Electronic Supplementary Information

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

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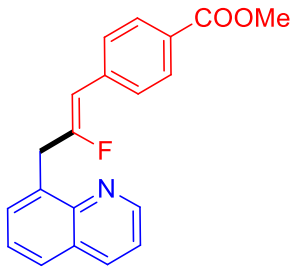
Table of Contents

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 ^1H 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.

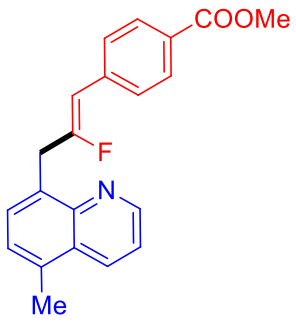
II. General procedures for the synthesis of compound 3

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**.



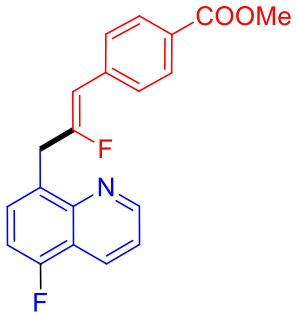
(*Z*)-Methyl 4-(2-fluoro-3-(quinolin-8-yl)prop-1-en-1-yl)benzoate (**3aa**)

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). ^1H 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, $J_{C\text{-}F}$ = 269.7 Hz), 149.9, 146.7, 138.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 136.5, 134.7, 129.8, 129.8, 128.6, 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.1 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.5, 126.4, 121.4, 107.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.12, 34.6 (d, $J_{C\text{-}F}$ = 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.



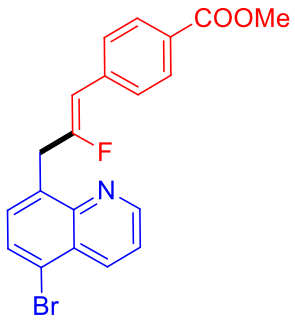
(*Z*)-Methyl 4-(2-fluoro-3-(5-methylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ba**)

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, $J_{C\text{-}F}$ = 269.8 Hz), 149.3, 146.8, 138.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 134.2, 132.8, 132.6 (d, $J_{C\text{-}F}$ = 1.9 Hz), 129.7, 129.5, 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.0 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.9, 126.9, 120.9, 106.9 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.1, 34.6 (d, $J_{C\text{-}F}$ = 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.



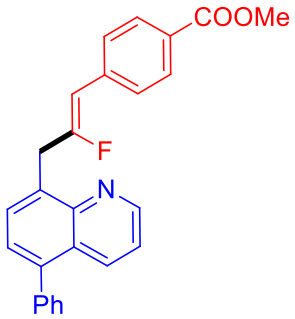
(*Z*)-Methyl 4-(2-fluoro-3-(5-fluoroquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ca**)

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, $J_{C\text{-}F}$ = 269.4, 0.9 Hz), 157.2 (d, $J_{C\text{-}F}$ = 253.3 Hz), 150.7, 147.0 (d, $J_{C\text{-}F}$ = 2.8 Hz), 138.5 (d, $J_{C\text{-}F}$ = 2.8 Hz), 130.6 (dd, $J_{C\text{-}F}$ = 4.6, 1.5 Hz), 129.8, 129.6 (d, $J_{C\text{-}F}$ = 4.8 Hz), 129.2 (d, $J_{C\text{-}F}$ = 8.6 Hz), 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.2 (d, $J_{C\text{-}F}$ = 2.4 Hz), 121.4 (d, $J_{C\text{-}F}$ = 2.9 Hz), 119.4 (d, $J_{C\text{-}F}$ = 16.2 Hz), 109.9 (d, $J_{C\text{-}F}$ = 19.1 Hz), 107.1 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.1, 34.2 (d, $J_{C\text{-}F}$ = 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.



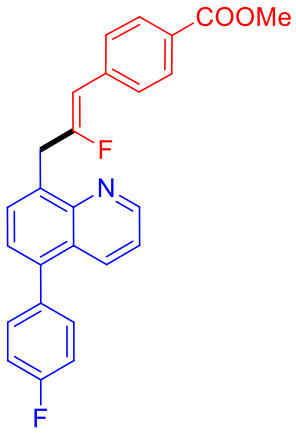
(*Z*)-Methyl 4-(3-(5-bromoquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3da**)

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, $J_{C\text{-}F}$ = 269.5 Hz), 150.5, 147.3, 138.4 (d, $J_{C\text{-}F}$ = 2.7 Hz), 135.9, 134.9 (d, $J_{C\text{-}F}$ = 1.2 Hz), 130.2, 130.0, 129.8, 128.4, 128.3, 127.9, 122.5, 121.2, 107.3 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.2, 34.5 (d, $J_{C\text{-}F}$ = 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.



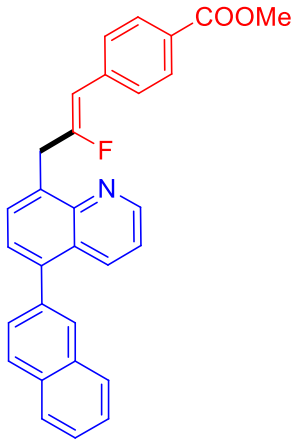
(*Z*)-Methyl 4-(2-fluoro-3-(5-phenylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ea**), *Z*/*E* = 15/1

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, $J_{C\text{-}F}$ = 269.7 Hz), 149.6, 146.8, 140.1, 139.4, 138.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 134.8, 134.0 (d, $J_{C\text{-}F}$ = 0.9 Hz), 130.2, 129.8, 129.2, 128.6, 128.3 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.1 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.8, 127.04, 127.0, 121.2, 107.2 (d, $J_{C\text{-}F}$ = 7.6 Hz), 52.1, 34.8 (d, $J_{C\text{-}F}$ = 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**)

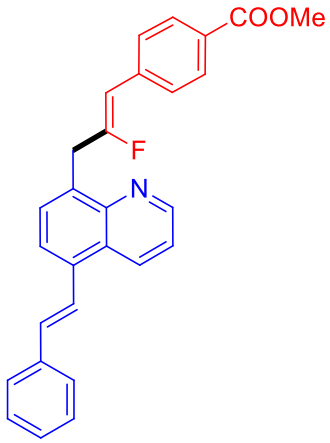
3fa was obtained according to the general procedure in 62% yield (51.3 mg), white solid, R_f = 0.3 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.1, 1.7 Hz, 1H), 8.19 (dd, J = 8.6, 1.7 Hz, 1H), 7.96 – 7.94 (m, 2H), 7.76 (d, J = 7.3 Hz, 1H), 7.53 – 7.51 (m, 2H), 7.45 (d, 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, $J_{C\text{-}F}$ = 245.6 Hz), 161.7 (d, $J_{C\text{-}F}$ = 269.7 Hz), 149.7, 146.8, 138.9, 138.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 135.3 (d, $J_{C\text{-}F}$ = 3.4 Hz), 134.5, 134.3 (d, $J_{C\text{-}F}$ = 0.9 Hz), 131.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 129.8, 129.2, 128.3 (d, $J_{C\text{-}F}$ = 7.8 Hz), 128.2 (d, $J_{C\text{-}F}$ = 2.3 Hz), 127.2, 127.0, 121.4, 115.6 (d, $J_{C\text{-}F}$ = 21.3 Hz), 107.2 (d, $J_{C\text{-}F}$ = 7.7 Hz), 52.13, 34.8 (d, $J_{C\text{-}F}$ = 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**)

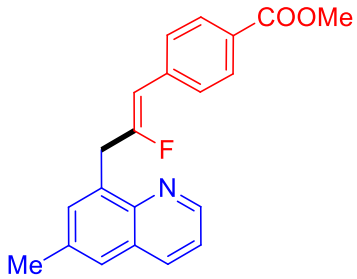
3ga was obtained according to the general procedure in 63% yield (56.8 mg), white solid, R_f = 0.4 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.97 (dd, J = 4.1, 1.7 Hz, 1H), 8.28 (dd, J = 8.6, 1.7 Hz, 1H), 7.98 – 7.86 (m, 6H), 7.80 (d, J = 7.3 Hz, 1H), 7.58 – 7.52 (m, 6H), 7.36 (dd, 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, $J_{C\text{-}F}$ = 269.7 Hz), 149.7, 146.8, 140.0, 138.7 (d, $J_{C\text{-}F}$ = 2.8 Hz), 136.9, 134.9, 134.2 (d, $J_{C\text{-}F}$ = 0.65 Hz), 133.5, 132.8, 129.8, 129.3, 129.1, 128.4, 128.3 (d, $J_{C\text{-}F}$ = 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**)

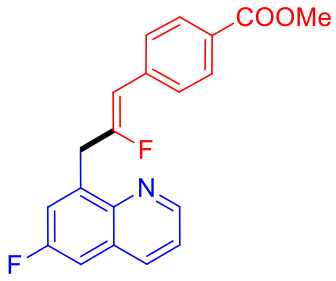
3ha was obtained according to the general procedure in 53% yield (45.0 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.55 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.82 – 7.67 (m, 3H), 7.59 – 7.58 (m, 2H), 7.51 – 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**)

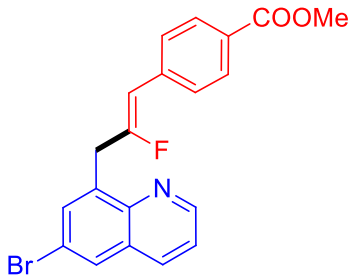
3ia was obtained according to the general procedure in 79% yield (52.9 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.54 (s, 1H), 7.51 – 7.49 (m, 3H), 7.36 (dd, *J* = 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.



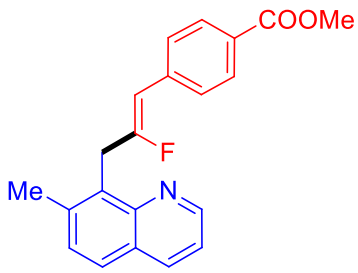
(*Z*)-Methyl 4-(2-fluoro-3-(6-fluoroquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ja**)

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.



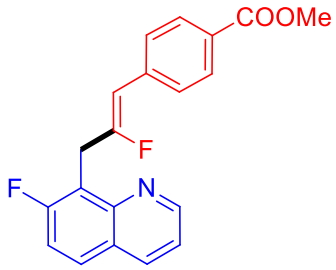
(*Z*)-Methyl 4-(3-(6-bromoquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3ka**)

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.



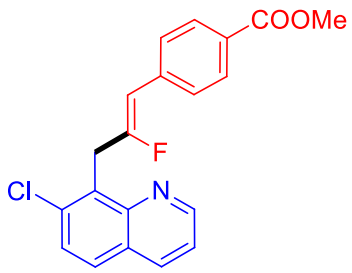
(*Z*)-Methyl 4-(2-fluoro-3-(7-methylquinolin-8-yl)prop-1-en-1-yl)benzoate (**3la**)

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.



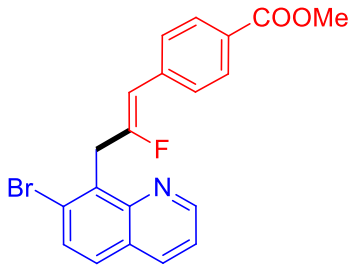
(*Z*)-Methyl 4-(2-fluoro-3-(7-fluoroquinolin-8-yl)prop-1-en-1-yl)benzoate (**3ma**)

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.



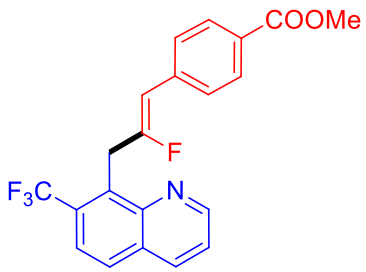
(*Z*)-Methyl 4-(3-(7-chloroquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3na**)

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, $J_{C\text{-}F}$ = 270.6 Hz), 150.9, 147.4, 138.6 (d, $J_{C\text{-}F}$ = 2.8 Hz), 136.3, 136.1, 132.1 (d, $J_{C\text{-}F}$ = 6.0 Hz), 129.7, 128.3, 128.24, 128.2, 128.0 (d, $J_{C\text{-}F}$ = 2.3 Hz), 127.1, 121.4, 106.1 (d, $J_{C\text{-}F}$ = 7.4 Hz), 52.1, 31.7 (d, $J_{C\text{-}F}$ = 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.



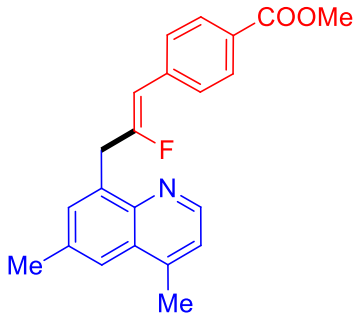
(*Z*)-Methyl 4-(3-(7-bromoquinolin-8-yl)-2-fluoroprop-1-en-1-yl)benzoate (**3oa**)

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, $J_{C\text{-}F}$ = 270.7 Hz), 150.8, 147.4, 138.6 (d, $J_{C\text{-}F}$ = 2.7 Hz), 136.3, 134.2 (d, $J_{C\text{-}F}$ = 6.7 Hz), 131.1, 129.6, 128.4, 128.2 (d, $J_{C\text{-}F}$ = 7.8 Hz), 127.9 (d, $J_{C\text{-}F}$ = 2.4 Hz), 127.4, 126.9, 121.6, 106.2 (d, $J_{C\text{-}F}$ = 7.3 Hz), 52.1, 34.4 (d, $J_{C\text{-}F}$ = 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.



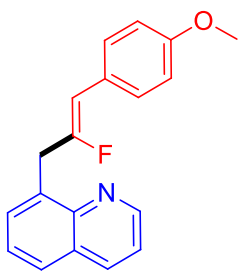
(*Z*)-Methyl 4-(2-fluoro-3-(7-(trifluoromethyl)quinolin-8-yl)prop-1-en-1-yl)benzoate (**3pa**)

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**)

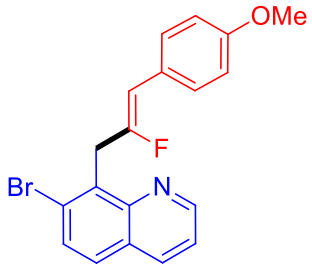
3qa was obtained according to the general procedure in 42% yield (29.1 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 15/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.3 Hz, 1H), 7.95 – 7.93 (m, 2H), 7.72 (s, 1H), 7.55 (s, 1H), 7.51 – 7.49 (m, 2H), 7.22 (d, J = 4.3 Hz, 1H), 5.61 (d, J = 38.6 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**)

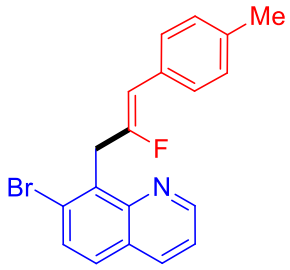
3ab was obtained according to the general procedure in 63% yield (37.2 mg), white solid, R_f = 0.20 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.14 (dd, J = 8.3, 1.7 Hz, 1H), 7.74 (d, J = 7.8 Hz, 2H), 7.56 – 7.47 (m, 1H), 7.45 – 7.35 (m, 3H), 6.83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



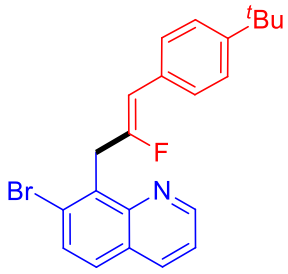
(*Z*)-7-Bromo-8-(2-fluoro-3-(4-methoxyphenyl)allyl)quinoline (**3ob**)

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.



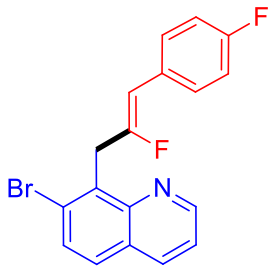
(*Z*)-7-Bromo-8-(2-fluoro-3-(p-tolyl)allyl)quinoline (**3oc**)

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.



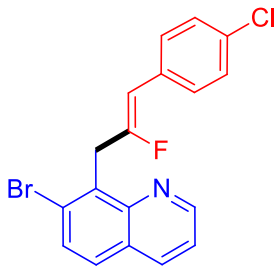
(*Z*)-7-Bromo-8-(3-(4-(tert-butyl)phenyl)-2-fluoroallyl)quinoline (**3od**)

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, $J_{C\text{-}F}$ = 265.8 Hz), 150.7, 149.6 (d, $J_{C\text{-}F}$ = 2.1 Hz), 147.6, 136.3, 134.8 (d, $J_{C\text{-}F}$ = 6.1 Hz), 131.2, 131.17, 128.2 (d, $J_{C\text{-}F}$ = 1.6 Hz), 128.1, 127.4, 126.9, 125.3, 121.5, 106.6 (d, $J_{C\text{-}F}$ = 8.0 Hz), 34.6, 34.4 (d, $J_{C\text{-}F}$ = 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.



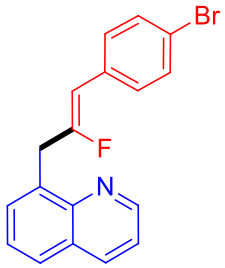
(*Z*)-7-Bromo-8-(2-fluoro-3-(4-fluorophenyl)allyl)quinoline (**3oe**)

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, $J_{C\text{-}F}$ = 244.7, 3.3 Hz), 158.3 (dd, $J_{C\text{-}F}$ = 266.0, 2.3 Hz), 150.8, 147.5, 136.4, 134.6 (d, $J_{C\text{-}F}$ = 6.5 Hz), 131.2, 130.02, 130.0 (d, $J_{C\text{-}F}$ = 15.4 Hz), 128.3, 127.5, 126.9, 121.6, 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 105.8 (d, $J_{C\text{-}F}$ = 8.0 Hz), 34.3 (d, $J_{C\text{-}F}$ = 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.



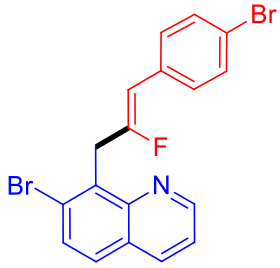
(*Z*)-7-bromo-8-(3-(4-chlorophenyl)-2-fluoroallyl)quinoline (**3of**)

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, $J_{C\text{-}F}$ = 267.6 Hz), 150.7, 147.4, 136.3, 134.4 (d, $J_{C\text{-}F}$ = 6.5 Hz), 132.4 (d, $J_{C\text{-}F}$ = 2.5 Hz), 132.1 (d, $J_{C\text{-}F}$ = 3.4 Hz), 131.1, 129.6 (d, $J_{C\text{-}F}$ = 7.6 Hz), 128.4, 128.2, 127.4, 126.8, 121.5, 105.7 (d, $J_{C\text{-}F}$ = 7.8 Hz), 34.3 (d, $J_{C\text{-}F}$ = 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**)

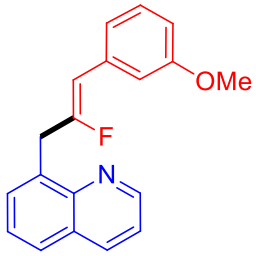
3ag was obtained according to the general procedure in 67% yield (46.1 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.7 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.55 – 7.48 (m, 1H), 7.44 – 7.35 (m, 3H), 7.31 – 7.29 (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, $J_{C\text{-}F}$ = 266.9 Hz), 149.9, 146.6, 136.5, 134.9 (d, $J_{C\text{-}F}$ = 1.2 Hz), 132.9 (d, $J_{C\text{-}F}$ = 2.7 Hz), 131.5, 130.0 (d, $J_{C\text{-}F}$ = 7.7 Hz), 129.7, 128.6, 127.4, 126.4, 121.3, 120.5 (d, $J_{C\text{-}F}$ = 3.5 Hz), 106.7 (d, $J_{C\text{-}F}$ = 8.0 Hz), 34.5 (d, $J_{C\text{-}F}$ = 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**)

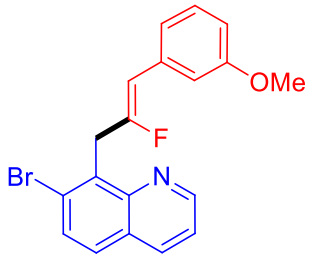
3og was obtained according to the general procedure in 96% yield (80.8 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, J = 4.2, 1.7 Hz, 1H), 8.10 (dd, J = 8.3, 1.7 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.62 – 7.60 (m, 1H), 7.41 (dd, J = 8.2, 4.2 Hz, 1H),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

= 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.



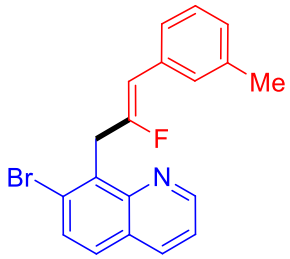
(*Z*)-8-(2-fluoro-3-(3-methoxyphenyl)allyl)quinoline (**3ah**)

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.



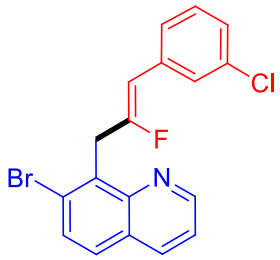
(*Z*)-7-Bromo-8-(2-fluoro-3-(3-methoxyphenyl)allyl)quinoline (**3oh**)

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.



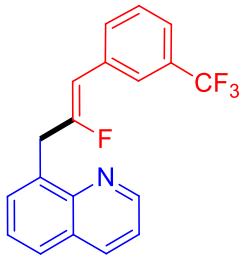
(*Z*)-7-Bromo-8-(2-fluoro-3-(m-tolyl)allyl)quinoline (**3oi**)

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.



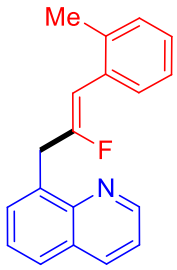
(*Z*)-7-bromo-8-(3-(3-chlorophenyl)-2-fluoroallyl)quinoline (**3oj**)

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.



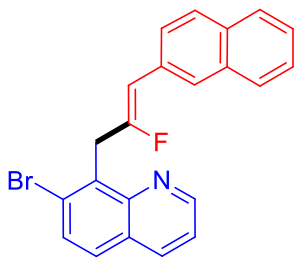
(*Z*)-8-(2-Fluoro-3-(3-(trifluoromethyl)phenyl)allyl)quinoline (**3ak**)

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.



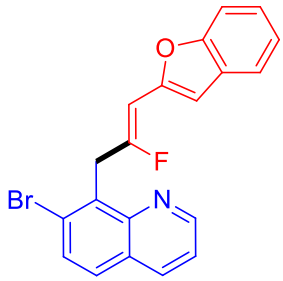
(*Z*)-8-(2-Fluoro-3-(o-tolyl)allyl)quinoline (**3al**)

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.



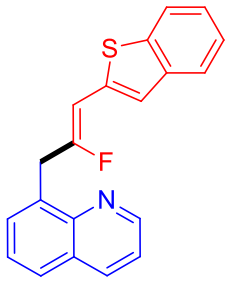
(*Z*)-7-Bromo-8-(2-fluoro-3-(naphthalen-2-yl)allyl)quinoline (**3om**)

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**)

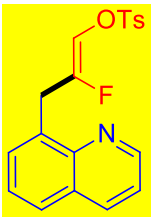
3on was obtained according to the general procedure in 35% yield (26.8 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 25/1).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.7 Hz, 1H), 7.76 – 7.74 (m, 1H), 7.68 – 7.66 (m, 1H), 7.51 – 7.42 (m, 2H), 7.32 – 7.31 (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**)

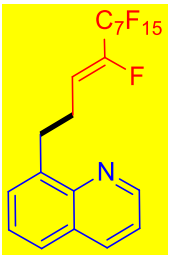
3al was obtained according to the general procedure (60 °C) in 32% yield (20.1 mg), white solid, R_f = 0.40 (hexanes/ethyl acetate = 25/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.3, 1.7 Hz, 1H), 7.78 – 7.73 (m, 3H), 7.69 – 7.62 (m, 1H), 7.57 – 7.50 (m, 1H), 7.42 (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, $J_{C\text{-}F}$ = 1.5 Hz), 122.4 (d, $J_{C\text{-}F}$ = 4.2 Hz), 122.1, 121.4, 102.8 (d, $J_{C\text{-}F}$ = 11.4 Hz), 34.0 (d, $J_{C\text{-}F}$ = 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.



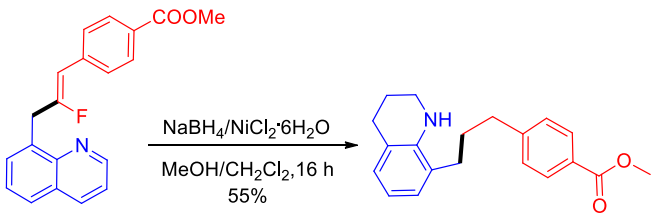
(*Z*)-2-Fluoro-3-(quinolin-8-yl)prop-1-en-1-yl 4-methylbenzenesulfonate (**3aq**)

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, $J_{C\text{-}F}$ = 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, $J_{C\text{-}F}$ = 11.6 Hz), 30.1 (d, $J_{C\text{-}F}$ = 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.



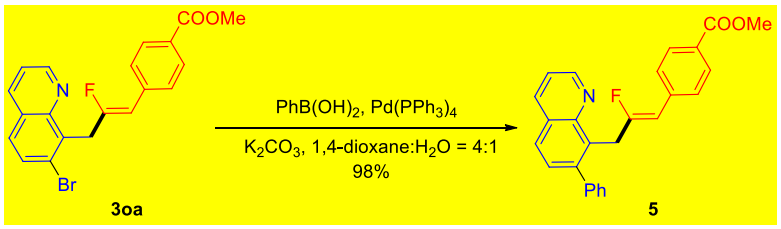
3aq was obtained according to the general procedure (80 °C) in 94% yield (108.7 mg), white solid, R_f = 0.30 (hexanes/ethyl acetate = 50/1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.2, 1.8 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.60 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.44 – 7.43 (m, 1H), 7.40 – 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, $J_{C\text{-}F}$ = 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.

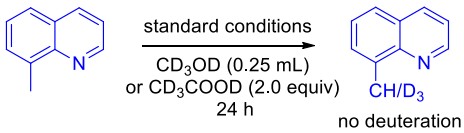


3oa **5**

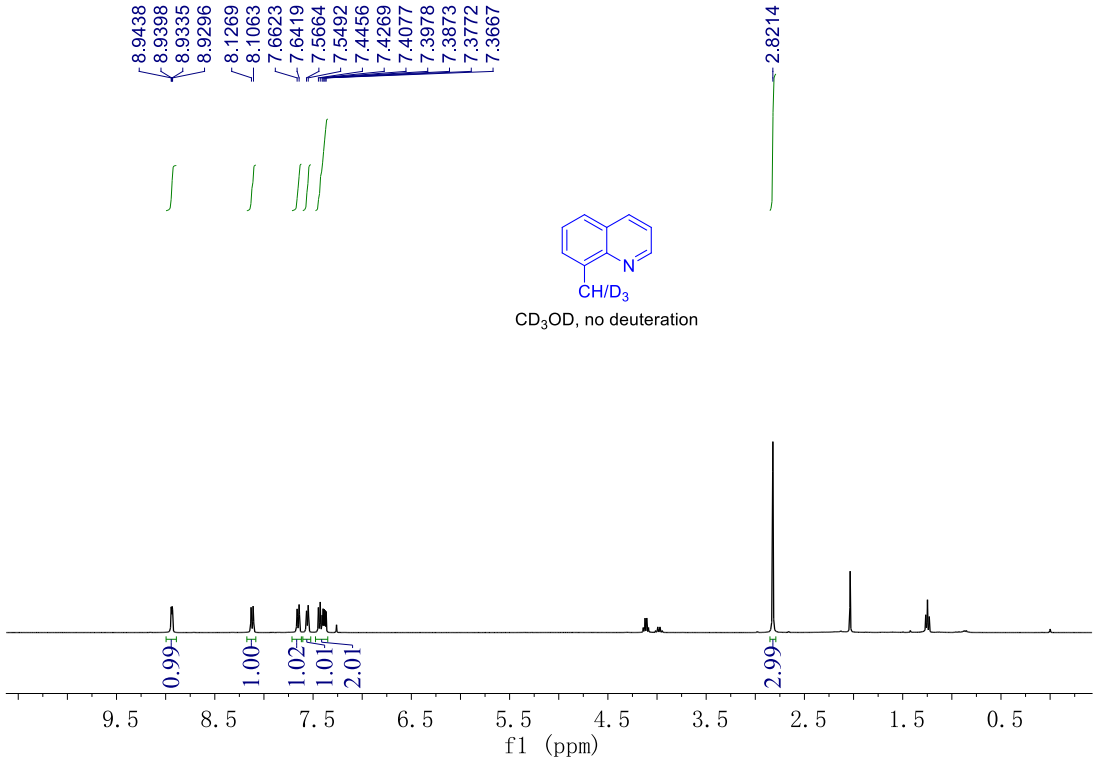
Olefin **3oa** (0.1 mmol, 40.0 mg), $PhB(OH)_2$ (0.15 mmol, 18.3 mg), $Pd(PPh_3)_4$ (5 mol%, 6.0 mg), K_2CO_3 (0.2 mmol, 34.0 mg), 1,4-dioxane (0.8 mL), and H_2O (0.2 mL) were charged into a pressure tube. The reaction mixture was stirred under N_2 at 90 ºC for 12 h. After the removal of the solvents, 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.

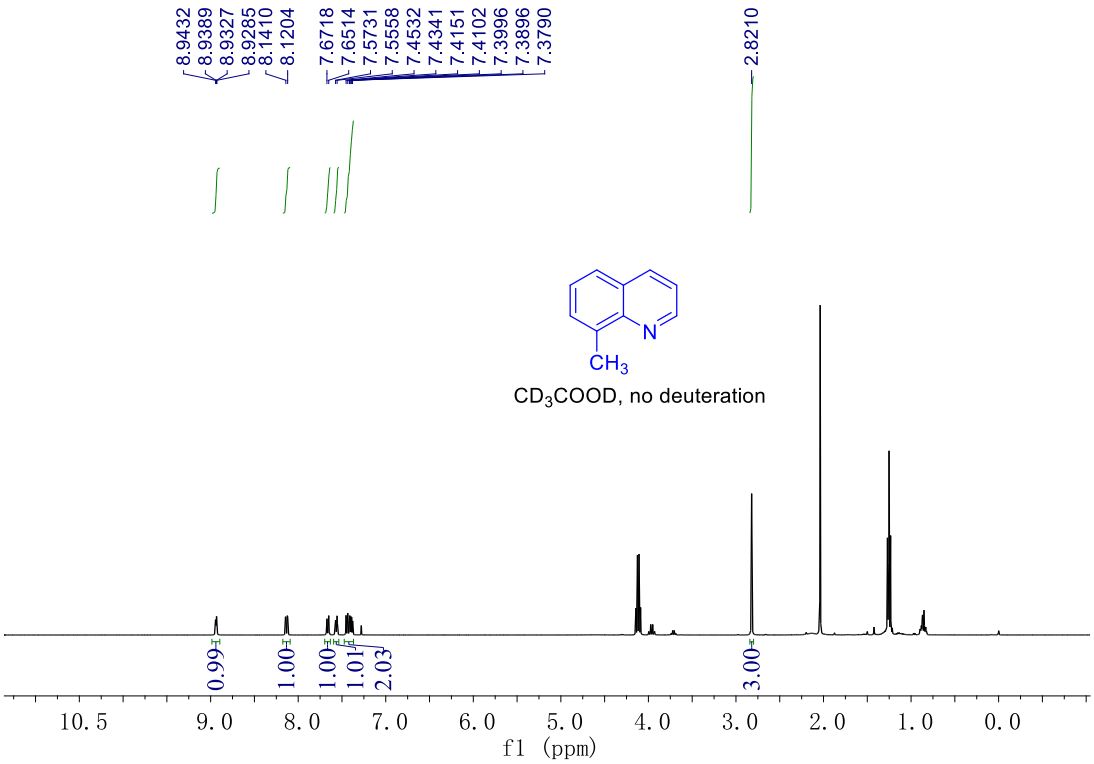
IV. Mechanistic Studies

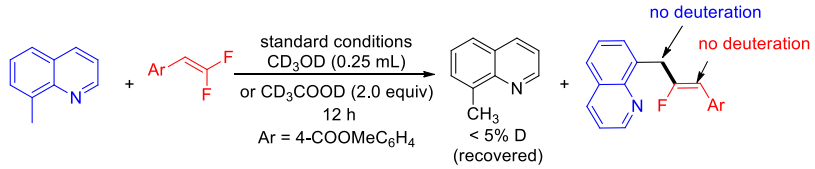
(a) H/D Exchange Experiments



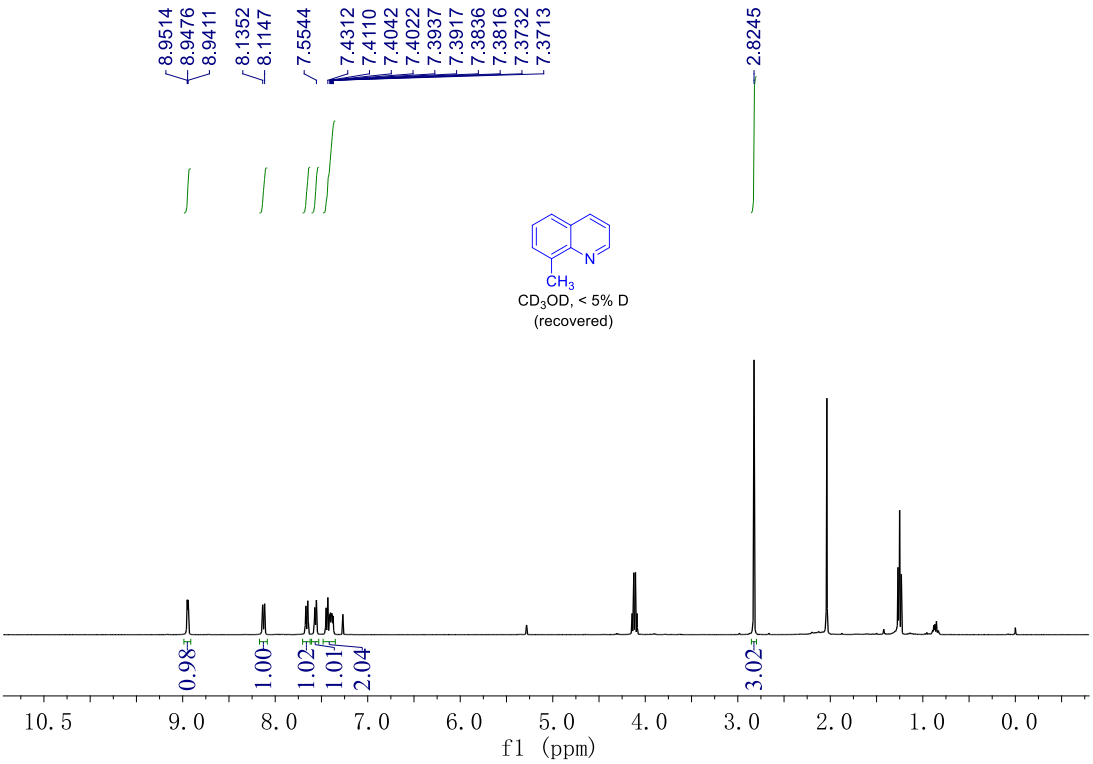
8-Methylquinoline (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (100 mg) were added to TFE (2 mL) in a pressure tube, and CD_3OD (0.25 mL) or CD_3COOD (2.0 equiv) was then introduced under N_2 atmosphere. The reaction mixture was 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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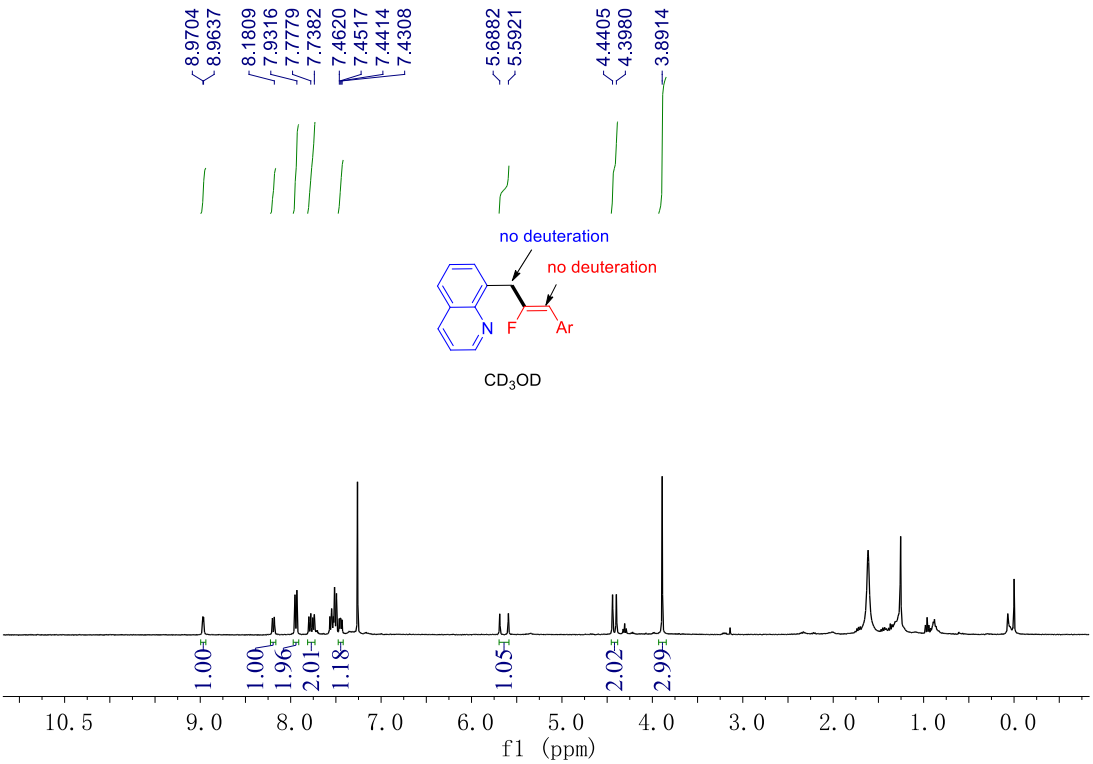
8.9411
8.1352
8.1147
7.5544
7.4312
7.4110
7.4042
7.4022
7.3937
7.3917
7.3836
7.3816
7.3732
7.3713
2.8245
N
CH3
CD3OD, < 5% D
(recovered)
0.98
1.00
1.02
1.01
2.04
3.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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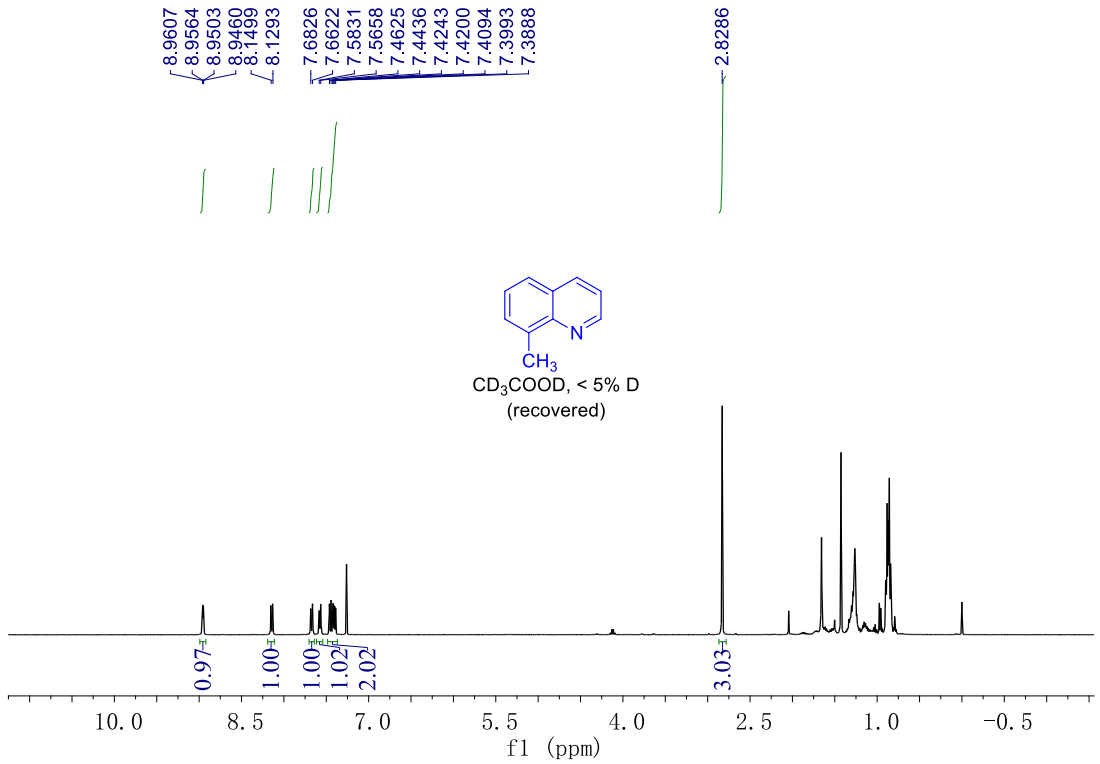
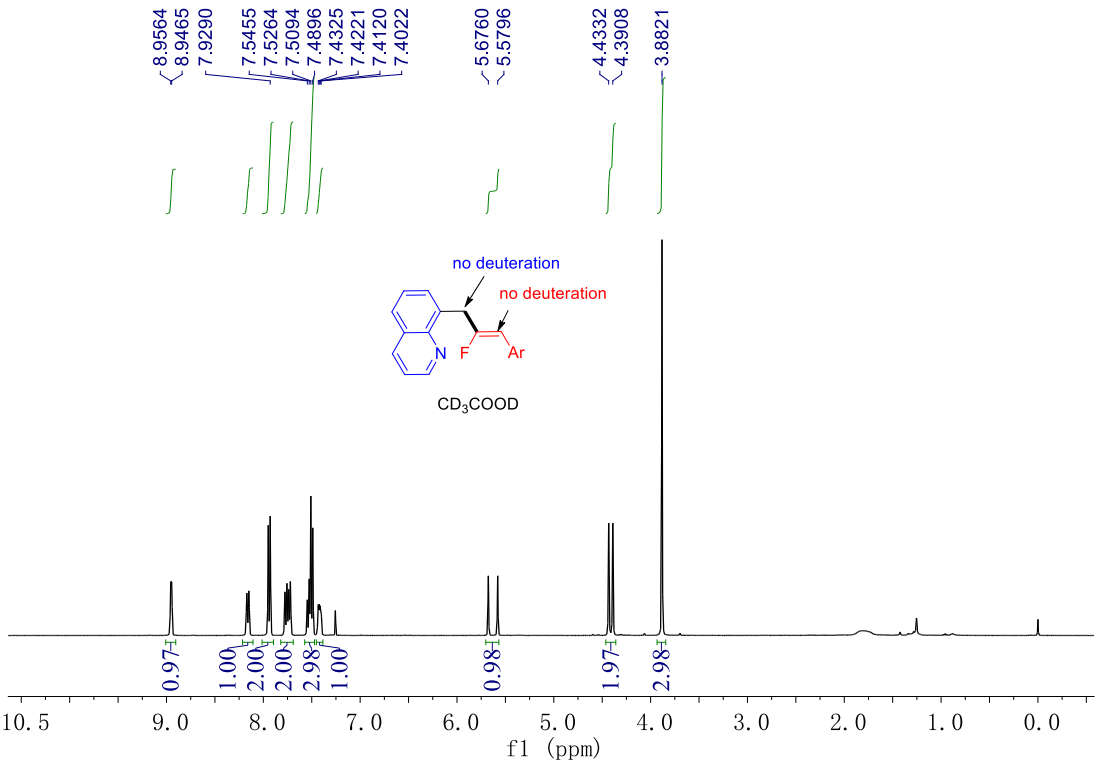
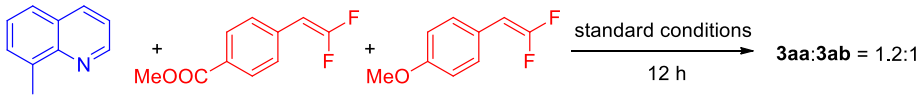
8.1809
7.9316
7.7779
7.7382
7.4620
7.4517
7.4414
7.4308
5.6882
5.5921
4.4405
4.3980
3.8914
no deuteration
no deuteration
N
F
Ar
CD3OD
1.00
1.00
1.96
2.01
1.18
1.05
2.02
2.99
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



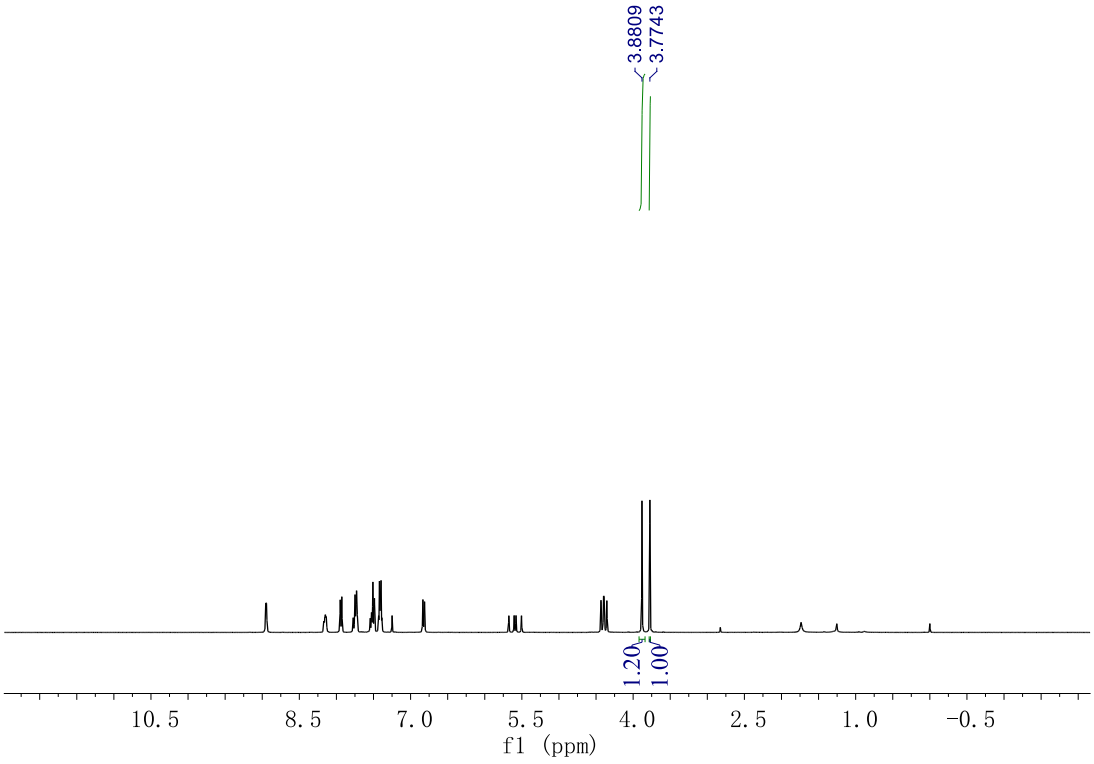


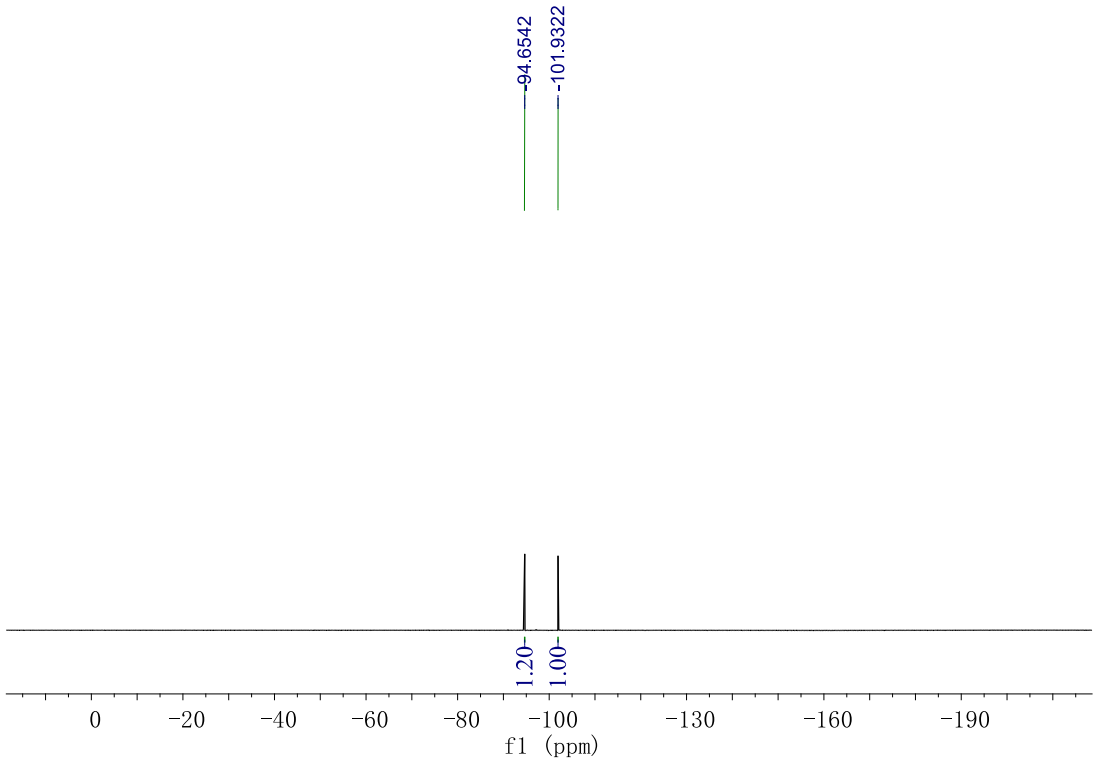
(b) Competition Reaction



1a (0.2 mmol) **2a** (0.2 mmol) **2b** (0.2 mmol)

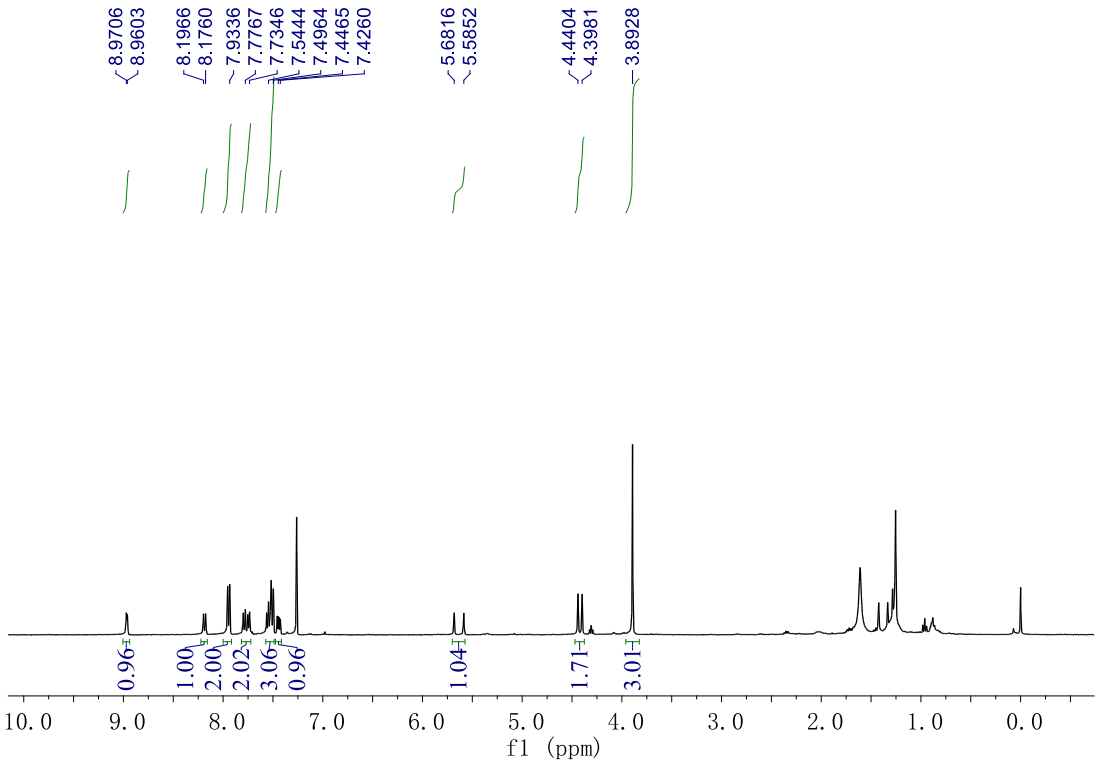
8-Methylquinoline **1a** (0.2 mmol), *gem*-difluoroalkene **2a** (0.2 mmol), **2b** (0.2 mmol), $[Cp^*RhCl_2]_2$ (5 mol%), $AgNTf_2$ (20 mol%), $Ca(OH)_2$ (3.0 equiv), $Zn(OAc)_2$ (50 mol%), and 4 Å M.S. (100 mg) were dissolved in TFE (2 mL) in a pressure tube under N_2 atmosphere. The reaction mixture 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 ^{1}H 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).

