Supporting Information

For

Redox-neutral tri-/difluoromethylation of *para*-quinone methides with sodium sulfinates

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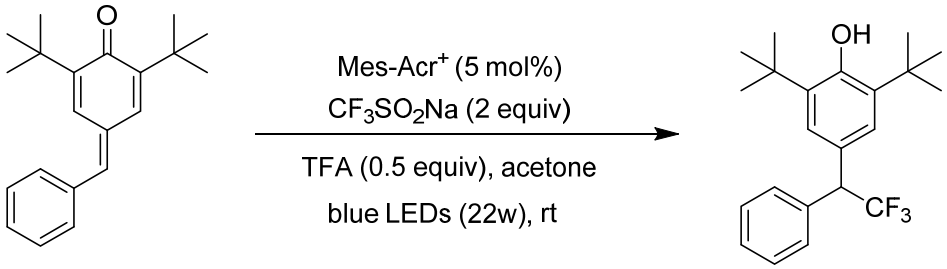
1. General remarks

^{1}H NMR spectra were recorded on 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR, 376 or 564 MHz for ^{19}F NMR) agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR). HRMS was recorded on a GCT Premier^{TM} (CI) Mass Spectrometer. Infrared (FT-IR) spectra were recorded on a Varian 1000FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW, X-4B and values are uncorrected. All commercially available reagents and solvents were used as received unless otherwise specified. The substrates we are readily prepared according to known methods (*Org. Lett*. **2015**, 17, 3390−3393; *Macromolecules* **2013**, 46, 5924−5928).

2. General procedure for synthesis of *p*-quinone methides

In a Dean-Stark apparatus, a mixture of aldehyde (1 equiv.) and 2,6-di-*tert*-butylphenol (1 equiv.) in toluene (0.25 M) was placed and refluxed. Piperidine (2 equiv.) was added to this reaction mixture in a drop-wise manner within an hour and the resultant mixture was stirred at reflux temperature for 12 h. The reaction mixture was cooled to 100 °C and acetic anhydride (2 equiv.) was added and the resulting solution was stirred for 30 more minutes at the same temperature. The reaction mixture was then cooled to room temperature and poured in to ice cold water (50 mL) and extracted with dichloromethane (50 mL × 2). The combined organic layer was dried over anhydrous sodium sulphate, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to obtain a pure *p*-quinone methide.

3. Typical experimental procedure

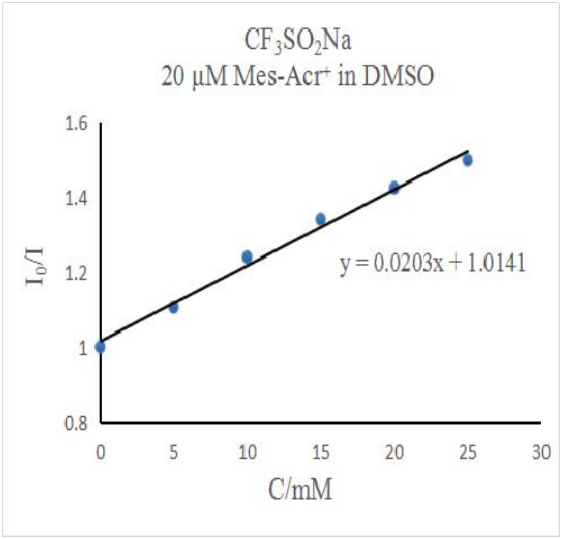


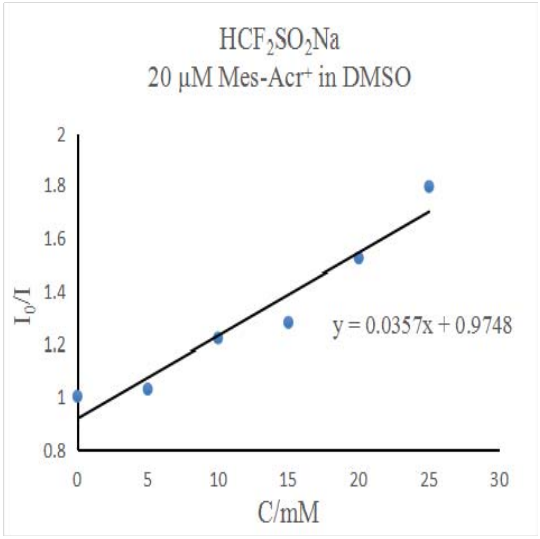
1a **2a**

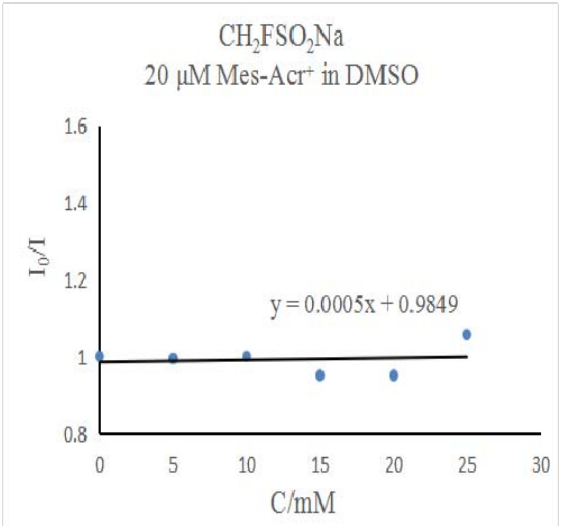
To a suspension of **1a** (58.8 mg, 0.2 mmol), CF_3SO_2Na (62.4 mg, 0.4 mmol) and *N*-methyl-9-mesityl acridinium perchlorate (4.1 mg, 0.01 mmol) in acetone (2 mL) was added TFA (7.7 μL, 0.1 mmol) at rt. The resulting mixture was stirred upon 22W blue LEDs irradiation under argon balloon. After the reaction was finished, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to give **2a** as colorless oil (71.0 mg, 98% yield).

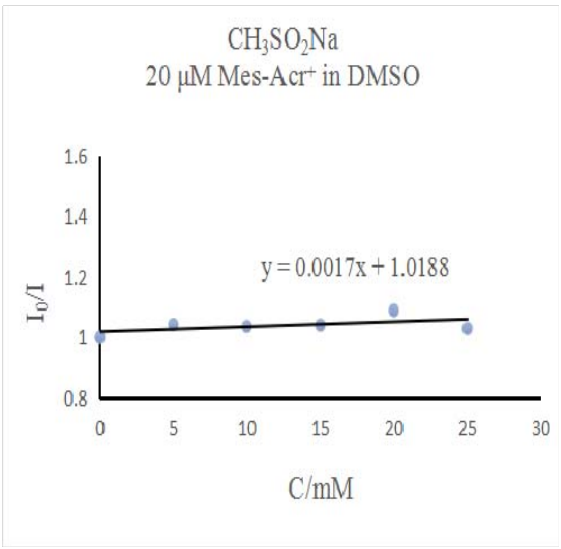
4. Fluorescence quenching experiments

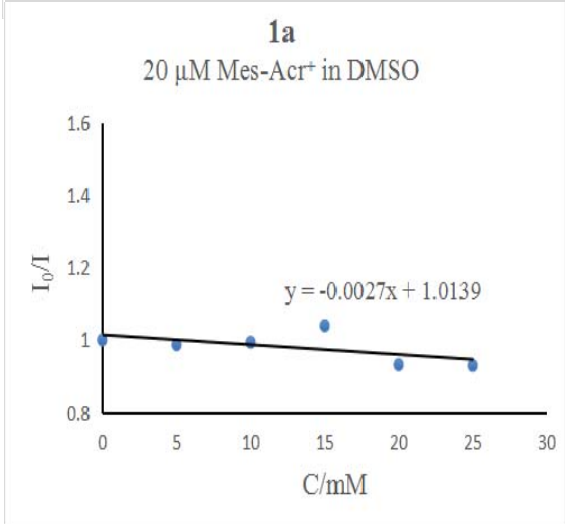
Emission intensities were recorded using LS55 Luminescence Spectrometer for all experiments. All Mes-Acr+ solutions were excited at 450 nm and the emission intensity was collected at 490-570 nm. In a typical experiment, the DMSO solution of Mes-Acr$^+$ (0.02 mM) was added the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing with nitrogen for 10 min, the emission spectra of the samples were collected. The results showed that CF_3SO_2Na and HCF_2SO_2Na quenched the photoexcited Mes-Acr$^+$ effectively.



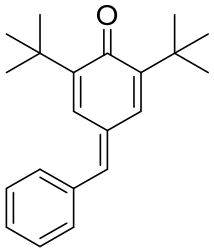




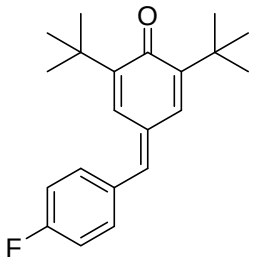




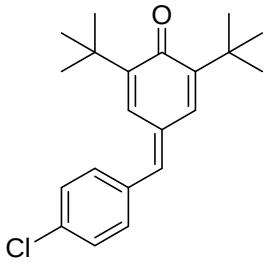
4. Characterization of the substrates and products



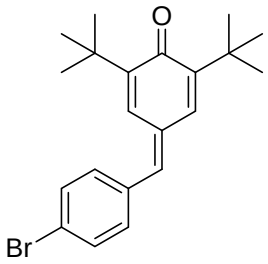
4-Benzylidene-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1a): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (d, J = 2.2 Hz, 1H), 7.48 – 7.43 (m, 4H), 7.41 – 7.37 (m, 1H), 7.19 (s, 1H), 7.03 (d, J = 2.3 Hz, 1H), 1.35 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 149.5, 147.9, 142.6, 136.0, 135.2, 132.1, 130.4, 129.2, 128.9, 127.9, 35.6, 35.1, 29.67, 29.65.



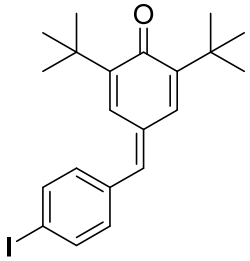
2,6-Di-tert-butyl-4-(4-fluorobenzylidene)cyclohexa-2,5-dien-1-one (1b): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 3H), 7.19 – 7.10 (m, 3H), 7.00 (s, 1H), 1.33 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.7, 163.17 (d, $J_{C\text{-}F}$ = 251.3 Hz), 149.7, 148.0, 141.1, 135.1, 132.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 132.22 (d, $J_{C\text{-}F}$ = 3.4 Hz) 132.0, 127.5, 116.1 (d, $J_{C\text{-}F}$ = 21.8 Hz), 35.6, 35.2, 29.7, 29.6.



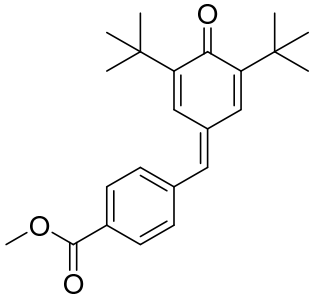
2,6-Di-tert-butyl-4-(4-chlorobenzylidene)cyclohexa-2,5-dien-1-one (1c): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 3H), 7.38 (d, J = 8.3 Hz, 2H), 7.11 (s, 1H), 6.99 (s, 1H), 1.33 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.7, 149.9, 148.2, 140.8, 135.3, 135.0, 134.5, 132.5, 131.6, 129.2, 127.4, 35.6, 35.2, 29.68, 29.65.



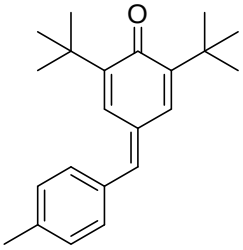
4-(4-Bromobenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1d): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 1H), 6.98 (s, 1H), 1.32 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 149.8, 148.2, 140.7, 134.9, 134.9, 132.5, 132.1, 131.8, 127.3, 123.6, 35.6, 35.1, 29.7, 29.6.



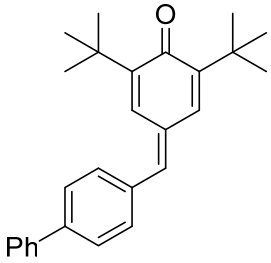
2,6-Di-tert-butyl-4-(4-iodobenzylidene)cyclohexa-2,5-dien-1-one (1e): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.43 (s, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.06 (s, 1H), 6.98 (s, 1H), 1.32 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 149.9, 148.2, 140.9, 138.1, 135.4, 135.0, 132.6, 131.9, 127.3, 95.5, 35.6, 35.2, 29.7, 29.6.



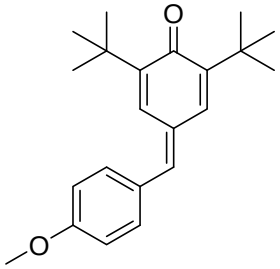
Methyl 4-((3,5-di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzoate (1f): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.45 (s, 1H), 7.17 (s, 1H), 7.01 (s, 1H), 3.95 (s, 3H), 1.33 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 186.7, 166.7, 150.1, 148.6, 140.6, 140.5, 134.9, 133.5, 130.3, 130.0, 127.5, 52.5, 35.7, 35.2, 29.67, 29.65.



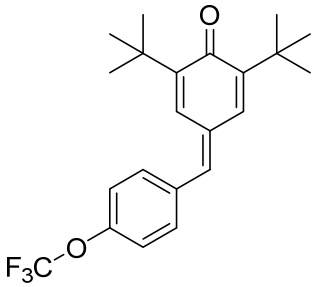
2,6-Di-tert-butyl-4-(4-methylbenzylidene)cyclohexa-2,5-dien-1-one (1g): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.37 (d, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 7.6 Hz, 2H), 7.16 (s, 1H), 7.01 (s, 1H), 2.40 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 149.2, 147.6, 143.0, 139.7, 135.4, 133.3, 131.5, 130.5, 129.7, 128.0, 35.6, 35.1, 29.69, 29.65, 21.6.



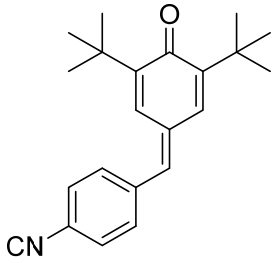
4-([1,1'-Biphenyl]-4-ylmethylene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 7.5 Hz, 2H), 7.62 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.2 Hz, 1H), 7.22 (s, 1H), 7.06 (s, 1H), 1.37 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.7, 149.5, 147.9, 142.2, 142.0, 140.1, 135.3, 135.1, 132.1, 131.1, 129.1, 128.0, 127.9, 127.5, 127.2, 35.6, 35.2, 29.73, 29.68.



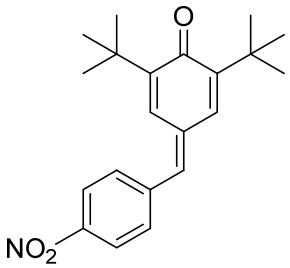
2,6-Di-tert-butyl-4-(4-methoxybenzylidene)cyclohexa-2,5-dien-1-one (1i): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.13 (s, 1H), 7.02 – 6.96 (m, 3H), 3.87 (s, 3H), 1.33 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 160.7, 149.1, 147.3, 142.8, 135.5, 132.3, 130.6, 128.8, 127.9, 114.6, 55.5, 35.6, 35.1, 29.72, 29.66.



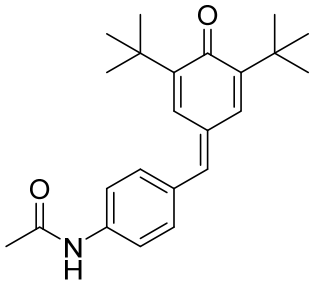
2,6-Di-tert-butyl-4-(4-(trifluoromethoxy)benzylidene)cyclohexa-2,5-dien-1-one (1j): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (s, 1H), 7.30 (d, *J* = 8.2 Hz, 2H), 7.13 (s, 1H), 7.00 (s, 1H), 1.33 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.7, 150.0, 149.6, 148.3, 140.3, 135.0, 134.6, 132.7, 131.8, 127.3, 121.2, 120.55 (d, J_{C-F} = 258.0 Hz), 35.6, 35.2, 29.7, 29.6.



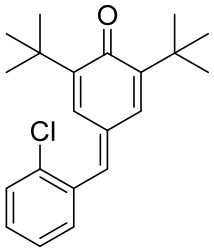
4-((3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)benzonitrile (1k): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 1H), 7.11 (s, 1H), 7.00 (s, 1H), 1.32 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.5, 150.6, 149.0, 140.5, 139.0, 134.6, 134.1, 132.5, 130.7, 126.8, 118.6, 112.2, 35.7, 35.3, 29.62, 29.59.



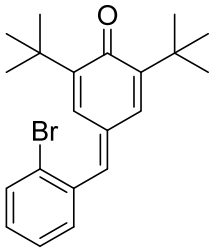
2,6-Di-tert-butyl-4-(4-nitrobenzylidene)cyclohexa-2,5-dien-1-one (1l): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 8.3 Hz, 2H), 7.37 (s, 1H), 7.15 (s, 1H), 7.01 (s, 1H), 1.33 (s, 9H), 1.29 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 150.9, 149.3, 147.6, 142.5, 138.4, 134.6, 134.5, 130.9, 126.8, 124.1, 35.8, 35.3, 29.7, 29.6.



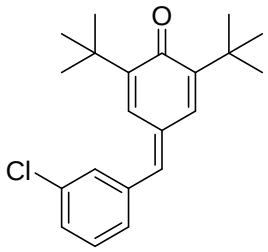
(4-((3,5-Di-tert-butyl-4-oxocyclohexa-2,5-dien-1-ylidene)methyl)phenyl)acetamide (1m): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.52 (s, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.12 (s, 1H), 7.00 (s, 1H), 2.22 (s, 3H), 1.32 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.7, 168.7, 149.4, 147.7, 142.2, 139.0, 135.4, 131.9, 131.5, 131.5, 127.9, 119.8, 35.6, 35.1, 29.70, 29.65, 24.9.



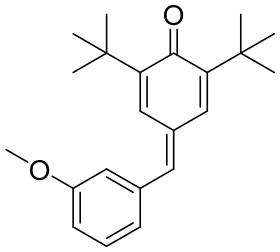
2,6-Di-tert-butyl-4-(2-chlorobenzylidene)cyclohexa-2,5-dien-1-one (1n): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.45 (m, 1H), 7.44 – 7.38 (m, 1H), 7.38 – 7.32 (m, 2H), 7.32 – 7.28 (m, 2H), 7.07 (s, 1H), 1.34 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$, Overlapping peaks) δ 186.7, 149.8, 148.4, 138.7, 135.0, 134.8, 134.2, 133.0, 132.3, 130.3, 130.1, 127.8, 126.8, 35.6, 35.2, 29.6.



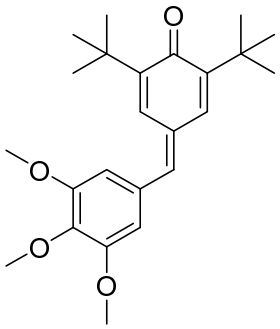
4-(2-Bromobenzylidene)-2,6-di-tert-butylcyclohexa-2,5-dien-1-one (1o): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.9 Hz, 1H), δ 7.44 – 7.36 (m, 2H), 7.31 – 7.21 (m, 3H), 7.08 (s, 1H), 1.35 (s, 9H), 1.27 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.7, 149.8, 148.4, 140.9, 136.0, 134.7, 133.4, 132.7, 132.4, 130.4, 127.8, 127.4, 125.2, 35.6, 35.3, 29.6.



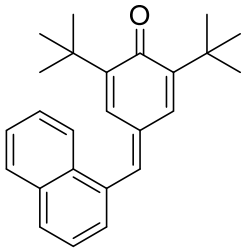
2,6-Di-tert-butyl-4-(3-chlorobenzylidene)cyclohexa-2,5-dien-1-one (1p): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 3.4 Hz, 2H), 7.39 – 7.28 (m, 3H), 7.08 (s, 1H), 6.99 (s, 1H), 1.33 (s, 9H), 1.30 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.6, 150.0, 148.4, 140.2, 137.7, 134.9, 134.8, 133.0, 130.2, 130.1, 129.0, 128.4, 127.4, 35.6, 35.2, 29.64, 29.63.



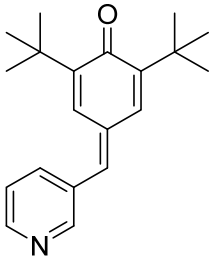
2,6-Di-tert-butyl-4-(3-methoxybenzylidene)cyclohexa-2,5-dien-1-one (1q): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.16 (s, 1H), 7.05 (d, *J* = 7.5 Hz, 1H), 7.01 (s, 1H), 6.99 (s, 1H), 6.95 (d, *J* = 8.2 Hz, 1H), 3.85 (s, 3H), 1.34 (s, 9H), 1.31 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.7, 159.9, 149.5, 148.0, 142.5, 137.3, 135.2, 132.2, 129.9, 128.0, 123.1, 115.4, 115.3, 55.4, 35.6, 35.1, 29.71, 29.65.



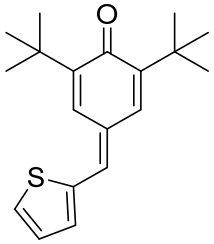
2,6-Di-tert-butyl-4-(3,4,5-trimethoxybenzylidene)cyclohexa-2,5-dien-1-one (1r): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.07 (s, 1H), 6.94 (s, 1H), 6.66 (s, 2H), 3.86 (s, 3H), 3.83 (s, 6H), 1.27 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.3, 153.3, 149.1, 147.5, 142.6, 139.2, 135.1, 131.4, 131.3, 127.7, 107.7, 60.9, 56.1, 35.4, 34.9, 29.6, 29.5.



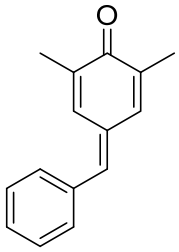
2,6-Di-tert-butyl-4-(naphthalen-1-ylmethylene)cyclohexa-2,5-dien-1-one (1s): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 1H), 7.92 (d, *J* = 6.9 Hz, 2H), 7.78 (s, 1H), 7.61 – 7.52 (m, 3H), 7.49 (d, *J* = 6.9 Hz, 1H), 7.39 (s, 1H), 7.20 (s, 1H), 1.39 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.9, 149.4, 148.1, 140.6, 134.8, 133.8, 133.4, 132.9, 132.1, 129.9, 129.5, 128.9, 128.7, 126.9, 126.6, 125.4, 124.8, 35.5, 35.2, 29.7, 29.6.



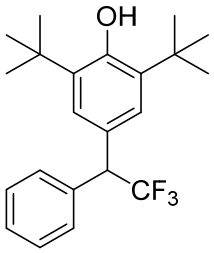
2,6-Di-tert-butyl-4-(pyridin-3-ylmethylene)cyclohexa-2,5-dien-1-one (1t): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 8.56 (d, *J* = 4.3 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.08 (s, 1H), 6.99 (s, 1H), 1.29 (s, 9H), 1.25 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.5, 150.9, 150.2, 149.5, 148.5, 137.7, 137.0, 134.6, 133.6, 131.9, 126.9, 123.6, 35.6, 35.1, 29.6, 29.5.



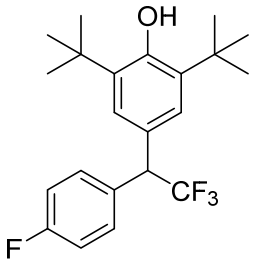
2,6-Di-tert-butyl-4-(thiophen-2-ylmethylene)cyclohexa-2,5-dien-1-one (1u): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.55 (d, *J* = 4.9 Hz, 1H), 7.32 (d, *J* = 3.0 Hz, 1H), 7.18 (s, 1H), 7.14 – 7.07 (m, 1H), 6.95 (s, 1H), 1.37 (s, 9H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 149.4, 147.5, 139.4, 135.3, 134.2, 134.1, 131.3, 129.1, 128.0, 127.1, 35.8, 35.1, 29.72, 29.66.



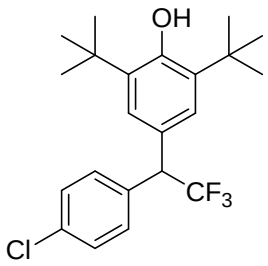
4-Benzylidene-2,6-dimethylcyclohexa-2,5-dien-1-one (1v): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.48 (s, 1H), 7.42 – 7.39 (m, 4H), 7.38 – 7.34 (m, 1H), 7.09 (s, 1H), 6.98 (s, 1H), 2.03 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 186.9, 142.6, 138.7, 137.2, 135.3, 131.4, 131.1, 130.2, 129.1, 128.5, 16.7, 16.0.



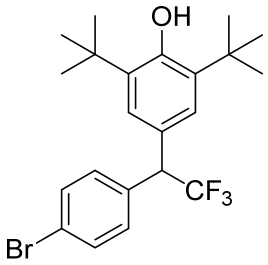
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-phenylethyl)phenol (2a): Colorless oil; 98% yield (71 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 2H), 7.38 (t, J = 7.3 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.19 (s, 2H), 5.23 (s, 1H), 4.60 (q, J = 10.1 Hz, 1H), 1.44 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 136.2, 136.0, 129.2, 128.7, 127.8, 126.6 (q, $J_{C\text{-}F}$ = 280.6 Hz), 126.1, 125.9, 55.7 (q, $J_{C\text{-}F}$ = 27.2 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.96 (d, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3638, 2958, 1149, 1104, 714; HRMS (CI) calcd $C_{22}H_{27}F_3O$ $[M]^+$: 364.2014, found: 364.2016.



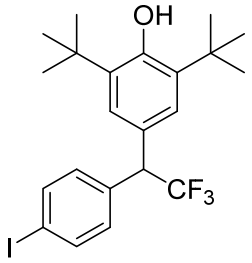
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(4-fluorophenyl)ethyl)phenol (2b): White solid; m.p. 84-86 ℃; 71% yield (54 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.14 (s, 2H), 7.06 (t, J = 8.5 Hz, 2H), 5.24 (s, 1H), 4.58 (q, J = 10.0 Hz, 1H), 1.43 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 162.4 (d, $J_{C\text{-}F}$ = 246.7 Hz), 153.6, 136.2, 132.0, 130.9 (d, $J_{C\text{-}F}$ = 8.0 Hz), 126.5 (q, $J_{C\text{-}F}$ = 280.5 Hz), 125.9, 125.8, 115.7 (d, $J_{C\text{-}F}$ = 21.5 Hz), 54.9 (q, $J_{C\text{-}F}$ = 27.4 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.25 (d, J = 10.1 Hz, 3F), -114.70 – -114.78 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3633, 2961, 1190, 1097, 802; HRMS (CI) calcd $C_{22}H_{26}F_4O$ $[M]^+$: 382.1920, found: 382.1927.



2,6-Di-tert-butyl-4-(1-(4-chlorophenyl)-2,2,2-trifluoroethyl)phenol (2c): White solid; m.p. 83-87 ℃; 83% yield (66 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 4H), 7.12 (s, 2H), 5.24 (s, 1H), 4.56 (q, J = 10.0 Hz, 1H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 136.2, 134.7, 133.8, 130.5, 128.9, 126.4 (q, J_{C-F} = 280.5 Hz), 125.8, 125.6, 55.0 (q, J_{C-F} = 27.4 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.15 (d, J = 10.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3621, 2923, 1184, 1095, 806; HRMS (CI) calcd $C_{22}H_{26}{}^{35}ClF_3O$ $[M]^+$: 398.1624, found: 398.1617.

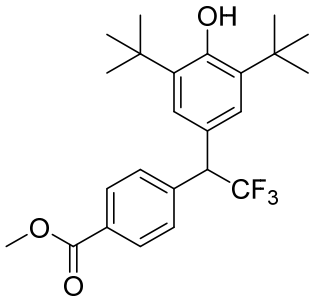


(1-(4-Bromophenyl)-2,2,2-trifluoroethyl)-2,6-di-tert-butylphenol (2d): White solid; m.p. 104-107 ℃; 79% yield (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 7.10 (s, 2H), 5.22 (s, 1H), 4.53 (q, J = 9.6 Hz, 1H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 136.2, 135.2, 131.9, 130.9, 126.3 (q, J_{C-F} = 280.5 Hz), 125.8, 125.5, 122.0, 55.1 (q, J_{C-F} = 27.5 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.12 (d, J = 10.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3626, 2966, 1182, 1105, 722; HRMS (CI) calcd $C_{22}H_{26}{}^{79}BrF_3O$ $[M]^+$: 442.1119, found: 442.1121.

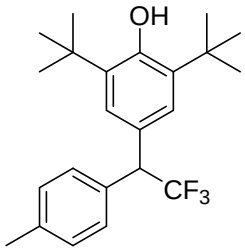


2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(4-iodophenyl)ethyl)phenol (2e): White solid; m.p. 102-105 ℃; 90% yield (88 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 7.13 (s, 2H), 5.24 (s, 1H), 4.53 (q, J = 10.0 Hz, 1H), 1.43 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 137.9, 136.2, 135.9, 131.1, 126.3 (q, J_{C-F} = 280.6 Hz), 125.8, 125.5, 93.6, 55.2 (q, J_{C-F} = 27.5 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.05 (d, J = 10.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1})

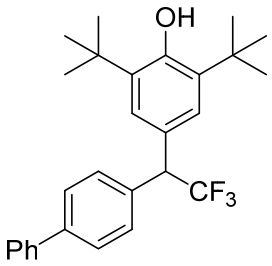
3617, 2957, 1184, 1108, 770; HRMS (CI) calcd $C_{22}H_{26}F_3IO$ $[M]^+$: 490.0981, found: 490.0968.



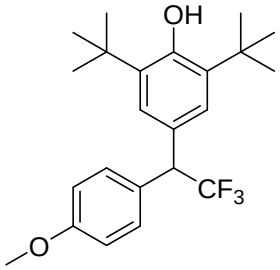
Methyl 4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,2,2-trifluoroethyl)benzoate (2f): White solid; m.p. 46-48 ℃; 83% yield (70 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.8 Hz, 2H), 7.49 (d, *J* = 7.8 Hz, 2H), 7.13 (s, 2H), 5.26 (s, 1H), 4.65 (q, *J* = 9.8 Hz, 1H), 3.92 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.8, 153.8, 141.2, 136.2, 130.0, 129.6, 129.2, 126.3 (q, J_{C-F} = 280.6 Hz), 125.9, 125.3, 55.5 (q, J_{C-F} = 27.5 Hz), 52.3, 34.5, 30.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.86 (d, *J* = 9.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3937, 2956, 1721, 1435, 1152; HRMS (CI) calcd $C_{24}H_{29}F_3O_3$ $[M + H]^+$: 423.2147, found: 423.2152.



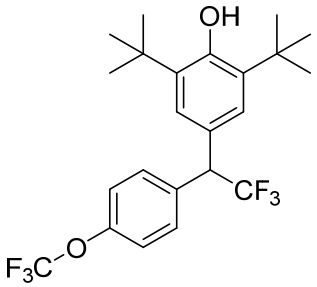
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(*p*-tolyl)ethyl)phenol (2g): White solid; m.p. 90-93 ℃; 80% yield (61 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 2H), 7.21 – 7.15 (m, 4H), 5.21 (s, 1H), 4.56 (q, *J* = 10.2 Hz, 1H), 2.36 (s, 3H), 1.44 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 137.5, 136.0, 133.2, 129.4, 129.0, 126.7 (d, J_{C-F} = 280.5 Hz), 126.3, 125.9, 55.4 (q, J_{C-F} = 27.2 Hz), 34.5, 30.4, 21.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.10 (d, *J* = 10.2 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3613, 2921, 1151, 1102, 639; HRMS (CI) calcd $C_{23}H_{29}F_3O$ $[M]^+$: 378.2171, found: 378.2163.



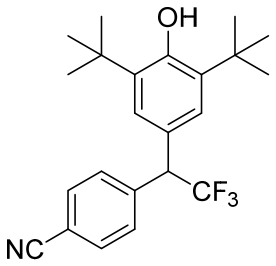
4-(1-([1,1'-Biphenyl]-4-yl)-2,2,2-trifluoroethyl)-2,6-di-tert-butylphenol (2h): White solid; m.p. 148-150 ℃; 77% yield (68 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.57 (m, 4H), 7.54 – 7.42 (m, 4H), 7.37 (t, *J* = 7.0 Hz, 1H), 7.23 (s, 2H), 5.25 (s, 1H), 4.64 (q, *J* = 10.0 Hz, 1H), 1.45 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 140.7, 140.6, 136.1, 135.2, 129.6, 128.9, 127.6, 127.5, 127.5 (q, J_{C-F} = 280.6 Hz), 127.2, 126.0, 125.9, 55.4 (q, J_{C-F} = 27.3 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.94 (d, *J* = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3619, 2963, 1145, 1103, 698; HRMS (CI) calcd $C_{28}H_{31}F_3O$ $[M]^+$: 440.2327, found: 440.2321.



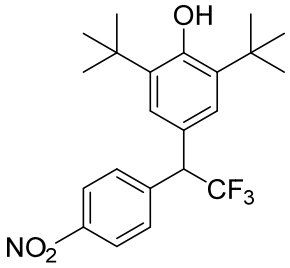
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(4-methoxyphenyl)ethyl)phenol (2i): White solid; m.p. 95-98 ℃; 83% yield (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.16 (s, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 5.21 (s, 1H), 4.54 (q, *J* = 10.2 Hz, 1H), 3.81 (s, 3H), 1.43 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1, 153.5, 136.0, 130.3, 128.3, 126.4, 126.9 (q, J_{C-F} = 280.5 Hz), 125.8, 114.1, 55.4, 54.8 (q, J_{C-F} = 27.2 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.30 (d, *J* = 10.2 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3598, 2961, 1146, 1030, 802; HRMS (CI) calcd $C_{23}H_{30}F_3O_2$ $[M + H]^+$: 395.2198, found: 395.2188.



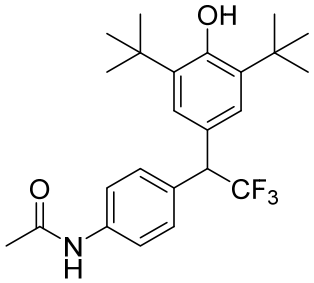
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(4-(trifluoromethoxy)phenyl)ethyl)phenol (2j): White solid; m.p. 46-49 ℃; 79% yield (71 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.14 (s, 2H), 5.25 (s, 1H), 4.60 (q, *J* = 9.9 Hz, 1H), 1.43 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 148.9, 136.3, 134.9, 130.6, 126.4 (q, J_{C-F} = 280.5 Hz), 125.8, 125.5, 121.1, 120.6 (q, J_{C-F} = 257.2 Hz), 55.0 (q, J_{C-F} = 27.5 Hz), 34.5, 30.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.85 (s，3F), -66.13 (d, *J* = 10.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3640, 2960, 1255, 1105, 808; HRMS (CI) calcd $C_{23}H_{27}F_6O_2$ $[M + H]^+$: 449.1915, found: 449.1910.



2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(4-isocyanophenyl)ethyl)phenol (2k): White solid; m.p. 99-101 ℃; 69% yield (53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.8 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.09 (s, 2H), 5.28 (s, 1H), 4.64 (q, *J* = 9.6 Hz, 1H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.9, 141.4, 136.5, 132.5, 129.9, 126.0 (q, J_{C-F} = 280.6 Hz), 125.8, 124.7, 118.6, 111.9, 55.5 (q, J_{C-F} = 27.7 Hz), 34.5, 30.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.83 (d, *J* = 9.8 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3631, 2959, 2231, 1437, 1154; HRMS (CI) calcd $C_{23}H_{27}F_3NO$ $[M + H]^+$: 390.2045, found: 390.2054.

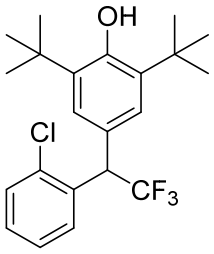


2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(4-nitrophenyl)ethyl)phenol (2l): White solid; m.p. 120-122 ℃; 68% yield (56 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.10 (s, 2H), 5.29 (s, 1H), 4.70 (q, *J* = 9.7 Hz, 1H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 147.5, 143.4, 136.5, 130.1, 126.0 (q, J_{C-F} = 280.7 Hz), 125.8, 124.6, 124.0, 55.4 (q, J_{C-F} = 27.8 Hz), 34.5, 30.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.86 (d, *J* = 9.7 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3605, 2920, 1523, 1119, 850; HRMS (CI) calcd $C_{22}H_{27}F_3NO_3$ $[M + H]^+$: 410.1943, found: 410.1930.

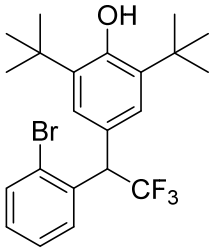


***N*-(4-(1-(3,5-di-tert-butyl-4-hydroxyphenyl)-2,2,2-trifluoroethyl)phenyl)acetamide (2m):** White solid; m.p. 208-214 ℃; 67% yield (57 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, *J* = 8.2 Hz, 2H), 7.41 (s, 1H), 7.33 (d, *J* = 8.1 Hz, 2H), 7.13 (s, 2H), 5.21 (s, 1H), 4.53 (q, *J* = 10.0 Hz, 1H), 2.16 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 153.5, 137.5, 136.1, 132.0, 129.8, 126.5 (d, J_{C-F} = 280.5 Hz),

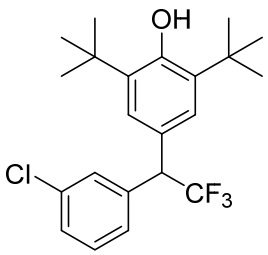
126.0, 125.8, 120.0, 55.1 (q, J_{C-F} = 54.7, 27.3 Hz), 34.5, 30.4, 24.7; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.16 (d, J = 9.7 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3620, 3910, 2959, 1148, 1103; HRMS (CI) calcd $C_{24}H_{31}F_3NO_2$ $[M + H]^+$: 422.2307, found: 422.2317.



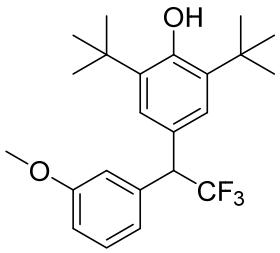
2,6-Di-tert-butyl-4-(1-(2-chlorophenyl)-2,2,2-trifluoroethyl)phenol (2n): White solid; m.p. 100-103 ℃; 90% yield (72 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, J = 7.7 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.32 (t, J = 7.4 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.18 (s, 2H), 5.34 – 5.17 (m, 2H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 136.0, 134.7, 134.2, 130.2, 129.2, 129.0, 127.2, 126.5 (d, J_{C-F} = 280.5 Hz), 126.2, 124.9, 51.0 (q, J_{C-F} = 27.9 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.48 (d, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3629, 2960, 1123, 1102, 755; HRMS (CI) calcd $C_{22}H_{26}{}^{35}ClF_3O$ $[M]^+$: 398.1624, found: 398.1629.



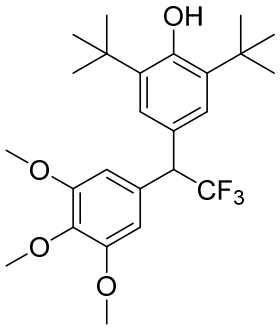
4-(1-(2-Bromophenyl)-2,2,2-trifluoroethyl)-2,6-di-tert-butylphenol (2o): White solid; m.p. 103-107 ℃; 80% yield (71 mg);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 7.7 Hz, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.20 (s, 2H), 7.19 – 7.13 (m, 1H), 5.34 – 5.16 (m, 2H), 1.43 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 136.0, 135.9, 133.6, 129.3, 129.3, 127.8, 126.5 (q, J_{C-F} = 280.7 Hz), 126.2, 125.7, 124.9, 53.7 (q, J_{C-F} = 27.8 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.36 (d, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3630, 2957, 1122, 1101, 754; HRMS (CI) calcd $C_{22}H_{26}{}^{79}BrF_3O$ $[M]^+$: 442.1119, found: 442.1108.



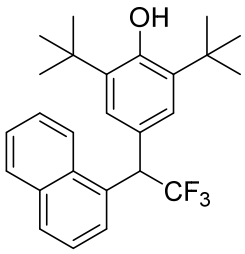
2,6-Di-tert-butyl-4-(1-(3-chlorophenyl)-2,2,2-trifluoroethyl)phenol (2p): White solid; m.p. 99-102 ℃; 82% yield (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.33 – 7.29 (m, 3H), 7.15 (s, 2H), 5.26 (s, 1H), 4.56 (q, J = 9.9 Hz, 1H), 1.44 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 138.1, 136.2, 134.6, 130.0, 129.5, 128.1, 127.2, 126.3 (q, J_{C-F} = 280.5 Hz), 125.9, 125.3, 55.3 (q, J_{C-F} = 27.6 Hz), 34.5, 30.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.98 (d, J = 10.0 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3636, 2956, 1143, 1108, 693; HRMS (CI) calcd $C_{22}H_{27}{}^{35}ClF_3O$ $[M + H]^+$: 399.1703, found: 399.1691.



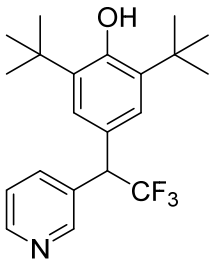
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(3-methoxyphenyl)ethyl)phenol (2q): White solid; m.p. 74-77 ℃; 83% yield (65 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.22 (m, 1H), 7.16 (s, 2H), 7.00 (d, J = 7.6 Hz, 1H), 6.94 (s, 1H), 6.84 (d, J = 7.8 Hz, 1H), 5.20 (s, 1H), 4.53 (q, J = 10.1 Hz, 1H), 3.79 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 153.6, 137.6, 136.0, 129.7, 126.6 (q, J_{C-F} = 280.5 Hz), 125.93, 125.88, 121.5, 115.3, 113.0, 55.6 (q, J_{C-F} = 54.7, 27.4 Hz), 55.3, 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -65.96 (d, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3614, 2962, 1264, 1144, 698; HRMS (CI) calcd $C_{23}H_{30}F_3O_2$ $[M + H]^+$: 395.2198, found: 395.2186.



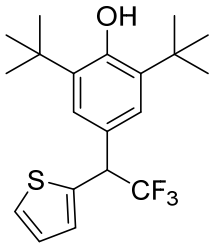
2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(3,4,5-trimethoxyphenyl)ethyl)phenol (2r): Colorless oil; 73% yield (66 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (s, 2H), 6.63 (s, 2H), 5.22 (s, 1H), 4.48 (q, J = 10.0 Hz, 1H), 3.87 – 3.82 (m, 9H), 1.43 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.7, 153.3, 137.7, 136.1, 131.4, 126.5 (q, J_{C-F} = 280.9 Hz), 125.8, 125.7, 106.5, 61.0, 56.2, 55.7 (q, J_{C-F} = 27.3 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.15 (d, J = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3636, 2956, 1237, 1007, 700; HRMS (CI) calcd $C_{25}H_{34}F_3O_4$ $[M + H]^+$: 455.2409, found: 455.2408.



2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(naphthalen-1-yl)ethyl)phenol (2s): White solid; m.p. 153-158 ℃; 70% yield (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.2 Hz, 1H), 7.92 – 7.75 (m, 3H), 7.59 – 7.43 (m, 3H), 7.22 (s, 2H), 5.45 (q, *J* = 9.8 Hz, 1H), 5.18 (s, 1H), 1.39 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.6, 135.9, 134.2, 131.9, 131.8, 129.2, 128.6, 127.0 (q, J_{C-F} = 280.7 Hz), 126.7, 126.2, 125.9, 125.8, 125.7, 125.4, 123.2, 50.4 (q, J_{C-F} = 27.2 Hz), 34.5, 30.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -64.82 (d, *J* = 10.8 Hz); ^{19}F NMR (564 MHz, $CDCl_3$) δ -64.82 (d, *J* = 10.8 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3616, 2920, 1182, 1103, 772; HRMS (CI) calcd $C_{26}H_{29}F_3O$ $[M]^+$: 414.2171, found: 414.2156.

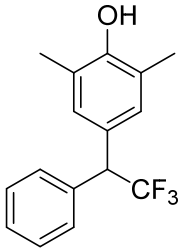


2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(pyridin-3-yl)ethyl)phenol (2t): Colorless liquid; 43% yield (31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) 8.65 – 8.52(m, 2H), 7.76 (d, *J* = 7.3 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.12 (s, 2H), 5.29 (s, 1H), 4.60 (q, *J* = 9.7 Hz, 1H), 1.41 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 150.4, 149.0, 136.44, 136.40, 132.2, 126.2 (q, J_{C-F} = 280.7 Hz), 125.8, 124.8, 123.7, 53.4 (q, J_{C-F} = 28.0 Hz), 34.5, 30.3; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.11 (d, *J* = 10.3 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3638, 2957, 1578, 1155, 865; HRMS (CI) calcd $C_{21}H_{27}F_3NO$ $[M + H]^+$: 366.2045, found: 366.2040.

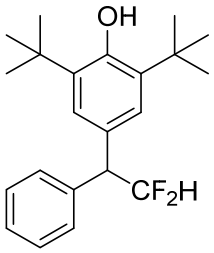


2,6-Di-tert-butyl-4-(2,2,2-trifluoro-1-(thiophen-2-yl)ethyl)phenol (2u): Yellowish oil; 20% yield (15 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (s, 1H), 7.21 (s, 2H), 7.09 – 7.06 (m, 1H), 7.01 – 6.95 (m, 1H), 5.24 (s, 1H), 4.79 (q, *J* = 9.5 Hz, 1H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.0, 138.1, 136.1, 127.5, 126.9, 125.9, 125.8 (q, J_{C-F} = 280.6 Hz), 125.7, 125.5, 51.3 (q, J_{C-F} = 28.8 Hz), 34.5, 30.4; ^{19}F NMR (564

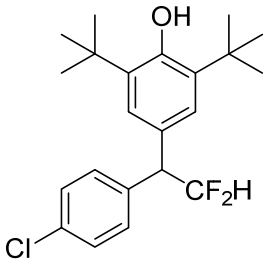
MHz, $CDCl_3$) δ -68.01 (d, *J* = 9.9 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3637, 2957, 1435, 1251, 701; HRMS (CI) calcd $C_{20}H_{26}F_3OS$ $[M + H]^+$: 371.1656, found: 371.1660.



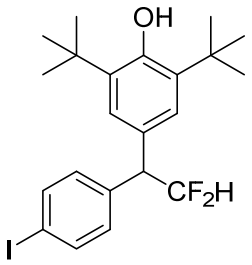
2,6-Dimethyl-4-(2,2,2-trifluoro-1-phenylethyl)phenol (2v): Yellowish oil; 34% yield (19 mg); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.0 Hz, 1H), 6.97 (s, 2H), 4.65 (s, 1H), 4.54 (q, *J* = 10.1 Hz, 1H), 2.22 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.1, 136.1, 129.4, 129.1, 128.8, 127.8, 127.1, 126.5 (q, J_{C-F} = 280.4 Hz), 123.4, 55.0 (q, J_{C-F} = 27.4 Hz), 16.1; ^{19}F NMR (564 MHz, $CDCl_3$) δ -66.06 (d, *J* = 10.1 Hz, 3F); FT-IR (thin film, KBr): ν (cm^{-1}) 3447, 2925, 1259, 1105, 699; HRMS (CI) calcd $C_{16}H_{16}F_3O$ $[M + H]^+$: 281.1153, found: 281.1146.



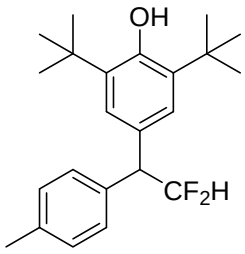
2,6-Di-tert-butyl-4-(2,2-difluoro-1-phenylethyl)phenol (3a): Yellowish oil; 81% yield (56 mg); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 7.10 (s, 2H), 6.26 (td, *J* = 56.1, 4.3 Hz, 1H), 5.18 (s, 1H), 4.31 (td, *J* = 16.3, 4.2 Hz, 1H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 137.8, 136.1, 129.2, 128.7, 127.8, 127.4, 125.8, 117.4 (t, J_{C-F} = 244.5 Hz), 55.2 (t, J_{C-F} = 20.4 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -117.26 (ddd, *J* = 276.9, 56.1, 15.5 Hz, 1F), -118.26 (ddd, *J* = 276.9, 56.2, 16.9 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3636, 2958, 1436, 1055, 699; HRMS (CI) calcd $C_{22}H_{29}F_2O$ $[M + H]^+$: 347.2186, found: 347.2181.



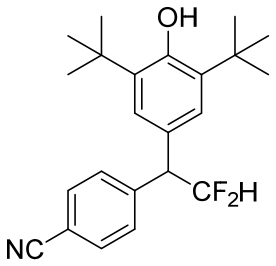
2,6-Di-tert-butyl-4-(1-(4-chlorophenyl)-2,2-difluoroethyl)phenol (3b): Yellowish oil; 63% yield (48 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.05 (s, 2H), 6.21 (td, *J* = 56.0, 3.9 Hz, 1H), 5.19 (s, 1H), 4.35 – 4.21 (m, 1H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 136.3, 136.2, 133.3, 130.6, 128.8, 127.3, 125.6, 117.1 (t, J_{C-F} = 244.8 Hz), 54.5 (t, J_{C-F} = 20.5 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -116.82 (ddd, *J* = 278.0, 55.9, 14.5 Hz, 1F), -119.10 (ddd, *J* = 278.0, 56.1, 18.2 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3635, 2958, 1436, 1053, 810; HRMS (CI) calcd $C_{22}H_{28}{}^{35}ClF_2O$ $[M + H]^+$: 381.1797, found: 381.1788.



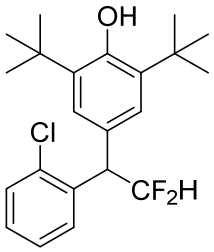
2,6-Di-tert-butyl-4-(2,2-difluoro-1-(4-iodophenyl)ethyl)phenol (3c): White solid; m.p. 115-117 ℃; 70% yield (66 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.06 (s, 2H), 6.22 (td, *J* = 56.0, 3.9 Hz, 1H), 5.20 (s, 1H), 4.29 – 4.21 (m, 1H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.4, 137.7, 137.4, 136.3, 131.3, 127.2, 125.6, 117.0 (t, J_{C-F} = 244.8 Hz), 93.1, 54.7 (t, J_{C-F} = 20.5 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -116.73 (ddd, *J* = 278.1, 55.8, 14.4 Hz, 1F), -119.06 (ddd, *J* = 278.1, 56.1, 18.2 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3616, 2957, 1434, 1208, 799; HRMS (CI) calcd $C_{22}H_{27}F_2IO$ $[M]^+$: 472.1075, found: 472.1089.



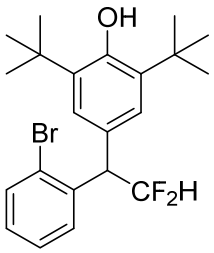
2,6-Di-tert-butyl-4-(2,2-difluoro-1-(p-tolyl)ethyl)phenol (3d): White solid; m.p. 83-86 ℃; 58% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.7 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.11 (s, 2H), 6.24 (td, *J* = 56.2, 4.1 Hz, 1H), 5.17 (s, 1H), 4.27 (td, *J* = 16.5, 3.8 Hz, 1H), 2.34 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.2, 137.0, 136.0, 134.7, 129.4, 129.0, 128.0, 125.7, 117.5 (t, J_{C-F} = 244.4 Hz), 54.9 (t, J_{C-F} = 20.4 Hz), 34.5, 30.4, 21.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -117.18 (ddd, *J* = 276.4, 56.1, 15.5 Hz, 1F), -118.32 (ddd, *J* = 276.4, 56.3, 17.0 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3611, 2959, 1436, 1109, 799; HRMS (CI) calcd $C_{23}H_{31}F_2O$ $[M + H]^+$: 361.2343, found: 361.2335.



2,6-Di-tert-butyl-4-(2,2-difluoro-1-(4-isocyanophenyl)ethyl)phenol (3e): White solid; m.p. 40-44 ℃; 42% yield (31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.04 (s, 1H), 6.25 (td, *J* = 55.7, 3.5 Hz, 1H), 5.24 (s, 1H), 4.45 – 4.30 (m, 1H), 1.41 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.5, 142.8, 136.4, 132.2, 130.0, 126.3, 125.5, 118.7, 116.6 (t, J_{C-F} = 245.3 Hz), 111.2, 54.9 (t, J_{C-F} = 20.5 Hz), 34.4, 30.2; ^{19}F NMR (564 MHz, $CDCl_3$) δ -116.18 (ddd, *J* = 279.8, 55.5, 13.5 Hz, 1F), -119.59 (ddd, *J* = 279.8, 55.9, 19.2 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3632, 2959, 2229, 1436, 810; HRMS (CI) calcd $C_{23}H_{28}F_2NO$ $[M + H]^+$: 372.2139, found: 372.2143.

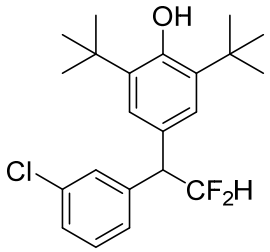


2,6-Di-tert-butyl-4-(1-(2-chlorophenyl)-2,2-difluoroethyl)phenol (3f): White solid; m.p. 59-64 ℃; 66% yield (50 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (s, 2H), 6.31 (td, *J* = 55.9, 4.3 Hz, 1H), 5.18 (s, 1H), 4.92 (td, *J* = 16.3, 4.2 Hz, 1H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.3, 136.0, 135.9, 134.8, 130.2, 129.7, 128.6, 127.1, 126.4, 126.0, 117.1 (t, J_{C-F} = 244.8 Hz), 50.9 (t, J_{C-F} = 21.2 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -117.39 (ddd, *J* = 277.8, 56.0, 15.5 Hz, 1F), -118.89 (ddd, *J* = 277.8, 55.8, 16.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3630, 2958, 1434, 1060, 751; HRMS (CI) calcd $C_{22}H_{27}{}^{35}ClF_2O$ $[M]^+$: 380.1718, found: 380.1721.

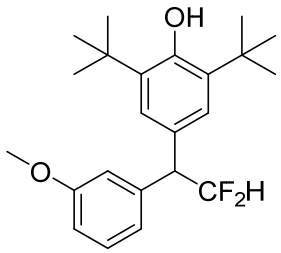


4-(1-(2-Bromophenyl)-2,2-difluoroethyl)-2,6-di-tert-butylphenol (3g): White solid; m.p. 81-84 ℃; 62% yield (53 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.9 Hz,

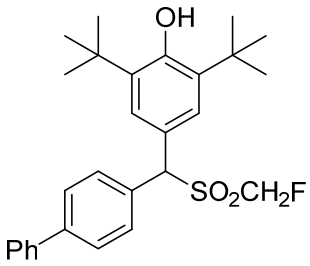
1H), 7.50 (d, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.11 (m, 3H), 6.30 (td, *J* = 55.9, 3.7 Hz, 1H), 5.18 (s, 1H), 4.93 (td, *J* = 16.3, 3.6 Hz, 1H), 1.42 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.3, 137.5, 136.0, 133.5, 129.7, 128.8, 127.7, 126.5, 126.0, 125.7, 117.2 (t, J_{C-F} = 244.9 Hz), 53.4 (t, J_{C-F} = 21.2 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -117.39 (ddd, *J* = 277.8, 56.0, 15.6 Hz, 1F), -119.02 (ddd, *J* = 277.7, 55.8, 16.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3631, 2958, 1435, 1022, 749; HRMS (CI) calcd $C_{22}H_{27}{}^{79}BrF_2O$ $[M]^+$: 424.1213, found: 424.1223.



