

Palladium-Catalyzed Cross-Coupling Reaction of Sulfoxonium Ylides and Benzyl Bromides by Carbene Migratory Insertion

Kaichuan Yan, Maoyao He, Jianglian Li, Hua He, Ruizhi Lai, Yi Luo, Li Guo* and Yong Wu*

Key Laboratory of Drug-Targeting and Drug Delivery System of the Education Ministry, Sichuan Engineering Laboratory for Plant-Sourced Drug and Sichuan Research Center for Drug Precision Industrial Technology, West China School of Pharmacy, Sichuan University, Chengdu, 610041 (P.R. China)

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1. General Information

Unless noted, all reactions were carried out in flame-dried glassware with magnetic stirring under an atmosphere of air. Solvents used were of analytical purity. All the reactions were monitored by thin-layer chromatography (TLC) and were visualized using UV light and Iodine. The product purification was done using silica gel column chromatography. Thin-layer chromatography (TLC) characterization was performed with precoated silica gel GF254 (0.2mm), while column chromatography characterization was performed with silica gel (100-200mesh). NMR spectra were recorded on a Varian spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C , and 376 MHz for ^{19}F). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform- d (δ 77.16) for ^{13}C NMR. Chemical shifts are reported in δ ppm. Coupling constants were given in Hz. HRMS spectra were recorded on a Waters Q-TOF Premier. Melting points were measured with YRT-3 melting point apparatus (Shantou Keyi Instrument & Equipment Co., Ltd., Shantou, China).

2. Experimental section

2.1. Synthesis of sulfoxonium ylides.

The substrates of sulfoxonium ylides were prepared according to the procedure reported by Burtoloso ¹. All the characteristic data are consistent with the data reported before ^{1,2}.

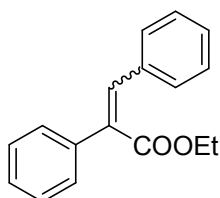
2.2. Typical procedure for Pd-catalyzed cross-coupling reaction.

In an oven-dried Schlenk tube, equipped with a magnetic stir bar, **1a** (0.1 mmol),

2a (1.2 eq), Pd(OAc)₂ (2.5 mol %), P(2-furyl)₃ (0.1 eq) and LiOtBu (2.0 eq)/Et₃N (0.5 eq) and 1 mL toluene were added. The tube was thoroughly flushed with argon, then the mixture was stirred for 24 hours at 80 °C. After completion of the reaction, the solvent was removed under vacuum, and the desired product was purified by column chromatography using PE/EA (40:1).

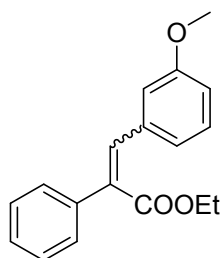
3. Characterization data for the products

ethyl 2,3-diphenylacrylate (**3a**)



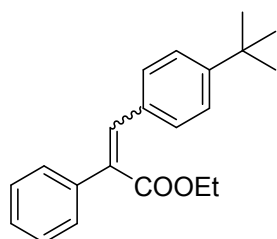
Yield: 87% (22 mg). Colorless oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.41 – 7.33 (m, 3H), 7.25 – 7.13 (m, 5H), 7.08 – 7.03 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.9, 140.2, 136.1, 134.9, 133.0, 130.7, 129.9, 129.0, 128.7, 128.3, 127.9, 61.3, 14.4; HRMS (ESI) *m/z* calculated for [C₁₇H₁₇O₂, M + H]⁺: 253.1223; Found: 253.1224

ethyl 3-(3-methoxyphenyl)-2-phenylacrylate (**3b**)



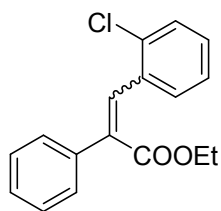
Yield: 90% (25.4 mg). Light yellow oil. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.35 (dd, *J* = 11.6, 7.1 Hz, 3H), 7.27 – 7.21 (m, 2H), 7.10 (t, *J* = 7.9 Hz, 1H), 6.78 – 6.71 (m, 2H), 6.49 (s, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.46 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 167.9, 159.2, 140.1, 136.2, 136.0, 133.1, 129.9, 129.3, 128.7, 127.9, 123.9, 116.1, 114.4, 61.3, 54.9, 14.4; HRMS (ESI) *m/z* calculated for [C₁₈H₁₉O₃, M + H]⁺: 283.1329; Found: 283.1327.

ethyl 3-(4-(tert-butyl) phenyl)-2-phenylacrylate (3c)



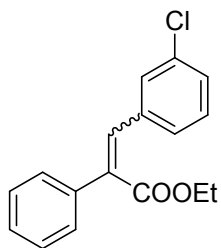
Yield: 94% (29 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.39 – 7.35 (m, 3H), 7.26 – 7.21 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.4$ Hz, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.24 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.1, 152.6, 140.1, 136.5, 131.9, 130.7, 129.9, 128.7, 128.2, 127.8, 125.3, 61.2, 34.8, 31.2, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{21}\text{H}_{25}\text{O}_2, \text{M} + \text{H}]^+$: 309.1849; Found: 309.1852.

ethyl 3-(2-chlorophenyl)-2-phenylacrylate (3d)



Yield: 79% (22.7 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.03 (s, 1H), 7.43 – 7.33 (m, 2H), 7.29 – 7.26 (m, 2H), 7.16 (dd, $J = 6.7, 3.0$ Hz, 2H), 7.11 (td, $J = 7.8, 1.7$ Hz, 1H), 6.88 (t, $J = 7.9$ Hz, 1H), 6.73 (dd, $J = 7.9, 1.7$ Hz, 1H), 4.31 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.5, 136.9, 135.2, 135.1, 135.0, 133.9, 131.3, 130.3, 129.7, 129.6, 128.4, 128.0, 126.2, 61.5, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{17}\text{H}_{16}\text{ClO}_2, \text{M} + \text{H}]^+$: 287.0833; Found: 287.0836.

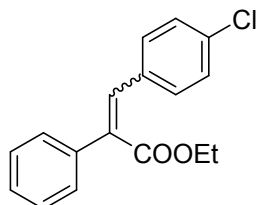
ethyl 3-(3-chlorophenyl)-2-phenylacrylate (3e)



Yield: 75% (21.5 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.40 – 7.33 (m, 3H), 7.23 – 7.12 (m, 3H), 7.06 (t, $J = 7.9$ Hz, 1H), 7.01 (s, 1H), 6.89 (d, $J = 7.9$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.6, 138.6, 136.7, 135.4, 134.4, 134.2, 130.5, 129.8,

129.5, 129.0, 128.8, 128.6, 128.2, 61.5, 14.4; **HRMS (ESI)** m/z calculated for $[C_{17}H_{16}ClO_2, M + H]^+$: 287.0833; Found: 287.0831.

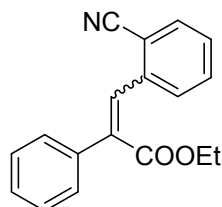
ethyl 3-(4-chlorophenyl)-2-phenylacrylate (3f)



Yield: 83% (23.8 mg). Colorless oil. 1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.41 – 7.31 (m, 3H), 7.23 – 7.17 (m, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 6.97 (d, $J = 8.6$ Hz, 2H),

4.27 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.7, 138.8, 135.7, 134.9, 133.6, 133.3, 131.8, 129.8, 128.8, 128.6, 128.1, 61.4, 14.4; **HRMS (ESI)** m/z calculated for $[C_{17}H_{16}ClO_2, M + H]^+$: 287.0833; Found: 287.0835.

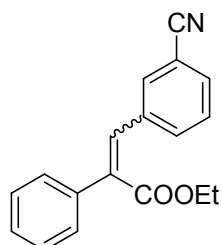
ethyl 3-(2-cyanophenyl)-2-phenylacrylate (3g)



Yield: 64% (17.8 mg). Colorless oil. 1H NMR (400 MHz, Chloroform-*d*) δ 8.07 (s, 1H), 7.75 – 7.61 (m, 1H), 7.58 – 7.51 (m, 1H), 7.47 – 7.38 (m, 1H), 7.38 – 7.29 (m, 3H), 7.27 – 7.17 (m,

2H), 6.90 (d, $J = 7.9$ Hz, 1H), 4.33 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 2H), 1.15 (t, $J = 7.1$ Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.0, 138.8, 137.6, 135.0, 133.1, 132.1, 130.3, 130.1, 128.9, 128.7, 128.6, 128.4, 117.6, 113.6, 61.8, 14.4; **HRMS (ESI)** m/z calculated for $[C_{18}H_{16}NO_2, M + H]^+$: 278.1176; Found: 278.1177.

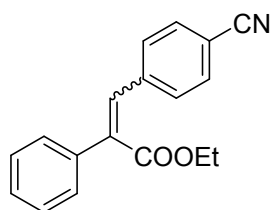
ethyl 3-(3-cyanophenyl)-2-phenylacrylate (3h)



Yield: 70% (19.4 mg). Colorless oil. 1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (s, 1H), 7.50 – 7.43 (m, 1H), 7.41 – 7.34 (m,

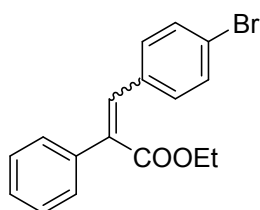
3H), 7.30 (s, 1H), 7.28 – 7.20 (m, 3H), 7.21 – 7.14 (m, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, Chloroform- d) δ 167.3, 137.3, 136.2, 135.7, 134.8, 134.4, 133.8, 132.0, 129.6, 129.1, 129.0, 128.5, 118.4, 112.7, 61.7, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{18}\text{H}_{16}\text{NO}_2, \text{M} + \text{H}]^+$: 278.1176; Found: 278.1174.

ethyl 3-(4-cyanophenyl)-2-phenylacrylate (3i)



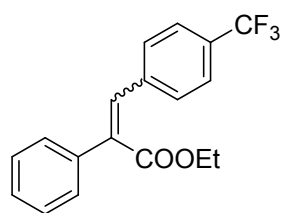
Yield: 73% (20.2 mg). White solid. m.p. 96.6-99.1°C. ^1H NMR (400 MHz, Chloroform- d) δ 7.78 (s, 1H), 7.43 (d, $J = 8.1$ Hz, 2H), 7.37 (s, 3H), 7.21 – 7.15 (m, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, Chloroform- d) δ 167.2, 139.5, 137.7, 136.3, 134.9, 132.0, 130.8, 129.7, 128.9, 128.5, 118.6, 112.1, 61.7, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{18}\text{H}_{16}\text{NO}_2, \text{M} + \text{H}]^+$: 278.1176; Found: 278.1176.

ethyl 3-(4-bromophenyl)-2-phenylacrylate (3j)



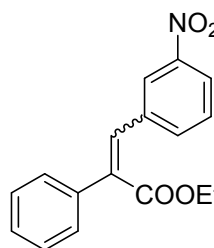
Yield: 68% (22.5 mg). White solid. m.p. 69.2-81.5°C. ^1H NMR (400 MHz, Chloroform- d) δ 7.74 (s, 1H), 7.36 (dd, $J = 5.3, 2.0$ Hz, 3H), 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 2H), 6.89 (d, $J = 8.3$ Hz, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, Chloroform- d) δ 167.7, 138.8, 135.6, 133.8, 133.8, 132.1, 131.6, 129.8, 128.8, 128.1, 123.3, 61.4, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{17}\text{H}_{16}\text{BrO}_2, \text{M} + \text{H}]^+$: 331.0328; Found: 331.0331.

ethyl 2-phenyl-3-(4-(trifluoromethyl) phenyl) acrylate (3k)



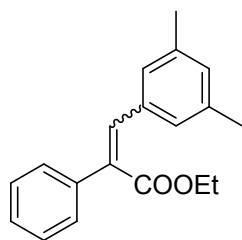
Yield: 75% (24.0 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.40 (d, $J = 8.2$ Hz, 2H), 7.39 – 7.33 (m, 3H), 7.20 (dd, $J = 6.6, 3.0$ Hz, 2H), 7.14 (d, $J = 8.1$ Hz, 2H), 4.29 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.5, 138.3, 135.4, 135.3, 130.7, 129.8, 129.0, 128.9, 128.8, 128.3, 125.2 (q, $J_{\text{C-F}} = 3.8$ Hz), 61.6, 14.4; $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.88; **HRMS (ESI)** m/z calculated for $[\text{C}_{18}\text{H}_{16}\text{F}_3\text{O}_2, \text{M} + \text{H}]^+$: 301.1097; Found: 301.1095.

ethyl 3-(3-nitrophenyl)-2-phenylacrylate (3l)



Yield: 69% (20.5mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.07 – 8.01 (m, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.44 – 7.36 (m, 3H), 7.32 (d, $J = 4.9$ Hz, 2H), 7.23 – 7.15 (m, 2H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.2, 148.2, 137.2, 136.6, 136.1, 136.0, 134.8, 129.6, 129.2, 129.0, 128.6, 125.2, 123.4, 61.7, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{17}\text{H}_{16}\text{NO}_4, \text{M} + \text{H}]^+$: 298.1074; Found: 298.1078.

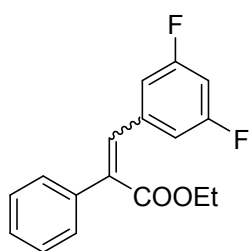
ethyl 3-(3,5-dimethylphenyl)-2-phenylacrylate (3m)



Yield: 86% (24.1 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.38 – 7.31 (m, 3H), 7.21 (dd, $J = 7.3, 2.3$ Hz, 2H), 6.84 (s, 1H), 6.63 (s, 2H), 4.26 (q, $J = 7.1$ Hz,

2H), 2.11 (s, 6H), 1.29 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, Chloroform- d) δ 168.0, 140.6, 137.6, 136.4, 134.6, 132.5, 130.8, 129.9, 128.7, 128.6, 127.7, 61.2, 21.3, 14.4; HRMS (ESI) m/z calculated for $[\text{C}_{19}\text{H}_{21}\text{O}_2, \text{M} + \text{H}]^+$: 281.1536; Found: 281.1540.

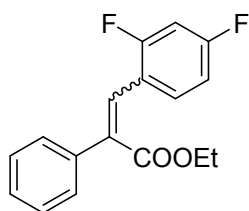
ethyl 3-(3,5-difluorophenyl)-2-phenylacrylate (3n)



Yield: 63% (18.1 mg). Colorless oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.62 (s, 1H), 7.35 – 7.27 (m, 3H), 7.11 (dd, $J = 6.6, 3.0$ Hz, 2H), 6.62 – 6.52 (m, 1H), 6.46 (d, $J = 6.7$ Hz, 2H), 4.20 (q, $J = 7.1$ Hz, 2H), 1.22 (t, $J = 7.1$ Hz, 3H); ^{13}C

NMR (101 MHz, Chloroform- d) δ 167.3, 162.7 (dd, $J_{\text{C-F}} = 248.1$ Hz, 12.8 Hz), 138.0 (t, $J_{\text{C-F}} = 9.8$ Hz), 137.5 (t, $J_{\text{C-F}} = 2.8$ Hz), 135.6, 134.9, 129.6, 128.9, 128.5, 113.2 (t, $J_{\text{C-F}} = 26.1$ Hz), 104.4 (t, $J_{\text{C-F}} = 25.5$ Hz), 61.7, 14.4; ^{19}F NMR (376 MHz, Chloroform- d) δ -109.82 (t, $J = 8.0$ Hz, 2F); HRMS (ESI) m/z calculated for $[\text{C}_{17}\text{H}_{15}\text{F}_2\text{O}_2, \text{M} + \text{H}]^+$: 289.1035; Found: 289.1031.

ethyl 3-(2,4-difluorophenyl)-2-phenylacrylate (3o)

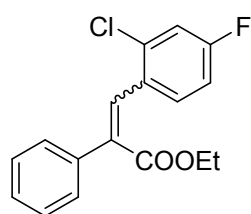


Yield: 72% (20.8 mg). Colorless oil. ^1H NMR (400 MHz, Chloroform- d) δ 7.92 (s, 1H), 7.44 – 7.30 (m, 3H), 7.24 – 7.10 (m, 2H), 6.77 (ddd, $J = 10.8, 8.7, 2.6$ Hz, 1H), 6.68 (td, $J = 8.6,$

6.4 Hz, 1H), 6.51 (td, $J = 8.5, 2.6$ Hz, 1H), 4.28 (q, $J = 7.1$ Hz, 2H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, Chloroform- d) δ 167.4, 163.7 (dd, $J_{\text{C-F}} = 150.4$ Hz, 12.1 Hz), 161.2 (dd, $J_{\text{C-F}} = 152.0$ Hz, 12.1 Hz), 135.4, 131.7 (dd, $J_{\text{C-F}} = 9.7$ Hz, 3.8 Hz), 130.9 (dd, $J_{\text{C-F}} = 5.2$ Hz, 1.5 Hz), 129.9, 128.7, 128.2, 126.9, 119.3 (dd, $J_{\text{C-F}} =$

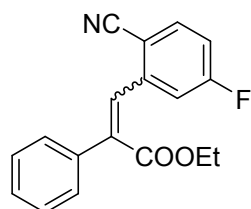
12.1 Hz, 4.0 Hz), 111.2 (dd, $J_{\text{C-F}} = 21.3$ Hz, 3.7 Hz), 104.0 (t, $J_{\text{C-F}} = 25.7$ Hz), 61.5, 14.4; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -107.46 (dt, $J = 16.0, 8.3$ Hz, 1F), -109.45 (q, $J = 9.2$ Hz, 1F); **HRMS (ESI)** m/z calculated for $[\text{C}_{17}\text{H}_{15}\text{F}_2\text{O}_2, \text{M} + \text{H}]^+$: 289.1035; Found: 289.1037.

ethyl 3-(2-chloro-4-fluorophenyl)-2-phenylacrylate (3p)



Yield: 65% (19.8 mg). Colorless oil. **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.44 – 7.33 (m, 1H), 7.31 – 7.27 (m, 2H), 7.20 – 7.08 (m, 3H), 6.71 (dd, $J = 8.9, 6.1$ Hz, 1H), 6.61 (td, $J = 8.4, 2.6$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.4, 162.2 (d, $J = 252.7$ Hz), 136.0 (d, $J = 10.3$ Hz), 135.7, 135.0, 132.5 (d, $J = 8.8$ Hz), 130.2, 130.0 (d, $J = 3.9$ Hz), 128.8, 128.5, 128.1, 117.0 (d, $J = 24.7$ Hz), 113.9 (d, $J = 21.2$ Hz), 61.6, 14.4; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -110.15 (q, $J = 8.0$ Hz); **HRMS (ESI)** m/z calculated for $[\text{C}_{17}\text{H}_{15}\text{ClFO}_2, \text{M} + \text{H}]^+$: 305.0735; Found: 305.0737.

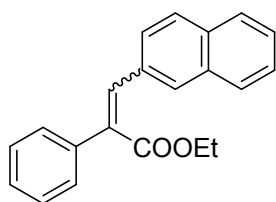
ethyl 3-(2-cyano-5-fluorophenyl)-2-phenylacrylate (3q)



Yield: 42% (19.8 mg). Colorless oil. **^1H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.64 (dd, $J = 8.6, 5.4$ Hz, 1H), 7.35 (dd, $J = 5.1, 2.0$ Hz, 3H), 7.17 (dd, $J = 6.5, 2.9$ Hz, 2H), 6.99 (td, $J = 8.1, 2.6$ Hz, 1H), 6.54 (dd, $J = 9.9, 2.6$ Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 1.35 (d, $J = 7.1$ Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.6, 164.2 (d, $J =$

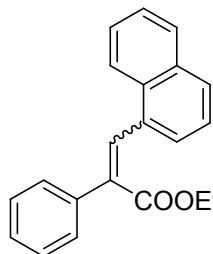
256.2 Hz), 141.8 (d, $J = 9.6$ Hz), 138.8, 135.3 (d, $J = 9.6$ Hz), 134.1, 133.7 (d, $J = 2.3$ Hz), 129.8, 128.9, 128.8, 117.6 (d, $J = 24.5$ Hz), 116.8, 116.6 (d, $J = 23.1$ Hz), 109.8 (d, $J = 3.4$ Hz), 62.0, 14.3; **^{19}F NMR** (376 MHz, Chloroform- d) δ -102.54; **HRMS (ESI)** m/z calculated for $[\text{C}_{18}\text{H}_{15}\text{FNO}_2, \text{M} + \text{H}]^+$: 296.1081; Found: 296.1083.

ethyl 3-(naphthalen-2-yl)-2-phenylacrylate (3r)



Yield: 85% (25.7 mg). Colorless oil. **^1H NMR** (400 MHz, Chloroform- d) δ 8.00 (s, 1H), 7.70 (d, $J = 6.6$ Hz, 1H), 7.65 (s, 2H), 7.53 (d, $J = 8.7$ Hz, 1H), 7.42 (t, $J = 6.2$ Hz, 2H), 7.39 – 7.33 (m, 3H), 7.29 – 7.22 (m, 2H), 6.99 (d, $J = 8.6$ Hz, 1H), 4.30 (q, $J = 7.1$ Hz, 2H), 1.32 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform- d) δ 168.0, 140.3, 136.1, 133.4, 133.1, 132.5, 131.6, 130.1, 128.9, 128.7, 128.6, 128.0, 127.6, 127.1, 127.1, 126.6, 126.4, 61.4, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{21}\text{H}_{19}\text{O}_2, \text{M} + \text{H}]^+$: 303.1380; Found: 303.1385.

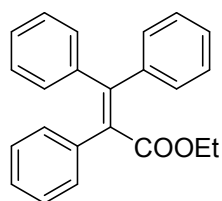
ethyl 3-(naphthalen-1-yl)-2-phenylacrylate (3s)



Yield: 83% (25.1 mg). Colorless oil. **^1H NMR** (400 MHz, Chloroform- d) δ 8.46 (s, 1H), 8.12 (d, $J = 8.2$ Hz, 1H), 7.83 (d, $J = 8.0$ Hz, 1H), 7.69 (d, $J = 8.2$ Hz, 1H), 7.61 – 7.48 (m, 3H), 7.21 – 7.12 (m, 5H), 6.96 (d, $J = 7.2$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform- d) δ 167.8, 138.6, 135.5, 135.4, 133.5, 132.5, 132.2, 130.4, 128.8, 128.8, 128.2, 128.1, 127.6, 126.6, 126.2,

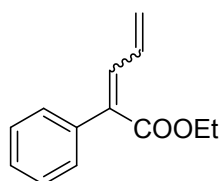
125.2, 124.3, 61.5, 14.5; **HRMS (ESI)** m/z calculated for $[C_{21}H_{19}O_2, M + H]^+$: 303.1380; Found: 303.1385.

ethyl 2,3,3-triphenylacrylate (3t)



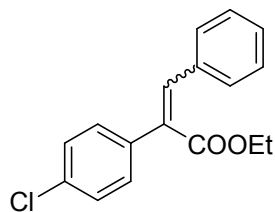
Yield: 18% (5.9 mg). White solid. m.p. 105.9-107.2°C. **1H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.29 (m, 5H), 7.22 – 7.10 (m, 8H), 7.02 (dd, $J = 7.8, 1.9$ Hz, 2H), 4.03 (q, $J = 7.1$ Hz, 2H), 0.98 (t, $J = 7.2$ Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.7, 146.1, 142.6, 140.7, 137.6, 133.9, 131.0, 130.0, 129.3, 128.3, 128.2, 128.2, 128.0, 127.8, 127.5, 61.1, 13.8; **HRMS (ESI)** m/z calculated for $[C_{23}H_{21}O_2, M + H]^+$: 329.1536; Found: 329.1533.

ethyl 2-phenylpenta-2,4-dienoate (3u)



Yield: 24% (4.9 mg). Colorless oil. **1H NMR** (400 MHz, Chloroform-*d*) δ 7.44 (d, $J = 11.4$ Hz, 1H), 7.42 – 7.29 (m, 3H), 7.23 (d, $J = 6.5$ Hz, 2H), 6.45 – 6.34 (m, 1H), 5.66 (dd, $J = 17.0, 1.8$ Hz, 1H), 5.41 (dd, $J = 10.0, 1.8$ Hz, 1H), 4.25 (q, $J = 7.1$ Hz, 2H), 1.29 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.5, 140.5, 135.1, 133.7, 133.4, 130.3, 128.0, 127.8, 125.6, 61.2, 14.4; **HRMS (ESI)** m/z calculated for $[C_{13}H_{15}O_2, M + H]^+$: 203.1067; Found: 203.1068.

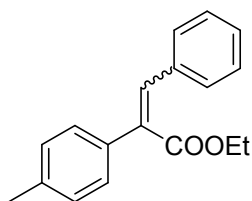
ethyl 2-(4-chlorophenyl)-3-phenylacrylate (3v)



Yield: 66% (18.9 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.25 – 7.11 (m, 5H), 7.05 (d, $J = 7.0$ Hz, 2H), 4.27 (q, $J = 7.1$ Hz,

2H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.6, 140.8, 134.5, 134.5, 133.9, 131.7, 131.5, 130.6, 129.3, 129.0, 128.4, 61.5, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{17}\text{H}_{16}\text{ClO}_2, \text{M} + \text{H}]^+$: 287.0833; Found: 287.0835.

