Electronic Supplementary Information

Rhodium(III)-Catalyzed Regio- and Stereoselective Benzylic *α*-Fluoroalkenylation with *gem*-Difluorostyrenes

Lingheng Kong,[a,b] Bingxian Liu,[c] Xukai Zhou,[a,b] Fen Wang,*[,a] Xingwei Li*[,a]

[a] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China*

[b] *University of Chinese Academy of Sciences, Beijing 100049, China*

[c] *School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang 453007, China*

Email: xwli@dicp.ac.cn， wangfen@dicp.ac.cn

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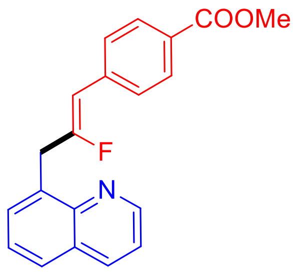
I. General Remarks

All chemicals were obtained from commercial sources and were used as received unless otherwise noted. All reactions were carried out using Schlenk techniques or in an N_2-filled glovebox. NMR Spectra were recorded on a 400 MHz NMR spectrometer in the solvent indicated. The chemical shift is given in dimensionless δ values and is frequency referenced relative to TMS in ^{1}H and ^{13}C NMR spectroscopy. HRMS data were obtained on a Thermo Scientific LTQ Orbitrap Discovery spectrometer (Bremen, Germany). Column chromatography was performed on silica gel (300-400 mesh) using ethyl acetate/hexanes. 8-Methylquinolines[1] and *gem*-difluoroalkenes[2] were prepared according to literature reports.

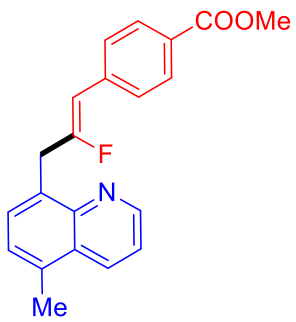
II. General procedures for the synthesis of compound 3

Typical Reaction Conditions. 8-Methylquinoline (0.2 mmol), *gem*-difluoroalkene (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), 4 Å M.S. (100 mg), and TFE (2 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 45 ºC for 24 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (40:1 to 20:1) to afford the product **3**.



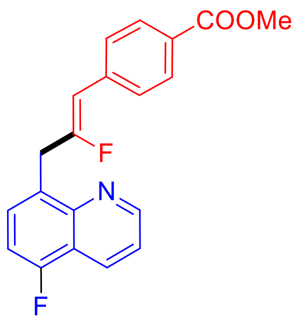
(*Z*)-Methyl 4-(2-fluoro-3-(quinolin-8-yl)prop-1-en-1-yl)benzoate (**3aa**)

3aa was obtained according to the general procedure in 81% yield (51.7 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.3, 1.7 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.76 (d, J = 8.2 Hz, 1H), 7.73 (d, J = 7.0 Hz, 1H), 7.58 – 7.47 (m, 3H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 5.63 (d, J = 38.6 Hz, 1H), 4.41 (d, J = 17.0 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.8 (d, J_{C-F} = 269.7 Hz), 149.9, 146.7, 138.6 (d, J_{C-F} = 2.8 Hz), 136.5, 134.7, 129.8, 129.8, 128.6, 128.3 (d, J_{C-F} = 7.8 Hz), 128.1 (d, J_{C-F} = 2.4 Hz), 127.5, 126.4, 121.4, 107.1 (d, J_{C-F} = 7.7 Hz), 52.12, 34.6 (d, J_{C-F} = 27.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.6. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{16}FNO_2$: 322.1238, found 322.1237.



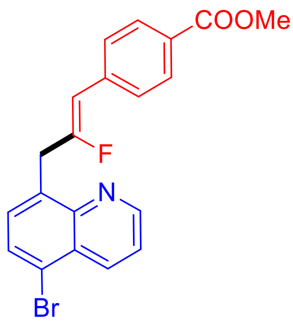
(Z)-Methyl 4-(2-fluoro-3-(5-methylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ba**)

3ba was obtained according to the general procedure in 72% yield (48.0 mg), white solid, $R_f = 0.30$ (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.1, 1.7 Hz, 1H), 8.32 (dd, J = 8.5, 1.7 Hz, 1H), 7.94 – 7.92 (m, 2H), 7.60 (d, J = 7.2 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.43 (dd, J = 8.5, 4.1 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 5.59 (d, J = 38.6 Hz, 1H), 4.37 (d, J = 16.6 Hz, 2H), 3.88 (s, 3H), 2.67 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.1 (d, J_{C-F} = 269.8 Hz), 149.3, 146.8, 138.7 (d, J_{C-F} = 2.8 Hz), 134.2, 132.8, 132.6 (d, J_{C-F} = 1.9 Hz), 129.7, 129.5, 128.3 (d, J_{C-F} = 7.8 Hz), 128.0 (d, J_{C-F} = 2.4 Hz), 127.9, 126.9, 120.9, 106.9 (d, J_{C-F} = 7.7 Hz), 52.1, 34.6 (d, J_{C-F} = 27.6 Hz), 18.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{18}FNO_2$: 336.1394, found 336.1398.



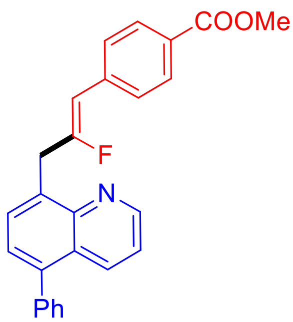
(Z)-Methyl 4-(2-fluoro-3-(5-fluoroquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ca**)

3ca was obtained according to the general procedure in 68% yield (46.1 mg), white solid, $R_f = 0.35$ (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (dd, J = 4.2, 1.8 Hz, 1H), 8.43 (dd, J = 8.4, 1.8 Hz, 1H), 7.99 – 7.90 (m, 2H), 7.66 – 7.63(m, 1H), 7.54 – 7.45 (m, 3H), 7.20 (dd, J = 9.5, 8.1 Hz, 1H), 5.62 (d, J = 38.5 Hz, 1H), 4.34 (d, J = 16.9 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.5 (dd, J_{C-F} = 269.4, 0.9 Hz), 157.2 (d, J_{C-F} = 253.3 Hz), 150.7, 147.0 (d, J_{C-F} = 2.8 Hz), 138.5 (d, J_{C-F} = 2.8 Hz), 130.6 (dd, J_{C-F} = 4.6, 1.5 Hz), 129.8, 129.6 (d, J_{C-F} = 4.8 Hz), 129.2 (d, J_{C-F} = 8.6 Hz), 128.3 (d, J_{C-F} = 7.8 Hz), 128.2 (d, J_{C-F} = 2.4 Hz), 121.4 (d, J_{C-F} = 2.9 Hz), 119.4 (d, J_{C-F} = 16.2 Hz), 109.9 (d, J_{C-F} = 19.1 Hz), 107.1 (d, J_{C-F} = 7.7 Hz), 52.1, 34.2 (d, J_{C-F} = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.2, -123.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{15}F_2NO_2$: 340.1144, found 340.1143.



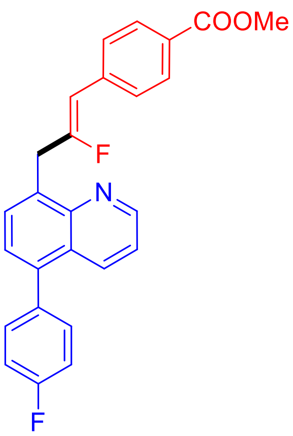
(*Z*)-Methyl 4-(3-(5-bromoquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3da**)

3da was obtained according to the general procedure in 60% yield (48.2 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.1, 1.6 Hz, 1H), 8.55 (dd, J = 8.5, 1.6 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.81 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.55 – 7.47 (m, 3H), 5.63 (d, J = 38.5 Hz, 1H), 4.36 (d, J = 17.1 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.1 (d, J_{C-F} = 269.5 Hz), 150.5, 147.3, 138.4 (d, J_{C-F} = 2.7 Hz), 135.9, 134.9 (d, J_{C-F} = 1.2 Hz), 130.2, 130.0, 129.8, 128.4, 128.3, 127.9, 122.5, 121.2, 107.3 (d, J_{C-F} = 7.6 Hz), 52.2, 34.5 (d, J_{C-F} = 27.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.2. HRMS: m/z: [M + H]$^+$ calculated for $C_{20}H_{15}BrFNO_2$: 400.0343, found 400.0343.



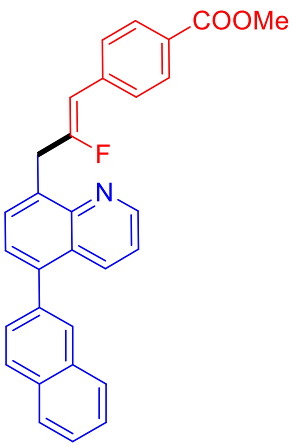
(*Z*)-Methyl 4-(2-fluoro-3-(5-phenylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ea**), *Z*/*E* = 15/1

3ea was obtained according to the general procedure in 71% yield (56.7 mg), white solid, R_f = 0.3 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 2.5 Hz, 1H), 8.25 (dd, J = 8.5, 1.1 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.76 (d, J = 7.2 Hz, 1H), 7.54 – 7.44 (m, 8H), 7.36 (dd, J = 8.5, 4.1 Hz, 1H), 5.70 (d, J = 38.6 Hz, 1H), 4.45 (d, J = 17.4 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.7 (d, J_{C-F} = 269.7 Hz), 149.6, 146.8, 140.1, 139.4, 138.6 (d, J_{C-F} = 2.7 Hz), 134.8, 134.0 (d, J_{C-F} = 0.9 Hz), 130.2, 129.8, 129.2, 128.6, 128.3 (d, J_{C-F} = 7.7 Hz), 128.1 (d, J_{C-F} = 2.4 Hz), 127.8, 127.04, 127.0, 121.2, 107.2 (d, J_{C-F} = 7.6 Hz), 52.1, 34.8 (d, J_{C-F} = 27.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.7. HRMS: m/z: [M + H]$^+$ calculated for $C_{26}H_{20}FNO_2$: 398.1551, found 398.1555.



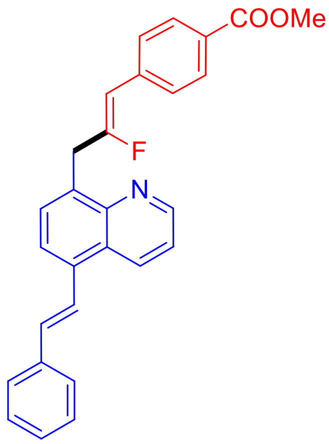
(*Z*)-Methyl 4-(2-fluoro-3-(5-(4-fluorophenyl)quinolin-8-yl)prop-1-en-1-yl)benzoate (**3fa**)

3fa was obtained according to the general procedure in 62% yield (51.3 mg), white solid, R_f = 0.3 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.1, 1.7 Hz, 1H), 8.19 (dd, J = 8.6, 1.7 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.76 (d, J = 7.3 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.45 (d, J = 7.3 Hz, 1H), 7.44 – 7.36 (m, 3H), 7.23 – 7.16 (m, 2H), 5.71 (d, J = 38.6 Hz, 1H), 4.45 (d, J = 17.5 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 162.6 (d, J_{C-F} = 245.6 Hz), 161.7 (d, J_{C-F} = 269.7 Hz), 149.7, 146.8, 138.9, 138.6 (d, J_{C-F} = 2.8 Hz), 135.3 (d, J_{C-F} = 3.4 Hz), 134.5, 134.3 (d, J_{C-F} = 0.9 Hz), 131.7 (d, J_{C-F} = 8.0 Hz), 129.8, 129.2, 128.3 (d, J_{C-F} = 7.8 Hz), 128.2 (d, J_{C-F} = 2.3 Hz), 127.2, 127.0, 121.4, 115.6 (d, J_{C-F} = 21.3 Hz), 107.2 (d, J_{C-F} = 7.7 Hz), 52.13, 34.8 (d, J_{C-F} = 27.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.8, -114.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{26}H_{19}F_2NO_2$: 416.1457, found 416.1458.



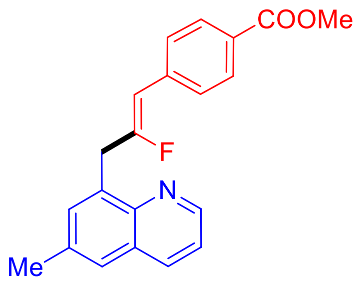
(*Z*)-Methyl 4-(2-fluoro-3-(5-(naphthalen-2-yl)quinolin-8-yl)prop-1-en-1-yl)benzoate (**3ga**)

3ga was obtained according to the general procedure in 63% yield (56.8 mg), white solid, R_f = 0.4 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (dd, J = 4.1, 1.7 Hz, 1H), 8.28 (dd, J = 8.6, 1.7 Hz, 1H), 7.98 – 7.86 (m, 6H), 7.80 (d, J = 7.3 Hz, 1H), 7.58 – 7.52 (m, 6H), 7.36 (dd, J = 8.6, 4.1 Hz, 1H), 5.71 (d, J = 38.6 Hz, 1H), 4.48 (d, J = 17.2 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 161.8 (d, J_{C-F} = 269.7 Hz), 149.7, 146.8, 140.0, 138.7 (d, J_{C-F} = 2.8 Hz), 136.9, 134.9, 134.2 (d, J_{C-F} = 0.65 Hz), 133.5, 132.8, 129.8, 129.3, 129.1, 128.4, 128.3 (d, J_{C-F} = 3.2 Hz), 128.2, 128.16, 128.1, 127.9, 127.4, 127.2, 126.7, 126.5, 121.3, 107.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.1, 34.8 (d, $J_{C\text{-}F}$ = 27.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.6. HRMS: m/z: $[M + H]^+$ calculated for $C_{30}H_{22}FNO_2$: 448.1707, found 448.1707.



Methyl4-((*Z*)-2-fluoro-3-(5-((*E*)-styryl)quinolin-8-yl)prop-1-en-1-yl)benzoate (**3ha**)

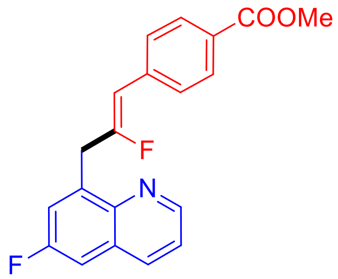
3ha was obtained according to the general procedure in 53% yield (45.0 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.82 – 7.67 (m, 3H), 7.59 – 7.58 (m, 2H), 7.51 – 7.49 (m, 2H), 7.45 (dd, *J* = 8.6, 4.1 Hz, 1H), 7.42 – 7.38 (m, 2H), 7.33 – 7.29 (m, 1H), 7.17 – 7.13 (m, 1H), 5.63 (d, *J* = 38.6 Hz, 1H), 4.41 (d, *J* = 16.8 Hz, 2H), 3.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.8 (d, $J_{C\text{-}F}$ = 269.7 Hz), 149.7, 146.8, 138.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 137.3, 135.0, 134.3 (d, $J_{C\text{-}F}$ = 1.5 Hz), 132.8, 132.5, 129.8, 129.7, 128.9, 128.3, 128.26, 128.1 (d, $J_{C\text{-}F}$ = 2.2 Hz), 126.9, 126.7, 124.2, 123.7, 121.1, 107.1 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.1, 34.8 (d, $J_{C\text{-}F}$ = 27.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{28}H_{22}FNO_2$: 424.1707, found 424.1711.



(*Z*)-Methyl 4-(2-fluoro-3-(6-methylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ia**)

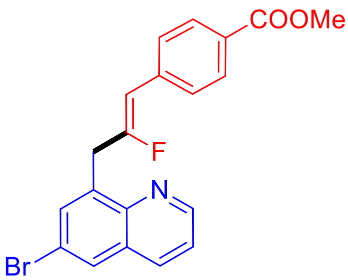
3ia was obtained according to the general procedure in 79% yield (52.9 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.54 (s, 1H), 7.51 – 7.49 (m, 3H), 7.36 (dd, *J* = 8.2, 4.2 Hz, 1H), 5.62 (d, *J* = 38.6 Hz, 1H), 4.37 (d, *J* = 17.1 Hz, 2H), 3.88 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.8 (d, $J_{C\text{-}F}$ = 269.8 Hz), 149.0, 145.2, 138.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 136.2, 135.7, 134.2 (d, $J_{C\text{-}F}$ = 1.4 Hz), 132.0, 129.7, 128.7, 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.1 (d, $J_{C\text{-}F}$ = 2.3 Hz), 126.3, 121.3, 107.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.1, 34.5 (d, $J_{C\text{-}F}$ = 27.5 Hz), 21.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.5.

HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{18}FNO_2$: 336.1394, found 336.1396.



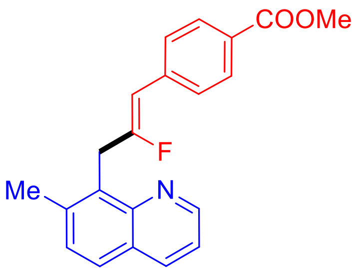
(*Z*)-Methyl 4-(2-fluoro-3-(6-fluoroquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ja**)

3ja was obtained according to the general procedure in 67% yield (45.4 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, J = 4.2, 1.6 Hz, 1H), 8.10 (dd, J = 8.3, 1.7 Hz, 1H), 7.99 – 7.91 (m, 2H), 7.56 – 7.48 (m, 3H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 7.37 (dd, J = 8.6, 2.8 Hz, 1H), 5.69 (d, J = 38.4 Hz, 1H), 4.40 (d, J = 17.9 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.7 (d, $J_{C\text{-}F}$ = 269.4 Hz), 160.1 (d, $J_{C\text{-}F}$ = 246.8 Hz), 149.1 (d, $J_{C\text{-}F}$ = 2.7 Hz), 143.8, 138.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 138.0 (d, $J_{C\text{-}F}$ = 8.6 Hz), 135.9 (d, $J_{C\text{-}F}$ = 5.5 Hz), 129.8, 129.4 (d, $J_{C\text{-}F}$ = 10.1Hz), 128.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.36, 122.2, 119.8 (d, $J_{C\text{-}F}$ = 26.2 Hz), 110.1 (d, $J_{C\text{-}F}$ = 21.1 Hz), 107.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.2, 34.5 (d, $J_{C\text{-}F}$ = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.6, -113.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{15}FNO_2$: 340.1144, found 340.1145.



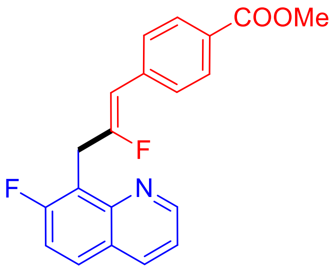
(*Z*)-Methyl 4-(3-(6-bromoquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3ka**)

3ka was obtained according to the general procedure in 63% yield (50.4 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.05 (dd, J = 8.3, 1.7 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.91 (d, J = 2.1 Hz, 1H), 7.79 (d, J = 1.1 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 5.67 (d, J = 38.4 Hz, 1H), 4.36 (d, J = 17.6 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.7 (d, $J_{C\text{-}F}$ = 269.5 Hz), 150.1, 145.3, 138.3 (d, $J_{C\text{-}F}$ = 2.9 Hz), 137.0, 135.5, 132.9, 129.8, 129.7, 129.4, 128.4 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.3, 122.2, 120.3, 107.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.1, 34.3 (d, $J_{C\text{-}F}$ = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{15}BrFNO_2$: 400.0343, found 400.0341.



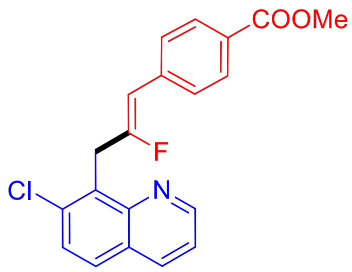
(*Z*)-Methyl 4-(2-fluoro-3-(7-methylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3la**)

3la was obtained according to the general procedure in 30% yield (20.1 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.2, 1.8 Hz, 1H), 8.13 (dd, J = 8.2, 1.8 Hz, 1H), 7.90 – 7.88 (m, 2H), 7.71 (d, J = 8.4 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.37 (dd, J = 8.2, 4.2 Hz, 1H), 5.24 (d, J = 39.2 Hz, 1H), 4.50 (d, J = 10.1 Hz, 2H), 3.87 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 161.8 (d, $J_{C\text{-}F}$ = 270.6 Hz), 150.0, 147.1, 138.8 (d, $J_{C\text{-}F}$ = 2.7 Hz), 138.8, 136.2, 131.6 (d, $J_{C\text{-}F}$ = 6.9 Hz), 129.9, 129.7, 128.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 127.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 126.9, 126.9, 120.5, 105.5 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.1, 30.8 (d, $J_{C\text{-}F}$ = 28.9 Hz), 20.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{18}FNO_2$: 336.1394, found 336.1394.



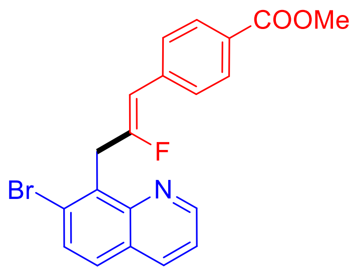
(*Z*)-Methyl 4-(2-fluoro-3-(7-fluoroquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ma**)

3ma was obtained according to the general procedure in 90% yield (61.0 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.2, 1.7 Hz, 1H), 8.13 (dd, J = 8.3, 1.7 Hz, 1H), 7.91 – 7.89 (m, 2H), 7.76 (dd, J = 9.0, 6.1 Hz, 1H), 7.45 – 7.43 (m, 2H), 7.41 – 7.34 (m, 2H), 5.51 (d, J = 38.5 Hz, 1H), 4.41 (d, J = 13.1 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.3 (d, $J_{C\text{-}F}$ = 248.2 Hz), 160.7 (dd, $J_{C\text{-}F}$ = 270.3, 1.0 Hz), 150.9, 147.5 (d, $J_{C\text{-}F}$ = 8.9 Hz), 138.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 136.3 (d, $J_{C\text{-}F}$ = 1.2 Hz), 129.7, 128.9 (d, $J_{C\text{-}F}$ = 10.5 Hz), 128.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 125.5 (d, $J_{C\text{-}F}$ = 0.8 Hz), 120.6 (d, $J_{C\text{-}F}$ = 2.5 Hz), 118.9 (dd, $J_{C\text{-}F}$ = 14.6, 4.2 Hz), 117.0 (d, $J_{C\text{-}F}$ = 26.3 Hz), 106.0 (d, $J_{C\text{-}F}$ = 7.4 Hz), 52.1, 27.4 (dd, $J_{C\text{-}F}$ = 29.9, 3.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -95.0 (d, J = 5.5 Hz, 1F), -110.9 (d, J = 5.5 Hz, 1F). HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{15}F_2NO_2$: 340.1144, found 340.1146.



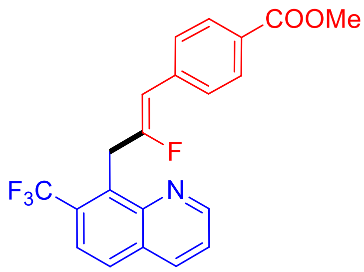
(*Z*)-Methyl 4-(3-(7-chloroquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3na**)

3na was obtained according to the general procedure in 92% yield (65.2 mg), white solid, R_f = 0.3 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, J = 4.2, 1.7 Hz, 1H), 8.03 (dd, J = 8.3, 1.7 Hz, 1H), 7.81 – 7.79 (m, 2H), 7.62 – 7.60 (m, 1H), 7.48 – 7.46 (m, 1H), 7.37 – 7.29 (m, 3H), 5.26 (d, J = 38.8 Hz, 1H), 4.49 (d, J = 11.1 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.5 (d, J_{C-F} = 270.6 Hz), 150.9, 147.4, 138.6 (d, J_{C-F} = 2.8 Hz), 136.3, 136.1, 132.1 (d, J_{C-F} = 6.0 Hz), 129.7, 128.3, 128.24, 128.2, 128.0 (d, J_{C-F} = 2.3 Hz), 127.1, 121.4, 106.1 (d, J_{C-F} = 7.4 Hz), 52.1, 31.7 (d, J_{C-F} = 30.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{15}ClFNO_2$: 356.0848, found 356.0849.



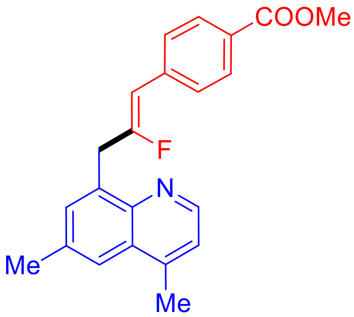
(*Z*)-Methyl 4-(3-(7-bromoquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3oa**)

3oa was obtained according to the general procedure in 94% yield (75.0 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.11 (dd, J = 8.3, 1.6 Hz, 1H), 7.90 – 7.89 (m, 2H), 7.73 – 7.71 (m, 1H), 7.63 – 7.61 (m, 1H), 7.43 – 7.40 (m, 3H), 5.32 (d, J = 38.9 Hz, 1H), 4.61 (d, J = 10.5 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 160.5 (d, J_{C-F} = 270.7 Hz), 150.8, 147.4, 138.6 (d, J_{C-F} = 2.7 Hz), 136.3, 134.2 (d, J_{C-F} = 6.7 Hz), 131.1, 129.6, 128.4, 128.2 (d, J_{C-F} = 7.8 Hz), 127.9 (d, J_{C-F} = 2.4 Hz), 127.4, 126.9, 121.6, 106.2 (d, J_{C-F} = 7.3 Hz), 52.1, 34.4 (d, J_{C-F} = 30.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{15}BrFNO_2$: 400.0343, found 400.0344.



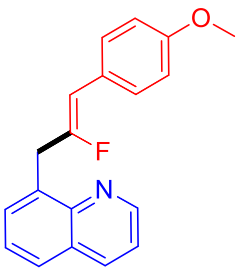
(*Z*)-Methyl 4-(2-fluoro-3-(7-(trifluoromethyl)quinolin-8-yl)prop-1-en-1-yl)benzoate (**3pa**)

3pa was obtained according to the general procedure in 74% yield (57.6 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.03 (dd, J = 3.9, 1.5 Hz, 1H), 8.20 (dd, J = 8.3, 1.3 Hz, 1H), 7.91 – 7.82 (m, 4H), 7.52 (dd, J = 8.3, 4.1 Hz, 1H), 7.39 – 7.37 (m, 2H), 5.15 (d, J = 38.8 Hz, 1H), 4.67 (d, J = 9.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 161.5 (d, $J_{C\text{-}F}$ = 270.5 Hz), 151.2, 146.7, 138.6 (d, $J_{C\text{-}F}$ = 2.6 Hz), 136.3, 134.5 (m), 130.1 (q, $J_{C\text{-}F}$ = 30.0 Hz), 129.8, 129.6, 128.2, 128.1, 128.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 124.4 (q, $J_{C\text{-}F}$ = 273.3 Hz), 123.1, 122.9 (q, $J_{C\text{-}F}$ = 5.4 Hz), 106.4 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.1, 30.9 (dq, $J_{C\text{-}F}$ = 30.9, 1.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -58.5 (d, J = 3.5 Hz, 3F), -93.3 (q, J = 3.5 Hz, 1F). HRMS: m/z: $[M + H]^+$ calculated for $C_{21}H_{15}F_4NO_2$: 390.1112, found 390.1115.



(*Z*)-Methyl 4-(3-(4,6-dimethylquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3qa**)

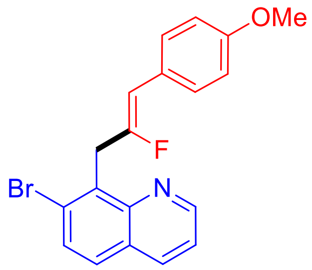
3qa was obtained according to the general procedure in 42% yield (29.1 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.3 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.72 (s, 1H), 7.55 (s, 1H), 7.51 – 7.49 (m, 2H), 7.22 (d, J = 4.3 Hz, 1H), 5.61 (d, J = 38.6 Hz, 1H), 4.38 (d, J = 17.0 Hz, 2H), 3.89 (s, 3H), 2.69 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 162.0 (d, $J_{C\text{-}F}$ = 269.8 Hz), 148.6, 144.9, 143.9, 138.8 (d, $J_{C\text{-}F}$ = 2.7 Hz), 135.9, 134.7 (d, $J_{C\text{-}F}$ = 1.3 Hz), 134.2, 131.7, 129.8, 128.7, 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.1 (d, $J_{C\text{-}F}$ = 2.4 Hz), 122.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 107.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.1, 34.9 (d, $J_{C\text{-}F}$ = 27.4 Hz), 22.1, 19.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -94.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{20}FNO_2$: 350.1551, found 350.1550.



(*Z*)-8-(2-Fluoro-3-(4-methoxyphenyl)allyl)quinoline (**3ab**)

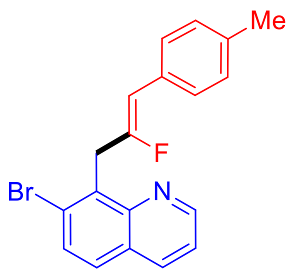
3ab was obtained according to the general procedure in 63% yield (37.2 mg), white solid, R_f = 0.20 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.14 (dd, J = 8.3, 1.7 Hz, 1H), 7.74 (d, J = 7.8 Hz, 2H), 7.56 – 7.47 (m, 1H), 7.45 – 7.35 (m, 3H), 6.83 – 6.80 (m, 2H), 5.55 (d, J = 39.4 Hz, 1H), 4.38 (d, J = 17.9 Hz, 2H), 3.77 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

158.41 (d, $J_{C\text{-}F}$ = 2.8 Hz), 158.4 (d, $J_{C\text{-}F}$ = 263.1 Hz), 149.8, 146.7, 136.5, 135.4, 129.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 129.5, 128.6, 127.2, 126.7 (d, $J_{C\text{-}F}$ = 2.6 Hz), 126.5, 121.2, 113.9, 107.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 55.3, 34.4 (d, $J_{C\text{-}F}$ = 28.0 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{16}FNO$: 294.1289, found 294.1286.



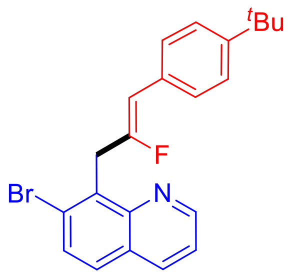
(*Z*)-7-Bromo-8-(2-fluoro-3-(4-methoxyphenyl)allyl)quinoline (**3ob**)

3ob was obtained according to the general procedure in 74% yield (54.7 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.1, 1.6 Hz, 1H), 8.11 (dd, J = 8.2, 1.5 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.62 – 7.60 (m, 1H), 7.42 (dd, J = 8.2, 4.2 Hz, 1H), 7.33 – 7.31 (m, 2H), 6.78 – 6.76 (m, 2H), 5.23 (d, J = 39.8 Hz, 1H), 4.58 (d, J = 10.9 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3 (d, $J_{C\text{-}F}$ = 2.7 Hz), 157.2 (d, $J_{C\text{-}F}$ = 264.2 Hz), 150.7, 147.6, 136.3, 134.9 (d, $J_{C\text{-}F}$ = 6.2 Hz), 131.2, 129.7 (d, $J_{C\text{-}F}$ = 7.5 Hz), 128.2, 127.5, 126.9, 126.8 (d, $J_{C\text{-}F}$ = 2.5 Hz), 121.5, 113.8, 106.3 (d, $J_{C\text{-}F}$ = 8.2 Hz), 55.3, 34.3 (d, $J_{C\text{-}F}$ = 30.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{15}BrFNO$: 372.0394, found 372.0397.



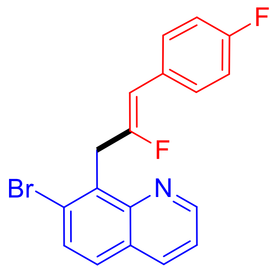
(*Z*)-7-Bromo-8-(2-fluoro-3-(p-tolyl)allyl)quinoline (**3oc**)

3oc was obtained according to the general procedure in 98% yield (69.5 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.8 Hz, 1H), 8.09 (dd, J = 8.3, 1.8 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.61 – 7.58 (m, 1H), 7.40 (dd, J = 8.2, 4.2 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.04 – 7.02 (m, 2H), 5.25 (d, J = 39.8 Hz, 1H), 4.58 (d, J = 10.8 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9 (d, $J_{C\text{-}F}$ = 265.6 Hz), 150.7, 147.6, 136.4 (d, $J_{C\text{-}F}$ = 2.4 Hz), 136.3, 134.8 (d, $J_{C\text{-}F}$ = 6.2 Hz), 131.2, 131.1 (d, $J_{C\text{-}F}$ = 2.5 Hz), 129.1, 128.3 (d, $J_{C\text{-}F}$ = 7.3 Hz), 128.2, 127.4, 126.9, 121.5, 106.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 34.3 (d, $J_{C\text{-}F}$ = 30.5 Hz), 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{15}BrFN$: 356.0445, found 372.0442.



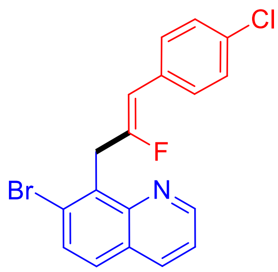
(*Z*)-7-Bromo-8-(3-(4-(tert-butyl)phenyl)-2-fluoroallyl)quinoline (**3od**)

3od was obtained according to the general procedure in 97% yield (77.0 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, J = 4.2, 1.7 Hz, 1H), 8.09 (dd, J = 8.2, 1.7 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.61 – 7.58 (m, 1H), 7.39 (dd, J = 8.2, 4.2 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.26 – 7.24 (m, 2H), 5.27 (d, J = 39.8 Hz, 1H), 4.59 (d, J = 10.9 Hz, 2H), 1.26 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.1 (d, J_{C-F} = 265.8 Hz), 150.7, 149.6 (d, J_{C-F} = 2.1 Hz), 147.6, 136.3, 134.8 (d, J_{C-F} = 6.1 Hz), 131.2, 131.17, 128.2 (d, J_{C-F} = 1.6 Hz), 128.1, 127.4, 126.9, 125.3, 121.5, 106.6 (d, J_{C-F} = 8.0 Hz), 34.6, 34.4 (d, J_{C-F} = 30.4 Hz), 31.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -99.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{21}BrFN$: 398.0914, found 398.0912.



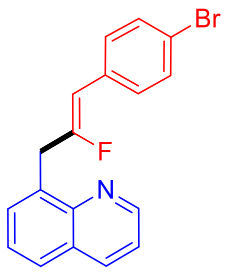
(*Z*)-7-Bromo-8-(2-fluoro-3-(4-fluorophenyl)allyl)quinoline (**3oe**)

3oe was obtained according to the general procedure in 75% yield (54.1 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, J = 2.7 Hz, 1H), 8.13 (d, J = 8.1 Hz, 1H), 7.75 – 7.72 (m, 1H), 7.64 – 7.62 (m, 1H), 7.43 (dd, J = 8.2, 4.1 Hz, 1H), 7.34 – 7.32 (m, 2H), 6.93 – 6.89 (m, 2H), 5.24 (d, J = 39.1 Hz, 1H), 4.59 (d, J = 10.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (dd, J_{C-F} = 244.7, 3.3 Hz), 158.3 (dd, J_{C-F} = 266.0, 2.3 Hz), 150.8, 147.5, 136.4, 134.6 (d, J_{C-F} = 6.5 Hz), 131.2, 130.02, 130.0 (d, J_{C-F} = 15.4 Hz), 128.3, 127.5, 126.9, 121.6, 115.2 (d, J_{C-F} = 21.2 Hz), 105.8 (d, J_{C-F} = 8.0 Hz), 34.3 (d, J_{C-F} = 30.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.0 (d, J = 1.0 Hz, 1F), -115.2 (d, J = 1.0 Hz, 1F). HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{12}BrF_2N$: 360.0194, found 360.0193.



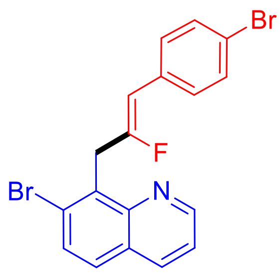
(*Z*)-7-bromo-8-(3-(4-chlorophenyl)-2-fluoroallyl)quinoline (**3of**)

3of was obtained according to the general procedure in 97% yield (73.2 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, J = 2.7 Hz, 1H), 8.12 (d, J = 8.1 Hz, 1H), 7.74 – 7.71 (m, 1H), 7.64 – 7.61 (m, 1H), 7.42 (dd, J = 8.1, 4.1 Hz, 1H), 7.30 – 7.28 (m, 2H), 7.19 – 7.17 (d, J = 8.3 Hz, 2H), 5.23 (d, J = 38.9 Hz, 1H), 4.59 (d, J = 10.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0 (d, J_{C-F} = 267.6 Hz), 150.7, 147.4, 136.3, 134.4 (d, J_{C-F} = 6.5 Hz), 132.4 (d, J_{C-F} = 2.5 Hz), 132.1 (d, J_{C-F} = 3.4 Hz), 131.1, 129.6 (d, J_{C-F} = 7.6 Hz), 128.4, 128.2, 127.4, 126.8, 121.5, 105.7 (d, J_{C-F} = 7.8 Hz), 34.3 (d, J_{C-F} = 30.2 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{12}BrClFN$: 375.9898, found 375.9898.



(*Z*)-8-(3-(4-Bromophenyl)-2-fluoroallyl)quinoline (**3ag**)

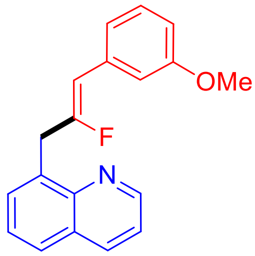
3ag was obtained according to the general procedure in 67% yield (46.1 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.7 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.55 – 7.48 (m, 1H), 7.44 – 7.35 (m, 3H), 7.31 – 7.29 (m, 2H), 5.52 (d, J = 38.6 Hz, 1H), 4.37 (d, J = 17.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5 (d, J_{C-F} = 266.9 Hz), 149.9, 146.6, 136.5, 134.9 (d, J_{C-F} = 1.2 Hz), 132.9 (d, J_{C-F} = 2.7 Hz), 131.5, 130.0 (d, J_{C-F} = 7.7 Hz), 129.7, 128.6, 127.4, 126.4, 121.3, 120.5 (d, J_{C-F} = 3.5 Hz), 106.7 (d, J_{C-F} = 8.0 Hz), 34.5 (d, J_{C-F} = 27.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{13}BrFN$: 342.0288, found 342.0288.



(*Z*)-7-bromo-8-(3-(4-bromophenyl)-2-fluoroallyl)quinoline (**3og**)

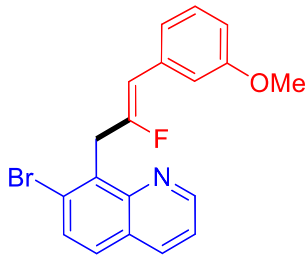
3og was obtained according to the general procedure in 96% yield (80.8 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.10 (dd, J = 8.3, 1.7 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.62 – 7.60 (m, 1H), 7.41 (dd, J = 8.2, 4.2 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.23 – 7.21 (m, 2H), 5.22 (d, J = 38.9 Hz, 1H), 4.57 (d, J = 10.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2 (d, J_{C-F} = 267.9 Hz), 150.8, 147.5, 136.4, 134.4 (d, J_{C-F} = 6.6 Hz), 132.9 (d, J_{C-F}

= 2.5 Hz), 131.4, 131.2, 130.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 128.3, 127.4, 126.9, 121.6, 120.3 (d, $J_{C\text{-}F}$ = 3.4 Hz), 105.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 34.4 (d, $J_{C\text{-}F}$ = 30.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -97.3. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{12}Br_2FN$: 419.9393, found 419.9393.



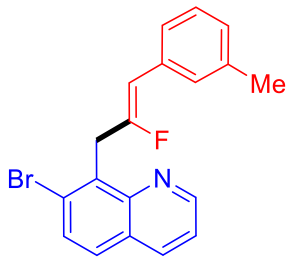
(*Z*)-8-(2-fluoro-3-(3-methoxyphenyl)allyl)quinoline (**3ah**)

3ah was obtained according to the general procedure in 79% yield (46.4 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.14 (dd, J = 8.3, 1.7 Hz, 1H), 7.75 – 7.732 (m, 2H), 7.53 – 7.49 (m, 1H), 7.40 (dd, J = 8.3, 4.2 Hz, 1H), 7.21 – 7.17 (m, 1H), 7.07 – 7.06 (m, 1H), 7.03 (d, J = 7.7 Hz, 1H), 6.74 (dd, J = 8.0, 2.2 Hz, 1H), 5.59 (d, J = 38.9 Hz, 1H), 4.39 (d, J = 17.7 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (d, $J_{C\text{-}F}$ = 266.3 Hz), 158.6, 149.8, 146.7, 136.4, 135.2 (d, $J_{C\text{-}F}$ = 2.6 Hz), 135.1 (d, $J_{C\text{-}F}$ = 1.0 Hz), 129.6, 129.4, 128.6, 127.3, 126.4, 121.3, 121.1 (d, $J_{C\text{-}F}$ = 6.9 Hz), 113.6 (d, $J_{C\text{-}F}$ = 8.2 Hz), 112.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 107.7 (d, $J_{C\text{-}F}$ = 7.8 Hz), 55.3, 34.5 (d, $J_{C\text{-}F}$ = 27.8 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{16}FNO$: 294.1289, found 294.1290.



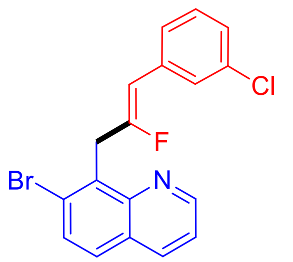
(*Z*)-7-Bromo-8-(2-fluoro-3-(3-methoxyphenyl)allyl)quinoline (**3oh**)

3oh was obtained according to the general procedure in 86% yield (63.8 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.11 (dd, J = 8.3, 1.7 Hz, 1H), 7.73 – 7.71 (m, 1H), 7.63 – 7.61 (m, 1H), 7.42 (dd, J = 8.2, 4.2 Hz, 1H), 7.16 – 7.12 (m, 1H), 6.98 – 6.97 (m, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.70 (dd, J = 8.0, 2.2 Hz, 1H), 5.27 (d, J = 39.2 Hz, 1H), 4.60 (d, J = 10.9 Hz, 2H), 3.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.6, 158.7 (d, $J_{C\text{-}F}$ = 267.2 Hz), 150.8, 147.6, 136.3, 135.2 (d, $J_{C\text{-}F}$ = 2.5 Hz), 134.6 (d, $J_{C\text{-}F}$ = 6.2 Hz), 131.2, 129.2, 128.3, 127.5, 126.9, 121.5, 121.1 (d, $J_{C\text{-}F}$ = 6.9 Hz), 113.5 (d, $J_{C\text{-}F}$ = 8.6Hz), 112.8 (d, $J_{C\text{-}F}$ = 2.0 Hz), 106.8 (d, $J_{C\text{-}F}$ = 7.4 Hz), 55.3, 34.4 (d, $J_{C\text{-}F}$ = 30.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.0. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{15}BrFNO$: 372.0394, found 372.0393.



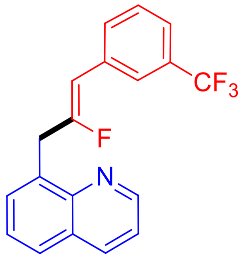
(*Z*)-7-Bromo-8-(2-fluoro-3-(m-tolyl)allyl)quinoline (**3oi**)

3oi was obtained according to the general procedure in 90% yield (64.3 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.8 Hz, 1H), 8.09 (dd, J = 8.3, 1.7 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.61 – 7.59 (m, 1H), 7.40 (dd, J = 8.2, 4.2 Hz, 1H), 7.20 – 7.19 (m, 2H), 7.14 – 7.10 (m, 1H), 6.94 (d, J = 7.4 Hz, 1H), 5.26 (d, J = 39.7 Hz, 1H), 4.59 (d, J = 10.8 Hz, 2H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4 (d, $J_{C\text{-}F}$ = 266.5 Hz), 150.7, 147.6, 137.8, 136.3, 134.8 (d, $J_{C\text{-}F}$ = 6.3 Hz), 133.9 (d, $J_{C\text{-}F}$ = 2.6 Hz), 131.2, 129.1 (d, $J_{C\text{-}F}$ = 7.1 Hz), 128.3, 128.2, 127.5 (d, $J_{C\text{-}F}$ = 2.2 Hz), 127.4, 126.9, 125.6 (d, $J_{C\text{-}F}$ = 7.4 Hz), 121.5, 106.9 (d, $J_{C\text{-}F}$ = 7.5 Hz), 34.4 (d, $J_{C\text{-}F}$ = 30.4 Hz), 21.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{15}BrFN$: 356.0445, found 356.0442.



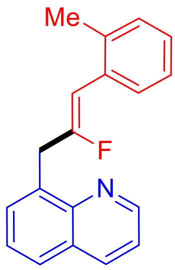
(*Z*)-7-bromo-8-(3-(3-chlorophenyl)-2-fluoroallyl)quinoline (**3oj**)

3oj was obtained according to the general procedure in 91% yield (68.7 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.1, 1.7 Hz, 1H), 8.12 (dd, J = 8.2, 1.6 Hz, 1H), 7.74 – 7.72 (m, 1H), 7.64 – 7.62 (m, 1H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 7.37 (s, 1H), 7.24 – 7.22 (m, 1H), 7.16 – 7.12 (m, 1H), 7.11 – 7.04 (m, 1H), 5.22 (d, J = 38.7 Hz, 1H), 4.60 (d, J = 10.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, $J_{C\text{-}F}$ = 268.8 Hz), 150.8, 147.5, 136.4, 135.7 (d, $J_{C\text{-}F}$ = 2.5 Hz), 134.4 (d, $J_{C\text{-}F}$ = 6.5 Hz), 134.2, 131.2, 129.5, 128.4, 128.3, 127.5, 126.9, 126.7 (d, $J_{C\text{-}F}$ = 2.0 Hz), 126.5 (d, $J_{C\text{-}F}$ = 7.5 Hz), 121.6, 105.8 (d, $J_{C\text{-}F}$ = 7.5 Hz), 34.4 (d, $J_{C\text{-}F}$ = 30.1 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -96.4. HRMS: m/z: $[M + H]^+$ calculated for $C_{18}H_{12}BrClFN$: 375.9898, found 375.9896.



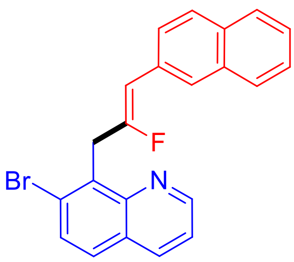
(*Z*)-8-(2-Fluoro-3-(3-(trifluoromethyl)phenyl)allyl)quinoline (**3ak**)

3ak was obtained according to the general procedure in 58% yield (38.5 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.3, 1.7 Hz, 1H), 7.78 – 7.72 (m, 2H), 7.68 (s, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.56 – 7.50 (m, 1H), 7.46 – 7.32 (m, 3H), 5.61 (d, J = 38.2 Hz, 1H), 4.41 (d, J = 17.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, $J_{C\text{-}F}$ = 268.1 Hz), 149.8, 146.6, 136.4, 134.61 (d, $J_{C\text{-}F}$ = 4.5 Hz), 134.6, 131.4 (dq, $J_{C\text{-}F}$ = 7.8, 1.4 Hz), 130.7 (q, $J_{C\text{-}F}$ = 31.8 Hz), 129.7, 128.7, 128.5, 127.4,126.3, 125.0 (m), 124.2 (q, $J_{C\text{-}F}$ = 270.6 Hz), 123.2 (m), 121.3, 106.4 (d, $J_{C\text{-}F}$ = 7.8 Hz), 34.4 (d, $J_{C\text{-}F}$ = 27.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7, -96.4. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{13}F_4N$: 332.1057, found 332.1057.



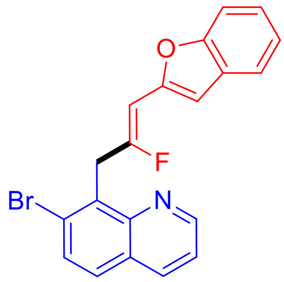
(*Z*)-8-(2-Fluoro-3-(o-tolyl)allyl)quinoline (**3al**)

3al was obtained according to the general procedure (60 °C) in 34% yield (15.5 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.1, 1.6 Hz, 1H), 8.17 (dd, J = 8.3, 1.6 Hz, 1H), 7.77 – 7.75 (m, 2H), 7.64 (d, J = 7.5 Hz, 1H), 7.57 – 7.49 (m, 1H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 7.21 – 7.03 (m, 3H), 5.76 (d, J = 38.2 Hz, 1H), 4.41 (d, J = 17.8 Hz, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, $J_{C\text{-}F}$ = 264.6 Hz), 149.8, 146.8, 136.5, 135.6, 135.4, 132.5 (d, $J_{C\text{-}F}$ = 1.8 Hz), 130.0, 129.5, 129.3 (d, $J_{C\text{-}F}$ = 9.5 Hz), 128.6, 127.3, 127.0 (d, $J_{C\text{-}F}$ = 0.9 Hz), 126.5, 125.9, 121.3, 105.4 (d, $J_{C\text{-}F}$ = 9.1 Hz), 34.7 (d, $J_{C\text{-}F}$ = 28.1 Hz), 20.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -101.9. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{16}FN$: 278.1340, found 278.1340.



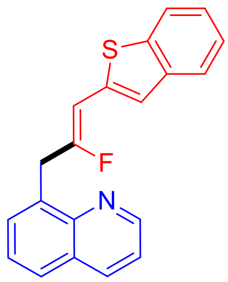
(*Z*)-7-Bromo-8-(2-fluoro-3-(naphthalen-2-yl)allyl)quinoline (**3om**)

3om was obtained according to the general procedure in 97% yield (76.2 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.06 (dd, J = 8.3, 1.6 Hz, 1H), 7.76 (s, 1H), 7.73 – 7.64 (m, 4H), 7.61 – 7.54 (m, 2H), 7.41 – 7.32 (m, 3H), 5.44 (d, J = 39.5 Hz, 1H), 4.64 (d, J = 10.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9 (d, $J_{C\text{-}F}$ = 267.3 Hz), 150.8, 147.5, 136.3, 134.7 (d, $J_{C\text{-}F}$ = 6.4 Hz), 133.5, 132.3 (d, $J_{C\text{-}F}$ = 1.6 Hz), 131.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 131.2, 128.3, 128.0, 127.8, 127.6, 127.5, 127.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 126.9, 126.7 (d, $J_{C\text{-}F}$ = 7.7 Hz), 126.0, 125.7, 121.5, 107.0 (d, $J_{C\text{-}F}$ = 7.6 Hz), 34.5 (d, $J_{C\text{-}F}$ = 30.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -98.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{22}H_{15}BrFN$: 392.0445, found 392.0441.



