Supporting Information

Ligand-Controlled Regioselective and Chemodivergent Defluorinative Functionalization of *gem*-Difluorocyclopropanes with Simple Ketones

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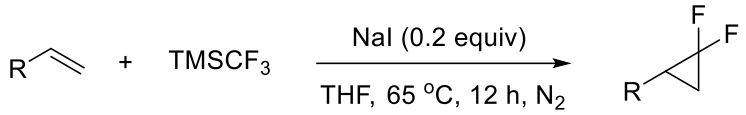
Contents

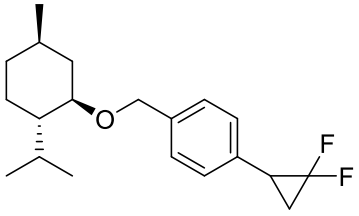
1. General information

^{1}H NMR spectra were recorded on Bruker 400 or 600 MHz spectrometer and the chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at Bruker 100 or 150 MHz and referenced to the internal solvent signals. ^{19}F NMR spectra were obtained at Bruker 376 or 565 MHz. $CDCl_3$ was used as the NMR solvent. High-resolution mass spectra (HRMS) were acquired on Thermo Q-Exactive instrument (quadrupole mass analyzer) using electrospray ionization mode (ESI). Flash column chromatography was performed over silica gel 200-300. All other reagents were purchased from Alfa, Aldrich, TCI, Energy, Innochem and Sinocompound Catalysts used without further purification. The Pd-PEPPSI catalyst were synthesized according to the reported literature.[1]

2. Synthesis of *gem*-difluorocyclopropane 1

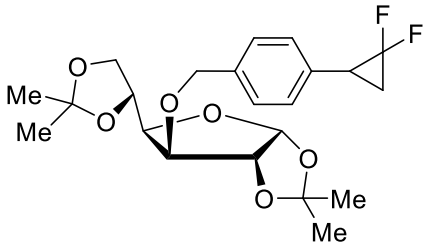


The *gem*-difluorocyclopropanes were prepared according to the known procedure.[2] A flame-dried reaction tube (50 cm^3) equipped with a magnetic stir bar was charged with anhydrous NaI (0.2 equiv), dry THF (10.0 mL), $TMSCF_3$ (2.5 equiv) and corresponding alkenes (4.0 mmol) under nitrogen atmosphere. The reaction tube was sealed with Teflon septum and stirred at 65 °C for 12 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of celite, and then evaporated to dryness under reduce pressure. The crude mixture was extracted with ethyl acetate (20.0 mL), washed with saturated $Na_2S_2O_3$ (10.0 mL) and brine (10.0 mL). The organic layer was dried over Na_2SO_4, filtered and concentrated, the residue was purified by column chromatography on silica gel to give the pure corresponding *gem*-difluorocyclopropanes. Characterization of new *gem*-difluorocyclopropanes **1n**, **1p-1t** are listed below.

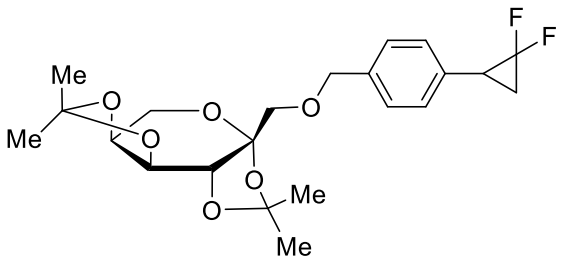


1-(2,2-Difluorocyclopropyl)-4-((((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)benzene (1n).

(petroleum ether: ethyl acetate = 50:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.64 (d, J = 11.4 Hz, 1H), 4.37 (d, J = 11.4 Hz, 1H), 3.16 (dt, J = 10.6, 4.0 Hz, 1H), 2.77-2.71 (m, 1H), 2.30-2.26 (m, 1H), 2.20-2.16 (m, 1H), 1.83-1.77 (m, 1H), 1.67-1.58 (m, 3H), 1.39-1.32 (m, 1H), 1.31-1.25 (m, 1H), 0.98-0.82 (m, 9H), 0.70 (dd, J = 7.0, 1.8 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.1, 132.7, 128.0, 127.9, 112.6 (dd, $J_{C\text{-}F}$ = 284.4, 284.2 Hz), 78.8, 70.0, 48.3, 40.3, 34.5, 31.6, 27.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 25.5, 23.2, 22.4, 21.0, 17.0 (d, $J_{C\text{-}F}$ = 11.4 Hz), 16.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.9 (dtd, J = 153.9, 12.8, 3.9 Hz, 1F), -142.3 (ddd, J = 153.9, 12.8, 4.8 Hz, 1F). HRMS (APCI) calcd for $C_{20}H_{29}F_2O$ [M + H $^+$], 323.2181; found: 323.2178.

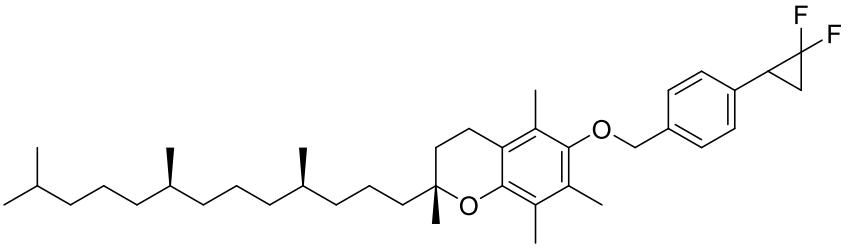


(3aR,5R)-6-((4-(2,2-Difluorocyclopropyl)benzyl)oxy)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxole (1p). (petroleum ether: ethyl acetate = 4:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 5.89 (d, J = 3.6 Hz, 1H), 4.67 (d, J = 11.8 Hz, 1H), 4.62 (d, J = 11.8 Hz, 1H), 4.58 (d, J = 3.6 Hz, 1H), 4.37-4.34 (m, 1H), 4.15-4.10 (m, 2H), 4.01-3.99 (m, 2H), 2.77-2.72 (m, 1H), 1.85-1.79 (m, 1H), 1.65-1.59 (m, 1H), 1.49 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 136.6, 133.3, 128.1, 127.8, 112.5 (dd, $J_{C\text{-}F}$ = 284.4, 284.2 Hz), 117.8, 109.0, 105.3, 82.6, 81.7, 81.3, 72.4, 72.0, 67.4, 26.9 (t, $J_{C\text{-}F}$ = 11.4 Hz), 26.8, 26.7, 26.2, 25.4, 17.0 (t, $J_{C\text{-}F}$ = 11.4 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.9 (dtd, J = 154.7, 12.6, 3.9 Hz, 1F), -142.3 (ddd, J = 154.7, 12.6, 5.0 Hz, 1F). HRMS (ESI) calcd for $C_{22}H_{28}F_2NaO_6$ [M + Na $^+$], 449.1746; found: 449.1745.

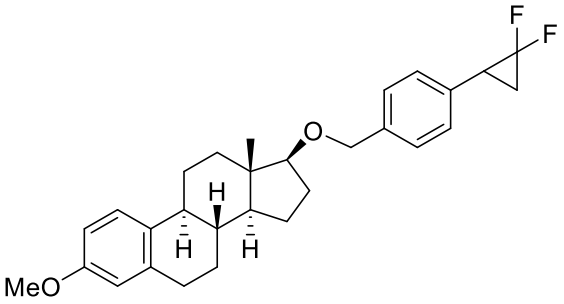


(3aR,5aS,8aS,8bR)-3a-(((4-(2,2-Difluorocyclopropyl)benzyl)oxy)methyl)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (1q). (petroleum ether: ethyl acetate = 4:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.66 (d, J = 12.2 Hz, 1H), 4.59 (dd, J = 8.0, 2.6 Hz, 1H), 4.56 (d, J = 12.2 Hz, 1H), 4.42 (d, J = 2.0 Hz, 1H), 4.23 (dd, J = 8.0, 0.8 Hz, 1H), 3.91 (dd, J = 12.8, 1.8 Hz,

1H), 3.73 (d, J = 12.8 Hz, 1H), 3.62 (d, J = 10.6 Hz, 1H), 3.58 (d, J = 10.6 Hz, 1H), 2.76-2.71 (m, 1H), 1.84-1.78 (m, 1H), 1.63-1.60 (m, 1H), 1.55 (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.1, 132.9, 127.9, 127.7, 112.5 (dd, $J_{C\text{-}F}$ = 284.4, 284.2 Hz), 108.9, 108.5, 102.7, 73.3, 71.6, 71.0, 70.2, 70.1, 61.0, 27.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 26.6, 25.8, 25.4, 24.0, 17.0 (t, $J_{C\text{-}F}$ = 11.4 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.9 (dtd, J = 154.7, 12.6, 3.9 Hz, 1F), -142.3 (ddd, J = 154.7, 12.6, 5.0 Hz, 1F). HRMS (ESI) calcd for $C_{22}H_{28}F_2NaO_6$ [M + Na^+], 449.1746; found: 449.1741.

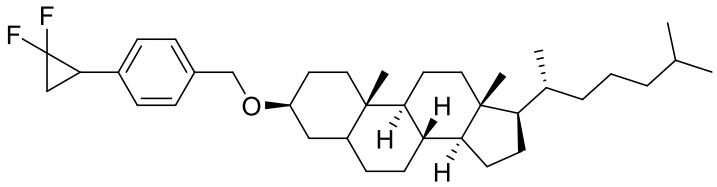


(2R)-6-((4-(2,2-Difluorocyclopropyl)benzyl)oxy)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chromane (1r). (petroleum ether: ethyl acetate = 20:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 7.8 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 4.67 (s, 2H), 2.79-2.73 (m, 1H), 2.58 (d, J = 6.6 Hz, 2H), 2.21 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 1.84-1.74 (m, 3H), 1.65-1.49 (m, 4H), 1.39-1.06 (m, 20H), 0.87-0.83 (m, 13H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.0, 147.9, 137.0, 133.1, 128.1, 127.9, 127.8, 125.9, 122.9, 117.6, 112.5 (dd, $J_{C\text{-}F}$ = 284.4, 284.2 Hz), 74.8, 74.2, 40.0, 39.4, 37.6, 37.5, 37.4, 37.3, 32.8, 32.7, 31.3, 31.2, 28.0, 27.0 (t, $J_{C\text{-}F}$ = 11.2 Hz), 24.8, 24.4, 23.9, 22.7, 22.6, 21.0, 20.7, 19.7, 19.6, 17.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 12.8, 12.0, 11.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.8 (dtd, J = 154.7, 12.6, 3.9 Hz, 1F), -142.2 (ddd, J = 154.7, 12.6, 5.0 Hz, 1F). HRMS (APCI) calcd for $C_{39}H_{59}F_2O_2$ [M + H^+], 597.4478; found: 597.4480.



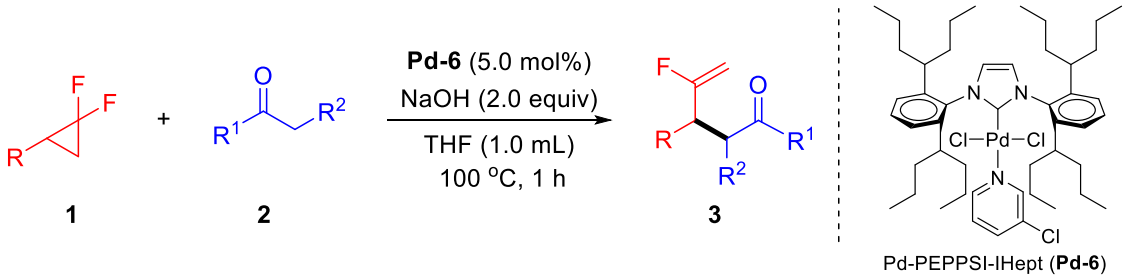
(8R,9S,13S,14S,17S)-17-((4-(2,2-Difluorocyclopropyl)benzyl)oxy)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene (1s). (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.31 (m, 2H), 7.20-7.19 (m, 3H), 6.71 (dd, J = 8.6, 2.4 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 4.55 (s, 2H), 3.77 (s, 3H), 3.49 (t, J = 8.4 Hz, 1H), 2.89-2.80 (m, 2H), 2.77-2.72 (m, 1H), 2.30-2.27 (m, 1H), 2.19-2.15 (m, 1H), 2.09-2.01 (m, 2H), 1.88-1.78 (m, 2H), 1.70-1.65 (m, 1H), 1.64-1.60 (m, 2H), 1.55-1.48 (m, 1H),

1.47-1.41 (m, 1H), 1.40-1.29 (m, 3H), 1.21-1.16 (m, 1H), 0.86 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.4, 138.3, 138.0, 132.7, 127.9, 127.4, 126.3, 113.8, 112.6 (dd, $J_{C\text{-}F}$ = 284.4, 284.2 Hz), 111.5, 88.4, 71.3, 55.2, 50.2, 43.9, 43.4, 38.6, 37.9, 29.8, 28.0, 27.2, 27.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 26.4, 23.1, 17.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 11.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.4 (dtd, J = 154.7, 12.6, 3.9 Hz, 1F), -142.0 (ddd, J = 154.7, 12.6, 5.0 Hz, 1F). HRMS (APCI) calcd for $C_{29}H_{35}F_2O_2$ [M + H $^+$], 453.2600; found: 453.2597.



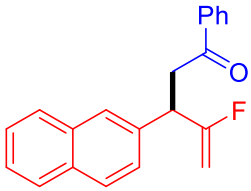
(3S,8R,9S,10S,13R,14S,17R)-3-((4-(2,2-Difluorocyclopropyl)benzyl)oxy)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthrene (1t). (petroleum ether: ethyl acetate = 50:1,R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 4.54 (d, J = 12.0 Hz, 1H), 4.62 (d, J = 12.0 Hz, 1H), 3.34-3.29 (m, 1H), 2.76-2.71 (m, 1H), 1.97-1.95 (m, 1H), 1.91-1.88 (m, 1H), 1.83-1.77 (m, 2H), 1.74-1.59 (m, 4H), 1.54-1.40 (m, 4H), 1.37-1.20 (m, 9H), 1.14-0.94 (m, 9H), 0.92-0.80 (m, 14H), 0.64-0.58 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 132.7, 128.0, 127.7, 112.6 (dd, $J_{C\text{-}F}$ = 284.4, 284.2 Hz), 78.1, 69.4, 56.5, 56.3, 54.4, 44.8, 42.6, 40.0, 39.5, 37.0, 36.2, 35.8, 35.5, 34.8, 32.1, 28.9, 28.3, 28.2, 28.0, 27.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 17.0 (t, $J_{C\text{-}F}$ = 11.4 Hz), 12.3, 12.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -125.9 (dtd, J = 154.7, 12.6, 3.9 Hz, 1F), -142.3 (ddd, J = 154.7, 12.6, 5.0 Hz, 1F). HRMS (APCI) calcd for $C_{37}H_{56}F_2NaO$ [M + H $^+$], 577.4191; found: 577.4186.

3. General procedure and characterization data for product 3

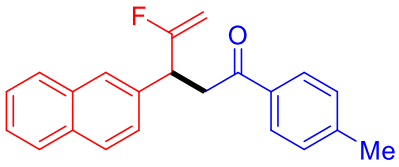


A flame-dried reaction tube (10 cm^3) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IHept (4.5 mg, 5 mol%). The reaction tube was transferred to the glovebox and charged with **1** (0.1 mmol), **2** (0.2 mmol), NaOH (8.0 mg) and THF (1.0 mL). After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 1 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (3.0 mL). The crude mixture was analyzed by GC-MS.

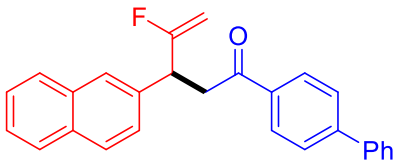
The solvent was evaporated *in vacuo* to give the crude product. NMR yield was determined by ^{1}H NMR using CH_2Br_2 as an internal standard. The residue was purified by column chromotography on silica gel to give the pure product **3**. **Note**: Use of the glovebox is not necessary. The reaction can be successfully performed with standard Schlenk line procedure.



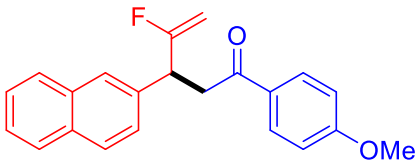
4-Fluoro-3-(naphthalen-2-yl)-1-phenylpent-4-en-1-one (3a). (29.0 mg, 95%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.94 (m, 2H), 7.81-7.79 (m, 4H), 7.55-7.53 (m, 1H), 7.49-7.46 (m, 1H), 7.45-7.42 (m, 4H), 4.68 (dd, J = 17.6, 3.2 Hz, 1H), 4.51 (dt, J = 16.6, 7.0 Hz, 1H), 4.42 (dd, J = 49.8, 3.2 Hz, 1H), 3.70 (dd, J = 17.4, 7.0 Hz, 1H), 3.55 (dd, J = 17.4, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 166.8 (d, $J_{C\text{-}F}$ = 259.8 Hz), 137.3, 136.6, 133.4, 133.3, 132.6, 128.6, 128.4, 128.0, 127.8, 127.6, 126.6, 126.1, 126.0, 125.8, 91.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.5 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.8 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.9 (1F). HRMS (APCI) calcd for $C_{21}H_{18}FO$ [M + H $^+$], 305.1336; found: 305.1334.



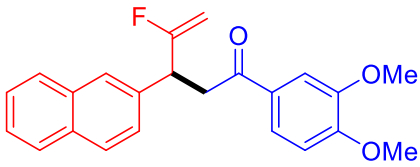
4-Fluoro-3-(naphthalen-2-yl)-1-(p-tolyl)pent-4-en-1-one (3b). (29.6 mg, 93%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 8.0 Hz, 2H), 7.81-7.78 (m, 4H), 7.48 (d, J = 8.4 Hz, 1H), 7.46-7.41 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 4.67 (dd, J = 17.5, 3.0 Hz, 1H), 4.50 (dt, J = 16.4, 7.0 Hz, 1H), 4.42 (dd, J = 49.9, 3.0 Hz, 1H), 3.66 (dd, J = 17.2, 7.0 Hz, 1H), 3.51 (dd, J = 17.2, 7.0 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 167.0 (d, $J_{C\text{-}F}$ = 260.0 Hz), 144.1, 137.4, 134.2, 133.4, 132.6, 129.3, 128.4, 128.2, 127.8, 127.6, 126.6, 126.1, 126.0, 125.8, 91.2 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.5 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.2 (d, $J_{C\text{-}F}$ = 2.8 Hz), 21.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (1F). HRMS (APCI) calcd for $C_{22}H_{20}FO$ [M + H $^+$], 319.1493; found: 319.1490.



1-([1,1'-Biphenyl]-4-yl)-4-fluoro-3-(naphthalen-2-yl)pent-4-en-1-one (3c). (33.4 mg, 88%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.82-7.79 (m, 4H), 7.65 (d, J = 8.4 Hz, 2H), 7.59 (d, J = 7.4 Hz, 2H), 7.50 (d, J = 7.8 Hz, 1H), 7.46-7.41 (m, 4H), 7.38 (t, J = 7.4 Hz, 1H), 4.70 (dd, J = 17.5, 3.0 Hz, 1H), 4.53 (dt, J = 16.4, 7.0 Hz, 1H), 4.44 (dd, J = 49.9, 3.0 Hz, 1H), 3.72 (dd, J = 17.2, 7.0 Hz, 1H), 3.47 (dd, J = 17.2, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 166.9 (d, $J_{C\text{-}F}$ = 260.4 Hz), 145.9, 139.7, 137.3, 135.3, 133.4, 132.6, 128.9, 128.6, 128.4, 128.3, 127.8, 127.6, 127.3, 127.2, 126.6, 126.1, 126.0, 125.8, 91.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.6 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.1 (1F). HRMS (APCI) calcd for $C_{27}H_{22}FO$ [M + H$^+$], 381.1649; found: 381.1643.

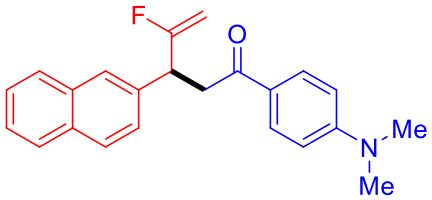


4-Fluoro-1-(4-methoxyphenyl)-3-(naphthalen-2-yl)pent-4-en-1-one (3d). (30.7 mg, 92%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 8.6 Hz, 2H), 7.80-7.78 (m, 4H), 7.48 (d, J = 8.4 Hz, 1H), 7.45-7.41 (m, 2H), 6.89 (d, J = 8.6 Hz, 2H), 4.67 (dd, J = 17.5, 3.0 Hz, 1H), 4.50 (dt, J = 16.4, 7.0 Hz, 1H), 4.42 (dd, J = 49.9, 3.0 Hz, 1H), 3.82 (s, 3H), 3.64 (dd, J = 17.2, 7.0 Hz, 1H), 3.48 (dd, J = 17.2, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.4, 167.0 (d, $J_{C\text{-}F}$ = 260.4 Hz), 163.6, 137.5, 133.4, 132.6, 130.3, 129.8, 128.3, 127.8, 127.5, 126.5, 126.1, 126.0, 125.8, 113.7, 91.2 (d, $J_{C\text{-}F}$ = 20.2 Hz), 55.4, 43.6 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.0 (d, $J_{C\text{-}F}$ = 2.8 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (1F). HRMS (APCI) calcd for $C_{22}H_{19}FNaO_2$ [M + Na$^+$], 357.1261; found: 357.1270.

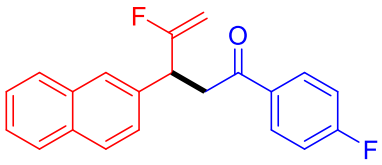


1-(3,4-Dimethoxyphenyl)-4-fluoro-3-(naphthalen-2-yl)pent-4-en-1-one (3e). (33.5 mg, 92%). Isolated by column chromatography (petroleum ether: ethyl acetate = 3:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82-7.79 (m, 4H), 7.60 (dd, J = 8.4, 1.6 Hz, 1H), 7.49-7.48 (m, 2H), 7.47-7.42 (m, 2H), 6.86 (d, J = 8.4 Hz, 1H), 4.69 (dd, J = 17.4, 3.0 Hz, 1H), 4.50 (dt, J = 16.8, 7.2 Hz, 1H), 4.43 (dd, J = 49.8, 3.0 Hz, 1H), 3.92 (s, 3H), 3.89 (s, 3H), 3.65 (dd, J = 17.0, 6.8 Hz, 1H), 3.51 (dd, J = 17.0, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.5, 167.0 (d, $J_{C\text{-}F}$ = 260.0 Hz), 153.4, 149.0, 137.4, 133.4, 132.6, 129.9, 128.4, 127.8, 127.6, 126.5, 126.1, 126.0, 125.8, 122.7, 110.1, 109.9, 91.2 (d, $J_{C\text{-}F}$ = 20.6 Hz), 56.0, 55.9, 43.8 (d, $J_{C\text{-}F}$ = 27.0 Hz), 40.8 (d, $J_{C\text{-}F}$ = 2.8 Hz); ^{19}F NMR (565 MHz,

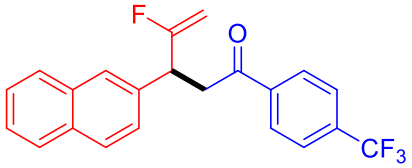
$CDCl_3$) δ -98.9 (1F). HRMS (APCI) calcd for $C_{23}H_{22}FO_3$ [M + H^+], 365.1548; found: 365.1544.



1-(4-(Dimethylamino)phenyl)-4-fluoro-3-(naphthalen-2-yl)pent-4-en-1-one (3f). (30.5 mg, 87%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, J = 9.0 Hz, 2H), 7.81-7.79 (m, 4H), 7.49 (d, J = 8.8 Hz, 1H), 7.46-7.42 (m, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.66 (dd, J = 17.6, 3.0 Hz, 1H), 4.51 (dt, J = 16.6, 7.2 Hz, 1H), 4.43 (dd, J = 49.9, 2.9 Hz, 1H), 3.60 (dd, J = 16.8, 7.2 Hz, 1H), 3.44 (dd, J = 16.8, 7.2 Hz, 1H), 3.04 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.8, 167.2 (d, $J_{C\text{-}F}$ = 260.2 Hz), 153.5, 137.8, 133.4, 132.5, 130.3, 128.3, 127.8, 127.5, 126.5, 126.1, 126.0, 125.7, 124.7, 110.6, 91.0 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.8 (d, $J_{C\text{-}F}$ = 26.8 Hz), 40.6 (d, $J_{C\text{-}F}$ = 2.2 Hz), 40.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.6 (1F). HRMS (APCI) calcd for $C_{23}H_{23}FNO$ [M + H^+], 348.1758; found: 348.1751.

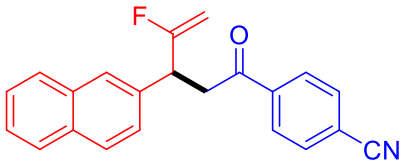


4-Fluoro-1-(4-fluorophenyl)-3-(naphthalen-2-yl)pent-4-en-1-one (3g). (29.0 mg, 90%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98-7.95 (m, 2H), 7.81-7.78 (m, 4H), 7.48-7.42 (m, 3H), 7.10 (t, J = 8.6 Hz, 2H), 4.68 (dd, J = 17.4, 3.0 Hz, 1H), 4.49 (dt, J = 16.4, 3.0 Hz, 1H), 4.42 (dd, J = 49.9, 3.0 Hz, 1H), 3.66 (dd, J = 17.4, 7.2 Hz, 1H), 3.48 (dd, J = 17.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 166.8 (d, $J_{C\text{-}F}$ = 260.4 Hz), 165.8 (d, $J_{C\text{-}F}$ = 255.4 Hz), 137.2, 133.4, 133.1 (d, $J_{C\text{-}F}$ = 3.0 Hz), 132.6, 130.7, 130.6, 128.5, 127.8, 127.6, 126.6, 126.2, 125.9, 115.8 (d, $J_{C\text{-}F}$ = 22.0 Hz), 91.4 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.5 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.3 (d, $J_{C\text{-}F}$ = 2.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (1F). HRMS (APCI) calcd for $C_{21}H_{17}F_2O$ [M + H^+], 323.1242; found: 323.1237.

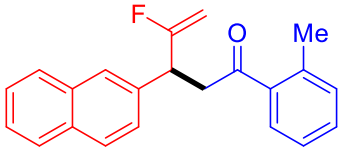


4-Fluoro-3-(naphthalen-2-yl)-1-(4-(trifluoromethyl)phenyl)pent-4-en-1-one (3h). (29.8 mg, 80%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 8.2 Hz, 2H), 7.83-7.78 (m, 4H), 7.71 (d, J = 8.2 Hz, 2H), 7.48-7.44 (m, 3H), 4.70 (dd, J = 17.5, 3.2 Hz, 1H), 4.50

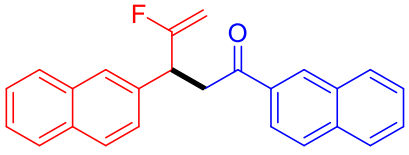
(dt, J = 16.4, 3.0 Hz, 1H), 4.43 (dd, J = 49.9, 3.2 Hz, 1H), 3.72 (dd, J = 17.4, 6.8 Hz, 1H), 3.57 (dd, J = 17.4, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.1, 166.6 (d, $J_{C\text{-}F}$ = 260.8 Hz), 139.3, 136.9, 134.6 (q, $J_{C\text{-}F}$ = 32.4 Hz), 133.4, 132.6, 128.5, 128.4, 127.8, 127.6, 126.6, 126.3, 126.0, 125.8, 125.7 (q, $J_{C\text{-}F}$ = 3.4 Hz), 123.4 (q, $J_{C\text{-}F}$ = 272.4 Hz), 91.6 (d, $J_{C\text{-}F}$ = 20.4 Hz), 43.5 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.7 (d, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (1F). HRMS (APCI) calcd for $C_{22}H_{17}F_4O$ [M + H $^+$], 373.1210; found: 373.1204.



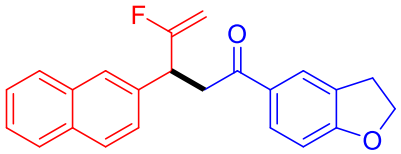
4-(4-Fluoro-3-(naphthalen-2-yl)pent-4-enoyl)benzonitrile (3i). (21.4 mg, 65%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.83-7.78 (m, 3H), 7.77 (s, 1H), 7.74 (d, J = 8.4 Hz, 2H), 7.48-7.44 (m, 3H), 4.70 (dd, J = 17.6, 3.2 Hz, 1H), 4.48 (dt, J = 16.4, 7.1 Hz, 1H), 4.42 (dd, J = 49.6, 3.2 Hz, 1H), 3.70 (dd, J = 17.4, 7.2 Hz, 1H), 3.56 (dd, J = 17.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.8, 166.4 (d, $J_{C\text{-}F}$ = 260.0 Hz), 139.5, 136.8, 133.4, 132.6, 132.5, 128.6, 128.4, 127.8, 127.6, 126.6, 126.3, 126.0, 125.8, 117.8, 116.6, 91.7 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.5 (d, $J_{C\text{-}F}$ = 27.1 Hz), 41.7 (d, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.4 (1F). HRMS (APCI) calcd for $C_{22}H_{16}FNNaO$ [M + Na $^+$], 352.1108; found: 352.1108.



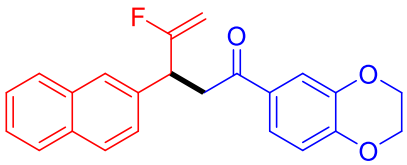
4-Fluoro-3-(naphthalen-2-yl)-1-(o-tolyl)pent-4-en-1-one (3j). (21.0 mg, 66%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82-7.78 (m, 3H), 7.75 (s, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.48-7.44 (m, 3H), 7.36 (t, J = 7.4 Hz, 1H), 7.26-7.23 (m, 1H), 7.21 (d, J = 7.5 Hz, 1H), 4.69 (dd, J = 17.6, 3.2 Hz, 1H), 4.47-4.36 (m, 2H), 3.60 (dd, J = 17.0, 7.0 Hz, 1H), 3.46 (dd, J = 17.0, 7.0 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.1, 166.9 (d, $J_{C\text{-}F}$ = 260.2 Hz), 138.2, 137.8, 137.1, 133.4, 132.6, 132.0, 131.4, 128.4, 128.2, 127.8, 127.6, 126.7, 126.2, 125.9, 125.8, 125.7, 91.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 44.4 (d, $J_{C\text{-}F}$ = 2.6 Hz), 43.9 (d, $J_{C\text{-}F}$ = 26.6 Hz), 20.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.6 (1F). HRMS (APCI) calcd for $C_{22}H_{20}FO$ [M + H $^+$], 319.1493; found: 319.1490.



4-Fluoro-1,3-di(naphthalen-2-yl)pent-4-en-1-one (3k). (31.5 mg, 89%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.01 (dd, J = 8.6, 1.5 Hz, 1H), 7.95 (d, J = 8.2 Hz, 1H), 7.87 (t, J = 8.6 Hz, 2H), 7.83-7.80 (m, 4H), 7.60 (t, J = 7.2 Hz, 1H), 7.55 (d, J = 7.4 Hz, 1H), 7.53 (dd, J = 8.6, 1.2 Hz, 1H), 7.47-7.43 (m, 2H), 4.71 (dd, J = 17.5, 3.0 Hz, 1H), 4.57 (dt, J = 16.4, 7.0 Hz, 1H), 4.46 (dd, J = 49.8, 3.0 Hz, 1H), 3.85 (dd, J = 17.2, 7.0 Hz, 1H), 3.69 (dd, J = 17.2, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 166.9 (d, $J_{C\text{-}F}$ = 260.0 Hz), 137.4, 135.7, 134.0, 133.4, 132.6, 132.4, 129.8, 129.6, 128.6, 128.5, 128.4, 127.8, 127.7, 127.6, 126.9, 126.6, 126.2, 126.0, 125.9, 123.7, 91.4 (d, $J_{C\text{-}F}$ = 20.1 Hz), 43.3 (d, $J_{C\text{-}F}$ = 27.0 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.8 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.9 (1F). HRMS (APCI) calcd for $C_{25}H_{20}FO$ [M + H $^+$], 355.1493; found: 355.1494.

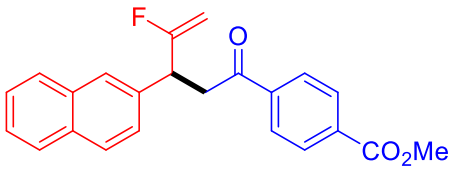


1-(2,3-Dihydrobenzofuran-6-yl)-4-fluoro-3-(naphthalen-2-yl)pent-4-en-1-one (3l). (30.8 mg, 89%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.81-7.80 (m, 1H), 7.80-7.78 (m, 4H), 7.48 (d, J = 8.4 Hz, 1H), 7.46-7.42 (m, 2H), 6.78 (d, J = 8.4 Hz, 1H), 4.67 (dd, J = 17.5, 3.0 Hz, 1H), 4.63 (t, J = 8.8 Hz, 2H), 4.50 (dt, J = 16.5, 7.0 Hz, 1H), 4.42 (dd, J = 49.8, 3.0 Hz, 1H), 3.62 (dd, J = 17.0, 7.0 Hz, 1H), 3.47 (dd, J = 17.0, 7.0 Hz, 1H), 3.20 (t, J = 8.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 167.0 (d, $J_{C\text{-}F}$ = 260.2 Hz), 164.5, 137.5, 133.4, 132.6, 130.1, 130.0, 128.3, 127.8, 127.6, 126.5, 126.1, 126.0, 125.8, 125.4, 109.0, 91.2 (d, $J_{C\text{-}F}$ = 20.6 Hz), 72.2, 43.7 (d, $J_{C\text{-}F}$ = 26.9 Hz), 41.0 (d, $J_{C\text{-}F}$ = 2.9 Hz), 28.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (1F). HRMS (APCI) calcd for $C_{20}H_{19}FNaO_2$ [M + Na $^+$], 369.1261; found: 369.1259.

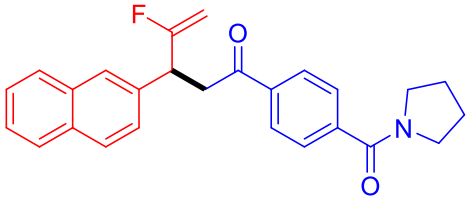


1-(2,3-Dihydrobenzo[b][1,4]dioxin-6-yl)-4-fluoro-3-(naphthalen-2-yl)pent-4-en-1-one (3m). (32.9 mg, 91%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.80 (m, 2H), 7.79-7.78 (m, 2H), 7.51-7.49 (m, 2H), 7.48-7.42 (m, 3H), 6.89 (d, J = 9.0 Hz, 1H), 4.67 (dd, J = 17.5, 3.0 Hz, 1H), 4.48 (dt, J = 16.4, 7.0 Hz, 1H), 4.41 (dd, J = 49.9, 3.0 Hz, 1H), 4.30-4.28 (m, 2H), 4.26-4.25 (m, 2H), 3.61 (dd, J = 17.0, 7.0 Hz, 1H), 3.47 (dd, J = 17.0, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.3, 167.0 (d, $J_{C\text{-}F}$ = 260.2 Hz), 148.2, 143.3, 137.4, 133.4, 132.6, 130.6, 128.4, 127.8, 127.6, 126.6, 126.1, 126.0, 125.8,

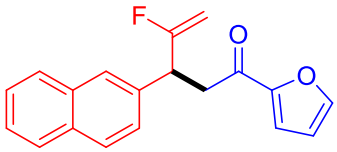
122.2, 117.6, 117.3, 91.2 (d, $J_{C\text{-}F}$ = 20.1 Hz), 64.7, 64.1, 43.6 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.0 (d, $J_{C\text{-}F}$ = 2.9 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.8 (1F). HRMS (APCI) calcd for $C_{23}H_{20}FO_3$ [M + H $^+$], 363.1391; found: 363.1387.



Methyl-4-(4-fluoro-3-(naphthalen-2-yl)pent-4-enoyl)benzoate (3n). (29.7 mg, 82%). Isolated by column chromatography (petroleum ether: ethyl acetate = 5:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.4 Hz, 2H), 7.82-7.79 (m, 4H), 7.48-7.43 (m, 3H), 4.70 (dd, J = 17.6, 3.2 Hz, 1H), 4.49 (dt, J = 16.4, 7.0 Hz, 1H), 4.42 (dd, J = 49.8, 3.2 Hz, 1H), 3.93 (s, 3H), 3.72 (dd, J = 17.4, 6.8 Hz, 1H), 3.57 (dd, J = 17.4, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 166.7 (d, $J_{C\text{-}F}$ = 260.4 Hz), 166.1, 139.8, 137.0, 134.0, 133.4, 132.6, 129.9, 128.5, 127.9, 127.8, 127.6, 126.6, 126.2, 125.9, 125.8, 91.5 (d, $J_{C\text{-}F}$ = 20.6 Hz), 52.5, 43.5 (d, $J_{C\text{-}F}$ = 26.9 Hz), 41.7 (d, $J_{C\text{-}F}$ = 2.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.1 (1F). HRMS (APCI) calcd for $C_{23}H_{19}FNaO_3$ [M + Na $^+$], 385.1210; found: 385.1204.

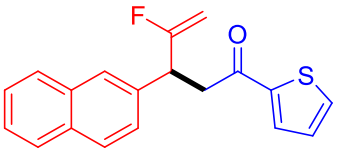


4-Fluoro-3-(naphthalen-2-yl)-1-(4-(pyrrolidine-1-carbonyl)phenyl)pent-4-en-1-one (3o). (38.1 mg, 95%). Isolated by column chromatography (petroleum ether: ethyl acetate = 2:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, J = 8.0 Hz, 2H), 7.82-7.78 (m, 4H), 7.57 (d, J = 8.0 Hz, 2H), 7.48-7.43 (m, 3H), 4.69 (dd, J = 17.4, 2.6 Hz, 1H), 4.49 (dt, J = 17.0, 7.0 Hz, 1H), 4.42 (dd, J = 49.8, 2.6 Hz, 1H), 3.69 (dd, J = 17.4, 6.6 Hz, 1H), 3.64 (t, J = 6.4 Hz, 2H), 3.56 (dd, J = 17.4, 6.6 Hz, 1H), 3.34 (t, J = 6.4 Hz, 2H), 1.97-1.93 (m, 2H), 1.89-1.85 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 168.4, 166.7 (d, $J_{C\text{-}F}$ = 260.2 Hz), 141.7, 137.4, 137.1, 133.4, 132.6, 128.4, 128.1, 127.8, 127.6, 127.3, 126.6, 126.2, 125.9, 91.4 (d, $J_{C\text{-}F}$ = 20.6 Hz), 49.4, 46.2, 43.6 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.6 Hz), 26.3, 24.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.1 (1F). HRMS (ESI) calcd for $C_{26}H_{24}FNNaO_2$ [M + Na $^+$], 424.1683; found: 424.1681.

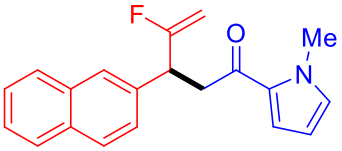


4-Fluoro-1-(furan-2-yl)-3-(naphthalen-2-yl)pent-4-en-1-one (3p). (27.3 mg, 87%). Isolated by column

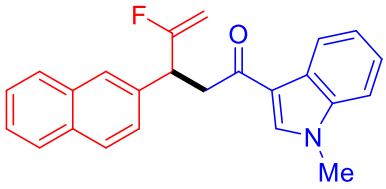
chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.79 (m, 4H), 7.56 (s, 1H), 7.48-7.43 (m, 3H), 7.19 (d, J = 3.6 Hz, 1H), 6.50 (d, J = 3.2 Hz, 1H), 4.68 (dd, J = 17.5, 3.0 Hz, 1H), 4.47 (dt, J = 16.4, 7.0 Hz, 1H), 4.44 (dd, J = 49.8, 3.0 Hz, 1H), 3.54 (dd, J = 17.2, 7.0 Hz, 1H), 3.40 (dd, J = 17.2, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 186.1, 166.6 (d, $J_{C\text{-}F}$ = 260.2 Hz), 152.5, 146.5, 137.0, 133.4, 132.6, 128.4, 127.8, 127.6, 126.7, 126.1, 125.9, 125.8, 117.4, 112.4, 91.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.3 (d, $J_{C\text{-}F}$ = 26.7 Hz), 41.4 (d, $J_{C\text{-}F}$ = 3.0 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.0 (1F). HRMS (APCI) calcd for $C_{19}H_{16}FO_2$ [M + H $^+$], 295.1129; found: 295.1128.



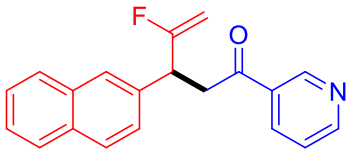
4-Fluoro-3-(naphthalen-2-yl)-1-(thiophen-2-yl)pent-4-en-1-one (3q). (27.8 mg, 96%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.70 (m, 4H), 7.64 (d, J = 3.7 Hz, 1H), 7.51 (d, J = 4.8 Hz, 1H), 7.39 (d, J = 8.4 Hz, 1H), 7.37-7.33 (m, 2H), 7.00 (t, J = 4.2 Hz, 1H), 4.60 (dd, J = 17.4, 3.0 Hz, 1H), 4.40 (dt, J = 16.4, 7.0 Hz, 1H), 4.35 (dd, J = 49.9, 3.0 Hz, 1H), 3.53 (dd, J = 16.7, 7.0 Hz, 1H), 3.47 (dd, J = 16.7, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 189.8, 166.5 (d, $J_{C\text{-}F}$ = 260.4 Hz), 143.9, 137.0, 134.0, 133.4, 132.6, 132.0, 128.4, 128.1, 127.8, 127.6, 126.6, 126.2, 125.9, 125.8, 91.5 (d, $J_{C\text{-}F}$ = 20.0 Hz), 43.7 (d, $J_{C\text{-}F}$ = 26.9 Hz), 42.0 (d, $J_{C\text{-}F}$ = 2.9 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.1 (1F). HRMS (APCI) calcd for $C_{19}H_{15}FNaOS$ [M + Na $^+$], 333.0720; found: 333.0717.



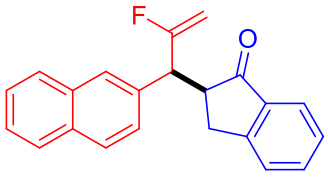
4-Fluoro-1-(1-methyl-1H-pyrrol-2-yl)-3-(naphthalen-2-yl)pent-4-en-1-one (3r). (25.8 mg, 84%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.78 (m, 4H), 7.48-7.42 (m, 3H), 7.02 (dd, J = 4.0, 1.2 Hz, 1H), 6.77 (br, 1H), 6.11 (dd, J = 4.0, 2.5 Hz, 1H), 4.66 (dd, J = 17.6, 3.0 Hz, 1H), 4.44 (dt, J = 16.4, 7.2 Hz, 1H), 4.43 (dd, J = 49.6, 2.4 Hz, 1H), 3.87 (s, 3H), 3.48 (dd, J = 16.4, 7.2 Hz, 1H), 3.35 (dd, J = 16.4, 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 187.4, 167.1 (d, $J_{C\text{-}F}$ = 260.0 Hz), 137.4, 133.4, 132.6, 131.3, 130.6, 128.3, 127.8, 127.6, 126.6, 126.1, 126.0, 125.8, 119.2, 108.1, 91.1 (d, $J_{C\text{-}F}$ = 20.5 Hz), 43.8 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.6 (d, $J_{C\text{-}F}$ = 2.4 Hz), 37.7; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.4 (1F). HRMS (APCI) calcd for $C_{20}H_{19}FNO$ [M + H $^+$], 308.1445; found: 308.1441.



4-Fluoro-1-(1-methyl-1H-indol-3-yl)-3-(naphthalen-2-yl)pent-4-en-1-one (3s). (25.0 mg, 70%). Isolated by column chromatography (petroleum ether: ethyl acetate = 2:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.37-8.35 (m, 1H), 7.81-7.76 (m, 4H), 7.64 (s, 1H), 7.51-7.49 (m, 1H), 7.44-7.39 (m, 2H), 7.28-7.24 (m, 3H), 4.66 (dd, J = 17.6, 2.8 Hz, 1H), 4.56 (dt, J = 17.2, 7.2 Hz, 1H), 4.47 (dd, J = 49.8, 2.8 Hz, 1H), 3.70 (s, 3H), 3.54 (dd, J = 16.0, 7.0 Hz, 1H), 3.35 (dd, J = 16.0, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 191.6, 167.1 (d, $J_{C\text{-}F}$ = 260.0 Hz), 137.8, 137.4, 135.4, 133.4, 132.5, 128.3, 127.8, 127.5, 126.5, 126.2, 126.0, 125.7, 123.4, 122.6, 122.5, 116.5, 109.6, 91.2 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.8 (d, $J_{C\text{-}F}$ = 26.6 Hz), 42.5 (d, $J_{C\text{-}F}$ = 2.0 Hz), 33.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.0 (1F). HRMS (APCI) calcd for $C_{24}H_{21}FNO$ [M + H $^+$], 358.1602; found: 358.1602.

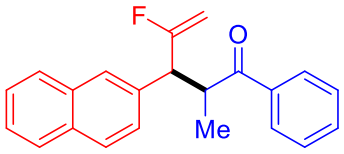


4-Fluoro-3-(naphthalen-2-yl)-1-(pyridin-3-yl)pent-4-en-1-one (3t). (22.6 mg, 74%). Isolated by column chromatography (petroleum ether: ethyl acetate = 1:2, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.10 (s, 1H), 8.67 (d, J = 4.2 Hz, 1H), 8.09 (d, J = 7.8 Hz, 1H), 7.74-7.70 (m, 4H), 7.40-7.35 (m, 3H), 7.29 (dd, J = 7.6, 5.0 Hz, 1H), 4.62 (dd, J = 17.4, 2.8 Hz, 1H), 4.41 (dt, J = 16.4, 7.0 Hz, 1H), 4.34 (dd, J = 49.9, 3.0 Hz, 1H), 3.62 (dd, J = 17.2, 7.0 Hz, 1H), 3.48 (dd, J = 17.2, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 195.9, 166.5 (d, $J_{C\text{-}F}$ = 260.2 Hz), 153.9, 149.5, 136.8, 135.3, 133.3, 132.6, 131.9, 128.5, 127.8, 127.6, 126.6, 126.2, 126.0, 125.8, 123.6, 91.6 (d, $J_{C\text{-}F}$ = 20.0 Hz), 43.4 (d, $J_{C\text{-}F}$ = 27.2 Hz), 41.6 (d, $J_{C\text{-}F}$ = 2.6 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (APCI) calcd for $C_{20}H_{17}FNO$ [M + H $^+$], 306.1289; found: 306.1286.

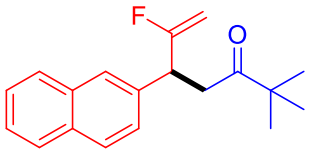


2-(2-Fluoro-1-(naphthalen-2-yl)allyl)-2,3-dihydro-1H-inden-1-one (3u). (dr = 1.6:1, 28.8 mg, 91%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.3); **Major** and **Minor**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86-7.70 (m, 5H), 7.62-7.48 (m, 2H), 7.46-7.40 (m, 2H), 7.39-7.28 (m, 2H), 4.85 (dd, J = 17.6, 3.2 Hz, 0.62H), 4.67 (dd, J = 18.4, 3.0 Hz, 0.38H), 4.60 (dd, J = 49.8, 3.2 Hz, 0.62H), 4.59 (dd, J = 12.6, 4.2 Hz, 0.38H),

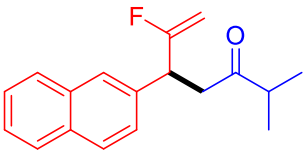
4.49 (dd, J = 18.8, 5.2 Hz, 0.64H), 4.19 (dd, J = 50.6, 3.0 Hz, 0.38H), 3.42-3.36 (m, 1.38H), 3.30-3.24 (m, 1H), 2.97 (dd, J = 17.2, 4.4 Hz, 0.62H); **Major** and **Minor**: ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.7, 205.6, 166.5 (d, $J_{C\text{-}F}$ = 258.8 Hz), 165.7 (d, $J_{C\text{-}F}$ = 261.4 Hz), 153.4, 153.3, 136.6, 136.3, 134.9, 133.4, 133.2, 132.6, 132.5, 128.4, 128.2, 127.9, 127.6, 127.5, 127.4, 127.1, 126.5, 126.4, 126.3, 126.1, 126.0, 125.9, 124.2, 124.0, 93.8 (d, $J_{C\text{-}F}$ = 19.6 Hz), 92.1 (d, $J_{C\text{-}F}$ = 20.2 Hz), 50.0, 49.5 (d, $J_{C\text{-}F}$ = 2.0 Hz), 48.5 (d, $J_{C\text{-}F}$ = 25.2 Hz), 48.1 (d, $J_{C\text{-}F}$ = 26.4 Hz), 30.4, 30.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -96.2, -97.0. HRMS (APCI) calcd for $C_{22}H_{18}FO$ [M + H $^+$], 317.1336; found: 317.1335.



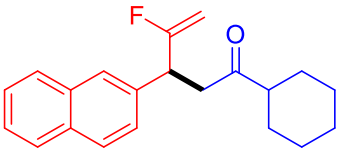
4-Fluoro-2-methyl-3-(naphthalen-2-yl)-1-phenylpent-4-en-1-one (3v). (dr = 2:1, 29.3 mg, 92%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); **Major**: ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 7.4 Hz, 1H), 7.87-7.82 (m, 3H), 7.73-7.68 (m, 3H), 7.53-7.45 (m, 2H), 7.39-7.34 (m, 3H), 4.67 (dd, J = 17.4, 3.0 Hz, 1H), 4.61 (dd, J = 49.8, 3.0 Hz, 1H), 4.41-4.34 (m, 1H), 4.20-4.14 (m, 1H), 1.41 (d, J = 7.0 Hz, 3H); **Major** and **Minor**: ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.7, 202.1, 166.1 (d, $J_{C\text{-}F}$ = 261.2 Hz), 165.5 (d, $J_{C\text{-}F}$ = 261.4 Hz), 137.0, 136.3, 136.1, 133.5, 133.3, 133.1, 132.8, 132.5, 128.8, 128.6, 128.5, 128.3, 128.1, 127.8, 127.6, 127.4, 126.7, 126.3, 126.2, 126.1, 125.9, 125.6, 92.7 (d, $J_{C\text{-}F}$ = 20.2 Hz), 91.4 (d, $J_{C\text{-}F}$ = 20.6 Hz), 51.5 (d, $J_{C\text{-}F}$ = 23.2 Hz), 51.3 (d, $J_{C\text{-}F}$ = 23.2 Hz), 42.3 (d, $J_{C\text{-}F}$ = 3.2 Hz), 42.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 17.6, 17.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -104.4, -98.1. HRMS (APCI) calcd for $C_{22}H_{20}FO$ [M + H $^+$], 319.1493; found: 319.1491.



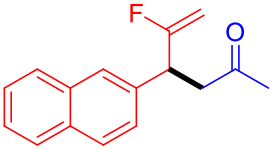
6-Fluoro-2,2-dimethyl-5-(naphthalen-2-yl)hept-6-en-3-one (3w). (22.7 mg, 80%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.79 (m, 3H), 7.73 (s, 1H), 7.47-7.41 (m, 3H), 4.64 (dd, J = 17.5, 3.0 Hz, 1H), 4.42-4.31 (m, 2H), 3.17 (dd, J = 17.6, 6.8 Hz, 1H), 3.07 (dd, J = 17.6, 6.8 Hz, 1H), 1.07 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 212.3, 167.1 (d, $J_{C\text{-}F}$ = 260.1 Hz), 137.5, 133.4, 132.5, 128.3, 127.8, 127.6, 126.6, 126.1, 125.9, 125.8, 91.0 (d, $J_{C\text{-}F}$ = 20.7 Hz), 44.1, 43.3 (d, $J_{C\text{-}F}$ = 26.6 Hz), 39.7 (d, $J_{C\text{-}F}$ = 2.2 Hz), 26.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.3 (1F). HRMS (APCI) calcd for $C_{19}H_{22}FO$ [M + H $^+$], 285.1649; found: 285.1647.



6-Fluoro-2-methyl-5-(naphthalen-2-yl)hept-6-en-3-one (3x). (16.5 mg, 61%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, J = 8.0 Hz, 3H), 7.73 (s, 1H), 7.48-7.44 (m, 2H), 7.42 (d, J = 8.4 Hz, 1H), 4.65 (dd, J = 17.6, 3.2 Hz, 1H), 4.38 (dd, J = 49.8, 3.2 Hz, 1H), 4.31 (dt, J = 16.6, 7.6 Hz, 1H), 3.15 (dd, J = 17.2, 6.8 Hz, 1H), 3.02 (dd, J = 17.2, 6.8 Hz, 1H), 2.55 (m, 1H). 1.07 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 211.3, 167.0(d, $J_{C\text{-}F}$ = 260.0 Hz), 137.3, 133.4, 132.6, 128.4, 127.8, 127.6, 126.6, 126.2, 125.9, 125.8, 91.1 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.3 (d, $J_{C\text{-}F}$ = 26.6 Hz), 43.2 (d, $J_{C\text{-}F}$ = 2.4 Hz), 41.3, 17.9, 17.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (ESI) calcd for $C_{18}H_{19}FNaO$ [M + Na^+], 293.1312; found: 393.1312.

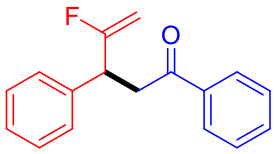


1-Cyclohexyl-4-fluoro-3-(naphthalen-2-yl)pent-4-en-1-one (3y). (24.5 mg, 79%). Isolated by column chromatography (petroleum ether: ethyl acetate = 50:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80-7.78 (m, 3H), 7.72 (s, 1H), 7.48-7.43 (m, 2H), 7.41 (dd, J = 8.6, 1.4 Hz, 1H), 4.64 (dd, J = 17.4, 3.0 Hz, 1H), 4.36 (dd, J = 49.8, 3.2 Hz, 1H), 4.31 (dt, J = 16.4, 7.0 Hz, 1H), 3.14 (dd, J = 17.4, 7.0 Hz, 1H), 3.00 (dd, J = 17.4, 7.0 Hz, 1H), 2.31-2.27 (m, 1H), 1.83-1.81 (m, 1H), 1.77-1.70 (m, 3H), 1.64-1.61 (m, 1H), 1.32-1.13 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 210.6, 167.0 (d, $J_{C\text{-}F}$ = 260.5 Hz), 137.4, 133.4, 132.6, 128.3, 127.8, 127.6, 126.6, 126.1, 125.9, 125.8, 90.1 (d, $J_{C\text{-}F}$ = 20.7 Hz), 51.1, 43.4 (d, $J_{C\text{-}F}$ = 2.2 Hz), 43.1 (d, $J_{C\text{-}F}$ = 26.6 Hz), 28.1, 28.0, 25.7, 25.5; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.1 (1F). HRMS (APCI) calcd for $C_{21}H_{24}FO$ [M + H^+], 311.1806; found: 311.1803.

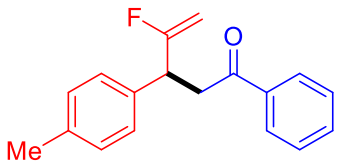


5-Fluoro-4-(naphthalen-2-yl)hex-5-en-2-one (3z). (18.2 mg, 75%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.80 (m, 3H), 7.73 (s, 1H), 7.48-7.44 (m, 2H), 7.41 (d, J = 8.4 Hz, 1H), 4.66 (dd, J = 17.4, 2.8 Hz, 1H), 4.36 (dd, J = 49.8, 2.8 Hz, 1H), 4.27 (dt, J = 17.4, 7.2 Hz, 1H), 3.13 (dd, J = 17.4, 7.0 Hz, 1H), 2.99 (dd, J = 17.4, 7.0 Hz, 1H), 2.12 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 205.5, 166.7 (d, $J_{C\text{-}F}$ = 260.2 Hz), 137.0, 133.4, 132.6, 128.4, 127.8, 127.6, 126.6, 126.2, 125.9, 125.8, 91.2 (d, $J_{C\text{-}F}$ = 20.6 Hz), 46.2 (d, $J_{C\text{-}F}$ = 2.4 Hz), 43.3 (d, $J_{C\text{-}F}$ = 26.8 Hz), 30.5; ^{19}F NMR (565 MHz,

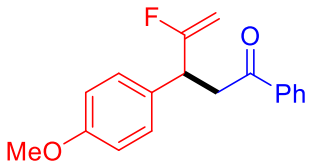
$CDCl_3$) δ -99.0 (1F). HRMS (APCI) calcd for $C_{16}H_{16}FO$ [M + H^+], 243.1180; found: 243.1170.



4-Fluoro-1,3-diphenylpent-4-en-1-one (3aa). (24.4 mg, 96%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.35-7.30 (m, 4H), 7.24 (t, J = 7.4 Hz, 1H), 4.64 (dd, J = 17.6, 3.0 Hz, 1H), 4.38 (dd, J = 49.8, 3.0 Hz, 1H), 4.33 (dt, J = 17.0, 7.0 Hz, 1H), 3.61 (dd, J = 17.4, 7.0 Hz, 1H), 3.44 (dd, J = 17.4, 7.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 167.0 (d, $J_{C\text{-}F}$ = 260.0 Hz), 140.0, 136.7, 133.3, 128.8, 128.7, 128.1, 127.9, 127.3, 91.1 (d, $J_{C\text{-}F}$ = 21.0 Hz), 43.5 (d, $J_{C\text{-}F}$ = 26.4 Hz), 41.5 (d, $J_{C\text{-}F}$ = 3.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (APCI) calcd for $C_{17}H_{16}FO$ [M + H^+], 255.1180; found: 255.1178.

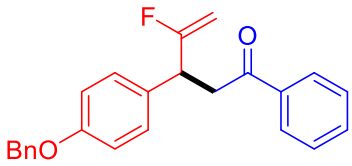


4-Fluoro-1-phenyl-3-(*p*-tolyl)pent-4-en-1-one (3ab) (24.7 mg, 92%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.23 (d, J = 7.6 Hz, 2H), 7.12 (d, J = 7.6 Hz, 2H), 4.62 (dd, J = 17.6, 3.0 Hz, 1H), 4.36 (dd, J = 49.8, 3.0 Hz, 1H), 4.29 (dt, J = 17.0, 7.2 Hz, 1H), 3.59 (dd, J = 17.2, 7.0 Hz, 1H), 3.42 (dd, J = 17.2, 7.0 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 167.1 (d, $J_{C\text{-}F}$ = 260.0 Hz), 136.9, 136.8, 133.2, 129.3, 128.6, 128.0, 127.6, 90.8 (d, $J_{C\text{-}F}$ = 20.8 Hz), 43.0 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 21.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.3 (1F). HRMS (APCI) calcd for $C_{18}H_{18}FO$ [M + H^+], 269.1336; found: 269.1332.

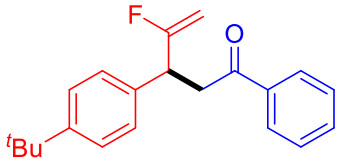


4-Fluoro-3-(4-methoxyphenyl)-1-phenylpent-4-en-1-one (3ac). (27.0 mg, 95%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 7.6 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 4.53 (dd, J = 17.5, 3.0 Hz, 1H), 4.26 (dd, J = 49.8, 3.0 Hz, 1H), 4.19 (dt, J = 16.4, 7.2 Hz, 1H), 3.68 (s, 3H), 3.49 (dd, J = 17.4, 6.8 Hz, 1H), 3.34 (dd, J = 17.4, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 167.3 (d, $J_{C\text{-}F}$ = 260.4 Hz),

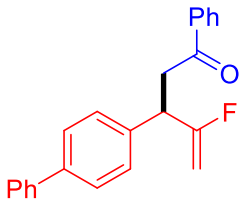
158.6, 136.7, 133.2, 131.9, 128.8, 128.6, 128.0, 114.0, 90.7 (d, $J_{C\text{-}F}$ = 20.5 Hz), 55.2, 42.6 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (APCI) calcd for $C_{18}H_{18}FO_2$ [M + H $^+$], 285.1285; found: 285.1279.



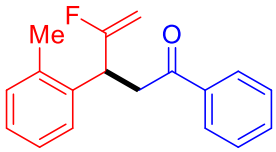
3-(4-(Benzyloxy)phenyl)-4-fluoro-1-phenylpent-4-en-1-one (3ad). (30.6 mg, 85%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.4 Hz, 2H), 7.54 (t, J = 7.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.40 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 5.01 (s, 2H), 4.61 (dd, J = 17.5, 3.0 Hz, 1H), 4.34 (dd, J = 49.8, 3.0 Hz, 1H), 4.27 (dt, J = 16.4, 7.2 Hz, 1H), 3.56 (dd, J = 17.4, 6.8 Hz, 1H), 3.40 (dd, J = 17.4, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 167.2 (d, $J_{C\text{-}F}$ = 260.4 Hz), 157.9, 136.9, 136.7, 133.2, 132.2, 128.8, 128.6, 128.5, 128.0, 127.9, 127.4, 114.9, 90.7 (d, $J_{C\text{-}F}$ = 20.5 Hz), 70.0, 42.6 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.4 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.3 (1F). HRMS (ESI) calcd for $C_{24}H_{21}FNaO_2$ [M + Na $^+$], 383.1418; found: 383.1417.



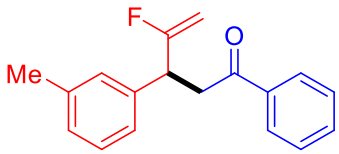
3-(4-(*Tert*-butyl)phenyl)-4-fluoro-1-phenylpent-4-en-1-one (3ae). (29.5 mg, 95%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.9 Hz, 2H), 7.55 (t, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 4.62 (dd, J = 17.6, 3.0 Hz, 1H), 4.37 (dd, J = 49.8, 2.9 Hz, 1H), 4.31 (dt, J = 17.8, 7.0 Hz, 1H), 3.61 (dd, J = 17.4, 7.4 Hz, 1H), 3.42 (dd, J = 17.4, 7.4 Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.1, 166.0 (d, $J_{C\text{-}F}$ = 260.0 Hz), 149.0, 135.8, 135.7, 132.2, 127.6, 127.0, 126.3, 124.6, 89.9 (d, $J_{C\text{-}F}$ = 20.9 Hz), 41.9 (d, $J_{C\text{-}F}$ = 26.6 Hz), 40.5 (d, $J_{C\text{-}F}$ = 2.2 Hz), 33.4, 30.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.5 (1F). HRMS (APCI) calcd for $C_{21}H_{24}FO$ [M + H $^+$], 311.1806; found: 311.1805.



3-([1,1'-Biphenyl]-4-yl)-4-fluoro-1-phenylpent-4-en-1-one (3af). (28.7 mg, 87%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.56-7.53 (m, 5H), 7.45-7.39 (m, 6H), 7.32 (t, J = 7.3 Hz, 1H), 4.66 (dd, J = 17.6, 2.9 Hz, 1H), 4.42 (dd, J = 49.8, 2.9 Hz, 1H), 4.40-4.35 (m, 1H), 3.63 (dd, J = 17.4, 7.0 Hz, 1H), 3.48 (dd, J = 17.4, 6.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 166.8 (d, $J_{C\text{-}F}$ = 259.8 Hz), 140.6, 140.1, 138.9, 136.6, 133.3, 128.7, 128.6, 128.2, 128.0, 127.4, 127.2, 127.0, 91.3 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.1 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.7 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (APCI) calcd for $C_{23}H_{20}FO$ [M + H $^+$], 331.1493; found: 331.1493.

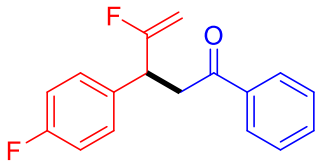


4-Fluoro-1-phenyl-3-(o-tolyl)pent-4-en-1-one (3ag). (23.3 mg, 87%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, J = 7.4 Hz, 2H), 7.58 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.31 (d, J = 7.2 Hz, 1H), 7.20-7.15 (m, 3H), 4.64 (dd, J = 17.6, 3.0 Hz, 1H), 4.60 (dt, J = 17.0, 7.4 Hz, 1H), 4.28 (dd, J = 49.8, 3.0 Hz, 1H), 3.65 (dd, J = 17.6, 7.0 Hz, 1H), 3.48 (dd, J = 17.6, 7.0 Hz, 1H), 2.47 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.1, 166.8 (d, $J_{C\text{-}F}$ = 260.0 Hz), 137.9, 136.7, 136.5, 133.3, 130.7, 128.6, 128.0, 127.0, 126.4, 126.2, 91.0 (d, $J_{C\text{-}F}$ = 20.8 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.2 Hz), 38.8 (d, $J_{C\text{-}F}$ = 26.4 Hz), 19.6; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.6 (1F). HRMS (APCI) calcd for $C_{18}H_{18}FO$ [M + H $^+$], 269.1336; found: 269.1332.

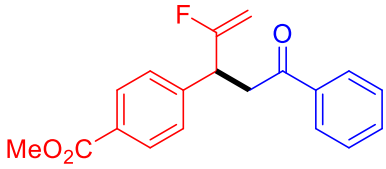


4-Fluoro-1-phenyl-3-(m-tolyl)pent-4-en-1-one (3ah). (24.7 mg, 92%). Isolated by column chromatography (petroleum ether: ethyl acetate = 50:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.20 (t, J = 7.6 Hz, 1H), 7.15-7.13 (m, 2H), 7.06 (d, J = 7.2 Hz, 1H), 4.63 (dd, J = 17.6, 2.8 Hz, 1H), 4.37 (dd, J = 49.6, 2.8 Hz, 1H), 4.29 (dt, J = 17.2, 7.2 Hz, 1H), 3.60 (dd, J = 17.2, 7.2 Hz, 1H), 3.41 (dd, J = 17.2, 7.2 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.0, 167.0 (d, $J_{C\text{-}F}$ = 260.0

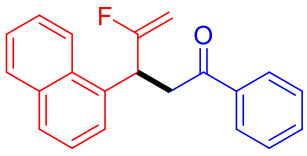
Hz), 139.9, 138.3, 136.7, 133.2, 128.6, 128.5, 128.4, 128.1, 128.0, 124.7, 90.9 (d, $J_{C\text{-}F}$ = 20.2 Hz), 43.4 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 21.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (ESI) calcd for $C_{18}H_{17}FNaO$ [M + Na^+], 291.1156; found: 291.1153.



4-Fluoro-3-(4-fluorophenyl)-1-phenylpent-4-en-1-one (3ai). (19.9 mg, 73%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.92 (m, 2H), 7.57 (t, J = 7.5 Hz, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.32-7.30 (m, 2H), 7.01-6.99 (m, 2H), 4.65 (dd, J = 17.6, 3.2 Hz, 1H), 4.37 (dd, J = 49.8, 3.2 Hz, 1H), 4.32 (dt, J = 17.0, 7.0 Hz, 1H), 3.58 (dd, J = 17.4, 6.5 Hz, 1H), 3.43 (dd, J = 17.4, 6.5 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8, 166.8 (d, $J_{C\text{-}F}$ = 260.0 Hz), 161.9 (d, $J_{C\text{-}F}$ = 245.2 Hz), 136.6, 135.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 133.4, 129.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 128.7, 128.0, 115.5 (d, $J_{C\text{-}F}$ = 21.4 Hz), 91.1 (d, $J_{C\text{-}F}$ = 20.6 Hz), 42.7 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.5 (1F), -115.4 (1F). HRMS (APCI) calcd for $C_{17}H_{15}F_2O$ [M + H^+], 273.1086; found: 273.1084.

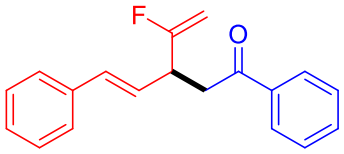


Methyl -4-(2-fluoro-5-oxo-5-phenylpent-1-en-3-yl)benzoate (3aj). (23.4 mg, 75%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, J = 8.2 Hz, 2H), 7.94-7.92 (m, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 4.68 (dd, J = 17.4, 3.2 Hz, 1H), 4.40 (dd, J = 49.8, 3.2 Hz, 1H), 4.40 (dt, J = 17.0, 7.2 Hz, 1H), 3.89 (s, 3H), 3.63 (dd, J = 17.4, 6.6 Hz, 1H), 3.48 (dd, J = 17.4, 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.5, 166.7, 166.1 (d, $J_{C\text{-}F}$ = 260.0 Hz), 145.1, 136.5, 133.4, 130.0, 129.1, 128.7, 128.0, 127.9, 91.5 (d, $J_{C\text{-}F}$ = 20.2 Hz), 52.0, 43.3 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.1 (d, $J_{C\text{-}F}$ = 2.2 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -97.2 (1F). HRMS (ESI) calcd for $C_{19}H_{18}FO_3$ [M + H^+], 313.1235; found: 313.1237.

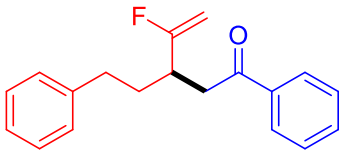


4-Fluoro-3-(naphthalen-1-yl)-1-phenylpent-4-en-1-one (3ak). (28.9 mg, 95%). Isolated by column

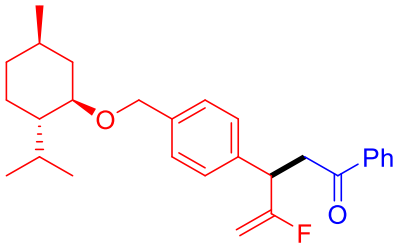
chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 8.5 Hz, 1H), 7.94 (d, J = 7.4 Hz, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.76 (d, J = 8.2 Hz, 1H), 7.54-7.51 (m, 3H), 7.47 (t, J = 7.4 Hz, 1H), 7.43-7.40 (m, 3H), 5.26-5.21 (m, 1H), 4.72 (dd, J = 17.6, 3.2 Hz, 1H), 4.37 (dd, J = 49.8, 3.0 Hz, 1H), 3.78 (dd, J = 17.6, 6.4 Hz, 1H), 3.48 (dd, J = 17.6, 6.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.0, 166.5 (d, $J_{C\text{-}F}$ = 260.0 Hz), 136.6, 135.9, 134.1, 133.3, 131.2, 129.0, 128.6, 128.0, 127.9, 126.5, 125.7, 125.4, 124.5, 122.9, 91.9 (d, $J_{C\text{-}F}$ = 20.6 Hz), 41.5 (d, $J_{C\text{-}F}$ = 3.0 Hz), 38.5 (d, $J_{C\text{-}F}$ = 27.0 Hz); ^{19}F NMR (565 MHz, $CDCl_3$) δ -97.2 (1F). HRMS (ESI) calcd for $C_{21}H_{18}FO$ [M + H $^+$], 305.1336; found: 305.1338.



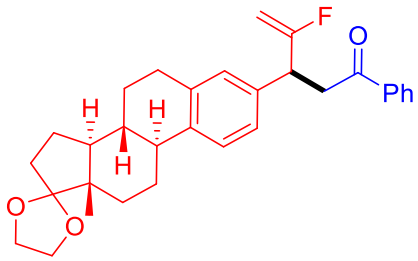
(E)-4-Fluoro-1-phenyl-3-styrylpent-4-en-1-one (3al). (21.8 mg, 78%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 8.5 Hz, 1H), 7.54 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 2H), 7.26-7.25 (m, 2H), 7.22 (t, J = 7.2 Hz, 2H), 6.26 (dd, J = 15.6, 7.4 Hz, 1H), 5.84 (dd, J = 25.4, 15.6 Hz, 1H), 4.59 (dd, J = 16.4, 2.4 Hz, 1H), 4.33 (dd, J = 48.8, 2.4 Hz, 1H), 4.24-4.21 (m, 1H), 3.43 (dd, J = 7.4, 1.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.6, 161.4 (d, $J_{C\text{-}F}$ = 251.6 Hz), 142.5, 137.0, 135.1 (d, $J_{C\text{-}F}$ = 2.8 Hz), 133.1, 128.7, 128.6, 128.0, 127.7, 126.8, 122.0 (d, $J_{C\text{-}F}$ = 24.2 Hz), 92.7 (d, $J_{C\text{-}F}$ = 21.4 Hz), 44.2, 43.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.2 (1F). HRMS (ESI) calcd for $C_{19}H_{18}FO$ [M + H $^+$], 281.1336; found: 281.1334.



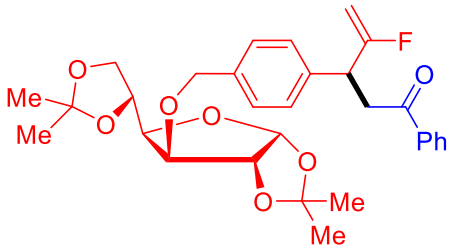
4-Fluoro-3-phenethyl-1-phenylpent-4-en-1-one (3am). (15.8 mg, 56%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.3 Hz, 2H), 7.29-7.26 (m, 2H), 7.19-7.16 (m, 3H), 4.62 (dd, J = 17.6, 2.8 Hz, 1H), 4.37 (dd, J = 50.6, 2.8 Hz, 1H), 3.30-3.25 (m, 1H), 3.09-3.00 (m, 2H), 2.78-2.73 (m, 1H), 2.66-2.62 (m, 1H), 1.90-1.79 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.0, 166.8 (d, $J_{C\text{-}F}$ = 260.0 Hz), 141.6, 137.0, 133.2, 128.6, 128.4, 128.1, 125.9, 91.4 (d, $J_{C\text{-}F}$ = 20.0 Hz), 41.0, 38.0 (d, $J_{C\text{-}F}$ = 25.6 Hz), 33.4, 33.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -106.7 (1F). HRMS (ESI) calcd for $C_{19}H_{19}FNaO$ [M + Na $^+$], 305.1312; found: 305.1308.



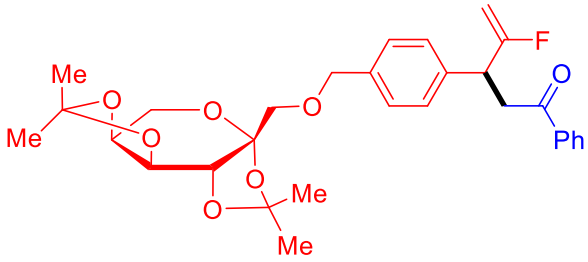
4-Fluoro-3-(4-((((2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)phenyl)-1-phenylpent-4-en-1-one (3an). (42.2 mg, 90%, dr = 1:1). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 7.6 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.64-4.60 (m, 2H), 4.38 (dd, J = 49.8, 3.0 Hz, 1H), 4.35-4.30 (m, 2H), 3.61-3.56 (m, 1H), 3.45-3.41 (m, 1H), 3.17-3.13 (m, 1H), 2.30-2.26 (m, 1H), 2.19-2.17 (m, 1H), 1.67-1.60 (m, 2H), 1.38-1.32 (m, 1H), 1.29-1.26 (m, 1H), 0.99-0.82 (m, 9H), 0.68 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 167.0 (d, $J_{C\text{-}F}$ = 259.8 Hz), 139.0, 138.1, 136.6, 133.2, 128.6, 128.2, 128.1, 128.0, 127.8, 90.9 (d, $J_{C\text{-}F}$ = 20.2 Hz), 78.7, 70.0, 48.2, 43.1 (d, $J_{C\text{-}F}$ = 26.6 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.7 Hz), 40.2, 34.5, 31.5, 25.4, 23.1, 22.3, 21.0, 16.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.0 (0.5F), -99.1 (0.5F). HRMS (APCI) calcd for $C_{28}H_{36}FO_2$ [M + H $^+$], 423.2694; found: 423.2689.



4-Fluoro-3-((8R,9S,13S,14S)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-1-phenylpent-4-en-1-one (3ao). (44.1 mg, 93%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 1H), 7.05 (s, 1H), 4.62 (dd, J = 17.4, 2.8 Hz, 1H), 4.38 (dd, J = 49.8, 2.8 Hz, 1H), 4.26 (dt, J = 17.4, 7.0 Hz, 1H), 3.96-3.86 (m, 4H), 3.60 (dd, J = 17.3, 7.4 Hz, 1H), 3.39 (dd, J = 17.3, 7.4 Hz, 1H), 2.85-2.84 (m, 2H), 2.33-2.30 (m, 1H), 2.27-2.23 (m, 1H), 2.04-2.00 (m, 1H), 1.90-1.88 (m, 1H), 1.86-1.81 (m, 1H), 1.79-1.73 (m, 2H), 1.65-1.60 (m, 1H), 1.54-1.32 (m, 5H), 0.87 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.0, 167.0 (d, $J_{C\text{-}F}$ = 260.0 Hz), 139.4, 137.1, 137.0, 136.7, 133.2, 128.6, 128.2, 128.0, 125.6, 124.8, 119.3, 90.8 (d, $J_{C\text{-}F}$ = 20.6 Hz), 65.2, 64.5, 49.4, 46.1, 43.9, 42.9 (d, $J_{C\text{-}F}$ = 27.0 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.4 Hz), 38.7, 34.2, 30.7, 29.5, 26.9, 25.8, 22.3, 14.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.3 (1F). HRMS (APCI) calcd for $C_{31}H_{36}FO_3$ [M + H $^+$], 475.2643; found: 475.2641.

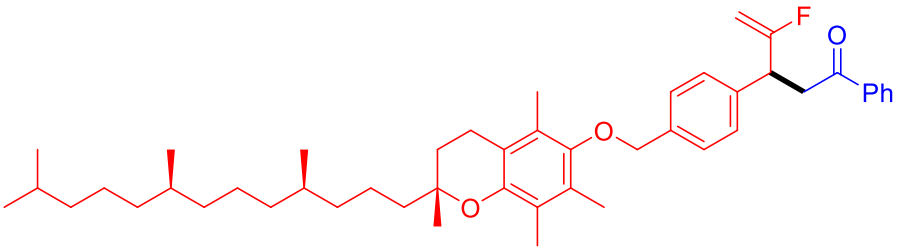


3-(4-((((3aR,5R)-5-((R)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)methyl)phenyl)-4-fluoro-1-phenylpent-4-en-1-one (3ap). (49.4 mg, 94%). Isolated by column chromatography (petroleum ether: ethyl acetate = 5:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 5.89 (s, 1H), 4.66-4.57 (m, 4H), 4.42-4.30 (m, 3H), 4.14-4.09 (m, 2H), 4.01-3.98 (m, 2H), 3.60 (dd, J = 17.4, 6.8 Hz, 1H), 3.45 (dd, J = 17.4, 6.8 Hz, 1H), 1.49 (s, 3H), 1.42 (d, J = 2.0 Hz, 3H), 1.36 (d, J = 5.8 Hz, 3H), 1.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.8, 166.8 (d, $J_{C\text{-}F}$ = 260.2 Hz), 139.5, 136.6, 133.3, 128.6, 128.0, 127.9, 111.7, 108.9, 105.2, 91.0 (d, $J_{C\text{-}F}$ = 20.4 Hz), 82.6, 81.6, 81.2, 72.4, 71.9, 67.3, 43.1 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 26.8, 26.7, 26.2, 25.4; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.3 (1F). HRMS (APCI) calcd for $C_{30}H_{35}FNaO_7$ [M + Na $^+$], 549.2259; found: 549.2253.

