Supporting Information

Direct benzylic C−H difluoroalkylation with difluoroenoxysilanes by transition metal-free photoredox catalysis

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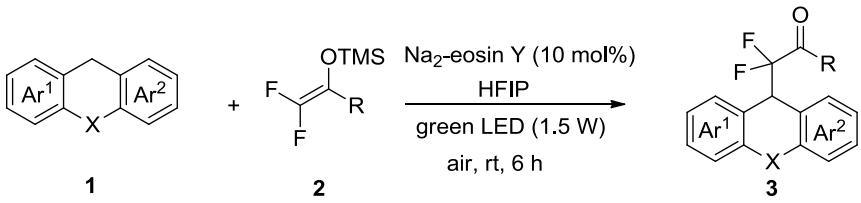
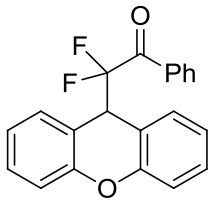
General information. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance 400 instrument at 400 (^{1}H NMR), 100 (^{13}C NMR), and 376 MHz (^{19}F NMR).Tetramethylsilane (TMS) and $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR) were used as references. Data for ^{1}H NMR were reported as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet, br = broad singlet), coupling constants (Hz), and integration. Data for ^{13}C NMR were reported as ppm. High-resolution mass spectra analyses were performed on a Waters SYNAPT G2-Si mass spectrometer. Melting points were determined using a X-4 digital micro melting point apparatus. Thin-layer chromatography (TLC) was performed, and visualization of the compounds was accomplished with UV light (254 nm). Flash column chromatography was performed on silica gel (200−300 mesh). Reactions were carried out using 1.5 W green LED (555nm) on a synLED-16 A discover. Known compounds xanthenes **1a**−**1k**,[1] **1p**,[2] **1q**,[2] acridines **1l**−**1n**,[3] thioxanthene **1o**[4] allylic and propargylic substrates **1w**−**1aa**,[5] and difluoroenoxysilanes **2**[6] were prepared according to literature procedures. Purchased reagents and solvents were used without further purification.

General procedure for preparation of products 3.

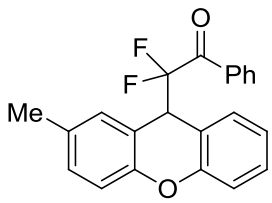


To a mixture of **1** (0.2 mmol) and **2** (0.4 mmol, 2.0 equiv) in HFIP (2.0 mL) was added Na_2-eosin Y (13.8 mg, 0.02 mmol, 10 mol%). The mixture was exposed to green LED (1.5 W) and stirred at room temperature under air for 6 h. Then the mixture was concentrated in vacuo, and purified by column chromatography on silica gel (PE/EA, 30:1 or 20:1) to afford the desired products **3**.



3a

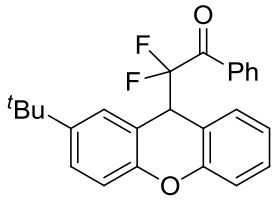
2,2-Difluoro-1-phenyl-2-(9*H*-xanthen-9-yl)ethanone (3a). Yellow solid; 56.4 mg, 84% yield, PE/EA = 30/1 as the eluent; mp = 62–63 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, J = 7.8 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.35–7.25 (m, 6H), 7.15 (d, J = 8.1 Hz, 2H), 7.04 (t, J = 7.6 Hz, 2H), 4.96 (t, J = 14.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.0 (t, J = 29.6 Hz), 153.5, 133.9, 133.1, 130.6, 129.8 (t, J = 3.6 Hz), 129.5, 128.3, 123.2, 118.0 (t, J = 260.5 Hz), 116.8, 116.2 (t, J = 3.2 Hz), 44.4 (t, J = 23.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.16 (d, J = 14.3 Hz, 2F). Physical and spectral properties of this material were identical to those previously reported in literature.[7]



3b

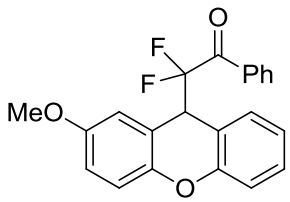
2,2-Difluoro-2-(2-methyl-9*H*-xanthen-9-yl)-1-phenylethanone (3b). Yellow oil; 56.7 mg, 81% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 6.7 Hz, 2H), 7.49 (t, J = 7.4 Hz, 1H), 7.33–7.26 (m, 4H), 7.17–6.99 (m, 5H), 4.89 (t, J = 14.3 Hz, 1H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1 (t, J = 29.4 Hz), 153.7, 151.4, 133.9, 133.2 (t, J = 1.9 Hz), 132.7, 130.8, 130.6, 130.1, 129.8 (t, J = 3.9 Hz), 129.4, 128.3, 123.1, 118.1 (t, J = 259.1 Hz), 116.8, 116.5, 116.2 (t, J = 3.2 Hz), 115.8 (t, J = 3.2 Hz), 44.5 (t, J = 23.9 Hz), 20.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.86 (dd, J = 259.4, 13.9 Hz, 1F), -103.62 (dd, J = 268.1, 14.3 Hz, 1F); **HRMS**

(ESI) *m*/*z* calcd for $[M + Na]^+$ $C_{22}H_{16}F_2O_2Na$ 373.1011, found 373.1017.



3c

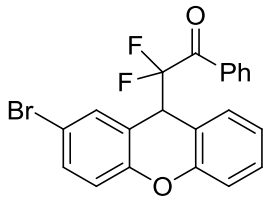
2-(2-(*tert*-Butyl)-9*H*-xanthen-9-yl)-2,2-difluoro-1-phenylethanone (3c). Yellow oil; 47.0 mg, 60% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.29–7.16 (m, 5H), 7.09 (s, 1H), 7.08 (d, J = 8.5 Hz, 1H), 7.02–6.97 (m, 2H), 4.85 (dd, J = 17.4, 11.7 Hz, 1H), 1.07 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8 (t, J = 28.6 Hz), 153.7, 151.3, 146.1, 133.8, 133.3, 130.7, 129.8 (t, J = 3.7 Hz), 129.4, 128.3, 127.3, 126.4, 123.1, 118.2 (t, J = 258.4 Hz), 116.7, 116.3, 116.2 (d, J = 4.9 Hz), 115.2 (d, J = 4.9 Hz), 44.9 (t, J = 23.9 Hz), 34.1, 31.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.31 (dd, J = 260.5, 12.2 Hz, 1F), -106.33 (dd, J = 260.2, 17.3 Hz, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{25}H_{22}F_2O_2Na$ 415.1480, found 415.1490.



3d

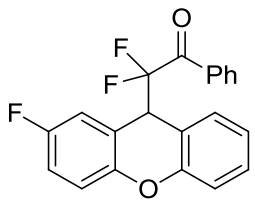
2,2-Difluoro-2-(2-methoxy-9*H*-xanthen-9-yl)-1-phenylethanone (3d). Yellow oil; 45.4 mg, 62% yield, PE/EA = 20/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, J =8.3 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.37–7.26 (m, 4H), 7.13 (d, J = 8.6 Hz, 1H), 7.09 (d, J = 8.8 Hz, 1H), 7.03 (t, J = 7.4 Hz, 1H), 6.87–6.82 (m, 2H), 4.92 (t, J = 14.2 Hz, 1H), 3.72 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.0 (t, J = 29.2 Hz), 155.3, 153.8, 147.6, 134.0, 133.2 (t, J = 1.9 Hz), 130.6, 129.8 (t, J

= 3.7 Hz), 129.4, 128.3, 123.0, 118.1 (t, *J* = 260.8 Hz), 117.6, 116.78 (t, *J* = 2.8 Hz), 116.77, 115.78 (t, *J* = 2.8 Hz), 115.77, 114.7, 55.7, 44.8 (t, *J* = 23.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.66 (dd, *J* = 265.8, 13.9 Hz, 1F), -103.40 (dd, *J* = 265.5, 14.5 Hz, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{22}H_{16}F_2O_3Na$ 389.0960, found 389.0971.



3e

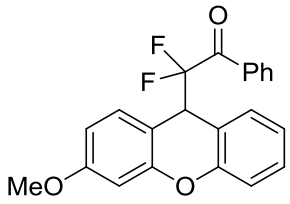
2-(2-Bromo-9*H*-xanthen-9-yl)-2,2-difluoro-1-phenylethanone (3e). Yellow oil; 78.0 mg, 94% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 7.2 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 1H), 7.47 (s, 1H), 7.39 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.33–7.26 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.06 (d, *J* = 6.2 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 4.92 (t, *J* = 13.2, Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.2 (t, *J* = 29.7 Hz), 153.1, 152.6, 134.1, 133.2, 132.9 (t, *J* = 2.0 Hz), 132.4, 130.6, 129.8 (t, *J* = 3.7 Hz), 129.7, 128.4, 123.6, 118.5, 118.4 (t, *J* = 3.0 Hz), 117.8 (t, *J* = 259.3 Hz), 116.9, 115.6 (t, *J* = 3.3 Hz), 115.3, 44.1 (t, *J* = 23.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.82 (dd, *J* = 271.5, 13.4 Hz, 1F), -103.73 (dd, *J* = 271.3, 14.9 Hz, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{21}H_{13}BrF_2O_2Na$ 436.9959, found 436.9966.



3f

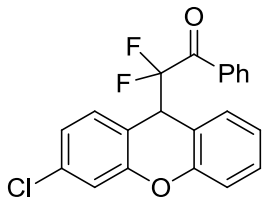
2,2-Difluoro-2-(2-fluoro-9*H*-xanthen-9-yl)-1-phenylethanone (3f). Yellow solid; 51.7 mg, 73% yield, PE/EA = 30/1 as the eluent; mp = 77–78 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.0

Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.37–7.27 (m, 4H), 7.16–6.98 (m, 5H), 4.95 (t, *J* = 14.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.4 (t, *J* = 29.4 Hz), 158.3 (d, *J* = 241.6 Hz), 153.5, 149.7 (d, *J* = 2.5 Hz), 134.1, 133.0 (t, *J* = 2.0 Hz), 130.6, 129.8 (t, *J* = 3.7 Hz), 129.6, 128.4, 123.1, 117.9 (d, *J* = 8.4 Hz), 117.8 (t, *J* = 259.5 Hz), 117.7 (t, *J* = 3.0 Hz), 116.9, 116.8 (d, *J* = 23.8 Hz), 116.4 (d, *J* = 23.5 Hz), 115.4 (t, *J* = 3.0 Hz), 44.4 (t, *J* = 23.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.16 (dd, *J* = 271.0, 13.7 Hz, 1F), -103.40 (dd, *J* = 270.7, 14.3 Hz, 1F), -120.03 – -120.09 (m, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{21}H_{13}F_3O_2Na$ 377.0760, found 377.0763.



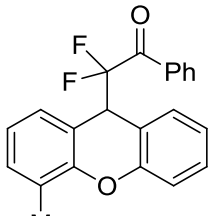
3g

2,2-Difluoro-2-(3-methoxy-9*H*-xanthen-9-yl)-1-phenylethanone (3g). Yellow oil; 61.5 mg, 84% yield, PE/EA = 20/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.50 (t, *J* = 7.4 Hz 1H), 7.34–7.27 (m, 4H), 7.20 (d, *J* = 8.5 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 2.5 Hz, 1H), 6.63 (dd, *J* = 8.5, 2.6 Hz, 1H), 4.90 (t, *J* = 14.1 Hz, 1H), 3.79 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1 (t, *J* = 29.6 Hz), 160.7, 154.4, 153.4, 133.9, 133.2 (t, *J* = 2.0 Hz), 131.1, 130.6, 129.8 (t, *J* = 3.7 Hz), 129.4, 128.3, 123.2, 118.1 (t, *J* = 258.5 Hz), 116.8, 116.5 (t, *J* = 3.0 Hz), 110.1, 108.2 (t, *J* = 3.3 Hz), 101.8, 55.4, 43.9 (t, *J* = 23.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.87 (dd, *J* = 265.5, 14.1 Hz, 1F), -103.65 (dd, *J* = 264.7, 14.3 Hz, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{22}H_{16}F_2O_3Na$ 389.0960, found 389.0968.



3h

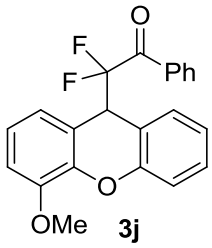
2-(3-Chloro-9*H*-xanthen-9-yl)-2,2-difluoro-1-phenylethanone (3h). Yellow solid; 57.1 mg, 77% yield, PE/EA = 30/1 as the eluent; mp = 75–76 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.36–7.25 (m, 5H), 7.17 (d, J = 2.1 Hz, 1H), 7.14 (d, J = 7.4 Hz 1H), 7.08–7.04 (m, 2H), 4.94 (t, J = 14.0 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.5 (t, J = 29.7 Hz), 154.0, 153.1, 134.9, 134.1, 132.9 (t, J = 2.1 Hz), 131.5, 130.6, 129.8 (t, J = 3.7 Hz), 129.6, 128.4, 123.6, 123.5, 117.8 (t, J = 260.9 Hz), 117.2, 116.9, 115.9 (t, J = 3.2 Hz), 115.0 (t, J = 3.1 Hz), 43.9 (t, J = 23.8 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.38 (dd, J = 270.5, 13.8 Hz, 1F), -103.46 (dd, J = 270.6, 14.6 Hz, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{21}H_{13}ClF_2O_2Na$ 393.0464, found 393.0468.



3i

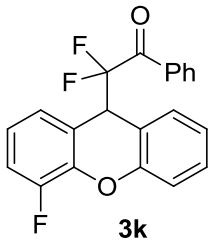
2,2-Difluoro-2-(4-methyl-9*H*-xanthen-9-yl)-1-phenylethanone (3i). Yellow oil; 52.5 mg, 75% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, J = 7.5 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.34–7.28 (m, 4H), 7.19 (dd, J = 8.6, 1.3 Hz, 1H), 7.13 (t, J = 7.2 Hz, 2H), 7.04 (td, J = 7.4, 1.3 Hz, 1H), 6.95 (t, J = 7.5 Hz, 1H), 4.94 (t, J = 14.4 Hz, 1H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1 (t, J = 29.1 Hz), 153.7, 151.7, 133.9, 133.3 (t, J = 1.9 Hz), 130.8, 130.5, 129.8 (t, J = 3.7 Hz), 129.3, 128.3, 128.1, 126.2, 123.2, 122.7, 118.2 (t, J = 260.7 Hz),

117.0, 116.5 (t, *J* = 3.0 Hz), 115.8 (t, *J* = 3.0 Hz), 44.7 (t, *J* = 23.8 Hz), 15.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.06 (dd, *J* = 264.0, 14.6 Hz, 1F), -103.85 (dd, *J* = 263.6, 14.6 Hz, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{22}H_{16}F_2O_2Na$ 373.1011, found 373.1016.



3j

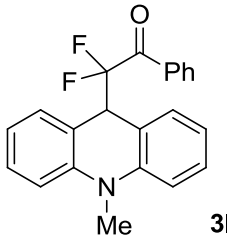
2,2-Difluoro-2-(4-methoxy-9*H*-xanthen-9-yl)-1-phenylethanone (3j). Yellow oil; 41.7 mg, 57% yield, PE/EA = 20/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 6.8 Hz, 2H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.34–7.26 (m, 5H), 7.05 (t, *J* = 9.6 Hz, 1H), 6.99 (t, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 8.5 Hz, 2H), 4.97 (t, *J* = 14.3 Hz, 1H), 3.93 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.1 (t, *J* = 29.6 Hz), 153.4, 148.2, 143.2, 133.9, 133.2 (t, *J* = 1.7 Hz), 130.5, 129.8 (t, *J* = 3.7 Hz), 129.4, 128.3, 123.4, 122.9, 122.2, 118.0 (t, *J* = 260.5 Hz), 117.1, 116.1 (t, *J* = 3.3 Hz), 111.8, 56.2, 44.4 (t, *J* = 23.9 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.34 (d, *J* = 14.1 Hz, 2F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{22}H_{16}F_2O_3Na$ 389.0960, found 389.0964.



3k

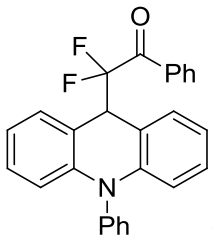
2,2-Difluoro-2-(4-fluoro-9*H*-xanthen-9-yl)-1-phenylethanone (3k). Yellow oil; 45.3 mg, 64% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.1 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.37–7.29 (m, 4H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.15–7.06 (m, 3H), 7.02–6.96 (m, 1H), 5.01 (t, *J* = 14.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.7 (t, *J* = 29.5 Hz), 152.9, 151.2

(d, *J* = 248.5 Hz), 142.0 (d, *J* = 11.6 Hz), 134.1, 133.0 (t, *J* = 1.7 Hz), 130.7, 129.8 (t, *J* = 3.7 Hz), 129.7, 128.5, 125.6 (d, *J* = 3.8 Hz), 123.9, 122.8 (d, *J* = 7.2 Hz), 119.0 (t, *J* = 2.9 Hz), 117.9 (t, *J* = 259.3 Hz), 117.2, 116.2 (d, *J* = 17.5 Hz), 115.9 (t, *J* = 2.9 Hz), 44.1 (t, *J* = 23.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.57 (dd, *J* = 268.5, 14.1 Hz, 1F), -103.43 (dd, *J* = 268.5, 14.2 Hz, 1F), -135.017 – -135.065 (m, 1F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{21}H_{13}F_3O_2Na$ 377.0760, found 377.0762.



3l

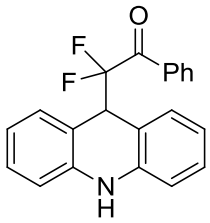
2,2-Difluoro-2-(10-methyl-9,10-dihydroacridin-9-yl)-1-phenylethanone (3l). Yellow solid; 67.0 mg, 96% yield, PE/EA = 30/1 as the eluent; mp = 125–126 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48–7.39 (m, 3H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.29–7.24 (m, 2H), 7.21 (t, *J* = 8.4 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 2H), 6.76 (d, *J* = 8.2 Hz, 2H), 4.88 (t, *J* = 13.6 Hz, 1H), 3.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.1 (t, *J* = 28.0 Hz), 143.3, 133.4, 133.3, 130.5, 129.6 (t, *J* = 3.7 Hz), 128.8, 127.9, 120.8, 118.7 (t, *J* = 259.8 Hz), 117.8 (t, *J* = 3.3 Hz), 112.7, 49.7 (t, *J* = 24.6 Hz), 32.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.67 (d, *J* = 13.6 Hz, 2F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{22}H_{17}F_2NONa$ 372.1170, found 372.1179.



3m

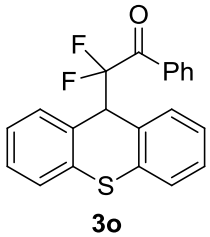
2,2-Difluoro-1-phenyl-2-(10-phenyl-9,10-dihydroacridin-9-yl)ethanone (3m). Brown solid; 42.7 mg, 52% yield, PE/EA = 30/1 as the eluent; mp = 102–103 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$)

δ 7.59–7.52 (m, 4H), 7.50–7.44 (m, 2H), 7.31 (d, J = 7.5 Hz, 2H), 7.25 (d, J = 9.2 Hz, 2H), 7.17 (d, J = 7.5 Hz, 2H), 7.05 (t, J = 7.0 Hz, 2H), 6.91 (t, J = 6.9 Hz, 2H), 6.30 (d, J = 8.3 Hz, 2H), 5.06 (t, J = 14.3 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.4 (t, J = 28.9 Hz), 143.0, 140.1, 133.6, 133.5, 130.80, 130.78, 130.7, 129.8 (t, J = 3.4 Hz), 128.5, 128.4, 128.2, 120.8, 118.6 (t, J = 260.5 Hz), 114.8 (t, J = 2.9 Hz), 114.5, 48.2 (t, J = 23.5 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.99 (d, J = 14.1 Hz, 2F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{27}H_{19}F_2NONa$ 434.1327, found 434.1331.



3n

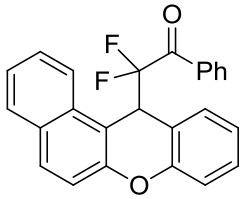
2-(9,10-Dihydroacridin-9-yl)-2,2-difluoro-1-phenylethanone (3n). Brown solid; 40.2 mg, 60% yield, PE/EA = 20/1 as the eluent; mp = 133–134 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.9 Hz, 2H), 7.46 (t, J = 7.5 Hz, 1H), 7.29–7.21 (m, 4H), 7.16 (t, J = 7.7 Hz, 2H), 6.88 (t, J = 7.5 Hz, 2H), 6.72 (d, J = 8.1 Hz, 2H), 6.19 (br, 1H), 4.98 (t, J = 14.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.8 (t, J = 28.7 Hz), 140.7, 133.6, 133.5, 130.9, 129.7 (t, J = 3.7 Hz), 128.8, 128.1, 120.9, 118.7 (t, J = 260.2 Hz), 114.1, 113.8 (t, J = 3.1 Hz), 47.7 (t, J = 23.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.89 (d, J = 14.7 Hz, 2F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{21}H_{15}F_2NONa$ 358.1014, found 358.1022.



3o

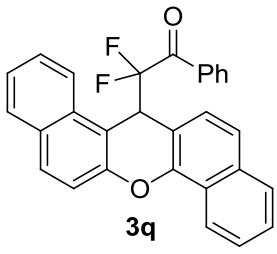
2,2-Difluoro-1-phenyl-2-(9*H*-thioxanthen-9-yl)ethanone (3o). White solid; 39.4 mg, 56% yield,

PE/EA = 30/1 as the eluent; mp = 96–97 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 2H), 7.47 (t, J = 7.5 Hz, 1H), 7.40–7.32 (m, 4H), 7.29–7.17 (m, 6H), 5.06 (t, J = 15.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.2 (t, J = 28.4 Hz), 134.3, 133.8, 133.3, 131.9, 129.8 (t, J = 3.9 Hz), 128.3, 128.2, 127.4, 126.7, 126.4, 119.3 (t, J = 262.3 Hz), 52.5 (t, J = 23.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -101.17 (d, J = 16.0 Hz, 2F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{21}H_{14}F_2NONa$ 375.0626, found 375.0630.



3p

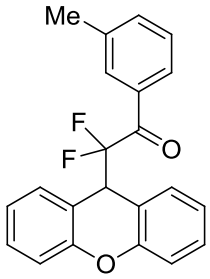
2-(12*H*-Benzo[*a*]xanthen-12-yl)-2,2-difluoro-1-phenylethanone (3p). Yellow solid; 74.1 mg, 96% yield, PE/EA = 30/1 as the eluent; mp = 97–98 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, J = 8.6 Hz, 1H), 7.88–7.77 (m, 2H), 7.60–7.55 (m, 3H), 7.46–7.36 (m, 4H), 7.34–7.28 (m, 1H), 7.26–7.21 (m, 3H), 7.06 (t, J = 7.5 Hz, 1H), 5.76 (dd, J = 19.4, 7.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.4 (dd, J = 30.8, 27.7 Hz), 153.6, 152.2, 133.9, 133.2, 132.5, 130.7, 130.4, 130.2, 129.7 (dd, J = 4.8, 2.7 Hz), 129.4, 128.5, 128.2, 127.0, 124.5, 123.7, 123.0, 118.9 (t, J = 262.3 Hz), 117.8, 116.8, 116.7 (dd, J = 5.9, 2.0 Hz), 109.3, 40.5 (t, J = 24.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.16 (dd, J = 263.1, 7.4 Hz, 1F), -107.40 (dd, J = 262.9, 19.4 Hz, 1F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{25}H_{16}F_2O_2Na$ 409.1011, found 409.1018.



3q

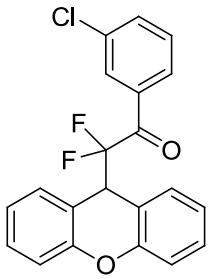
2-(14*H*-Dibenzo[*a,h*]xanthen-14-yl)-2,2-difluoro-1-phenylethanone (3q). White solid; 60.2 mg,

69% yield, PE/EA = 30/1 as the eluent; mp = 173–174 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.48 (d, J = 8.3 Hz, 1H), 8.19 (d, J = 8.6 Hz, 1H), 7.89–7.79 (m, 3H), 7.62–7.54 (m, 7H), 7.48–7.42 (m, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.16 (t, J = 7.8 Hz, 2H), 5.89 (dd, J = 18.4, 7.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 191.3 (t, J = 30.4 Hz), 152.2, 149.4, 134.0, 133.8, 133.1, 132.5, 130.9, 130.2, 129.6 (dd, J = 4.2, 3.2 Hz), 128.5, 128.1, 127.6, 127.1, 127.0, 126.9, 126.2, 124.6, 124.1, 123.3, 123.1, 121.7, 119.0 (t, J = 258.7 Hz), 117.8, 110.7 (dd, J = 5.4, 2.4 Hz), 109.5 (t, J = 2.0 Hz), 40.8 (t, J = 24.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -97.45 (dd, J = 263.5, 7.3 Hz, 1F), -106.64 (dd, J = 263.5, 18.3 Hz, 1F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{29}H_{18}F_2O_2Na$ 459.1167, found 459.1172.



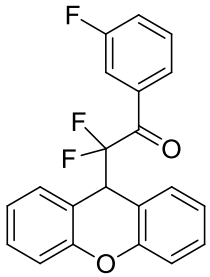
3r

2,2-Difluoro-1-(*m*-tolyl)-2-(9*H*-xanthen-9-yl)ethanone (3r). White solid; 49.7 mg, 71% yield, PE/EA = 30/1 as the eluent; mp = 67–68 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34 (d, J = 7.9 Hz, 1H), 7.29 (s, 1H), 7.21–7.09 (m, 5H), 7.08–7.00 (m, 3H), 6.92 (t, J = 7.4 Hz, 2H), 4.82 (t, J = 14.3 Hz, 1H), 2.14 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 119.2 (t, J = 29.2 Hz), 153.5, 138.1, 134.7, 133.1, 130.7, 130.3 (t, J = 3.8 Hz), 129.4, 128.2, 127.0 (t, J = 3.8 Hz), 123.2, 118.1 (t, J = 260.7 Hz), 116.8, 116.3 (t, J = 3.2 Hz), 44.4 (t, J = 23.9 Hz), 21.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.06 (d, J = 14.0 Hz, 2F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{22}H_{16}F_2O_2Na$ 373.1011, found 373.1018.



3s

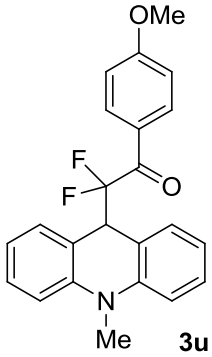
1-(3-Chlorophenyl)-2,2-difluoro-2-(9*H*-xanthen-9-yl)ethanone (3s). Yellow solid; 60.8 mg, 82% yield, PE/EA = 30/1 as the eluent; mp = 87–88 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.46 (d, J = 8.1 Hz, 1H), 7.34–7.30 (m, 4H), 7.23 (t, J = 7.9 Hz, 1H), 7.15 (d, J = 7.3 Hz, 2H), 7.07 (t, J = 7.5 Hz, 2H), 4.93 (t, J = 14.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.0 (t, J = 29.9 Hz), 153.4, 134.6, 134.6, 133.9, 130.6, 129.73 (t, J = 3.8 Hz), 129.66, 129.6, 127.8 (t, J = 3.8 Hz), 123.4, 117.9 (t, J = 260.4 Hz), 116.9, 116.0 (t, J = 3.4 Hz), 44.6 (t, J = 23.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.10 (d, J = 14.6 Hz, 2F); **HRMS (ESI)** *m/z* calcd for $[M + Na]^+$ $C_{21}H_{13}ClF_2O_2Na$ 393.0464, found 393.0470.



3t

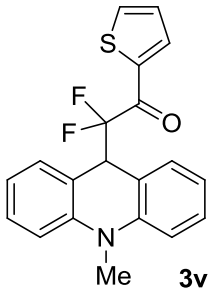
2,2-Difluoro-1-(3-fluorophenyl)-2-(9*H*-xanthen-9-yl)ethanone (3t). Yellow solid; 41.1 mg, 58% yield, PE/EA = 30/1 as the eluent; mp = 49–50 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (d, J = 7.8 Hz, 1H), 7.34–7.24 (m, 6H), 7.20 (td, J = 8.1, 1.6 Hz, 1H), 7.15 (d, J = 8.6 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 4.93 (t, J = 14.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (td, J = 30.0, 2.3 Hz), 162.3 (d, J = 248.0 Hz), 153.5, 134.9 (d, J = 7.1 Hz), 130.6, 130.0 (d, J = 7.8 Hz), 129.7, 125.6 (q, J = 3.8 Hz), 123.4, 121.1 (d, J = 21.6 Hz), 118.0 (t, J = 260.4 Hz), 116.9, 116.6 (dt, J = 23.5, 3.6

Hz), 116.1 (t, J = 3.2 Hz), 44.6 (t, J = 23.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.14 (d, J = 14.1 Hz, 2F), -111.53 – -111.64 (m, 1F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{21}H_{13}F_3O_2Na$ 377.0760, found 377.0766.



3u

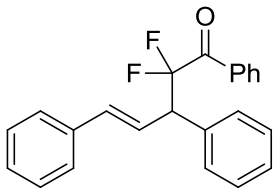
2,2-Difluoro-1-(4-methoxyphenyl)-2-(10-methyl-9,10-dihydroacridin-9-yl)ethanone (3u). Brown solid; 70.5 mg, 93% yield, PE/EA = 30/1 as the eluent; mp = 95–96 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 7.4 Hz, 2H), 7.29–7.24 (m, 2H), 6.98 (t, J = 6.9 Hz, 2H), 6.78 (d, J = 8.2 Hz, 2H), 6.68 (d, J = 9.0 Hz, 2H), 4.86 (t, J = 13.6 Hz, 1H), 3.81 (s, 3H), 3.06 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.5 (t, J = 27.2 Hz), 163.6, 143.3, 132.2 (t, J = 4.1 Hz), 130.5, 128.8, 126.5, 120.7, 118.9 (t, J = 258.0 Hz), 117.9 (t, J = 3.5 Hz), 113.2, 112.6, 55.4, 49.7 (t, J = 24.8 Hz), 32.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.61 (d, J = 14.0 Hz, 2F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{23}H_{19}F_2NO_2Na$ 402.1276, found 402.1278.



3v

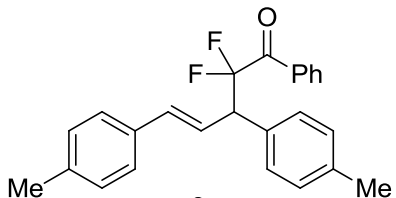
2,2-Difluoro-2-(10-methyl-9,10-dihydroacridin-9-yl)-1-(thiophen-2-yl)ethanone (3v). Brown oil; 63.2 mg, 89% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, J = 5.0 Hz, 1H), 7.34 (d, J = 7.5 Hz, 2H), 7.26 (t, J = 7.8 Hz, 2H), 6.99 (t, J = 6.9 Hz, 2H), 6.92 (d, J

= 2.4 Hz, 1H), 6.82 (dd, *J* = 4.9, 3.9 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 2H), 4.82 (t, *J* = 13.1 Hz, 1H), 3.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 181.6 (t, *J* = 30.0 Hz), 143.2, 140.2, 135.20 (t, *J* = 5.9 Hz), 135.18, 130.5, 128.9, 128.3, 120.8, 118.1 (t, *J* = 257.4 Hz), 117.7 (t, *J* = 3.5 Hz), 112.6, 50.0 (t, *J* = 24.9 Hz), 32.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -104.51 (d, *J* = 12.8 Hz, 2F); **HRMS (ESI)** *m/z* calcd for $[M + Na]^+$ $C_{20}H_{15}F_2NOSNa$ 378.0735, found 378.0744.