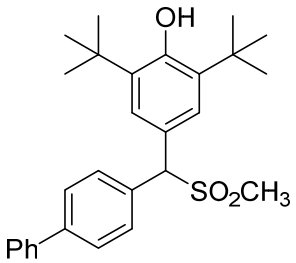
2,6-Di-tert-butyl-4-(2,2-difluoro-1-(3-methoxyphenyl)ethyl)phenol (3h): White solid; m.p. 68-70 ℃; 52% yield (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.3 Hz, 1H), 7.13 (s, 2H), 6.31 (td, *J* = 55.9, 4.3 Hz, 1H), 5.18 (s, 1H), 4.92 (td, *J* = 16.3, 4.1 Hz, 1H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 153.3, 136.0, 135.9, 134.7, 130.2, 129.7, 128.6 127.0, 126.4, 126.0, 117.1 (t, J_{C-F} = 244.8 Hz), 50.9 (t, J_{C-F} = 21.2 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -117.39 (ddd, *J* = 277.8, 56.0, 15.5 Hz, 1F), -118.89 (ddd, *J* = 277.7, 55.8, 16.8 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3630, 2959, 1434, 1060, 751; HRMS (CI) calcd $C_{22}H_{28}{}^{35}ClF_2O$ $[M + H]^+$: 381.1797, found: 381.1796.



2,6-Di-tert-butyl-4-(2,2-difluoro-1-(3-methoxyphenyl)ethyl)phenol (3i): Colorless oil; 59% yield (45 mg); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H), 7.10 (s, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.87 (s, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 6.23 (td, *J* = 56.1, 4.3 Hz, 1H), 5.16 (s, 1H), 4.26 (td, *J* = 16.1, 4.2 Hz, 1H), 3.79 (s, 3H), 1.41 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.8, 153.3, 139.3 136.1, 129.6, 127.6, 125.7, 121.5, 117.4 (t, J_{C-F} = 244.6 Hz), 115.3, 112.5, 55.3, 55.3 (t, J_{C-F} = 20.5 Hz), 34.5, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -117.24 (ddd, *J* = 276.8, 56.1, 15.5 Hz, 1F), -118.14 (ddd, *J* = 276.9, 56.2, 16.6 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3634, 2957, 1434, 1053, 771; HRMS (CI) calcd $C_{23}H_{31}F_2O_2$ $[M + H]^+$: 377.2292, found: 377.2297.



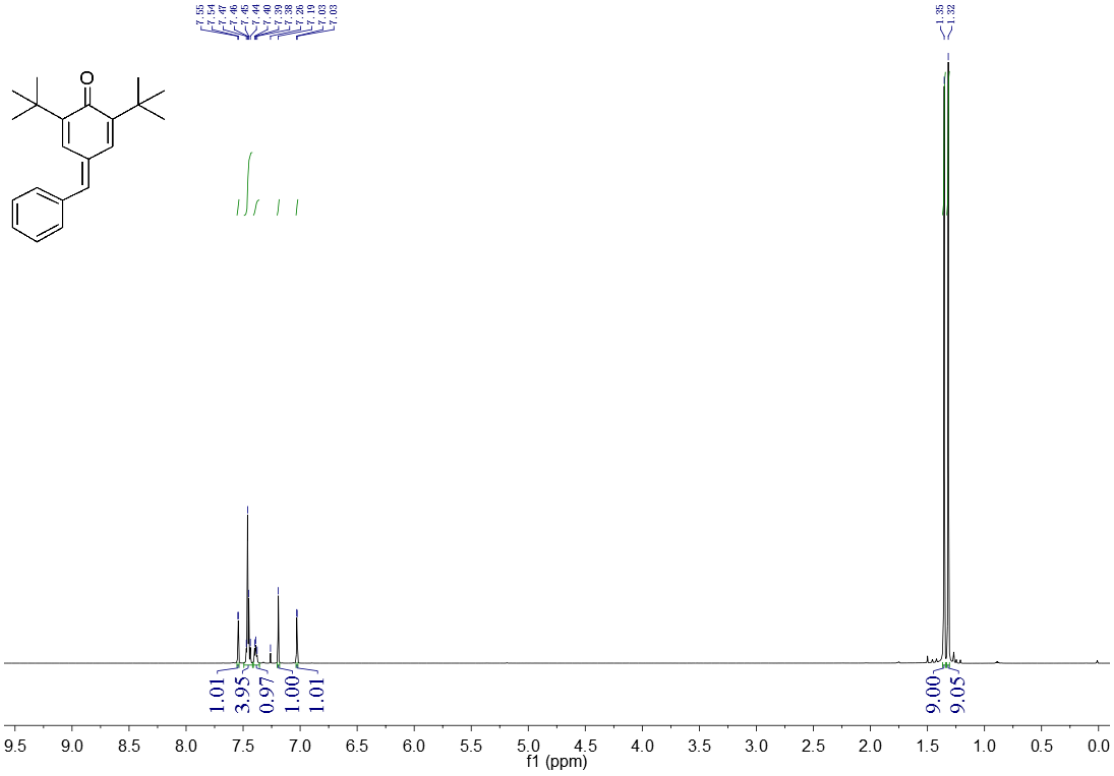
4-**([1,1'-Biphenyl]-4-yl((fluoromethyl)sulfonyl)methyl)-2,6-di-tert-butylphenol (4a):** White solid; m.p. 51-55 ℃; 59% yield (55 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.42 (m, 4H), 7.37 (t, *J* = 7.2 Hz, 1H), 5.54 (s, 1H), 5.36 (s, 1H), 4.92 (d, *J* = 46.9 Hz, 2H), 1.45 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.9, 142.2, 140.3, 136.8, 130.9, 130.4, 129.0, 127.94, 127.87, 127.3, 126.9, 121.7, 88.3 (d, J_{C-F} = 219.2 Hz), 70.8, 34.6, 30.4; ^{19}F NMR (564 MHz, $CDCl_3$) δ -211.91 (td, *J* = 46.9, 1.9 Hz, 1F); FT-IR (thin film, KBr): ν (cm^{-1}) 3629, 2957, 1434, 1140, 740; HRMS (CI) calcd $C_{28}H_{34}FO_3S$ $[M + H]^+$: 469.2213, found: 469.2223.



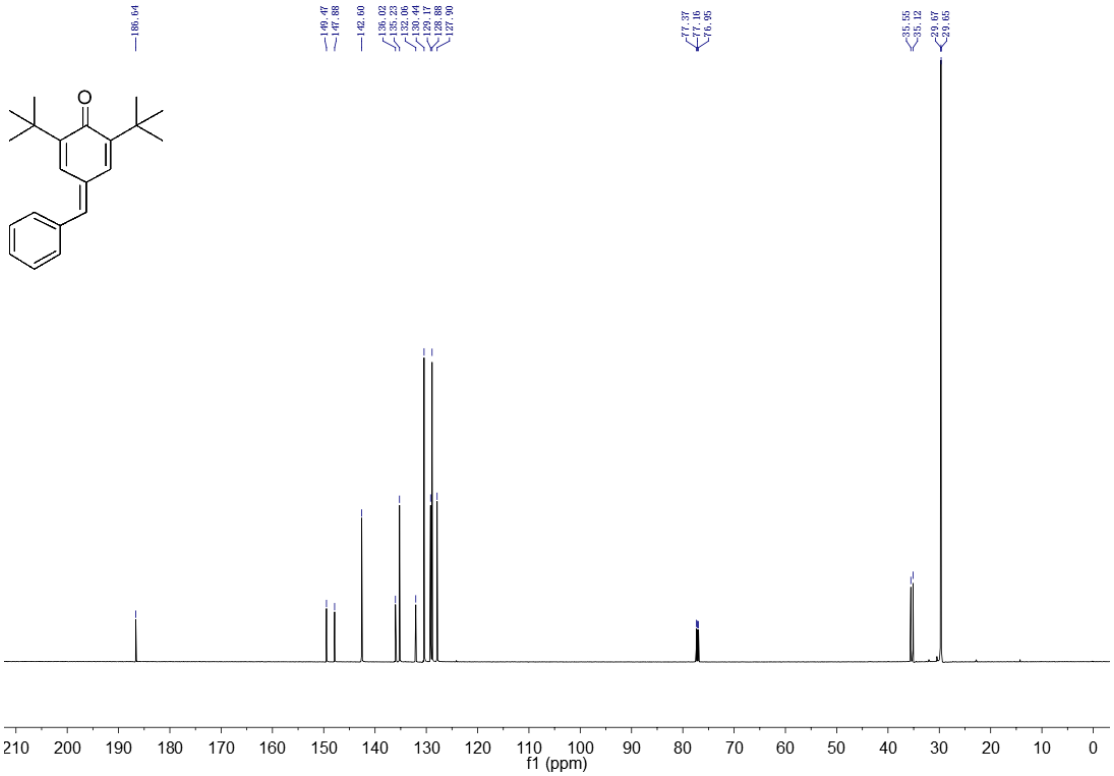
4-([1,1'-Biphenyl]-4-yl(methylsulfonyl)methyl)-2,6-di-tert-butylphenol (4b): White solid; m.p. 75-80 ℃; 58% yield (52 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.36 (t, *J* = 7.2 Hz, 1H), 5.33 (s, 1H), 5.29 (s, 1H), 2.78 (s, 3H), 1.45 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$, overlapping peaks) δ 154.6, 141.7, 140.4, 136.5, 132.3, 130.2, 128.9, 127.7, 127.2, 126.6, 123.2, 74.8, 40.0, 34.6, 30.4; FT-IR (thin film, KBr): ν (cm^{-1}) 3629, 2956, 1435, 1133, 730; HRMS (CI) calcd $C_{28}H_{35}O_3S$ $[M + H]^+$: 451.2307, found: 451.2304.