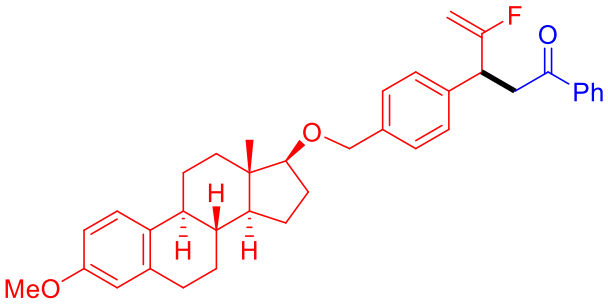


4-Fluoro-1-phenyl-3-(4-((((3aR,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methoxy)methyl)phenyl)pent-4-en-1-one (3aq). (51 mg, 97%). Isolated by column chromatography (petroleum ether: ethyl acetate = 5:1, R_f = 0.3); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.8 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 4.66-4.61 (m, 2H), 4.58 (dd, J = 8.0, 2.2 Hz, 1H), 4.55 (dd, J = 12.4, 2.4 Hz, 1H), 4.42-4.41 (m, 1H), 4.40-4.30 (m, 2H), 4.22 (d, J = 8.0 Hz, 1H), 3.91 (dd, J = 13.0, 1.6 Hz, 1H), 3.72 (d, J = 13.0 Hz, 1H), 3.62-3.56 (m, 3H), 3.43 (dd, J = 17.4, 4.2 Hz, 1H), 1.54 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 166.9 (d, $J_{C\text{-}F}$ = 260.2 Hz), 139.2, 137.1, 136.6, 133.2, 128.6, 128.0, 127.8, 127.7, 108.8, 108.5, 102.6, 91.0 (d, $J_{C\text{-}F}$ = 20.4 Hz), 73.3, 73.2, 71.5, 71.4, 70.9, 70.1, 70.0, 60.9, 43.1 (d, $J_{C\text{-}F}$ = 26.8 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 26.5, 25.7, 25.4, 23.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (APCI) calcd for $C_{30}H_{35}FNaO_7$ [M + Na $^+$], 549.2259;

found: 549.2254.

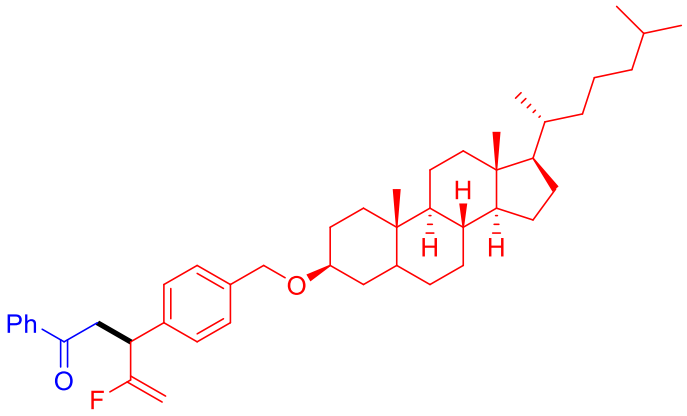


4-Fluoro-1-phenyl-3-(4-((((R)-2,5,7,8-tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)pent-4-en-1-one (3ar). (61.2 mg, 88%). Isolated by column chromatography (petroleum ether: ethyl acetate = 5:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46-7.43 (m, 4H), 7.38 (d, J = 7.8 Hz, 2H), 4.65 (s, 2H), 4.64 (dd, J = 17.4, 3.0 Hz, 1H), 4.38 (dd, J = 49.8, 3.0 Hz, 1H), 4.36 (dt, J = 17.4, 7.0 Hz, 1H), 3.61 (dd, J = 17.4, 7.0 Hz, 1H), 3.47 (dd, J = 17.4, 7.0 Hz, 1H), 2.57 (t, J = 6.7 Hz, 2H), 2.20 (s, 3H), 2.15 (s, 3H), 2.10 (s, 3H), 1.84-1.79 (m, 1H), 1.77-1.73 (m, 1H), 1.61-1.49 (m, 3H), 1.47-1.24 (m, 15H), 1.20-1.07 (m, 6H), 0.87 (s, 3H), 0.86 (s, 3H), 0.85 (s, 3H), 0.84 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 167.0 (d, $J_{C\text{-}F}$ = 260.2 Hz), 148.1, 148.0, 139.5, 137.1, 136.8, 133.4, 128.7, 128.1, 128.0, 127.9, 126.0, 123.0, 117.6, 91.1 (d, $J_{C\text{-}F}$ = 20.2 Hz), 74.9, 74.4, 43.3 (d, $J_{C\text{-}F}$ = 26.7 Hz), 41.5 (d, $J_{C\text{-}F}$ = 2.2 Hz), 40.1, 40.0, 39.4, 37.6, 37.5, 37.4, 37.3, 32.9, 32.8, 32.7, 31.4, 31.3, 28.0, 24.9, 24.5, 24.0, 22.8, 22.7, 21.1, 20.7, 19.9, 19.8, 19.7, 12.9, 12.0, 11.9; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.1 (1F). HRMS (APCI) calcd for $C_{47}H_{65}FNaO_3$ [M + Na $^+$], 719.4810; found: 719.4800.



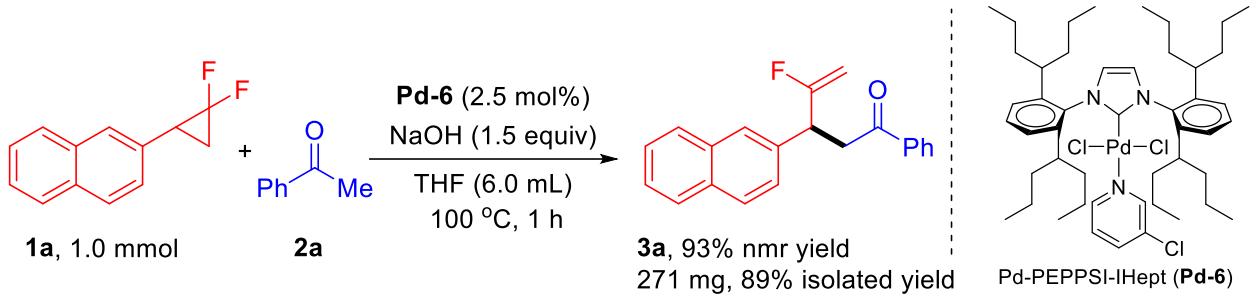
4-Fluoro-3-(4-((((8R,9S,13S,14S,17S)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl)oxy)methyl)phenyl)-1-phenylpent-4-en-1-one (3as). (52.5 mg, 95%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.3 Hz, 1H), 7.44 (t, J = 7.3 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 7.30 (d, J = 8.2 Hz, 2H), 7.19 (d, J = 8.3 Hz, 1H), 6.70 (dd, J = 8.6, 2.0 Hz, 1H), 6.62 (d, J = 1.6 Hz, 1H), 4.63 (dd, J = 17.4, 2.8 Hz, 1H), 4.53 (s, 2H), 4.38 (dd, J = 17.4, 2.8 Hz, 1H), 4.33 (dt, J = 15.8, 7.2 Hz, 1H), 3.76 (s, 3H), 3.59 (dd, J = 17.4, 6.8 Hz, 1H), 3.48 (t, J = 8.3 Hz, 1H), 3.44 (dd, J = 17.4, 6.8 Hz, 1H), 2.88-2.79 (m, 2H), 2.28-2.25 (m, 1H), 2.18-2.14 (m,

1H), 2.06-2.00 (m, 2H), 1.87-1.84 (m, 1H), 1.68-1.64 (m, 1H), 1.61-1.28 (m, 6H), 2.00-1.15 (m, 1H), 0.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 167.0 (d, $J_{C\text{-}F}$ = 260.0 Hz), 157.4, 138.9, 138.3, 137.9, 136.7, 133.2, 132.6, 128.6, 128.0, 127.7, 127.6, 126.3, 113.7, 111.4, 91.0 (d, $J_{C\text{-}F}$ = 19.8 Hz), 88.4, 71.3, 55.1, 50.2, 43.9, 43.4, 43.1 (d, $J_{C\text{-}F}$ = 26.4 Hz), 41.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 38.6, 37.9, 29.8, 28.0, 27.2, 26.4, 23.1, 11.8; ^{19}F NMR (565 MHz, $CDCl_3$) δ -98.6 (1F). HRMS (ESI) calcd for $C_{37}H_{41}FNaO_3$ [M + Na $^+$], 575.2932; found: 575.2938.



3-(4-((((3S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)phenyl)-4-fluoro-1-phenylpent-4-en-1-one (3at). (60.2 mg, 92%). Isolated by column chromatography (petroleum ether: ethyl acetate = 10:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.62 (dd, J = 17.4, 3.0 Hz, 1H), 4.52 (d, J = 12.4 Hz, 1H), 4.49 (d, J = 12.4 Hz, 1H), 4.36 (dd, J = 49.9, 3.0 Hz, 1H), 4.35-4.29 (m, 1H), 3.59 (dd, J = 17.3, 6.9 Hz, 1H), 3.43 (dd, J = 17.3, 6.9 Hz, 1H), 3.34-3.29 (m, 1H), 1.97-1.94 (m, 1H), 1.90-1.88 (m, 1H), 1.83-1.77 (m, 1H), 1.72-1.63 (m, 3H), 1.57-1.40 (m, 4H), 1.37-1.19 (m, 9H), 1.14-0.93 (m, 9H), 0.90-0.83 (m, 11H), 0.80 (s, 3H), 0.64 (s, 3H), 0.62-0.57 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 167.0 (d, $J_{C\text{-}F}$ = 260.2 Hz), 139.0, 138.2, 136.7, 133.2, 128.6, 128.0, 127.9, 127.8, 91.0 (d, $J_{C\text{-}F}$ = 20.4 Hz), 78.1, 69.4, 56.5, 56.2, 44.8, 43.1 (d, $J_{C\text{-}F}$ = 27.0 Hz), 42.6, 41.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 40.0, 39.5, 37.0, 36.1, 35.8, 35.7, 35.4, 34.8, 32.1, 28.8, 28.2, 28.0, 24.2, 23.8, 22.8, 22.5, 21.2, 18.6, 12.3, 12.0; ^{19}F NMR (565 MHz, $CDCl_3$) δ -99.2 (1F). HRMS (APCI) calcd for $C_{45}H_{64}FO_2$ [M + H $^+$], 655.4885; found: 655.4870.

4. Scale up synthesis of product 3a



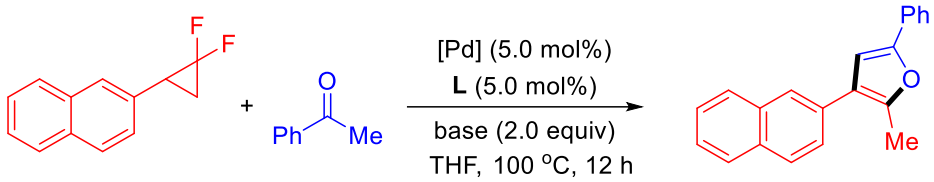
1a, 1.0 mmol **2a** **3a**, 93% nmr yield
271 mg, 89% isolated yield

Pd-PEPPSI-IHept (**Pd-6**)

A flame-dried reaction tube (50 cm^3) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IHept (22.6 mg, 2.5 mol%). The reaction tube was transferred to the glovebox and charged with **1a** (1.0 mmol), **2a** (2.0 mmol), NaOH (60.0 mg) and THF (6.0 mL). After that, the reaction mixture was sealed with Teflon cap, moved out of glovebox, and stirred at 100 °C for 1 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (10.0 mL). The solvent was evaporated *in vacuo* to give the crude product. NMR yield (93%) was determined by ^1H NMR using CH_2Br_2 as an internal standard. The residue was purified by column chromotography on silica gel to give the pure product **3a** (271 mg, 89% isolated yield).

5. Optimization of the reaction conditions for furan product

Table S1. Optimization of the reaction conditions[a]



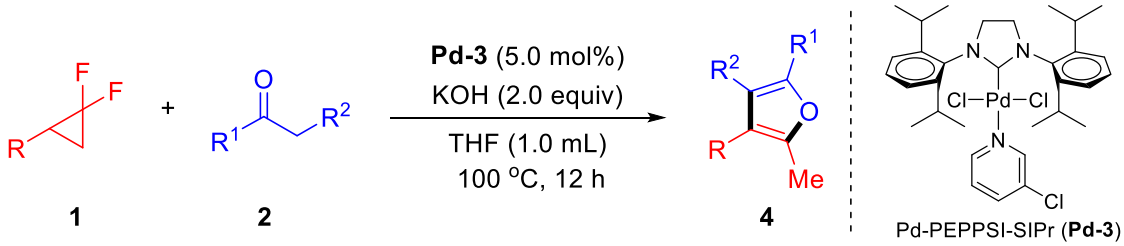
1a **2a** **4a**

entry	[Pd]	**L**	base	yield **4a** (%)[b]
1	$Pd(OAc)_2$	XanPhos	KOH	trace
2	$Pd(OAc)_2$	RuPhos	KOH	N.D.
3	$Pd(OAc)_2$	DPEPhos	KOH	N.D.
4[c]	$Pd(OAc)_2$	PPh_3	KOH	N.D.
5	$Pd(OAc)_2$	dppe	KOH	N.D.
6	$Pd(OAc)_2$	dppf	KOH	N.D.
7	$Pd(OAc)_2$	dtbbpy	KOH	N.D.
8	$Pd(OAc)_2$	IMes•HCl	KOH	trace
9	$Pd(OAc)_2$	SIMes•HCl	KOH	trace
10	$Pd(OAc)_2$	ICy•HCl	KOH	N.D.
11	$Pd(OAc)_2$	IPr•HCl	KOH	54

12	$Pd(OAc)_2$	SIPr•HCl	KOH	75
13	Pd-PEPPSI-SIPr	-	KOH	75
14	Pd-PEPPSI-SIPr	-	NaOH	67
15	Pd-PEPPSI-SIPr	-	NaOMe	58
16	Pd-PEPPSI-SIPr	-	LiO^{t}Bu	N.D.
17	Pd-PEPPSI-SIPr	-	DBU	N.D.
18	Pd-PEPPSI-SIPr	-	K_3PO_4	N.D.
19	Pd-PEPPSI-SIPr	-	K_2CO_3	N.D.
20	Pd-PEPPSI-SIPr	-	Cs_2CO_3	N.D.
21	$Pd(OAc)_2$	-	KOH	N.D.

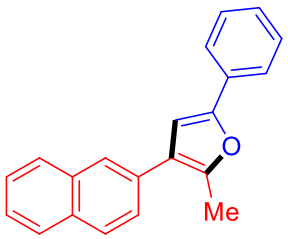
[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), palladium catalyst (5.0 mol%), ligand (5.0 mol%), base (0.2 mmol), THF (1.0 mL), 100 °C, 12 h under N_2 unless otherwise noted. [b]NMR yields were based on **1a** and determined by ^{1}H NMR using CH_2Br_2 as an internal standard. [c]ligand (10%). N.D. = not detected.

6. General procedure and characterization data for product 4

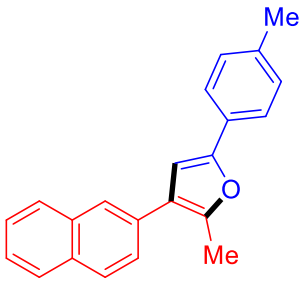


1 **2** **4**

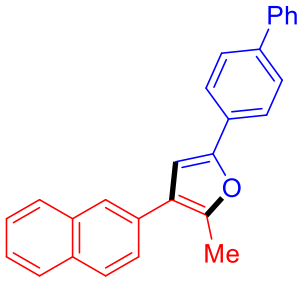
A flame-dried reaction tube (10 cm^3) equipped with a magnetic stir bar was charged with Pd-PEPPSI-SIPr (3.4 mg, 5 mol%). The reaction tube was transferred to the glovebox and charged with **1** (0.1 mmol), **2** (0.2 mmol), KOH (11.2 mg) and THF (1.0 mL). After that, the reaction mixture was sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 12 h. After the mixture was cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by EtOAc (3.0 mL). The solvent was evaporated *in vacuo* to give the crude product. The crude mixture was analyzed by GC-MS. NMR yield was determined by ^{1}H NMR using CH_2Br_2 as an internal standard. The residue was purified by column chromotography on silica gel to give the pure product **4**. **Note**: Use of the glovebox is not necessary. The reaction can be successfully performed with standard Schlenk line procedure.



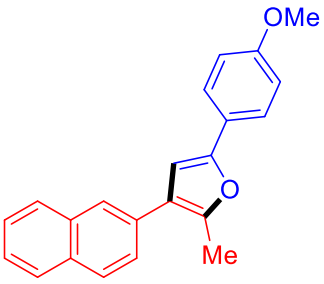
2-Methyl-3-(naphthalen-2-yl)-5-phenylfuran (4a). (21 mg, 73%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.88 (m, 4H), 7.76-7.74 (m, 2H), 7.63 (dd, J = 8.4, 1.7 Hz, 1H), 7.56-7.48 (m, 2H), 7.45-7.42 (m, 2H), 7.31-7.28 (m, 1H), 6.93 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 148.0, 133.6, 132.1, 131.5, 130.9, 128.7, 128.2, 127.8, 127.7, 127.1, 126.3, 126.1, 125.9, 125.7, 123.5, 123.1, 106.6, 13.4. HRMS (APCI) calcd for $C_{21}H_{17}O$ [M + H^+], 285.1274; found: 285.1270.



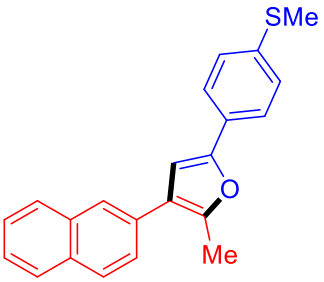
2-Methyl-3-(naphthalen-2-yl)-5-(p-tolyl)furan (4b). (21 mg, 72%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.83 (m, 4H), 7.60-7.57 (m, 3H), 7.50-7.44 (m, 2H), 7.20 (d, J = 8.0 Hz, 2H), 6.83 (s, 1H), 2.58 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0, 147.5, 136.9, 133.6, 132.1, 131.6, 129.3, 128.2, 128.1, 127.8, 127.7, 126.2, 126.1, 125.8, 125.6, 123.4, 122.9, 105.8, 21.3, 13.3; HRMS (APCI) calcd for $C_{22}H_{19}O$ [M + H^+], 299.1430; found: 299.1425.



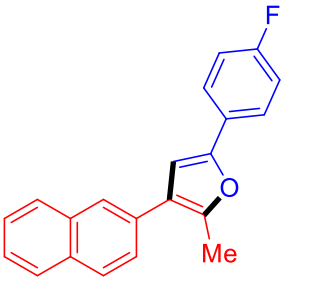
5-([1,1'-Biphenyl]-4-yl)-2-methyl-3-(naphthalen-2-yl)furan (4c). (25 mg, 69%). Isolated by column chromatography (petroleum ether: ethyl acetate = 60:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.88 (m, 4H), 7.81 (d, J = 8.4 Hz, 2H), 7.69-7.66 (m, 4H), 7.64 (dd, J = 8.4, 1.8 Hz, 1H), 7.56-7.47 (m, 4H), 7.40-7.36 (m, 1H), 6.97 (s, 1H), 2.65 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 148.2, 140.7, 139.7, 133.6, 132.2, 131.5, 129.8, 128.8, 128.2, 127.8, 127.7, 127.4, 127.3, 126.9, 126.3, 126.1, 125.9, 125.7, 123.9, 123.2, 106.8, 13.4; HRMS (APCI) calcd for $C_{27}H_{21}O$ [M + H^+], 361.1587; found: 361.1582.



5-(4-Methoxyphenyl)-2-methyl-3-(naphthalen-2-yl)furan (4d). (22 mg, 70%). Isolated by column chromatography (petroleum ether: ethyl acetate = 100:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92-7.87 (m, 4H); 7.67 (d, J = 8.8 Hz, 2H), 7.62 (dd, J = 8.4, 1.7 Hz, 1H), 7.54-7.48 (m, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.79 (s, 1H), 3.88 (s, 3H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.9, 151.8, 147.2, 133.6, 132.1, 131.7, 128.2, 127.8, 127.7, 126.3, 126.1, 125.8, 125.6, 124.9, 124.0, 122.9, 114.2, 105.0, 55.4, 13.3. HRMS (APCI) calcd for $C_{22}H_{19}O_2$ [M + H$^+$], 315.1380; found: 315.1379.

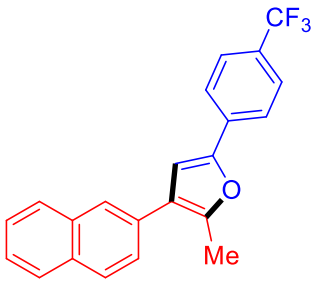


2-Methyl-5-(4-(methylthio)phenyl)-3-(naphthalen-2-yl)furan (4e). (22 mg, 68%). Isolated by column chromatography (petroleum ether: ethyl acetate = 100:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, J = 8.6 Hz, 1H), 7.90-7.87 (m, 3H), 7.65 (d, J = 8.6 Hz, 2H), 7.61 (dd, J = 8.4, 1.7 Hz, 1H), 7.54-7.48 (m, 2H), 7.32 (d, J = 8.6 Hz, 2H), 6.88 (s, 1H), 2.62 (s, 3H), 2.55 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 147.8, 137.1, 133.6, 132.1, 131.5, 128.2, 127.9, 127.8, 127.7, 126.9, 126.3, 126.1, 125.9, 125.7, 123.9, 123.1, 106.3, 15.9, 13.4. HRMS (APCI) calcd for $C_{22}H_{19}OS$ [M + H$^+$], 331.1151; found: 331.1157.

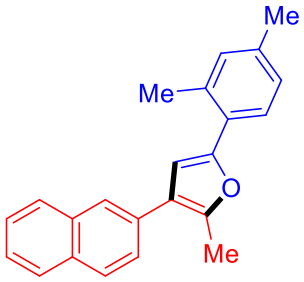


5-(4-Fluorophenyl)-2-methyl-3-(naphthalen-2-yl)furan (4f). (20 mg, 66%). Isolated by column chromatography (petroleum ether: ethyl acetate = 60:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.88 (m, 4H), 7.72-7.68 (m, 2H), 7.61 (dd, J = 8.4, 1.6 Hz, 1H), 7.55-7.49 (m, 2H), 7.12 (t, J = 8.6 Hz, 2H), 6.85 (s, 1H), 2.62 (s, 3H); ^{13}C NMR

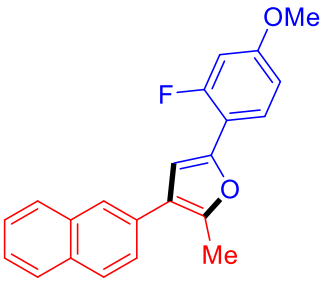
(150 MHz, $CDCl_3$) δ 162.0 (d, $J_{C\text{-}F}$ = 246.4 Hz), 151.0, 147.9, 133.6, 132.1, 131.4, 128.2, 127.8, 127.7, 127.2 (d, $J_{C\text{-}F}$ = 3.0 Hz), 126.3, 126.0, 125.9, 125.7, 125.2, 125.1, 123.1, 115.7 (d, $J_{C\text{-}F}$ = 21.8 Hz), 106.2, 13.3; HRMS (APCI) calcd for $C_{21}H_{16}FO$ [M + H^+], 303.1180; found: 303.1179.



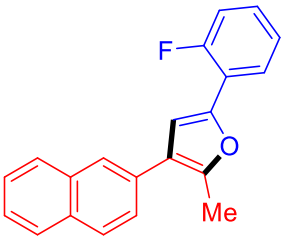
2-Methyl-3-(naphthalen-2-yl)-5-(4-(trifluoromethyl)phenyl)furan (4g). (22 mg, 63%). Isolated by column chromatography (petroleum ether: ethyl acetate = 60:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94-7.88 (m, 4H), 7.82 (d, J = 8.4 Hz, 2H), 7.67 (d, J = 8.4 Hz, 2H), 7.61 (dd, J = 8.4, 1.6 Hz, 1H), 7.56-7.50 (m, 2H), 7.04 (s, 1H), 2.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.3, 149.2, 133.9, 133.6, 132.2, 131.0, 128.5 (q, $J_{C\text{-}F}$ = 34.0 Hz), 128.3, 127.8, 127.7, 126.4, 126.0, 125.9, 125.8, 125.7 (q, $J_{C\text{-}F}$ = 3.4 Hz), 124.2 (q, $J_{C\text{-}F}$ = 272.0 Hz), 122.9, 108.6, 13.4; HRMS (ESI) calcd for $C_{22}H_{16}F_3O$ [M + H^+], 353.1148; found: 353.1144.



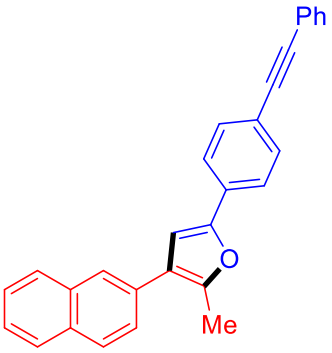
5-(2,4-Dimethylphenyl)-2-methyl-3-(naphthalen-2-yl)furan (4h). (22 mg, 71%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.88 (m, 4H), 7.69 (d, J = 8.6 Hz, 1H), 7.64 (dd, J = 8.6, 1.8 Hz, 1H), 7.55-7.48 (m, 2H), 7.13-7.11 (m, 2H), 6.75 (s, 1H), 2.63 (s, 3H), 2.57 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 147.1, 137.0, 134.2, 133.7, 132.1, 131.9, 131.8, 128.2, 127.8, 127.7, 127.4, 126.8, 126.7, 126.3, 126.2, 125.8, 125.6, 122.7, 109.6, 21.9, 21.1, 13.3. HRMS (APCI) calcd for $C_{23}H_{21}O$ [M + H^+], 313.1587; found: 313.1584.



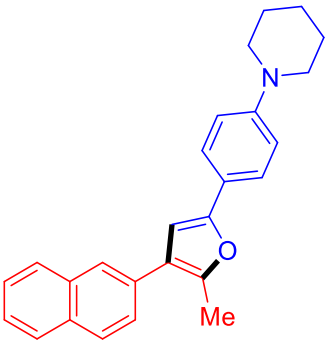
5-(2-Fluoro-4-methoxyphenyl)-2-methyl-3-(naphthalen-2-yl)furan (4i). (24 mg, 72%). Isolated by column chromatography (petroleum ether: ethyl acetate = 60:1, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92-7.87 (m, 4H), 7.79 (t, J = 8.8 Hz, 1H), 7.63 (dd, J = 8.6, 1.5 Hz, 1H), 7.55-7.47 (m, 2H), 6.98 (d, J = 3.6 Hz, 1H), 6.80 (dd, J = 8.6, 2.6 Hz, 1H), 6.74 (dd, J = 12.8, 2.6 Hz, 1H), 3.87 (s, 3H), 2.62 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.1 (d, $J_{C\text{-}F}$ = 250.4 Hz), 159.6 (d, $J_{C\text{-}F}$ = 10.8 Hz), 147.1, 146.0 (d, $J_{C\text{-}F}$ = 3.2 Hz), 133.6, 131.8 (d, $J_{C\text{-}F}$ = 54.8 Hz), 128.2, 127.8, 127.7, 126.4 (d, $J_{C\text{-}F}$ = 5.2 Hz), 126.2, 126.1, 125.9, 125.6, 123.1, 112.1 (d, $J_{C\text{-}F}$ = 12.8 Hz), 110.2 (d, $J_{C\text{-}F}$ = 2.8 Hz), 109.7 (d, $J_{C\text{-}F}$ = 10.8 Hz), 102.1 (d, $J_{C\text{-}F}$ = 25.1 Hz), 55.6, 13.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.0. HRMS (APCI) calcd for $C_{22}H_{18}FO_2$ [M + H$^+$], 333.1285; found: 333.1291.



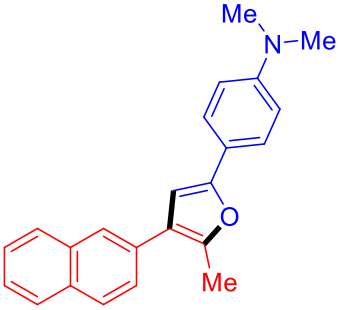
5-(2-Fluorophenyl)-2-methyl-3-(naphthalen-2-yl)furan (4j). (21 mg, 68%). Isolated by column chromatography (petroleum ether, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93-7.88 (m, 5H), 7.64 (dd, J = 8.6, 1.6 Hz, 1H), 7.55-7.48 (m, 2H), 7.27-7.21 (m, 2H), 7.19-7.14 (m, 1H), 7.13-7.12 (m, 1H), 2.64 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.4 (d, $J_{C\text{-}F}$ = 250.0 Hz), 147.9 (d, $J_{C\text{-}F}$ = 1.0 Hz), 145.9 (d, $J_{C\text{-}F}$ = 3.0 Hz), 133.6, 132.2, 131.4, 128.2, 127.9 (d, $J_{C\text{-}F}$ = 8.2 Hz), 127.8, 127.7, 126.3, 126.1, 125.9, 125.7, 125.6 (d, $J_{C\text{-}F}$ = 3.4 Hz), 124.3 (d, $J_{C\text{-}F}$ = 3.4 Hz), 123.4 (d, $J_{C\text{-}F}$ = 1.6 Hz), 119.1 (d, $J_{C\text{-}F}$ = 12.1 Hz), 115.9 (d, $J_{C\text{-}F}$ = 21.5 Hz), 111.8 (d, $J_{C\text{-}F}$ = 11.6 Hz), 13.3; ^{19}F NMR (565 MHz, $CDCl_3$) δ -114.1. HRMS (APCI) calcd for $C_{21}H_{16}FO$ [M + H$^+$], 303.1180; found: 303.1170.



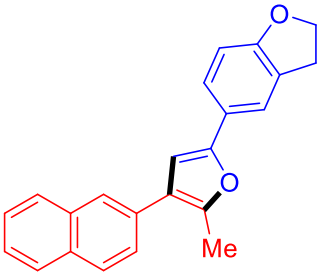
2-Methyl-3-(naphthalen-2-yl)-5-(4-(phenylethynyl)phenyl)furan (4k). (23 mg, 61%). Isolated by column chromatography (petroleum ether: ethyl acetate = 100:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.92 (d, J = 8.6 Hz, 1H), 7.90-7.88 (m, 3H), 7.72 (d, J = 8.6 Hz, 2H), 7.63-7.56 (m, 5H), 7.54-7.49 (m, 2H), 7.41-7.36 (m, 3H), 6.97 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2, 148.5, 133.6, 132.2, 132.0, 131.6, 131.3, 130.5, 128.4, 128.3, 127.8, 127.7, 126.3, 126.1, 126.0, 125.8, 123.4, 123.3, 123.2, 121.6, 107.6, 90.2, 89.6, 13.4. HRMS (APCI) calcd for $C_{29}H_{21}O$ [M + H$^+$], 385.1587; found: 385.1588.



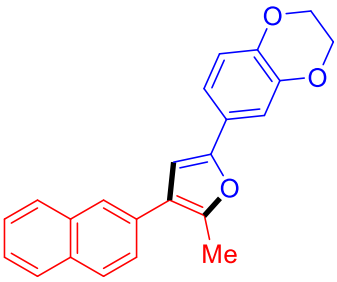
1-(4-(5-Methyl-4-(naphthalen-2-yl)furan-2-yl)phenyl)piperidine (4l). (19 mg, 52%). Isolated by column chromatography (petroleum ether: ethyl acetate = 60:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90-7.86 (m, 4H), 7.63-7.61 (m, 3H), 7.53-7.47 (m, 2H), 7.00 (br, 2H), 7.76 (s, 1H), 3.24 (t, J = 5.6 Hz, 4H), 2.61 (s, 3H), 1.78-1.73 (m, 4H), 1.65-1.61 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.3, 146.8, 133.6, 132.0, 131.9, 128.1, 127.8, 127.7, 126.2, 126.1, 125.8, 125.6, 124.5, 122.8, 116.3, 104.4, 50.4, 25.7, 24.3, 13.3. HRMS (ESI) calcd for $C_{26}H_{26}NO$ [M + H$^+$], 368.2009; found: 368.2022.



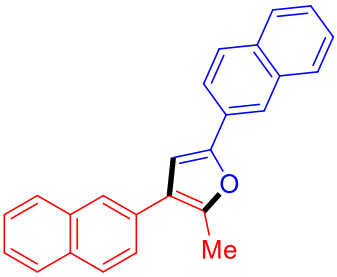
***N*,*N*-Dimethyl-4-(5-methyl-4-(naphthalen-2-yl)furan-2-yl)aniline (4m).** (17 mg, 53%). Isolated by column chromatography (petroleum ether:ethyl acetate = 20:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.83 (m, 4H), 7.60-7.58 (m, 3H), 7.50-7.44 (m, 2H), 6.76 (d, J = 8.8 Hz, 2H), 6.69 (s, 1H), 2.99 (s, 6H), 2.58 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.6, 149.7, 146.4, 133.6, 132.0, 131.9, 128.0, 127.8, 127.6, 126.2, 125.7, 125.5, 124.7, 122.7, 119.8, 112.5, 103.6, 40.5, 13.3; HRMS (APCI) calcd for $C_{23}H_{22}NO$ [M + H$^+$], 328.1696; found: 328.1692.



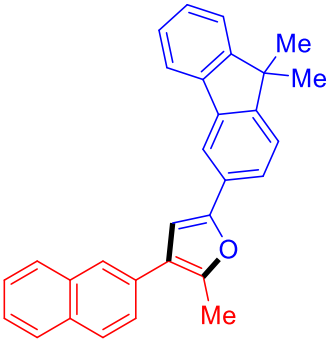
6-(5-Methyl-4-(naphthalen-2-yl)furan-2-yl)-2,3-dihydrobenzofuran (4n). (17 mg, 51%). Isolated by column chromatography (petroleum ether:ethyl acetate = 30:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.84 (m, 4H), 7.58 (d, J = 8.4 Hz, 1H), 7.56 (s, 1H), 7.50-7.45 (m, 3H), 6.82 (d, J = 8.2 Hz, 1H), 6.72 (s, 1H), 4.60 (t, J = 8.6 Hz, 2H), 3.25 (t, J = 8.6 Hz, 2H), 2.58 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 152.2, 146.9, 133.6, 132.0, 131.7, 128.1, 127.8, 127.6, 127.5, 126.2, 126.1, 125.8, 125.6, 124.0, 123.9, 122.8, 120.5, 109.4, 104.6, 71.4, 29.7, 13.3; HRMS (ESI) calcd for $C_{23}H_{19}O_2$ [M + H$^+$], 327.1380; found: 327.1375.



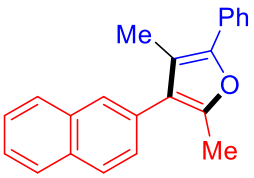
6-(5-Methyl-4-(naphthalen-2-yl)furan-2-yl)-2,3-dihydrobenzo[b][1,4]dioxine (4o) (18 mg, 53%). Isolated by column chromatography (petroleum ether:ethyl acetate = 30:1, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87-7.82 (m, 4H), 7.57 (dd, J = 8.4, 1.4 Hz, 1H), 7.49-7.44 (m, 2H), 7.23-7.18 (m, 2H), 6.88 (d, J = 8.4 Hz, 1H), 6.73 (s, 1H), 4.27 (s, 4H), 2.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 147.3, 143.7, 142.9, 133.6, 132.0, 131.6, 128.1, 127.8, 127.6, 126.2, 126.1, 125.8, 125.6, 124.8, 122.9, 117.5, 117.0, 112.5, 105.4, 64.5, 64.4, 13.3; HRMS (APCI) calcd for $C_{23}H_{19}O_3$ [M + H$^+$], 343.1329; found: 343.1322.



2-Methyl-3,5-di(naphthalen-2-yl)furan (4p). (21 mg, 63%). Isolated by column chromatography (petroleum ether: ethyl acetate = 60:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.95-7.83 (m, 8H), 7.66 (dd, J = 8.5, 1.6 Hz, 1H), 7.57-7.47 (m, 4H), 7.05 (s, 1H), 2.68 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.9, 148.3, 133.6, 132.6, 132.2, 131.5, 128.4, 128.2, 128.1, 127.8, 127.7, 126.5, 126.3, 126.1, 125.9, 125.8, 125.7, 123.3, 122.2, 121.6, 107.3, 13.4; HRMS (APCI) calcd for $C_{25}H_{19}O$ [M + H$^+$], 335.1430; found: 335.1427.

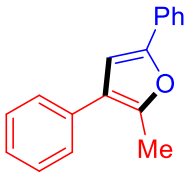


5-(9,9-Dimethyl-9H-fluoren-3-yl)-2-methyl-3-(naphthalen-2-yl)furan (4q). (26 mg, 65%). Isolated by column chromatography (petroleum ether, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88-7.84 (m, 4H), 7.78 (s, 1H), 7.73-7.68 (m, 3H), 7.60 (dd, J = 8.4, 1.4 Hz, 1H), 7.50-7.48 (m, 1H), 7.47-7.43 (m, 2H), 7.34-7.29 (m, 2H), 6.94 (s, 1H), 2.62 (s, 3H), 1.54 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 154.1, 153.8, 152.3, 147.8, 138.9, 138.2, 133.6, 132.1, 131.5, 129.8, 128.2, 127.8, 127.7, 127.2, 127.0, 126.3, 126.1, 125.8, 125.6, 123.2, 122.6, 122.5, 120.3, 119.9, 117.6, 106.4, 46.9, 27.2, 13.4; HRMS (APCI) calcd for $C_{30}H_{25}O$ [M + H$^+$], 401.1890; found: 401.1895.

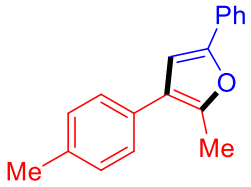


2,4-Dimethyl-3-(naphthalen-2-yl)-5-phenylfuran (4r). (16 mg, 44%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, J = 8.4 Hz, 1H), 7.88-7.85 (m, 2H), 7.74 (s, 1H), 7.68 (d, J = 7.6 Hz, 2H), 7.52-7.47 (m, 2H), 7.45-7.41 (m, 3H), 7.27-7.25 (m, 1H), 2.40 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 147.5, 147.0, 133.5, 132.2, 131.9, 131.1, 128.5, 128.3, 128.0, 127.9, 127.8, 127.7, 126.4, 126.1, 125.8, 125.3, 124.8, 116.6, 12.5, 10.9; HRMS (APCI) calcd for $C_{27}H_{21}O$ [M + H$^+$], 361.1587; found:

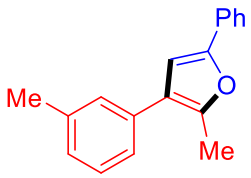
361.1589.



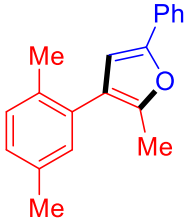
2-Methyl-3,5-diphenylfuran (4s).[3] (17 mg, 74%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.48-7.46 (m, 2H), 7.45-7.39 (m, 4H), 7.33-7.30 (m, 1H), 7.29-7.26 (m, 1H), 6.82 (s, 1H), 2.56 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.8, 147.8, 134.3, 131.1, 128.9, 128.8, 127.7, 127.2, 126.7, 123.6, 123.2, 106.6, 13.4.



2-Methyl-5-phenyl-3-(*p*-tolyl)furan (4t).[4] (18 mg, 73%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.42-7.39 (m, 2H), 7.38-7.35 (m, 2H), 7.28-7.25 (m, 3H), 6.80 (s, 1H), 2.54 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 147.3, 136.1, 131.1, 130.9, 129.3, 128.6, 127.4, 127.0, 123.4, 122.9, 106.5, 21.2, 13.2.

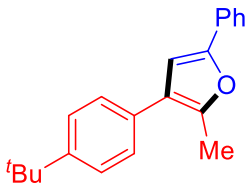


2-Methyl-5-phenyl-3-(m-tolyl)furan (4u). (17.6 mg, 71%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.6 Hz, 1H), 7.25-7.22 (m, 3H), 7.10 (d, J = 7.4 Hz, 1H), 6.78 (s, 1H), 2.52 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 147.5, 138.2, 134.0, 130.9, 128.6, 128.5, 128.2, 127.2, 127.0, 124.6, 123.4, 123.0, 106.5, 21.5, 13.2; HRMS (APCI) calcd for $C_{18}H_{17}O$ [M + H^+], 249.1274; found: 249.1271.

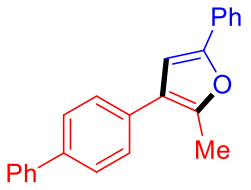


3-(2,5-Dimethylphenyl)-2-methyl-5-phenylfuran (4v). (18 mg, 70%). Isolated by column chromatography

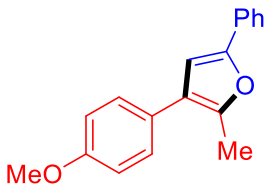
(petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.70-7.69 (m, 2H), 7.42-7.39 (m, 2H), 7.28-7.24 (m, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 7.07 (s, 1H), 6.64 (s, 1H), 2.37 (s, 3H), 2.32 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.2, 148.0, 135.1, 133.6, 133.4, 131.0, 130.8, 130.1, 128.6, 128.0, 126.9, 123.3, 122.7, 108.2, 20.9, 19.8, 12.5. HRMS (APCI) calcd for $C_{19}H_{19}O$ [M + H^+], 263.1430; found: 263.1434.



3-(4-(*tert*-Butyl)phenyl)-2-methyl-5-phenylfuran (4w). (20 mg, 68%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.49-7.47 (m, 2H), 7.43-7.39 (m, 4H), 7.28-7.25 (m, 1H), 6.81 (s, 1H), 2.56 (s, 3H), 1.40 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 149.4, 147.4, 131.1, 130.9, 128.6, 127.2, 127.0, 125.6, 123.4, 122.8, 106.5, 34.5, 31.4, 13.3. HRMS (APCI) calcd for $C_{21}H_{23}O$ [M + H^+], 291.1743; found: 291.1742.

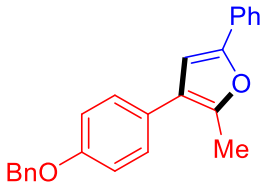


3-([1,1'-Biphenyl]-4-yl)-2-methyl-5-phenylfuran (4x). (22 mg, 71%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, J = 7.9 Hz, 2H), 7.65-7.61 (m, 4H), 7.51 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.24 (t, J = 7.4 Hz, 1H), 6.82 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.7, 147.7, 140.7, 139.2, 133.0, 130.8, 128.8, 128.6, 127.8, 127.3, 127.2, 127.0, 126.9, 123.4, 122.6, 106.3, 13.3; HRMS (APCI) calcd for $C_{23}H_{19}O$ [M + H^+], 311.1430; found: 311.1427.

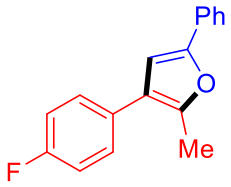


3-(4-Methoxyphenyl)-2-methyl-5-phenylfuran (4y). (17 mg, 63%). Isolated by column chromatography (petroleum ether: ethyl acetate = 100:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.42-7.37 (m, 4H), 7.28-7.25 (m, 1H), 6.99 (d, J = 8.7 Hz, 2H), 6.77 (s, 1H), 3.87 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 158.3, 151.4, 147.0, 130.9, 128.6, 126.9, 126.6, 123.4, 122.6, 114.1, 106.6, 55.3, 13.1. HRMS (APCI)

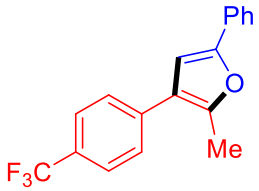
calcd for $C_{18}H_{17}O_2$ [M + H^+], 265.1223; found: 265.1219.



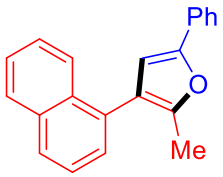
3-(4-(Benzyloxy)phenyl)-2-methyl-5-phenylfuran (4z). (21 mg, 61%). Isolated by column chromatography (petroleum ether: ethyl acetate = 100:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.70 (m, 2H), 7.50-7.49 (m, 2H), 7.45-7.42 (m, 2H), 7.41-7.37 (m, 5H), 7.27-7.25 (m, 1H), 7.06 (d, J = 8.7 Hz, 2H), 6.78 (s, 1H), 5.14 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.5, 151.5, 147.0, 137.0, 130.9, 128.7, 128.6, 128.0, 127.5, 127.0, 126.9, 123.4, 122.6, 115.0, 106.5, 70.1, 13.1. HRMS (APCI) calcd for $C_{24}H_{21}O_2$ [M + H^+], 341.1536; found: 341.1543.



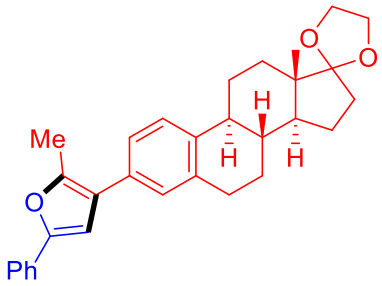
3-(4-Fluorophenyl)-2-methyl-5-phenylfuran (4aa).[3] (18 mg, 72%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.43-7.40 (m, 4H), 7.30-7.26 (m, 1H), 7.15-7.12 (m, 2H), 6.76 (s, 1H), 2.52 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 161.6 (d, $J_{C\text{-}F}$ = 245.8 Hz), 151.7, 141.4, 130.8, 130.1 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 128.7, 127.1, 123.4, 122.2, 115.5 (d, $J_{C\text{-}F}$ = 21.2 Hz), 106.4, 13.1; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.1.



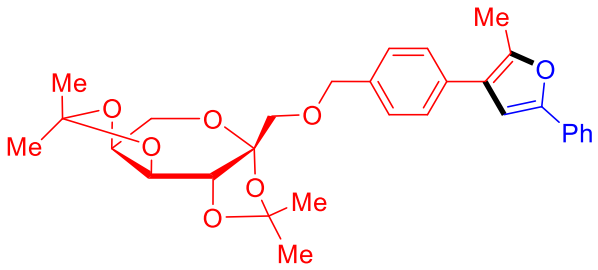
2-Methyl-5-phenyl-3-(4-(trifluoromethyl)phenyl)furan (4ab). (22 mg, 73%). Isolated by column chromatography (petroleum ether, R_f = 0.5); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.66 (d, J = 7.8 Hz, 2H), 7.66-7.64 (m, 2H), 7.52 (d, J = 7.8 Hz, 2H), 7.40-7.37 (m, 2H), 7.27-7.24 (m, 1H), 6.78 (s, 1H), 2.53 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.1, 148.4, 137.7, 130.5, 128.7, 128.4 (q, $J_{C\text{-}F}$ = 32.8 Hz), 127.5, 127.3, 125.5 (q, $J_{C\text{-}F}$ = 3.4 Hz), 124.3 (q, $J_{C\text{-}F}$ = 271.4 Hz), 123.5, 122.0, 105.9, 13.3. HRMS (APCI) calcd for $C_{18}H_{14}F_3O$ [M + H^+], 303.0991; found: 303.0987.



2-Methyl-3-(naphthalen-1-yl)-5-phenylfuran (4ac). (16 mg, 55%). Isolated by column chromatography (petroleum ether, R_f = 0.6); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 (d, J = 7.8 Hz, 1H), 7.90 (d, J = 7.8 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.53-7.46 (m, 3H), 7.43-7.39 (m, 3H), 7.27-7.25 (m, 1H), 6.80 (s, 1H), 2.32 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 148.9, 133.8, 132.2, 131.8, 130.9, 128.7, 128.3, 127.6, 127.4, 127.0, 126.0, 125.8, 125.4, 123.4, 121.5, 108.9, 12.6; HRMS (ESI) calcd for $C_{21}H_{17}O$ [M + H^+], 285.1274; found: 285.1272.

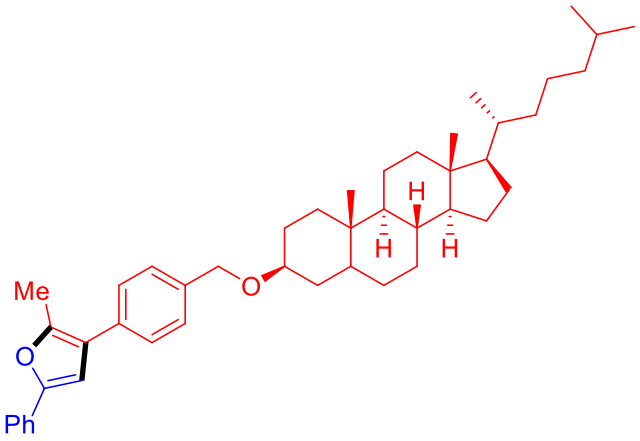


(8R,9S,13S,14S)-13-Methyl-3-(2-methyl-5-phenylfuran-3-yl)-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolane] (4ae). (27.7 mg, 61%). Isolated by column chromatography (petroleum ether: ethyl acetate = 50:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.42-7.37 (m, 3H), 7.27-7.24 (m, 2H), 7.19 (s, 1H), 4.02-3.91 (m, 4H), 2.96-2.94 (m, 2H), 2.54 (s, 3H), 2.44-2.33 (m, 2H), 2.10-2.05 (m, 1H), 1.99-1.95 (m, 1H), 1.92-1.80 (m, 3H), 1.73-1.67 (m, 1H), 1.62-1.36 (m, 8H), 0.93 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.5, 147.4, 138.8, 137.0, 131.3, 130.9, 128.6, 128.0, 126.9, 125.7, 124.8, 123.4, 122.8, 119.5, 106.6, 65.3, 64.6, 49.5, 46.2, 44.1, 38.9, 34.3, 30.8, 29.7, 27.0, 26.0, 22.4, 14.4, 13.2. HRMS (APCI) calcd for $C_{31}H_{35}O_3$ [M + H^+], 455.2581; found: 455.2573.

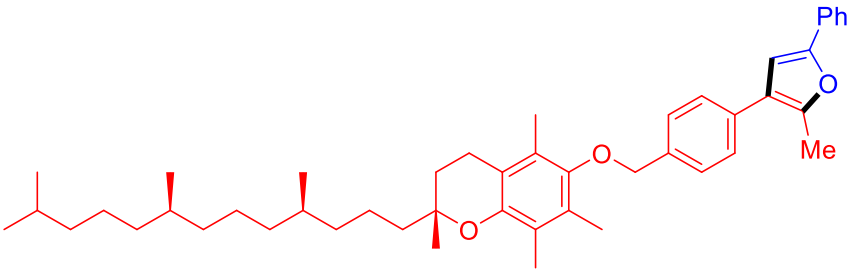


(3aR,5aS,8aS,8bR)-2,2,7,7-Tetramethyl-3a-(((4-(2-methyl-5-phenylfuran-3-yl)benzyl)oxy)methyl)tetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (4af). (27.3 mg, 54%). Isolated by column chromatography (petroleum

ether: ethyl acetate = 4:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 2H), 7.41-7.36 (m, 6H), 7.24 (t, J = 7.6 Hz, 1H), 6.77 (s, 1H), 4.70 (d, J = 12.2 Hz, 1H), 4.62-4.60 (m, 2H), 4.46 (d, J = 1.8 Hz, 1H), 4.23 (d, J = 7.8 Hz, 1H), 3.93 (d, J = 13.0 Hz, 1H), 3.74 (d, J = 13.0 Hz, 1H), 3.66 (d, J = 10.6 Hz, 1H), 3.62 (d, J = 10.6 Hz, 1H), 2.51 (s, 3H), 1.56 (s, 3H), 1.45 (s, 3H), 1.42 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 147.6, 136.3, 133.3, 130.8, 128.6, 127.9, 127.4, 127.0, 123.4, 122.8, 108.9, 108.5, 106.4, 102.7, 73.5, 71.6, 71.0, 70.3, 70.2, 61.0, 26.6, 25.8, 24.0, 13.2; HRMS (ESI) calcd for $C_{30}H_{35}O_7$ [M + H$^+$], 507.2377; found: 507.2374.



3-(4-((((3S,8R,9S,10S,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)methyl)phenyl)-2-methyl-5-phenylfuran (4ag). (36.1 mg, 57%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (d, J = 7.6 Hz, 2H), 7.41-7.36 (m, 6H), 7.25-7.23 (m, 1H), 6.77 (s, 1H), 4.58 (d, J = 11.8 Hz, 1H), 4.56 (d, J = 11.8 Hz, 1H), 3.39-3.33 (m, 1H), 2.51 (s, 3H), 1.97-1.92 (m, 2H), 1.82-1.77 (m, 1H), 1.74-1.64 (m, 3H), 1.54-1.46 (m, 4H), 1.37-1.22 (m, 10H), 1.14-1.03 (m, 6H), 0.95-0.80 (m, 16H), 0.65-0.59 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 147.5, 137.4, 133.1, 130.8, 128.6, 127.9, 127.4, 127.0, 123.4, 122.8, 106.4, 78.1, 69.6, 56.5, 56.3, 54.4, 44.9, 42.6, 40.0, 39.5, 37.0, 36.2, 35.8, 35.7, 35.5, 34.9, 32.1, 28.9, 28.3, 28.2, 28.0, 24.2, 23.8, 22.8, 22.6, 21.2, 18.7, 13.2, 12.3, 12.1; HRMS (APCI) calcd for $C_{45}H_{63}O_2$ [M + H$^+$], 635.4823; found: 635.4821.

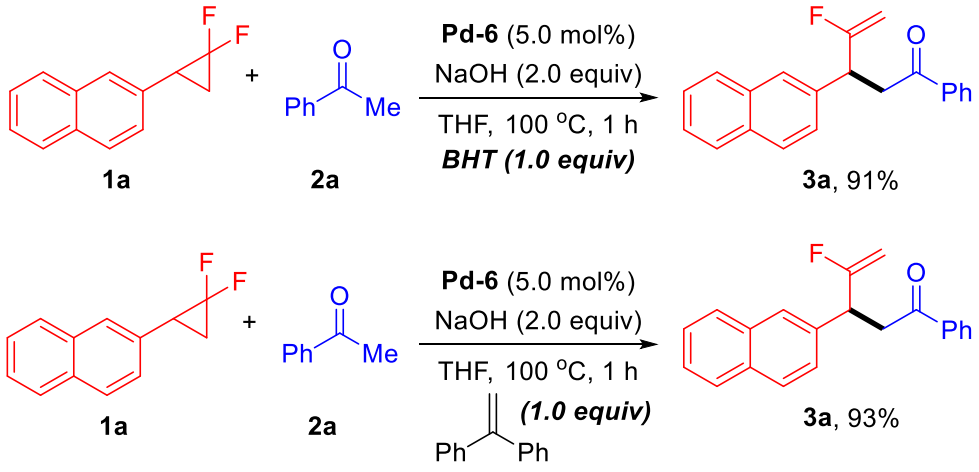


(R)-2,5,7,8-tetramethyl-6-((4-(2-Methyl-5-phenylfuran-3-yl)benzyl)oxy)-2-((4R,8R)-4,8,12-trimethyltridecyl)

chromane (4ah). (37.2 mg, 55%). Isolated by column chromatography (petroleum ether: ethyl acetate = 20:1, R_f = 0.4); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, J = 7.6 Hz, 2H), 7.55 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.6 Hz, 2H), 7.24 (t, J = 7.6 Hz, 1H), 6.79 (s, 1H), 4.72 (s, 2H), 2.60 (t, J = 6.2 Hz, 2H), 2.53 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H), 2.12 (s, 3H), 1.86-1.75 (m, 2H), 1.54-1.08 (m, 26H), 0.87-0.84 (m, 12H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.6, 148.1, 147.9, 147.6, 136.2, 133.6, 130.8, 128.6, 128.0, 127.9, 127.6, 127.0, 125.9, 123.4, 122.9, 122.8, 117.6, 106.4, 74.8, 74.5, 40.1, 39.4, 37.6, 37.5, 37.4, 37.3, 32.8, 32.7, 32.6, 31.3, 31.2, 28.0, 24.8, 24.4, 23.9, 22.7, 22.6, 21.0, 20.7, 19.8, 19.7, 19.6, 13.2, 12.9, 12.0, 11.8; HRMS (APCI) calcd for $C_{47}H_{65}O_3$ [M + H^+], 677.4928; found: 677.4925.

7. Control experiments

BHT (0.1 mmol) or 1,1-diphenylethylene (0.1 mmol) was added and the other operations were following the general procedure. The yield of product **3a** was not affected in either case.

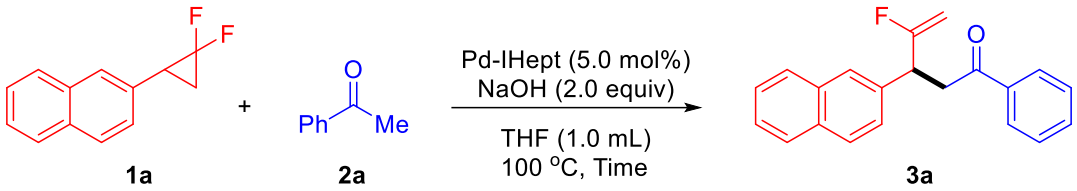


Scheme S1. Control experiements with BHT or 1,1-diphenylethylene as additive

8. Time-course reaction

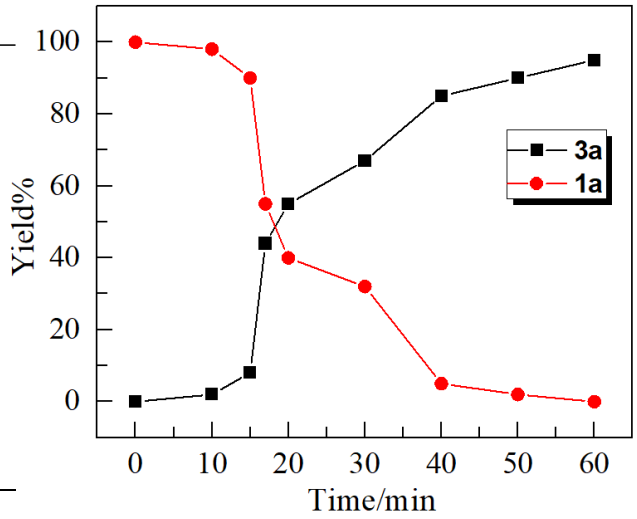
A set of flame-dried reaction tubes (10 cm^3) equipped with a magnetic stir bar was charged with Pd-PEPPSI-IHept (4.5 mg, 5 mol%) respectively. These reaction tubes were transferred to the glovebox and charged with **1a** (0.1 mmol), **2a** (0.2 mmol), NaOH (8.0 mg) and THF (1.0 mL), respectively. After that, the corresponding reaction mixtures were sealed with aluminum cap, moved out of glovebox, and stirred at 100 °C for 10 min, 15 min, 17 min, 20 min, 30 min, 40 min, 50 min and 60 min, respectively. Once stirred at the indicated time, the reaction mixture was quickly cooled to room temperature, the resulting solution was directly filtered through a pad of silica gel by

EtOAc (3.0 mL). The solvent was evaporated *in vacuo* to give the crude product. The yield of **3a** and remaining **1a** were determined by ^{1}H NMR using CH_2Br_2 as an internal standard. The corresponding data and time-course plot were shown in Scheme S2.



1a + **2a** → **3a**

Entry	Time/min	**3a** (%)	**1a** (%)
1	0	0	100
2	10	2	96
3	15	8	90
4	17	44	55
5	20	55	40
6	30	67	32
7	40	85	5
8	50	90	2
9	60	95	0



Scheme S2. Time-course reaction

9. References

[1] (a) Chartoire, A.; Frogneux, X.; Boreux, A.; Slawin, A. M. Z.; Nolan, S. P. [Pd(IPr*)(3-Cl-pyridinyl)Cl_2]: A Novel and Efficient PEPPSI Precatalyst. *Organometallics* **2012,** *31*, 6947-6951. (b) Valente, C.; Çalimsiz, S.; Hoi, K. H.; Mallik, D.; Sayah, M.; Organ, M. G. The Development of Bulky Palladium NHC Complexes for the Most-Challenging Cross-Coupling Reactions. *Angew. Chem. Int. Ed.* **2012,** *51*, 3314-3332. (c) Valente, C.; Pompeo, M.; Sayah, M.; Organ, M. G. Carbon–Heteroatom Coupling Using Pd-PEPPSI Complexes. *Org. Process Res. Dev.* **2014,** *18*, 180-190.

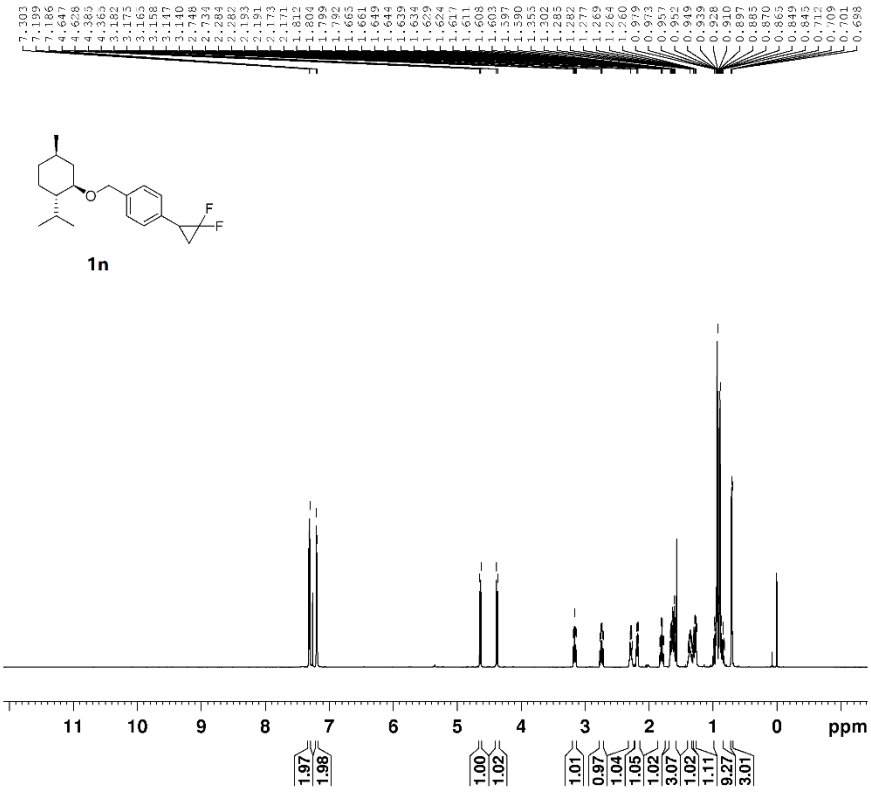
[2] (a) F. Wang, T. Luo, J. Hu, Y. Wang, H. S. Krishnan, P. V. Jog, S. K. Ganesh, G. K. S. Prakash, G. A. Olah, *Angew. Chem. Int. Ed.* **2011**, *50*, 7153-7157. (b) J. Xu, E.-A. Ahmed, B. Xiao, Q.-Q. Lu, Y.-L. Wang, C.-G. Yu, Y. Fu, *Angew. Chem. Int. Ed.* **2015**, *54*, 8231-8235. (c) Lv, L.; Li, C. J. Palladium-Catalyzed Defluorinative Alkylation of gem-Difluorocyclopropanes: Switching Regioselectivity via Simple Hydrazones. *Angew. Chem. Int. Ed.* **2021,**

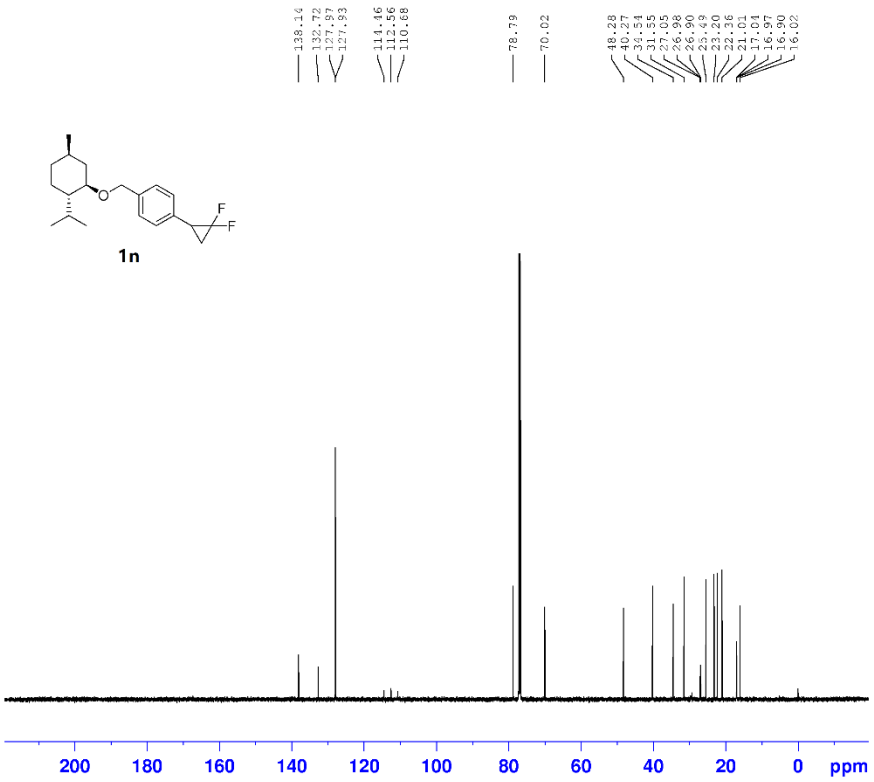
60, 13098-13104.

[3] Tan, W. W.; Yoshikai, N. Copper-Catalyzed Coupling of 2-Siloxy-1-alkenes and Diazocarbonyl Compounds: Approach to Multisubstituted Furans, Pyrroles, and Thiophenes. *J. Org. Chem.* **2016,** *81*, 5566-5573.

[4] Xia, Y.; Xia, Y.; Ge, R.; Liu, Z.; Xiao, Q.; Zhang, Y.; Wang, J. Oxidative Cross-Coupling of Allenyl Ketones and Organoboronic Acids: Expeditious Synthesis of Highly Substituted Furans. *Angew. Chem. Int. Ed.* **2014,** *53*, 3917-3921.

10. Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for new compounds

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31.55
27.05
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26.00
25.49
23.20
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17.04
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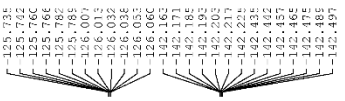

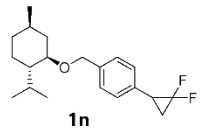

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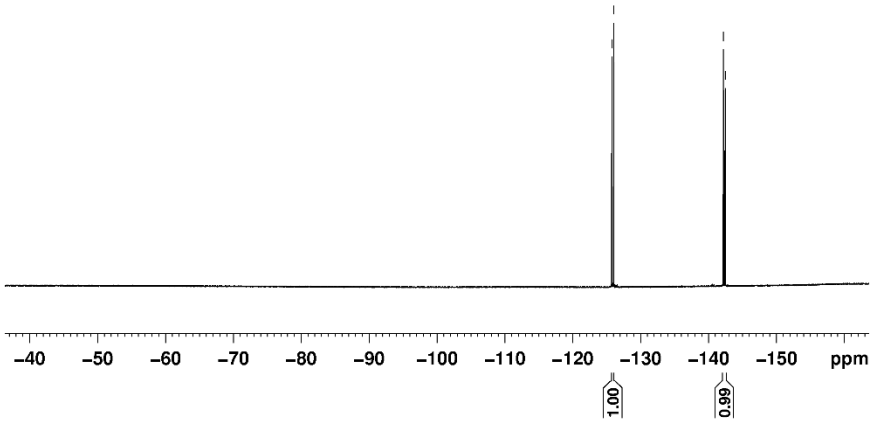

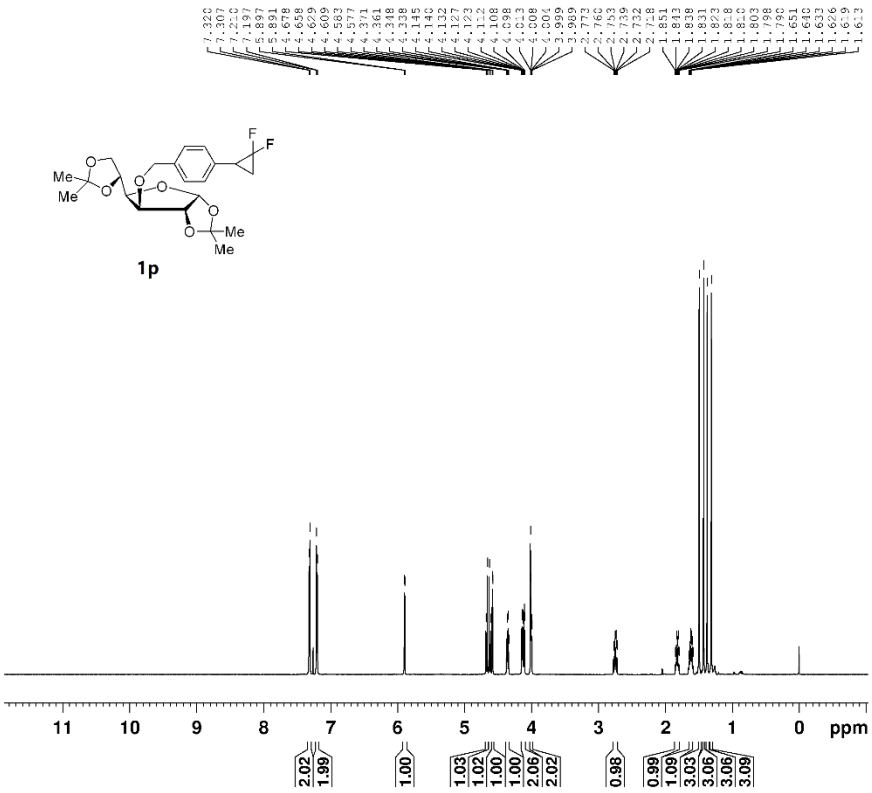
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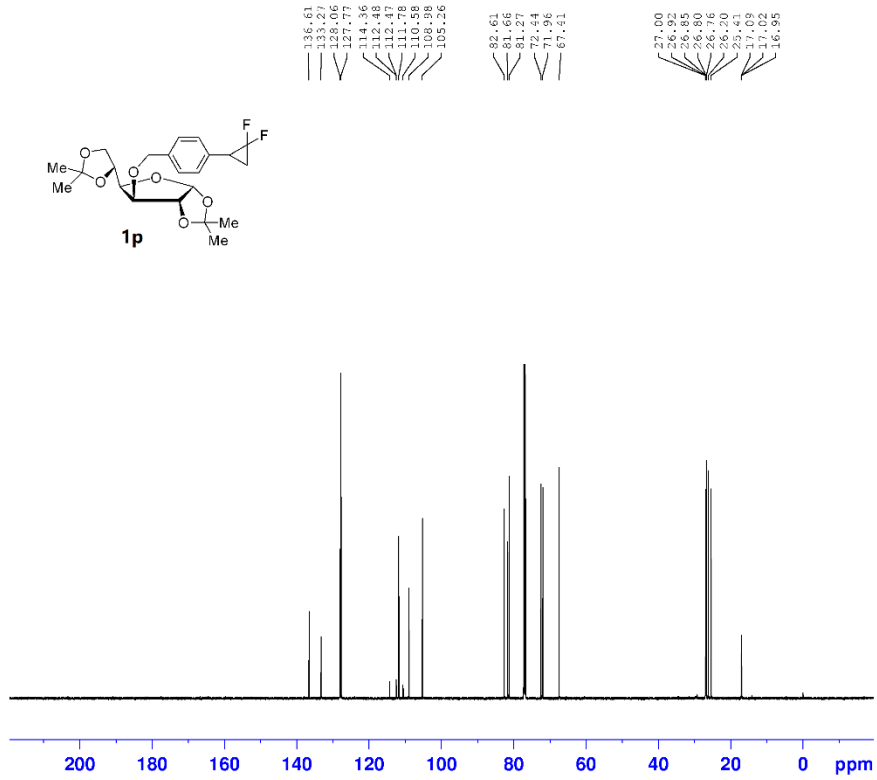
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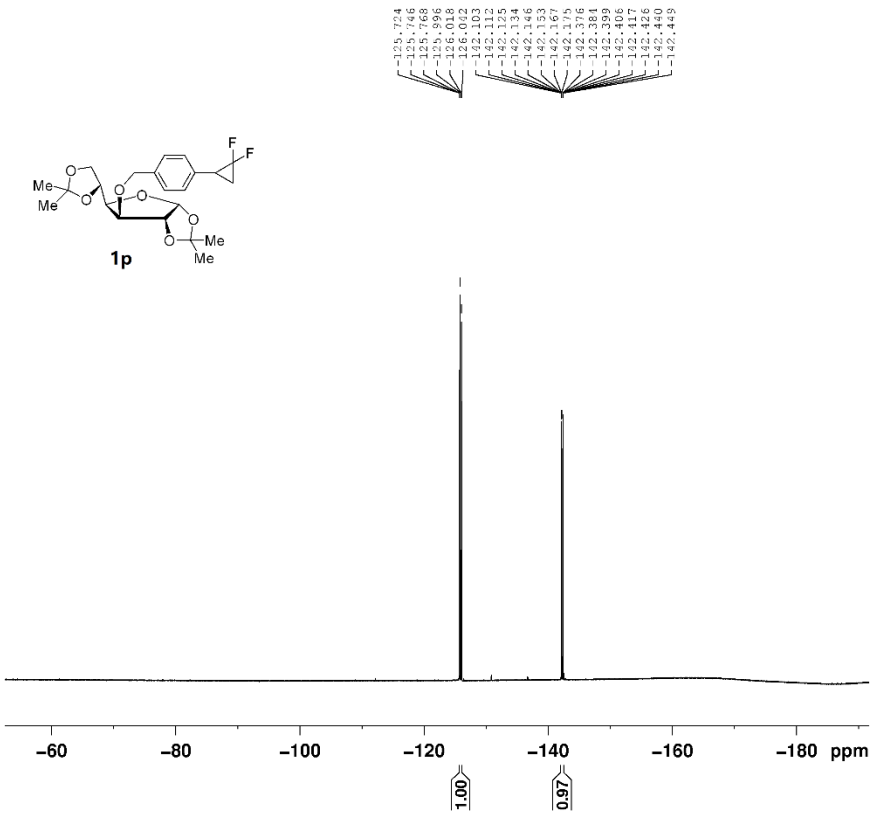
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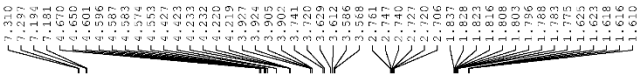