(*Z*)-8-(3-(benzofuran-2-yl)-2-fluoroallyl)-7-bromoquinoline (**3on**)

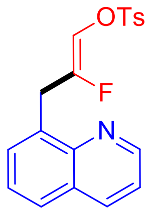
3on was obtained according to the general procedure in 35% yield (26.8 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.7 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.68 – 7.66 (m, 1H), 7.51 – 7.42 (m, 2H), 7.32 – 7.31 (m, 1H), 7.16 – 7.13 (m, 2H), 6.82 (s, 1H), 5.43 (d, J = 37.5 Hz, 1H), 4.66 (d, J = 9.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.7 (d, $J_{C\text{-}F}$ = 271.5 Hz), 153.8 (d, $J_{C\text{-}F}$ = 1.0 Hz), 151.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 150.9, 147.5, 136.4, 134.0 (d, $J_{C\text{-}F}$ = 7.3 Hz), 131.2, 129.4, 128.5, 127.5, 127.0, 124.0, 122.8, 121.7, 120.8, 110.8, 105.1 (d, $J_{C\text{-}F}$ = 11.3 Hz), 98.0 (d, $J_{C\text{-}F}$ = 10.1 Hz), 34.2 (d, $J_{C\text{-}F}$ = 28.9 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -89.5. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{13}BrFNO$: 382.0237, found 382.0240.



(*Z*)-8-(3-(Benzo[b]thiophen-2-yl)-2-fluoroallyl)quinoline (**3ao**)

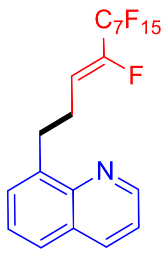
3al was obtained according to the general procedure (60 ºC) in 32% yield (20.1 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.3, 1.7 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.69 – 7.62 (m, 1H), 7.57 – 7.50 (m, 1H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 7.31 – 7.22 (m, 2H), 7.15 (s, 1H), 5.95 (d, J = 37.7 Hz, 1H), 4.44 (d, J = 16.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4 (d, $J_{C\text{-}F}$ = 267.9 Hz), 149.9, 146.7, 140.1 (d, $J_{C\text{-}F}$ = 7.5 Hz), 139.5, 136.5, 134.6 (d, $J_{C\text{-}F}$ = 1.5 Hz), 132.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 129.9, 128.6, 127.5, 126.5, 124.3, 124.2, 123.2

(d, J_{C-F} = 1.5 Hz), 122.4 (d, J_{C-F} = 4.2 Hz), 122.1, 121.4, 102.8 (d, J_{C-F} = 11.4 Hz), 34.0 (d, J_{C-F} = 26.7 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.7. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{14}FNS$: 320.0904, found 320.0903.



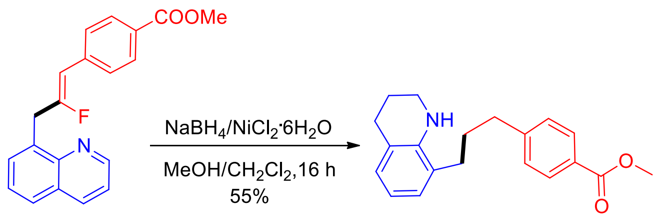
(*Z*)-2-Fluoro-3-(quinolin-8-yl)prop-1-en-1-yl 4-methylbenzenesulfonate (**3aq**)

3ap was obtained according to the general procedure (100 °C, DCE) in 61% yield (43.8 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 8/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.90 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.16 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.75 – 7.73 (m, 1H), 7.70 – 7.67 (m, 2H), 7.48 – 7.38 (m, 3H), 7.18 – 7.16 (m, 2H), 6.18 (d, *J* = 19.1 Hz, 1H), 4.09 (d, *J* = 19.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4 (d, J_{C-F} = 262.2 Hz), 149.8, 146.4, 145.3, 136.5, 133.3, 131.9, 129.7, 129.4, 128.5, 128.4, 127.6, 126.3, 121.4, 119.0 (d, J_{C-F} = 11.6 Hz), 30.1 (d, J_{C-F} = 23.2 Hz), 21.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -117.8. HRMS: m/z: $[M + H]^+$ calculated for $C_{19}H_{16}FNO_3S$: 358.0908, found 358.0907.



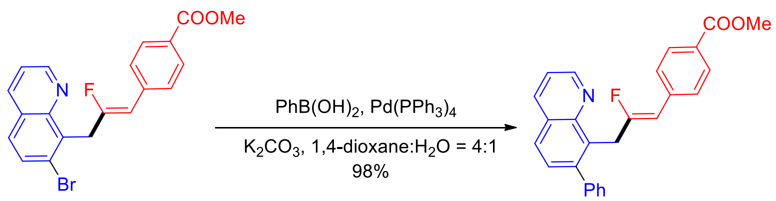
3aq was obtained according to the general procedure (80 °C) in 94% yield (108.7 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 50/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.60 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.44 – 7.43 (m, 1H), 7.40 – 7.34 (m, 1H), 7.31 – 7.28 (m, 1H), 5.62 (dt, *J* = 34.0, 7.8 Hz, 1H), 3.33 (t, *J* = 7.5 Hz, 2H), 2.76 – 2.63 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 146.9 (t, *J* = 28.6 Hz), 146.7, 144.3 (t, *J* = 22.5 Hz), 138.9, 136.4, 129.1, 128.5, 126.7, 126.2, 121.0, 118.6 (m), 116.0 (m), 112.8 (m), 110.6 (m), 108.2(m), 30.3, 24.5 (d, J_{C-F} = 2.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.9 (m), -117.4 (m), -122.1 (m), -122.8 (m), -123.2 (m), -126.2 (m), -132.2 (m). HRMS: m/z: $[M + H]^+$ calculated for $C_{29}H_{11}F_{16}N$: 570.0709, found 570.0705.

III. Derivatization of coupled product 3aa and 3oa



3aa **4**

Olefin **3aa** (0.2 mmol, 64.2 mg) and $NiCl_6 \cdot H_2O$ (10 mol%, 5.0 mg, 0.02 mmol) were dissolved in MeOH (2 mL), to which was added CH_2Cl_2 (1 mL) and $NaBH_4$ (3 mmol, 114 mg) in portions with stirring under cooling for 1 h. Then the stirring was continued for another 16 h at rt. After the removal of the solvents, the residue was absorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:8) to afford compound **4** as a white solid (55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 6.89 – 6.80 (m, 2H), 6.59 – 6.57 (m, J = 7.4 Hz, 1H), 3.90 (s, 3H), 3.34 – 3.26 (m, 2H), 2.79 – 2.73 (m, 4H), 2.45 – 2.37 (m, 2H), 1.98 – 1.88 (m, 4H). The NH was not visible due to exchange. ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 147.9, 142.3, 129.8, 128.6, 128.0, 127.7, 126.8, 124.9, 121.5, 116.6, 52.1, 42.4, 35.9, 30.3, 29.6, 27.6, 22.2. HRMS: m/z: $[M + H]^+$ calculated for $C_{20}H_{23}NO_2$: 310.1802, found 310.1806.

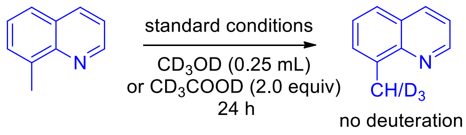


3oa **5**

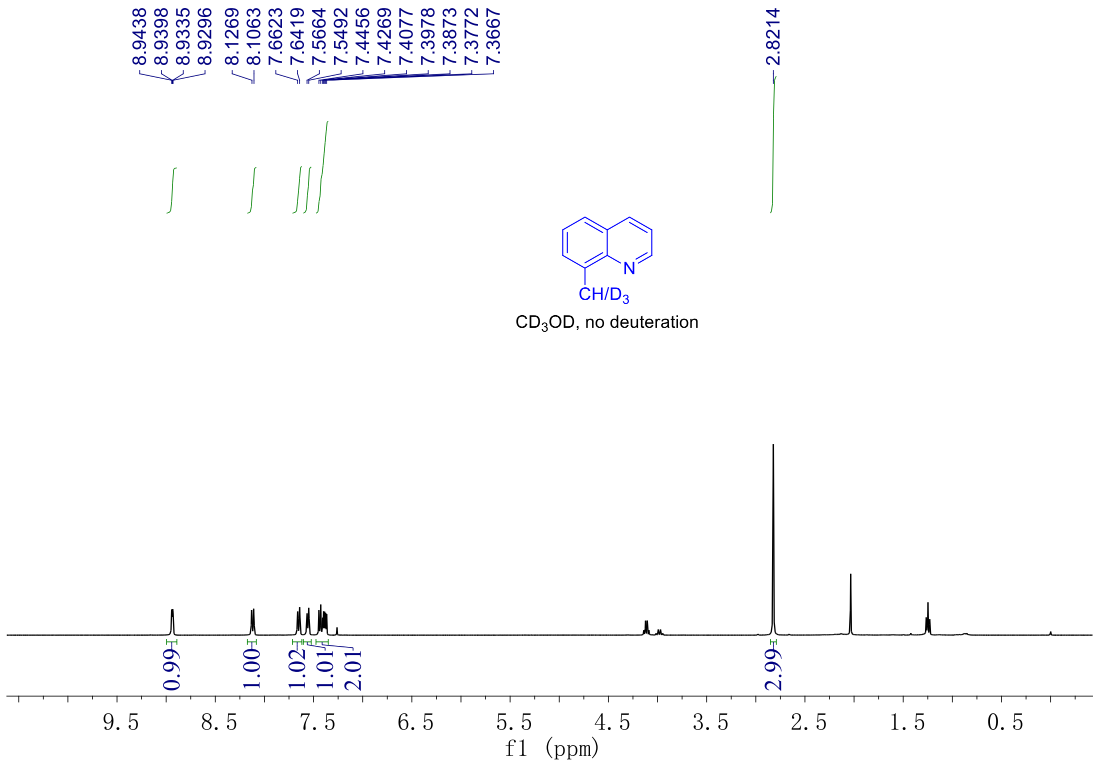
Olefin **3oa** (0.1 mmol, 40.0 mg), $PhB(OH)_2$ (0.15 mmol, 18.3 mg), $Pd(PPh_3)_4$ (5 mol%, 6.0 mg), K_2CO_3 (0.2 mmol, 34.0 mg), 1,4-dioxane (0.8 mL), and H_2O (0.2 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 90 °C for 12 h. After the removal of the solvents, the residue was absorbed onto small amounts of silica. The purification was performed by flash column chromatography on silica gel (eluent: EtOAc/petroleum ether = 1:25) to afford compound **5** as a white solid (39.0 mg, 98%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.99 (dd, J = 4.2, 1.8 Hz, 1H), 8.19 (dd, J = 8.2, 1.7 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.83 (d, J = 8.4 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.48 – 7.38 (m, 6H), 7.36 – 7.34 (m, 2H), 5.09 (d, J = 39.1 Hz, 1H), 4.37 (d, J = 10.0 Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 162.7 (d, $J_{C\text{-}F}$ = 270.6 Hz), 150.4, 147.0, 143.9, 141.2, 138.9 (d, $J_{C\text{-}F}$ = 2.6Hz), 136.3, 131.3 (d, $J_{C\text{-}F}$ = 7.0 Hz), 129.6, 129.2, 129.15, 128.5, 128.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 127.8 (d, $J_{C\text{-}F}$ = 2.3 Hz), 127.7, 127.6, 127.1, 121.3, 106.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.1, 32.0 (d, $J_{C\text{-}F}$ = 29.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ -93.1. HRMS: m/z: $[M + H]^+$ calculated for $C_{26}H_{20}FNO_2$: 398.1551, found 398.1555.

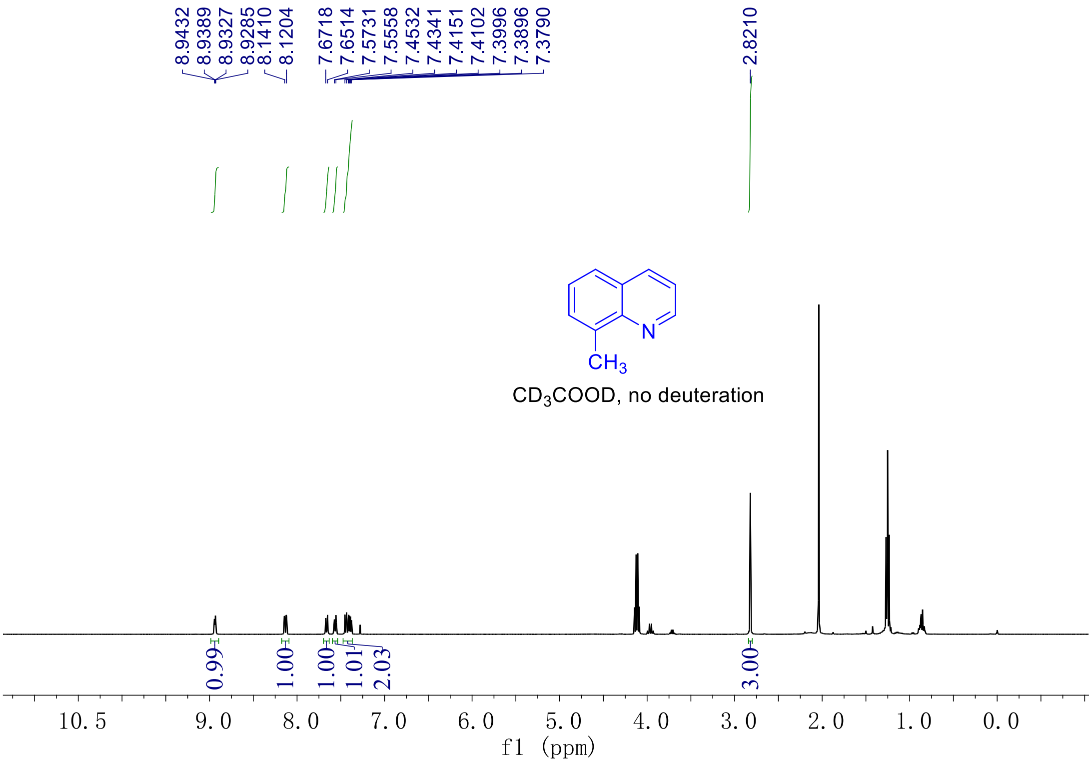
IV. Mechanistic Studies

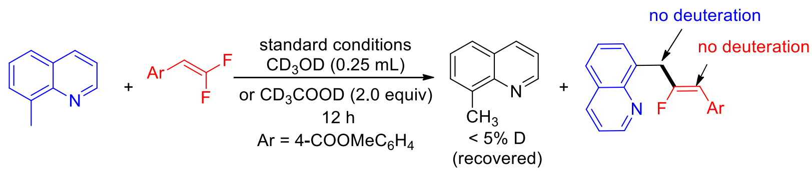
(a) H/D Exchange Experiments



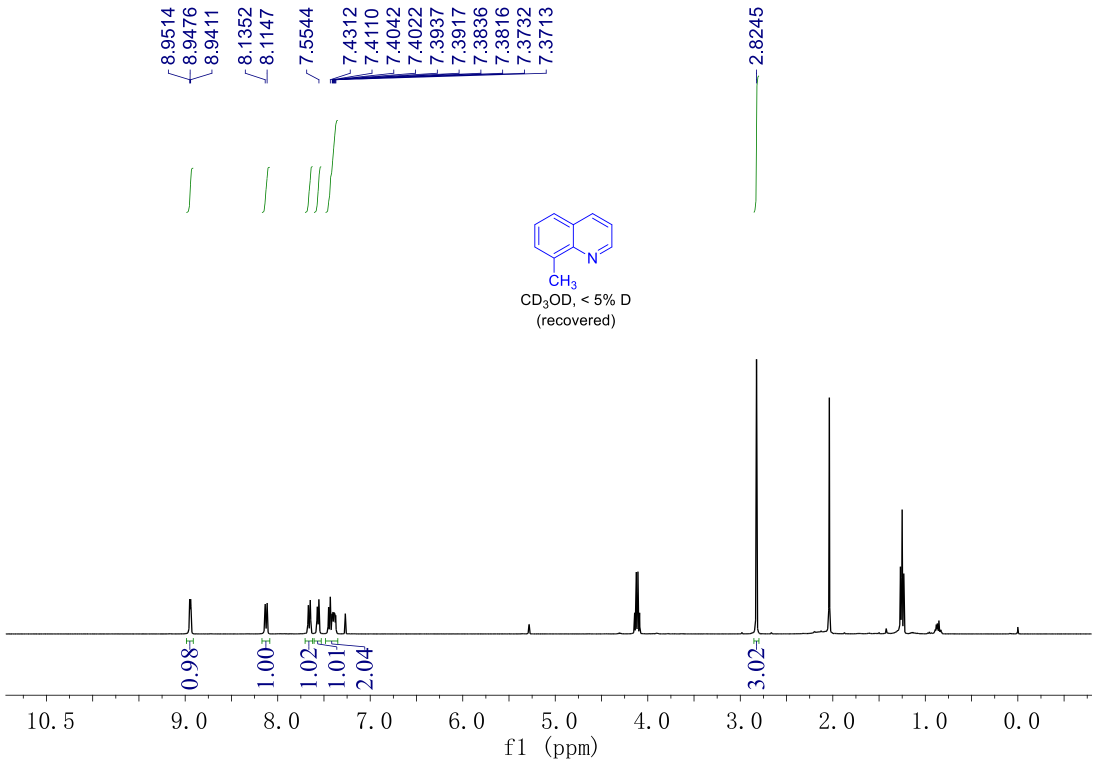
8-Methylquinoline (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (100 mg) were added to TFE (2 mL) in a pressure tube, and CD_3OD (0.25 mL) or CD_3COOD (2.0 equiv) was then introduced under N_2 atmosphere. The reaction mixture was stirred at 45 °C for 24 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford an oil, which was characterized by ^1H NMR spectroscopy. The methyl group was not be deuterated.







8-Methylquinoline (0.2 mmol), *gem*-difluoroalkene **2a** (0.3 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (100 mg) were dissolved in TFE (2 mL), and CD_3OD (0.25 mL) or CD_3COOD (2.0 equiv) in a pressure tube under N_2 atmosphere. The reaction mixture was stirred at 45 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford the recovered 8-methyl-quinoline and the product **3aa**, which were characterized by ^1H NMR spectroscopy.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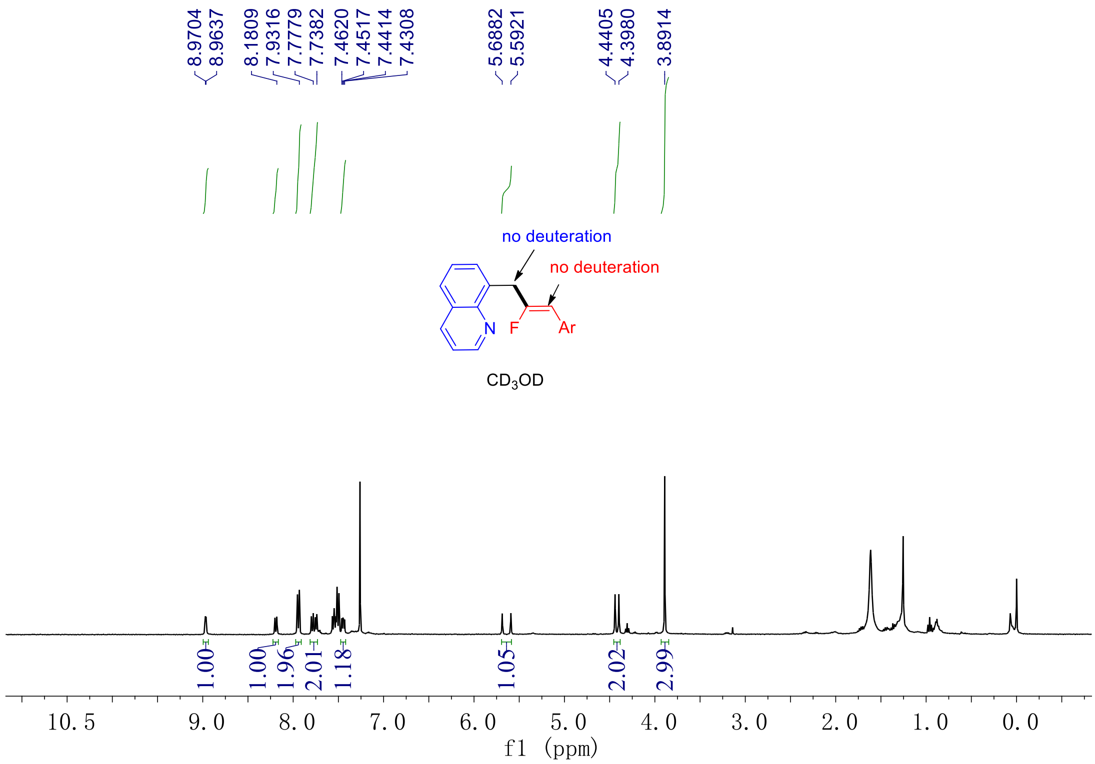
8.9476
8.9411
8.1352
8.1147
7.5544
7.4312
7.4110
7.4042
7.4022
7.3937
7.3917
7.3836
7.3816
7.3732
7.3713
2.8245
N
CH_3
CD_3OD, < 5% D
(recovered)
0.98
1.00
1.02
1.01
2.04
3.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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7.7779
7.7382
7.4620
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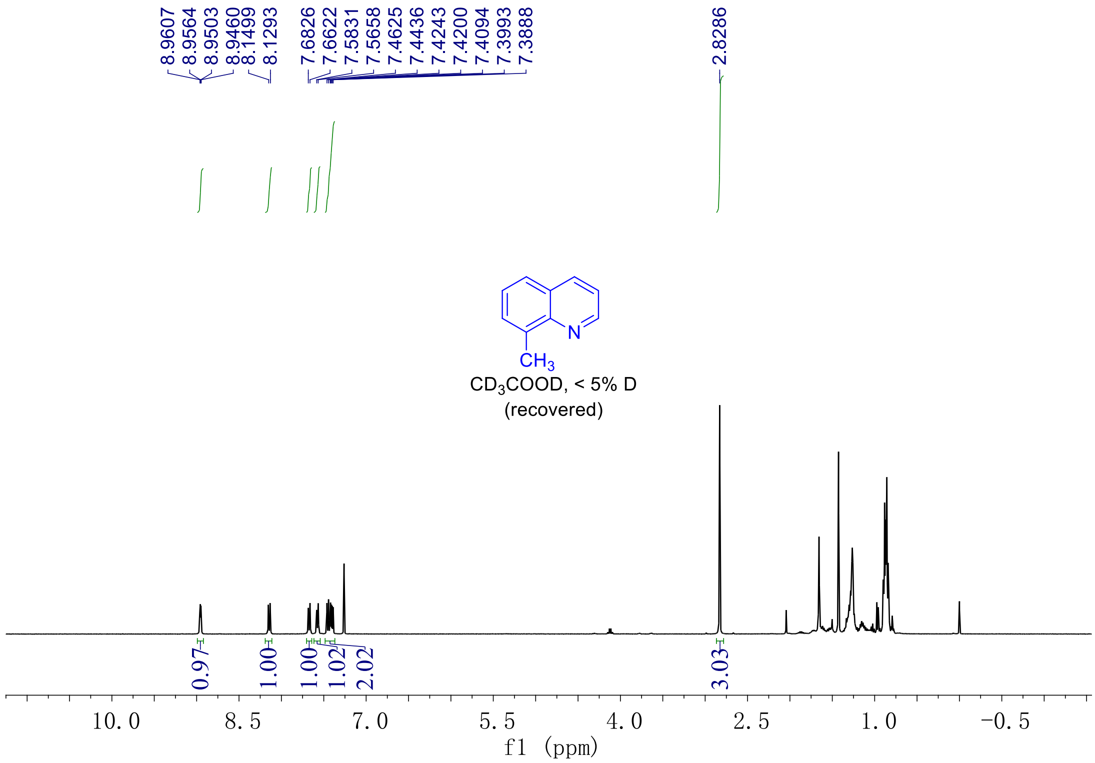
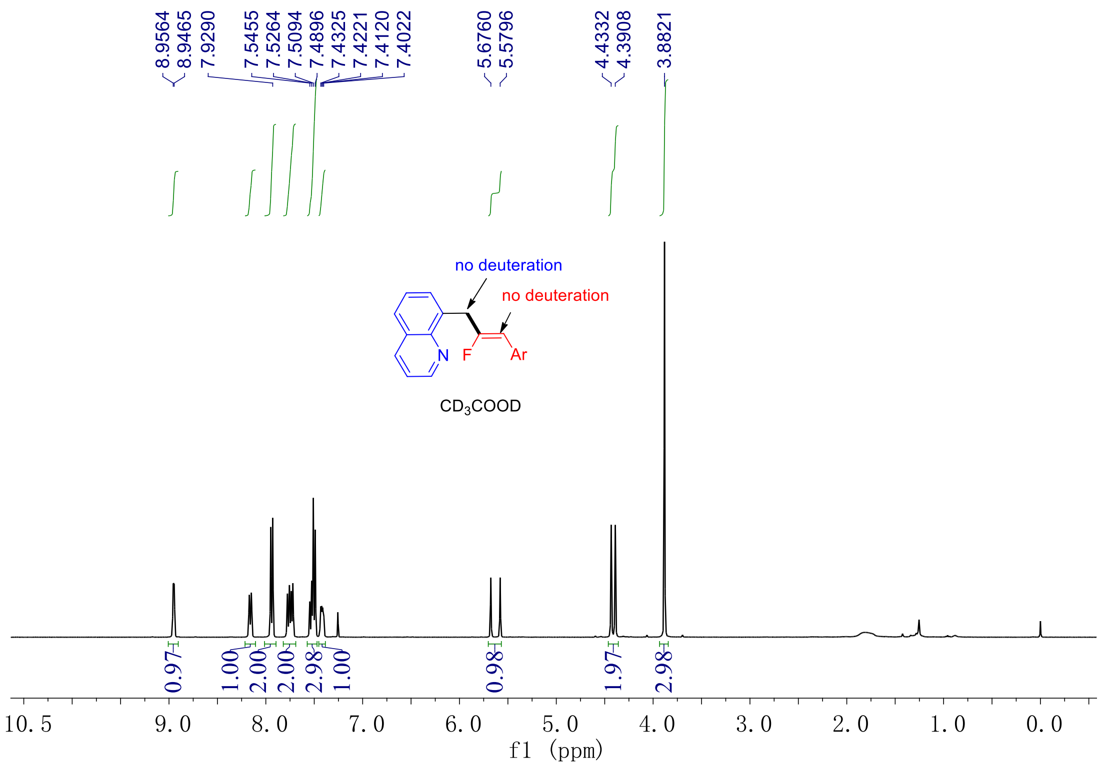
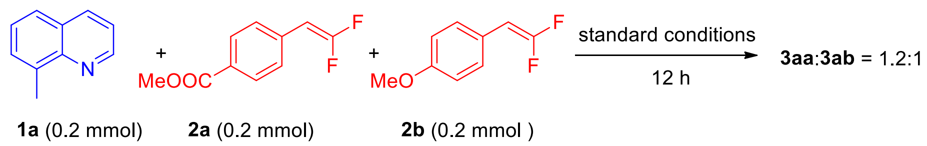
7.4414
7.4308
5.6882
5.5921
4.4405
4.3980
3.8914
no deuteration
no deuteration
N
F
Ar
CD_3OD
1.00
1.00
1.96
2.01
1.18
1.05
2.02
2.99
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

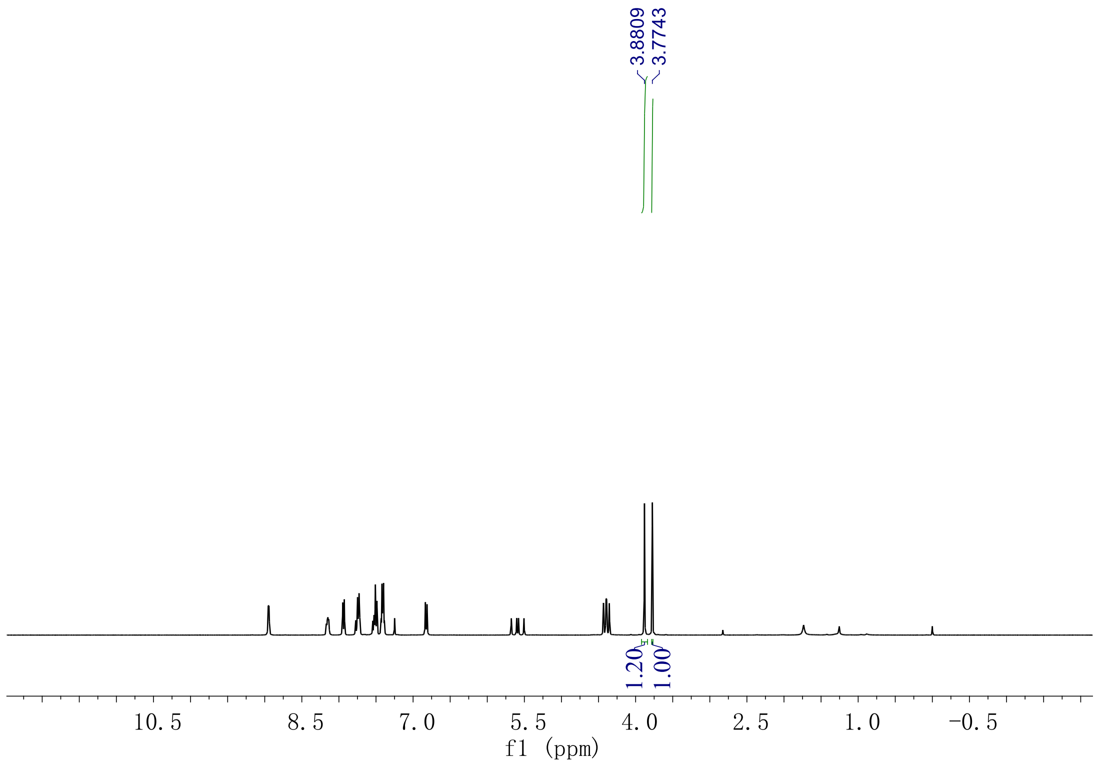


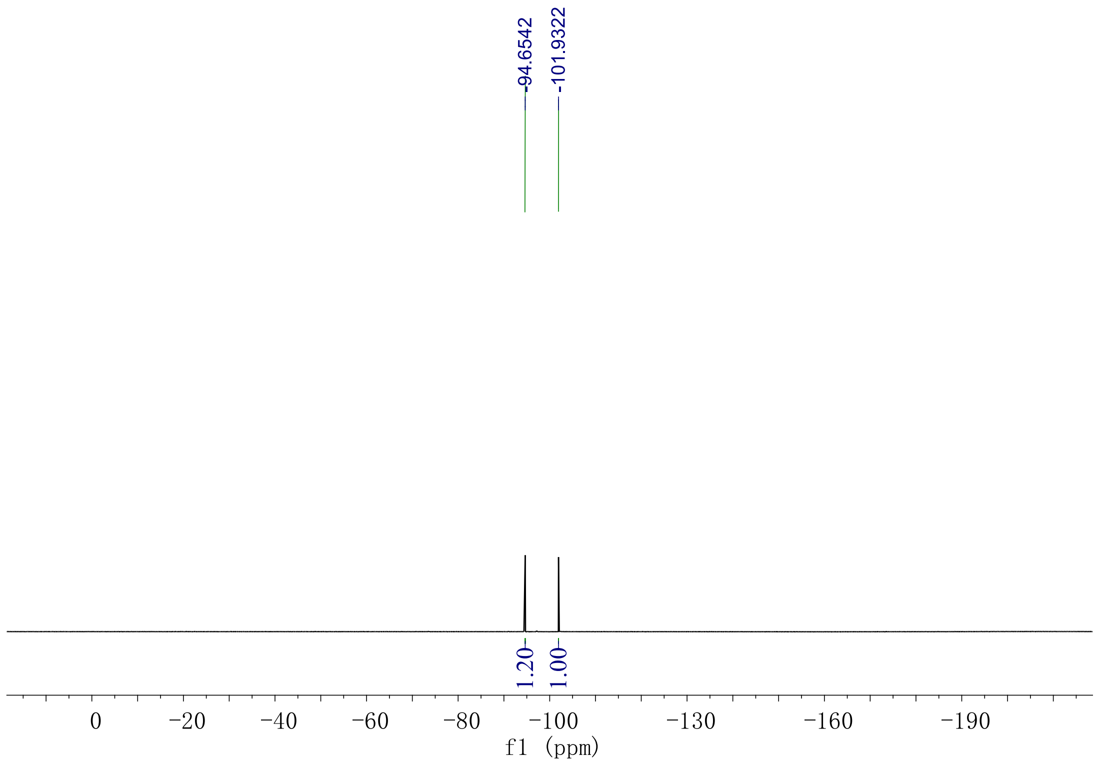


(b) Competition Reaction



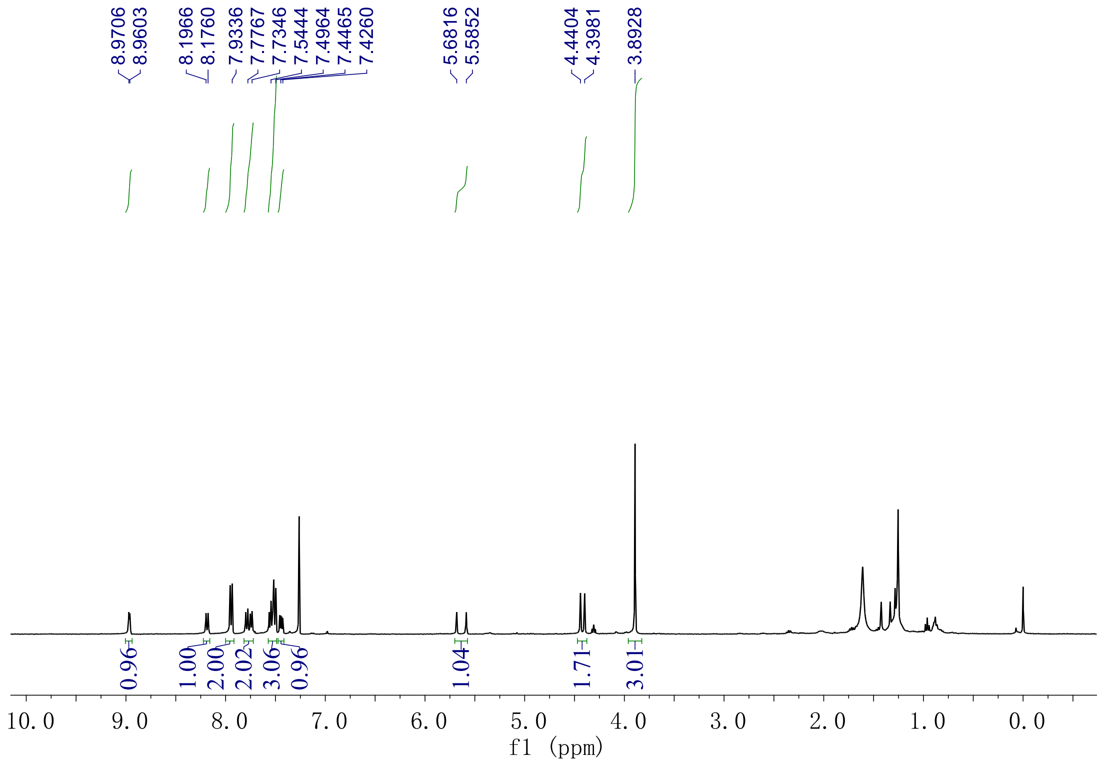
8-Methylquinoline **1a** (0.2 mmol), *gem*-difluoroalkene **2a** (0.2 mmol), **2b** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (100 mg) were dissolved in TFE (2 mL) in a pressure tube under N_2 atmosphere. The reaction mixture was stirred at 45 °C for 12 h. After that, the solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using PE/EA to afford **3aa** and **3ab**, which were characterized by ^1H NMR spectroscopy.





(c) KIE Study

Two pressure tubes were separately charged with **1a** or **1a**-d_3 (0.1 mmol), and to each tube was added *gem*-difluoroalkene **2a** (0.15 mmol) $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (50 mg) were dissolved in TFE (1 mL) in a pressure tube under N_2 atmosphere. The two reaction mixtures were stirred side by side in an oil bath preheated at 45 °C for 5 min. The resulting mixtures in the two tubes were rapidly combined and the solvent was rapidly removed under reduced pressure. The resulting residue was purified by silica gel chromatography using EA/PE to afford the rude products. The KIE value was determined to be k_H/k_D= 5.9 on the basis of ^{1}H NMR analysis.



(d) Synthetic method of 2 mmol scale

7-Bromo-8-methylquinoline **1q** (2.0 mmol), *gem*-difluoroalkene **2a** (3.0 mmol), $[Cp^*RhCl_2]_2$ (3 mol%), $AgNTf_2$ (12 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (1.0 g), and TFE (20 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 45 ºC for 24 h. After the solvent was removed under reduced pressure, the residue was purified by silica gel chromatography using PE/EA (40:1) to afford the product **3qa** in 60% (480.6 mg).

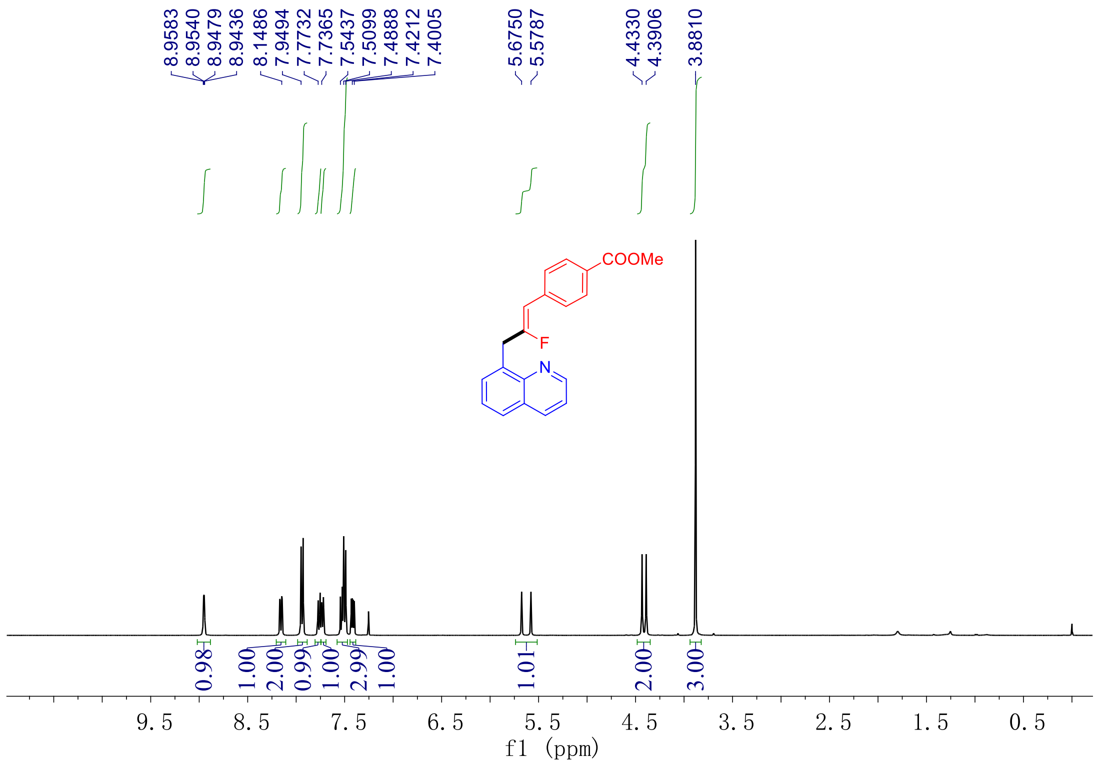
V. References

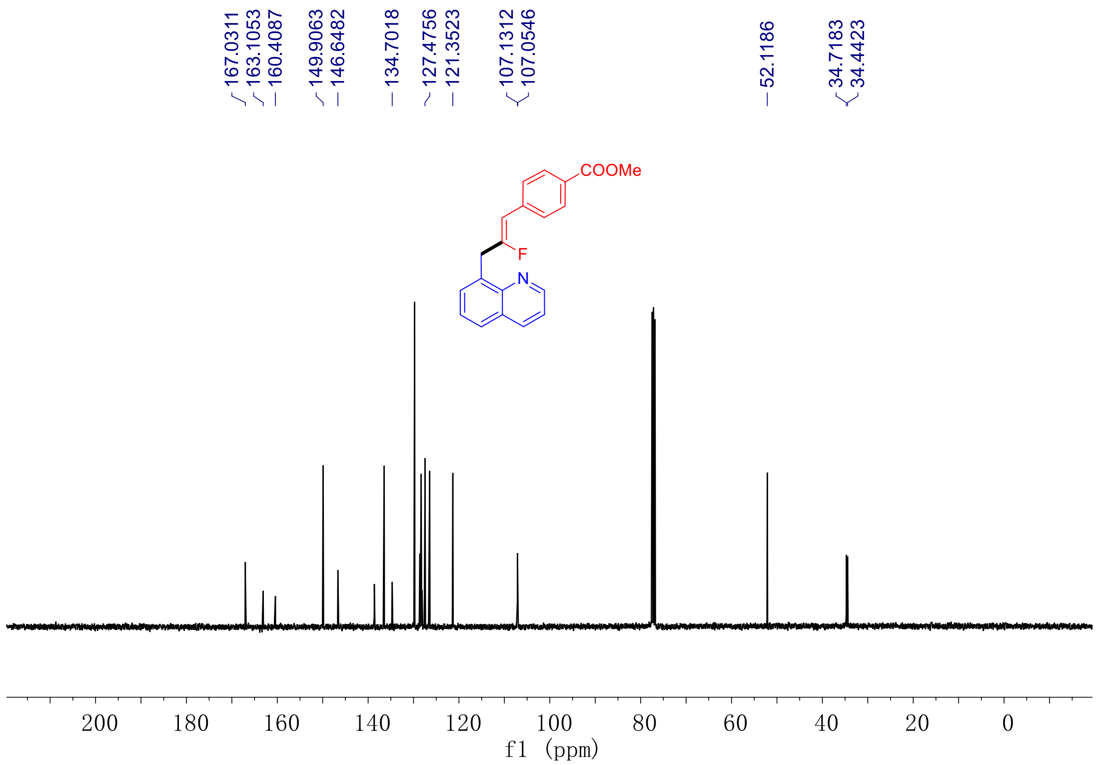
(1) (a) P. Evans, P. Hogg, R. Grigg, M. Nurnabi, J. Hinsley, V. Sridharan, S. Suganthan, S. Korn, S. Collard and J. E. Muir, *Tetrahedron*, 2005, **61**, 9696; (b) N. Gandhamsetty, S. Joung, S.-W. Park, S. Park and S. Chang, *J. Am. Chem. Soc*., 2014, **48**, 16780. (c) T. M. Heidelbaugh, P. X. Nguyen, K. Chow and M. E. Garst, WO2008/88937 A1, 2008.

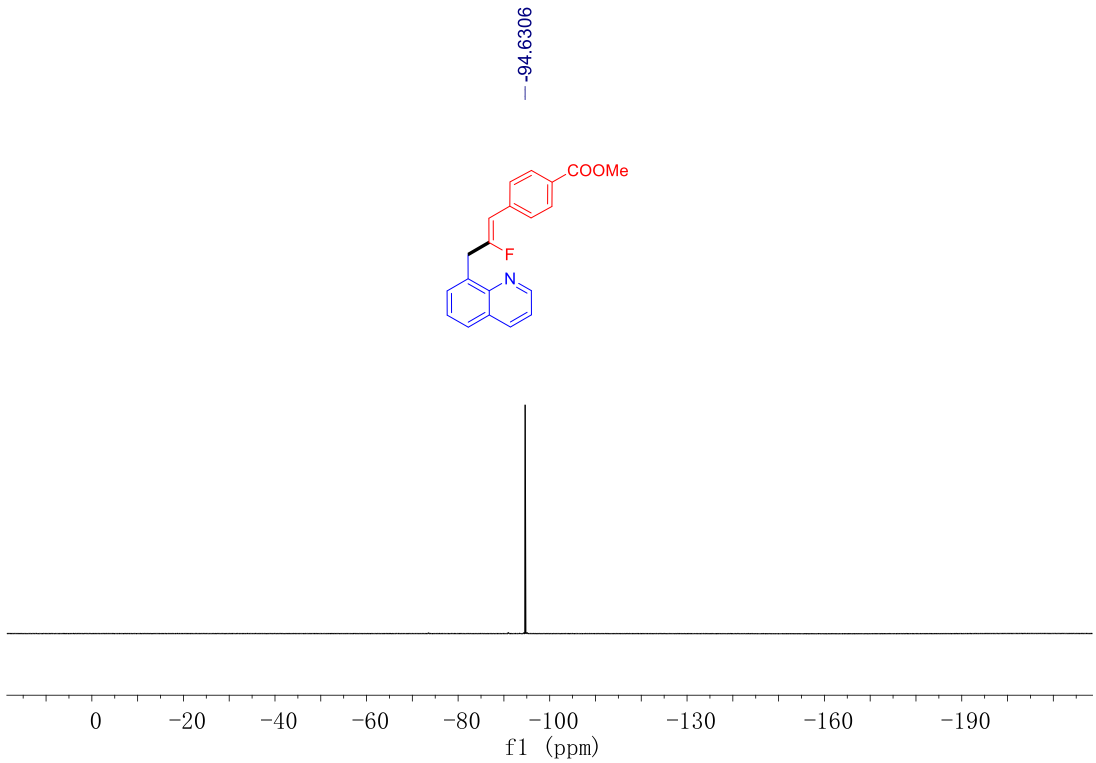
(2) C. S. Thomoson, H. Martinez and W. R. D. Jr, *J. Fluorine Chem.,* 2013, **150***,* 53.

