Supplementary Information (SI) for Chemical Science.
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Supporting Information

Single-Carbon-Atom Transfer to *para*-Quinone Methides from $TMSCF_2Br$

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Content

1. General Information

Reagents and Solvents: PE refers to petroleum ether b. p. 60-90 °C, EA refers to ethyl acetate, and DCM refers to dichloromethane. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

Chromatography: Flash column chromatography was carried out using commercially available 200-300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA or DCM/MeOH, they were listed as volume ratios.

Data collection: ^{1}H, ^{13}C and ^{19}F NMR spectra were collected on BRUKER AV-300 (300 MHz) spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane ($\delta = 0.00$ ppm) with the solvent resonance as an internal standard ($CDCl_3$: $\delta = 7.26$ ppm, DMSO-d_6: $\delta = 2.50$ ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: $\delta = 77.16$ ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 65451 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m. p.) was measured on a microscopic melting point apparatus. X-ray diffraction analyses were carried out on a microcrystalline powder using a Rigaku Oxford Diffraction XtaLAB Synergy-S diffractometer using Mo radiation ($\lambda = 0.71073$ Å).

2. General Procedure for the Synthesis of *p*-QMs Derivatives

The *p*-QMs Derivatives **2a – 2q** were prepared according to the reported literature procedures.[1]

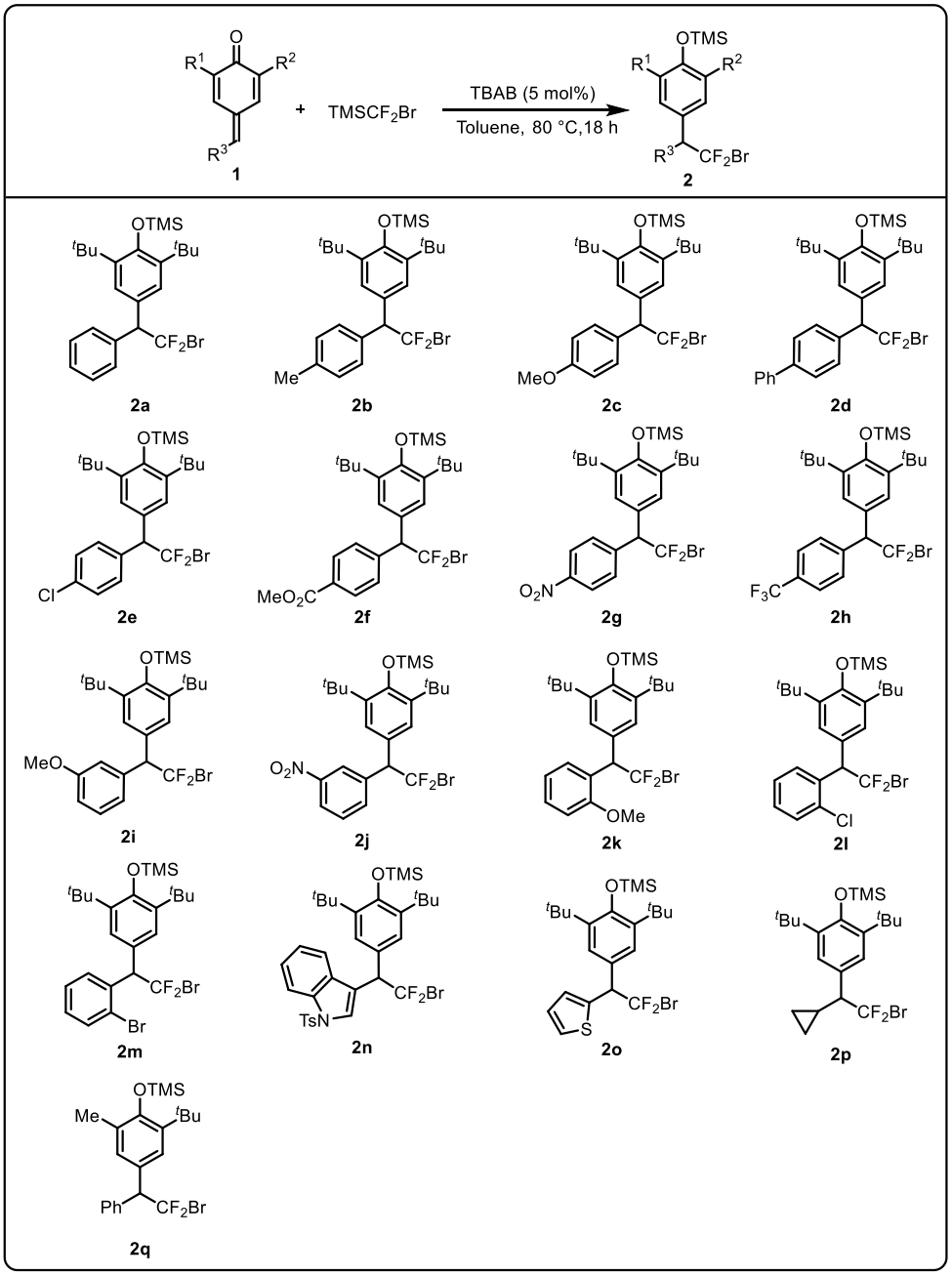


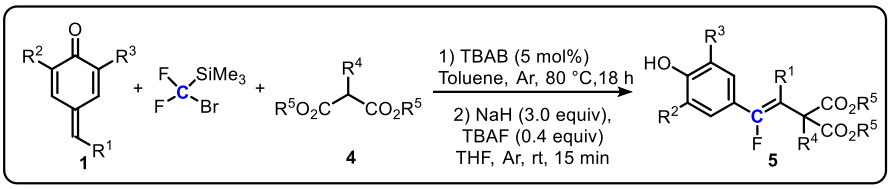
Figure S1. Synthesis of *p*-QMs Derivatives **2**

To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added *p*-QMs (1.0 mmol, 1.0 equiv) and TBAB (16 mg, 0.05 mmol, 5 mol %). Then the Schlenk tube was evacuated and filled with argon for three times. After that, $TMSCF_2Br$ (406.2 mg, 2.0 mmol, 2.0 equiv) dissolved in toluene (2.0 mL) was added

[1] J. Zhu, M. Xu, B. Gong, A. Lin, S. Gao, *Org. Lett.* **2023**, *25*, 3271.

under argon atmosphere via a syringe. The reaction mixture was stirred at 80 °C in oil bath for 18 h. After completed consumption of starting material, the resulting mixture was then poured into ice water (5 mL), extracted with EA (3 × 5 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the crude material was purified by flash chromatography on silica gel (PE) to afford the desired product **2a** – **2q**.

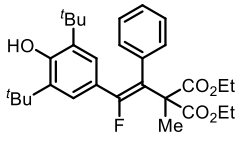
3. General Procedure A for the Synthesis of Monofluoroalkenes 5



To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added *p*-QMs **1** (0.5 mmol, 1.0 equiv) and TBAB (8.0 mg, 0.025 mmol, 5 mol %), then the Schlenk tube was evacuated and filled with argon for three times. After that, $TMSCF_2Br$ (203.1 mg, 1.0 mmol, 2.0 equiv) dissolved in toluene (1.0 mL) was added under argon atmosphere via a syringe. The reaction mixture was stirred at 80 ℃ in oil bath for 18 h to afford the toluene solution of crude intermediate.

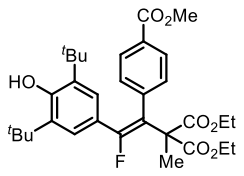
To another oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added 60% NaH (60.0 mg, 1.5 mmol, 3.0 equiv), then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous THF (0.5 mL) and **4** (1.0 mmol, 2.0 equiv, dissolved in 0.5 mL THF) was added under argon atmosphere via a syringe. After stirred for 30 min at room temperature, the toluene solution of crude intermediate was added, and then TBAF (0.2 mmol, 0.4 equiv, 1 M solution in THF) was dropped slowly under argon atmosphere stirred for 15 min at room temperature. When the starting material was completely consumed, saturated solution of NH_4Cl (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with EA (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **5**.

diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-phenylvinyl)-2-methylmalonate (5aa)



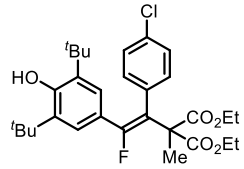
Prepared through general procedure A to give **5aa** in 187.0 mg, 75% yield, white solid, **m.p.** 120 – 122 ℃, R_f = 0.45 (PE/EA = 10/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.32 – 7.19 (m, 5H), 6.94 (s, 2H), 5.27 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 4H), 1.65 (s, 3H), 1.22 – 1.17 (m, 24H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.2, 156.4 (d, ^1J = 252.4 Hz), 154.2, 136.6 (d, ^3J = 8.4 Hz), 135.0, 130.8 (d, ^4J = 3.1 Hz), 128.6, 127.6, 125.3 (d, ^3J = 7.6 Hz), 123.0 (d, ^2J = 28.2 Hz), 117.8 (d, ^2J = 19.5 Hz), 61.6, 58.8, 34.3, 30.1, 22.0 (d, ^4J = 3.1 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ – 96.19 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{30}H_{39}FO_5 - H]^-$ 497.2709, found 497.2701.

diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-(4-(methoxycarbonyl)phenyl)vinyl)-2-methylmalonate (5ba)



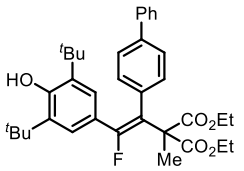
Prepared through general procedure A to give **5ba** in 167.0 mg, 60% yield, colorless oil, R_f = 0.2 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.91 (s, 2H), 5.31 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 4H), 3.91 (s, 3H), 1.67 (s, 3H), 1.22 – 1.18 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 170.5, 166.4, 156.5 (d, ^1J = 254.5 Hz), 154.1, 141.5 (d, ^3J = 8.5 Hz), 134.8, 130.6 (d, ^4J = 3.0 Hz), 129.4, 128.8, 125.0 (d, ^3J = 7.1 Hz), 122.2 (d, ^2J = 28.2 Hz), 116.7 (d, ^2J = 20.4 Hz), 61.4, 58.2, 51.9, 33.9, 29.6, 21.7 (d, ^4J = 2.6 Hz), 13.6 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 93.54 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{32}H_{41}FO_7 - H]^-$ 555.2764, found 555.2768.

diethyl (Z)-2-(1-(4-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluorovinyl)-2-methylmalonate (5ca)



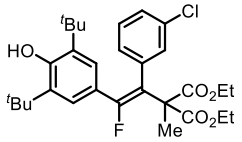
Prepared through general procedure A to give **5ca** in 177.9 mg, 67% yield, yellow solid, **m.p.** 78 – 80 °C, R_f = 0.35 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.44 (d, *J* = 8.5 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.08 (s, 2H), 5.50 (s, 1H), 4.30 (q, *J* = 7.1 Hz, 4H), 1.83 (s, 3H), 1.41 (s, 18H), 1.37 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.0, 156.8 (d, ^1J = 252.4 Hz), 154.4, 135.3, 135.2, 133.7, 132.3 (d, ^4J = 3.4 Hz), 128.8, 125.3 (d, ^3J = 7.3 Hz), 122.7 (d, ^2J = 28.0 Hz), 116.7 (d, ^2J = 20.0 Hz), 61.7, 58.6, 34.3, 30.0, 22.0 (d, ^4J = 3.3 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 94.43 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}ClFO_5 - H]^-$ 531.2319, found 531.2310.

diethyl (Z)-2-(1-([1,1'-biphenyl]-4-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluorovinyl)-2-methylmalonate (5da)



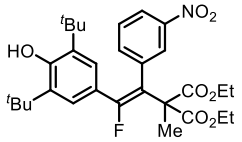
Prepared through general procedure A to give **5da** in 163.8 mg, 57% yield, white solid, **m.p.** 96 – 98 °C, R_f = 0.4 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.18 – 7.14 (m, 4H), 7.09 – 7.04 (m, 2H), 7.00 – 6.91 (m, 3H), 6.62 (s, 2H), 4.92 (s, 1H), 3.78 (q, *J* = 7.1 Hz, 4H), 1.35 (s, 3H), 0.90 – 0.81 (m, 24H) ppm.**^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.2, 156.4(d, ^1J = 251.3 Hz), 154.2, 141.0, 140.7, 135.7 (d, ^3J = 8.4 Hz), 135.1, 131.2 (d, ^4J = 2.9 Hz), 128.9, 127.4, 127.1, 125.2 (d, ^3J = 7.8 Hz), 123.0 (d, ^2J = 28.1 Hz), 117.4 (d, ^2J = 19.5 Hz), 61.7, 58.8, 34.3, 30.0, 22.1 (d, ^4J = 3.0 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 96.35 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{36}H_{43}FO_5 - H]^-$ 573.3022, found 573.3029.

diethyl (Z)-2-(1-(3-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluorovinyl)-2-methylmalonate (5ea)



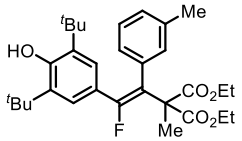
Prepared through general procedure A to give **5ea** in 207.9 mg, 78% yield, white solid, **m.p.** 101 – 103 ℃, R_f = 0.45 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.26 – 7.21 (m, 3H), 7.14 – 7.08 (m, 1H), 6.95 (s, 2H), 5.34 (s, 1H), 4.14 (q, J = 7.1 Hz, 4H), 1.67 (s, 3H), 1.29 – 1.19 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 170.9, 156.9 (d, ^1J = 252.4 Hz), 154.5, 138.6 (d, ^3J = 8.7 Hz), 135.2, 134.4, 130.9 (d, ^4J = 3.3 Hz), 130.0, 129.0 (d, ^4J = 3.1 Hz), 127.8, 125.3 (d, ^3J = 7.6 Hz), 122.5 (d, ^2J = 27.9 Hz), 116.6 (d, ^2J = 20.3 Hz), 61.8, 58.7, 34.3, 30.0, 22.0 (d, ^4J = 3.1 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 94.52 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}ClFO_5 - H]^-$ 531.2319, found 531.2311.

diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-(3-nitrophenyl)vinyl)-2-methylmalonate (5fa)



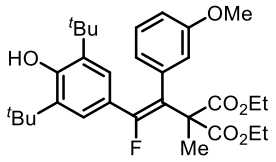
Prepared through general procedure A to give **5fa** in 171.6 mg, 63% yield, white solid, **m.p.** 108 – 110 ℃, R_f = 0.3 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.15 – 8.10 (m, 2H), 7.60 – 7.56 (m, 1H), 7.49 (t, J = 7.8 Hz, 1H), 6.89 (s, 2H), 5.36 (s, 1H), 4.15 (q, J = 7.2 Hz, 4H), 1.72 (s, 3H), 1.26 – 1.18 (s, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 170.7, 158.0 (d, ^1J = 255.3 Hz), 154.7, 148.3, 138.9 (d, ^3J = 9.0 Hz), 137.3 (d, ^4J = 3.0 Hz), 135.5, 129.5, 126.0 (d, ^4J = 3.3 Hz), 125.6 (d, ^3J = 6.6 Hz), 122.5, 122.2 (d, ^2J = 27.8 Hz), 116.1 (d, ^2J = 21.2 Hz), 62.0, 58.6, 34.3, 30.0, 22.2 (d, ^4J = 3.6 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 90.92 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}FNO_7 - H]^-$ 542.2560, found 542.2572.

diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-(m-tolyl)vinyl)-2-methylmalonate (5ga)



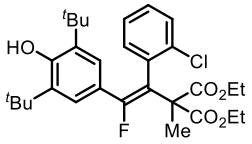
Prepared through general procedure A to give **5ga** in 130.3 mg, 51% yield, yellow solid, **m.p.** 110 – 112 ℃, R_f = 0.4 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.26 – 7.15 (m, 1H), 7.07 – 6.96 (m, 5H), 5.28 (s, 1H), 4.13 (q, J = 7.1 Hz, 4H), 2.29 (s, 3H), 1.63 (s, 3H), 1.28 – 1.18 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.3, 156.1 (d, ^1J = 250.4 Hz), 154.1, 138.1, 136.3 (d, ^3J = 8.3 Hz), 134.9, 131.3 (d, ^4J = 3.0 Hz), 128.6, 128.4, 127.7 (d, ^4J = 3.0 Hz), 125.1 (d, ^3J = 7.9 Hz), 123.0 (d, ^2J = 28.3 Hz), 117.7 (d, ^2J = 19.2 Hz), 61.6, 58.7, 34.2, 30.0, 22.0 (d, ^4J = 2.8 Hz), 21.3, 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 97.08 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{31}H_{41}FO_5 - H]^-$ 511.2865, found 511.2867.

diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-(3-methoxyphenyl)vinyl)-2-methylmalonate (5ha)



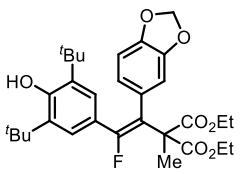
Prepared through general procedure A to give **5ha** in 148.6 mg, 56% yield, white solid, **m.p.** 88 – 90 ℃, R_f = 0.4 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.21 (t, *J* = 7.9 Hz, 1H), 6.99 (s, 2H), 6.82 – 6.74 (m, 3H), 5.30 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 4H), 3.71 (s, 3H), 1.64 (s, 3H), 1.24 – 1.19 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.2, 159.8, 156.3 (d, ^1J = 251.0 Hz), 154.2, 137.8 (d, ^3J = 8.4 Hz), 135.0, 129.6, 125.1 (d, ^3J = 7.5 Hz), 123.1 (d, ^4J = 3.0 Hz), 123.0 (d, ^2J = 28.1 Hz), 117.5 (d, ^2J = 19.5 Hz), 116.3 (d, ^4J = 3.1 Hz), 113.4, 61.6, 58.6, 55.3, 34.2, 30.0, 22.0 (d, ^4J = 2.7 Hz), 13.9 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 96.35 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{31}H_{41}FO_6 - H]^-$ 527.2814, found 527.2819.

diethyl (E)-2-(1-(2-chlorophenyl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluorovinyl)-2-methylmalonate (5ia)



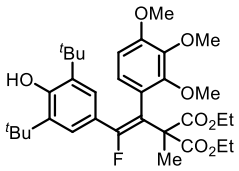
Prepared through general procedure A to give **5ia** in 151.9 mg, 57% yield, white solid, **m.p.** 96 – 98 ℃, R_f = 0.35 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.38 – 7.35 (m, 1H), 7.28 – 7.17 (m, 3H), 6.99 (s, 2H), 5.29 (s, 1H), 4.26 (q, *J* = 7.0 Hz, 2H), 4.05 – 3.97 (m, 2H), 1.66 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.25 (s, 18H), 1.15 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.2, 157.6 (d, ^1J = 255.0 Hz), 154.5, 136.1 (d, ^4J = 2.9 Hz), 136.0 (d, ^3J = 9.2 Hz), 135.2, 132.8 (d, ^4J = 3.1 Hz), 129.7, 129.2, 127.0, 124.7 (d, ^3J = 7.3 Hz), 122.9 (d, ^2J = 28.3 Hz), 114.8 (d, ^2J = 22.2 Hz), 61.7 (d, ^4J = 4.5 Hz), 58.6, 34.3, 30.1, 21.5, 14.1, 13.9 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 93.06 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}ClFO_5 - H]^-$ 531.2319, found 531.2312.

diethyl (Z)-2-(1-(benzo[d][1,3]dioxol-5-yl)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluorovinyl)-2-methylmalonate (5ja)



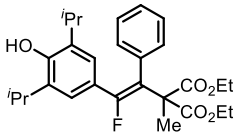
Prepared through general procedure A to give **5ja** in 188.6 mg, 69% yield, colorless oil, R_f = 0.25 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.02 (s, 2H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.72 – 6.70 (m, 2H), 5.93 (s, 2H), 5.34 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 4H), 1.66 (s, 3H), 1.30 – 1.23 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.2, 156.5 (d, ^1J = 251.1 Hz), 154.2, 147.7, 147.1, 135.0, 130.0 (d, ^3J = 8.9 Hz), 125.1 (d, ^3J = 7.9 Hz), 124.3 (d, ^4J = 3.3 Hz), 123.0 (d, ^2J = 28.1 Hz), 117.1 (d, ^2J = 20.2 Hz), 111.4 (d, ^4J = 3.4 Hz), 108.6, 101.0, 61.6, 58.7, 34.3, 30.1, 22.0 (d, ^4J = 2.9 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 96.04 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{31}H_{39}FO_7 - H]^-$ 541.2607, found 541.2615.

diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-(2,3,4-trimethoxyphenyl)vinyl)-2-methylmalonate (5ka)



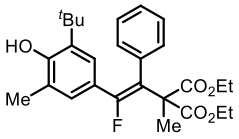
Prepared through general procedure A to give **5ka** in 209.1 mg, 71% yield, colorless oil, R_f = 0.2 (PE/EA = 5/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.03 (s, 2H), 6.42 (s, 2H), 5.31 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.82 (s, 3H), 3.74 (s, 6H), 1.67 (s, 3H), 1.27 (s, 18H), 1.22 (t, *J* = 7.2 Hz, 6H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.1, 156.4 (d, ^1J = 251.7 Hz), 154.2, 153.4, 137.5, 135.1, 132.1 (d, ^3J = 8.8 Hz), 125.0 (d, ^3J = 7.6 Hz), 123.0 (d, ^2J = 28.2 Hz), 117.6 (d, ^2J = 20.0 Hz), 107.9 (d, ^4J = 3.2 Hz), 61.6, 60.8, 58.8, 56.2, 34.3, 30.1, 22.0 (d, ^4J = 3.0 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 96.50 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{33}H_{45}FO_8 - H]^-$ 587.3026, found 587.3019.

diethyl (Z)-2-(2-fluoro-2-(4-hydroxy-3,5-diisopropylphenyl)-1-phenylvinyl)-2-methylmalonate (5la)



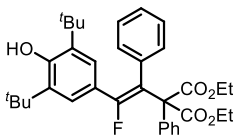
Prepared through general procedure A to give **5la** in 180.0 mg, 76% yield, colorless oil, R_f = 0.35 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.29 – 7.19 (m, 5H), 6.78 (s, 2H), 5.08 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 4H), 3.05 – 2.91 (m, 2H), 1.66 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 6H), 1.00 (d, *J* = 6.9 Hz, 12H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.3, 156.3 (d, ^1J = 251.3 Hz), 150.4, 136.6 (d, ^3J = 8.5 Hz), 132.9, 130.9 (d, ^4J = 3.2 Hz), 128.6, 127.7, 124.1 (d, ^2J = 28.7 Hz), 123.7 (d, ^3J = 7.3 Hz), 117.9 (d, ^2J = 19.1 Hz), 61.7, 58.8, 26.9, 22.5, 22.0 (d, ^4J = 2.4 Hz), 14.0 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 96.24 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{28}H_{35}FO_5 - H]^-$ 469.2396, found 469.2389.

diethyl (Z)-2-(2-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)-2-fluoro-1-phenylvinyl)-2-methylmalonate (5ma)



Prepared through general procedure A to give **5ma** in 182.0 mg, 80% yield, colorless oil, R_f = 0.25 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.30 – 7.14 (m, 5H), 6.90 (s, 1H), 6.71 (s, 1H), 5.27 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 4H), 2.09 (s, 3H), 1.65 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 6H), 1.10 (s, 9H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.3, 156.2 (d, ^1J = 251.2 Hz), 153.2, 136.4 (d, ^3J = 8.2 Hz), 134.7, 130.7 (d, ^4J = 3.0 Hz), 128.5, 127.8 (d, ^3J = 7.3 Hz), 127.6, 126.1 (d, ^3J = 7.0 Hz), 123.3 (d, ^2J = 28.7 Hz), 122.6, 117.8 (d, ^2J = 19.1 Hz), 61.7, 58.7, 34.4, 29.3, 21.9 (d, ^4J = 3.0 Hz), 16.0, 13.9 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 95.38 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{27}H_{33}FO_5 - H]^-$ 455.2239, found 455.2227.

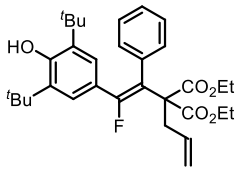
diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-phenylvinyl)-2-phenylmalonate (5ab)



Prepared through general procedure A to give **5ab** in 145.8 mg, 52% yield, yellow solid, **m.p.** 132 – 134 °C, R_f = 0.4 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.63 – 7.59 (m, 2H), 7.37 – 7.22 (m, 8H), 7.00 (s, 2H), 5.32 (s, 1H), 4.10 – 3.94 (m, 4H), 1.23 (s,

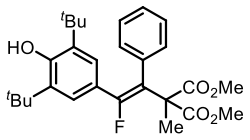
18H), 1.06 (t, J = 7.1 Hz, 6H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 169.8, 156.5 (d, ^1J = 251.2 Hz), 154.4, 137.1 (d, ^3J = 7.9 Hz), 136.5, 135.1, 130.9 (d, ^4J = 3.0 Hz), 129.3, 128.6, 127.7, 127.6, 127.4, 125.3 (d, ^3J = 7.9 Hz), 122.7 (d, ^2J = 27.7 Hz), 116.1 (d, ^2J = 19.7 Hz), 62.0, 34.3, 30.0, 13.8 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 90.19 ppm. **HRMS (ESI)** *m*/*z* Calcd for [$C_{35}H_{41}FO_5$ – H]$^-$ 559.2865, found 559.2870.

diethyl (Z)-2-allyl-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-phenylvinyl) malonate (5ac)



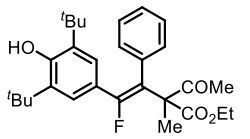
Prepared through general procedure A to give **5ac** in 134.0 mg, 52% yield, white solid, **m.p.** 114 – 116 ℃, R_f = 0.45 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.22 – 7.11 (m, 5H), 6.84 (s, 2H), 6.05 – 5.91 (m, 1H), 5.20 (s, 1H), 5.03 – 4.95 (m, 2H), 4.02 (q, J = 7.1 Hz, 4H), 2.71 (d, J = 7.2 Hz, 2H), 1.14 – 1.07 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 170.2, 156.5 (d, ^1J = 252.0 Hz), 154.2, 136.7 (d, ^3J = 8.3 Hz), 135.0, 134.6, 130.9 (d, ^4J = 2.9 Hz), 128.5, 127.5, 125.3 (d, ^3J = 7.3 Hz), 123.0 (d, ^2J = 28.2 Hz), 118.2, 116.4 (d, ^2J = 19.3 Hz), 62.5, 61.4, 39.9 (d, ^4J = 2.8 Hz), 34.2, 30.0, 13.9 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 94.24 ppm. **HRMS (ESI)** *m*/*z* Calcd for [$C_{32}H_{41}FO_5$ – H]$^-$ 523.2865, found 523.2858.

dimethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-phenylvinyl)-2-me thylmalonate (5ad)



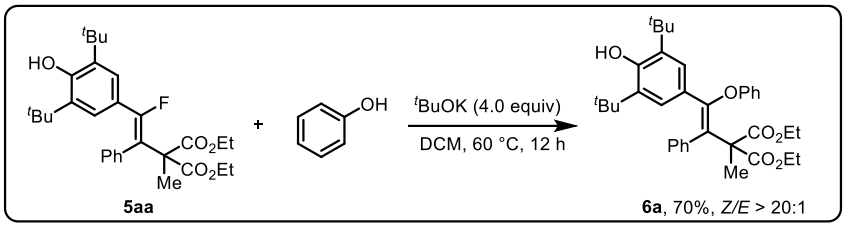
Prepared through general procedure A to give **5ad** in 164.7 mg, 70% yield, white solid, **m.p.** 140 – 142 ℃, R_f = 0.45 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.26 – 7.16 (m, 3H), 7.13 – 7.10 (m, 2H), 6.88 (s, 2H), 5.22 (s, 1H), 3.58 (s, 6H), 1.54 (s, 3H), 1.13 (s, 18H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.7 (d, ^4J = 1.0 Hz), 156.4 (d, ^1J = 250.3 Hz), 154.3, 136.3 (d, ^3J = 8.4 Hz), 135.0 (d, ^4J = 1.2 Hz), 130.7 (d, ^4J = 3.0 Hz), 128.7, 127.8, 125.2 (d, ^3J = 8.0 Hz), 122.7 (d, ^2J = 28.2 Hz), 117.3 (d, ^2J = 19.3 Hz), 58.6 (d, ^3J = 1.1 Hz), 52.8, 34.3, 30.0, 22.1 (d, ^4J = 2.6 Hz) ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 97.51 ppm. **HRMS (ESI)** *m*/*z* Calcd for [$C_{28}H_{35}FO_5$ – H]$^-$ 469.2396, found 469.2388.

methyl (Z)-2-acetyl-4-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-fluoro-2-methyl-3-phen ylbut-3-enoate (8aa)

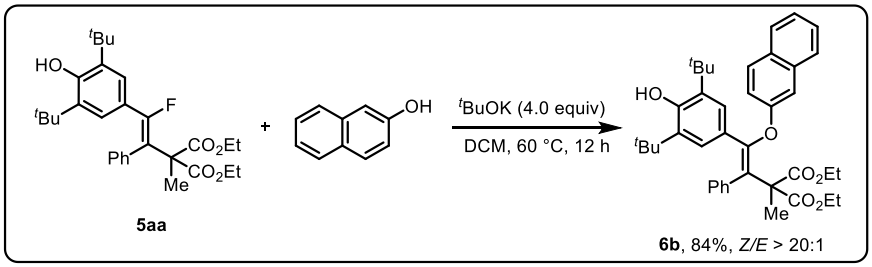


Prepared through general procedure A to give **8aa** in 110.1 mg, 47% yield, yellow solid, **m.p.** 120 – 122 ℃**,** R_f = 0.45 (PE/EA = 10/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.34 – 7.26 (m, 3H), 7.18 – 7.16 (m, 2H), 6.95 (s, 2H), 5.33 (s, 1H), 4.09 – 3.98 (m, 2H), 2.48 (s, 3H), 1.48 (s, 3H), 1.23 (s, 18H), 1.14 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 205.0, 171.5, 156.4 (d, ^1J = 249.7 Hz), 154.5, 136.3 (d, ^3J = 8.9 Hz), 135.2, 130.5 (d, ^4J = 2.0 Hz), 128.9, 127.9, 125.2 (d, ^3J = 7.8 Hz), 122.5 (d, ^2J = 27.9 Hz), 118.1 (d, ^2J = 20.0 Hz), 64.0, 61.5, 34.3, 30.1, 27.2 (d, ^4J = 4.7 Hz), 20.9, 13.9 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ – 96.01 ppm. **HRMS (ESI)** *m/z* Calcd for [$C_{29}H_{37}FO_4$ + H]$^+$ 469.2749, found 469.2760.

4. Intermolecular S_NV Reaction with 5aa

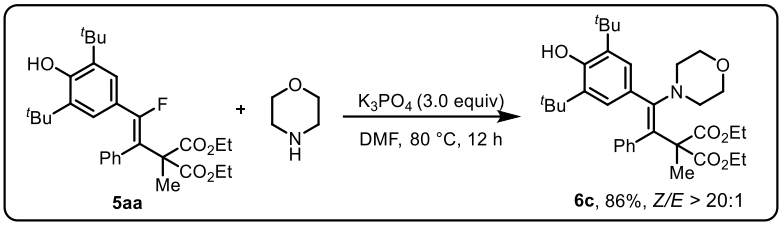


diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-phenoxy-1-phenylvinyl)-2-methylmalonate (6a) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.8 mg, 0.8 mmol, 4.0 equiv), **5aa** (99.7 mg, 0.2 mmol, 1.0 equiv) and phenol (37.6 mg, 0.4 mmol, 2.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 12 h at 60 °C. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **6a** as a white solid (80.1 mg, 70%, *Z/E* > 20:1). **m.p.** 134 – 135 °C, R_f = 0.3 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.22 – 7.08 (m, 7H), 6.86 – 6.78 (m, 5H), 5.01 (s, 1H), 4.10 – 3.90 (m, 4H), 1.61 (s, 3H), 1.13 – 1.09 (m, 24H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.7, 156.2, 153.0, 150.0, 138.6, 134.6, 131.2, 128.8, 128.1, 127.3, 126.8, 125.1, 125.0, 121.7, 118.2, 61.4, 59.0, 34.1, 30.2, 22.4, 14.0 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{36}H_{44}O_6 + H]^+$ 573.3211, found 573.3224.

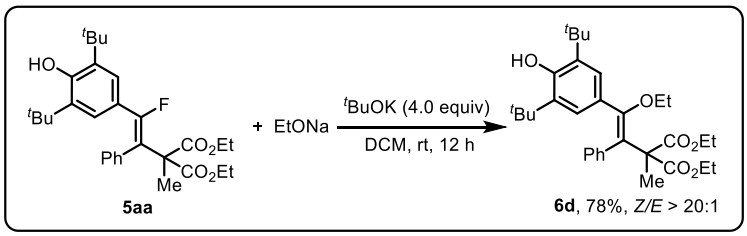


diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(naphthalen-2-yloxy)-1-phenylvinyl)-2-methylmalonate (6b) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.8 mg, 0.8 mmol, 4.0 equiv), **5aa** (99.7 mg, 0.2 mmol, 1.0 equiv) and 2-hydroxynaphthalene (57.6 mg, 0.4 mmol, 2.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 12 h at 60 °C. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding

product **6b** as a white solid (104.4 mg, 84% yield, *Z/E* > 20:1). **m.p.** 116 – 118 ℃, R_f = 0.3 (PE/EA = 20/1). The regioselectivity of this reaction (C1 vs OH) was determined by the proton NMR with "Heavy Water Exchange NMR Experiment". **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.70 – 7.57 (m, 3H), 7.38 – 7.14 (m, 9H), 6.86 (s, 2H), 4.99 (s, 1H), 4.07 – 3.90 (m, 3H), 1.12 – 1.07 (m, 24H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.7, 154.0, 153.1, 150.2, 138.5, 134.6, 134.1, 131.2, 129.5, 128.85, 128.1, 127.7, 127.2, 127.0, 126.9, 126.1, 125.5, 125.1, 124.0, 119.6, 113.8, 61.5, 59.0, 34.1, 30.2, 22.5, 14.0 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{40}H_{46}O_6 + Na]^+$ 645.3187, found 645.3204.

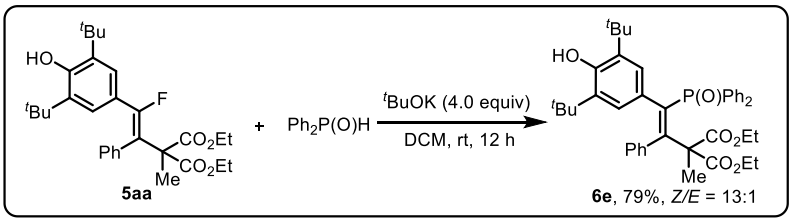


diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-morpholino-1-phenylvinyl)-2-methylmalonate (6c) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added K_3PO_4 (127.4 mg, 0.6 mmol, 3.0 equiv), **5aa** (99.7 mg, 0.2 mmol, 1.0 equiv) and morpholine (34.8 mg, 0.4 mmol, 2.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DMF (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 12 h at 80 ℃. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with EA (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **6c** as yellow oil (97.6 mg, 86% yield), R_f = 0.4 (PE/EA = 5/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 6.99 – 6.88 (m, 3H), 6.87 – 6.83 (m, 2H), 6.60 (s, 2H), 4.92 (s, 1H), 4.20 (q, *J* = 7.1 Hz, 4H), 3.69 (t, *J* = 4.6 Hz, 4H), 2.66 (t, *J* = 4.6 Hz, 4H), 1.49 (s, 3H), 1.29 – 1.24 (m, 24H) ppm. **^{13}C NMR (75 MHz, CDCl3)** δ 171.9, 152.0, 149.8, 138.8, 136.8, 134.1, 130.1, 127.3, 126.9, 125.9, 125.3, 66.5, 61.1, 58.6, 50.2, 33.9, 30.2, 23.8, 14.0 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{34}H_{47}NO_6 + H]^+$ 566.3477, found 566.3475.

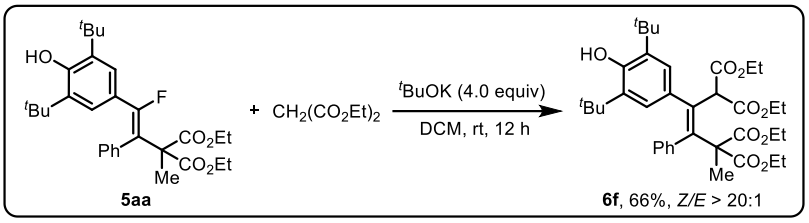


diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethoxy-1-phenylvinyl)-2-methylmalonate (6d) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.8 mg, 0.8 mmol, 4.0 equiv), **5aa** (99.7 mg, 0.2 mmol, 1.0 equiv) and EtONa (136.1 mg, 20 wt% in EtOH, 0.4 mmol, 2.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that,

anhydrous DCM (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 12 h at rt. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **6d** as colorless oil (81.9 mg, 78% yield, *Z*/*E* > 20:1), R_f = 0.3 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 2H), 7.25 – 7.20 (m, 5H), 5.25 (s, 1H), 4.29 – 4.10 (m, 2H), 3.94 – 3.81 (m, 4H), 1.42 (s, 3H), 1.32 – 1.19 (m, 27H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.7, 154.3, 149.0, 135.2, 134.9, 130.5, 128.6, 127.1, 124.7, 121.4, 121.1, 114.7, 64.1, 61.2, 59.3, 59.1, 34.3, 30.1, 17.3, 15.4, 15.3, 14.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{32}H_{44}O_6 + H]^+$ 525.3211, found 525.3217.

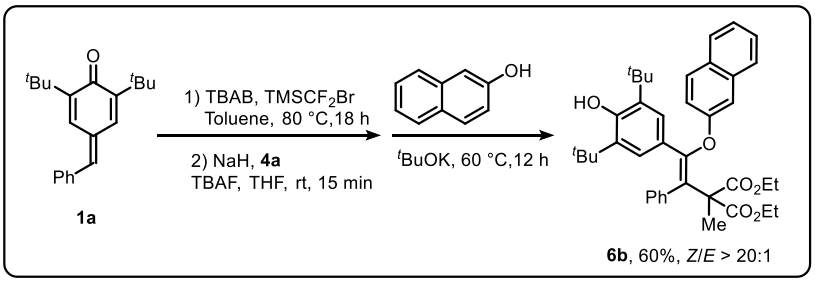


diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-((diphenylphosphoryl)oxy)-1-phenylvinyl)-2-methylmalonate (6e) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.8 mg, 0.8 mmol, 4.0 equiv), **5aa** (99.7 mg, 0.2 mmol, 1.0 equiv) and diphenylphosphine oxide (80.8 mg, 0.4 mmol, 2.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 12 h at rt. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (DCM/MeOH) to afford the corresponding product **6e** as a white solid (107.0 mg, 79% yield, *Z*/*E* = 13:1). **m.p.** 198 – 200 ℃, R_f = 0.3 (DCM/MeOH = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.48 – 7.41 (m, 4H), 7.20 – 7.04 (m, 10H), 6.99 – 6.90 (m, 3H), 5.02 (s, 1H), 3.90 (dq, *J* = 10.7, 7.1 Hz, 2H), 3.70 (dq, *J* = 10.7, 7.1 Hz, 2H)., 1.29 (s, 18H), 1.20 (s, 3H), 1.14 (t, *J* = 7.15 Hz, 6H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.0 (d, *J* = 1.3 Hz), 153.3 (d, *J* = 11.1 Hz), 152.8 (d, *J* = 2.6 Hz), 140.6 (d, *J* = 91.4 Hz), 136.9 (d, *J* = 8.1 Hz), 135.4, 134.8 (d, *J* = 1.9 Hz), 134.1, 133.1 (d, *J* = 9.1 Hz), 131.2 (d, *J* = 1.6 Hz), 131.0 (d, *J* = 8.7 Hz), 130.1 (d, *J* = 2.8 Hz), 127.6 (d, *J* = 5.0 Hz), 127.4 (d, *J* = 12.0 Hz), 126.5, 62.4 (d, *J* = 12.8 Hz), 61.5, 34.2, 30.1, 24.1, 13.9 ppm. **^{31}P NMR (121 MHz, $CDCl_3$)** δ 24.84 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{42}H_{49}O_6P + Na]^+$ 703.3159, found 703.3167.



tetraethyl (E)-2-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-phenylpent-2-ene-1,1,4,4-tetracarboxylate (6f) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.8 mg, 0.8 mmol, 4.0 equiv), **5aa** (99.7 mg, 0.2 mmol, 1.0 equiv) and dimethyl malonate (60.1 mg, 0.4 mmol, 2.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 12 h at rt. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **6f** as a white solid (84.2 mg, 66% yield, *Z/E* > 20:1). **m.p.** 163 – 165 ℃, R_f = 0.4 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.35 – 7.26 (m, 7H), 5.15 (s, 1H), 4.21 (s, 1H), 3.93 – 3.82 (m, 6H), 3.77 – 3.69 (m, 2H), 1.42 (s, 18H), 1.25 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 6H), 1.02 (t, *J* = 7.1 Hz, 6H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.3, 168.4, 153.2, 140.8, 140.2, 135.9, 134.4, 129.6, 128.4, 127.9, 127.5, 61.3, 61.1, 60.6, 59.9, 34.4, 30.4, 30.3, 24.2, 14.0 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{37}H_{50}O_9 + H]^+$ 639.3528, found 639.3548.

5. One-pot Reaction for the Synthesis of tetra-Substituted Alkene 6b

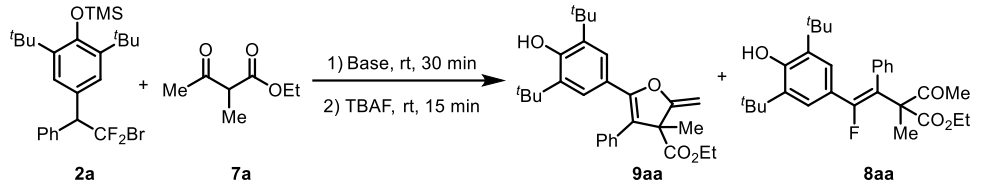


To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added *p*-QM **1a** (147.2 mg, 0.5 mmol, 1.0 equiv) and TBAB (8.0 mg, 0.025 mmol, 5 mol%), then the Schlenk tube was evacuated and backfilled with argon for three times. After that, $TMSCF_2Br$ (203.1 mg, 1.0 mmol, 2.0 equiv) dissolved in toluene (1.0 mL) was added under argon atmosphere via a syringe. The reaction mixture was stirred at 80 ℃ (oil bath) for 18 h to afford the solution of intermediate **2a** in toluene.

To another oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added NaH (60 mg, 1.5 mmol, 3.0 equiv), then the Schlenk tube was evacuated and backfilled with argon for three times. Compound **4a** (1.0 mmol, 2.0 equiv) dissolved in 1.0 mL anhydrous THF was added under argon atmosphere via a syringe, and the reaction mixture was stirred at room temperature for 30 min. Then the solution of crude **2a** in toluene was added, followed by the dropwise addition of TBAF (0.4 mmol, 0.4 equiv, 0.3 M solution in THF) under argon atmosphere. After stirring at room temperature for 15 min, ^{t}BuOK (224.4 mg, 2.0 mmol, 4.0 equiv) and 2-hydroxynaphthalene (144.2 mg, 1.0 mmol, 2.0 equiv) were directly added to the above-mentioned solution under argon atmosphere. After stirred at 60 ℃ for 12 h, saturated solution of NH_4Cl (5.0 mL) was added to quench the reaction. The reaction mixture was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **6b** (186.8 mg, 60% yield, *Z*/*E* > 20:1).

6. Optimization of Reaction Parameters for the Synthesis of 9aa

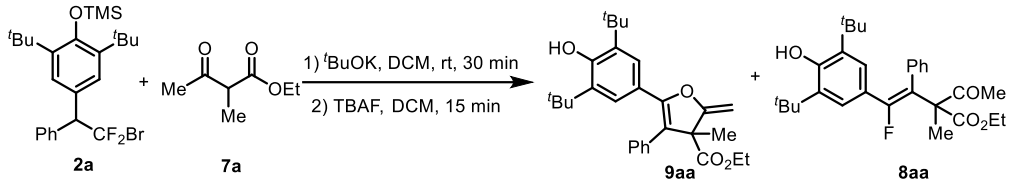
Table S1. Base, Solvent Screening[a, b]



Entry	Base	The equiv of base	Solvent	Yield of **9aa** (%)	Yield of **8aa** (%)
1	^{t}BuOK	3.0	DCM	51	41
2	^{t}BuONa	3.0	DCM	45	29
3	KOH	3.0	DCM	17	51
4	K_2CO_3	3.0	DCM	n.d.	71
5	DBU	3.0	DCM	9	25
6	LDA	3.0	DCM	n.d.	n.d.
7	^{t}BuOK	2.0	DCM	3	60
8	^{t}BuOK	2.5	DCM	20	50
9	^{t}BuOK	3.5	DCM	49	40
10	^{t}BuOK	4.0	DCM	65	30
11	^{t}BuOK	4.0	Toluene	18	77
12	^{t}BuOK	4.0	DMF	8	60
13	^{t}BuOK	4.0	MTBE	48	46
14	^{t}BuOK	4.0	HMPA	4	69

[a] ^{t}BuOK (0.8 mmol, 4.0 equiv) and **7a** (0.4 mmol, 2.0 equiv) in DCM were stirred at rt for 30 min. Then TBAF (1 M in THF) and **2a** (0.2 mmol, 1.0 equiv) were added under Ar. [b]The yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as internal standard.

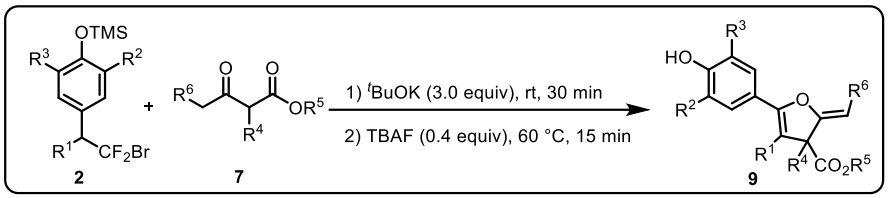
Table S2. Screening of temperature and the equivalent of TBAF[a, b]



Entry	Temperature (℃)	The equiv of TBAF	Yield of **9aa** (%)	Yield of **8aa** (%)
1	r.t.	1.1	65	30
2	40	1.1	60	36
3	60	1.1	79	13
4	80	1.1	78	5
5	100	1.1	76	n.d.
6	60	0.2	72	8
7	60	0.4	85	3
8	60	0.6	80	13
9	60	0.8	78	5
10	60	1.0	75	23

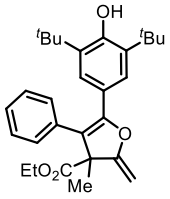
[a]**7a** (0.4 mmol, 2.0 equiv) and ^{t}BuOK (0.8 mmol, 4.0 equiv) in DCM were stirred at rt for 30 min. Then TBAF (1 M in THF) and **2a** (0.2 mmol, 1.0 equiv) were added under Ar. [b]The yields were determined by ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as internal standard.

7. General Procedure B for the Synthesis of Product 9



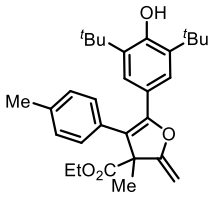
To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.7 mg, 0.8 mmol, 4.0 equiv), then the Schlenk tube was evacuated and filled with argon for three times. After that, compound **7** (0.4 mmol, 2.0 equiv) dissolved in 1.0 mL anhydrous DCM was added under argon atmosphere via a syringe. The above-mentioned solution was stirred at room temperature for 30 min, followed by the sequential addition of TBAF (0.08 mL, 0.4 equiv, 1 M solution in THF, dissolved in 0.5 mL DCM) and **2** (0.2 mmol in 0.5 mL DCM) under argon atmosphere. After the starting material was completely consumed (typically 15 min at 60 ℃), ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **9**.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-phenyl-2,3-dihydrofuran-3-carboxylate (9aa)



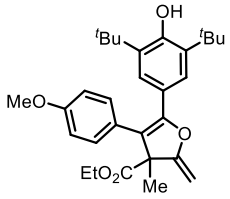
Prepared through general procedure B to give **9aa** in 70.9 mg, 79% yield, white solid, m.p. 165 – 166 ℃, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.37 – 7.22 (m, 7H), 5.31 (s, 1H), 4.74 (d, J = 2.7 Hz, 1H), 4.31 (d, J = 2.6 Hz, 1H), 4.26 – 4.16 (m, 2H), 1.56 (s, 3H), 1.28 – 1.23 (m, 21H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.7, 165.1, 154.6, 150.7, 135.5, 133.9, 130.4, 128.8, 127.6, 124.6, 120.7, 114.4, 83.8, 61.7, 60.0, 34.4, 30.1, 23.9, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{29}H_{36}O_4 + H]^+$ 449.2686, found 449.2698.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-(p-tolyl)-2,3-dihydrofuran-3-carboxylate (9ab)



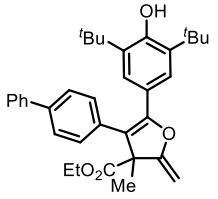
Prepared through general procedure B to give **9ab** in 62.8 mg, 68% yield, yellow solid, m.p. 130 – 131 ℃, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl3)** δ 7.23 (s, 1H), 7.18 – 7.05 (m, 2H), 5.28 (s, 1H), 4.71 (d, J = 2.6 Hz, 1H), 4.28 (d, J = 2.6 Hz, 1H), 4.23 – 4.12 (m, 2H), 2.33 (s, 3H), 1.53 (s, 3H), 1.34 – 1.22 (m, 21H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.7, 165.1, 154.5, 150.4, 137.3, 135.5, 130.7, 130.3, 129.5, 124.5, 120.8, 114.4, 83.7, 61.6, 60.0, 34.4, 30.1, 23.9, 21.3, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}O_4 + H]^+$ 463.2843, found 463.2857.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(4-methoxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9ac)



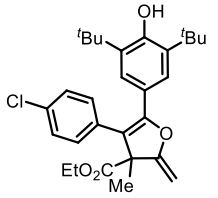
Prepared through general procedure B to give **9ac** in 66.9 mg, 70% yield, yellow solid, m.p. 146 – 147 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.26 (s, 2H), 7.17 – 7.12 (m, 2H), 6.90 – 6.85 (m, 2H), 5.30 (s, 1H), 4.72 (d, *J* = 2.6 Hz, 1H), 4.28 (d, *J* = 2.6 Hz, 1H), 4.24 – 4.14 (m, 2H), 3.80 (s, 3H), 1.53 (s, 3H), 1.28 – 1.22 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.7, 165.1, 159.2, 154.5, 150.4, 135.4, 131.6, 125.9, 124.4, 120.8, 114.4, 114.0, 83.7, 61.6, 59.9, 55.5, 34.4, 30.1, 23.9, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}O_5 + H]^+$ 479.2792, found 479.2807.

ethyl 4-([1,1'-biphenyl]-4-yl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9ad)



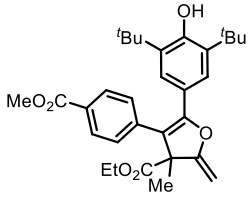
Prepared through general procedure B to give **9ad** in 68.1 mg, 65% yield, yellow solid, m.p. 156 – 157 °C, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** 7.71 – 7.67 (m, 4H), 7.57 (t, *J* = 7.3 Hz, 2H), 7.50 – 7.36 (m, 5H), 5.44 (s, 1H), 4.88 (d, *J* = 2.7 Hz, 1H), 4.45 (d, *J* = 2.7 Hz, 1H), 4.40 – 4.27 (m, 2H), 1.72 (s, 3H), 1.40 – 1.37 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.7, 165.0, 154.6, 150.9, 141.1, 140.5, 135.5, 132.9, 130.8, 128.9, 127.6, 127.4, 127.2, 124.6, 120.6, 114.0, 84.0, 61.7, 59.9, 34.4, 30.1, 24.0, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{35}H_{40}O_4 + H]^+$ 525.2999, found 525.3014.

ethyl 4-(4-chlorophenyl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9ae)



Prepared through general procedure B to give **9ae** in 64.6 mg, 67% yield, purple solid, m.p. 141 – 142 °C, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.35 – 7.32 (m, 2H), 7.24 (s, 2H), 7.21 – 7.18 (m, 2H), 5.37 (s, 1H), 4.77 (d, *J* = 2.8 Hz, 1H), 4.35 (d, *J* = 2.7 Hz, 1H), 4.28 – 4.15 (m, 2H), 1.57 (s, 3H), 1.32 – 1.24 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.5, 164.7, 154.8, 151.2, 135.6, 133.5, 132.5, 131.8, 129.0, 124.6, 120.3, 113.0, 84.3, 61.8, 59.7, 34.4, 30.1, 23.9, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{29}H_{35}ClO_4 + H]^+$ 483.2297, found 483.2312.

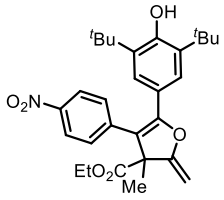
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(4-(methoxycarbonyl)phenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9af)



Prepared through general procedure B to give **9af** in 57.7 mg, 57% yield, yellow solid, m.p. 135 – 136 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.98 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.23 (s, 2H), 5.36 (s, 1H), 4.75 (d, *J* = 2.8 Hz, 1H), 4.34 (d, *J* = 2.8 Hz, 1H), 4.26 – 4.12 (m, 2H), 3.92 (s, 2H), 1.55 (s, 3H), 1.27 – 1.20 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.4, 167.0, 164.7, 155.0, 151.9, 139.2, 135.7, 130.1, 130.0, 128.9, 124.9, 120.2, 113.4, 84.4, 61.8, 59.6, 52.3, 34.4, 30.1, 23.9, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{31}H_{38}O_6 + H]^+$

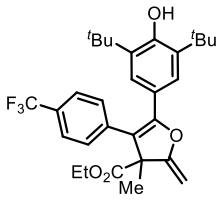
507.2741, found 507.2751.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-(4-nitrophenyl)-2,3-dihydrofuran-3-carboxylate (9ag)



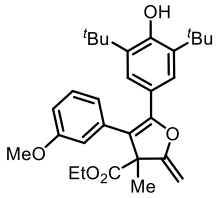
Prepared through general procedure B to give **9ag** in 45.4 mg, 46% yield, yellow solid, m.p. 185 – 186 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.15 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.22 (s, 2H), 5.42 (s, 1H), 4.78 (d, *J* = 2.9 Hz, 1H), 4.39 (d, *J* = 2.9 Hz, 1H), 4.30 – 4.14 (m, 2H), 1.58 (s, 3H), 1.29 – 1.21 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.4, 164.4, 155.5, 153.7, 146.6, 141.6, 136.0, 130.5, 125.2, 123.9, 119.9, 112.4, 85.1, 62.0, 59.3, 34.5, 30.1, 24.0, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{29}H_{35}NO_6 + H]^+$ 494.2537, found 494.2547.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-(4-(trifluoromethyl)phenyl)-2,3-dihydrofuran-3-carboxylate (9ah)



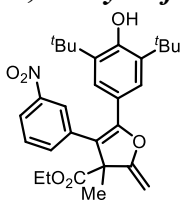
Prepared through general procedure B to give **9ah** in 64.0 mg, 62% yield, white solid, m.p. 140 – 141 °C, R_f = 0.7 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.62 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 2H), 5.38 (s, 1H), 4.79 (d, *J* = 2.6 Hz, 1H), 4.38 (d, *J* = 2.6 Hz, 1H), 4.27 – 4.20 (m, 2H), 1.59 (s, 3H), 1.36 – 1.25 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.4, 164.6, 155.0, 151.9, 130.2, 129.6 (q, ^2J = 32.4 Hz), 125.7 (q, ^3J = 3.8 Hz), 124.7, 124.3 (q, ^1J = 270.2 Hz), 120.1, 112.9, 84.6, 61.9, 59.7, 34.4, 30.1, 24.0, 14.2 ppm. **^{19}F NMR (282 MHz, CDCl$_3$)** δ –62.76 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{35}F_3O_4 + H]^+$ 517.2560, found 517.2559.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(3-methoxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9ai)



Prepared through general procedure B to give **9ai** in 66.9 mg, 70% yield, yellow solid, m.p. 150 – 151 °C, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.27 (s, 2H), 7.26 – 7.22 (m, 1H), 6.85 – 6.76 (m, 3H), 5.31 (s, 1H), 4.72 (d, *J* = 2.6 Hz, 1H), 4.29 (d, *J* = 2.7 Hz, 1H), 4.25 – 4.15 (m, 2H), 3.74 (s, 3H), 1.54 (s, 3H), 1.28 – 1.23 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.7, 165.0, 160.0, 154.6, 150.7, 135.5, 135.1, 129.8, 124.6, 122.8, 120.6, 115.8, 114.2, 113.3, 83.8, 61.7, 59.9, 55.3, 34.4, 30.2, 23.9, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}O_5 + H]^+$ 479.2792, found 479.2808.

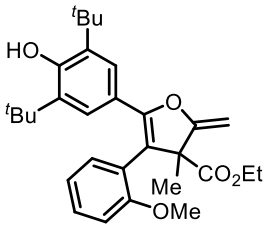
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-(3-nitrophenyl)-2,3-dihydrofuran-3-carboxylate (9aj)



Prepared through general procedure B to give **9aj** in 52.3 mg, 53% yield, green solid, m.p. 133 – 134 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.16 – 8.12 (m, 2H), 7.59 – 7.48 (m, 2H), 7.20 (s, 2H), 5.39 (s, 1H), 4.79 (d, *J* = 2.8 Hz, 1H), 4.39 (d, *J* = 2.9 Hz, 1H), 4.32 – 4.14 (m, 2H), 1.58 (s, 3H), 1.29 – 1.25 (m, 21H) ppm. **^{13}C**

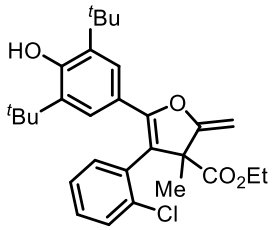
NMR (75 MHz, $CDCl_3$) δ 172.3, 164.3, 155.2, 152.6, 148.6, 136.7, 136.1, 135.9, 129.7, 125.2, 124.8, 122.3, 119.8, 111.7, 85.0, 62.1, 59.5, 34.4, 30.1, 24.1, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{29}H_{35}NO_6 + H]^+$ 494.2537, found 494.2548.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(2-methoxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9ak)



Prepared through general procedure B to give **9ak** in 67.9 mg, 71% yield, green solid, m.p. 159 – 160 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.27 (s, 2H), 7.26 – 7.22 (m, 1H), 6.84 – 6.76 (m, 3H), 5.31 (s, 1H), 4.75 (d, *J* = 2.6 Hz, 1H), 4.32 (d, *J* = 2.7 Hz, 1H), 4.25 – 4.15 (m, 2H), 3.74 (s, 3H), 1.54 (s, 3H), 1.28 – 1.23 (m, 21H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.7, 165.0, 160.0, 154.6, 150.7, 135.5, 135.1, 129.8, 124.6, 122.8, 120.6, 115.8, 114.2, 113.3, 83.8, 61.7, 59.9, 55.3, 34.4, 30.1, 23.9, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}O_5 + H]^+$ 479.2792, found 479.2806.

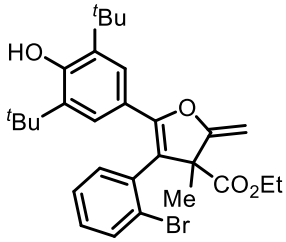
ethyl 4-(2-chlorophenyl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9al)



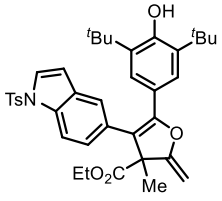
Prepared through general procedure B to give **9al** in 75.2 mg, 78% yield, yellow solid, m.p. 115 – 116 °C, R_f = 0.4 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.39 – 7.35 (m, 1H), 7.20 – 7.12 (m, 5H), 5.23 (s, 1H), 4.70 (d, *J* = 2.6 Hz, 1H), 4.21 (d, *J* = 2.8 Hz, 1H), 4.18 – 4.09 (m, 2H), 1.47 (s, 3H), 1.26 – 1.13 (m, 21H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.3, 165.0, 154.8, 151.6, 136.3, 135.6, 132.9, 132.5, 130.2, 129.3, 127.2, 123.9, 120.6, 109.8, 84.4, 61.7, 34.4 (two overlapping carbon signals), 30.1 (two overlapping carbon signals), 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{29}H_{35}ClO_4 + H]^+$ 483.2297, found 483.2312.

ethyl 4-(2-bromophenyl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9am)

Prepared through general procedure B to give **9am** in 86.3 mg, 82% yield, yellow solid, m.p. 119 – 120 °C, R_f = 0.4 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.18 (m, 5H), 5.35 (s, 1H), 4.79 (d, *J* = 2.4 Hz,1H), 4.32 – 4.26 (m, 3H), 1.60 (s, 3H), 1.35 – 1.27 (m, 21H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.5, 165.0, 154.8, 151.5, 135.5, 134.9, 133.5, 132.2, 129.5, 127.9, 127.2, 123.9, 120.6, 111.3, 84.1, 61.7, 61.4, 34.4, 30.1, 22.7, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{29}H_{35}BrO_4 + H]^+$ 527.1791, found 527.1802.