5. NMR Spectra for the substrates and products

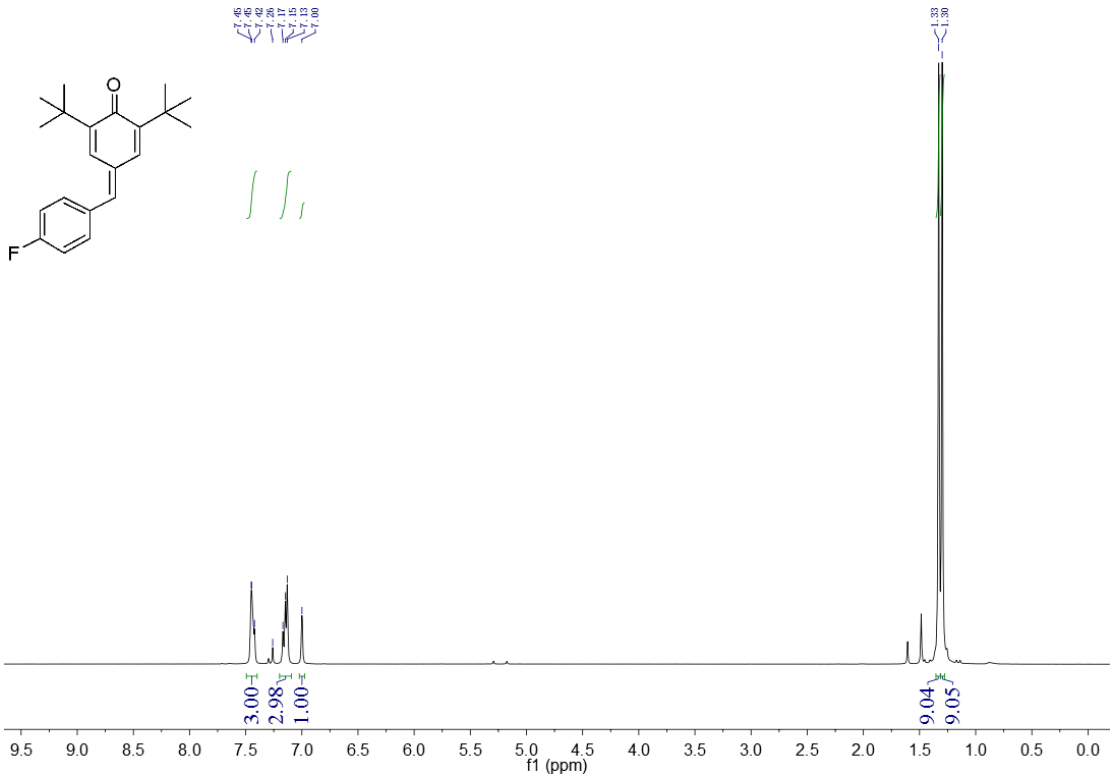
1H NMR of **1a**



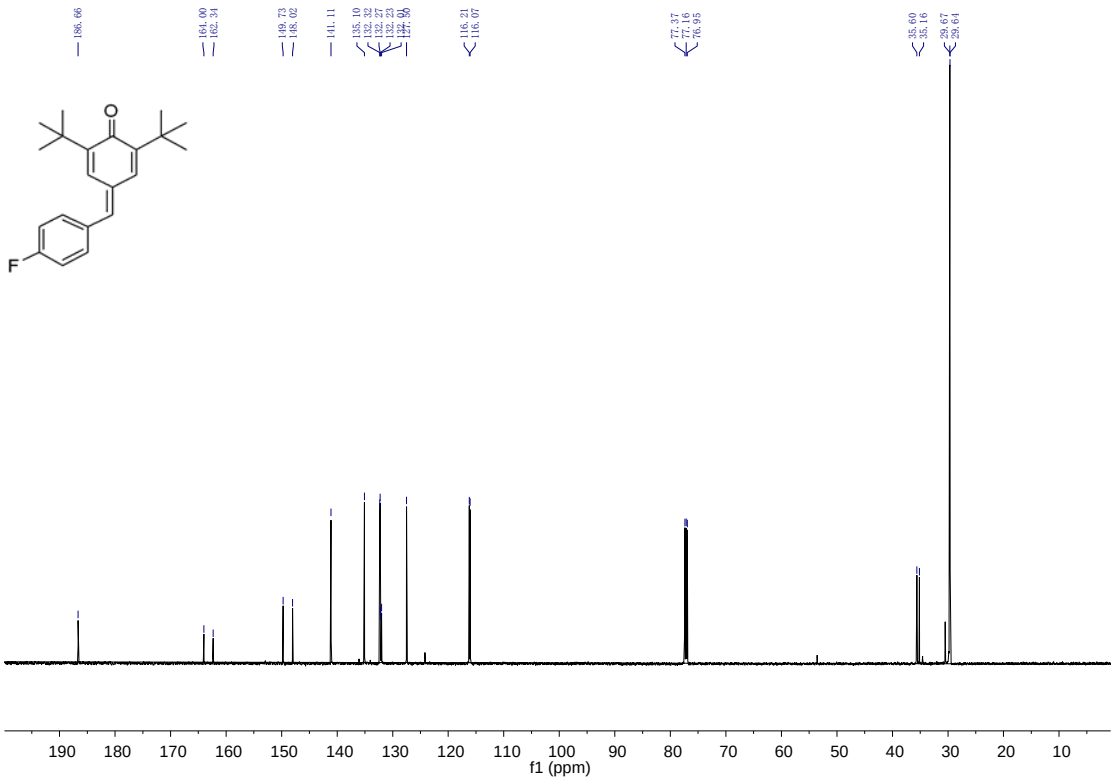
^{13}C NMR of **1a**



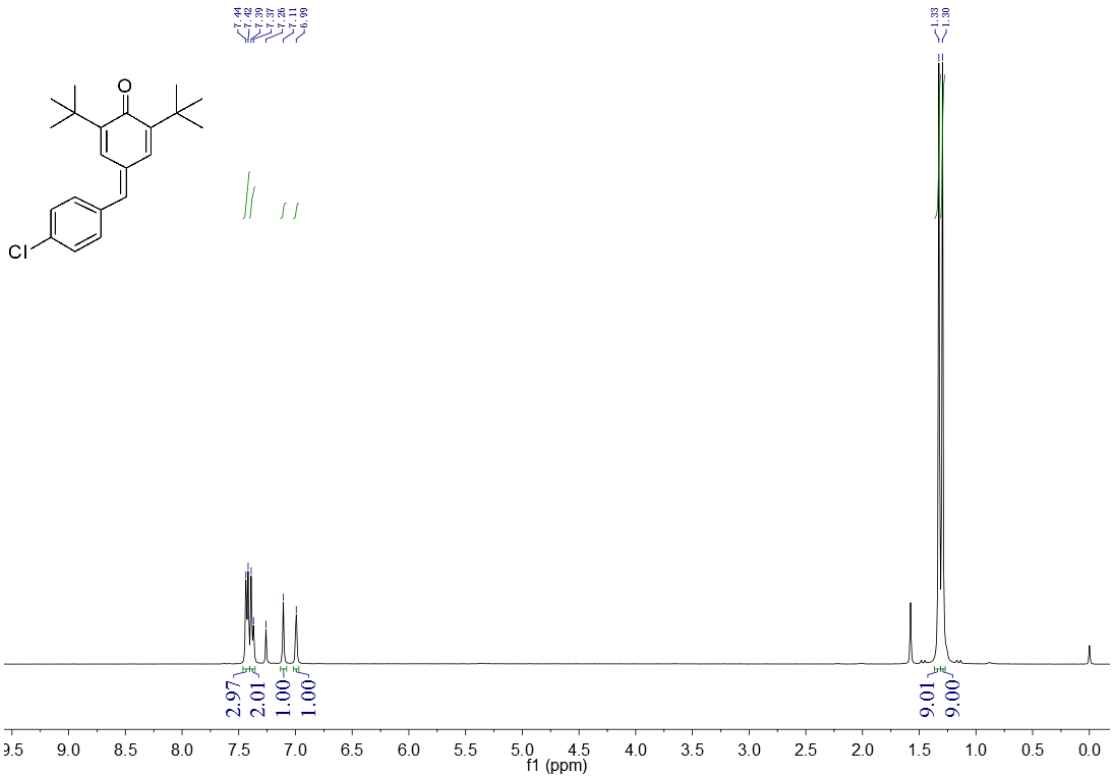
^{1}H NMR of **1b**



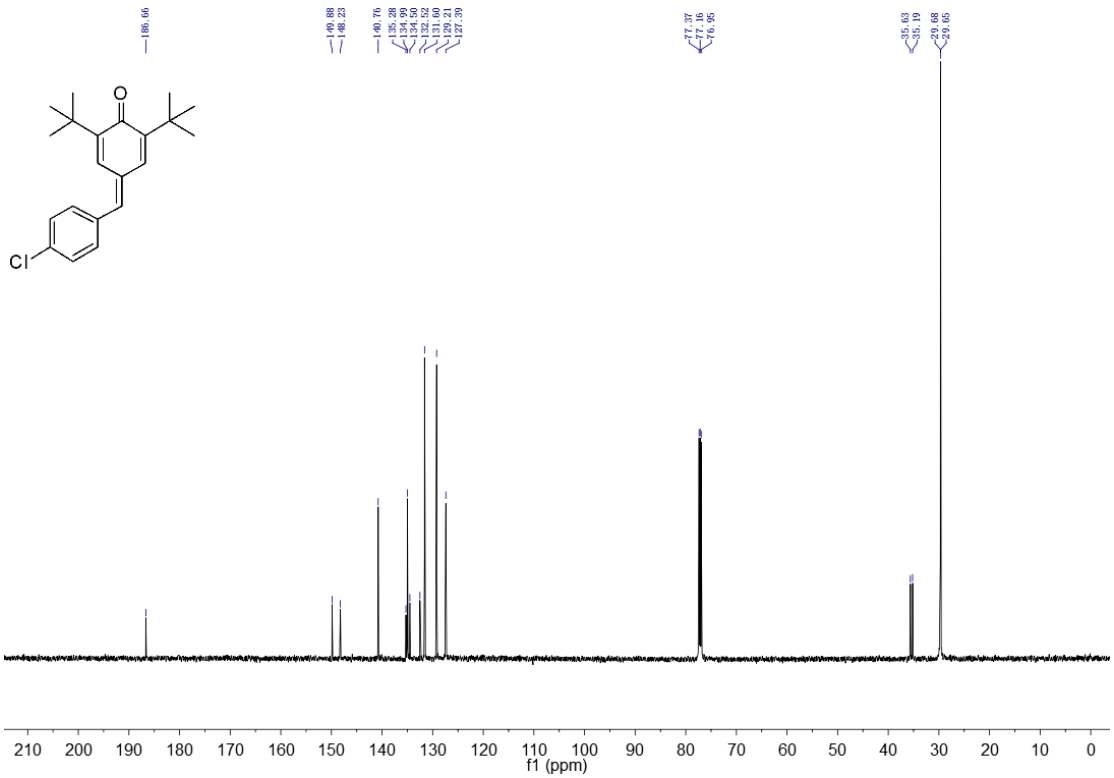
^{13}C NMR of **1b**



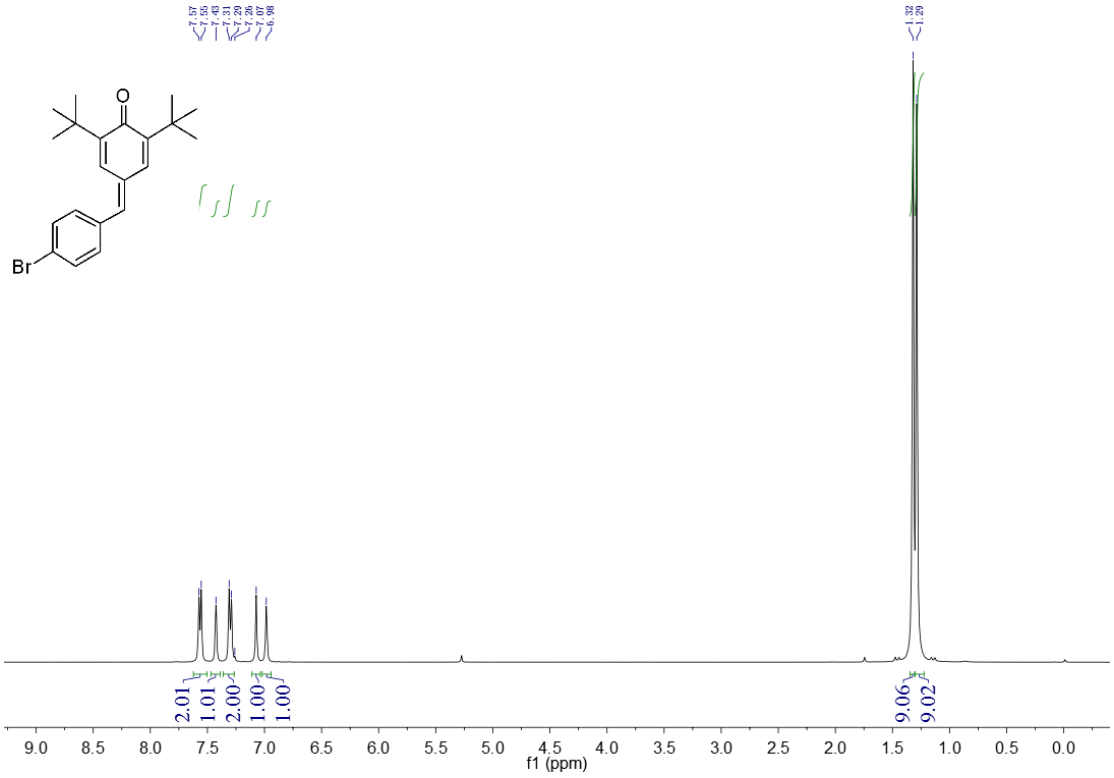
^{1}H NMR of **1c**



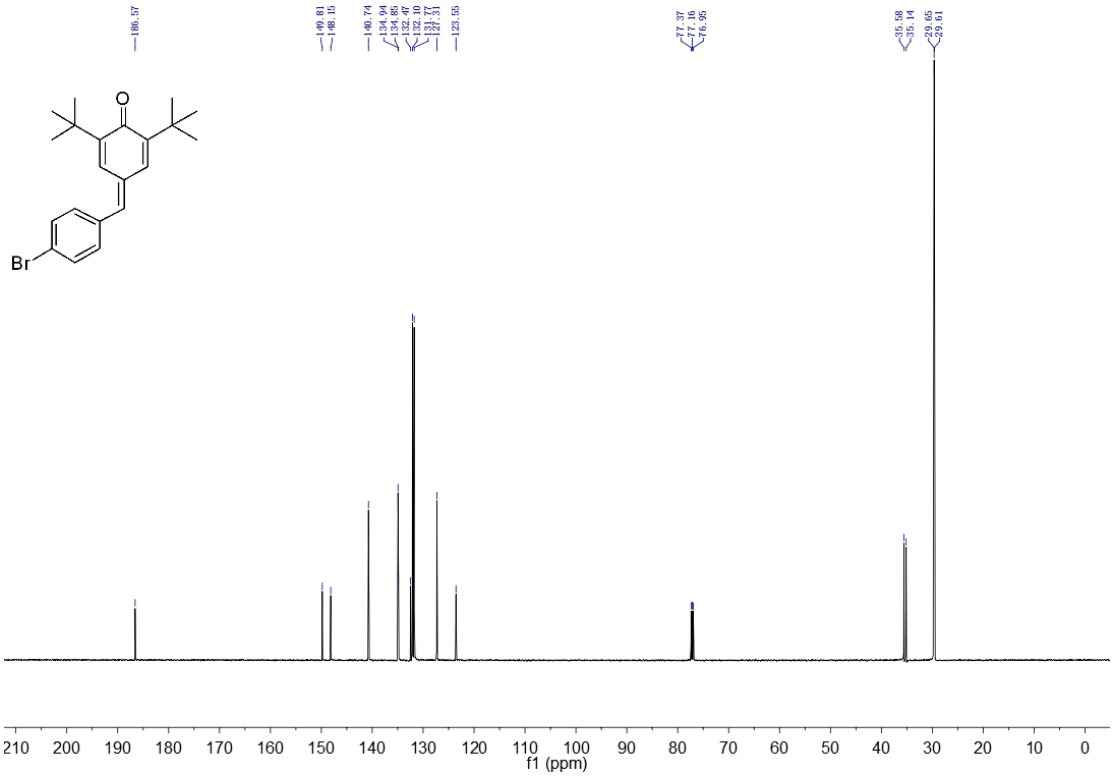
^{13}C NMR of **1c**



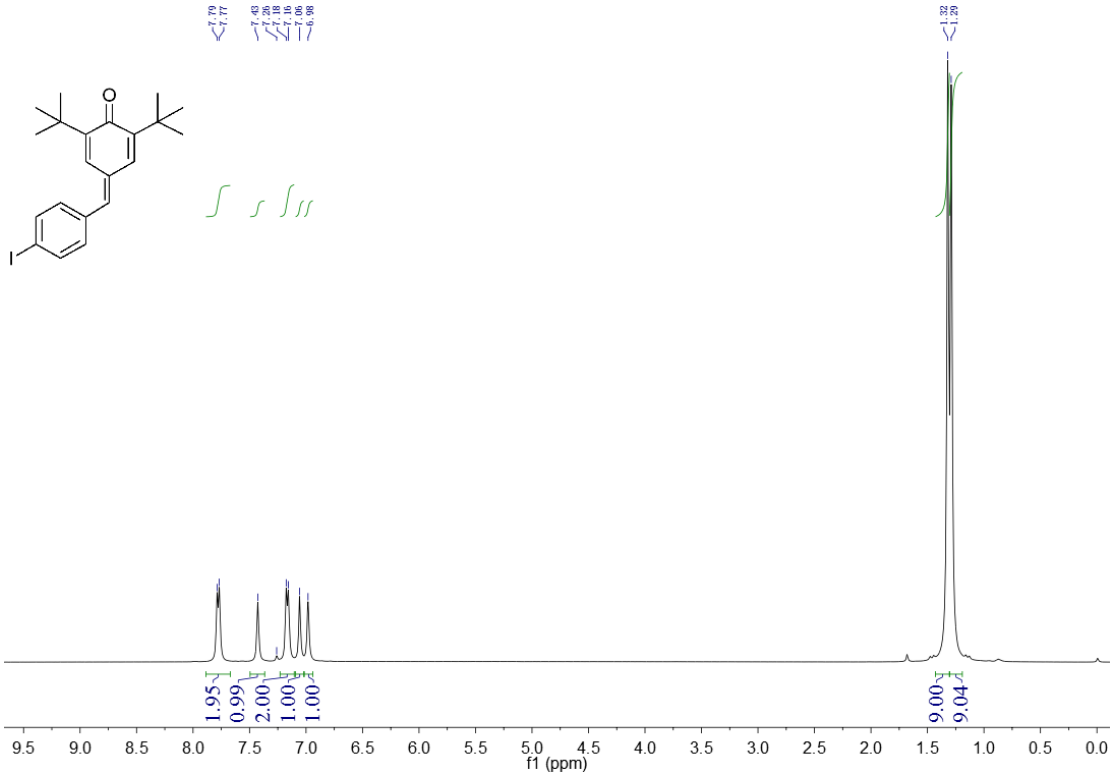
^{1}H NMR of **1d**



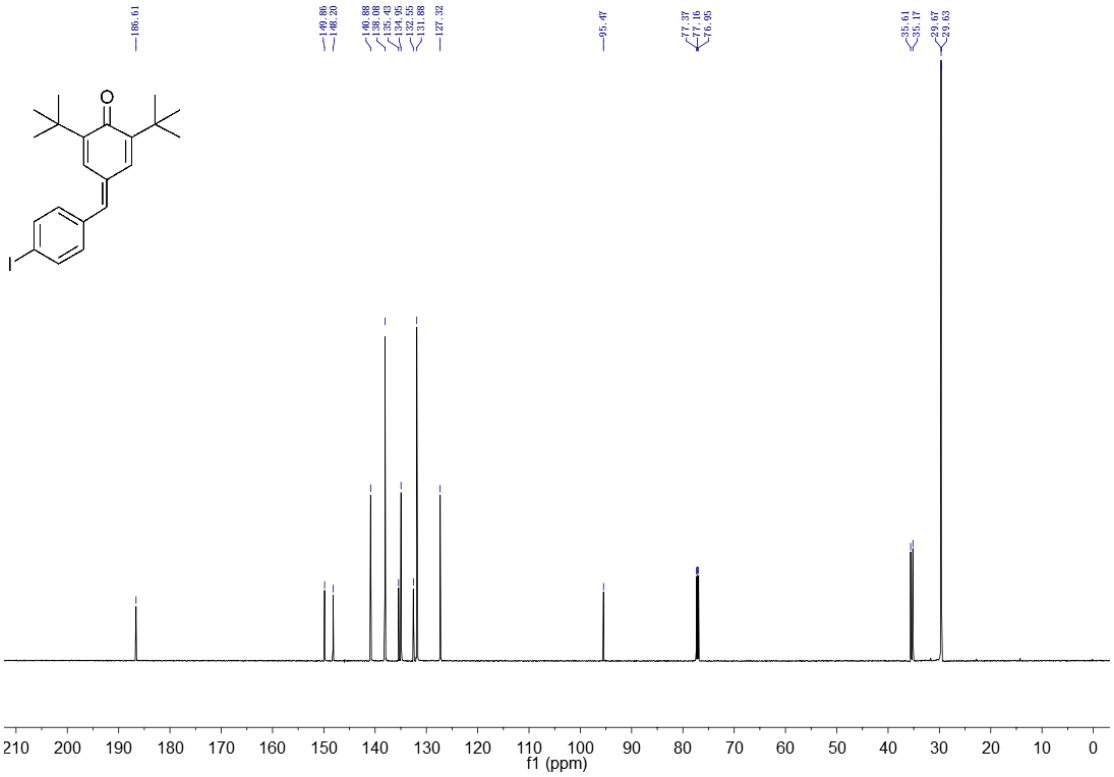
^{13}C NMR of **1d**



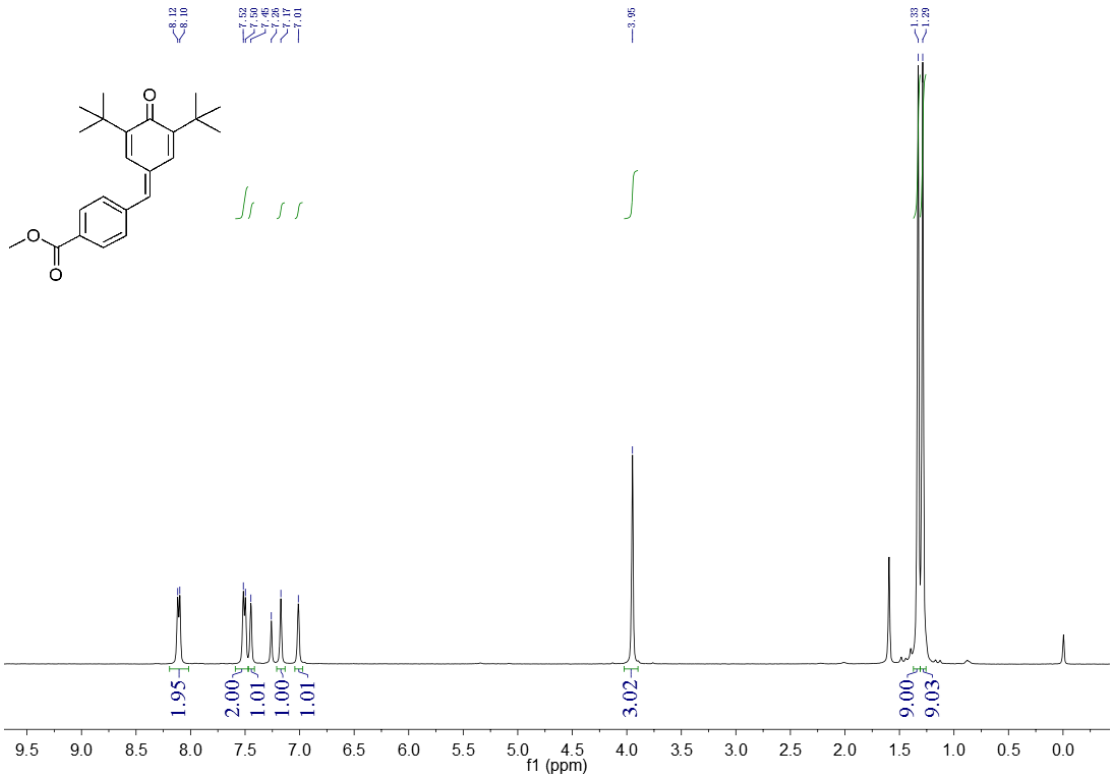
^{1}H NMR of **1e**



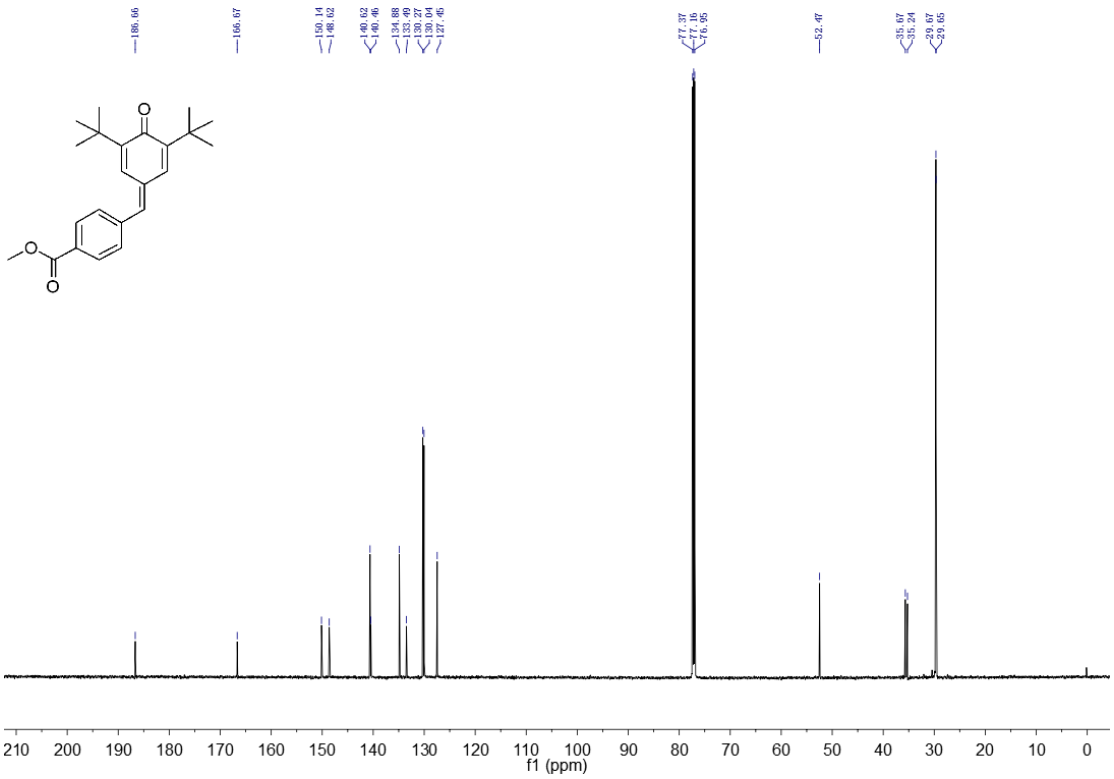
^{13}C NMR of **1e**



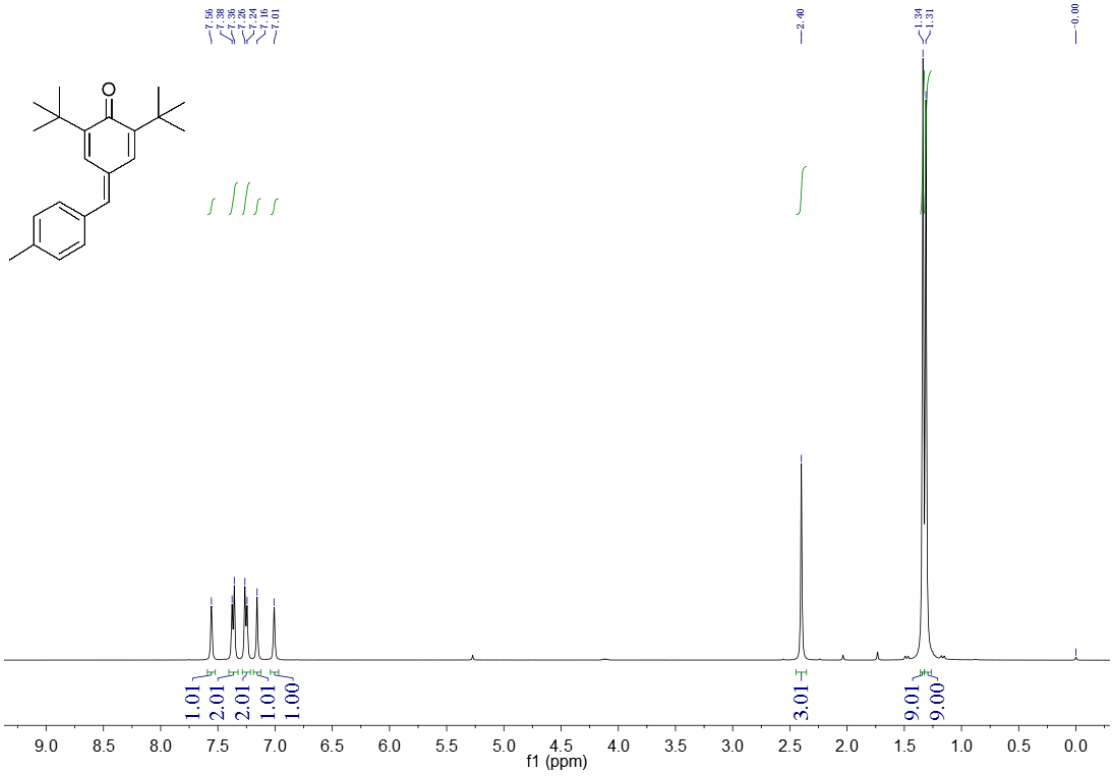
^{1}H NMR of **1f**



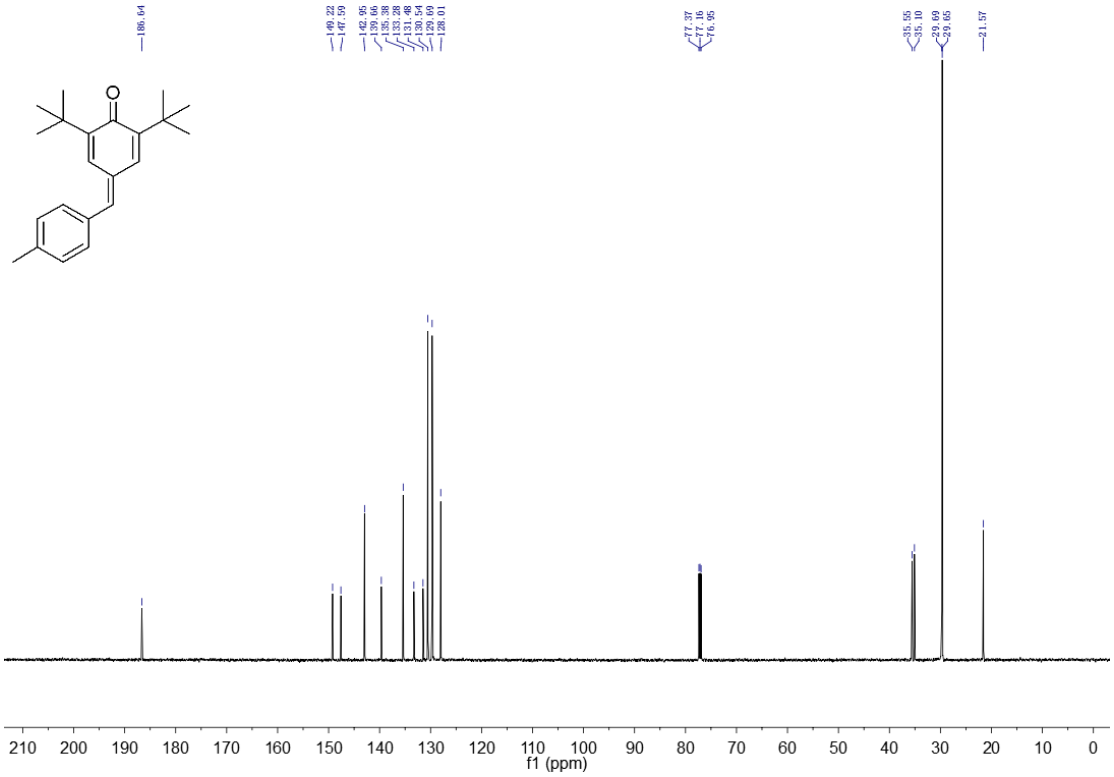
^{13}C NMR of **1f**



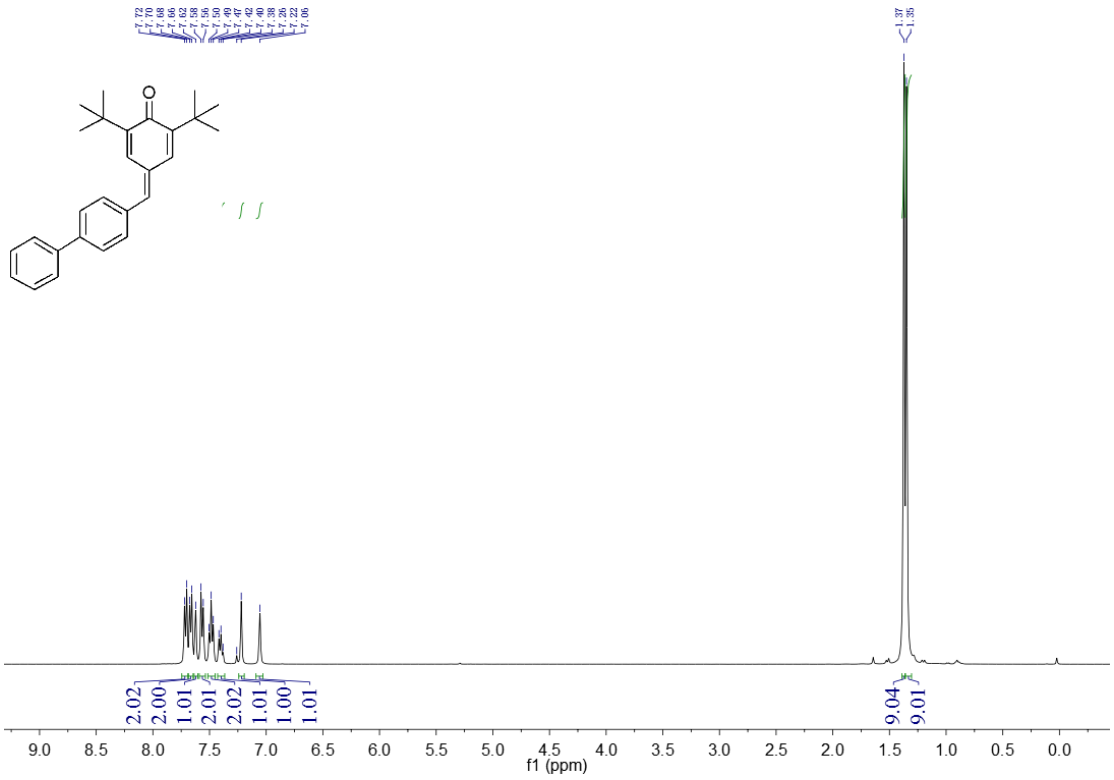
^{1}H NMR of **1g**



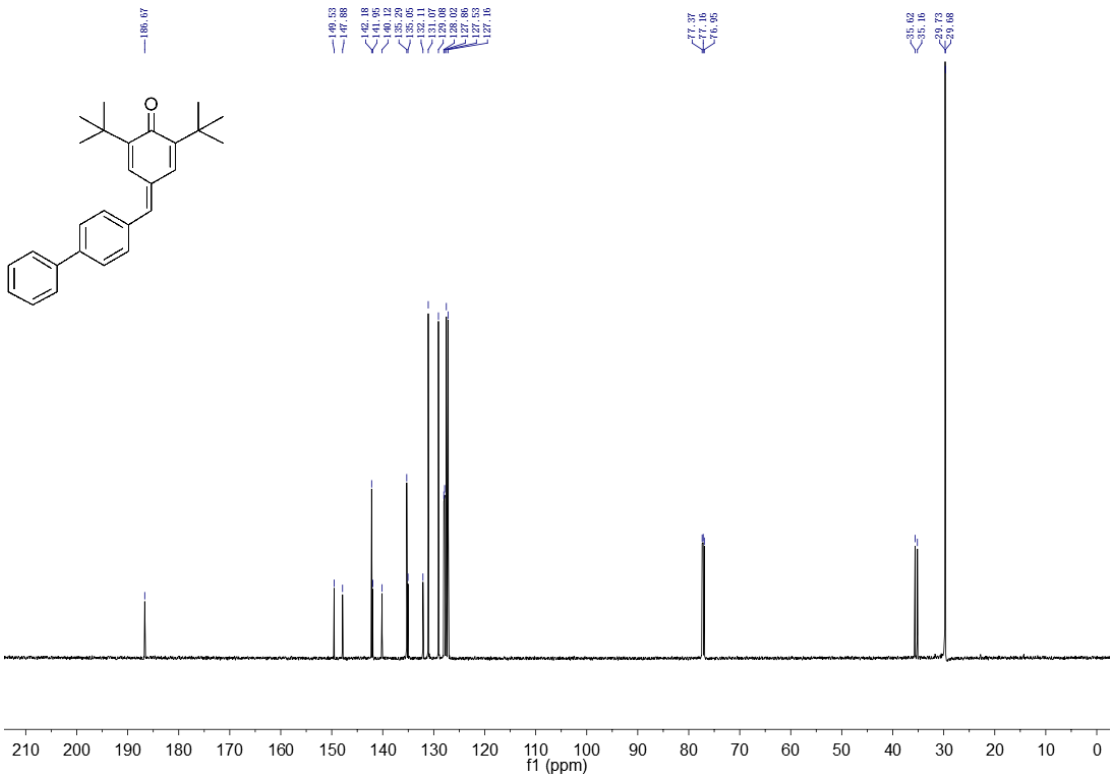
^{13}C NMR of **1g**



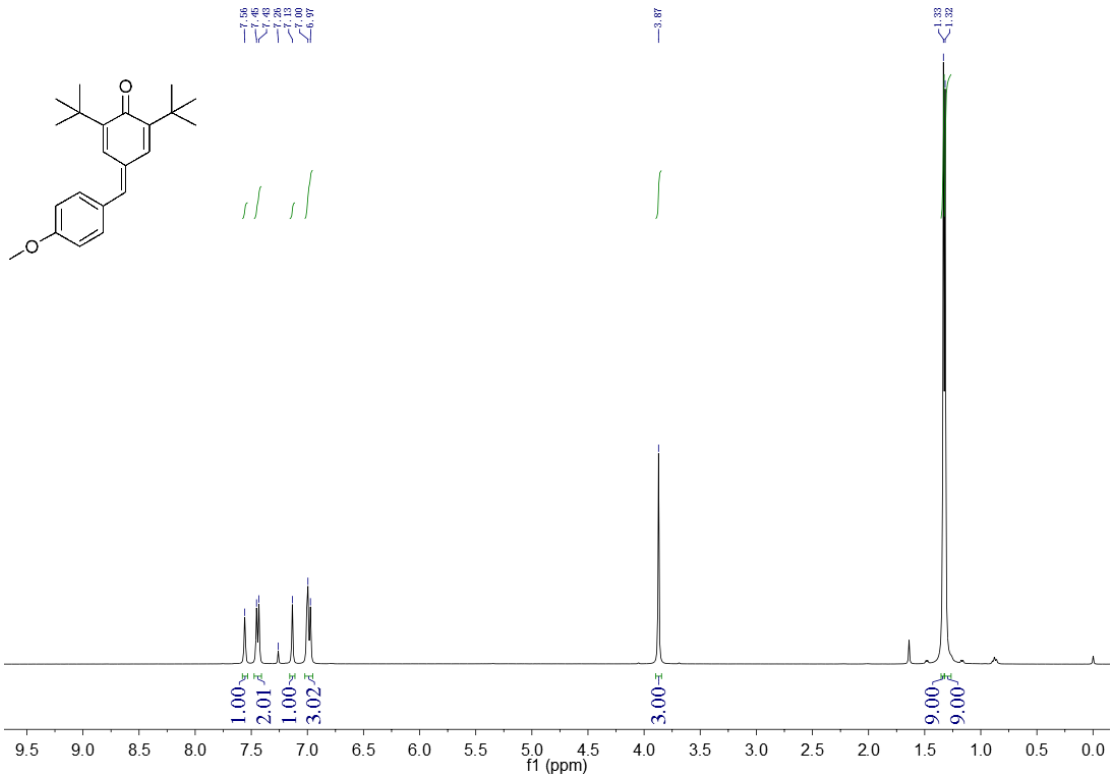
^{1}H NMR of **1h**



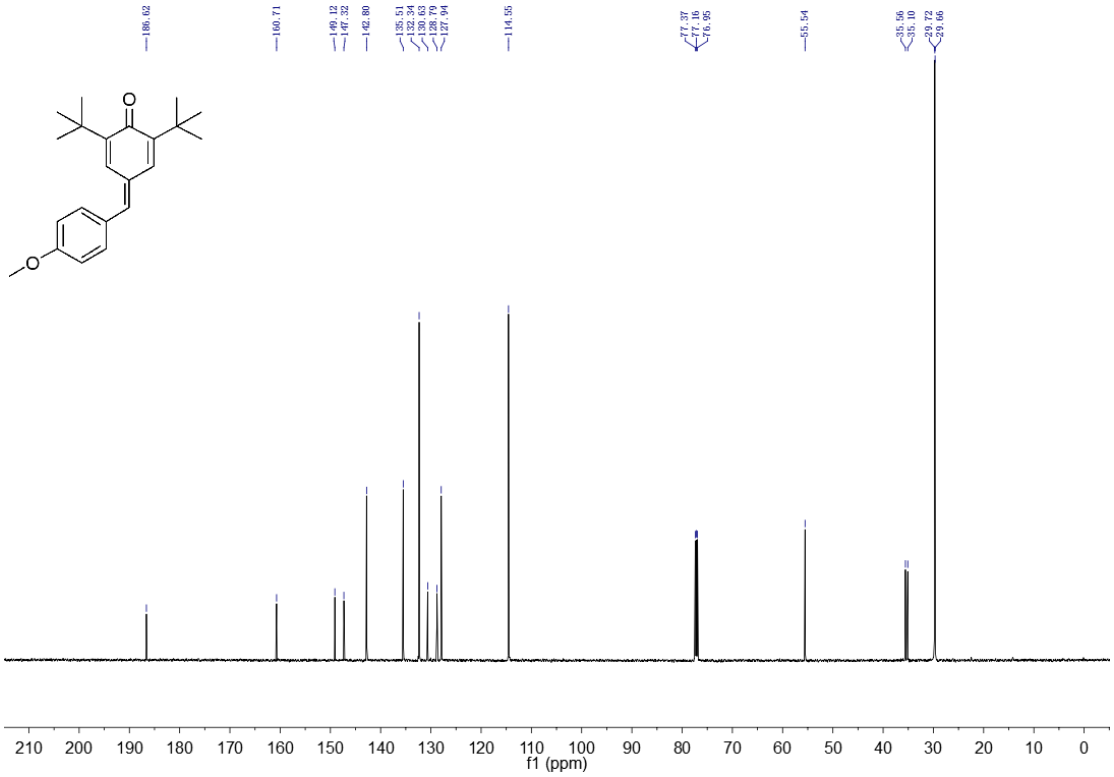
^{13}C NMR of **1h**



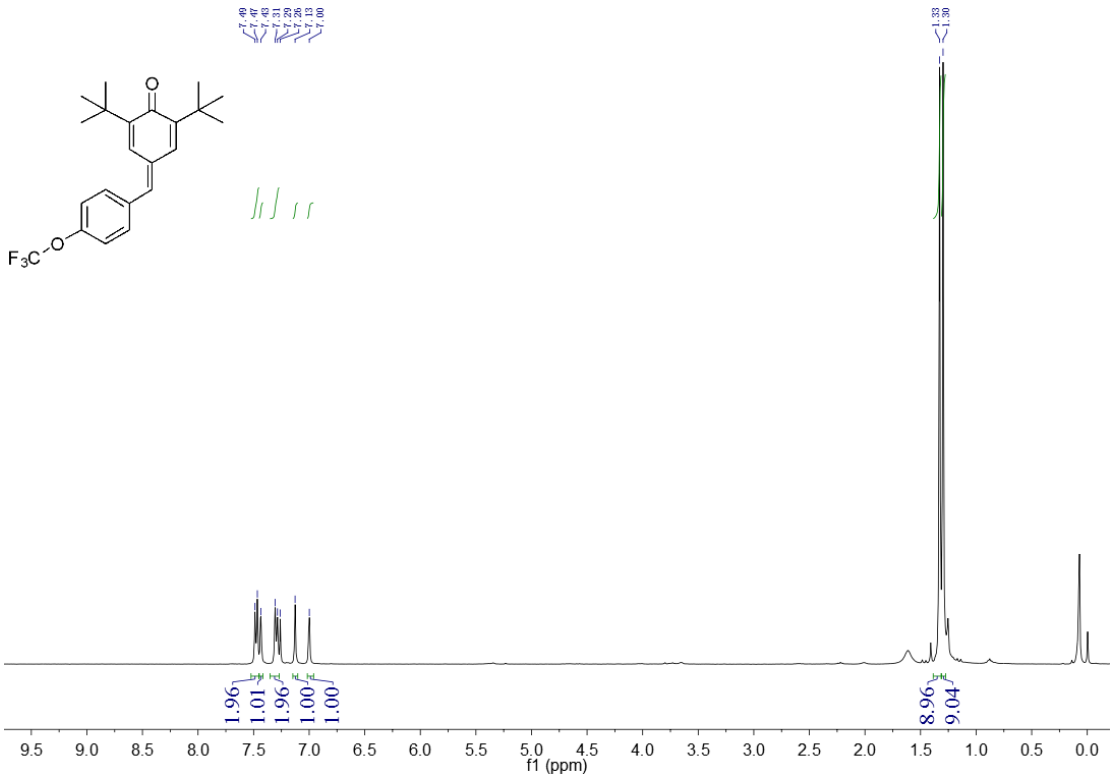
^{1}H NMR of **1i**



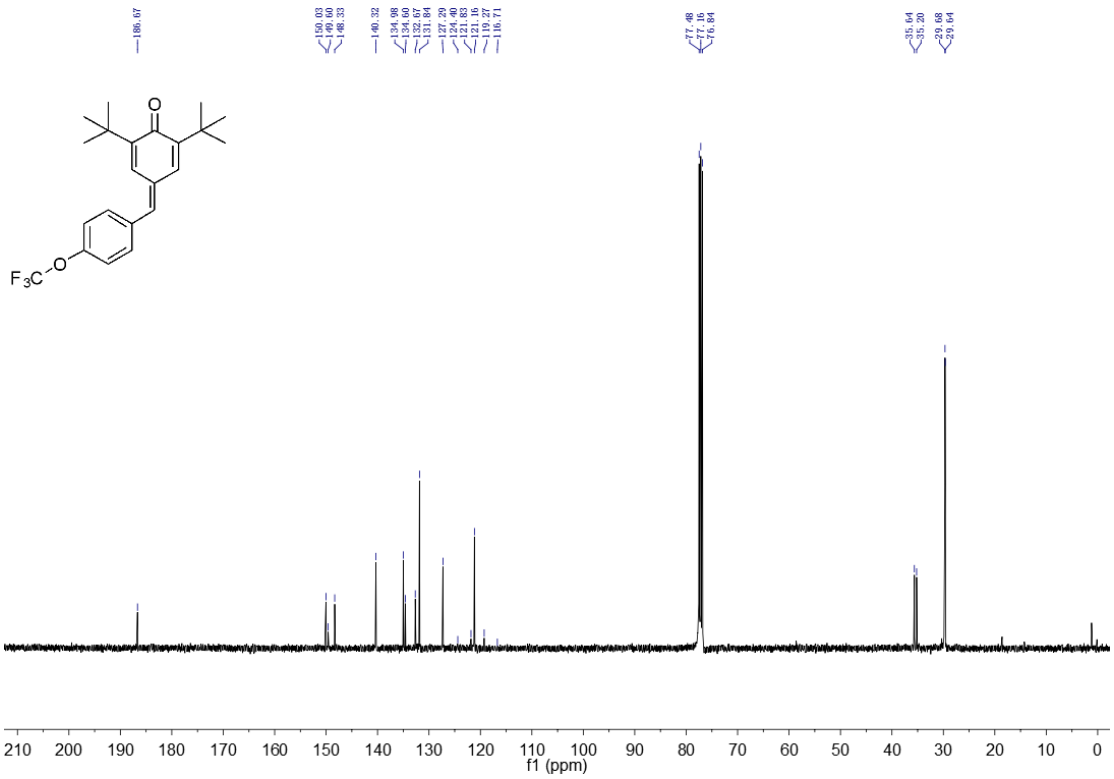
^{13}C NMR of **1i**



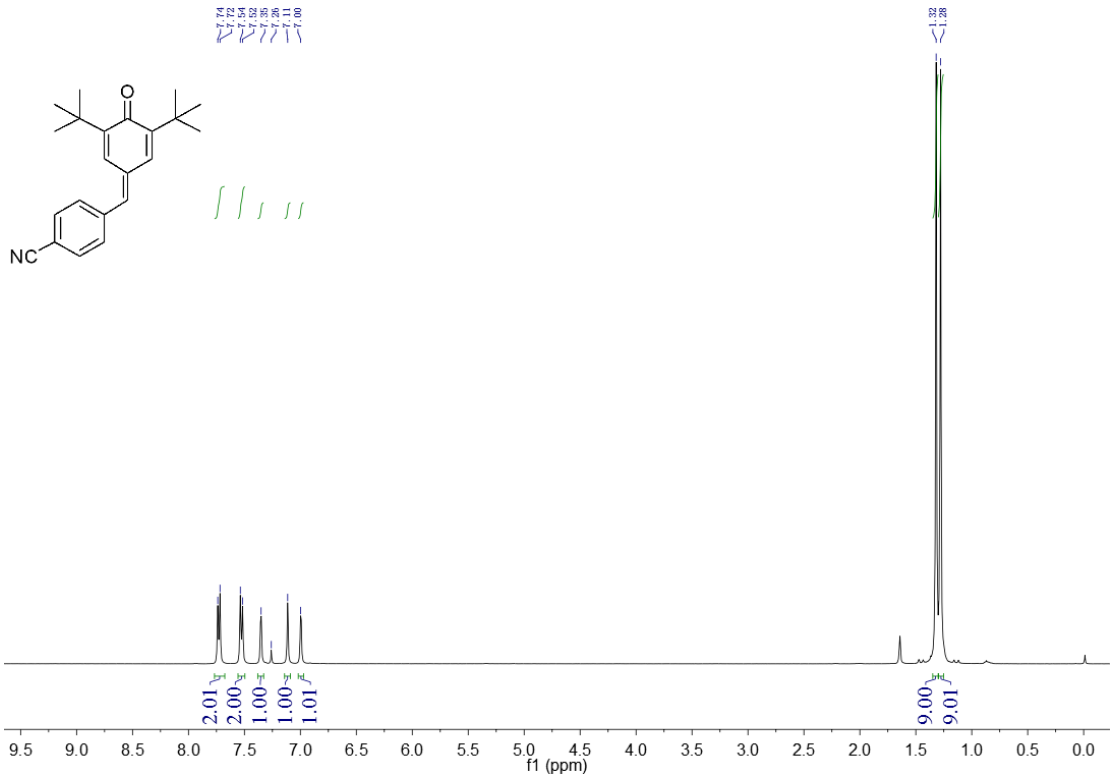
^{1}H NMR of **1j**



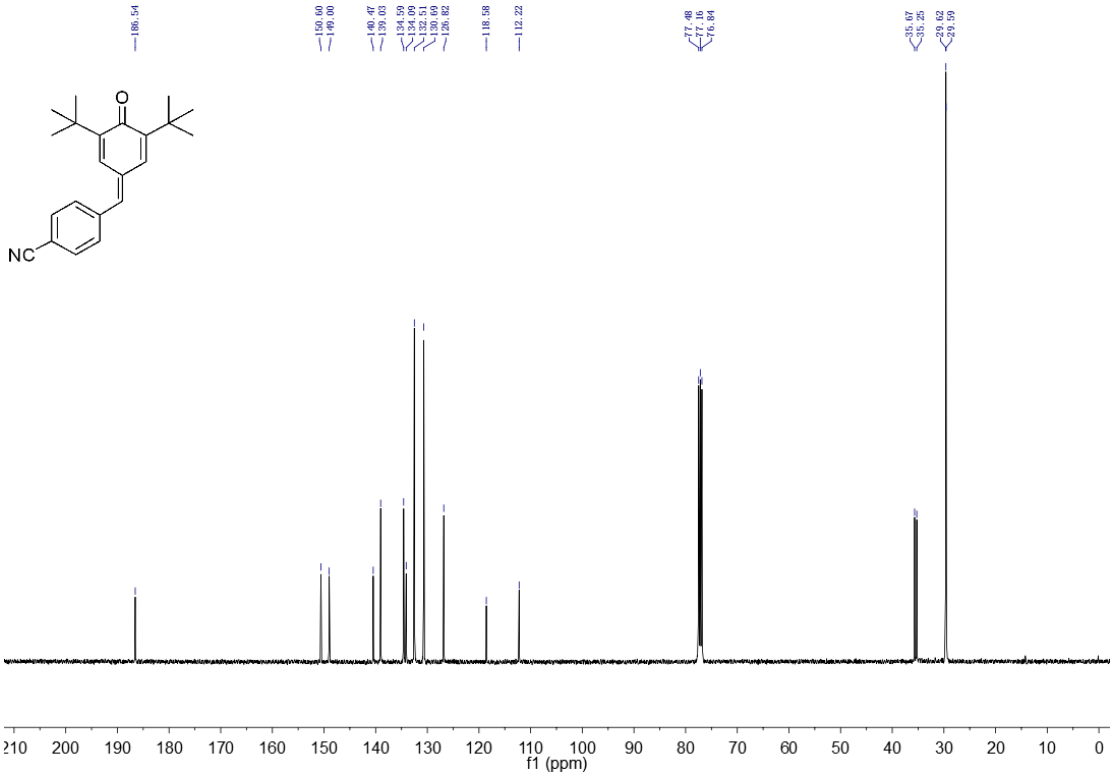
^{13}C NMR of **1j**



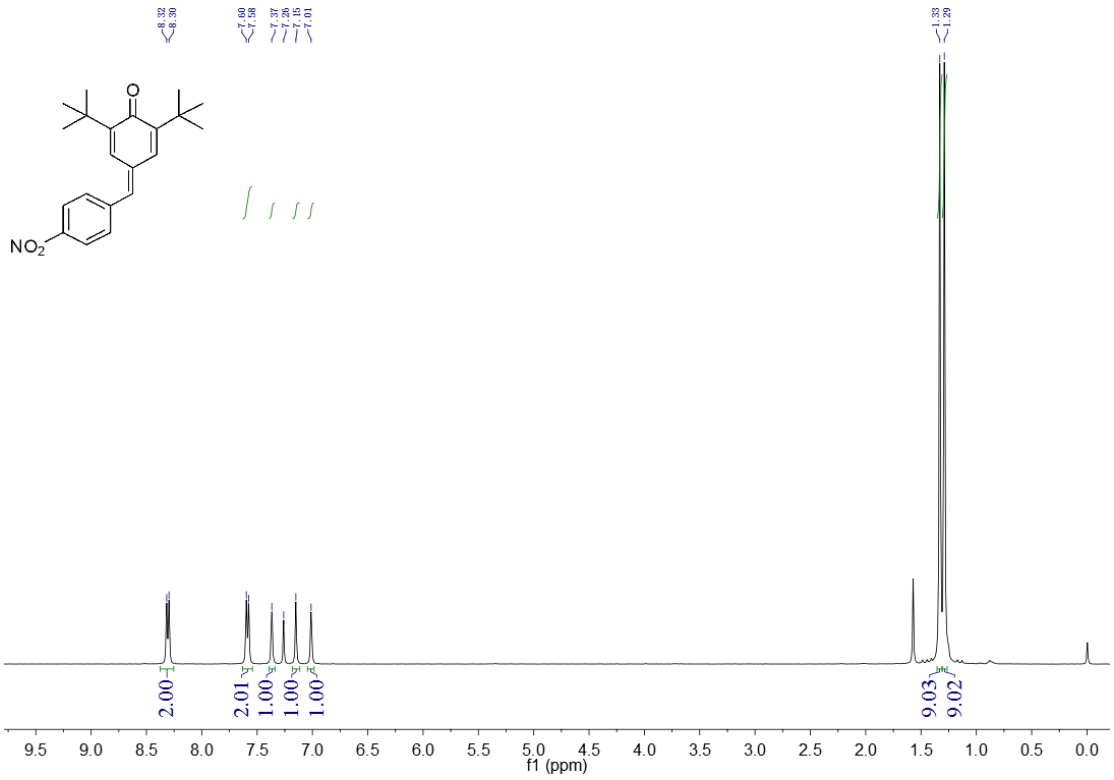
^{1}H NMR of **1k**



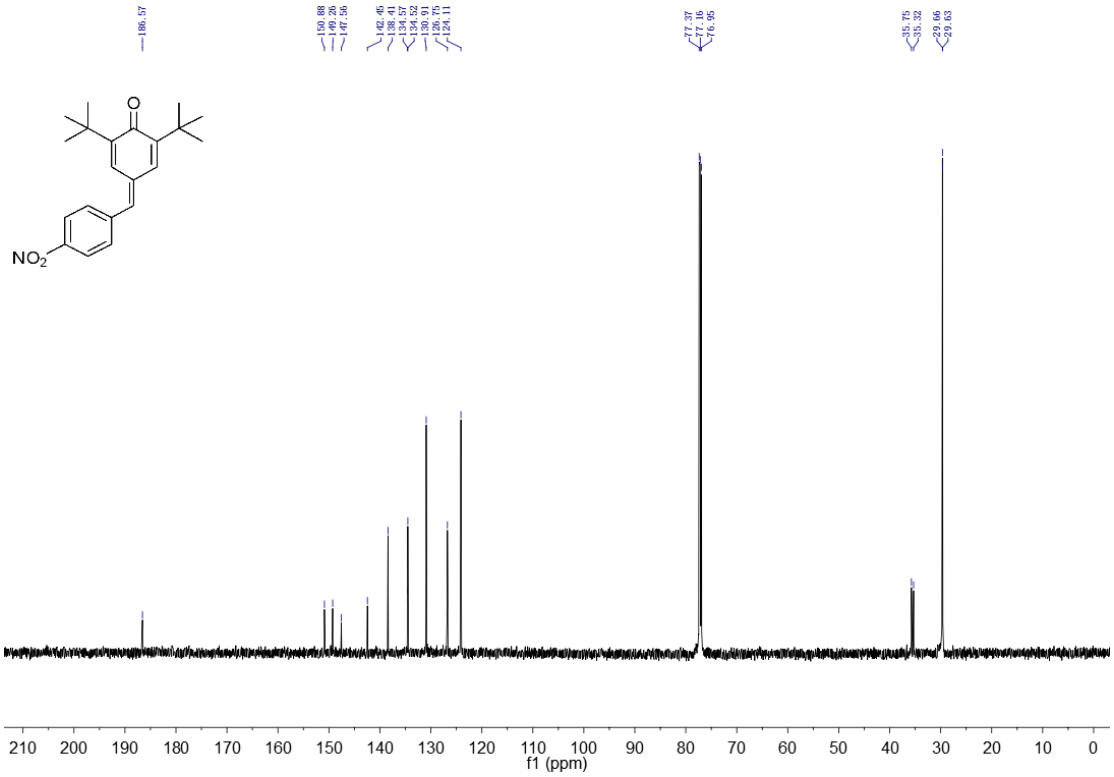
^{13}C NMR of **1k**



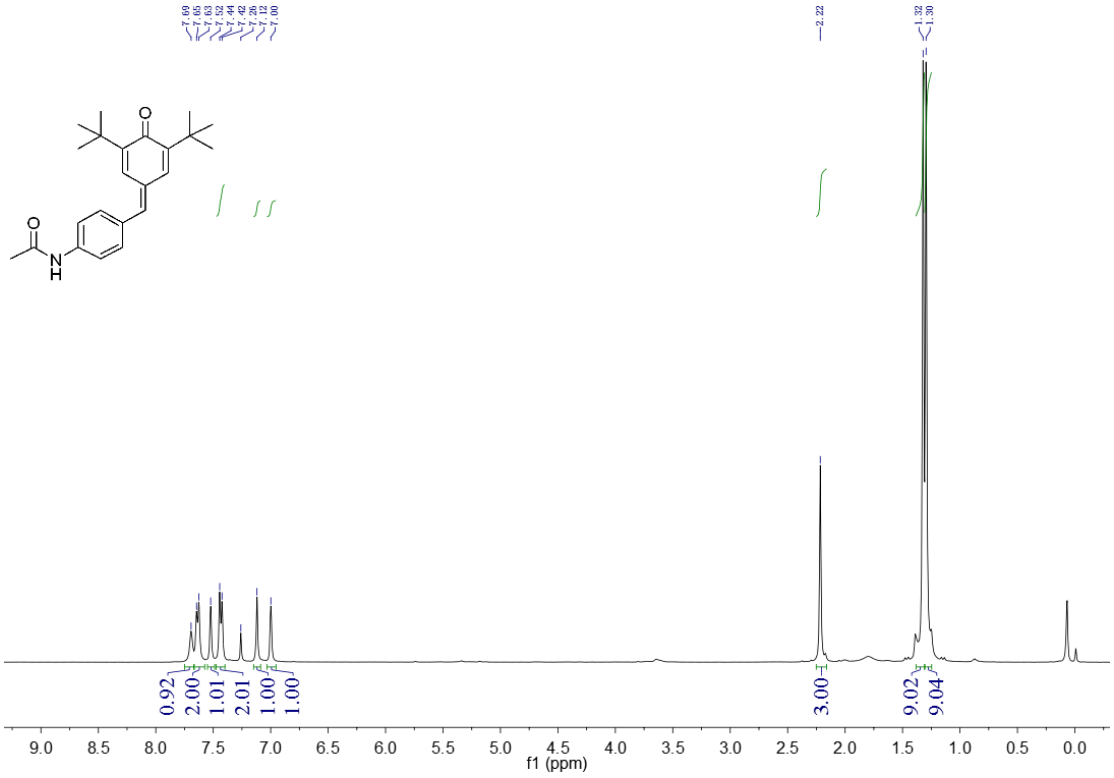
^{1}H NMR of **1l**



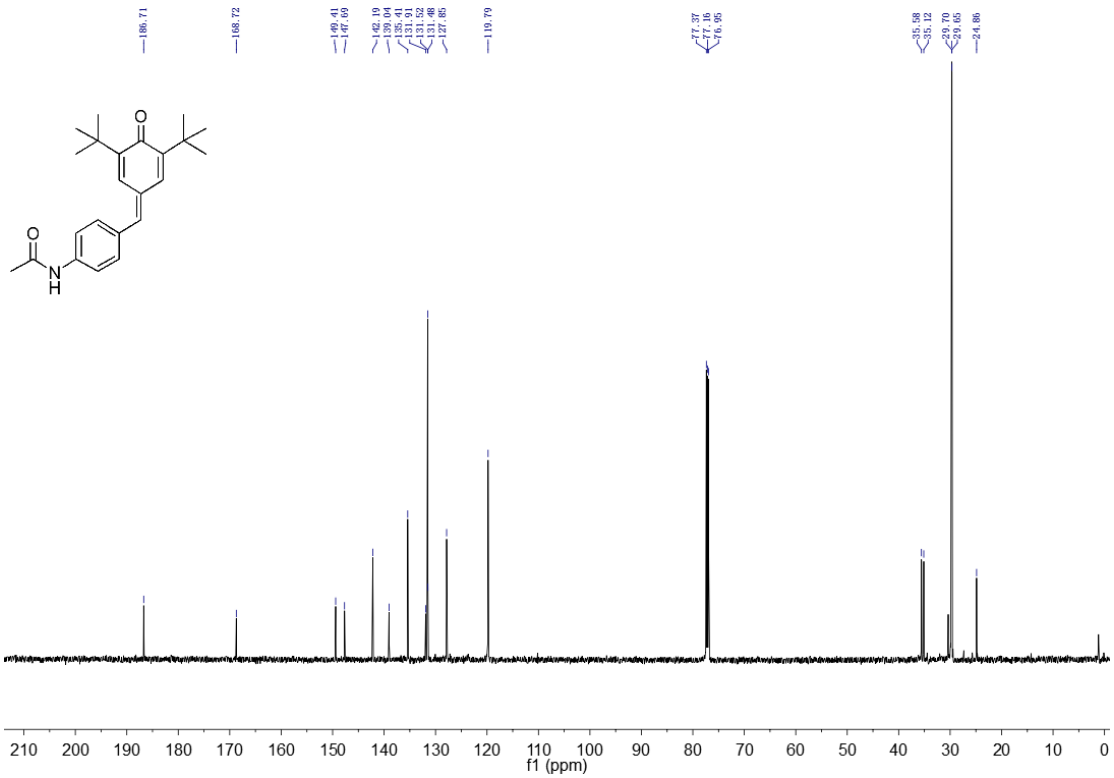
^{13}C NMR of **1l**



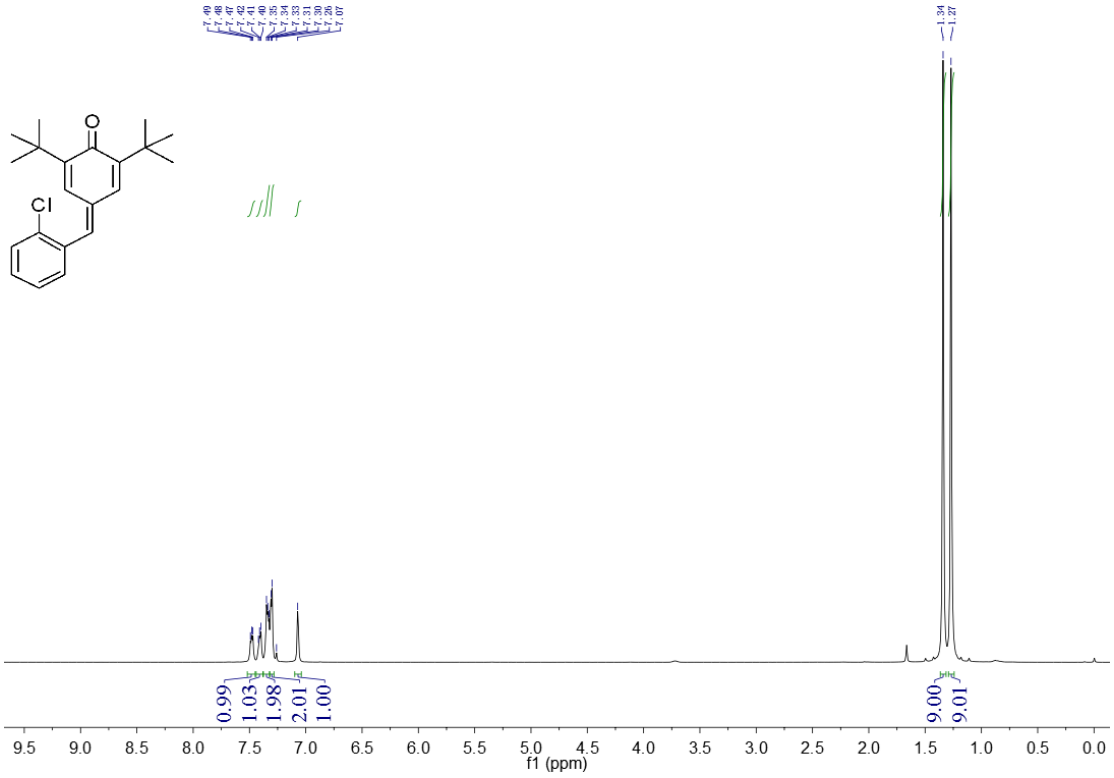
^{1}H NMR of **1m**



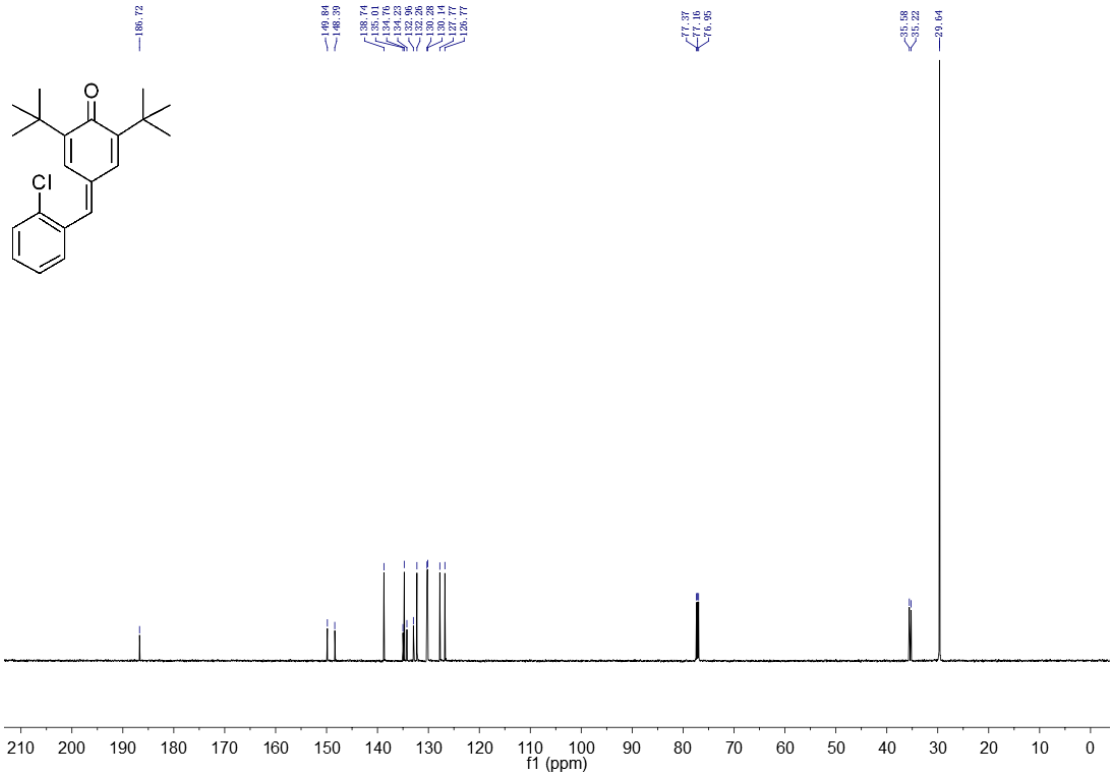
^{13}C NMR of **1m**



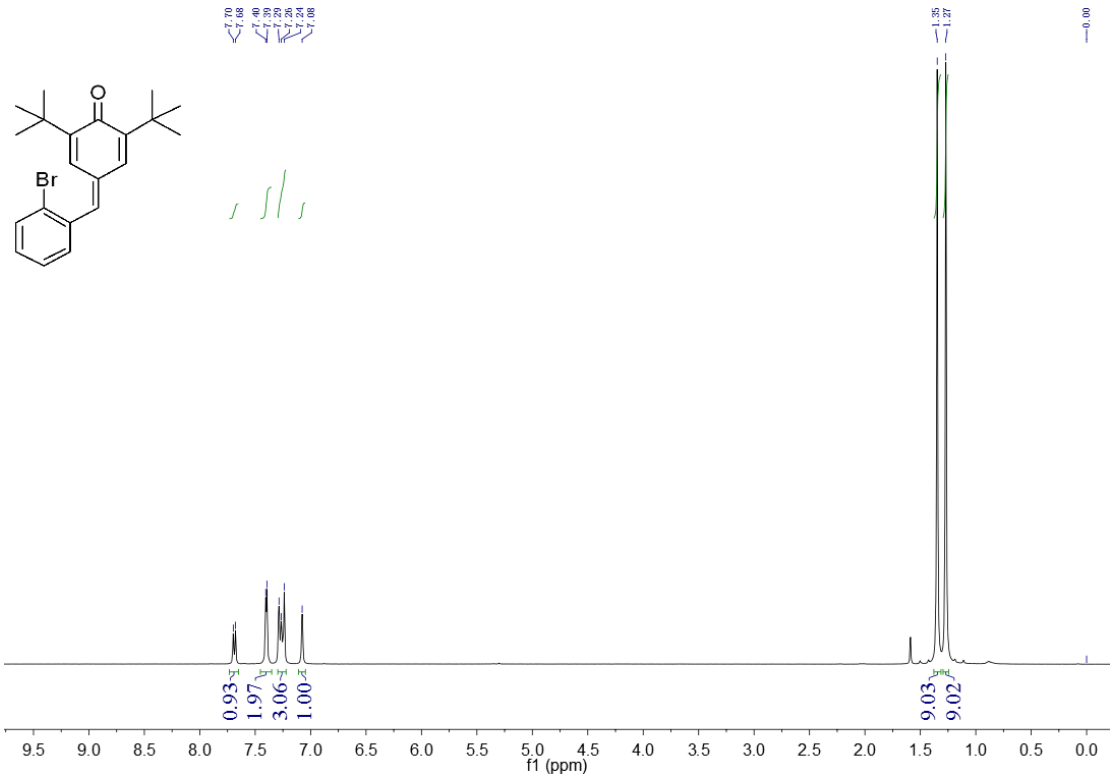
^{1}H NMR of **1n**



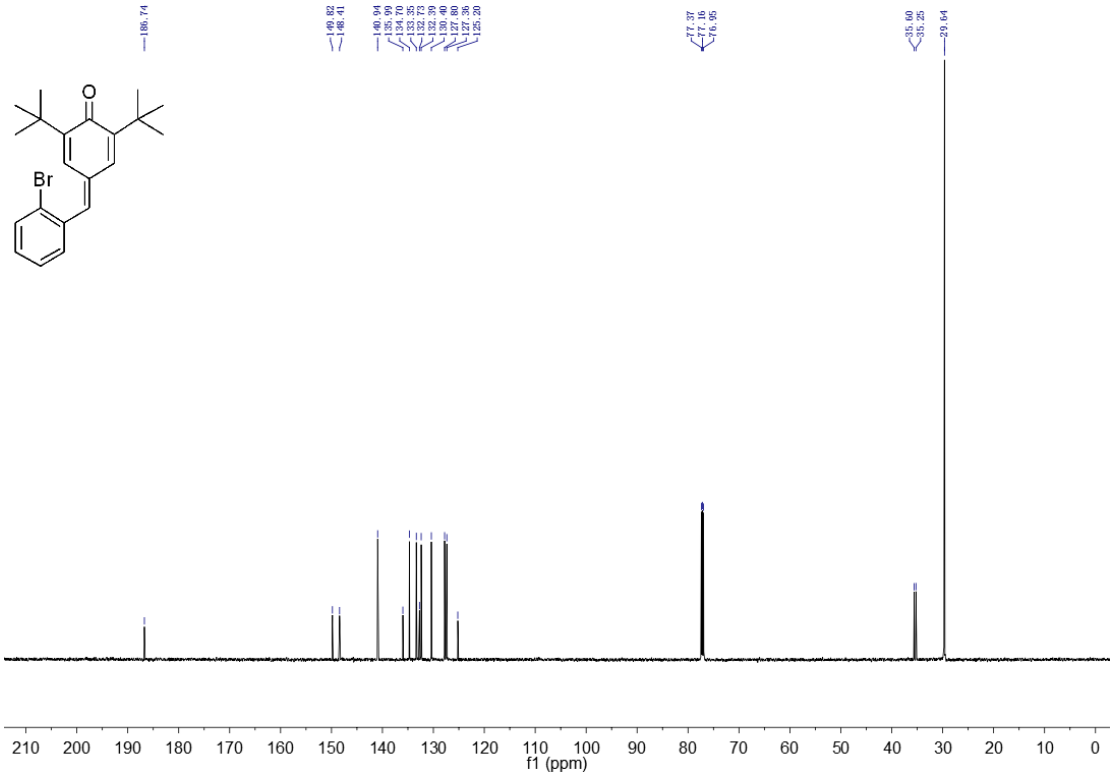
^{13}C NMR of **1n**



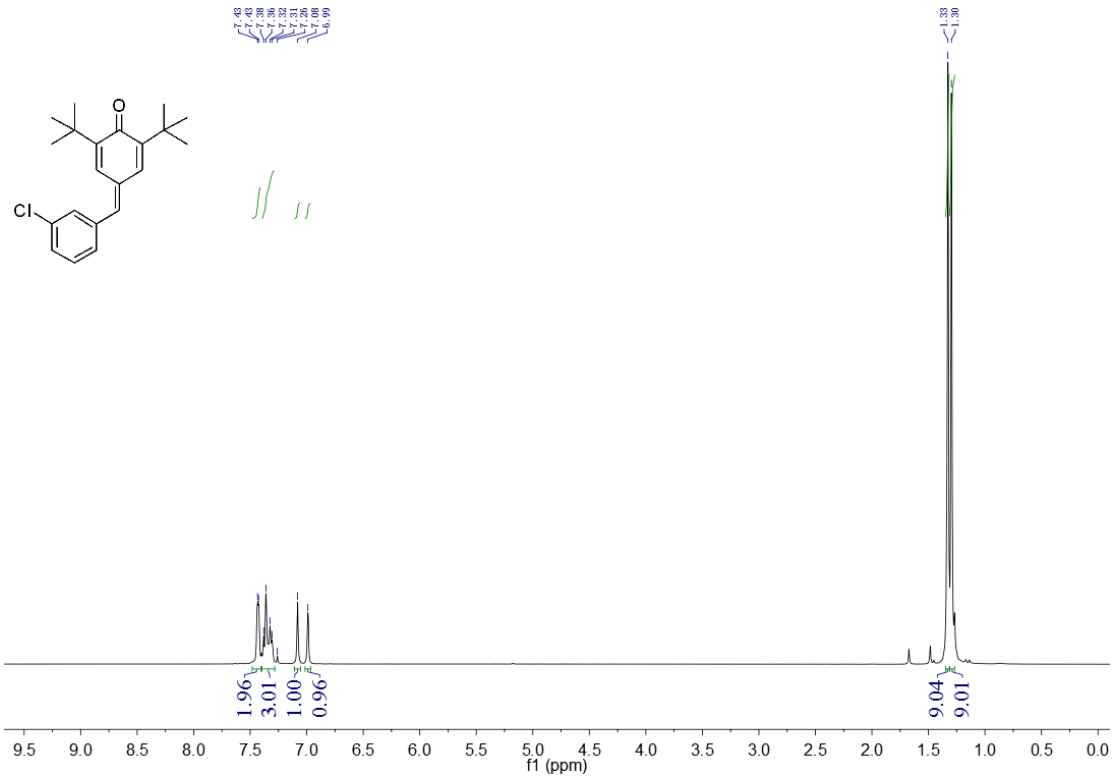
^{1}H NMR of **1o**



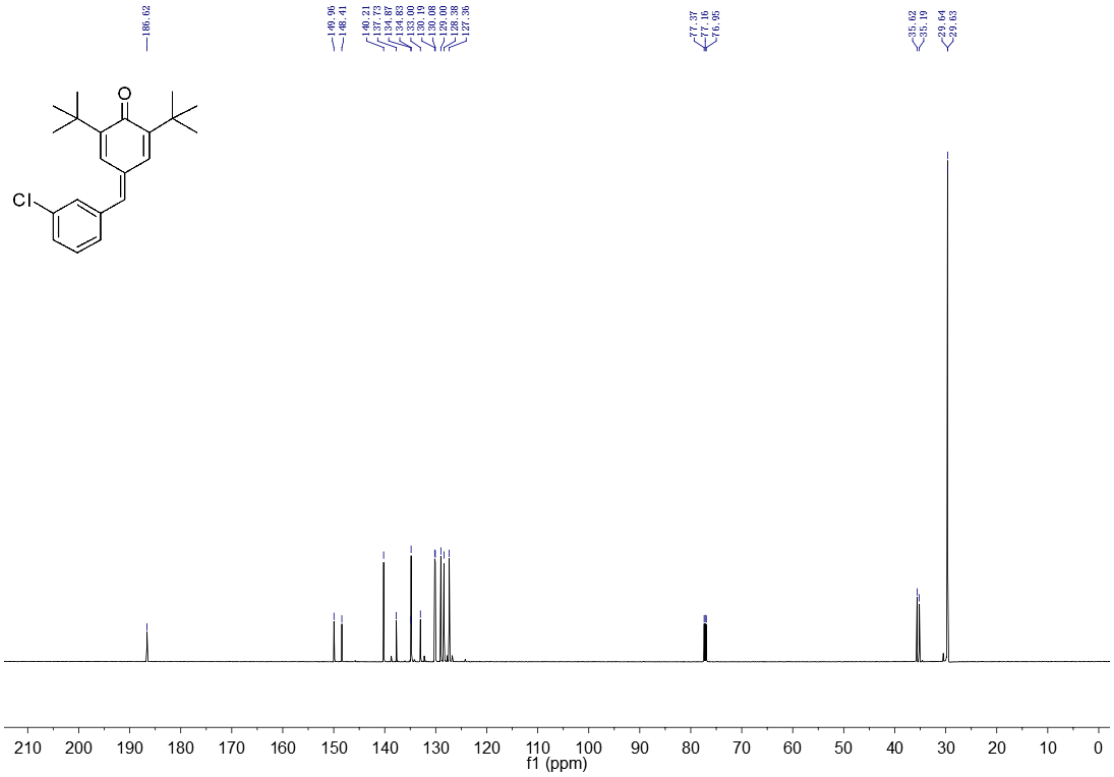
^{13}C NMR of **1o**



^{1}H NMR of **1p**



^{13}C NMR of **1p**



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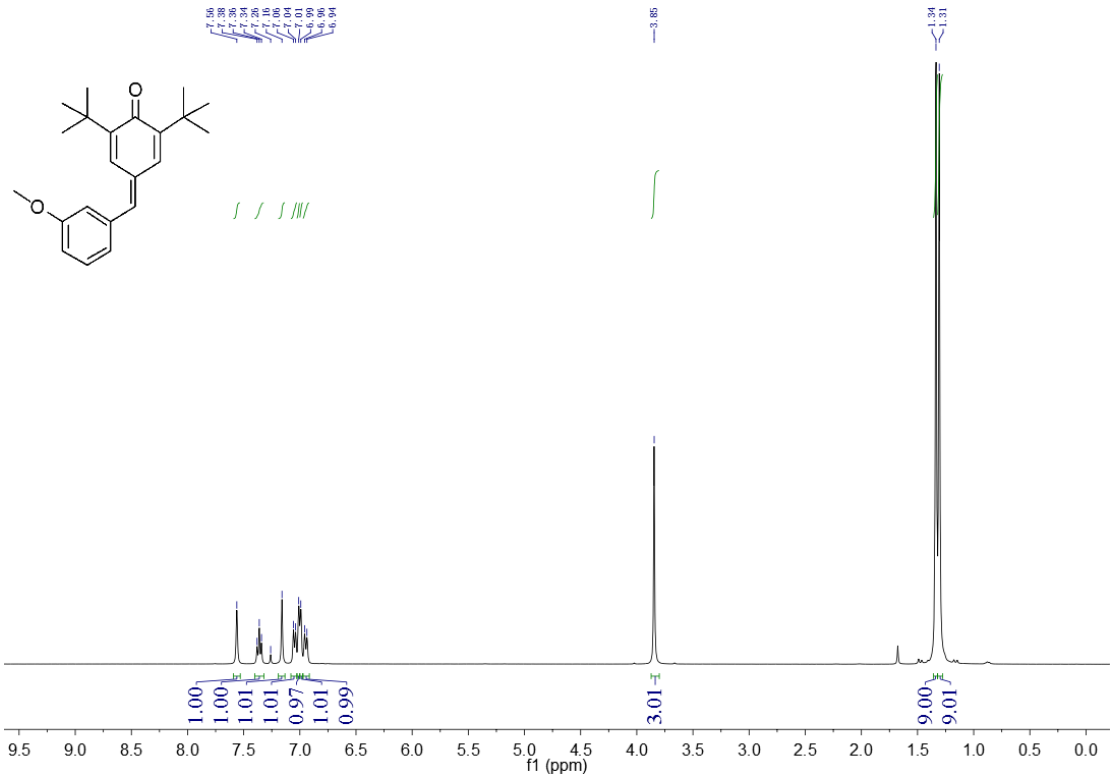

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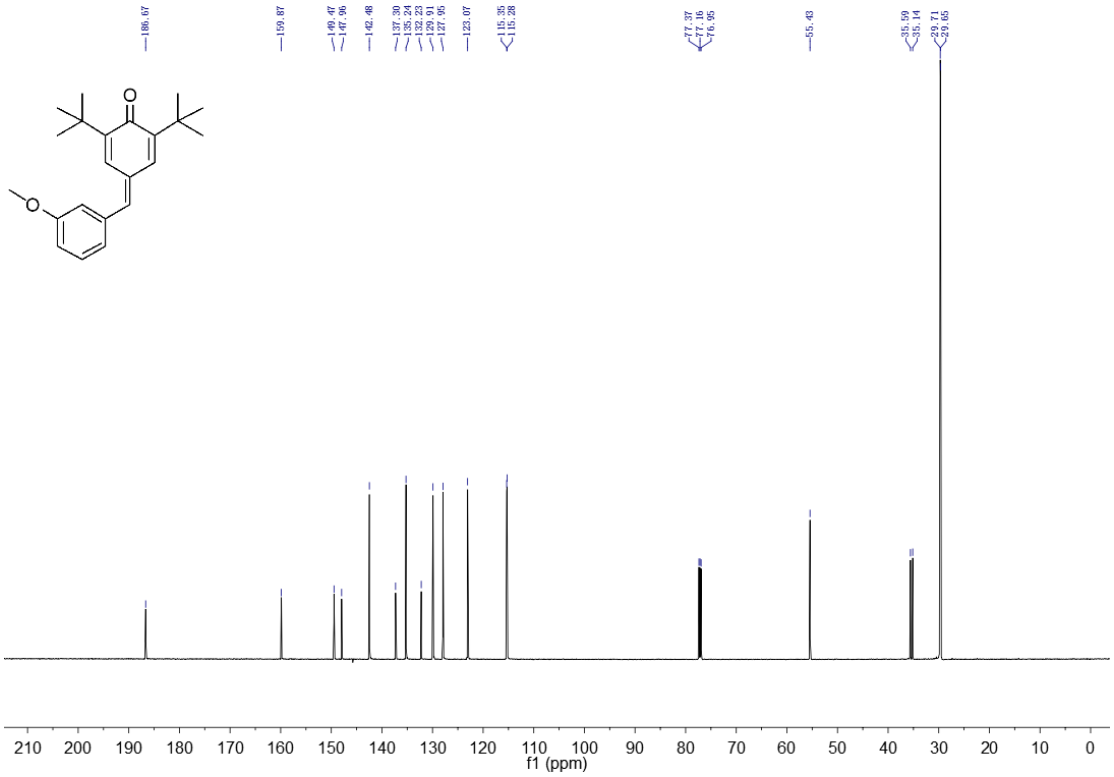

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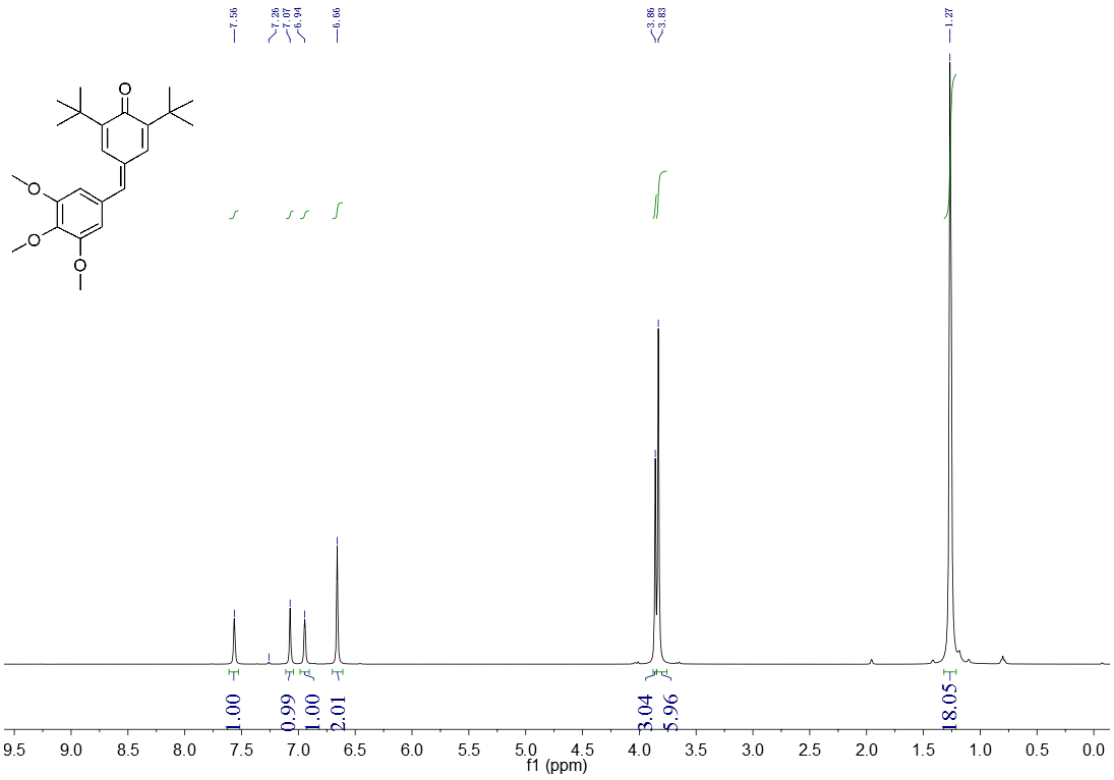

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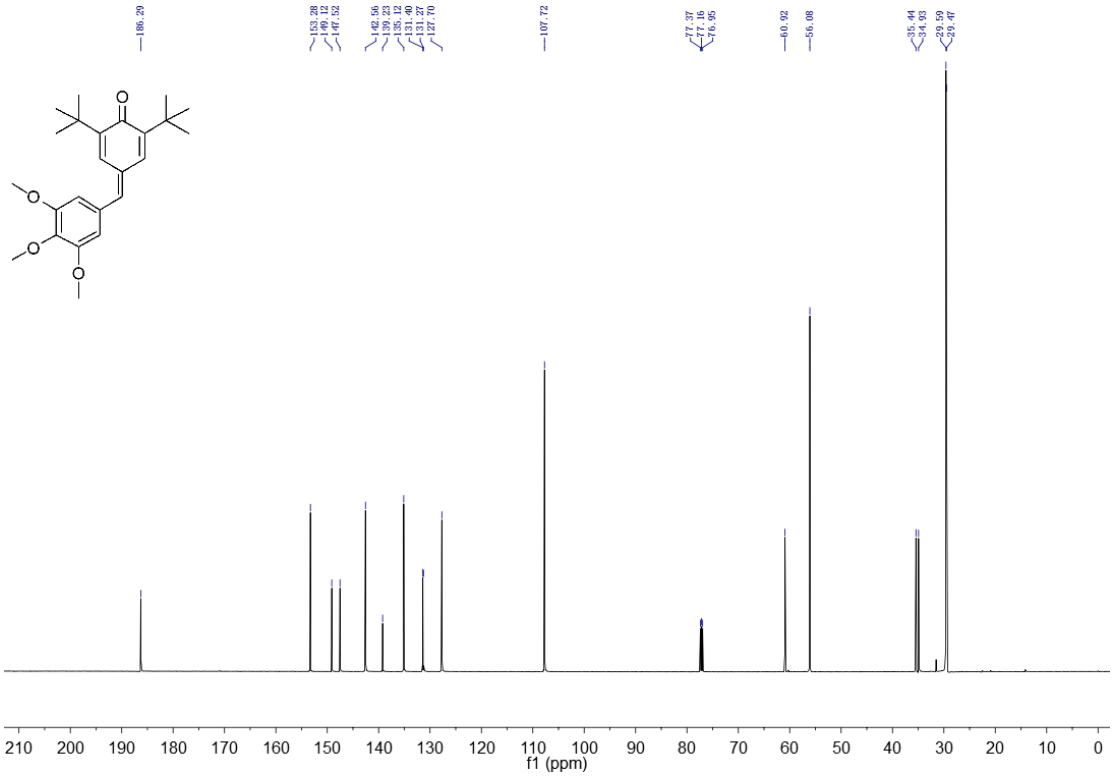

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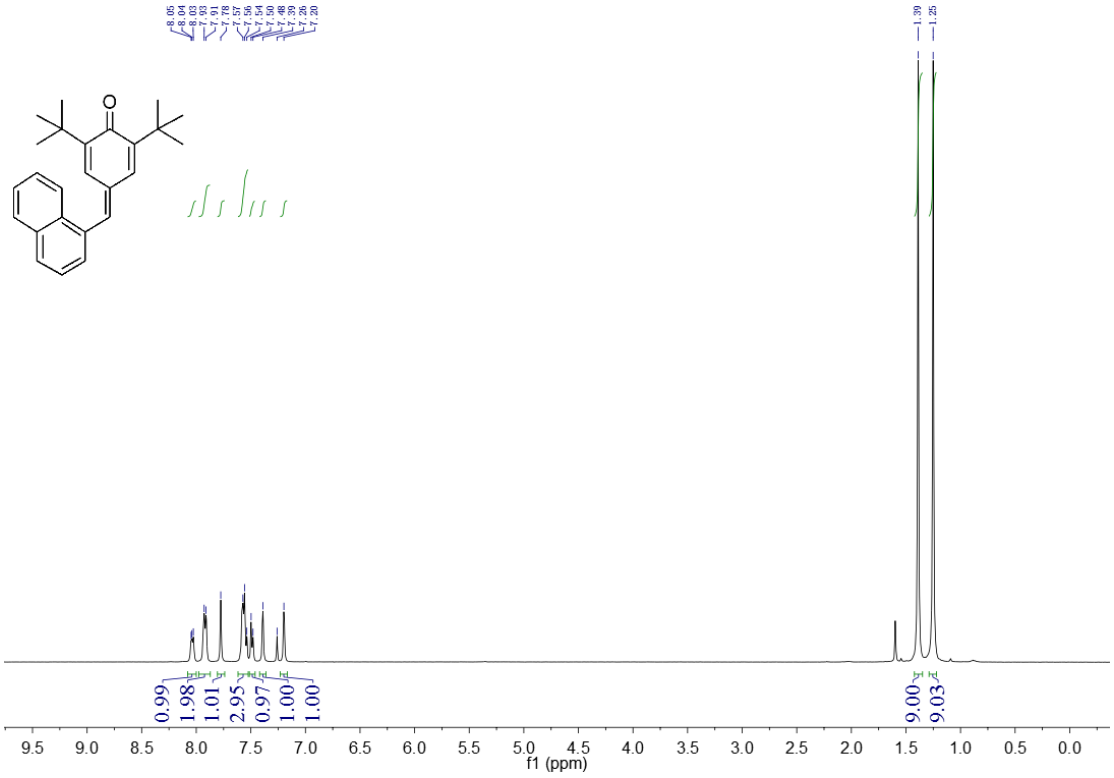

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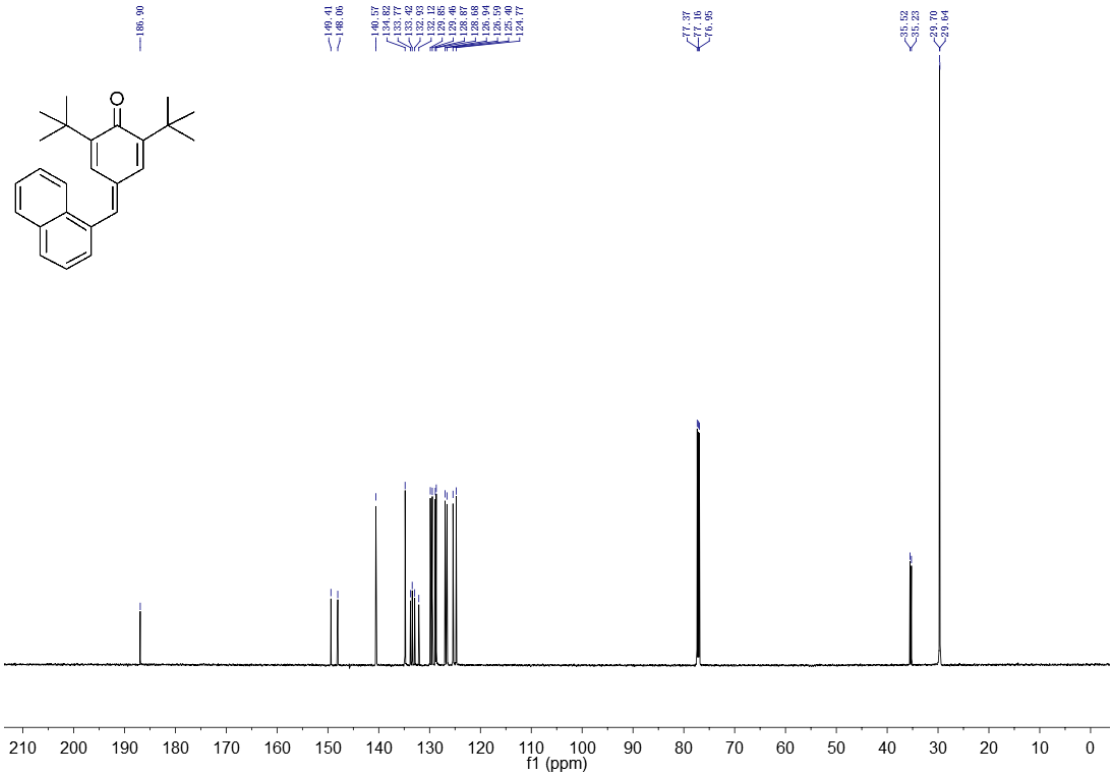
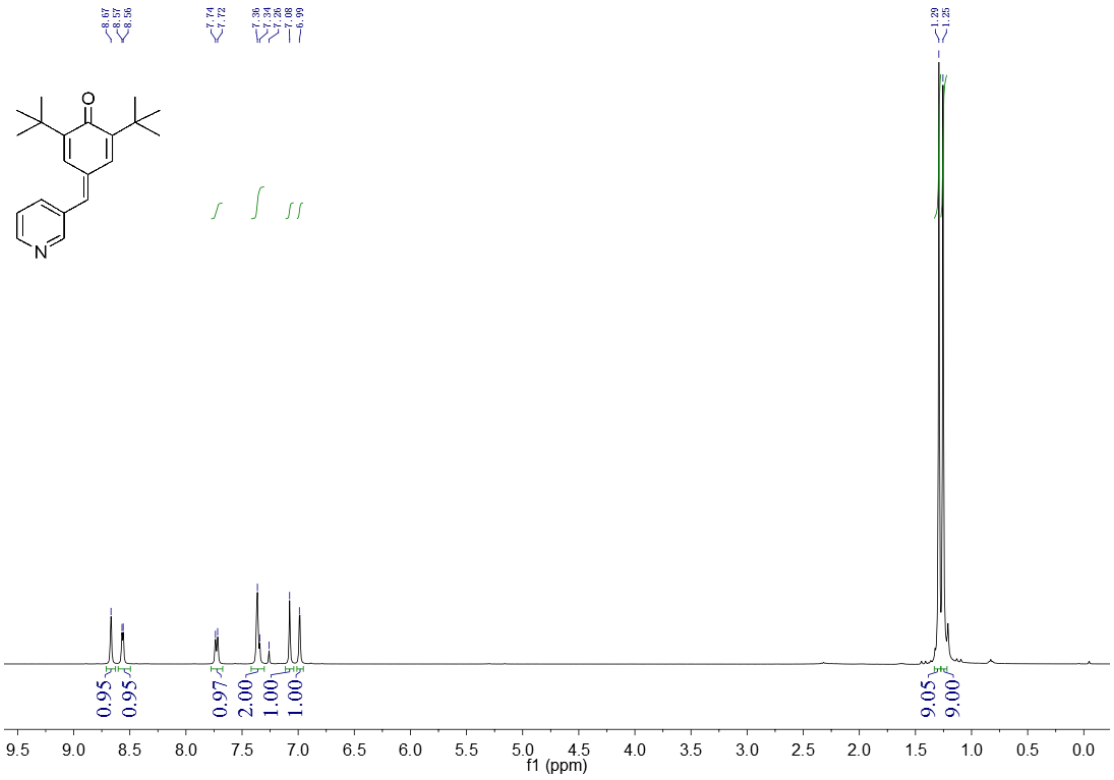
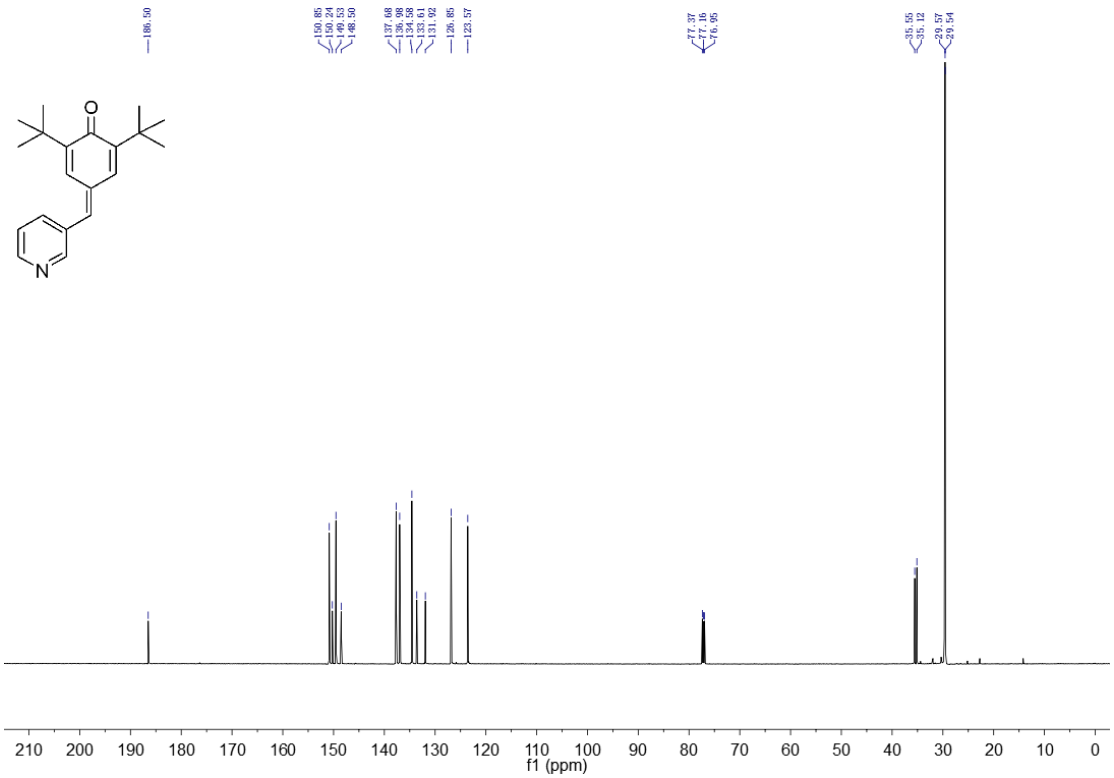


