Supporting Information

Three-Component Approach to the Modular Synthesis of Tetra-Substituted Furans/Pyrroles

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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, they were listed as volume/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 (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm, DMSO-d_6: δ = 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 ($CDCl_3$: δ = 77.16 ppm, DMSO-d_6: δ = 39.52 ppm). High Resolution Mass measurement was performed on Agilent Q-TOF 6520 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 (λ = 0.71073 Å).

2. General Procedure for the Synthesis of *p*-QMs 1

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

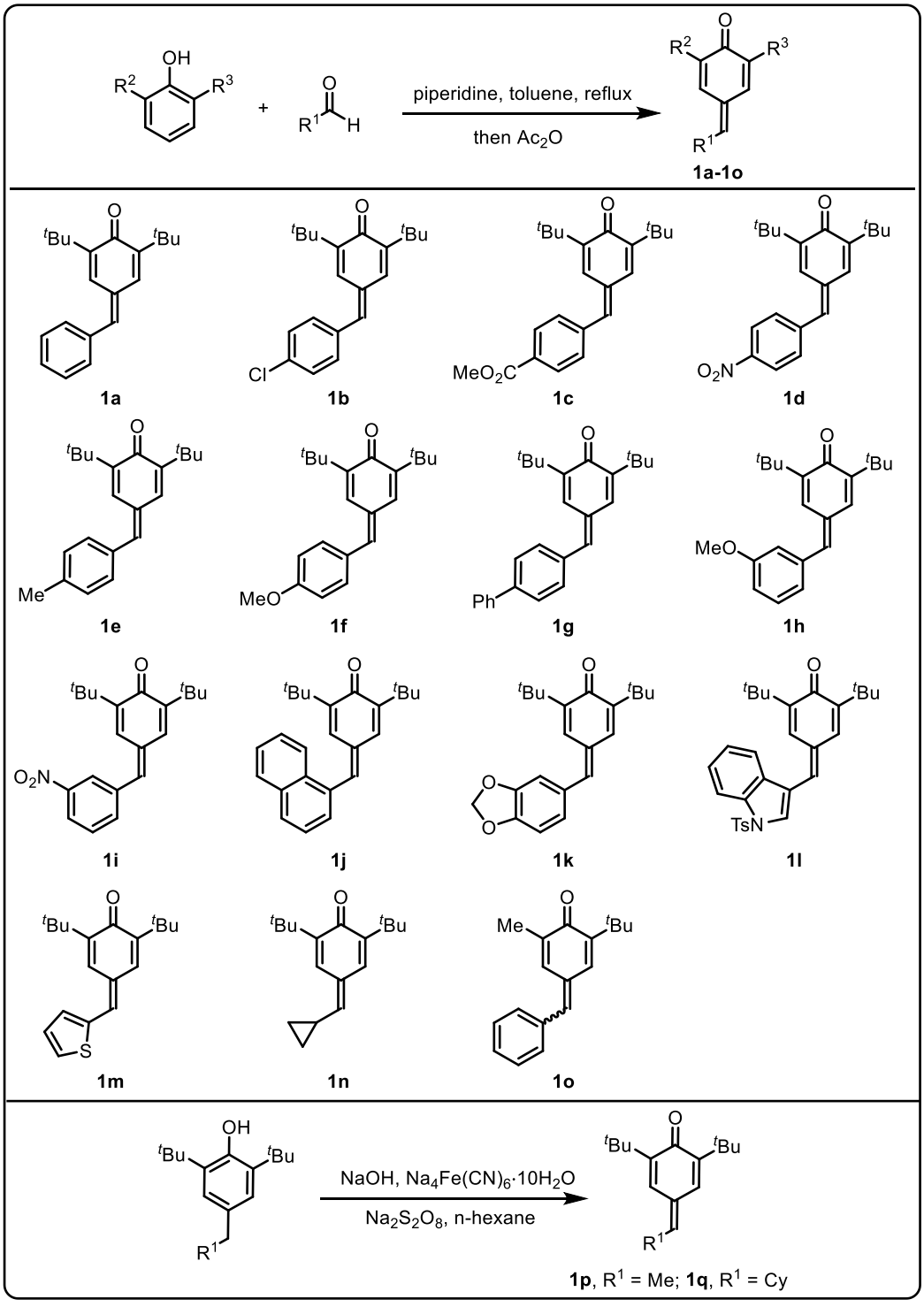


Figure S1. Synthesis of *p*-QMs

3. General Procedure for the Synthesis of 2

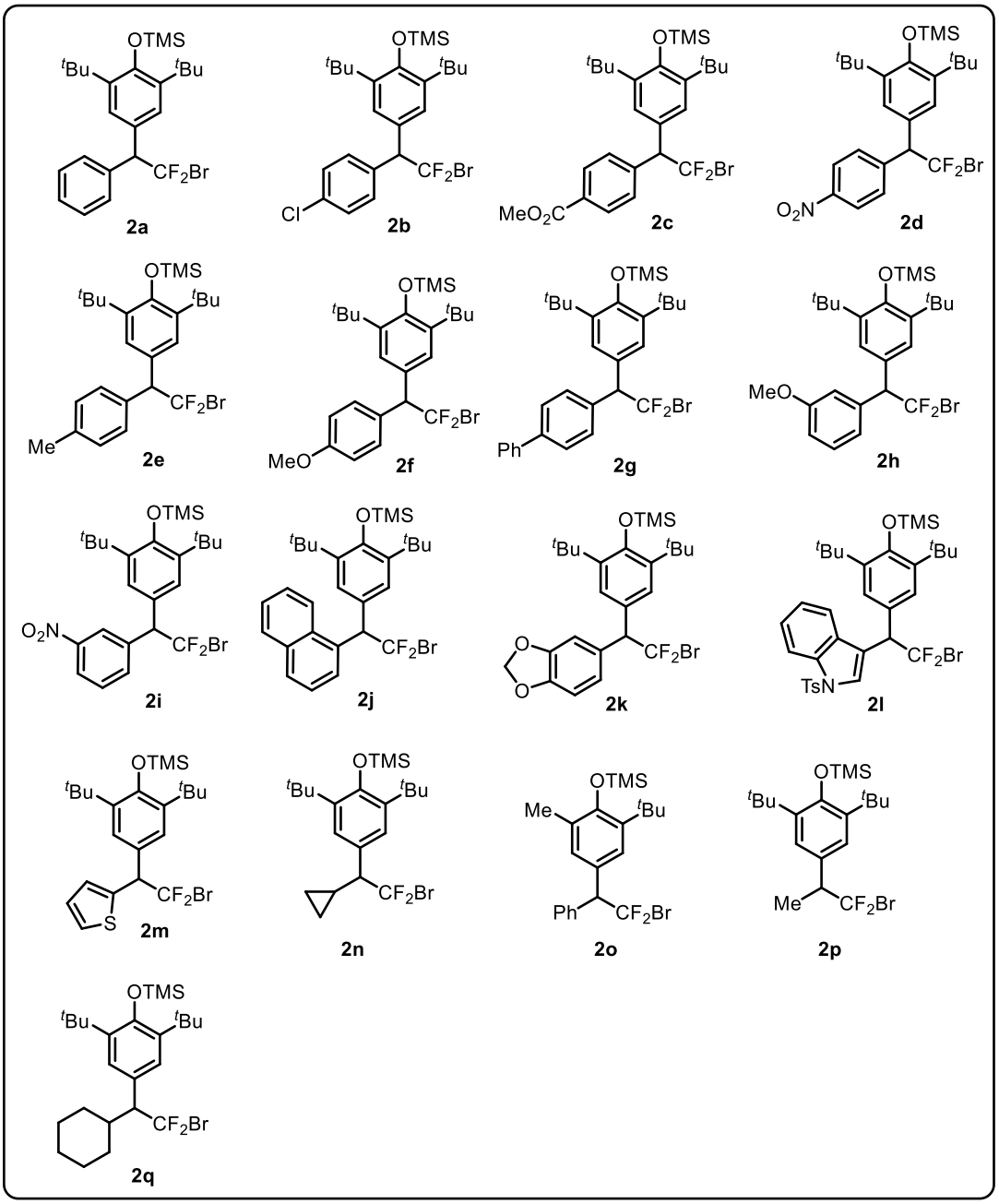
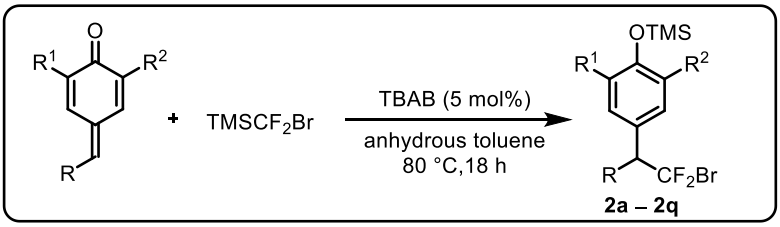


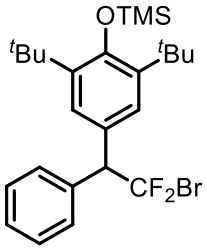
Figure S2. Structures of *p*-QMs Derivatives



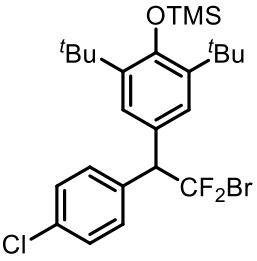
Scheme S1. General procedure for the synthesis of 2

To an oven-dried 10 mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added *p*-QMs (1 mmol, 1.0 eq.) 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 eq.) dissolved in toluene (2.0 mL) was added 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 ethyl acetate (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**.

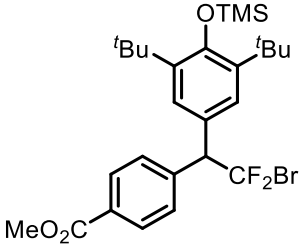
4. Characterization of the *p*-QMs Derived Adducts 2



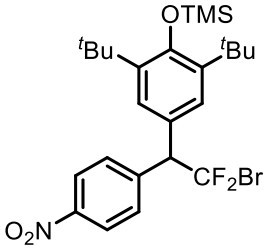
(4-(2-bromo-2,2-difluoro-1-phenylethyl)-2,6-di-tert-butylphenoxy) trimethylsilane (2a) Prepared through general procedure to give **2a** in 476.3 mg, 97% yield. White solid, m.p. 70 – 72 ℃, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.26 – 7.16 (m, 5H), 7.05 (s, 2H), 5.18 (dd, *J* = 18.3, 5.4 Hz, 1H), 1.34 (s, 18H), 0.43 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 154.8, 140.8, 135.5 (*app.* d, ^3J = 4.2 Hz), 129.8, 129.1, 128.3, 124.7 (dd, ^3J = 27.0, 25.4 Hz), 124.0 (dd, ^4J = 5.1, 5.2 Hz), 120.0 (dd, ^1J = 250.9, 248.9 Hz), 56.0 (dd, ^2J = 33.6, 29.9 Hz), 35.3, 31.3 ppm.^{19}F NMR (282 MHz, $CDCl_3$) δ -93.6 (d, *J* = 236.3 Hz), -102.9 (d, *J* = 235.9 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{35}BrF_2OSi + Na]^+$ 519.1495, found 519.1496.



(4-(2-bromo-1-(4-chlorophenyl)-2,2-difluoroethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2b) Prepared through general procedure to give **2b** in 493.0 mg, 93% yield. White solid, m.p. 72 – 74 ℃, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.19 – 7.16 (m, 2H), 7.13 – 7.09 (m, 2H), 6.98 (s, 2H), 5.07 (dd, *J* = 17.8, 5.9 Hz, 1H), 1.28 (s, 18H), 0.37 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 140.9, 135.0, 134.0 (*app.* d, ^3J = 4.4 Hz), 131.0, 128.4, 124.4 (dd, ^3J = 26.3, 26.3 Hz), 124.4 (dd, ^4J = 5.8, 5.8 Hz), 119.7 (dd, ^1J = 248.5, 248.5 Hz), 54.8 (dd, ^2J = 30.5, 30.6 Hz), 35.3, 31.2, 3.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.9 (d, *J* = 235.4 Hz), -104.0 (d, *J* = 235.7 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{34}BrClF_2OSi + H]^+$ 531.1292, found 531.1294.

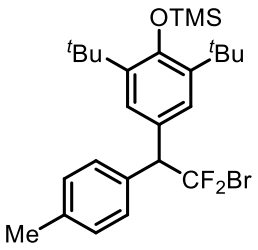


methyl 4-(2-bromo-1-(3,5-di-tert-butyl-4-((trimethylsilyl)oxy) phenyl)-2,2-difluoroethyl)benzoate (2c) Prepared through general procedure to give **2c** in 520.9 mg, 94% yield. White solid, m.p. 84 – 86 ℃, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.01 (s, 2H), 5.17 (dd, *J* = 17.4, 6.1 Hz, 1H), 3.89 (s, 3H), 1.27 (s, 18H), 0.36 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.3, 154.8, 140.9, 142.2 (*app.* d, ^3J = 4.1 Hz), 130.6, 129.6, 129.4, 124.4 (dd, ^3J = 26.2, 26.2 Hz), 123.8 (dd, ^4J = 5.8, 5.8 Hz), 119.6 (dd, ^1J = 249.6, 249.2 Hz), 54.8 (dd, ^2J = 34.3, 30.4 Hz), 52.3, 35.2, 31.1, 3.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.6 (d, *J* = 236.4 Hz), -103.4 (d, *J* = 236.6 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{27}H_{37}BrF_2O_3Si + Na]^+$ 577.1556, found 577.1546.

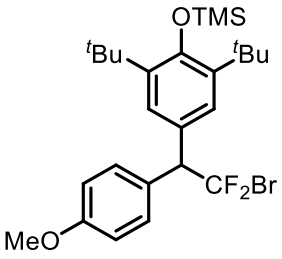


(4-(2-bromo-2,2-difluoro-1-(4-nitrophenyl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2d) Prepared through general procedure to give **2d** in 481.5 mg, 89% yield. White solid, m.p. 100 – 102 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.08 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.02 (s, 2H), 5.21 (dd, *J* = 16.6, 6.6 Hz, 1H), 1.28 (s, 18H), 0.37 (s, 9H) ppm.

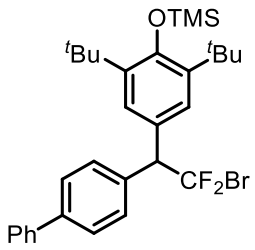
^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 147.9, 142.4 (*app.* d, ^3J = 4.0 Hz), 141.2, 130.8, 124.2 (dd, ^3J = 26.2,26.2 Hz), 123.7 (dd, ^4J = 5.9, 5.9 Hz), 123.3, 119.4 (dd, ^1J = 250.3, 250.0 Hz), 53.8 (dd, ^2J = 34.8, 31.2 Hz), 35.2, 31.1, 3.7 ppm. ^{19}F NMR (282 MHz, CDCl3) δ -94.0 (d, J = 237.9 Hz), -103.1 (d, J = 237.7 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{34}BrF_2NO_3Si + H]^+$ 542.1532, found 542.1535.



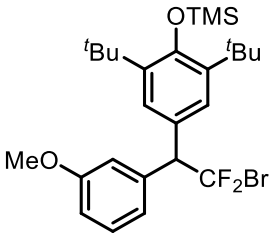
(4-(2-bromo-2,2-difluoro-1-(p-tolyl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2e) Prepared through general procedure to give **2e** in 397.9 mg, 78% yield. White solid, m.p. 100 – 102 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.06 (d, J = 8.1 Hz, 2H), 7.01 – 6.97 (m, 4H), 5.07 (dd, J = 18.3, 5.8 Hz, 1H), 2.28 (s, 3H), 1.27 (s, 18H), 0.36 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 140.7, 139.0, 132.5 (*app*. d, ^3J = 4.4 Hz), 129.5, 128.9, 124.8 (dd, ^3J = 25.8, 26.0 Hz), 124.0 (dd, ^4J = 5.5, 5.4 Hz), 119.9 (dd, ^1J = 248.8 249.1 Hz), 55.9 (dd, ^2J = 33.4, 30.0 Hz), 35.2, 31.2, 21.2, 3.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.8 (d, J = 235.0 Hz), -103.7 (d, J = 234.9 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{38}BrF_2OSi + H]^+$ 511.1838, found 511.1827**.**



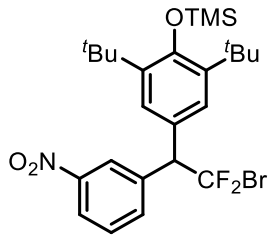
(4-(2-bromo-2,2-difluoro-1-(4-methoxyphenyl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2f) Prepared through general procedure to give **2f** in 420.0 mg, 80% yield. White solid, m.p. 104 – 106 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, J = 8.3 Hz, 2H), 7.01 (s, 2H), 6.74 (d, J = 8.7 Hz, 2H), 5.10 (dd, J = 18.1, 5.8 Hz, 1H), 3.76 (s, 3H), 1.30 (d, J = 1.2 Hz, 18H), 0.38 (d, J = 1.5 Hz, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0, 154.6, 140.6, 130.8, 127.5 (*app.* d, ^3J = 4.4 Hz), 124.8 (d, ^3J = 26.1, 26.2 Hz), 123.9 (dd, ^4J = 5.4, 5.5 Hz) 119.9 (dd, ^1J = 248.7, 248.3 Hz). 113.5, 55.7 (dd, ^2J = 31.4, 28.0 Hz), 55.3, 35.2, 31.1, 3.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.5 (d, J = 235.0 Hz), -103.8 (d, J = 235.0 Hz). HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{37}BrF_2O_2Si + Na]^+$ 549.1606, found 549.1632.



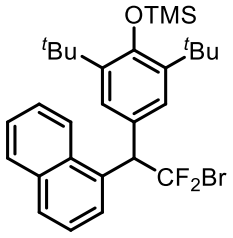
(4-(1-([1,1'-biphenyl]-4-yl)-2-bromo-2,2-difluoroethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2g) Prepared through general procedure to give **2g** in 571.3 mg, 90% yield, white solid, m.p. 73 – 75 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.51 – 7.47 (m, 2H), 7.44 – 7.38 (m, 4H), 7.36 – 7.30 (m, 1H), 7.28 – 7.24 (m, 2H), 7.03 (s, 2H), 5.16 (dd, J = 18.4, 5.5 Hz, 1H), 1.26 (s, 18H), 0.36 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 142.1, 140.8, 140.5, 134.4 (*app.* d, ^3J = 4.3 Hz), 130.1, 129.0, 127.7, 127.2, 127.0, 124.7 (dd, ^3J = 25.7, 25.8 Hz), 124.0 (dd, ^4J = 5.3, 5.4 Hz), 119.9 (dd, ^1J = 249.1, 249.2 Hz), 55.7 (dd, ^2J = 33.7, 30.0 Hz), 35.3, 31.2, 3.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.2 (d, J = 235.4 Hz), -103.6 (d, J = 235.2 Hz). HRMS (ESI) *m*/*z* Calcd for $[C_{31}H_{39}BrF_2OSi + Na]^+$ 595.1814, found 595.1810.



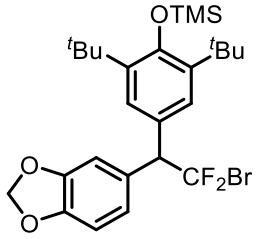
(4-(2-bromo-2,2-difluoro-1-(3-methoxyphenyl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2h) Prepared through general procedure to give **2h** in 489.0 mg, 93% yield. White solid, m.p. 58 – 60 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.10 (t, *J* = 7.9 Hz, 1H), 7.01 (s, 2H), 6.82 – 6.72 (m, 2H), 6.68 (s, 1H), 5.08 (dd, *J* = 18.1, 5.6 Hz, 1H), 3.67 (s, 3H), 1.27 (s, 18H), 0.37 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.3, 154.7, 140.7, 136.7 (*app.* d, ^3J = 4.4 Hz), 129.2, 124.6 (dd, ^3J = 25.9, 25.7 Hz), 123.9 (dd, ^4J = 5.4, 5.4 Hz), 122.0, 119.9 (dd, ^1J = 249.0, 249.2 Hz), 115.1, 114.7, 55.8 (dd, ^2J = 33.8, 29.8 Hz), 55.2, 35.2, 31.2, 3.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.3 (d, *J* = 235.5 Hz), -103.4 (d, *J* = 235.4 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{37}BrF_2O_2Si + Na]^+$ 549.1606, found 549.1609.



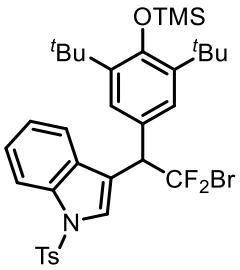
(4-(2-bromo-2,2-difluoro-1-(3-nitrophenyl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2i) Prepared through general procedure to give **2i** in 481.6 mg, 89% yield. White solid, m.p. 78 – 80 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.15 – 8.11 (m, 1H), 7.99 – 7.98 (m, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.04 (s, 2H), 5.25 (dd, *J* = 16.4, 6.4 Hz, 1H), 1.28 (s, 18H), 0.36 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 147.8, 141.2, 137.6 (*app*. d, ^3J = 4.1 Hz), 135.7, 129.3, 124.6, 123.9 (dd, ^3J = 26.0, 26.0 Hz), 123.7, 123.6 (*app.* t, ^4J = 5.5 Hz), 119.5 (dd, ^1J = 249.6, 249.9 Hz), 53.8 (dd, ^2J = 34.9, 31.3 Hz), 35.2, 31.1, 3.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -94.2 (d, *J* = 238.1 Hz), -103.0 (d, *J* = 238.1 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{34}BrF_2NO_3Si + Na]^+$ 564.1352, found 564.1336.



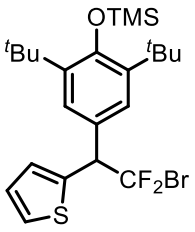
(4-(2-bromo-2,2-difluoro-1-(naphthalen-1-yl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2j) Prepared through general procedure to give **2j** in 398.7 mg, 73% yield. White solid, m.p. 104 – 106 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.10 – 8.06 (m, 1H), 7.75 – 7.67 (m, 2H), 7.50 – 7.45 (m, 1H), 7.37 – 7.34 (m, 1H), 7.28 – 7.23 (m, 1H), 7.19 – 7.14 (m, 1H), 6.90 (s, 2H), 6.12 (dd, *J* = 20.1, 3.7 Hz, 1H), 1.09 (s, 18H), 0.22 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.5, 140.5, 133.1, 131.5 (*app.* d, ^3J = 5.1 Hz), 130.7, 130.1 (*app.* d, ^4J = 2.0 Hz), 128.8, 126.6, 125.6, 125.3, 124.4 (dd, ^3J = 25.8, 25.9 Hz), 123.8 (dd, ^4J = 5.4, 5.4 Hz), 121.7, 119.7 (dd, ^1J = 251.8, 249.5 Hz), 50.0 (dd, ^2J = 33.5, 28.3 Hz), 35.0, 30.9, 3.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -91.9 (d, J = 231.3 Hz), -105.4 (d, J = 231.2 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{37}BrF_2OSi + Na]^+$ 569.1657, found 569.1636.



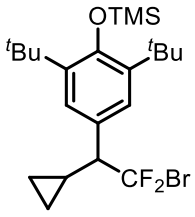
(4-(1-(benzo[d][1,3]dioxol-5-yl)-2-bromo-2,2-difluoroethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2k) Prepared through general procedure to give **2k** in 529.3 mg, 98% yield. White solid, m.p. 88 – 90 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.04 (s, 2H), 6.79 – 6.78 (m, 1H), 6.61 – 6.56 (m, 2H), 5.90 (s, 2H), 5.05 (dd, *J* = 17.7, 5.9 Hz, 1H), 1.30 (s, 18H), 0.37 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.7, 148.2, 147.6, 140.8, 129.1 (*app.* d, ^3J = 4.3 Hz), 124.7 (dd, ^3J = 25.9, 25.8 Hz), 123.9 (dd, ^4J = 5.5, 5.4 Hz), 123.5, 119.9 (dd, ^1J = 249.6, 248.9 Hz), 110.0, 107.6, 101.4, 55.9 (dd, ^2J = 34.0, 30.0 Hz), 35.3, 31.2, 3.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.6 (d, *J* = 235.9 Hz), -103.1 (d, *J* = 236.0 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{35}BrF_2O_3Si + H]^+$ 541.1580, found 541.1582.



3-(2-bromo-1-(3,5-di-tert-butyl-4-((trimethylsilyl)oxy)phenyl)-2,2-difluoroethyl)-1-tosyl-1H-indole (2l) Prepared through general procedure to give **2l** in 592.7 mg, 86% yield. White solid, m.p. 64 – 66 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.67 (s, 1H), 7.22 – 7.13 (m, 4H), 7.09 – 7.05 (m, 3H), 5.43 (dd, *J* = 17.7, 5.8 Hz, 1H), 2.25 (s, 3H), 1.16 (s, 18H), 0.35 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 145.3, 140.8, 134.8, 134.5, 130.1, 128.6, 127.2, 126.9, 125.0, 124.4 (dd, ^3J = 25.7, 25.8 Hz), 123.6 (dd, ^4J = 5.1 5.3 Hz), 123.4, 120.3 (dd, ^1J = 248.4, 248.3 Hz), 117.1 (*app.* d, ^3J = 4.8 Hz), 113.4, 47.6 (dd, ^2J = 36.4, 33.4 Hz), 35.0, 30.9, 21.6, 3.9 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.2 (d, *J* = 235.1 Hz), -101.1 (d, *J* = 235.0 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{34}H_{42}BrF_2NO_3SSi + Na]^+$ 712.1698, found 712.1686.

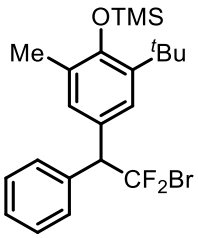


(4-(2-bromo-2,2-difluoro-1-(thiophen-2-yl)ethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2m) Prepared through general procedure to give **2m** in 215.9 mg, 43% yield. White solid, m.p. 72 – 74 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.26 – 7.24 (m, 1H), 7.13 (s, 2H), 6.90 – 6.89 (m, 1H), 6.84 – 6.81 (m, 1H), 5.43 (dd, *J* = 17.6, 5.8 Hz, 1H), 1.31 (s, 18H), 0.36 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.9, 140.9, 138.0 (*app.* d, ^3J = 4.6 Hz), 129.2, 127.4, 126.5, 124.5 (dd, ^3J = 25.9, 25.9 Hz), 123.8 (dd, ^4J = 5.4, 5.4 Hz), 119.4 (dd, ^1J = 249.0, 248.9 Hz), 50.3 (dd, ^2J = 36.7, 32.3 Hz), 35.3, 31.3, 3.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.9 (d, *J* = 235.8 Hz), -103.5 (d, *J* = 235.6 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{23}H_{33}BrF_2OSSi + H]^+$ 503.1246, found 503.1267.

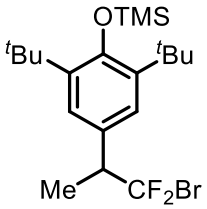


(4-(2-bromo-1-cyclopropyl-2,2-difluoroethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2n) Prepared through general procedure to give **2n** in 432.6 mg, 94% yield. White solid, m.p. 64 – 66 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.37 (s, 2H), 3.63 – 3.53 (m, 1H), 1.41 (s, 18H), 1.24 – 1.15 (m, 1H), 0.75 – 0.55 (m, 2H),

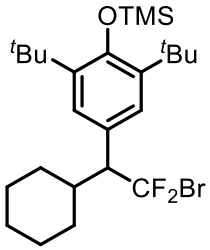
0.41 (s, 9H), 0.36 – 0.28 (m, 1H), 0.13 – 0.04 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8, 141.0, 125.7 (dd, ^3J = 25.7, 25.6 Hz), 123.8 (dd, ^4J = 5.5, 5.7 Hz), 120.4 (dd, ^1J = 246.7, 246.9 Hz), 61.9 (dd, ^2J = 30.8, 30.8 Hz), 35.4, 31.3, 15.0 (dd, ^3J = 3.0, 2.9 Hz), 10.4, 6.2, 3.8 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -90.9 (d, J = 239.5 Hz), -103.3 (d, J = 239.5 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{22}H_{35}BrF_2OSi + H]^+$ 461.1682, found 461.1688.



(4-(2-bromo-2,2-difluoro-1-phenylethyl)-2-(tert-butyl)-6-methylphenoxy)trimethylsilane (2o) Prepared through general procedure to give **2o** in 445.0 mg, 98% yield. White solid, m.p. 72 – 74 °C, R_f = 0.7 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.31 – 7.17 (m, 5H), 6.95 (d, J = 1.5 Hz, 1H), 6.76 (d, J = 1.6 Hz, 1H), 5.12 (dd, J = 17.5, 6.5 Hz, 1H), 2.19 (s, 3H), 1.19 (s, 9H), 0.32 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.6, 139.8, 135.3 (*app.* d, ^3J = 4.0 Hz), 129.8, 129.0, 128.3, 128.2, 126.9 (dd, ^4J = 5.4, 5.4 Hz), 125.4 (dd, ^3J = 26.1, 26.1 Hz), 123.8 (dd, ^4J = 5.4, 5.2 Hz), 119.8 (dd, ^1J = 248.6, 248.7 Hz), 55.8 (dd, ^2J = 33.3, 30.5 Hz), 34.8, 30.1, 20.1, 2.2 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.6 (d, J = 236.3 Hz), -102.9 (d, J = 236.5 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{22}H_{29}F_2OSi + H]^+$ 455.1212, found 455.1187.

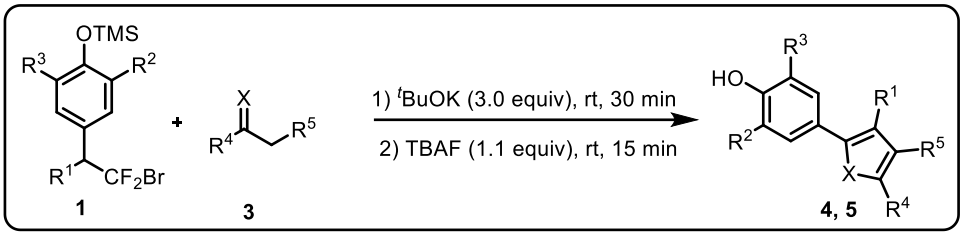


(4-(1-bromo-1,1-difluoropropan-2-yl)-2,6-di-tert-butylphenoxy)trimethylsilane (2p) Prepared through general procedure to give **2p** in 412 mg, 95% yield. White solid, m.p. 62 – 64 °C, R_f = 0.6 (PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (s, 2H), 4.42 – 4.27 (m, 1H), 1.67 (d, J = 7.0 Hz, 3H), 1.41 (s, 18H), 0.41 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.8 (dd, ^6J = 26.0, 26.0 Hz), 140.9, 125.1 (dd, ^3J = 26.3, 26.3 Hz), 123.6 (dd, ^4J = 5.8, 5.9 Hz), 120.6 (dd, ^1J = 246.5, 246.5 Hz), 49.2 (dd, ^2J = 33.1, 33.1 Hz), 20.0 (dd, ^3J = 2.5, 2.6 Hz), 4.2, 4.0, 3.8, 3.4 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -96.1 (d, J = 240.1 Hz), -103.5 (d, J = 240.1 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{20}H_{33}BrF_2OSi + H]^+$ 435.1525, found 435.1528.



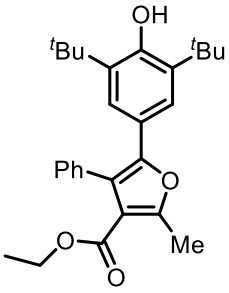
(4-(2-bromo-1-cyclohexyl-2,2-difluoroethyl)-2,6-di-tert-butylphenoxy)trimethylsilane (2q) Prepared through general procedure to give **2q** in 402.0 mg, 80% yield. White solid, m.p. 96 – 98 °C, R_f = 0.5 (PE). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (s, 2H), 4.14 (dd, J = 16.8, 11.0 Hz, 1H), 1.79 – 1.54 (m, 4H), 1.46 – 1.41 (m, 21H), 1.29 – 1.07 (m, 4H), 0.40 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) 154.7, 141.1, 126.3 (dd, ^3J = 26.0, 26.0 Hz), 123.2 (dd, ^4J = 5.8, 5.9 Hz), 120.9 (dd, ^1J = 247.0, 247.0 Hz), 63.6 (dd, ^2J = 29.0, 29.0 Hz), 38.8 (*app.* d, ^4J = 1.7 Hz), 35.3, 32.2, 31.2, 28.1 (*app.* d, ^4J = 1.6 Hz), 26.2, 25.8 (*app.* d, ^4J = 1.3 Hz), 3.7 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -89.1 (d, J = 241.2 Hz), -98.5 (d, J = 241.2 Hz) ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{41}BrF_2OSi + Na]^+$ 525.1970, found 525.1967.

5. General Procedure for the Synthesis of Tetra-substituted Pyrrole/Furans



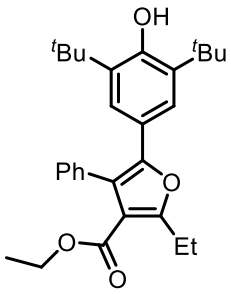
To an oven-dried 8-mL disposable culture tube equipped with a Teflon coated magnetic stir bar was added ^{t}BuOK (67.3 mg, 0.6 mmol, 3.0 equiv in 0.5 mL DCM), and **3** (0.4 mmol, 2.0 equiv in 0.5 mL DCM) under air, stirred for 30 min at ambient temperature, at which time TBAF (47.6 mg, 0.22 mmol, 1.1 equiv in 0.5 mL DCM) was added, and then put **1** (0.2 mmol in 0.5 mL DCM) into the reaction mixture stirred for 5-15 min at ambient temperature (monitored by TLC). After 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 **4** or **5**.

6. Characterization of the Products of Tetra-substituted Pyrrole/Furans

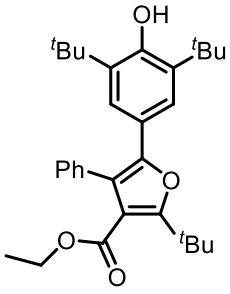


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (4a) Prepared through general procedure to give **4a** in 78.2 mg, 90% yield. White solid, m.p. 128 – 130 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.19 (s, 2H), 5.19 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.27 (s, 18H), 1.02 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 157.5, 153.4, 148.5, 135.8, 134.7, 130.5, 128.2, 127.2, 122.7, 121.8, 120.3, 115.5, 59.8, 34.4, 30.2, 14.4, 13.9 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{28}H_{34}O_4 + H]^+$ 435.2530, found 435.2533.

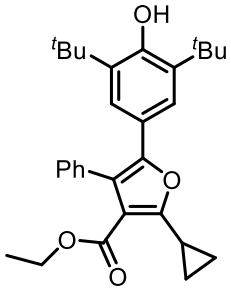
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethyl-4-phenylfuran-3-carboxylate (4b)



Prepared through general procedure to give **4b** in 81.6 mg, 91% yield. White solid, m.p. 114 – 116 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.20 (s, 2H), 5.20 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.10 (q, *J* = 7.5 Hz, 2H). 1.36 (t, *J* = 7.5 Hz, 3H), 1.28 (s, 18H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 162.2, 153.4, 148.4, 135.7, 134.7, 10.5, 128.2, 127.1, 122.7, 121.9, 120.2, 114.6, 59.8, 34.3, 30.1, 21.7, 13.8, 12.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{36}O_4 + H]^+$ 449.2686, found 449.2681.

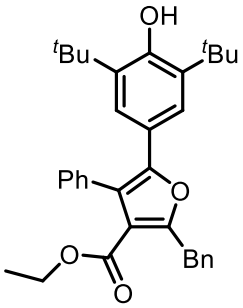


ethyl 2-(tert-butyl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylfuran-3-carboxylate (4c) Prepared through general procedure to give **4c** in 52.4 mg, 55% yield. White solid, m.p. 110 – 112 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.38 – 7.26 (m, 5H), 7.22 (s, 2H), 5.20 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 1.48 (s, 9H), 1.28 (s, 18H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.4, 162.7, 153.4, 146.7, 135.8, 134.5, 130.2, 128.4, 127.2, 122.7, 122.0, 120.7, 115.4, 60.4, 34.6, 34.3, 30.1, 28.8, 13.7 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{31}H_{40}O_4 + H]^+$ 477.2999, found 477.2998.

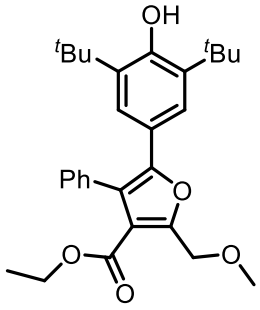


ethyl 2-cyclopropyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylfuran-3-carboxylate (4d) Prepared through general procedure to give **4d** in 82.9 mg, 90% yield. White solid, m.p. 118 – 120 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.11 (s, 2H), 5.19 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.90 – 2.81 (m, 1H), 1.26 (s, 18H), 1.21 – 1.17 (m, 2H), 1.13 – 1.07 (m, 2H), 1.00 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 161.3, 153.3, 147.1, 135.7, 134.6, 130.4, 128.2, 127.1, 122.5, 121.8, 120.5, 115.1, 59.8, 34.3, 30.1, 13.9, 9.5, 8.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{30}H_{36}O_4 + H]^+$ 461.2686, found 461.2673.

ethyl 2-cyclohexyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylfuran-3-carboxylate (4e) Prepared through general procedure to give **4e** in 95.5 mg, 95% yield. White solid, m.p. 138 – 140 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.39 – 7.26 (m, 5H), 7.20 (s, 2H), 5.19 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.51 – 3.41 (m, 1H), 2.03 – 1.97 (m, 2H), 2.03 – 1.97 (m, 2H), 1.78 – 1.63 (m, 3H), 1.50 – 1.34 (m, 3H), 1.28 (s, 1.28), 0.99 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 164.4, 153.3, 148.1, 135.8, 134.8, 130.5, 128.2, 127.1, 122.7, 122.0, 120.0, 113.8, 59.7, 37.4, 34.3, 31.2, 30.1, 26.4, 26.1, 13.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{33}H_{42}O_4 + H]^+$ 503.3156, found 503.3156.

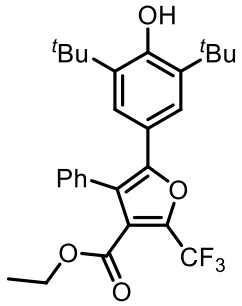


ethyl 2-benzyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylfuran-3-carboxylate (4f) Prepared through general procedure to give **4f** in 92.9 mg, 91% yield. White solid, m.p. 124 – 126 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.43 – 7.36 (m, 3H), 7.34 – 7.27 (m, 6H), 7.25 – 7.20 (m, 1H), 7.17 (s, 2H), 5.19 (s, 1H), 4.44 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.26 (s, 18H), 1.00 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 158.4, 153.5, 149.1, 137.8, 135.8, 134.5, 130.5, 129.1, 128.6, 128.3, 127.2, 126.7, 122.8, 121.7, 120.2, 115.6, 60.00, 34.3, 34.1, 30.1, 13.9 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{34}H_{38}O_4 + H]^+$ 511.2843, found 511.2844.

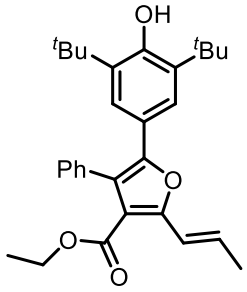


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(methoxymethyl)-4-phenylfuran-3-carboxylate (4g) Prepared through general procedure to give **4g** in 86.5 mg, 93% yield. White solid, m.p. 112-114 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.41 – 7.28 (m, 5H), 7.23 (s, 2H), 5.24 (s, 1H), 4.82 (s, 2H), 4.44 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.50 (s, 3H),1.27 (s, 18H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 154.7, 153.8, 150.6, 135.8, 134.2, 130.5,

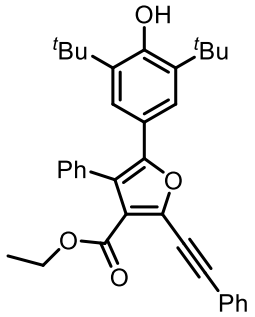
128.3, 127.3, 123.2, 121.4, 120.3, 118.6, 65.3, 60.2, 58.6, 34.3, 30.1, 13.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{36}O_5 + H]^+$ 465.2636, found 465.2637.



ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenyl-2-(trifluoromethyl)furan-3-carboxylate (4h) Prepared through general procedure to give **4h** in 63.5 mg, 65% yield. White solid, m.p. 108 – 110 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.43 – 7.30 (m, 5H), 7.25 (s, 2H), 5.35 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.28 (s, 18H), 1.12 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5, 154.7, 152.0, 140.0 (q, ^2J = 42.4 Hz), 136.0, 132.0, 130.3, 128.6, 128.0, 127.9, 123.6, 121.6 (q, ^3J = 2.3 Hz), 120.8, 120.1, 119.1 (q, ^1J = 268.9 Hz), 61.3, 34.3, 30.0, 13.6 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -61.5 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{28}H_{31}F_3O_4 + H]^+$ 489.2247, found 489.2244.

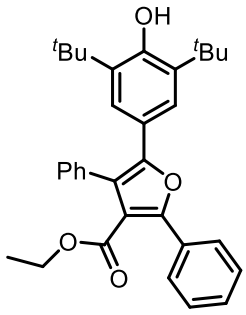


ethyl (E)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenyl-2-(prop-1-en-1-yl)furan-3-carboxylate (4i) Prepared through general procedure to give **4i** in 70.9 mg, 77% yield. White solid, m.p. 128 – 130 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.40 – 7.28 (m, 5H), 7.23 (s, 2H), 7.03 (dd, *J* = 15.9, 1.8 Hz, 1H), 6.62 (dq, *J* = 15.8, 6.9 Hz, 1H), 5.22 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 1.99 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.28 (s, 18H), 1.00 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 154.9, 153.7, 148.9, 135.8, 134.5, 130.5, 130.4, 128.3, 127.2, 123.0, 121.7, 121.0, 119.5, 114.5, 60.0, 34.4, 30.1, 19.0, 13.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{30}H_{36}O_4 + H]^+$ 461.2686, found 461.2684.

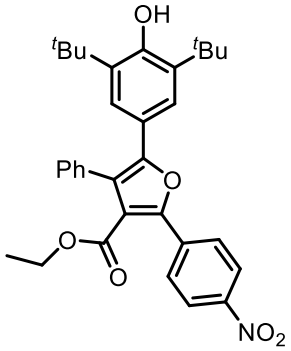


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenyl-2-(phenylethynyl)furan-3-carboxylate (4j) Prepared through general procedure to give **4j** in 98.9 mg, 95% yield. White solid, m.p. 96 – 98 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.65 – 7.62 (m, 2H), 7.43 – 7.33 (m, 8H), 7.27 (s, 2H), 5.29 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.28 (s, 18H), 1.14 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 154.2, 151.7, 138.3, 135.9, 133.4, 131.8, 130.5, 129.2, 128.6, 128.5, 127.7, 123.4, 123.2, 122.2, 121.2, 121.0, 97.9, 79.8, 60.5, 34.4, 30.1, 14.1 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{35}H_{36}O_4 + H]^+$ 521.2686, found 521.2667.

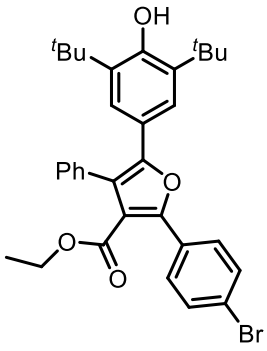
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,4-diphenylfuran-3-carboxylate (4k)



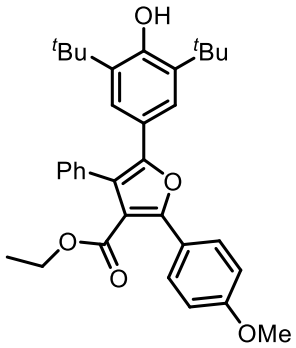
Prepared through general procedure to give **4k** in 71.5 mg, 72% yield. White solid, m.p. 121 – 123 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.94 – 7.91 (m, 2H), 7.48 – 7.42 (m, 2H), 7.41 – 7.32 (m, 6H), 7.30 (s, 2H), 5.26 (s, 1H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.29 (s, 18H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.6, 153.8, 153.7, 149.5, 135.9, 134.2, 130.4, 130.2, 128.9, 128.5, 128.4, 127.8, 127.4, 123.1, 121.8, 121.6, 116.8, 60.5, 34.4, 30.1, 13.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{33}H_{36}O_4 + H]^+$ 497.2686, found 497.2687.



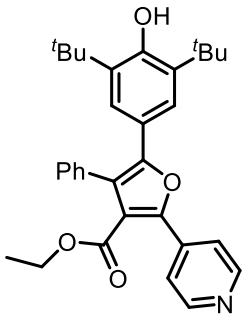
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-nitrophenyl)-4-phenylfuran-3-carboxylate (4l) Prepared through general procedure to give **4l** in 88.8 mg, 82% yield. White solid, m.p. 168 – 170 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.31 (d, *J* = 9.0 Hz, 2H), 8.14 (d, *J* = 9.0 Hz, 2H), 7.45 – 7.34 (m, 5H), 7.31 (s, 2H), 5.34 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 1.30 (s, 18H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 154.4, 151.4, 150.2, 147.2, 136.1, 135.9, 133.5, 130.2, 128.6, 127.8 (two overlapping carbon signals), 123.9, 123.4, 122.5, 120.9, 119.9, 61.1, 34.4, 30.1, 13.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{33}H_{35}NO_6 + H]^+$ 542.2537, found 542.2537.



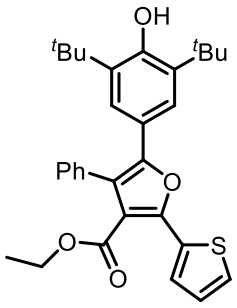
ethyl 2-(4-bromophenyl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenylfuran-3- carboxylate (4m) Prepared through general procedure to give **4m** in 102.4 mg, 89% yield. White solid, m.p. 118 – 120 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.43 – 7.33 (m, 5H), 7.28 (s, 2H), 5.26 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 1.29 (s, 18H), 0.91 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 154.0, 152.5, 149.9, 136.0, 134.1, 131.6, 130.4, 129.3, 129.2, 128.5, 127.5, 123.1 (two overlapping carbon signals), 122.0, 121.4, 117.3, 60.6, 34.4, 30.1, 13.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{33}H_{35}BrO_4 + H]^+$ 575.1791, found 575.1780.



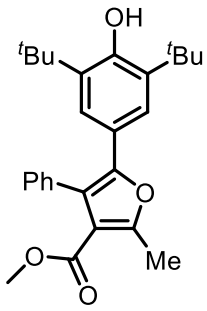
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(4-methoxyphenyl)-4-phenylfuran-3- carboxylate (4n) Prepared through general procedure to give **4n** in 73.7 mg, 70% yield. White solid, m.p. 128 –130 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.44 – 7.32 (m, 5H), 7.28 (s, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 5.23 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.87 (s, 3H), 1.30 (s, 18H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.7, 160.3, 154.3, 153.7, 149.0, 135.9, 134.5, 130.4, 129.5, 128.4, 127.3 (two overlapping carbon signals), 123.0 (two overlapping carbon signals), 121.7, 115.6, 113.8, 60.4, 55.5, 34.4, 30.2, 13.7 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{34}H_{38}O_5 + H]^+$ 527.2792, found 527.2795.



ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenyl-2-(pyridin-4-yl)furan-3- carboxylate (4o) Prepared through general procedure to give **4o** in 87.6 mg, 88% yield. White solid, m.p. 155 – 157 ℃, R_f = 0.4 (PE/EA = 20/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.71 – 8.69 (m, 2H), 7.87 – 7.85 (m, 2H), 7.45 – 7.35 (m, 2H), 7.32 (s, 2H), 5.48 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.31 (s, 18H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 154.3, 151.1, 150.0, 149.5, 137.0, 136.1, 133.5, 130.2, 128.6, 127.7, 123.3, 122.3, 120.9, 120.8, 120.0, 61.0, 34.4, 30.1, 13.5 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{32}H_{35}NO_4 + H]^+$ 498.2639, found 498.2637.

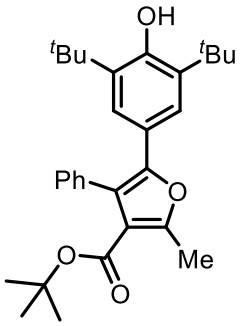


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-phenyl-2-(thiophen-2-yl)furan-3- carboxylate (4p) Prepared through general procedure to give **4p** in 78.4 mg, 78% yield. White solid, m.p. 150 – 152 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.00 – 7.99 (m, 1H), 7.43 – 7.40 (m, 2H), 7.38 – 7.33 (m, 4H), 7.29 (s, 2H), 7.15 – 7.12 (m, 1H), 5.26 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.29 (s, 18H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 153.8, 150.3, 148.9, 135.9, 134.4, 132.1, 130.4, 128.4, 128.0, 127.5, 127.5, 127.4, 123.0, 121.6, 121.3, 115.0, 60.4, 34.4, 30.1, 13.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{31}H_{34}O_4S + H]^+$ 503.2251, found 503.2258.

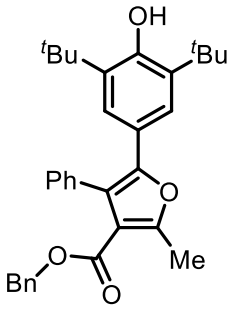


methyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (4q) Prepared through general procedure to give **4q** in 68.1 mg, 81% yield. White solid, m.p. 152 – 154 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.17 (s, 2H), 5.20 (s, 1H), 3.63 (s, 3H), 2.68 (s, 3H), 1.27 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 157.6, 153.4, 148.7, 135.7, 134.4, 130.4, 128.3, 127.2, 122.8, 121.7, 120.3, 115.2, 51.1, 34.3, 30.1, 14.5 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{27}H_{32}O_4 + H]^+$

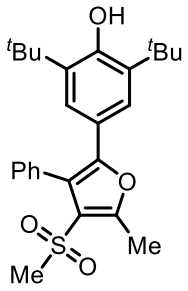
421.2373, found 421.2372.



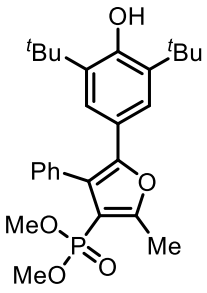
tert-butyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (4r) Prepared through general procedure to give **4r** in 87.0 mg, 94% yield. White solid, m.p. 178 – 180 °C, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.31 – 7.25 (m, 3H), 7.18 (s, 2H), 5.17 (s, 1H), 2.65 (s, 3H), 1.27 (s, 18H), 1.22 (s, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 157.1, 153.3, 148.2, 135.7, 135.2, 130.4, 128.3, 127.0, 122.6, 122.0, 120.2, 116.9, 80.2, 34.4, 30.2, 28.0, 14.1 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{30}H_{38}O_4 + H]^+$ 463.2843, found 463.2841.



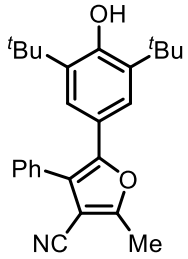
benzyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (4s) Prepared through general procedure to give **4s** in 86.4 mg, 87% yield. White solid, m.p. 136 – 138 °C, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.24 – 7.21 (m, 3H), 7.17 (s, 2H), 6.99 – 6.96 (m, 2H), 5.19 (s, 1H), 5.09 (s, 2H), 2.68 (s, 3H), 1.27 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 158.1, 153.4, 148.7, 135.9, 135.8, 134.6, 130.5, 128.5, 128.4, 127.8 (two overlapping carbon signals), 127.3, 122.7, 121.7, 120.0, 115.2, 65.8, 34.3, 30.1, 14.5 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{33}H_{36}O_4 + H]^+$ 497.2686, found 497.2690.



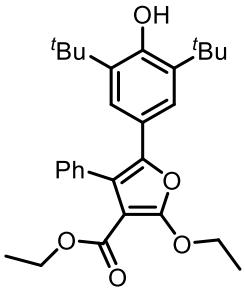
2,6-di-tert-butyl-4-(5-methyl-4-(methylsulfonyl)-3-phenylfuran-2-yl)phenol (4t) Prepared through general procedure to give **4t** in 64.3 mg, 73% yield. White solid, m.p. 190 – 192 °C, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.44 – 7.38 (m, 5H), 7.14 (s, 2H), 5.26 (s, 1H), 2.73 (s, 3H), 2.70 (s, 3H), 1.27 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.2, 154.0, 149.8, 136.0, 131.7, 131.3, 129.0, 128.5, 123.1, 123.0, 120.8, 117.6, 44.7, 34.4, 30.1, 13.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{32}O_4S + Na]^+$ 463.1914, found 463.1900.



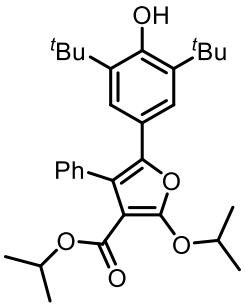
Dimethyl (5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-yl)phosphonate (4u) Prepared through general procedure to give **4u** in 43.2 mg, 46% yield. White solid, m.p. 168 – 170 °C, R_f = 0.4 (PE/EA = 20/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.38 – 7.31 (m, 5H), 7.16 (s, 2H), 5.23 (s, 1H), 3.54 (s, 3H), 3.50 (s, 3H), 2.68 (d, J = 2.2 Hz, 3H), 1.27 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.0 (d, ^2J = 26.9 Hz), 153.5, 149.4 (d, ^2J = 14.7 Hz), 135.8, 133.9, 130.5, 128.4, 127.6, 122.9, 121.5, 121.1 (d, ^2J = 12.0 Hz), 108.6 (d, ^1J = 212.0 Hz), 52.1, 52.1, 34.4, 30.1, 14.1 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{27}H_{35}O_5P + H]^+$ 471.2295, found 471.2309.



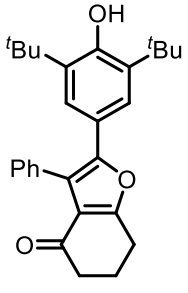
5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-carbonitrile (4v) Prepared through general procedure to give **4v** in 67.4 mg, 87% yield. White solid, m.p. 148 – 150 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.44 – 7.33 (m, 5H), 7.26 (s, 2H), 5.31 (s, 1H), 2.58 (s, 3H), 1.31 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 154.3, 149.7, 136.1, 131.4, 129.4, 129.0, 128.2, 123.4, 120.7, 120.0, 114.3, 97.9, 34.4, 30.2, 13.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{29}NO_2 + Na]^+$ 410.2091, found 410.2083.



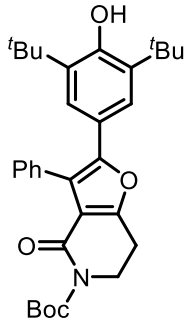
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethoxy-4-phenylfuran-3-carboxylate (4w) Prepared through general procedure to give **4w** in 53.0 mg, 57% yield. White solid, m.p. 112 – 114 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.40 – 7.29 (m, 5H), 7.11 (s, 2H), 5.17 (s, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 4.06 (q, *J* = 7.1 Hz, 2H), 1.55 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 18H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 161.3, 153.1, 140.4, 135.9, 134.2, 130.4, 128.2, 127.3, 122.2, 121.6, 120.5, 94.8, 68.0, 59.6, 34.3, 30.1, 15.2, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{36}O_5 + H]^+$ 465.2636, found 465.2640.



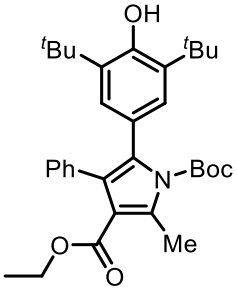
isopropyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-isopropoxy-4-phenylfuran-3-carboxylate (4x) Prepared through general procedure to give **4x** in 62.1 mg, 63% yield, white solid, m.p. 110 – 112 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.44 – 7.25 (m, 5H), 7.13 (s, 2H), 5.16 (s, 1H), 5.05 – 4.91 (m, 2H)), 1.52 (d, *J* = 6.2 Hz, 6H), 1.27 (s, 18H), 1.01 (d, *J* = 6.3 Hz, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 160.9, 153.0, 140.4, 135.8, 134.6, 130.5, 128.2, 122.2, 121.8, 120.4, 96.8, 77.1, 66.8, 34.4, 30.1, 22.6, 21.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{31}H_{40}O_5 + H]^+$ 493.2949, found 493.2945.



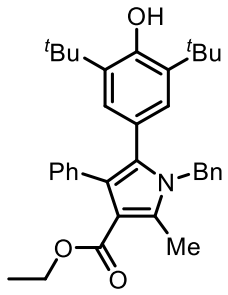
2-(3,5-di-tert-butyl-4-hydroxyphenyl)-3-phenyl-6,7-dihydrobenzofuran-4(5H)-one (4y) Prepared through general procedure to give **4y** in 45.2 mg, 54% yield. White solid, m.p. 190 – 192 ℃, R_f = 0.4 (PE/EA = 20/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.37 – 7.29 (m, 5H), 7.21 (s, 2H), 5.24 (s, 1H), 2.99 (t, *J* = 6.2 Hz, 2H), 2.49 (t, *J* = 6.3 Hz, 2H), 2.25 – 2.17 (m, 2H), 1.29 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.3, 165.6, 153.8, 150.4, 135.9, 132.9, 130.3, 128.3, 127.4, 123.4, 121.4 (two overlapping carbon signals), 117.8, 38.7, 34.4, 30.2, 23.9, 22.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{28}H_{32}O_3 + H]^+$ 417.2424, found 417.2426.



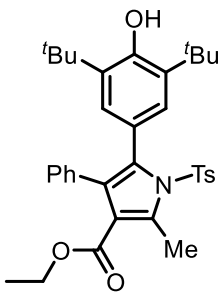
tert-butyl 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-oxo-3-phenyl-6,7-dihydrofuro[3,2-c]pyridine-5(4H)-carboxylate (4z) Prepared through general procedure to give **4z** in 83.7 mg, 81% yield. White solid, m.p. 98 – 100 °C, R_f = 0.4 (PE/EA = 20/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.43 – 7.28 (m, 5H), 7.19 (s, 2H), 5.26 (s, 1H), 4.15 (t, *J* = 6.4 Hz, 2H), 3.05 (t, *J* = 6.4 Hz, 2H), 1.51 (s, 9H), 1.28 (s, 18H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4, 159.6, 153.8, 153.3, 151.1, 135.8, 132.4, 130.5, 128.4, 127.5, 123.2, 121.3, 119.3, 116.8, 82.9, 44.4, 34.3, 30.1, 28.2, 23.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{32}H_{39}NO_5 + Na]^+$ 540.2720, found 540.2710.



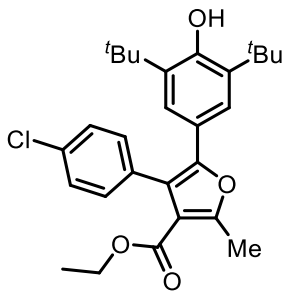
1-(tert-butyl) 3-ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenyl-1H-pyrrole-1,3-dicarboxylate (4aa) Prepared through general procedure to give **4aa** in 66.1 mg, 62% yield. White solid, m.p. 172 – 174 °C, R_f = 0.5 (PE/EA = 20/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.18 – 7.11 (m, 3H), 7.08 – 7.05 (m, 2H), 6.86 (s, 2H), 5.10 (s, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.75 (s, 3H), 1.30 (s, 18H), 1.22 (s, 9H), 0.96 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 153.0, 150.0, 136.7, 135.4, 135.0, 132.3, 130.8, 127.0, 126.9, 126.0, 125.2, 124.0, 114.8, 84.3, 59.7, 34.2, 30.3, 27.4, 13.9, 13.2 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{33}H_{43}NO_5 + Na]^+$ 556.3033, found 556.3018.



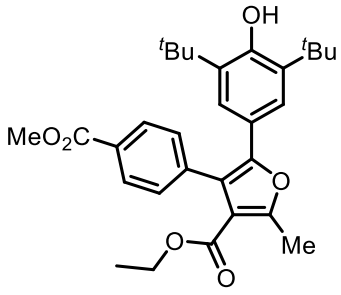
ethyl 1-benzyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenyl-1H-pyrrole-3-carboxylate (4ab) Prepared through general procedure to give **4ab** in 48.1 mg, 46% yield. White solid, m.p. 130 – 132 °C, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.37 – 7.28 (m, 3H), 7.19 – 7.11 (m, 5H), 7.03 – 7.01 (m, 2H), 6.72 (s, 2H), 5.10 (s, 2H), 5.08 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.51 (s, 3H), 1.11 (s, 18H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 153.2, 138.3, 136.7, 135.7, 135.3, 133.4, 131.0, 129.0, 127.9, 127.3, 127.1, 125.6, 125.5, 123.3, 122.1, 111.6, 59.4, 48.1, 34.2, 30.1, 14.0, 11.9 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{35}H_{41}NO_3 + H]^+$ 524.3159, found 524.3167.



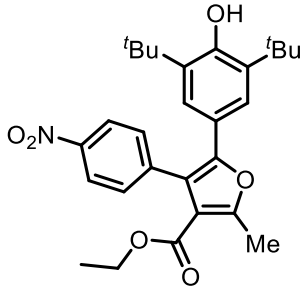
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-phenyl-1-tosyl-1H-pyrrole-3-carboxylate (4ac) Prepared through general procedure to give **4ac** in 49.3 mg, 42% yield. White solid, m.p. 183 – 185 °C, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.20 – 7.17 (m, 2H), 7.07 – 7.04 (m, 5H), 6.88 – 6.84 (m, 2H), 6.63 (s, 2H), 5.13 (s, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.93 (s, 3H), 2.33 (s, 3H), 1.23 (s, 18H), 0.92 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 153.6, 144.5, 138.2, 136.7, 134.7, 134.2, 134.1, 130.1, 129.9, 129.4, 127.3, 127.1, 126.8, 126.1, 120.8, 117.2, 60.3, 34.1, 30.3, 21.8, 14.4, 13.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{35}H_{41}NO_5S + H]^+$ 588.2778, found 588.2779.



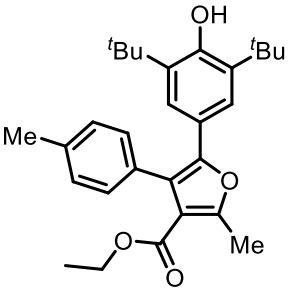
ethyl 4-(4-chlorophenyl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylfuran-3-carboxylate (5a) Prepared through general procedure to give **5a** in 76.8 mg, 82% yield. White solid, m.p. 130 – 132 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.27 – 7.24 (m, 2H), 7.15 (s, 2H), 5.23 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.29 (s, 18H), 1.08 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 157.8, 153.6, 148.8, 135.9, 133.2, 133.2, 132.0, 128.4, 122.8, 121.5, 119.0, 115.2, 60.0, 34.4, 30.1, 14.4, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{28}H_{33}ClO_4 + H]^+$ 469.2140, found 469.2149.



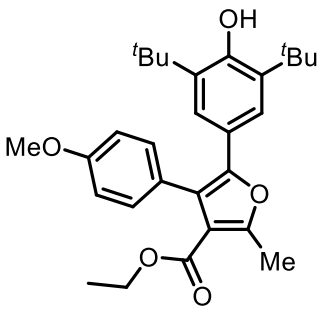
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(4-(methoxycarbonyl)phenyl)-2-methylfuran-3-carboxylate (5b) Prepared through general procedure to give **5b** in 94.5 mg, 96% yield. White solid, m.p. 110 – 112 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.15 (s, 2H), 5.24 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 3H), 2.69 (s, 3H), 1.27 (s, 18H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.2, 164.1, 157.9, 153.7, 148.8, 140.0, 135.9, 130.7, 129.5, 128.8, 122.8, 121.3, 119.2, 115.2, 60.0, 52.2, 34.4, 30.1, 14.4, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{30}H_{36}O_6 + H]^+$ 493.2585, found 493.2583.



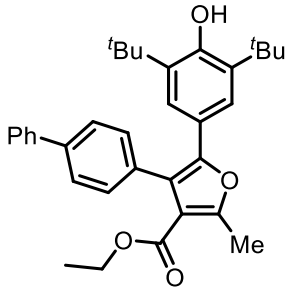
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-(4-nitrophenyl)furan-3-carboxylate (5c) Prepared through general procedure to give **5c** in 70.9 mg, 74% yield. White solid, m.p. 118 – 120 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 2H), 7.51 (d, *J* = 8.6 Hz, 2H), 7.09 (s, 2H), 5.28 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.27 (s, 18H), 1.09 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8, 158.3, 154.0, 149.4, 147.0, 142.3, 136.1, 131.8, 123.4, 123.1, 120.8, 118.1, 114.9, 60.2, 34.4, 30.1, 14.5, 14.1 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{28}H_{33}NO_6 + Na]^+$ 502.2200, found 502.2215.



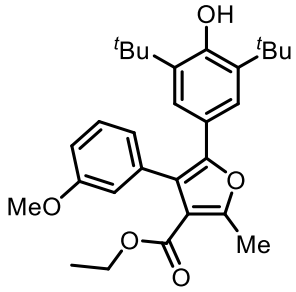
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-(p-tolyl)furan-3-carboxylate (5d) Prepared through general procedure to give **5d** in 75.3 mg, 84% yield, white solid, m.p. 116 – 118 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.23 – 7.18 (m, 6H), 5.18 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 2.36 (s, 3H), 1.28 (s, 18H), 1.07 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 157.3, 153.3, 148.5, 136.7, 135.7, 131.5, 130.3, 128.9, 122.6, 121.9, 120.3, 115.5, 59.8, 34.4, 30.1, 21.3, 14.4, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{36}O_4 + H]^+$ 449.2686, found 449.2688.



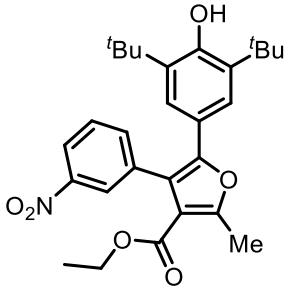
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(4-methoxyphenyl)-2-methylfuran-3-carboxylate (5e) Prepared through general procedure to give **5e** in 86.5 mg, 93% yield. White solid, m.p. 103 – 105 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 4H), 6.93 – 6.90 (m, 2H), 5.18 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 3H), 2.67 (s, 3H), 1.29 (s, 18H), 1.09 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 158.9, 157.3, 153.3, 148.6, 135.7, 131.6, 126.8, 122.7, 121.9, 119.9, 115.5, 113.8, 59.8, 55.5, 34.4, 30.1, 14.4, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{36}O_5 + H]^+$ 465.2636, found 465.2621



ethyl 4-([1,1'-biphenyl]-4-yl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylfuran-3-carboxylate (5f) Prepared through general procedure to give **5f** in 76.5 mg, 75% yield. White solid, m.p. 108 – 110 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.62 – 7.58 (m, 4H), 7.49 – 7.42 (m, 2H), 7.41 – 7.34 (m, 3H), 7.22 (s, 2H), 5.20 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.28 (s, 18H), 1.07 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 157.6, 153.5, 148.7, 141.5, 140.2, 135.8, 133.8, 130.9, 128.9, 127.2 (two overlapping carbon signals), 127.1, 122.7, 121.8, 119.9, 115.4, 59.9, 34.4, 30.1, 14.4, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{34}H_{38}O_4 + H]^+$ 511.2843, found 511.2838.