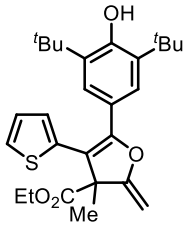


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-(1-tosyl-1H-indol-5-yl)-2,3-dihydrofuran-3-carboxylate (9an)



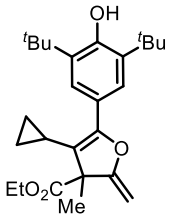
Prepared through general procedure B to give **9an** in 55.1 mg, 43% yield, white solid, m.p. 199 – 200 ℃, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.52 (s, 1H), 7.33 – 7.25 (m, 3H), 7.17 – 7.07 (m, 4H), 5.27 (s, 1H), 4.82 (d, *J* = 2.7 Hz, 1H), 4.40 (d, *J* = 2.7 Hz, 1H), 4.19 – 4.10 (m, 2H), 2.37 (s, 3H), 1.57 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 1.03 (s, 18H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.5, 164.5, 154.7, 152.2, 145.1, 135.3, 135.1, 135.0, 130.4, 130.1, 127.1, 125.0, 124.4, 124.2, 123.3, 121.8, 120.1, 115.5, 113.6, 104.2, 84.6, 61.8, 60.1, 34.1, 29.7, 24.4, 21.7, 14.1 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{38}H_{43}NO_6S + H]^+$ 642.2884, found 642.2900.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-(thiophen-2-yl)-2,3-dihydrofuran-3-carboxylate (9ao)



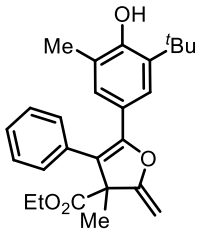
Prepared through general procedure B to give **9ao** in 55.4 mg, 61% yield, yellow solid, m.p. 135 – 136 ℃, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.29 (s, 2H), 7.22 – 7.18 (m, 1H), 6.95 – 6.92 (m, 1H), 6.82 – 6.81 (m, 1H), 5.29 (s, 1H), 4.66 (d, *J* = 2.8 Hz, 1H), 4.26 (d, *J* = 2.9 Hz, 1H), 4.18 – 4.07 (m, 2H), 1.51 (s, 3H), 1.25 – 1.16 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.4, 164.6, 155.0, 152.4, 135.6, 134.6, 128.1, 127.4, 126.5, 124.8, 120.2, 107.6, 84.5, 61.8, 59.7, 34.4, 30.2, 24.0, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{27}H_{34}O_4S + H]^+$ 455.2251, found 455.2264.

ethyl 4-cyclopropyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-2,3-dihydrofuran-3-carboxylate (9ap)



Prepared through general procedure B to give **9ap** in 35 mg, 42% yield, white solid, m.p. 134 – 136 ℃, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.65 (s, 2H), 5.37 (s, 1H), 4.59 (d, *J* = 2.6 Hz, 1H), 4.24 – 4.07 (m, 3H), 1.60 (s, 3H), 1.52 – 1.47 (m, 19H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.85 – 0.68 (m, 2H), 0.55 – 0.47 (m, 1H), 0.41 – 0.33 (m, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 173.6, 165.2, 154.3, 151.6, 135.5, 124.8, 121.4, 113.6, 83.0, 61.5, 59.3, 34.6, 30.4, 24.4, 14.1, 7.4, 6.9, 6.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{26}H_{36}O_4 + H]^+$ 413.2686, found 413.2689.

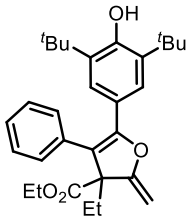
ethyl 5-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)-3-methyl-2-methylene-4-phenyl-2,3-dihydrofuran-3-carboxylate (9aq)



Prepared through general procedure B to give **9aq** in 51.9 mg, 64% yield, yellow solid, m.p. 81 – 82 ℃, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.34 – 7.18 (m, 6H), 7.07 (s, 1H), 4.92 (s, 1H), 4.71 (d, *J* = 2.7 Hz, 1H), 4.30 (d, *J* = 2.4 Hz, 1H), 4.23 – 4.16 (m, 2H), 2.16 (s, 3H), 1.54 (s, 3H), 1.24 (t, *J* = 7.0 Hz, 3H), 1.16 (s, 9H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.7, 165.0, 153.4, 150.4,

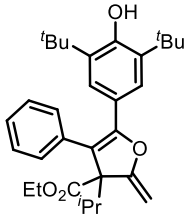
135.2, 133.7, 130.3, 128.8, 127.6, 127.6, 125.2, 122.8, 121.2, 114.6, 83.9, 61.7, 59.9, 34.5, 29.5, 23.8, 16.0, 14.2 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{26}H_{30}O_4 + H]^+$ 407.2217, found 407.2230.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-ethyl-2-methylene-4-phenyl-2,3-dihydrofuran-3-carboxylate (9ba)



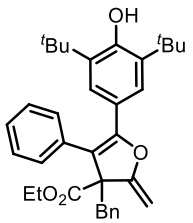
Prepared through general procedure B to give **9ba** in 65.6 mg, 71% yield, white solid, m.p. 183 – 184 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.34 – 7.19 (m, 7H), 5.31 (s, 1H), 4.80 (d, *J* = 2.6 Hz, 1H), 4.23 (d, *J* = 2.7 Hz, 1H), 4.23 – 4.11 (m, 2H), 1.95 (q, *J* = 7.4 Hz, 2H), 1.27 (s, 18H), 1.21 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.7, 162.5, 154.6, 151.8, 135.4, 133.9, 130.2, 128.8, 127.5, 124.7, 120.6, 111.5, 84.1, 65.1, 61.5, 34.4, 30.1, 27.6, 14.2, 8.5 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}O_4 + H]^+$ 463.2843, found 463.2860.

ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-isopropyl-2-methylene-4-phenyl-2,3-dihydrofuran-3-carboxylate (9ca)



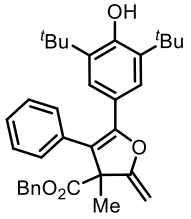
Prepared through general procedure B to give **9ca** in 42.8 mg, 45% yield, purple solid, m.p. 141 – 142 °C, R_f = 0.7 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.48 – 7.37 (m, 5H), 7.31 (s, 2H), 5.40 (s, 1H), 5.04 (d, *J* = 2.5 Hz, 1H), 4.46 (d, *J* = 2.5 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 2.65 – 2.56 (m, 1H), 1.38 (s, 18H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 6.6 Hz, 3H), 1.03 (d, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.6, 161.0, 154.4, 151.3, 135.3, 134.8, 130.9, 128.7, 127.5, 124.8, 120.7, 111.8, 86.7, 69.1, 61.2, 34.3, 33.4, 30.1, 18.1, 16.9, 14.1 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{31}H_{40}O_4 + H]^+$ 477.2999, found 477.3012.

ethyl 3-benzyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylene-4-phenyl-2,3-dihydrofuran-3-carboxylate (9da)



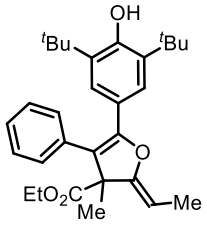
Prepared through general procedure B to give **9da** in 87.0 mg, 83% yield, yellow solid, m.p. 132 – 133 °C, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.39 – 7.31 (m, 3H), 7.26 – 7.20 (m, 9H), 5.41 (s, 1H), 4.92 (d, *J* = 2.9 Hz, 1H), 4.41 – 4.34 (m, 3H), 3.56 – 3.40 (m, 2H), 1.39 – 1.32 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.6, 162.2, 154.7, 152.4, 136.5, 135.5, 133.6, 130.6, 129.6, 128.5, 127.8, 127.1, 126.6, 125.1, 120.8, 112.4, 85.8, 64.5, 61.8, 41.1, 34.3, 30.2, 14.1 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{35}H_{40}O_4 + H]^+$ 525.2999, found 525.3011.

benzyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-2-methylene-4-phenyl-2,3-dihydrofuran-3-carboxylate (9ea)



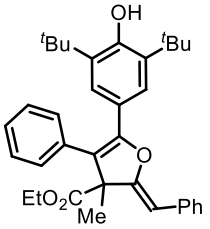
Prepared through general procedure B to give **9ea** in 71.4 mg, 70% yield, yellow solid, m.p. 177 – 178 ℃, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.30 – 7.29 (m, 5H), 7.23 – 7.21 (m, 5H), 7.07– 7.04 (m, 2H), 5.30 (s, 1H), 5.27 – 5.10 (m, 2H), 4.74 (d, *J* = 2.7 Hz, 1H), 4.29 (d, *J* = 2.7 Hz, 1H), 1.55 (s, 3H), 1.26 (s, 18H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.4, 164.8, 154.6, 150.9, 135.9, 135.5, 133.6, 130.3, 128.8, 128.5, 128.3, 128.2, 127.5, 124.7, 120.6, 114.2, 84.2, 67.2, 59.9, 34.3, 30.1, 23.7 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{34}H_{38}O_4 + H]^+$ 511.2843, found 511.2858.

ethyl (Z)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethylidene-3-methyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (9fa)



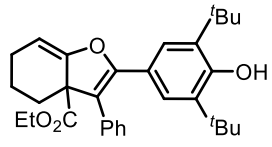
Prepared through general procedure B to give **9fa** in 52.8 mg, 57% yield, yellow solid, m.p. 164 – 166 ℃, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.33 – 7.20 (m, 7H), 5.29 (s, 1H), 4.65 (q, *J* = 6.9 Hz, 1H), 4.26 – 4.09 (m, 2H), 1.79 (d, *J* = 6.9 Hz, 3H), 1.50 (s, 3H), 1.27 – 1.20 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 173.1, 157.6, 154.5, 150.4, 135.4, 134.1, 130.5, 128.7, 127.4, 124.6, 121.0, 114.2, 94.8, 61.5, 59.3, 34.3, 30.1, 23.9, 14.3, 10.6 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{30}H_{38}O_4 + H]^+$ 463.2843, found 463.2841.

ethyl (Z)-2-benzylidene-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (9ga)



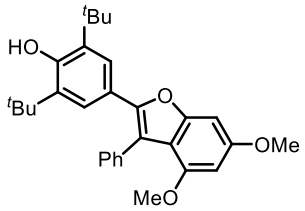
Prepared through general procedure B at room temperature to give **9ga** in 52.7 mg, 50% yield, yellow solid, m.p. 163 – 165 ℃, R_f = 0.5 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.75 (d, *J* = 7.6 Hz, 2H), 7.38 – 7.27 (m, 9H), 7.23 – 7.17 (m, 1H), 5.59 (s, 1H), 5.34 (s, 1H), 4.26 – 4.14 (m, 2H), 1.63 (s, 3H), 1.31 – 1.21 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.5, 158.2, 154.6, 150.6, 135.6, 133.5, 130.5, 128.9, 128.4, 128.3, 127.8, 126.0, 124.5, 120.6, 114.3, 100.5, 61.8, 61.5, 34.4, 30.1, 23.8, 14.3 ppm. **HRMS (ESI)** *m*/*z* Calcd for $[C_{35}H_{40}O_4 + H]^+$ 525.3000, found 525.2997.

ethyl 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-phenyl-5,6-dihydrobenzofuran-3a(4H)-carboxylate (9ha)



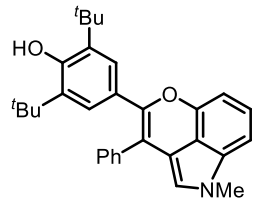
Prepared through general procedure B to give **9ha** in 40.1 mg, 42% yield, green solid, m.p. 165 – 167 ℃, R_f = 0.4 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.34 – 7.19 (m, 7H), 5.29 – 5.27 (m, 2H), 4.26 – 4.08 (m, 2H), 2.47 – 2.42 (m, 1H), 2.27 – 2.21 (m, 1H), 1.84 – 1.76 (m, 1H), 1.63 – 1.46 (m, 2H), 1.26 (s, 18H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.2, 155.1, 154.6,

152.6, 135.4, 134.3, 130.0, 128.7, 127.2, 124.9, 121.0, 113.2, 99.0, 61.2, 58.9, 34.4, 30.2, 29.2, 22.2, 18.9, 14.4 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{31}H_{38}O_4 + H]^+$ 475.2843, found 475.2836.



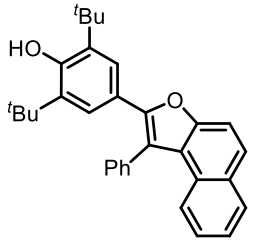
2,6-di-tert-butyl-4-(4,6-dimethoxy-3-phenylbenzofuran-2-yl)phenol (9ia) Prepared through general procedure B in 25 min to give **9ia** in 40.3 mg, 44% yield, yellow solid, m.p. 178 – 181 ℃, R_f = 0.7 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.48 – 7.44 (m, 2H), 7.41 – 7.31 (m, 5H), 6.74 (d, *J* = 2.0 Hz, 1H), 6.28 (d, *J* = 2.0 Hz, 1H), 5.23 (s, 1H), 3.87 (s, 3H), 3.65 (s, 3H), 1.30 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 158.8, 155.6, 154.7, 153.7, 150.0, 135.7, 134.6, 130.9, 128.1, 127.0, 123.8, 122.3, 115.4, 113.5, 94.5, 88.2, 55.9, 55.6, 34.4, 30.2 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{30}H_{34}O_4 + H]^+$ 459.2530, found 459.2523.

2,6-di-tert-butyl-4-(5-methyl-3-phenyl-5H-pyrano[4,3,2-cd]indol-2-yl)phenol (9ja)



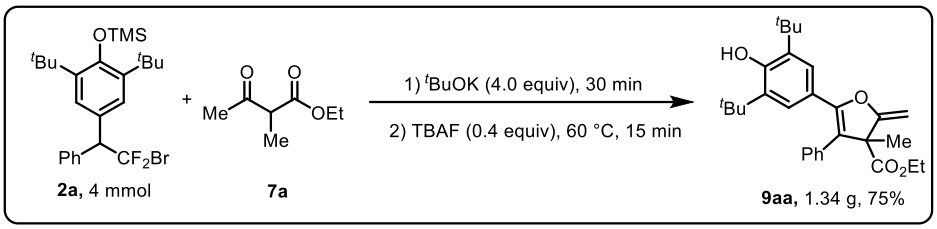
Prepared through general procedure B to give **9ja** in 42.5 mg, 47% yield, yellow oil, R_f = 0.7 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.57 – 7.43 (m, 6H), 7.38 – 7.33 (m, 1H), 7.28 – 7.15 (m, 2H), 7.07 (s, 1H), 6.83 (s, 1H), 5.23 (s, 1H), 3.83 (s, 3H), 1.35 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.7, 149.5, 147.2, 136.2, 135.9, 134.6, 130.3, 128.9, 128.3, 127.2, 123.8, 122.8, 122.2, 116.7, 114.3, 113.4, 105.6, 97.2, 34.5, 33.6, 30.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{31}H_{33}NO_2 + H]^+$ 452.2584, found 452.2583.

2,6-di-tert-butyl-4-(1-phenylnaphtho[2,1-b]furan-2-yl)phenol (9ka)



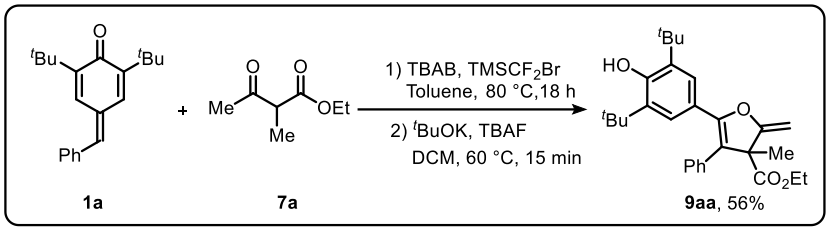
Prepared through general procedure B to give **9ka** in 60.1 mg, 67% yield, m.p. 173 – 174 ℃, R_f = 0.6 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.90 (d, *J* = 8.1 Hz, 1H), 7.76 – 7.69 (m, 2H), 7.57 – 7.46 (m, 8H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.21 (m, 1H), 5.27 (s, 1H), 1.32 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 153.9, 151.3, 151.0, 135.9, 135.5, 130.92, 130.87, 129.4, 128.9, 128.2, 128.0, 125.8, 125.0, 124.1, 124.0, 123.5, 123.2, 122.2, 117.5, 112.3, 34.4, 30.1 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{32}H_{32}O_2 + Na]^+$ 471.2295, found 471.2296.

8. Gram-scale Reaction for the Synthesis of 9aa



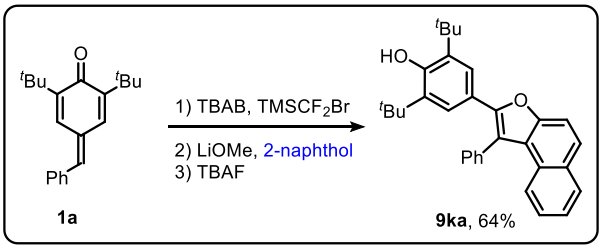
To a 100 mL two necked bottle equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (1.79 g, 16.0 mmol, 4.0 equiv) and **7a** (8.0 mmol, 2.0 equiv). Then the bottle was evacuated and filled with argon for three times. After that, anhydrous DCM (10 mL) was added under argon atmosphere via a syringe. The above-mentioned solution was stirred at room temperature for 30 min. Then TBAF (1.6 mL, 1.6 mmol, 1 M in THF) dissolved in 10 mL DCM, and compound **2a** (4.0 mmol in 10 mL DCM) was added in sequential under argon atmosphere. After stirring at 60 ℃ for 15 min, ice water (15 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **9aa** as a white solid (1.34 g, 75% yield).

9. One-pot Reaction for the Synthesis of 9aa and 9ka



To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **1a** (147.2 mg, 0.5 mmol, 1.0 equiv) and TBAB (8.0 mg, 0.025 mmol, 5 mol%), then the Schlenk tube was evacuated and backfilled with argon for three times. After that, $TMSCF_2Br$ (203.1 mg, 1.0 mmol, 2.0 equiv) dissolved in toluene (1.0 mL) was added under argon atmosphere via a syringe. The reaction mixture was stirred at 80 ℃ (oil bath) for 18 h to afford the toluene solution of crude intermediate.

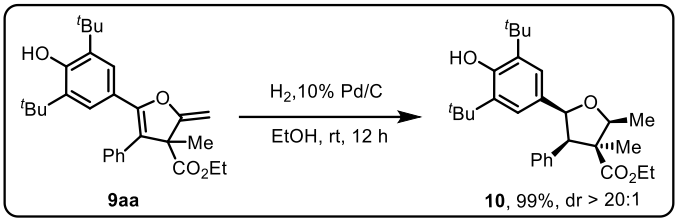
To another oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (224.4 mg, 2.0 mmol, 4.0 equiv), then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (1.0 mL) and **7a** (1.0 mmol, 2.0 equiv, dissolved in 1.0 mL THF) was added under argon atmosphere via a syringe. After stirred at room temperature for 30 min, the toluene solution of crude intermediate was added, and then TBAF (0.5 mmol, 0.4 equiv, 1 M solution in THF) dissolved in 1.0 mL DCM was dropped slowly under argon atmosphere. The reaction mixture was stirred at 60 ℃ for 15 min. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 5 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **9aa** as a white solid (125.6 mg, 56% yield).



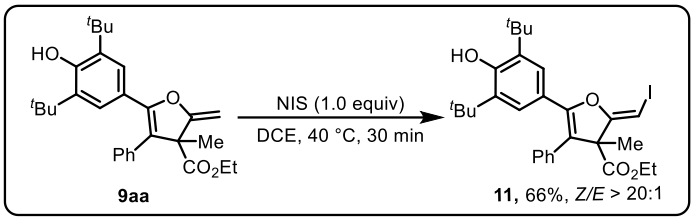
2,6-di-tert-butyl-4-(1-phenylnaphtho[2,1-b]furan-2-yl)phenol (15) To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added *p*-QM **1a** (147.2 mg, 0.5 mmol, 1.0 equiv) and TBAB (8 mg, 0.025 mmol, 5 mol%), then the Schlenk tube was evacuated and filled with argon for three times. After that, $TMSCF_2Br$ (203.1 mg, 1.0 mmol, 2.0 equiv) dissolved in toluene (1.0 mL) was added under argon atmosphere via a syringe. The reaction mixture was stirred at 80 ℃ in oil bath for 18 h to afford the toluene solution of crude intermediate. To another oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added LiOMe (75.8 mg, 2.0 mmol, 4.0 equiv), then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (0.5 mL) and 2-naphthol (1.0 mmol, 2.0

equiv, dissolved in 0.5 mL DCM) was added under argon atmosphere via a syringe. After stirred for 30 min at room temperature, the toluene solution of crude intermediate was added, and then TBAF (0.2 mmol, 0.4 equiv, dissolved in 1.0 mL DCM) was dropped slowly under argon atmosphere stirred for 15 min at room temperature. When the starting material was completely consumed, saturated solution of NH_4Cl (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **9ka** as a purple solid (143.6 mg, 64% yield).

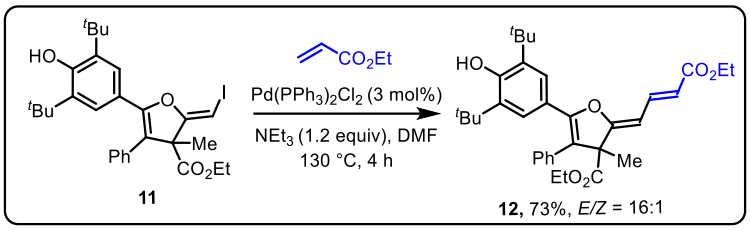
10. Transformations of the Products



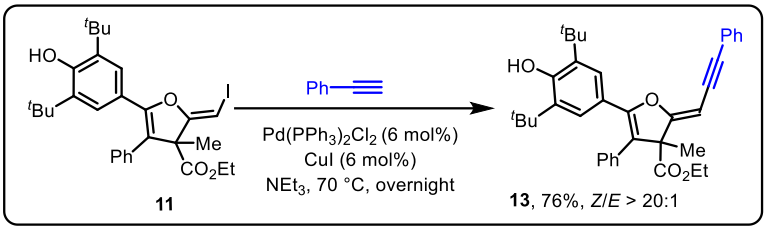
ethyl (2S,3S,4R,5S)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,3-dimethyl-4-phenyltetrahydrofuran-3-carboxylate (10) To an oven-dried 50 mL two necked bottle equipped with a Teflon coated magnetic stir bar was added **9aa** (89.7 mg, 0.2 mmol, 1.0 equiv), 10% Pd/C (17.9 mg, 20% wt) and 2 mL EtOH. The bottle was evacuated and filled with H_2 for three times then stirred at room temperature under H_2 atmosphere for 12 h. After **9aa** was completely consumed, the reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. Purification by flash chromatography on silica gel (PE/EA) to afford **10** as a white solid (89.5 mg, 99% yield). **m.p.** 106 – 107 °C, R_f = 0.3 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 6.92 – 6.84 (m, 3H), 6.77 (s, 2H), 6.57 (d, *J* = 7.3 Hz, 2H), 5.25 (d, *J* = 8.2 Hz, 1H), 4.88 (s, 1H), 3.95 – 3.89 (m, 1H), 3.80 – 3.61 (m, 2H), 3.53 (d, *J* = 8.9 Hz, 1H), 1.47 (d, *J* = 6.5 Hz, 3H), 1.32 (s, 3H), 1.20 (s, 18H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 172.2, 152.2, 136.9, 134.5, 130.9, 129.7, 127.0, 126.3, 123.7, 83.3, 81.5, 63.5, 59.8, 58.0, 34.2, 30.2, 23.4, 15.3, 14.0 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{29}H_{40}O_4 + Na]^+$ 475.2819, found 475.2834.



ethyl (Z)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(iodomethylene)-3-methyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (11) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added NIS (45.0 mg, 0.2 mmol, 1.0 equiv) and **9aa** (89.7 mg, 0.2 mmol, 1.0 equiv). Then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCE (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 30 min at 40 °C. After **9aa** was completely consumed, the mixture was concentrated and the residue was purified by chromatography on silica gel (PE/EA) to afford **11** as a white solid (75.8 mg, 66% yield, *Z/E* > 20:1). **m.p.** 170 – 172 °C, R_f = 0.4 (PE/EA = 20/1). **^{1}H NMR (300 MHz, CDCl$_3$)** δ 7.35 – 7.21 (m, 7H), 5.33 (s, 1H), 5.19 (s, 1H), 4.23 – 4.16 (m, 2H), 1.55 (s, 3H), 1.28 – 1.22 (m, 22H) ppm. **^{13}C NMR (75 MHz, CDCl$_3$)** δ 171.4, 163.9, 154.8, 150.3, 135.6, 133.4, 130.5, 128.9, 127.9, 124.6, 120.1, 115.4, 62.0, 61.0, 44.5, 34.4, 30.1, 23.6, 14.2 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{29}H_{35}IO_4 + H]^+$ 575.1653, found 575.1636.

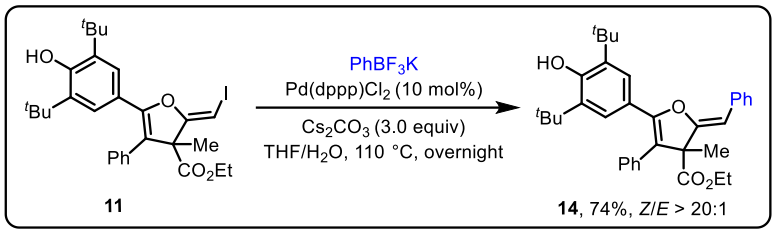


ethyl (Z)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-((E)-4-ethoxy-4-oxobut-2-en-1-ylidene)-3-methyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (12) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (114.9 mg, 0.2 mmol, 1.0 equiv) and $Pd(PPh_3)_2Cl_2$ (4.2 mg, 0.006 mmol, 3 mol%). Then the Schlenk tube was evacuated and filled with argon for three times. After that, ethyl acrylate (56.1 mg, 0.56 mmol, 2.8 equiv) and NEt_3 (24.3 mg, 0.24 mmol, 1.2 equiv) in anhydrous DMF (2 ml) was added via a syringe under argon atmosphere. After stirring for 4 h at 130 °C, the reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. Purification by flash chromatography on silica gel (PE/EA) to afford **12** as a white solid (79.6 mg, 73% yield, *E/Z* = 16:1). **m.p.** 167 – 169 °C, R_f = 0.2 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.86 (dd, *J* = 15.5, 11.3 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.31 (s, 2H), 7.28 – 7.20 (m, 3H), 5.89 (d, *J* = 15.5 Hz, 1H), 5.51 (d, *J* = 11.4 Hz, 1H), 5.38 (s, 1H), 4.28 – 4.18 (m, 4H), 1.59 (s, 3H), 1.35 – 1.23 (m, 6H), 1.31 (s, 18H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 171.5, 167.6, 165.1, 154.9, 150.6, 138.4, 135.7, 132.9, 130.4, 129.0, 128.0, 124.5, 120.0, 117.6, 114.8, 98.8, 62.0, 61.1, 60.2, 34.4, 30.1, 23.1, 14.4, 14.2 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{34}H_{42}O_6 + H]^+$ 547.3055, found 547.3058.

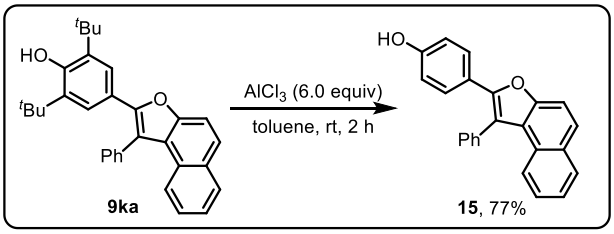


ethyl (Z)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-methyl-4-phenyl-2-(3-phenylprop-2-yn-1-ylidene)-2,3-dihydrofuran-3-carboxylate (13) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (114.9 mg, 0.2 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (8.4 mg, 0.012 mmol, 6 mol%), and CuI (2.3 mg, 0.012 mmol, 6 mol%). Then the Schlenk tube was evacuated and filled with argon for three times. After that, phenylacetylene (24.5 mg, 0.24 mmol, 1.2 equiv) in anhydrous NEt_3 (2 mL) was added via a syringe under argon atmosphere. After stirring at 70 °C overnight, the reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. Purification by flash chromatography on silica gel (PE/EA) to afford **13** as a white solid (83.4 mg, 76% yield, *Z/E* > 20:1). **m.p.** 142– 144 °C, R_f = 0.3 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.49 – 7.46 (m, 2H), 7.39 – 7.23 (m, 10H), 5.33 (s, 1H), 5.04 (s, 1H), 4.29 – 4.15 (m, 2H), 1.58 (s, 3H), 1.30 – 1.23 (m, 21H) ppm. **^{13}C NMR (75 MHz, CDCl3)** δ 171.6, 168.3, 154.8, 150.6, 135.6, 133.2, 131.3, 130.5, 129.0, 128.4, 128.0, 127.8, 124.6, 124.3, 120.2, 114.8, 94.5, 84.3, 80.8, 62.0, 61.0, 34.4, 30.1,

23.6, 14.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{37}H_{41}O_4 + H]^+$ 549.3000, found 549.2991.

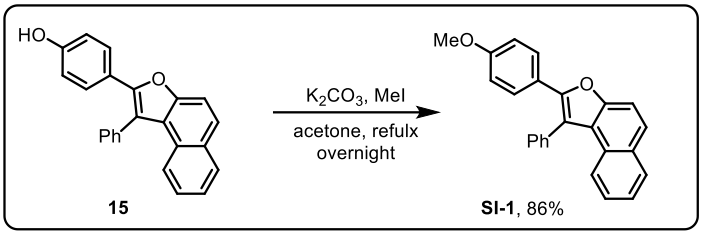


ethyl (Z)-2-benzylidene-5-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)-3-methyl-4-phenyl-2,3-dihydrofuran-3-carboxylate (14) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (114.9 mg, 0.2 mmol, 1.0 equiv), Cs_2CO_3 (211.7 mg, 0.6 mmol, 3.0 equiv), $PhBF_3K$ (44.2 mg, 0.24 mmol, 1.2 equiv), and $Pd(dppp)Cl_2$ (11.8 mg, 0.02 mmol, 10 mol%). Then the Schlenk tube was evacuated and filled with argon for three times. After that, THF (2.0 mL) and H_2O (0.6 mL) were added under argon atmosphere via a syringe. After stirred at 110 ℃ overnight, the reaction was quenched with brine and extracted with EA (3 × 4 mL). The combined organic phase was washed with brine, dried over $MgSO_4$, evaporated to give the crude products. The residue was purified by flash chromatography (PE/EA) to afford **14** as a yellow solid (77.7 mg, 74% yield, *Z/E* > 20:1). **m.p.** 163 – 165 ℃, R_f = 0.3 (PE/EA = 20/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.76 – 7.73 (m, 2H), 7.38 – 7.16 (m, 10H), 5.58 (s, 1H), 5.33 (s, 1H), 4.29 – 4.11 (m, 2H), 1.62 (s, 3H), 1.30 (s, 18H), 1.23 (t, *J* = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 172.5, 158.3, 154.7, 150.6, 135.7, 133.5, 130.6, 128.9, 128.4, 128.3, 127.8, 126.0, 124.5, 120.6, 114.3, 100.5, 61.8, 61.5, 34.4, 30.1, 23.8, 14.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{35}H_{40}O_4 + H]^+$ 525.3000, found 525.2998.



4-(1-phenylnaphtho[2,1-b]furan-2-yl)phenol (15) To an oven dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added $AlCl_3$ (160.0 mg, 1.2 mmol, 6.0 equiv). Then the Schlenk tube was evacuated and filled with argon for three times. After that, **9ka** (89.7 mg, 0.2 mmol, 1.0 equiv) dissolved in toluene (4.0 mL) was added. The reaction was stirred for 2 h under at room temperature. After complete consumption of **9ka**, ice-water was added to quench the reaction. The reaction mixture was extracted with EA (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE/EA) to afford product **15** as yellow oil (51.8 mg, 77% yield), R_f = 0.3 (PE/EA = 5/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.65 (*app.* s, 2H), 7.54 – 7.48 (m, 6H), 7.41 – 7.30 (m, 3H), 7.24 – 7.19 (m, 1H),

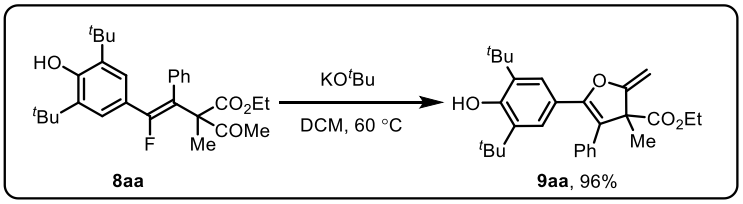
6.65 (d, J = 8.7 Hz, 2H), 5.52 (s, 1H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 155.3, 151.2, 150.3, 134.9, 131.0, 130.8, 129.5, 129.1, 128.4, 128.2, 128.0, 126.0, 125.6, 124.3, 124.0, 123.8, 123.2, 118.1, 115.6, 112.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{24}H_{16}O_2 + H]^+$ 337.1223, found 337.1225.



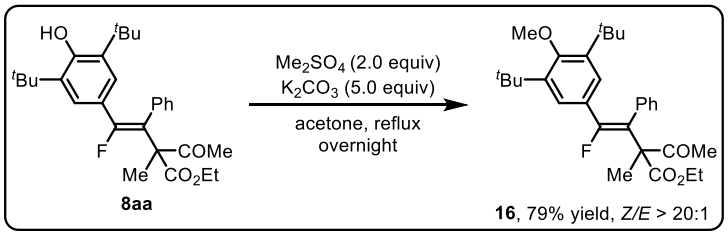
2-(4-methoxyphenyl)-1-phenylnaphtho[2,1-b]furan (SI-1) To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **15** (67.3 mg, 0.2 mmol, 1.0 equiv) and K_2CO_3 (138.2 mg, 1.0 mmol, 5.0 equiv). Then the Schlenk tube was evacuated and filled with argon for three times. After that, MeI (56.8 mg, 0.4 mmol, 2.0 equiv) dissolved in acetone (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred at 70 ℃ overnight. When the starting material was completely consumed, water was slowly added to quench the reaction. The reaction mixture was extracted with EA (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford **SI-1** as a white solid (60.1 mg, 86% yield). **m.p.** 110 – 111 ℃, R_f = 0.4 (PE/EA = 5/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.88 (d, J = 8.1 Hz, 1H), 7.68 (s, 2H), 7.56 – 7.44 (m, 8H), 7.38 – 7.32 (m, 1H), 7.25 – 7.18 (m, 1H), 6.80 – 6.75 (m, 2H), 3.73 (s, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 159.4, 151.2, 150.4, 135.0, 131.0, 130.9, 130.8, 129.6, 129.5, 129.5, 129.0, 128.3, 128.2, 127.8, 127.7, 125.9, 125.5, 124.3, 123.8, 123.7, 123.2, 118.1, 114.0, 112.2, 55.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{25}H_{18}O_2 + H]^+$ 351.1380, found 351.1379. Product **SI-1** is a known compound. The regioselectivity in forming **9ka** was unambiguously established by NMR spectral congruence with reported data.[2]

[2] V. K. Rao, G. M. Shelke, R. Tiwari, K. Parang and A. Kumar, *Org. Lett.* **2013**, *15*, 2190.

11. Control Experiments



To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (89.8 mg, 0.8 mmol, 4.0 equiv) and **8aa** (99.7 mg, 0.2 mmol, 1.0 equiv) then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous DCM (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred for 15 min at 60 ℃. After the starting material was completely consumed, ice water (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford the corresponding product **9aa** as a white solid (86.0 mg, 96% yield).



To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **8aa** (93.7 mg, 0.2 mmol, 1.0 equiv) and K_2CO_3 (138.2 mg, 1.0 mmol, 5.0 equiv). Then the Schlenk tube was evacuated and filled with argon for three times. After that, Me_2SO_4 (50.5 mg, 0.4 mmol, 2.0 equiv) dissolved in acetone (2 mL) was added under argon atmosphere via a syringe under argon atmosphere stirred at 70 ℃ overnight. When the starting material was completely consumed, water was slowly added to quench the reaction. The reaction mixture was extracted with EA (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$. After removal of the solvent in vacuo, the residue was purified by flash chromatography on silica gel (PE/EA) to afford **16** as a white solid (76.2 mg, 79% yield, *Z/E* > 20:1). **m.p.** 131 – 133 ℃, R_f = 0.6 (PE/EA = 10/1). **^{1}H NMR (300 MHz, $CDCl_3$)** δ 7.37 – 7.24 (m, 3H), 7.19 – 7.16 (m, 2H), 7.01 (s, 2H), 4.10 – 3.98 (m, 2H), 3.60 (s, 3H), 2.48 (d, J = 1.9 Hz, 3H), 1.48 (s, 3H), 1.20 (s, 19H), 1.14 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR (75 MHz, $CDCl_3$)** δ 204.7 (d, ^4J = 2.3 Hz), 171.4, 160.1, 156.1 (d, ^1J = 250.1 Hz), 143.2, 136.1 (d, ^3J = 8.6 Hz), 130.4 (d, ^4J = 3.0 Hz), 128.9, 128.0, 126.6 (d, ^3J = 7.5 Hz), 125.7 (d, ^2J = 28.0 Hz), 119.2 (d, ^2J = 19.4 Hz), 64.2, 64.0, 61.6, 35.7, 31.8, 27.3 (d, ^4J = 4.6 Hz), 20.9 (d, ^4J = 1.6 Hz), 13.9 ppm. **^{19}F NMR (282 MHz, $CDCl_3$)** δ -96.3 ppm. **HRMS (ESI)** *m/z* Calcd for $[C_{30}H_{39}FO_4 + Na]^+$ 505.2725, found 505.2727.

12. Calculation Studies

To validate bond order quantification, semi-empirical quantum mechanical (QM) calculations were performed using the PM7 Hamiltonian as implemented in MOPAC v22.1.1 (Digital Object Identifier (DOI): 10.5281/zenodo.6511958). Initial molecular geometries were defined through Cartesian coordinates, with explicit generation of Mayer bond order matrices enabled by the BONDS keyword. All geometry optimizations were conducted under gas-phase conditions to simulate isolated molecular environments.

The computational results are presented as follows.

Intermediate I (INT-I)

C	-0.00000038	0.01144502	0.00234211
C	2.09269800	1.21919308	-0.00000046
C	1.39504438	2.42769771	-0.00354261
C	0.00021938	2.42761922	-0.00402101
C	-0.69738200	1.21941765	-0.00068200
H	-0.54975692	-0.94087567	0.00044960
H	3.19237342	1.21927944	0.00482213
O	-0.71509425	3.66584907	-0.00766095
C	-2.23738196	1.21967394	-0.00093409
C	-2.71308564	1.94172337	1.24194665
C	-2.71281788	1.93482693	-1.24784514
C	-2.71316312	-0.21766301	0.00296366
H	-2.33913584	1.42529621	2.15841942
H	-2.33838435	2.99339448	1.24774255
H	-3.82888196	1.96398262	1.27935692
H	-2.33823551	1.41374577	-2.16142981
H	-3.82862522	1.95635430	-1.28582080
H	-2.33862626	2.98664312	-1.25922127
H	-3.82899581	-0.26104966	0.00346840
H	-2.33912787	-0.75323909	-0.90241572
H	-2.33860715	-0.74847827	0.91093958
C	2.16554888	3.76108276	-0.00621100
C	1.78218598	4.52943596	-1.25323472
C	1.78066425	4.53545807	1.23655888
C	3.64804661	3.45364488	-0.00452897
H	2.04483861	3.94366483	-2.16665881
H	0.68419383	4.73133546	-1.26306274
H	2.32145066	5.50643129	-1.29286009
H	2.04162095	3.95394379	2.15319252
H	2.32034527	5.51239051	1.27232182
H	0.68275082	4.73793835	1.24390106
H	4.24405320	4.39796238	-0.00695329

H	3.92185032	2.86531815	0.90396380
H	3.92282722	2.86018141	-0.90939029
C	1.39515962	0.01144458	0.00234166
C	2.04664035	-1.11490464	-0.74616120
C	2.04411989	-1.11357837	0.75493997
H	1.41112866	-1.84072875	-1.28314242
F	1.26471187	-1.99969824	1.41054253
F	3.19997999	-0.88184161	1.41280433
C	3.36779261	-0.85214179	-1.49256083
C	3.34534058	-0.38612883	-2.80739894
C	4.58683438	-1.07991601	-0.85412194
C	4.54170803	-0.14861393	-3.48379625
H	2.38410696	-0.20738771	-3.31071129
C	5.78365748	-0.84143958	-1.53025310
H	4.60471337	-1.44703666	0.18223311
C	5.76128801	-0.37598971	-2.84493673
H	4.52409000	0.21810517	-4.52037872
H	6.74466839	-1.02072786	-1.02647937
H	6.70445212	-0.18859034	-3.37843392

Atomic orbital electron populations

Atom		s	px	py	pz
1	C	1.08707	0.96466	1.08074	1.00091
2	C	1.08926	1.09612	0.95474	0.98780
3	C	1.10260	1.00651	1.01235	1.00362
4	C	1.11508	0.88846	0.85767	0.67963
5	C	1.10414	1.02353	0.99565	0.99395
6	H	0.83158			
7	H	0.82287			
8	O	1.87871	1.72964	1.44210	1.39942
9	C	1.04659	0.90773	0.94832	0.96041
10	C	1.05918	1.15276	1.16978	1.08133
11	C	1.05962	1.16652	1.16255	1.07665
12	C	1.06070	1.16325	1.07476	1.16955
13	H	0.85437			
14	H	0.82835			
15	H	0.85560			
16	H	0.85728			
17	H	0.85486			
18	H	0.83095			
19	H	0.85134			
20	H	0.85607			
21	H	0.85324			
22	C	1.04624	0.93256	0.92071	0.95805

23	C	1.05931	1.18351	1.14378	1.07665
24	C	1.05913	1.19082	1.13089	1.08159
25	C	1.06070	1.05379	1.18125	1.17265
26	H	0.85797			
27	H	0.83354			
28	H	0.85520			
29	H	0.85400			
30	H	0.85646			
31	H	0.83012			
32	H	0.85045			
33	H	0.85225			
34	H	0.85520			
35	C	1.04935	0.99300	0.95344	1.08859
36	C	1.06769	1.07998	1.07754	0.99898
37	C	1.09675	0.80899	0.90580	0.85537
38	H	0.80461			
39	F	1.96710	1.78153	1.65448	1.75621
40	F	1.96685	1.47258	1.95075	1.76152
41	C	1.05723	0.95407	1.00333	0.98701
42	C	1.08491	1.06116	1.01514	0.99000
43	C	1.08449	0.98300	1.03620	1.04892
44	C	1.08358	0.98641	1.03225	1.04186
45	H	0.83705			
46	C	1.08364	1.05291	1.01249	0.99173
47	H	0.83993			
48	C	1.08420	1.04809	0.99484	1.01933
49	H	0.84830			
50	H	0.84878			
51	H	0.85065			

(Valencies) bond orders

1 C (3.968) 5 C 1.883 35 C 1.025 6 H 0.953 8 O 0.037 4 C 0.013 10 C 0.013
11 C 0.012

2 C (3.965) 3 C 1.881 35 C 1.025 7 H 0.950 8 O 0.038 4 C 0.014 24 C 0.013
23 C 0.012

3 C (3.984) 2 C 1.881 22 C 0.985 4 C 0.976 8 O 0.048 36 C 0.019 5 C 0.019
37 C 0.017

4 C (3.836) 8 O 1.819 3 C 0.976 5 C 0.972 2 C 0.014 1 C 0.013

5 C (3.985) 1 C 1.883 9 C 0.986 4 C 0.972 8 O 0.048 36 C 0.019 3 C 0.019 37 C 0.017

6 H (0.972) 1 C 0.953

7 H (0.969) 2 C 0.950

8 O (2.015) 4 C 1.819 5 C 0.048 3 C 0.048 2 C 0.038 1 C 0.037

9 C (3.984) 12 C 0.994 10 C 0.990 11 C 0.990 5 C 0.986

10 C (3.924) 9 C 0.990 13 H 0.971 15 H 0.970 14 H 0.960 1 C 0.013

11 C (3.925) 9 C 0.990 16 H 0.972 17 H 0.970 18 H 0.961 1 C 0.012

12 C (3.930) 9 C 0.994 20 H 0.971 21 H 0.970 19 H 0.968

13 H (0.979) 10 C 0.971

14 H (0.971) 10 C 0.960

15 H (0.979) 10 C 0.970

16 H (0.980) 11 C 0.972

17 H (0.979) 11 C 0.970

18 H (0.971) 11 C 0.961

19 H (0.978) 12 C 0.968

20 H (0.979) 12 C 0.971

21 H (0.978) 12 C 0.970

22 C (3.983) 25 C 0.995 23 C 0.990 24 C 0.990 3 C 0.985

23 C (3.926) 22 C 0.990 26 H 0.972 28 H 0.970 27 H 0.962 2 C 0.012

24 C (3.925) 22 C 0.990 29 H 0.971 30 H 0.970 31 H 0.961 2 C 0.013

25 C (3.929) 22 C 0.995 34 H 0.970 33 H 0.969 32 H 0.968

26 H (0.980) 23 C 0.972

27 H (0.972) 23 C 0.962

28 H (0.979) 23 C 0.970

29 H (0.979) 24 C 0.971

30 H (0.979) 24 C 0.970

31 H (0.971) 24 C 0.961

32 H (0.978) 25 C 0.968

33 H (0.978) 25 C 0.969

34 H (0.979) 25 C 0.970

35 C (3.977) 1 C 1.025 2 C 1.025 37 C 0.924 36 C 0.913 39 F 0.022 40 F 0.021

36 C (3.949) 41 C 1.005 37 C 0.973 38 H 0.940 35 C 0.913 39 F 0.022 40 F 0.022
5 C 0.019 3 C 0.019

37 C (3.884) 36 C 0.973 40 F 0.966 39 F 0.959 35 C 0.924 3 C 0.017 5 C 0.017

38 H (0.962) 36 C 0.940

39 F (1.054) 37 C 0.959 40 F 0.039 36 C 0.022 35 C 0.022

40 F (1.059) 37 C 0.966 39 F 0.039 36 C 0.022 35 C 0.021

41 C (3.992) 43 C 1.430 42 C 1.415 36 C 1.005 48 C 0.114

42 C (3.973) 44 C 1.452 41 C 1.415 45 H 0.960 46 C 0.112

43 C (3.974) 46 C 1.439 41 C 1.430 47 H 0.961 44 C 0.111

44 C (3.976) 42 C 1.452 48 C 1.434 49 H 0.964 43 C 0.111

45 H (0.973) 42 C 0.960

46 C (3.976) 48 C 1.446 43 C 1.439 50 H 0.964 42 C 0.112

47 H (0.974) 43 C 0.961

48 C (3.977) 46 C 1.446 44 C 1.434 51 H 0.965 41 C 0.114

49 H (0.977) 44 C 0.964

50 H (0.977) 46 C 0.964

51 H (0.978) 48 C 0.965

13. Crystal Structure of Product 10

Vapor diffusion crystallization method was used for crystal growth of **10**. The compound **10** was dissolved in diethyl ether to make saturated solution in small vial and placed in closed bottle with another solvent as *n*-hexane.

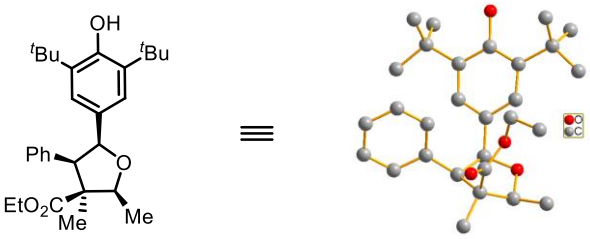
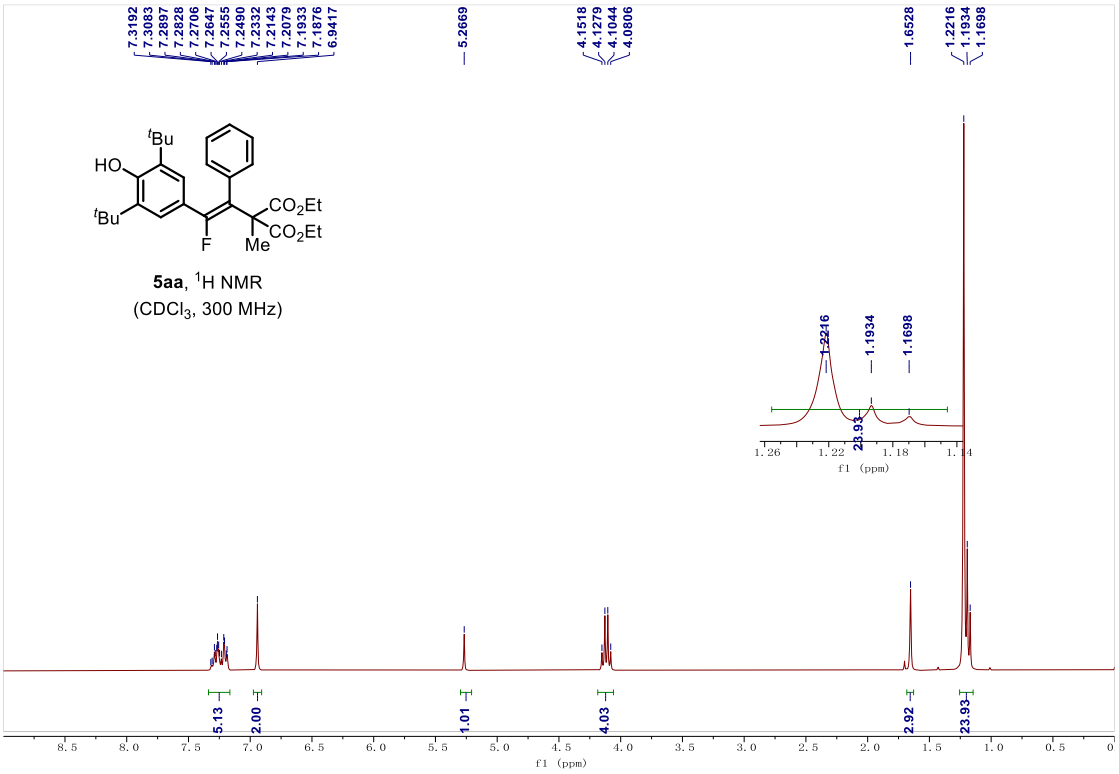


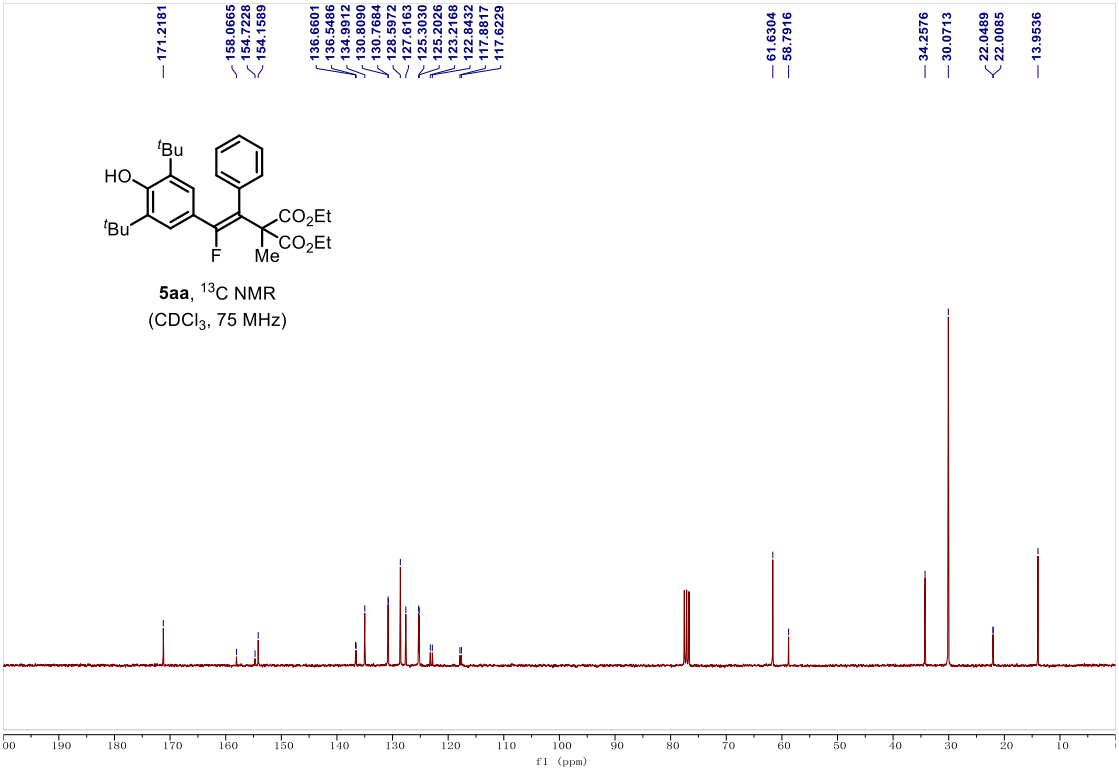
Figure S1. ORTEP plot of the crystal structure of compound **10** and thermal ellipsoid is set at 50% probability

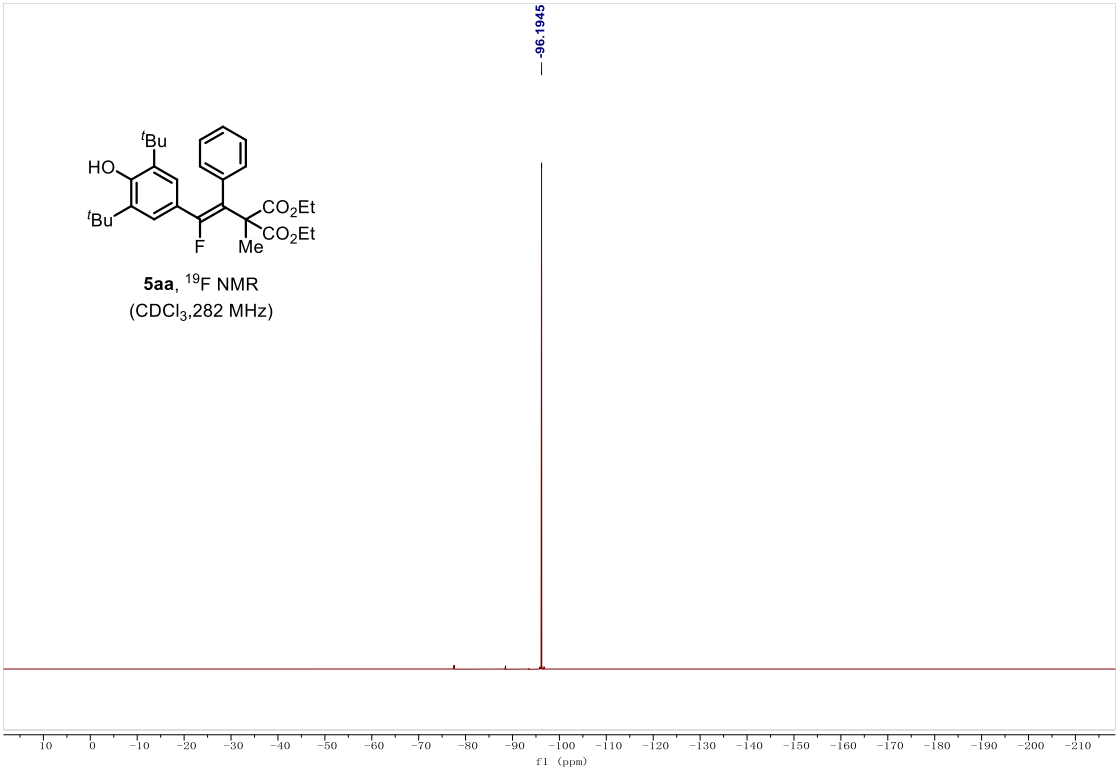
Table S3 X-ray Crystallographic Data of **10**

CCDC number	2356255
Bond precision	C-C = 0.0050 A Wavelength = 0.71073
Cell	a=10.6394 (6) b=10.7112 (6) c=23.9695 (13) alpha=90.188 (2) beta=102.380 (2) gamma=104.147 (2)
Temperature	170 K
Volume	2582.7 (3)
Space group	P -1
Hall group	-P 1
Sum formula	$C_{29}H_{40}O_4$
Mr	452.61
Dx, g cm-3	1.164
Z	4
Mu (mm-1)	0.076
F000	984.0
F000’	984.44
h, k, lmax	0, 0, 0
Nref	10326
Tmin, Tmax	0.524, 0.856
Tmin’	0.989
Correction method	# Reported T Limits: Tmin=0.524, Tmax=0.856
AbsCorr	MULTI-SCAN
Data completeness	0.971
Theta(max)	26.423
R(reflections)	0.0866 (6371)
wR2(reflections)	wR2 (reflections) =0.2458 (10326)
S	1.049
Npar	615
Ellipsoid contour % probability levels	50

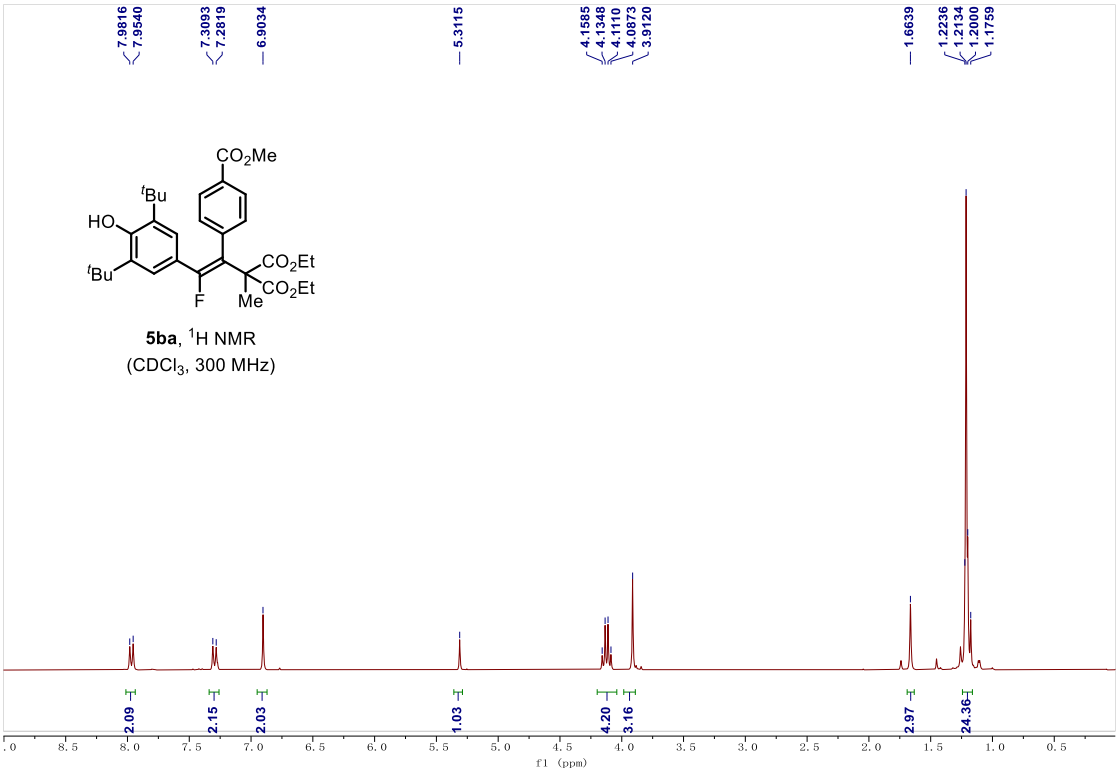
14. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Title Compounds



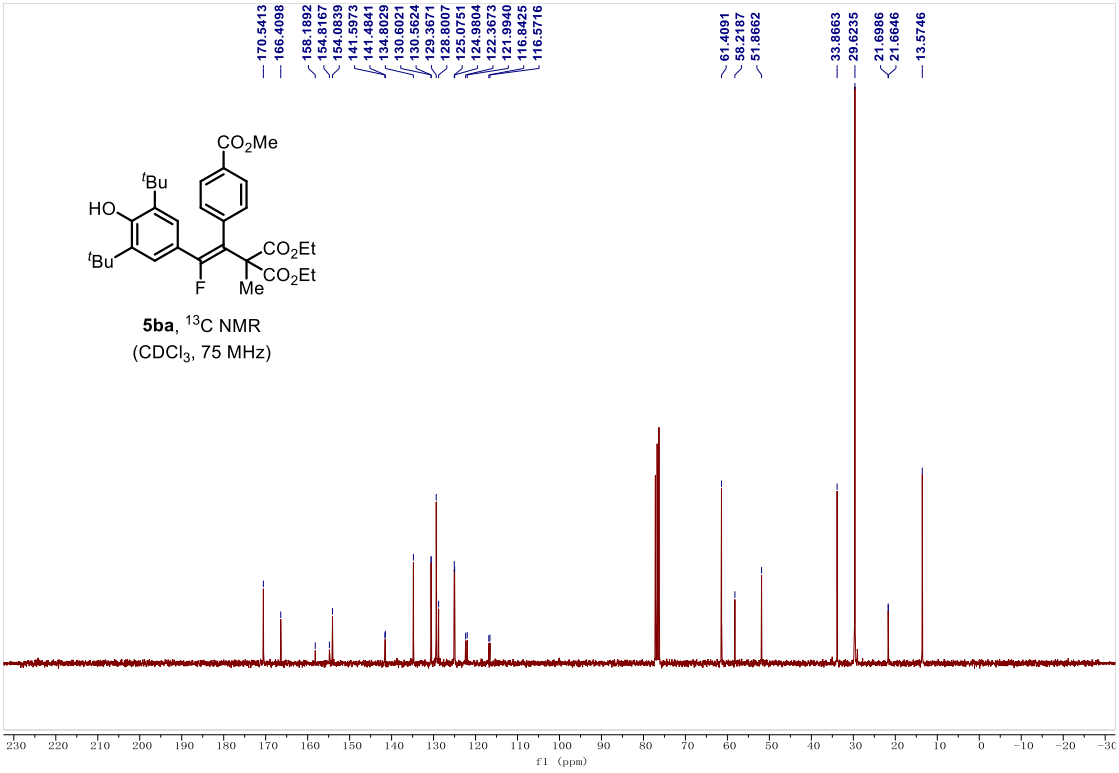




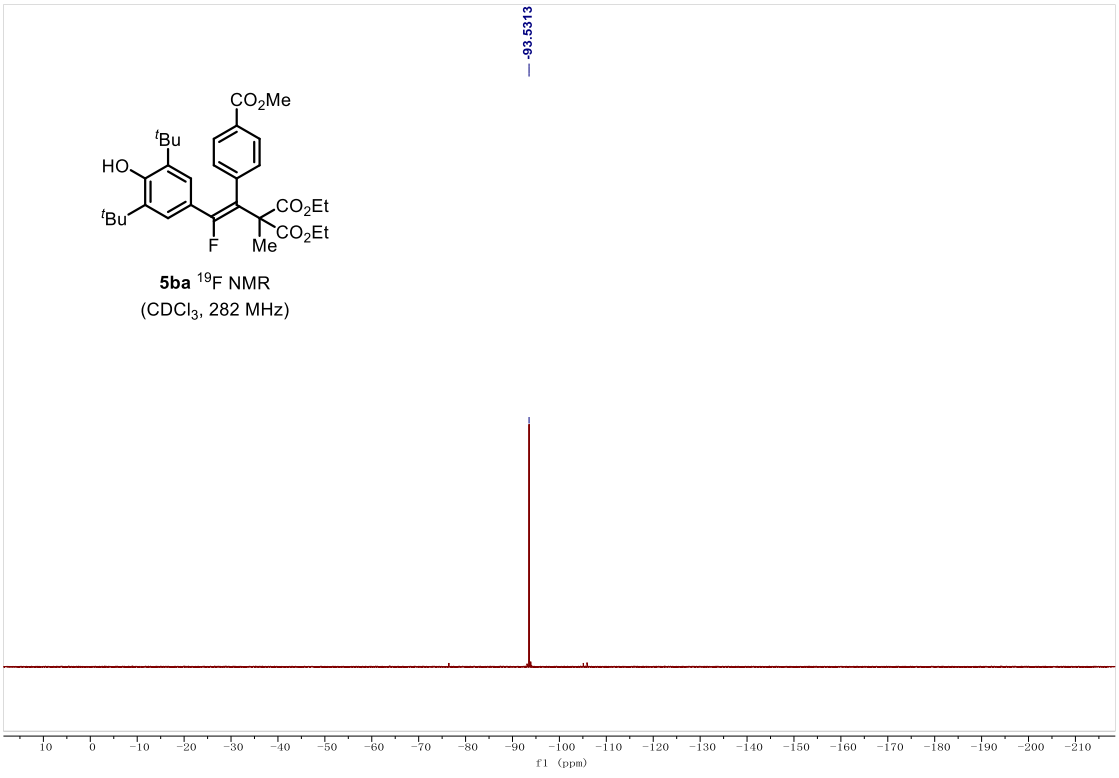
5aa, ^{19}F NMR
($CDCl_3$,282 MHz)