3w

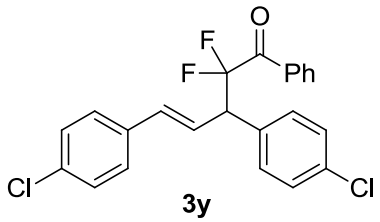
(*E*)-2,2-Difluoro-1,3,5-triphenylpent-4-en-1-one (3w). White solid; 29.8 mg, 43% yield, PE/EA = 30/1 as the eluent; mp = 86–87 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 – 7.94 (m, 2H), 7.62 – 7.58 (m, 1H), 7.45 (t, *J* = 7.1 Hz, 2H), 7.39 – 7.28 (m, 9H), 7.26 – 7.23 (m, 1H), 6.55 (s, 2H), 4.49 (t, *J* = 16.2 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.9 (t, *J* = 29.8 Hz), 136.5, 135.4, 135.3, 134.0, 132.9, 129.8 (d, *J* = 3.4 Hz), 129.6, 128.6 (t, *J* = 7.6 Hz), 127.9, 126.5, 123.6 (t, *J* = 3.9 Hz), 118.7 (t, *J* = 258.9 Hz), 53.3 (t, *J* = 22.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.53 (dd, *J* = 275.3, 16.9 Hz, 1F), -103.38 (dd, *J* = 275.3, 16.7 Hz, 1F); **HRMS (ESI)** *m/z* $[M + Na]^+$ calcd for $C_{23}H_{18}F_2ONa$ 371.1223, found 371.1216. Physical and spectral properties of this material were identical to those previously reported in literature.[7]



3x

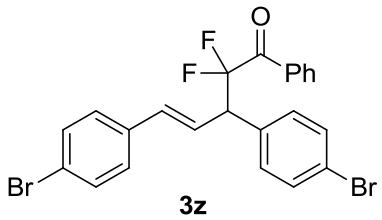
(*E*)-2,2-Difluoro-1-phenyl-3,5-di-*p*-tolylpent-4-en-1-one (3x). White solid; 42.1 mg, 56% yield,

PE/EA = 30/1 as the eluent; mp = 94–95 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.26 – 7.21 (m, 4H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.50 – 6.41 (m, 2H), 4.45 – 4.36 (m, 1H), 2.30 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.1 (t, *J* = 29.7 Hz), 137.8, 137.6, 135.0, 134.0, 133.9, 133.0, 132.5, 129.9 (t, *J* = 3.4 Hz), 129.5, 129.4, 129.3, 128.6, 126.5, 122.7 (t, *J* = 4.2 Hz), 118.8 (t, *J* = 258.6 Hz), 53.1 (t, *J* = 22.0 Hz), 21.2 (d, *J* = 10.7 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.19 (d, *J* = 16.2 Hz, 2F); **HRMS (ESI)** *m/z* $[M + Na]^+$ alcd for $C_{25}H_{22}F_2ONa$ 399.1536, found 399.1542. Physical and spectral properties of this material were identical to those previously reported in literature.[7]



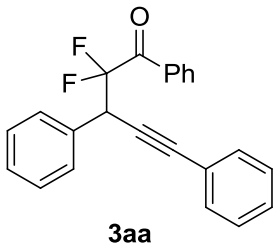
3y

(*E*)-3,5-Bis(4-chlorophenyl)-2,2-difluoro-1-phenylpent-4-en-1-one (3y). White solid; 31.6 mg, 38% yield, PE/EA = 30/1 as the eluent; mp = 116–117 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.62 (dd, *J* = 10.6, 4.3 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.32 (m, 4H), 7.28 (s, 4H), 6.57 – 6.49 (m, 2H), 4.54 (tdd, *J* = 16.0, 4.5, 2.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.2 (t, *J* = 29.9 Hz), 134.7, 134.3, 134.2, 133.8, 133.7, 133.6, 132.5 (d, *J* = 1.7 Hz), 130.9, 129.8 (t, *J* = 3.3 Hz), 128.8, 128.6, 127.6, 123.7 (t, *J* = 4.1 Hz), 118.3 (t, *J* = 259.4 Hz), 52.4 (t, *J* = 22.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.01 (dd, *J* = 278.9, 16.1 Hz, 1F), -102.84 (dd, *J* = 278.8, 15.6 Hz, 1F); **HRMS (ESI)** *m/z* $[M + Na]^+$ calcd for $C_{23}H_{16}Cl_2F_2ONa$ 416.0546, found 416.0551. Physical and spectral properties of this material were identical to those previously reported in literature.[7]



3z

(*E*)-3,5-Bis(4-bromophenyl)-2,2-difluoro-1-phenylpent-4-en-1-one (3z). White solid; 41.5 mg, 41% yield, PE/EA = 30/1 as the eluent; mp = 143–144 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 2H), 7.64 – 7.60 (m, 1H), 7.48 (t, *J* = 8.1 Hz, 4H), 7.44 – 7.41 (m, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.23 – 7.19 (m, 2H), 6.55 – 6.45 (m, 2H), 4.50 (td, *J* = 16.1, 6.5 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.4 (t, *J* = 30.0 Hz), 135.3, 134.5, 134.4, 134.3 (t, *J* = 2.1 Hz), 132.6, 131.9, 131.8, 131.4, 130.0 (t, *J* = 3.3 Hz), 128.8, 128.1, 124.0 (t, *J* = 4.2 Hz), 122.2, 122.0, 118.4 (t, *J* = 259.5 Hz), 52.6 (t, *J* = 22.1 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.01 (dd, *J* = 279.7, 16.4 Hz, 1F), -102.81 (dd, *J* = 280.0, 16.2 Hz, 1F); **HRMS (ESI)** *m/z* $[M + Na]^+$ calcd for $C_{23}H_{16}Br_2F_2ONa$ 528.9413, found 528.9420. Physical and spectral properties of this material were identical to those previously reported in literature.[7]

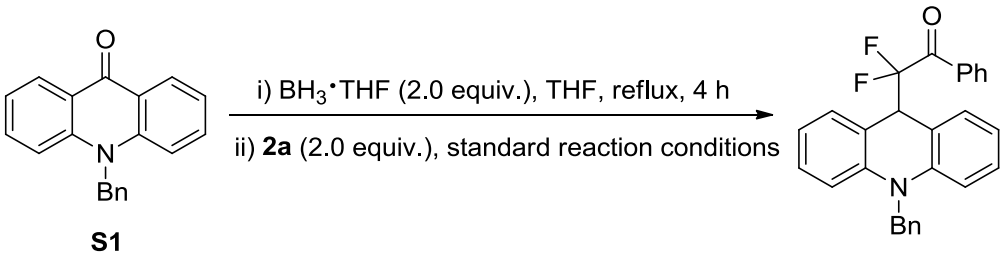


3aa

2,2-Difluoro-1,3-diphenylpent-4-yn-1-one (3aa): Yellow oil; 33.2 mg, 48% yield, PE/EA = 30/1 as the eluent; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.57 (dd, *J* = 14.0, 6.8 Hz, 3H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.43 – 7.37 (m, 5H), 7.32 – 7.26 (m, 3H), 4.89 (dd, *J* = 18.3, 10.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6 (dd, *J* = 30.2, 28.6 Hz), 134.2, 133.1, 132.9 (t, *J* = 1.7 Hz), 132.4 (d, *J* = 1.9 Hz), 131.7, 130.1, 130.0 (dd, *J* = 3.9, 3.2 Hz), 122.4, 116.9 (dd, *J* = 263.3, 259.9 Hz), 86.2, 83.4 (dd, *J* = 9.4, 2.2 Hz), 43.6 (dd, *J* = 27.4, 23.1 Hz); **^{19}F NMR** (376 MHz,

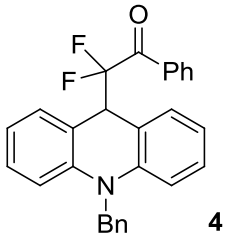
$CDCl_3$) δ -100.50 (dd, *J* = 267.7, 11.7 Hz, 1F), -105.72 (dd, *J* = 267.8, 20.0 Hz, 1F); **HRMS (ESI)** *m/z* $[M + Na]^+$ calcd for $C_{23}H_{16}F_2ONa$ 369.1067, found 369.1061. Physical and spectral properties of this material were identical to those previously reported in literature.[7]

Procedure for preparation of compound 4.



To a slurry of *N*-benzylacridine-9(10*H*)-one **SI** (142.5 mg, 0.5 mmol, 1.0 equiv) in THF (2 mL) BH_3•THF solution (1.0 M in THF; 1 mL, 1.0 mmol, 2.0 equiv) was added dropwise and the mixture was refluxed for 4 hours under Ar-atmosphere. Then the mixture was cooled to 0-5 ℃ and cautiously quenched by the addition of brine (5 mL) followed by 2 M aq. NaOH (1 mL). The organic layer was separated, and the aqueous layer was extracted with Et_2O (1 × 10 mL). The collected organic layers were dried over $MgSO_4$ and evaporated.[3]

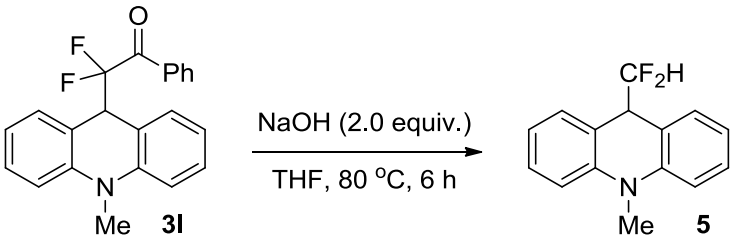
The obtained 10-benzyl-9,10-dihydroacridine without any further purification was transferred to a vial equipped with a magnetic stirring bar with HFIP (5.0 mL). **2a** (237 mg, 1.0 mmol, 2.0 equiv) and Na_2-eosin Y (34.5 mg, 0.05 mmol, 10 mol%) were added to the vial. The mixture was exposed to green LED (1.5 W) and stirred at room temperature under air for 6 h. Then the mixture was concentrated in vacuo, and purified by column chromatography on silica gel (PE/EA, 30:1) to afford the desired products **4** (182.8 mg, 86% yield) as a brown solid.



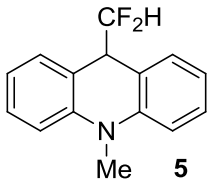
4

2-(10-Benzyl-9,10-dihydroacridin-9-yl)-2,2-difluoro-1-phenylethanone (4). Brown solid; 182.8 mg, 86% yield, PE/EA = 30/1 as the eluent; mp = 119–120 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50–7.43 (m, 3H), 7.33 (d, J = 6.8 Hz, 2H), 7.30–7.23 (m, 5H), 7.12 (t, J = 7.0 Hz, 2H), 7.07 (d, J = 6.6 Hz, 2H), 6.95 (t, J = 6.9 Hz, 2H), 6.62 (d, J = 8.3 Hz, 2H), 4.96 (t, J = 13.7 Hz, 1H), 4.76 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 190.0 (t, J = 28.0 Hz), 142.3, 136.5, 133.50, 133.45, 130.7, 129.7 (t, J = 3.7 Hz), 129.0, 128.8, 128.1, 127.0, 125.9, 121.0, 118.7 (t, J = 260.1 Hz), 117.1 (t, J = 3.0 Hz), 113.8, 50.9, 49.1 (t, J = 24.0 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -103.40 (d, J = 13.3 Hz, 2F); **HRMS (ESI)** *m*/*z* calcd for $[M + Na]^+$ $C_{28}H_{21}F_2NONa$ 448.1483, found 448.1494.

Procedure for preparation of compound 5.



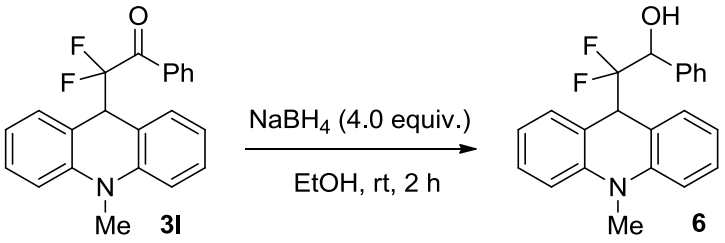
Compound **3l** (69.8 mg, 0.2 mmol, 1.0 equiv), NaOH (16 mg, 0.4 mmol, 2.0 equiv) and THF (2.0 mL) were added to a sealed tube. After the reaction was stirred at 80 ^{o}C for 6 h, the resulting mixture was cooled to room temperature, concentrated in vacuo, and purified by flash column chromatography on silica gel (PE/EA, 50:1) to give product **5** (30.9 mg, 63% yield) as a green solid.[8]



5

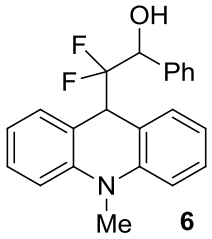
9-(Difluoromethyl)-10-methyl-9,10-dihydroacridine (5). Green solid; 30.9 mg, 63% yield, PE/EA = 50/1 as the eluent; mp = 89–90 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.34–7.24 (m, 4H), 7.05–6.92 (m, 4H), 5.60 (td, J = 57.1, 6.0 Hz, 1H), 4.30 (td, J = 12.9, 5.9 Hz, 1H), 3.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.8, 130.2, 128.6, 120.9, 119.0 (t, J = 4.0 Hz), 115.1 (t, J = 245.5 Hz), 112.4, 48.5 (t, J = 13.3 Hz), 33.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -120.83 (dd, J = 57.0, 13.1 Hz, 2F); **HRMS (ESI)** *m/z* calcd for $[M + H]^+$ $C_{15}H_{14}F_2N$ 246.1089, found 246.1088.

Procedure for preparation of compound 6.



3l **6**

An oven-dried Schlenk tube under an N_2 atmosphere was charged with compound **3l** (69.8 mg, 0.2 mmol, 1.0 equiv), EtOH (2.0 mL), $NaBH_4$ (30.4 mg, 0.8 mmol, 4.0 equiv). After the reaction was stirred at room temperature for 2 h, aqueous solution HCl (1 M, 2.0 mL) was added. The resulting mixture was extracted with ethyl acetate (2 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4, concentrated in vacuo, and purified by silica gel column chromatography (PE/EA, 10:1) to give product **6** (60.4 mg, 86% yield, >20:1 dr) as a white solid.[7]

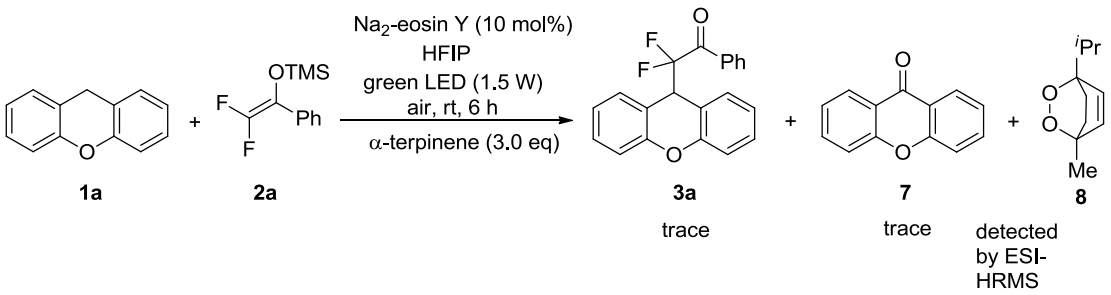


6

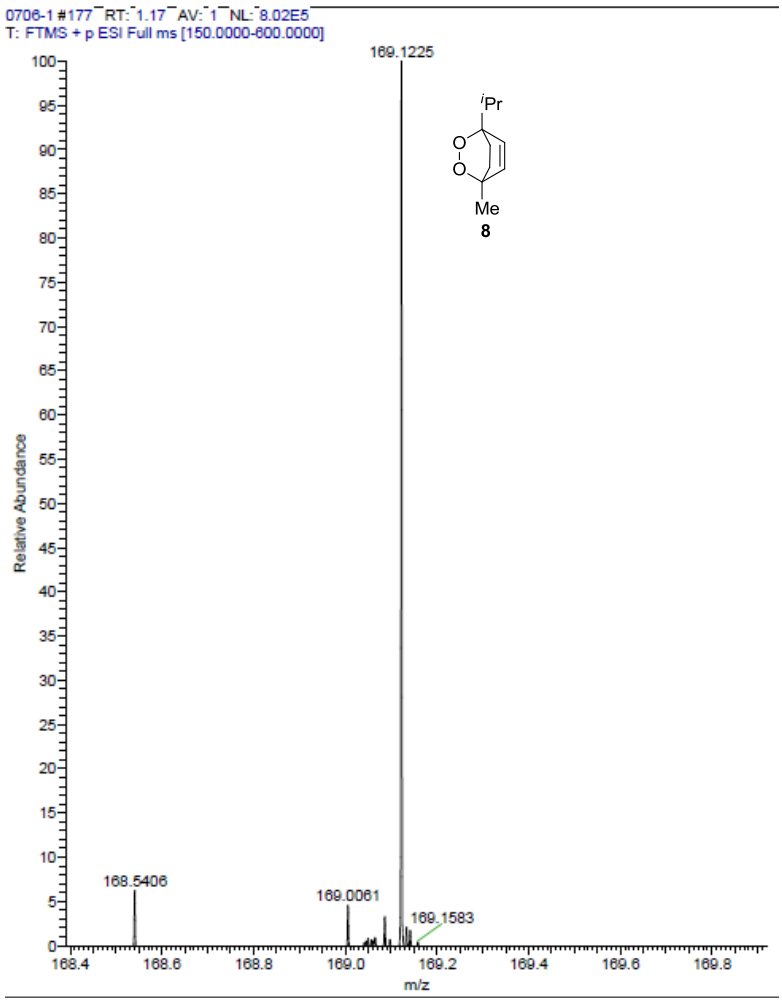
2,2-Difluoro-2-(10-methyl-9,10-dihydroacridin-9-yl)-1-phenylethanol (6). White solid; 60.4 mg, 86% yield, PE/EA = 10/1 as the eluent; mp = 174–175 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.5 Hz, 1H), 7.35–7.24 (m, 8H), 7.06–6.95 (m, 3H), 6.93 (d, J = 8.3 Hz, 1H), 4.84 (dd, J = 24.0, 7.0 Hz, 1H), 4.68 (d, J = 20.9 Hz, 1H), 3.38 (s, 3H), 2.36 (d, J = 5.1 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.6, 130.6 (d, J = 65.5 Hz), 128.5, 128.4, 128.1, 128.0, 121.9 (dd, J = 256.0, 251.3 Hz) , 120.5 (d, J = 10.2 Hz), 118.8 (dd, J = 59.1, 6.1 Hz), 112.6 (d, J = 30.4 Hz), 72.1 (dd, J = 33.4, 24.0 Hz), 47.2 (t, J = 24.9 Hz), 33.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.76 (dd, J = 252.2, 24.0 Hz, 1F), -117.68 (ddd, J = 252.1, 21.0, 7.0 Hz, 1F); **HRMS (ESI)** m/z calcd for $[M + Na]^+$ $C_{22}H_{19}F_2NONa$ 374.1327, found 374.1331.

The singlet oxygen capture experiment with α-terpinene

To a mixture of **1a** (0.2 mmol), **2a** (0.4 mmol, 2.0 equiv) and α-terpinene (0.6 mmol, 3.0 equiv) in HFIP (2.0 mL) was added Na_2-eosin Y (13.8 mg, 0.02 mmol, 10 mol%). The mixture was exposed to green LED (1.5 W) and stirred at room temperature under air for 6 h. As expected, only trace amount of **3a** and **7** were found and the adduct of singlet oxygen ($^1O_2$) with α-terpinene **8** is detected by ESI-HRMS.



1a + **2a** → **3a** trace + **7** trace + **8** detected by ESI-HRMS



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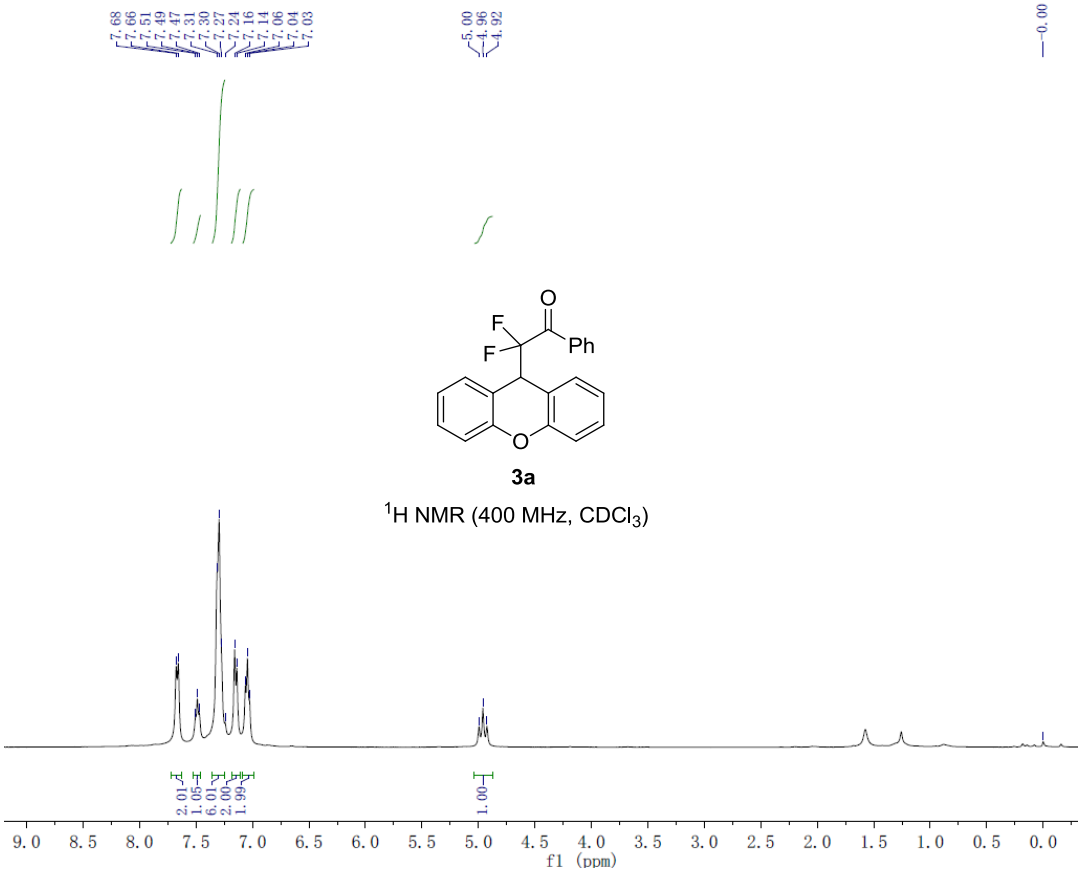
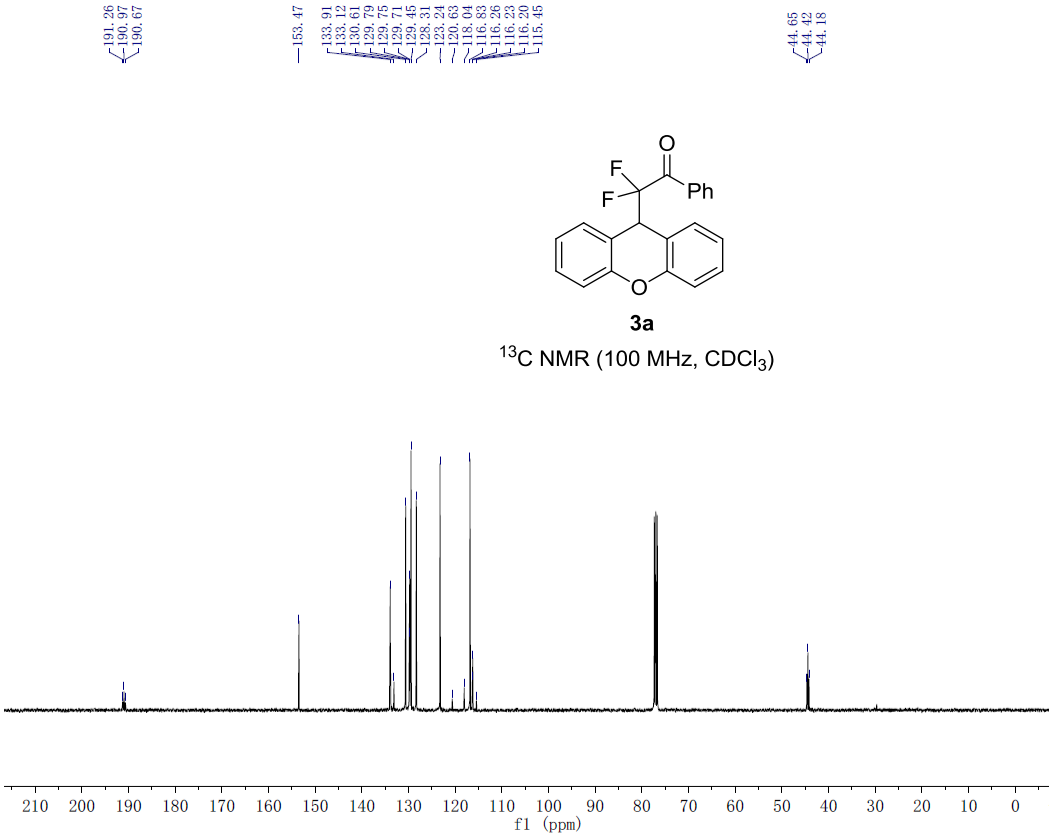
Copies of ^{1}H, ^{13}C and ^{19}F NMR spectra



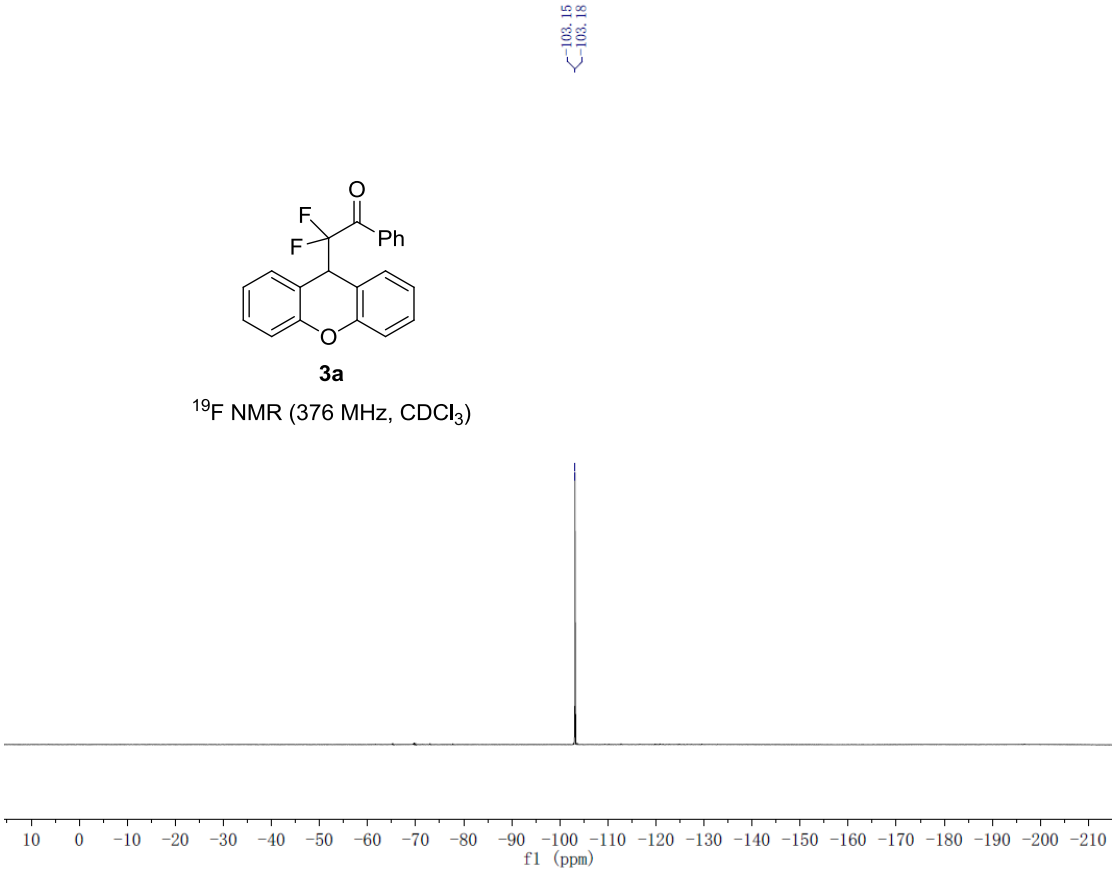
3a

^{1}H NMR (400 MHz, $CDCl_3$)



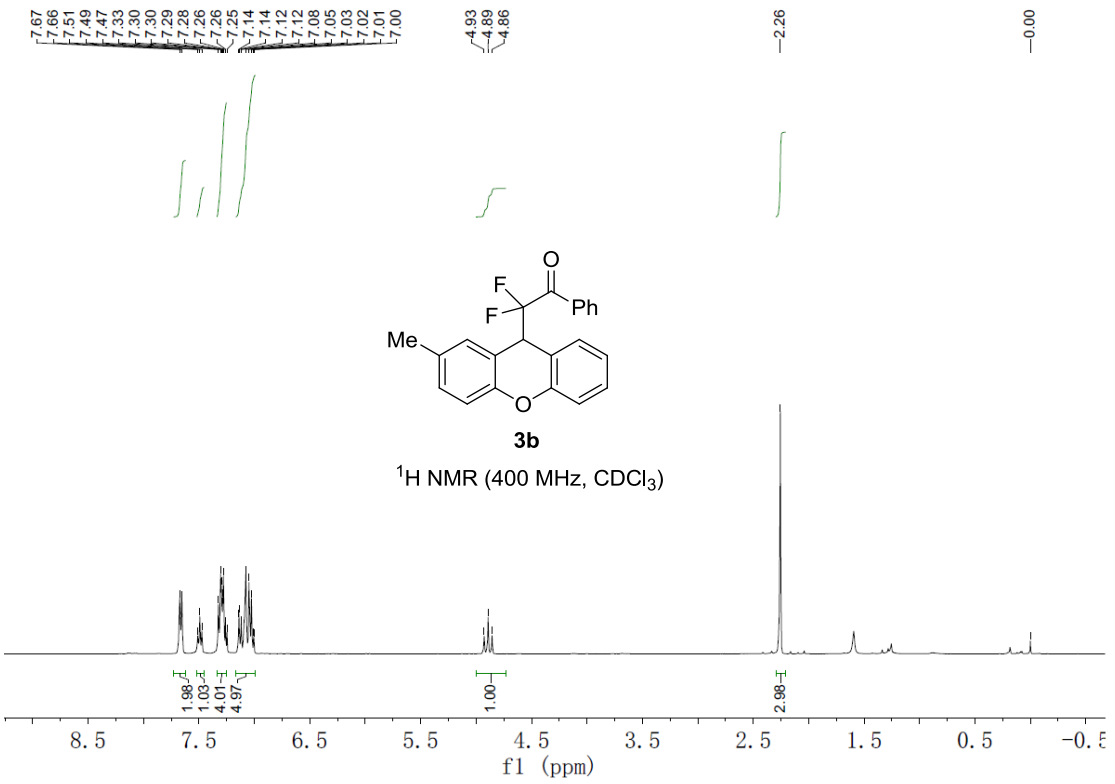
3a

^{13}C NMR (100 MHz, $CDCl_3$)



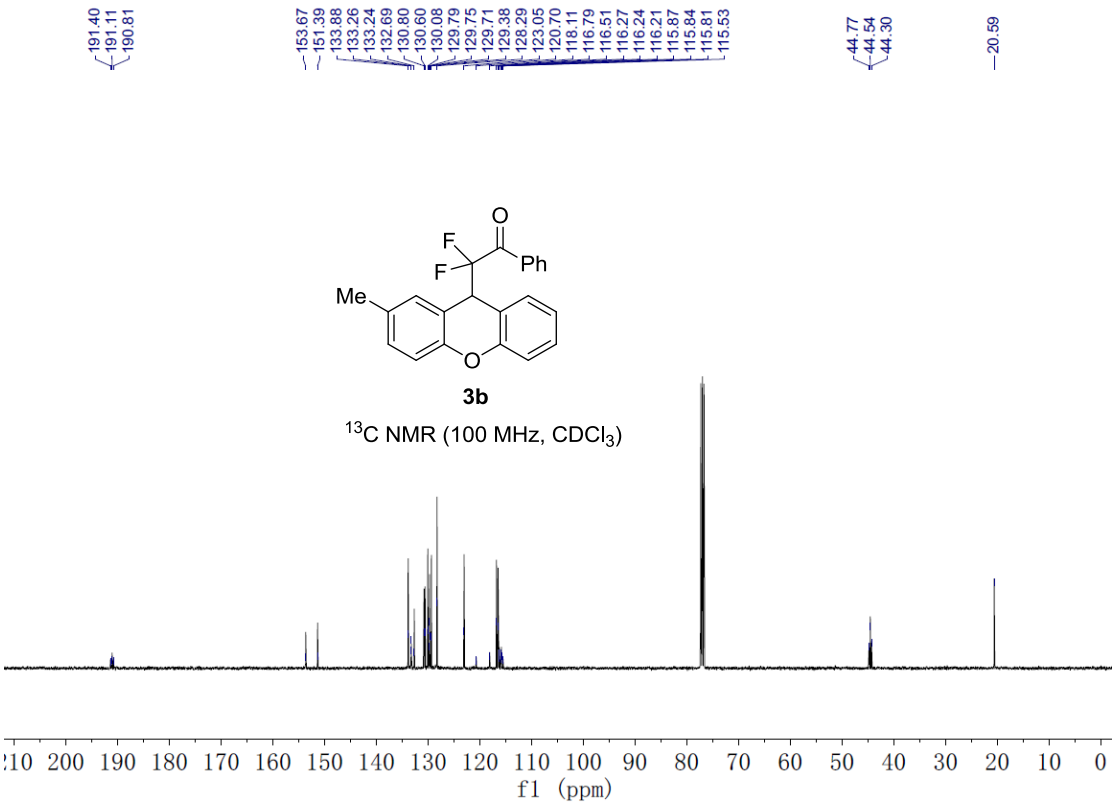
3a

^{19}F NMR (376 MHz, $CDCl_3$)



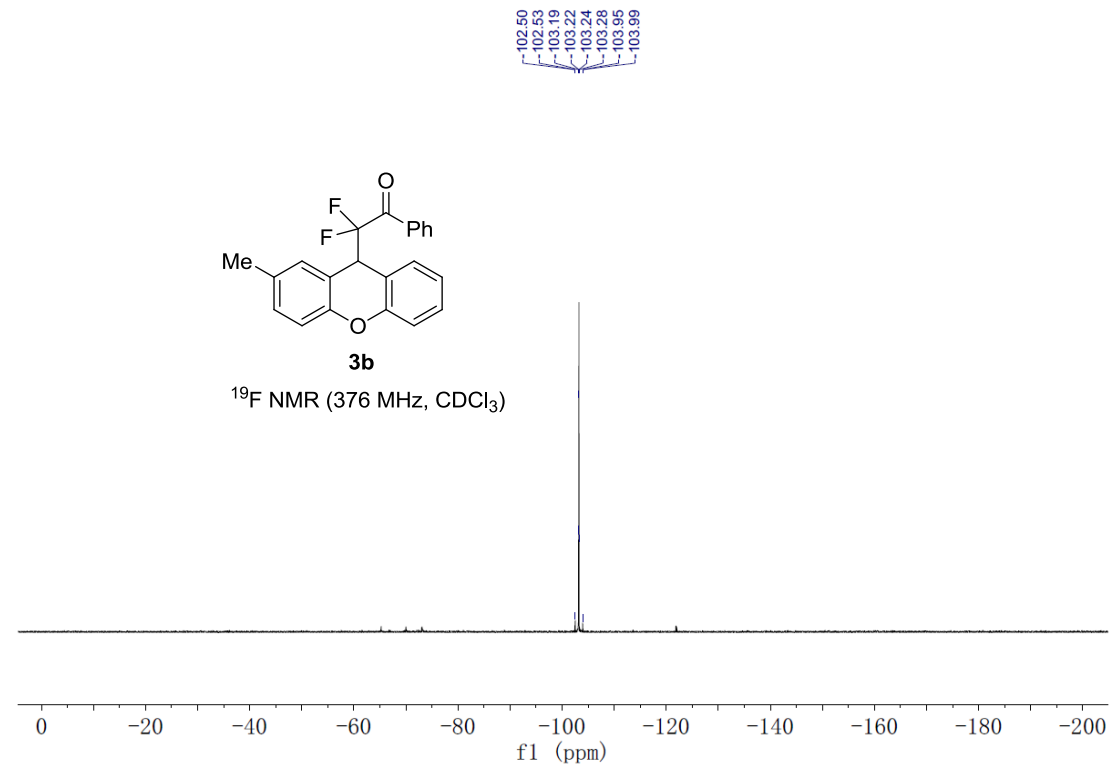
3b

^{1}H NMR (400 MHz, $CDCl_3$)



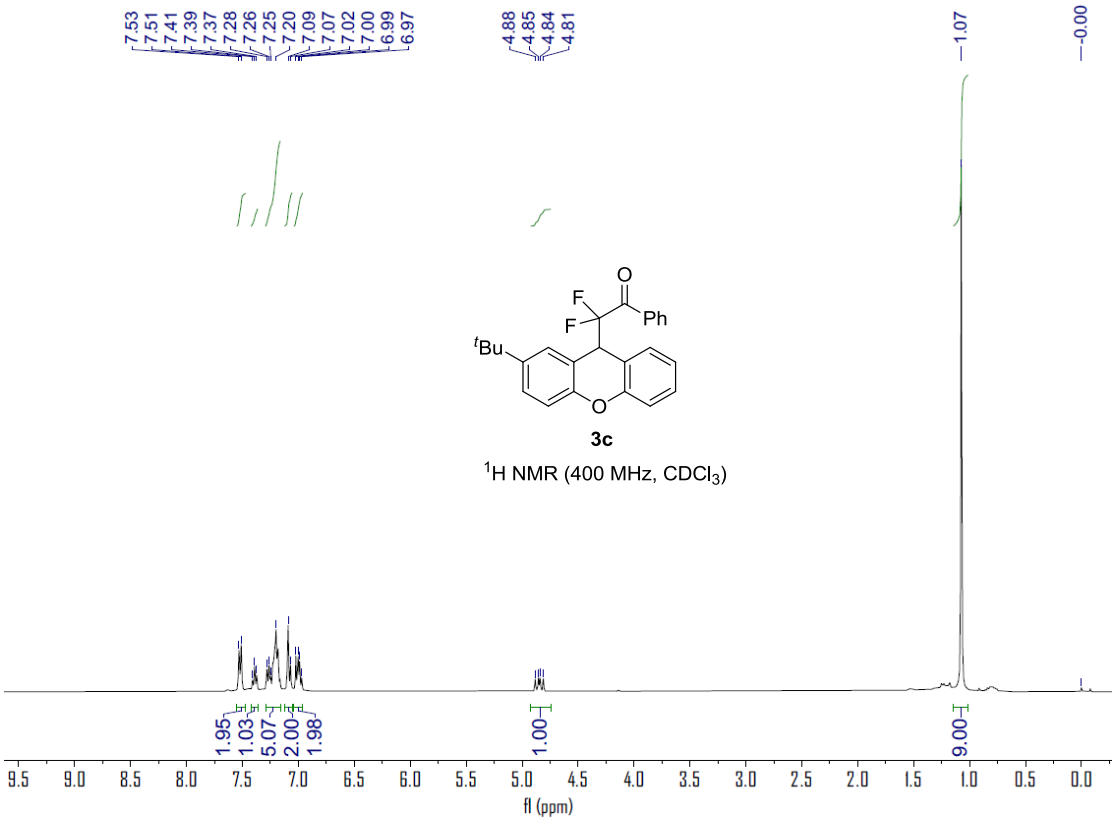
3b

^{13}C NMR (100 MHz, $CDCl_3$)