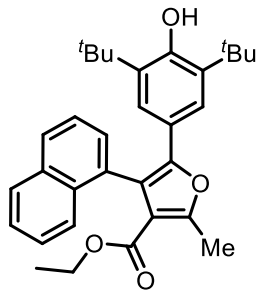


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-4-(3-methoxyphenyl)-2-methylfuran-3-carboxylate (5g) Prepared through general procedure to give **5g** in 77.1 mg, 83% yield. White solid, m.p. 90 – 92 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.31 – 7.23 (m, 3H), 6.92 – 6.86 (m, 3H), 5.21 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 2.68 (s, 3H), 1.29 (s, 18H), 1.04 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 159.6, 157.4, 153.4, 148.4, 136.0, 135.8, 129.3, 123.0, 122.6, 121.7, 120.0, 115.8, 115.5, 113.0, 59.8, 55.4, 34.4, 30.1, 14.4, 13.9 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{36}O_5 + H]^+$ 465.2636, found 465.2610.

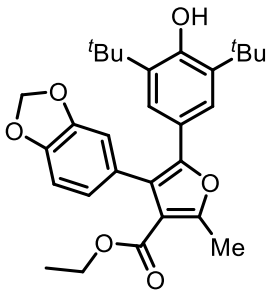


ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-(3-nitrophenyl)furan-3- carboxylate (5h) Prepared through general procedure to give **5h** in 79.5 mg, 83% yield. White solid, m.p. 108 – 110 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.24 – 8.18 (m, 2H), 7.69 – 7.65 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.12 (s, 2H), 5.26 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.27 (s, 18H), 1.06 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9, 158.3, 154.0, 149.5, 148.2, 137.2, 136.7, 136.1, 129.0, 125.9, 123.0, 122.1, 120.9, 117.7, 115.0, 60.1, 34.4, 30.1,

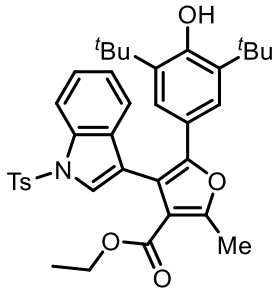
14.5, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{28}H_{33}NO_6 + H]^+$ 480.2381, found 480.2380.



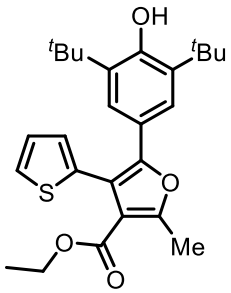
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-ethyl-4-(naphthalen-1-yl)furan-3-carboxylate (5i) Prepared through general procedure to give **5i** in 72.6 mg, 75% yield. White solid, m.p. 148 – 150 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.88 – 7.82 (m, 2H), 7.74 – 7.71 (m, 1H), 7.49 – 7.41 (m, 2H), 7.39 – 7.33 (m, 2H), 7.08 (s, 2H), 5.12 (s, 1H), 3.86 – 3.75 (m, 2H), 2.76 (s, 3H), 1.11 (s, 18H), 0.52 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 157.9, 153.4, 149.1, 135.8, 133.8, 133.3, 132.8, 128.1, 127.7 (two overlapping carbon signals), 126.2, 126.1, 125.7, 125.6, 122.3, 121.7, 117.7, 116.5, 59.5, 34.2, 30.0, 14.3, 13.2 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{32}H_{36}O_4 + H]^+$ 485.2686, found 485.2681.



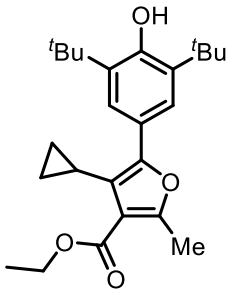
ethyl 4-(benzo[d][1,3]dioxol-5-yl)-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylfuran-3-carboxylate (5j) Prepared through general procedure to give **5j** in 84.2 mg, 88% yield. White solid, m.p. 98 – 100 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.23 (s, 2H), 6.90 – 6.73 (m, 3H), 5.95 (s, 2H), 5.21 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.66 (s, 18H), 1.32 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 157.4, 153.4, 148.7, 147.5, 146.7, 135.8, 128.1, 123.9, 122.7, 121.8, 119.8, 115.5, 111.2, 108.4, 101.0, 59.9, 34.4, 30.2, 14.5, 14.1 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{29}H_{34}O_6 + H]^+$ 479.2428, found 479.2424.



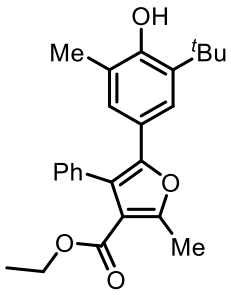
ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-(1-tosyl-1H-indol-3-yl)furan-3-carboxylate (5k) Prepared through general procedure to give **5k** in 80.3 mg, 64% yield, white solid, m.p. 100 – 102 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 8.03 (d, *J* = 8.3 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.57 (s, 1H), 7.32 – 7.26 (m, 1H), 7.23 – 7.08 (m, 6H), 5.18 (s, 1H), 3.90 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 2.33 (s, 3H), 1.10 (s, 18H), 0.65 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 158.1, 153.6, 150.1, 144.9, 135.8, 135.5, 134.8, 131.0, 130.0, 127.1, 125.2, 124.6, 123.2, 122.5, 121.4, 121.2, 115.9, 115.7, 113.5, 109.3, 59.8, 34.2, 29.9, 21.6, 14.3, 13.4 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{37}H_{41}NO_6S + H]^+$ 628.2727, found 628.2732.



ethyl 5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methyl-4-(thiophen-2-yl)furan-3-carboxylate (5l) Prepared through general procedure to give **5l** in 75.7 mg, 86% yield. White solid, m.p. 94 – 96 ℃, R_f= 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.37 – 7.35 (m, 1H), 7.32 (s, 2H), 7.07 – 7.04 (m, 1H), 6.98 – 6.96 (m, 1H), 5.26 (s, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 1.32 (s, 18H), 1.10 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1, 157.6, 153.8, 150.3, 135.8, 135.0, 128.1, 127.0, 126.2, 122.9, 121.4, 116.1, 112.2, 59.9, 34.4, 30.2, 14.3, 14.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{32}O_4S + H]^+$ 440.2021, found 440.2005.

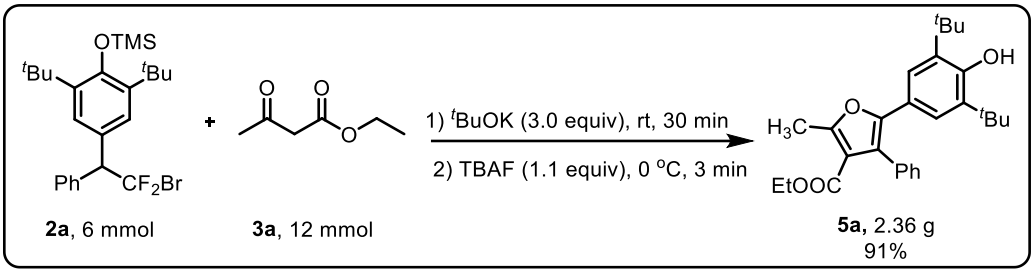


ethyl 4-cyclopropyl-5-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-methylfuran-3-carboxylate (5m) Prepared through general procedure to give **5m** in 47.8 mg, 60% yield. White solid, m.p. 78 – 80 ℃, R_f= 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.51 (s, 2H), 5.29 (s, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 2.57 (s, 3H), 1.93 – 1.84 (m, 1H), 1.48 (s, 18H), 1.38 (t, *J* = 7.1 Hz, 3H), 0.91 – 0.85 (m, 1H), 0.34 – 0.29 (m, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 157.3, 153.5, 150.6, 135.5, 124.2, 122.1, 120.1, 116.3, 60.0, 34.6, 30.5, 14.5, 14.3, 8.9, 6.9, 1.2 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{34}O_4 + H]^+$ 399.2530, found 399.2520.



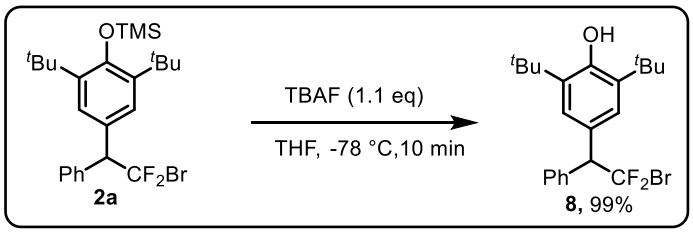
ethyl 5-(3-(tert-butyl)-4-hydroxy-5-methylphenyl)-2-methyl-4-phenylfuran-3-carboxylate (5n) Prepared through general procedure to give **5n** in Prepared through general procedure. 66.7 mg, 85% yield. White solid, m.p. 122 – 124 ℃, R_f= 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.15 (d, *J* = 1.9 Hz, 1H), 6.98 (d, *J* = 1.8 Hz, 1H), 4.85 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.67 (s, 3H), 2.16 (s, 3H), 1.16 (s, 9H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 157.6, 152.3, 148.2, 135.4, 134.4, 130.4, 128.2, 127.2, 125.8, 123.3, 123.1, 122.3, 120.4, 115.5, 59.9, 34.5, 29.5, 16.2, 14.4, 13.9 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{25}H_{28}O_4 + H]^+$ 393.2060, found 393.2068.

7. Gram-scale Reactions



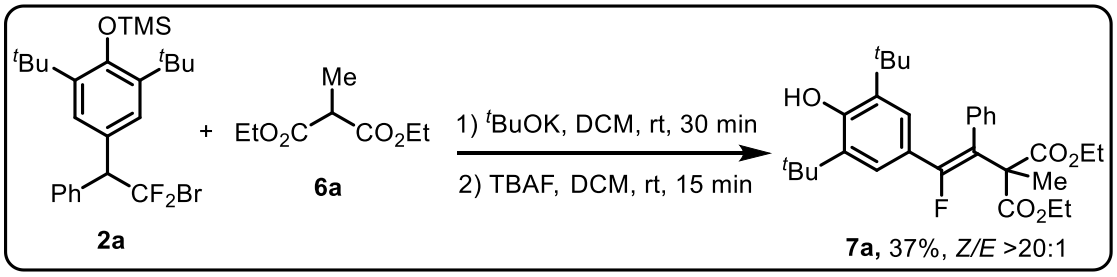
To an oven-dried 250 mL round-bottomed flask equipped with a Teflon coate d magnetic stir bar was added ^{t}BuOK (2.0 g, 18 mmol, 3.0 equiv in 15 mL DCM) and **3a** (1.56 g, 12 mmol, 2.0 equiv in 15 mL DCM) under air. The reaction mixture was stirred for 30 min at ambient temperature, at which time TBAF (1.42 g, 6.6 mmol, 1.1 equiv in 15 mL DCM) was added, and then **2a** (2.98g, 6 mmol in 15 mL DCM) was added dropwise to the reaction mixture at 0 ℃. Then the reaction mixture was stirred at this temperature for 3 min. After the material was completely consumed (monitored by TLC), saturated solution of NH_4Cl (5 mL) was slowly added to quench the reaction. The reaction mixture was extracted with DCM (3 × 30 mL). The combined organic layers were 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 **5a** as a white solid (2.36 g, 91% yield).

8. Mechanism Studies



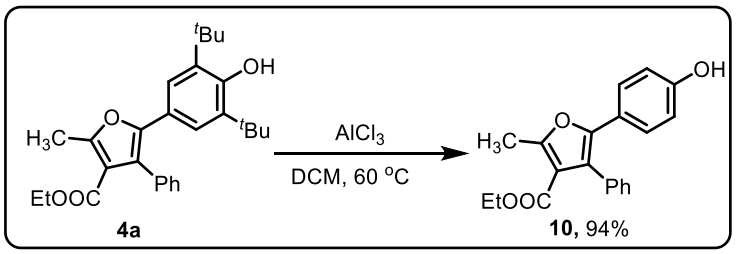
4-(2-bromo-2,2-difluoro-1-phenylethyl)-2,6-di-tert-butylphenol (8) To an oven-dried 8 mL disposable culture tube equipped with a Teflon coated magnetic stir bar was added **2a** (99.2 mg, 0.2 mmol in 0.5 mL THF). After the reaction mixture was cooled to -78 ℃, TBAF (47.6 mg, 0.22 mmol, 1.1 equiv in 0.5 mL THF) was added. Then the reaction mixture was stirred for about 10 min at this temperature. After the starting material was consumed completely (monitored by TLC), saturated solution of NH_4Cl (5 mL) was slowly added to quench the reaction at -78 ℃, and then 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 crude material was purified by flash chromatography on silica gel (PE/EA) to afford product as white solid (83.9 mg, 99% yield). M.p. 76 – 78 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 5H), 6.82 (s, 2H), 5.26 (s, 1H), 5.04 (dd, J = 17.4, 6.0 Hz, 1H), 1.22 (s, 18H). ^{13}C NMR (75 MHz, $CDCl_3$), δ 155.3, 135.4, 135.3 (*app.* d, ^{3}J = 4.0 Hz), 129.9, 129.0, 128.2, 123.9 (dd, ^{3}J =25.7, 25.7 Hz), 123.4 (dd, ^{4}J = 5.4, 5.6 Hz), 120.0 (dd, ^{1}J =

248.6, 248.6 Hz), 55.9 (dd, ^{2}J = 33.4, 31.0 Hz), 34.4, 30.1 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ -93.4 (d, J = 235.4 Hz), -101.8 (d, J = 235.4 Hz) ppm. HRMS (ESI) m/z Calcd for $[C_{22}H_{27}BrF_2O + K]^+$ 463.0845, found 463.0844.



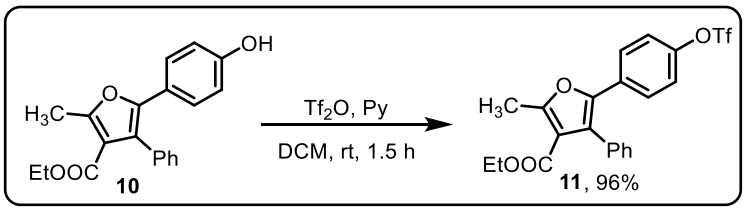
Diethyl (Z)-2-(2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-fluoro-1-phenylvinyl)-2-methylmalonate (7a) Prepared through general procedure to give **7a** in 36.9 mg, 37% yield, *Z*/*E* > 20:1. The configuration of the olefin motif was confirmed by X-ray analysis. White solid, m. p. 120 – 122 °C, R_f = 0.45 (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, ^{1}J = 252.4 Hz), 154.2, 136.6 (d, ^{3}J = 8.4 Hz), 135.0, 130.8 (d, ^{4}J = 3.1 Hz), 128.6, 127.6, 125.3 (d, ^{3}J = 7.6 Hz), 123.0 (d, ^{2}J = 28.2 Hz), 117.8 (d, ^{2}J = 19.5 Hz), 61.6, 58.8, 34.3, 30.1, 22.0 (d, ^{4}J = 3.1 Hz), 14.0 ppm. ^{19}F NMR (282 MHz, $CDCl_3$) δ – 96.2 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{30}H_{39}FO_5+H]^+$ 497.2709, found 497.2704.

9. Derivatization of Products

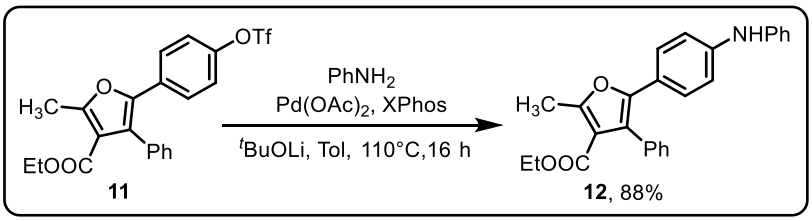


ethyl 5-(4-hydroxyphenyl)-2-methyl-4-phenylfuran-3-carboxylate (10) [2] To an oven-dried 25-mL two-necked flask equipped with a Teflon coated magnetic stir bar was added $AlCl_3$ **(**26.7 mg, 0.12 mmol, 6.0 eq.). Then the Schlenk tube was evacuated and filled with argon for three times. After that, **4a** (92.0 mg, 0.2 mmol) dissolved in DCM (4.0 mL) was added. The reaction was stirred for 15 min under at 60 ℃. After complete consumption of **4a**, 1 M HCl was added to quench the reaction. The reaction mixture was extracted with DCM (3 × 10 mL). The organic layers were combined and dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by flash chromatography on silica gel (PE/EA) to afford product **10** as a white solid (60.5 mg, 94% yield). M.p. 96 – 98 ℃, R_f = 0.3 (PE/EA = 5/1). ^{1}H NMR (300 Hz, DMSO-d_6) δ 9.65 (s, 1H), 7.41 – 7.34 (m, 3H), 7.25 – 7.22 (m, 2H), 7.07 (d, J = 8.7 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 3.99 (q, J = 7.1 Hz, 2H), 2.61 (s, 3H), 0.96 (t, J = 7.1 Hz, 3H) ppm. ^{13}C

NMR (75 MHz, DMSO-d_6) δ 163.0, 157.2, 156.9, 147.4, 133.3, 130.1, 128.0, 127.2, 126.9, 120.7, 119.6, 115.3, 115.0, 59.4, 13.8, 13.6 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{20}H_{19}O_4 + H]^+$ 323.1278, found 323.1283.

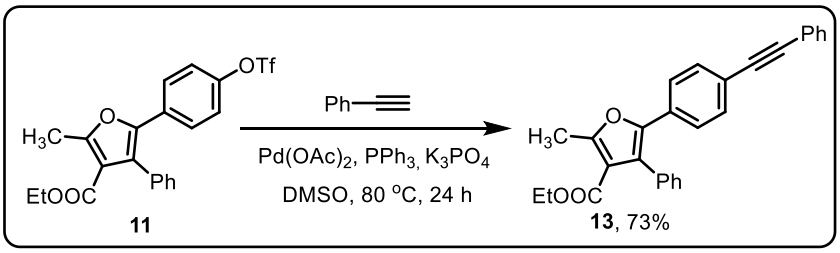


Ethyl 2-methyl-4-phenyl-5-(4-(((trifluoromethyl)sulfonyl)oxy)phenyl)furan-3-carboxylate (11) [4] To a solution of **10** (0.2 g, 0.56 mmol, 1.0 equiv) and pyridine (88.0 mg, 1.12 mmol, 2.0 equiv) in DCM (1 mL) was slowly added trifluoromethanesulfonic anhydride in DCM (0.19 g, 0.67 mmol, 1.2 equiv, 0.5M) at 0 ℃. Then the reaction mixture was warmed to room temperature and stirred about 1.5 h at this temperature. After **10** was completely consumed, the mixture was poured into 10% aqueous hydrochloric acid solution and extracted with DCM (3 × 5 mL). The combined organic layers were washed with brined and dried over Na_2SO_4. After filtration, the organic phase was concentrated under reduced pressure and the residues were purified by flash column chromatography on silica gel (PE/EA) to give the product (0.24 g, 96% yield) as white solid. M.p. 98 – 100 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, DMSO-d_6) δ 7.44 – 7.36 (m, 7H), 7.30 – 7.26 (m, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 2.64 (s, 3H), 0.95 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 162.6, 158.7, 148.0, 145.0, 132.6, 130.2, 129.7, 128.3, 127.8, 126.8, 123.5, 121.8, 118.2 (q, *J* = 319.0 Hz), 115.5, 59.6, 13.8, 13.5 ppm. ^{19}F NMR (282 MHz, DMSO-d_6) δ -73.0 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{21}H_{17}F_3O_6S + H]^+$ 455.0771, found 455.0775.

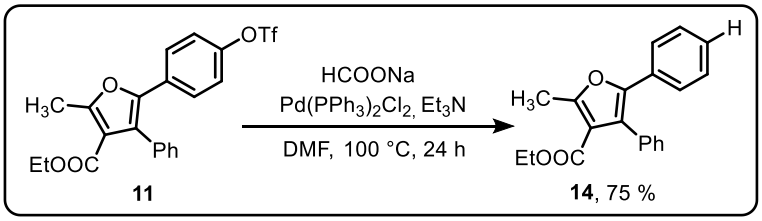


ethyl 2-methyl-4-phenyl-5-(4-(phenylamino)phenyl)furan-3-carboxylate(12)[7] To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (90.8 mg, 0.2 mmol, 1.0 eq.), $Pd(OAc)_2$ (4.5 mg, 10 mol%), Xphos (19 mg, 20 mol%) and ^{t}BuOLi (35.2 mg, 0.44 mmol, 2.2 eq.). Then the schlenk tube was evacuated and filled with argon for three times. After that, benzenamine (20.5 mg, 0.22 mmol, 1.1 eq.) in toluene (1 mL) was added under argon atmosphere via a syringe. After stirred at 110 ℃ of 16 h, 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 the desired product as a white solid (69.9 mg, 88% yield). M.p. 178 – 180 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.33 – 7.31 (m, 5H), 7.24 – 7.18 (m, 4H), 7.02 – 6.99 (m, 2H), 6.93 – 6.83 (m, 3H) 5.71 (s, 1H), 4.07 (q, *J* = 7.1 Hz, 2H), 2.66 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.5, 152.9,

143.0, 137.9, 137.6, 129.3, 125.6, 124.6, 123.4, 122.5, 122.0, 118.1, 116.8, 115.7, 113.8, 111.9, 110.8, 55.1, 9.5, 9.1 ppm. HRMS (ESI) *m/z* Calcd for $[C_{26}H_{23}NO_3 + H]^+$ for 398.1751, found 398.1741.

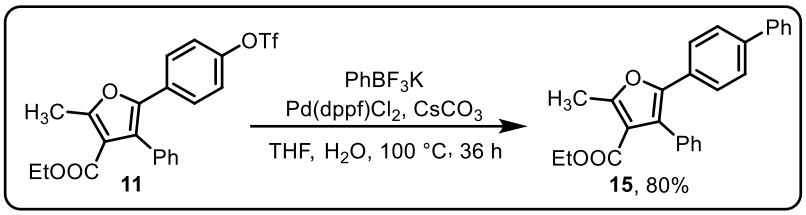


ethyl 2-methyl-4-phenyl-5-(4-(phenylethynyl)phenyl)furan-3-carboxylate (13) To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (90.8 mg, 0.2 mmol, 1.0 eq.), $Pd(OAc)_2$ (1.4 mg, 3 mol%), PPh_3 (6.3 mg, 4.0 eq. to Pd), and K_3PO_4 (51.7 mg, 0.24 mmol, 1.2 eq.). Then the Schlenk tube was evacuated and filled with argon for three times. After that, phenylacetylene (30.6 mg, 0.3 mmol, 1.5 eq.) in DMSO (2 mL) was added via a syringe[6]. After stirring at 80 ℃ of 24 h, 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 the desired product as a white solid (59.3 mg, 73% yield). M.p. 106 – 108 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.52 – 7.49 (m, 2H), 7.41 – 7.29 (m, 12H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.71(s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 158.7, 146.9, 133.6, 131.7, 131.6, 130.2, 130.1, 128.4, 128.4, 127.7, 125.2, 123.4, 123.3, 122.0, 116.0, 90.4, 89.4, 60.0, 14.4, 13.9 ppm. HRMS (ESI) *m/z* Calcd for $[C_{28}H_{22}O_3 + H]^+$ 407.1642, found 407.1629.

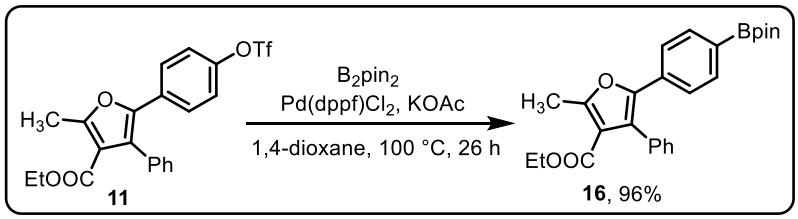


ethyl 2-methyl-4,5-diphenylfuran-3-carboxylate (14)[5] To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (90.8 mg, 0.2 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol, 10 mol %), and HCO_2Na (27.6 mg, 0.4 mmol, 2.0 eq.). Then the Schlenk tube was evacuated and filled with argon for three times. After that, Et_3N (60.7 mg, 0.6 mmol, 3.0 eq.) and anhydrous DMF (2.0 mL) were added under argon atmosphere via a syringe. The reaction mixture was stirred at 100 ℃ (oil bath) for 24 h. After complete consumption of **11**, the reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EA) to afford the desired product **14** as a white solid **(**45.9 mg, 75% yield). M.p. 68 – 70 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, DMSO-d_6) δ 7.38 – 7.36 (m, 3H), 7.26 – 7.21 (m, 7H), 3.98 (q, *J* = 7.1 Hz, 2H), 2.62 (s, 3H), 0.94 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 168.1, 163.1, 151.9, 138.3, 135.1, 134.8, 133.7, 133.4, 132.9, 132.7, 130.3, 127.2, 120.5,

64.7, 19.0, 18.8 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{20}H_{18}O_3 + H]^+$ 307.1329, found 307.1325.

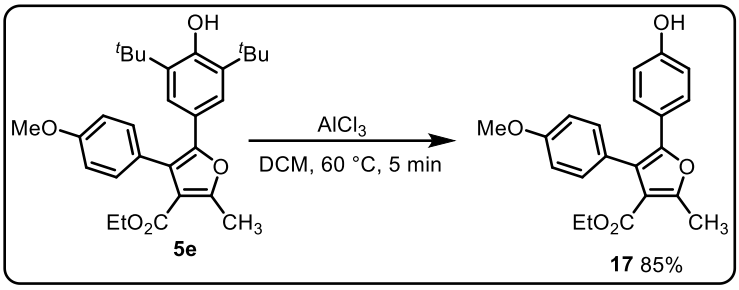


ethyl 5-([1,1'-biphenyl]-4-yl)-2-methyl-4-phenylfuran-3-carboxylate (15)[8] To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (90.8 mg, 0.2 mmol, 1.0 equiv), Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), $PhBF_3K$ (38.6 mg, 0.21 mmol, 1.0 equiv), $Pd(dppf)Cl_2$ (14.6 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 100 ℃ for 36 h, the reaction was quenched with brine and extracted with EA (3 × 4 mL). The combined organic phase was washed with brine, dried over Mg_2SO_4, evaporated to give the crude products. The residue was purified by flash chromatography (PE/EA) to give the desired product as a white solid (61.1 mg, 80% yield). M.p. 88 – 90 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.45 – 7.29 (m, 12H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.70 (s, 3H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) 164.8, 159.1, 147.9, 141.2, 140.6, 134.5, 130.9, 130.0, 129.5, 129.0, 128.2, 128.1, 127.7, 127.6, 126.5, 123.3, 116.5, 60.6, 15.0, 14.5 ppm. HRMS (ESI) *m*/*z* Calcd for $[C_{26}H_{22}O_3 + H]^+$ for 383.1642, found 383.1634.

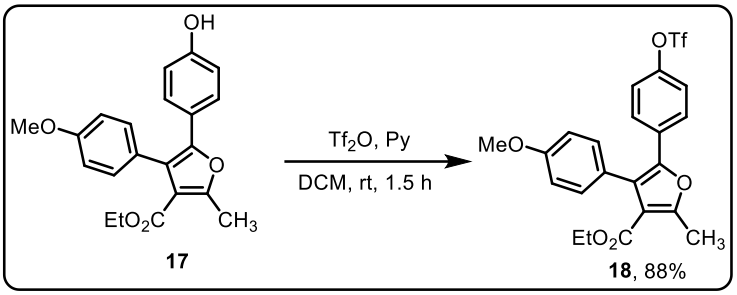


ethyl 2-methyl-4-phenyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)furan-3-carboxylate (16) [8] To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **11** (90.8 mg, 0.2 mmol, 1.0 eq.), bis(pinacolato)diboron (76.2 mg, 0.3 mmol, 1.5 eq.), potassium acetate (58.8 mg, 0.6 mmol, 3.0 eq.) and $Pd(dppf)Cl_2$ (14.6 mg, 10 mol%) sequentially. Then the Schlenk tube was evacuated and filled with argon for three times. After that, anhydrous 1,4-dioxane (1.0 mL) was added under argon atmosphere via a syringe. After stirred at 100 ℃ of 26 h, the reaction mixture was filtered through a pad of celite, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EA) to afford the desired product as a white solid (58.8 mg, 96% yield). M.p. 93 – 95 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.64 – 7.62 (m, 2H), 7.33 – 7.28 (m, 7H), 4.08 (q, *J* = 7.1 Hz, 2H), 2.68 (s, 3H), 1.30 (s, 12H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0, 158.7, 147.4, 134.8, 133.7, 132.8, 130.2,

128.2, 127.5 (two carbon signals overlapped), 124.6, 123.4, 115.9, 83.8, 59.9, 24.9, 14.4, 13.9 ppm. HRMS (ESI) *m/z* Calcd for $[C_{20}H_{18}O_3 + H]^+$ 306.1250, found 306.1262.

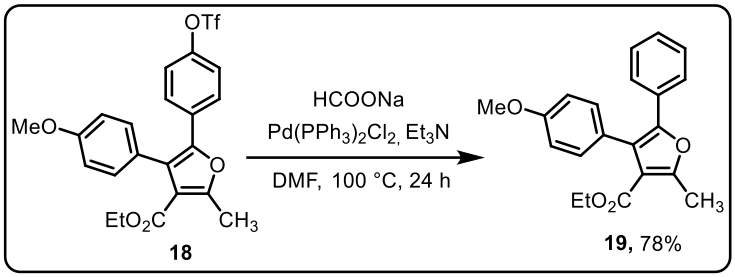


ethyl 5-([1,1'-biphenyl]-4-yl)-2-methyl-4-phenylfuran-3-carboxylate (17)[2] To an oven-dried 25-mL two-necked flask equipped with a Teflon coated magnetic stir bar was added $AlCl_3$ **(**26.7 mg, 0.12 mmol, 6.0 eq.). Then the Schlenk tube was evacuated and filled with argon for three times. After that, **5e** (92.8 mg, 0.2 mmol) dissolved in DCM (4.0 mL) was added. The reaction was stirred for 15 min under at 60 ℃. After complete conversion of **5e**, 1 M HCl was 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 crude material was purified by flash chromatography on silica gel (PE/EA) to afford product **17** as a white solid (59.8 mg, 85% yield). M.p. 108 – 110 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 9.63 (s, 1H), 7.15 – 7.08 (m, 4H), 6.92 (d, J = 8.6 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 4.01 (q, J = 7.1 Hz, 2H), 3.78 (s, 3H), 2.58 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.6, 159.0, 157.6, 157.2, 147.9, 131.7, 127.3, 125.7, 121.4, 119.8, 115.8, 115.6, 114.0, 59.9, 55.5, 14.4, 14.2 ppm. HRMS (ESI) *m/z* Calcd for $[C_{21}H_{20}O_5 + H]^+$ for 353.1384, found 353.1380.

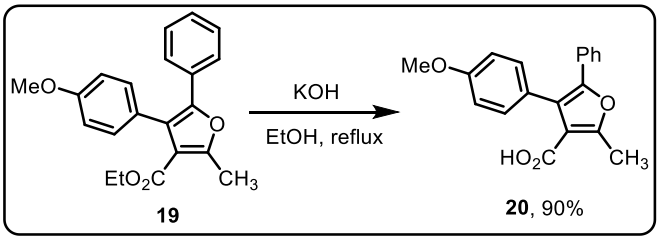


ethyl 5-([1,1'-biphenyl]-4-yl)-2-methyl-4-phenylfuran-3-carboxylate (18) To a solution of **17** (70.4 mg, 0.2 mmol, 1.0 equiv) and pyridine (31.6 mg, 0.4 mmol, 2.0 equiv) in DCM (1 mL) was slowly added trifluoromethanesulfonic anhydride in DCM (67.7 mg, 0.24 mmol, 1.2 equiv, 0.5M) at 0 ℃. Then the reaction mixture was warmed to room temperature and stirred for 1.5 h at this temperature. After **17** was completely consumed, the mixture was poured into 10% HCl (aq.) and extracted with DCM. The organic layers were washed with brined and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA) to give the product as white solid (85.1 mg, 88% yield). M.p. 120 – 122 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.45 – 7.38 (m, 4H), 7.19 (d,

J = 8.6 Hz, 2H), 6.98 (d, *J* = 8.6 Hz, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 2.63 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.2, 159.4, 159.0, 148.5, 145.5, 131.5, 130.9, 127.3, 124.8, 123.8, 122.4, 118.7 (q, *J* = 320.8 Hz), 116.2, 114.3,60.1, 55.6, 14.4, 14.2 ppm. ^{19}F NMR (282 MHz, DMSO-d_6) δ -72.9 ppm. HRMS (ESI) m/z Calcd for $[C_{22}H_{19}F_3O_7$ S+ H]$^+$ for 485.0876, found 485.0862.



ethyl 5-([1,1'-biphenyl]-4-yl)-2-methyl-4-phenylfuran-3-carboxylate (19) To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **18** (96.8 mg, 0.2 mmol, 1.0 eq.), $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol, 10 mol %), and HCO_2Na (27.6 mg, 0.4 mmol, 2.0 eq.). The Schlenk tube was evacuated and filled with argon for three times. After that, Et_3N (60.7 mg, 0.6 mmol, 3.0 eq.) and anhydrous DMF (2.0 mL) were added under argon atmosphere via a syringe. The reaction mixture was stirred at 100 °C in oil bath for 24 h.[5] After **18** was completely consumed, the reaction mixture was filtered through a pad of celite and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (PE/EA) to afford the desired product **19** as a white solid (52.4 mg, 78% yield). M.p. 108 – 110 ℃, R_f = 0.4 (PE/EA = 50/1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 7.27 – 7.15 (m, 7H), 6.95 (d, *J* = 8.5 Hz, 2H), 4.02 (q, *J* = 7.0 Hz, 2H), 3.79 (s, 3H), 2.62 (s, 3H), 1.01 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 163.4, 159.2, 158.2, 147.2, 131.6, 130.3, 129.0, 128.1, 125.5, 125.4, 122.2, 115.9, 114.1, 60.0, 55.5, 14.4, 14.2 ppm. HRMS (ESI) *m*/*z* Calcd for HRMS (ESI) *m*/*z* Calcd for $[C_{21}H_{20}O_4$ + H]$^+$ for 337.1434, found 337.1434.



ethyl 5-([1,1'-biphenyl]-4-yl)-2-methyl-4-phenylfuran-3-carboxylate (20) To an oven-dried 10-mL Schlenk tube equipped with a Teflon coated magnetic stir bar was added **19** (67.2 mg, 0.2 mmol, 1.0 eq), KOH (33.6 mg, 0.6 mmol, 3.0 eq) and EtOH (2 mL) were added sequentially. The resulting mixture was stirred at 80 ℃ for 12 h. After **19** was completely consumed, cooled to room temperature, the reaction was quenched by water. Then the mixture was extracted with EA (3 × 30 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo. The crude material was purified by flash chromatography on silica gel (PE/EA) to generate the title compound as white solid (55.5 mg, 90% yield). M.p. 128 – 130 ℃, R_f = 0.4 (PE/EA =

50/1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 12.33 (s, 1H), 7.24 – 7.15 (m, 7H), 6.94 (d, J = 8.5 Hz, 2H), 3.78 (s, 3H), 2.62 (s, 3H) ppm. ^{13}C NMR (75 MHz, DMSO-d_6) δ 164.9, 158.9, 158.0, 147.0, 131.5, 130.3, 128.9, 127.9, 125.5 (two carbon signals overlapped), 122.4, 116.4, 114.0, 55.4, 14.4 ppm. HRMS (ESI) m/z Calcd $[C_{19}H_{16}O_4 + H]^+$ for 309.1121, found 309.1124.

10. Crystal Structure of 4x and 7a

Vapor diffusion crystallization method was used for crystal growth of 4x: The compound **4x** was dissolved in diethyl ether to make saturated solution in small vial and placed in closed bottle with another solvent as *n*-hexane.

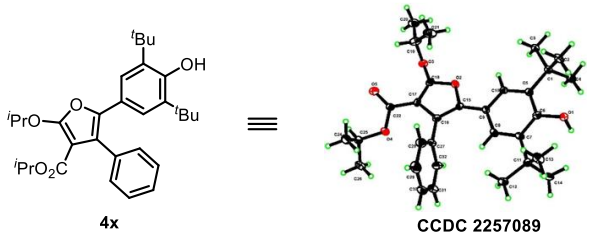


Figure S1. ORTEP plot of the crystal structure of compound 4x and thermal ellipsoid is set at 50% probability

Table S1 X-ray Crystallographic Data of **4x**

CCDC number	2257089
Bond precision	C-C = 0.0078 A Wavelength = 0.71073
Cell	a=9.5453 (7) b=11.8954 (8) c=13.9574 (10) alpha=109.552 (2) beta=107.835 (2) gamma=90.633 (2)
Temperature	100 K
Volume	1410.21 (17)
Space group	P 1
Hall group	P 1
Sum formula	$C_{31}H_{40}O_5$
Mr	492.63
Dx, g cm-3	1.160
Z	2
Mu (mm-1)	0.077
F000	532.0
F000’	532.25
h, k, lmax	0, 0, 0
Nref	9940
Tmin, Tmax	0.456,0.586
Tmin’	0.993
Correction method	# Reported T Limits: Tmin=0.456 Tmax=0.586
AbsCorr	MULTI-SCAN
Data completeness	1.73/0.87
Theta(max)	26.379
R(reflections)	0.0745(5665)
wR2(reflections)	0.2211(9940)
S	1.043
Npar	671
Ellipsoid contour % probability levels	50

Vapor diffusion crystallization method was used for crystal growth of 7a: The compound **7a** was dissolved in dichloromethane to make saturated solution in small vial and placed in closed bottle with another solvent as *n*-hexane.

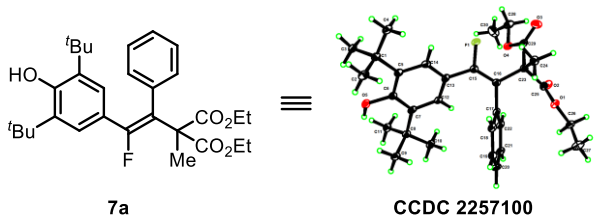


Figure S2. ORTEP plot of the crystal structure of compound **7a** and thermal ellipsoid is set at 50% probability

Table S2. X-ray Crystallographic Data of **7a**

CCDC number	2257100
Bond precision	C-C = 0.0050 A Wavelength=0.71073
Cell	a=18.8386 (14) b=15.4558 (11) c=19.3981 (14) alpha=90 beta=105.066 (2) gamma=90
Temperature	100 K
Volume	5453.9(7)
Space group	P 1 21/c 1
Hall group	-p 2ybc
Sum formula	$C_{30}H_{39}FO_5$
Mr	498.61
Dx, g cm-3	1.214
Z	8
Mu (mm-1)	0.086
F000	2144.0
F000’	2145.12
h, k, lmax	23, 19, 24
Nref	10860
Tmin, Tmax	0.671,0.745
Tmin’	0.990
Correction method	# Reported T Limits: Tmin=0.671 Tmax=0.745
AbsCorr	MULTI-SCAN
Data completeness	0.972
Theta(max)	26.384
R(reflections)	0.0768(6945)
wR2(reflections)	0.2538(10860)
S	1.078
Npar	688
Ellipsoid contour % probability levels	50

Reference

[1] (a) Koutek, B.; Pavličková, L.; Souček, M. *Synth. Commun.* **1976**, *6*, 305. (b) Chu, W.; Zhang, L.; Bao, X.; Zhao, X.; Zeng, C.; Du, J.; Zhang, G.; Wang, F.; Ma, X.; Fan, C. *Angew. Chem., Int. Ed.* **2013**, *52*, 9229. (c) Caruana, L.; Kniep, F.; Johansen, T. K.; Poulsen, P. H.; Jørgensen, K. A. *J. Am. Chem. Soc.* **2014**, *136*, 15929. (d) Richter, D.; Hampel, N.; Singer, T.; Ofial, A. R.; Mayr, H. *Eur. J. Org. Chem.* **2009**, *19*, 3203. (e) López, A.; Parra, A.; Jarava-Barrera, C.; Tortosa, M. *Chem. Comm.* **2015**, *51*, 17684; (f) Gai, K.; Fang, X.; Li, X.; Xu, J.; Wu, X.; Lin, A.; Yao, H. *Chem. Commun.* **2015**, *51*, 15831.

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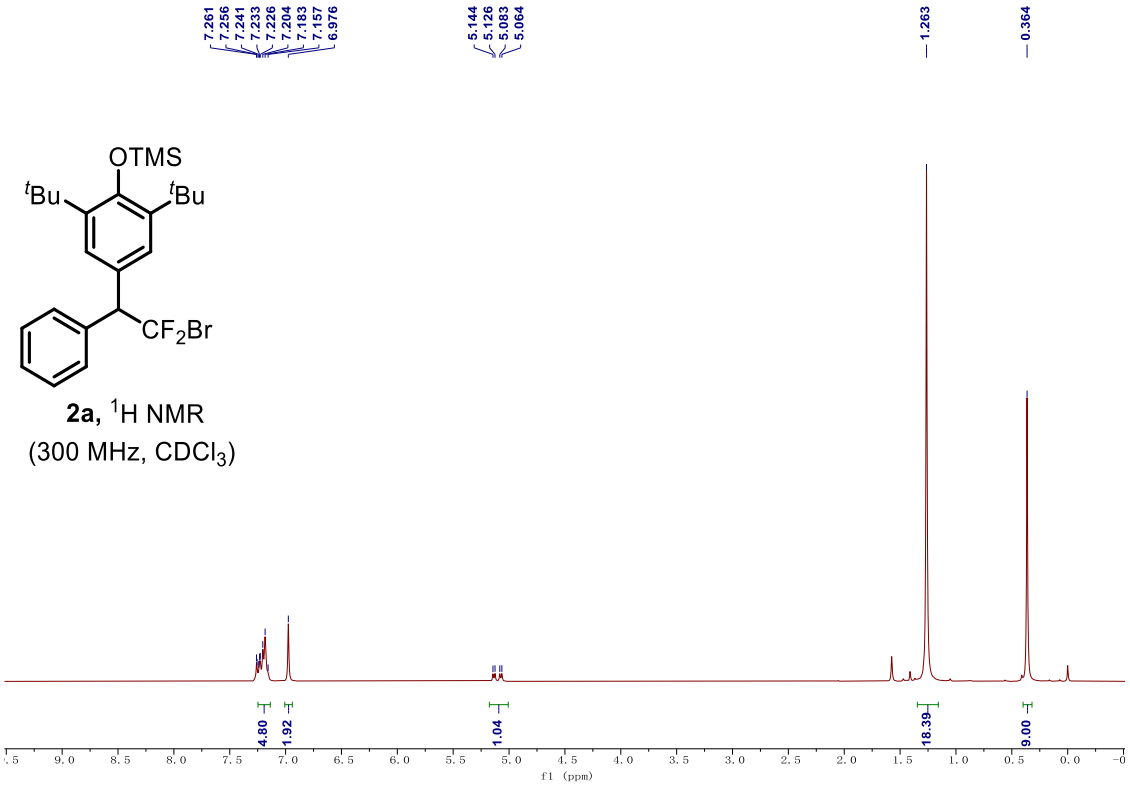
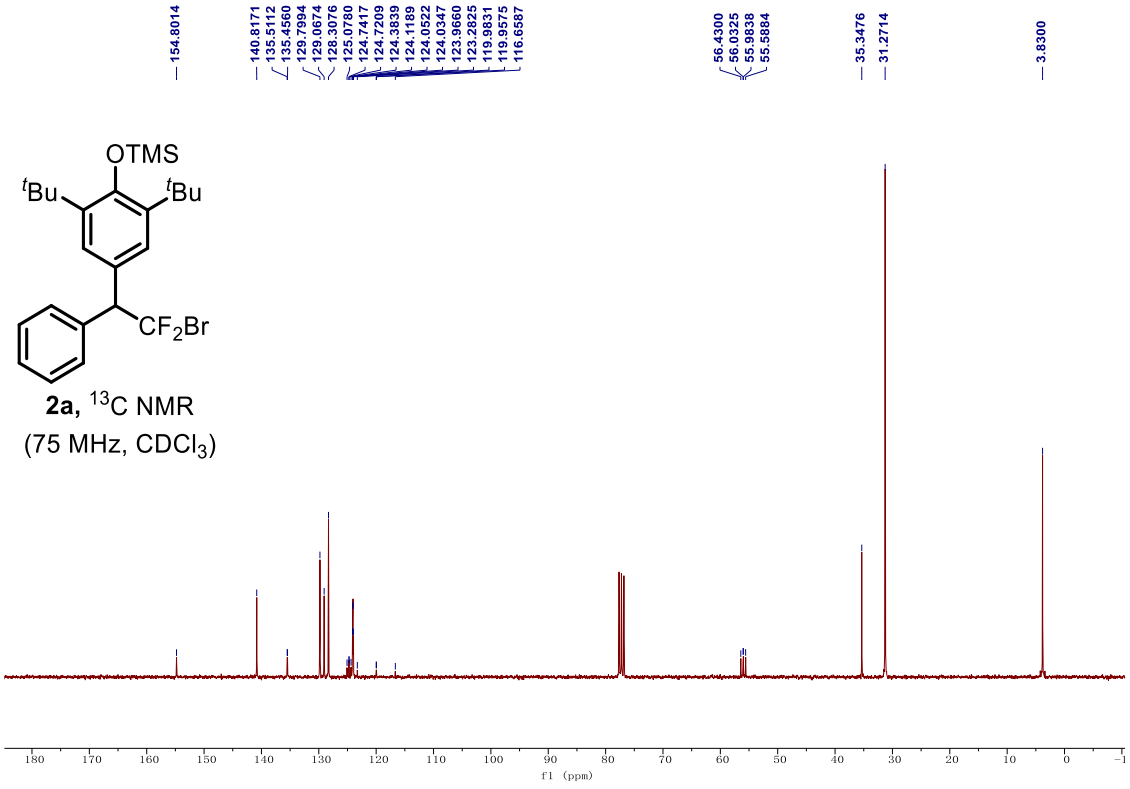
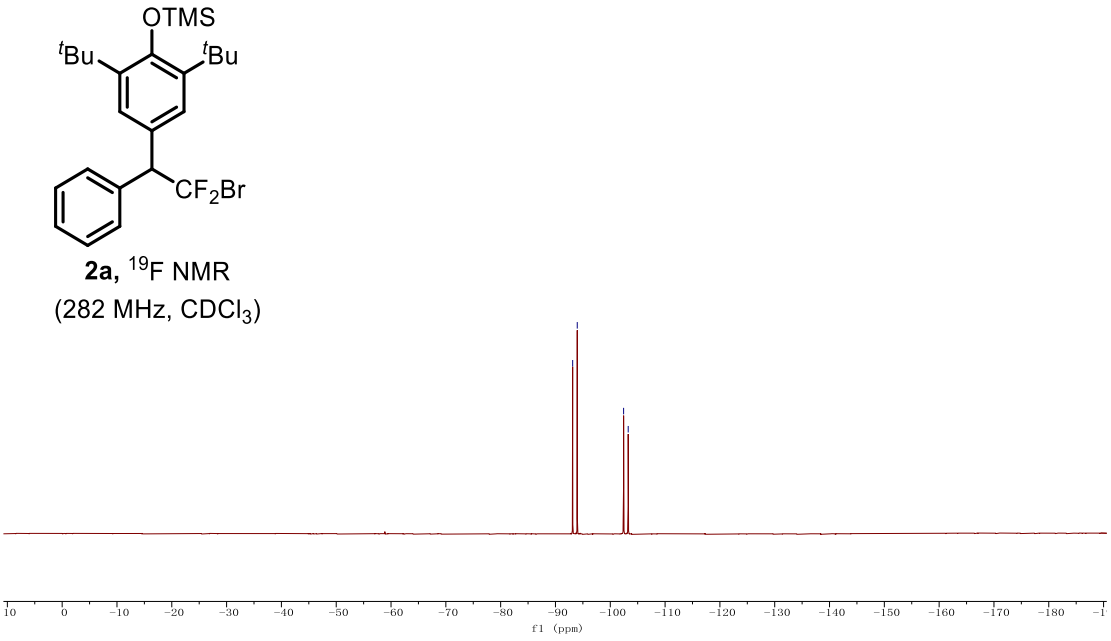
11. ^{1}H, ^{13}C and ^{19}F NMR Spectra of Title Compounds



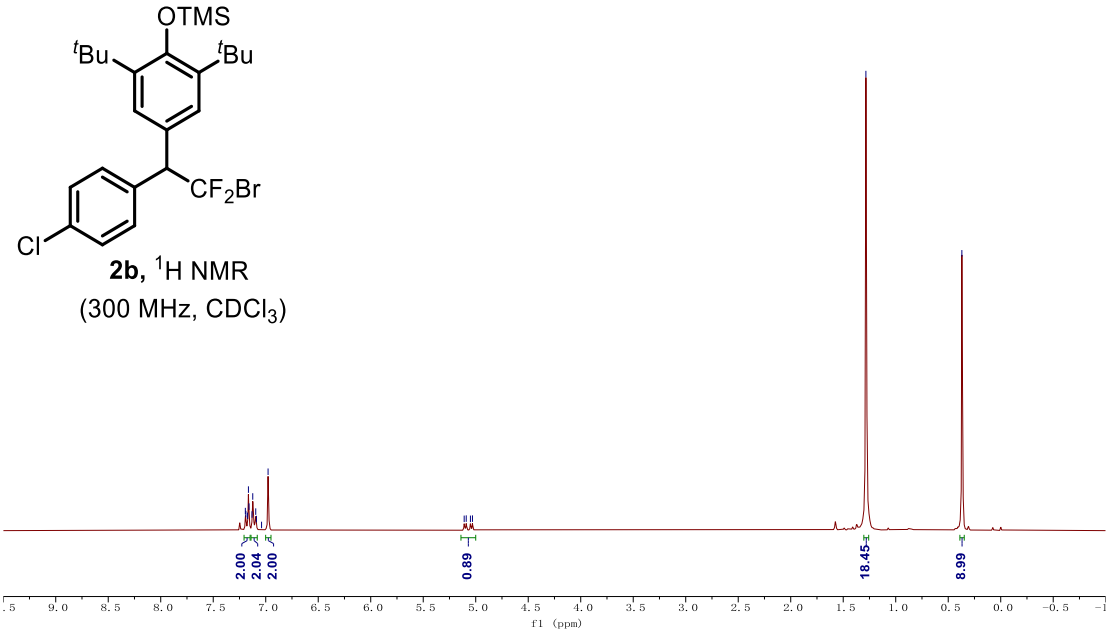
2a, ^{1}H NMR
(300 MHz, $CDCl_3$)



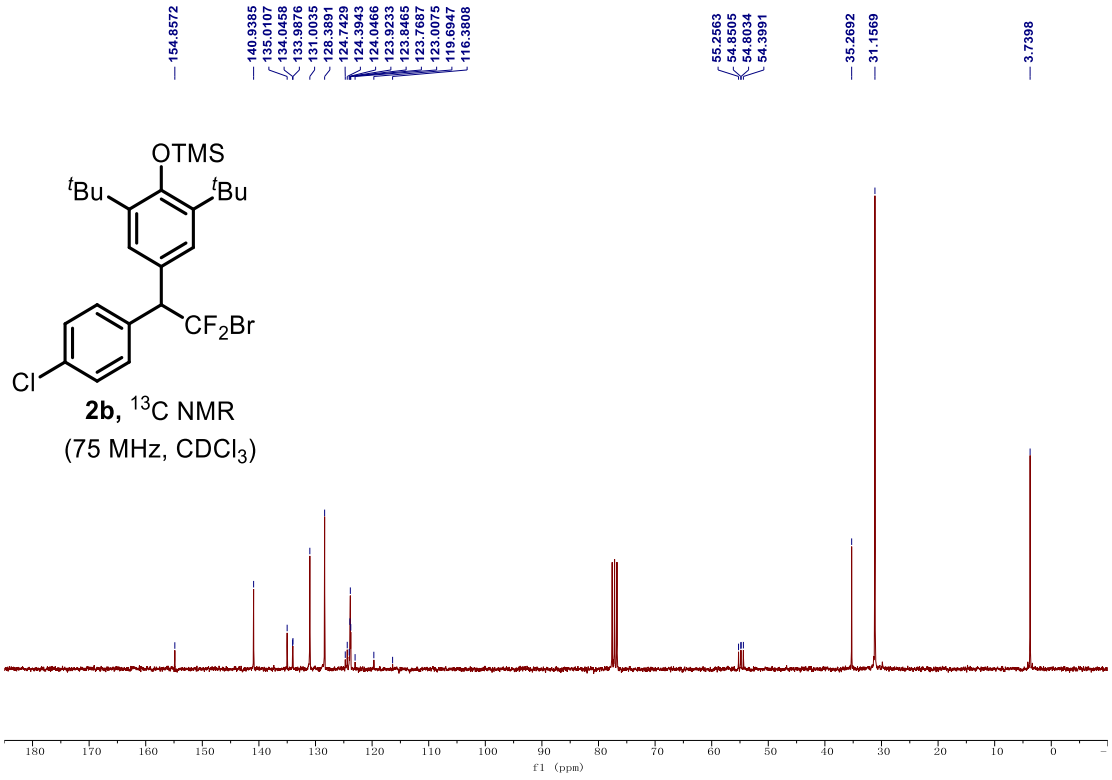
2a, ^{13}C NMR
(75 MHz, $CDCl_3$)



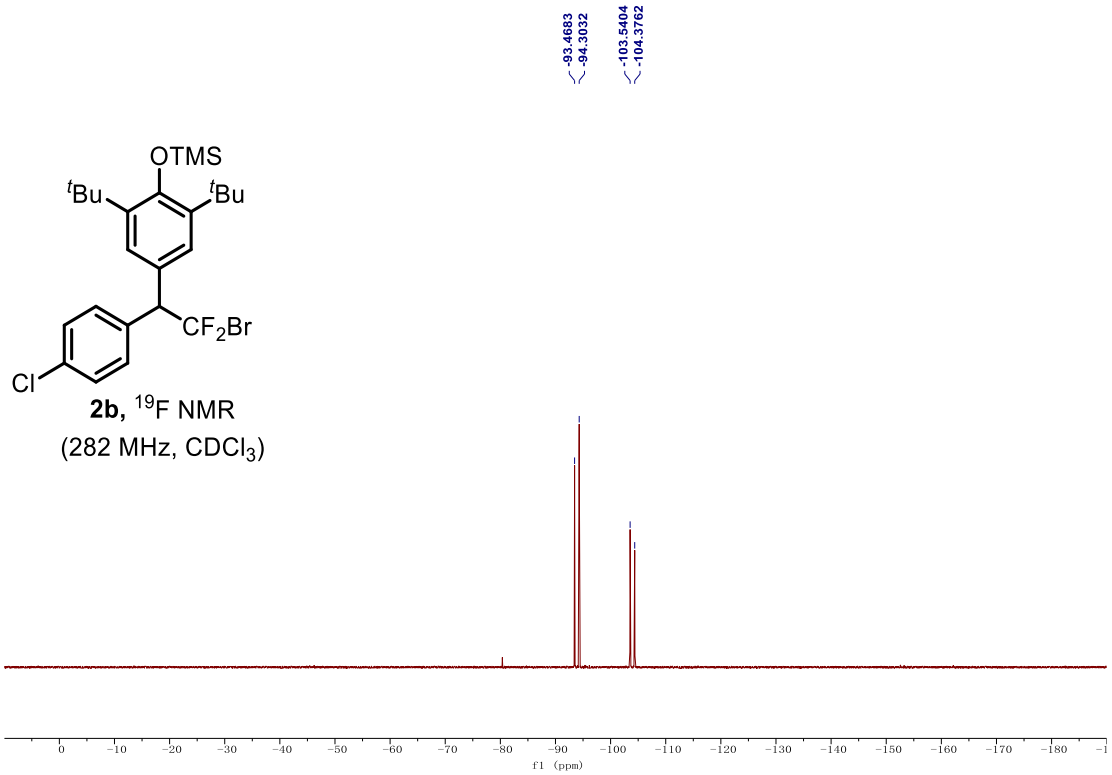
2a, ^{19}F NMR
(282 MHz, $CDCl_3$)



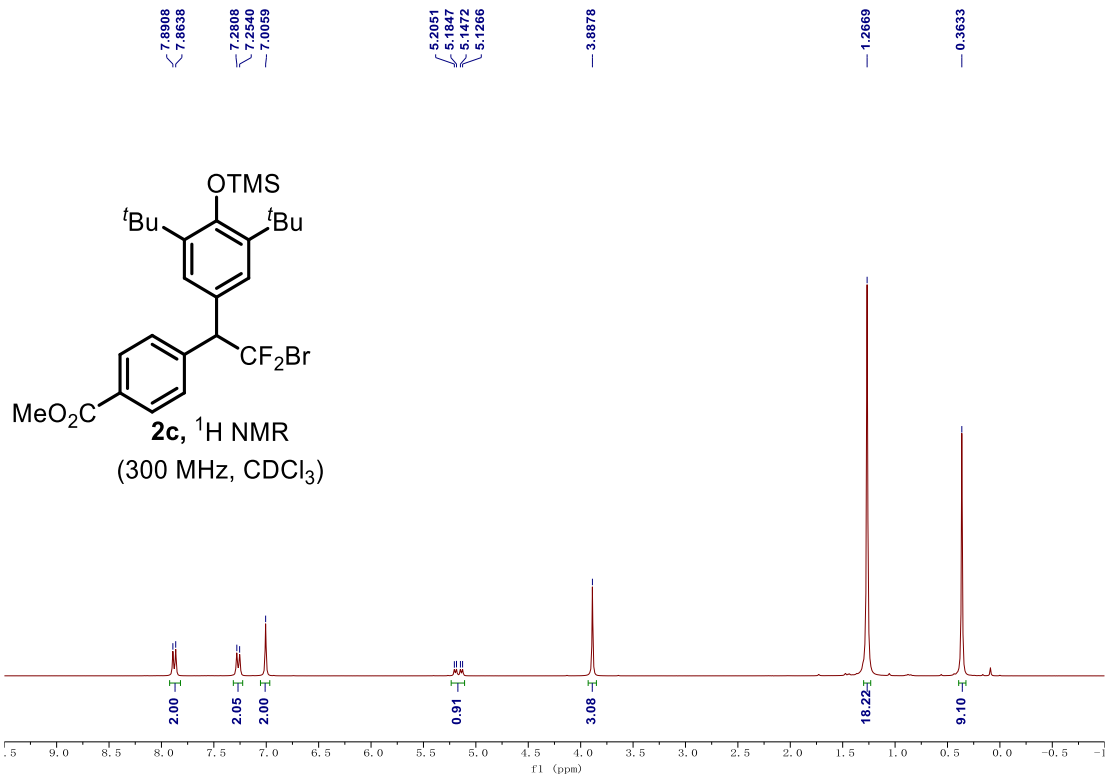
2b, ^{1}H NMR
(300 MHz, $CDCl_3$)



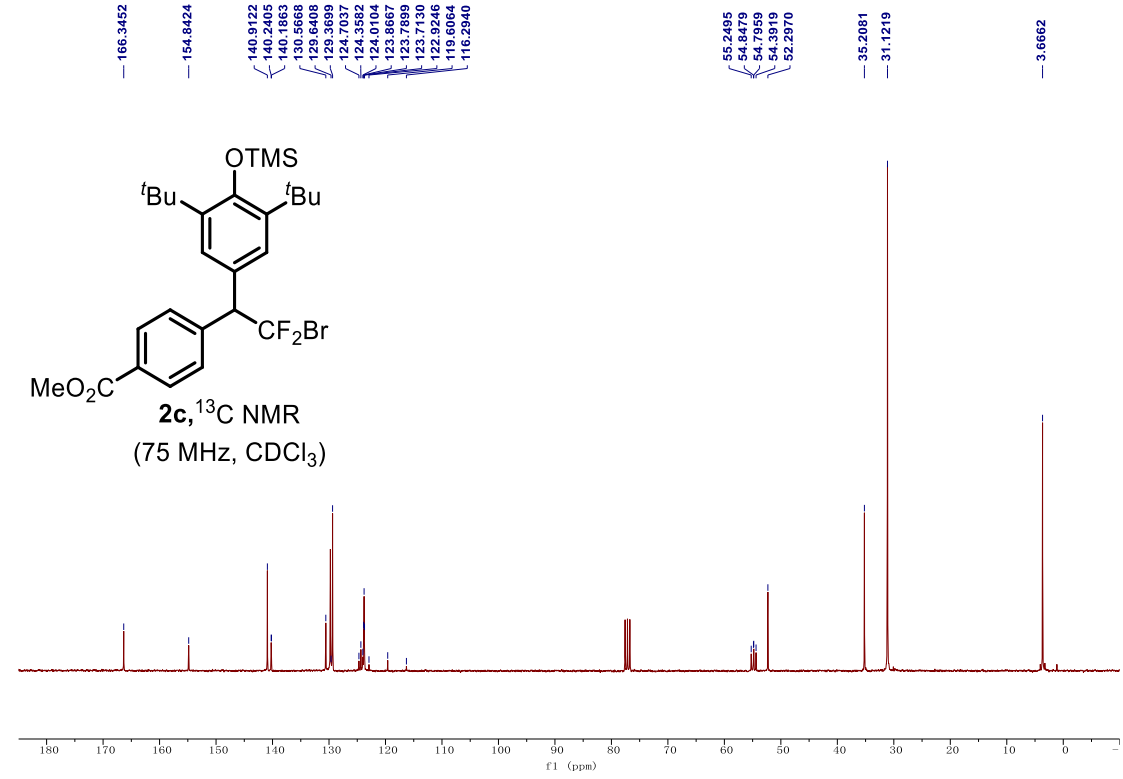
2b, ^{13}C NMR
(75 MHz, $CDCl_3$)



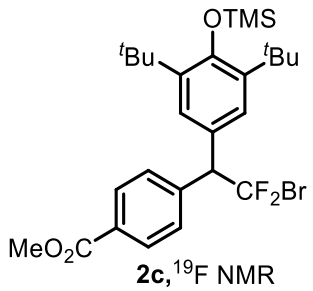
2b, ^{19}F NMR
(282 MHz, $CDCl_3$)



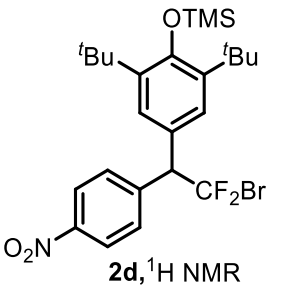
2c, ^{1}H NMR
(300 MHz, $CDCl_3$)



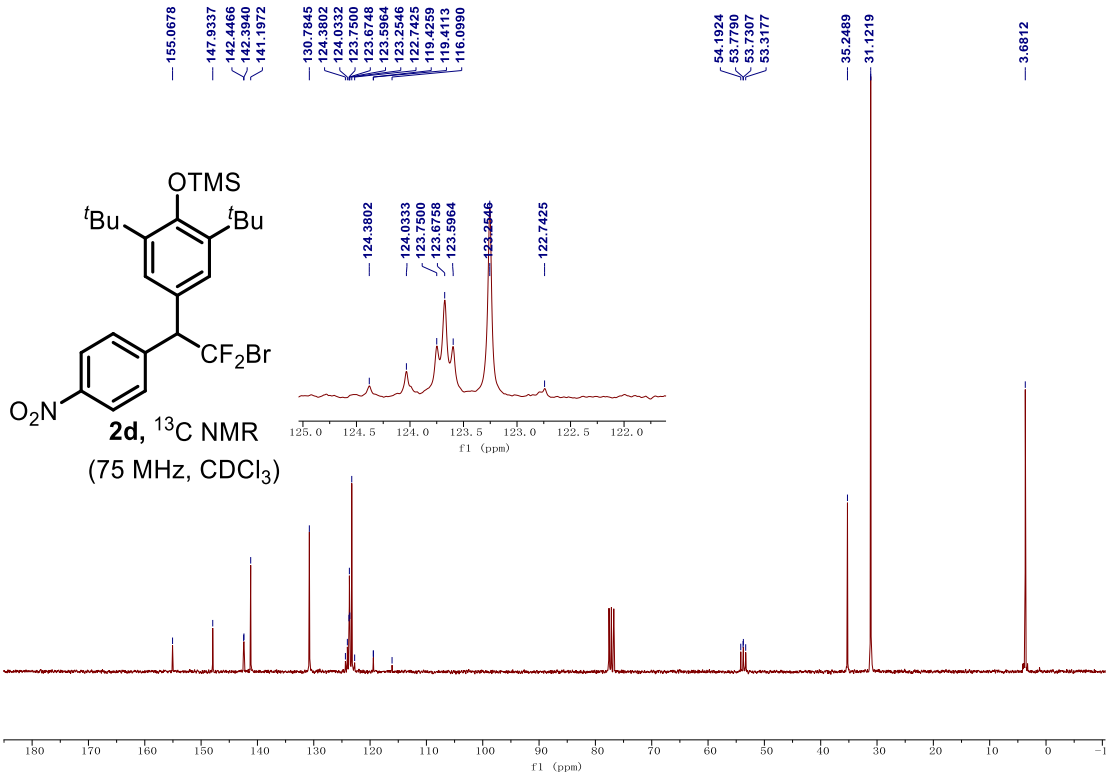
2c,^{13}C NMR
(75 MHz, $CDCl_3$)



2c,^{19}F NMR
(282 MHz, $CDCl_3$)