VI. NMR Spectra of Coupled Products

3aa







-94.6306
COOMe
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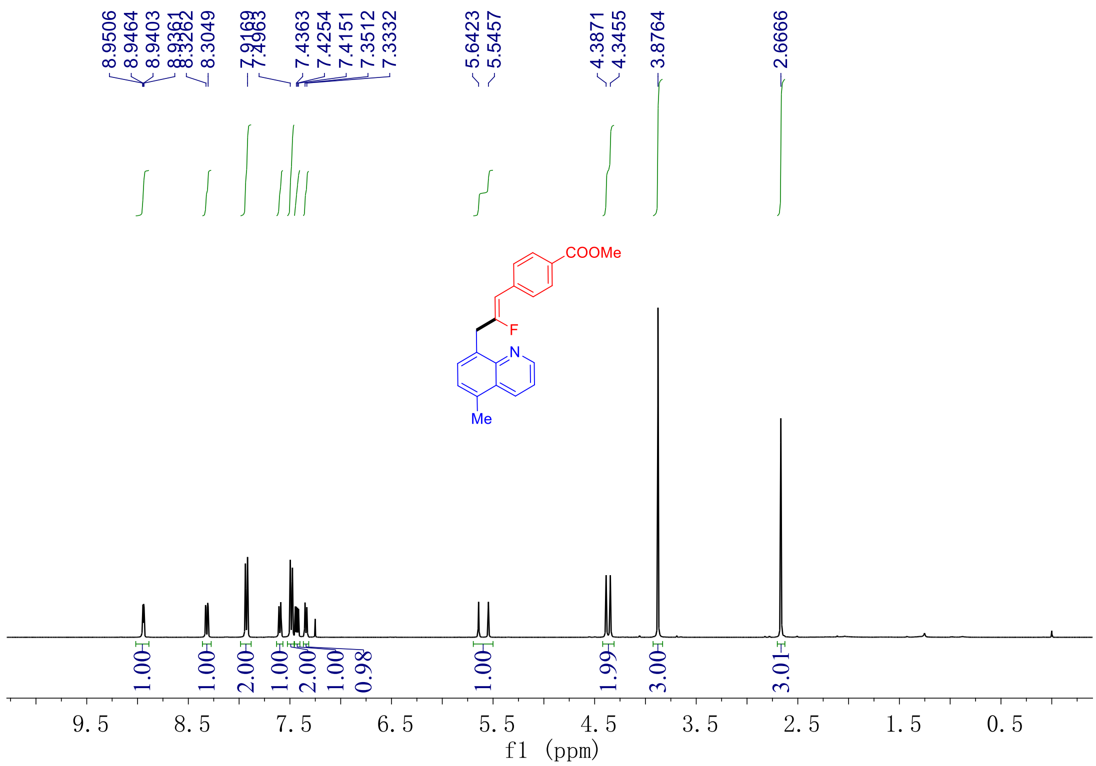
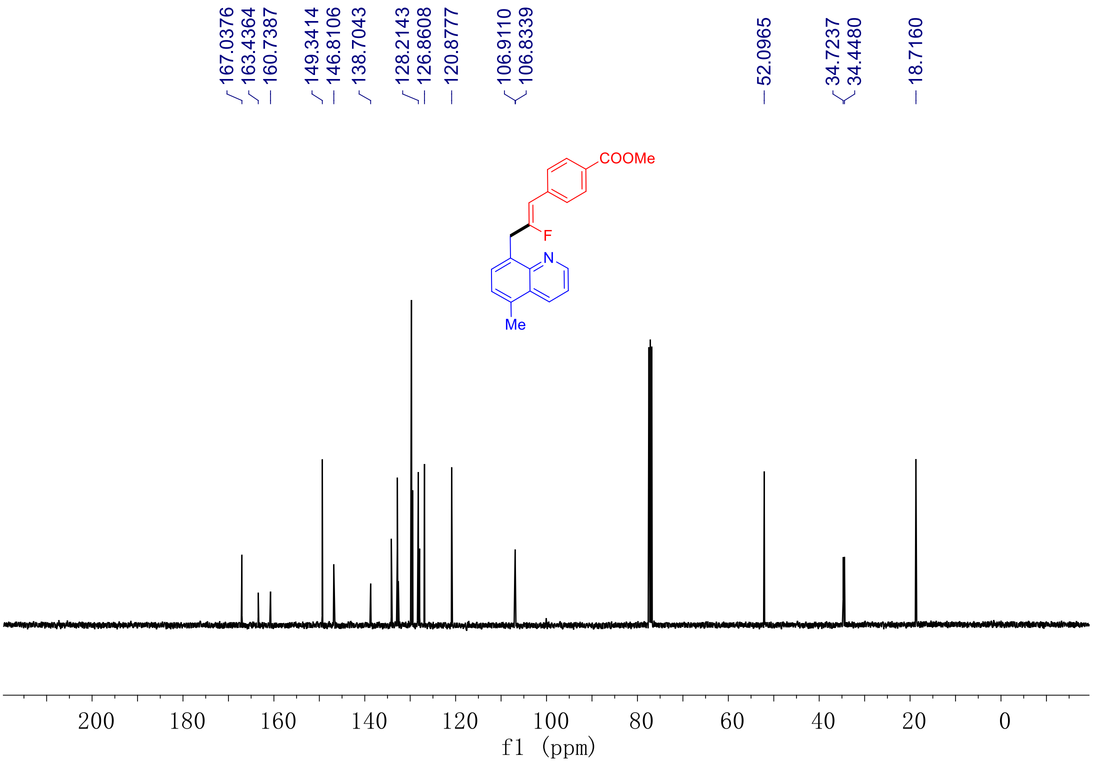
N
0
−20
−40
−60
−80
−100
−130
−160
−190
f1 (ppm)

3ba



8.9506
8.9464
8.9403
8.9361
8.3262
8.3049
7.9169
7.4953
7.4363
7.4254
7.4151
7.3512
7.3332
5.6423
5.5457
4.3871
4.3455
3.8764
2.6666
COOMe
F
N
Me
1.00
1.00
2.00
1.00
2.00
1.00
0.98
1.00
1.99
3.00
3.01
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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160.7387
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146.8106
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120.8777
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106.8339
52.0965
34.7237
34.4480
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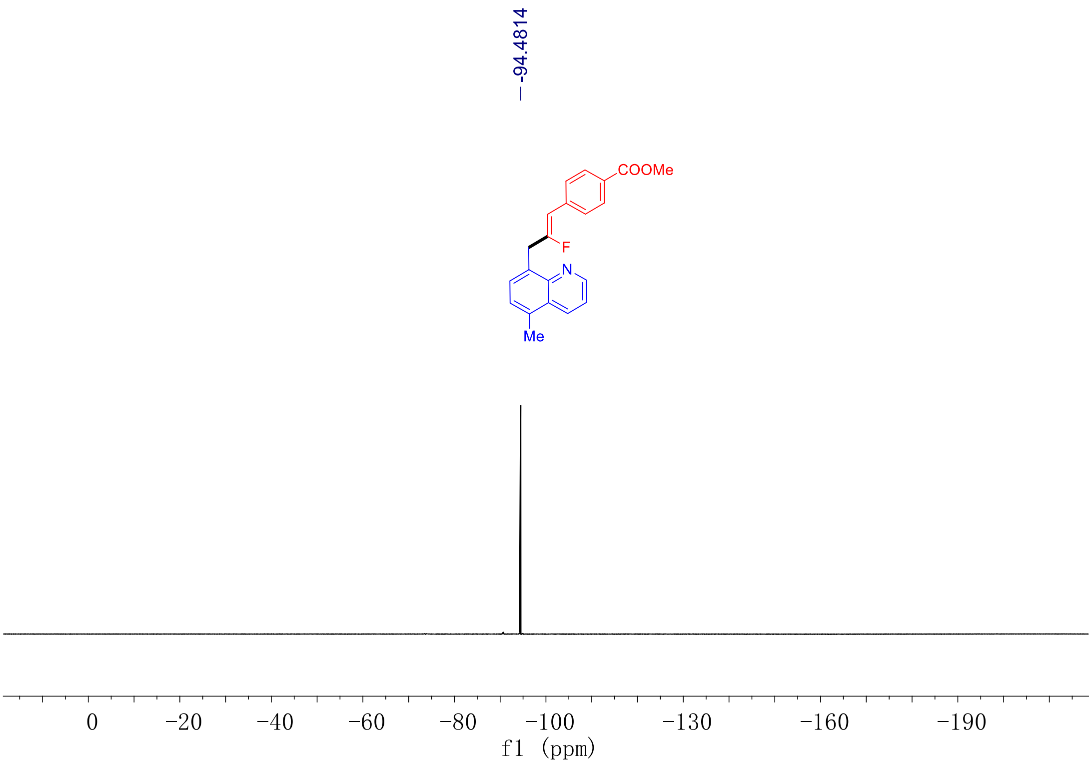
N
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Me
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-100
-130
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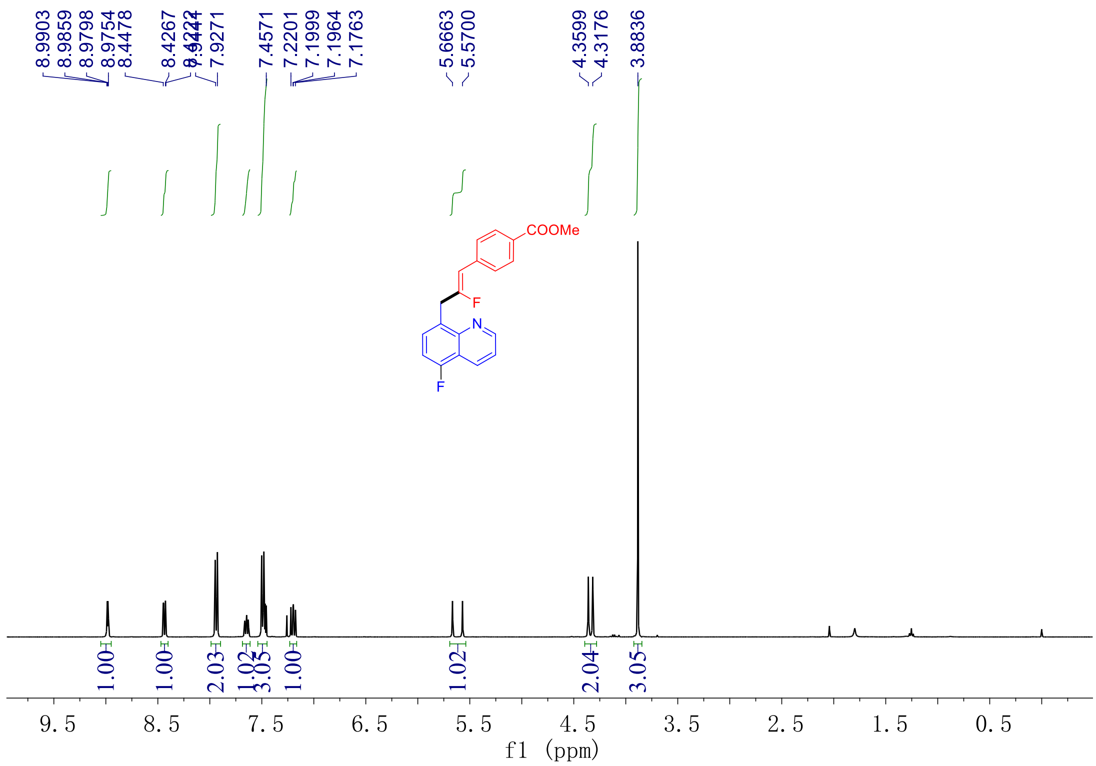
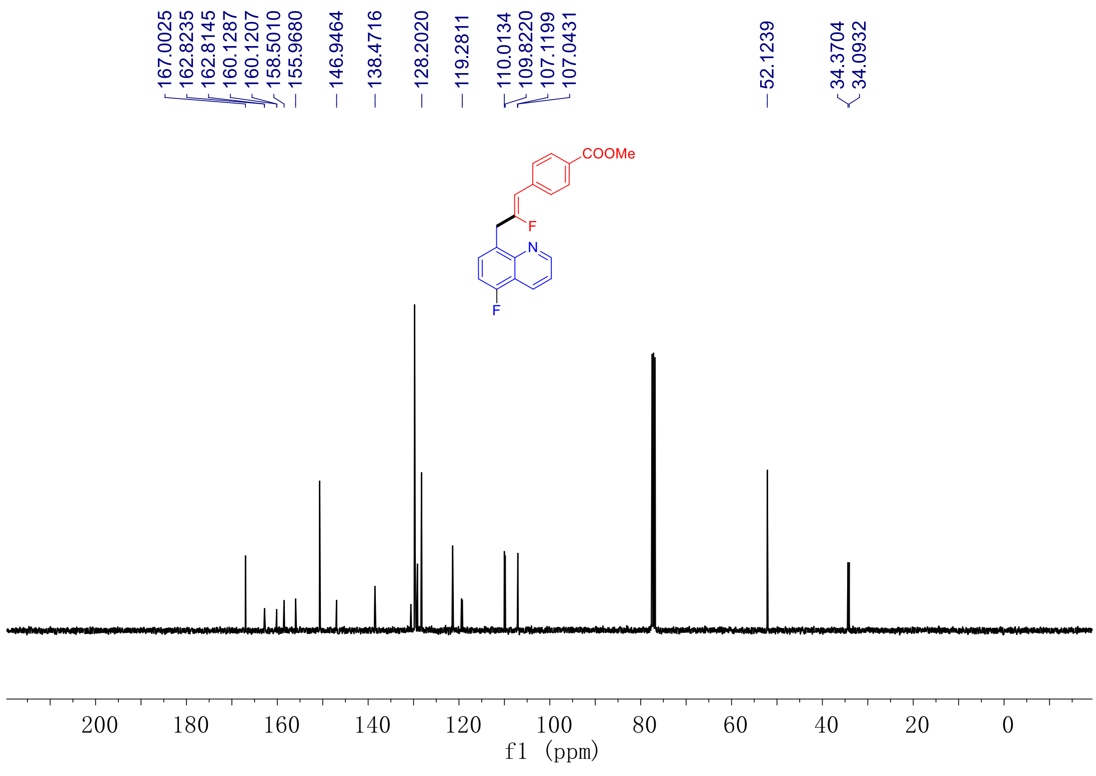
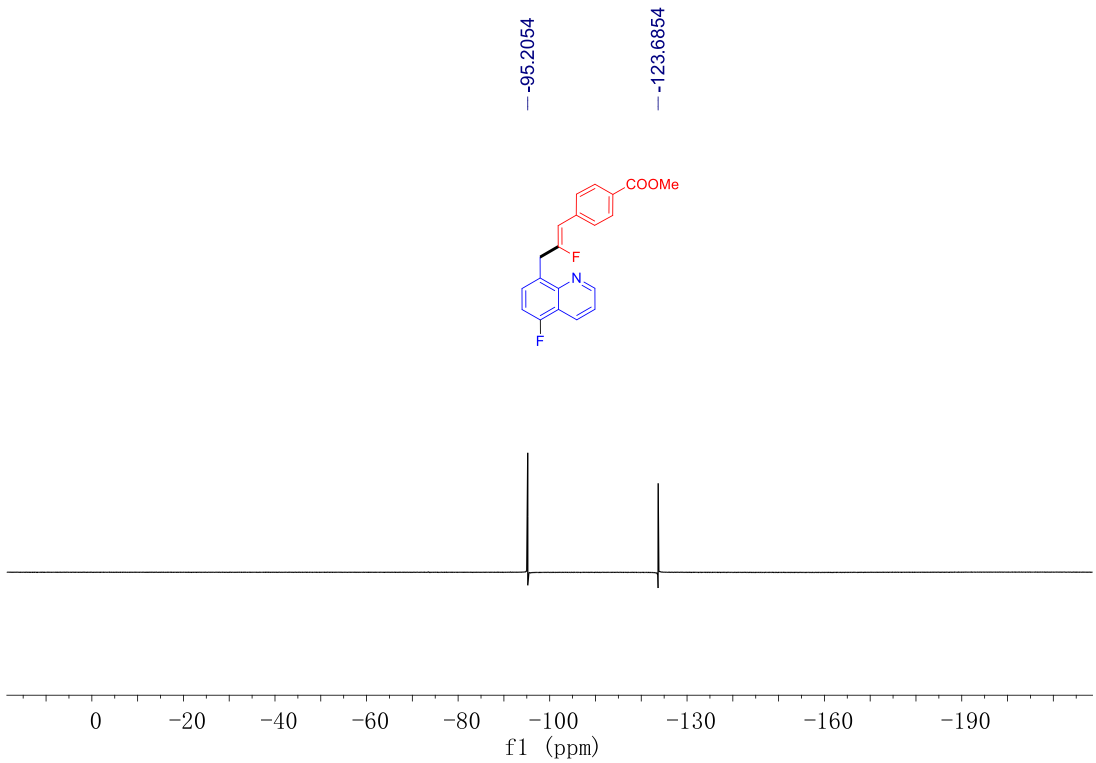
-190
f1 (ppm)

3ca



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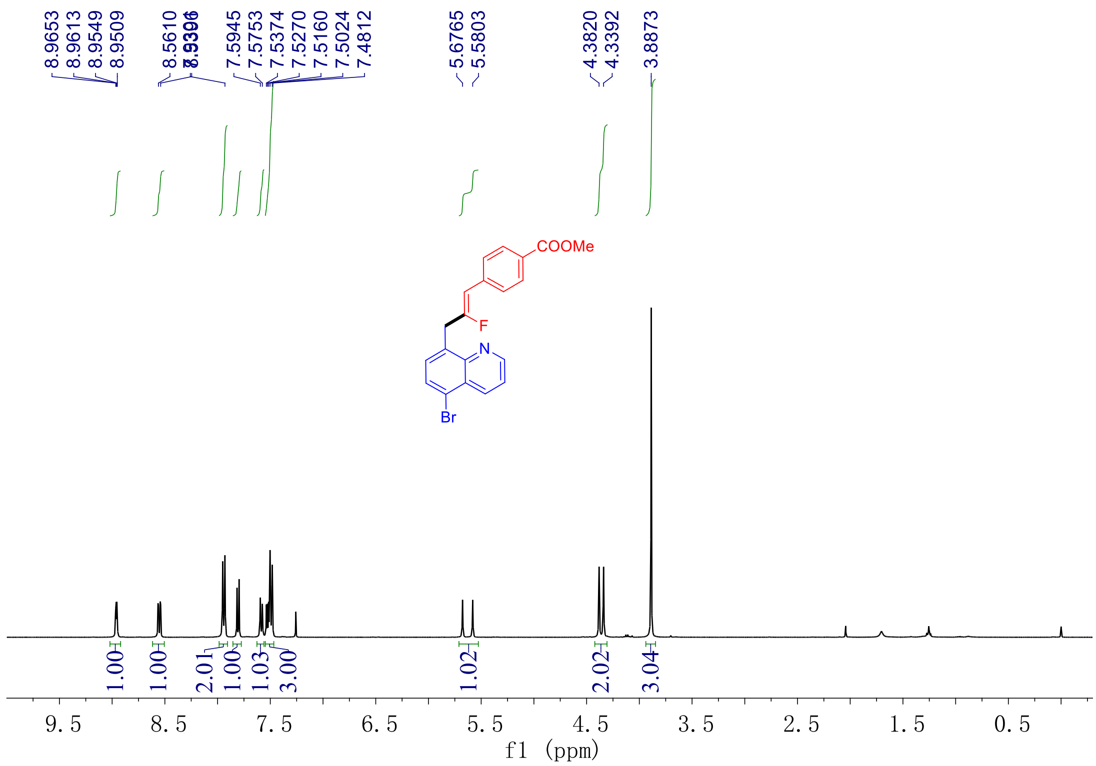
F
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3da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7.4812
5.6765
5.5803
4.3820
4.3392
3.8873
COOMe
F
N
Br
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1.00
2.01
1.00
1.03
3.00
1.02
2.02
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5.5
4.5
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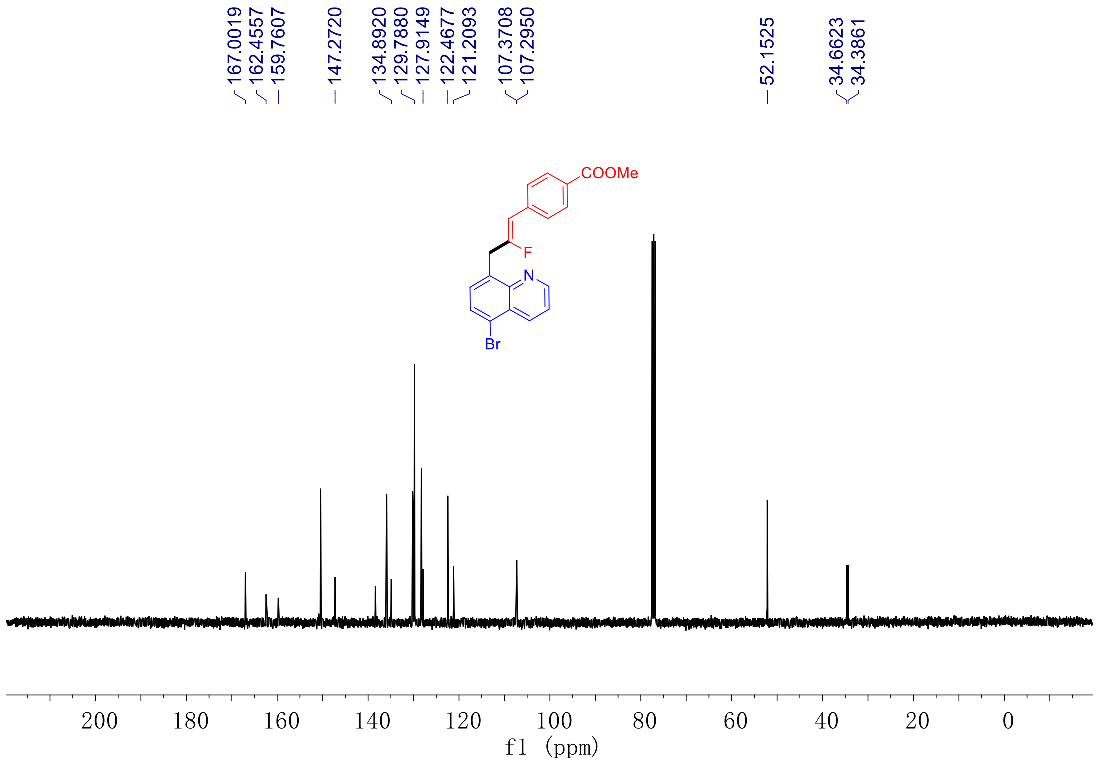
1.5
0.5
f1 (ppm)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52.1525
34.6623
34.3861
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N
Br
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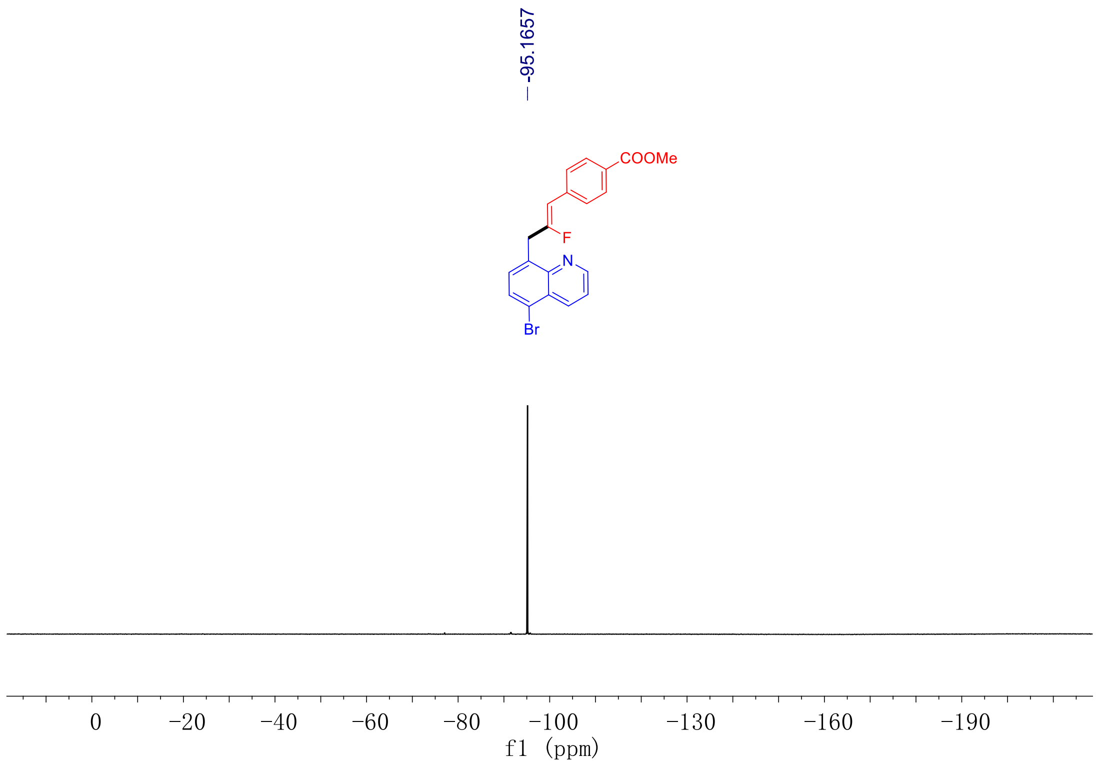
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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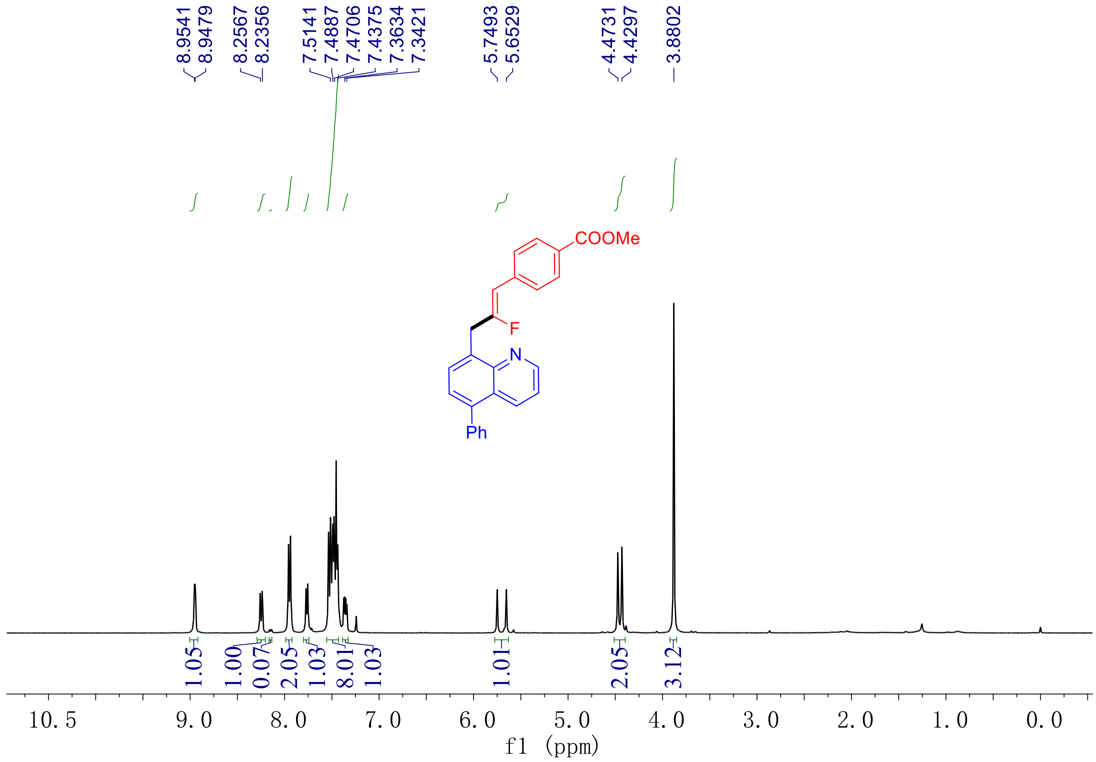
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5.6529
4.4731
4.4297
3.8802
COOMe
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N
Ph
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1.00
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2.05
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8.01
1.03
1.01
2.05
3.12
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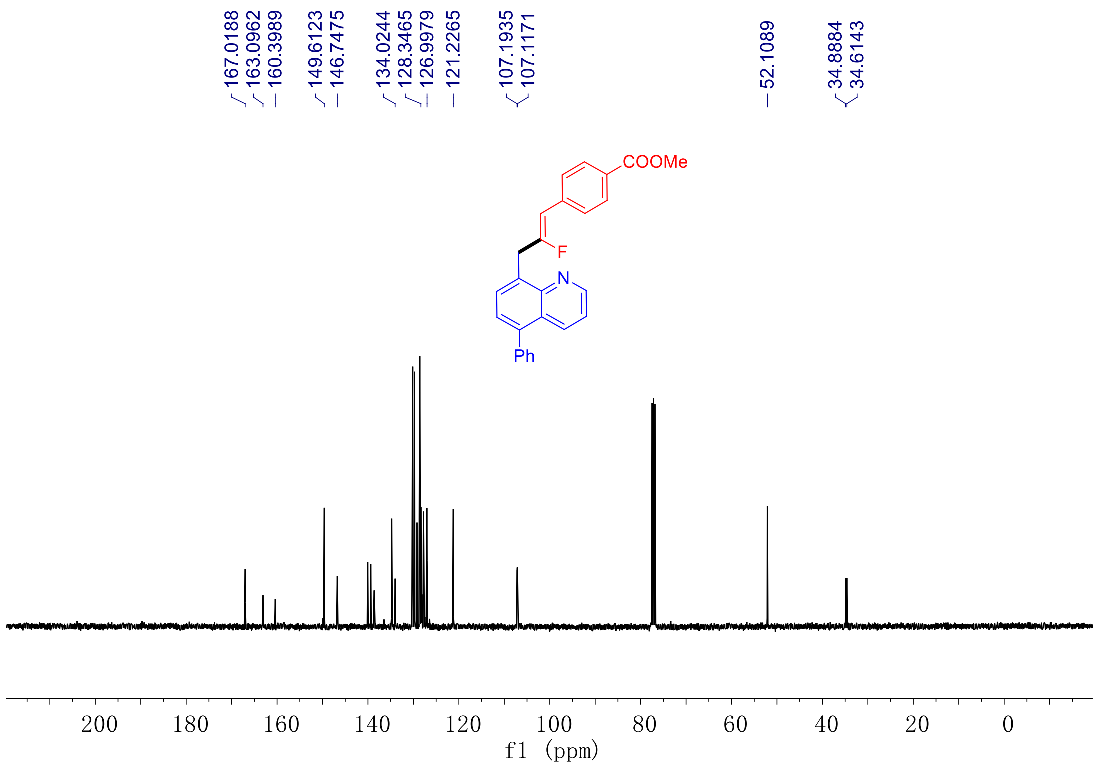
f1 (ppm)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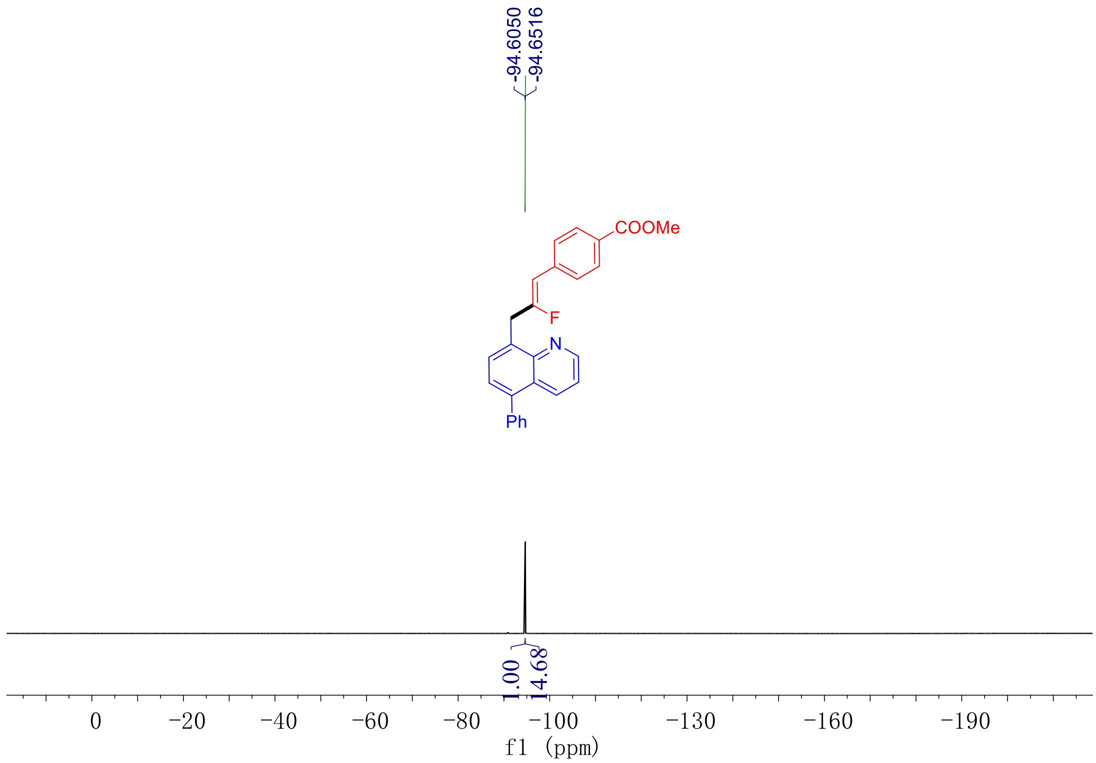
f1 (ppm)



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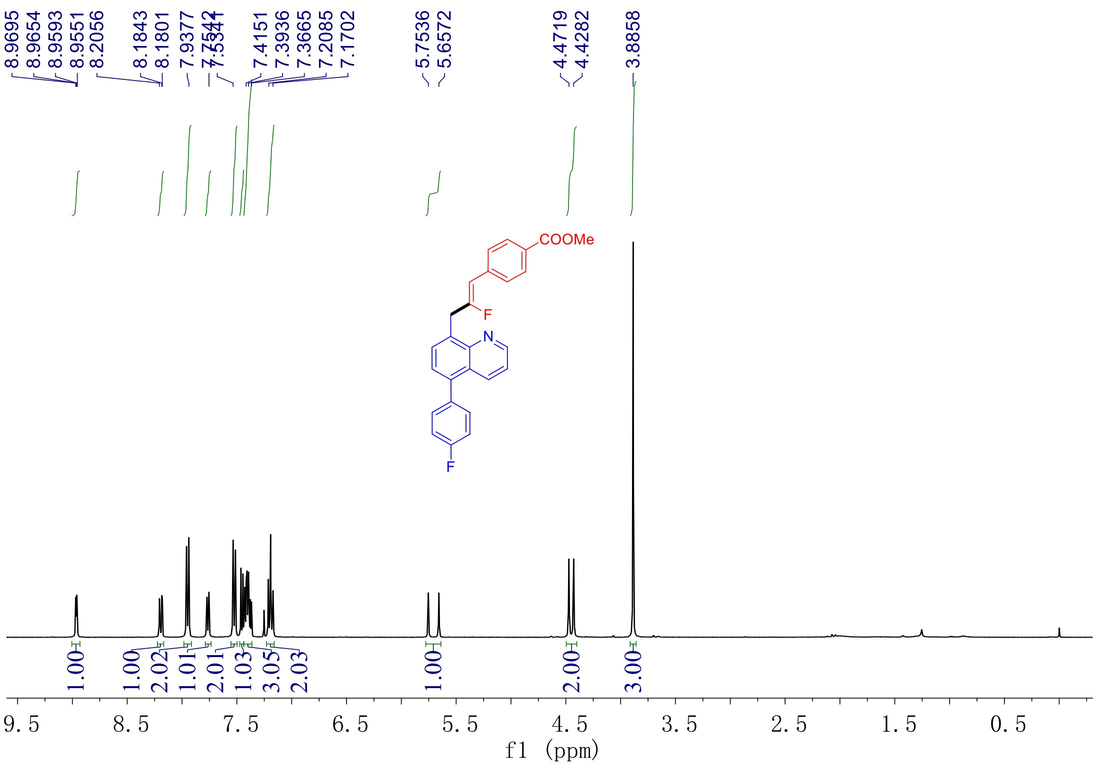

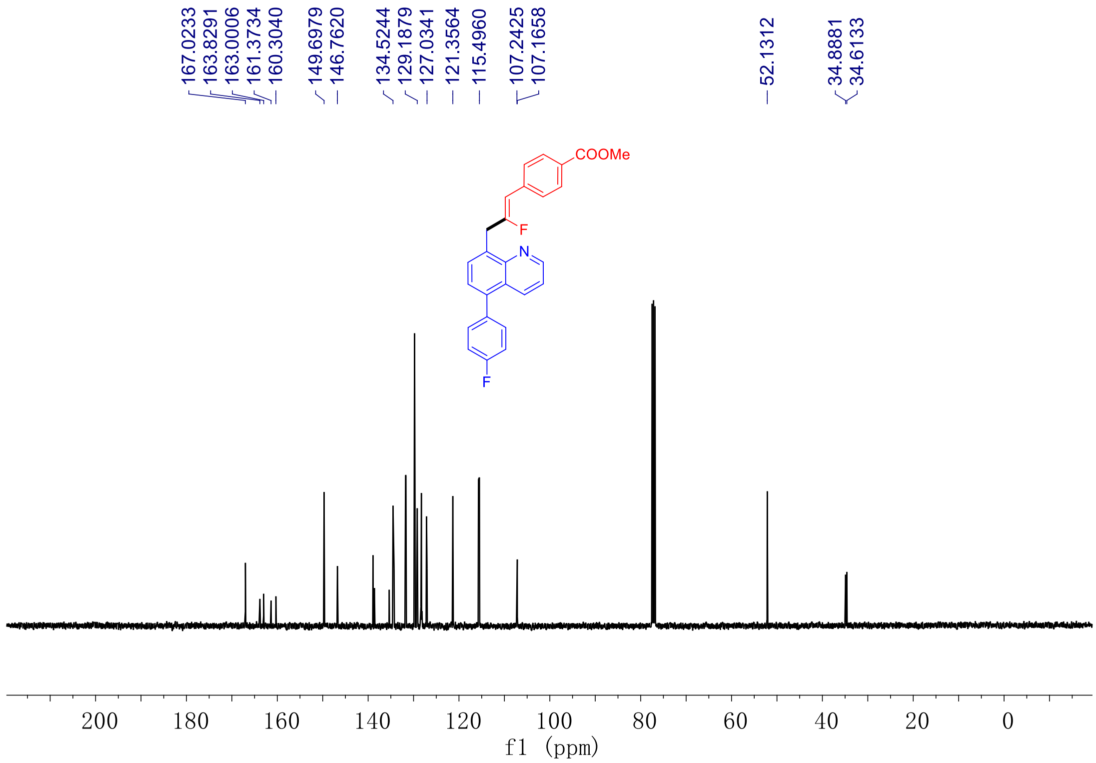
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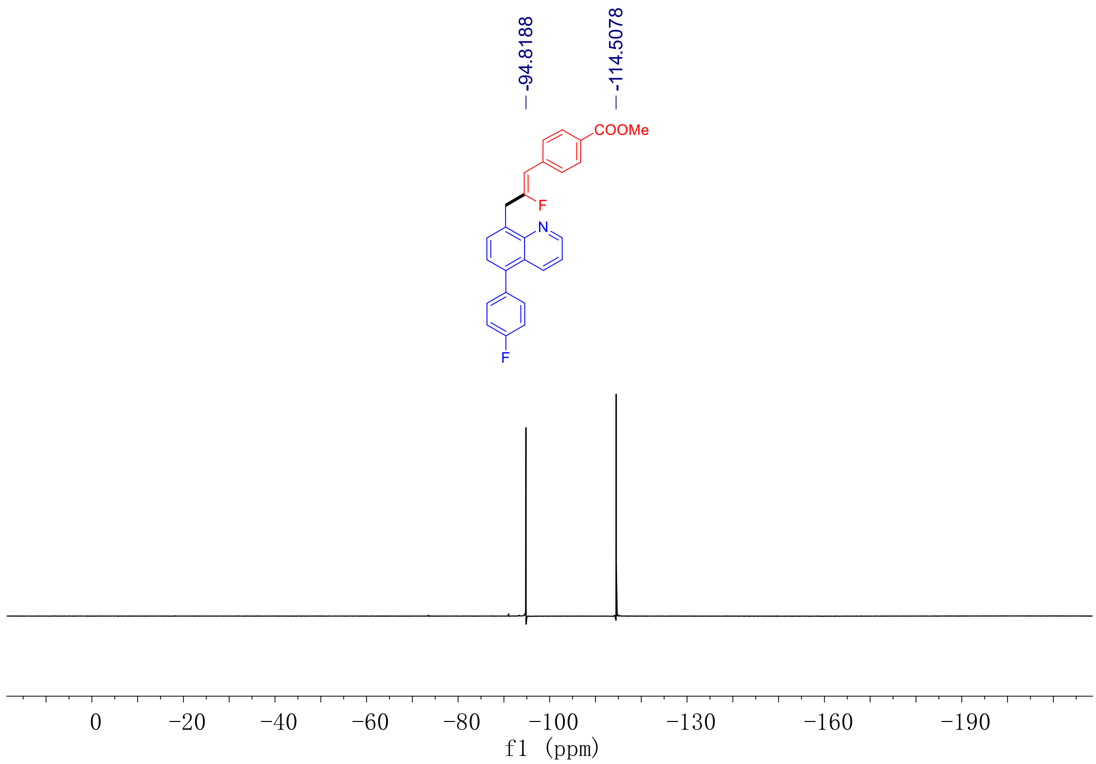
f1 (ppm)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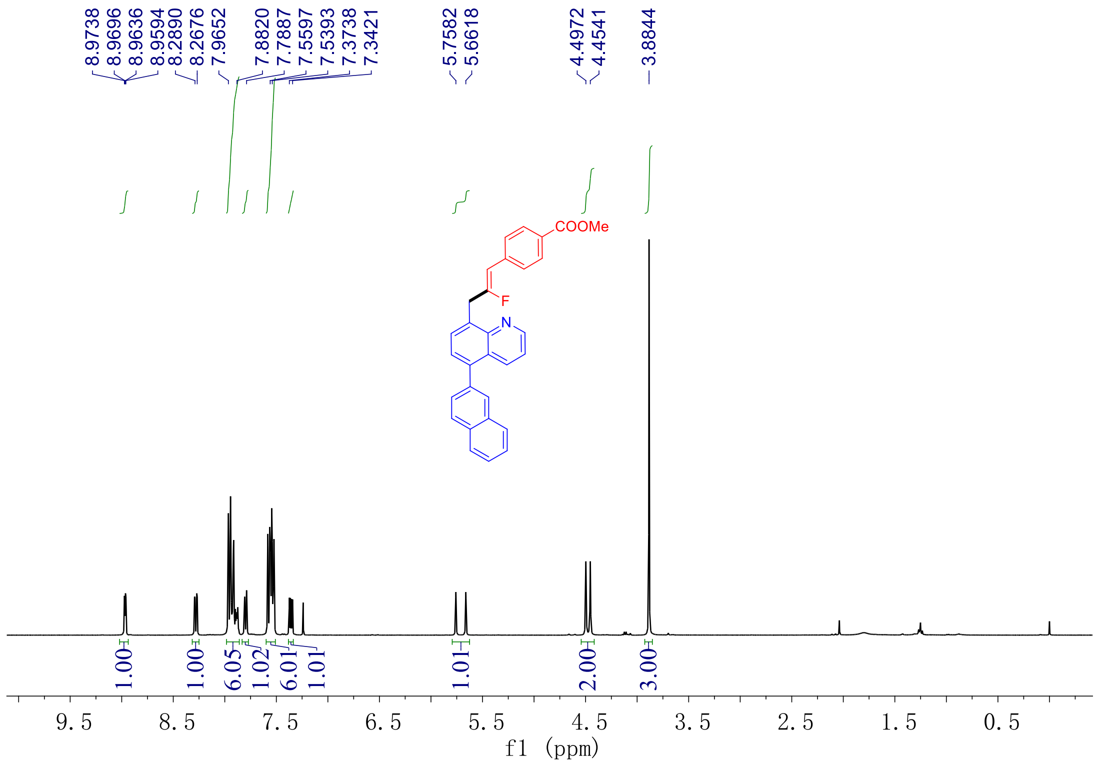
f1 (ppm)

3ga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COOMe
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N
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1.02
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1.01
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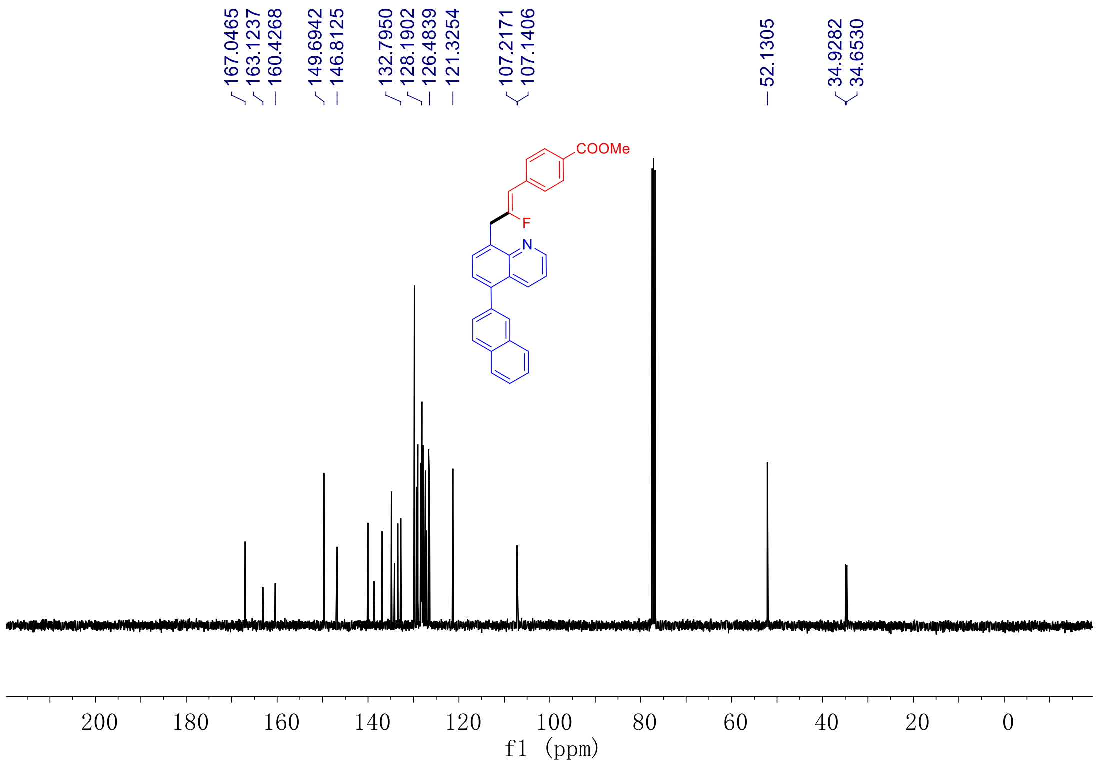
f1 (ppm)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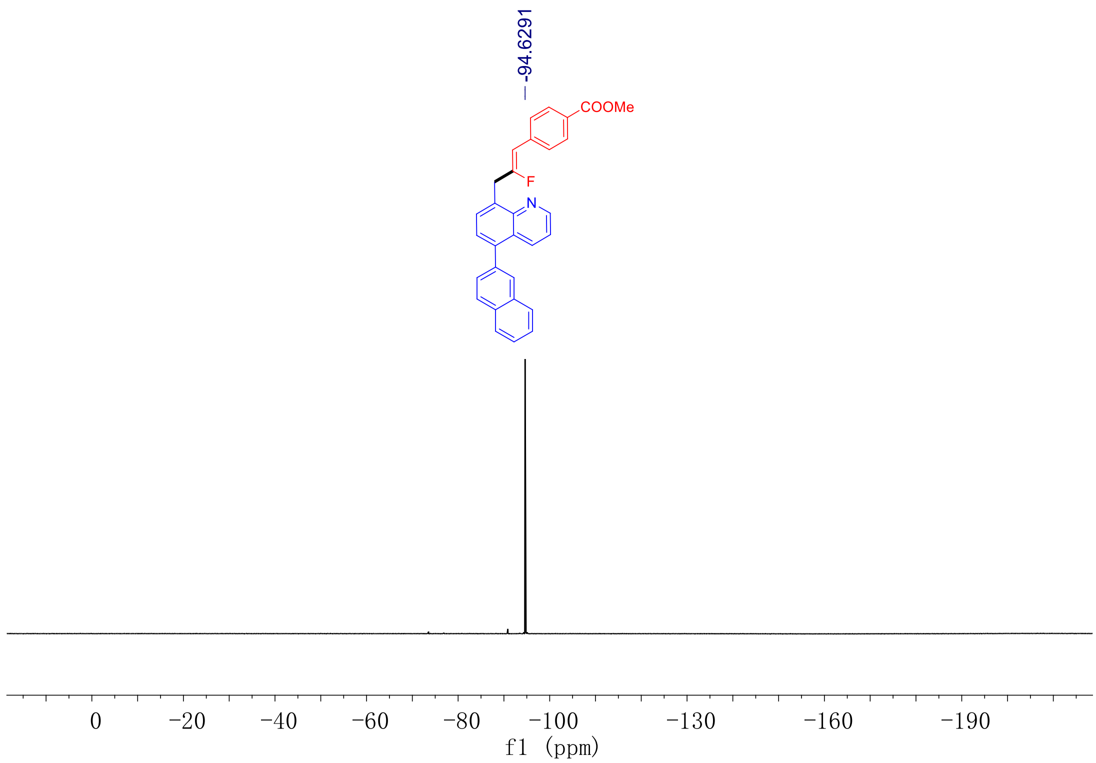
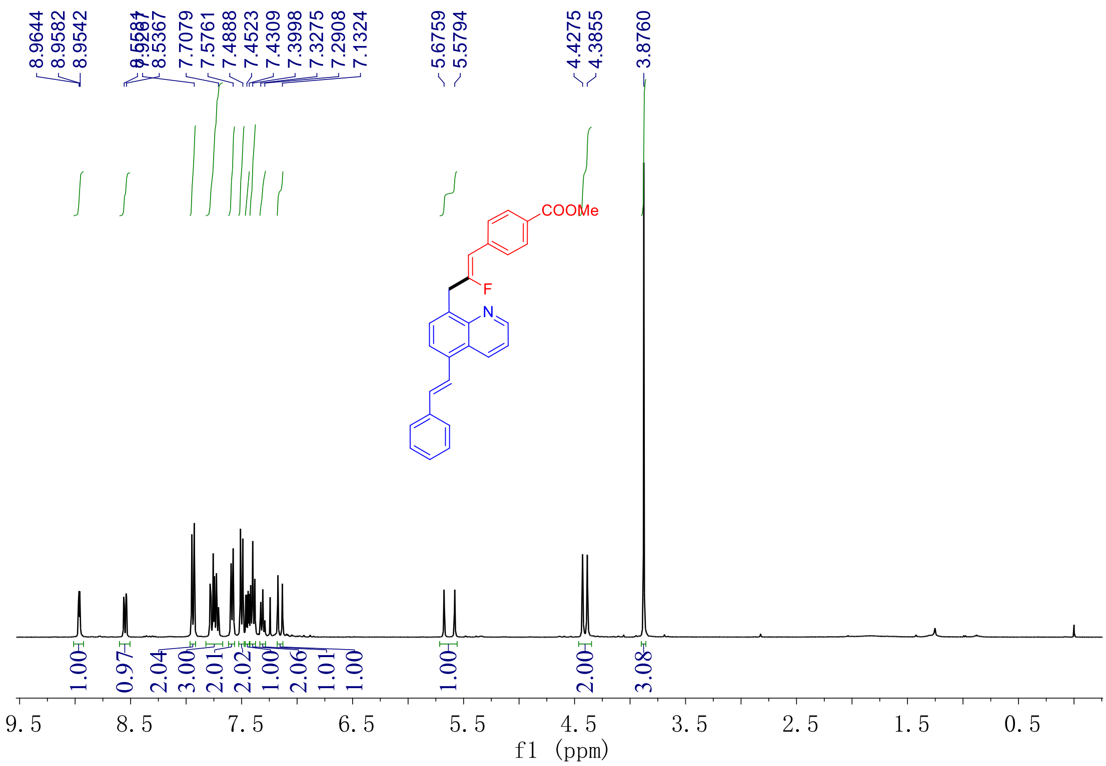
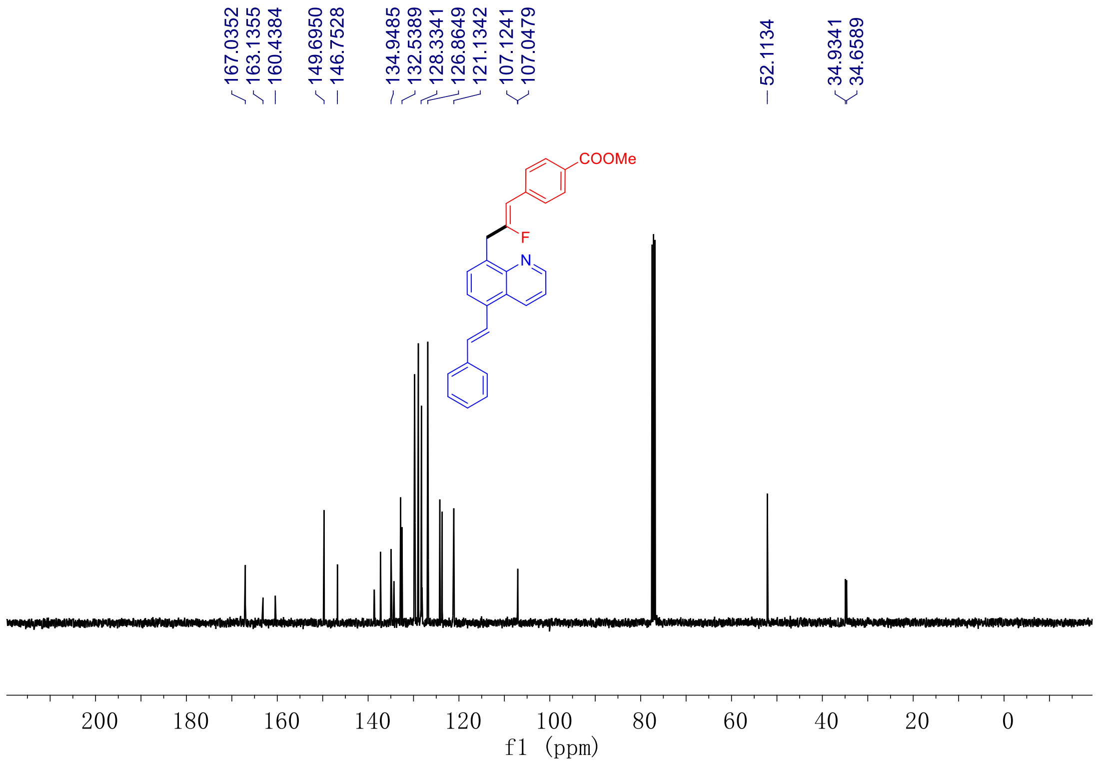


3ha





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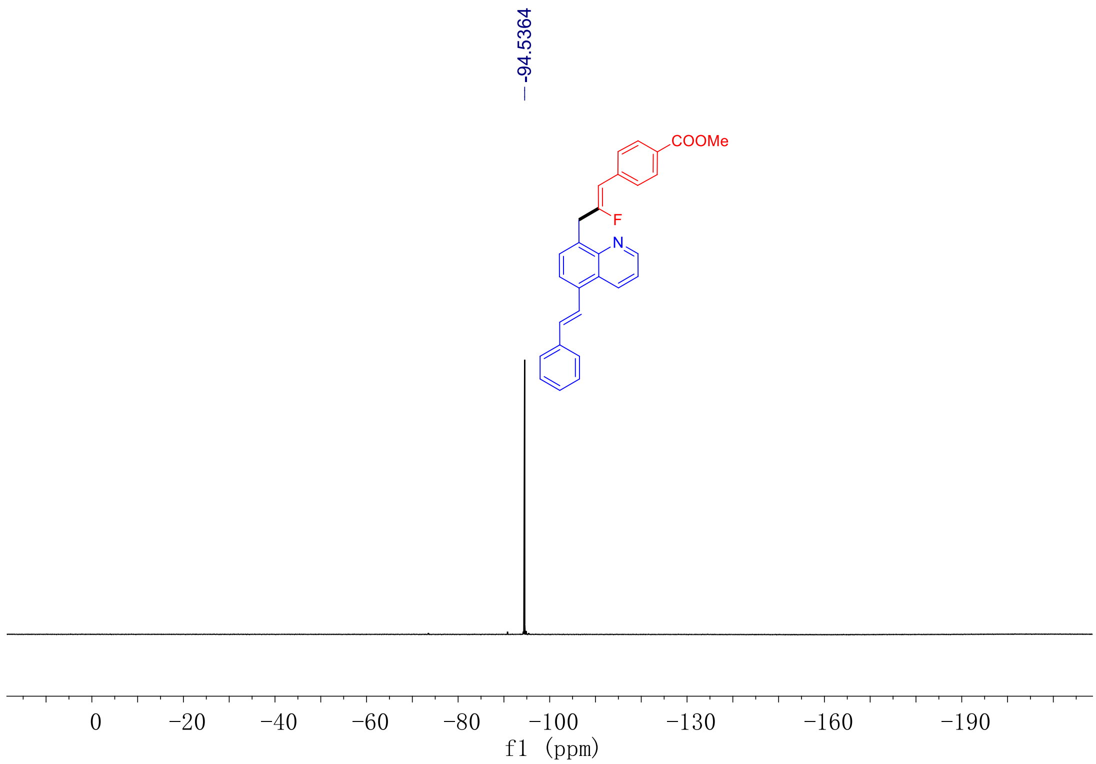
34.6589
COOMe
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