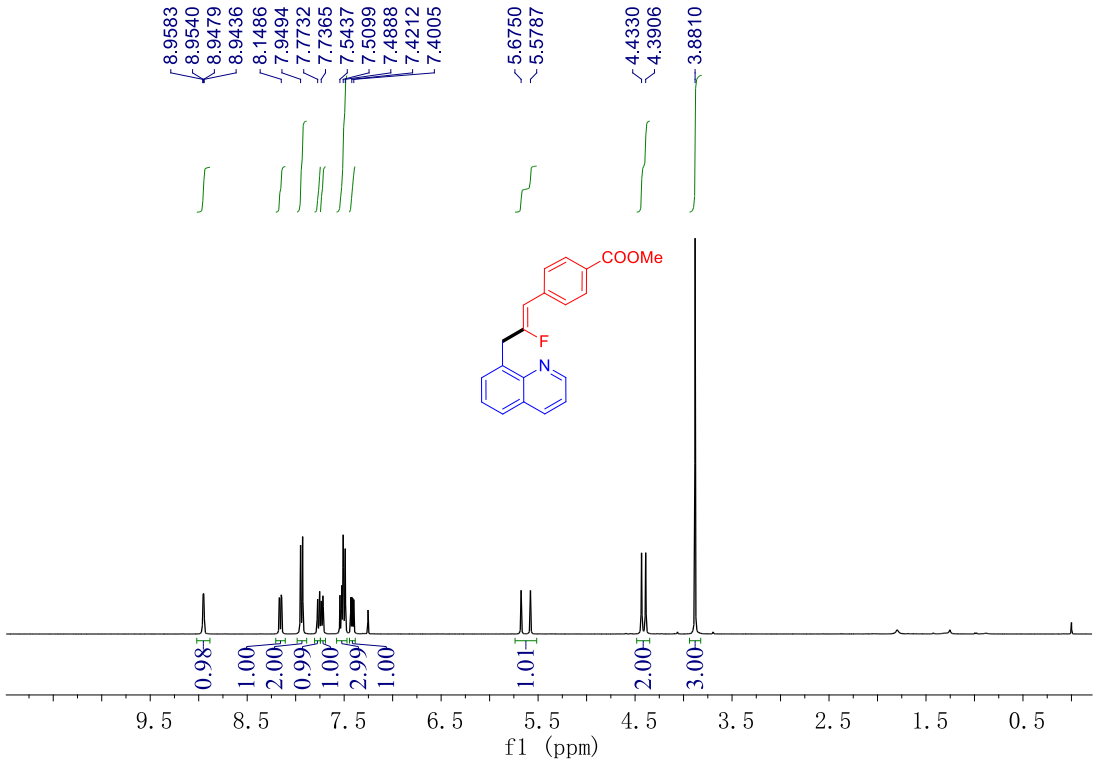
V. References

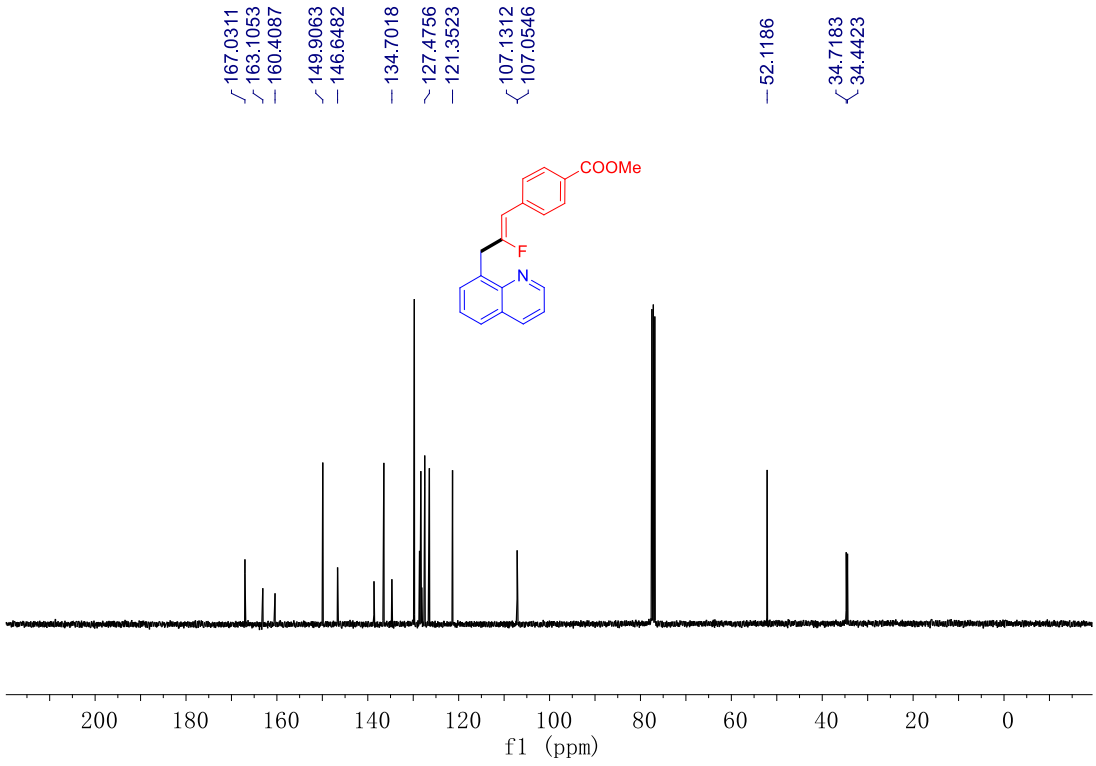
(1) (a) P. Evans, P. Hogg, R. Grigg, M. Nurnabi, J. Hinsley, V. Sridharan, S. Suganthan, S. Korn, S. Collard and J. E. Muir, *Tetrahedron*, 2005, **61**, 9696; (b) N. Gandhamsetty, S. Joung, S.-W. Park, S. Park and S. Chang, *J. Am. Chem. Soc*., 2014, **48**, 16780. (c) T. M. Heidelbaugh, P. X. Nguyen,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

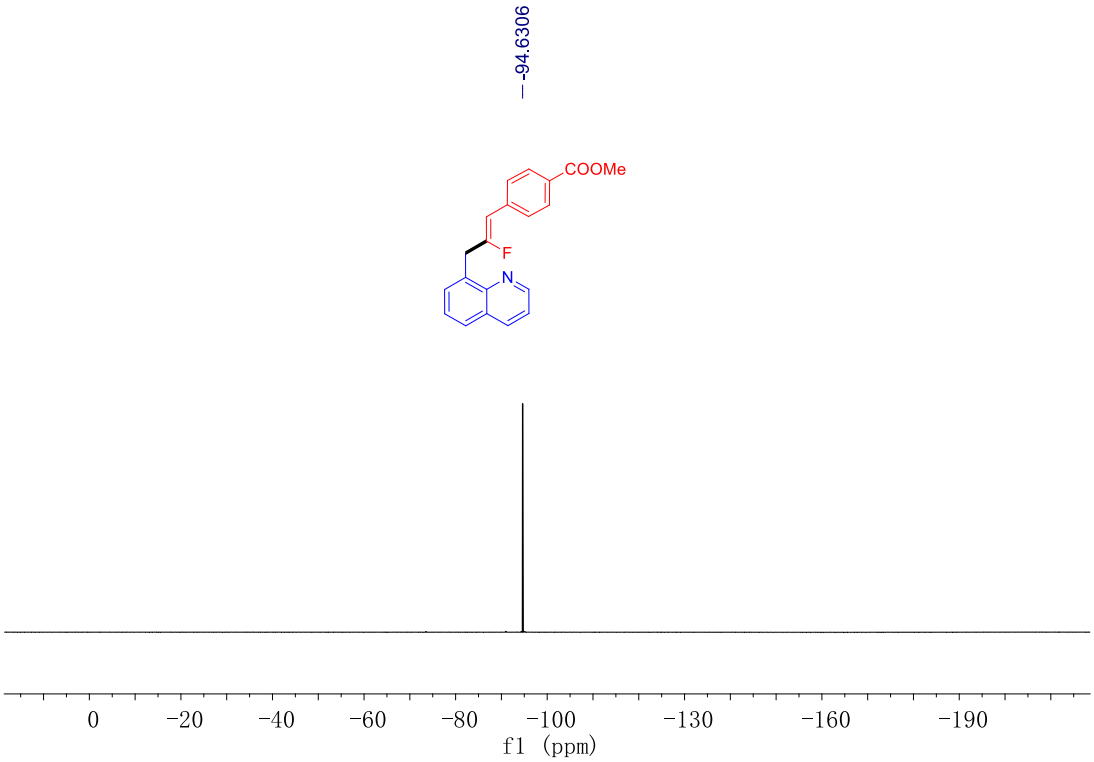
(2) C. S. Thomoson, H. Martinez and W. R. D. Jr, *J. Fluorine Chem.,* 2013, **150***,* 53.

VI. NMR Spectra of Coupled Products

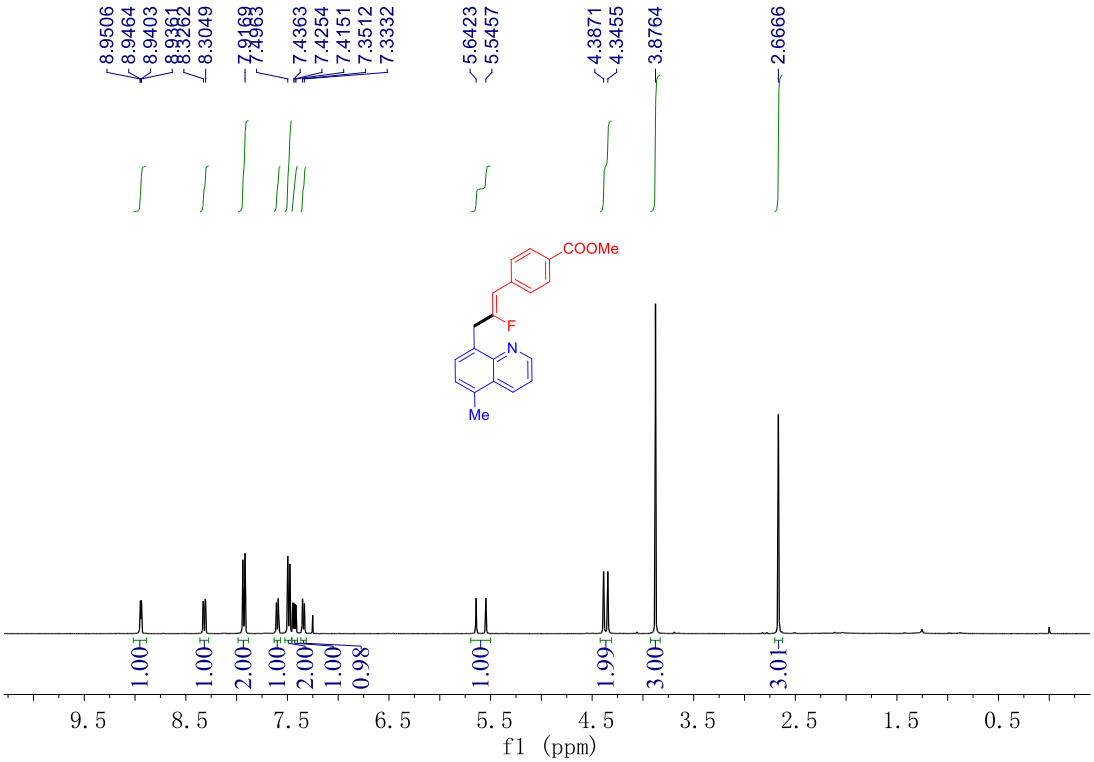
3aa






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

3ba


8.9506
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8.9403
8.3049
7.4363
7.4254
7.4151
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7.3332
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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
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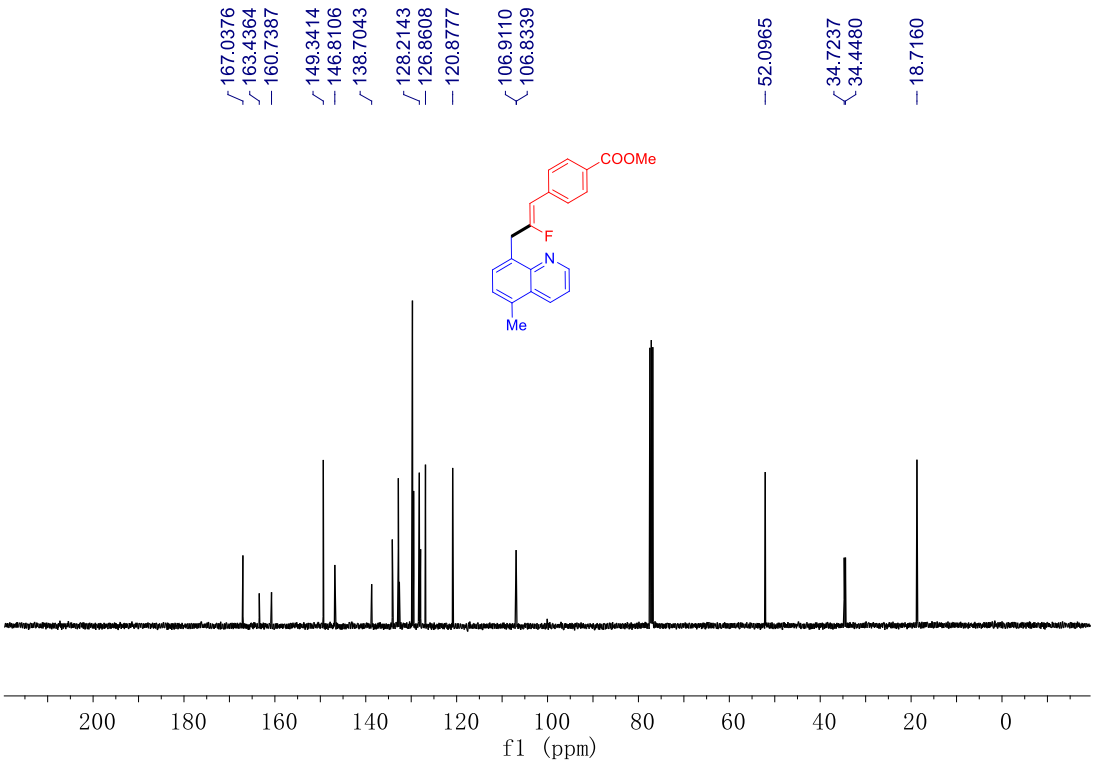
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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106.8339
52.0965
34.7237
34.4480
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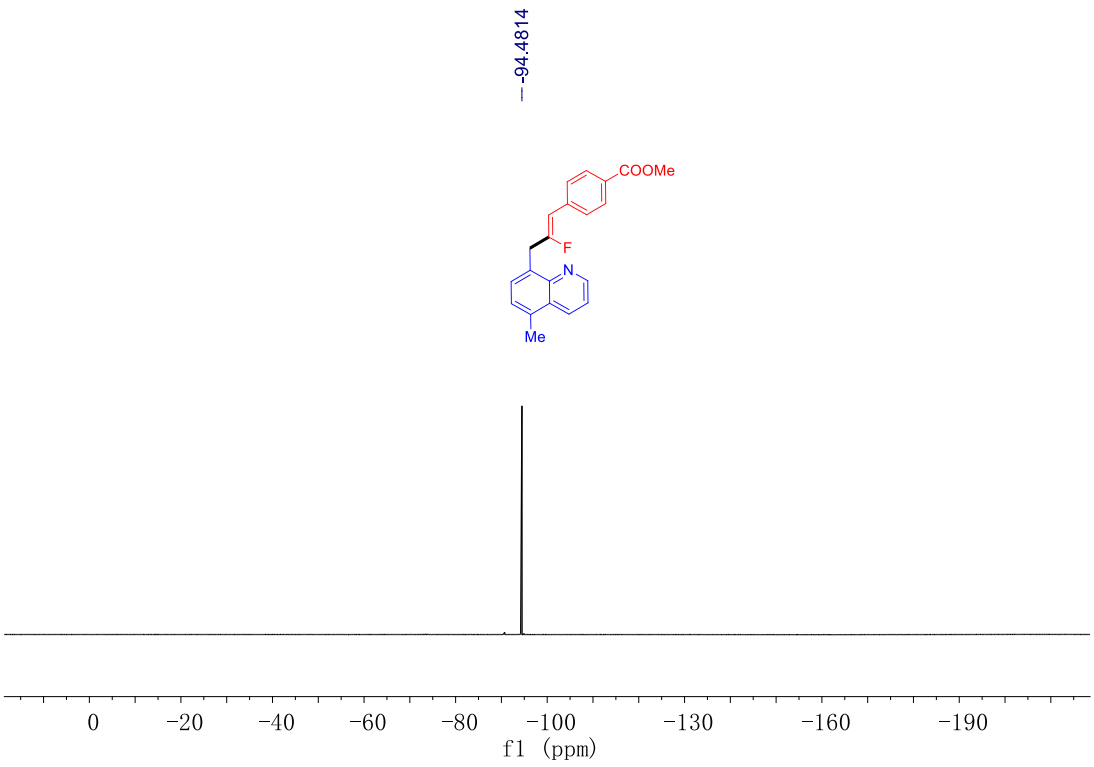
COOMe
F
N
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Me
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-20
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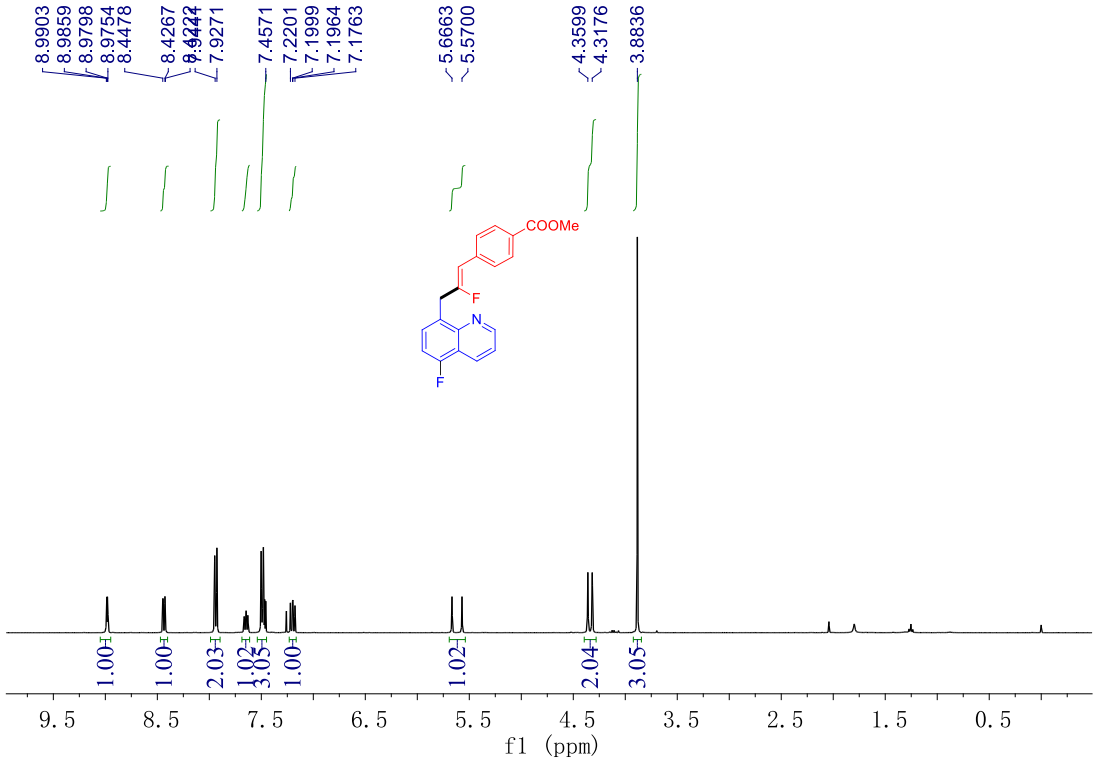
f1 (ppm)

3ca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8.9754
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7.2201
7.1999
7.1964
7.1763
5.6663
5.5700
4.3599
4.3176
3.8836
COOMe
F
N
F
1.00
1.00
2.03
1.02
3.05
1.00
1.02
2.04
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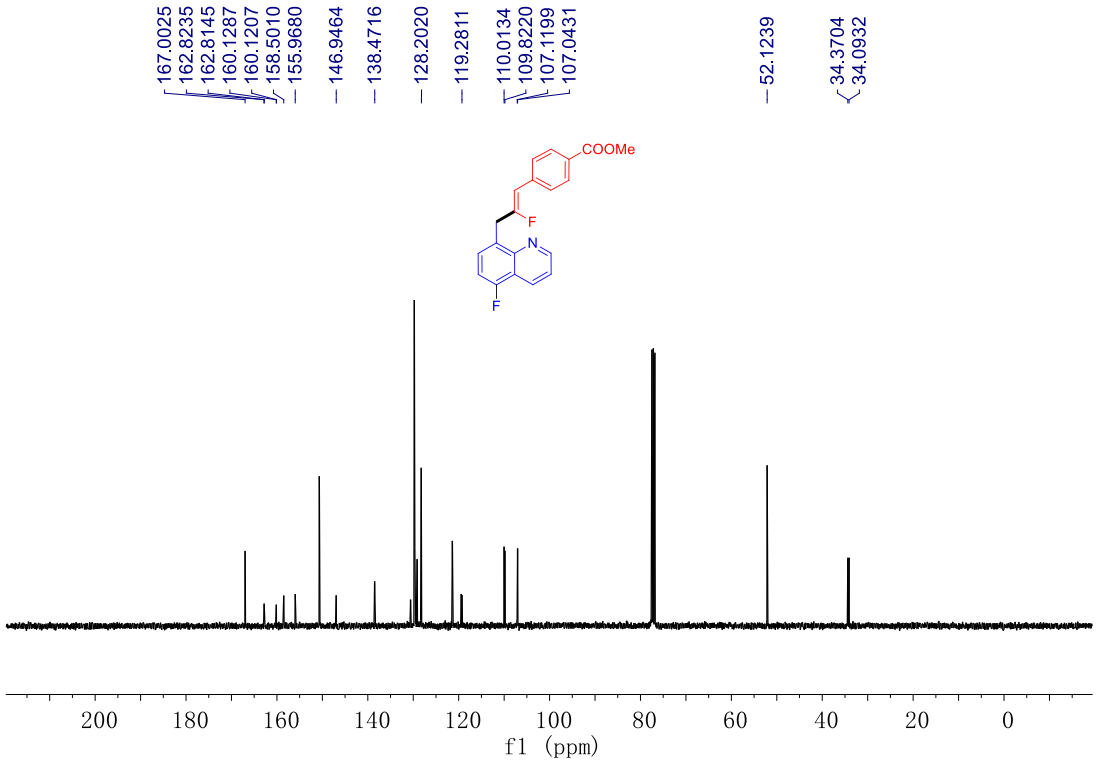
2.5
1.5
0.5
f1 (ppm)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119.2811
110.0134
109.8220
107.1199
107.0431
52.1239
34.3704
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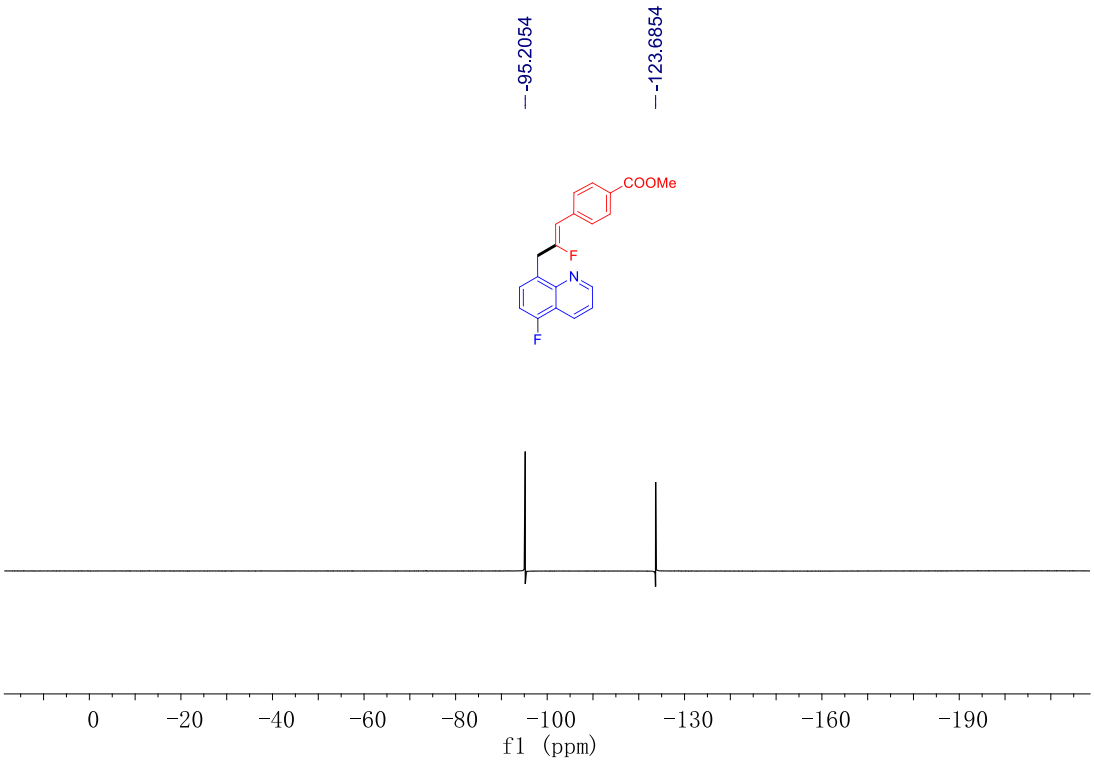
COOMe
F
N
F
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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COOMe
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F
0
-20
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-60
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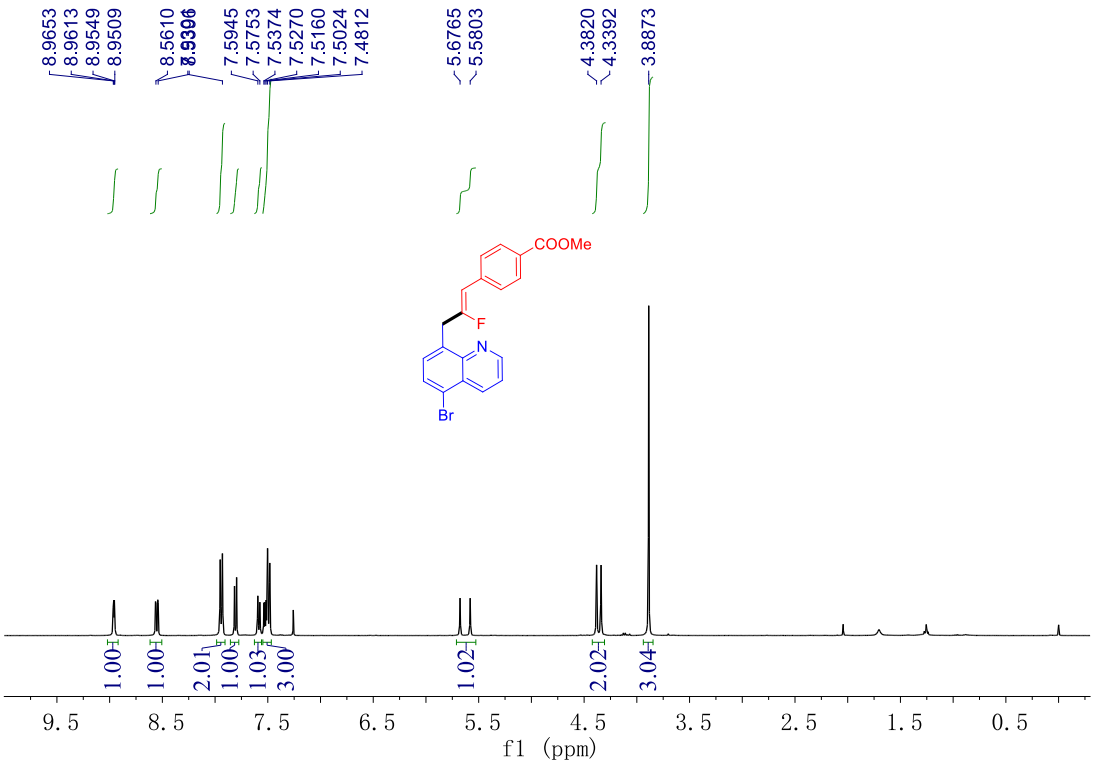
-130
-160
-190
f1 (ppm)

3da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4.3392
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COOMe
F
N
Br
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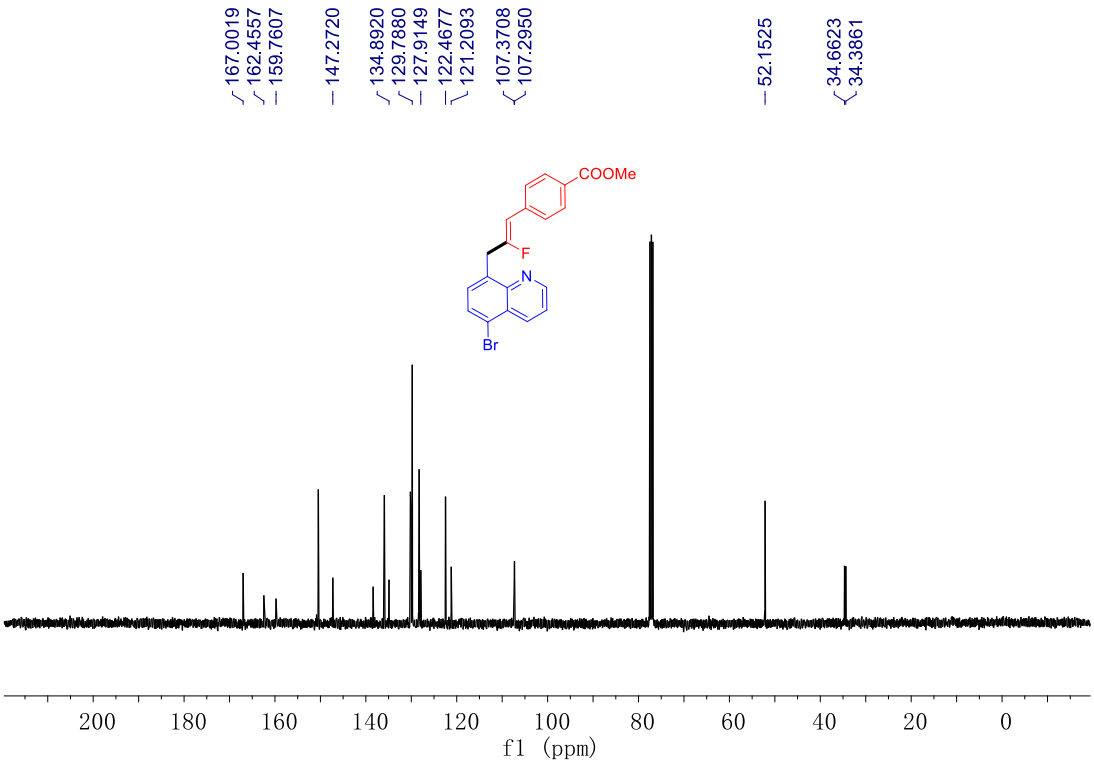
1.00
2.01
1.00
1.03
3.00
1.02
2.02
3.04
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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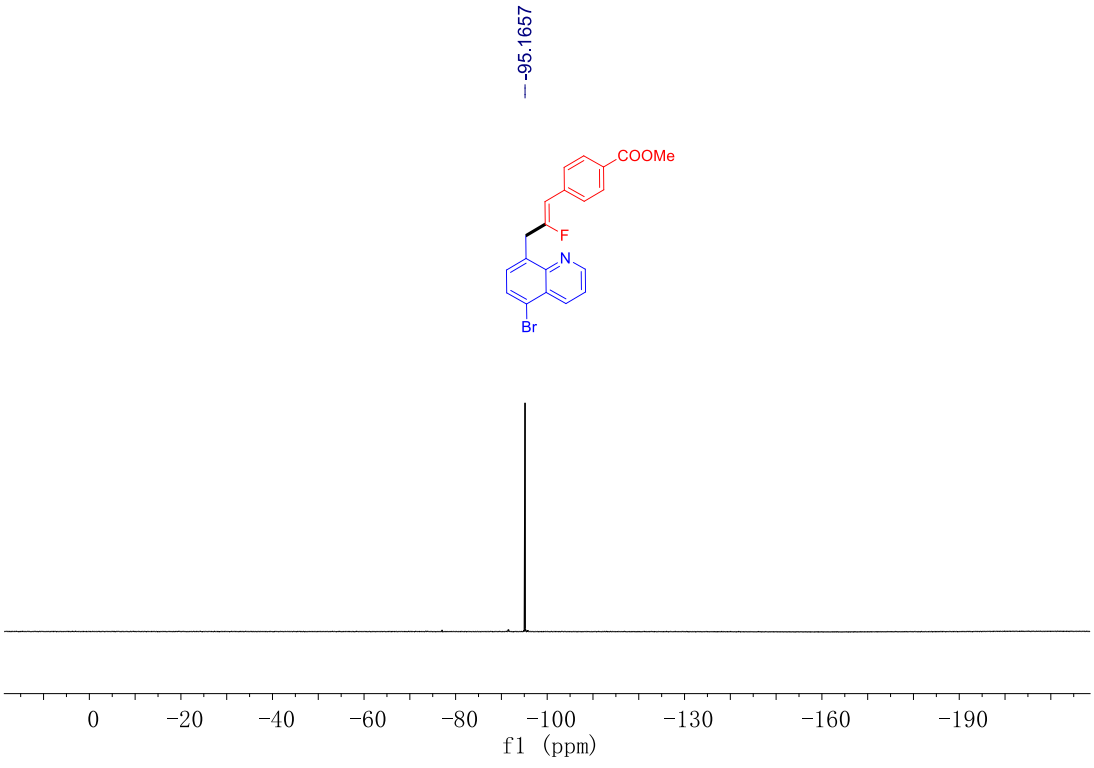
129.7880
127.9149
122.4677
121.2093
107.3708
107.2950
52.1525
34.6623
34.3861
COOMe
F
N
Br
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Br
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-80
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-130
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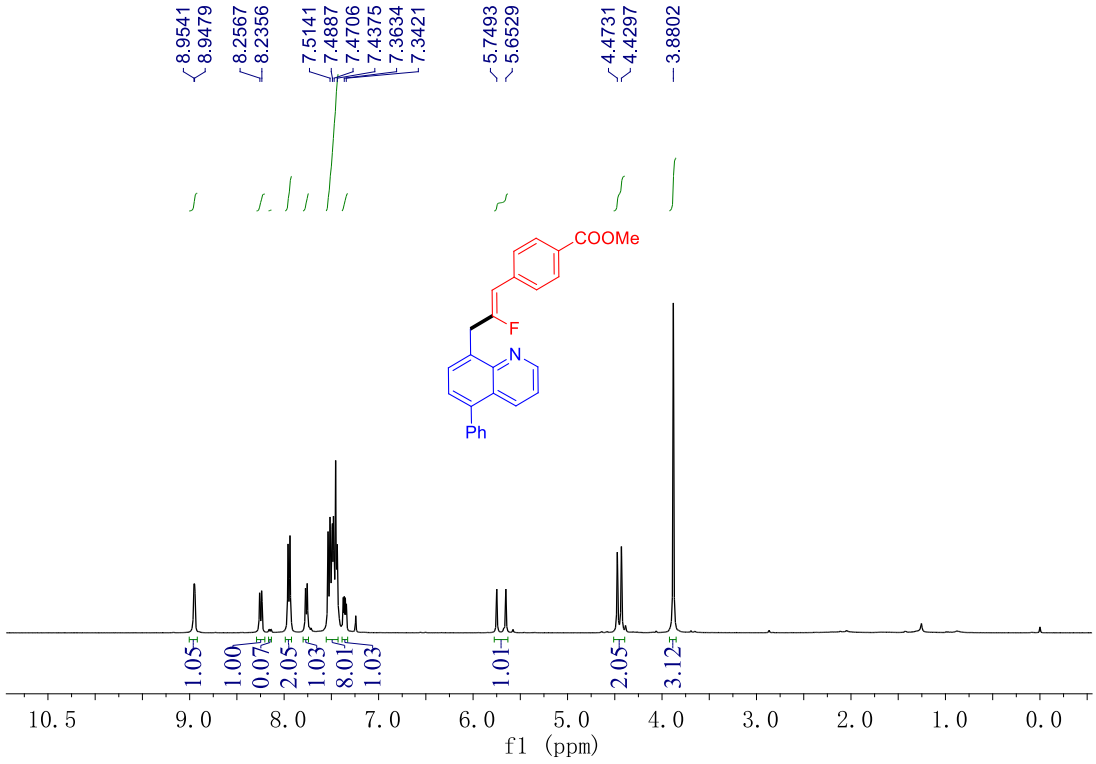
-190
f1 (ppm)