2d,^{1}H NMR
(300 MHz, $CDCl_3$)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119.4113
116.0990
54.1924
53.7790
53.7307
53.3177
35.2489
31.1219
3.6812
OTMS
tBu
tBu
CF2Br
O2N
2d, 13C NMR
(75 MHz, CDCl3)
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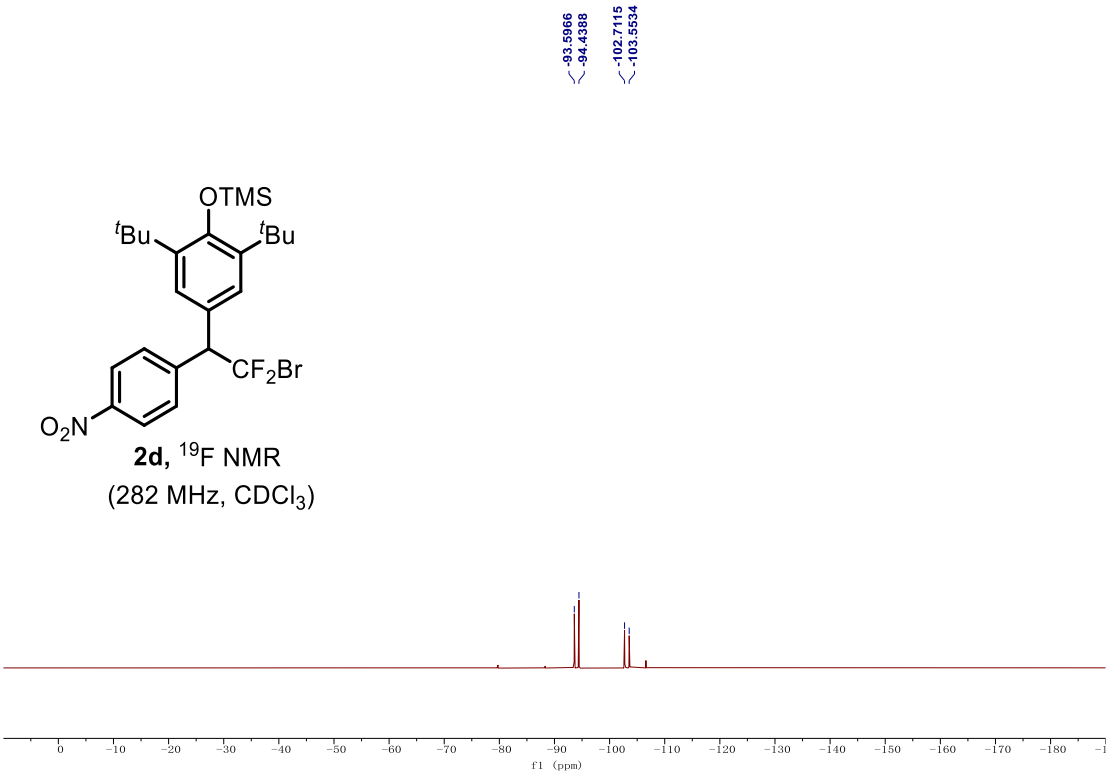
124.0333
123.7500
123.6758
123.5964
123.2646
122.7425
f1 (ppm)
f1 (ppm)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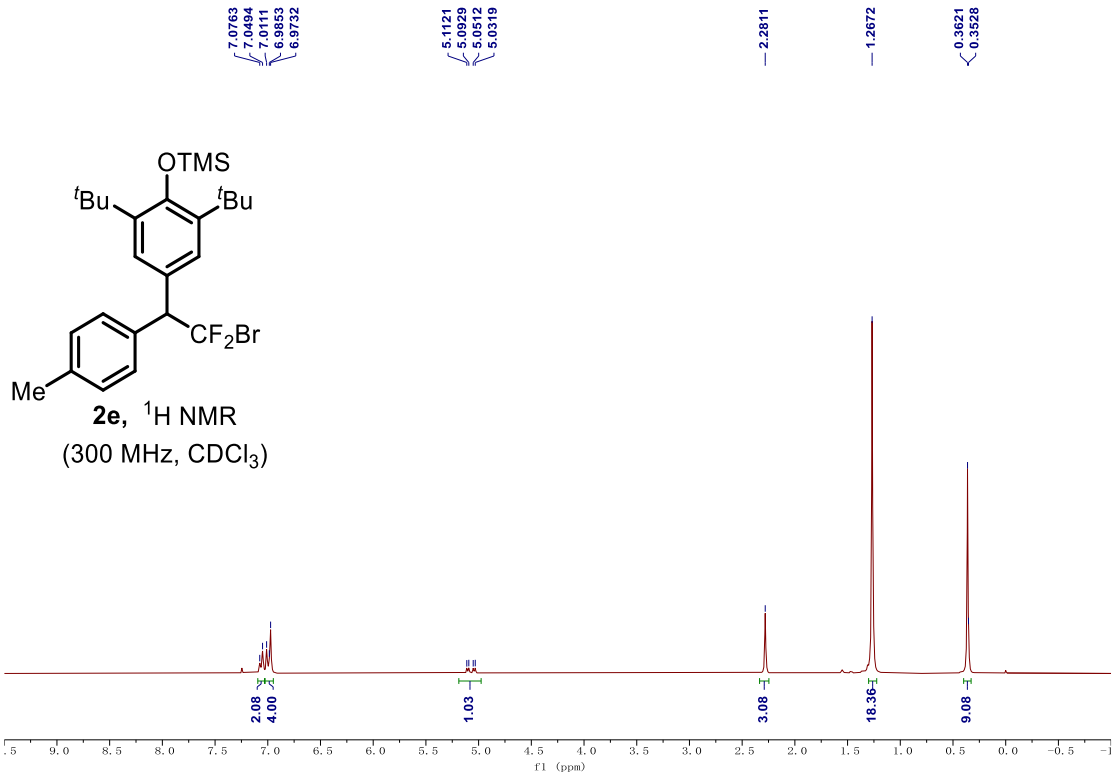
tBu
tBu
CF2Br
O2N
2d, 19F NMR
(282 MHz, CDCl3)
f1 (ppm)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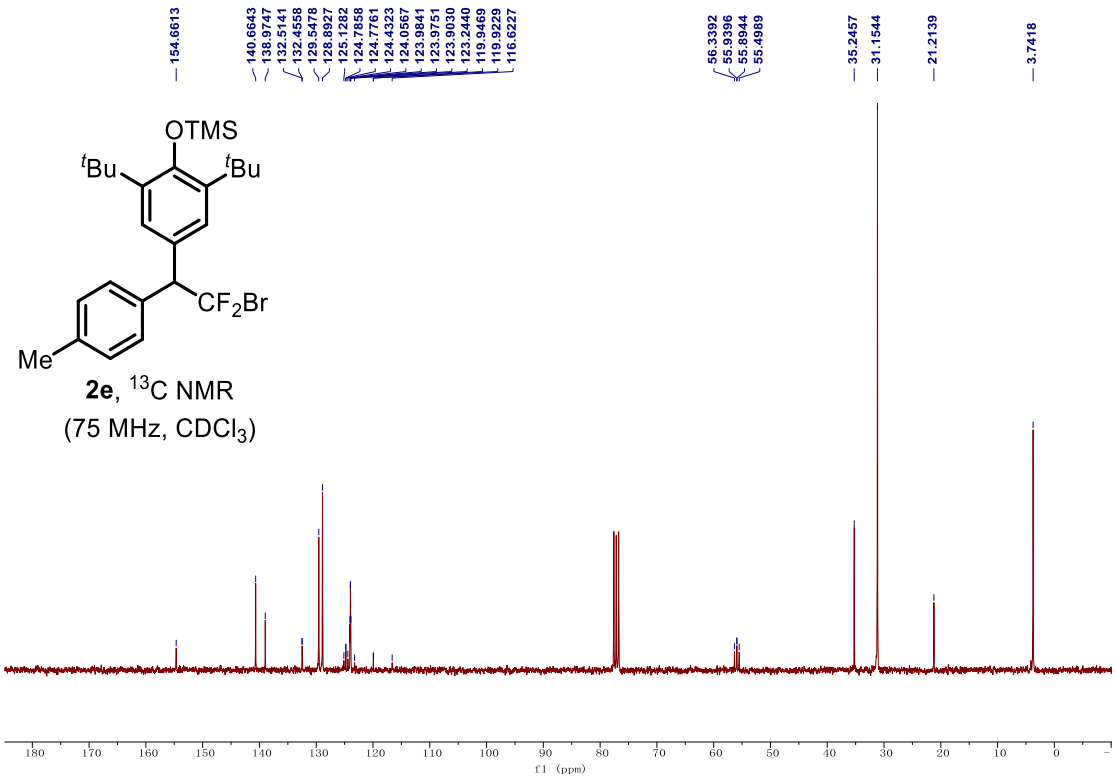
5.0929
5.0512
5.0319
2.2811
1.2672
0.3621
0.3528
OTMS
tBu
tBu
CF2Br
Me
2e, 1H NMR
(300 MHz, CDCl3)
2.08
4.00
1.03
3.08
18.36
9.08
f1 (ppm)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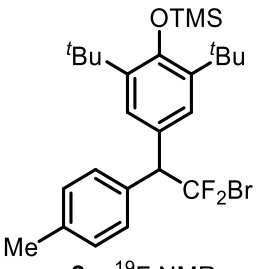
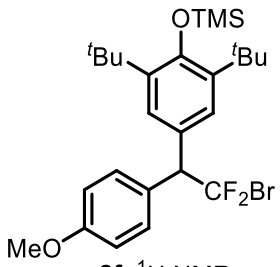
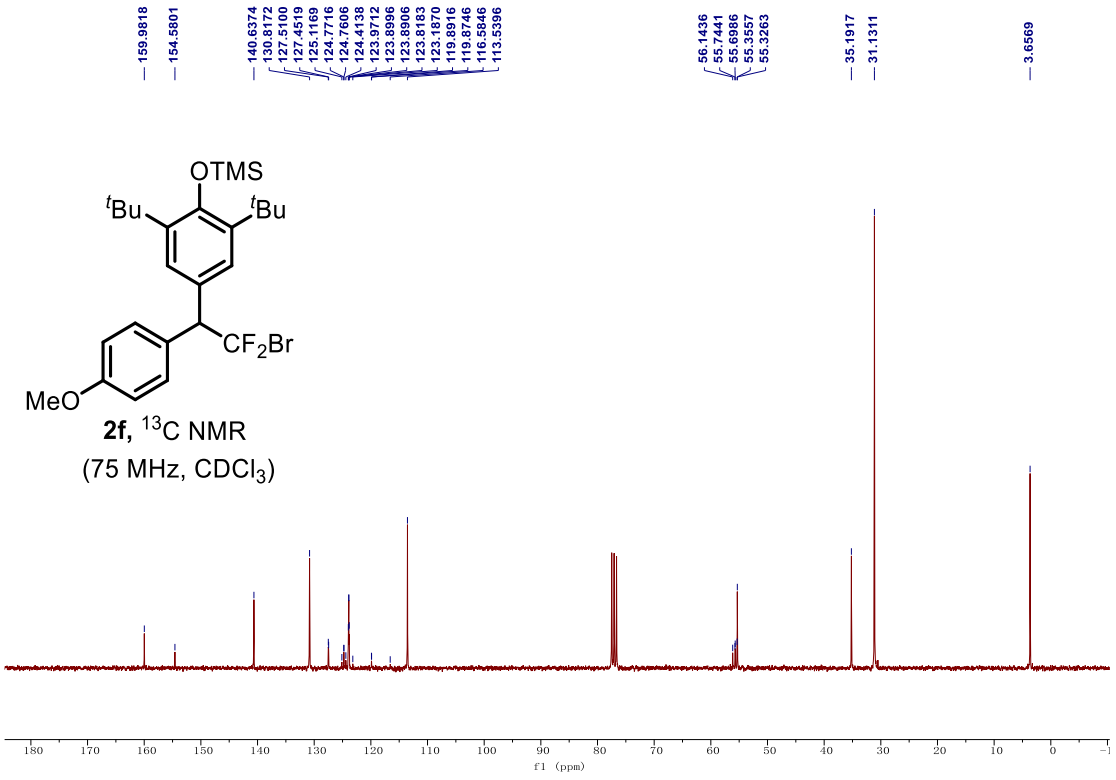
124.0567
123.9841
123.9751
123.9030
123.2440
119.9469
119.9229
116.6227
56.3392
55.9396
55.8944
55.4989
35.2457
31.1544
21.2139
3.7418
OTMS
tBu
tBu
CF2Br
Me
2e, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



2e, ^{19}F NMR
(282 MHz, $CDCl_3$)



2f, ^{1}H NMR
(300 MHz, $CDCl_3$)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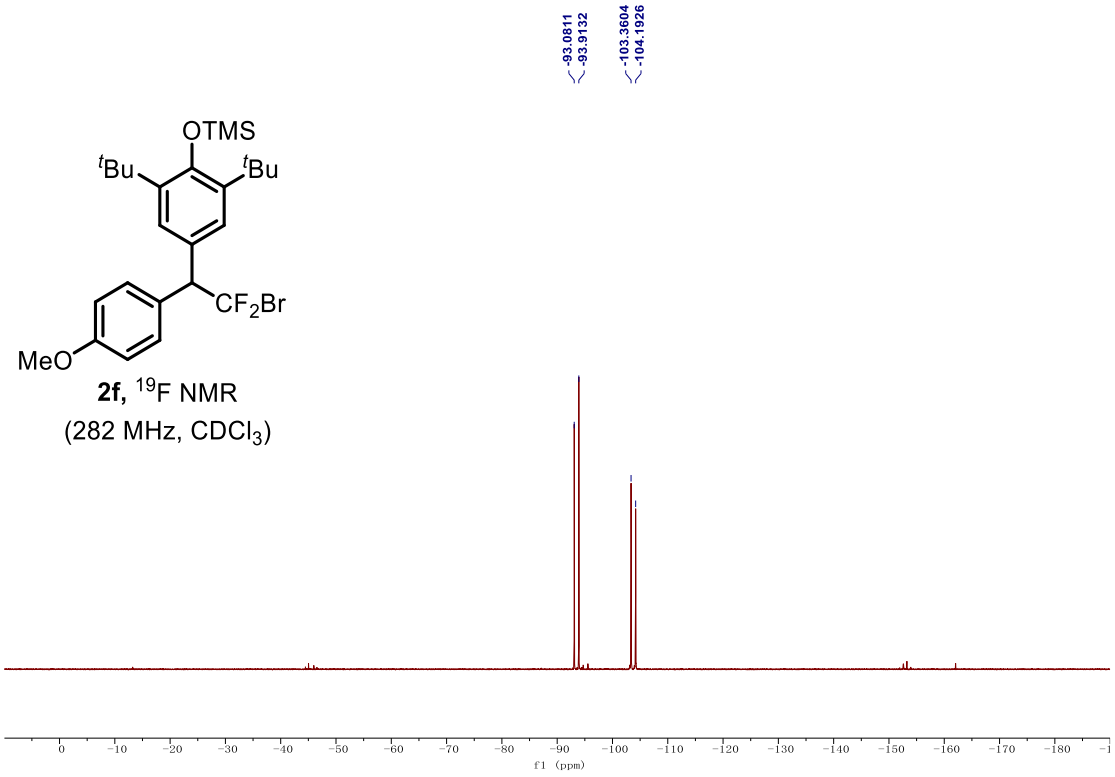
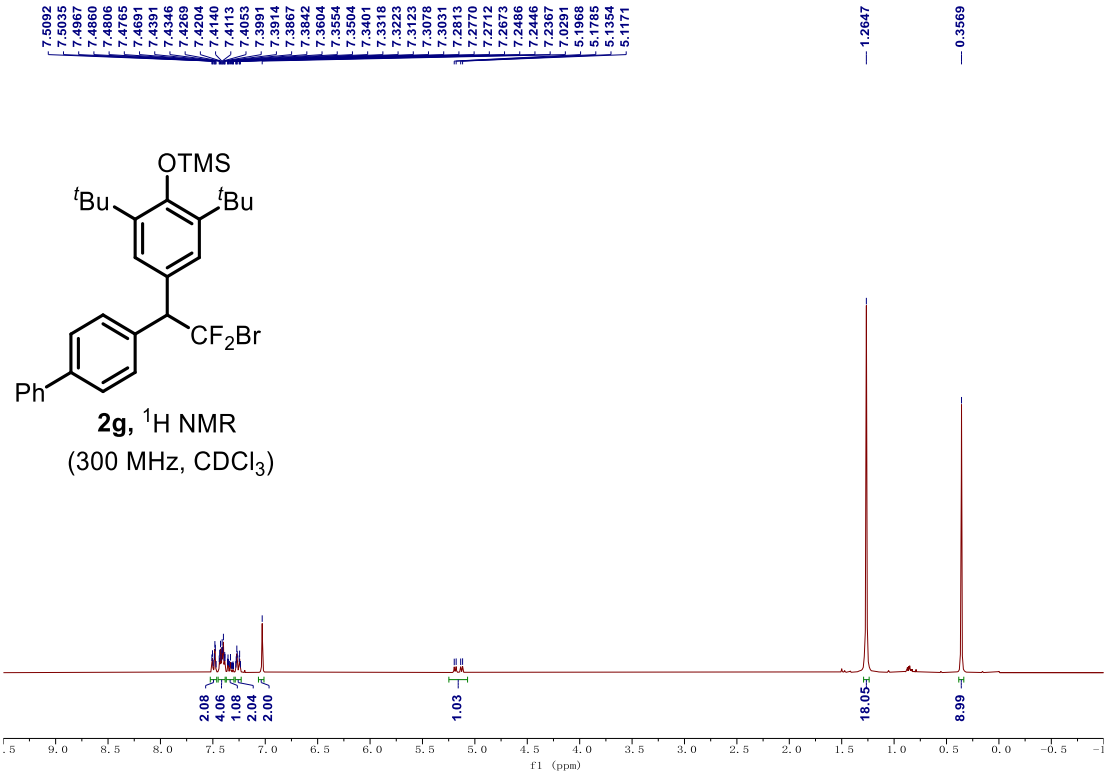
140.6374
130.8172
127.5100
127.4519
125.1169
124.7716
124.7606
124.4138
123.9712
123.8996
123.8906
123.8183
123.1870
119.8916
119.8746
116.5846
113.5396
56.1436
55.7441
55.6986
55.3557
55.3263
35.1917
31.1311
3.6569
OTMS
tBu
tBu
CF2Br
MeO
2f, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)


-93.0811
-93.9132
-103.3604
-104.1926
OTMS
tBu
tBu
CF2Br
MeO
2f, 19F NMR
(282 MHz, CDCl3)
f1 (ppm)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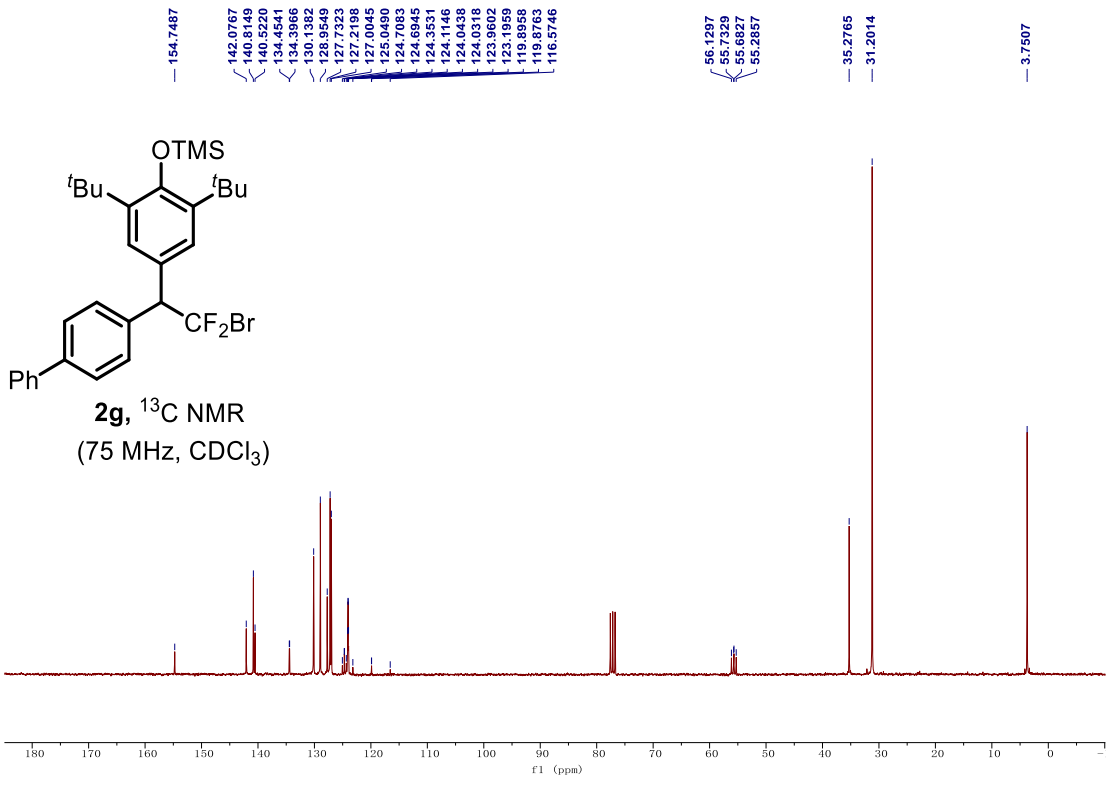
7.5035
7.4967
7.4860
7.4806
7.4765
7.4691
7.4391
7.4346
7.4269
7.4204
7.4140
7.4113
7.4053
7.3991
7.3914
7.3867
7.3842
7.3604
7.3554
7.3504
7.3401
7.3318
7.3223
7.3123
7.3078
7.3031
7.2813
7.2770
7.2712
7.2673
7.2486
7.2446
7.2367
7.0291
5.1968
5.1785
5.1354
5.1171
1.2647
0.3569
OTMS
tBu
tBu
CF2Br
Ph
2g, 1H NMR
(300 MHz, CDCl3)
2.08
4.06
1.08
2.04
2.00
1.03
18.05
8.99
f1 (ppm)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142.0767
140.8149
140.5220
134.4541
134.3966
130.1382
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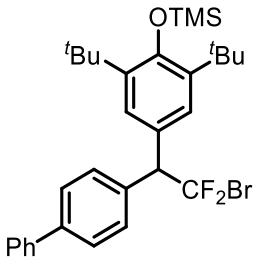
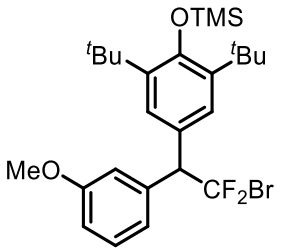
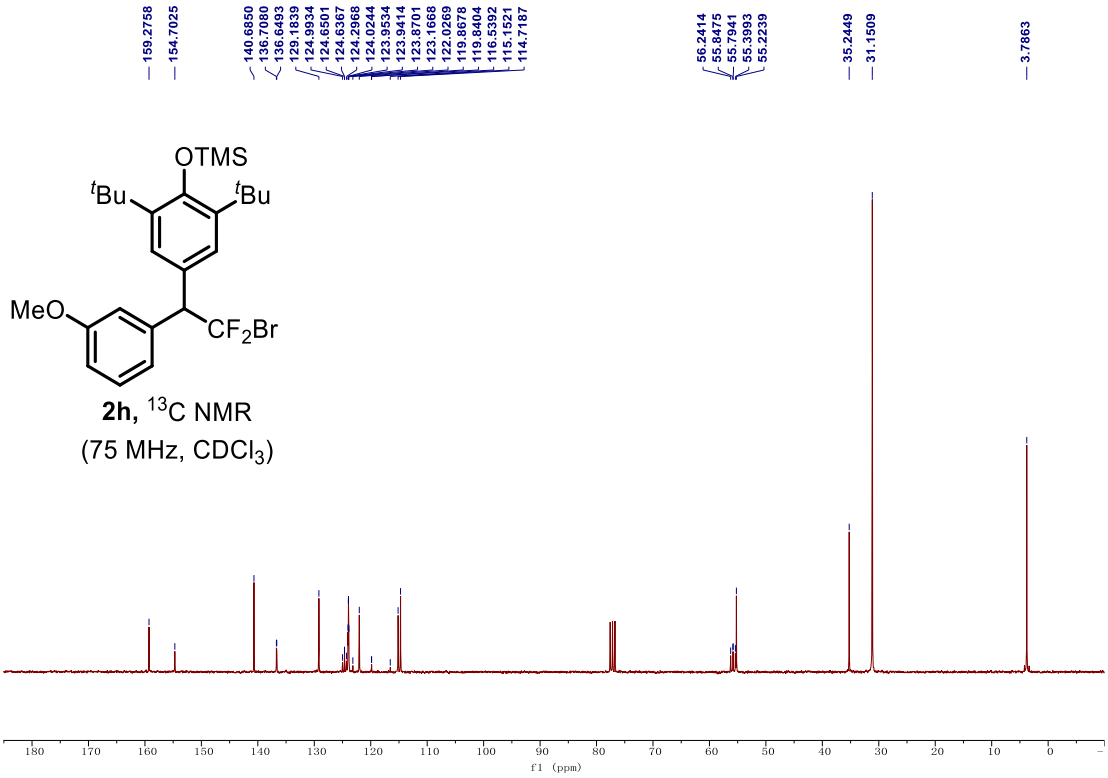
127.2198
127.0045
125.0490
124.7083
124.6945
124.3531
124.1146
124.0438
124.0318
123.9602
123.1959
119.8958
119.8763
116.5746
56.1297
55.7329
55.6827
55.2857
35.2765
31.2014
3.7507
OTMS
tBu
tBu
CF2Br
Ph
2g, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



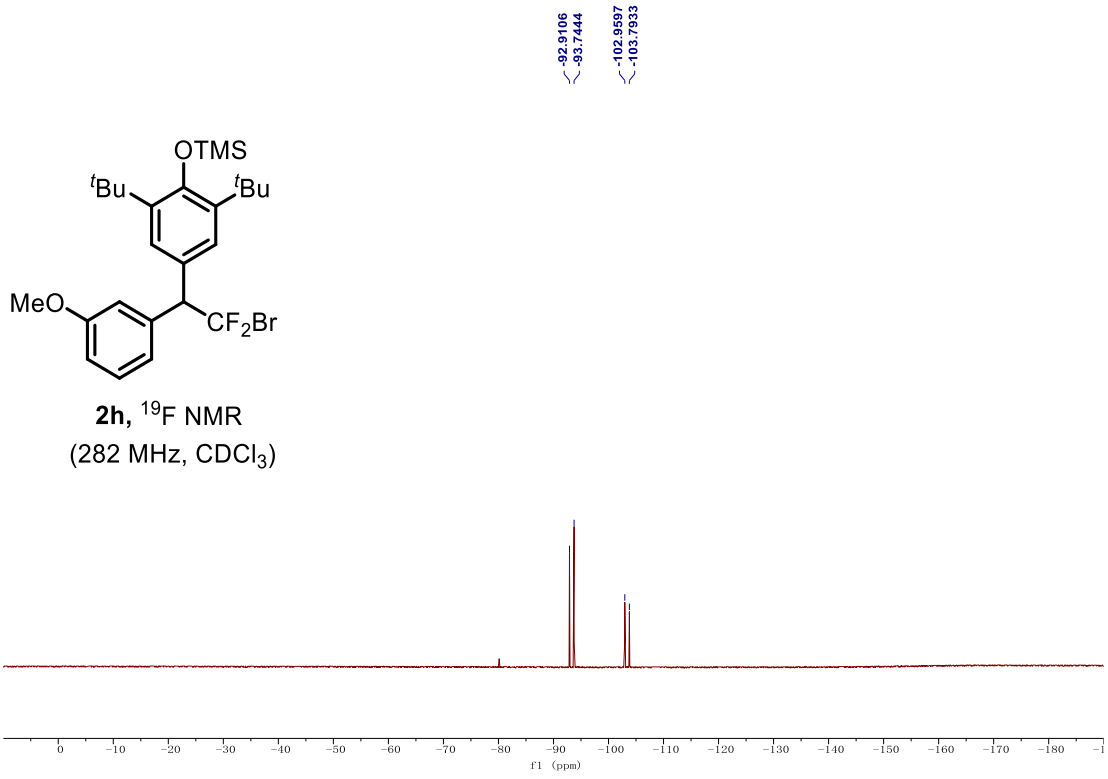
2g, ^{19}F NMR
(282 MHz, $CDCl_3$)



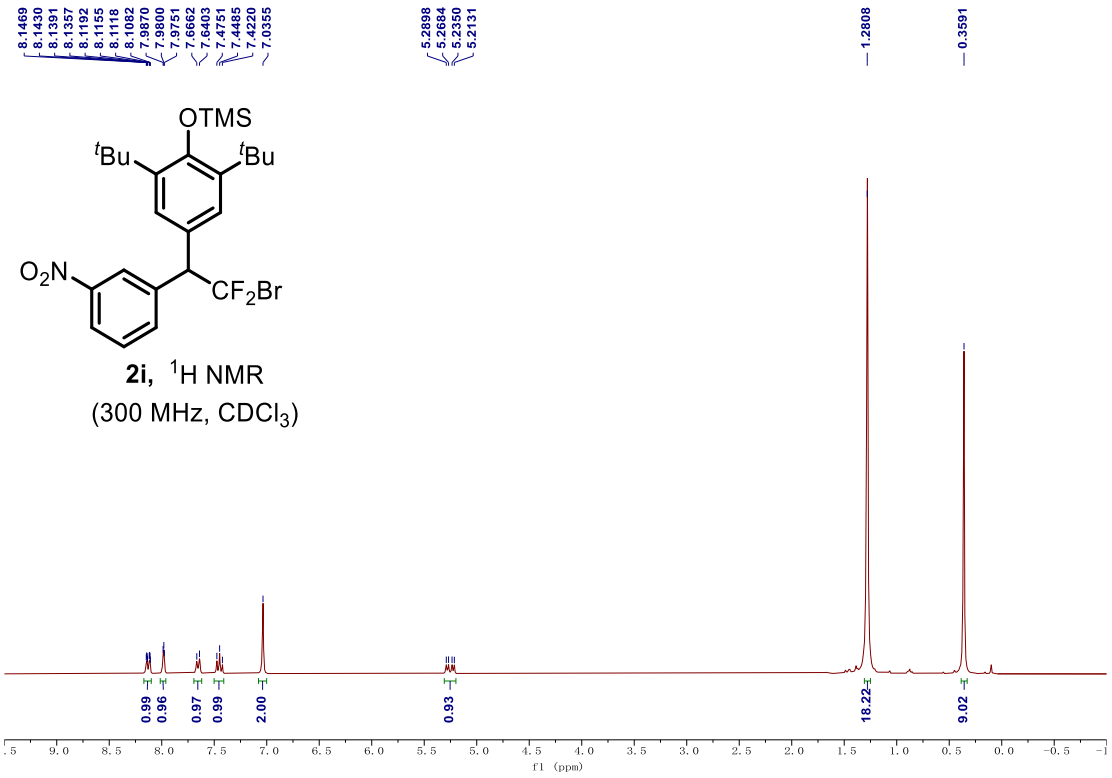
2h, ^{1}H NMR
(300 MHz, $CDCl_3$)

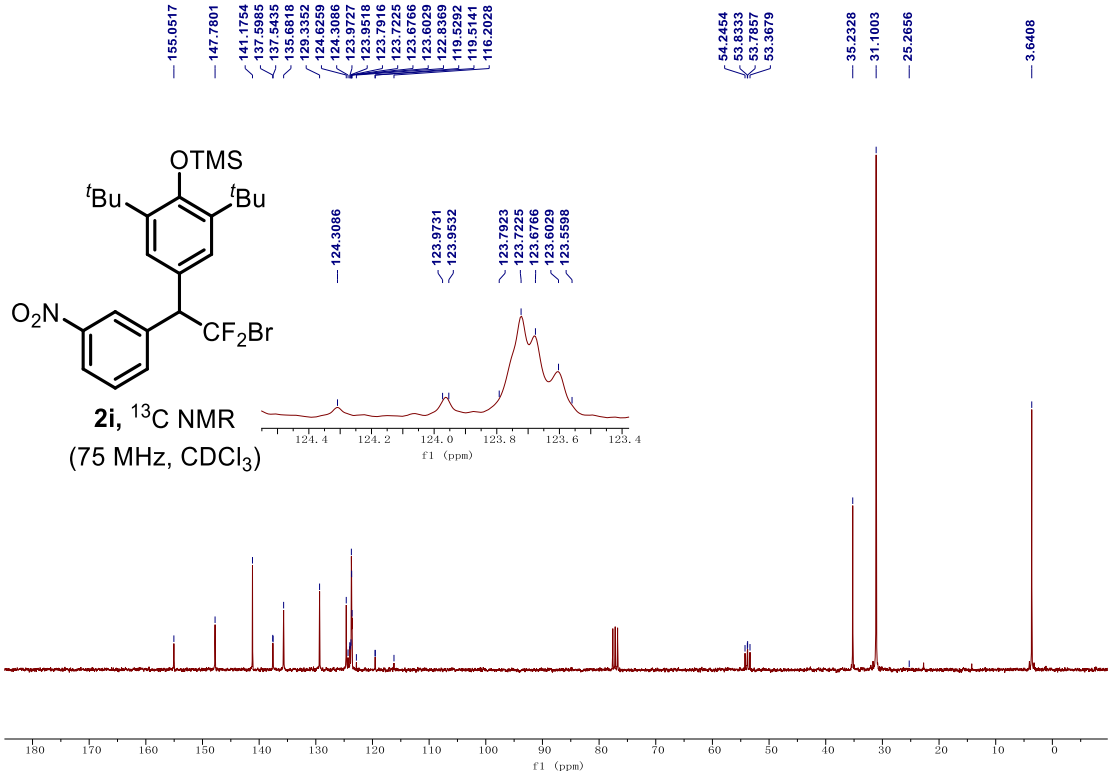


2h, ^{13}C NMR
(75 MHz, $CDCl_3$)



2h, ^{19}F NMR
(282 MHz, $CDCl_3$)


8.1469
8.1430
8.1391
8.1357
8.1192
8.1155
8.1118
8.1082
7.9870
7.9800
7.9751
7.6662
7.6403
7.4751
7.4485
7.4220
7.0355
5.2898
5.2684
5.2350
5.2131
1.2808
0.3591
OTMS
tBu
tBu
O2N
CF2Br
2i, 1H NMR
(300 MHz, CDCl3)
0.99
0.96
0.97
0.99
2.00
0.93
18.22
9.02
f1 (ppm)


155.0517
147.7801
141.1754
137.5985
137.5435
135.6818
129.3352
124.6259
124.3086
123.9727
123.9518
123.7916
123.7225
123.6766
123.6029
122.8369
119.5292
119.5141
116.2028
54.2454
53.8333
53.7857
53.3679
35.2328
31.1003
25.2656
3.6408
OTMS
tBu
tBu
O2N
CF2Br
2i, 13C NMR
(75 MHz, CDCl3)
124.3086
123.9731
123.9532
123.7923
123.7225
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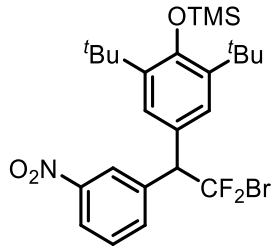
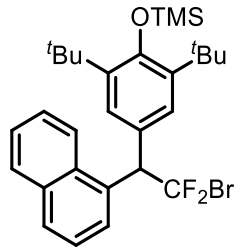
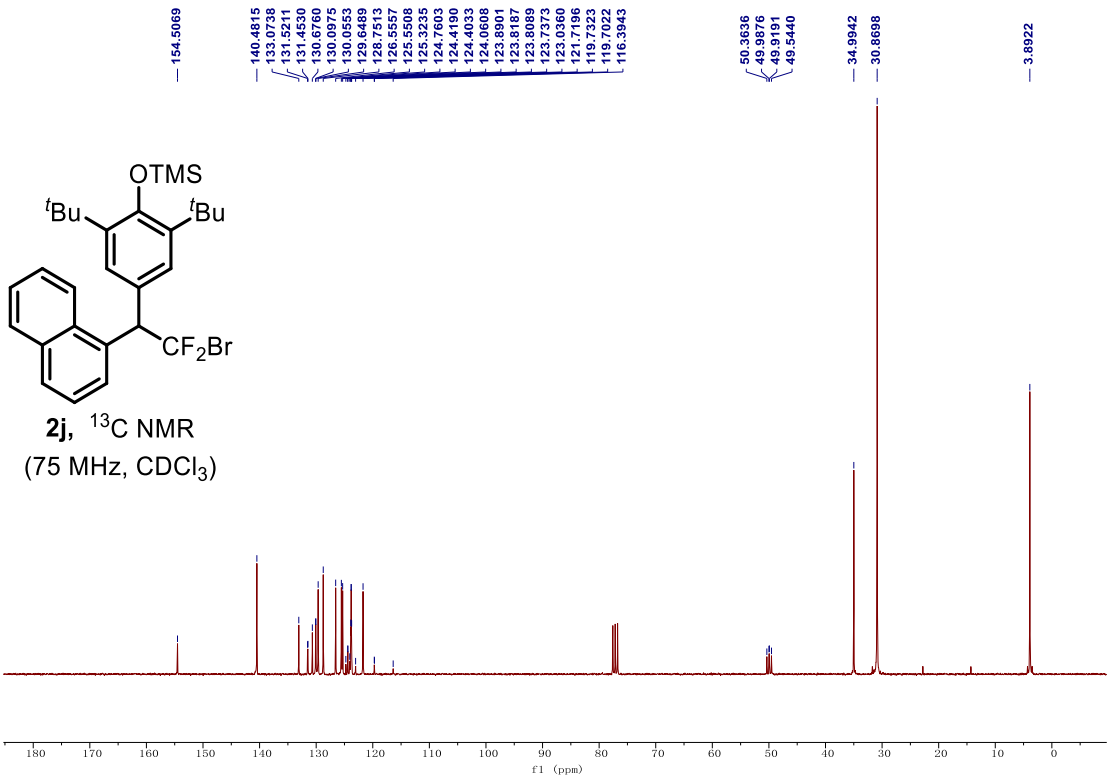
123.6029
123.5598
f1 (ppm)
f1 (ppm)



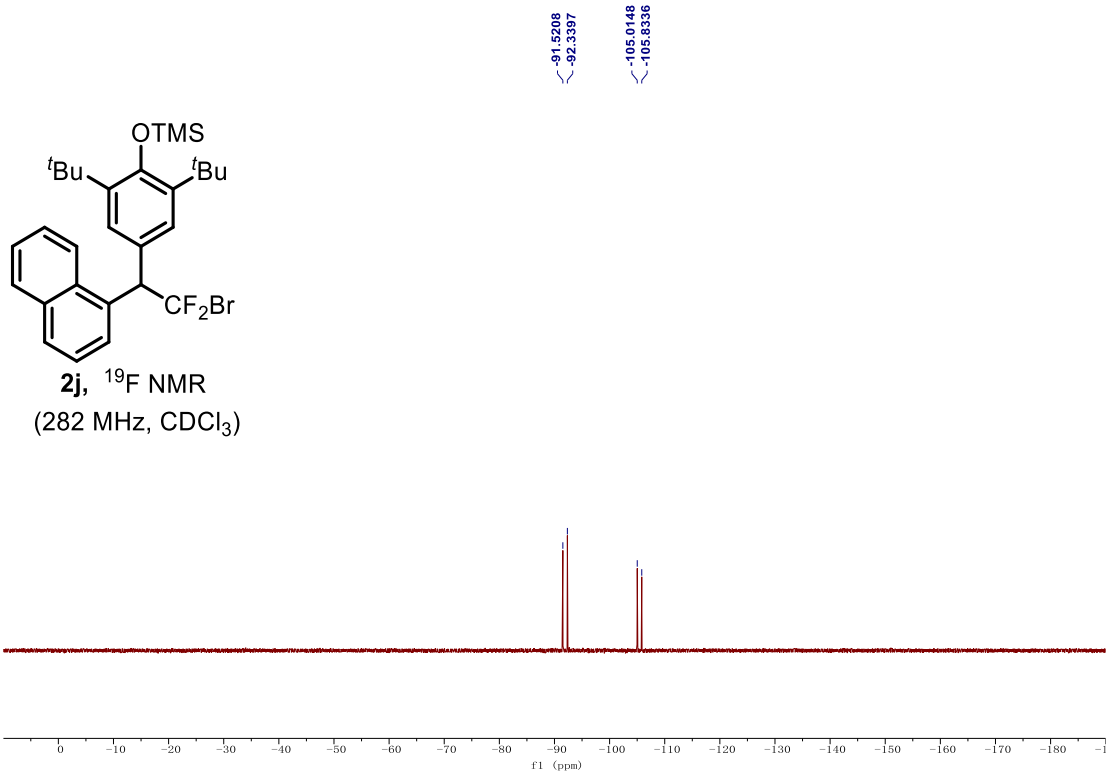
2i, ^{19}F NMR
(282 MHz, $CDCl_3$)



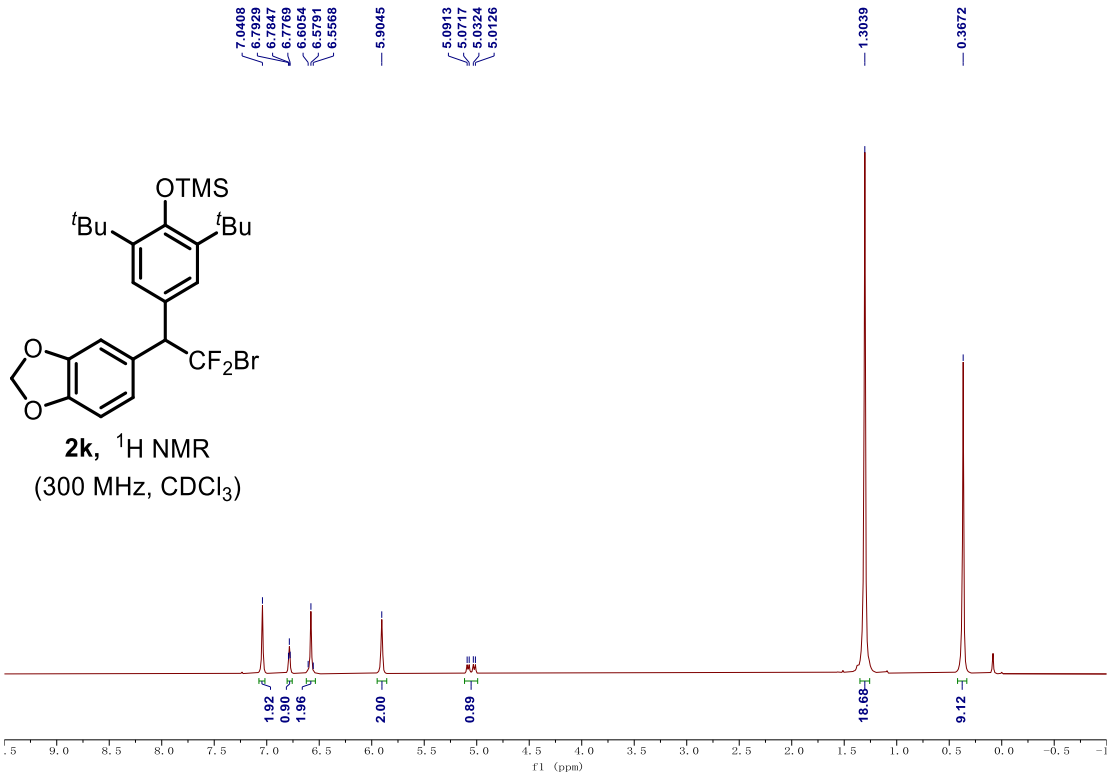
2j, ^{1}H NMR
(300 MHz, $CDCl_3$)



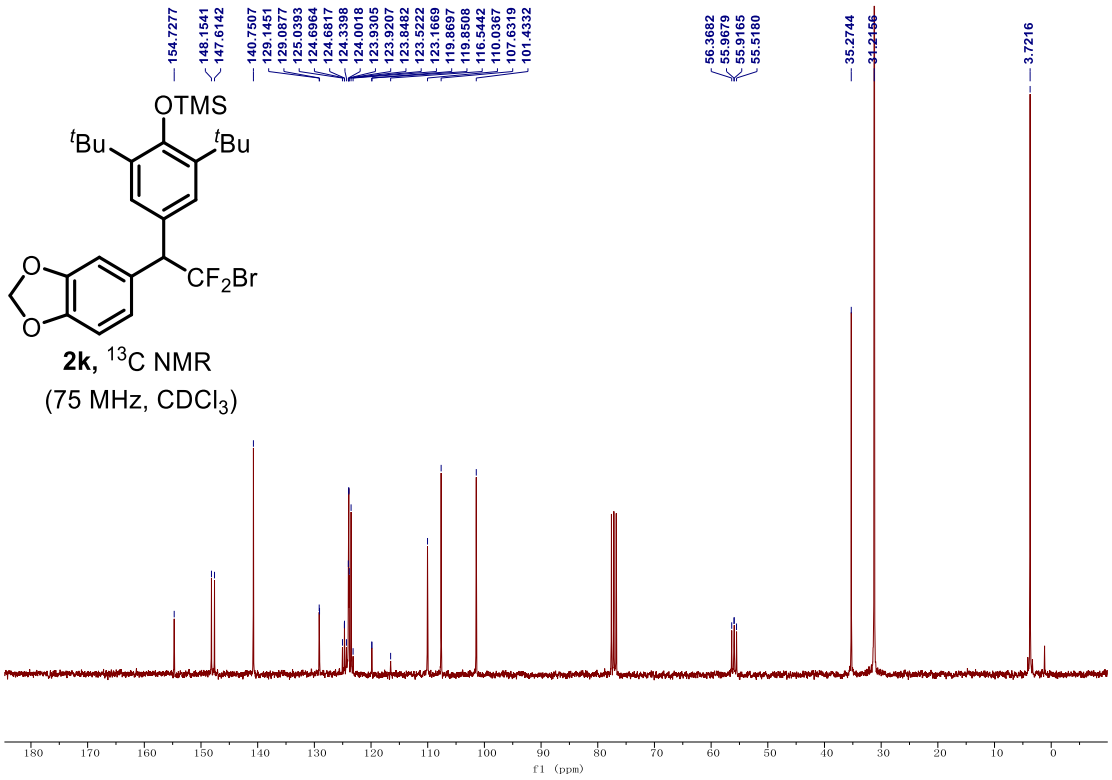
2j, ^{13}C NMR
(75 MHz, $CDCl_3$)



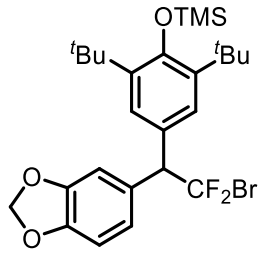
2j, ^{19}F NMR
(282 MHz, $CDCl_3$)



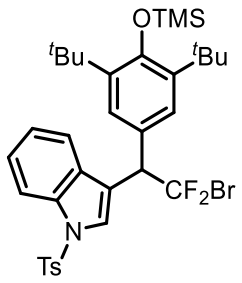
2k, ^{1}H NMR
(300 MHz, $CDCl_3$)



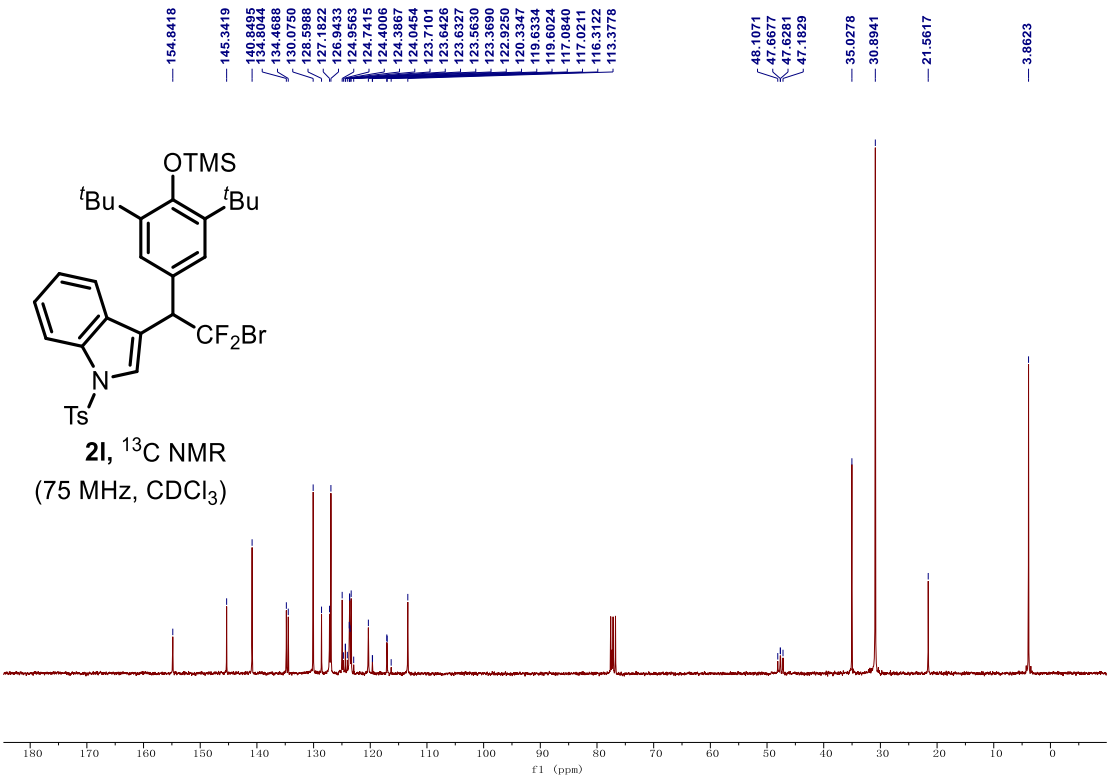
2k, ^{13}C NMR
(75 MHz, $CDCl_3$)



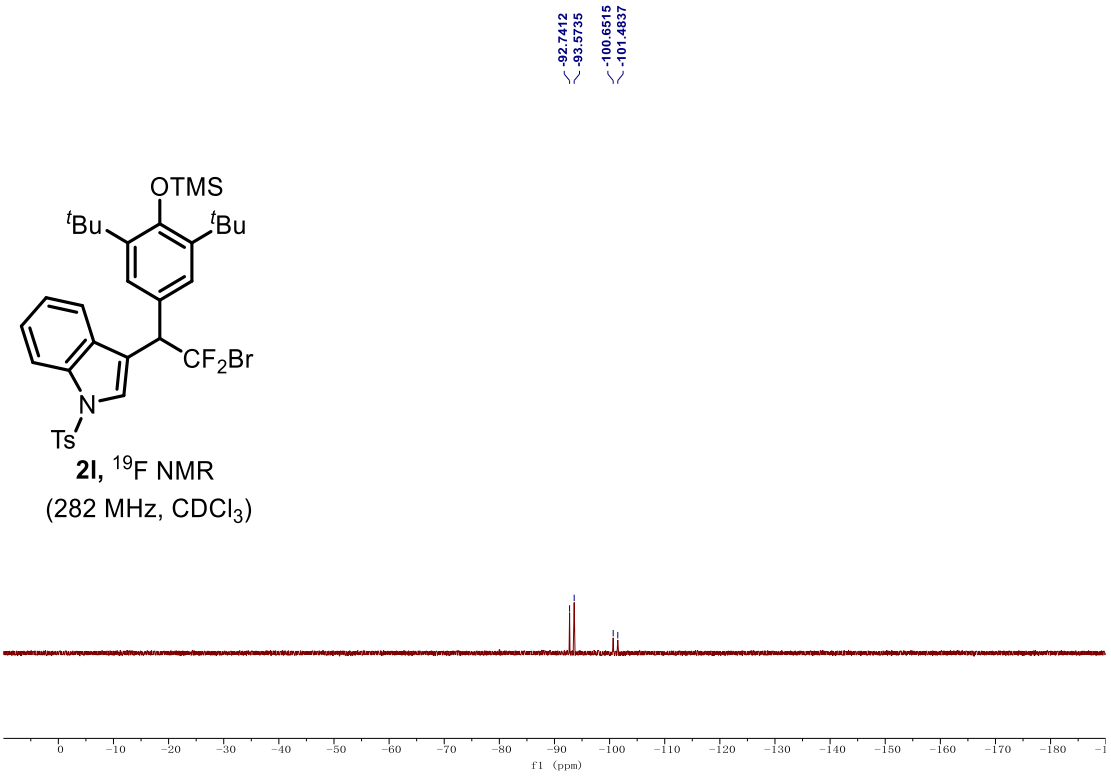
2k, ^{19}F NMR
(282 MHz, $CDCl_3$)



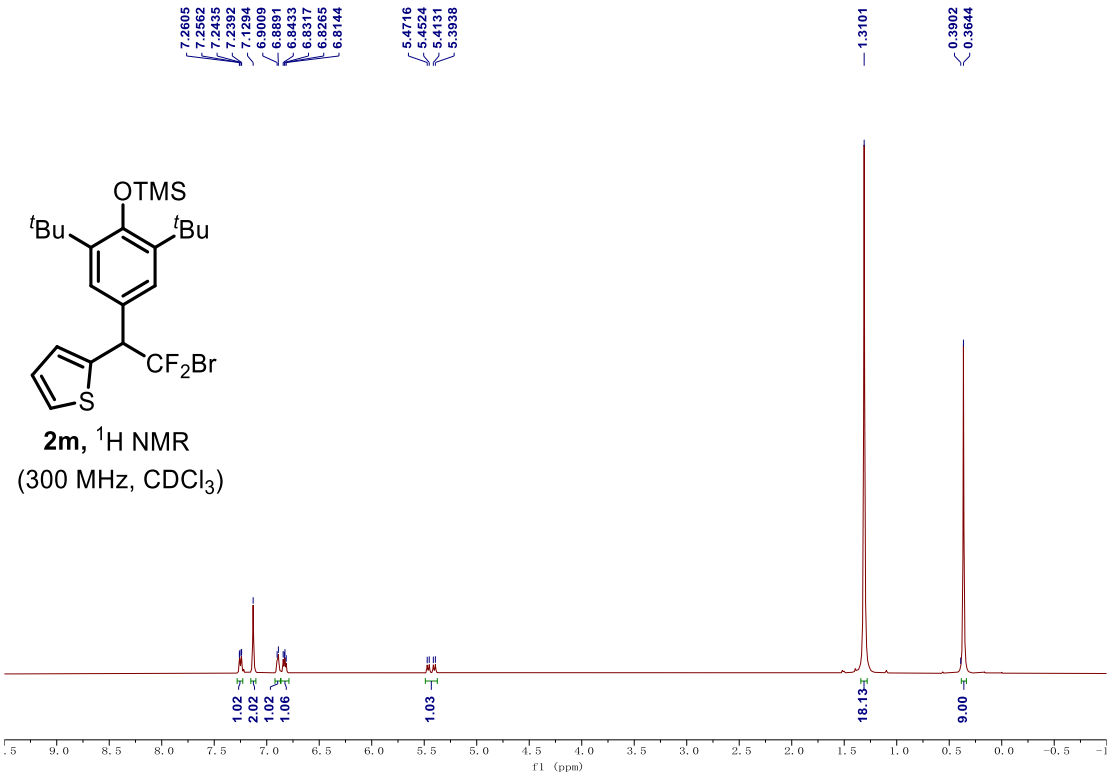
2l, ^{1}H NMR
(300 MHz, $CDCl_3$)



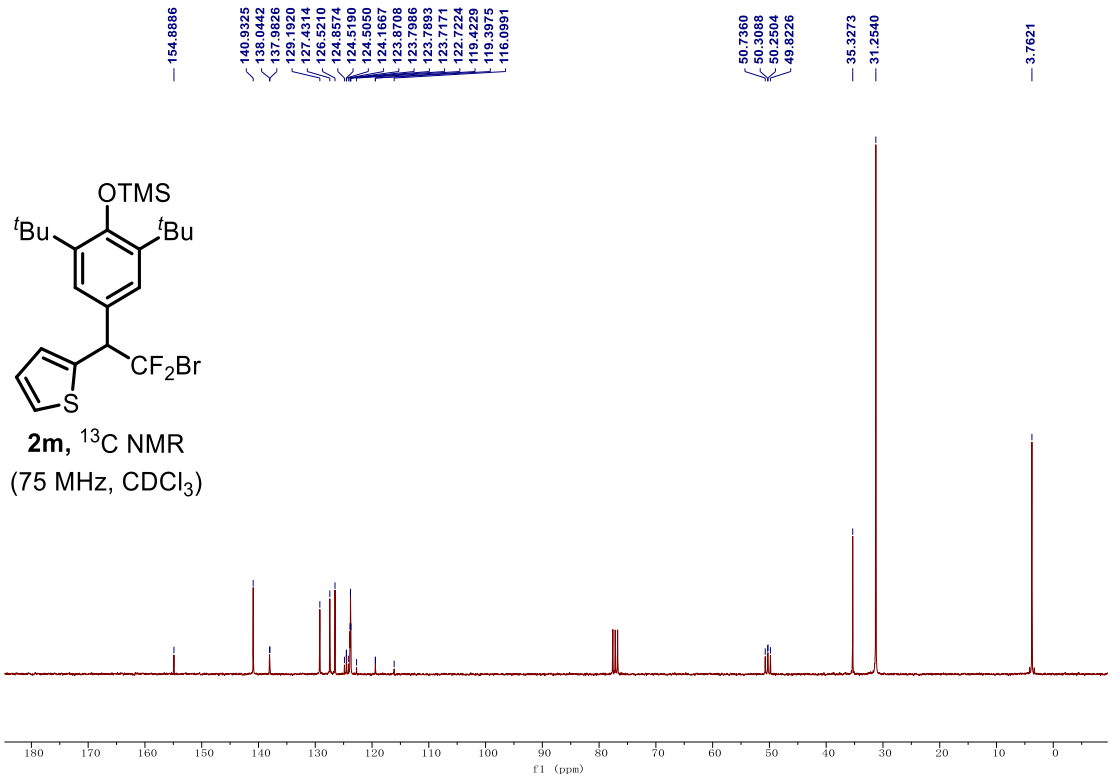
2l, ^{13}C NMR
(75 MHz, $CDCl_3$)



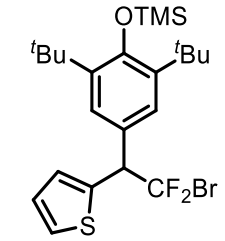
2l, ^{19}F NMR
(282 MHz, $CDCl_3$)



2m, ^{1}H NMR
(300 MHz, $CDCl_3$)

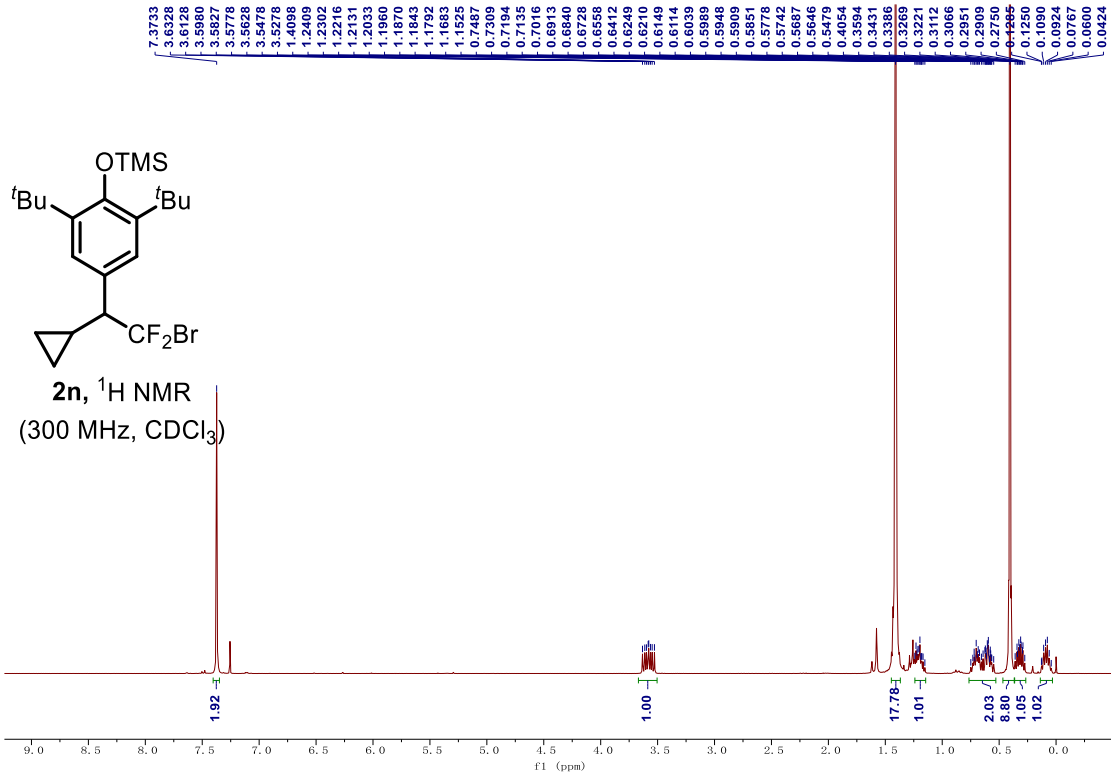


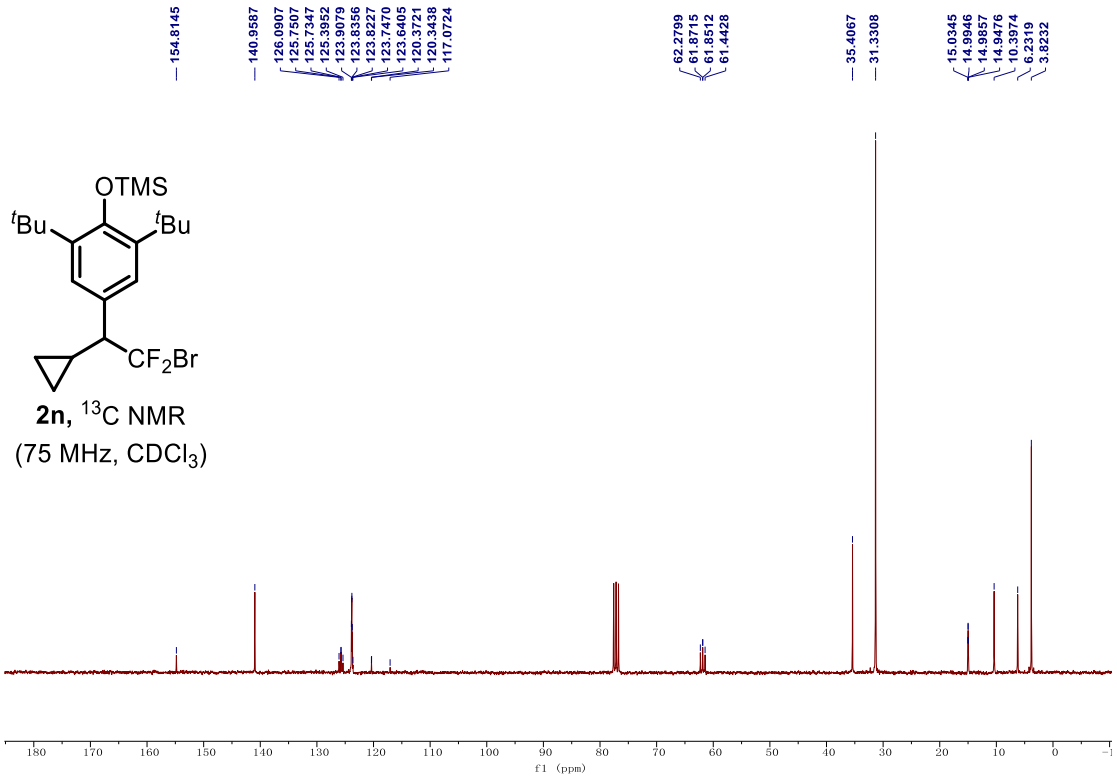
2m, ^{13}C NMR
(75 MHz, $CDCl_3$)



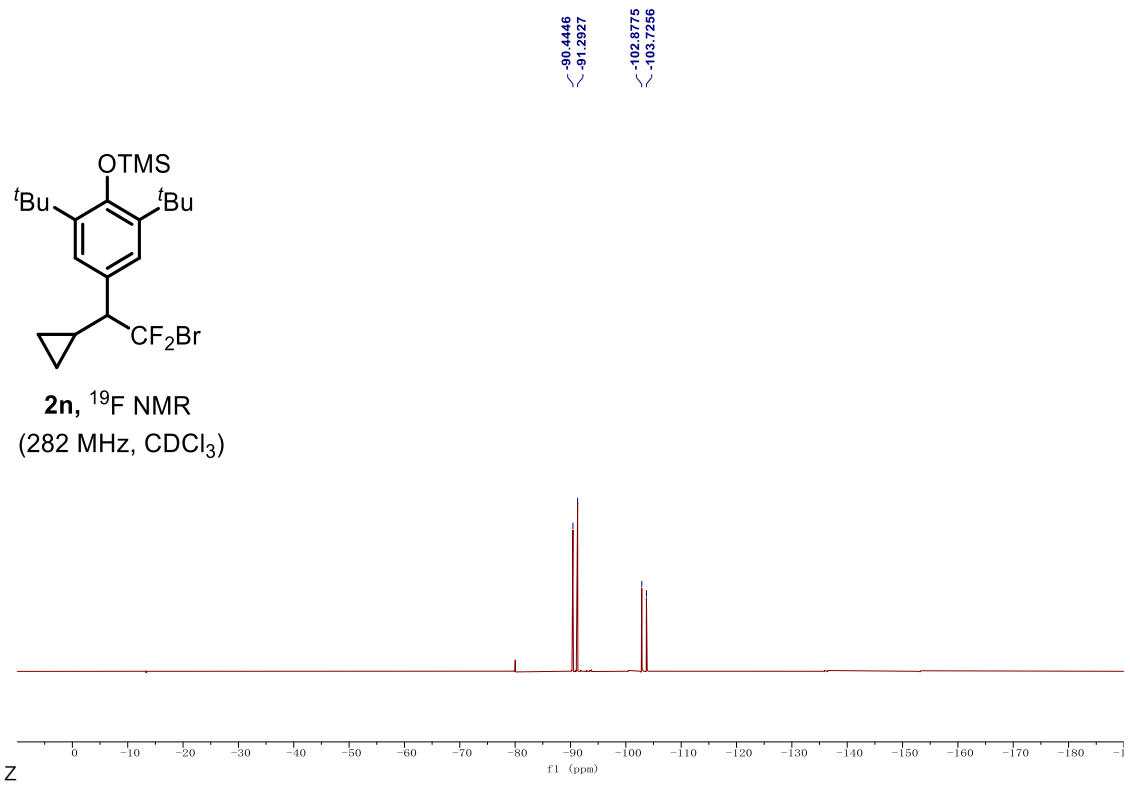
2m, ^{19}F NMR
(282 MHz, $CDCl_3$)

2n, ^{1}H NMR
(300 MHz, $CDCl_3$)

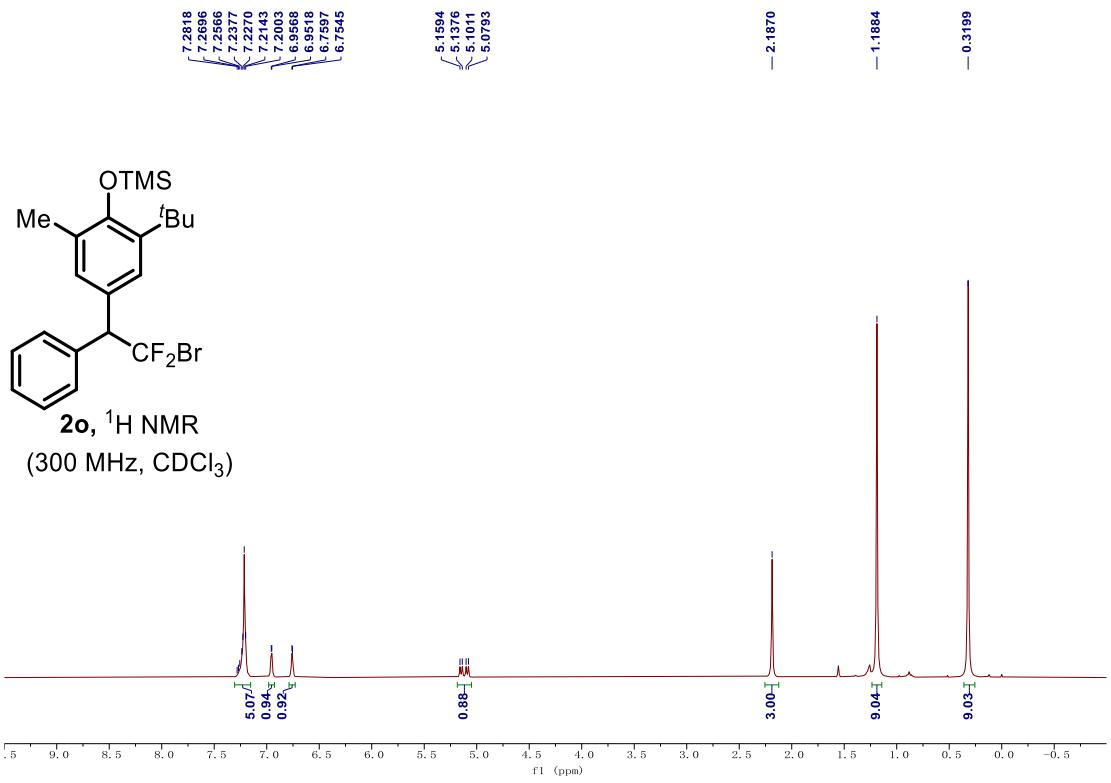




2n, ^{13}C NMR
(75 MHz, $CDCl_3$)