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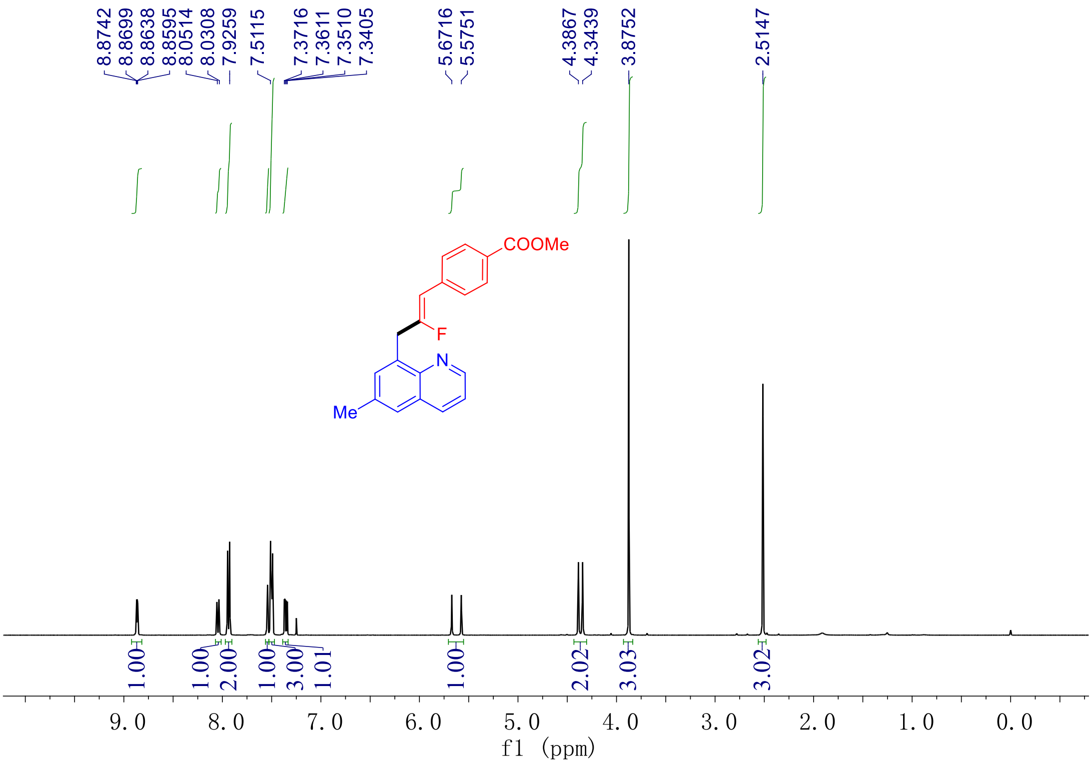
−130
−160
−190
f1 (ppm)

3ia



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7.9259
7.5115
7.3716
7.3611
7.3510
7.3405
5.6716
5.5751
4.3867
4.3439
3.8752
2.5147
COOMe
F
N
Me
1.00
1.00
2.00
1.00
3.00
1.01
1.00
2.02
3.03
3.02
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7.0
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5.0
4.0
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2.0
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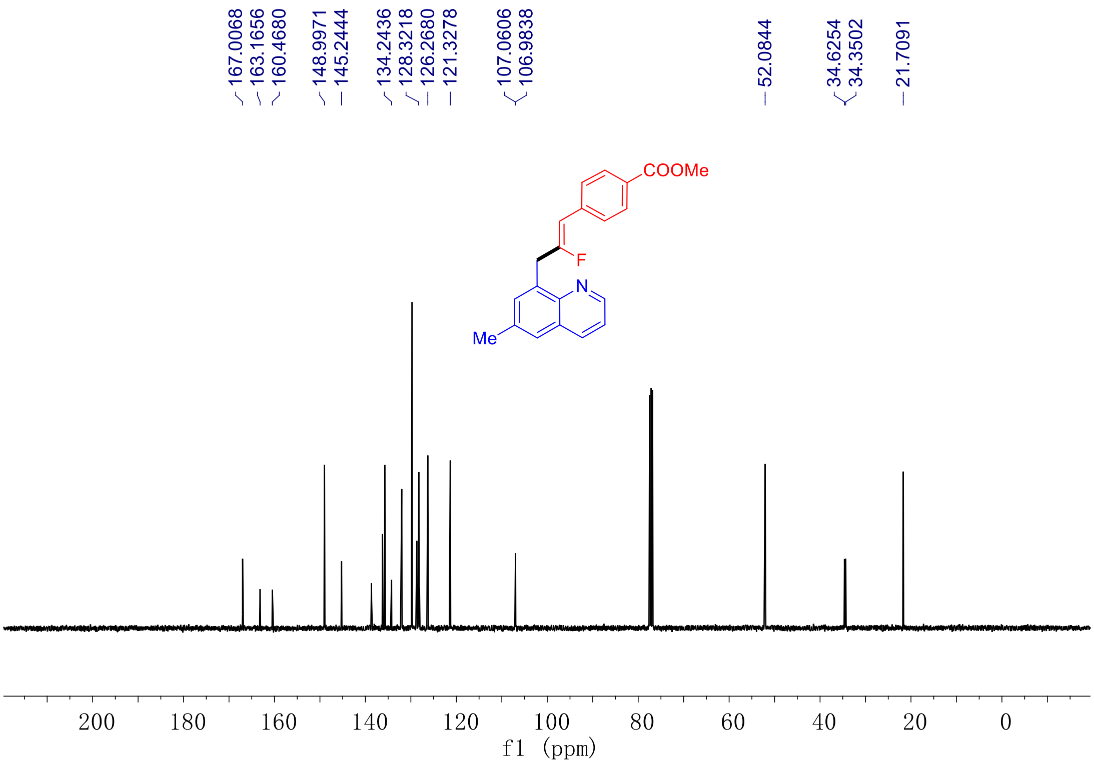
f1 (ppm)



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148.9971
145.2444
134.2436
128.3218
126.2680
121.3278
107.0606
106.9838
52.0844
34.6254
34.3502
21.7091
COOMe
F
N
Me
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180
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140
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100
80
60
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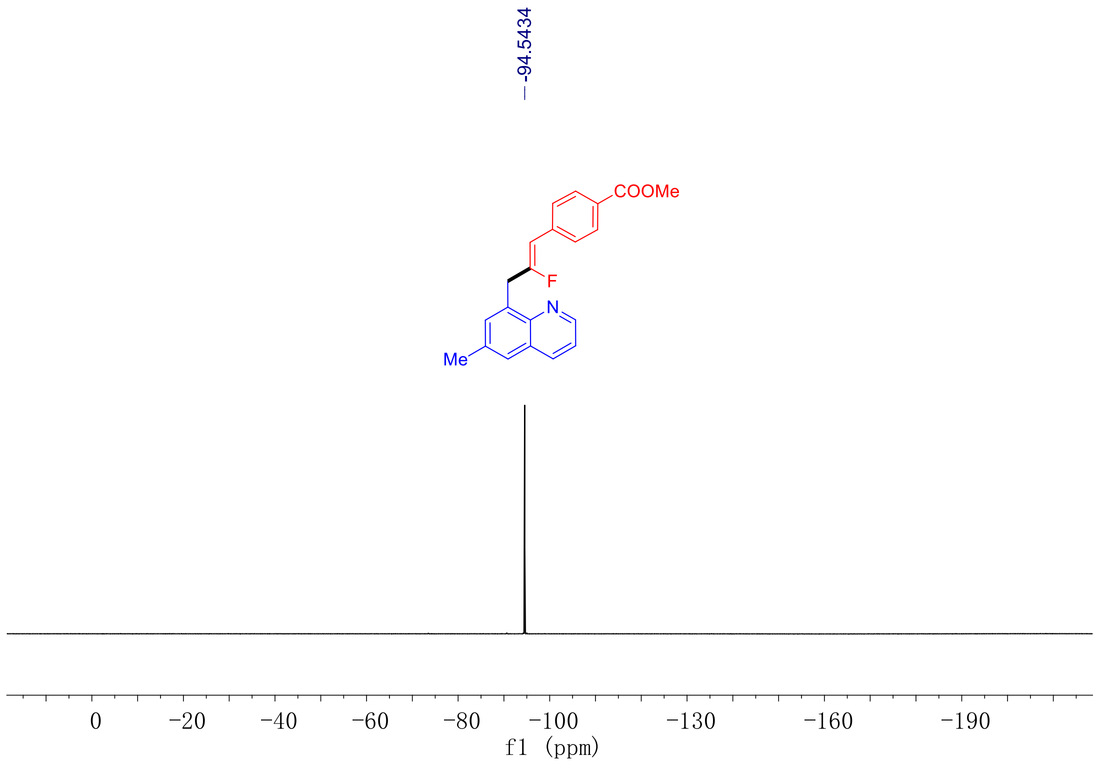
20
0
f1 (ppm)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F
N
Me
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−20
−40
−60
−80
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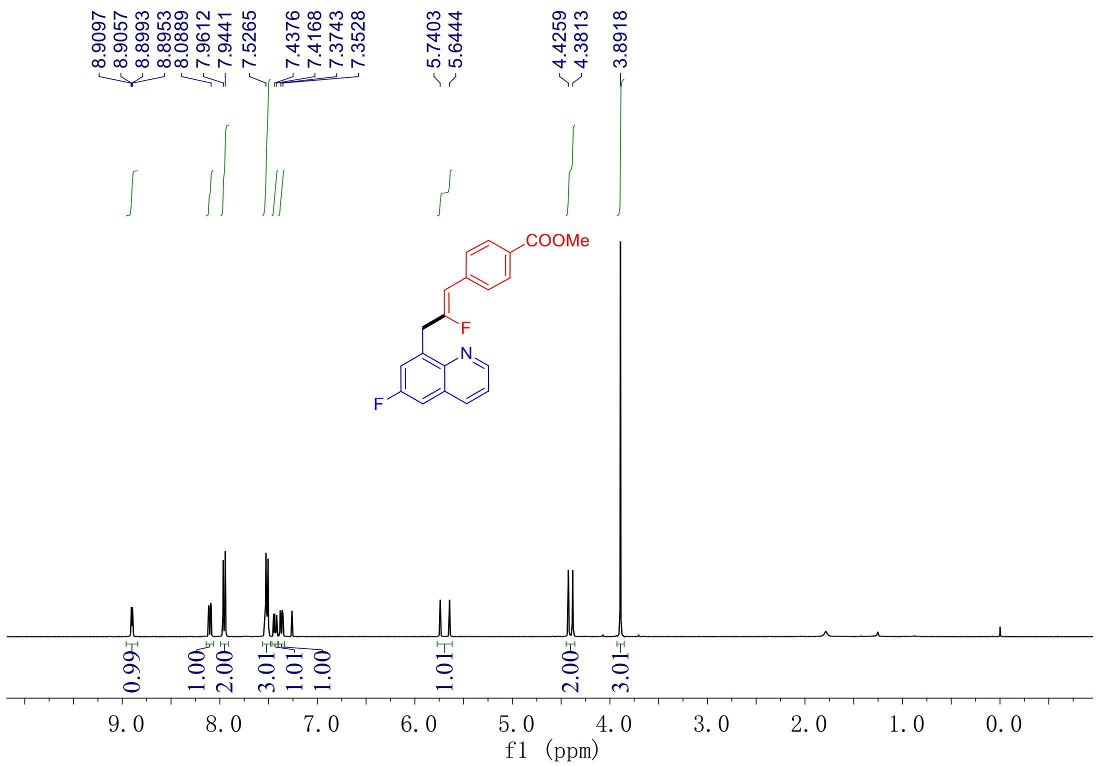
−130
−160
−190
f1 (ppm)

3ja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8.9057
8.8993
8.8953
8.0889
7.9612
7.9441
7.5265
7.4376
7.4168
7.3743
7.3528
5.7403
5.6444
4.4259
4.3813
3.8918
COOMe
F
N
F
0.99
1.00
2.00
3.01
1.01
1.00
1.01
2.00
3.01
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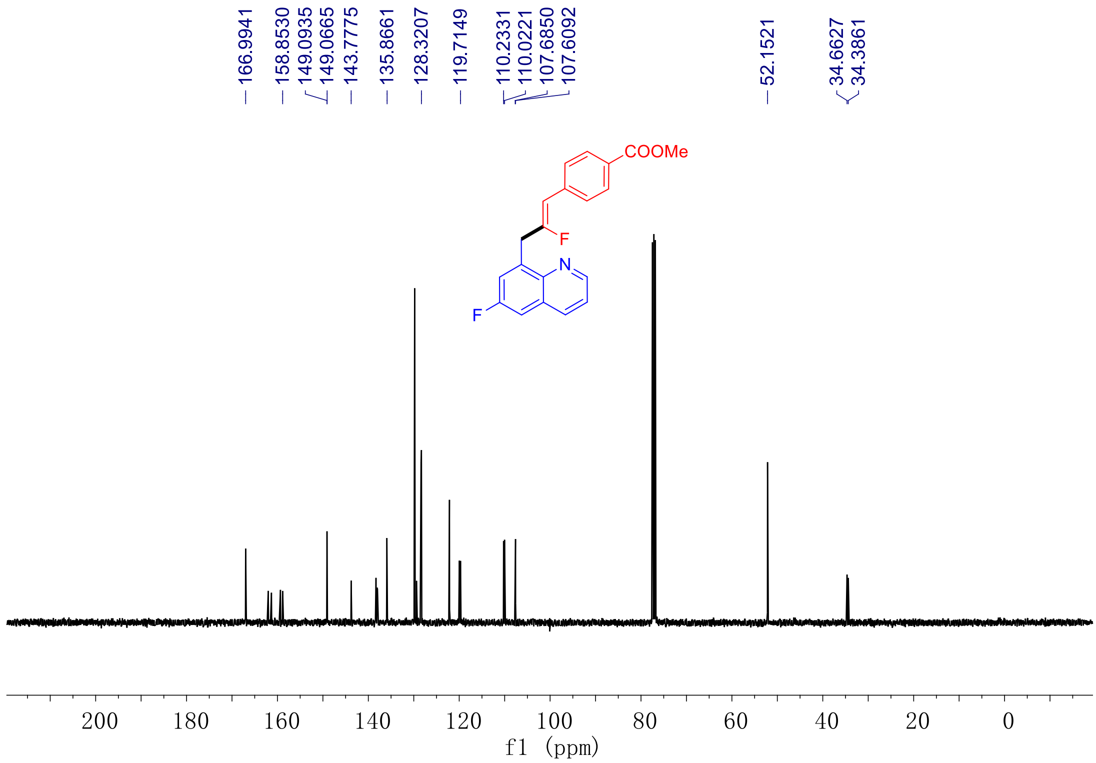
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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143.7775
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128.3207
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110.0221
107.6850
107.6092
52.1521
34.6627
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COOMe
F
N
F
200
180
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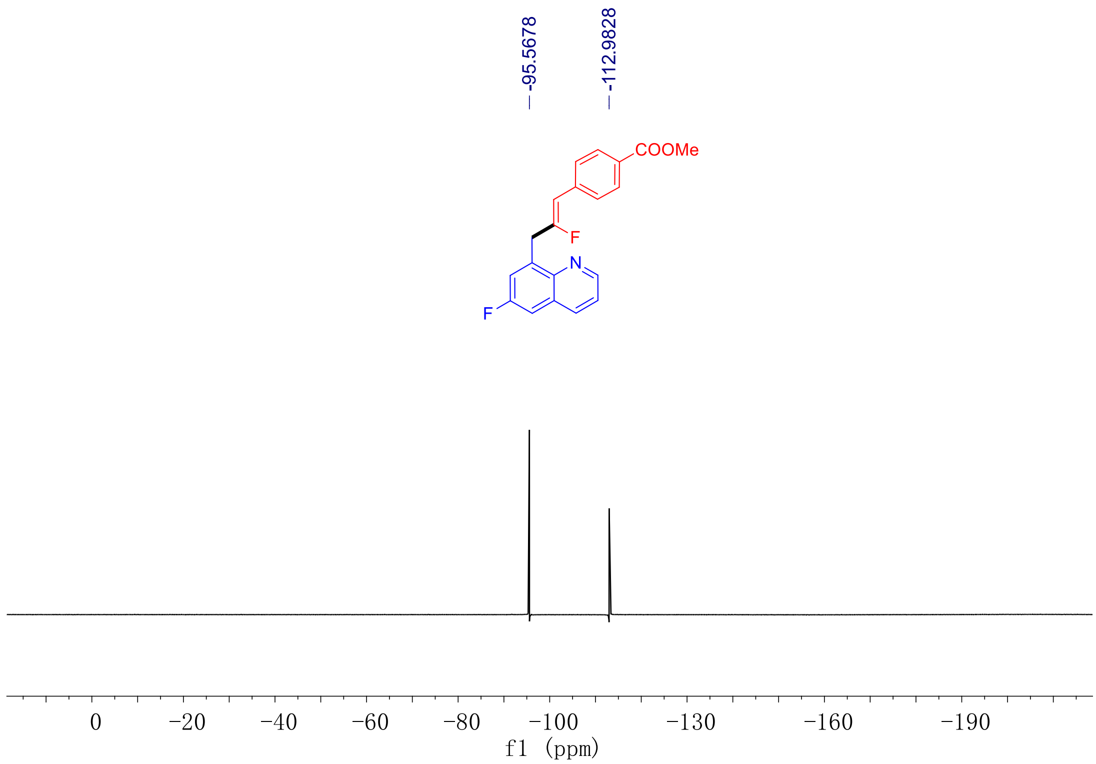
140
120
100
80
60
40
20
0
f1 (ppm)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F
0
−20
−40
−60
−80
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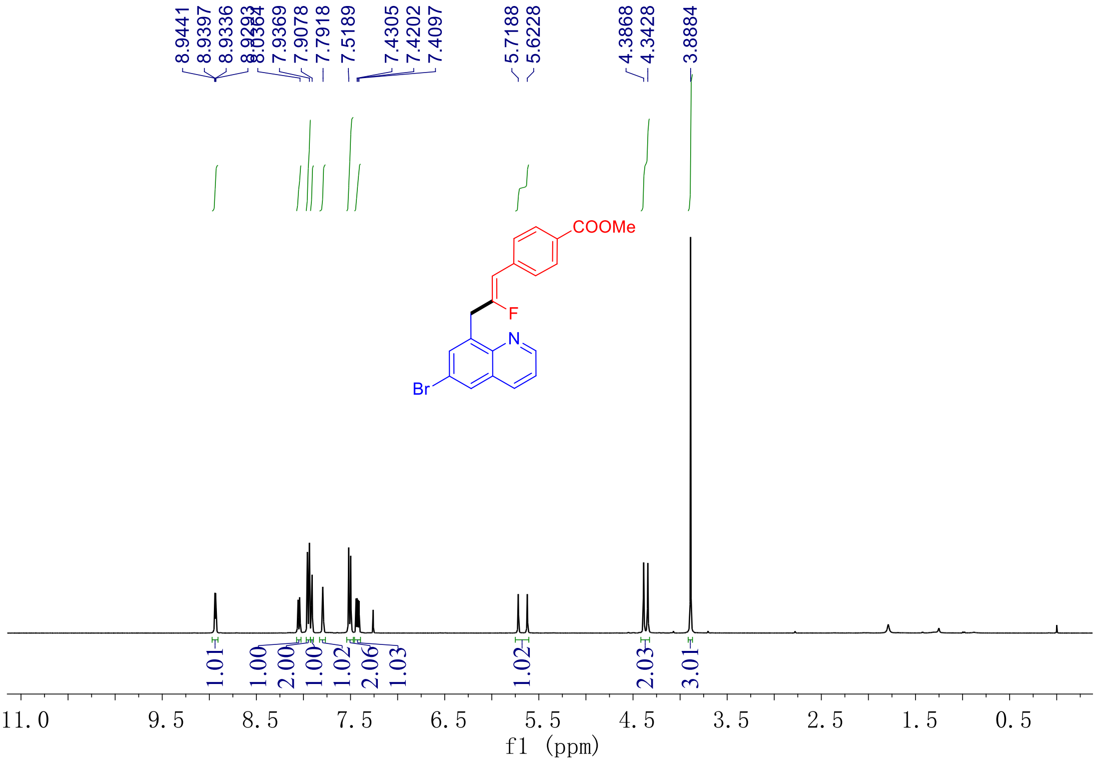
−130
−160
−190
f1 (ppm)

3ka


8.9441
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8.9336
8.9293
8.0364
7.9369
7.9078
7.7918
7.5189
7.4305
7.4202
7.4097
5.7188
5.6228
4.3868
4.3428
3.8884
COOMe
F
N
Br
1.01
1.00
2.00
1.00
1.02
2.06
1.03
1.02
2.03
3.01
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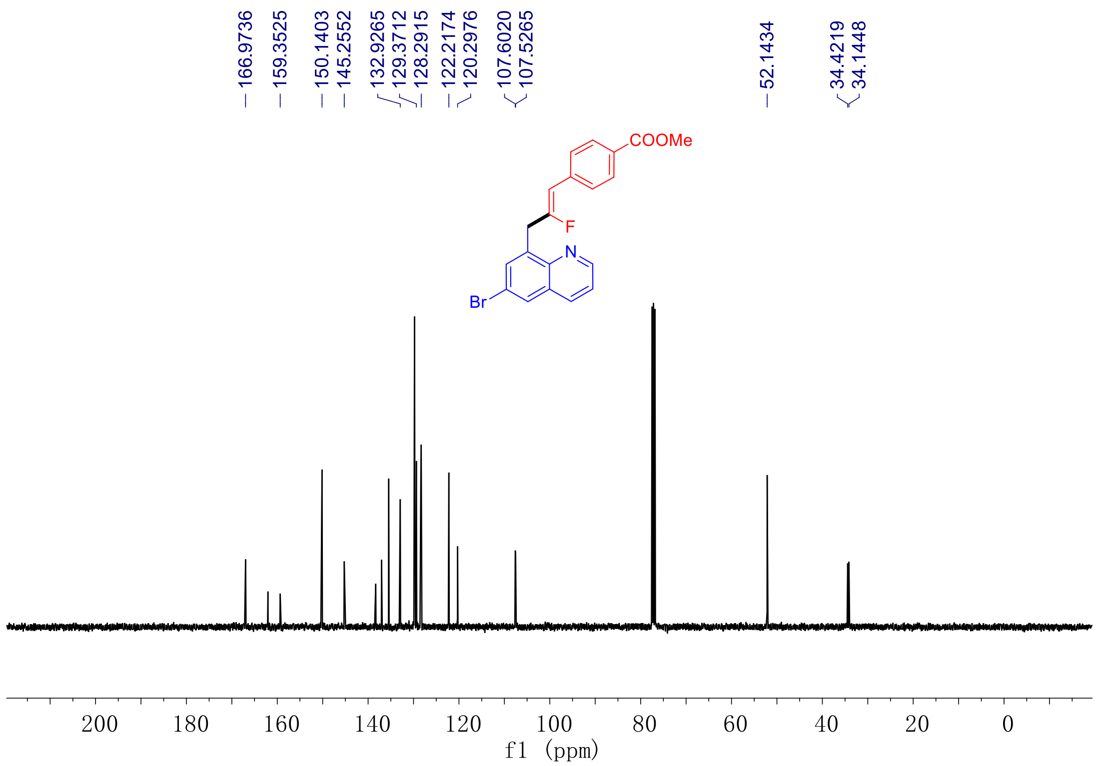
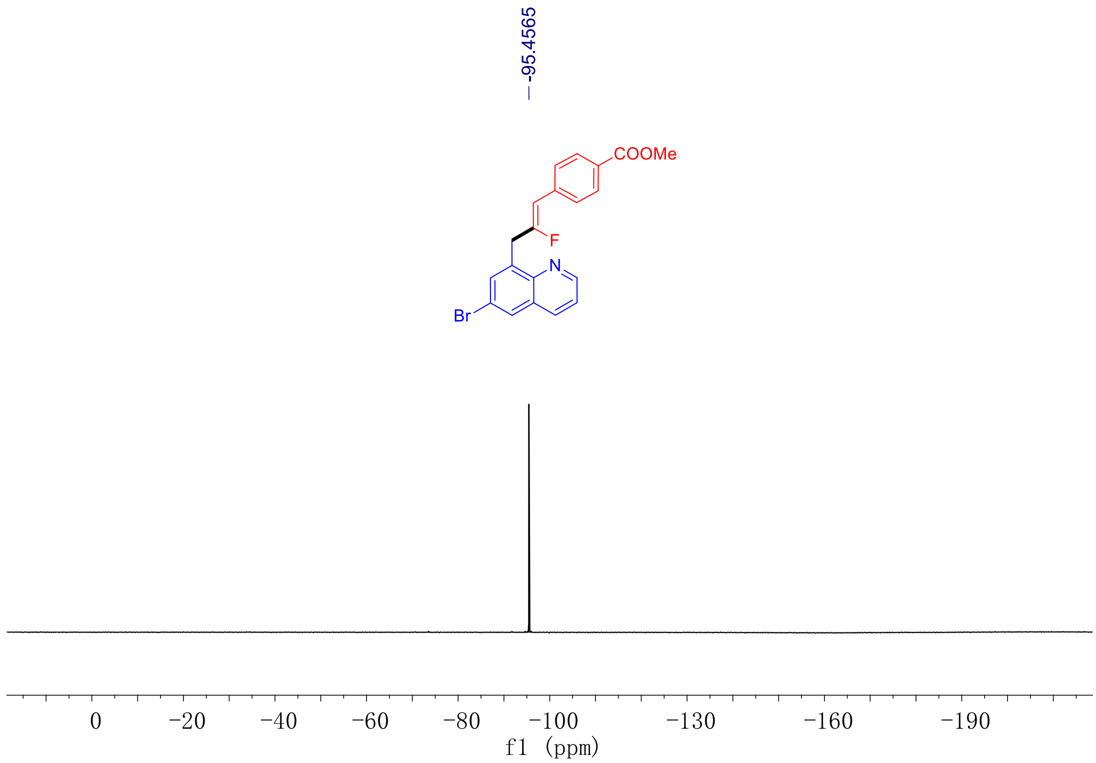
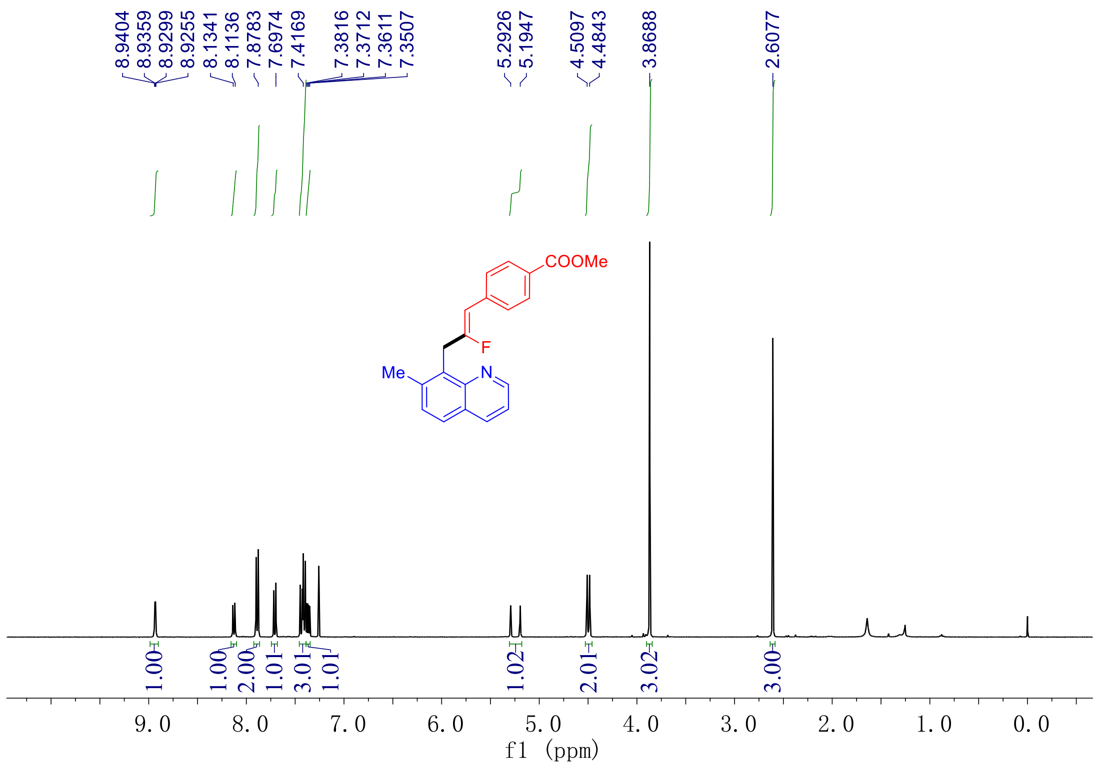
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


166.9736
159.3525
150.1403
145.2552
132.9265
129.3712
128.2915
122.2174
120.2976
107.6020
107.5265
52.1434
34.4219
34.1448
COOMe
F
N
Br
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

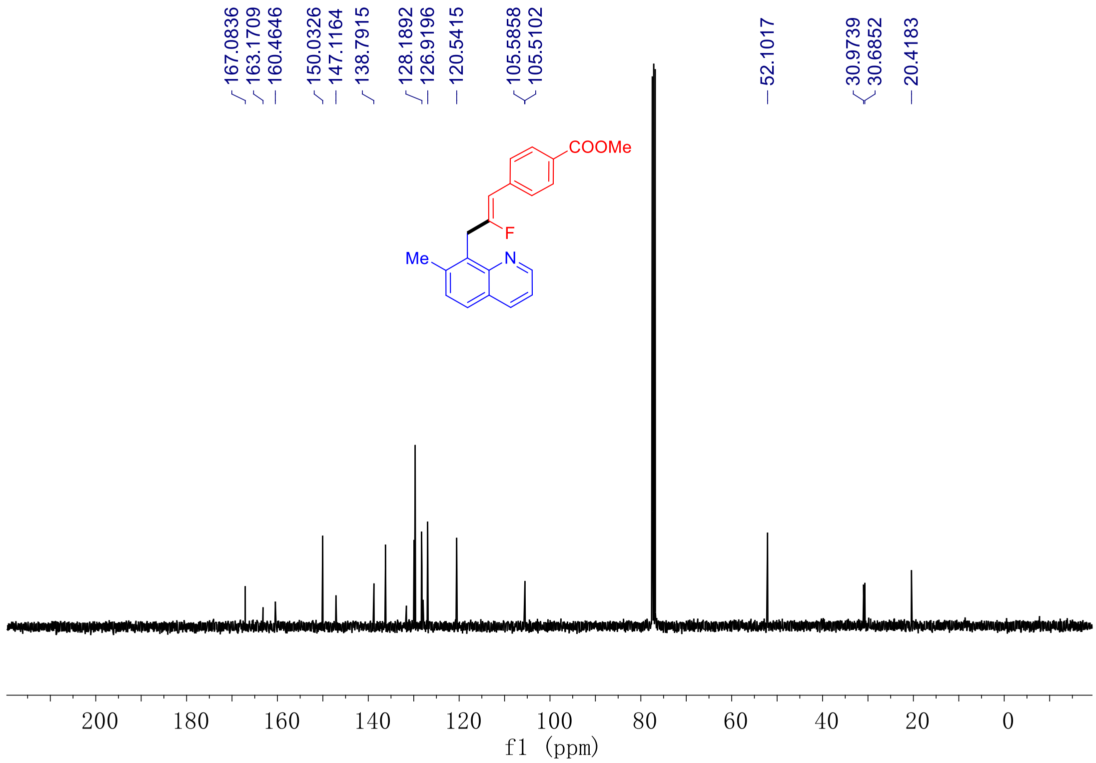


-95.4565
COOMe
F
N
Br
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3la



8.9404
8.9359
8.9299
8.9255
8.1341
8.1136
7.8783
7.6974
7.4169
7.3816
7.3712
7.3611
7.3507
5.2926
5.1947
4.5097
4.4843
3.8688
2.6077
COOMe
F
Me
N
1.00
1.00
2.00
1.01
3.01
1.01
1.02
2.01
3.02
3.00
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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160.4646
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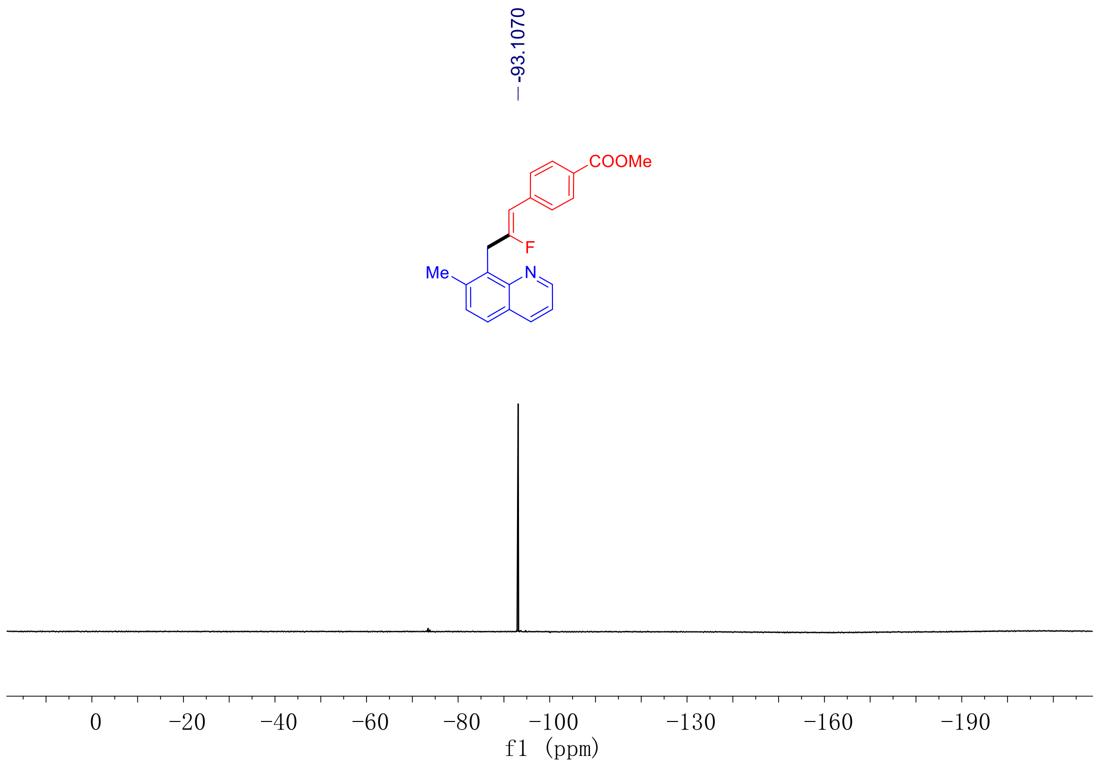
147.1164
138.7915
128.1892
126.9196
120.5415
105.5858
105.5102
52.1017
30.9739
30.6852
20.4183
COOMe
F
Me
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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F
Me
N
0
-20
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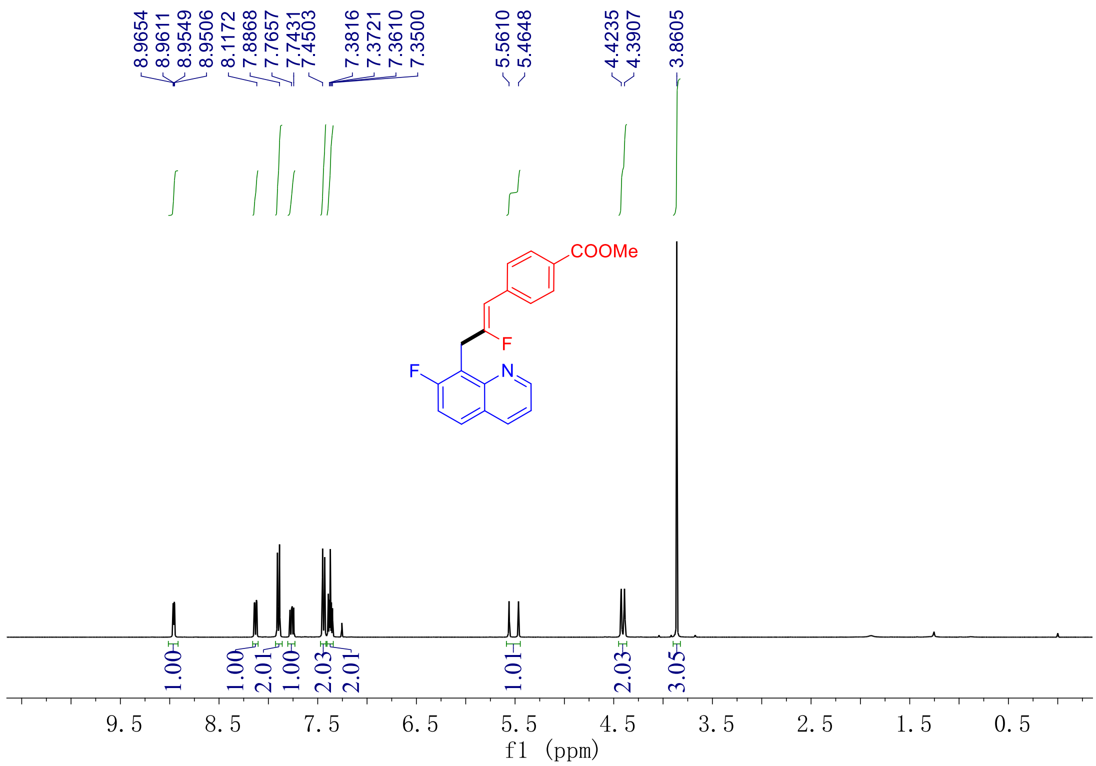
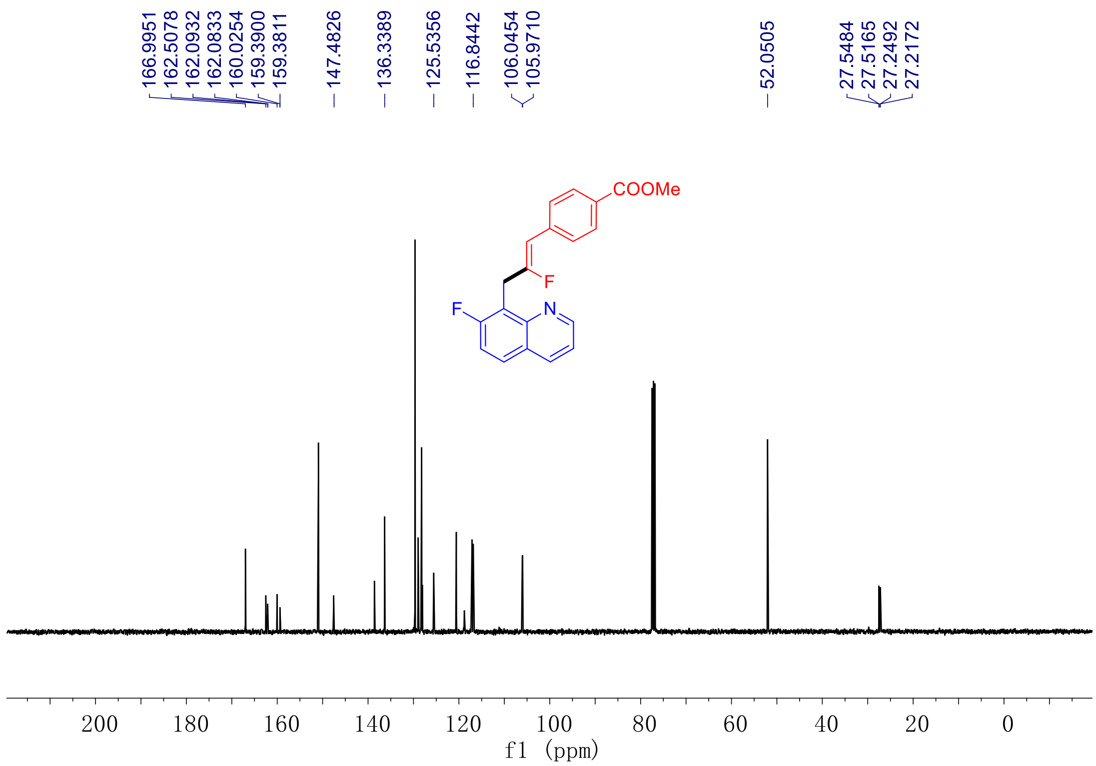
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ma



8.9654
8.9611
8.9549
8.9506
8.1172
7.8868
7.7657
7.7431
7.4503
7.3816
7.3721
7.3610
7.3500
5.5610
5.4648
4.4235
4.3907
3.8605
COOMe
F
F
N
1.00
1.00
2.01
1.00
2.03
2.01
1.01
2.03
3.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



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159.3900
159.3811
147.4826
136.3389
125.5356
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105.9710
52.0505
27.5484
27.5165
27.2492
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COOMe
F
F
N
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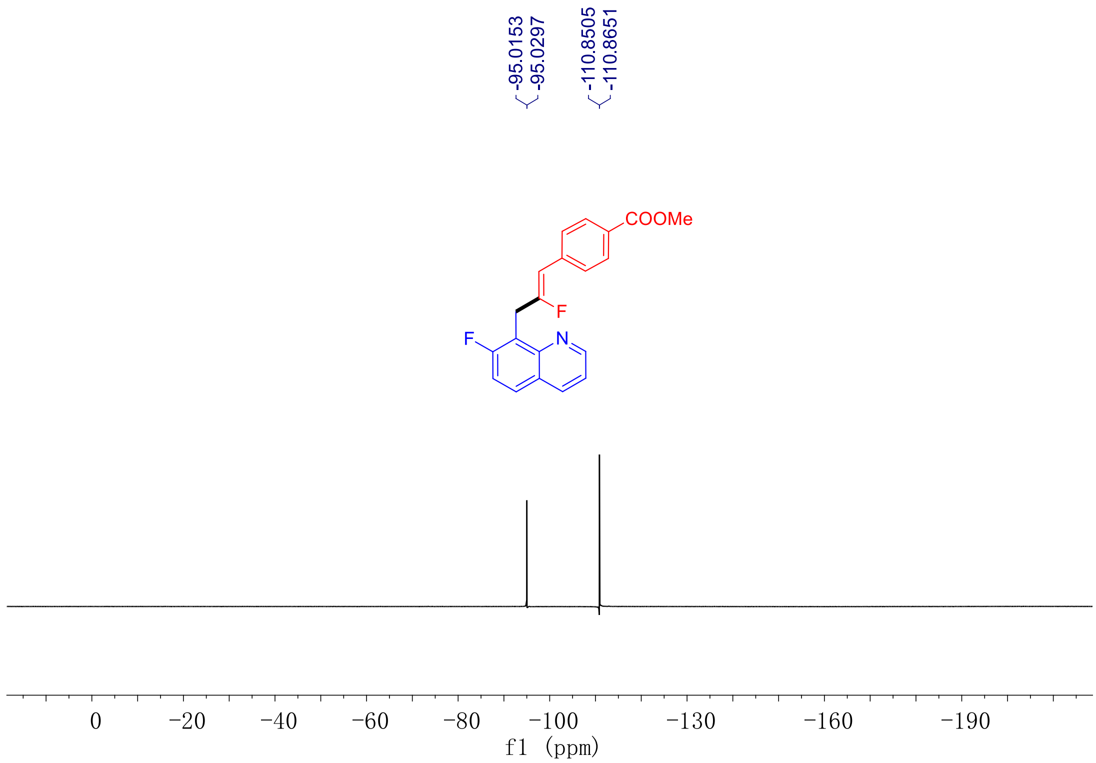
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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F
N
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−80
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−130
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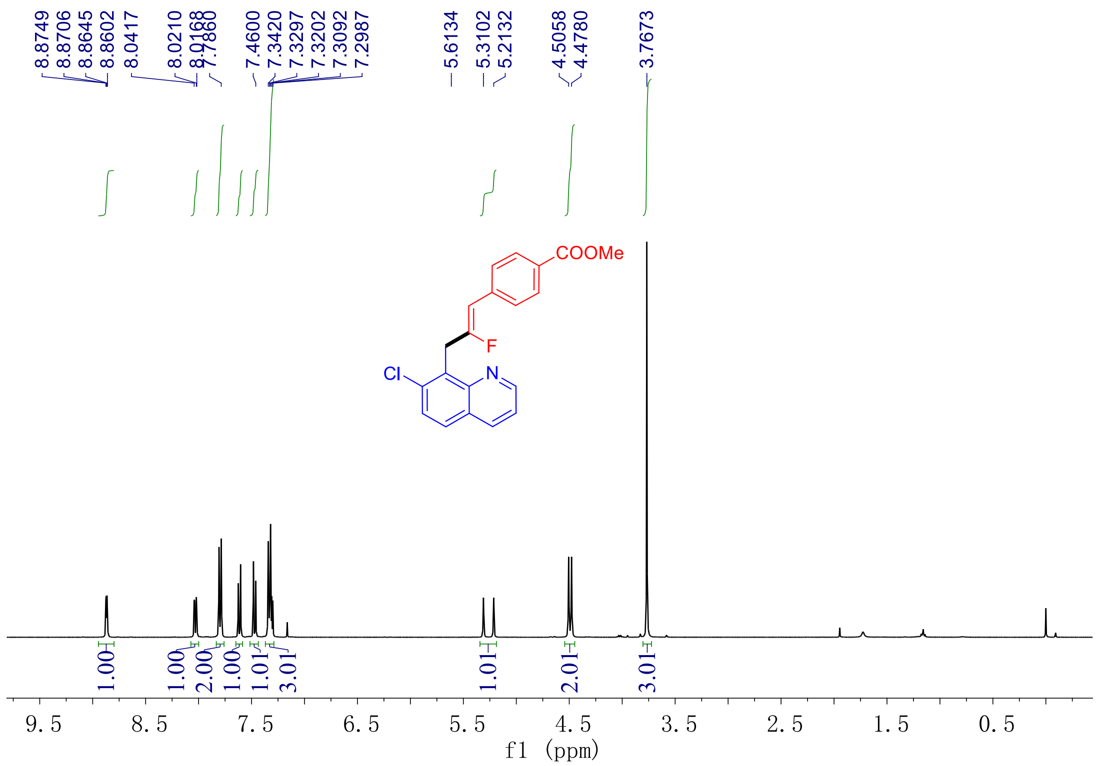
−190
f1 (ppm)