^{1}H NMR of **1t**



^{13}C NMR of **1t**



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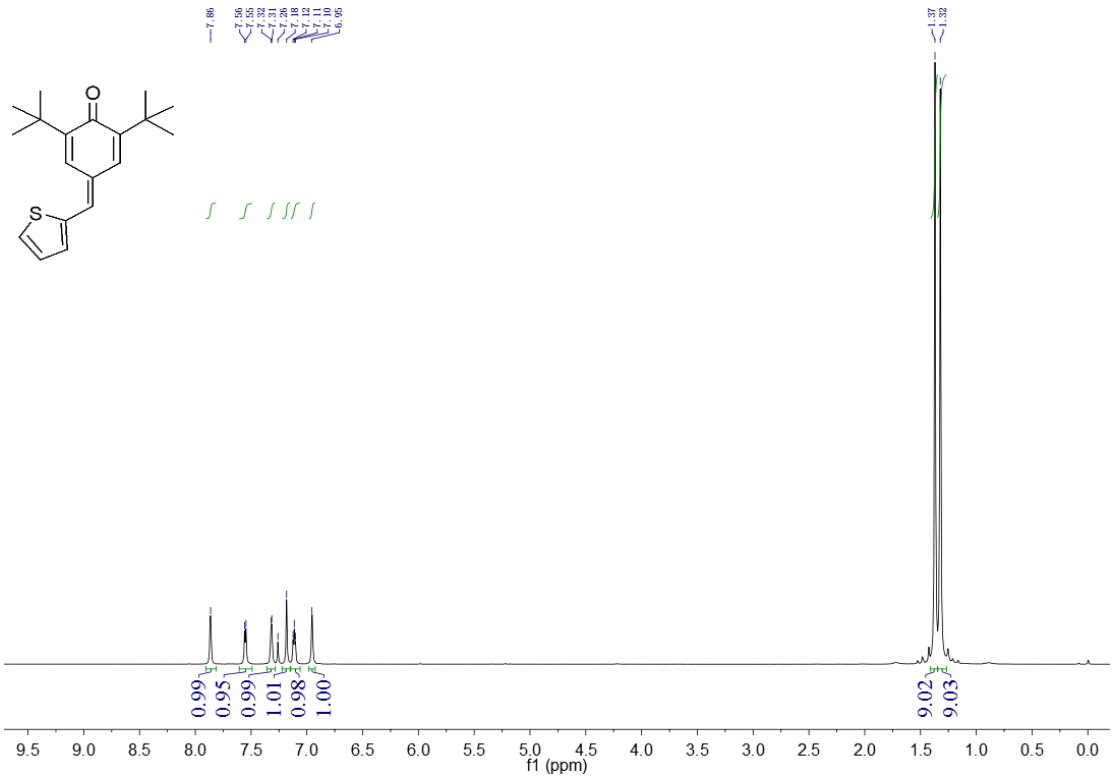
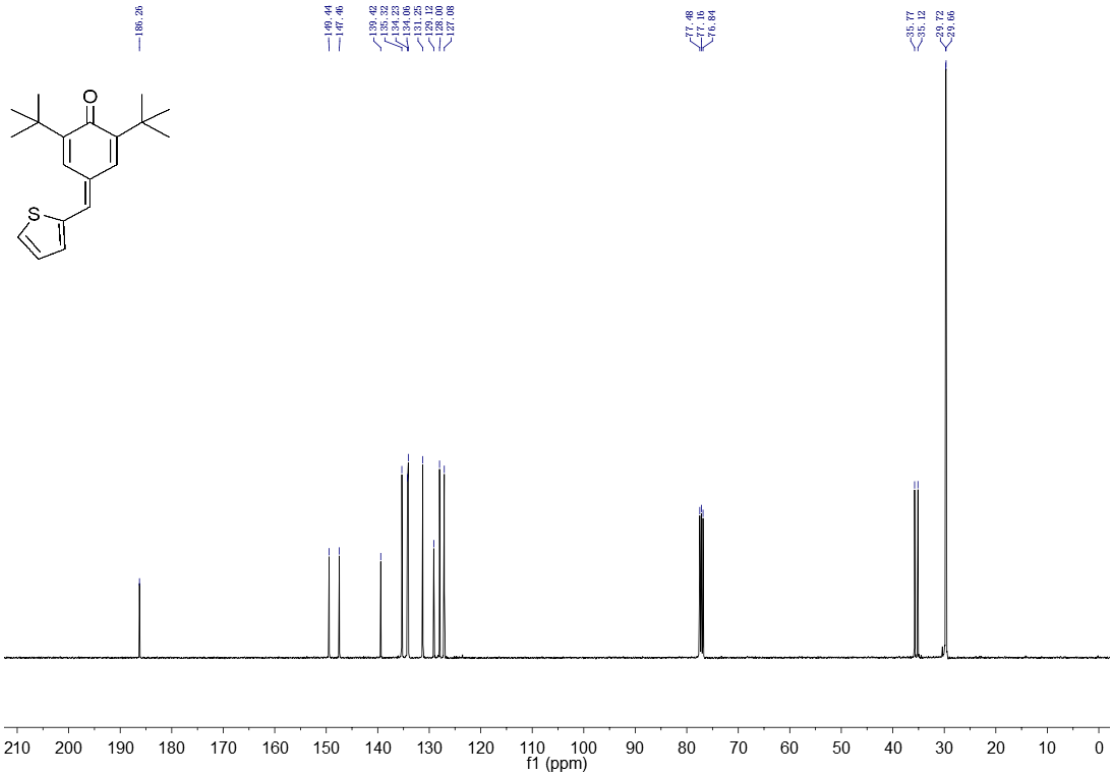
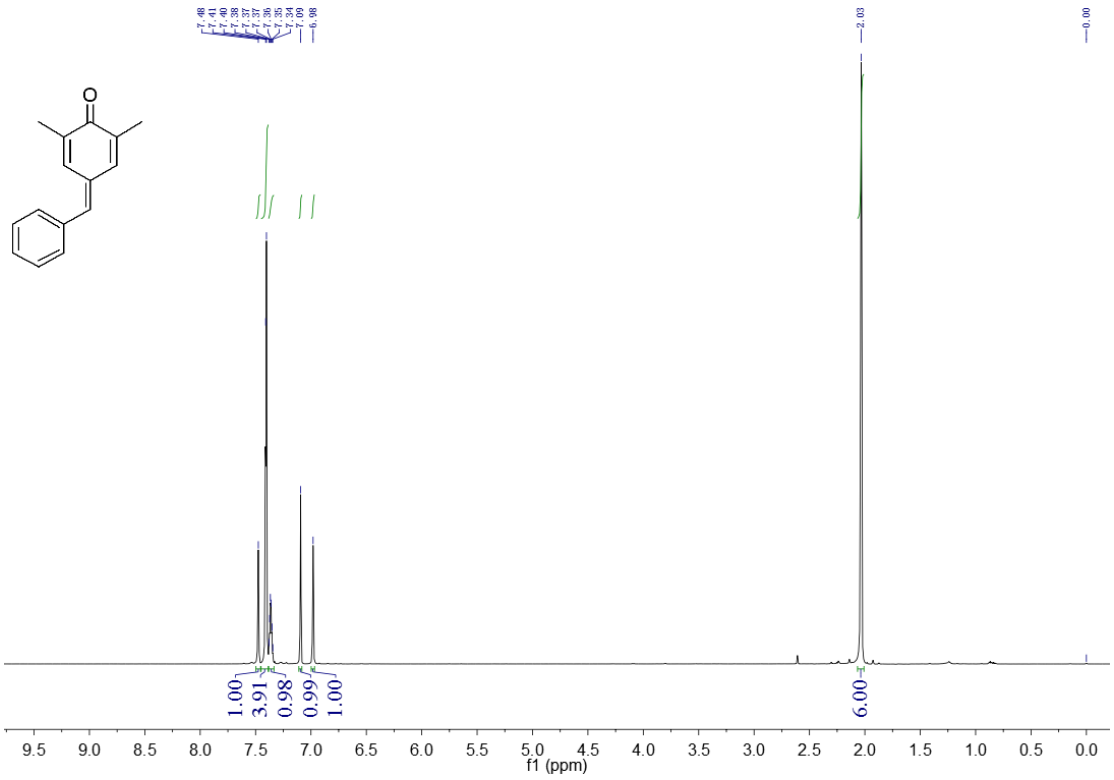


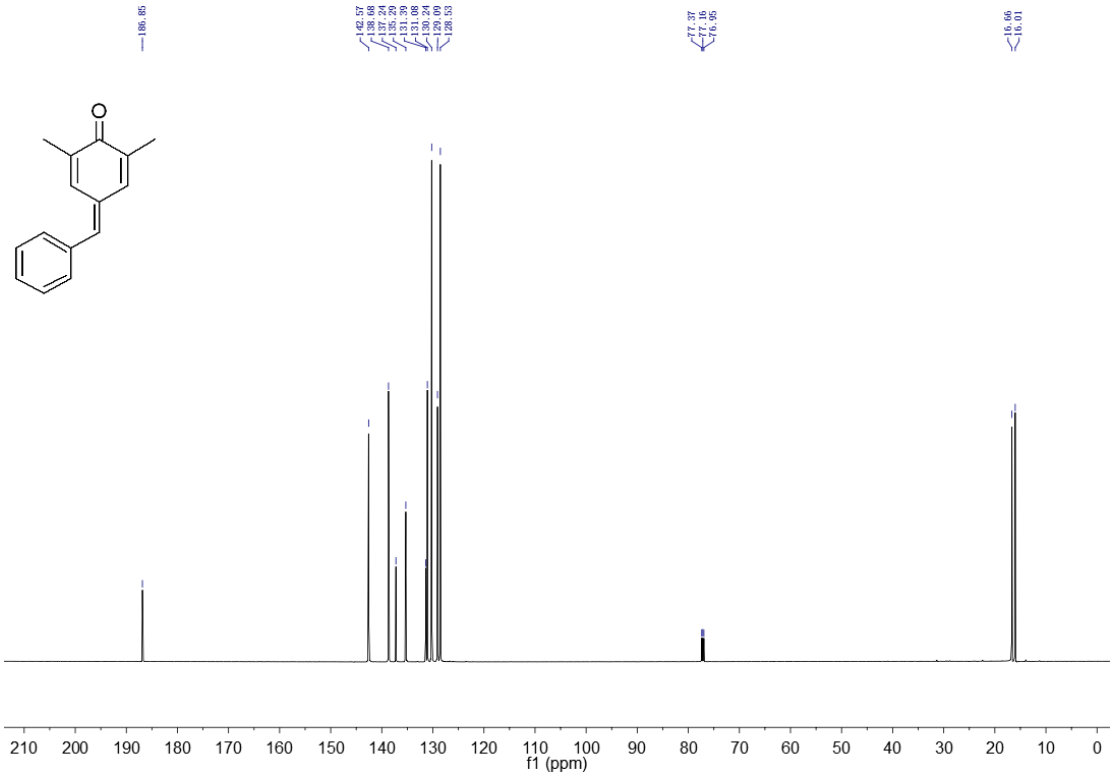
^{13}C NMR of **1u**



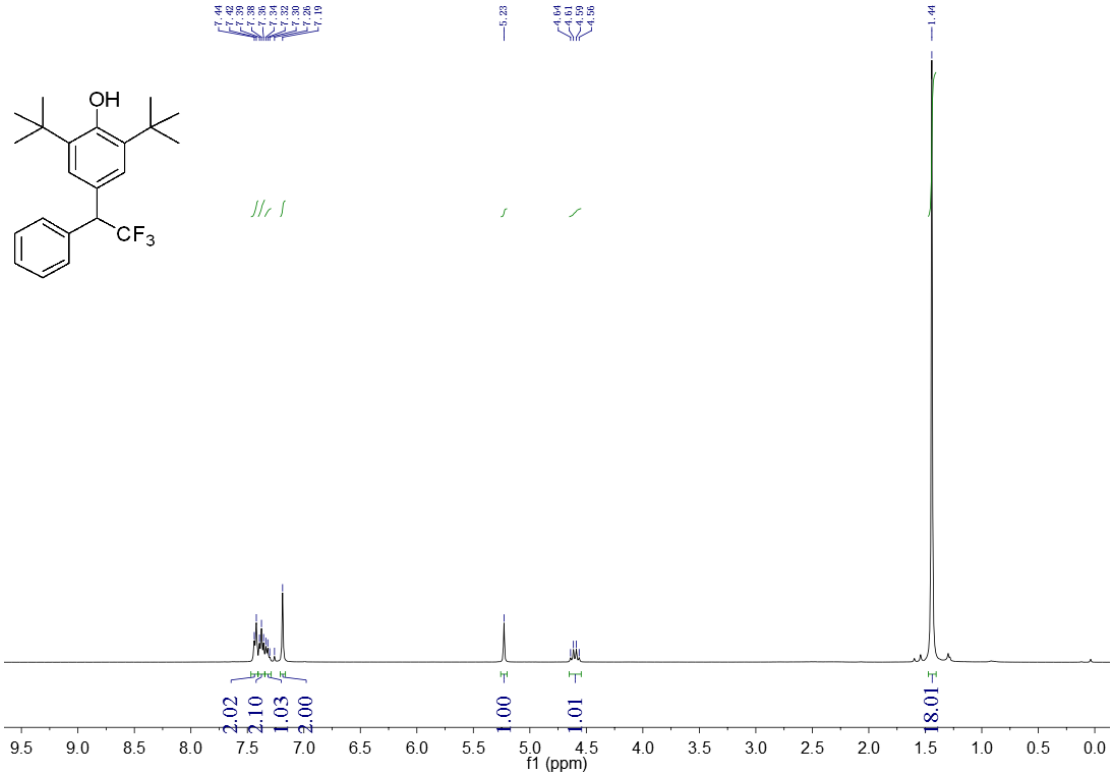
^{1}H NMR of **1v**



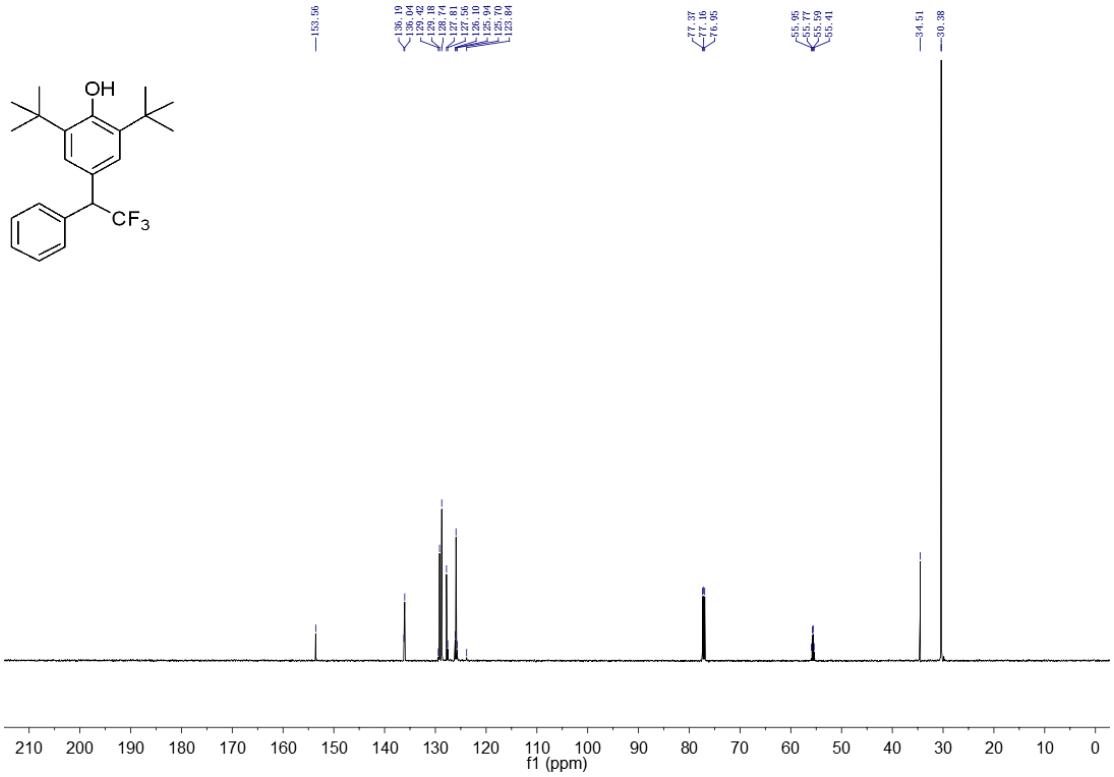
^{13}C NMR of **1v**



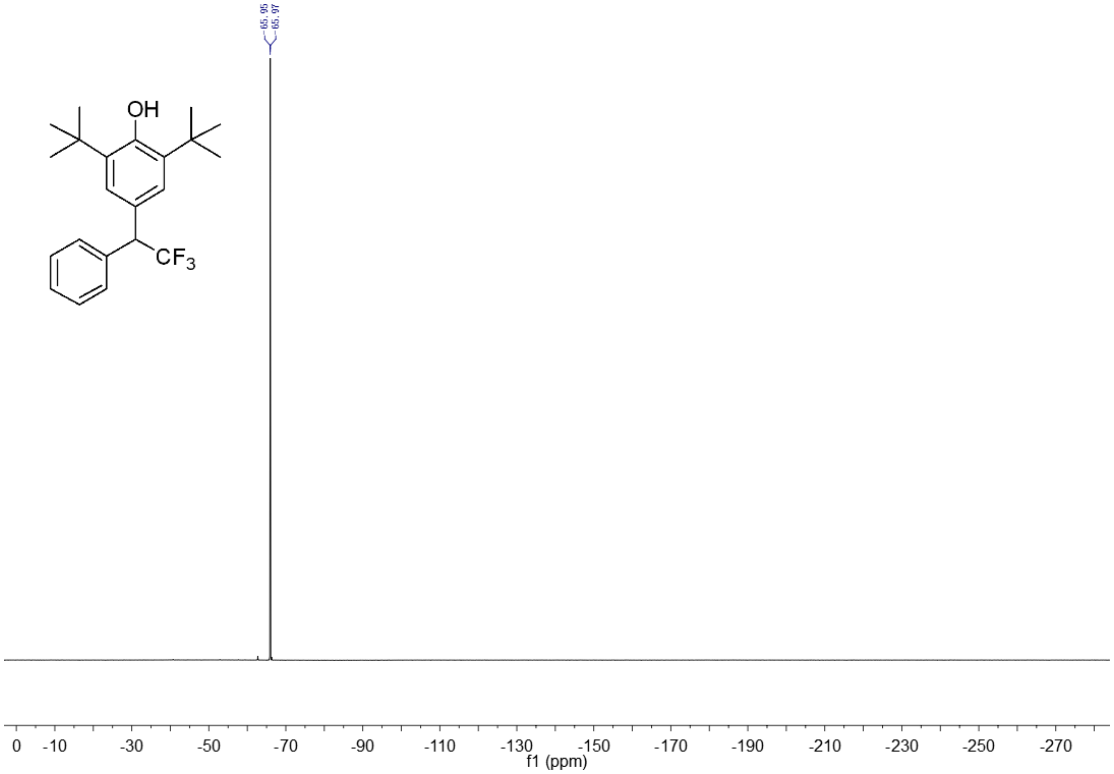
^{1}H NMR of **2a**



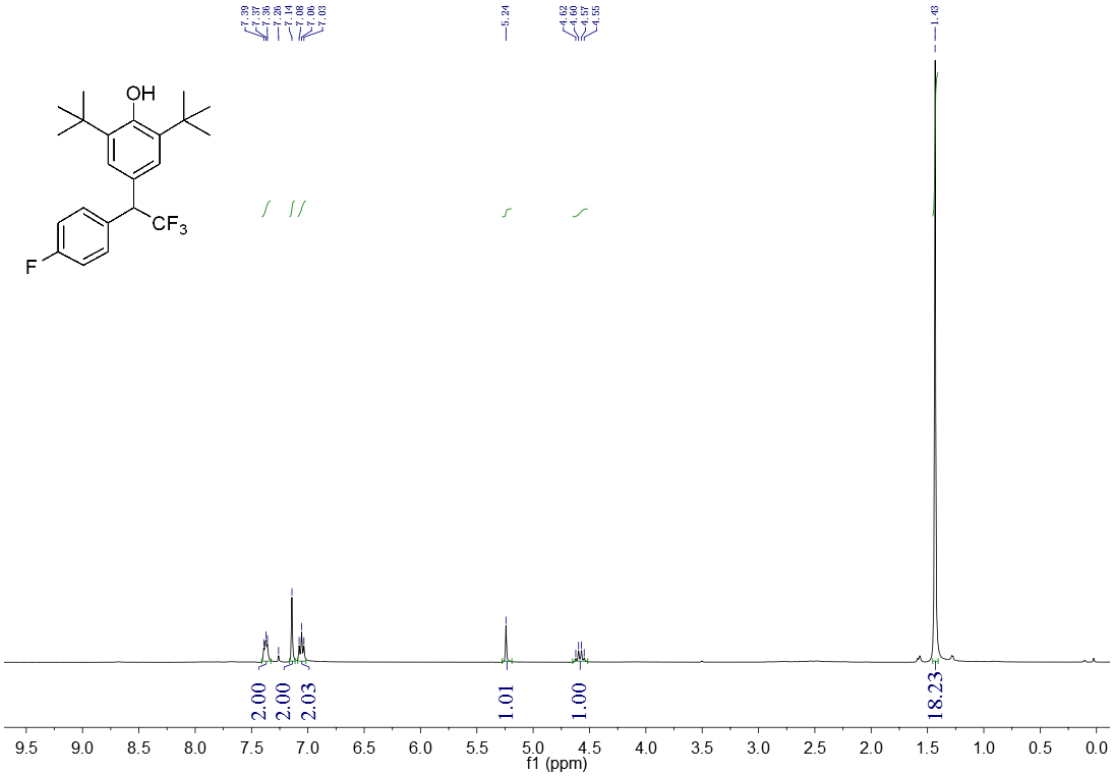
^{13}C NMR of **2a**



^{19}F NMR of **2a**



^{1}H NMR of **2b**



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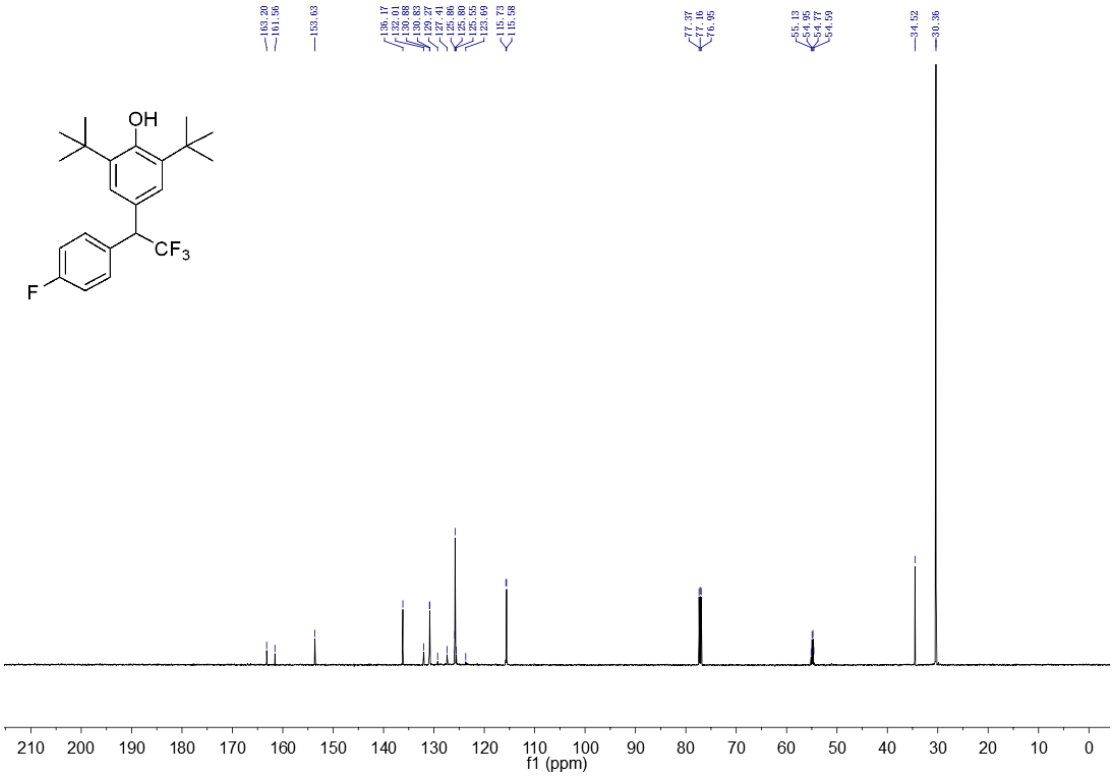
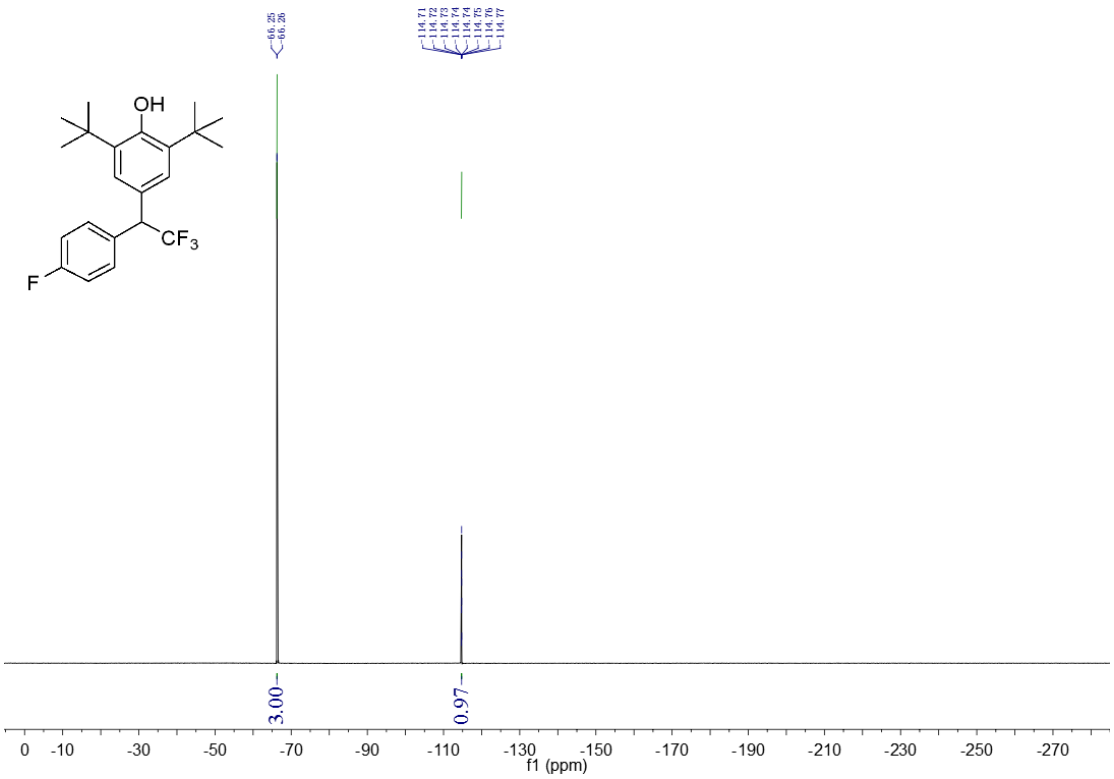
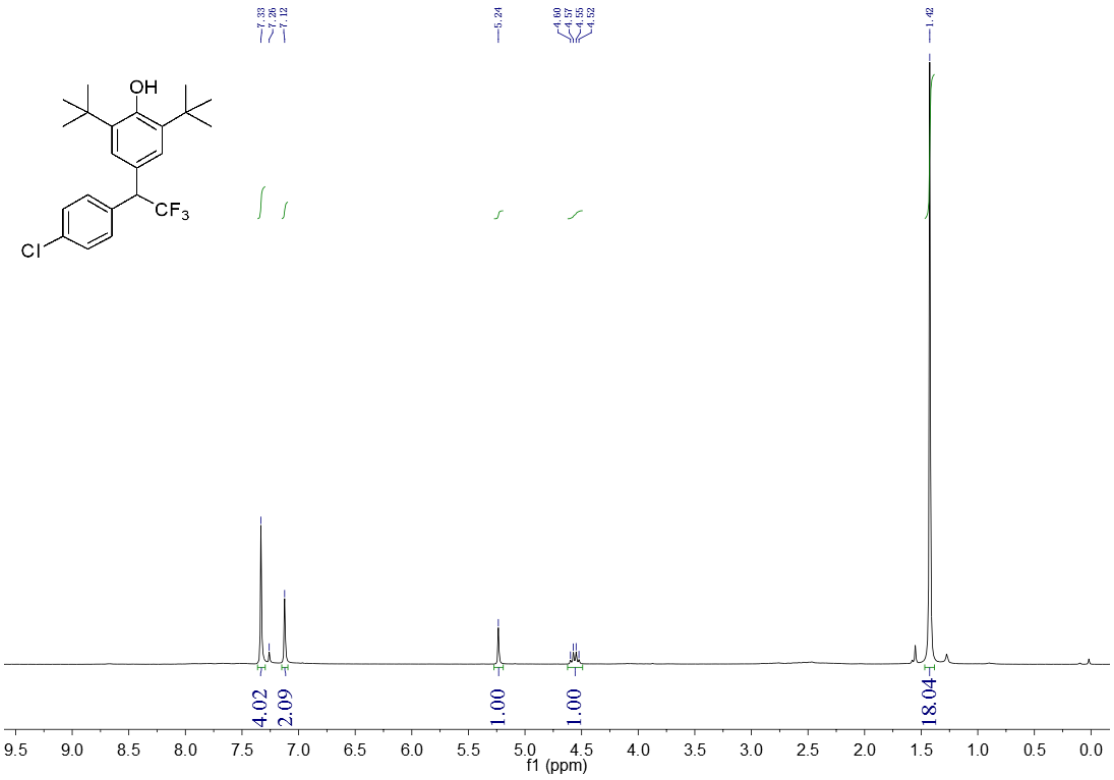


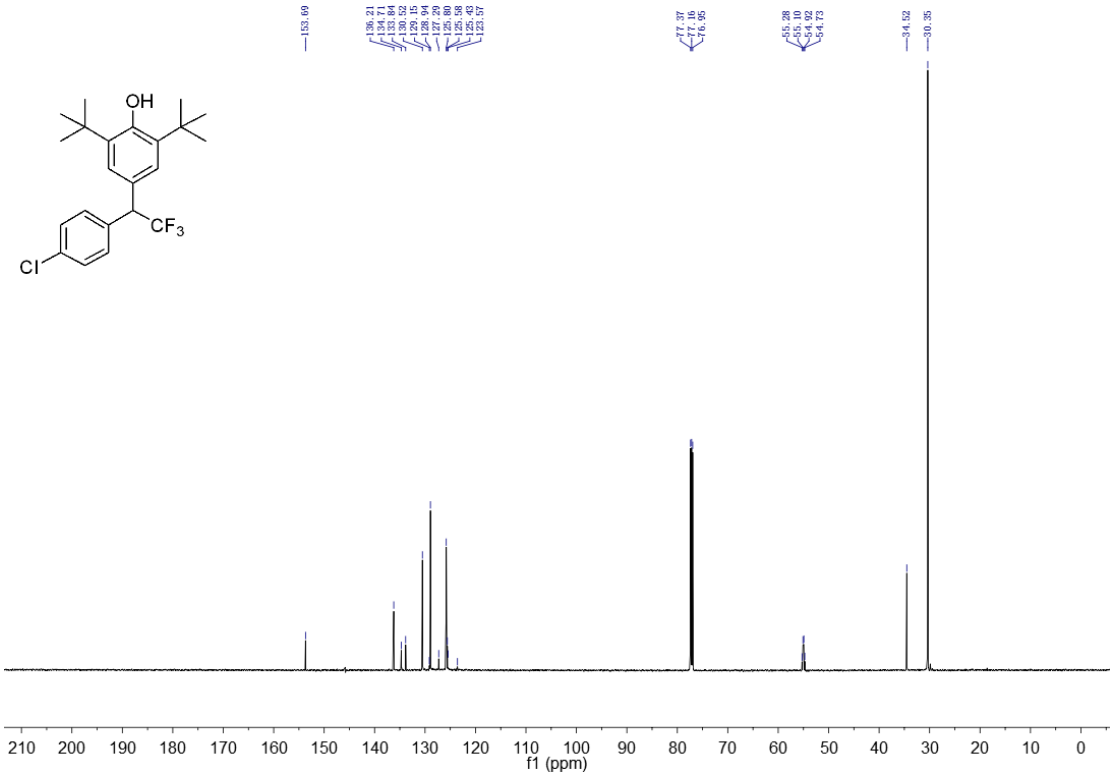
^{19}F NMR of **1v**



^{1}H NMR of **2c**



^{13}C NMR of **2c**



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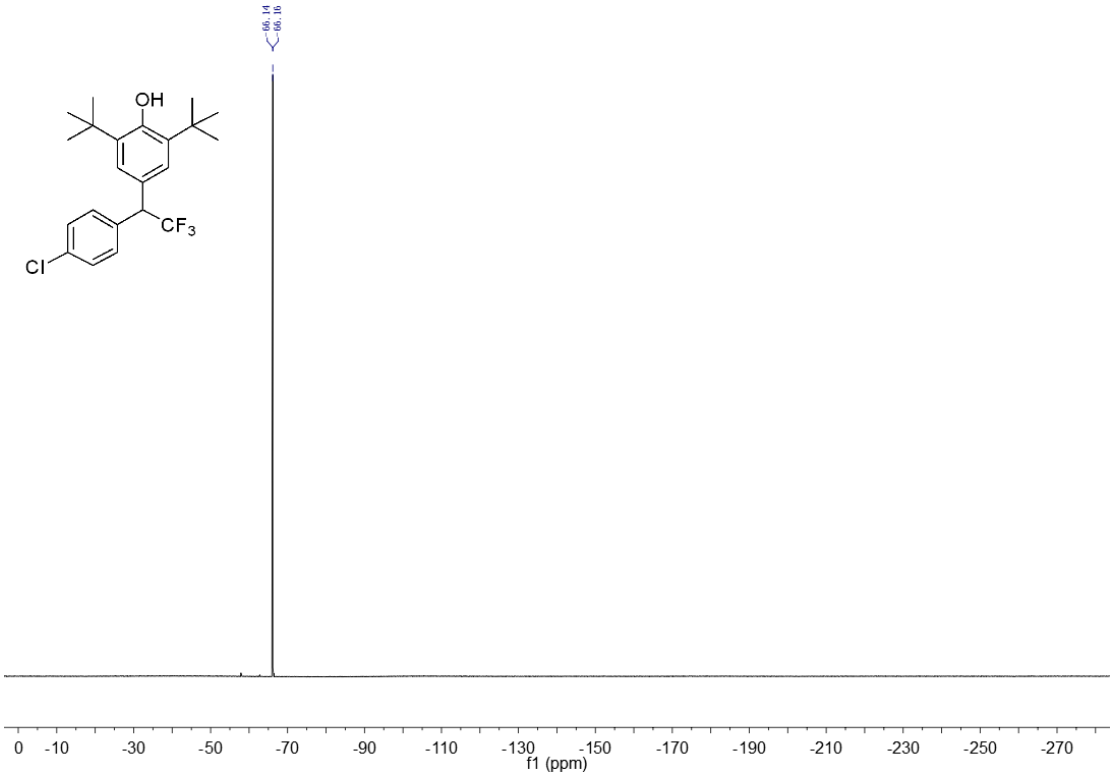

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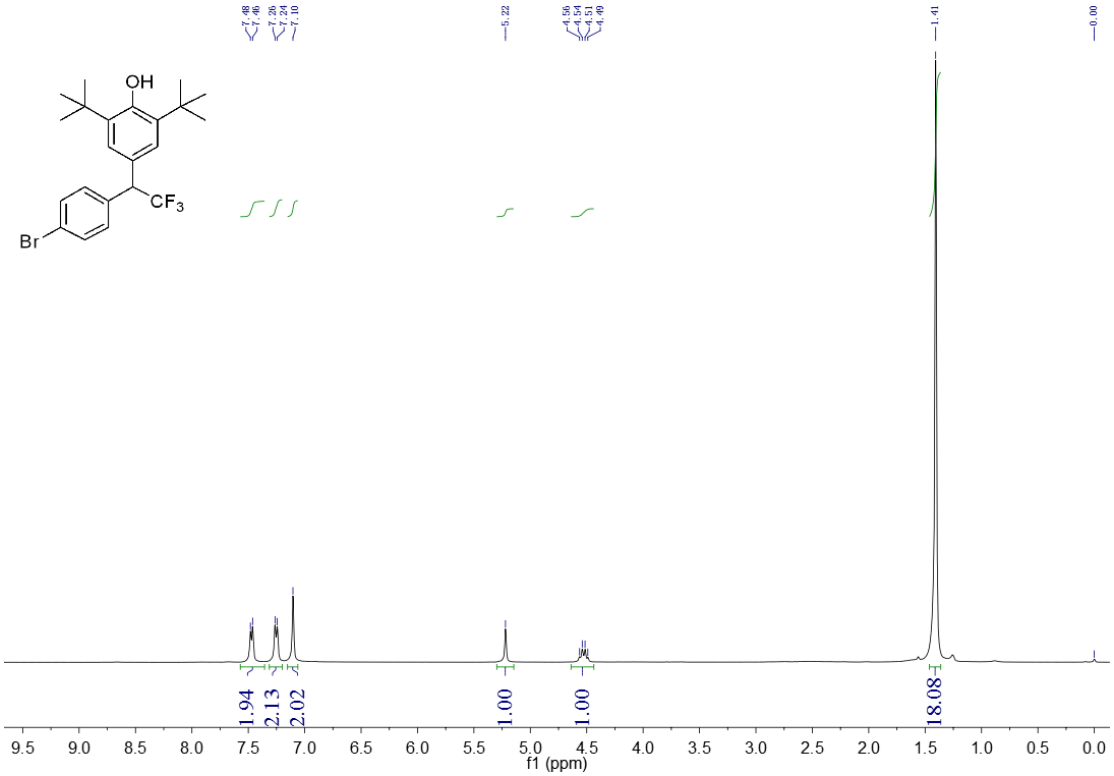
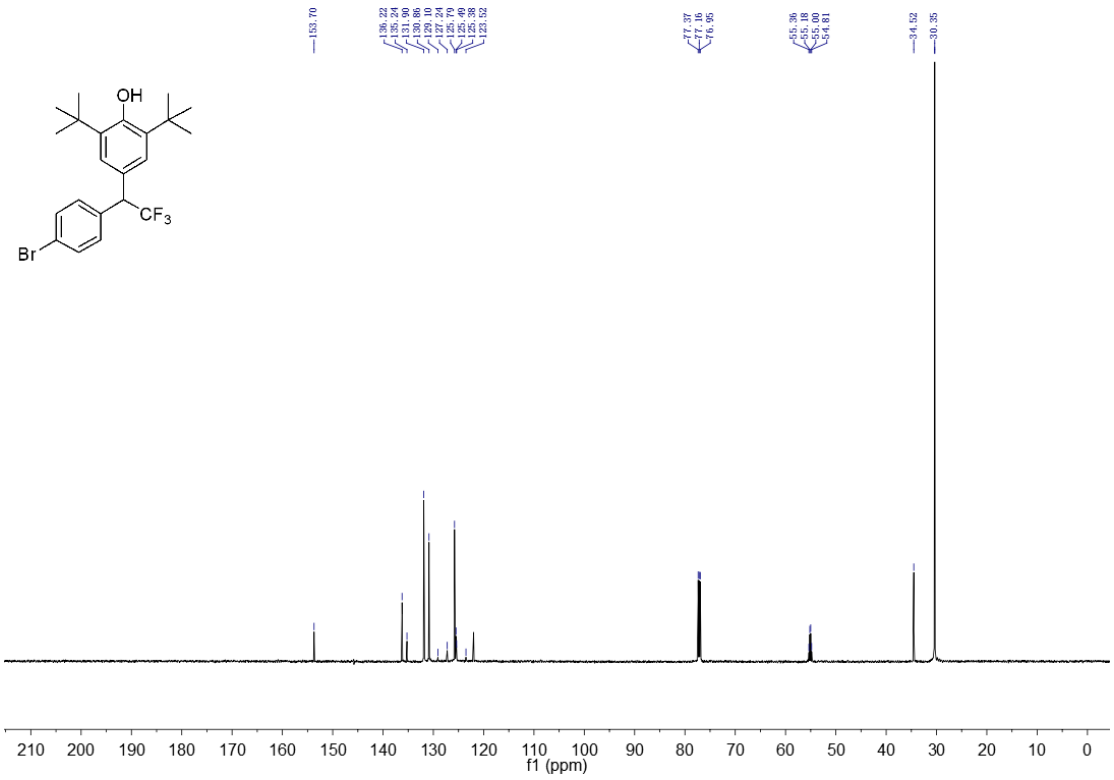


^{13}C NMR of **2d**



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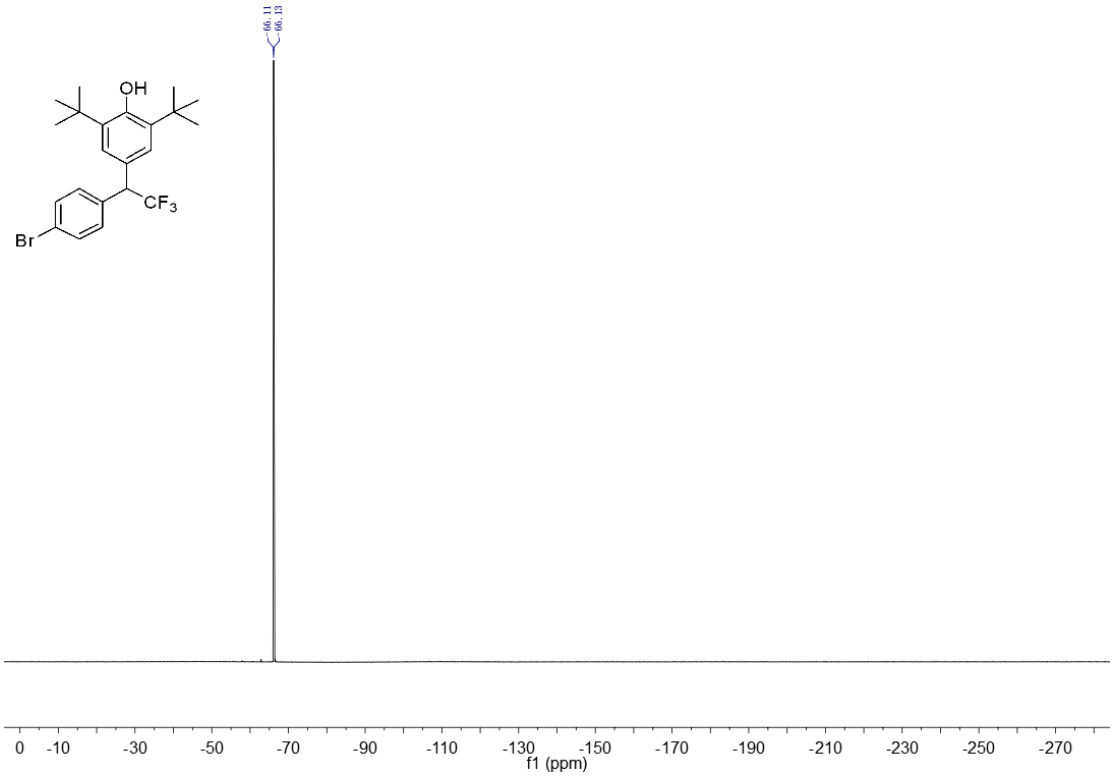

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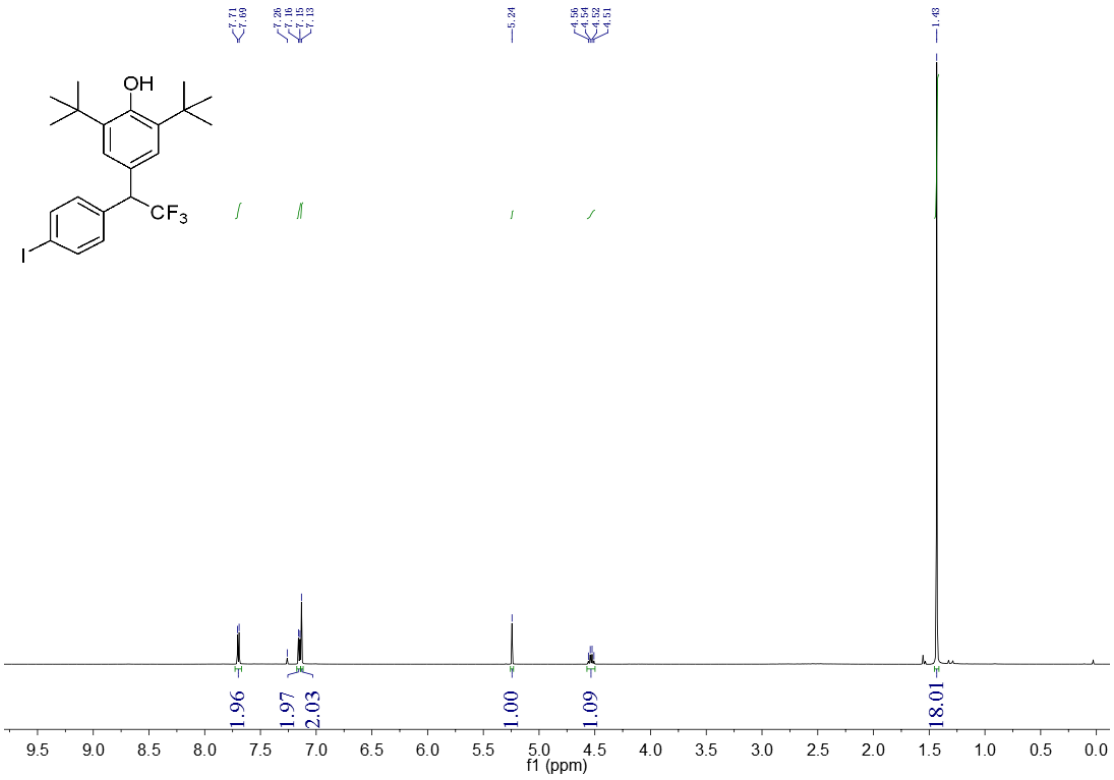

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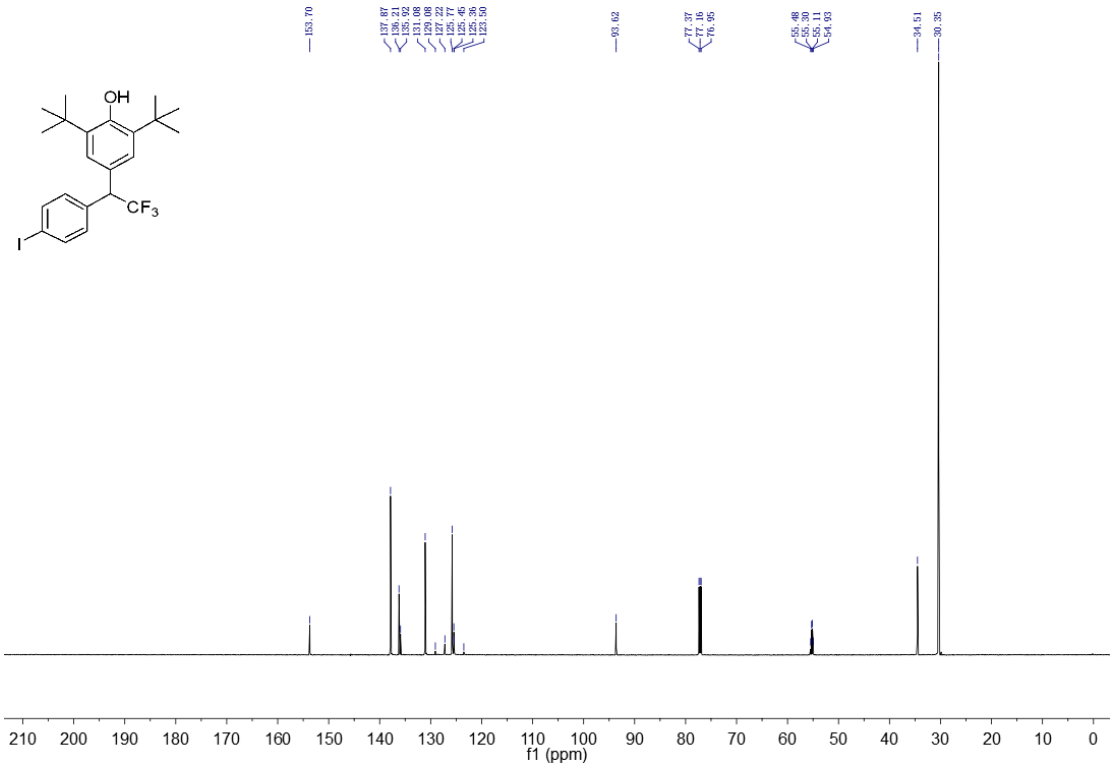

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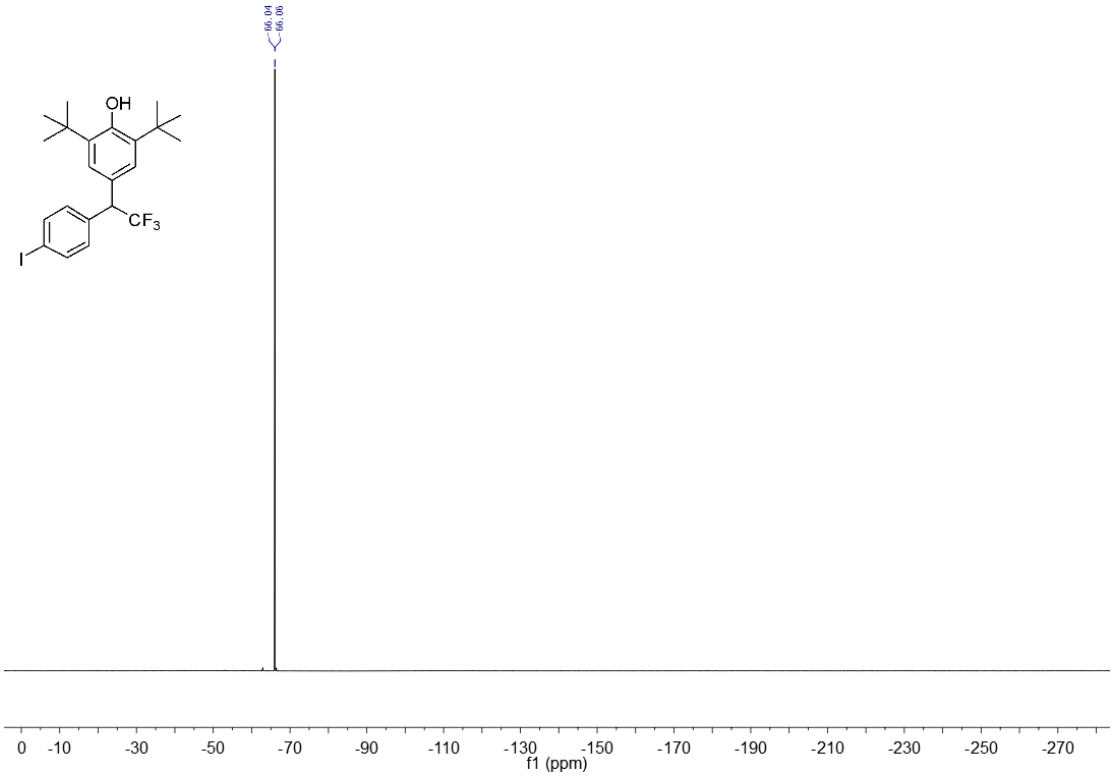