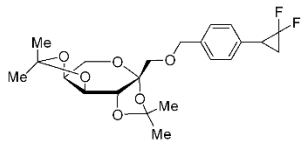

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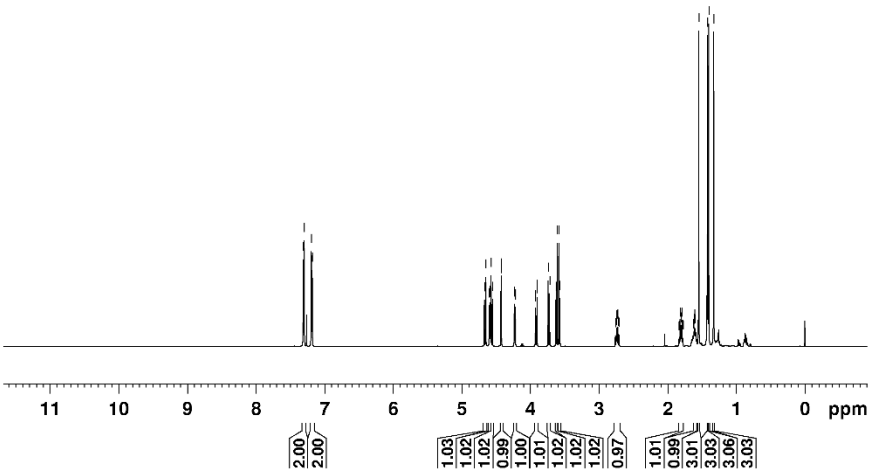
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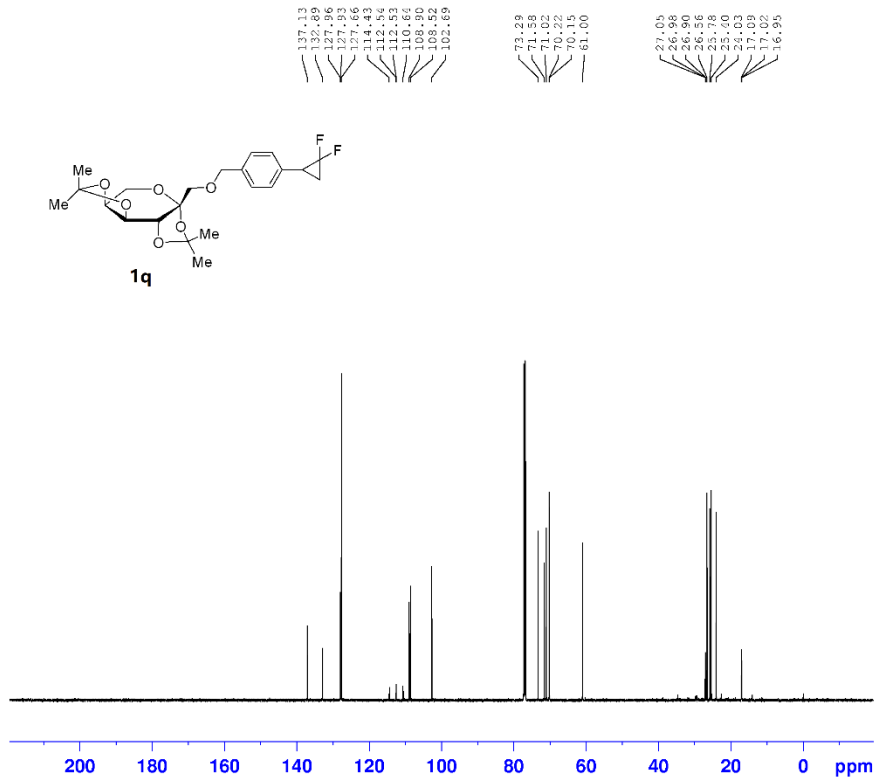
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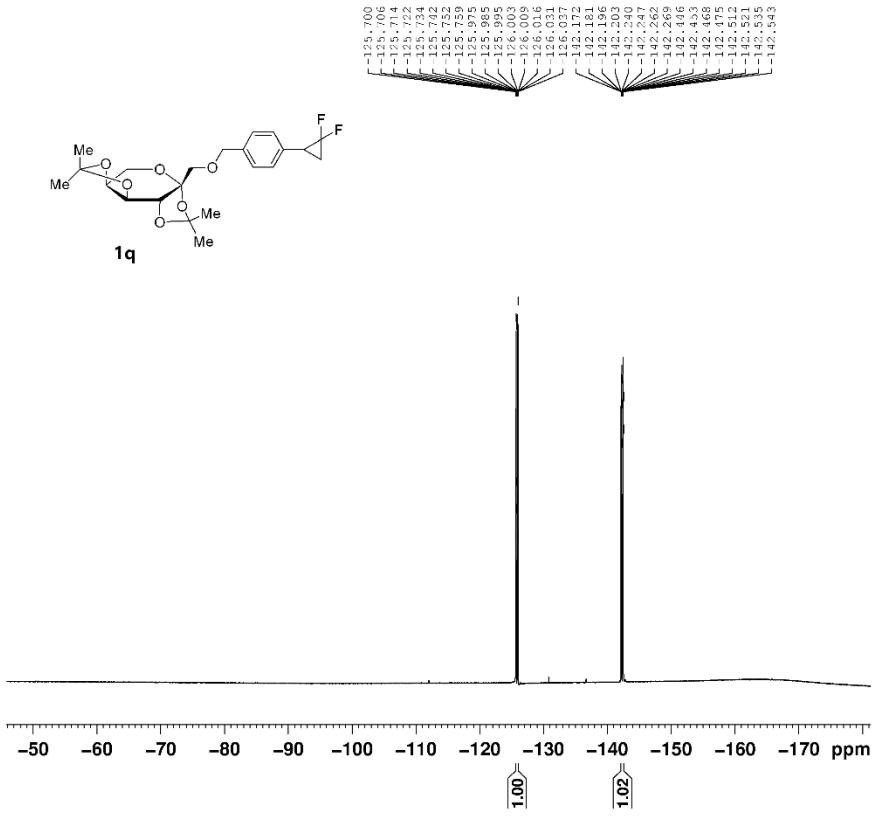
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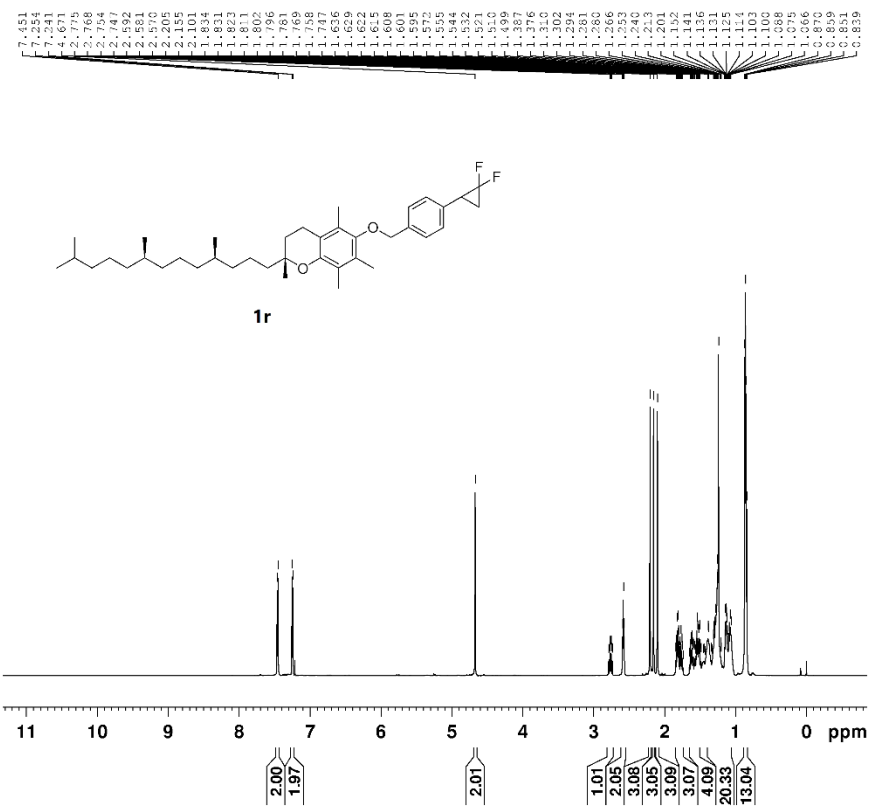
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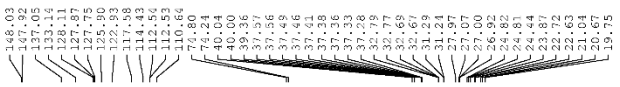
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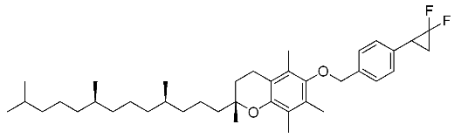
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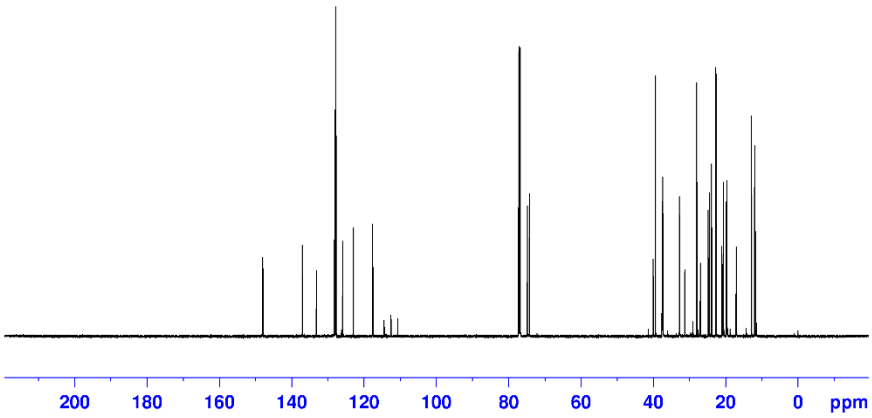
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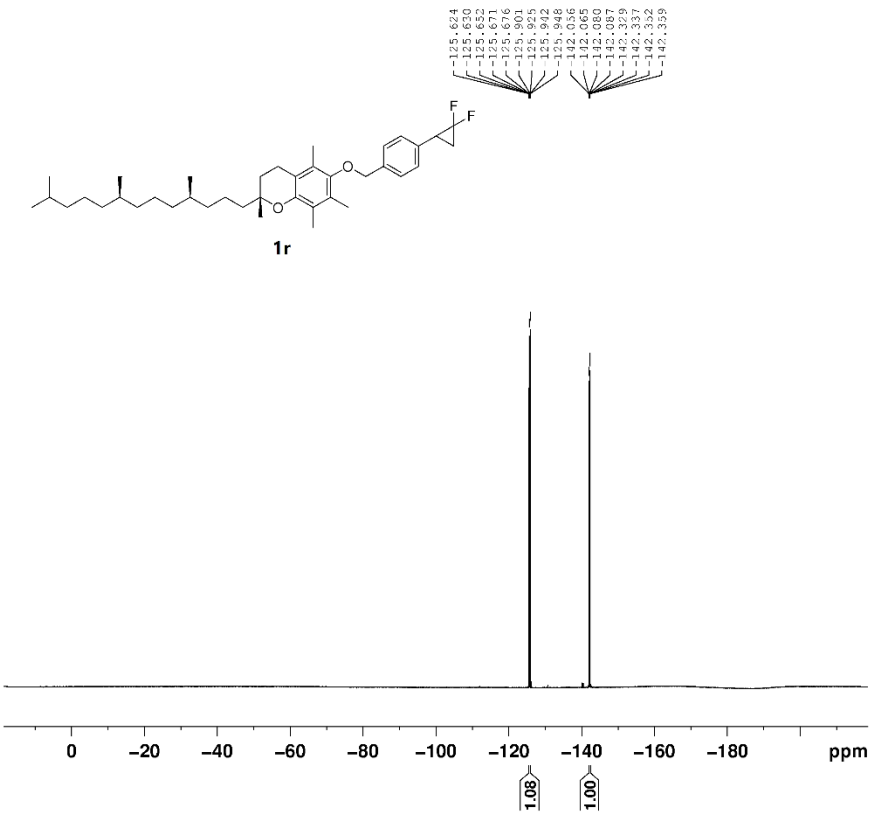
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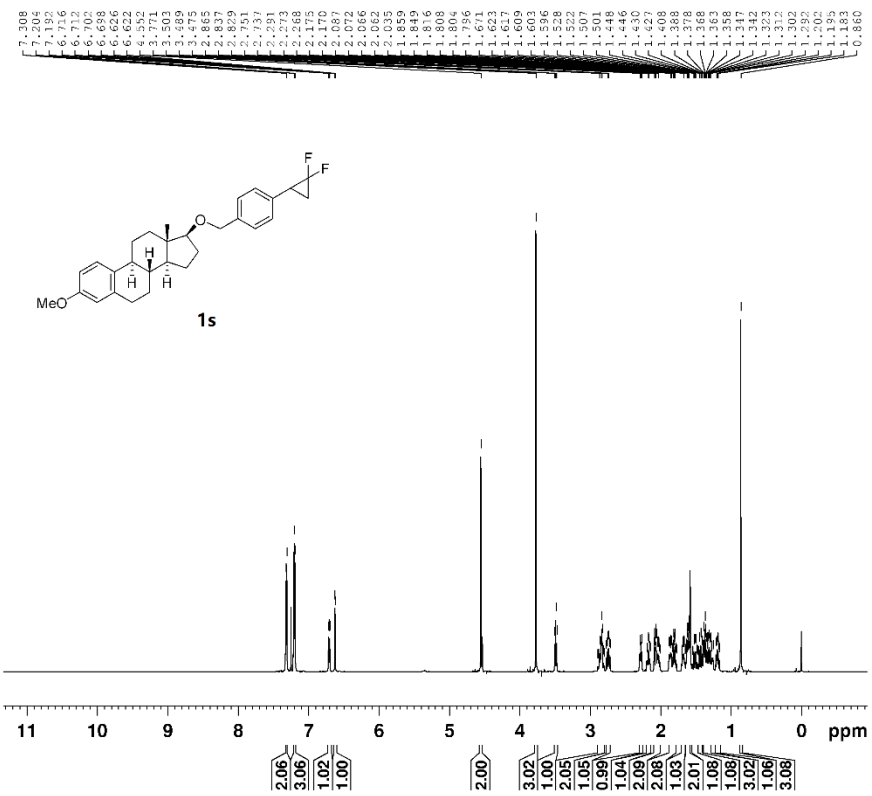
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H
H
H
MeO
1s
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
3.06
1.02
1.00
2.00
3.02
1.00
2.05
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2.09
2.08
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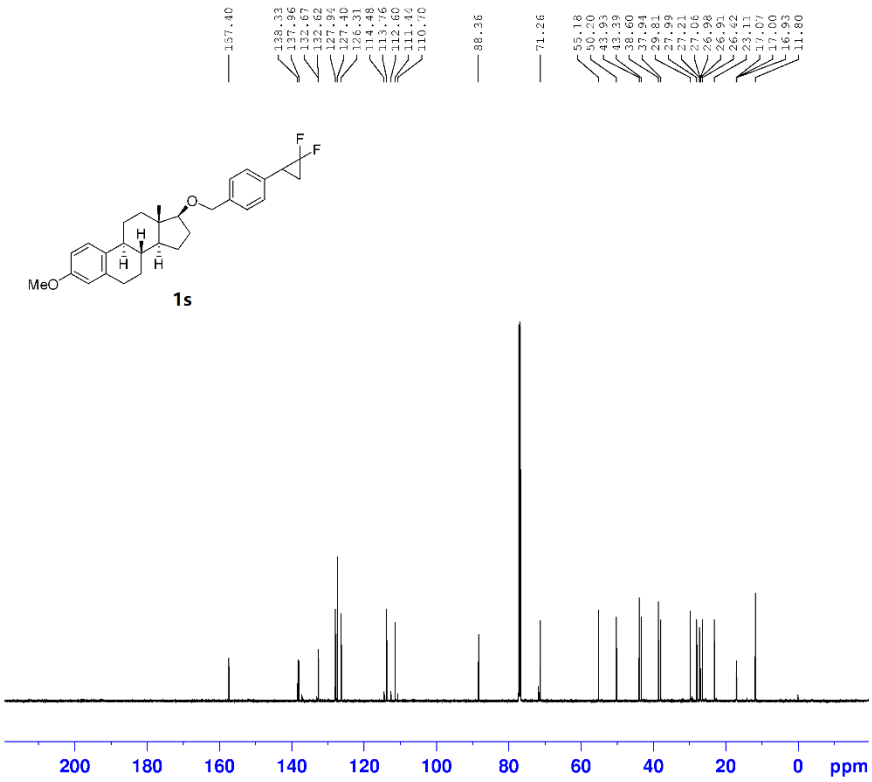
2.01
1.08
1.08
3.02
1.06
3.08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71.26
55.18
50.20
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43.39
38.60
37.94
29.81
27.99
27.21
27.06
26.98
26.91
26.42
23.11
21.01
17.00
16.93
11.80
F
F
O
H
H
H
MeO
1s
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120
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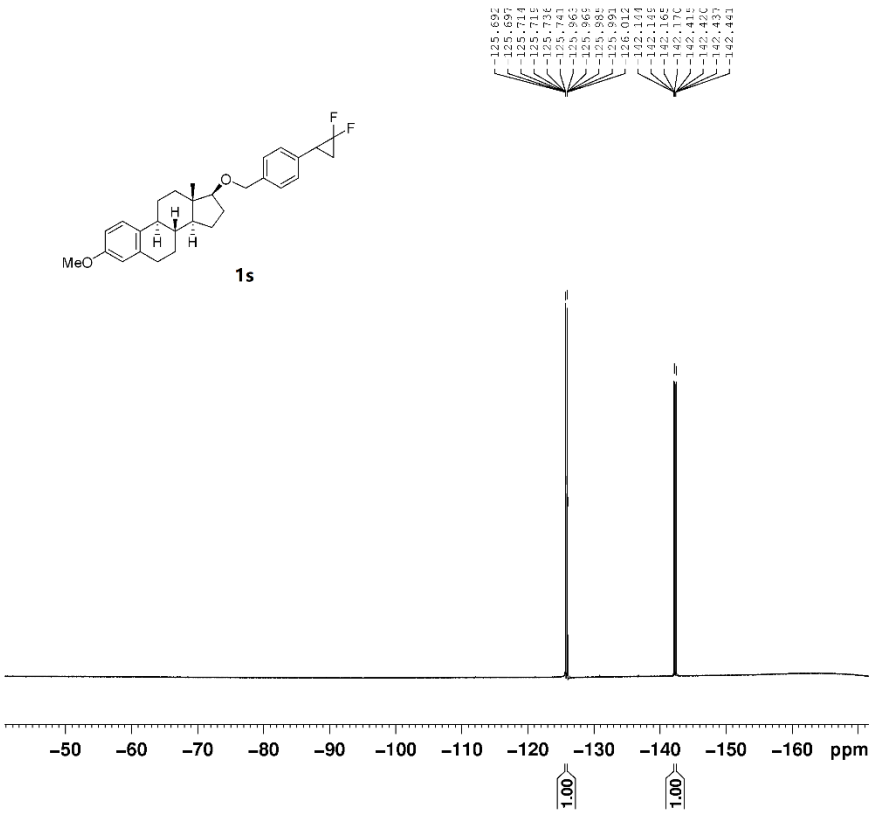
60
40
20
0
ppm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-126.012
-142.104
-142.149
-142.165
-142.170
-142.415
-142.420
-142.437
-142.441
F
F
O
H
H
H
MeO
1s
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-90
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-110
-120
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-150
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ppm
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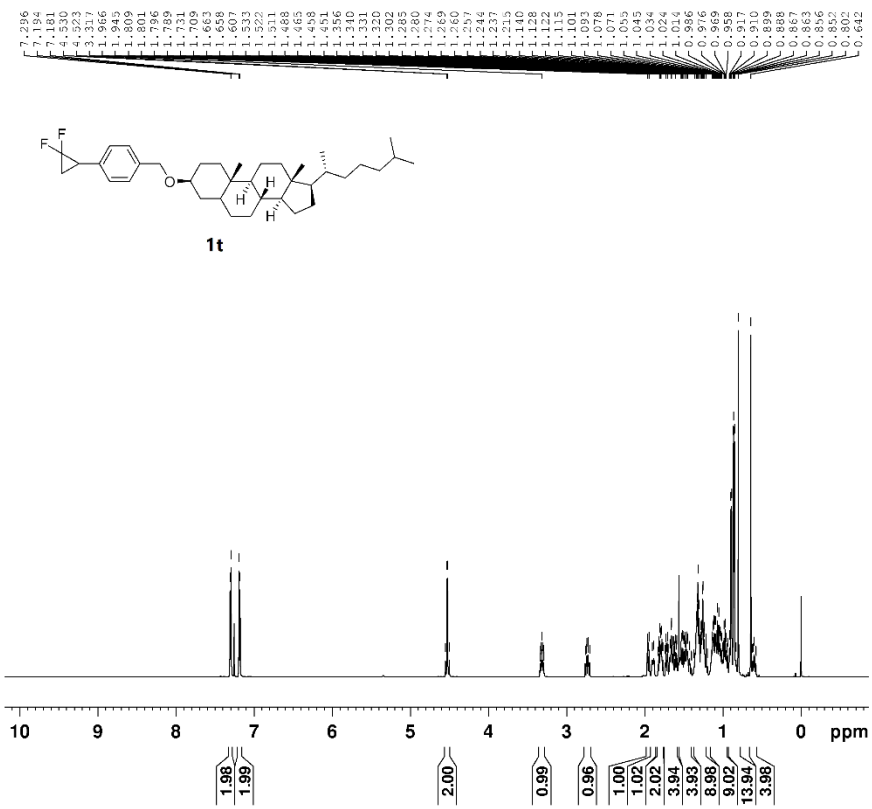
1.00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1.945
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1.731
1.709
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1.658
1.607
1.533
1.522
1.511
1.488
1.465
1.458
1.451
1.356
1.310
1.301
1.291
1.280
1.285
1.280
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1.260
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1.246
1.237
1.215
1.140
1.128
1.122
1.115
1.101
1.093
1.078
1.071
1.053
1.045
1.034
1.024
1.014
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0.976
0.969
0.958
0.917
0.910
0.899
0.888
0.867
0.863
0.856
0.852
0.802
0.642
F
F
O
H
H
H
1t
10
9
8
7
6
5
4
3
2
1
0
ppm
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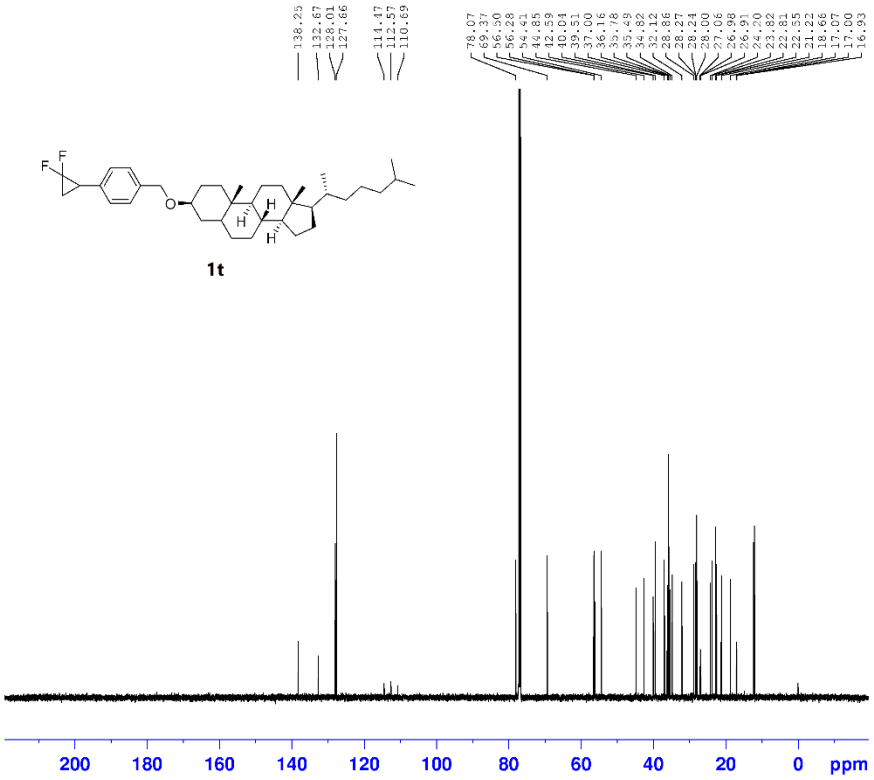
3.98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78.07
69.37
56.90
56.28
54.41
44.85
42.59
40.04
39.51
37.00
36.16
33.78
35.49
34.82
32.12
28.86
28.27
28.24
28.00
27.06
26.98
26.91
24.20
23.82
22.81
22.55
21.22
18.66
17.07
17.00
16.93
F
F
O
H
H
H
1t
200
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120
100
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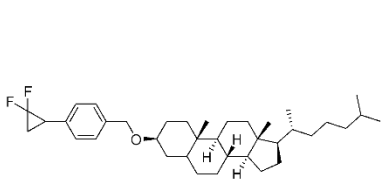
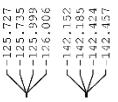
60
40
20
0
ppm


F
F
O
H
H
H

1t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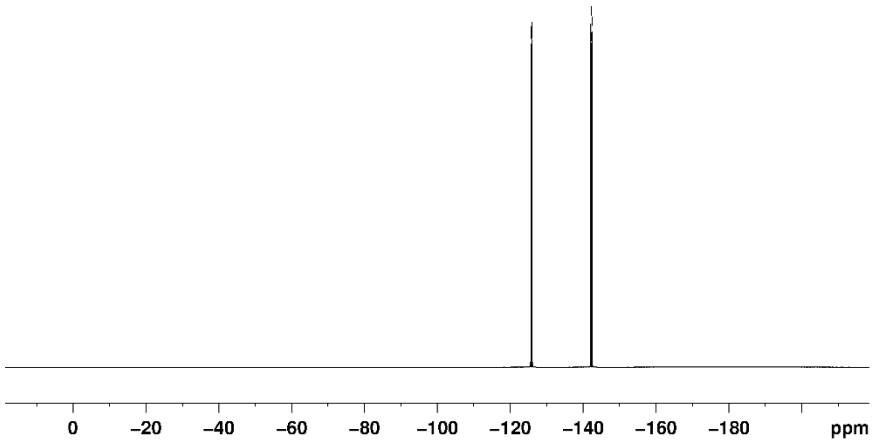
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-40
-60
-80
-100
-120
-140
-160
-180
ppm


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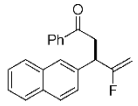
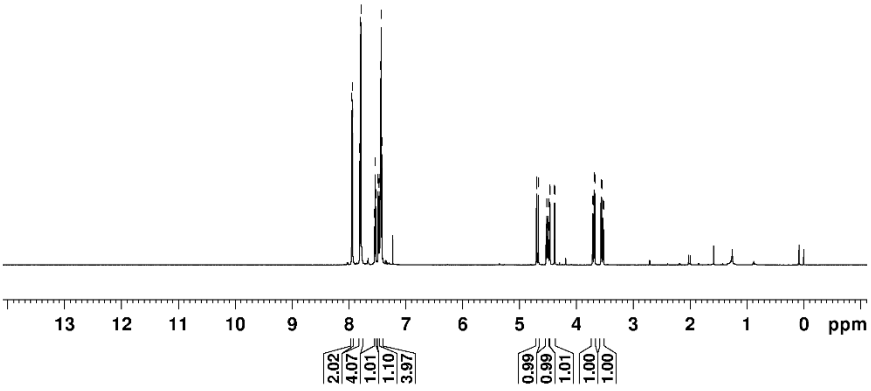
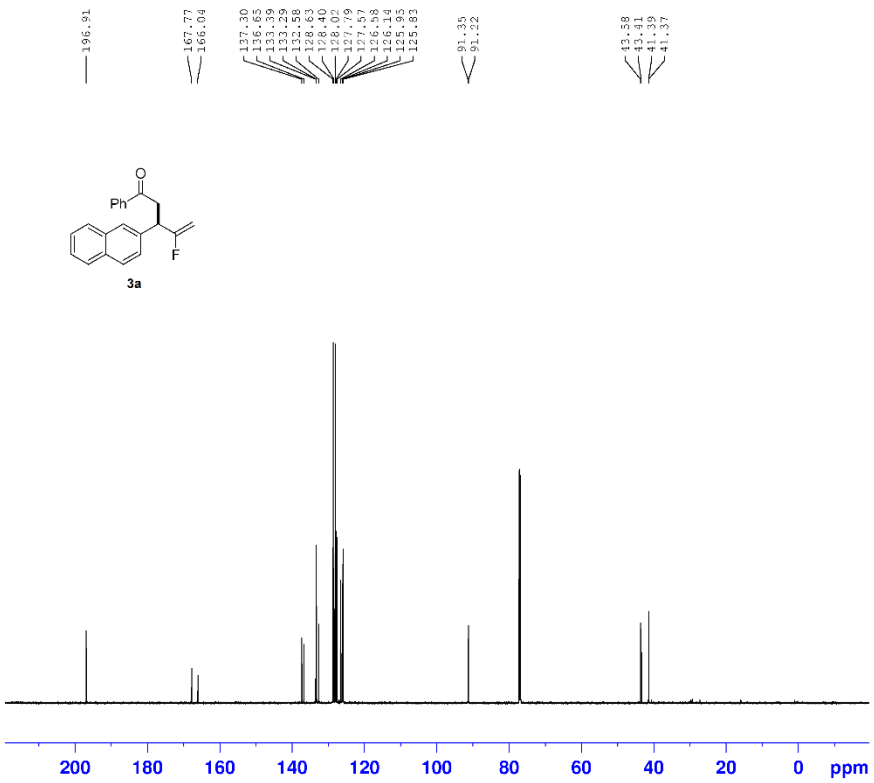
7.812
7.798
7.788
7.552
7.540
7.528
7.488
7.474
7.472
7.465
7.463
7.454
7.452
7.446
7.442
7.439
7.433
7.420
4.701
4.695
4.672
4.667
4.532
4.521
4.509
4.505
4.493
4.481
4.468
4.463
4.385
4.380
3.716
3.704
3.687
3.675
3.566
3.554
3.537
3.523


O
Ph
F

3a


13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
4.07
1.01
1.10
3.97
0.99
0.99
1.01
1.00
1.00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166.04
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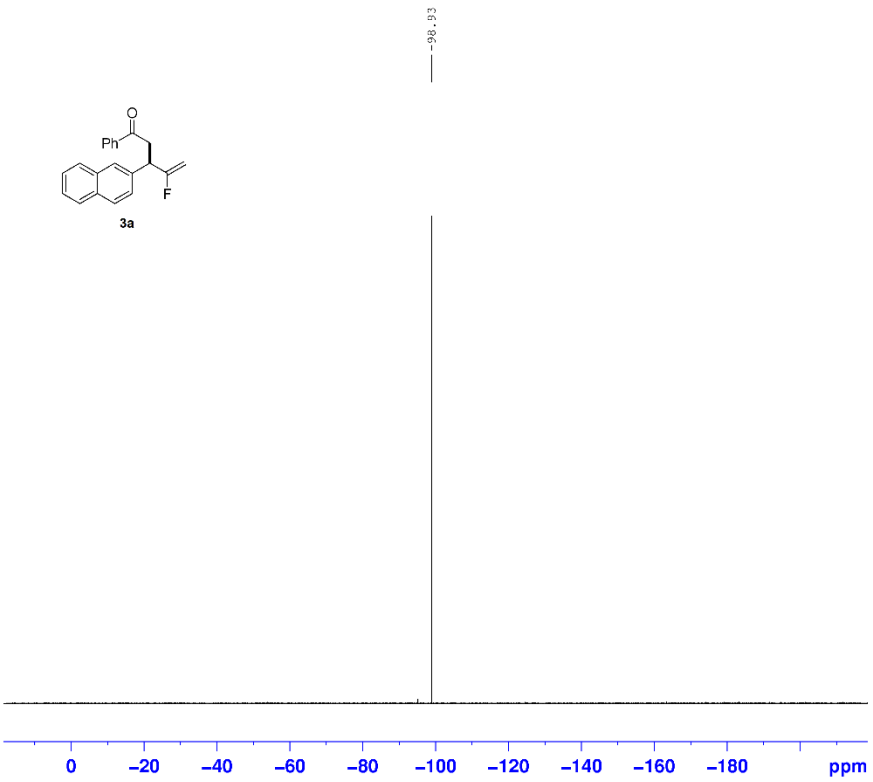
136.65
133.39
133.29
132.58
128.65
128.40
128.02
127.79
127.57
126.58
126.14
125.95
125.83
91.35
91.22
43.58
43.41
41.39
41.37
O
Ph
F
3a
200
180
160
140
120
100
80
60
40
20
0
ppm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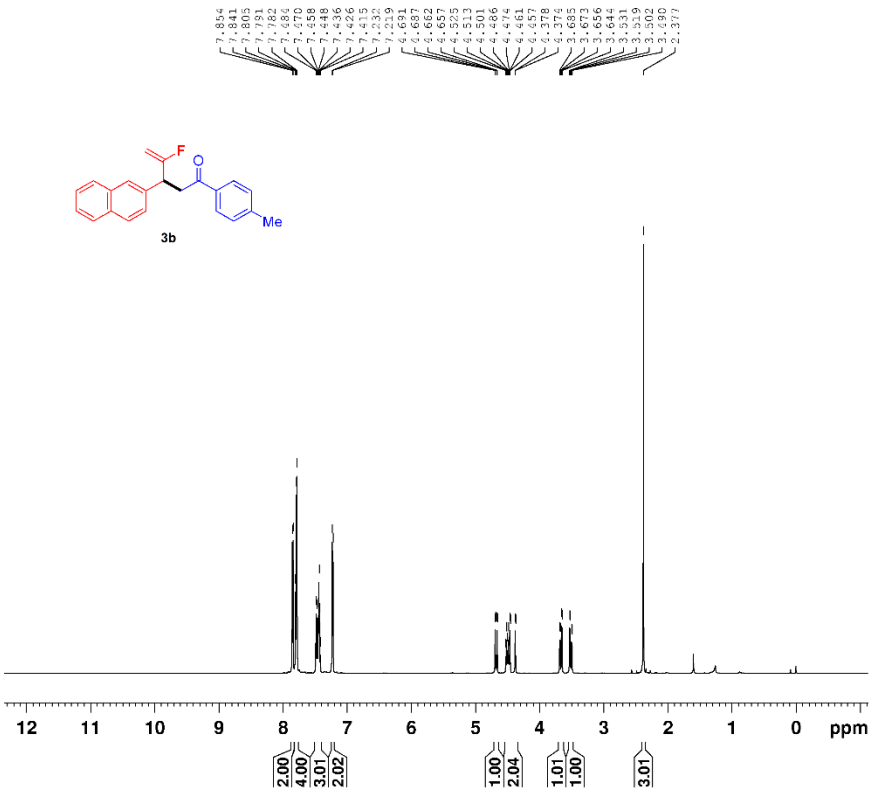
O
Ph
F
3a
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm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7.415
7.232
7.219
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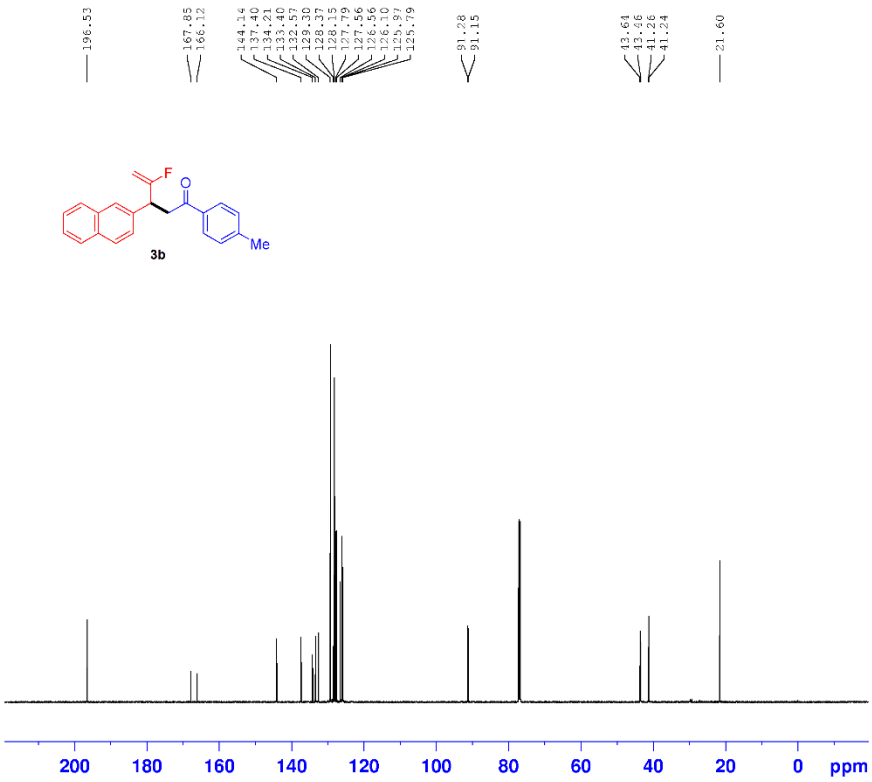
4.687
4.662
4.657
4.525
4.513
4.501
4.486
4.474
4.461
4.457
4.378
4.376
3.685
3.673
3.656
3.644
3.531
3.519
3.502
3.490
2.377
F
O
Me
3b
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.00
3.01
2.02
1.00
2.04
1.01
1.00
3.01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133.40
132.57
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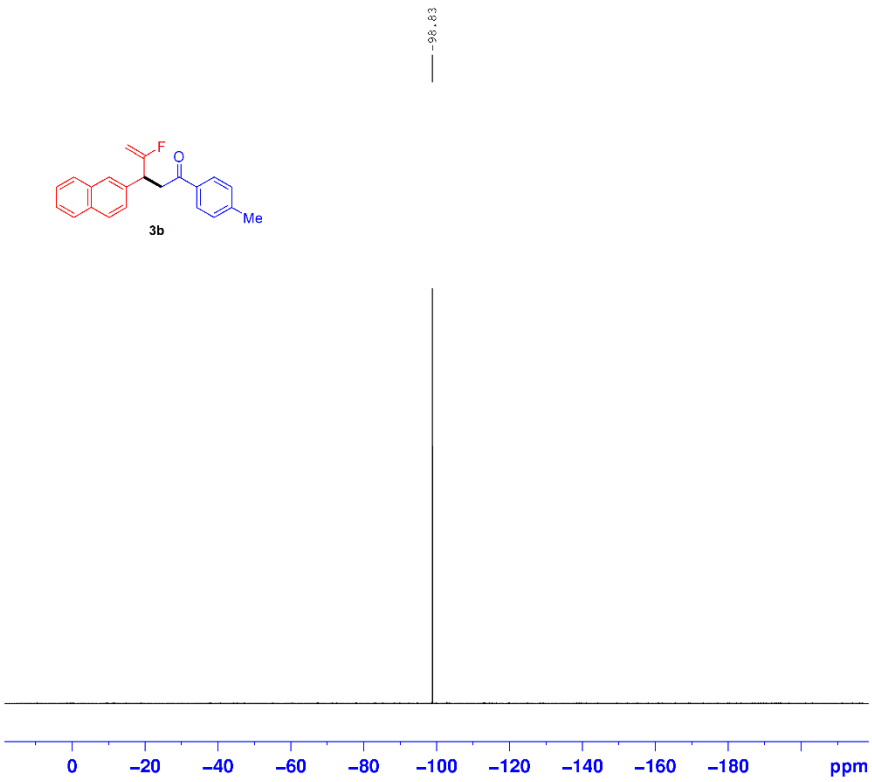
128.37
128.15
127.79
127.56
126.56
126.10
125.97
125.79
91.28
91.15
43.64
43.26
41.26
41.24
21.60
F
O
Me
3b
200
180
160
140
120
100
80
60
40
20
0
ppm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O
Me
3b
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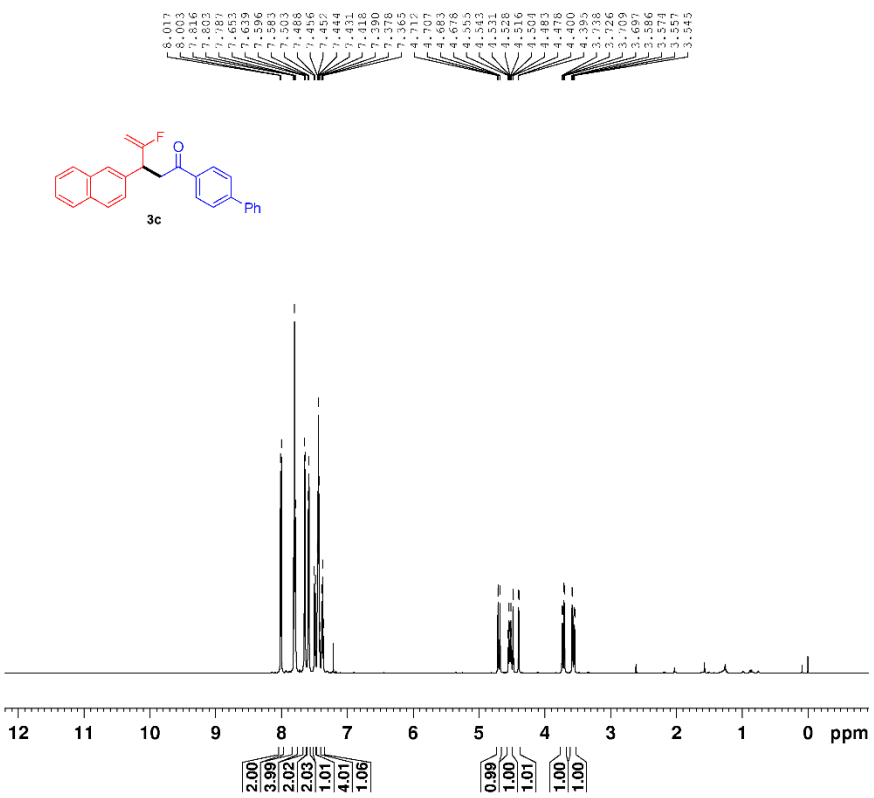
−60
−80
−100
−120
−140
−160
−180
ppm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7.583
7.503
7.488
7.456
7.444
7.390
7.378
7.365
4.712
4.707
4.683
4.678
4.543
4.531
4.528
4.516
4.504
4.483
4.478
4.400
4.395
3.738
3.726
3.709
3.697
3.586
3.574
3.557
3.545
F
O
Ph
3c
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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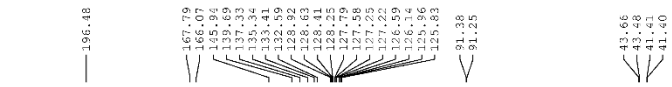
3.99
2.02
2.03
1.01
4.01
1.06
0.99
1.00
1.01
1.00
1.00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133.41
132.59
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128.63
128.41
128.25
127.79
127.58
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126.14
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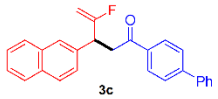
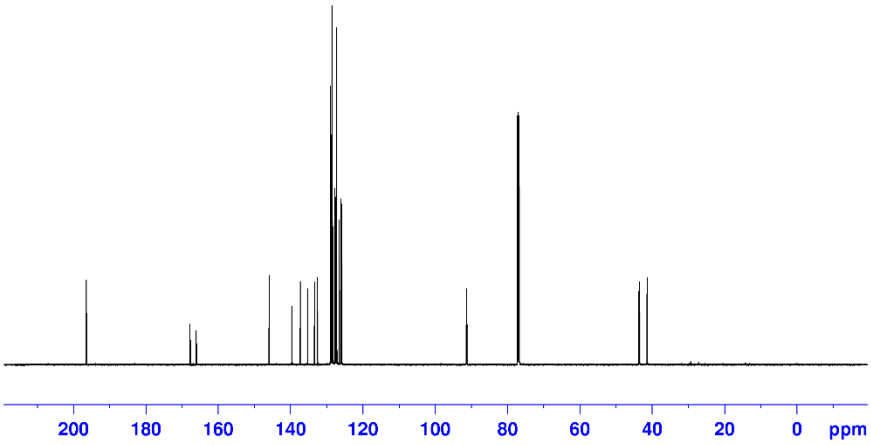
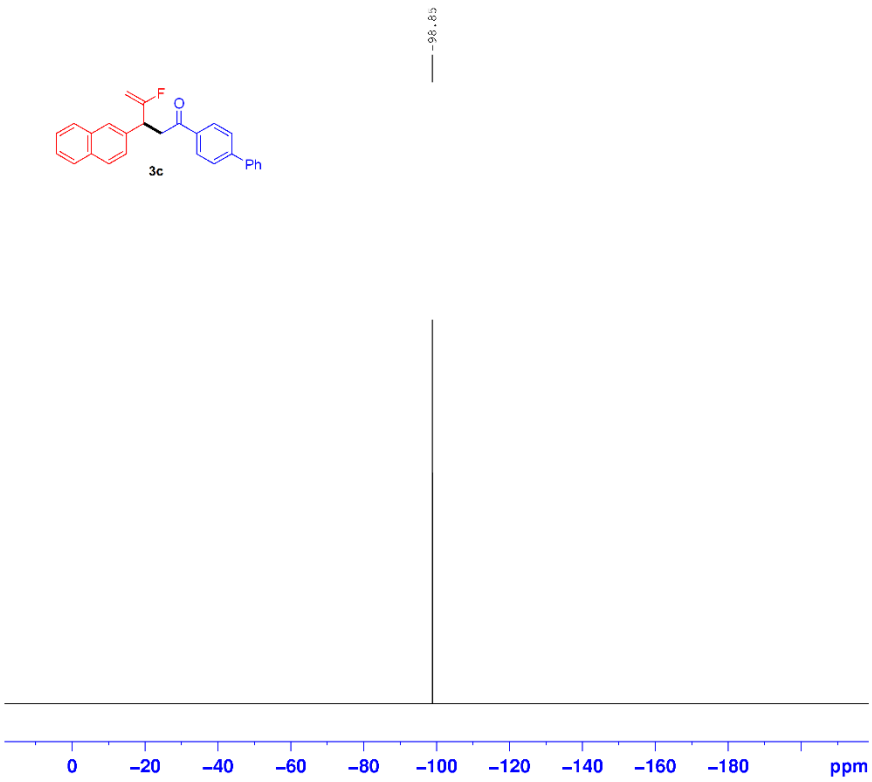
41.41
41.40


F
O
Ph

3c


200
180
160
140
120
100
80
60
40
20
0
ppm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O
Ph
3c
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−80
−100
−120
−140
−160
−180
ppm


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7.788
7.781
7.484
7.470
7.454
7.444
7.433
7.422
7.411
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6.885
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4.684
4.660
4.655
4.652
4.511
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4.482
4.471
4.462
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3.615
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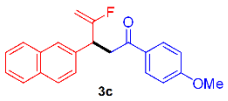
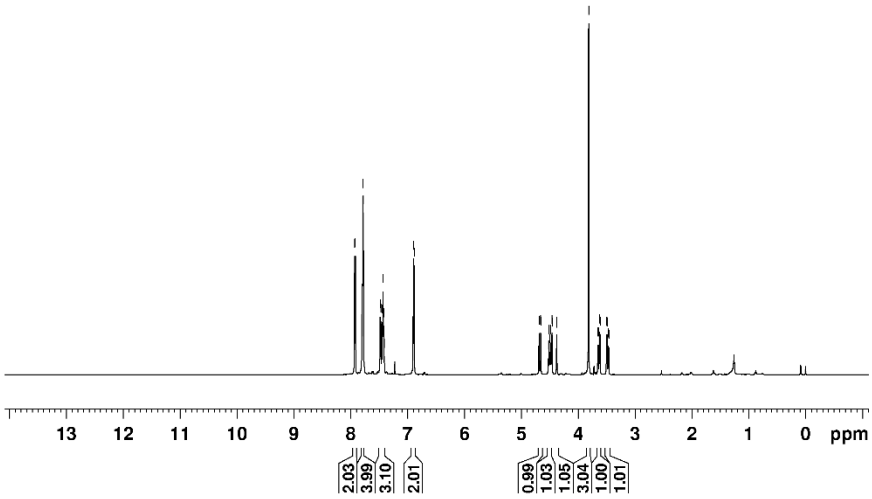
3.474
3.462


F
O
OMe

3c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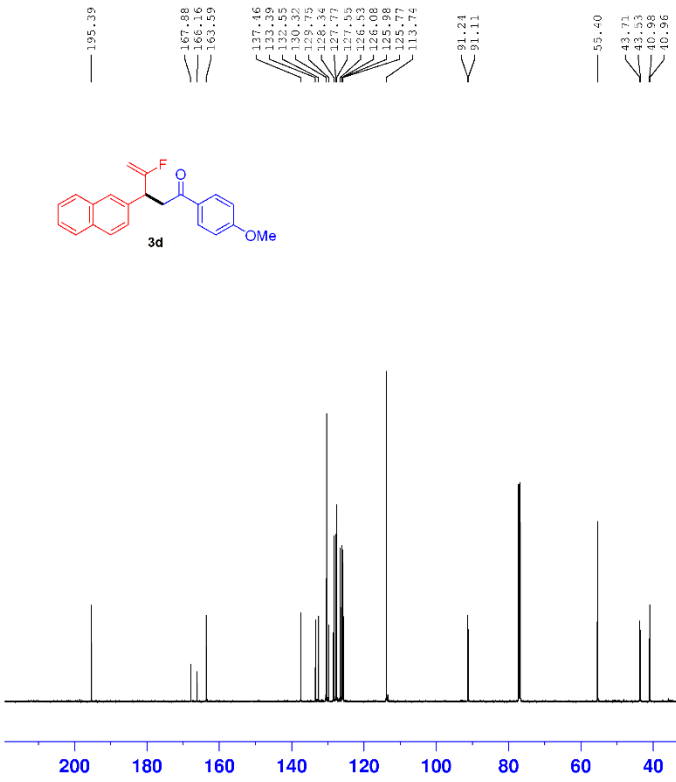
10
9
8
7
6
5
4
3
2
1
0
ppm
2.03
3.99
3.10
2.01
0.99
1.03
1.05
3.04
1.00
1.01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127.55
126.53
126.08
125.98
125.77
113.74
91.24
91.11
55.40
43.71
43.53
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O
OMe
3d
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120
100
80
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40
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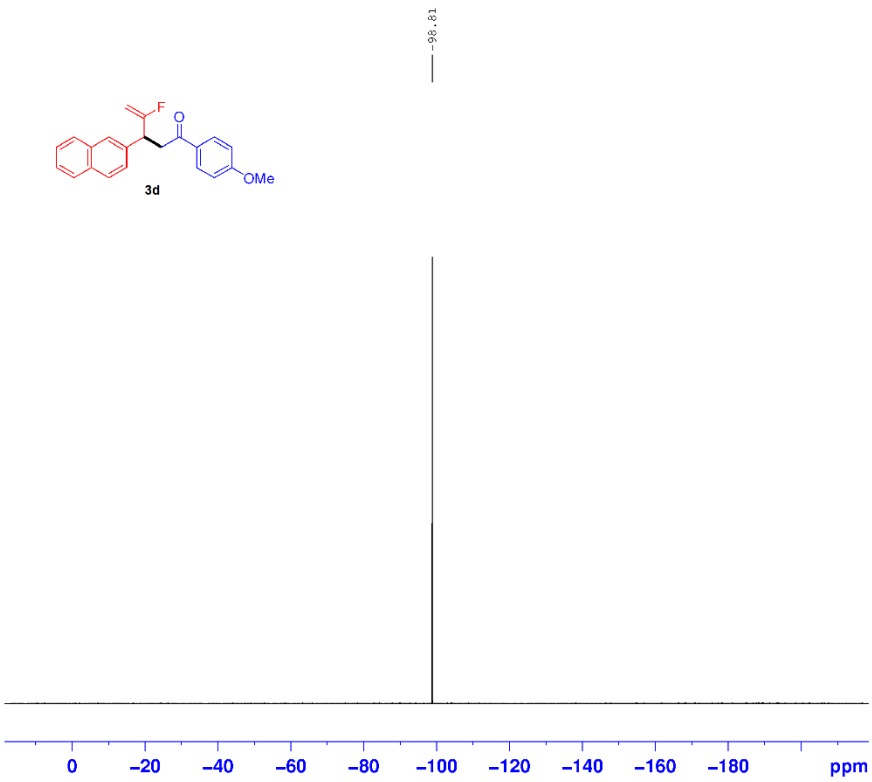
0
ppm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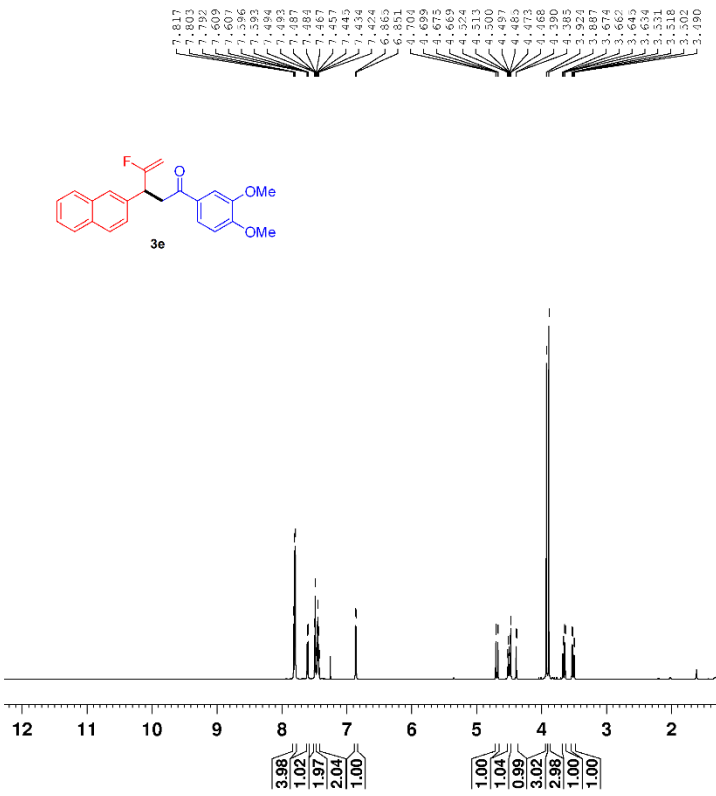
ppm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7.487
7.484
7.467
7.457
7.445
7.434
7.424
6.863
6.851
4.704
4.699
4.673
4.659
4.524
4.513
4.500
4.497
4.483
4.473
4.468
4.390
4.385
3.924
3.887
3.674
3.662
3.644
3.634
3.531
3.518
3.502
3.490
F
O
OMe
OMe
3e
12
11
10
9
8
7
6
5
4
3
2
1
0
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2.04
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1.00
1.04
0.99
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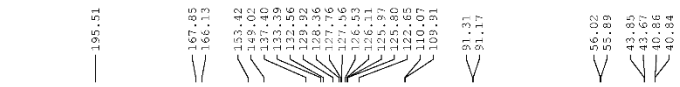
1.00
1.00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127.56
126.53
126.11
125.97
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110.07
109.91
91.31
91.17
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55.89
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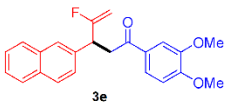
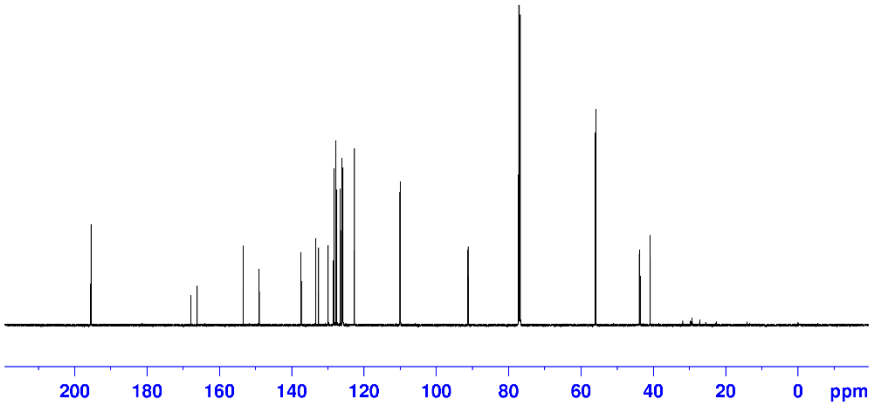
43.67
40.86
40.84


F
O
OMe
OMe

3e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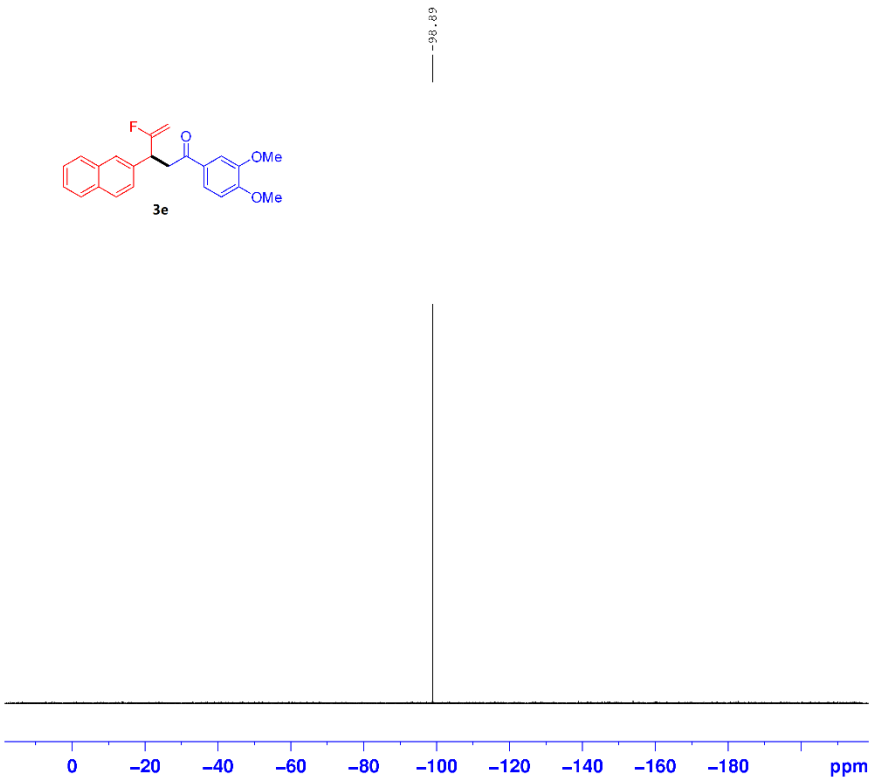
120
100
80
60
40
20
0
ppm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F
O
OMe
OMe
3e
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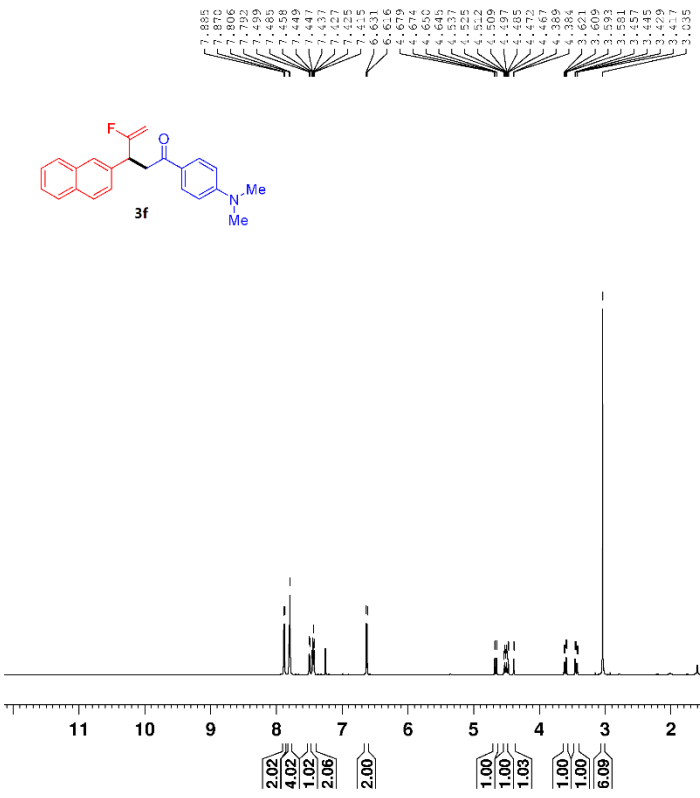
−180
ppm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7.425
7.415
6.631
6.616
4.679
4.674
4.650
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4.609
4.597
4.485
4.472
4.467
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4.384
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3.593
3.581
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3.145
3.129
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F
O
N
Me
Me
3f
11
10
9
8
7
6
5
4
3
2
1
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1.02
2.06
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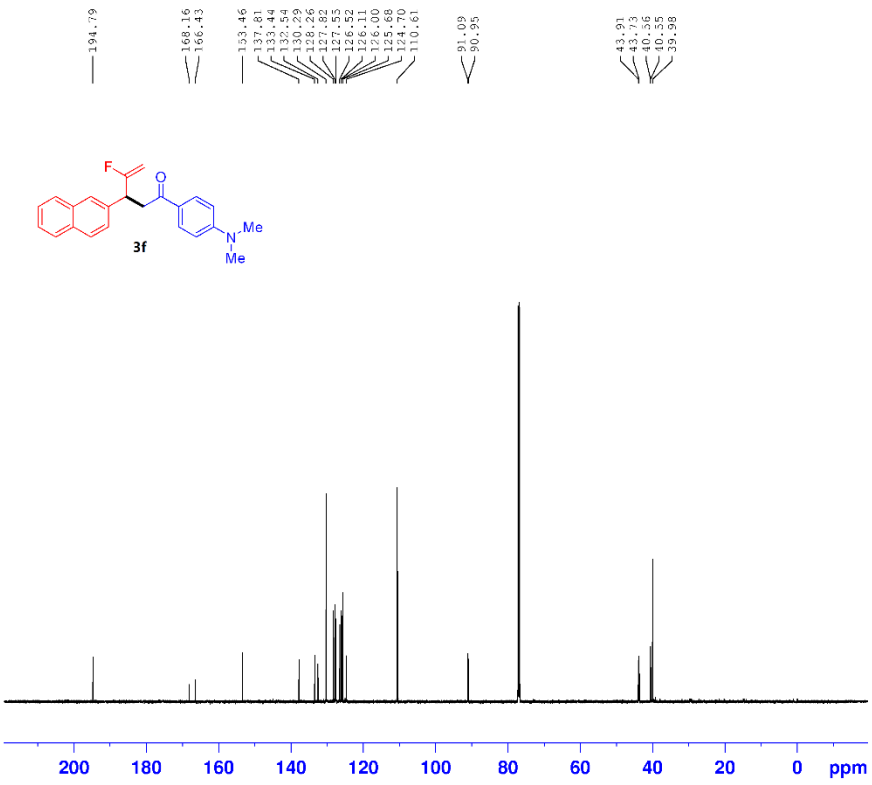
1.00
1.00
1.03
1.00
1.00
6.09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133.44
132.54
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127.82
127.55
126.52
126.11
126.00
125.68
124.70
110.61
91.09
90.95
43.91
43.73
40.56
40.35
39.98
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N
Me
Me
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40
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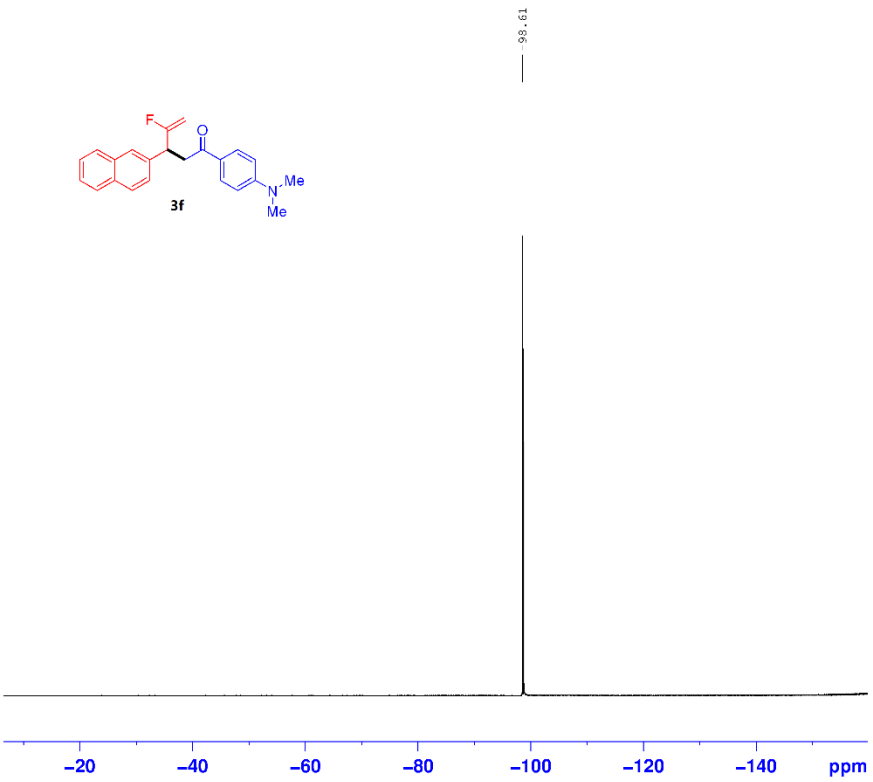
0
ppm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N
Me
Me
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−60
−80
−100
−120
−140
ppm


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7.968
7.963
7.953
7.814
7.800
7.787
7.781
7.479
7.462
7.460
7.438
7.427
7.114
7.100
7.085
4.703
4.698
4.678
4.669
4.313
4.301
4.489
4.485
4.473
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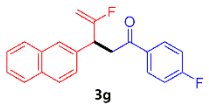
3.641
3.531
3.519
3.502
3.490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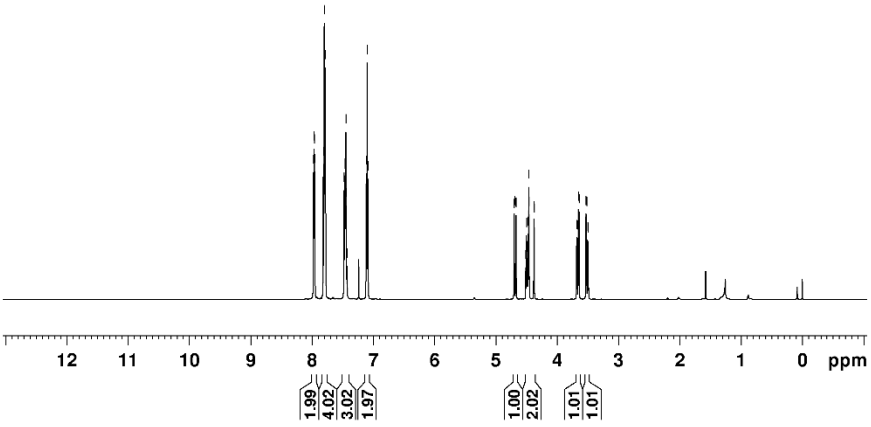
O
F

3g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8
7
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1
0
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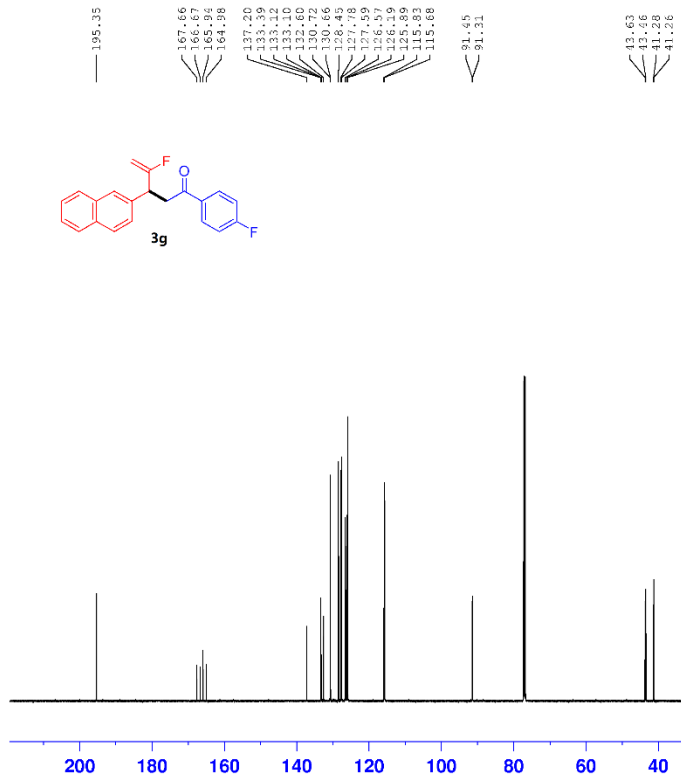
3.02
1.97
1.00
2.02
1.01
1.01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133.39
133.12
133.10
132.60
130.72
130.66
128.45
127.78
127.59
126.57
126.19
125.89
115.83
115.68
91.45
91.31
43.63
43.26
41.28
41.26
F
O
F
3g
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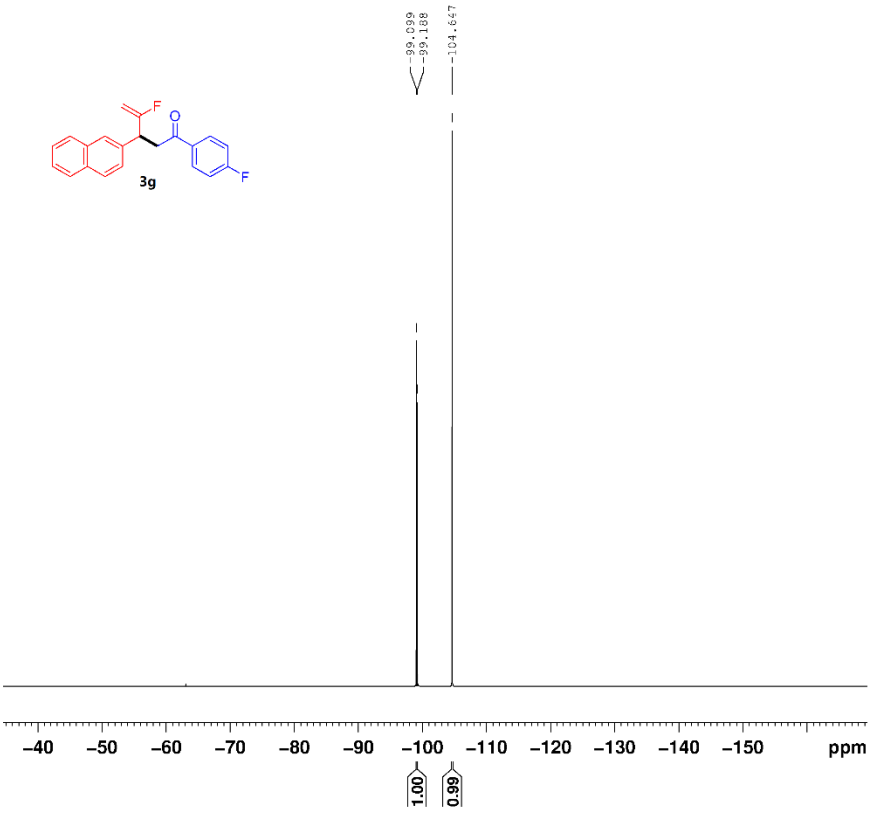
120
100
80
60
40
20
0
ppm


F
O
F
3g
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-99.188
-104.647
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
ppm
1.00
0.99


8.047
8.033
7.838
7.814
7.804
7.792
7.783
7.719
7.705
7.482
7.474
7.466
7.463
7.456
7.453
7.451
7.442
4.719
4.714
4.690
4.685
4.522
4.510
4.498
4.495
4.483
4.469
4.463
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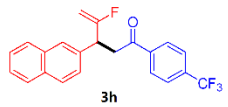
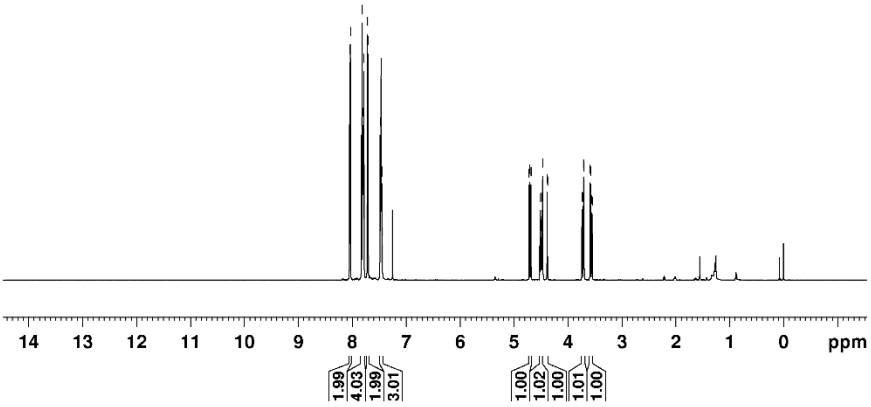
4.380
3.741
3.729
3.712
3.700
3.591
3.579
3.567
3.550


F
O
CF3

3h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10
9
8
7
6
5
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3
2
1
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ppm
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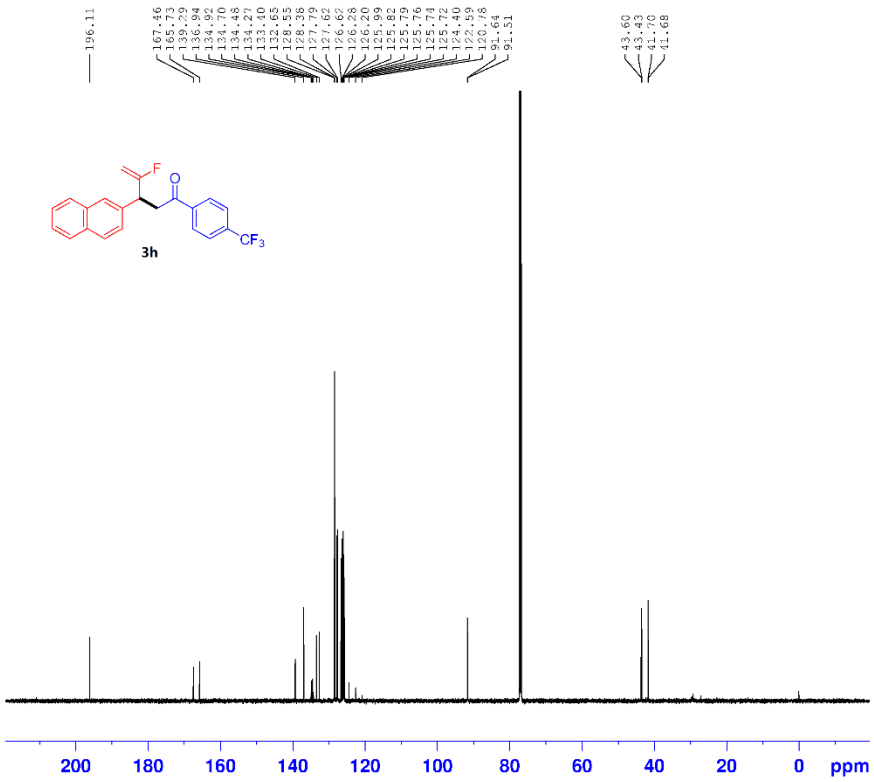
1.99
3.01
1.00
1.02
1.00
1.01
1.00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165.73
139.29
136.94
134.92
134.70
134.48
134.27
133.10
132.65
128.55
128.36
127.79
127.62
126.67
126.28
126.20
125.99
125.82
125.79
125.76
125.74
125.72
124.40
122.59
120.78
91.64
91.51
43.60
43.43
41.70
41.68
F
O
CF3
3h
200
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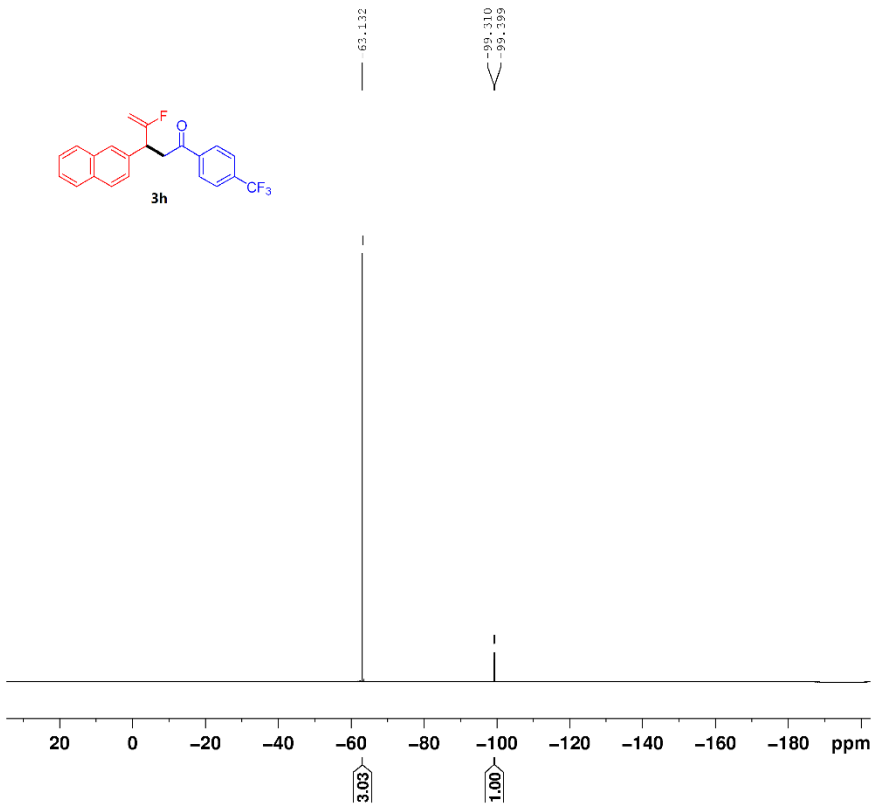
140
120
100
80
60
40
20
0
ppm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-99.399
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O
CF3
3h
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-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
3.03
1.00


8.016
8.003
7.835
7.811
7.801
7.798
7.787
7.771
7.746
7.733
7.486
7.469
7.465
7.460
7.456
7.454
7.445
4.720
4.715
4.691
4.686
4.504
4.492
4.490
4.476
4.465
4.460
4.453
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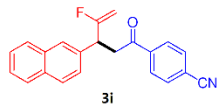
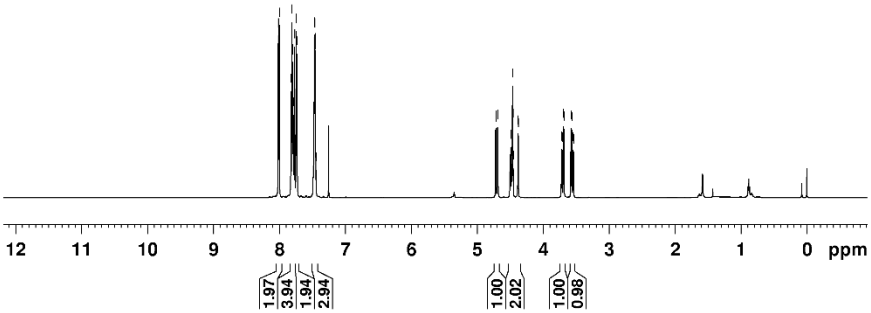
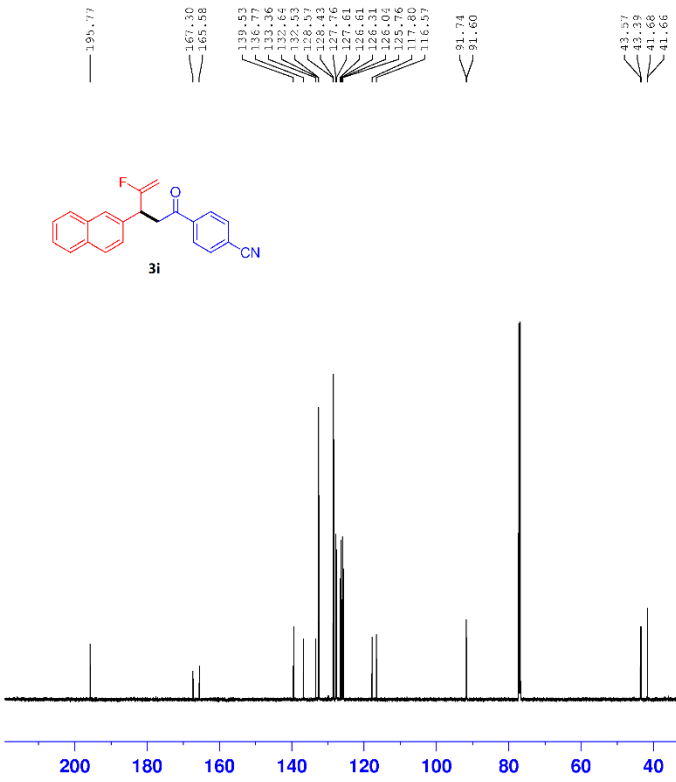
4.377
3.723
3.712
3.694
3.682
3.579
3.566
3.549
3.537


F
O
CN

3i


12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
3.94
1.94
2.94
1.00
2.02
1.00
0.98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132.53
128.57
128.43
127.76
127.61
126.61
126.31
126.04
125.76
117.80
116.57
91.74
91.60
43.97
43.39
41.68
41.66
F
O
CN
3i
200
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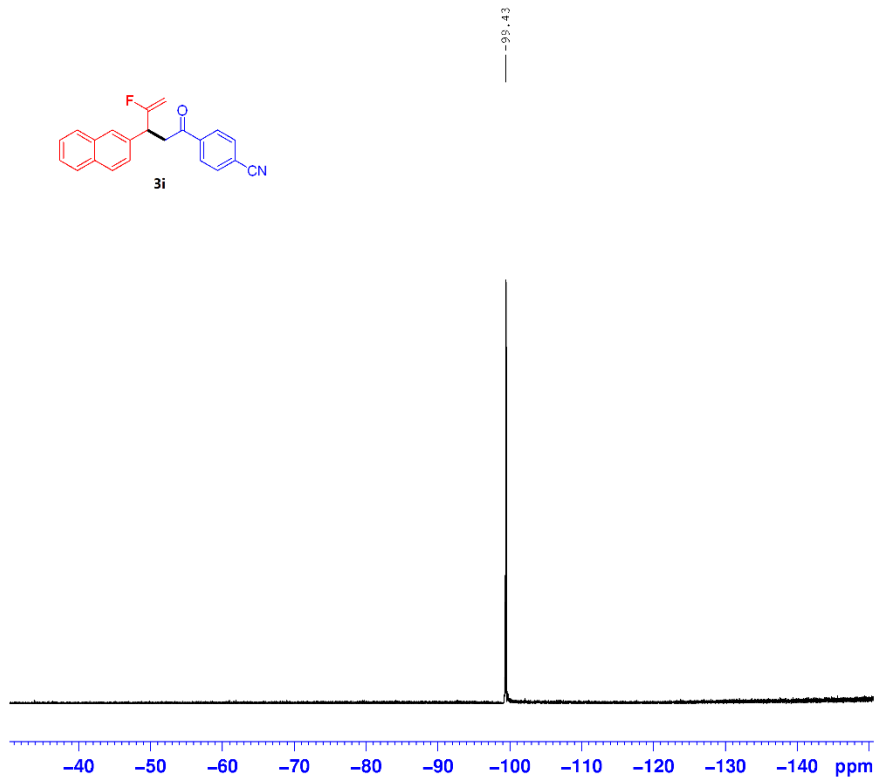
120
100
80
60
40
20
0
ppm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F
O
CN
3i
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−50
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−70
−80
−90
−100
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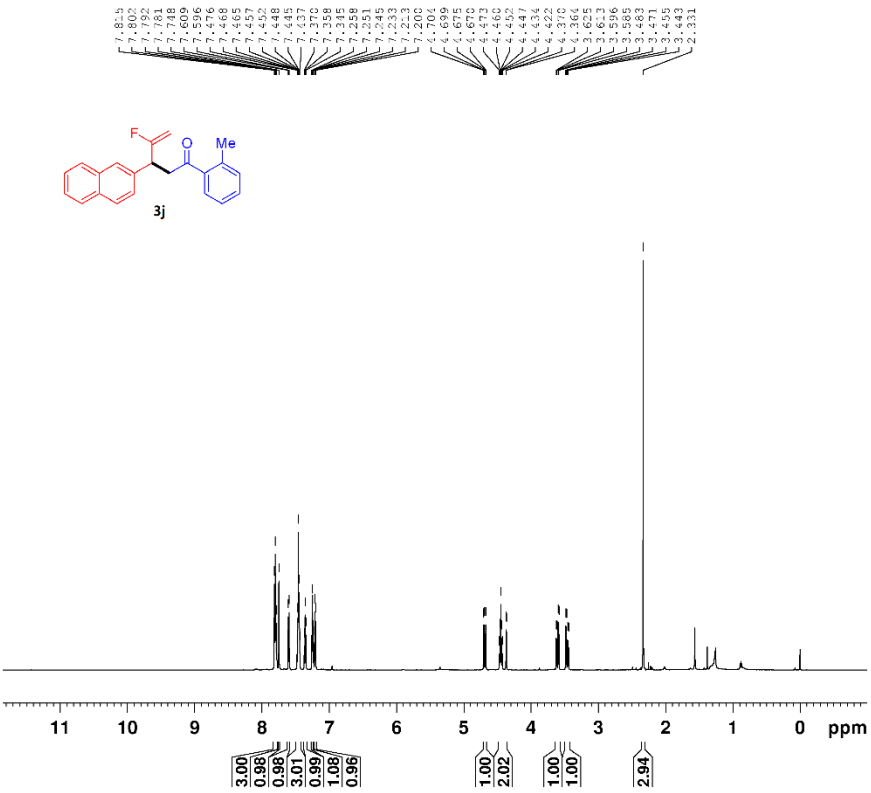
−120
−130
−140
ppm