3ea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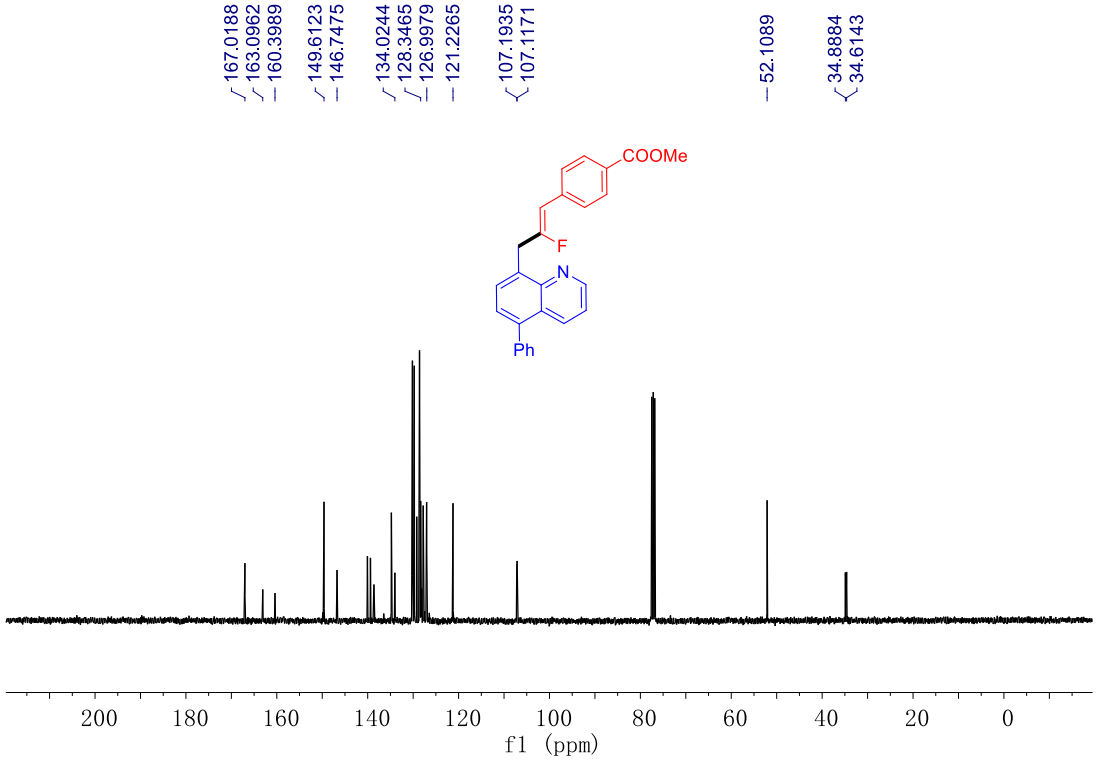
8.2567
8.2356
7.5141
7.4887
7.4706
7.4375
7.3634
7.3421
5.7493
5.6529
4.4731
4.4297
3.8802
COOMe
F
N
Ph
1.05
1.00
0.07
2.05
1.03
8.01
1.03
1.01
2.05
3.12
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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128.3465
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121.2265
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52.1089
34.8884
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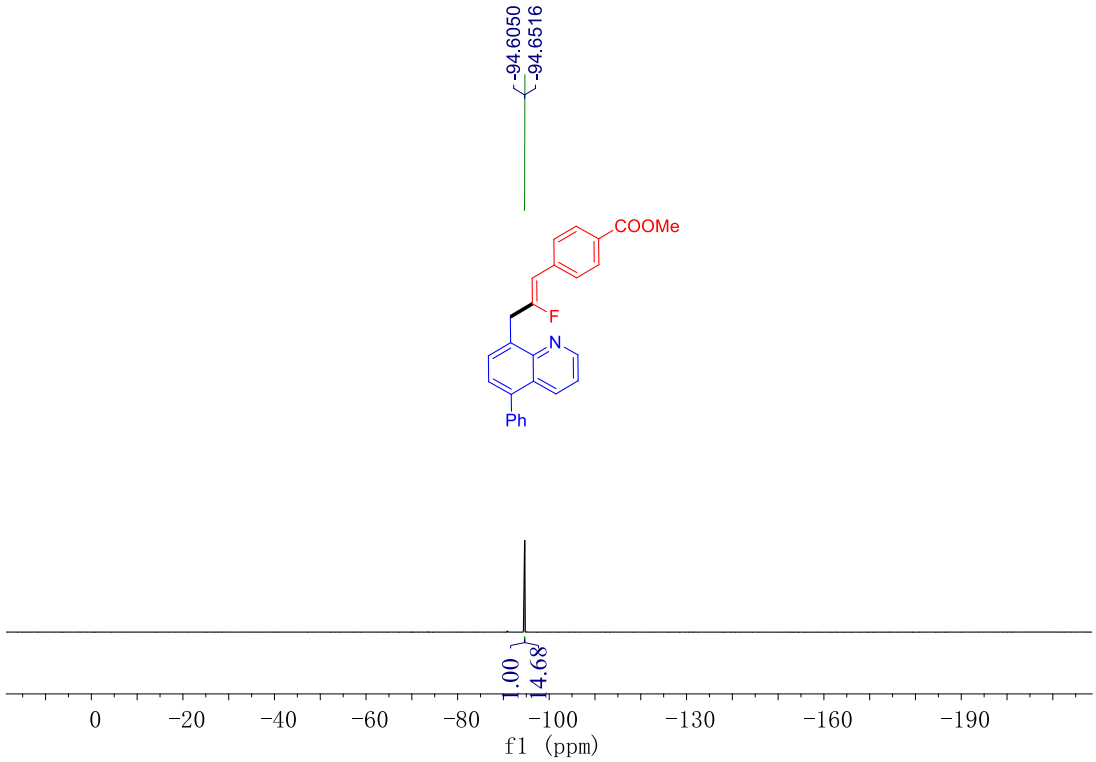
COOMe
F
N
Ph
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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COOMe
F
N
Ph
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-60
-80
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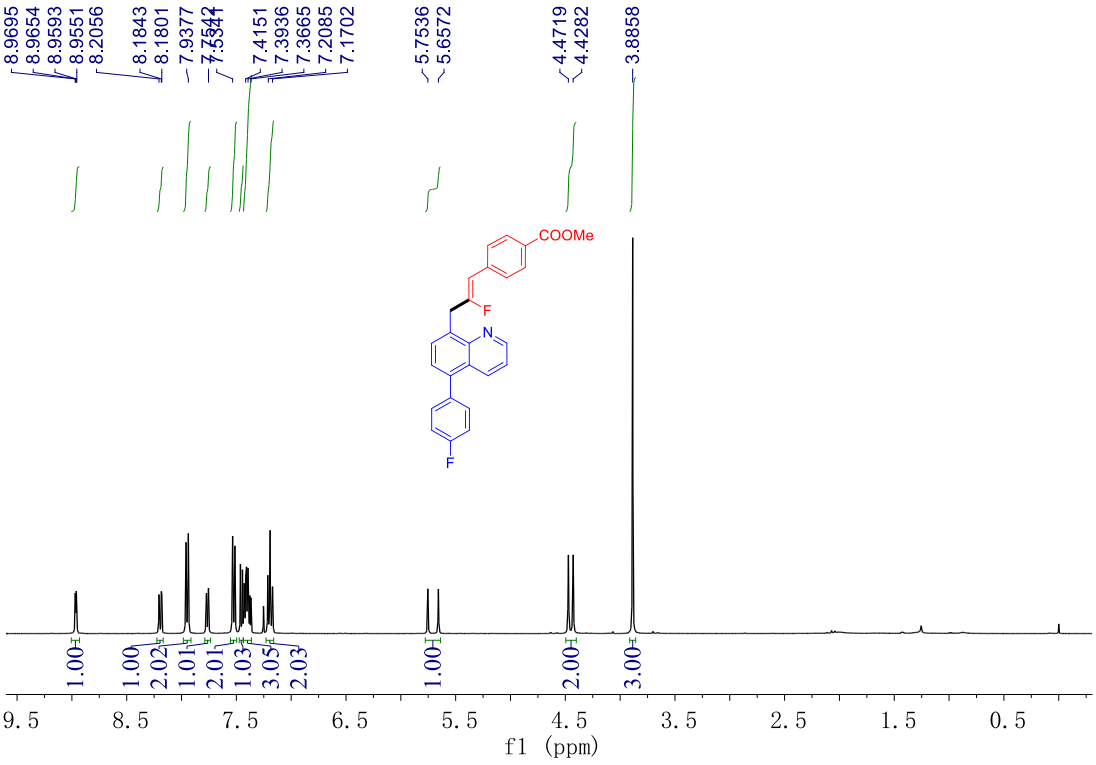
-130
-160
-190
f1 (ppm)

3fa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8.9593
8.9551
8.2056
8.1843
8.1801
7.9377
7.4151
7.3936
7.3665
7.2085
7.1702
5.7536
5.6572
4.4719
4.4282
3.8858
COOMe
F
N
F
1.00
1.00
2.02
1.01
2.01
1.03
3.05
2.03
1.00
2.00
3.00
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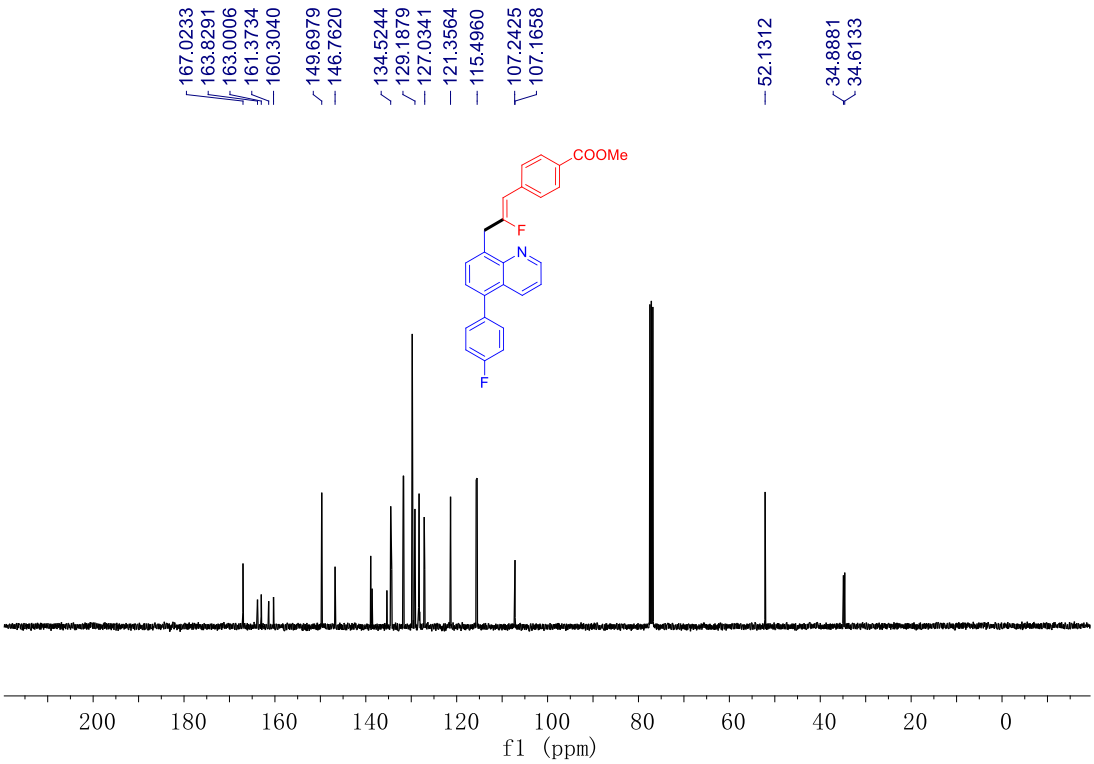
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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163.0006
161.3734
160.3040
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146.7620
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129.1879
127.0341
121.3564
115.4960
107.2425
107.1658
52.1312
34.8881
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COOMe
F
N
F
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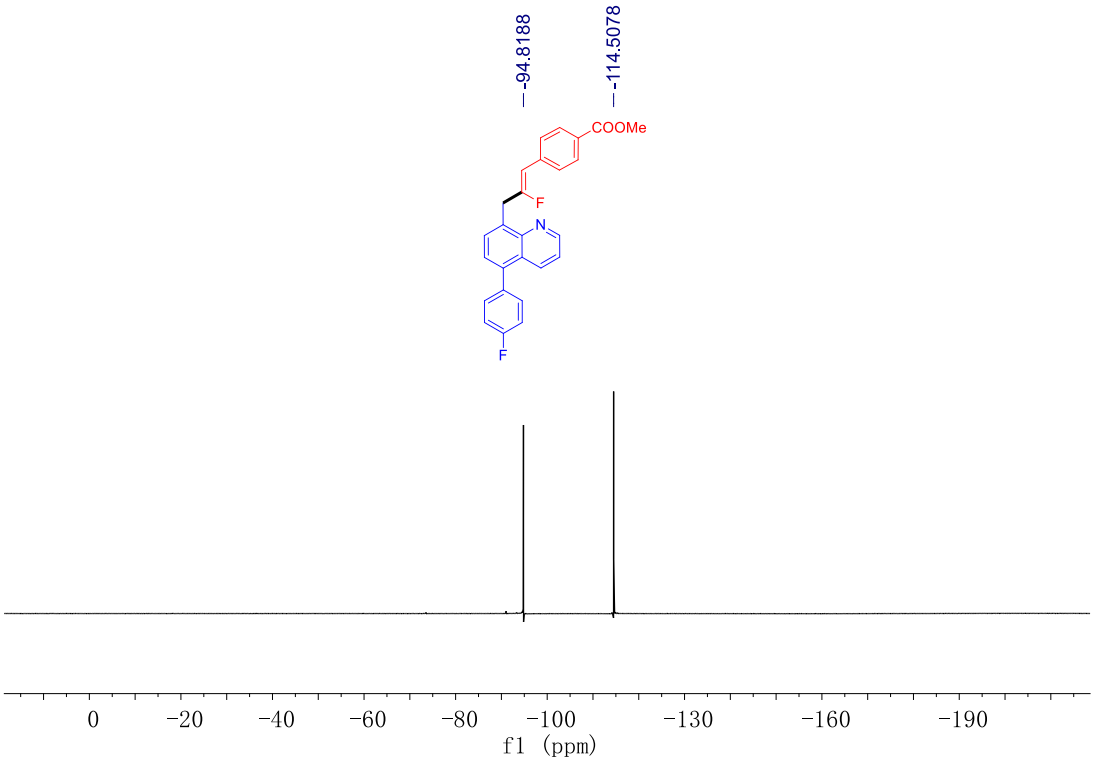
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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-114.5078
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F
0
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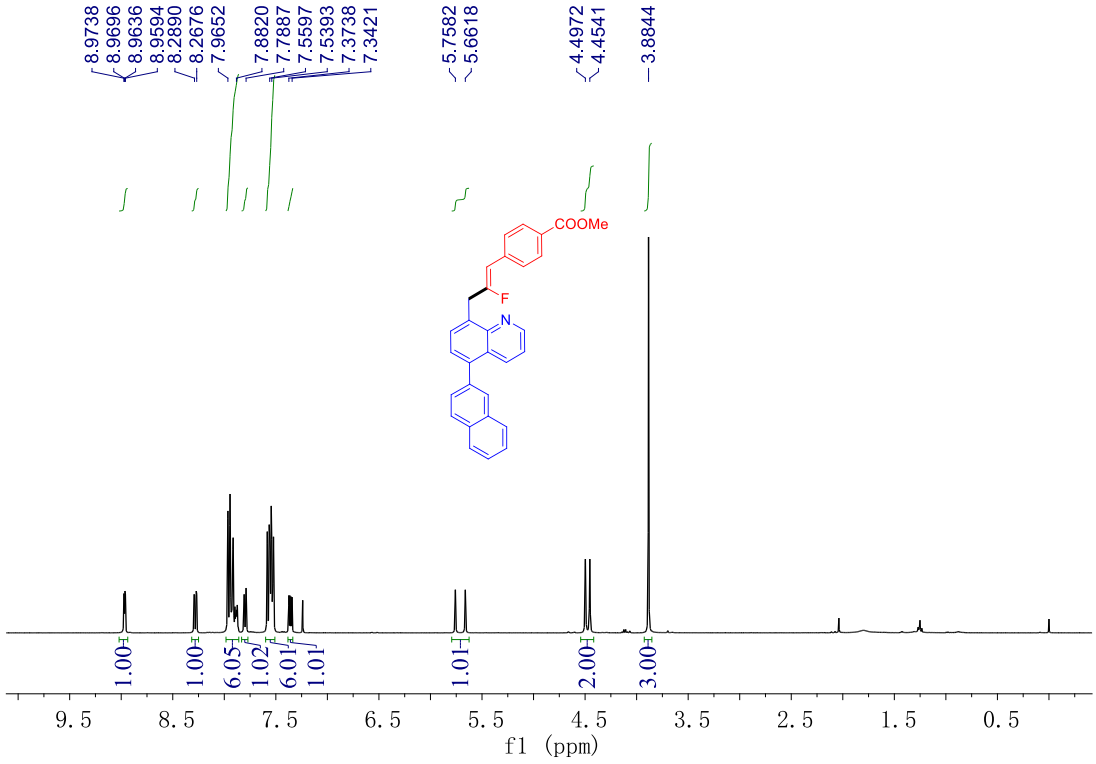
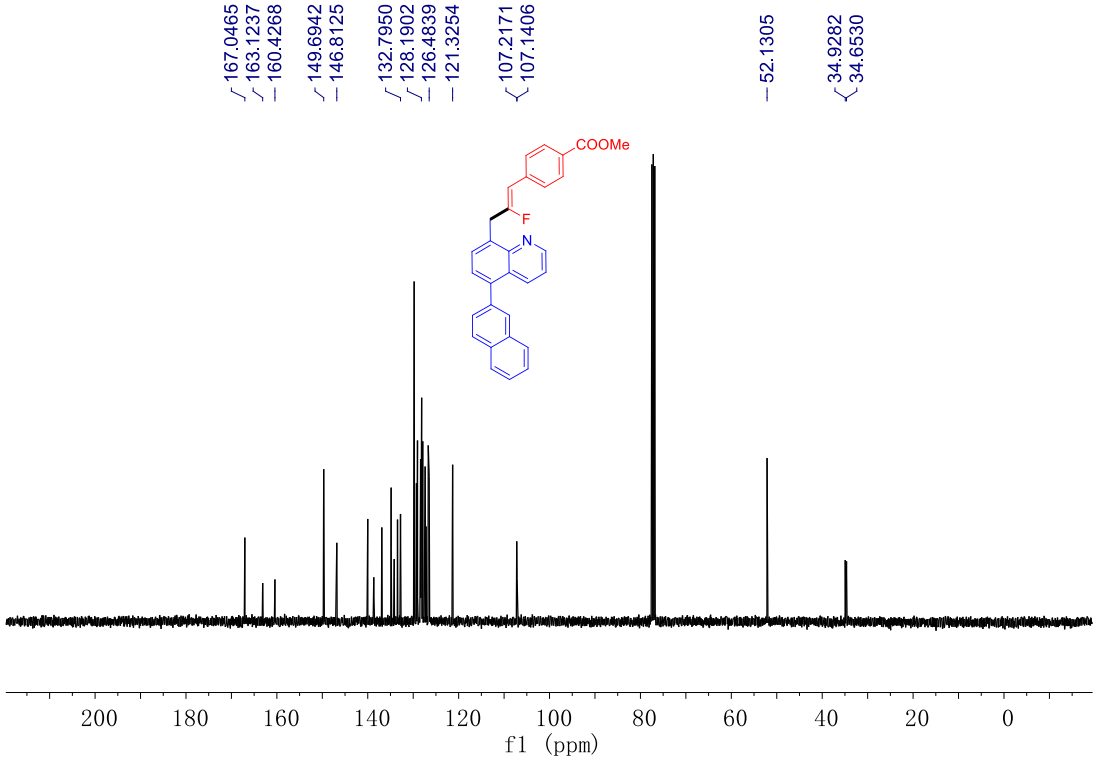
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ga


8.9738
8.9696
8.9636
8.9594
8.2890
8.2676
7.9652
7.8820
7.7887
7.5597
7.5393
7.3738
7.3421
5.7582
5.6618
4.4972
4.4541
3.8844
COOMe
F
N
1.00
1.00
6.05
1.02
6.01
1.01
1.01
2.00
3.00
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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160.4268
149.6942
146.8125
132.7950
128.1902
126.4839
121.3254
107.2171
107.1406
52.1305
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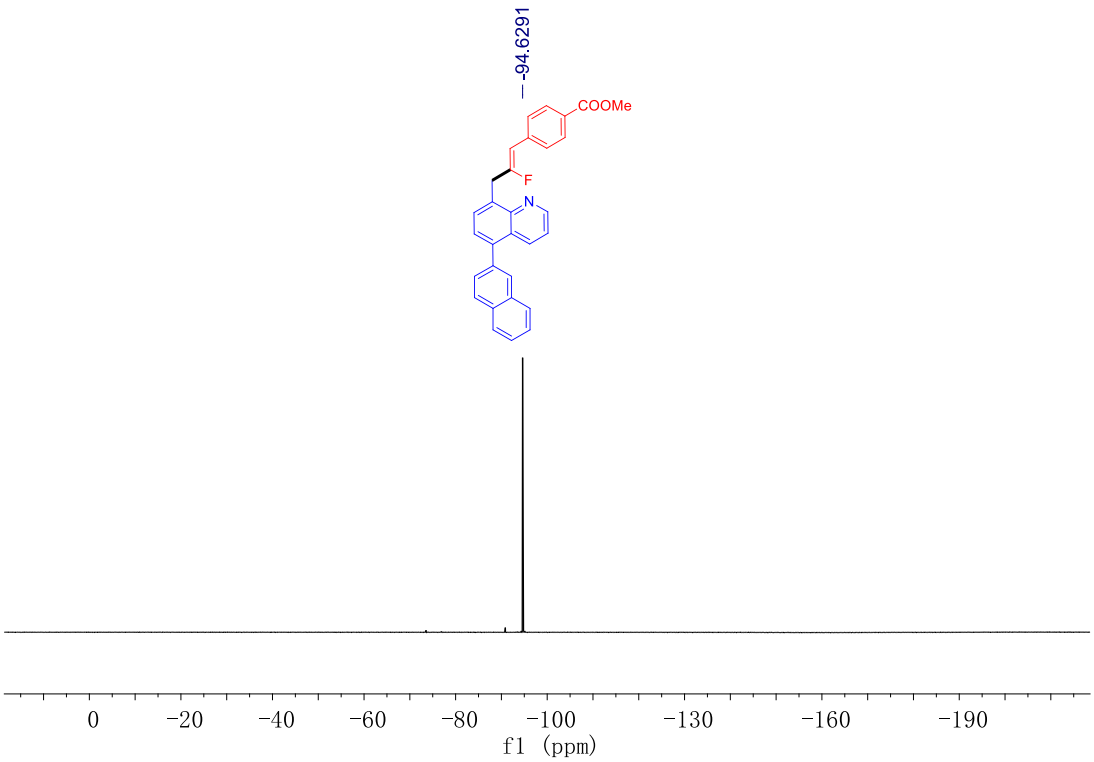
COOMe
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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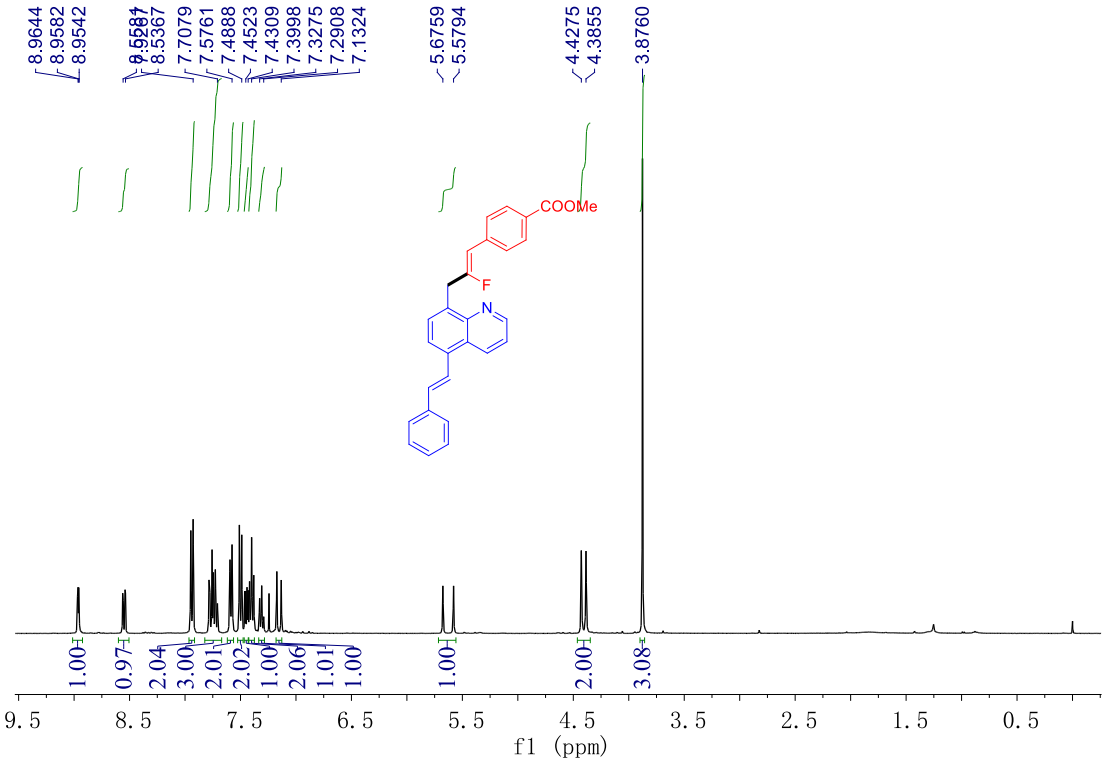
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ha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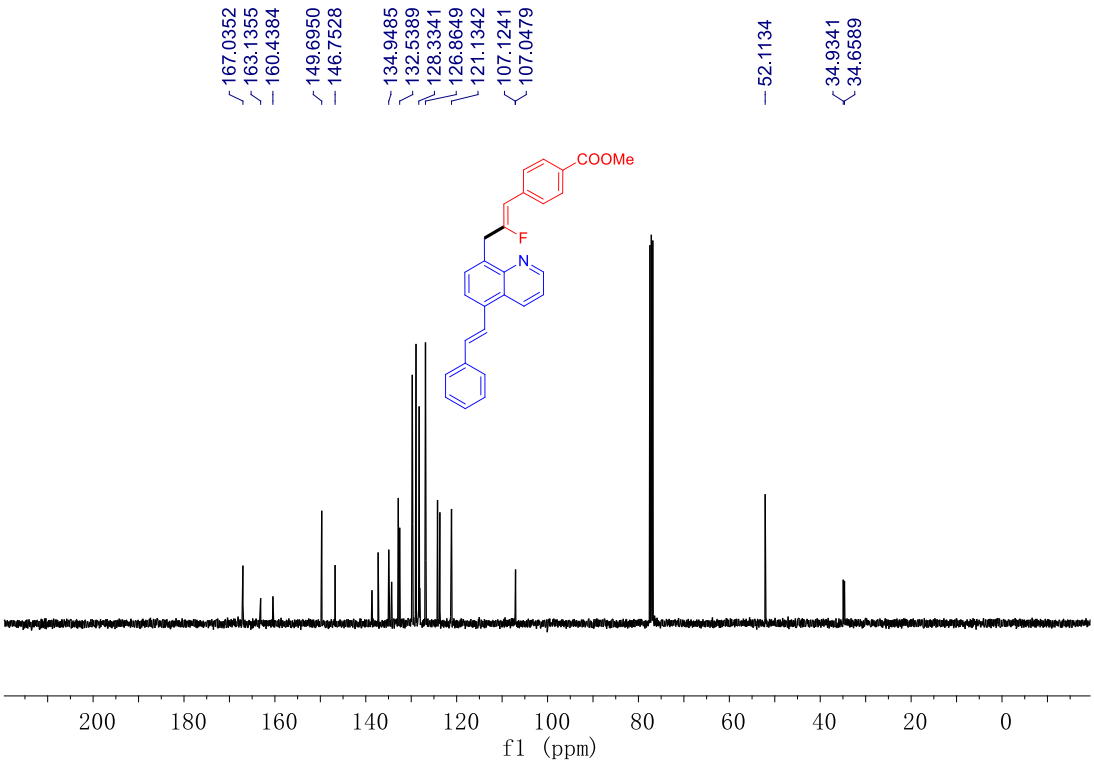
8.9582
8.9542
8.5367
7.7079
7.5761
7.4888
7.4523
7.4309
7.3998
7.3275
7.2908
7.1324
5.6759
5.5794
4.4275
4.3855
3.8760
COOMe
F
N
1.00
0.97
2.04
3.00
2.01
2.02
1.00
2.06
1.01
1.00
1.00
2.00
3.08
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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146.7528
134.9485
132.5389
128.3341
126.8649
121.1342
107.1241
107.0479
52.1134
34.9341
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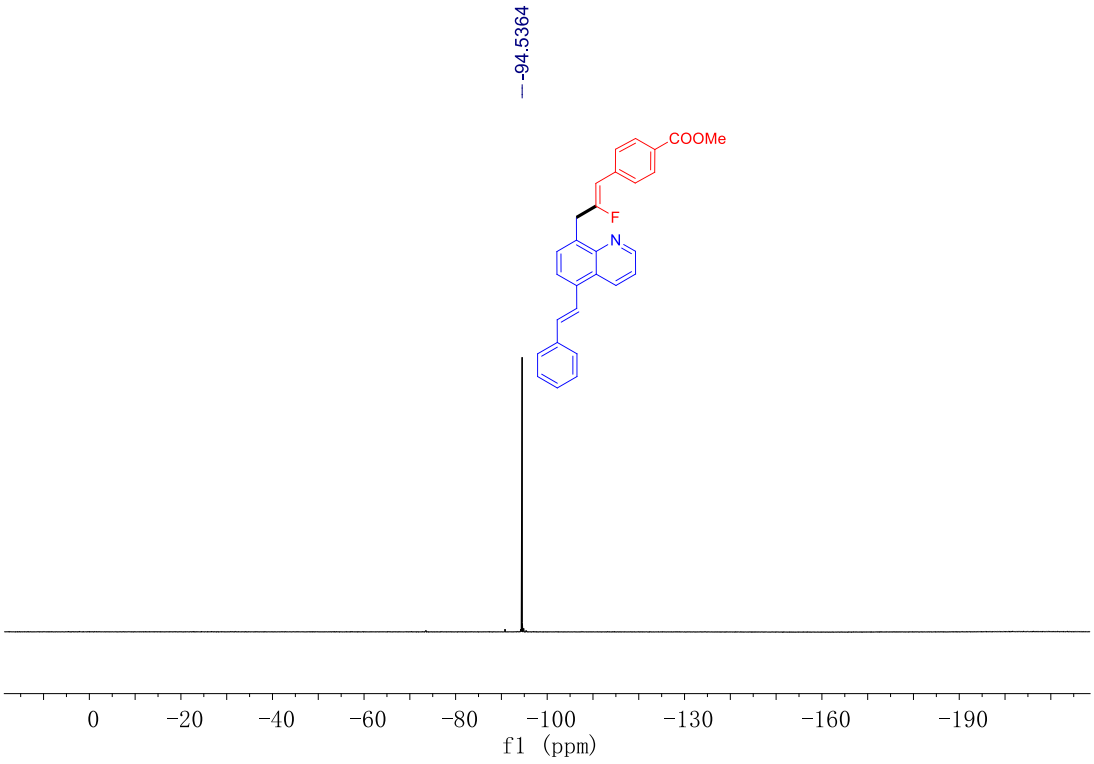
COOMe
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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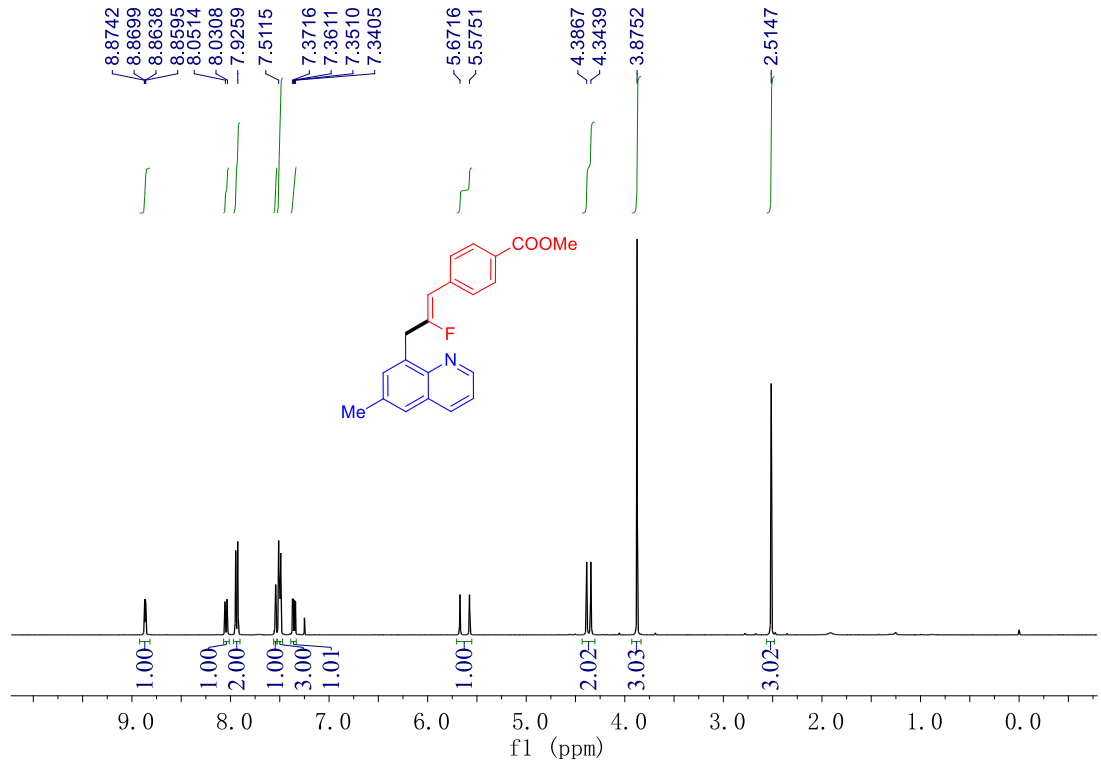
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ia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8.8638
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7.9259
7.5115
7.3716
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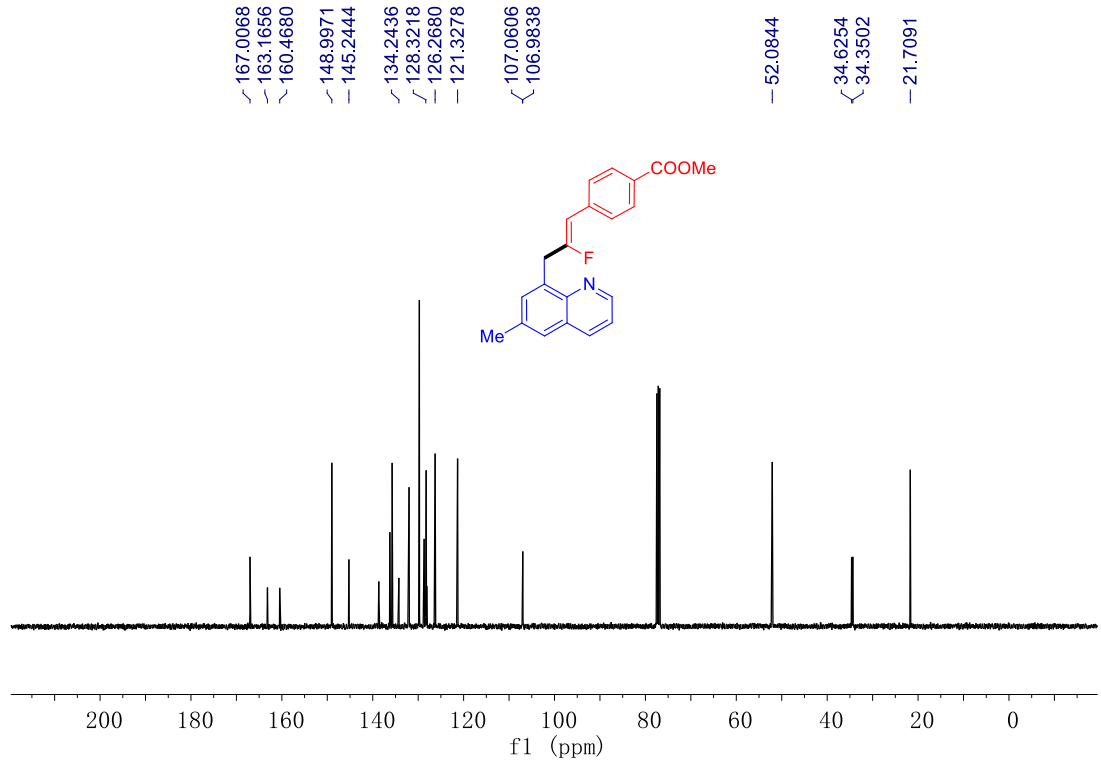
7.3510
7.3405
5.6716
5.5751
4.3867
4.3439
3.8752
2.5147
COOMe
F
N
Me
1.00
1.00
2.00
1.00
3.00
1.01
1.00
2.02
3.03
3.02
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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52.0844
34.6254
34.3502
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COOMe
F
N
Me
200
180
160
140
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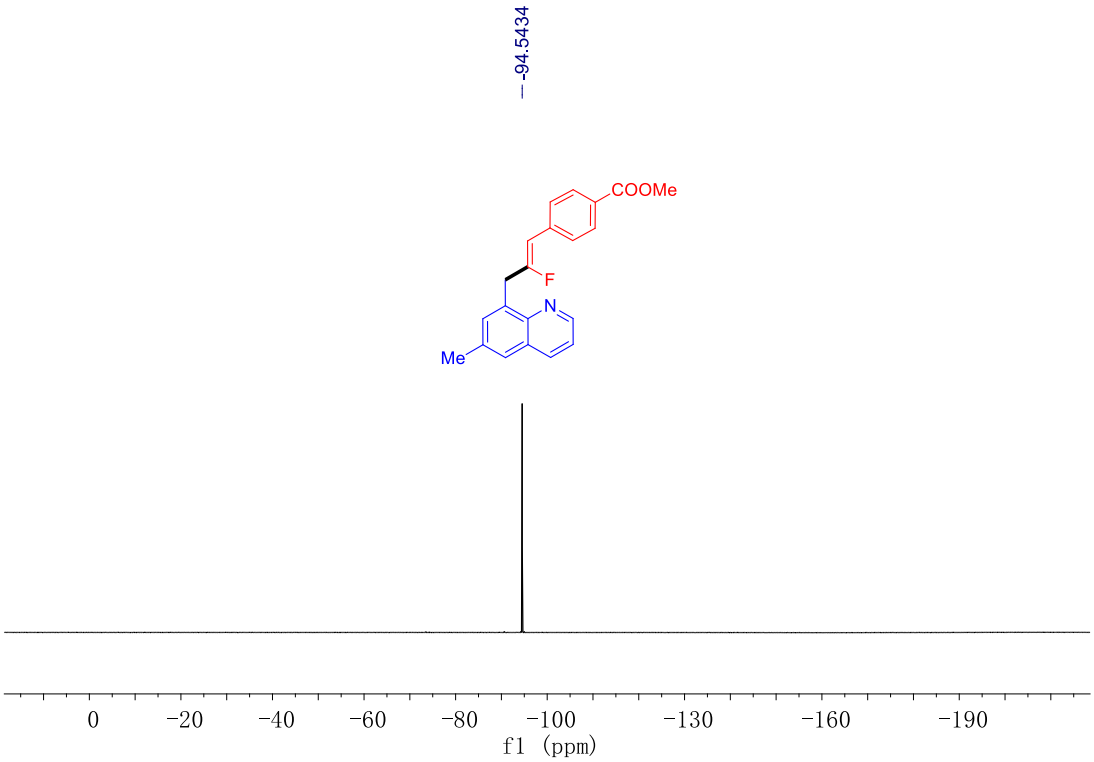
100
80
60
40
20
0
f1 (ppm)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F
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Me
0
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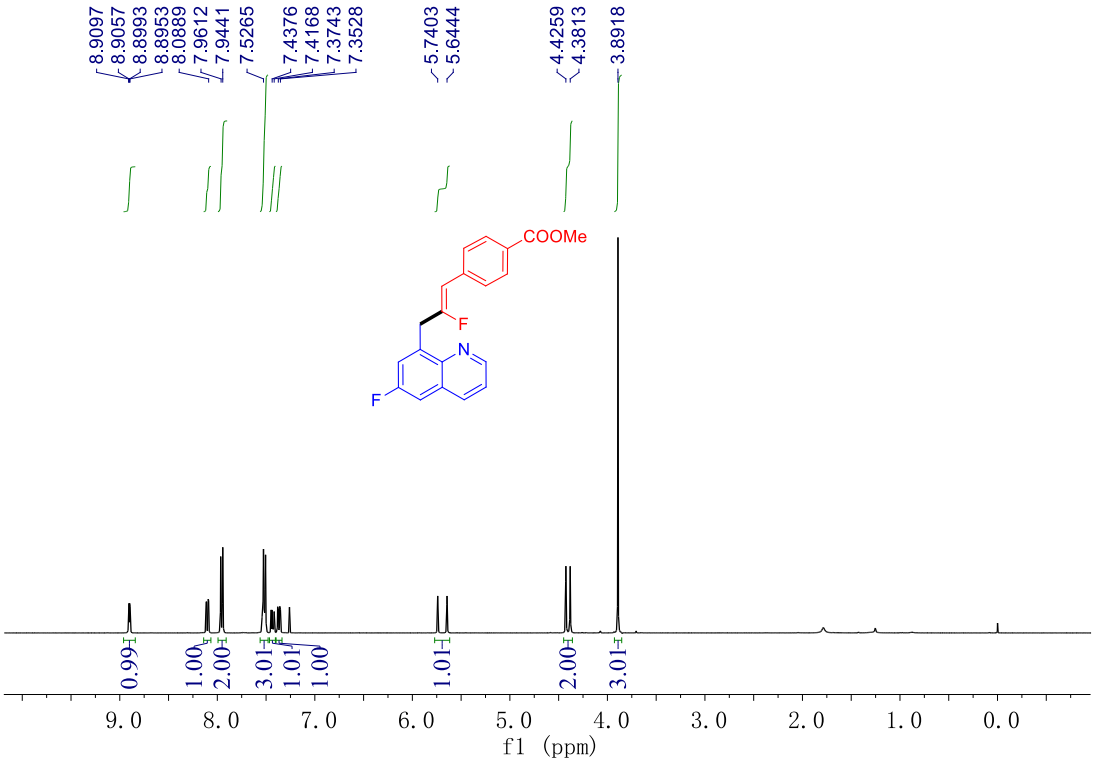
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ja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7.9441
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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
9.0
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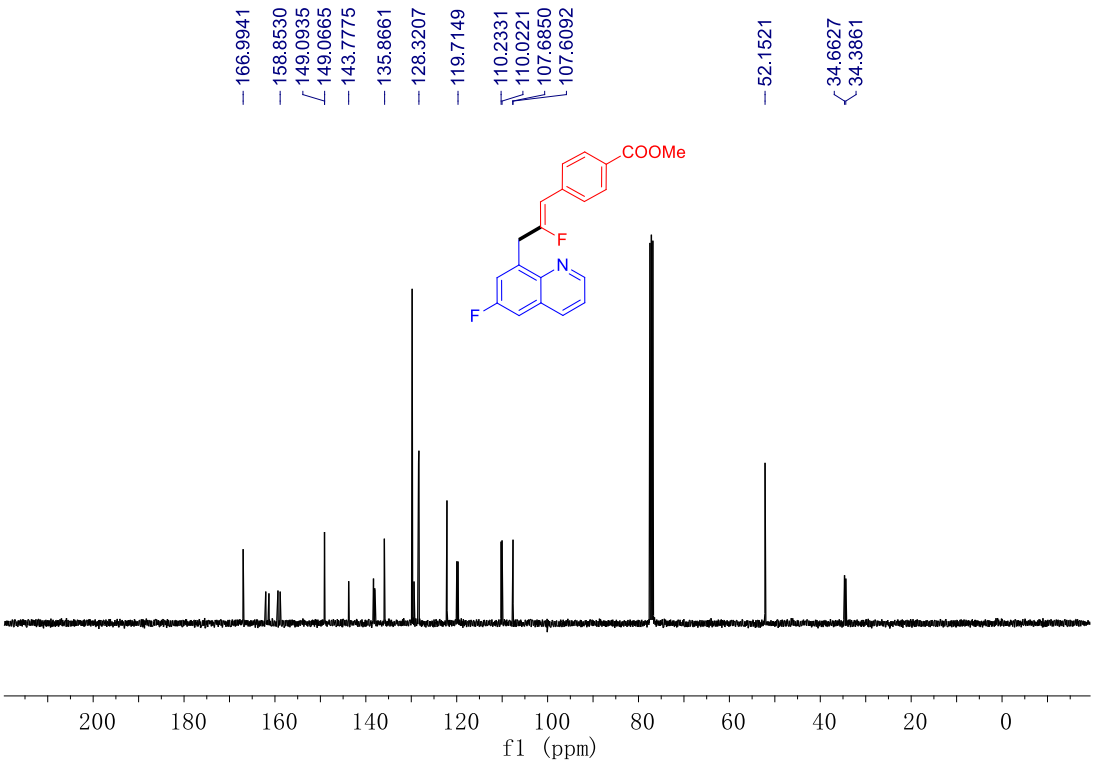
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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143.7775
135.8661
128.3207
119.7149
110.2331
110.0221
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107.6092
52.1521
34.6627
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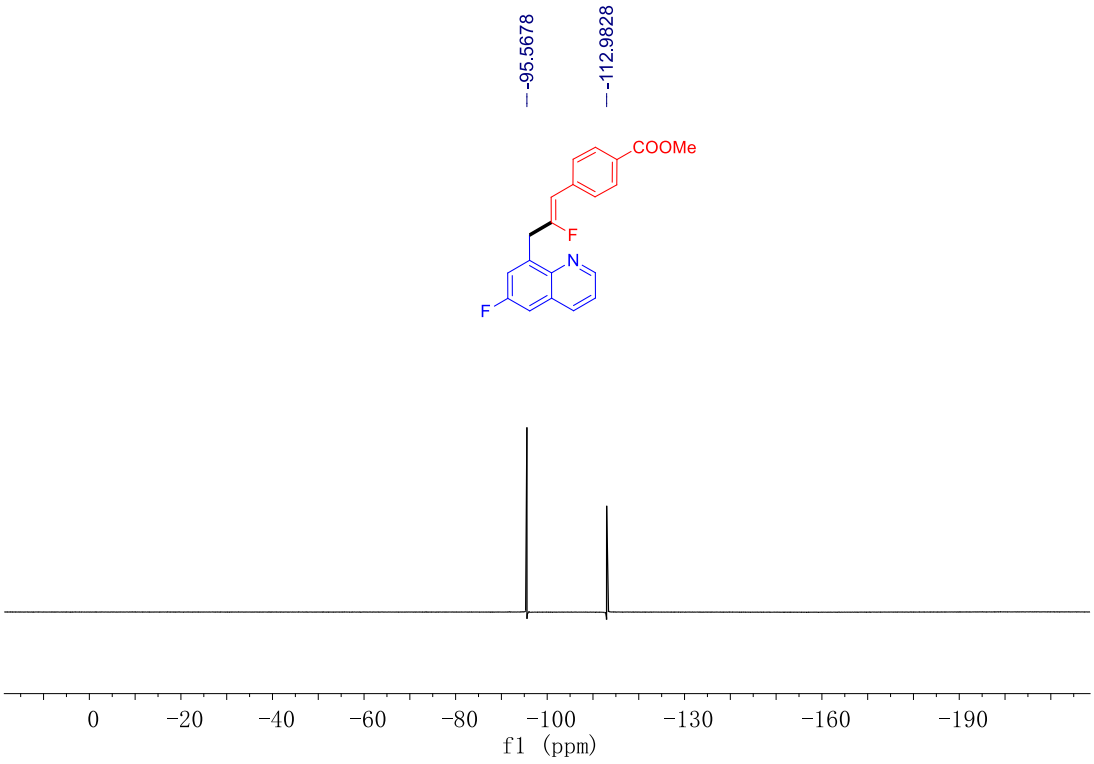
COOMe
F
N
F
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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0
-20
-40
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-130
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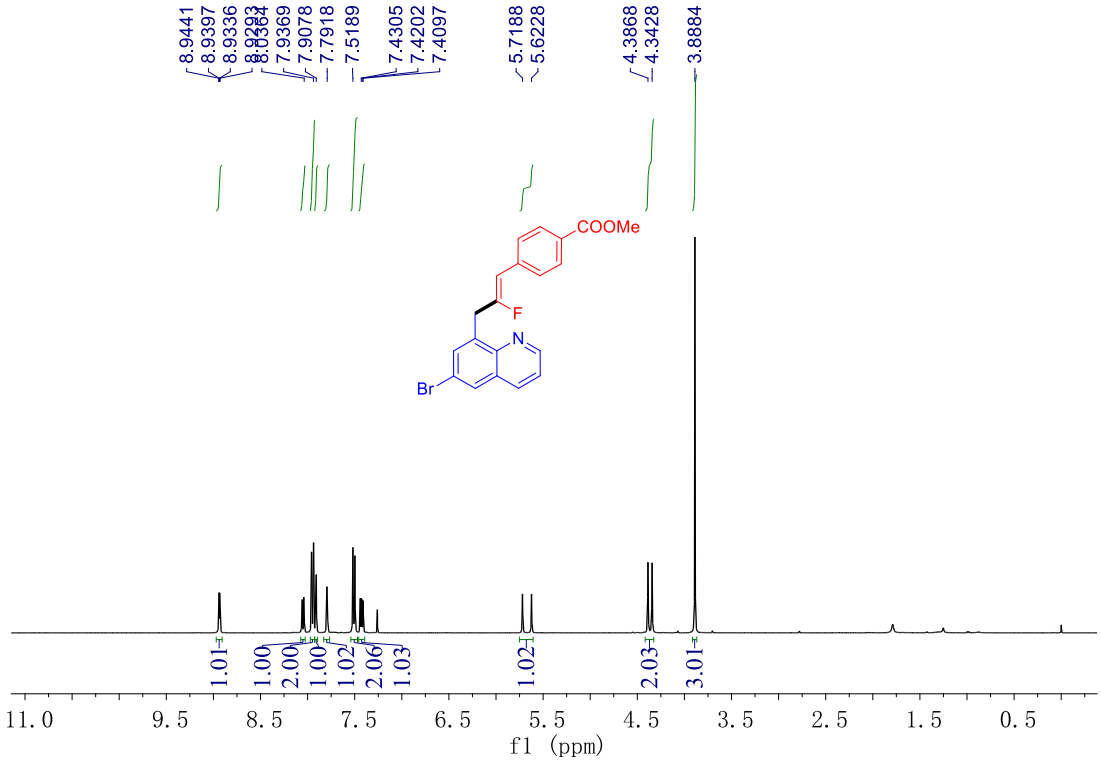
-190
f1 (ppm)