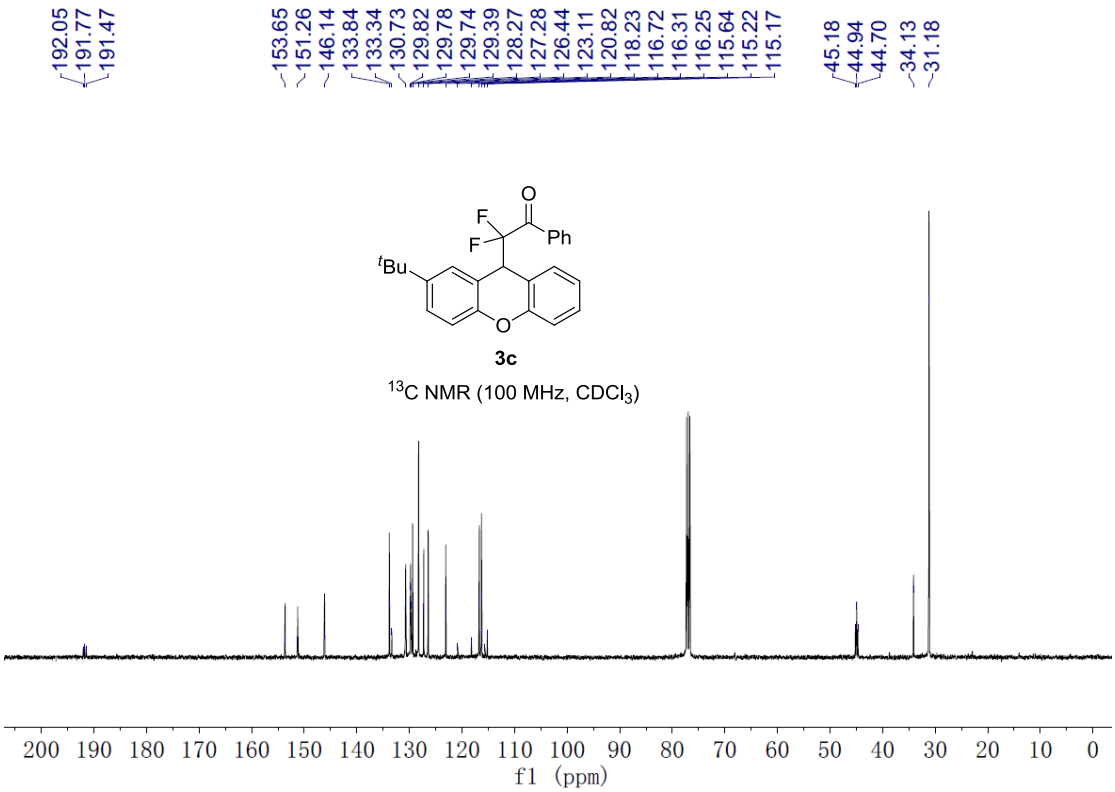
3b

^{19}F NMR (376 MHz, $CDCl_3$)



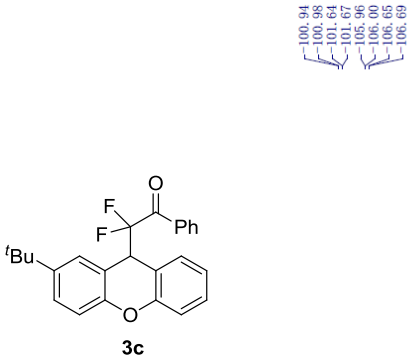
3c

^{1}H NMR (400 MHz, $CDCl_3$)



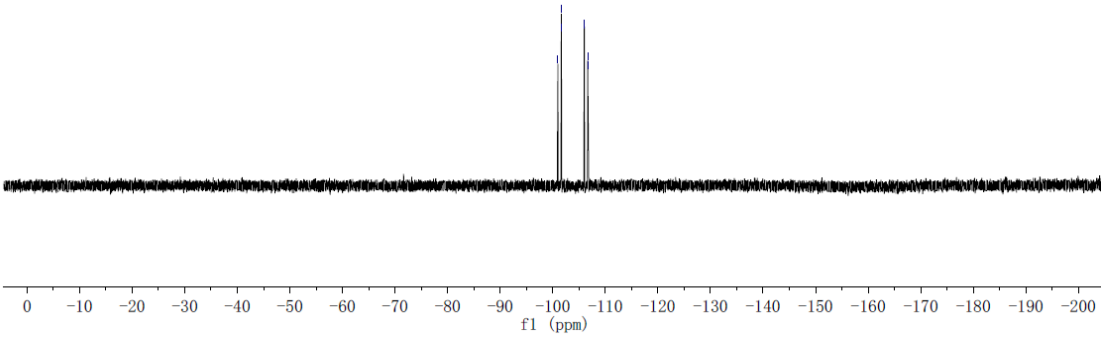
3c

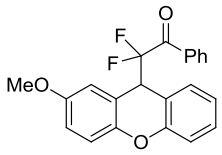
^{13}C NMR (100 MHz, $CDCl_3$)



3c

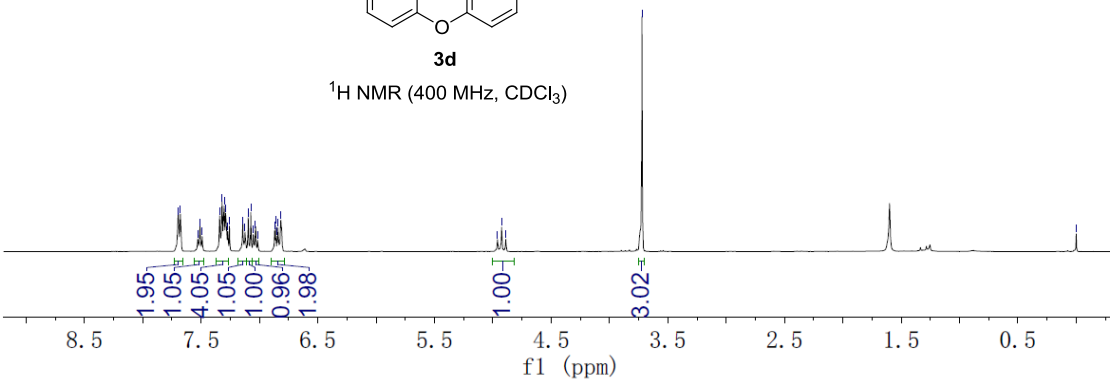
^{19}F NMR (376 MHz, $CDCl_3$)

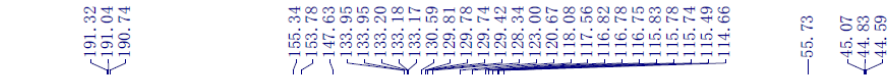


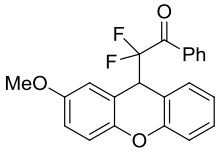


3d

^{1}H NMR (400 MHz, $CDCl_3$)

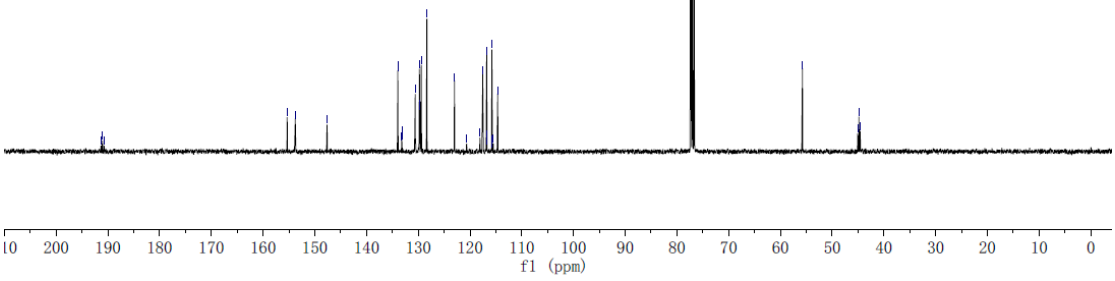


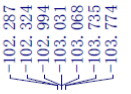


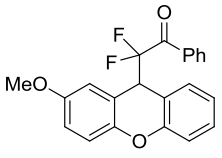


3d

^{13}C NMR (100 MHz, $CDCl_3$)

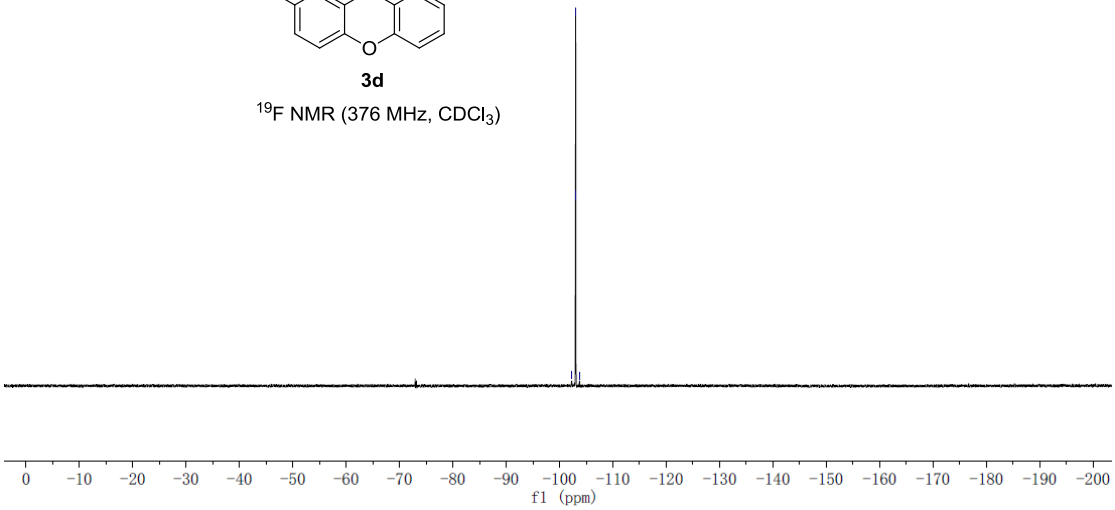


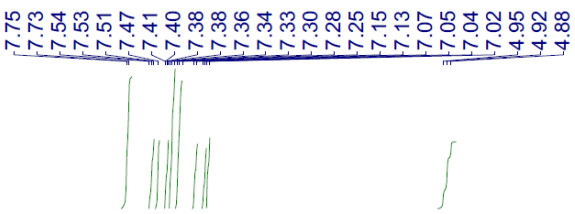


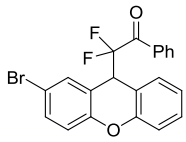


3d

^{19}F NMR (376 MHz, $CDCl_3$)

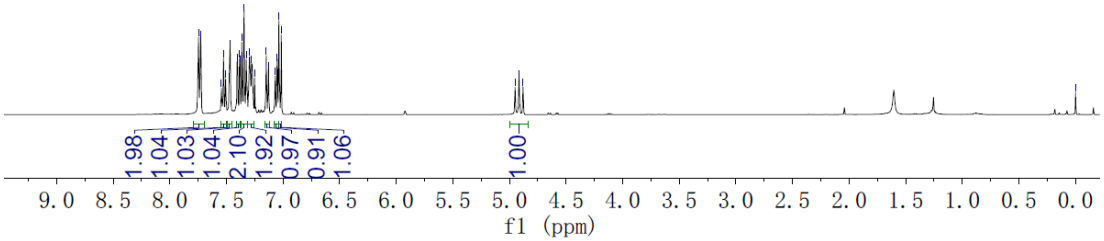


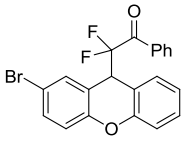




3e

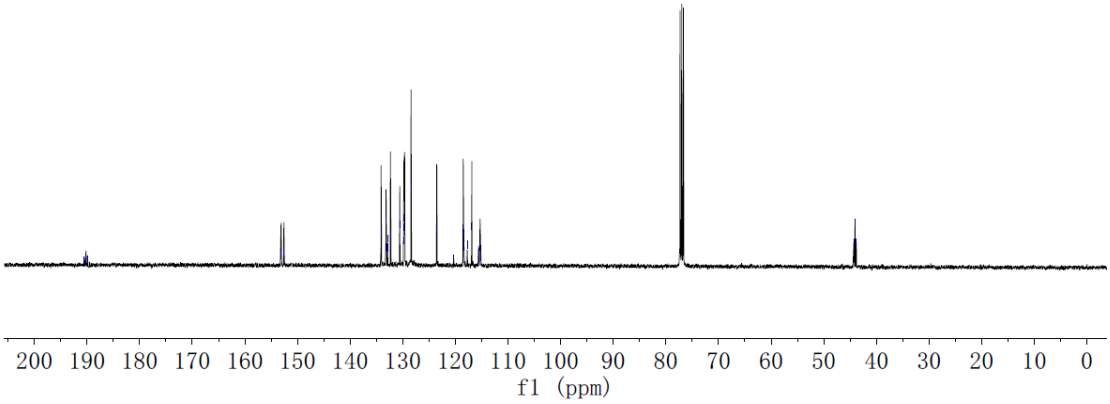
^{1}H NMR (400 MHz, $CDCl_3$)

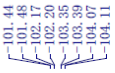


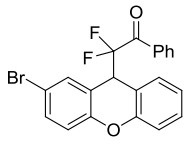


3e

^{13}C NMR (100 MHz, $CDCl_3$)

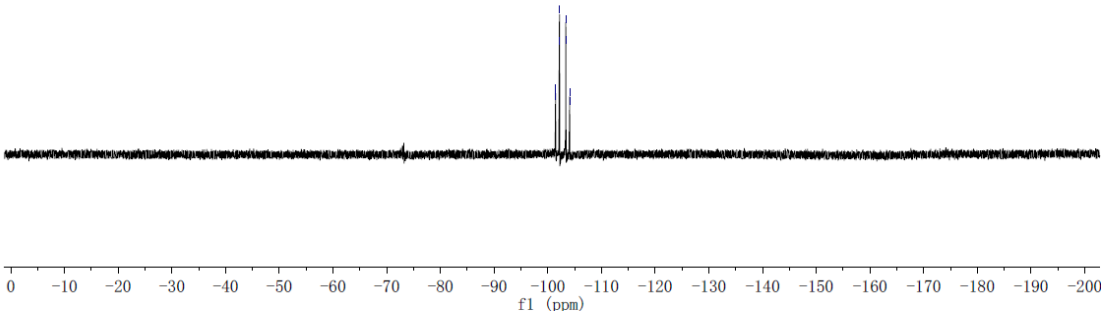


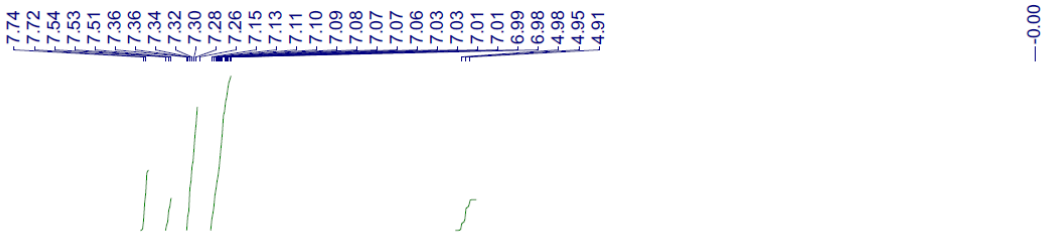


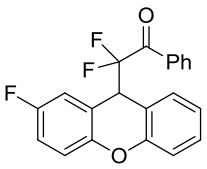


3e

^{19}F NMR (376 MHz, $CDCl_3$)

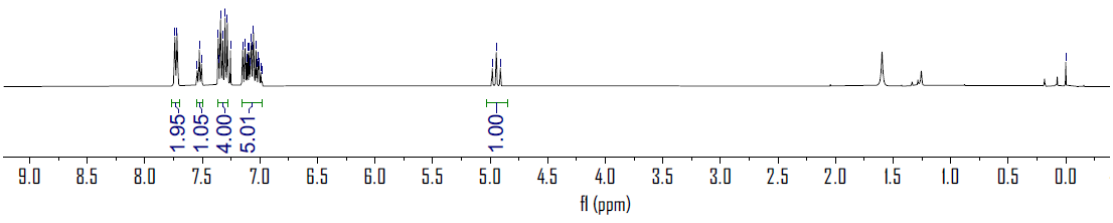


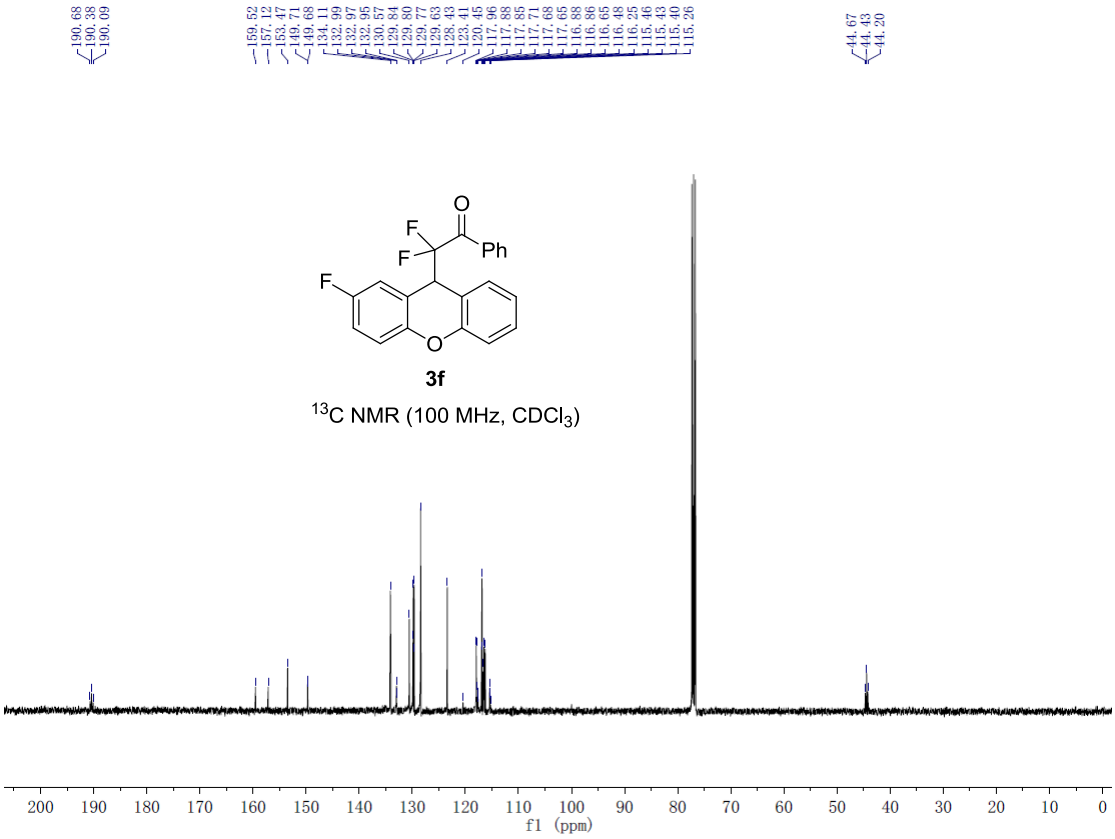




3f

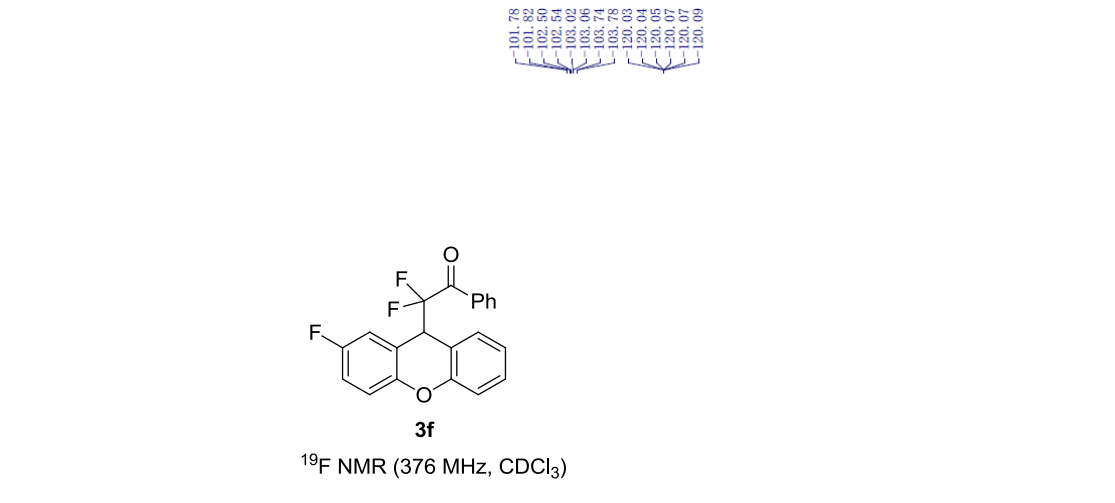
^{1}H NMR (400 MHz, $CDCl_3$)





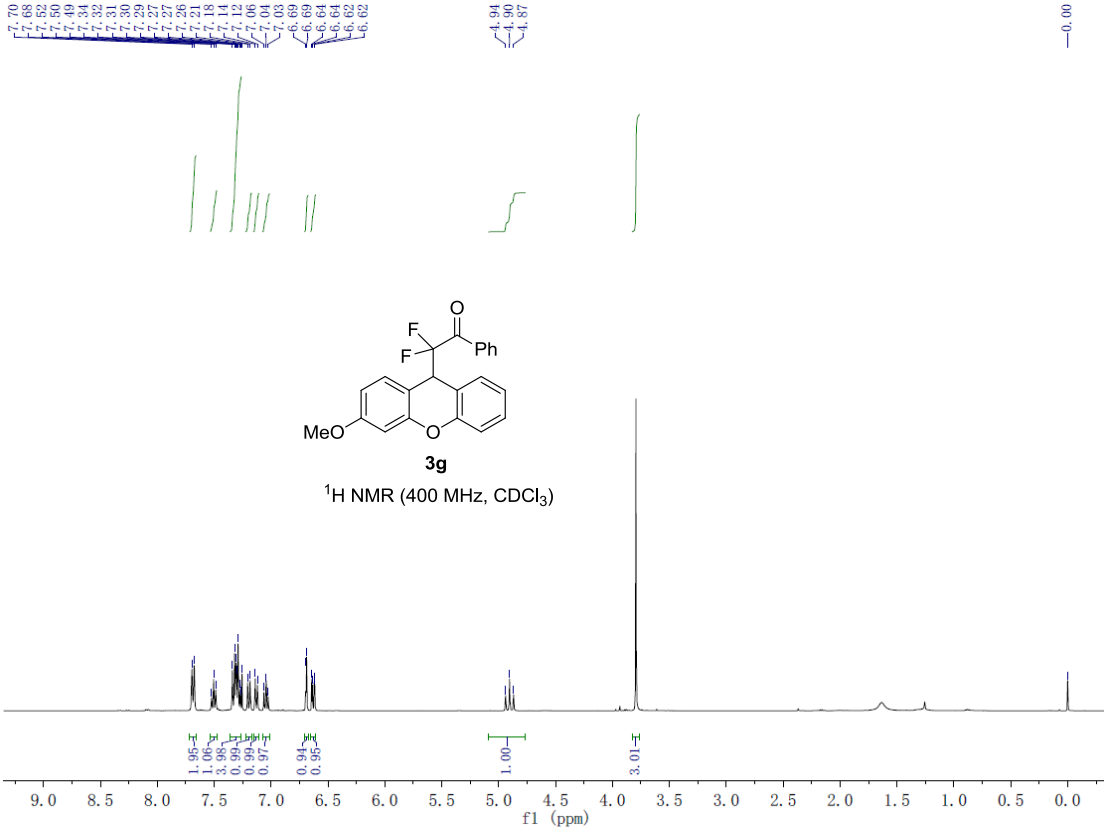
3f

^{13}C NMR (100 MHz, $CDCl_3$)



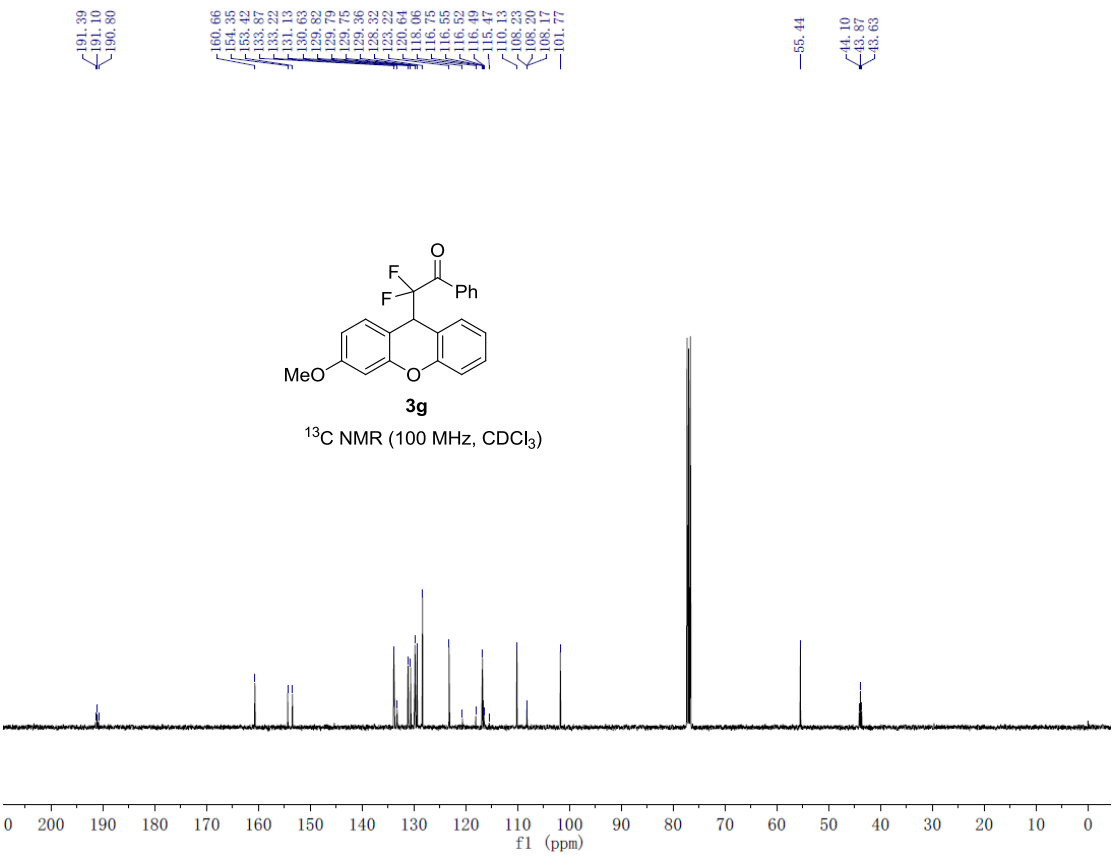
3f

^{19}F NMR (376 MHz, $CDCl_3$)



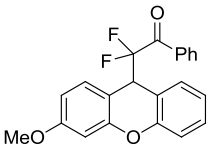
3g

^{1}H NMR (400 MHz, $CDCl_3$)



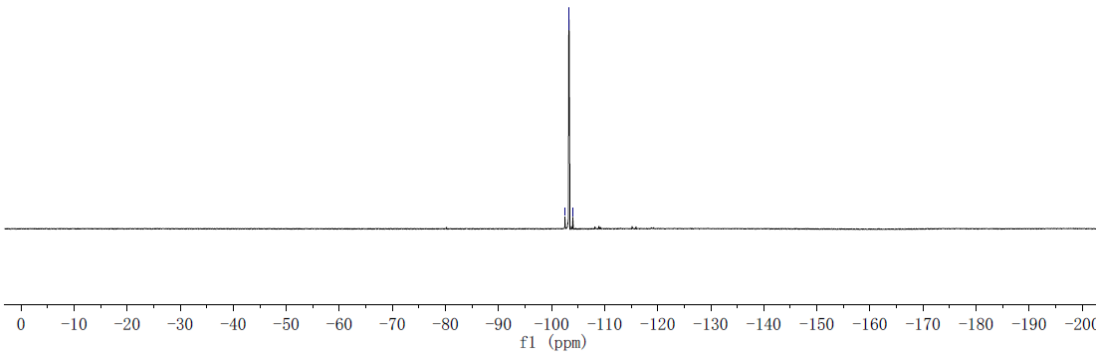
3g

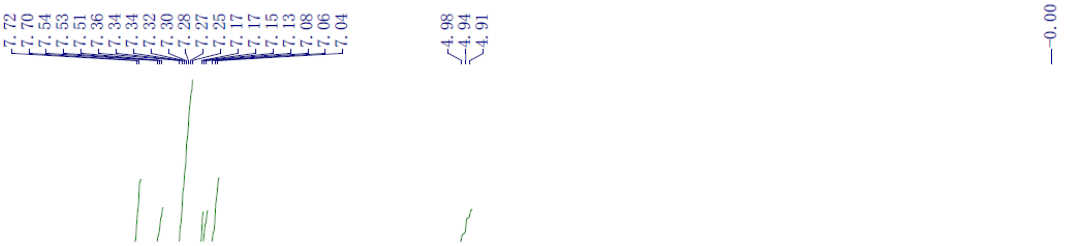
^{13}C NMR (100 MHz, $CDCl_3$)

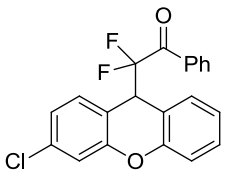


3g

^{19}F NMR (376 MHz, $CDCl_3$)

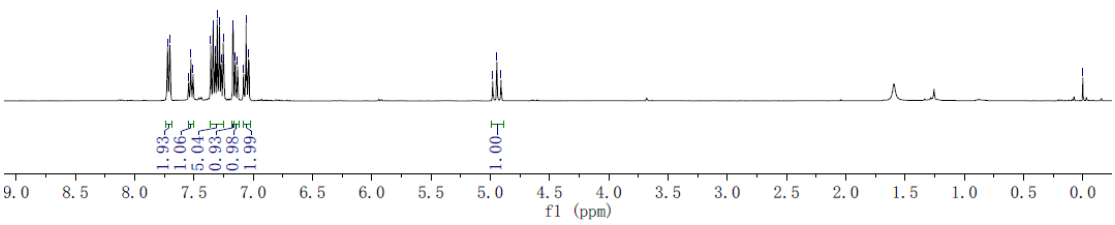


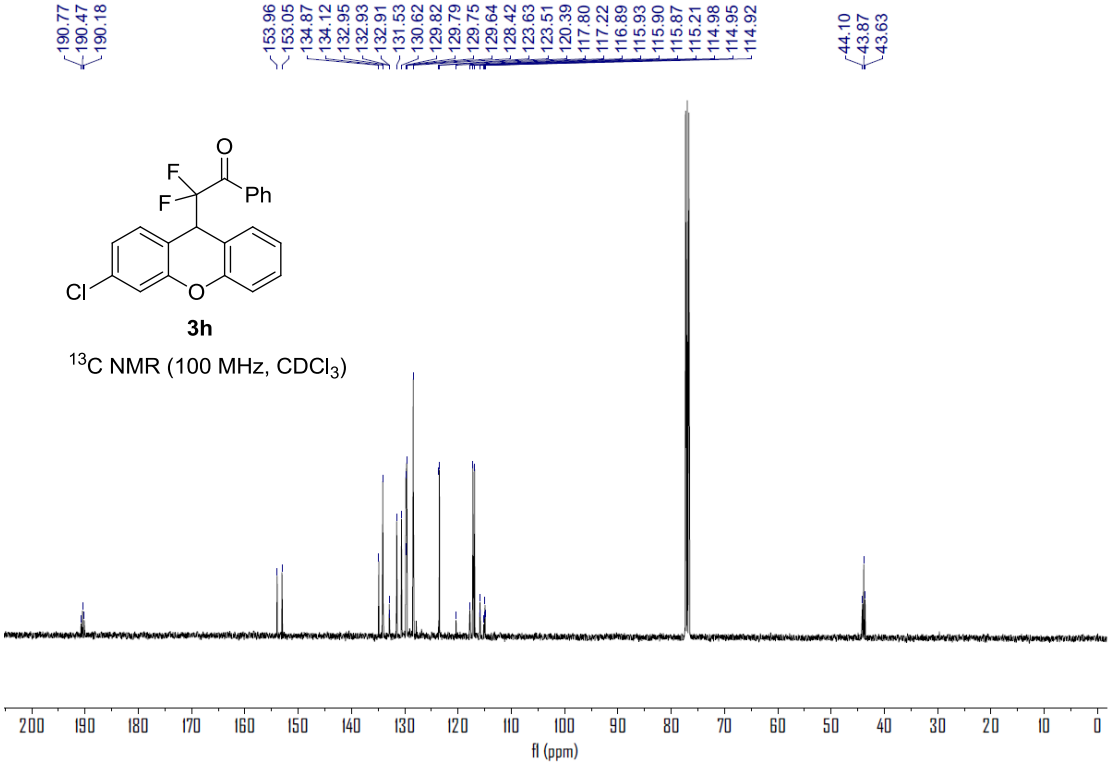




3h

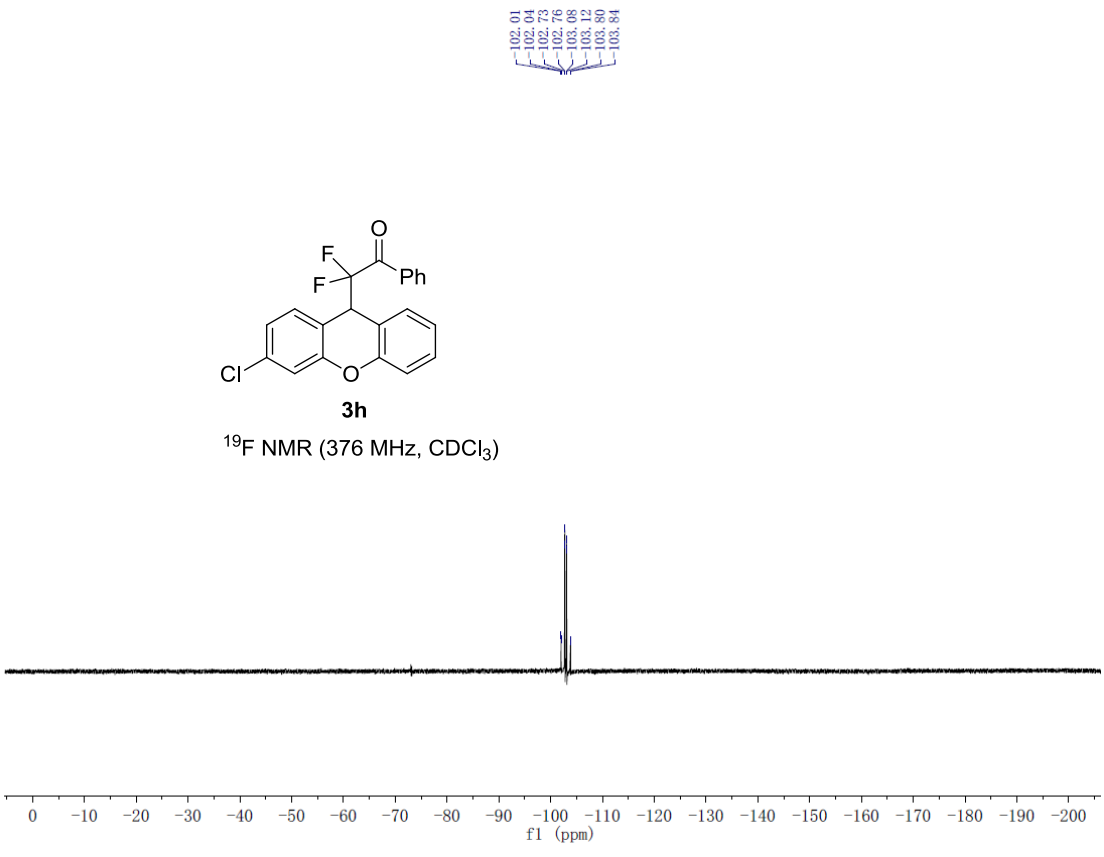
^{1}H NMR (400 MHz, $CDCl_3$)