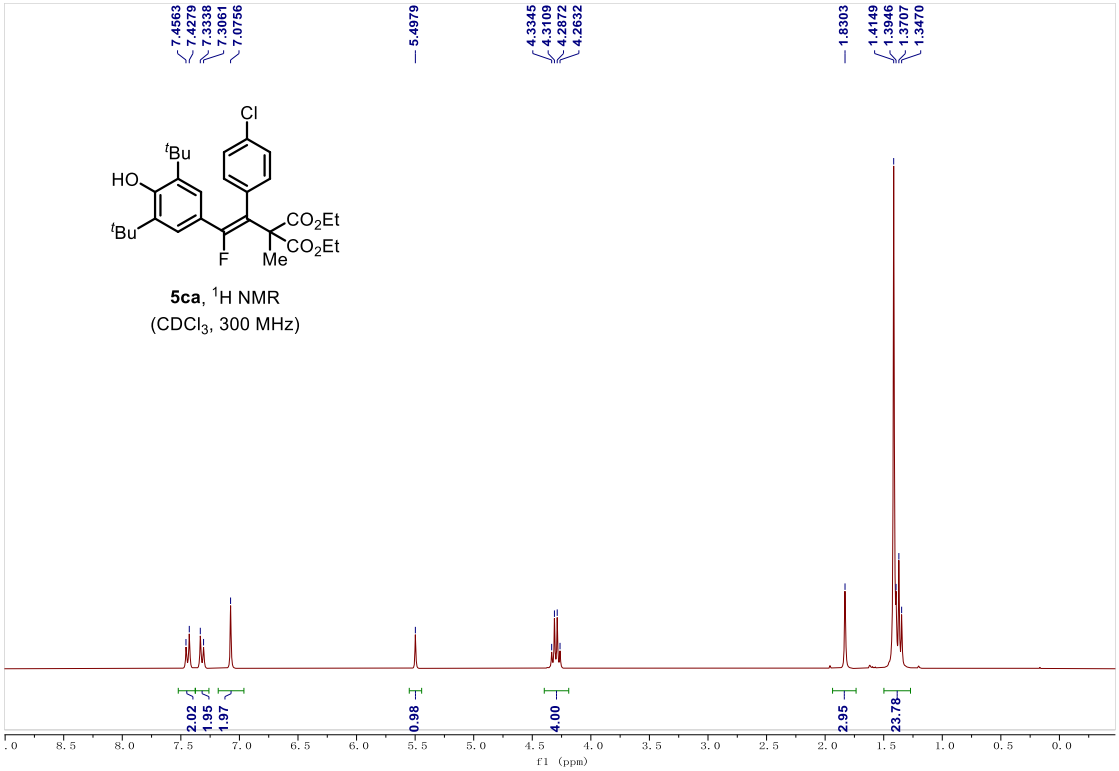
5ba, ^{1}H NMR
($CDCl_3$, 300 MHz)



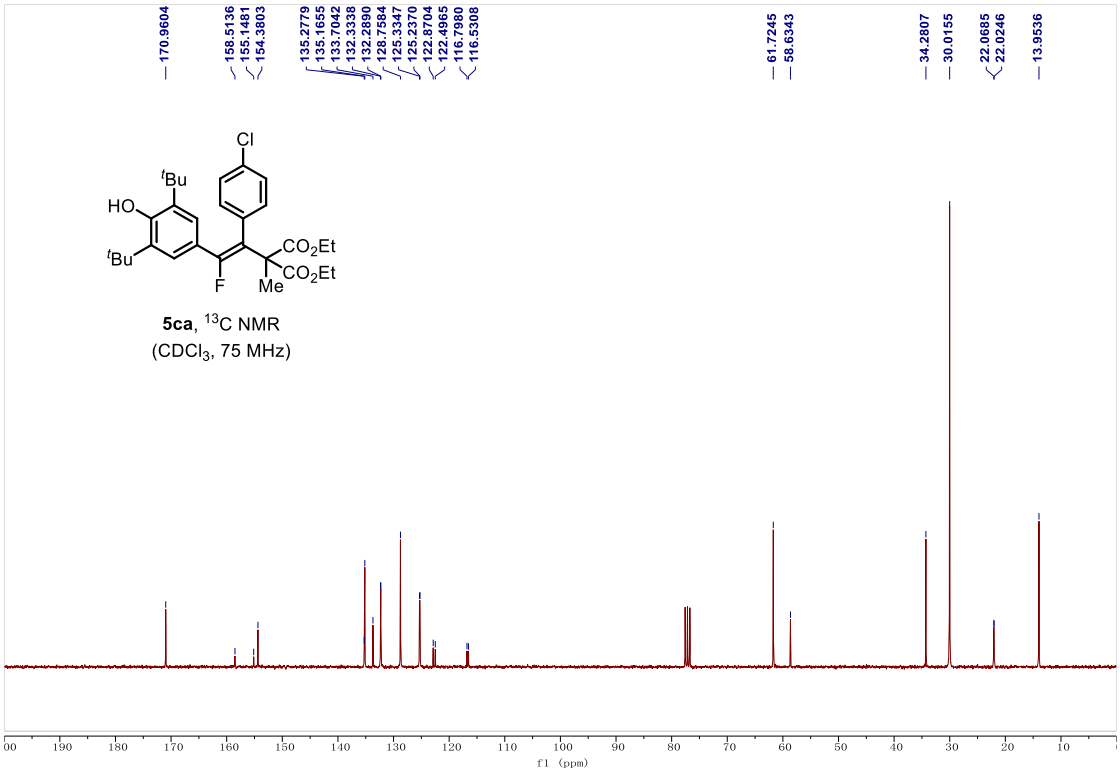
5ba, ^{13}C NMR
($CDCl_3$, 75 MHz)



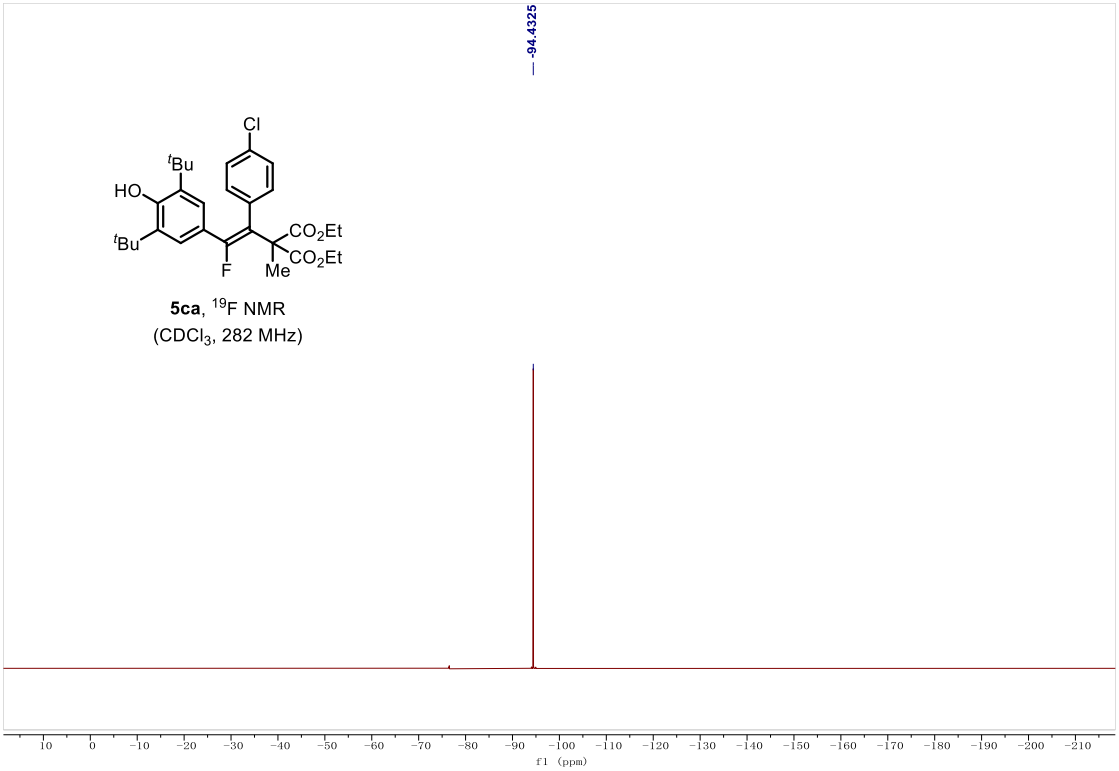
5ba ^{19}F NMR
($CDCl_3$, 282 MHz)



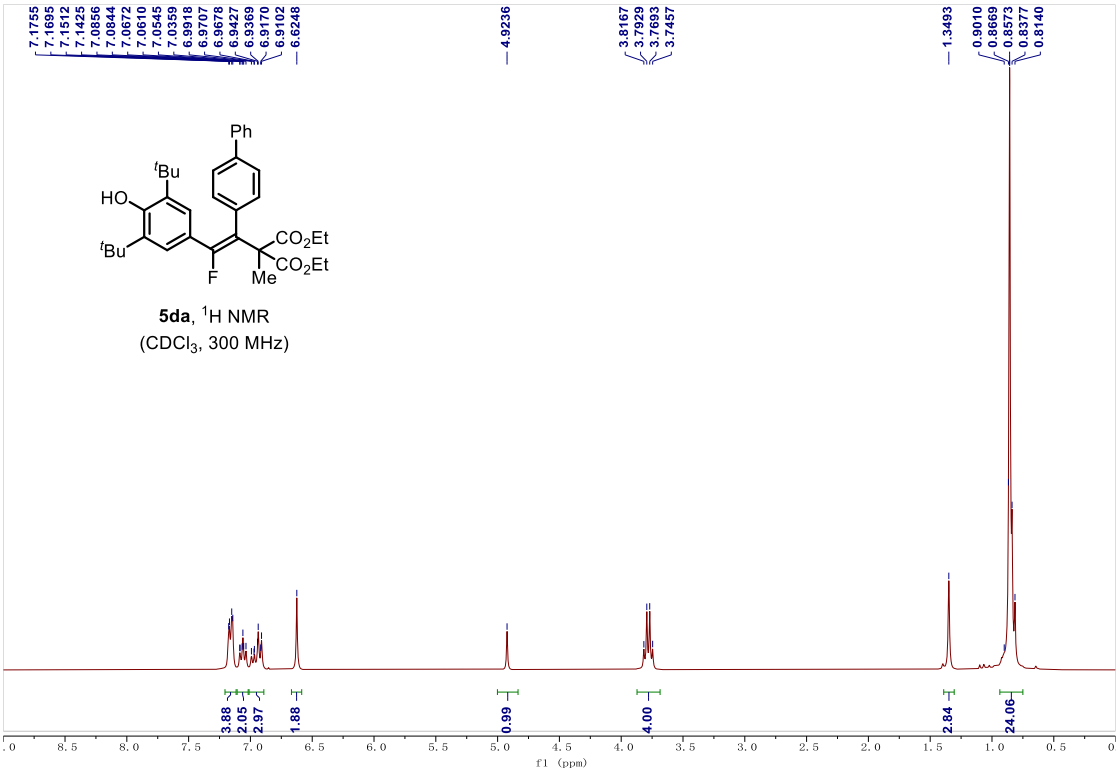
5ca, ^{1}H NMR
($CDCl_3$, 300 MHz)



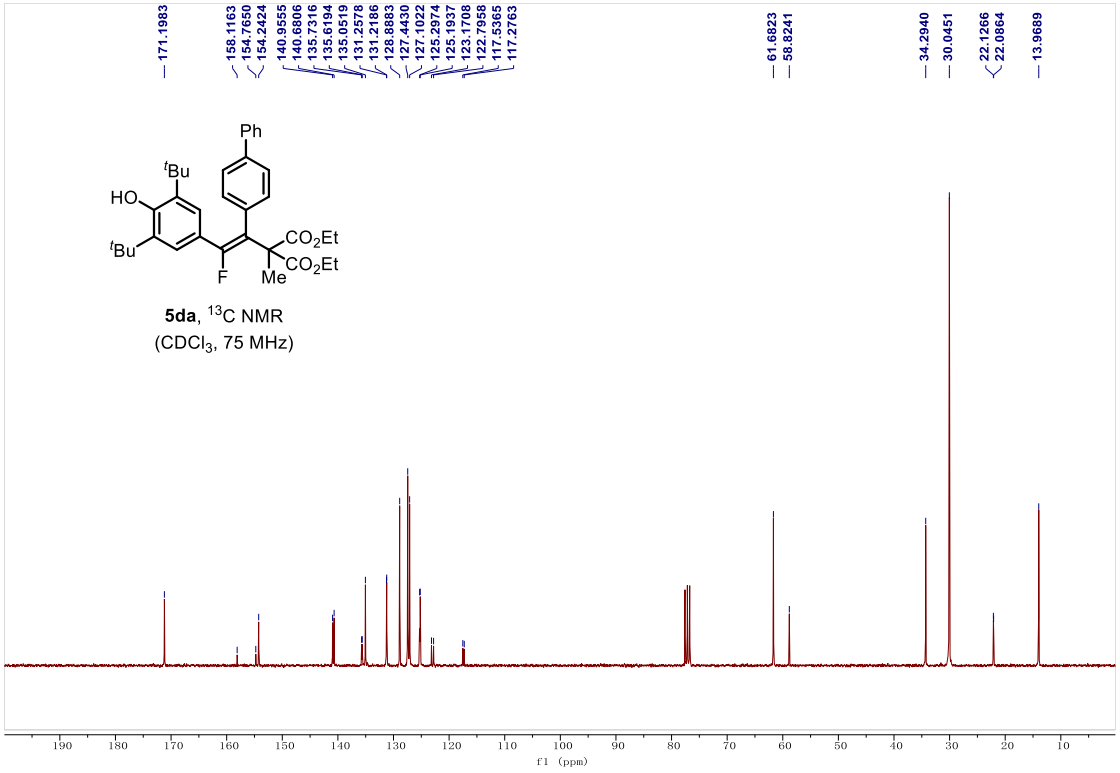
5ca, ^{13}C NMR
($CDCl_3$, 75 MHz)



5ca, ^{19}F NMR
($CDCl_3$, 282 MHz)



5da, ^{1}H NMR
($CDCl_3$, 300 MHz)


171.1983
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154.7650
154.2424
140.9555
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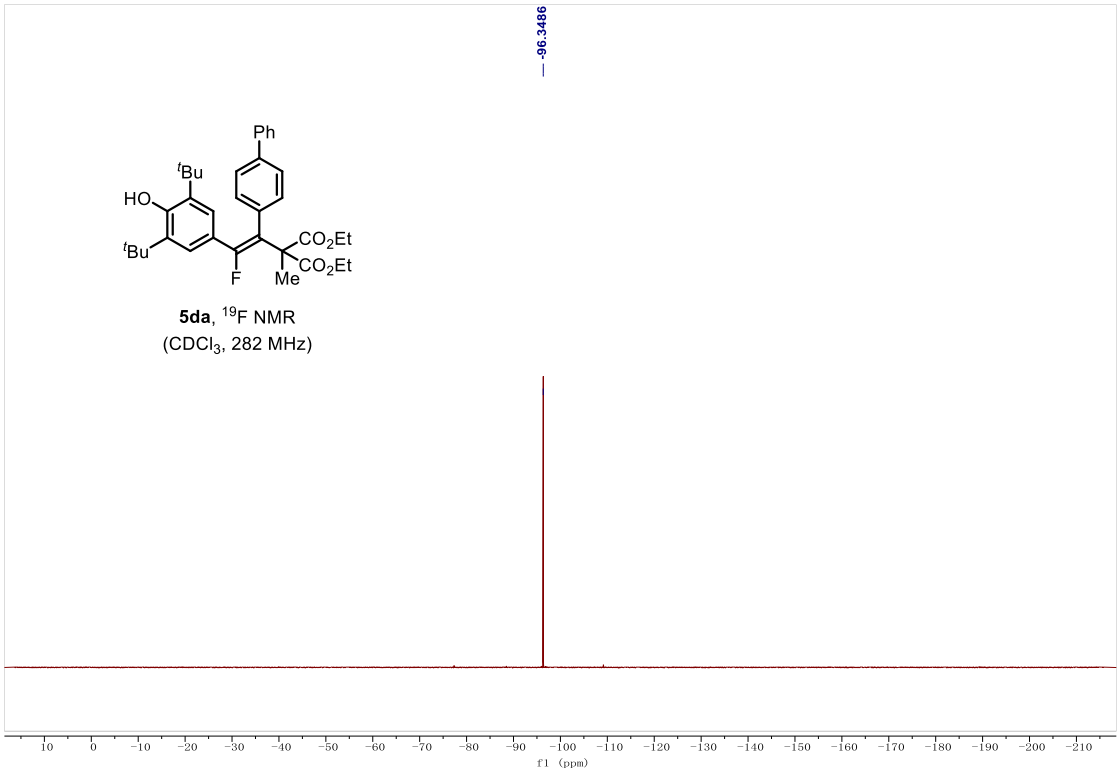
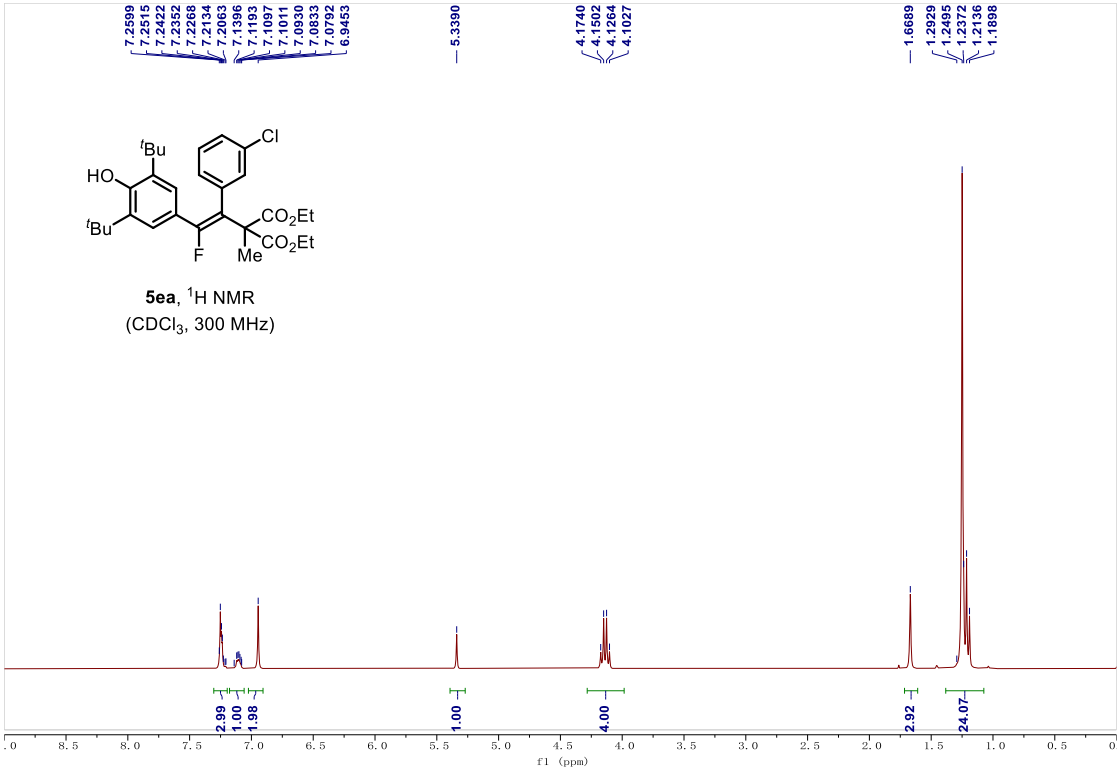
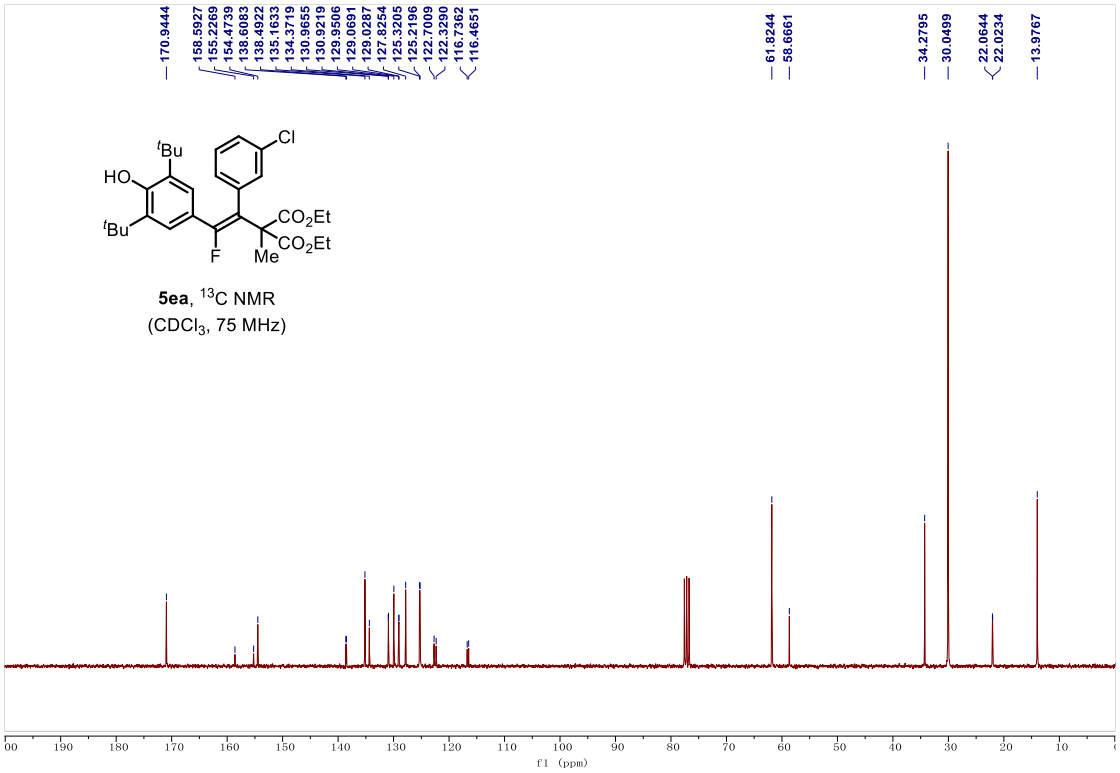
131.2578
131.2186
128.8883
127.4430
127.1022
125.2974
125.1937
123.1708
122.7958
117.5365
117.2763
61.6823
58.8241
34.2940
30.0451
22.1266
22.0864
13.9689
Ph
tBu
HO
tBu
CO2Et
CO2Et
F
Me
5da, 13C NMR
(CDCl3, 75 MHz)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

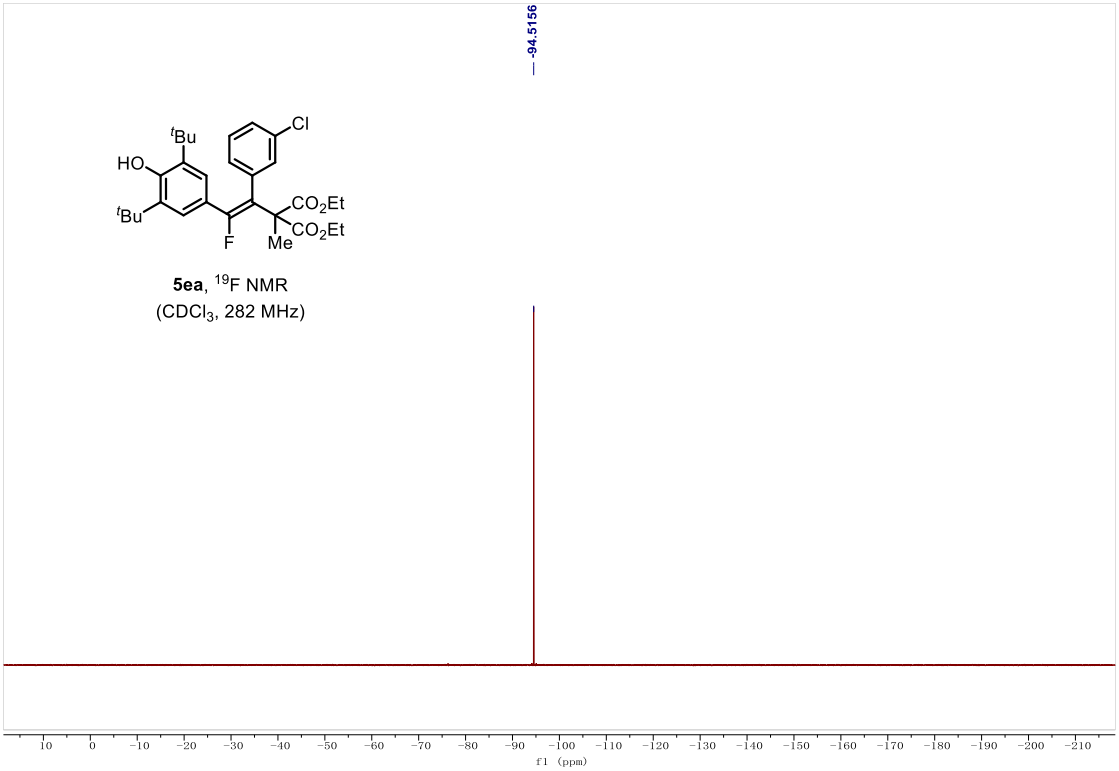

-96.3486
Ph
tBu
HO
tBu
CO2Et
CO2Et
F
Me
5da, 19F NMR
(CDCl3, 282 MHz)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)



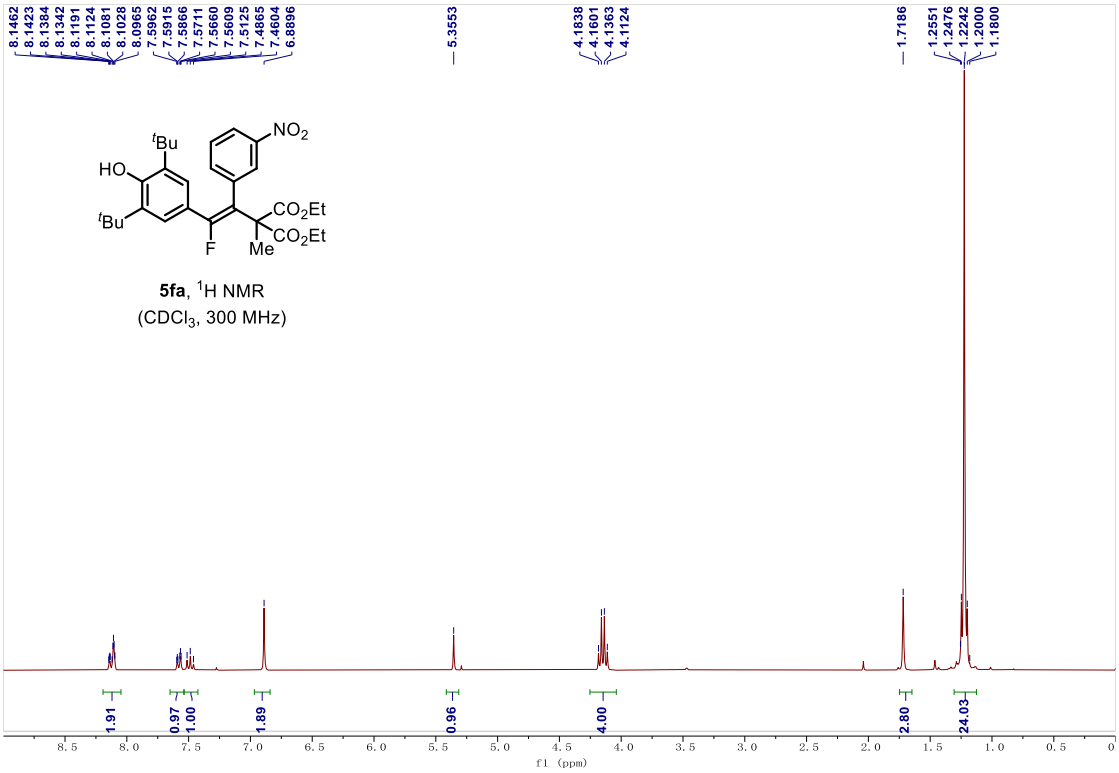
5ea, ^{1}H NMR
($CDCl_3$, 300 MHz)



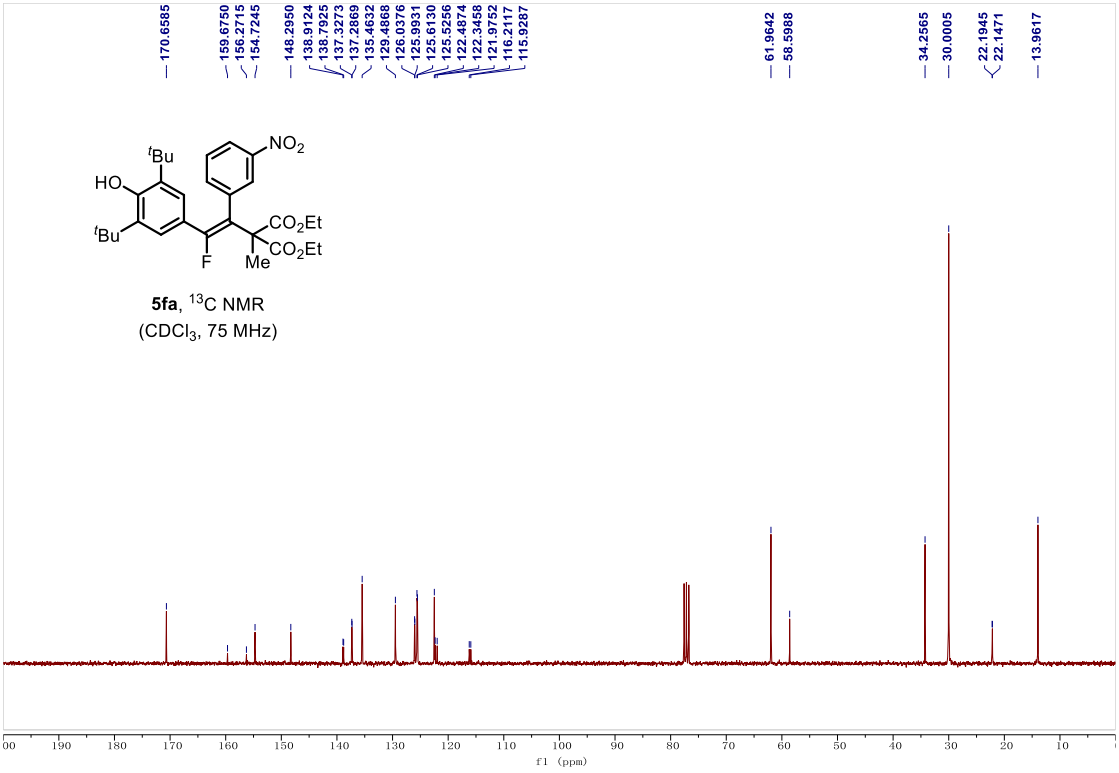
5ea, ^{13}C NMR
($CDCl_3$, 75 MHz)



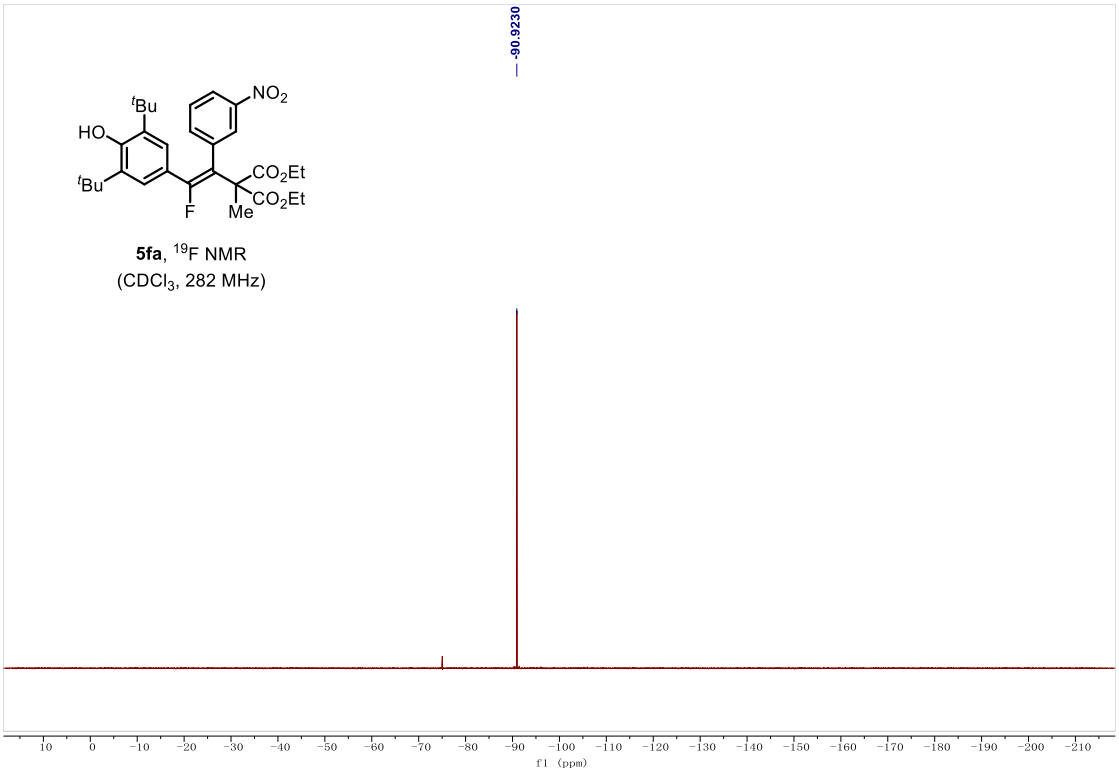
5ea, ^{19}F NMR
($CDCl_3$, 282 MHz)



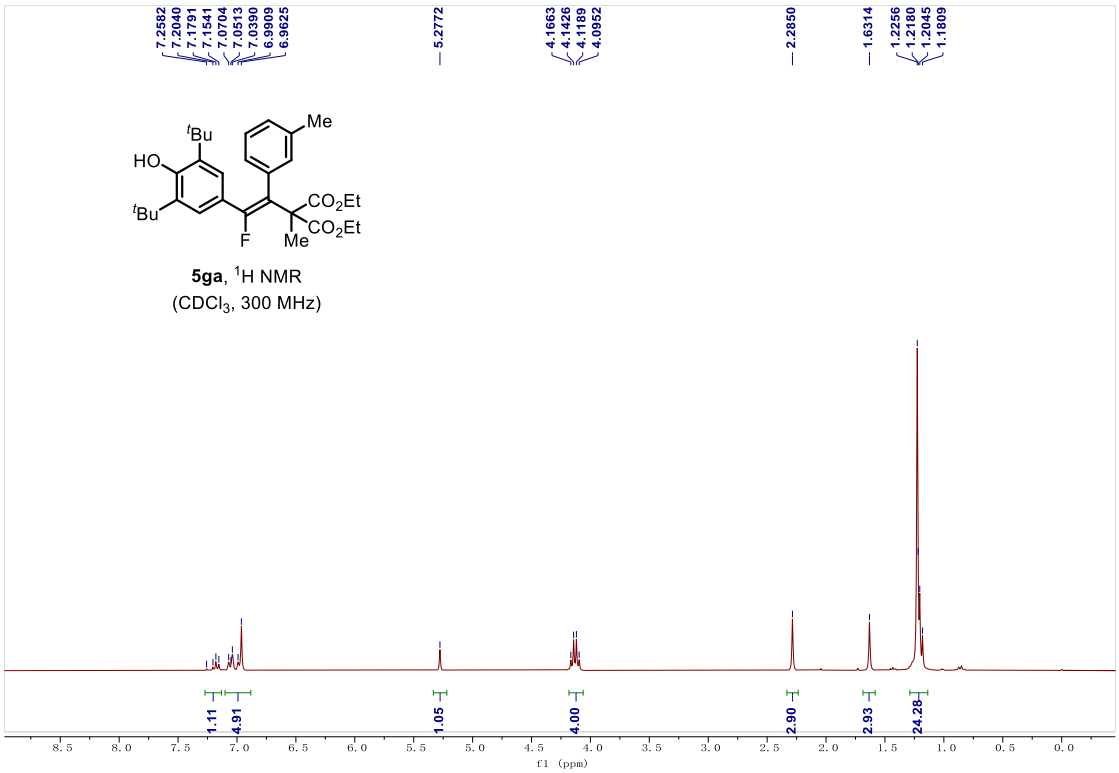
5fa, ^{1}H NMR
($CDCl_3$, 300 MHz)



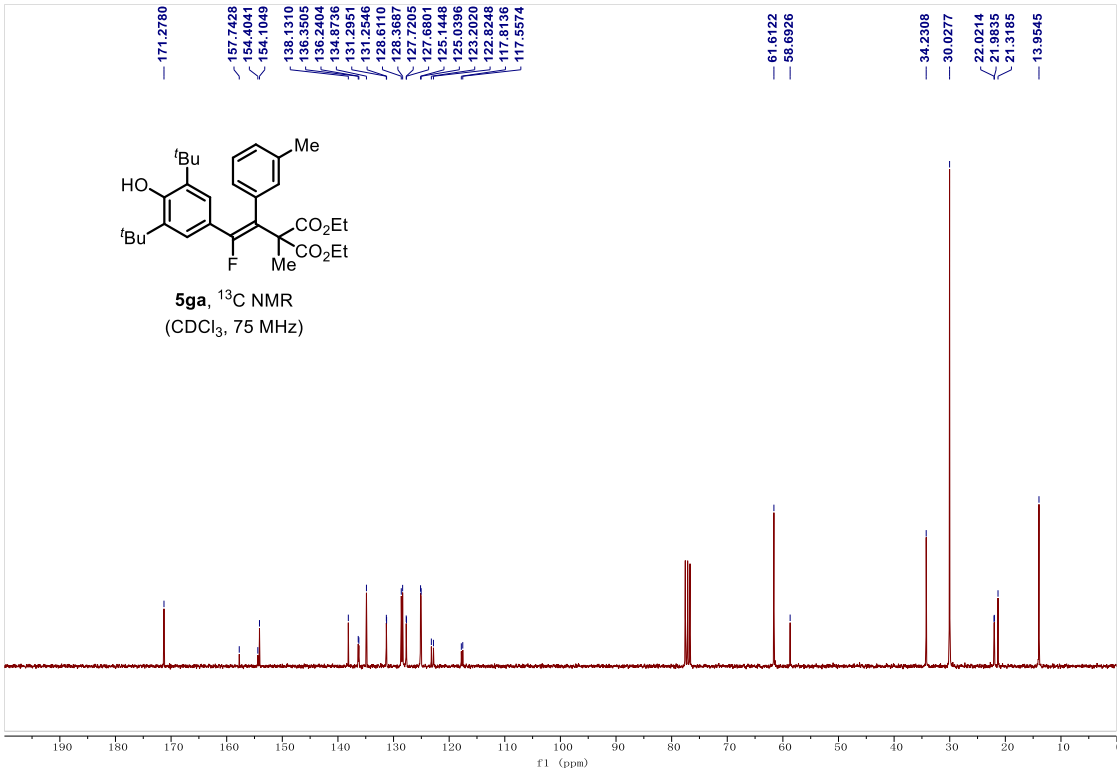
5fa, ^{13}C NMR
($CDCl_3$, 75 MHz)



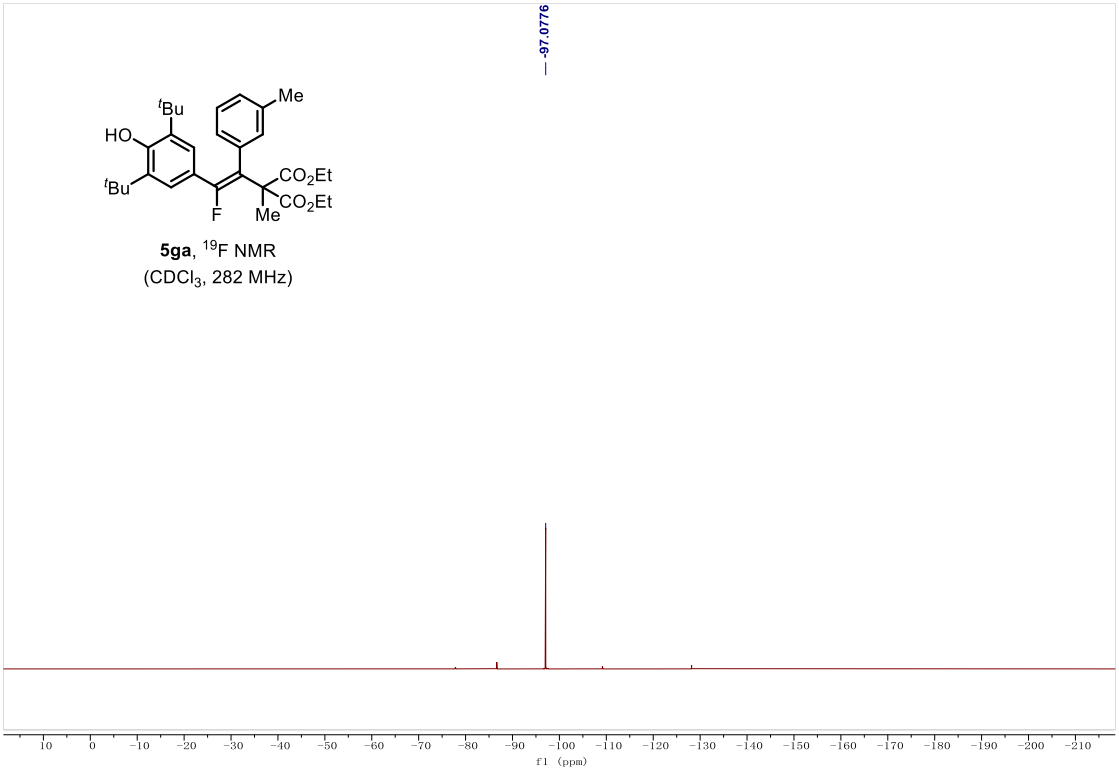
5fa, ^{19}F NMR
($CDCl_3$, 282 MHz)



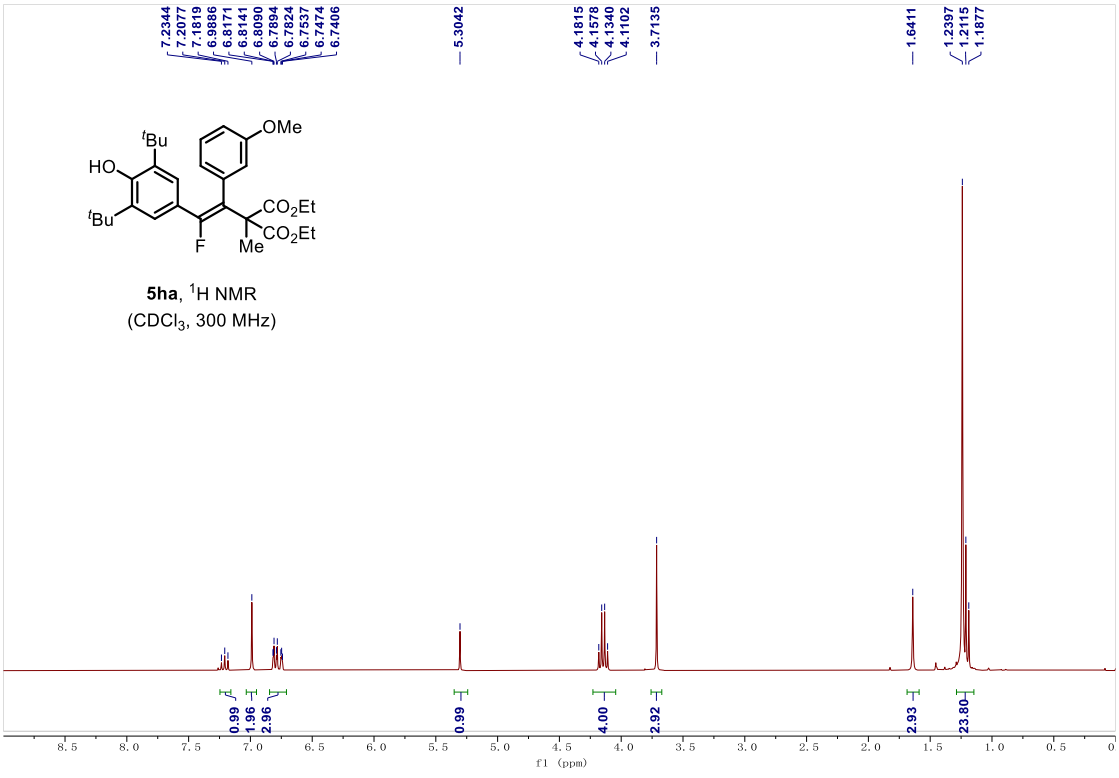
5ga, ^{1}H NMR
($CDCl_3$, 300 MHz)



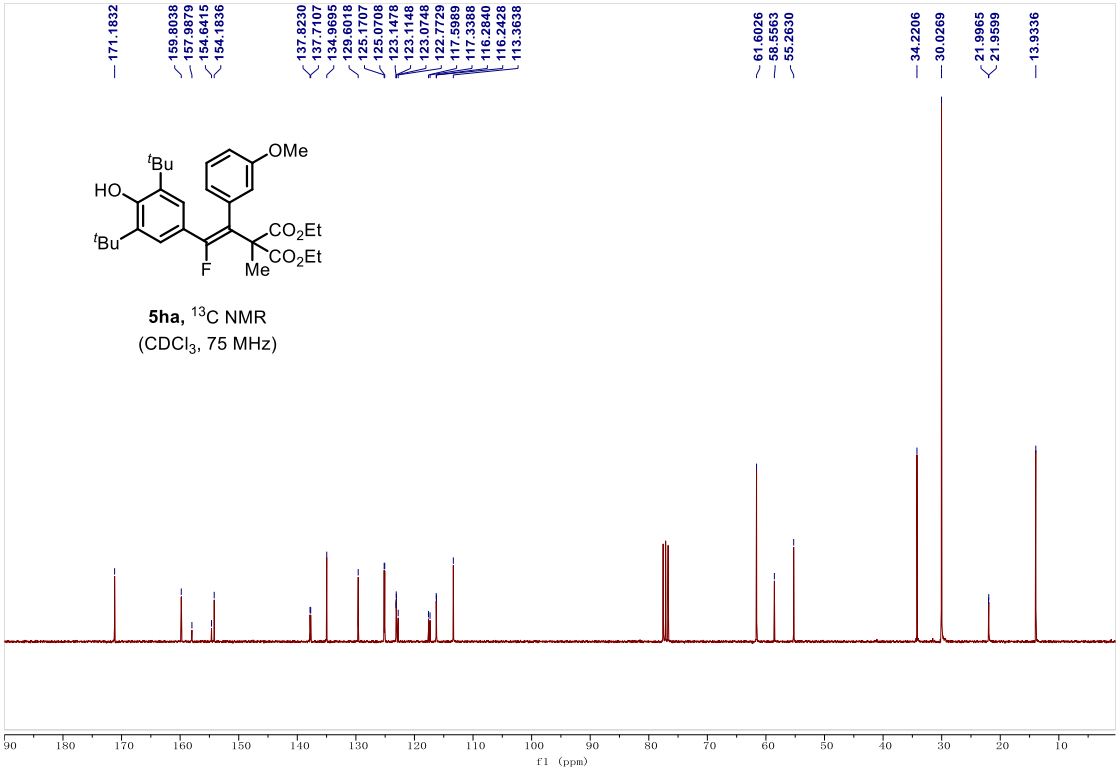
5ga, ^{13}C NMR
($CDCl_3$, 75 MHz)



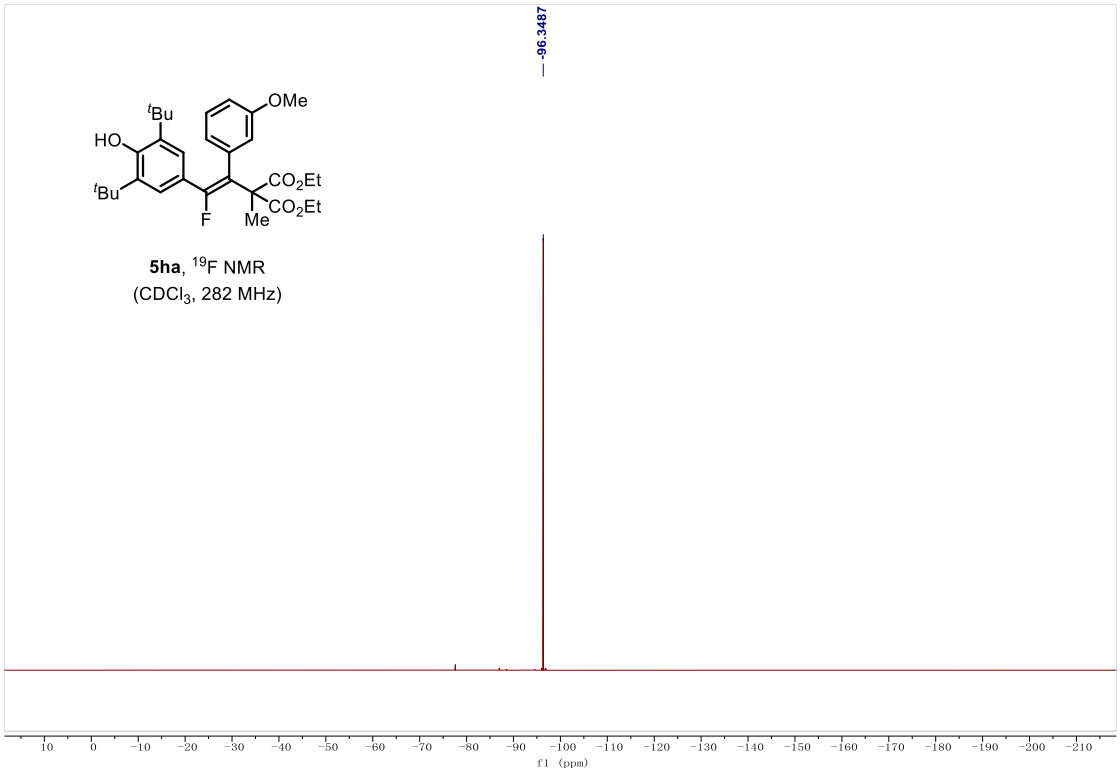
5ga, ^{19}F NMR
($CDCl_3$, 282 MHz)



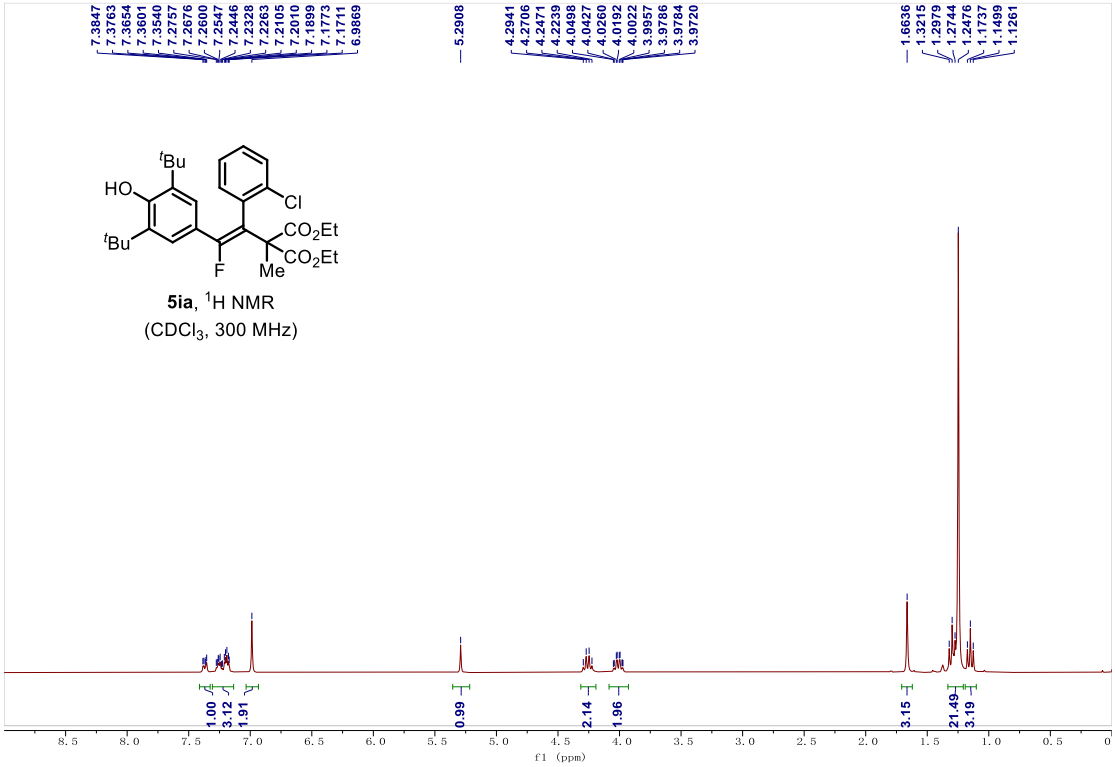
5ha, ^{1}H NMR
($CDCl_3$, 300 MHz)



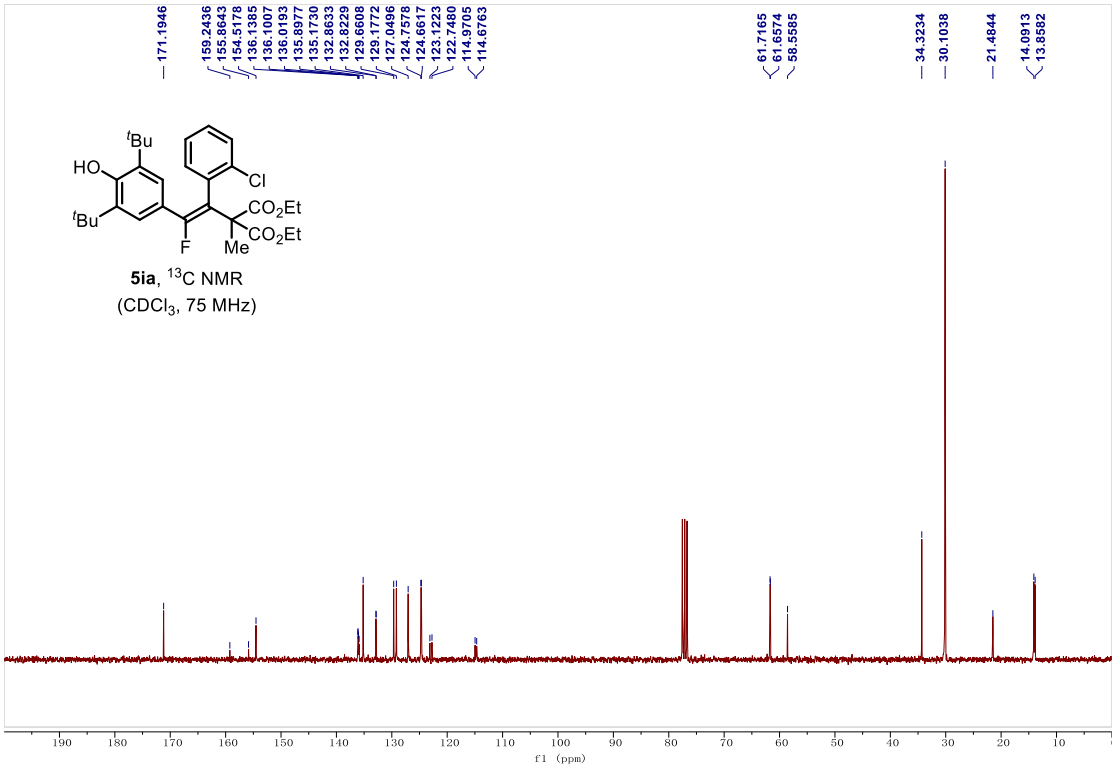
5ha, ^{13}C NMR
($CDCl_3$, 75 MHz)



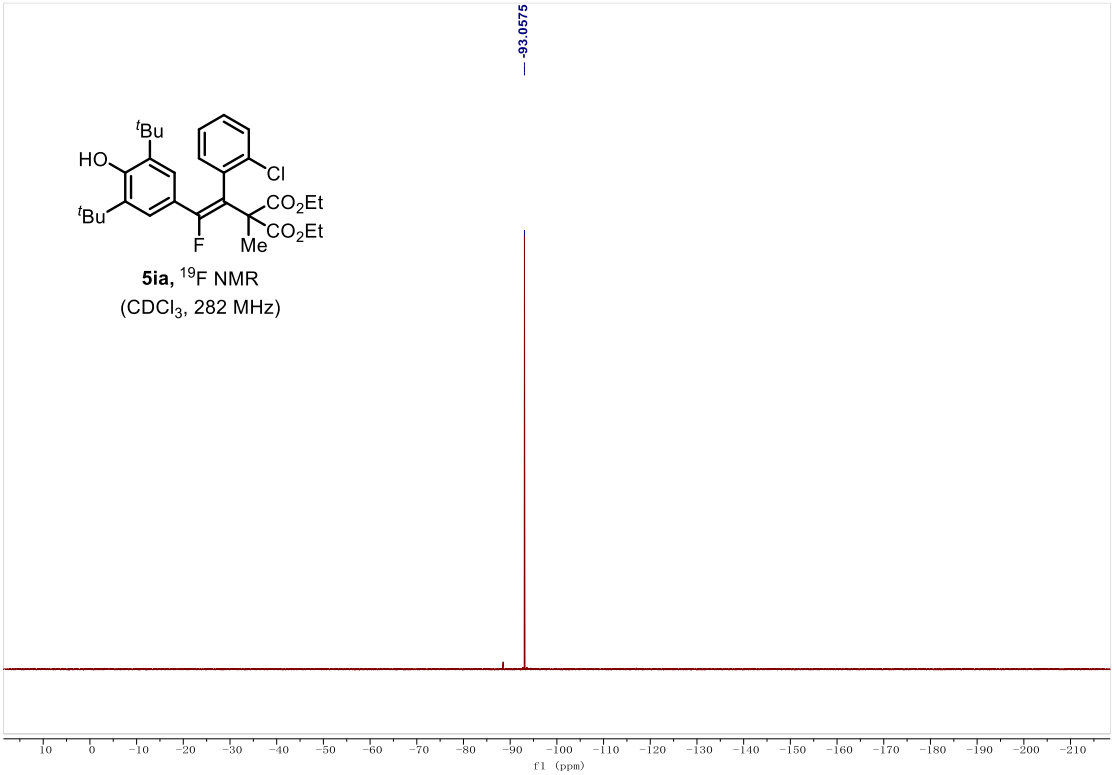
5ha, ^{19}F NMR
($CDCl_3$, 282 MHz)



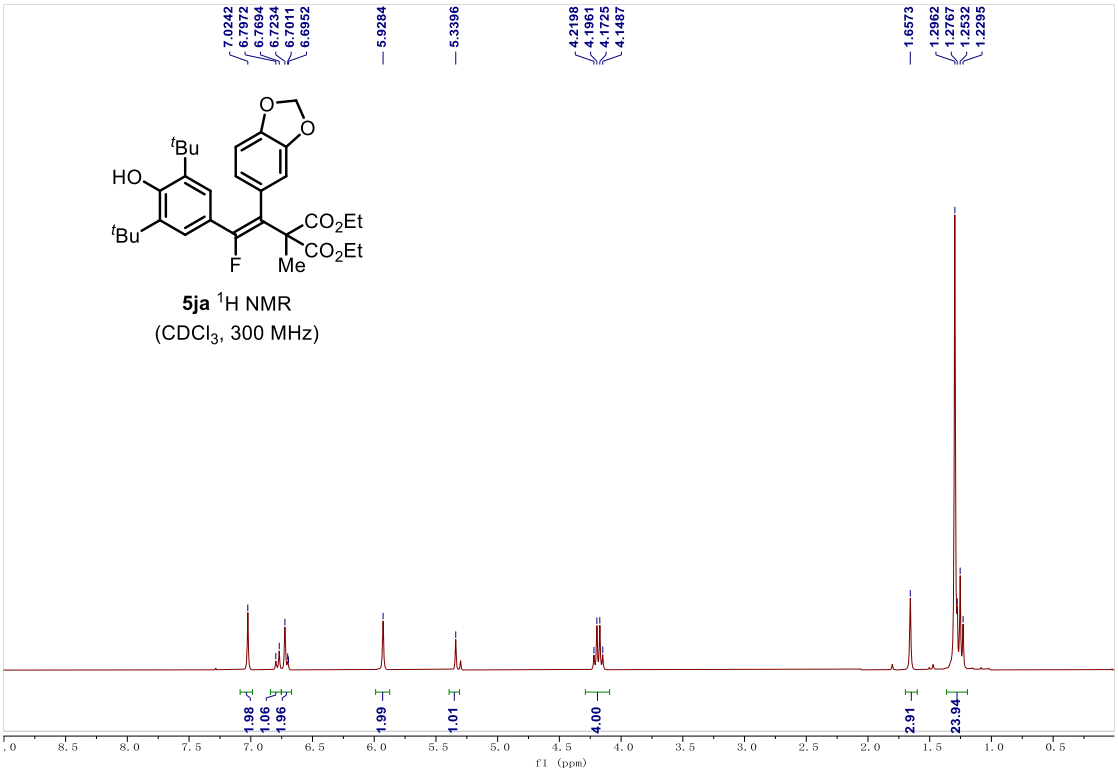
5ia, ^{1}H NMR
($CDCl_3$, 300 MHz)