3na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8.0168
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7.4600
7.3420
7.3297
7.3202
7.3092
7.2987
5.6134
5.3102
5.2132
4.5058
4.4780
3.7673
COOMe
F
Cl
N
1.00
1.00
2.00
1.00
1.01
3.01
1.01
2.01
3.01
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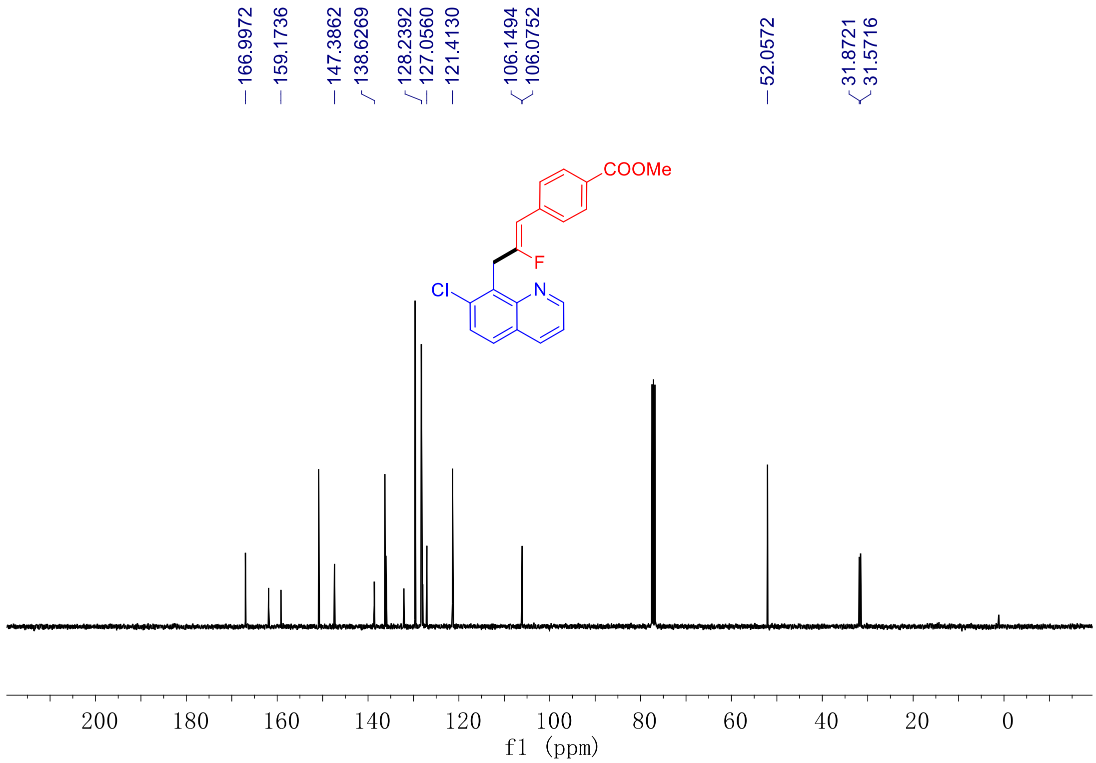
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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138.6269
128.2392
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121.4130
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106.0752
52.0572
31.8721
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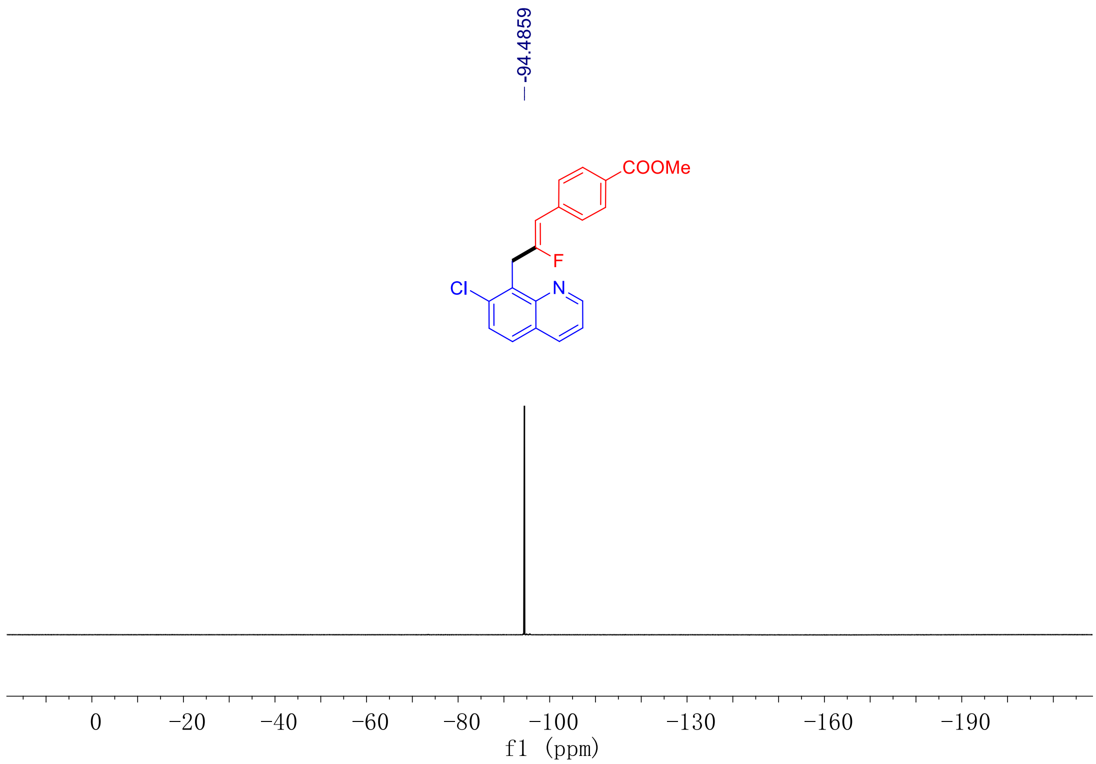
COOMe
F
Cl
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Cl
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-80
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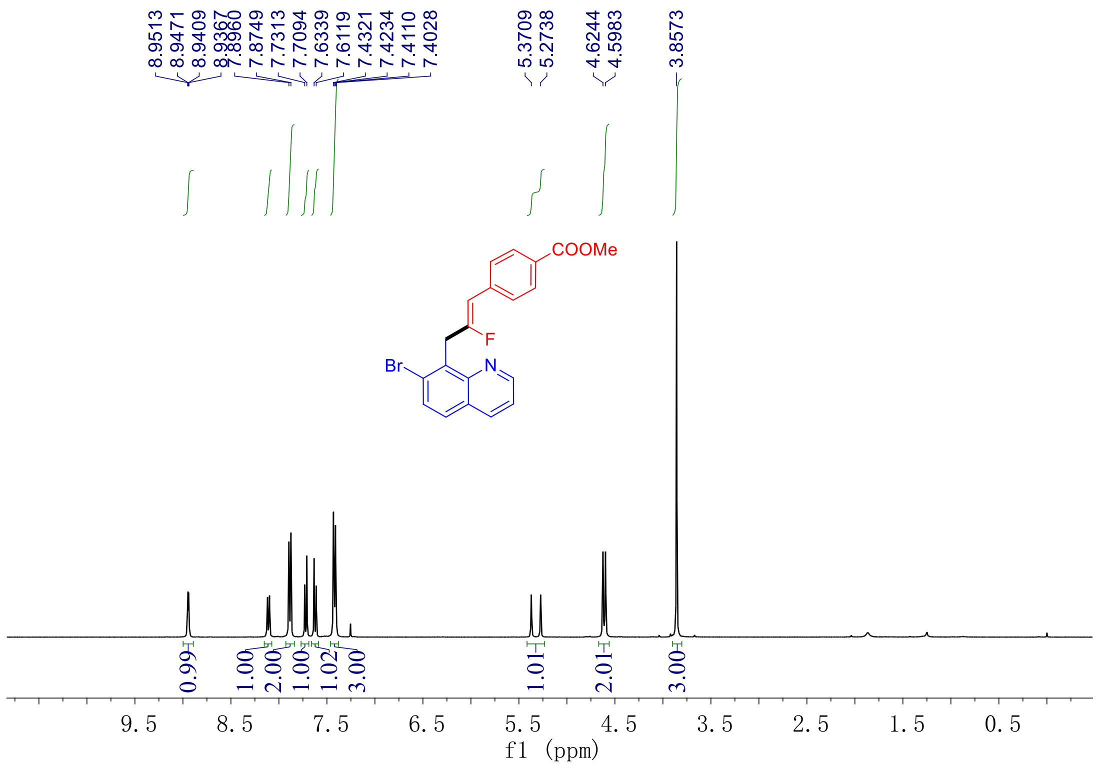
f1 (ppm)

3oa



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7.4234
7.4110
7.4028
5.3709
5.2738
4.6244
4.5983
3.8573
COOMe
F
Br
N
0.99
1.00
2.00
1.00
1.02
3.00
1.01
2.01
3.00
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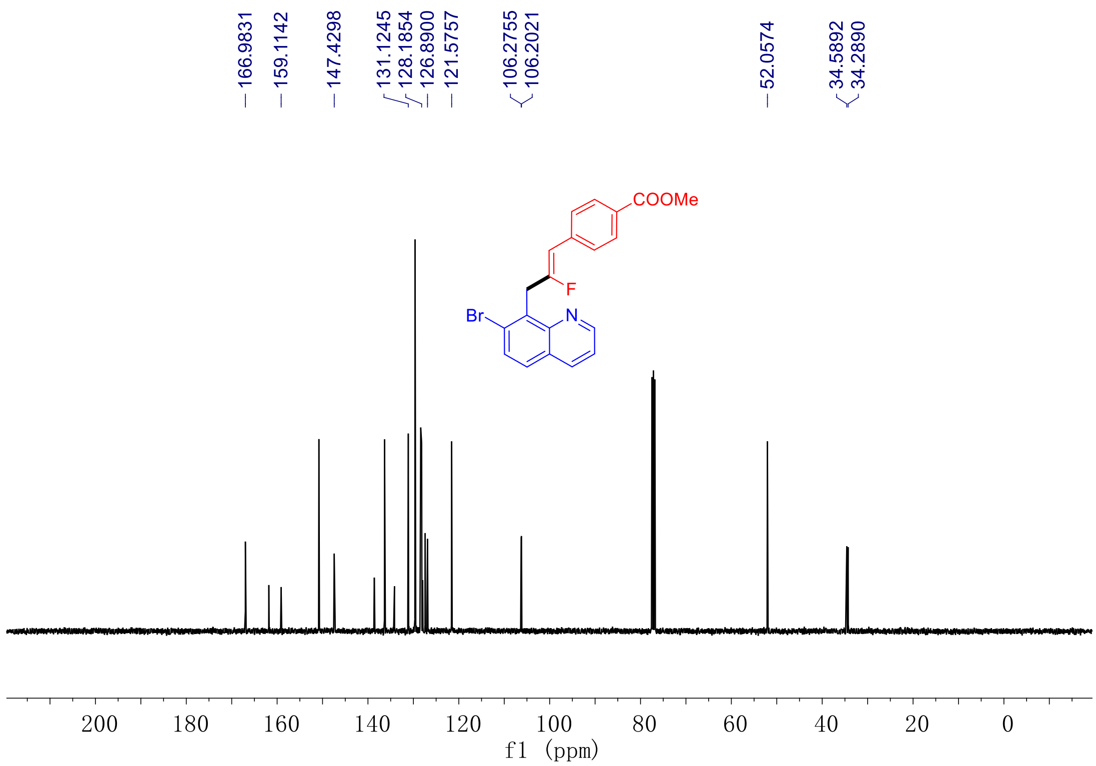
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



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121.5757
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52.0574
34.5892
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Br
N
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100
80
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20
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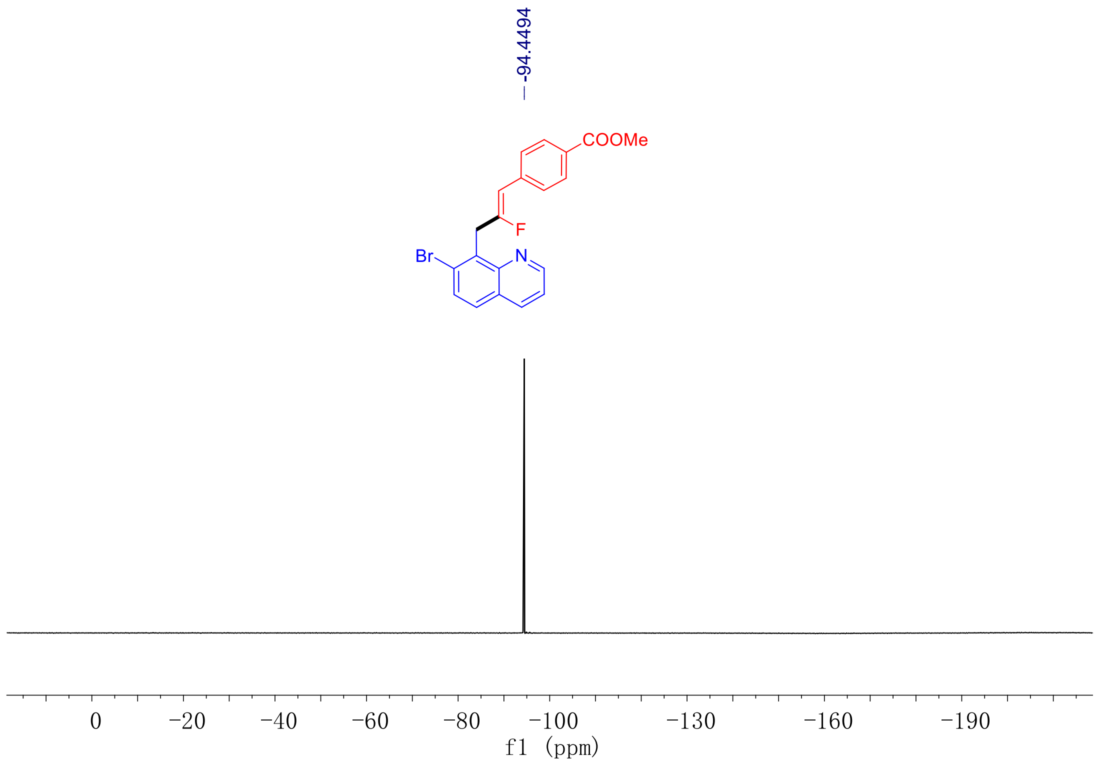
f1 (ppm)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Br
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−80
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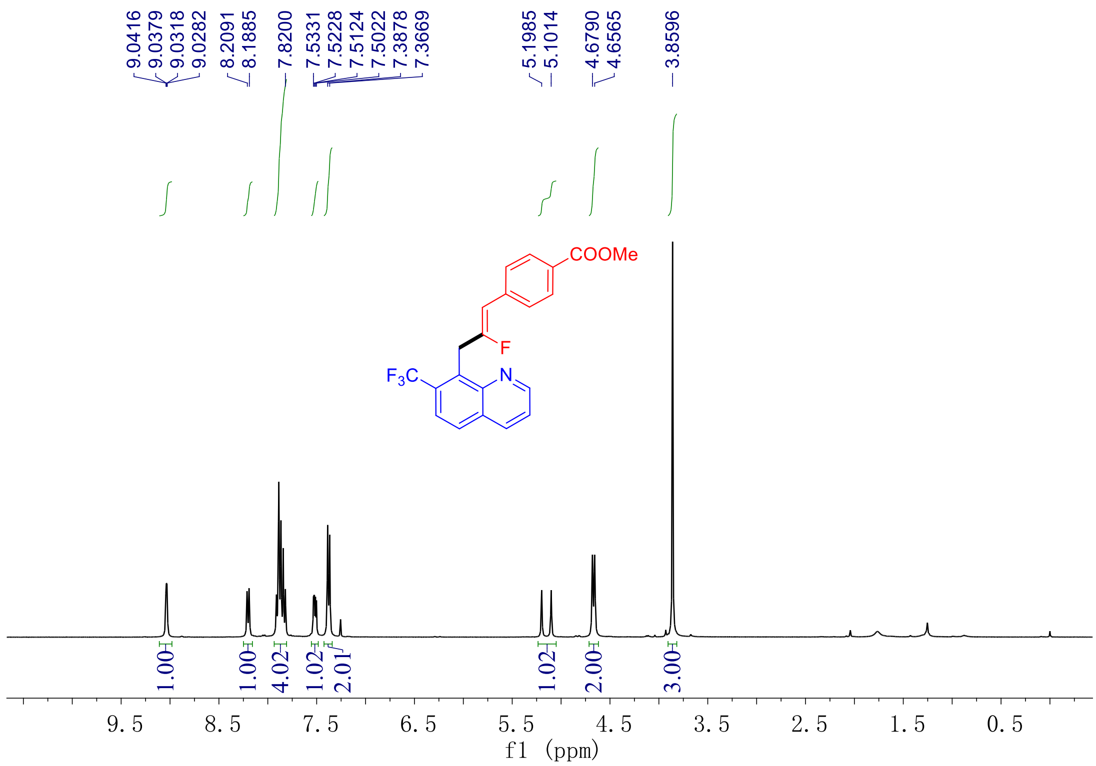
f1 (ppm)

3pa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9.0318
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8.1885
7.8200
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7.5228
7.5124
7.5022
7.3878
7.3669
5.1985
5.1014
4.6790
4.6565
3.8596
COOMe
F
F3C
N
1.00
1.00
4.02
1.02
2.01
1.02
2.00
3.00
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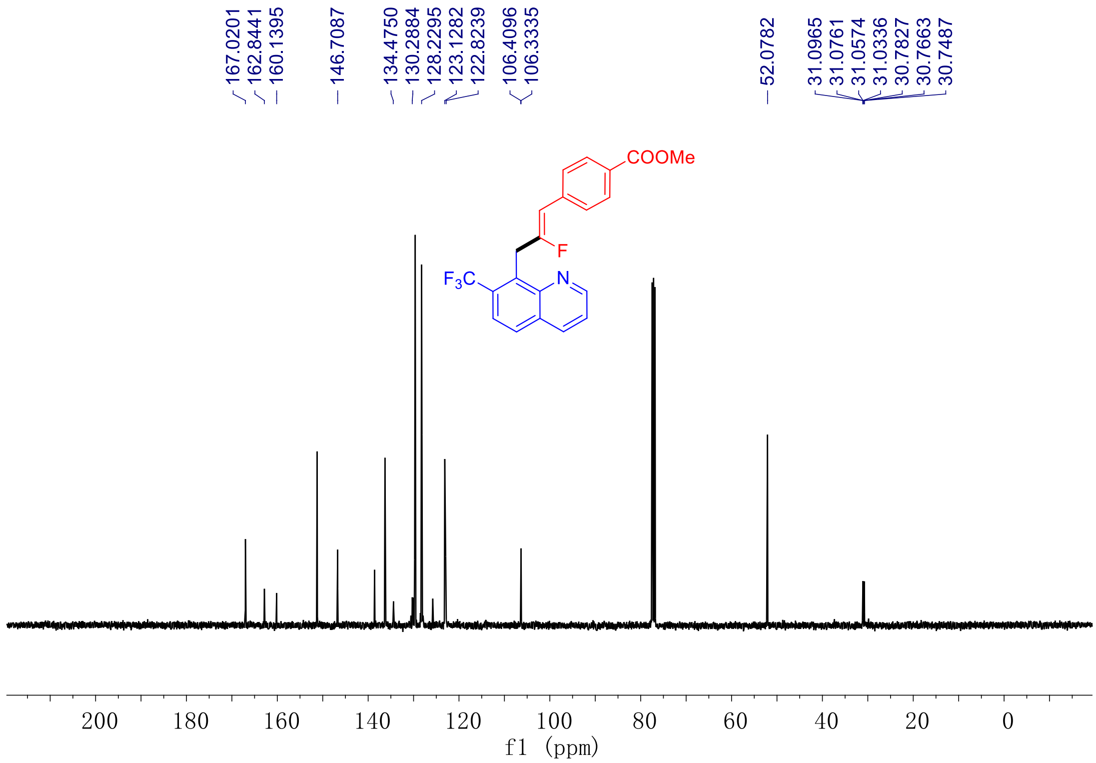
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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31.0761
31.0574
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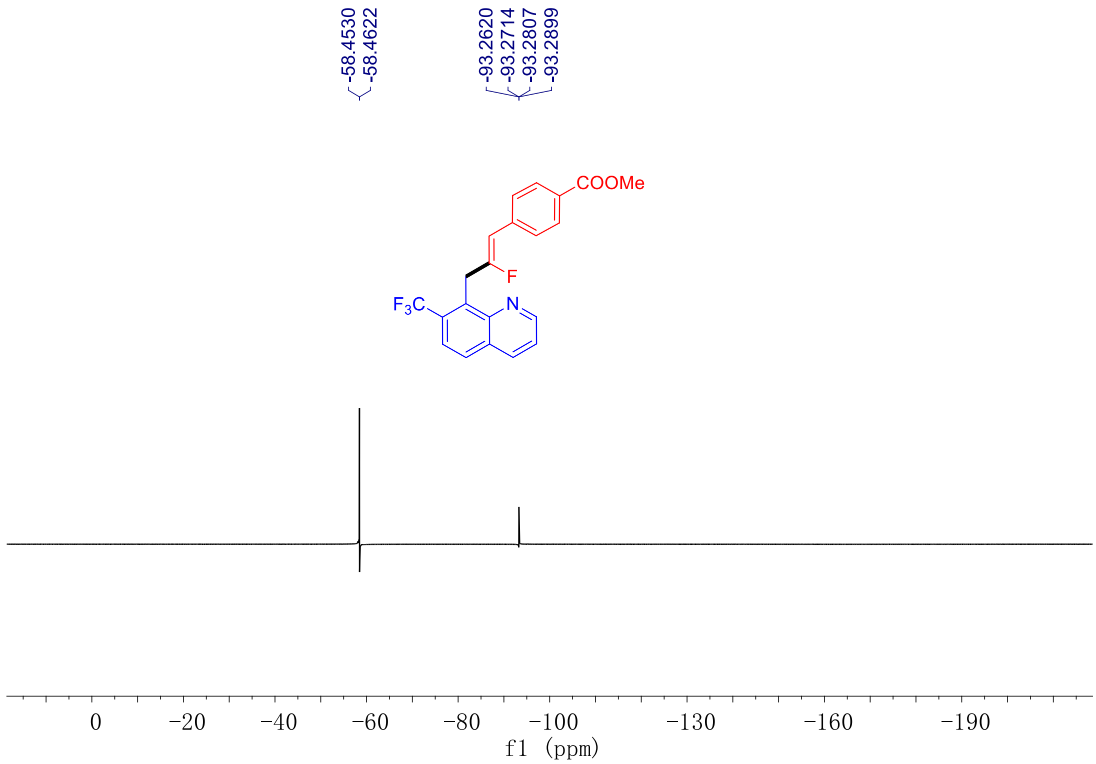
COOMe
F
F_3C
N
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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-93.2714
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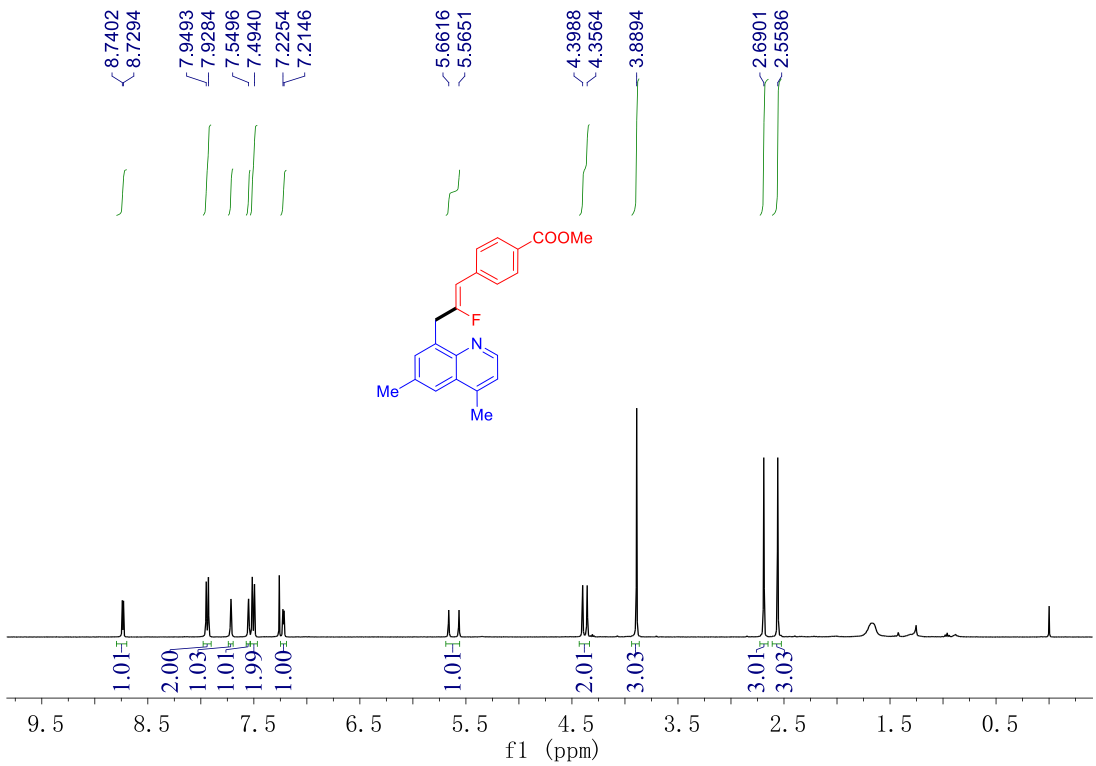
-93.2899
COOMe
F
F_3C
N
0 −20 −40 −60 −80 −100 −130 −160 −190
f1 (ppm)

3qa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7.2254
7.2146
5.6616
5.5651
4.3988
4.3564
3.8894
2.6901
2.5586
COOMe
F
N
Me
Me
1.01
2.00
1.03
1.01
1.99
1.00
1.01
2.01
3.03
3.01
3.03
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7.5
6.5
5.5
4.5
3.5
2.5
1.5
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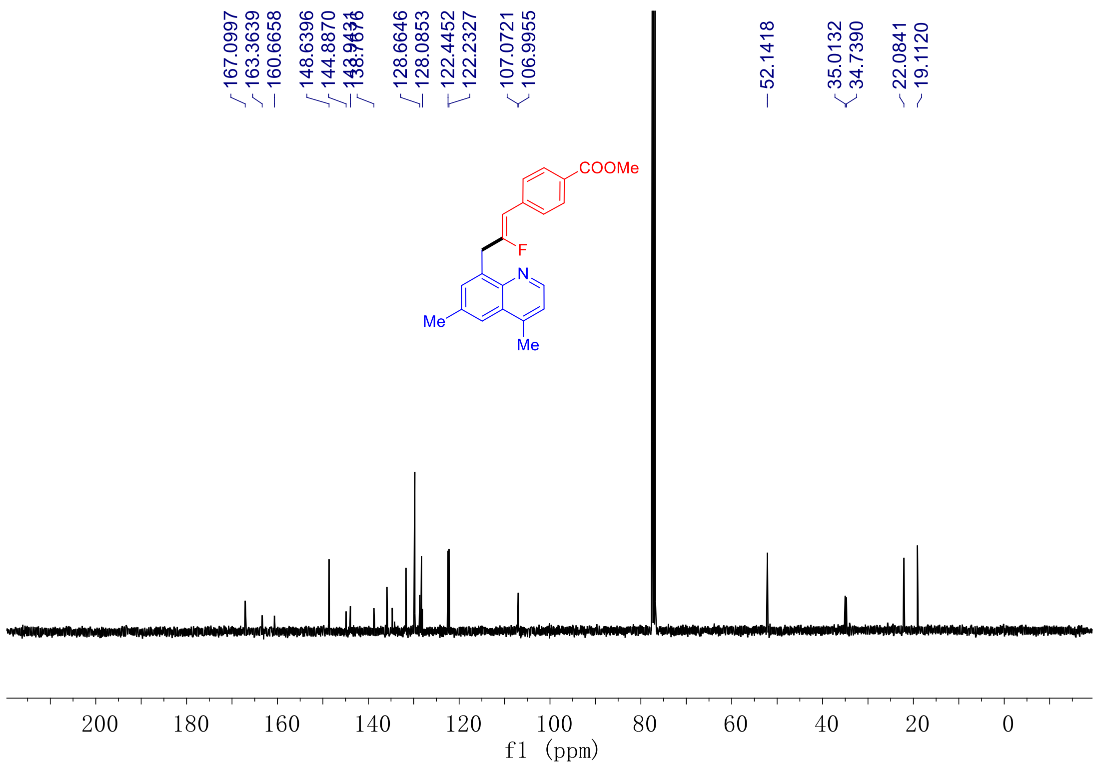
f1 (ppm)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122.4452
122.2327
107.0721
106.9955
52.1418
35.0132
34.7390
22.0841
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COOMe
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N
Me
Me
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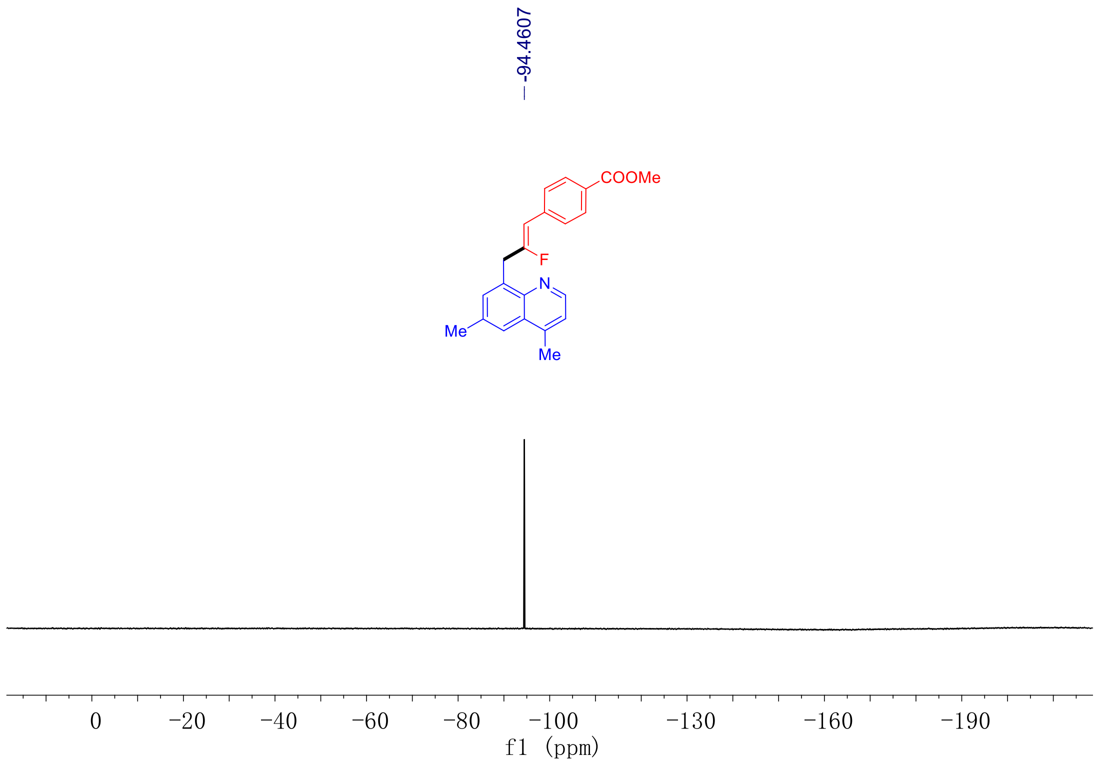
140
120
100
80
60
40
20
0
f1 (ppm)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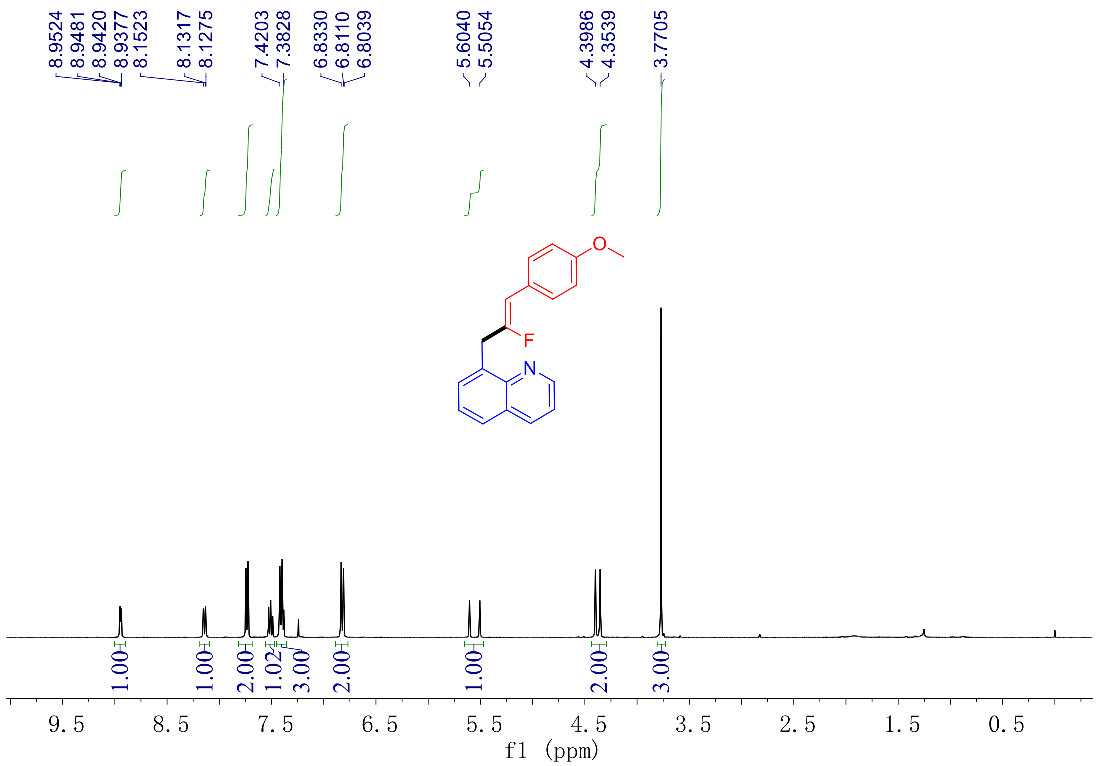
F
N
Me
Me
f1 (ppm)

3ab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8.1275
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7.3828
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6.8110
6.8039
5.6040
5.5054
4.3986
4.3539
3.7705
O
F
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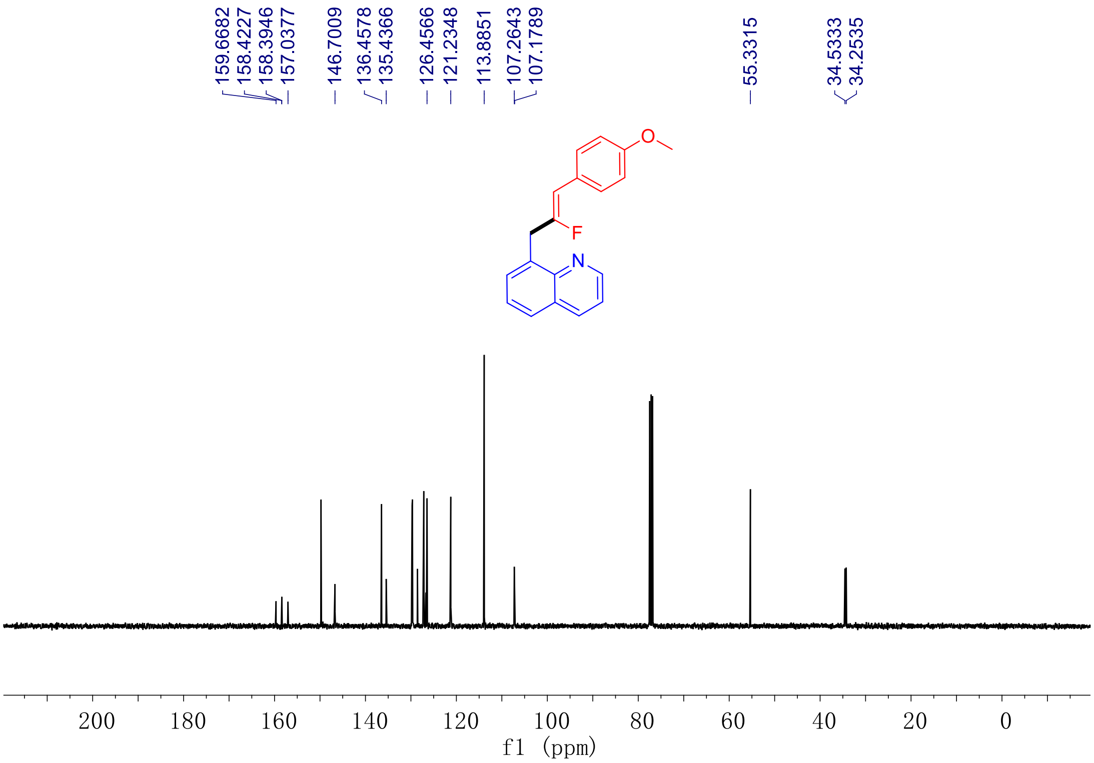
1.00
2.00
1.02
3.00
2.00
1.00
2.00
3.00
f1 (ppm)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135.4366
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121.2348
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107.1789
55.3315
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N
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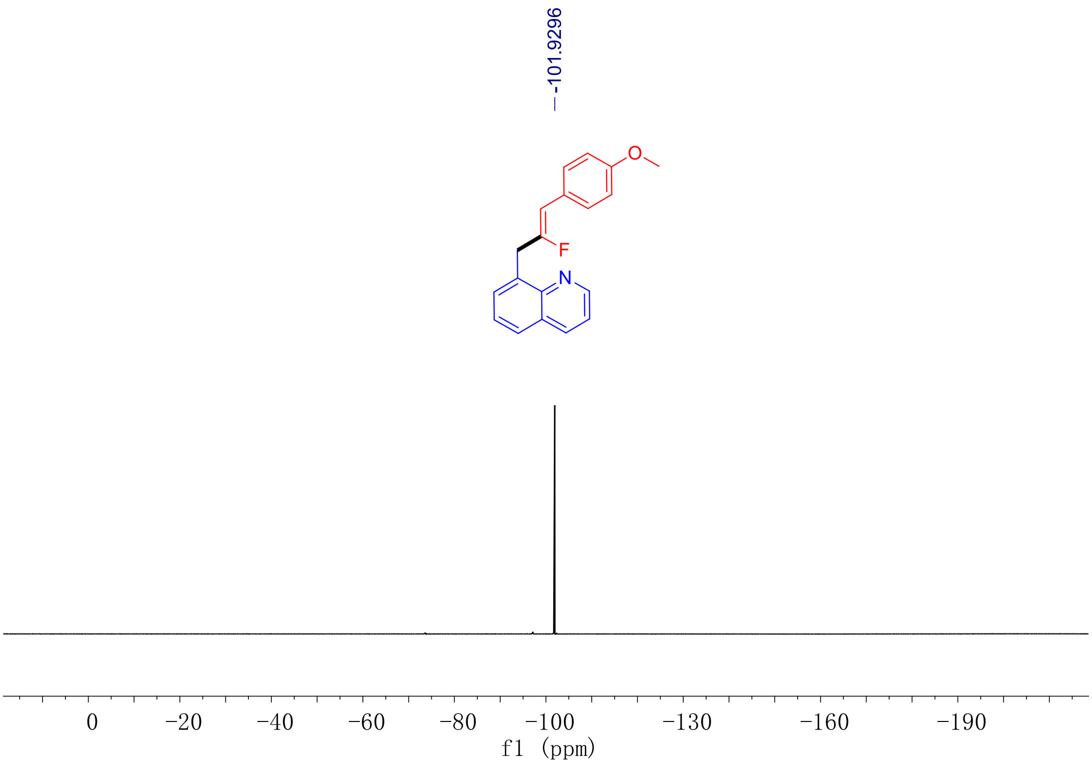
140
120
100
80
60
40
20
0
f1 (ppm)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O
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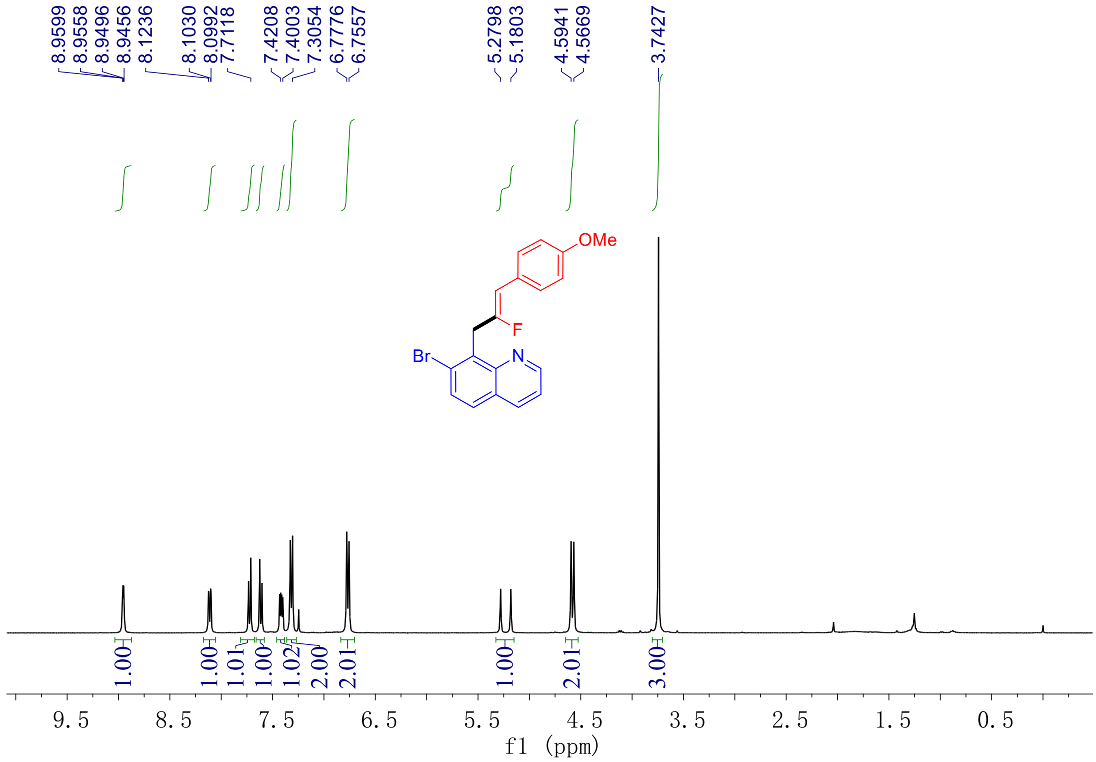
-190
f1 (ppm)

3ob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7.4003
7.3054
6.7776
6.7557
5.2798
5.1803
4.5941
4.5669
3.7427
OMe
F
Br
N
1.00
1.00
1.01
1.00
1.02
2.00
2.01
1.00
2.01
3.00
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7.5
6.5
5.5
4.5
3.5
2.5
1.5
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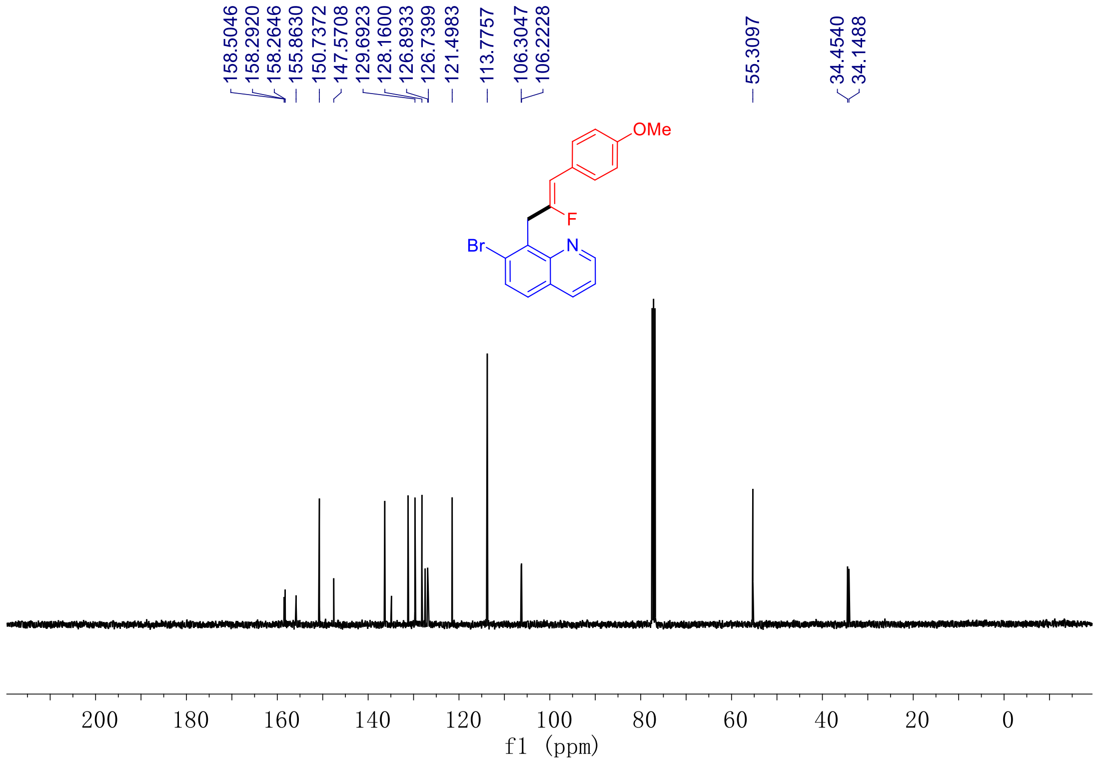
f1 (ppm)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147.5708
129.6923
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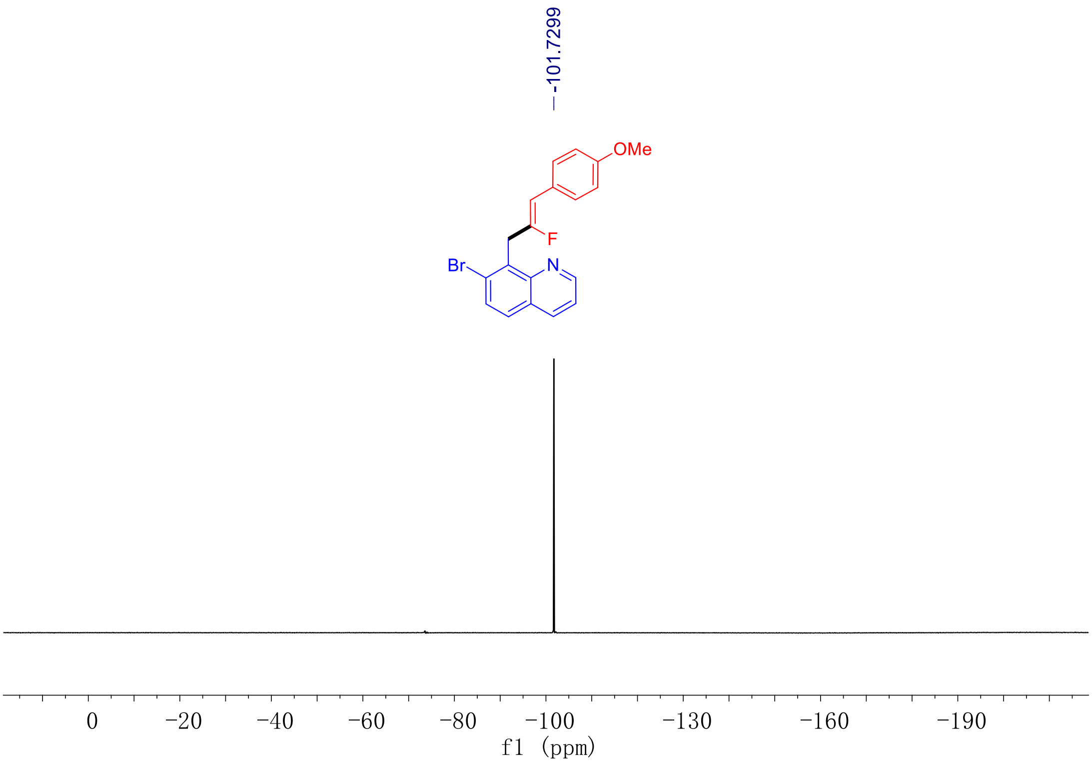
126.8933
126.7399
121.4983
113.7757
106.3047
106.2228
55.3097
34.4540
34.1488
OMe
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Br
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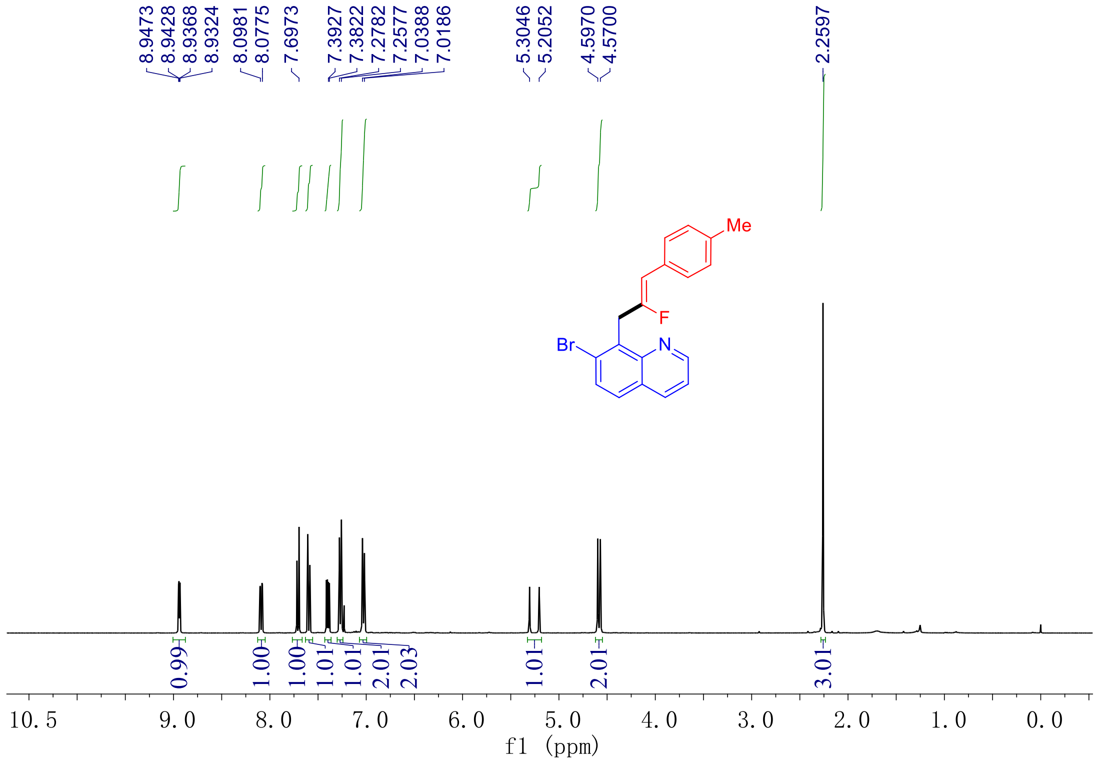
−130
−160
−190
f1 (ppm)