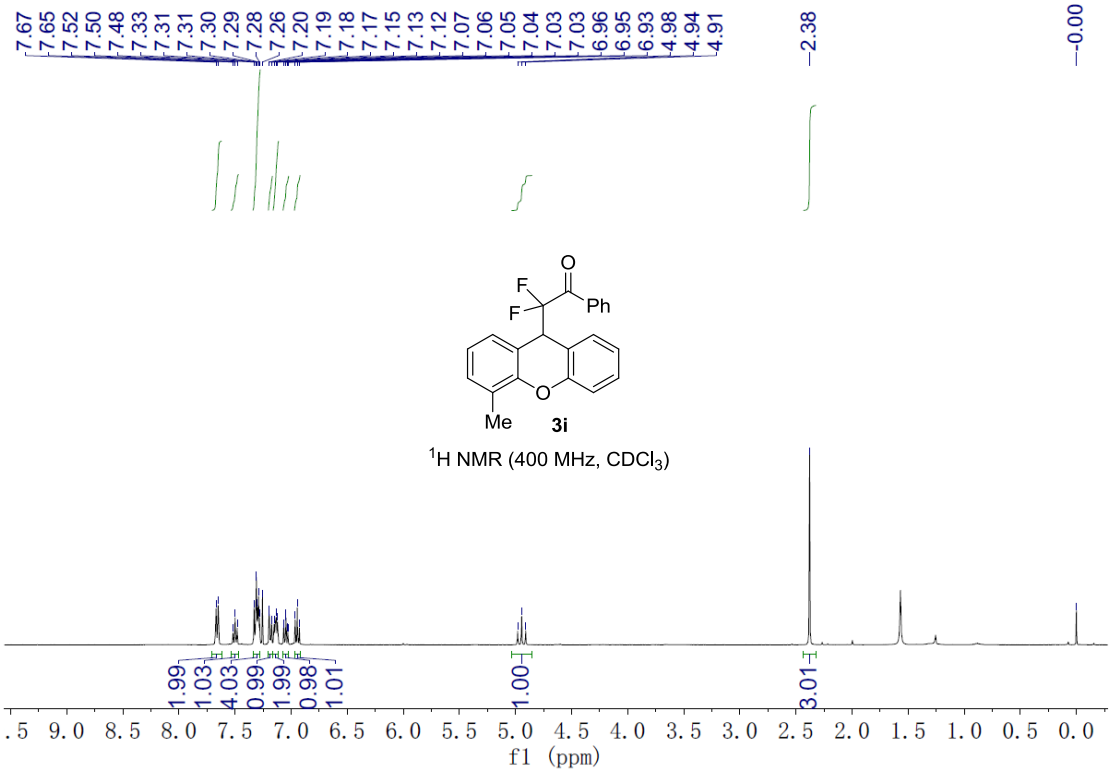
3h

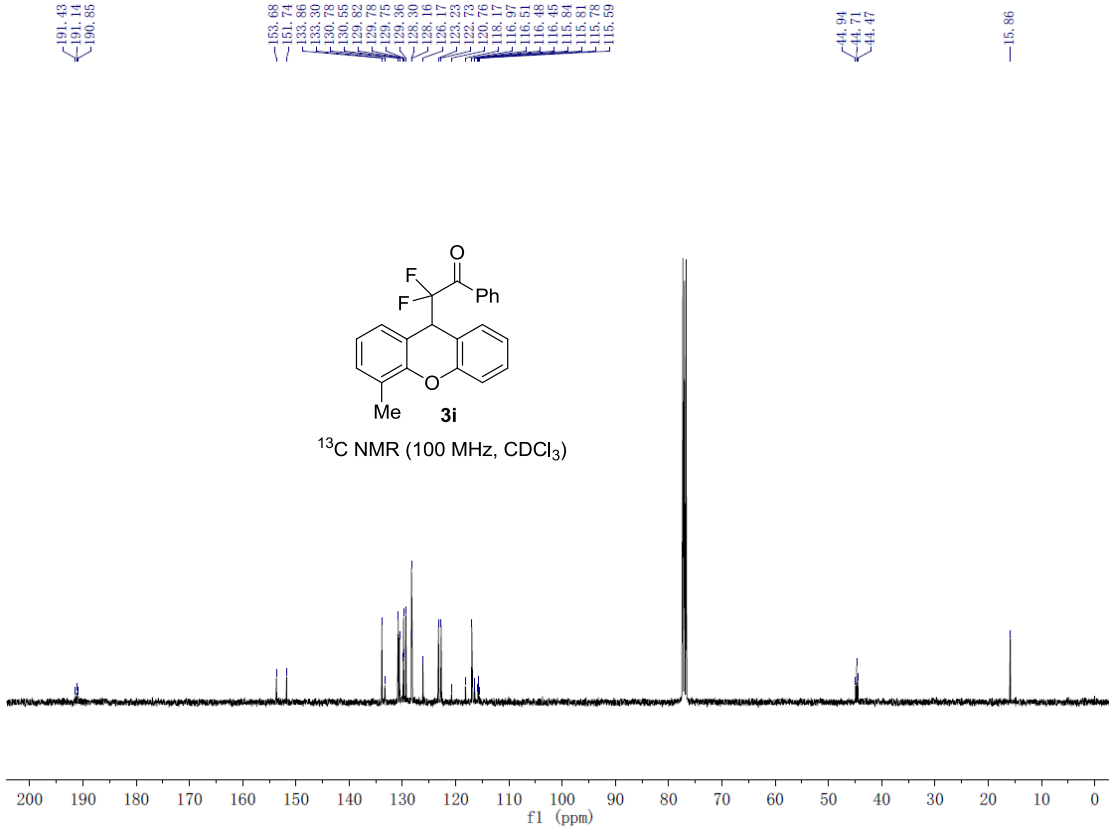
^{13}C NMR (100 MHz, $CDCl_3$)

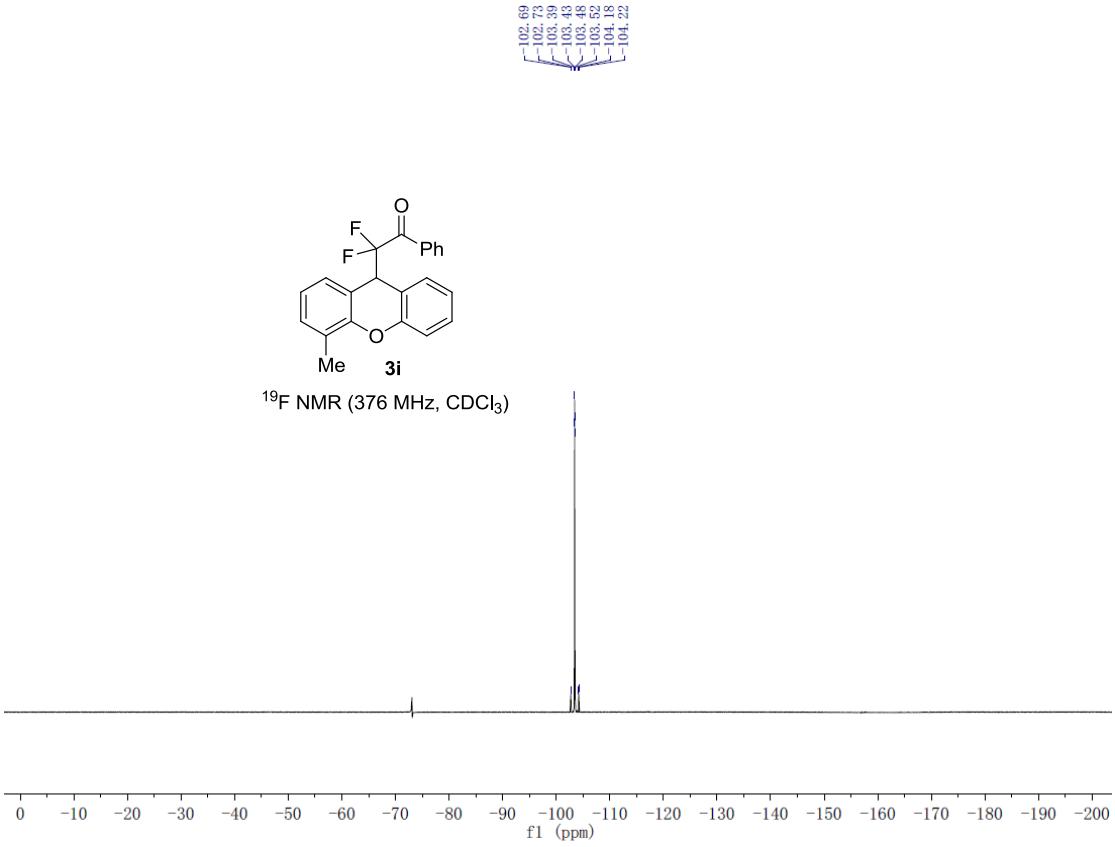


3h

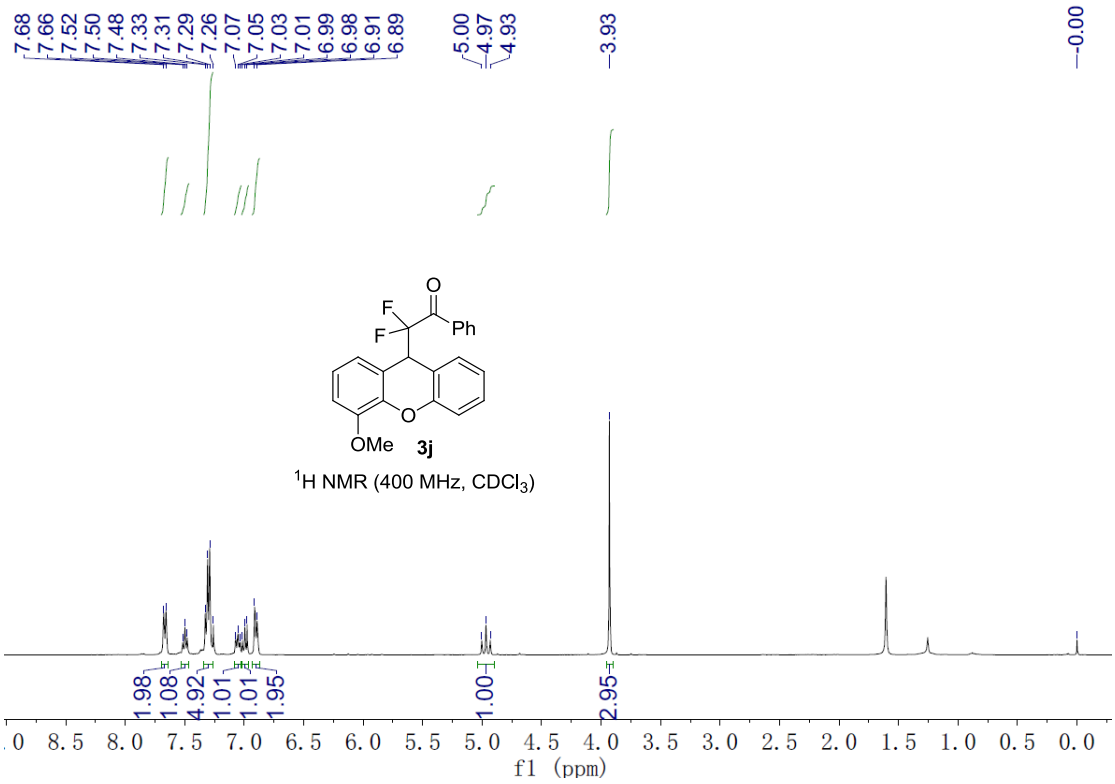
^{19}F NMR (376 MHz, $CDCl_3$)


7.67
7.65
7.52
7.50
7.48
7.33
7.31
7.31
7.30
7.29
7.28
7.26
7.20
7.19
7.18
7.17
7.15
7.13
7.12
7.07
7.06
7.05
7.04
7.03
7.03
6.96
6.95
6.93
4.98
4.94
4.91
2.38
0.00
O
F
F
Ph
O
Me
3i
1H NMR (400 MHz, CDCl3)
1.99
1.03
4.03
0.99
1.99
0.98
1.01
1.00
3.01
f1 (ppm)

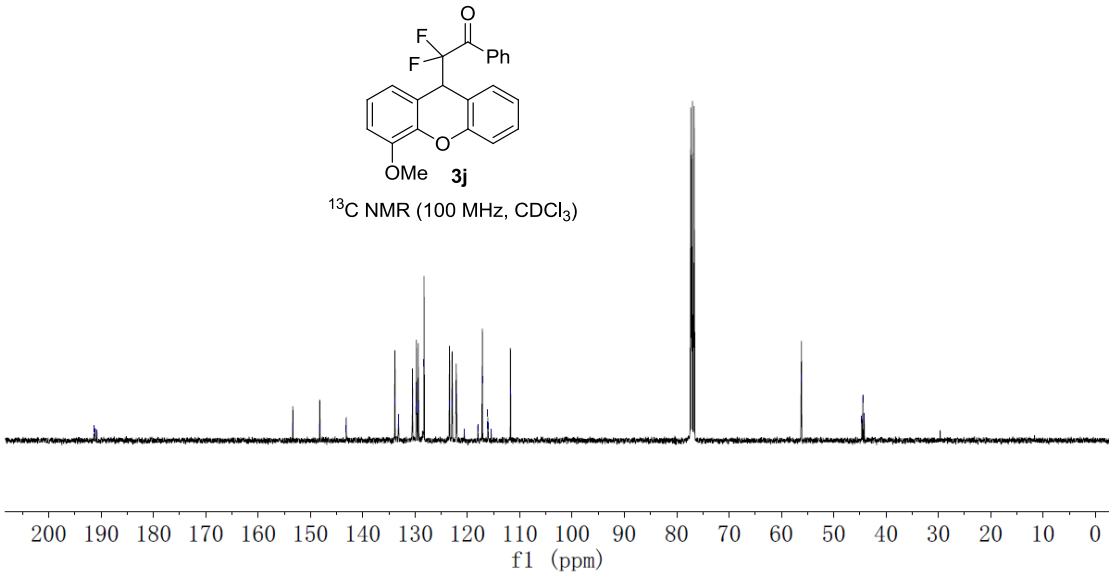

191.43
191.14
190.85
153.68
151.74
133.86
133.30
130.78
130.55
129.82
129.78
129.75
129.36
128.30
128.16
126.17
123.23
122.73
120.76
118.17
116.97
116.51
116.48
116.45
115.84
115.81
115.78
115.59
44.94
44.71
44.47
15.86
O
F
F
Ph
O
Me
3i
13C NMR (100 MHz, CDCl3)
f1 (ppm)



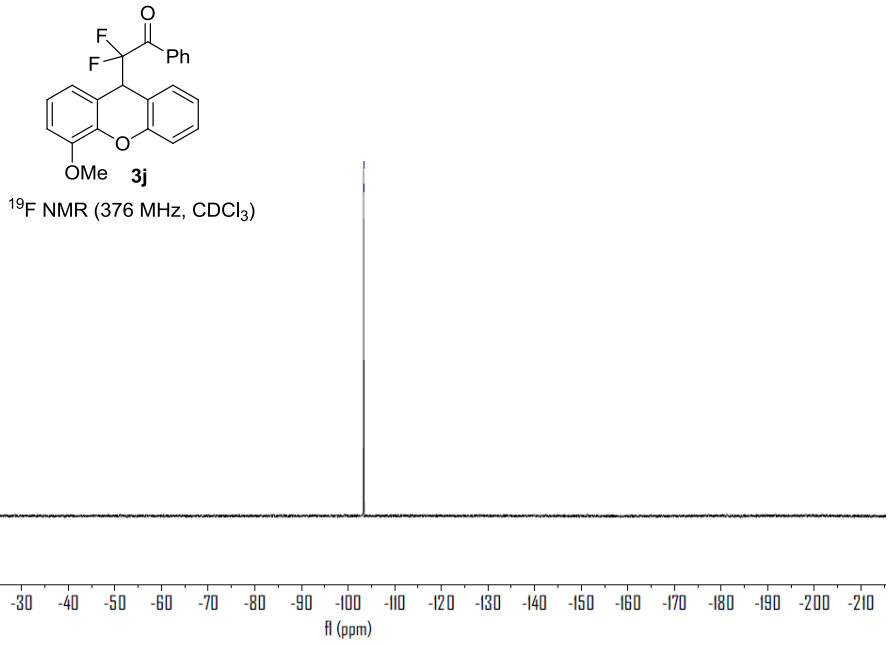
^{19}F NMR (376 MHz, $CDCl_3$)



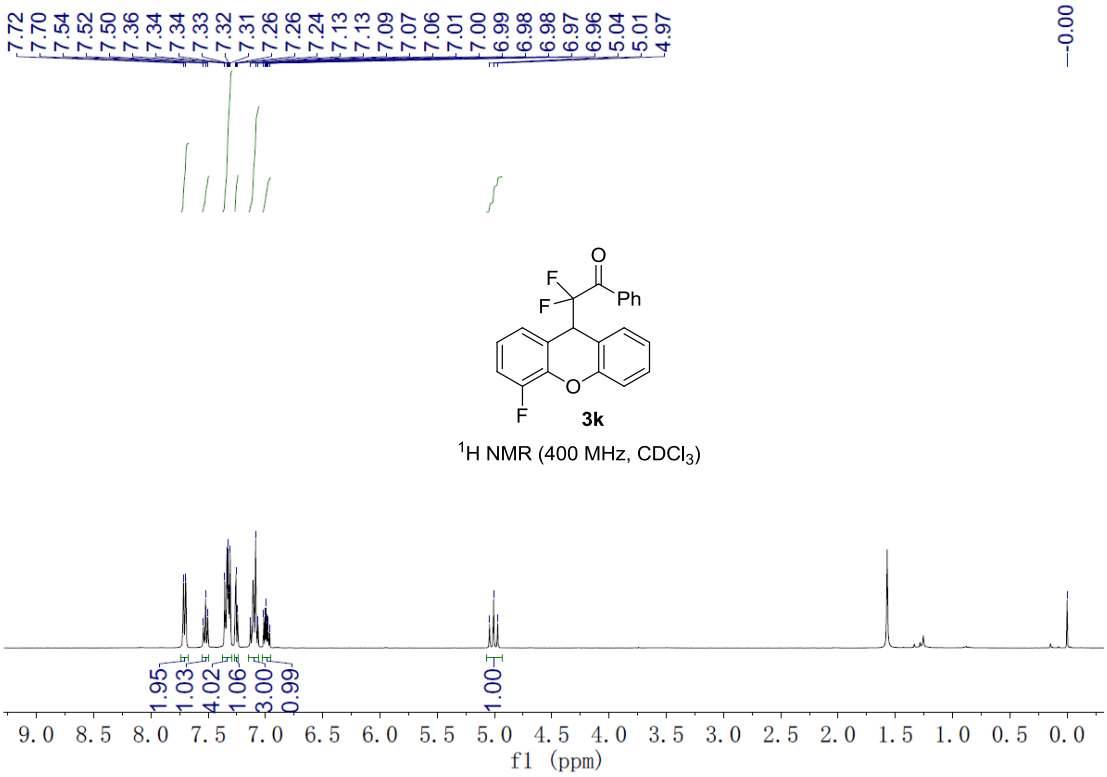
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

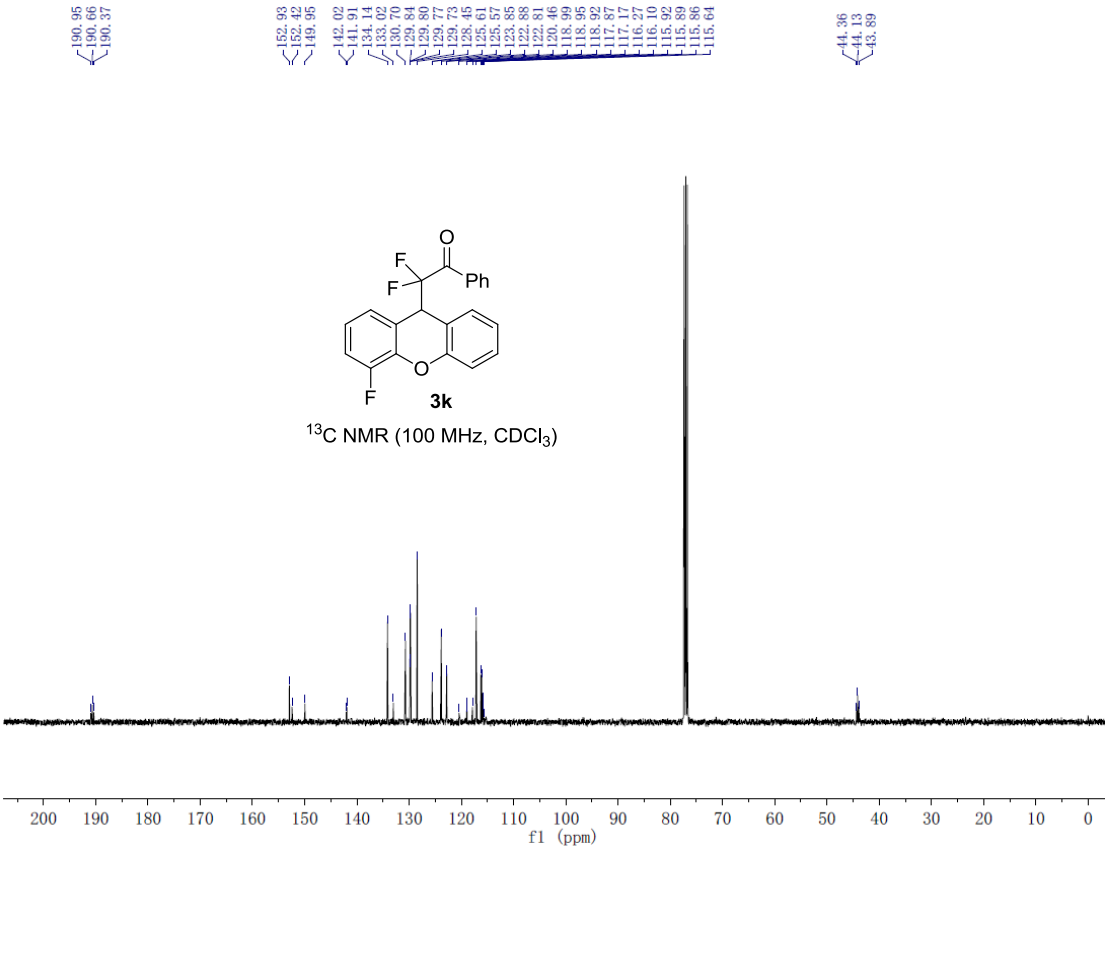


^{19}F NMR (376 MHz, $CDCl_3$)



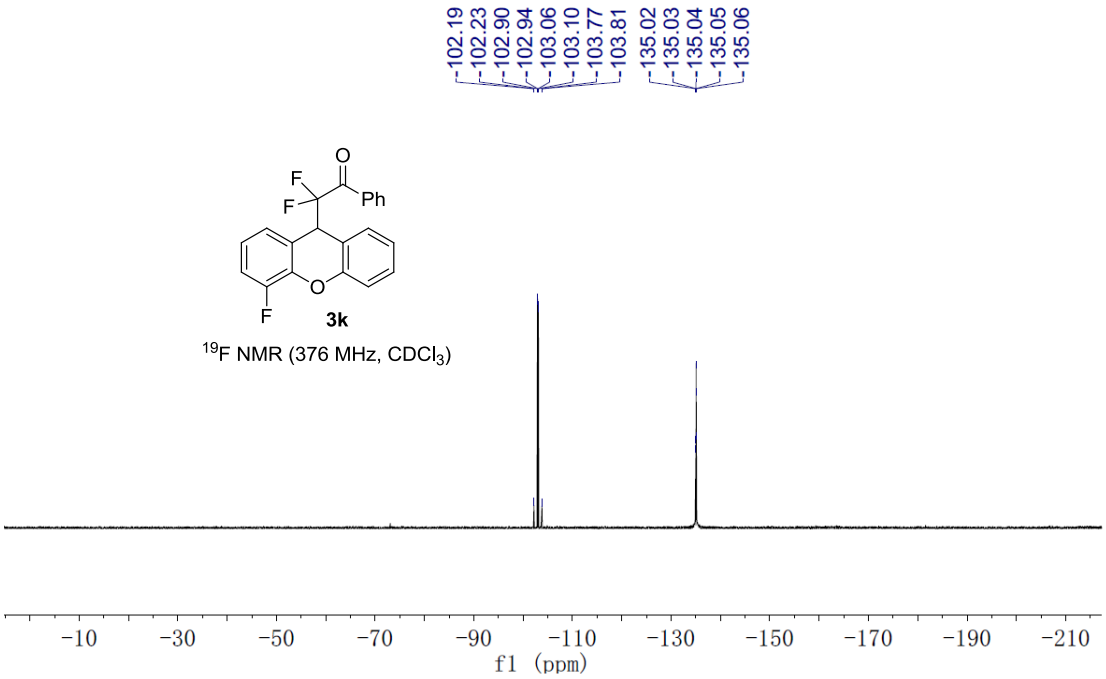
3k

^{1}H NMR (400 MHz, $CDCl_3$)

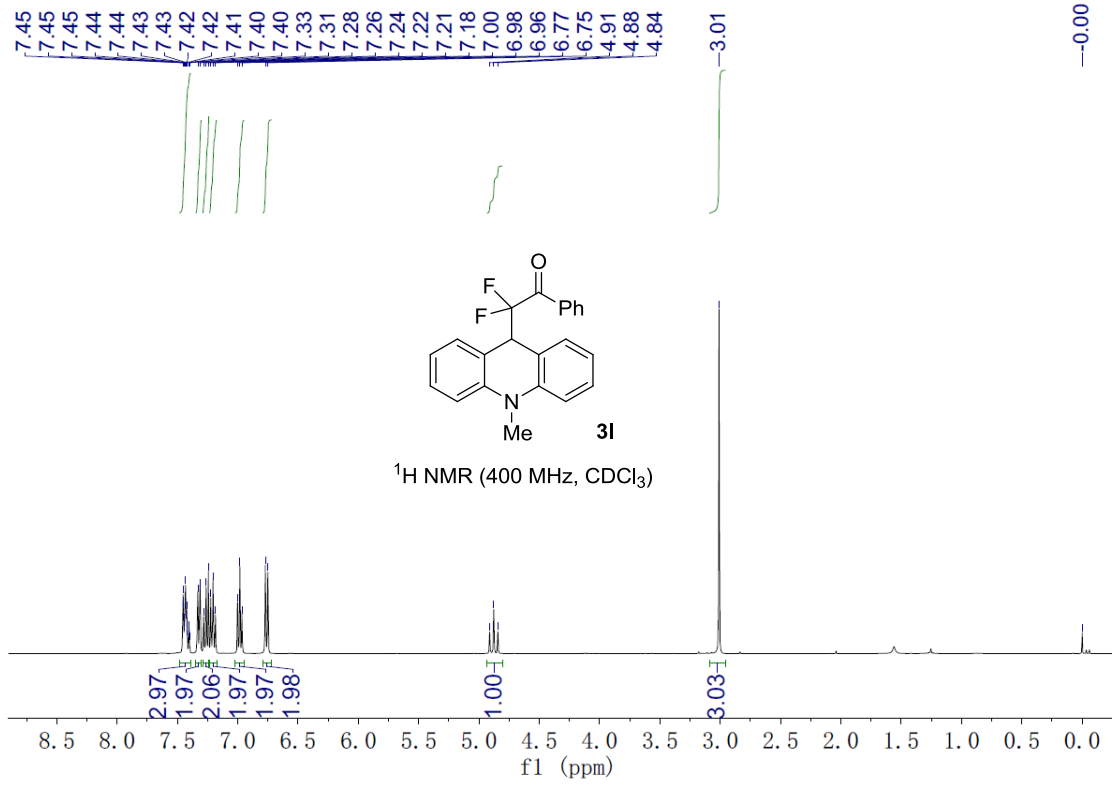


3k

^{13}C NMR (100 MHz, $CDCl_3$)

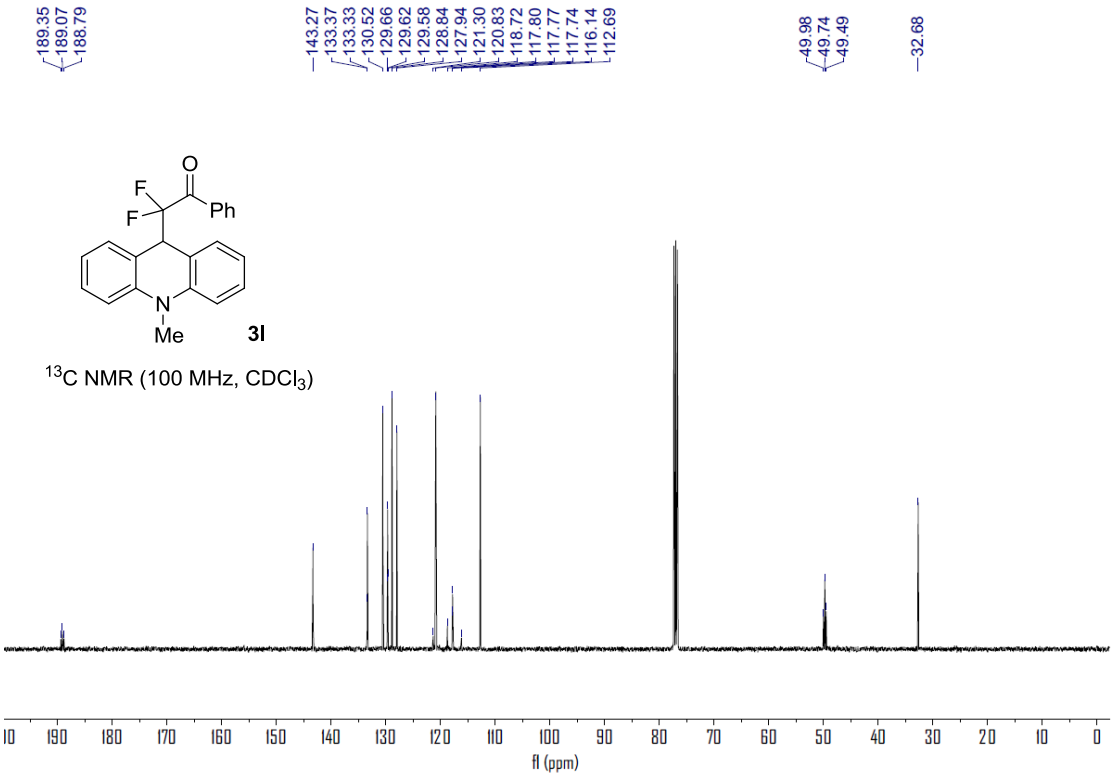


^{19}F NMR (376 MHz, $CDCl_3$)



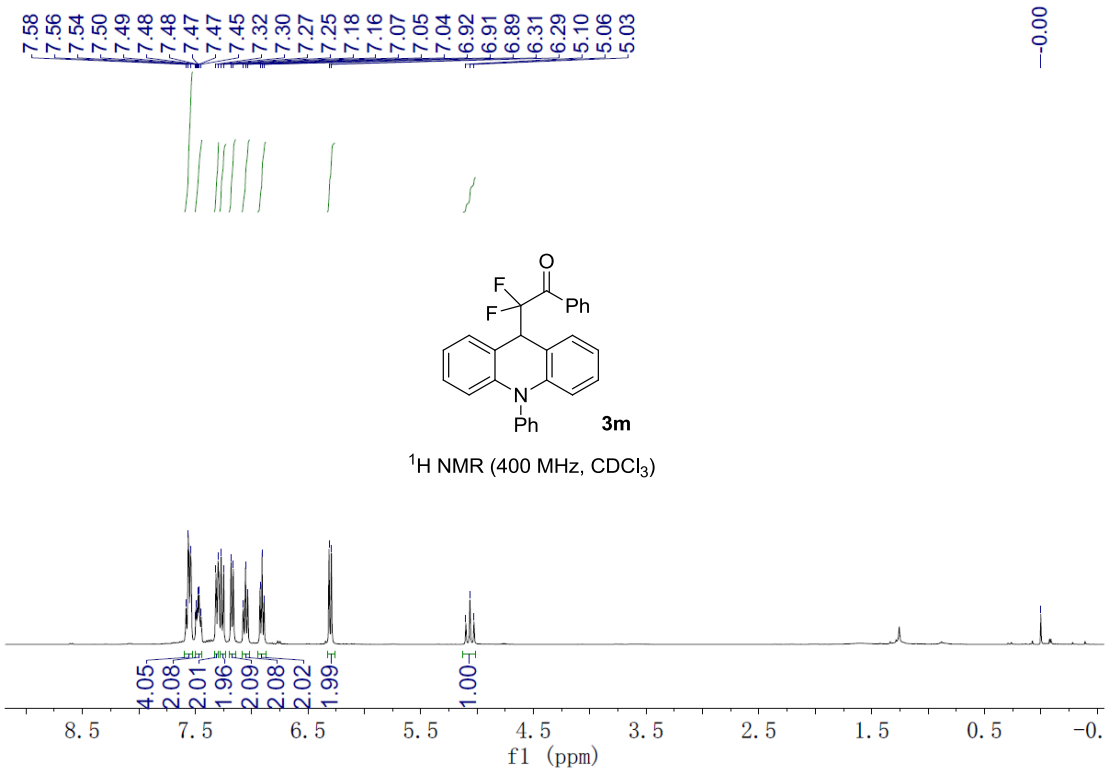
3l

^{1}H NMR (400 MHz, $CDCl_3$)