3ka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8.9336
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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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9.5
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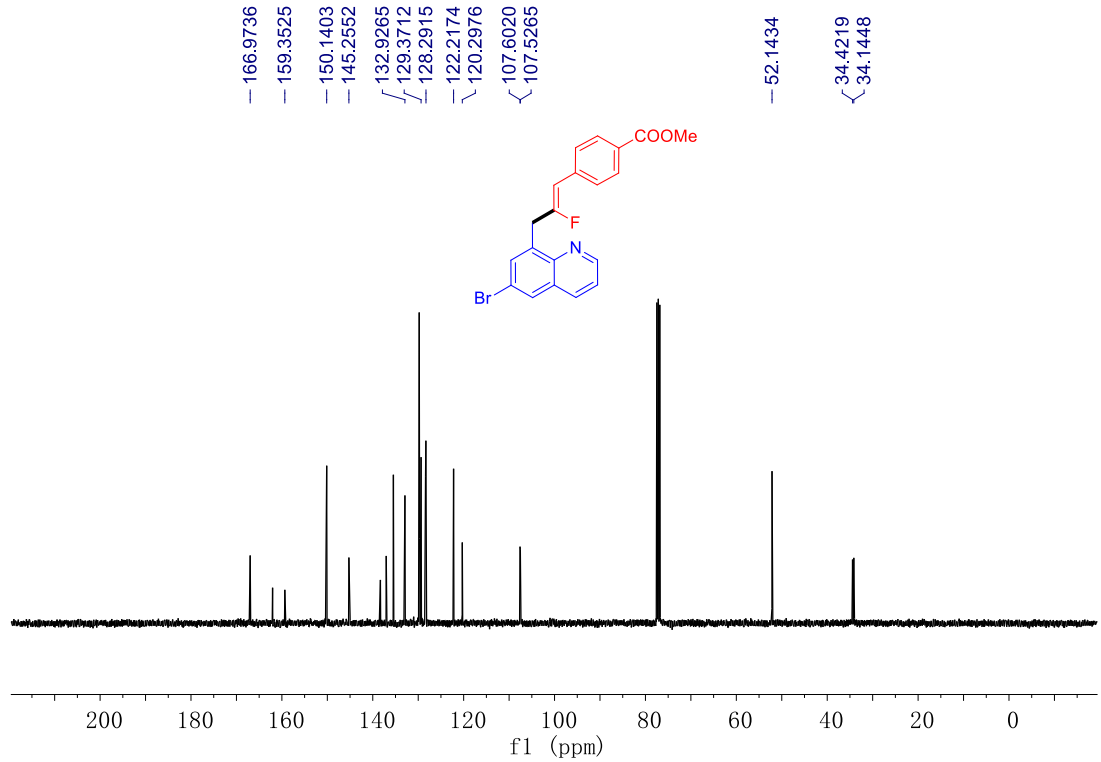
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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150.1403
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132.9265
129.3712
128.2915
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120.2976
107.6020
107.5265
52.1434
34.4219
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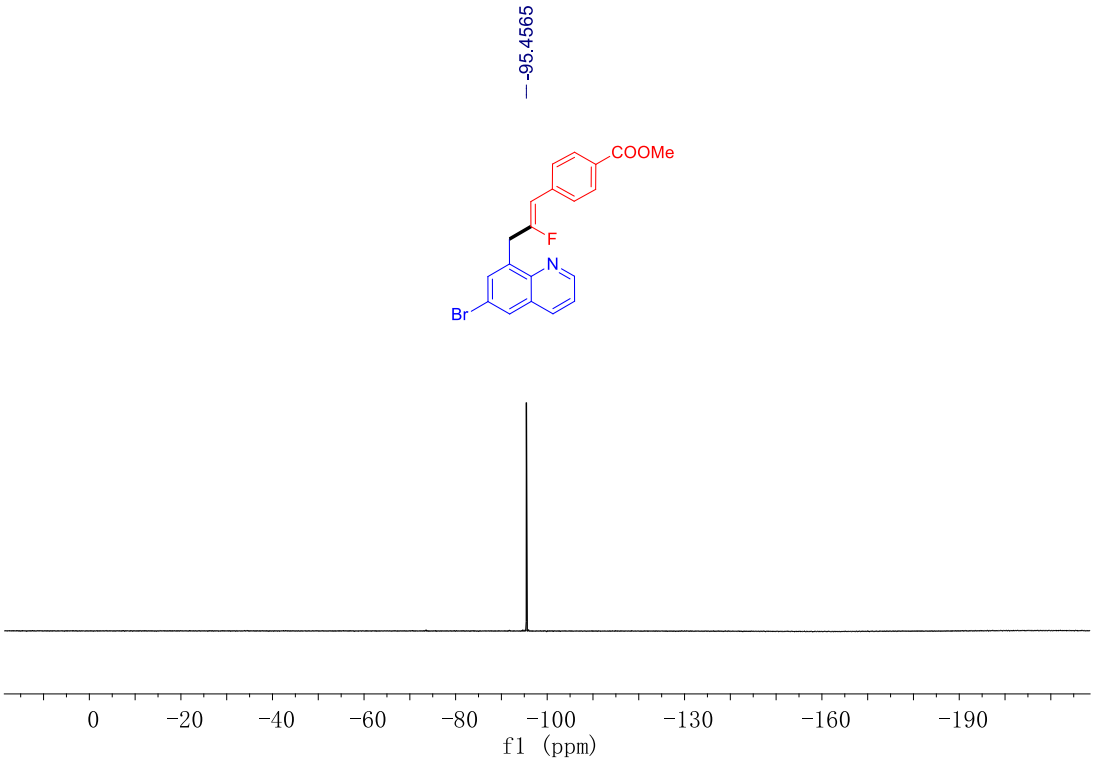
COOMe
F
N
Br
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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F
N
Br
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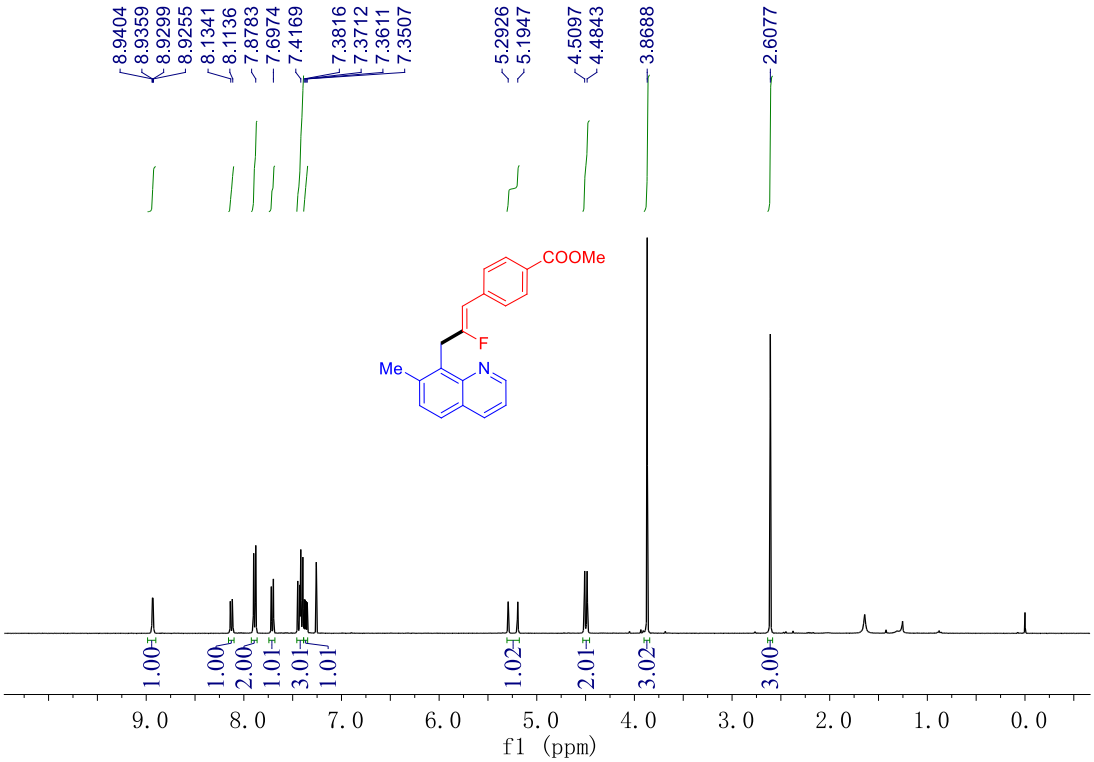
-60
-80
-100
-130
-160
-190
f1 (ppm)

3la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7.3712
7.3611
7.3507
5.2926
5.1947
4.5097
4.4843
3.8688
2.6077
COOMe
F
Me
N
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1.00
2.00
1.01
3.01
1.01
1.02
2.01
3.02
3.00
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7.0
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5.0
4.0
3.0
2.0
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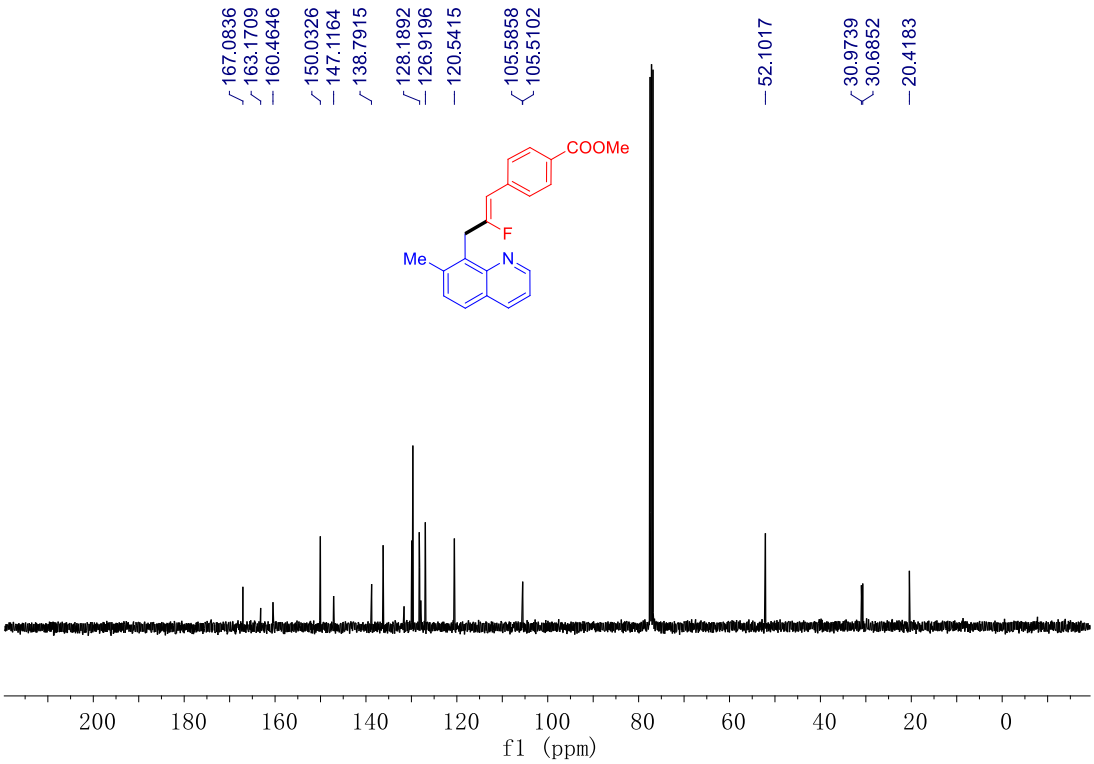
0.0
f1 (ppm)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52.1017
30.9739
30.6852
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Me
N
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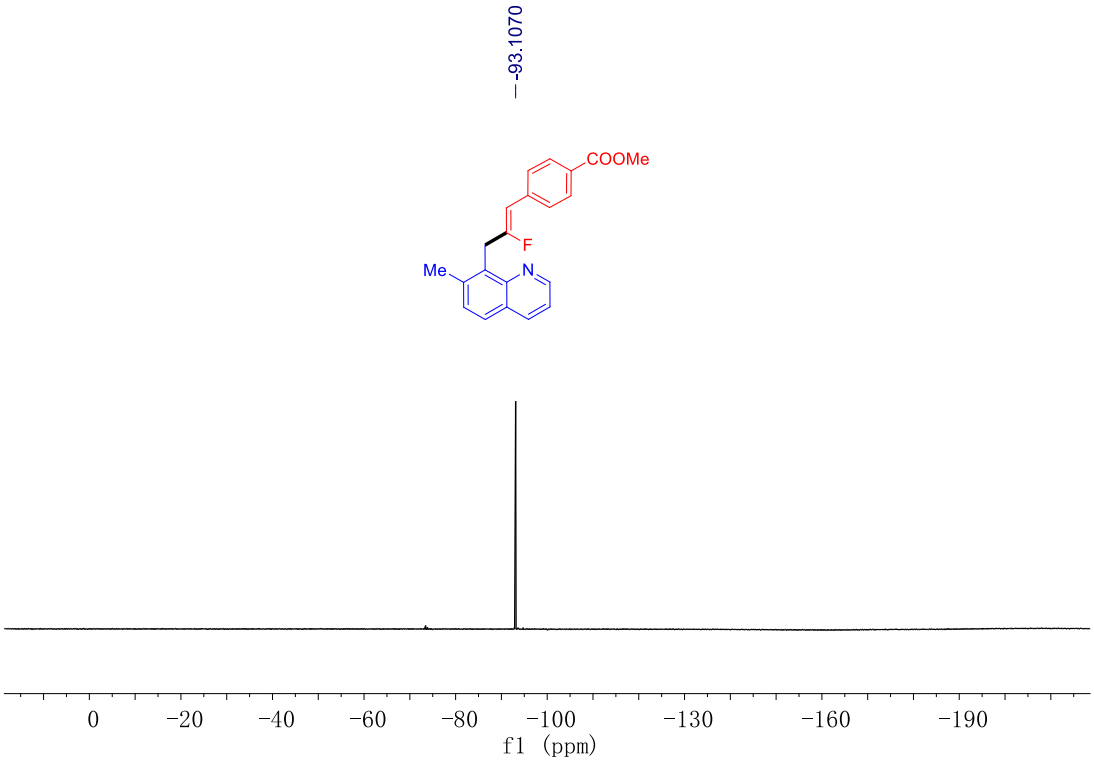
100
80
60
40
20
0
f1 (ppm)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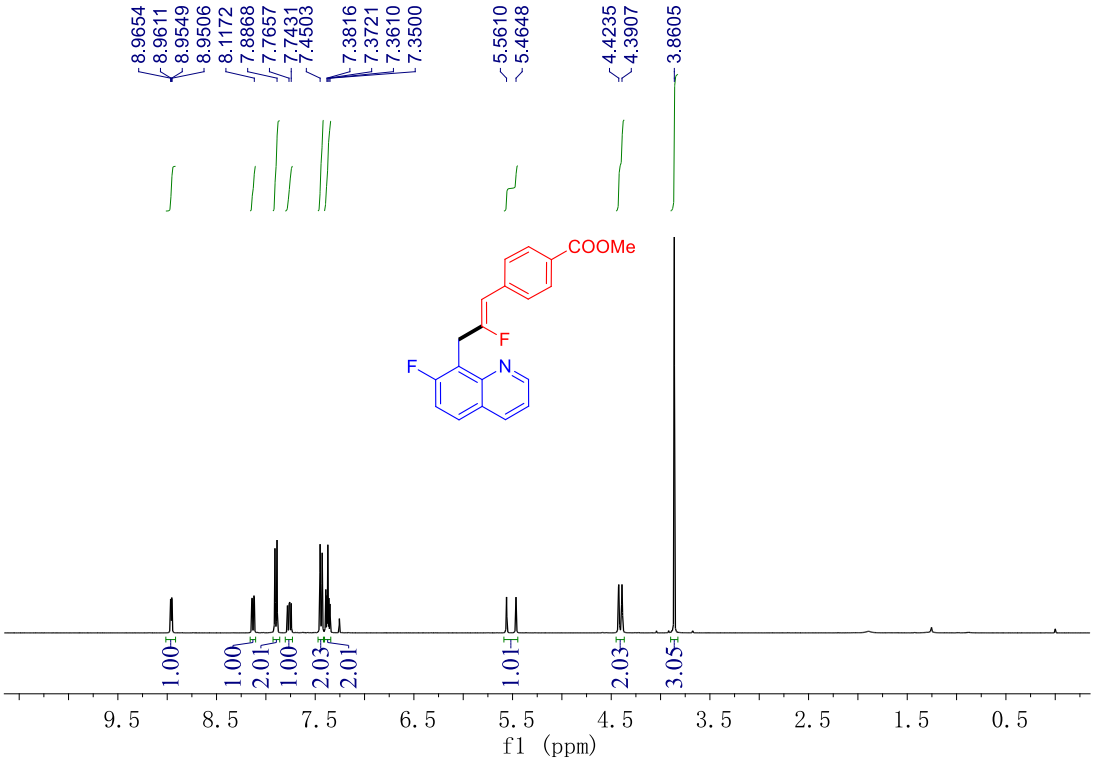
3ma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7.7431
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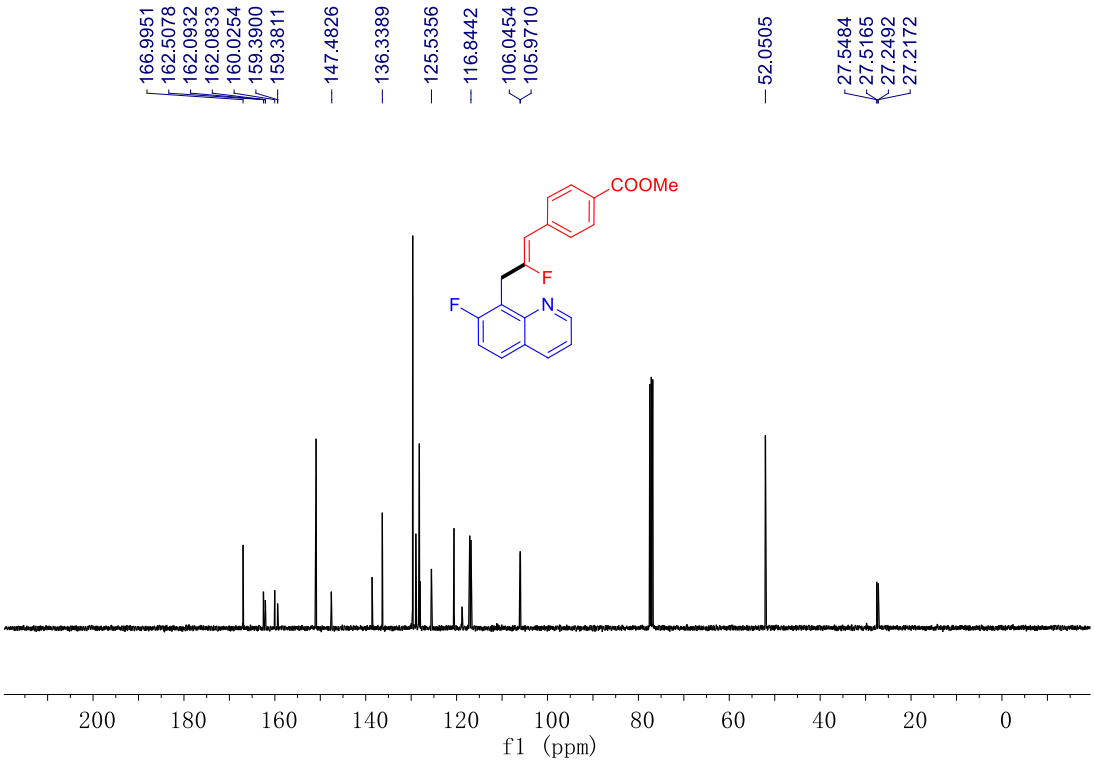
7.3721
7.3610
7.3500
5.5610
5.4648
4.4235
4.3907
3.8605
COOMe
F
F
N
1.00
1.00
2.01
1.00
2.03
2.01
1.01
2.03
3.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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136.3389
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116.8442
106.0454
105.9710
52.0505
27.5484
27.5165
27.2492
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COOMe
F
F
N
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180
160
140
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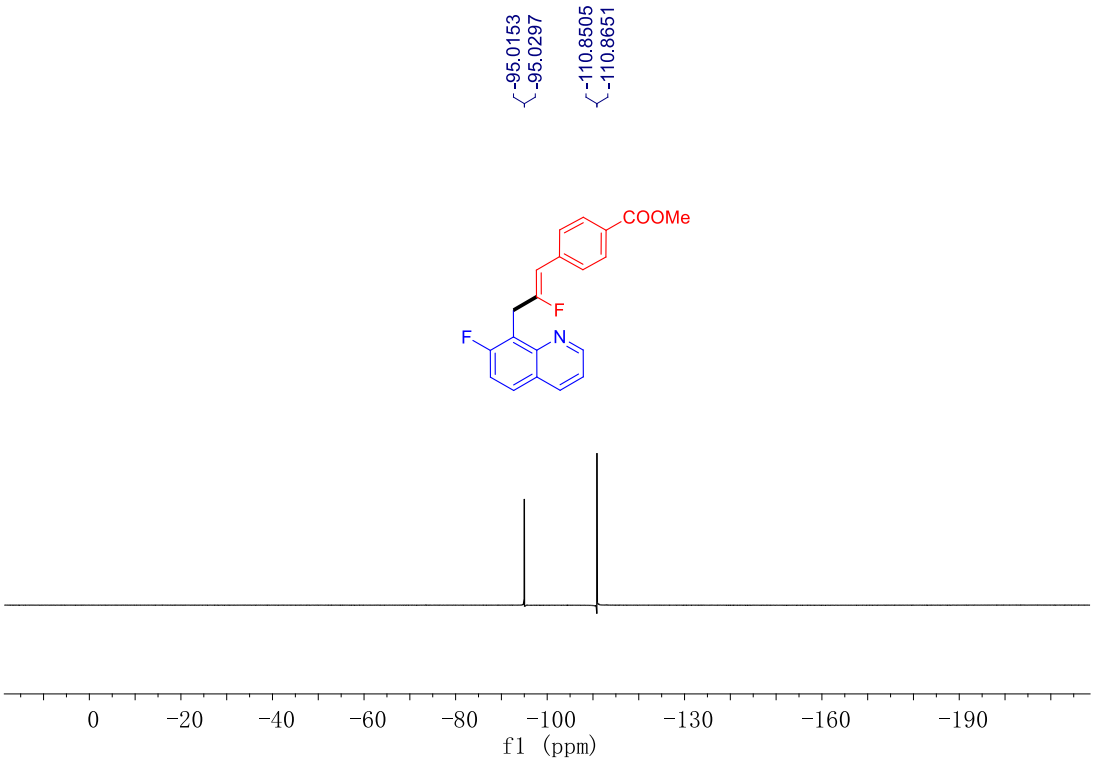
100
80
60
40
20
0
f1 (ppm)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N
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-20
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-60
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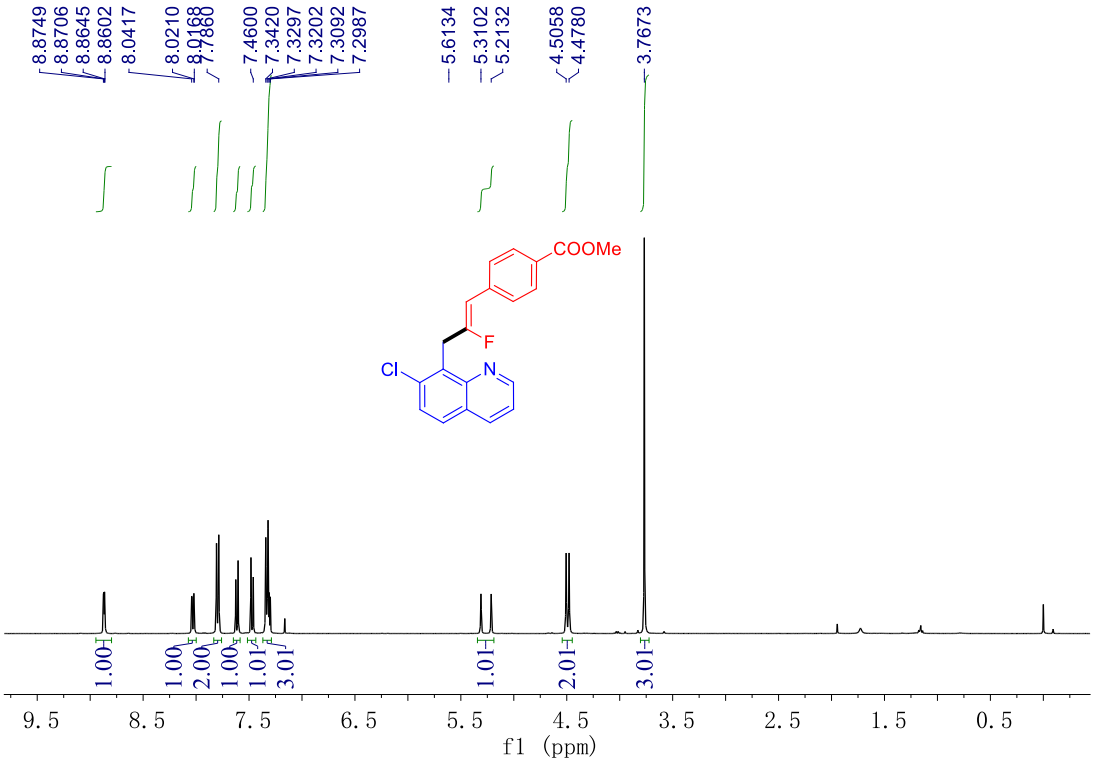
-130
-160
-190
f1 (ppm)

3na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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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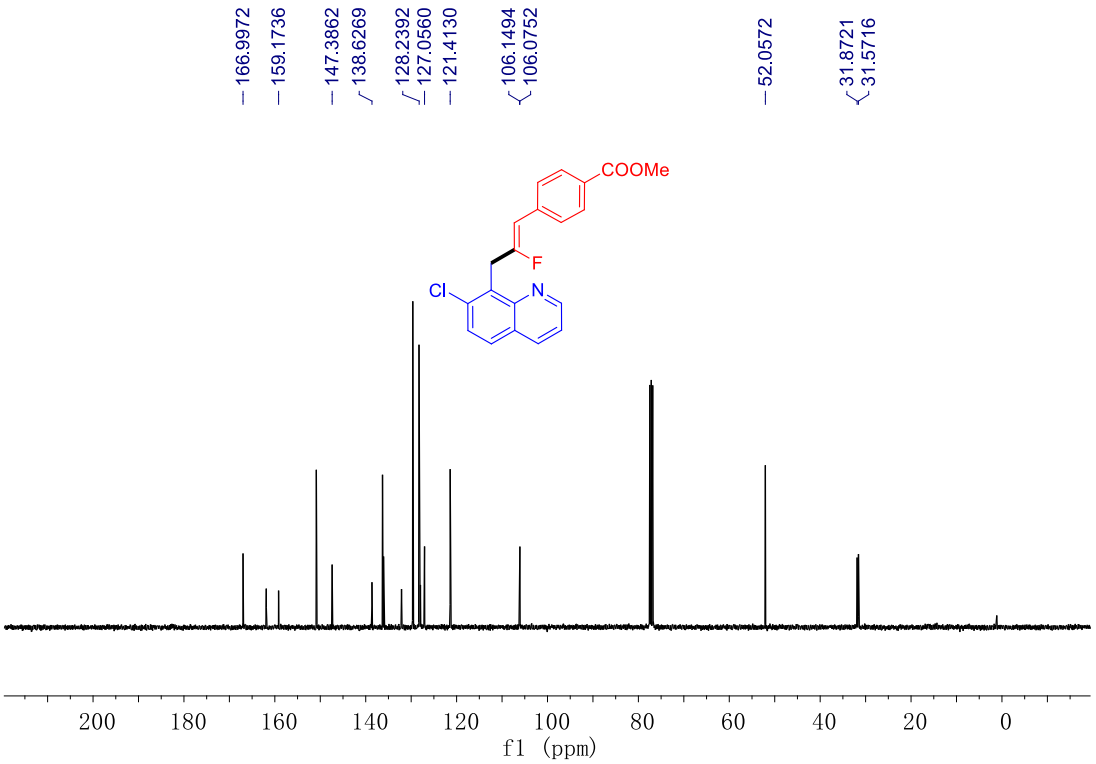
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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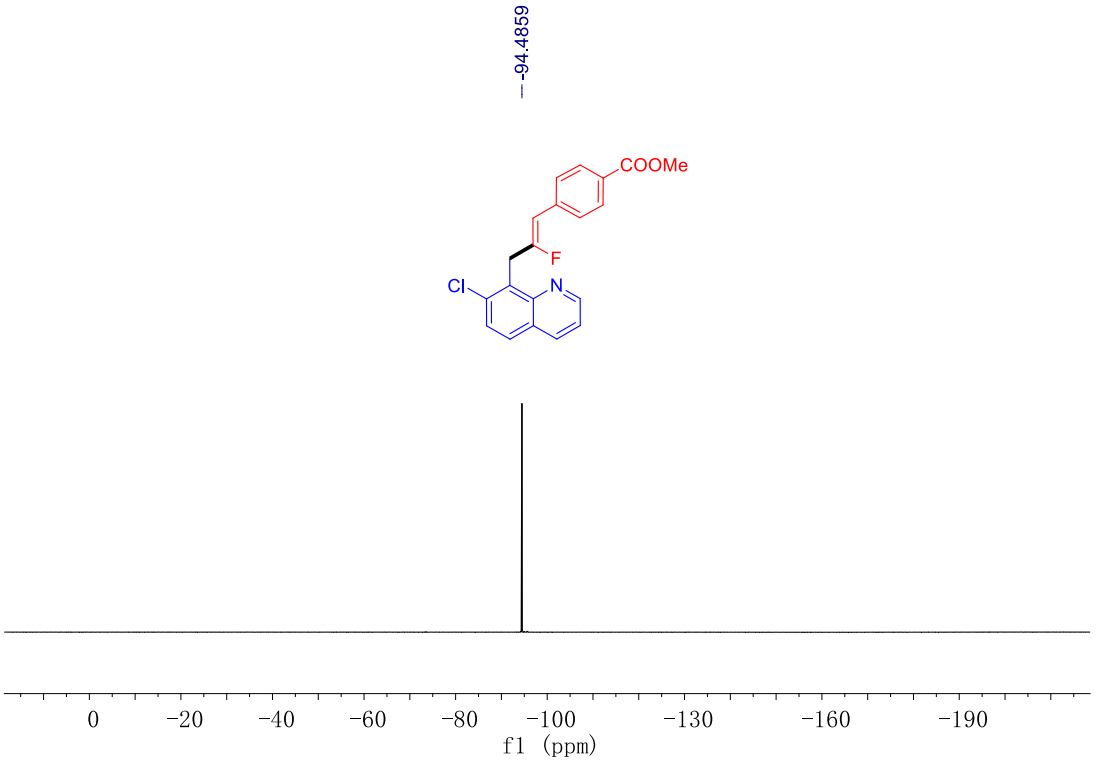
147.3862
138.6269
128.2392
127.0560
121.4130
106.1494
106.0752
52.0572
31.8721
31.5716
COOMe
F
Cl
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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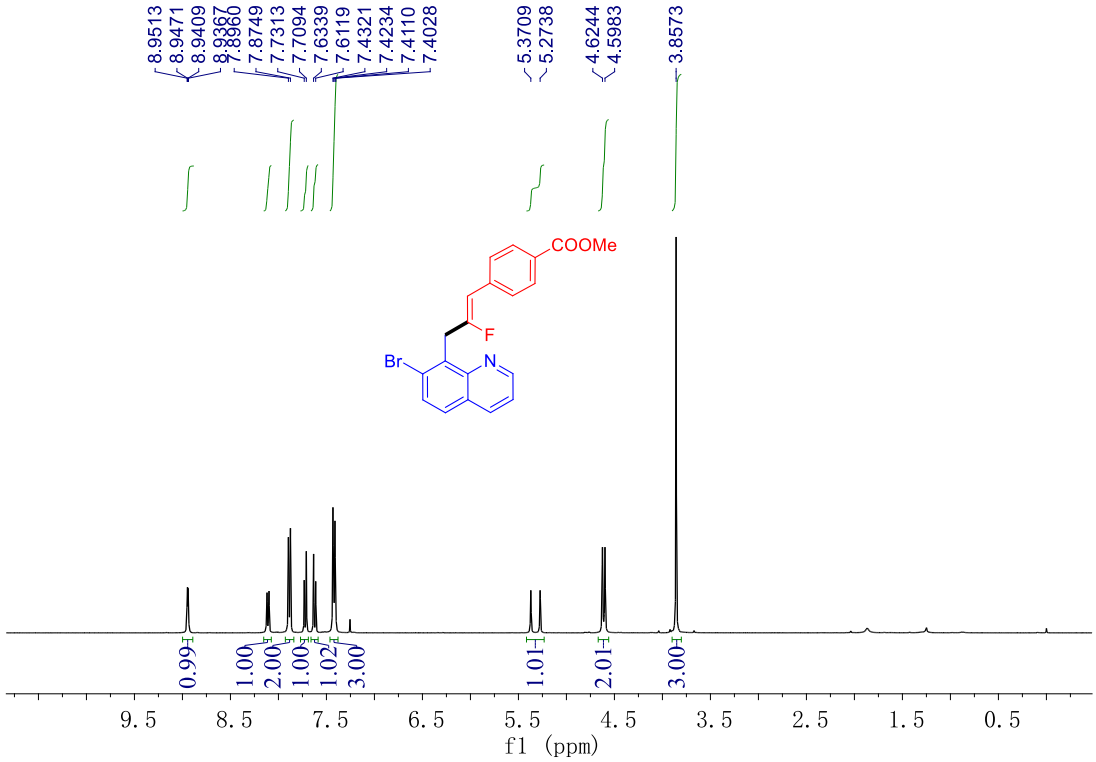
-60
-80
-100
-130
-160
-190
f1 (ppm)

3oa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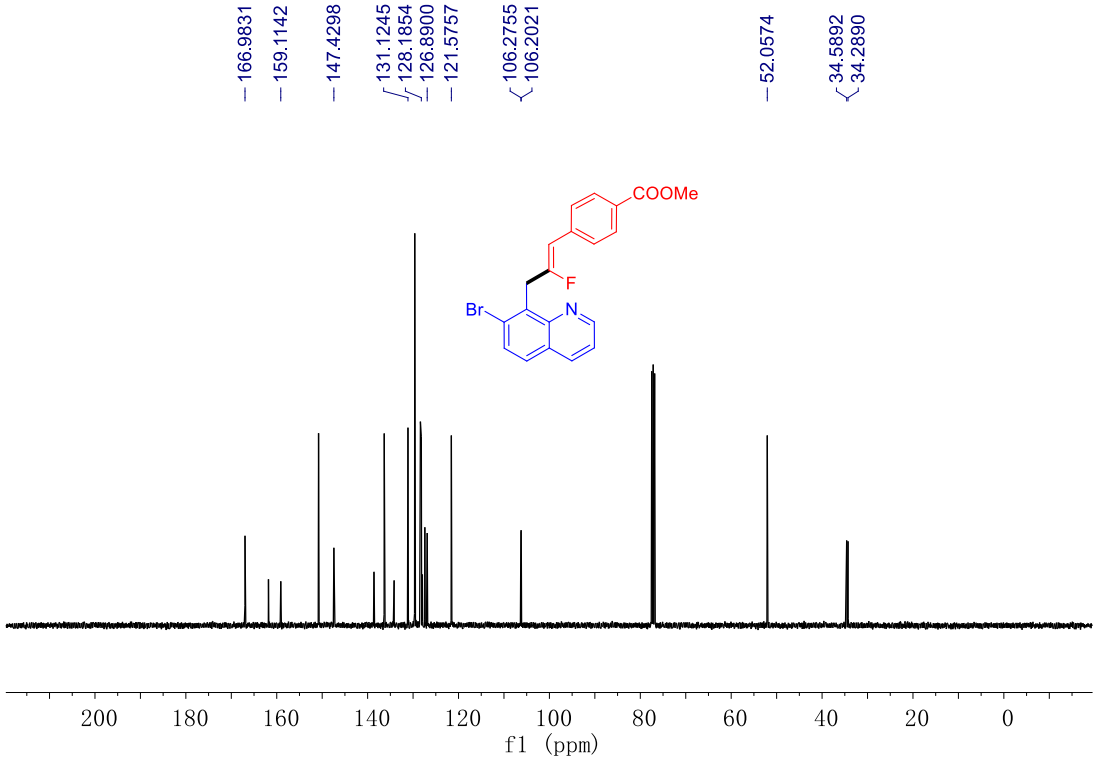
8.9471
8.9409
7.8960
7.8749
7.7313
7.7094
7.6339
7.6119
7.4321
7.4234
7.4110
7.4028
5.3709
5.2738
4.6244
4.5983
3.8573
COOMe
F
Br
N
0.99
1.00
2.00
1.00
1.02
3.00
1.01
2.01
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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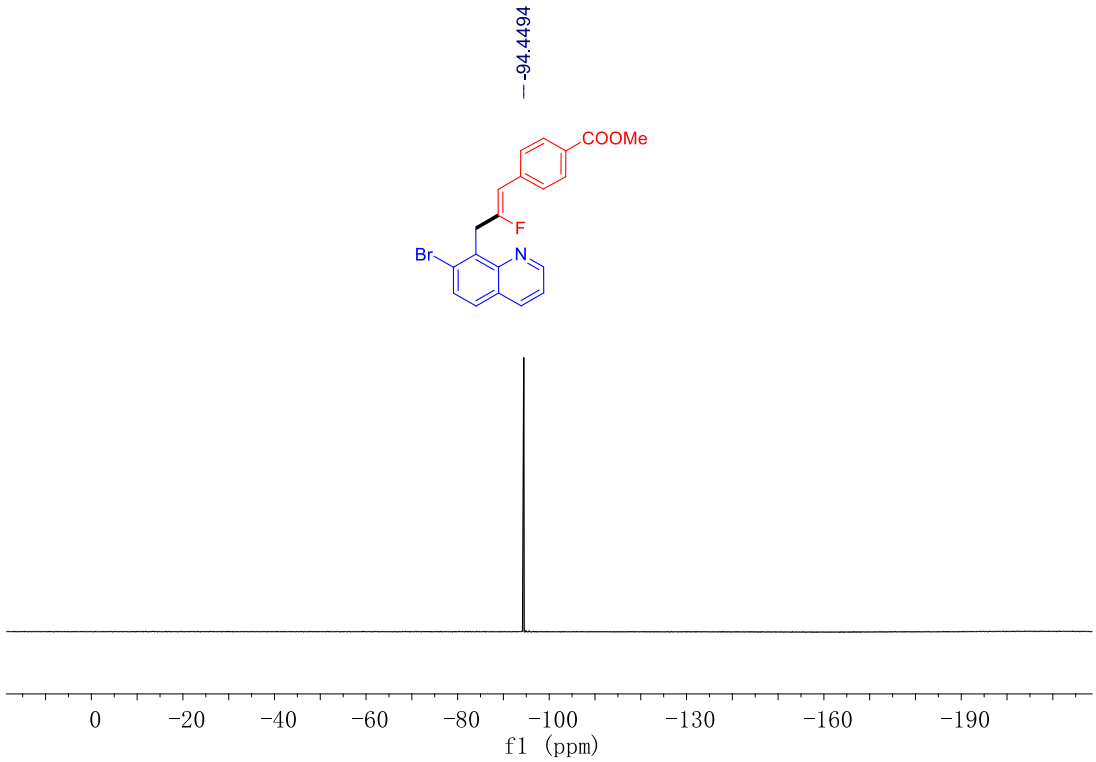
159.1142
147.4298
131.1245
128.1854
126.8900
121.5757
106.2755
106.2021
52.0574
34.5892
34.2890
COOMe
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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COOMe
F
Br
N
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-20
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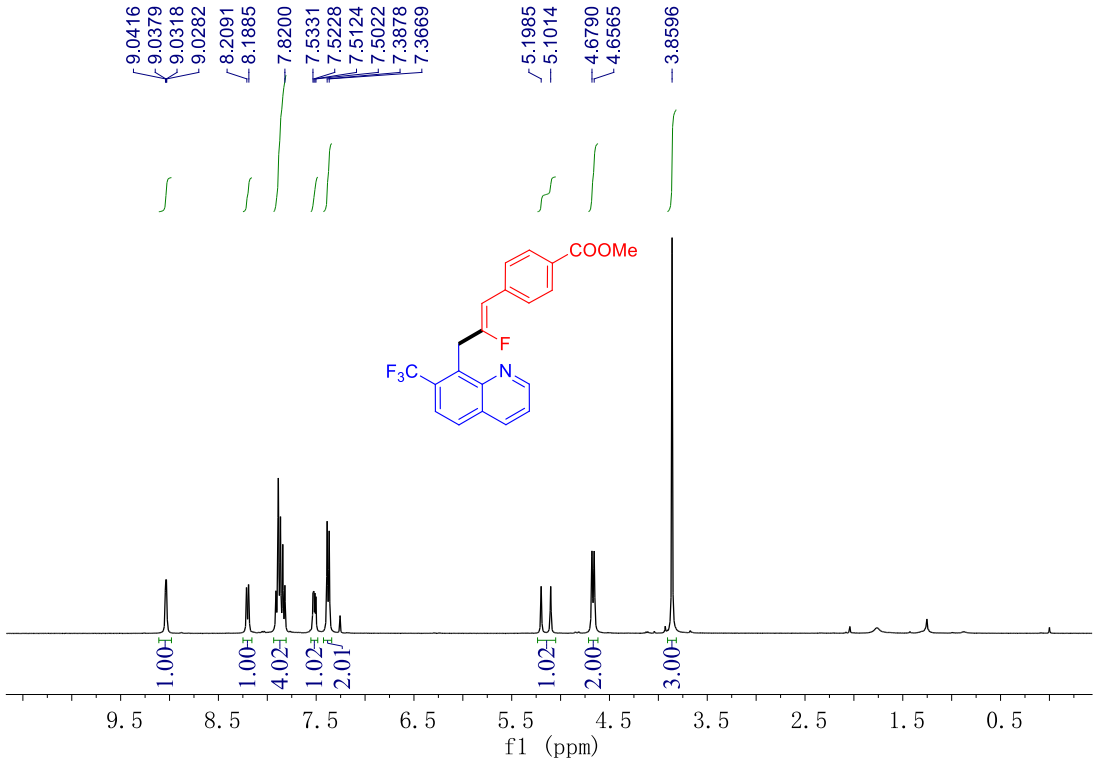
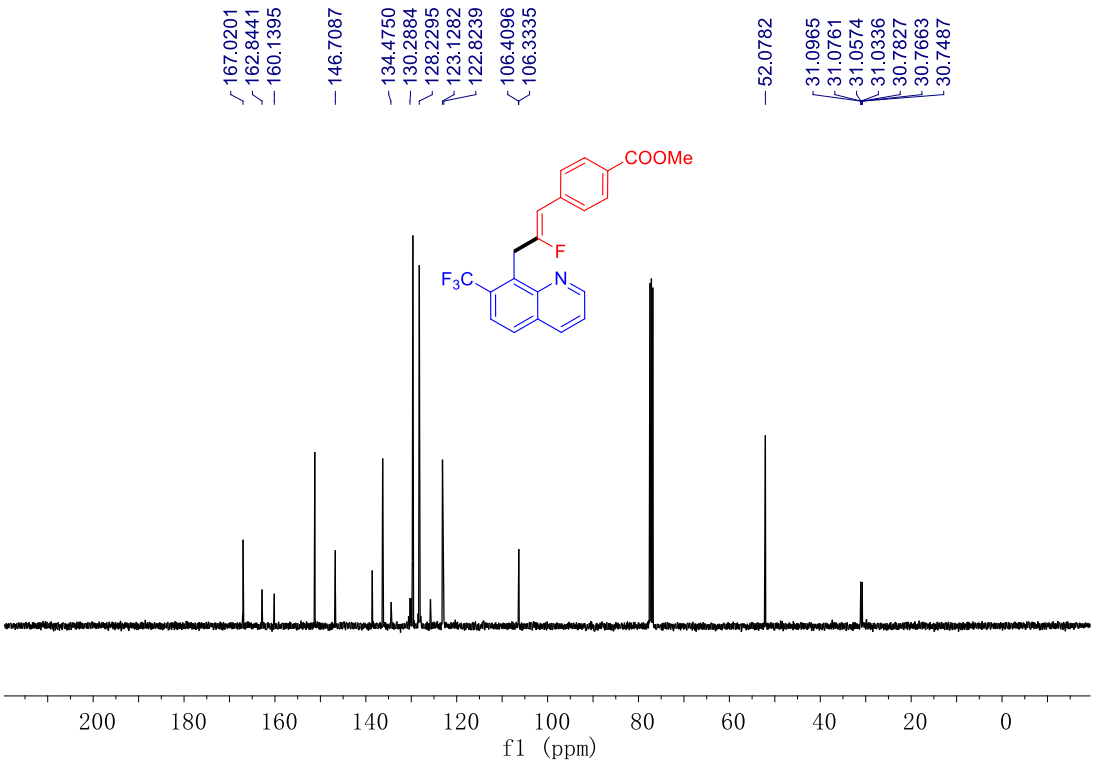
-60
-80
-100
-130
-160
-190
f1 (ppm)