3oc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7.3822
7.2782
7.2577
7.0388
7.0186
5.3046
5.2052
4.5970
4.5700
2.2597
Me
F
Br
N
0.99
1.00
1.00
1.01
1.01
2.01
2.03
1.01
2.01
3.01
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7.0
6.0
5.0
4.0
3.0
2.0
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0.0
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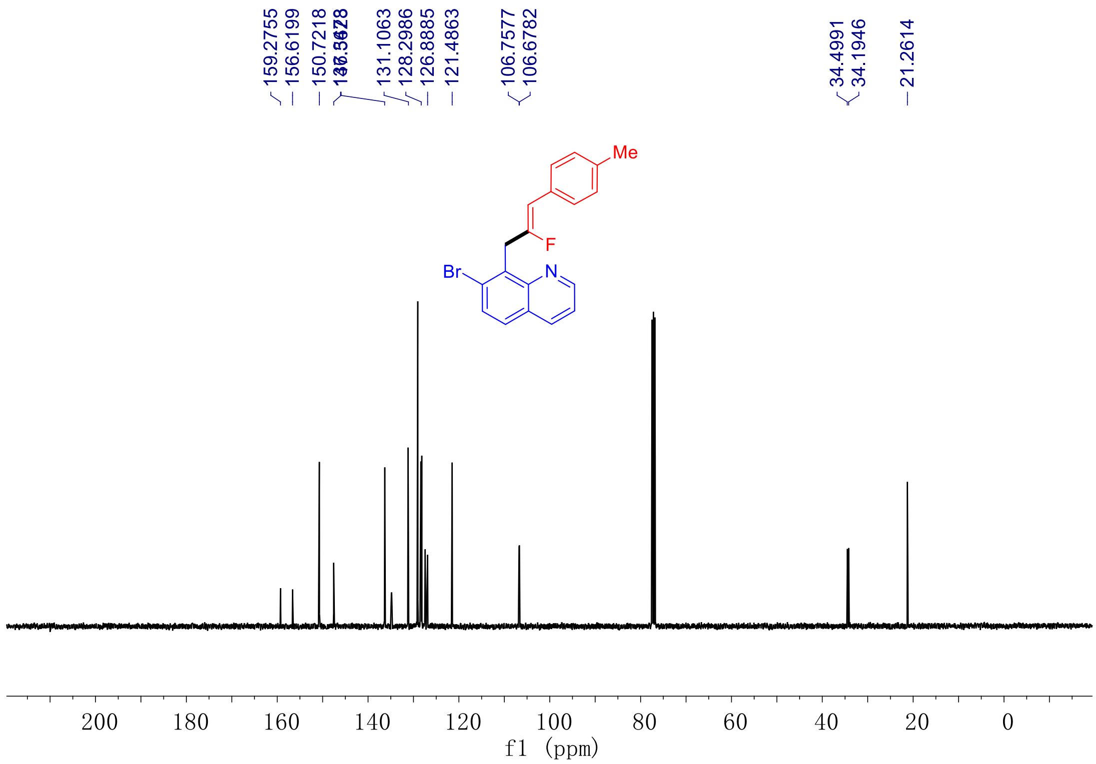
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126.8885
121.4863
106.7577
106.6782
34.4991
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Me
F
Br
N
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100
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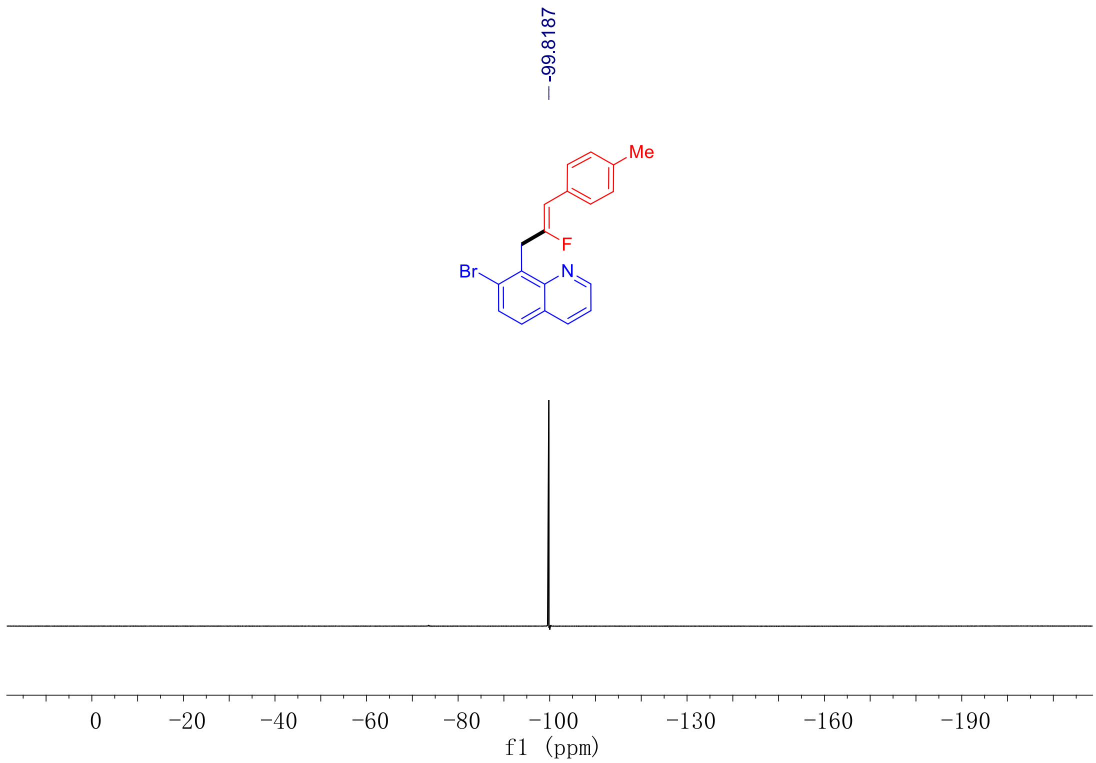
f1 (ppm)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Br
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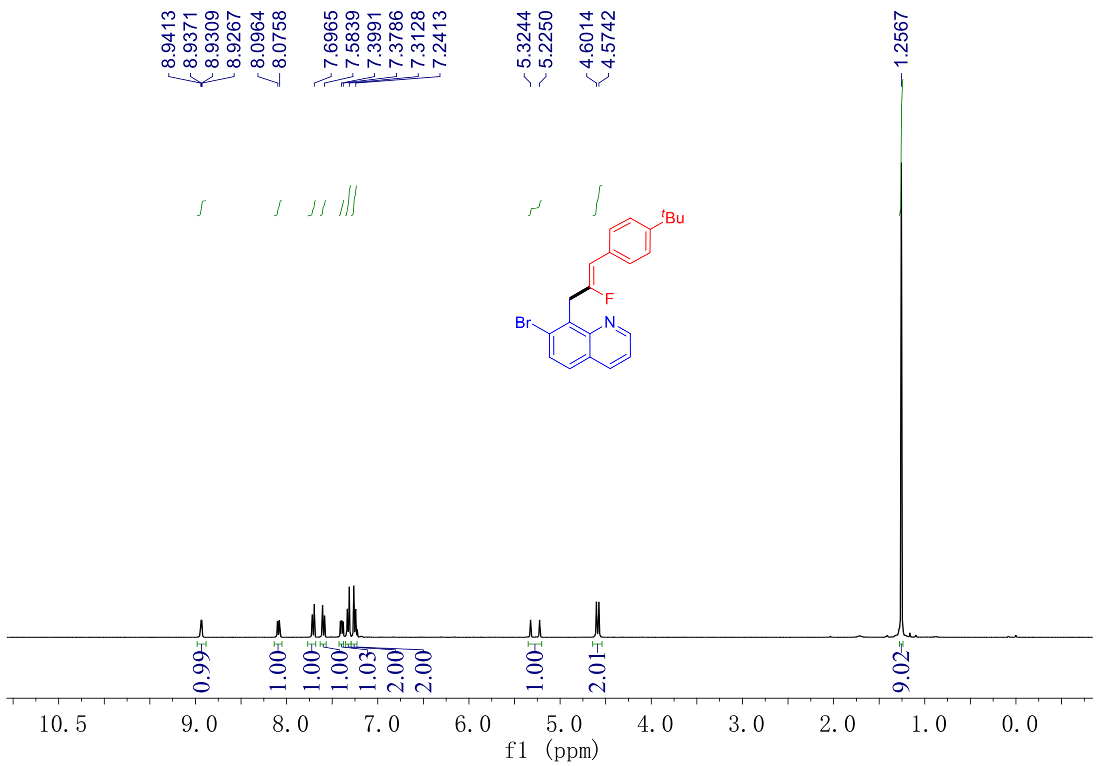
f1 (ppm)

3od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7.3128
7.2413
5.3244
5.2250
4.6014
4.5742
1.2567
tBu
F
Br
N
0.99
1.00
1.00
1.00
1.03
2.00
2.00
1.00
2.01
9.02
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7.0
6.0
5.0
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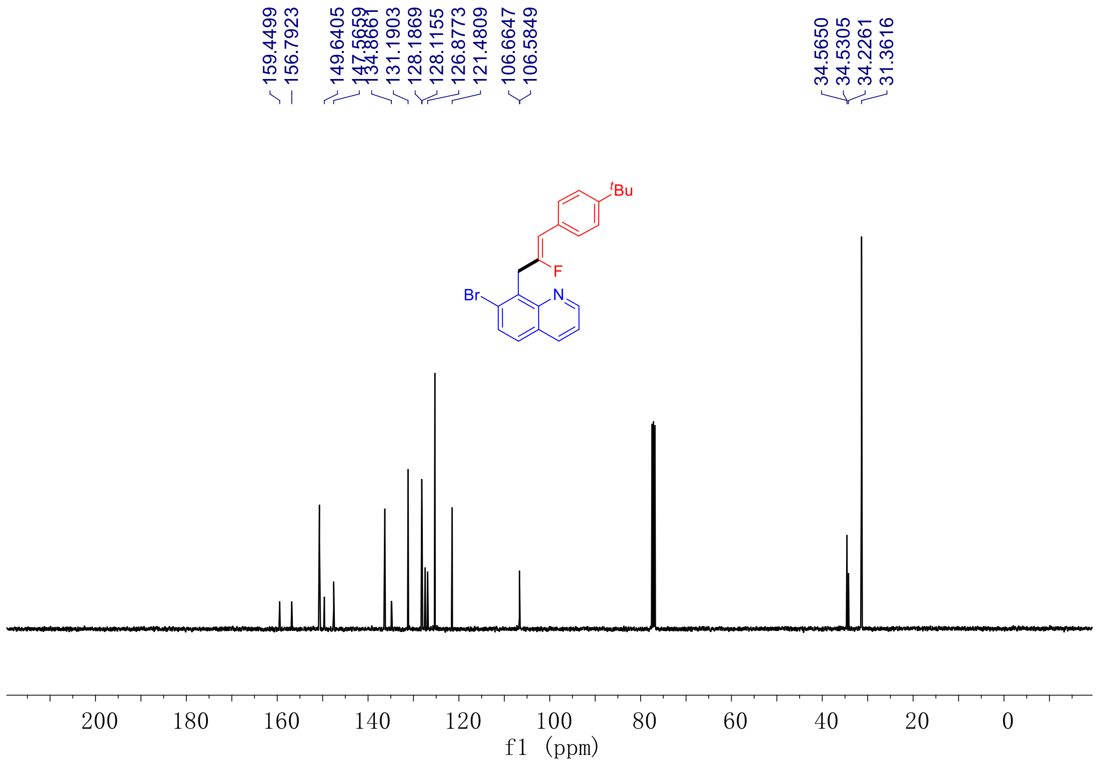
f1 (ppm)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106.6647
106.5849
34.5650
34.5305
34.2261
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F
Br
N
200
180
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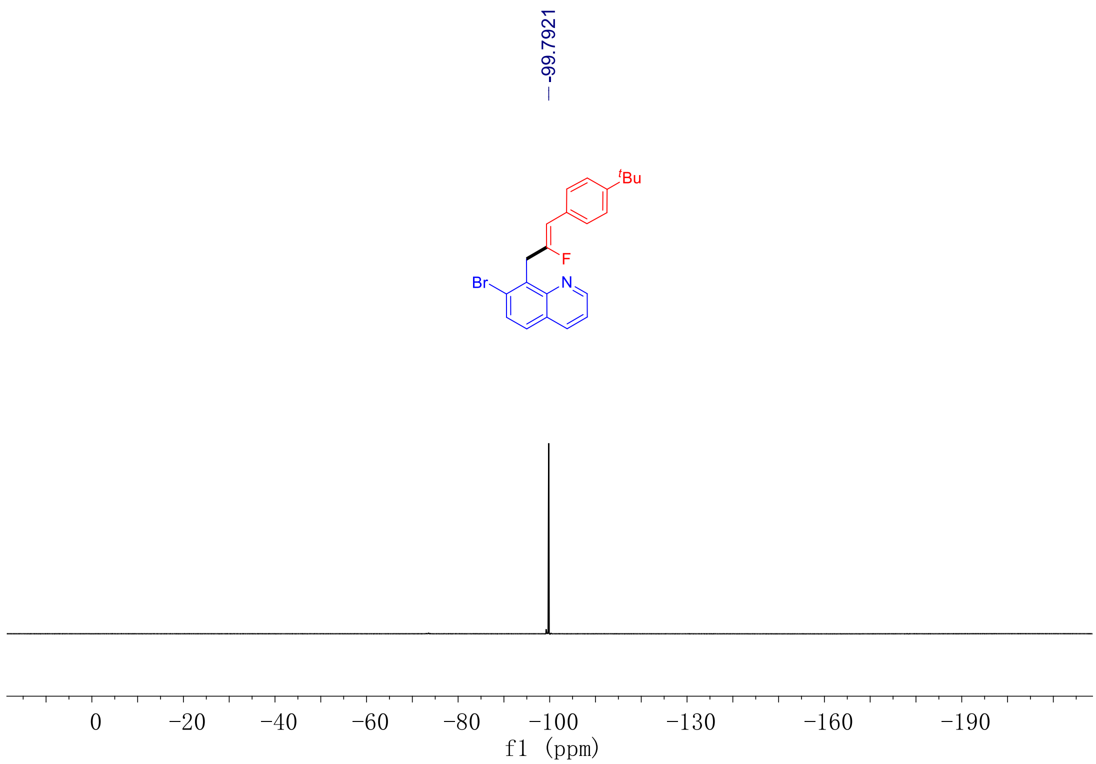
100
80
60
40
20
0
f1 (ppm)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F
Br
N
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-60
-80
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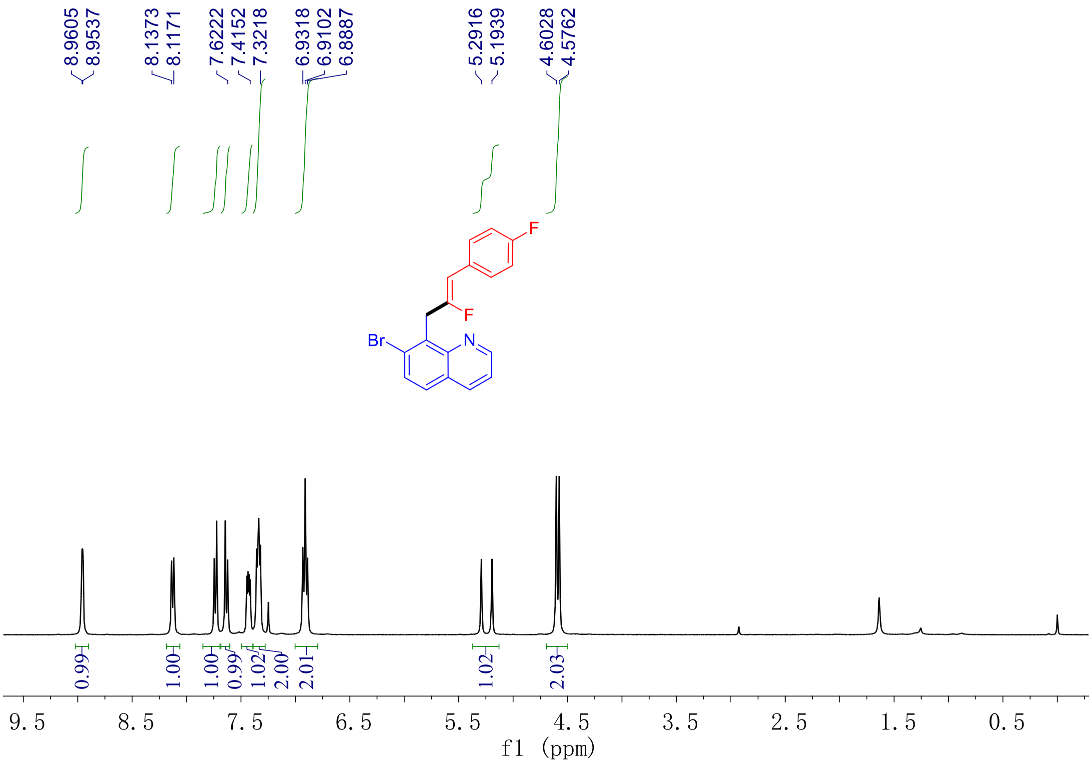
f1 (ppm)

3oe



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7.6222
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6.9102
6.8887
5.2916
5.1939
4.6028
4.5762
F
F
Br
N
0.99
1.00
1.00
0.99
1.02
2.00
2.01
1.02
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7.5
6.5
5.5
4.5
3.5
2.5
1.5
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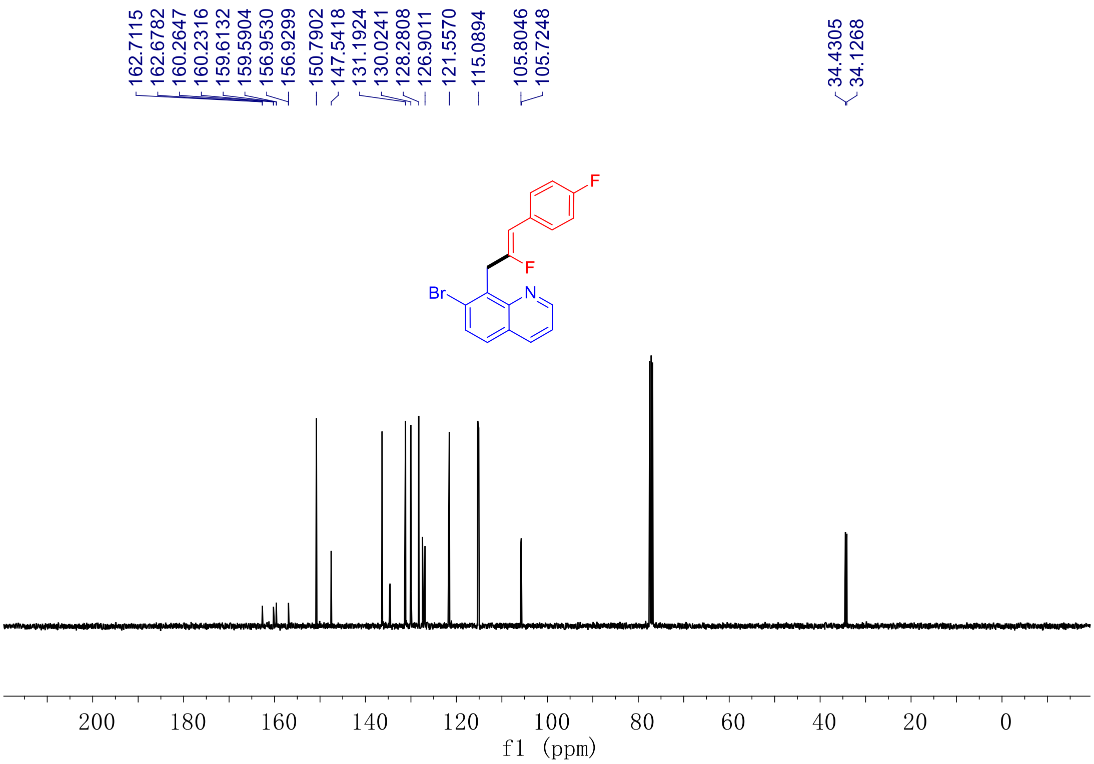
f1 (ppm)



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150.7902
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130.0241
128.2808
126.9011
121.5570
115.0894
105.8046
105.7248
34.4305
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F
F
Br
N
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100
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60
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20
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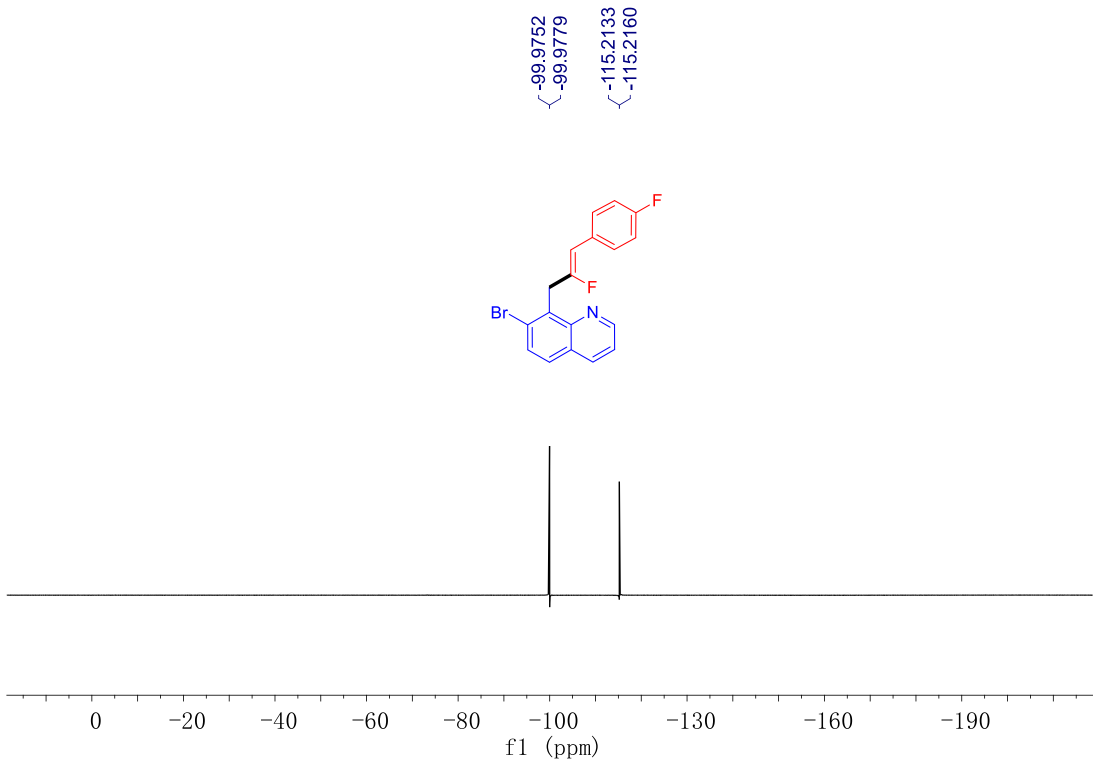
f1 (ppm)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F
F
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N
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−80
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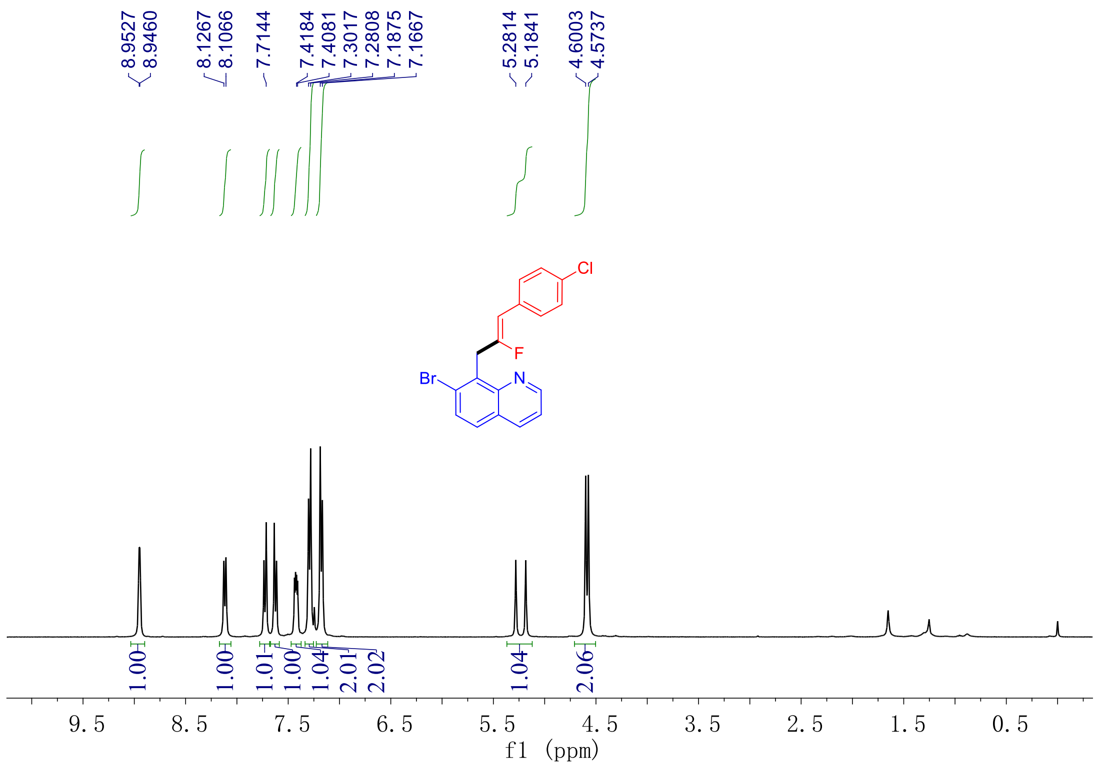
−130
−160
−190
f1 (ppm)

3of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7.4081
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7.2808
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7.1667
5.2814
5.1841
4.6003
4.5737
Cl
F
Br
N
1.00
1.00
1.01
1.00
1.04
2.01
2.02
1.04
2.06
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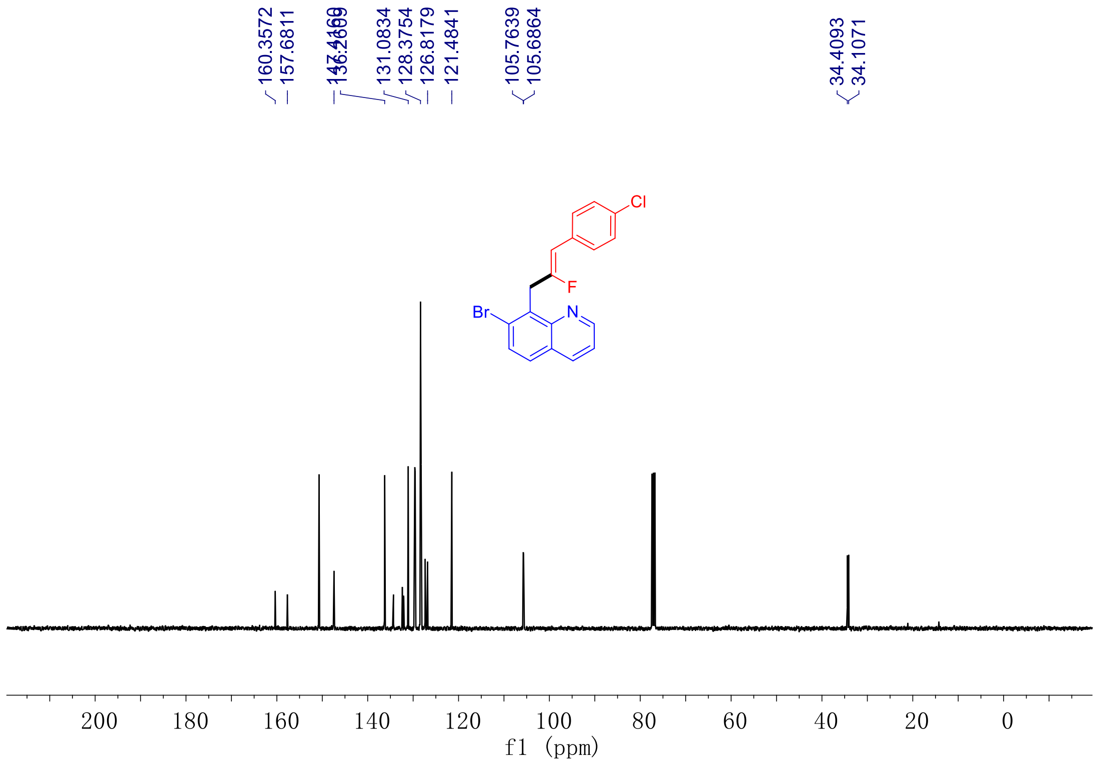
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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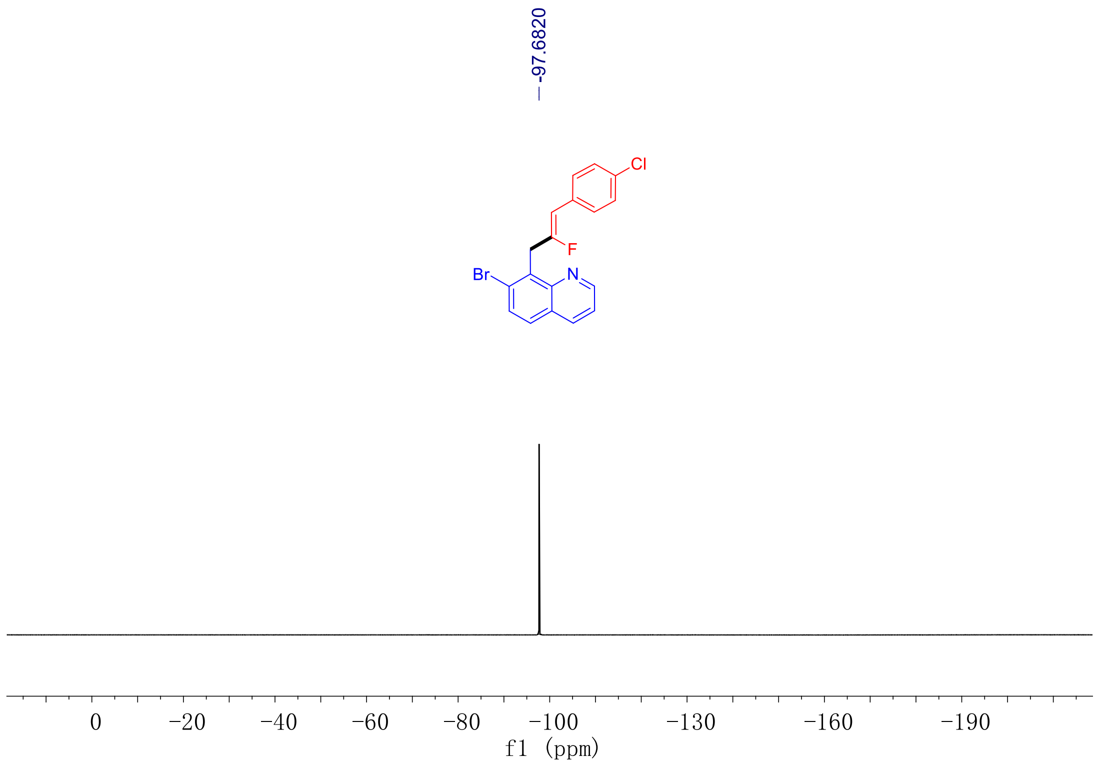
F
Br
N
f1 (ppm)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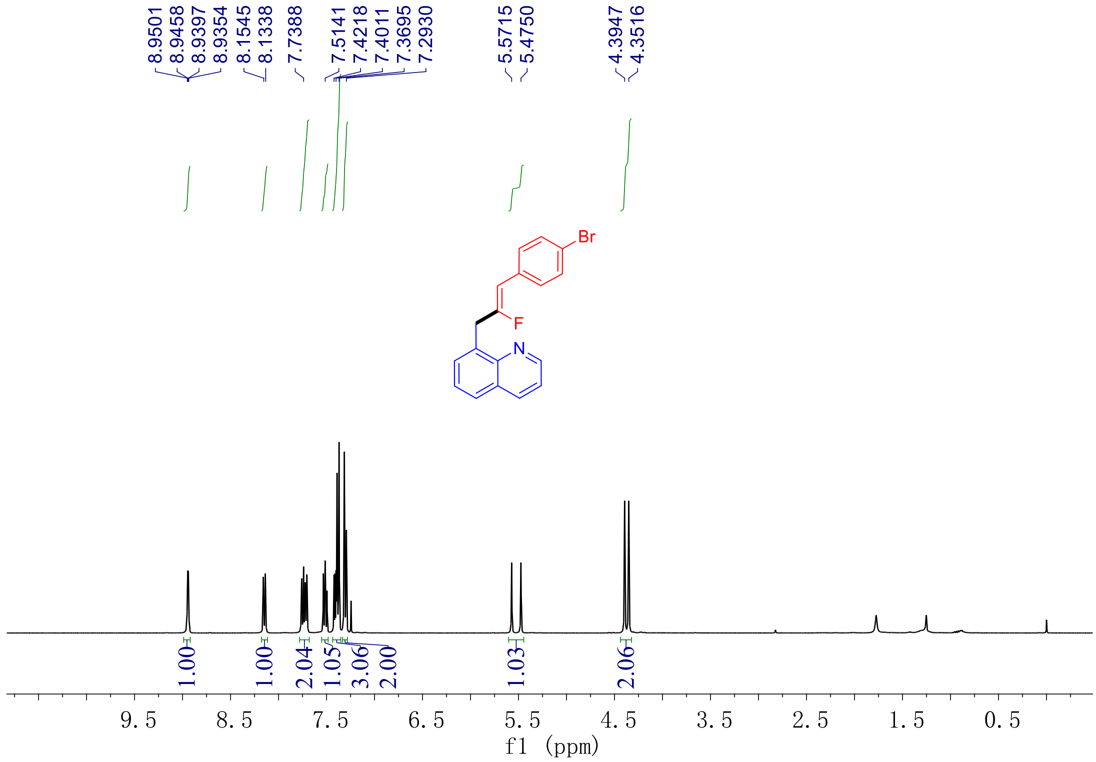
F
Br
N
f1 (ppm)

3ag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7.3695
7.2930
5.5715
5.4750
4.3947
4.3516
Br
F
N
1.00
1.00
2.04
1.05
3.06
2.00
1.03
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9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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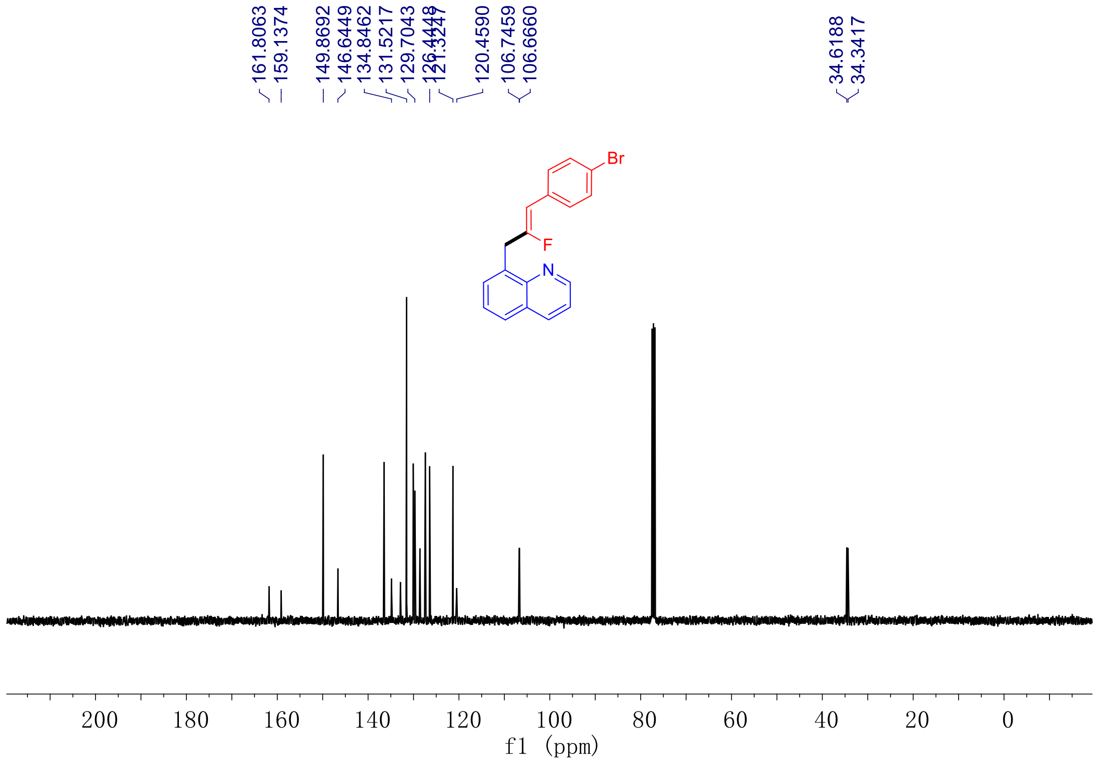
f1 (ppm)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129.7043
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106.7459
106.6660
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Br
F
N
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180
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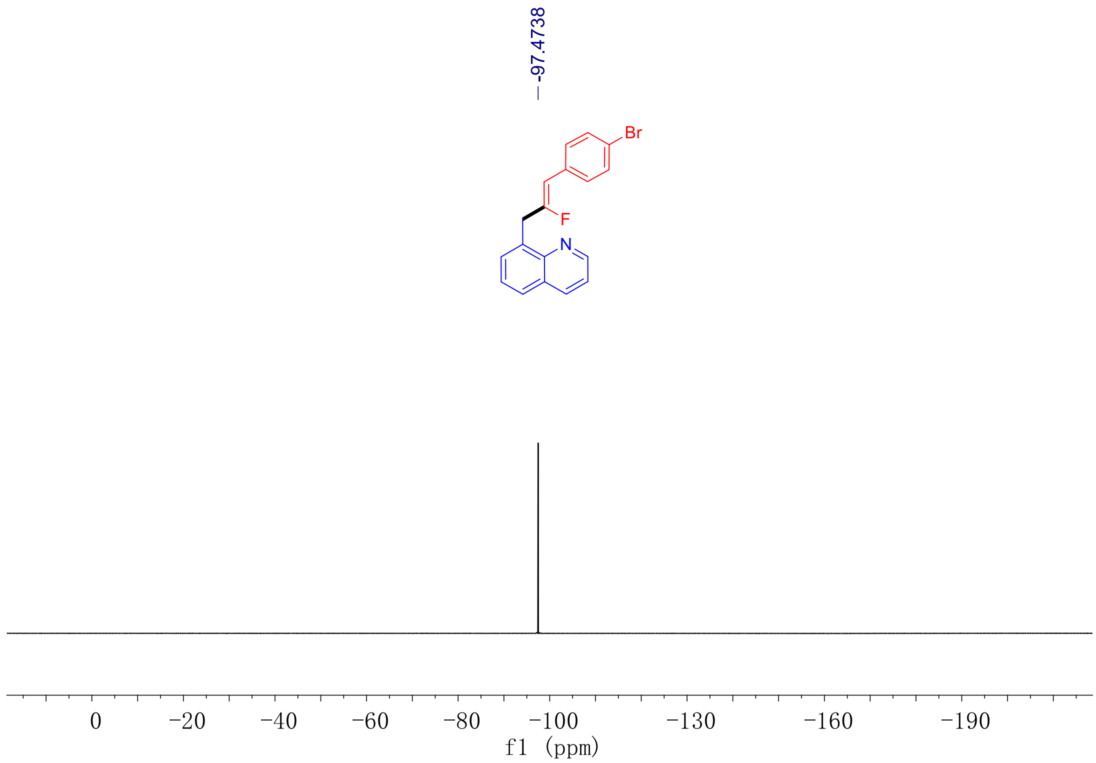
140
120
100
80
60
40
20
0
f1 (ppm)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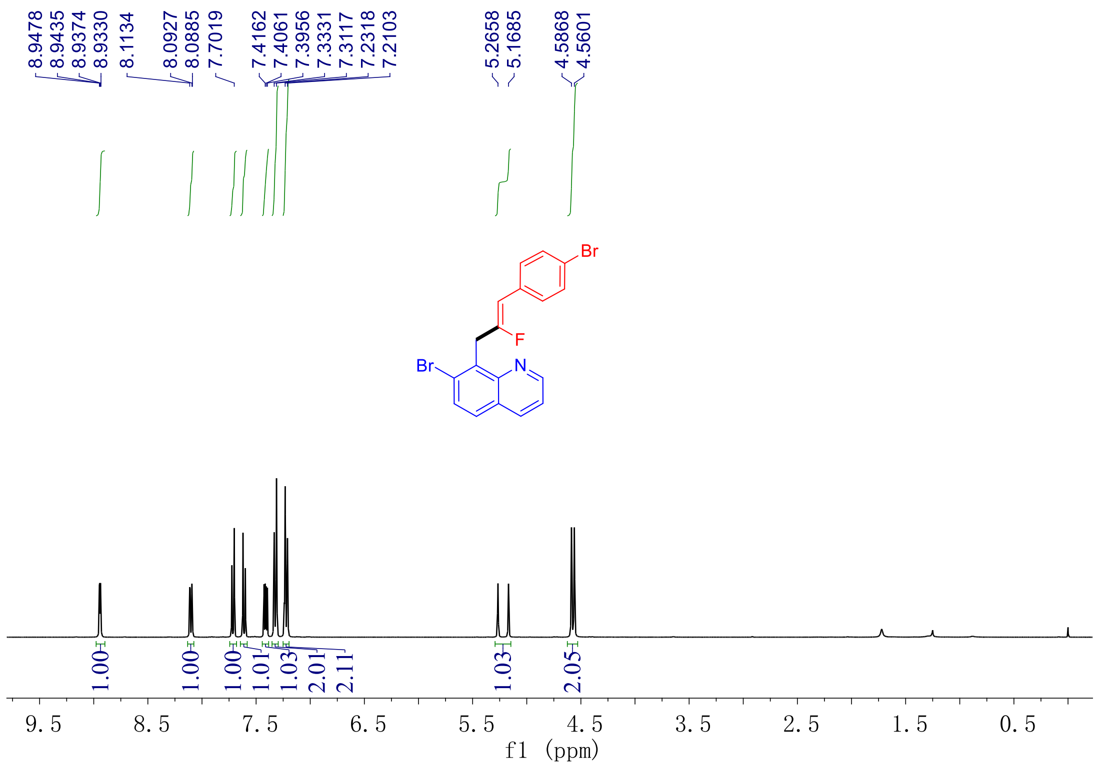
3og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7.3956
7.3331
7.3117
7.2318
7.2103
5.2658
5.1685
4.5868
4.5601
Br
F
Br
N
1.00
1.00
1.00
1.01
1.03
2.01
2.11
1.03
2.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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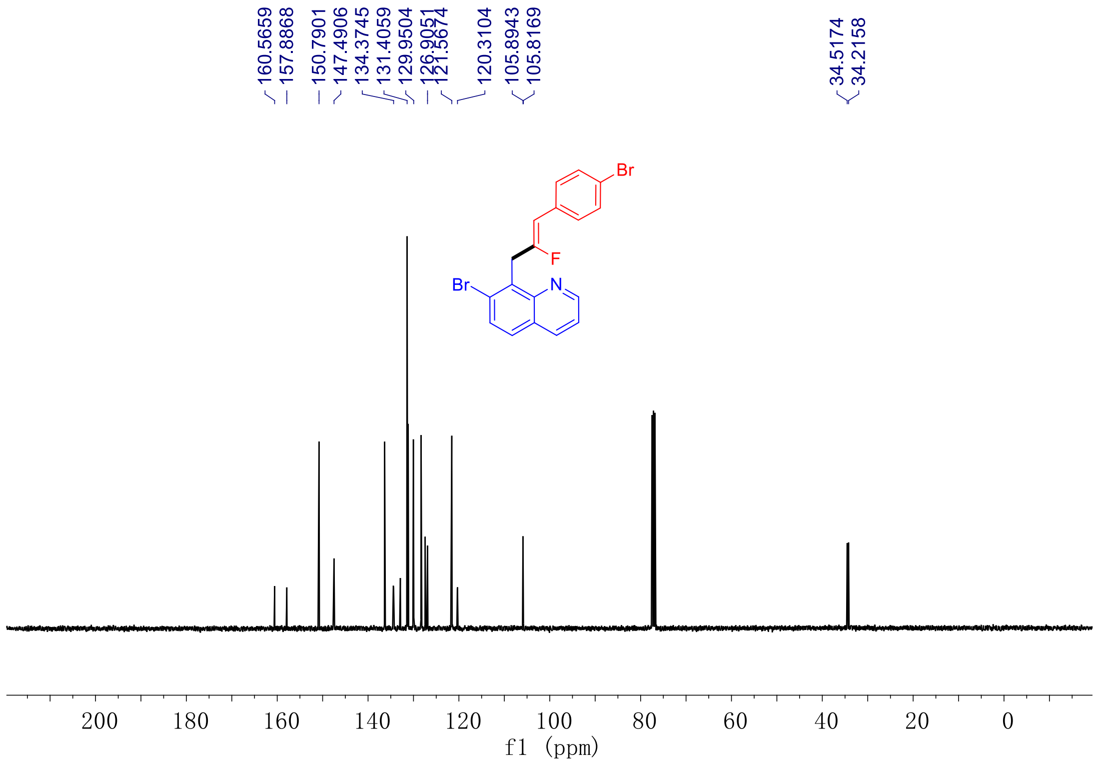
f1 (ppm)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129.9504
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105.8943
105.8169
34.5174
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F
Br
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100
80
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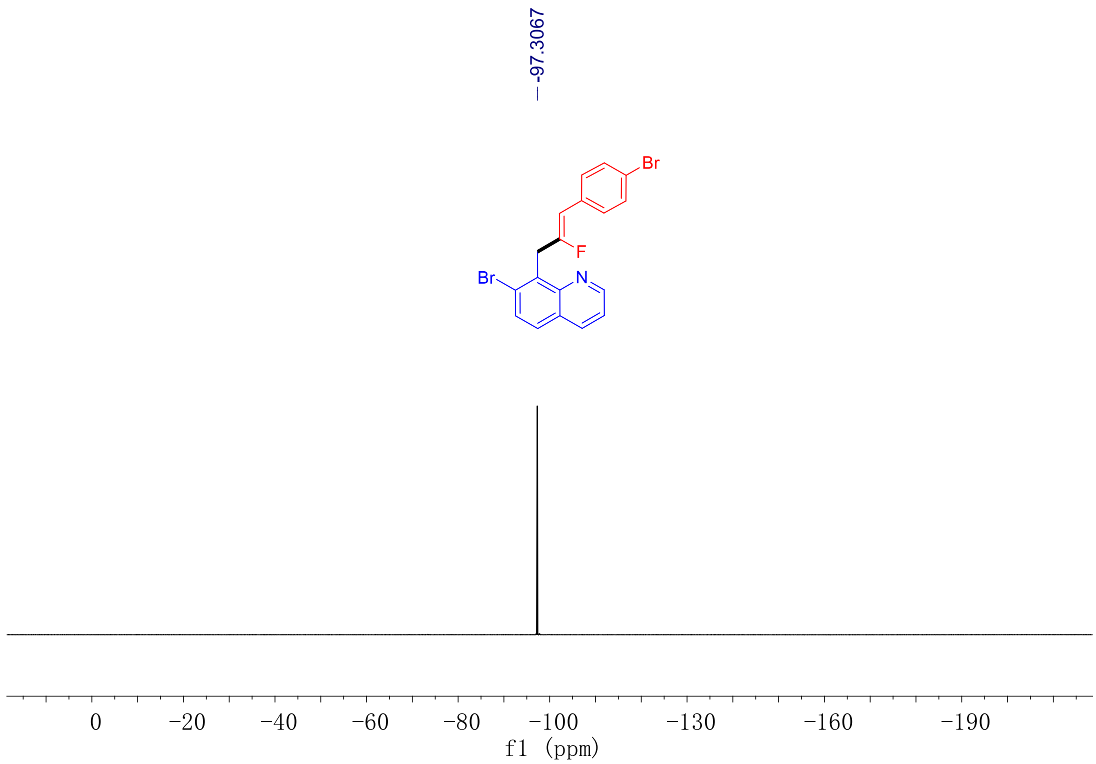
f1 (ppm)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Br
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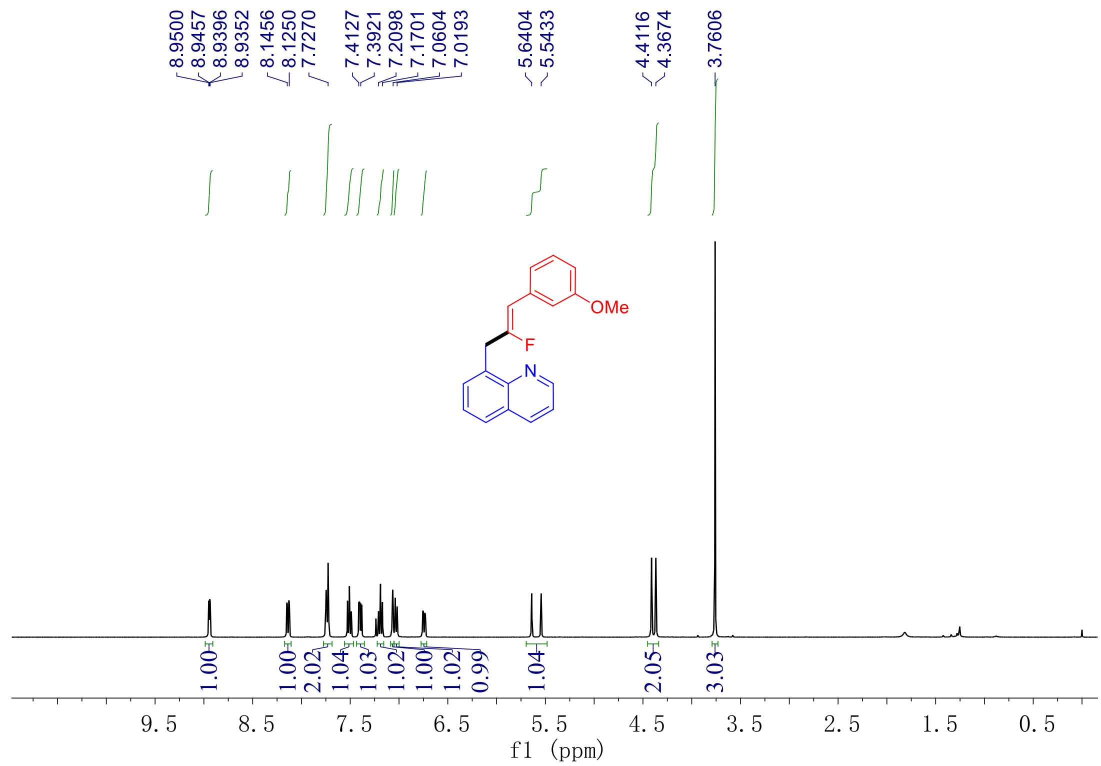
f1 (ppm)