F
O
Me
3j
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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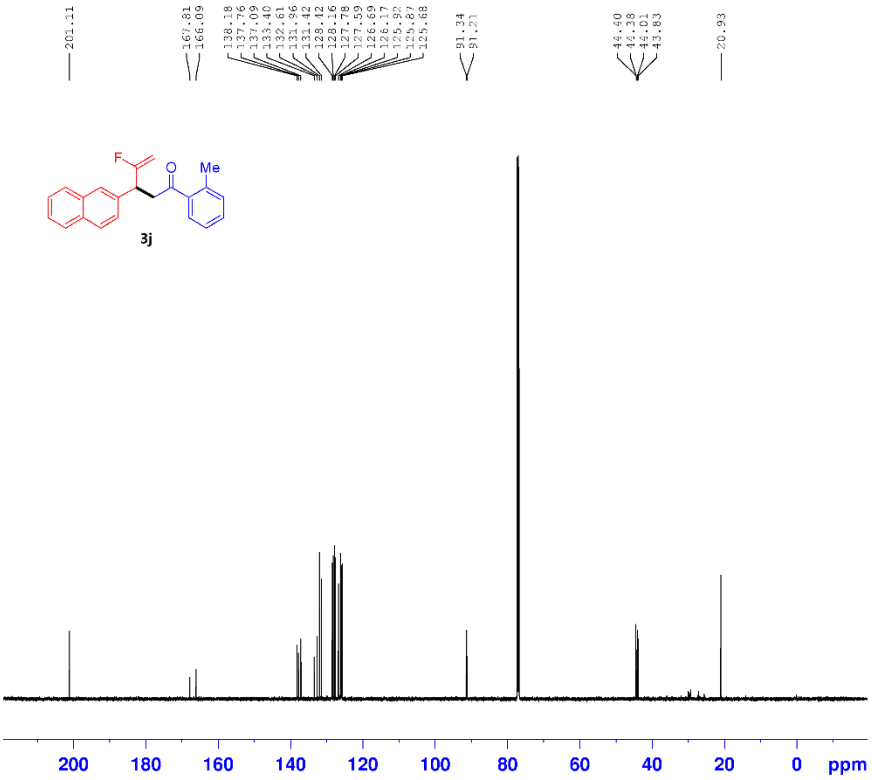
0.98
3.01
0.99
1.08
0.96
1.00
2.02
1.00
1.00
2.94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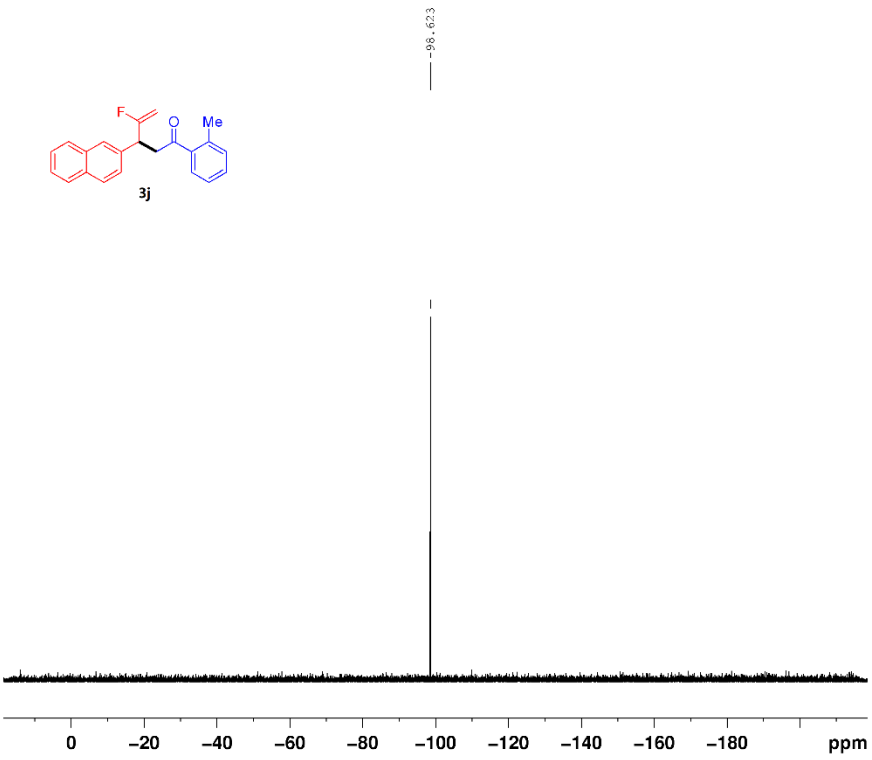
137.76
137.09
133.40
132.61
131.96
131.42
128.42
128.16
127.78
127.59
126.69
126.17
125.92
125.87
125.68
91.34
91.21
44.40
44.38
44.01
43.83
20.93
F
O
Me
3j
200
180
160
140
120
100
80
60
40
20
0
ppm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Me
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−100
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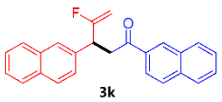
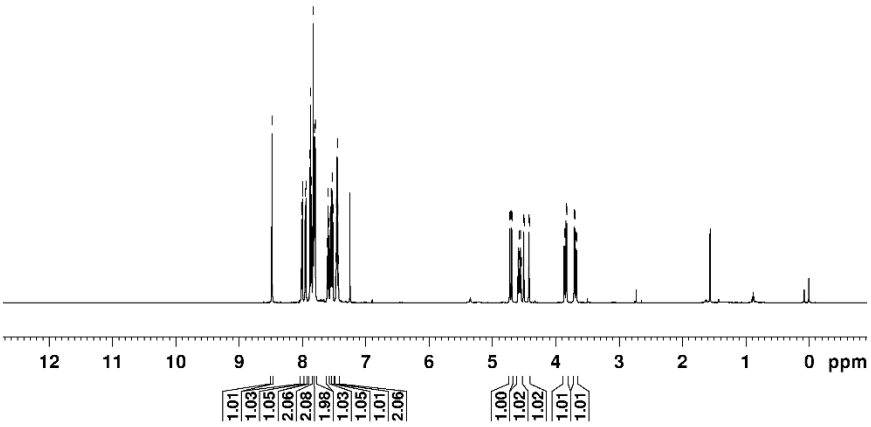
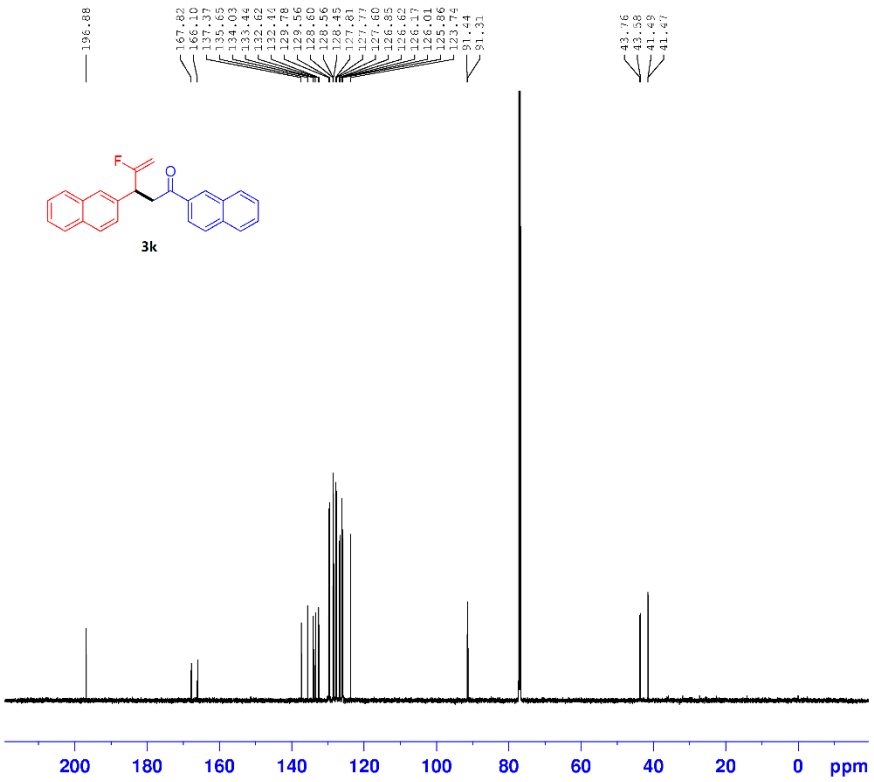
−180
ppm


F
O

3k


12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.01
1.03
1.05
2.06
2.08
1.98
1.03
1.05
1.01
2.06
1.00
1.02
1.02
1.01
1.01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134.03
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132.62
132.46
131.78
129.56
128.60
128.56
128.45
127.81
127.77
127.60
126.85
126.62
126.17
126.01
125.86
123.74
91.44
91.31
43.76
43.58
41.49
41.47
F
O
3k
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160
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120
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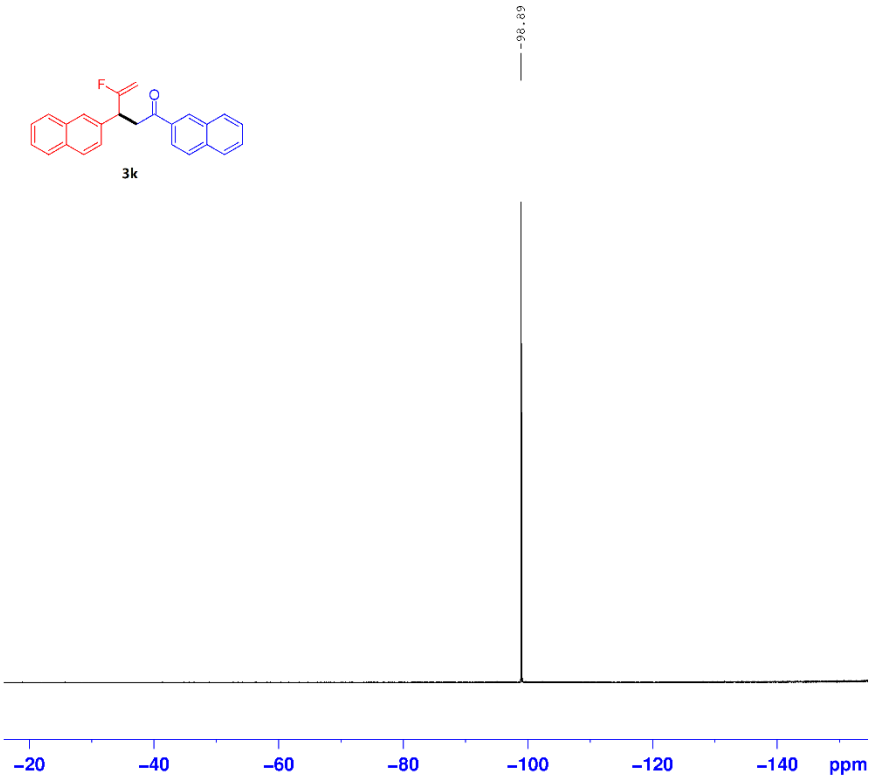
80
60
40
20
0
ppm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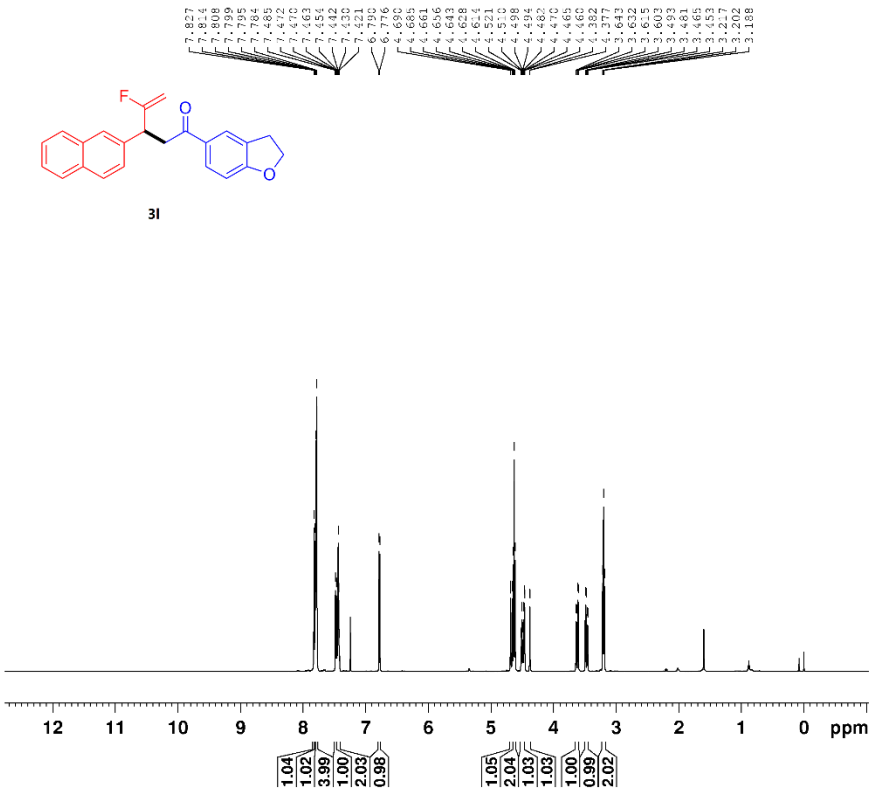
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7.463
7.455
7.442
7.430
7.421
6.790
6.776
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4.685
4.661
4.656
4.643
4.628
4.624
4.621
4.510
4.498
4.494
4.482
4.470
4.465
4.462
4.382
4.377
3.643
3.632
3.615
3.603
3.483
3.481
3.465
3.453
3.217
3.202
3.188
F
O
O
3l
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.02
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1.00
2.03
0.98
1.05
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1.03
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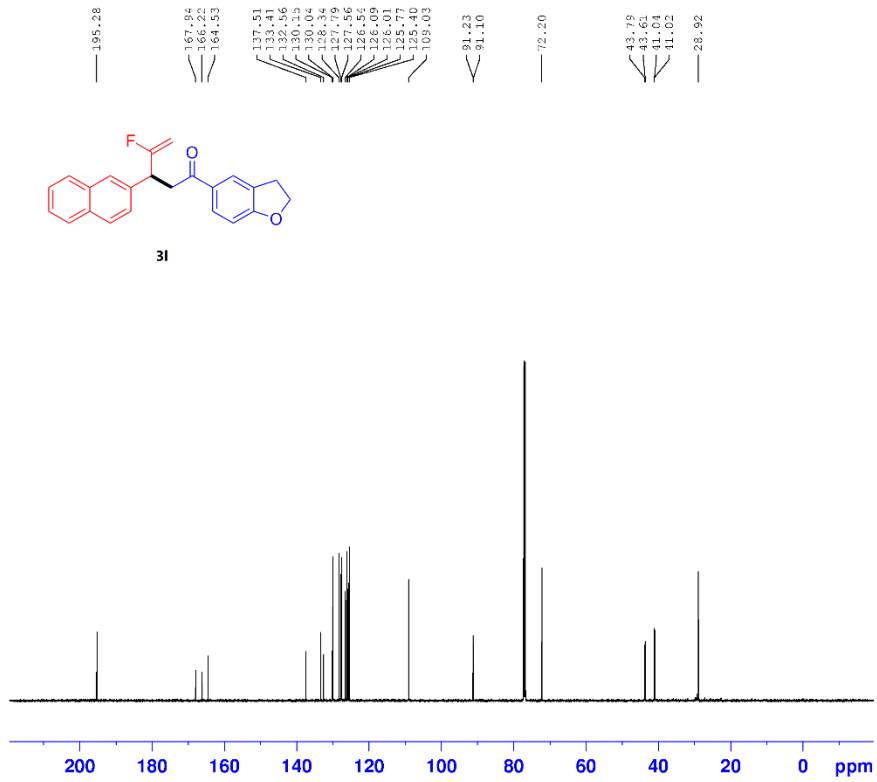
1.00
0.99
2.02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164.53
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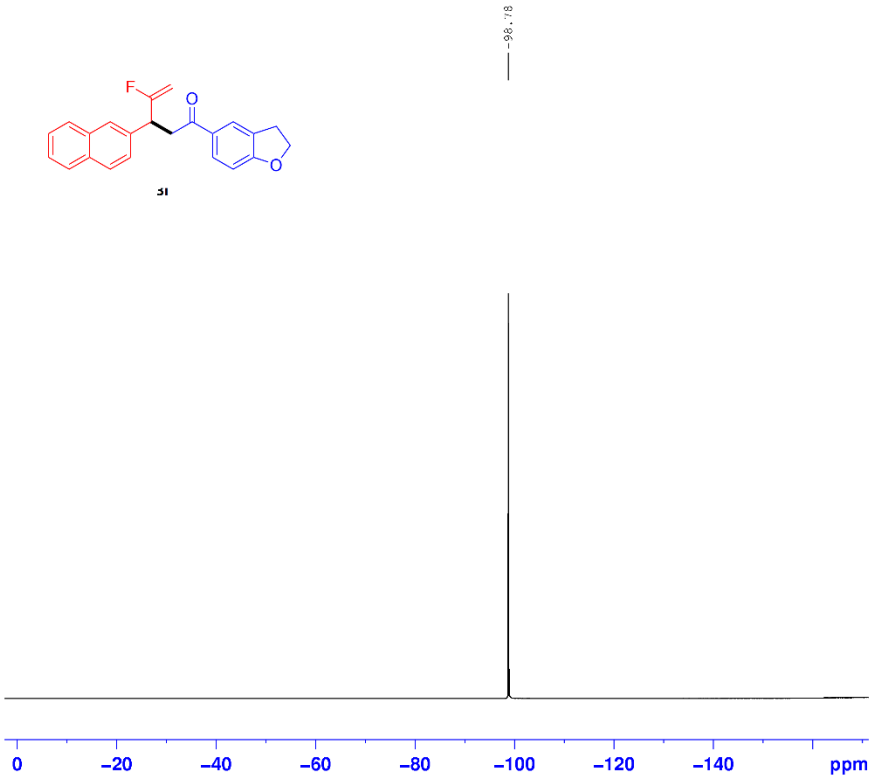
132.56
130.15
130.04
128.34
127.79
127.56
126.56
126.09
126.01
125.71
125.40
109.03
91.23
91.10
72.20
43.78
43.61
41.04
41.02
28.92
F
O
O
3l
200
180
160
140
120
100
80
60
40
20
0
ppm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F
O
O
0
−20
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−60
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−100
−120
−140
ppm


7.853
7.801
7.800
7.790
7.778
7.503
7.500
7.493
7.482
7.467
7.459
7.447
7.437
7.426
6.896
6.882
4.689
4.686
4.659
4.654
4.506
4.494
4.482
4.478
4.466
4.459
4.454
4.376
4.311
4.302
4.296
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3.590
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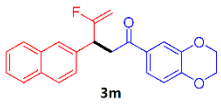
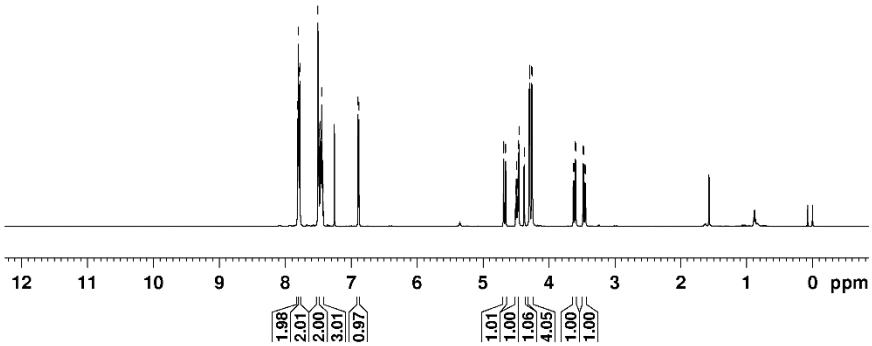
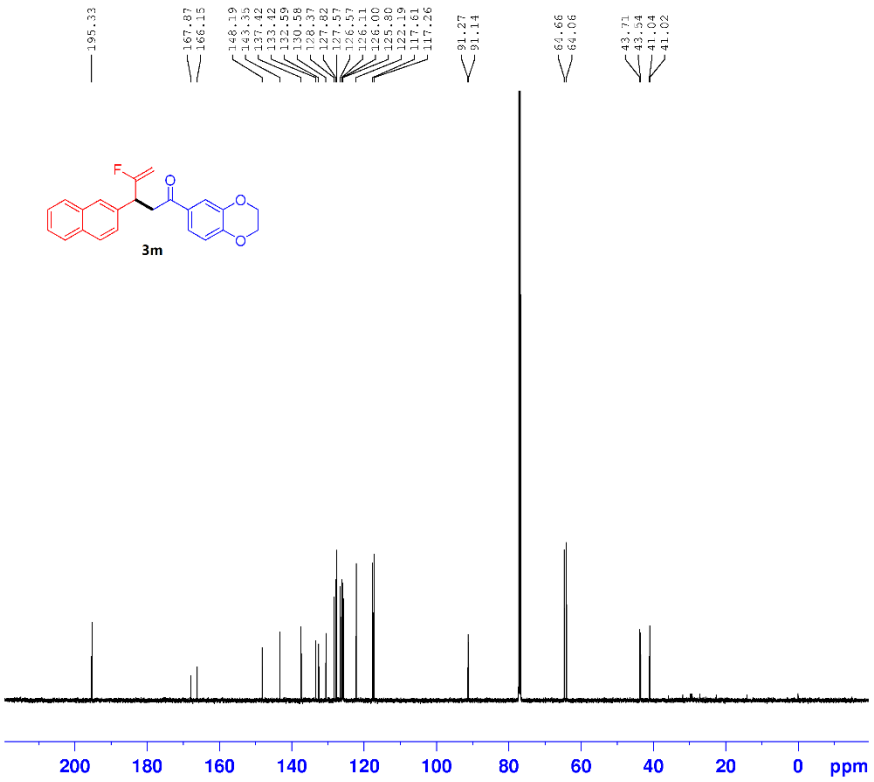
3.470
3.454
3.442


F
O
O
O

3m


12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.98
2.01
2.00
3.01
0.97
1.01
1.00
1.06
4.05
1.00
1.00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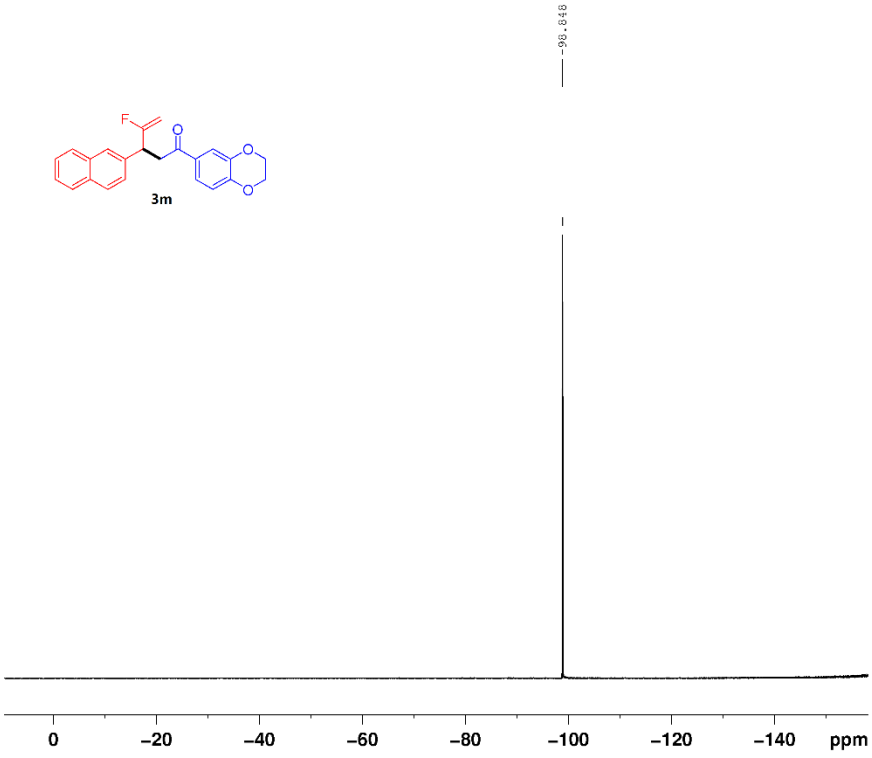
143.35
137.42
133.42
132.59
130.58
128.37
127.82
127.57
126.57
126.11
126.00
125.80
122.19
117.61
117.26
91.27
91.14
64.66
64.06
43.71
43.54
41.04
41.02
F
O
O
O
3m
200
180
160
140
120
100
80
60
40
20
0
ppm


-96.848
F
O
O
O
3m
0
−20
−40
−60
−80
−100
−120
−140
ppm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7.992
7.978
7.820
7.805
7.799
7.794
7.786
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7.481
7.470
7.467
7.463
7.461
7.455
7.452
7.448
7.443
7.440
7.431
7.429
4.713
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4.508
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4.492
4.480
4.470
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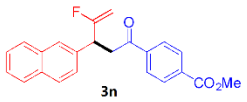
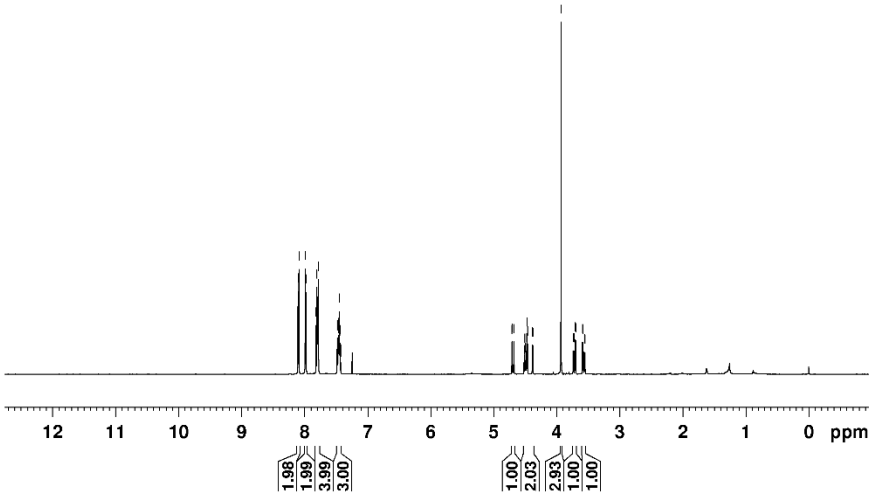
3.563
3.551


F
O
CO2Me

3n


12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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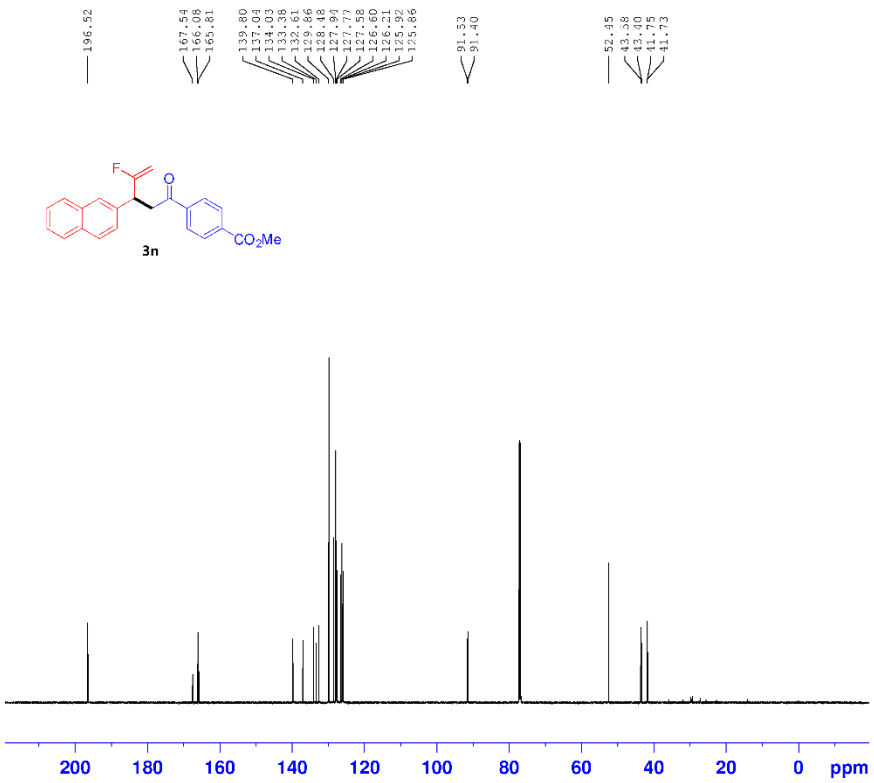
1.99
3.99
3.00
1.00
2.03
2.93
1.00
1.00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134.03
133.38
132.61
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127.94
127.77
127.58
126.60
126.21
125.92
125.86
91.53
91.40
52.45
43.38
43.40
41.75
41.73
F
O
CO2Me
3n
200
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140
120
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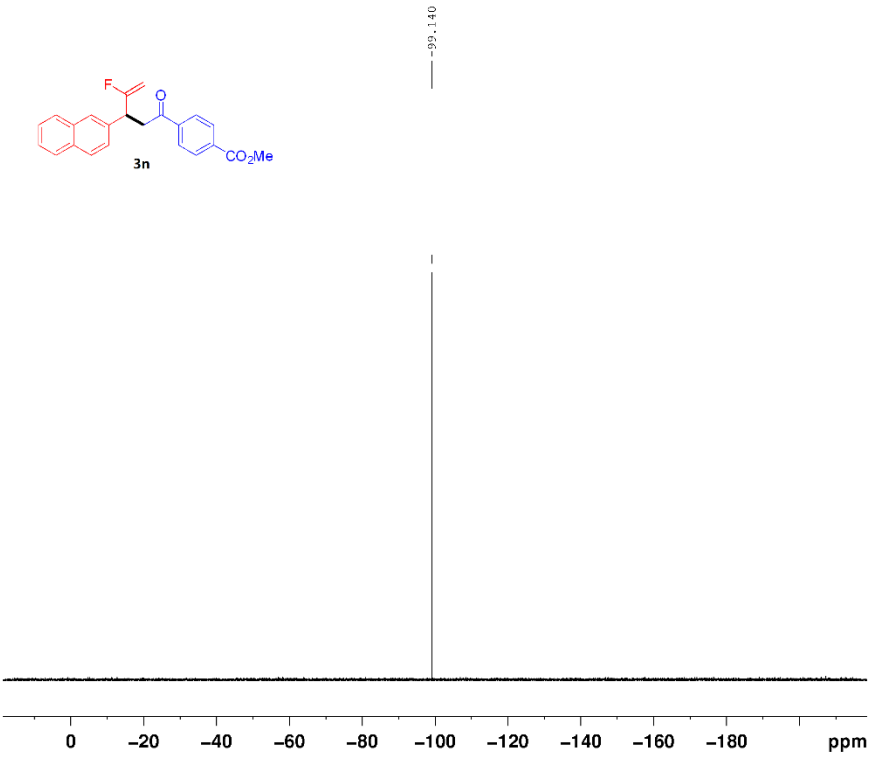
80
60
40
20
0
ppm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CO2Me
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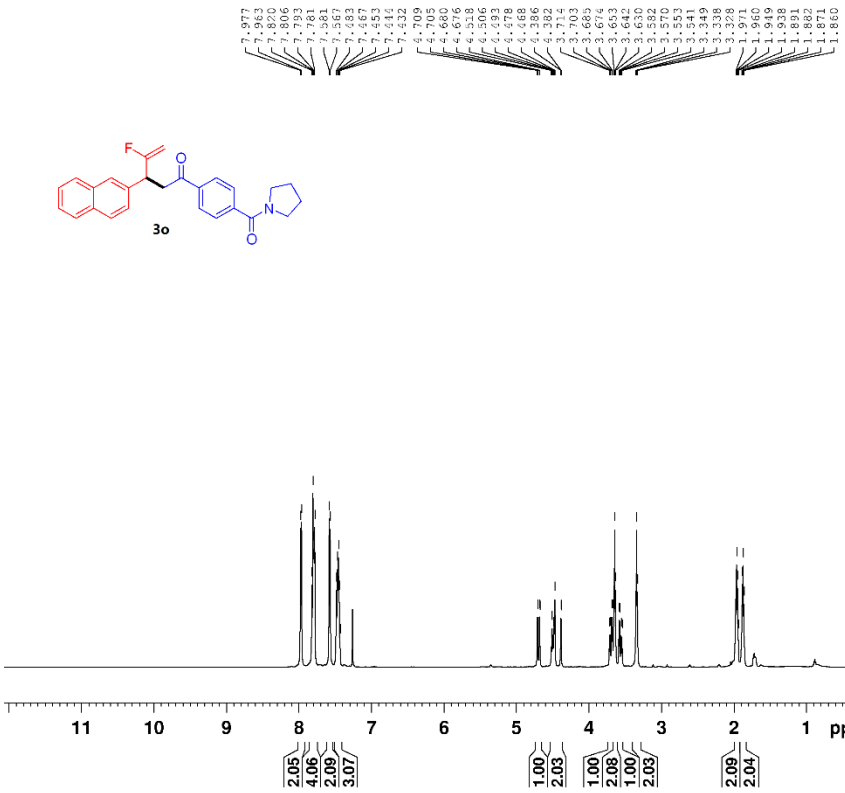
−180
ppm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7.667
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7.432
4.709
4.705
4.680
4.676
4.518
4.506
4.493
4.478
4.388
4.386
3.792
3.775
3.703
3.685
3.674
3.653
3.642
3.630
3.582
3.570
3.553
3.541
3.349
3.338
3.328
3.311
1.960
1.949
1.938
1.891
1.882
1.871
1.860
F
O
N
O
3o
11
10
9
8
7
6
5
4
3
2
1
ppm
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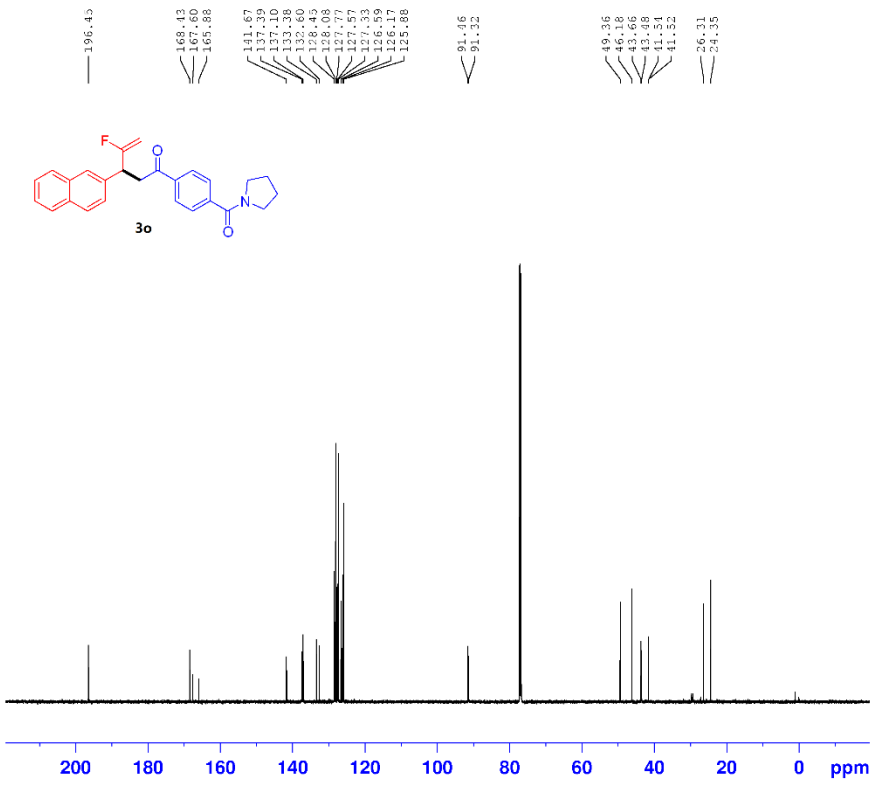
4.06
2.09
3.07
1.00
2.03
1.00
2.08
1.00
2.03
2.09
2.04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165.88
141.67
137.39
137.10
133.38
132.60
128.45
128.08
127.77
127.57
127.33
126.59
126.17
125.88
91.46
91.32
49.36
46.18
43.66
43.48
41.54
41.52
26.31
24.35
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O
O
N
3o
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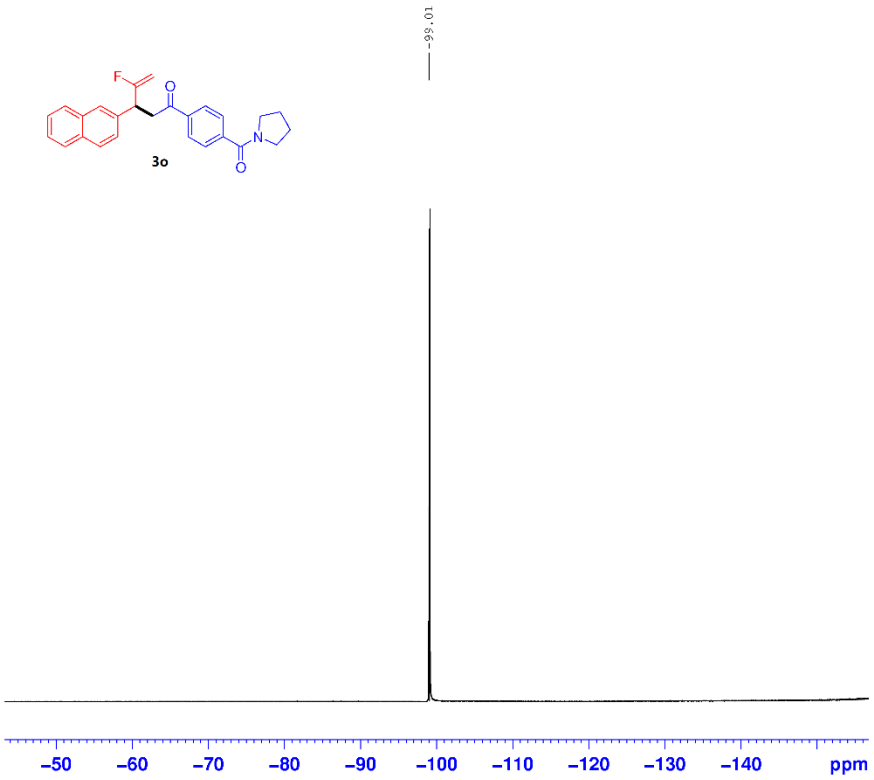
120
100
80
60
40
20
0
ppm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3o
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−90
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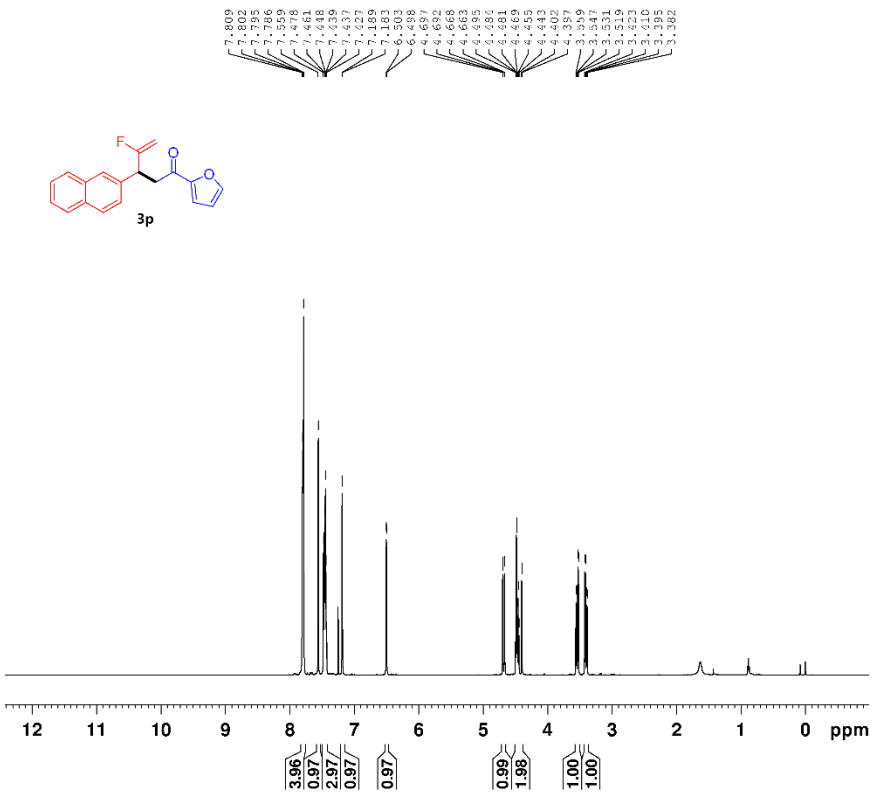
−140
ppm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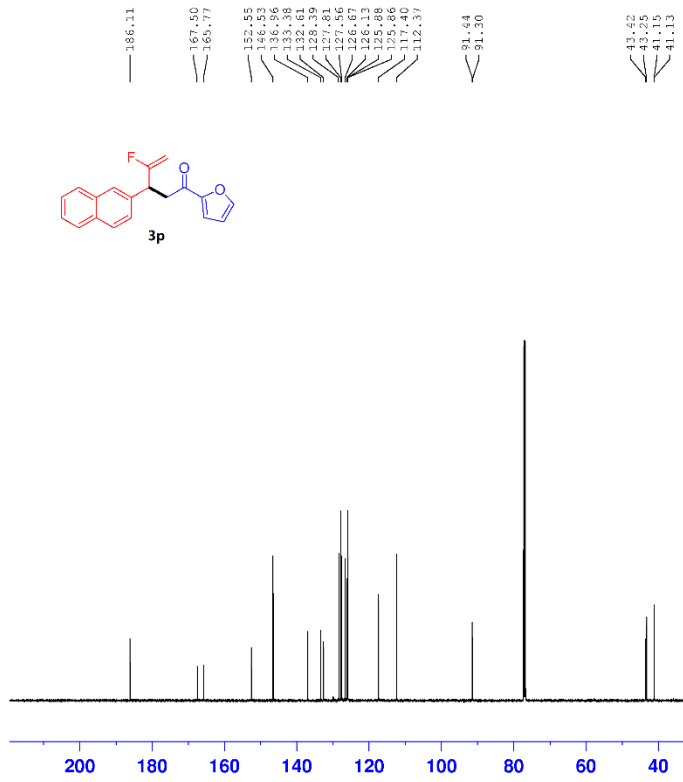
7.448
7.439
7.437
7.427
7.189
7.183
6.503
6.498
4.697
4.692
4.668
4.663
4.485
4.480
4.481
4.469
4.455
4.443
4.402
4.397
3.559
3.547
3.531
3.519
3.423
3.410
3.395
3.382
F
O
O
3p
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.96
0.97
2.97
0.97
0.97
0.99
1.98
1.00
1.00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167.50
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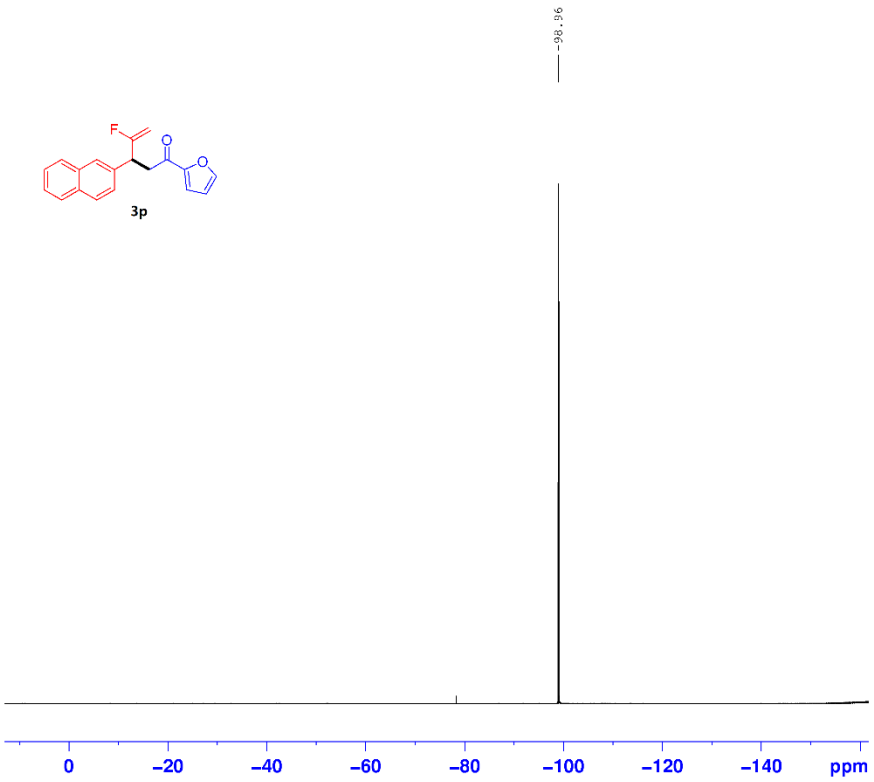
152.55
142.53
136.96
133.38
132.61
128.39
127.81
127.56
126.67
126.13
125.88
125.86
117.40
112.37
91.64
91.30
43.42
43.25
41.15
41.13
F
O
O
3p
200
180
160
140
120
100
80
60
40
20
0
ppm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O
O
3p
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−40
−60
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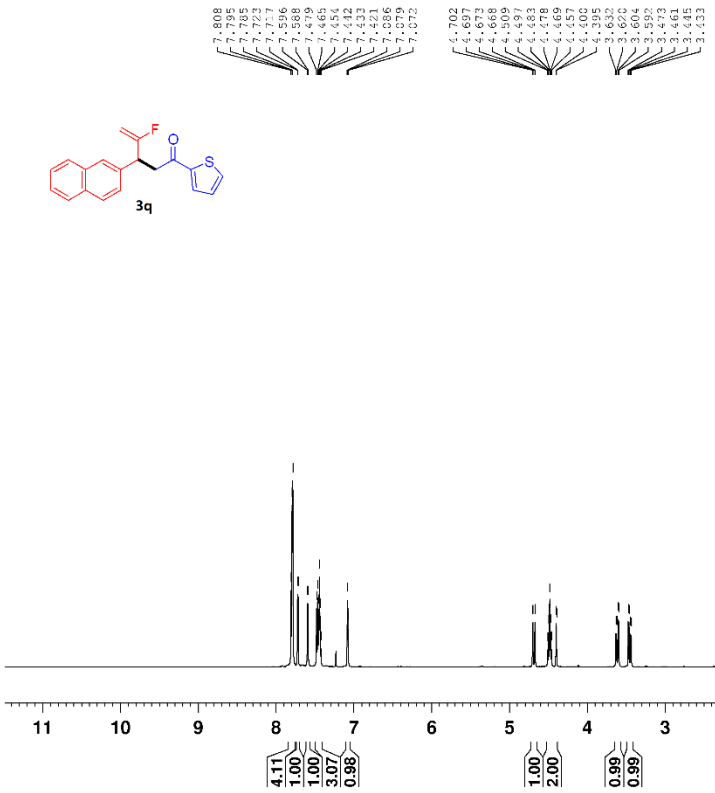
−100
−120
−140
ppm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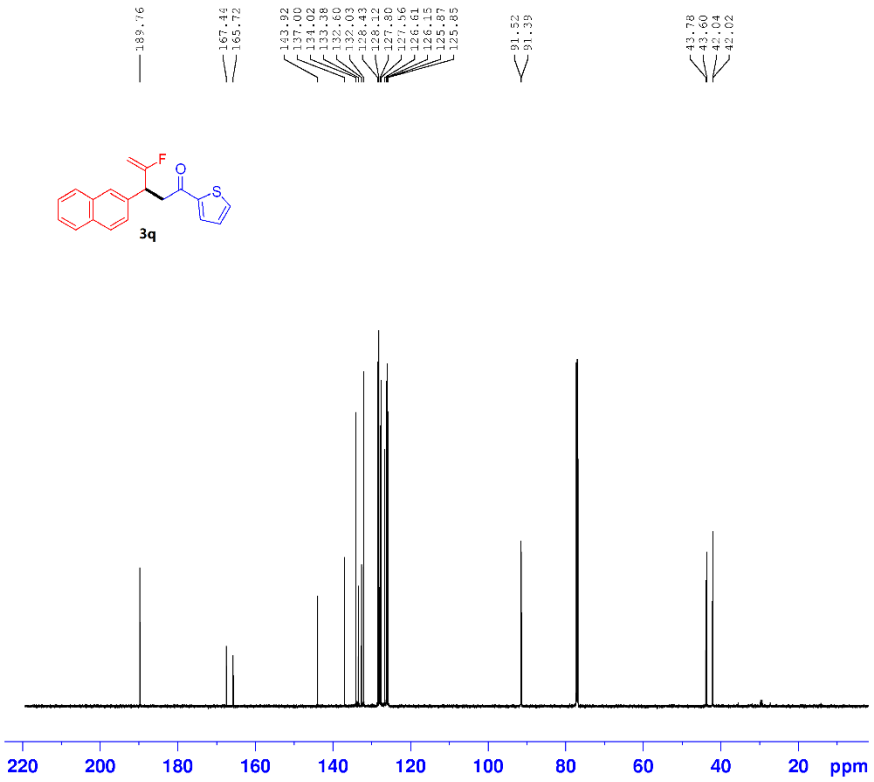
7.705
7.723
7.717
7.596
7.588
7.469
7.465
7.454
7.442
7.433
7.421
7.086
7.079
7.073
4.702
4.697
4.673
4.668
4.599
4.594
4.483
4.478
4.469
4.457
4.400
4.395
3.632
3.620
3.604
3.592
3.473
3.461
3.445
3.433
F
O
S
3q
11
10
9
8
7
6
5
4
3
2
ppm
4.11
1.00
1.00
3.07
0.98
1.00
2.00
0.99
0.99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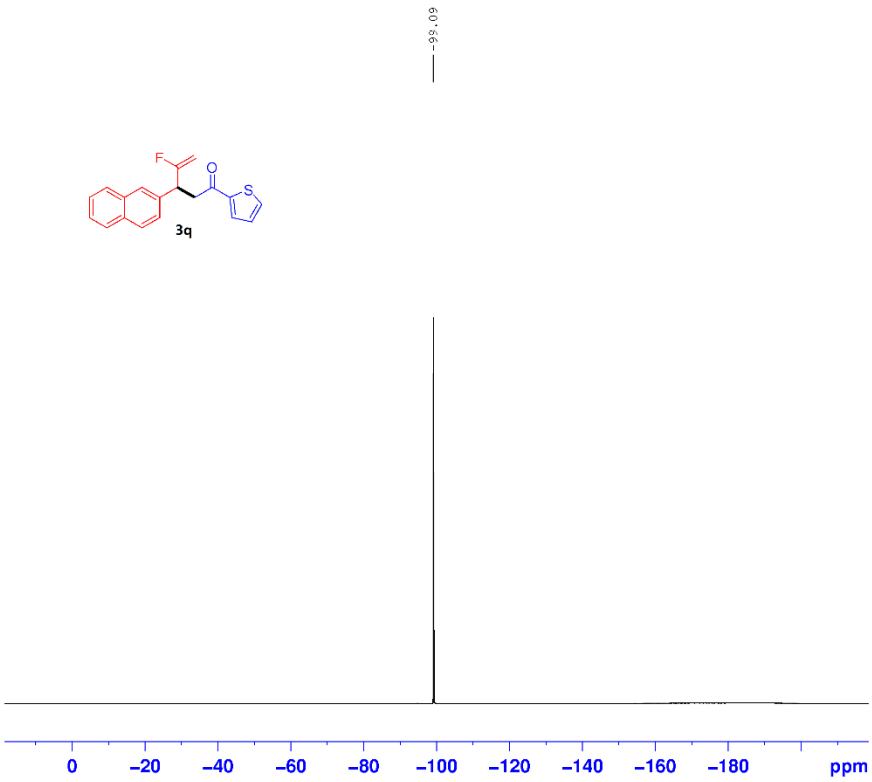
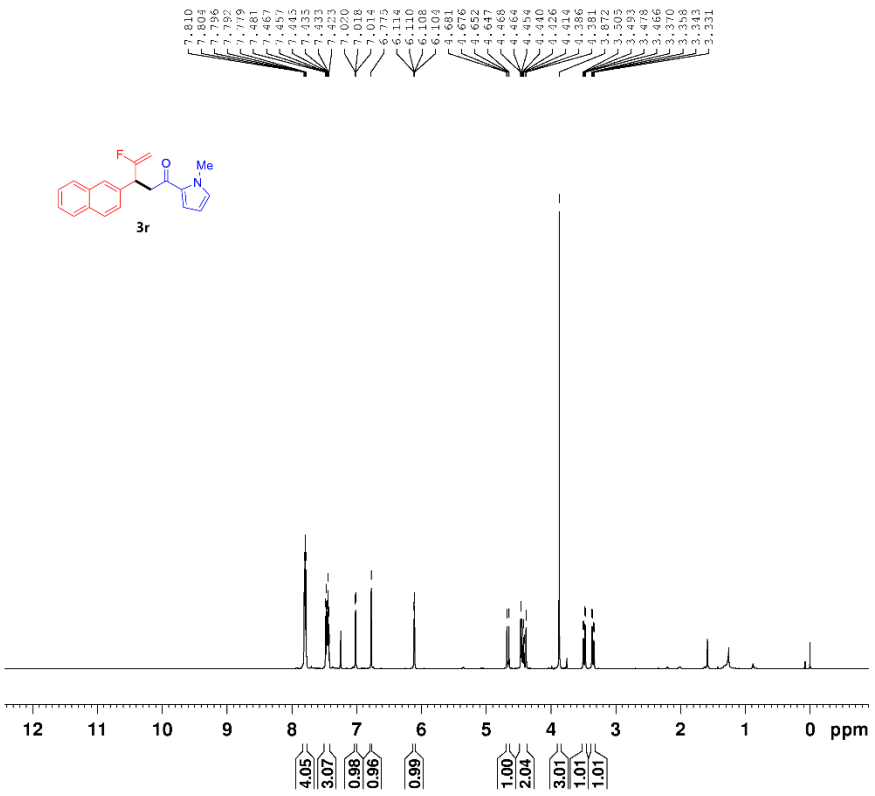
167.44
165.72
143.92
137.00
134.02
133.38
132.60
132.03
128.43
128.12
127.80
127.56
126.61
126.15
125.87
125.85
91.52
91.39
43.78
43.60
42.04
42.02
F
O
S
3q
220
200
180
160
140
120
100
80
60
40
20
ppm


-99.09
F
O
S
3q
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm


7.810
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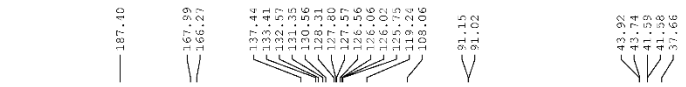
7.779
7.481
7.467
7.457
7.445
7.433
7.423
7.020
7.018
7.014
6.773
6.114
6.110
6.108
6.104
4.681
4.676
4.652
4.647
4.468
4.464
4.454
4.440
4.426
4.414
4.386
4.381
3.872
3.505
3.493
3.478
3.466
3.330
3.358
3.343
3.331
F
O
Me
N
3r
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.05
3.07
0.98
0.96
0.99
1.00
2.04
3.01
1.01
1.01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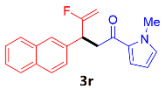
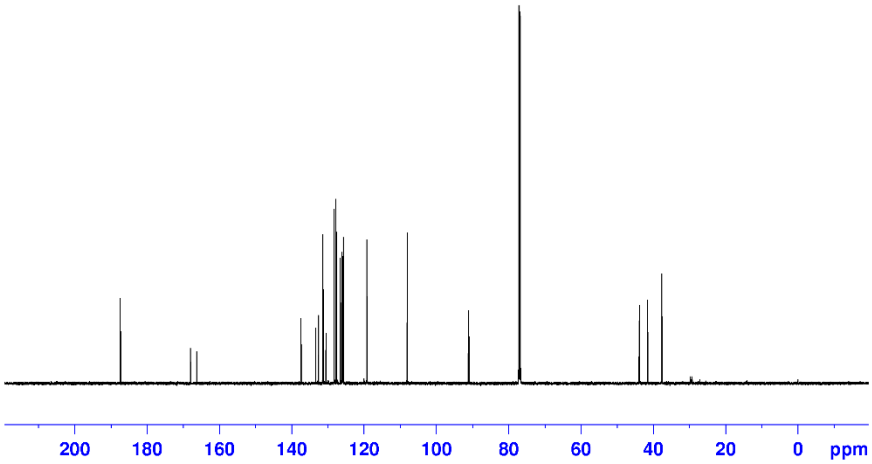
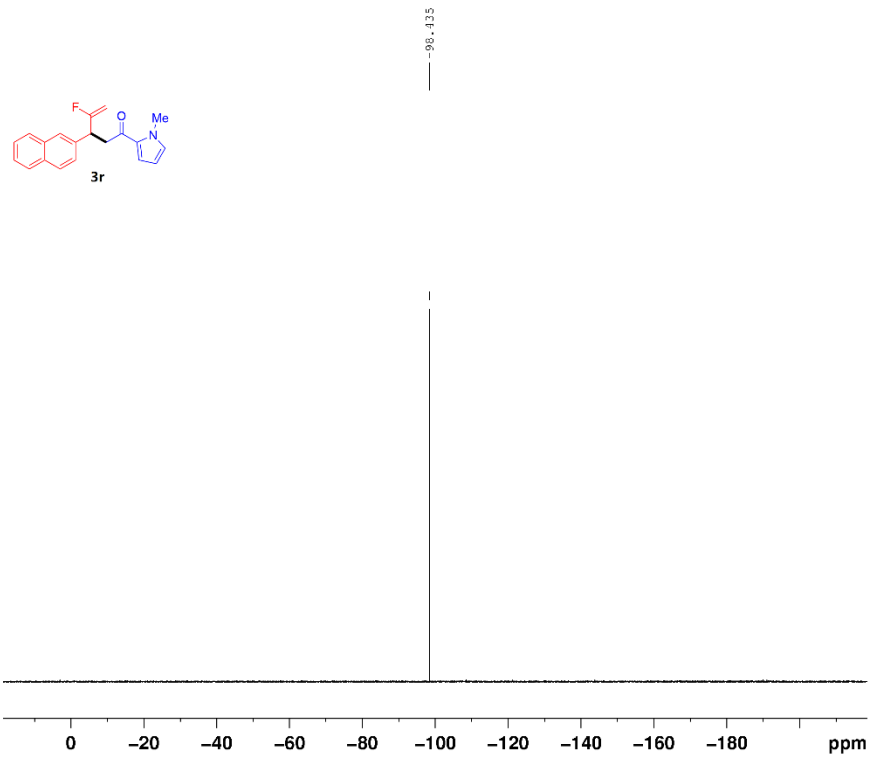
133.41
132.57
131.35
130.56
128.31
127.80
127.57
126.56
126.06
126.02
125.75
119.26
108.06
91.15
91.02
43.92
43.74
41.55
41.38
37.66


F
O
Me
N

3r


200
180
160
140
120
100
80
60
40
20
0
ppm


-98.435
F
O
Me
N
3r
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−80
−100
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−140
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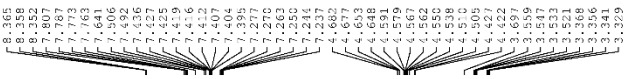
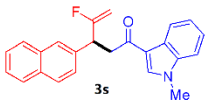
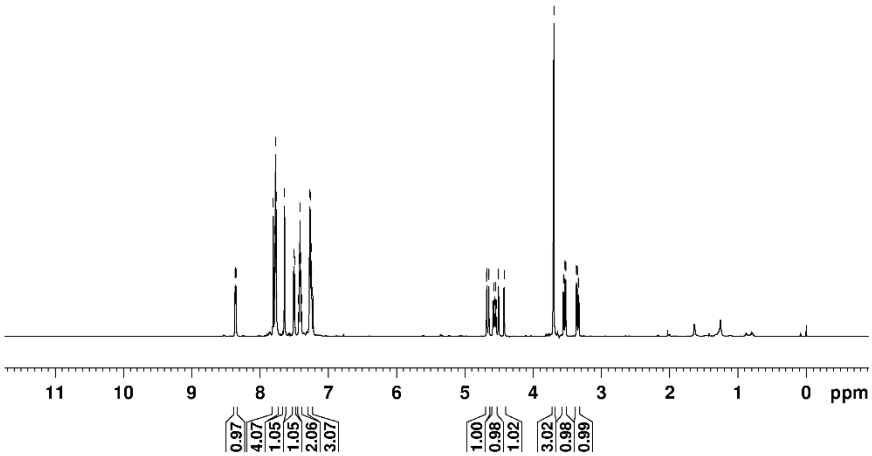
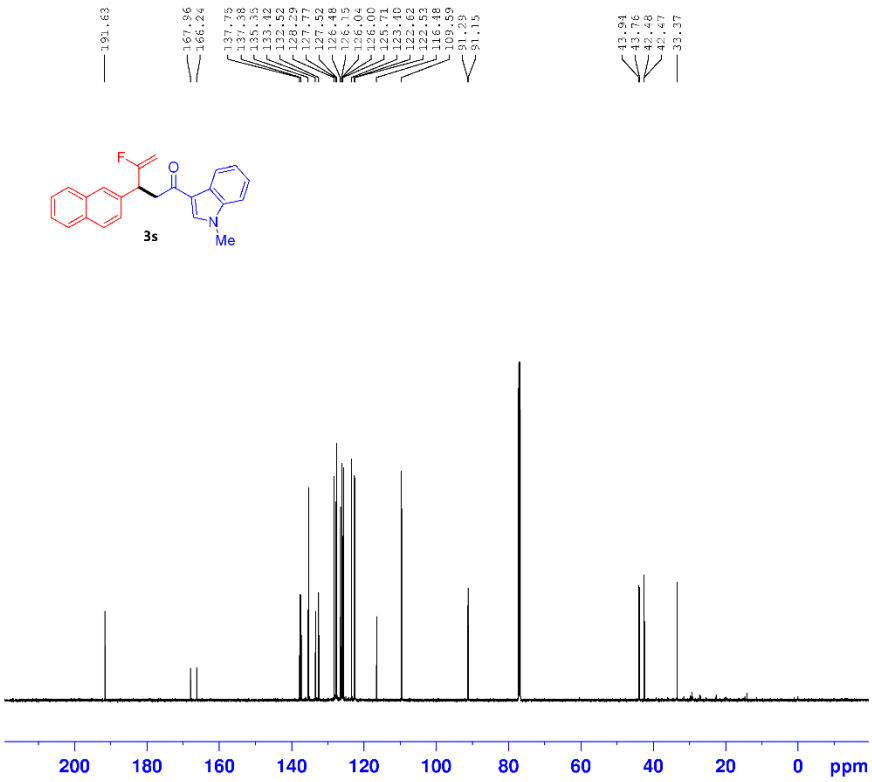
−180
ppm




F
O
N
Me
3s


11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.97
4.07
1.05
1.05
2.06
3.07
1.00
0.98
1.02
3.02
0.98
0.99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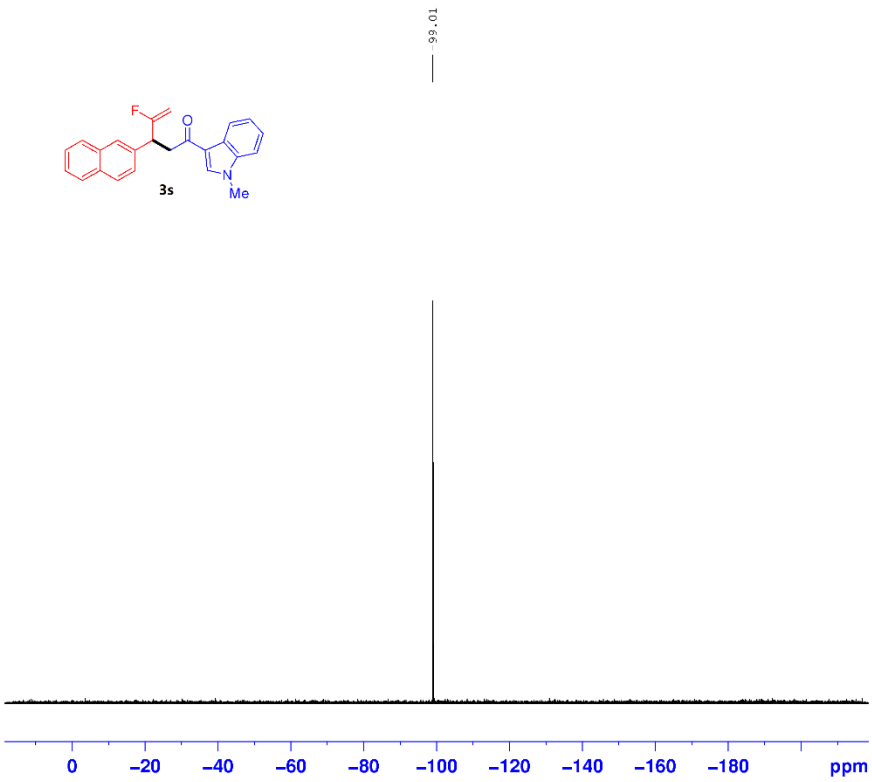
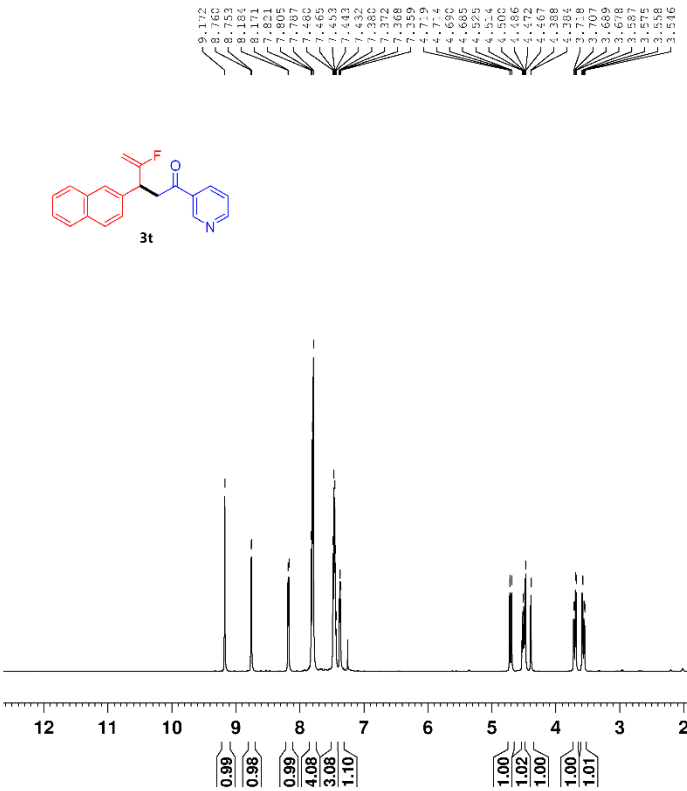
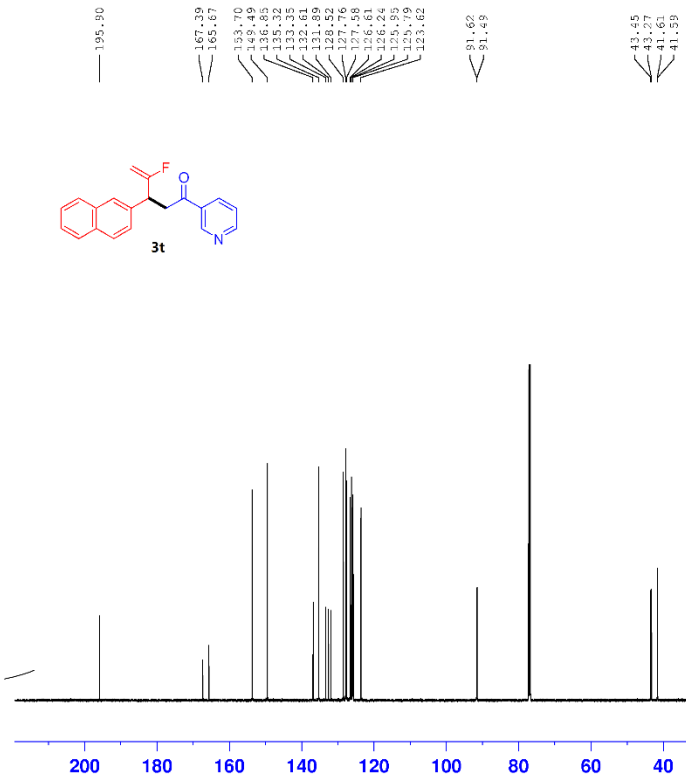
167.96
166.24
137.75
137.38
135.35
133.42
132.52
128.29
127.77
127.52
126.48
126.15
126.04
126.00
125.71
123.40
122.62
122.53
116.48
109.59
91.29
91.15
43.94
43.76
43.58
43.47
33.37
F
O
N
Me
3s
200
180
160
140
120
100
80
60
40
20
0
ppm


99.01
F
O
N
Me
3s
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm


9.172
8.760
8.753
8.184
8.171
7.821
7.805
7.787
7.460
7.465
7.453
7.443
7.432
7.380
7.372
7.368
7.359
4.719
4.714
4.690
4.685
4.525
4.514
4.500
4.466
4.472
4.467
4.388
4.384
3.718
3.707
3.689
3.678
3.587
3.575
3.558
3.546
F
O
N
3t
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
0.99
0.98
0.99
4.08
3.08
1.10
1.00
1.02
1.00
1.00
1.01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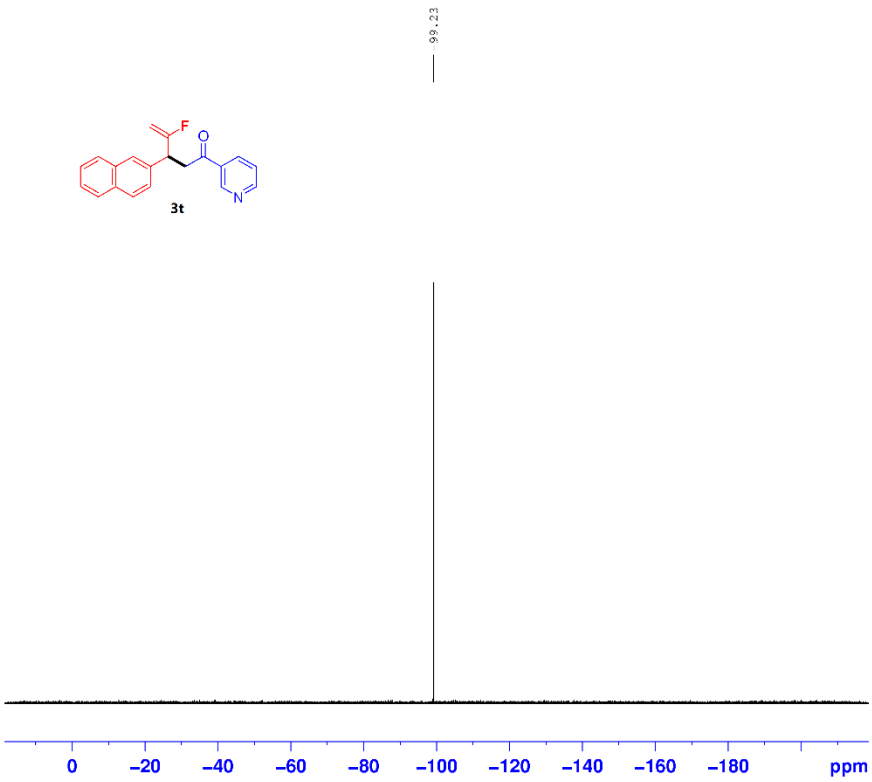
165.67
153.70
149.49
136.85
135.32
133.35
132.61
131.89
128.52
127.76
127.58
126.61
126.24
125.95
125.79
123.62
91.62
91.49
43.45
43.27
41.61
41.39
F
O
N
3t
200
180
160
140
120
100
80
60
40
20
0
ppm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F
O
N
3t
0
−20
−40
−60
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−100
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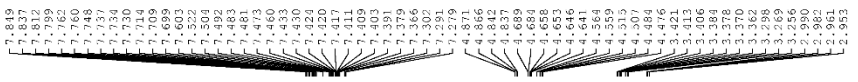
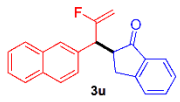
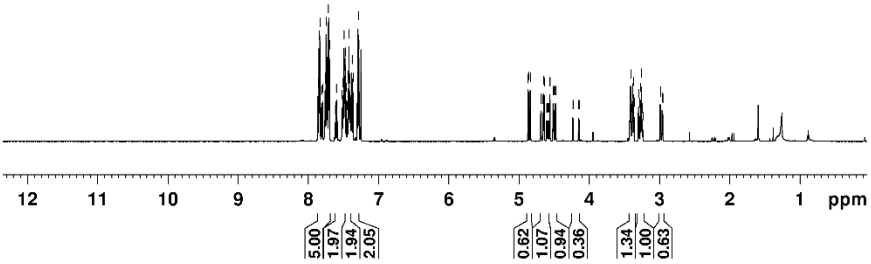
−140
−160
−180
ppm

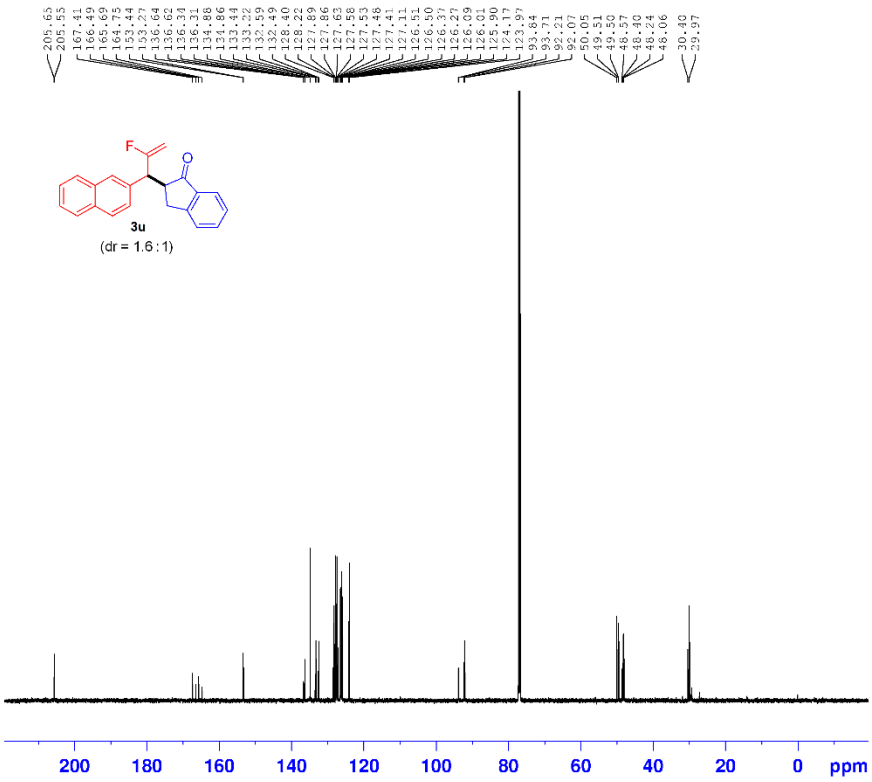


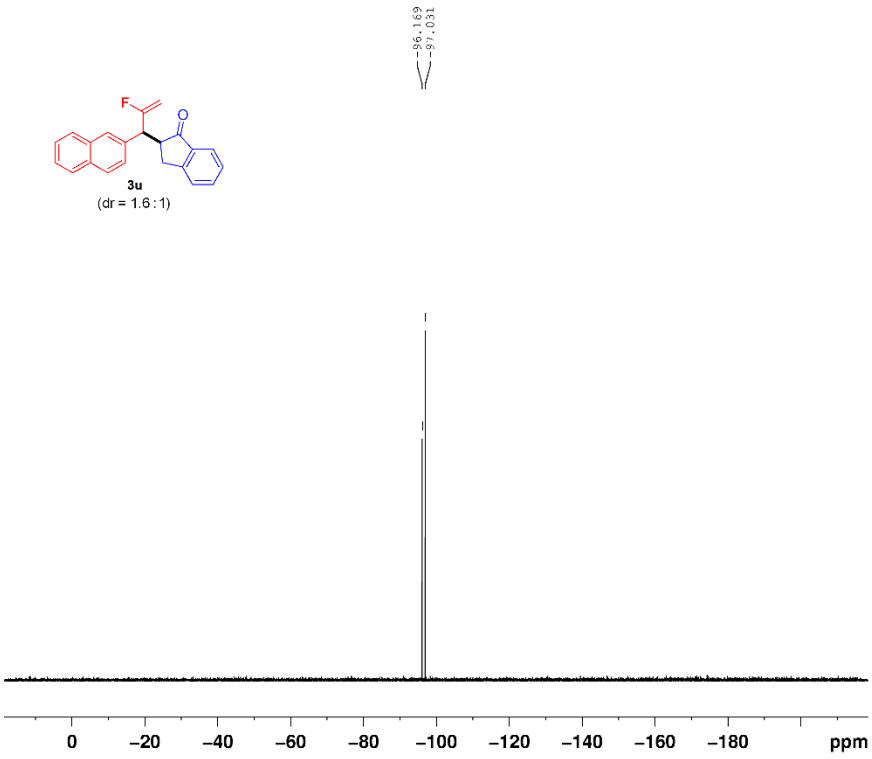

F
O

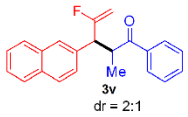
3u

(dr = 1.6 : 1)


12
11
10
9
8
7
6
5
4
3
2
1
ppm
5.00
1.97
1.94
2.05
0.62
1.07
0.94
0.36
1.34
1.00
0.63

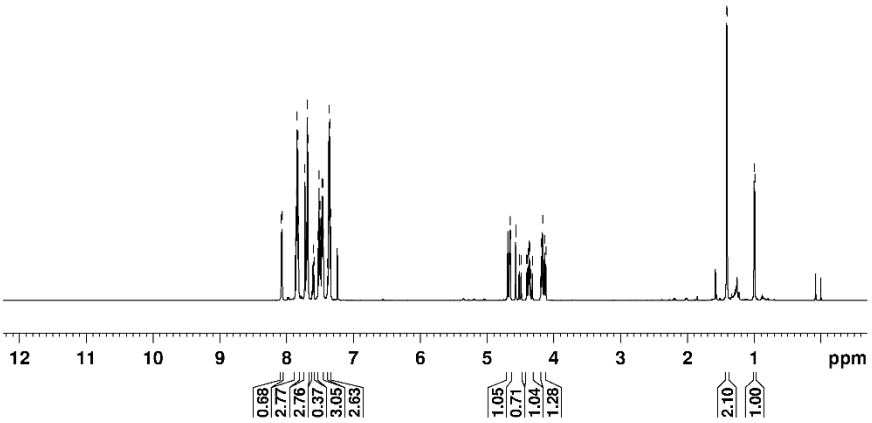

205.63
205.55
167.41
166.49
165.69
164.75
153.44
153.27
136.64
136.62
136.34
136.31
134.88
134.66
133.44
133.22
132.59
132.49
128.40
128.22
127.89
127.86
127.63
127.58
127.53
127.46
127.41
127.11
126.51
126.40
126.37
126.27
126.09
126.01
125.90
124.17
123.97
93.84
93.71
92.21
92.07
50.05
49.51
49.50
48.57
48.40
48.24
48.06
30.40
29.97
F
O
3u
(dr = 1.6 : 1)
200
180
160
140
120
100
80
60
40
20
0
ppm

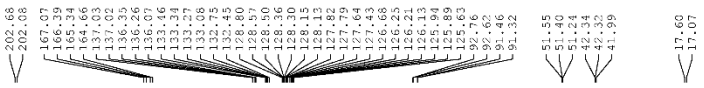

-96.169
-97.031
F
O
3u
(dr = 1.6 : 1)
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm


F
O
Me

3v

dr = 2:1


12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.68
2.77
2.76
0.37
3.05
2.63
1.05
0.71
1.04
1.28
2.10
1.00