3pa


9.0416
9.0379
9.0318
9.0282
8.2091
8.1885
7.8200
7.5331
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
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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160.1395
146.7087
134.4750
130.2884
128.2295
123.1282
122.8239
106.4096
106.3335
52.0782
31.0965
31.0761
31.0574
31.0336
30.7827
30.7663
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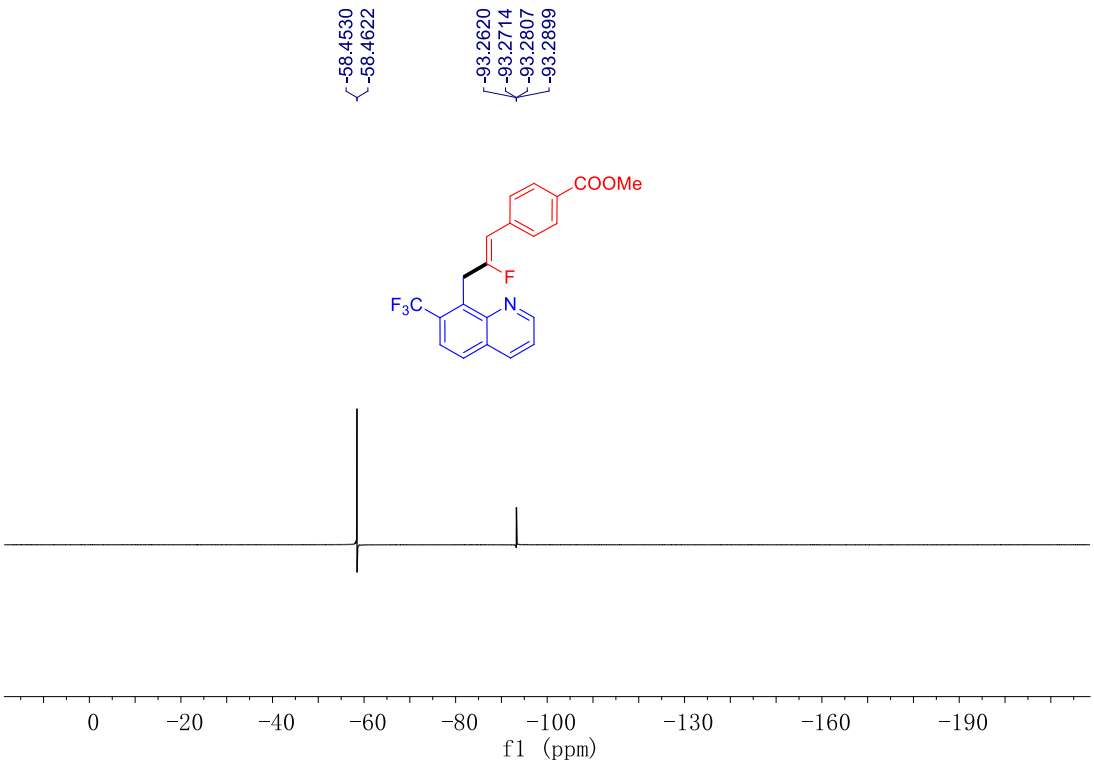
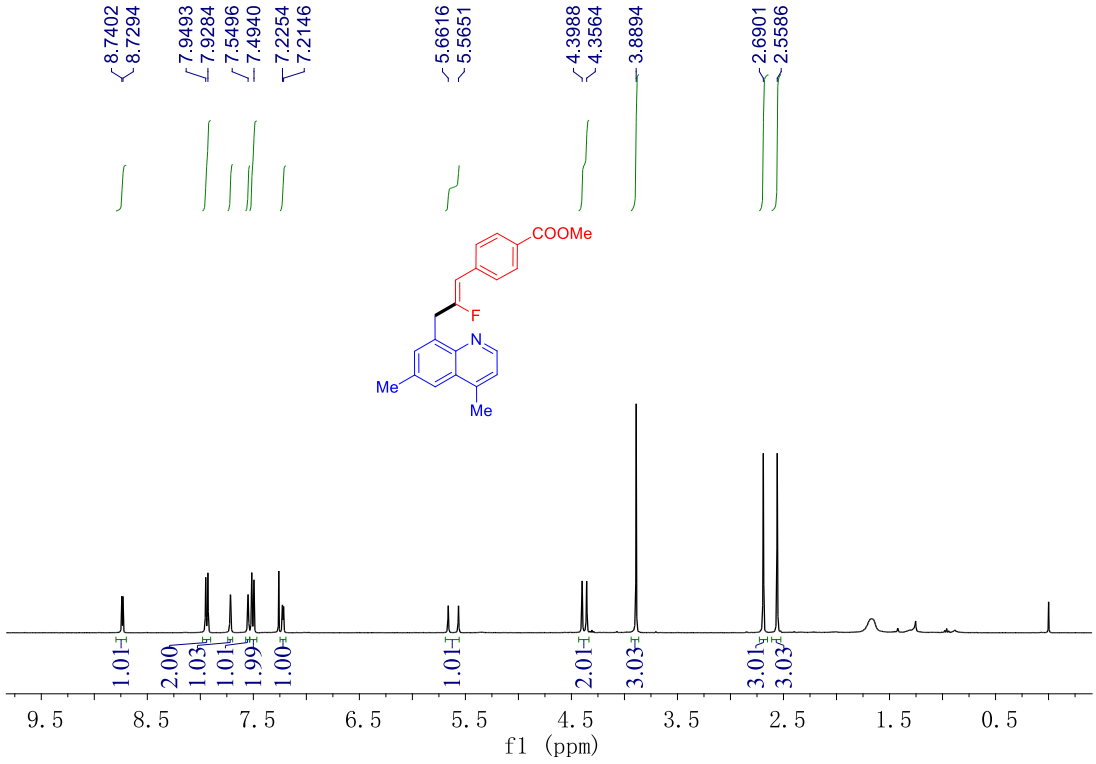
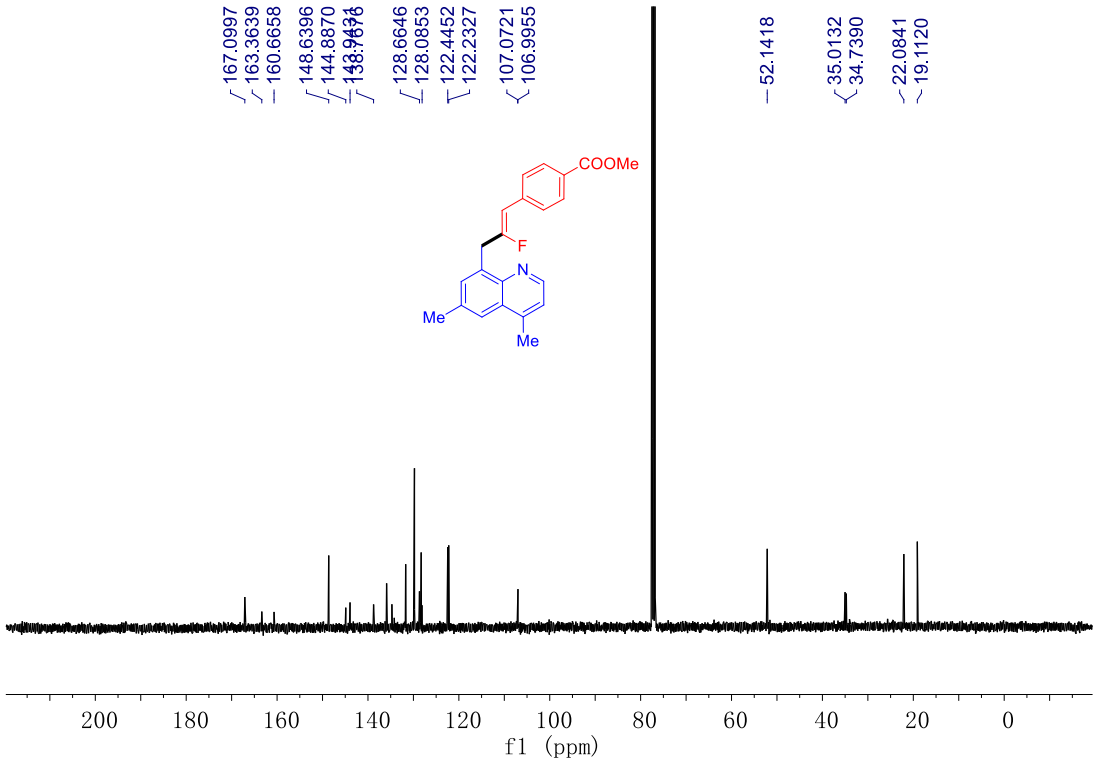
COOMe
F
F3C
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-58.4530
-58.4622
-93.2620
-93.2714
-93.2807
-93.2899
COOMe
F
F3C
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3qa


8.7402
8.7294
7.9493
7.9284
7.5496
7.4940
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
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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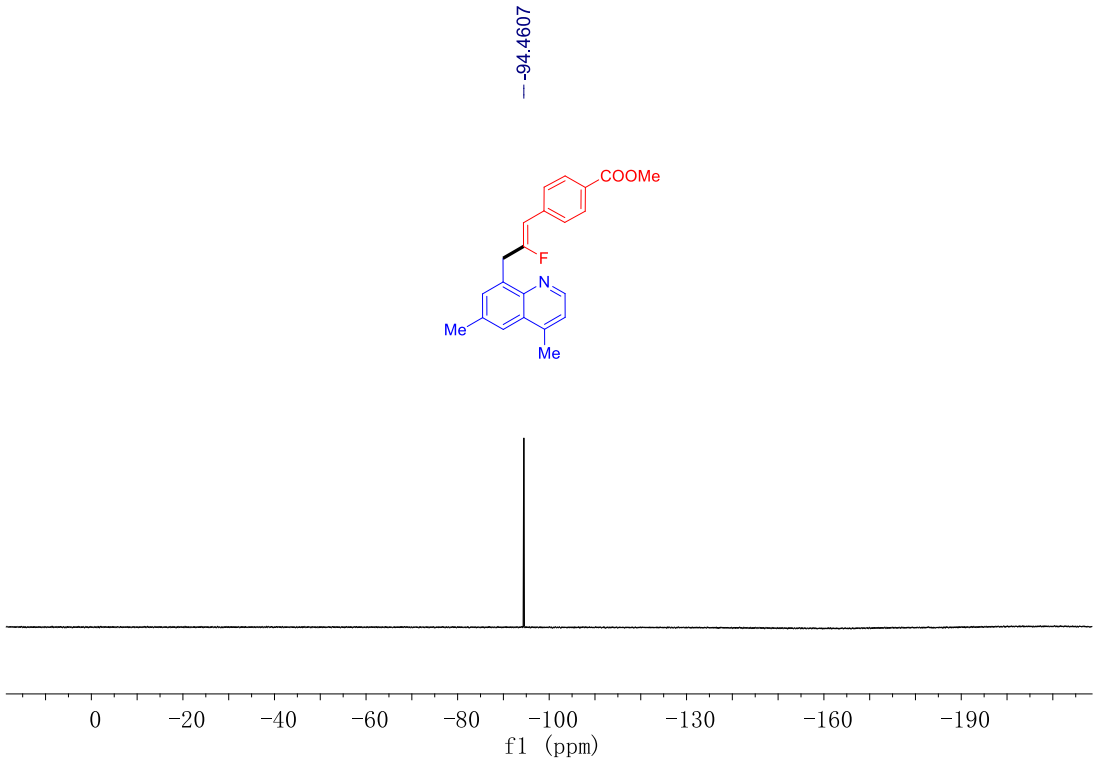
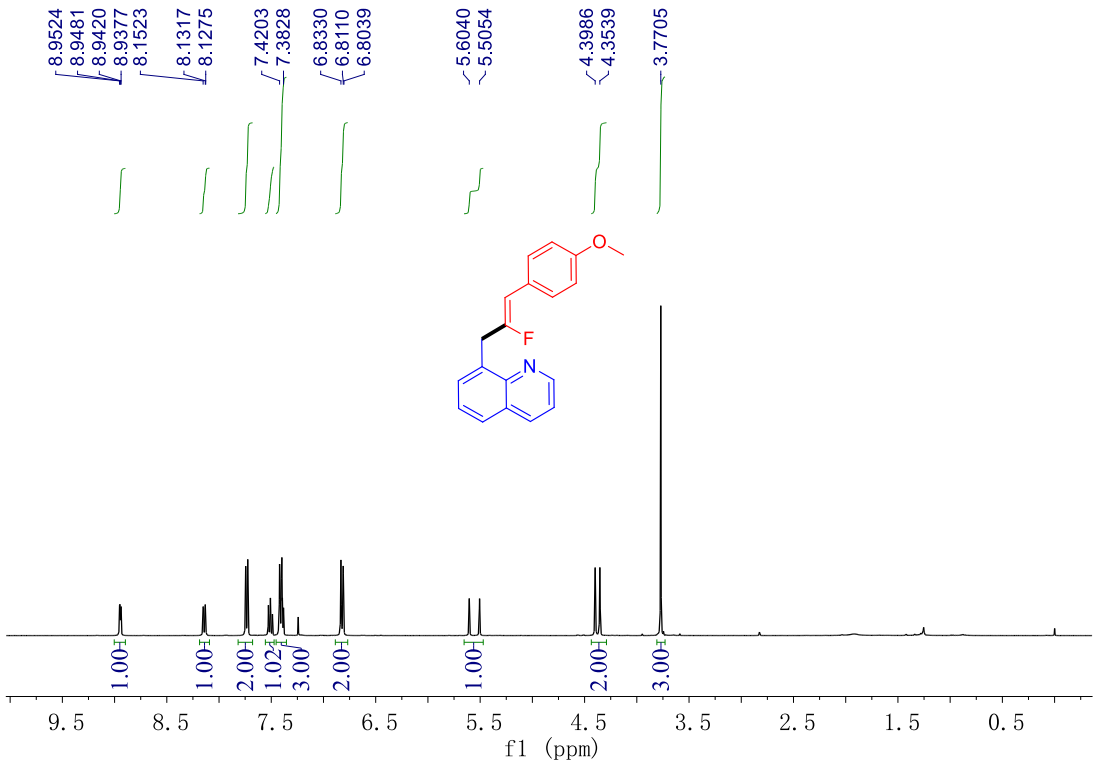
160.6658
148.6396
144.8870
128.6646
128.0853
122.4452
122.2327
107.0721
106.9955
52.1418
35.0132
34.7390
22.0841
19.1120
COOMe
F
N
Me
Me
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


-94.4607
COOMe
F
N
Me
Me
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ab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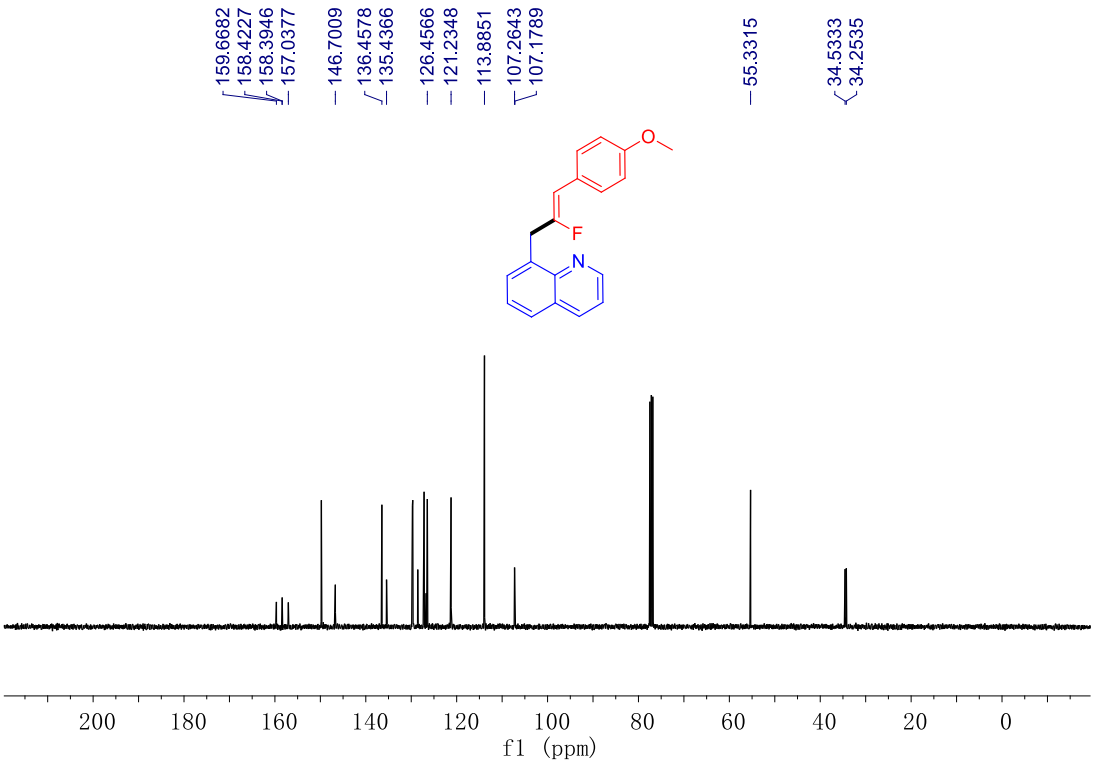
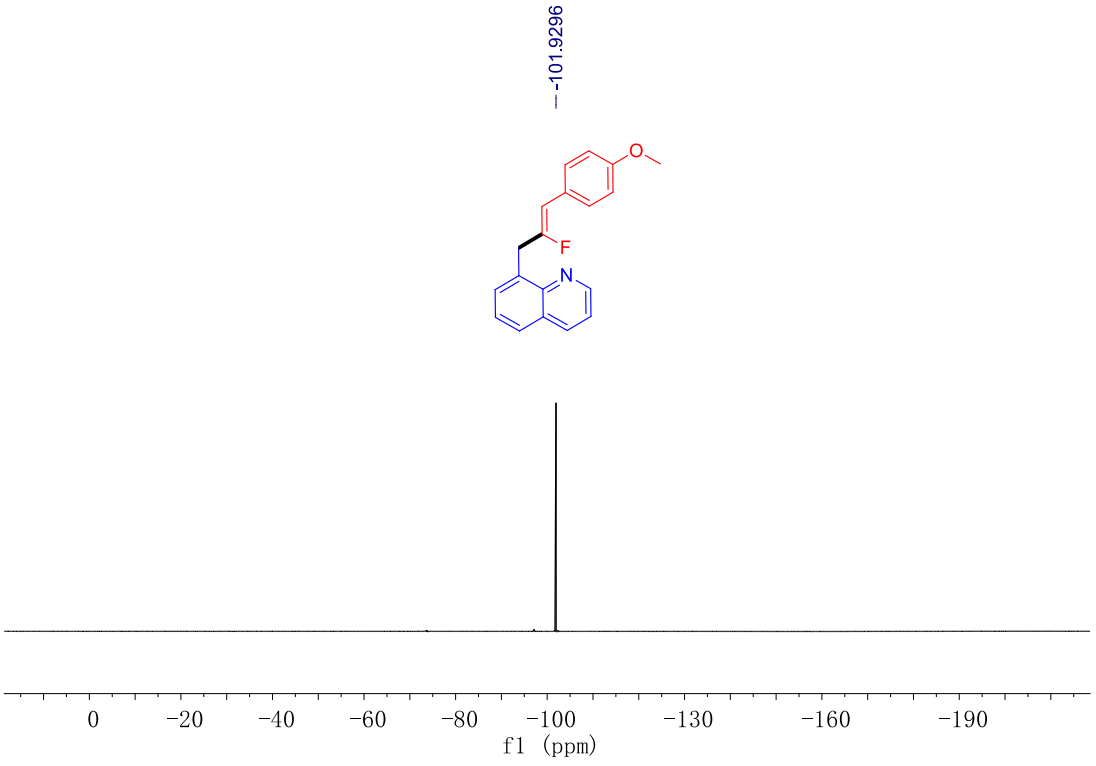
8.9420
8.9377
8.1523
8.1317
8.1275
7.4203
7.3828
6.8330
6.8110
6.8039
5.6040
5.5054
4.3986
4.3539
3.7705
O
F
N
1.00
1.00
2.00
1.02
3.00
2.00
1.00
2.00
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


159.6682
158.4227
158.3946
157.0377
146.7009
136.4578
135.4366
126.4566
121.2348
113.8851
107.2643
107.1789
55.3315
34.5333
34.2535
O
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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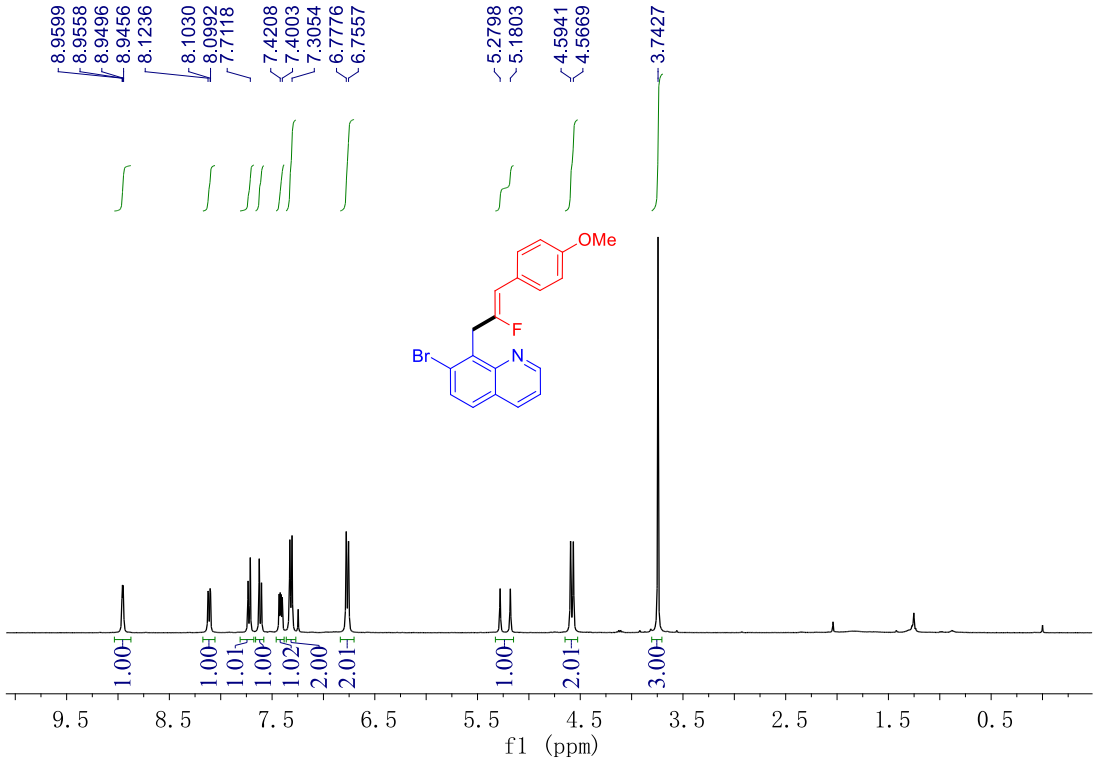
O
F
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ob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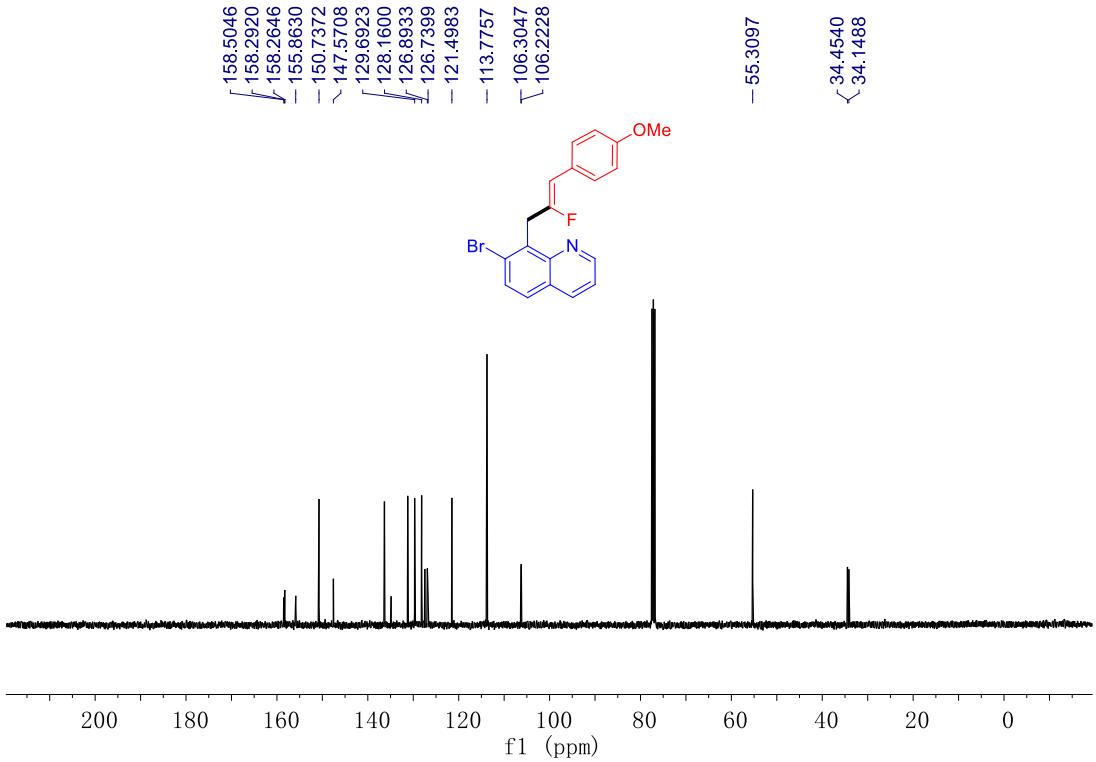
8.9558
8.9496
8.9456
8.1236
8.1030
8.0992
7.7118
7.4208
7.4003
7.3054
6.7776
6.7557
5.2798
5.1803
4.5941
4.5669
3.7427
OMe
F
Br
N
1.00
1.00
1.01
1.00
1.02
2.00
2.01
1.00
2.01
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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129.6923
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126.8933
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113.7757
106.3047
106.2228
55.3097
34.4540
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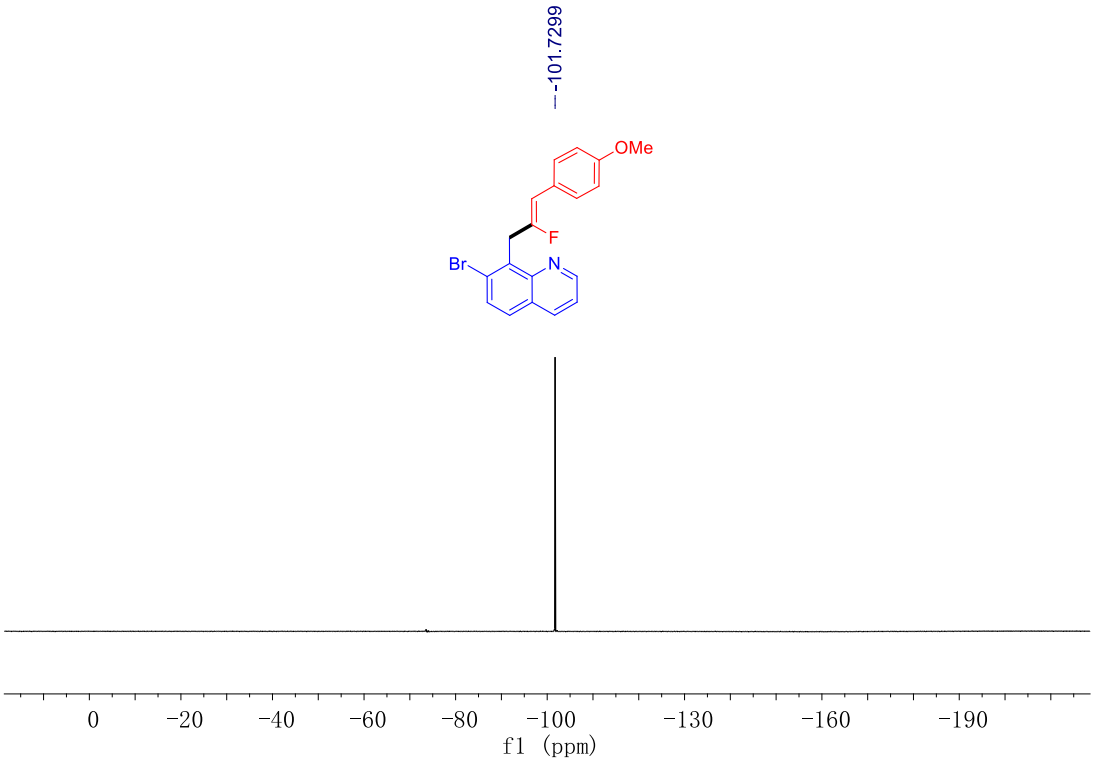
OMe
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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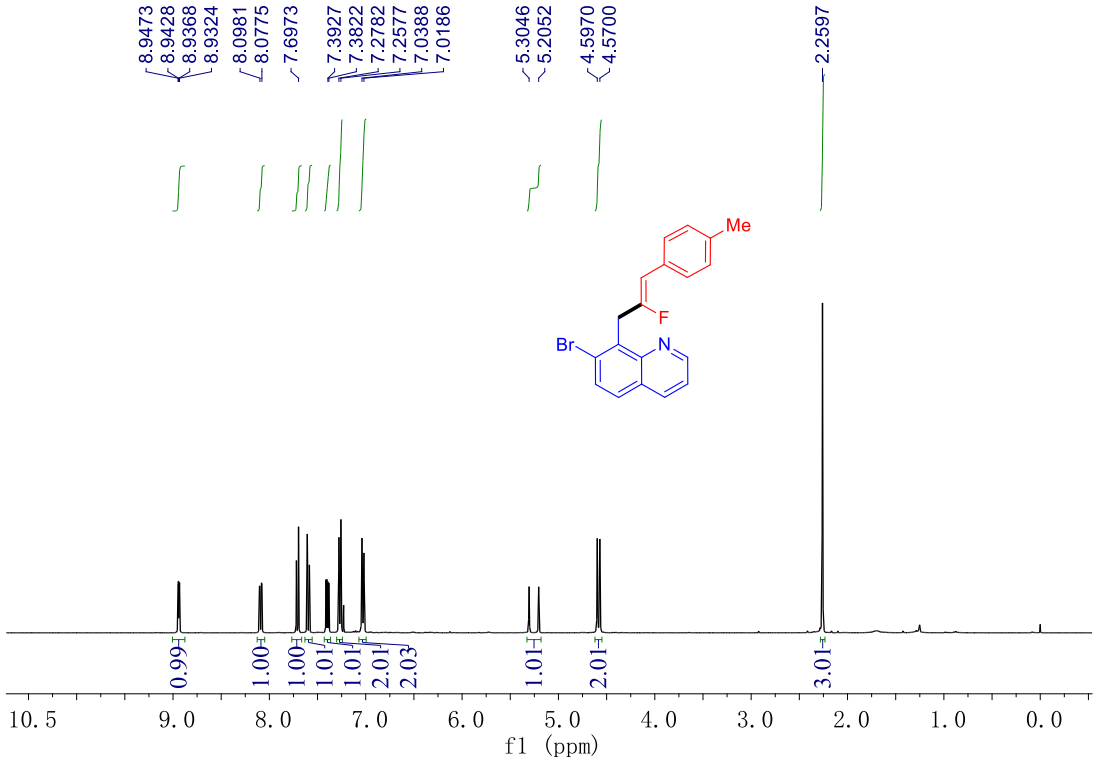
OMe
F
Br
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3oc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8.9368
8.9324
8.0981
8.0775
7.6973
7.3927
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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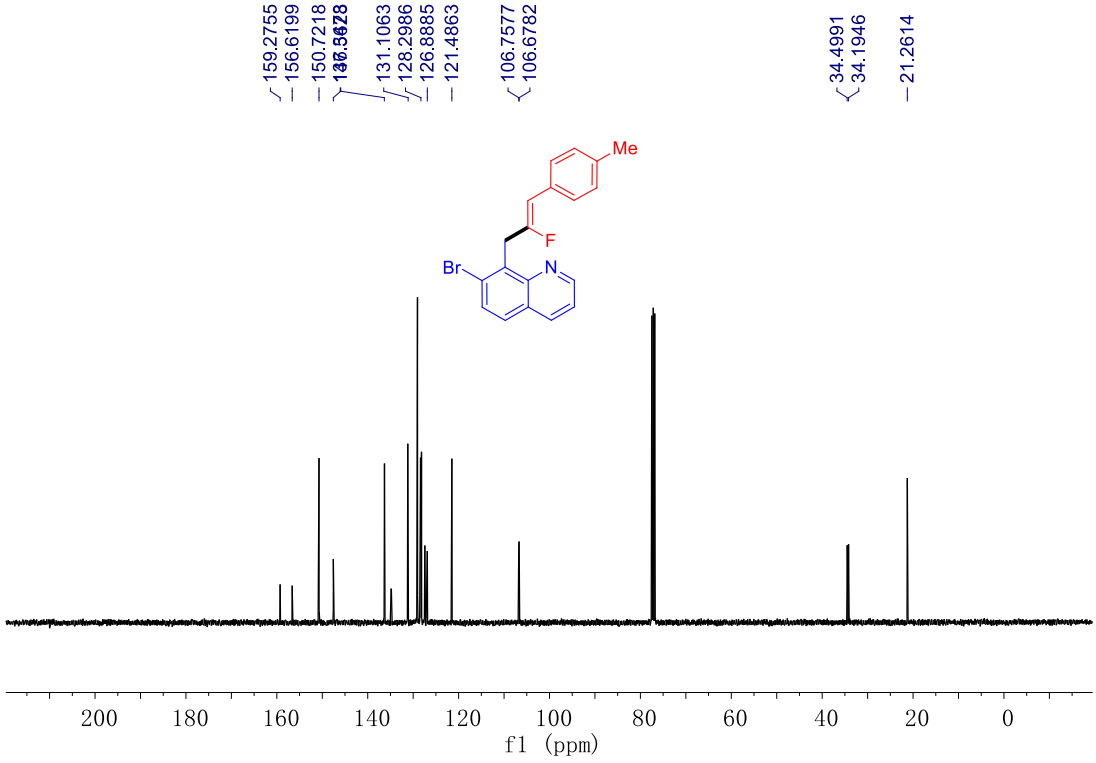
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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131.1063
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121.4863
106.7577
106.6782
34.4991
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Me
F
Br
N
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140
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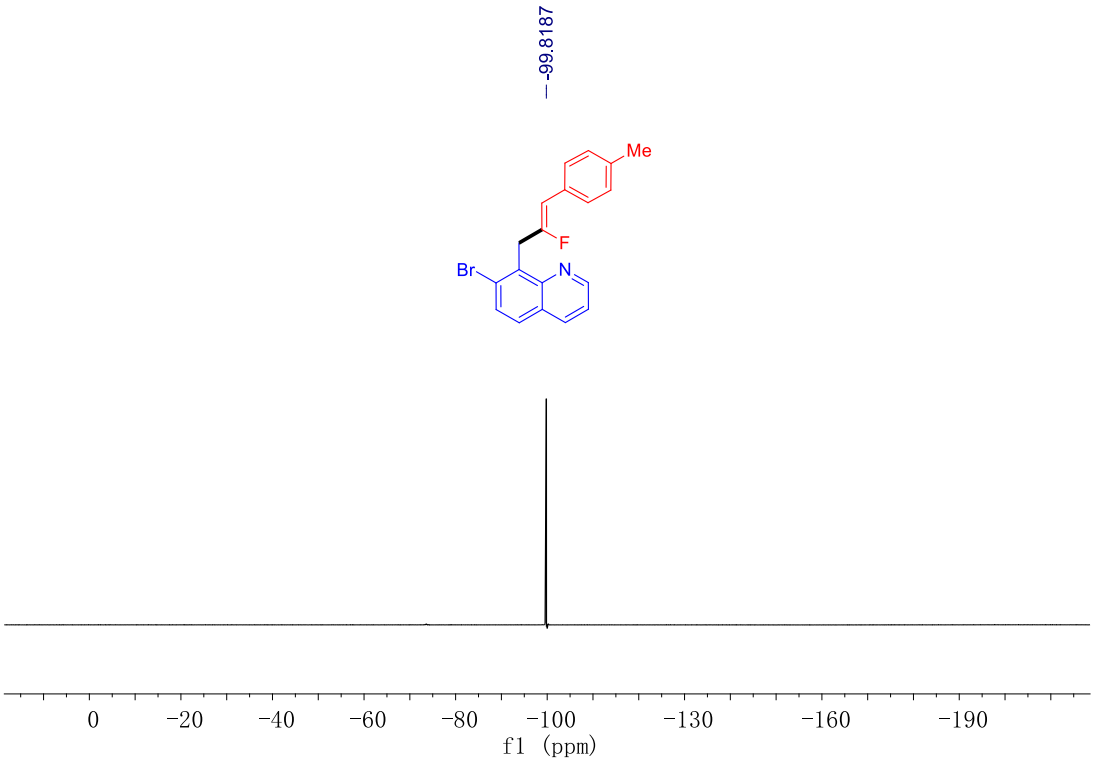
100
80
60
40
20
0
f1 (ppm)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F
Br
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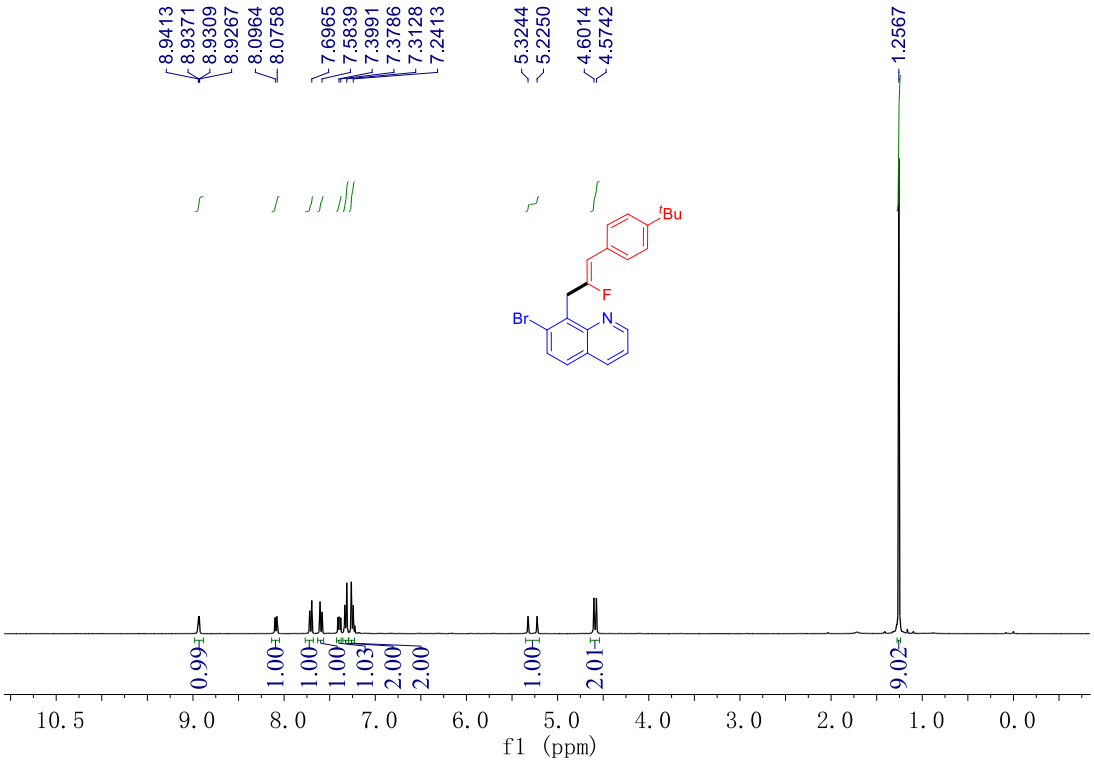
-80
-100
-130
-160
-190
f1 (ppm)

3od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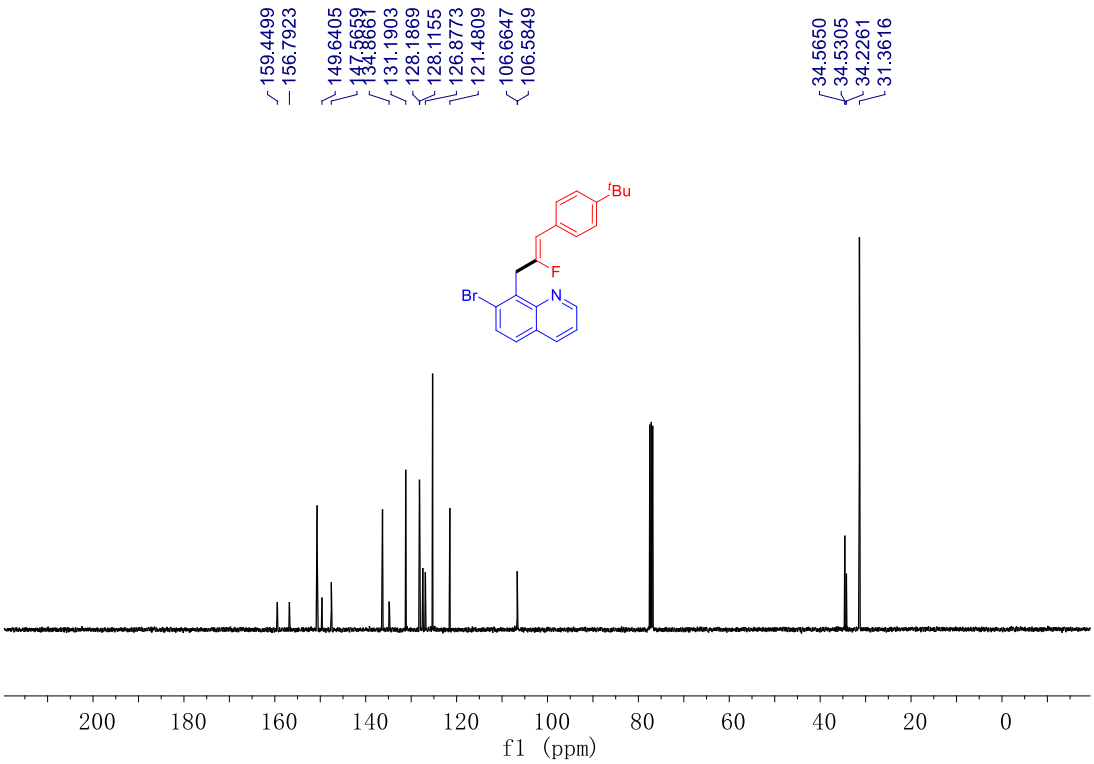
8.9309
8.9267
8.0964
8.0758
7.6965
7.5839
7.3991
7.3786
7.3128
7.2413
5.3244
5.2250
4.6014
4.5742
1.2567
tBu
F
Br
N
0.99
1.00
1.00
1.00
1.03
2.00
2.00
1.00
2.01
9.02
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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128.1869
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126.8773
121.4809
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106.5849
34.5650
34.5305
34.2261
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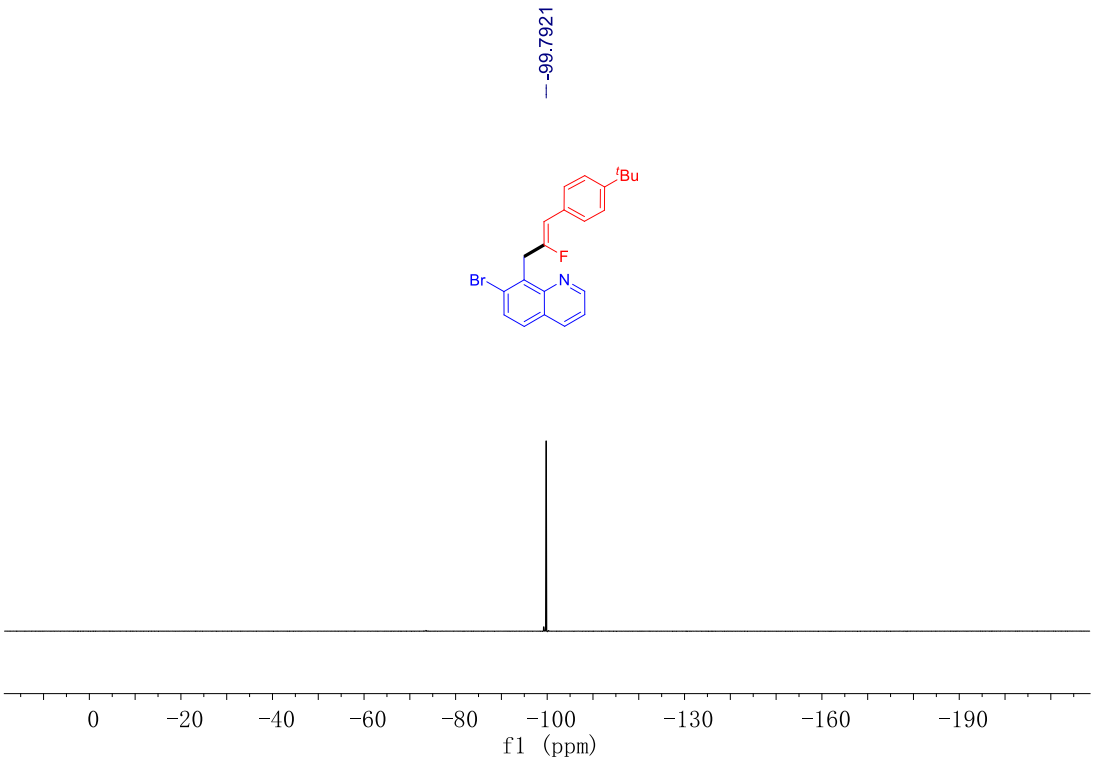
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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F
Br
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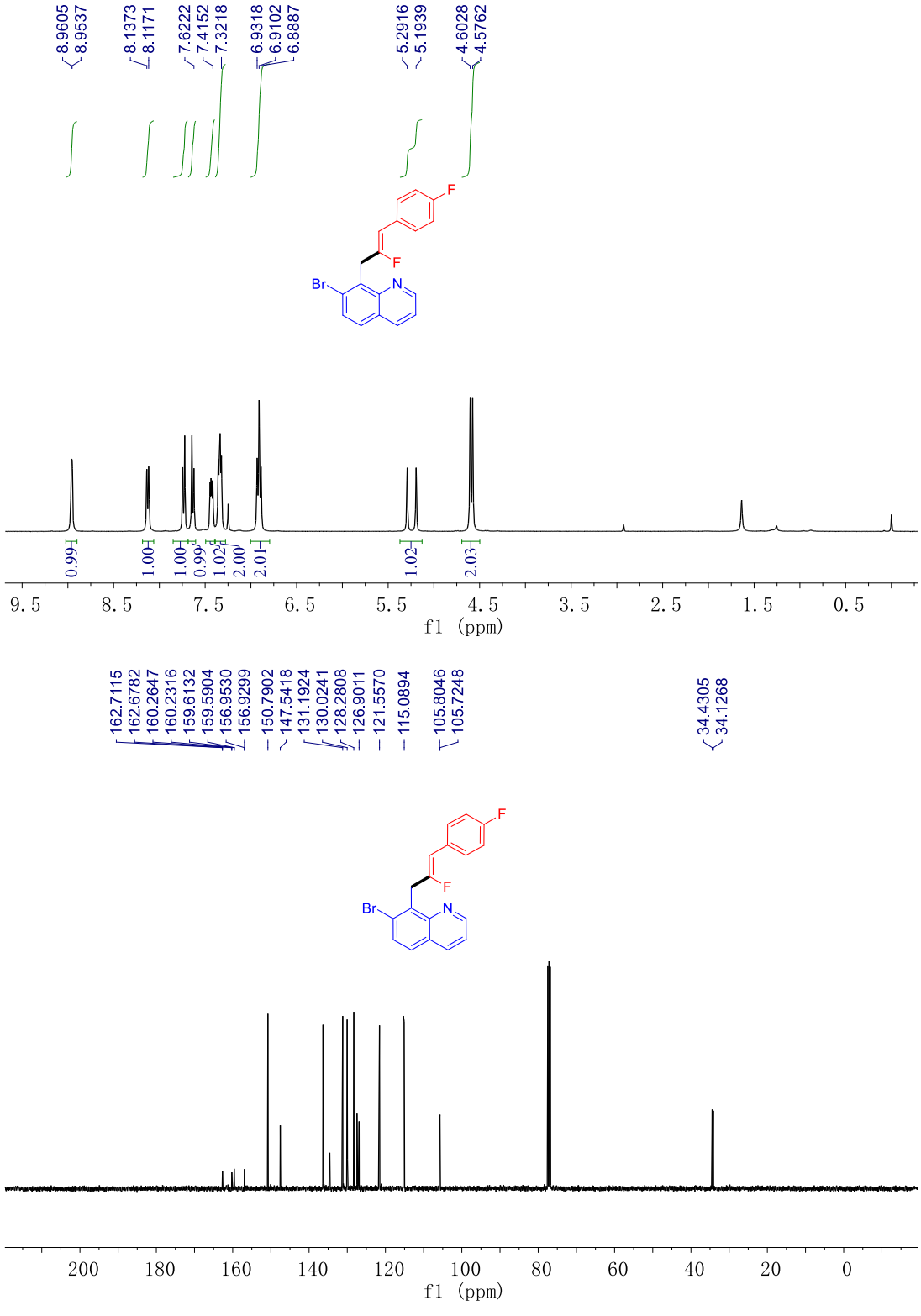
-60
-80
-100
-130
-160
-190
f1 (ppm)