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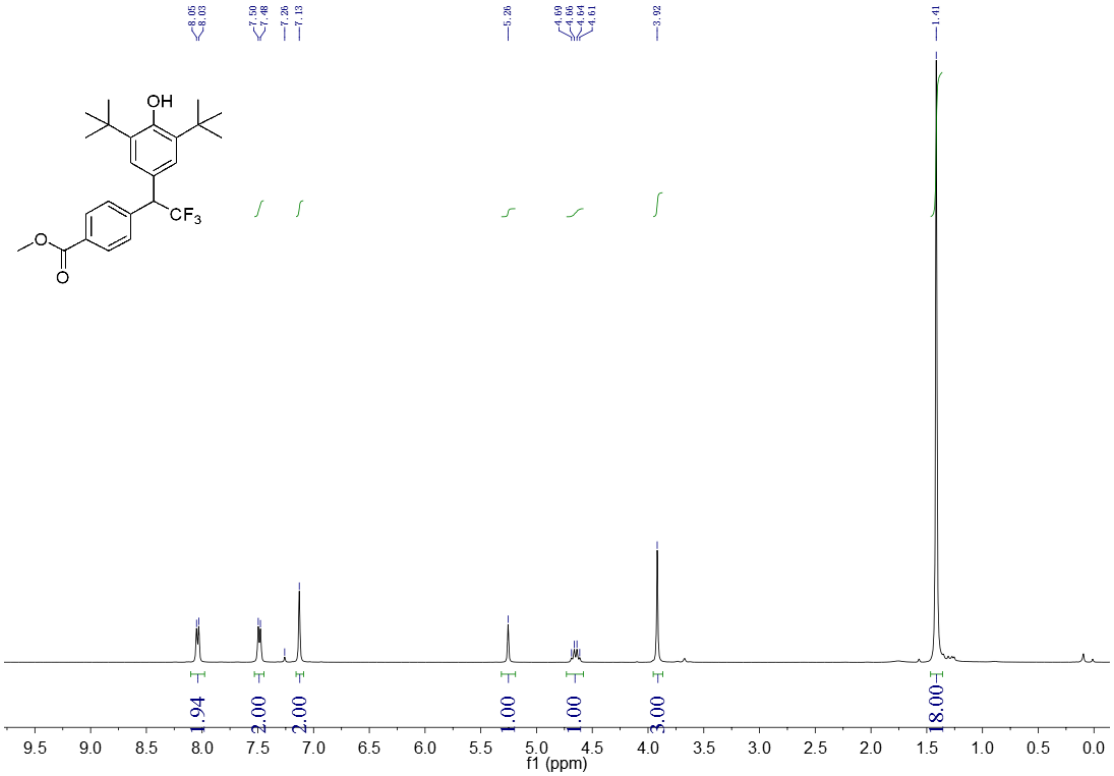

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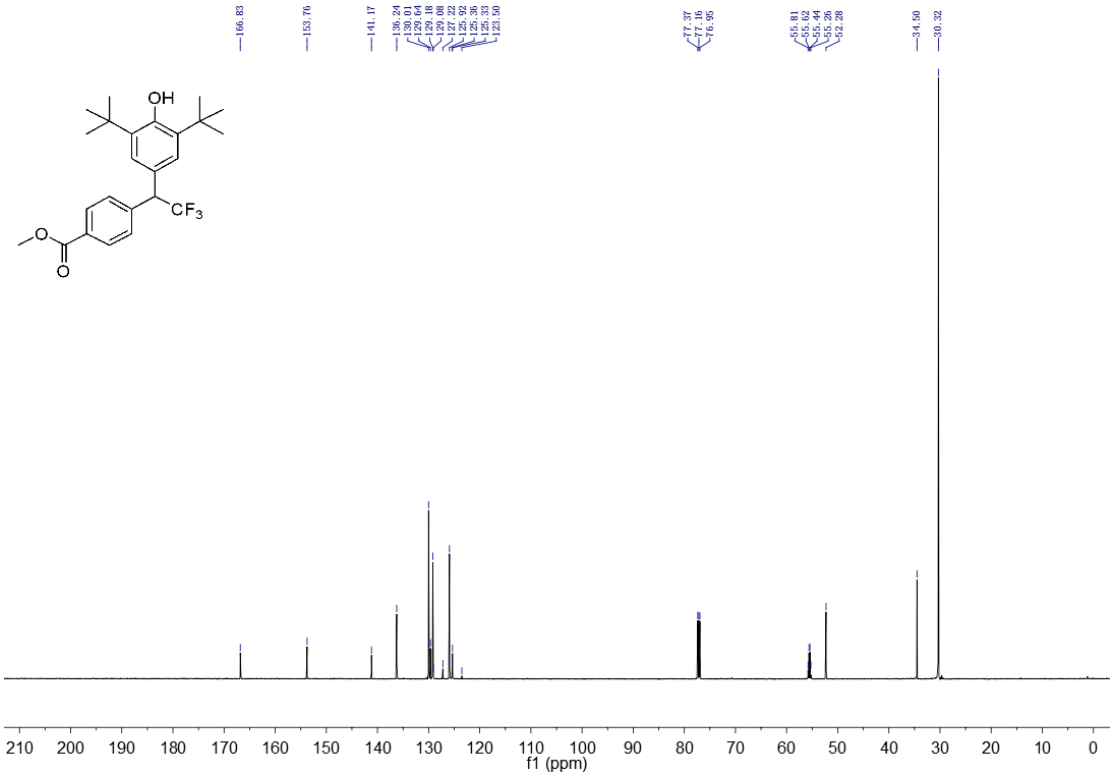

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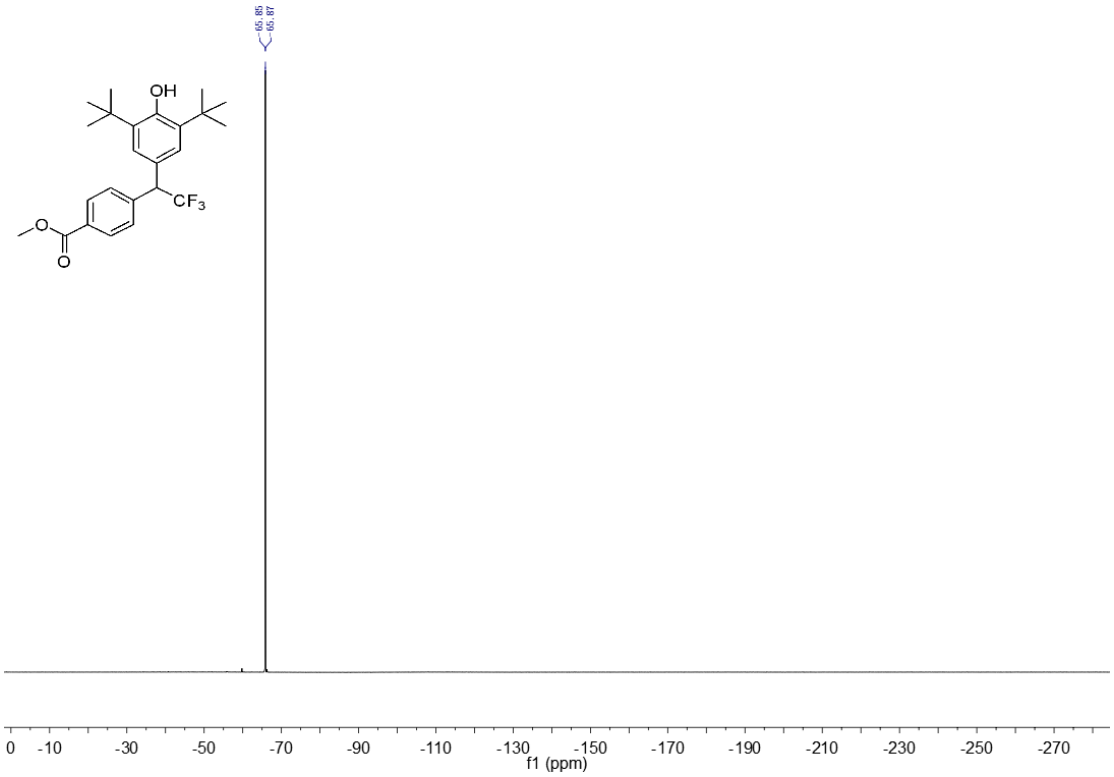
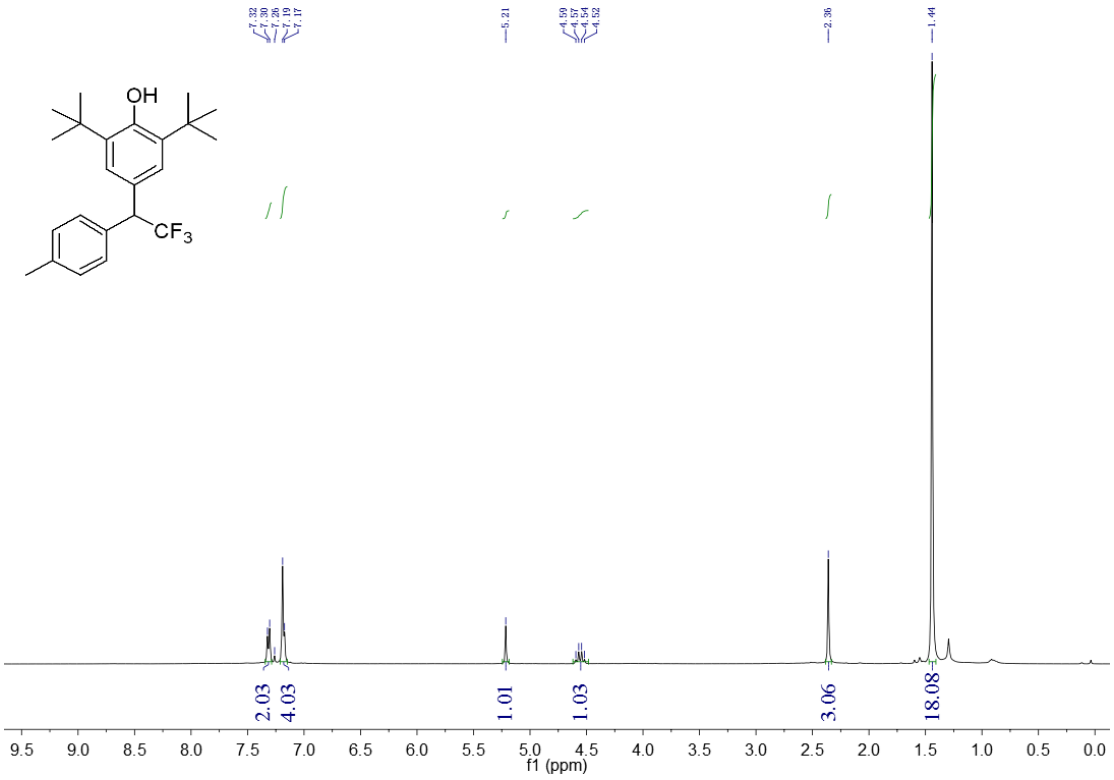


^{1}H NMR of **2g**



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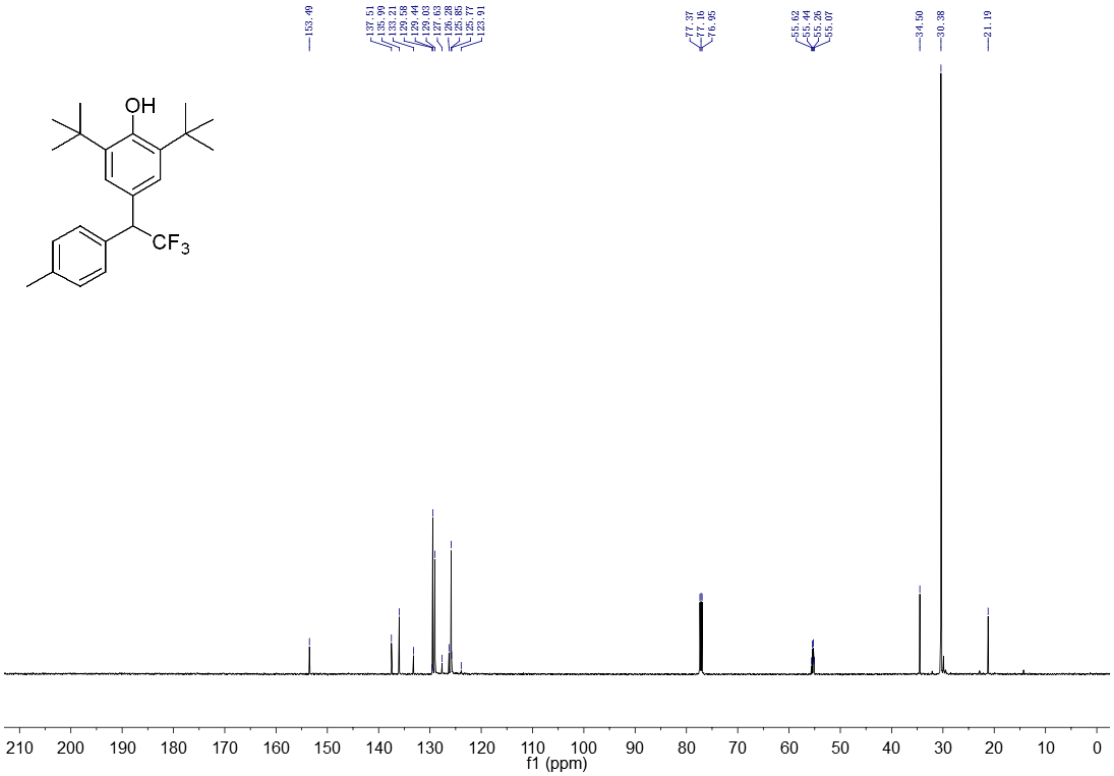

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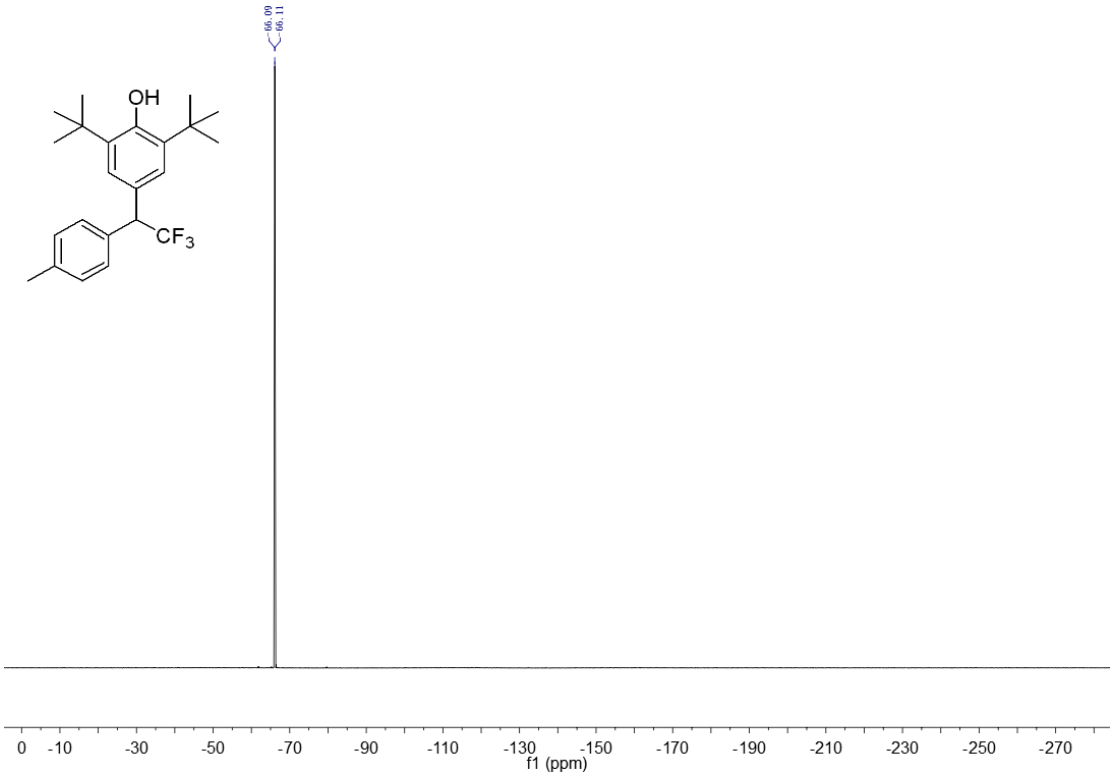

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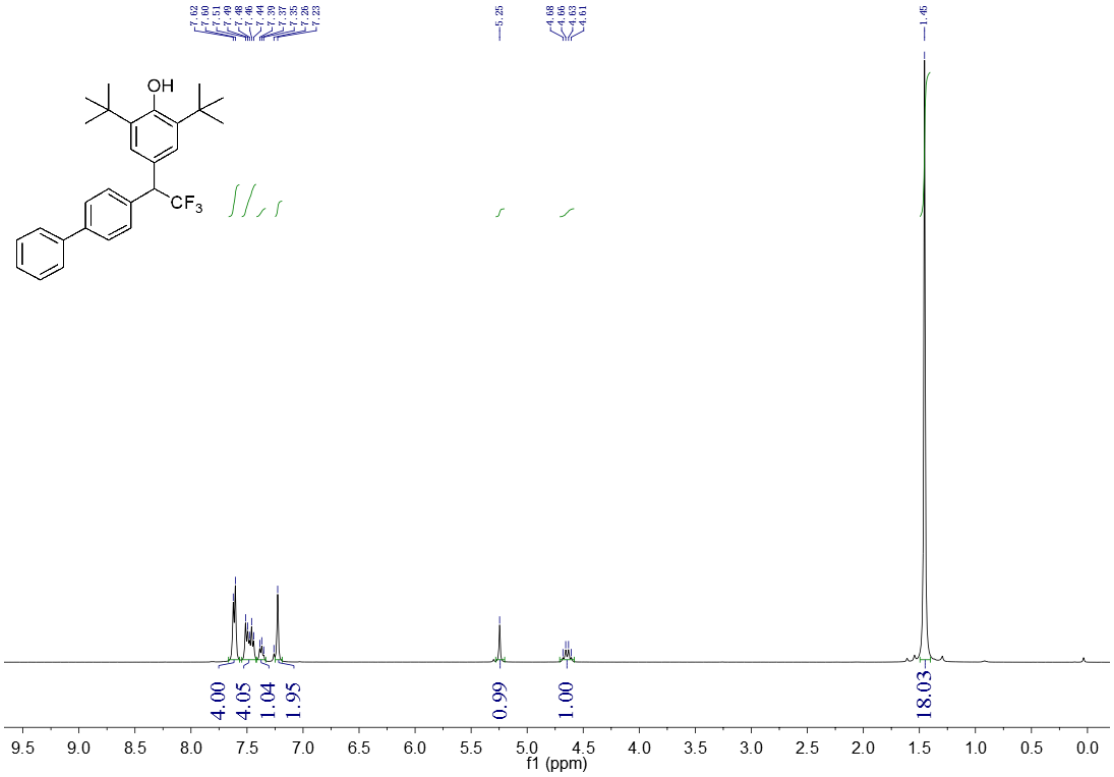

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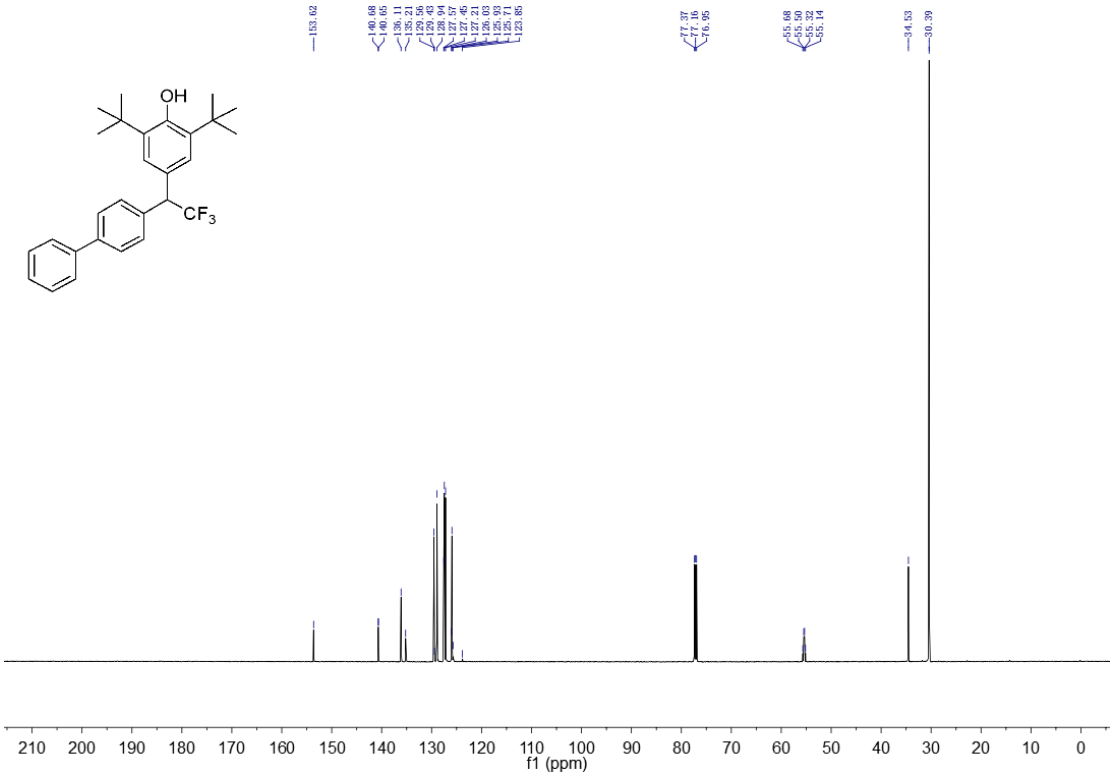

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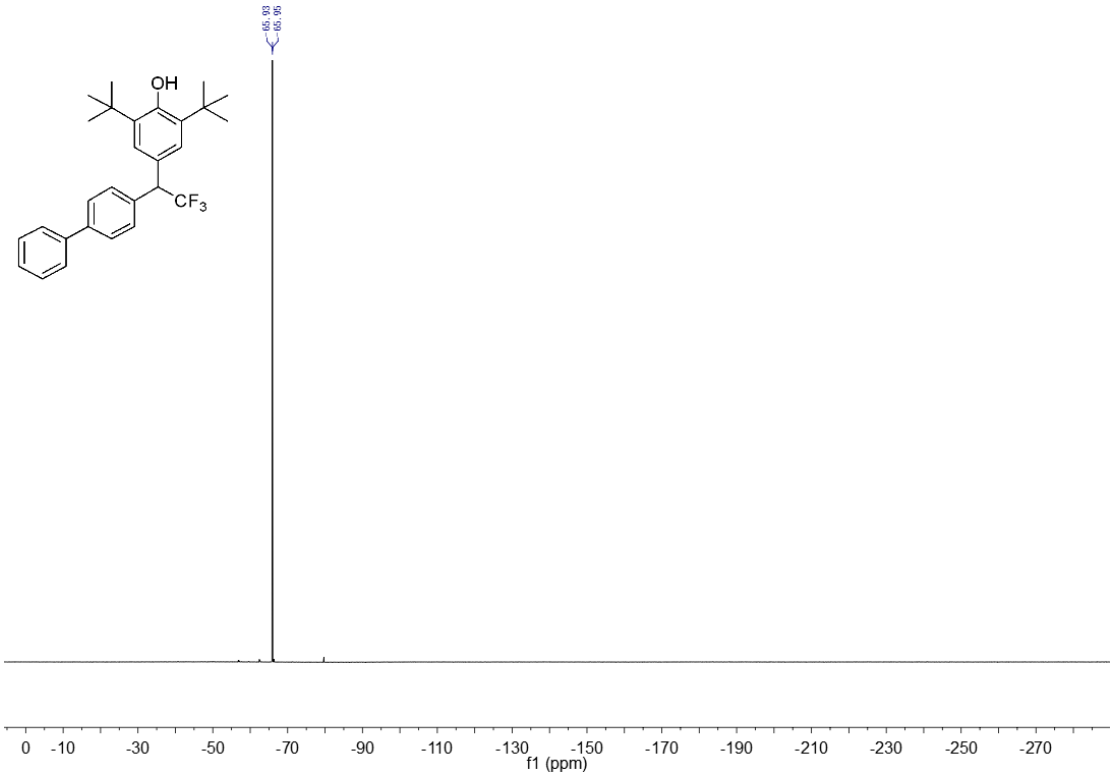
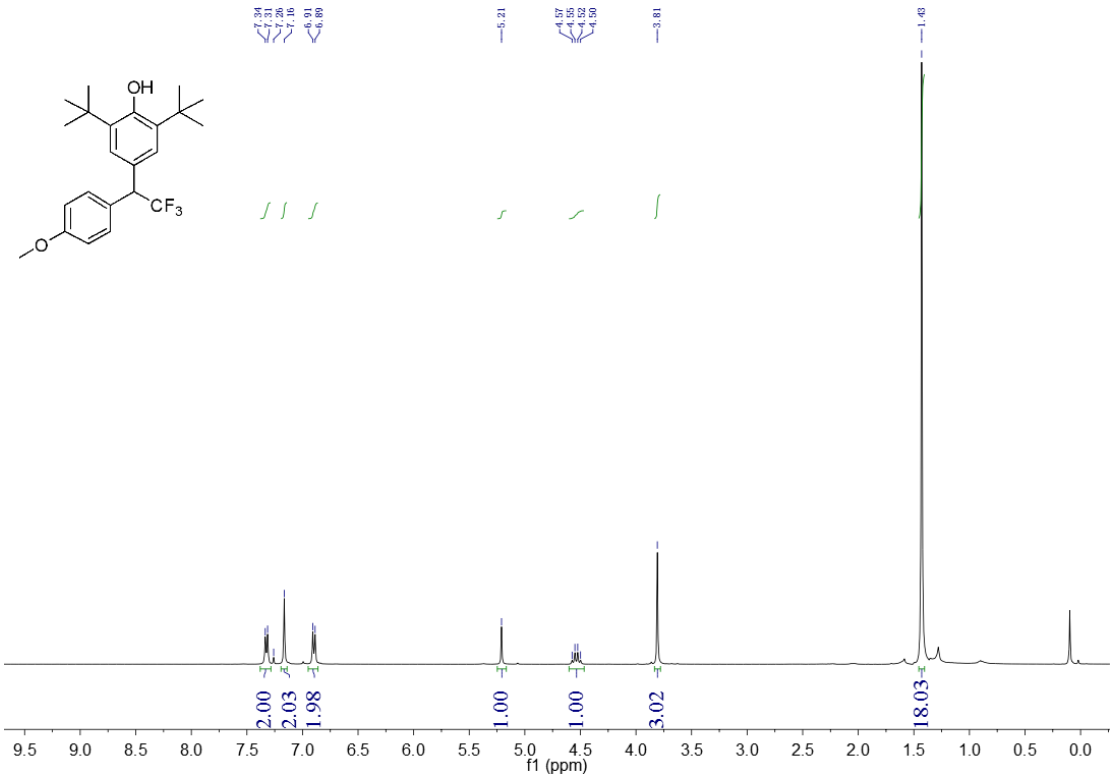
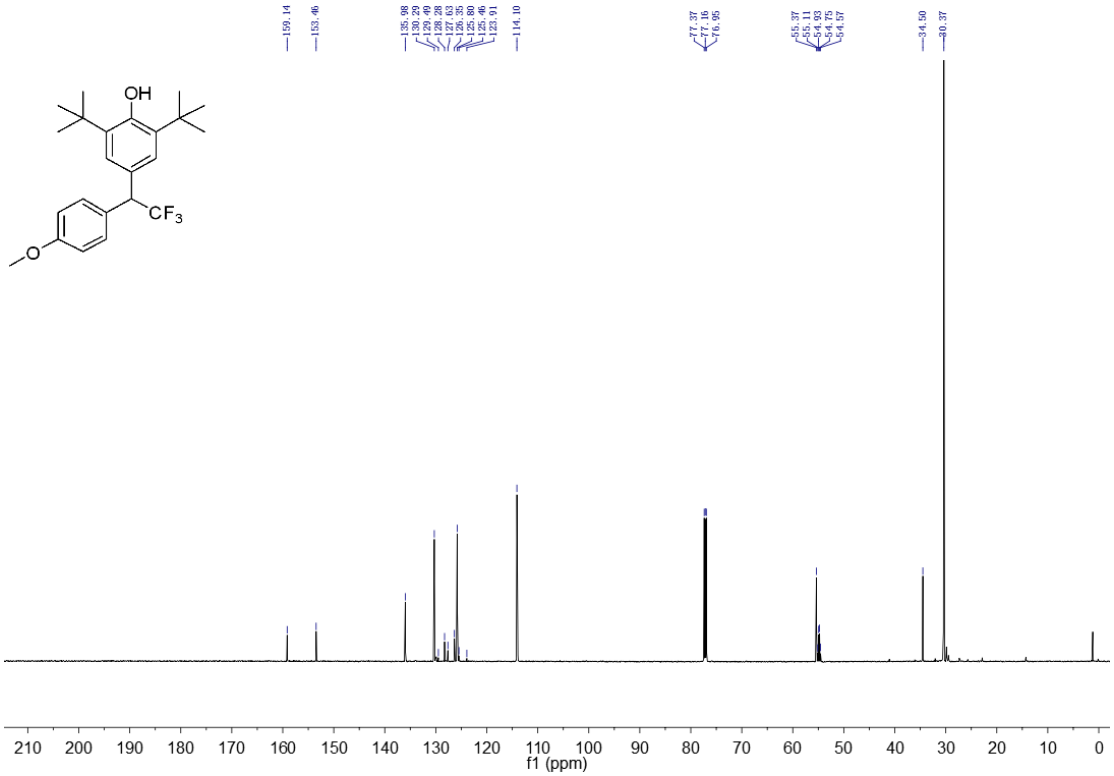


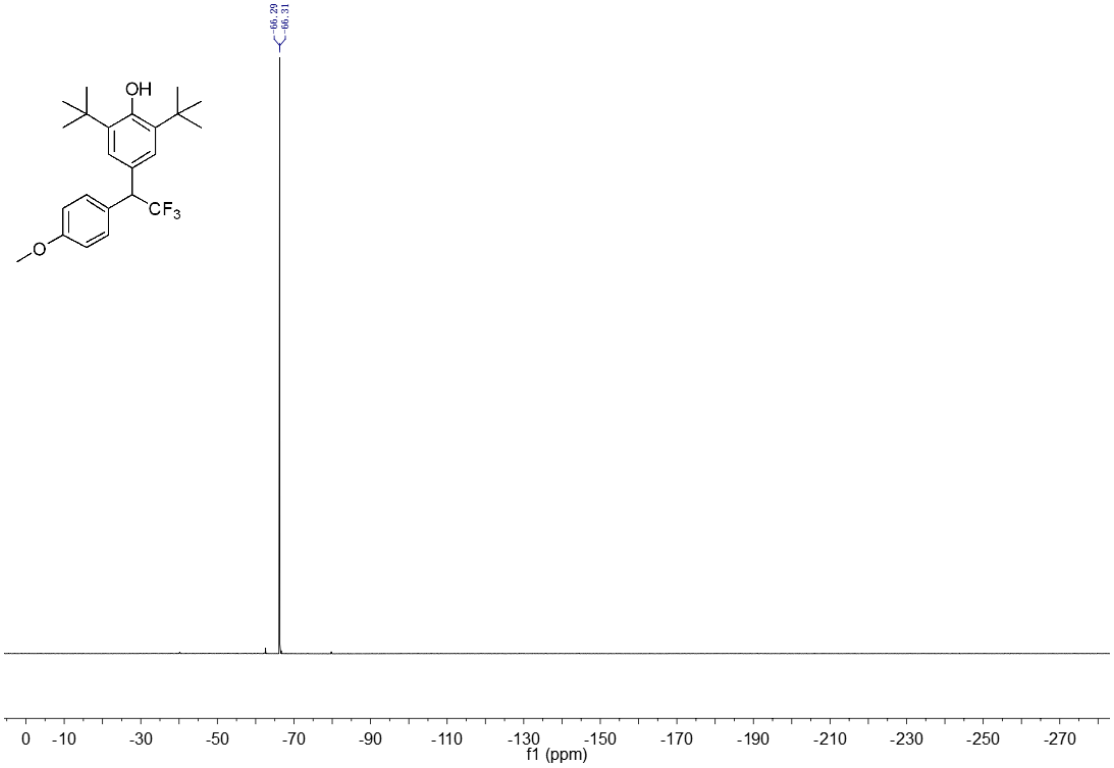
^{1}H NMR of **2i**



^{13}C NMR of **2i**



^{19}F NMR of **2i**



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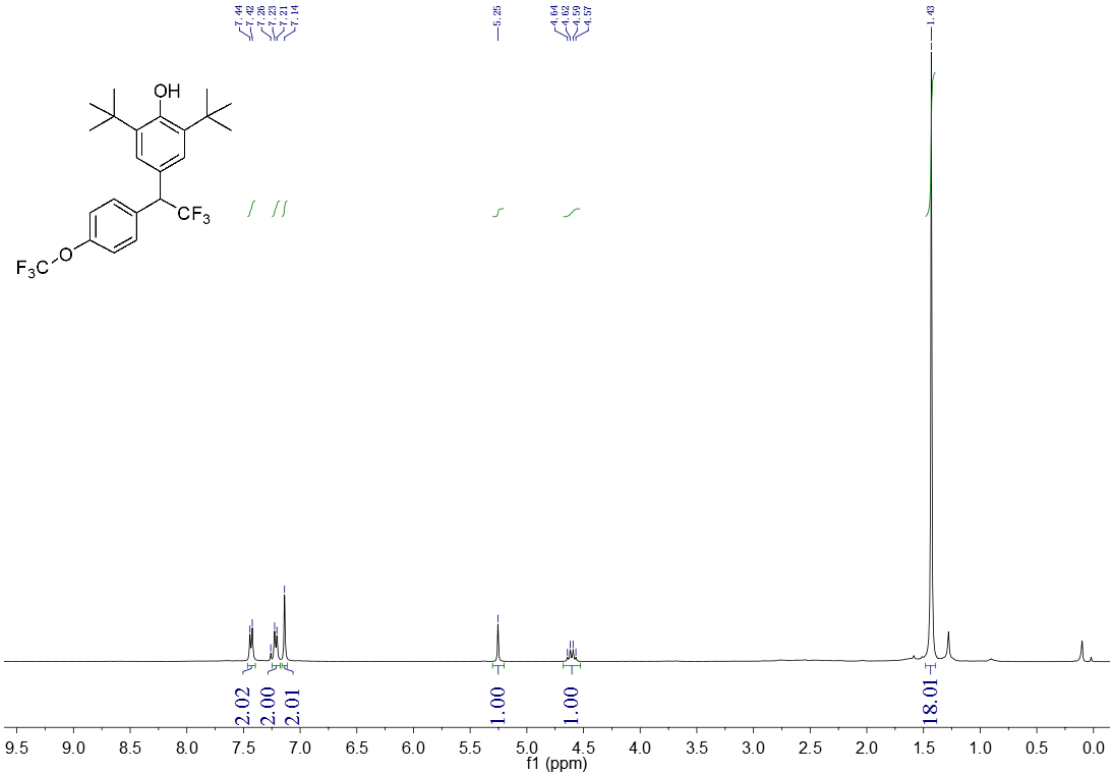

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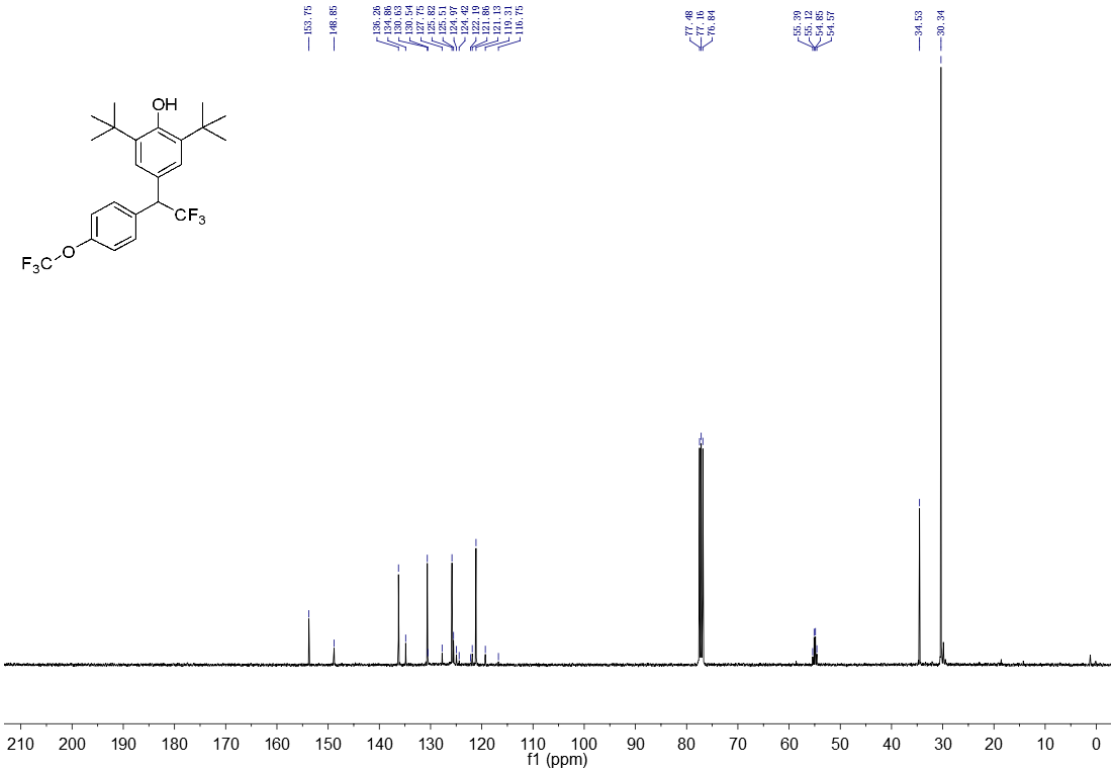

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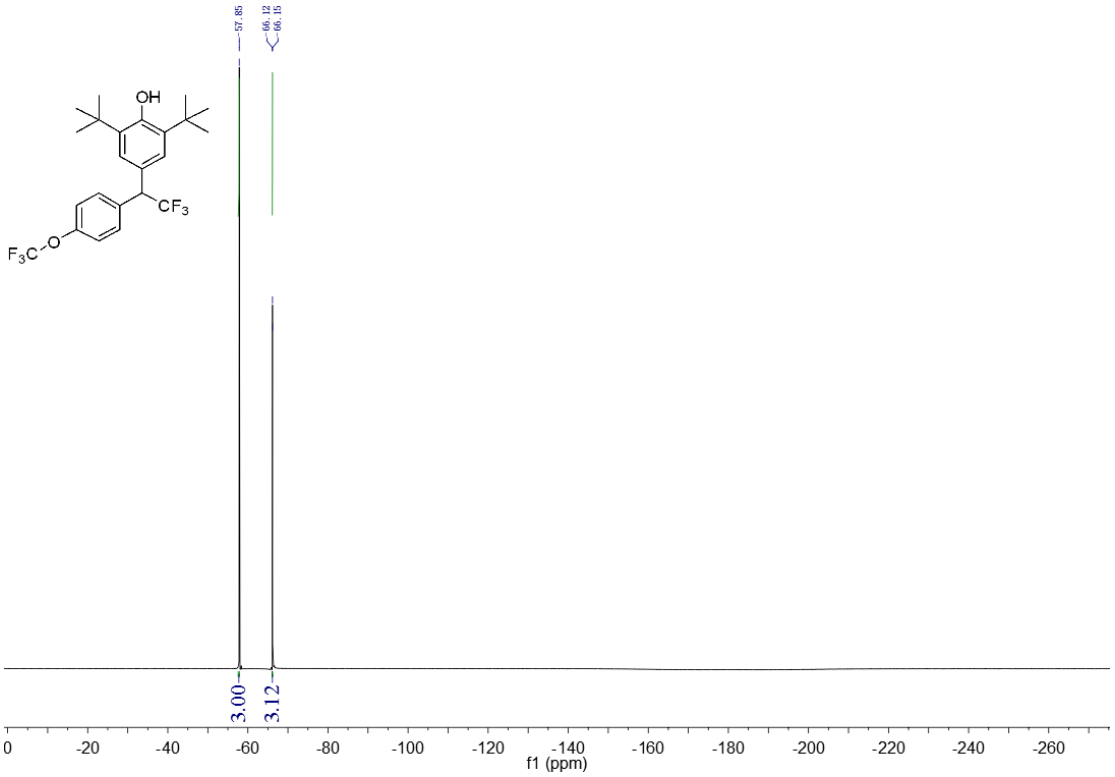

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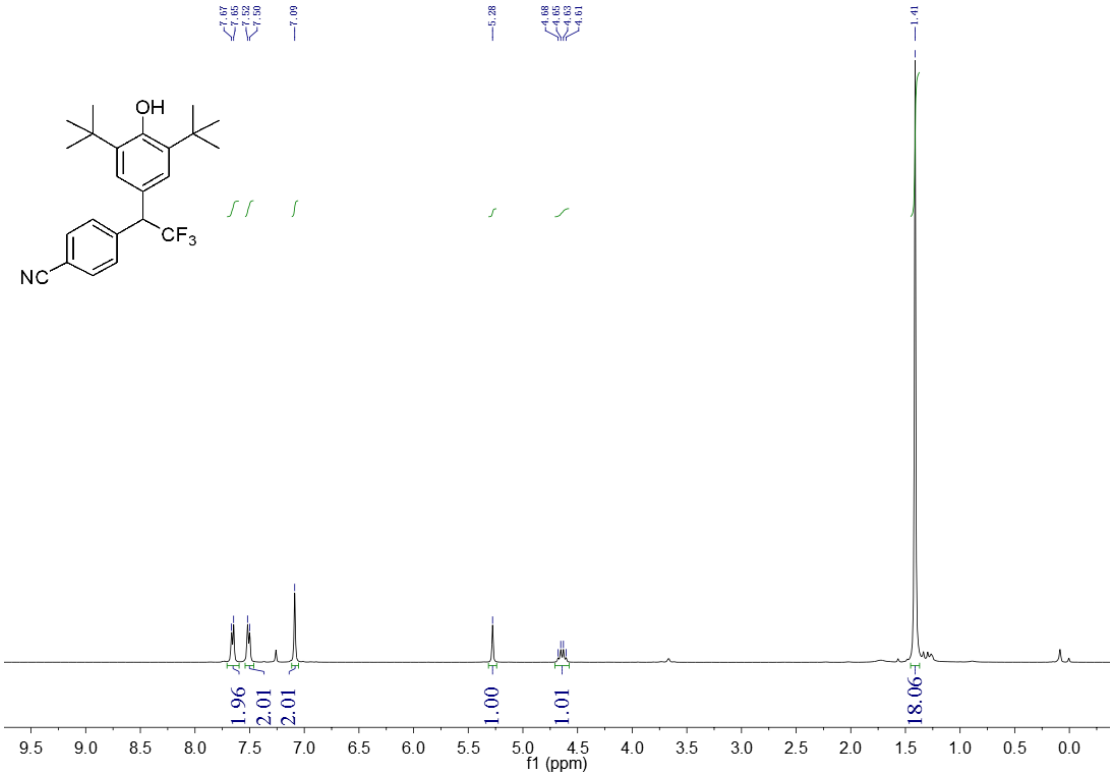

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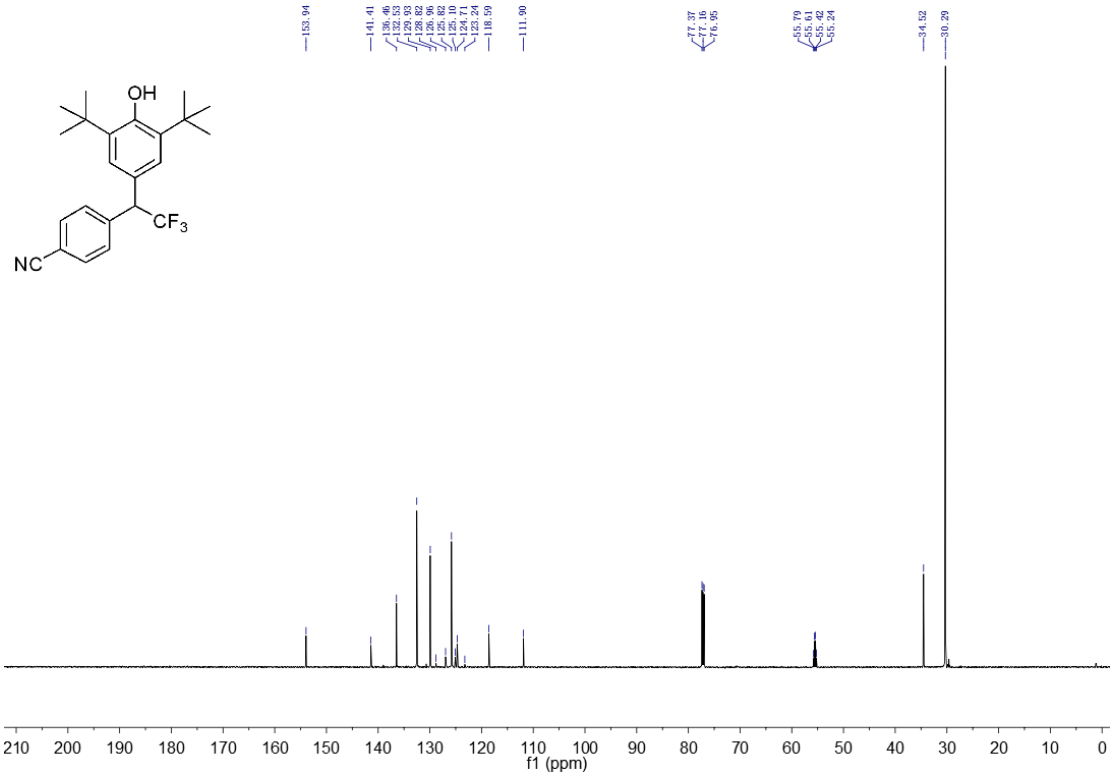

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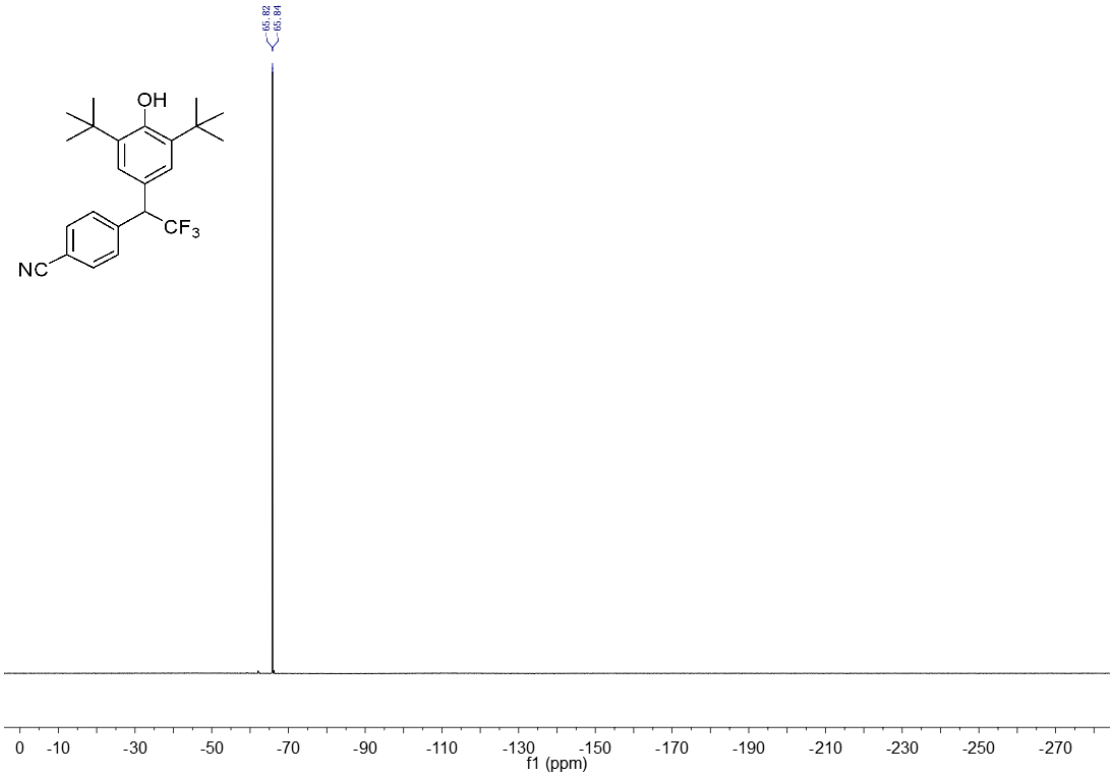

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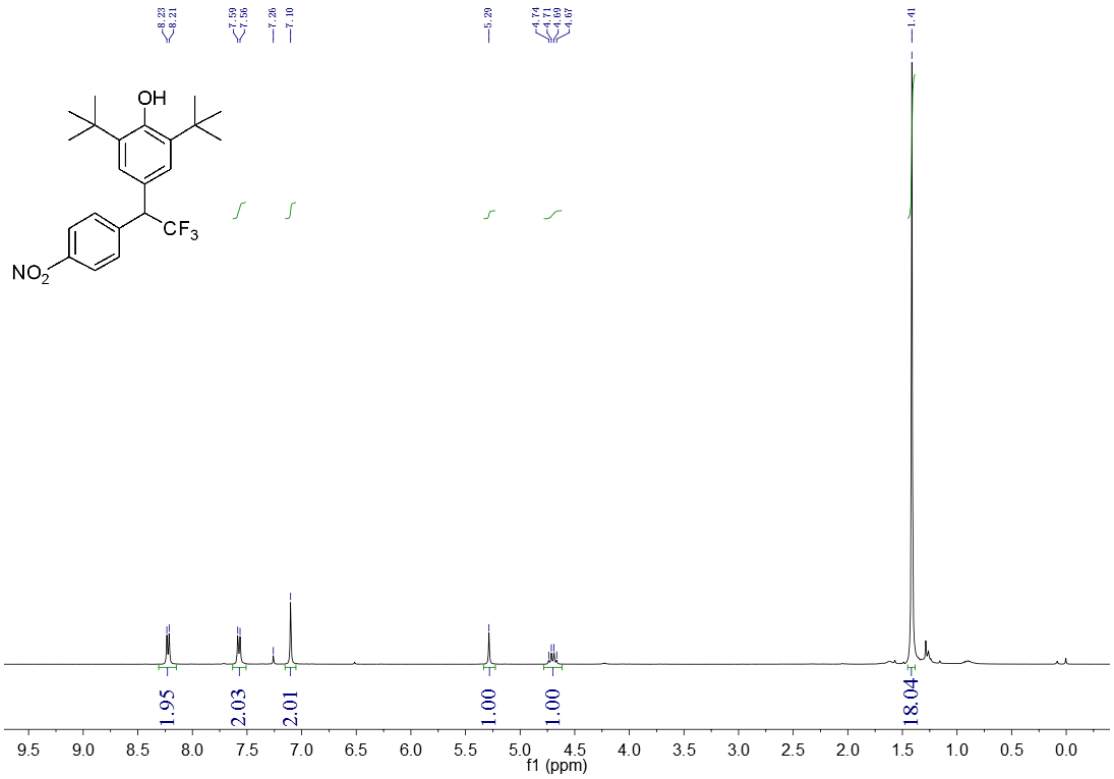

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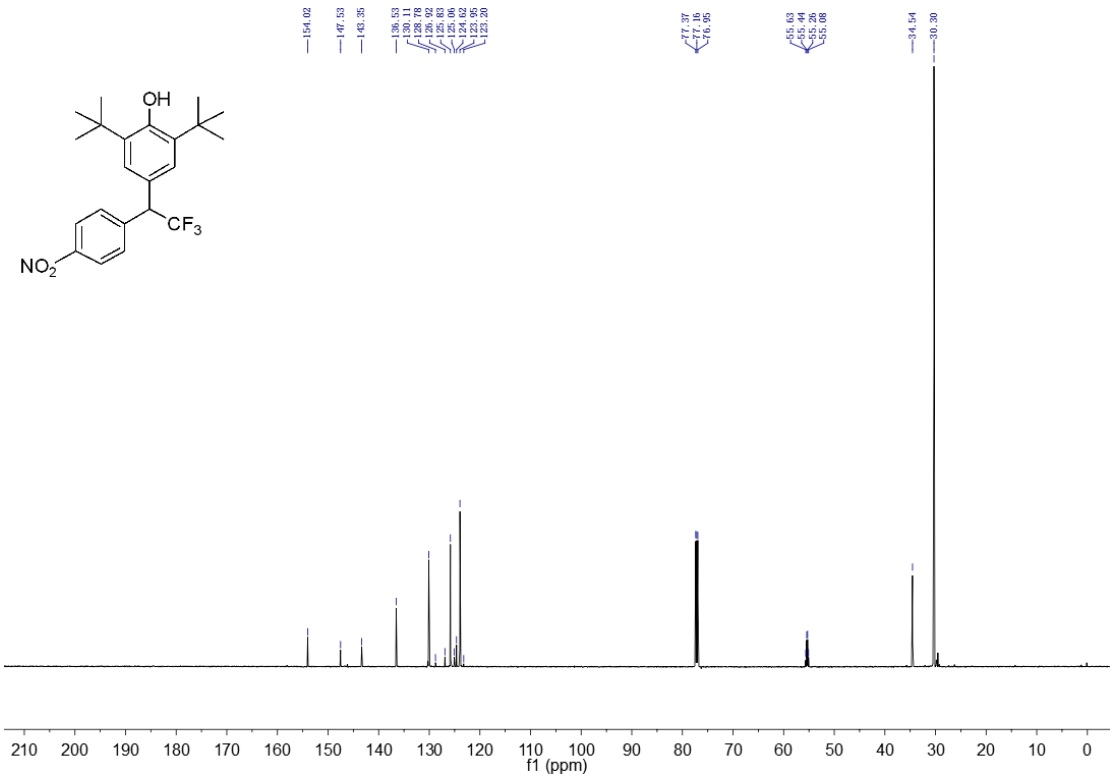
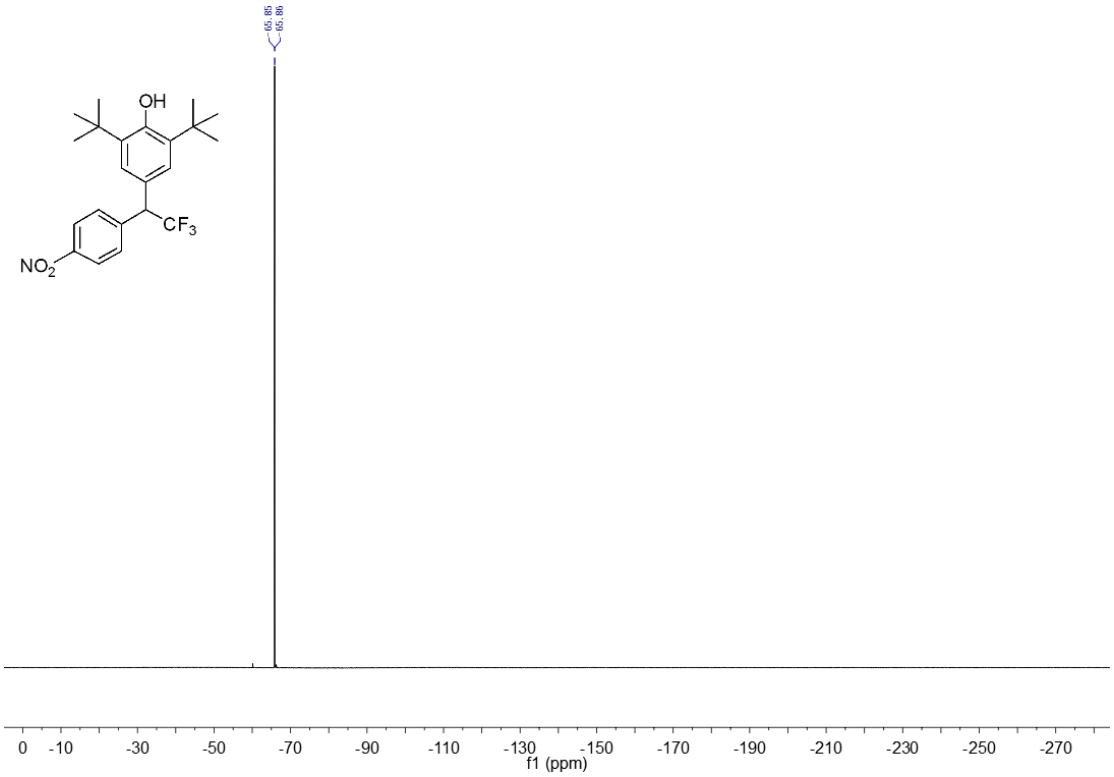
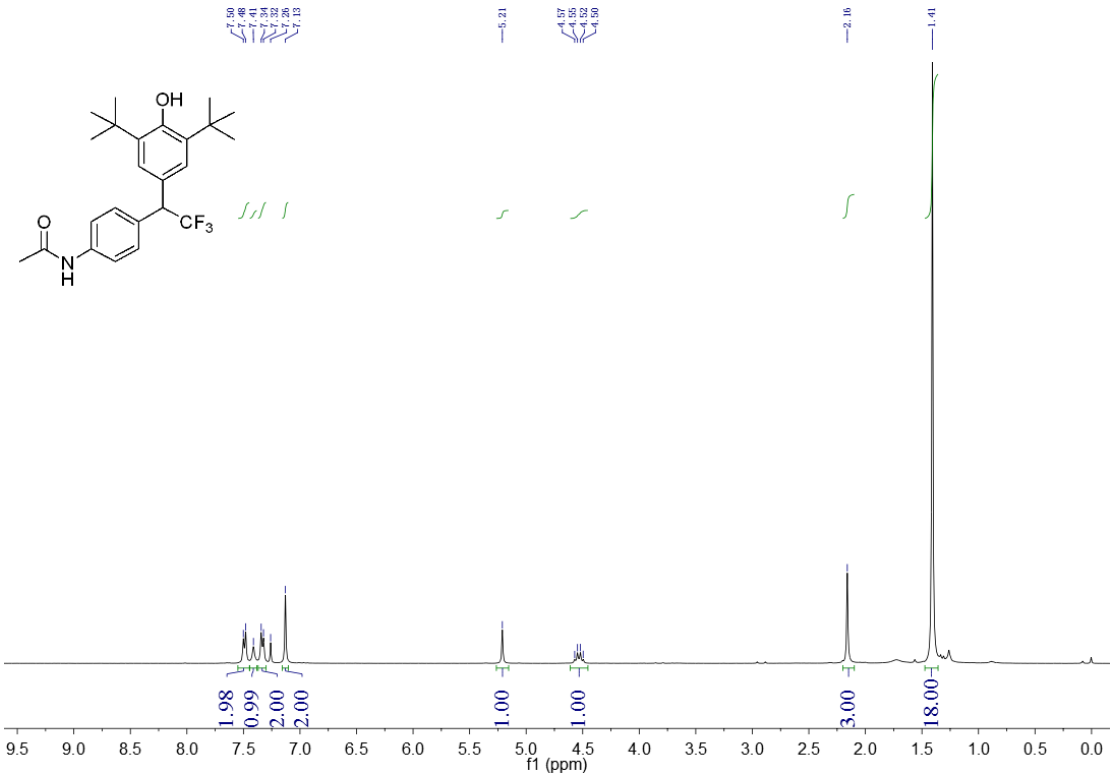