202.68
202.08
167.07
166.39
165.34
164.66
137.03
137.02
136.35
136.26
136.07
133.46
133.34
133.27
133.06
132.75
132.45
128.80
128.57
128.50
128.36
128.30
128.15
128.13
127.82
127.79
127.64
127.43
126.68
126.25
126.21
126.13
125.94
125.89
125.63
92.76
92.62
91.46
91.32
51.55
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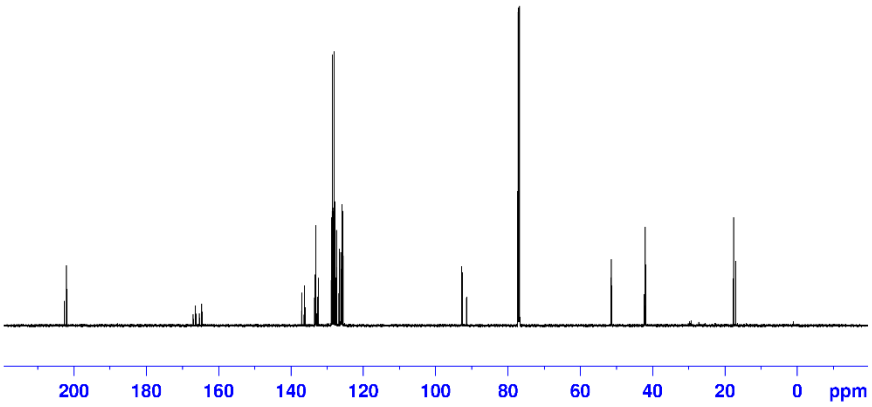
51.24
42.34
42.32
41.99
17.60
17.07


F
O
Me

3v
dr = 2:1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120
100
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60
40
20
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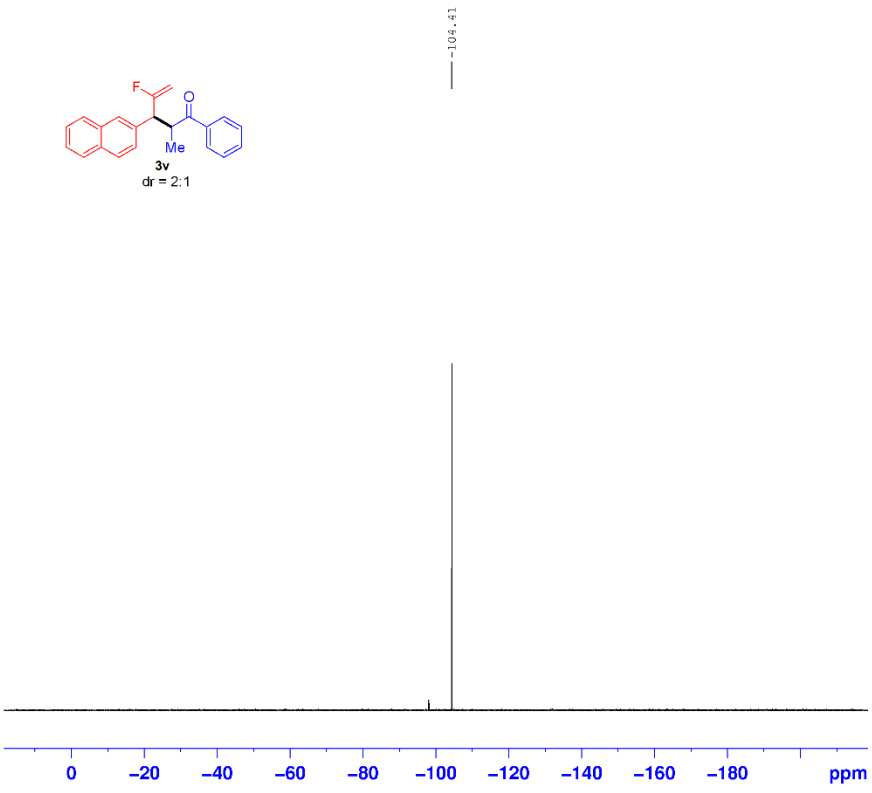
ppm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F
O
Me
3v
dr = 2:1
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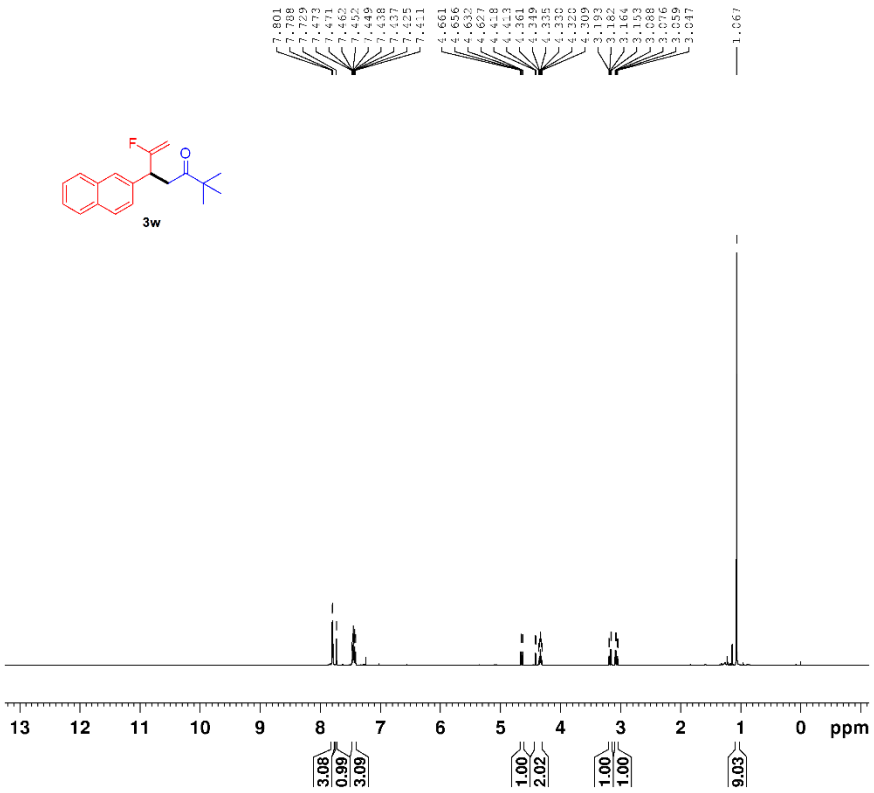
−40
−60
−80
−100
−120
−140
−160
−180
ppm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7.471
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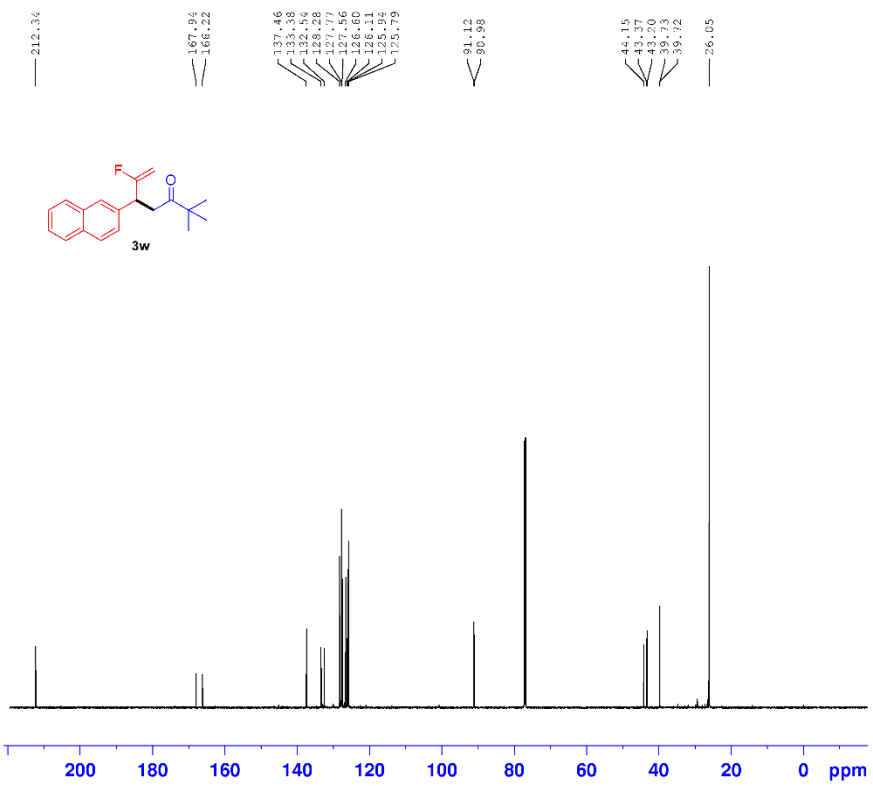
7.452
7.449
7.438
7.437
7.425
7.411
4.661
4.656
4.632
4.627
4.443
4.361
4.349
4.335
4.330
4.320
4.309
3.193
3.182
3.164
3.153
3.088
3.076
3.059
3.047
1.067
F
O
3w
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.08
0.99
3.09
1.00
2.02
1.00
1.00
9.03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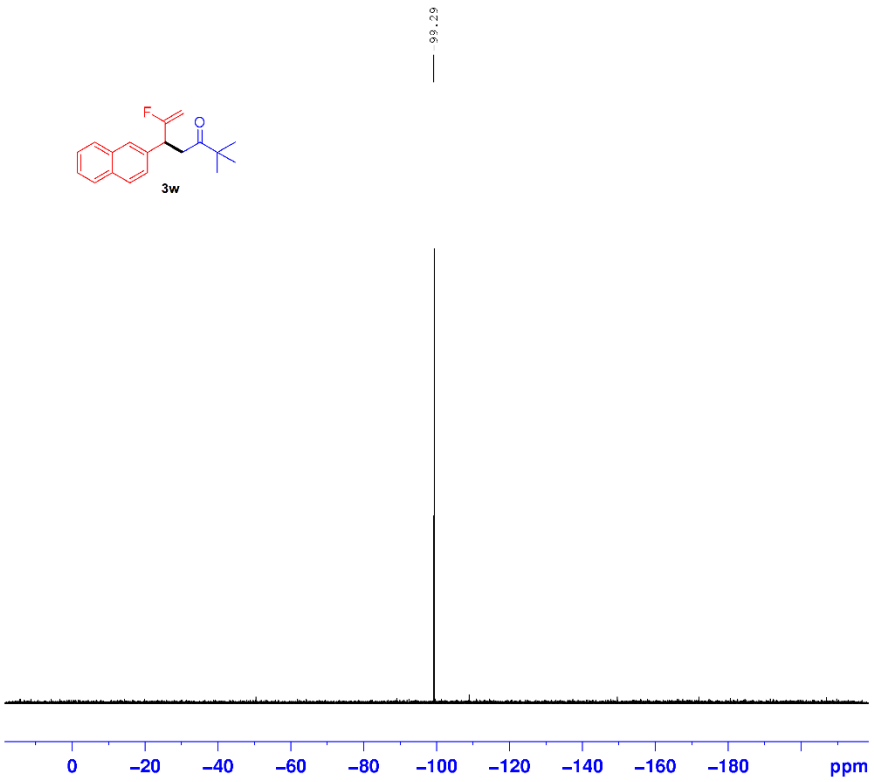
166.22
137.46
133.38
132.54
128.28
127.77
127.56
126.60
126.11
125.94
125.79
91.12
90.98
44.15
43.37
43.20
39.73
39.32
26.05
F
O
3w
200
180
160
140
120
100
80
60
40
20
0
ppm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−100
−120
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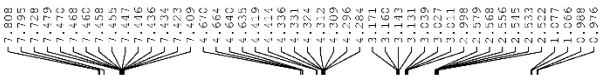
−160
−180
ppm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7.460
7.458
7.455
7.447
7.446
7.436
7.434
7.423
7.409
4.670
4.664
4.647
4.635
4.619
4.614
4.336
4.331
4.324
4.312
4.309
4.296
4.284
3.171
3.160
3.143
3.131
3.039
3.027
3.011
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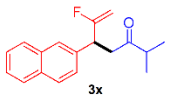
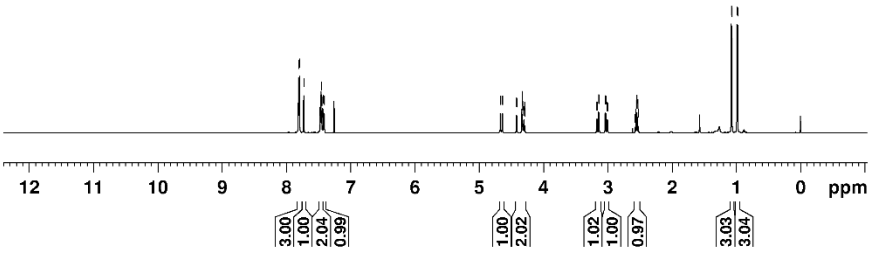
2.568
2.556
2.545
2.533
2.522
1.077
1.066
0.988
0.976


F
O

3x


12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
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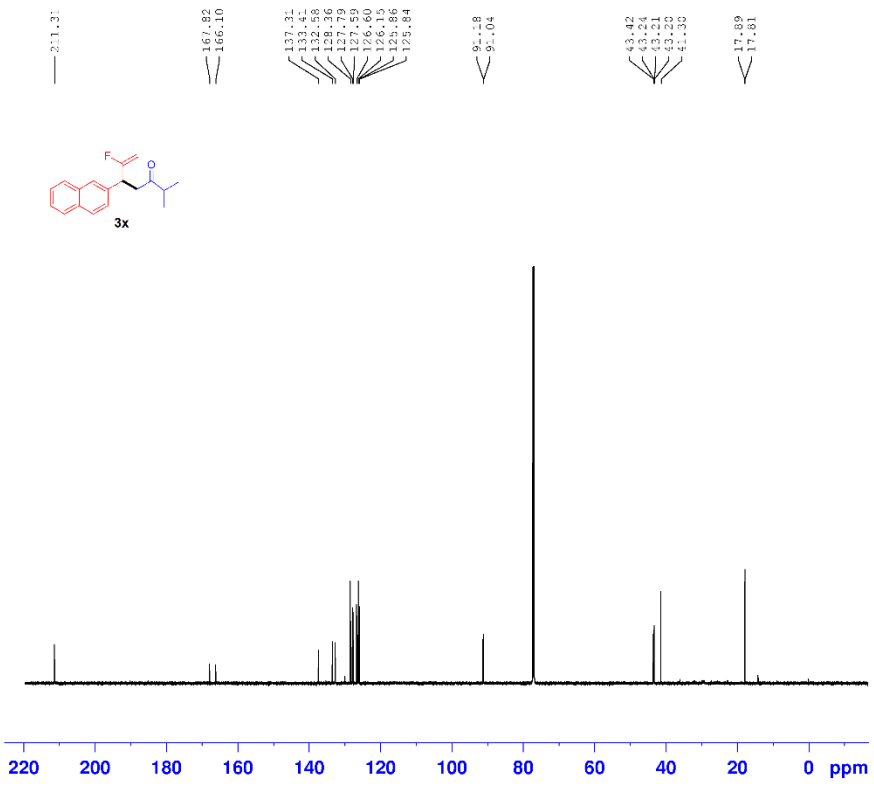
1.00
2.04
0.99
1.00
2.02
1.02
1.00
0.97
3.03
3.04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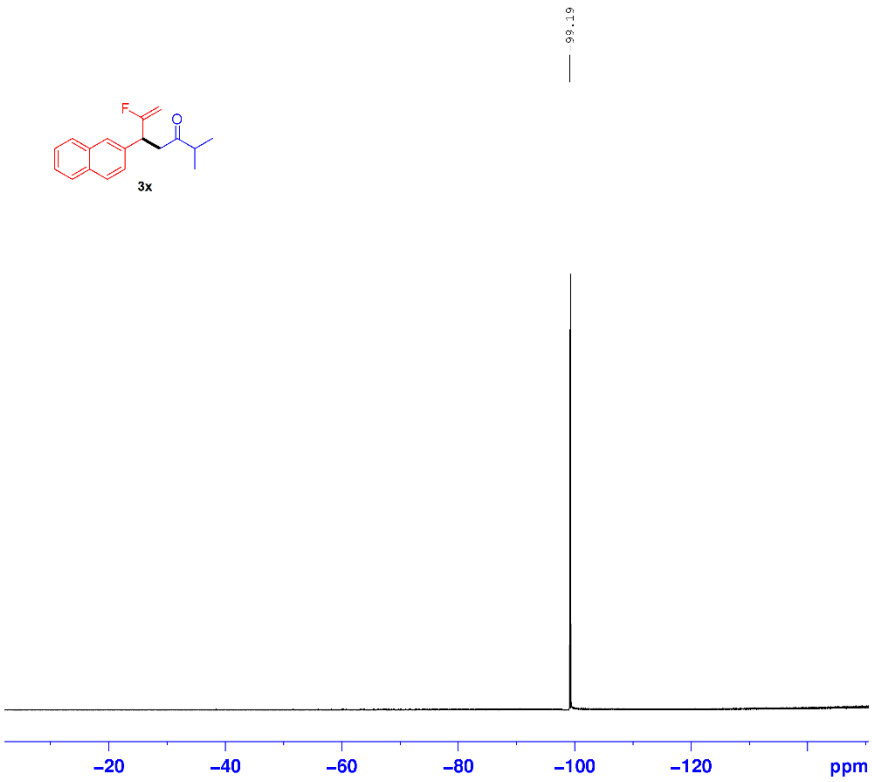
137.31
133.41
132.58
128.36
127.79
127.59
126.60
126.15
125.86
125.84
95.18
91.04
43.42
43.24
43.21
43.20
41.30
17.89
17.81
F
O
3x
220
200
180
160
140
120
100
80
60
40
20
0
ppm


99.19
F
O
3x
−20
−40
−60
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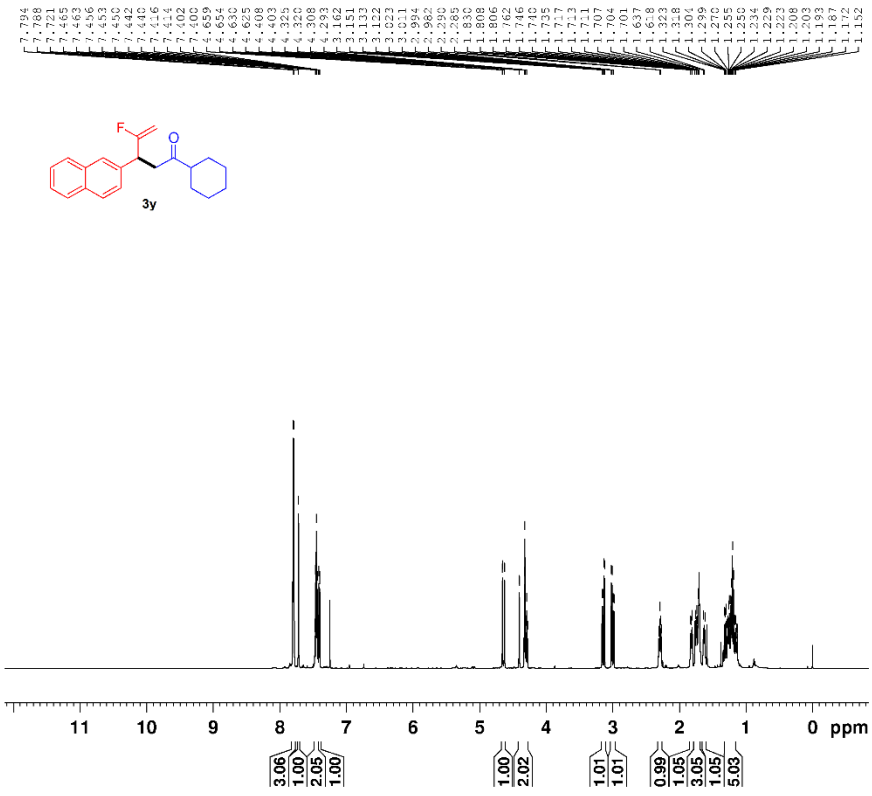
−100
−120
ppm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7.721
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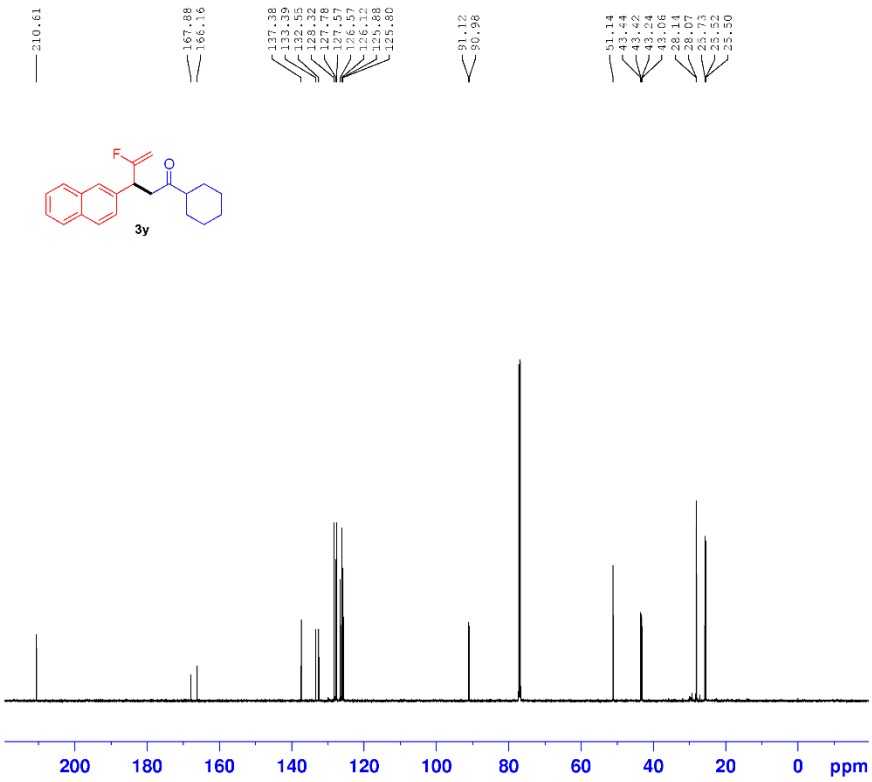
7.463
7.456
7.453
7.450
7.442
7.440
7.416
7.414
7.402
7.400
7.659
7.654
7.630
7.625
7.408
7.403
4.325
4.320
4.308
4.293
3.162
3.151
3.133
3.122
3.023
3.011
2.994
2.982
2.290
2.285
1.830
1.808
1.806
1.762
1.746
1.740
1.735
1.727
1.723
1.721
1.707
1.704
1.701
1.637
1.618
1.323
1.318
1.301
1.299
1.270
1.255
1.250
1.234
1.229
1.223
1.208
1.203
1.193
1.187
1.172
1.152
F
O
3y
11
10
9
8
7
6
5
4
3
2
1
0 ppm
3.06
1.00
2.05
1.00
1.00
2.02
1.01
1.01
0.99
1.05
3.05
1.05
5.03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166.16
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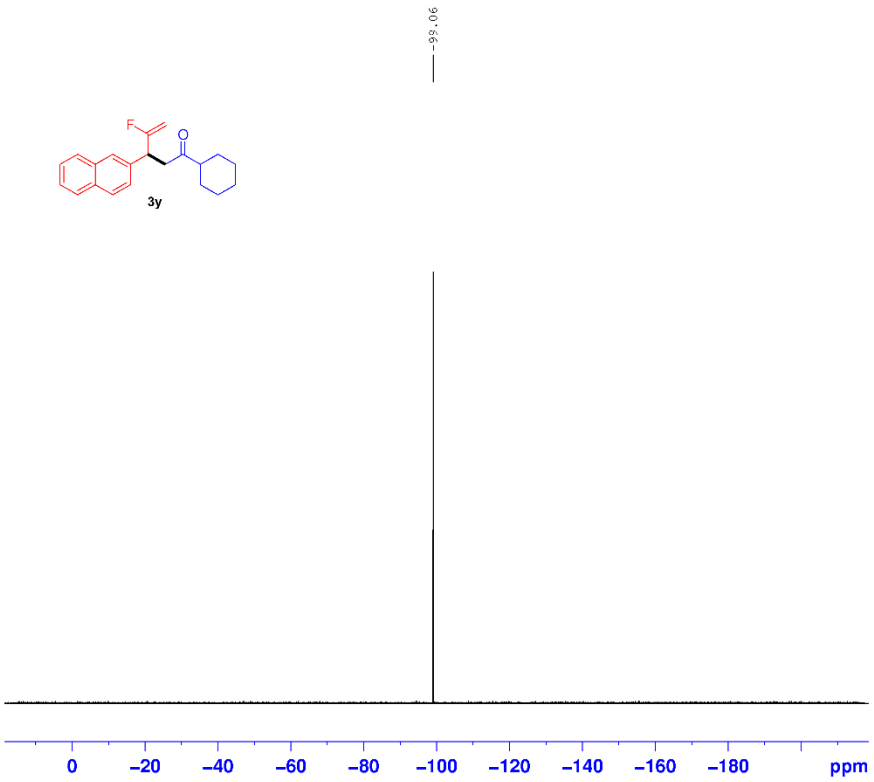
133.39
132.55
128.32
127.78
127.57
126.57
126.12
125.88
125.80
91.12
90.98
51.14
43.44
43.22
43.04
42.06
28.11
28.07
25.73
25.52
25.50
F
O
3y
200
180
160
140
120
100
80
60
40
20
0
ppm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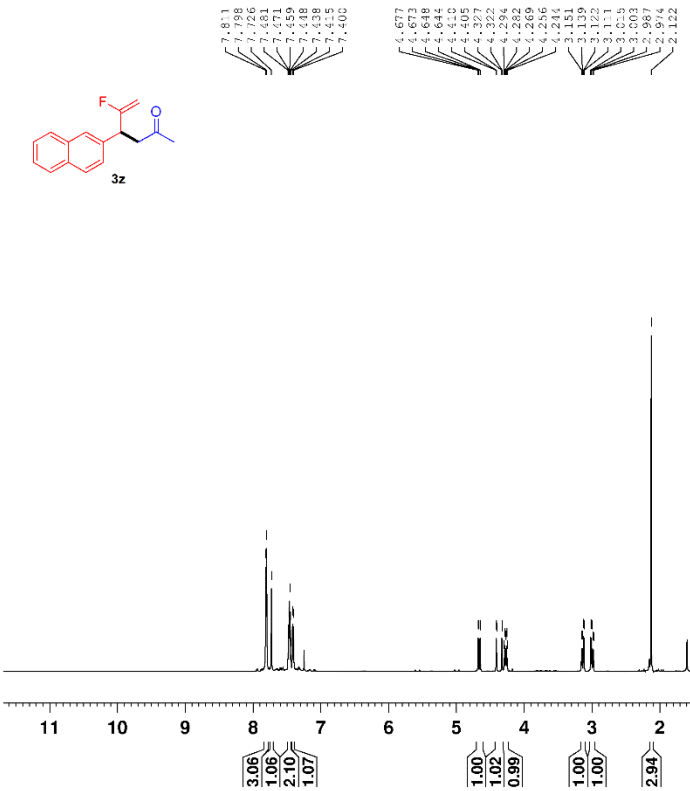
F
O
3y
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm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7.471
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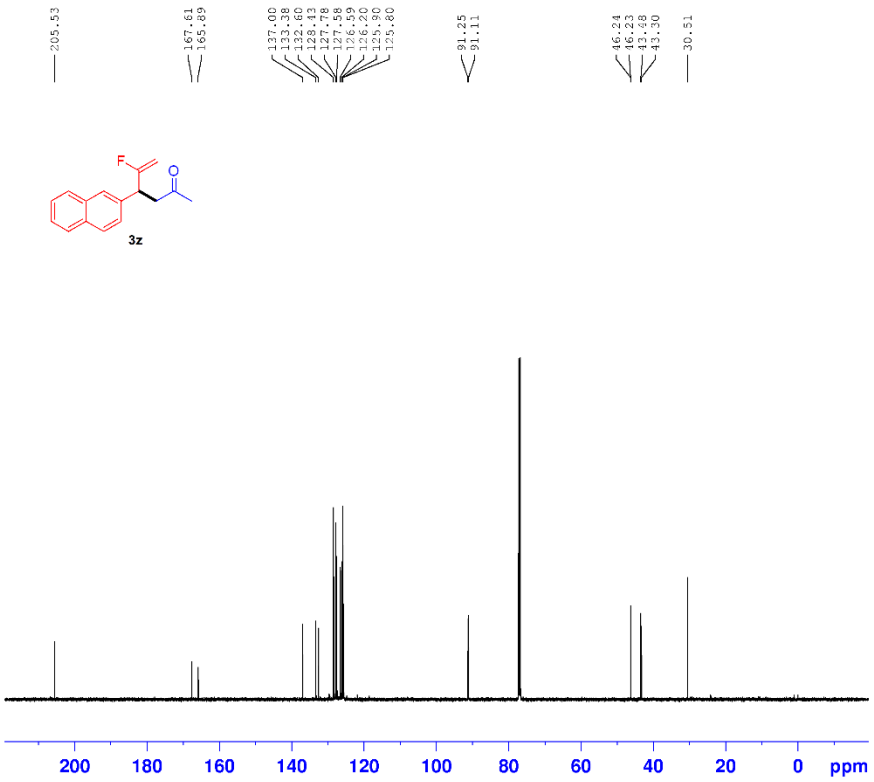
7.448
7.438
7.425
7.400
4.677
4.673
4.648
4.644
4.410
4.405
4.327
4.322
4.294
4.282
4.269
4.256
4.244
4.141
3.139
3.122
3.111
3.005
3.003
2.987
2.974
2.122
F
O
3z
11
10
9
8
7
6
5
4
3
2
1
0
ppm
3.06
1.06
2.10
1.07
1.00
1.02
0.99
1.00
1.00
2.94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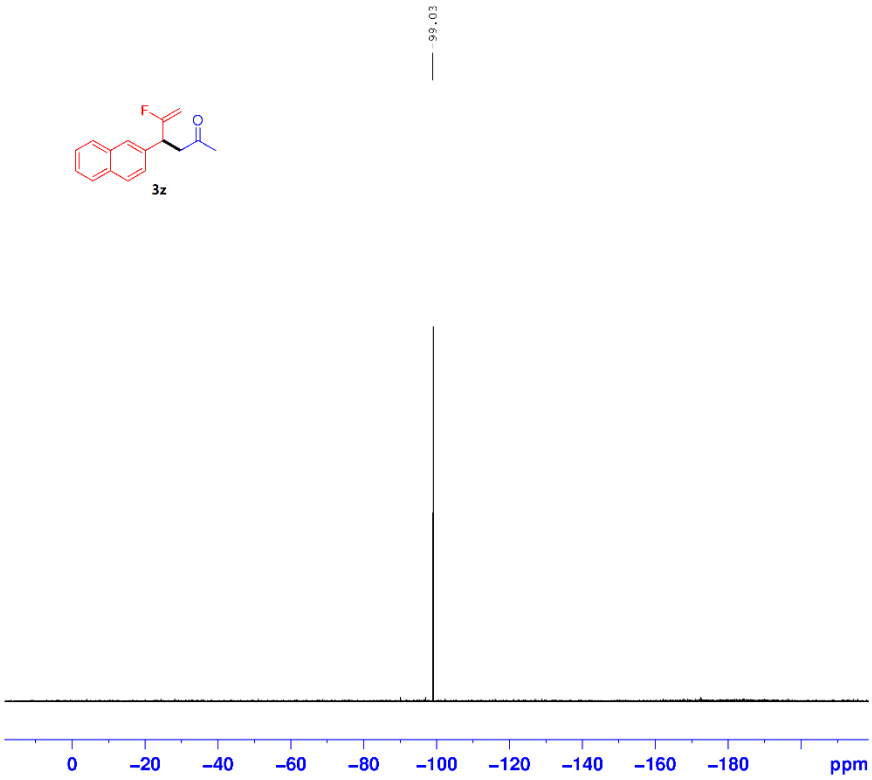
132.60
128.43
127.78
127.58
126.59
126.20
125.90
125.80
91.25
91.11
46.24
46.23
43.68
43.30
30.51
F
O
3z
200
180
160
140
120
100
80
60
40
20
0
ppm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F
O
3z
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
ppm


7.941
7.928
7.561
7.549
7.537
7.454
7.441
7.428
7.353
7.340
7.326
7.314
7.301
7.252
7.240
7.228
4.655
4.650
4.626
4.620
4.420
4.415
4.357
4.343
4.336
4.332
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4.303
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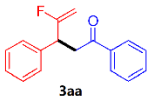
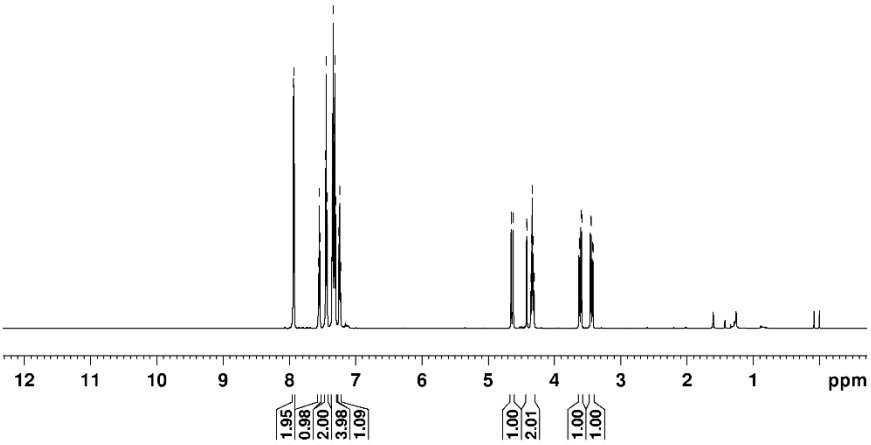
3.417


F
O

3aa


12
11
10
9
8
7
6
5
4
3
2
1
ppm
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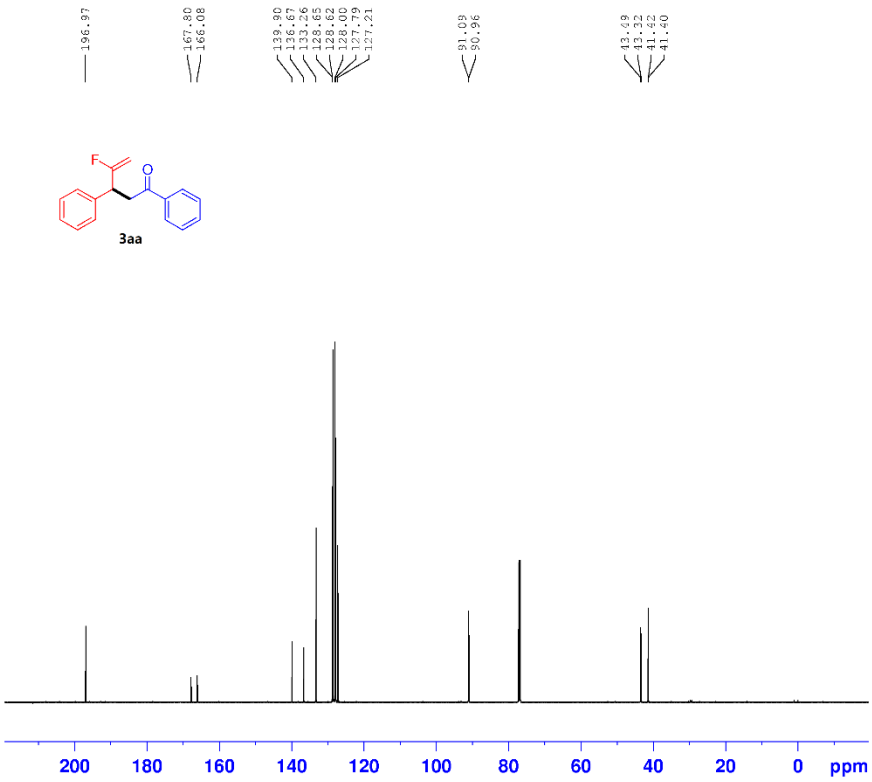
0.98
2.00
3.98
1.09
1.00
2.01
1.00
1.00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133.26
128.65
128.62
128.00
127.79
127.21
91.09
90.96
43.69
43.32
41.62
41.40
F
O
3aa
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180
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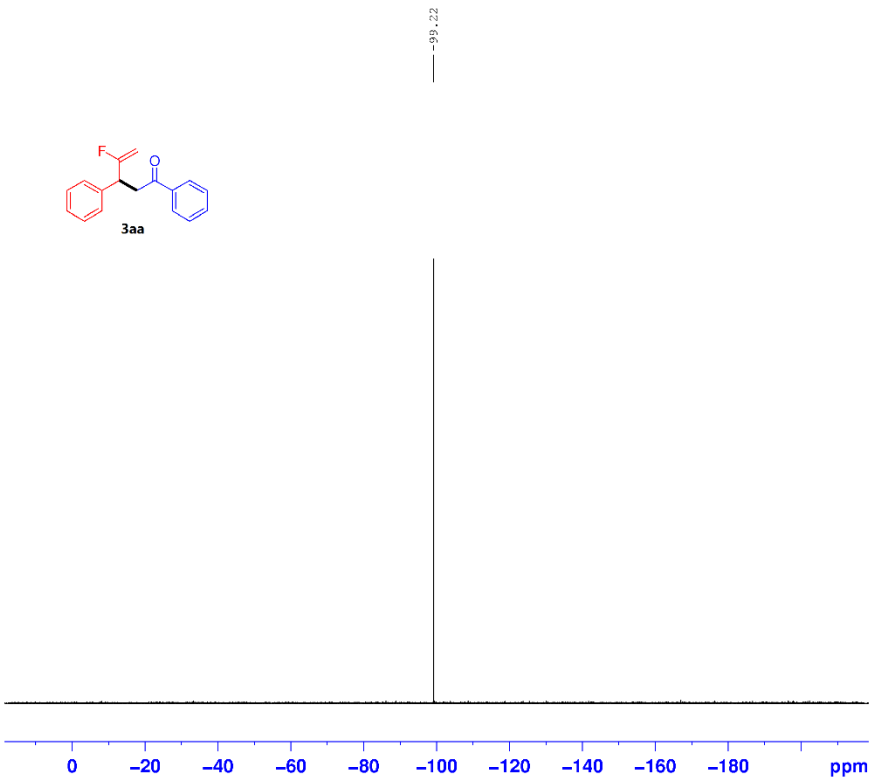
140
120
100
80
60
40
20
0
ppm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−40
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−140
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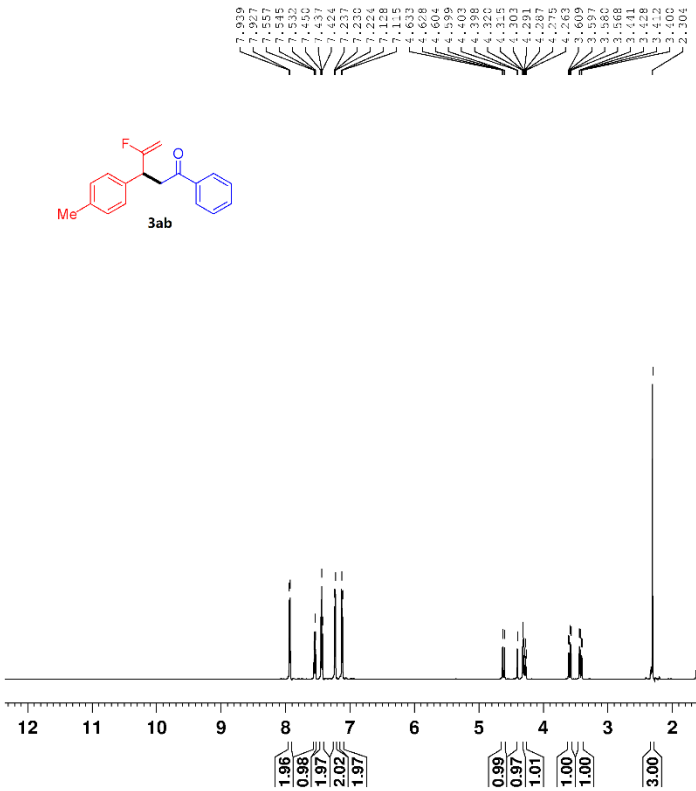
−180
ppm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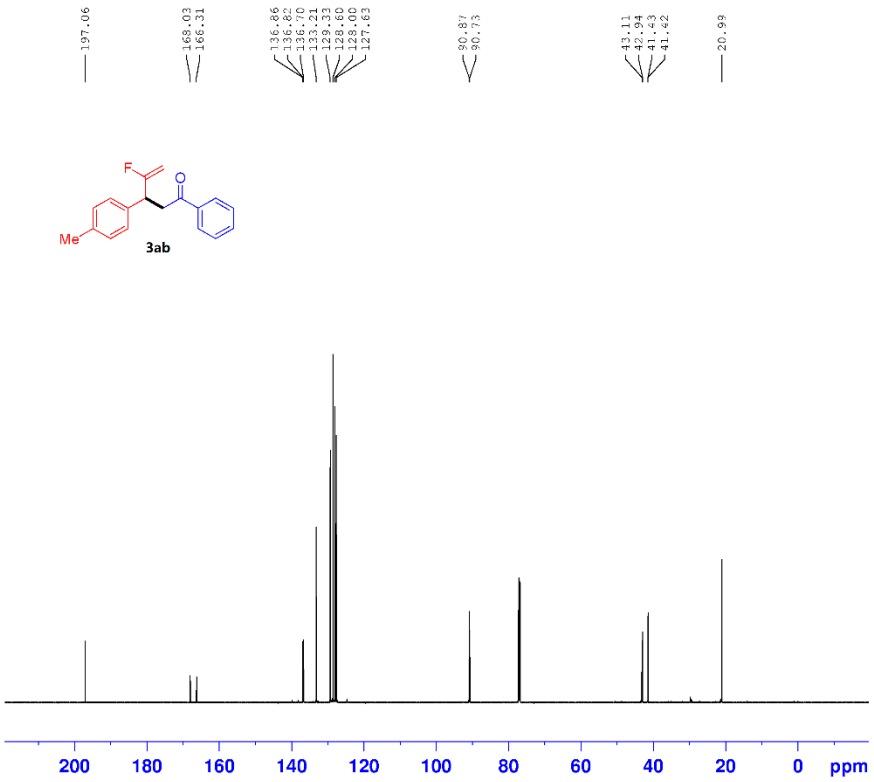
7.532
7.450
7.437
7.424
7.237
7.230
7.224
7.128
7.115
4.633
4.608
4.604
4.599
4.403
4.398
4.325
4.315
4.303
4.291
4.287
4.275
4.263
3.609
3.597
3.586
3.568
3.441
3.428
3.412
3.402
2.304
F
O
Me
3ab
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.96
0.98
1.97
2.02
1.97
0.99
0.97
1.01
1.00
1.00
3.00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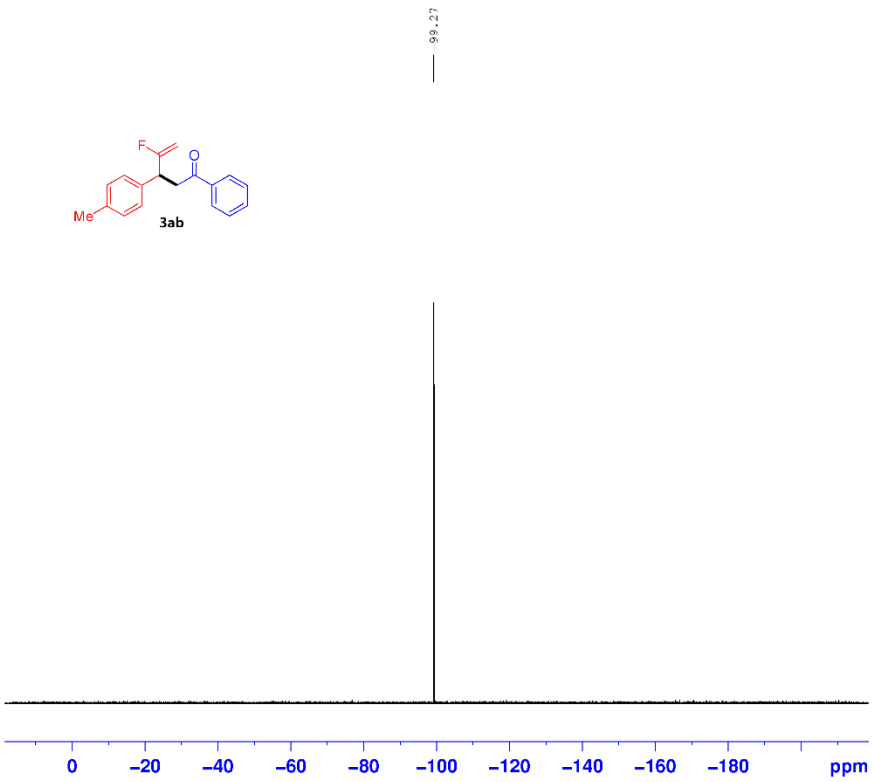
136.82
136.70
133.21
133.23
128.60
128.00
127.63
90.87
90.73
43.11
42.94
41.43
41.42
20.99
F
O
Me
3ab
200
180
160
140
120
100
80
60
40
20
0
ppm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Me
3ab
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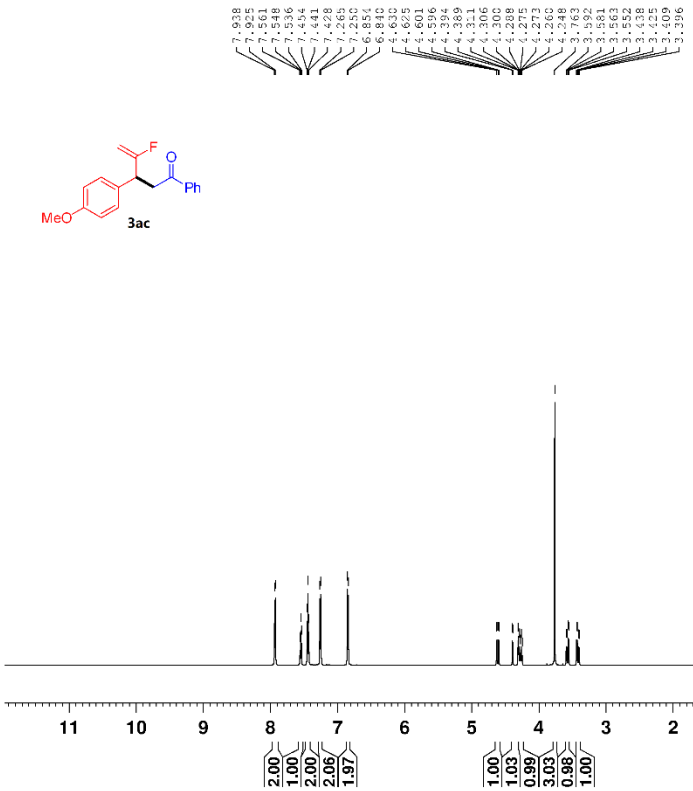
−180
ppm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7.428
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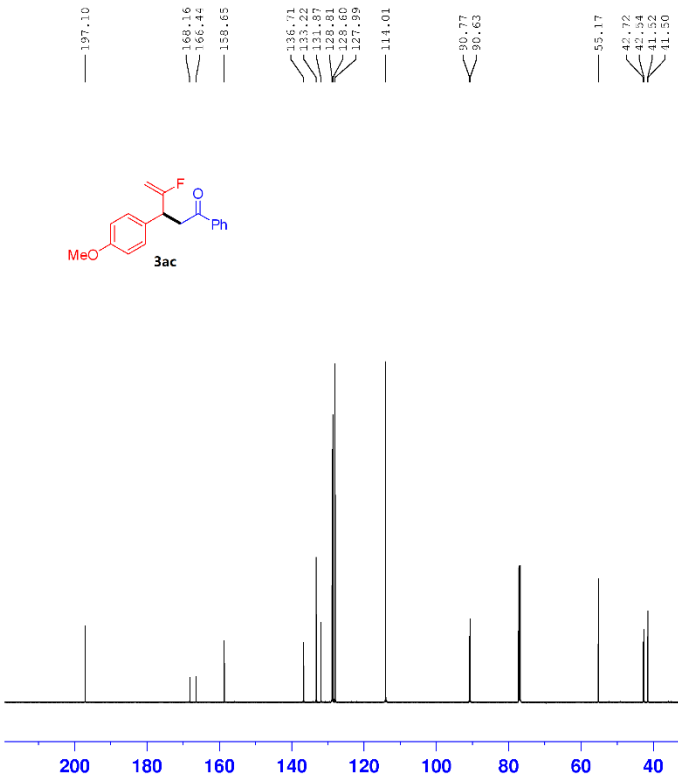
6.840
4.630
4.605
4.601
4.596
4.394
4.389
4.311
4.306
4.300
4.288
4.275
4.273
4.260
4.248
3.763
3.592
3.561
3.551
3.552
3.438
3.425
3.409
3.396
F
O
Ph
MeO
3ac
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
1.00
2.00
2.06
1.97
1.00
1.03
0.99
3.03
0.98
1.00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133.22
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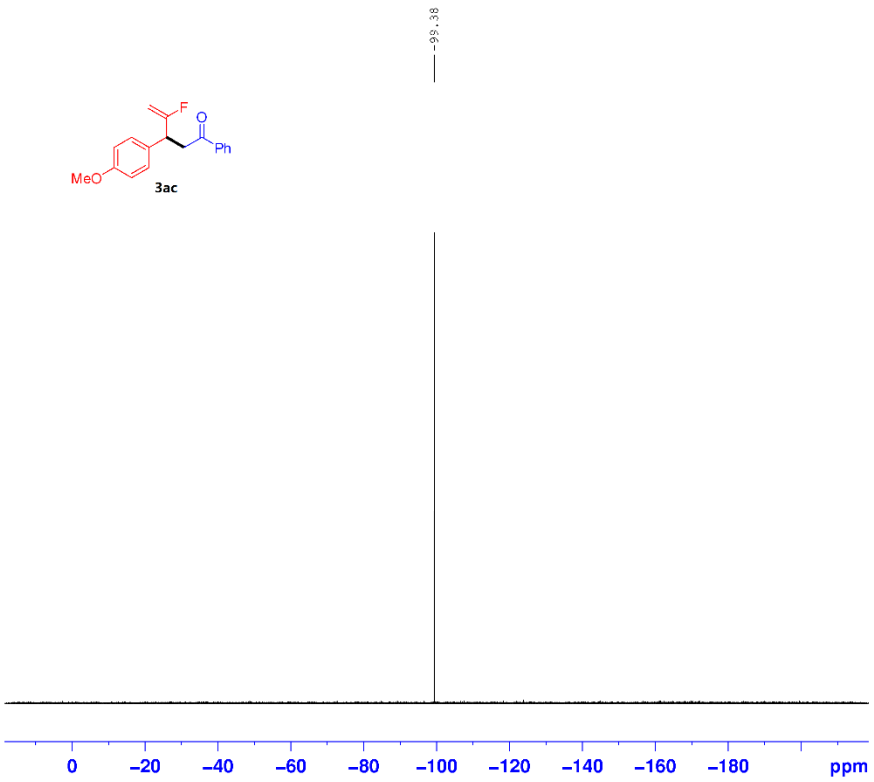
128.81
128.60
127.99
114.01
90.77
90.63
55.17
42.72
42.54
41.52
41.50
F
O
Ph
MeO
3ac
200
180
160
140
120
100
80
60
40
20
0
ppm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O
Ph
MeO
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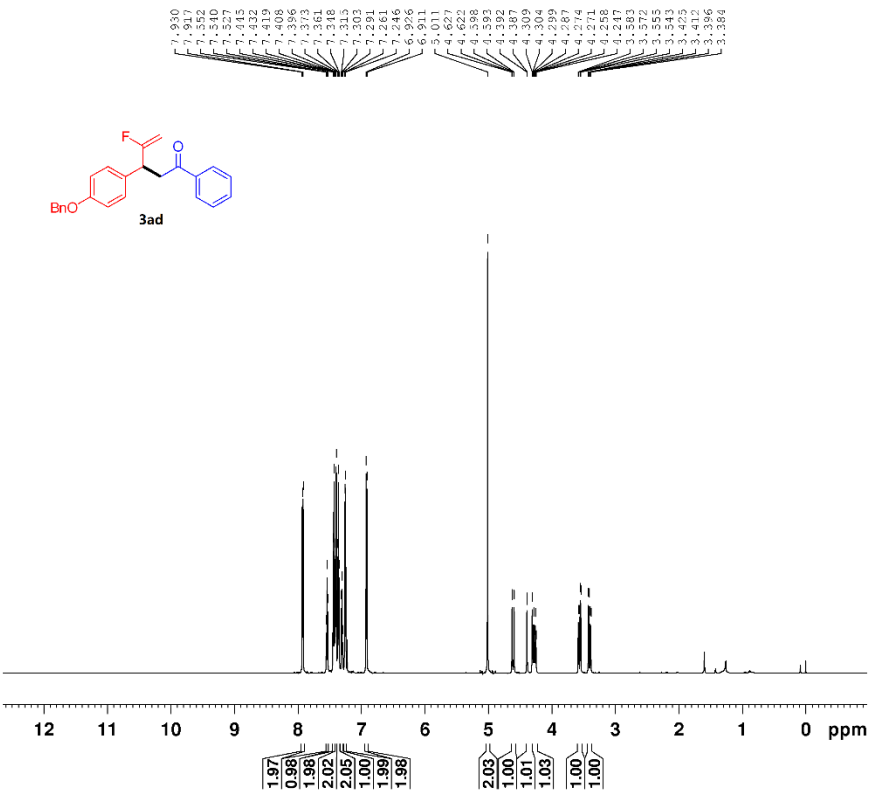
−180
ppm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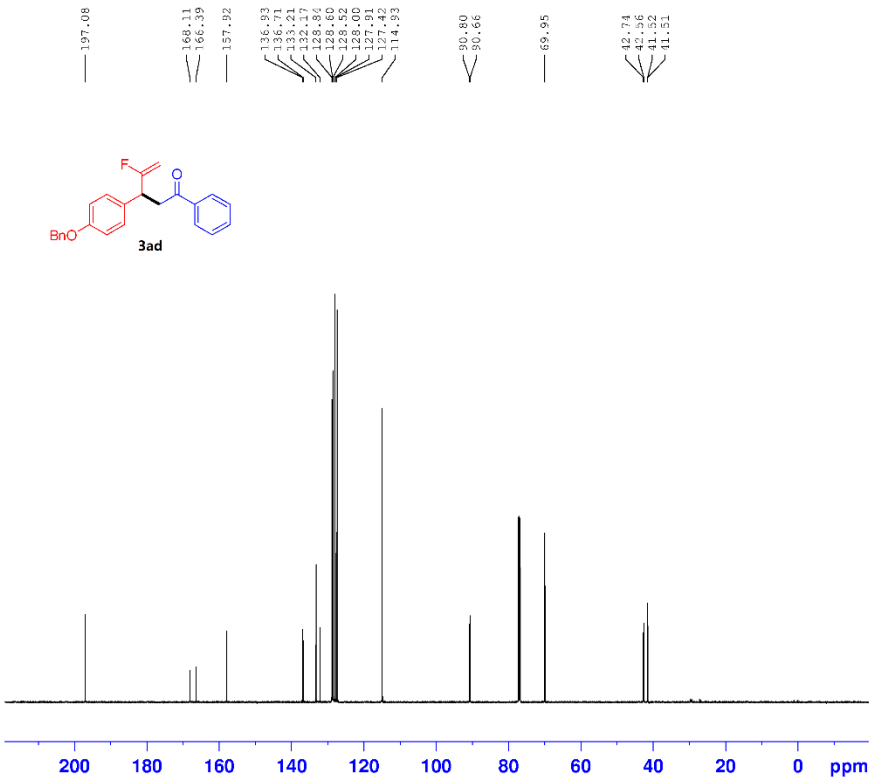
7.419
7.408
7.396
7.373
7.361
7.348
7.315
7.303
7.291
7.261
7.246
6.926
6.911
5.011
4.627
4.613
4.588
4.573
4.392
4.387
4.309
4.304
4.299
4.287
4.274
4.271
4.258
4.247
3.593
3.572
3.565
3.543
3.425
3.412
3.396
3.384
F
O
BnO
3ad
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.97
0.98
1.98
2.02
2.05
1.00
1.99
1.98
2.03
1.00
1.01
1.03
1.00
1.00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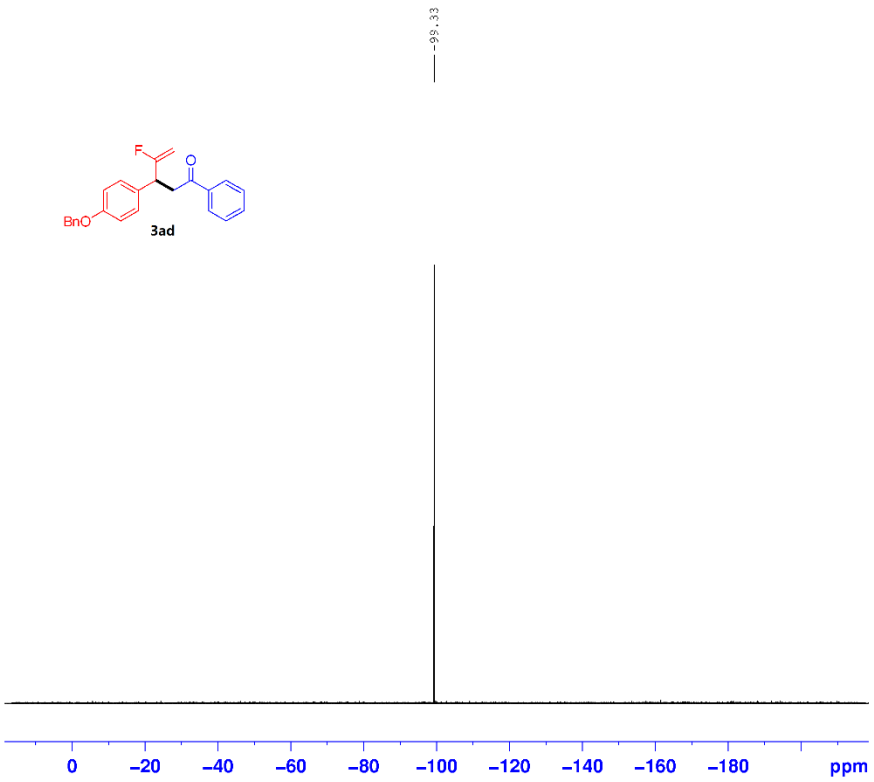
136.71
133.21
132.17
128.84
128.60
128.52
128.00
127.91
127.43
114.93
90.80
90.66
69.95
42.74
42.96
41.52
41.51
F
O
BnO
3ad
200
180
160
140
120
100
80
60
40
20
0
ppm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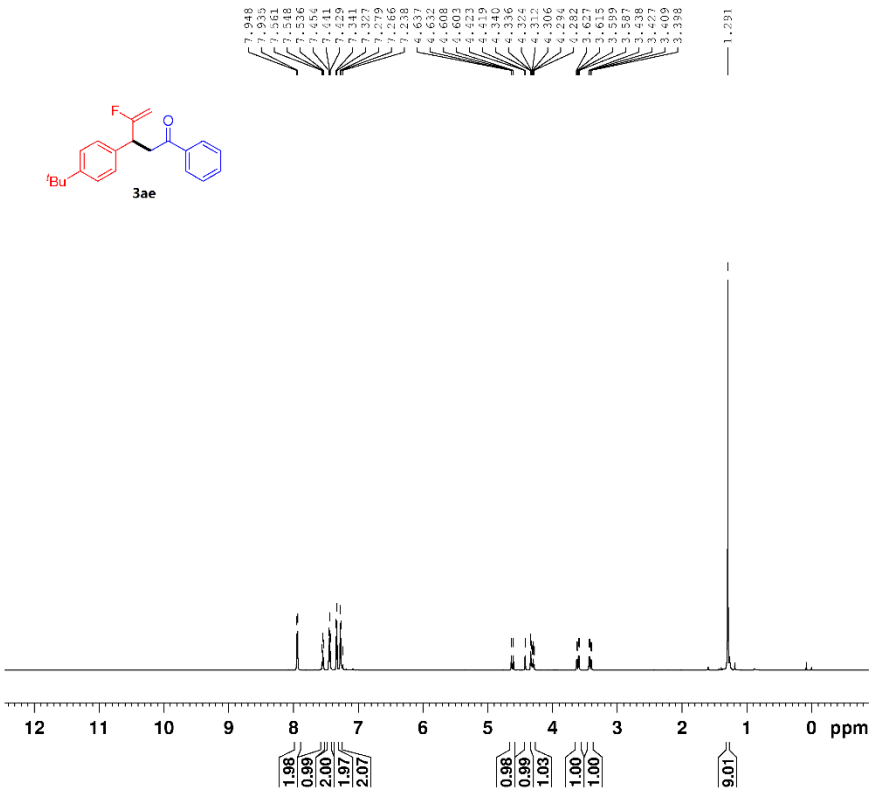
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7.238
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4.632
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4.603
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4.336
4.324
4.312
4.306
4.294
4.292
4.277
3.615
3.599
3.587
3.438
3.427
3.409
3.398
1.291
F
O
tBu
3ae
12
11
10
9
8
7
6
5
4
3
2
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2.07
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0.99
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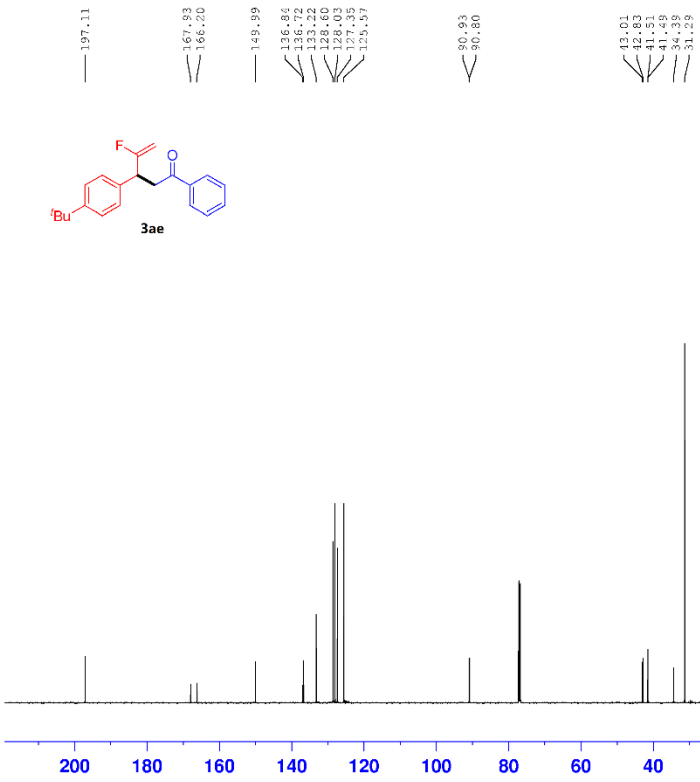
9.01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90.93
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41.19
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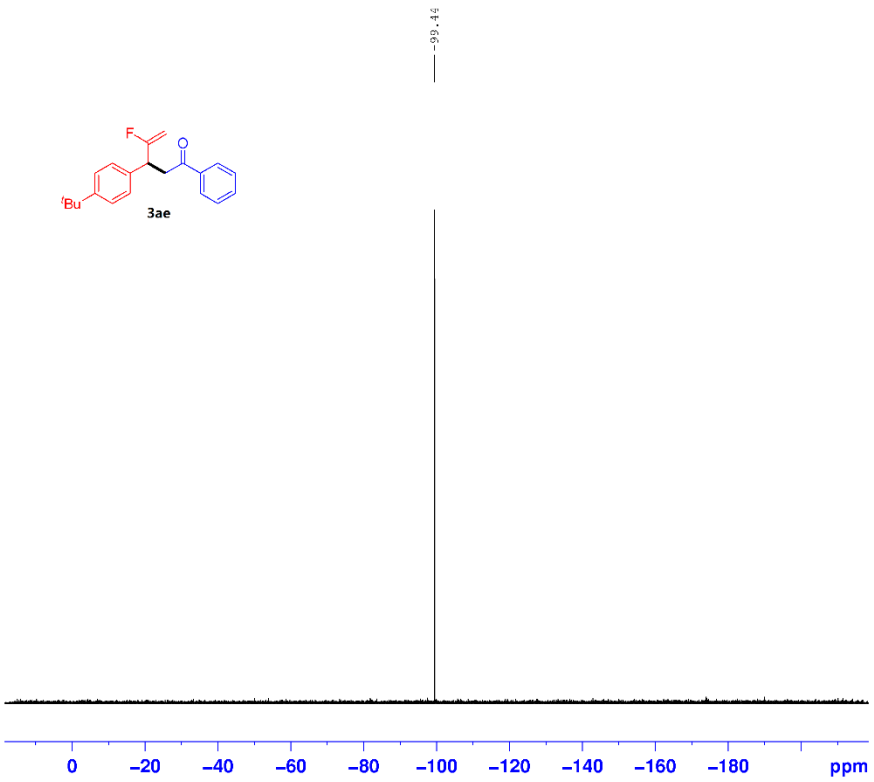
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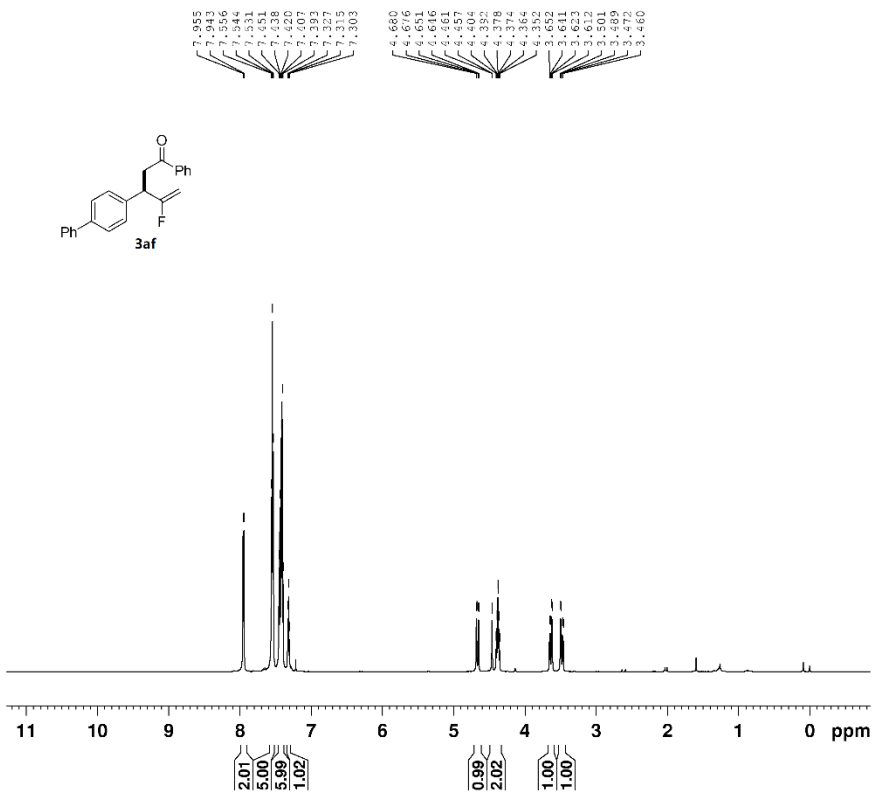
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7.303
4.680
4.676
4.651
4.646
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4.657
4.404
4.392
4.378
4.374
4.364
4.352
3.652
3.641
3.623
3.622
3.501
3.489
3.477
3.460
O
Ph
Ph
F
3af
11
10
9
8
7
6
5
4
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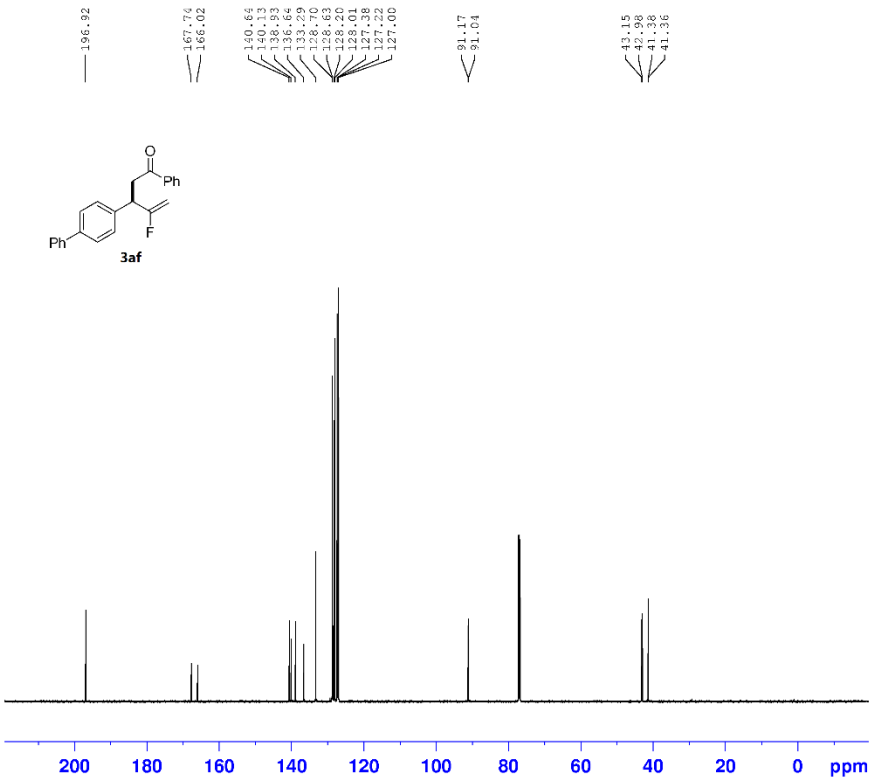
1.00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127.22
127.00
91.17
91.04
43.15
42.98
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Ph
Ph
F
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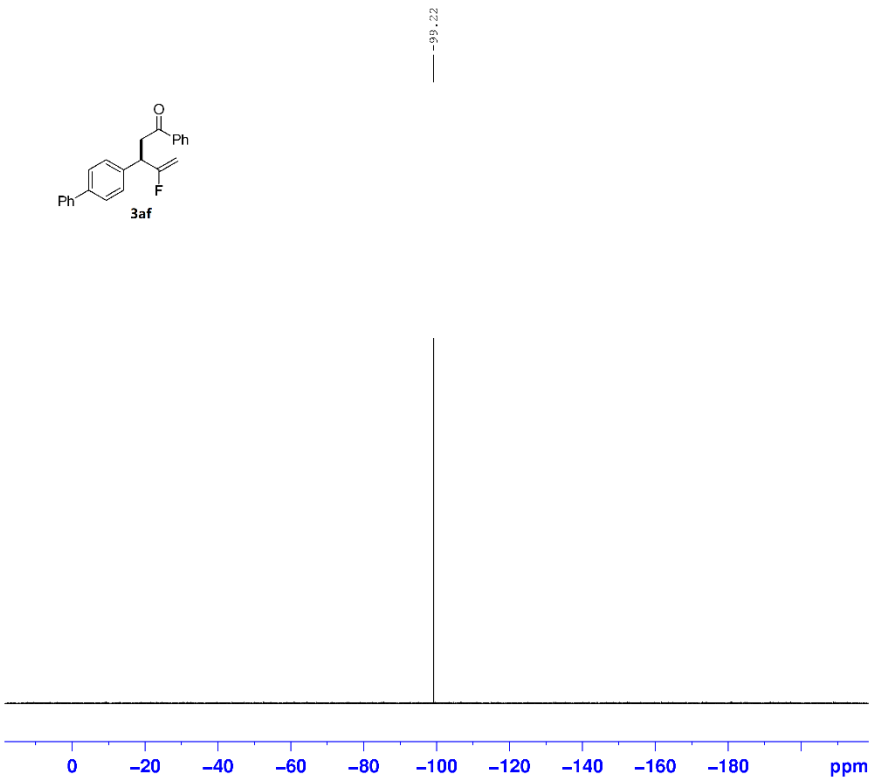
ppm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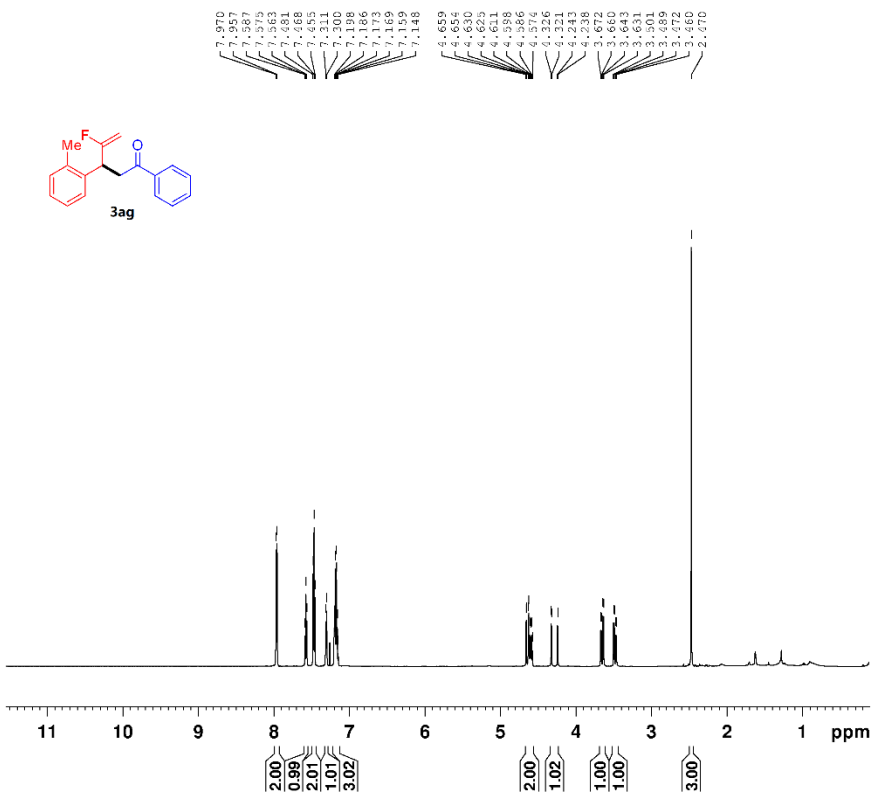
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7.468
7.455
7.211
7.200
7.198
7.186
7.173
7.169
7.159
7.148
6.659
6.654
6.630
6.625
6.611
6.598
6.586
6.576
6.326
6.321
6.243
6.238
3.672
3.660
3.643
3.631
3.501
3.489
3.472
3.460
2.270
F
Me
O
3ag
11
10
9
8
7
6
5
4
3
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0.99
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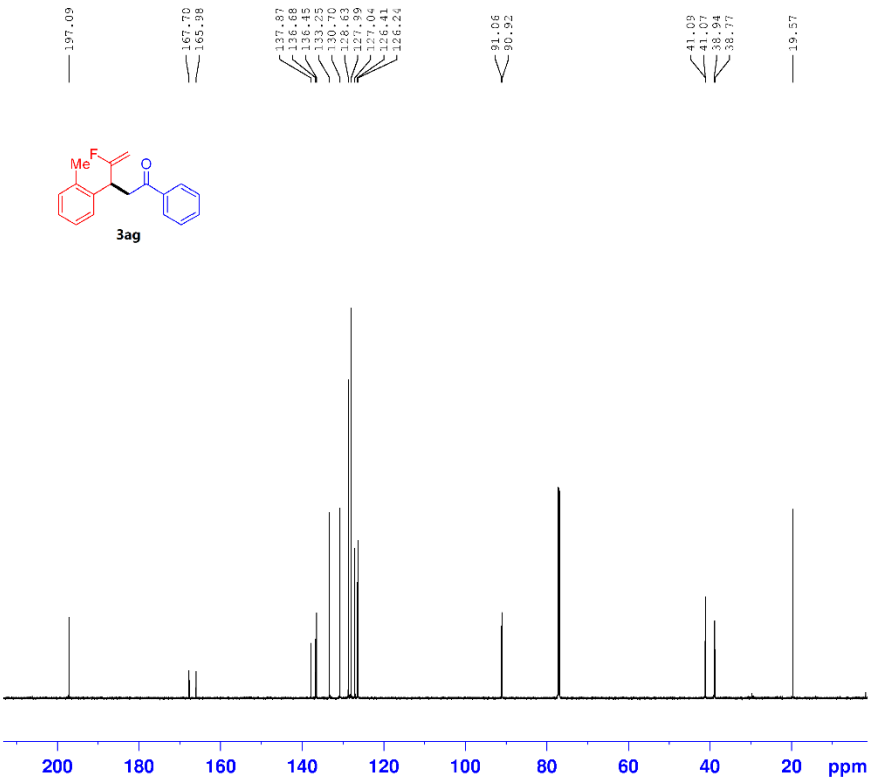
1.01
3.02
2.00
1.02
1.00
1.00
3.00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130.70
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127.99
127.04
126.41
126.24
91.06
90.92
41.09
41.07
38.94
38.77
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F
O
3ag
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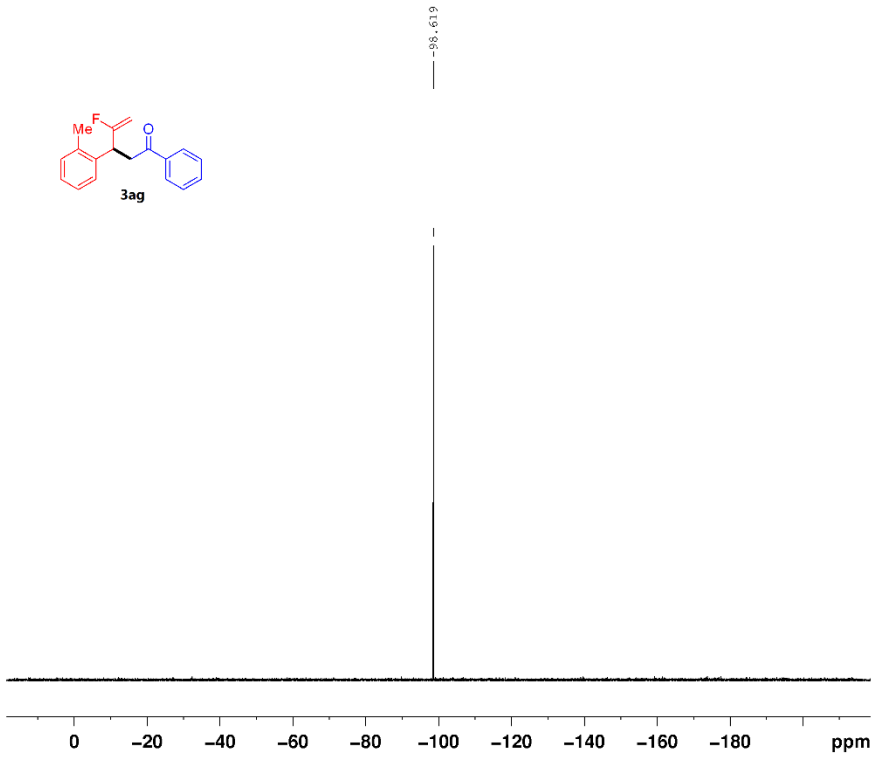
160
140
120
100
80
60
40
20
ppm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O
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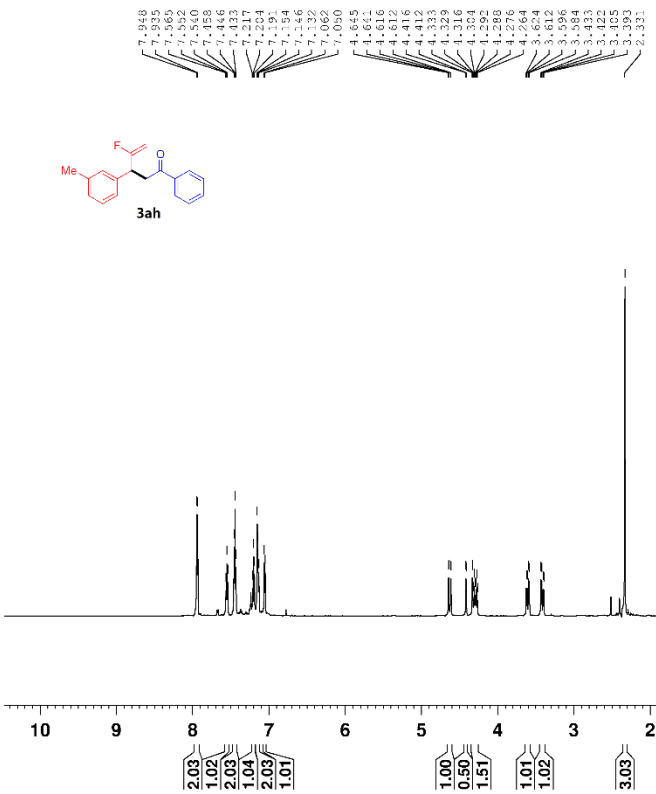
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7.433
7.217
7.204
7.191
7.154
7.146
7.132
7.062
7.050
4.645
4.641
4.616
4.612
4.416
4.412
4.333
4.329
4.316
4.304
4.292
4.288
4.276
4.264
3.624
3.612
3.596
3.584
3.433
3.422
3.405
3.393
2.331
F
O
Me
3ah
10
9
8
7
6
5
4
3
2
1
0
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1.04
2.03
1.01
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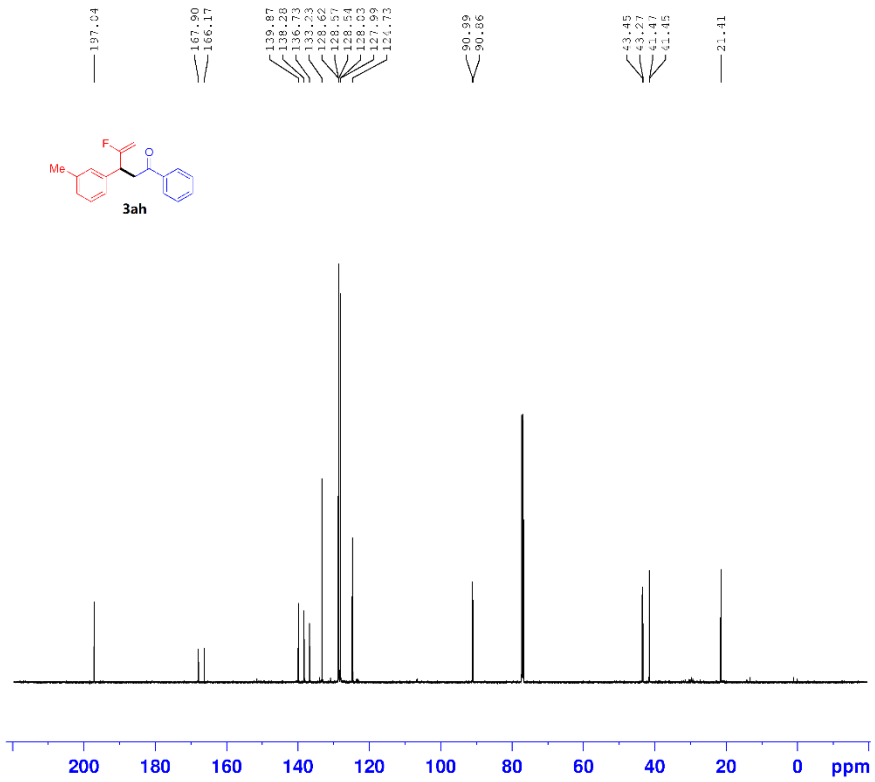
1.02
3.03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127.99
121.73
90.99
90.86
43.45
43.27
42.47
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O
Me
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120
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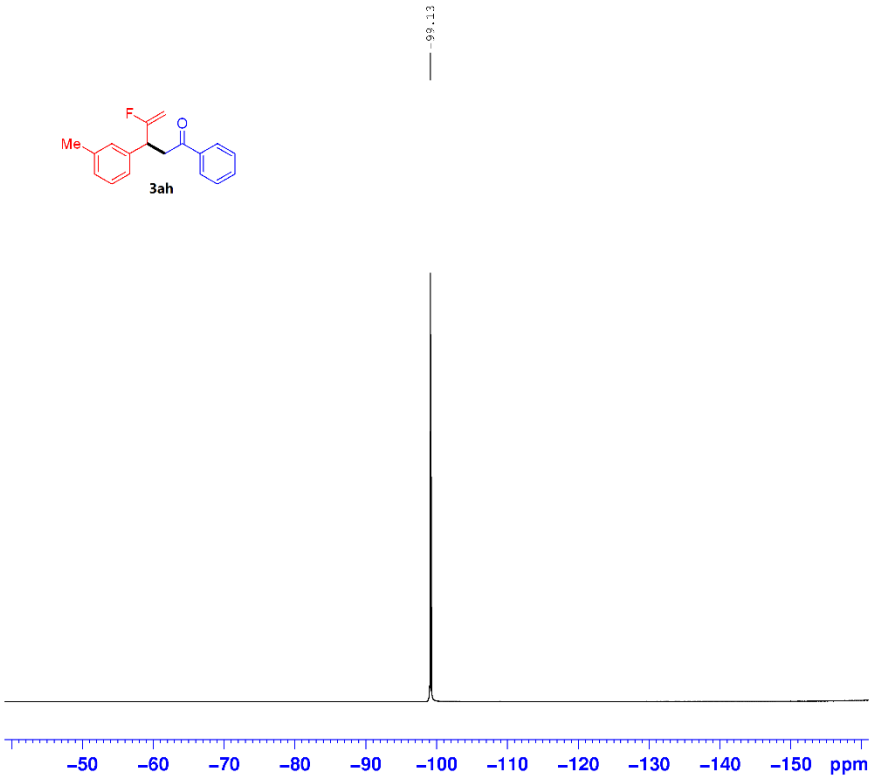
20
0
ppm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O
Me
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−90
−100
−110
−120
−130
−140
−150
ppm