3ah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7.7270
7.4127
7.3921
7.2098
7.1701
7.0604
7.0193
5.6404
5.5433
4.4116
4.3674
3.7606
OMe
F
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1.00
1.00
2.02
1.04
1.03
1.02
1.00
1.02
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1.04
2.05
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5.5
4.5
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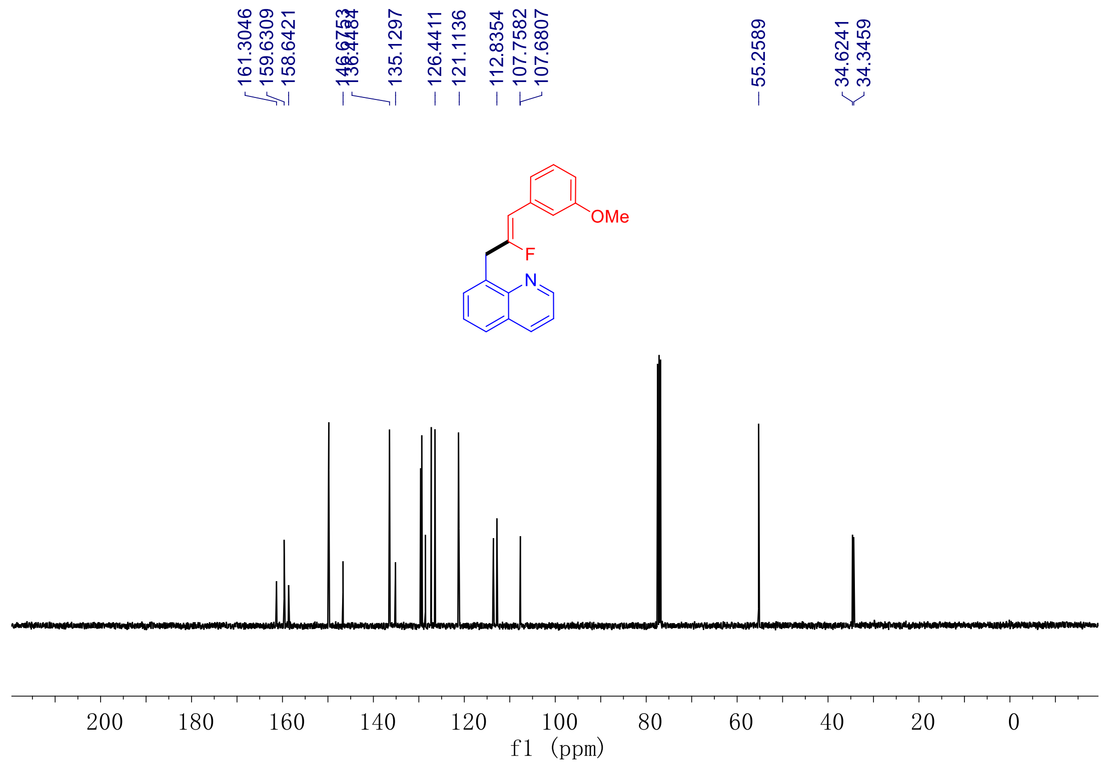
f1 (ppm)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135.1297
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121.1136
112.8354
107.7582
107.6807
55.2589
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100
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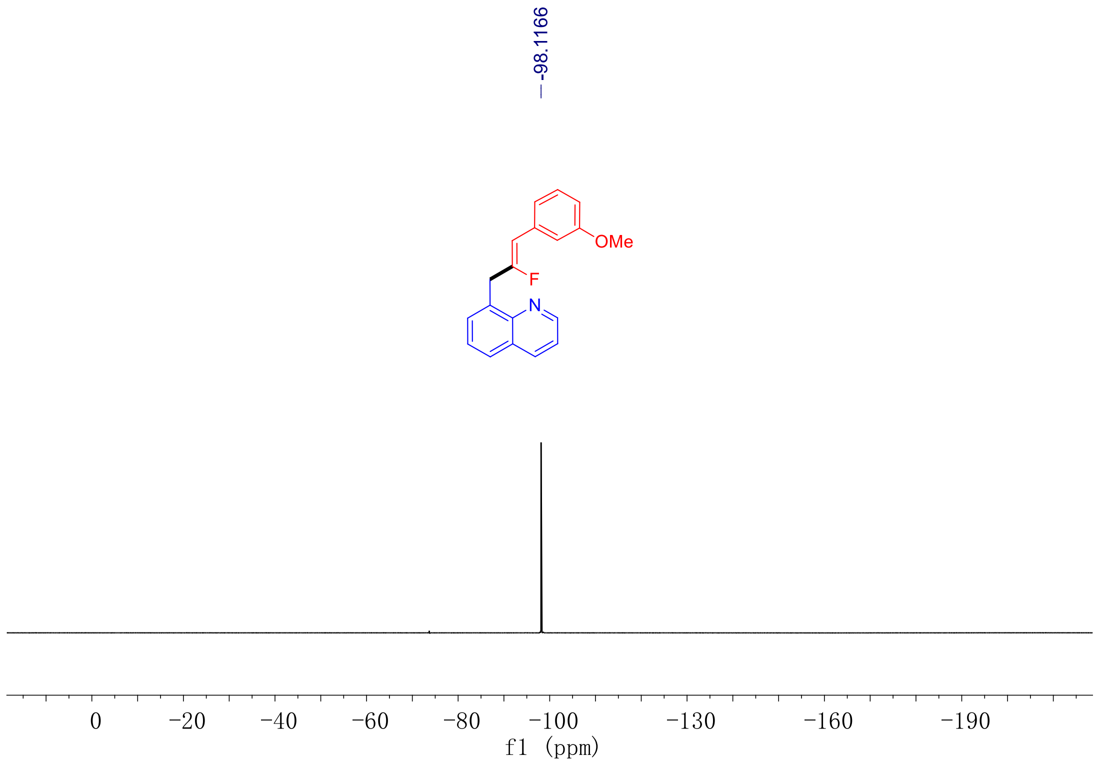
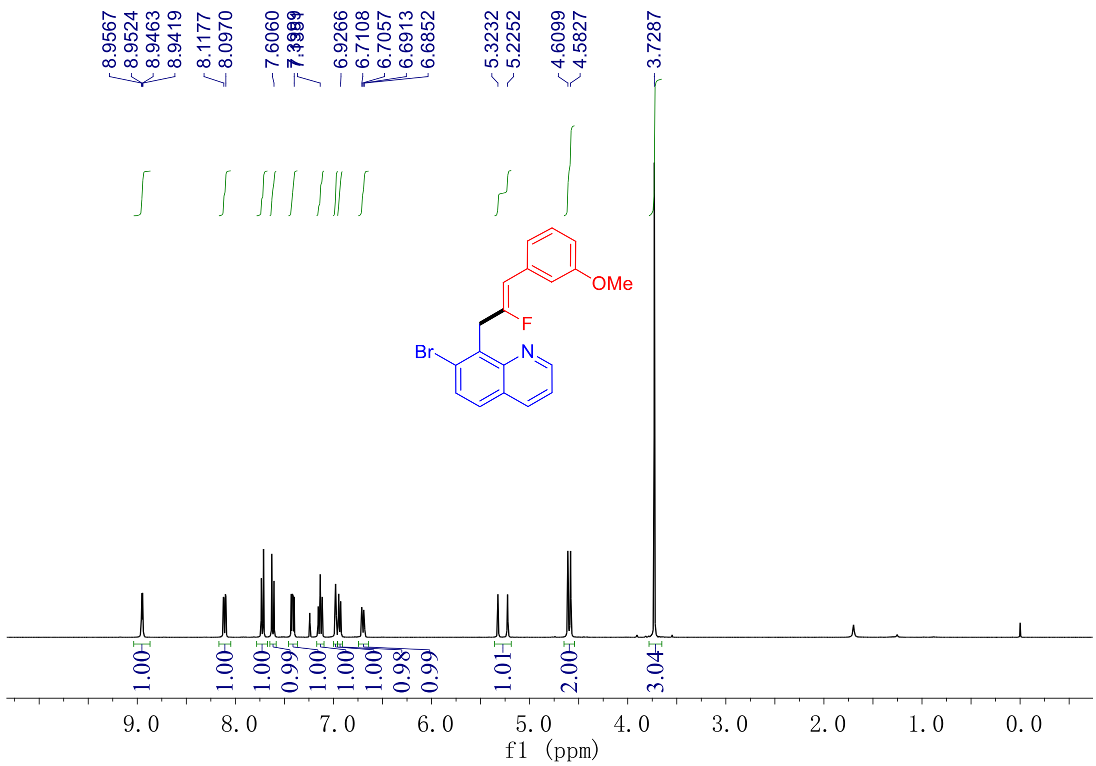
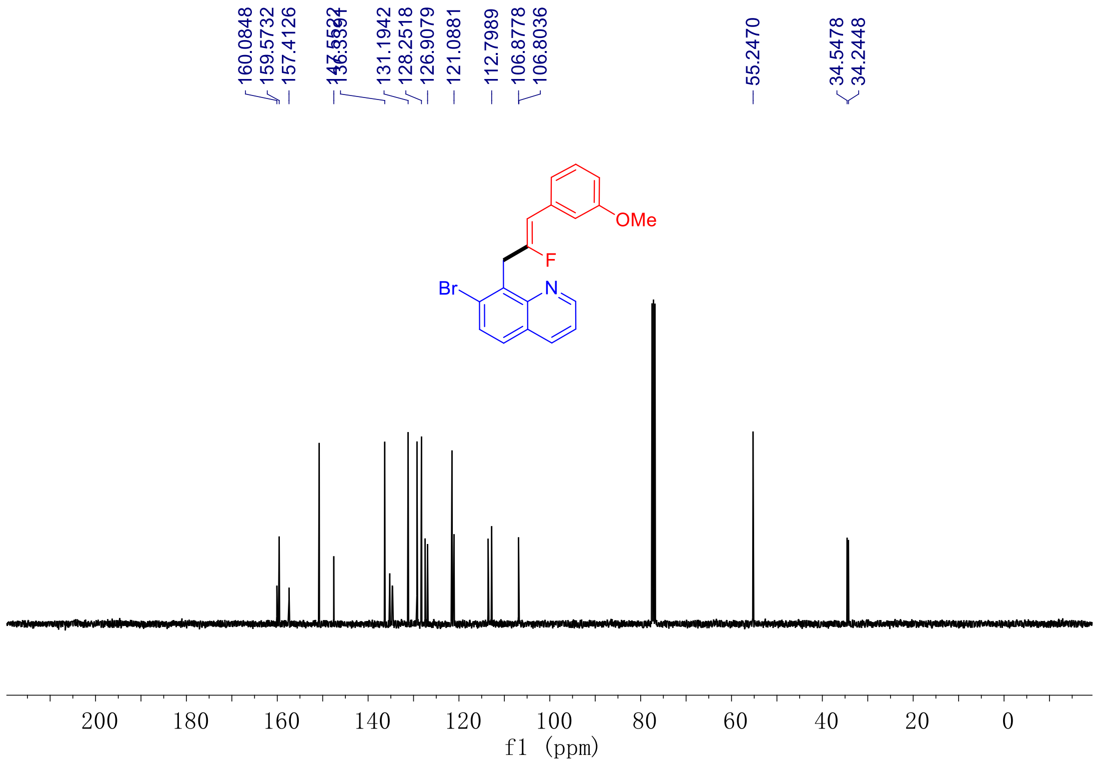


3oh

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106.8778
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55.2470
34.5478
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Br
N
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140
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100
80
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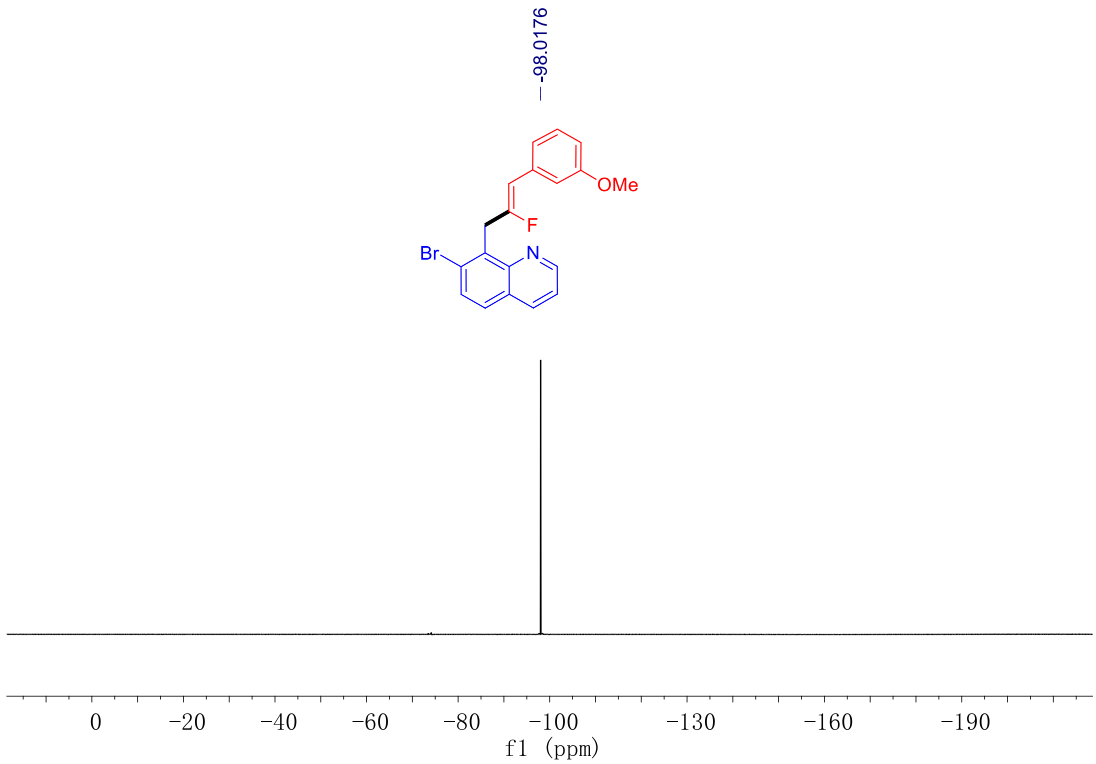
f1 (ppm)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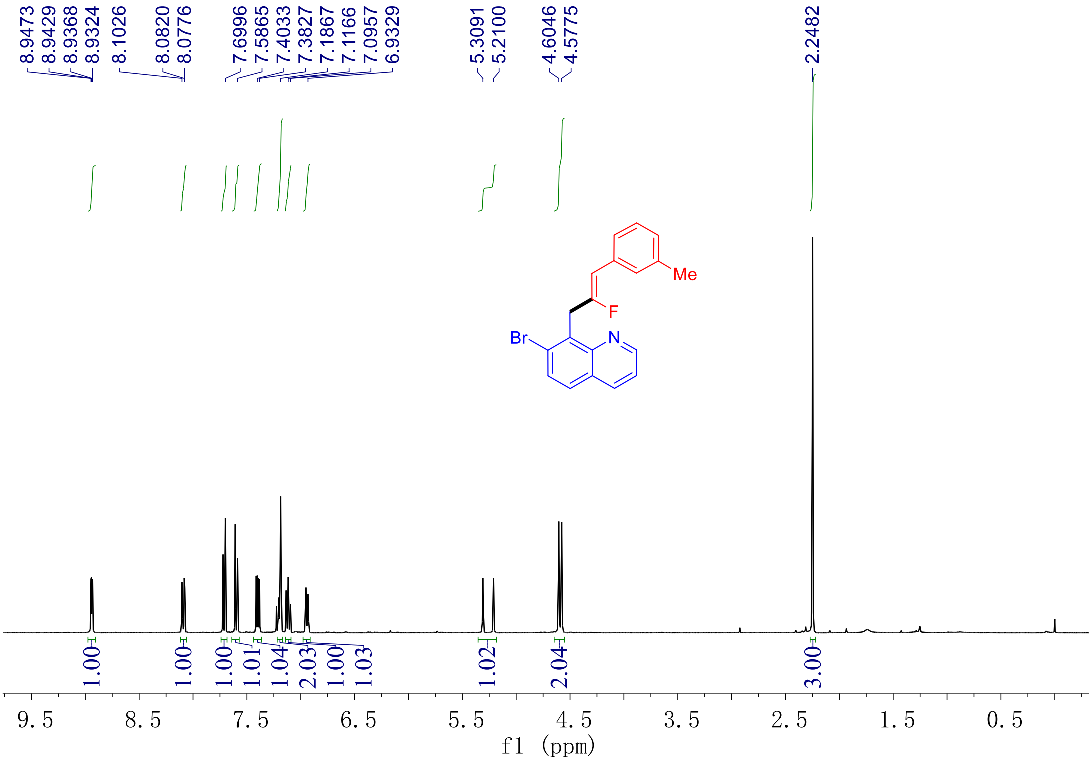
3oi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8.0776
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7.1867
7.1166
7.0957
6.9329
5.3091
5.2100
4.6046
4.5775
2.2482
Br
N
F
Me
1.00
1.00
1.00
1.01
1.04
2.03
1.00
1.03
1.02
2.04
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5.5
4.5
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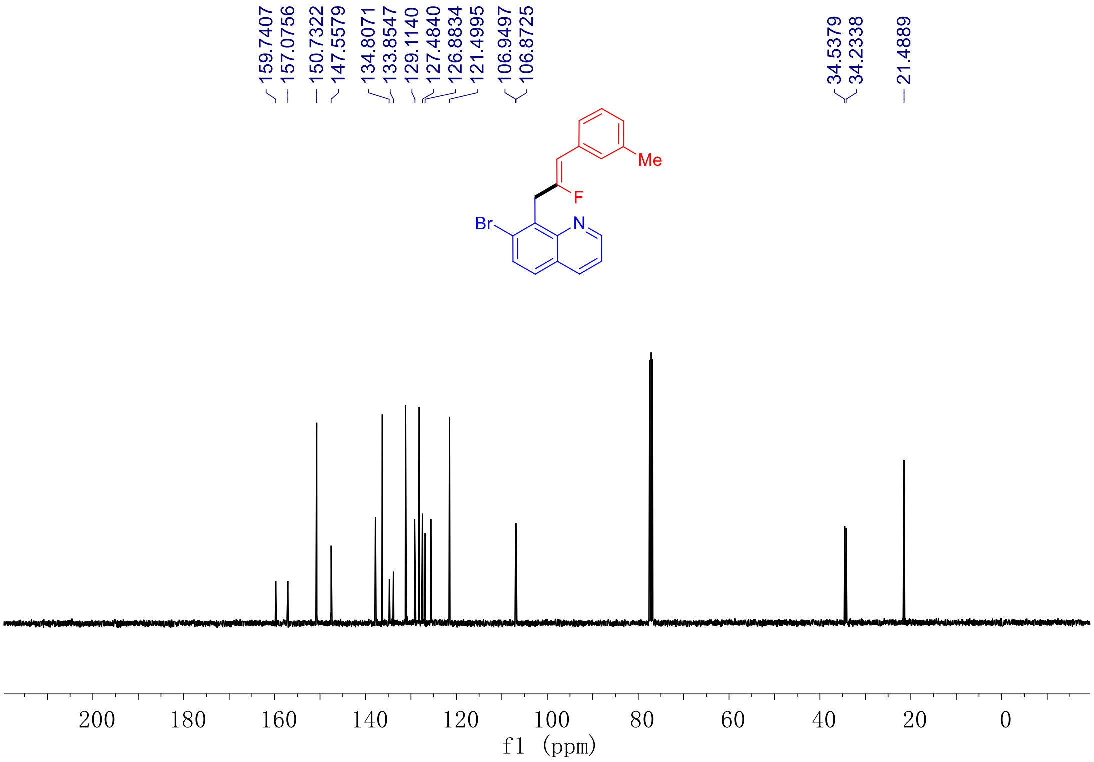
f1 (ppm)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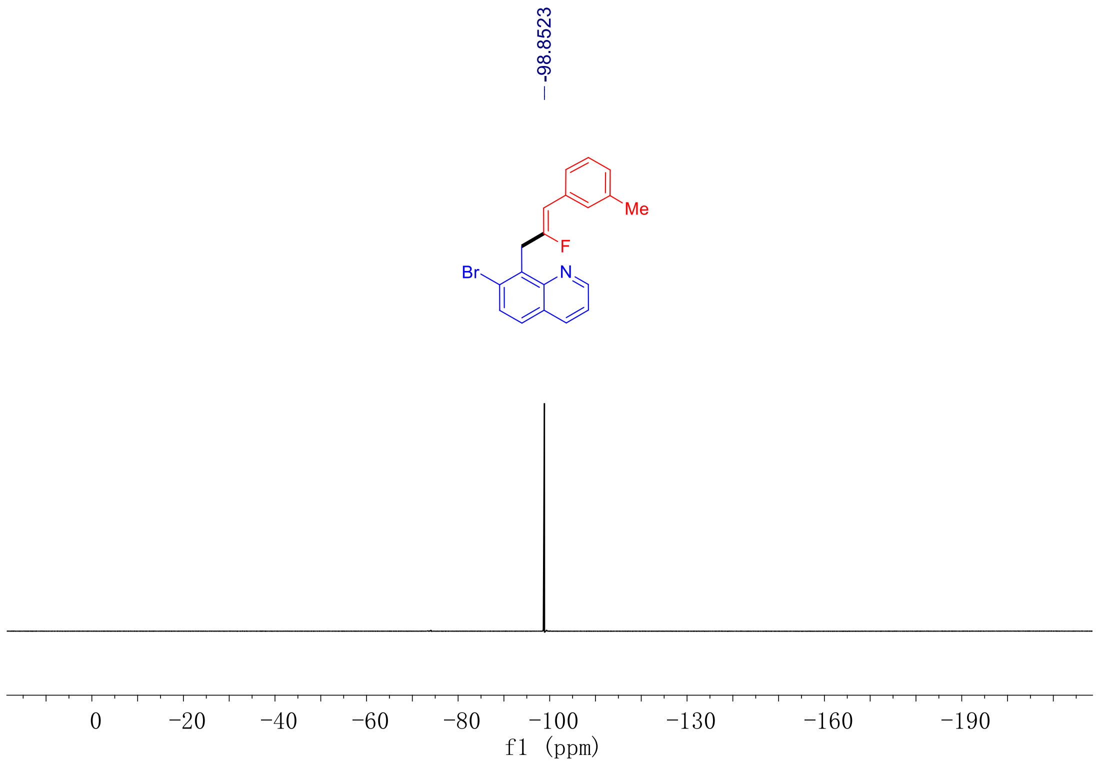
f1 (ppm)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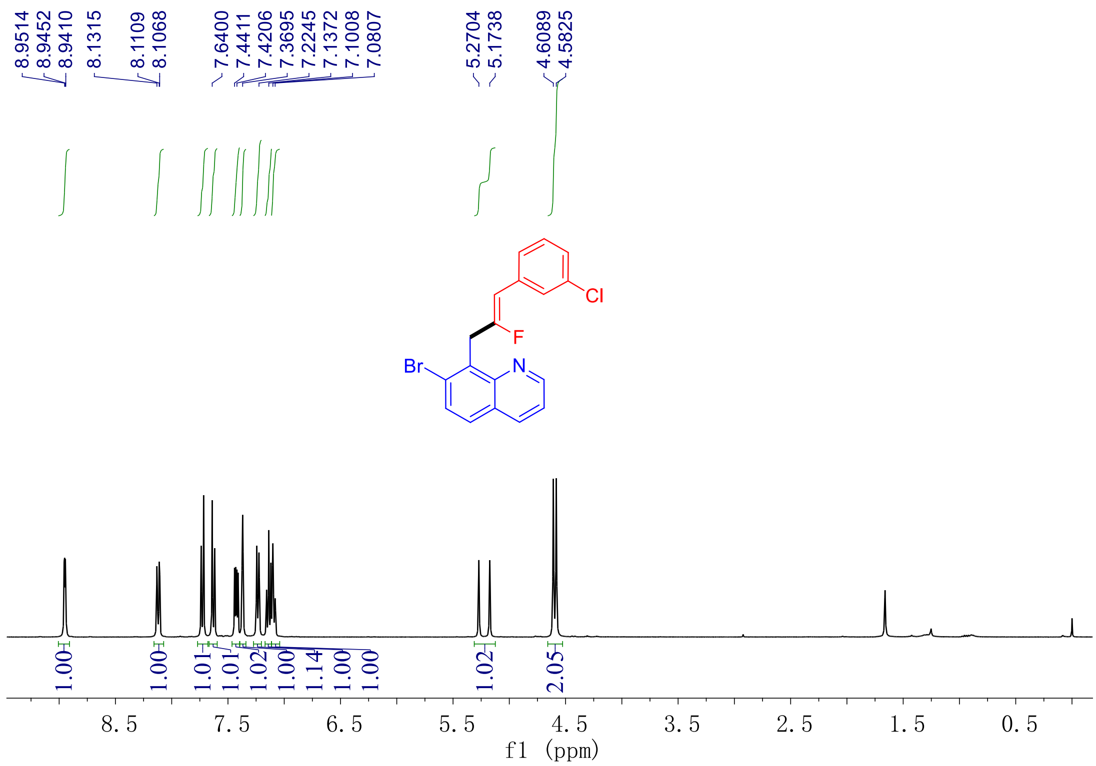
−190
f1 (ppm)

3oj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7.1008
7.0807
5.2704
5.1738
4.6089
4.5825
Cl
F
Br
N
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1.00
1.01
1.01
1.02
1.00
1.14
1.00
1.00
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7.5
6.5
5.5
4.5
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2.5
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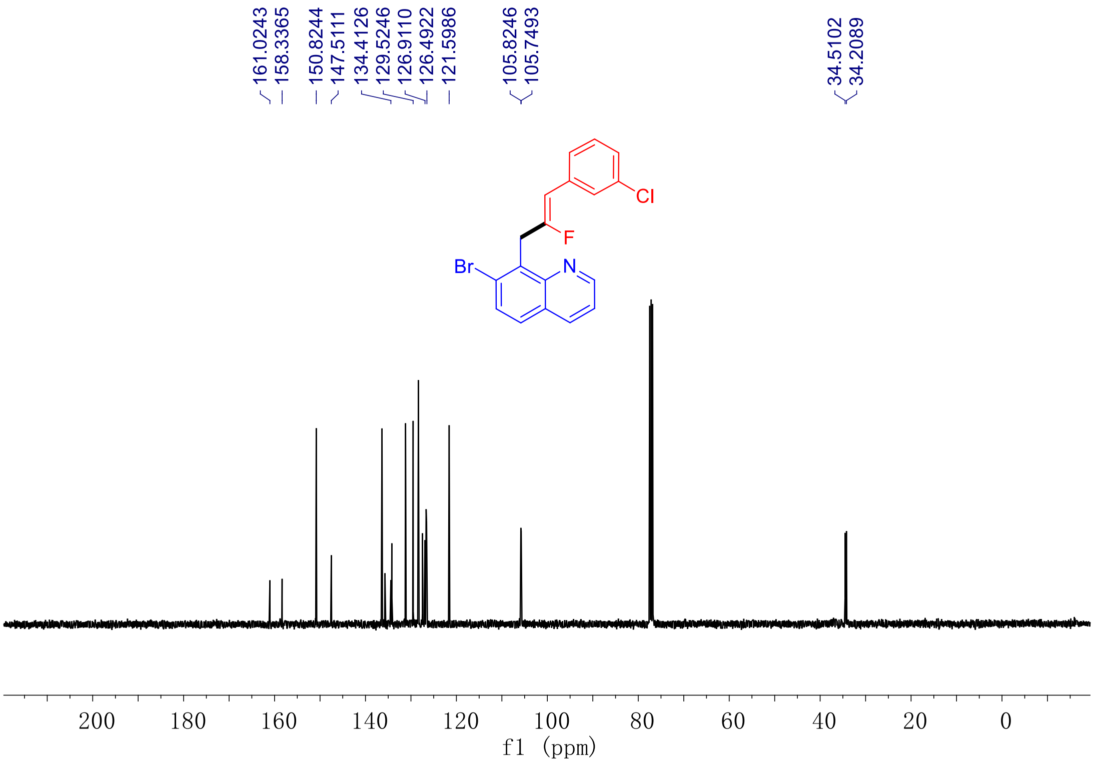
f1 (ppm)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105.7493
34.5102
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N
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80
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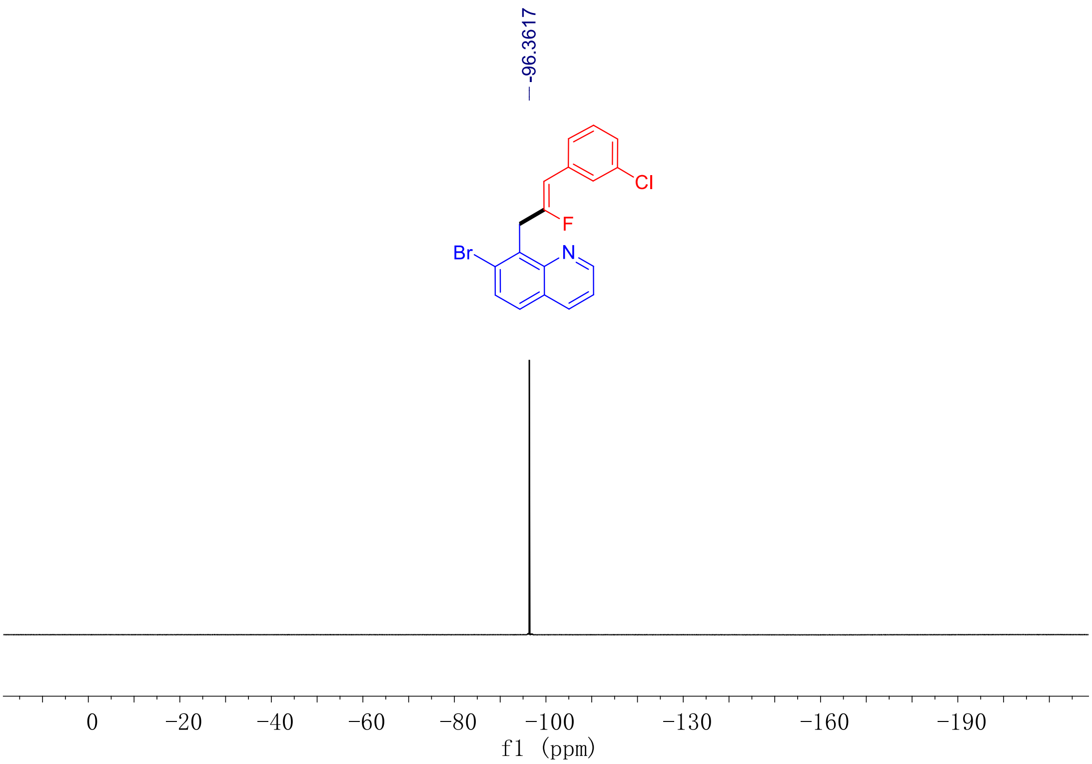
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−80
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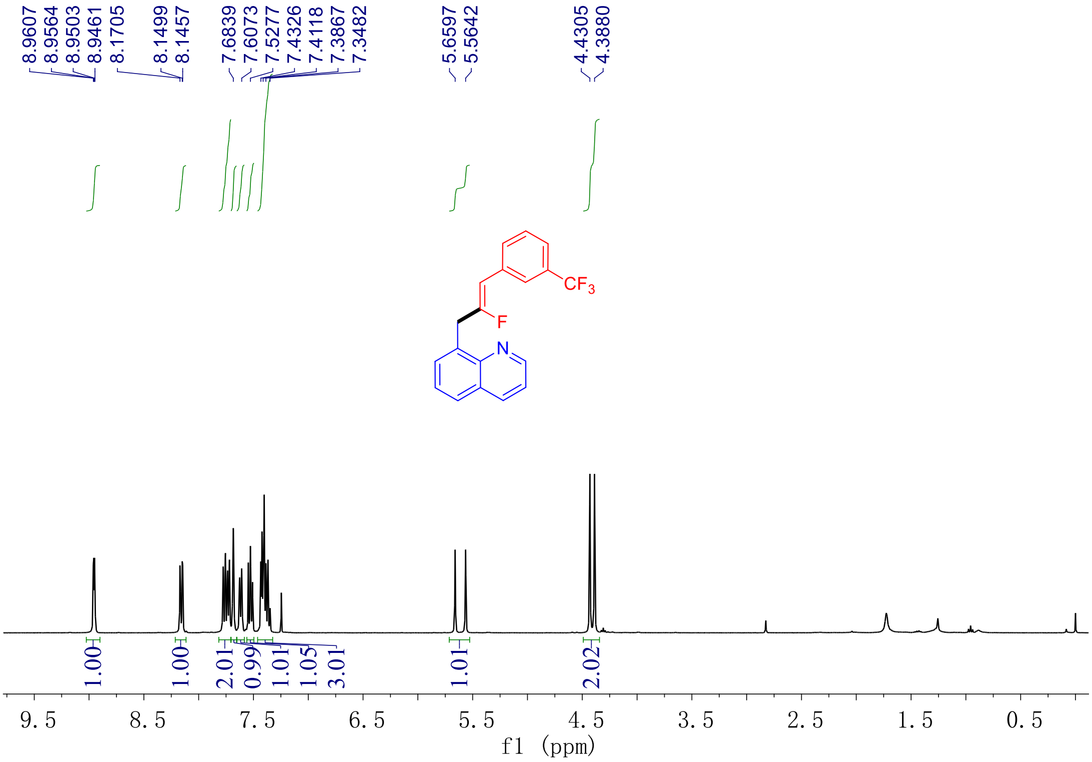
−190
f1 (ppm)

3ak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7.4118
7.3867
7.3482
5.6597
5.5642
4.4305
4.3880
CF3
F
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1.00
2.01
0.99
1.01
1.05
3.01
1.01
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7.5
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2.5
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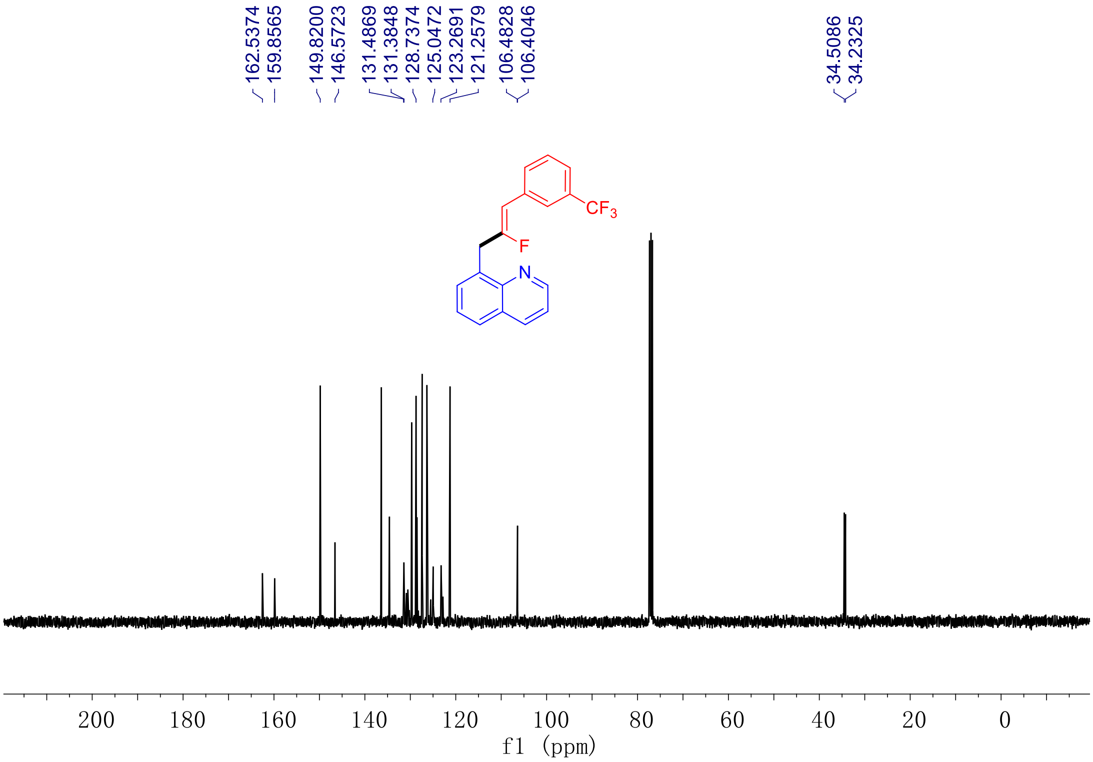
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106.4046
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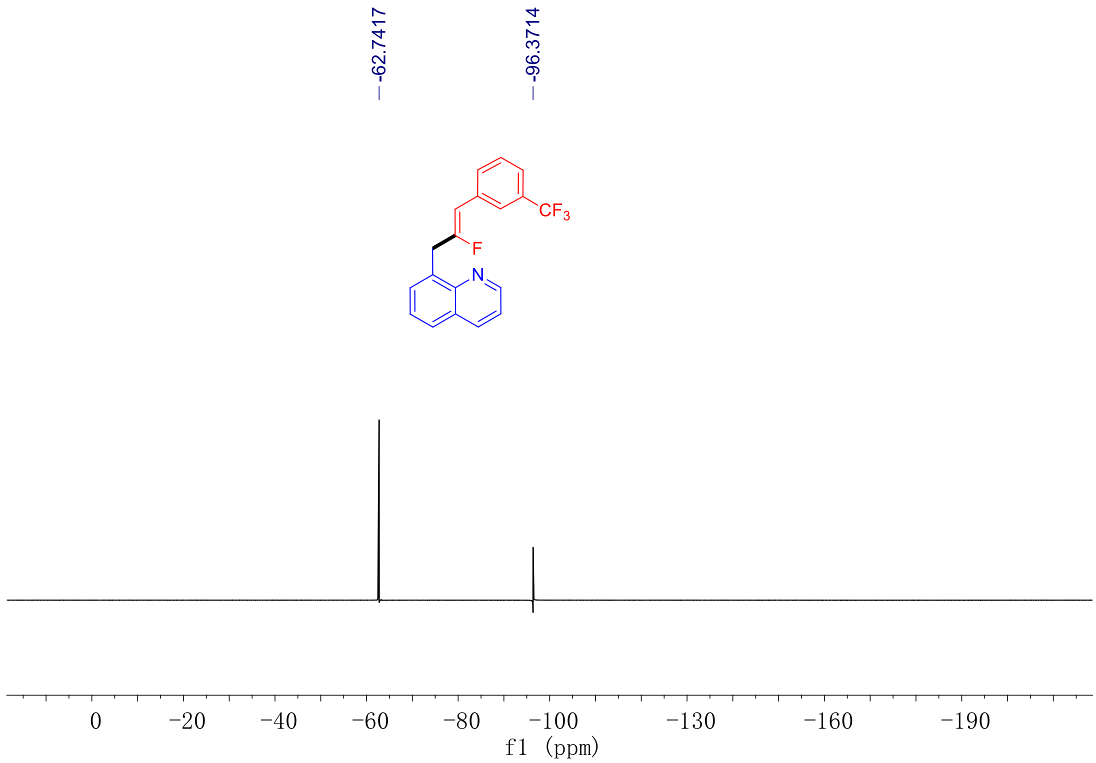
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CF3
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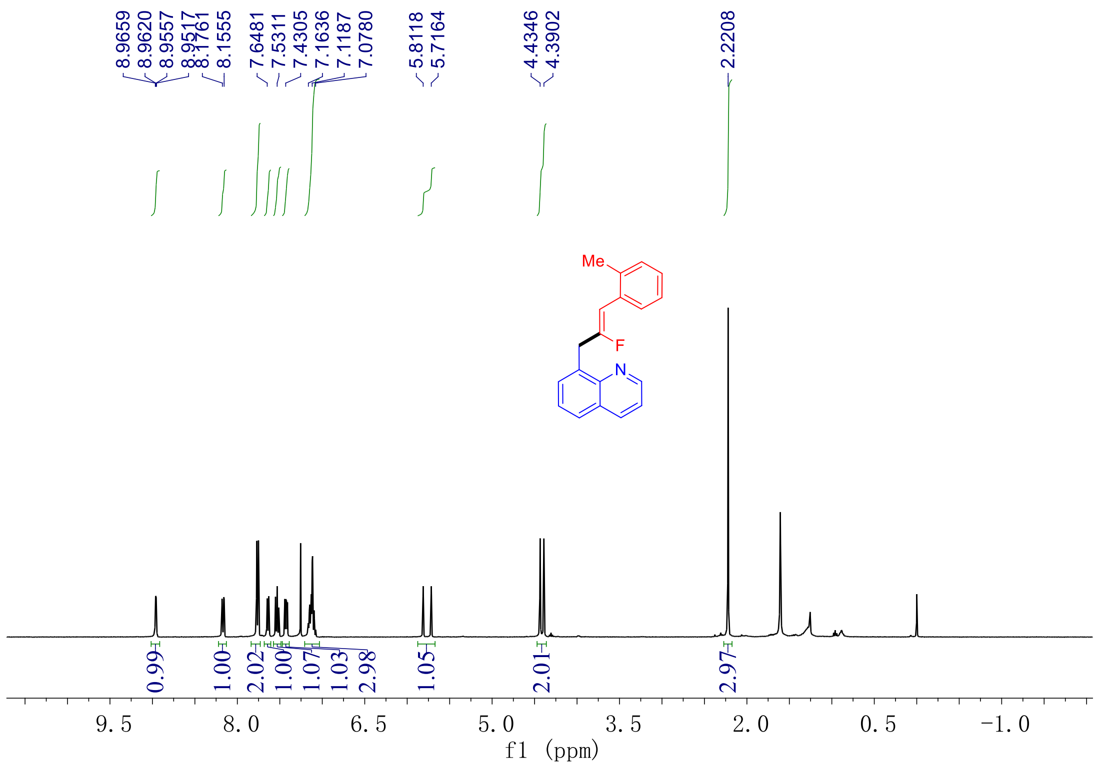
-190
f1 (ppm)

3al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7.1187
7.0780
5.8118
5.7164
4.4346
4.3902
2.2208
Me
F
N
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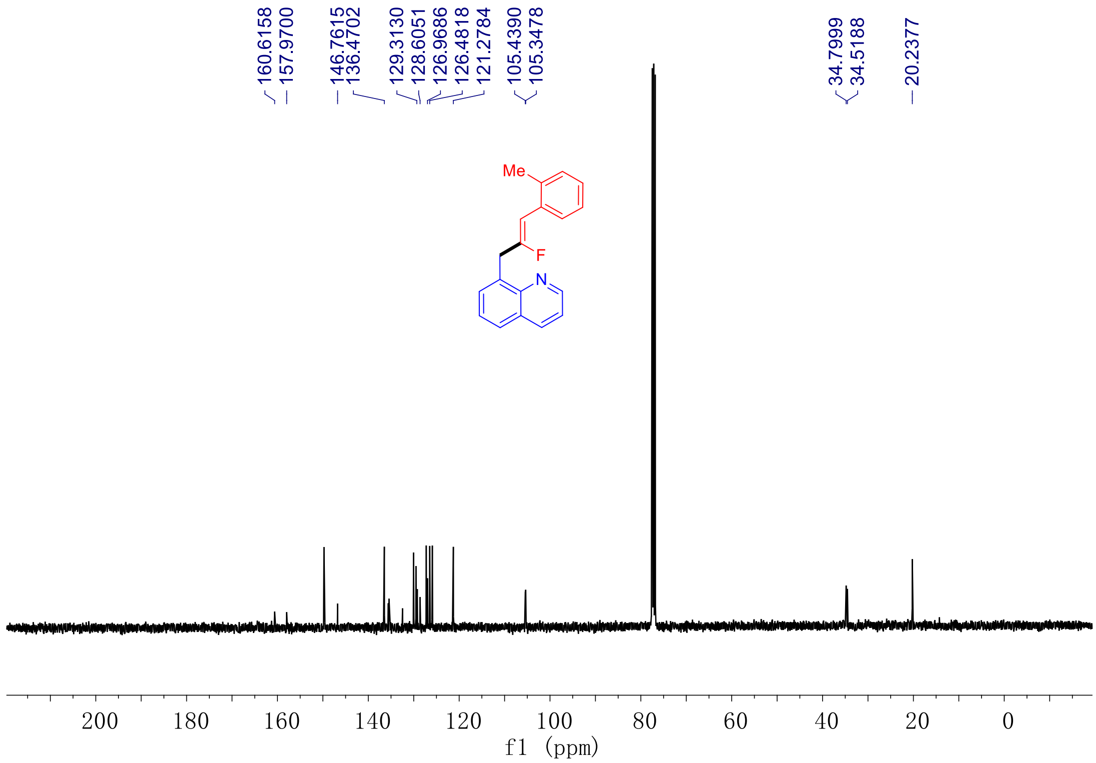
1.00
2.02
1.00
1.07
1.03
2.98
1.05
2.01
2.97
9.5
8.0
6.5
5.0
3.5
2.0
0.5
-1.0
f1 (ppm)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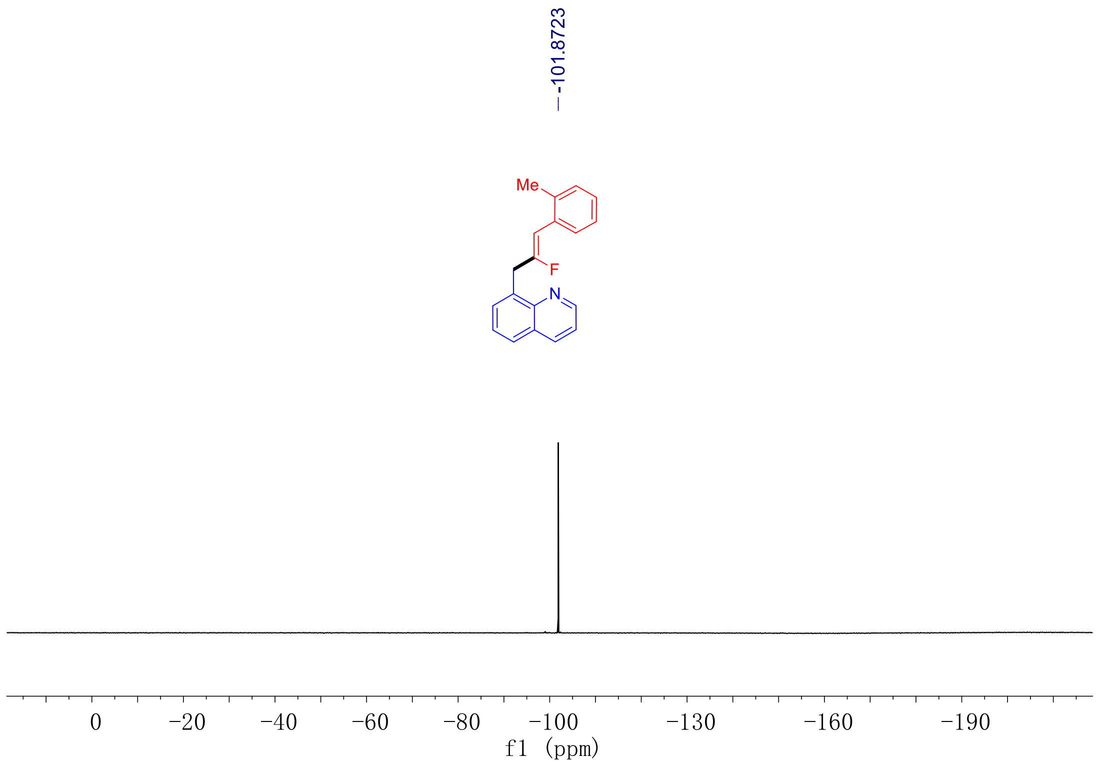
157.9700
146.7615
136.4702
129.3130
128.6051
126.9686
126.4818
121.2784
105.4390
105.3478
34.7999
34.5188
20.2377
Me
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Me
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N
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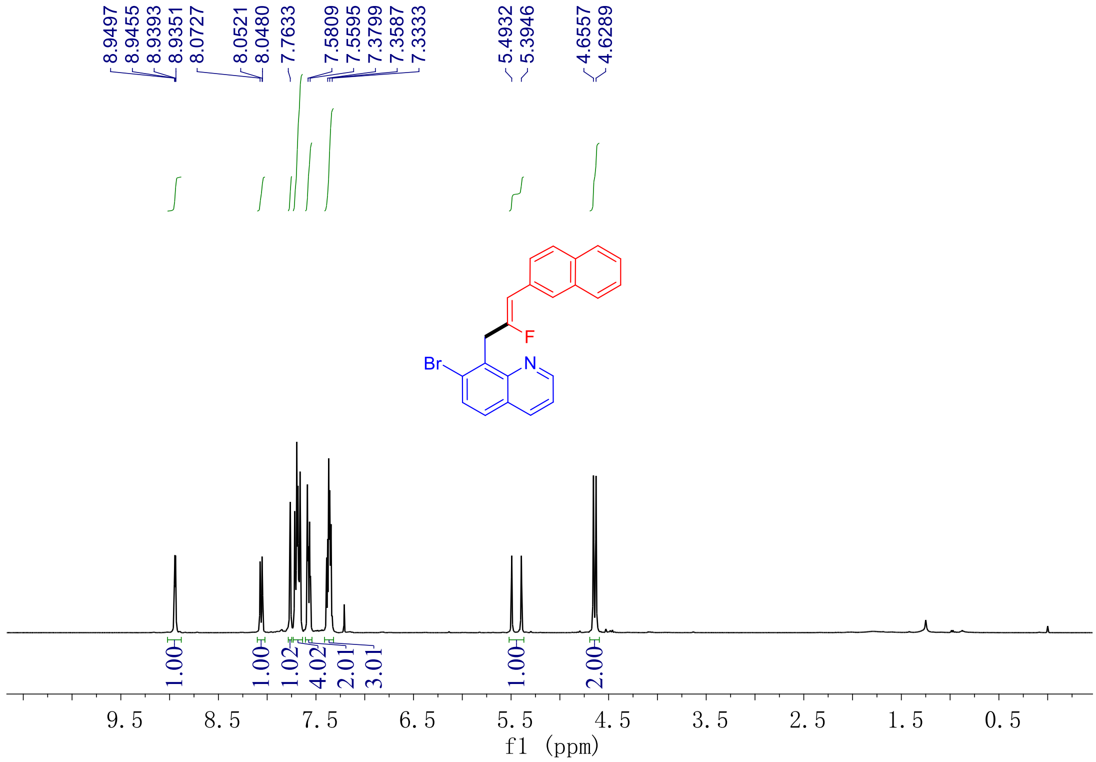
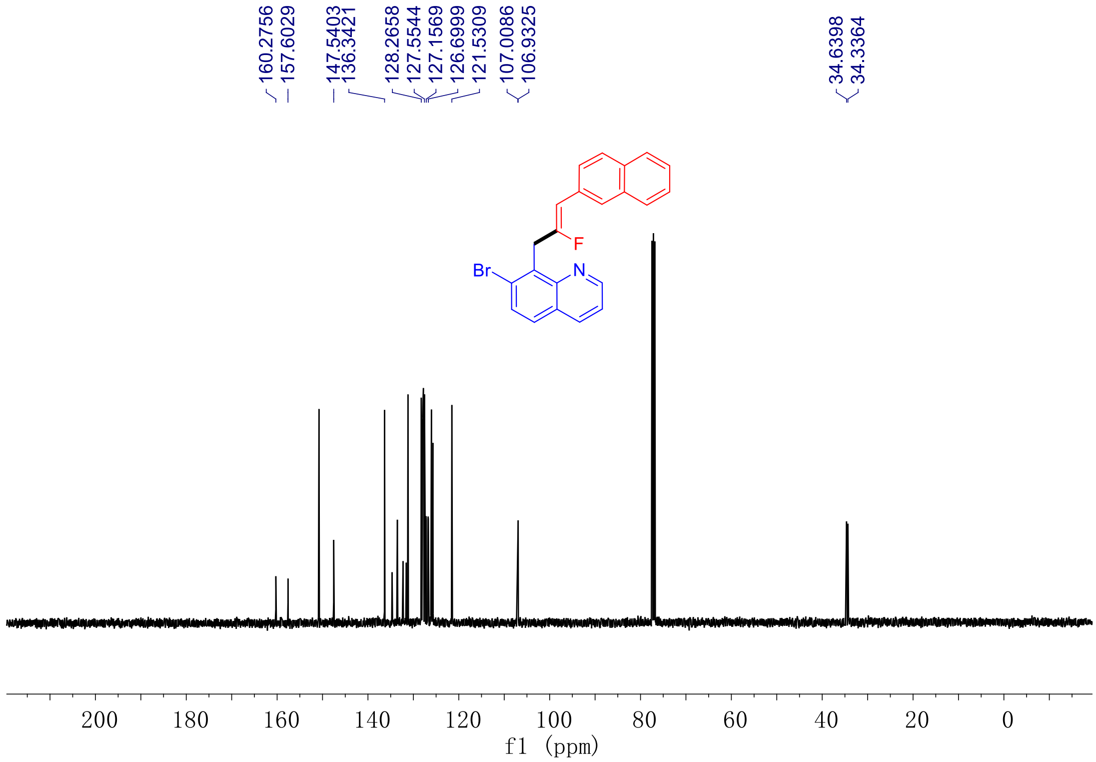
−60
−80
−100
−130
−160
−190
f1 (ppm)

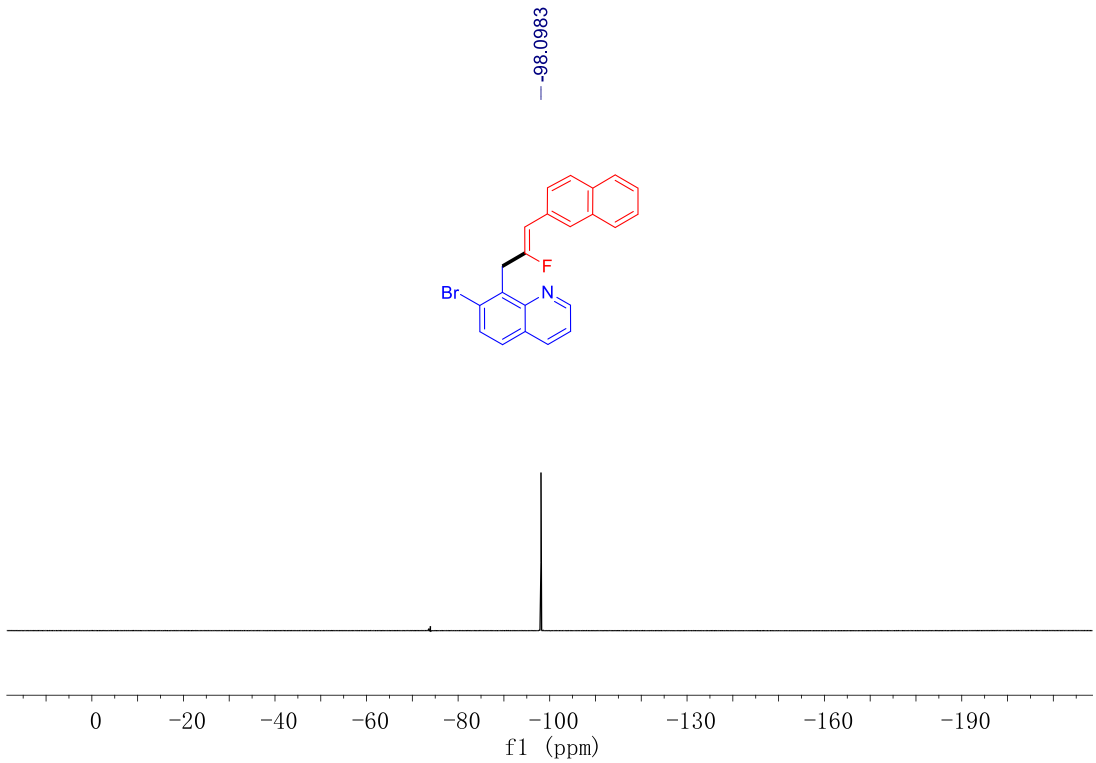
3om



8.9497
8.9455
8.9393
8.9351
8.0727
8.0521
8.0480
7.7633
7.5809
7.5595
7.3799
7.3587
7.3333
5.4932
5.3946
4.6557
4.6289
Br
N
F
1.00
1.00
1.02
4.02
2.01
3.01
1.00
2.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