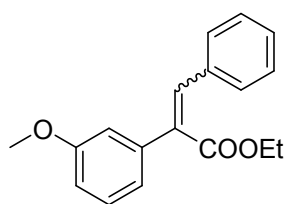
ethyl 3-phenyl-2-(*p*-tolyl) acrylate (3w)



Yield: 61% (16.2 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.22 – 7.13 (m, 5H), 7.12 – 7.04 (m, 4H), 4.26 (q, $J = 7.1$ Hz, 2H), 2.38 (s, 3H), 1.30 (t, $J = 7.1$

Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.2, 140.0, 137.6, 135.0, 133.0, 132.9, 130.7, 129.8, 129.4, 129.0, 128.3, 61.3, 21.5, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{18}\text{H}_{19}\text{O}_2, \text{M} + \text{H}]^+$: 267.1380; Found: 267.1385.

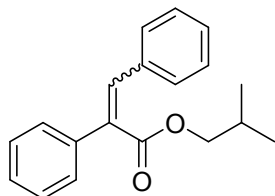
ethyl 2-(3-methoxyphenyl)-3-phenylacrylate (3x)



Yield: 63% (17.8 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.28 (d, $J = 7.9$ Hz, 1H), 7.22 – 7.13 (m, 3H), 7.07 (d, $J = 6.6$ Hz, 2H), 6.89 (dd, $J = 7.8, 2.2$

Hz, 1H), 6.80 (d, $J = 7.6$ Hz, 1H), 6.77 (dd, $J = 2.7, 1.5$ Hz, 1H), 4.27 (q, $J = 7.1$ Hz, 2H), 3.76 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.9, 159.8, 140.3, 137.4, 134.8, 132.8, 130.7, 129.8, 129.2, 128.3, 122.3, 115.2, 113.8, 61.3, 55.4, 14.4; **HRMS (ESI)** m/z calculated for $[\text{C}_{18}\text{H}_{19}\text{O}_3, \text{M} + \text{H}]^+$: 283.1329; Found: 283.1325.

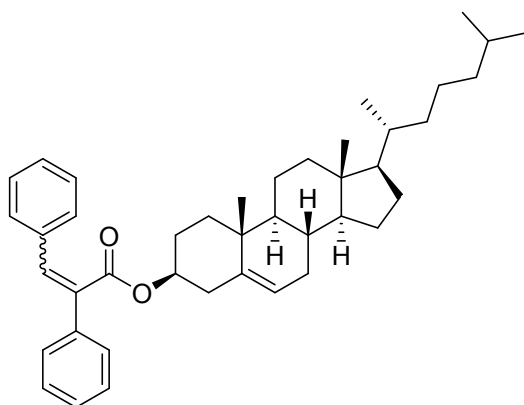
isobutyl 2,3-diphenylacrylate (3z)



Yield: 75% (21.1 mg). Colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.86 (s, 1H), 7.42 – 7.28 (m, 4H), 7.25 – 7.12 (m, 4H), 7.07 (d, $J = 7.1$ Hz, 2H), 3.99 (d, $J = 6.4$ Hz, 2H), 2.02 – 1.88 (m, 1H), 0.9 (d, $J = 6.8$ Hz, 6H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 168.0, 140.2, 136.1, 134.8, 133.0, 130.7, 129.8, 129.1, 128.6, 128.3, 127.8, 71.3, 27.9, 19.2; **HRMS (ESI)** m/z calculated for $[\text{C}_{19}\text{H}_{21}\text{O}_2, \text{M} + \text{H}]^+$: 281.1536; Found: 281.1537.

(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)

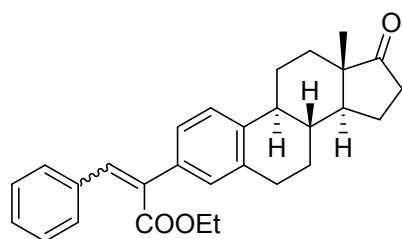
2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H cyclopenta[a]phenanthren-3-yl 2,3-diphenylacrylate (4)



Yield: 34% (20.1 mg). colorless oil. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.38 – 7.30 (m, 3H), 7.25 – 7.09 (m, 5H), 7.08 – 6.98 (m, 2H), 5.38 (dd, $J = 5.0$, 2.4 Hz, 1H), 4.74 (tt, $J = 11.1$, 4.9 Hz, 1H), 2.44 – 2.31 (m, 2H), 2.05 – 1.81 (m, 6H), 1.66 – 1.41 (m, 11H), 1.19 – 1.04 (m, 8H), 1.02 (s, 3H), 0.98 – 0.92 (m, 1H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.87 (dd, $J = 6.6$, 1.8 Hz, 6H), 0.68 (s, 3H); $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 167.4, 139.9, 139.9, 136.1,

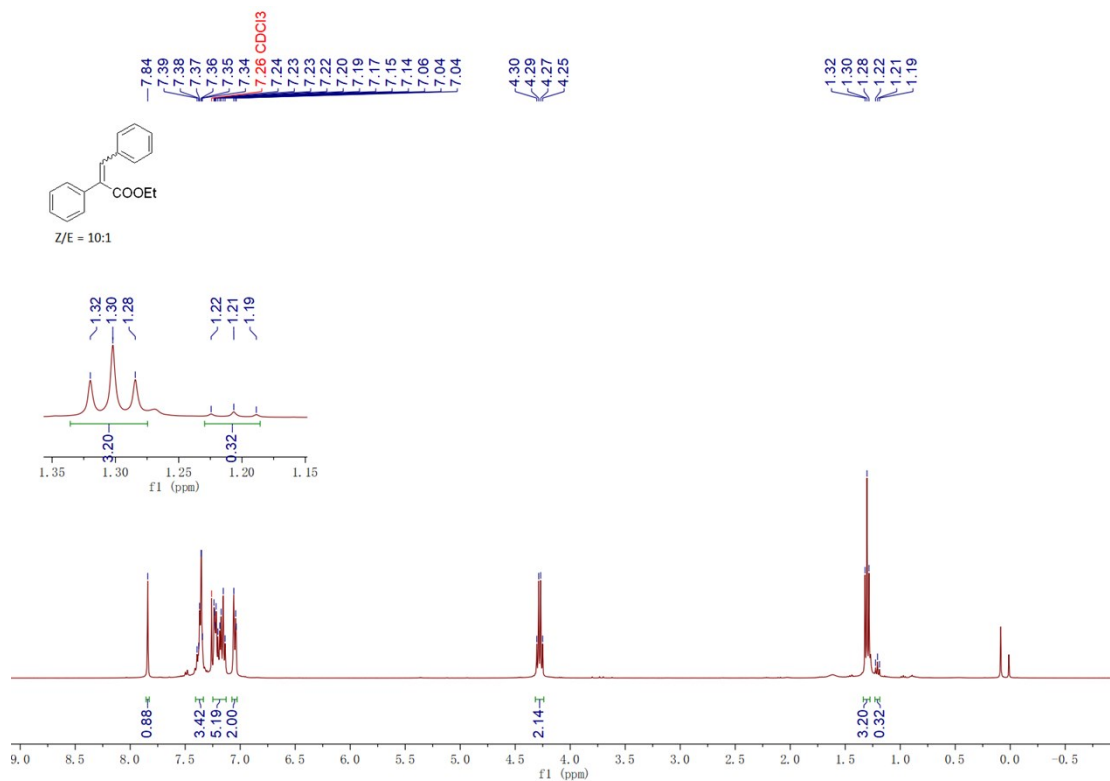
135.0, 133.3, 130.7, 130.0, 129.0, 128.6, 128.3, 127.8, 122.8, 75.0, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.3, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 27.9, 24.4, 24.0, 23.0, 21.2, 19.5, 18.9, 12.0; **HRMS (ESI)** m/z calculated for $[C_{42}H_{57}O_2, M + H]^+$: 593.4353; Found: 593.4355.

ethyl 2-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-3-phenylacrylate (5)

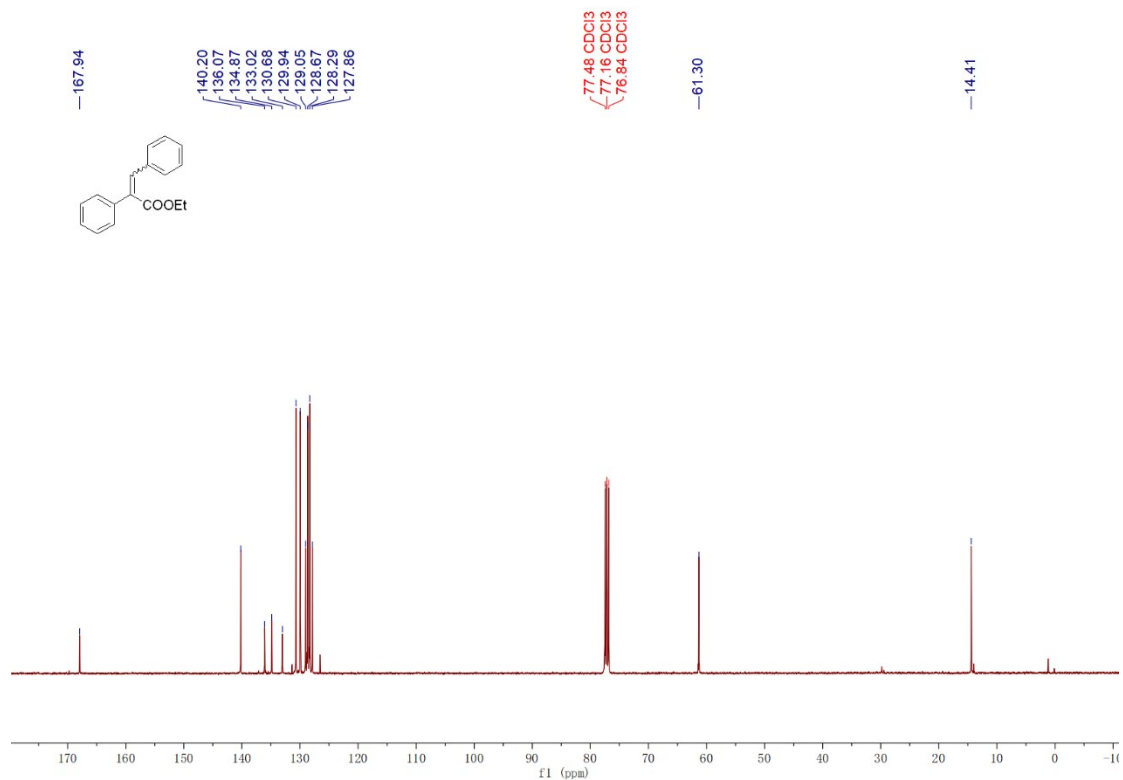


Yield: 78% (20.1 mg). Colorless oil. **¹H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.41 – 7.29 (m, 1H), 7.26 – 7.06 (m, 5H), 7.05 – 6.86 (m, 2H), 4.28 (q, $J = 7.3$ Hz, 2H), 2.99 – 2.81 (m, 2H), 2.52 (dd, $J = 18.8, 8.6$ Hz, 1H), 2.47 – 2.30 (m, 2H), 2.22 – 2.11 (m, 1H), 2.13 – 1.94 (m, 3H), 1.69 – 1.48 (m, 6H), 1.32 (t, $J = 7.1$ Hz, 2H), 1.20 (t, $J = 7.1$ Hz, 1H), 0.94 (s, 3H); **¹³C NMR** (101 MHz, Chloroform-*d*) δ 221.2, 168.2, 139.7, 139.4, 136.7, 135.0, 133.2, 132.8, 130.7, 130.3, 129.0, 128.3, 127.3, 125.6, 61.3, 50.8, 48.2, 44.6, 38.2, 36.0, 31.8, 29.4, 26.7, 25.7, 21.7, 14.5, 14.1; **HRMS (ESI)** m/z calculated for $[C_{29}H_{33}O_3, M + H]^+$: 429.2424; Found: 429.2421.

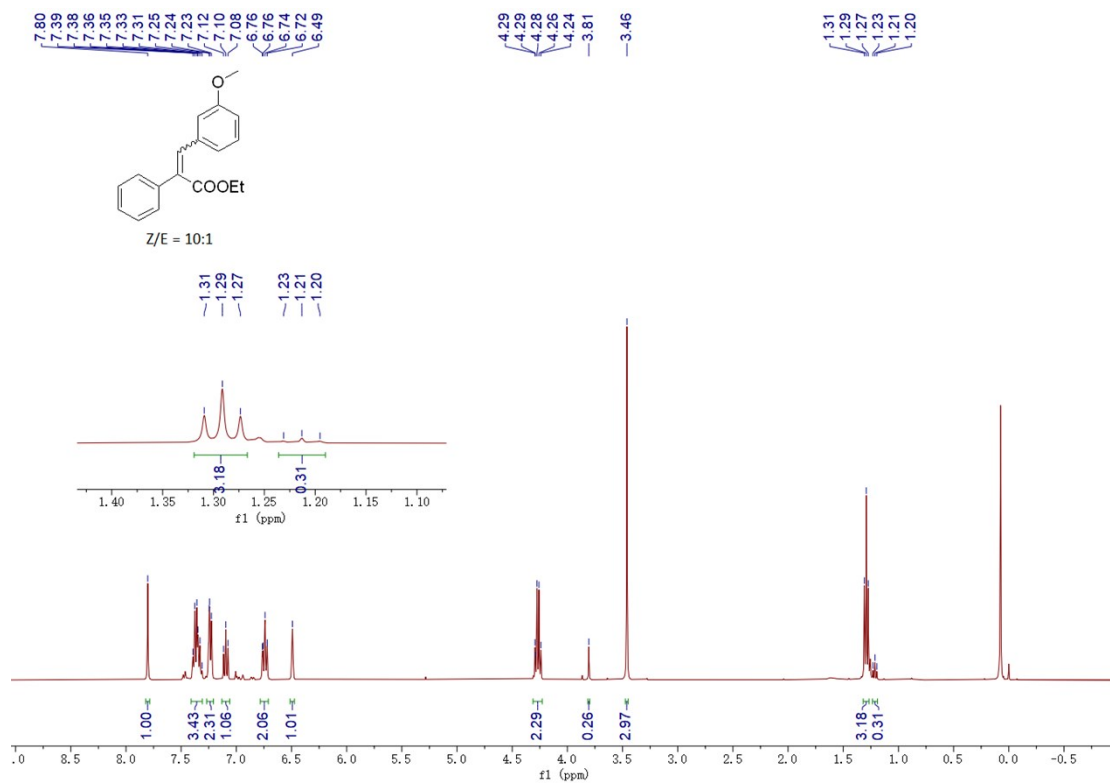
4. ¹H NMR, ¹³C NMR and ¹⁹F NMR Spectra of Products.