3oe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7.3218
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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
2.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)
162.7115
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160.2647
160.2316
159.6132
159.5904
156.9530
156.9299
150.7902
147.5418
131.1924
130.0241
128.2808
126.9011
121.5570
115.0894
105.8046
105.7248
34.4305
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F
Br
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140
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100
80
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20
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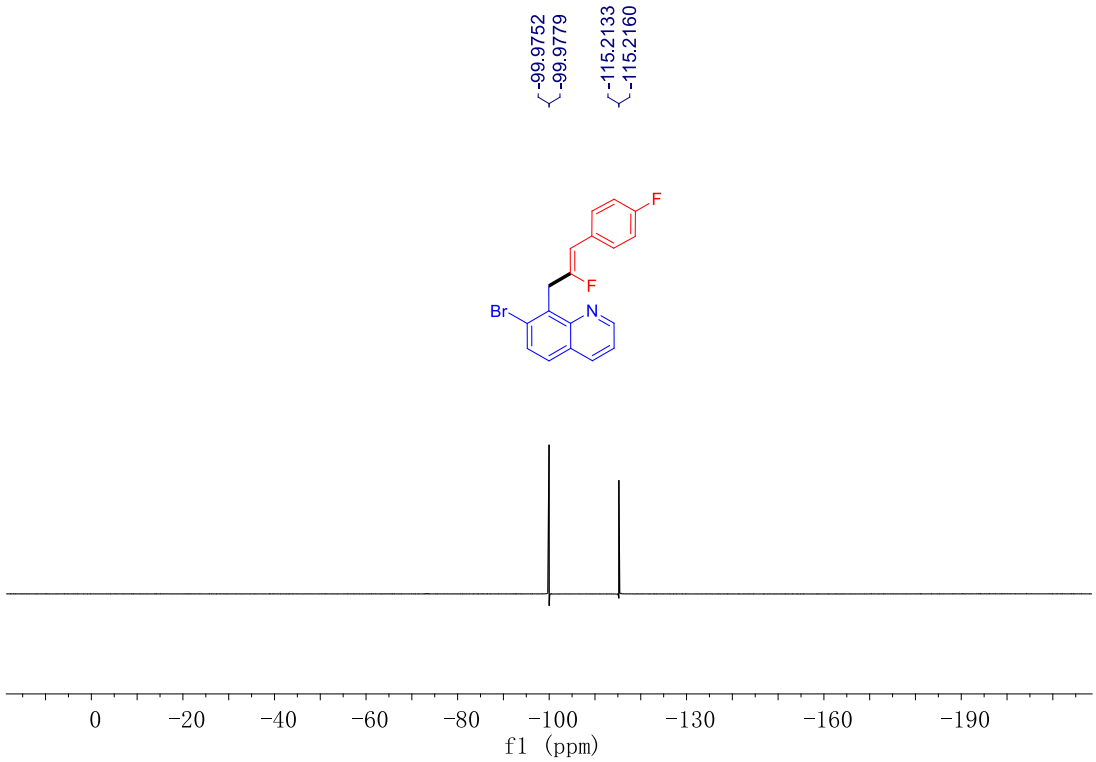
f1 (ppm)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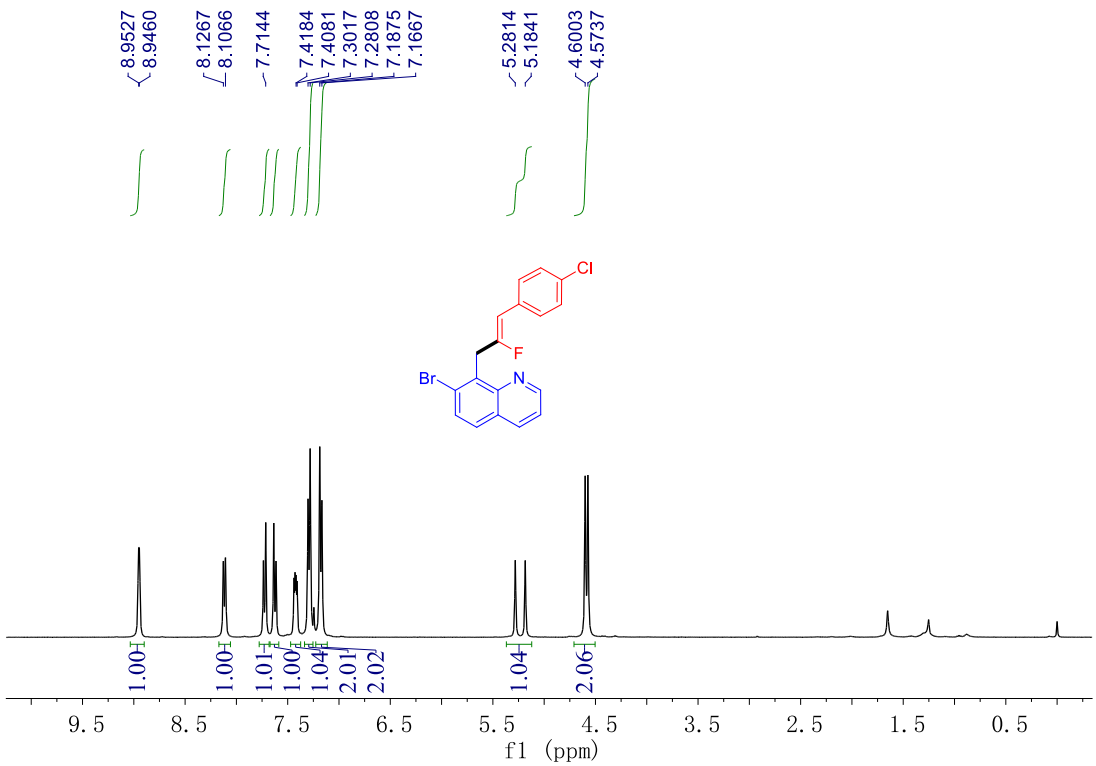
-115.2160
F
F
Br
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3of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8.1267
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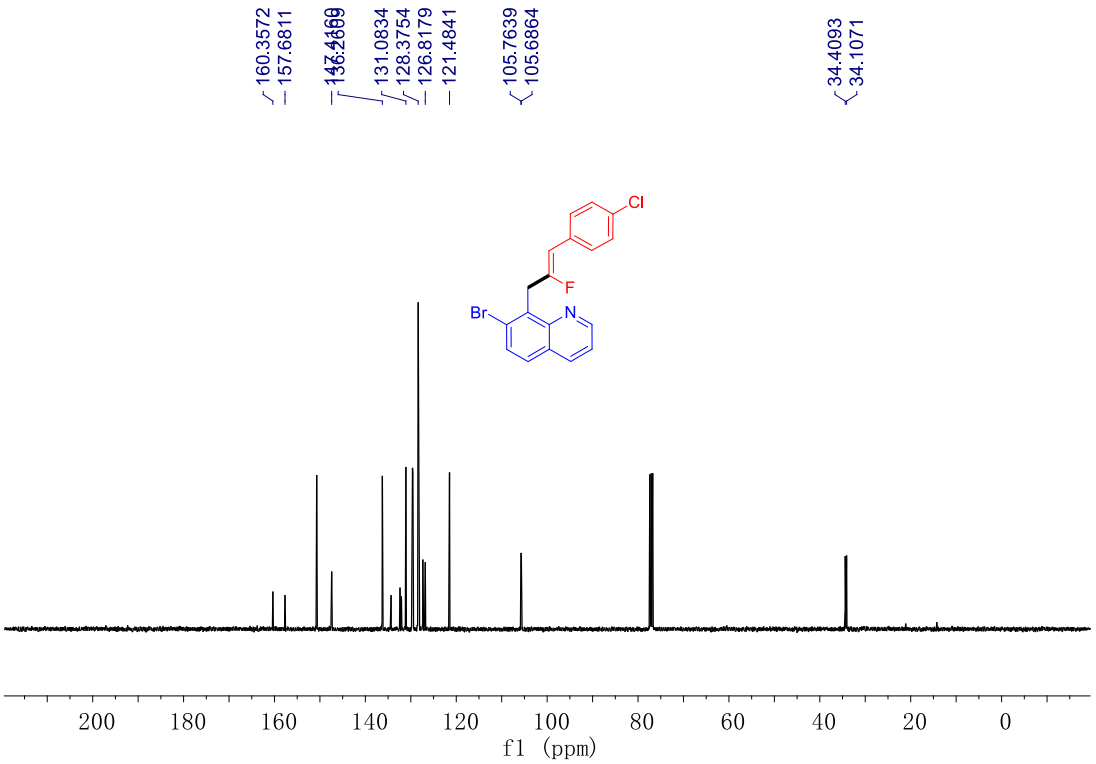
7.7144
7.4184
7.4081
7.3017
7.2808
7.1875
7.1667
5.2814
5.1841
4.6003
4.5737
Cl
F
Br
N
1.00
1.00
1.01
1.00
1.04
2.01
2.02
1.04
2.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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131.0834
128.3754
126.8179
121.4841
105.7639
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34.4093
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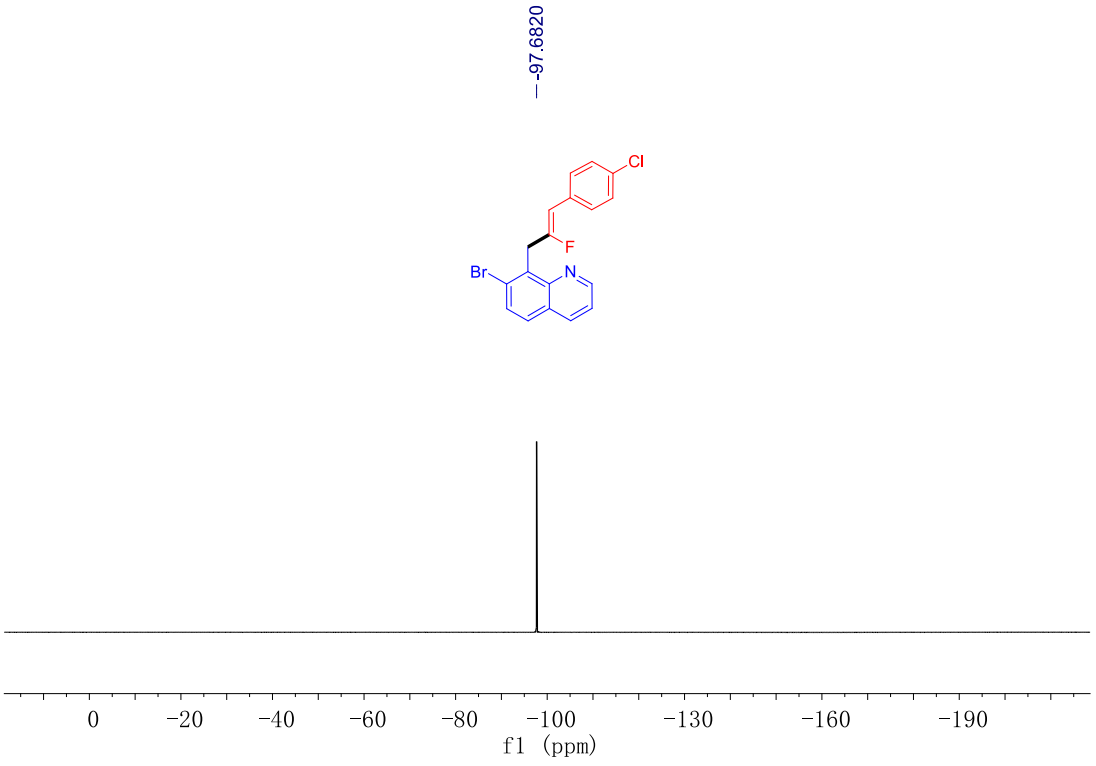
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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Br
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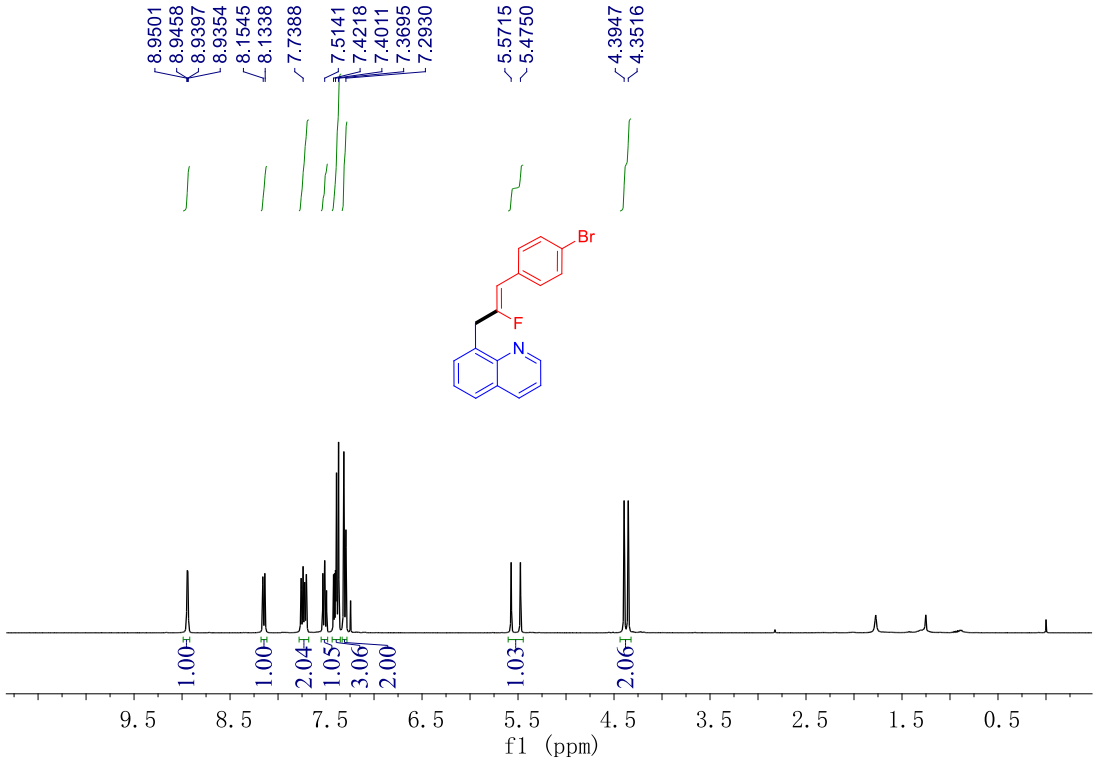
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ag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7.4218
7.4011
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
2.06
9.5
8.5
7.5
6.5
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4.5
3.5
2.5
1.5
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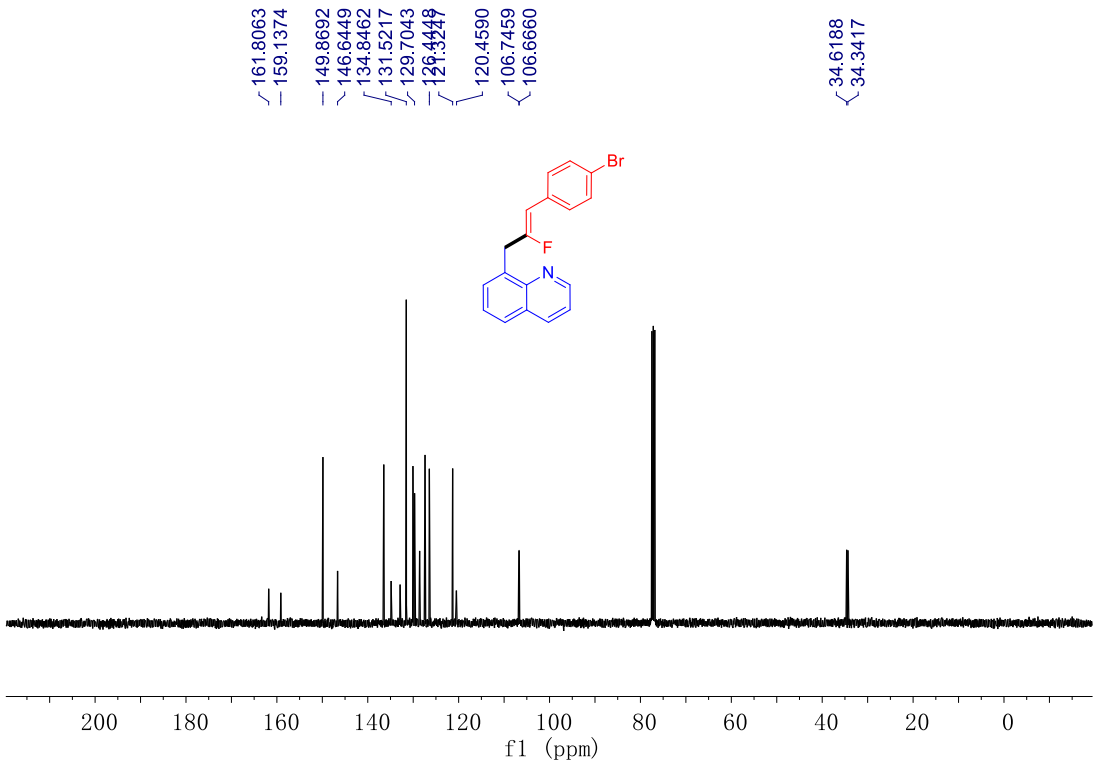
f1 (ppm)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134.8462
131.5217
129.7043
120.4590
106.7459
106.6660
34.6188
34.3417
Br
F
N
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180
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140
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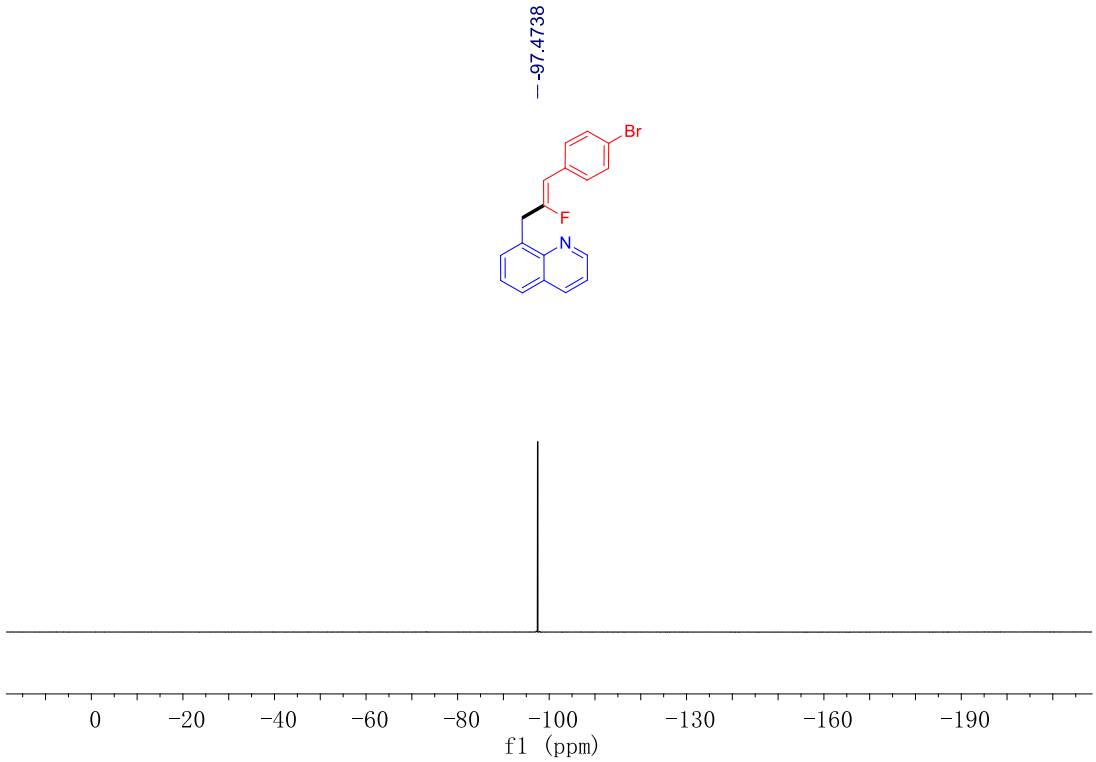
100
80
60
40
20
0
f1 (ppm)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-80
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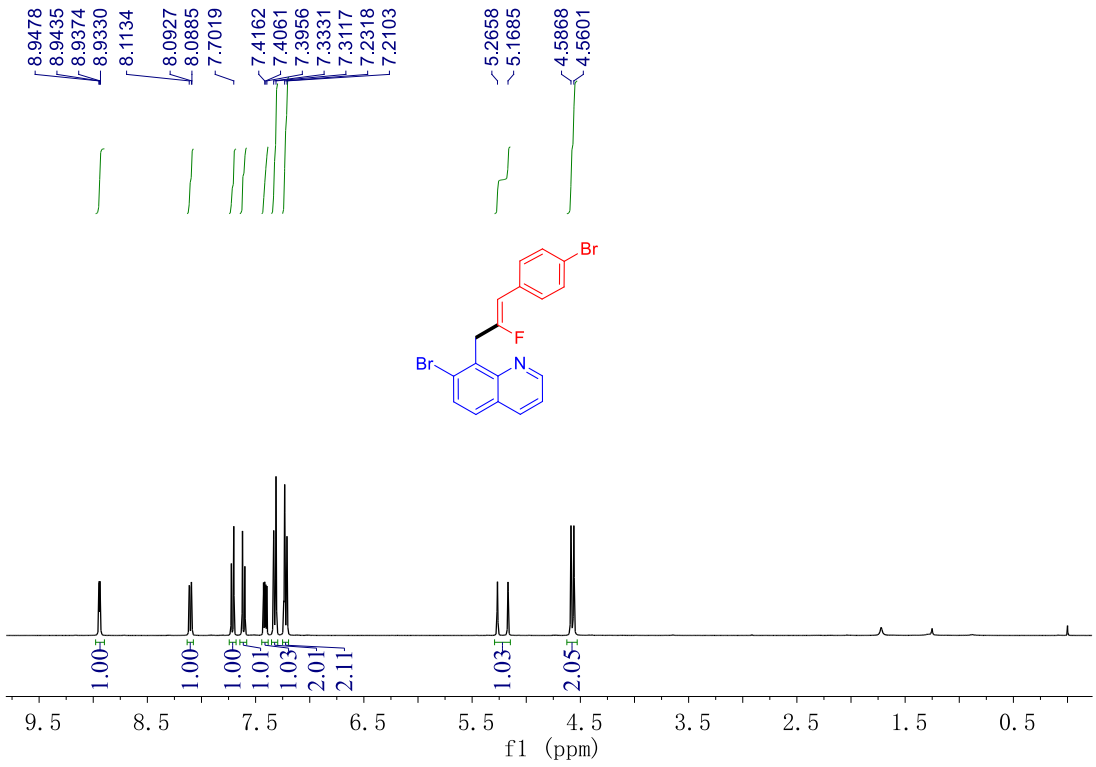
-190
f1 (ppm)

3og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8.9374
8.9330
8.1134
8.0927
8.0885
7.7019
7.4162
7.4061
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
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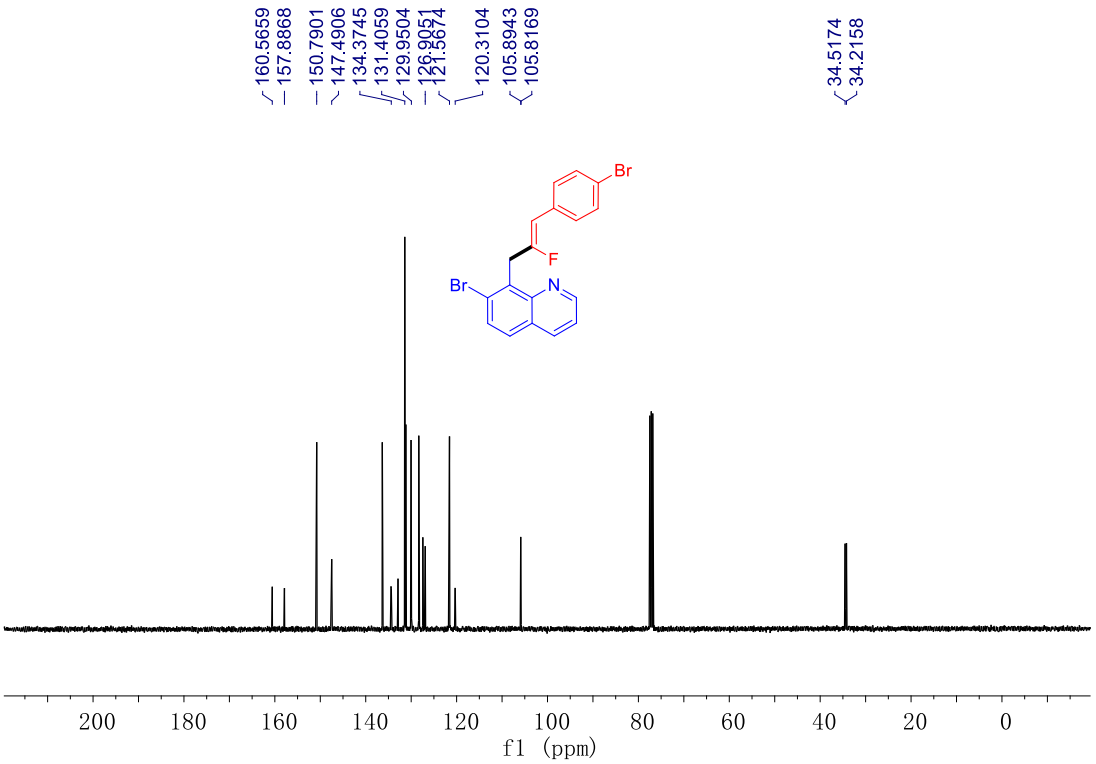
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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134.3745
131.4059
129.9504
126.9051
121.5674
120.3104
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105.8169
34.5174
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F
Br
N
200
180
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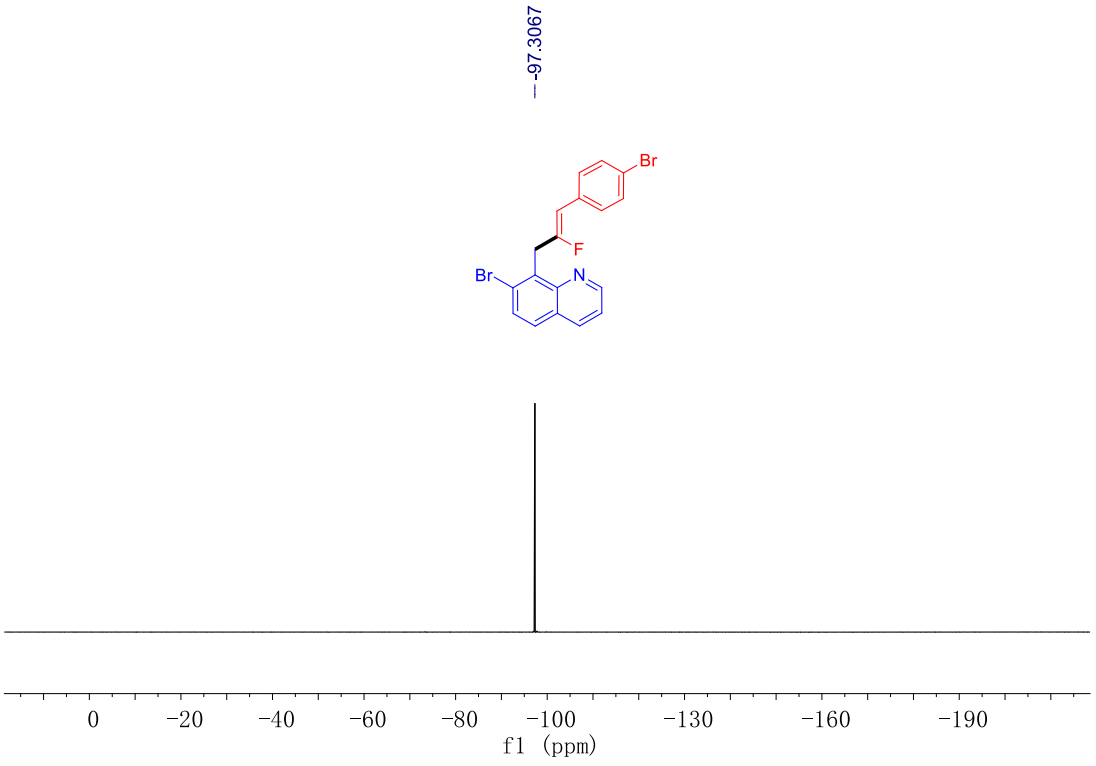
140
120
100
80
60
40
20
0
f1 (ppm)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Br
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-60
-80
-100
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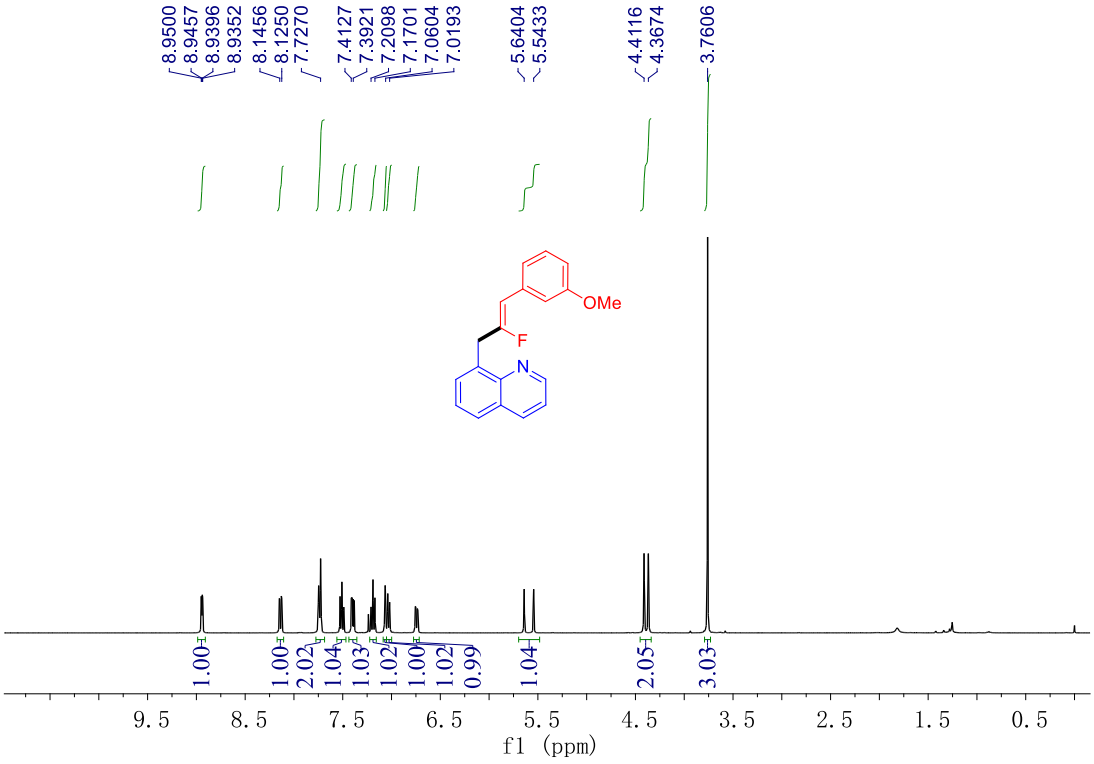
-190
f1 (ppm)

3ah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8.9396
8.9352
8.1456
8.1250
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
N
1.00
1.00
2.02
1.04
1.03
1.02
1.00
1.02
0.99
1.04
2.05
3.03
9.5
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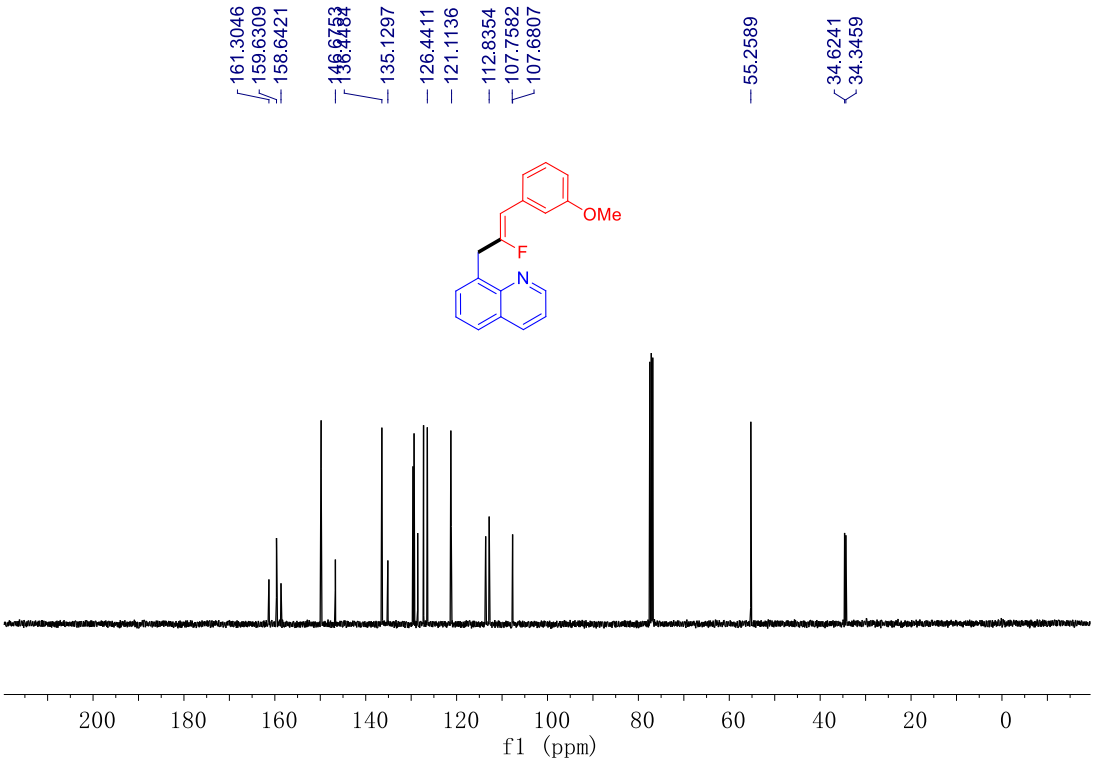
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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158.6421
135.1297
126.4411
121.1136
112.8354
107.7582
107.6807
55.2589
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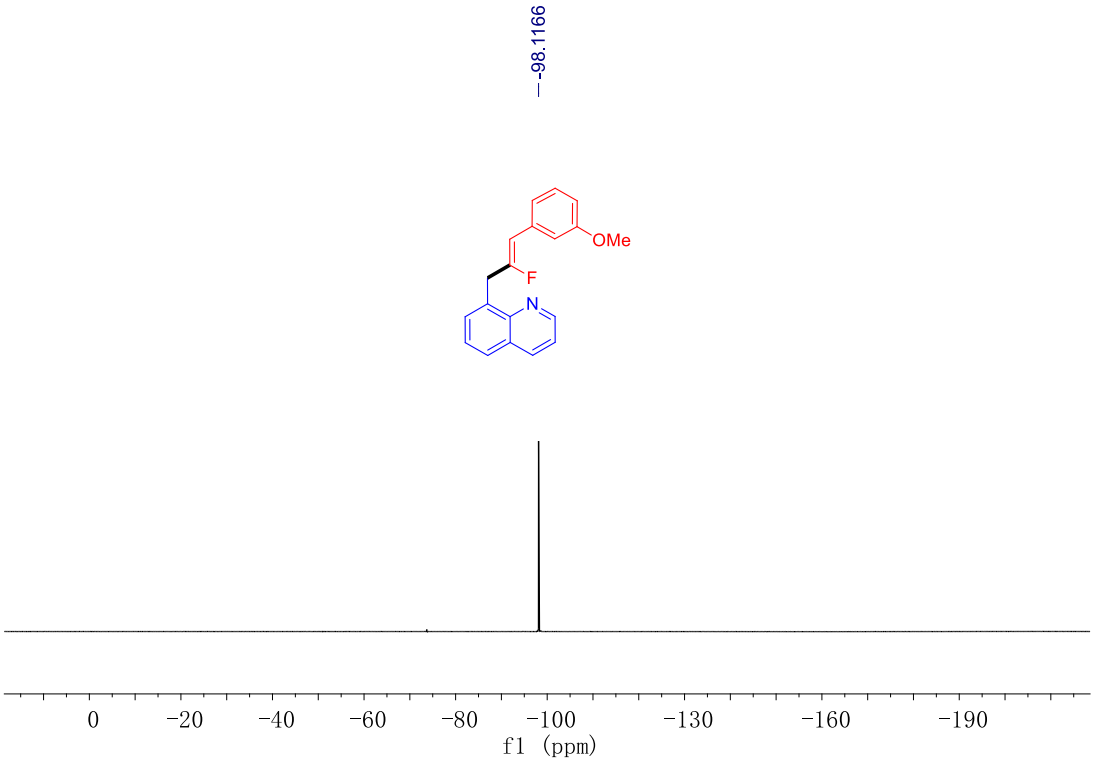
OMe
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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0
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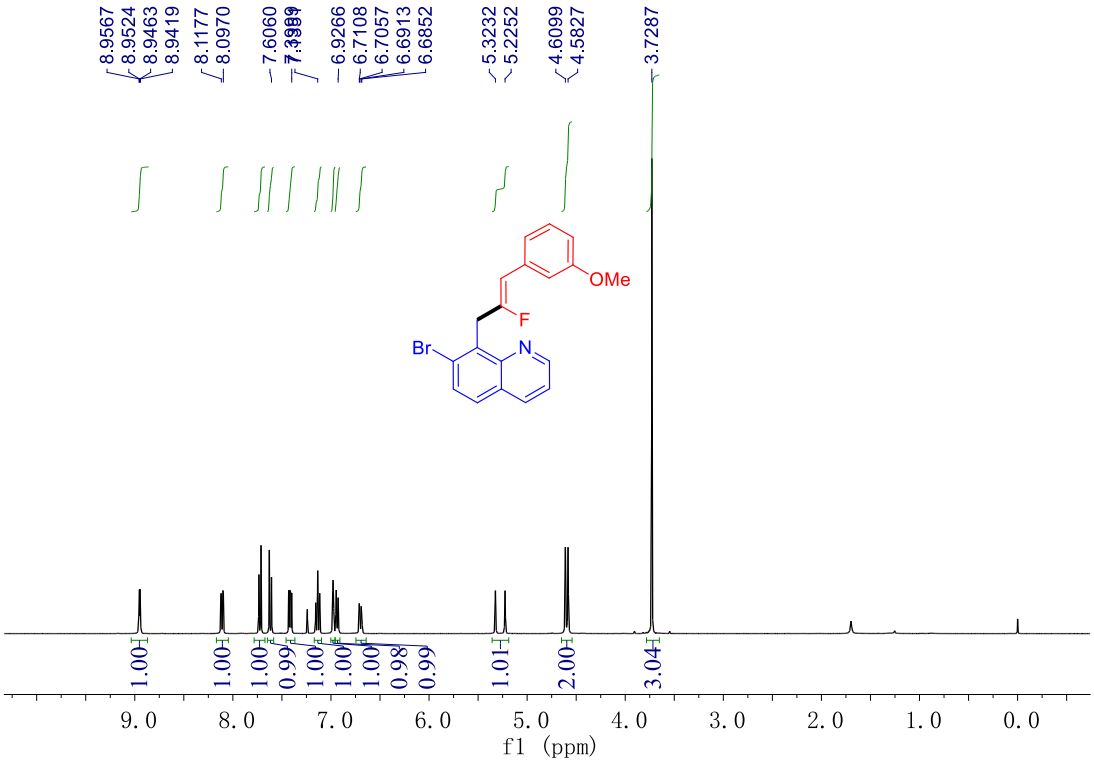
-80
-100
-130
-160
-190
f1 (ppm)