160.2756
157.6029
147.5403
136.3421
128.2658
127.5544
127.1569
126.6999
121.5309
107.0086
106.9325
34.6398
34.3364
Br
N
F
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-98.0983
Br
N
F
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−60
−80
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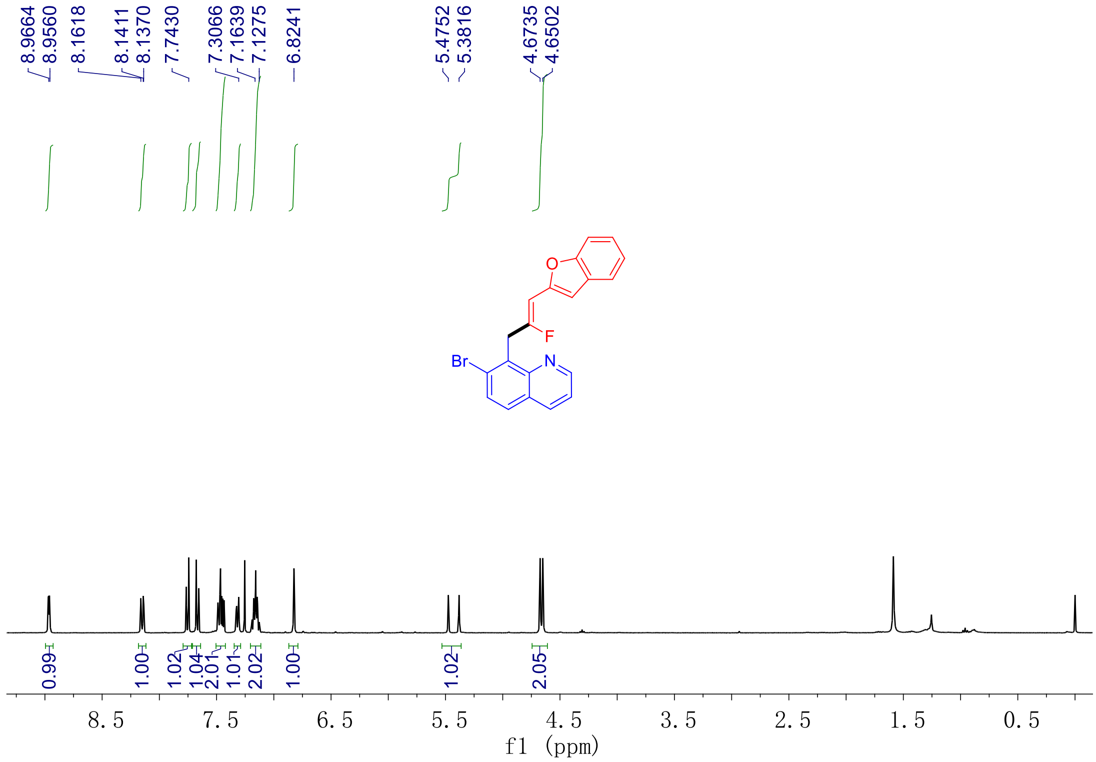
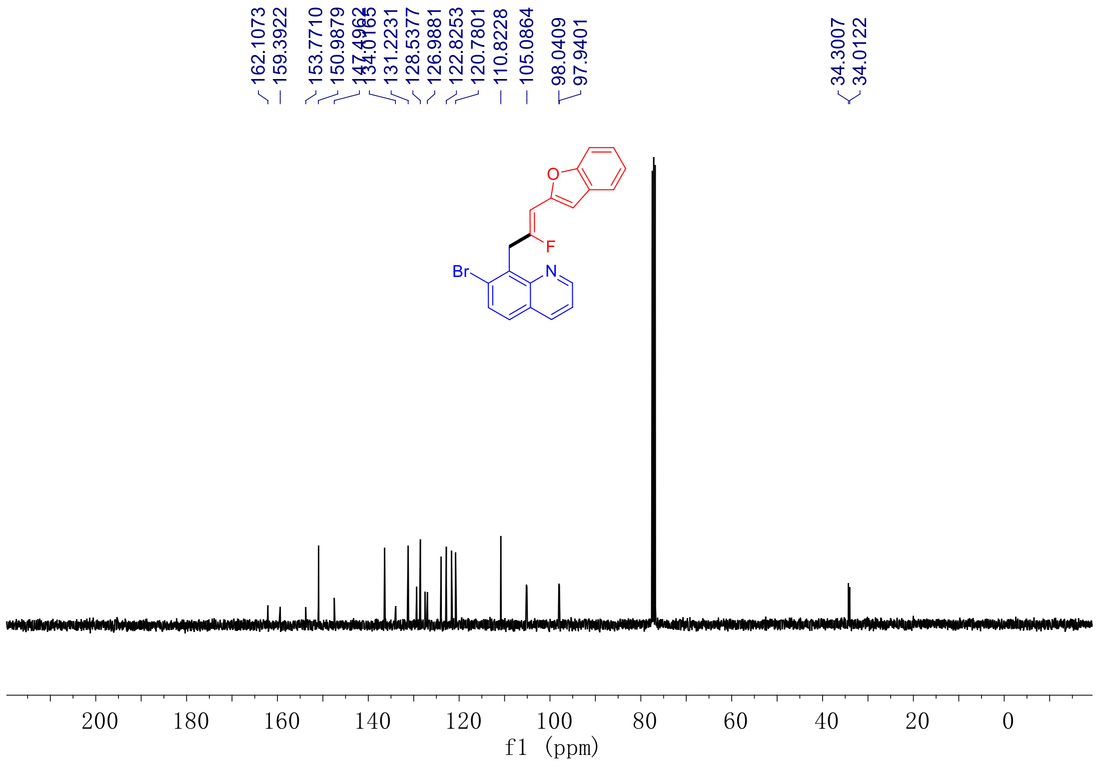
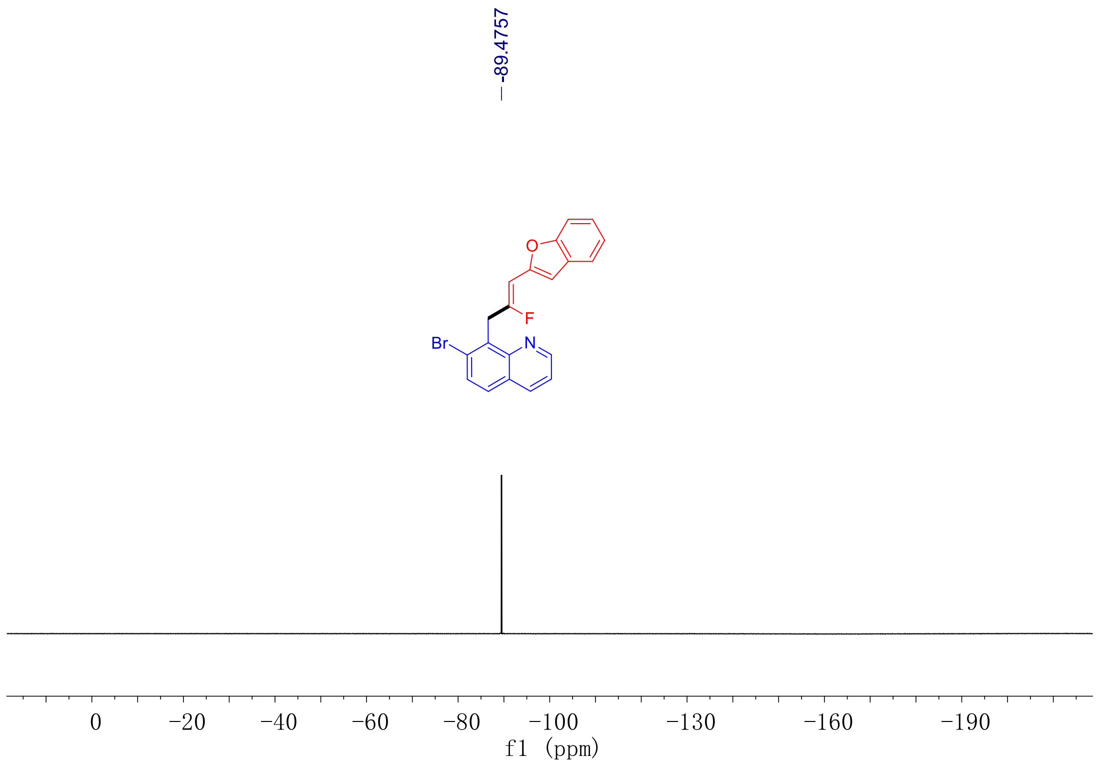
−130
−160
−190
f1 (ppm)

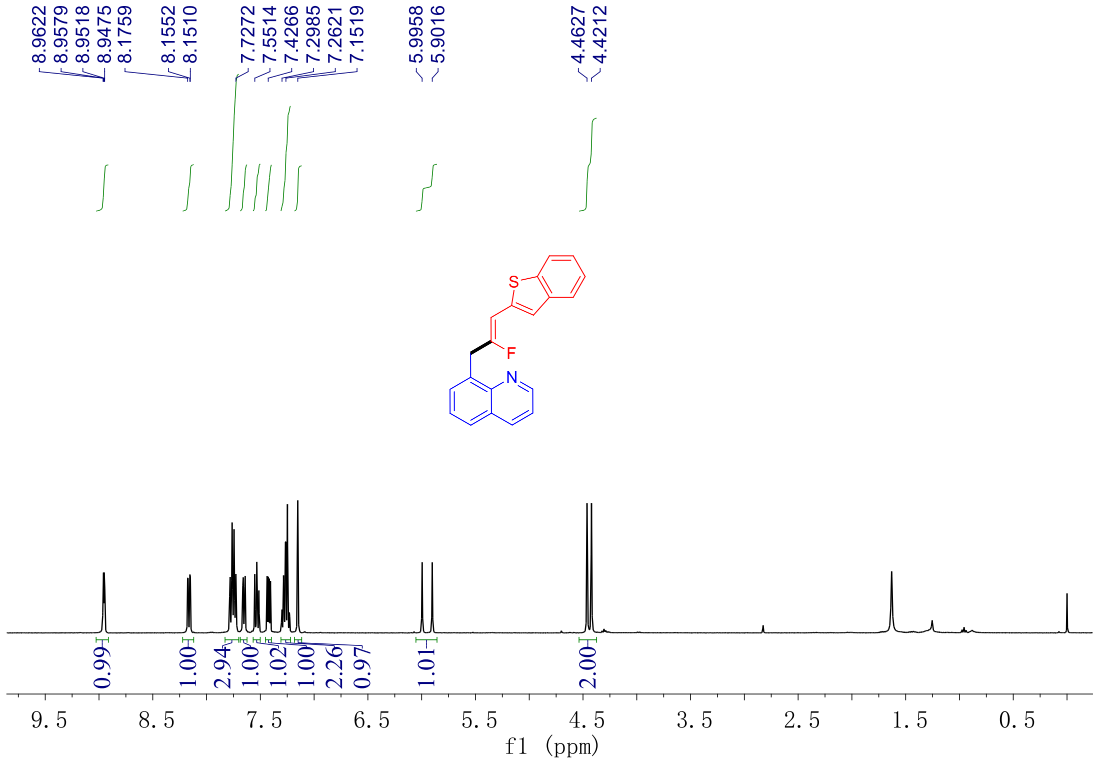
3on

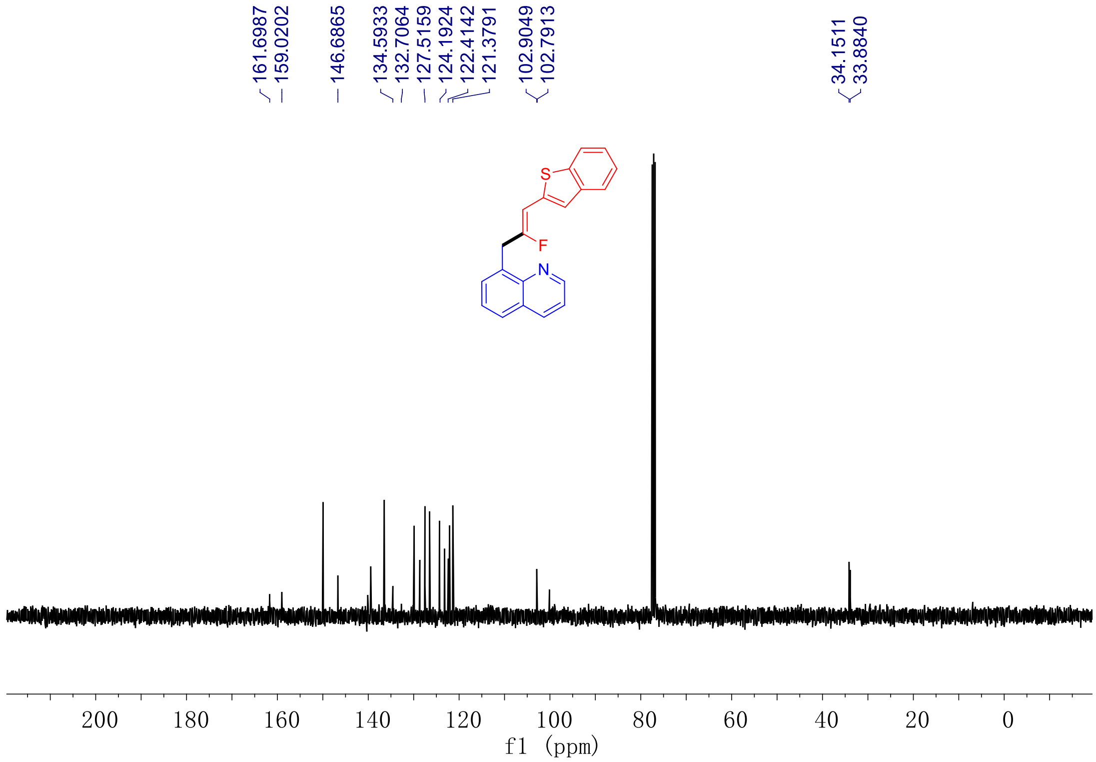

8.9664
8.9560
8.1618
8.1411
8.1370
7.7430
7.3066
7.1639
7.1275
6.8241
5.4752
5.3816
4.6735
4.6502
O
F
Br
N
0.99
1.00
1.02
1.04
2.01
1.01
2.02
1.00
1.02
2.05
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


162.1073
159.3922
153.7710
150.9879
147.4962
134.0165
131.2231
128.5377
126.9881
122.8253
120.7801
110.8228
105.0864
98.0409
97.9401
34.3007
34.0122
O
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-89.4757
O
F
Br
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ao


8.9622
8.9579
8.9518
8.9475
8.1759
8.1552
8.1510
7.7272
7.5514
7.4266
7.2985
7.2621
7.1519
5.9958
5.9016
4.4627
4.4212
S
F
N
0.99
1.00
2.94
1.00
1.02
1.00
2.26
0.97
1.01
2.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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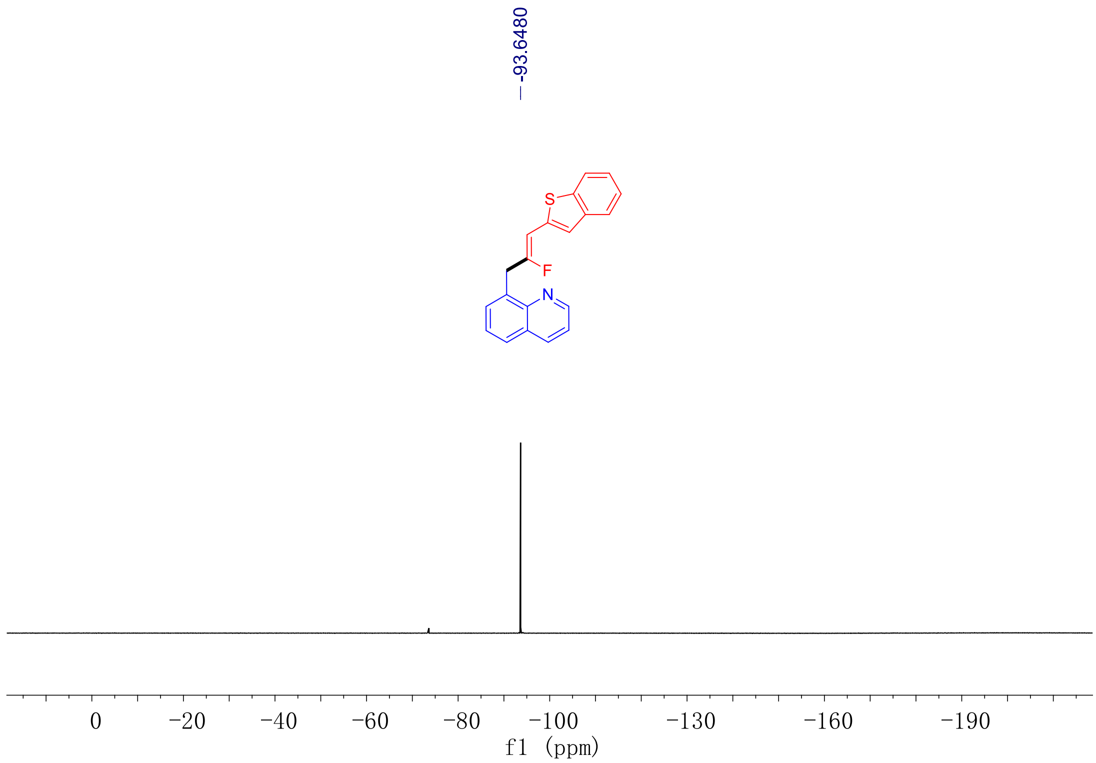
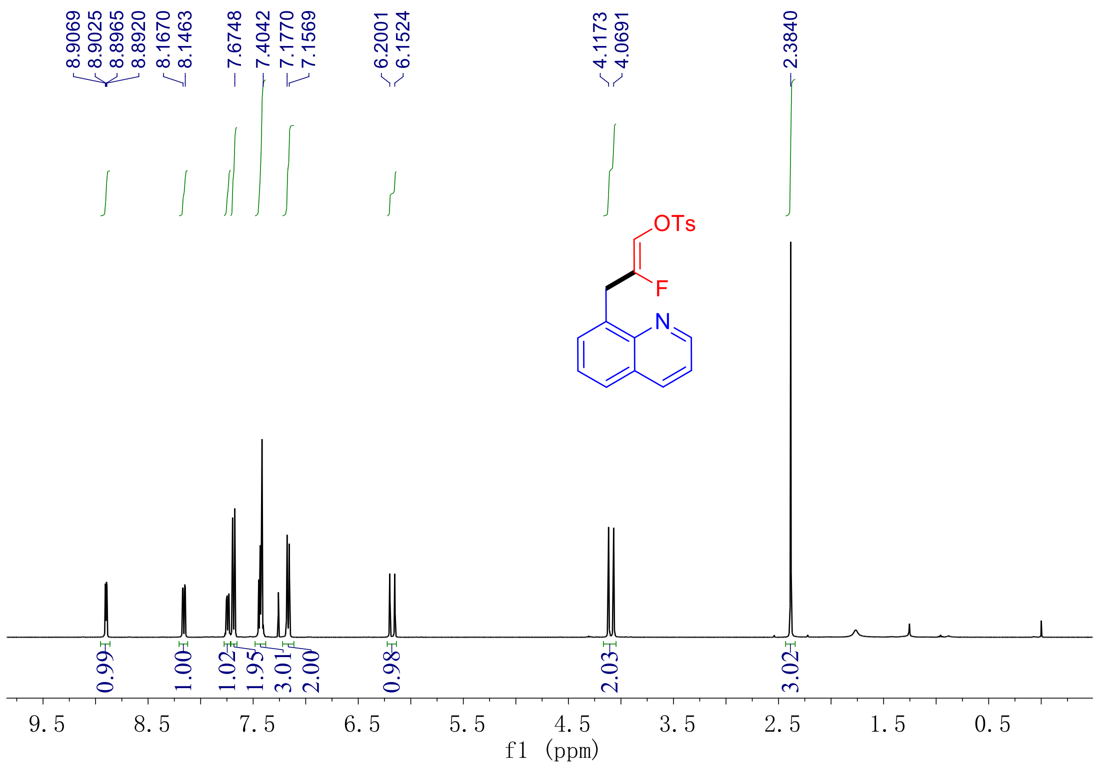
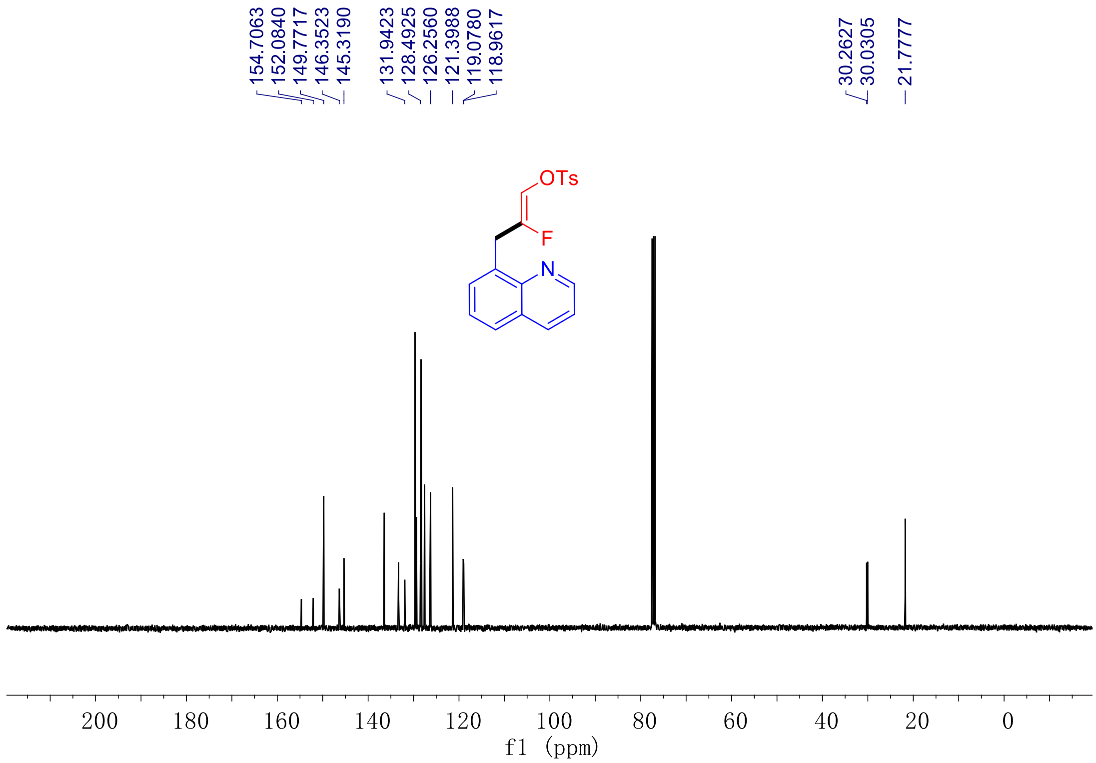
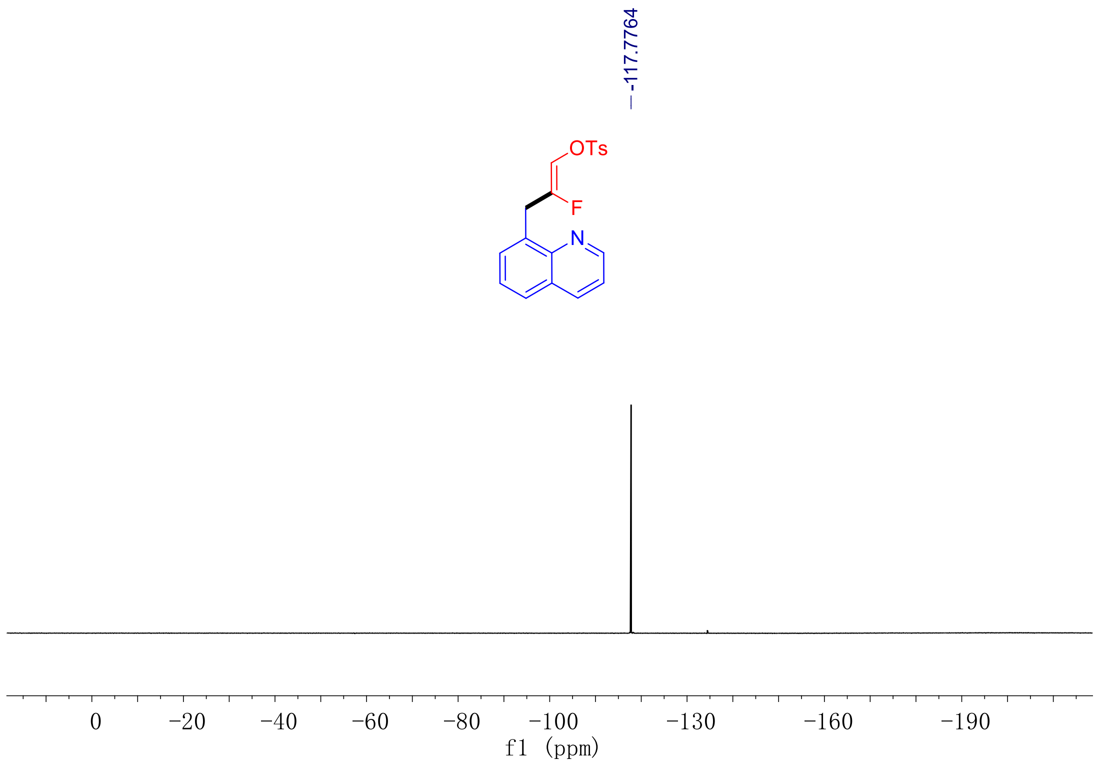
159.0202
146.6865
134.5933
132.7064
127.5159
124.1924
122.4142
121.3791
102.9049
102.7913
34.1511
33.8840
S
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-93.6480
S
F
N
0
−20
−40
−60
−80
−100
−130
−160
−190
f1 (ppm)

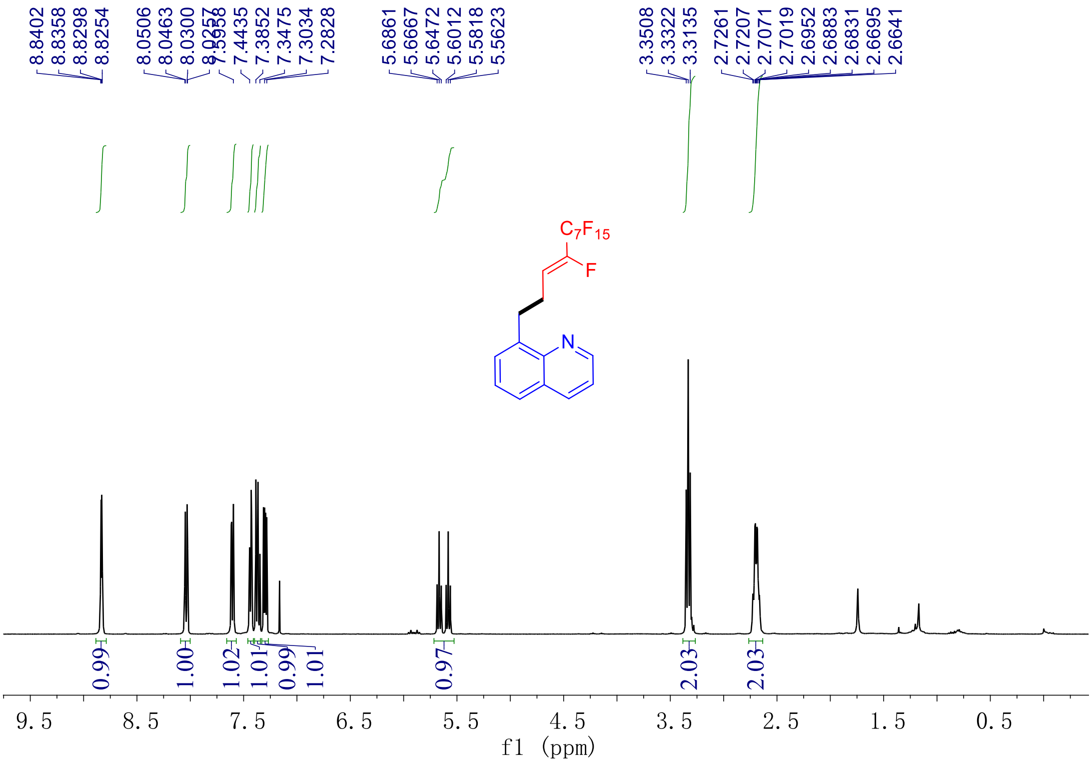
3ap


8.9069
8.9025
8.8965
8.8920
8.1670
8.1463
7.6748
7.4042
7.1770
7.1569
6.2001
6.1524
4.1173
4.0691
2.3840
OTs
F
N
0.99
1.00
1.02
1.95
3.01
2.00
0.98
2.03
3.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

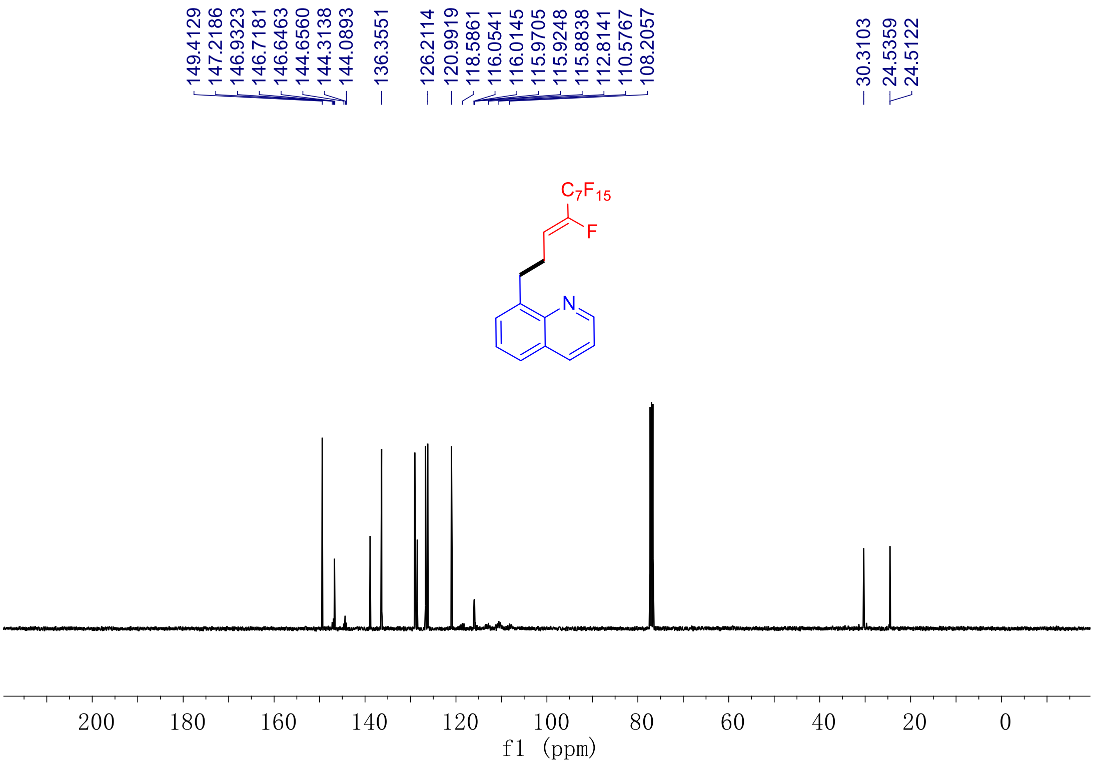

154.7063
152.0840
149.7717
146.3523
145.3190
131.9423
128.4925
126.2560
121.3988
119.0780
118.9617
30.2627
30.0305
21.7777
OTs
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-117.7764
OTs
F
N
0
−20
−40
−60
−80
−100
−130
−160
−190
f1 (ppm)

3aq



8.8402
8.8358
8.8298
8.8254
8.0506
8.0463
8.0300
7.5958
7.4435
7.3852
7.3475
7.3034
7.2828
5.6861
5.6667
5.6472
5.6012
5.5818
5.5623
3.3508
3.3322
3.3135
2.7261
2.7207
2.7071
2.7019
2.6952
2.6883
2.6831
2.6695
2.6641
C_7F_{15}
F
N
0.99
1.00
1.02
1.01
0.99
1.01
0.97
2.03
2.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)



149.4129
147.2186
146.9323
146.7181
146.6463
144.6560
144.3138
144.0893
136.3551
126.2114
120.9919
118.5861
116.0541
116.0145
115.9705
115.9248
115.8838
112.8141
110.5767
108.2057
30.3103
24.5359
24.5122
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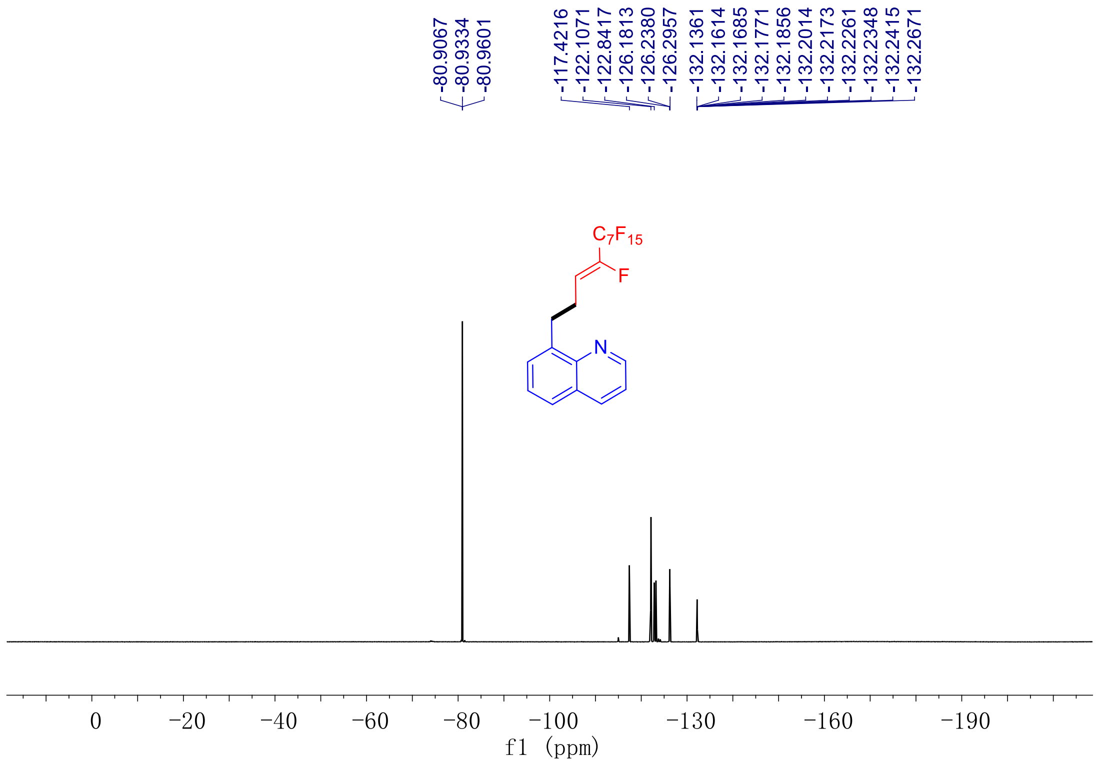
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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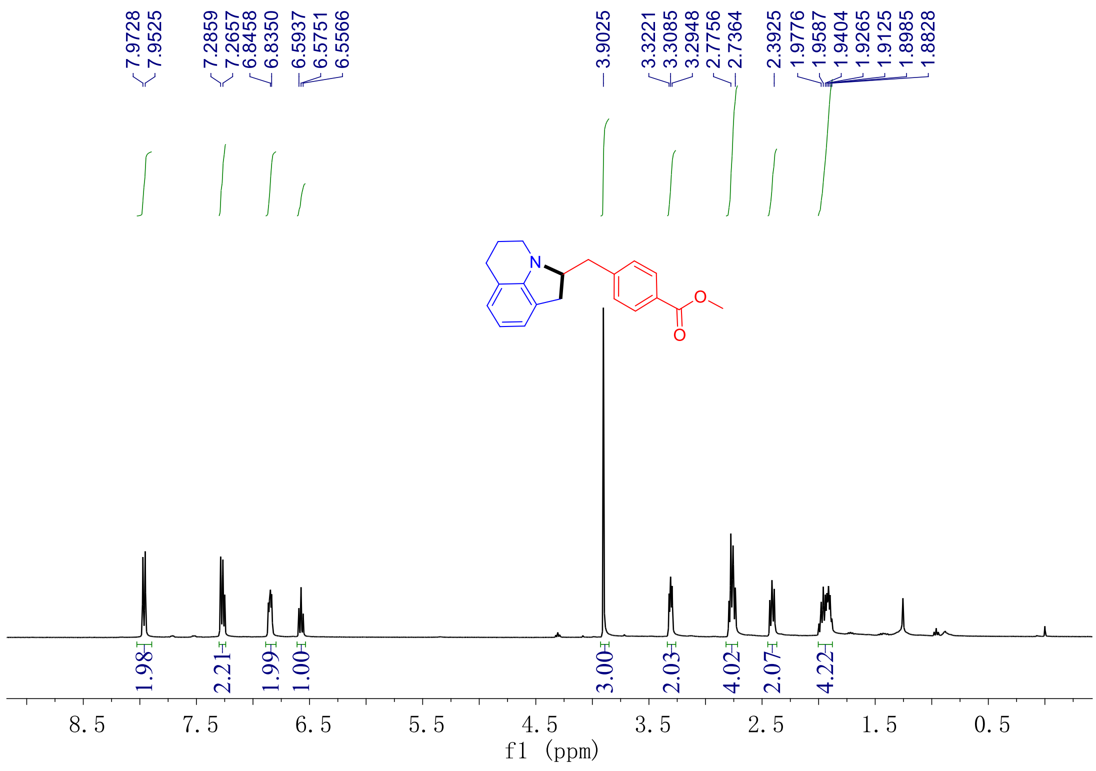
-80.9601
-117.4216
-122.1071
-122.8417
-126.1813
-126.2380
-126.2957
-132.1361
-132.1614
-132.1685
-132.1771
-132.1856
-132.2014
-132.2173
-132.2261
-132.2348
-132.2415
-132.2671
C_7F_{15}
F
N
0
−20
−40
−60
−80
−100
−130
−160
−190
f1 (ppm)

4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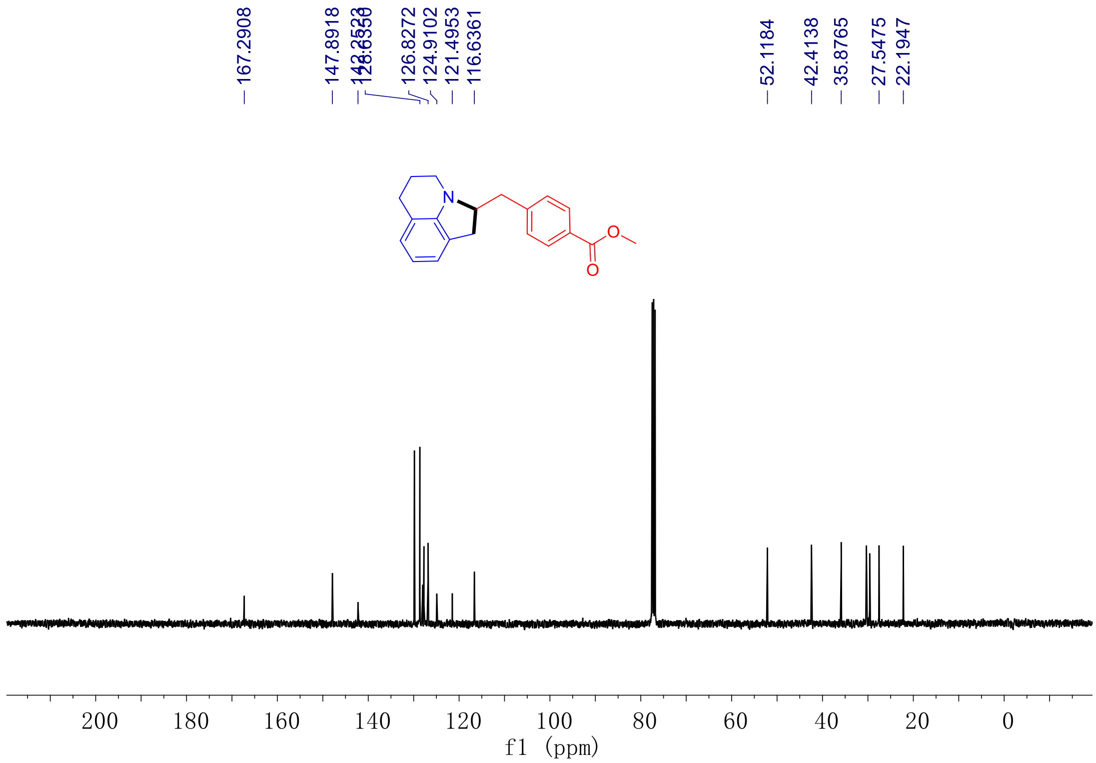
7.2859
7.2657
6.8458
6.8350
6.5937
6.5751
6.5566
3.9025
3.3221
3.3085
3.2948
2.7756
2.7364
2.3925
1.9776
1.9587
1.9404
1.9265
1.9125
1.8985
1.8828
N
O
O
1.98
2.21
1.99
1.00
3.00
2.03
4.02
2.07
4.22
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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142.2523
128.6350
126.8272
124.9102
121.4953
116.6361
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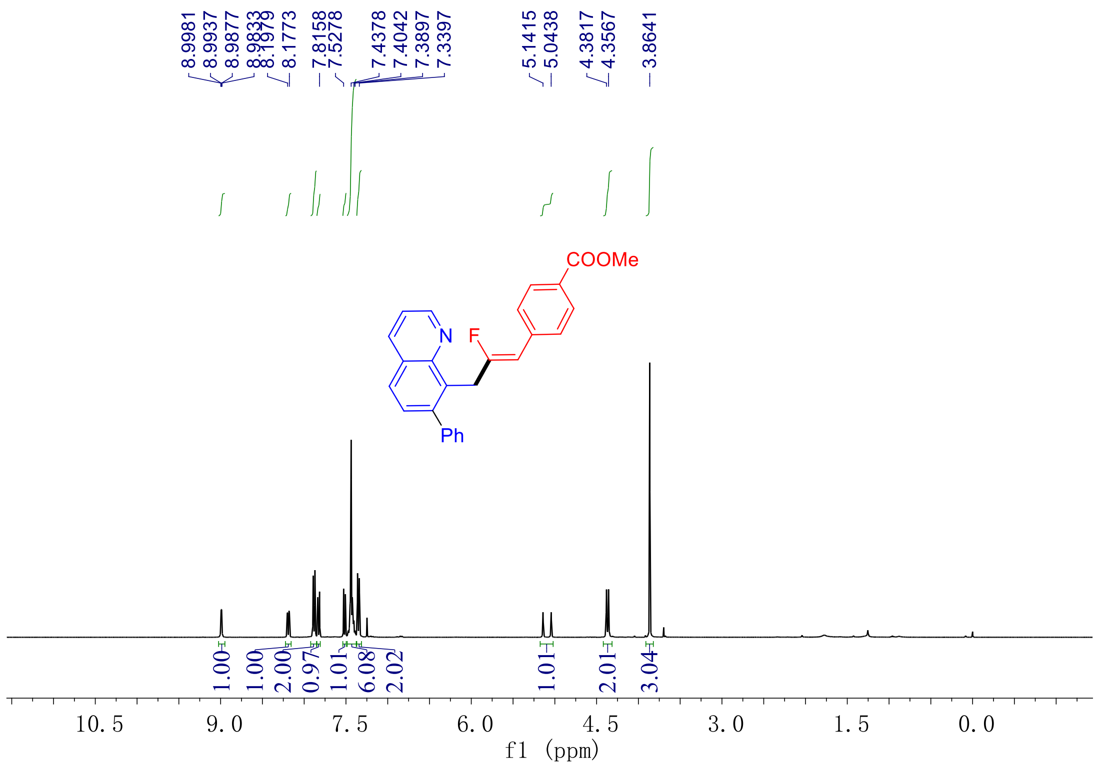
42.4138
35.8765
27.5475
22.1947
N
O
O
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

5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8.9877
8.9833
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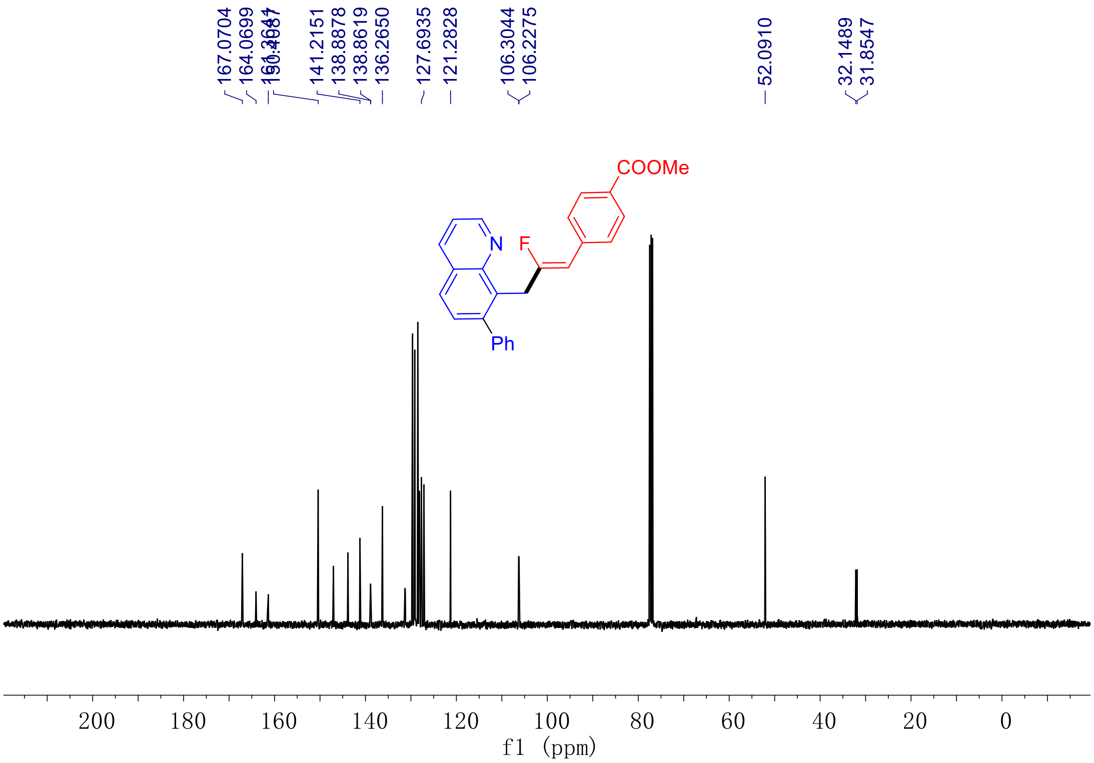
8.1773
7.8158
7.5278
7.4378
7.4042
7.3897
7.3397
5.1415
5.0438
4.3817
4.3567
3.8641
COOMe
N
F
Ph
1.00
1.00
2.00
0.97
1.01
6.08
2.02
1.01
2.01
3.04
10.5 9.0 7.5 6.0 4.5 3.0 1.5 0.0
f1 (ppm)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127.6935
121.2828
106.3044
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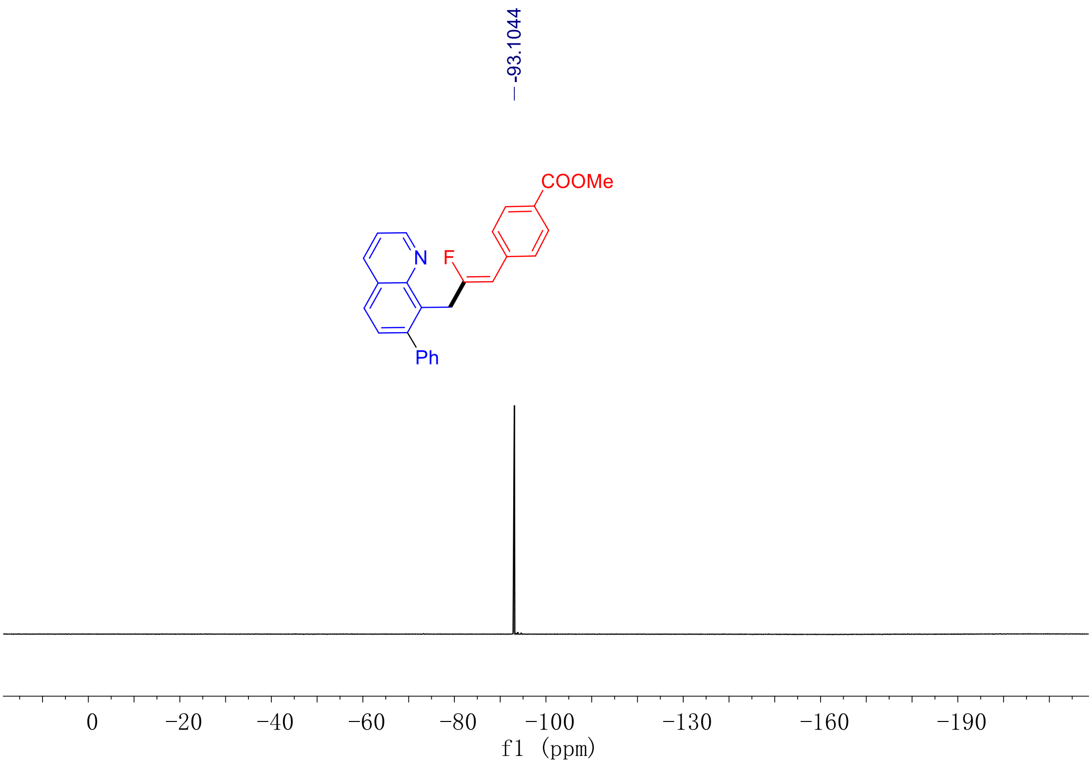
32.1489
31.8547
COOMe
F
N
Ph
200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


-93.1044
COOMe
F
N
Ph
0 -20 -40 -60 -80 -100 -130 -160 -190
f1 (ppm)