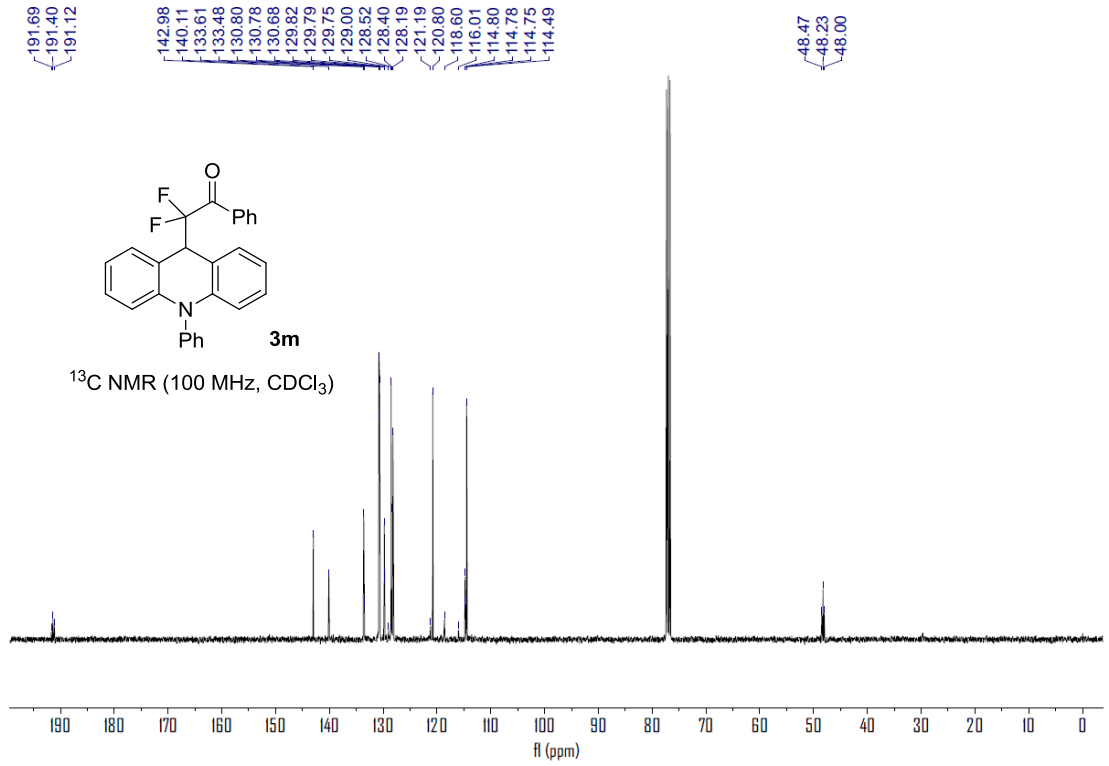


^{13}C NMR (100 MHz, $CDCl_3$)

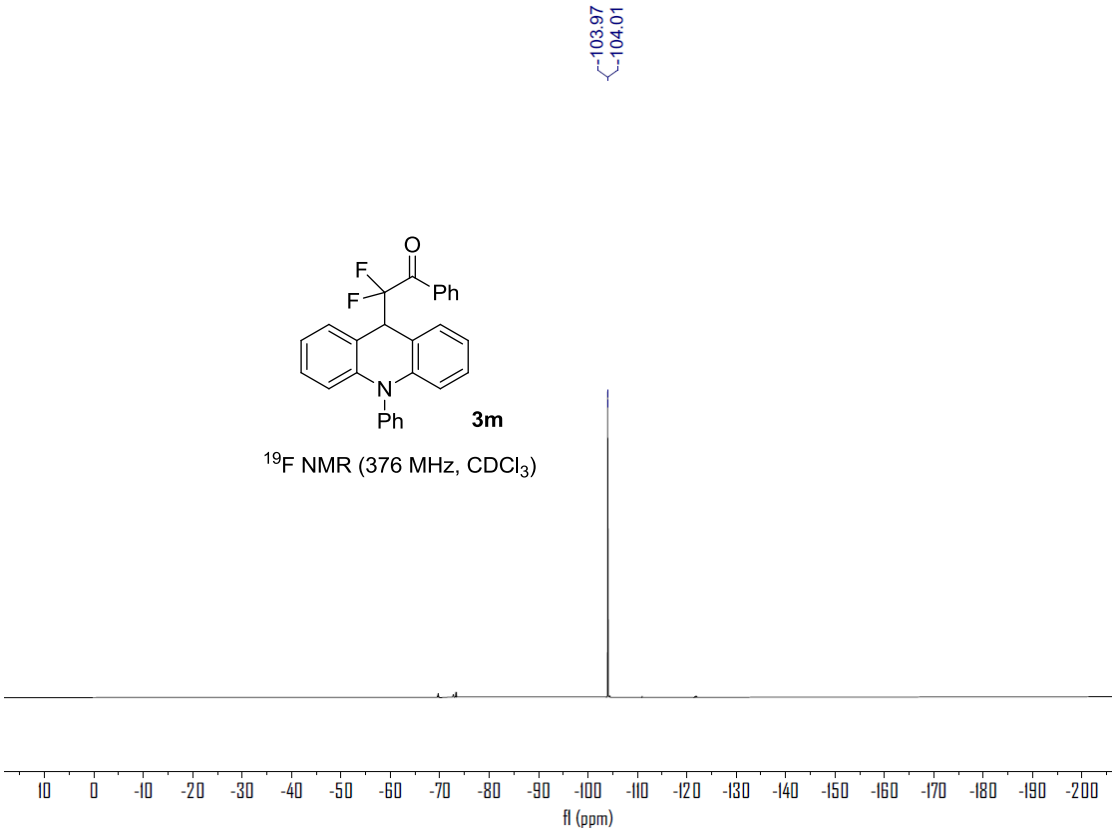
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

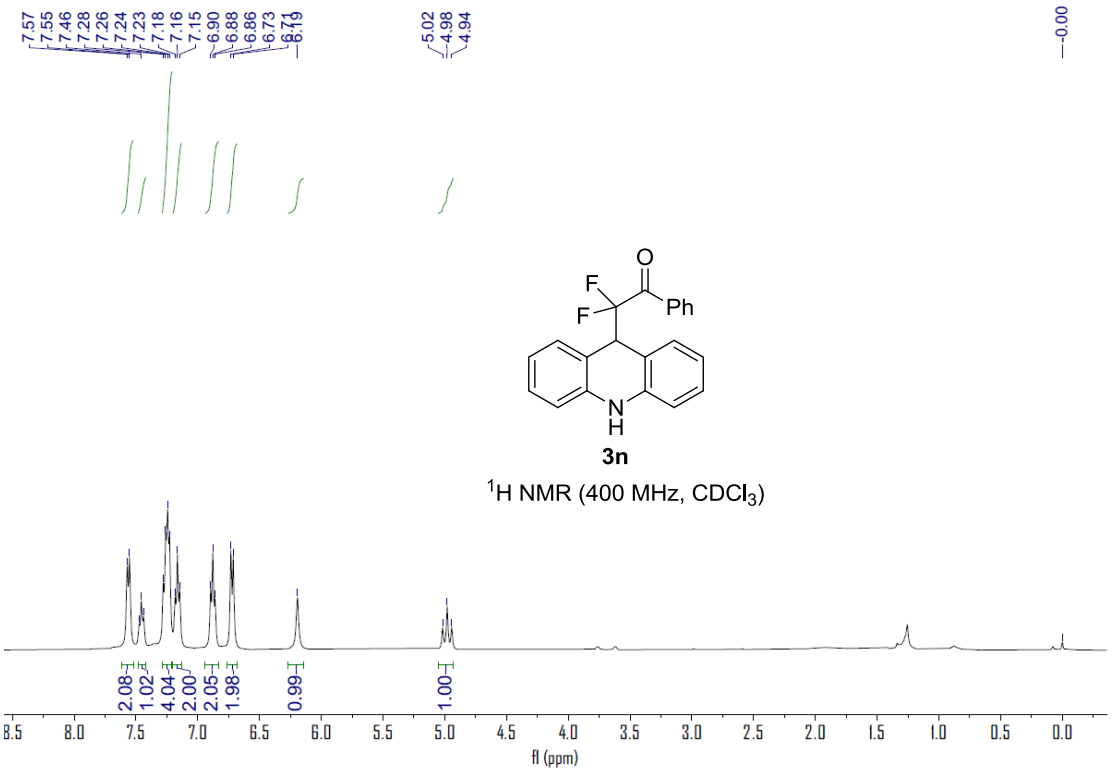


^{13}C NMR (100 MHz, $CDCl_3$)



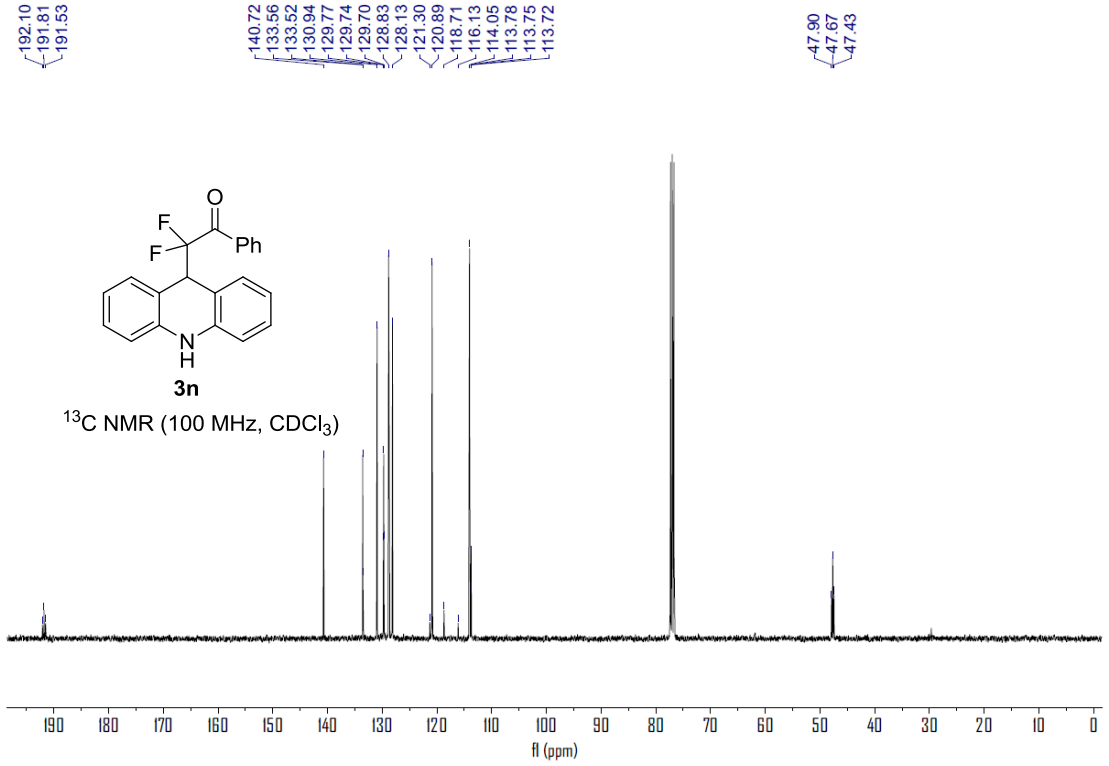
3m

^{19}F NMR (376 MHz, $CDCl_3$)



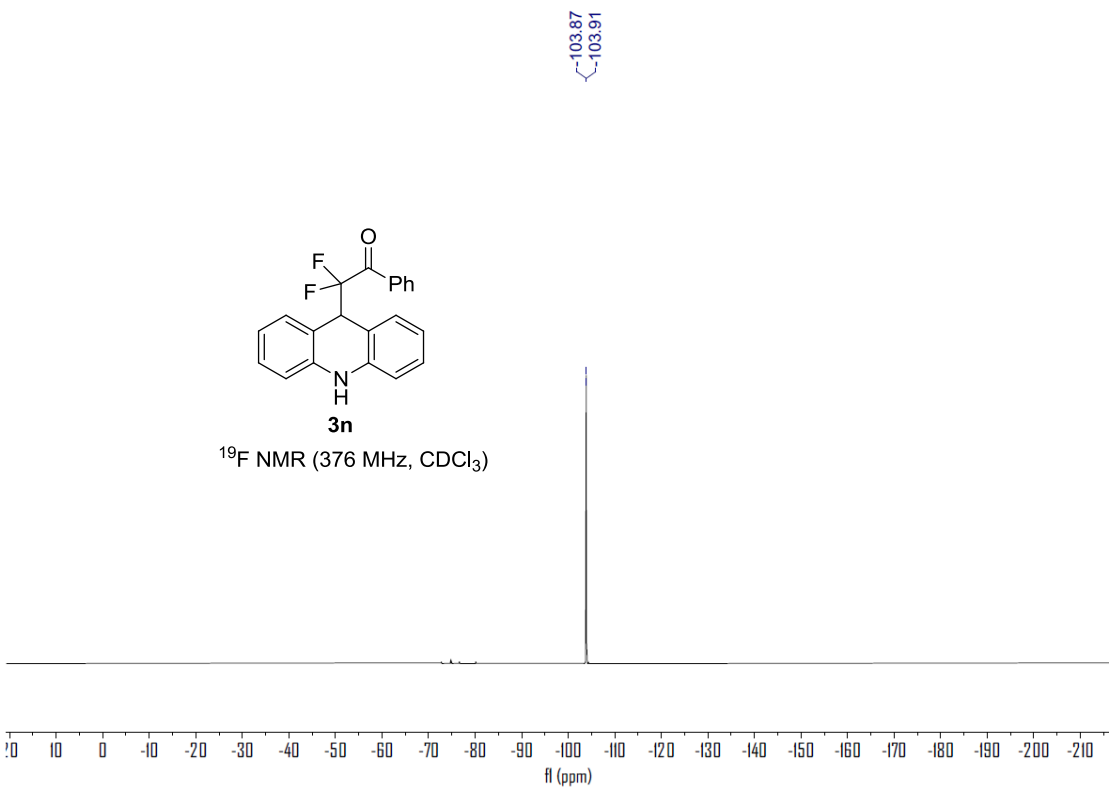
3n

^{1}H NMR (400 MHz, $CDCl_3$)



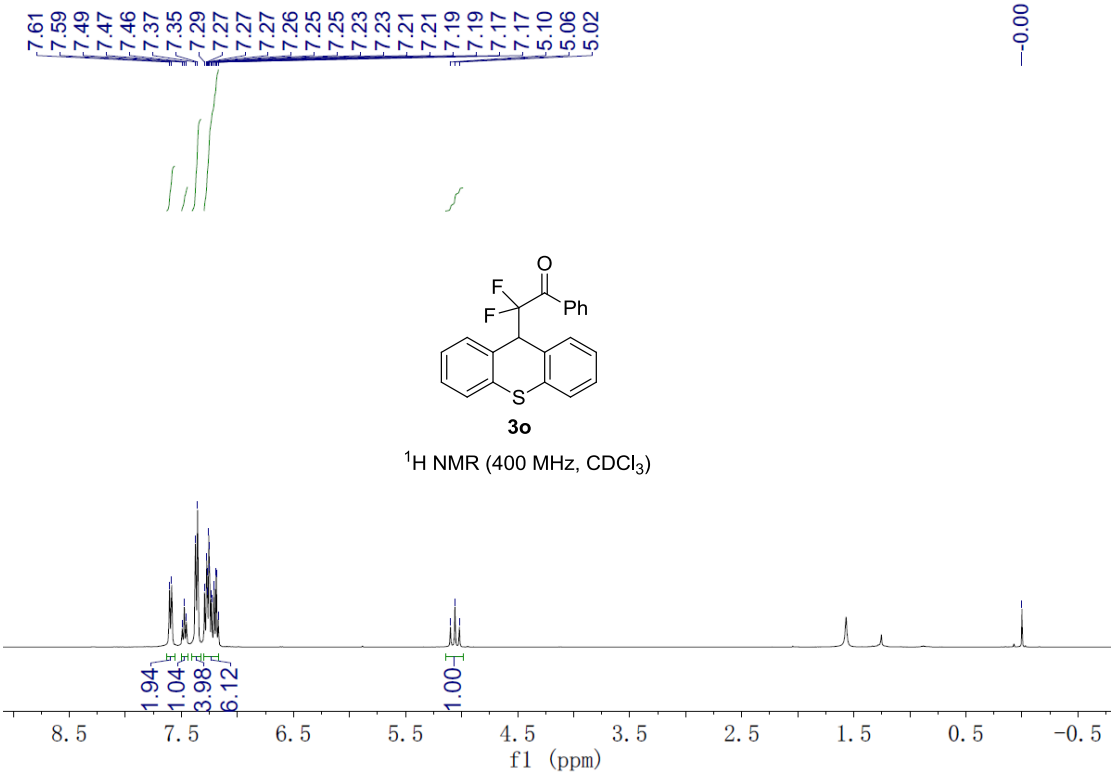
3n

^{13}C NMR (100 MHz, $CDCl_3$)



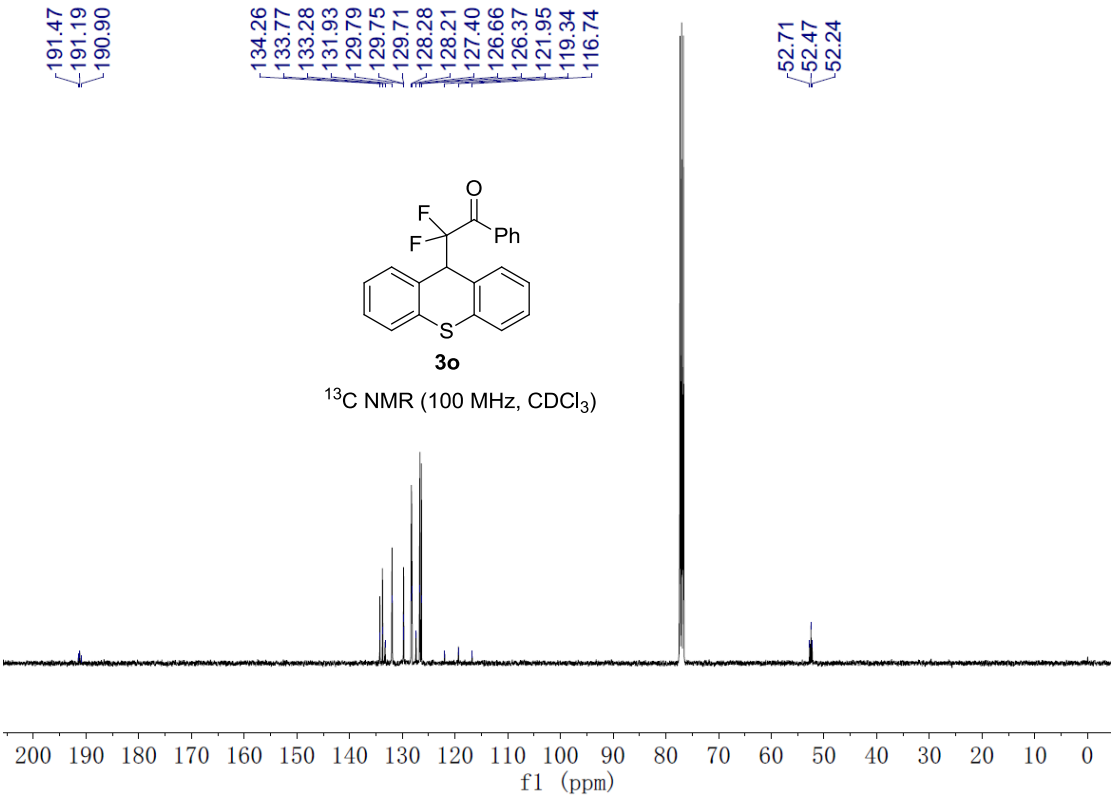
3n

^{19}F NMR (376 MHz, $CDCl_3$)



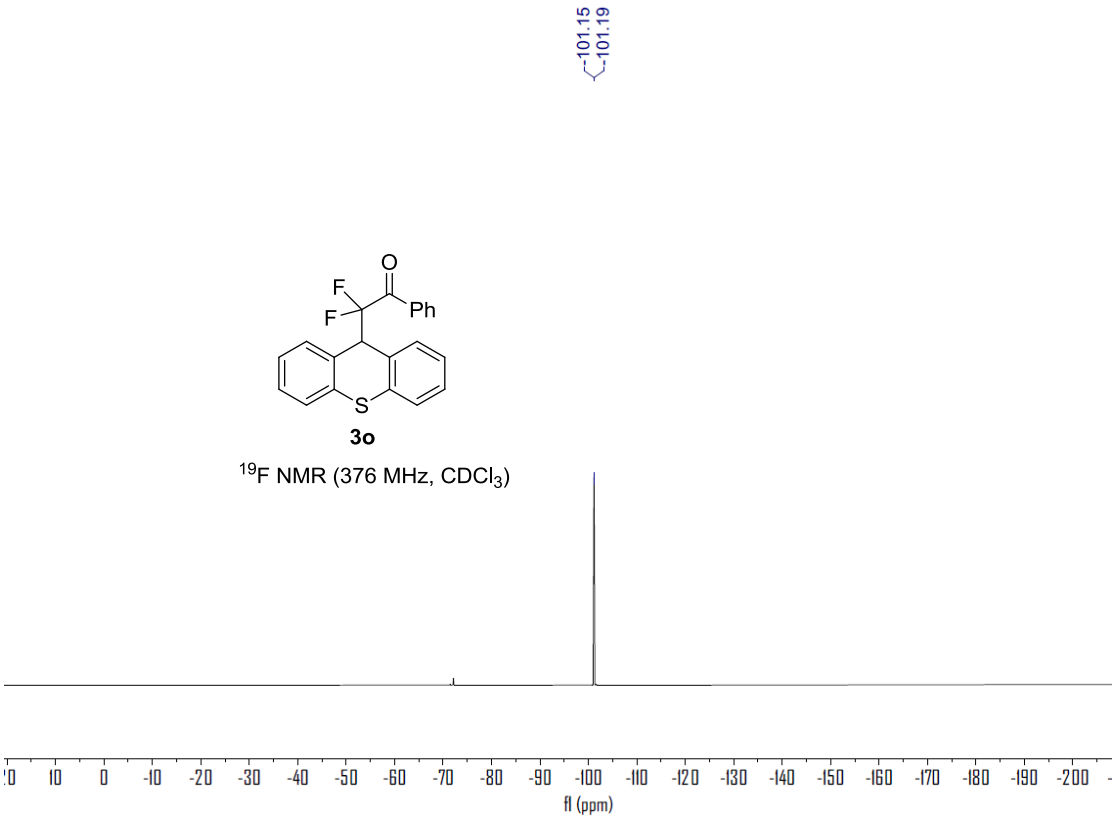
3o

^{1}H NMR (400 MHz, $CDCl_3$)



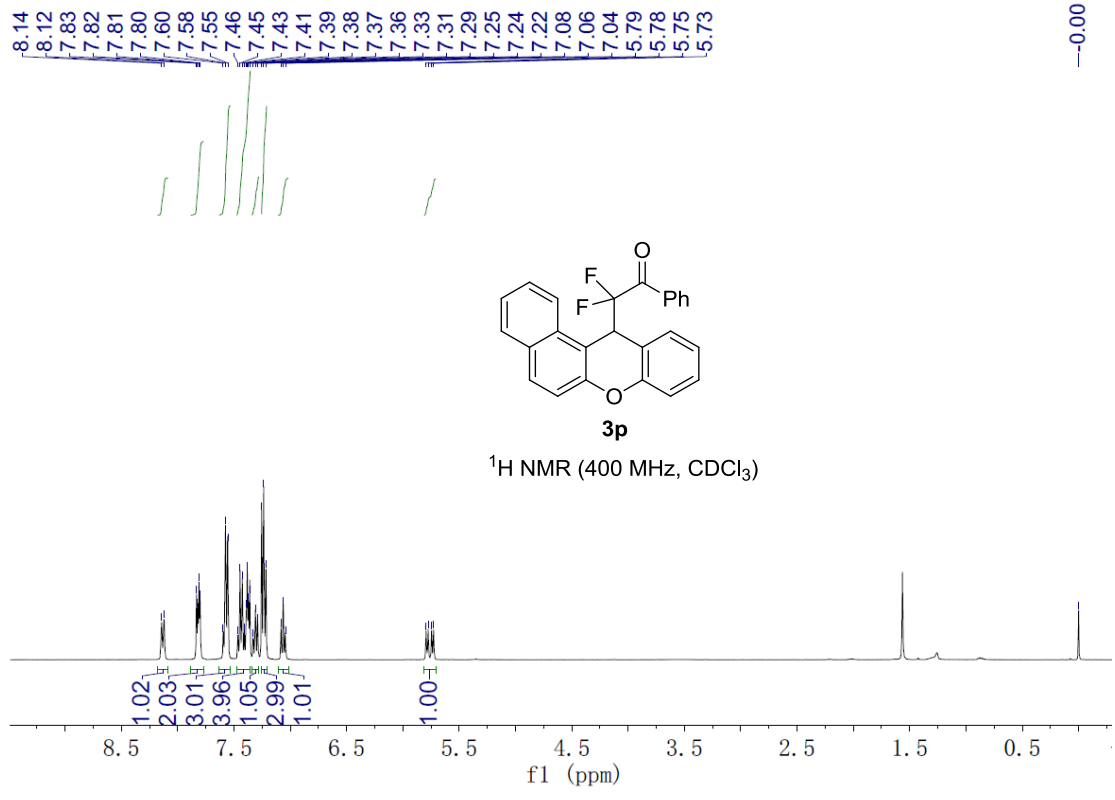
3o

^{13}C NMR (100 MHz, $CDCl_3$)



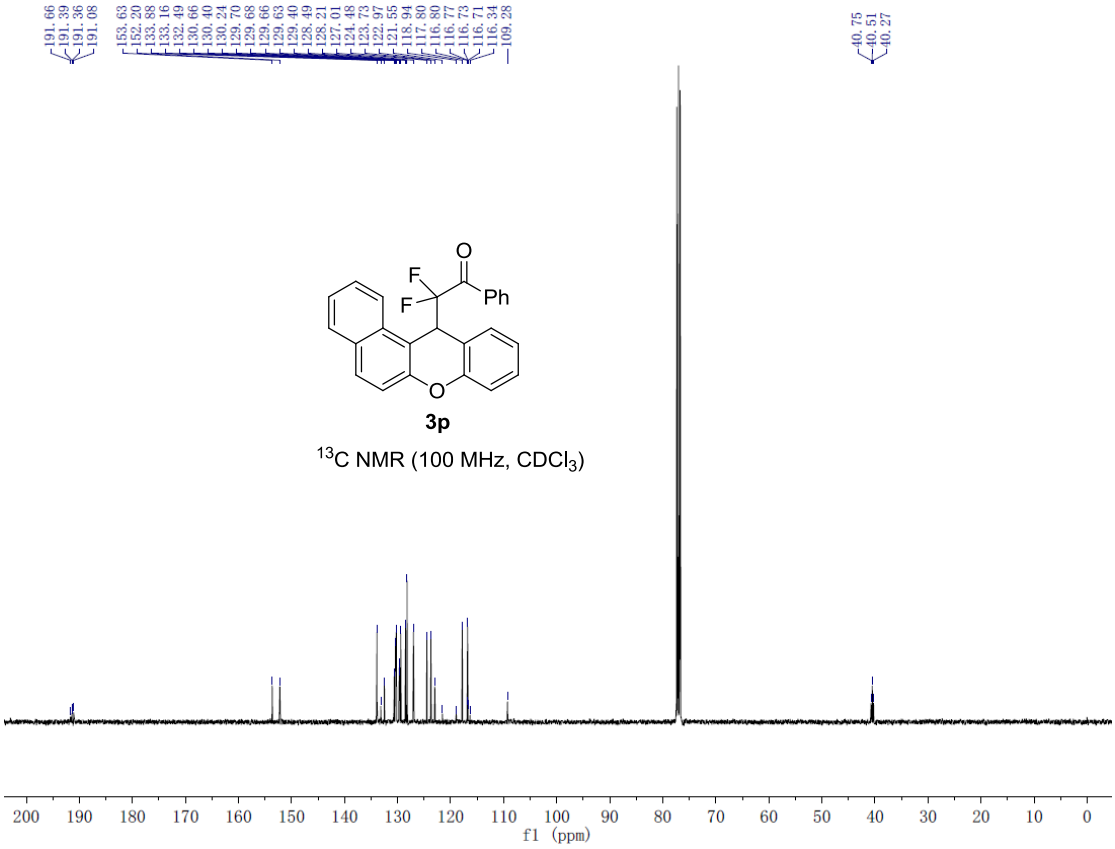
3o

^{19}F NMR (376 MHz, $CDCl_3$)



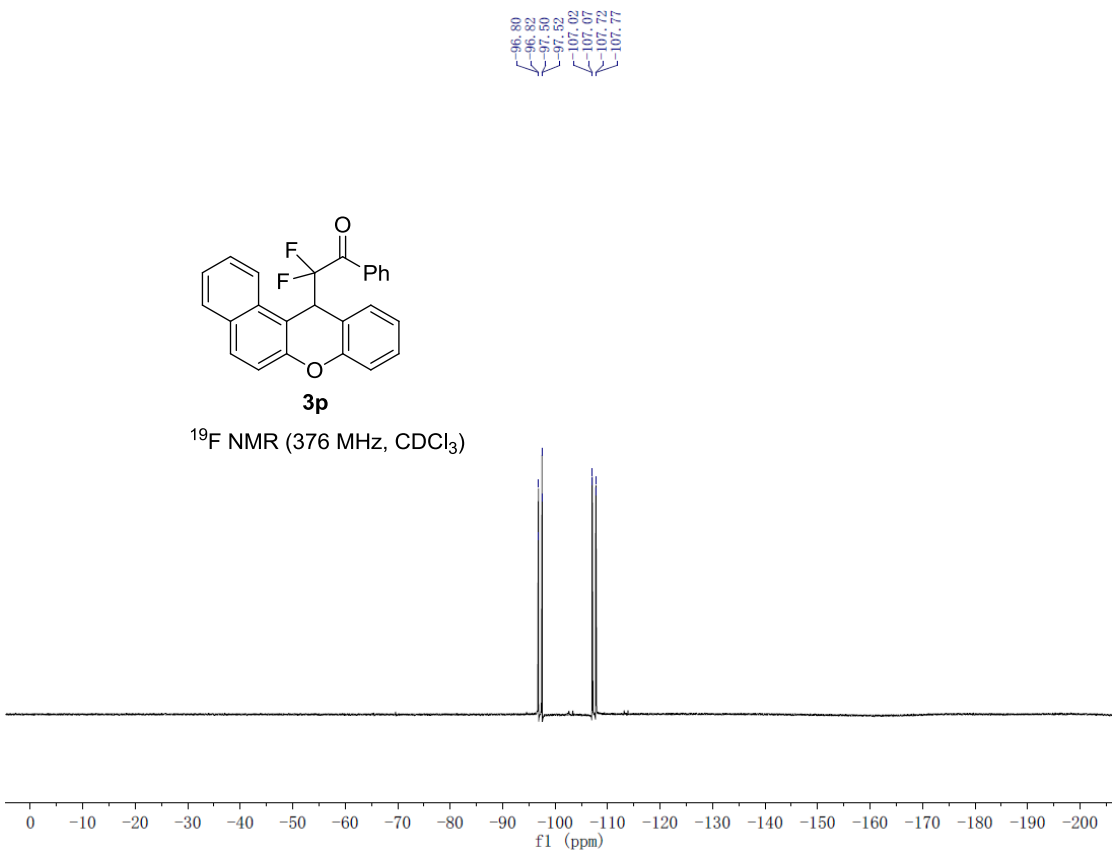
3p

^{1}H NMR (400 MHz, $CDCl_3$)



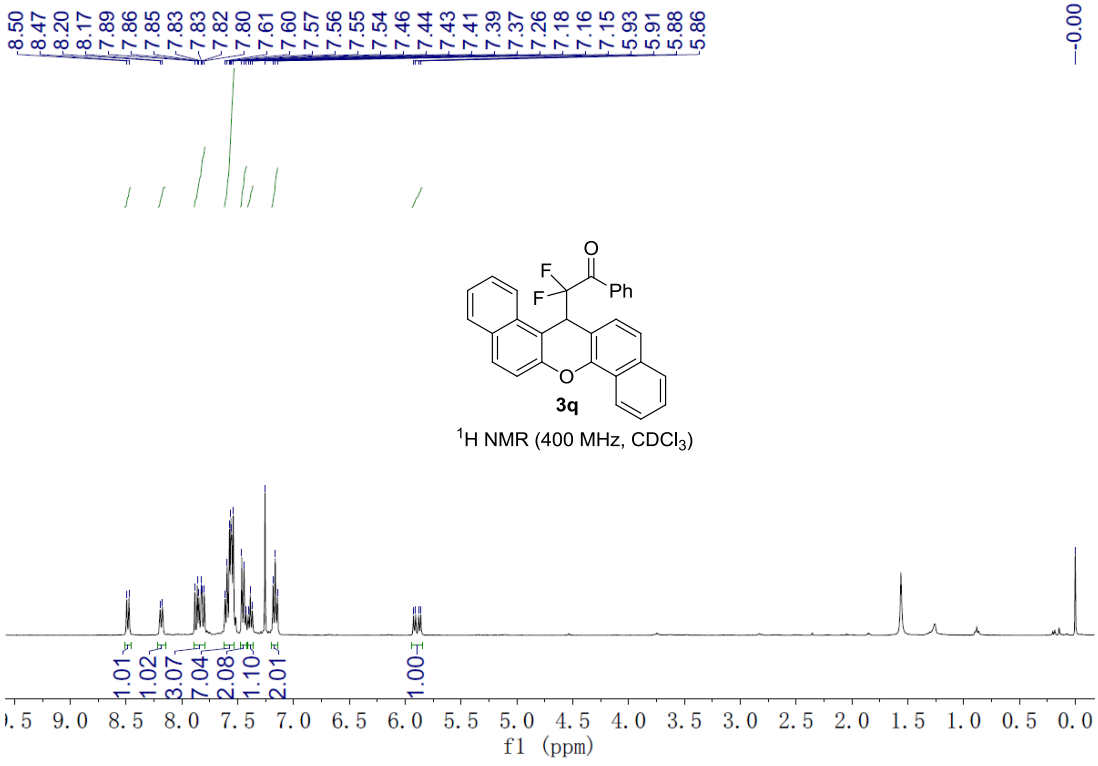
3p

^{13}C NMR (100 MHz, $CDCl_3$)

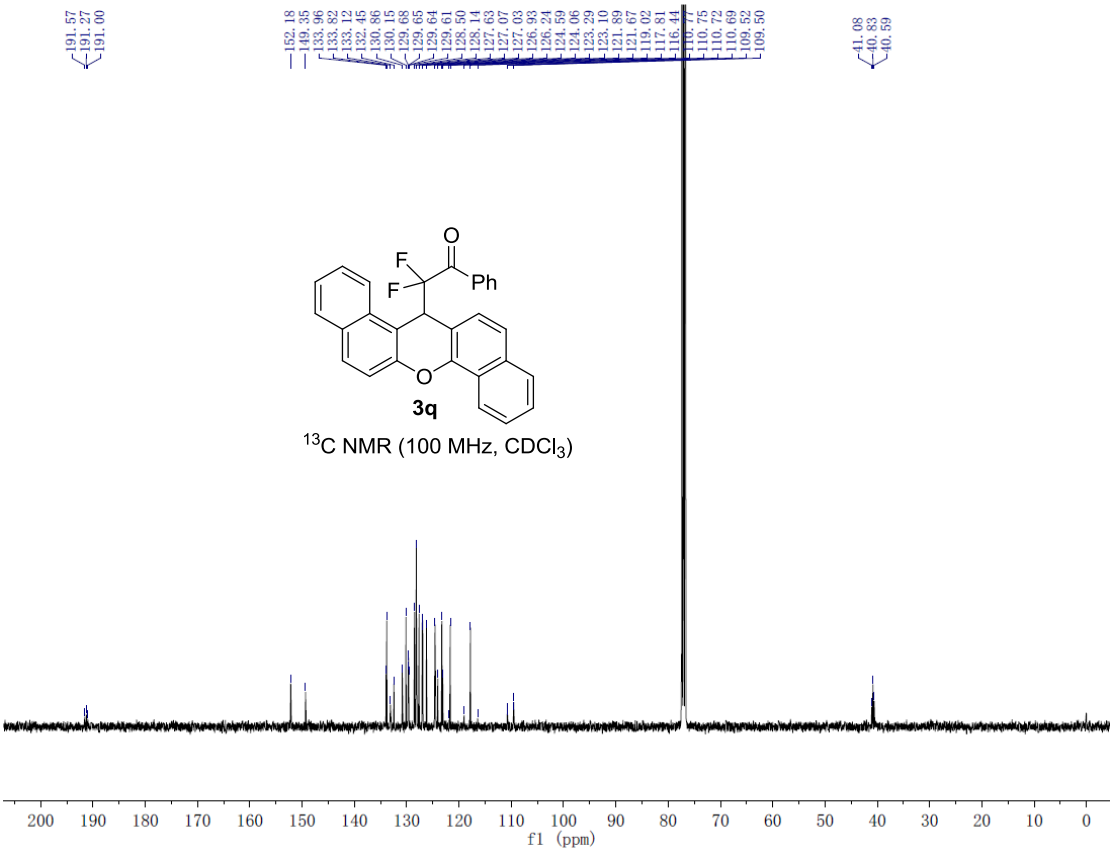


3p

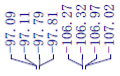
^{19}F NMR (376 MHz, $CDCl_3$)