^{19}F NMR of **2l**



^{1}H NMR of **2m**



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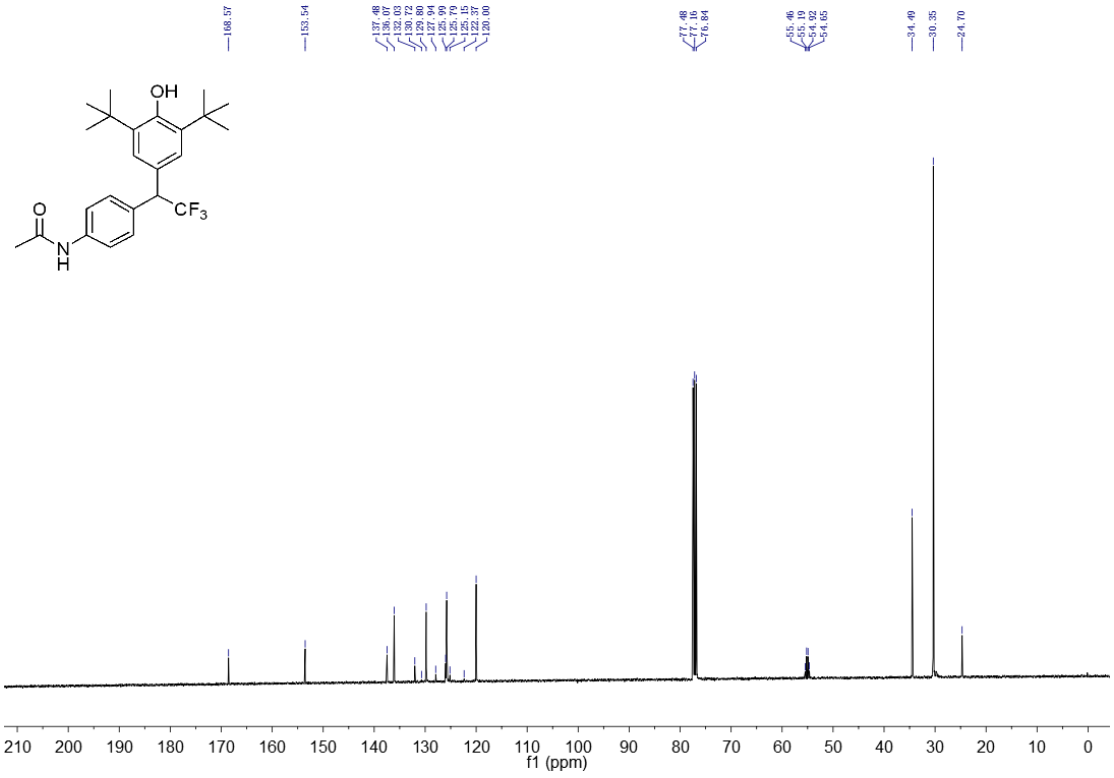

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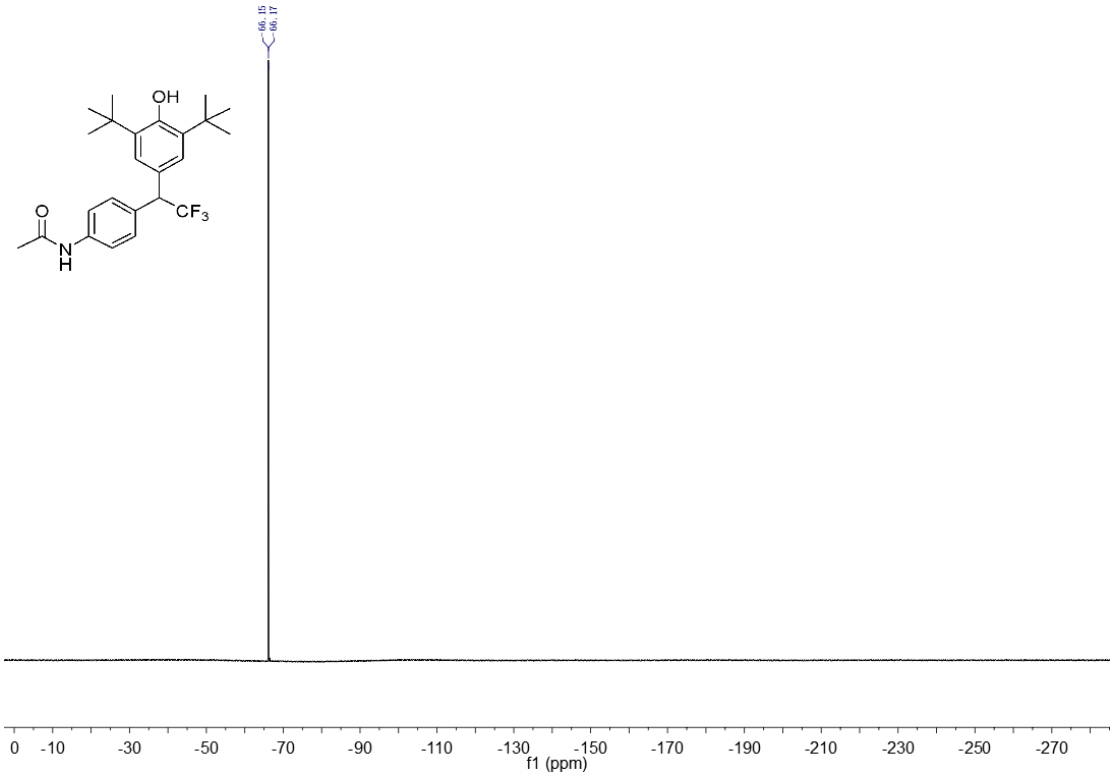
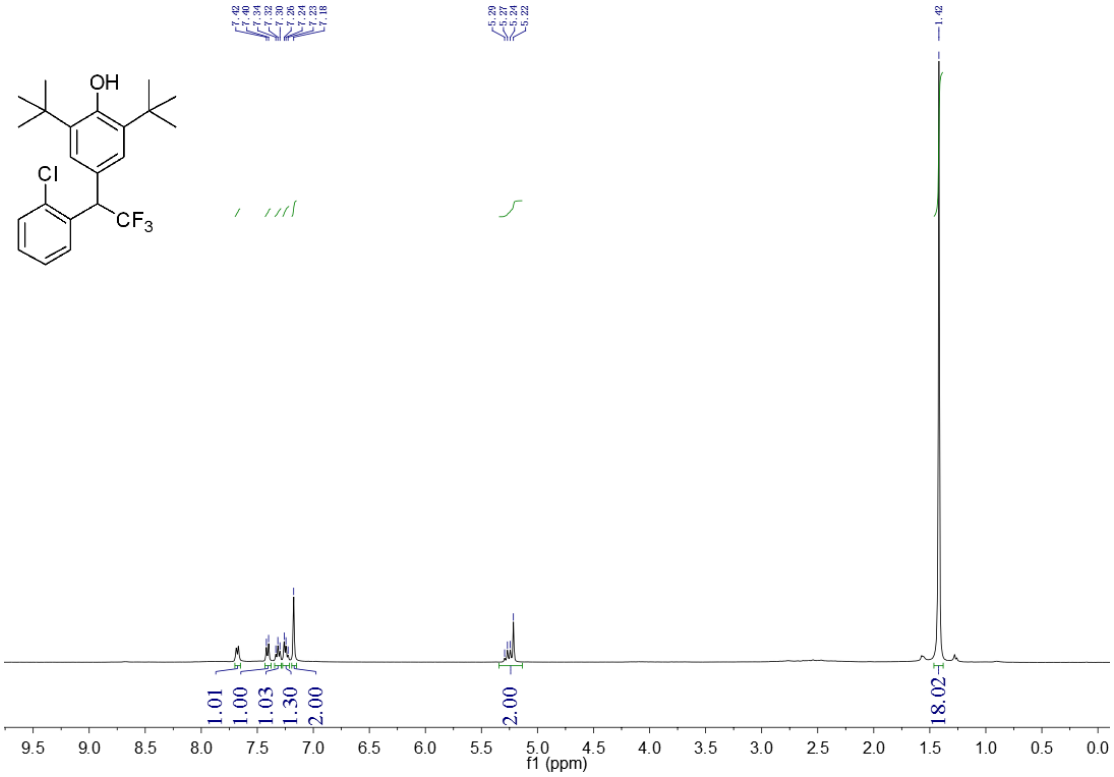


^{1}H NMR of **2n**



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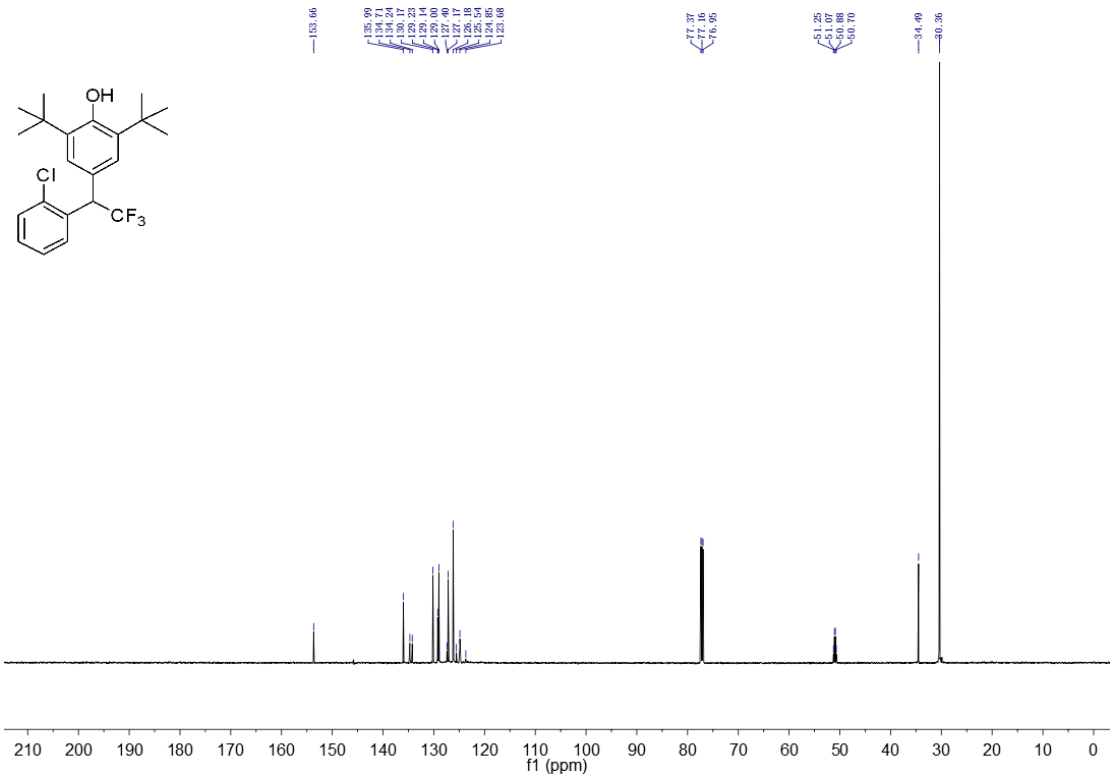

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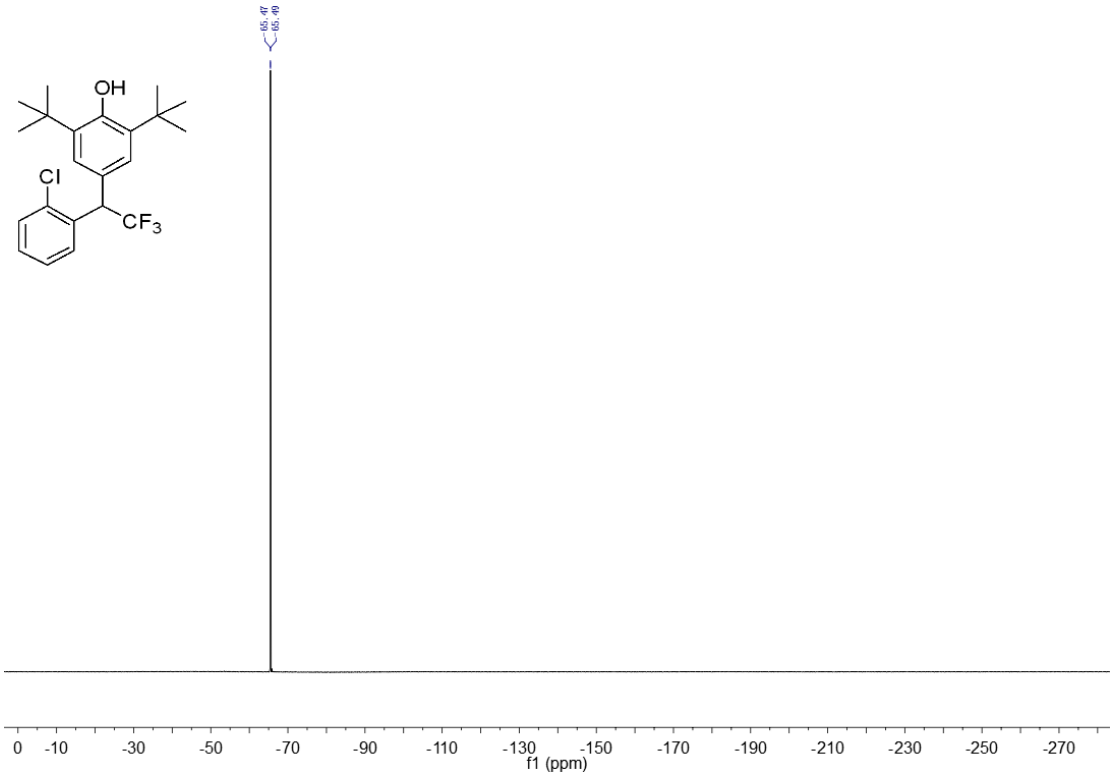

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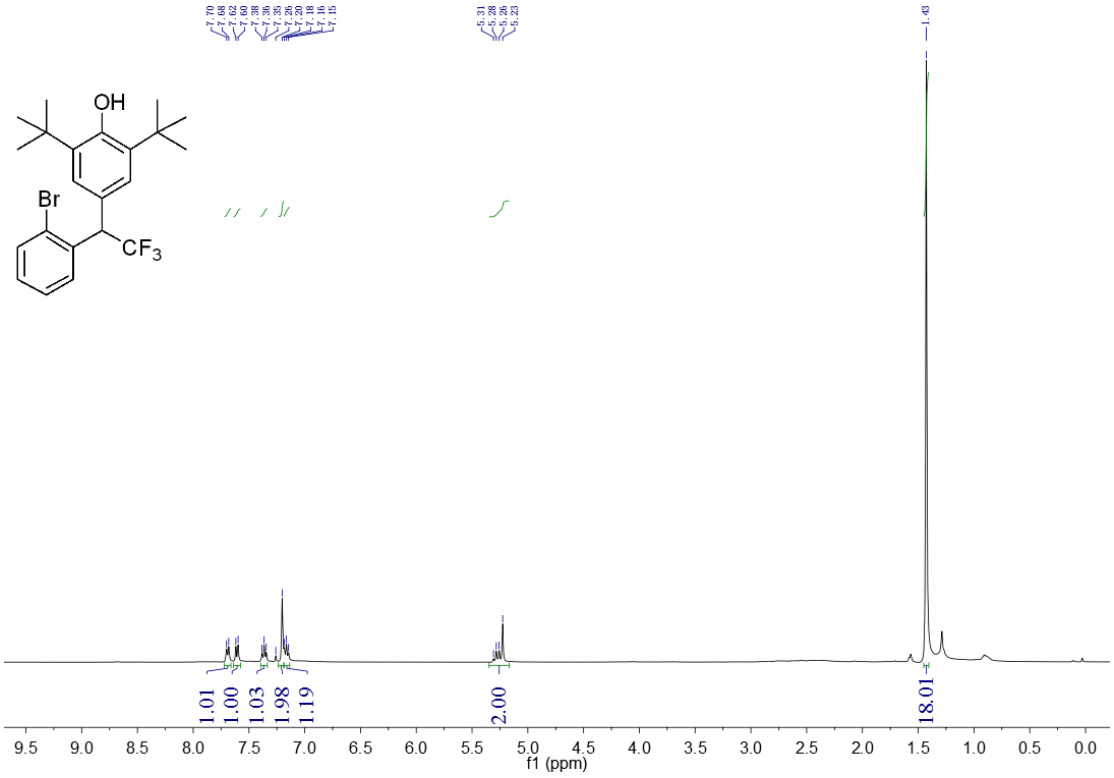

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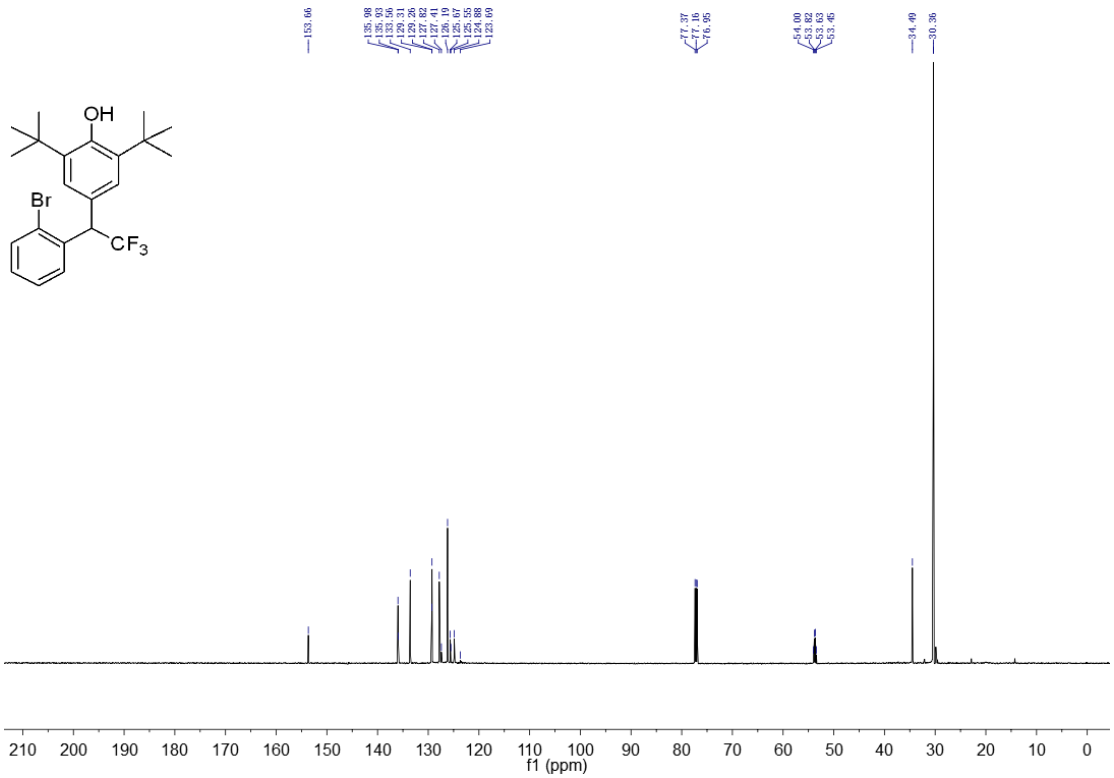
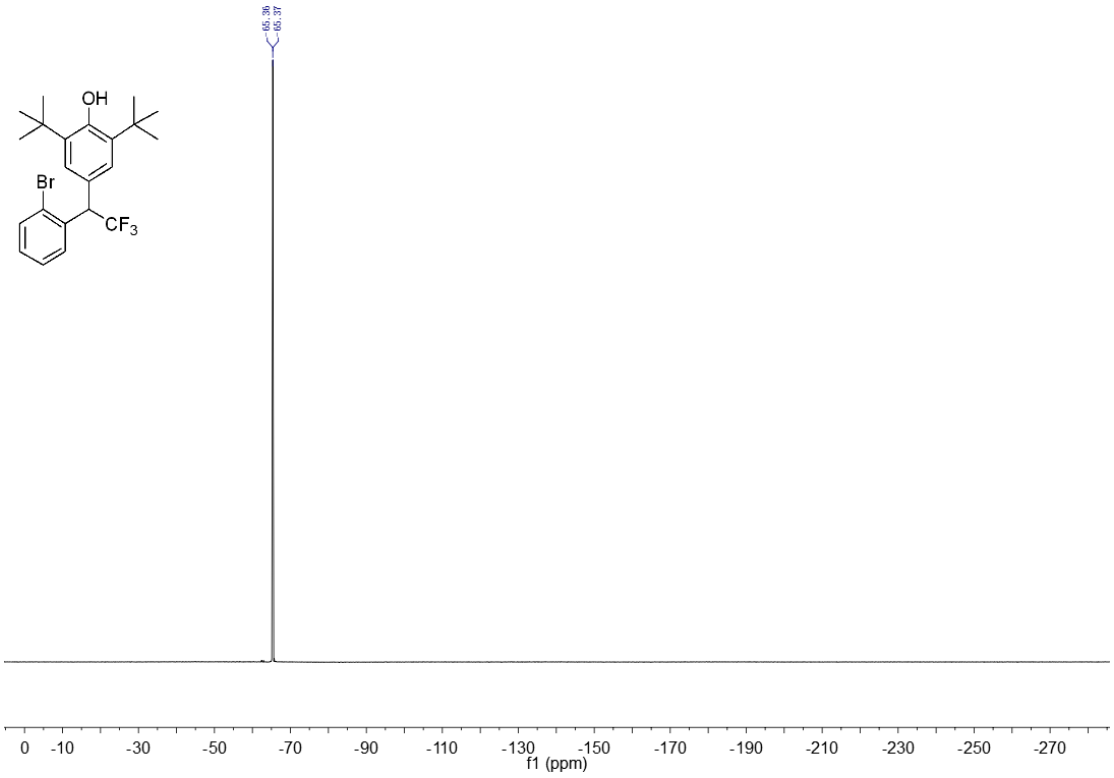
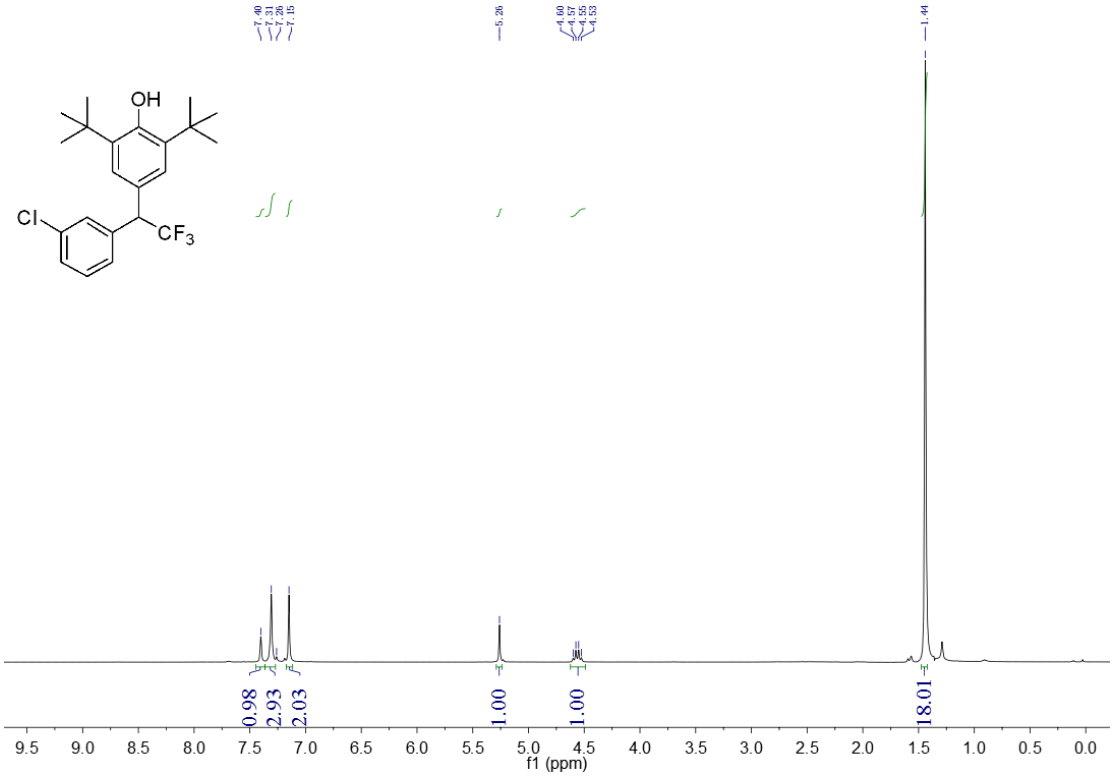


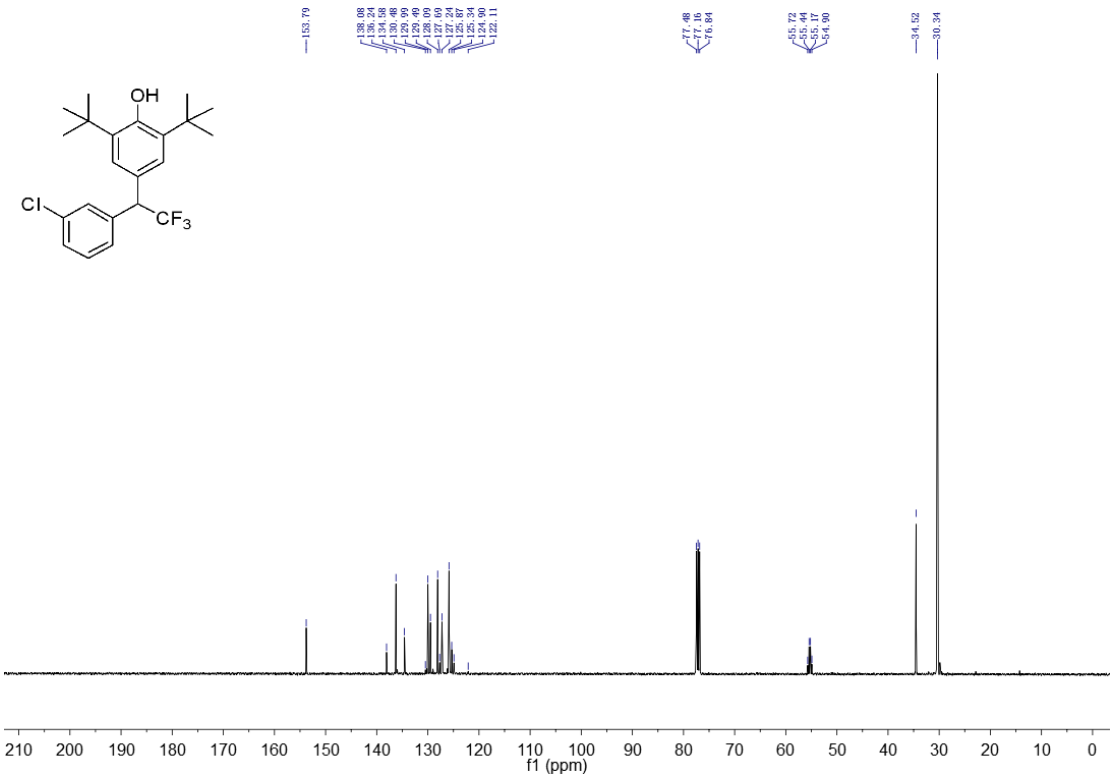
^{19}F NMR of **2o**



^{1}H NMR of **2p**



^{13}C NMR of **2p**



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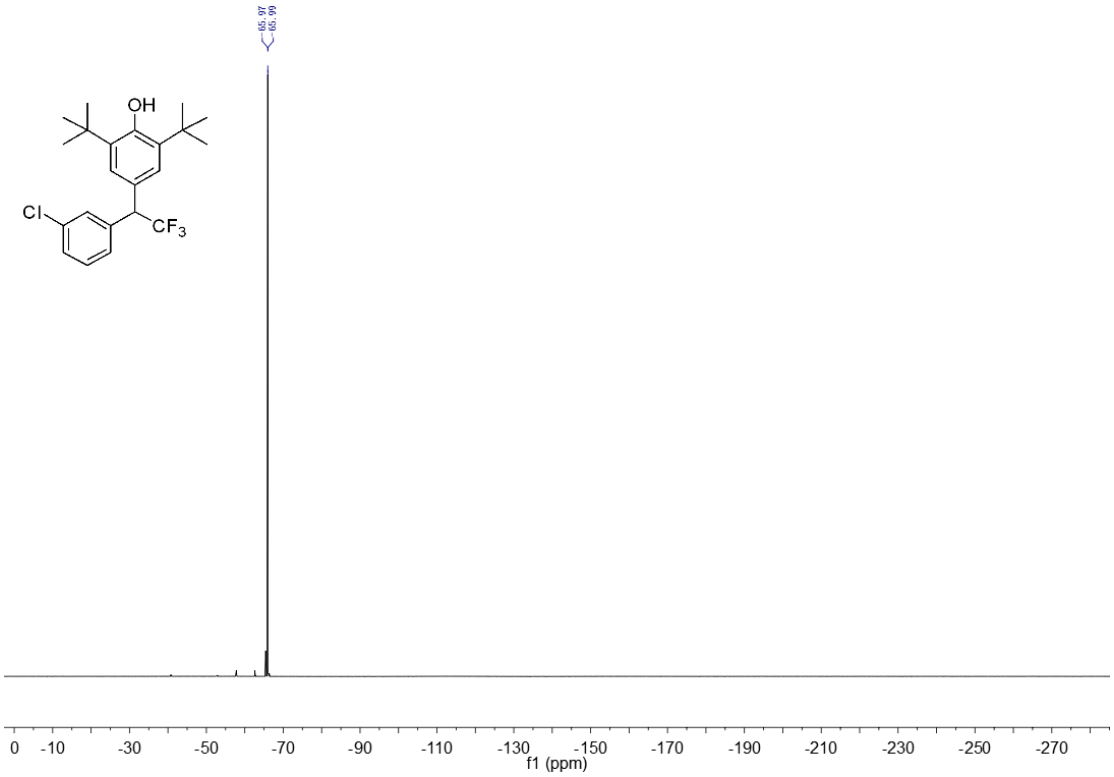
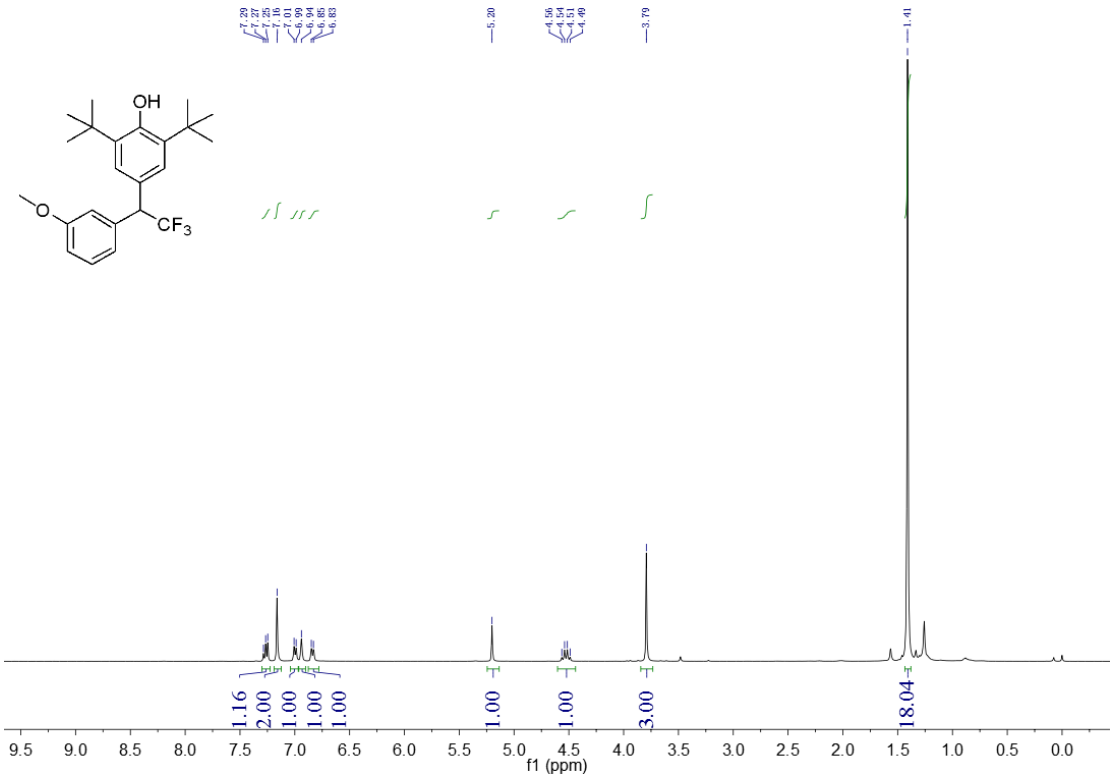
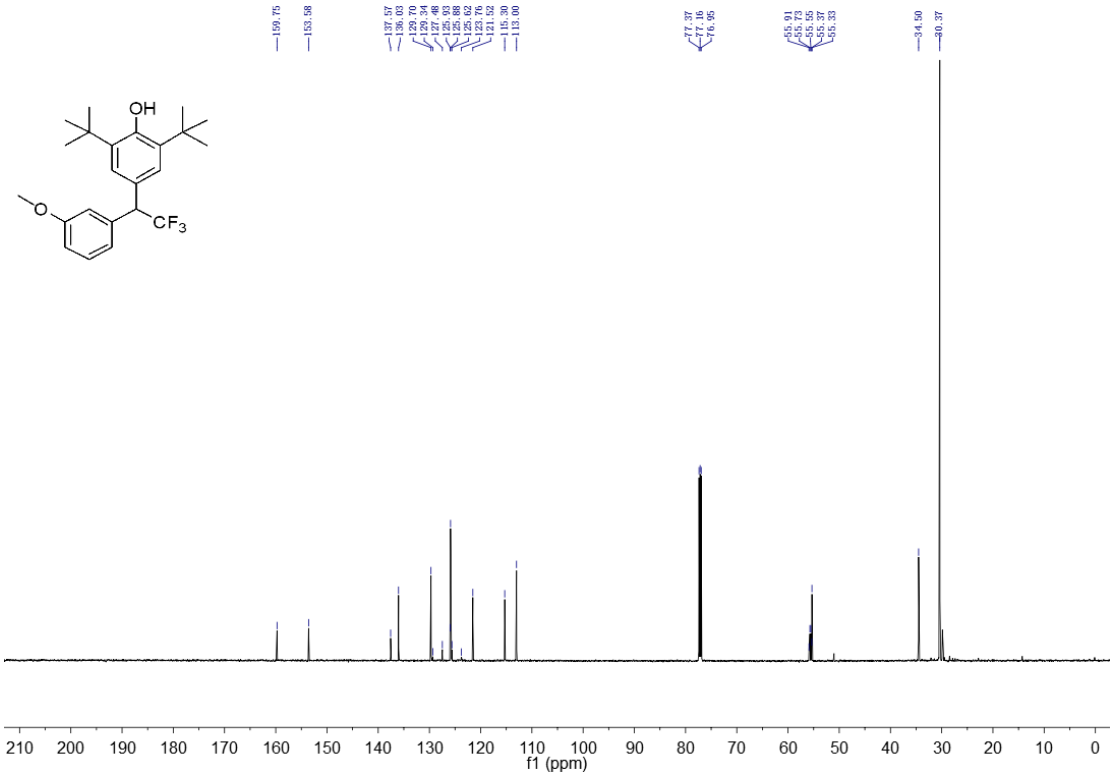


^{1}H NMR of **2q**



^{13}C NMR of **2q**



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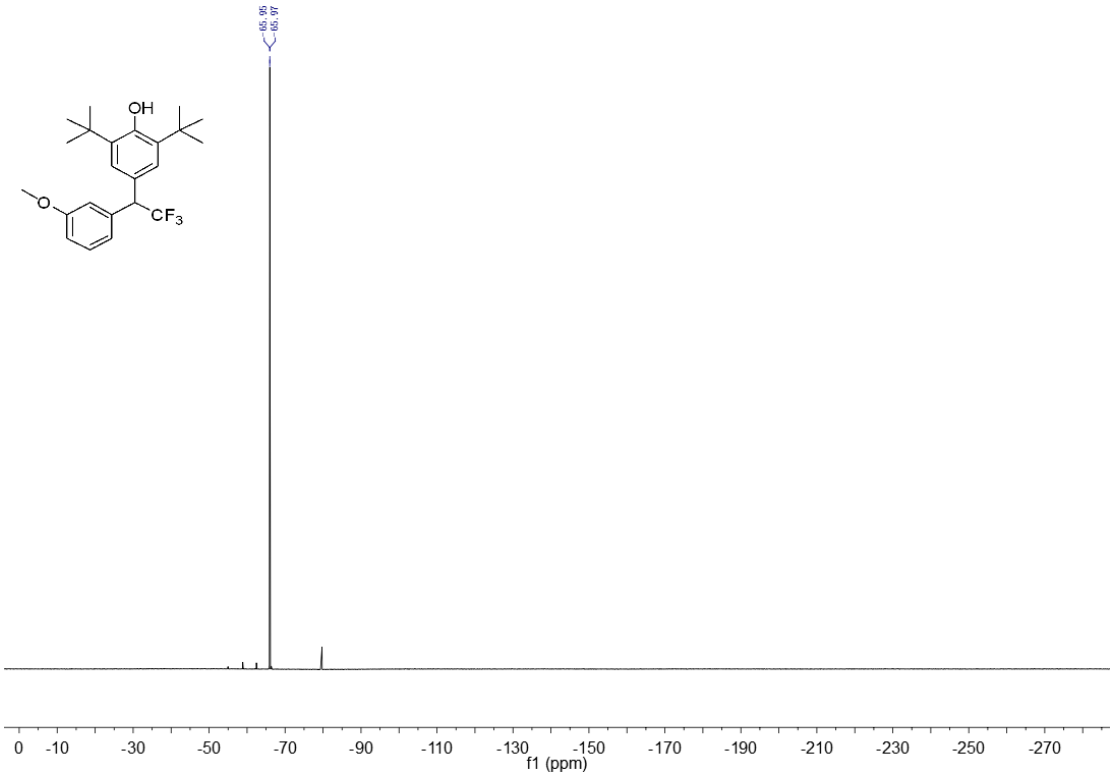
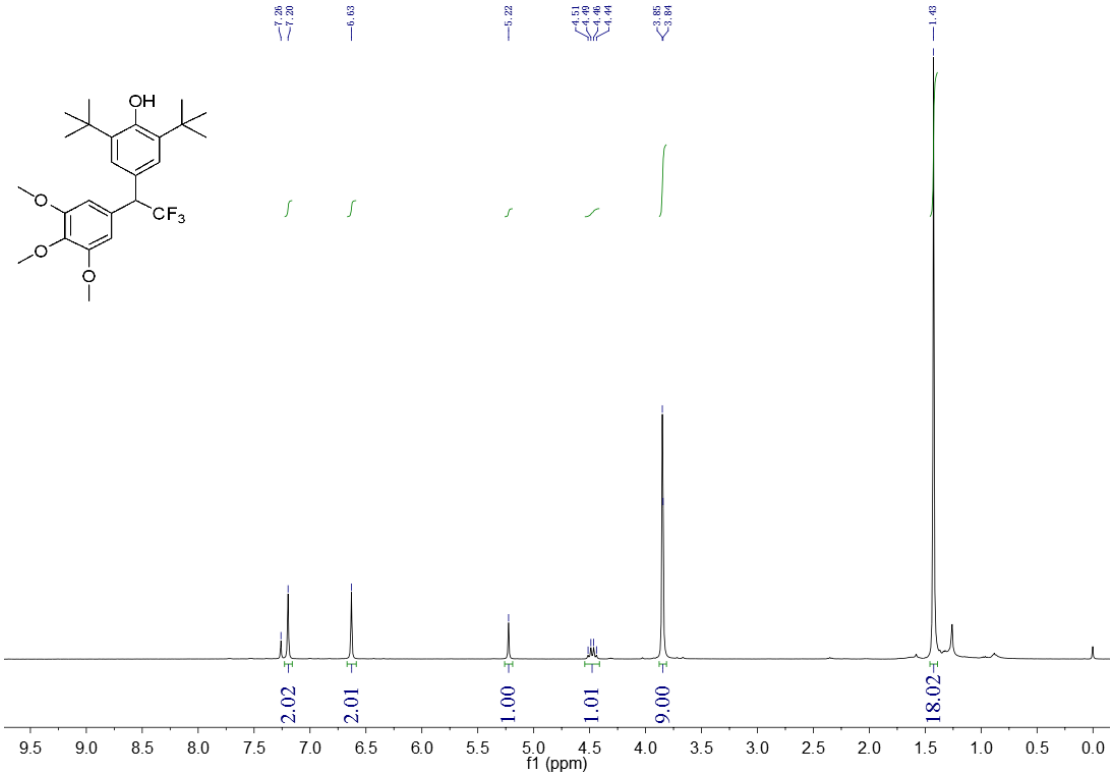
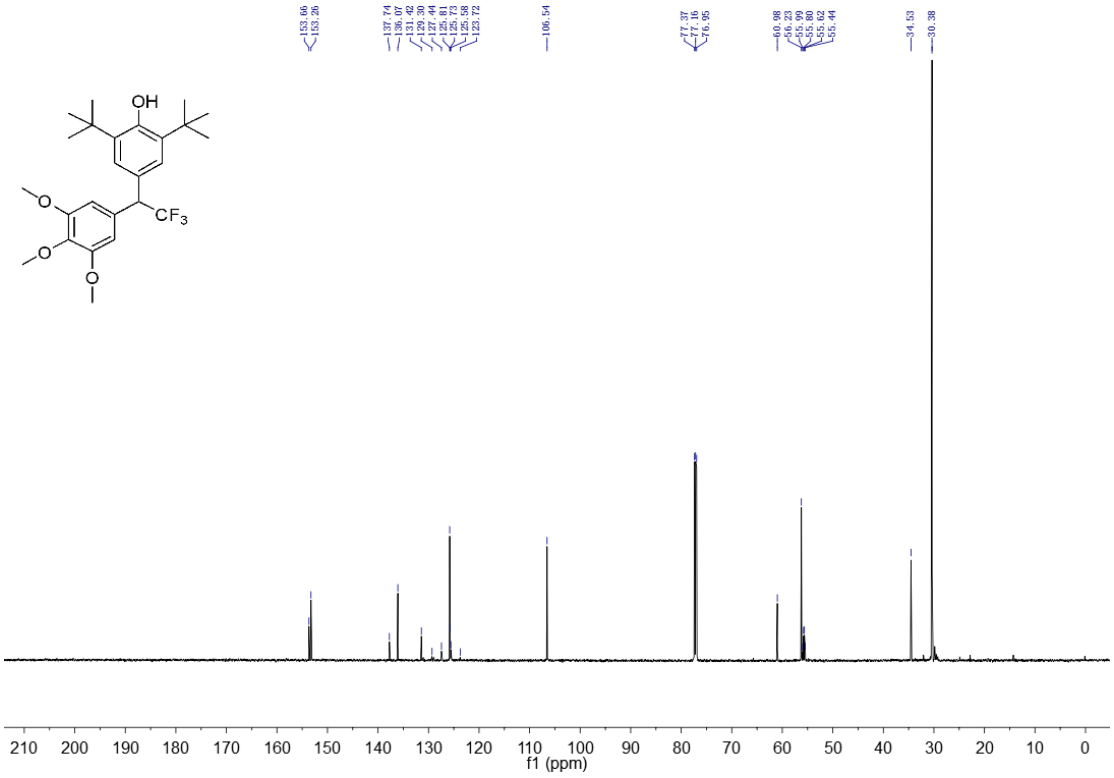


^{1}H NMR of **2r**



^{13}C NMR of **2r**



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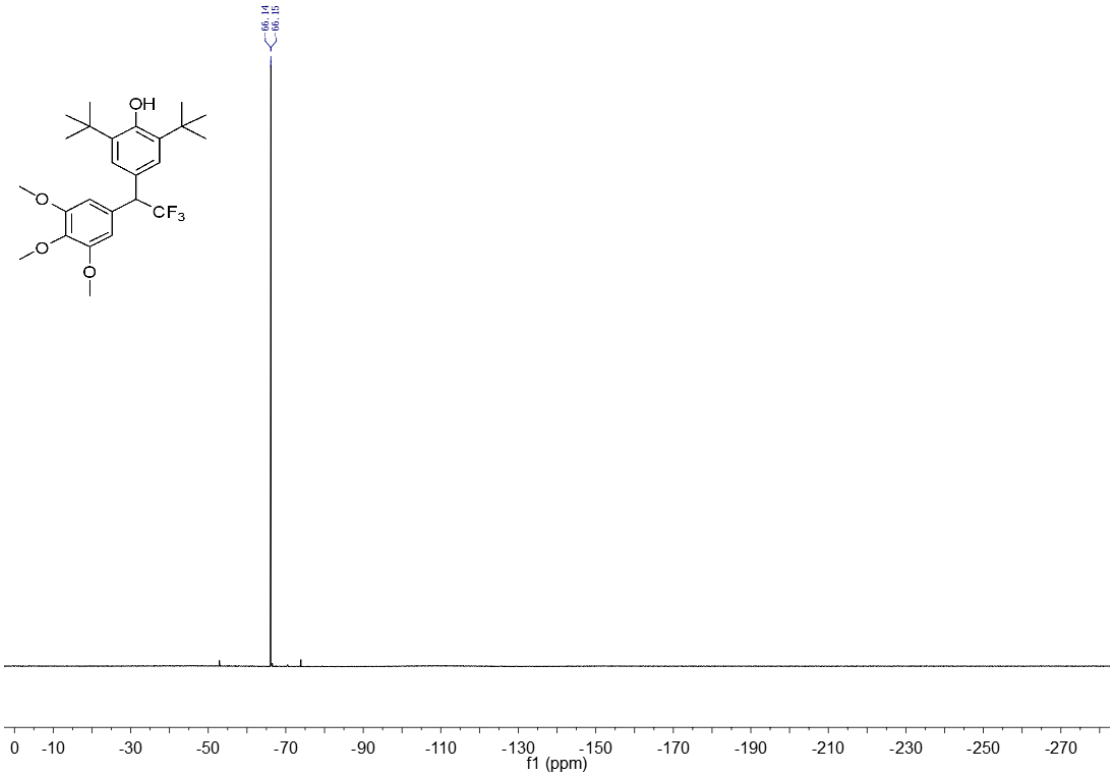

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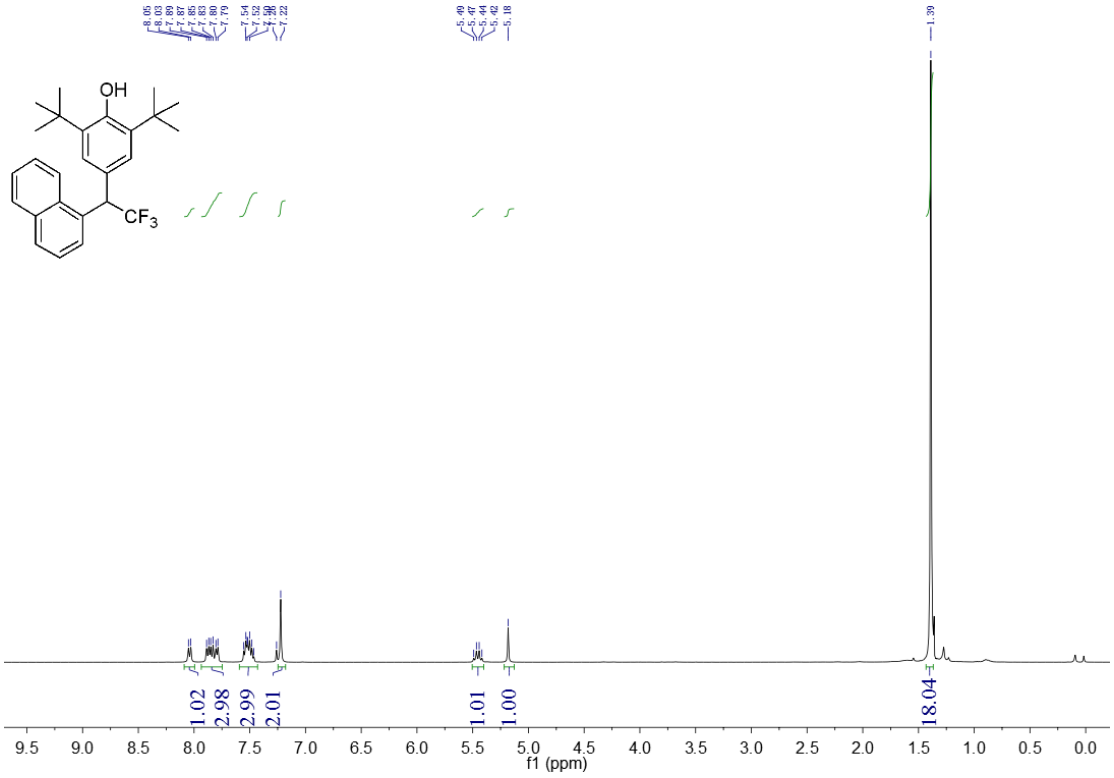

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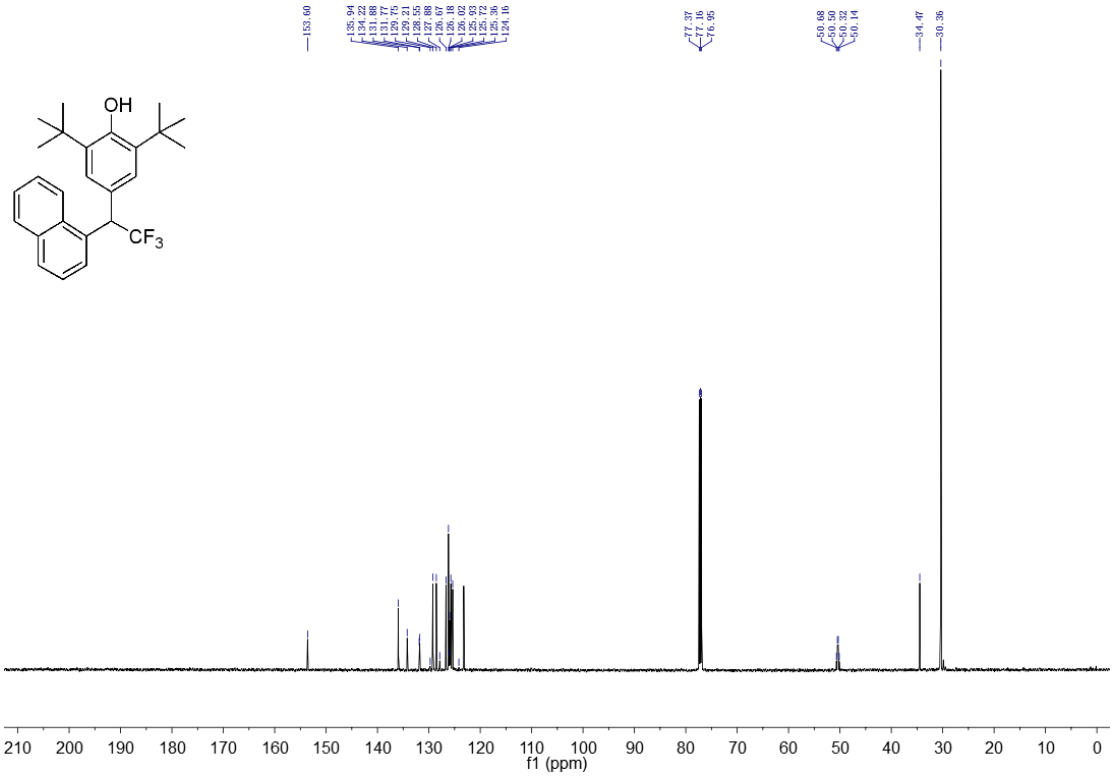