2n, ^{19}F NMR
(282 MHz, $CDCl_3$)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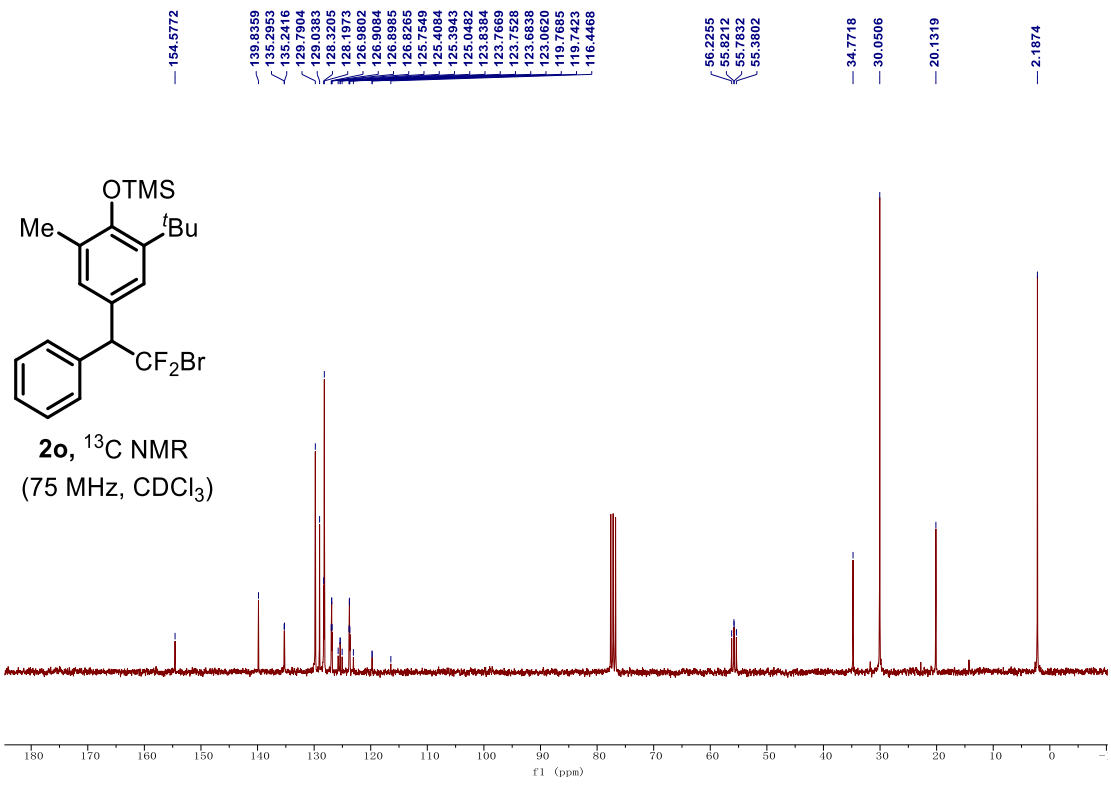
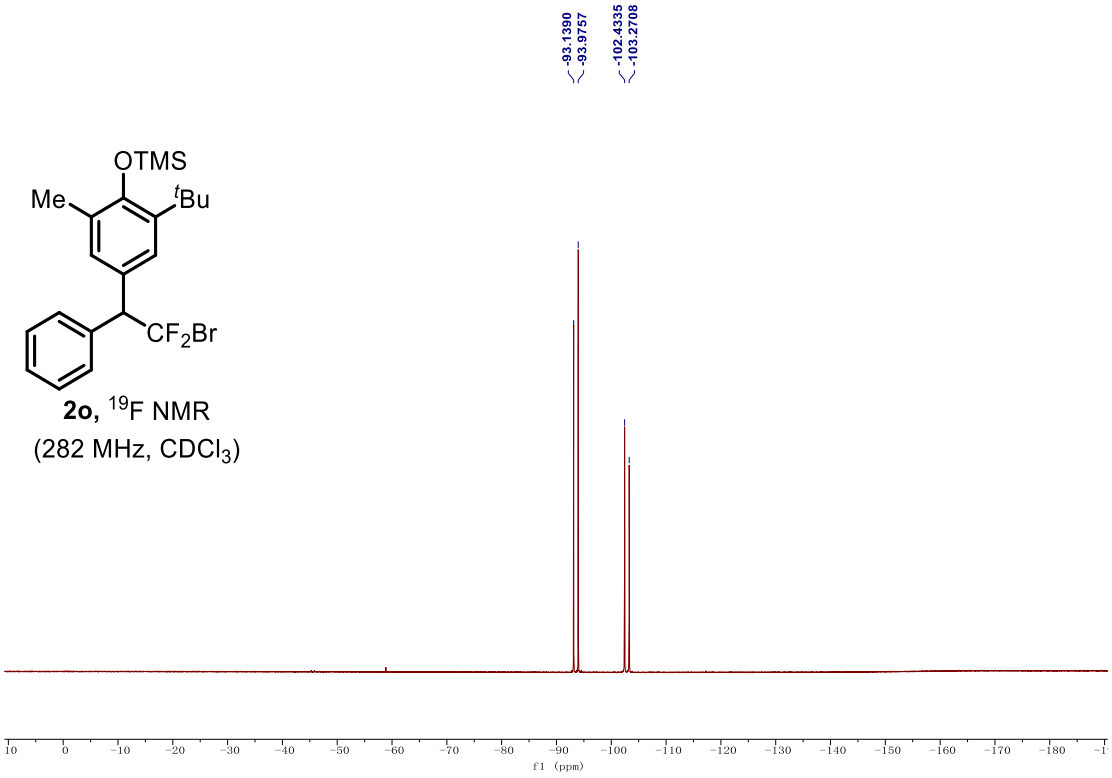
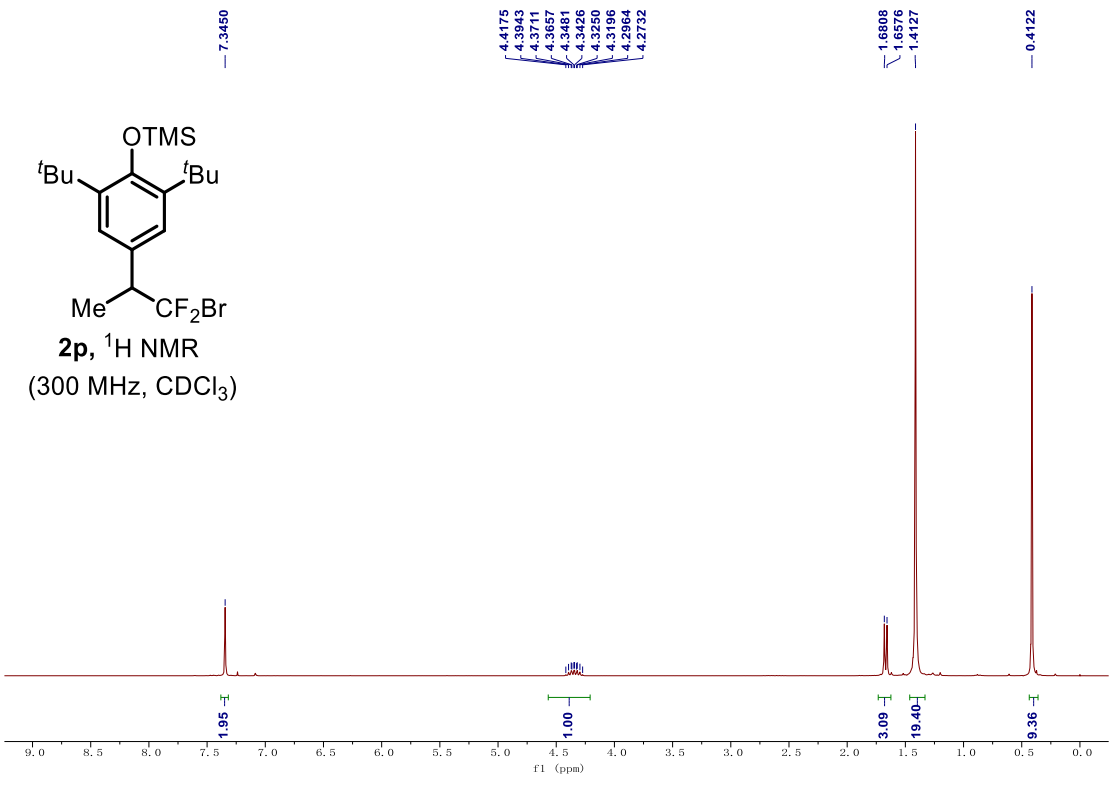
7.2696
7.2566
7.2377
7.2270
7.2143
7.2003
6.9568
6.9518
6.7597
6.7545
5.1594
5.1376
5.1011
5.0793
2.1870
1.1884
0.3199
OTMS
Me
tBu
CF2Br
2o, 1H NMR
(300 MHz, CDCl3)
5.07
0.94
0.92
0.88
3.00
9.04
9.03
f1 (ppm)

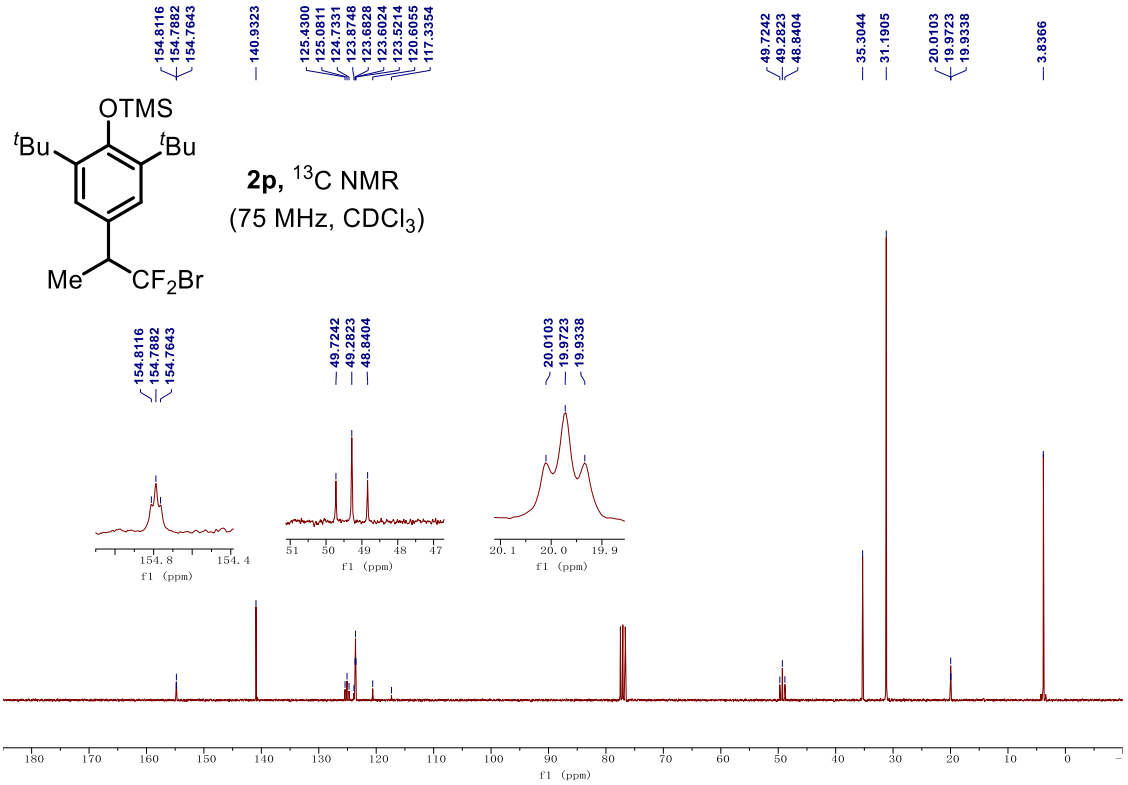

154.5772
139.8359
135.2953
135.2416
129.7904
129.0383
128.3205
128.1973
126.9802
126.9084
126.8985
126.8265
125.7549
125.4084
125.3943
125.0482
123.8384
123.7669
123.7528
123.6838
123.0620
119.7685
119.7423
116.4468
56.2255
55.8212
55.7832
55.3802
34.7718
30.0506
20.1319
2.1874
OTMS
Me
tBu
CF2Br
2o, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



2o, ^{19}F NMR
(282 MHz, $CDCl_3$)



2p, ^{1}H NMR
(300 MHz, $CDCl_3$)


154.8116
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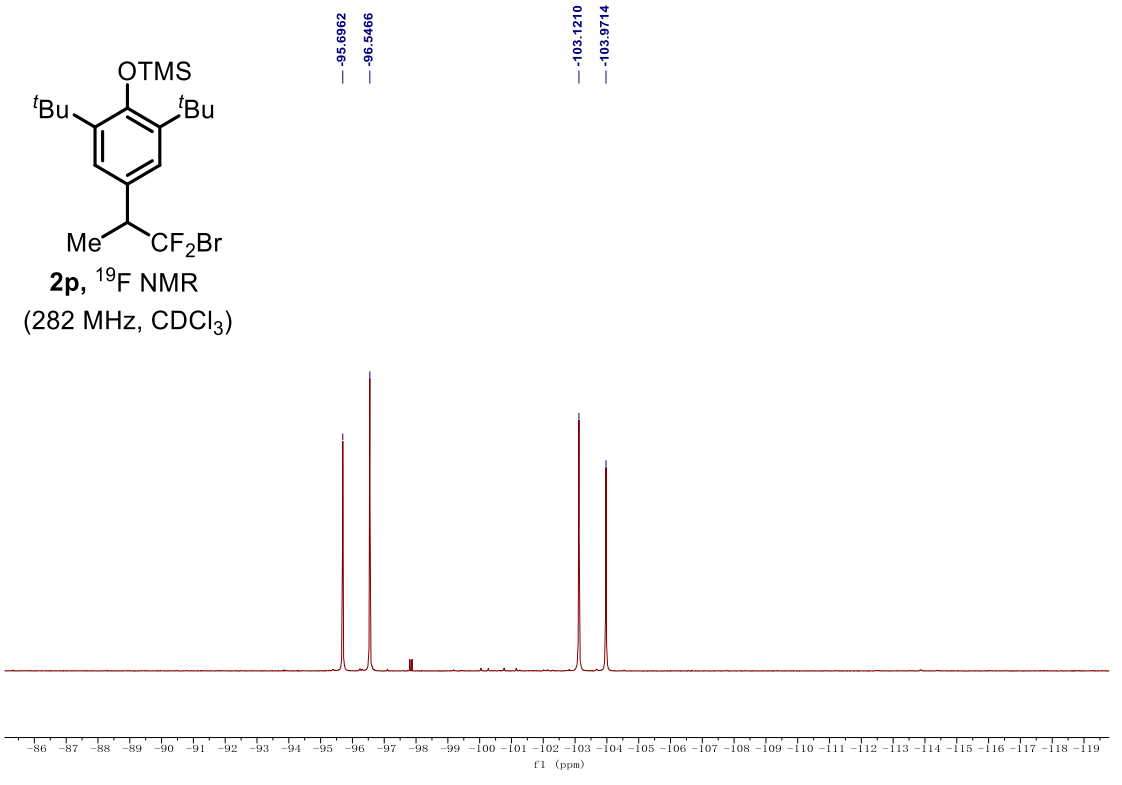
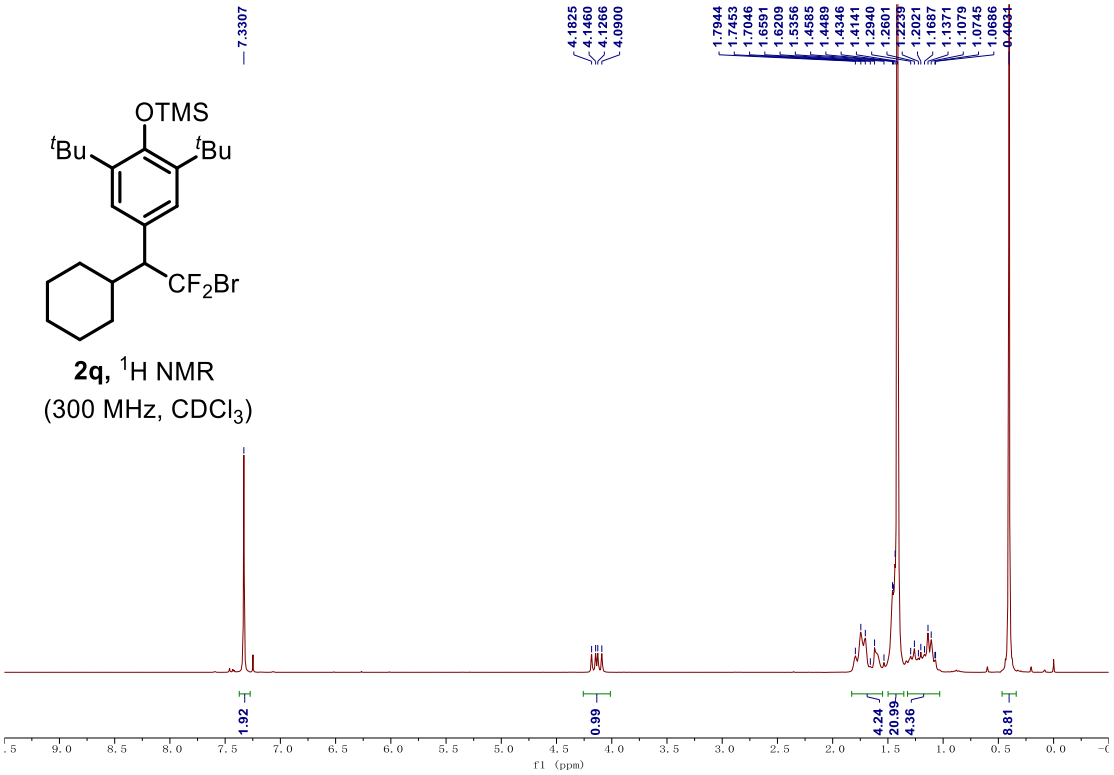
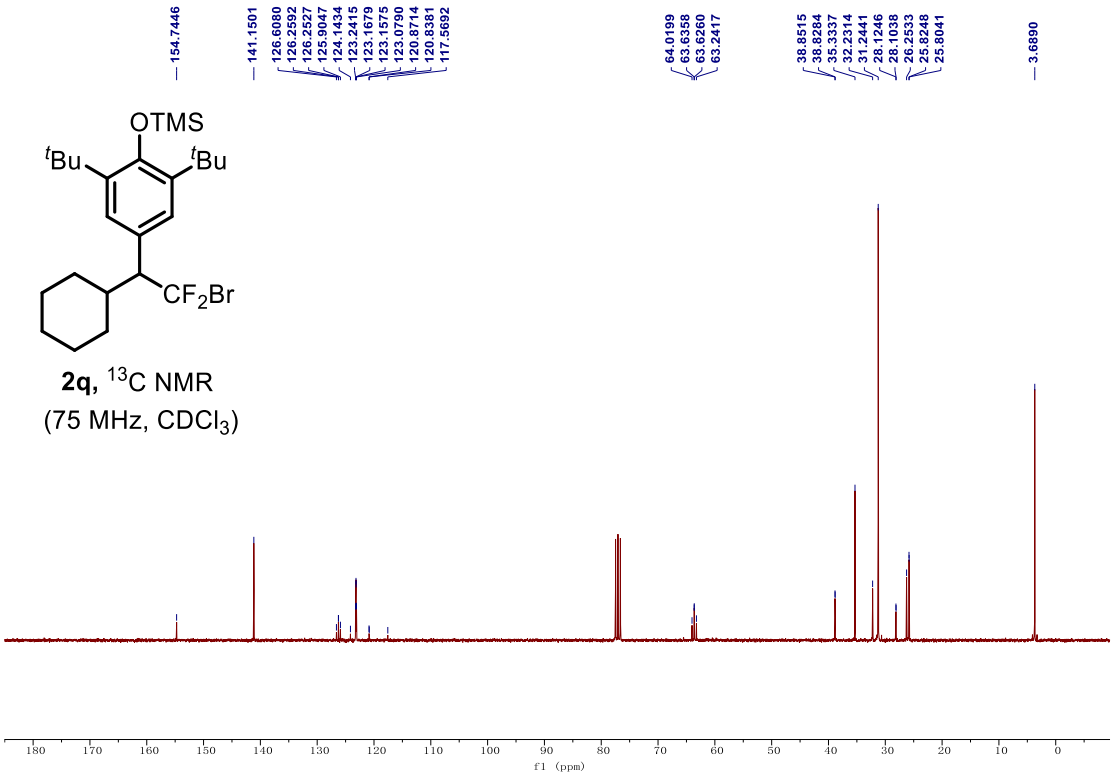
125.4300
125.0811
124.7331
123.8748
123.6828
123.6024
123.5214
120.6055
117.3354
49.7242
49.2823
48.8404
35.3044
31.1905
20.0103
19.9723
19.9338
3.8366
OTMS
tBu
tBu
Me
CF2Br
2p, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)

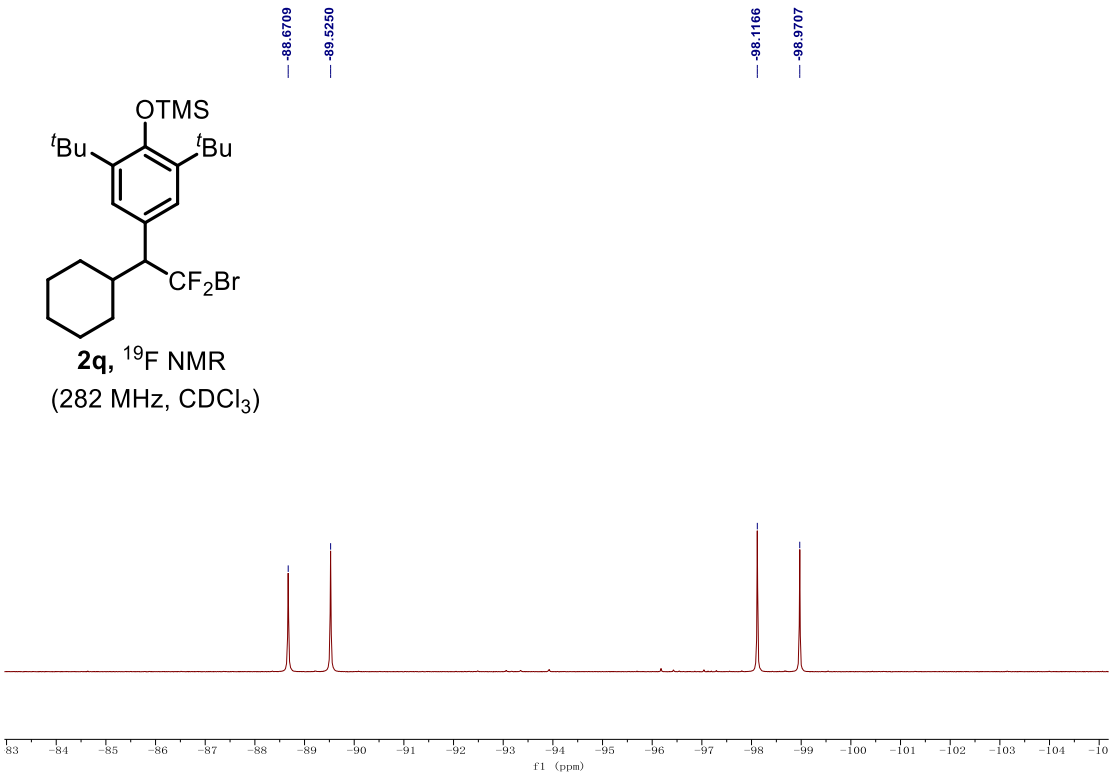

-95.6962
-96.5466
-103.1210
-103.9714
OTMS
tBu
tBu
Me
CF2Br
2p, 19F NMR
(282 MHz, CDCl3)
f1 (ppm)



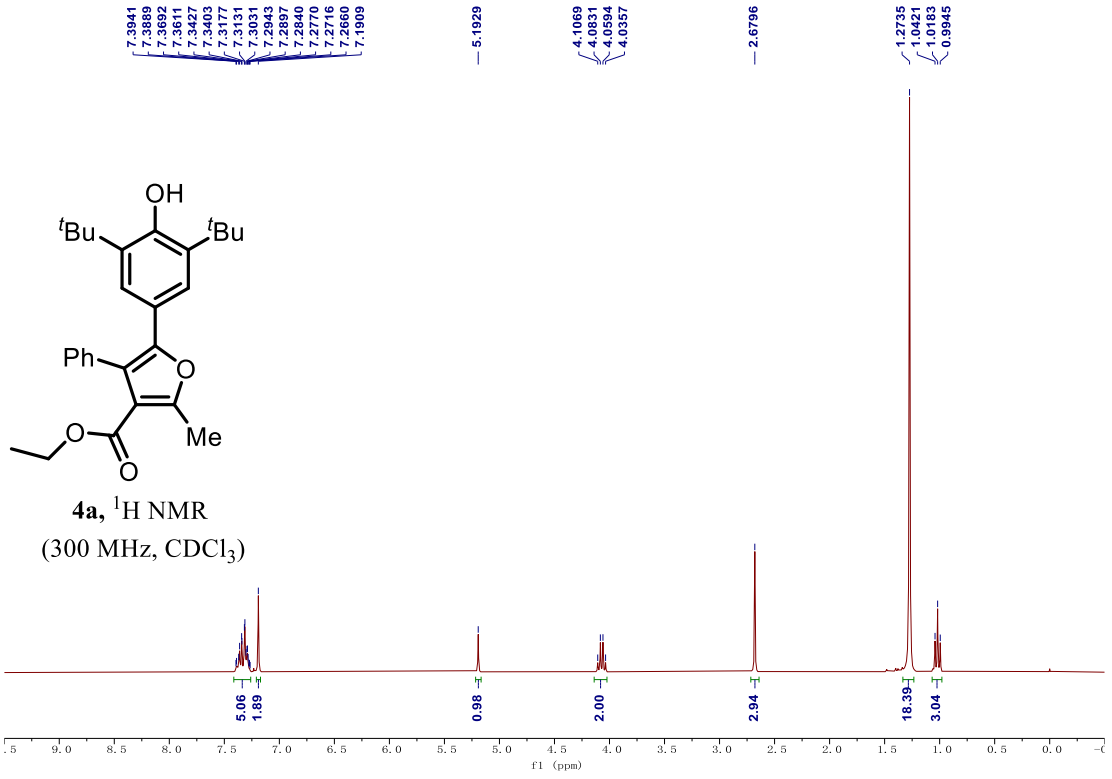
2q, ^{1}H NMR
(300 MHz, $CDCl_3$)



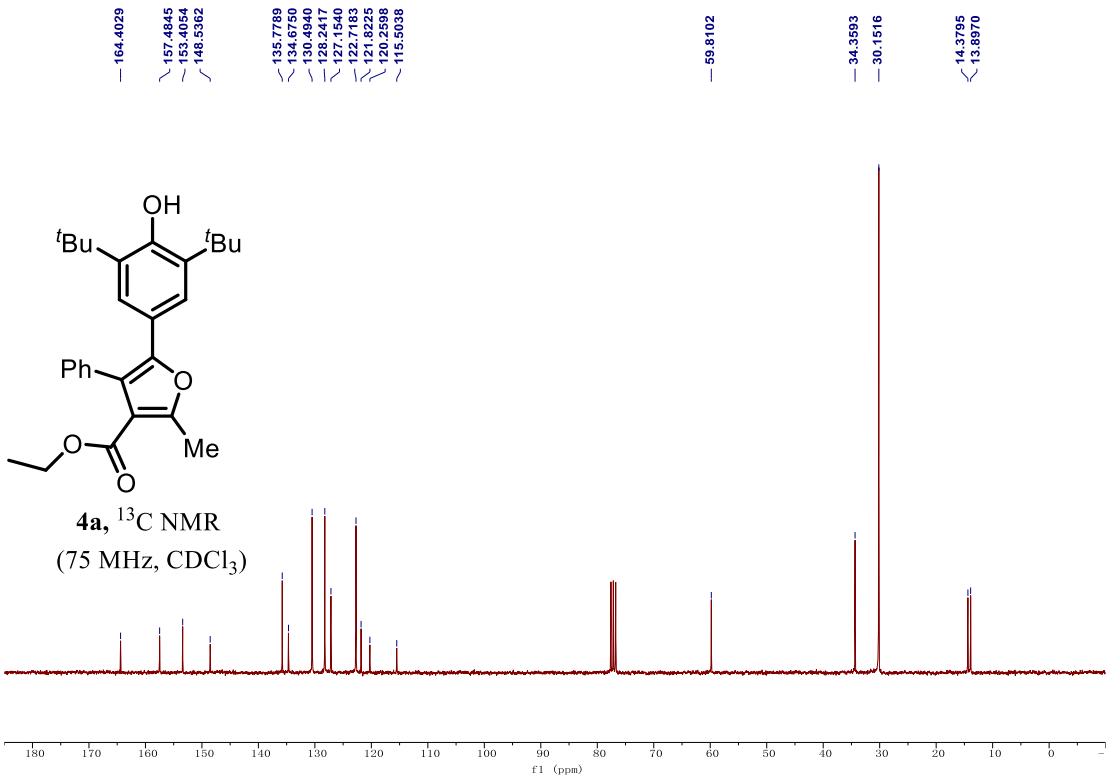
2q, ^{13}C NMR
(75 MHz, $CDCl_3$)



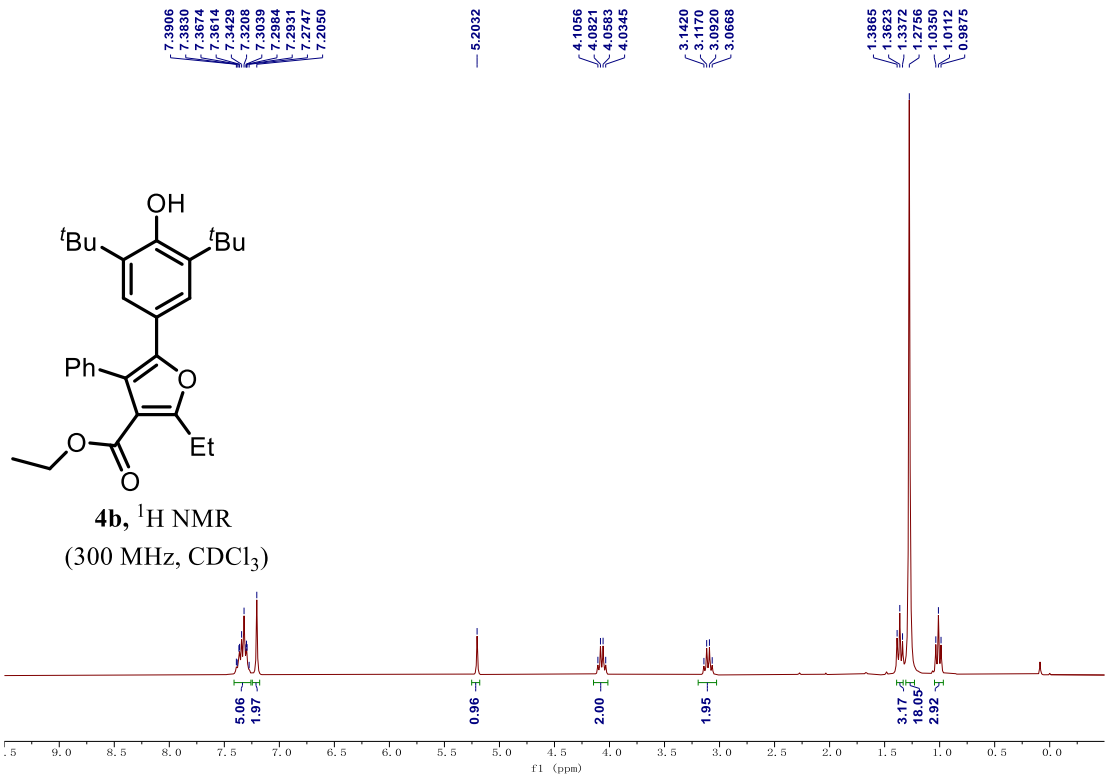
2q, ^{19}F NMR
(282 MHz, $CDCl_3$)



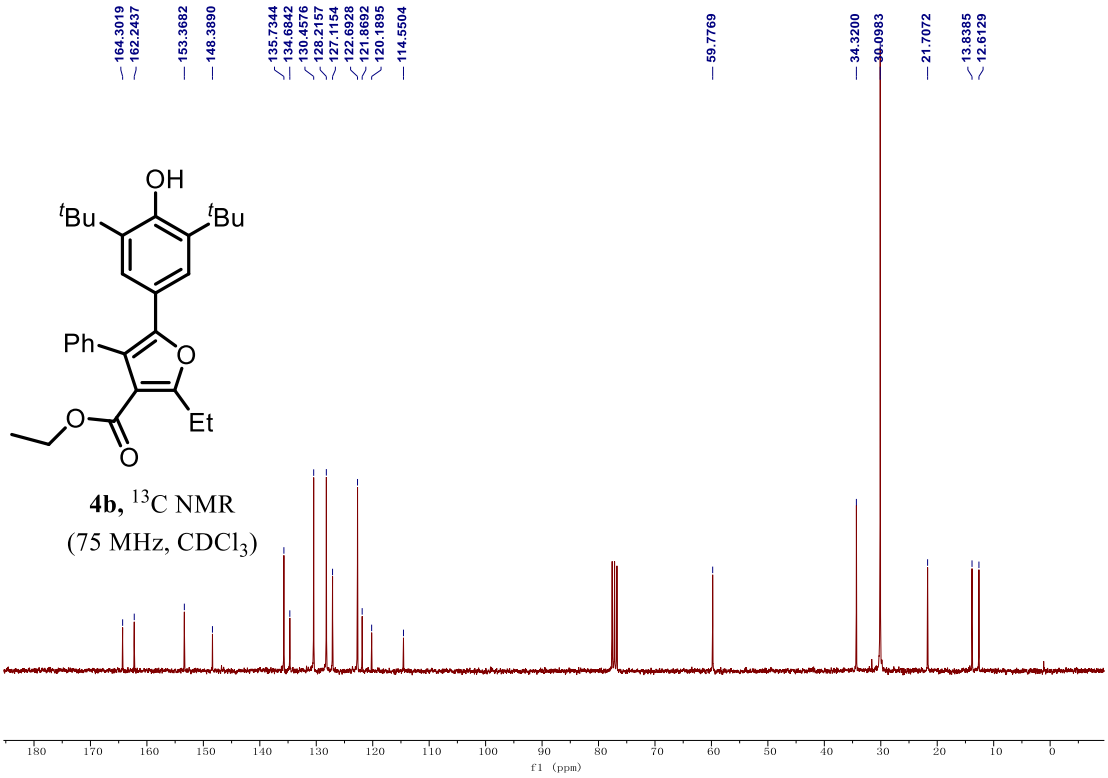
4a, ^{1}H NMR
(300 MHz, $CDCl_3$)



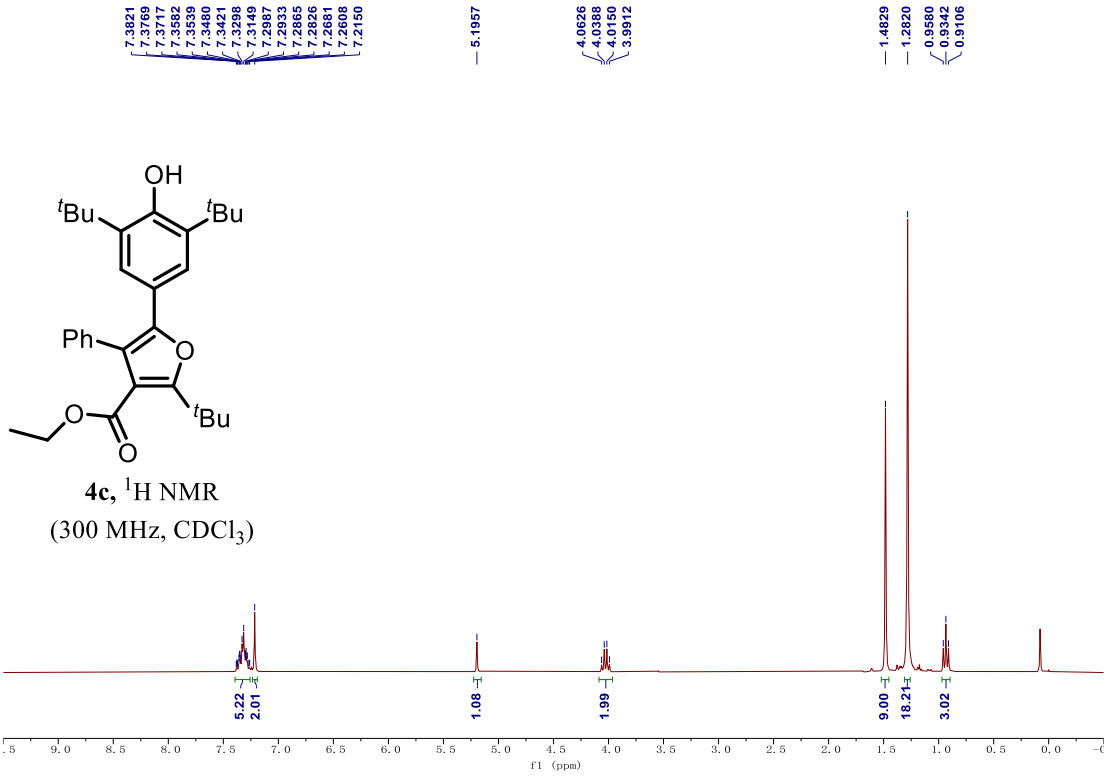
4a, ^{13}C NMR
(75 MHz, $CDCl_3$)



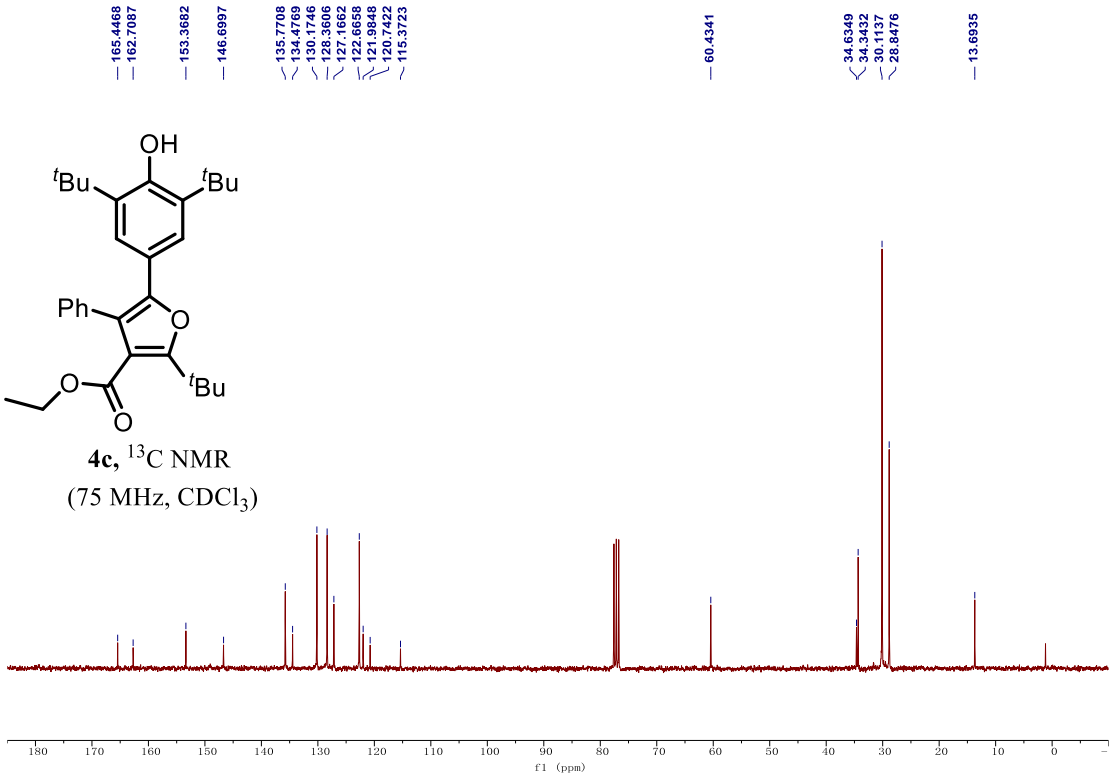
4b, ^{1}H NMR
(300 MHz, $CDCl_3$)



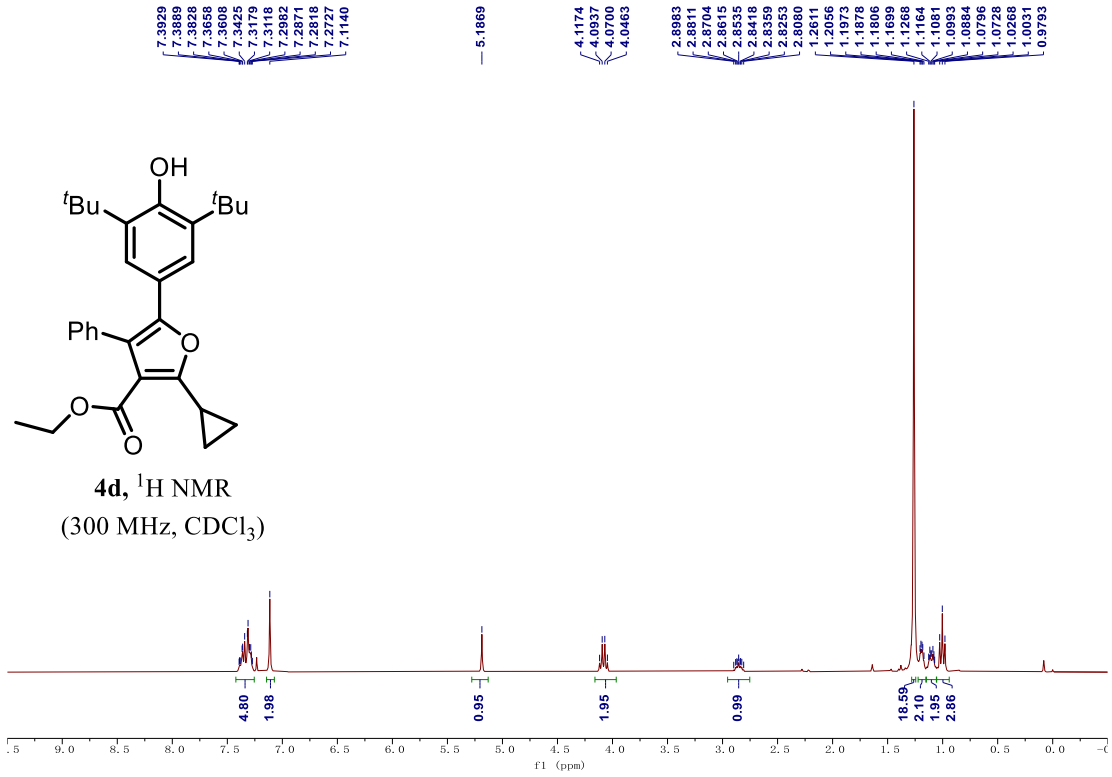
4b, ^{13}C NMR
(75 MHz, $CDCl_3$)



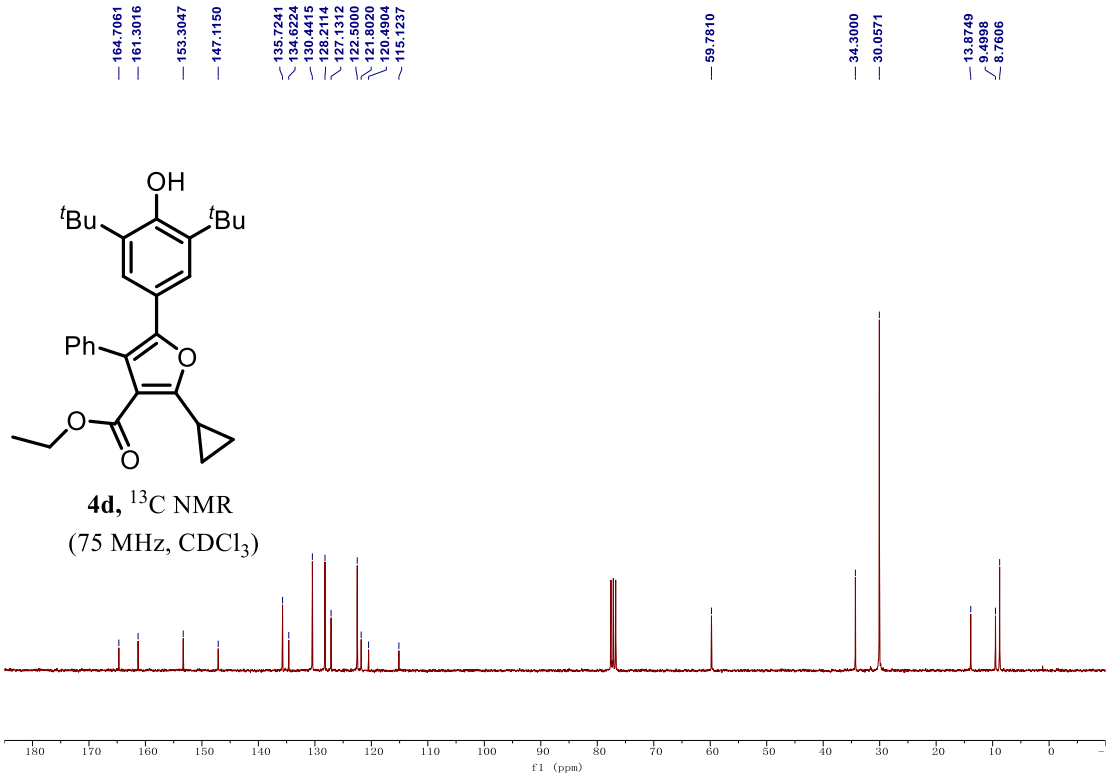
4c, ^{1}H NMR
(300 MHz, $CDCl_3$)



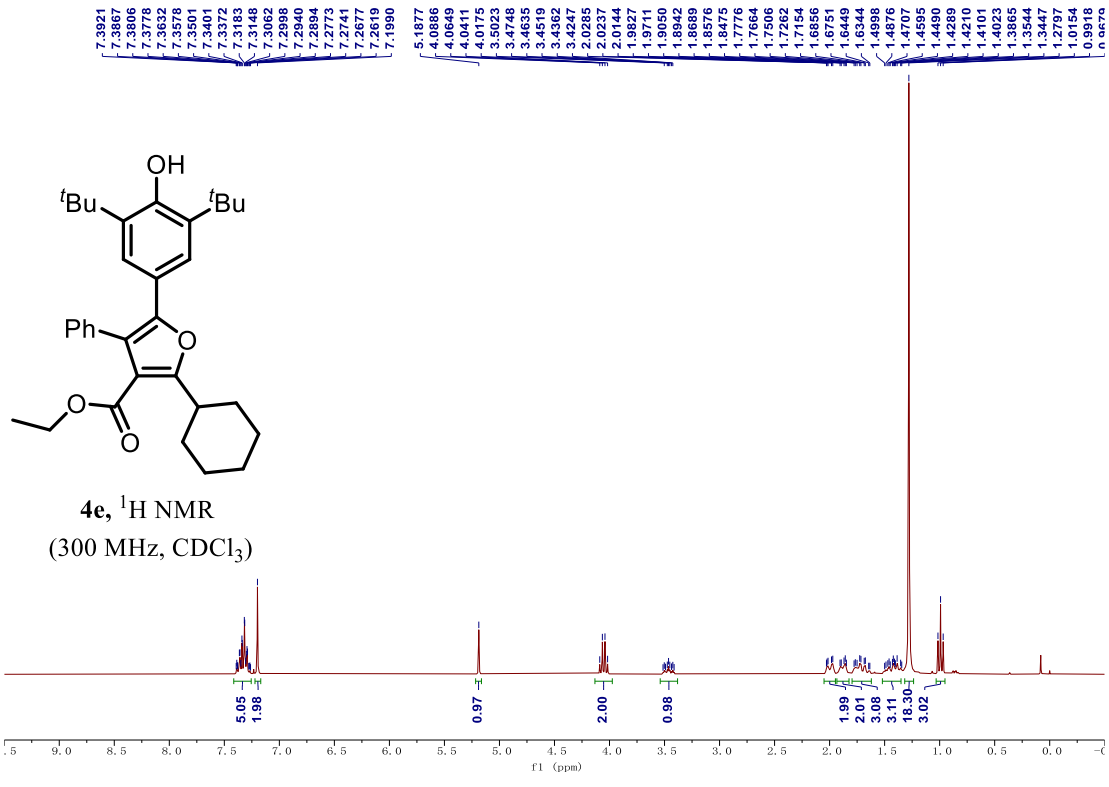
4c, ^{13}C NMR
(75 MHz, $CDCl_3$)



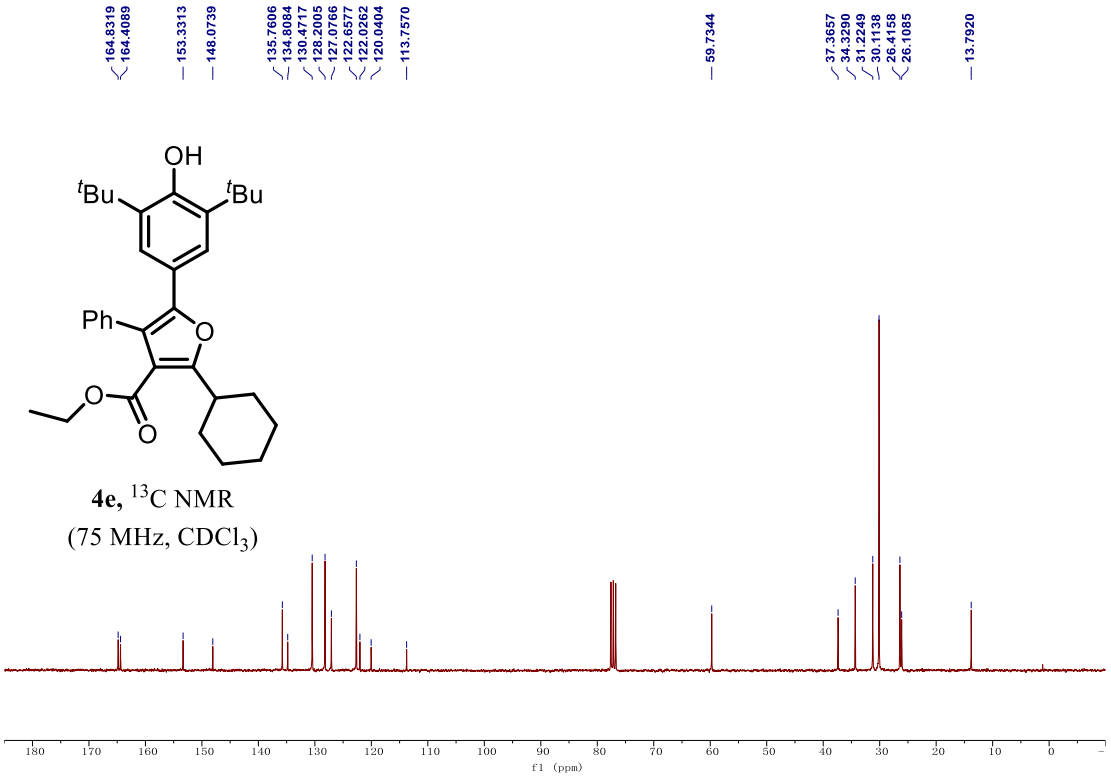
4d, ^{1}H NMR
(300 MHz, $CDCl_3$)



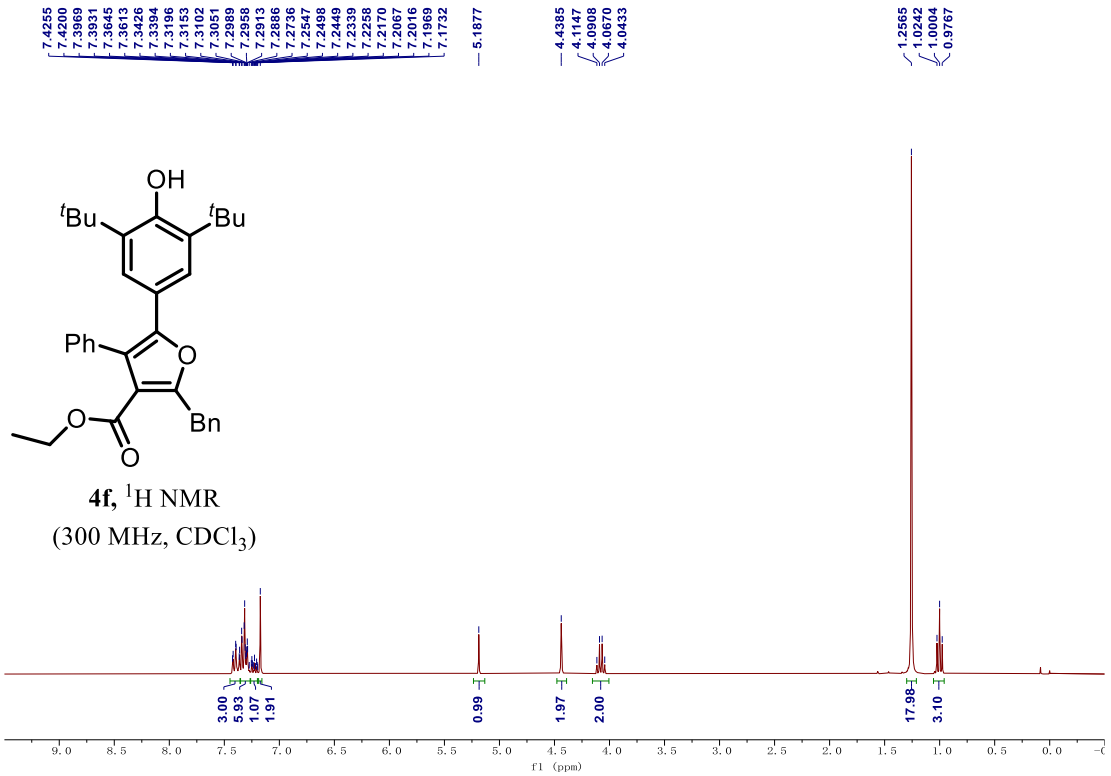
4d, ^{13}C NMR
(75 MHz, $CDCl_3$)



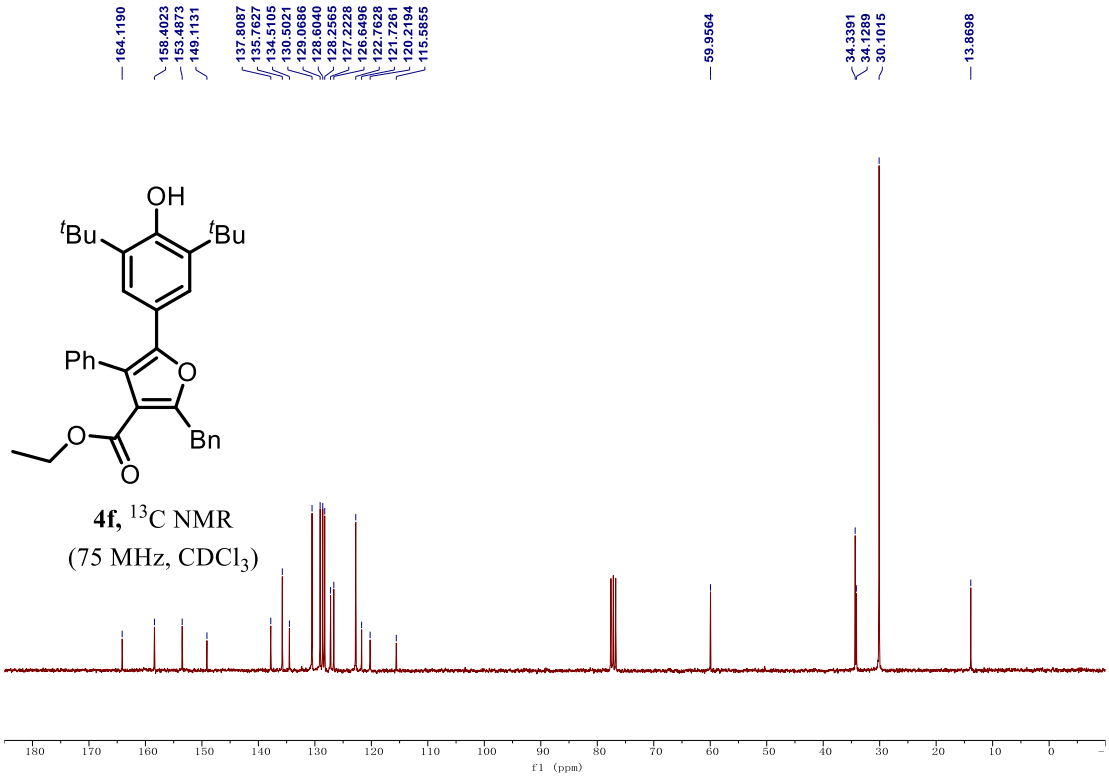
4e, ^{1}H NMR
(300 MHz, $CDCl_3$)



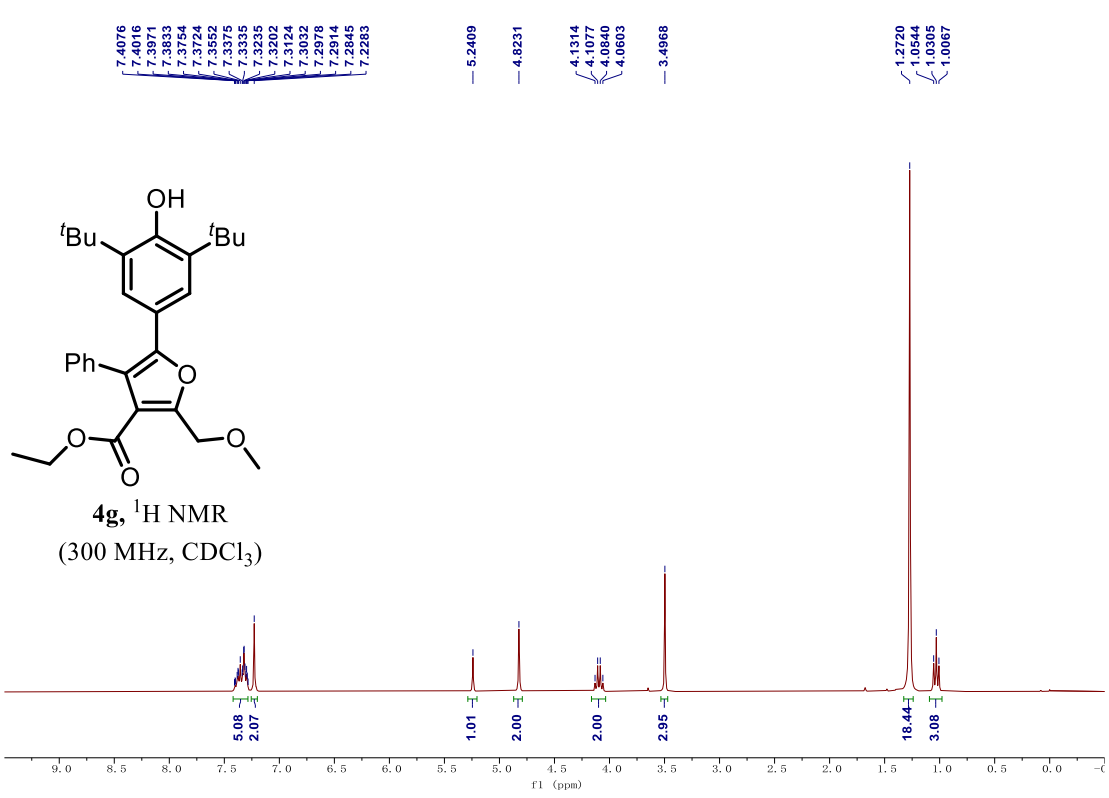
4e, ^{13}C NMR
(75 MHz, $CDCl_3$)



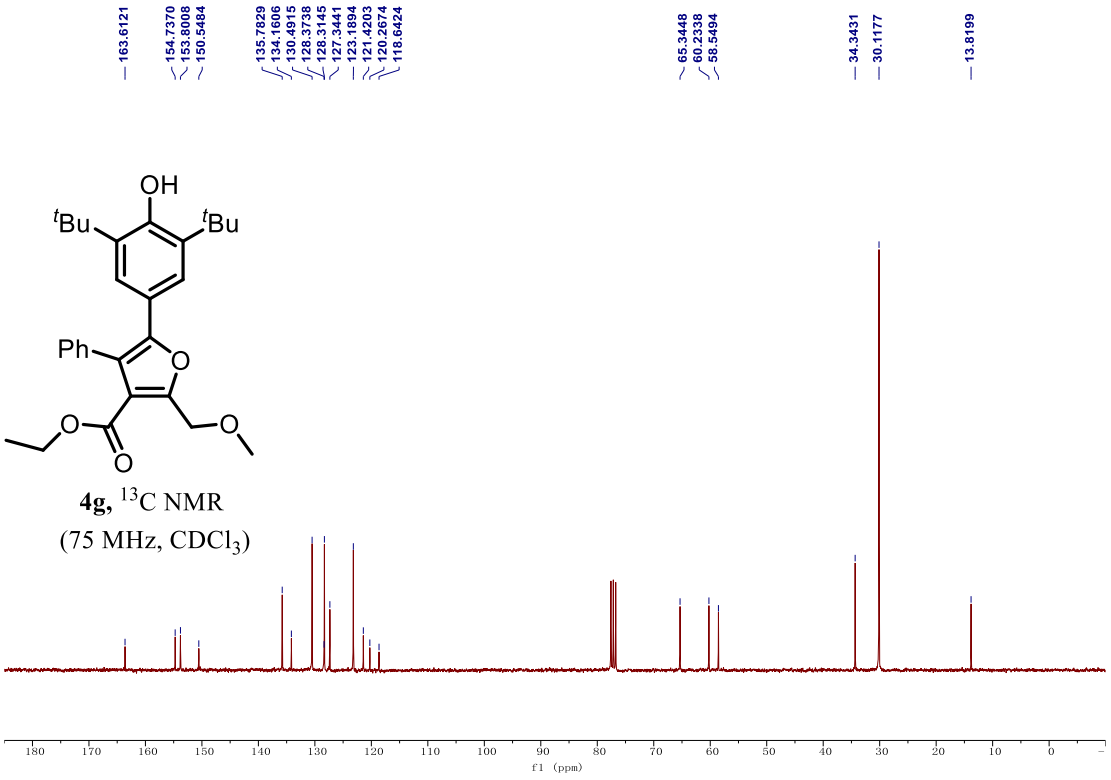
4f, ^{1}H NMR
(300 MHz, $CDCl_3$)



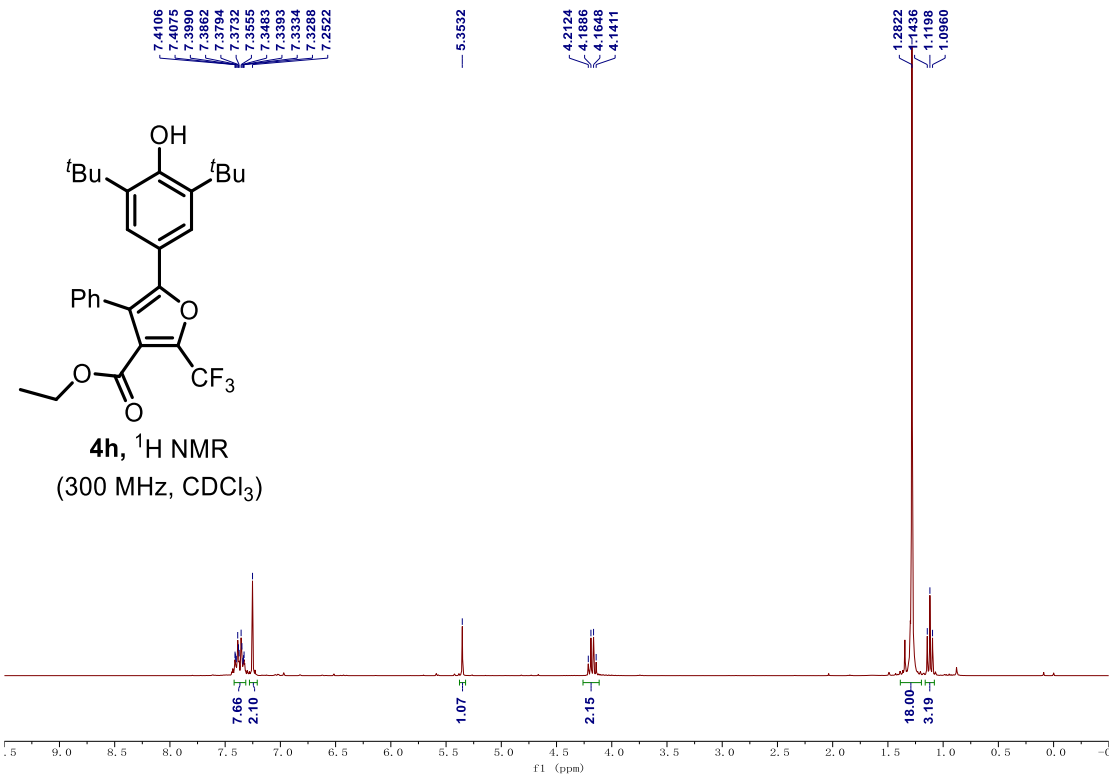
4f, ^{13}C NMR
(75 MHz, $CDCl_3$)



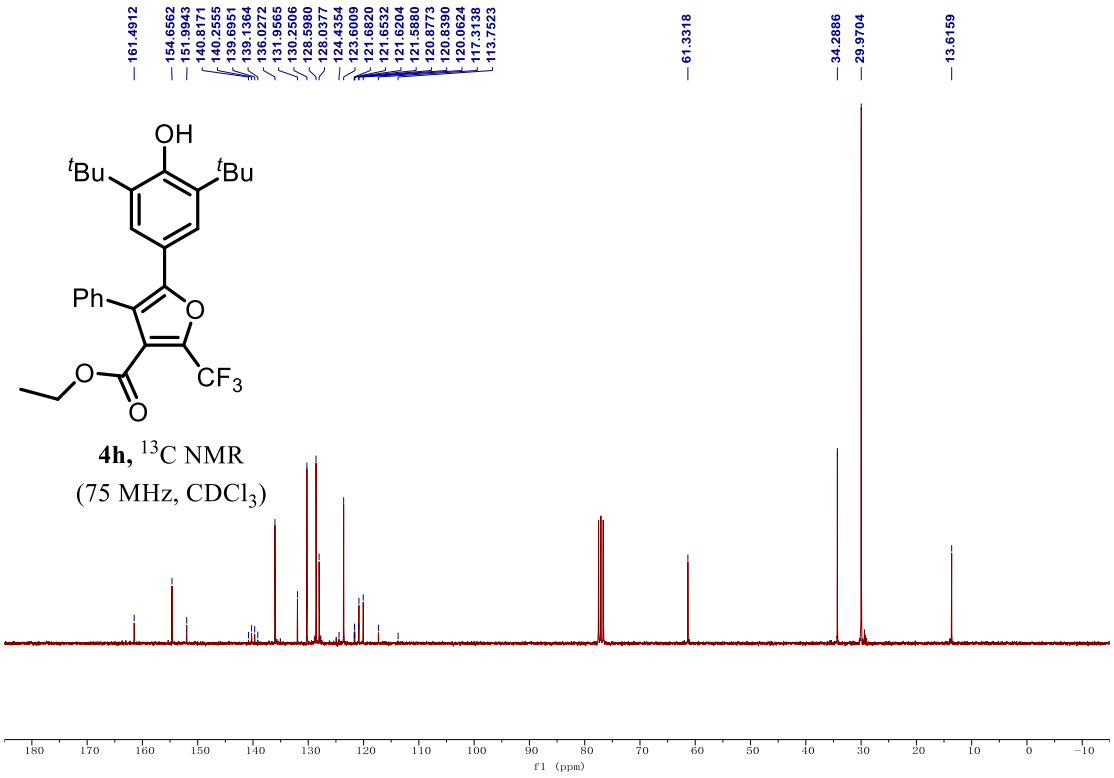
4g, ^{1}H NMR
(300 MHz, $CDCl_3$)