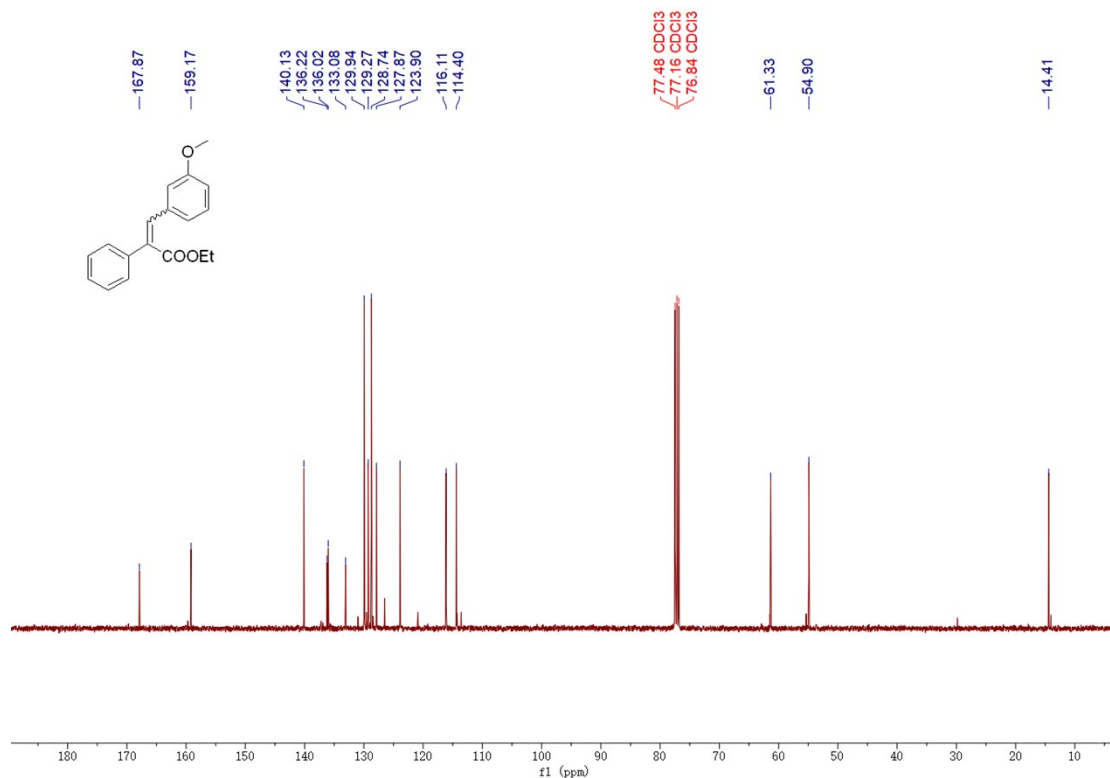
¹H NMR of 3a



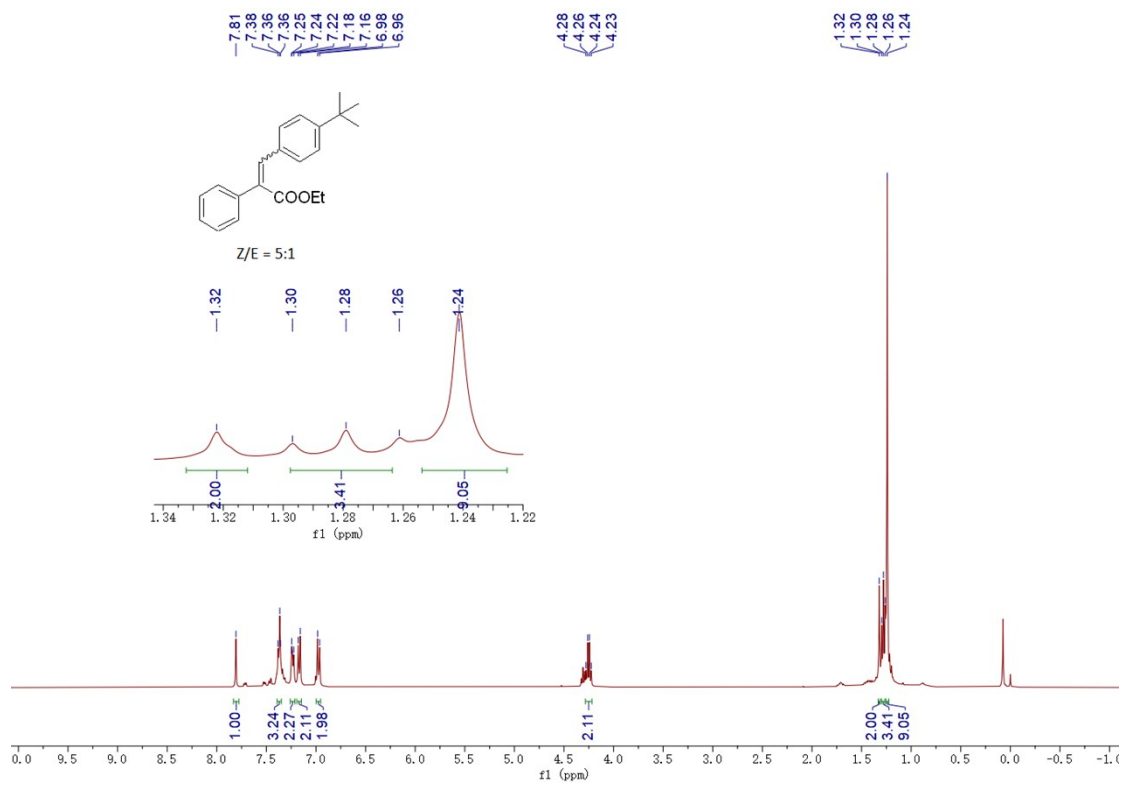
¹³C NMR of 3a



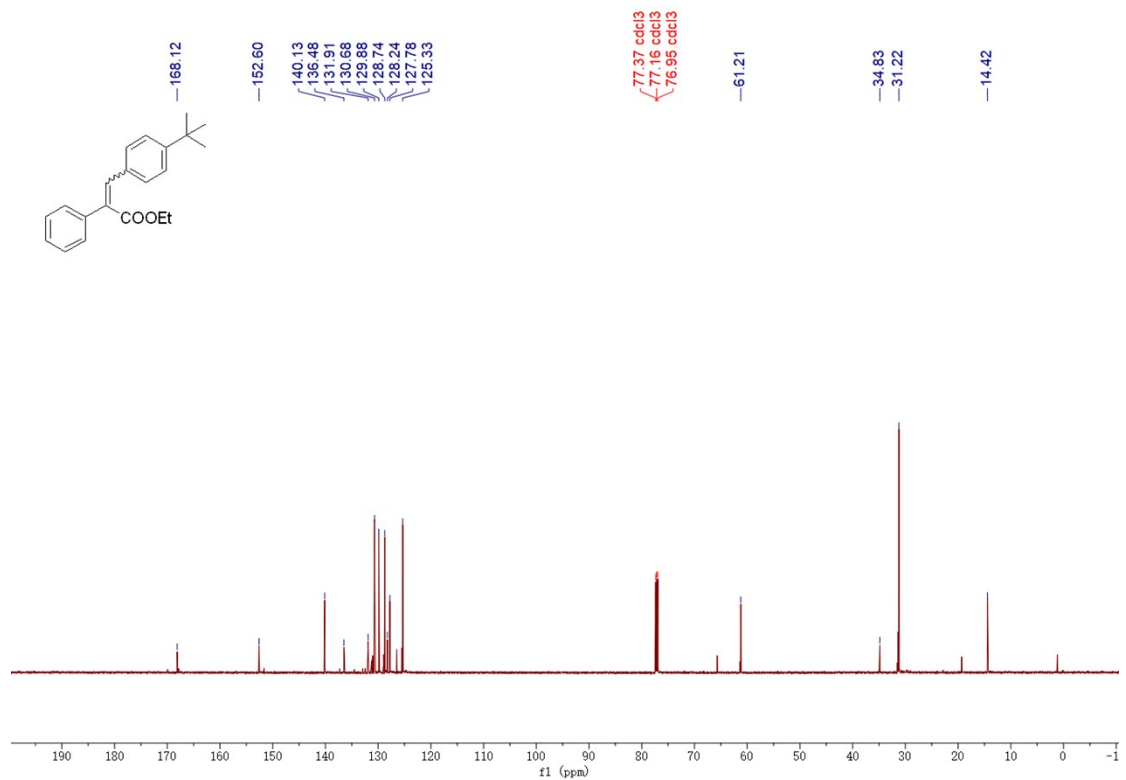
$^1\text{H NMR}$ of **3b**



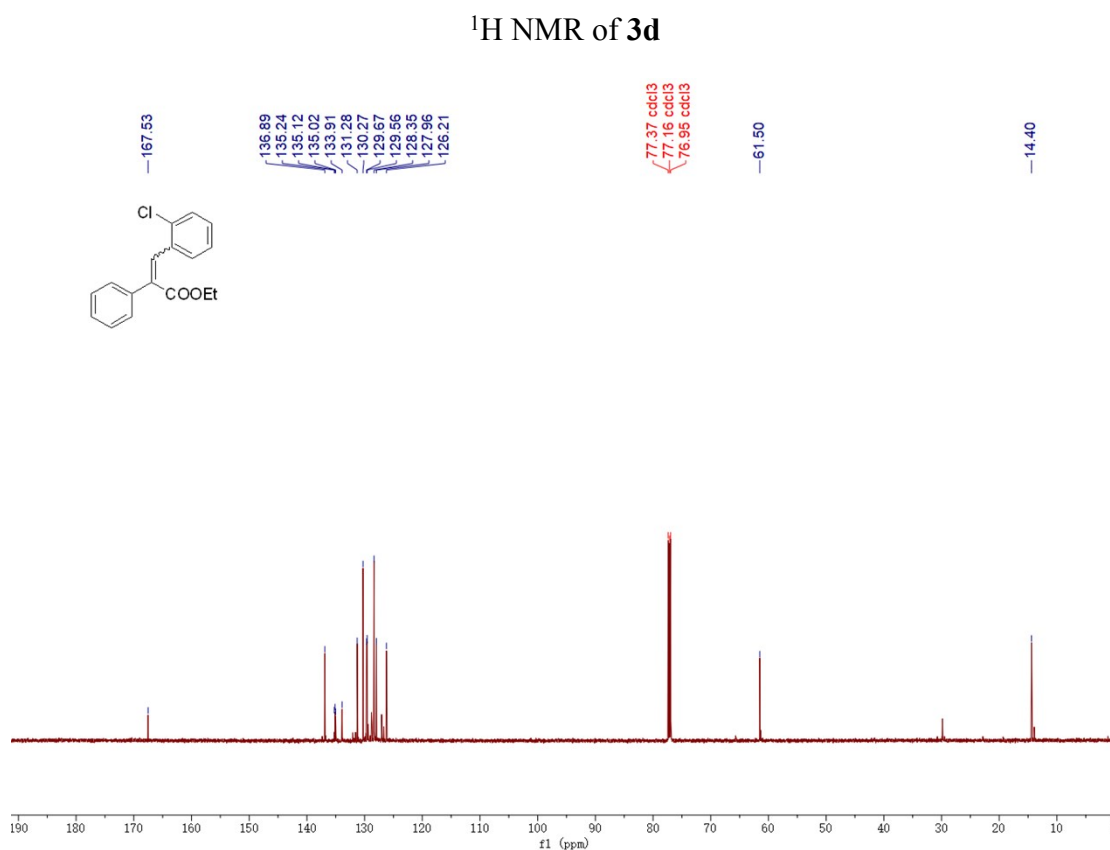
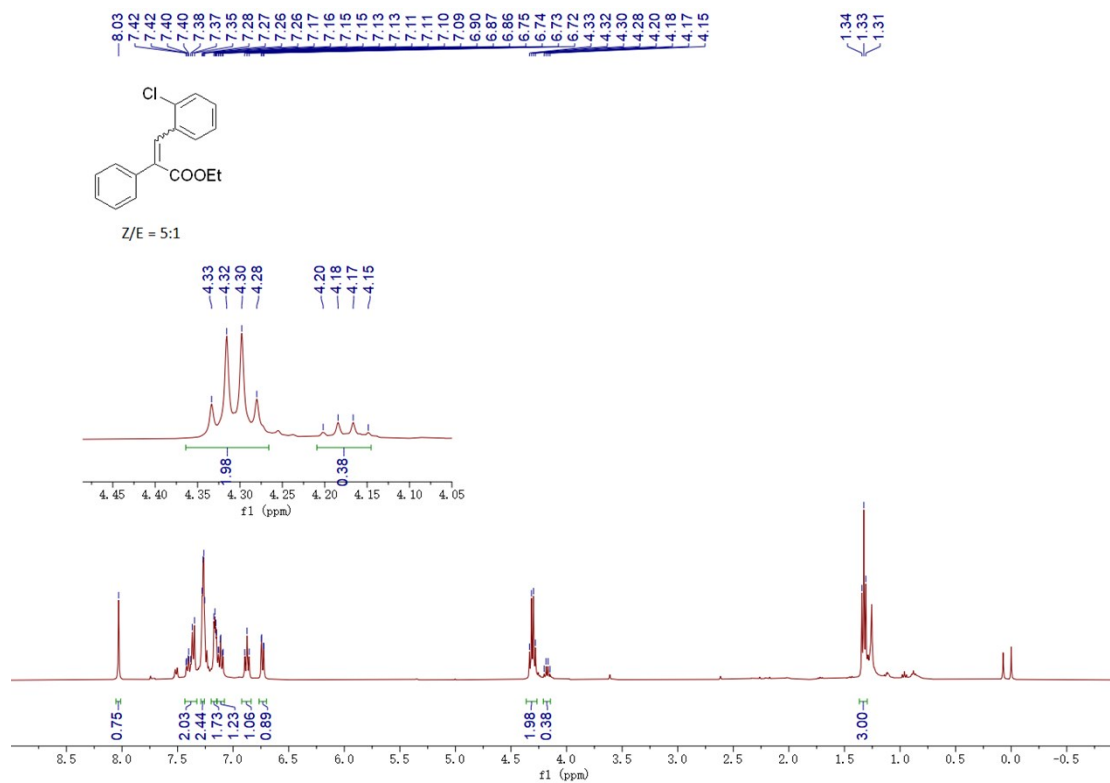
$^{13}\text{C NMR}$ of **3b**

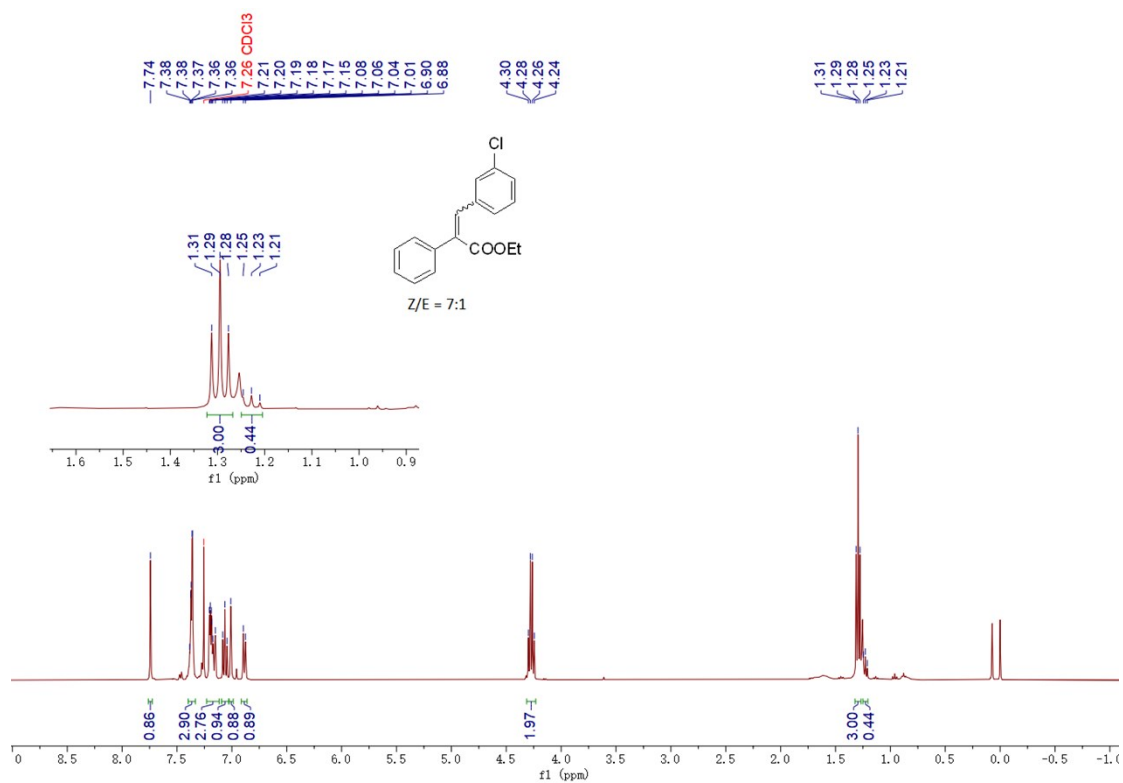


¹H NMR of 3c

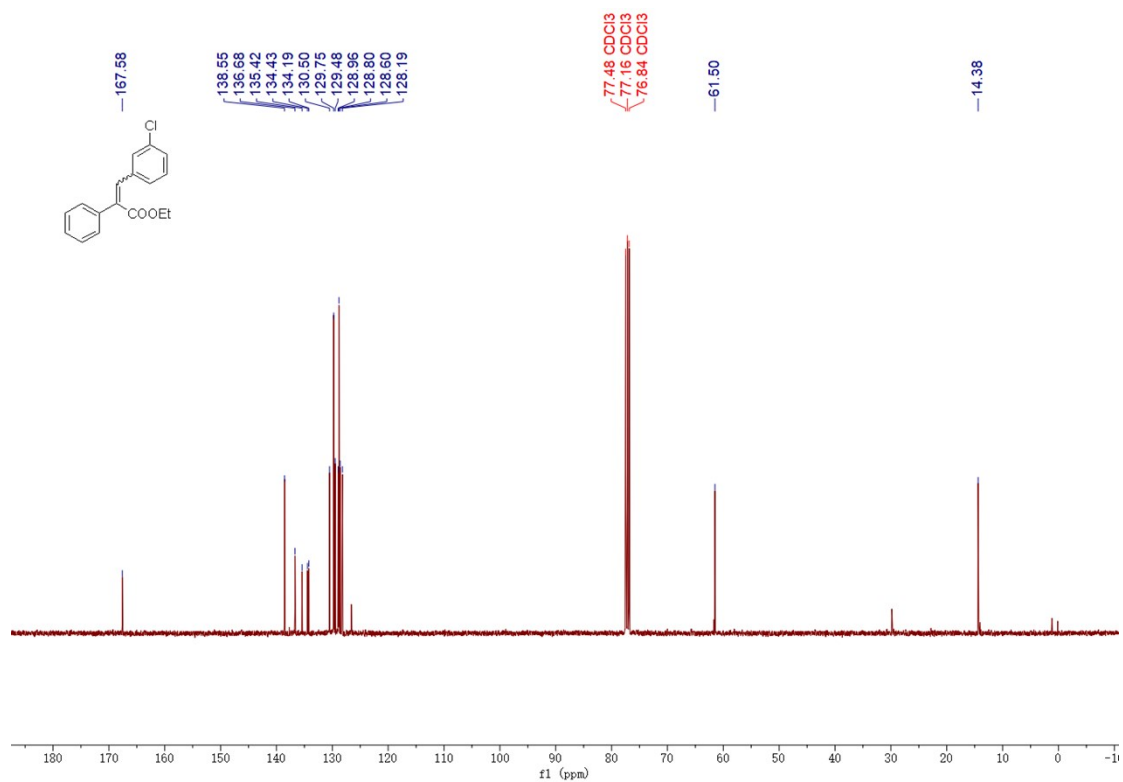


¹³C NMR of 3c

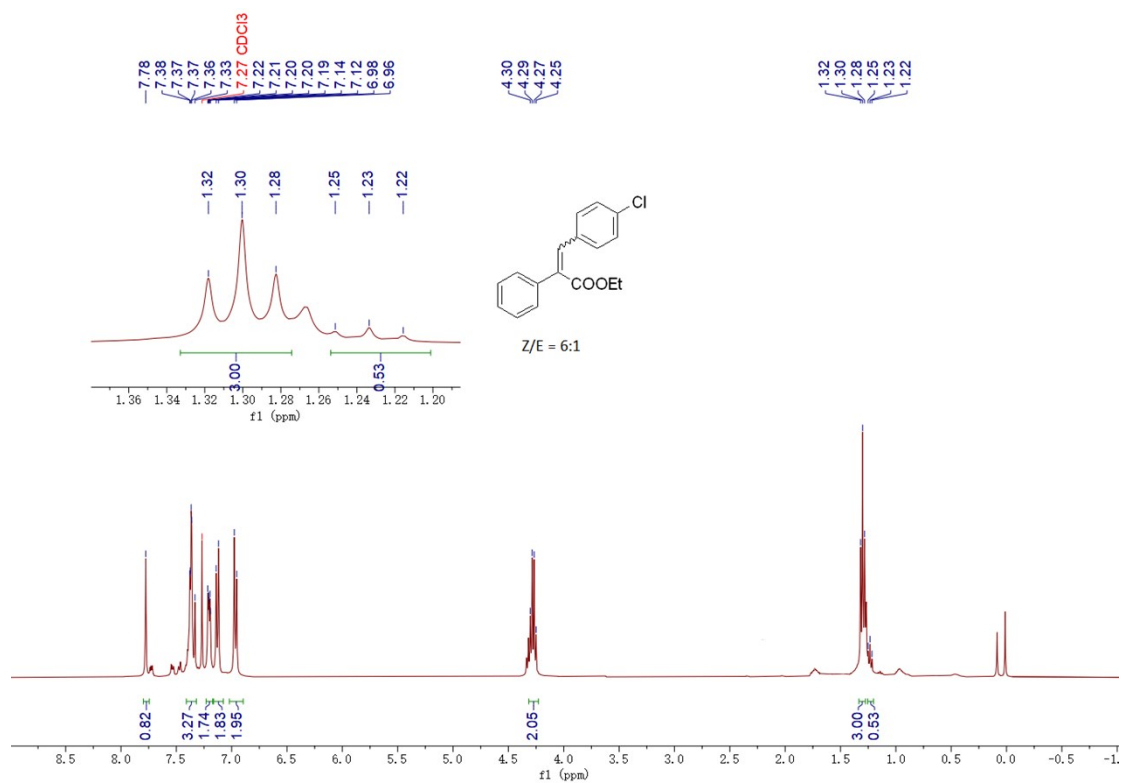




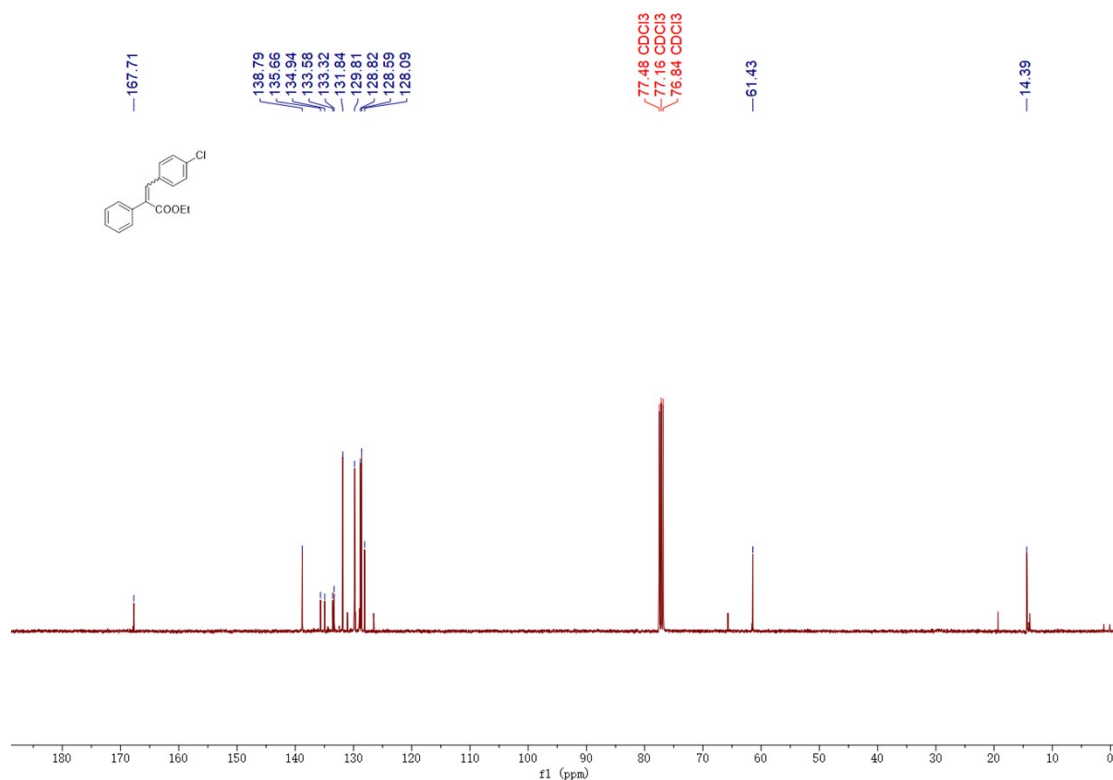
¹H NMR of 3e



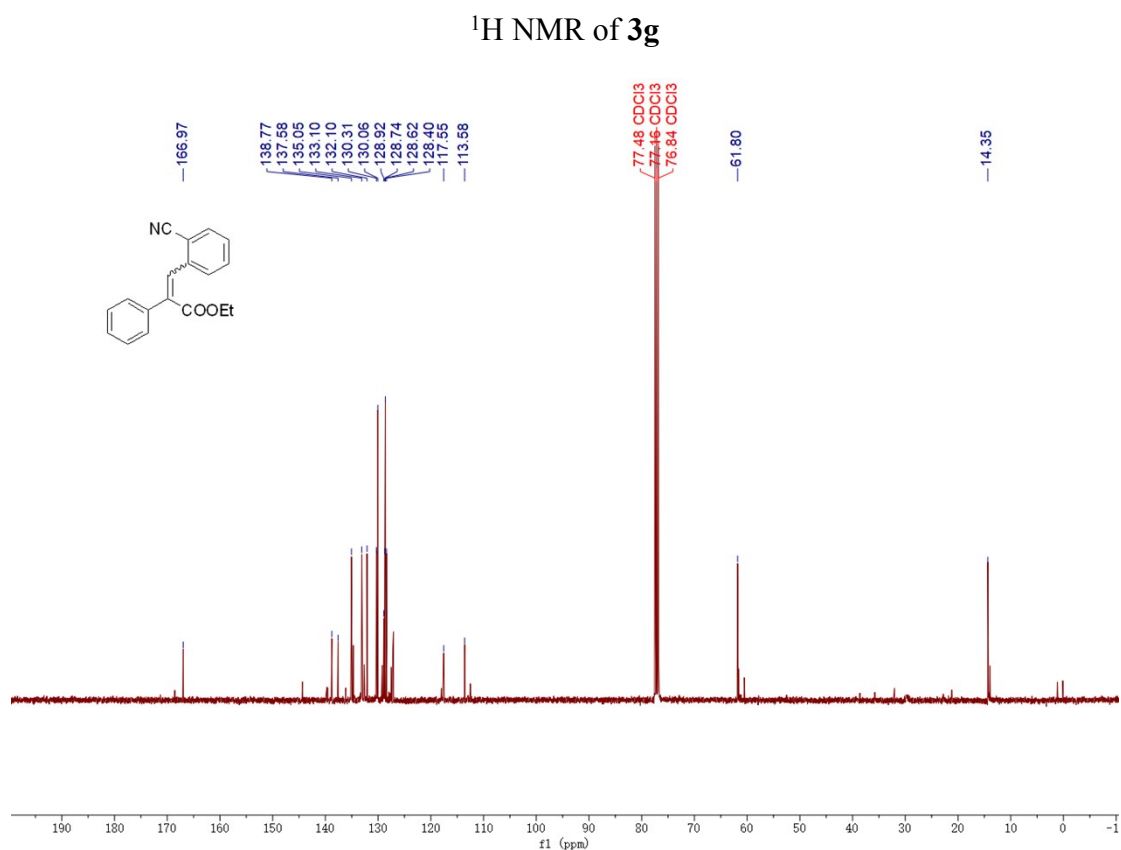
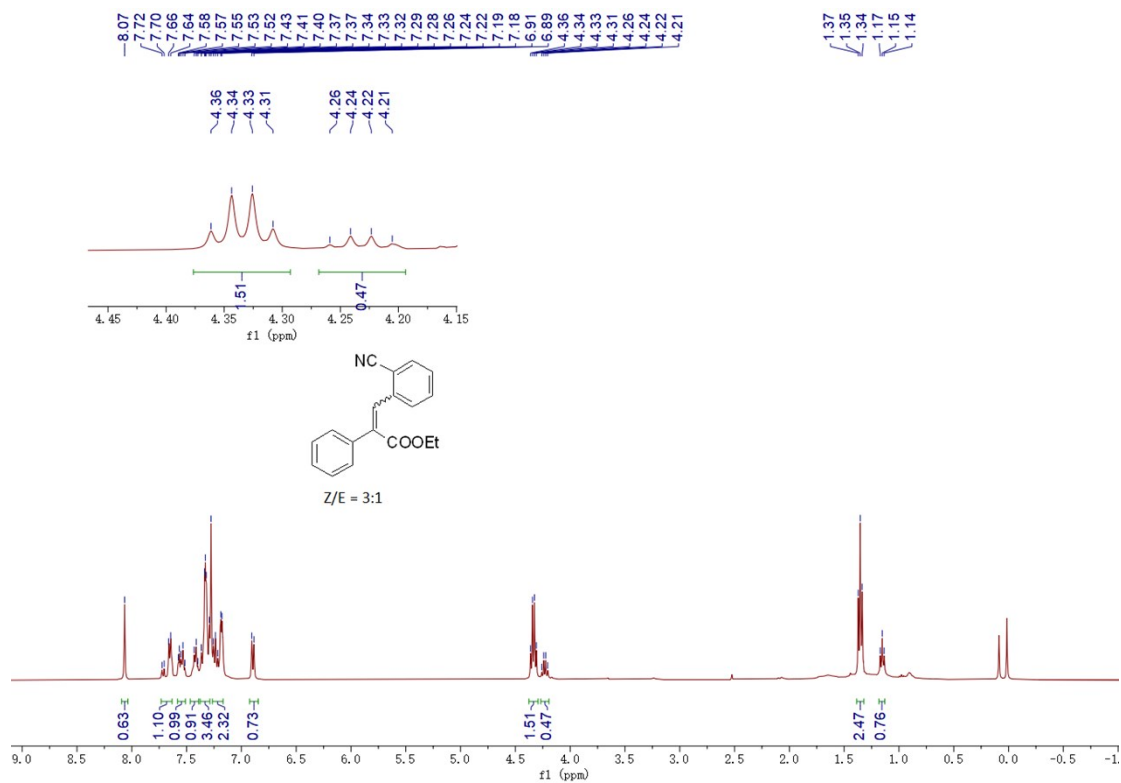
¹³C NMR of 3e