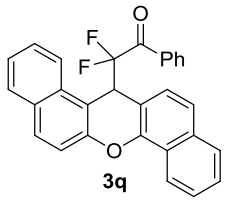


^{1}H NMR (400 MHz, $CDCl_3$)



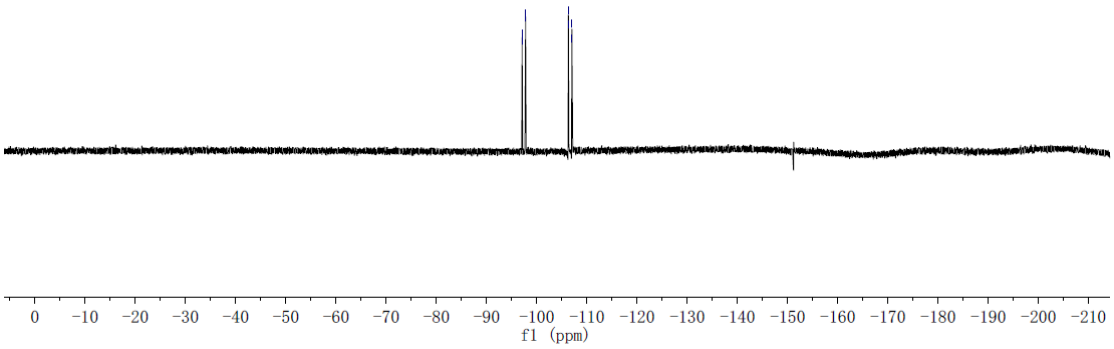
^{13}C NMR (100 MHz, $CDCl_3$)

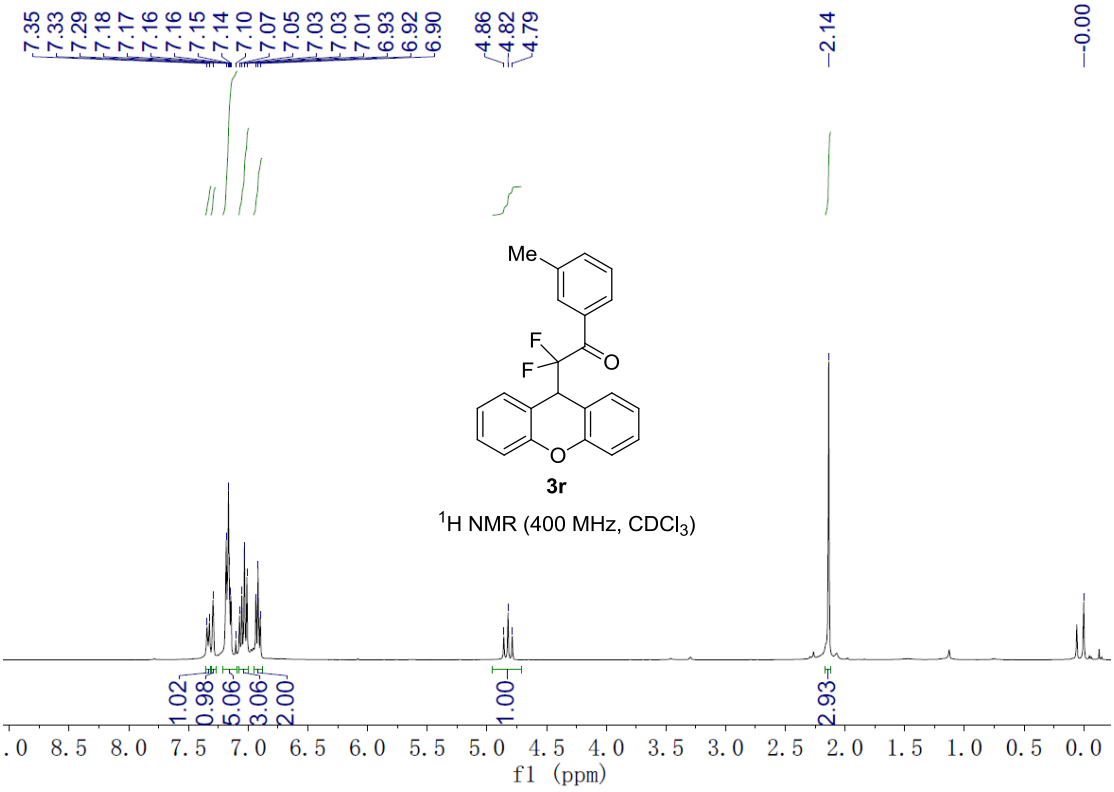




3q

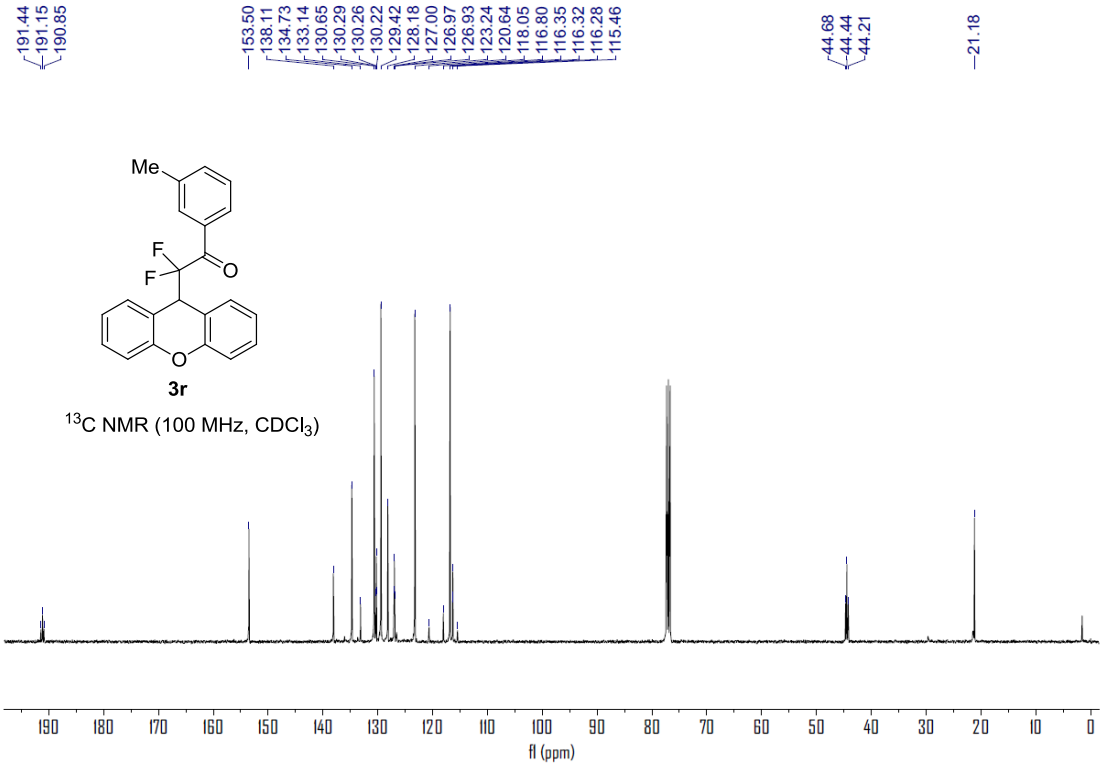
^{19}F NMR (376 MHz, $CDCl_3$)





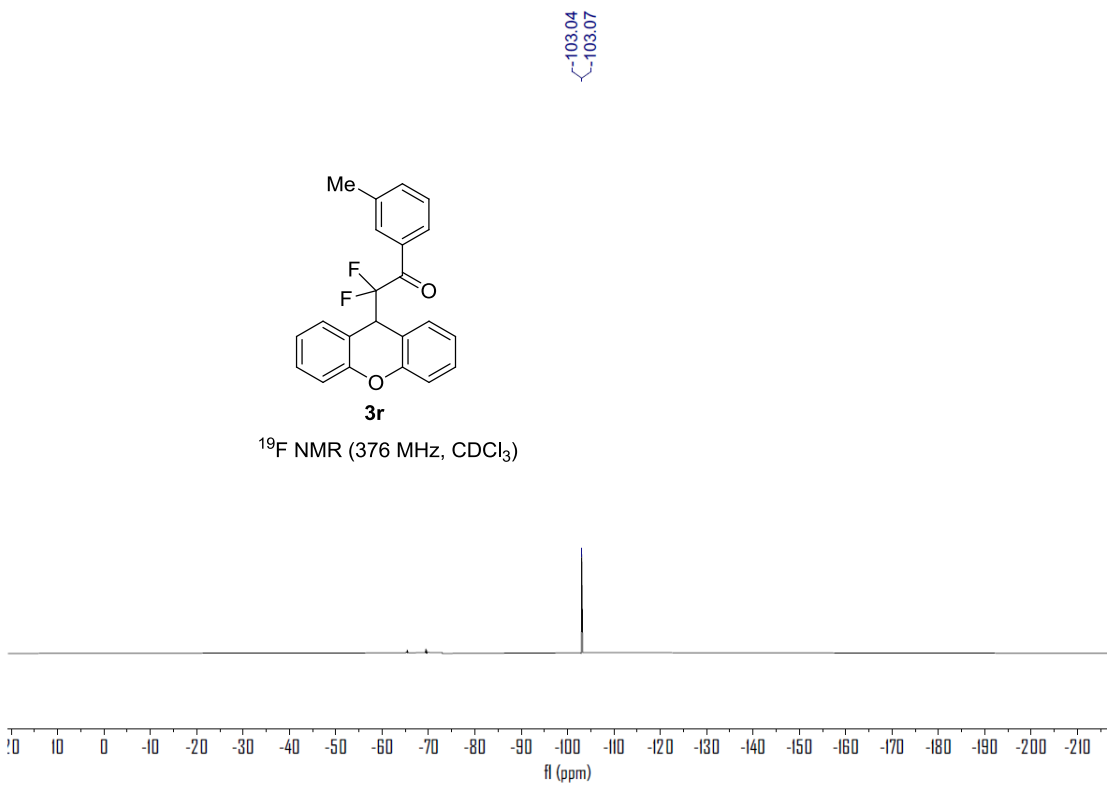
3r

^{1}H NMR (400 MHz, $CDCl_3$)



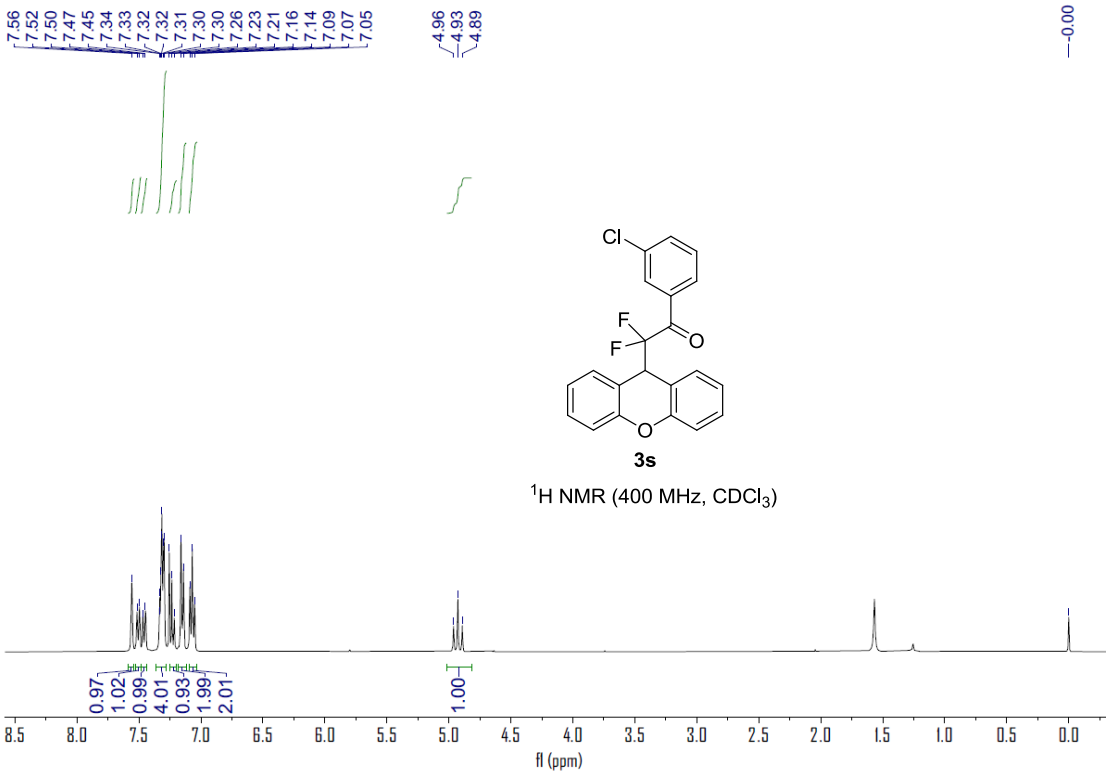
3r

^{13}C NMR (100 MHz, $CDCl_3$)



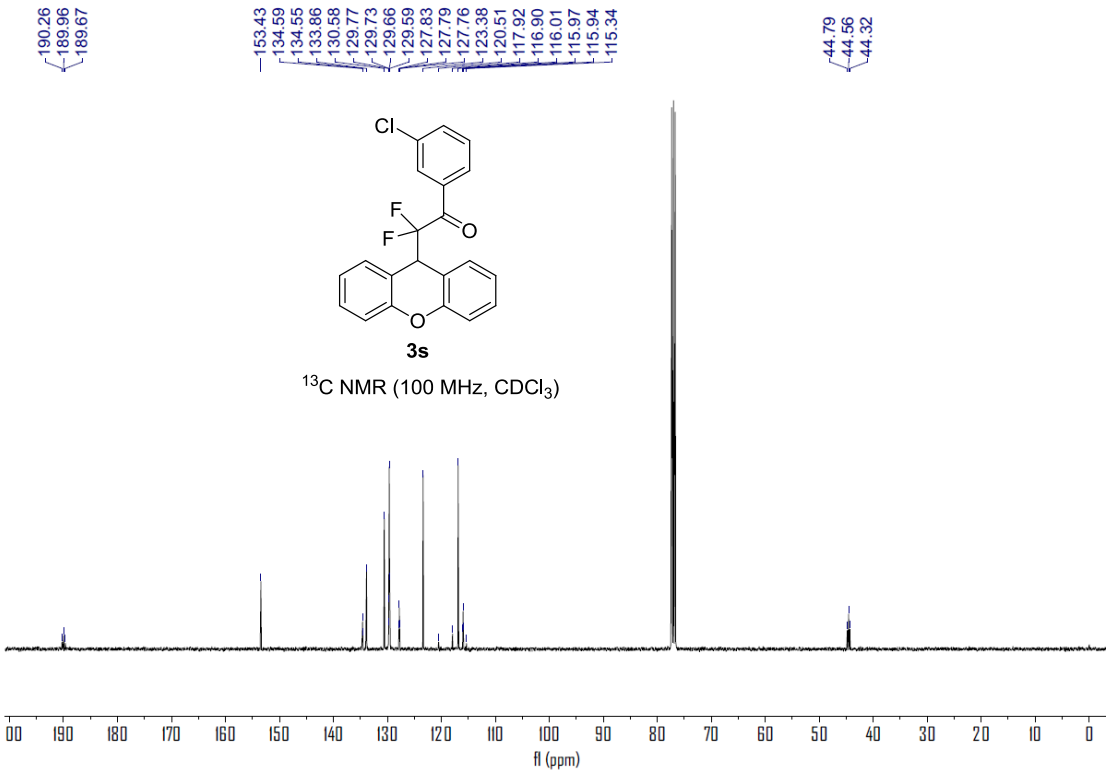
3r

^{19}F NMR (376 MHz, $CDCl_3$)



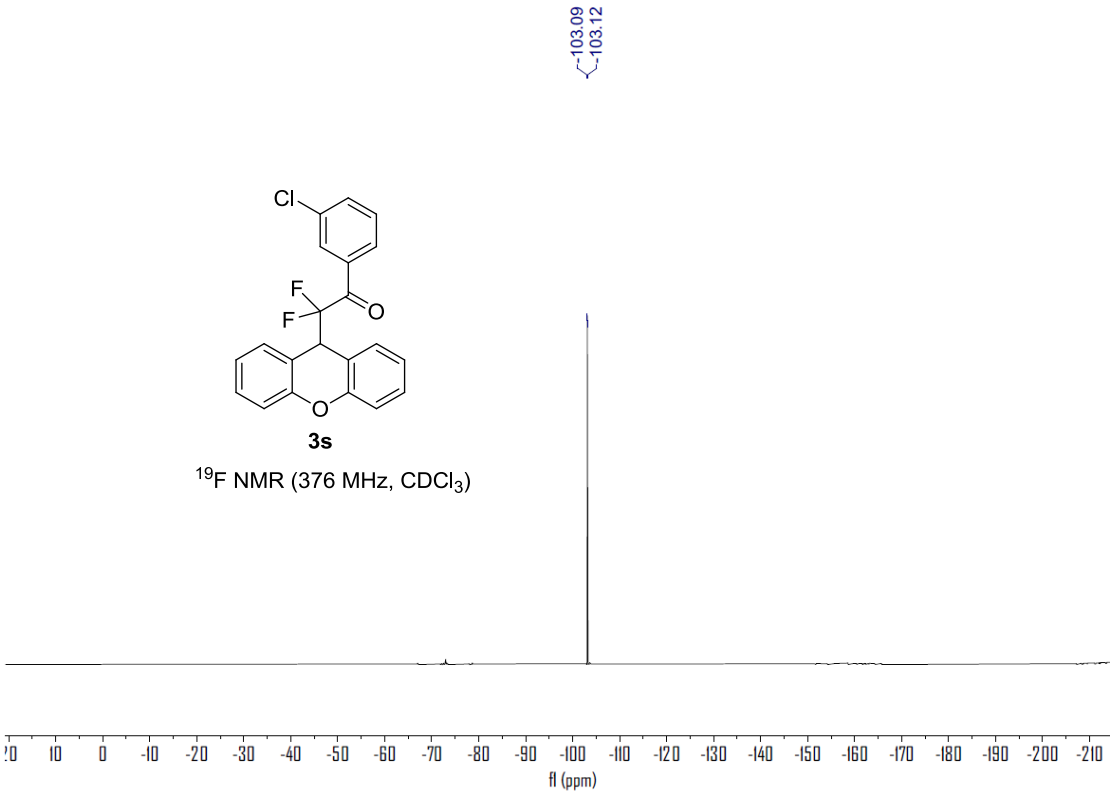
3s

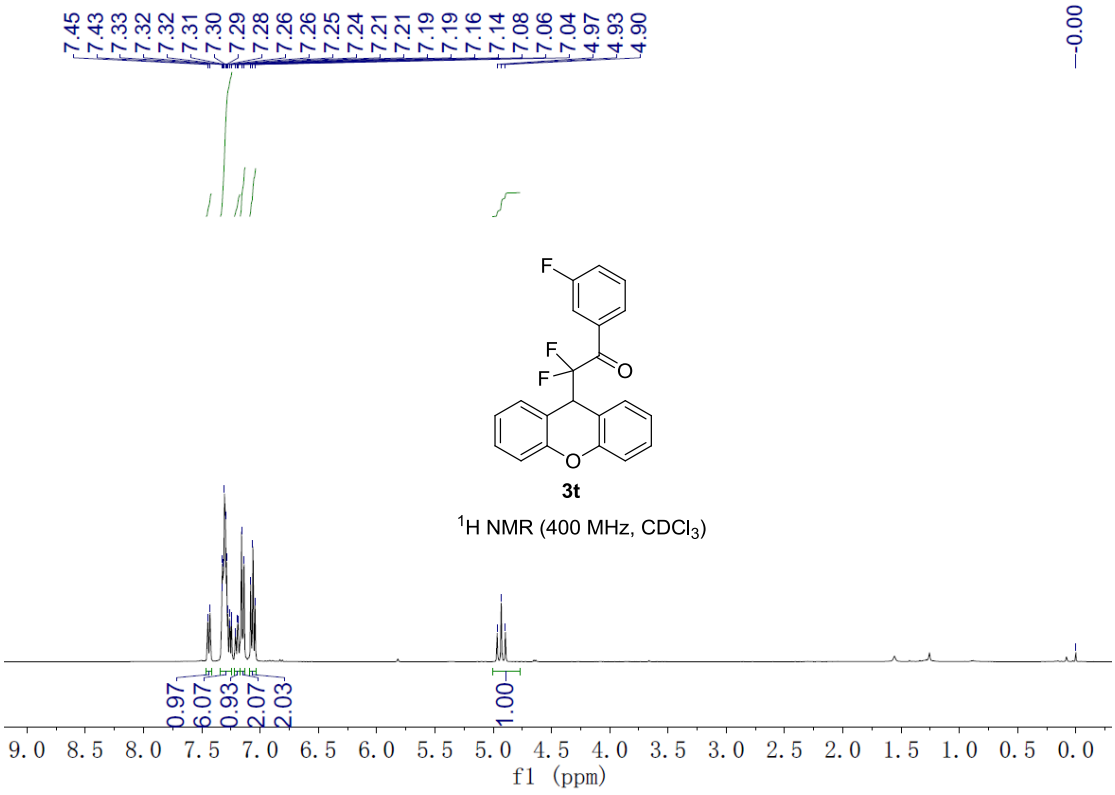
^{1}H NMR (400 MHz, $CDCl_3$)

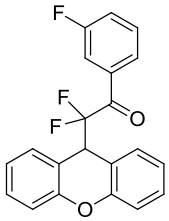


3s

^{13}C NMR (100 MHz, $CDCl_3$)

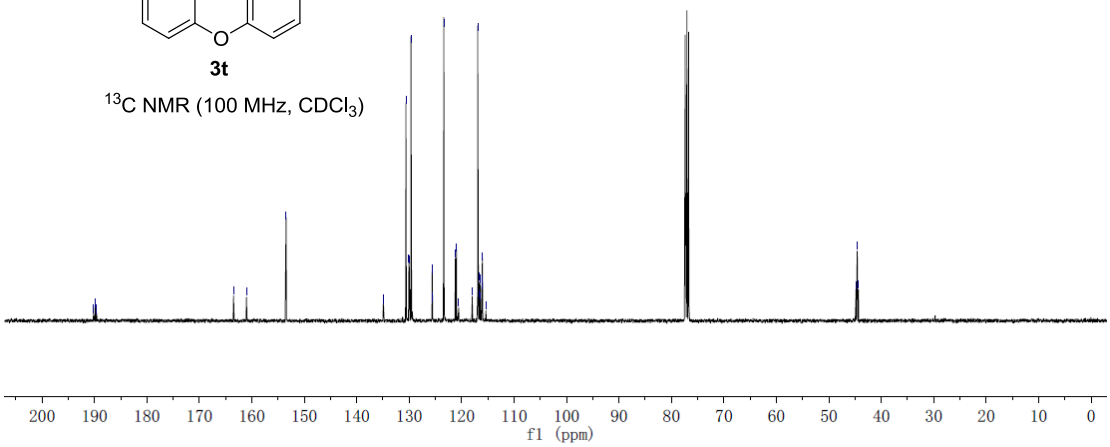

-103.09
-103.12
Cl
F
F
O
O
3s
19F NMR (376 MHz, CDCl3)
f1 (ppm)

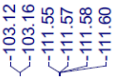

7.45
7.43
7.33
7.32
7.32
7.31
7.30
7.29
7.28
7.26
7.26
7.25
7.24
7.21
7.21
7.19
7.19
7.16
7.14
7.08
7.06
7.04
4.97
4.93
4.90
-0.00
F
F
F
O
O
3t
1H NMR (400 MHz, CDCl3)
0.97
6.07
0.93
2.07
2.03
1.00
f1 (ppm)

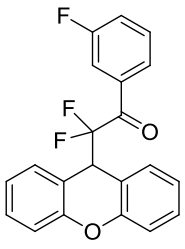


3t

^{13}C NMR (100 MHz, $CDCl_3$)

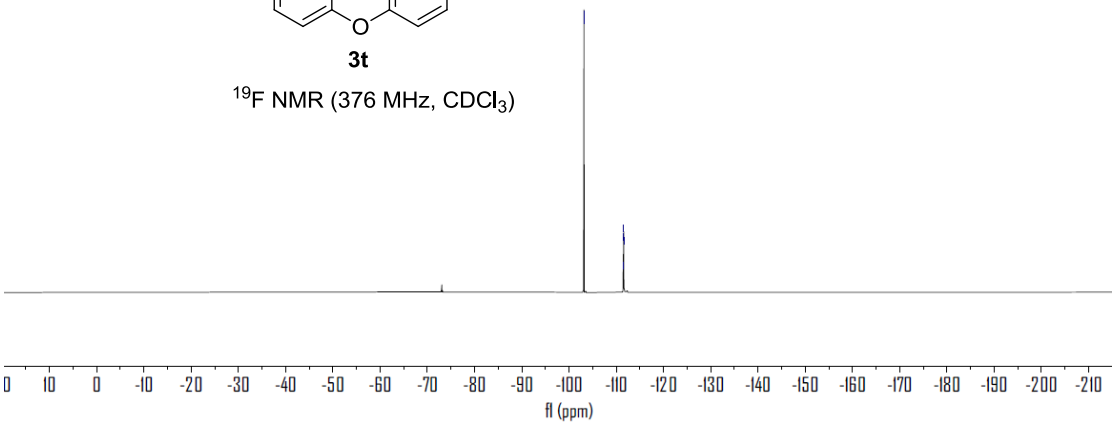


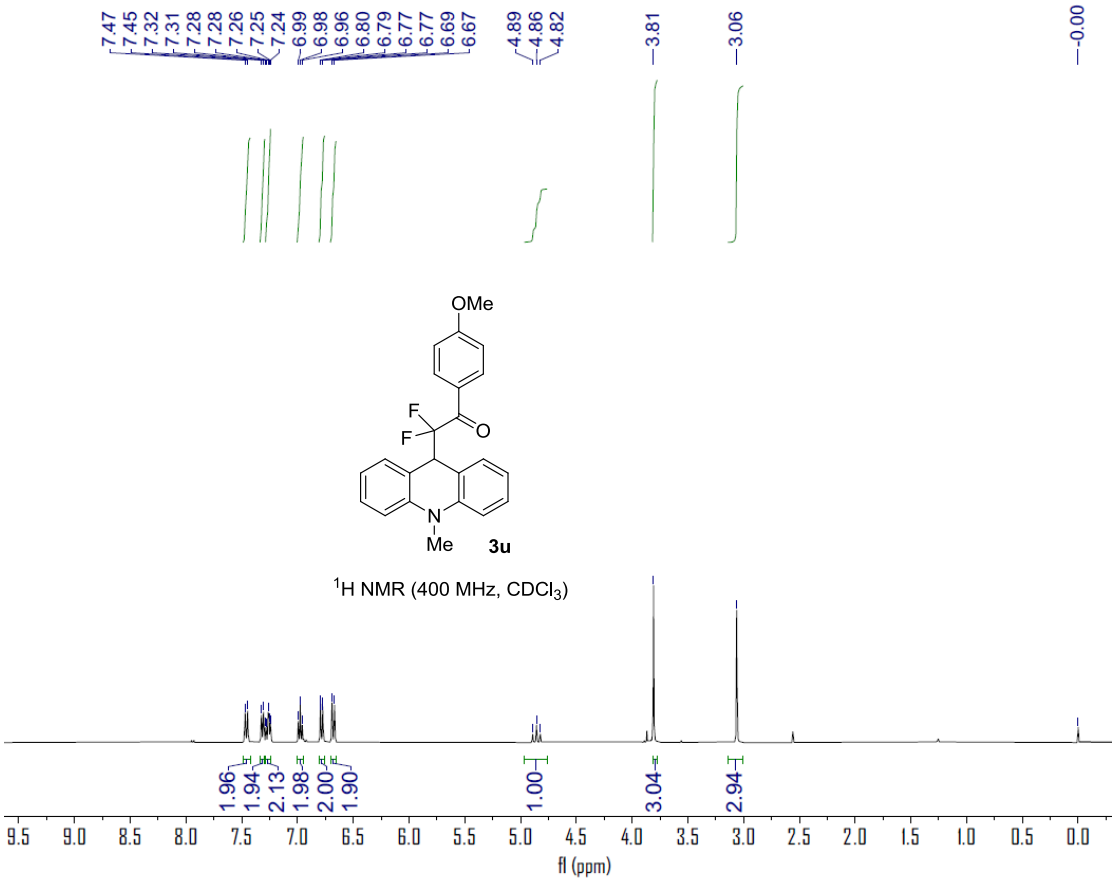


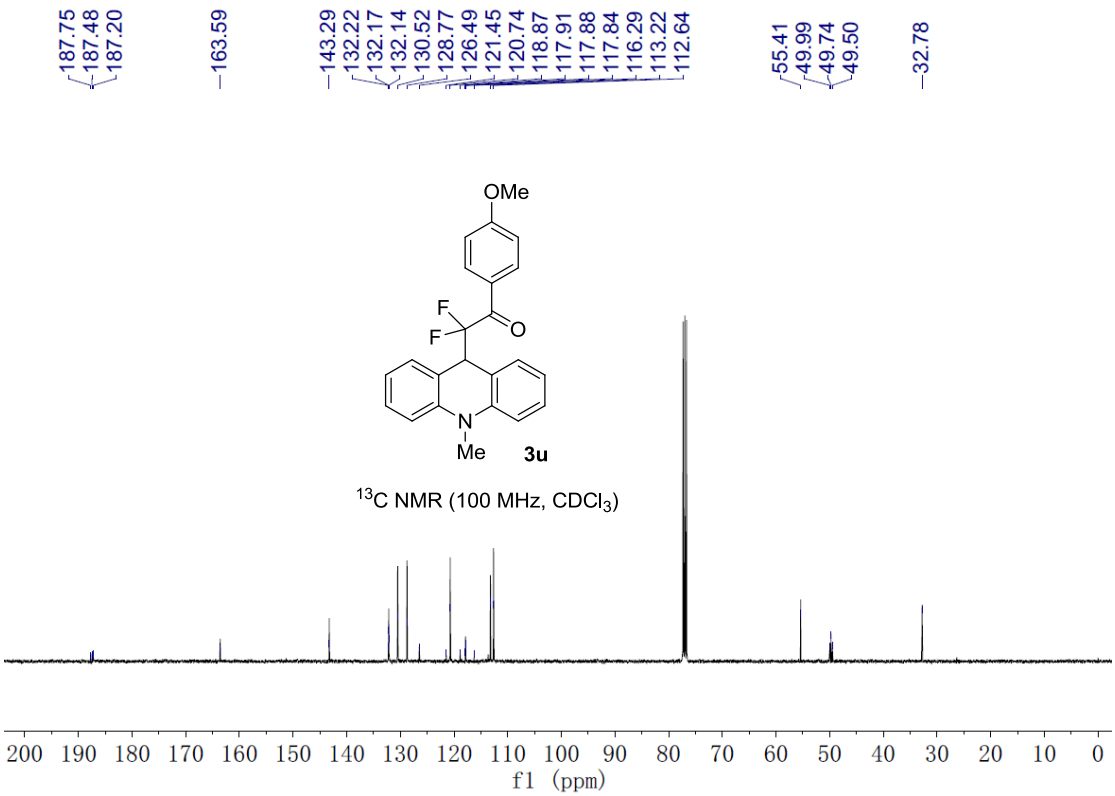


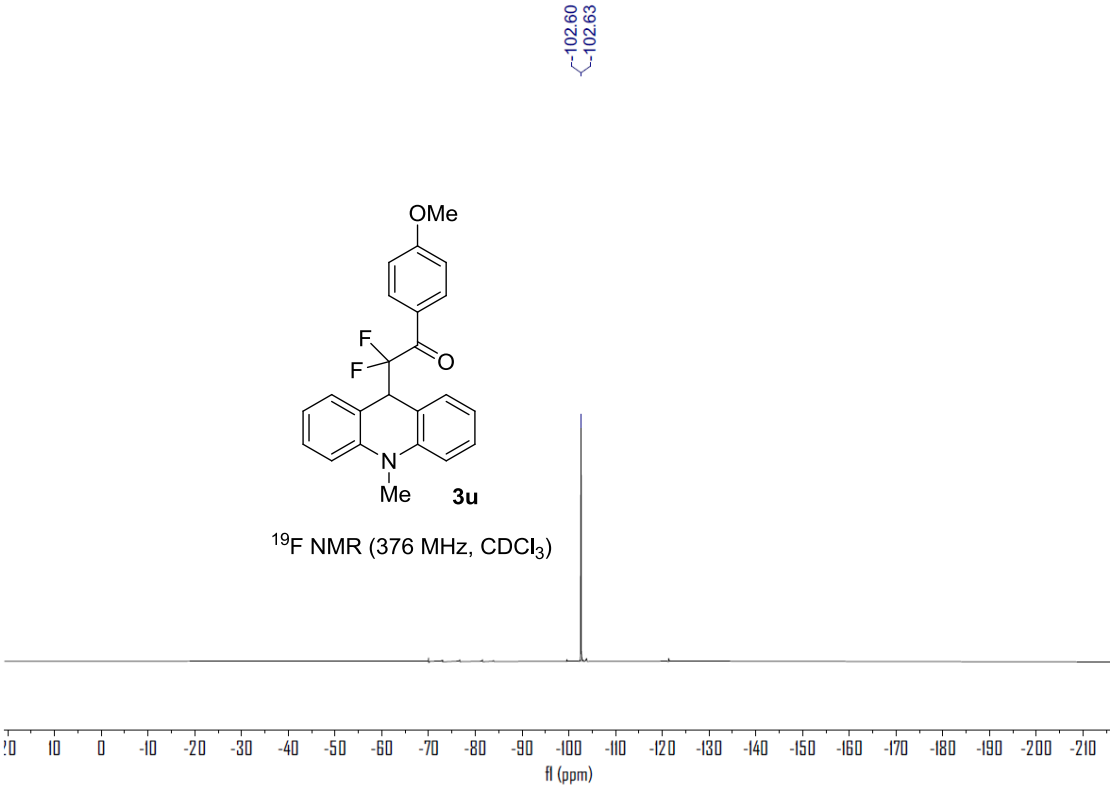
3t

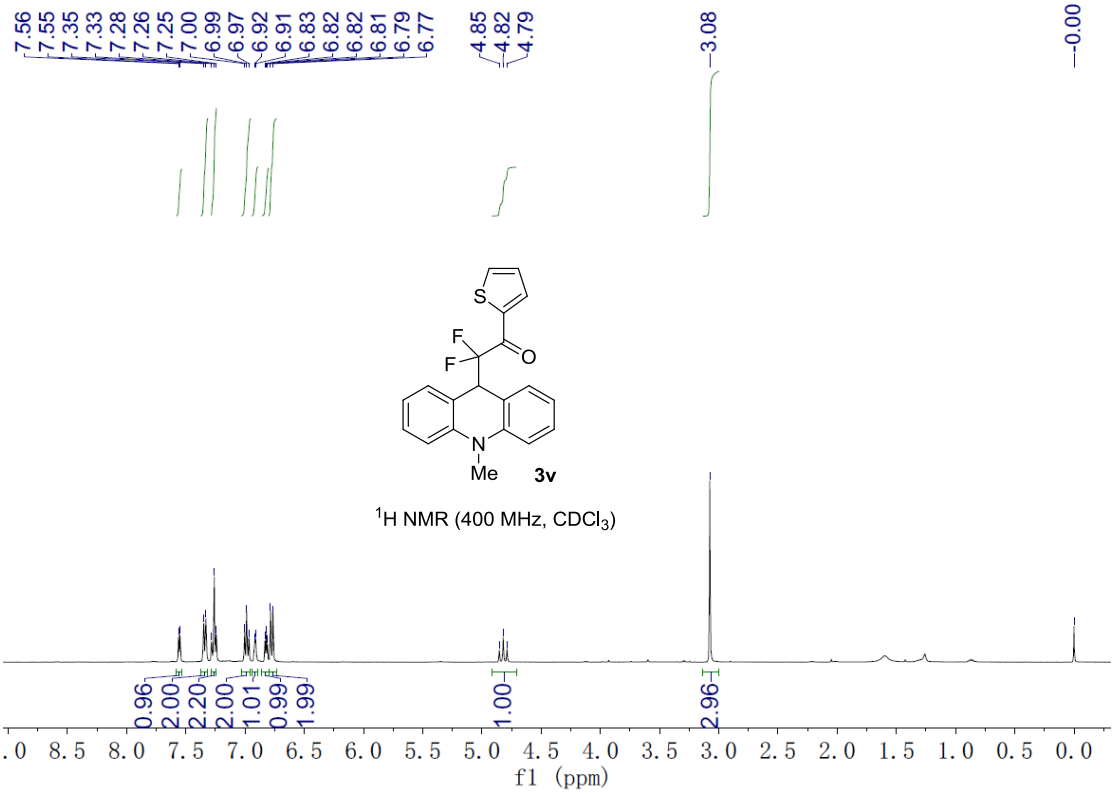
^{19}F NMR (376 MHz, $CDCl_3$)