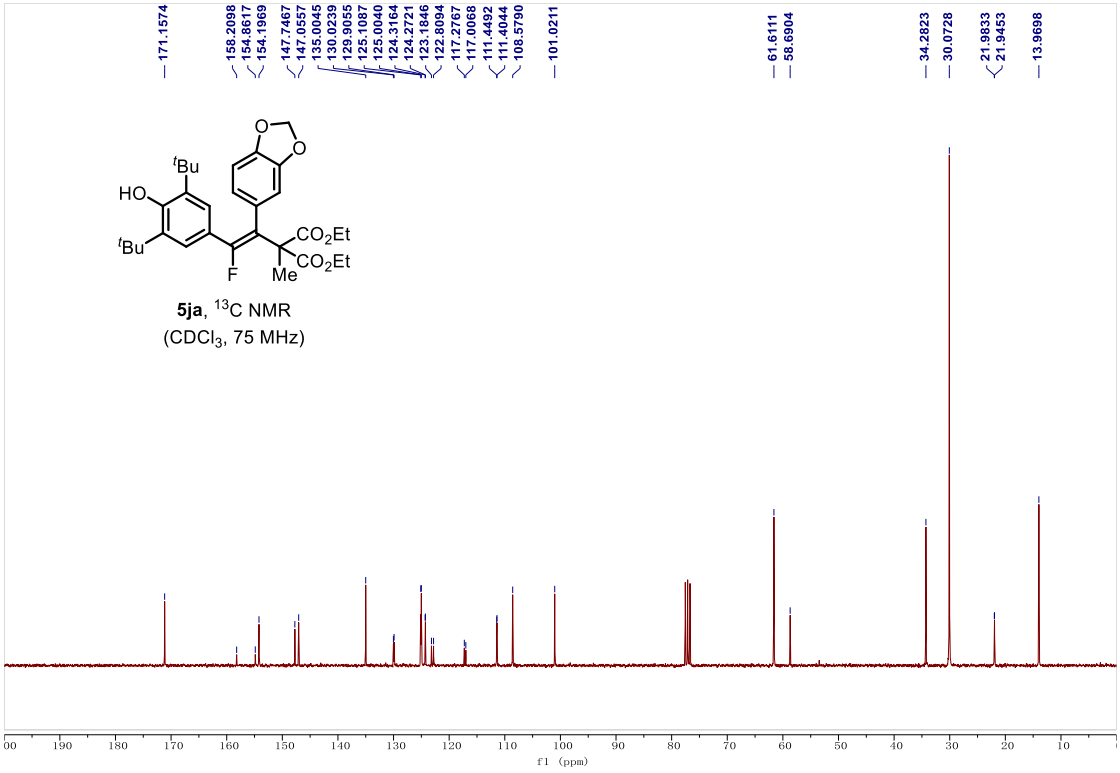
5ia, ^{13}C NMR
($CDCl_3$, 75 MHz)



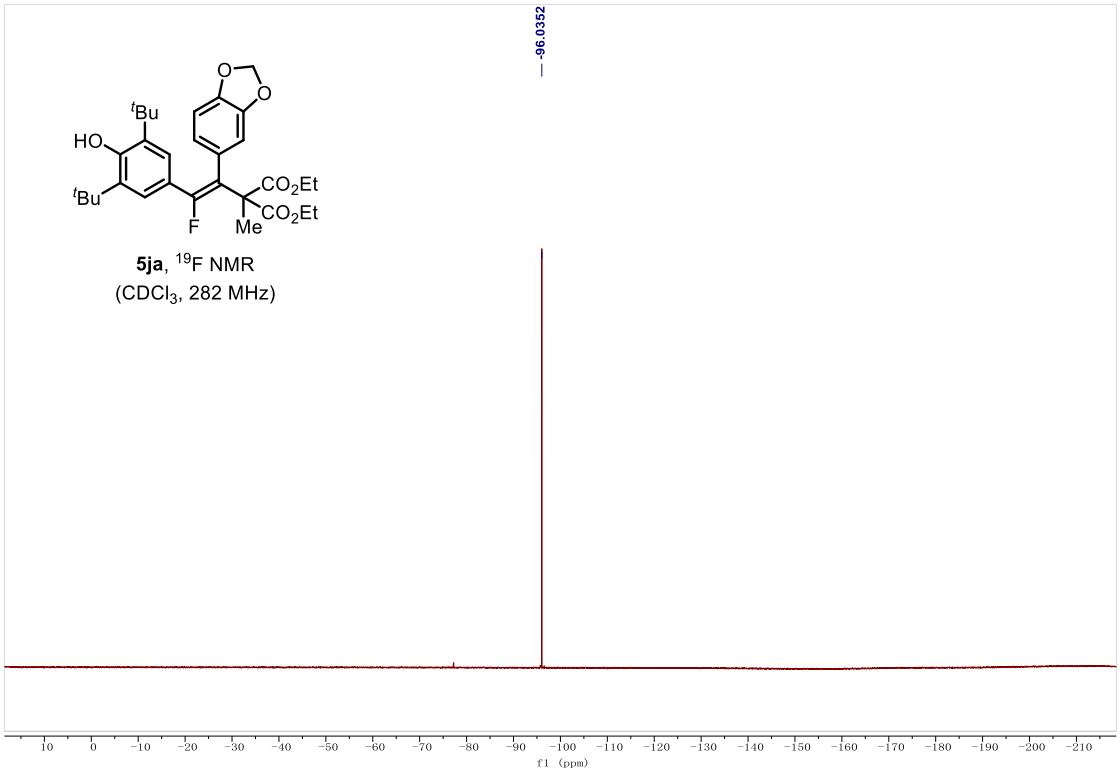
5ia, ^{19}F NMR
($CDCl_3$, 282 MHz)



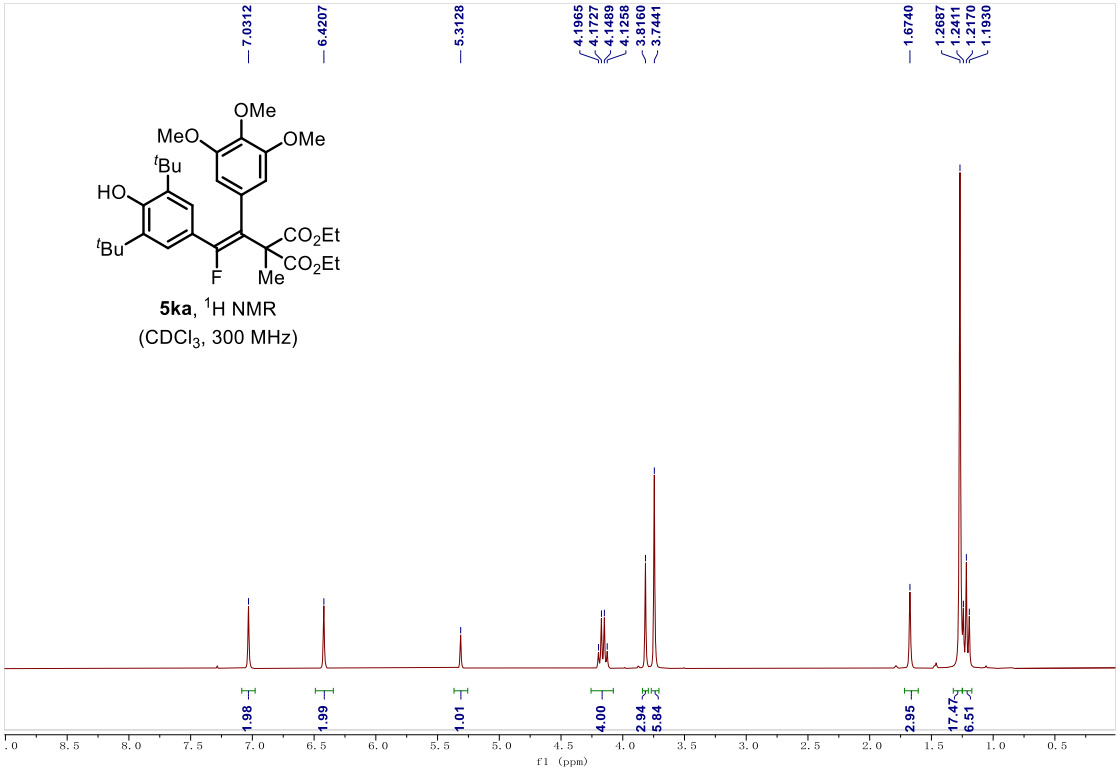
5ja ^{1}H NMR
($CDCl_3$, 300 MHz)



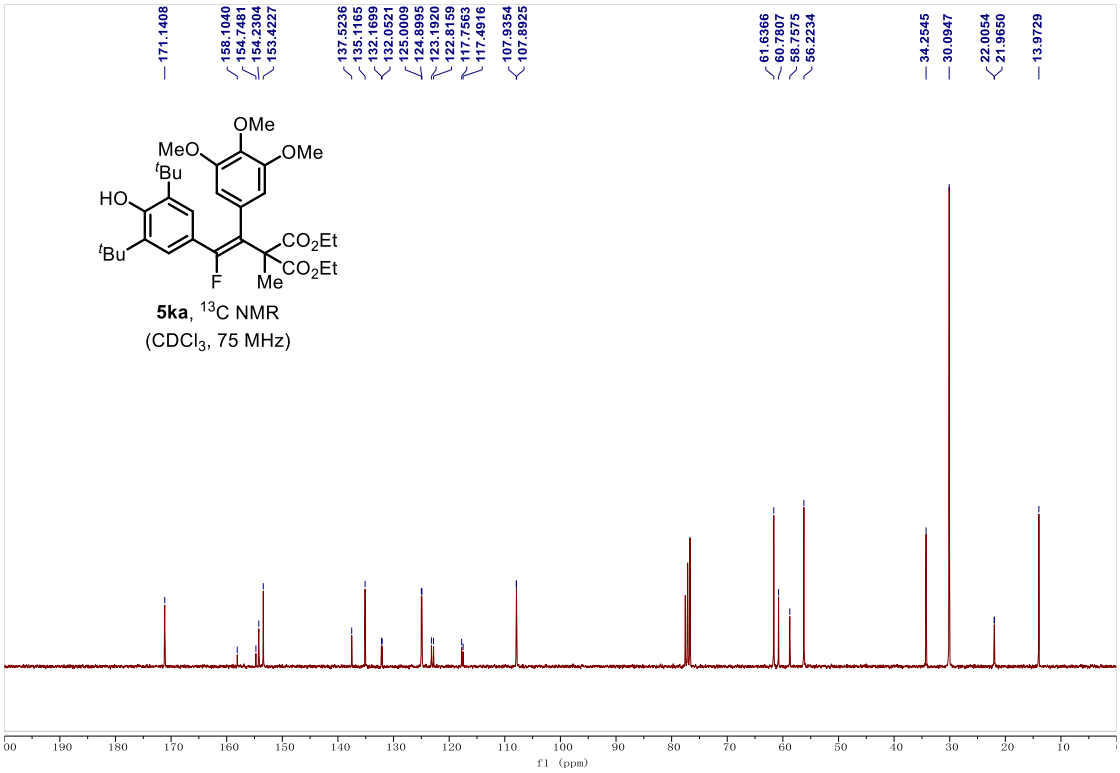
5ja, ^{13}C NMR
($CDCl_3$, 75 MHz)



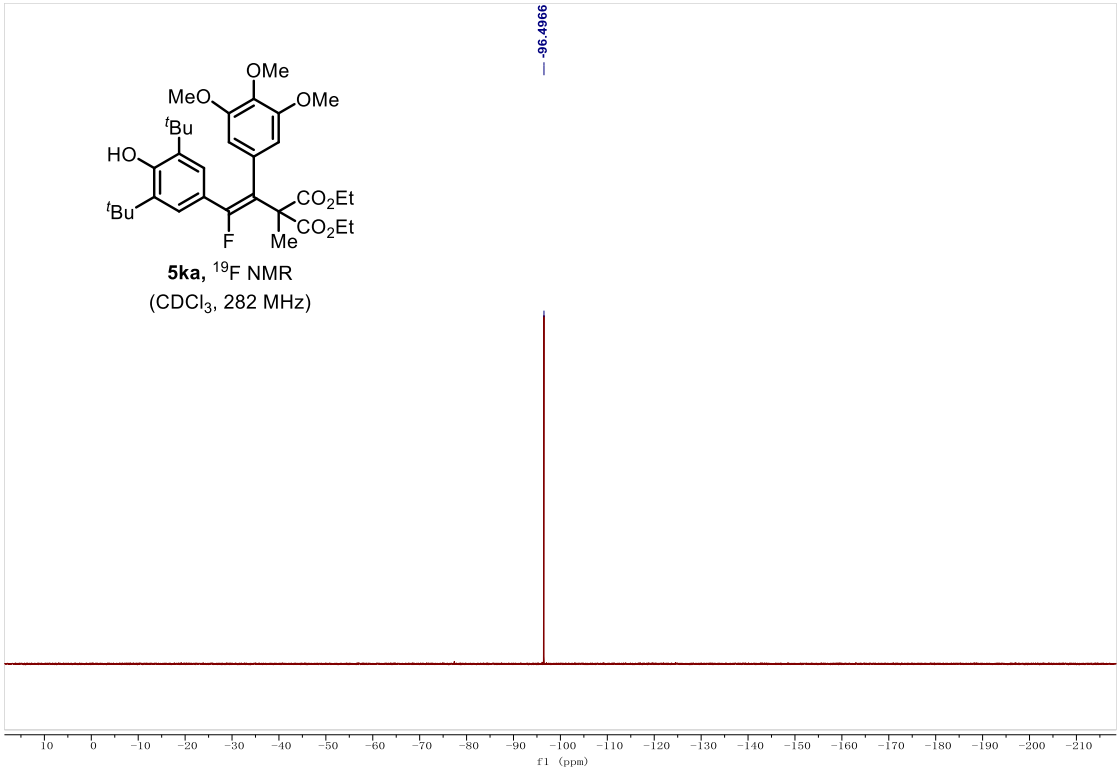
5ja, ^{19}F NMR
($CDCl_3$, 282 MHz)



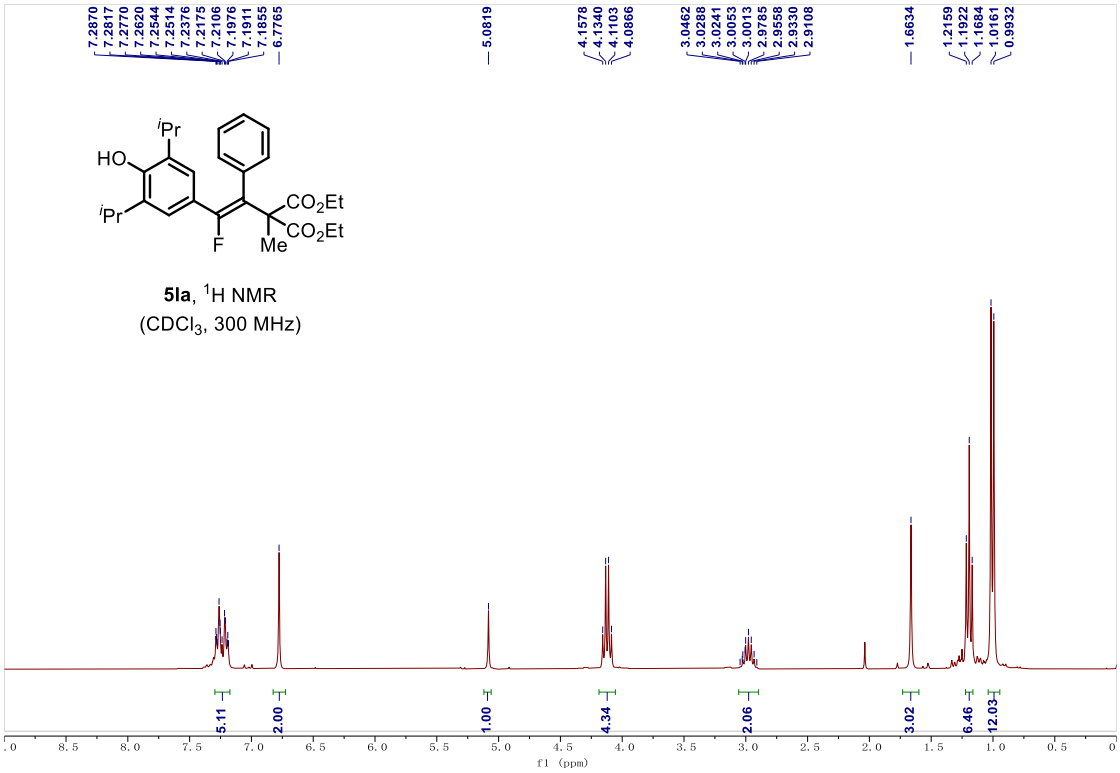
5ka, ^{1}H NMR
($CDCl_3$, 300 MHz)



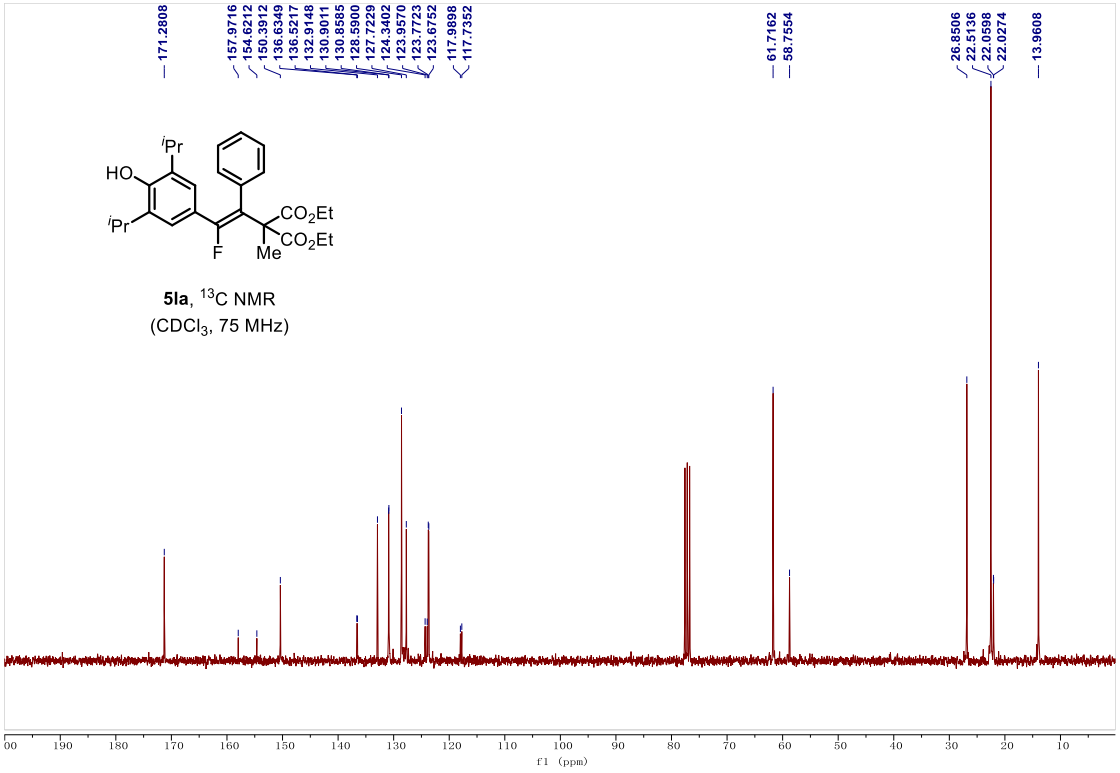
5ka, ^{13}C NMR
($CDCl_3$, 75 MHz)



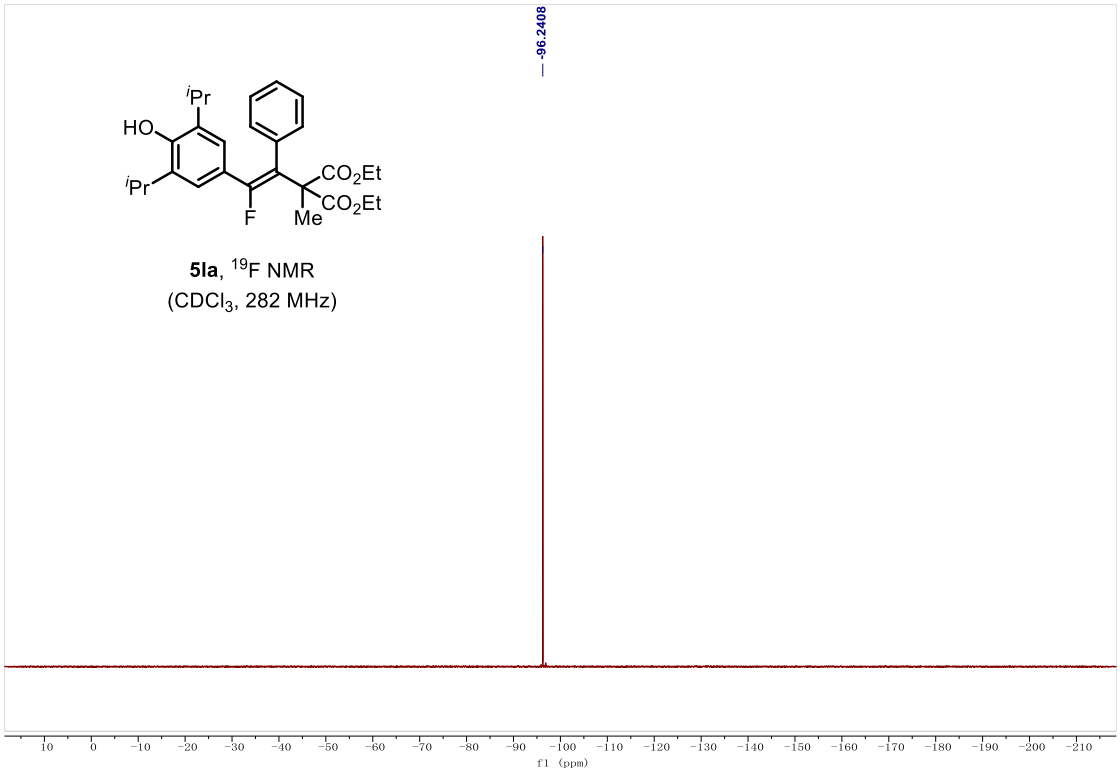
5ka, ^{19}F NMR
($CDCl_3$, 282 MHz)



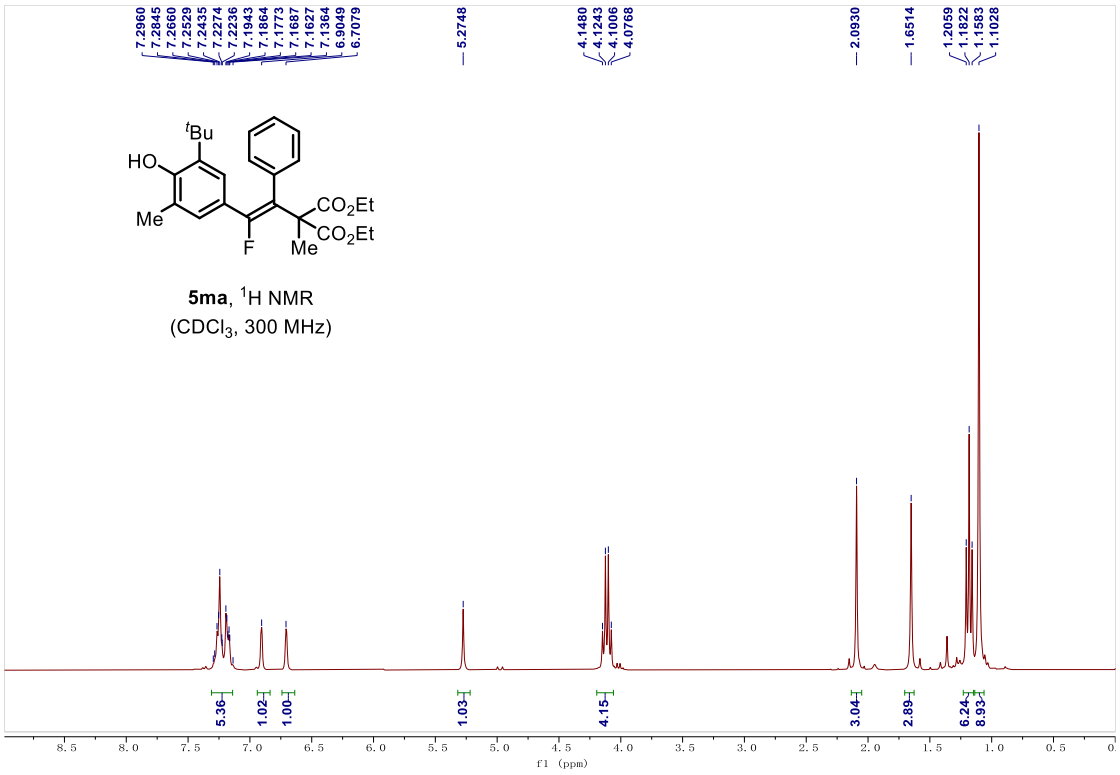
5la, ^{1}H NMR
($CDCl_3$, 300 MHz)



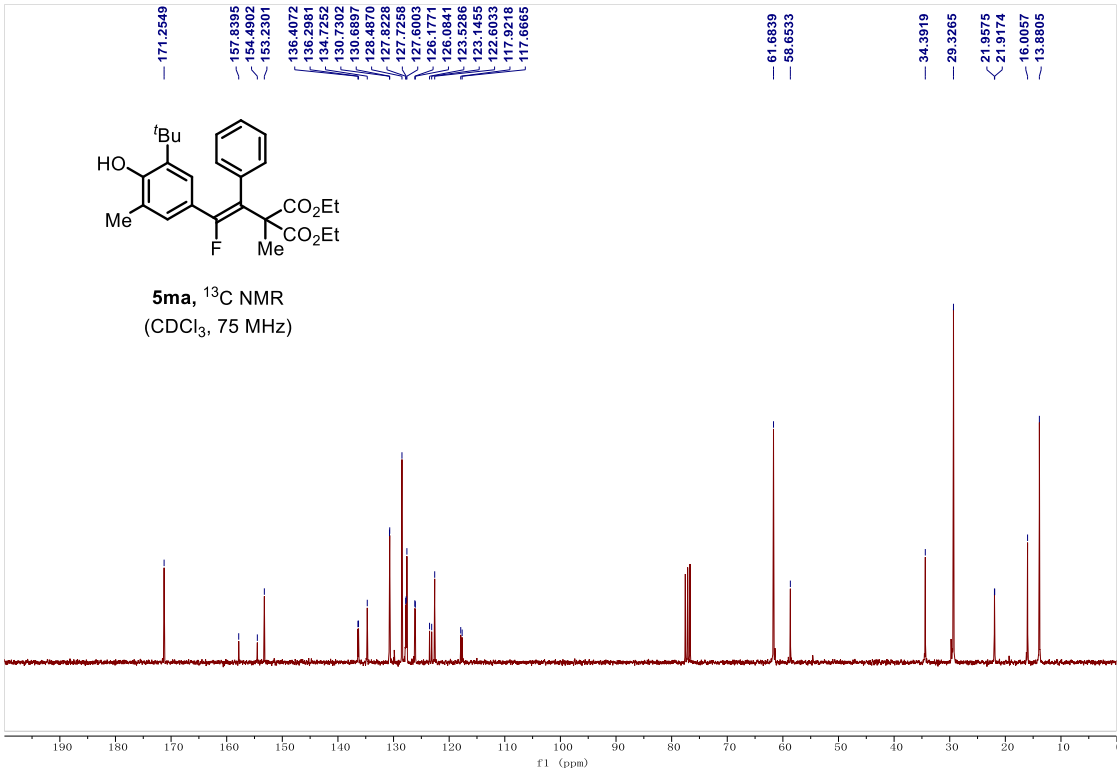
5la, ^{13}C NMR
($CDCl_3$, 75 MHz)



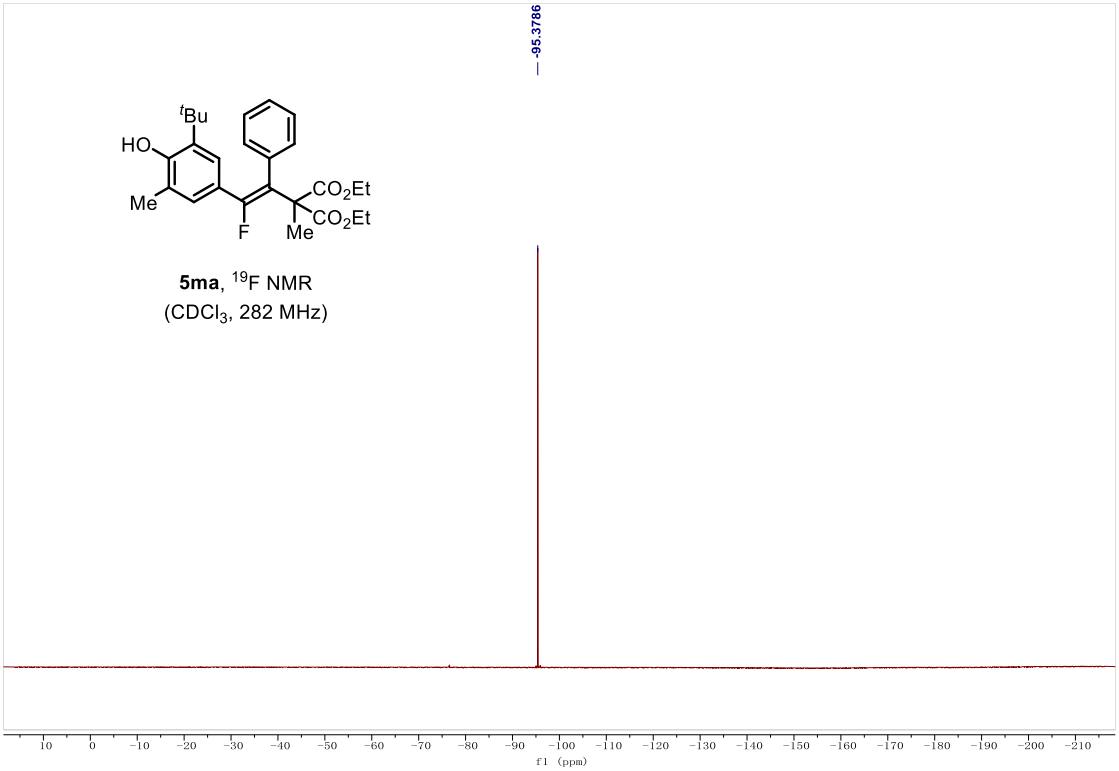
5la, ^{19}F NMR
($CDCl_3$, 282 MHz)



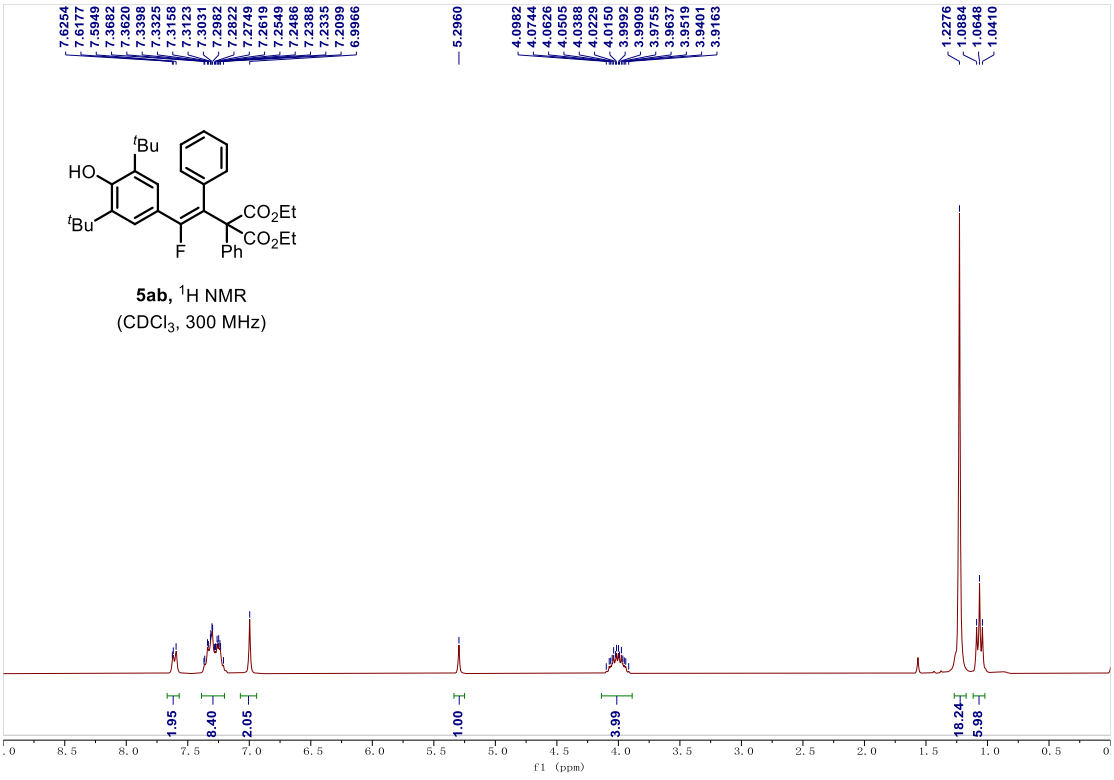
5ma, ^{1}H NMR
($CDCl_3$, 300 MHz)



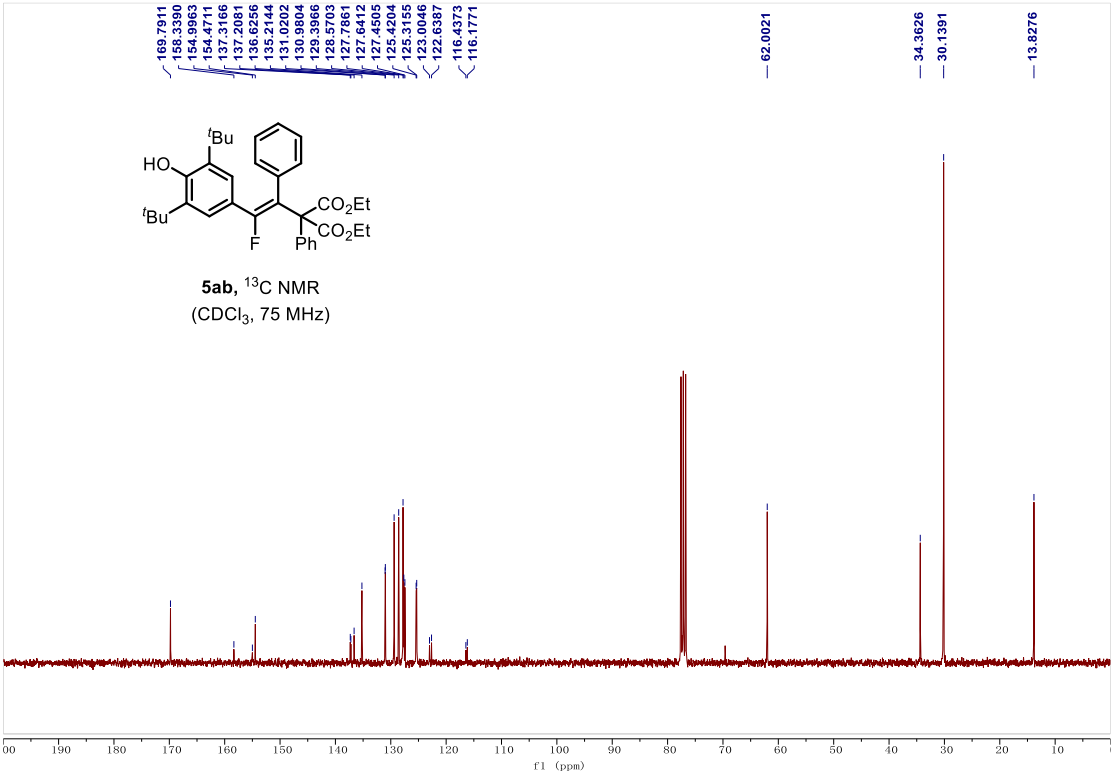
5ma, ^{13}C NMR
($CDCl_3$, 75 MHz)



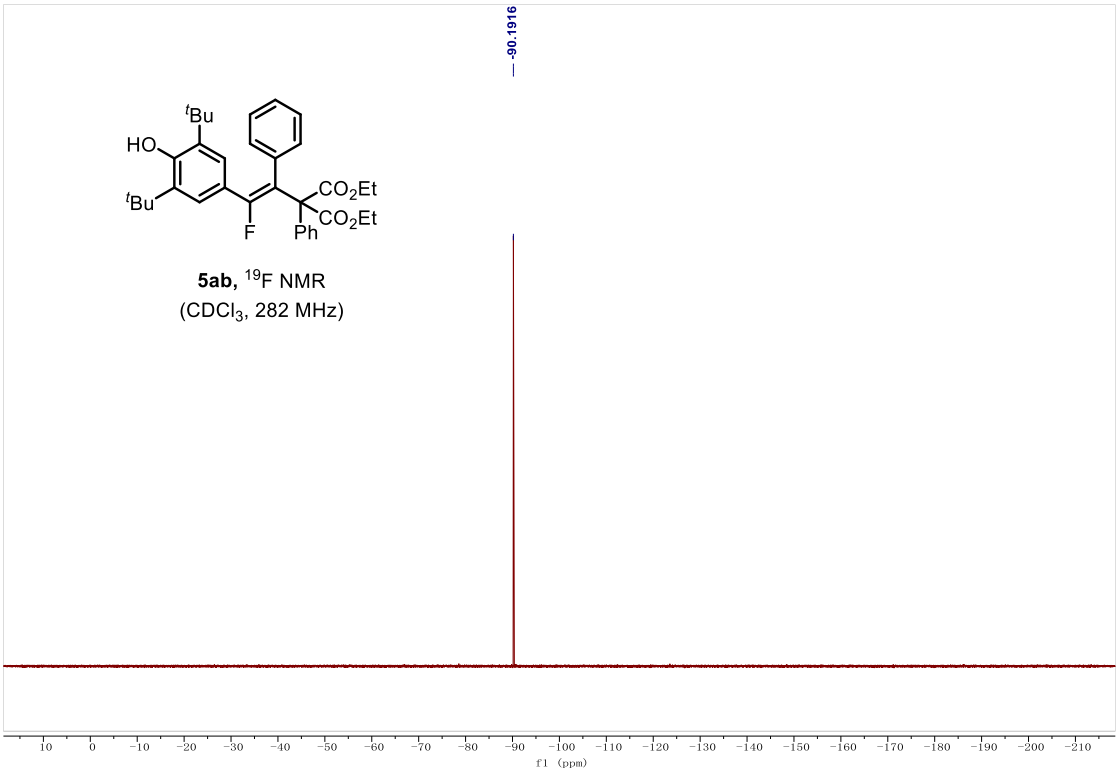
5ma, ^{19}F NMR
($CDCl_3$, 282 MHz)



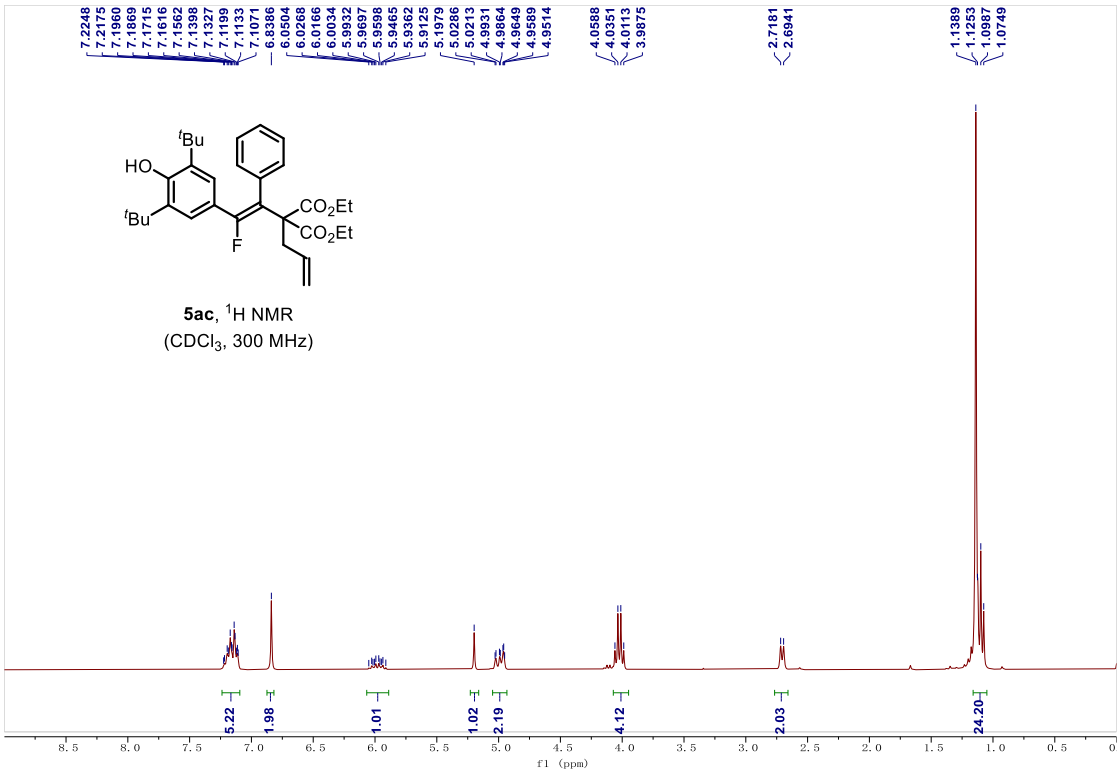
5ab, ^{1}H NMR
($CDCl_3$, 300 MHz)



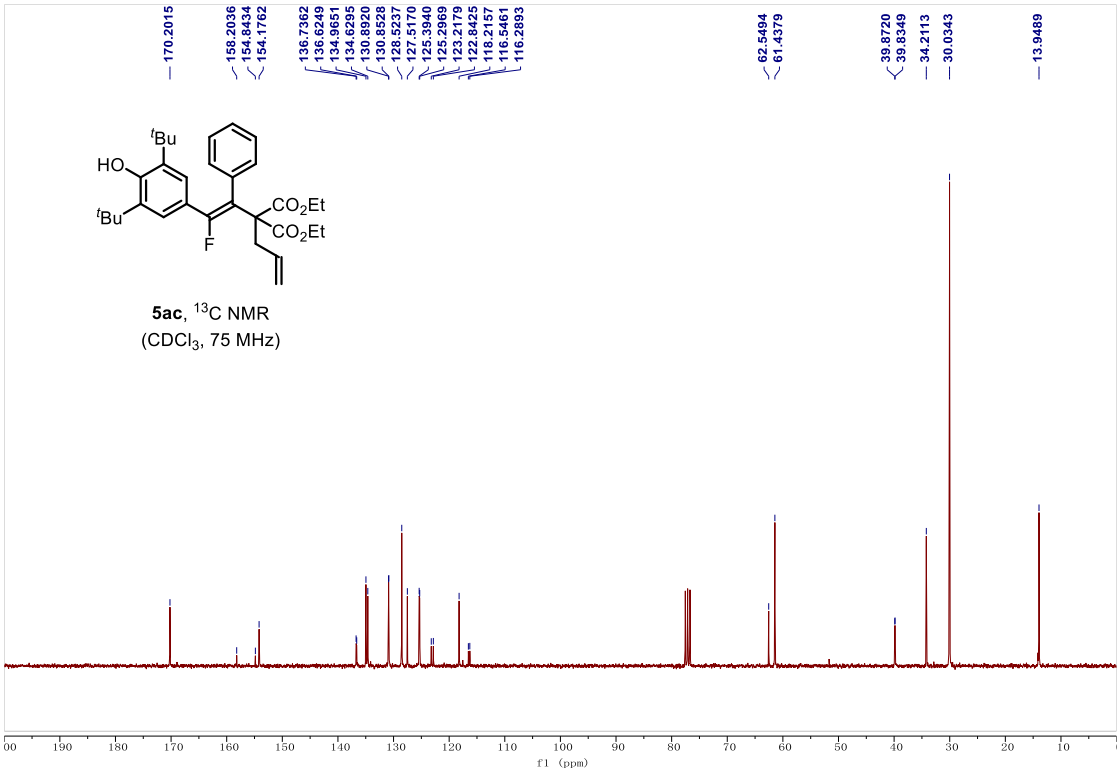
5ab, ^{13}C NMR
($CDCl_3$, 75 MHz)



5ab, ^{19}F NMR
($CDCl_3$, 282 MHz)

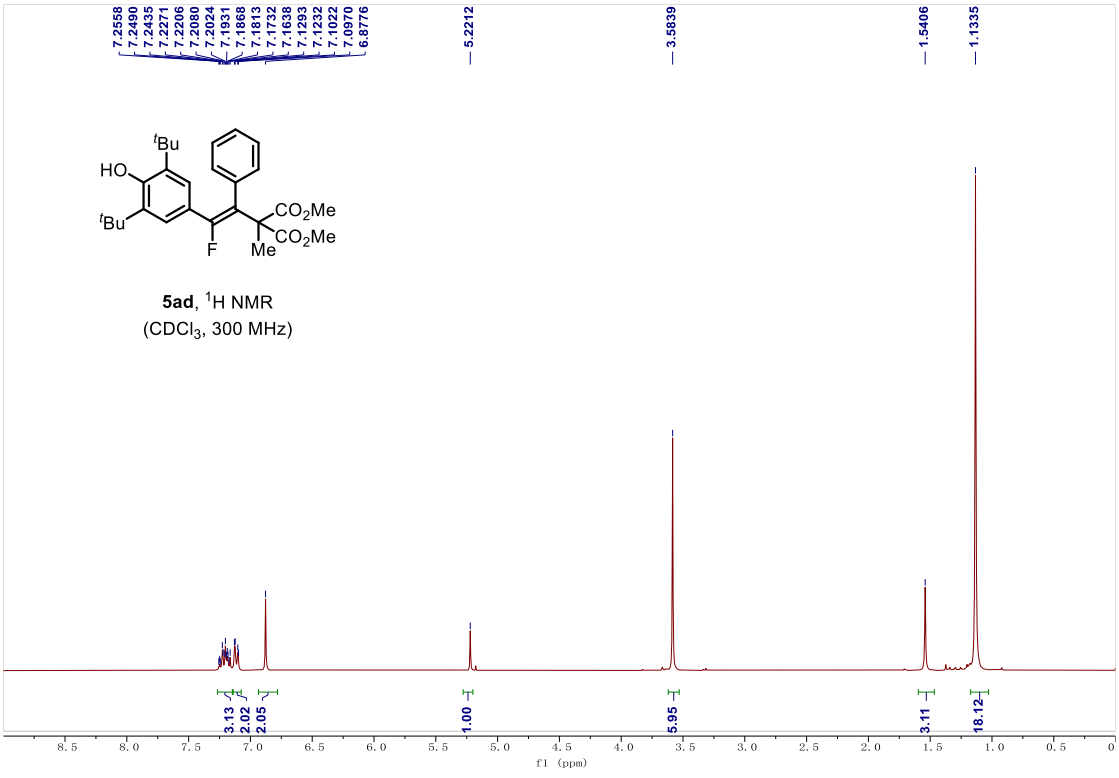


5ac, ^{1}H NMR
($CDCl_3$, 300 MHz)

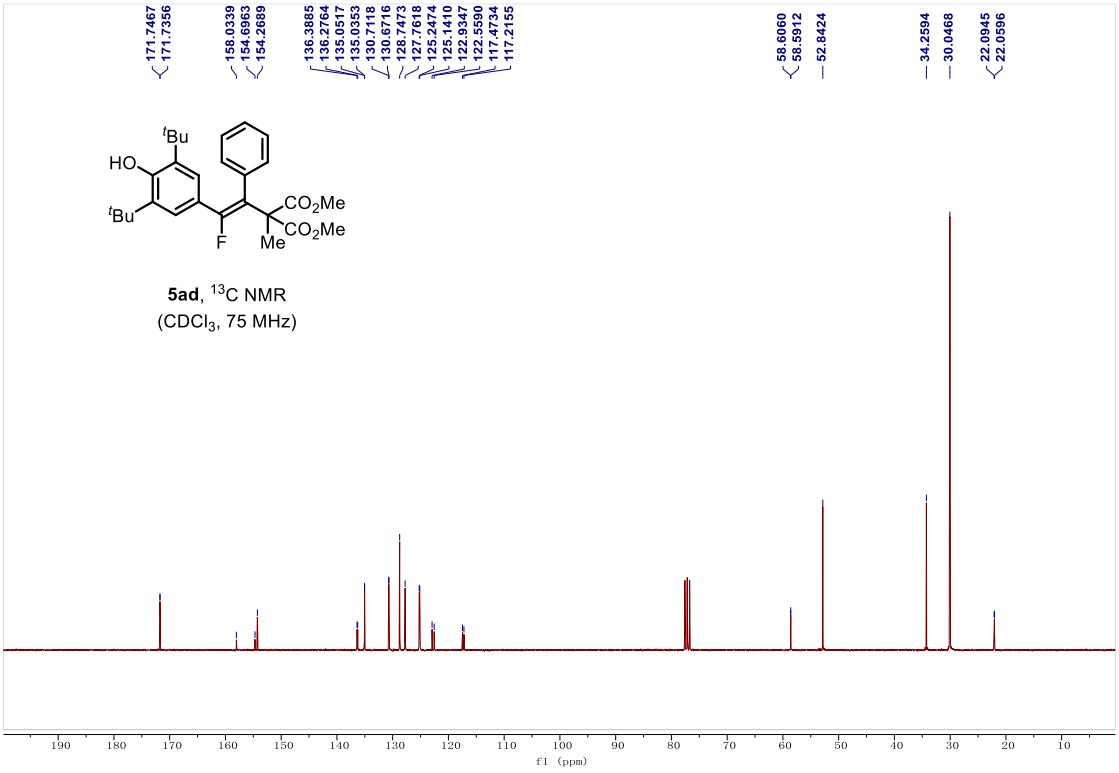


5ac, ^{13}C NMR
($CDCl_3$, 75 MHz)

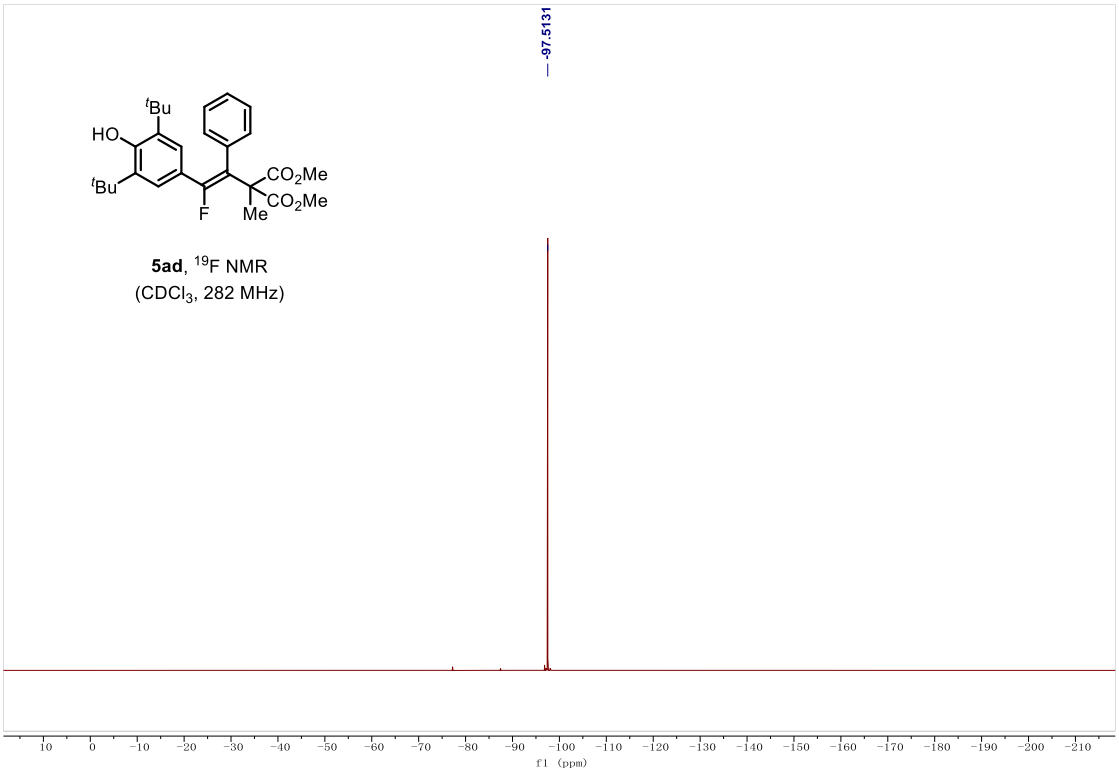
5ac, ^{19}F NMR
($CDCl_3$, 282 MHz)



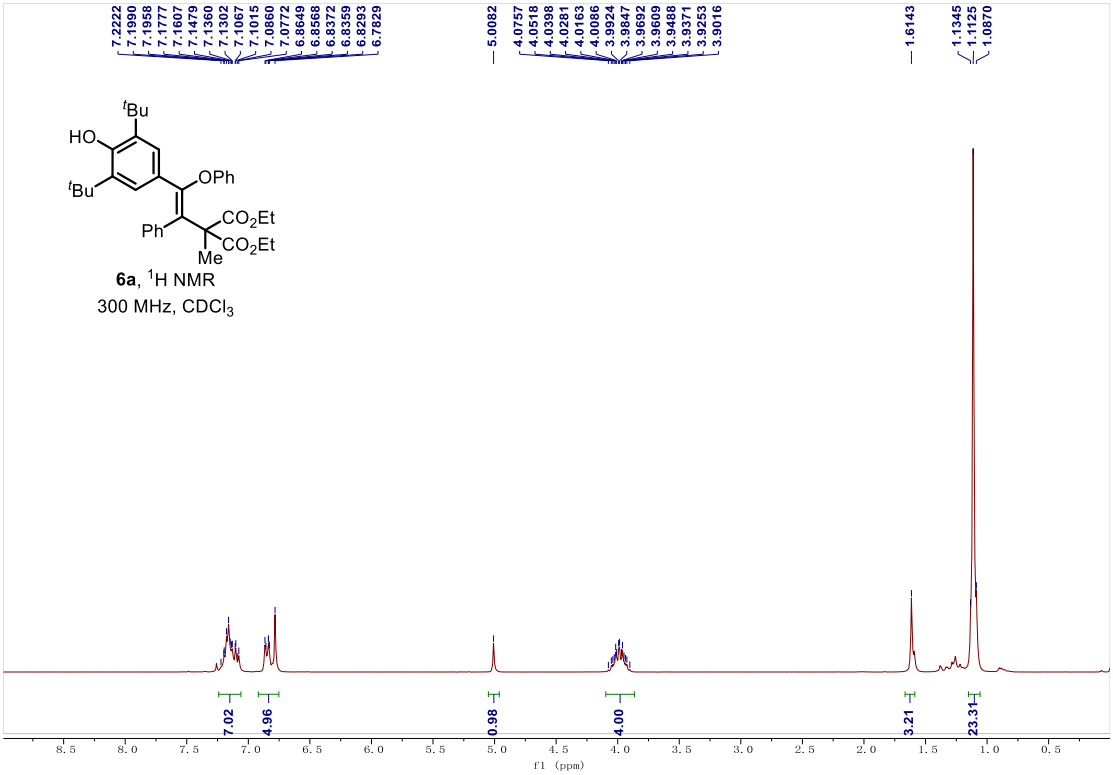
5ad, ^{1}H NMR
($CDCl_3$, 300 MHz)

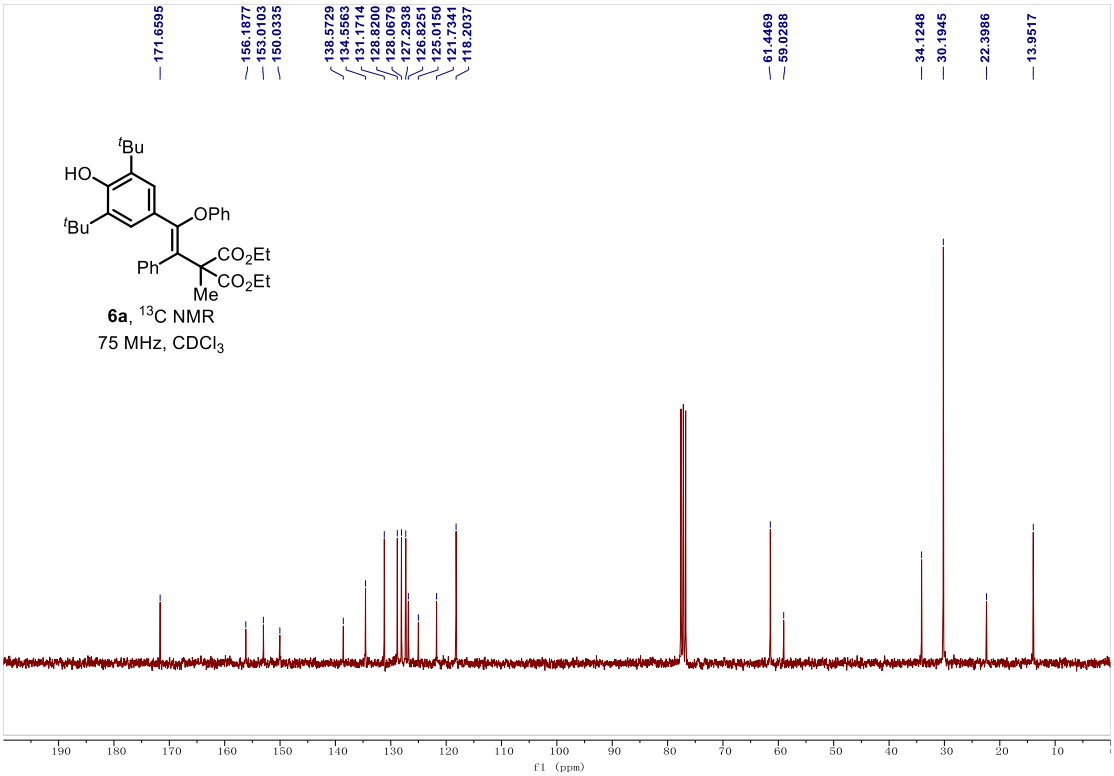


5ad, ^{13}C NMR
($CDCl_3$, 75 MHz)



5ad, ^{19}F NMR
($CDCl_3$, 282 MHz)


7.2222
7.1990
7.1958
7.1777
7.1607
7.1479
7.1360
7.1302
7.1067
7.1015
7.0860
7.0772
6.8649
6.8568
6.8372
6.8359
6.8293
6.7829
5.0082
4.0757
4.0518
4.0398
4.0281
4.0163
4.0086
3.9924
3.9847
3.9692
3.9609
3.9488
3.9371
3.9253
3.9016
1.6143
1.1345
1.1125
1.0870
tBu
HO
tBu
OPh
Ph
CO2Et
CO2Et
Me
6a, 1H NMR
300 MHz, CDCl3
7.02
4.96
0.98
4.00
3.21
23.31
f1 (ppm)