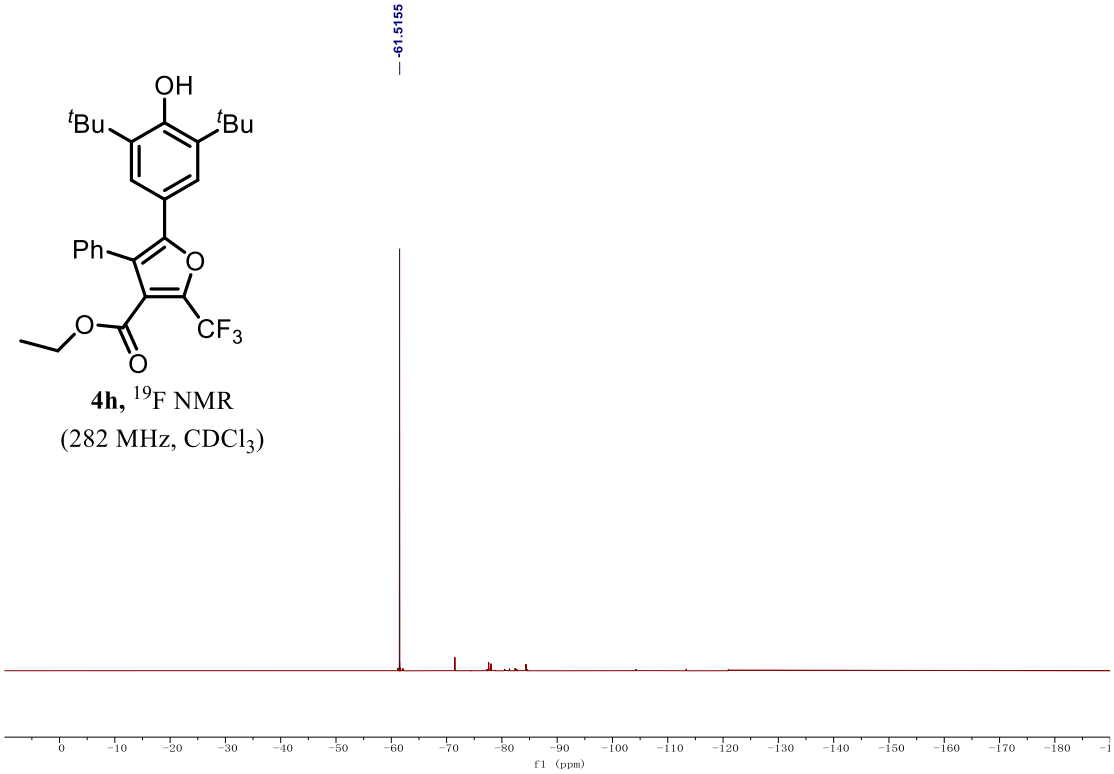
4g, ^{13}C NMR
(75 MHz, $CDCl_3$)



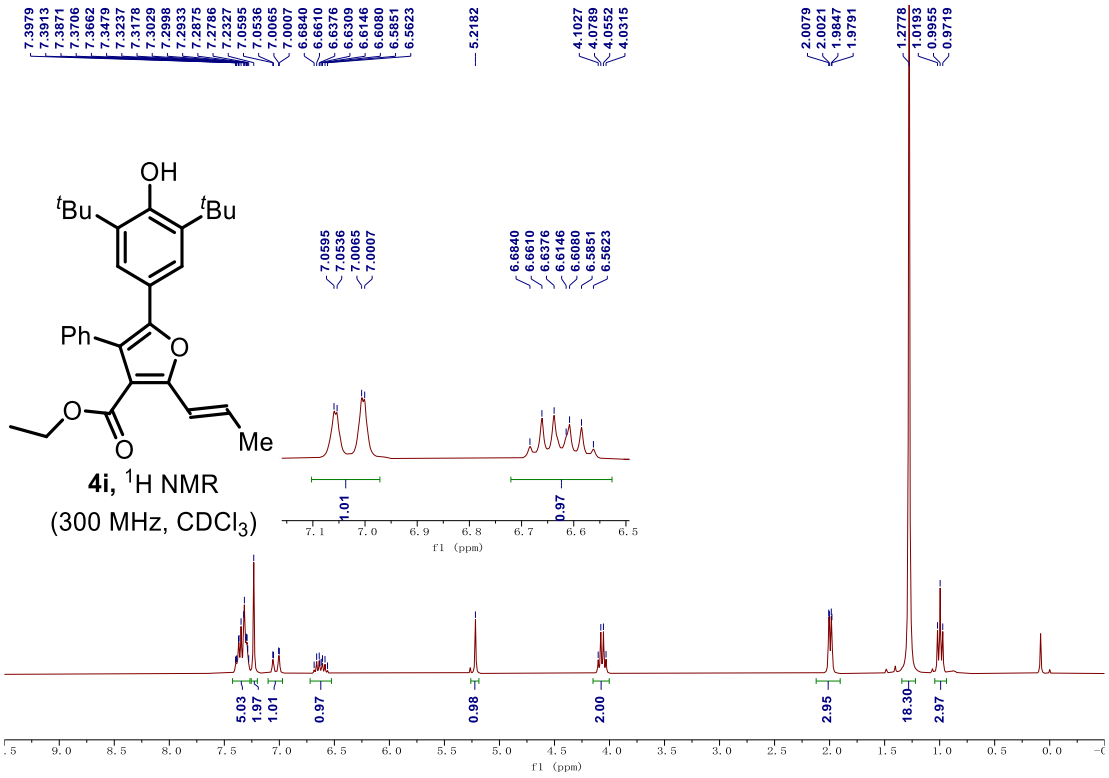
4h, ^{1}H NMR
(300 MHz, $CDCl_3$)

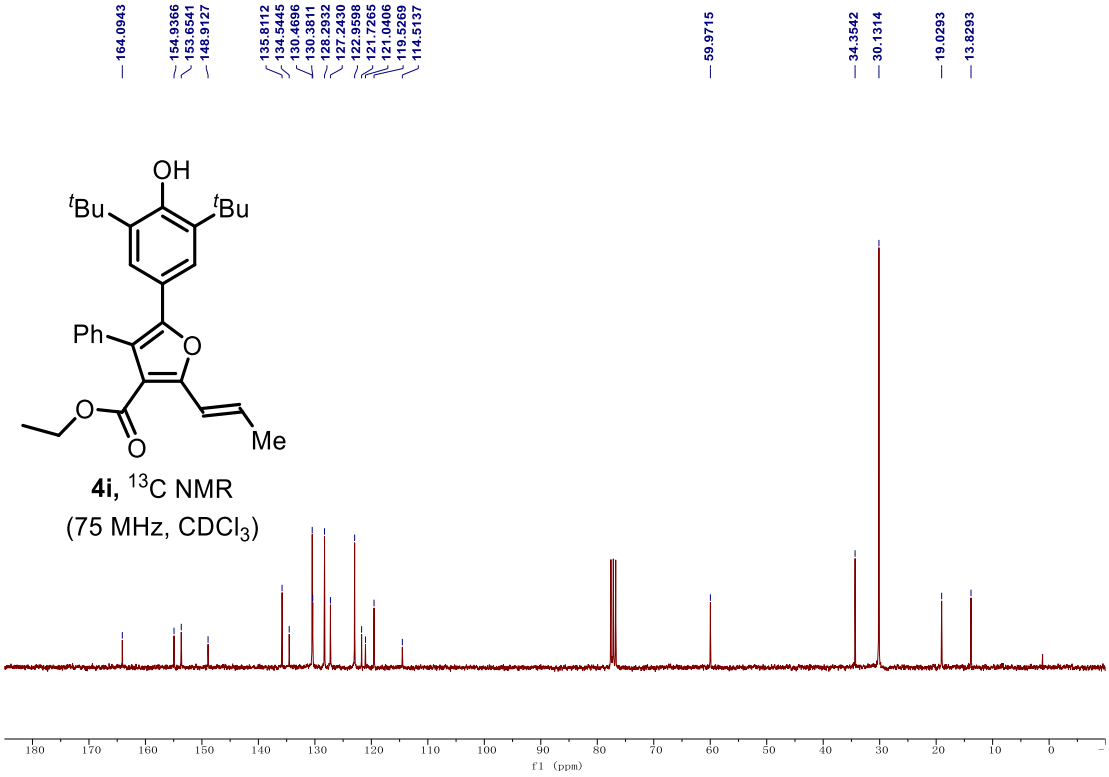


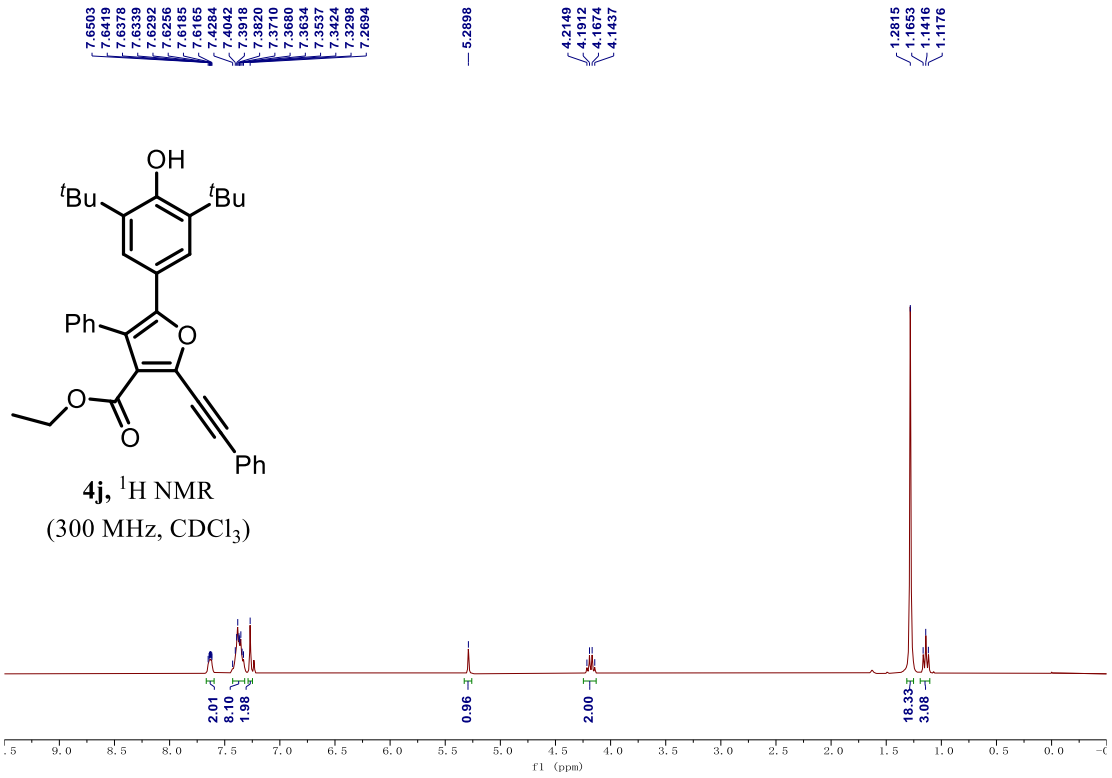
4h, ^{13}C NMR
(75 MHz, $CDCl_3$)



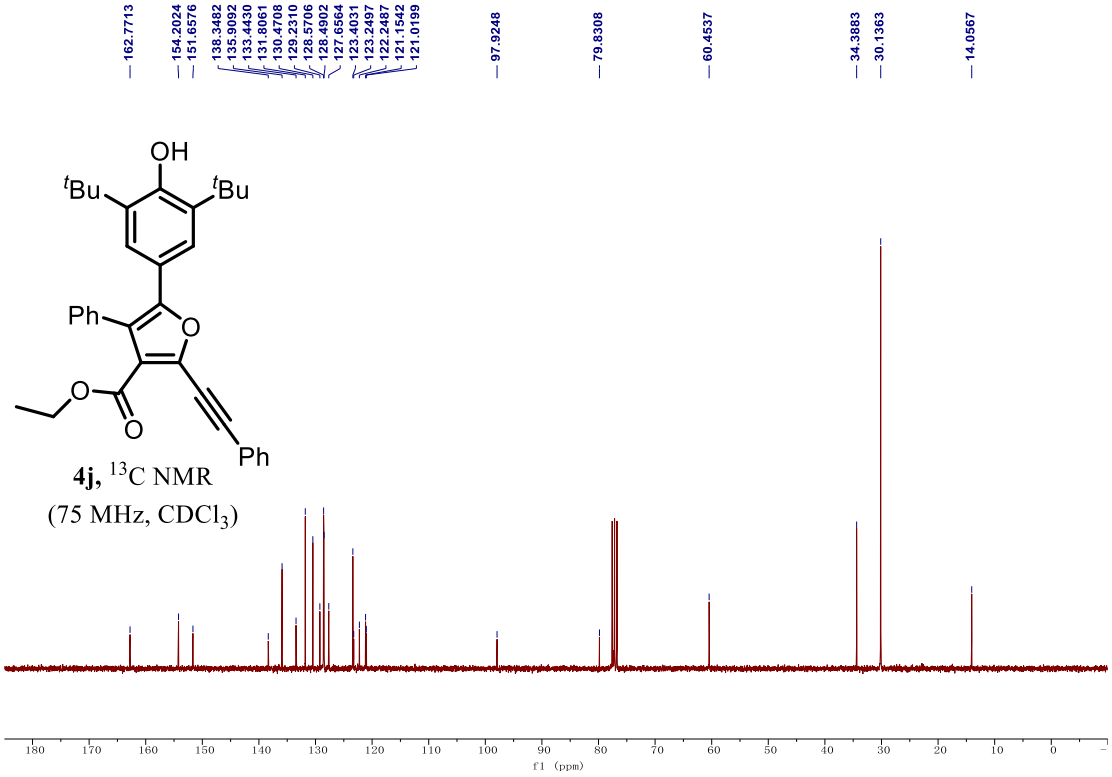
4h, ^{19}F NMR
(282 MHz, $CDCl_3$)


OH
tBu
tBu
Ph
O
O
O
Me
4i, 1H NMR
(300 MHz, CDCl3)
f1 (ppm)

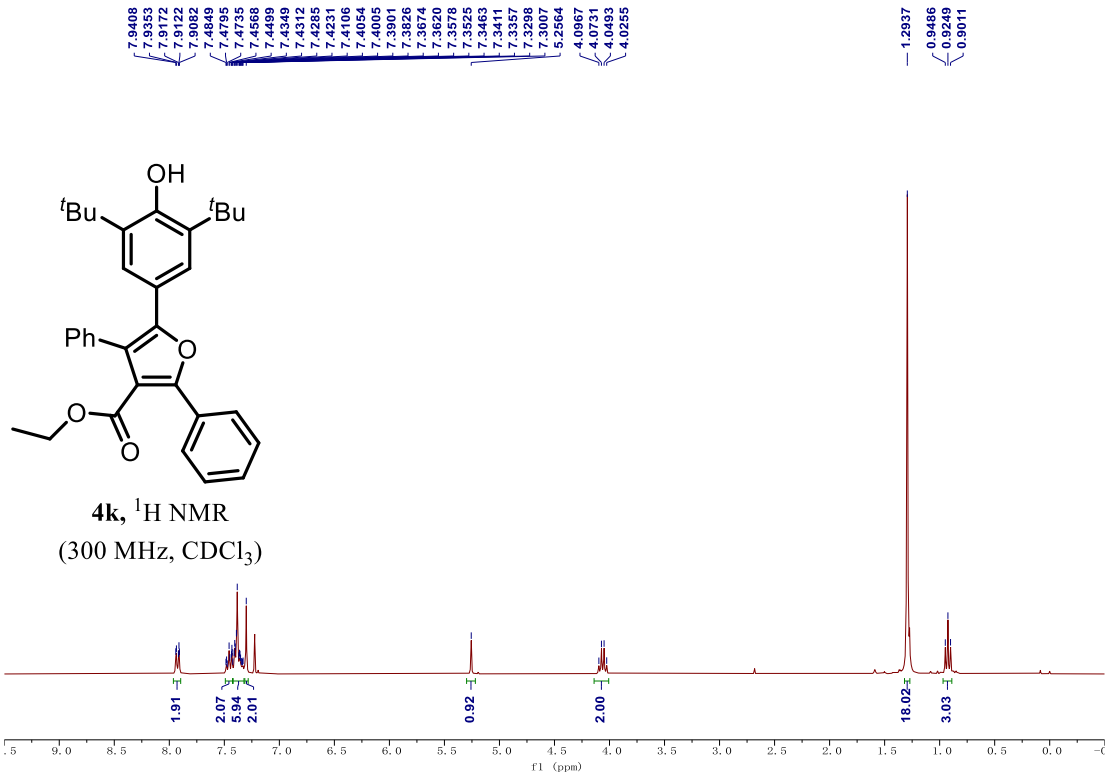

OH
tBu
tBu
Ph
O
O
O
Me
4i, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



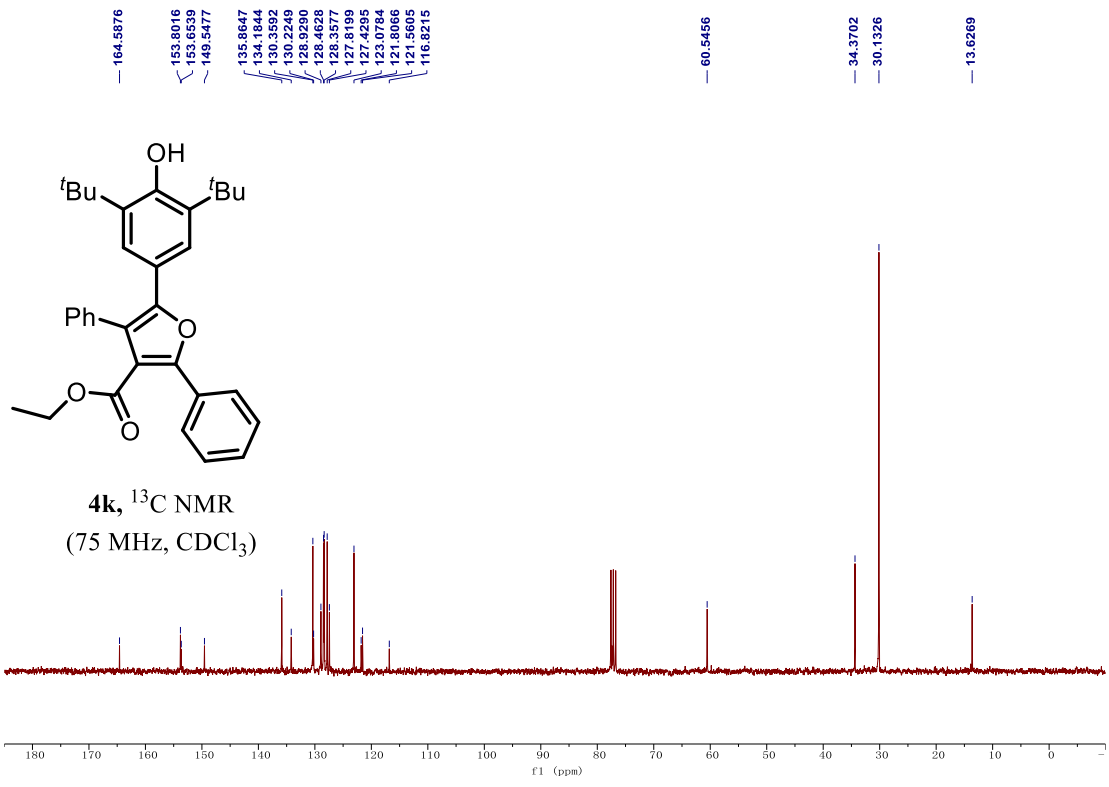
4j, ^{1}H NMR
(300 MHz, $CDCl_3$)



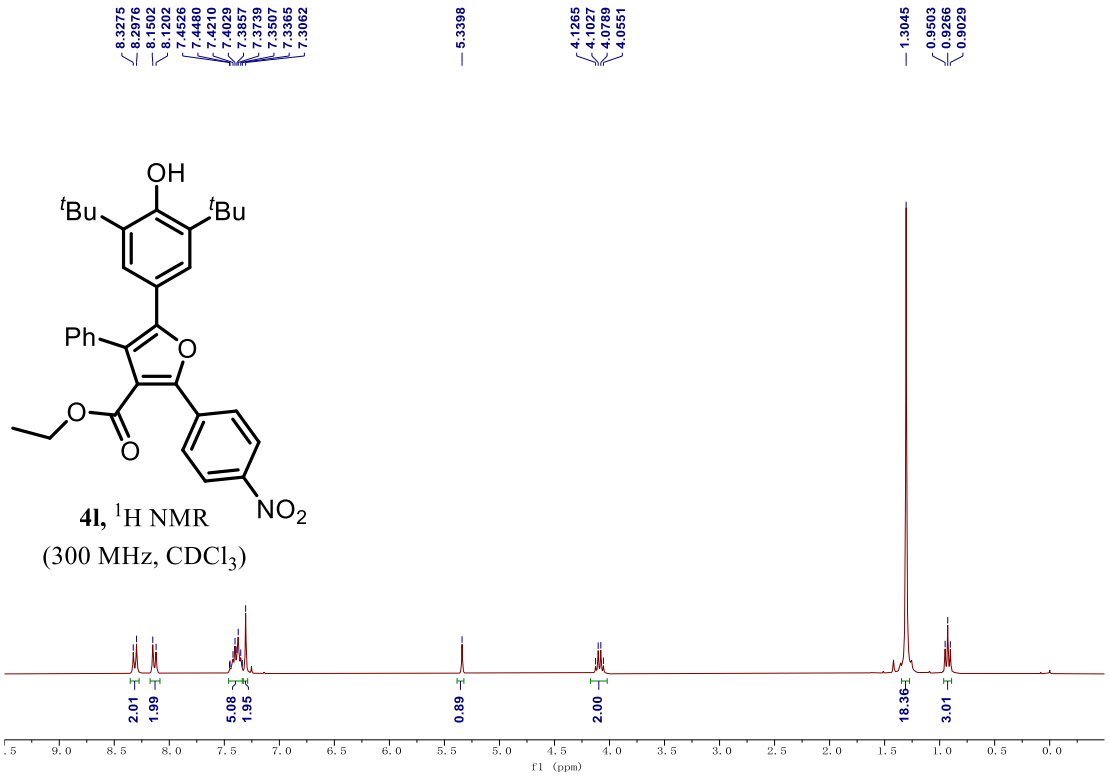
4j, ^{13}C NMR
(75 MHz, $CDCl_3$)



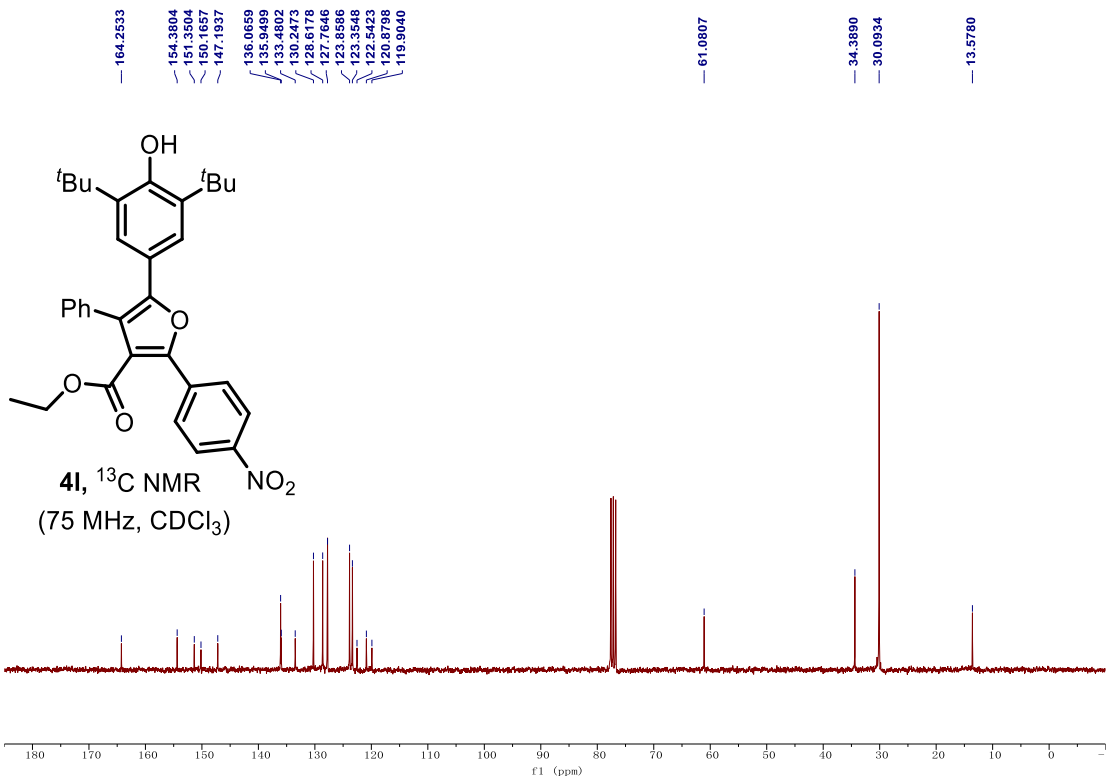
4k, ^{1}H NMR
(300 MHz, $CDCl_3$)



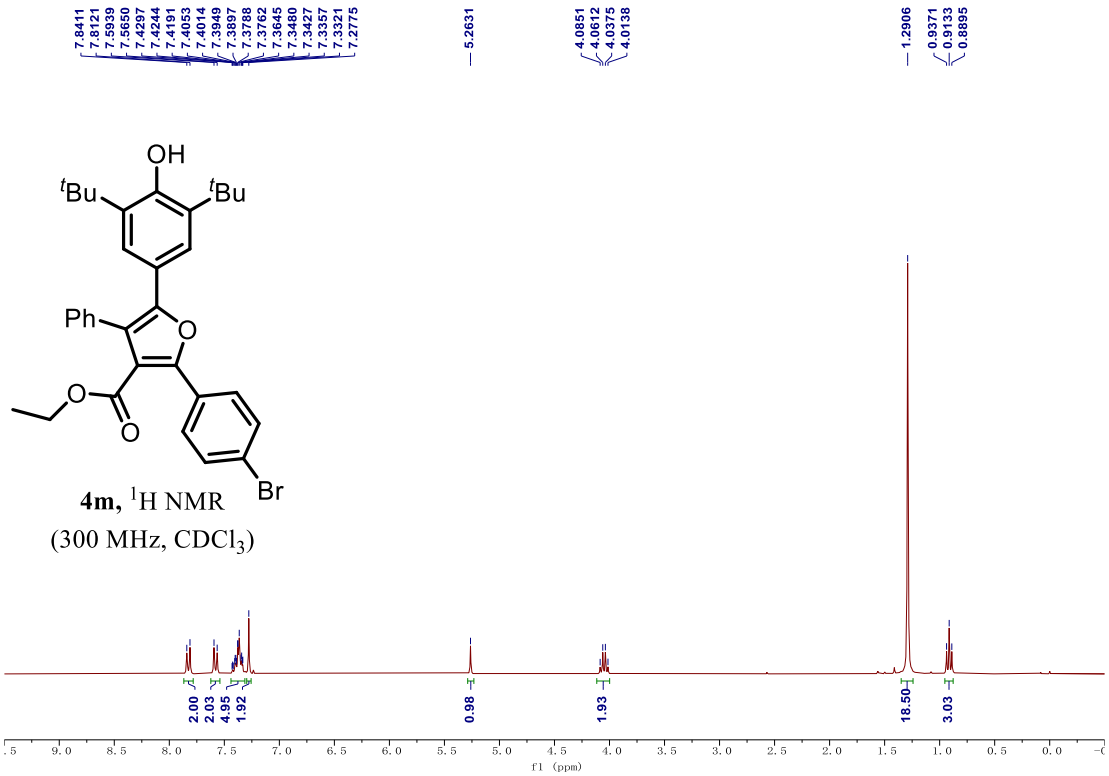
4k, ^{13}C NMR
(75 MHz, $CDCl_3$)



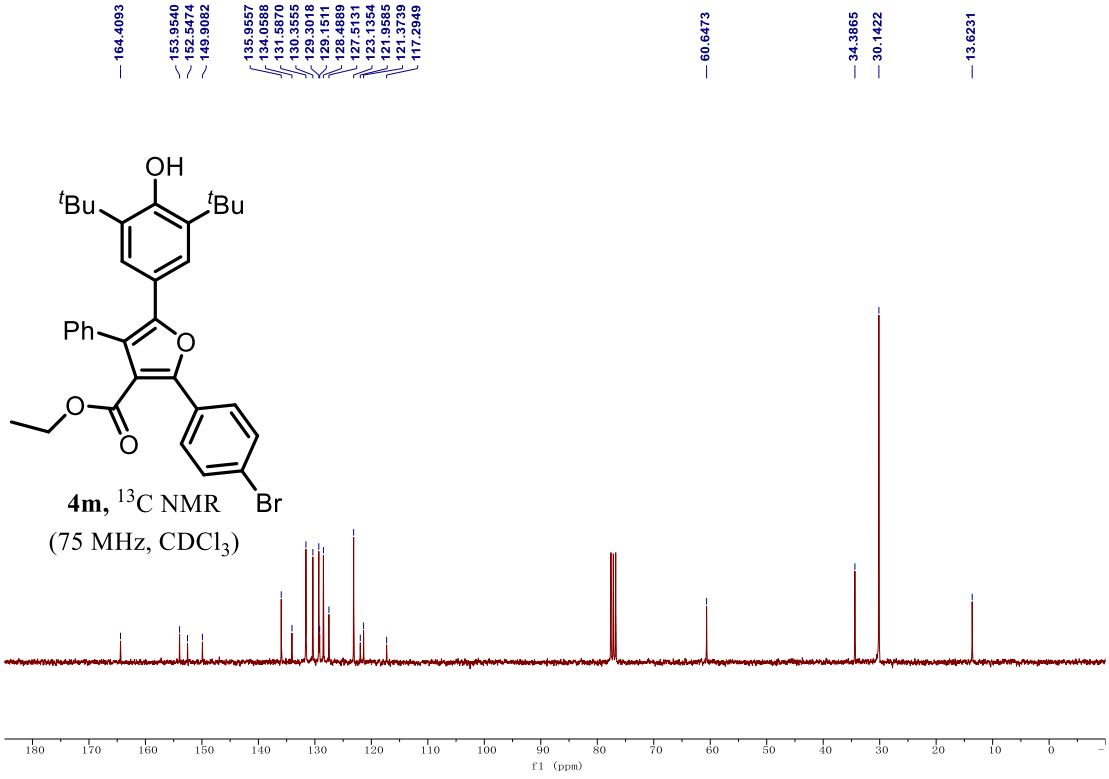
4l, ^{1}H NMR
(300 MHz, $CDCl_3$)



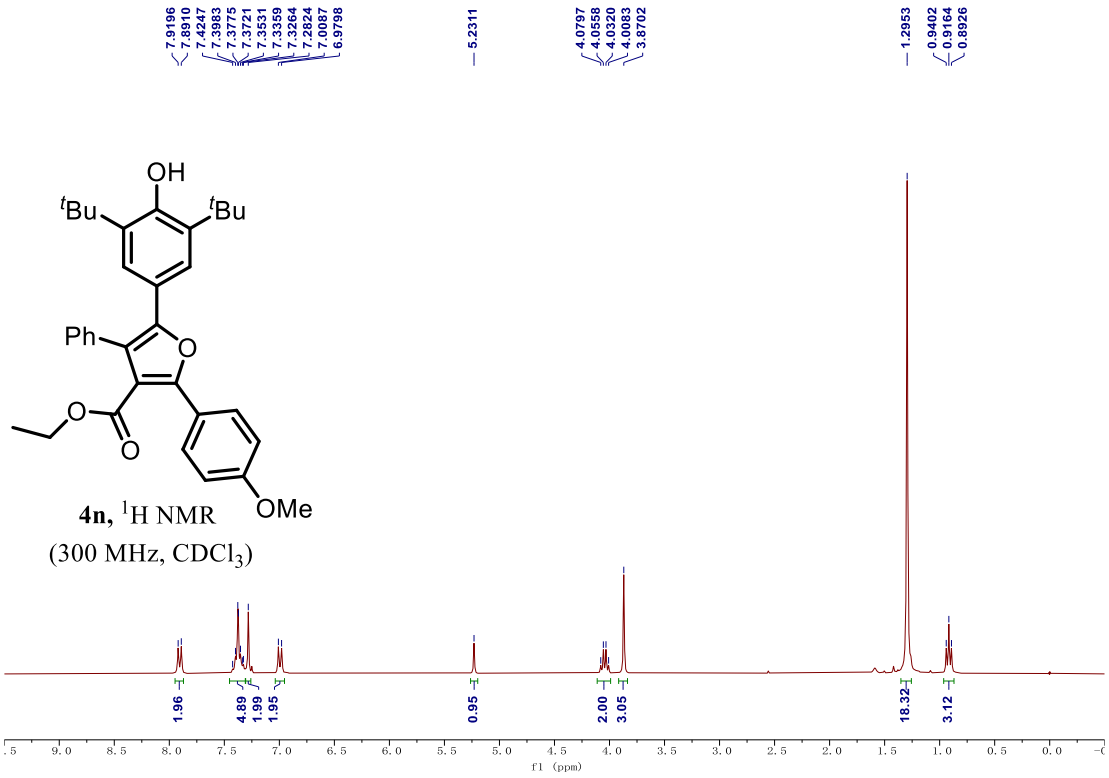
4l, ^{13}C NMR
(75 MHz, $CDCl_3$)

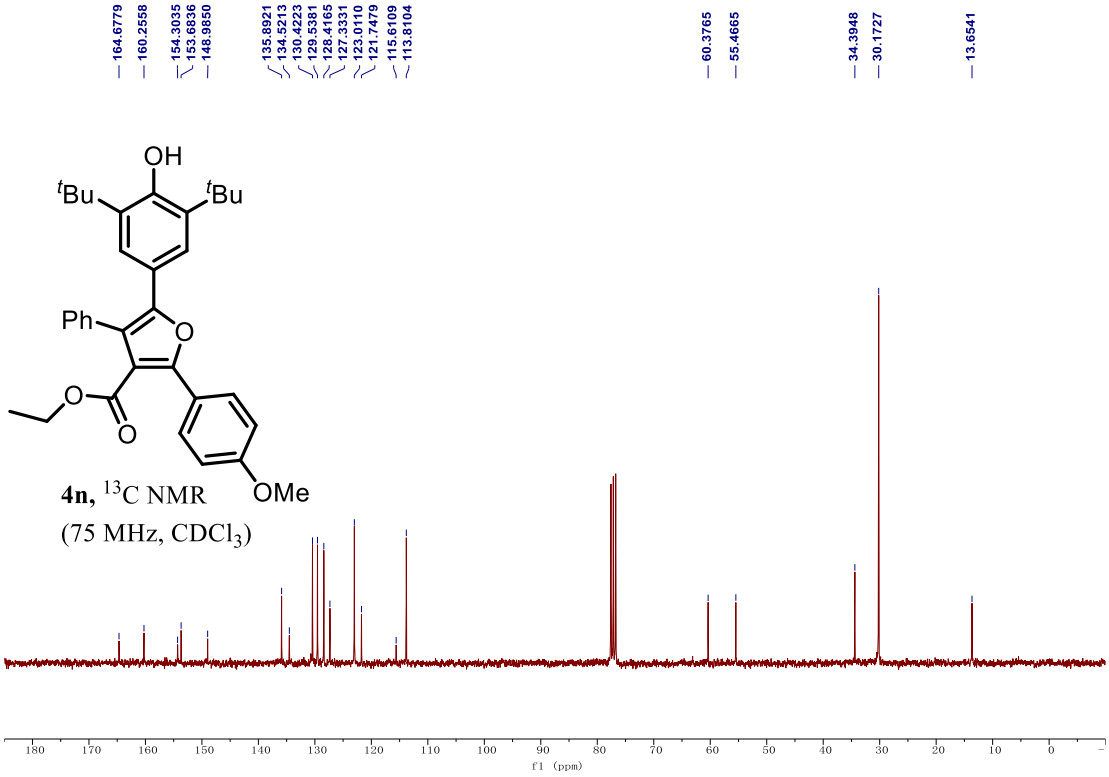


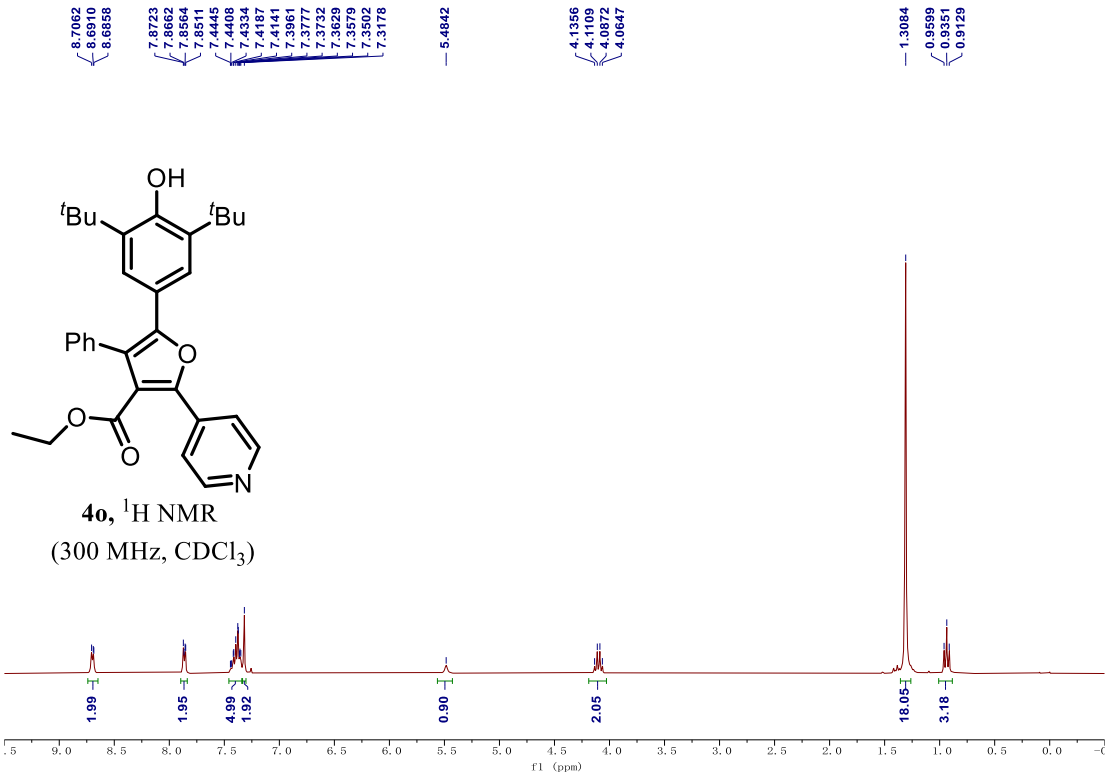
4m, ^{1}H NMR
(300 MHz, $CDCl_3$)



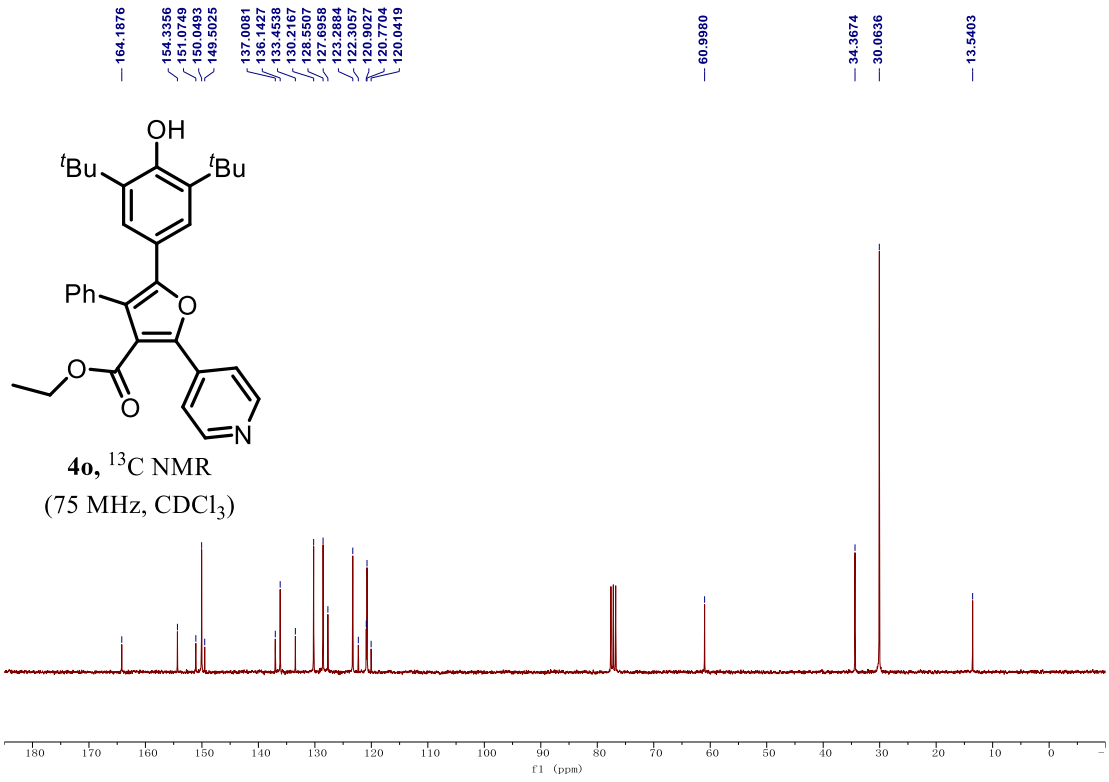
4m, ^{13}C NMR
(75 MHz, $CDCl_3$)


7.9196
7.8910
7.4247
7.3983
7.3775
7.3721
7.3531
7.3359
7.3264
7.2824
7.0087
6.9798
5.2311
4.0797
4.0558
4.0320
4.0083
3.8702
1.2953
0.9402
0.9164
0.8926
OH
tBu
tBu
Ph
O
O
O
OMe
4n, 1H NMR
(300 MHz, CDCl3)
1.96
4.89
1.99
1.95
0.95
2.00
3.05
18.32
3.12
f1 (ppm)

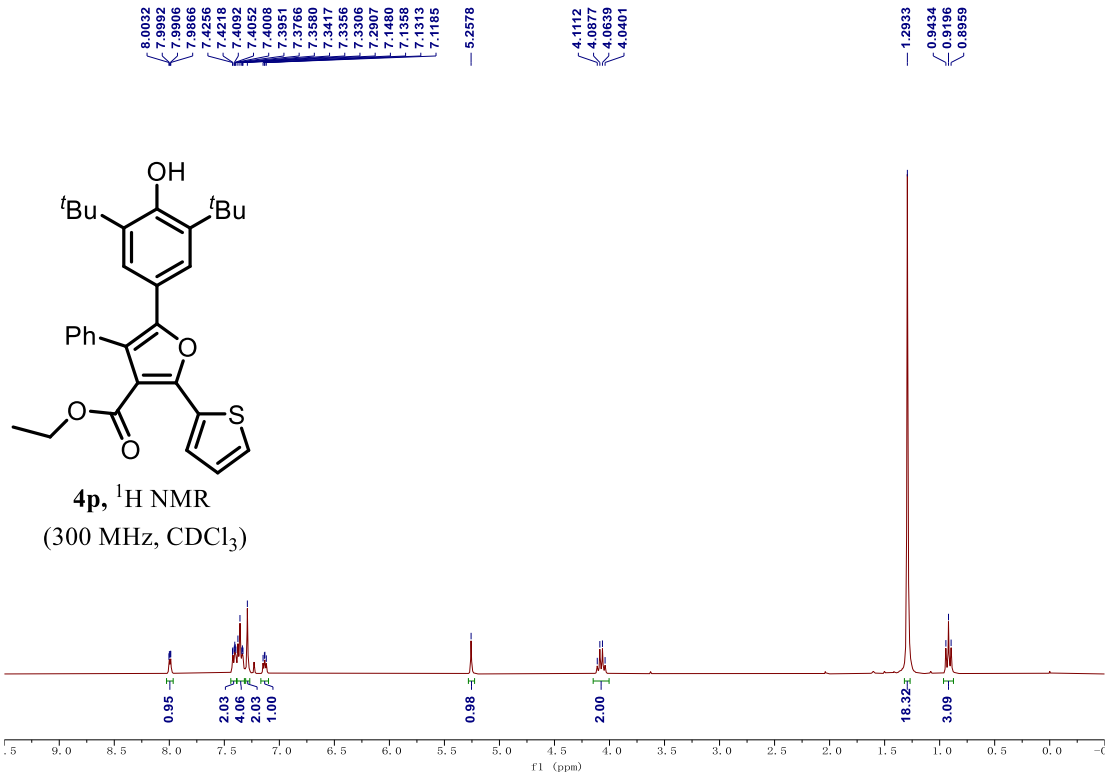

164.6779
160.2558
154.3035
153.6836
148.9850
135.8921
134.5213
130.4223
129.5381
128.4165
127.3331
123.0110
121.7479
115.6109
113.8104
60.3765
55.4665
34.3948
30.1727
13.6541
OH
tBu
tBu
Ph
O
O
O
OMe
4n, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



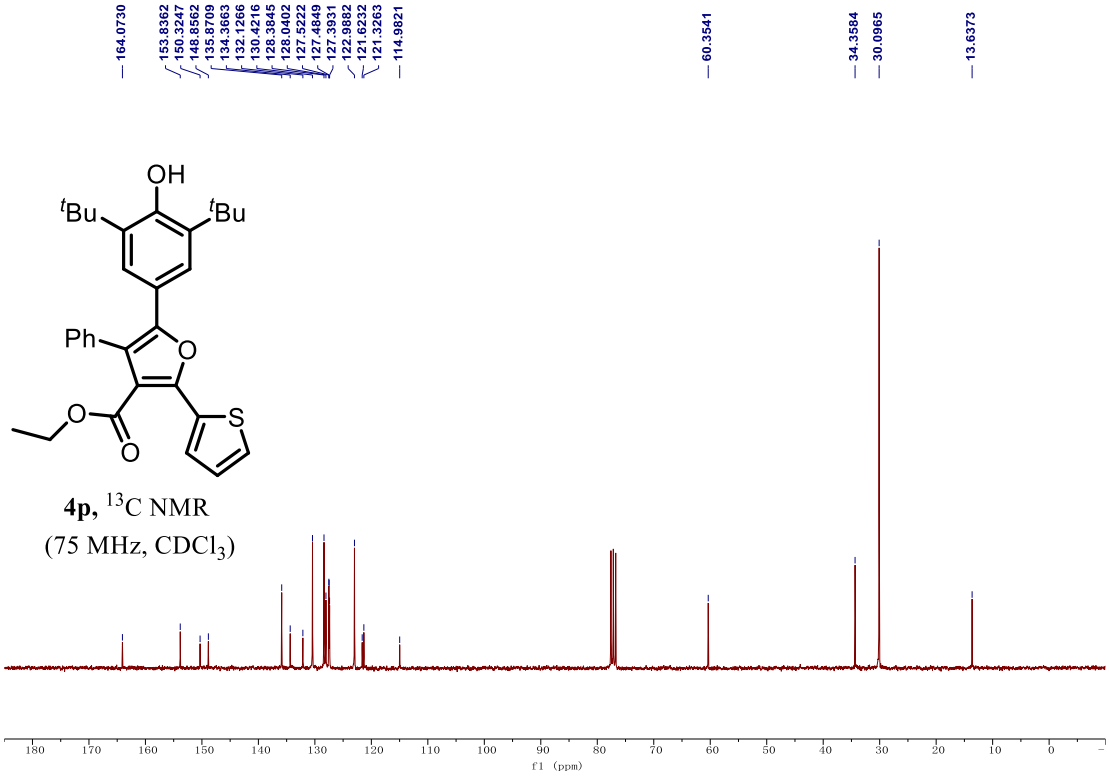
4o, ^{1}H NMR
(300 MHz, $CDCl_3$)



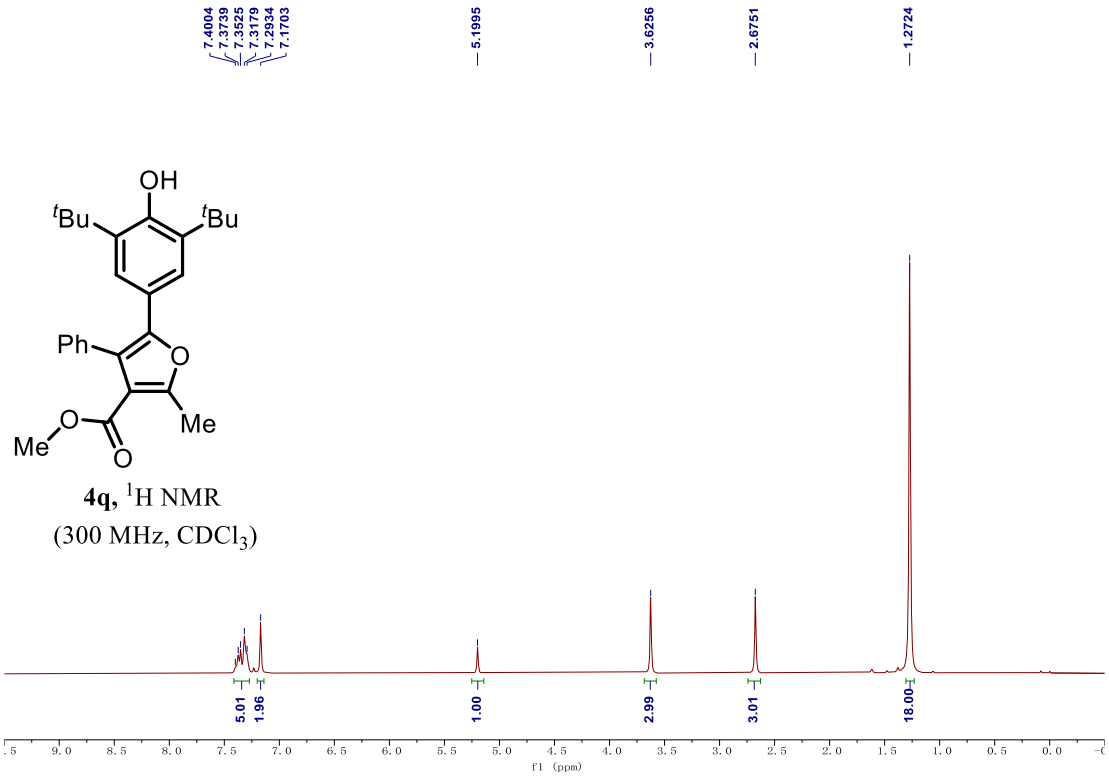
4o, ^{13}C NMR
(75 MHz, $CDCl_3$)



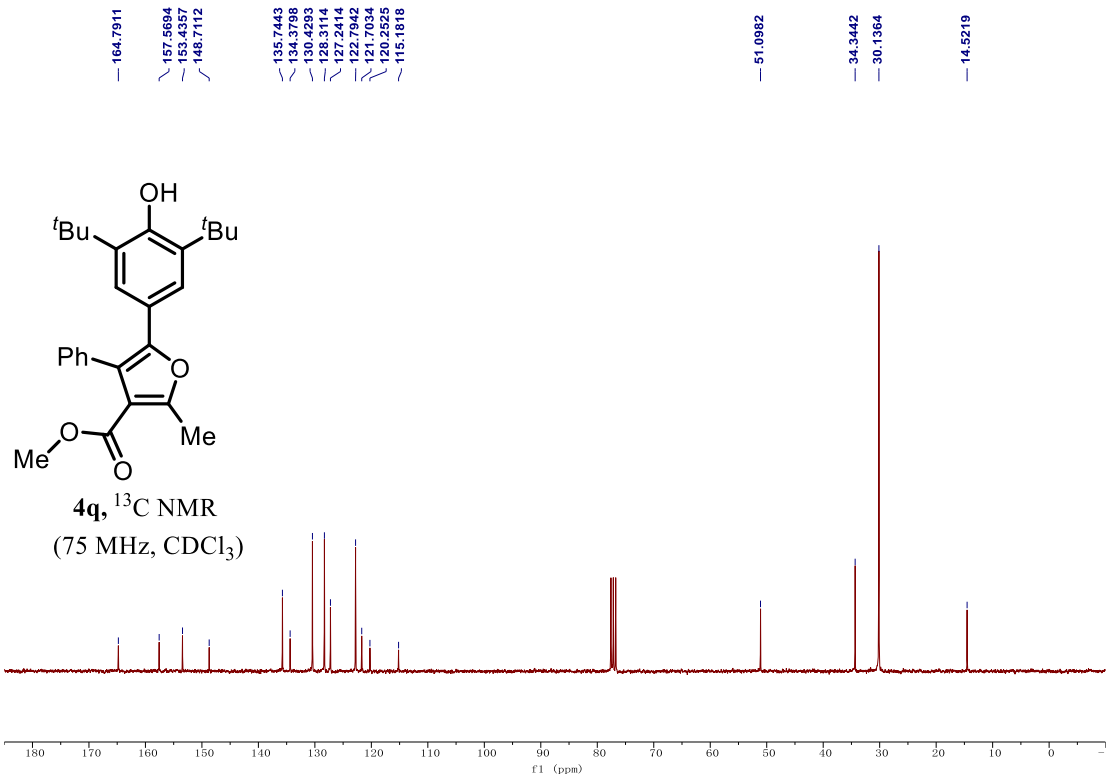
4p, ^{1}H NMR
(300 MHz, $CDCl_3$)



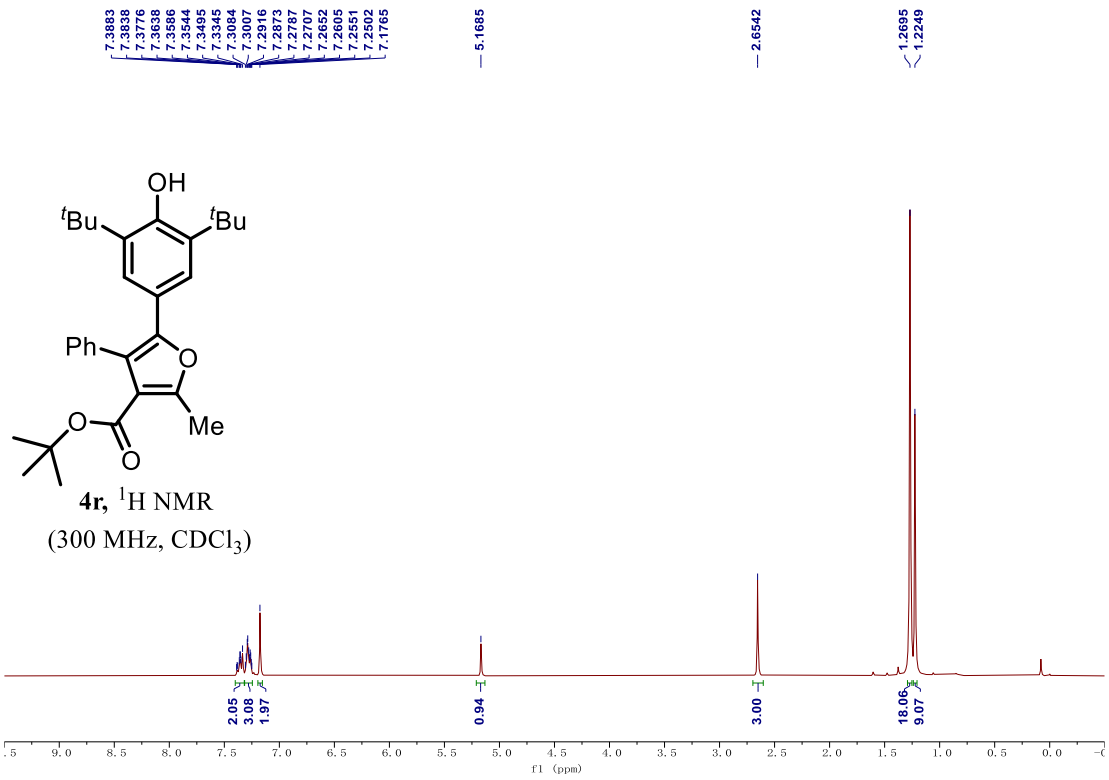
4p, ^{13}C NMR
(75 MHz, $CDCl_3$)



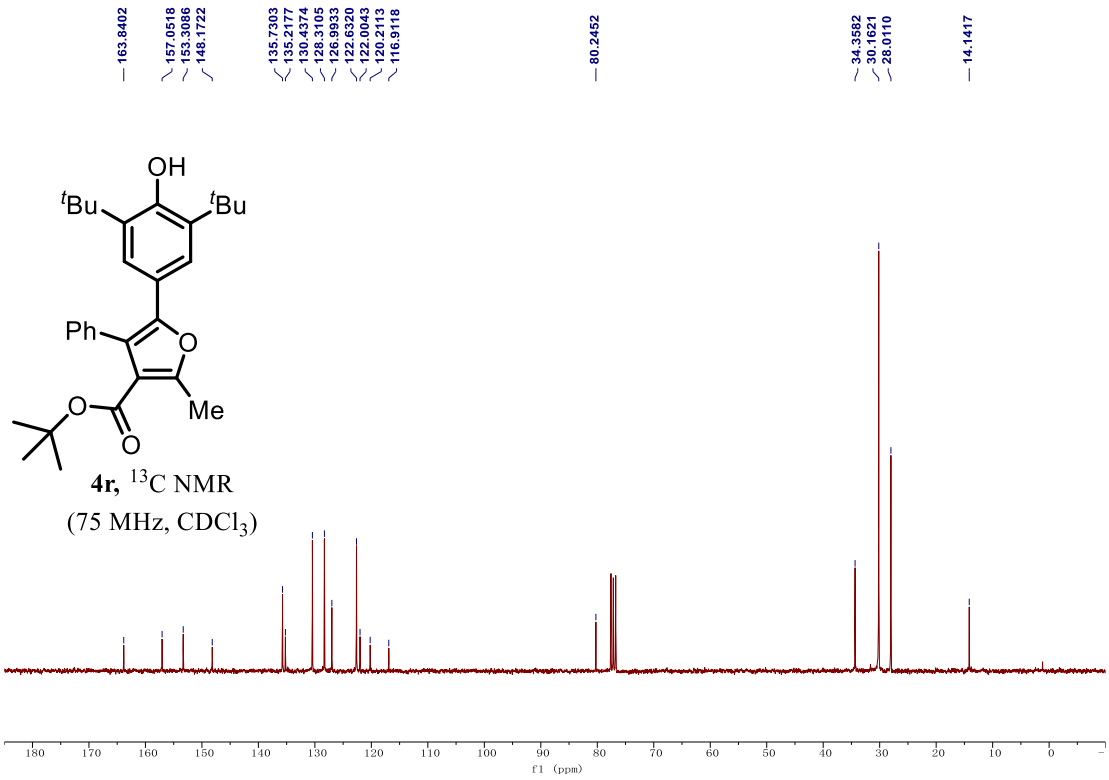
4q, ^{1}H NMR
(300 MHz, $CDCl_3$)



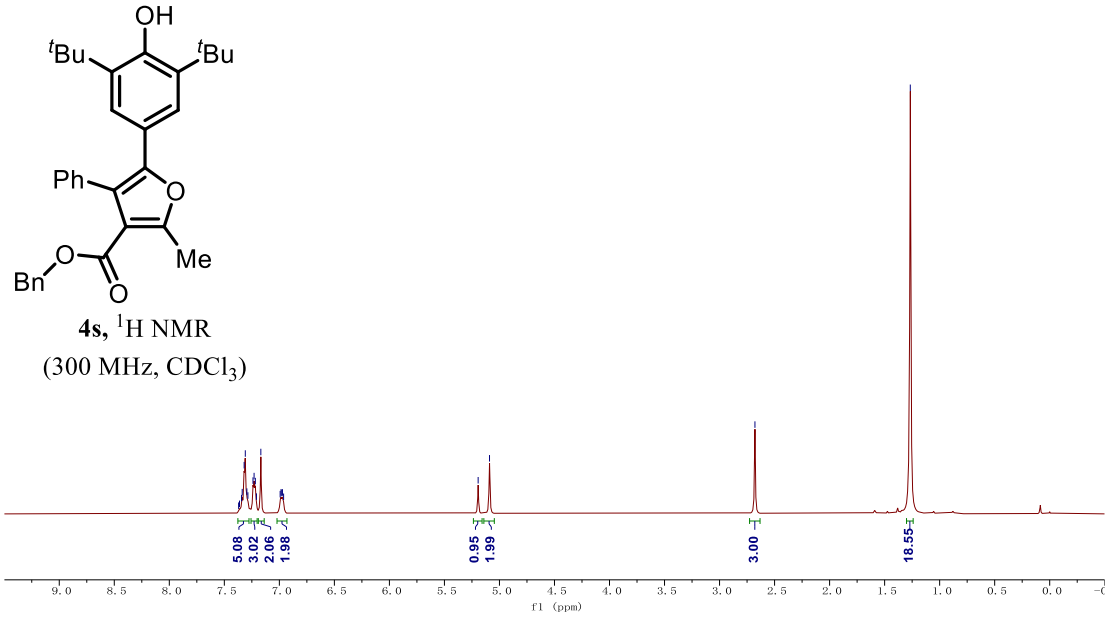
4q, ^{13}C NMR
(75 MHz, $CDCl_3$)



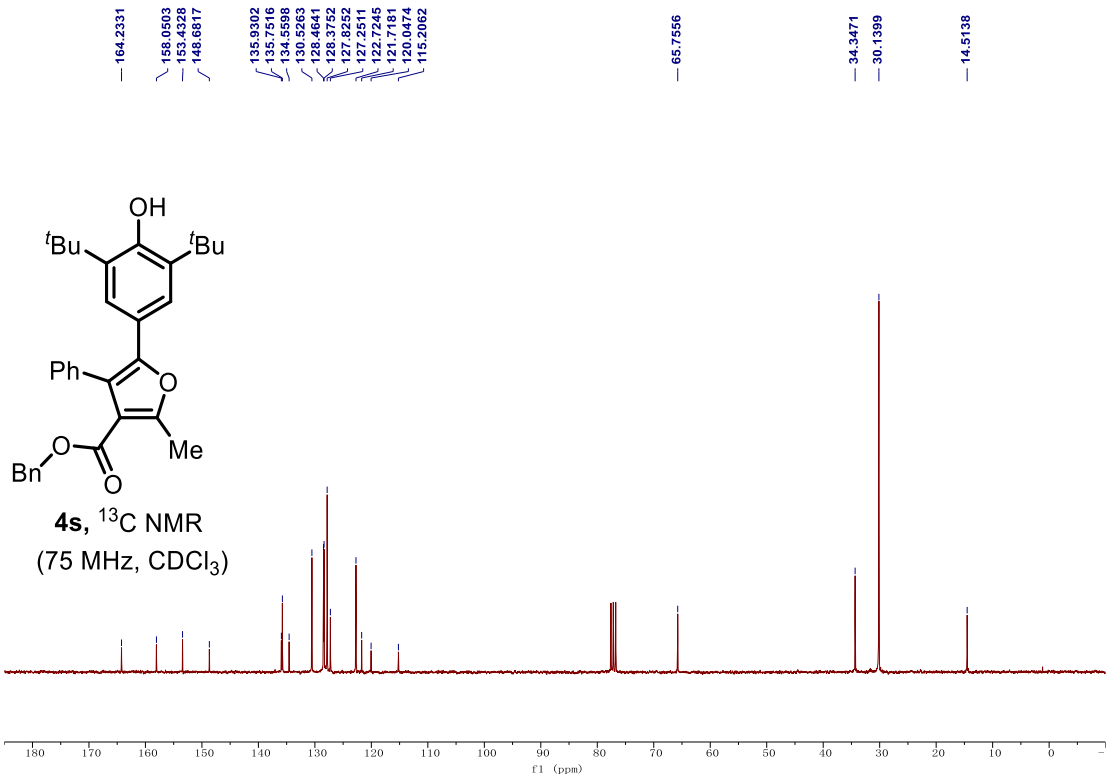
4r, ^{1}H NMR
(300 MHz, $CDCl_3$)



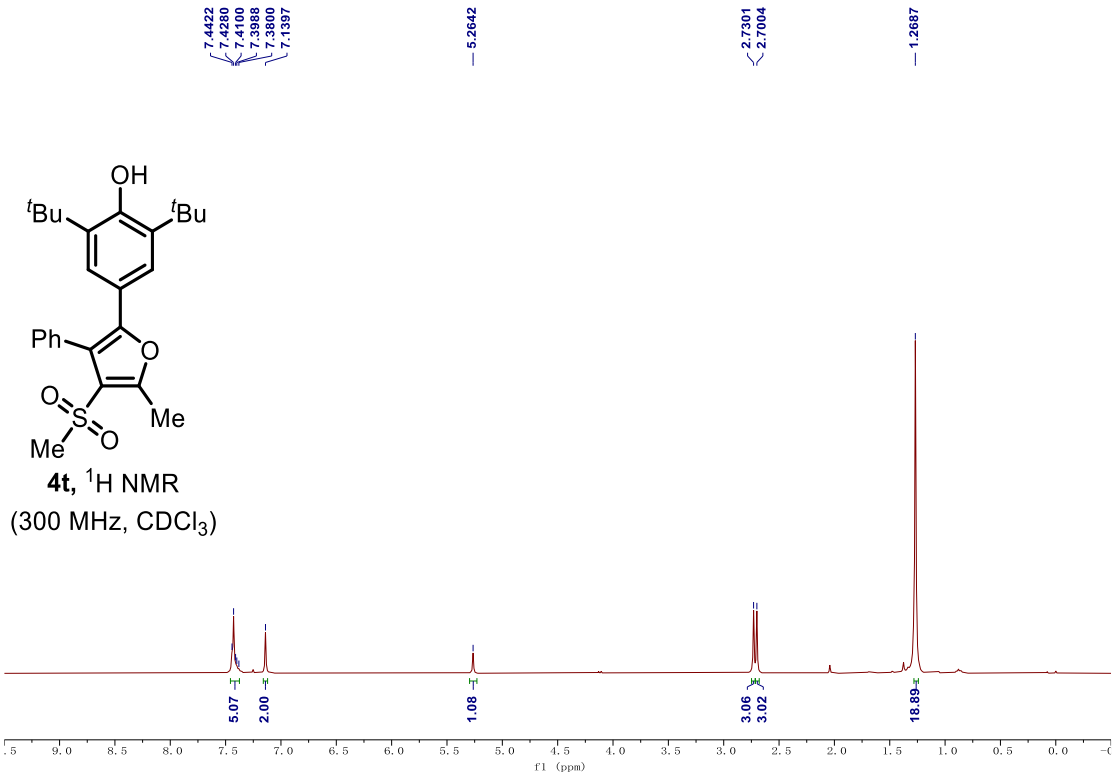
4r, ^{13}C NMR
(75 MHz, $CDCl_3$)