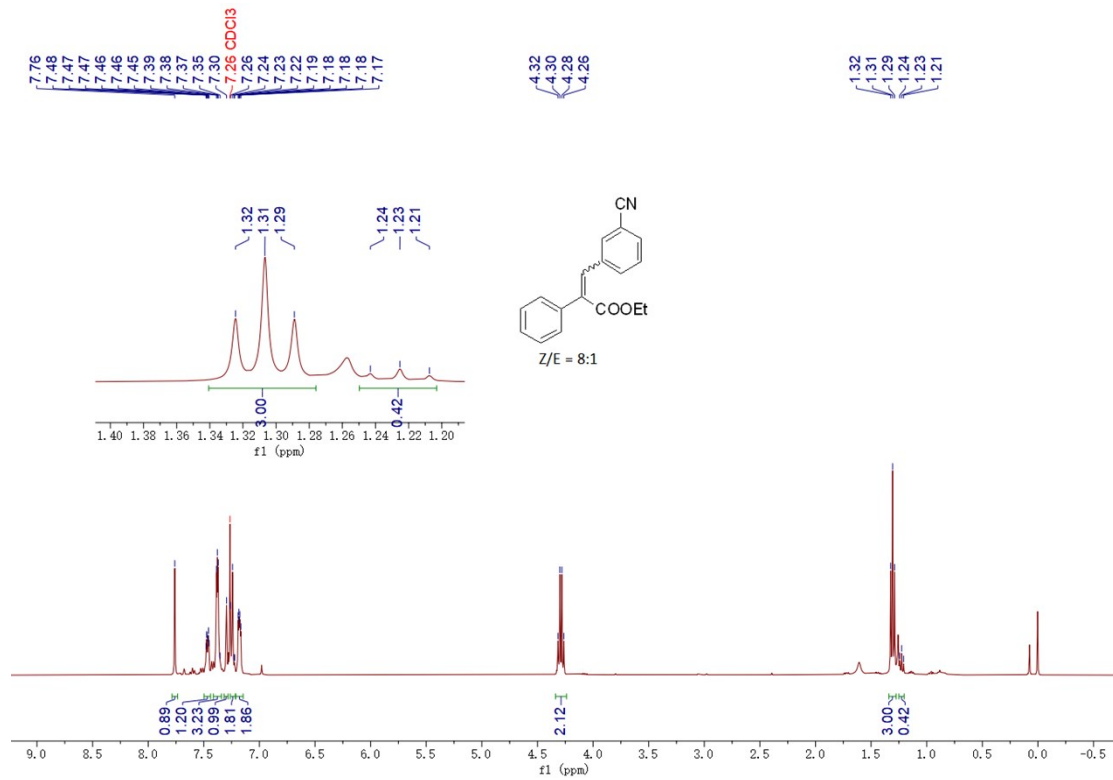


¹H NMR of 3f

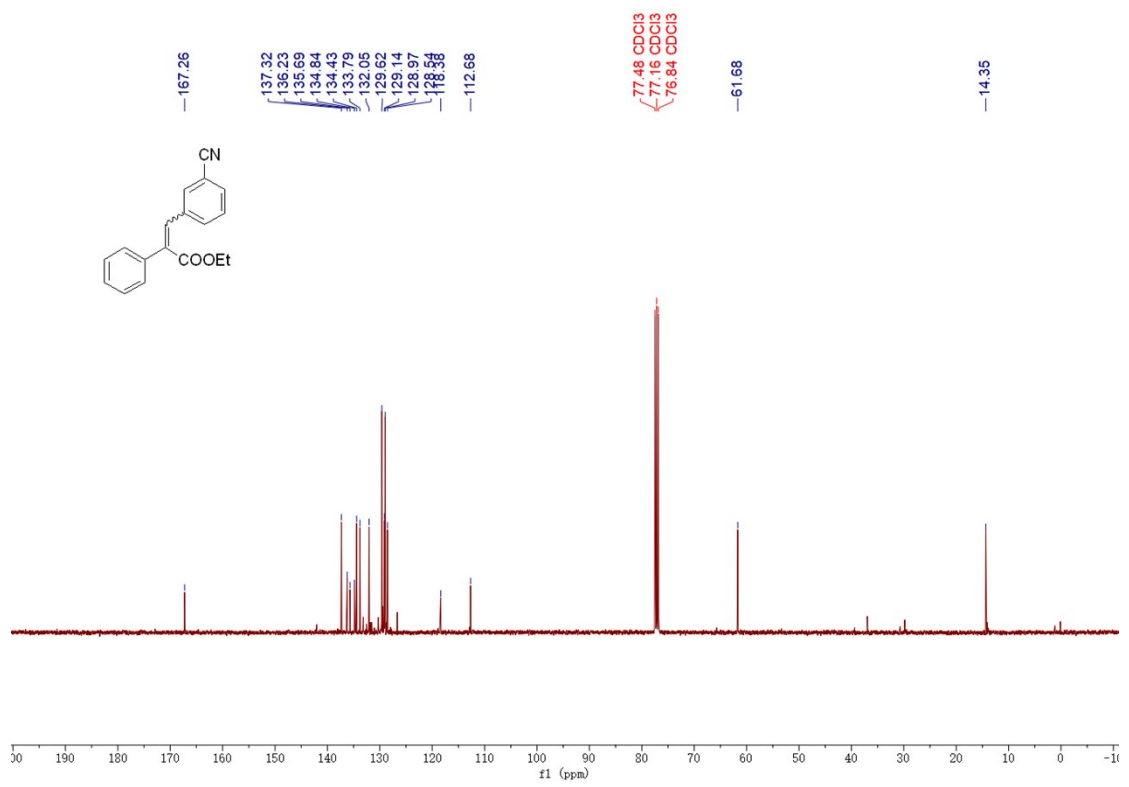


¹³C NMR of 3f

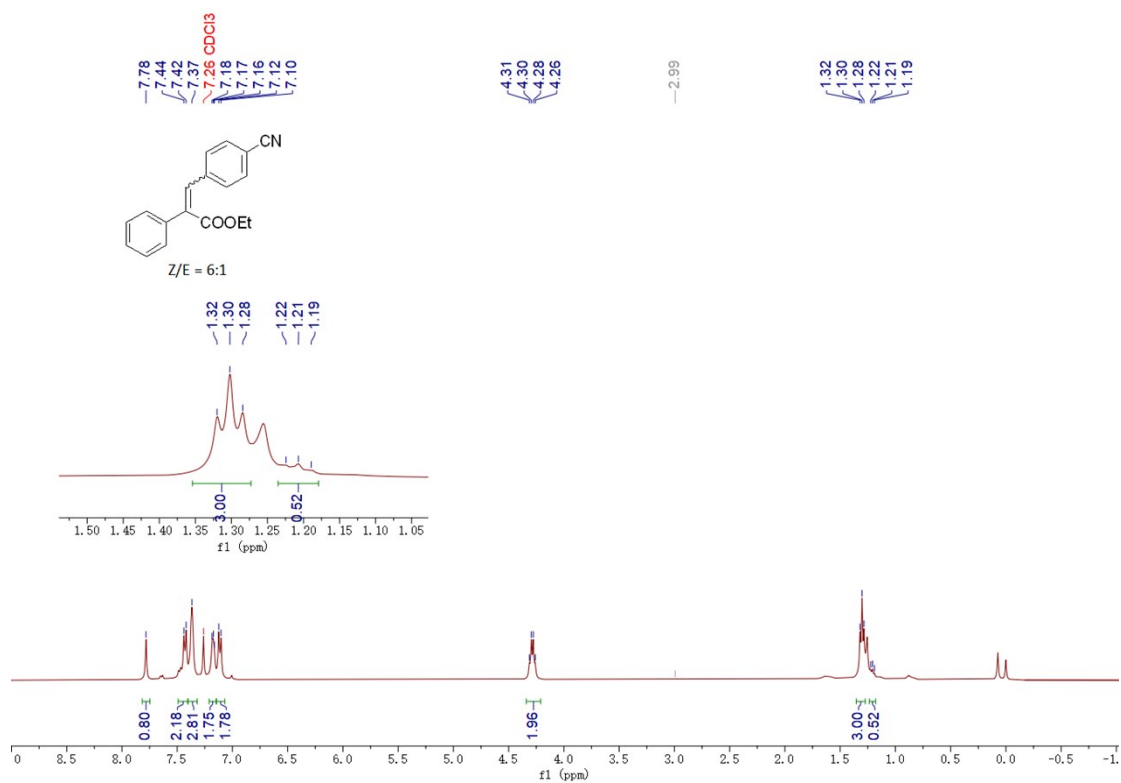




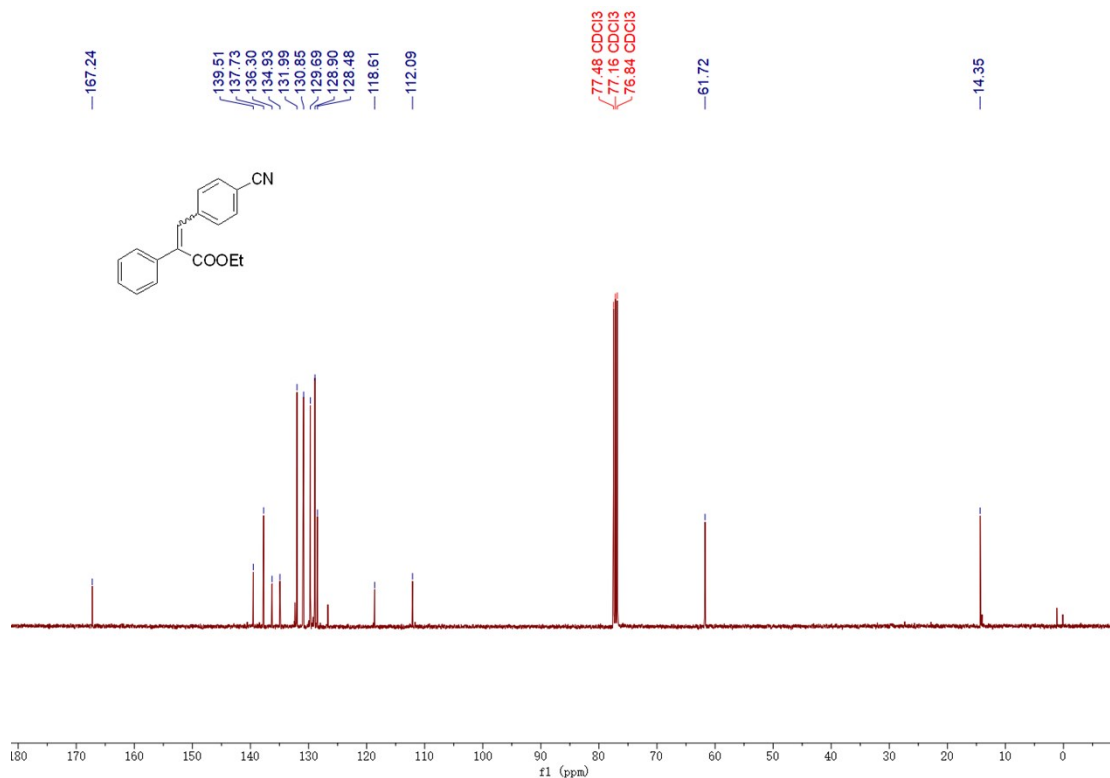
¹H NMR of 3h



¹³C NMR of 3h



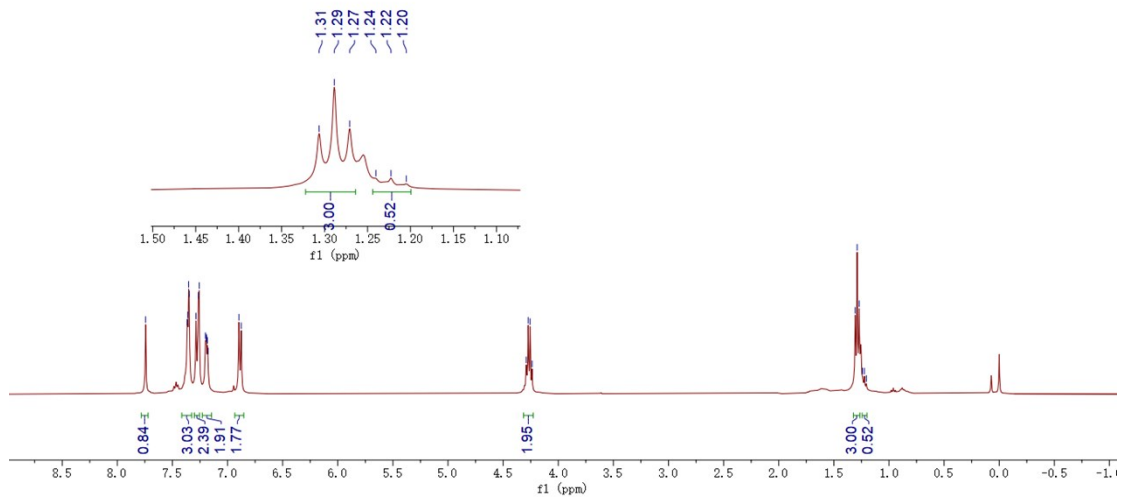
$^1\text{H NMR}$ of **3i**



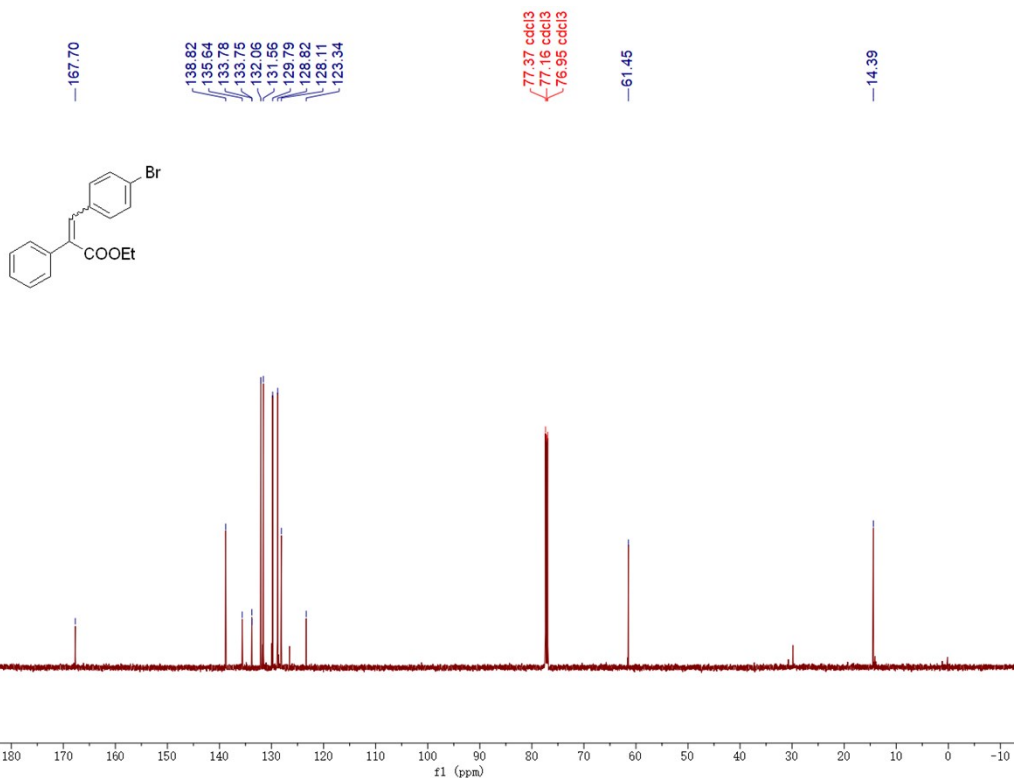
$^{13}\text{C NMR}$ of **3i**



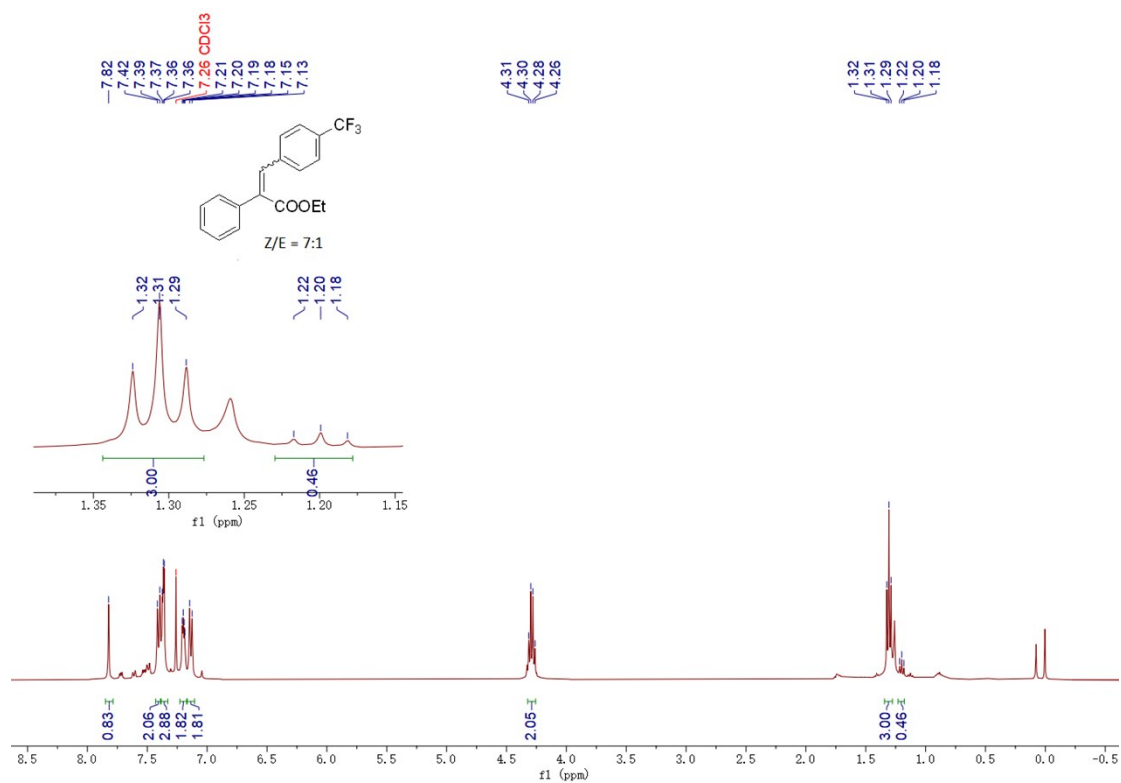
Z/E = 6:1



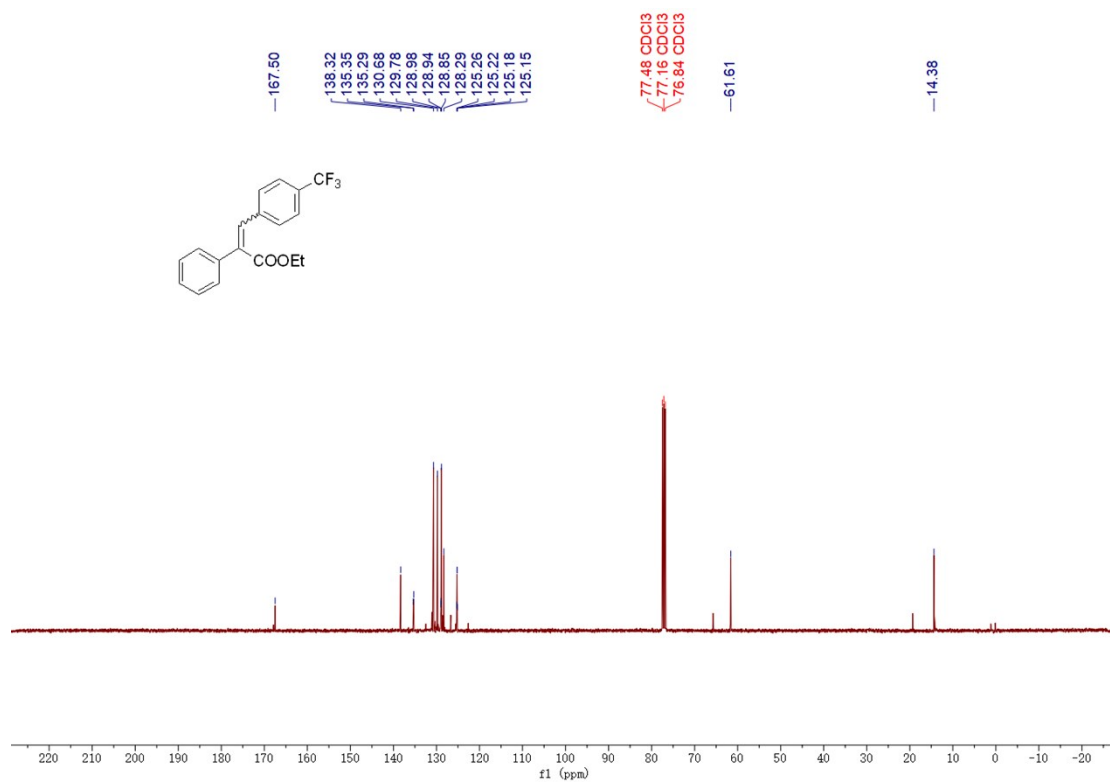
¹H NMR of **3j**



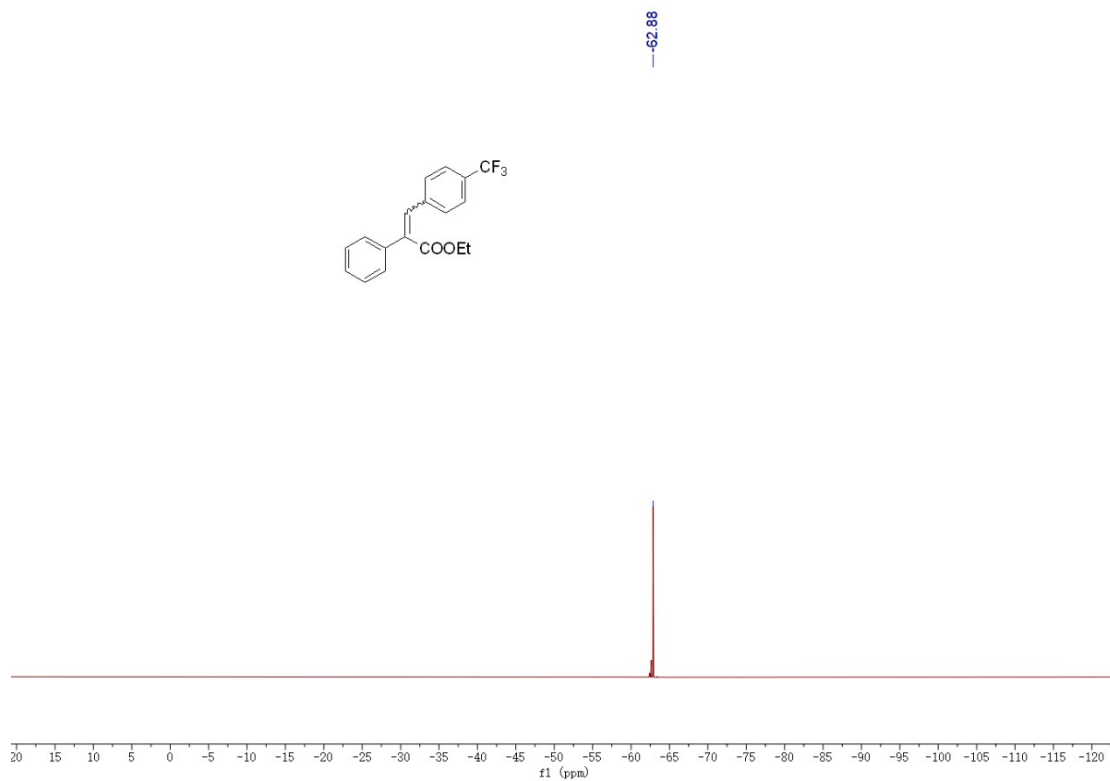