171.6595
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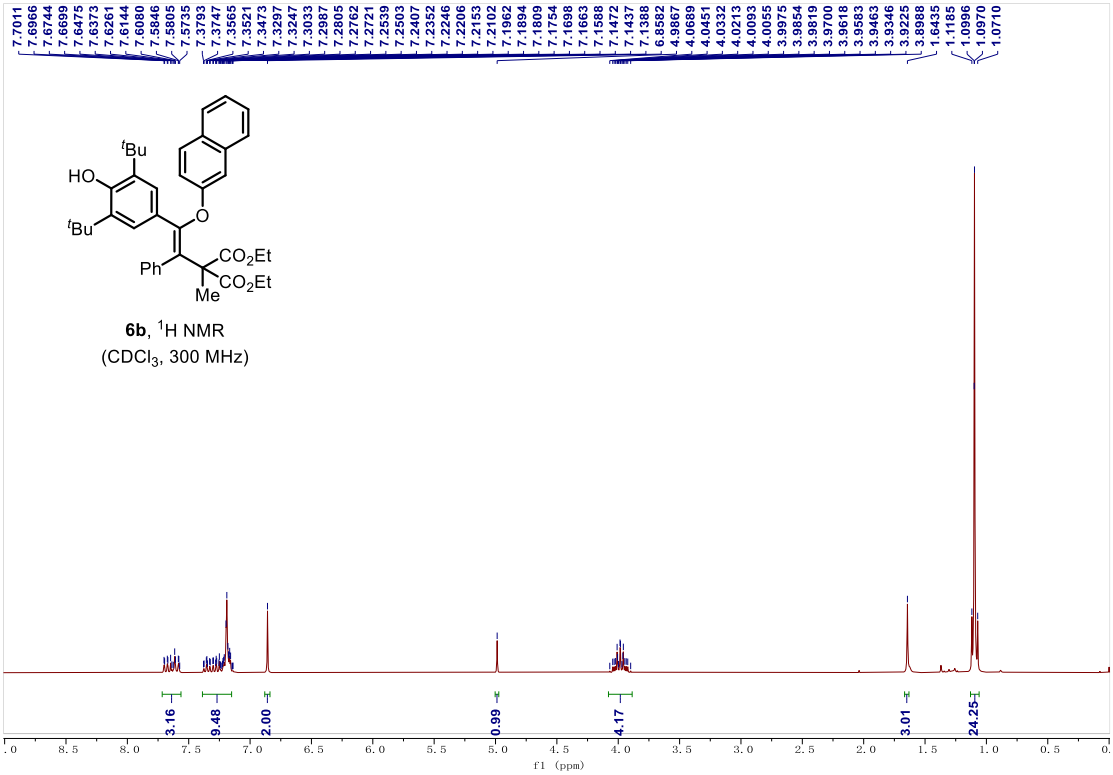
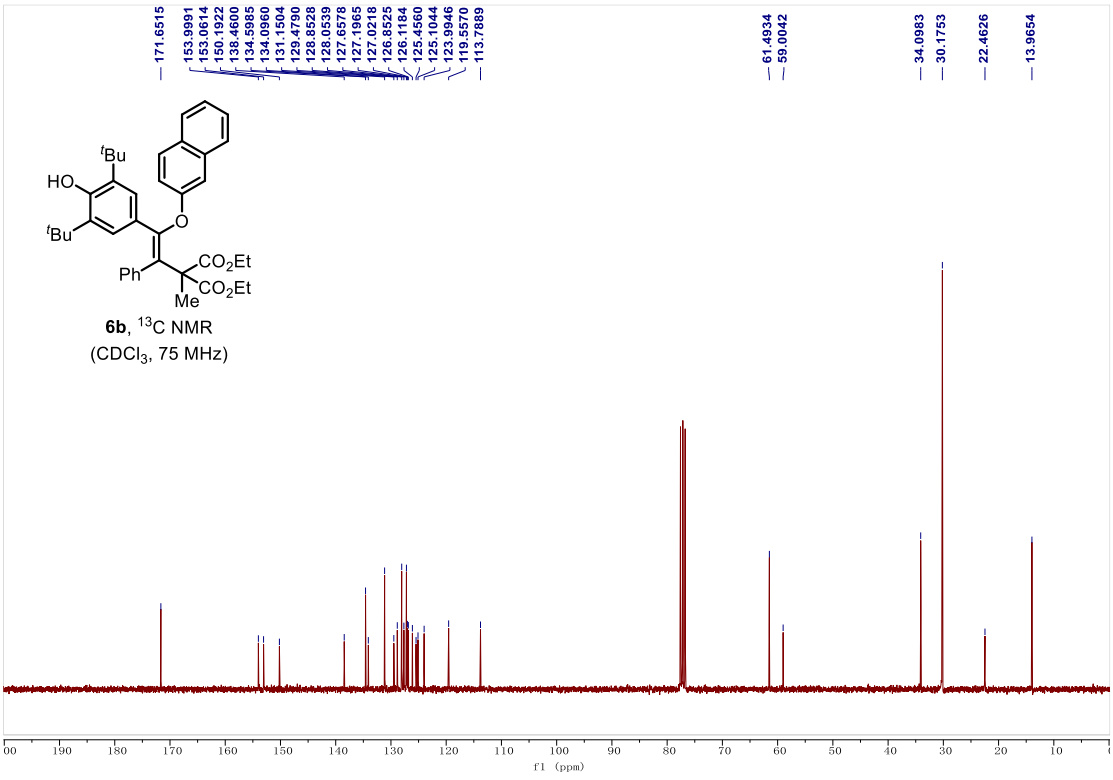
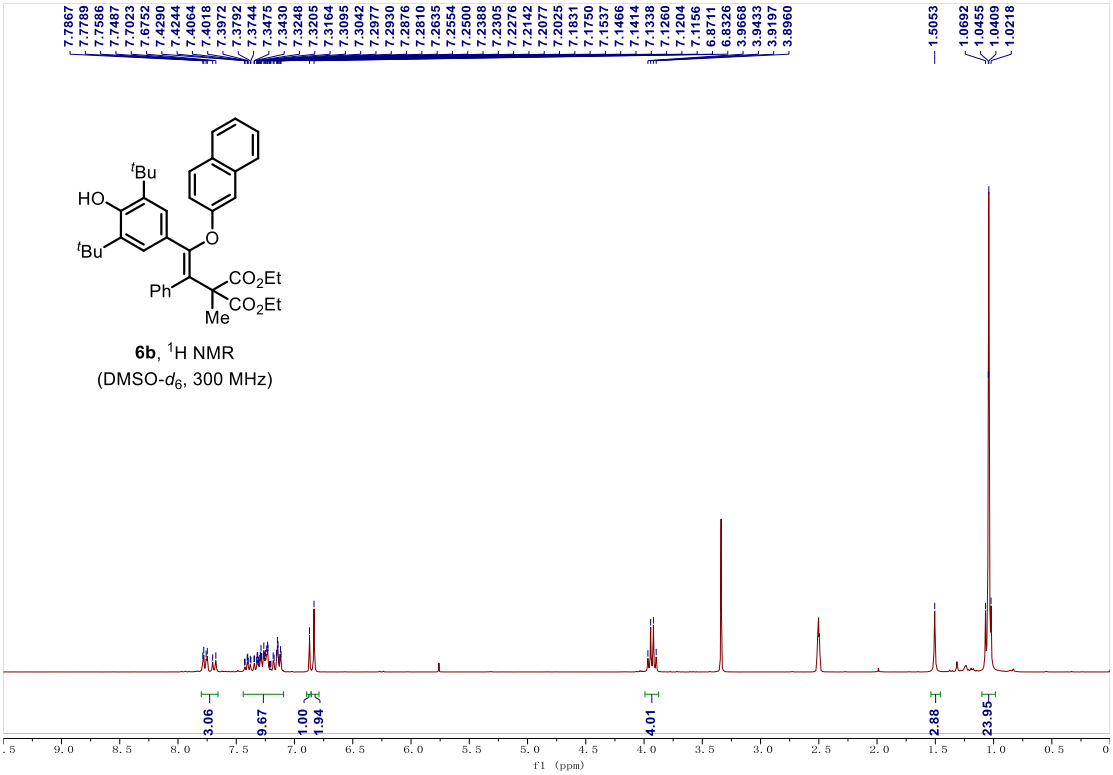
153.0103
150.0335
138.5729
134.5563
131.1714
128.8200
128.0679
127.2938
126.8251
125.0150
121.7341
118.2037
61.4469
59.0288
34.1248
30.1945
22.3986
13.9517
tBu
HO
tBu
OPh
Ph
CO2Et
CO2Et
Me
6a, 13C NMR
75 MHz, CDCl3
f1 (ppm)



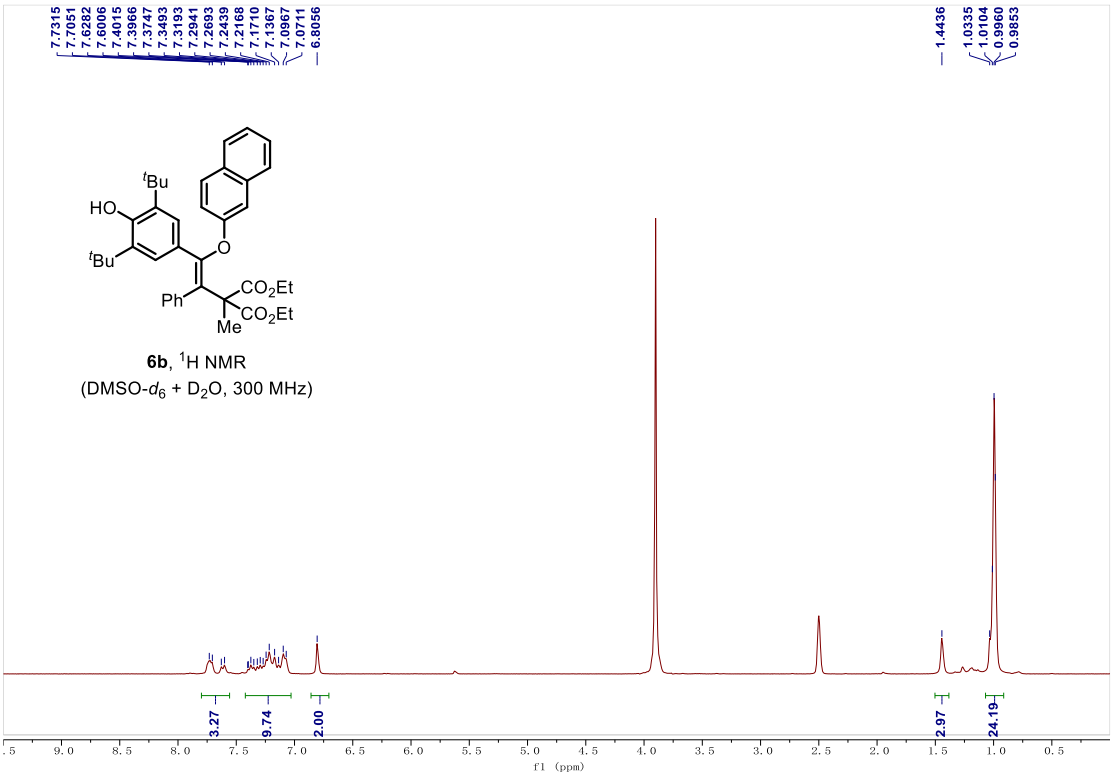
6b, ^{1}H NMR
($CDCl_3$, 300 MHz)



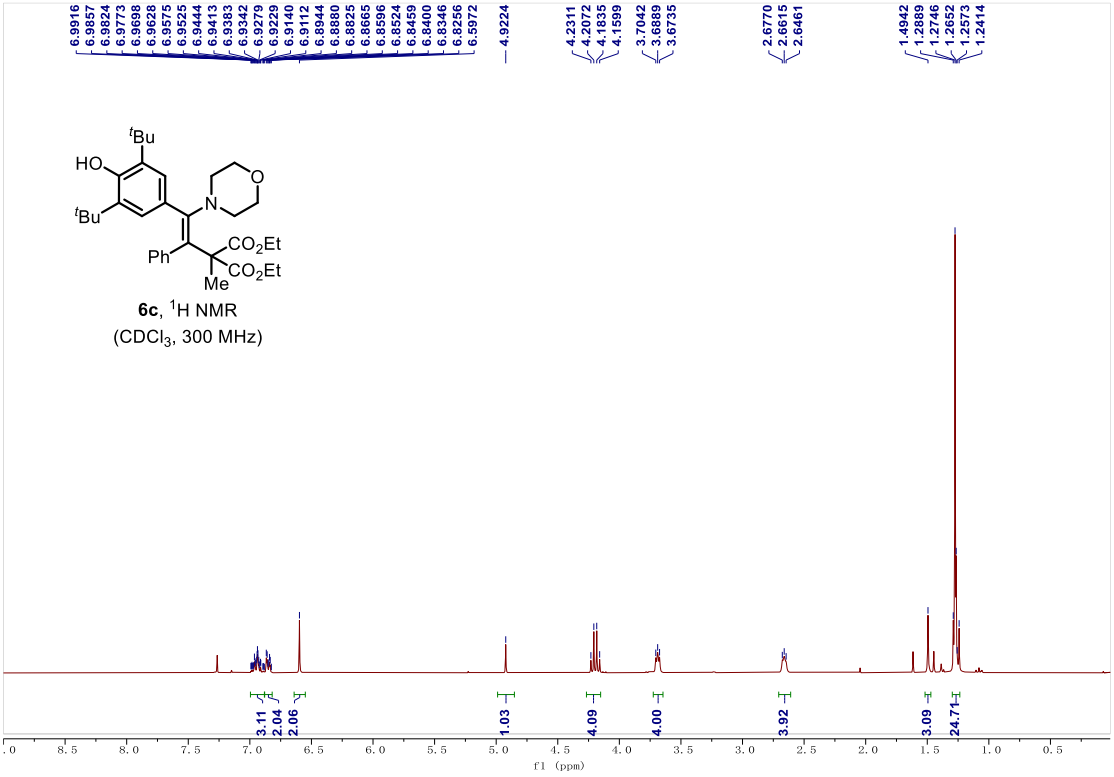
6b, ^{13}C NMR
($CDCl_3$, 75 MHz)



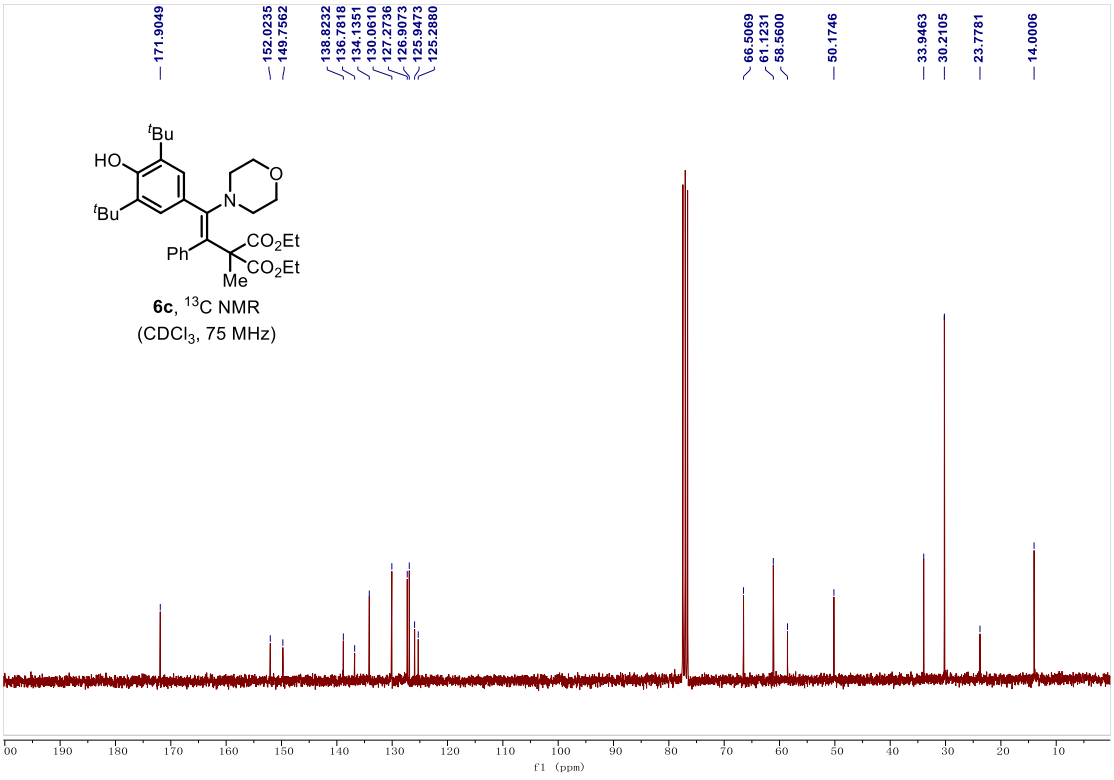
6b, ^{1}H NMR
(DMSO-d_6, 300 MHz)



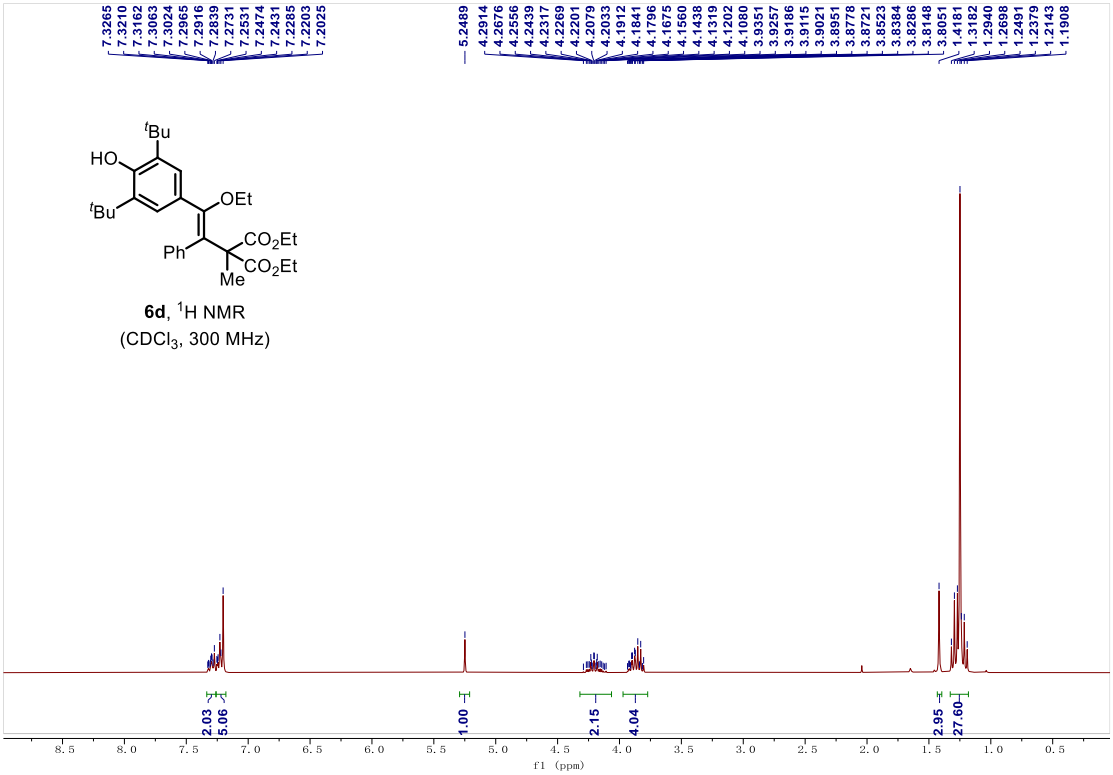
6b, ^{1}H NMR
(DMSO-d_6 + D_2O, 300 MHz)

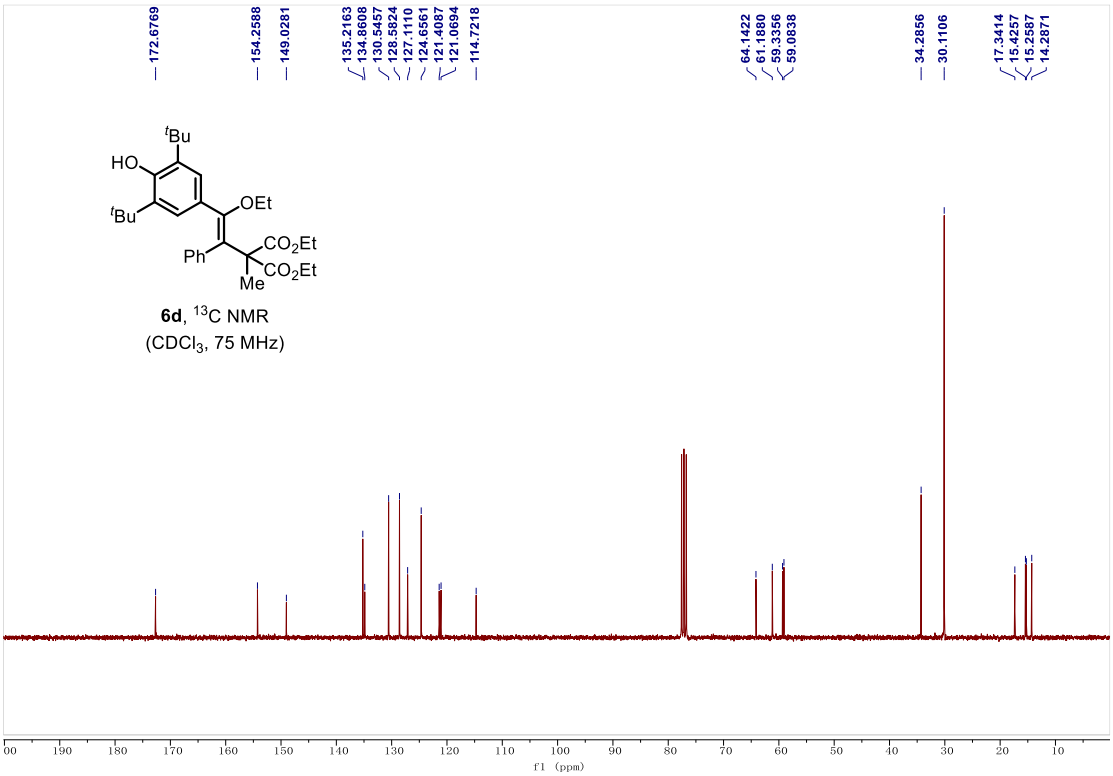


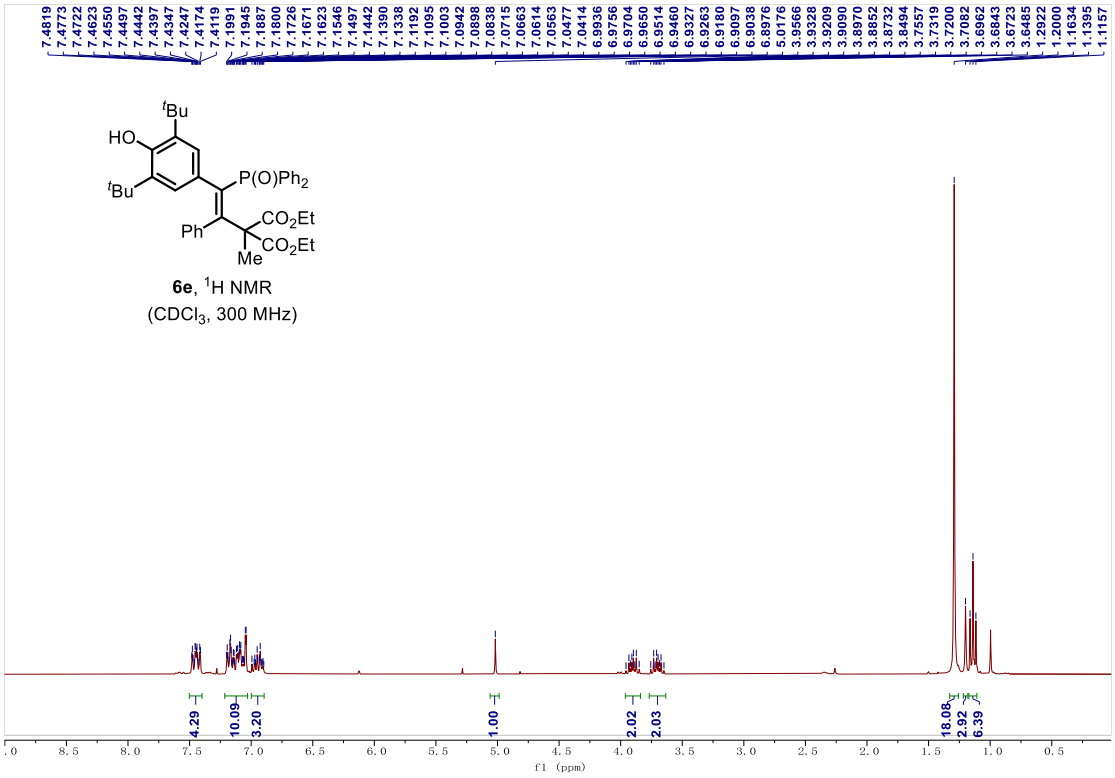
6c, ^{1}H NMR
($CDCl_3$, 300 MHz)



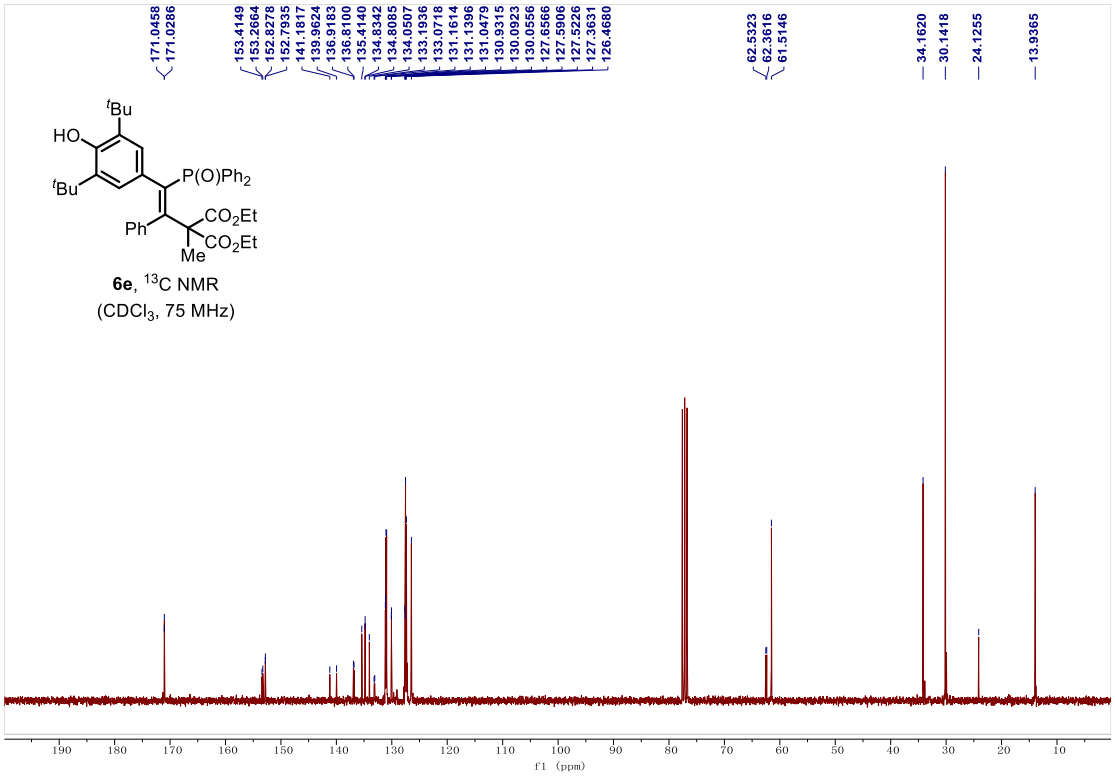
6c, ^{13}C NMR
($CDCl_3$, 75 MHz)


7.3265
7.3210
7.3162
7.3063
7.3024
7.2965
7.2916
7.2839
7.2731
7.2531
7.2474
7.2431
7.2285
7.2203
7.2025
5.2489
4.2914
4.2676
4.2556
4.2439
4.2317
4.2269
4.2201
4.2079
4.2033
4.1912
4.1841
4.1796
4.1675
4.1560
4.1438
4.1319
4.1202
4.1080
3.9351
3.9257
3.9186
3.9115
3.9021
3.8951
3.8778
3.8721
3.8523
3.8384
3.8286
3.8148
3.8051
1.4181
1.3182
1.2940
1.2698
1.2491
1.2379
1.2143
1.1908
tBu
HO
tBu
OEt
Ph
CO2Et
CO2Et
Me
6d, 1H NMR
(CDCl3, 300 MHz)
2.03
5.06
1.00
2.15
4.04
2.95
27.60
f1 (ppm)

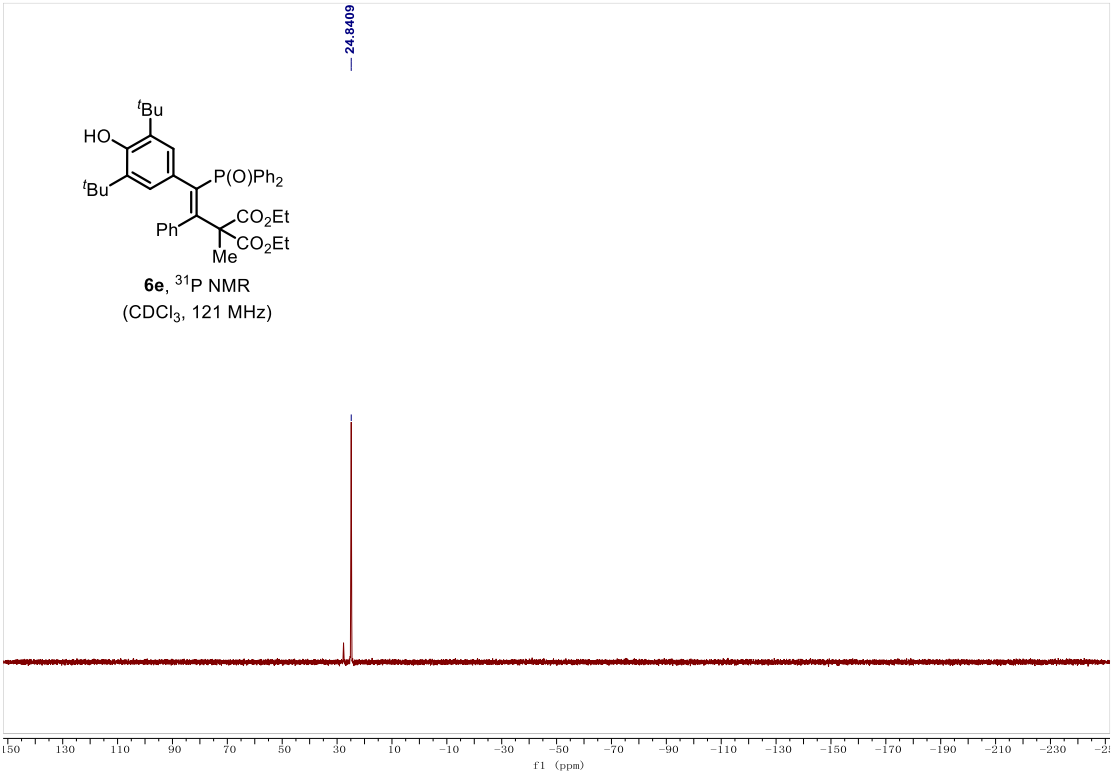

172.6769
154.2588
149.0281
135.2163
134.8608
130.5457
128.5824
127.1110
124.6561
121.4087
121.0694
114.7218
64.1422
61.1880
59.3356
59.0838
34.2856
30.1106
17.3414
15.4257
15.2587
14.2871
tBu
HO
tBu
OEt
Ph
CO2Et
CO2Et
Me
6d, 13C NMR
(CDCl3, 75 MHz)
f1 (ppm)



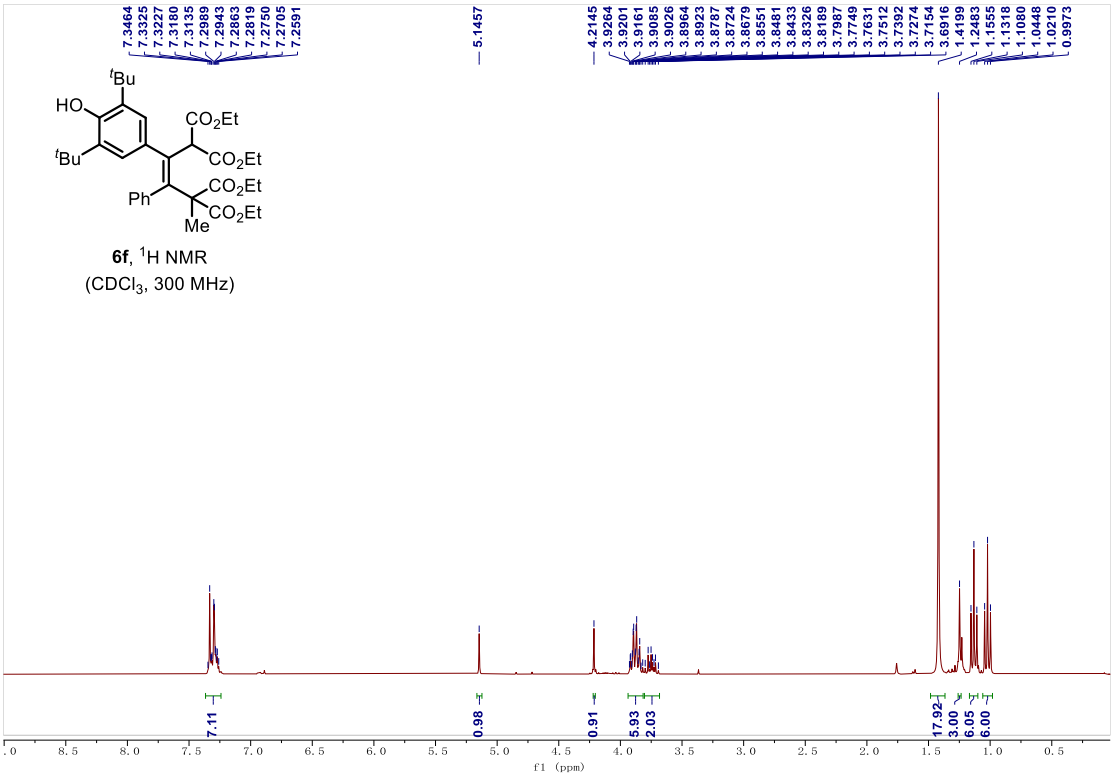
6e, ^{1}H NMR
($CDCl_3$, 300 MHz)



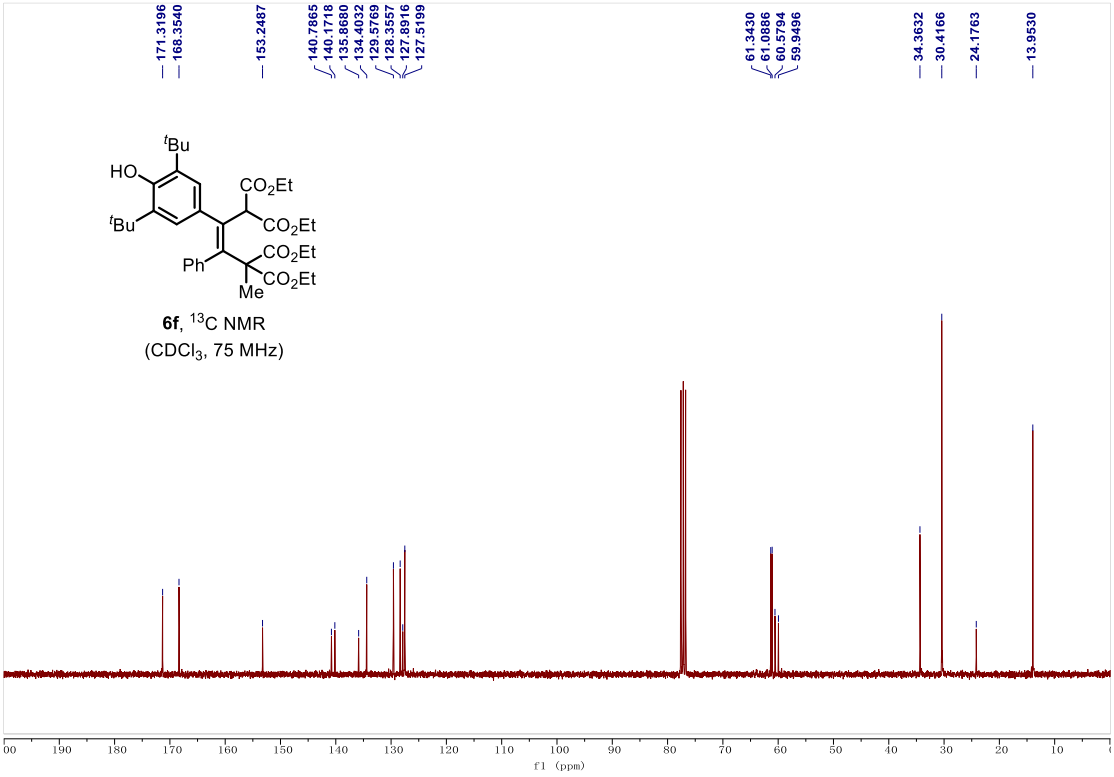
6e, ^{13}C NMR
($CDCl_3$, 75 MHz)



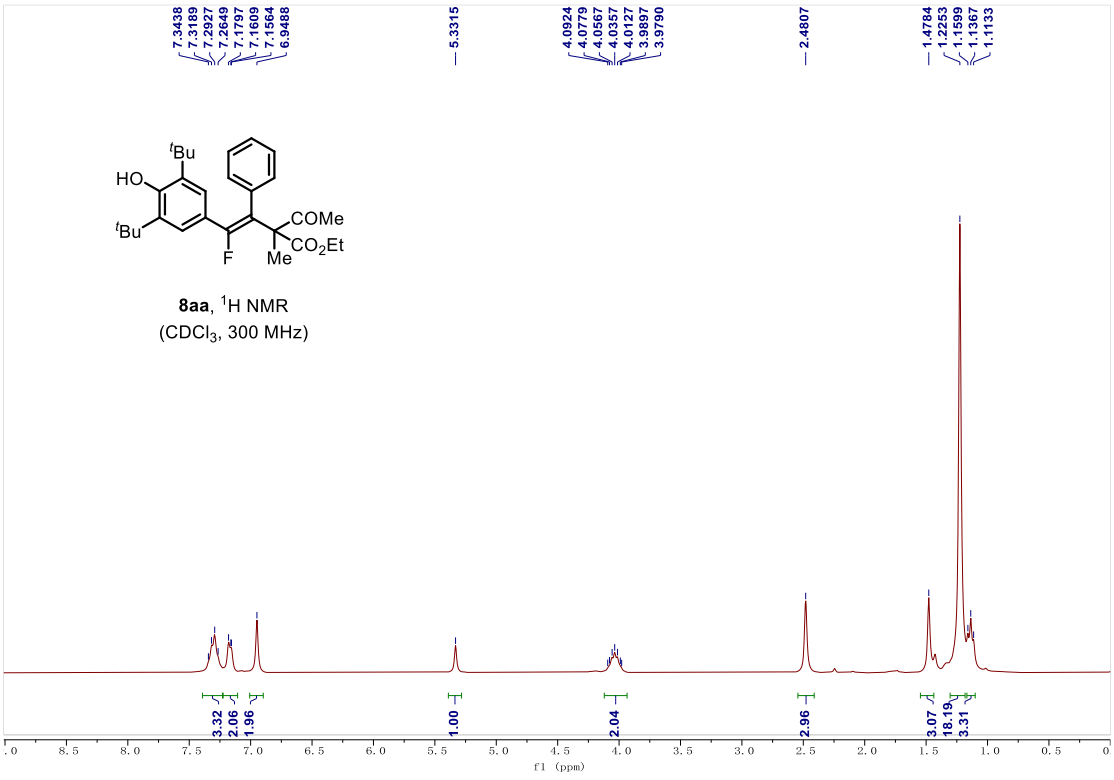
6e, ^{31}P NMR
($CDCl_3$, 121 MHz)



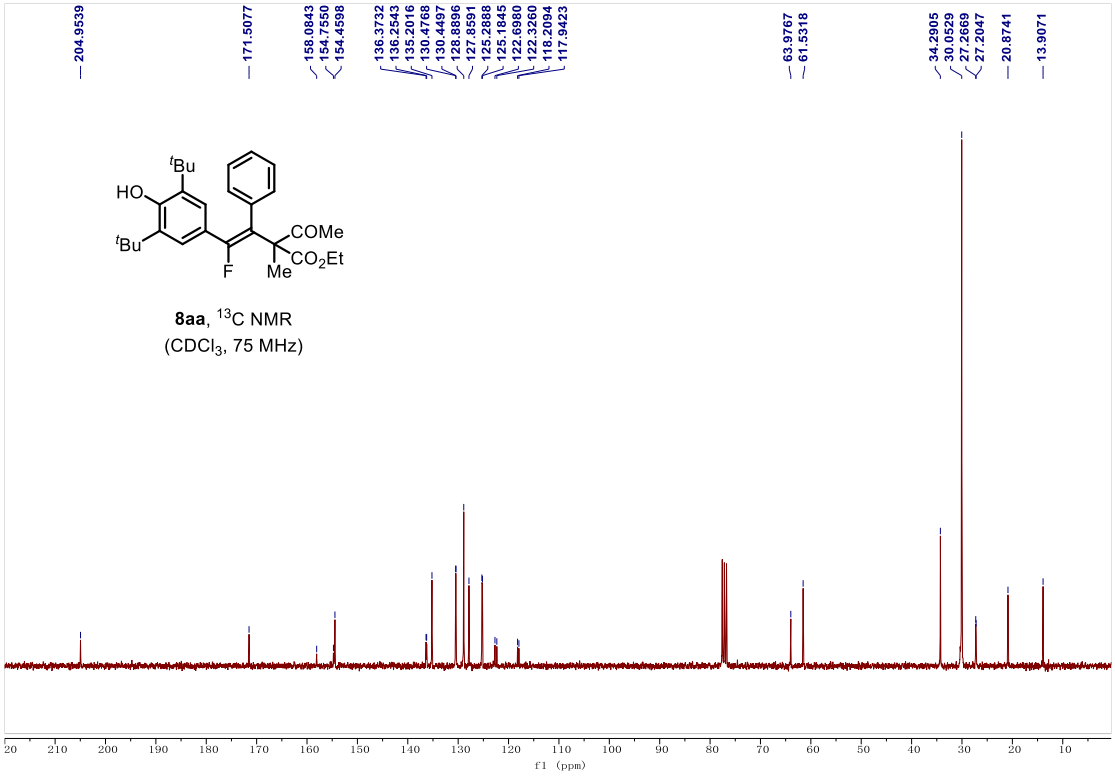
6f, ^{1}H NMR
($CDCl_3$, 300 MHz)



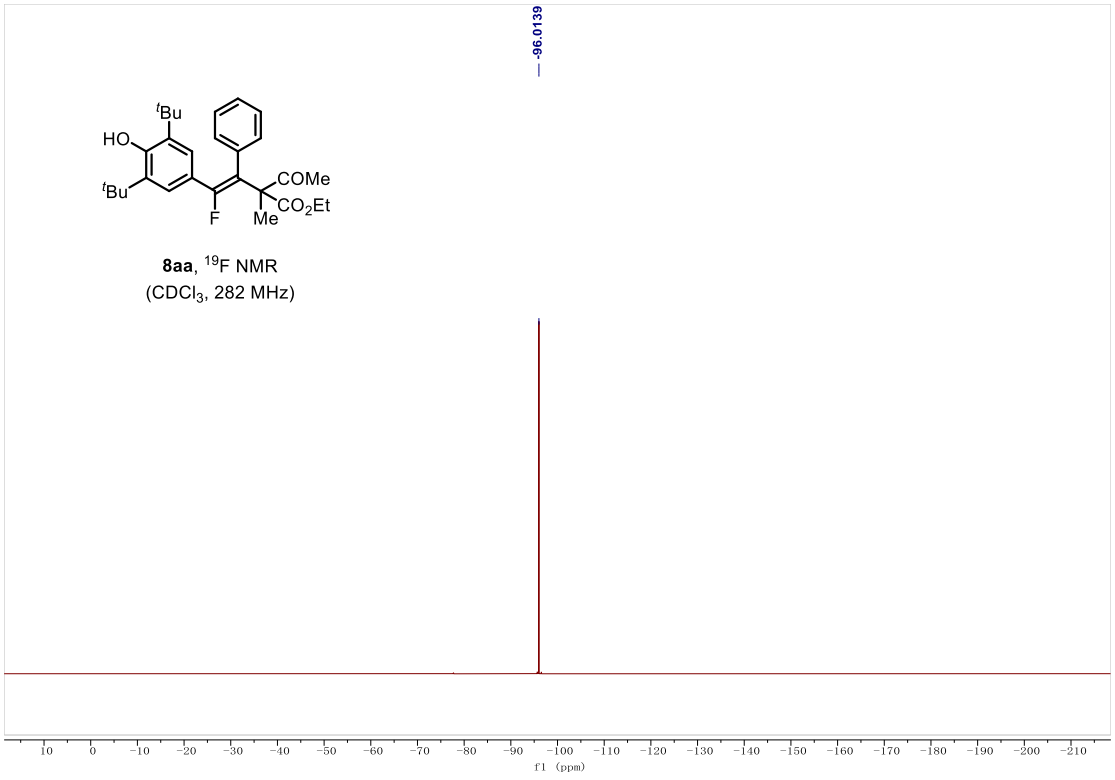
6f, ^{13}C NMR
($CDCl_3$, 75 MHz)



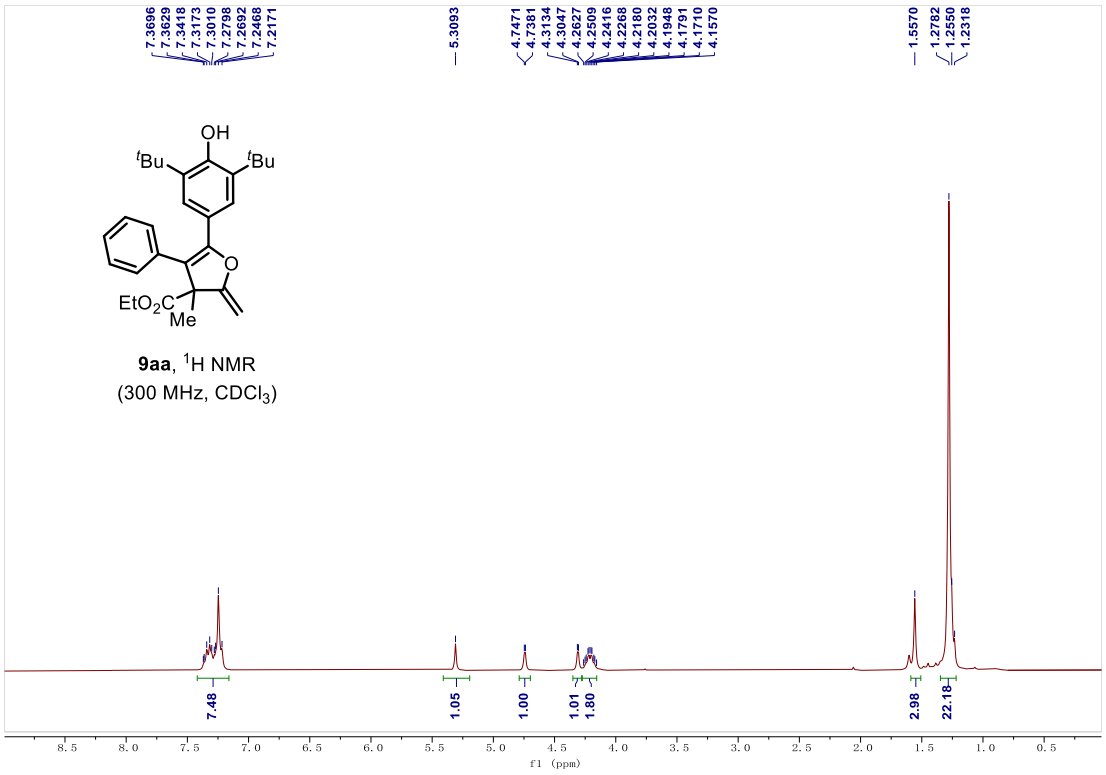
8aa, ^{1}H NMR
($CDCl_3$, 300 MHz)



8aa, ^{13}C NMR
($CDCl_3$, 75 MHz)



8aa, ^{19}F NMR
($CDCl_3$, 282 MHz)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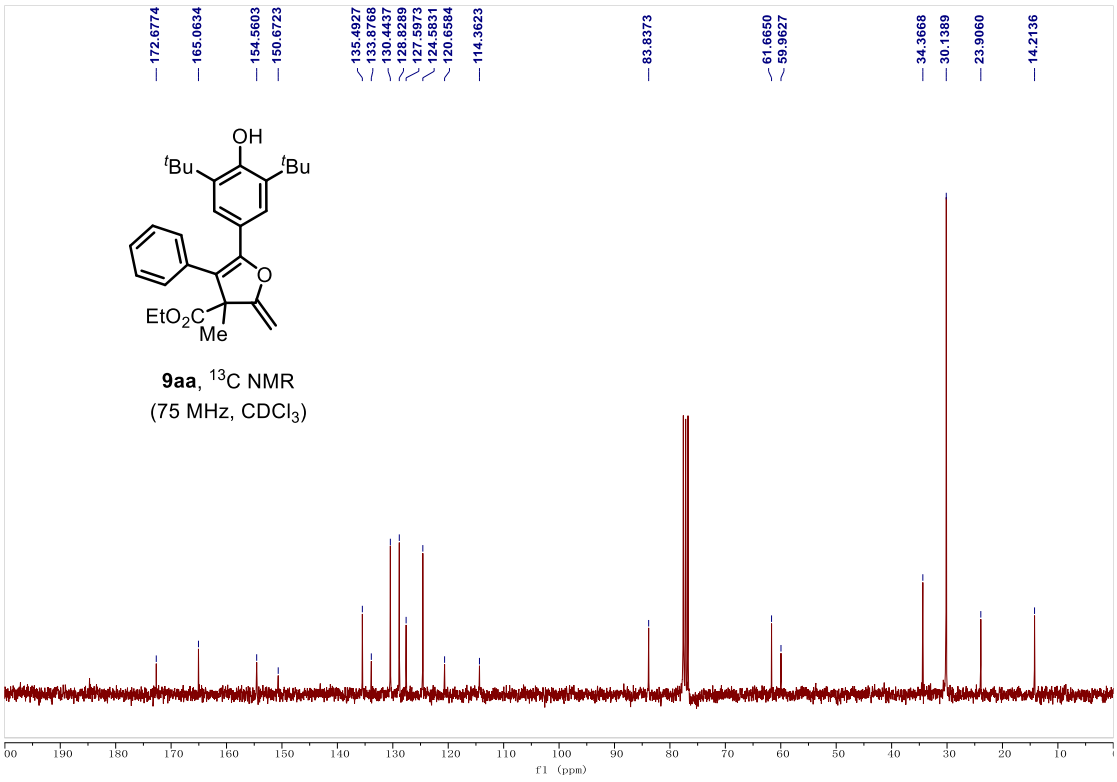
7.3629
7.3418
7.3173
7.3010
7.2798
7.2692
7.2468
7.2171
5.3093
4.7471
4.7381
4.3134
4.3047
4.2627
4.2509
4.2416
4.2268
4.2180
4.2032
4.1948
4.1791
4.1710
4.1570
1.5570
1.2782
1.2550
1.2318
OH
tBu
tBu
O
EtO2C
Me
9aa, 1H NMR
(300 MHz, CDCl3)
7.48
1.05
1.00
1.01
1.80
2.98
22.18
f1 (ppm)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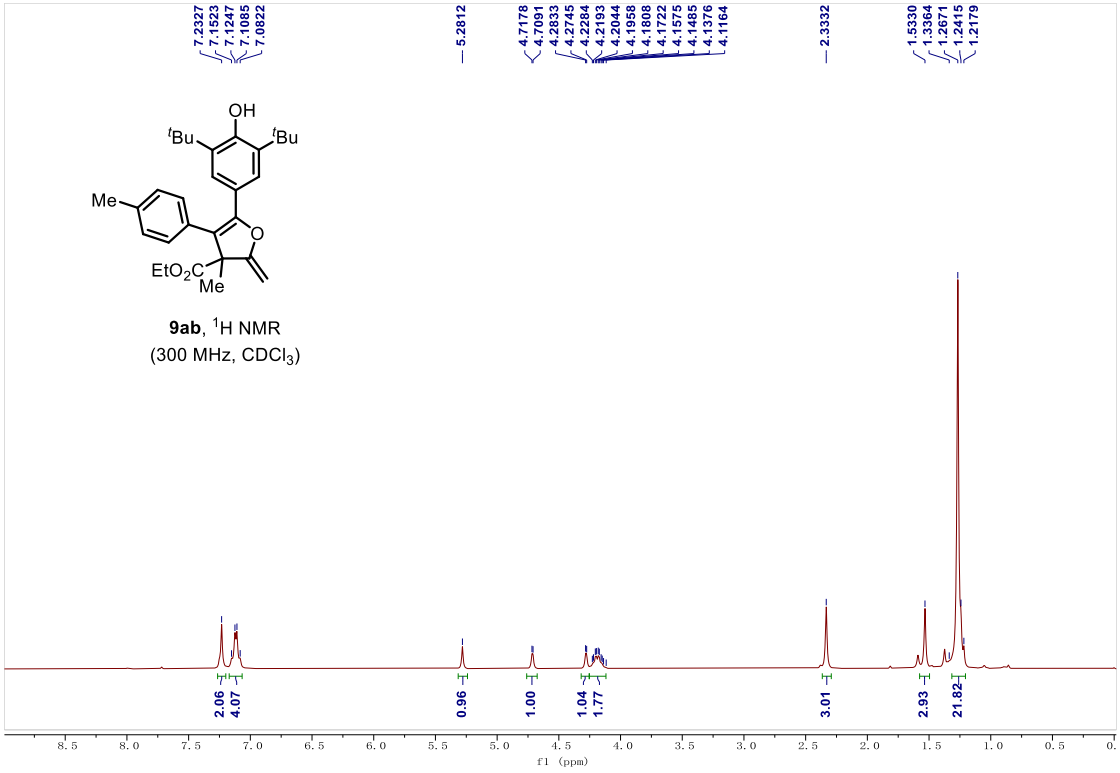
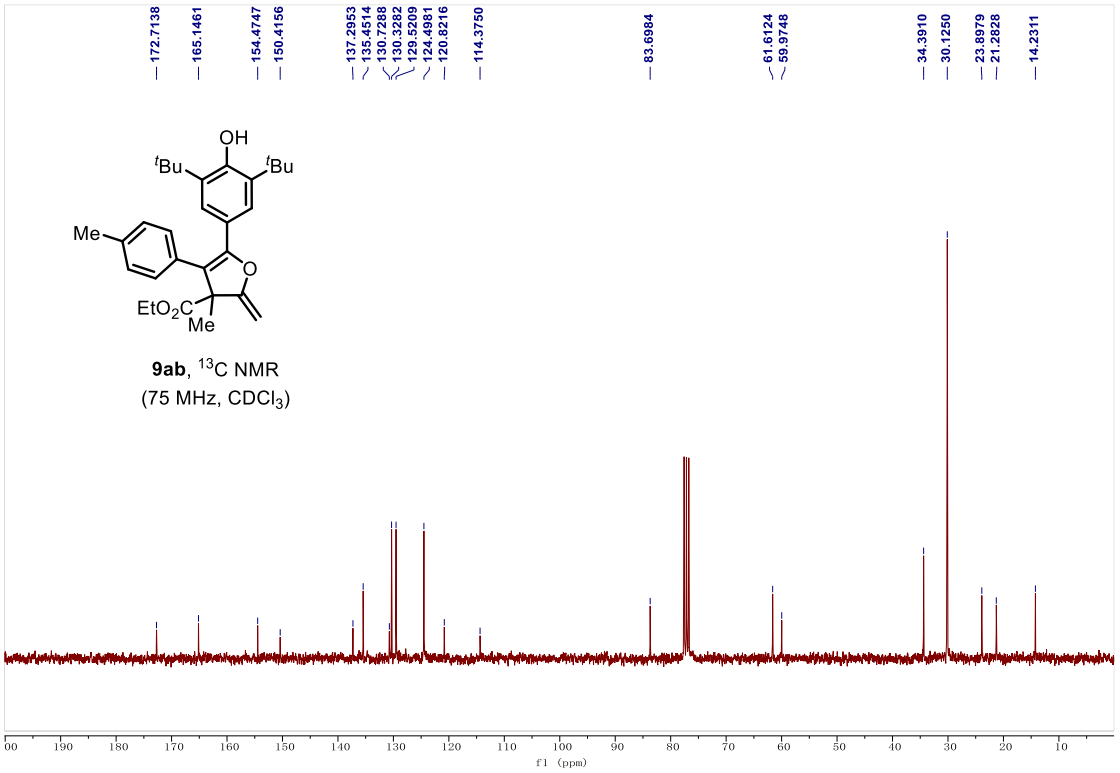
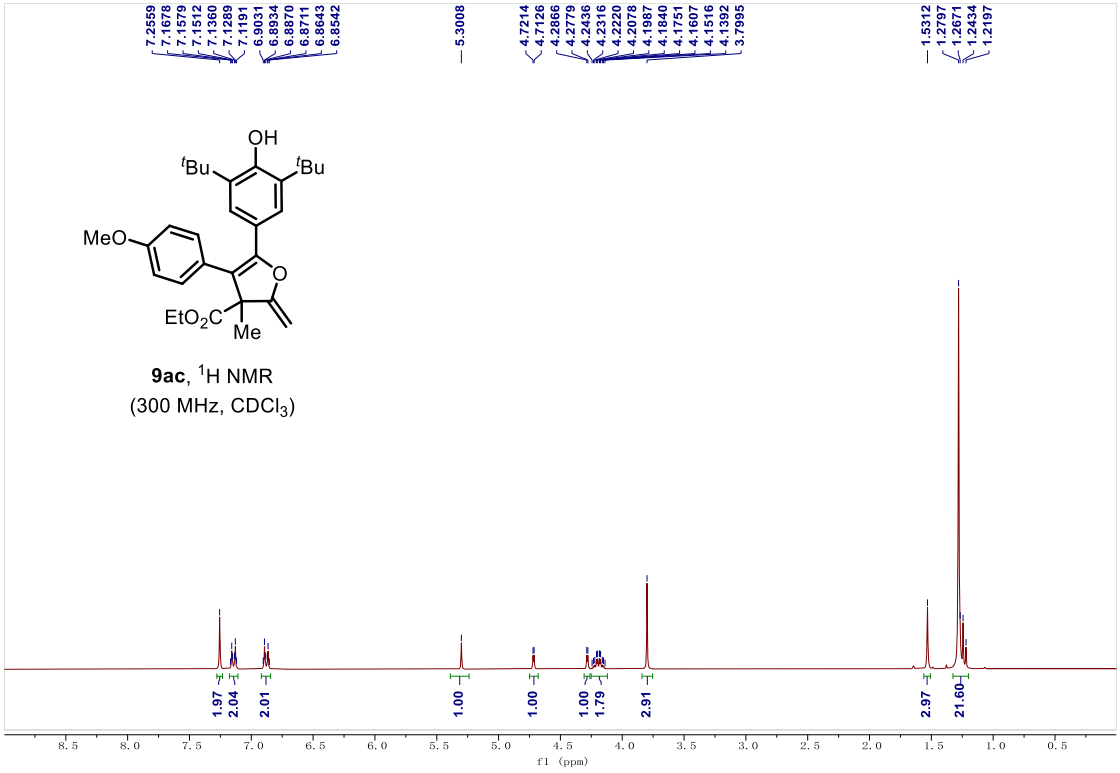
154.5603
150.6723
135.4927
133.8768
130.4437
128.8289
127.5973
124.5831
120.6584
114.3623
83.8373
61.6650
59.9627
34.3668
30.1389
23.9060
14.2136
OH
tBu
tBu
O
EtO2C
Me
9aa, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



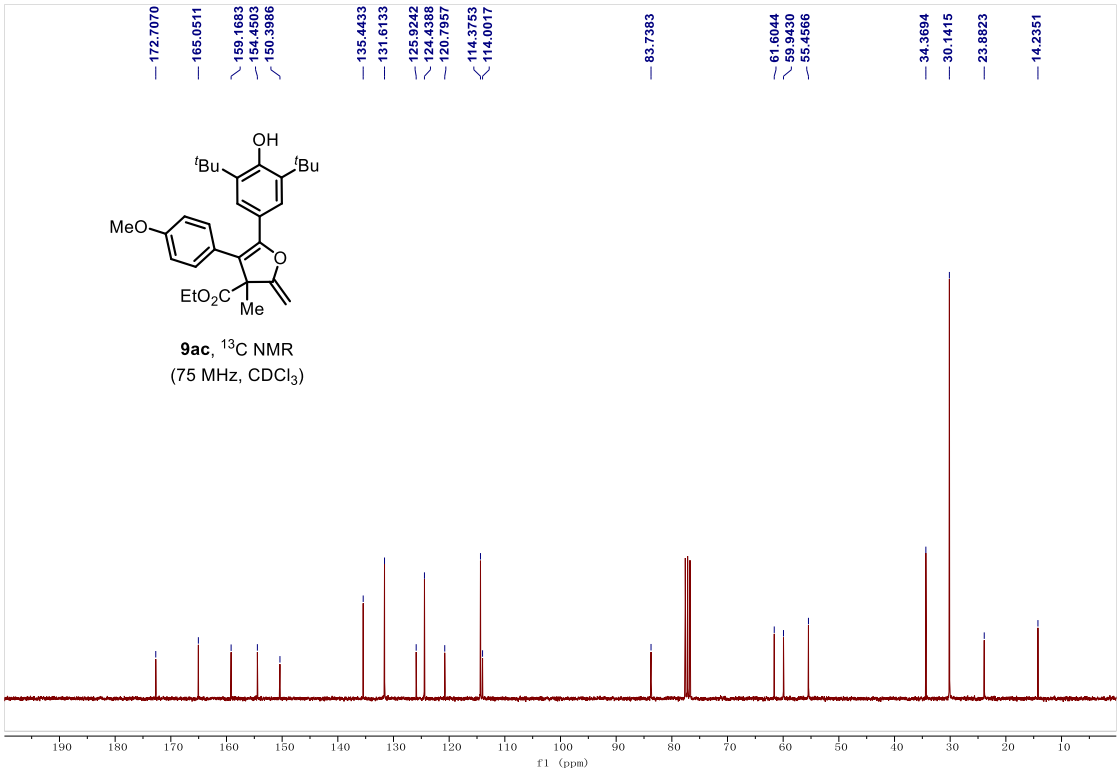
9ab, ^{1}H NMR
(300 MHz, $CDCl_3$)



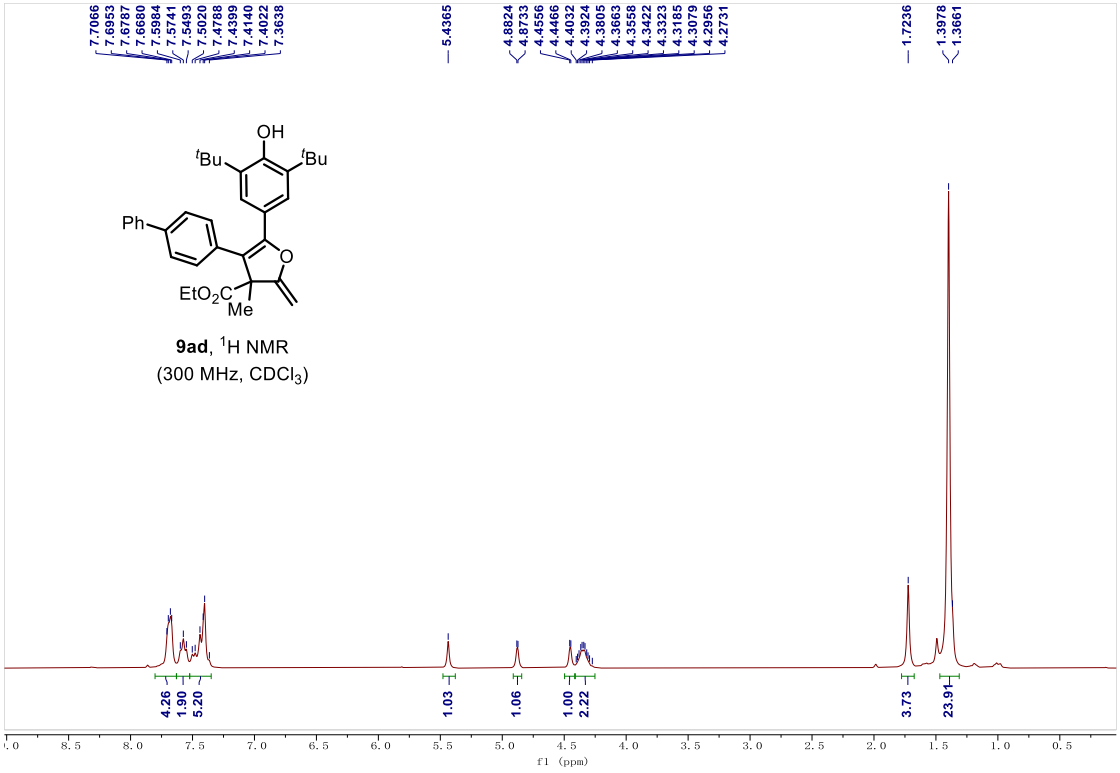
9ab, ^{13}C NMR
(75 MHz, $CDCl_3$)



