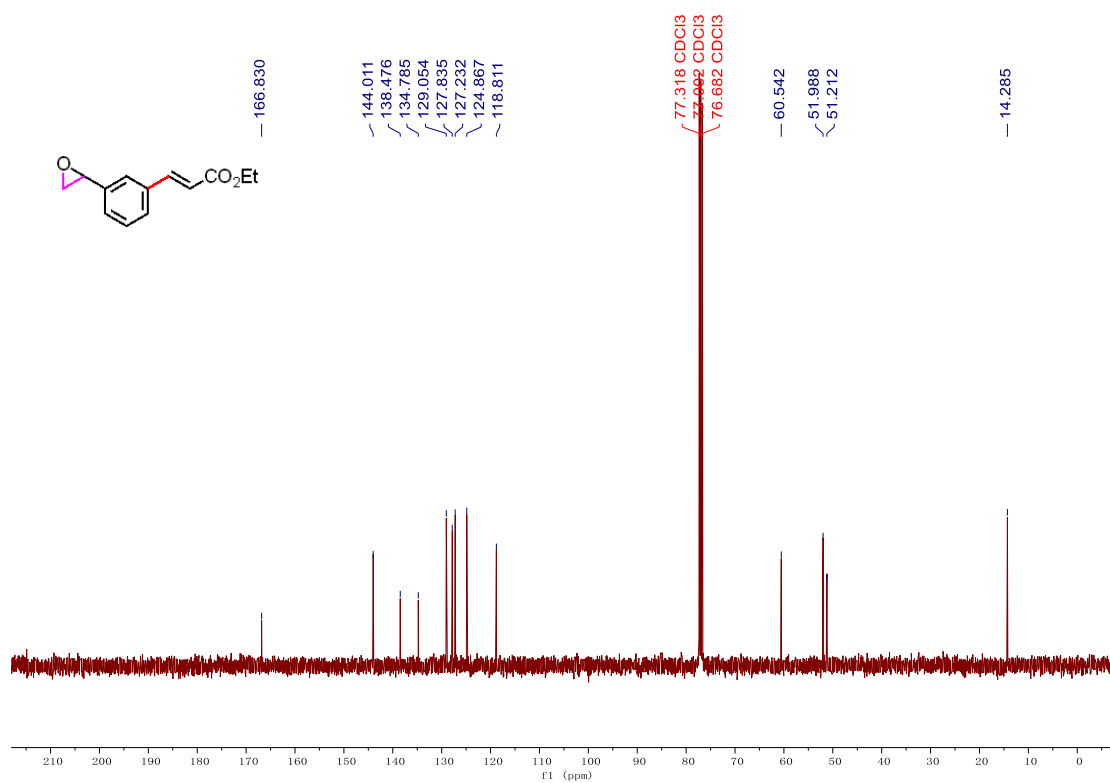
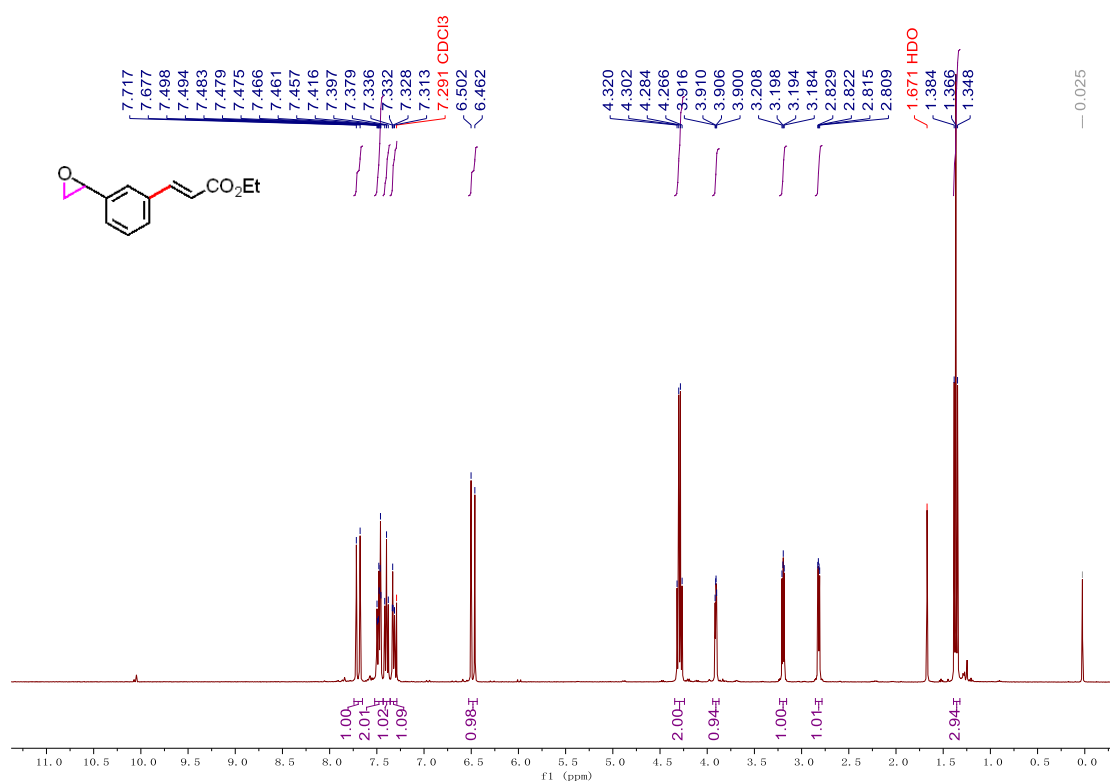
¹H and ¹³C NMR spectra of compound 8



¹H and ¹³C NMR spectra of compound 9



¹H and ¹³C NMR spectra of compound 10



¹H and ¹³C NMR spectra of compound **11**