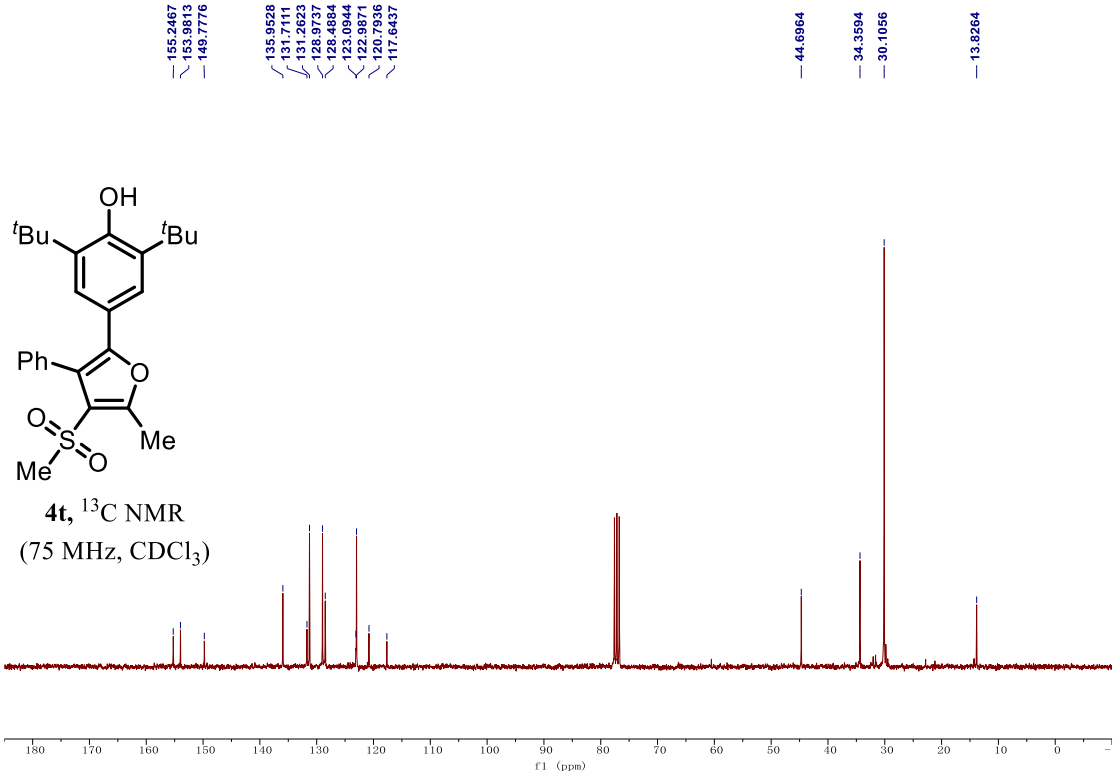
4s, ^{1}H NMR
(300 MHz, $CDCl_3$)



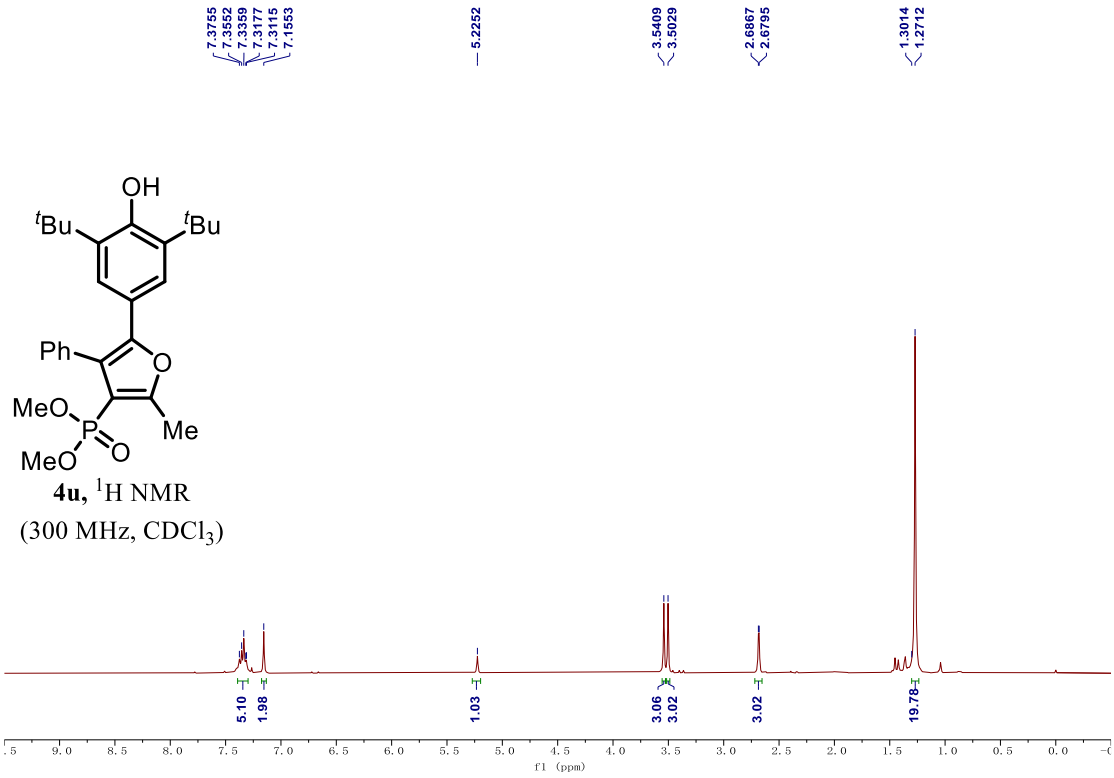
4s, ^{13}C NMR
(75 MHz, $CDCl_3$)



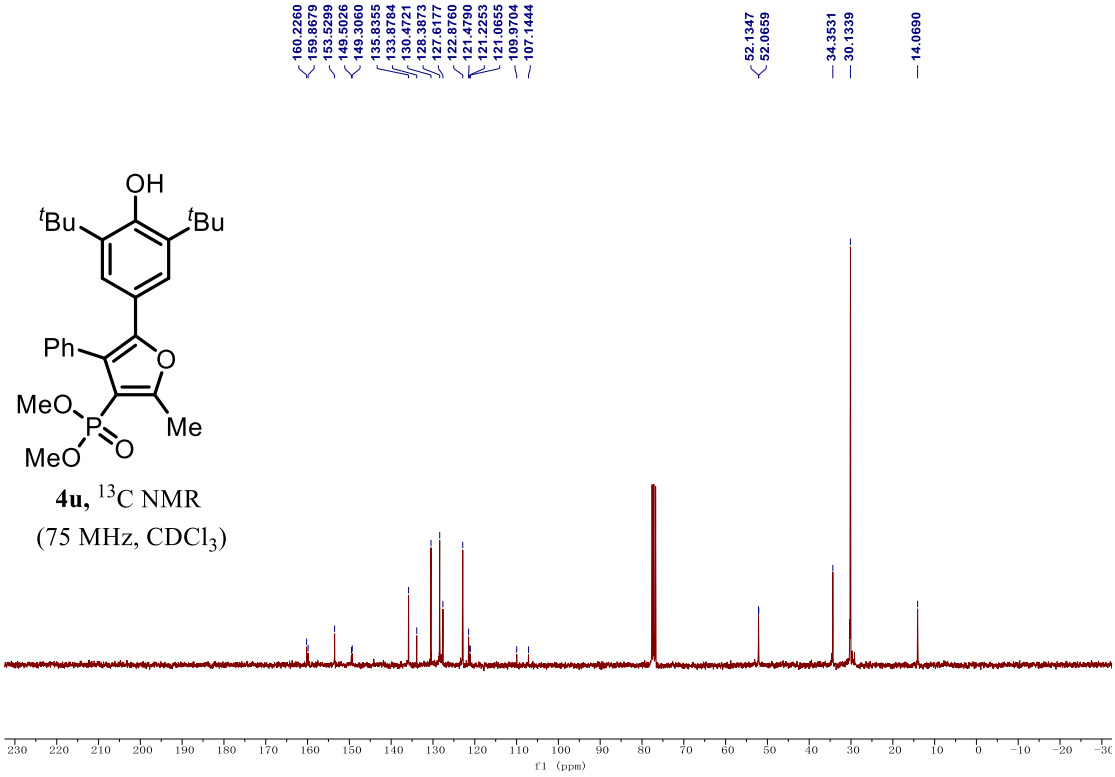
4t, ^{1}H NMR
(300 MHz, $CDCl_3$)



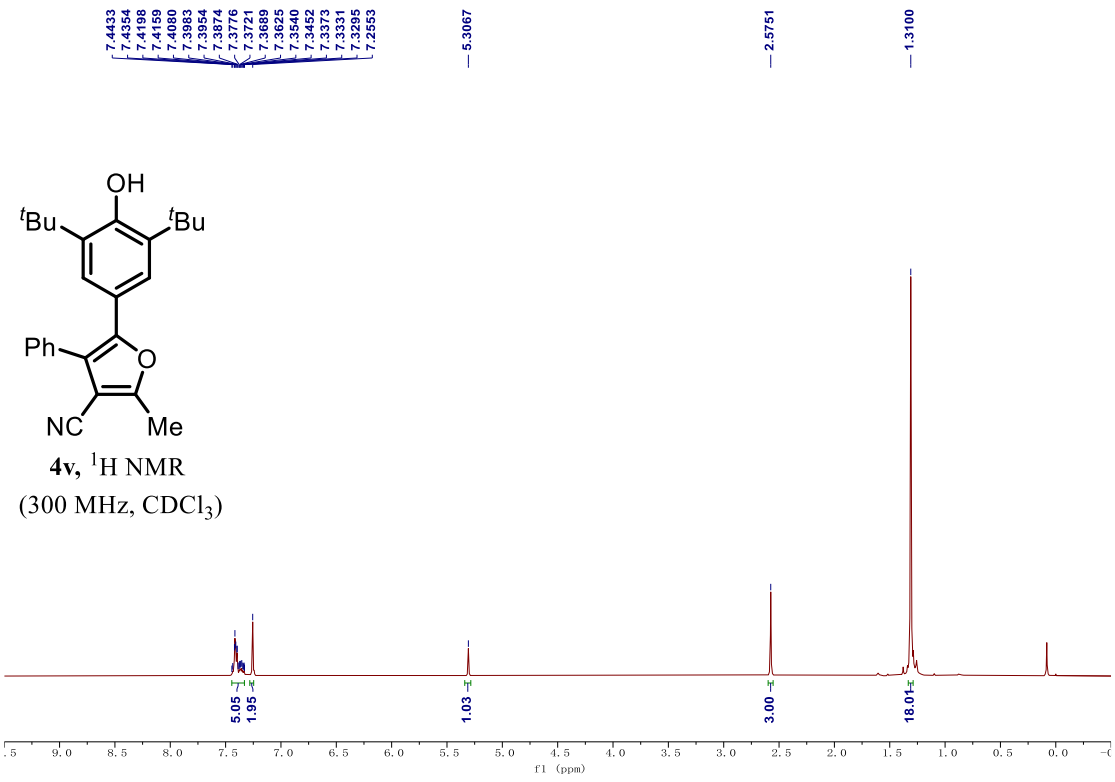
4t, ^{13}C NMR
(75 MHz, $CDCl_3$)



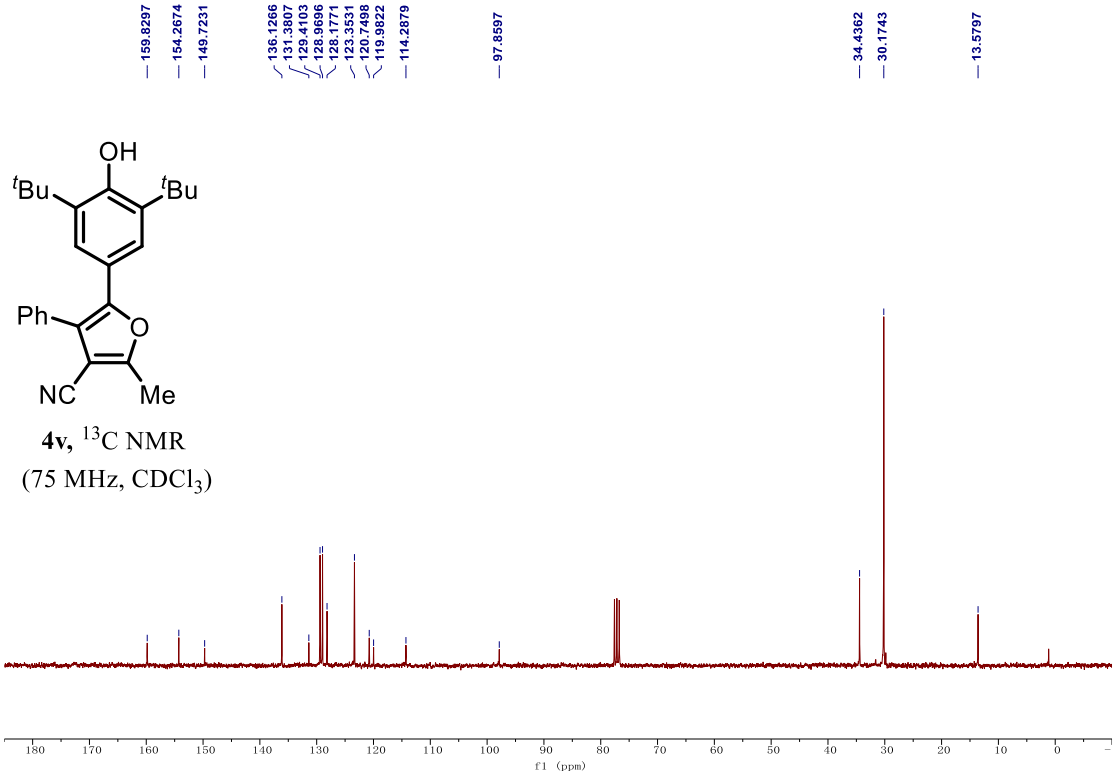
4u, ^{1}H NMR
(300 MHz, $CDCl_3$)



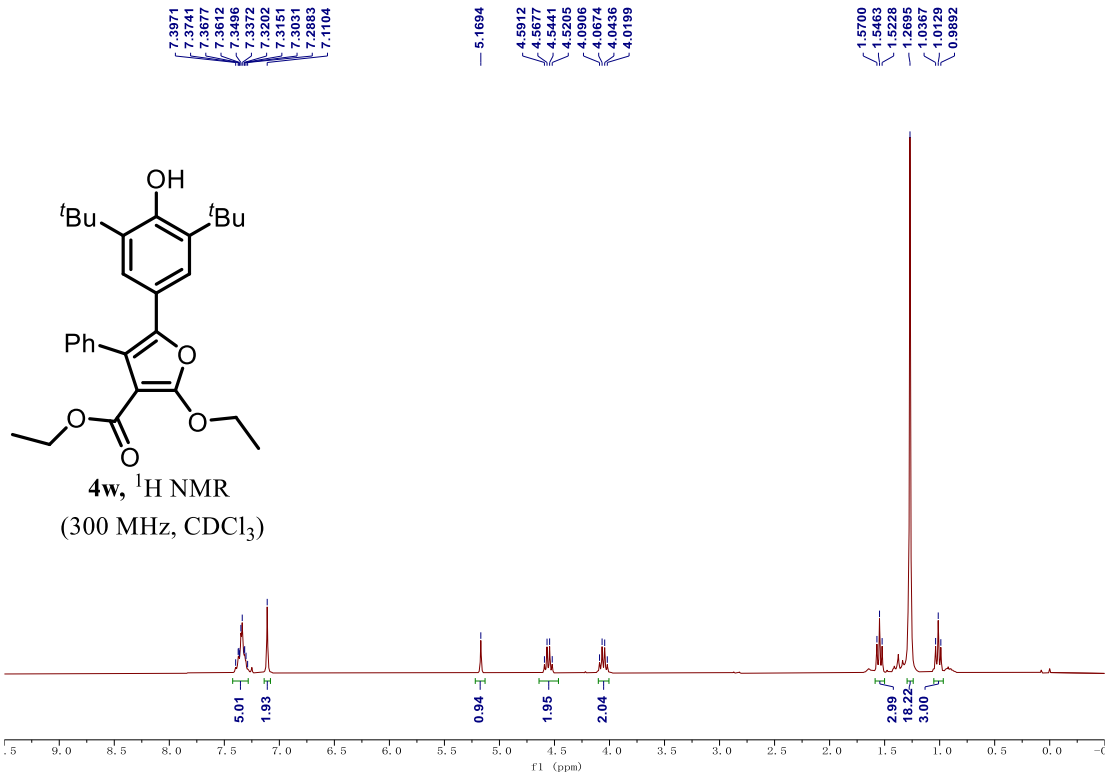
4u, ^{13}C NMR
(75 MHz, $CDCl_3$)



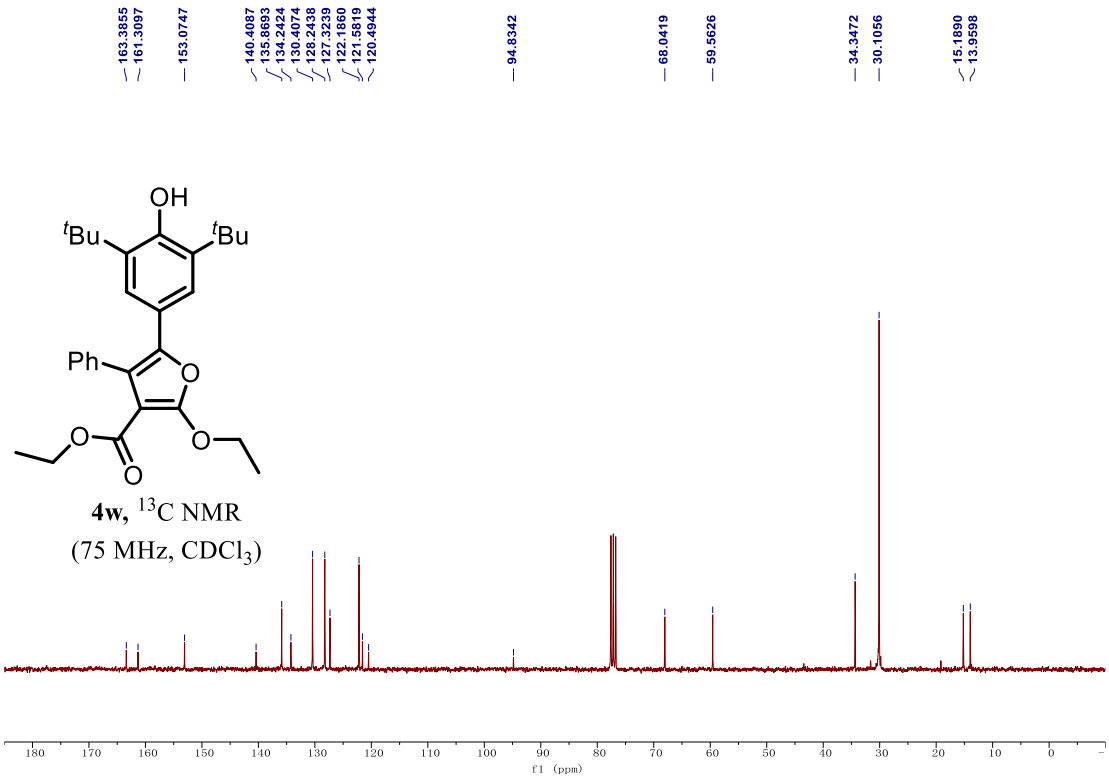
4v, ^{1}H NMR
(300 MHz, $CDCl_3$)



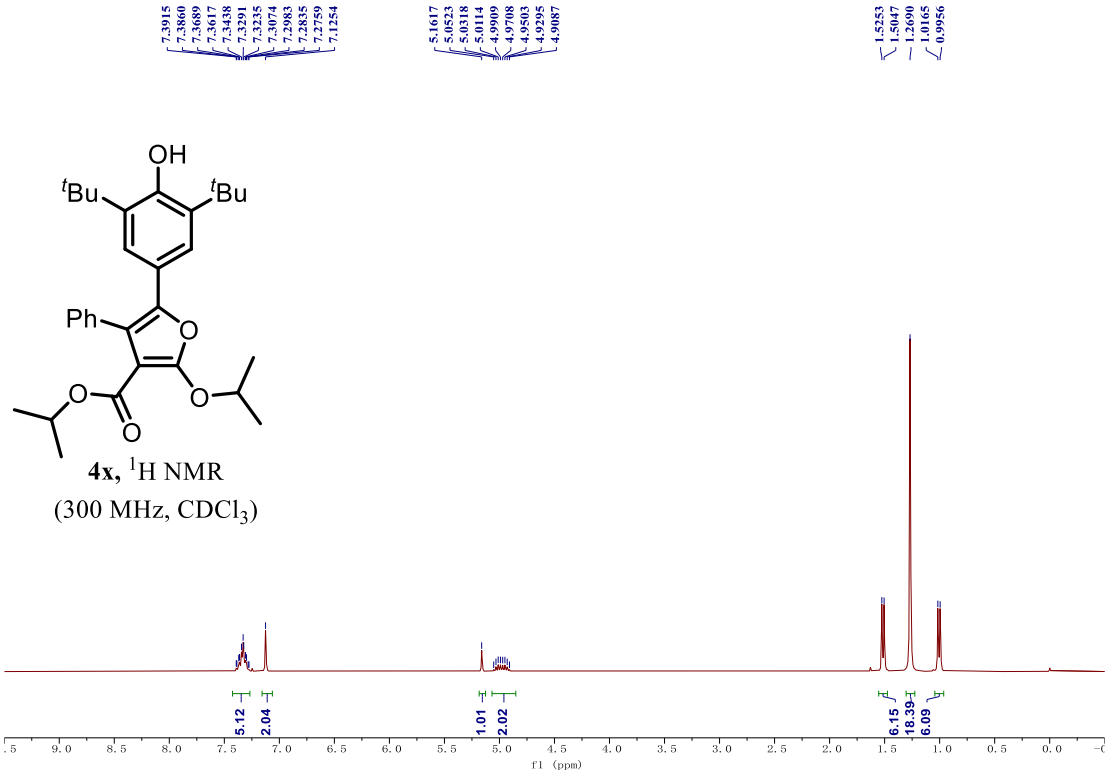
4v, ^{13}C NMR
(75 MHz, $CDCl_3$)

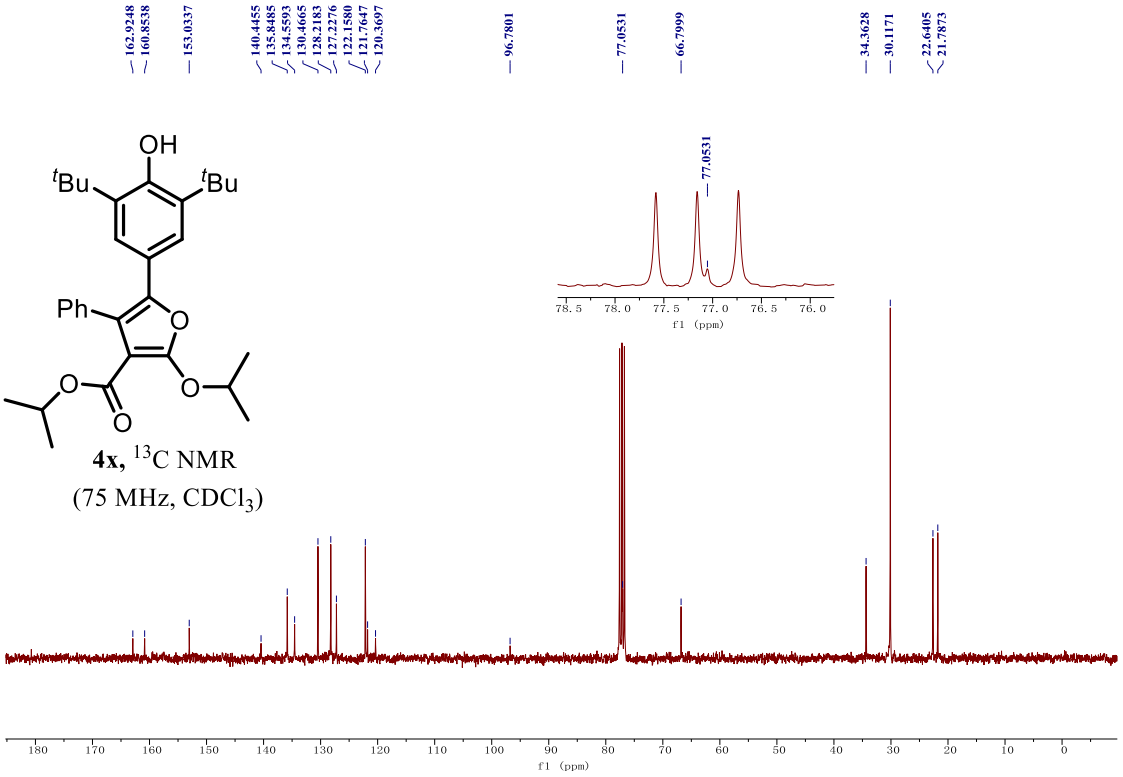


4w, ^{1}H NMR
(300 MHz, $CDCl_3$)



4w, ^{13}C NMR
(75 MHz, $CDCl_3$)


7.3915
7.3860
7.3689
7.3617
7.3438
7.3291
7.3235
7.3074
7.2983
7.2835
7.2759
7.1254
5.1617
5.0523
5.0318
5.0114
4.9909
4.9708
4.9503
4.9295
4.9087
1.5253
1.5047
1.2690
1.0165
0.9956
OH
tBu
tBu
Ph
O
O
O
O
4x, 1H NMR
(300 MHz, CDCl3)
5.12
2.04
1.01
2.02
6.15
18.39
6.09
f1 (ppm)


162.9248
160.8538
153.0337
140.4455
135.8485
134.5593
130.4665
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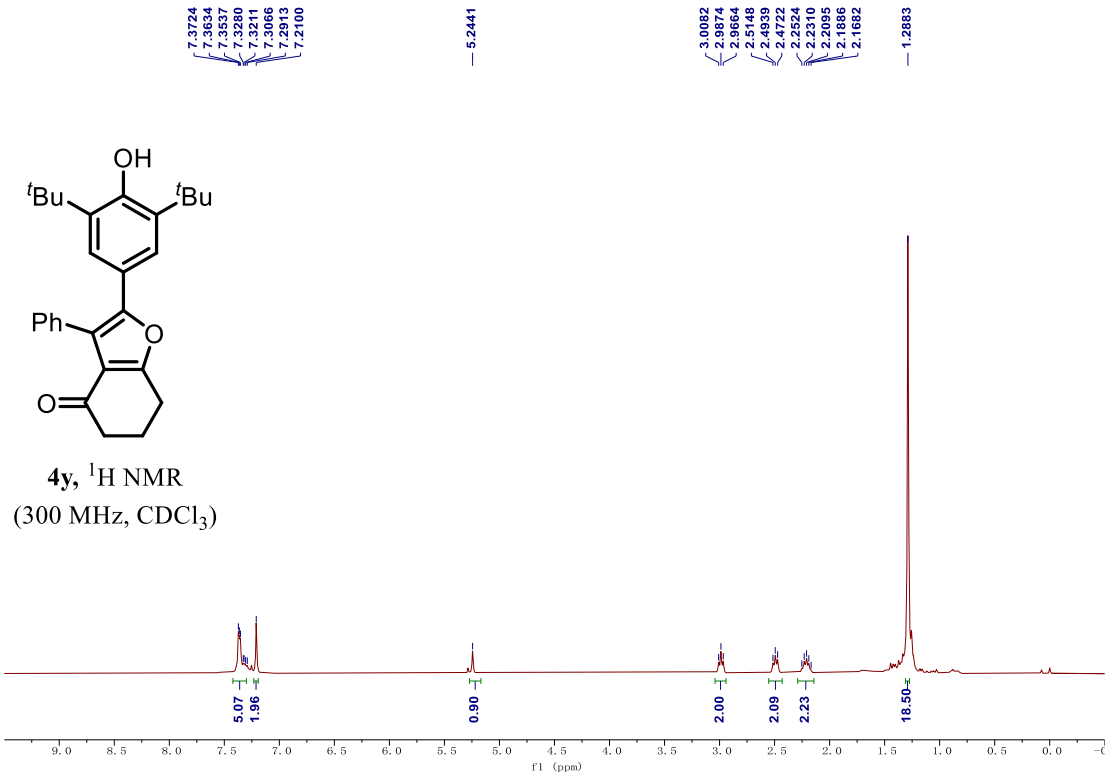
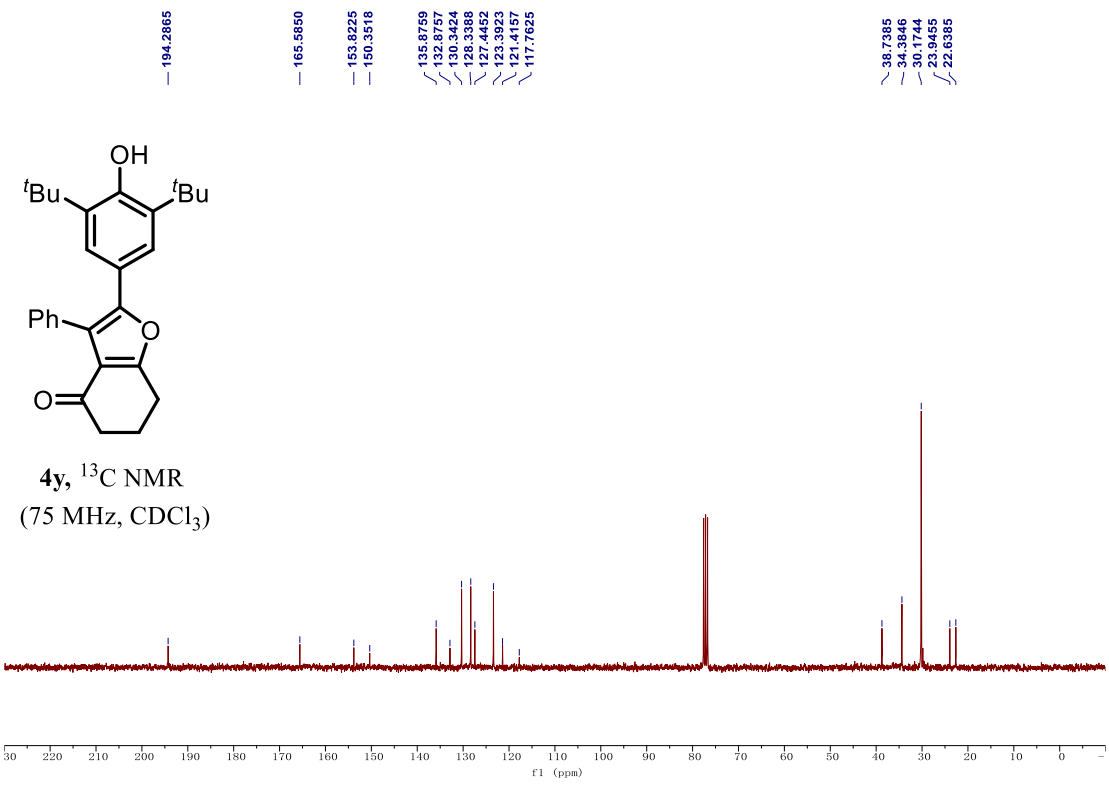
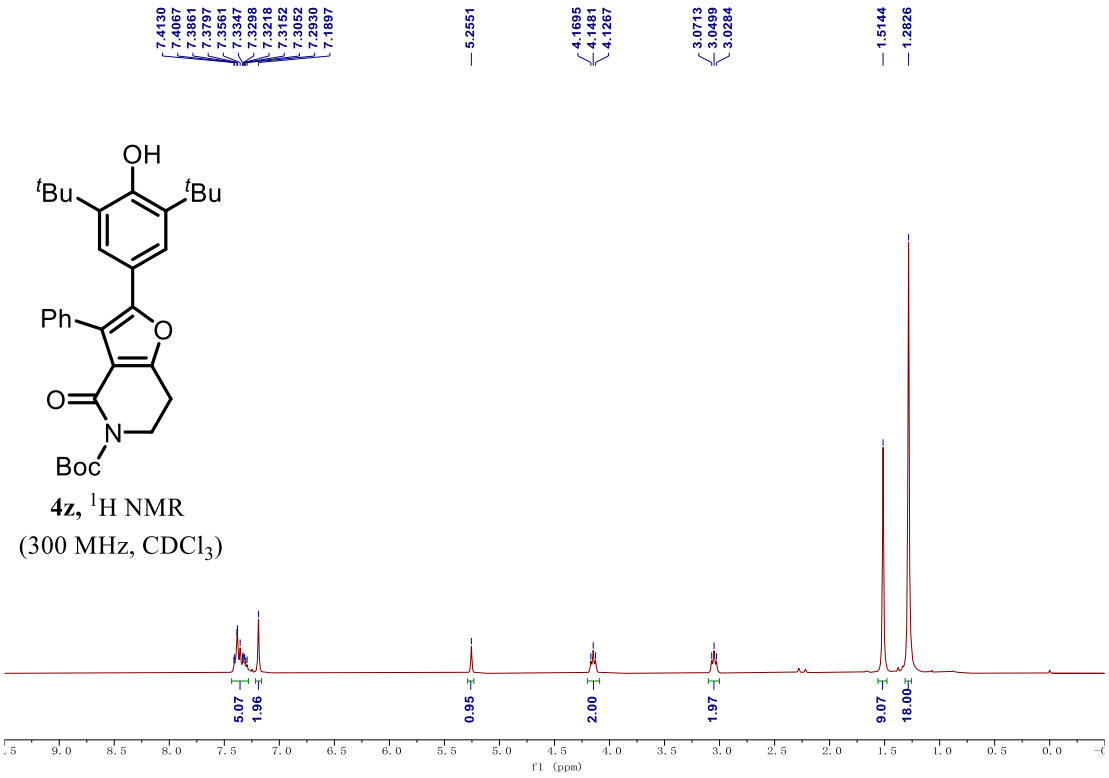
127.2276
122.1580
121.7647
120.3697
96.7801
77.0531
66.7999
34.3628
30.1171
22.6405
21.7873
OH
tBu
tBu
Ph
O
O
O
O
4x, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



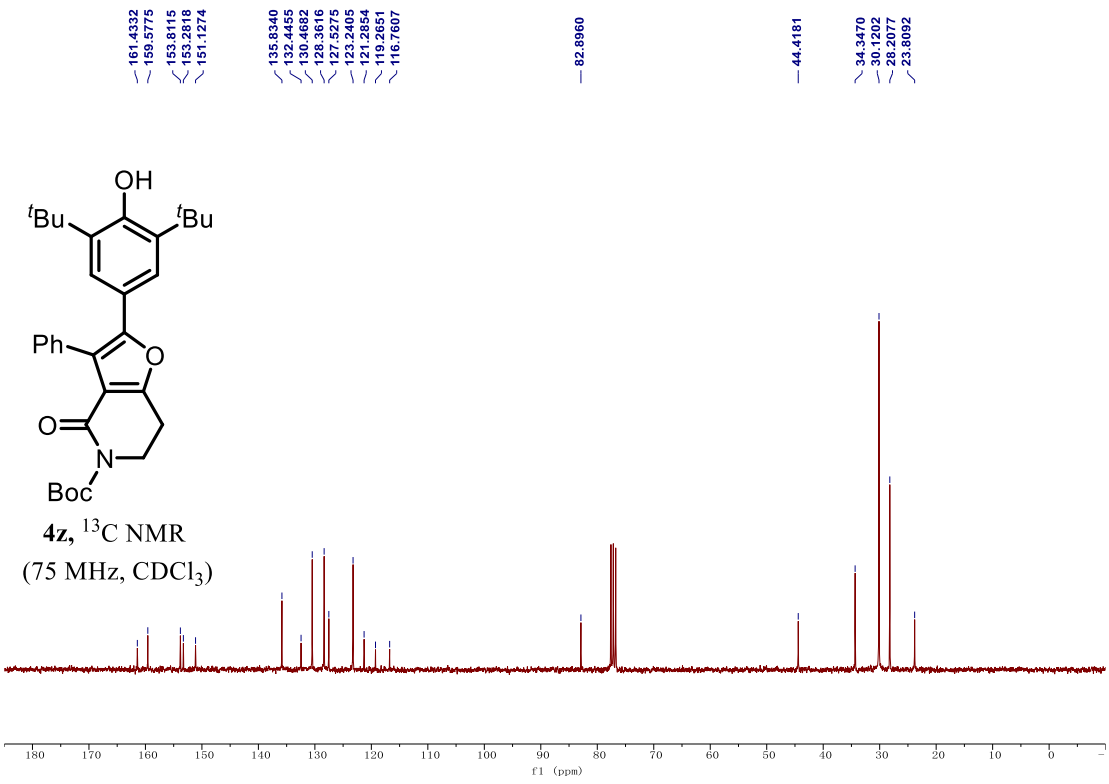
4y, ^{1}H NMR
(300 MHz, $CDCl_3$)



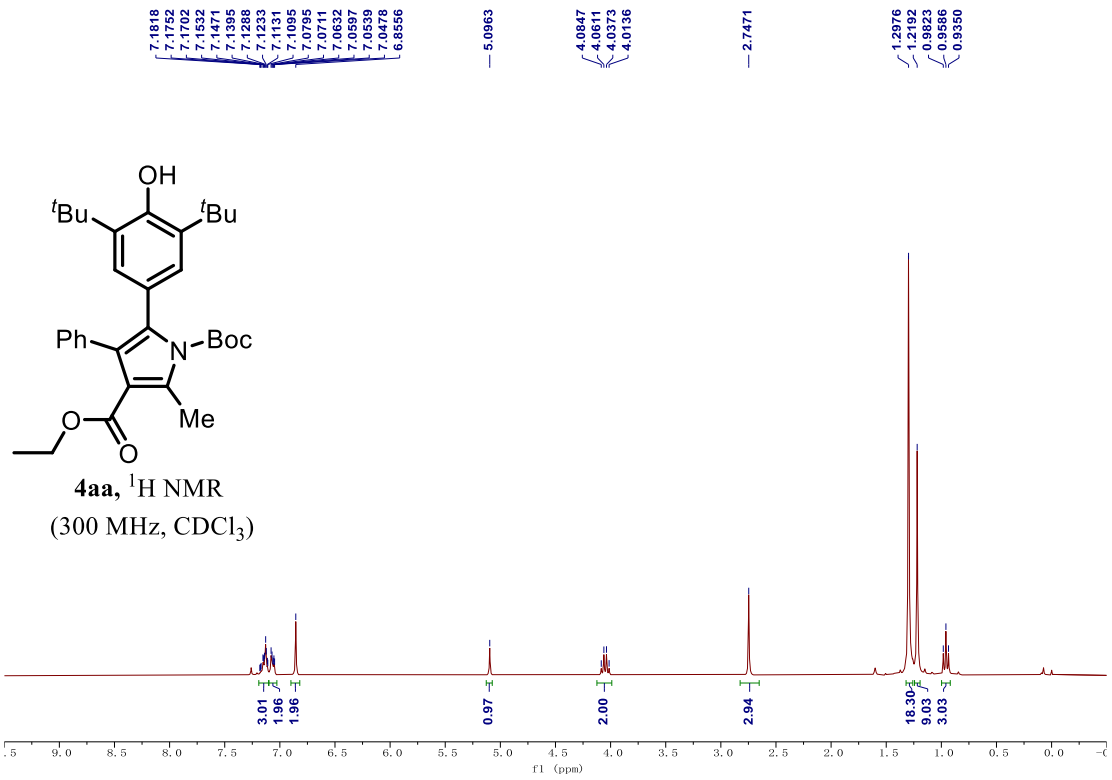
4y, ^{13}C NMR
(75 MHz, $CDCl_3$)



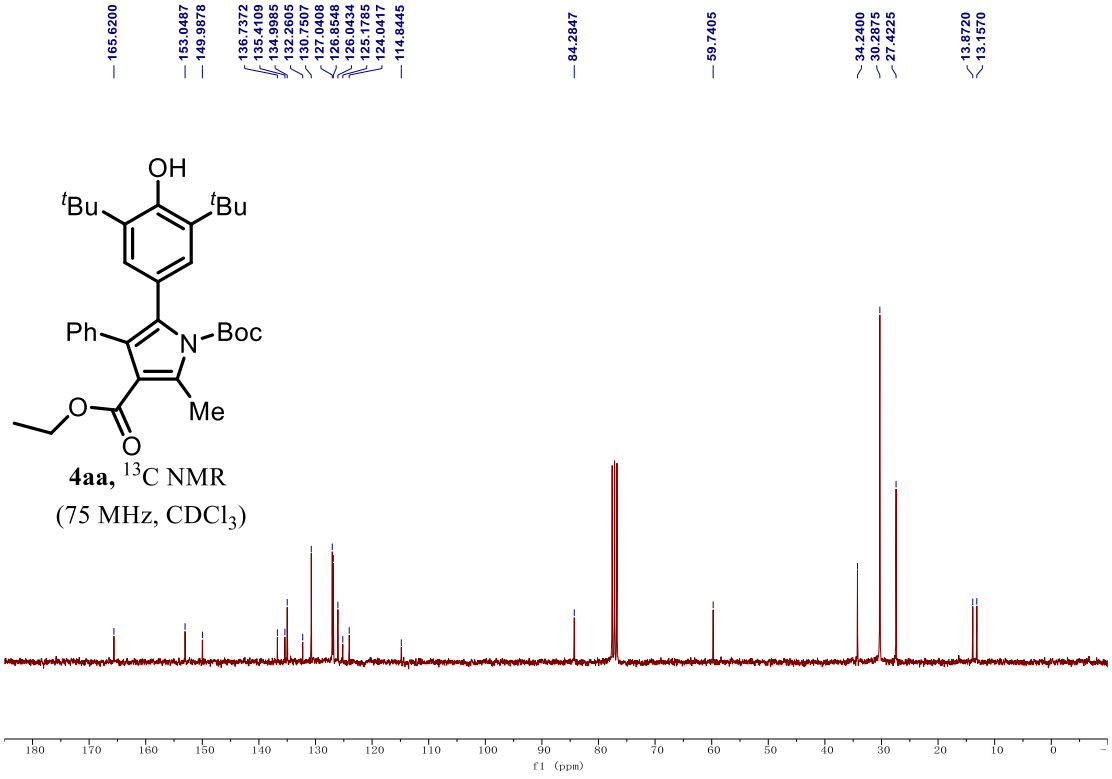
4z, ^{1}H NMR
(300 MHz, $CDCl_3$)



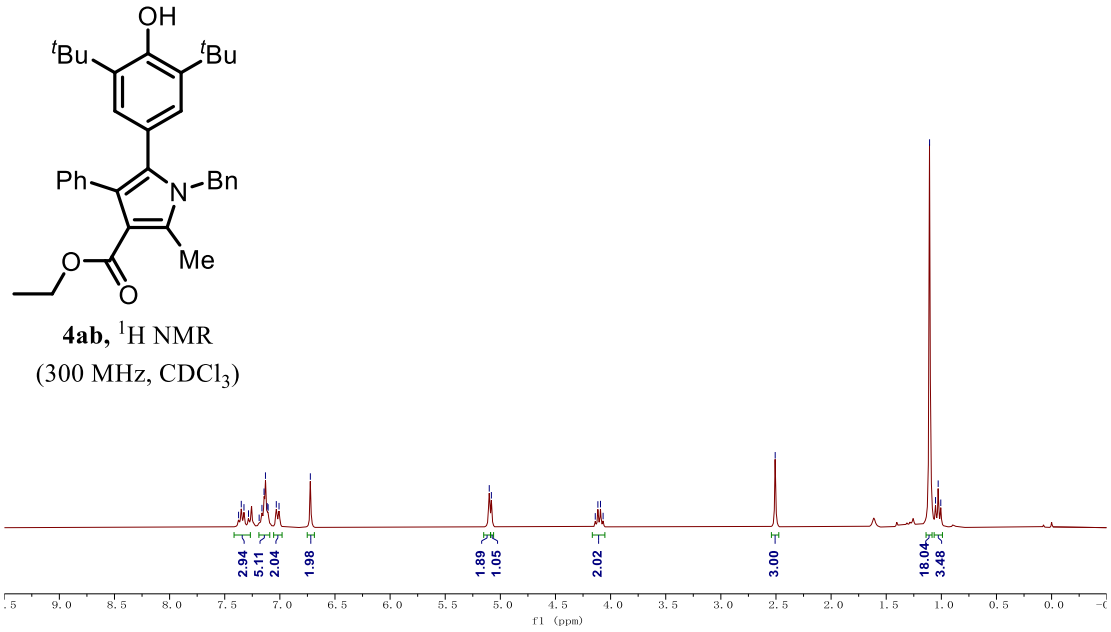
4z, ^{13}C NMR
(75 MHz, $CDCl_3$)



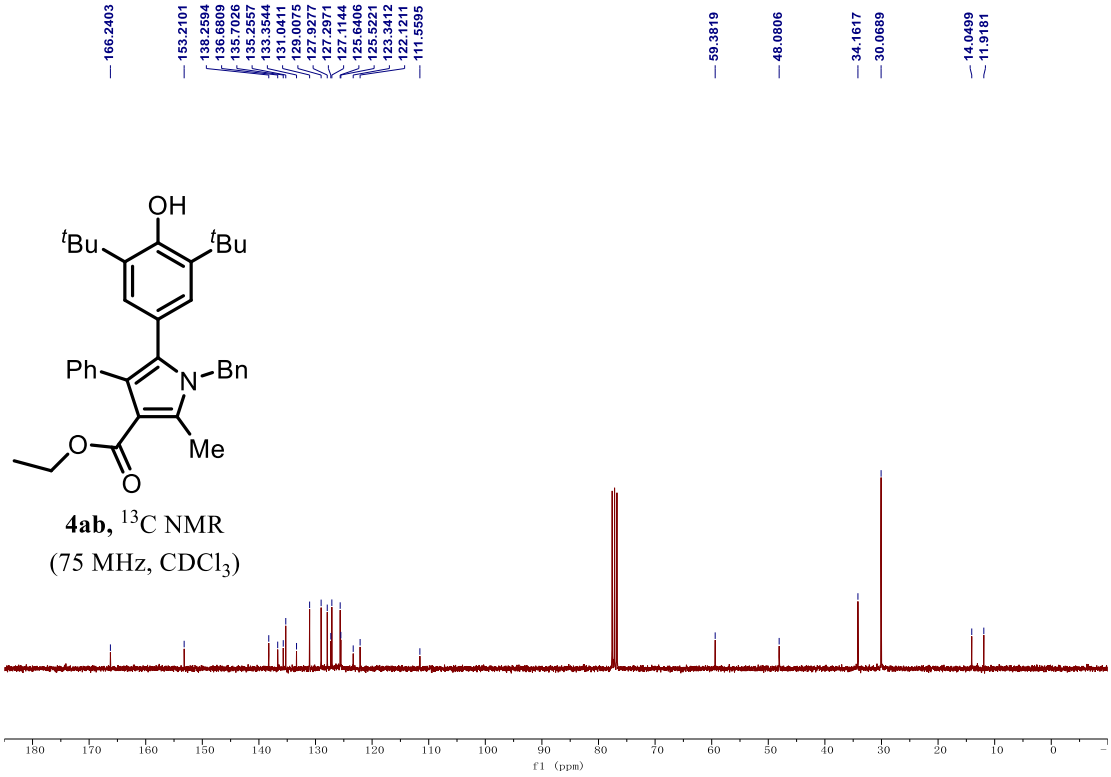
4aa, ^{1}H NMR
(300 MHz, $CDCl_3$)



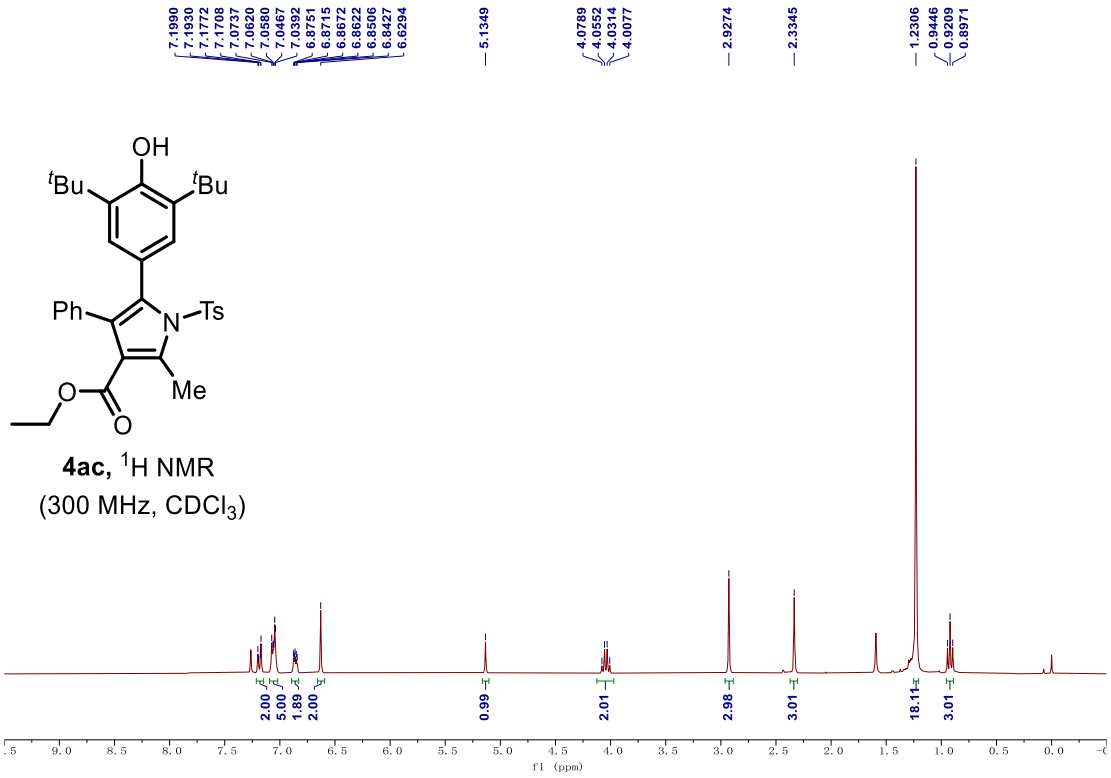
4aa, ^{13}C NMR
(75 MHz, $CDCl_3$)



4ab, ^{1}H NMR
(300 MHz, $CDCl_3$)



4ab, ^{13}C NMR
(75 MHz, $CDCl_3$)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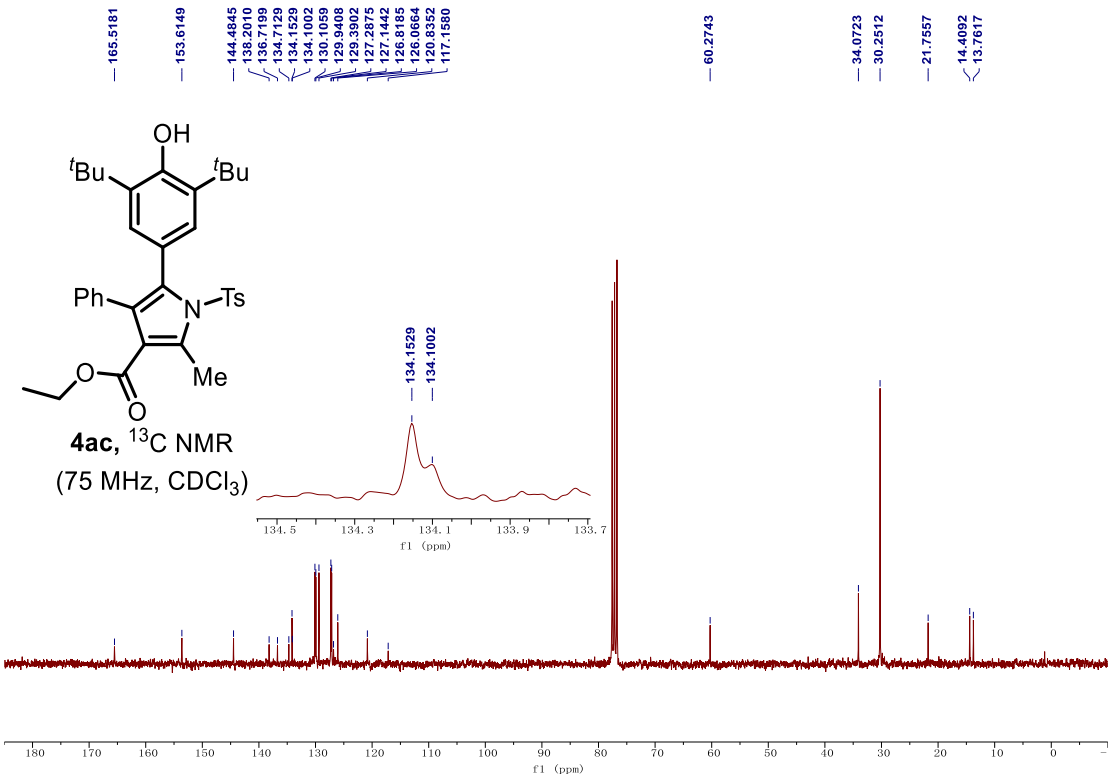
7.1772
7.1708
7.0737
7.0620
7.0580
7.0467
7.0392
6.8751
6.8715
6.8672
6.8622
6.8506
6.8427
6.6294
5.1349
4.0789
4.0552
4.0314
4.0077
2.9274
2.3345
1.2306
0.9446
0.9209
0.8971
OH
tBu
tBu
Ph
N
Ts
Me
O
O
4ac, 1H NMR
(300 MHz, CDCl3)
2.00
5.00
1.89
2.00
0.99
2.01
2.98
3.01
18.11
3.01
f1 (ppm)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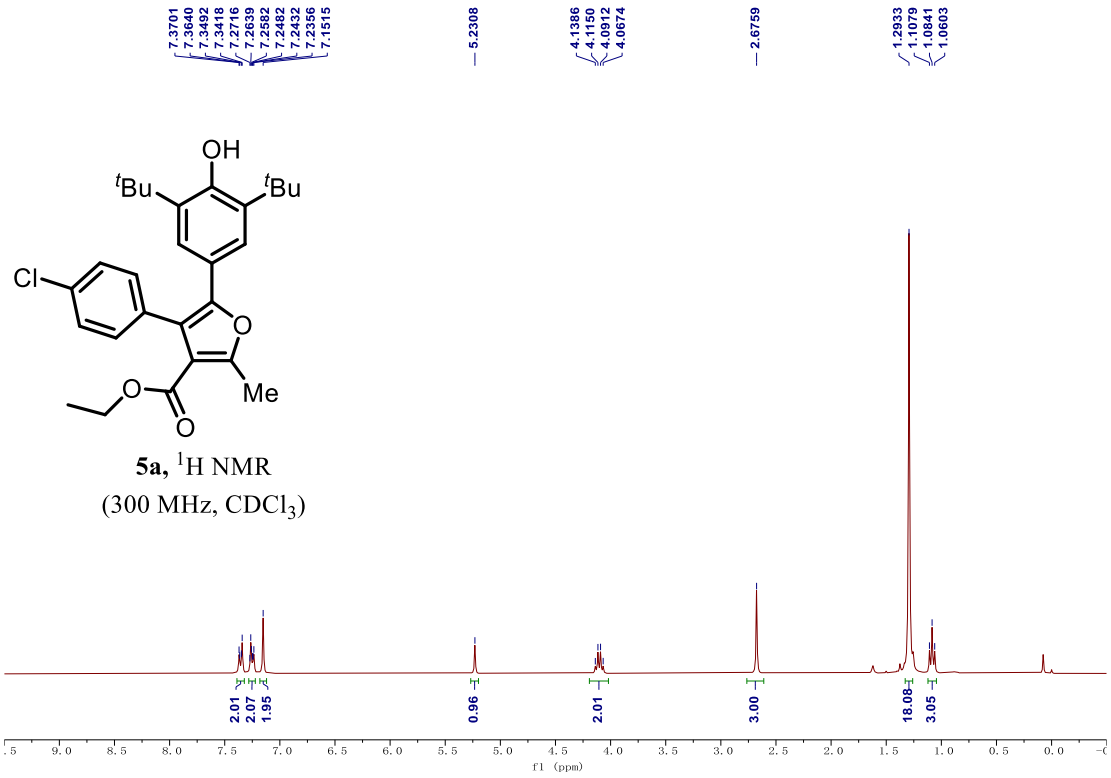
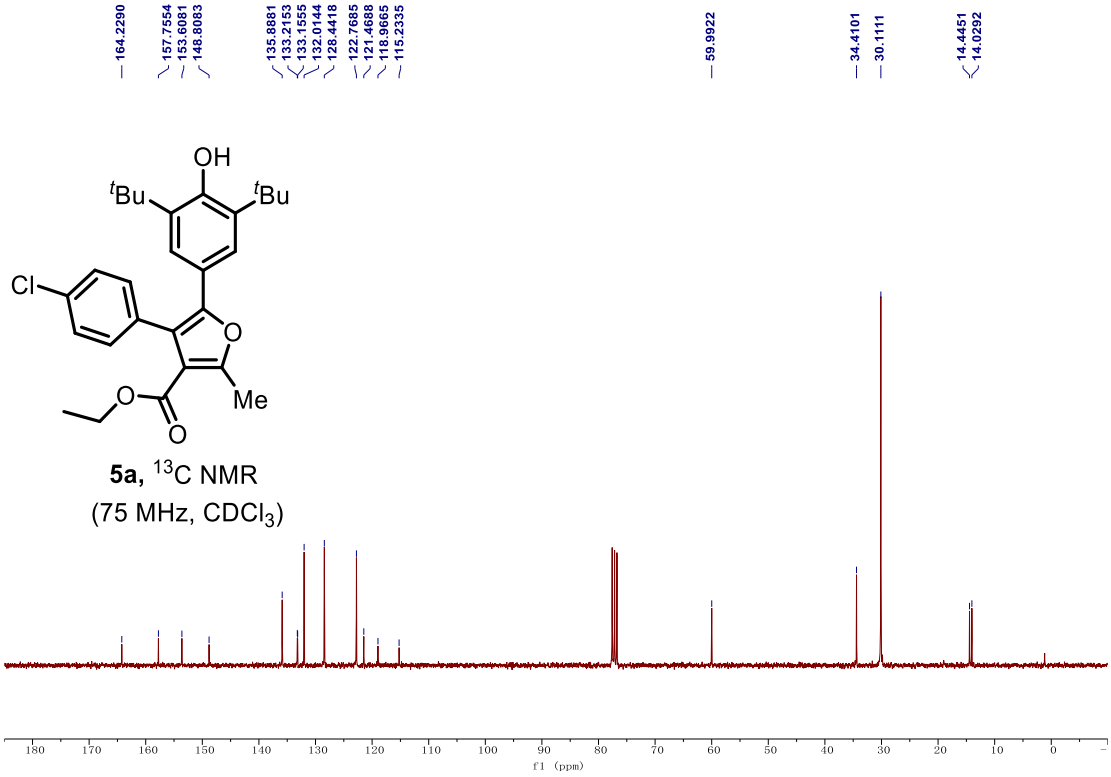
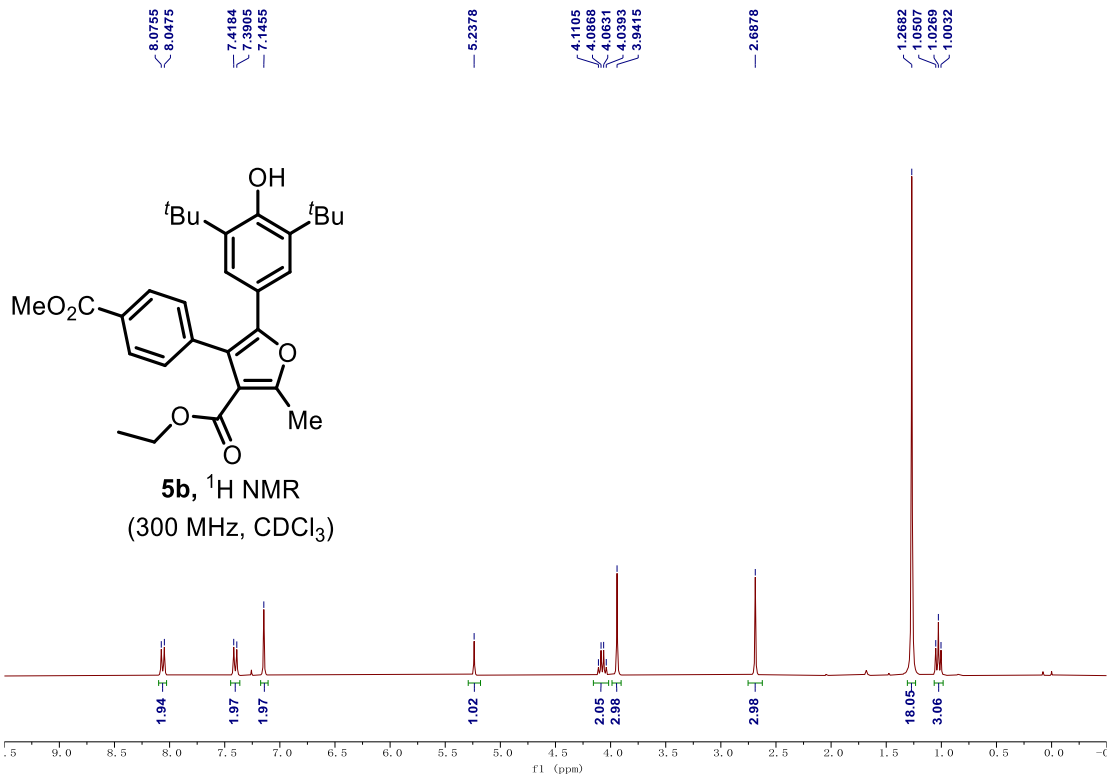
153.6149
144.4845
138.2010
136.7199
134.7129
134.1529
134.1002
130.1059
129.9408
129.3902
127.2875
127.1442
126.8185
126.0664
120.8352
117.1580
60.2743
34.0723
30.2512
21.7557
14.4092
13.7617
OH
tBu
tBu
Ph
N
Ts
Me
O
O
4ac, 13C NMR
(75 MHz, CDCl3)
134.1529
134.1002
f1 (ppm)
f1 (ppm)



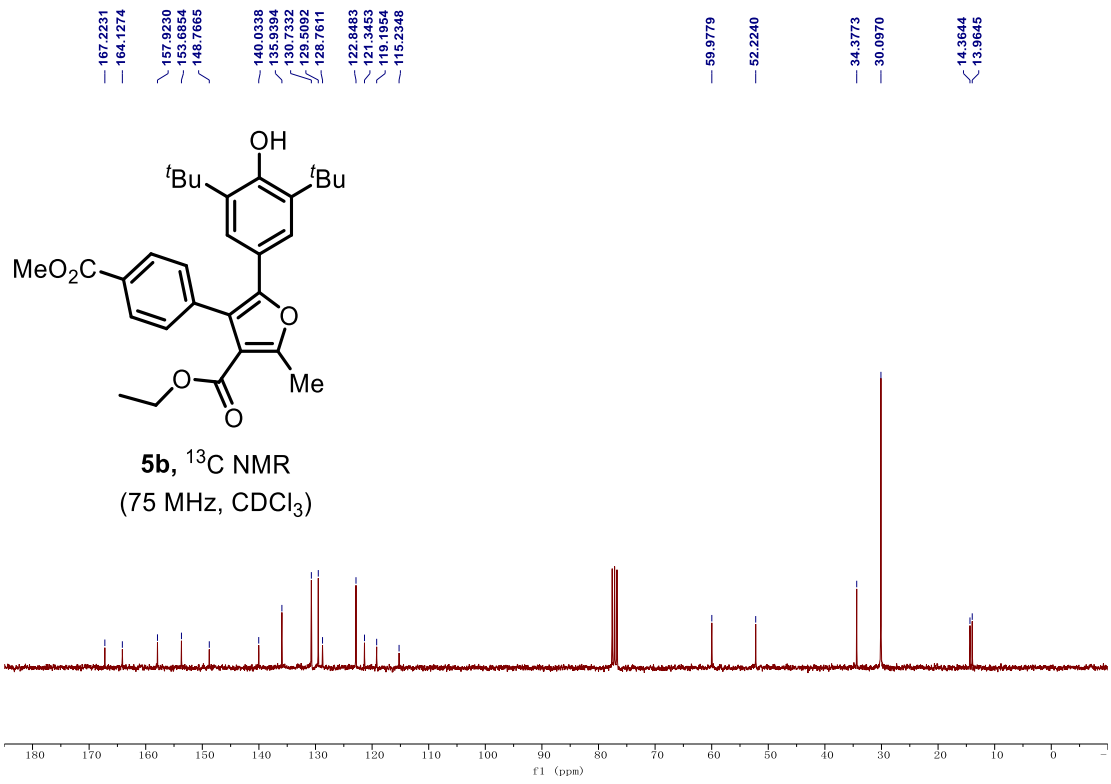
5a, ^{1}H NMR
(300 MHz, $CDCl_3$)



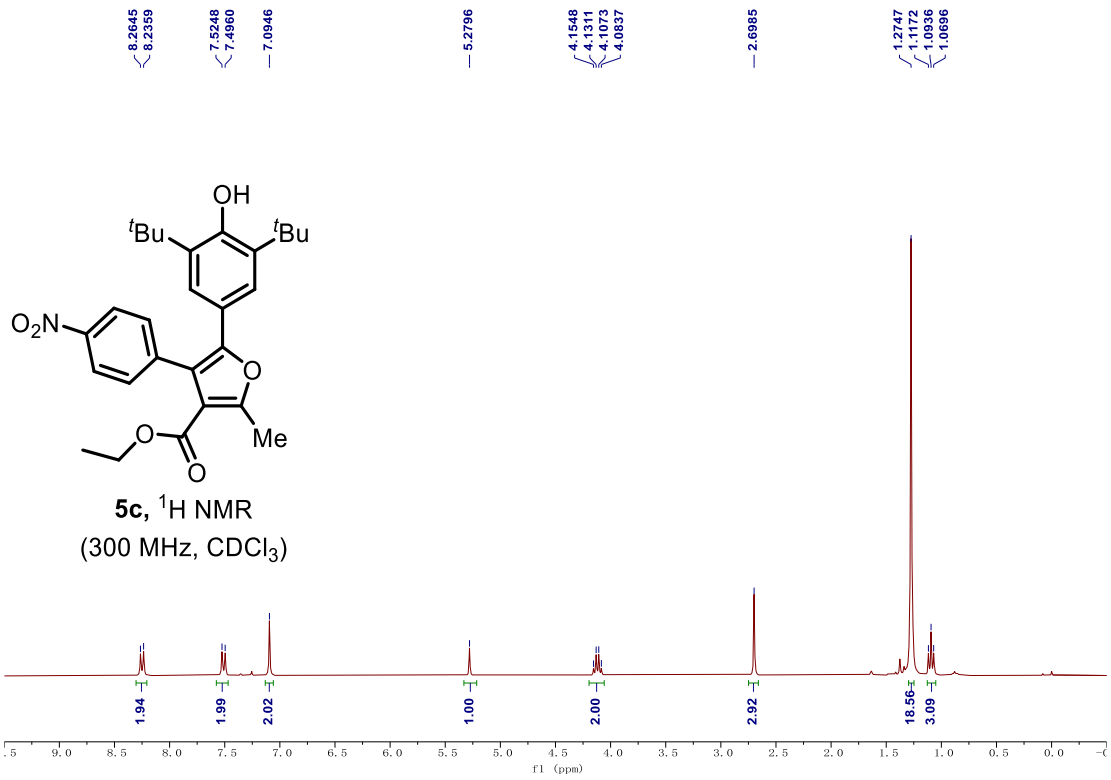
5a, ^{13}C NMR
(75 MHz, $CDCl_3$)