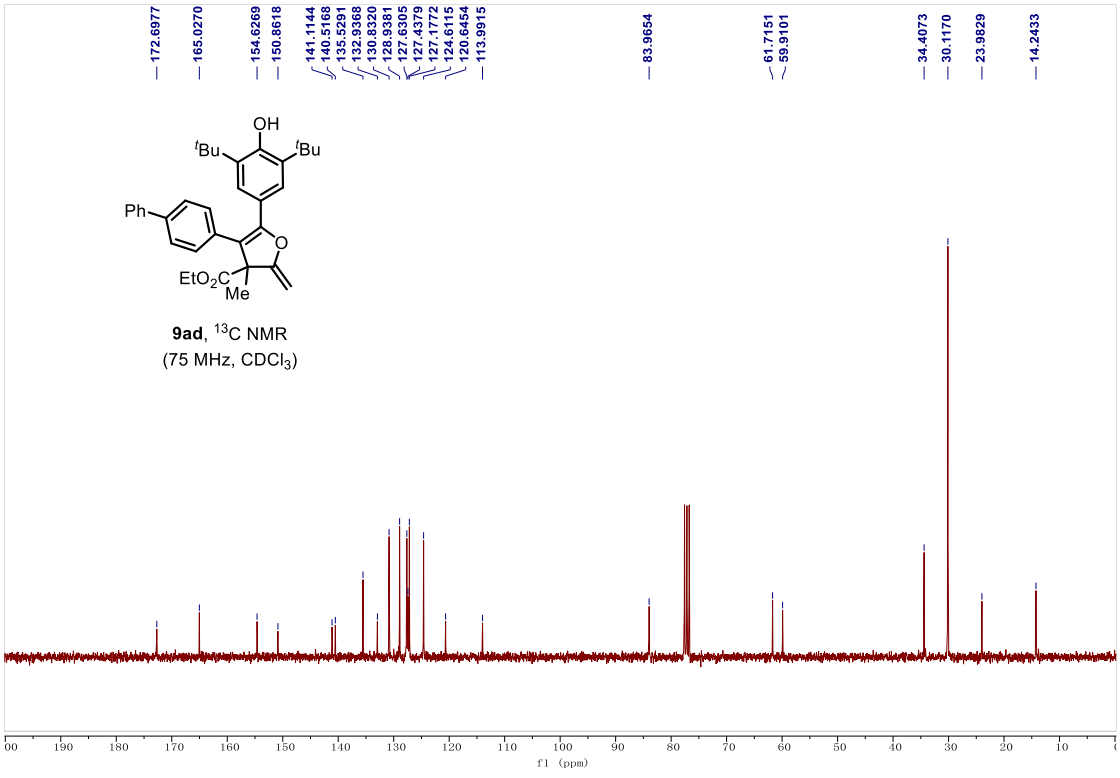
9ac, ^{1}H NMR
(300 MHz, $CDCl_3$)



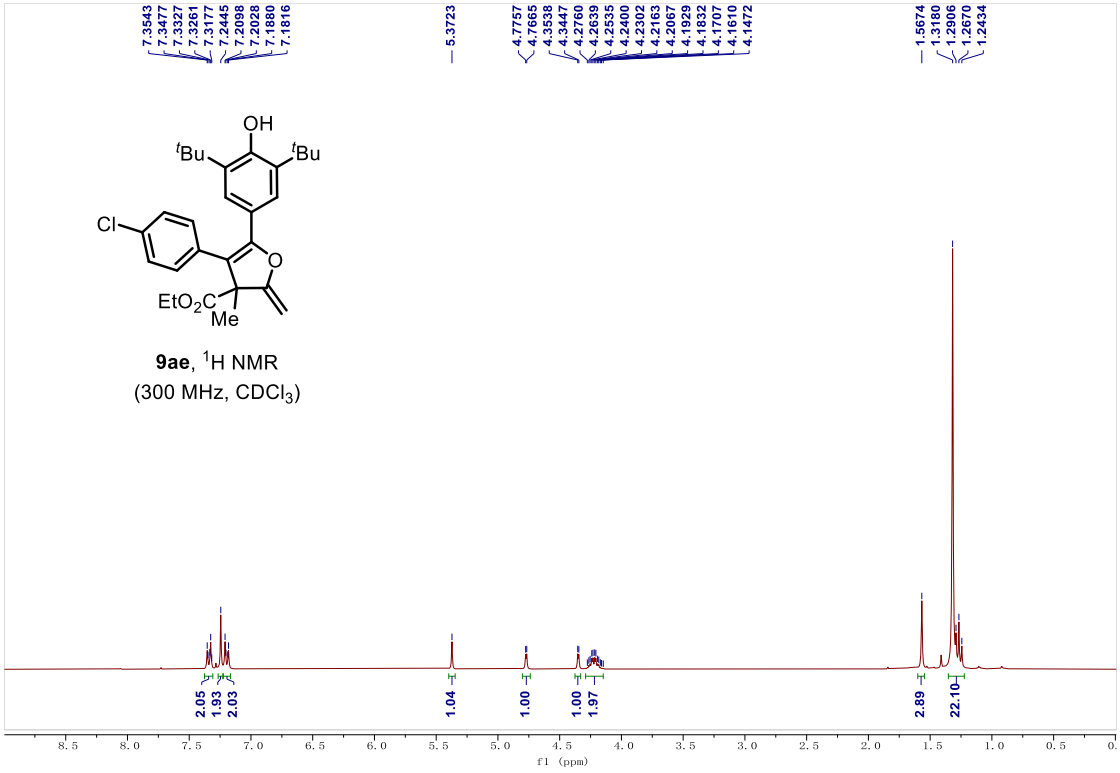
9ac, ^{13}C NMR
(75 MHz, $CDCl_3$)



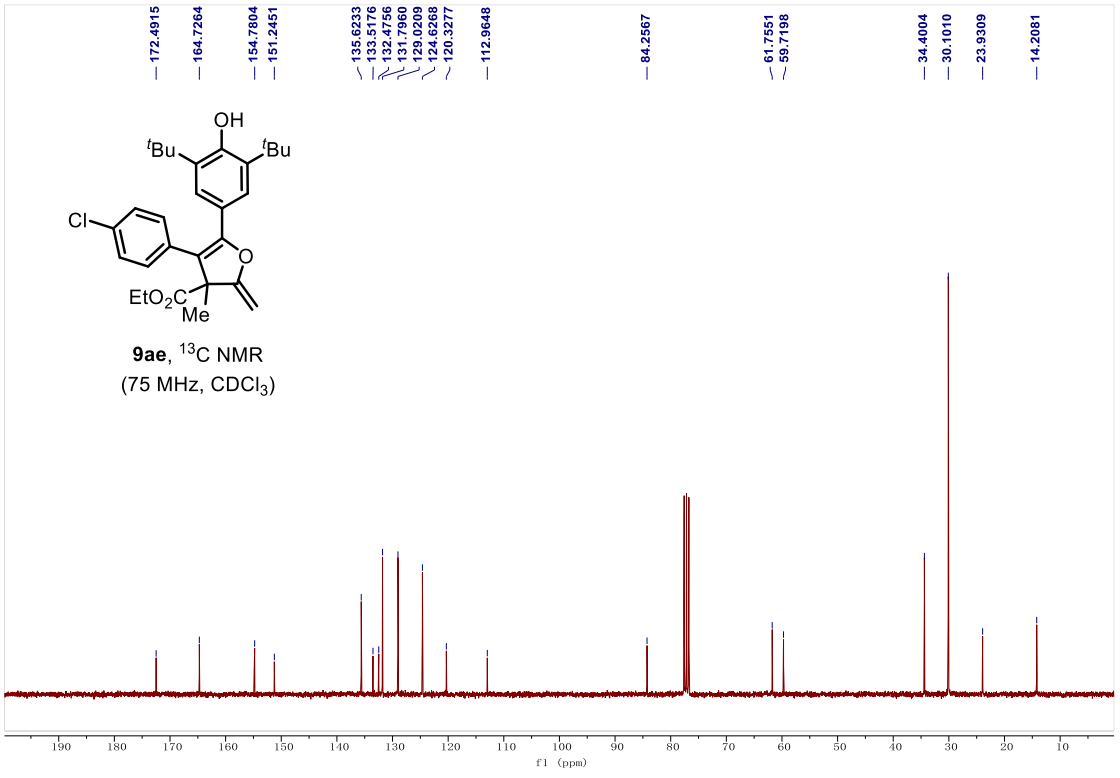
9ad, ^{1}H NMR
(300 MHz, $CDCl_3$)



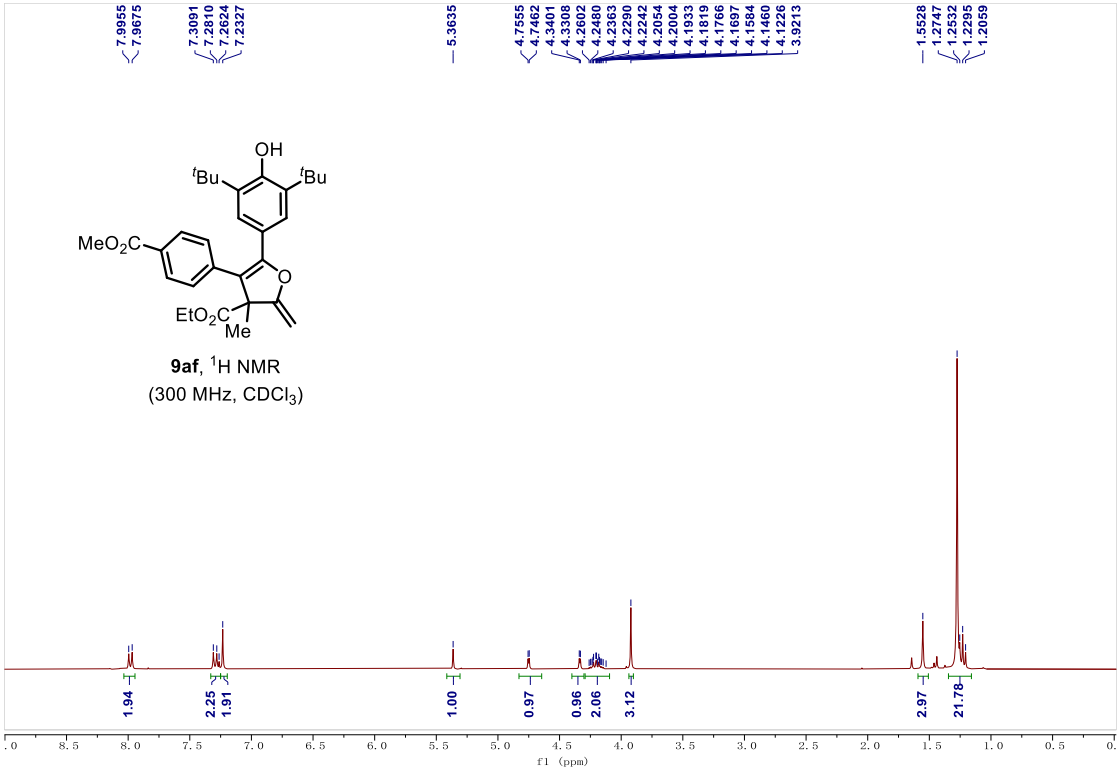
9ad, ^{13}C NMR
(75 MHz, $CDCl_3$)



9ae, ^{1}H NMR
(300 MHz, $CDCl_3$)



9ae, ^{13}C NMR
(75 MHz, $CDCl_3$)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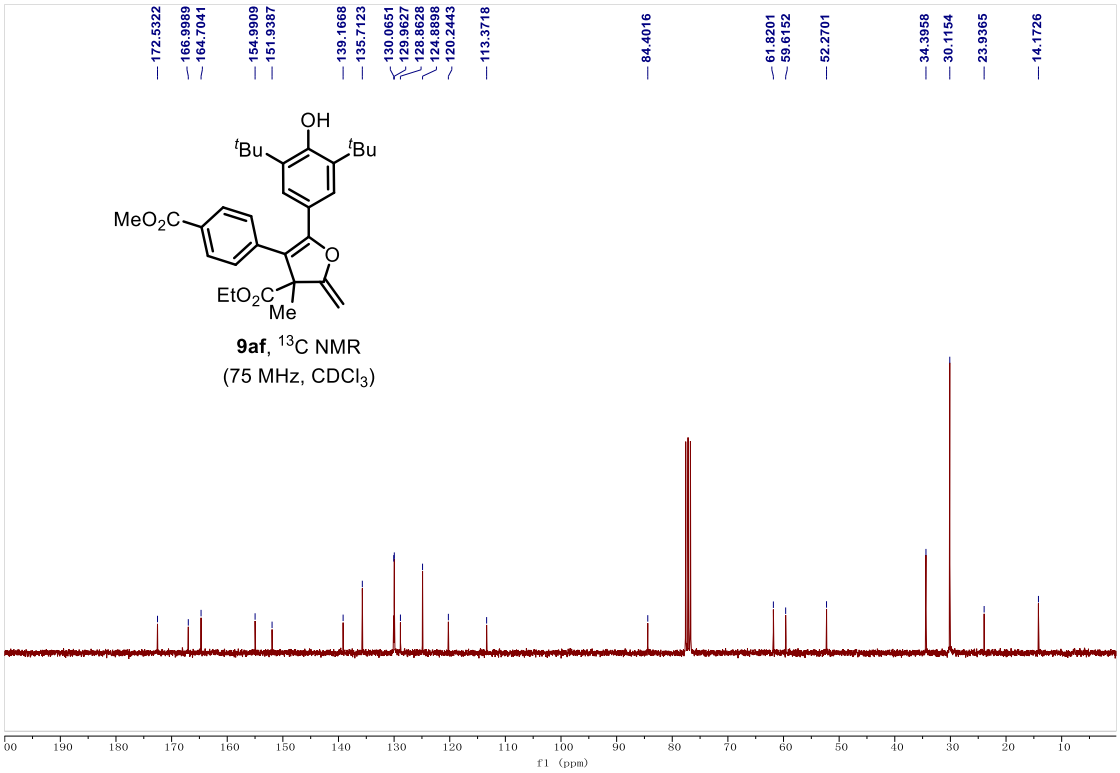
7.9675
7.3091
7.2810
7.2624
7.2327
5.3635
4.7555
4.7462
4.3401
4.3308
4.2602
4.2480
4.2363
4.2290
4.2242
4.2054
4.2004
4.1933
4.1819
4.1766
4.1697
4.1584
4.1460
4.1226
3.9213
1.5528
1.2747
1.2532
1.2295
1.2059
OH
tBu
tBu
MeO2C
O
EtO2C
Me
9af, 1H NMR
(300 MHz, CDCl3)
1.94
2.25
1.91
1.00
0.97
0.96
2.06
3.12
2.97
21.78
f1 (ppm)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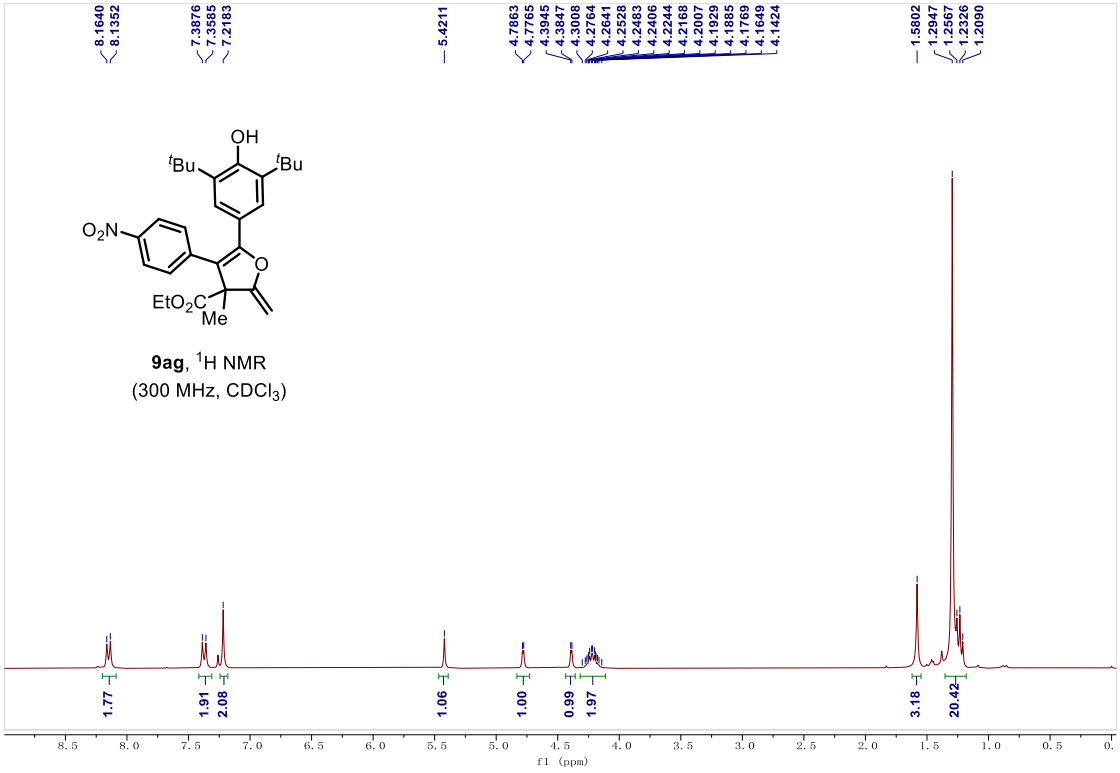
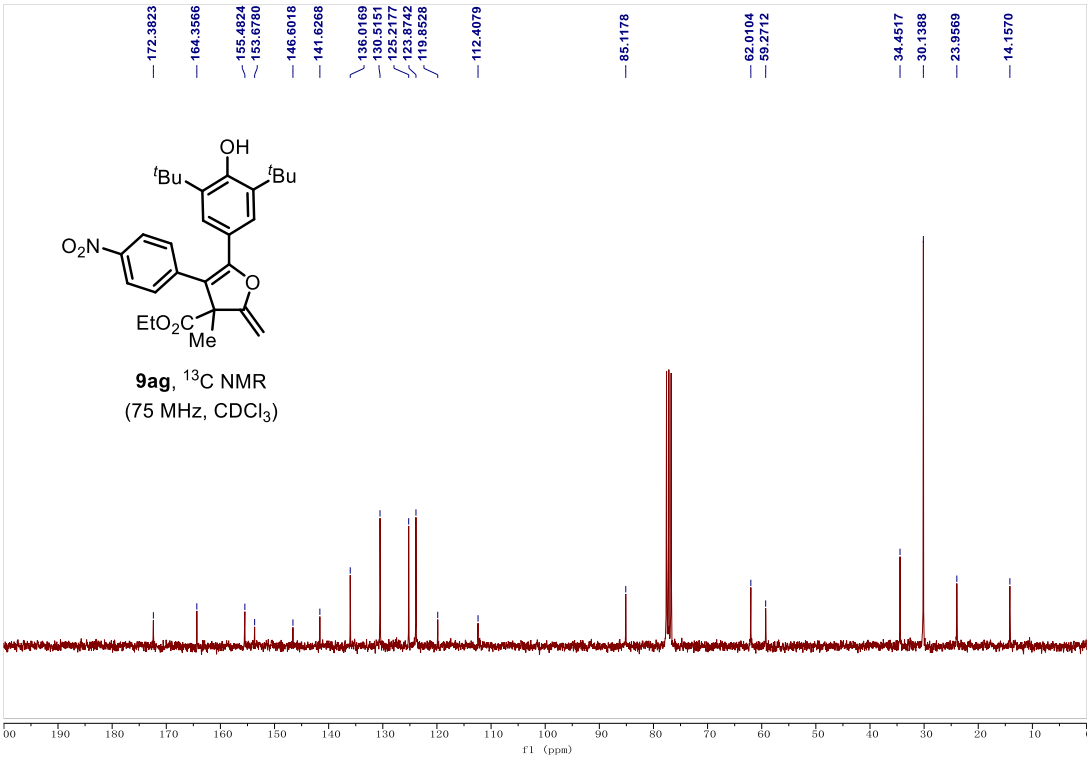
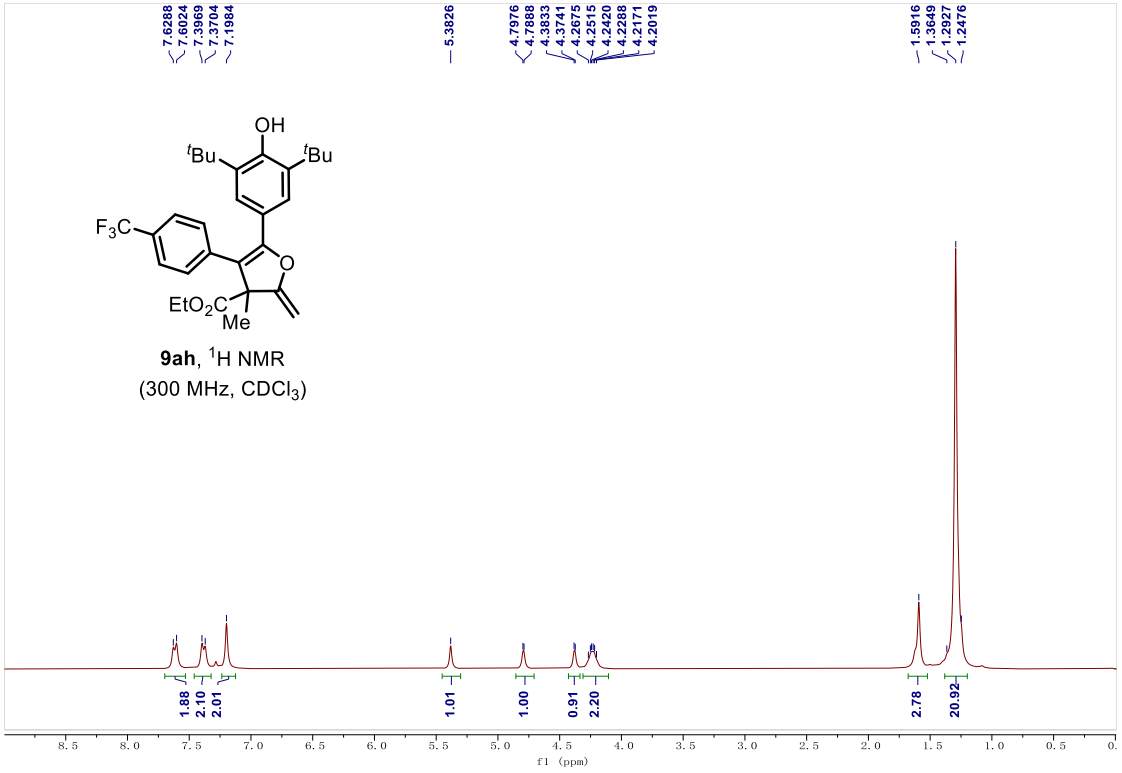
164.7041
154.9909
151.9387
139.1668
135.7123
130.0651
129.9627
128.8628
124.8898
120.2443
113.3718
84.4016
61.8201
59.6152
52.2701
34.3958
30.1154
23.9365
14.1726
OH
tBu
tBu
MeO2C
O
EtO2C
Me
9af, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



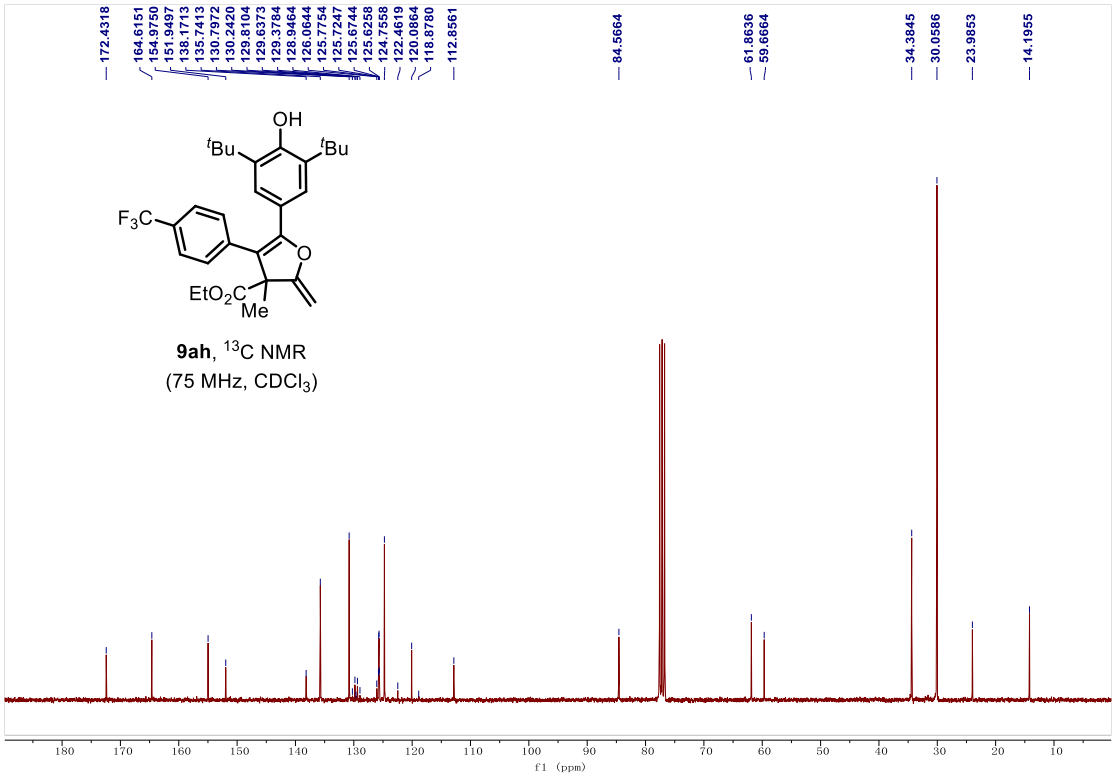
9ag, ^{1}H NMR
(300 MHz, $CDCl_3$)



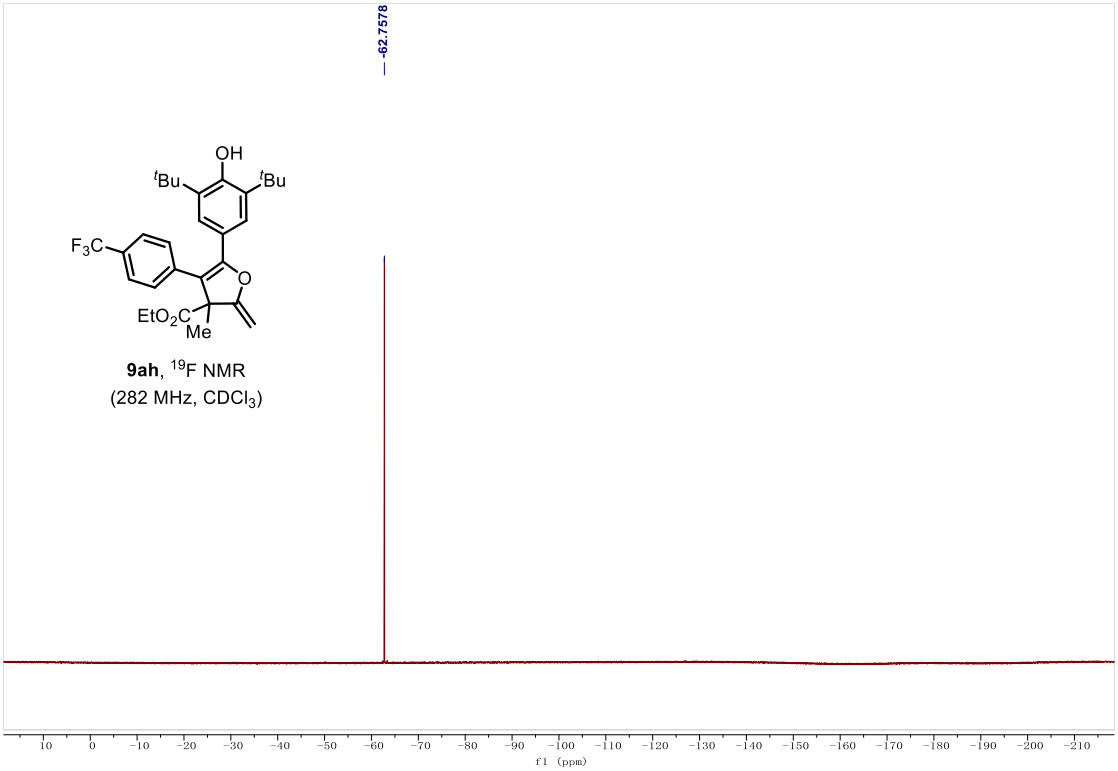
9ag, ^{13}C NMR
(75 MHz, $CDCl_3$)



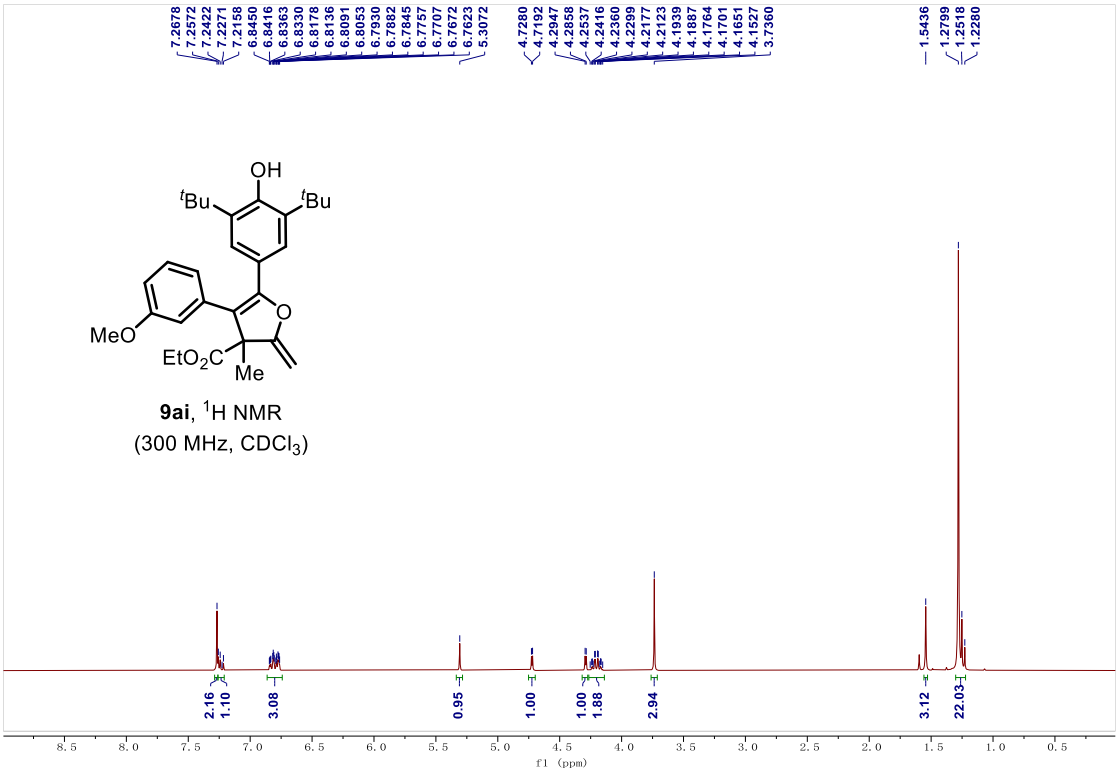
9ah, ^{1}H NMR
(300 MHz, $CDCl_3$)



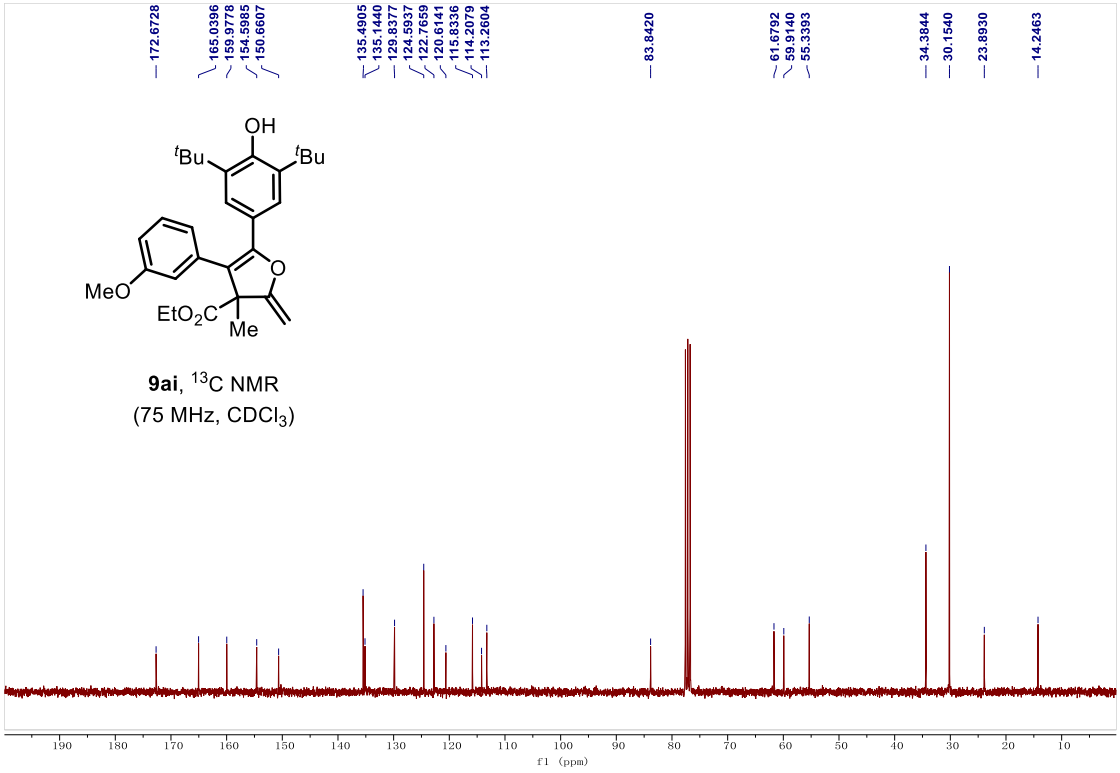
9ah, ^{13}C NMR
(75 MHz, $CDCl_3$)



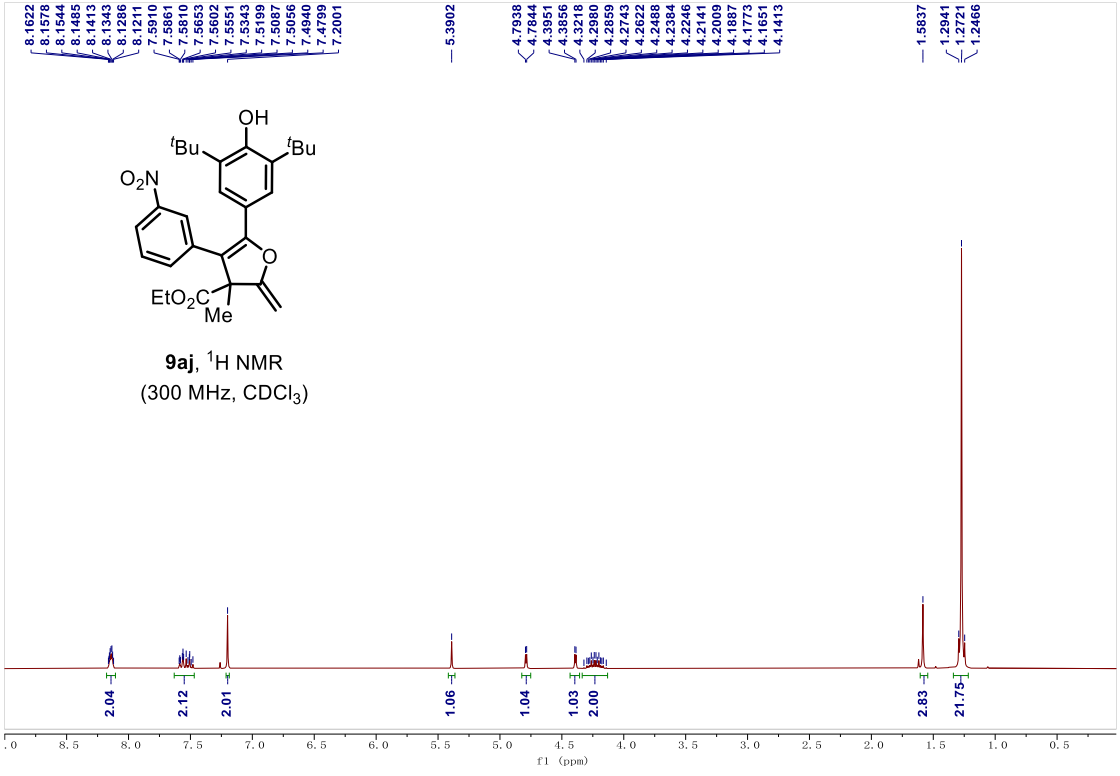
9ah, ^{19}F NMR
(282 MHz, $CDCl_3$)



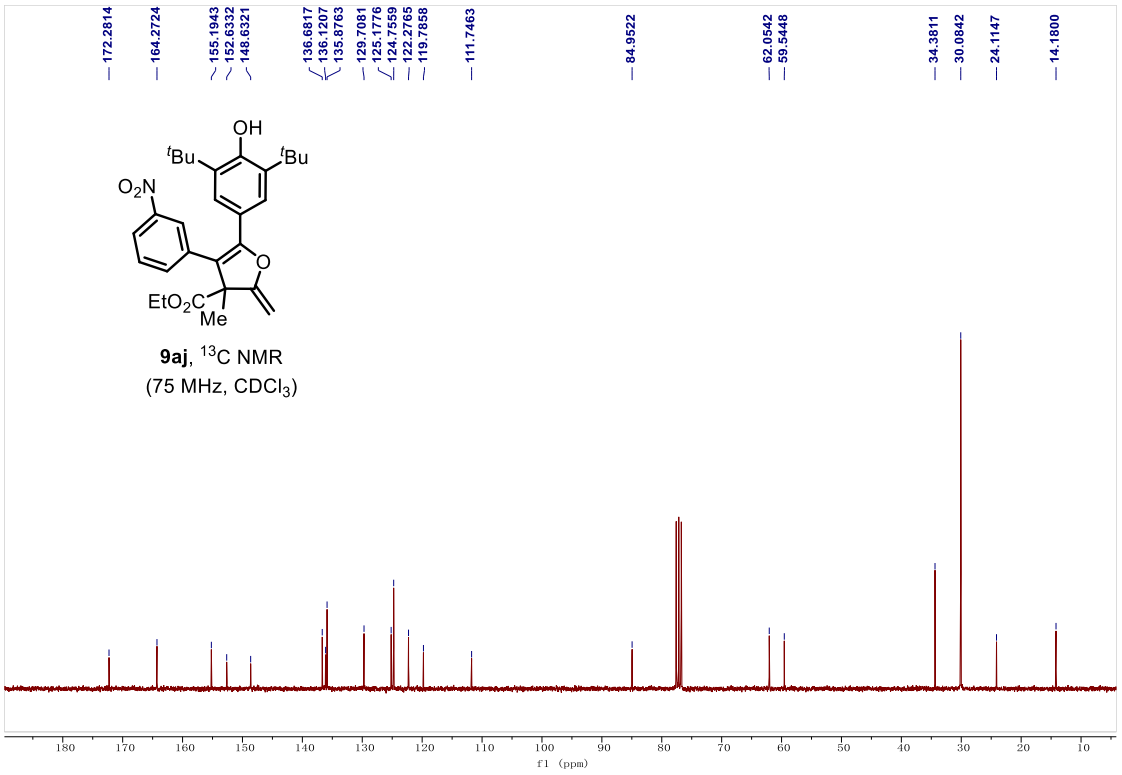
9ai, ^{1}H NMR
(300 MHz, $CDCl_3$)



9ai, ^{13}C NMR
(75 MHz, $CDCl_3$)



9aj, ^{1}H NMR
(300 MHz, $CDCl_3$)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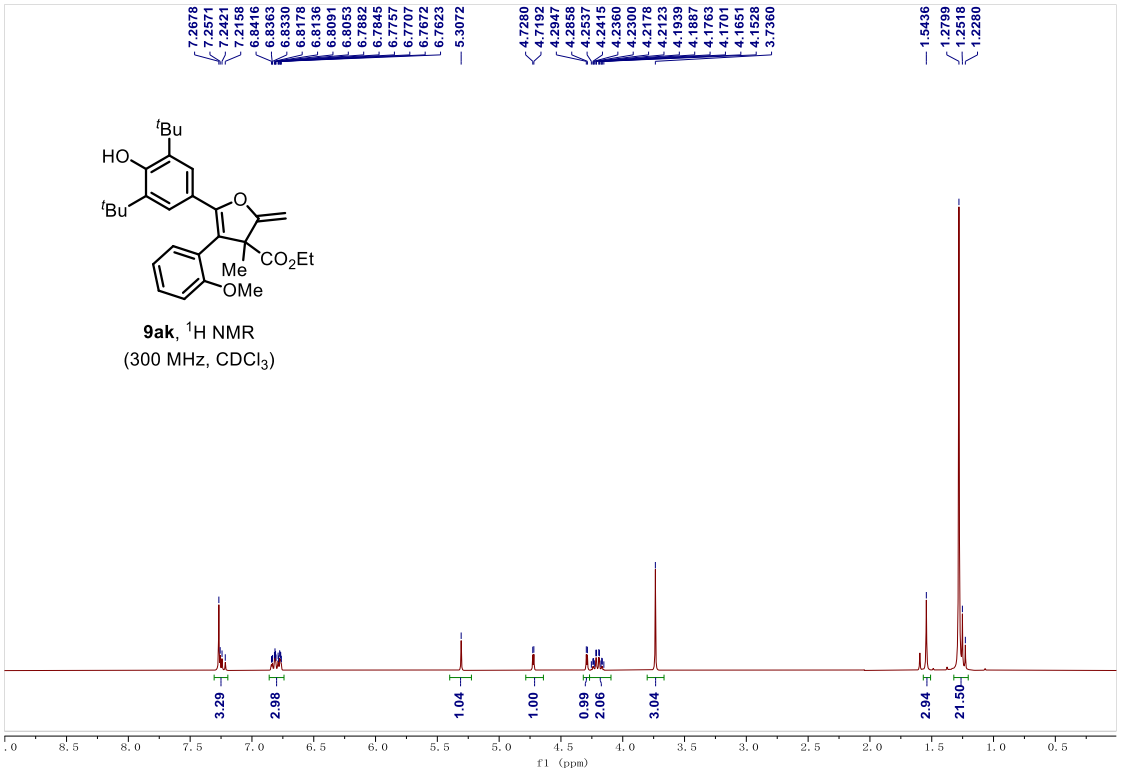
155.1943
152.6332
148.6321
136.6817
136.1207
135.8763
129.7081
125.1776
124.7559
122.2765
119.7858
111.7463
84.9522
62.0542
59.5448
34.3811
30.0842
24.1147
14.1800
OH
tBu
tBu
O2N
O
EtO2C
Me
9aj, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)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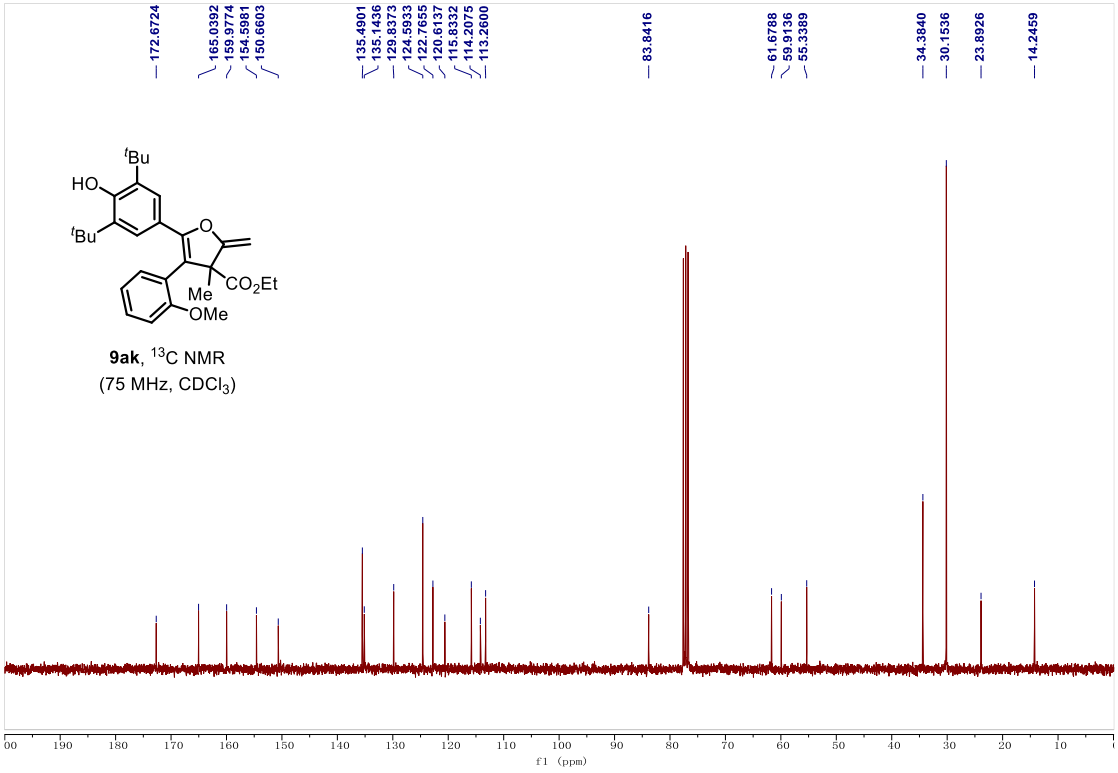
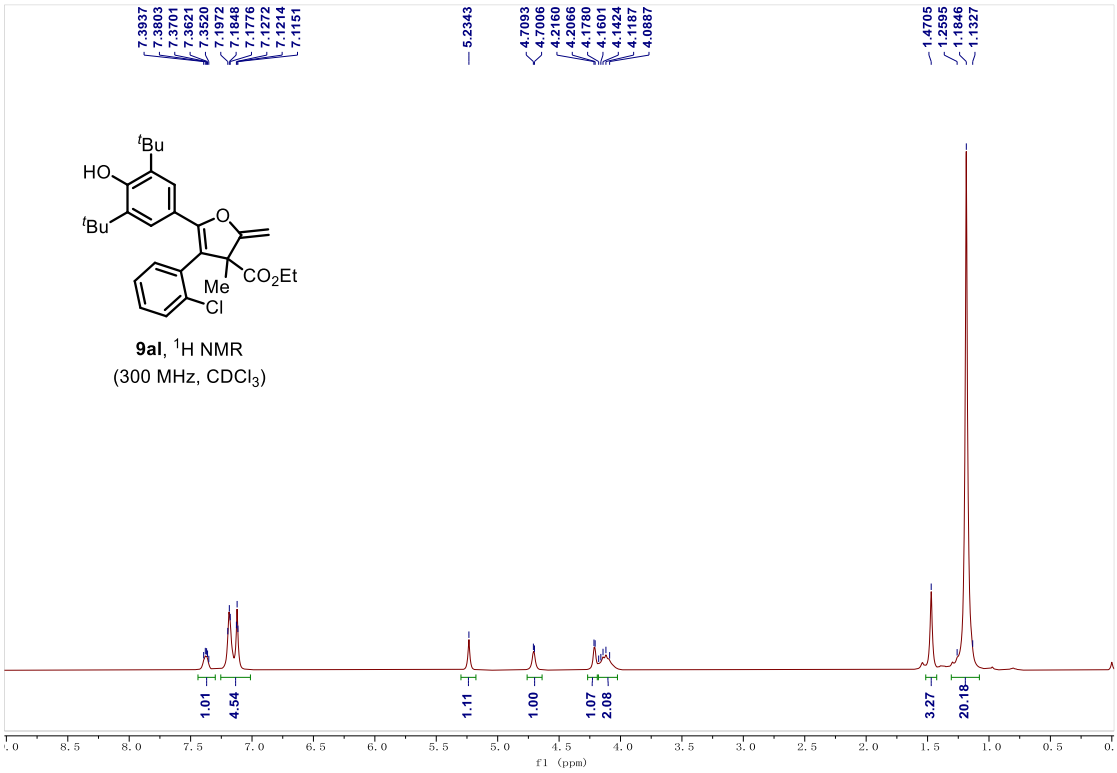
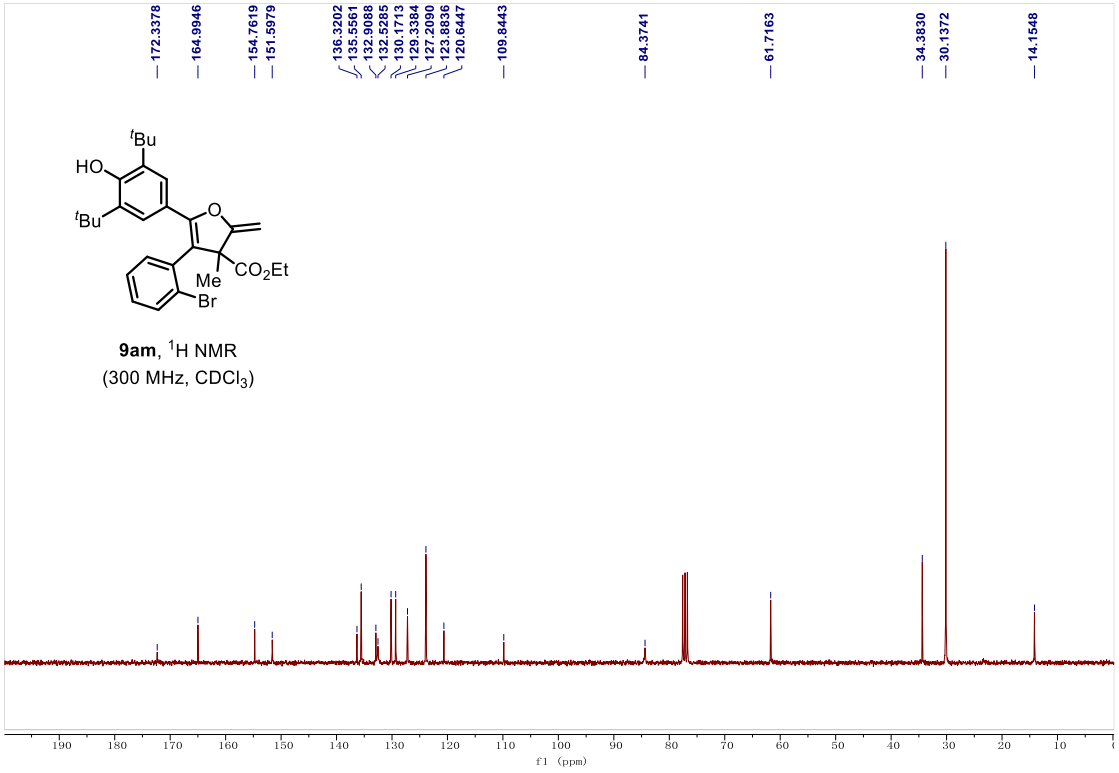
7.2421
7.2158
6.8416
6.8363
6.8330
6.8178
6.8136
6.8091
6.8053
6.7882
6.7845
6.7757
6.7707
6.7672
6.7623
5.3072
4.7280
4.7192
4.2947
4.2858
4.2537
4.2415
4.2360
4.2300
4.2178
4.2123
4.1939
4.1887
4.1763
4.1701
4.1651
4.1528
3.7360
1.5436
1.2799
1.2518
1.2280
tBu
HO
tBu
O
CO2Et
Me
OMe
3.29
2.98
1.04
1.00
0.99
2.06
3.04
2.94
21.50
9ak, 1H NMR
(300 MHz, CDCl3)
f1 (ppm)

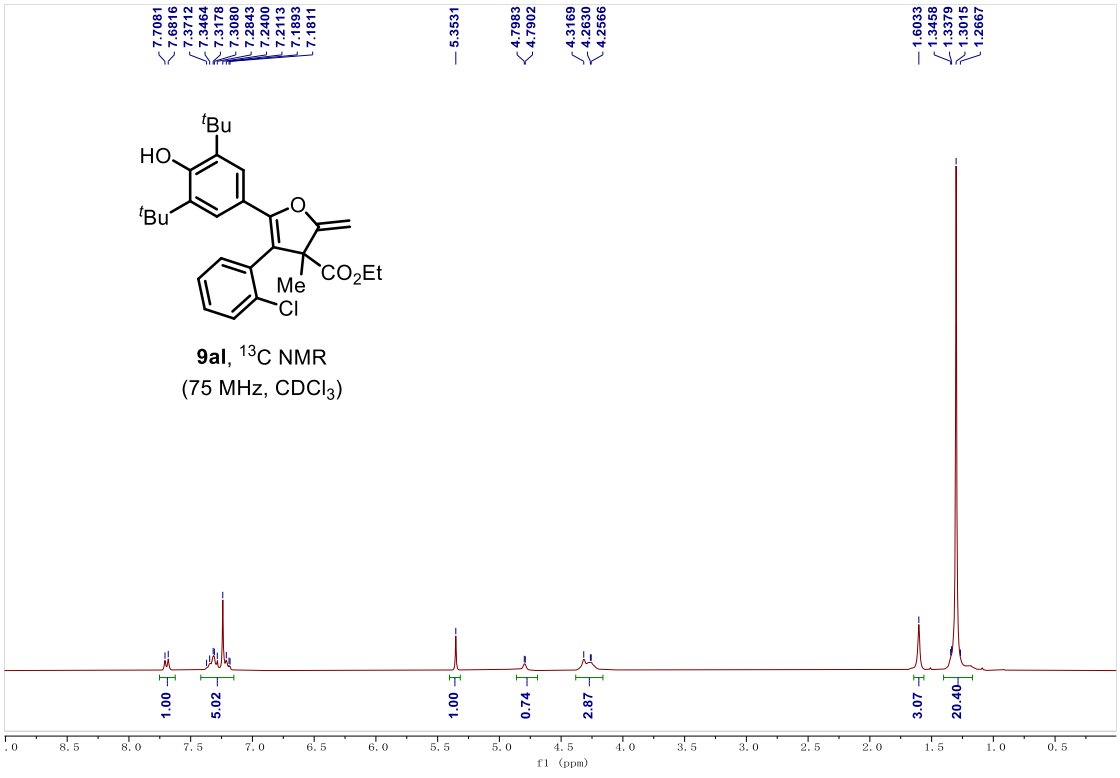


9ak, ^{13}C NMR
(75 MHz, $CDCl_3$)



9al, ^{1}H NMR
(300 MHz, $CDCl_3$)


172.3378
164.9946
154.7619
151.5979
136.3202
135.5561
132.9088
132.5285
130.1713
129.3384
127.2090
123.8836
120.6447
109.8443
84.3741
61.7163
34.3830
30.1372
14.1548
tBu
HO
tBu
O
CO2Et
Me
Br
9am, 1H NMR
(300 MHz, CDCl3)
f1 (ppm)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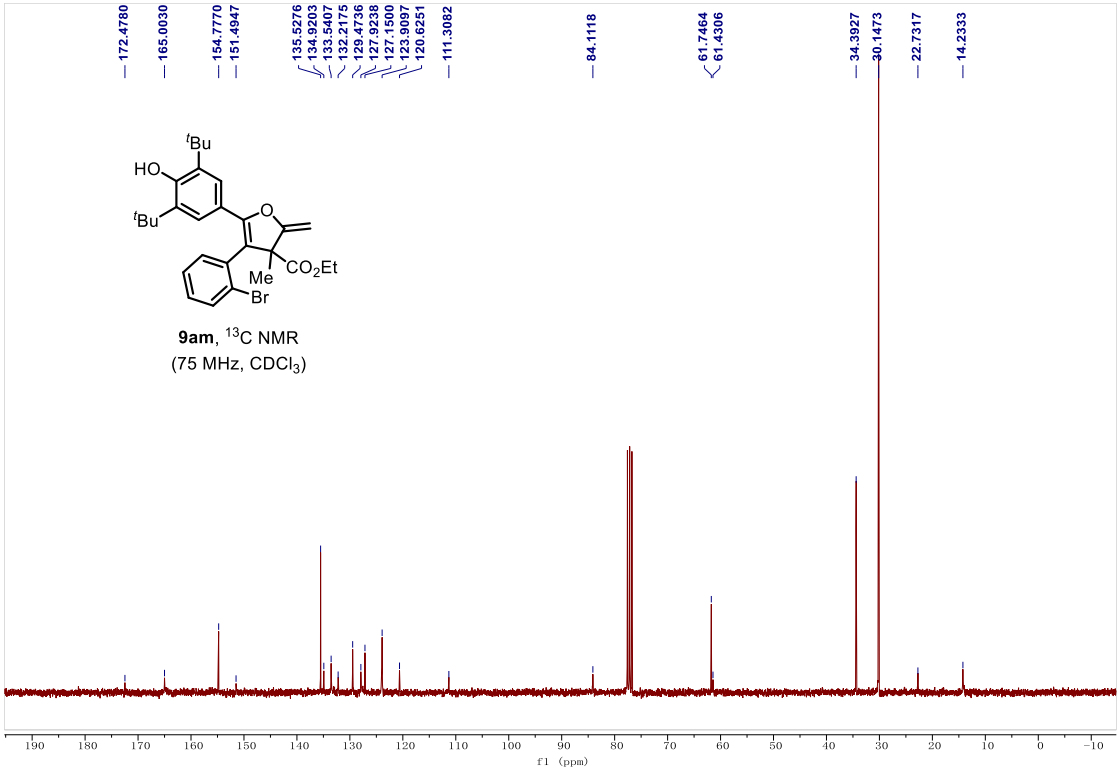
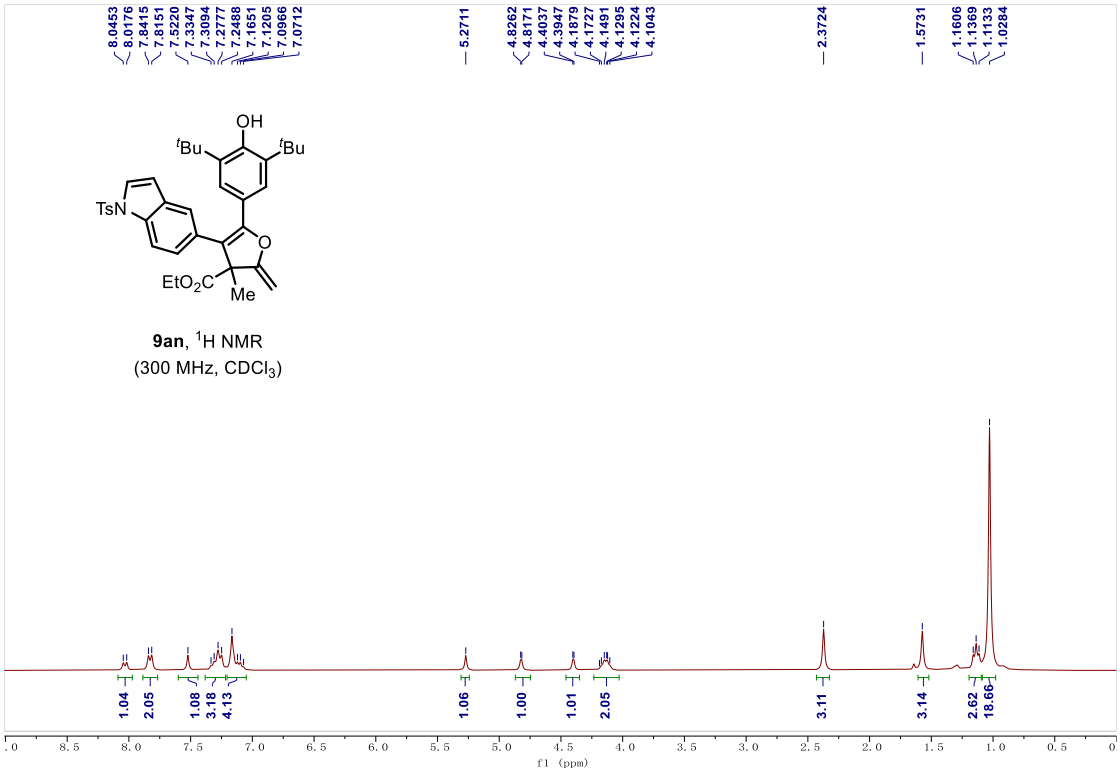
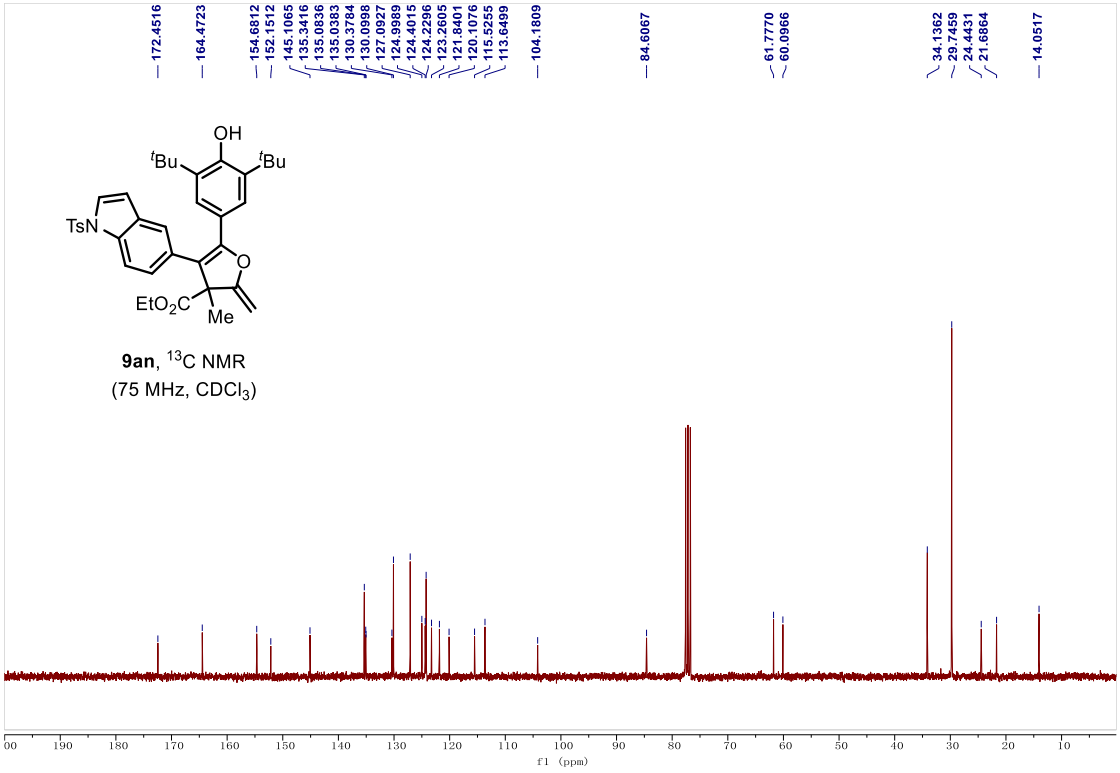
7.3712
7.3464
7.3178
7.3080
7.2843
7.2400
7.2113
7.1893
7.1811
5.3531
4.7983
4.7902
4.3169
4.2630
4.2566
1.6033
1.3458
1.3379
1.3015
1.2667
1.00
5.02
1.00
0.74
2.87
3.07
20.40
tBu
HO
tBu
O
CO2Et
Me
Cl
9al, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