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7.924
7.579
7.566
7.554
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7.455
7.442
7.323
7.314
7.309
7.300
7.014
7.011
7.000
6.988
6.985
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4.657
4.634
4.628
4.418
4.413
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4.330
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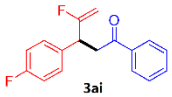
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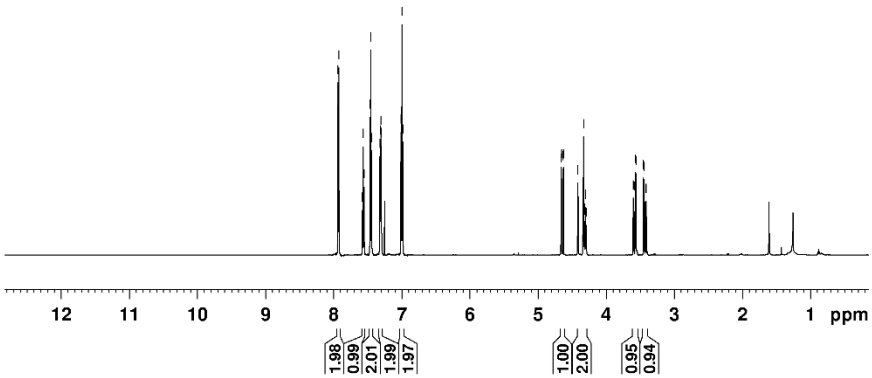
O
F

3ai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10
9
8
7
6
5
4
3
2
1
ppm
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2.01
1.99
1.97
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2.00
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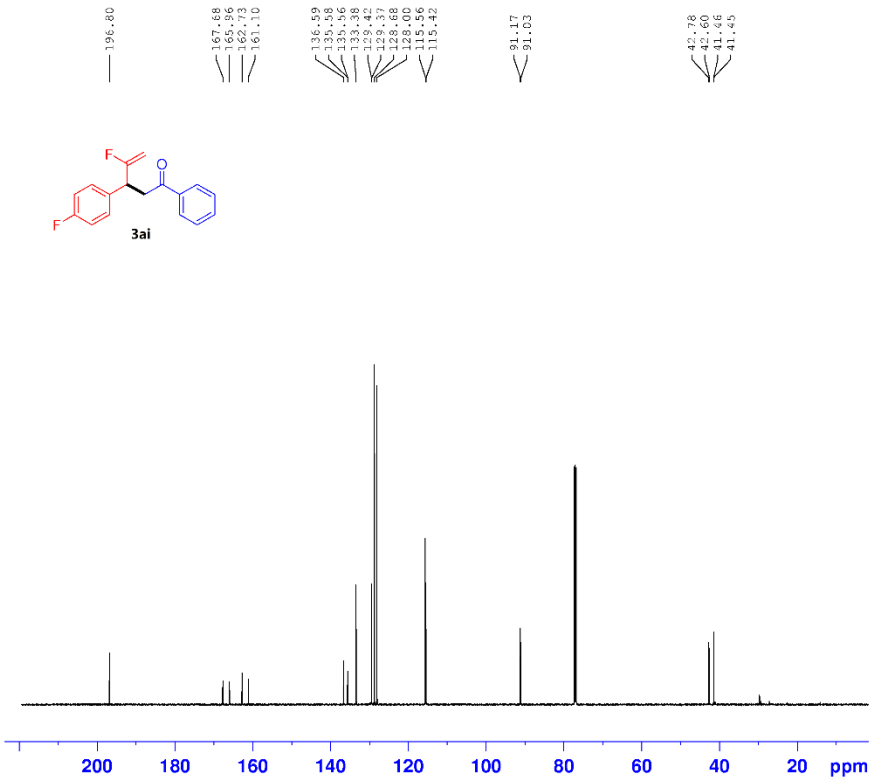
0.94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135.56
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133.42
129.37
128.68
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115.56
115.42
91.17
91.03
42.78
42.66
41.66
41.45
F
O
F
3ai
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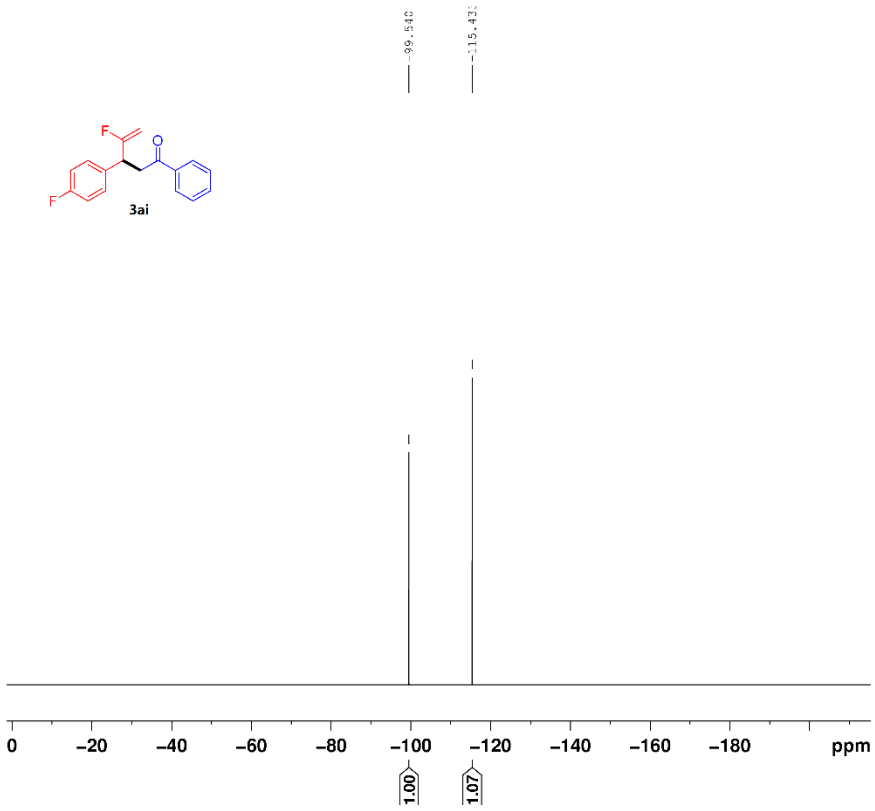
140
120
100
80
60
40
20
ppm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-115.431
F
O
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ppm
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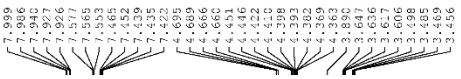
1.07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7.422
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4.669
4.666
4.662
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4.446
4.422
4.410
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4.393
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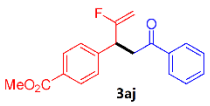
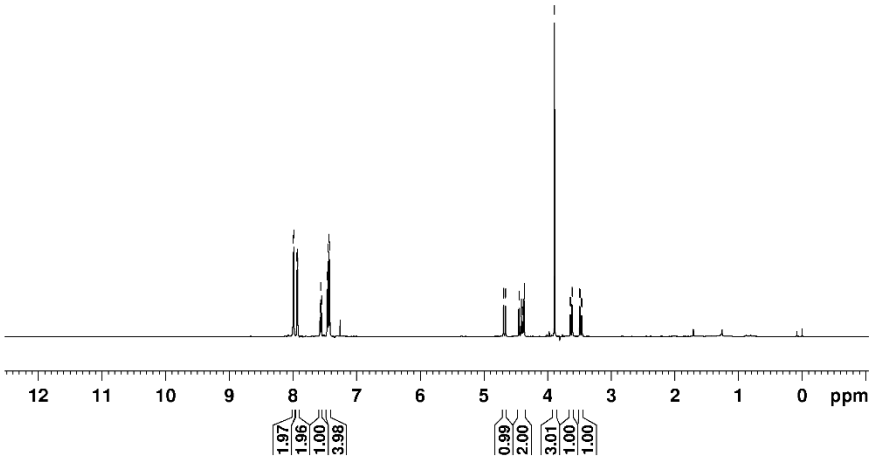
3.469
3.456


F
O
MeO2C

3aj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9
8
7
6
5
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3
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ppm
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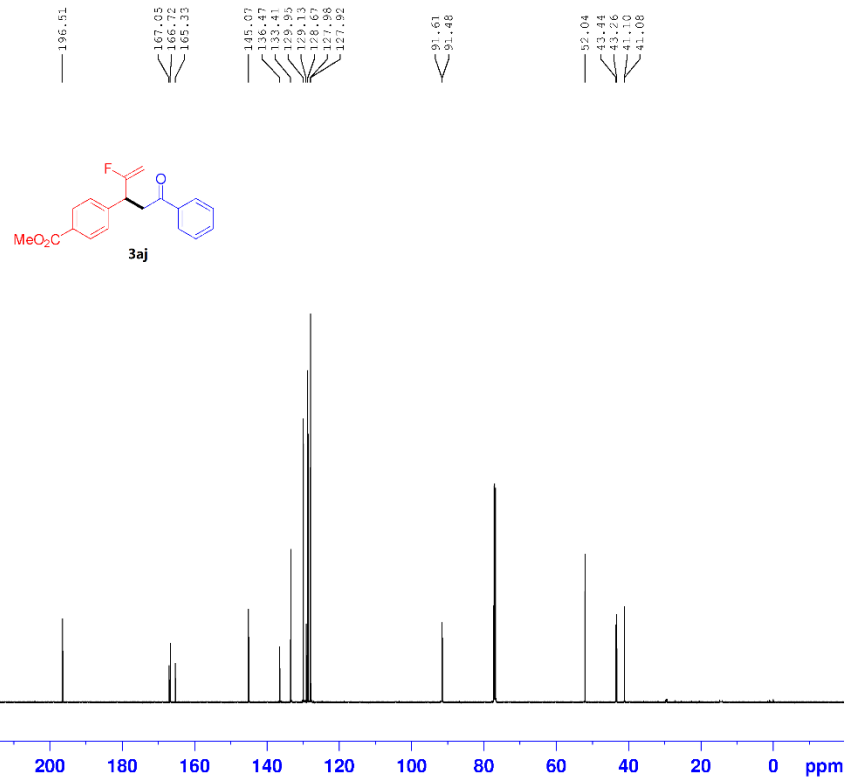
3.01
1.00
1.00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91.61
91.48
52.04
43.44
43.26
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O
MeO2C
3aj
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120
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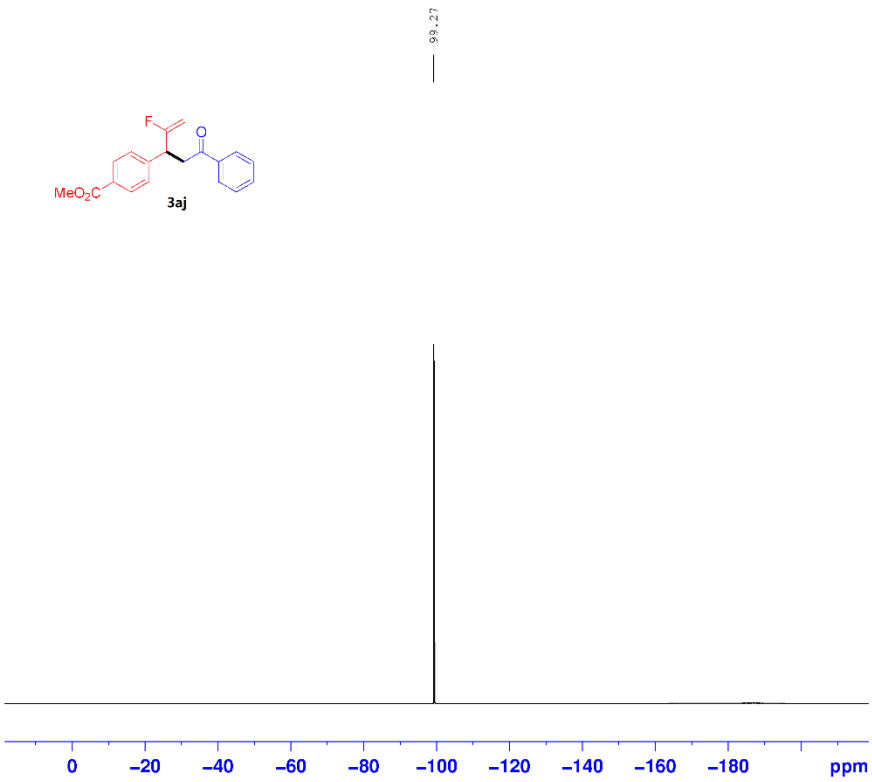
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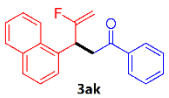
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O

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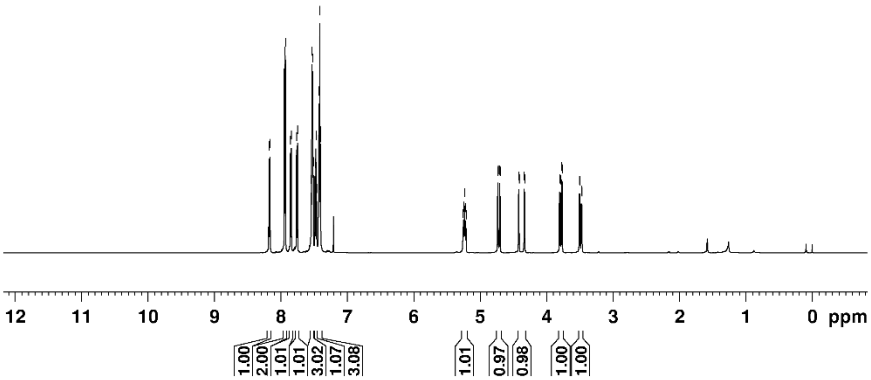
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9
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7
6
5
4
3
2
1
0 ppm
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1.07
3.08
1.01
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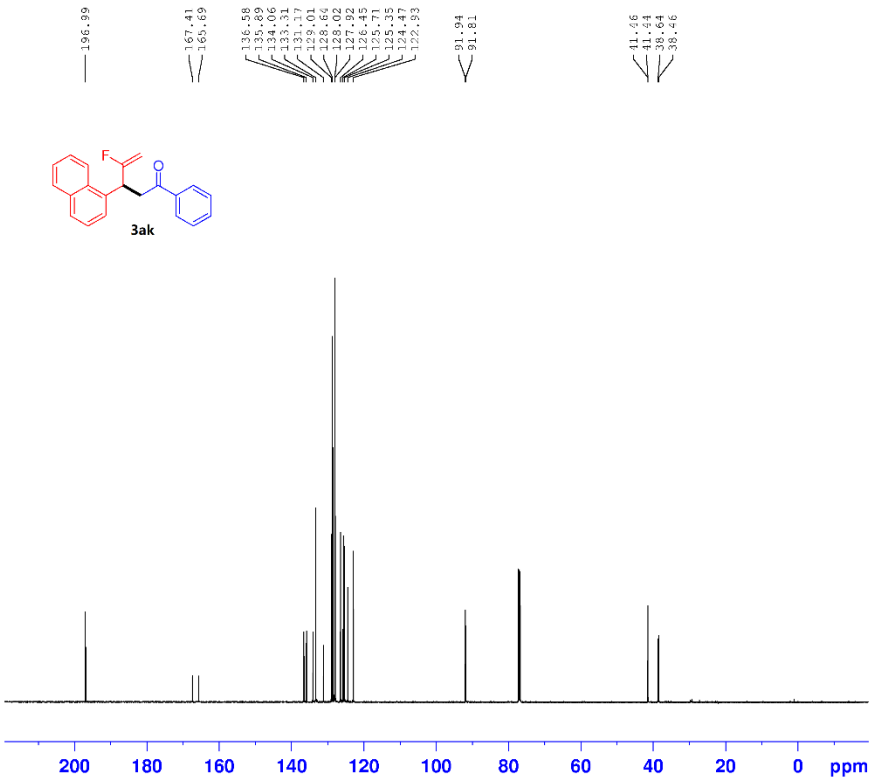
1.00
1.00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128.02
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126.45
125.71
125.35
124.47
122.93
91.94
91.81
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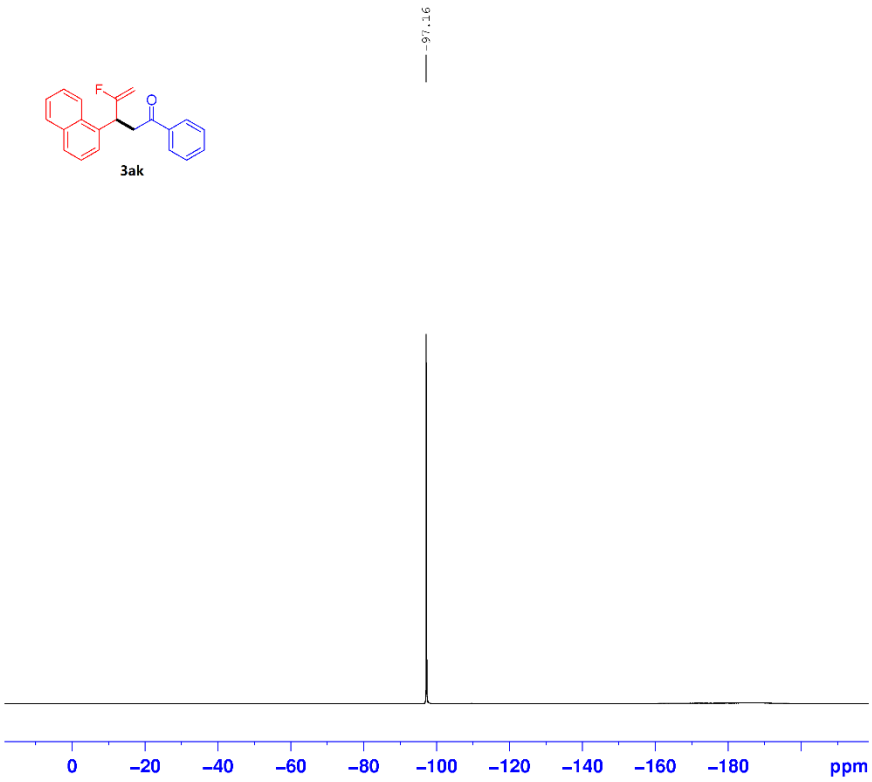
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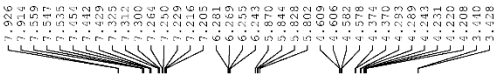
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7.230
7.229
7.216
7.205
6.281
6.269
6.255
6.243
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5.828
5.802
4.609
4.606
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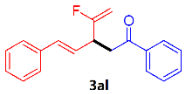
3.428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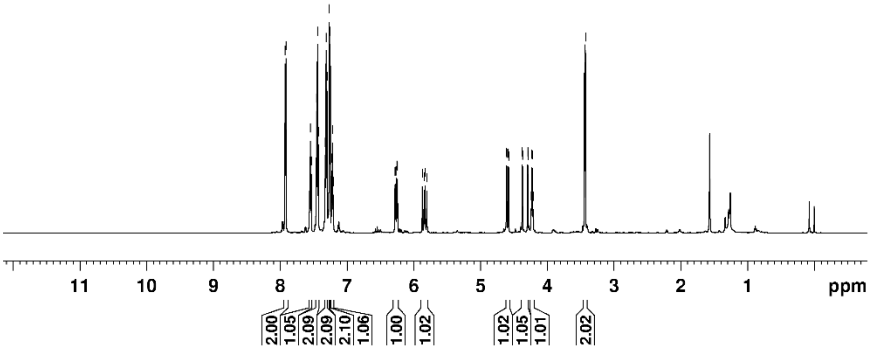
3al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7
6
5
4
3
2
1
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1.02
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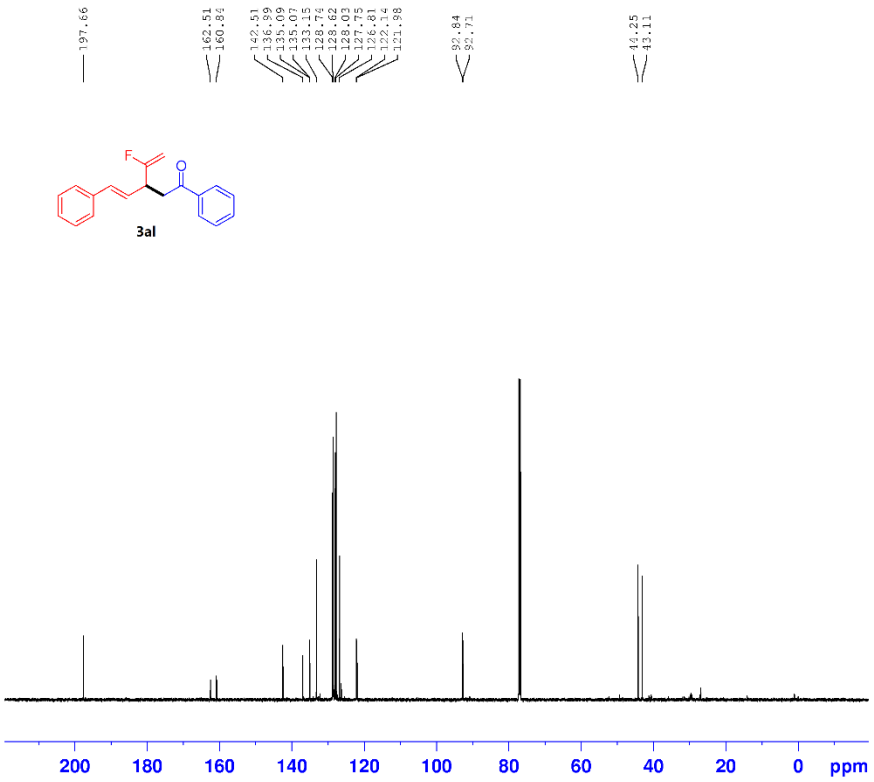
1.01
2.02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127.75
126.81
122.14
121.98
92.84
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O
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120
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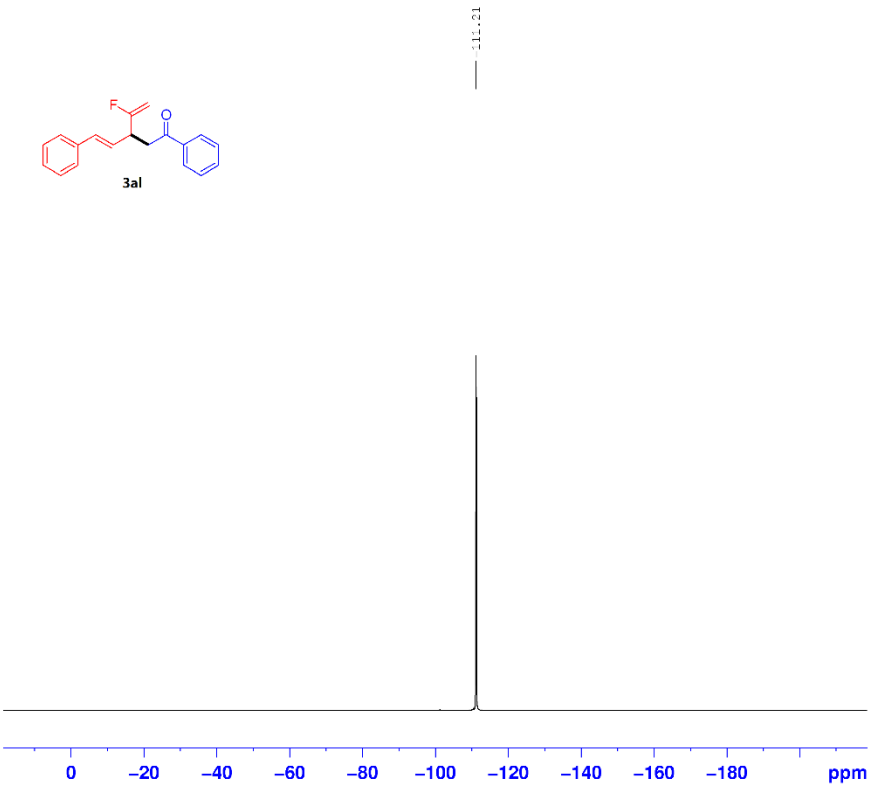
ppm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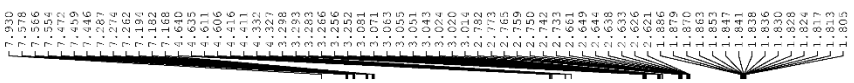
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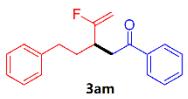
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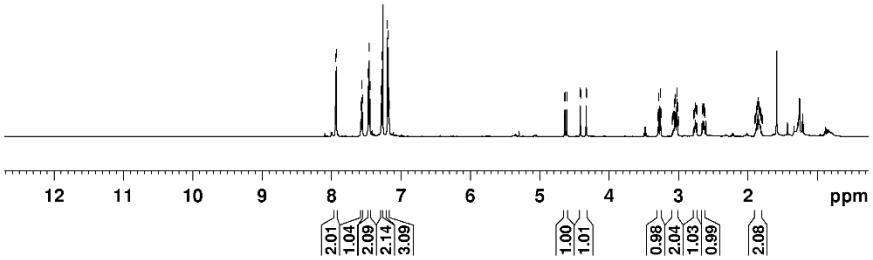
3am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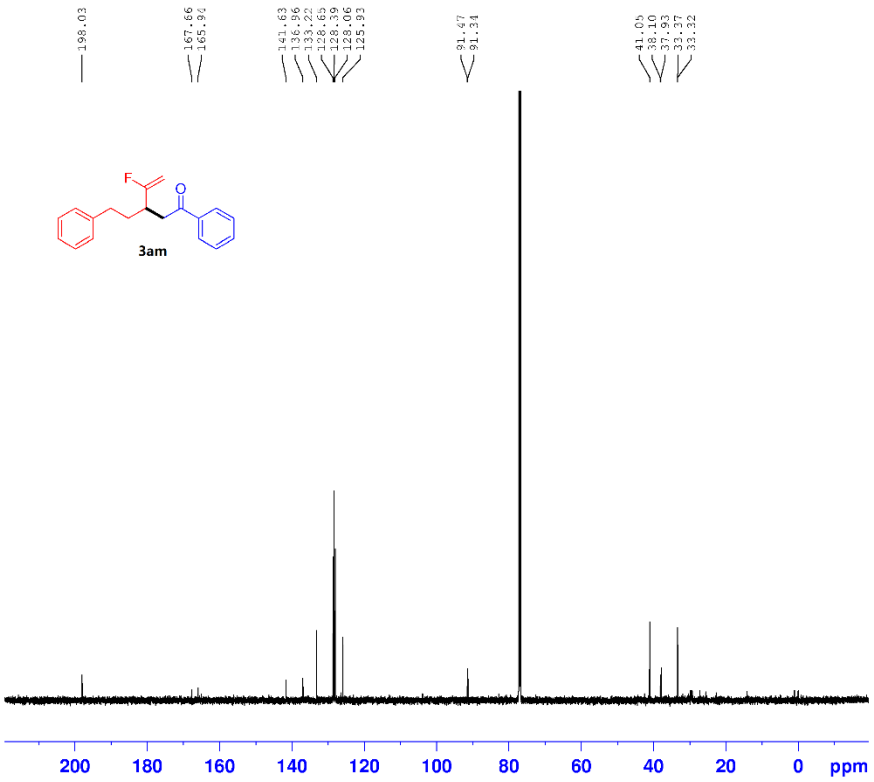
2.08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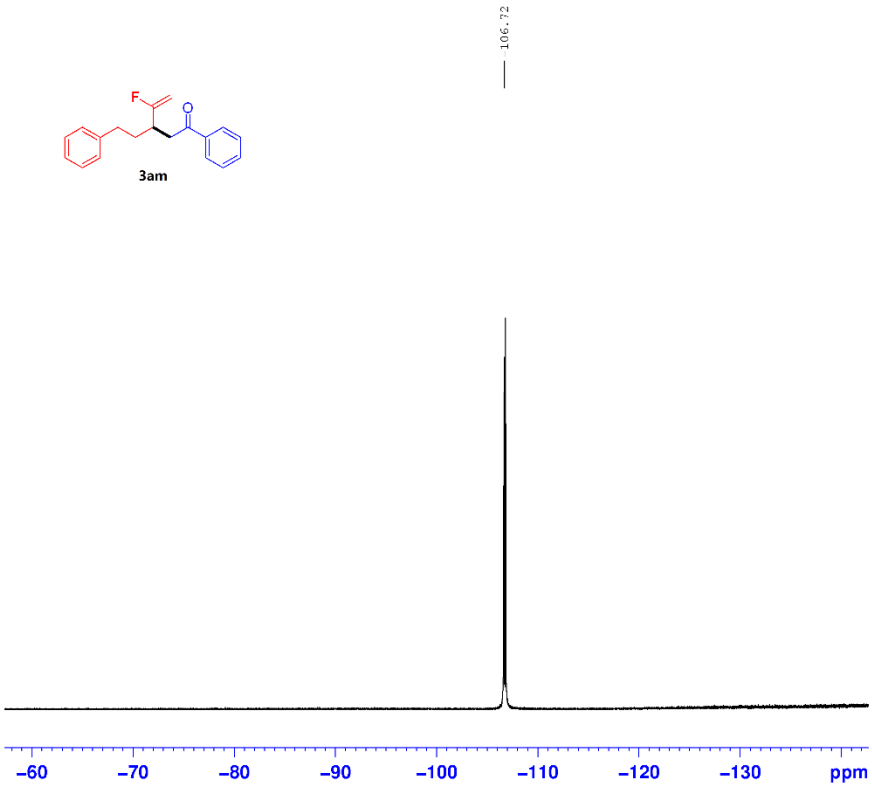
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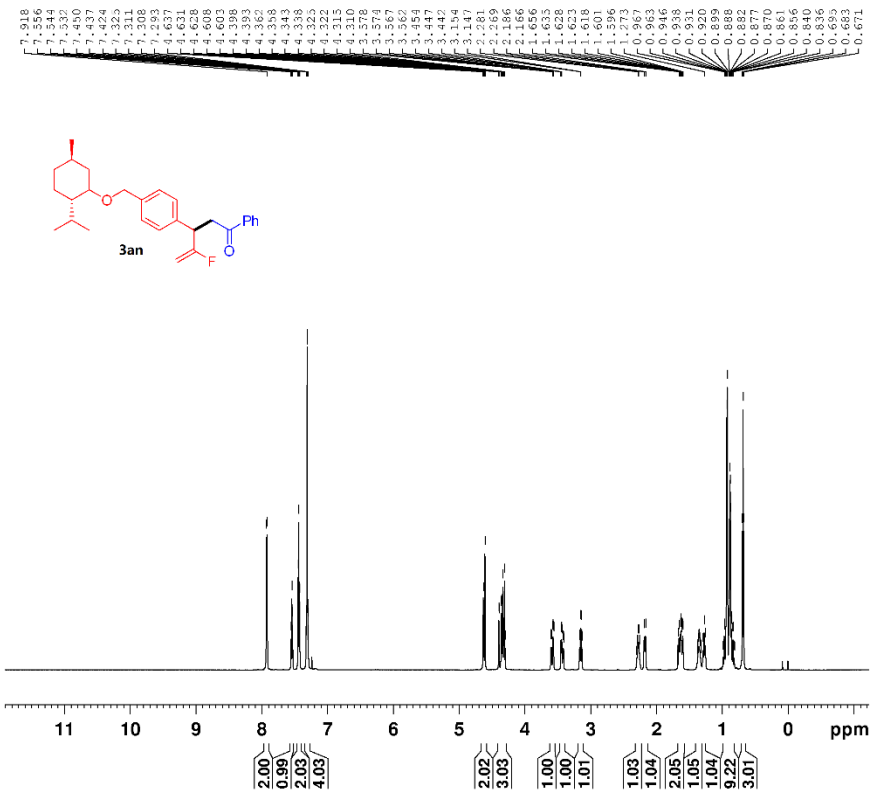
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O
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1.03
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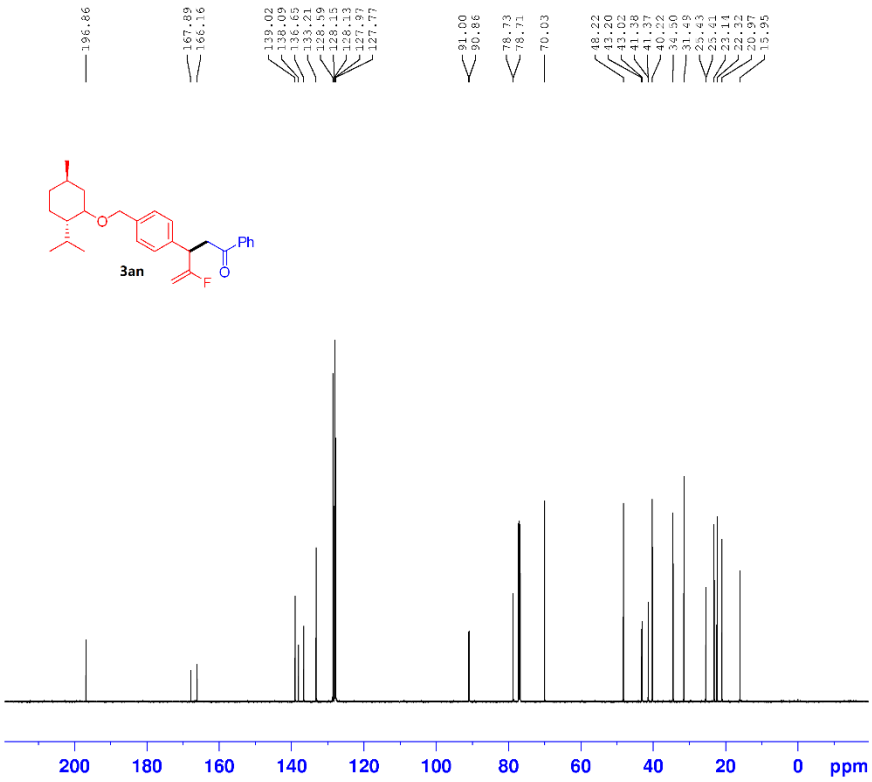
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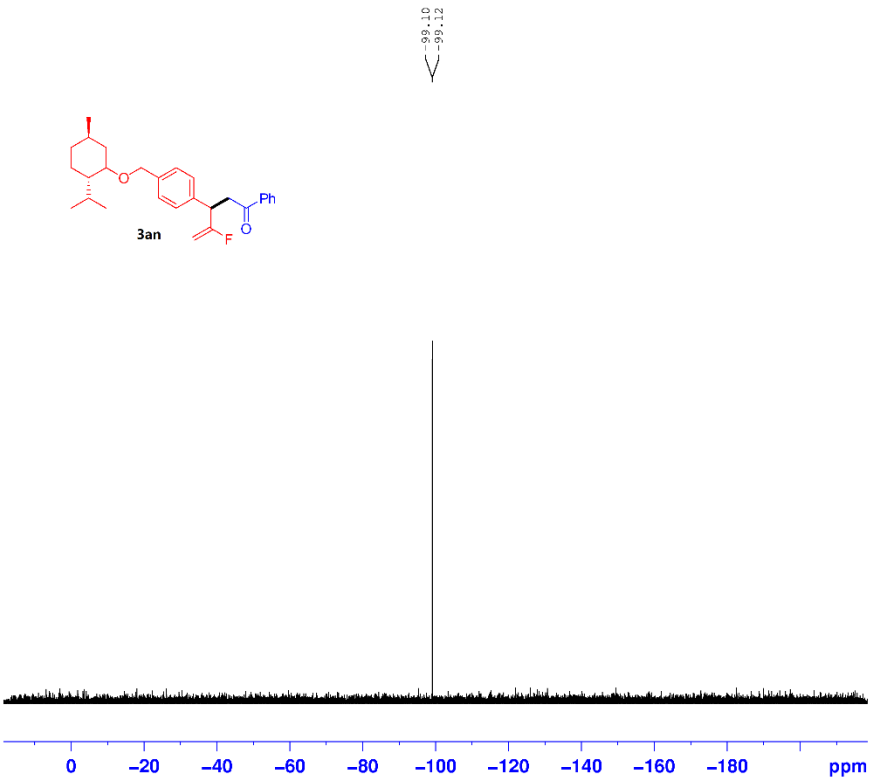
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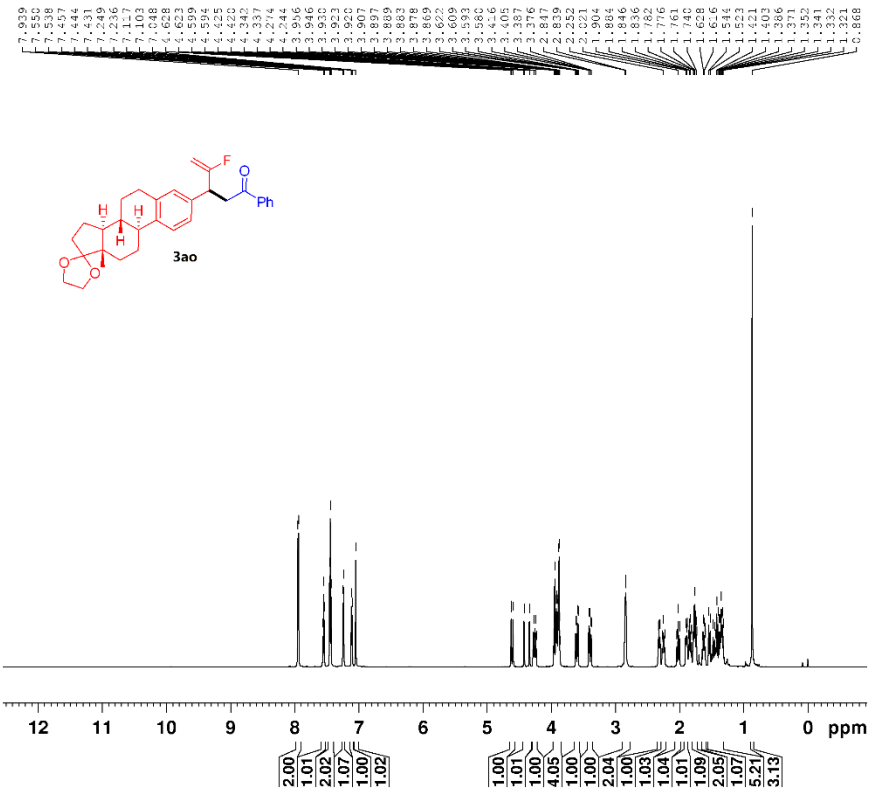
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4.594
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4.420
4.342
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4.274
4.244
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3.923
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1.332
1.321
0.868
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O
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H
H
H
O
O
3ao
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11
10
9
8
7
6
5
4
3
2
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1.01
2.02
1.07
1.00
1.02
1.00
1.01
1.00
4.05
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5.21
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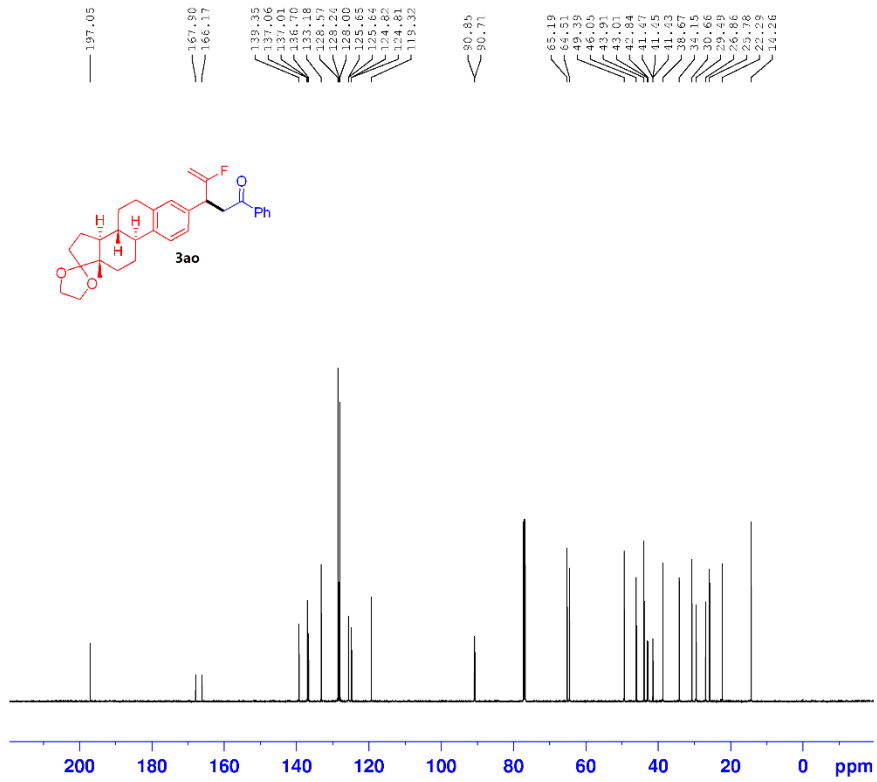
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41.45
41.23
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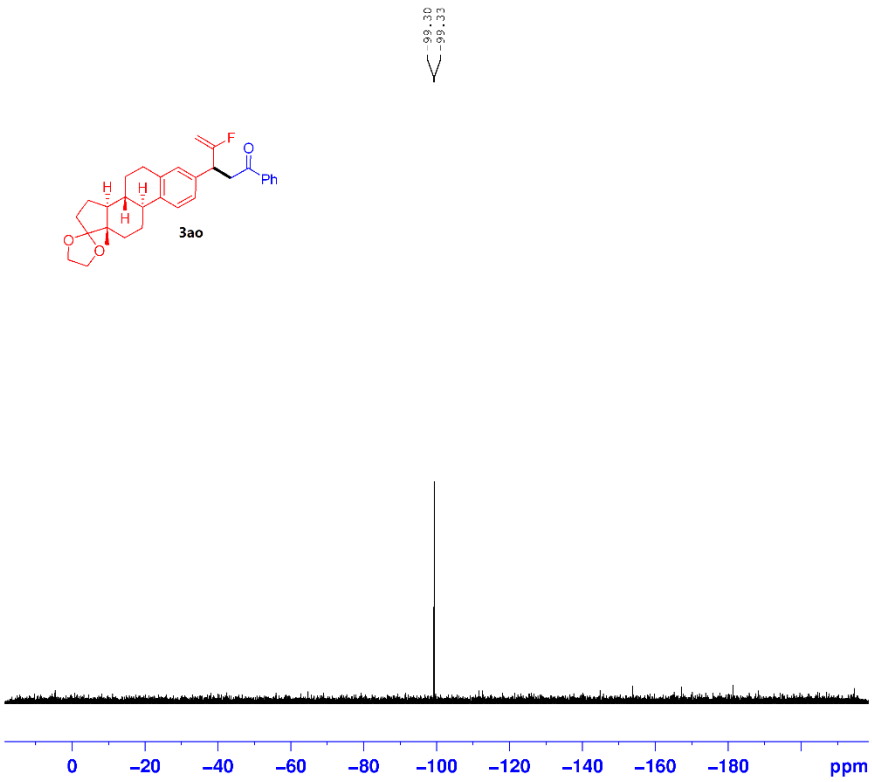
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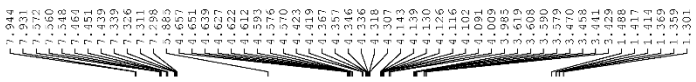

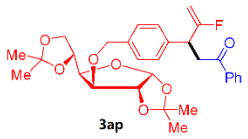
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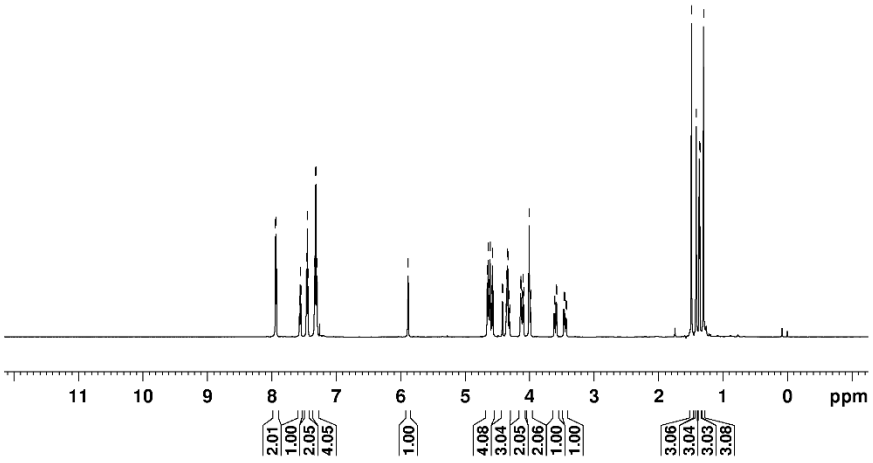
O
Ph
Me
Me