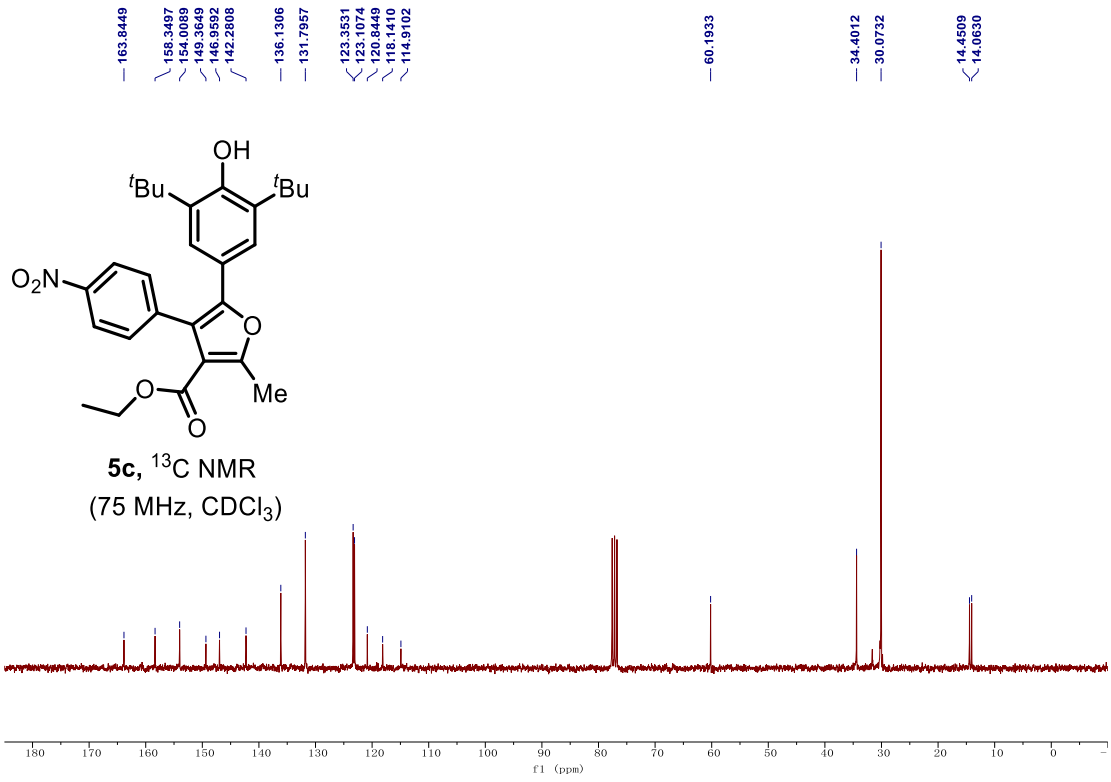
5b, ^{1}H NMR
(300 MHz, $CDCl_3$)



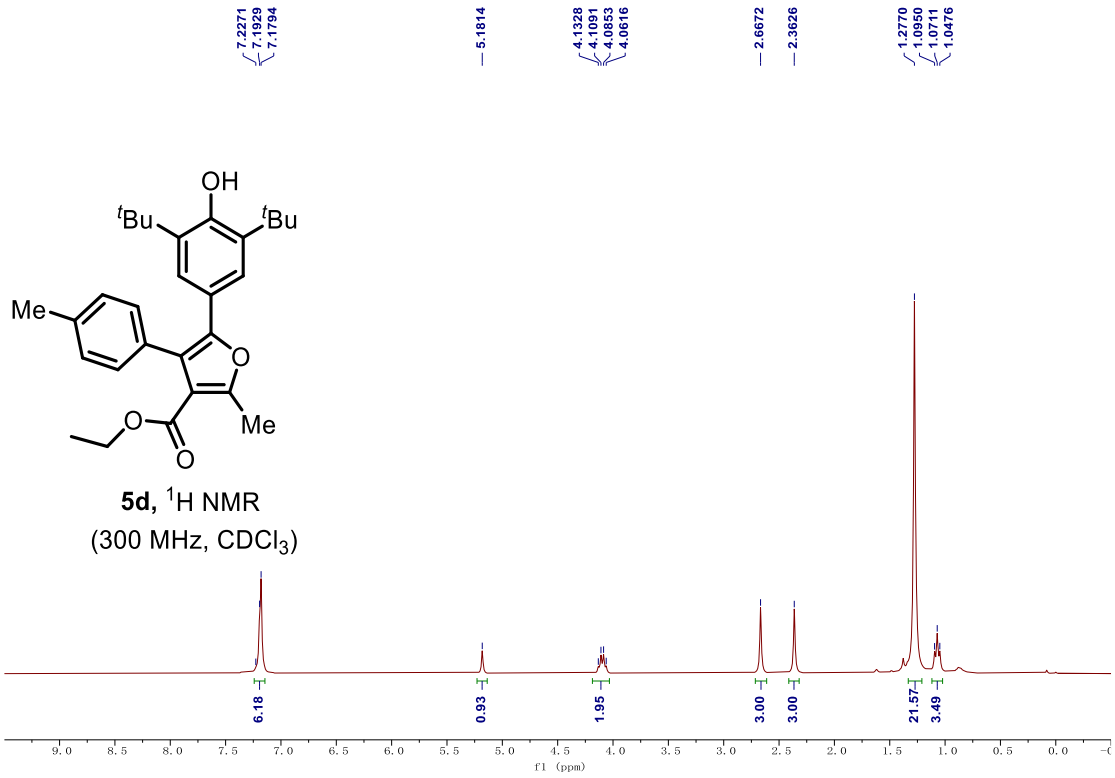
5b, ^{13}C NMR
(75 MHz, $CDCl_3$)



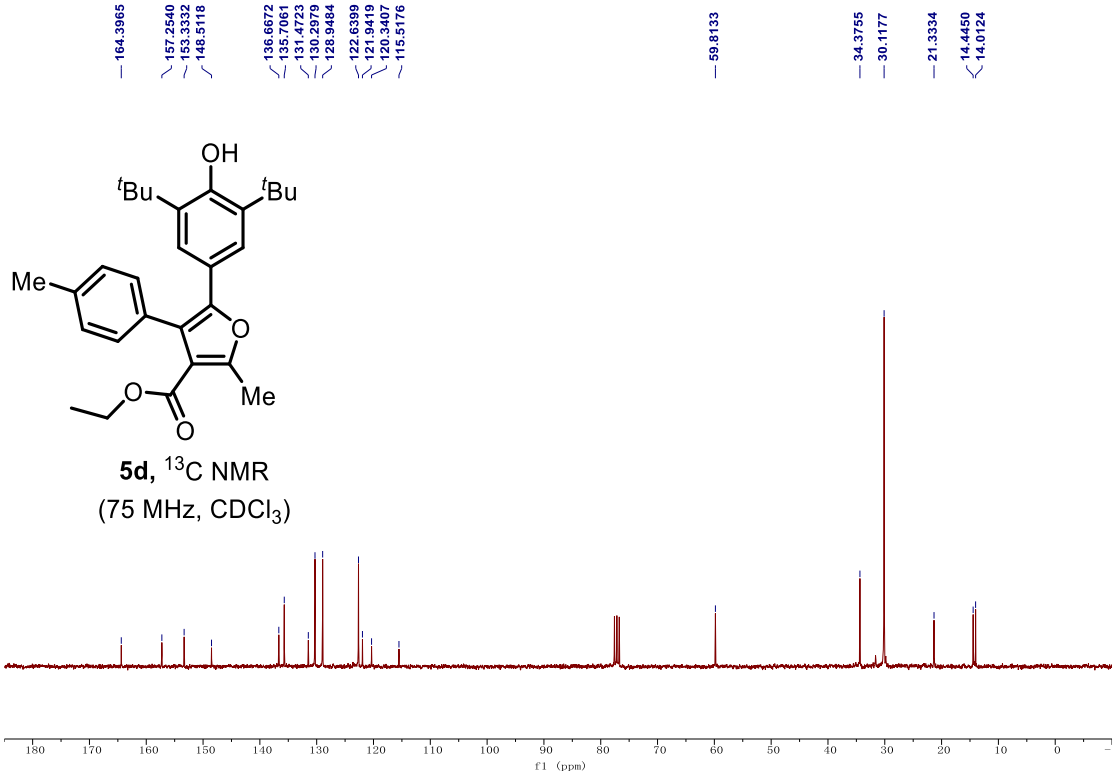
5c, ^{1}H NMR
(300 MHz, $CDCl_3$)



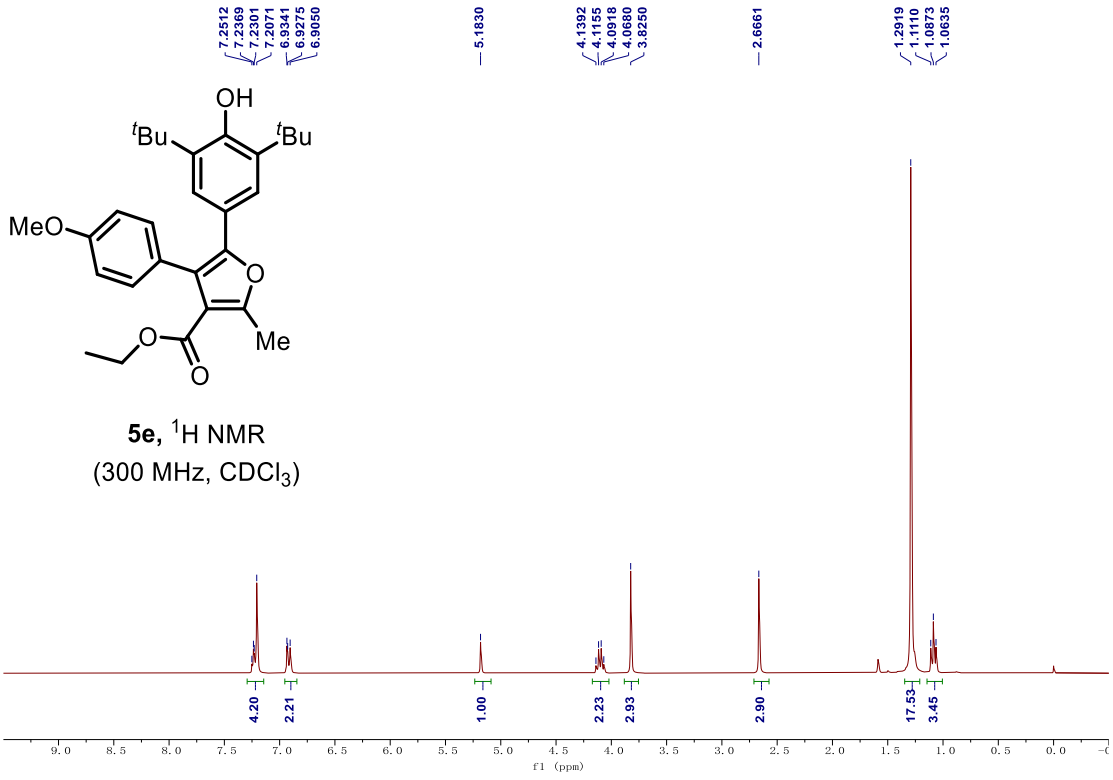
5c, ^{13}C NMR
(75 MHz, $CDCl_3$)



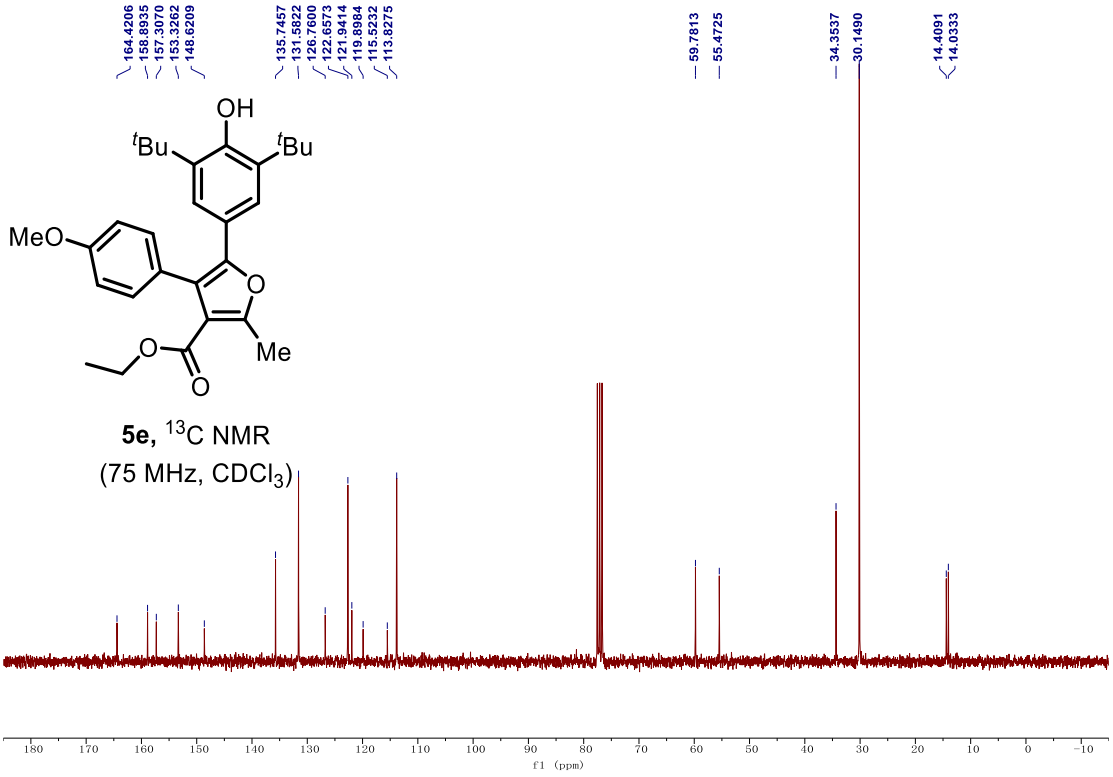
5d, ^{1}H NMR
(300 MHz, $CDCl_3$)



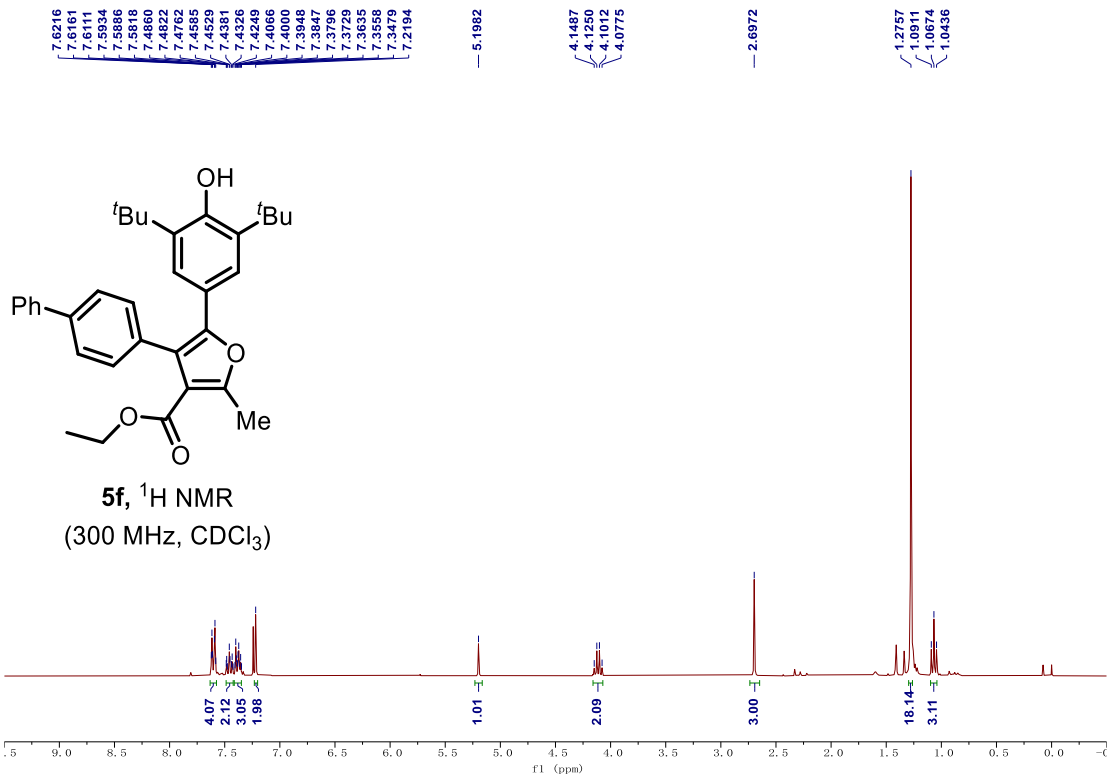
5d, ^{13}C NMR
(75 MHz, $CDCl_3$)



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



5e, ^{13}C NMR
(75 MHz, $CDCl_3$)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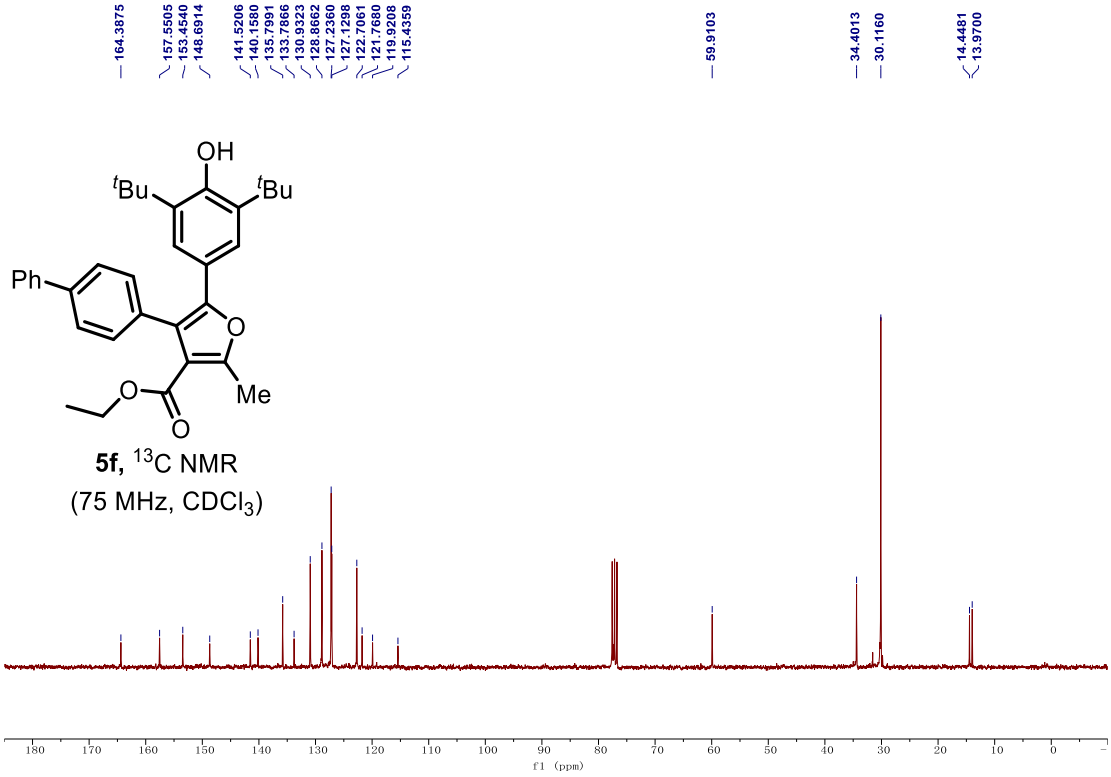
7.6111
7.5934
7.5886
7.5818
7.4860
7.4822
7.4762
7.4585
7.4529
7.4381
7.4326
7.4249
7.4066
7.4000
7.3948
7.3847
7.3796
7.3729
7.3635
7.3558
7.3479
7.2194
5.1982
4.1487
4.1250
4.1012
4.0775
2.6972
1.2757
1.0911
1.0674
1.0436
OH
tBu
tBu
Ph
O
O
O
Me
5f, 1H NMR
(300 MHz, CDCl3)
4.07
2.12
3.05
1.98
1.01
2.09
3.00
18.14
3.11
f1 (ppm)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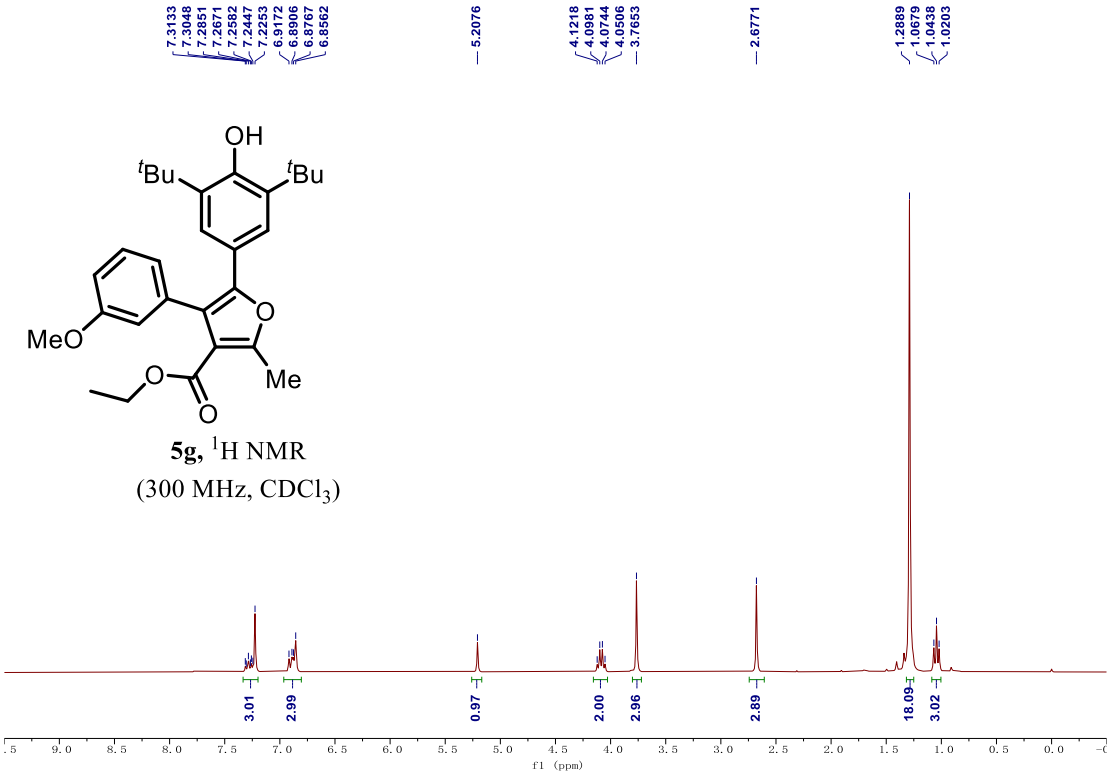
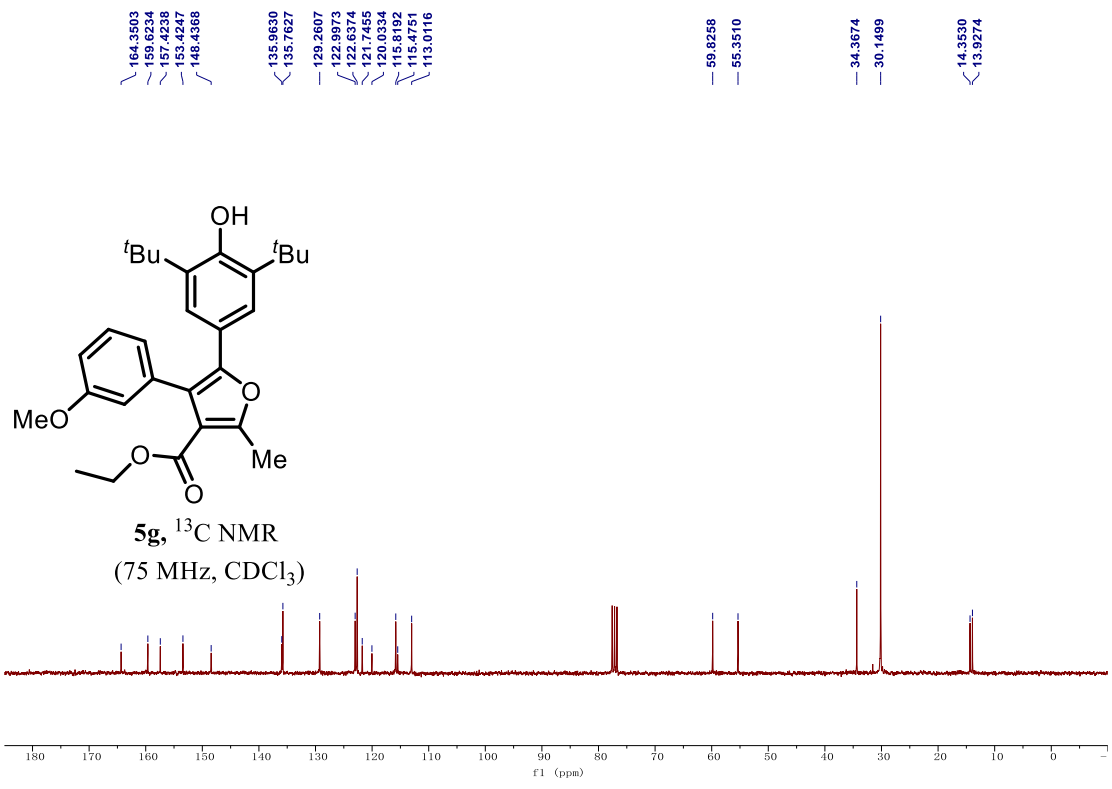
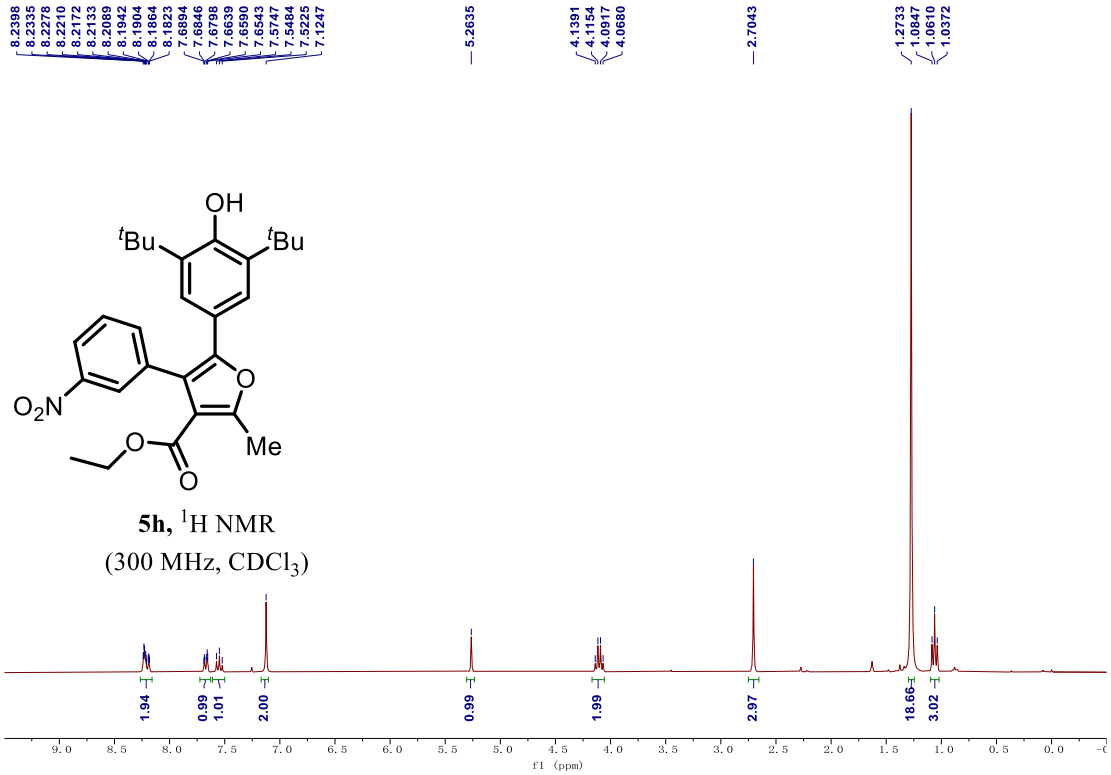
153.4540
148.6914
141.5206
140.1580
135.7991
133.7866
130.9323
128.8662
127.2360
127.1298
122.7061
121.7680
119.9208
115.4359
59.9103
34.4013
30.1160
14.4481
13.9700
OH
tBu
tBu
Ph
O
O
O
Me
5f, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)



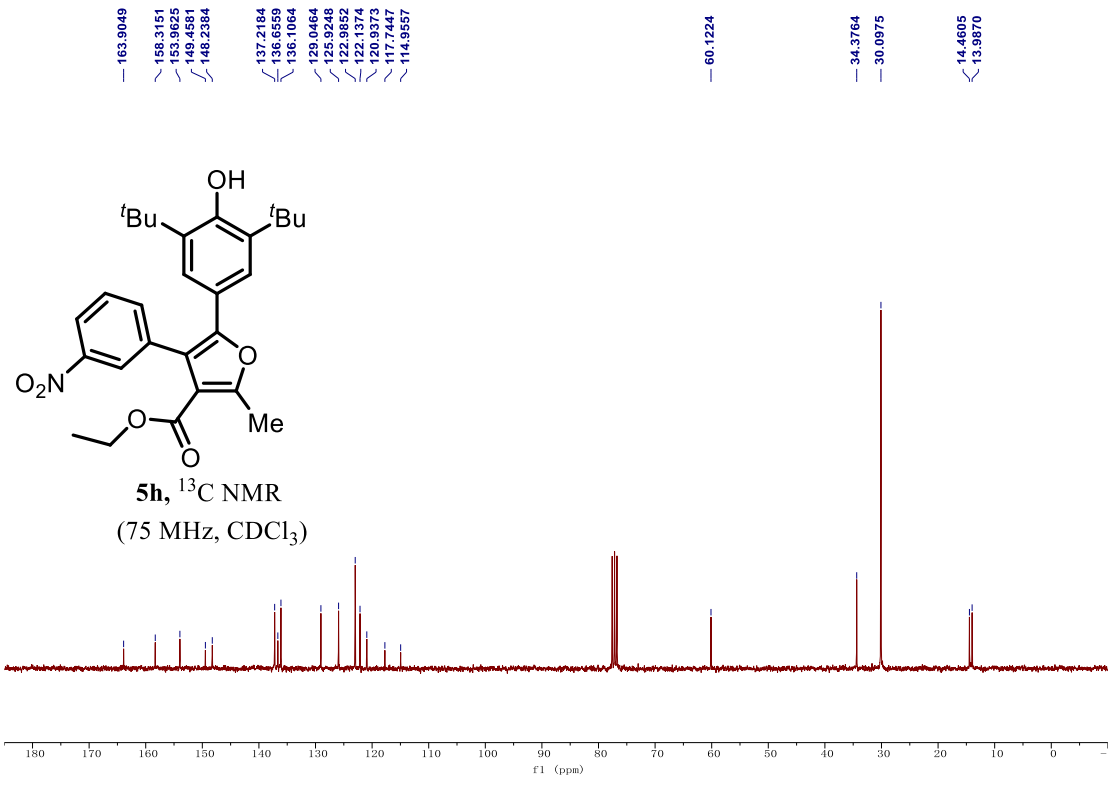
5g, ^{1}H NMR
(300 MHz, $CDCl_3$)



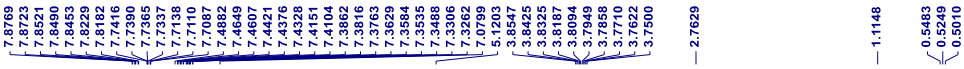
5g, ^{13}C NMR
(75 MHz, $CDCl_3$)

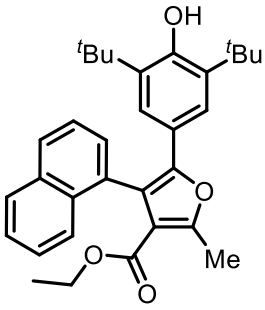


5h, ^{1}H NMR
(300 MHz, $CDCl_3$)

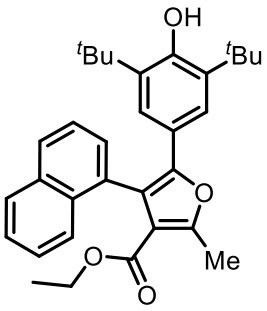


5h, ^{13}C NMR
(75 MHz, $CDCl_3$)

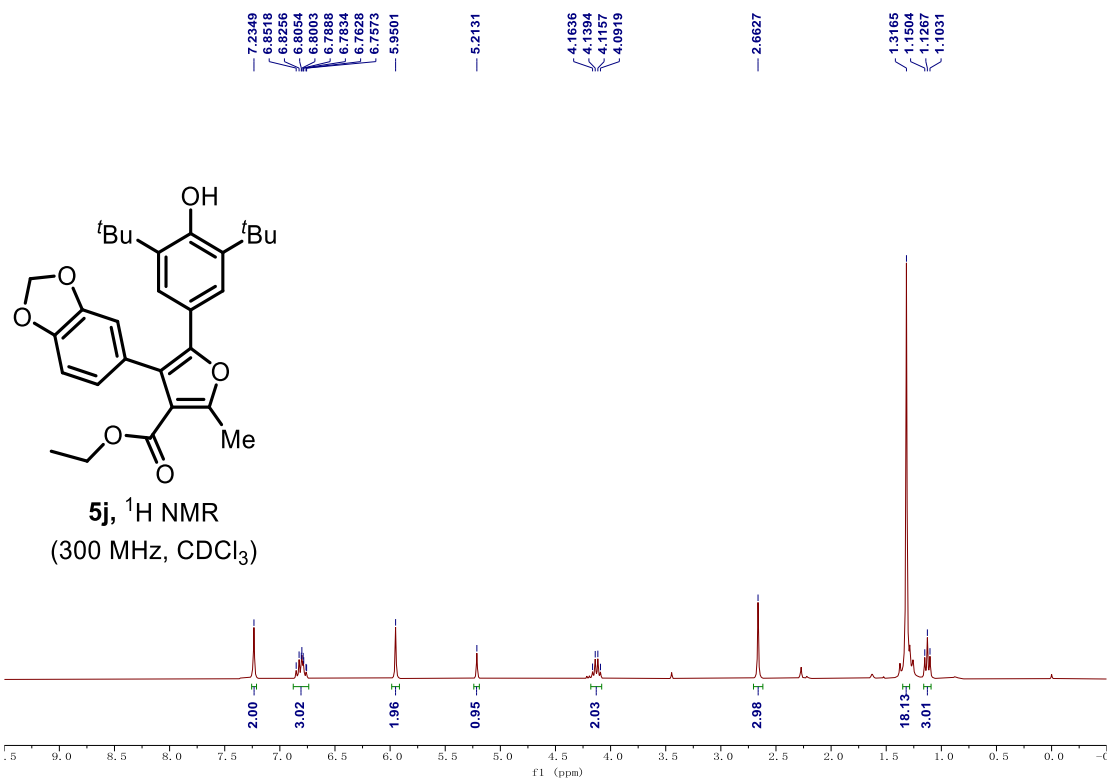




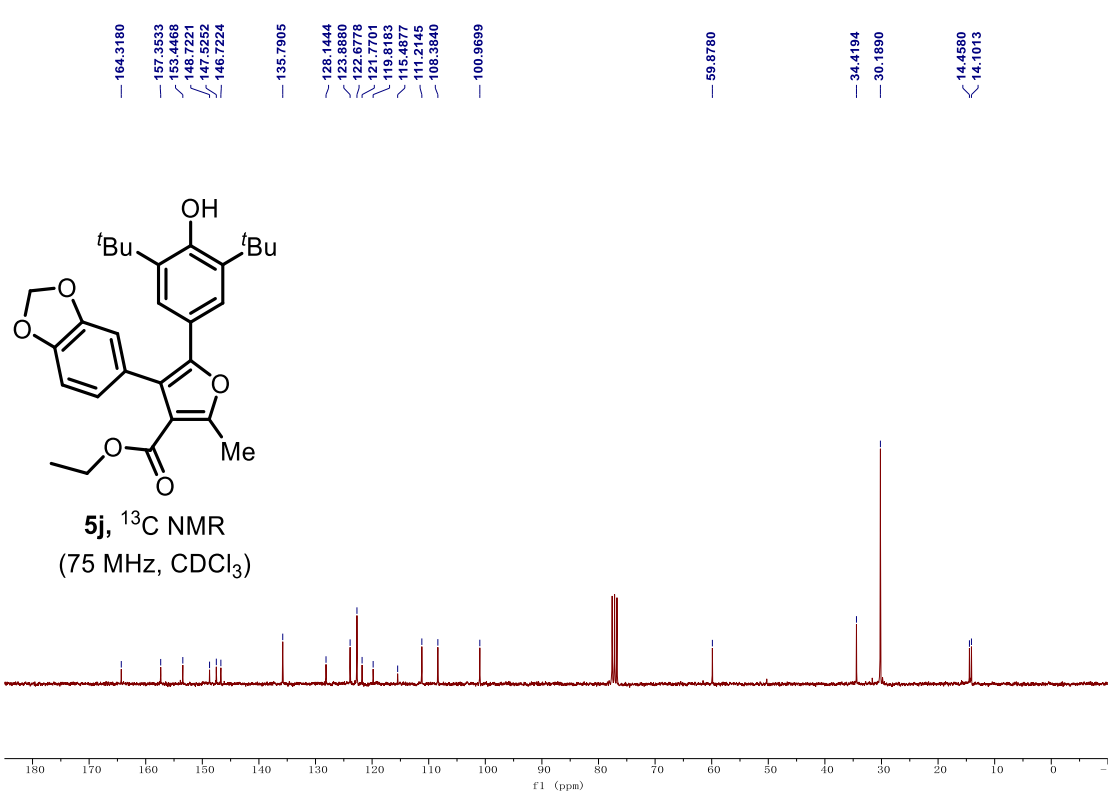
5i, ^{1}H NMR
(300 MHz, $CDCl_3$)



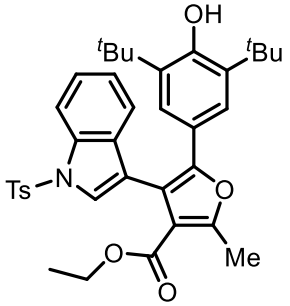
5i, ^{13}C NMR
(75 MHz, $CDCl_3$)



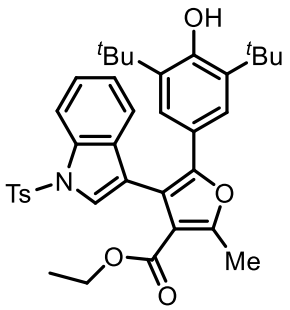
5j, ^{1}H NMR
(300 MHz, $CDCl_3$)



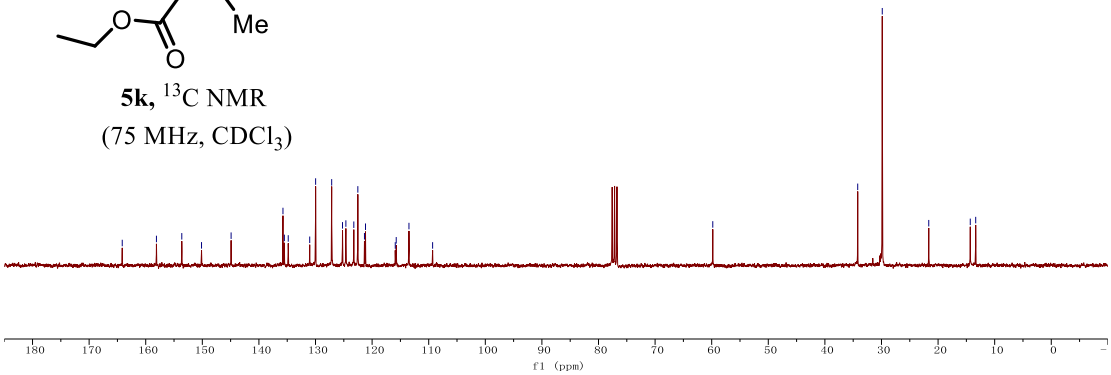
5j, ^{13}C NMR
(75 MHz, $CDCl_3$)

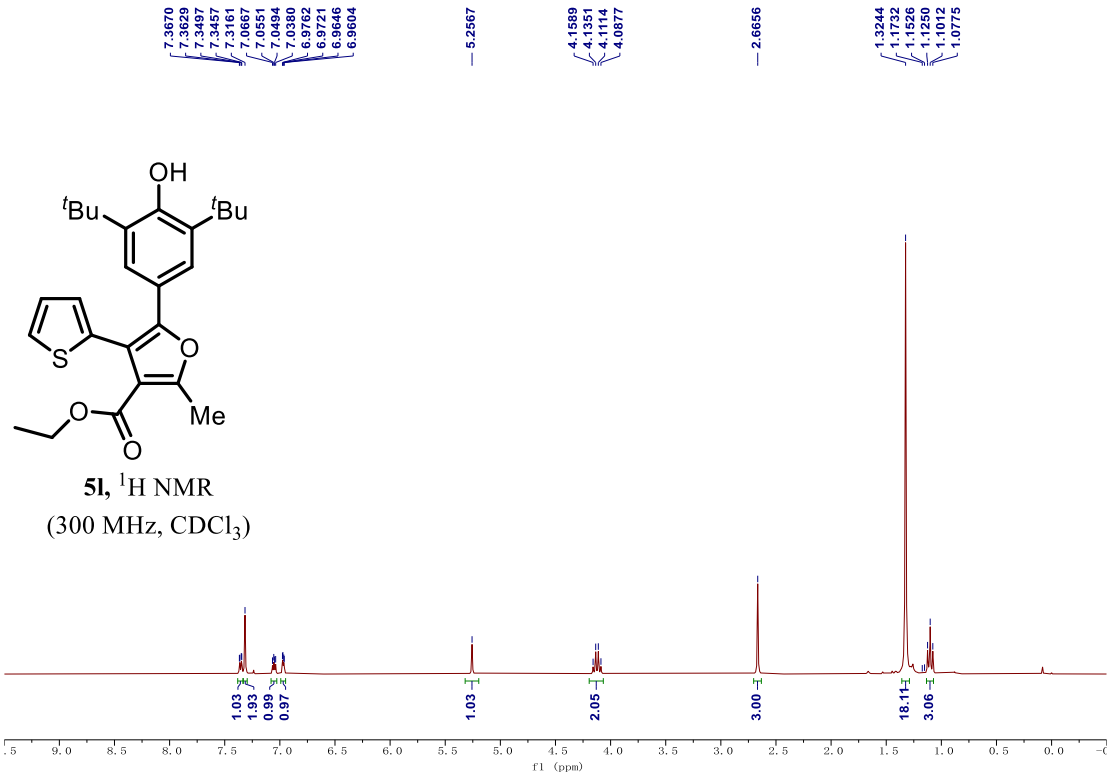


5k, ^{1}H NMR
(300 MHz, $CDCl_3$)

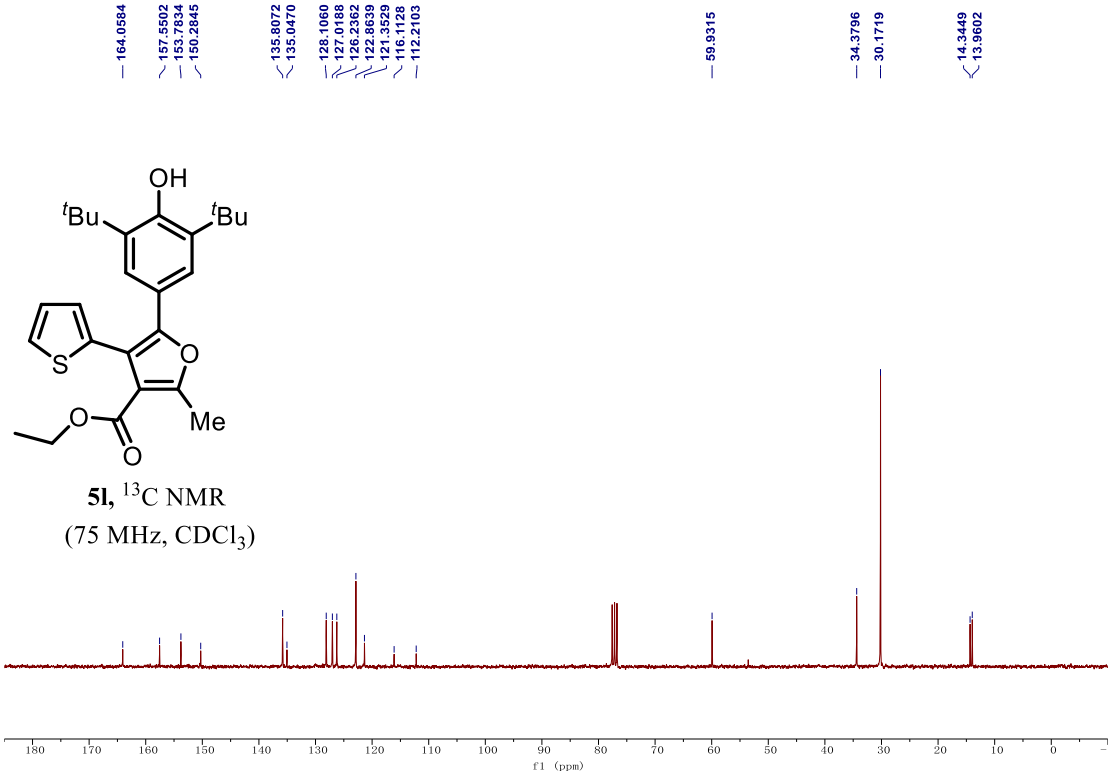


5k, ^{13}C NMR
(75 MHz, $CDCl_3$)

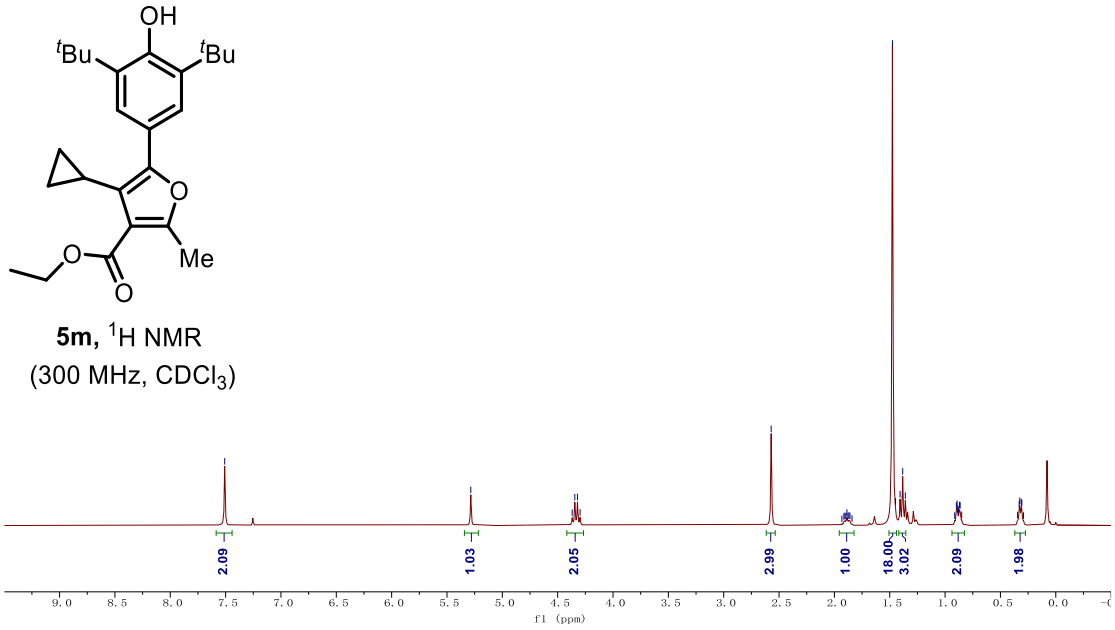




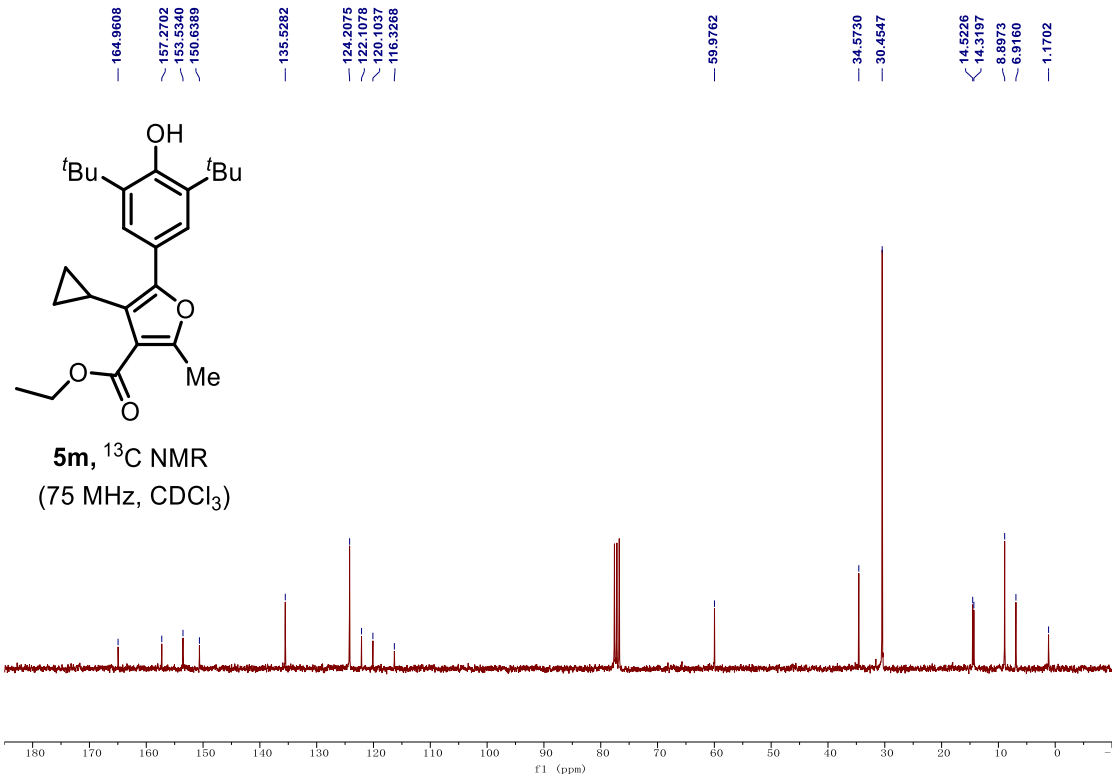
5l, ^{1}H NMR
(300 MHz, $CDCl_3$)



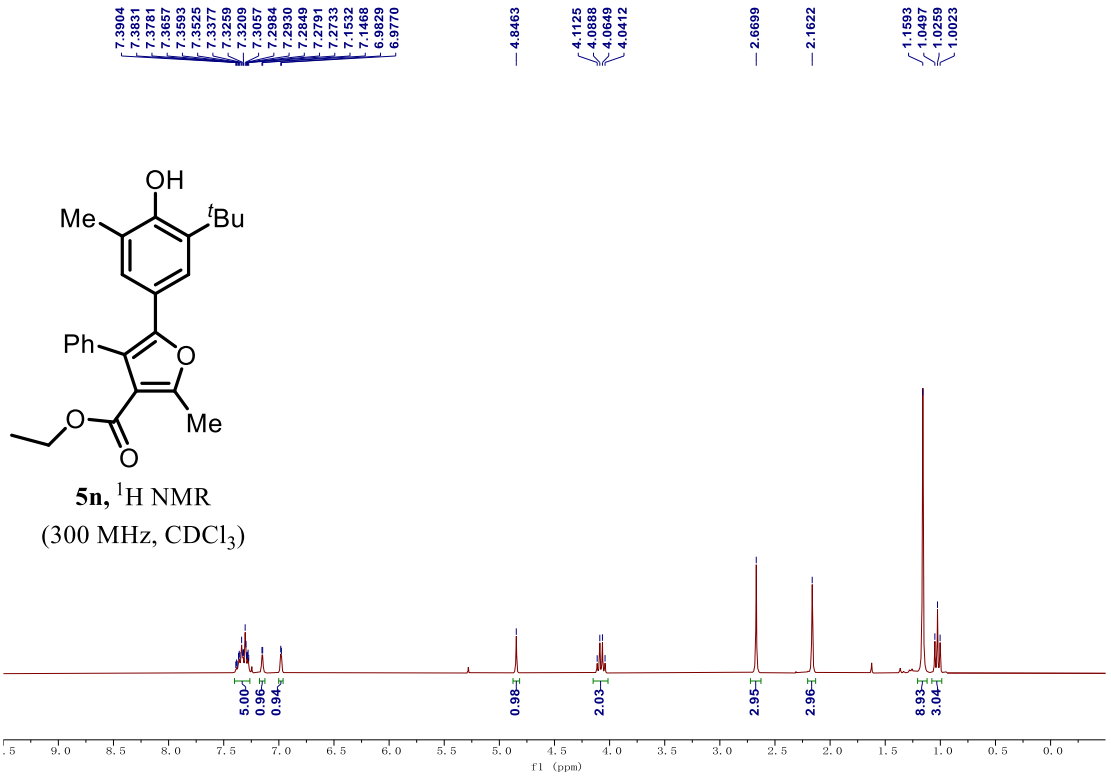
5l, ^{13}C NMR
(75 MHz, $CDCl_3$)



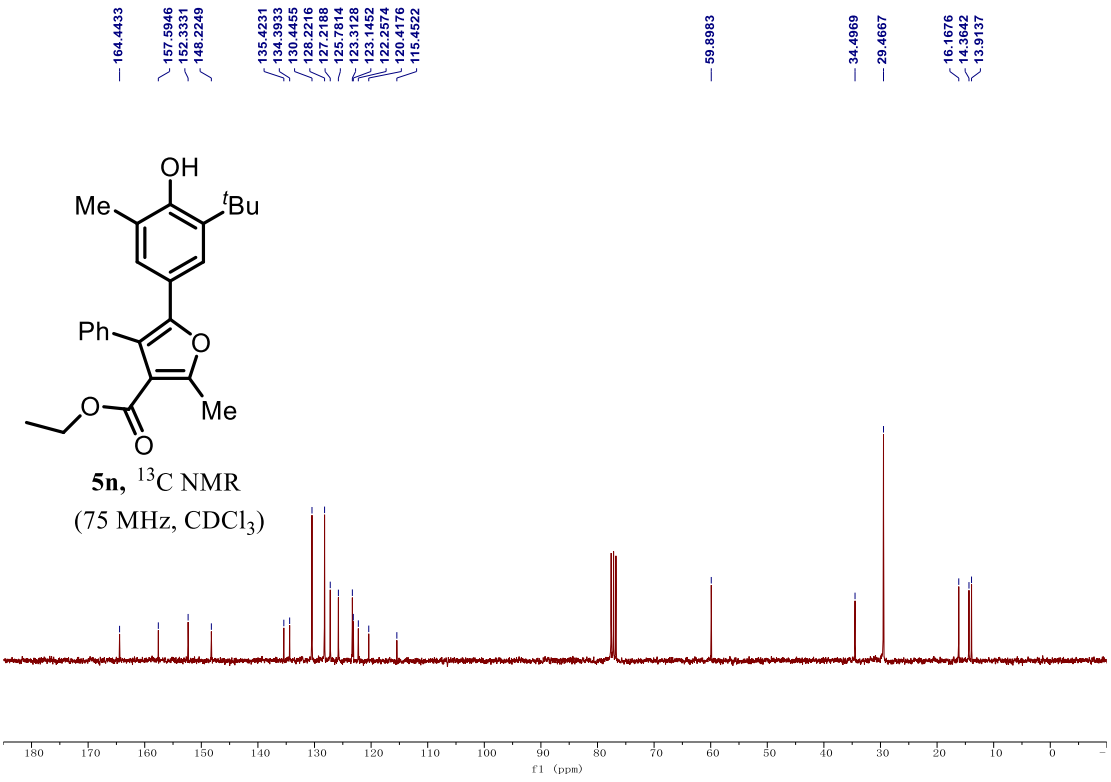
5m, ^{1}H NMR
(300 MHz, $CDCl_3$)



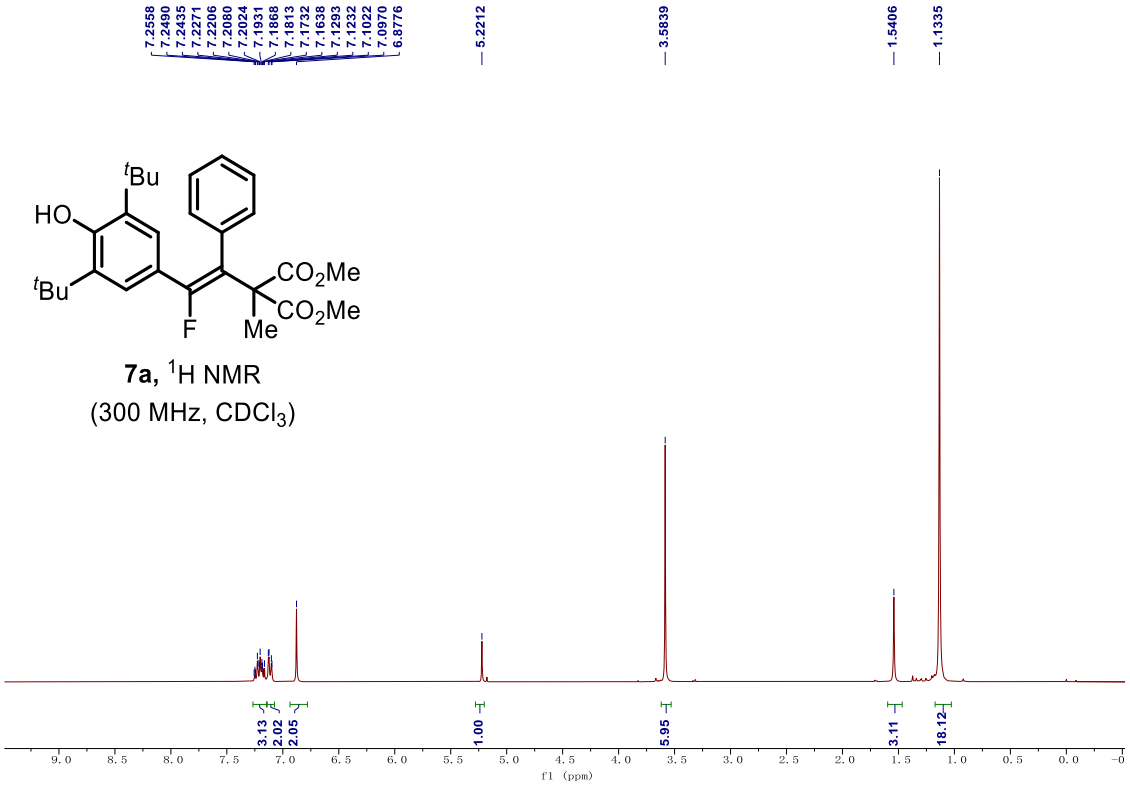
5m, ^{13}C NMR
(75 MHz, $CDCl_3$)



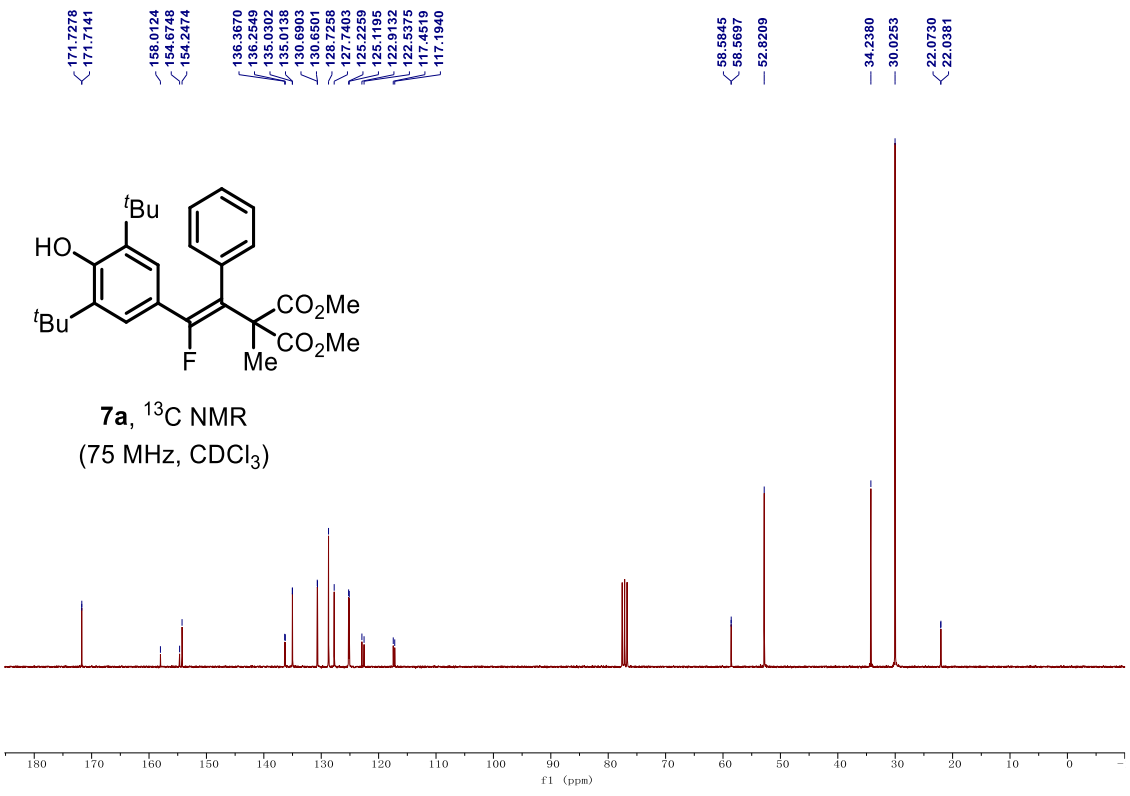
5n, ^{1}H NMR
(300 MHz, $CDCl_3$)



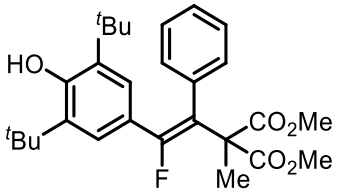
5n, ^{13}C NMR
(75 MHz, $CDCl_3$)



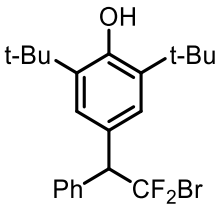
7a, ^{1}H NMR
(300 MHz, $CDCl_3$)



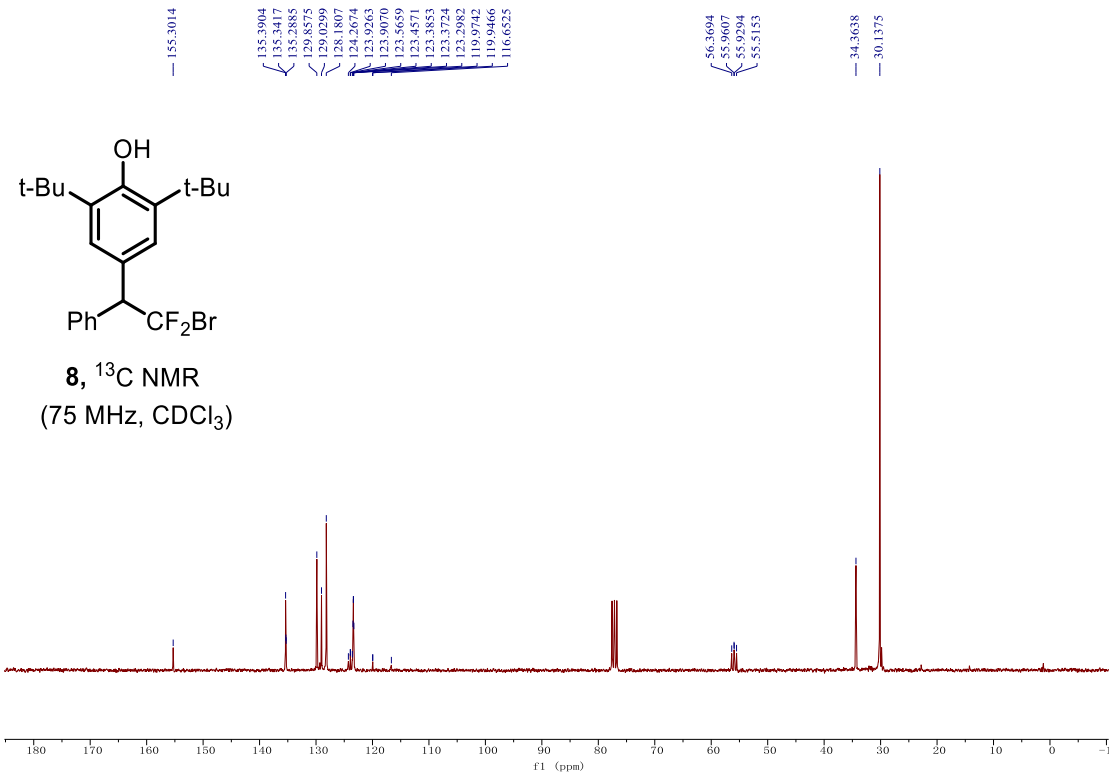
7a, ^{13}C NMR
(75 MHz, $CDCl_3$)



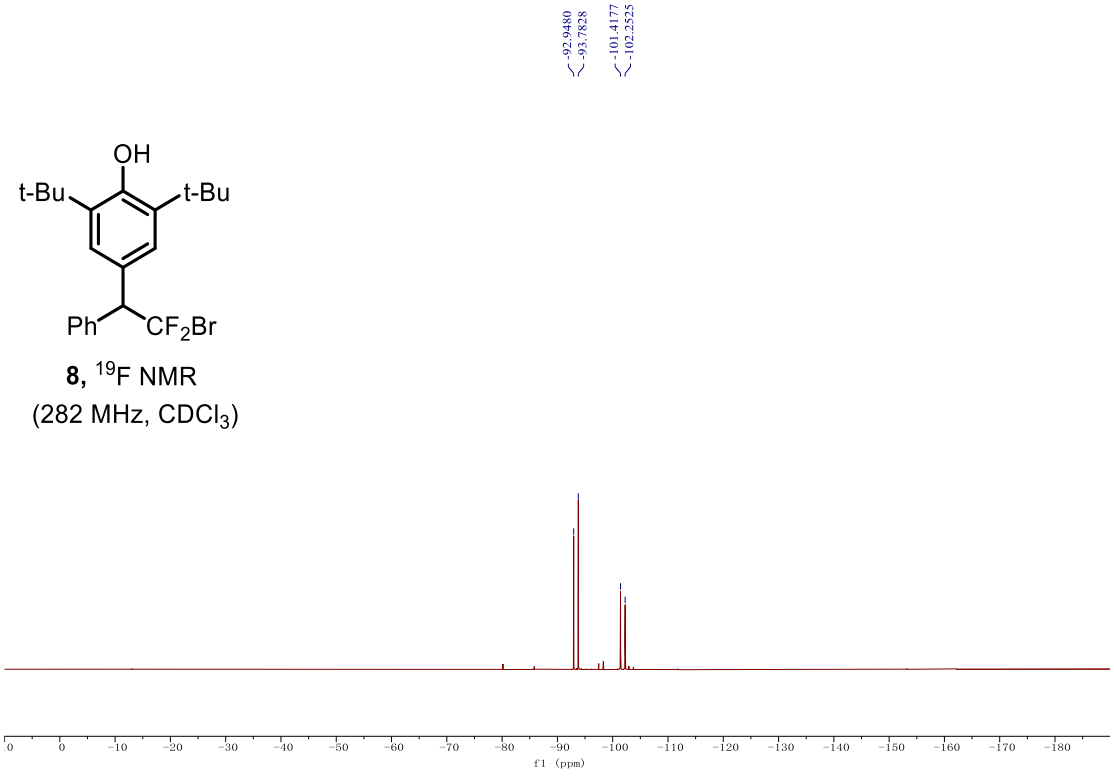
7a, ^{19}F NMR
(282 MHz, $CDCl_3$)