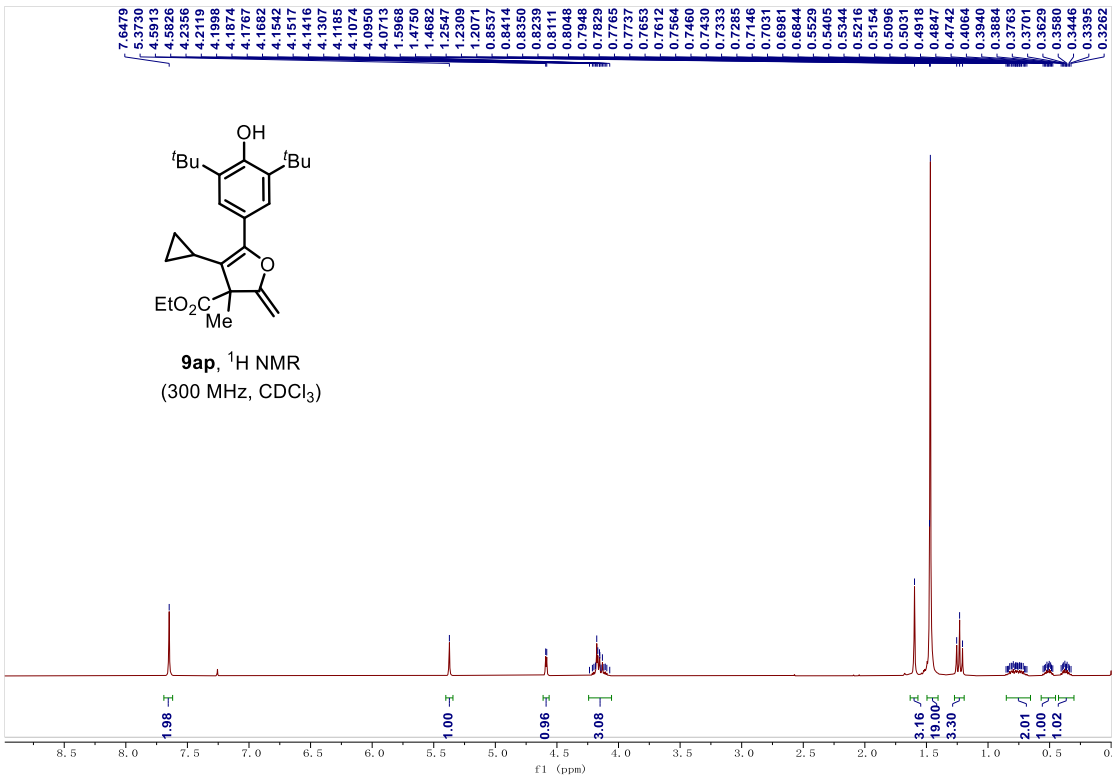
9am, ^{13}C NMR
(75 MHz, $CDCl_3$)



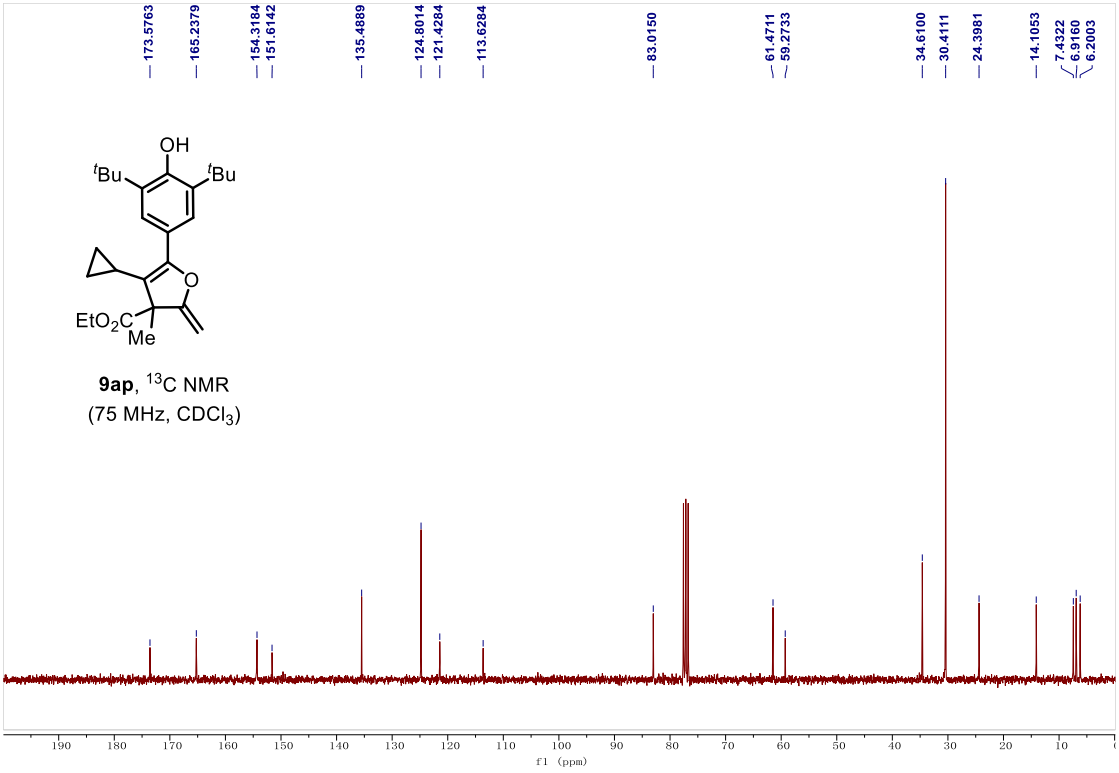
9an, ^{1}H NMR
(300 MHz, $CDCl_3$)



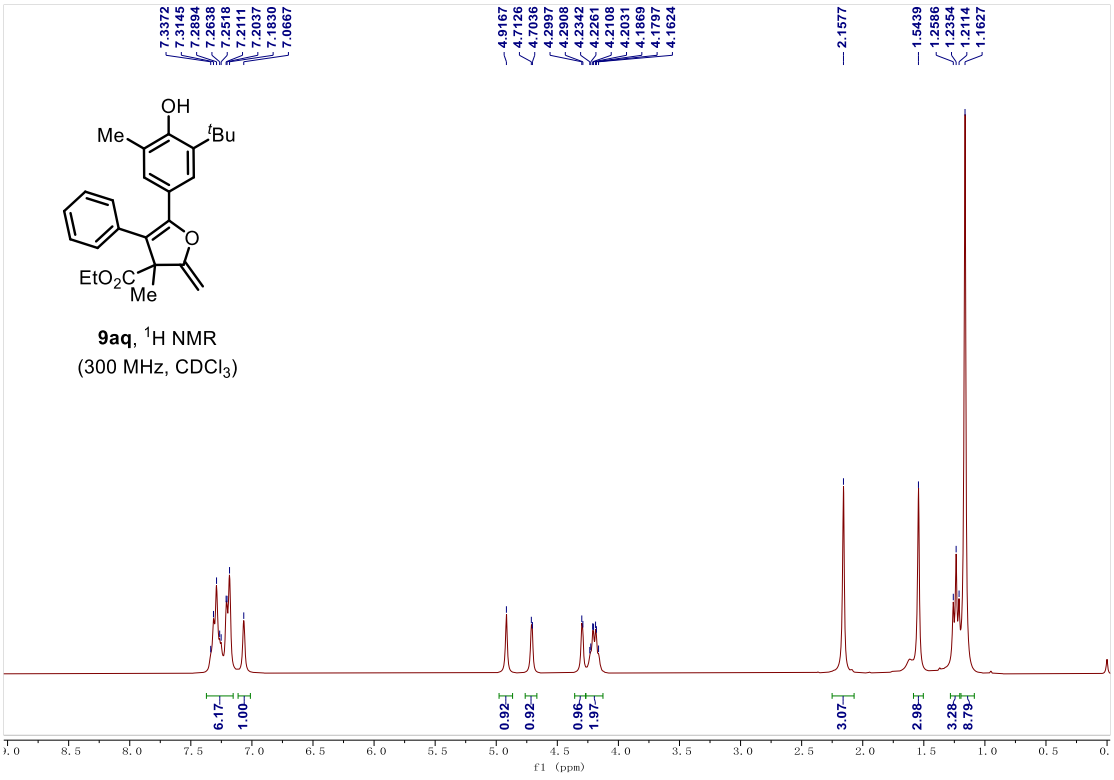
9an, ^{13}C NMR
(75 MHz, $CDCl_3$)



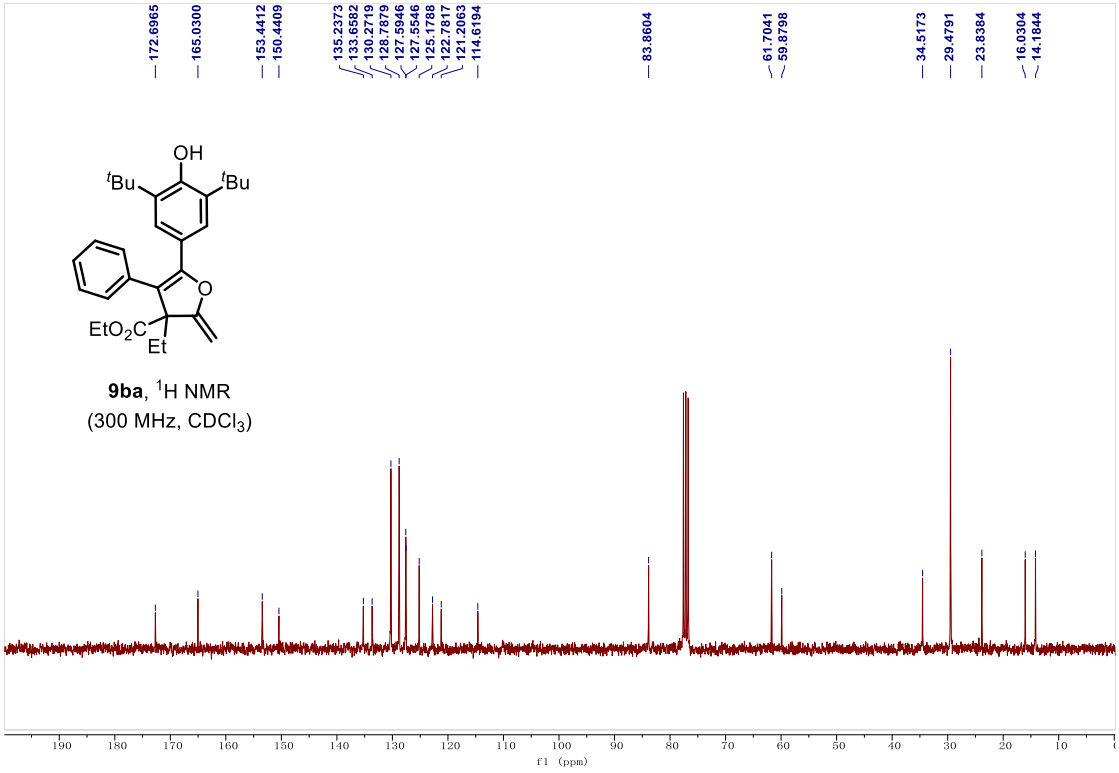
9ap, ^{1}H NMR
(300 MHz, $CDCl_3$)

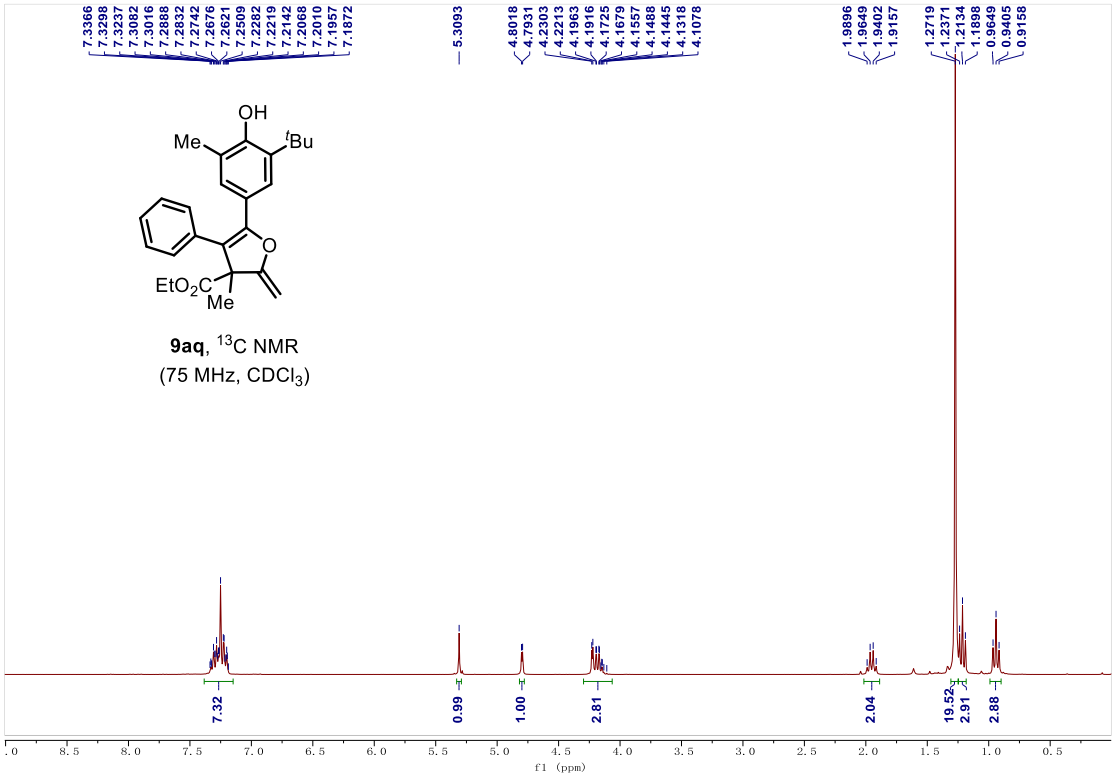


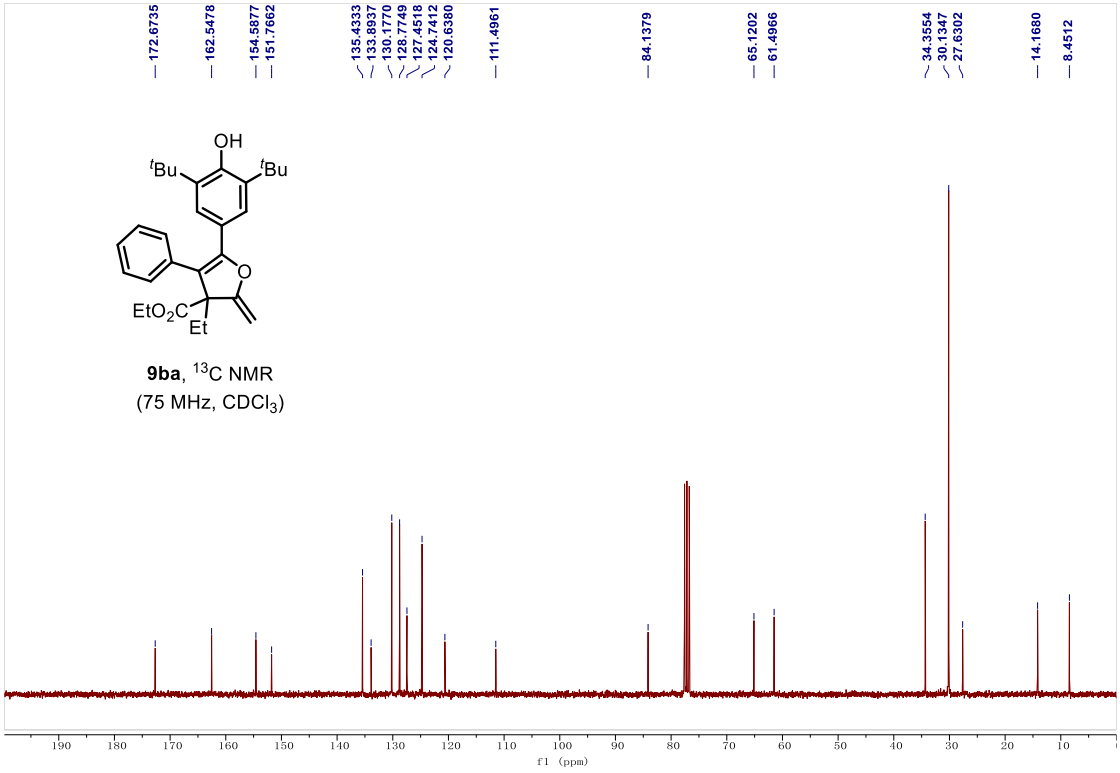
9ap, ^{13}C NMR
(75 MHz, $CDCl_3$)



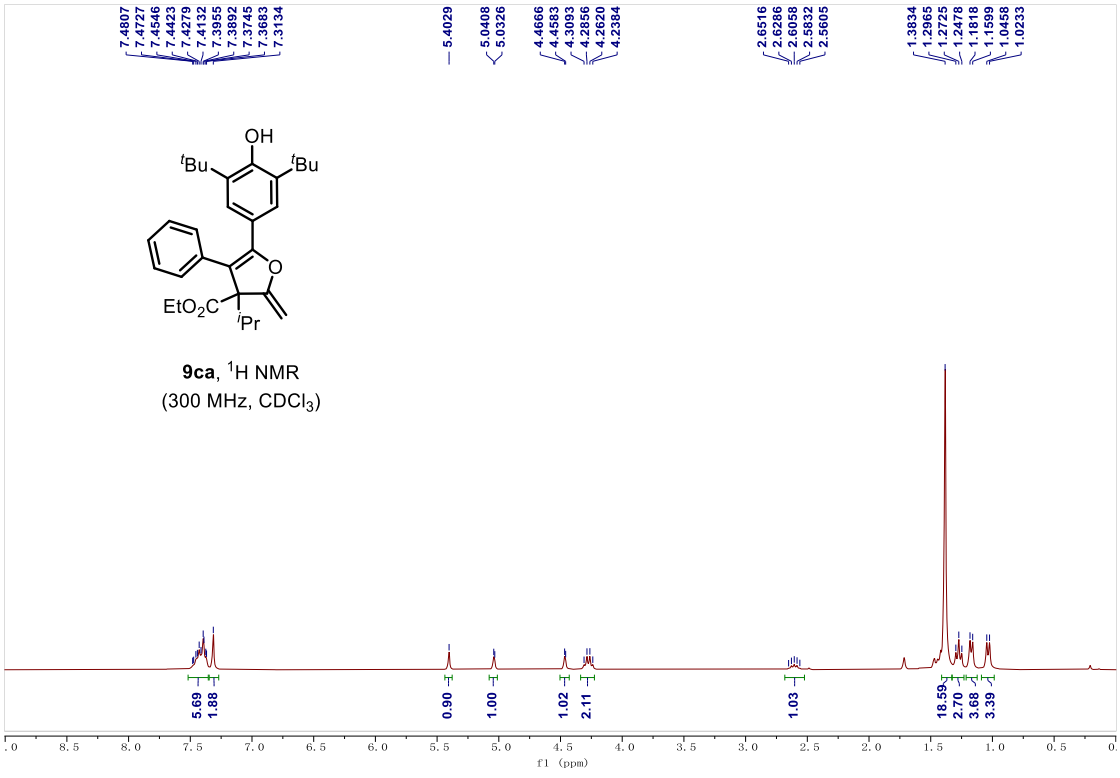
9aq, ^{1}H NMR
(300 MHz, $CDCl_3$)


172.6965
165.0300
153.4412
150.4409
135.2373
133.6582
130.2719
128.7879
127.5946
127.5546
125.1788
122.7817
121.2063
114.6194
83.8604
61.7041
59.8798
34.5173
29.4791
23.8384
16.0304
14.1844
OH
tBu
tBu
O
EtO2C
Et
9ba, 1H NMR
(300 MHz, CDCl3)
f1 (ppm)

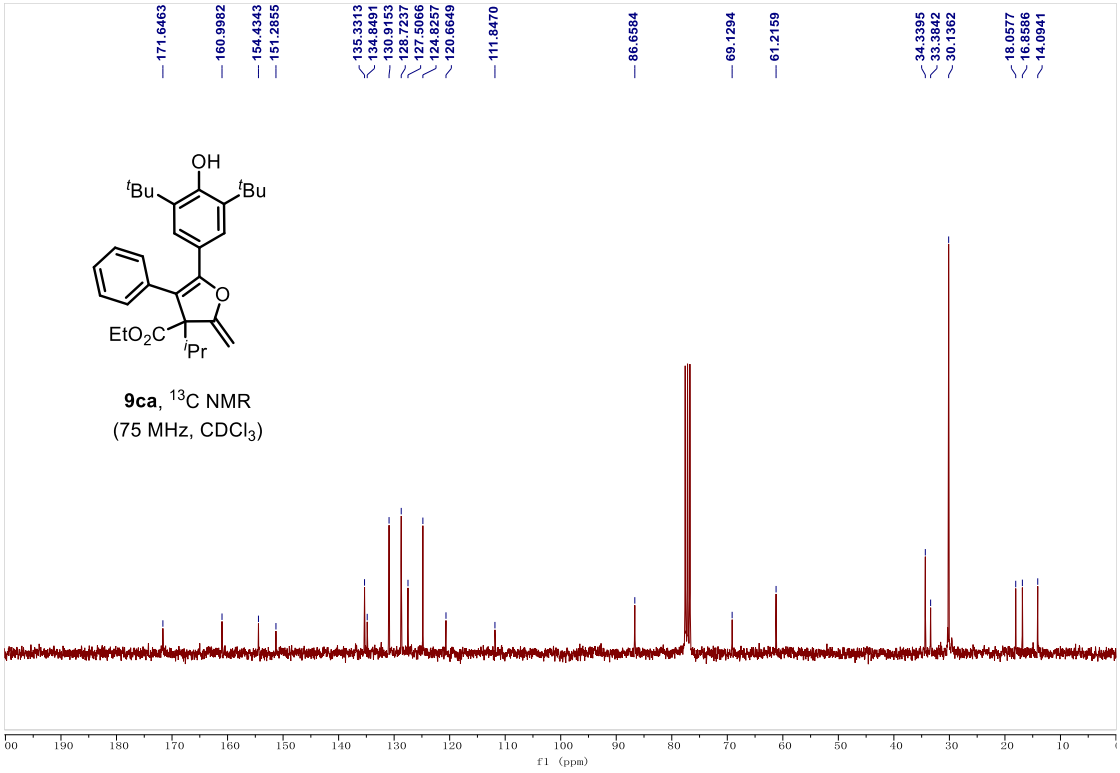

7.3366
7.3298
7.3237
7.3082
7.3016
7.2888
7.2832
7.2742
7.2676
7.2621
7.2509
7.2282
7.2219
7.2142
7.2068
7.2010
7.1957
7.1872
5.3093
4.8018
4.7931
4.2303
4.2213
4.1963
4.1916
4.1725
4.1679
4.1557
4.1488
4.1445
4.1318
4.1078
1.9896
1.9649
1.9402
1.9157
1.2719
1.2371
1.2134
1.1898
0.9649
0.9405
0.9158
OH
Me
tBu
O
EtO2C
Me
9aq, 13C NMR
(75 MHz, CDCl3)
7.32
0.99
1.00
2.81
2.04
19.52
2.91
2.88
f1 (ppm)



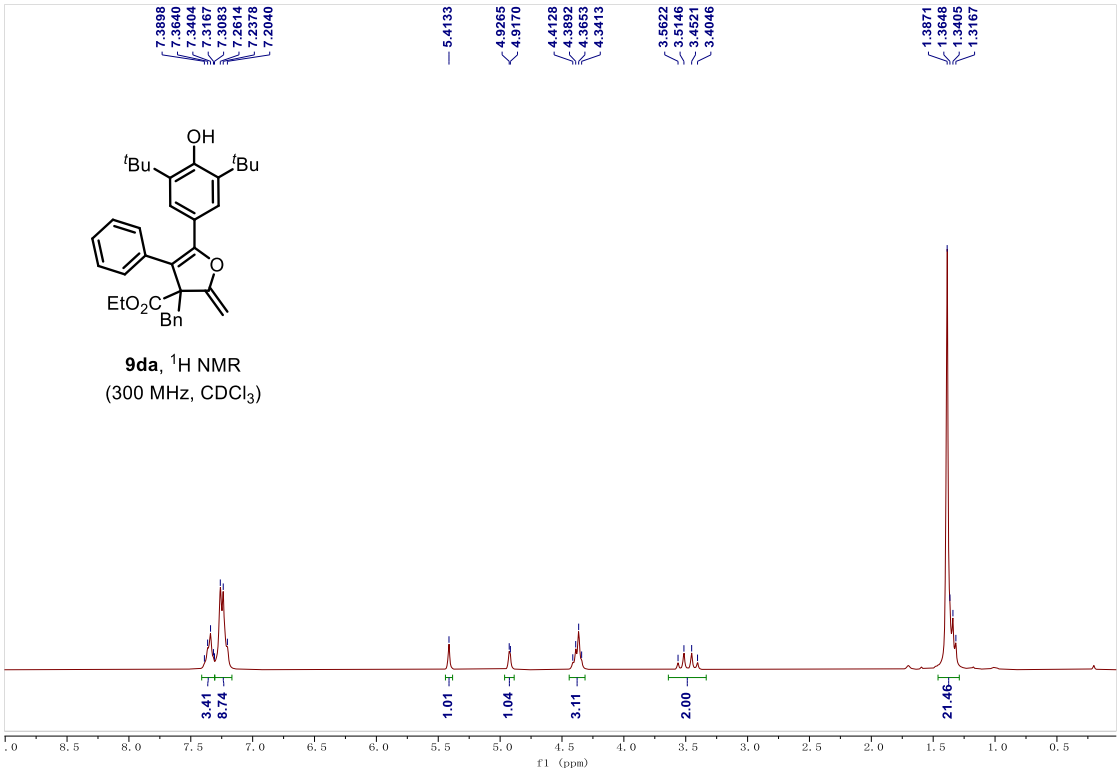
9ba, ^{13}C NMR
(75 MHz, $CDCl_3$)



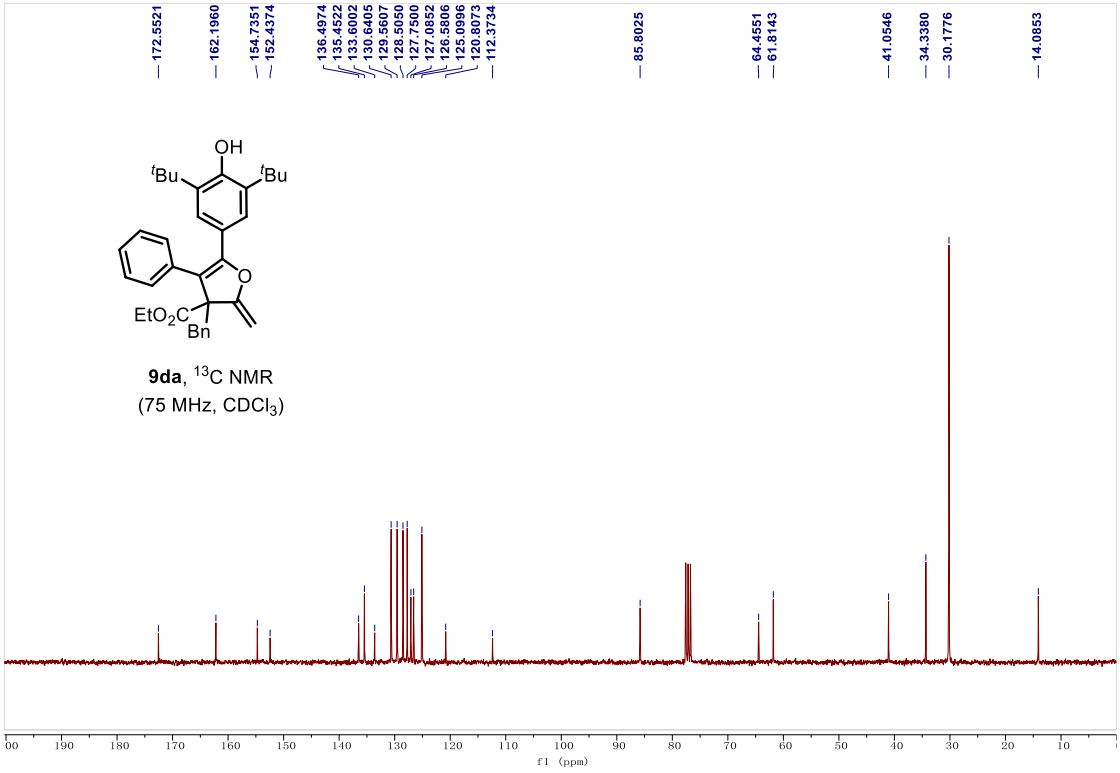
9ca, ^{1}H NMR
(300 MHz, $CDCl_3$)



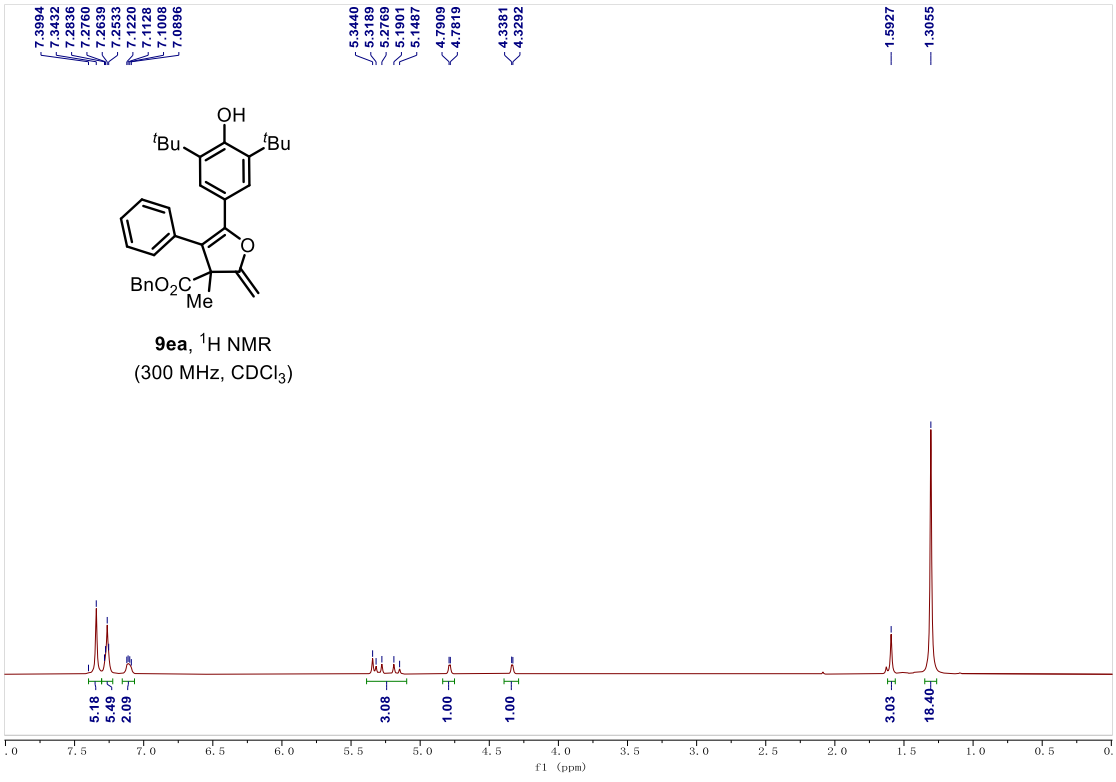
9ca, ^{13}C NMR
(75 MHz, $CDCl_3$)



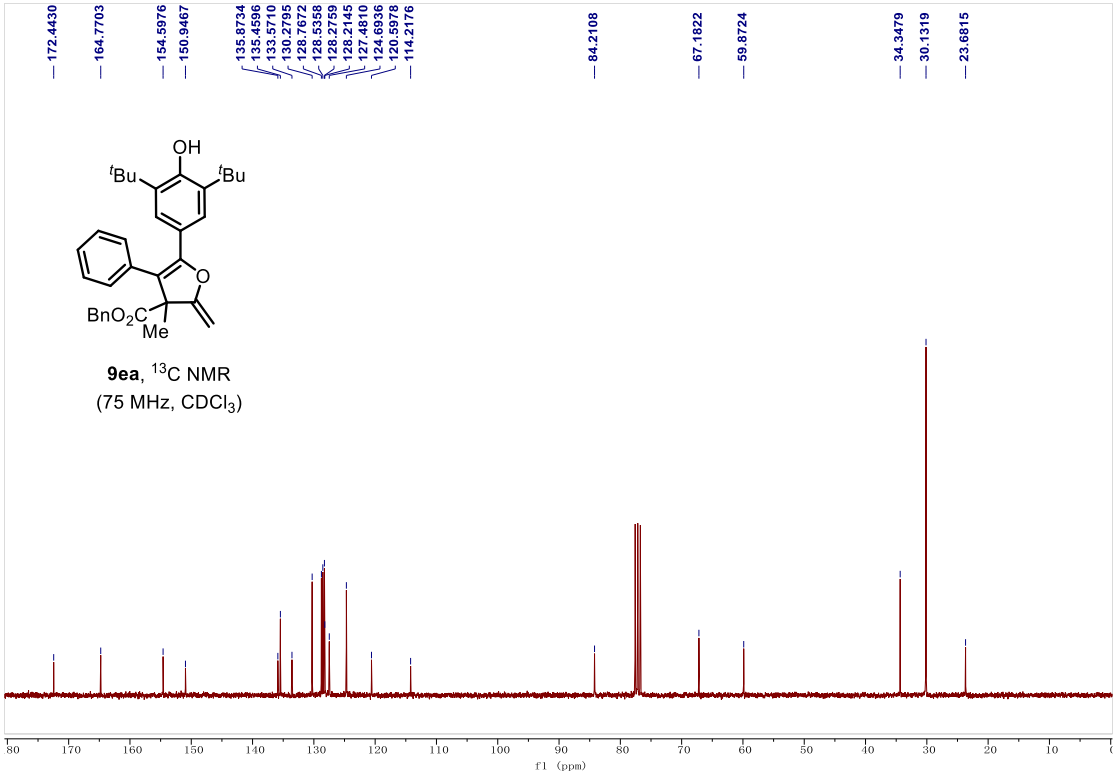
9da, ^{1}H NMR
(300 MHz, $CDCl_3$)



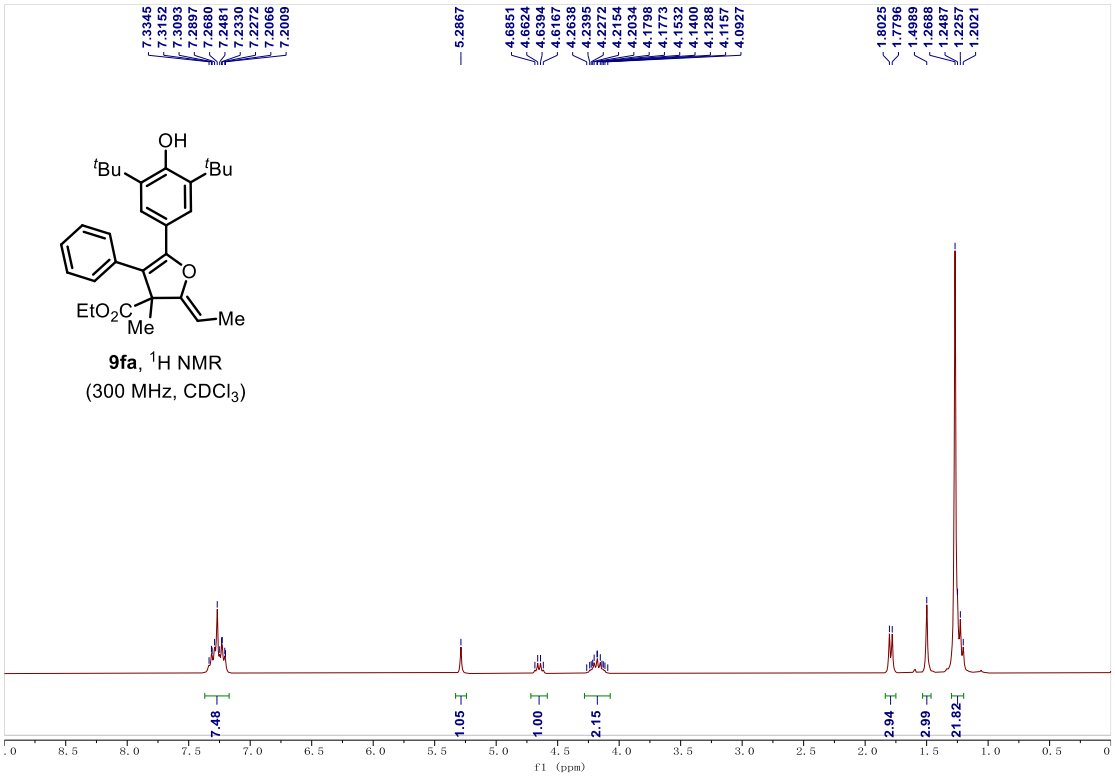
9da, ^{13}C NMR
(75 MHz, $CDCl_3$)



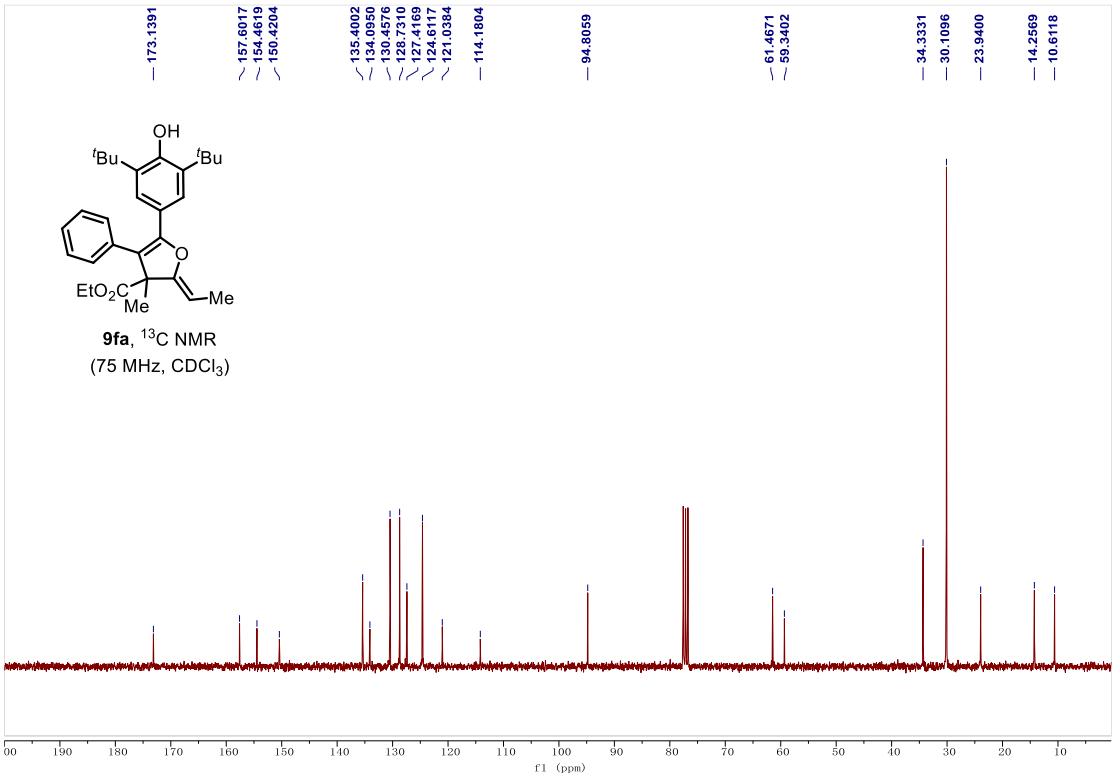
9ea, ^{1}H NMR
(300 MHz, $CDCl_3$)



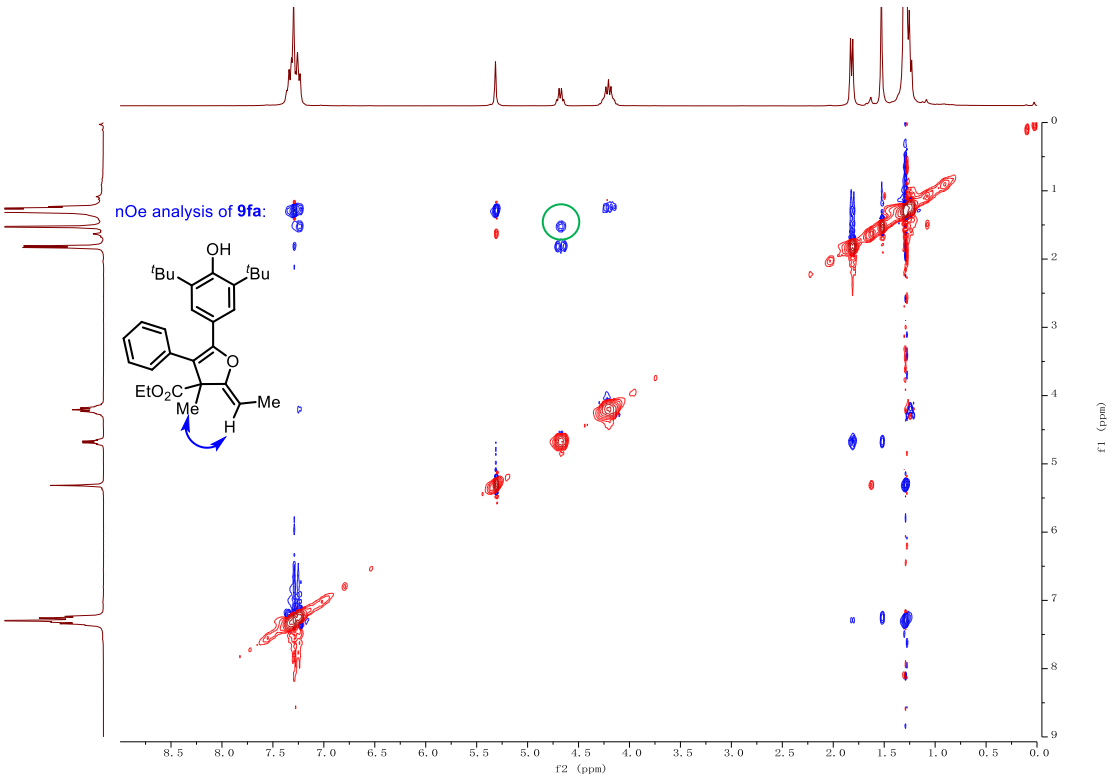
9ea, ^{13}C NMR
(75 MHz, $CDCl_3$)

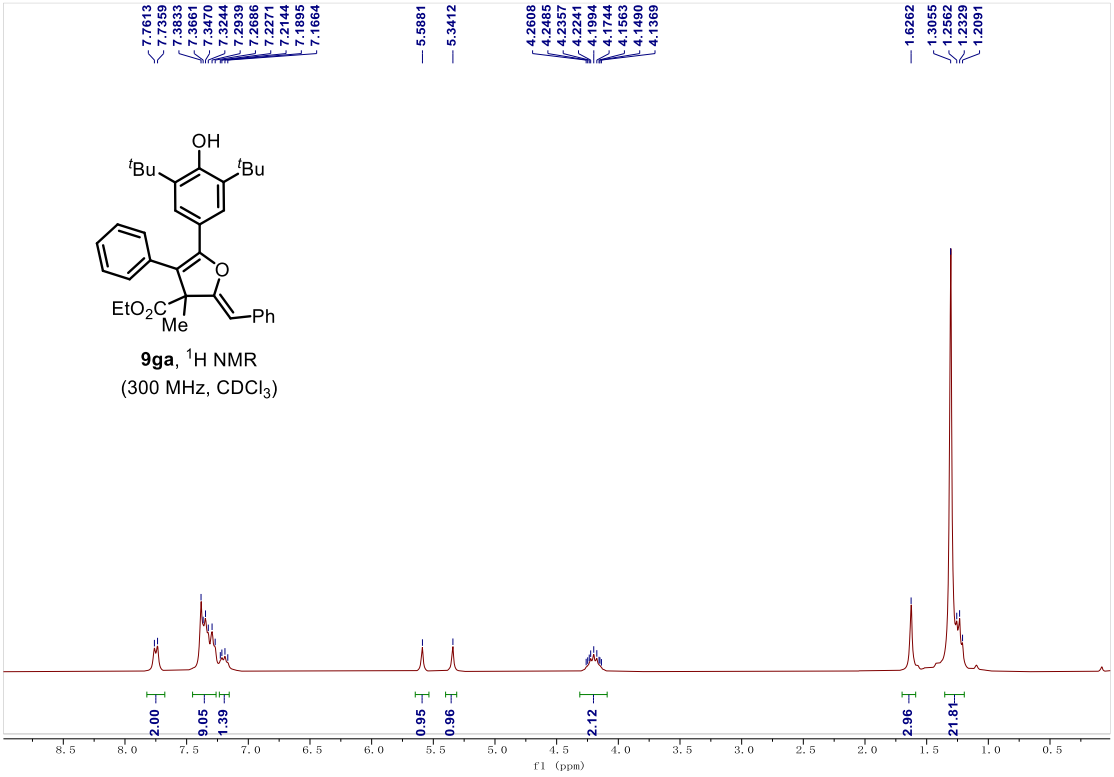


9fa, ^{1}H NMR
(300 MHz, $CDCl_3$)

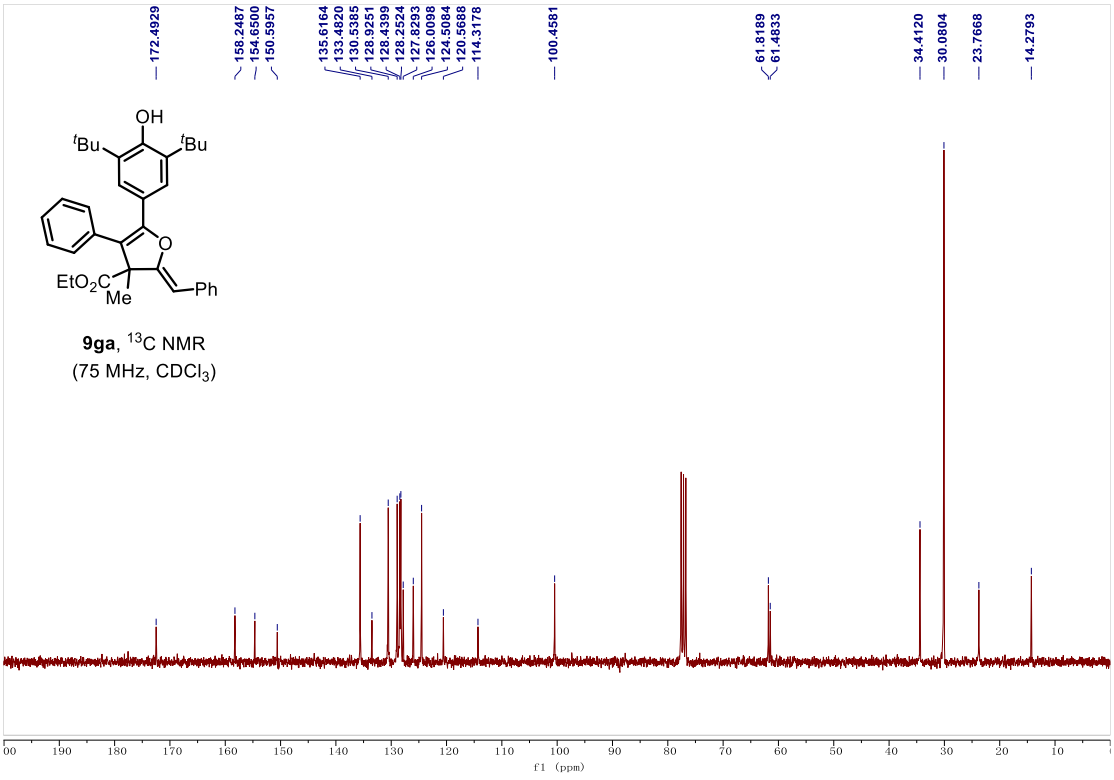


9fa, ^{13}C NMR
(75 MHz, $CDCl_3$)

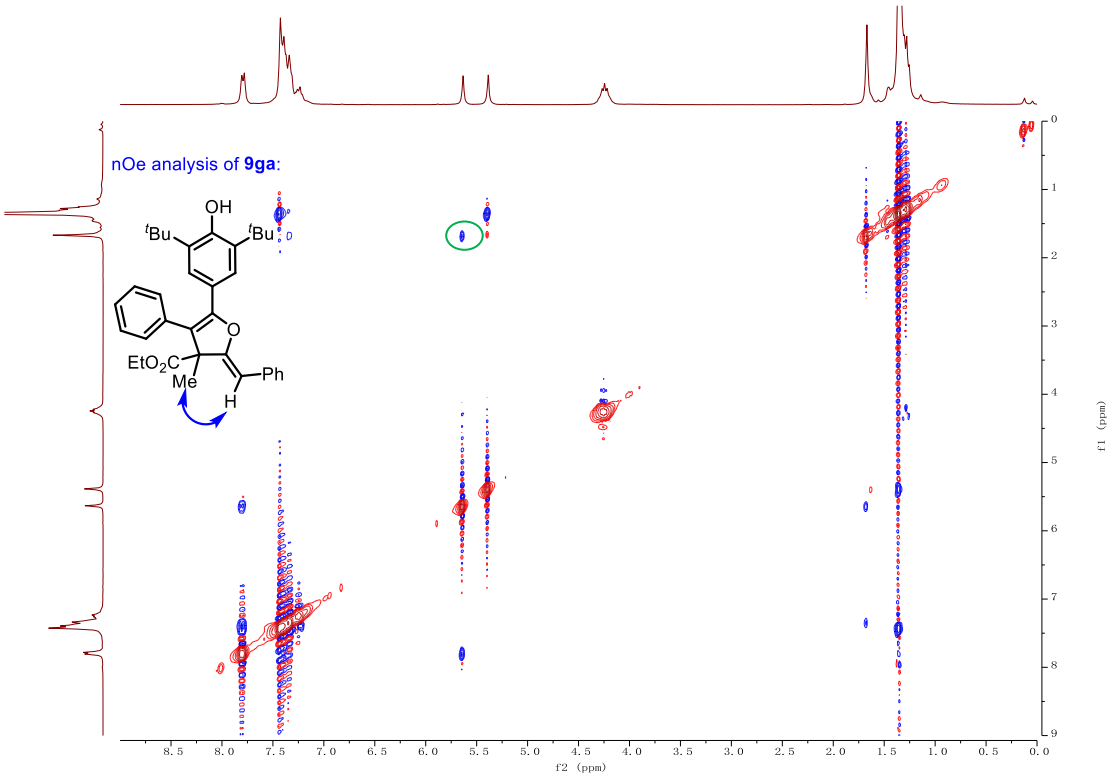


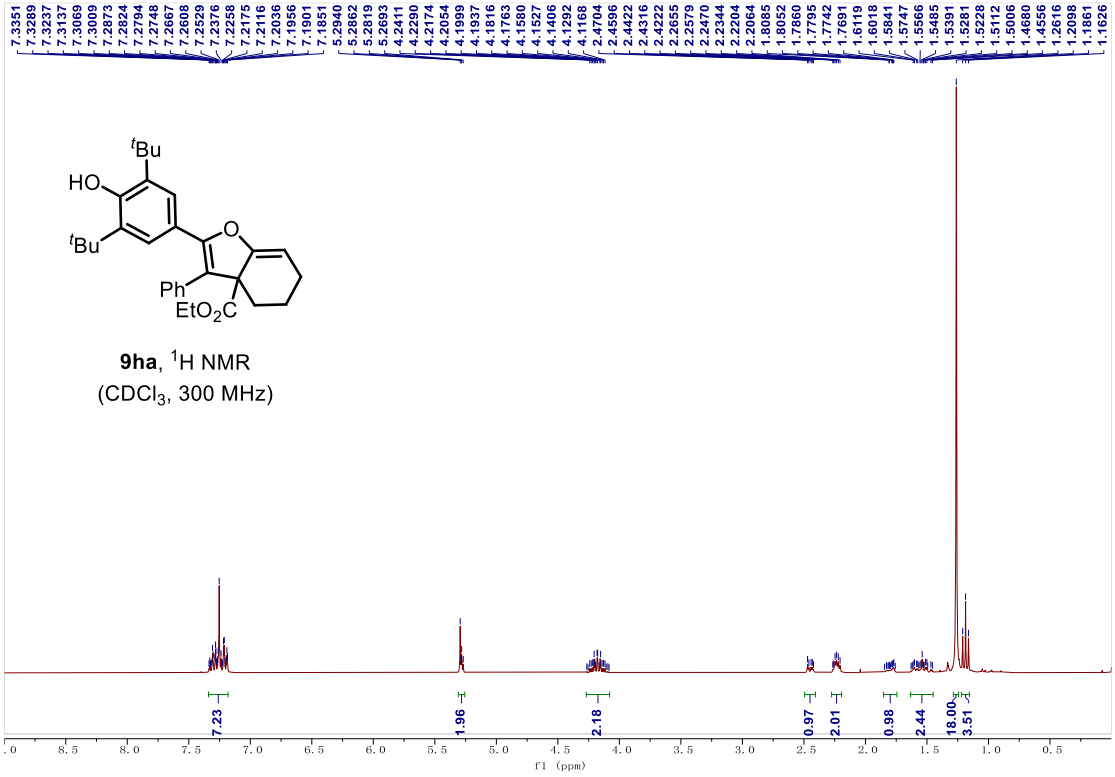


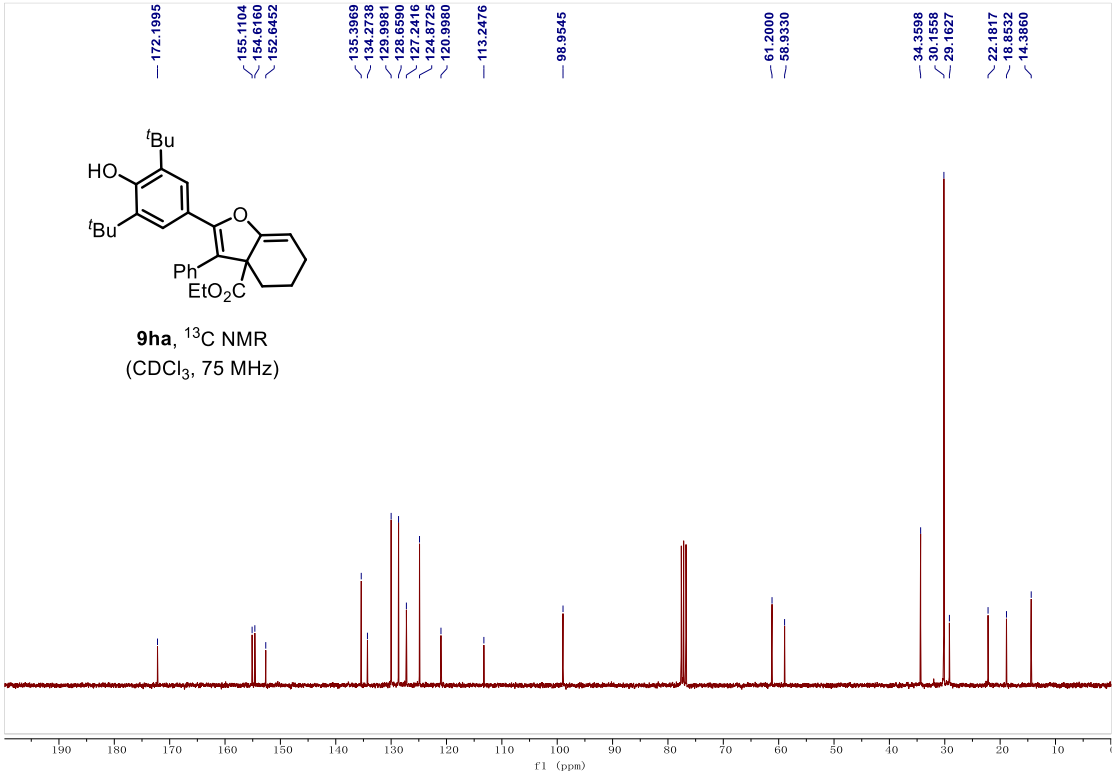
9ga, ^{1}H NMR
(300 MHz, $CDCl_3$)



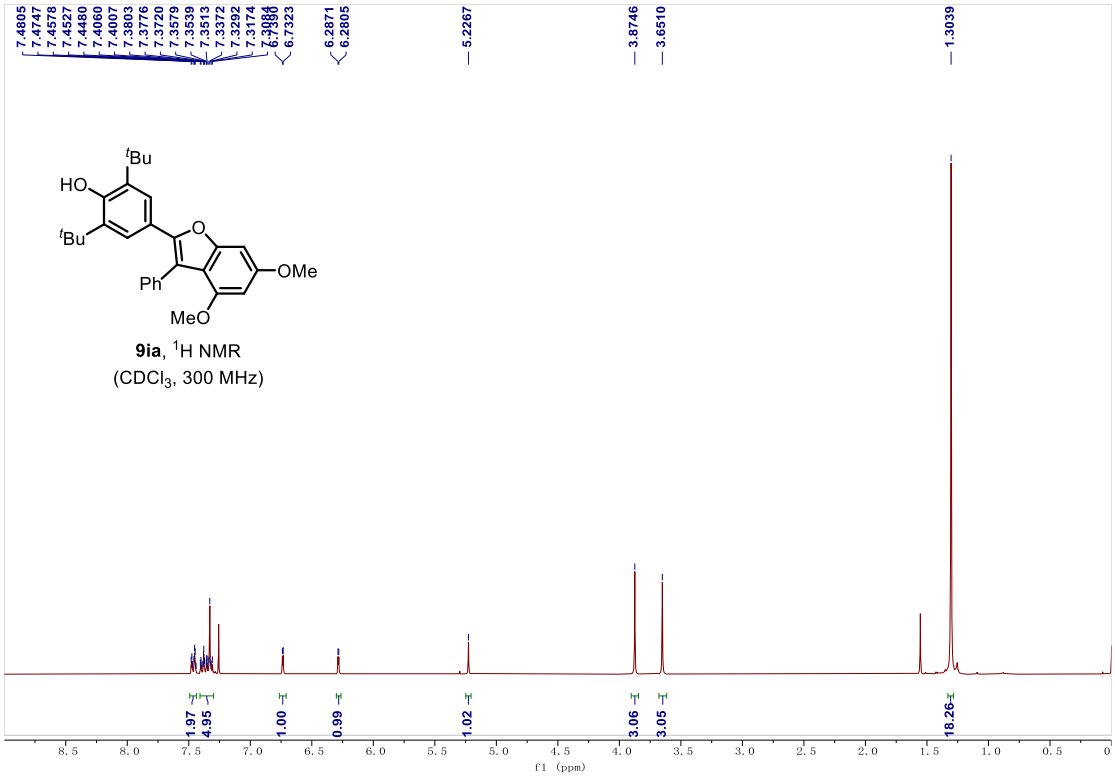
9ga, ^{13}C NMR
(75 MHz, $CDCl_3$)


nOe analysis of 9ga:
OH
tBu
tBu
O
EtO2C
Me
Ph
H
f2 (ppm)
f1 (ppm)

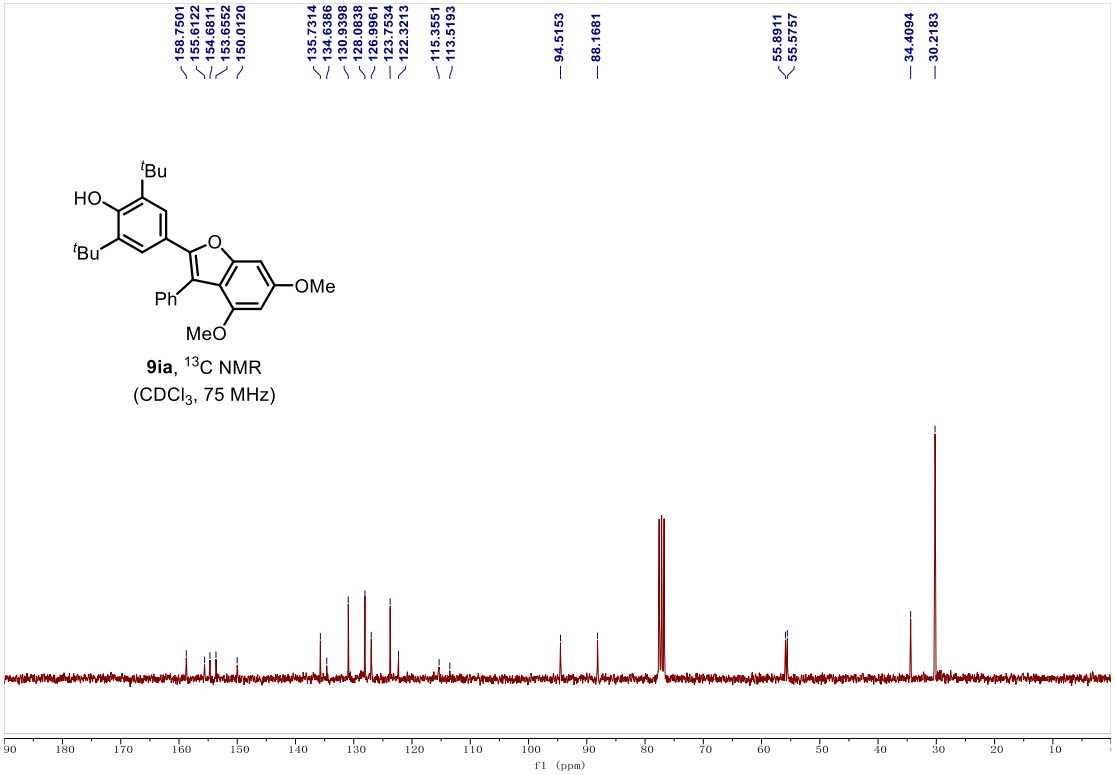

tBu
HO
tBu
O
Ph
EtO2C
9ha, 1H NMR
(CDCl3, 300 MHz)
7.23
1.96
2.18
0.97
2.01
0.98
2.44
18.00
3.51
f1 (ppm)