3oh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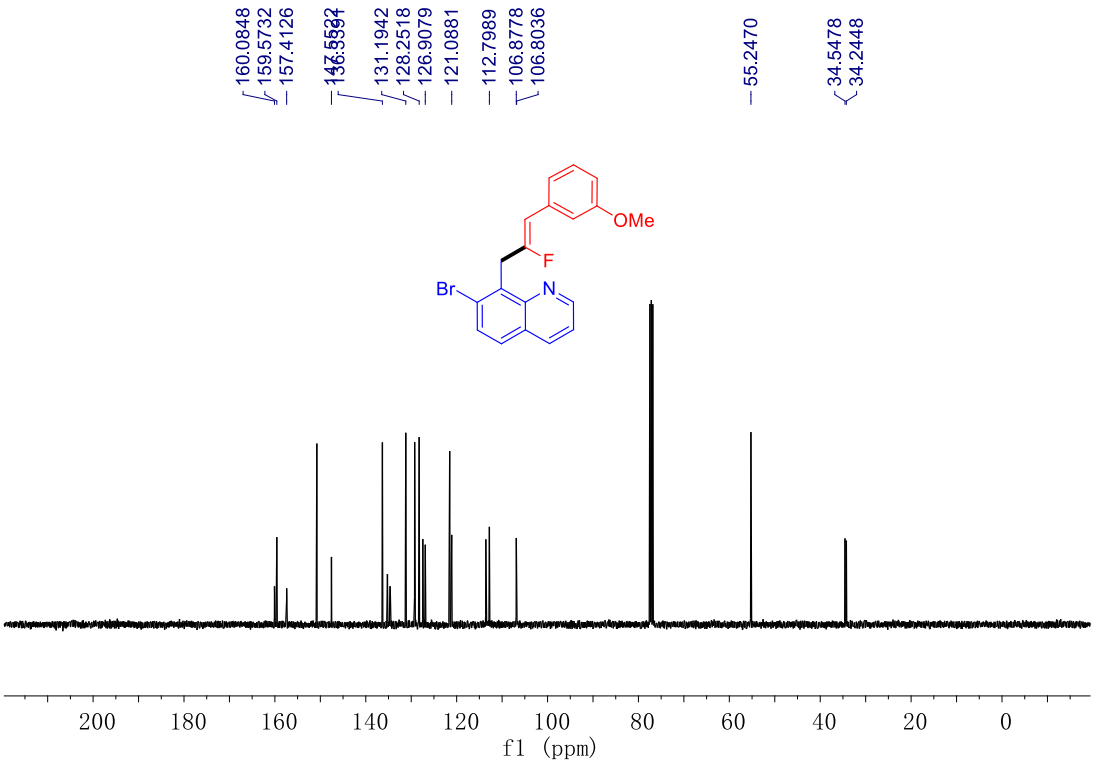
8.9524
8.9463
8.9419
8.1177
8.0970
7.6060
6.9266
6.7108
6.7057
6.6913
6.6852
5.3232
5.2252
4.6099
4.5827
3.7287
OMe
F
Br
N
1.00
1.00
1.00
0.99
1.00
1.00
1.00
0.98
0.99
1.01
2.00
3.04
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)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157.4126
131.1942
128.2518
126.9079
121.0881
112.7989
106.8778
106.8036
55.2470
34.5478
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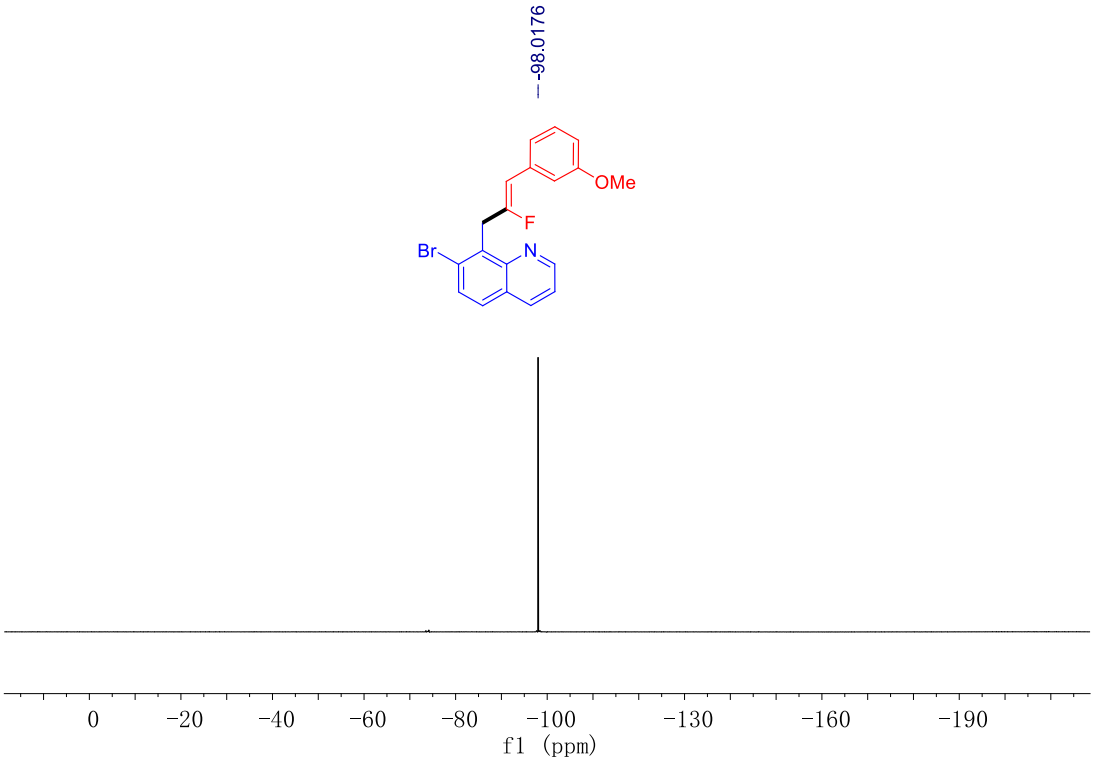
F
Br
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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-20
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-80
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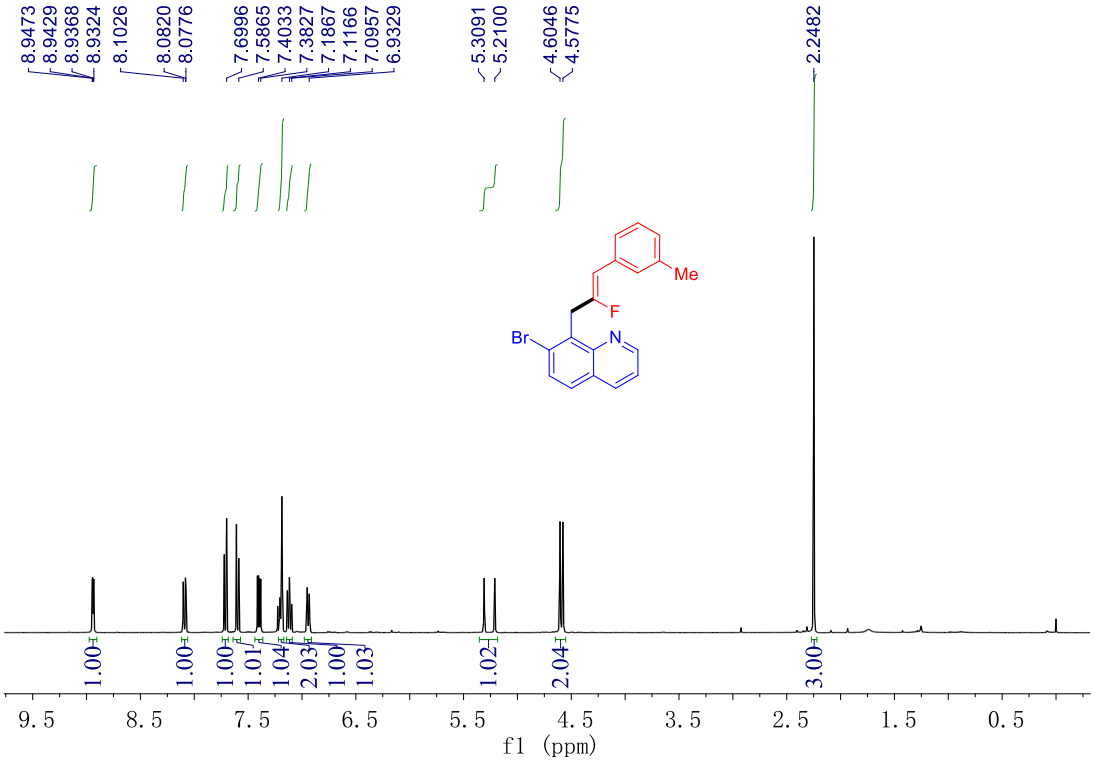
-160
-190
f1 (ppm)

3oi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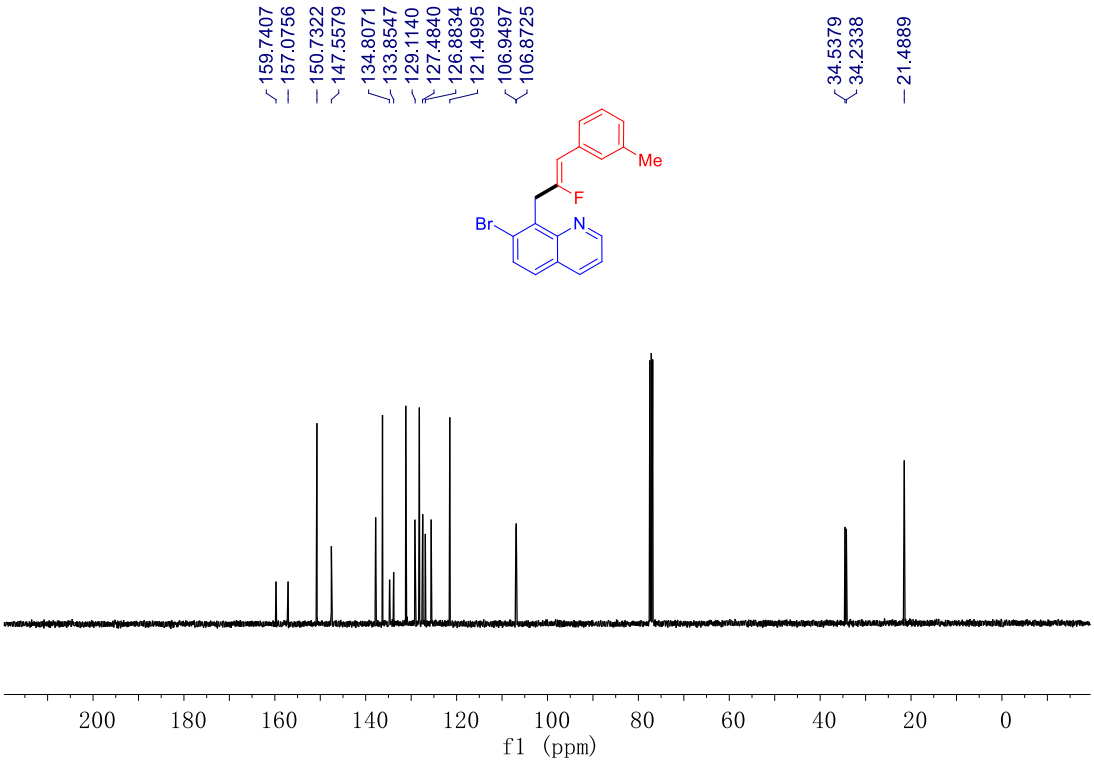
8.9368
8.9324
8.1026
8.0820
8.0776
7.6996
7.5865
7.4033
7.3827
7.1867
7.1166
7.0957
6.9329
5.3091
5.2100
4.6046
4.5775
2.2482
Me
F
Br
N
1.00
1.00
1.00
1.01
1.04
2.03
1.00
1.03
1.02
2.04
3.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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121.4995
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34.5379
34.2338
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Br
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140
120
100
80
60
40
20
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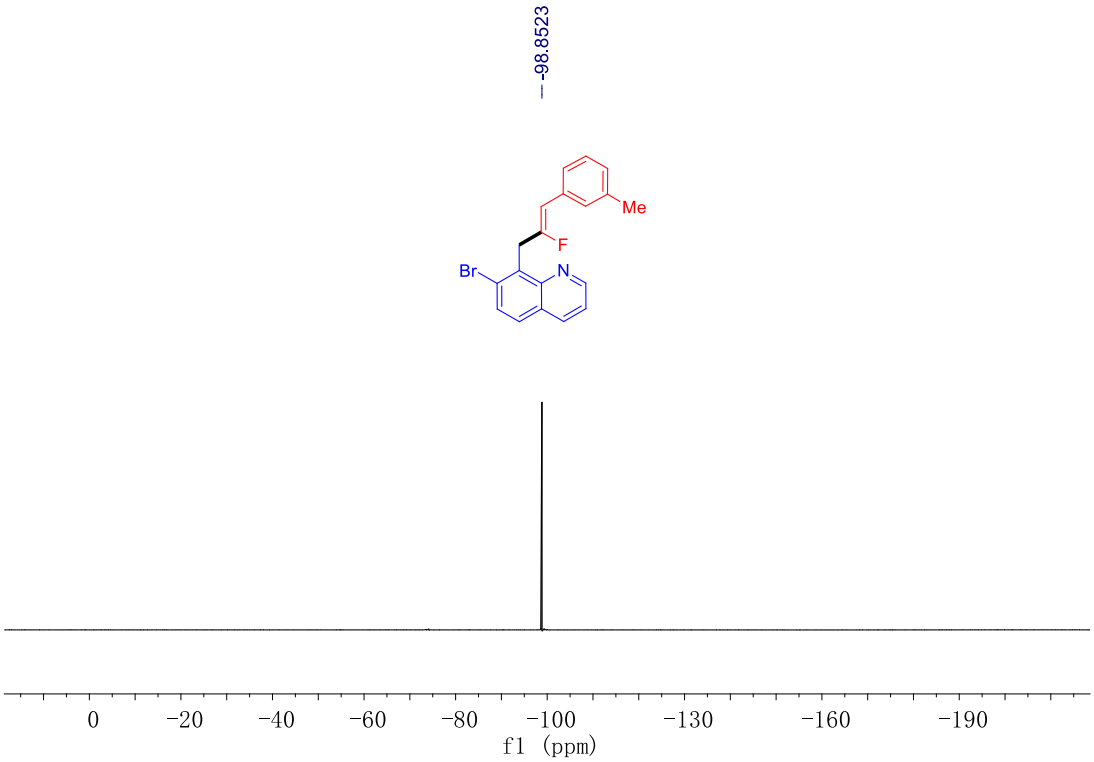
f1 (ppm)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Me
F
Br
N
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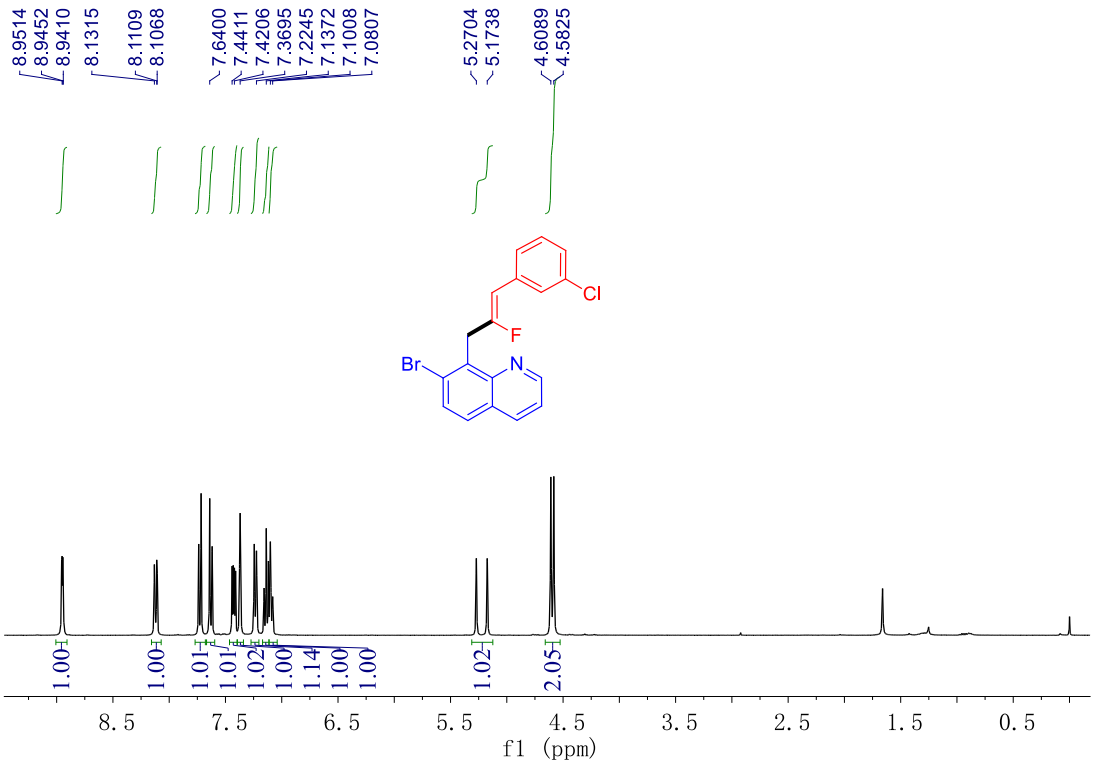
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3oj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8.1068
7.6400
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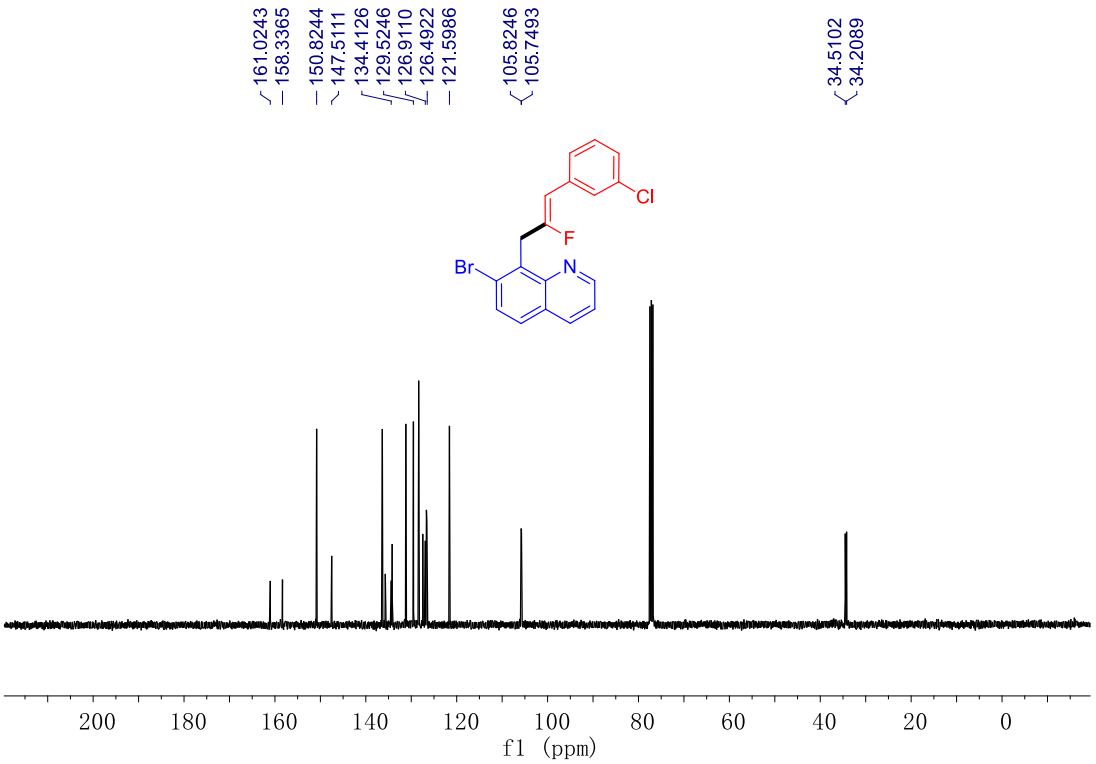
7.4206
7.3695
7.2245
7.1372
7.1008
7.0807
5.2704
5.1738
4.6089
4.5825
Cl
F
Br
N
1.00
1.00
1.01
1.01
1.02
1.00
1.14
1.00
1.00
1.02
2.05
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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126.9110
126.4922
121.5986
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105.7493
34.5102
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F
Br
N
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140
120
100
80
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40
20
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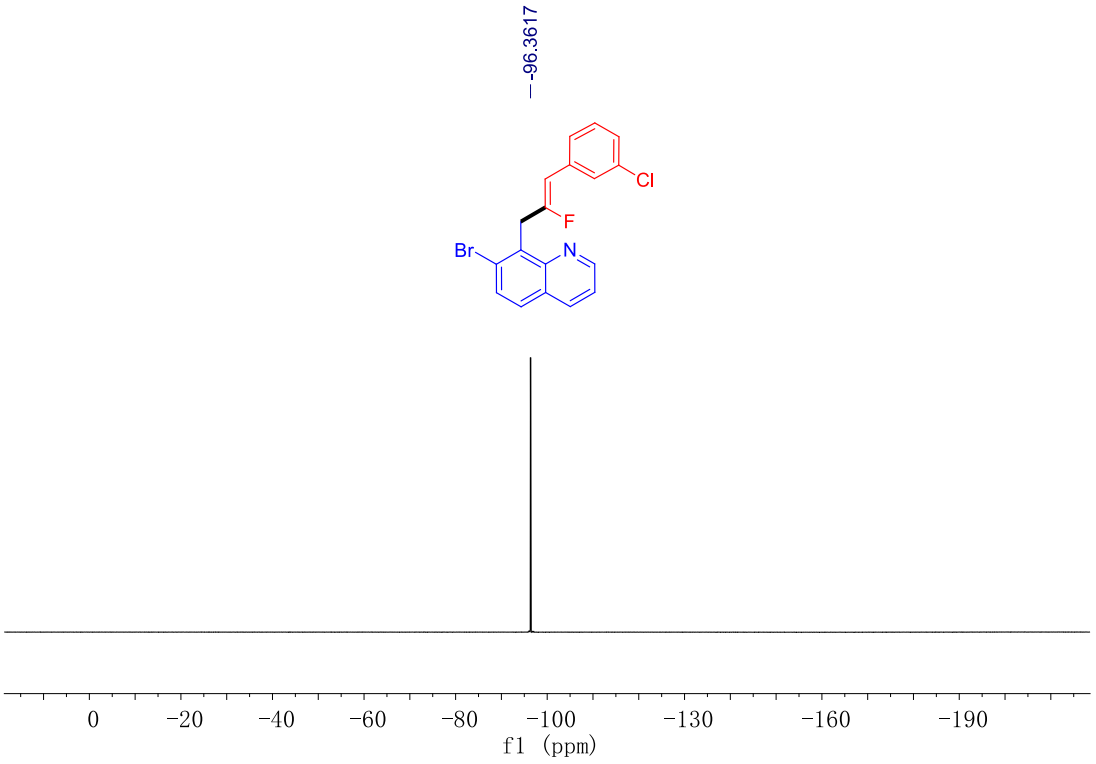
f1 (ppm)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F
Br
N
0
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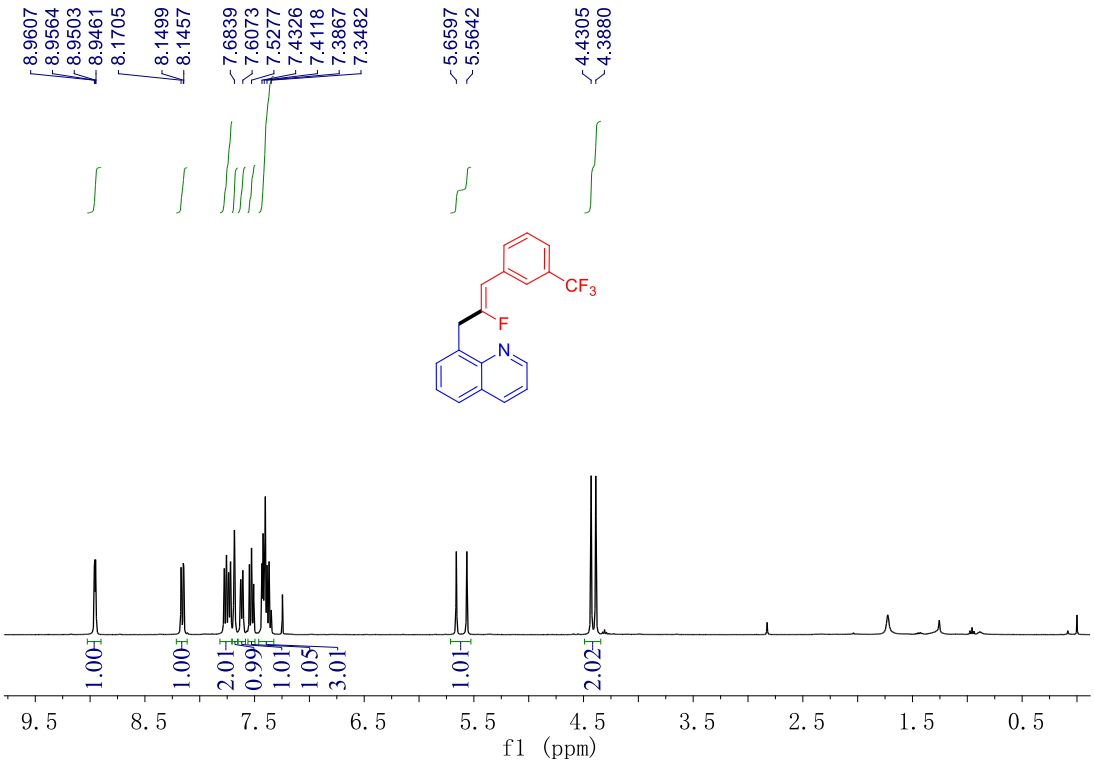
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ak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8.9461
8.1705
8.1499
8.1457
7.6839
7.6073
7.5277
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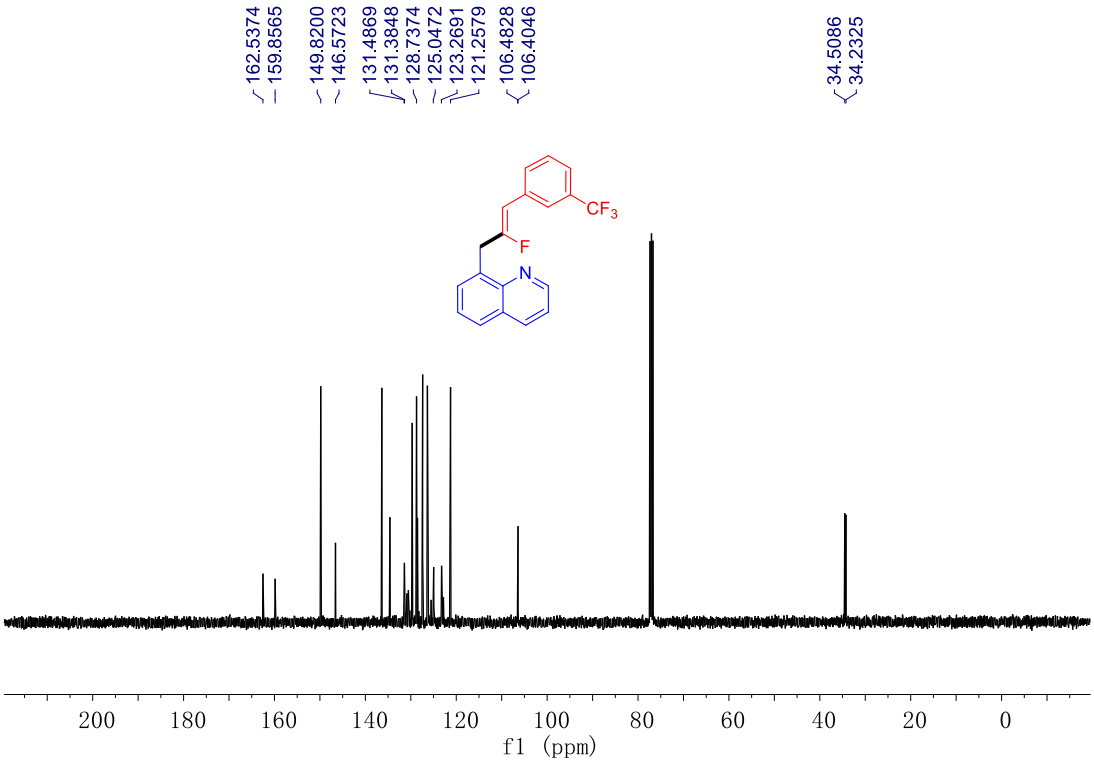
7.3867
7.3482
5.6597
5.5642
4.4305
4.3880
CF3
F
N
1.00
1.00
2.01
0.99
1.01
1.05
3.01
1.01
2.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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128.7374
125.0472
123.2691
121.2579
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106.4046
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CF3
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180
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140
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100
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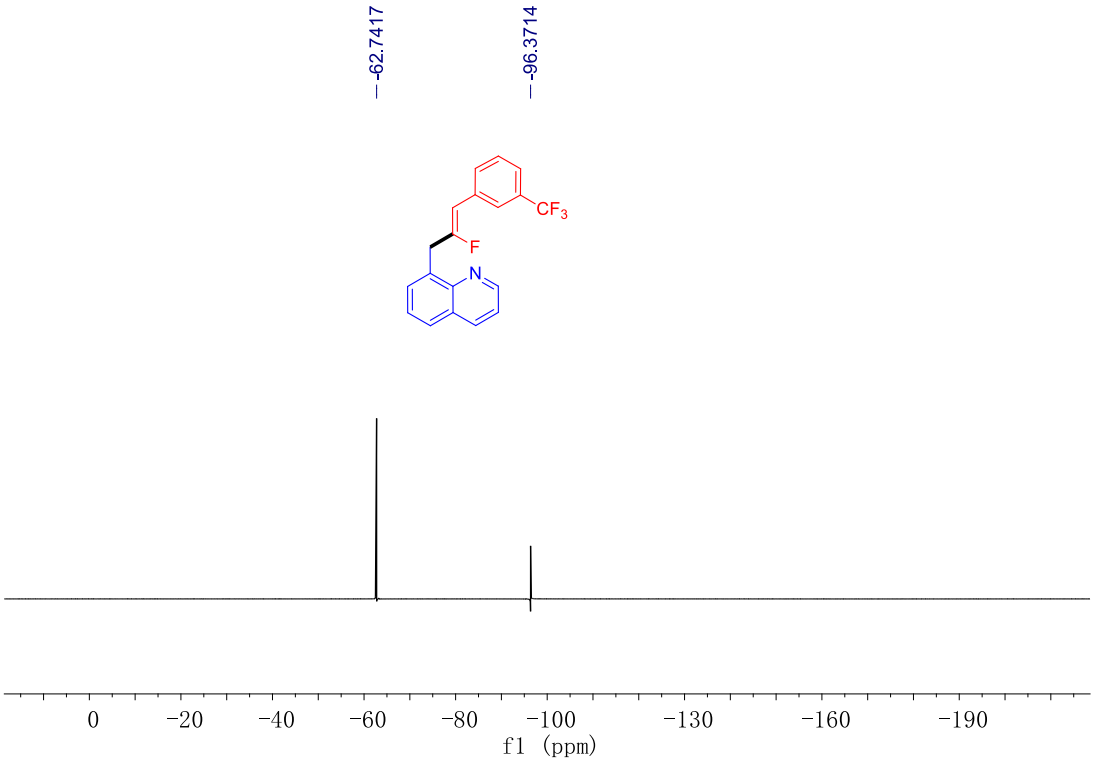
f1 (ppm)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CF3
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N
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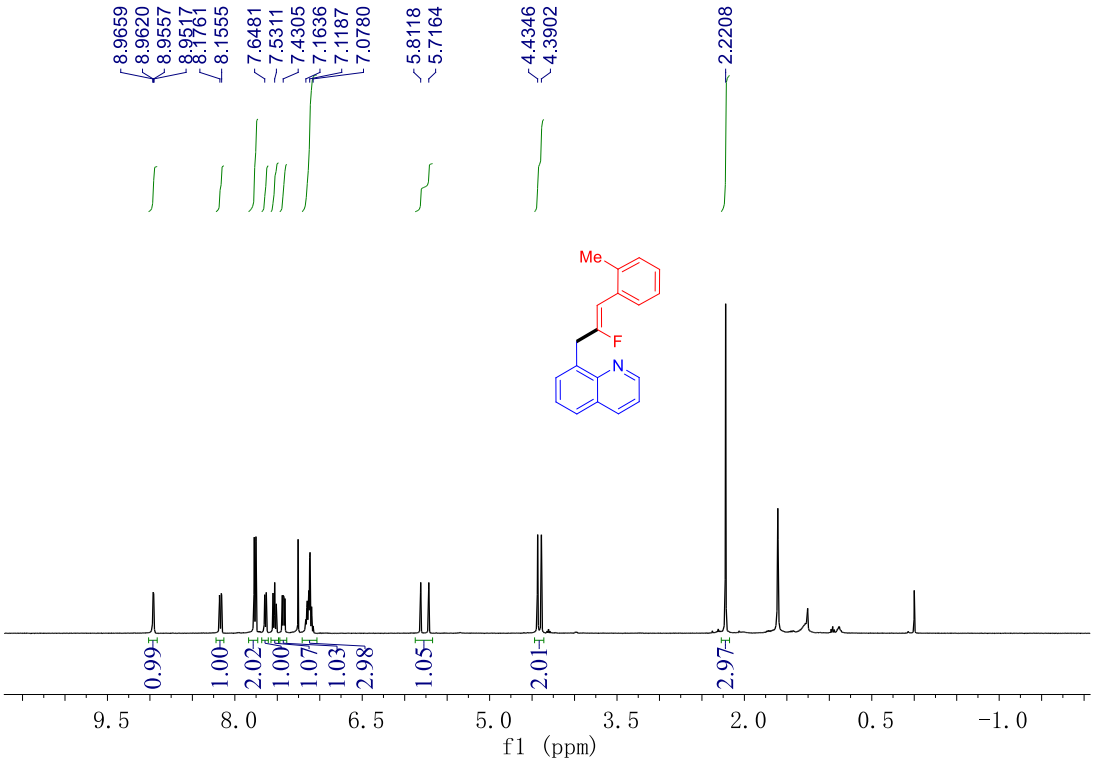
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3al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8.1761
8.1555
7.6481
7.5311
7.4305
7.1636
7.1187
7.0780
5.8118
5.7164
4.4346
4.3902
2.2208
Me
F
N
0.99
1.00
2.02
1.00
1.07
1.03
2.98
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2.01
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9.5
8.0
6.5
5.0
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2.0
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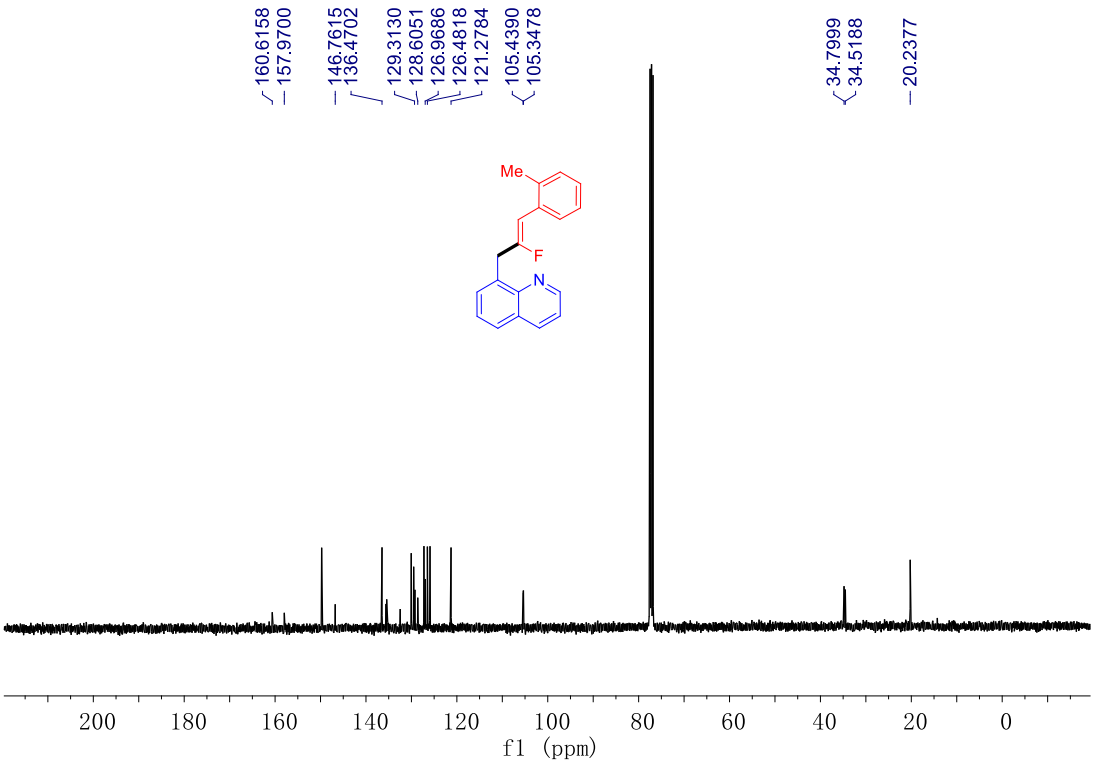
-1.0
f1 (ppm)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105.3478
34.7999
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140
120
100
80
60
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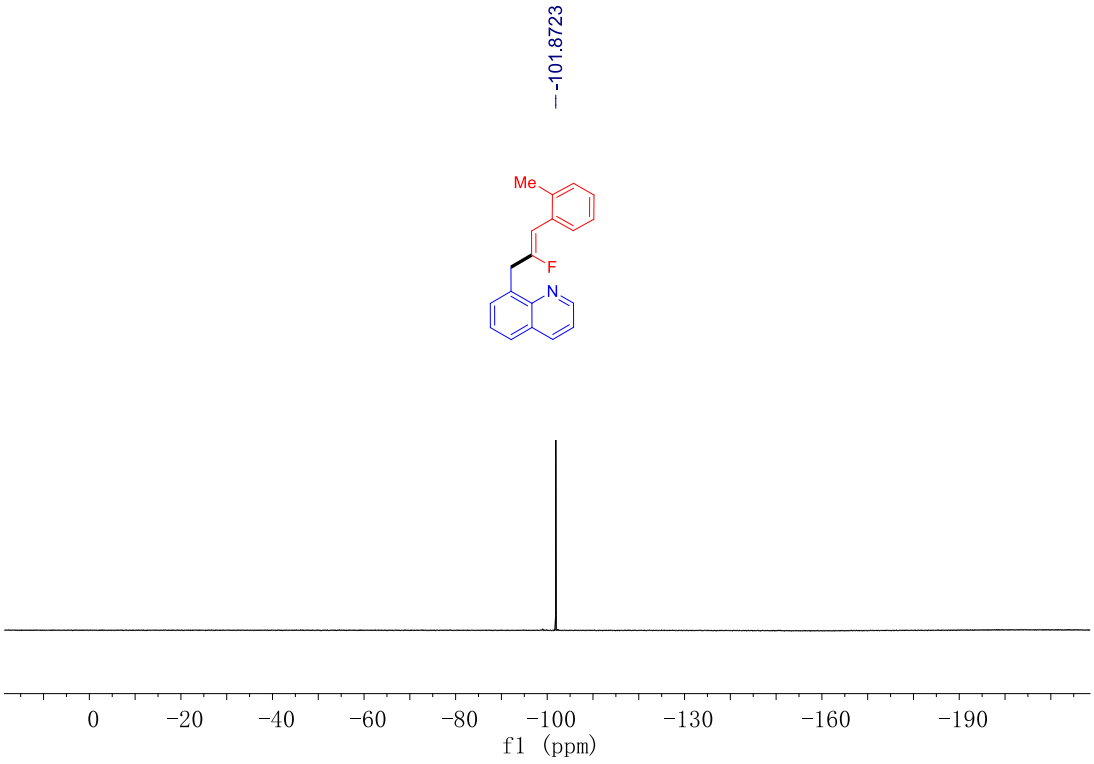
20
0
f1 (ppm)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N
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-20
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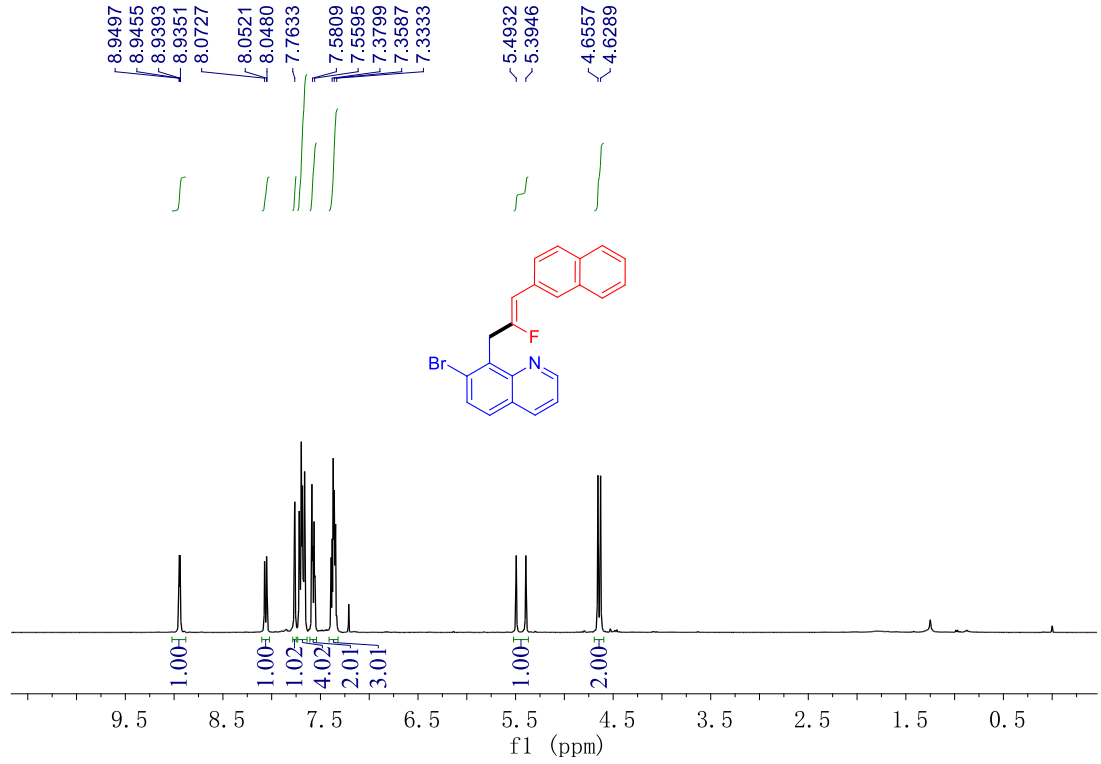
-60
-80
-100
-130
-160
-190
f1 (ppm)

3om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8.0521
8.0480
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7.5809
7.5595
7.3799
7.3587
7.3333
5.4932
5.3946
4.6557
4.6289
F
Br
N
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1.00
1.02
4.02
2.01
3.01
1.00
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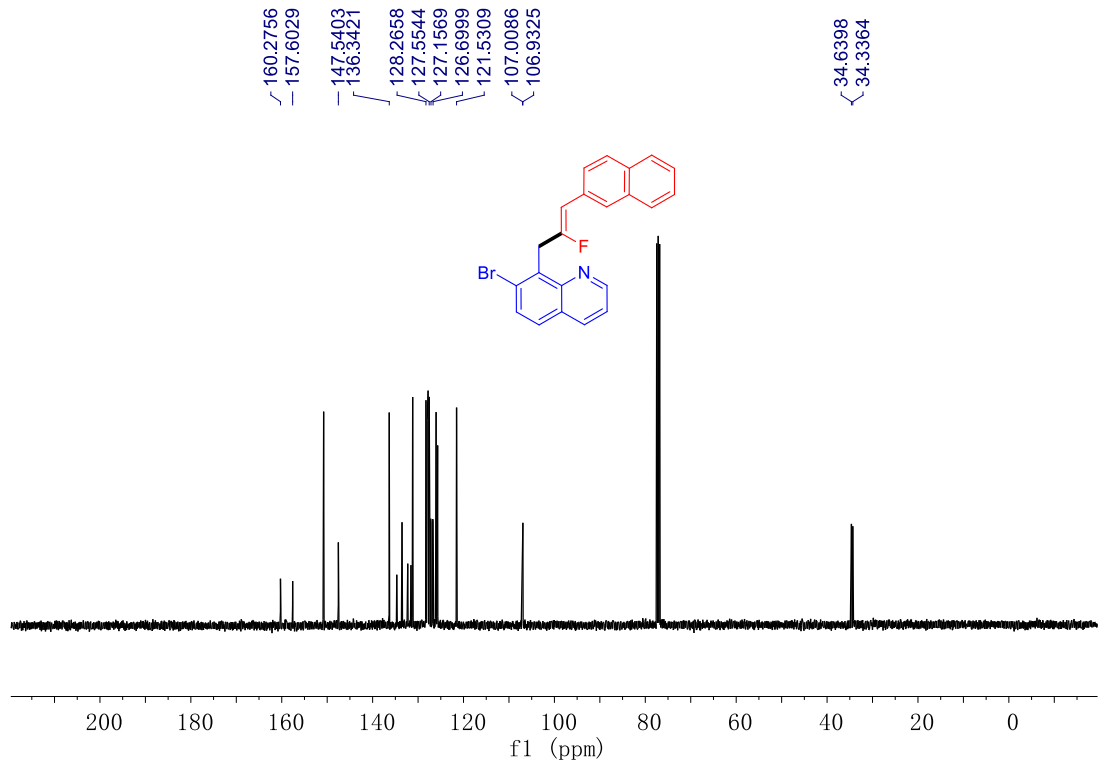
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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106.9325
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Br
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100
80
60
40
20
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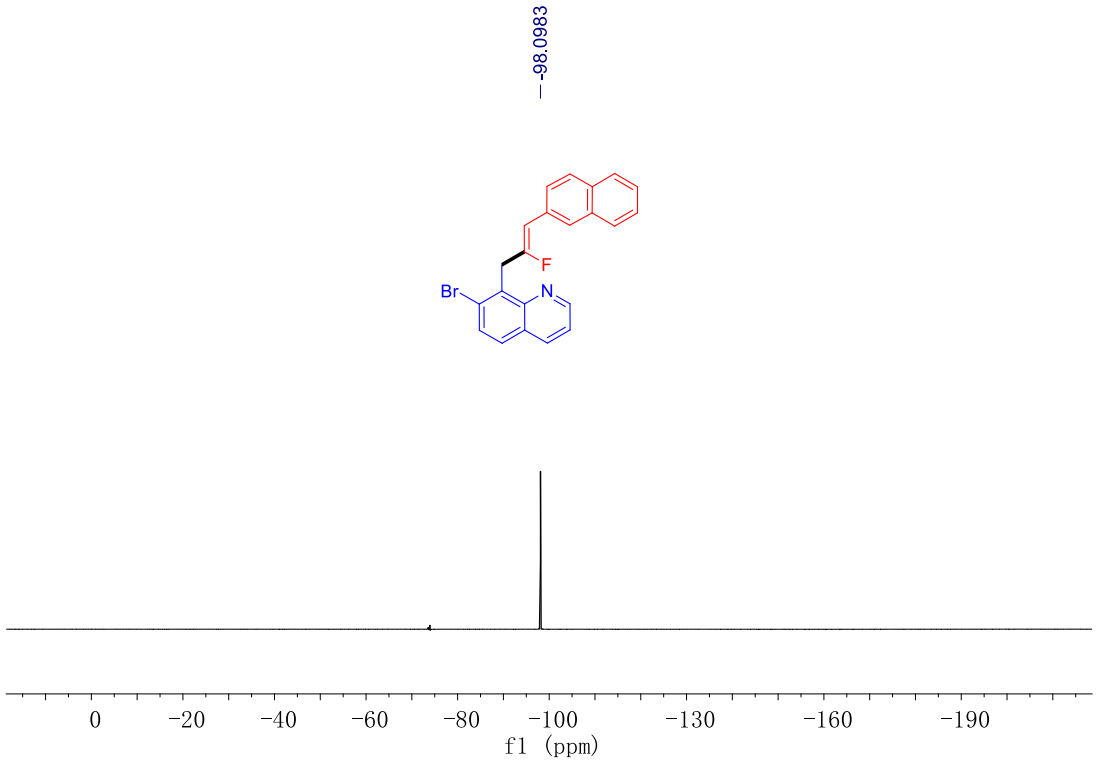
f1 (ppm)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-80
-100
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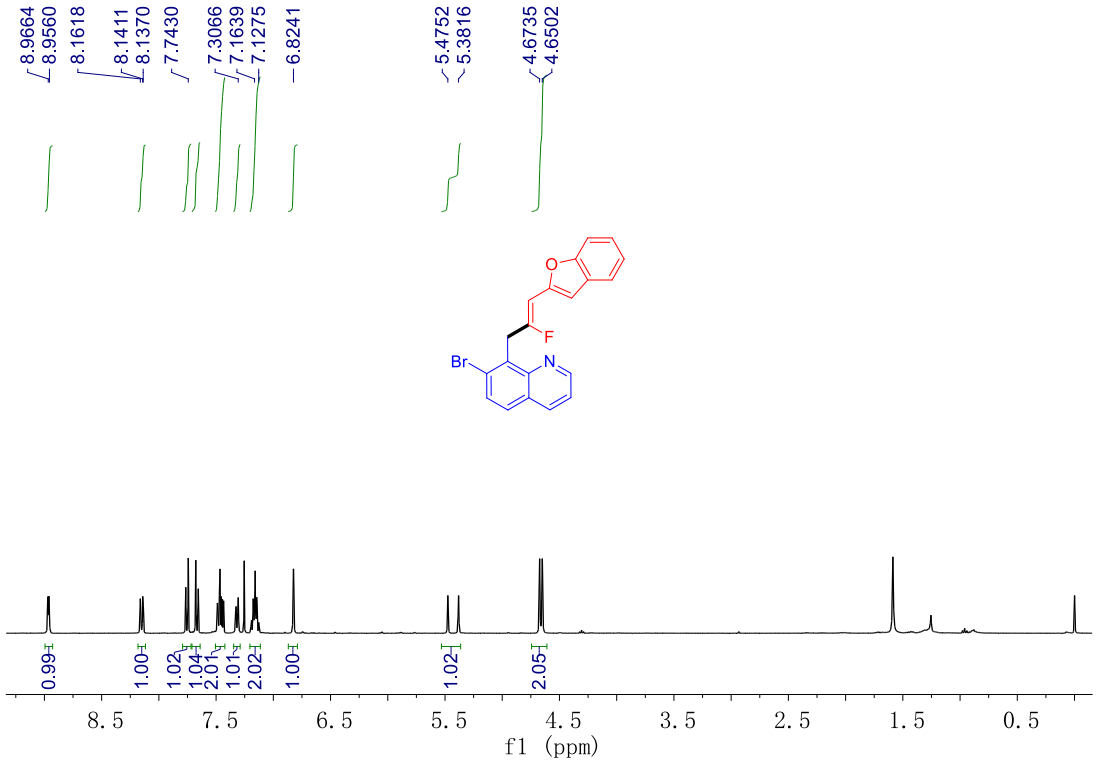
-190
f1 (ppm)