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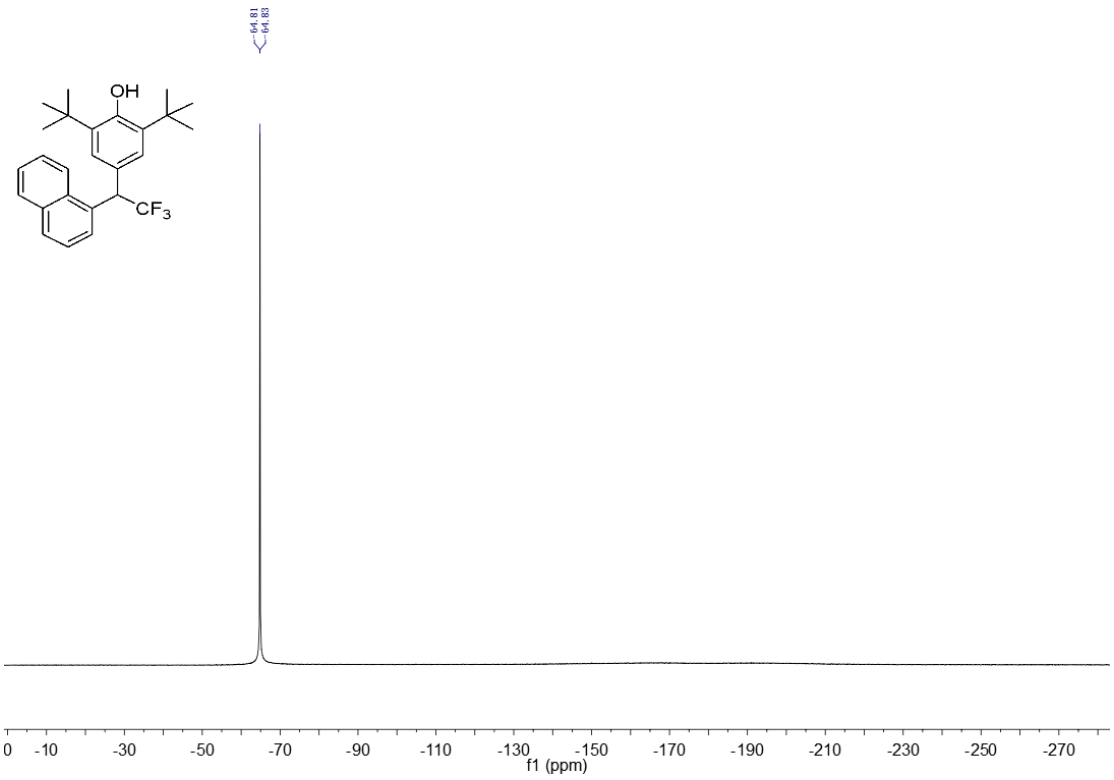
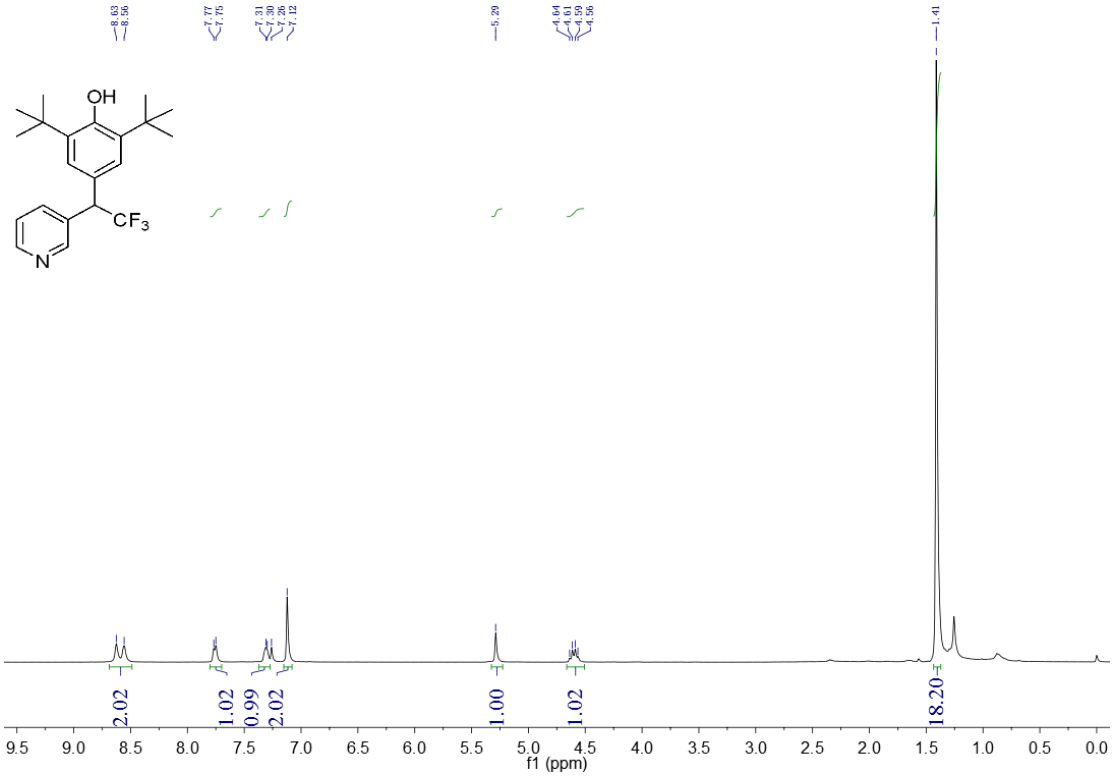


^{1}H NMR of **2t**



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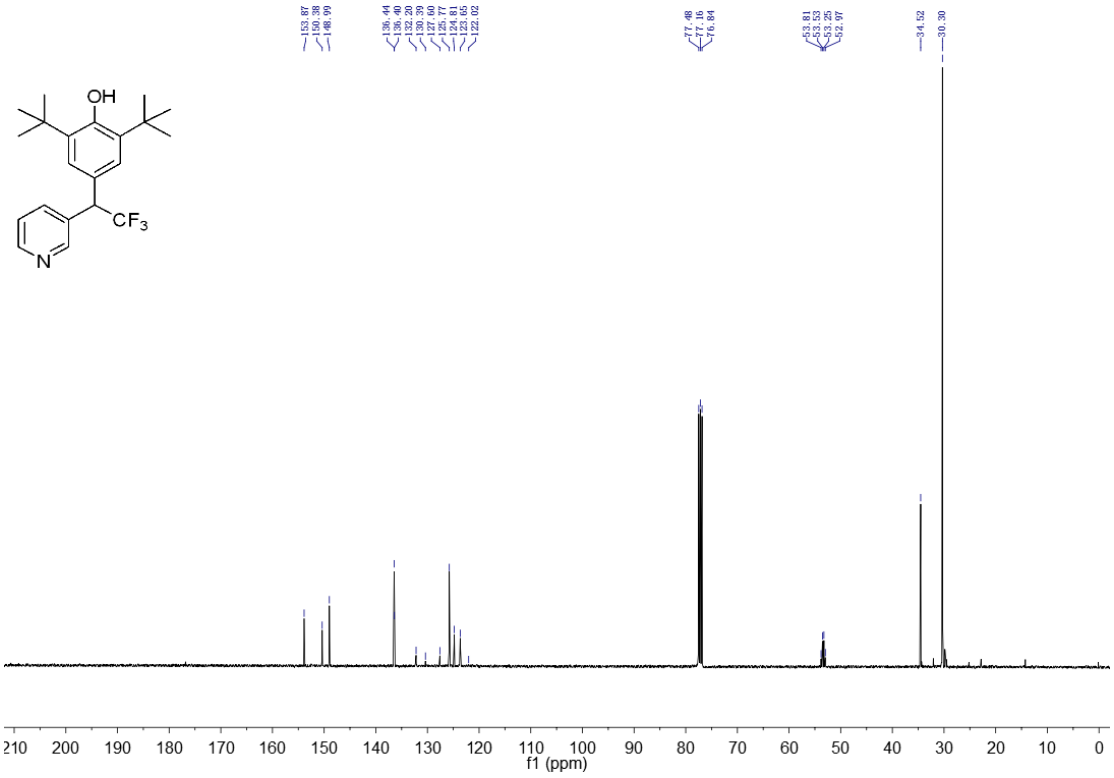
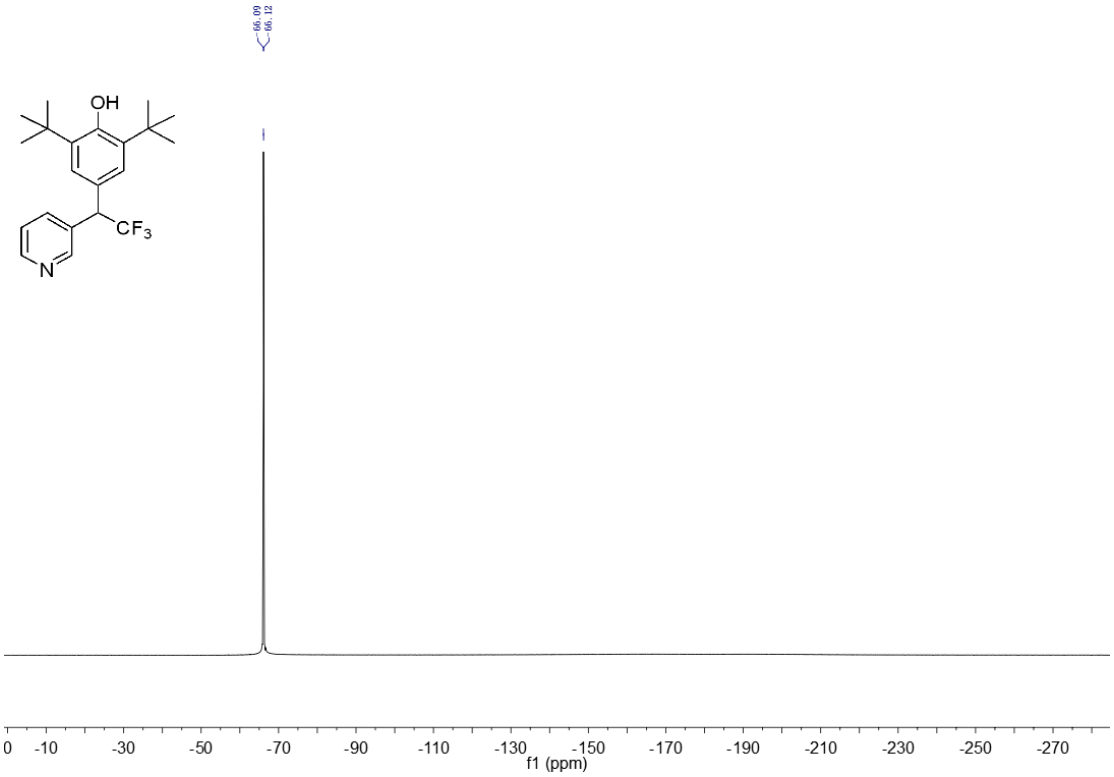
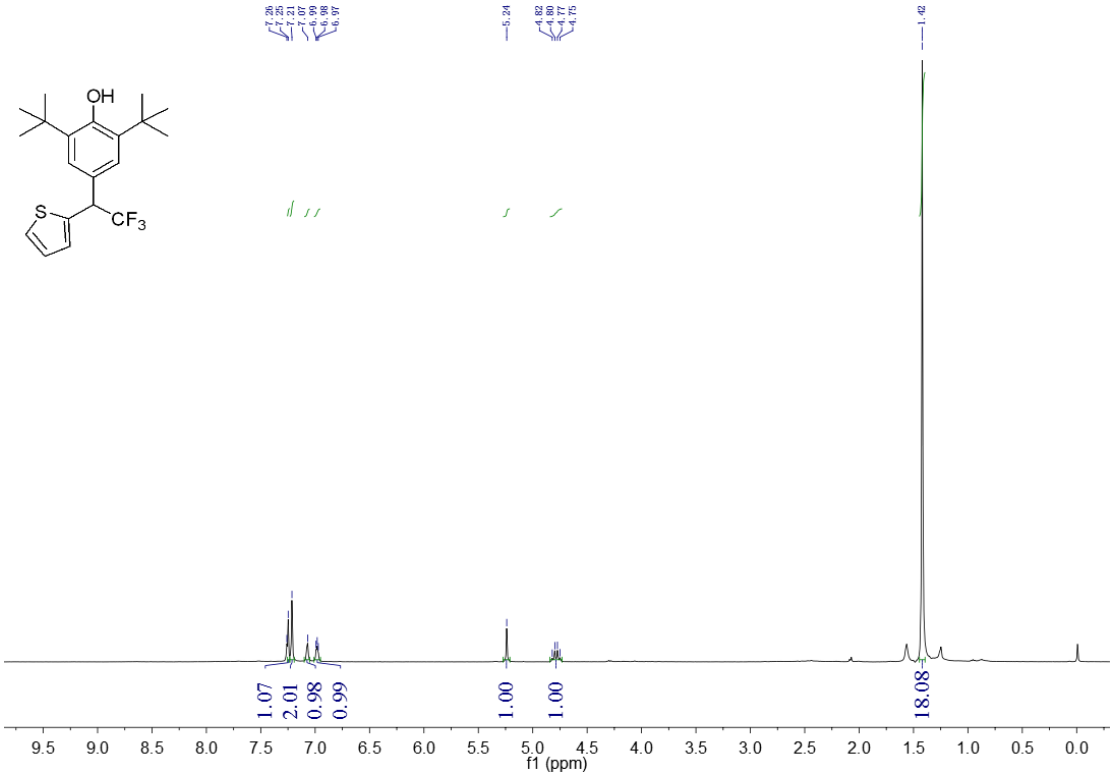


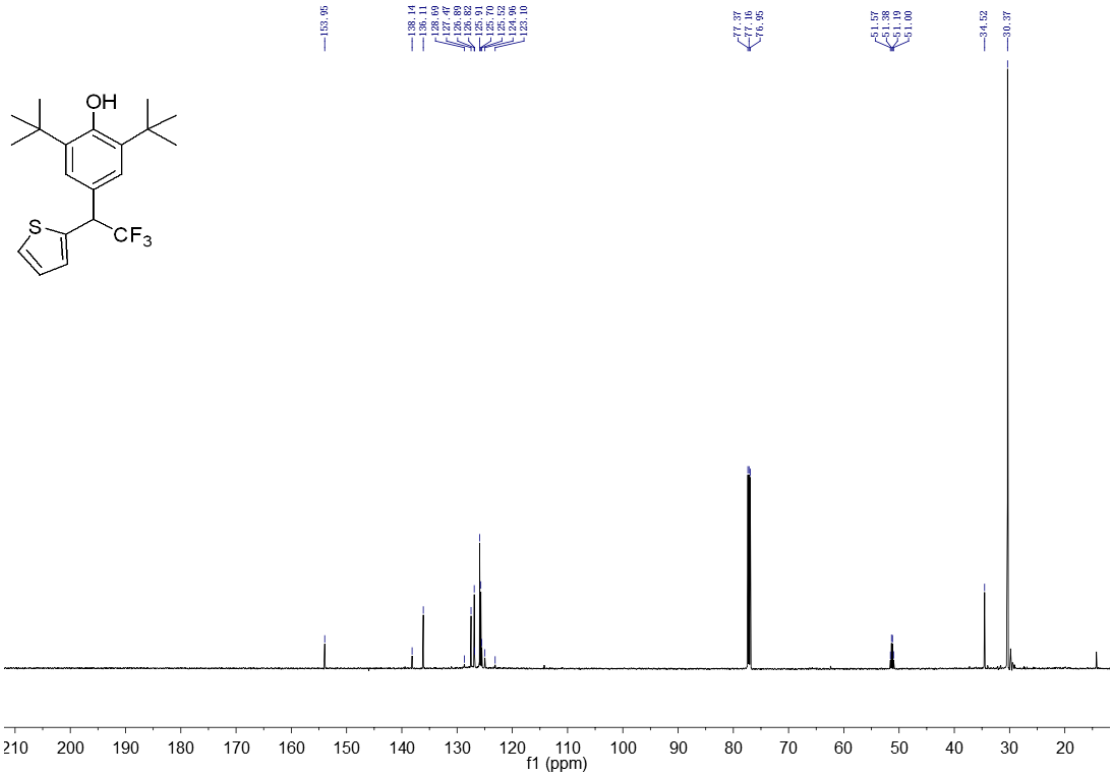
^{19}F NMR of **2t**



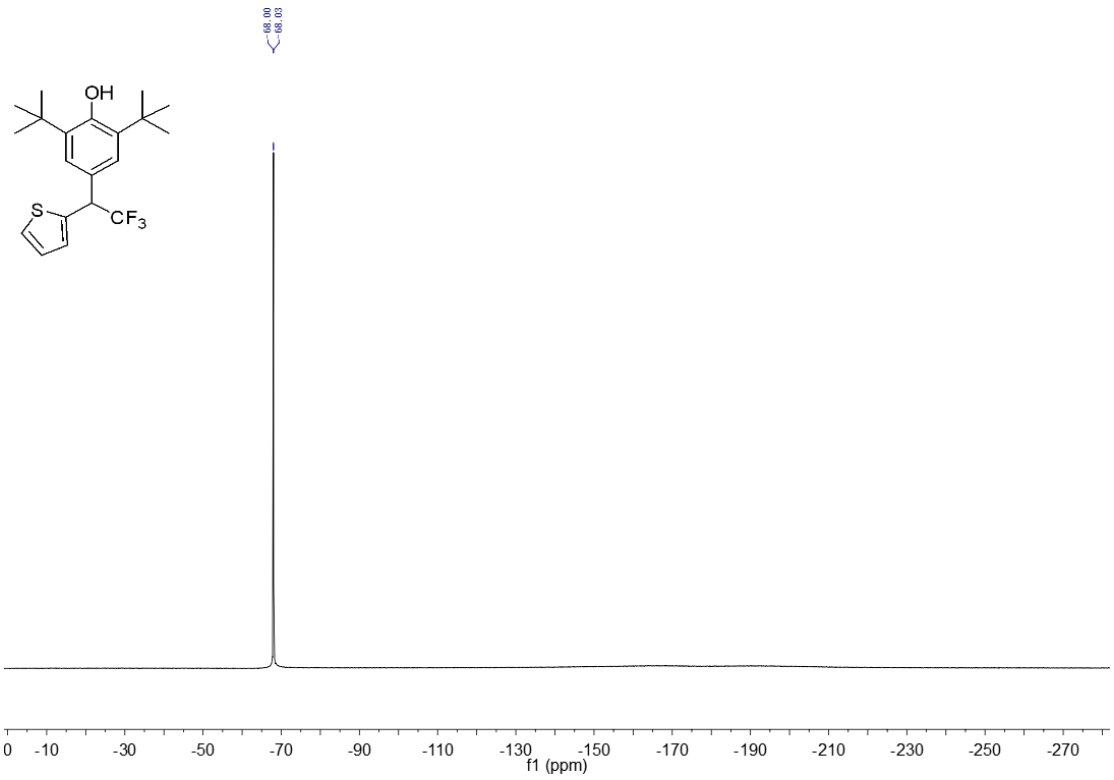
^{1}H NMR of **2u**



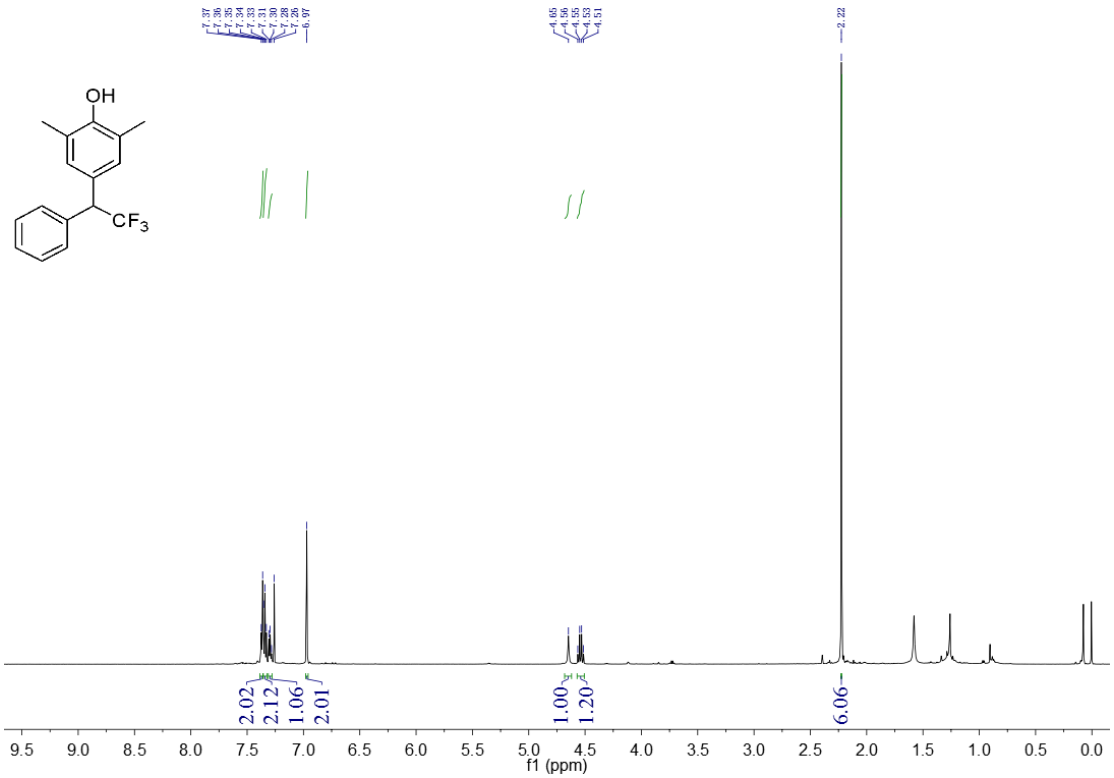
^{13}C NMR of **2u**



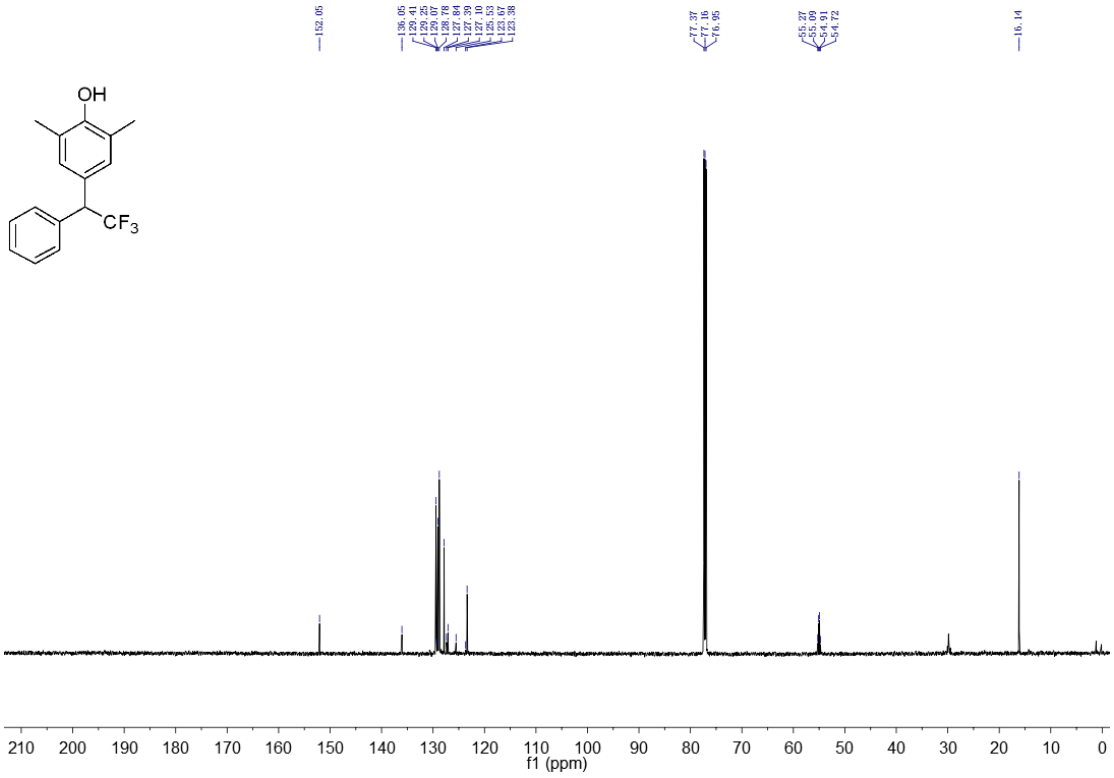
^{19}F NMR of **2u**



^{1}H NMR of **2v**



^{13}C NMR of **2v**



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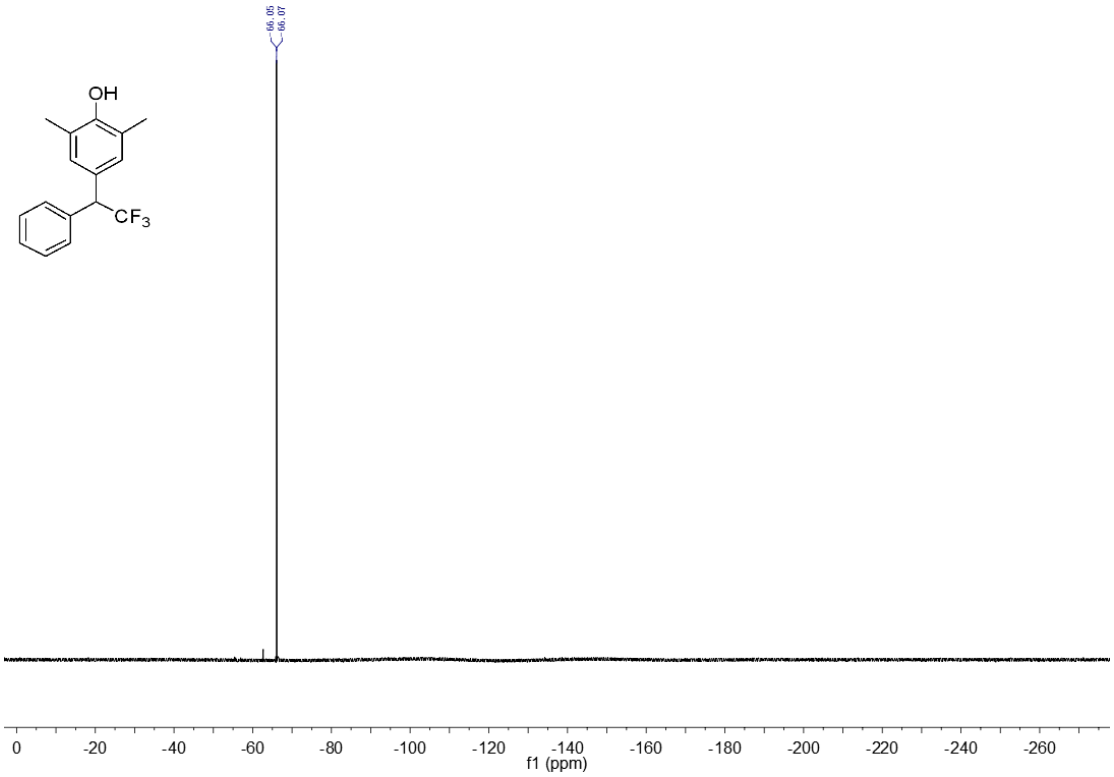
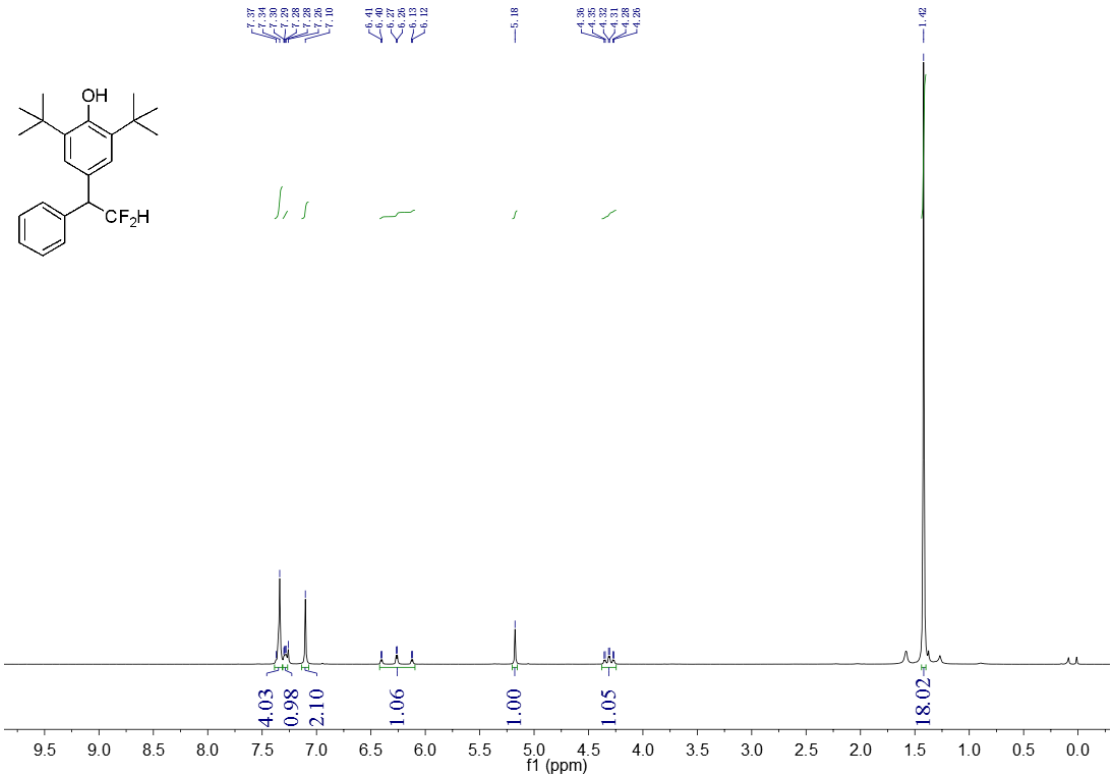


^{1}H NMR of **3a**



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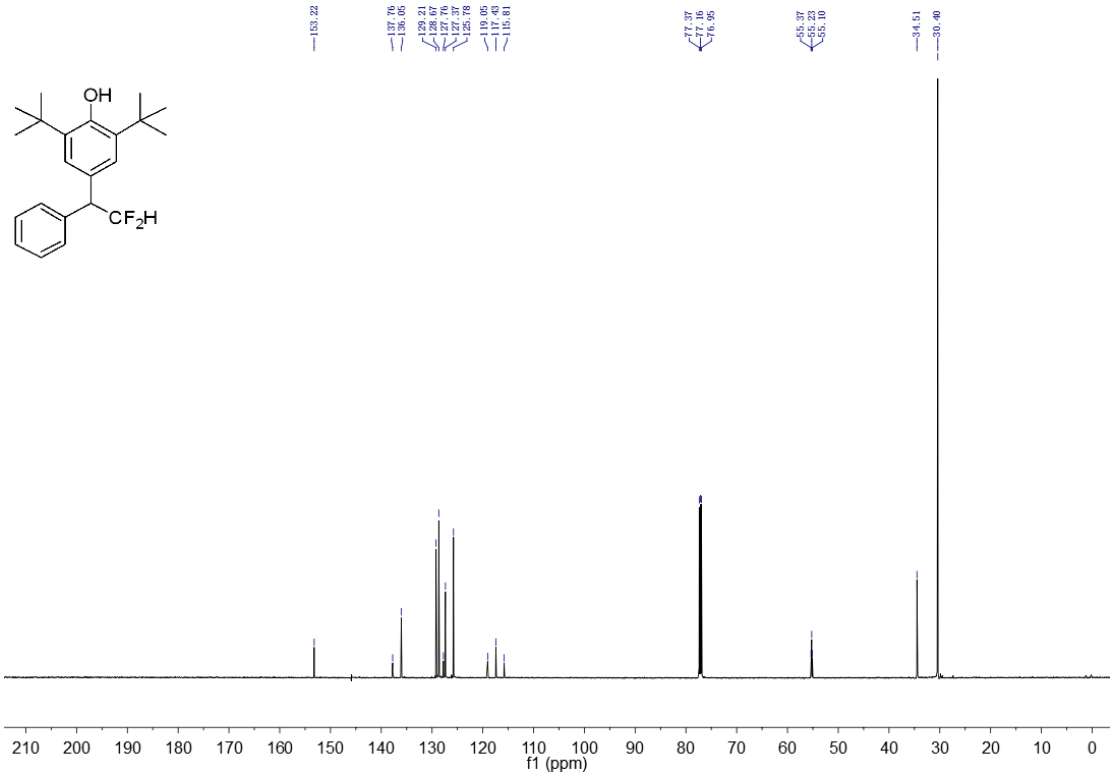
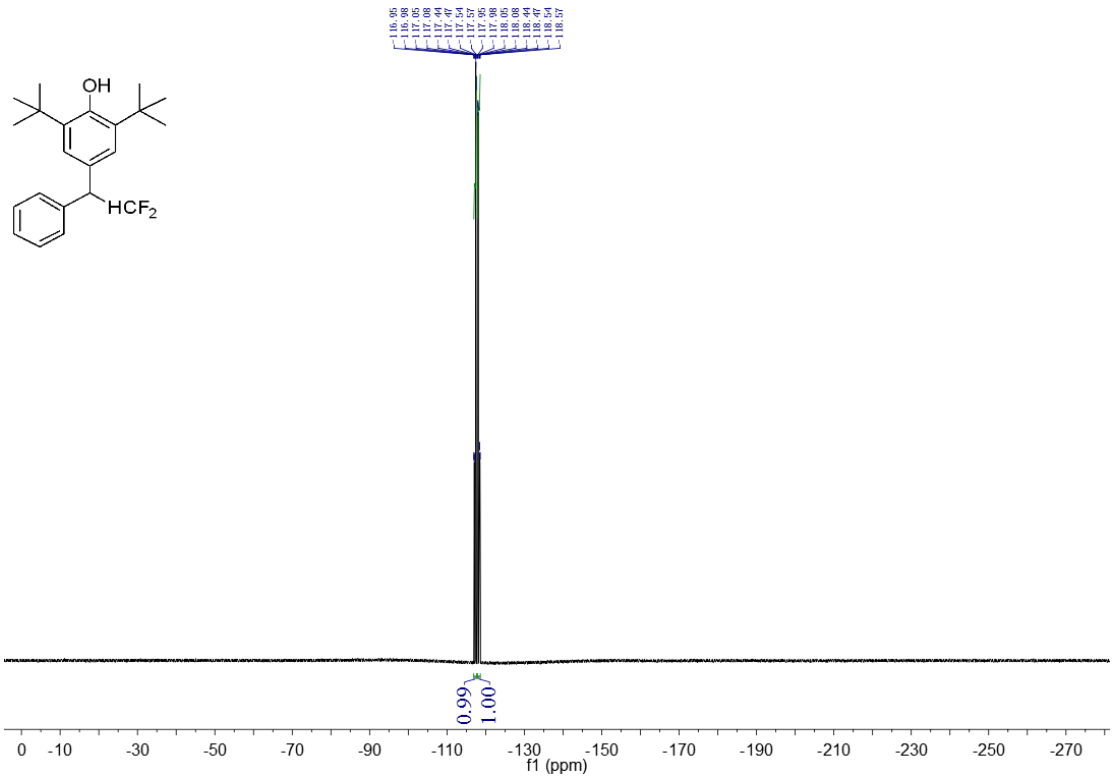
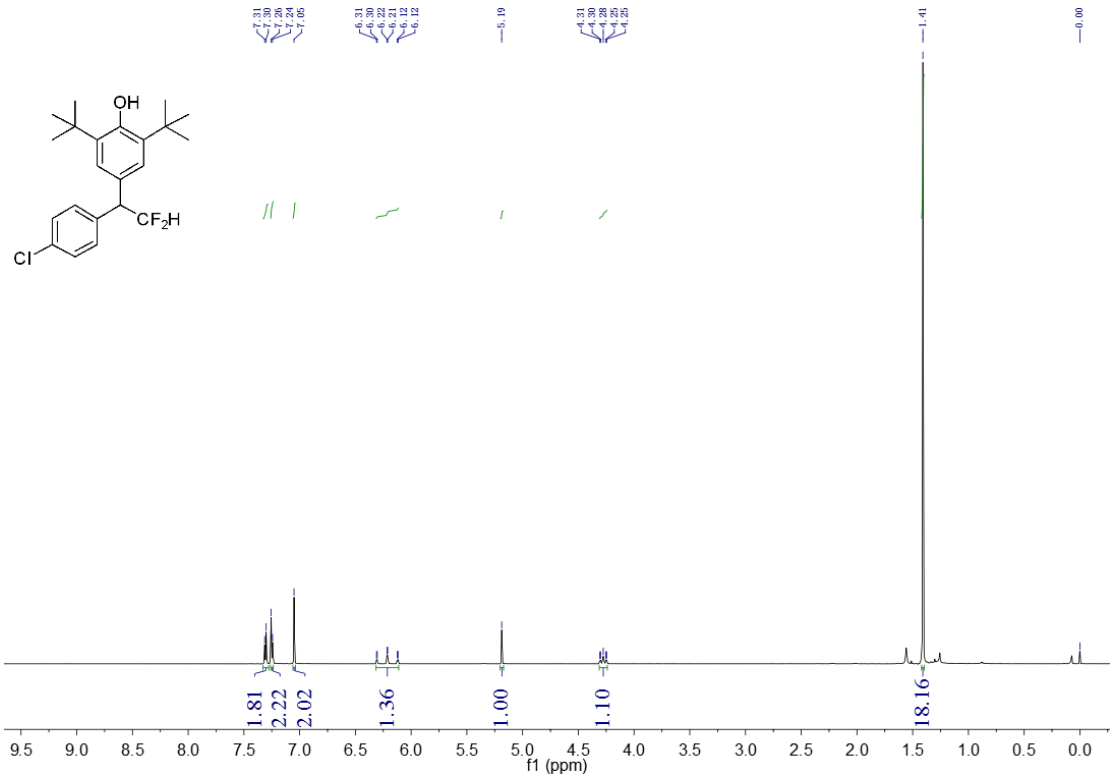


^{19}F NMR of **3a**



^{1}H NMR of **3b**



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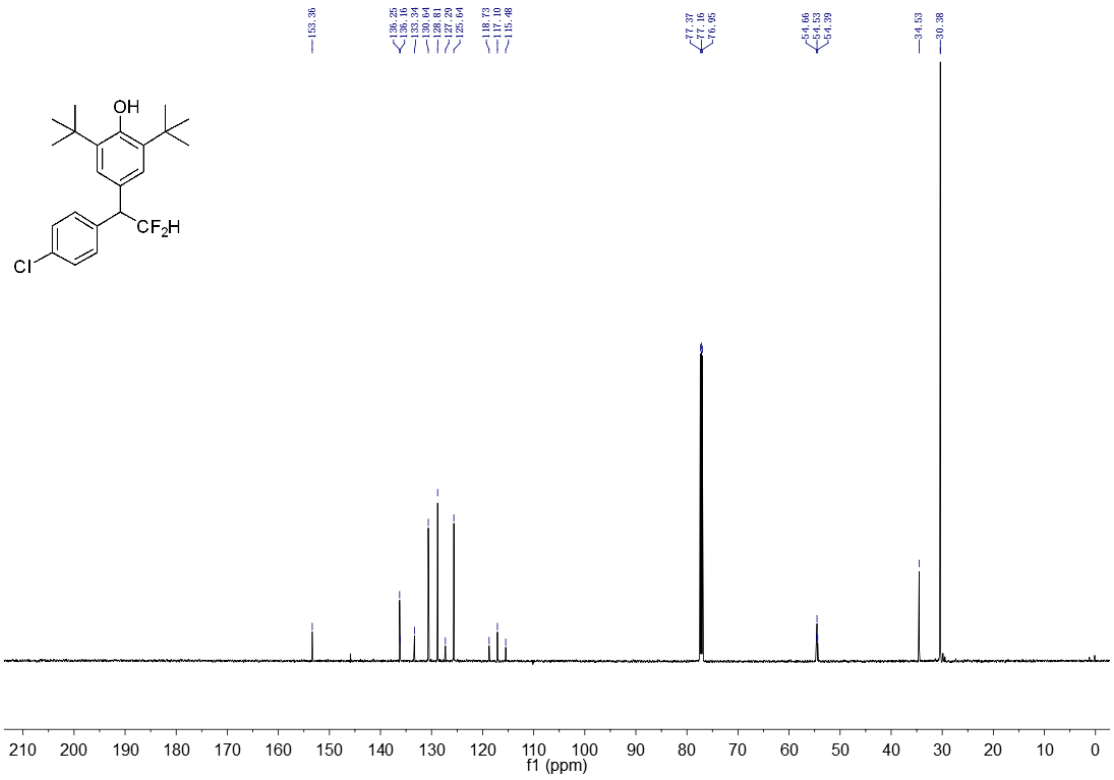

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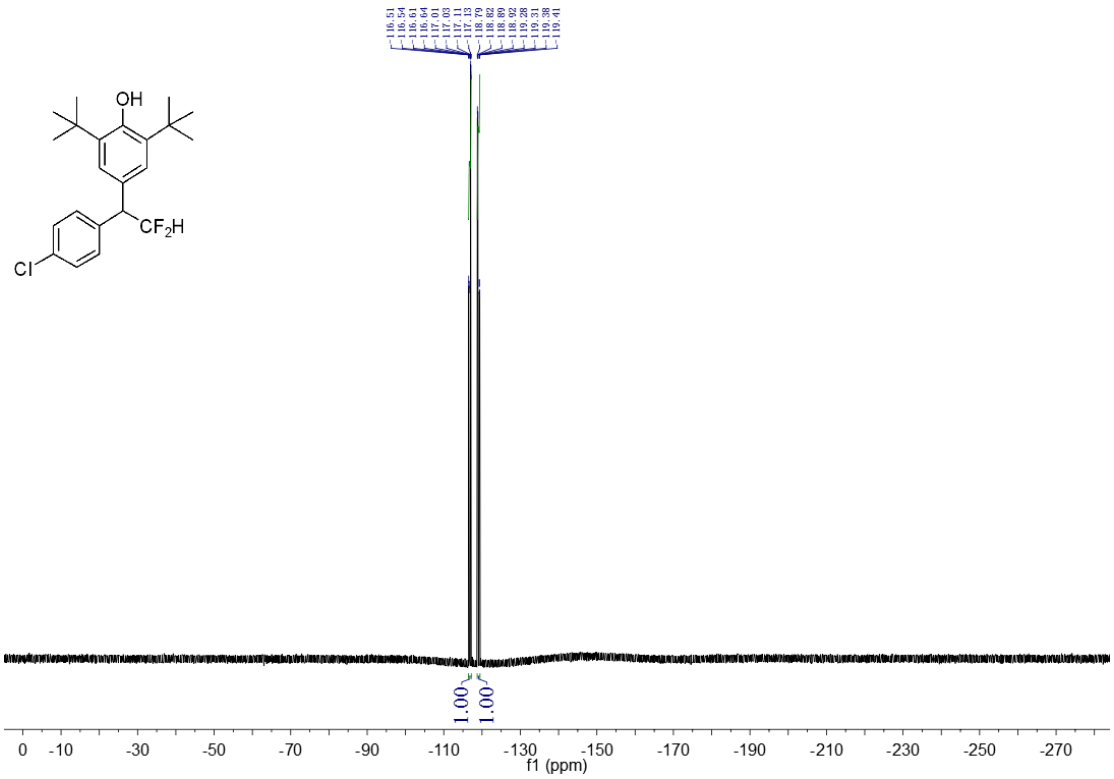
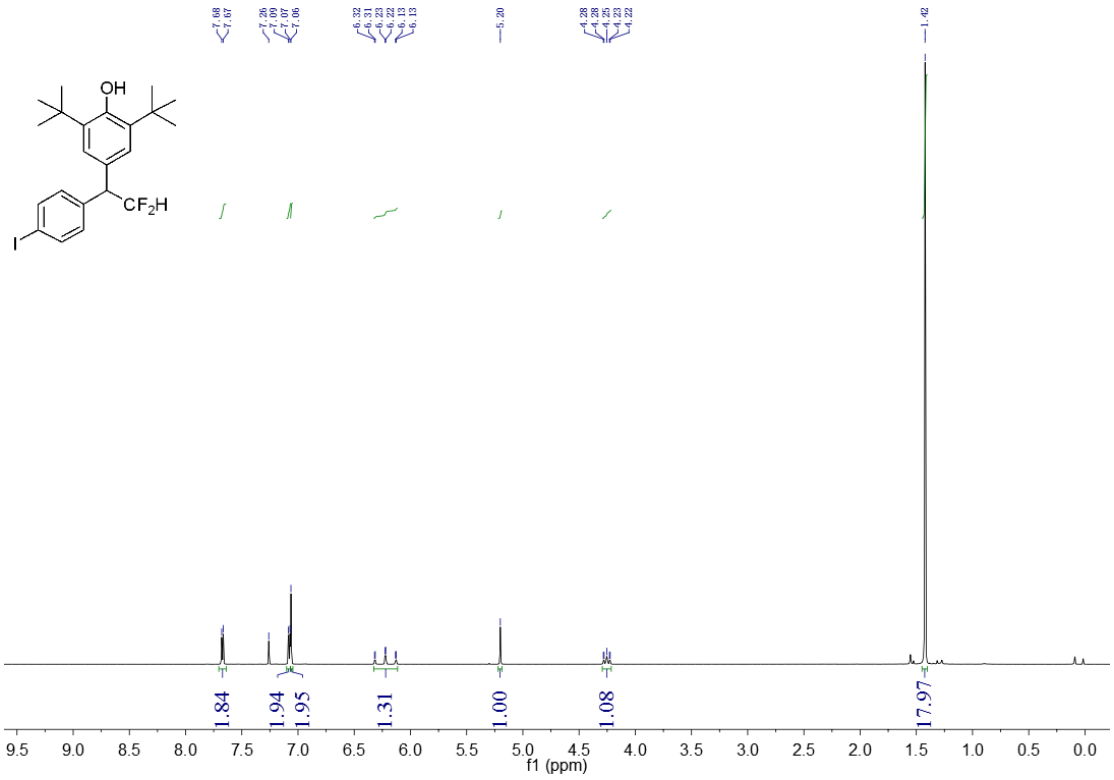
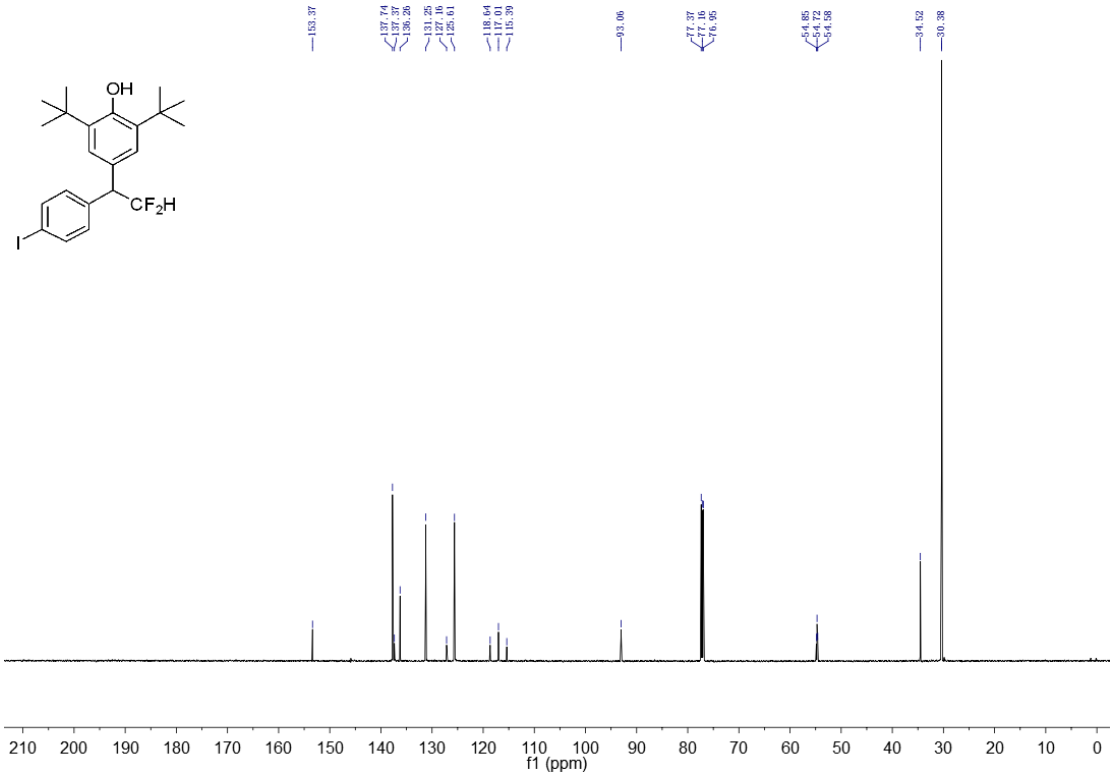


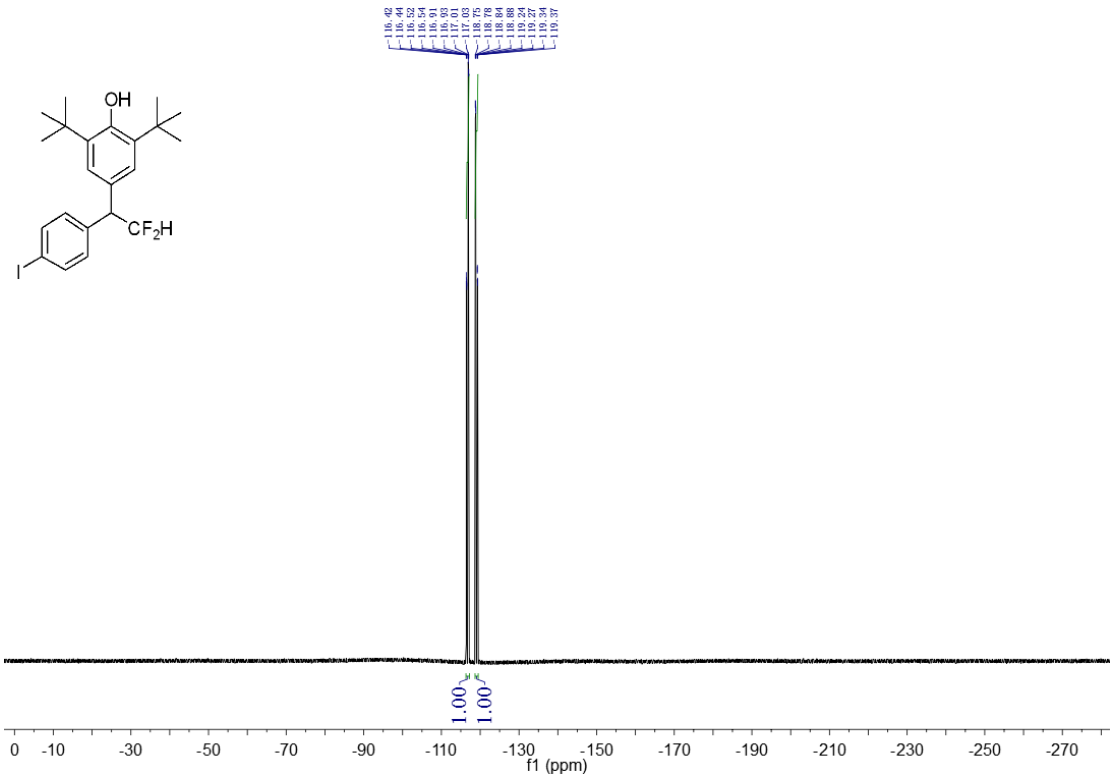
^{1}H NMR of **3c**



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



^{19}F NMR of **3c**



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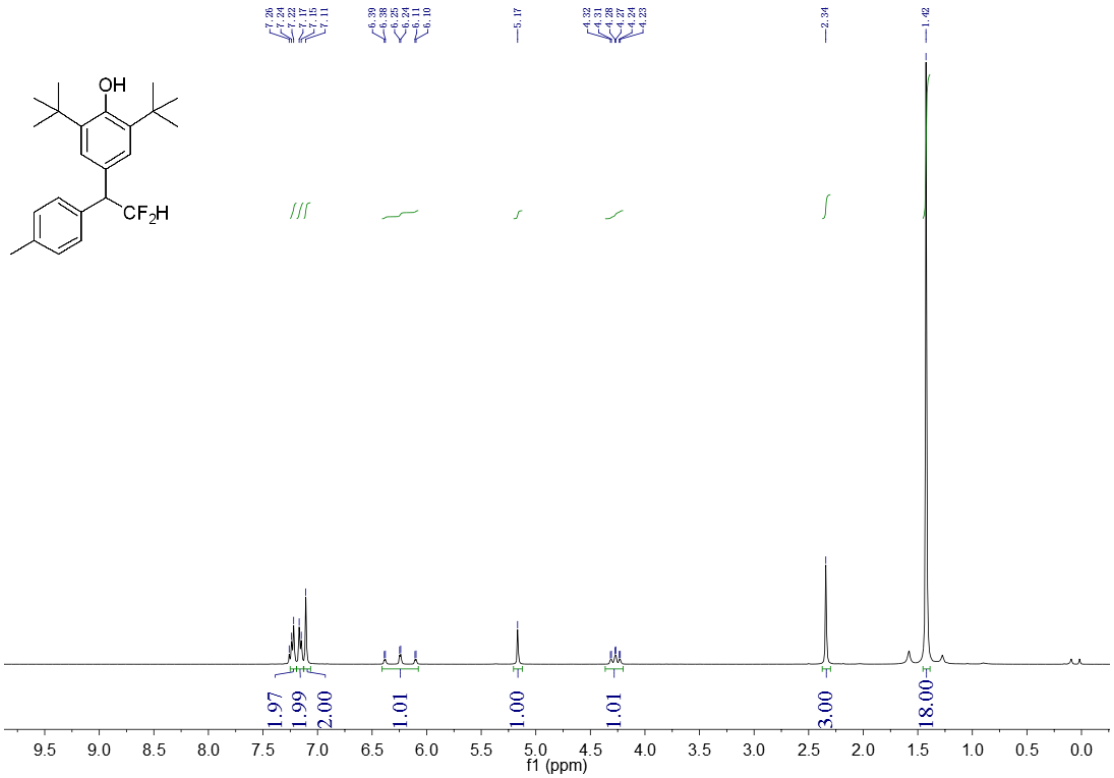

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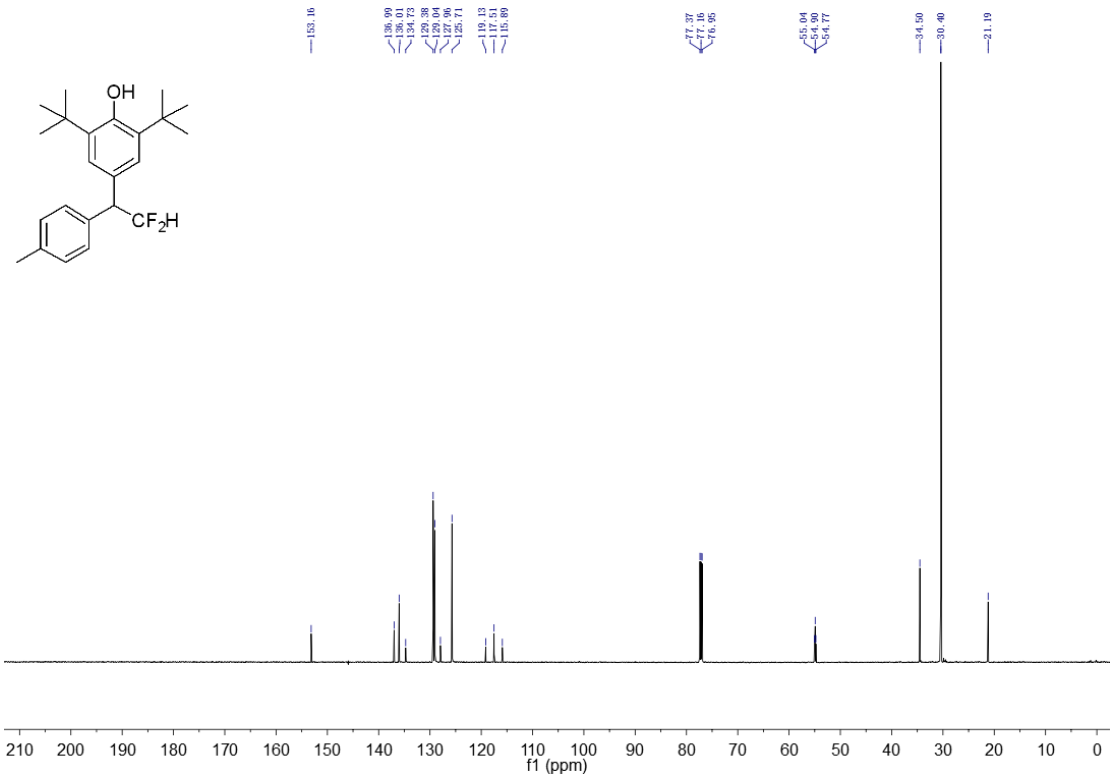