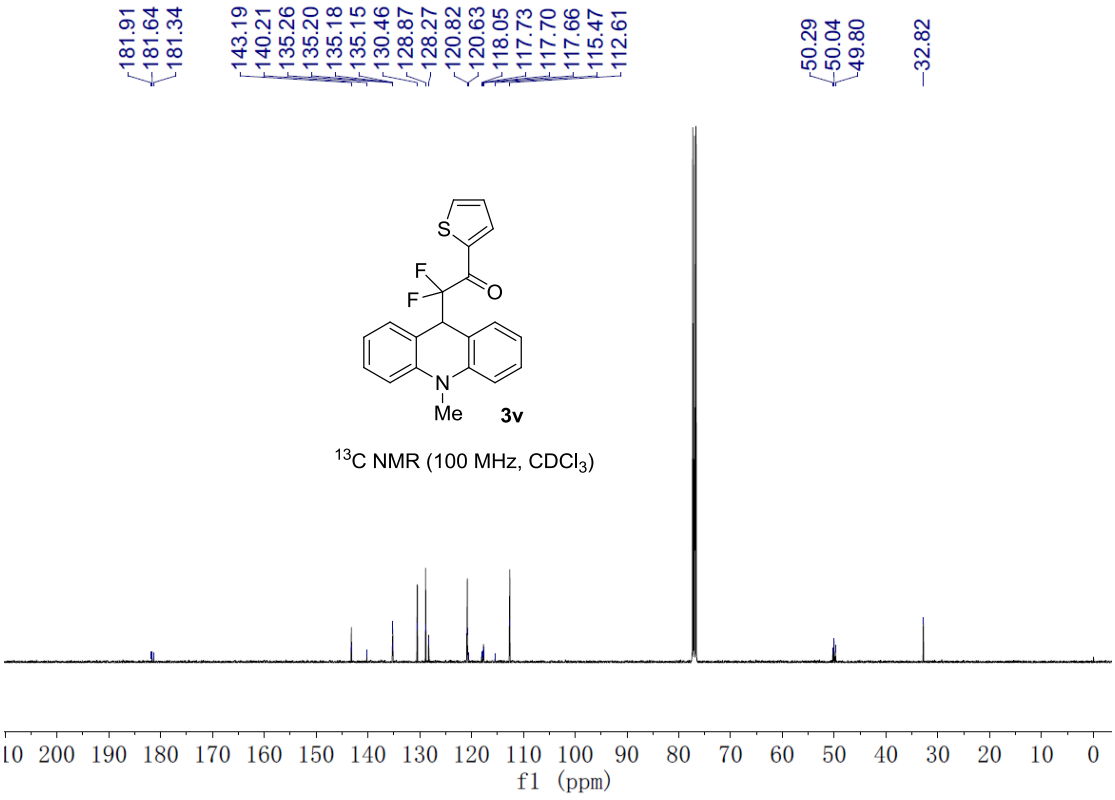



7.47
7.45
7.32
7.31
7.28
7.28
7.26
7.25
7.24
6.99
6.98
6.96
6.80
6.79
6.77
6.77
6.69
6.67
4.89
4.86
4.82
3.81
3.06
0.00
OMe
F
F
O
N
Me
3u
1H NMR (400 MHz, CDCl3)
1.96
1.94
2.13
1.98
2.00
1.90
1.00
3.04
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

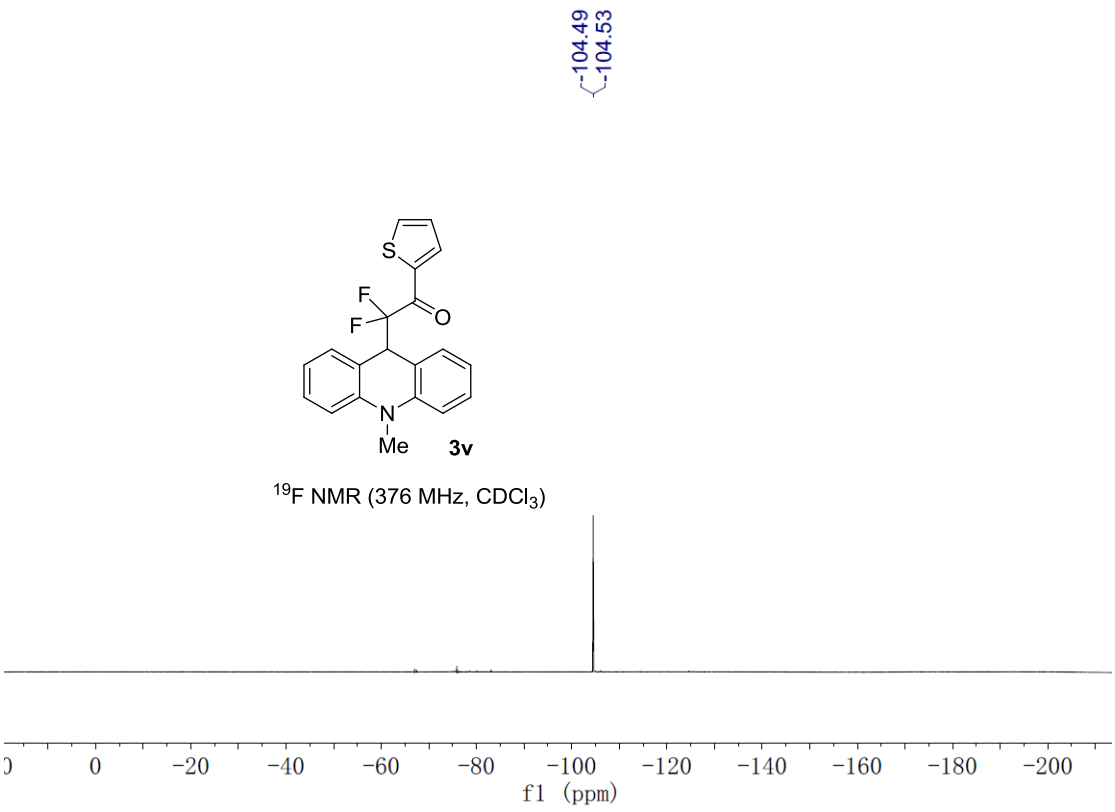

187.75
187.48
187.20
163.59
143.29
132.22
132.17
132.14
130.52
128.77
126.49
121.45
120.74
118.87
117.91
117.88
117.84
116.29
113.22
112.64
55.41
49.99
49.74
49.50
32.78
OMe
F
F
O
N
Me
3u
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-102.60
-102.63
OMe
F
F
O
N
Me
3u
^{19}F NMR (376 MHz, CDCl$_3$)
f1 (ppm)

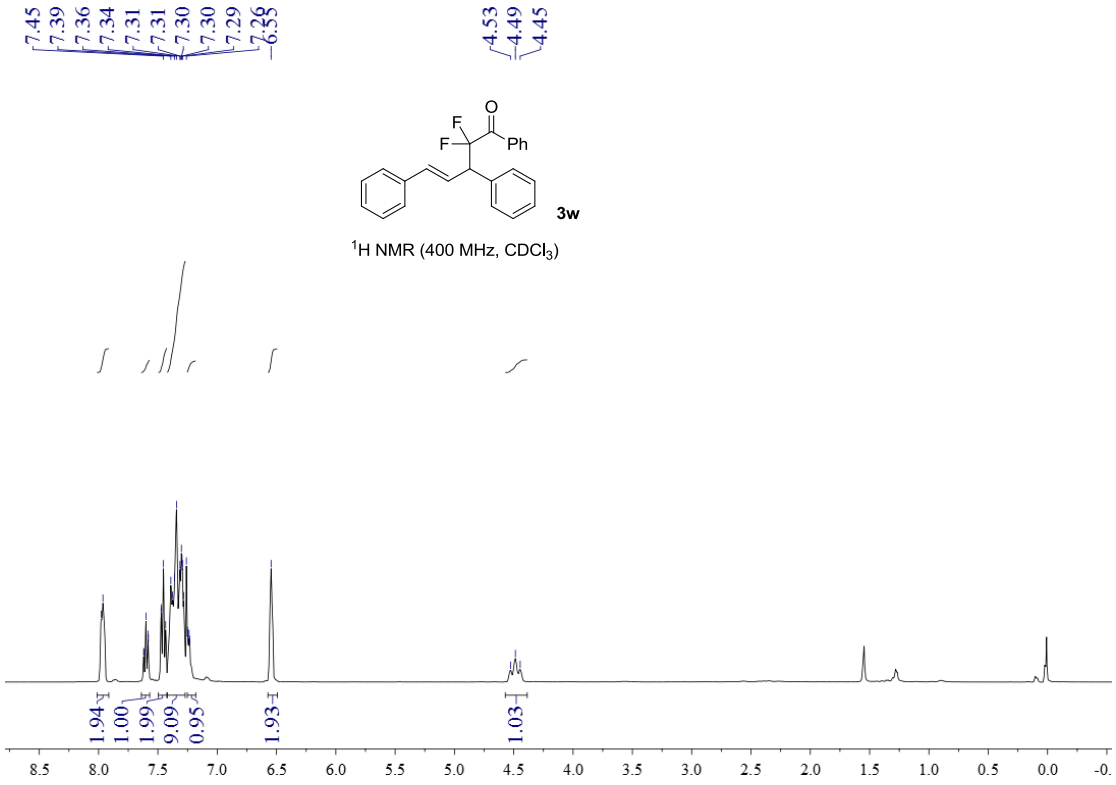

7.56
7.55
7.35
7.33
7.28
7.26
7.25
7.00
6.99
6.97
6.92
6.91
6.83
6.82
6.82
6.81
6.79
6.77
4.85
4.82
4.79
3.08
0.00
S
F
F
O
N
Me
3v
^{1}H NMR (400 MHz, CDCl$_3$)
0.96
2.00
2.20
2.00
1.01
0.99
1.99
1.00
2.96
f1 (ppm)



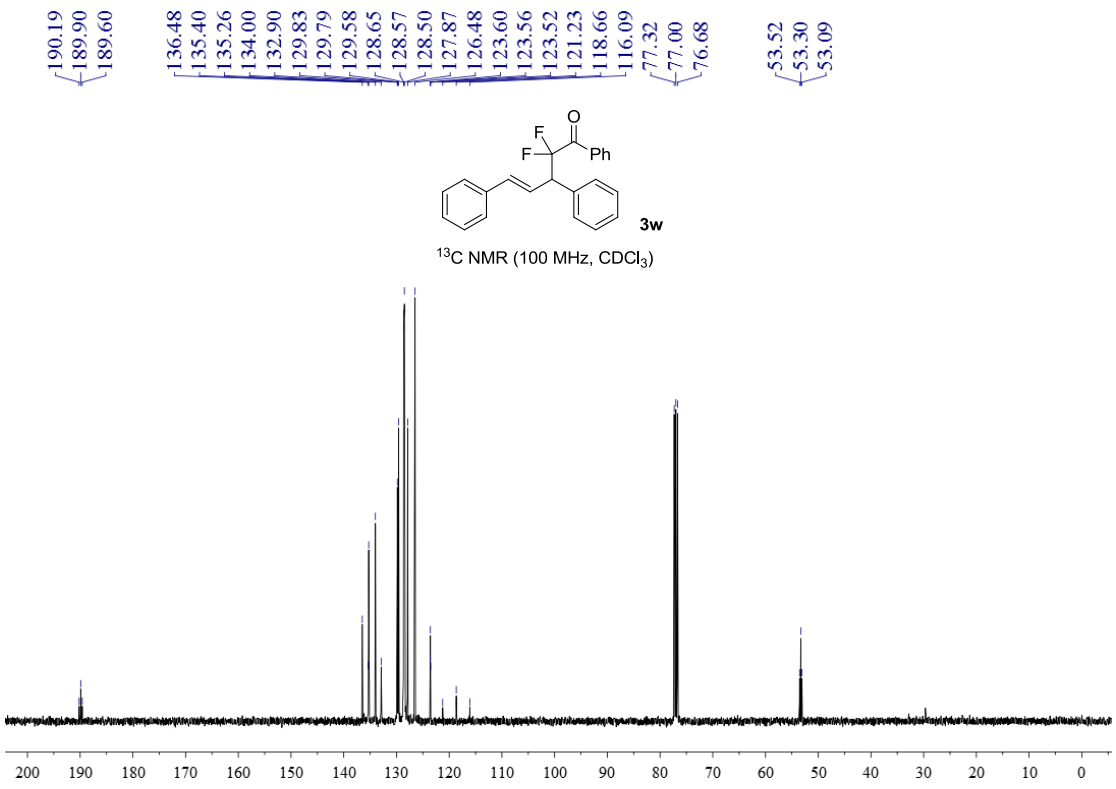
^{13}C NMR (100 MHz, $CDCl_3$)



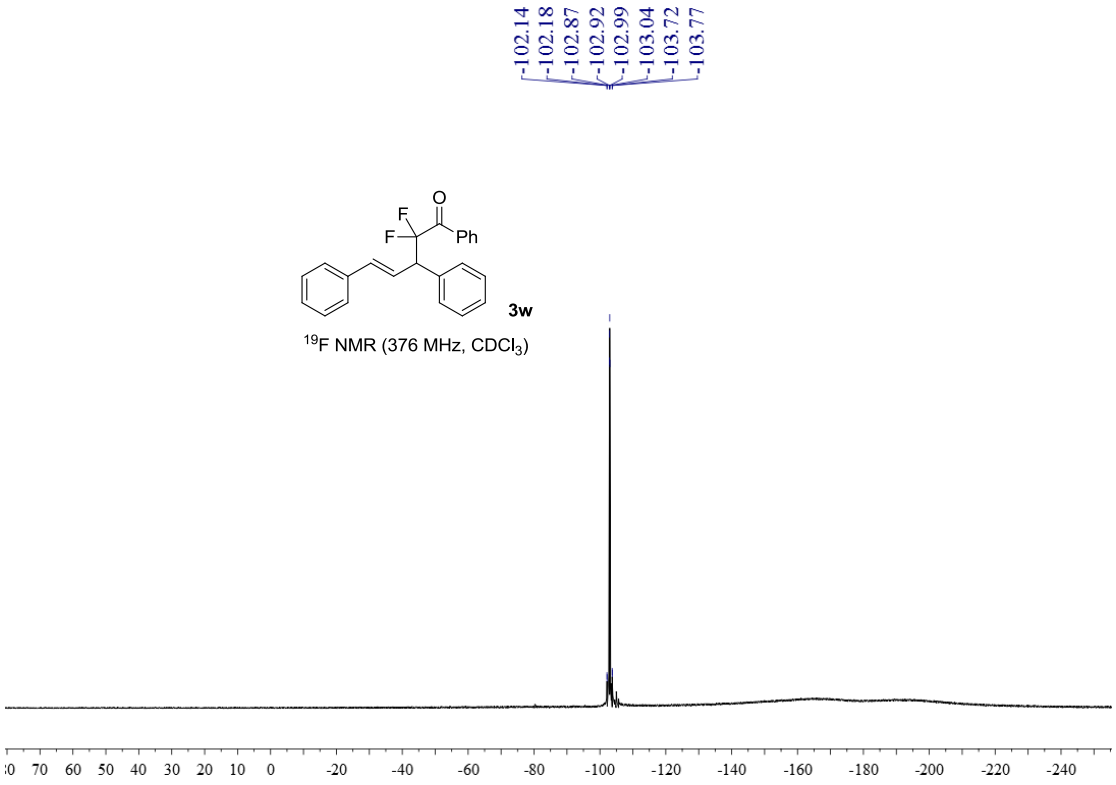
^{19}F NMR (376 MHz, $CDCl_3$)

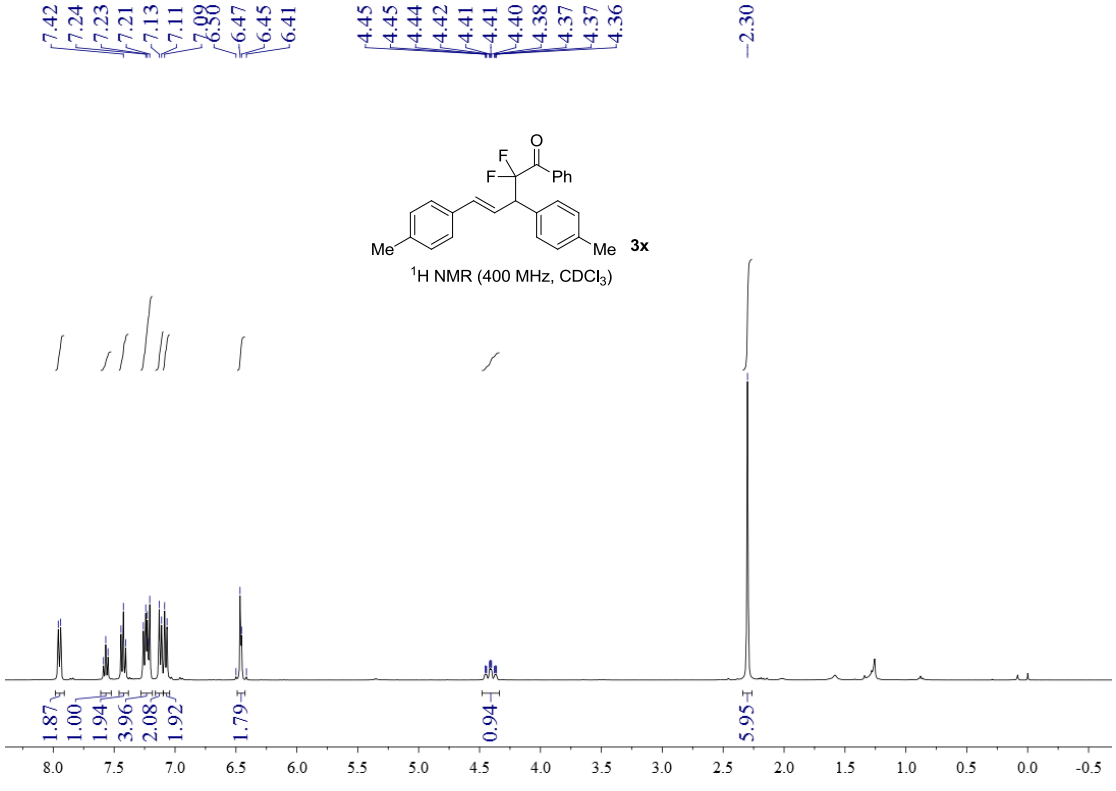


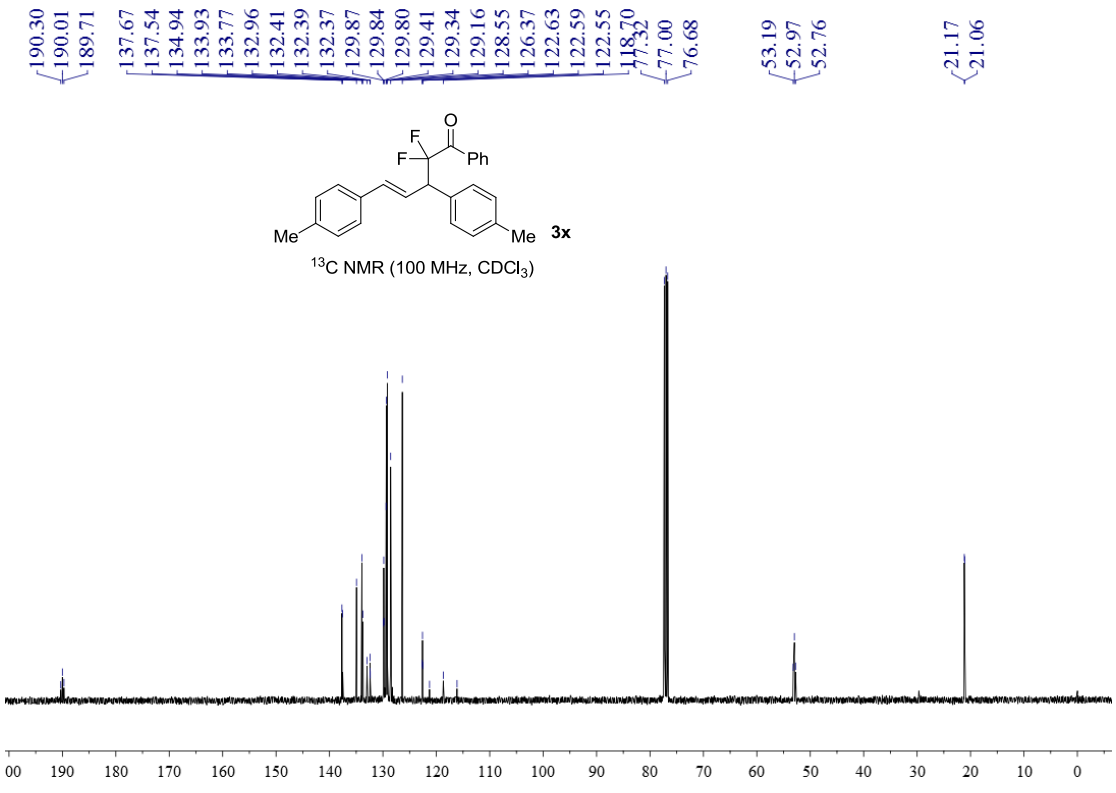
^{1}H NMR (400 MHz, $CDCl_3$)

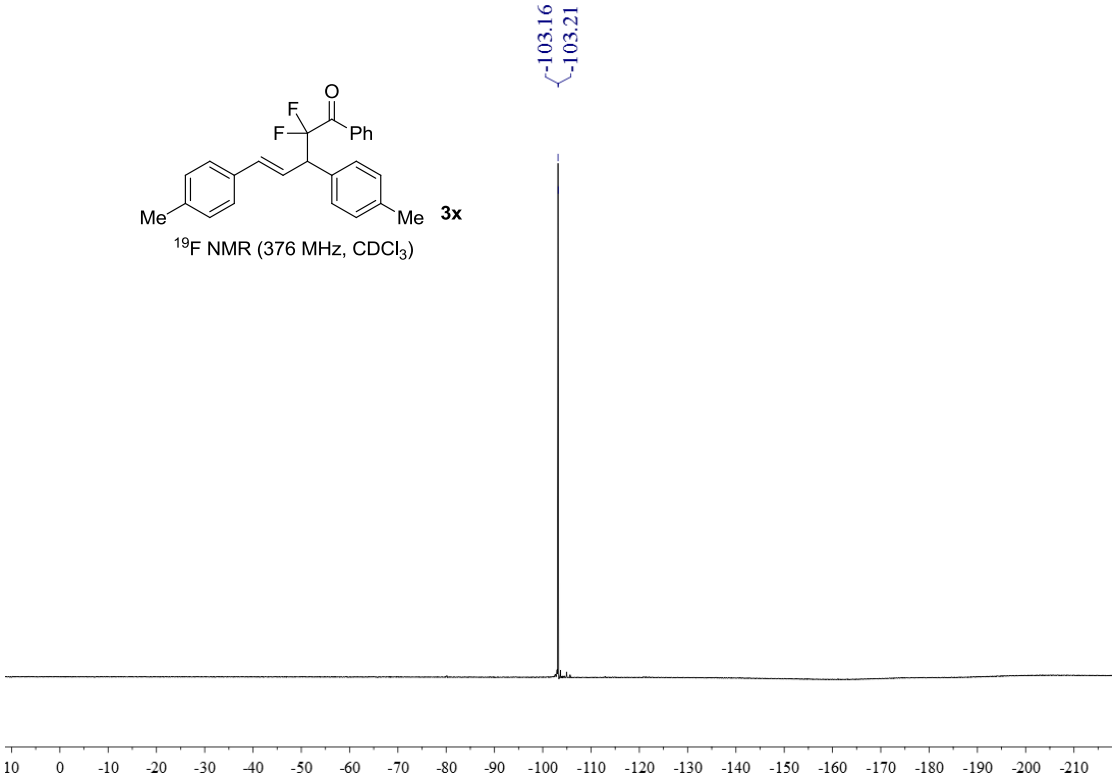


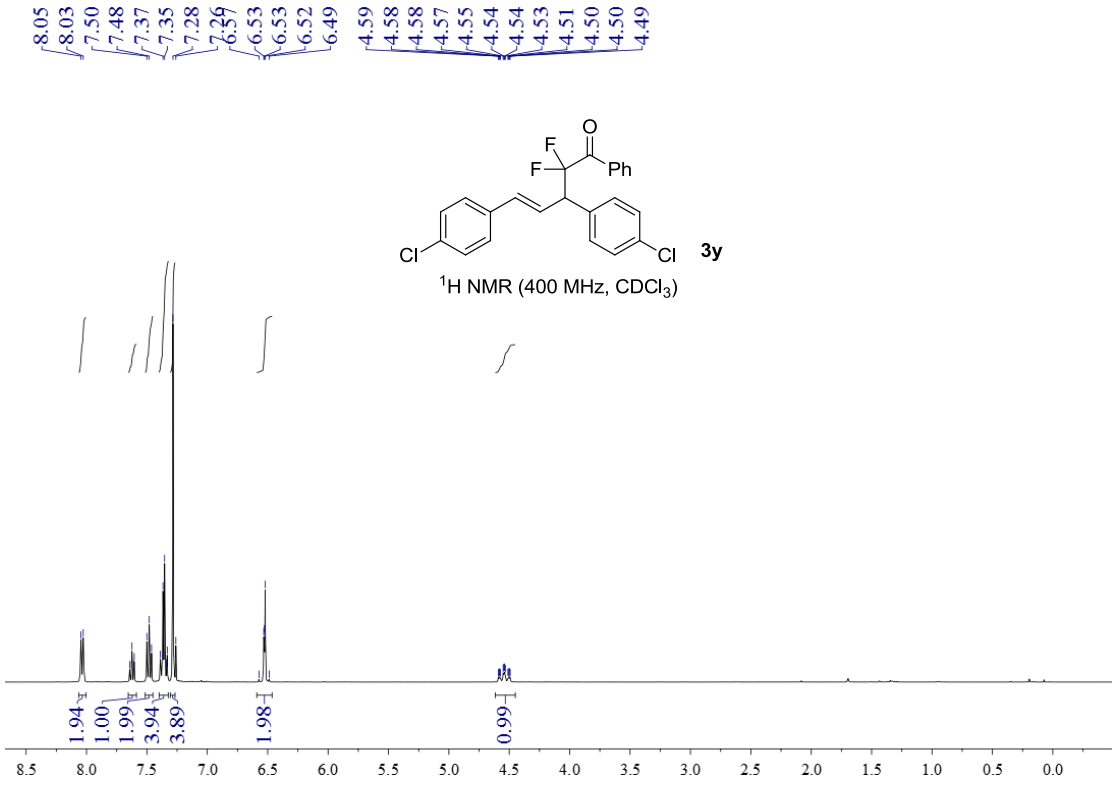
^{13}C NMR (100 MHz, $CDCl_3$)

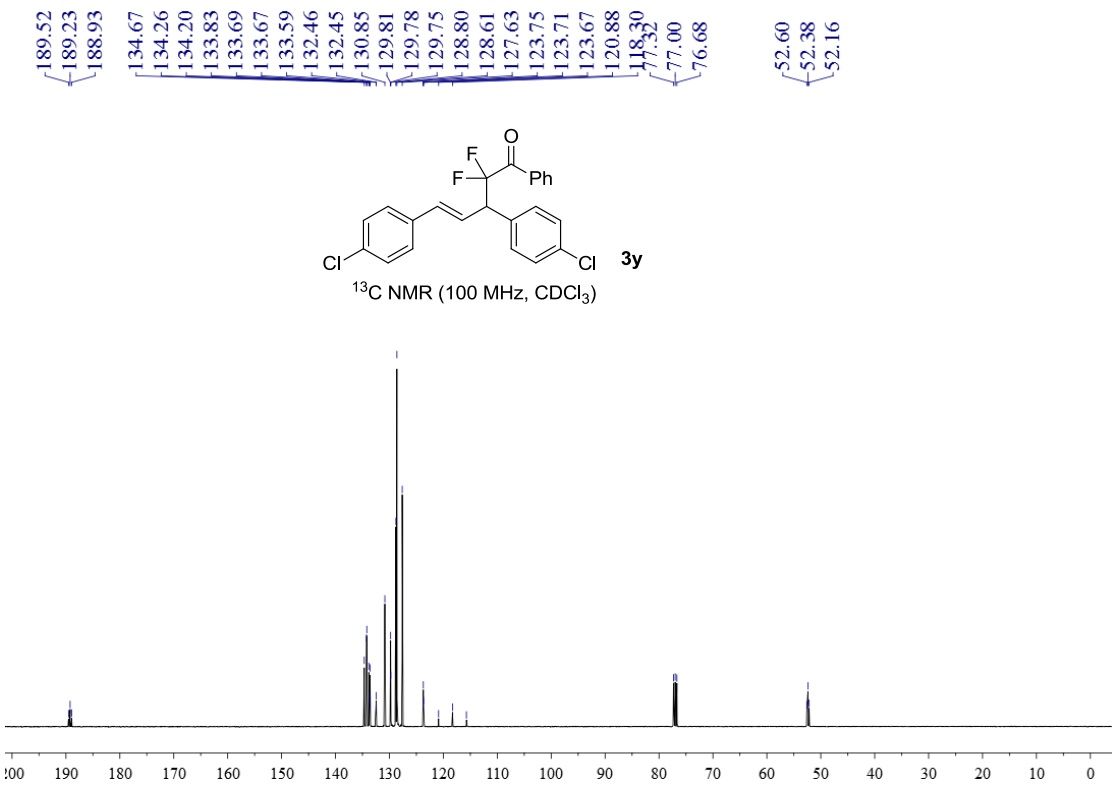

-102.14
-102.18
-102.87
-102.92
-102.99
-103.04
-103.72
-103.77
F
F
O
Ph
3w
^{19}F NMR (376 MHz, CDCl$_3$)
70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240

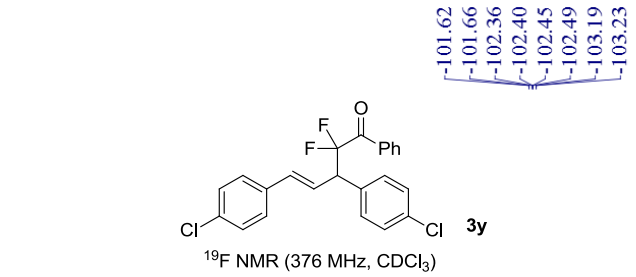

7.42
7.24
7.23
7.21
7.13
7.11
7.09
6.50
6.47
6.45
6.41
4.45
4.45
4.44
4.42
4.41
4.41
4.40
4.38
4.37
4.37
4.36
2.30
F
F
O
Ph
Me
Me
3x
^{1}H NMR (400 MHz, CDCl$_3$)
1.87
1.00
1.94
3.96
2.08
1.92
1.79
0.94
5.95
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5


190.30
190.01
189.71
137.67
137.54
134.94
133.93
133.77
132.96
132.41
132.39
132.37
129.87
129.84
129.80
129.41
129.34
129.16
128.55
126.37
122.63
122.59
122.55
118.70
77.32
77.00
76.68
53.19
52.97
52.76
21.17
21.06
O
F
F
Ph
Me
Me
3x
^{13}C NMR (100 MHz, CDCl$_3$)
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

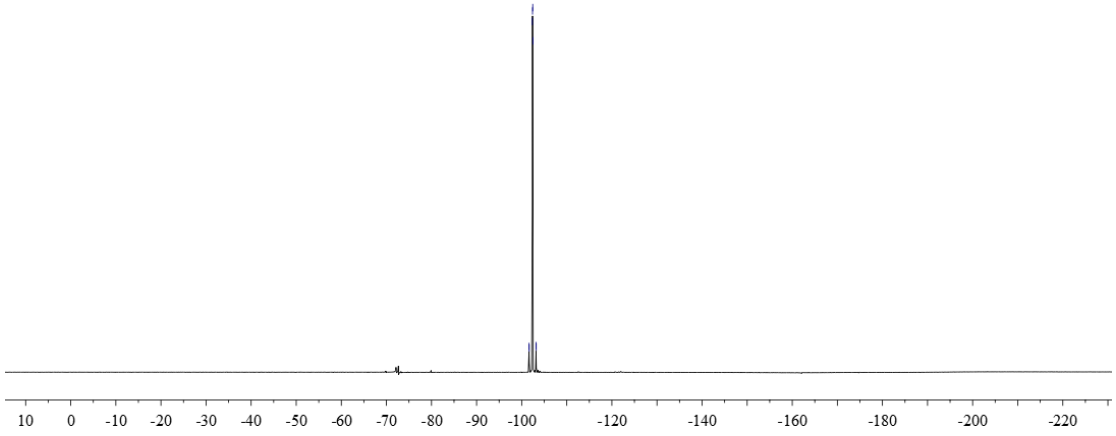

-103.16
-103.21
O
F
F
Ph
Me
Me
3x
^{19}F NMR (376 MHz, CDCl$_3$)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210

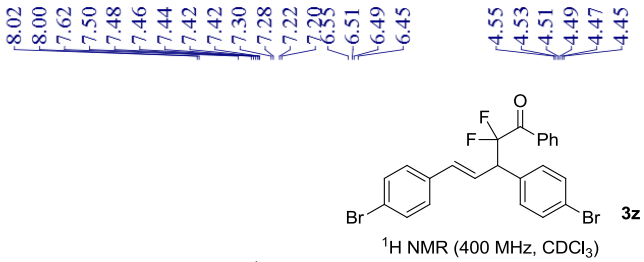

8.05
8.03
7.50
7.48
7.37
7.35
7.28
7.26
6.57
6.53
6.53
6.52
6.49
4.59
4.58
4.58
4.57
4.55
4.54
4.54
4.53
4.51
4.50
4.50
4.49
F
F
O
Ph
Cl
Cl
3y
1H NMR (400 MHz, CDCl3)
1.94
1.00
1.99
3.94
3.89
1.98
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