3on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8.1370
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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
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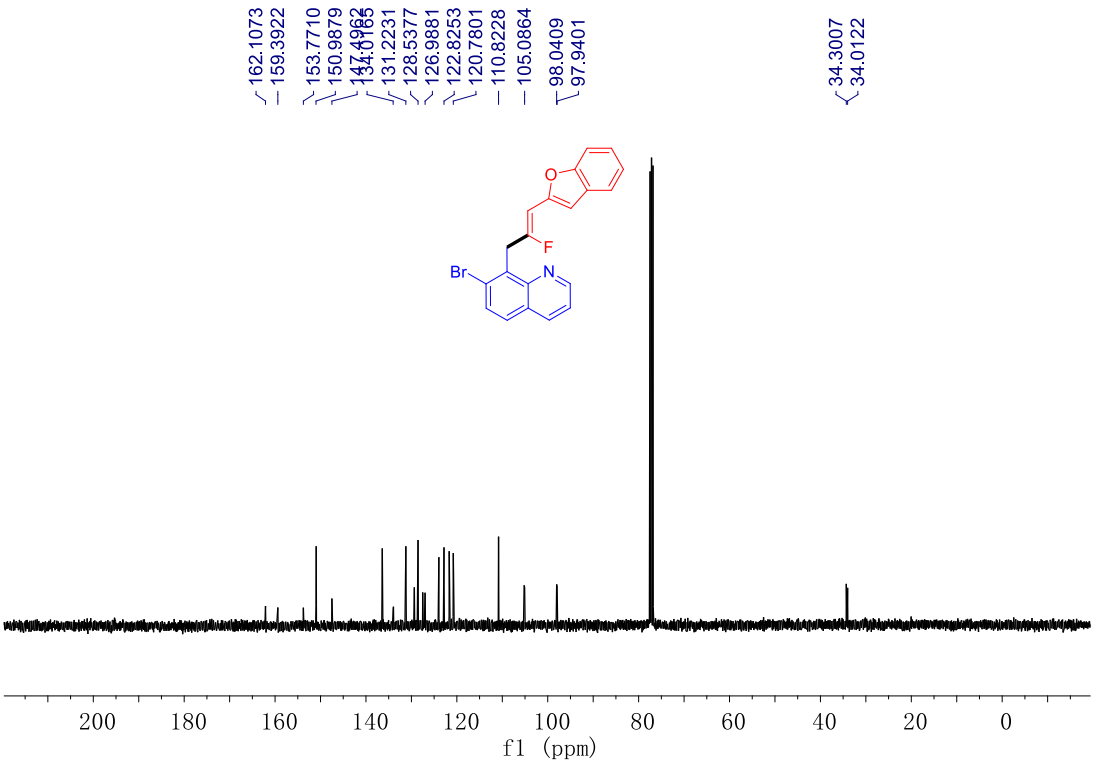
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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131.2231
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126.9881
122.8253
120.7801
110.8228
105.0864
98.0409
97.9401
34.3007
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F
Br
N
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180
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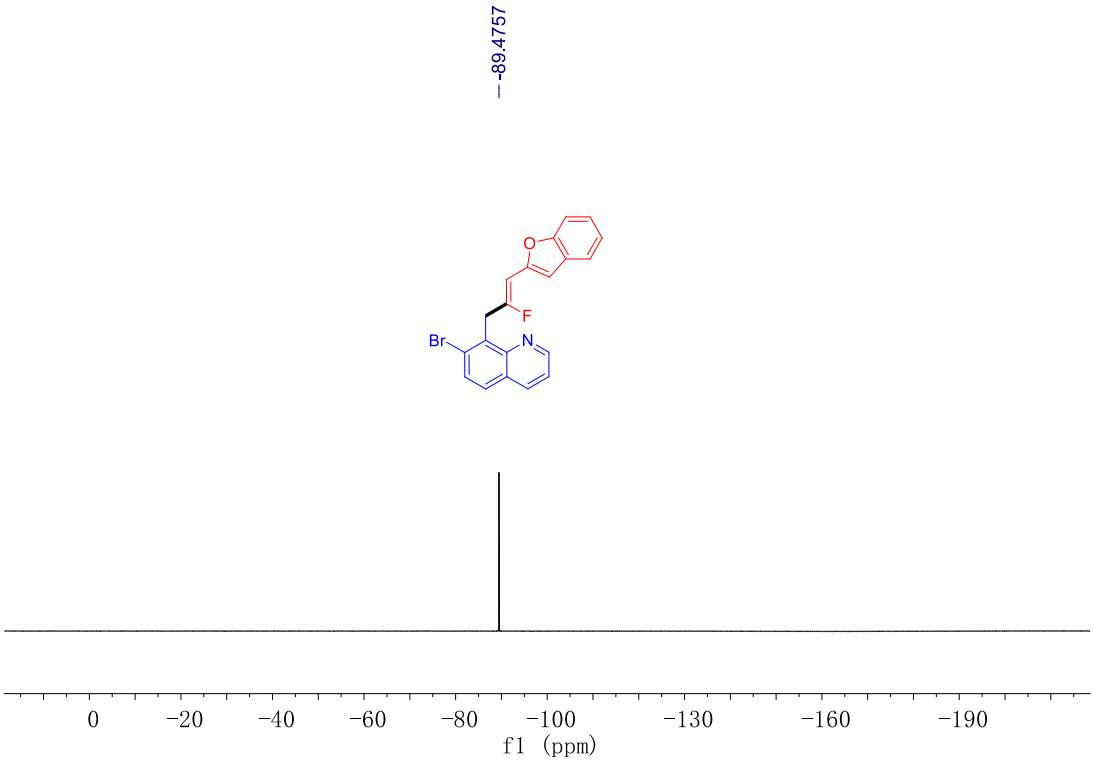
140
120
100
80
60
40
20
0
f1 (ppm)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-60
-80
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-130
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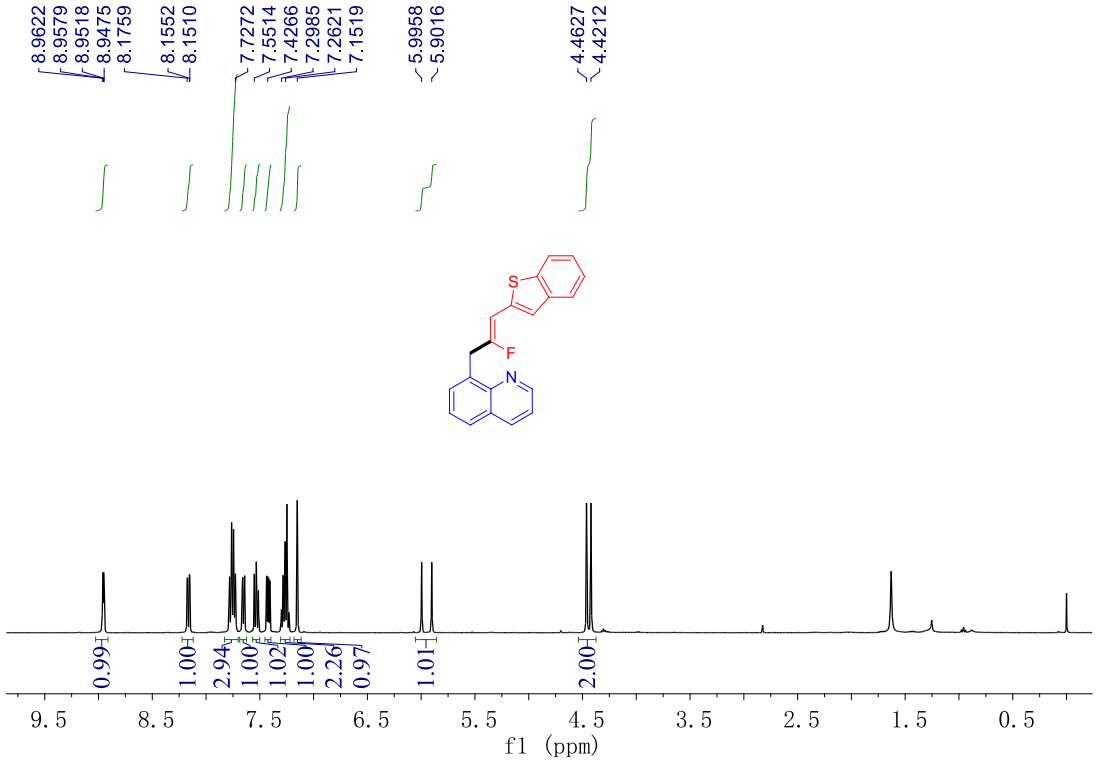
-190
f1 (ppm)

3ao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8.1510
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7.5514
7.4266
7.2985
7.2621
7.1519
5.9958
5.9016
4.4627
4.4212
S
F
N
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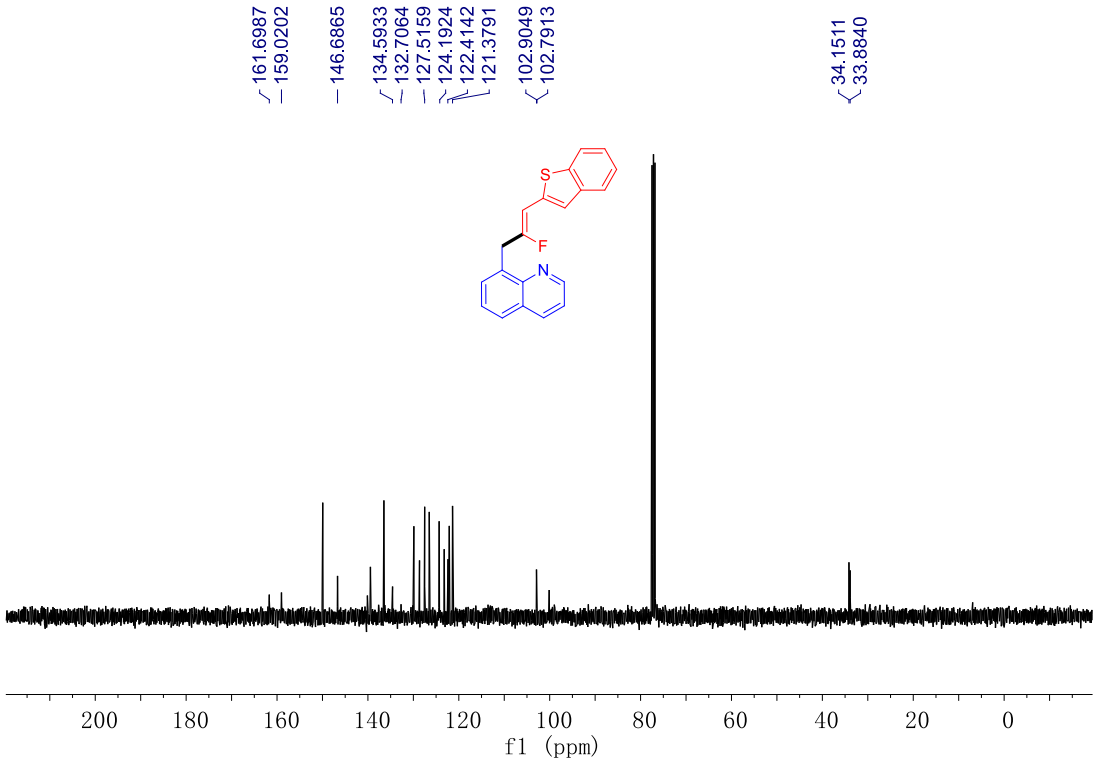
1.00
2.94
1.00
1.02
1.00
2.26
0.97
1.01
2.00
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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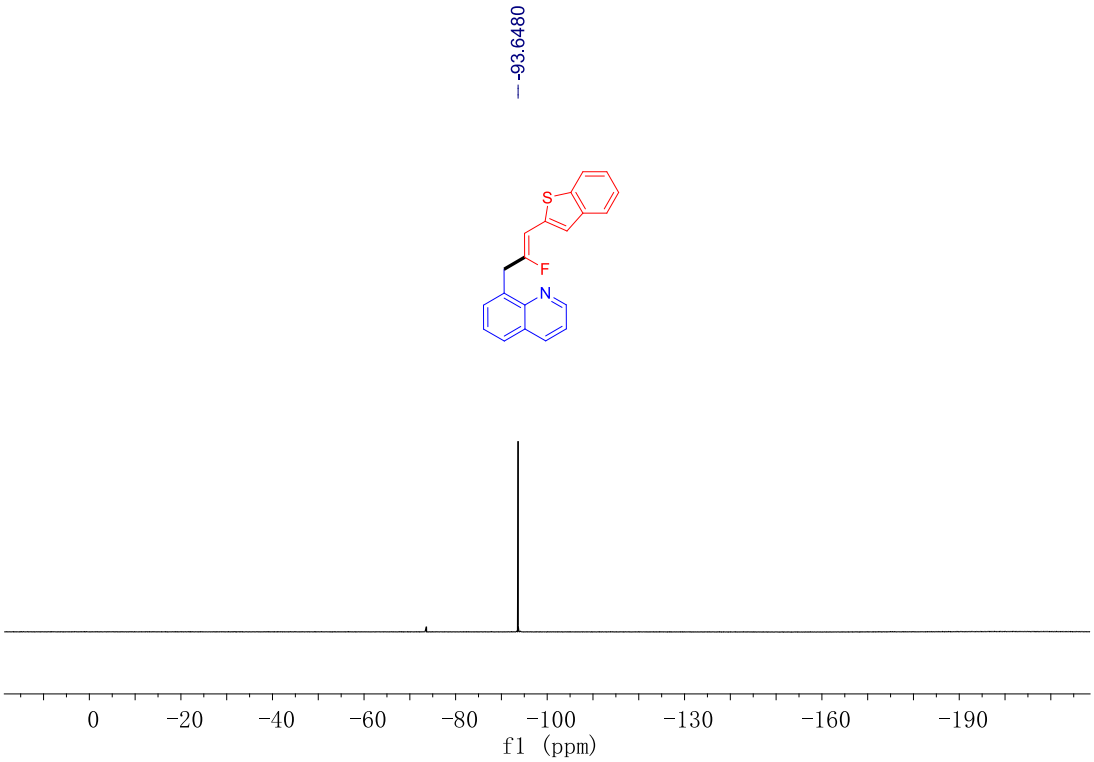
159.0202
146.6865
134.5933
132.7064
127.5159
124.1924
122.4142
121.3791
102.9049
102.7913
34.1511
33.8840
S
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


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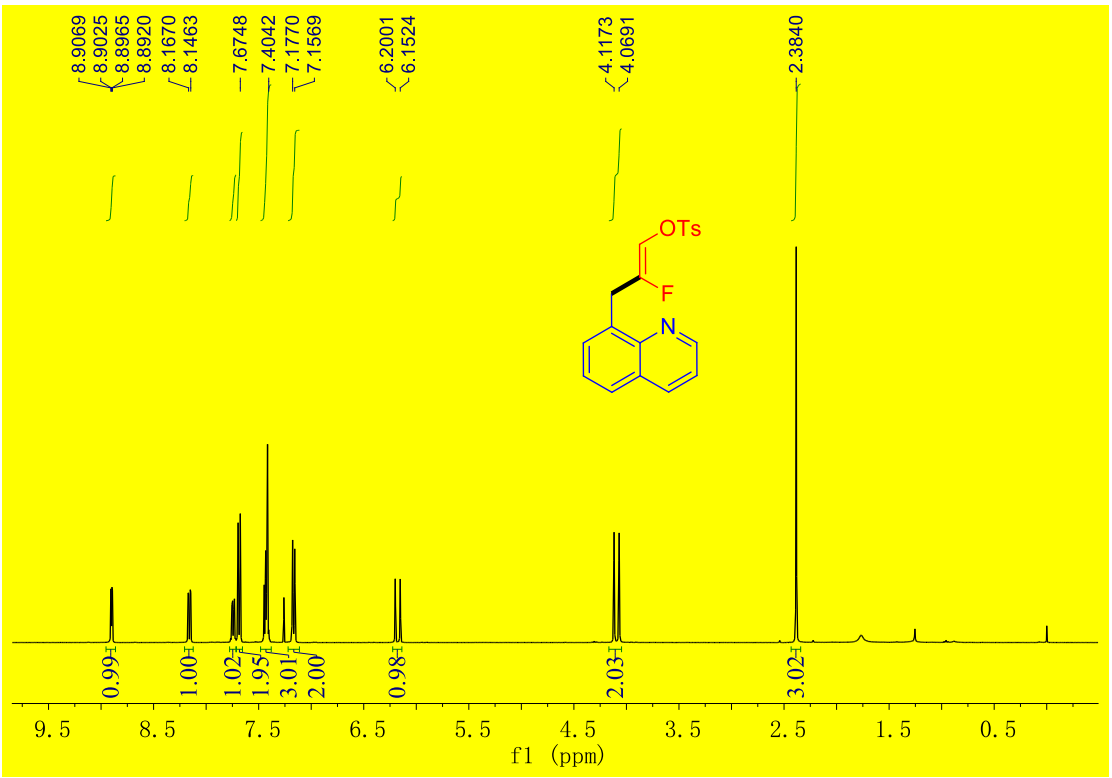
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

3ap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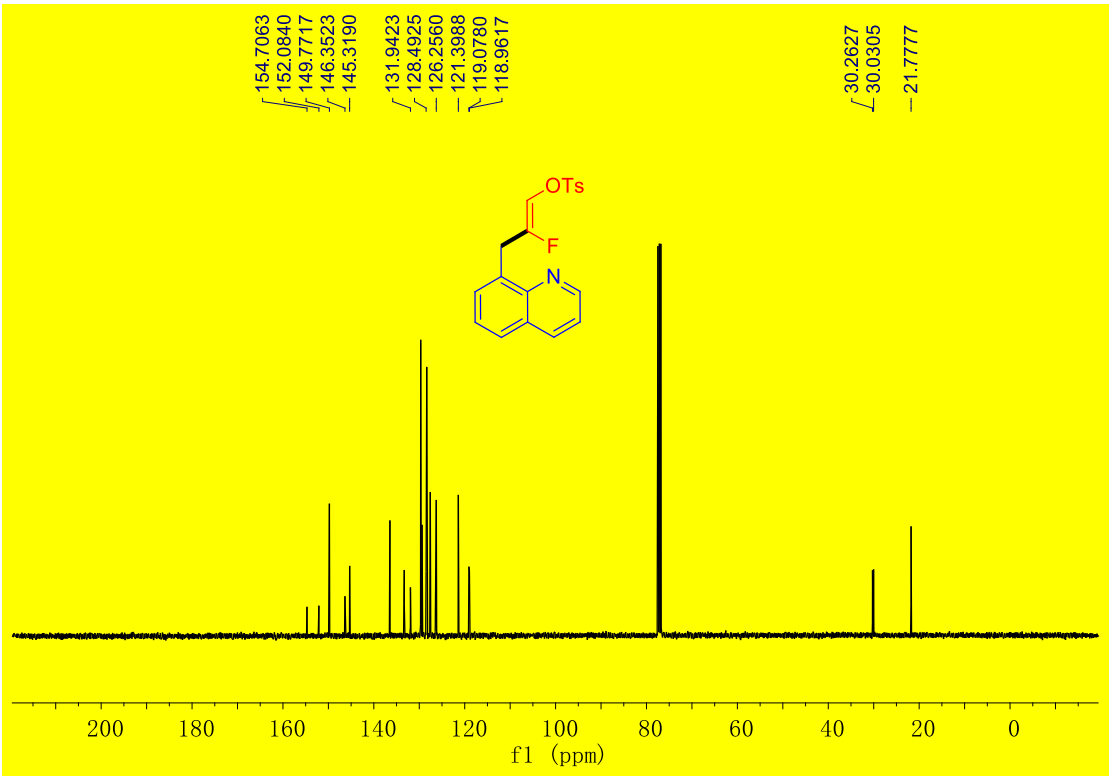
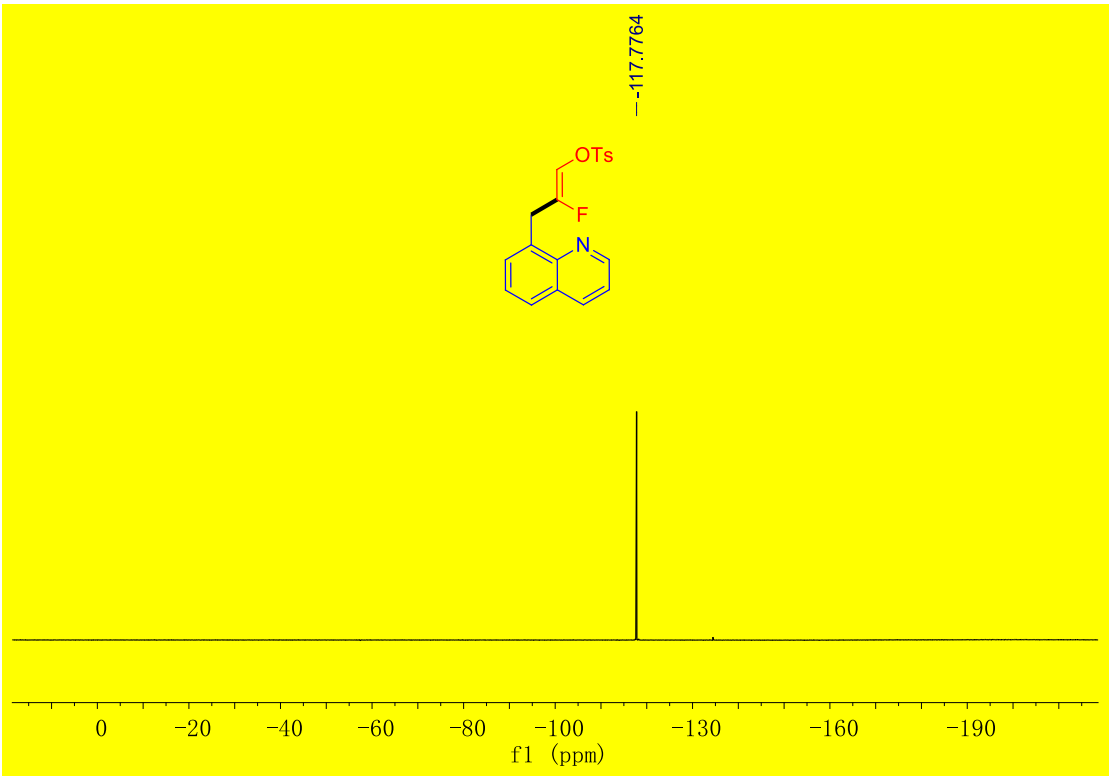
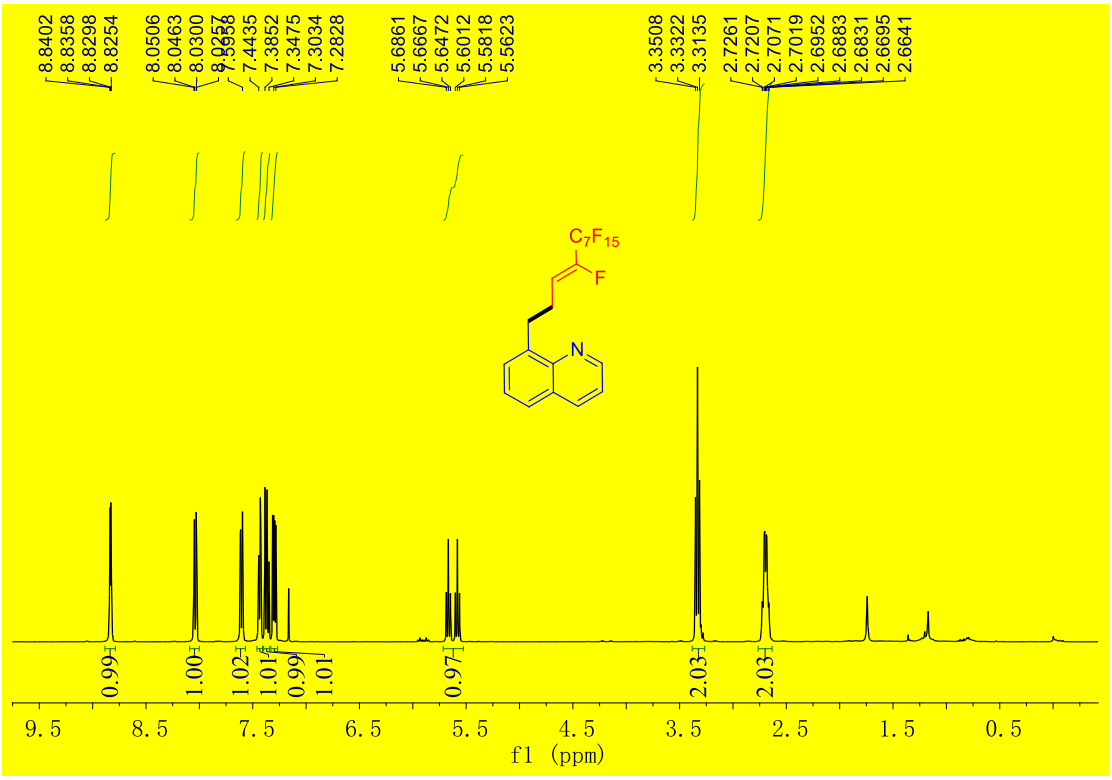
8.9025
8.8965
8.8920
8.1670
8.1463
7.6748
7.4042
7.1770
7.1569
6.2001
6.1524
4.1173
4.0691
2.3840
OTs
F
N
0.99
1.00
1.02
1.95
3.01
2.00
0.98
2.03
3.02
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


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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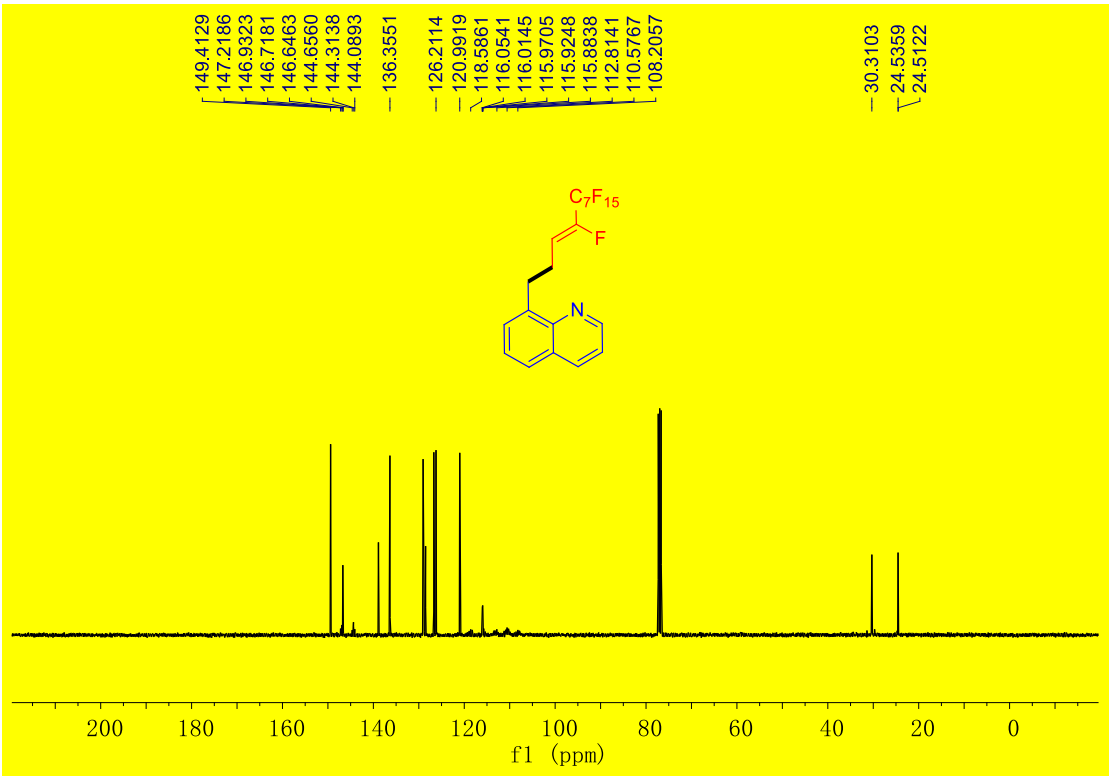
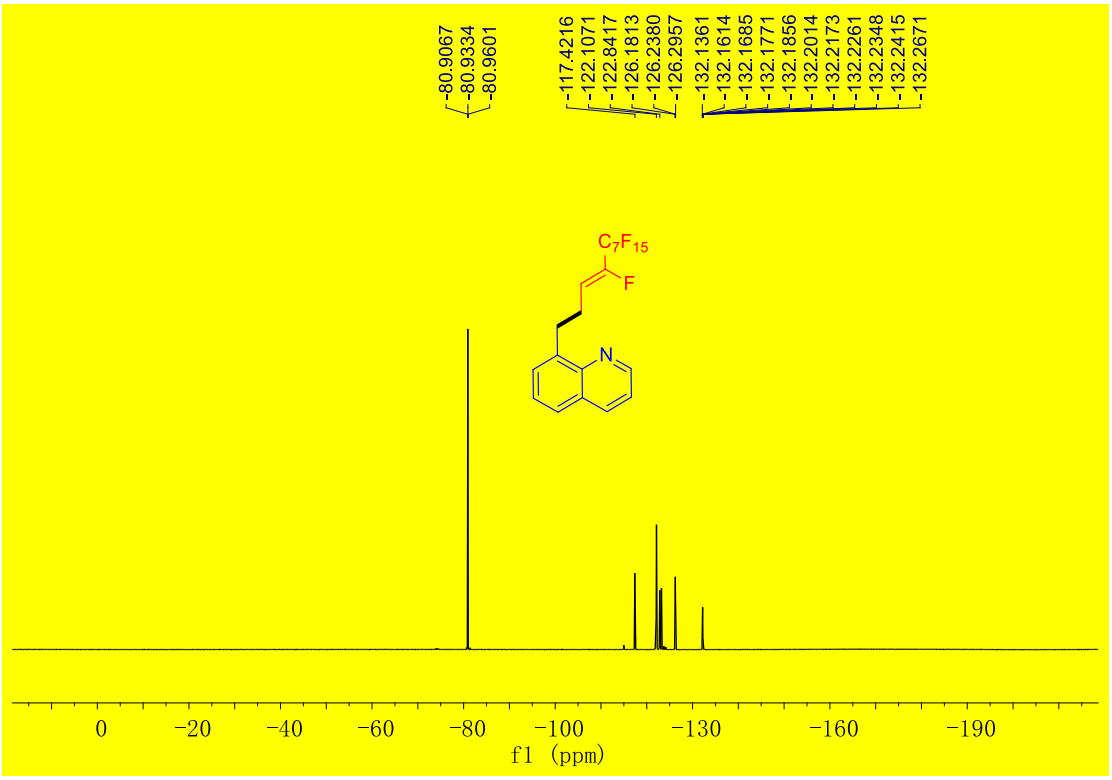
8.8358
8.8298
8.8254
8.0506
8.0463
8.0300
7.4435
7.3852
7.3475
7.3034
7.2828
5.6861
5.6667
5.6472
5.6012
5.5818
5.5623
3.3508
3.3322
3.3135
2.7261
2.7207
2.7071
2.7019
2.6952
2.6883
2.6831
2.6695
2.6641
C7F15
F
N
0.99
1.00
1.02
1.01
0.99
1.01
0.97
2.03
2.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (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
C7F15
F
N
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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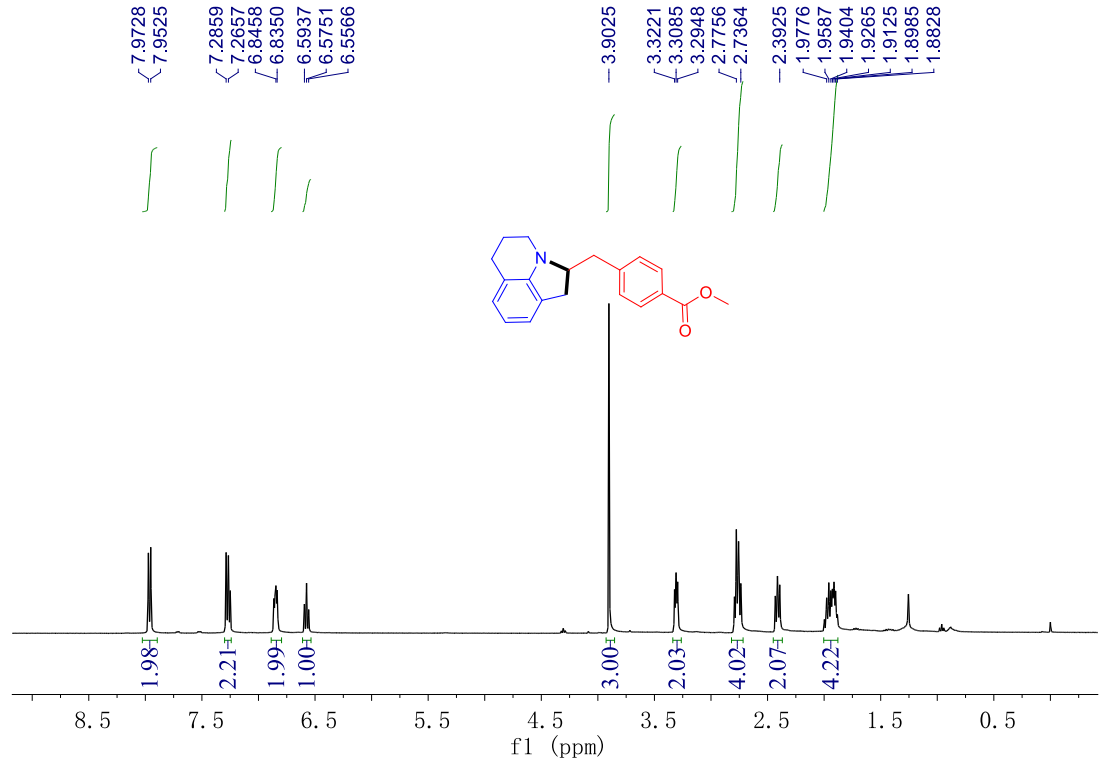
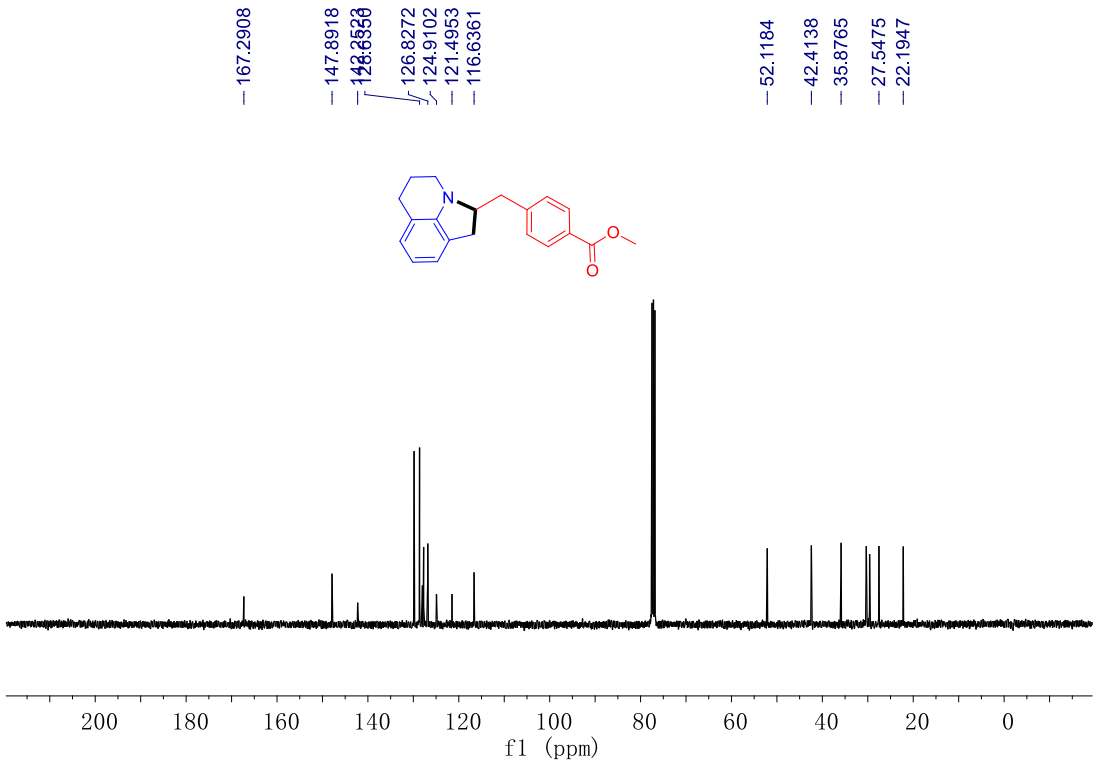
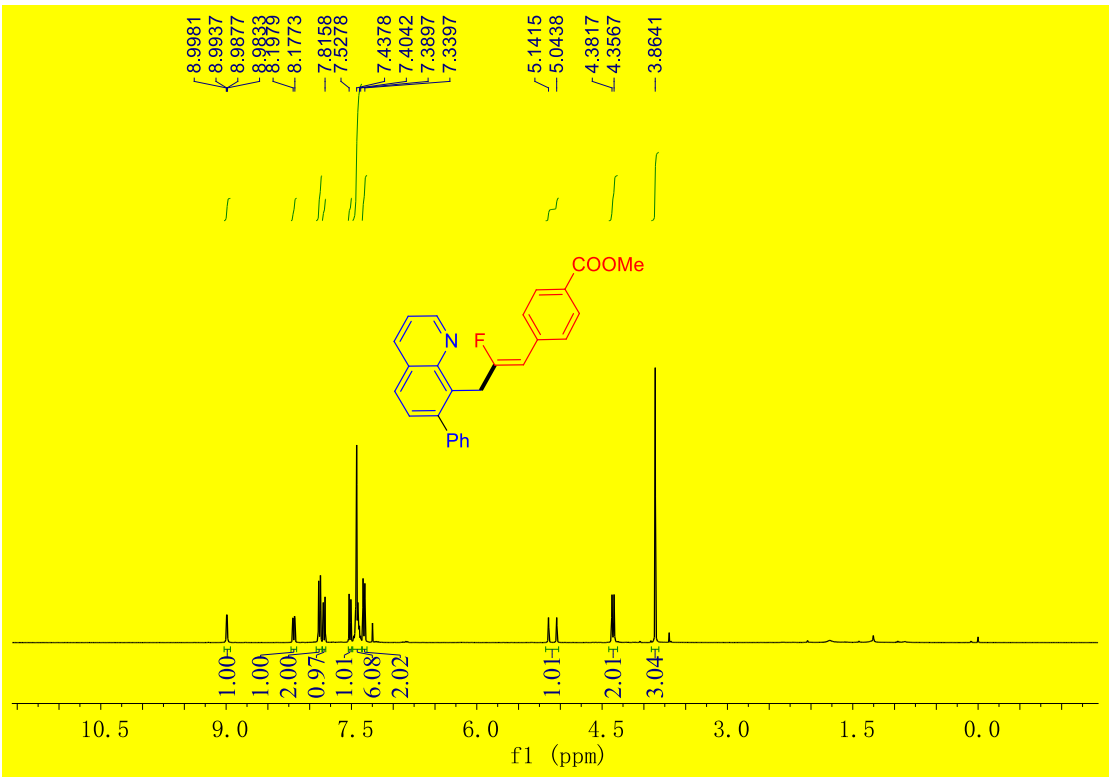
-80.9334
-80.9601
-117.4216
-122.1071
-122.8417
-126.1813
-126.2380
-126.2957
-132.1361
-132.1614
-132.1685
-132.1771
-132.1856
-132.2014
-132.2173
-132.2261
-132.2348
-132.2415
-132.2671
C7F15
F
N
0
-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)

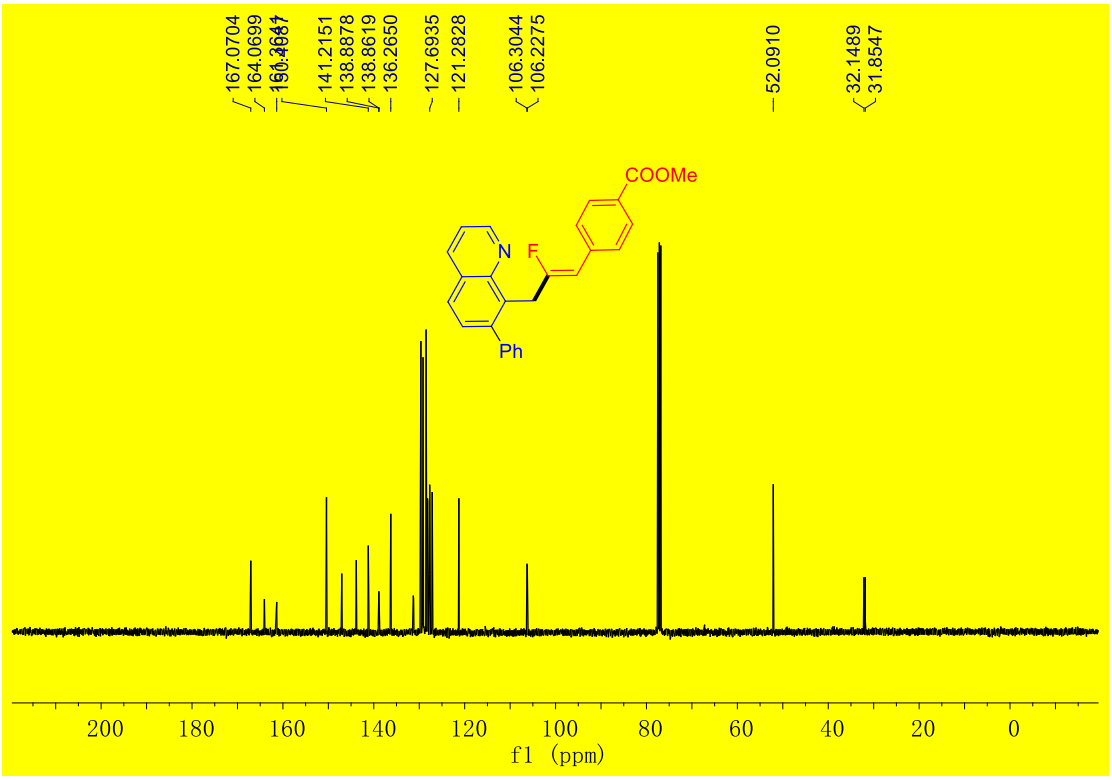
4

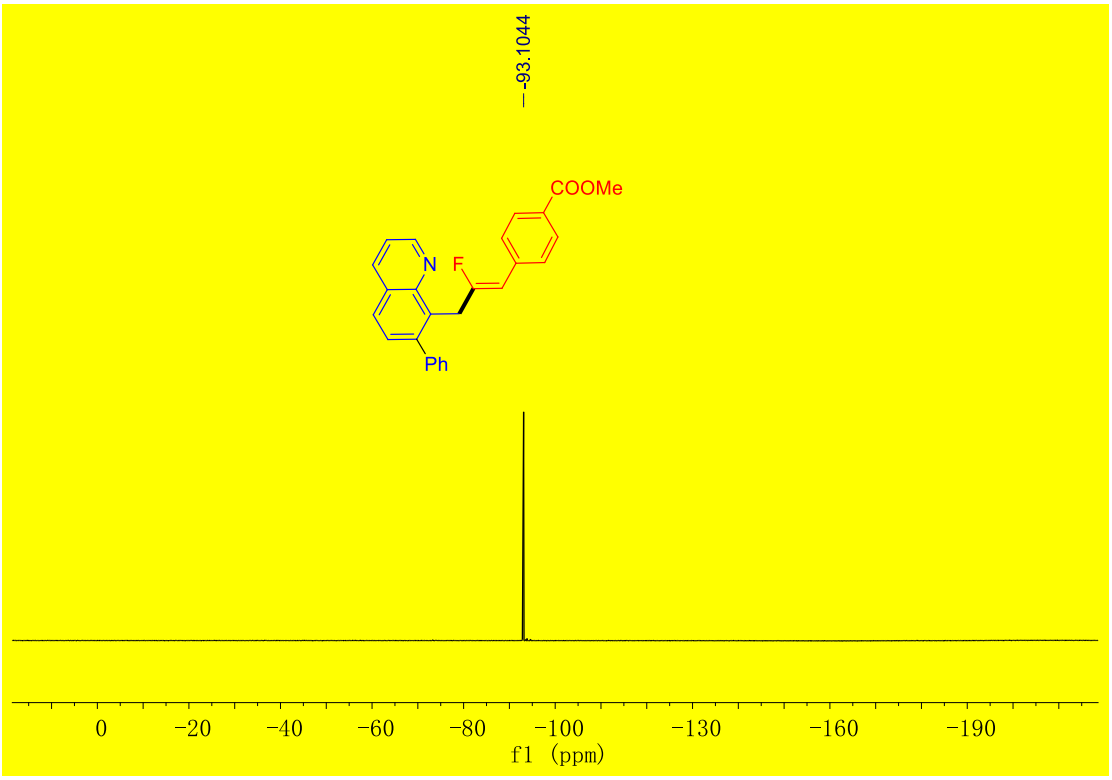

7.9728
7.9525
7.2859
7.2657
6.8458
6.8350
6.5937
6.5751
6.5566
3.9025
3.3221
3.3085
3.2948
2.7756
2.7364
2.3925
1.9776
1.9587
1.9404
1.9265
1.9125
1.8985
1.8828
N
O
O
1.98
2.21
1.99
1.00
3.00
2.03
4.02
2.07
4.22
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


167.2908
147.8918
126.8272
124.9102
121.4953
116.6361
52.1184
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


8.9981
8.9937
8.9877
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)


167.0704
164.0699
141.2151
138.8878
138.8619
136.2650
127.6935
121.2828
106.3044
106.2275
52.0910
32.1489
31.8547
COOMe
N
F
Ph
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)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COOMe
N
F
Ph
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-20
-40
-60
-80
-100
-130
-160
-190
f1 (ppm)