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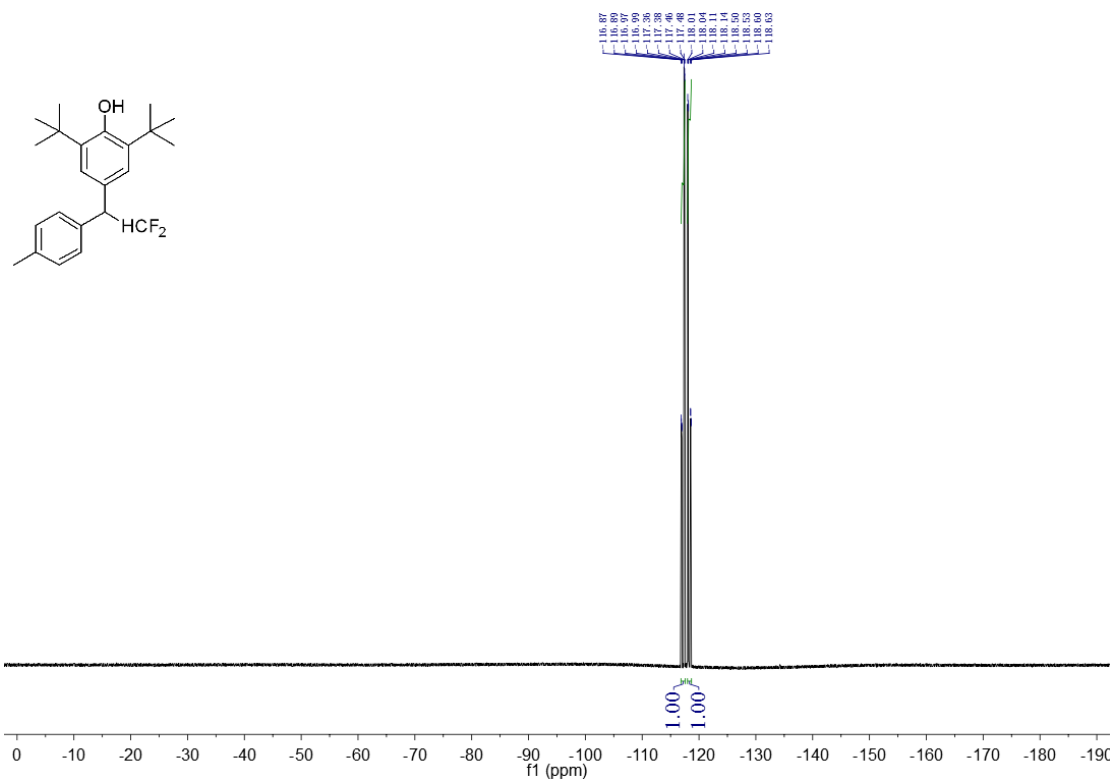

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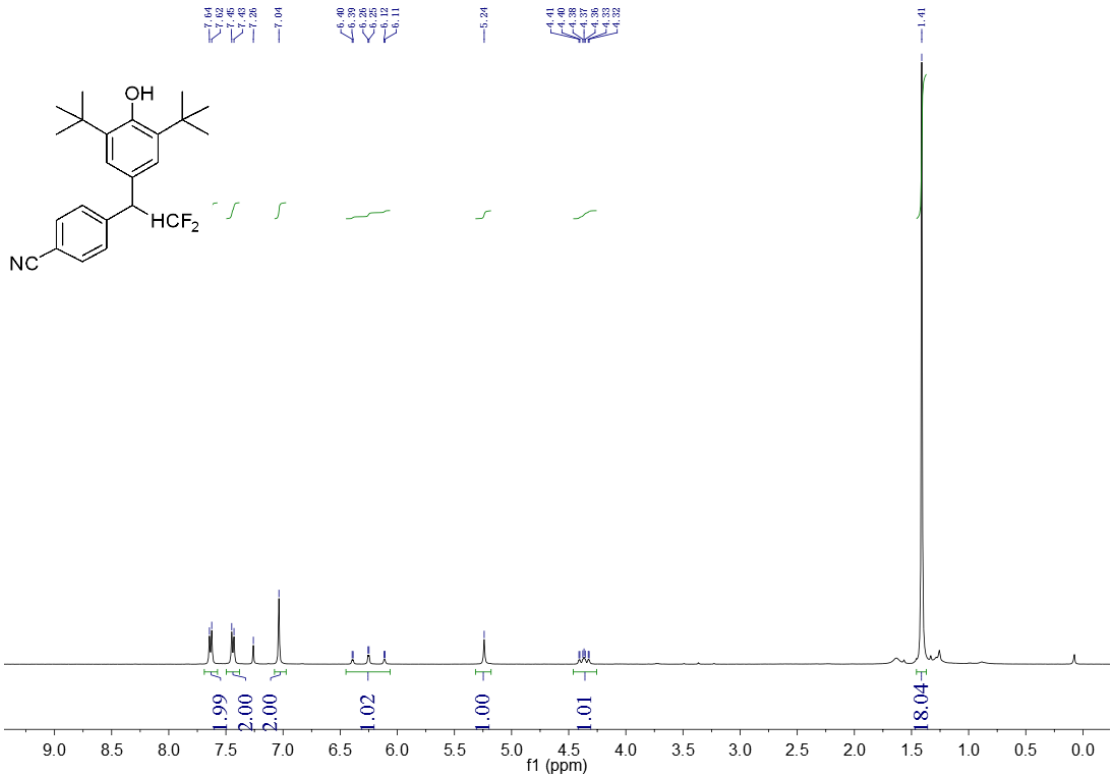

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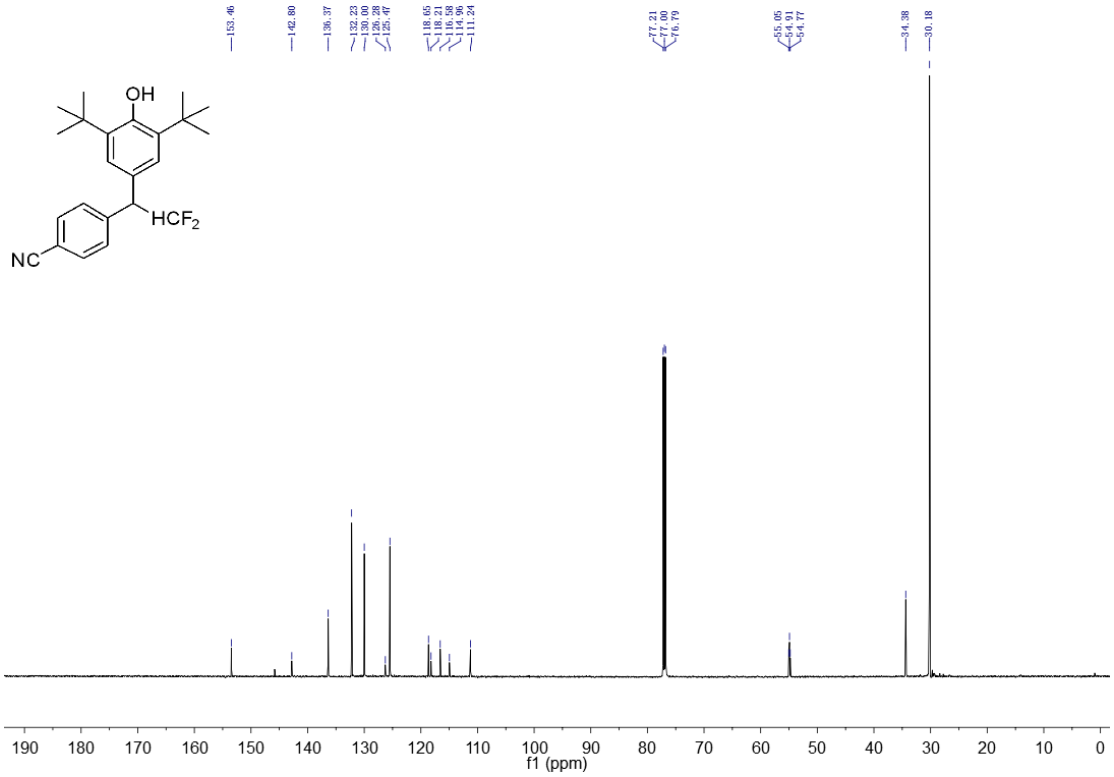

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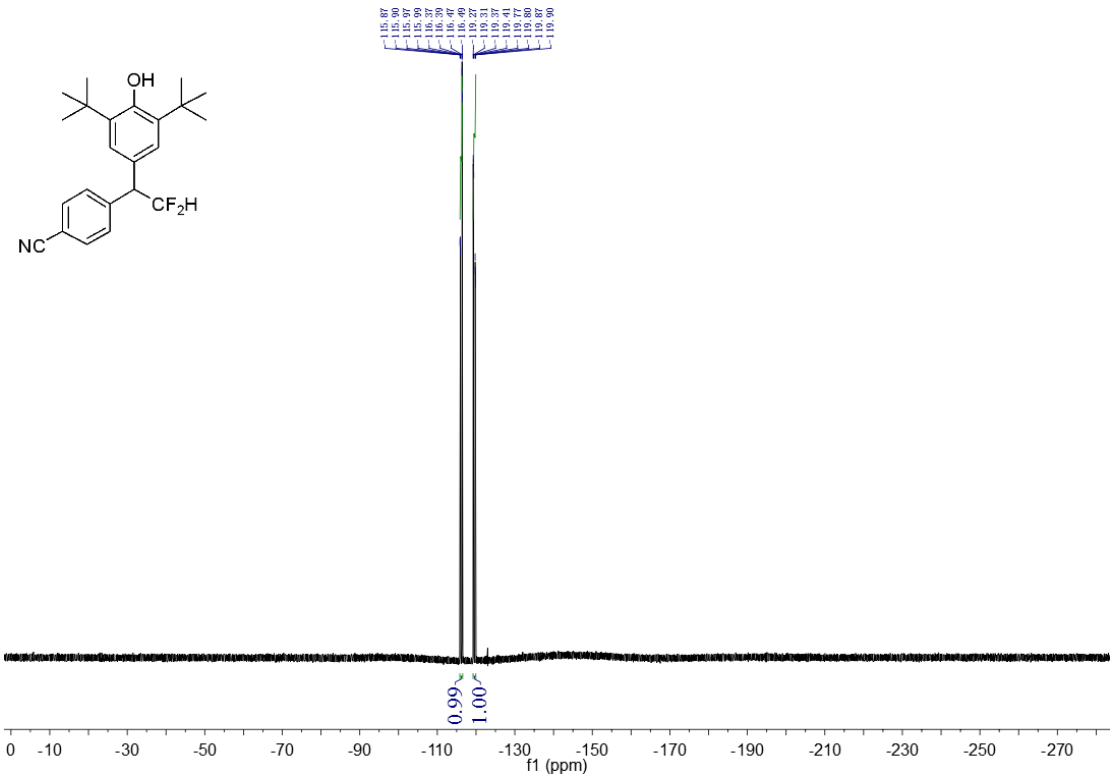

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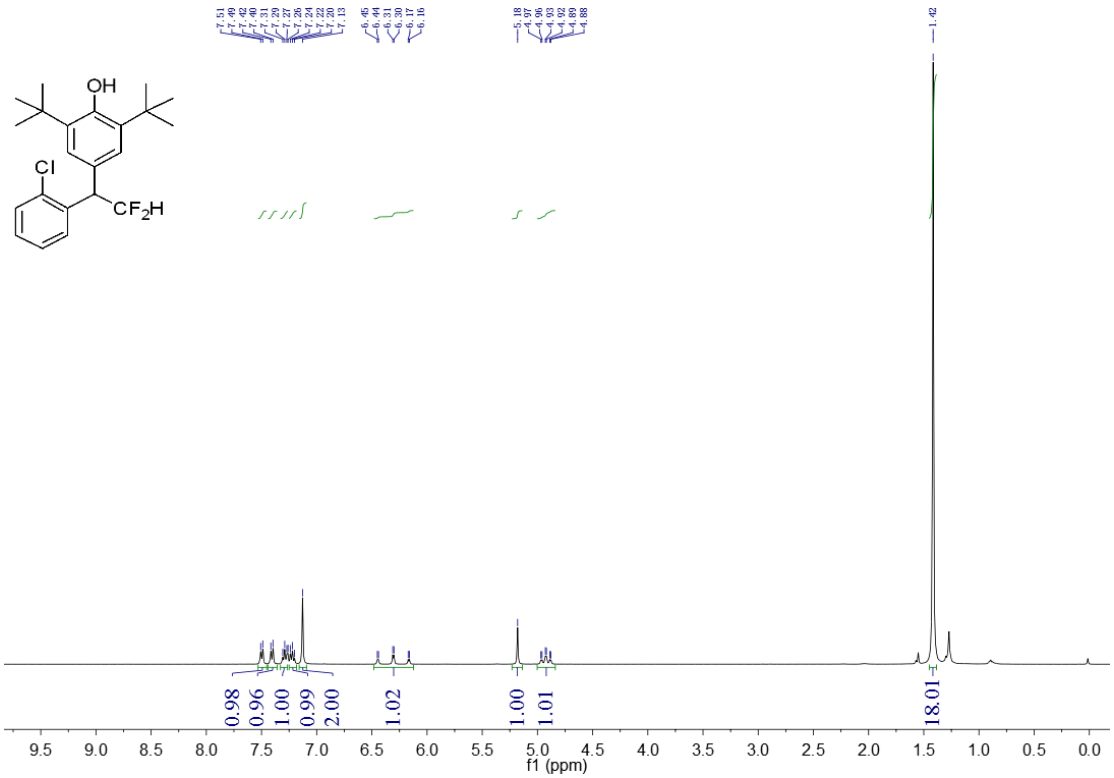

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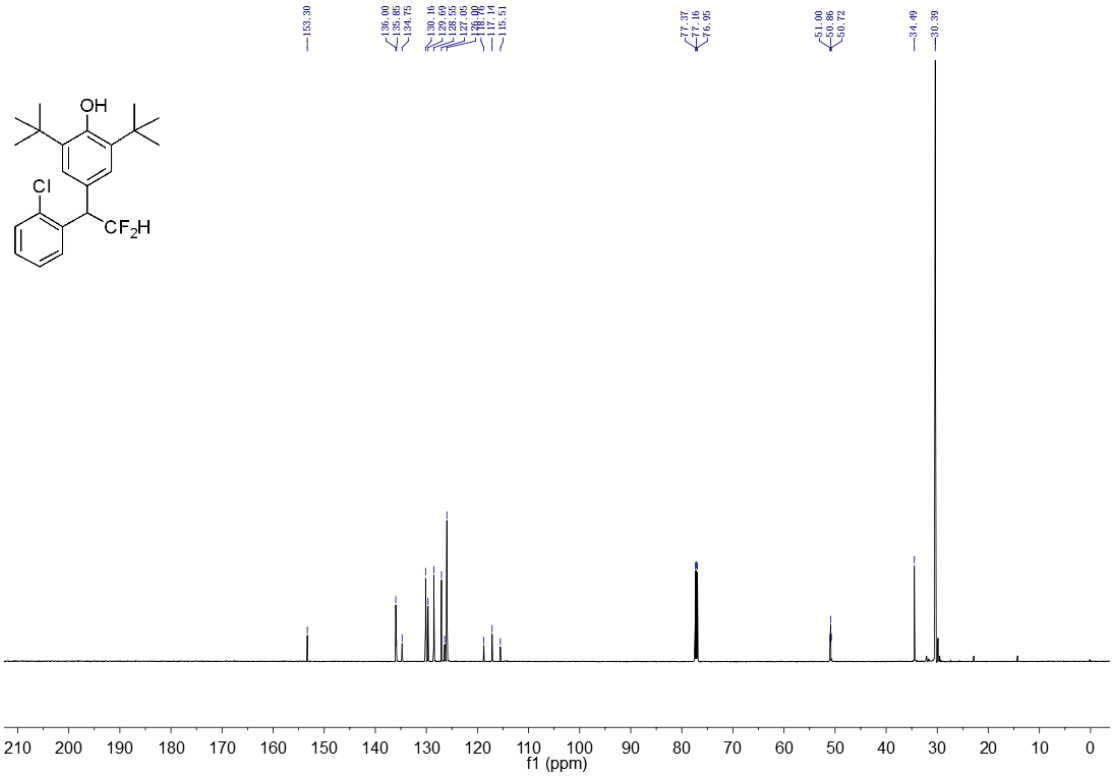
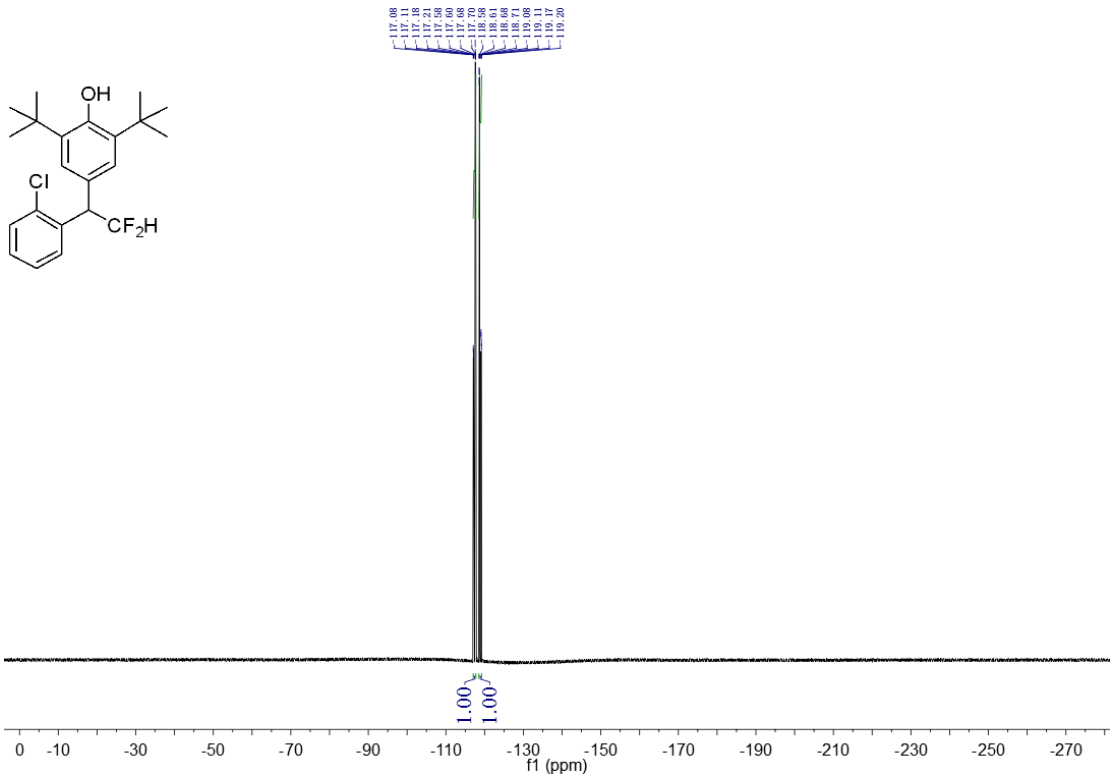
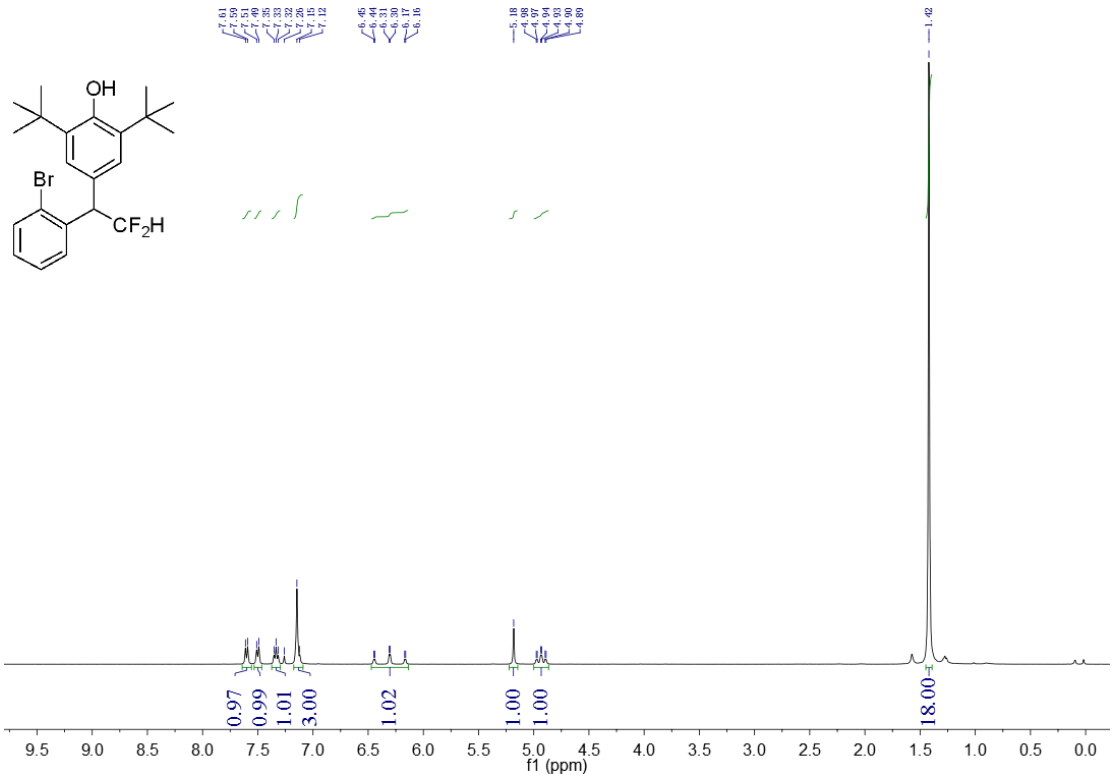


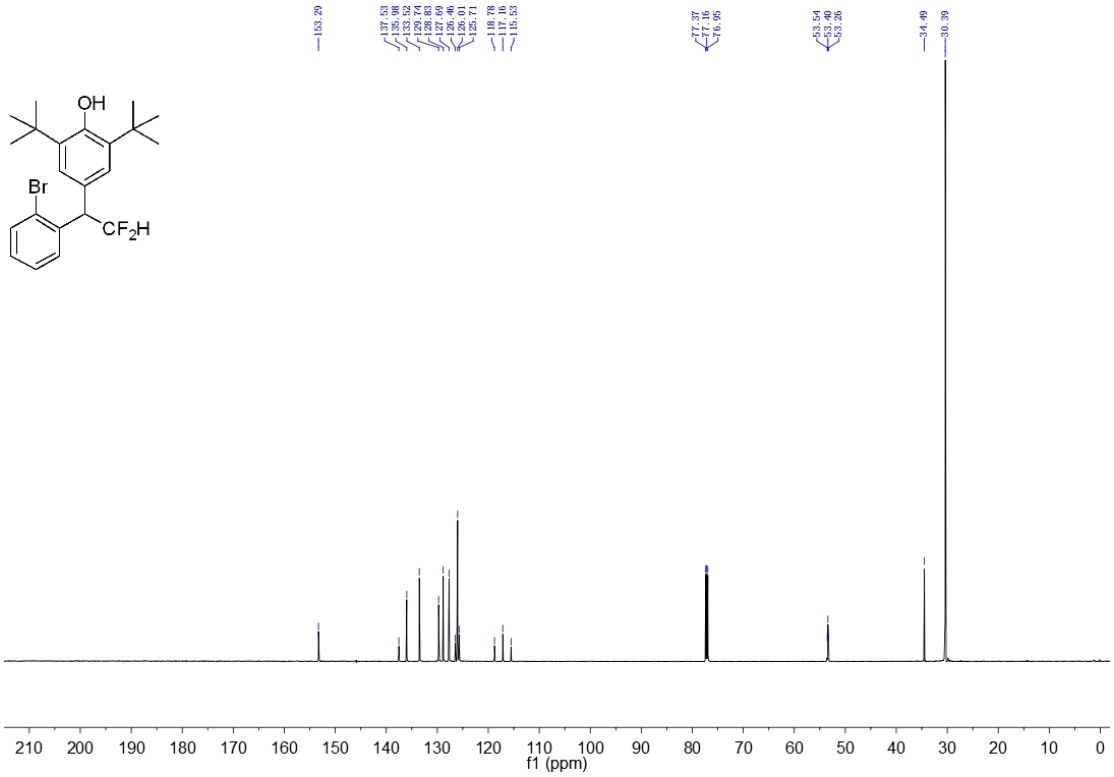
^{19}F NMR of **3f**



^{1}H NMR of **3g**



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



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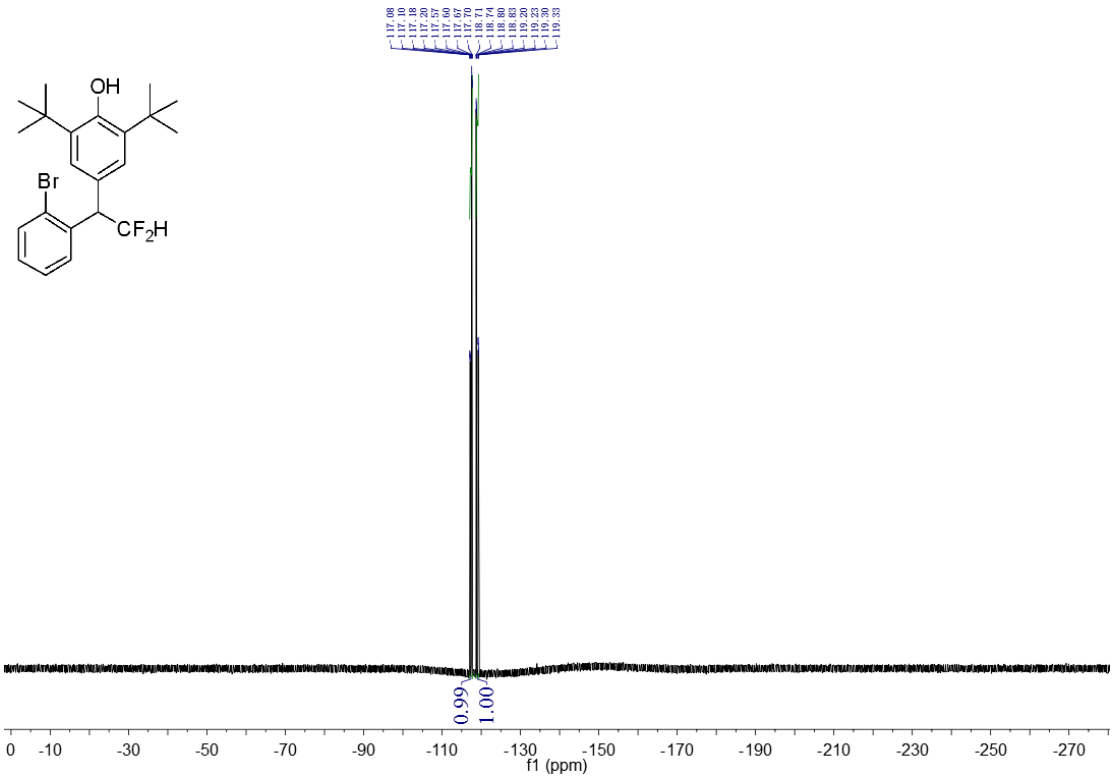
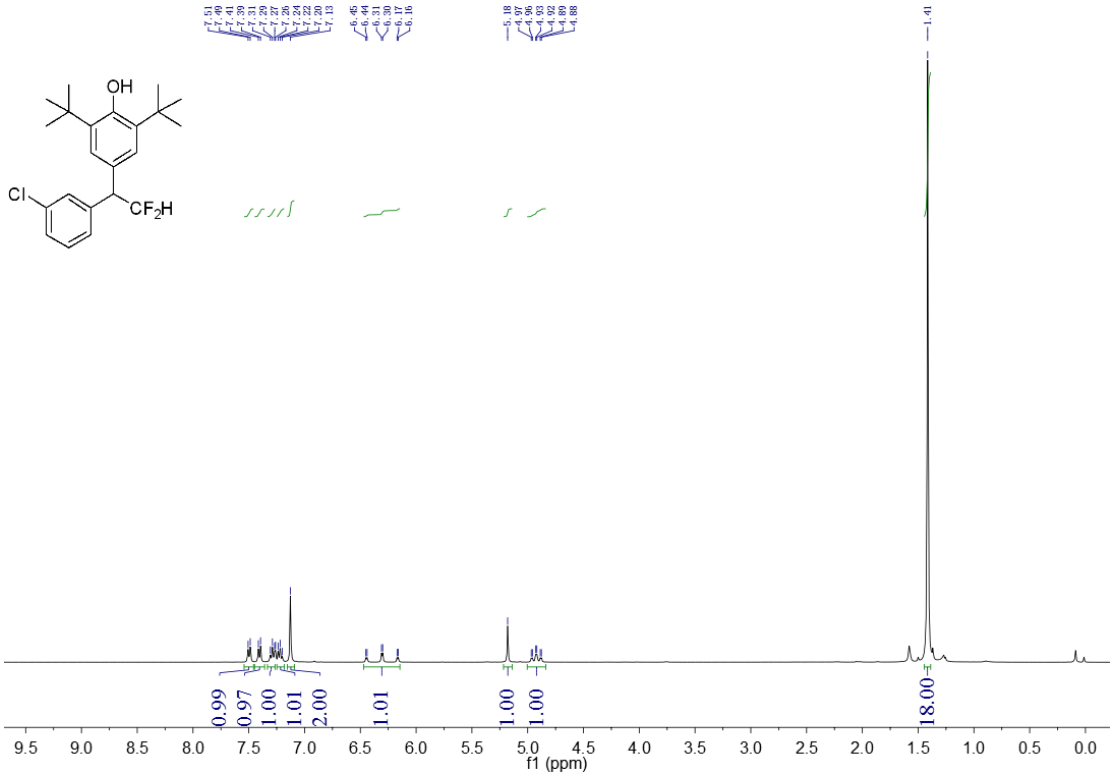


^{1}H NMR of **3h**



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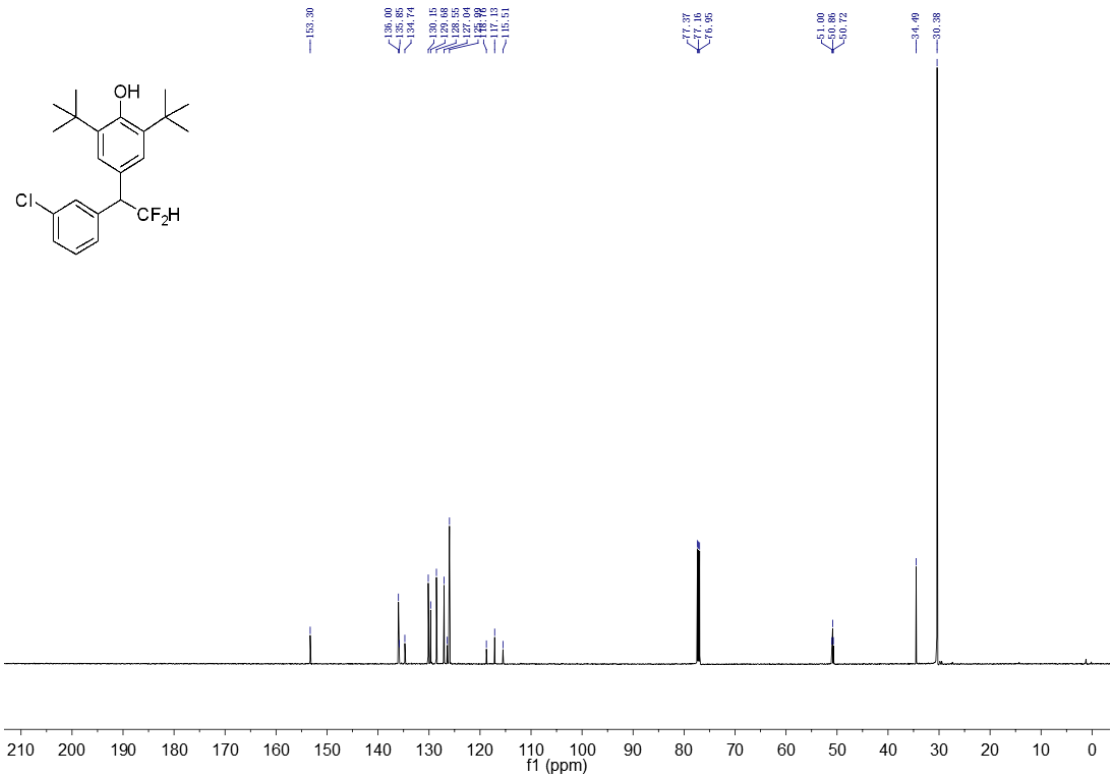

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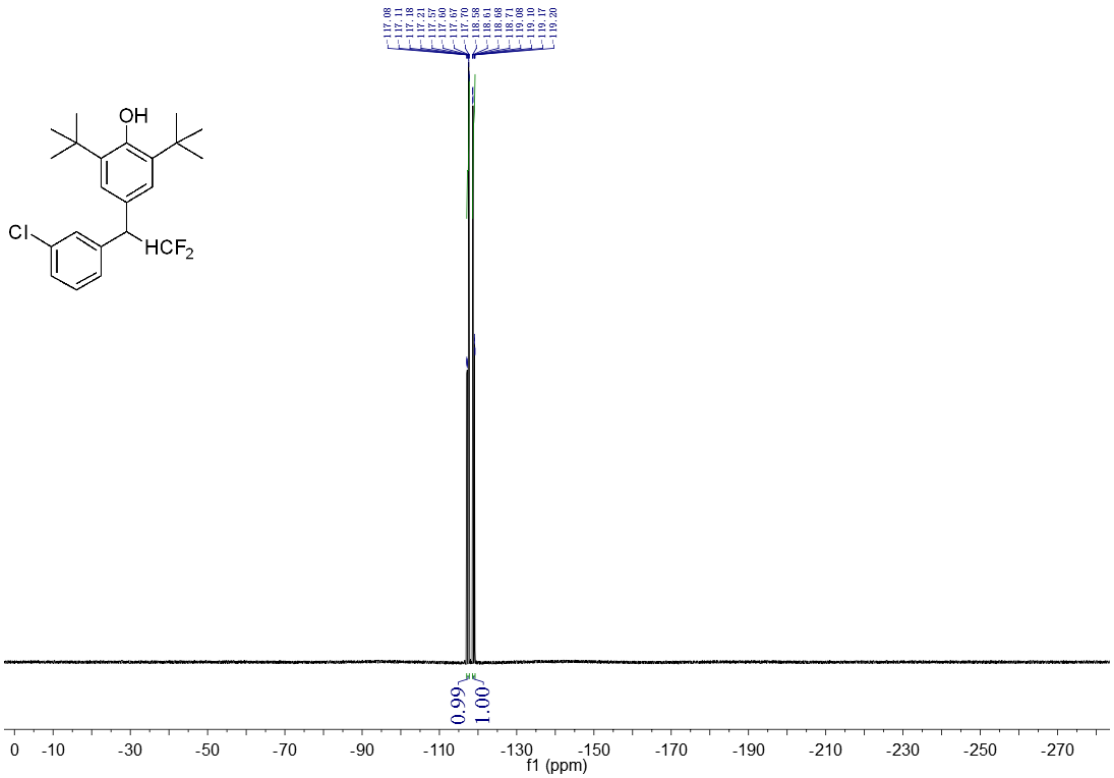
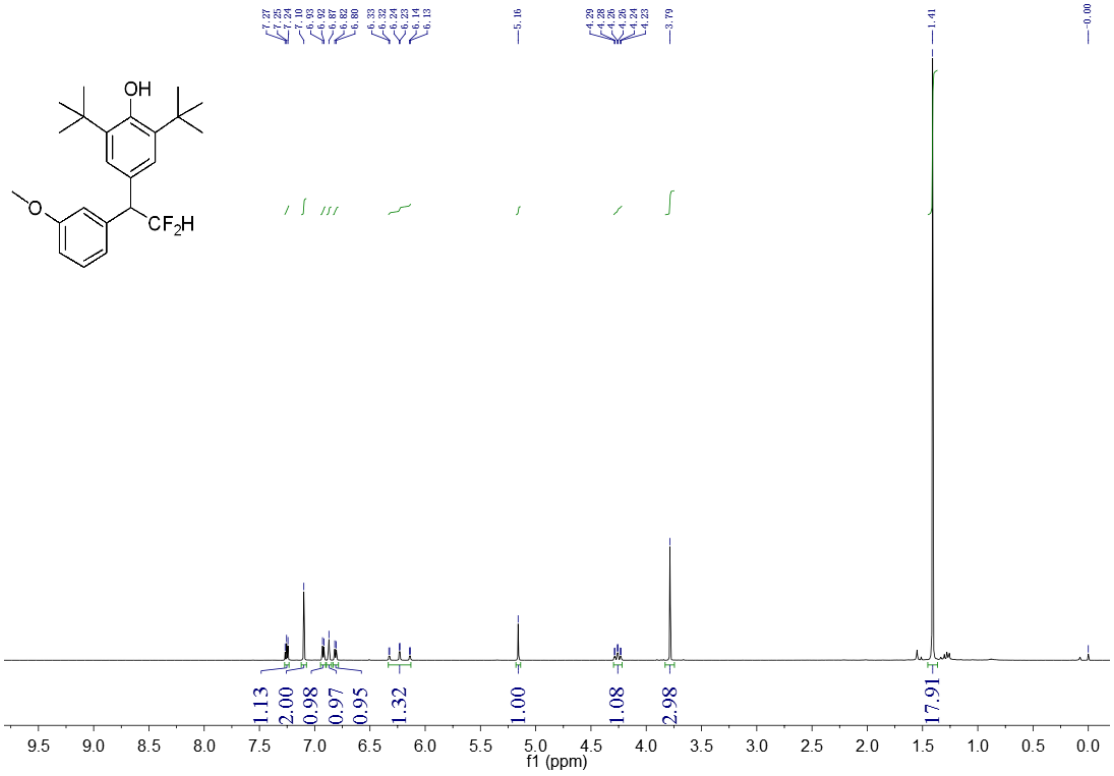
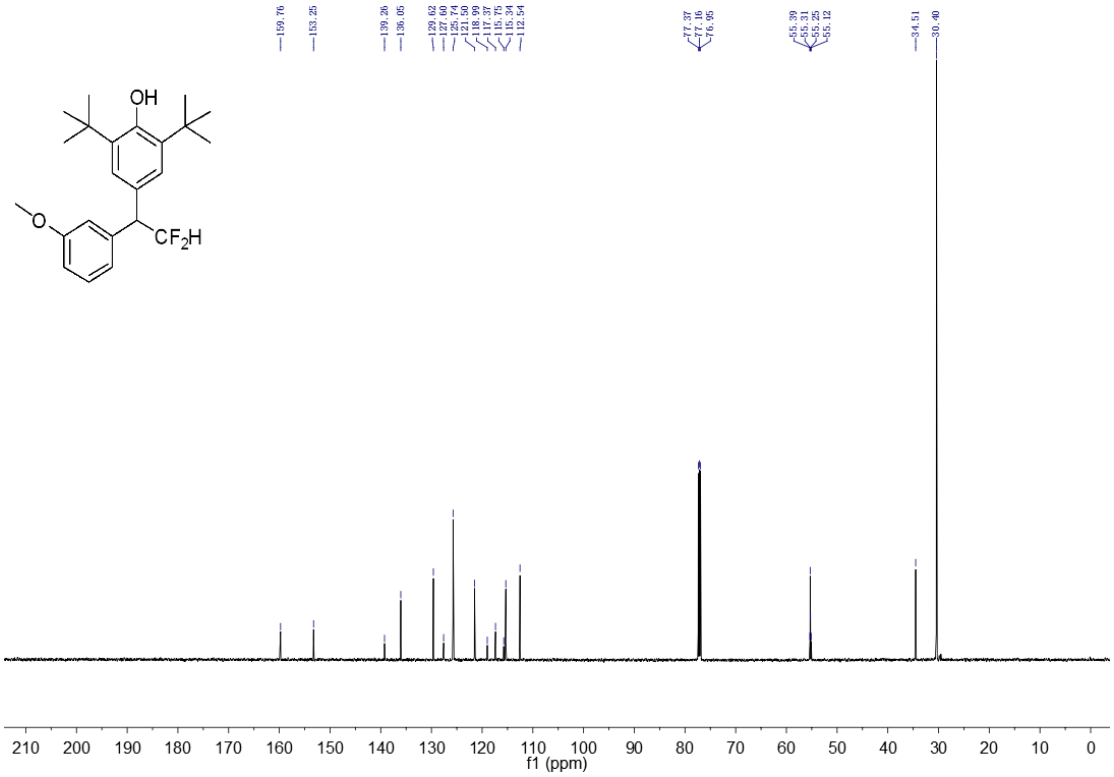


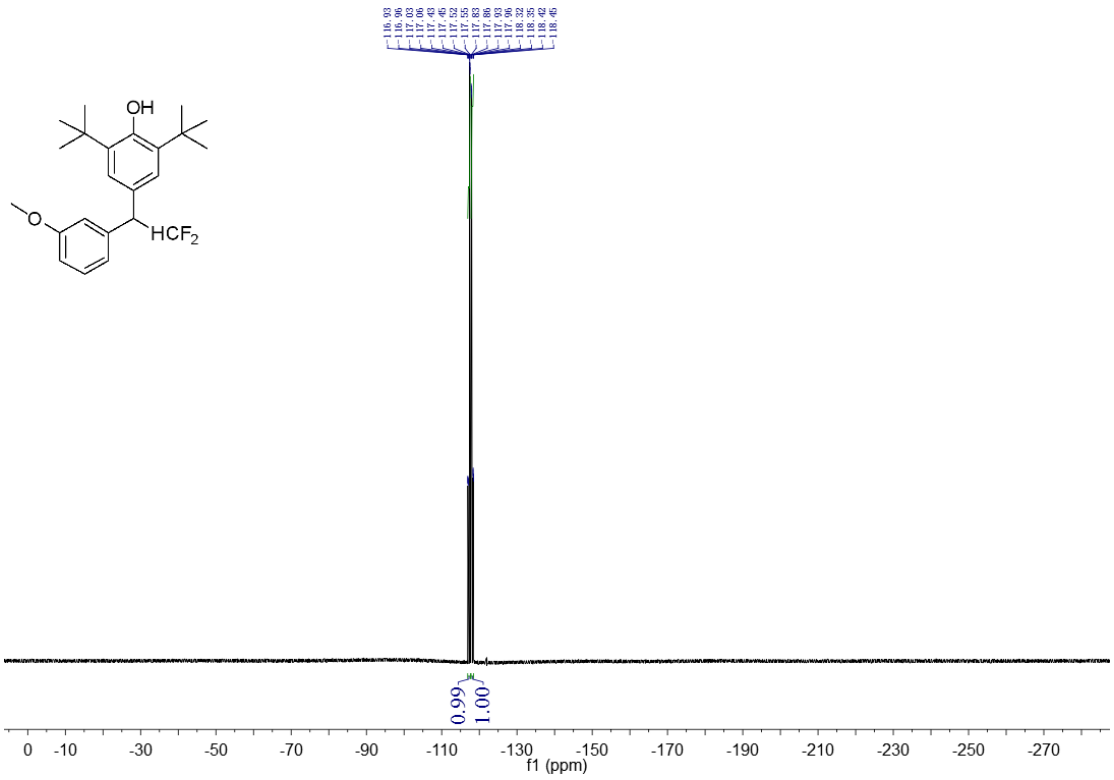
^{1}H NMR of **3i**



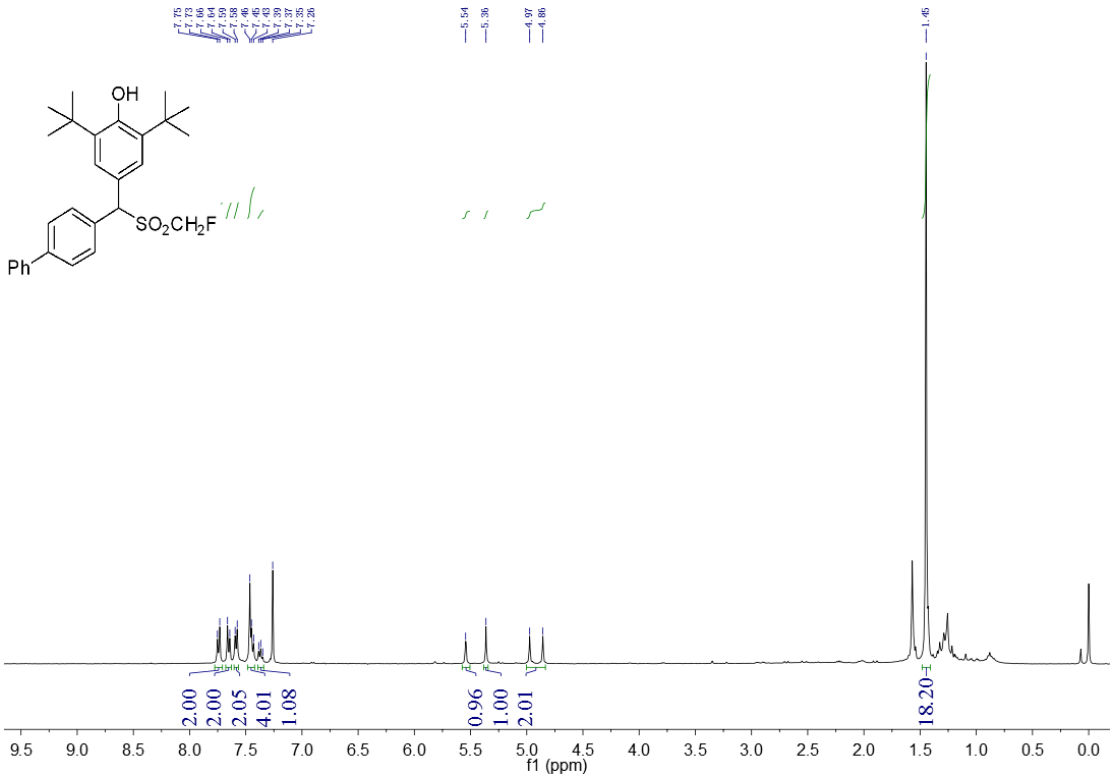
^{13}C NMR of **3i**



^{19}F NMR of **3i**



^{1}H NMR of **4a**



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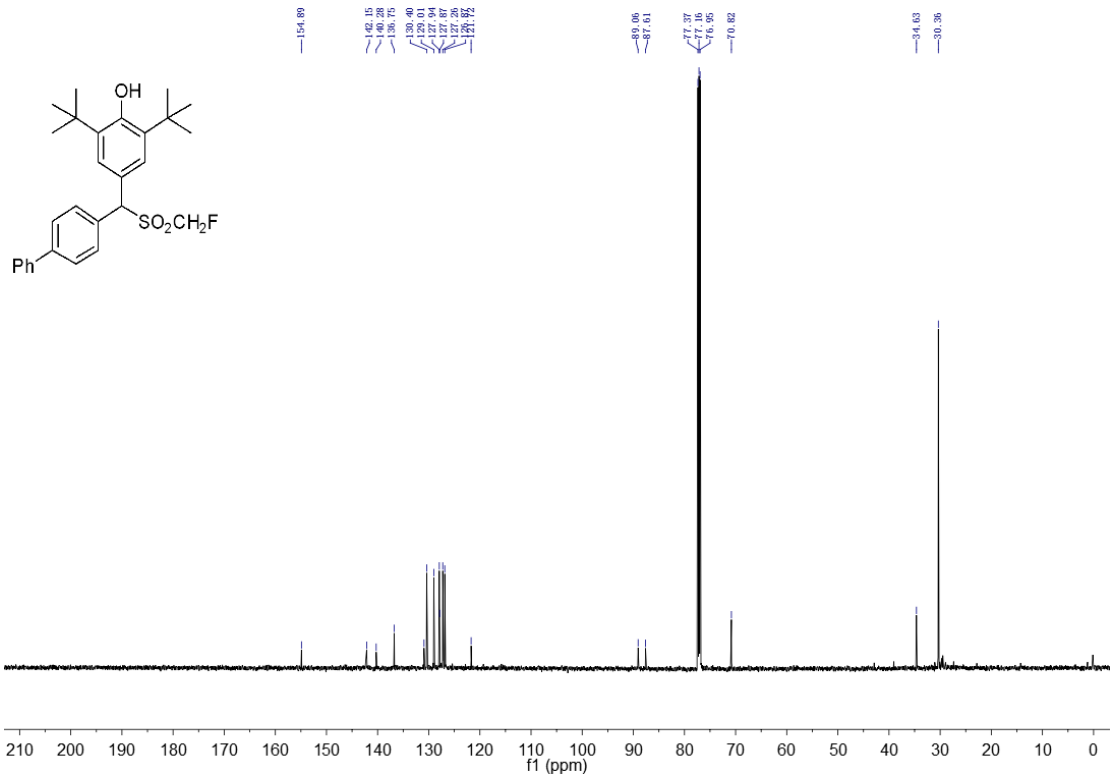
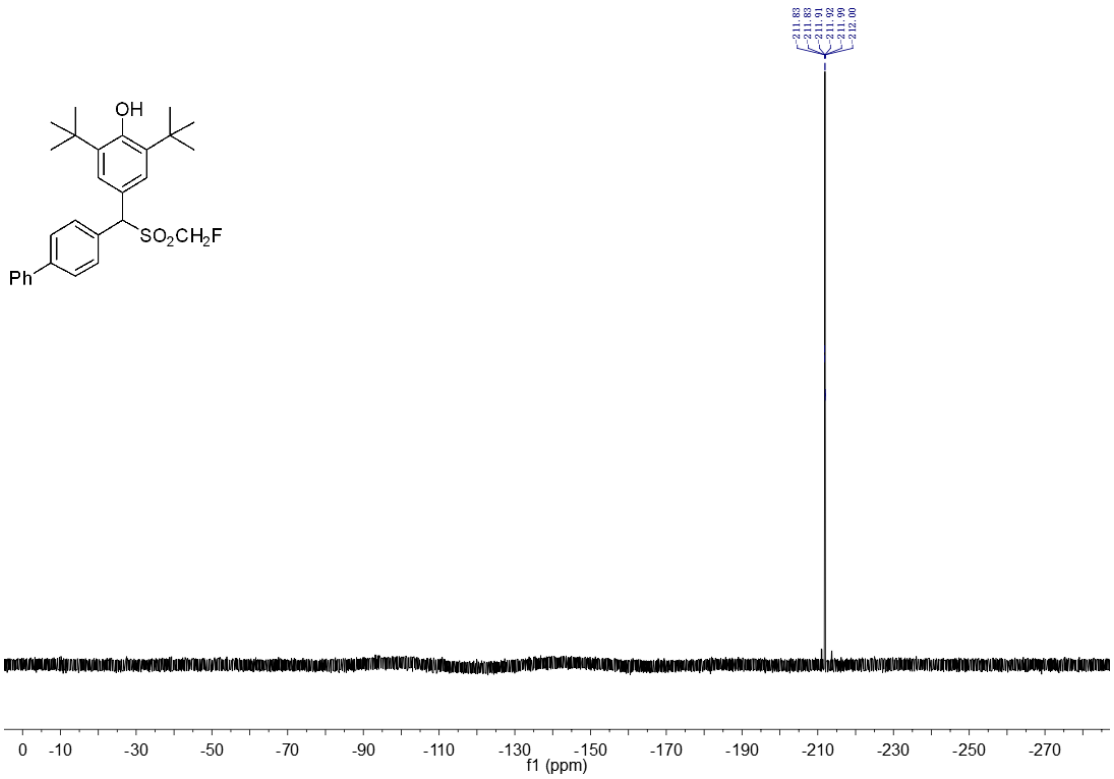
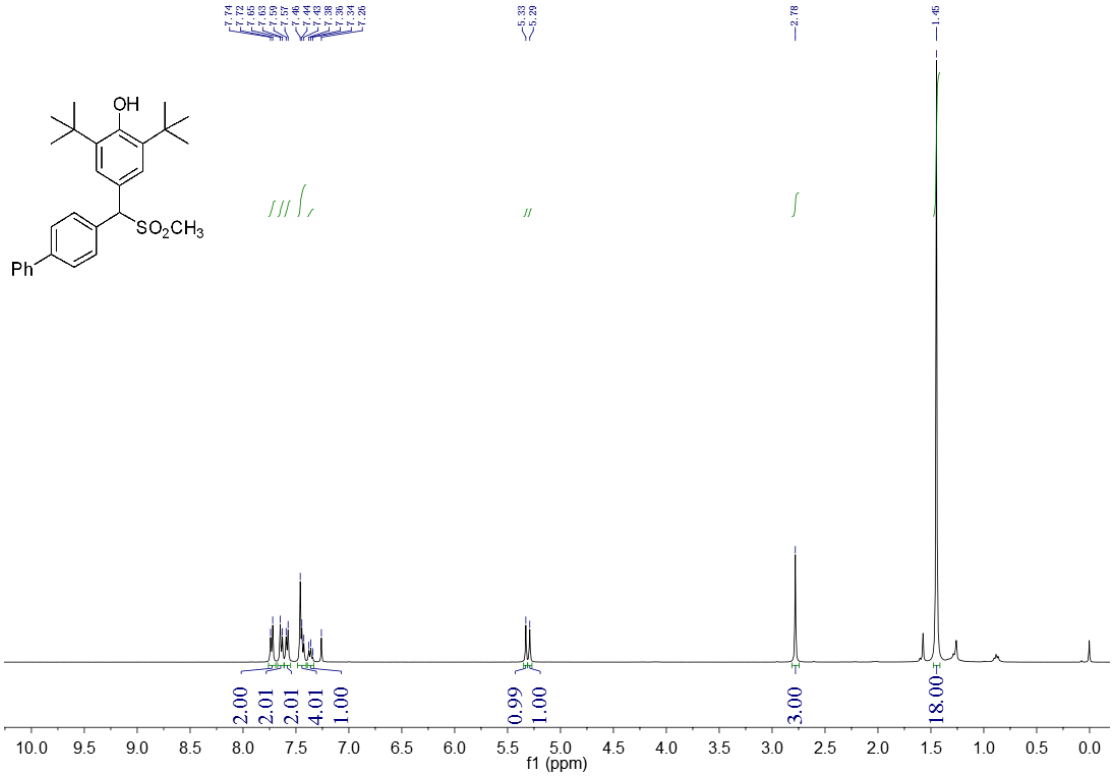


^{19}F NMR of **4a**



^{1}H NMR of **4b**



^{13}C NMR of **4b**