¹³C NMR of **3j**



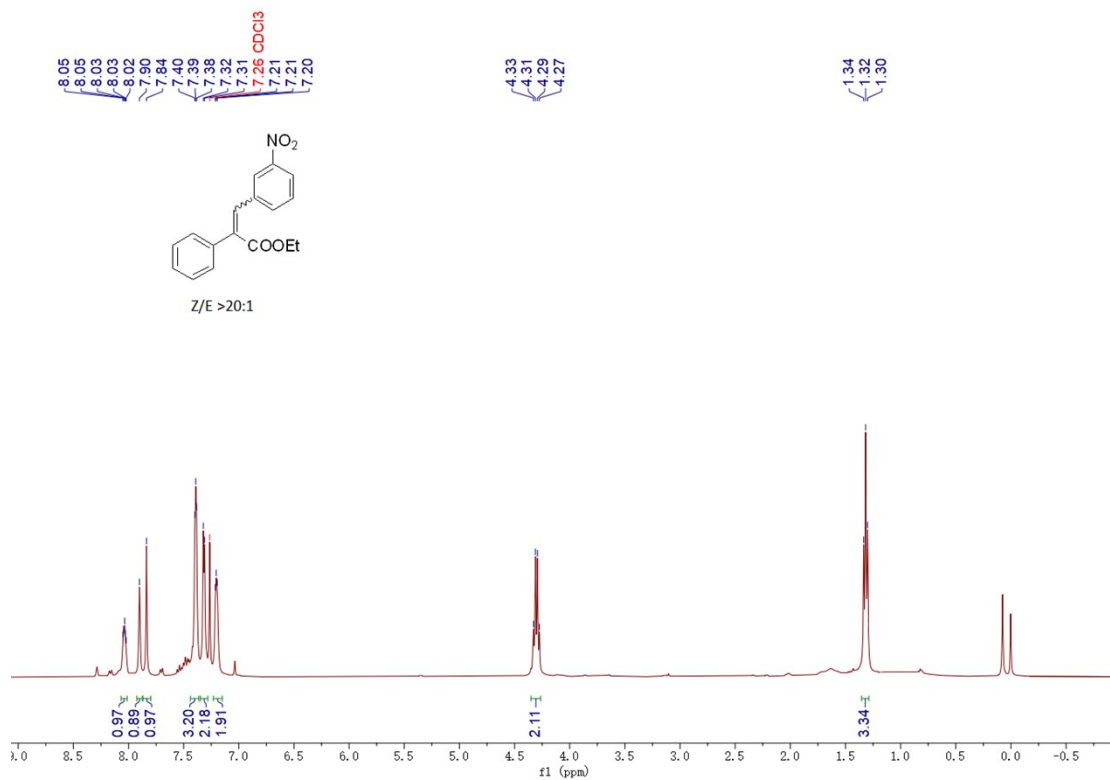
¹H NMR of 3k



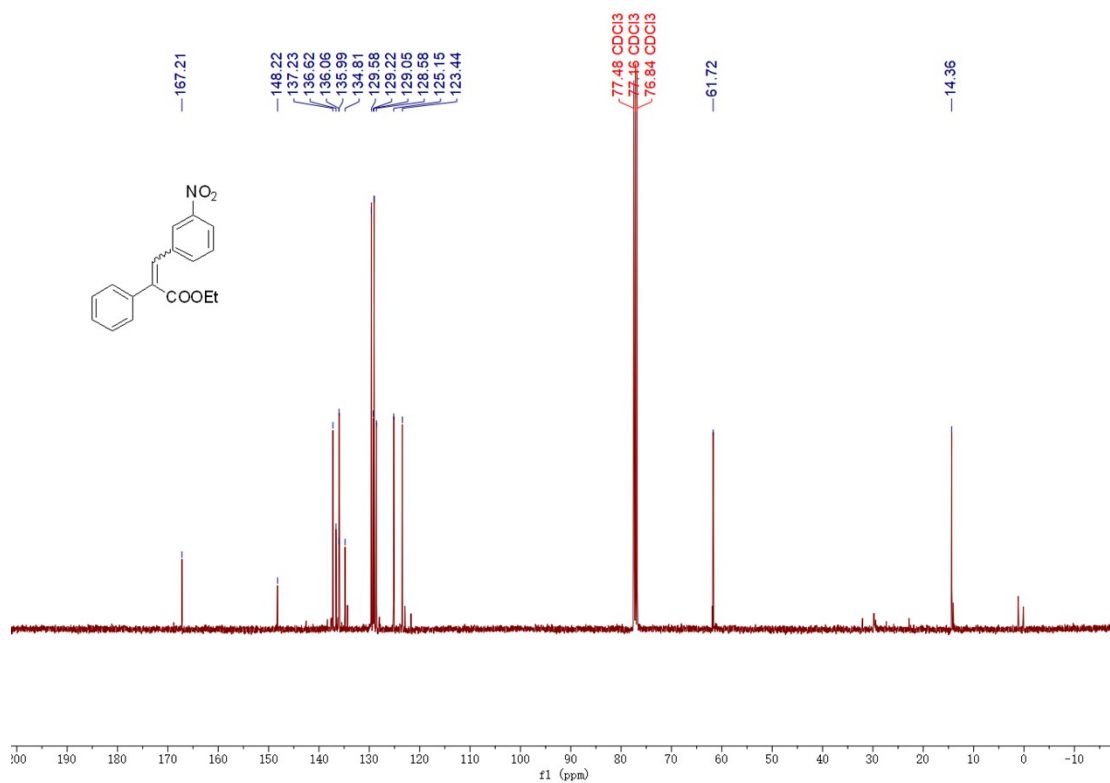
¹³C NMR of 3k



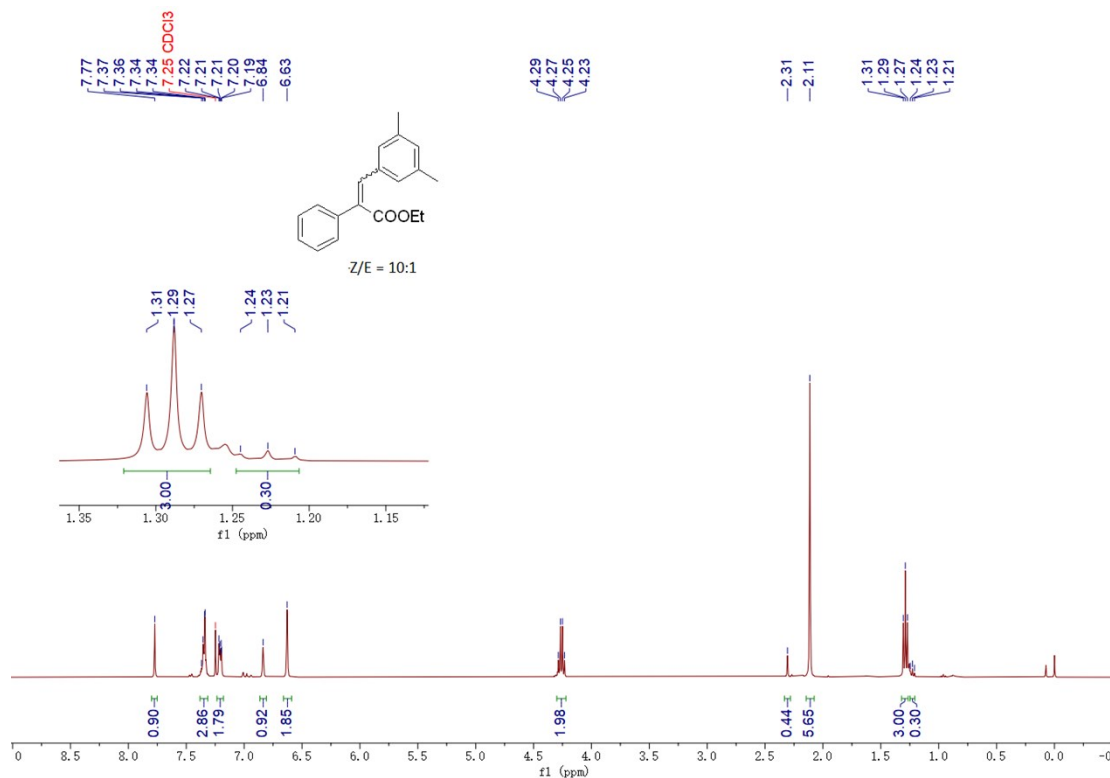
¹⁹F NMR of **3k**



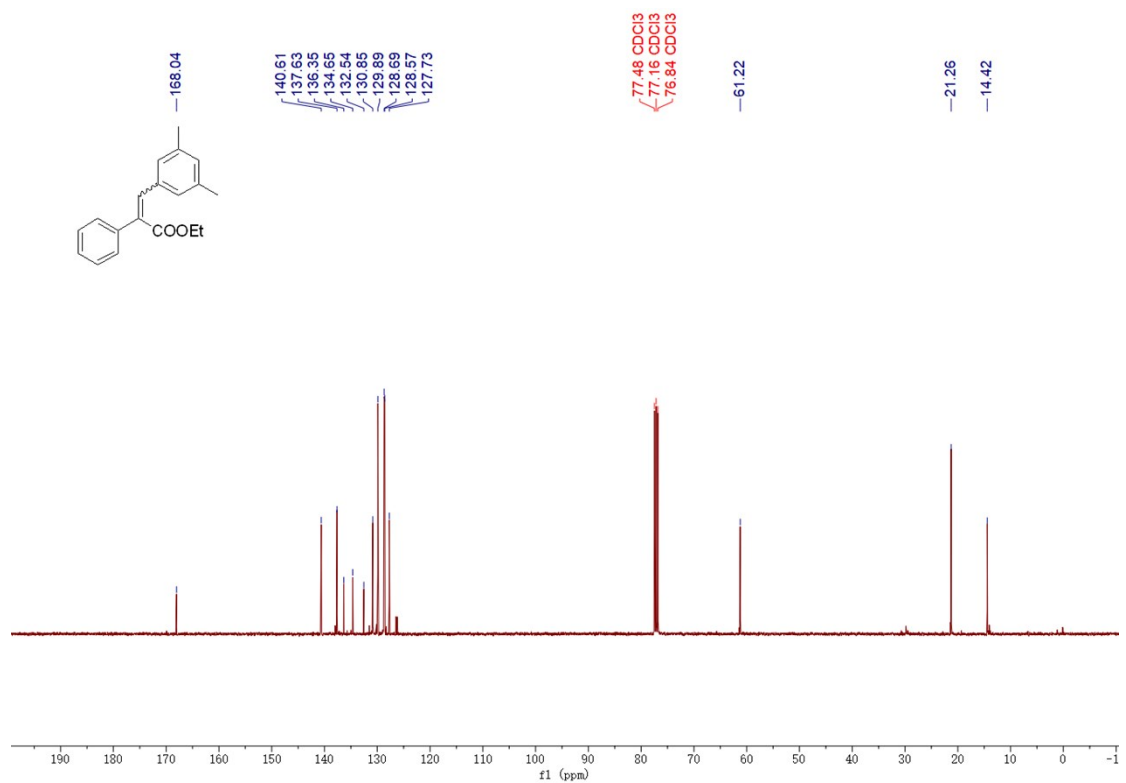
¹H NMR of **3l**



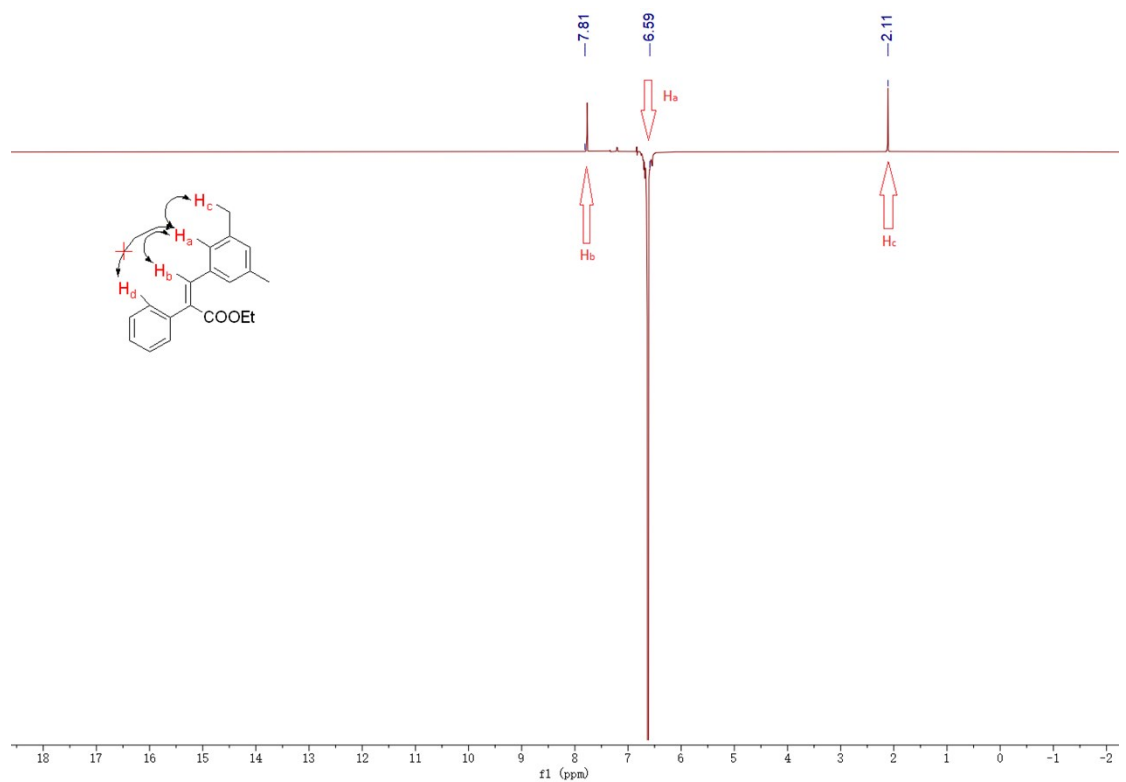
¹³C NMR of **31**



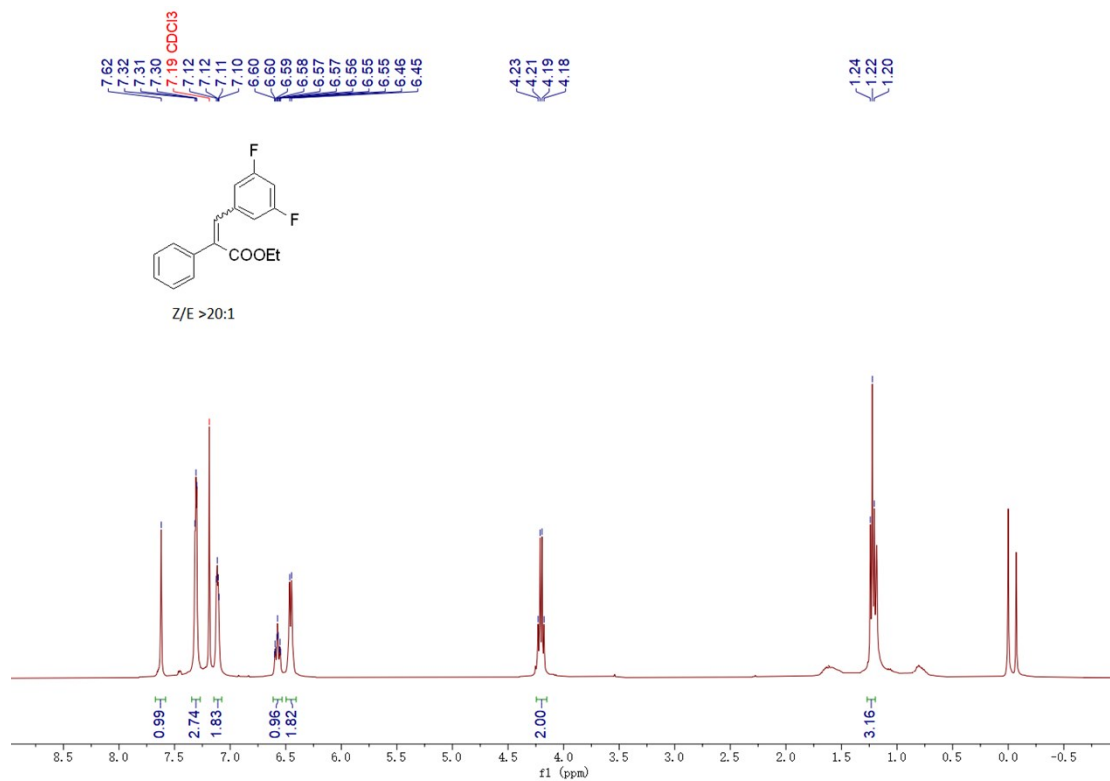
¹H NMR of **3m**



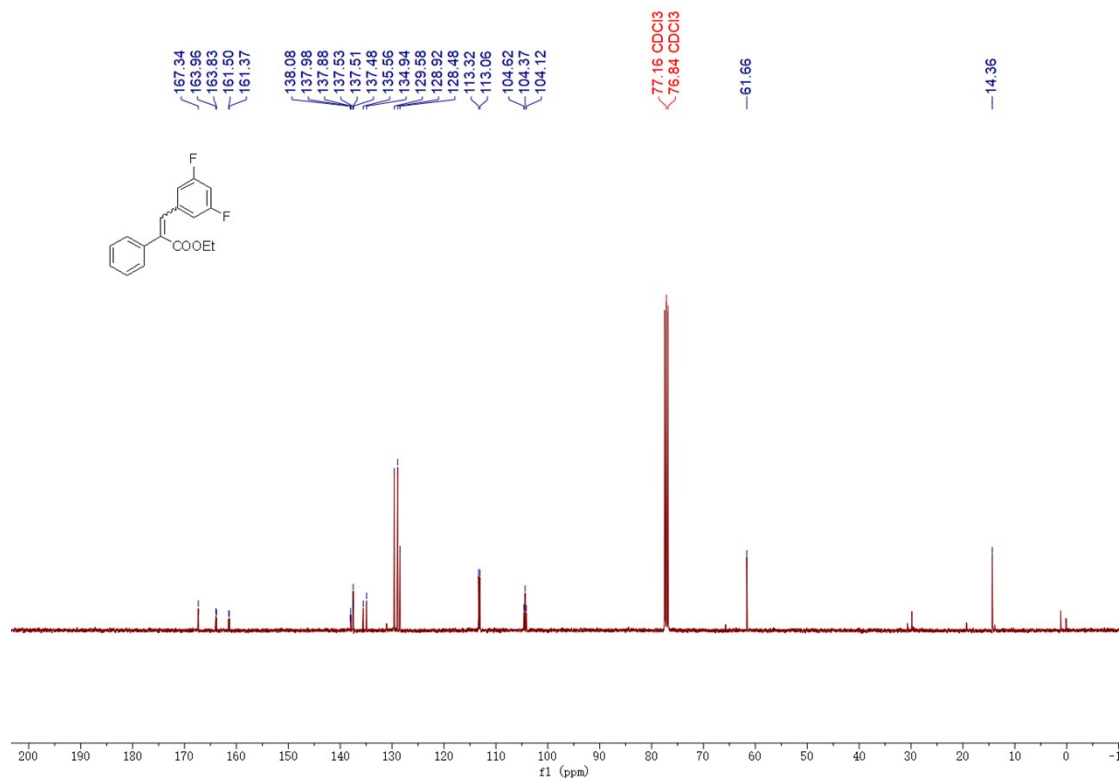
^{13}C NMR of **3m**



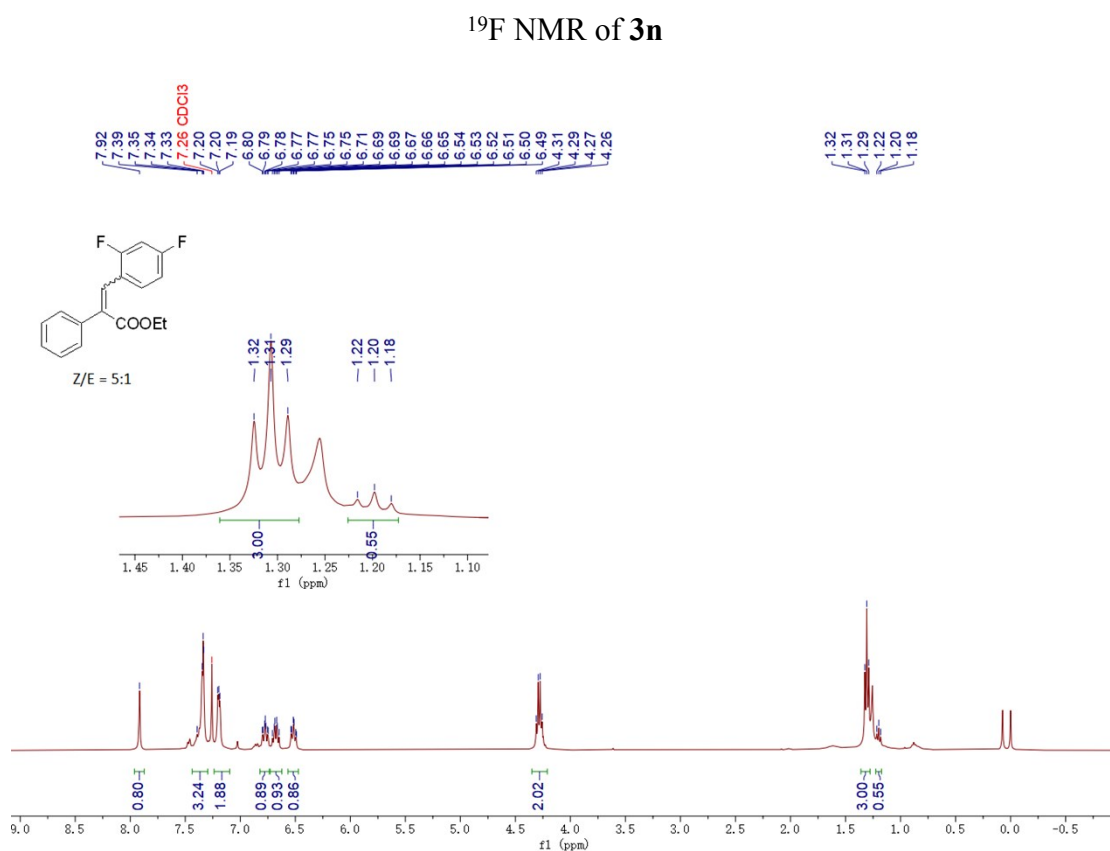
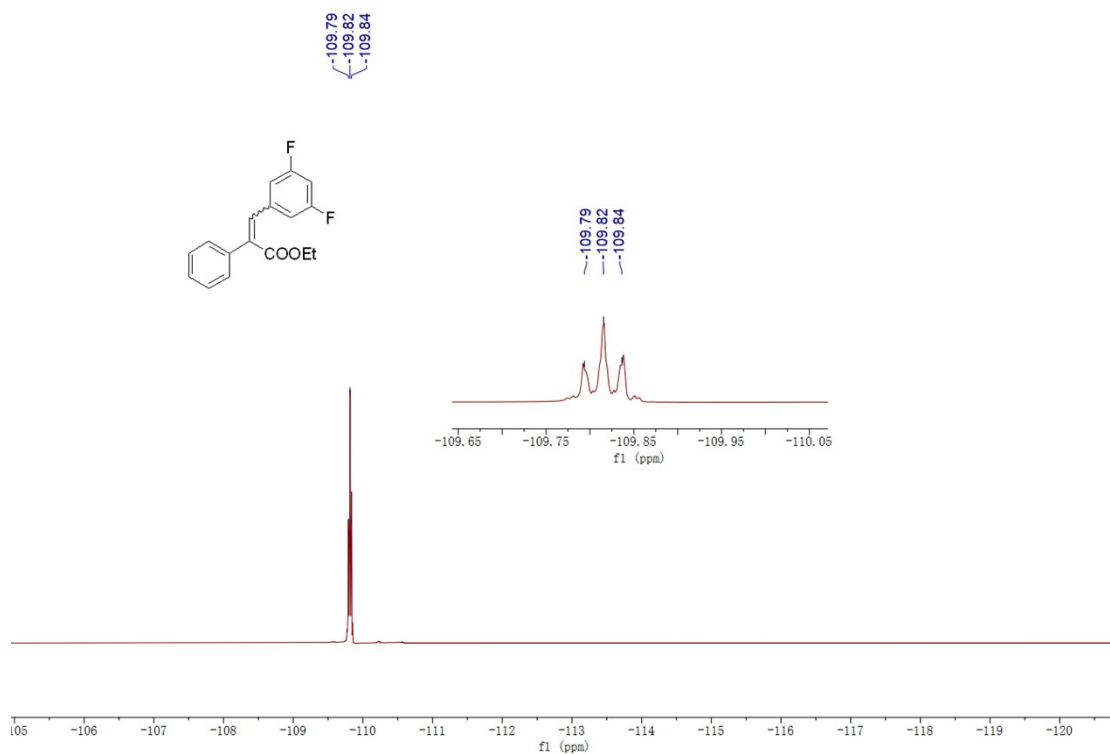
NOESY of **3m**