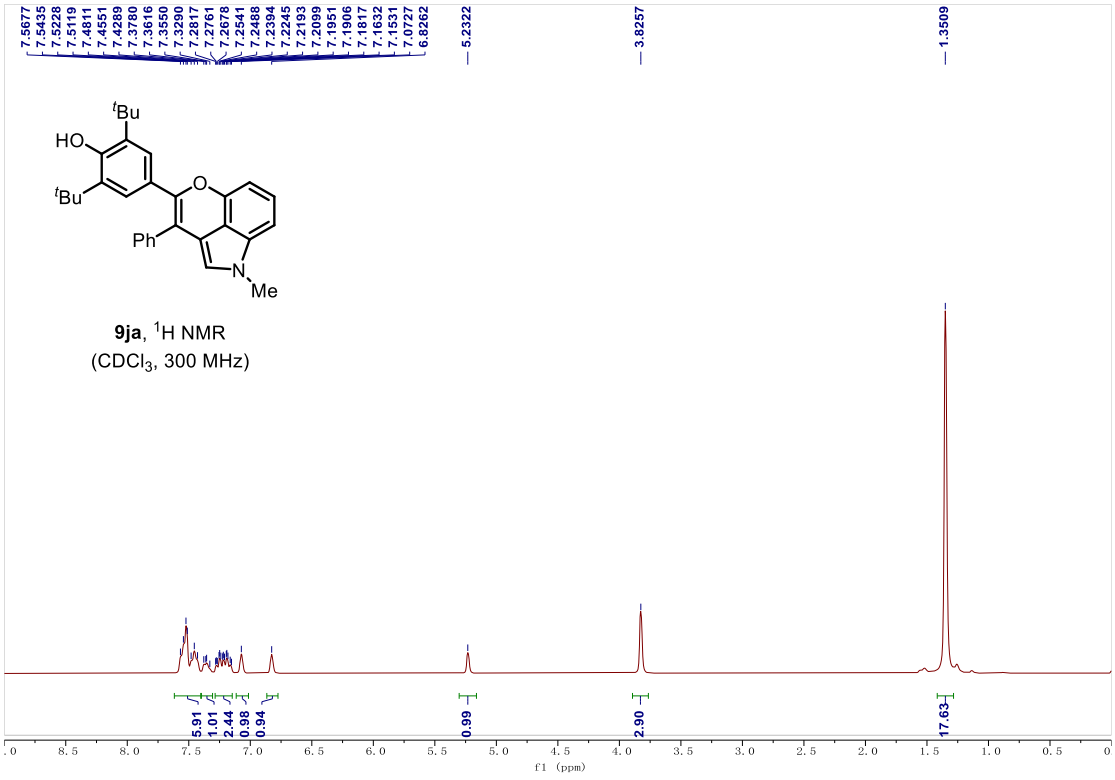
9ha, ^{13}C NMR
($CDCl_3$, 75 MHz)



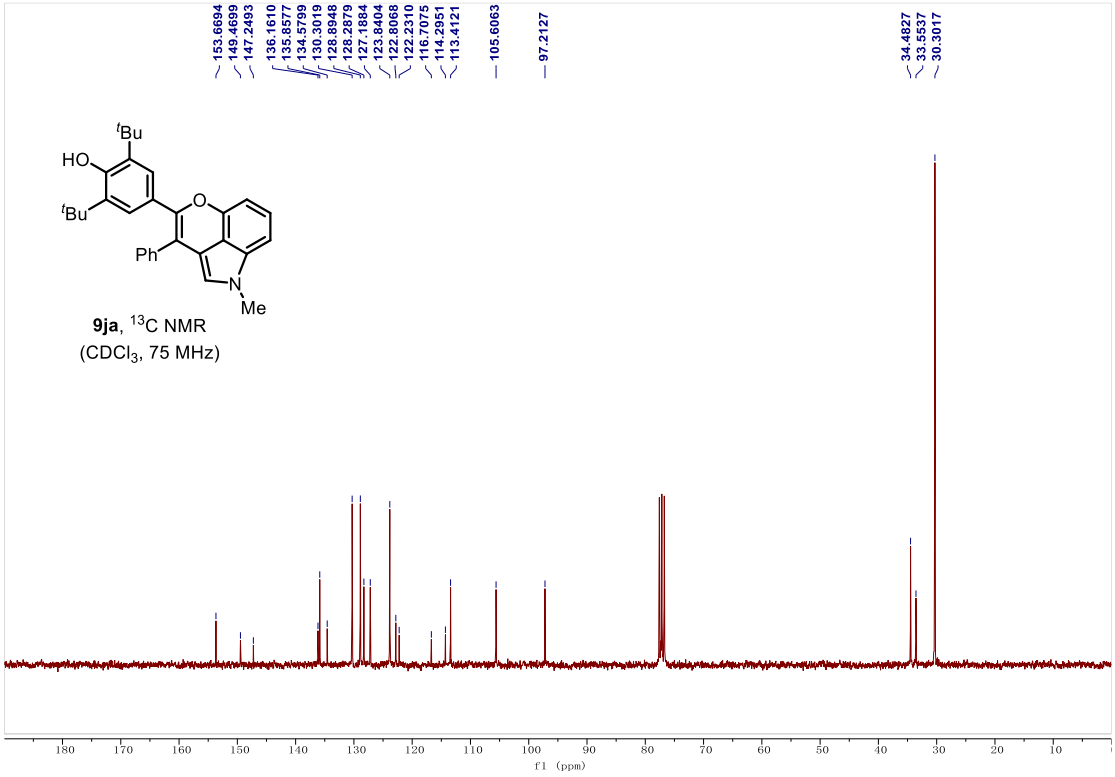
9ia, ^{1}H NMR
($CDCl_3$, 300 MHz)



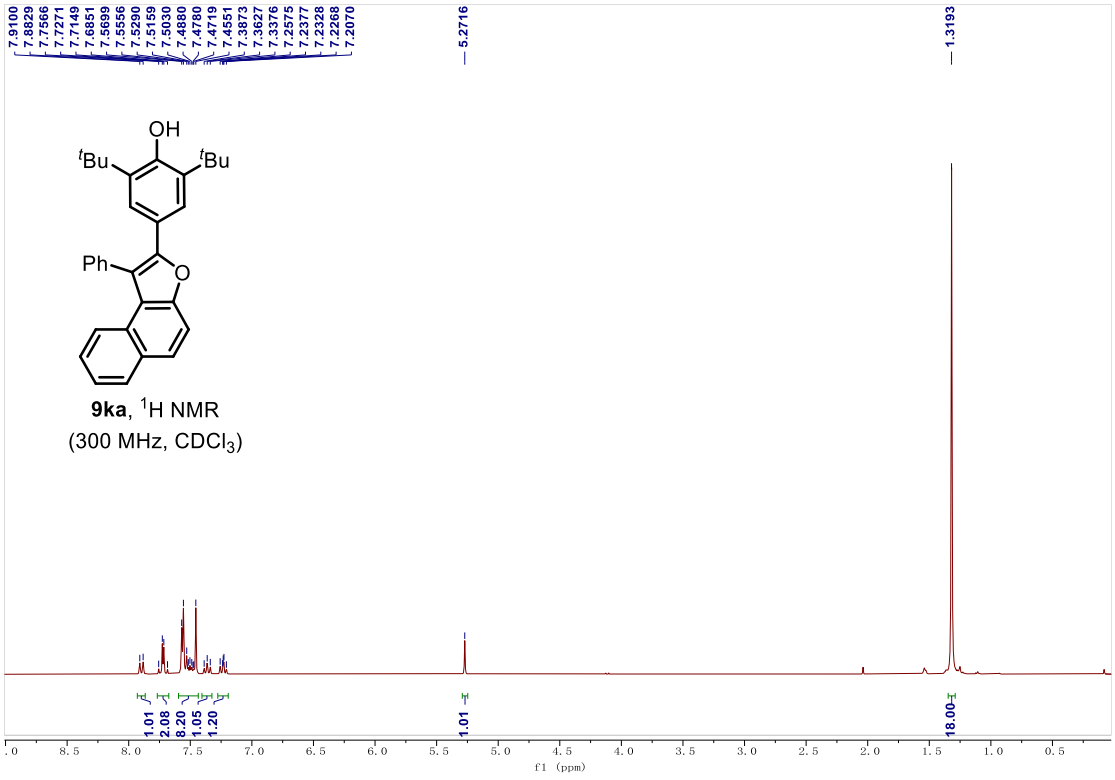
9ia, ^{13}C NMR
($CDCl_3$, 75 MHz)



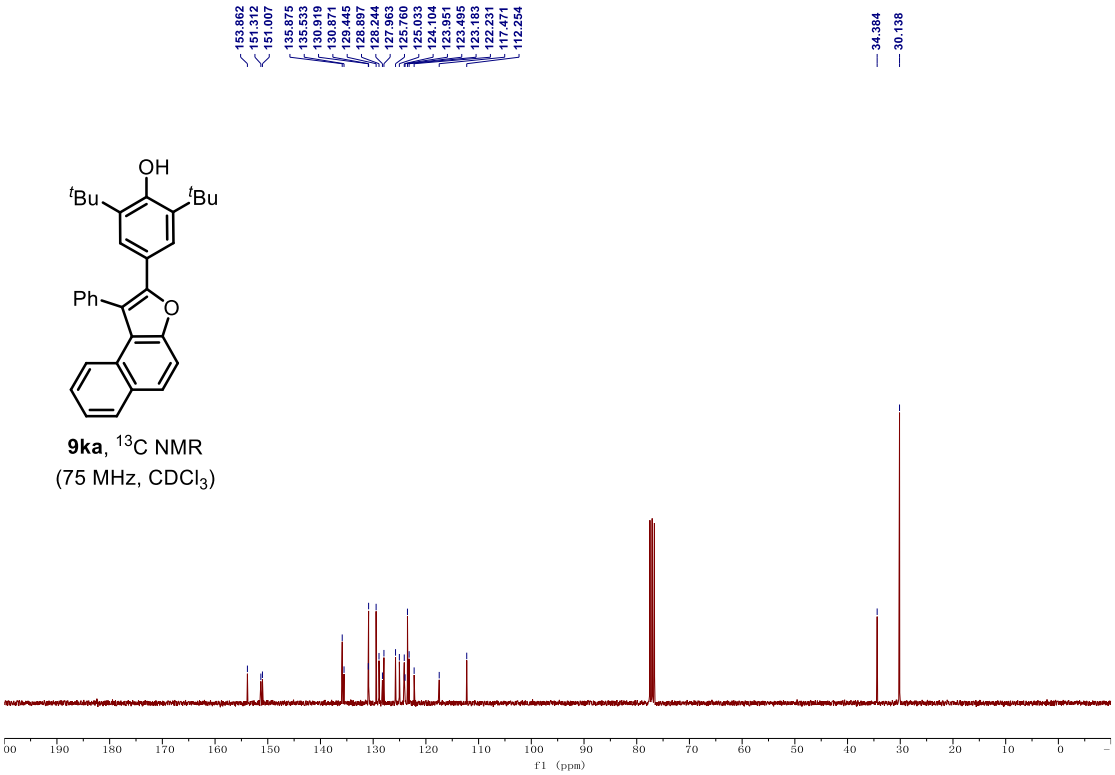
9ja, ^{1}H NMR
($CDCl_3$, 300 MHz)



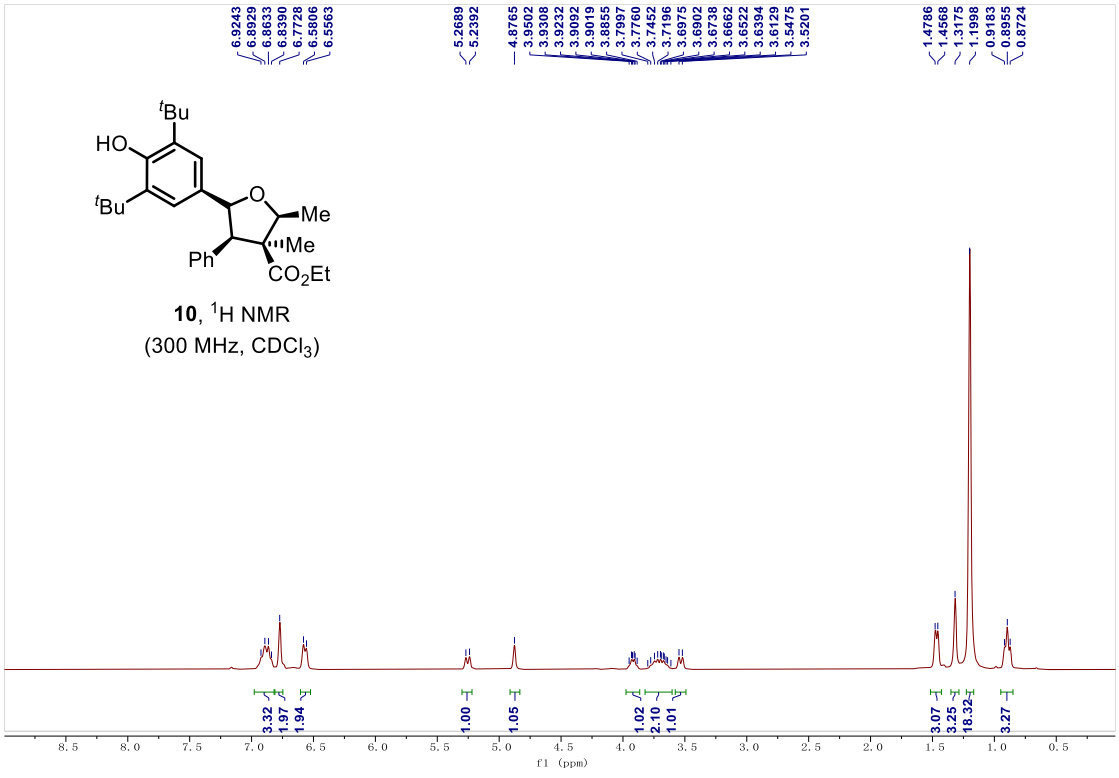
9ja, ^{13}C NMR
($CDCl_3$, 75 MHz)



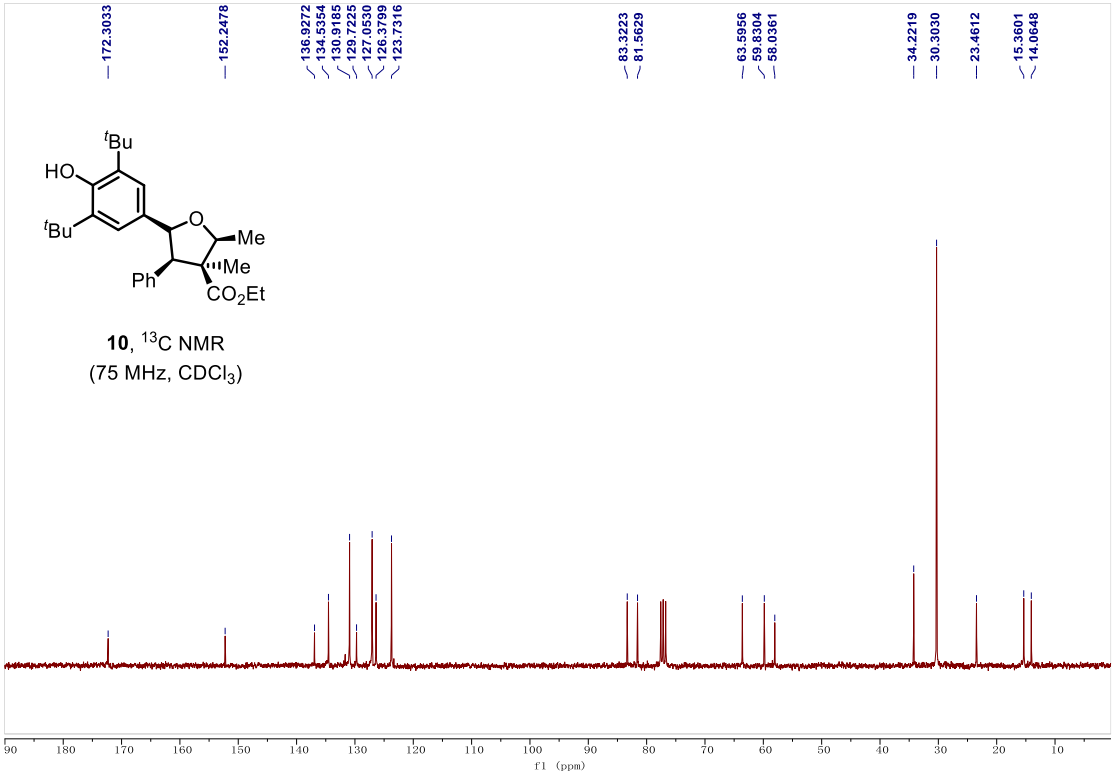
9ka, ^{1}H NMR
(300 MHz, $CDCl_3$)



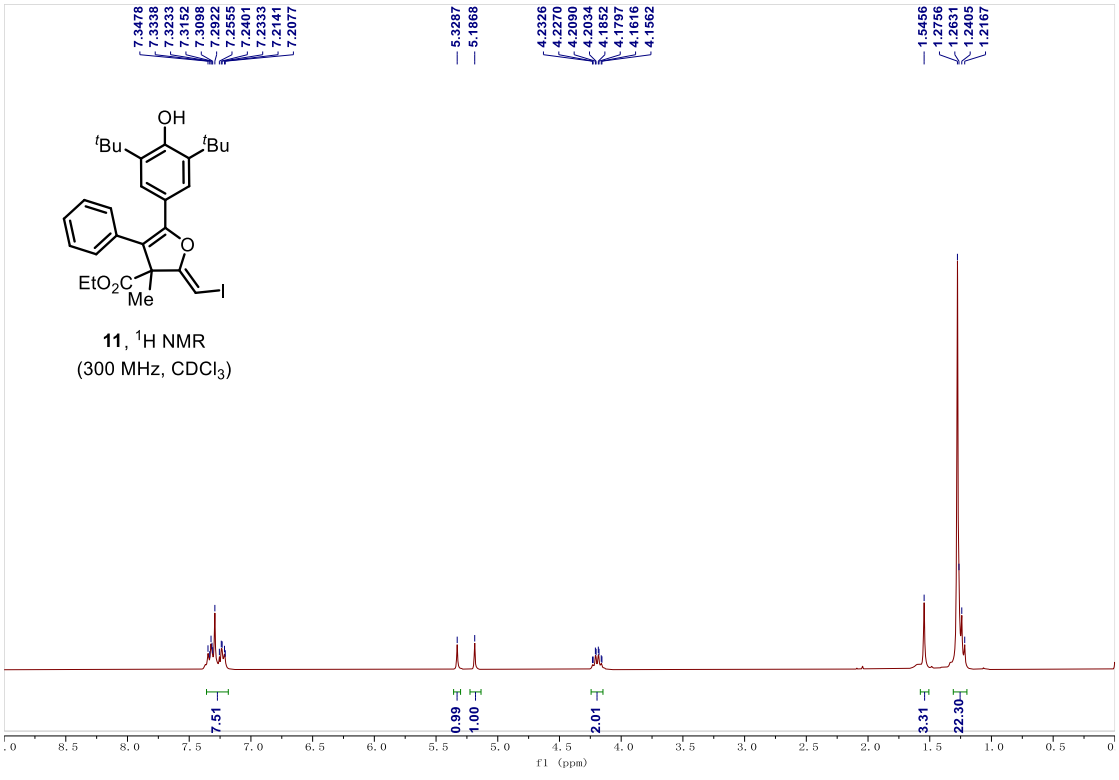
9ka, ^{13}C NMR
(75 MHz, $CDCl_3$)



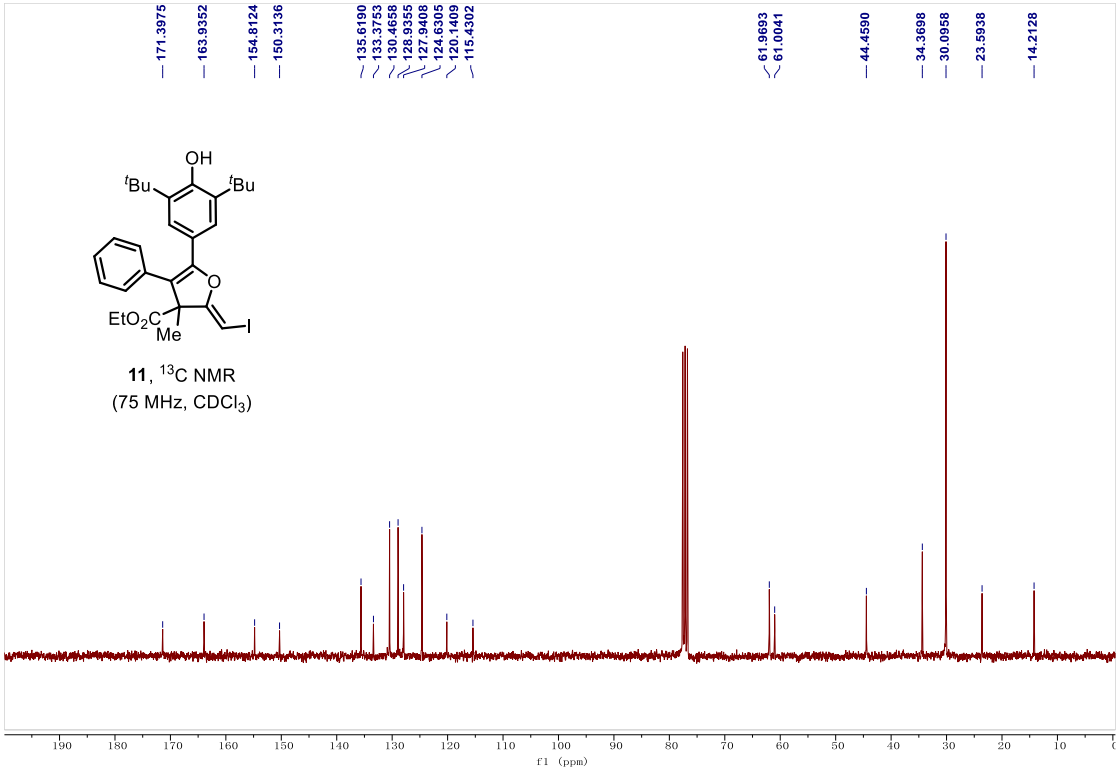
10, ^{1}H NMR
(300 MHz, $CDCl_3$)

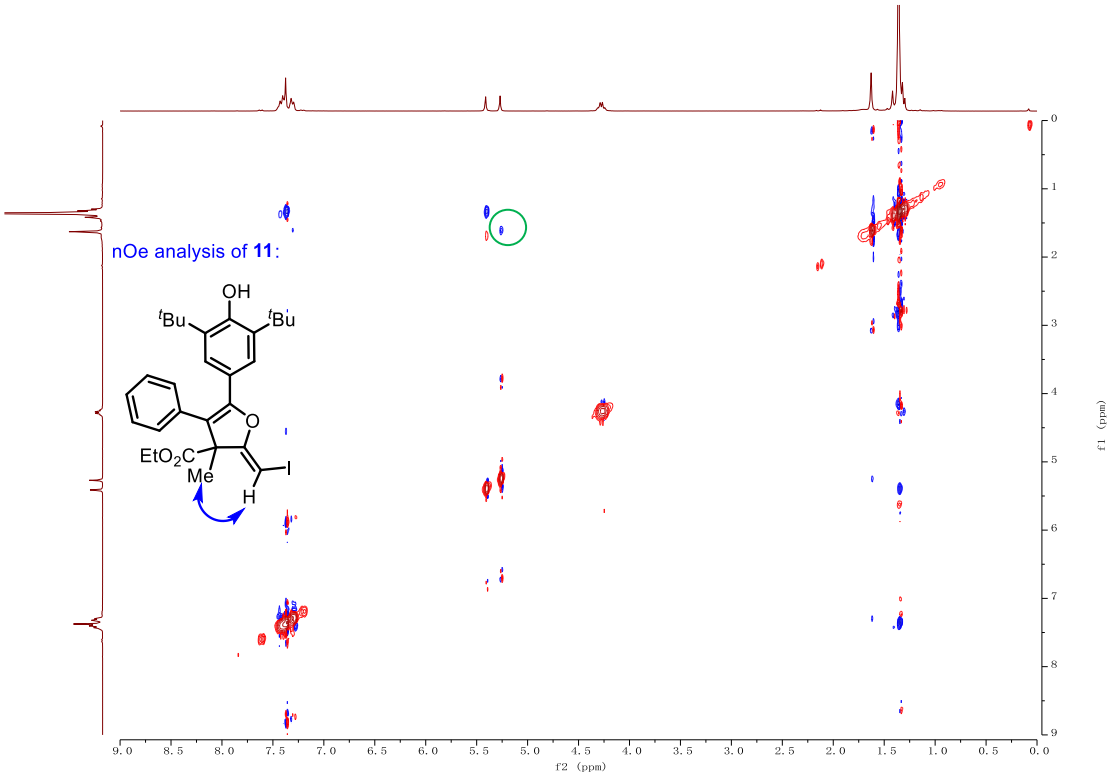


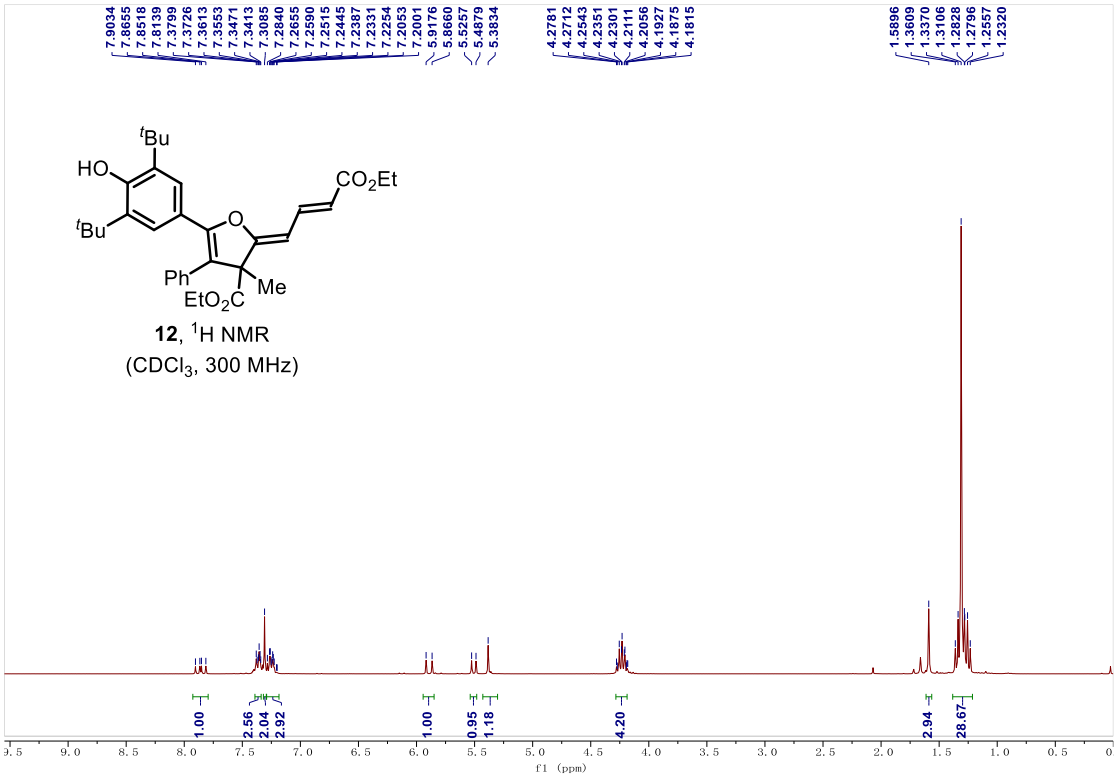
10, ^{13}C NMR
(75 MHz, $CDCl_3$)



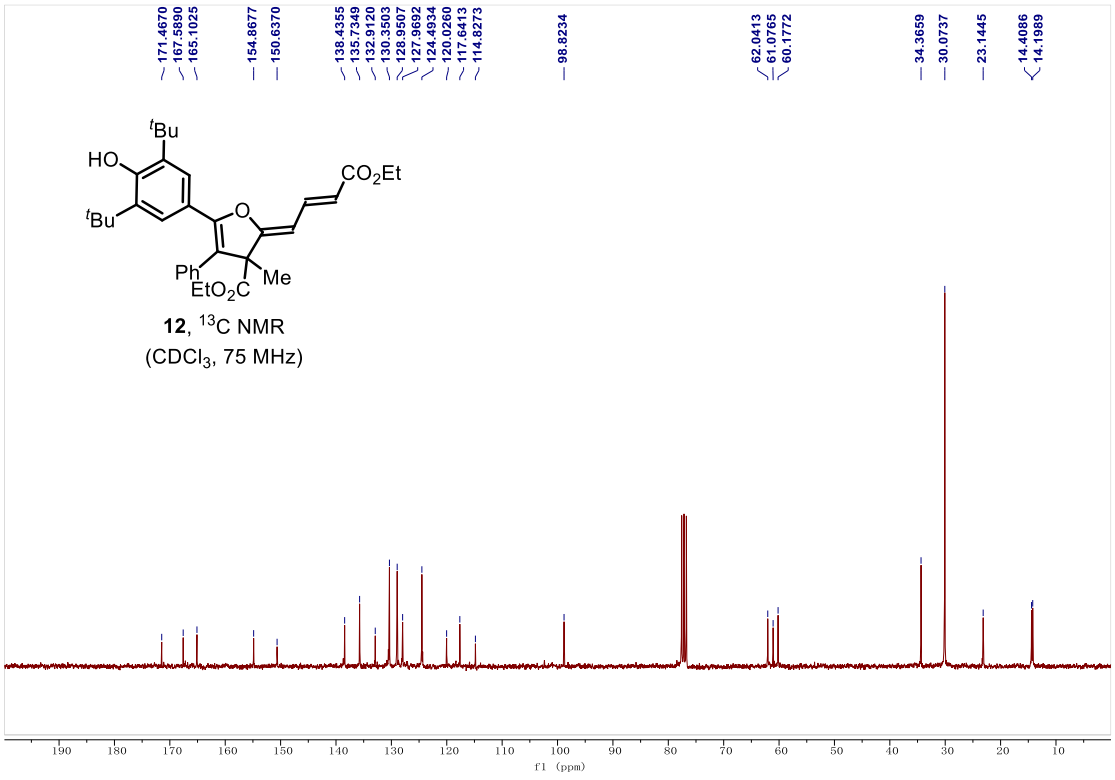
11, ^{1}H NMR
(300 MHz, $CDCl_3$)


171.3975
163.9352
154.8124
150.3136
135.6190
133.3753
130.4658
128.9355
127.9408
124.6305
120.1409
115.4302
61.9693
61.0041
44.4590
34.3698
30.0958
23.5938
14.2128
OH
tBu
tBu
O
EtO2C
Me
I
11, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)

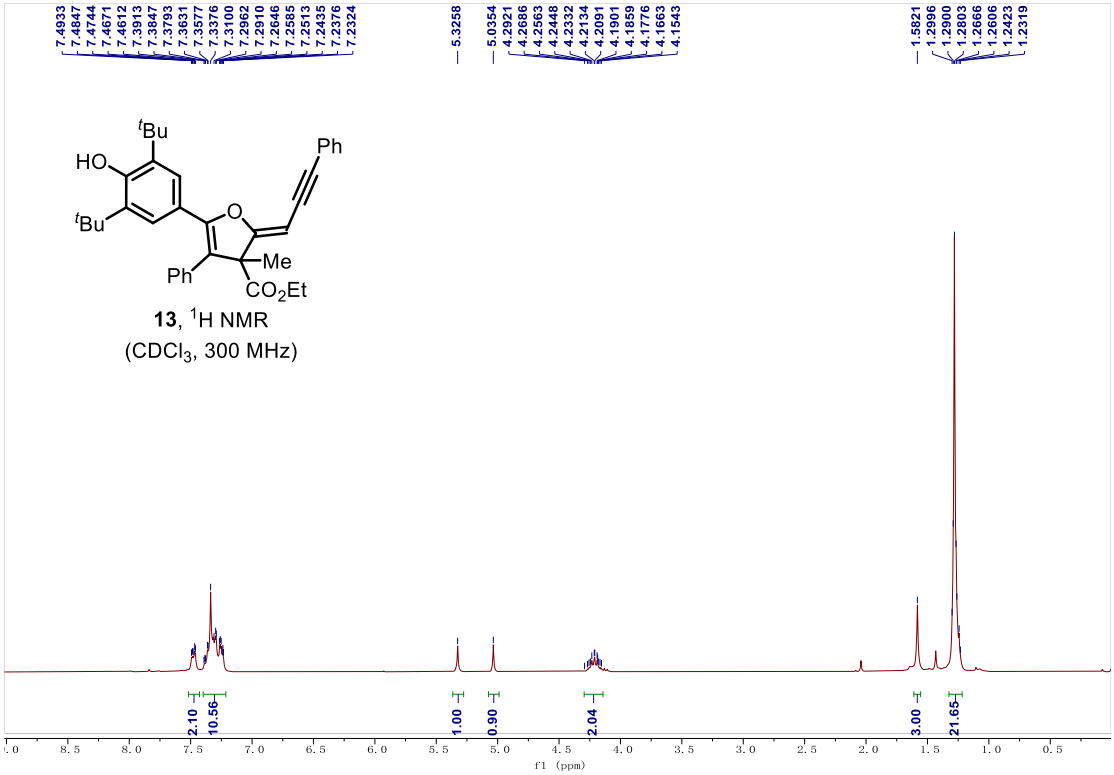

nOe analysis of 11:
OH
tBu
tBu
O
EtO2C
Me
I
H
f2 (ppm)
f1 (ppm)



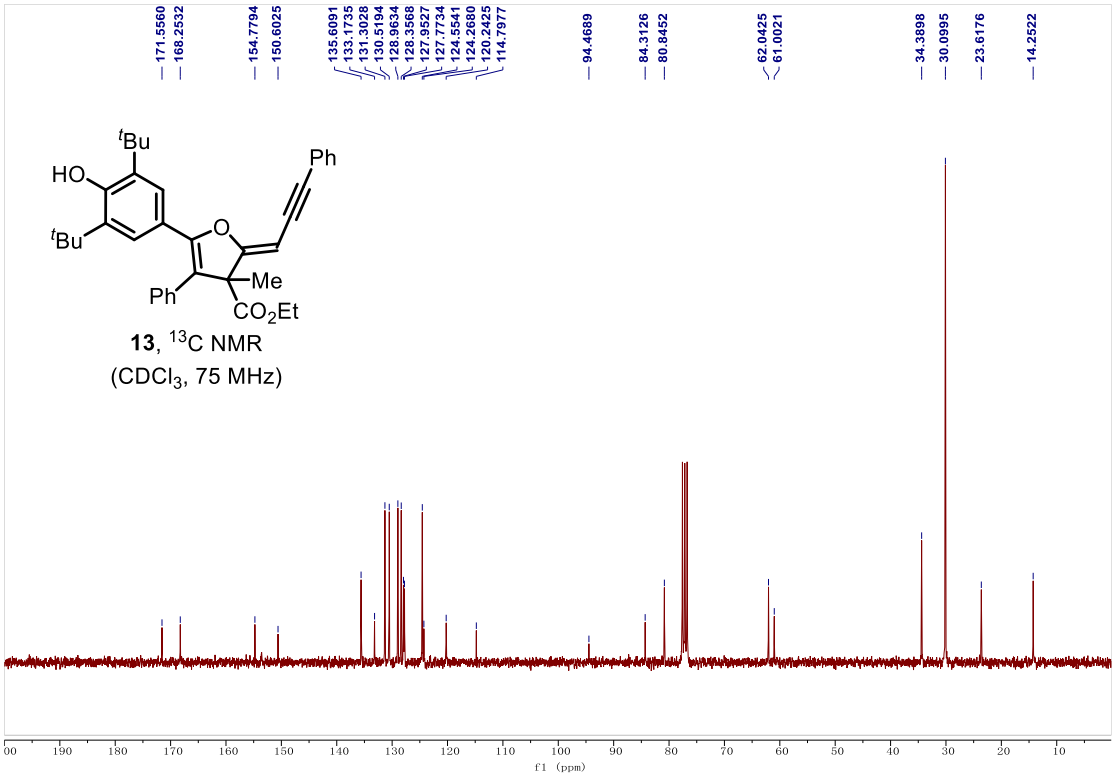
12, ^{1}H NMR
($CDCl_3$, 300 MHz)



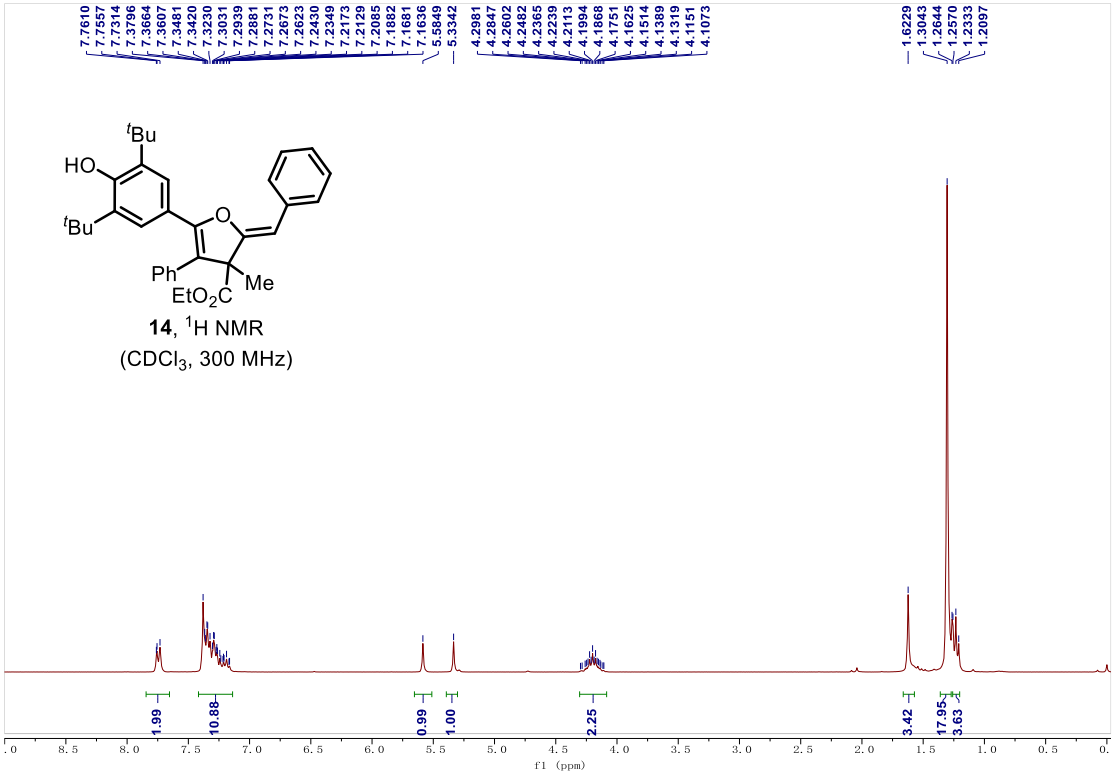
12, ^{13}C NMR
($CDCl_3$, 75 MHz)



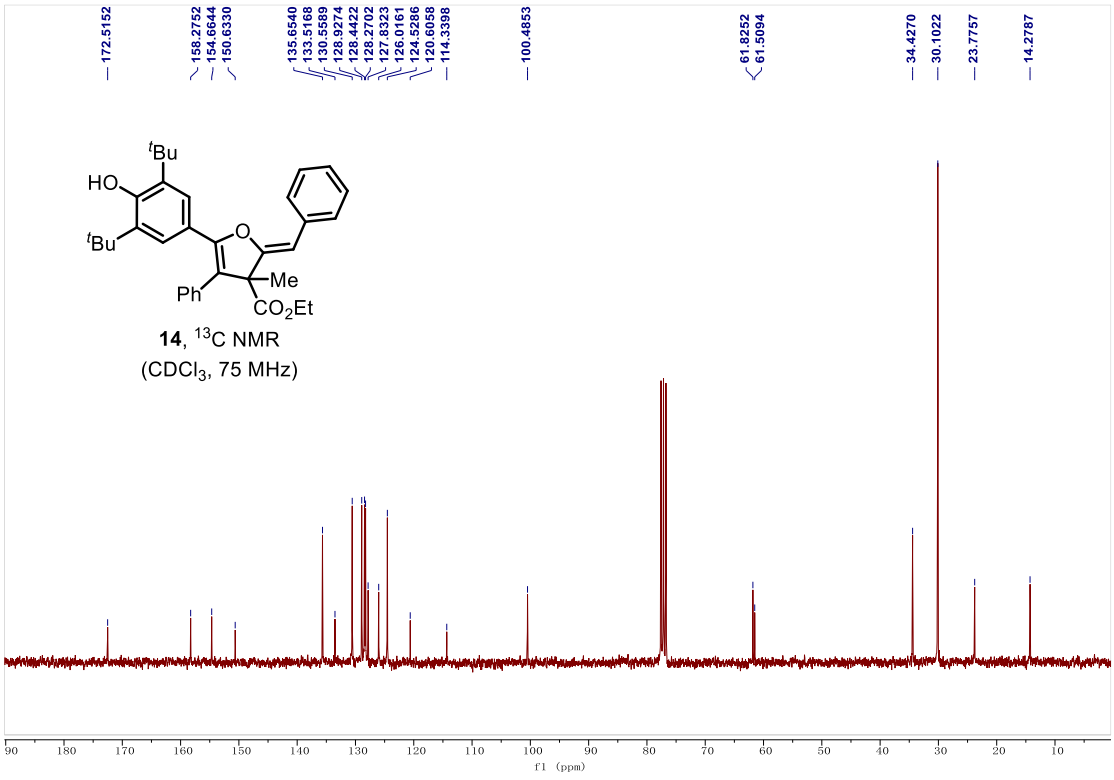
13, ^{1}H NMR
($CDCl_3$, 300 MHz)



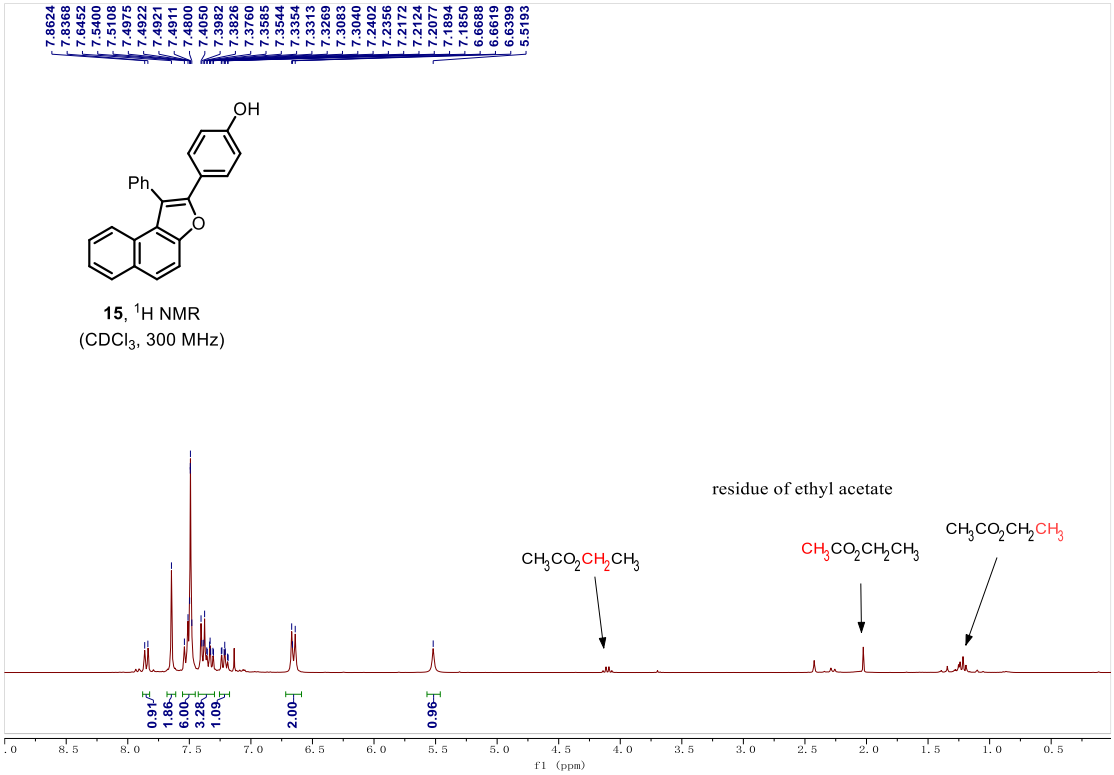
13, ^{13}C NMR
($CDCl_3$, 75 MHz)

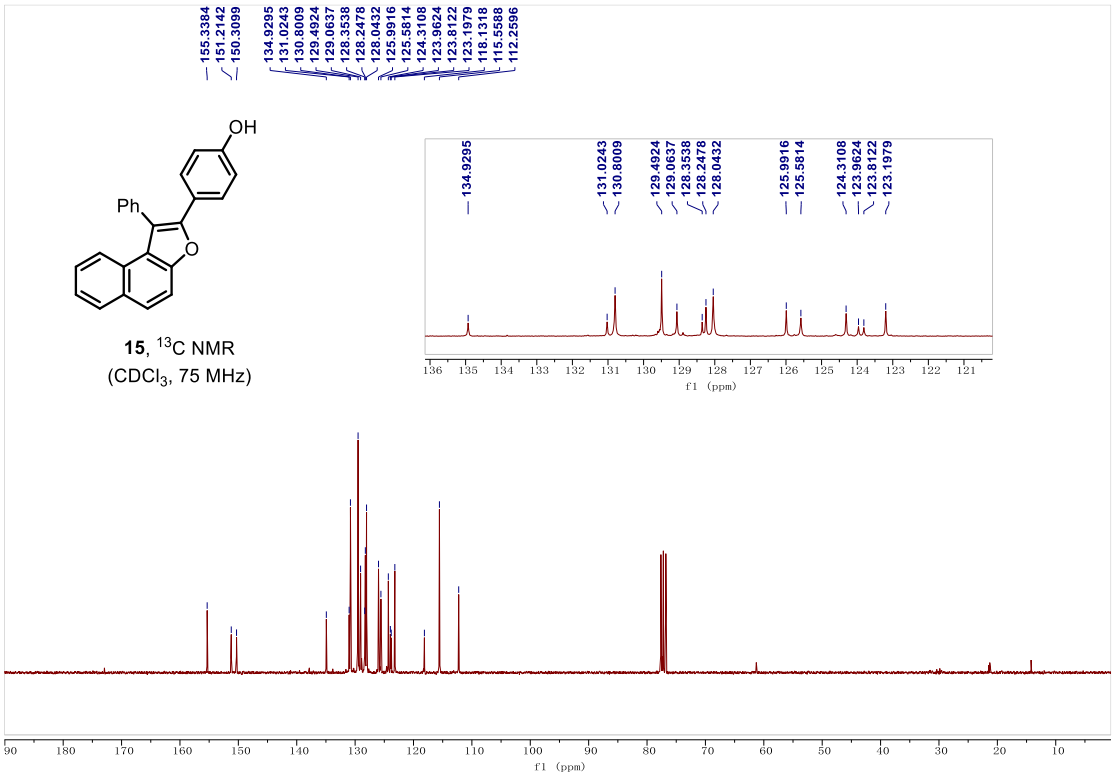


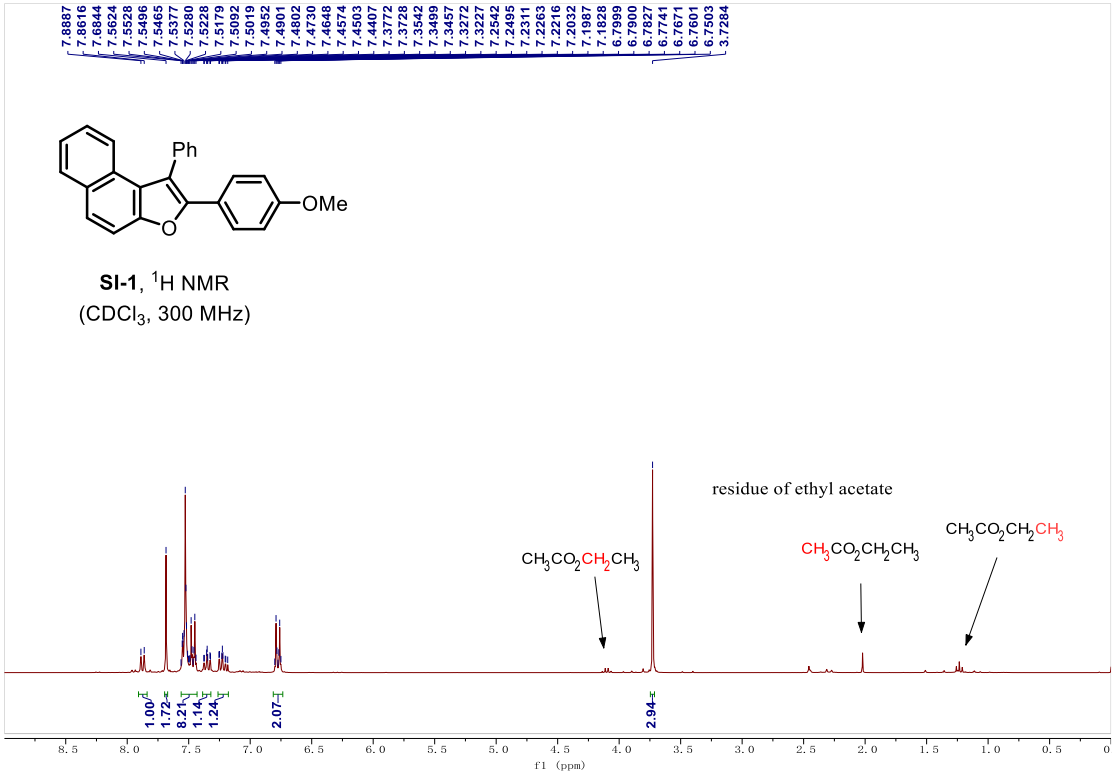
14, ^{1}H NMR
($CDCl_3$, 300 MHz)

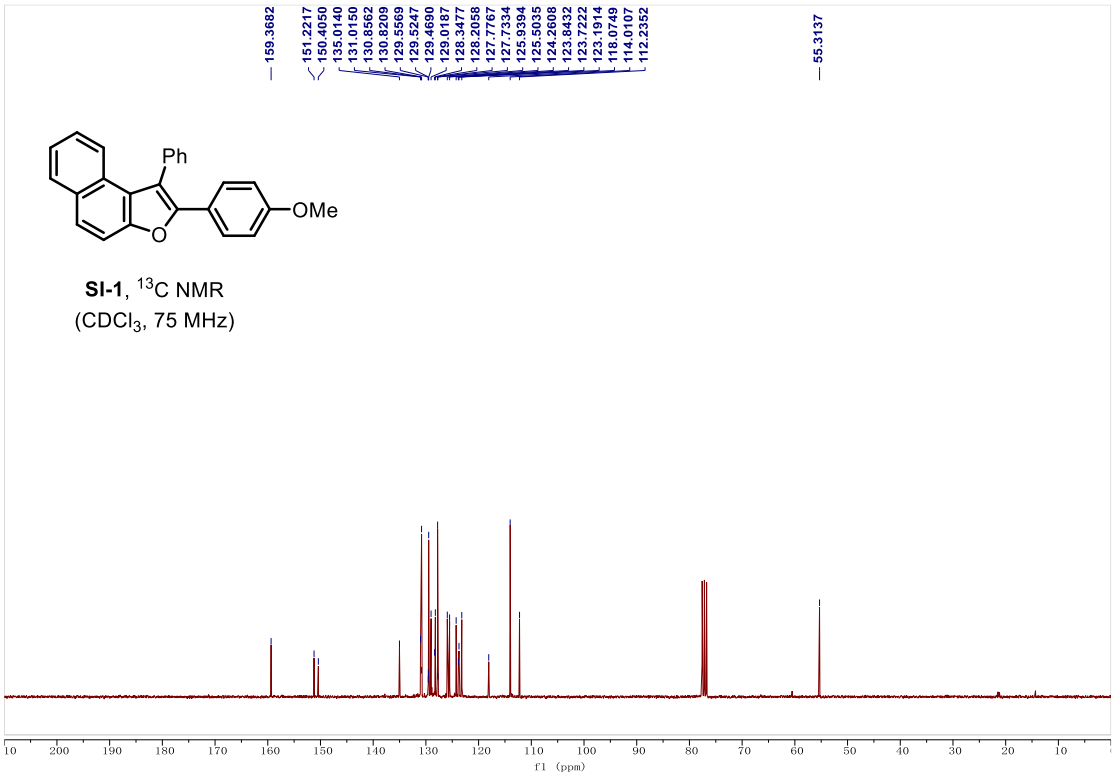


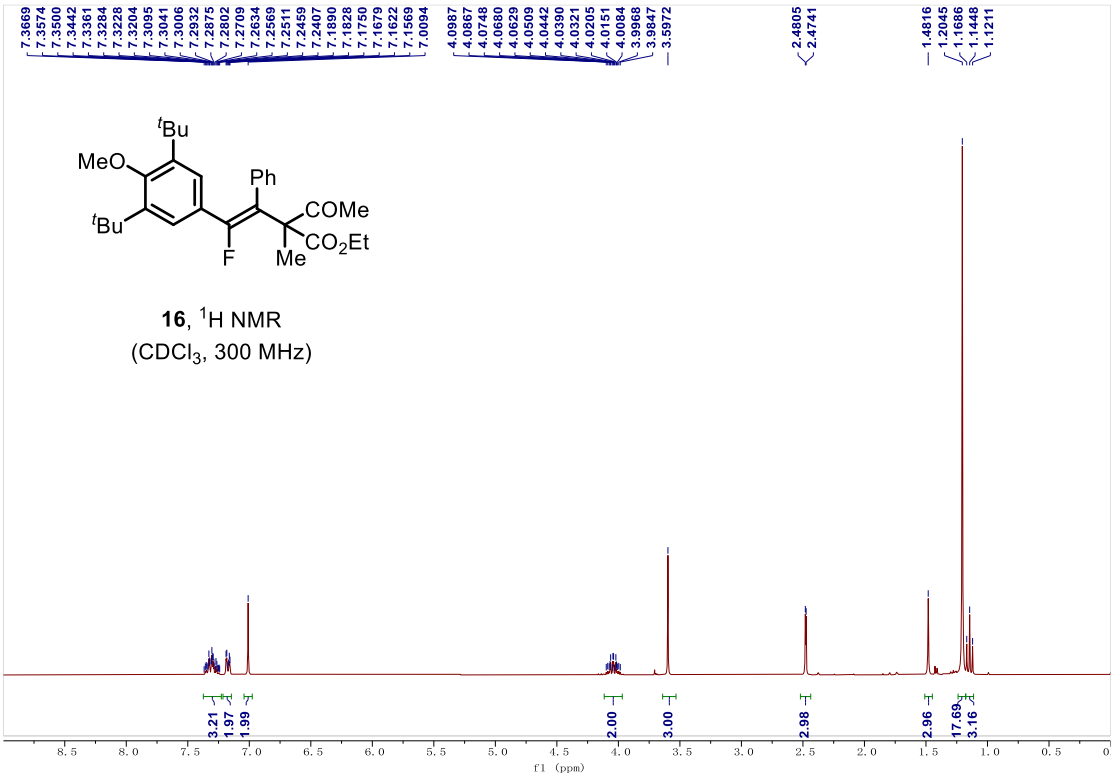
14, ^{13}C NMR
($CDCl_3$, 75 MHz)


7.8624
7.8368
7.6452
7.5400
7.5108
7.4975
7.4922
7.4921
7.4911
7.4800
7.4050
7.3982
7.3826
7.3760
7.3585
7.3544
7.3354
7.3313
7.3269
7.3083
7.3040
7.2402
7.2356
7.2172
7.2124
7.2077
7.1894
7.1850
6.6688
6.6619
6.6399
5.5193
OH
Ph
O
15, 1H NMR
(CDCl3, 300 MHz)
residue of ethyl acetate
CH3CO2CH2CH3
CH3CO2CH2CH3
CH3CO2CH2CH3
0.91
1.86
6.00
3.28
1.09
2.00
0.96
f1 (ppm)

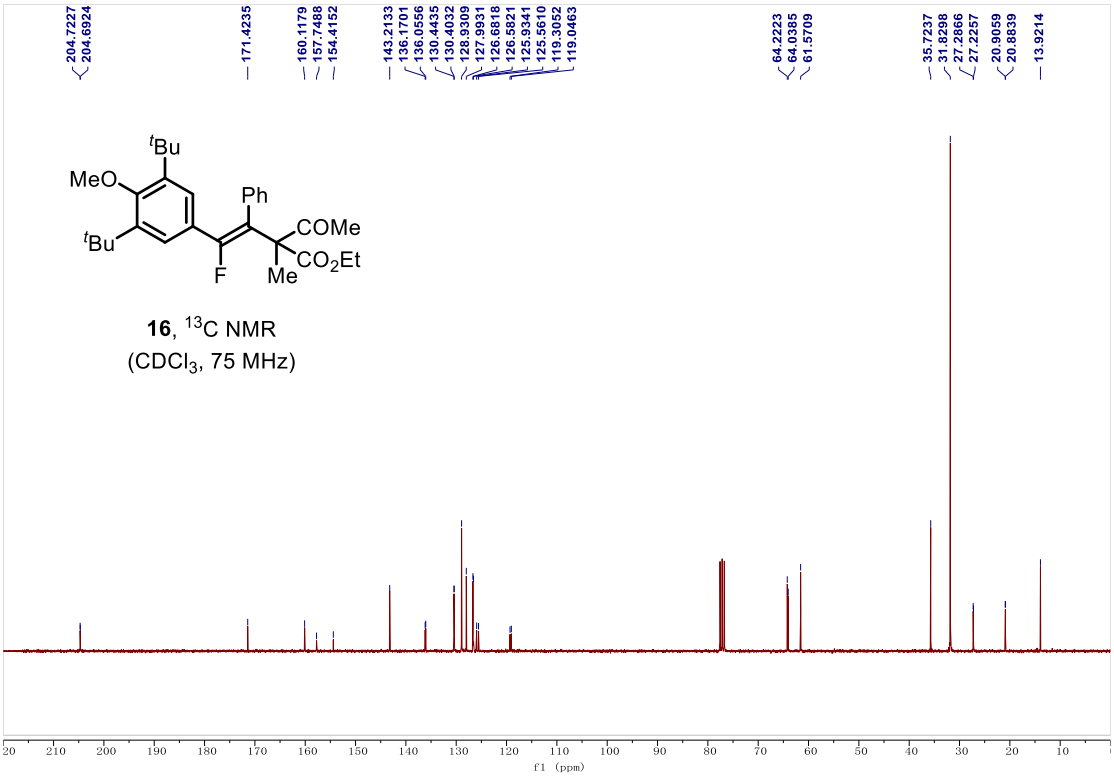

155.3384
151.2142
150.3099
134.9295
131.0243
130.8009
129.4924
129.0637
128.3538
128.2478
128.0432
125.9916
125.5814
124.3108
123.9624
123.8122
123.1979
118.1318
115.5588
112.2596
OH
Ph
O
15, 13C NMR
(CDCl3, 75 MHz)
f1 (ppm)


7.8887
7.8616
7.6844
7.5624
7.5528
7.5496
7.5465
7.5377
7.5280
7.5228
7.5179
7.5092
7.5019
7.4952
7.4901
7.4802
7.4730
7.4648
7.4574
7.4503
7.4407
7.3772
7.3728
7.3542
7.3499
7.3457
7.3272
7.3227
7.2542
7.2495
7.2311
7.2263
7.2216
7.2032
7.1987
7.1828
6.7999
6.7900
6.7827
6.7741
6.7671
6.7601
6.7503
3.7284
Ph
OMe
O
SI-1, 1H NMR
(CDCl3, 300 MHz)
residue of ethyl acetate
CH3CO2CH2CH3
CH3CO2CH2CH3
CH3CO2CH2CH3
1.00
1.72
8.21
1.14
1.24
2.07
2.94
f1 (ppm)

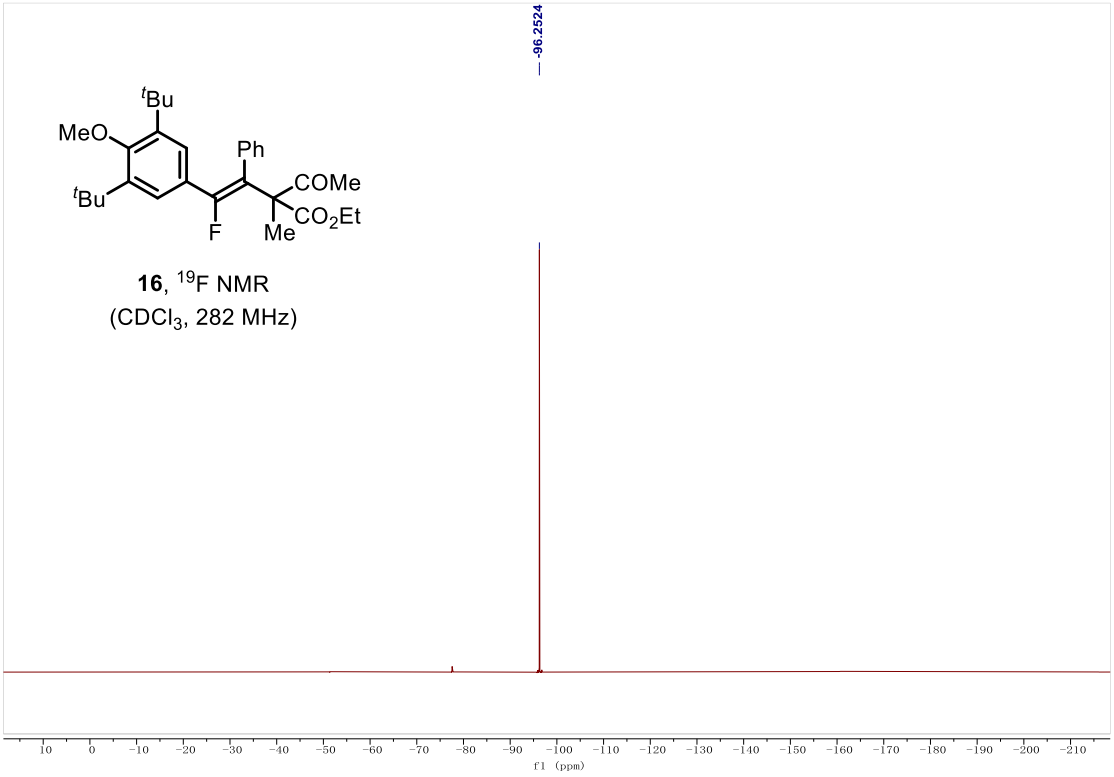

159.3682
151.2217
150.4050
135.0140
131.0150
130.8562
130.8209
129.5569
129.5247
129.4690
129.0187
128.3477
128.2058
127.7767
127.7334
125.9394
125.5035
124.2608
123.8432
123.7222
123.1914
118.0749
114.0107
112.2352
55.3137
Ph
OMe
O
SI-1, 13C NMR
(CDCl3, 75 MHz)
f1 (ppm)



16, ^{1}H NMR
($CDCl_3$, 300 MHz)



16, ^{13}C NMR
($CDCl_3$, 75 MHz)



16, ^{19}F NMR
($CDCl_3$, 282 MHz)