3ap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ppm
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1.00
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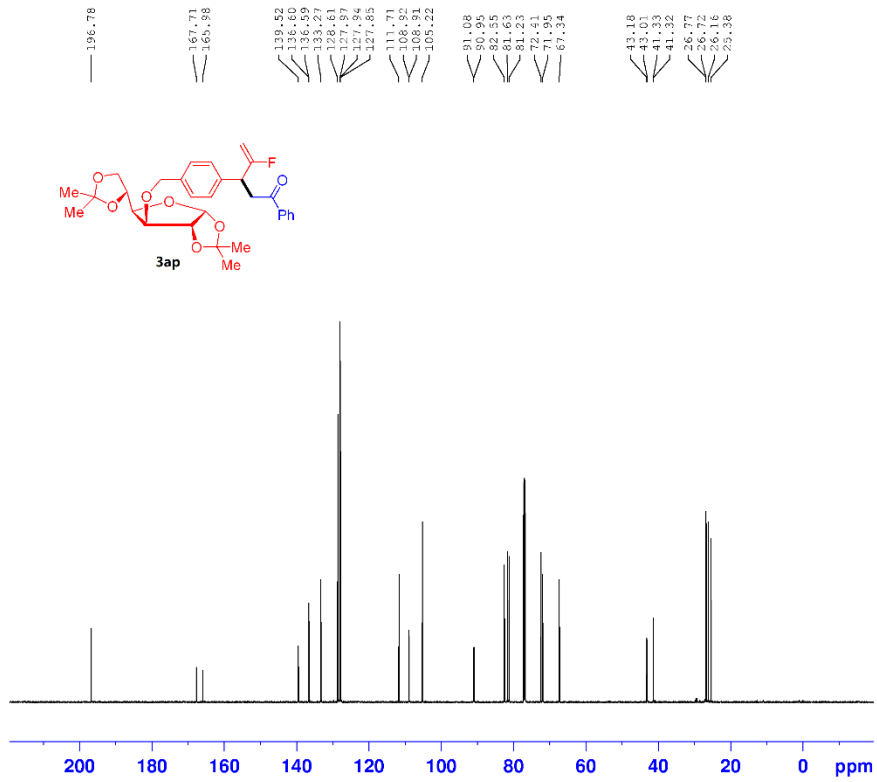
3.08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71.95
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41.33
41.32
26.77
26.72
26.16
25.38
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O
Ph
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Me
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Me
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120
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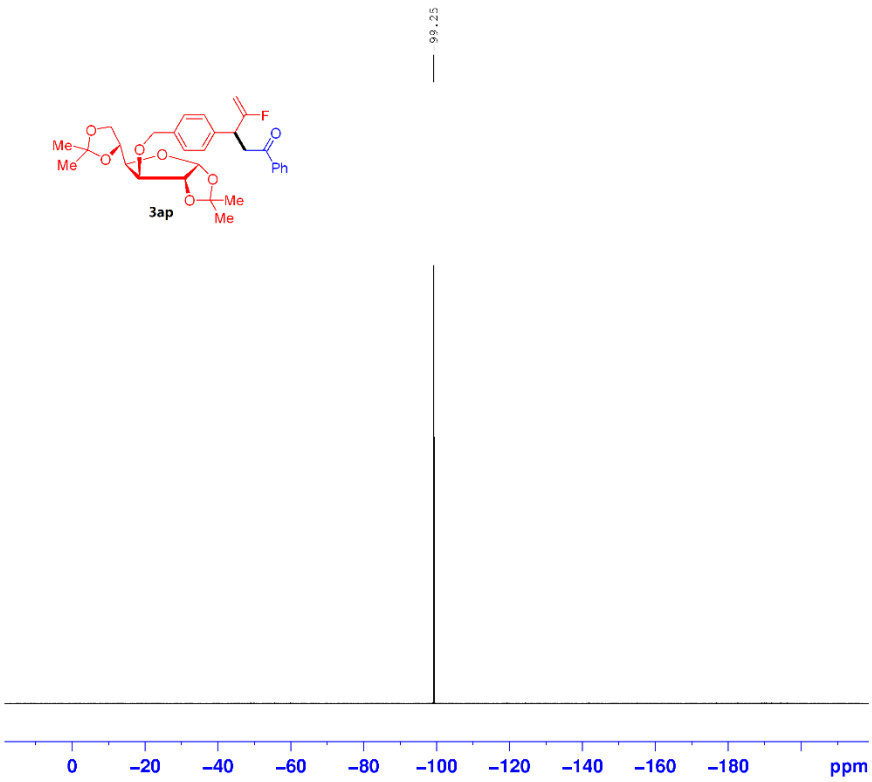
20
0
ppm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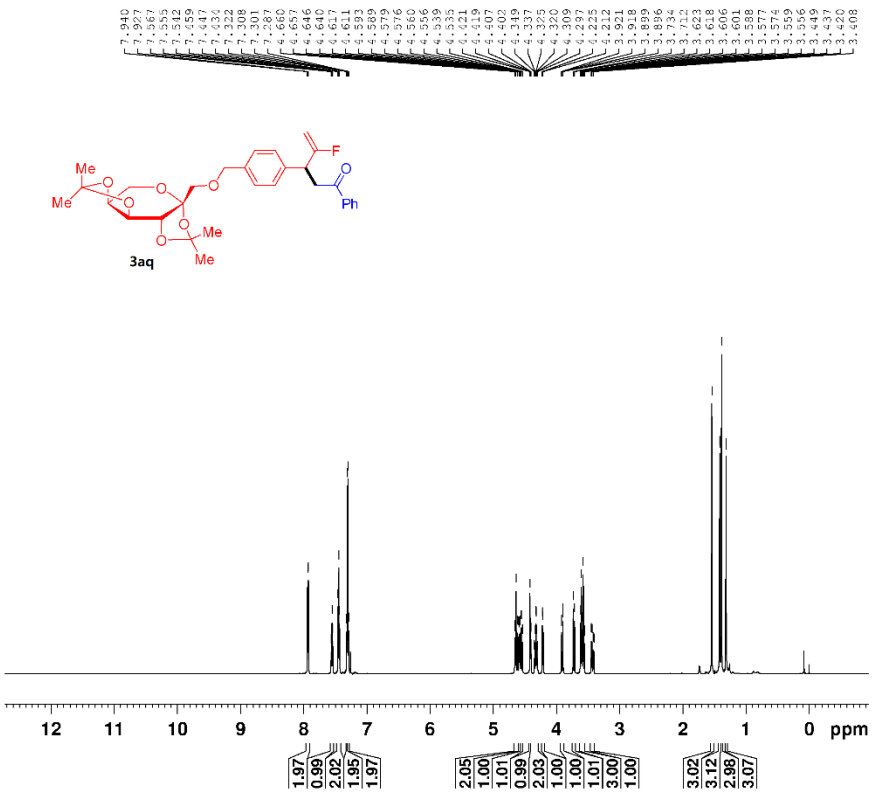
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O
O
O
F
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Ph
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Me
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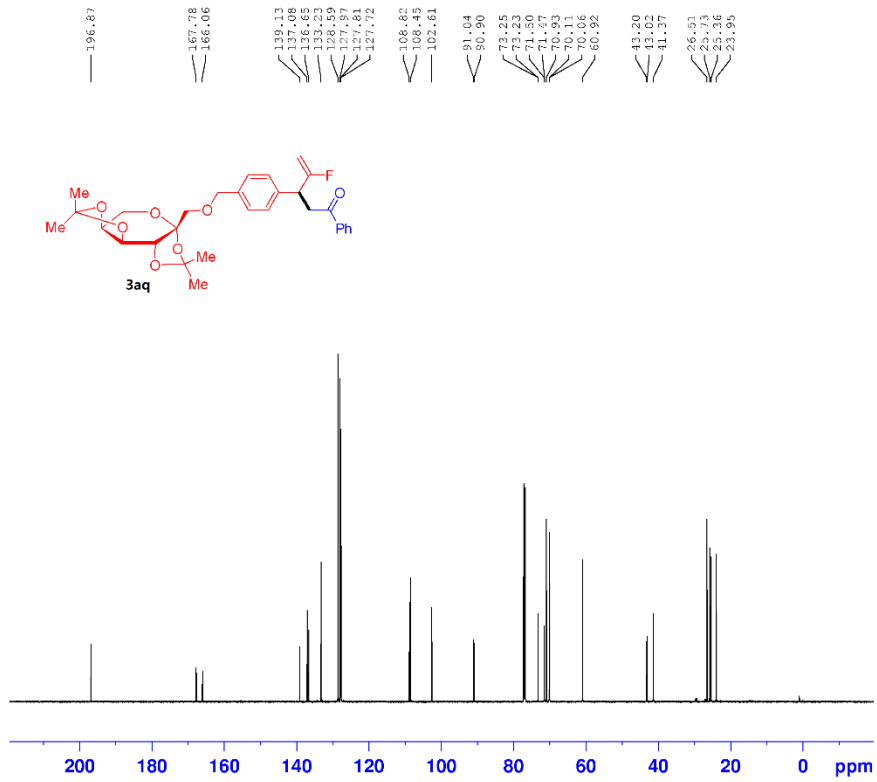
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70.11
70.06
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41.37
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Me
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O
O
O
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Ph
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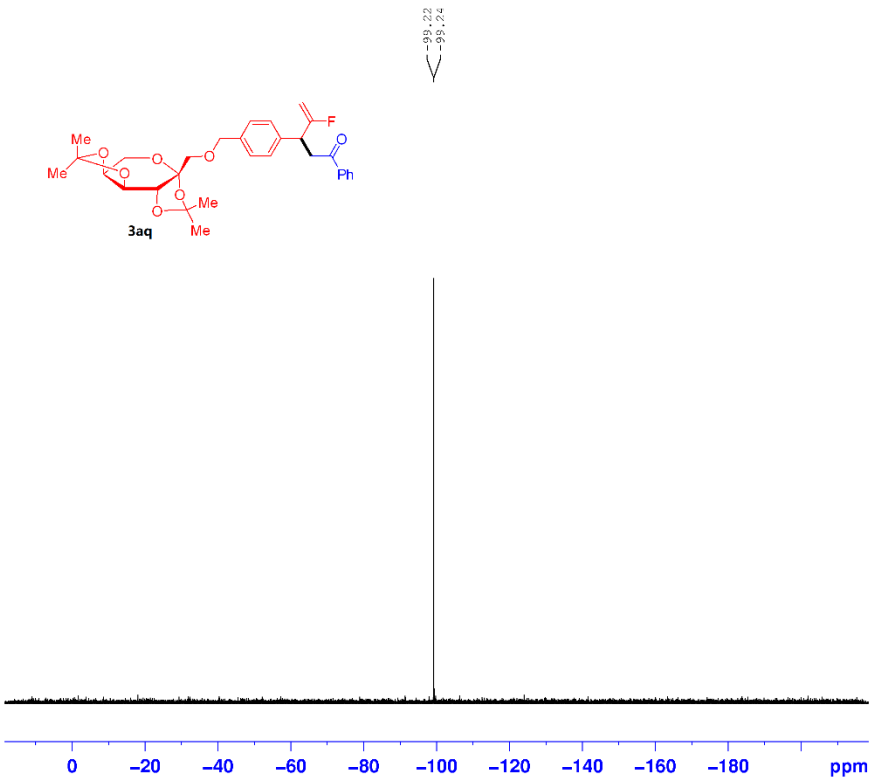
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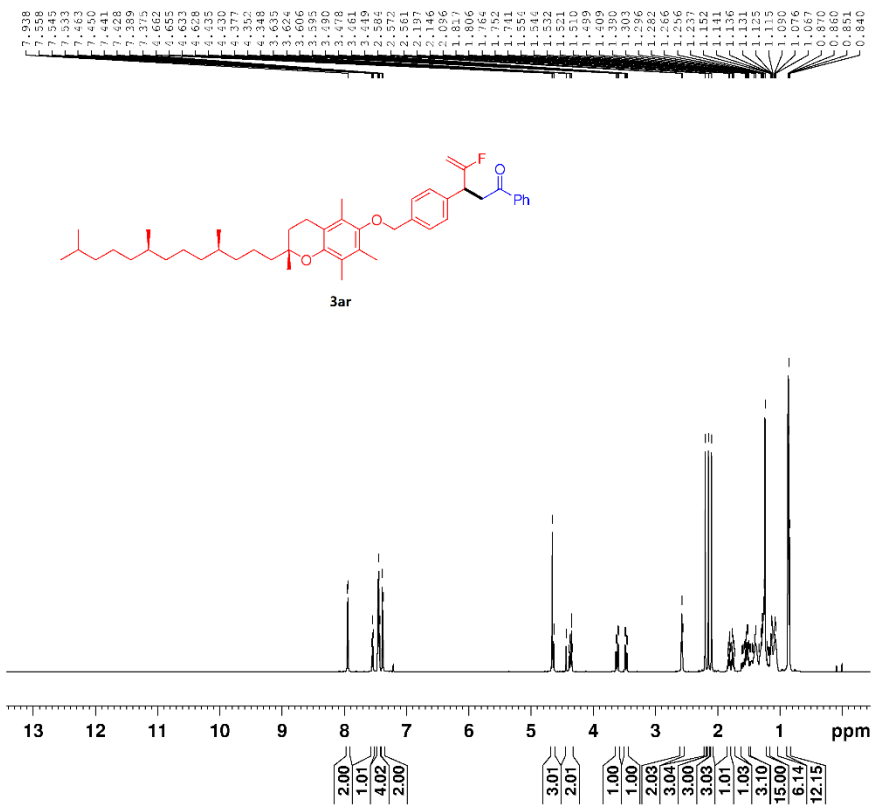
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1.764
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Ph
O
O
3ar
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12
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10
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6
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4
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ppm
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2.01
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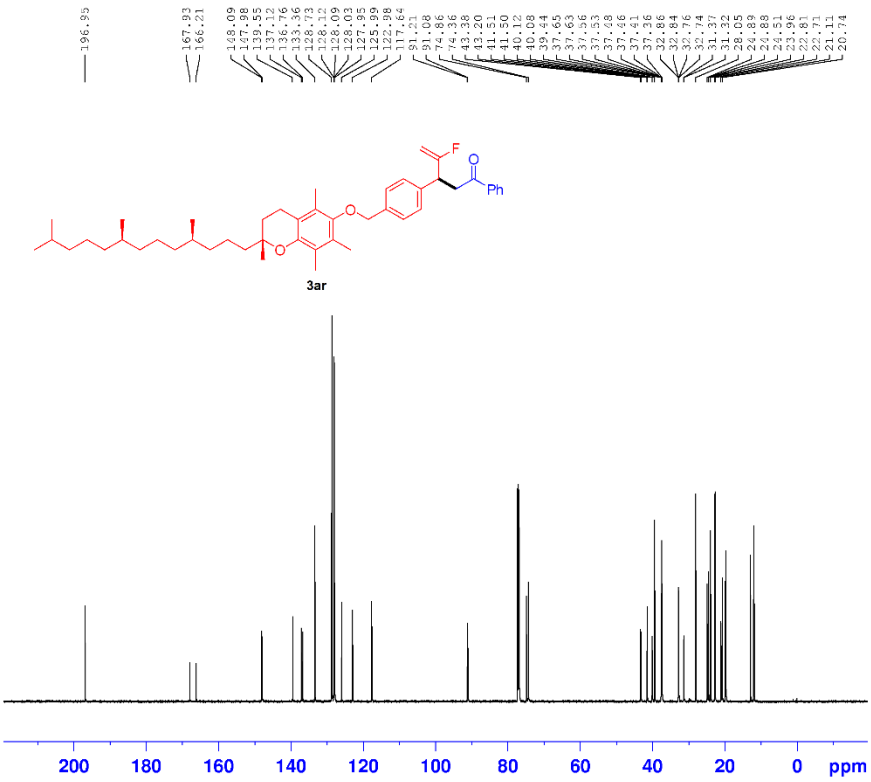
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43.20
41.51
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37.96
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37.28
37.16
37.11
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28.05
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24.88
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22.81
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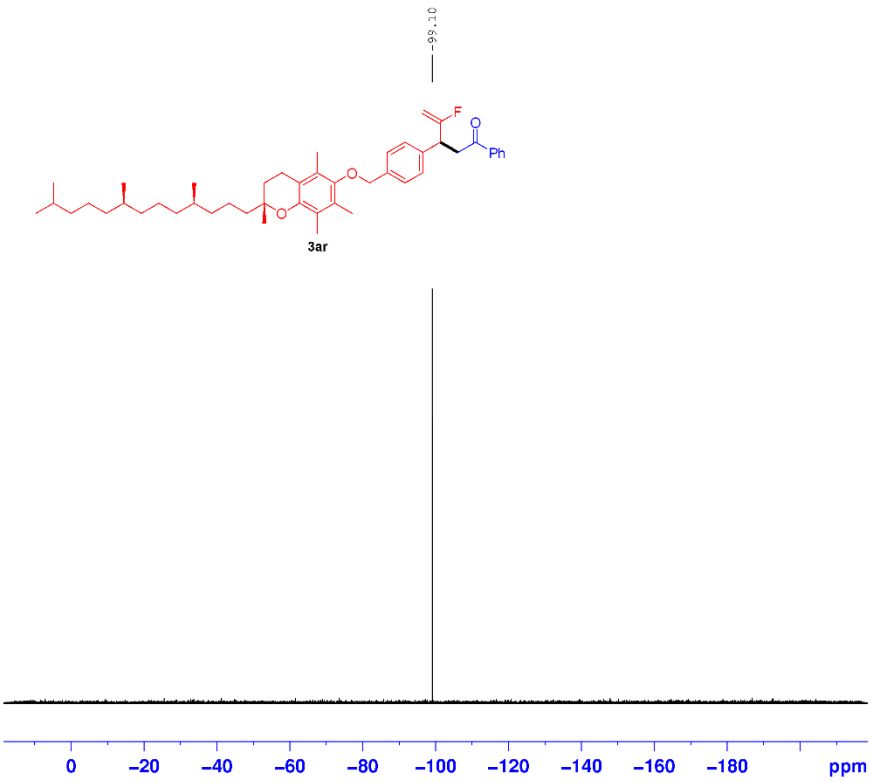
ppm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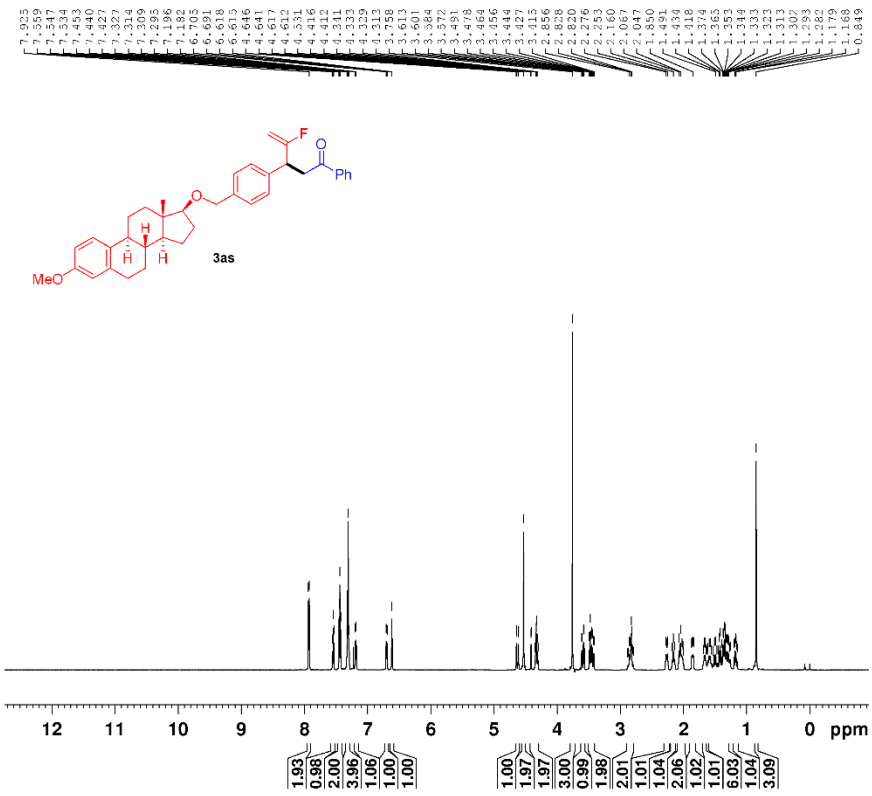
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MeO
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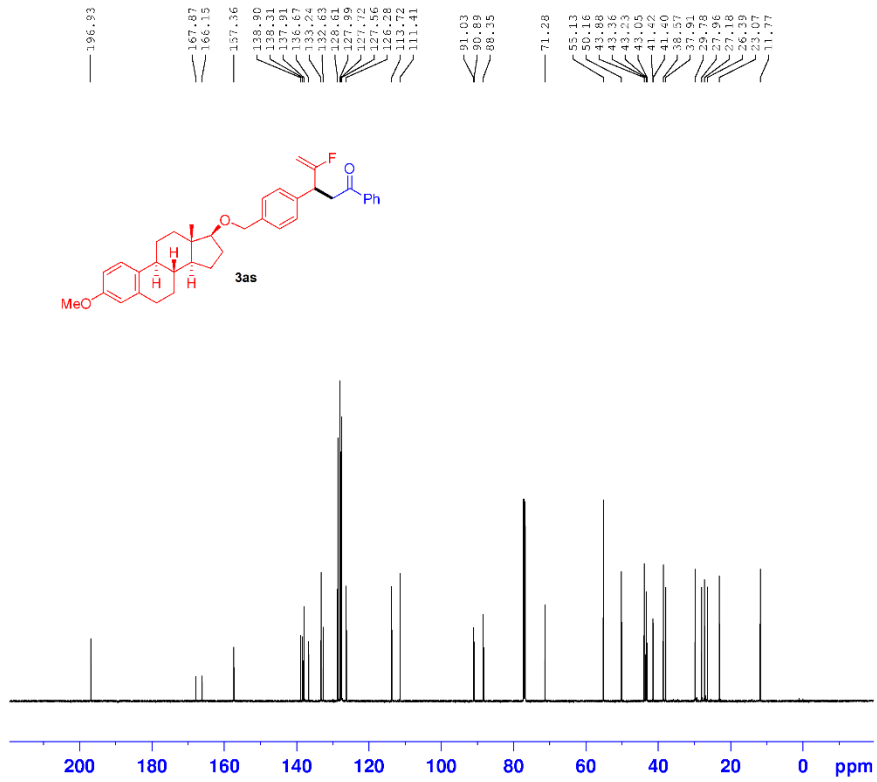
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41.42
41.40
38.57
37.91
29.78
27.96
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23.07
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Ph
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MeO
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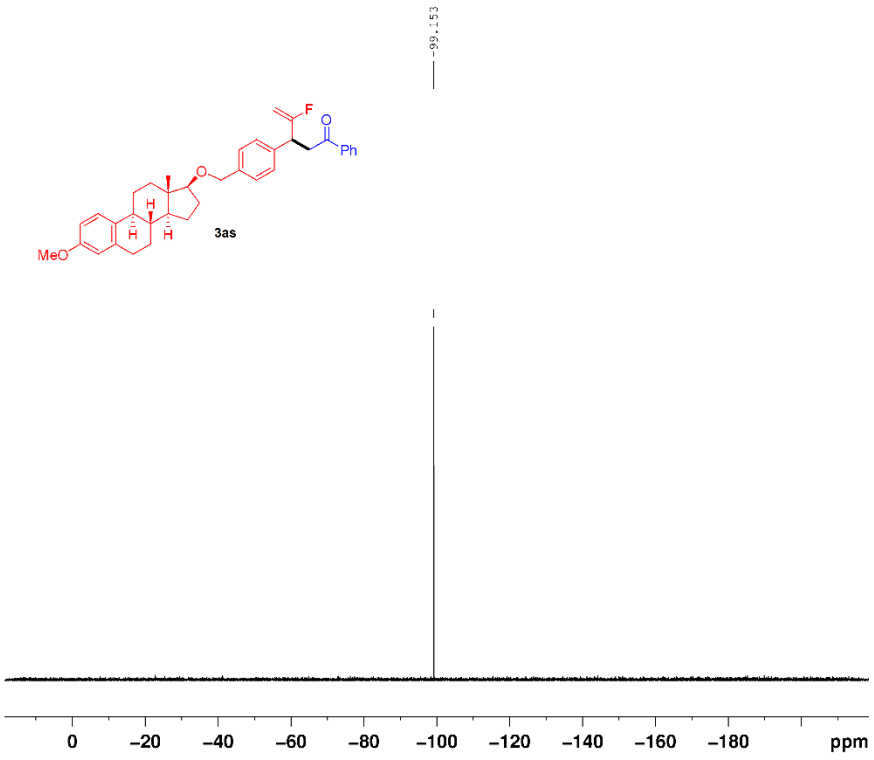
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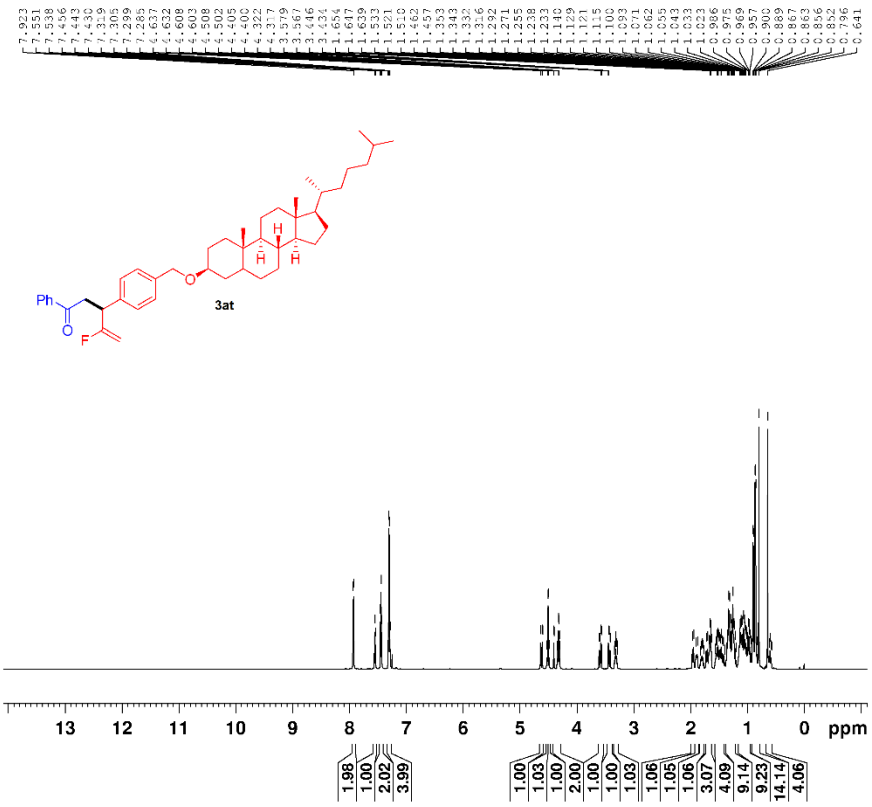
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4.603
4.598
4.593
4.405
4.400
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3.434
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1.055
1.043
1.033
1.023
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0.900
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0.867
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0.856
0.852
0.796
0.641
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O
F
H
H
H
O
3at
13
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11
10
9
8
7
6
5
4
3
2
1
0
ppm
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1.00
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3.99
1.00
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1.00
2.00
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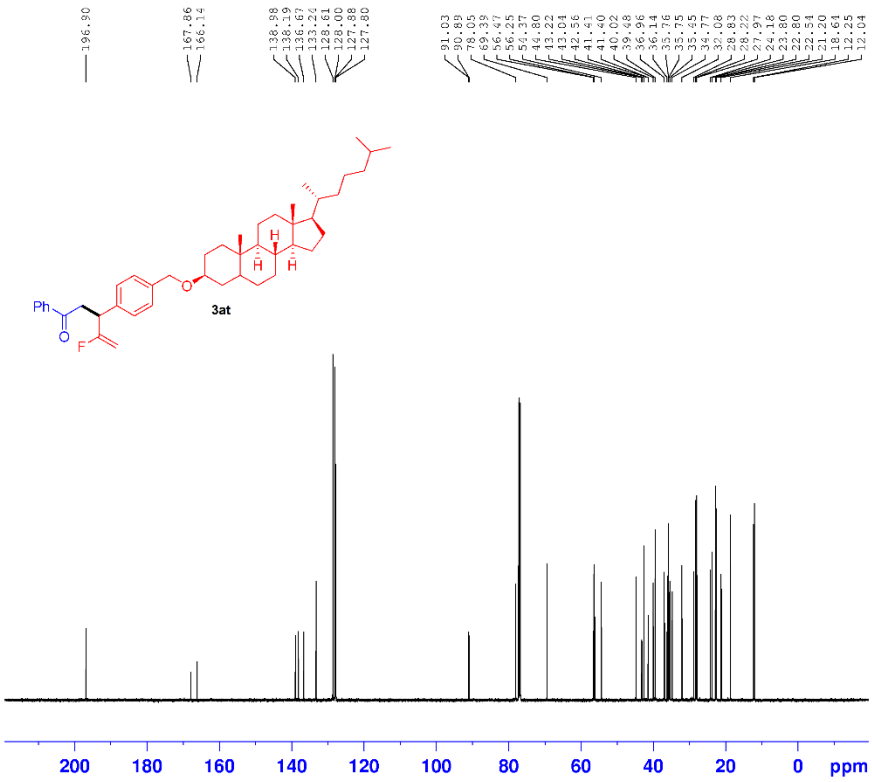
4.06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43.04
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41.41
41.40
40.02
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35.45
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34.08
29.83
28.22
27.97
24.18
23.80
22.80
22.54
21.20
18.64
12.25
12.04
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H
H
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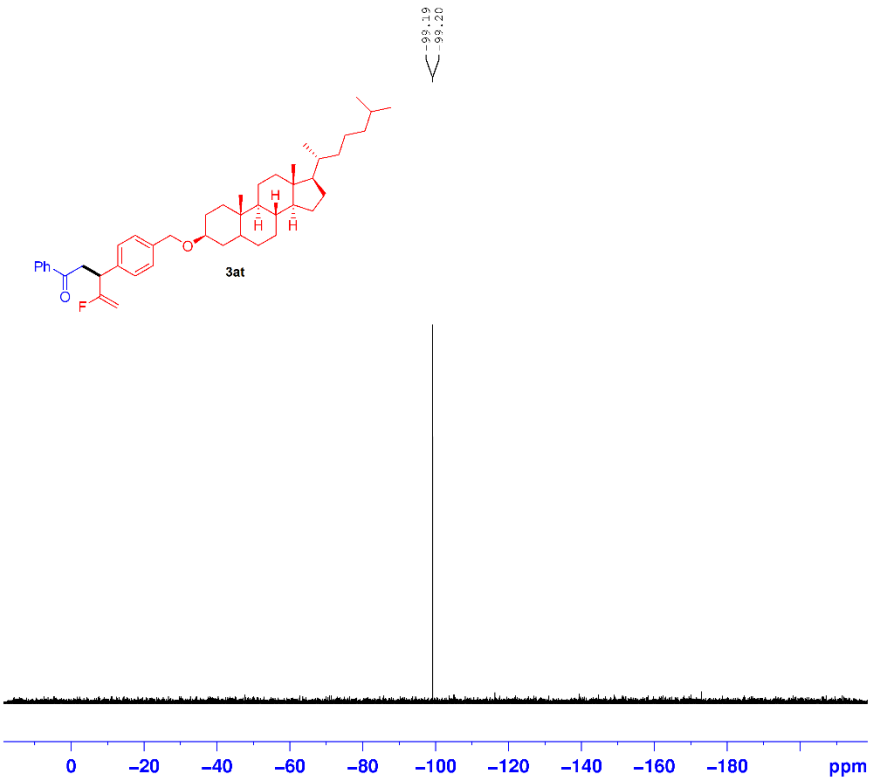
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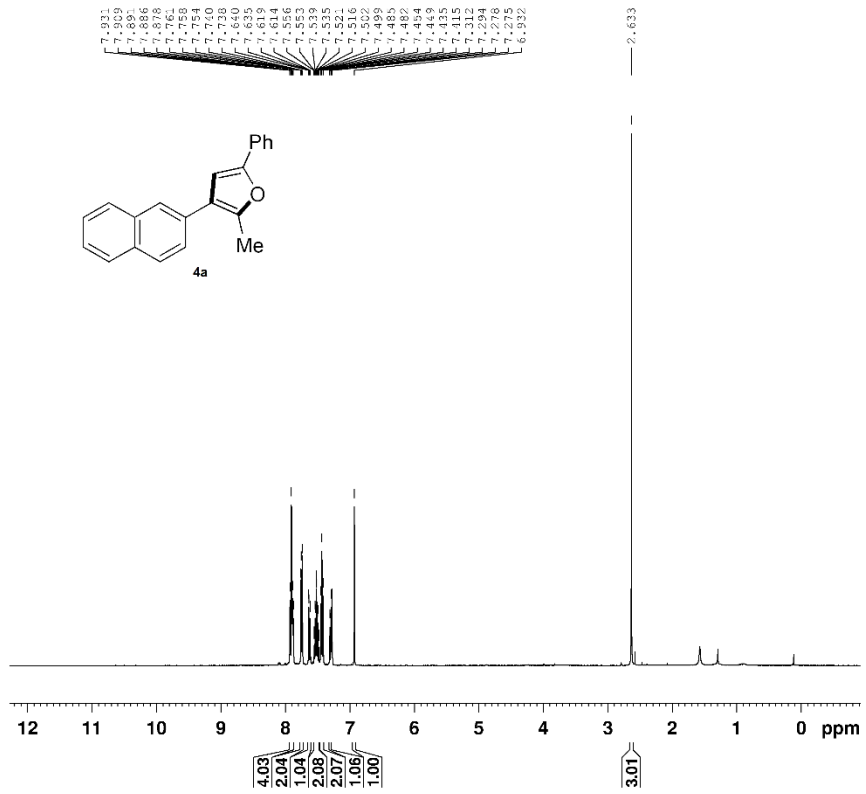
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Ph
O
Me
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8
7
6
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2.08
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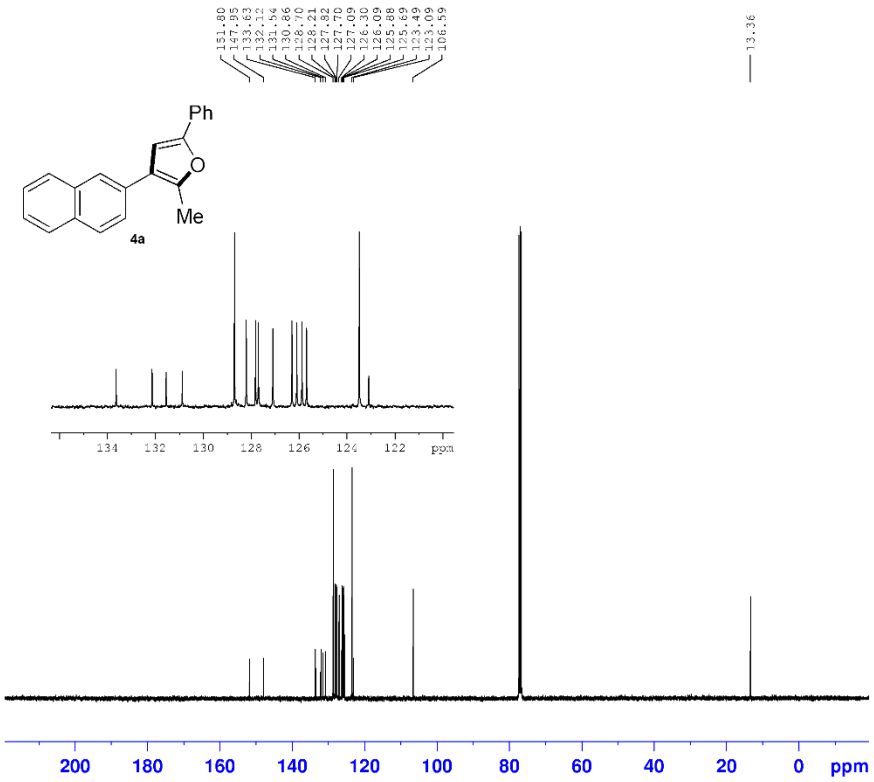
1.00
3.01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127.09
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126.09
125.88
125.69
123.49
123.09
106.59
13.36
Ph
O
Me
4a
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132
130
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126
124
122
ppm
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120
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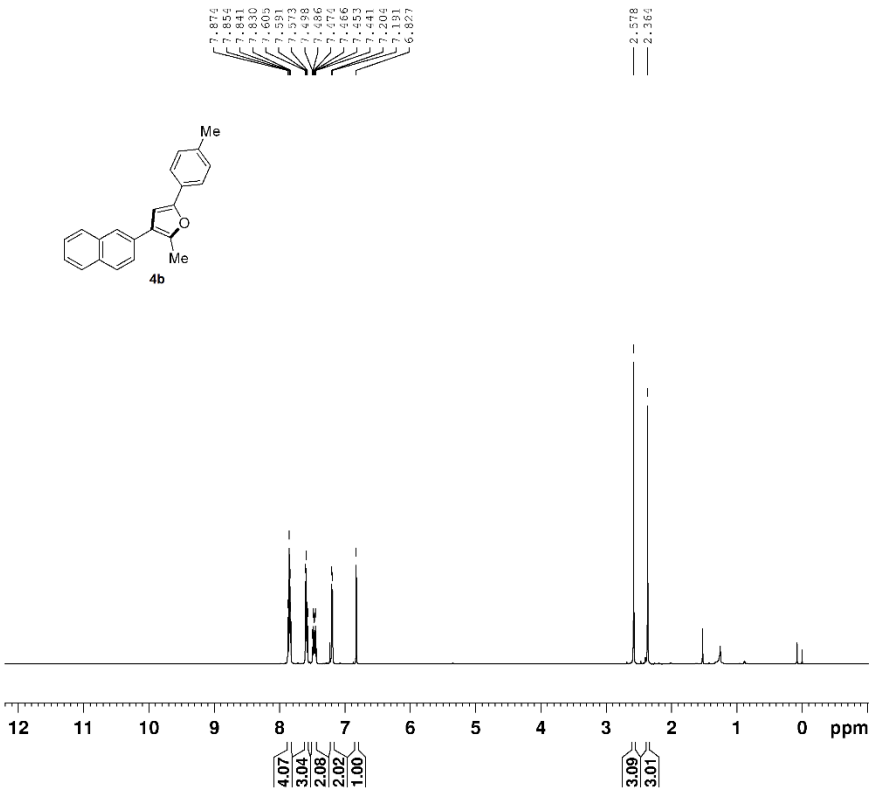
40
20
0
ppm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7.573
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7.486
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7.466
7.453
7.441
7.206
7.191
6.827
2.578
2.361
Me
O
Me
4b
12
11
10
9
8
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1
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3.04
2.08
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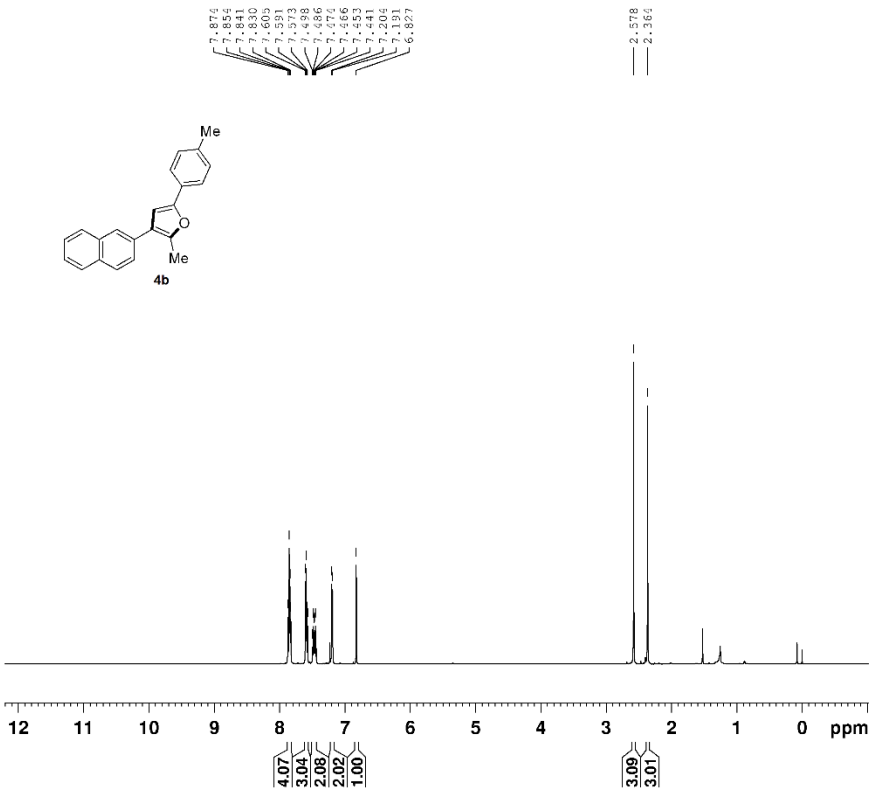
3.09
3.01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7.206
7.191
6.827
2.578
2.361
Me
O
Me
4b
12
11
10
9
8
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1
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ppm
4.07
3.04
2.08
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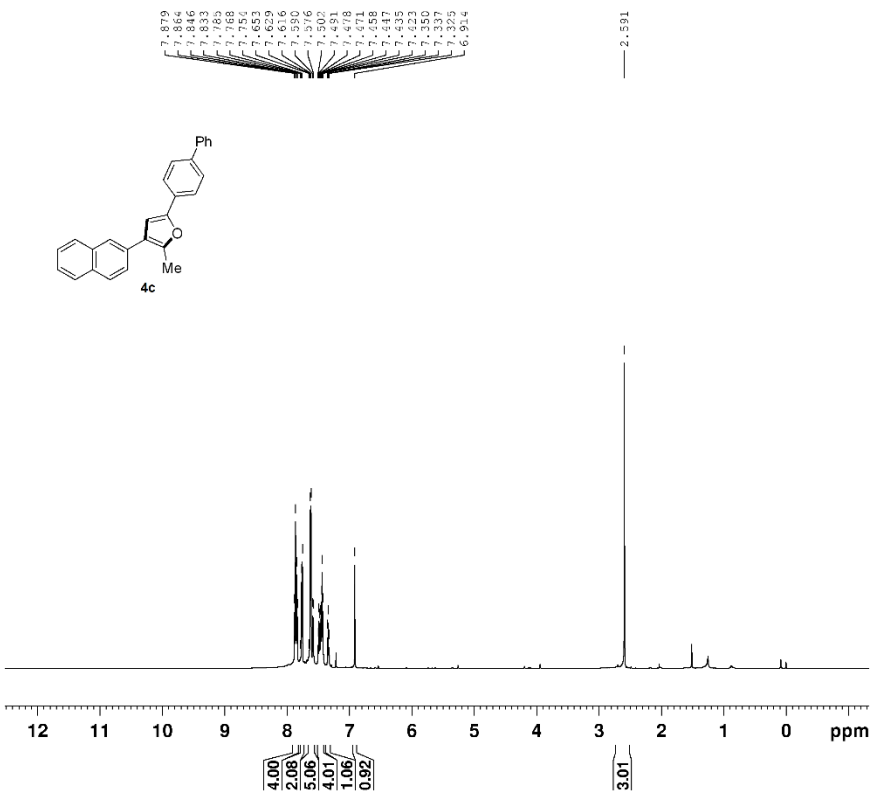
3.09
3.01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7.491
7.478
7.471
7.458
7.447
7.435
7.423
7.350
7.337
7.325
6.914
2.591
Ph
O
Me
4c
12
11
10
9
8
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5
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2
1
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ppm
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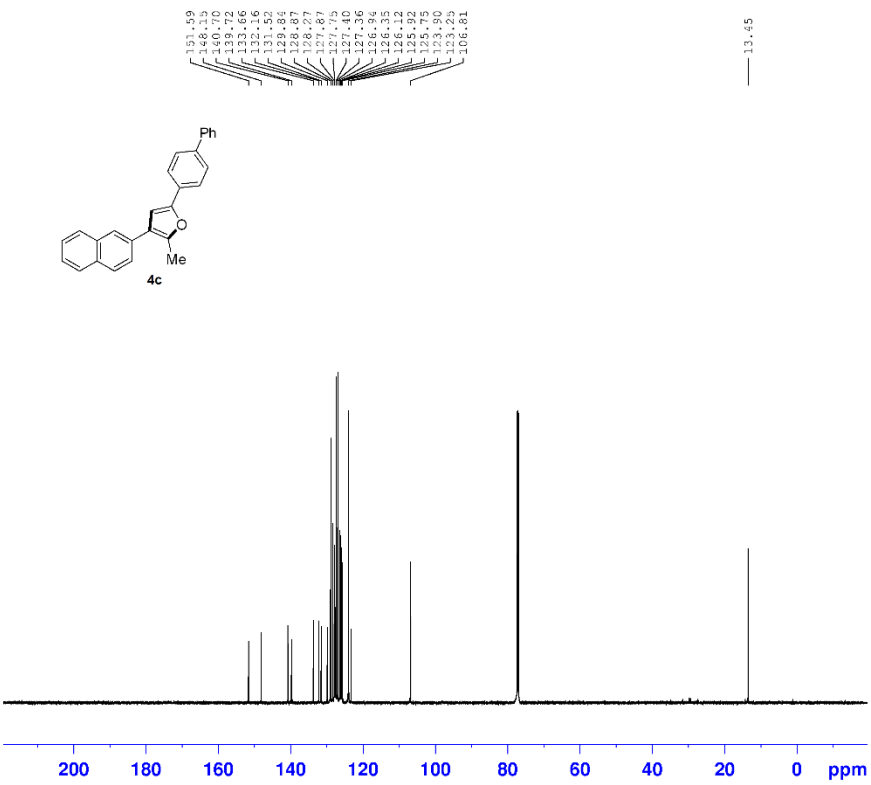
0.92
3.01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127.36
126.94
126.35
126.12
125.92
125.75
123.90
123.25
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Ph
O
Me
4c
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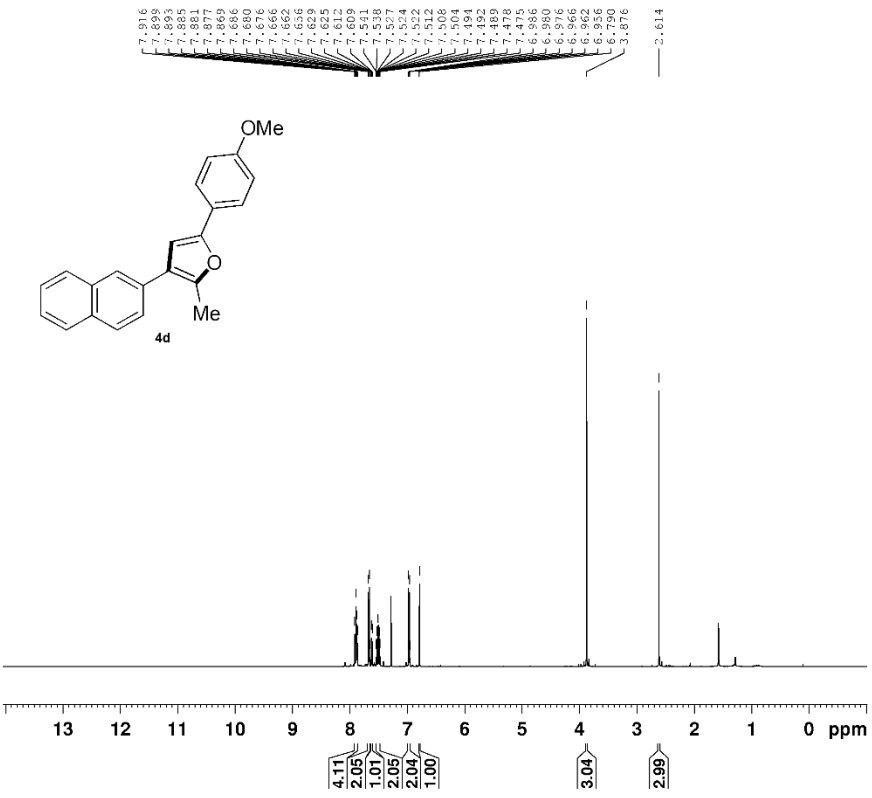
0
ppm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7.662
7.636
7.629
7.625
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7.609
7.541
7.538
7.527
7.524
7.522
7.512
7.508
7.504
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7.192
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6.976
6.966
6.962
6.956
6.790
3.876
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OMe
O
Me
4d
13
12
11
10
9
8
7
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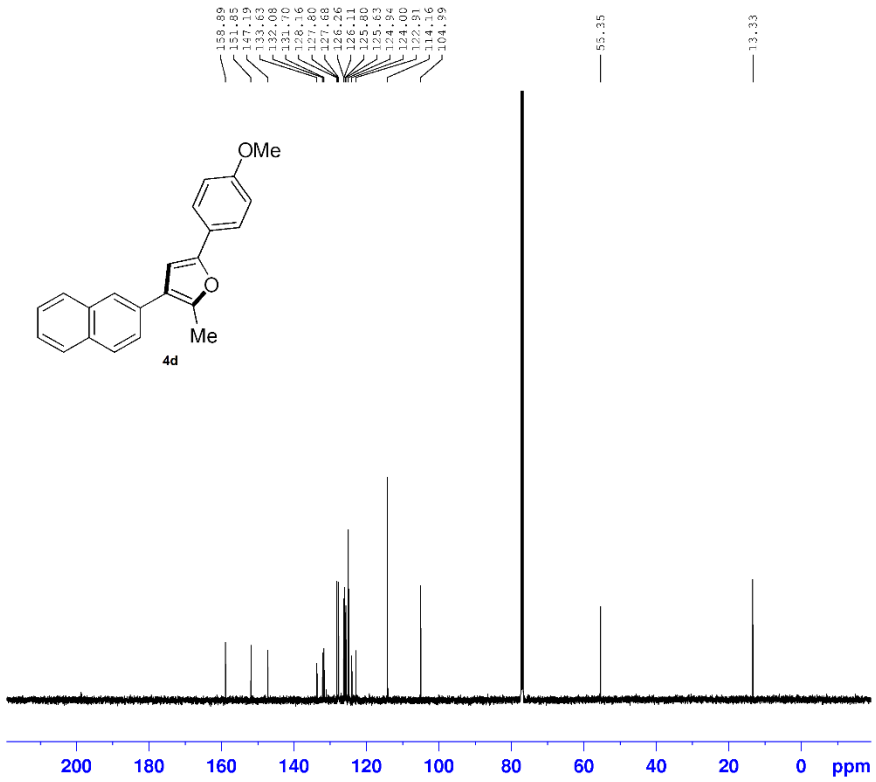
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125.63
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124.00
122.91
114.16
104.99
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O
Me
4d
200
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120
100
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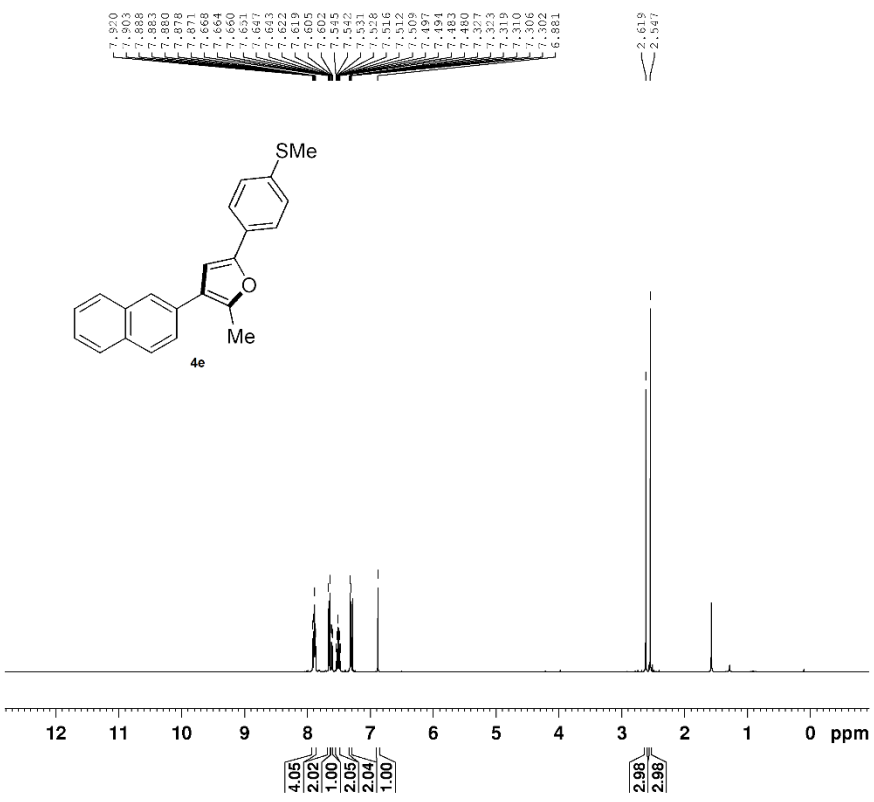
40
20
0
ppm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7.528
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7.512
7.509
7.497
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7.323
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7.310
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7.302
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2.547
SMe
O
Me
4e
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11
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7
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2.05
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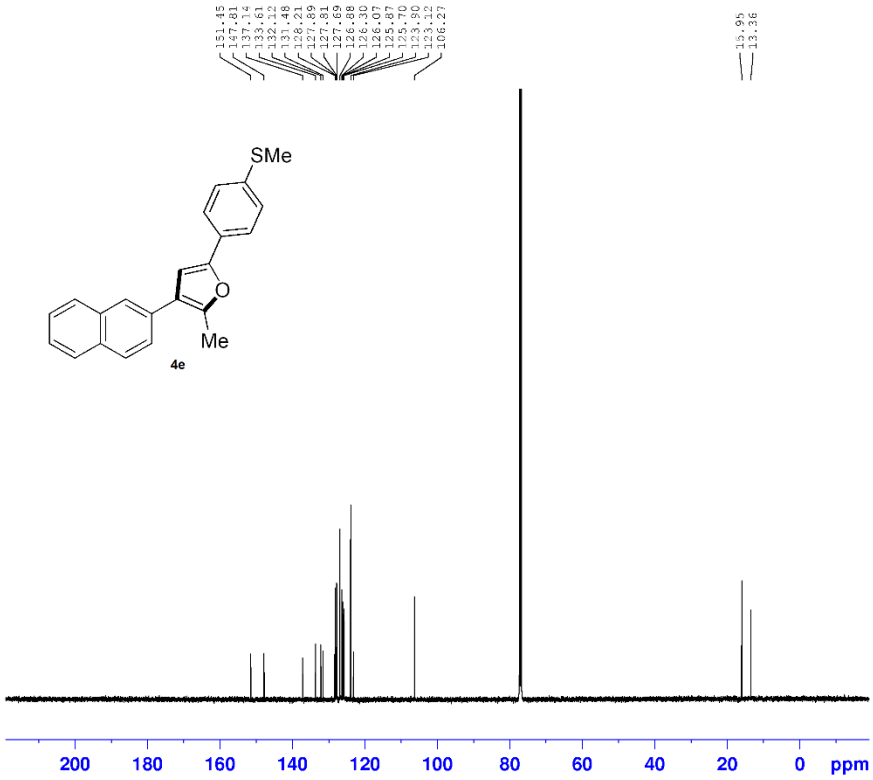
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126.07
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125.70
123.90
123.12
106.27
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O
Me
4e
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120
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40
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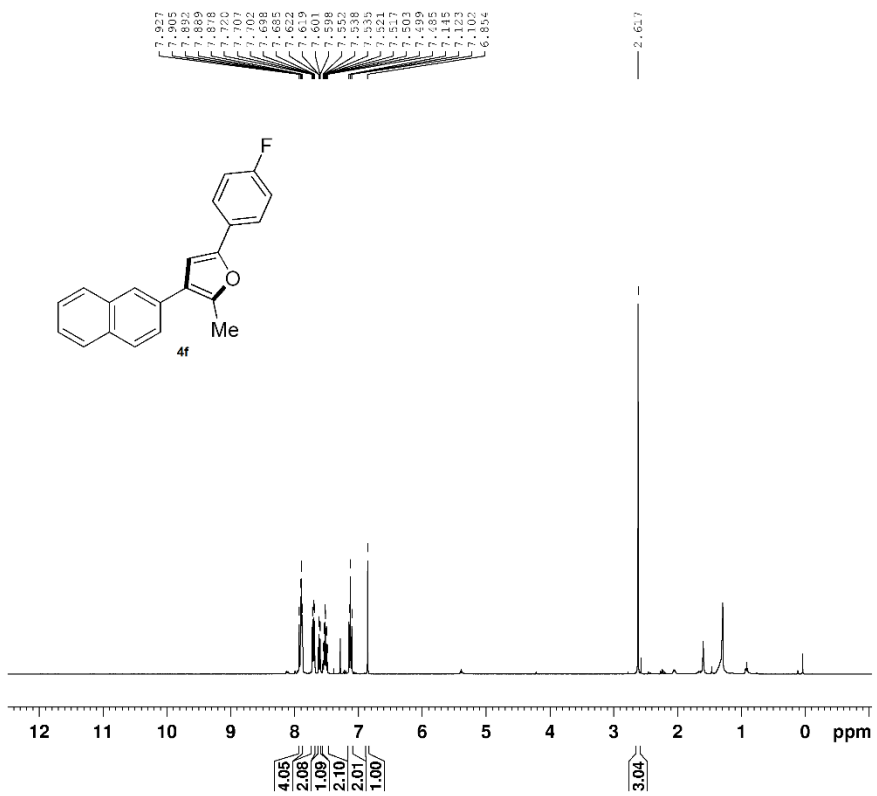
0
ppm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7.598
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7.485
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O
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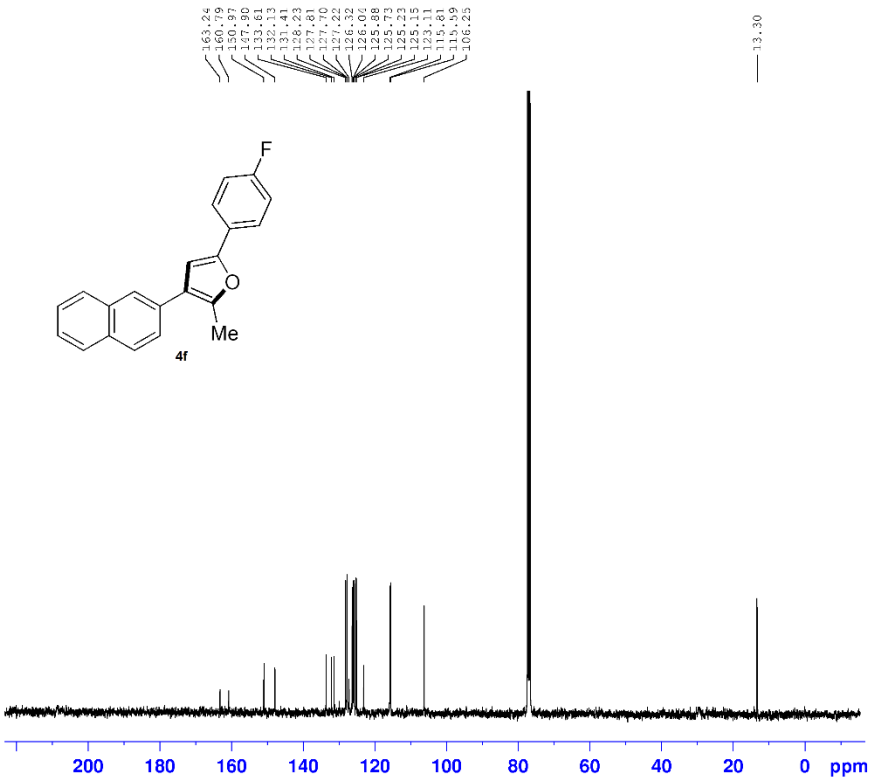
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126.32
126.04
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125.73
125.23
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123.11
115.81
115.59
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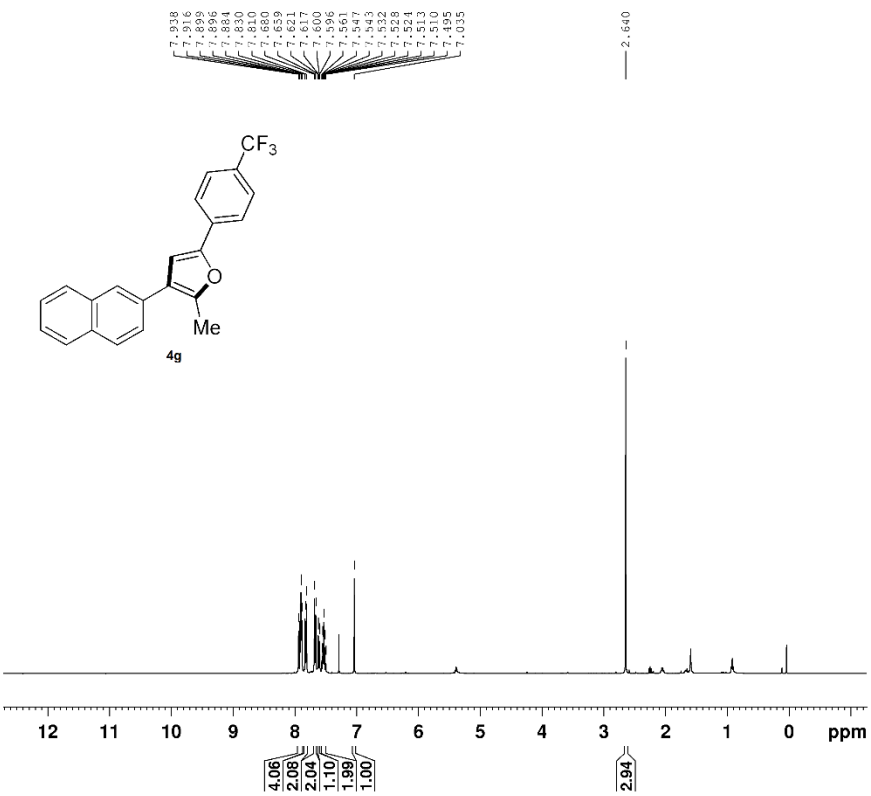
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7.561
7.547
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7.532
7.528
7.524
7.513
7.510
7.495
7.035
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CF3
O
Me
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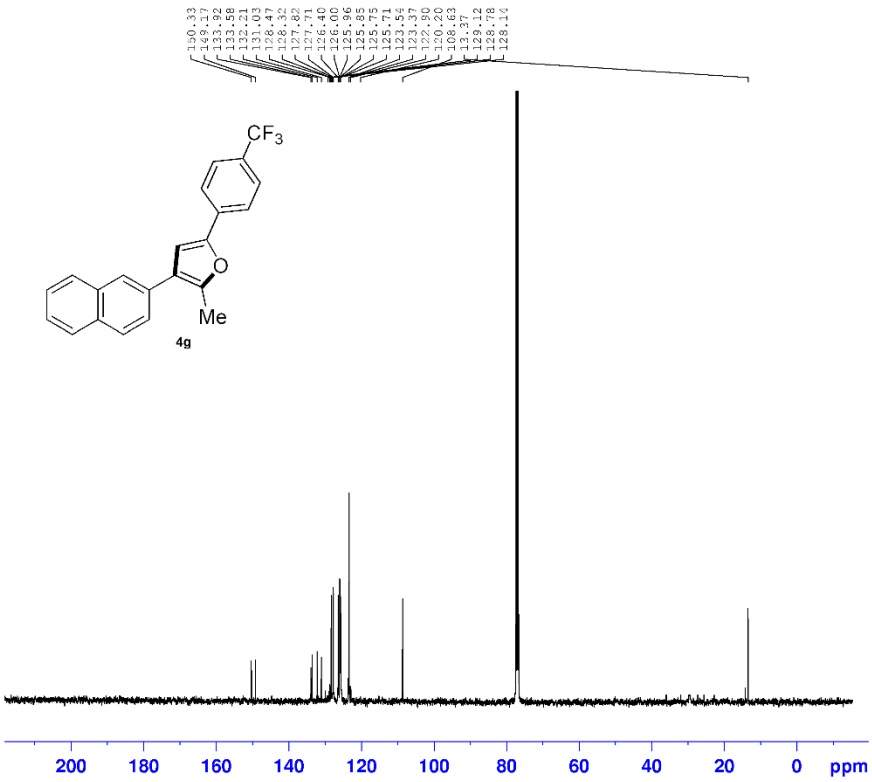
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125.96
125.85
125.75
125.71
123.54
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108.63
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129.12
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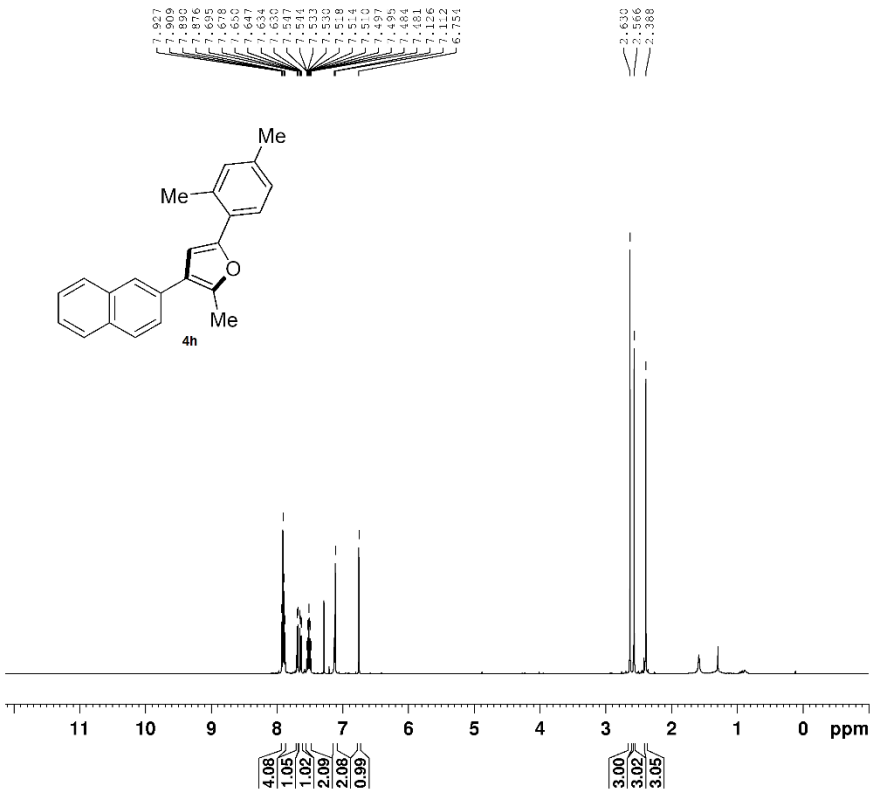
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7.510
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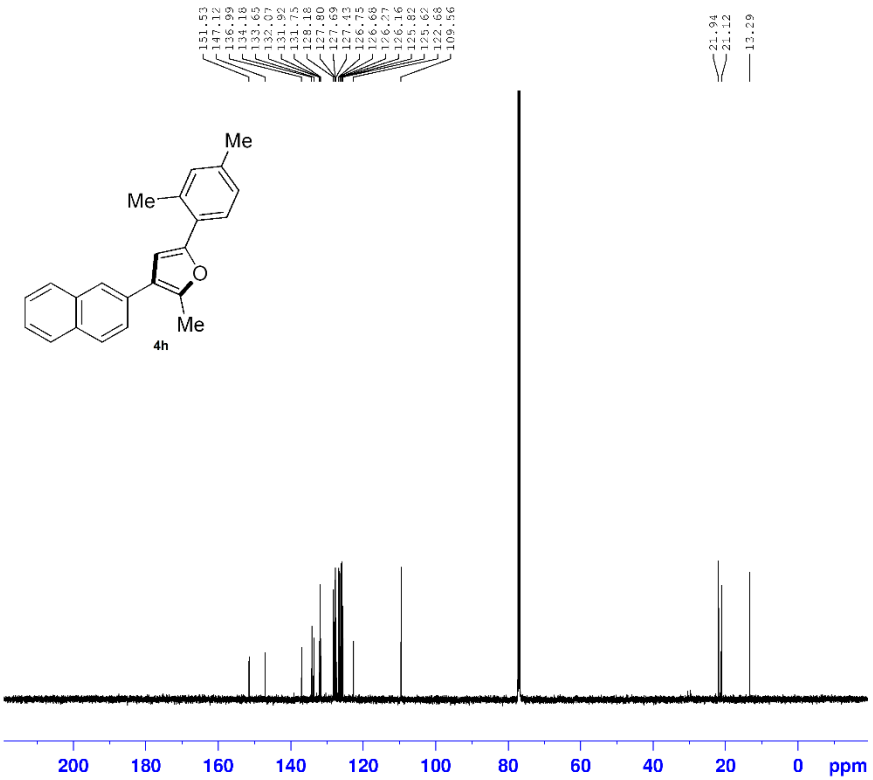
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125.82
125.62
122.68
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Me
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120