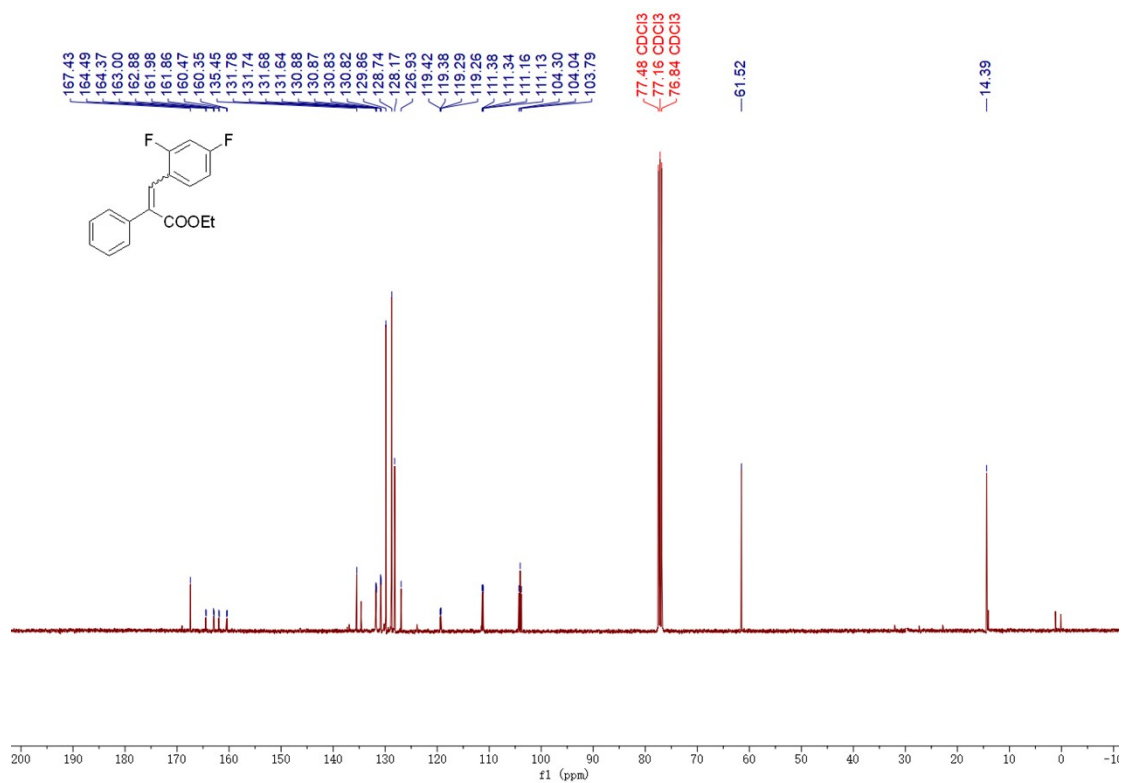


¹H NMR of **3n**

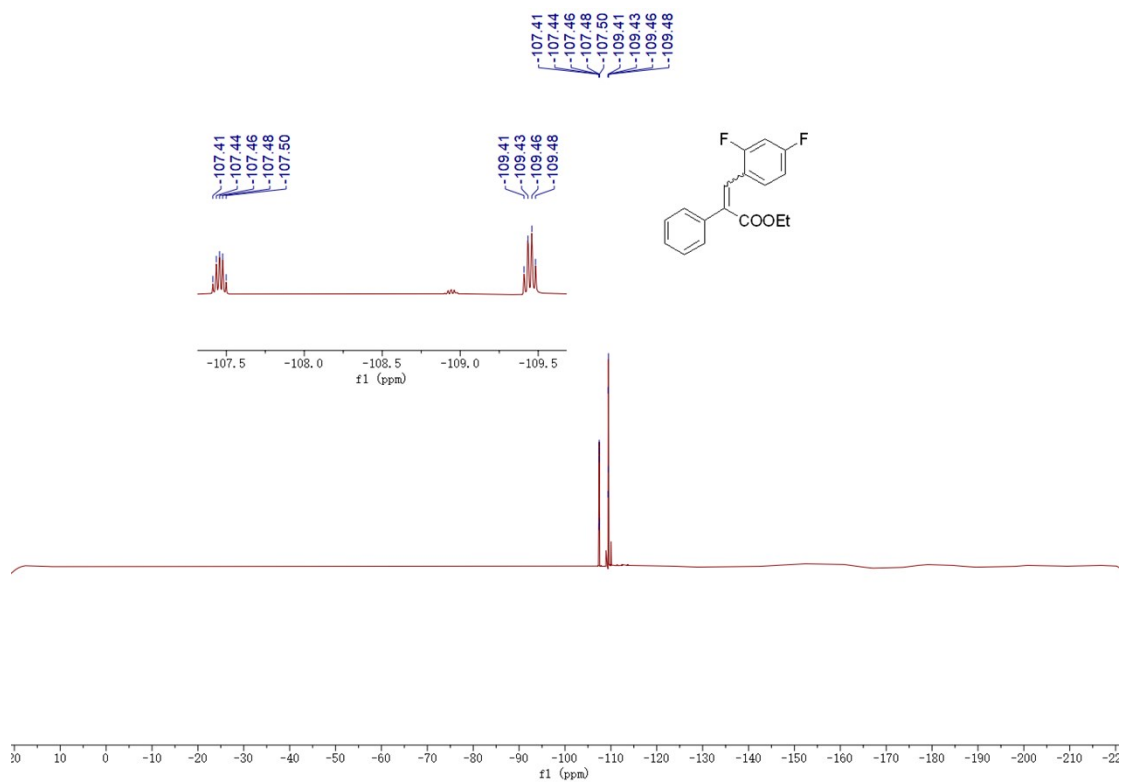


¹³C NMR of **3n**

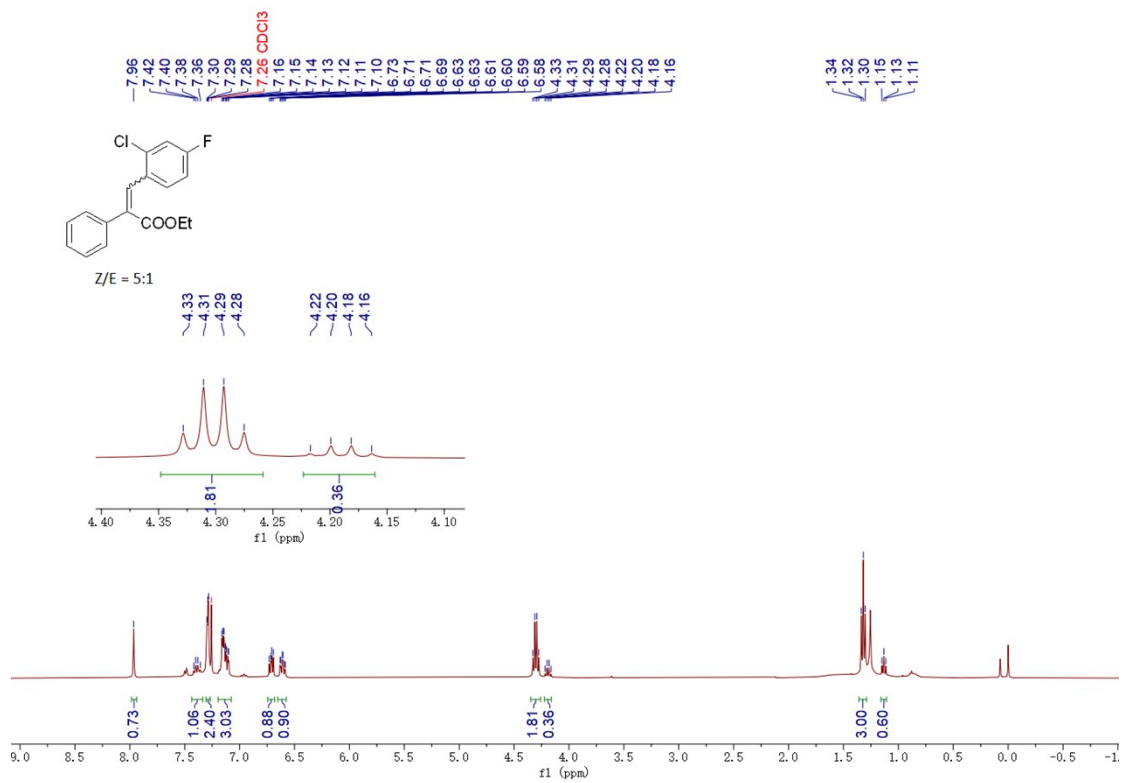




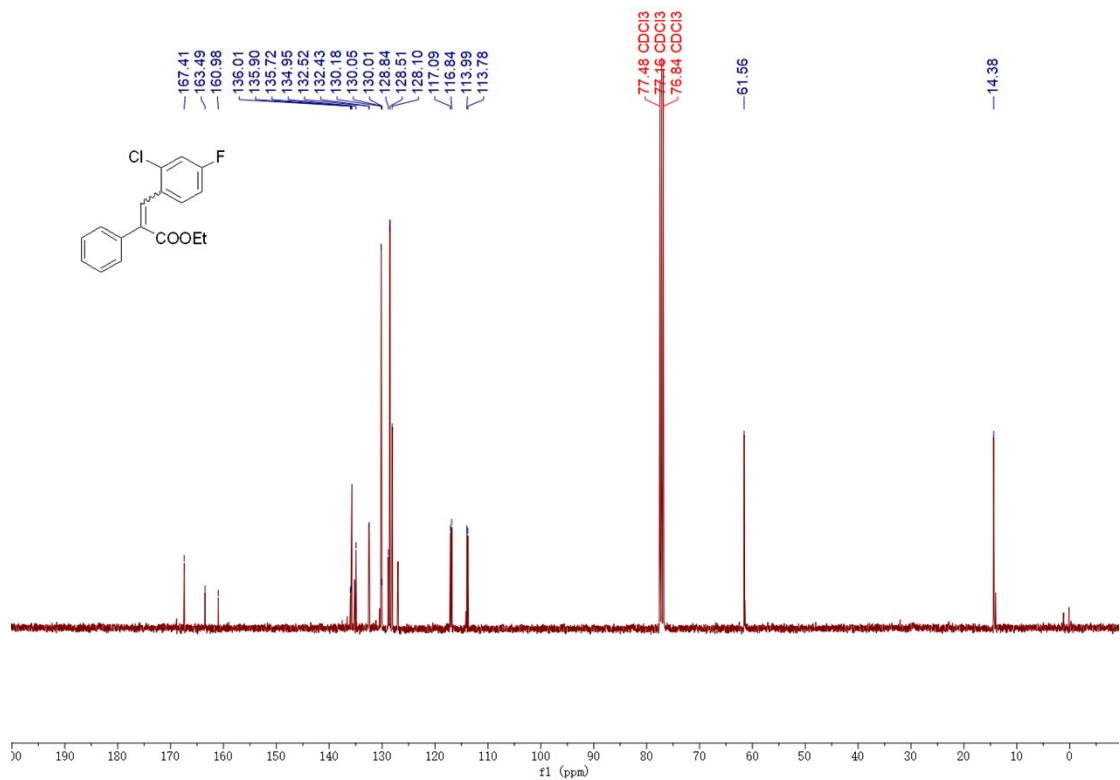
¹³C NMR of **30**



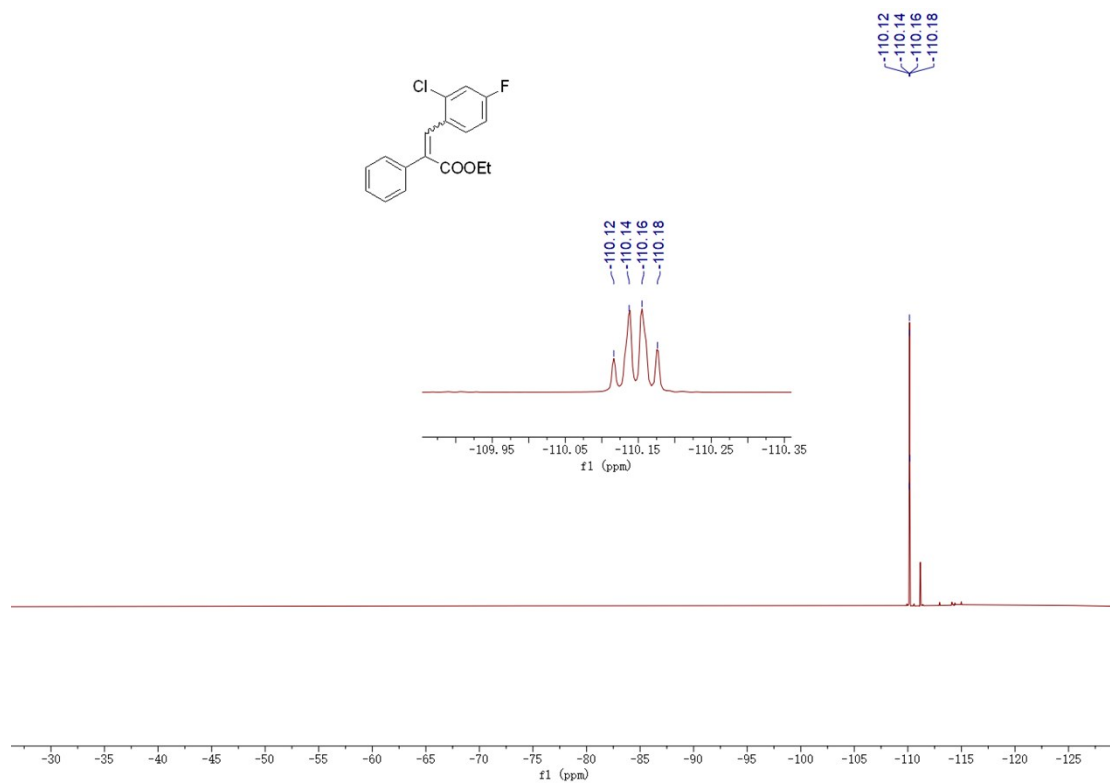
¹⁹F NMR of **30**



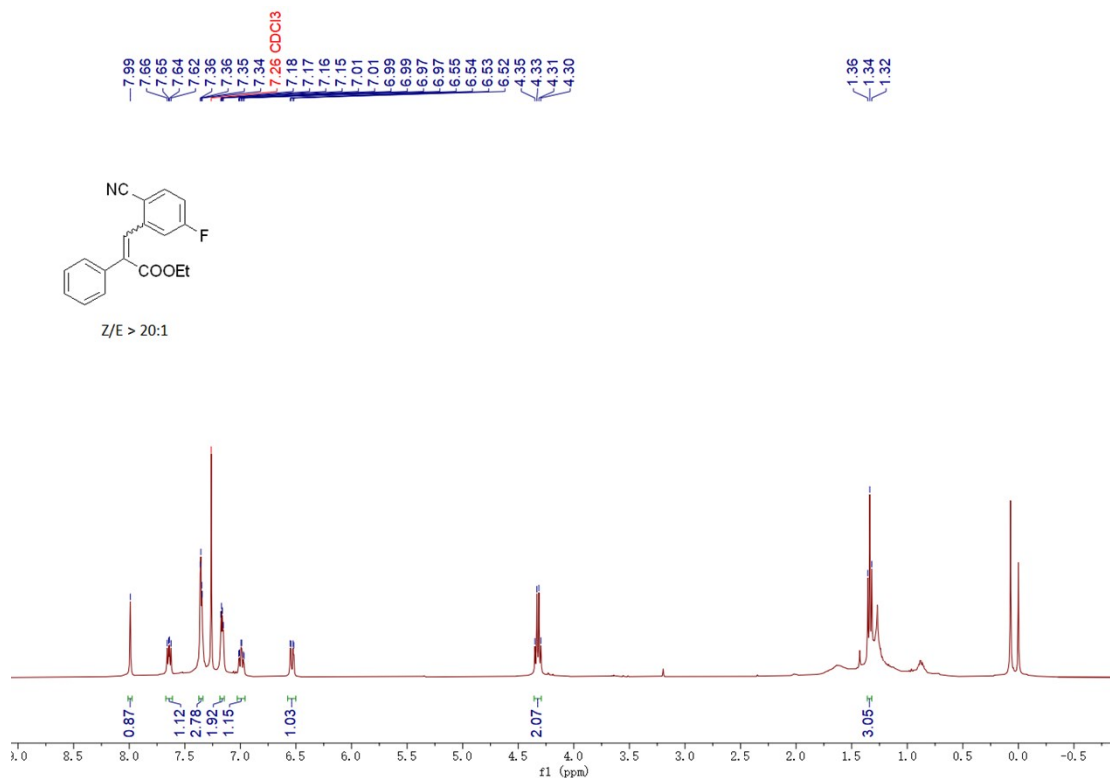
¹H NMR of 3p



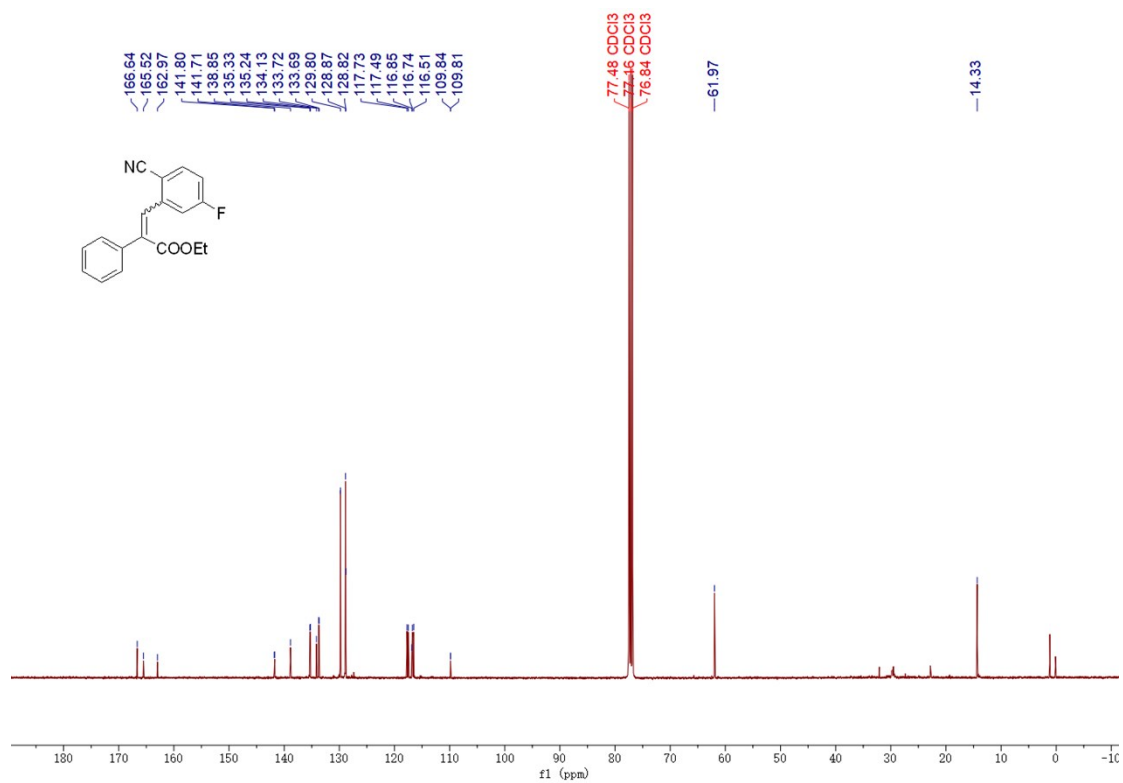
¹³C NMR of 3p



^{19}F NMR of 3p



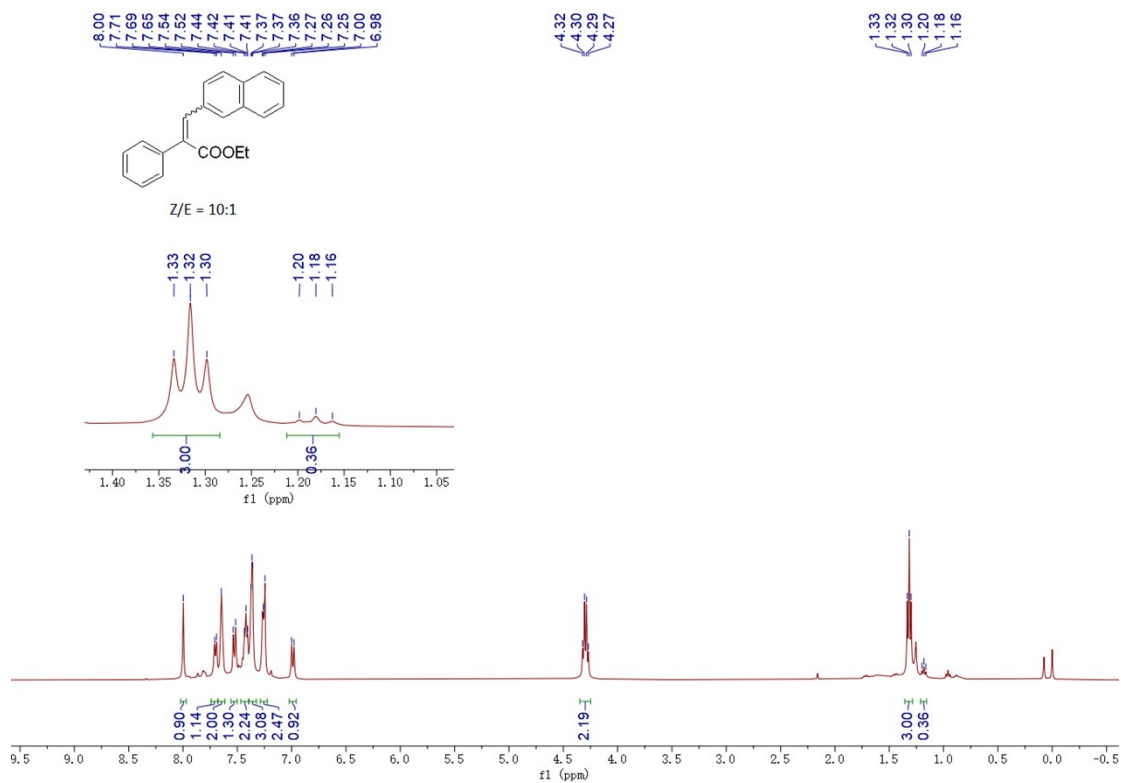
^1H NMR of 3q



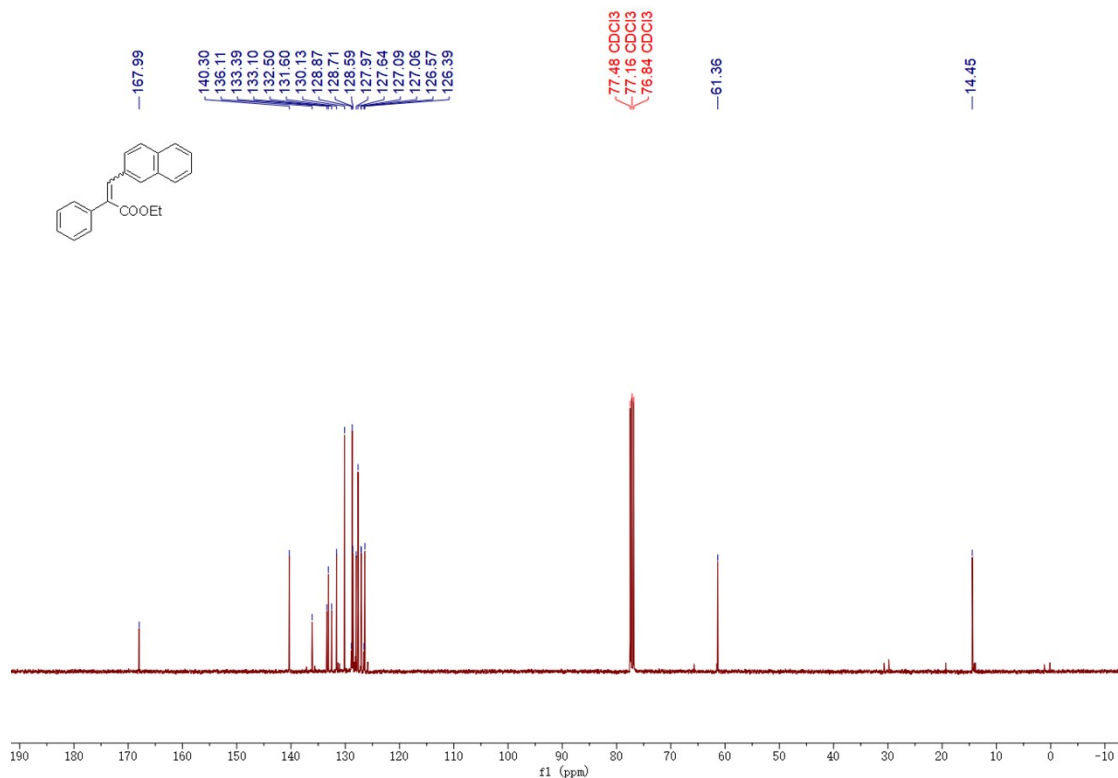
¹³C NMR of **3q**



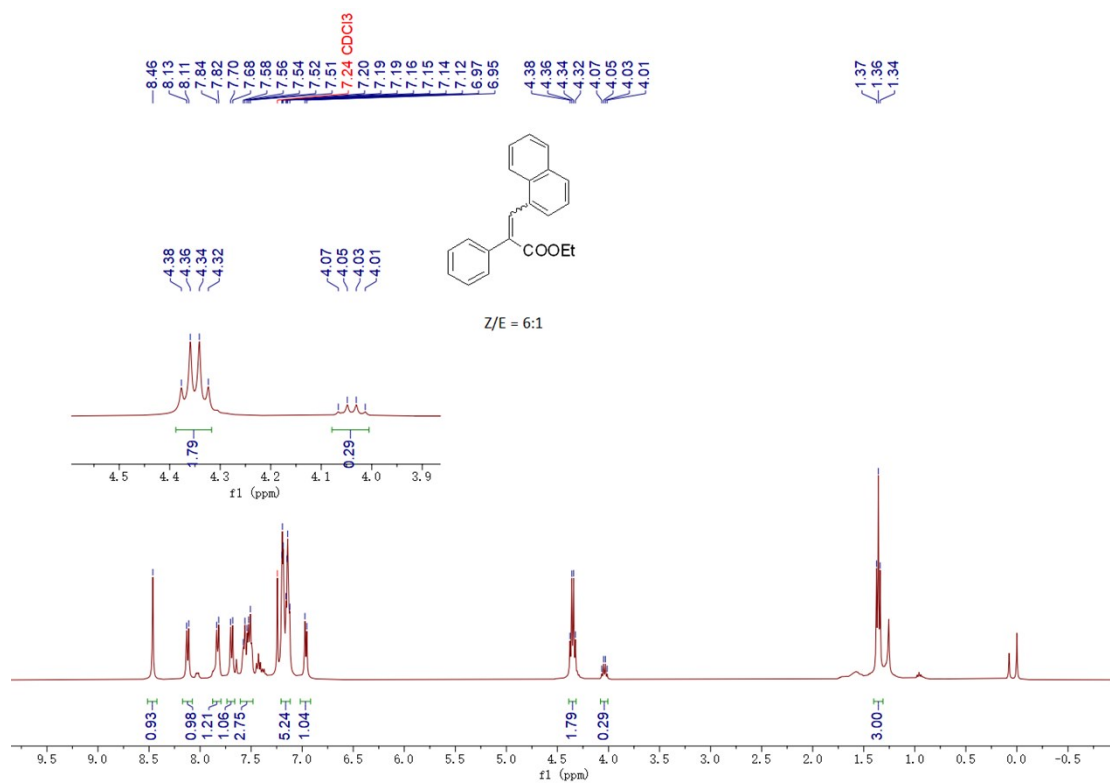
¹⁹F NMR of **3q**



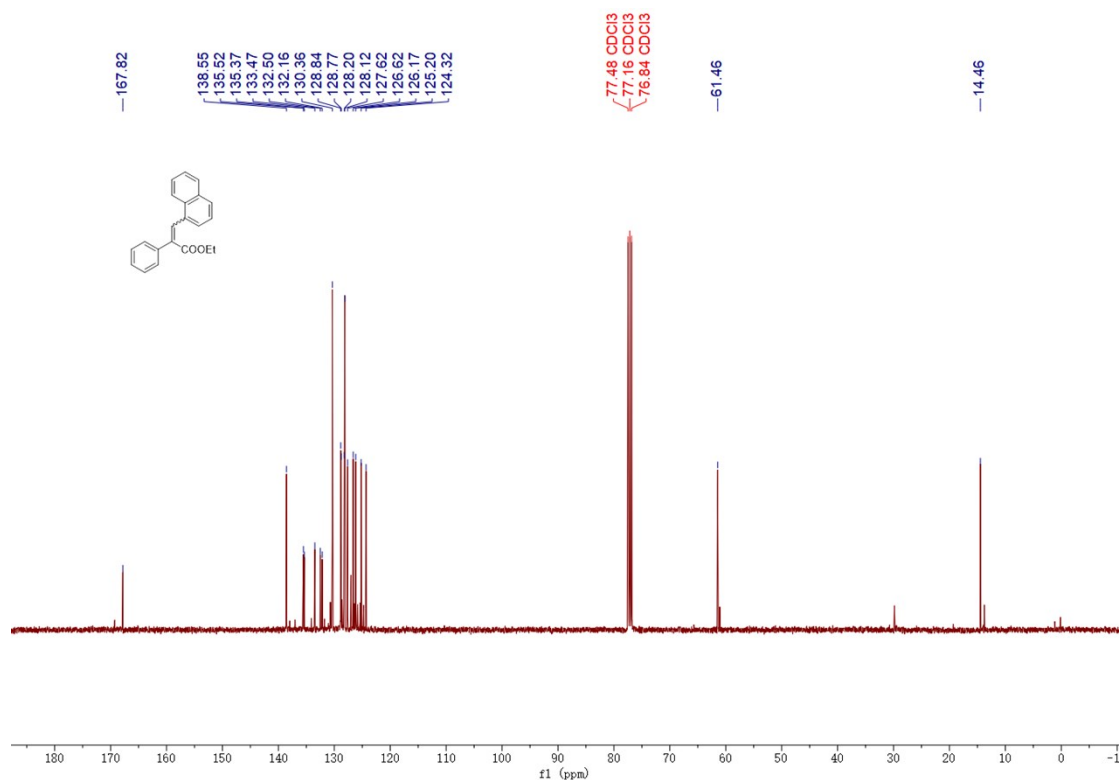
$^1\text{H NMR}$ of **3r**



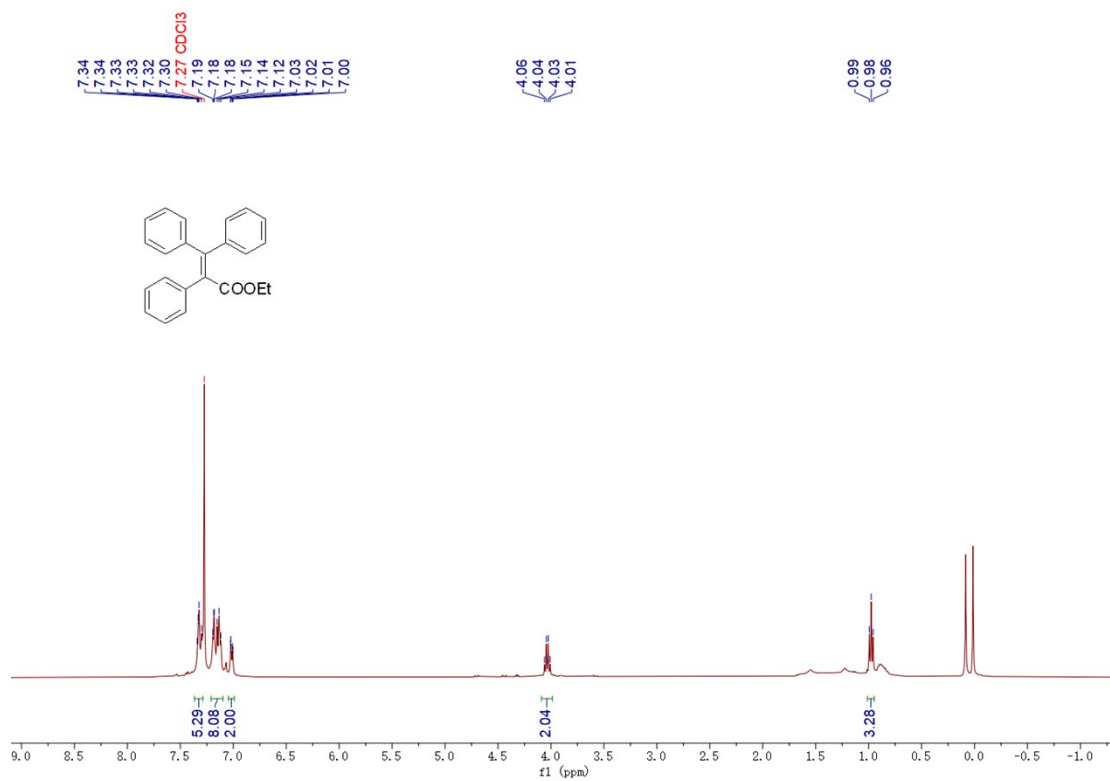
$^{13}\text{C NMR}$ of **3r**



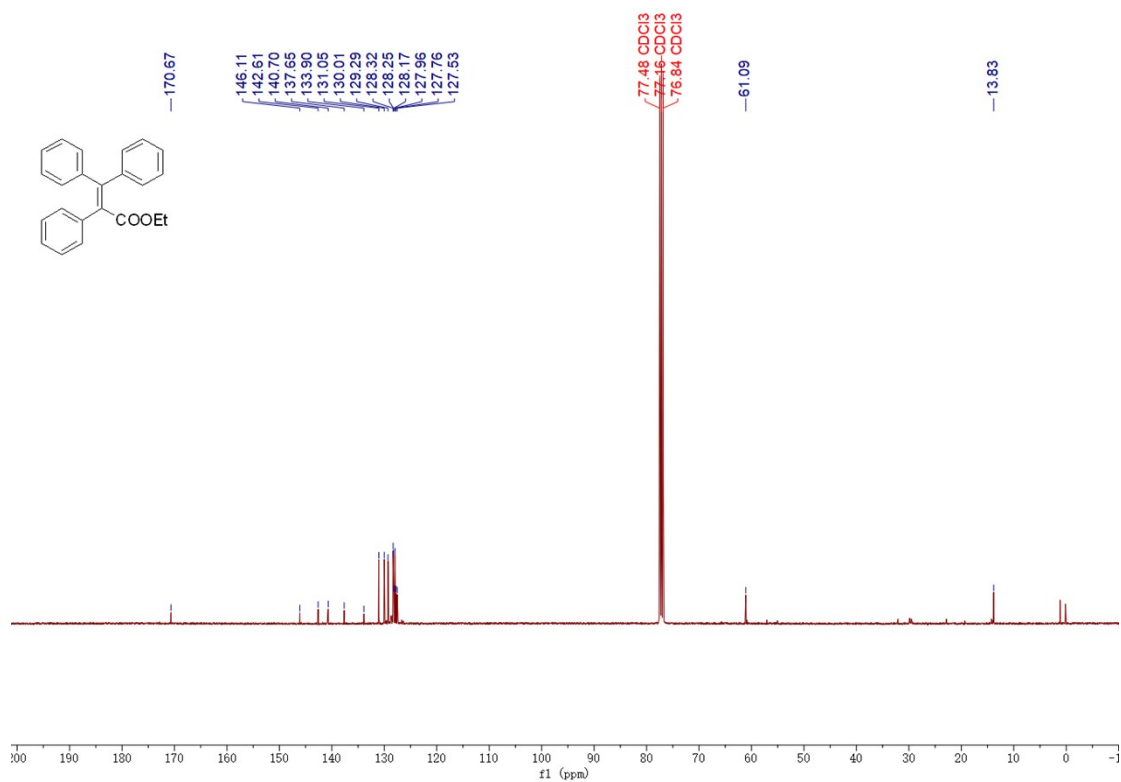
¹H NMR of 3s