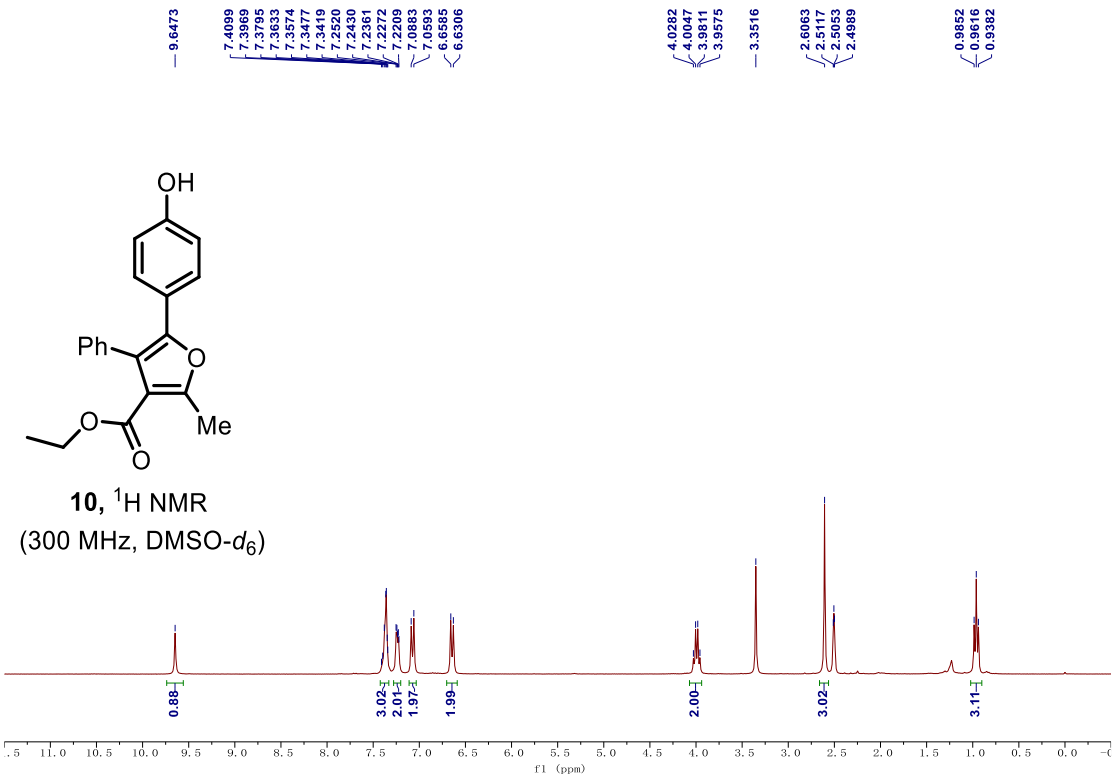
8, ^{1}H NMR
(300 MHz, $CDCl_3$)



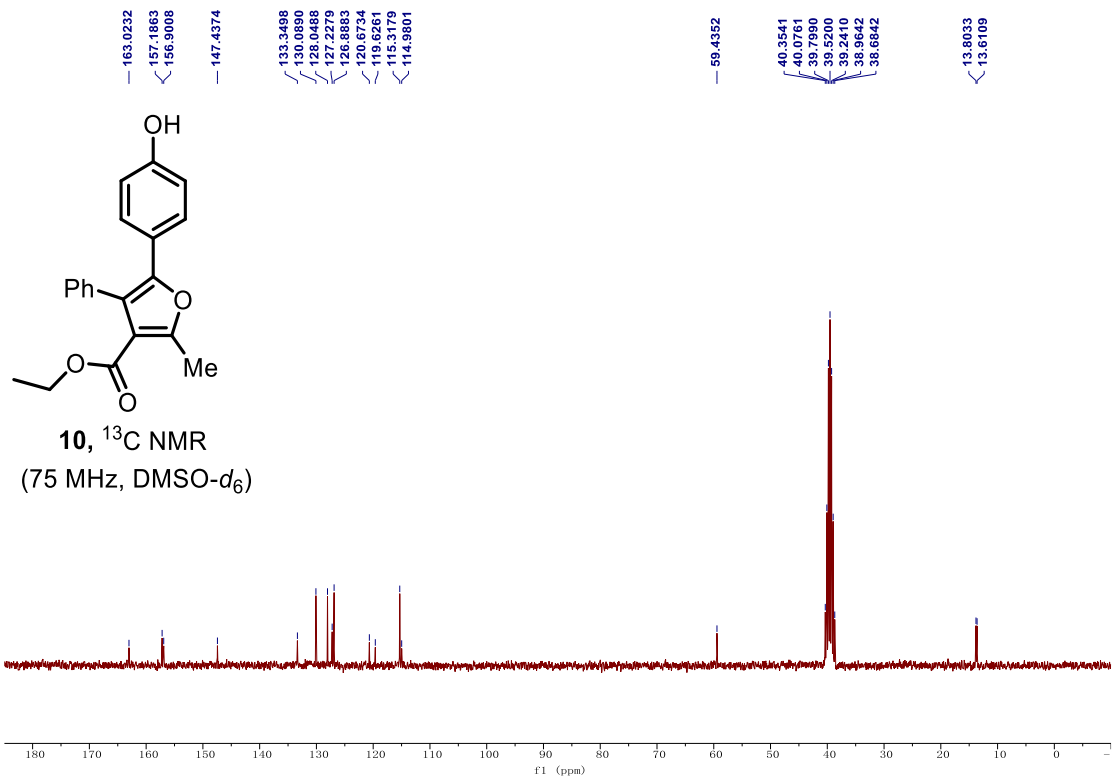
8, ^{13}C NMR
(75 MHz, $CDCl_3$)



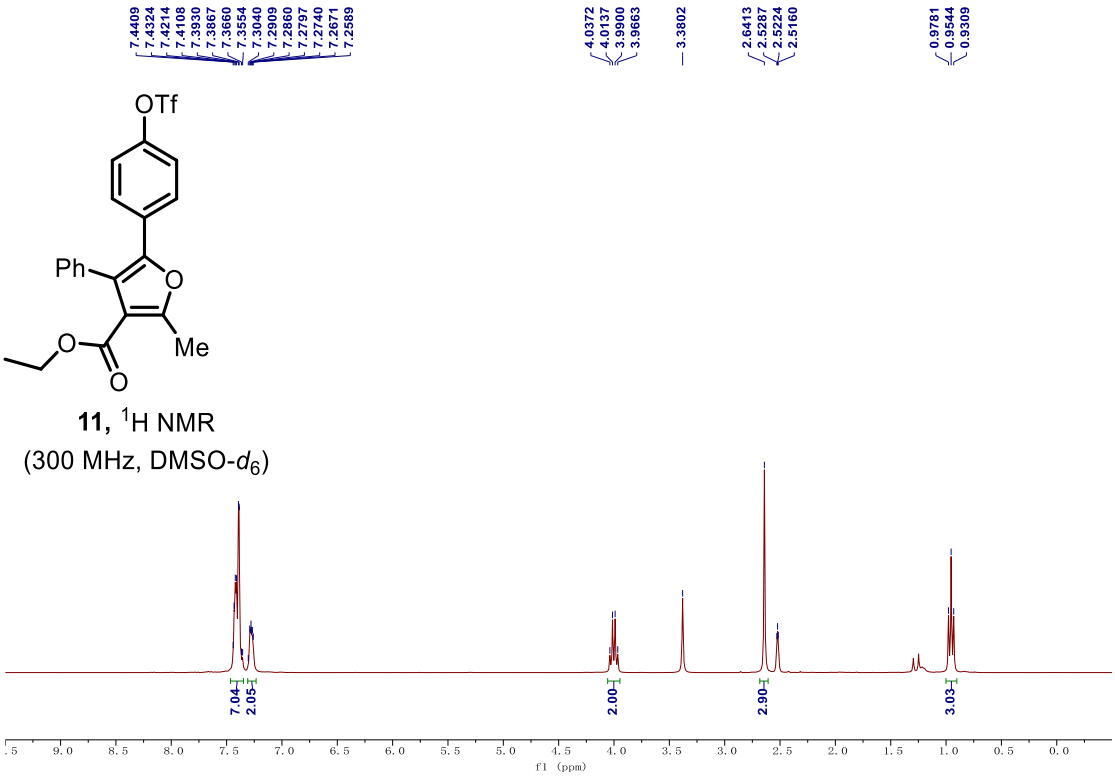
8, ^{19}F NMR
(282 MHz, $CDCl_3$)



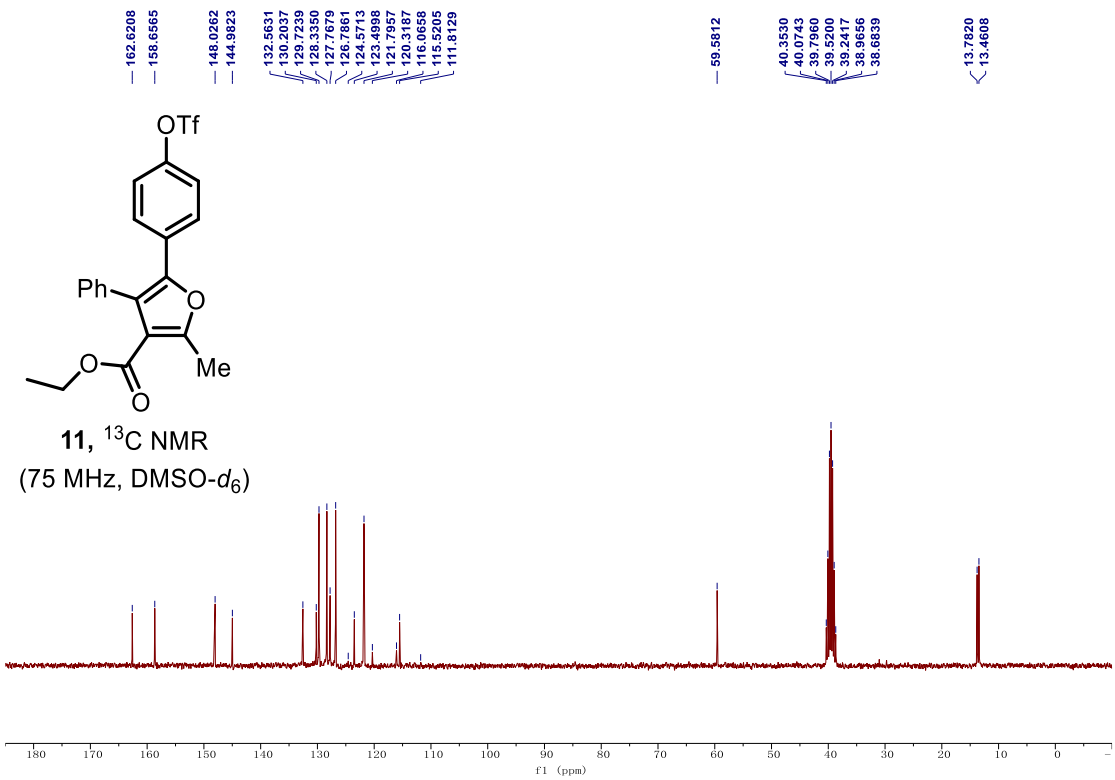
10, ^{1}H NMR
(300 MHz, DMSO-d_6)



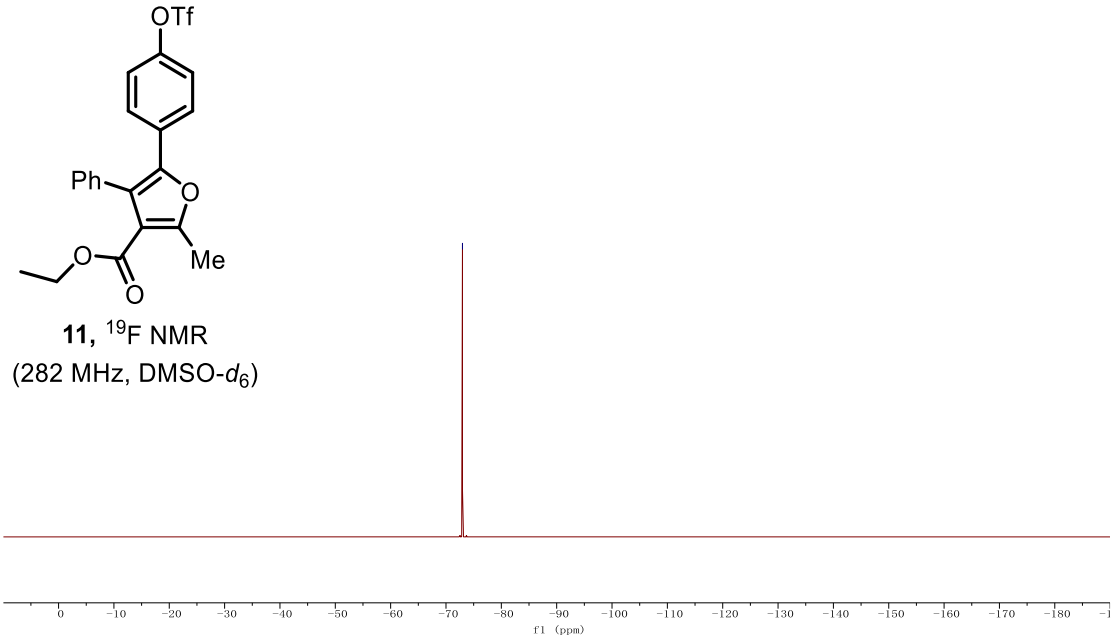
10, ^{13}C NMR
(75 MHz, DMSO-d_6)



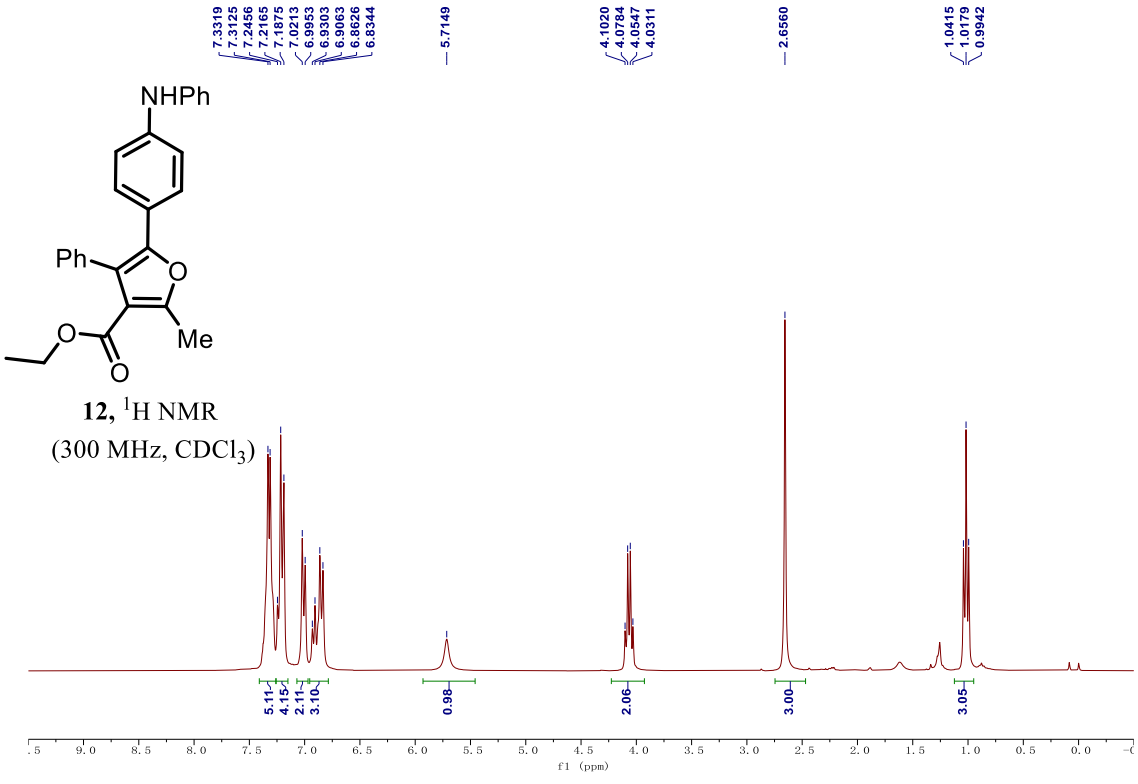
11, ^{1}H NMR
(300 MHz, DMSO-d_6)



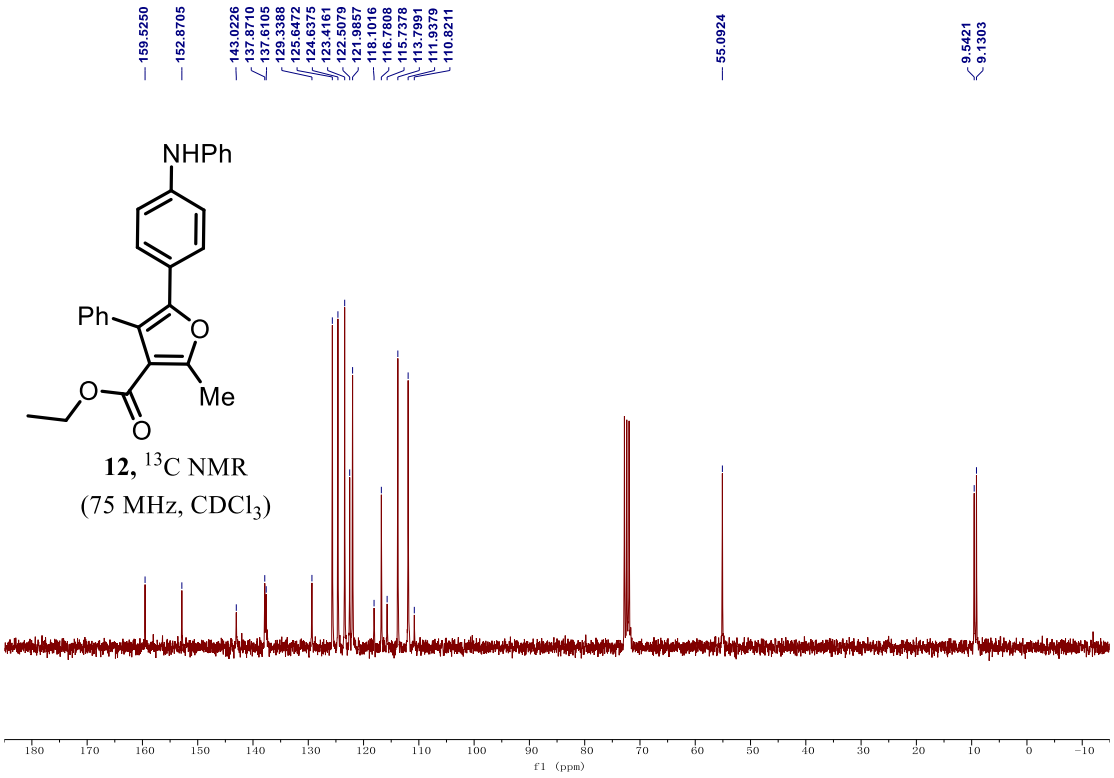
11, ^{13}C NMR
(75 MHz, DMSO-d_6)



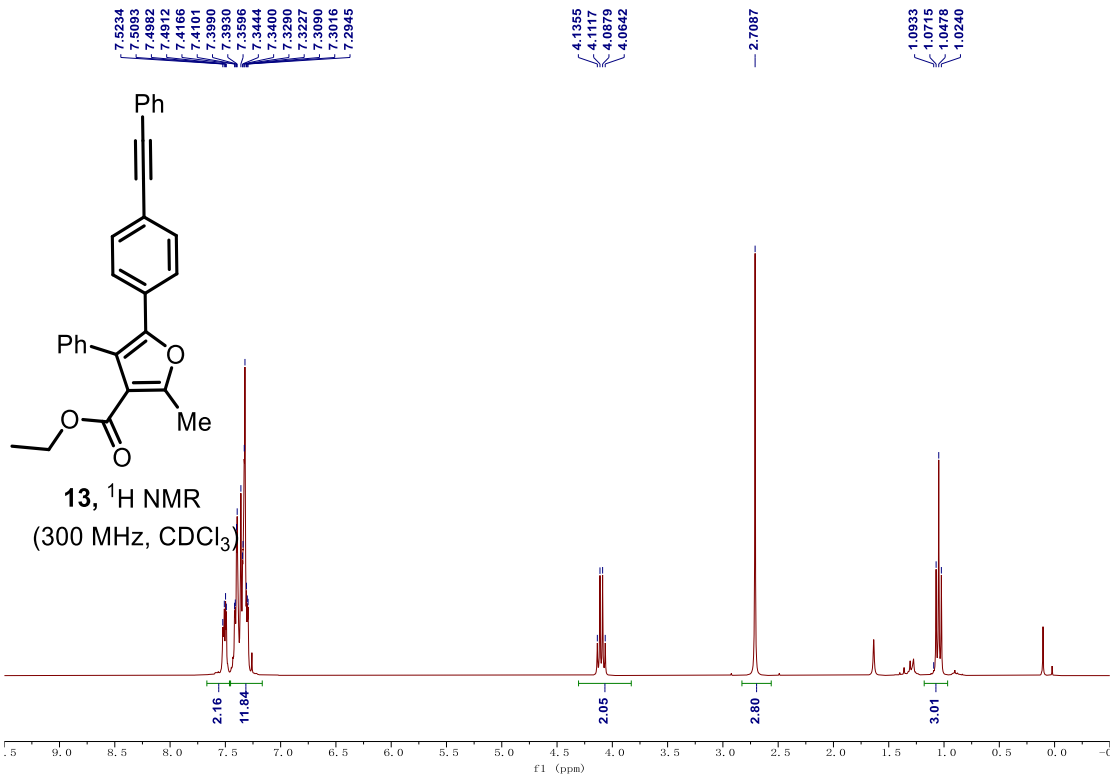
11, ^{19}F NMR
(282 MHz, DMSO-d_6)



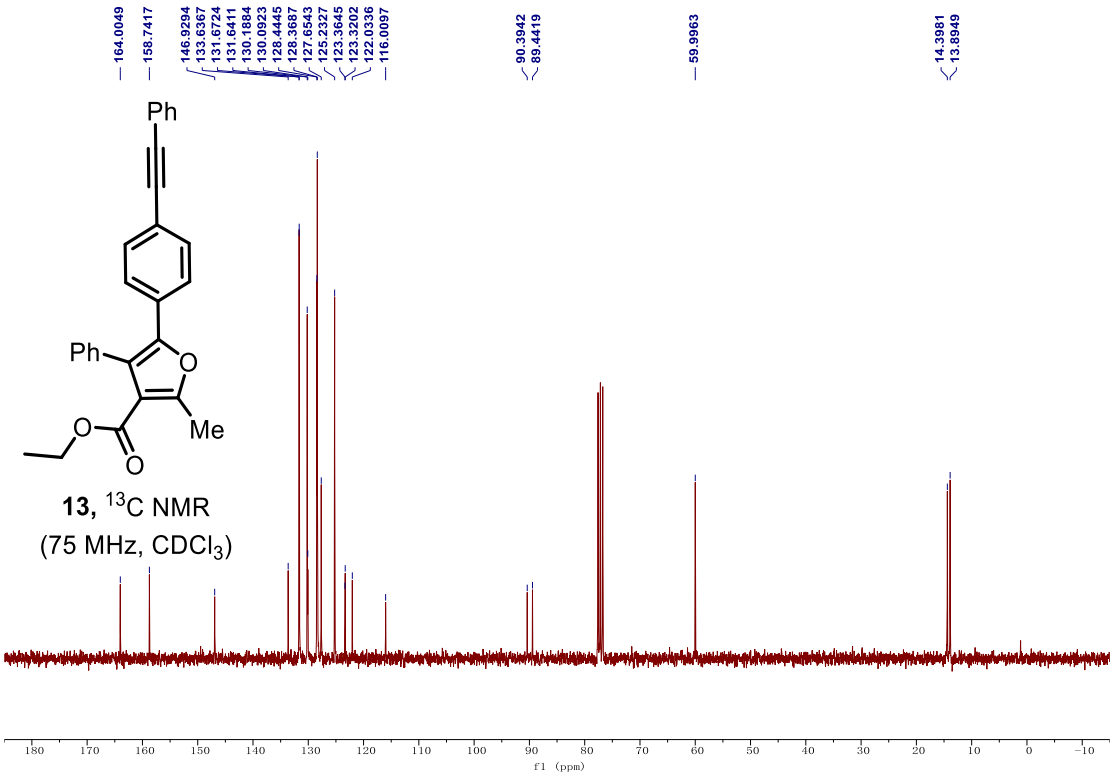
12, ^{1}H NMR
(300 MHz, $CDCl_3$)

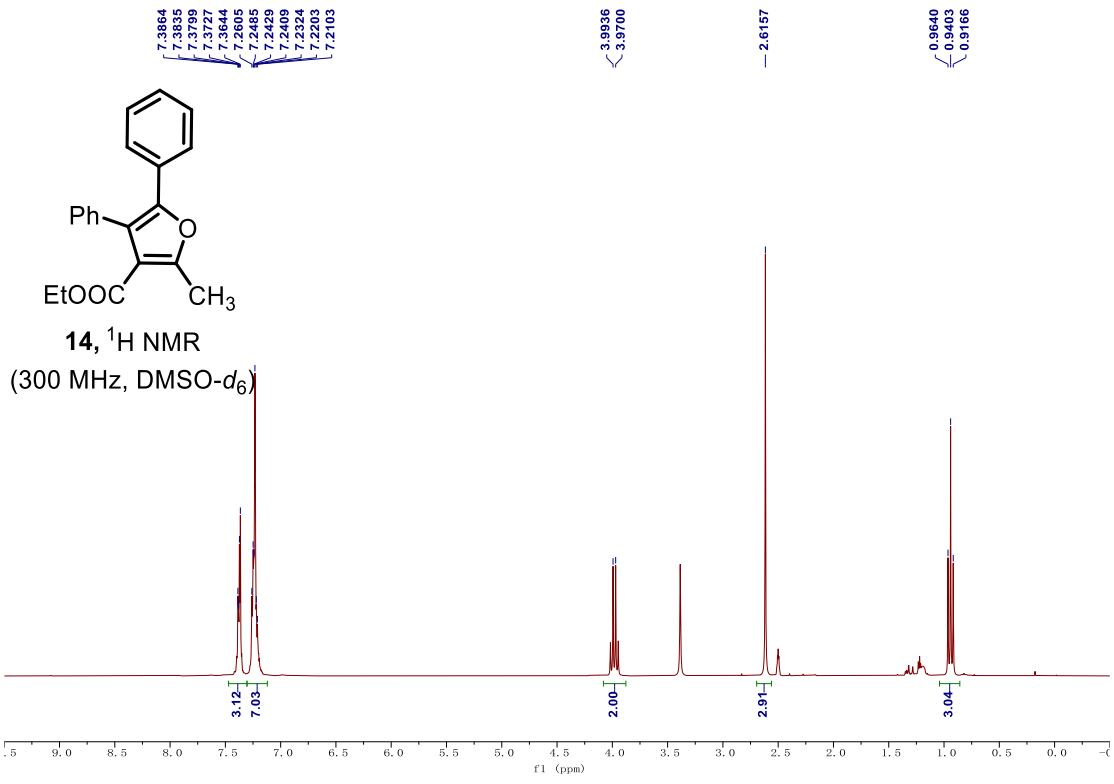


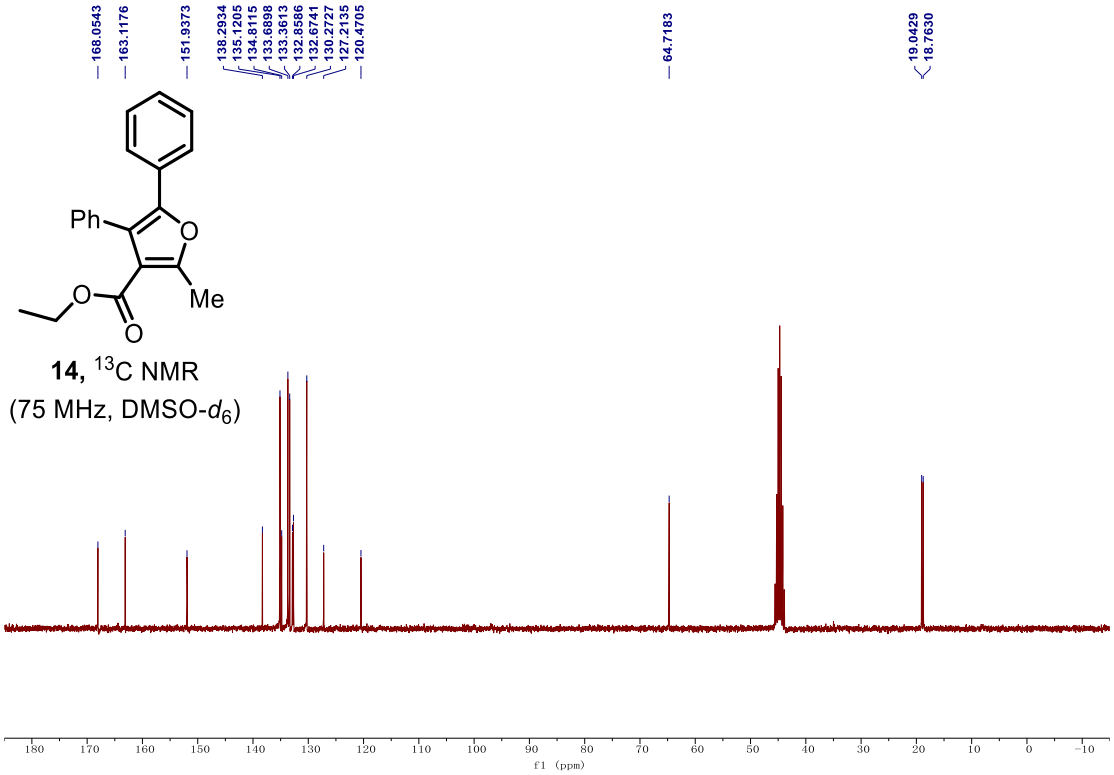
12, ^{13}C NMR
(75 MHz, $CDCl_3$)

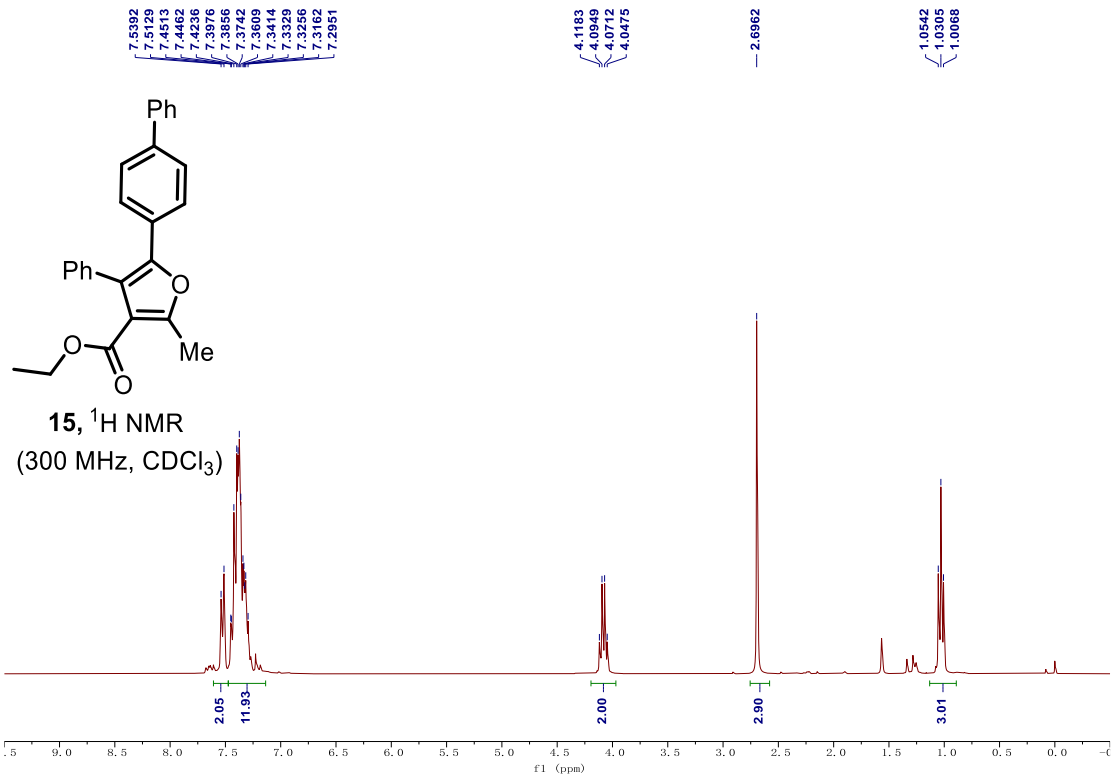


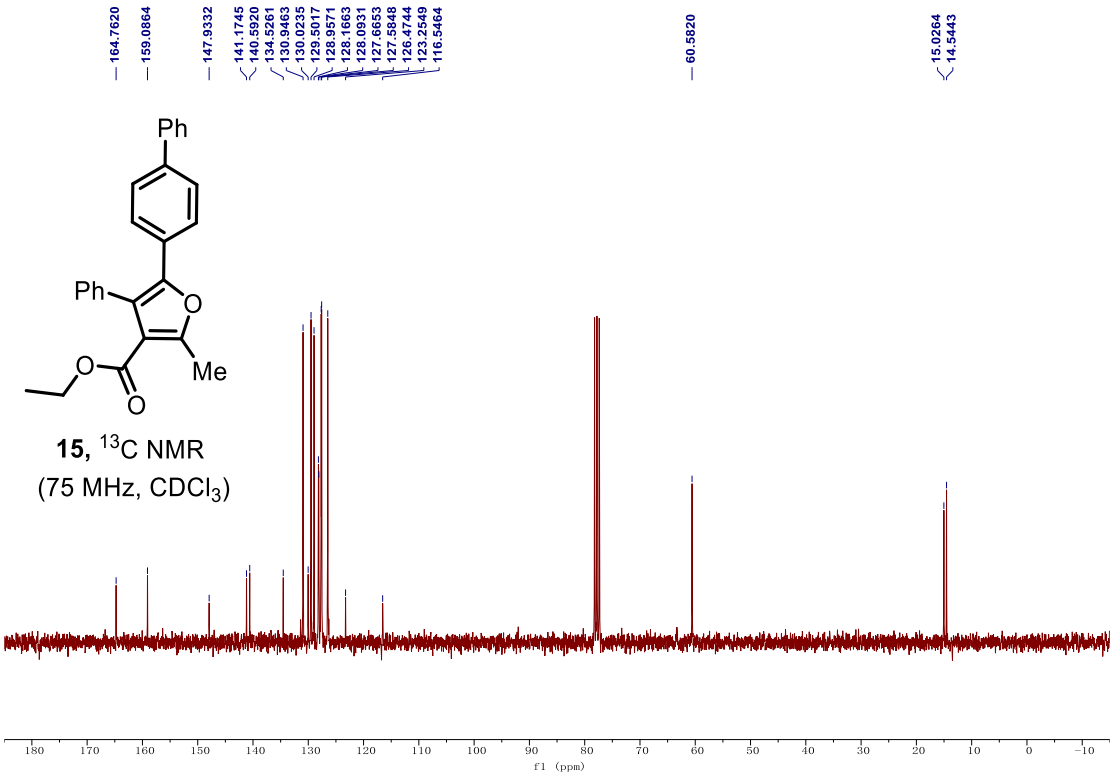
13, ^{1}H NMR
(300 MHz, $CDCl_3$)

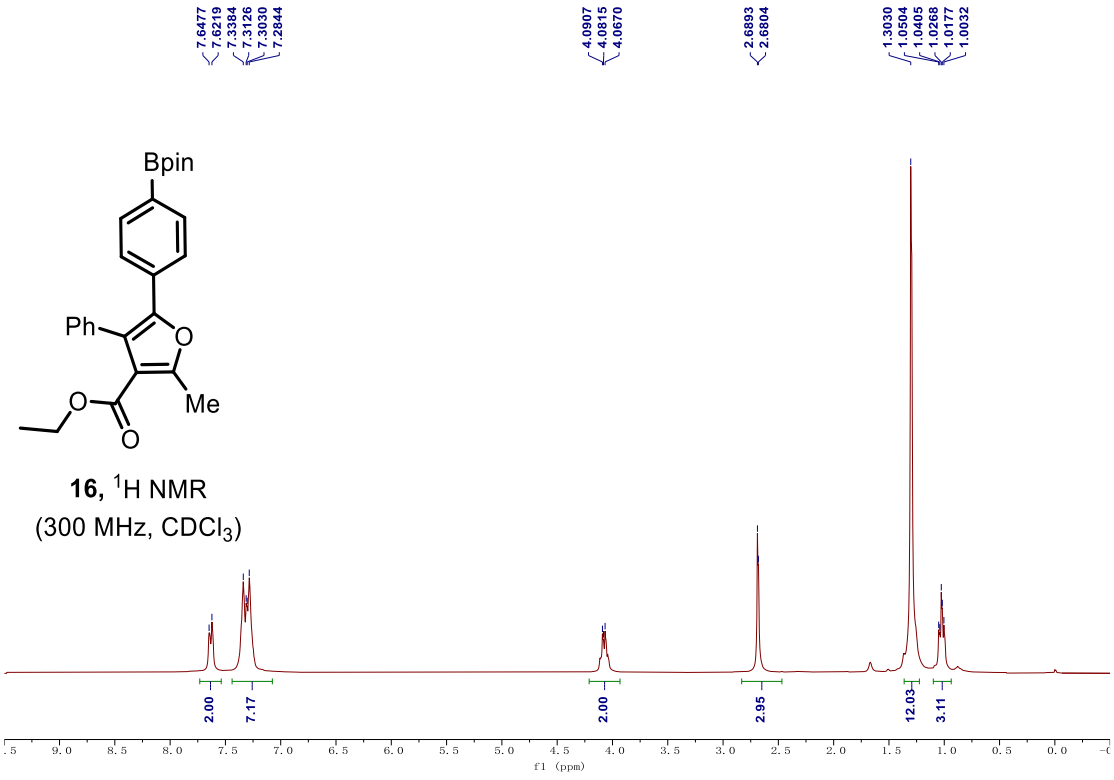

164.0049
158.7417
146.9294
133.6367
131.6724
131.6411
130.1884
130.0923
128.4445
128.3687
127.6543
125.2327
123.3645
123.3202
122.0336
116.0097
90.3942
89.4419
59.9963
14.3981
13.8949
Ph
Ph
O
O
Me
O
13, 13C NMR
(75 MHz, CDCl3)
f1 (ppm)

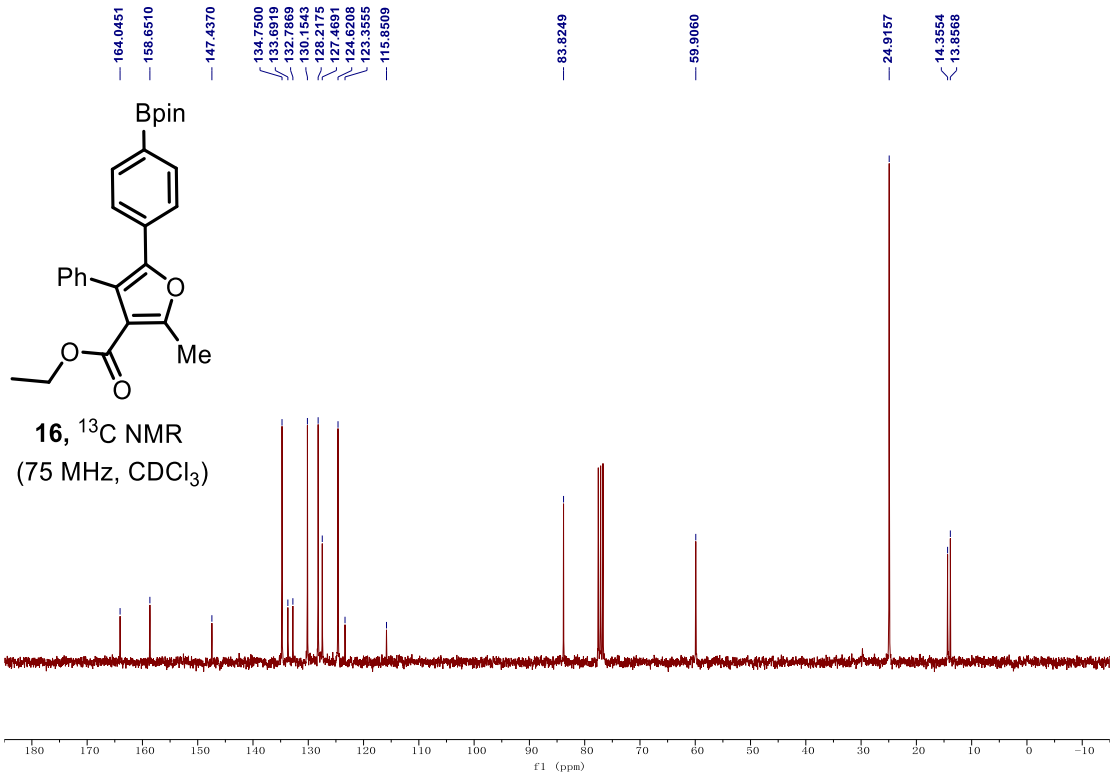

7.3864
7.3835
7.3799
7.3727
7.3644
7.2605
7.2485
7.2429
7.2409
7.2324
7.2203
7.2103
3.9936
3.9700
2.6157
0.9640
0.9403
0.9166
Ph
O
EtOOC
CH3
14, 1H NMR
(300 MHz, DMSO-d6)
3.12
7.03
2.00
2.91
3.04
f1 (ppm)


168.0543
163.1176
151.9373
138.2934
135.1205
134.8115
133.6898
133.3613
132.8586
132.6741
130.2727
127.2135
120.4705
64.7183
19.0429
18.7630
Ph
O
O
O
Me
14, 13C NMR
(75 MHz, DMSO-d6)
f1 (ppm)

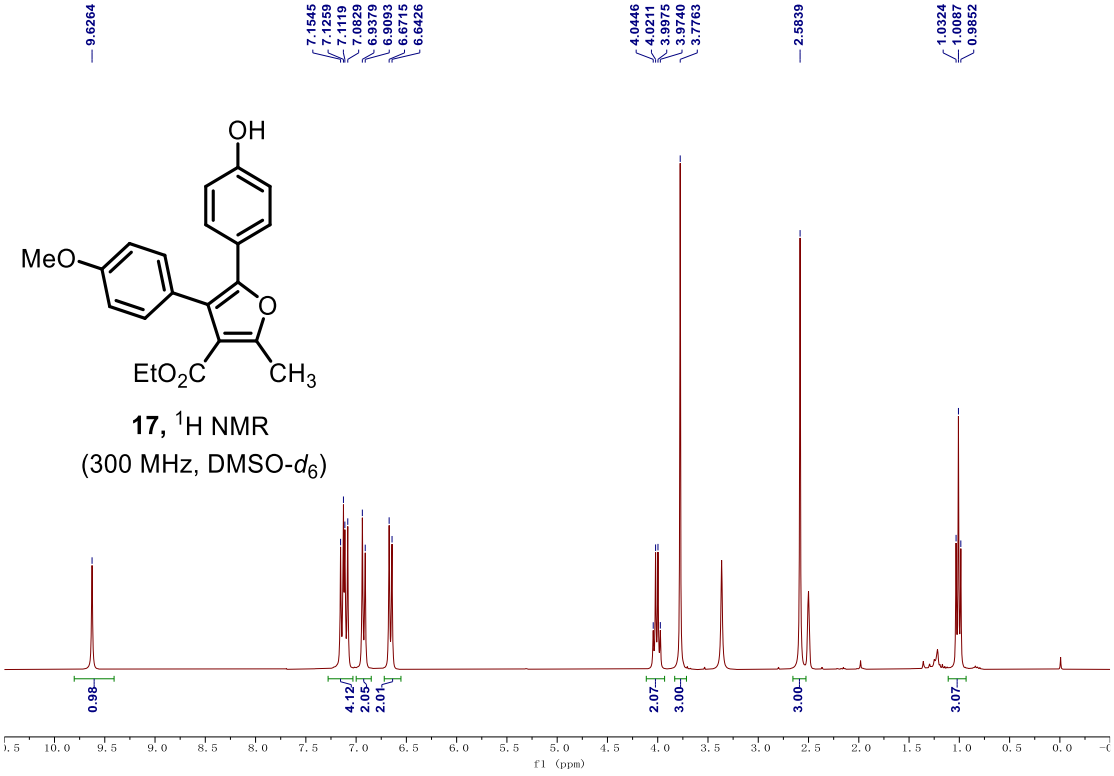

7.5392
7.5129
7.4513
7.4462
7.4236
7.3976
7.3856
7.3742
7.3609
7.3414
7.3329
7.3256
7.3162
7.2951
4.1183
4.0949
4.0712
4.0475
2.6962
1.0542
1.0305
1.0068
Ph
Ph
O
O
O
Me
15, 1H NMR
(300 MHz, CDCl3)
2.05
11.93
2.00
2.90
3.01
f1 (ppm)


164.7620
159.0864
147.9332
141.1745
140.5920
134.5261
130.9463
130.0235
129.5017
128.9571
128.1663
128.0931
127.6653
127.5848
126.4744
123.2549
116.5464
60.5820
15.0264
14.5443
Ph
Ph
O
O
O
Me
O
15, 13C NMR
(75 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

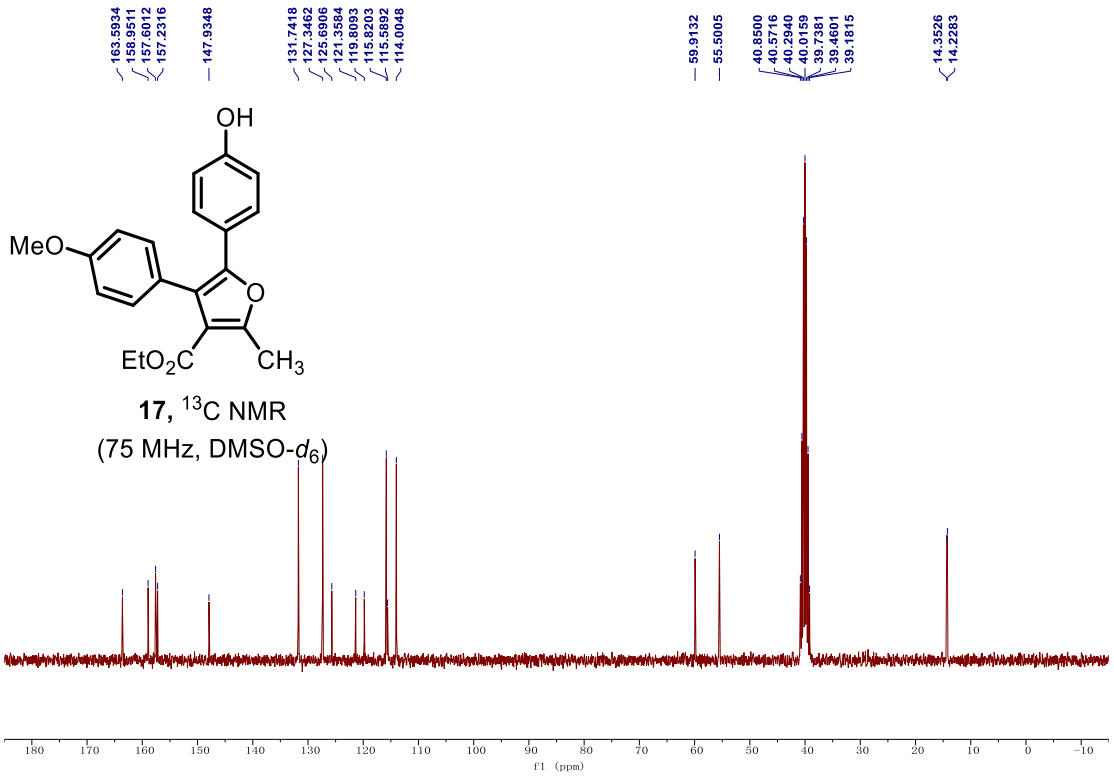

7.6477
7.6219
7.3384
7.3126
7.3030
7.2844
4.0907
4.0815
4.0670
2.6893
2.6804
1.3030
1.0504
1.0405
1.0268
1.0177
1.0032
Bpin
Ph
O
O
O
Me
16, 1H NMR
(300 MHz, CDCl3)
2.00
7.17
2.00
2.95
12.03
3.11
f1 (ppm)



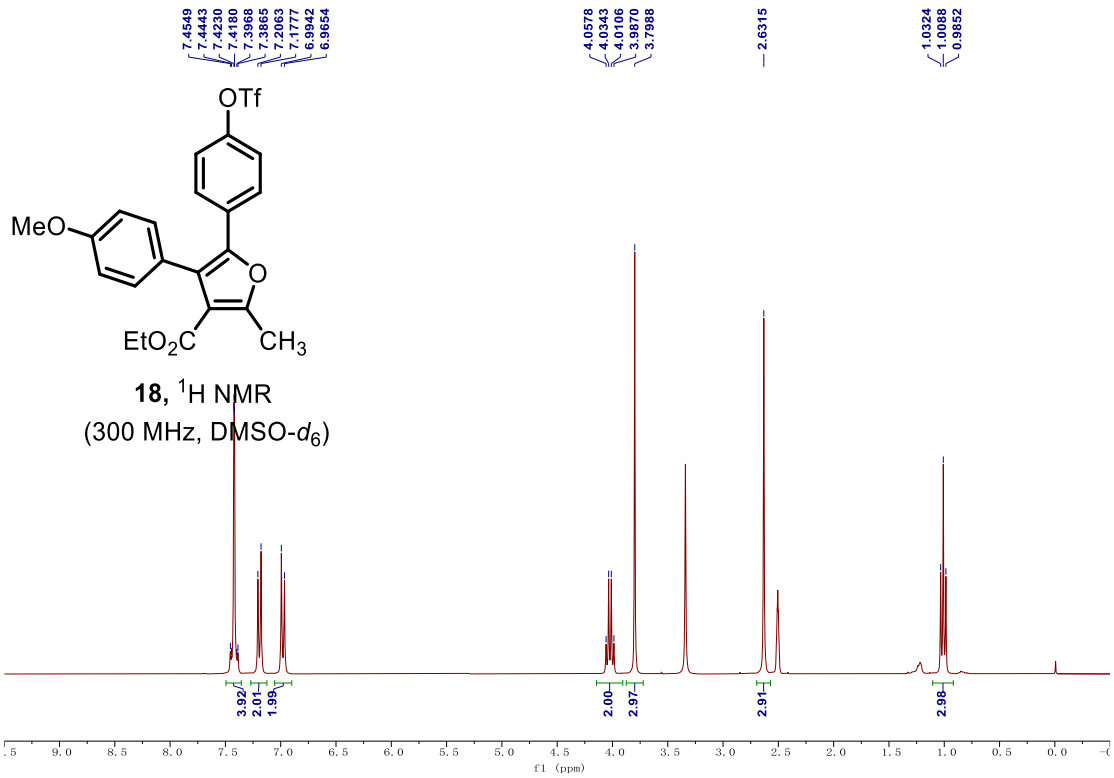
16, ^{13}C NMR
(75 MHz, $CDCl_3$)



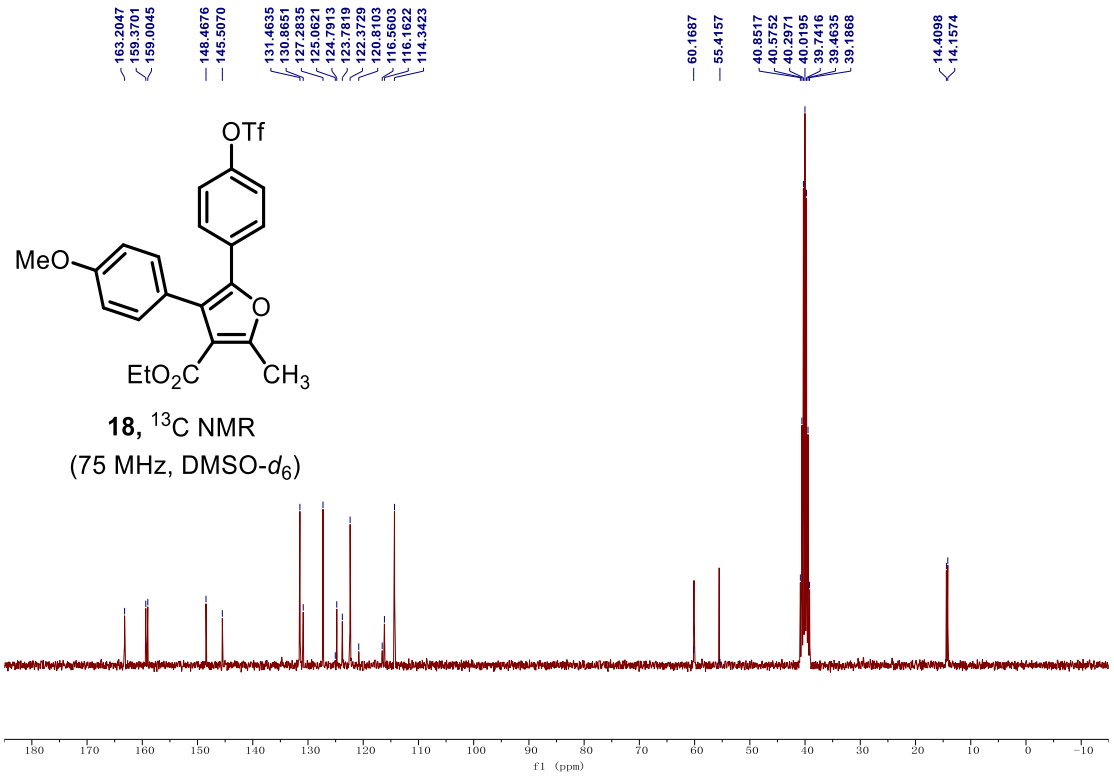
17, ^{1}H NMR
(300 MHz, DMSO-d_6)



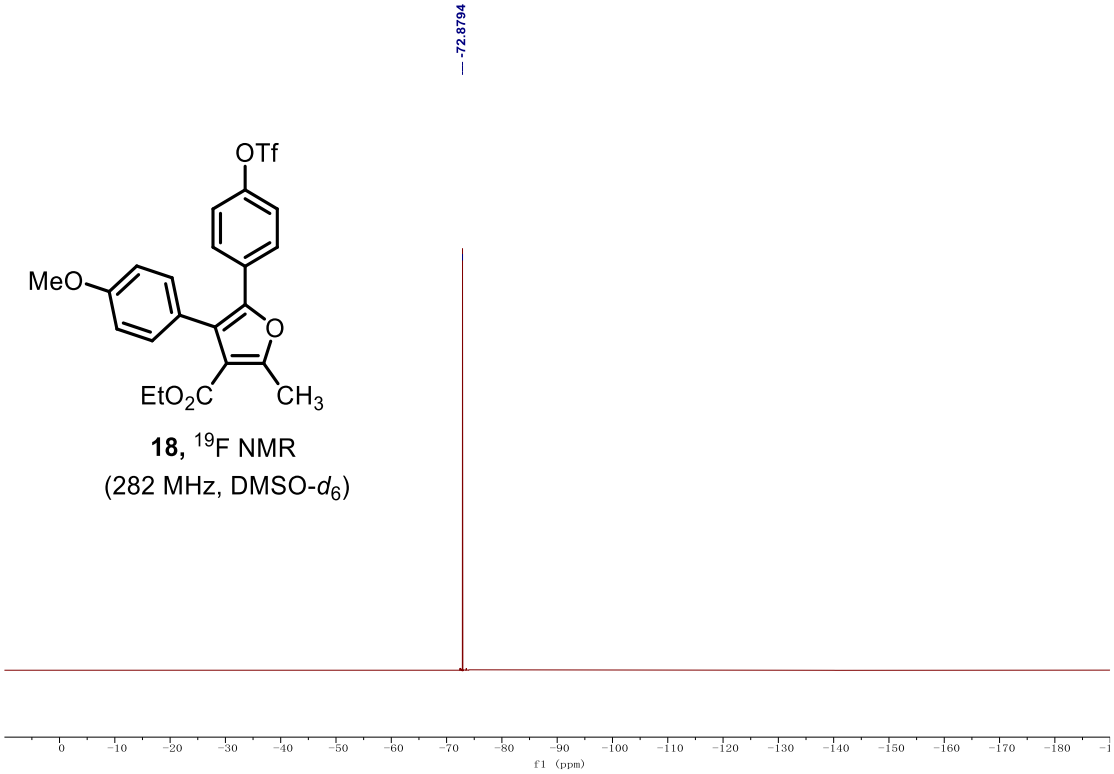
17, ^{13}C NMR
(75 MHz, DMSO-d_6)



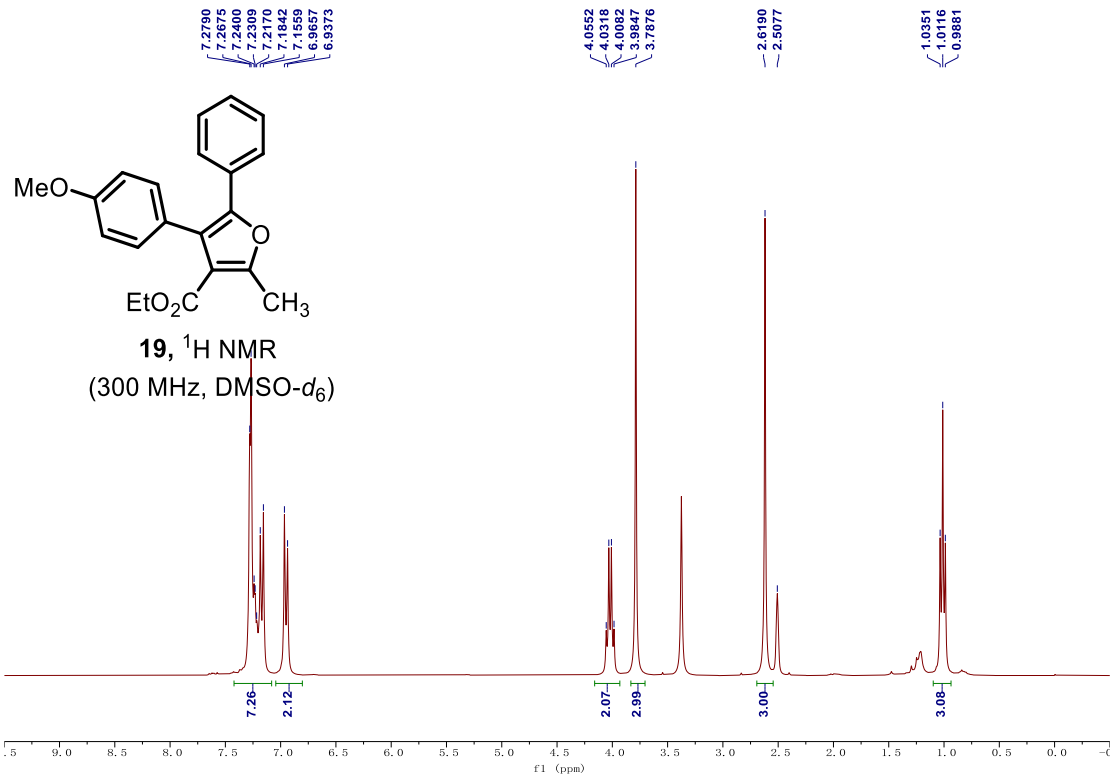
18, ^{1}H NMR
(300 MHz, DMSO-d_6)



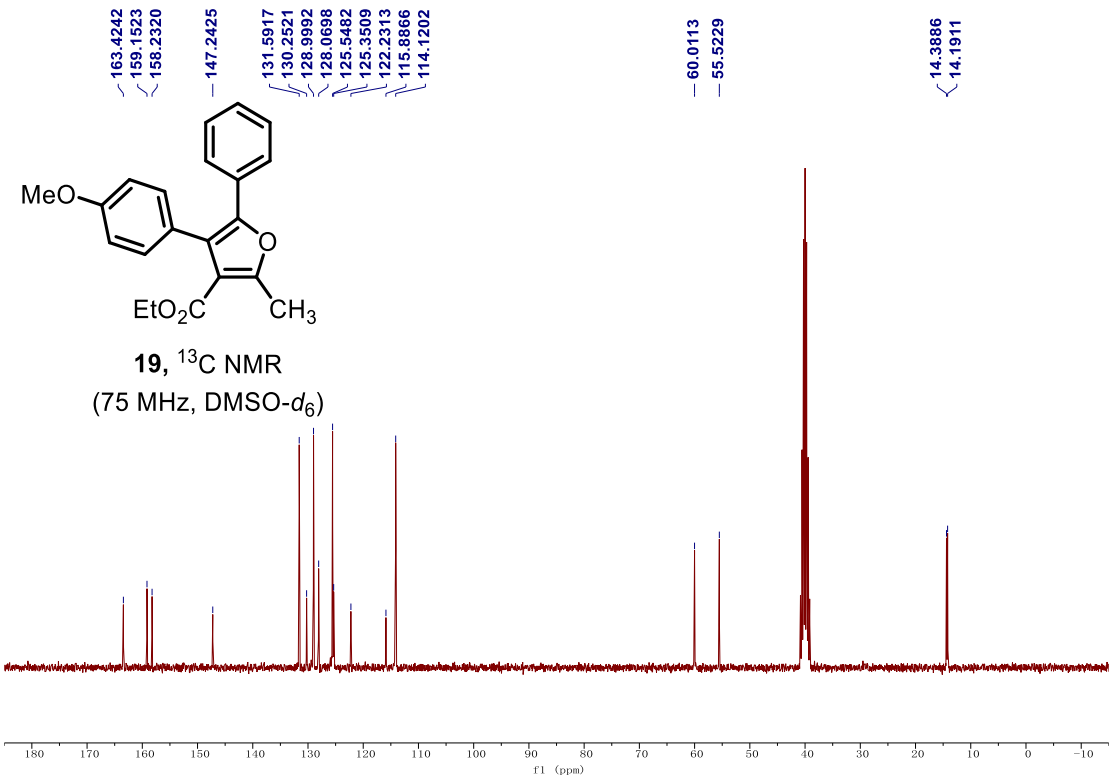
18, ^{13}C NMR
(75 MHz, DMSO-d_6)



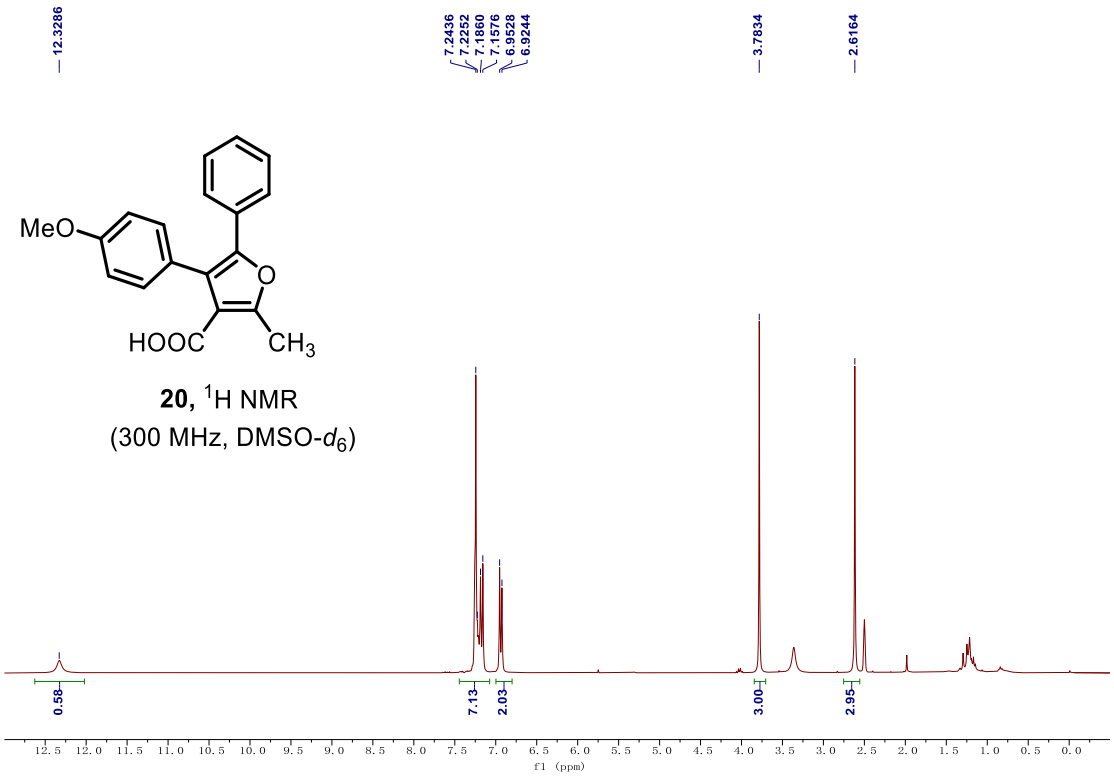
18, ^{19}F NMR
(282 MHz, DMSO-d_6)



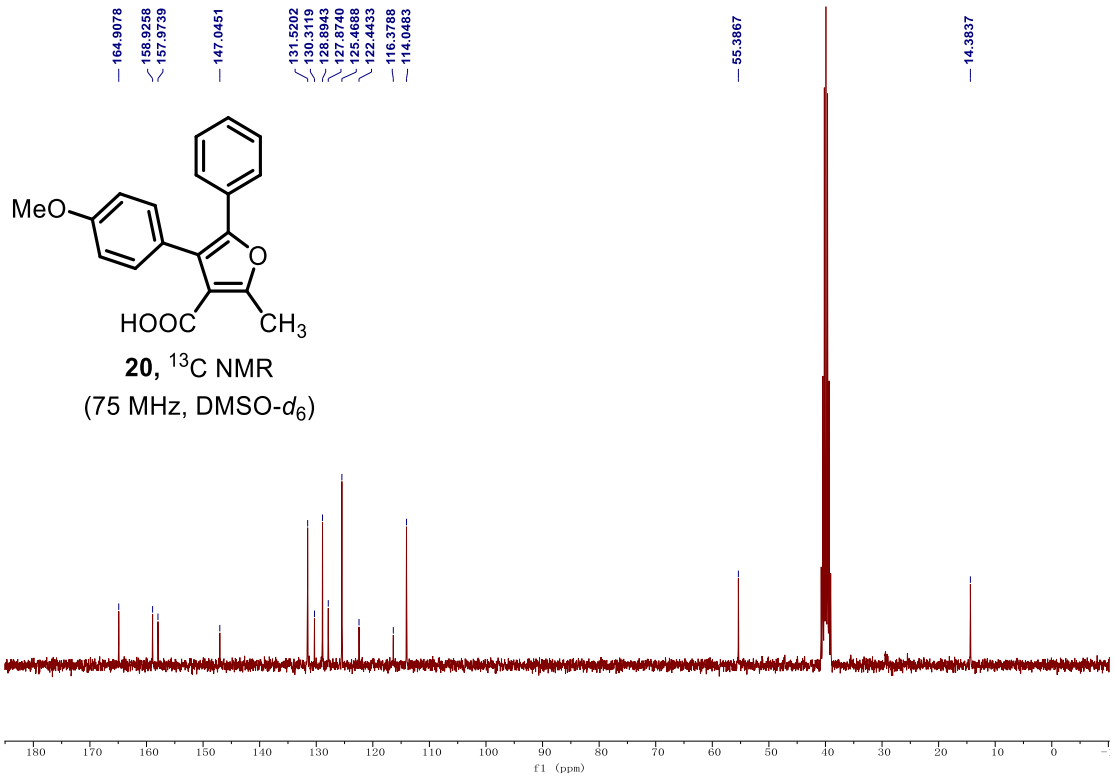
19, ^{1}H NMR
(300 MHz, DMSO-d_6)



19, ^{13}C NMR
(75 MHz, DMSO-d_6)



20, ^{1}H NMR
(300 MHz, DMSO-d_6)



20, ^{13}C NMR
(75 MHz, DMSO-d_6)