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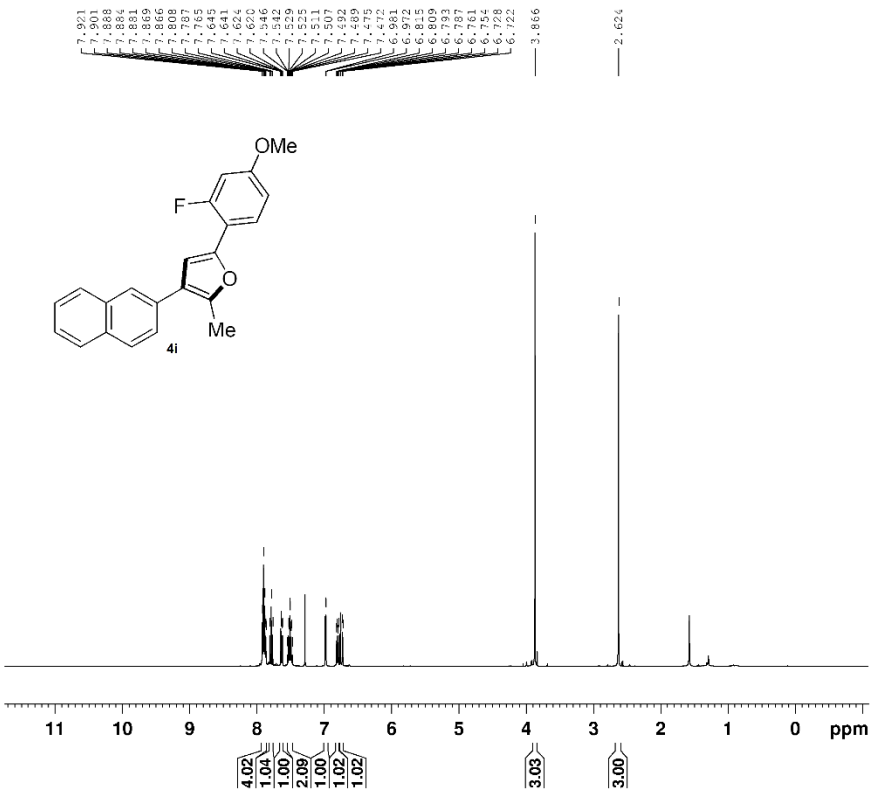
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7.641
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7.620
7.546
7.542
7.529
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7.511
7.507
7.492
7.489
7.475
7.472
6.981
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6.815
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6.793
6.787
6.761
6.754
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6.722
3.866
2.624
OMe
F
O
Me
4i
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7
6
5
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1.00
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1.00
1.02
1.02
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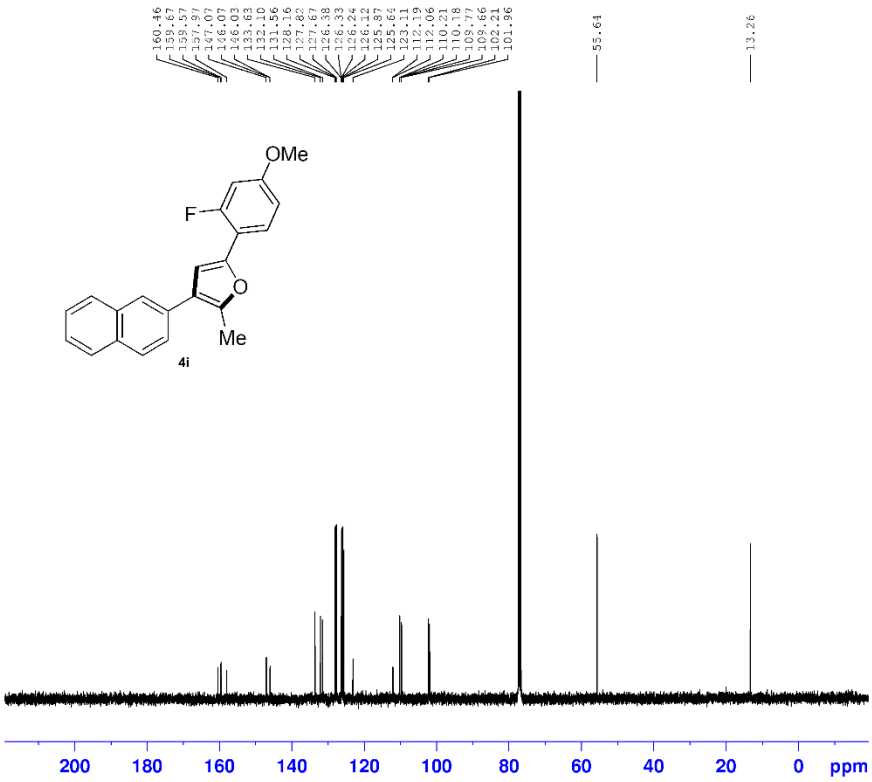
3.00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125.64
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112.06
110.21
110.18
109.77
109.66
102.21
101.96
55.61
13.26
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Me
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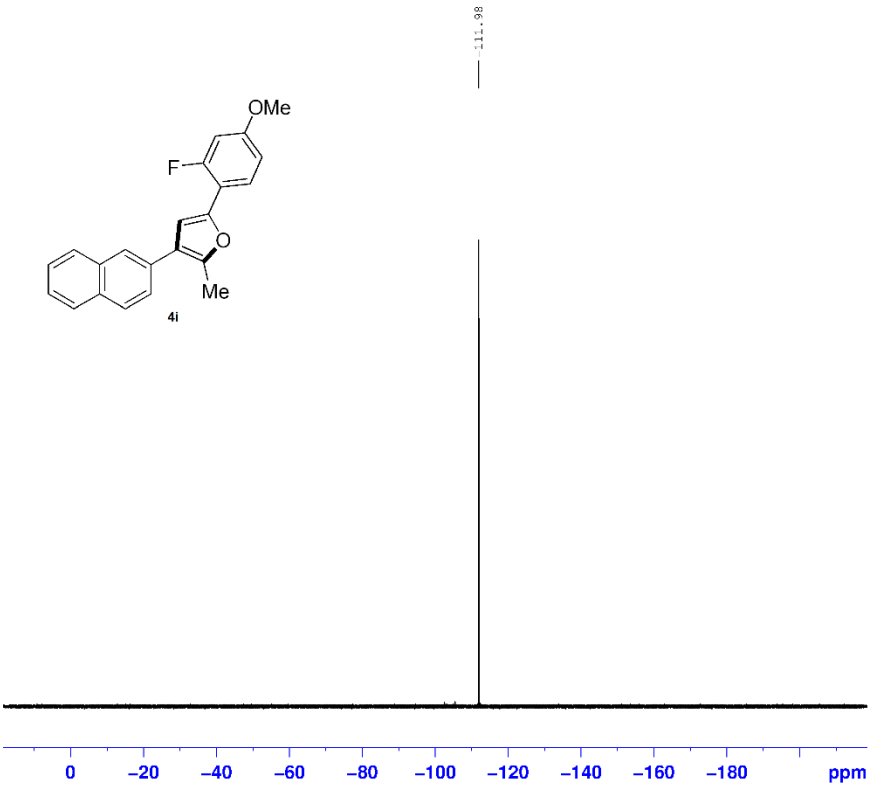
ppm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−180
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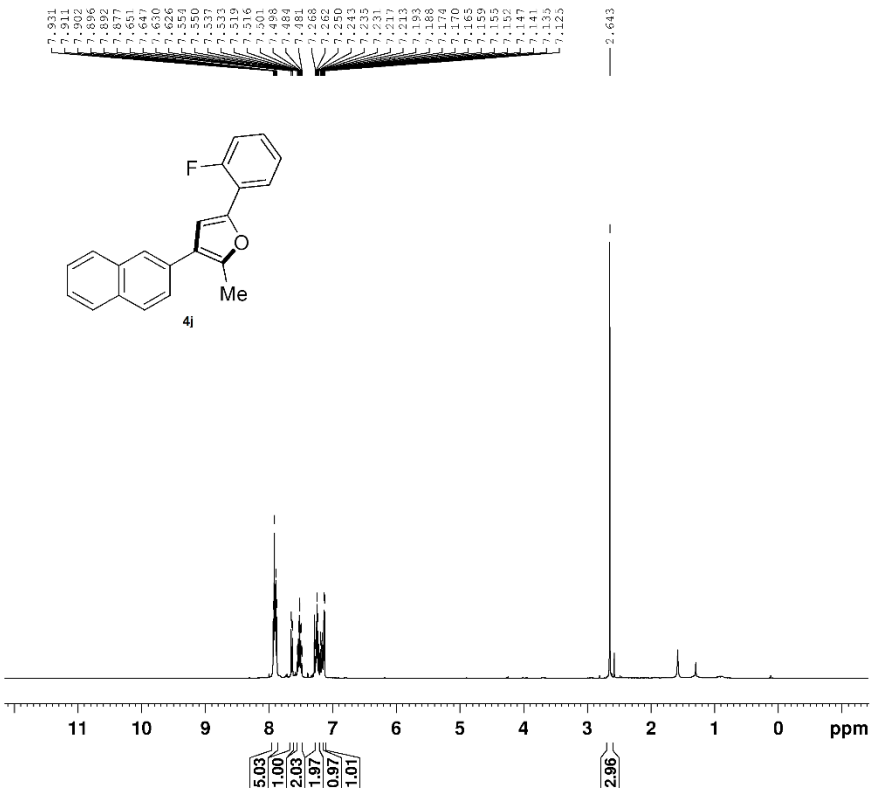
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7.519
7.516
7.501
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7.268
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7.235
7.231
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7.213
7.193
7.188
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7.170
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7.159
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7.152
7.147
7.141
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2.643
F
O
Me
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6
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4
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ppm
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2.03
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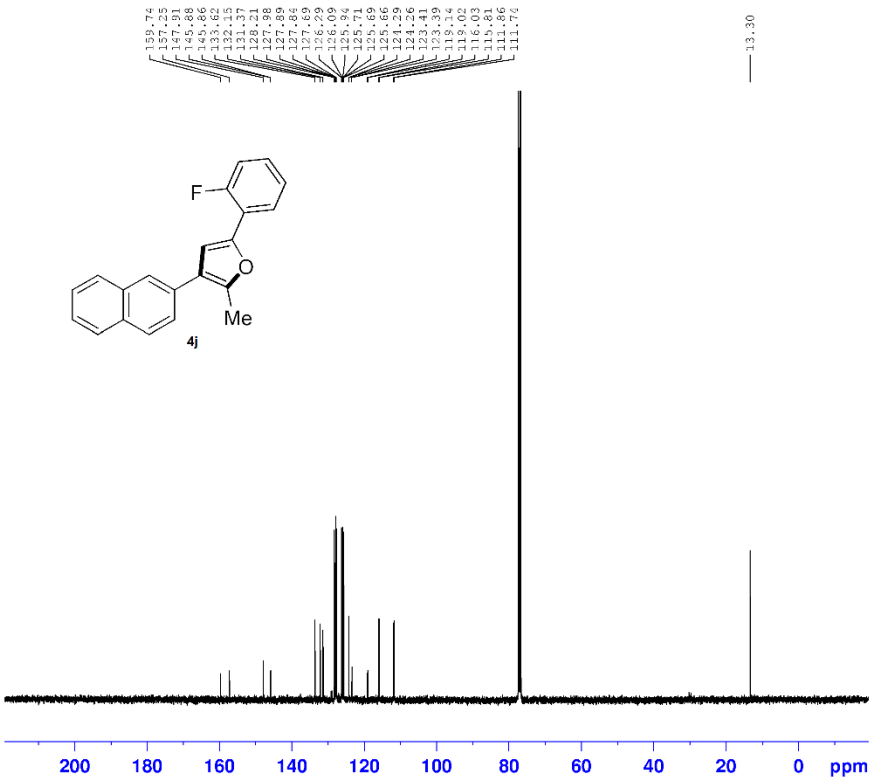
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119.02
116.03
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O
Me
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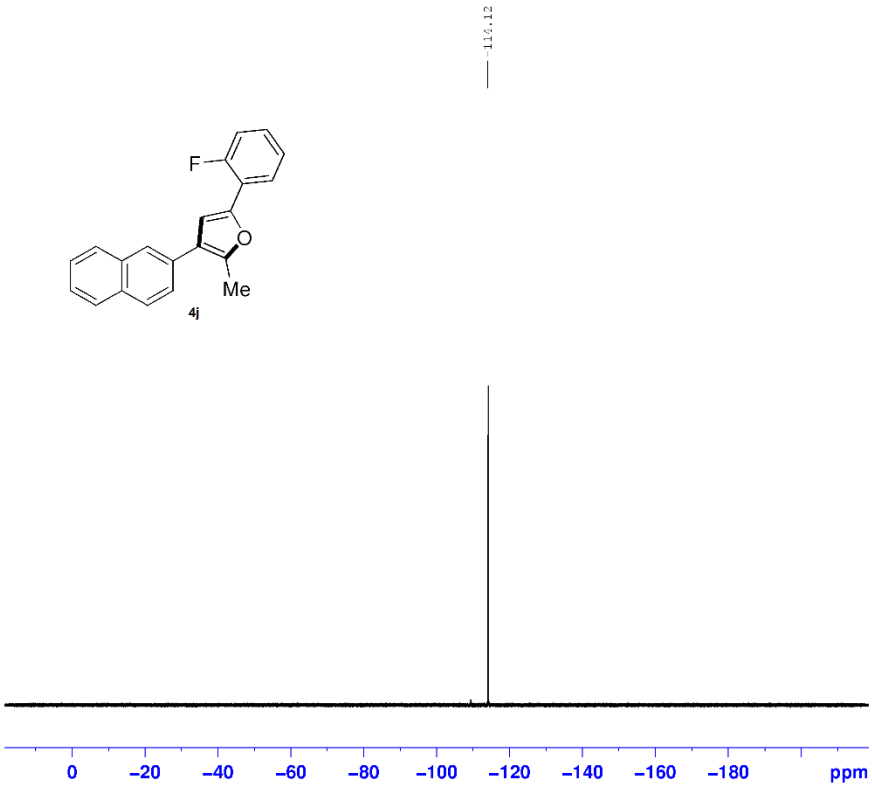
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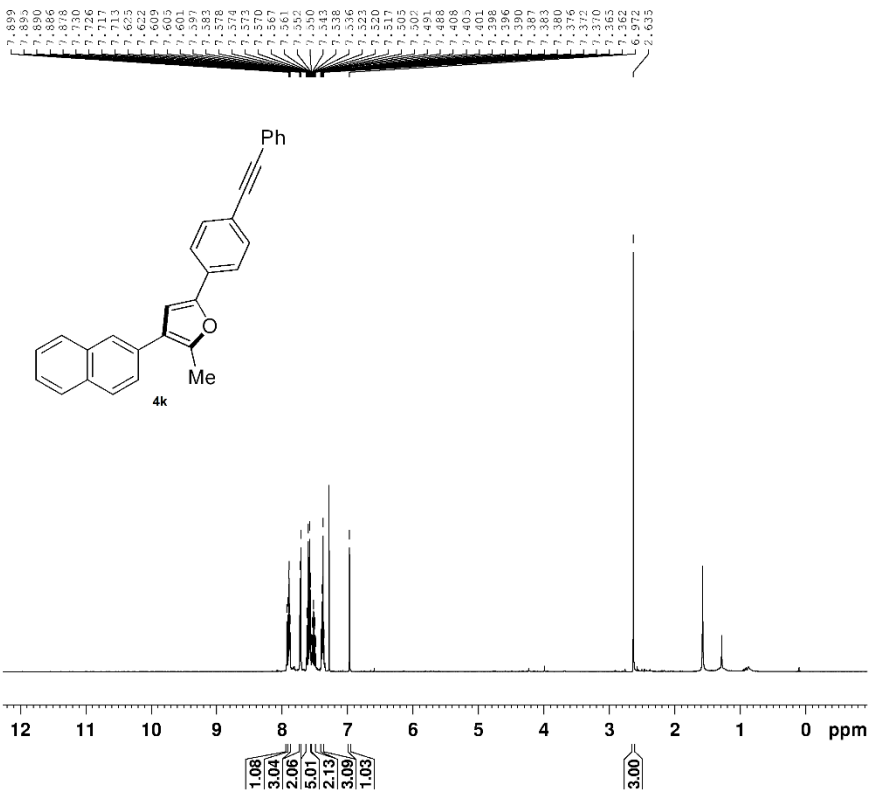
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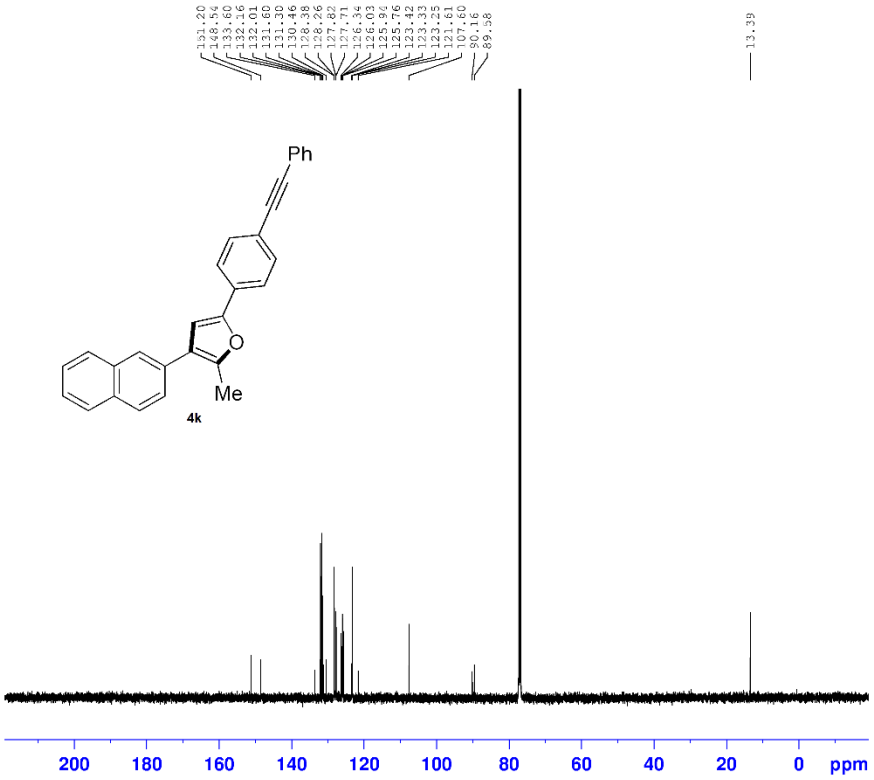
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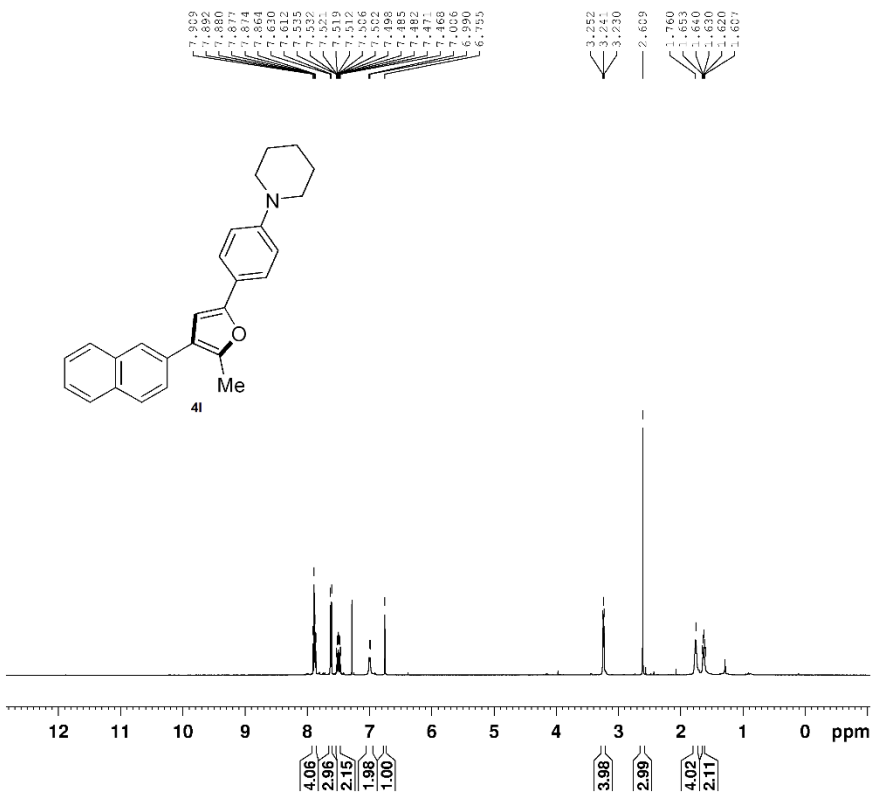
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7.502
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7.406
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3.241
3.230
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1.653
1.640
1.630
1.620
1.607
N
O
Me
4l
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11
10
9
8
7
6
5
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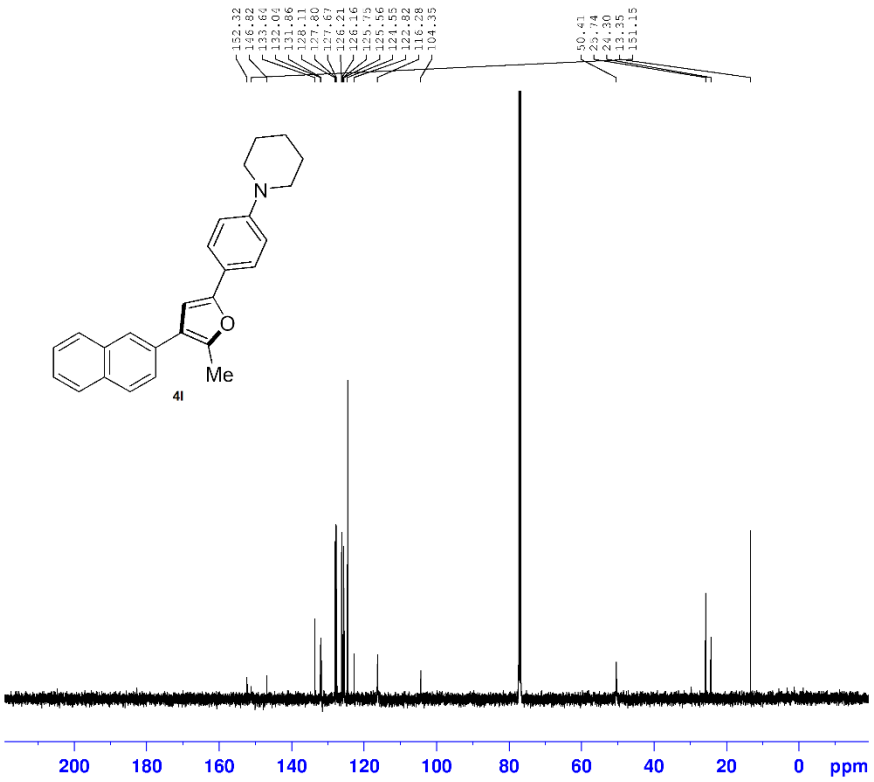
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22.70
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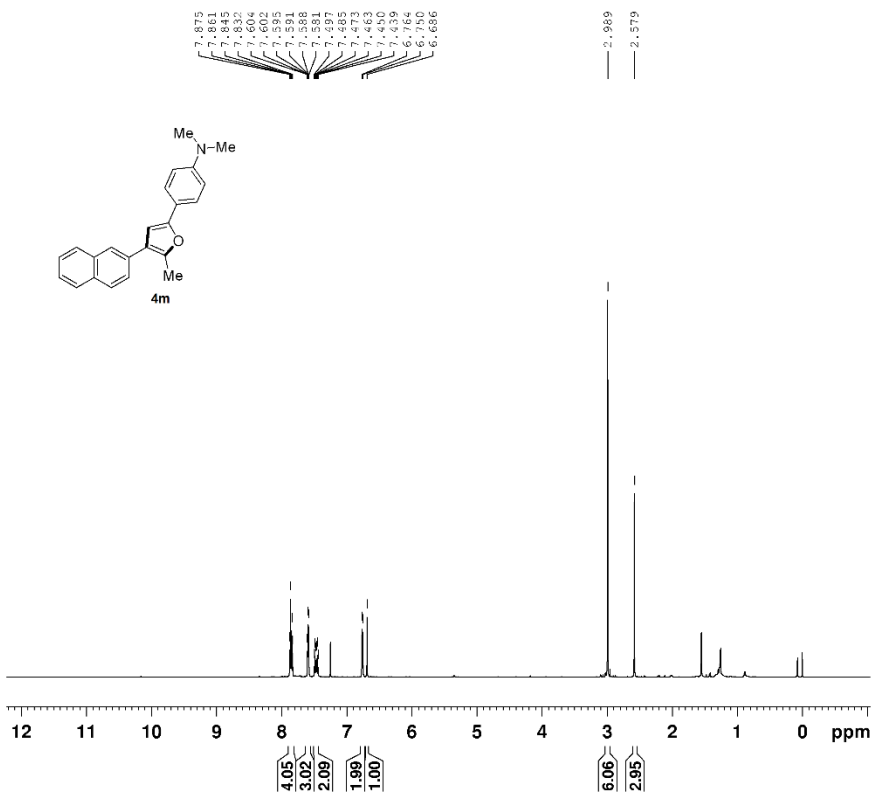
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7.450
7.439
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6.686
2.989
2.579
Me
N–Me
O
Me
4m
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11
10
9
8
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1.00
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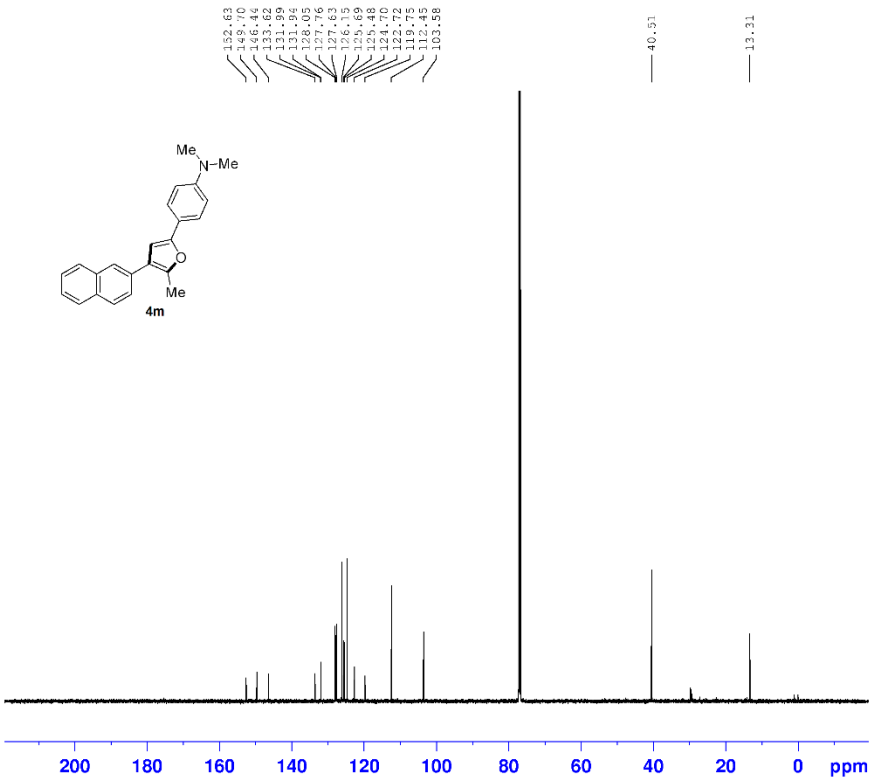
2.95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40.91
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Me
O
Me
4m
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120
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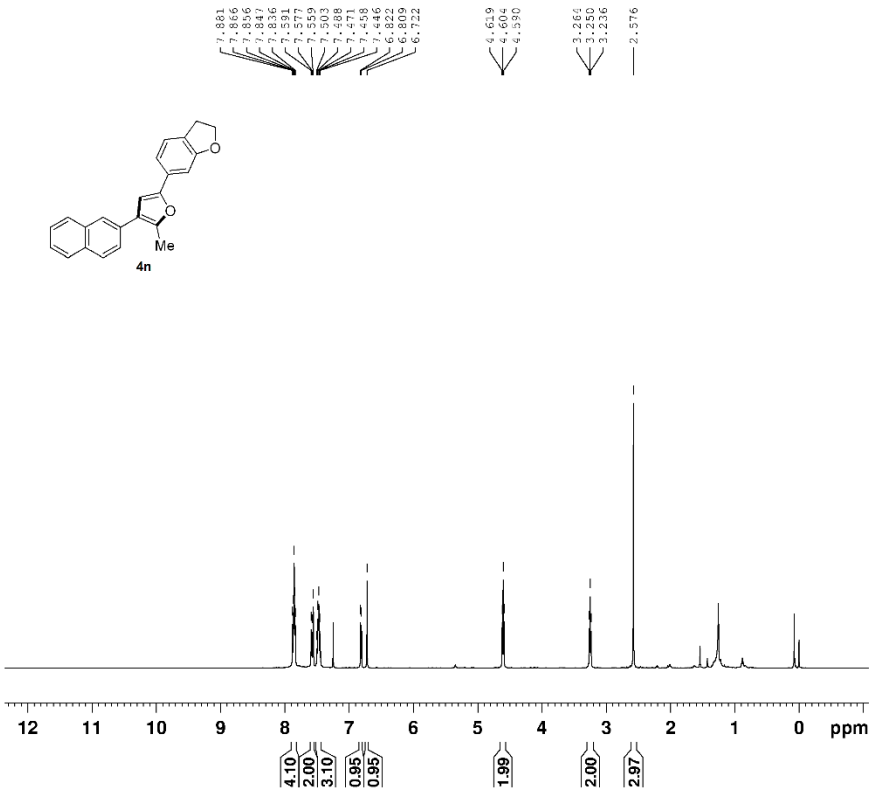
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7.426
6.822
6.809
6.722
4.619
4.604
4.590
3.261
3.250
3.236
2.576
O
O
Me
4n
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10
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8
7
6
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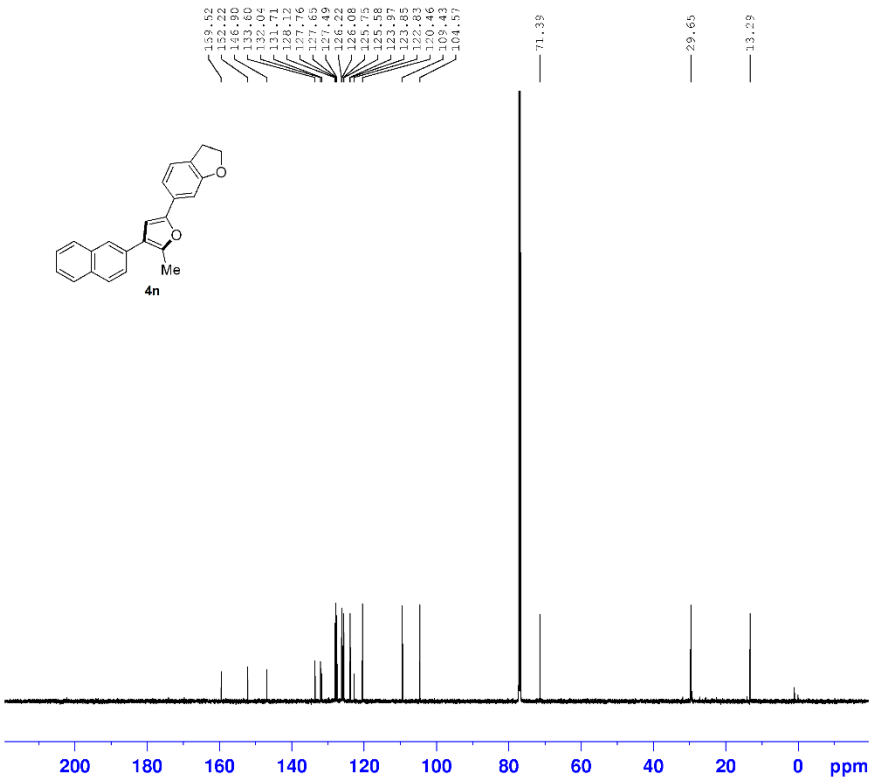
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125.58
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123.85
122.83
120.46
109.43
104.57
71.39
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O
Me
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120
100
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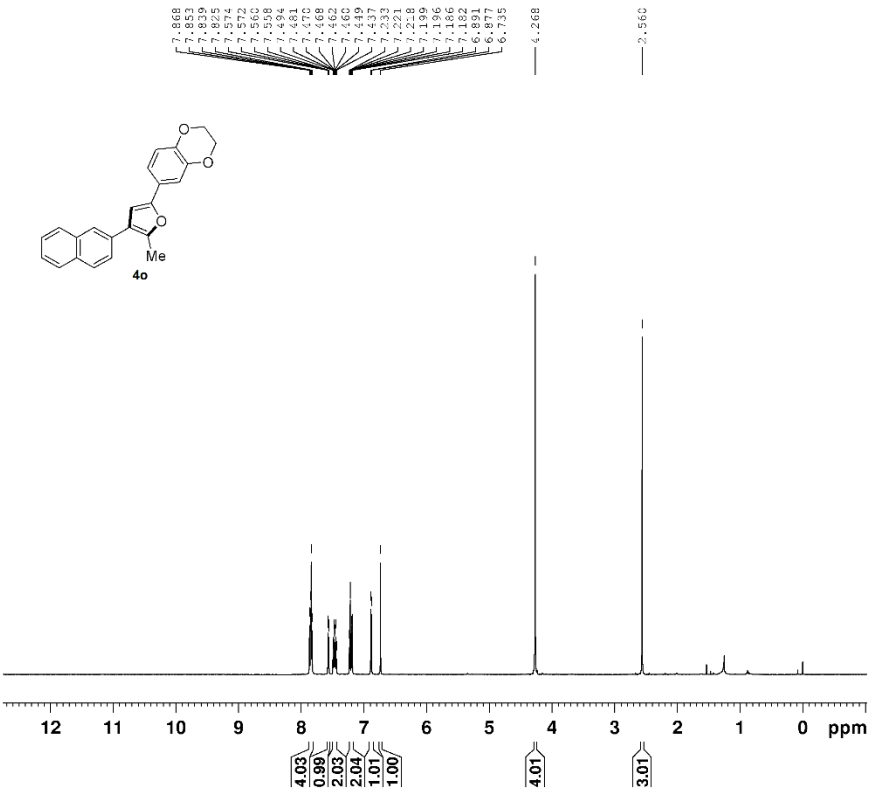
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7.462
7.460
7.449
7.437
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7.196
7.186
7.182
6.891
6.891
6.877
6.735
4.268
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O
O
Me
4o
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9
8
7
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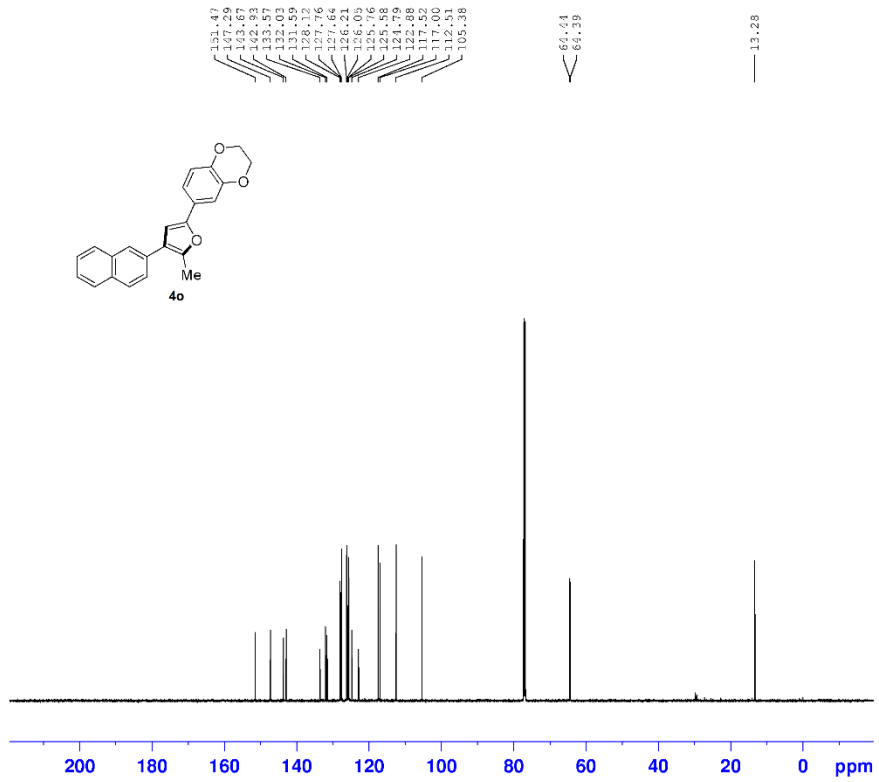
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122.88
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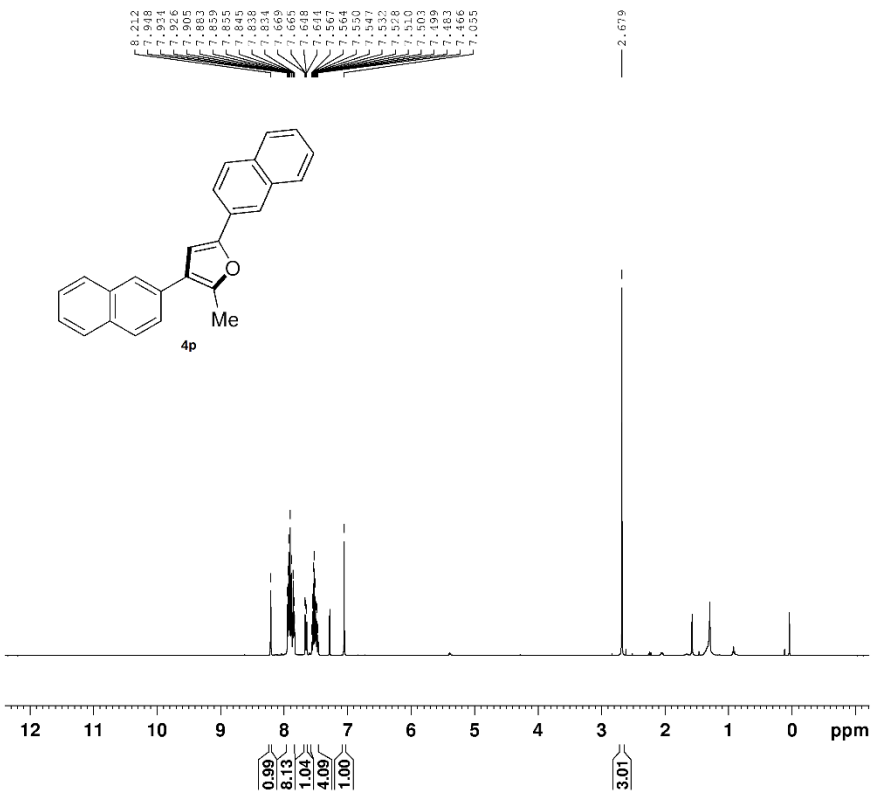
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7.648
7.641
7.567
7.564
7.550
7.547
7.532
7.528
7.510
7.503
7.499
7.483
7.466
7.055
2.679
O
Me
4p
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11
10
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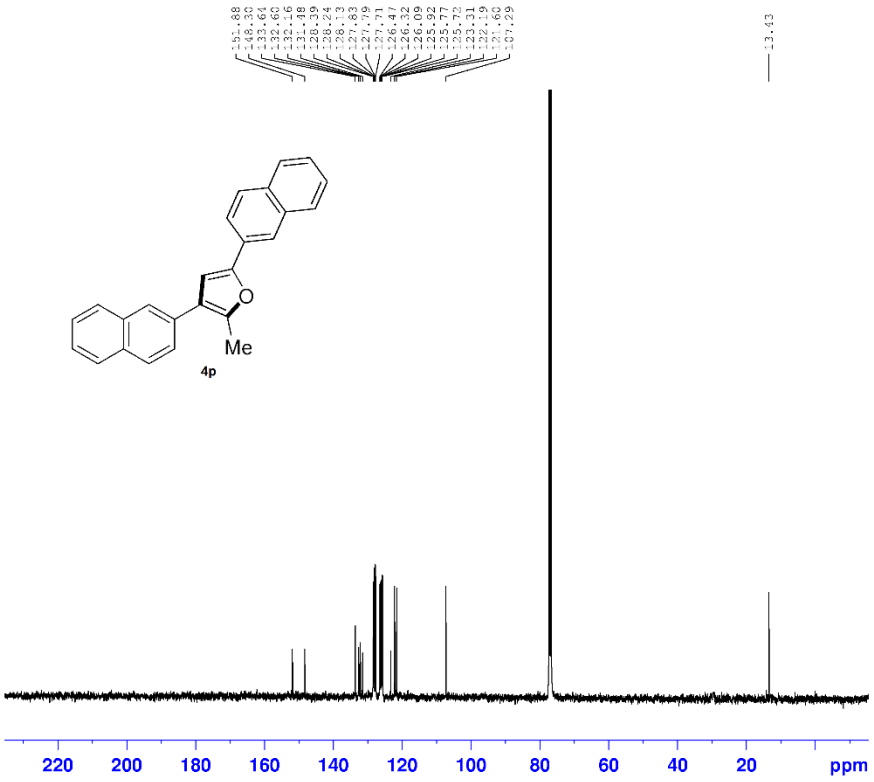
3.01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125.77
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122.19
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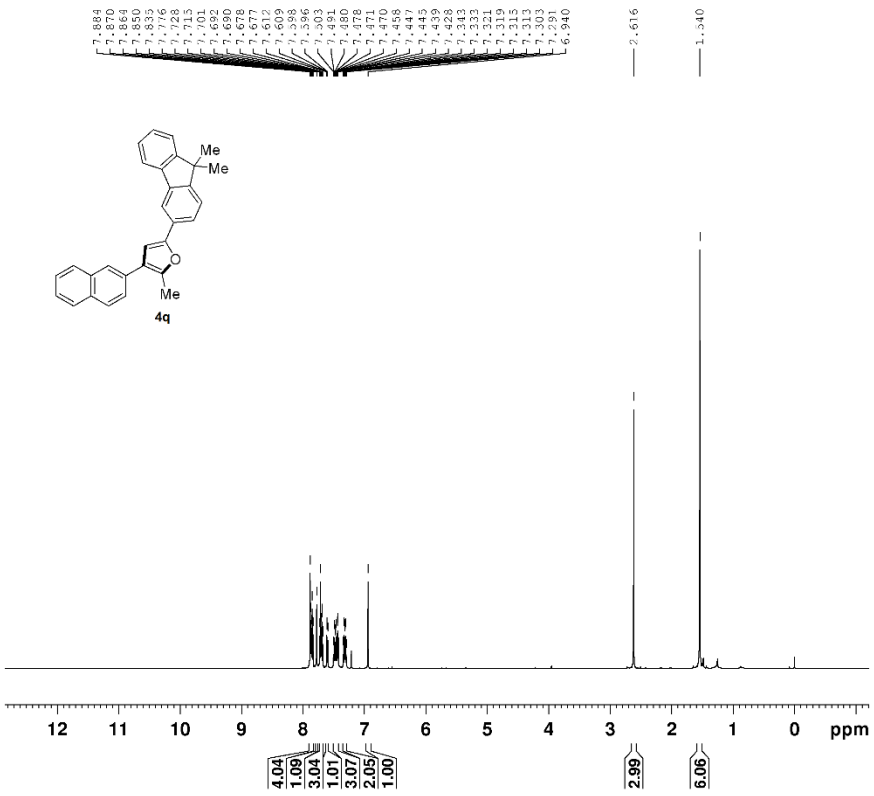
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Me
Me
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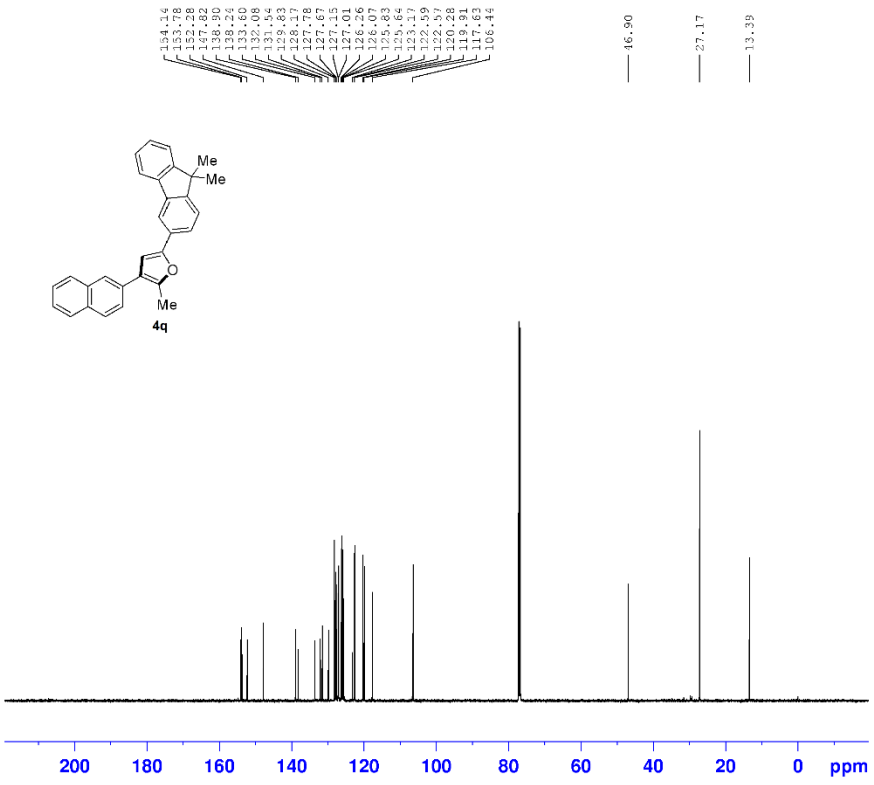
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122.57
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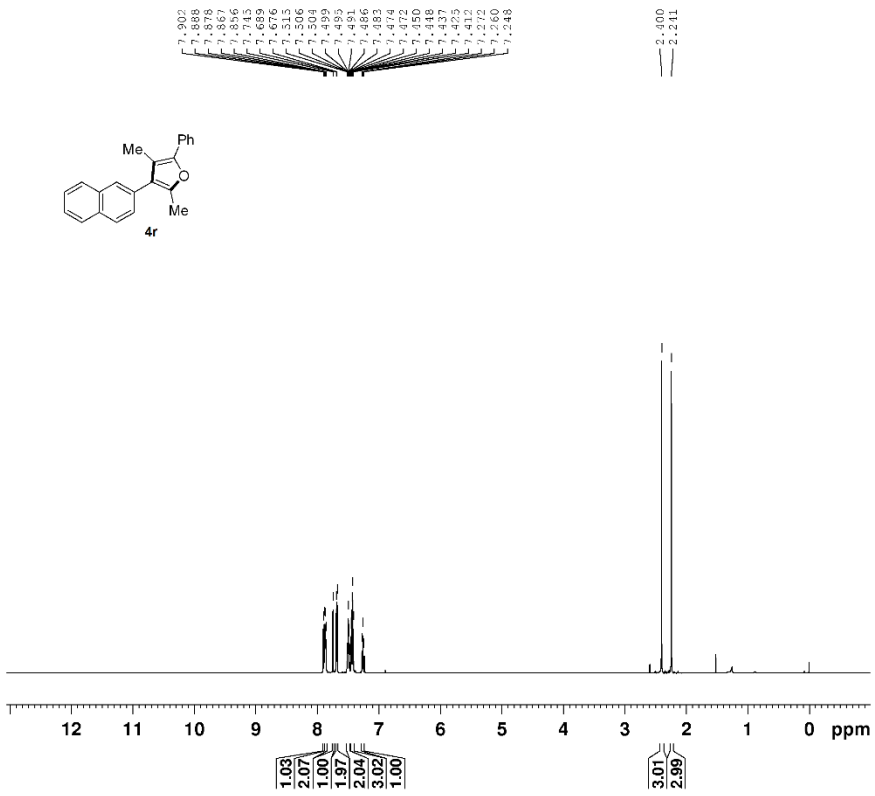
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7.483
7.474
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7.272
7.260
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Me
Ph
O
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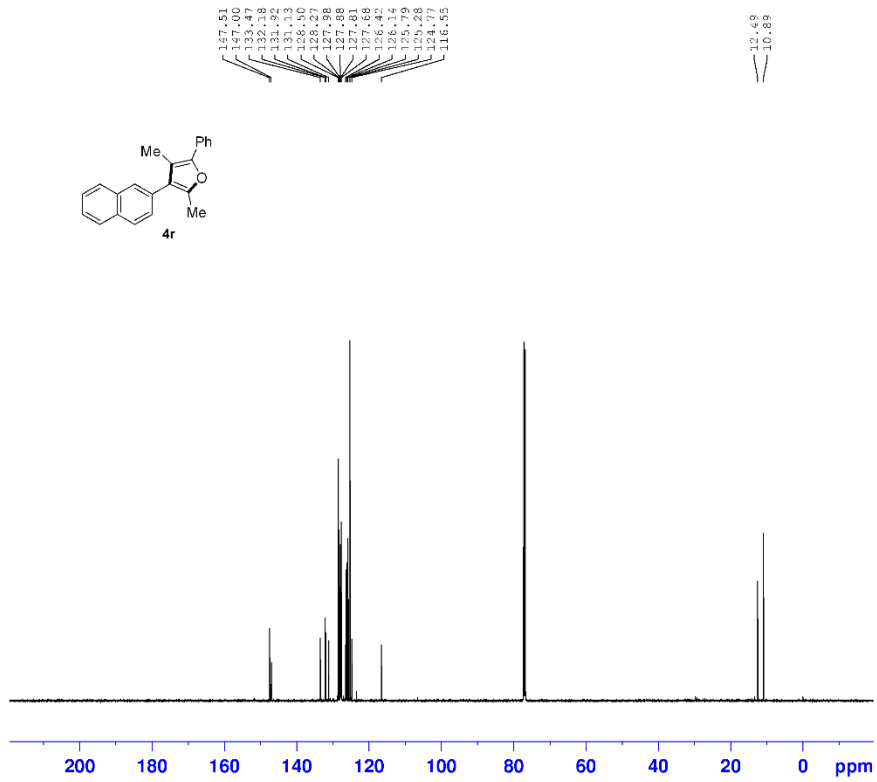
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116.55
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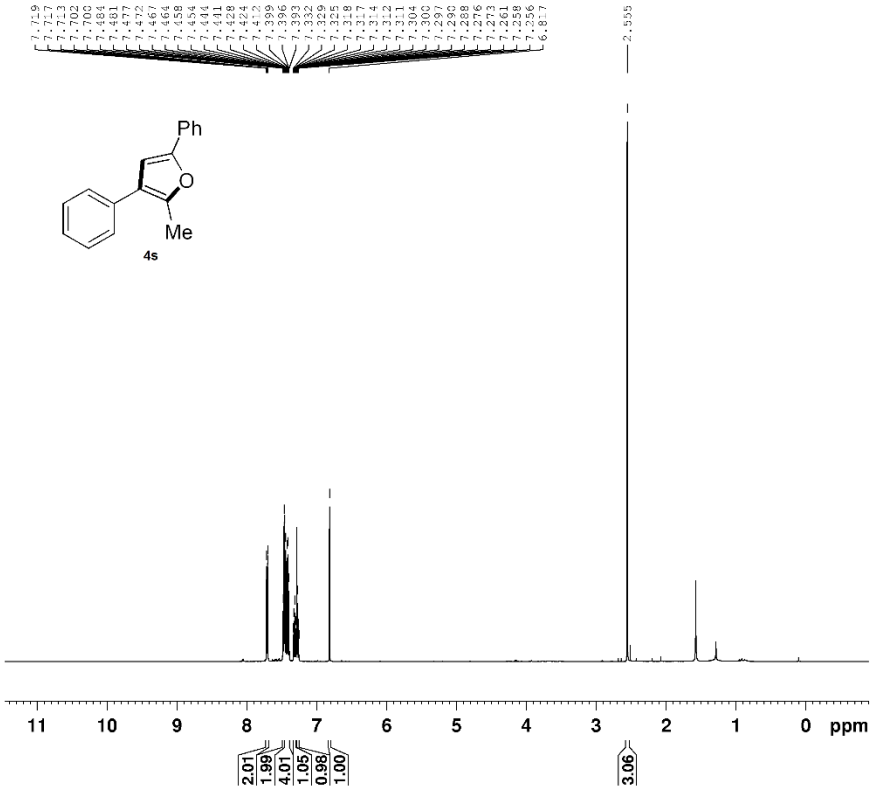
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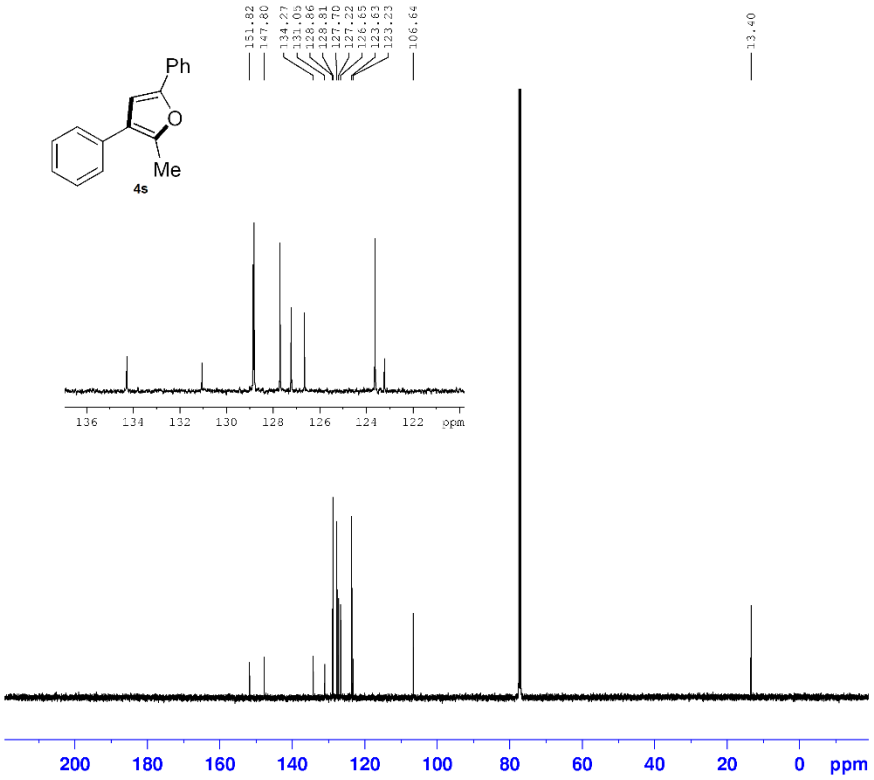
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O
Me
4s
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126
124
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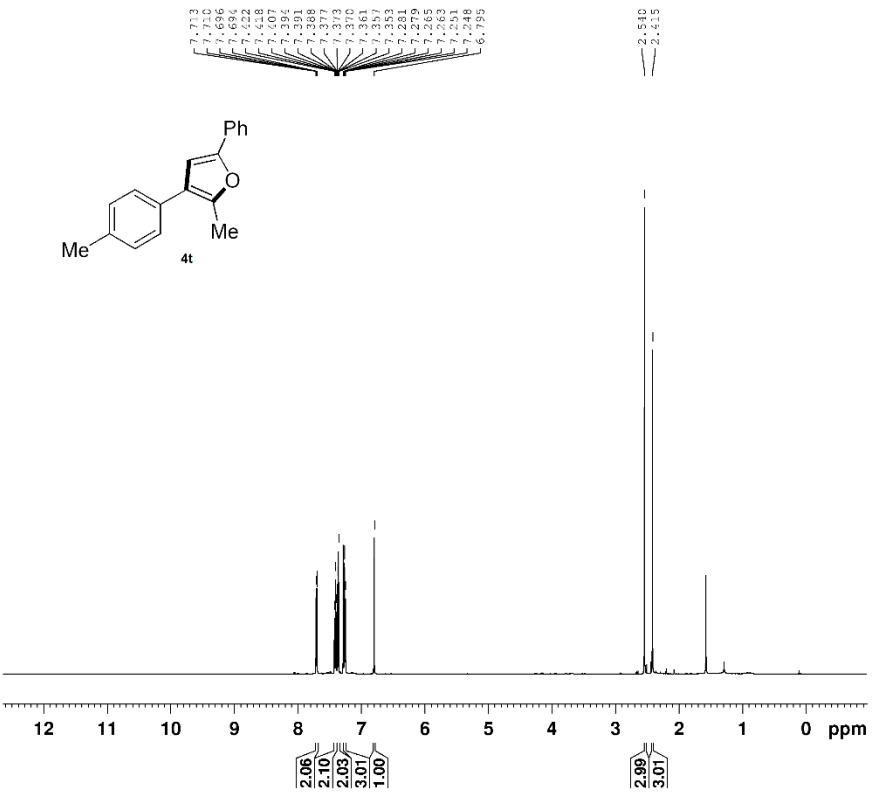
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7.353
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7.263
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Me
Me
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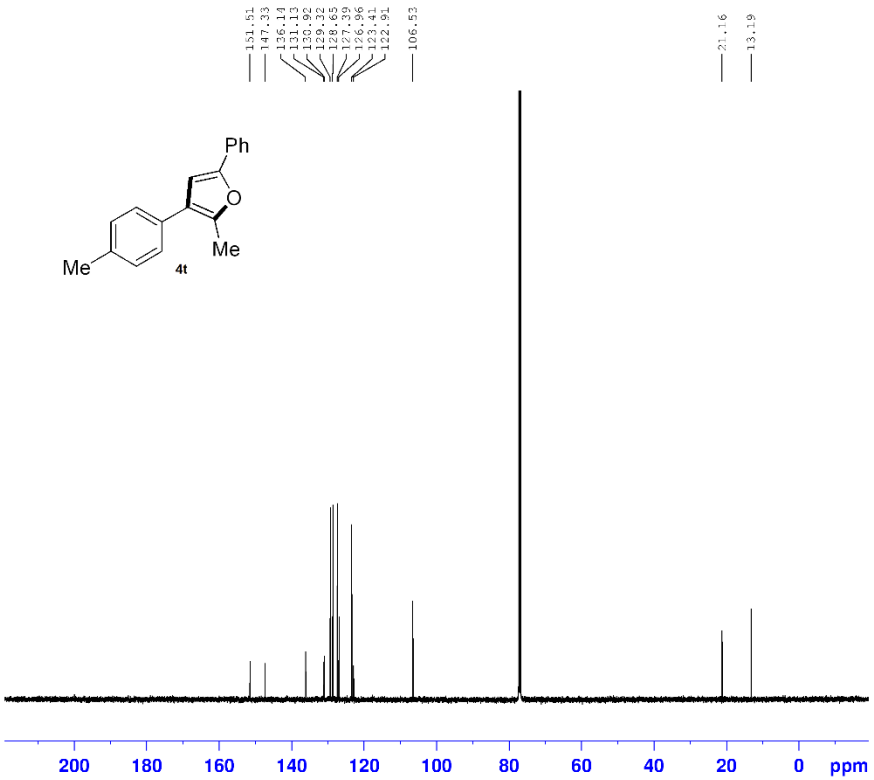
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Me
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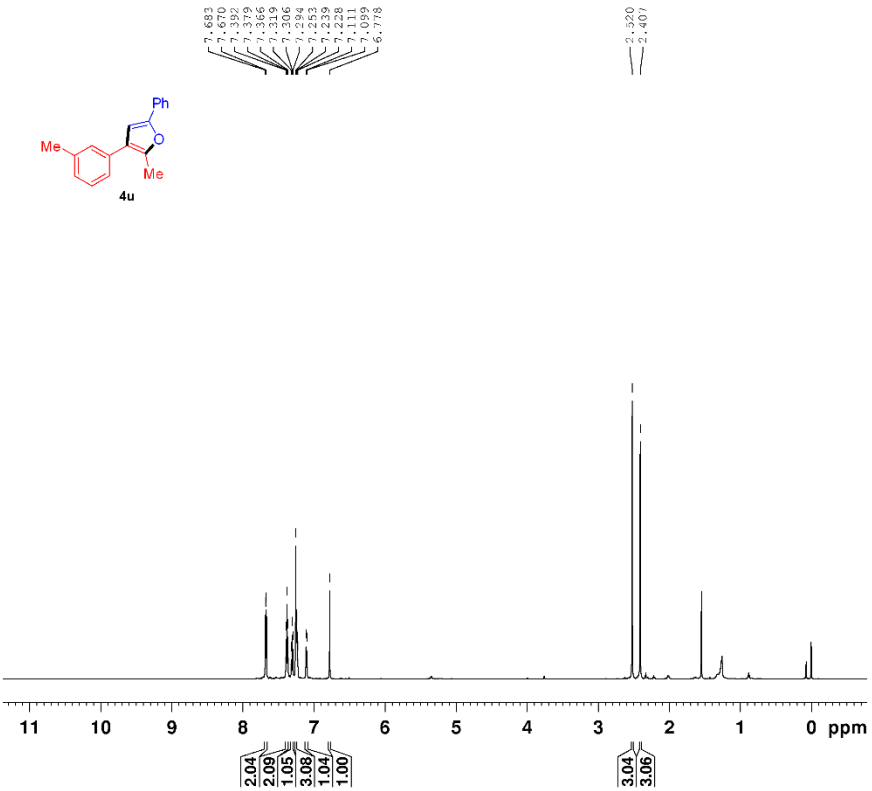
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2.407
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O
Me
4u
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10
9
8
7
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3.08
1.04
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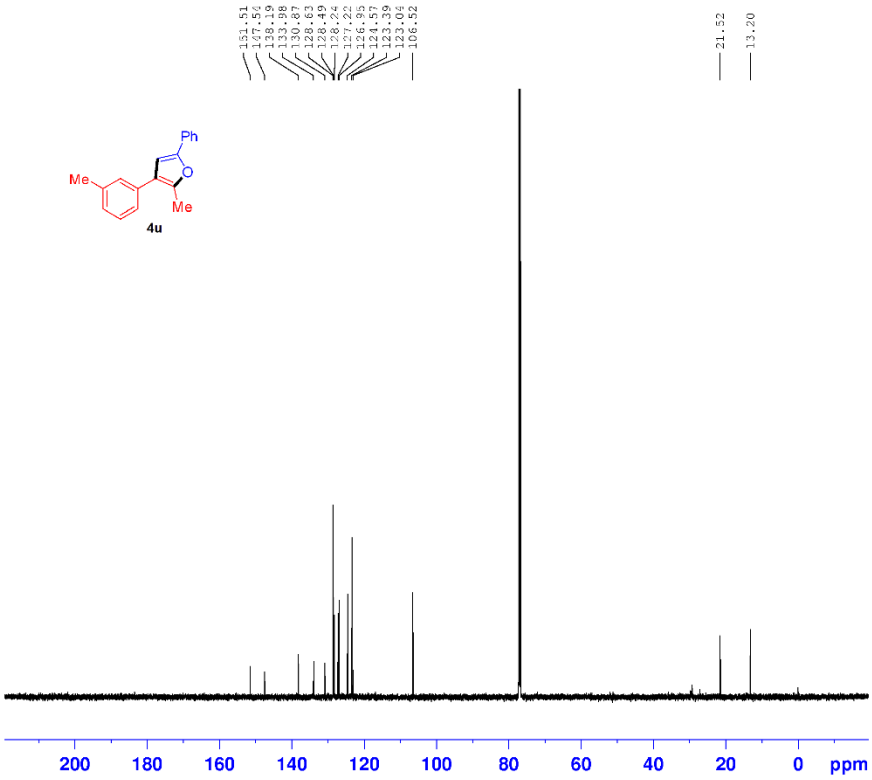
3.06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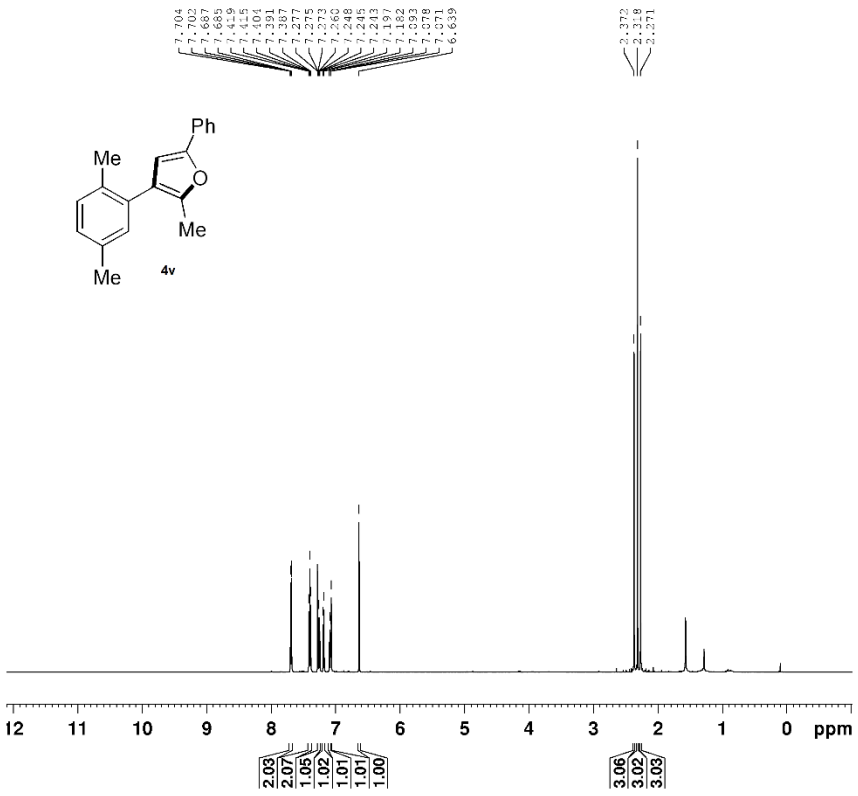
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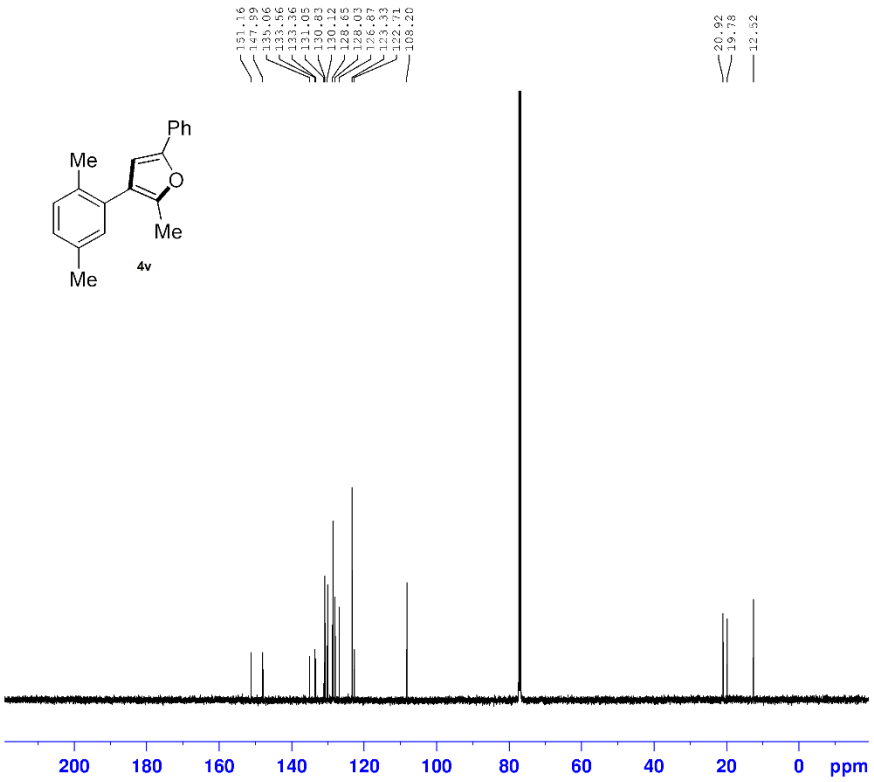
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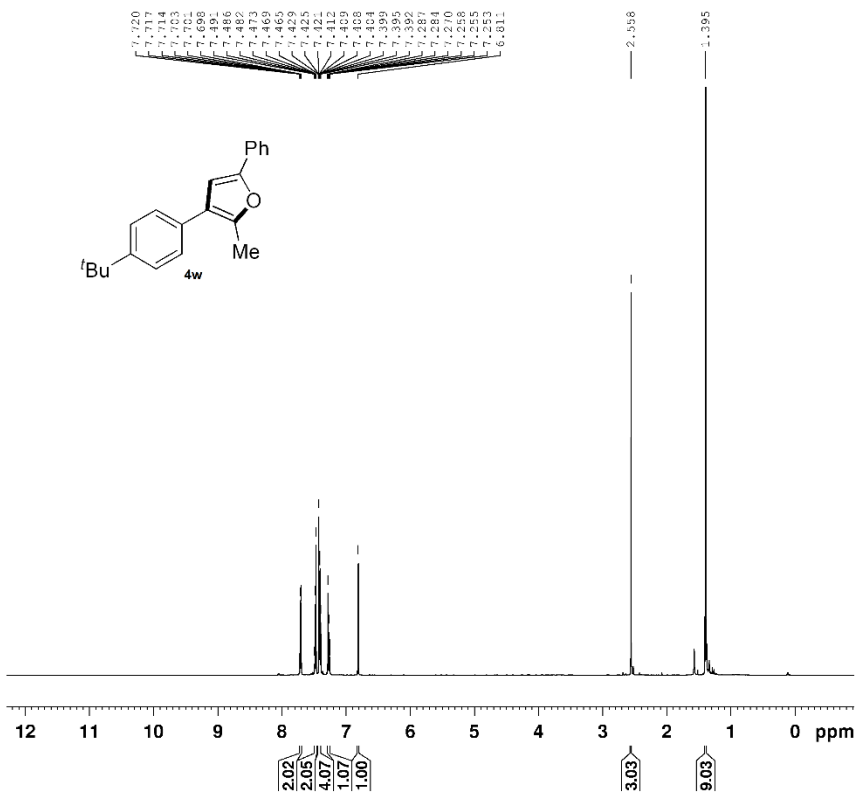
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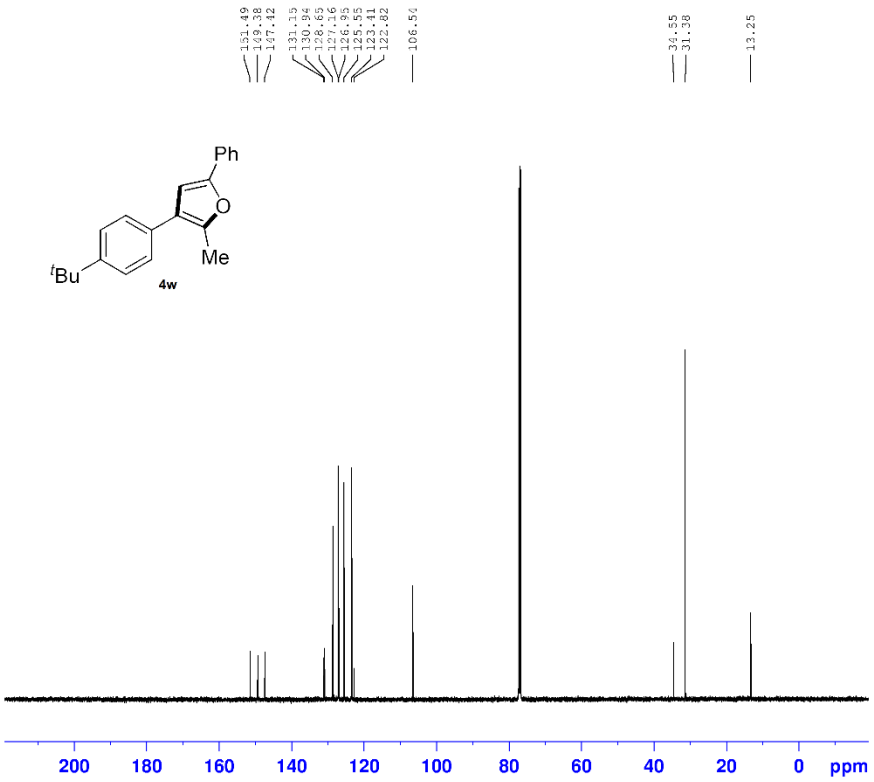
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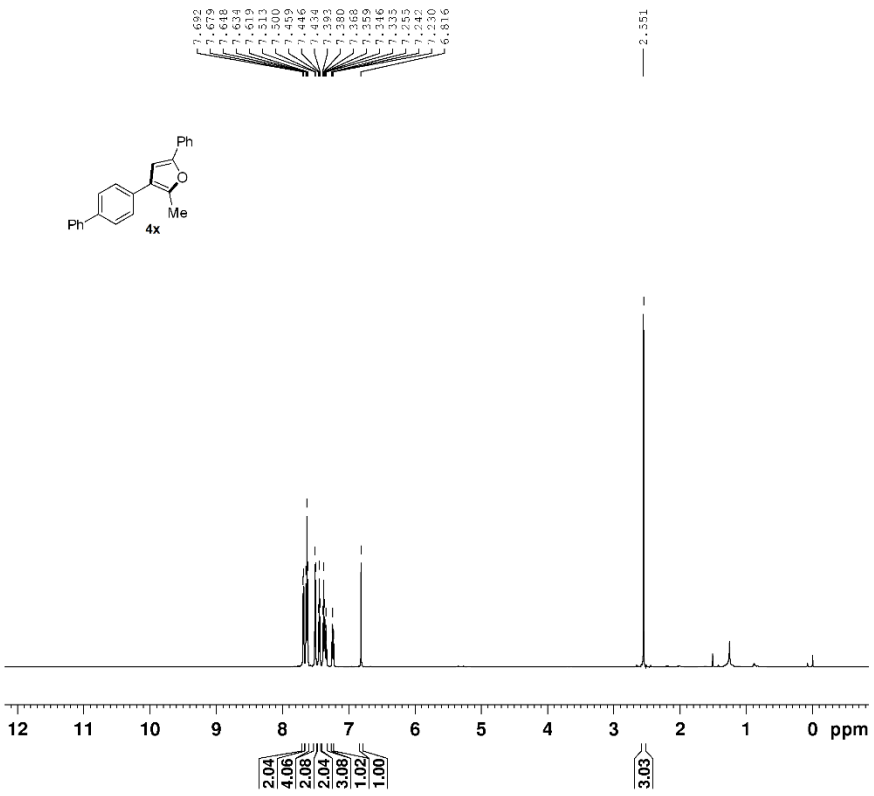
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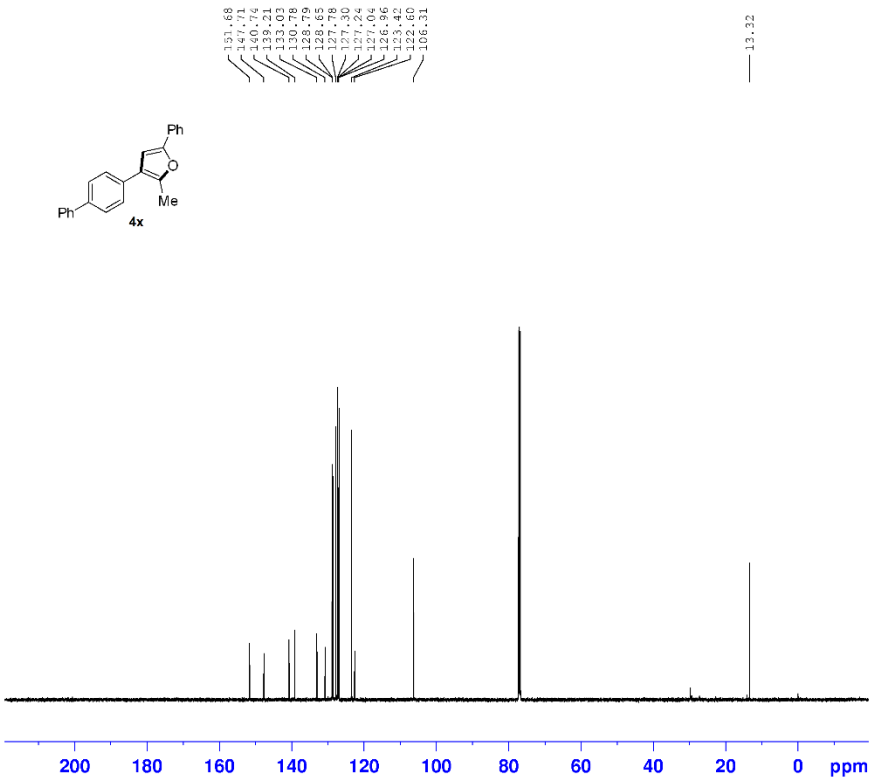
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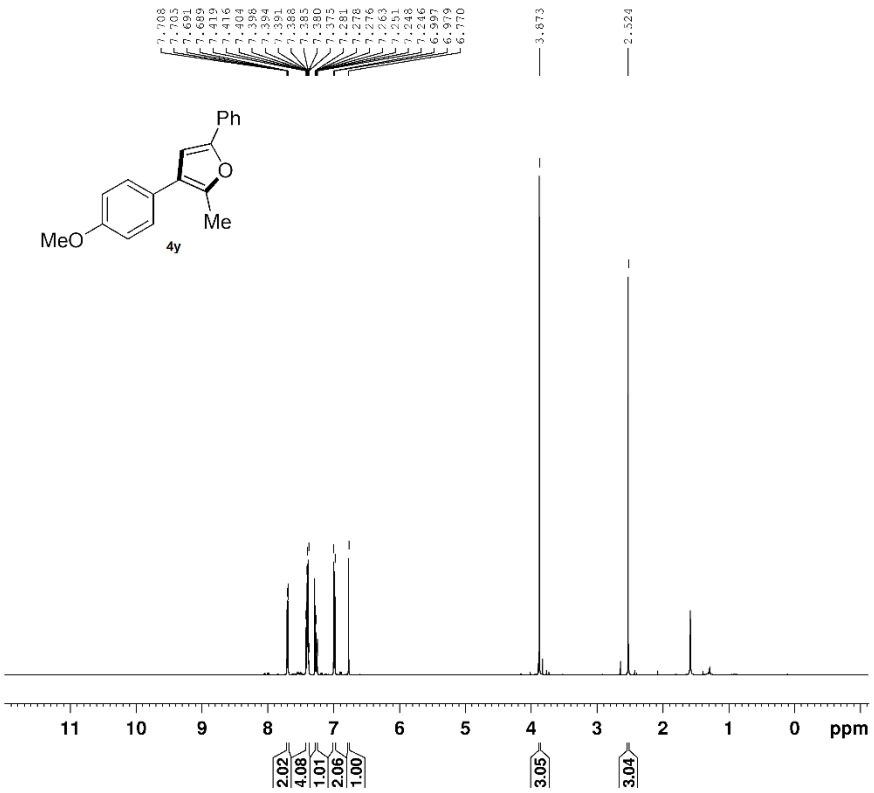
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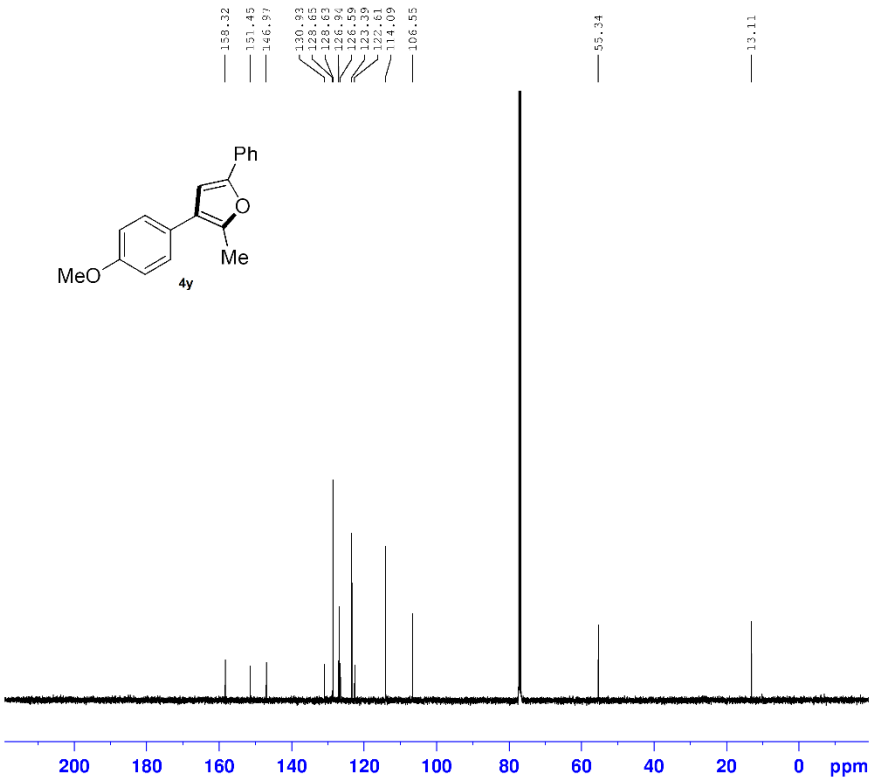
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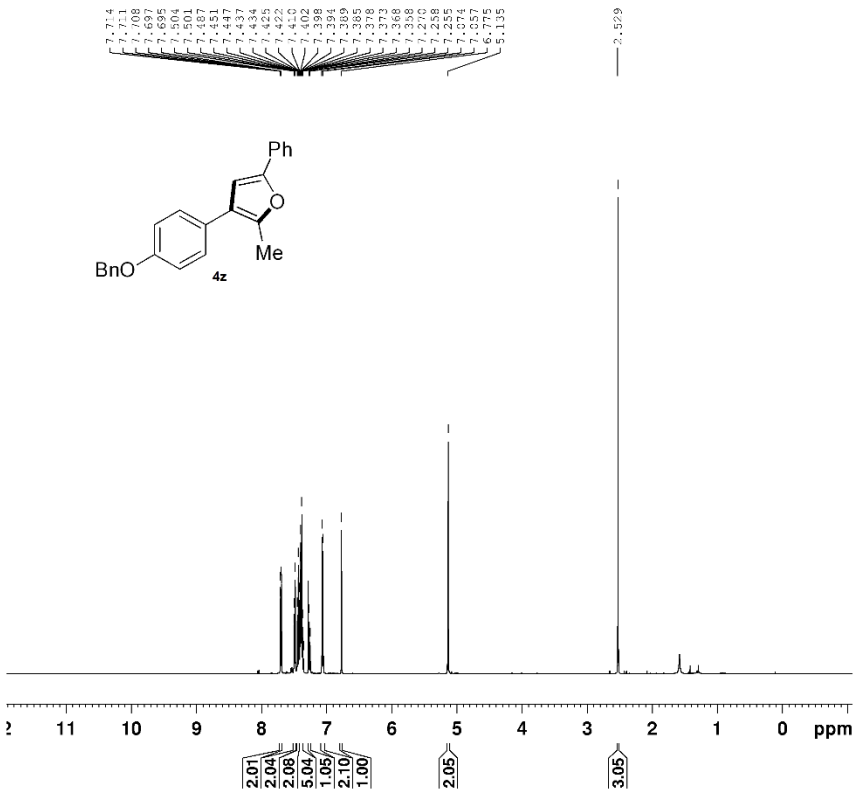
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Me
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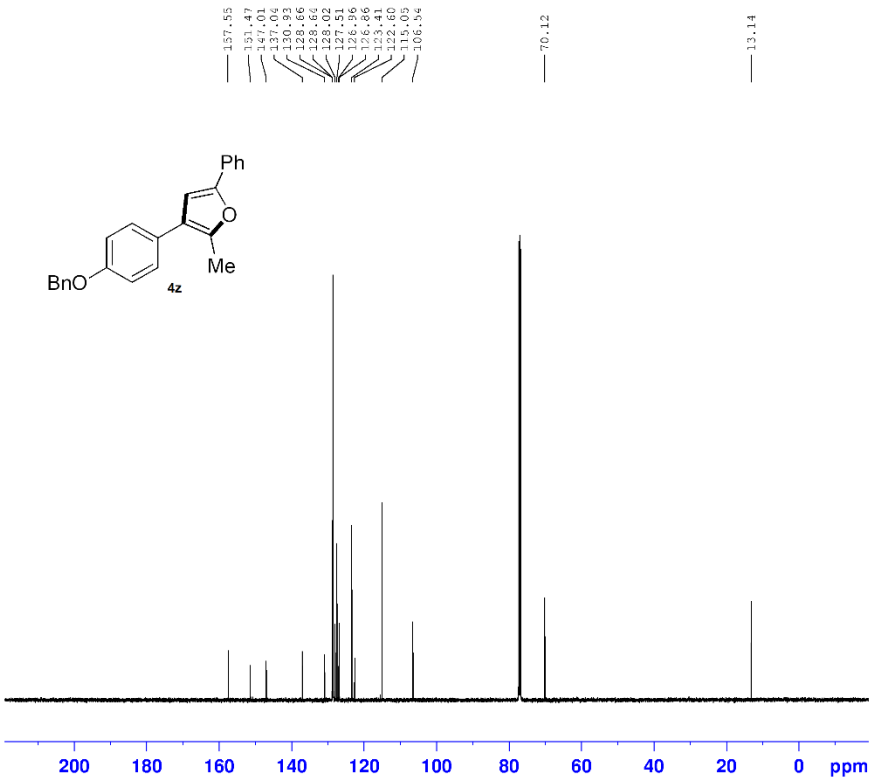
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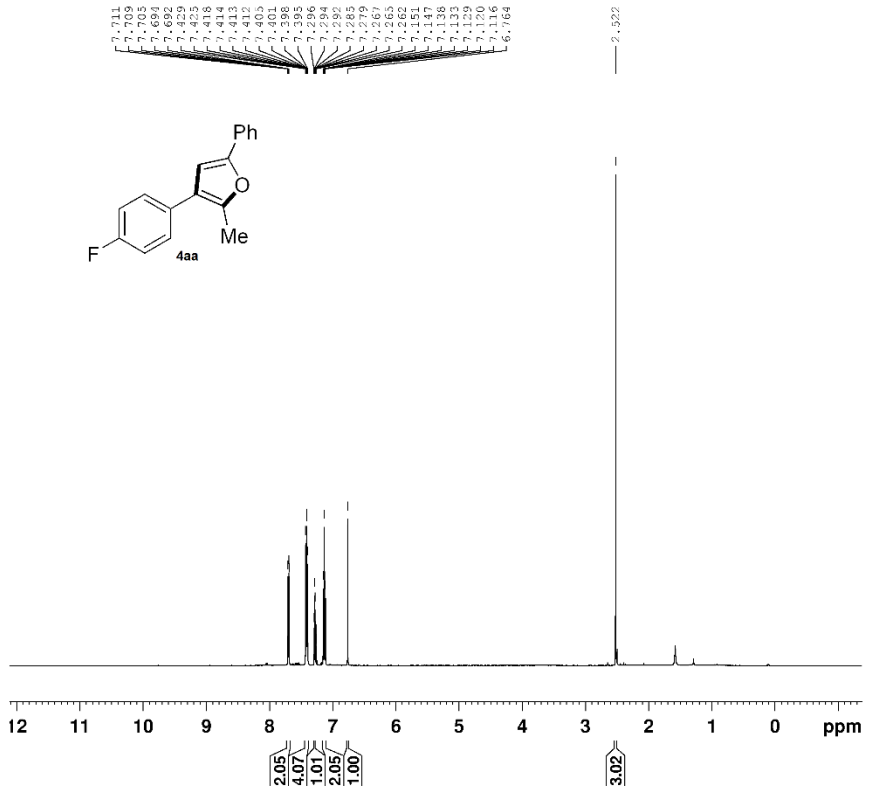
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Me
F
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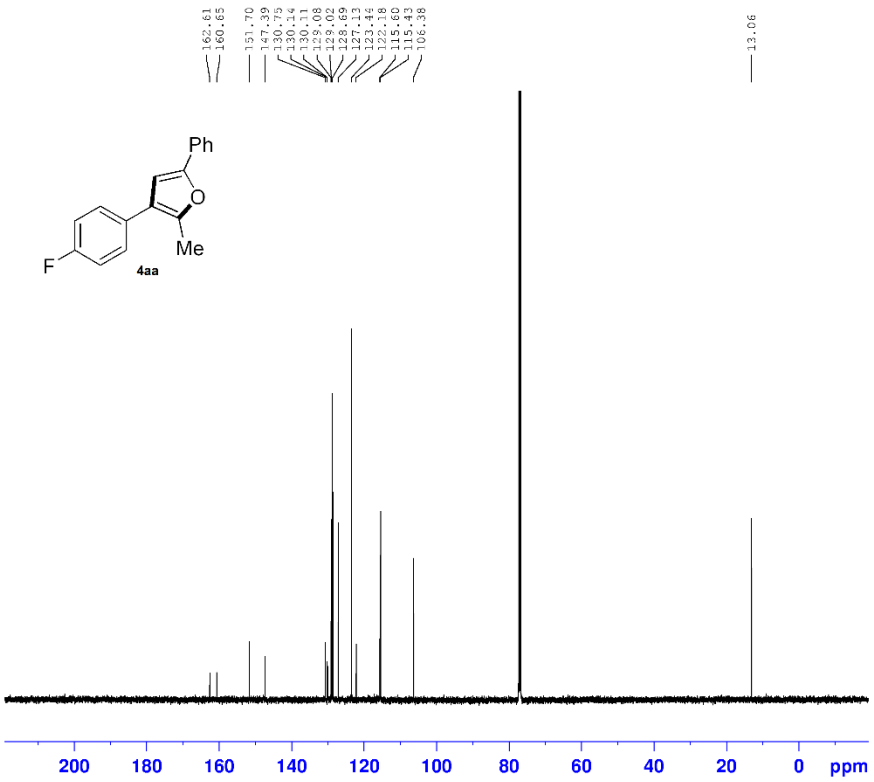
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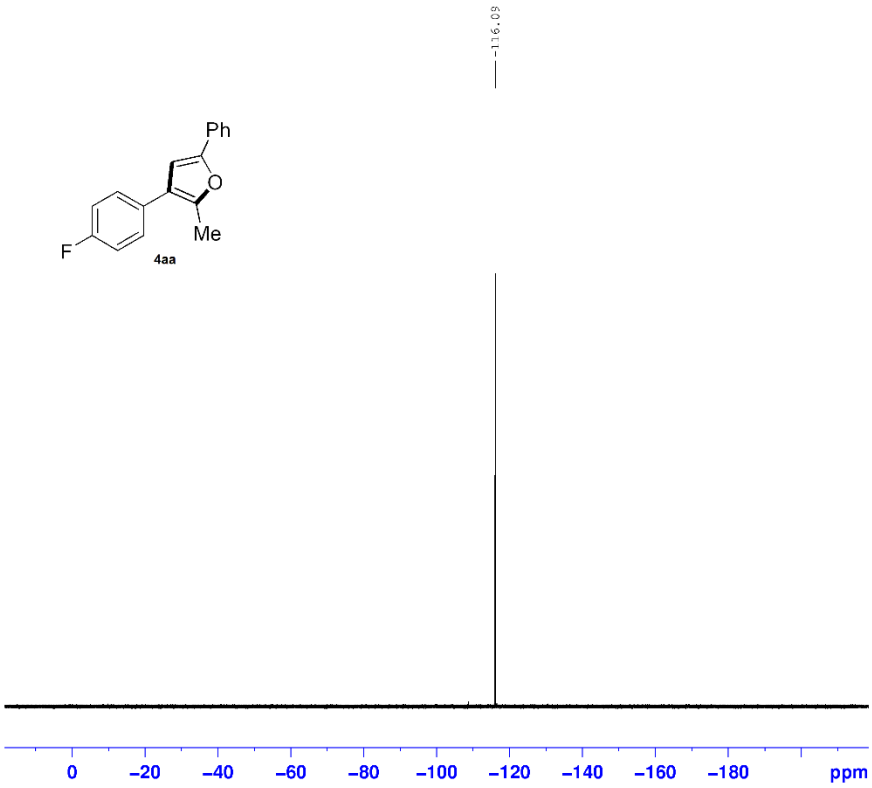
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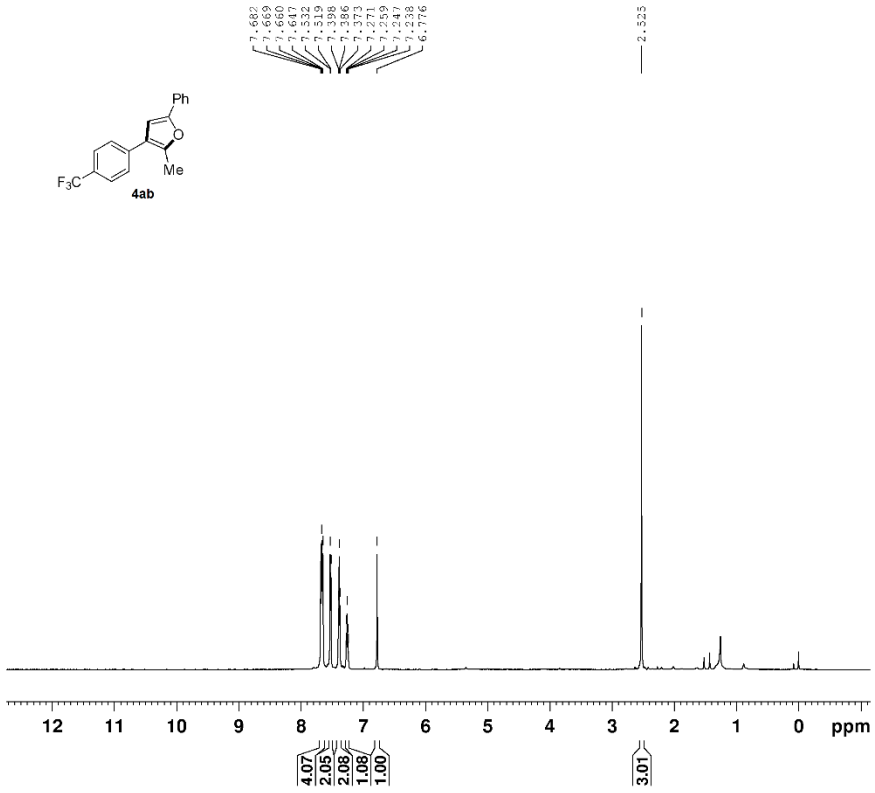
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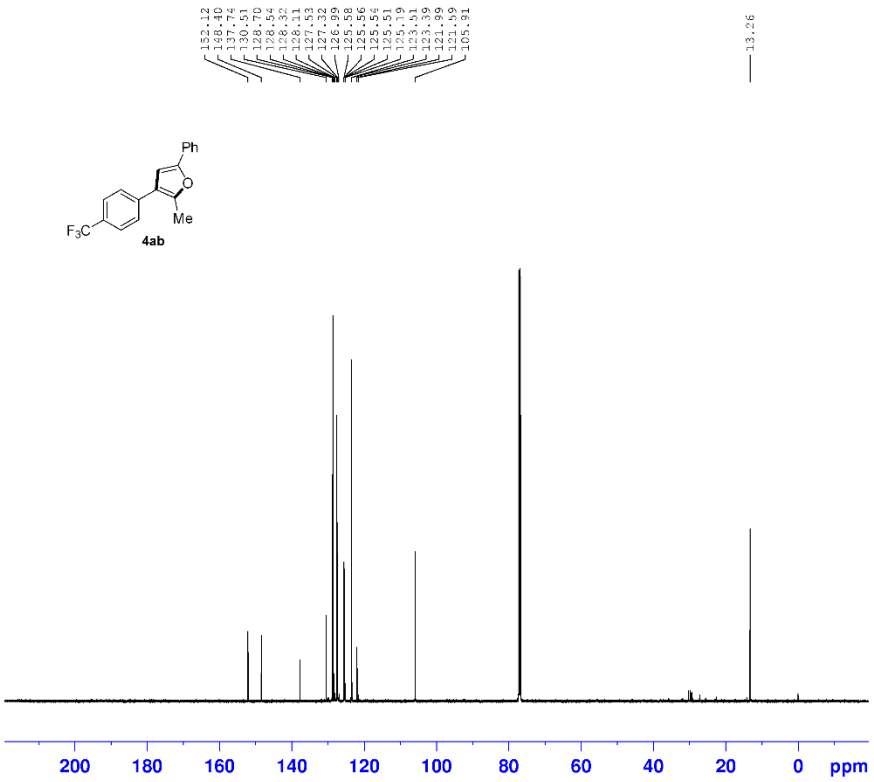
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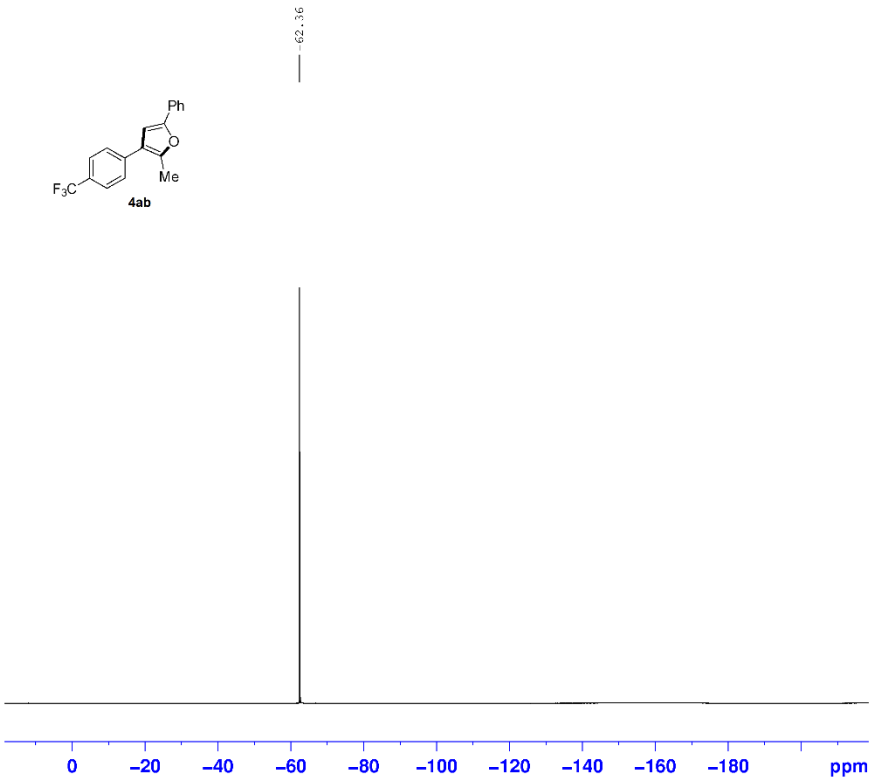
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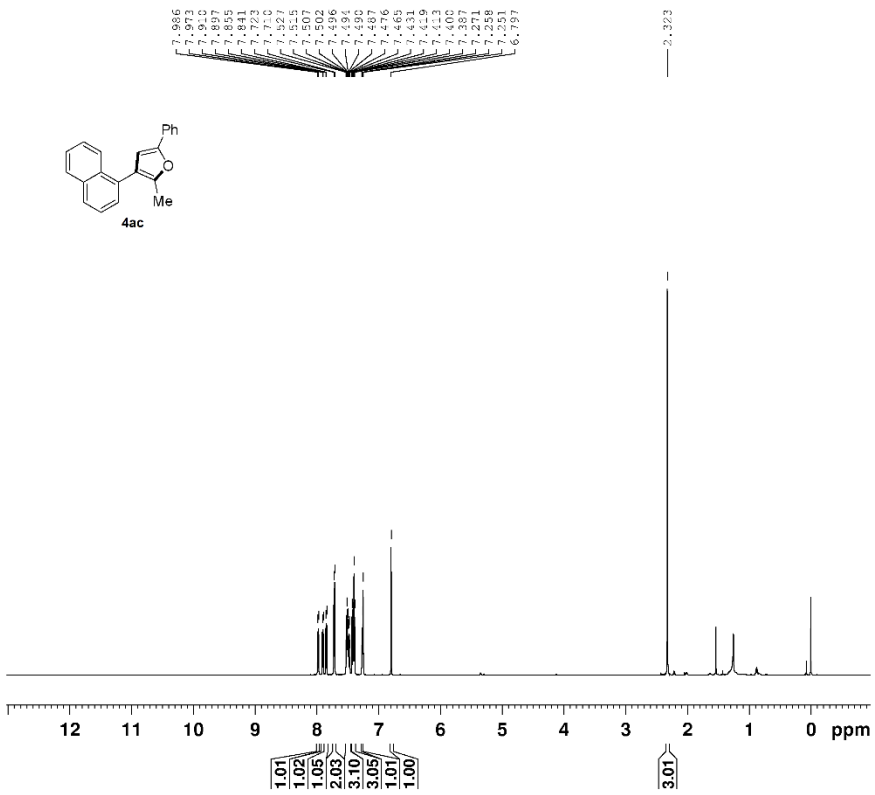
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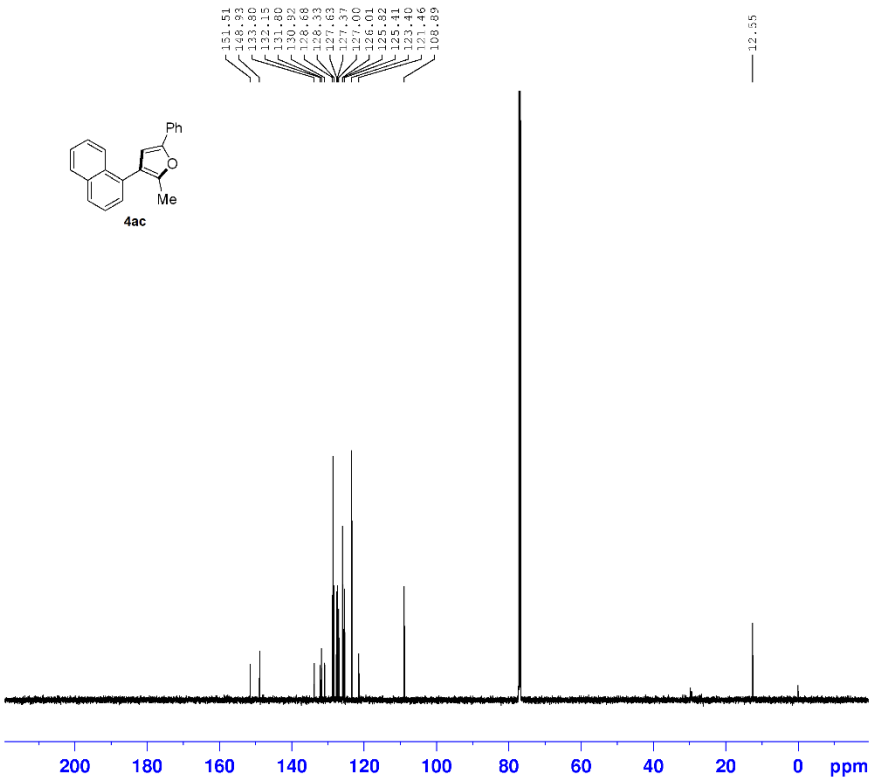
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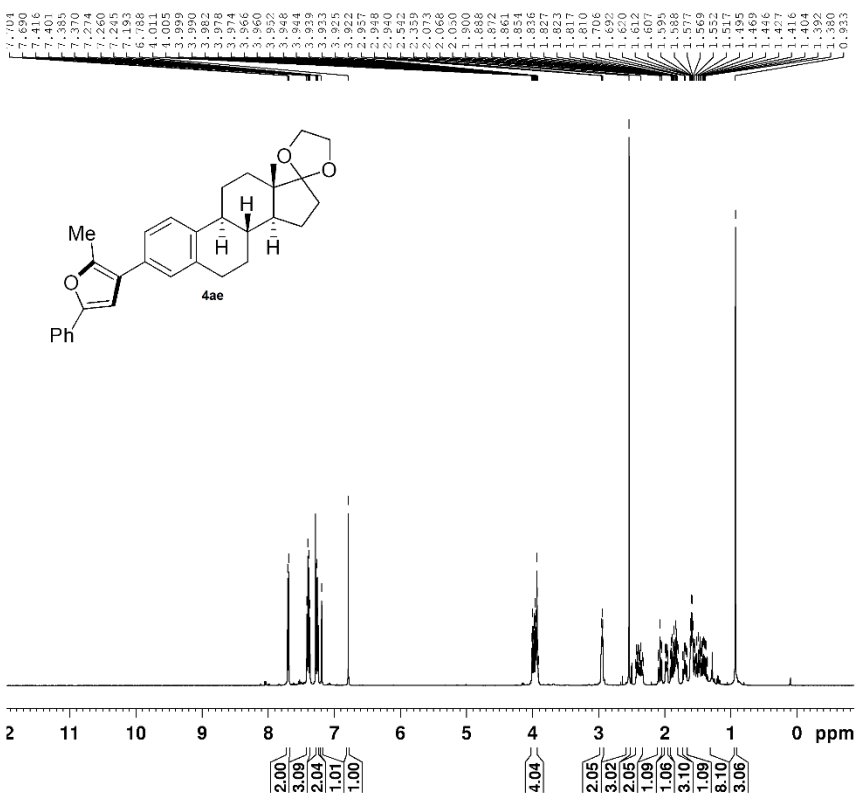
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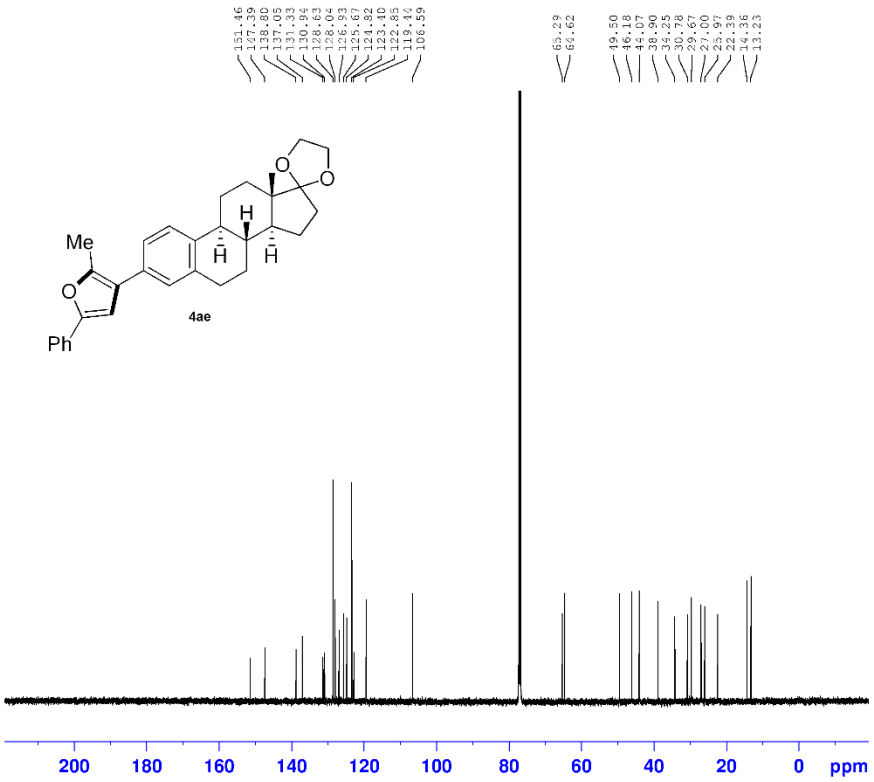
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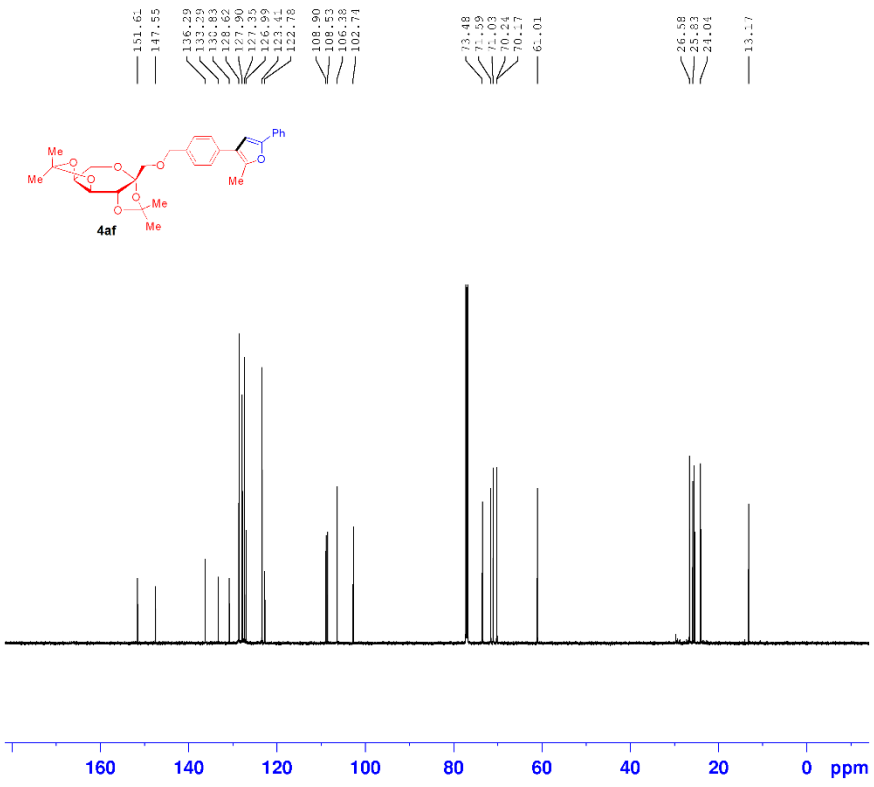
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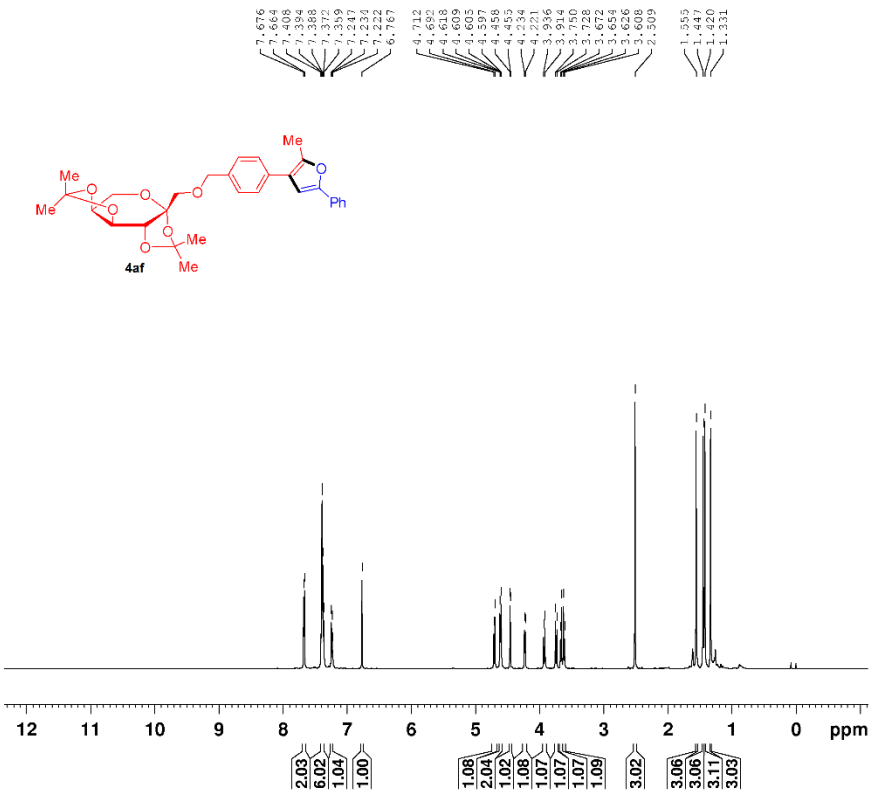
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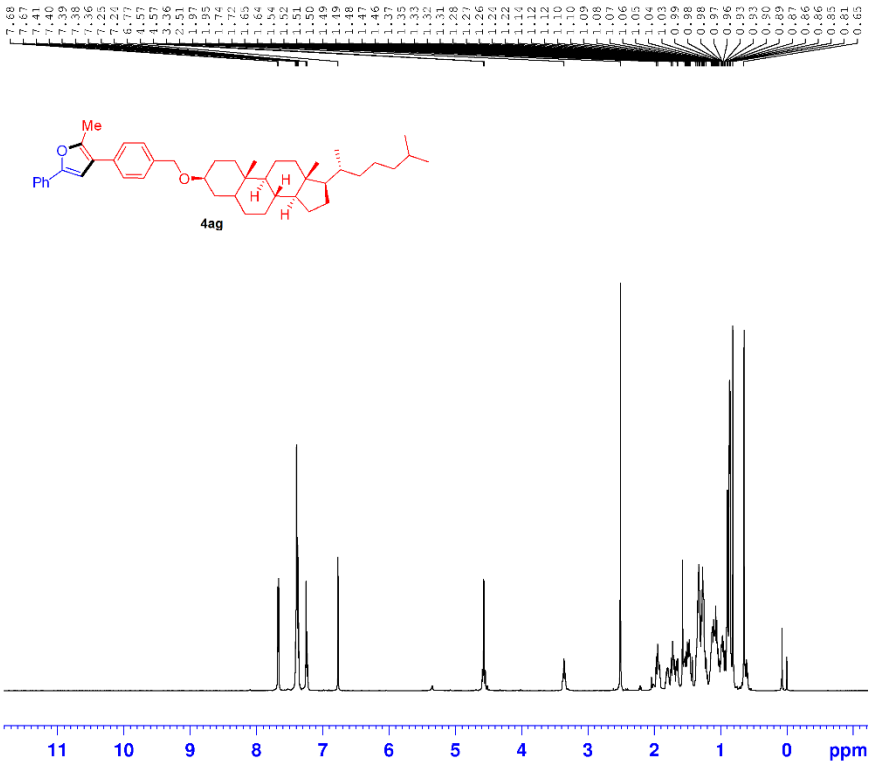
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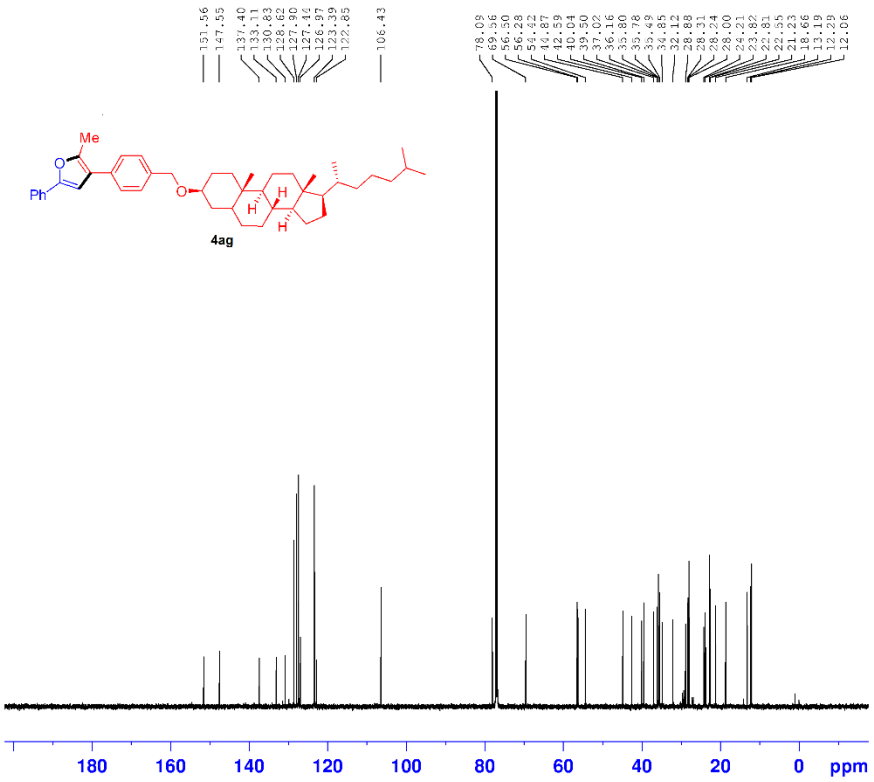
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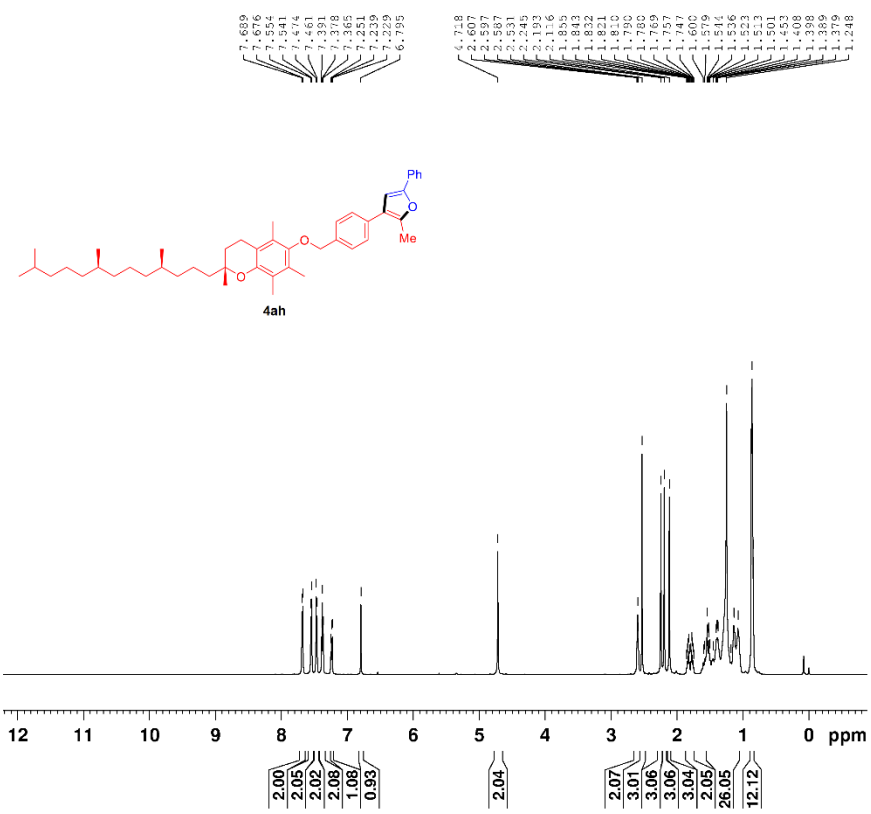
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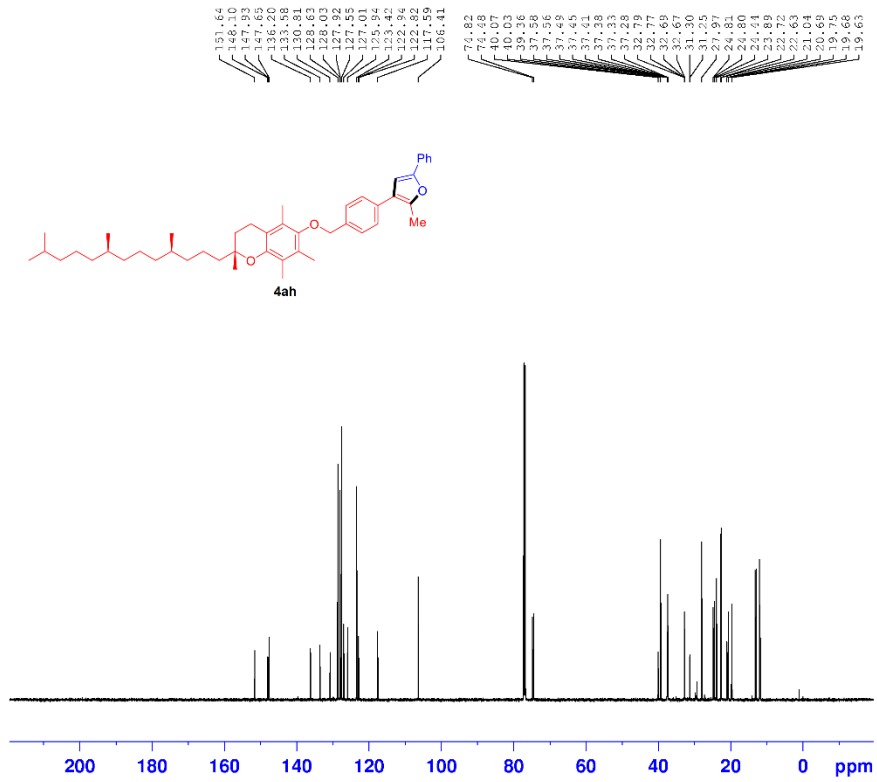
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122.82
117.59
106.41
74.82
74.48
40.07
40.03
39.36
37.58
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37.49
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32.69
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24.81
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21.84
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