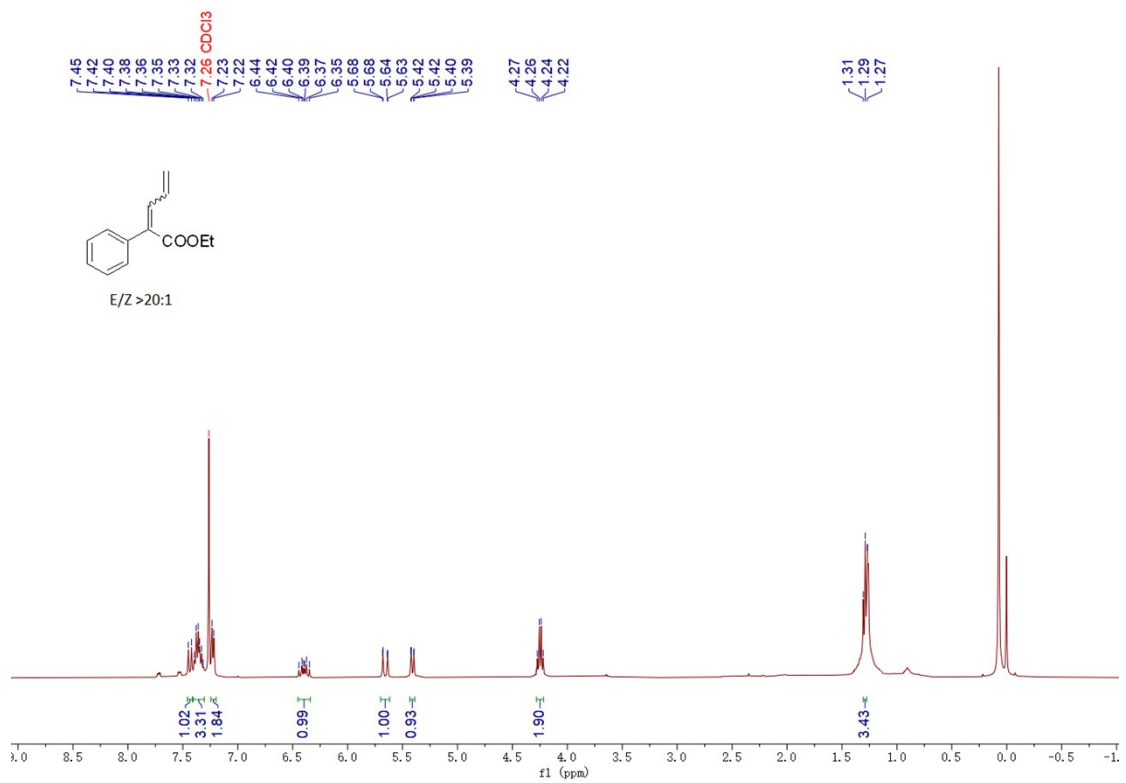
¹³C NMR of 3s



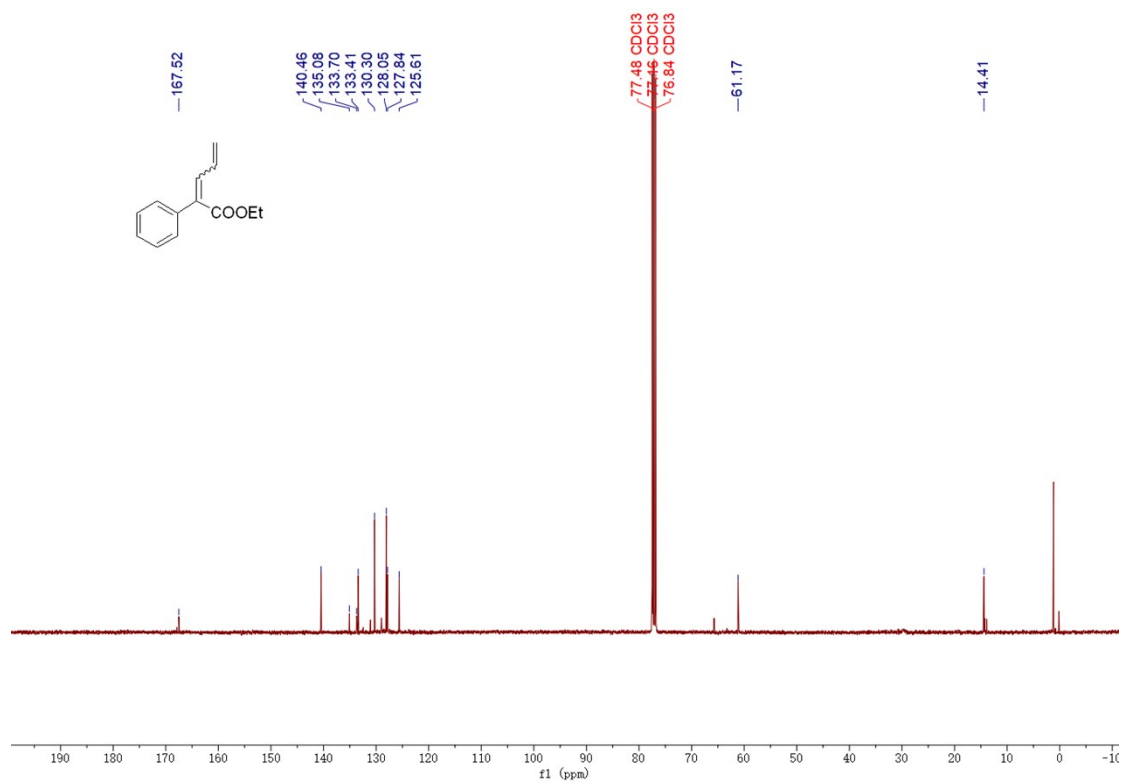
$^1\text{H NMR}$ of 3t



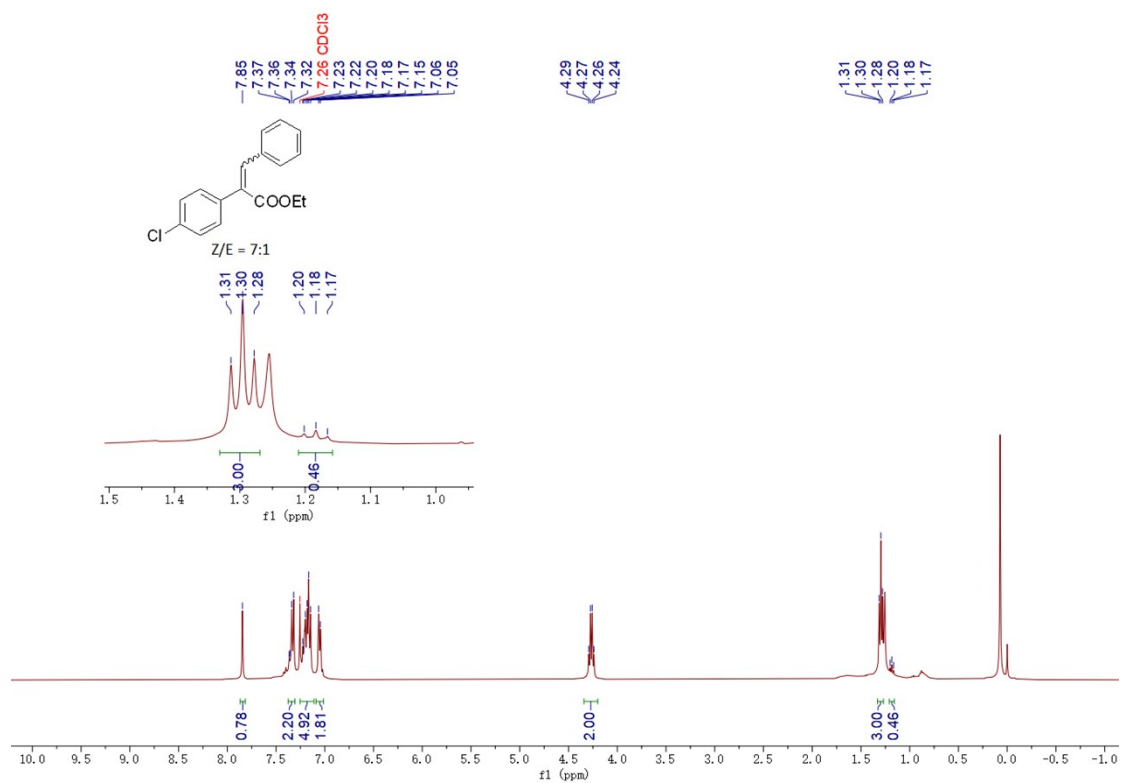
$^{13}\text{C NMR}$ of 3t



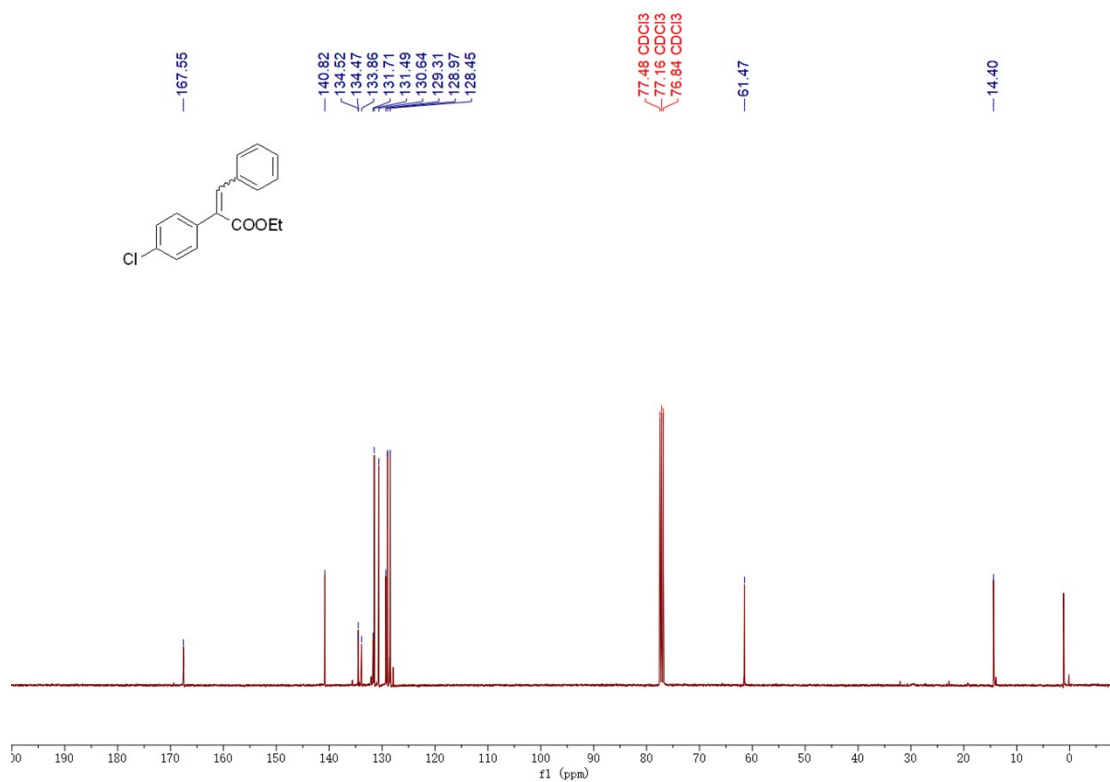
¹H NMR of 3u



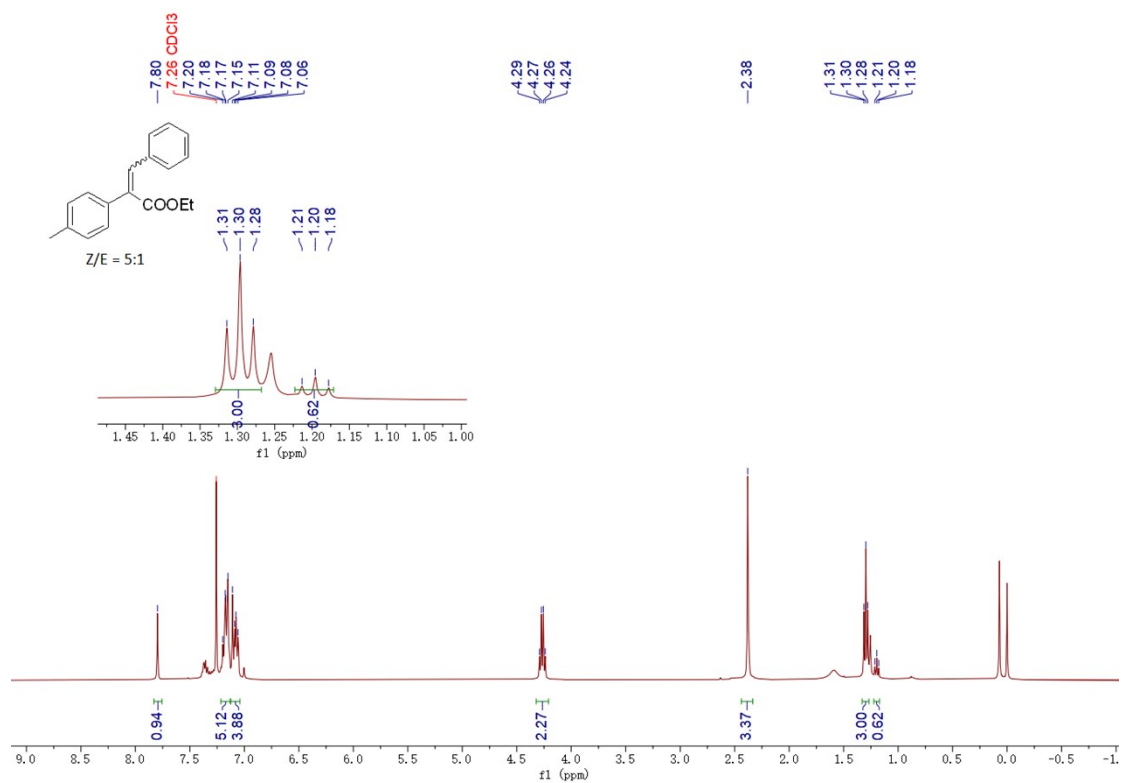
¹³C NMR of 3u



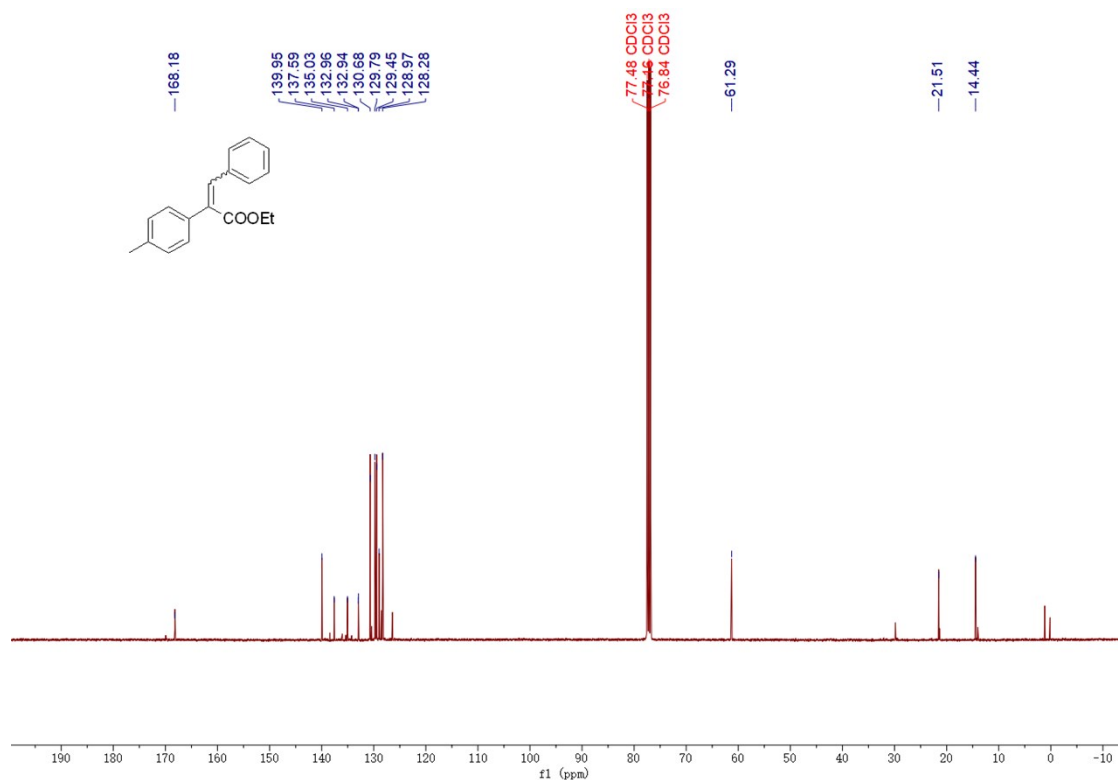
¹H NMR of 3v



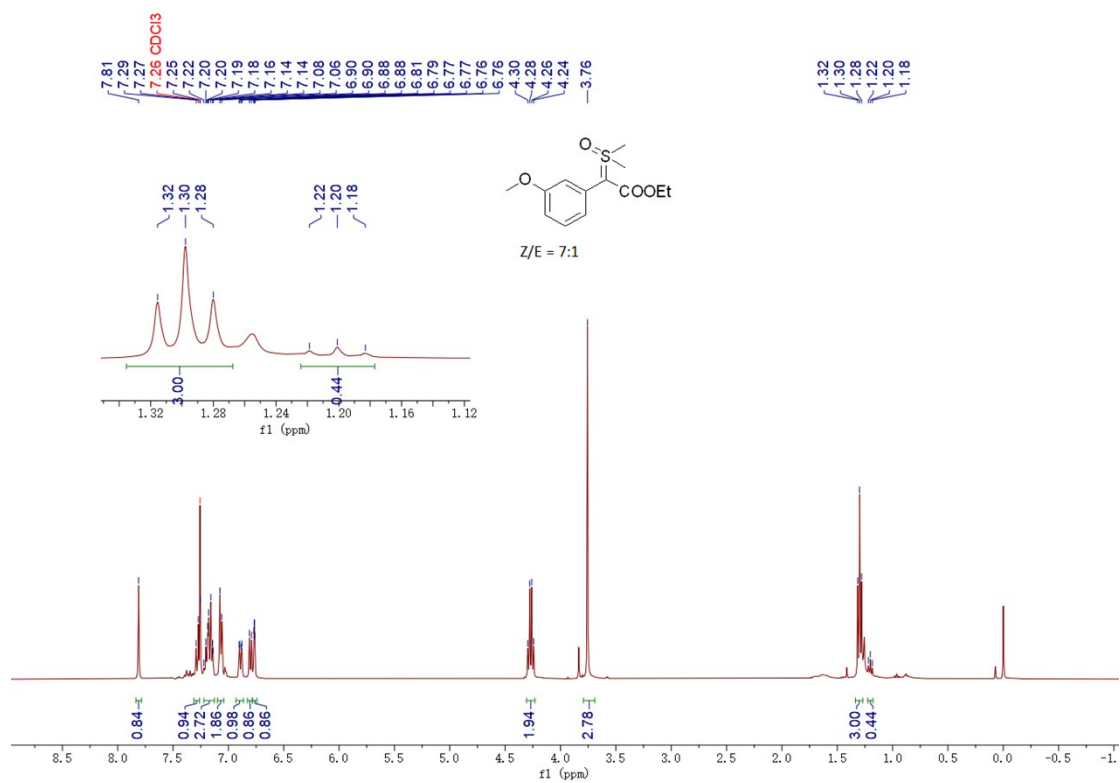
¹³C NMR of 3v



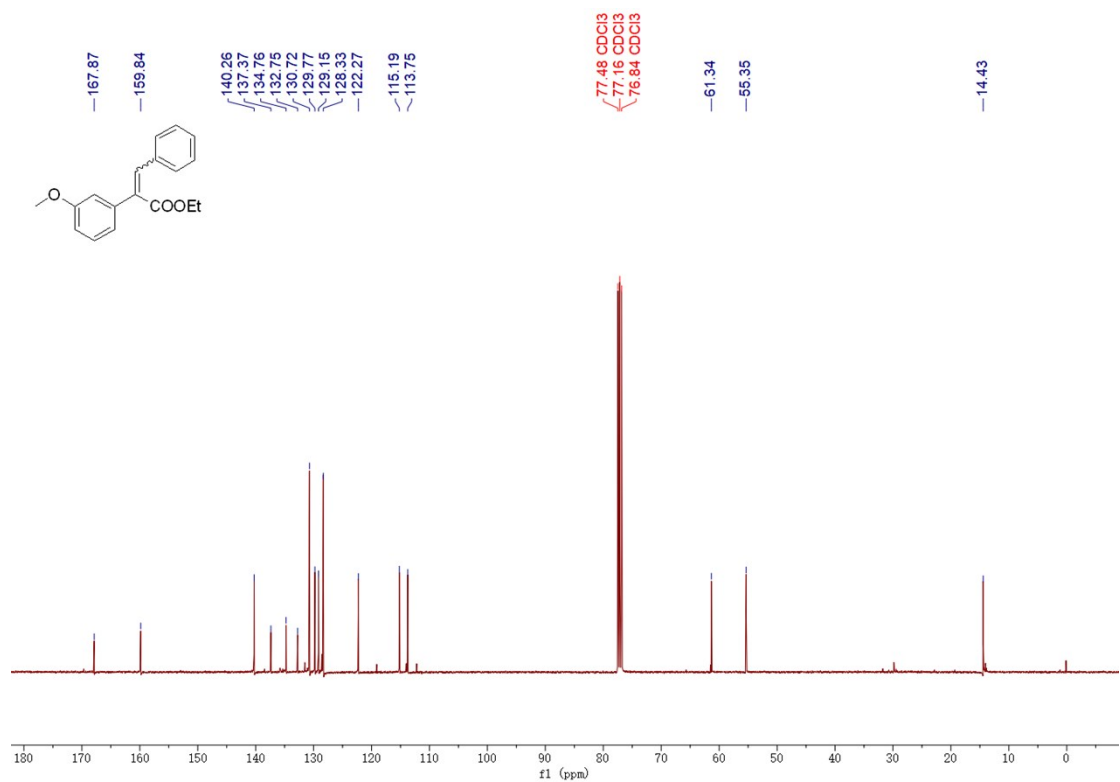
¹H NMR of 3w



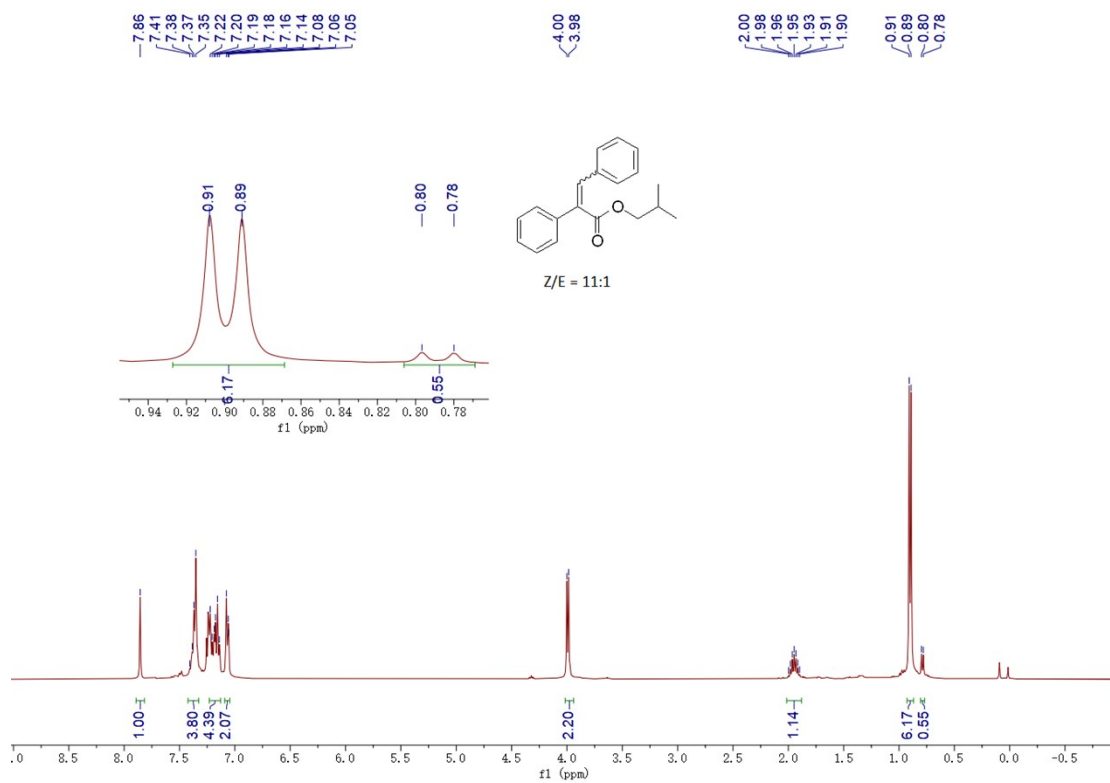
¹³C NMR of 3w



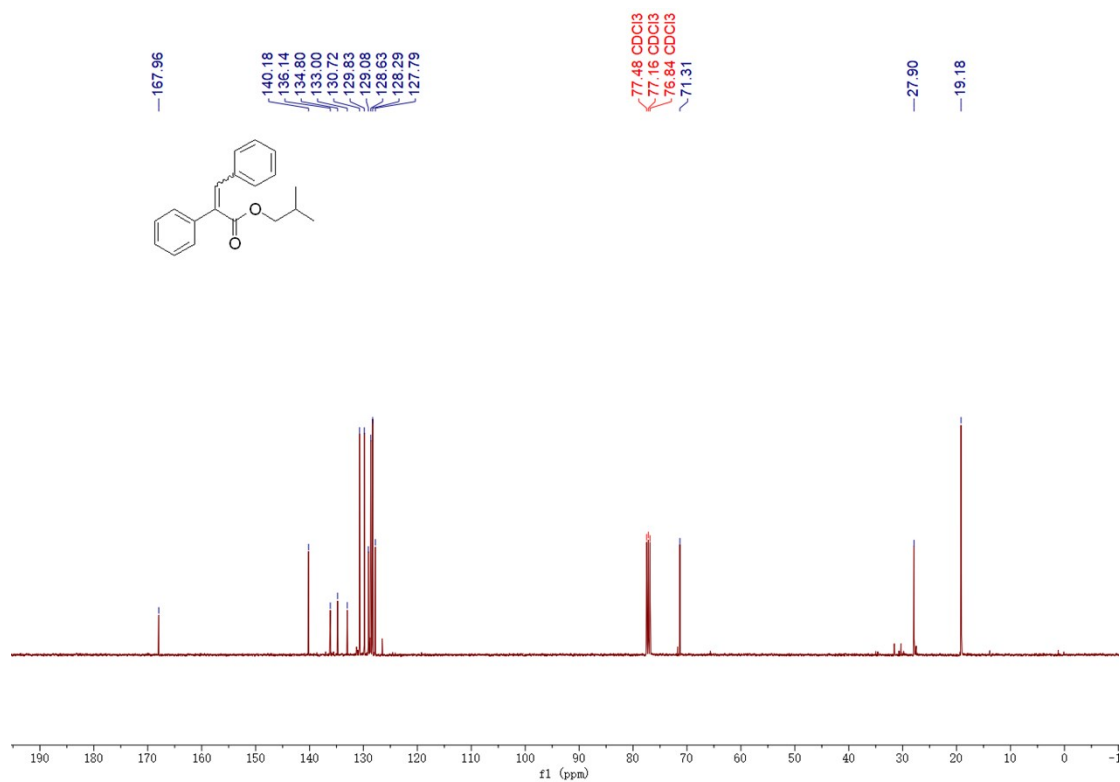
¹H NMR of 3x



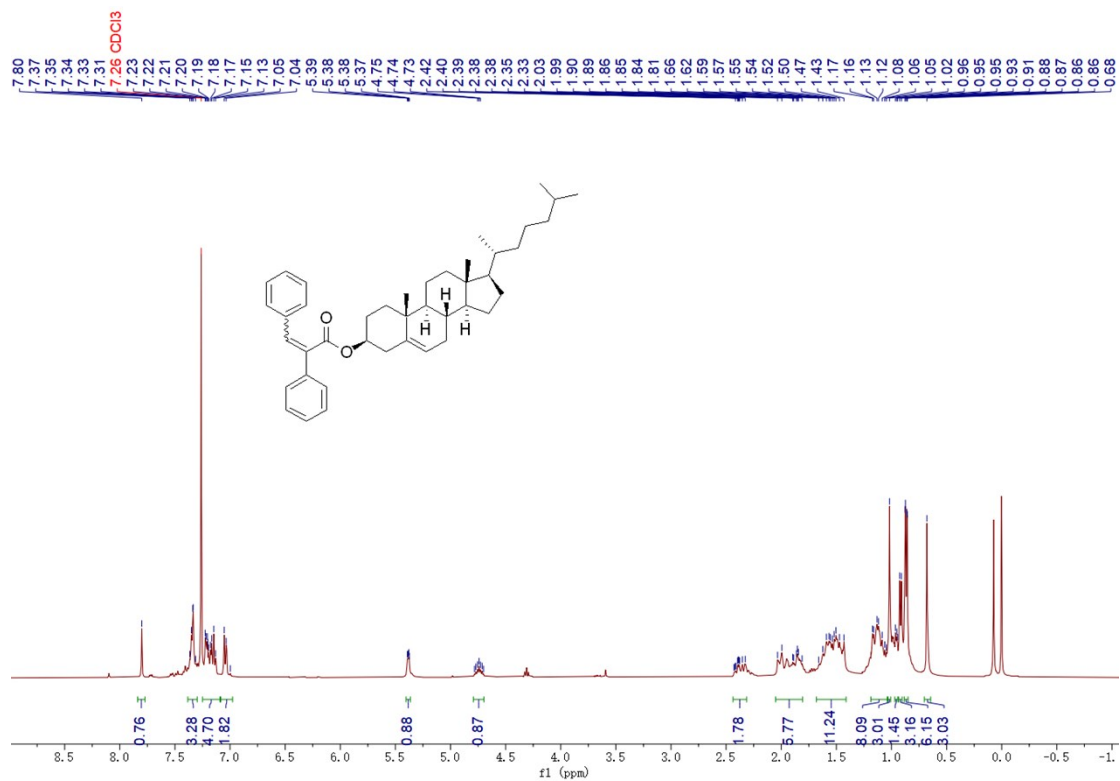
¹³C NMR of 3x



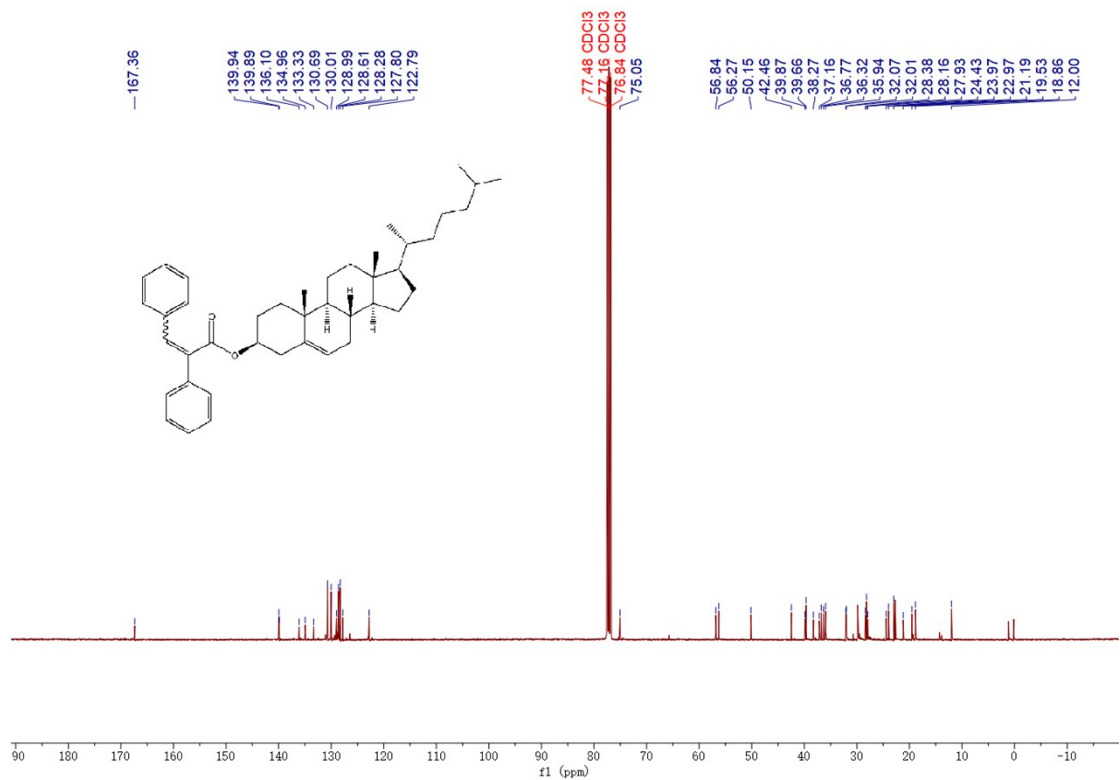
¹H NMR of 3z



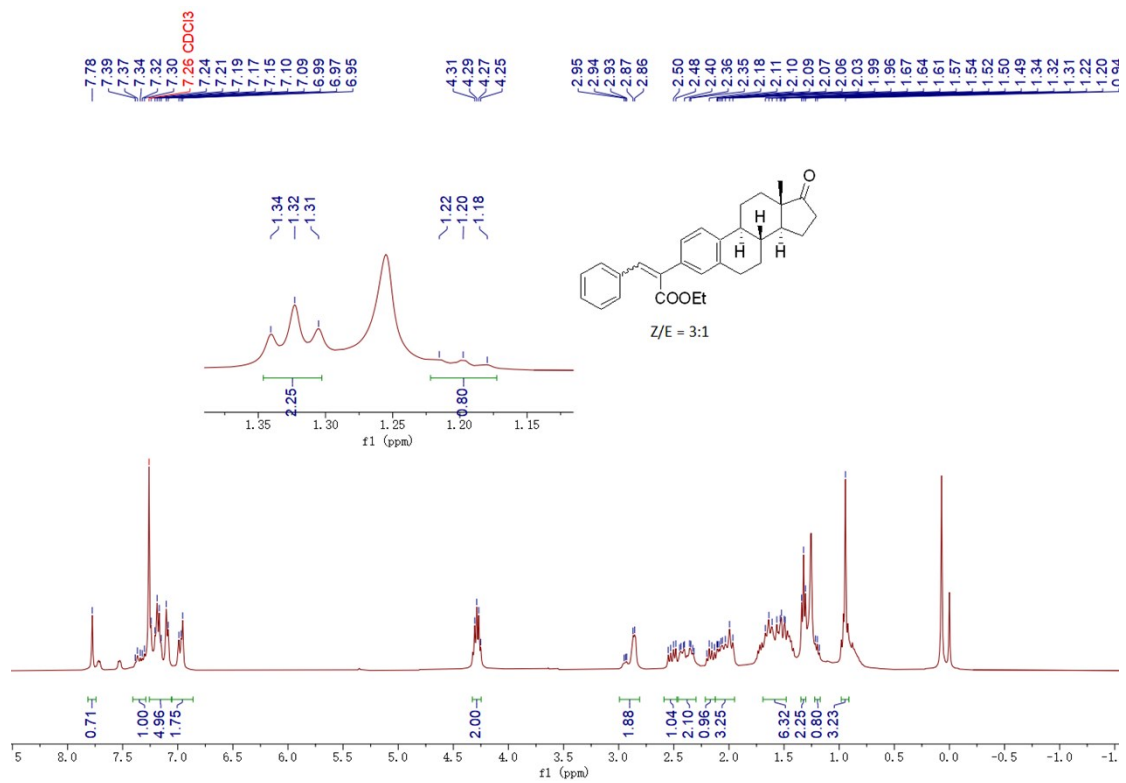
¹³C NMR of 3z



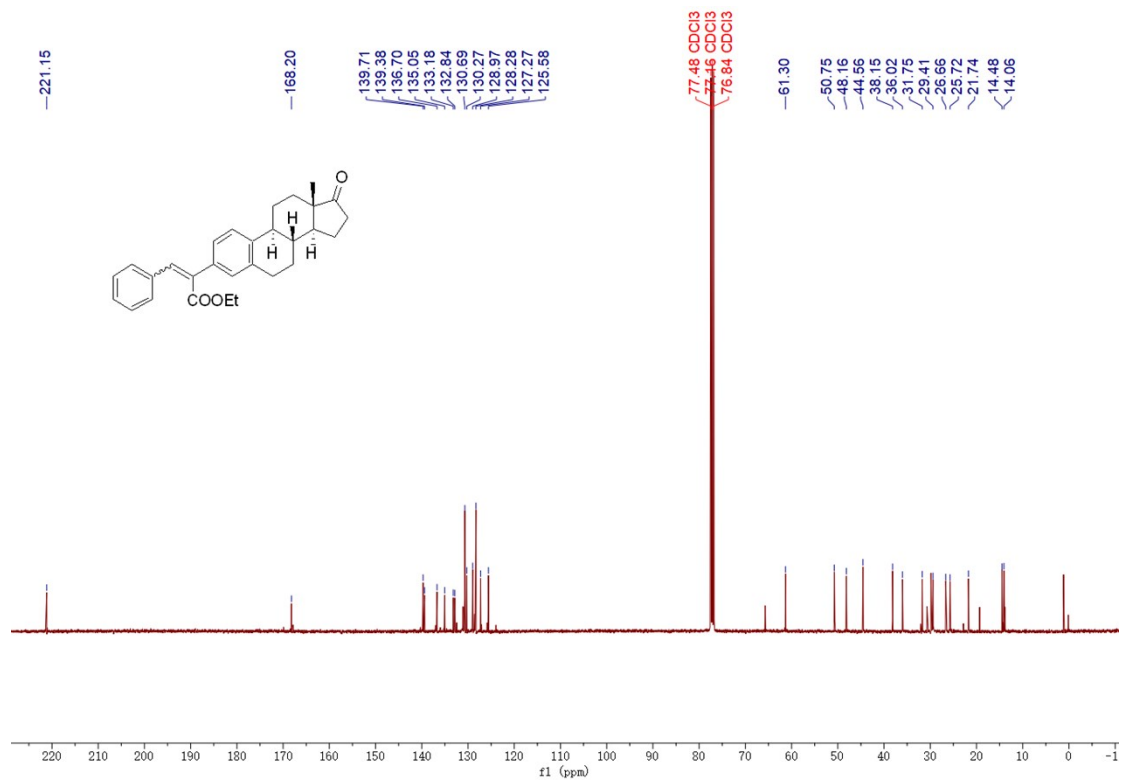
¹H NMR of 4



¹³C NMR of 4