189.52
189.23
188.93
134.67
134.26
134.20
133.83
133.69
133.67
133.59
132.46
132.45
130.85
129.81
129.78
129.75
128.80
128.61
127.63
123.75
123.71
123.67
120.88
118.30
77.32
77.00
76.68
52.60
52.38
52.16
F
F
O
Ph
Cl
Cl
3y
13C NMR (100 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

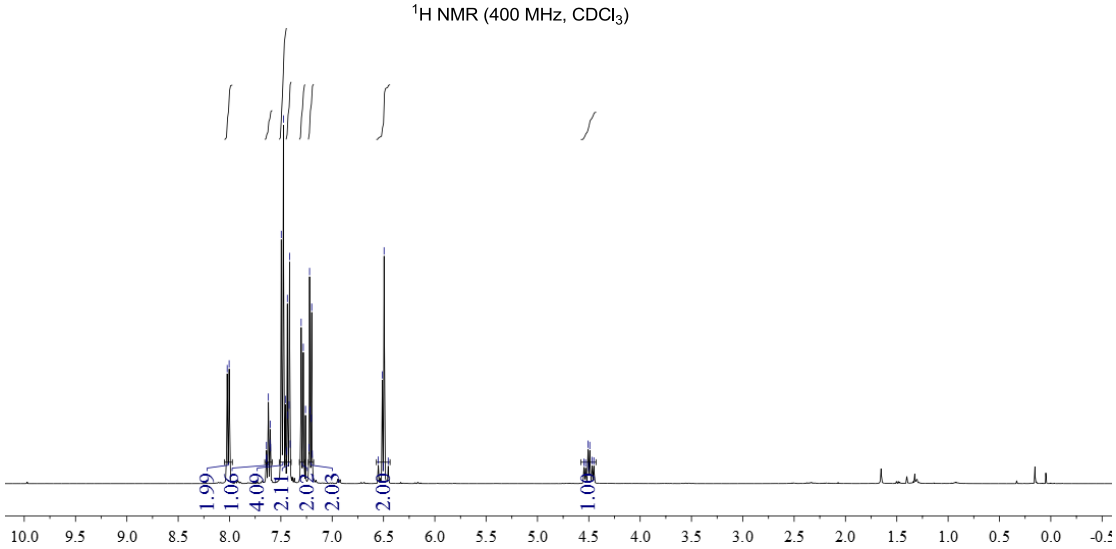


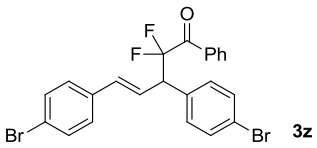
^{19}F NMR (376 MHz, $CDCl_3$)





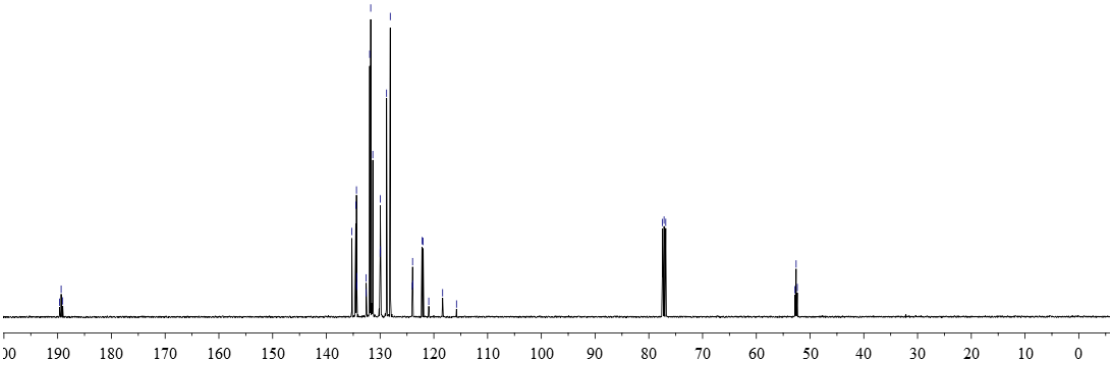
^{1}H NMR (400 MHz, $CDCl_3$)

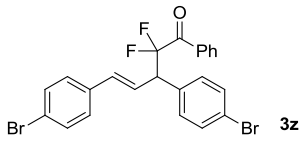




3z

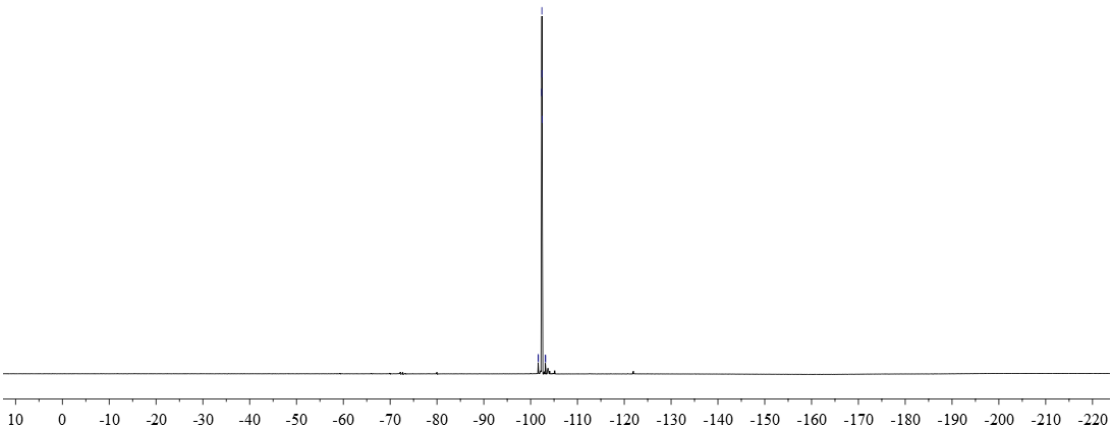
^{13}C NMR (100 MHz, $CDCl_3$)

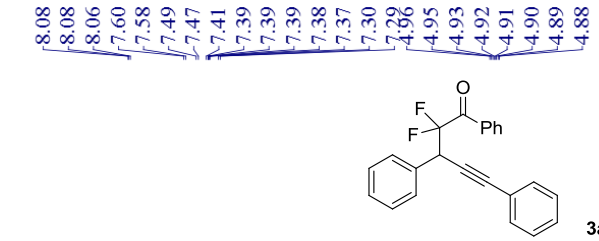




3z

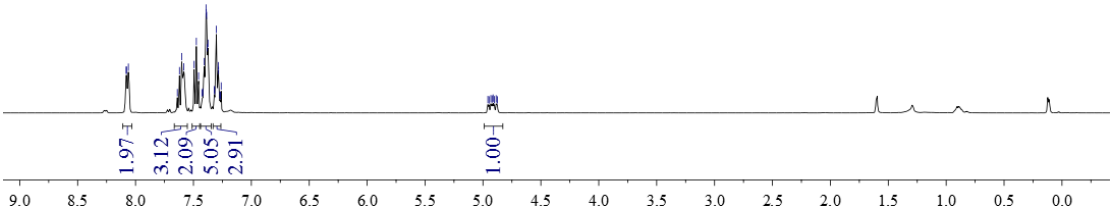
^{19}F NMR (376 MHz, $CDCl_3$)

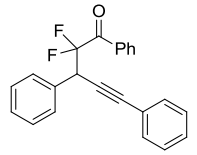




3aa

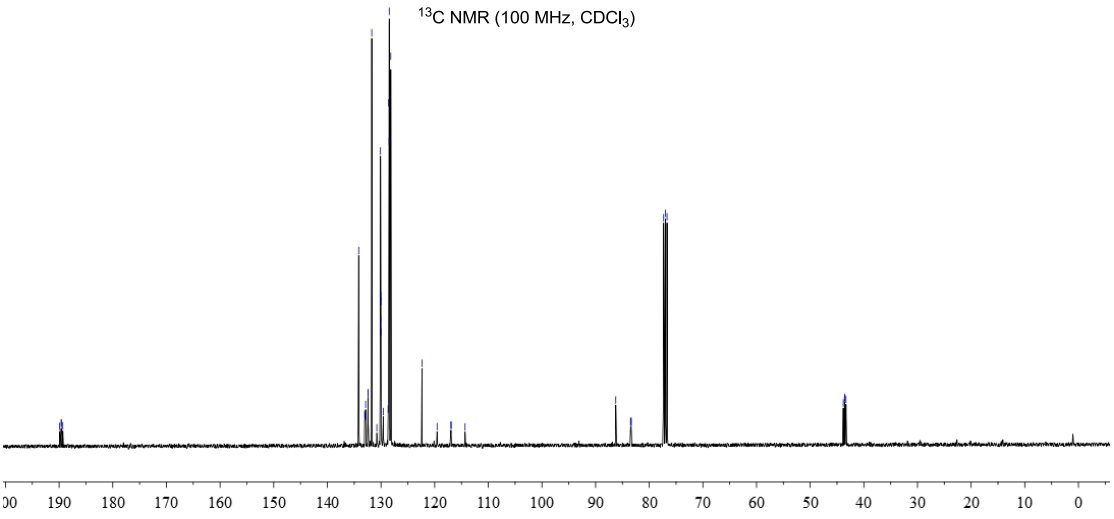
^{1}H NMR (400 MHz, $CDCl_3$)

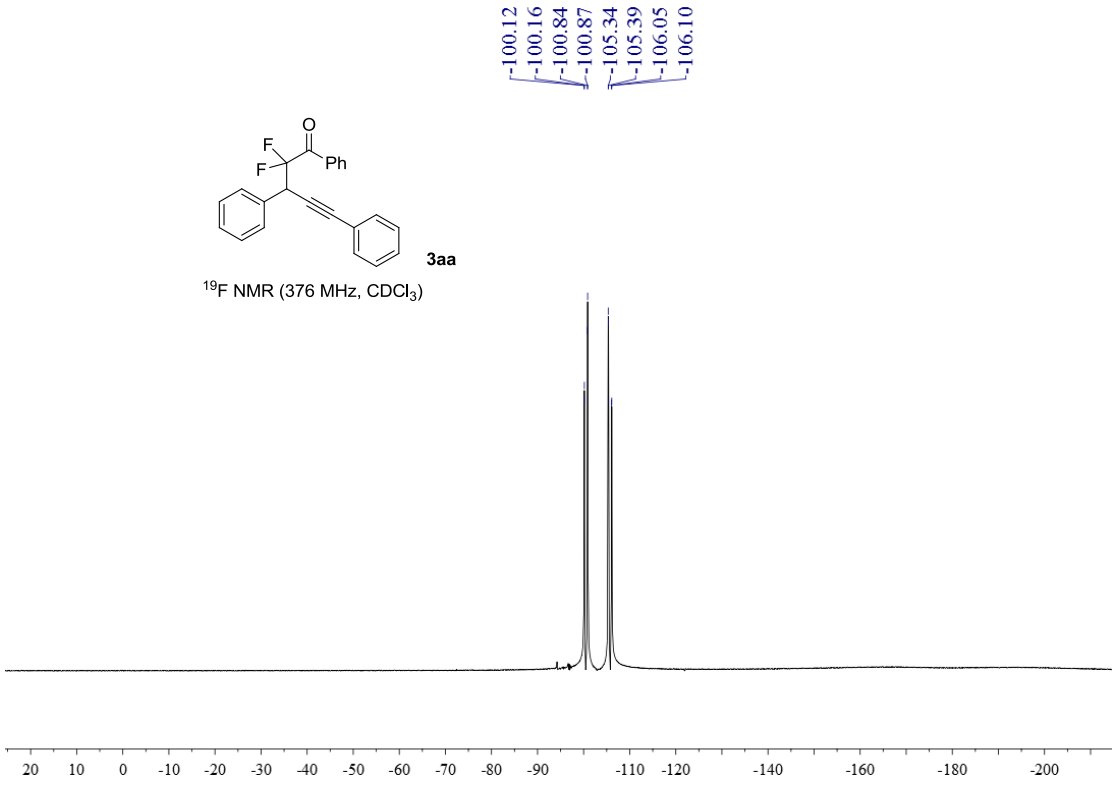




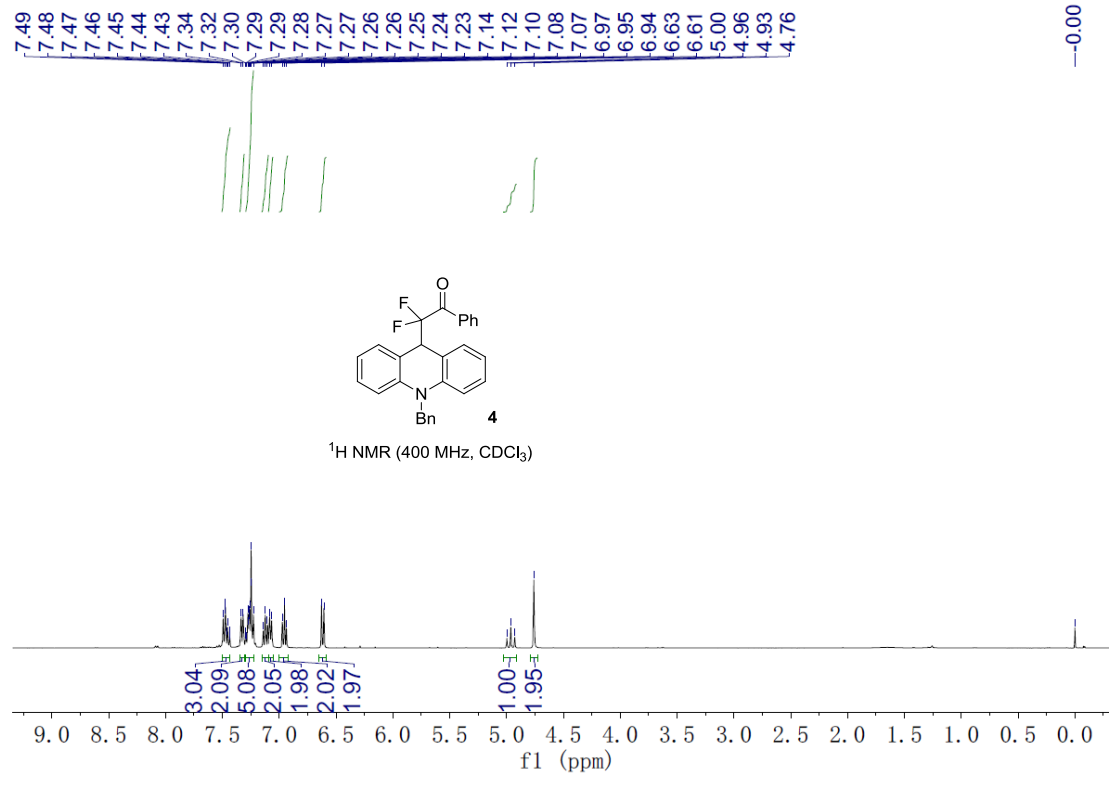
3aa

^{13}C NMR (100 MHz, $CDCl_3$)

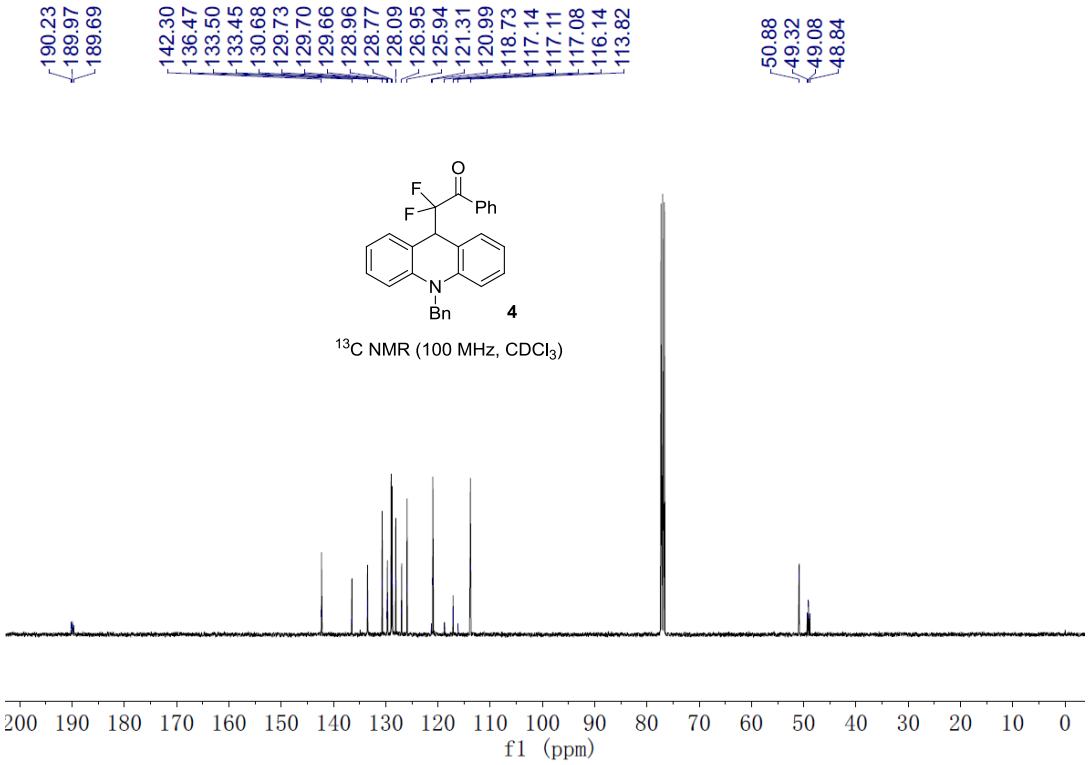




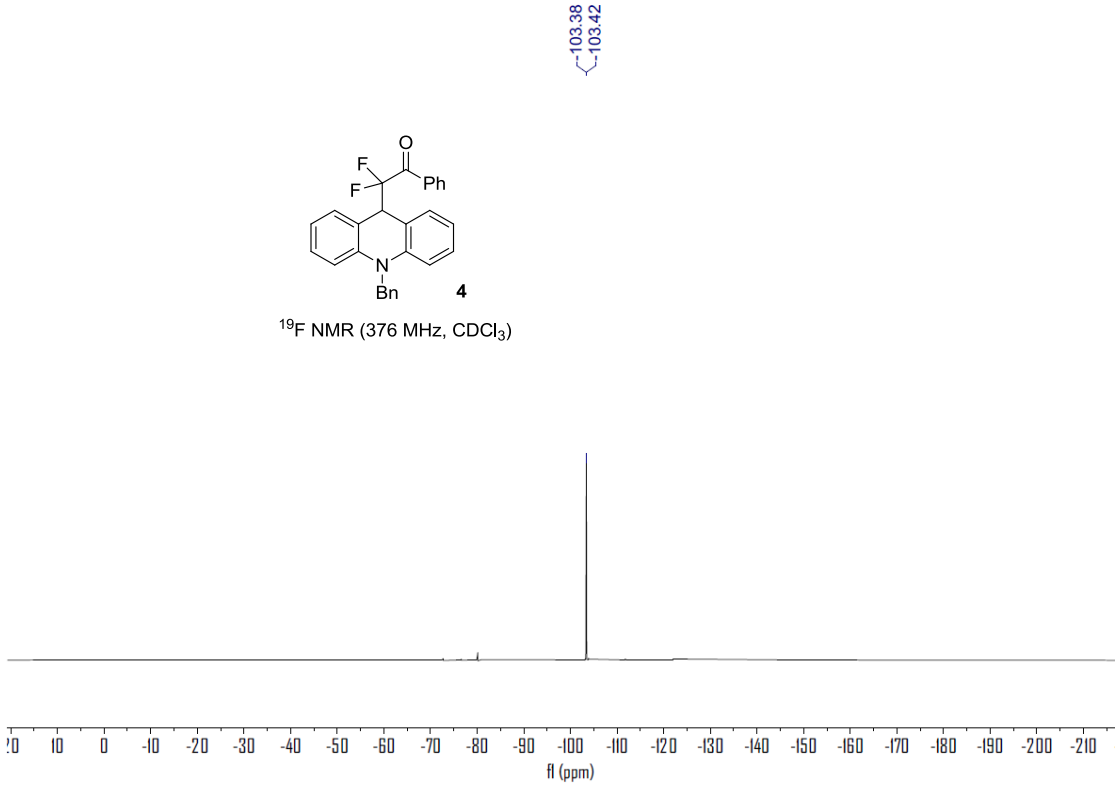
^{19}F NMR (376 MHz, $CDCl_3$)



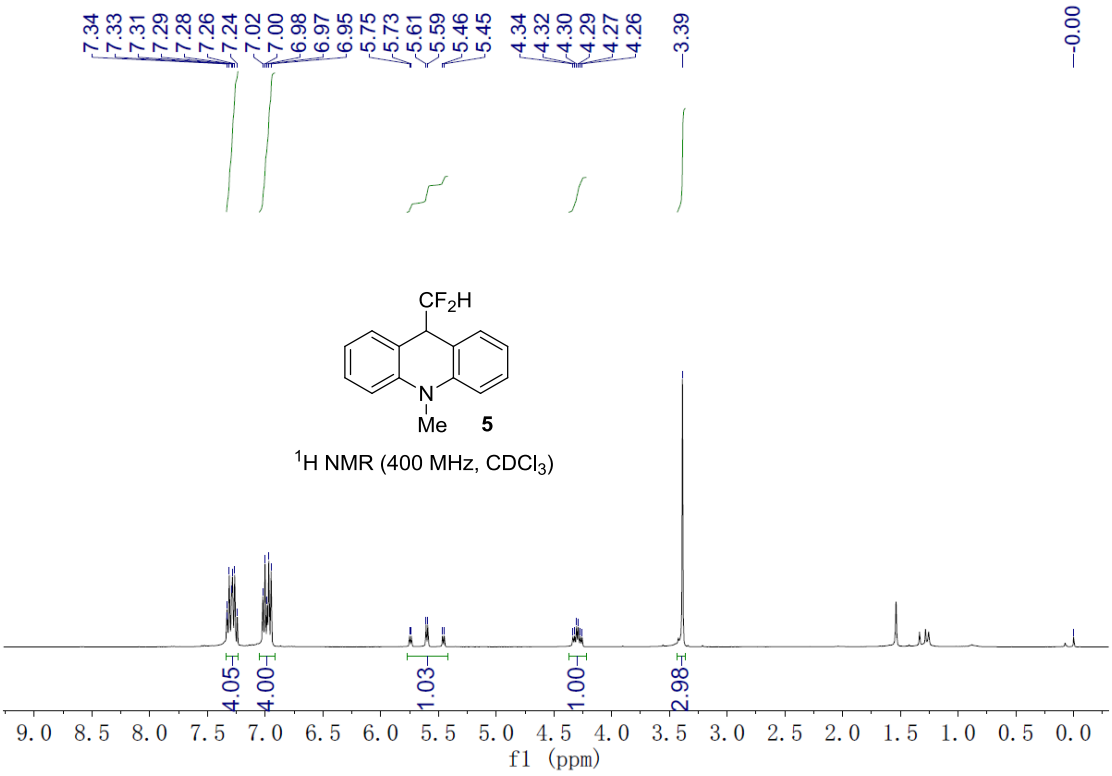
^{1}H NMR (400 MHz, $CDCl_3$)



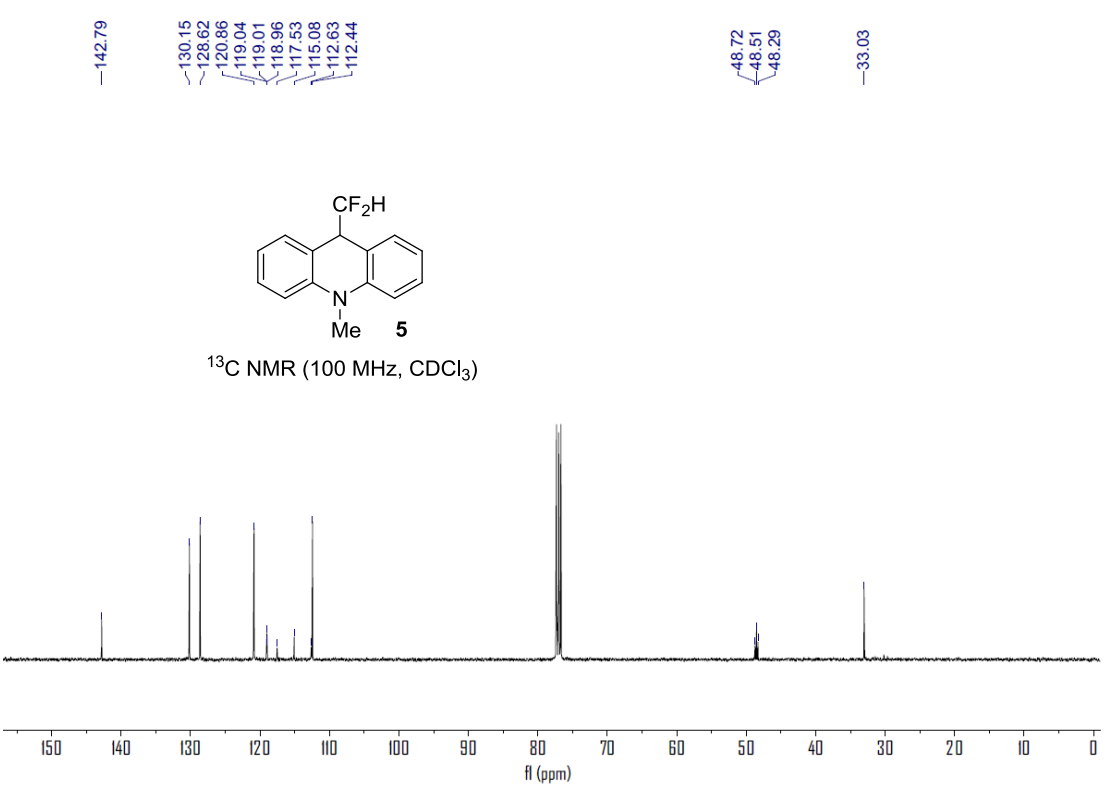
^{13}C NMR (100 MHz, $CDCl_3$)



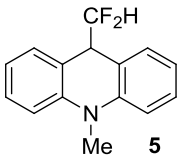
^{19}F NMR (376 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



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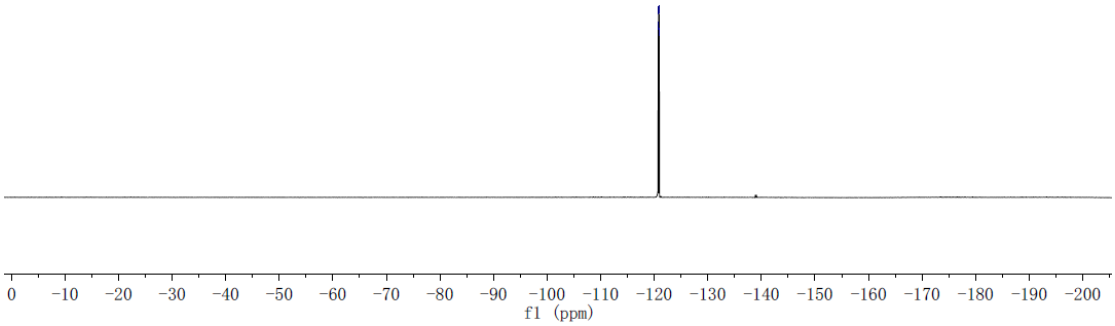
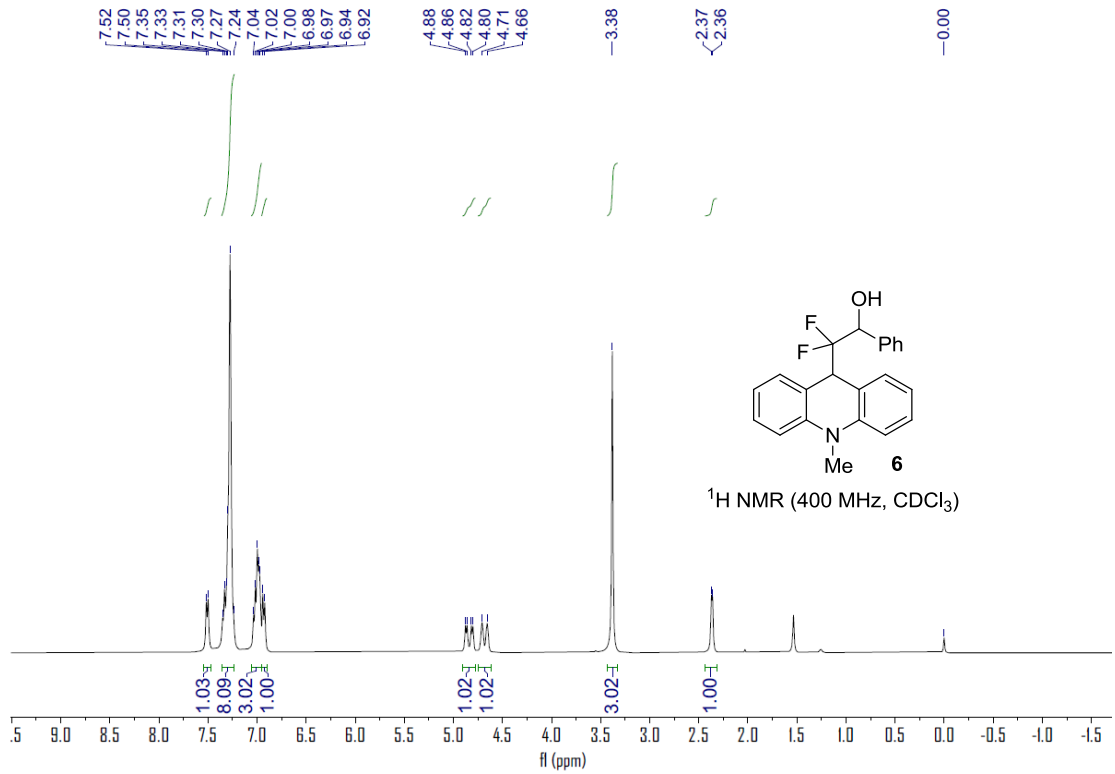
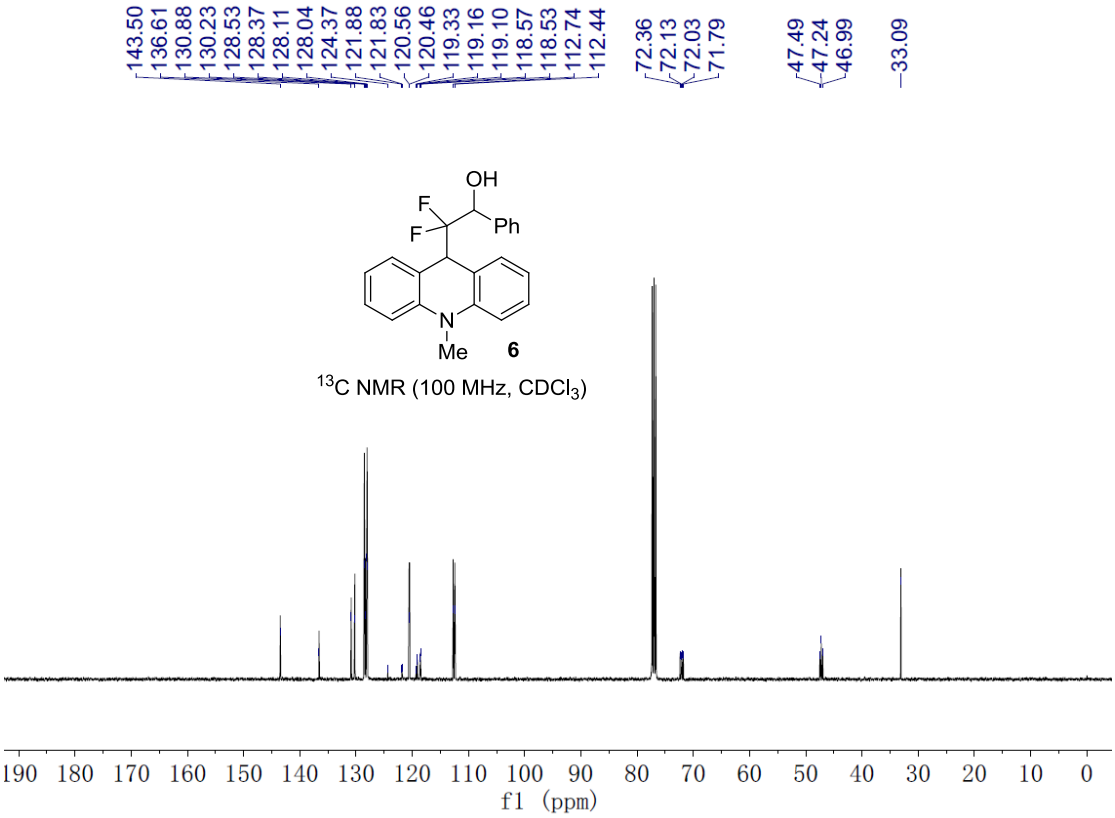
^{19}F NMR (376 MHz, $CDCl_3$)



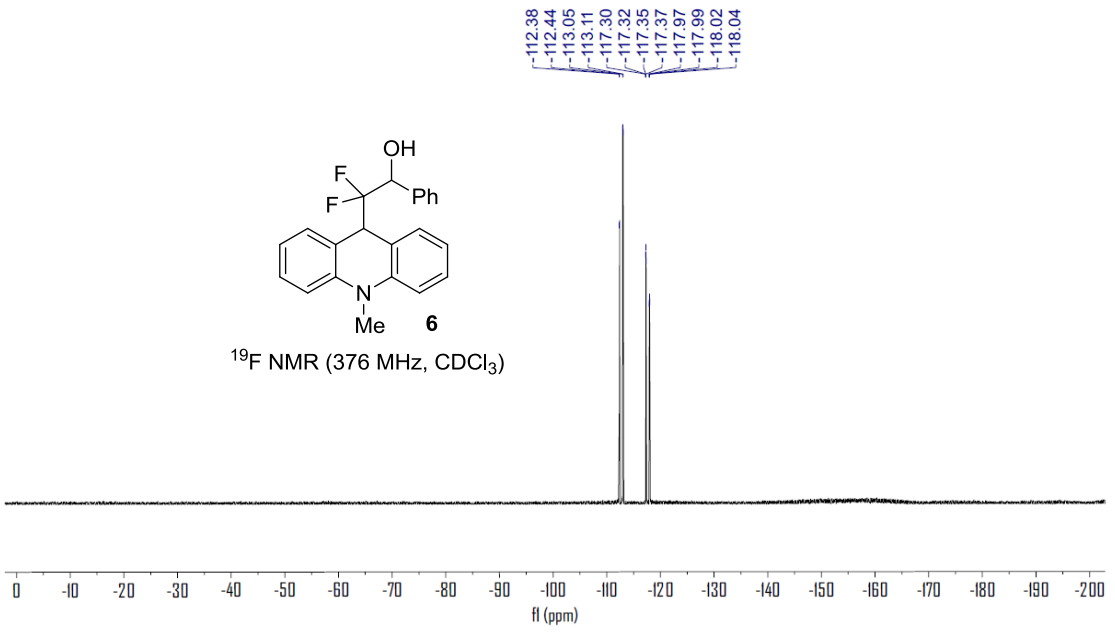


6

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)



^{19}F NMR (376 MHz, $CDCl_3$)