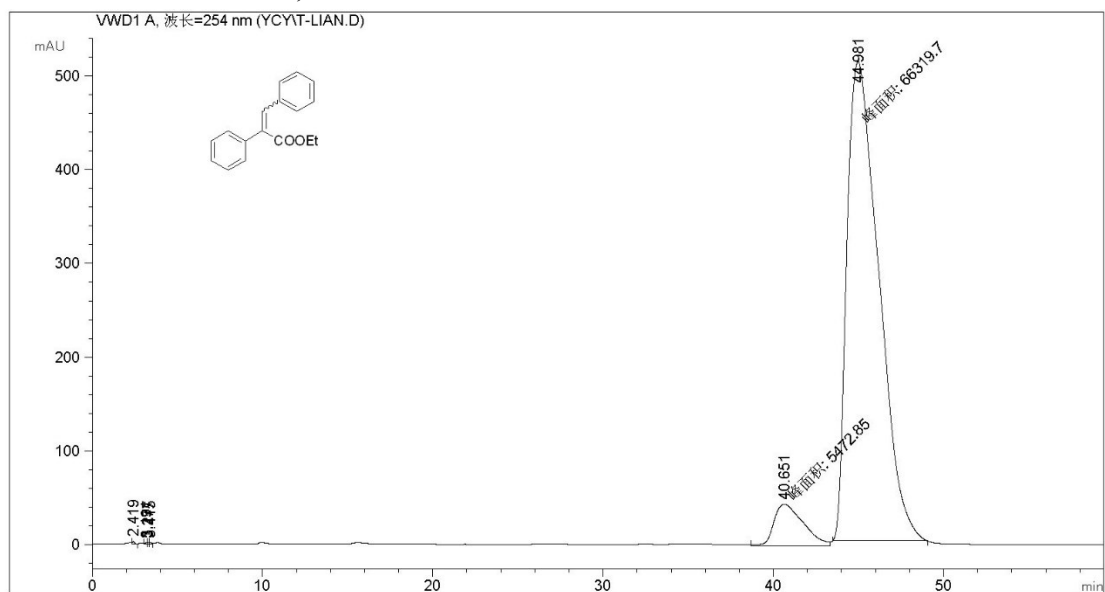


¹H NMR of 5

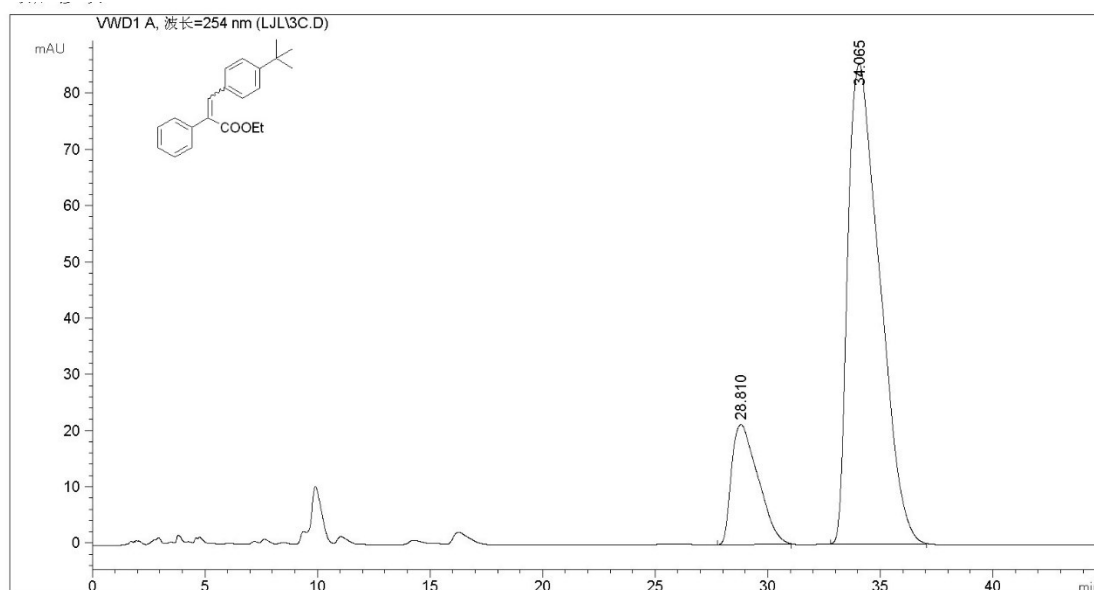


¹³C NMR of 5

5. HPLC Charts of 3a, 3c



峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
4	3.415	VV	0.1397	16.91923	1.78534	0.0235
5	40.651	MM	2.0277	5472.85059	44.98375	7.6159
6	44.981	MM	2.1613	6.63197e4	511.41574	92.2889
总量 :				7.18610e4	564.75053	



信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	28.810	BB	1.1892	1745.13696	21.35743	17.2812
2	34.065	BB	1.4287	8353.35840	85.34573	82.7188
总量 :				1.00985e4	106.70315	

6. references.

- (a) C. Janot, P. Palamini, B. C. Dobson, J. Muir, C. Aissa, *Org. Lett.* 2019, **21**, 296; (b): C. A. D. Caiuby, M. P. Jesus, A. C. B. Burtoloso, *J. Org. Chem.* 2020, **85**, 7433.
- H. He, K. Yan, J. Li, R. Lai, Y. Luo, M. Guan, Y. Wu, *Synthesis*. DOI: 10.1055/s-0040-1707186.