Supporting Information to

Cu-catalyzed cascade difluoroalkylation/5-endo cyclization/β-fluorine cleavage of ynones

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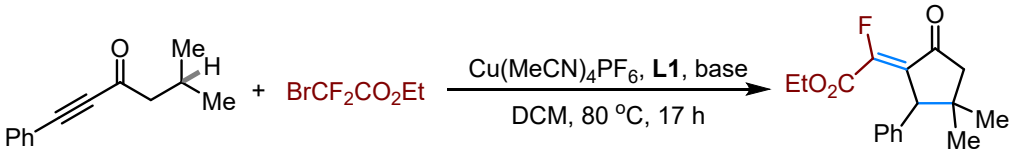
1. General Information

Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. Ynones were prepared according to the method reported in the literature.[1] Melting points reported here were measured by a melting point instrument and were uncorrected. ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured on a 600 MHz or 400 MHz NMR spectrometer. Chemical shifts are given in parts per million on the delta (δ) scale, and the coupling constants are given in hertz. ^{1}H NMR chemical shifts were determined relative to the internal standard tetramethylsilane (TMS) at 0.00 ppm, ^{13}C NMR shifts were determined relative to the residual solvent peaks of $CDCl_3$ at δ 77.00 ppm, and ^{19}F NMR chemical shifts were determined relative to outside standard $CFCl_3$ at δ 0.00 ppm. High-resolution mass spectrometry (HRMS) analysis was carried out using a TOF MS instrument with an ESI source. Flash column chromatography was carried out on the silica gel (200-300 mesh).

2. Supplementary optimization of the reaction condition.

Tables S1. Base screening[a]



1a **2a** **3a**

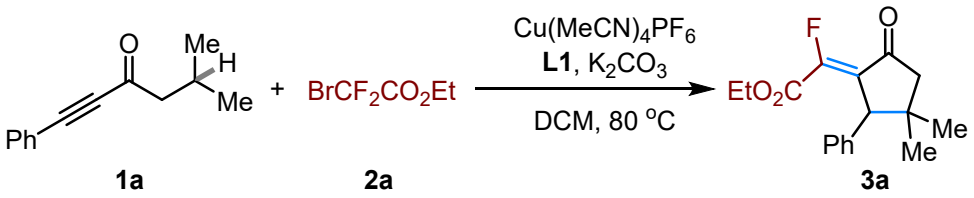
Entry	Base	Yield (%)[b]	*Z*/*E*[c]
1	Na_2CO_3	8	1.5:1
2	Cs_2CO_3	58	6.6:1
3	Li_2CO_3	trace	-
4	$NaHCO_3$	8	3.7:1
5	KOMe	8	3.0:1
6	K_2HPO_4	21	8.2:1
7	KH_2PO_4	36	8.6:1

[1] (a) Q.-X. Wang, and J. A. May, Formation of β-oxo-*N*-vinylimidates via intermolecular ester incorporation in Huisgen cyclization/carbene cascade reactions. *Org. Lett.,* 2020, **22**, 9579; (b) T. P. Reddy, J. Gujral, P. Roy, and D. B. Ramachary, Catalytic ynone-amidine formal [4 + 2]-cycloaddition for the regioselective synthesis of tricyclic azepines. *Org. Lett.,* 2020, **22**, 9653.

8	KOAc	8	3.8:1
9	KF	35	7.0:1

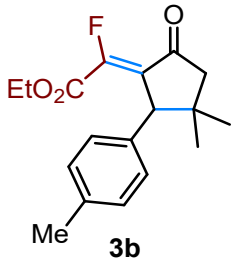
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.7 mmol), base (0.4 mmol), [Cu] (20 mol%), ligand (40 mol%), solvent (2 mL), 80 °C, 17 h. [b] GC yield with 1.0 equivalent naphthene as internal standard. [c] Determined by ^{19}F NMR.

3. General Procedures for Experiments and Analytical Data



1a **2a** **3a**

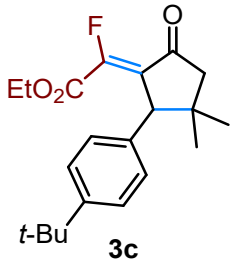
To a mixture of $Cu(MeCN)_4PF_6$ (14.9 mg, 0.04 mmol), **L1** (18.9 mg, 0.08 mmol), **2a** (142.1 mg, 0.7 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of DCM was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After stirring at 80 °C for 17 h, the reaction mixture was quenched with water, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 42 mg (72% yield) of **3a** as a yellow oil, *Z*/*E* = 10:1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.25 – 7.21 (m, 1H), 7.06 – 7.04 (m, 2H), 4.27 (s, 1H), 4.16 – 4.08 (m 2H), 2.51 (d, J = 18.0 Hz, 1H), 2.21 (dd, J = 18.0, 1.5 Hz, 1H), 1.20 (s, 3H), 1.18 (t, J = 7.1 Hz, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.10, 160.25 (d, J = 35.1 Hz), 147.59 (d, J = 290.8 Hz), 141.24 (d, J = 3.3 Hz), 129.65 (d, J = 2.5 Hz), 128.26, 128.19, 126.80, 62.34, 56.36, 51.34, 38.52, 30.80, 25.31, 13.85; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.12; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{19}FO_3$+H^+: 291.1391; Found 291.1393.



3b

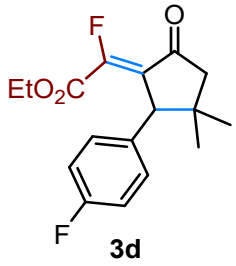
*Compound **3b:*** 44 mg, 75% yield, yellow oil, *Z*/*E* > 20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.09 (d, J = 7.8 Hz, 2H), 6.93 (d, J

= 7.8 Hz, 2H), 4.23 (s, 1H), 4.18 – 4.06 (m, 2H), 2.50 (d, J = 18.0 Hz, 1H), 2.31 (s, 3H), 2.19 (dd, J = 18.0, 1.5 Hz, 1H), 1.21 – 1.17 (m, 6H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.31, 160.29 (d, J = 34.8 Hz), 147.43 (d, J = 290.5 Hz), 138.22 (d, J = 3.3 Hz), 136.36, 129.92, 128.94, 128.05, 62.32, 56.01, 51.29, 38.49, 30.79, 25.30, 21.01, 13.88; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.52; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{18}H_{21}FO_3$+H^+: 305.1547; Found 305.1538.



3c

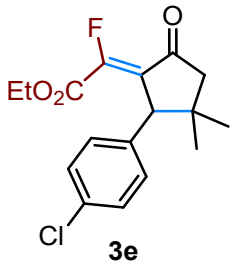
Compound ***3c:*** 48 mg, 70% yield, yellow oil, Z/E > 20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 8.4 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 4.17 (s, 1H), 4.09 – 4.01 (m, 2H), 2.45 (d, J = 18.0 Hz, 1H), 2.12 (dd, J = 18.0, 1.5 Hz, 1H), 1.22 (s, 9H), 1.12 (s, 3H), 1.09 (t, J = 7.1 Hz, 3H), 0.70 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.32, 160.32 (d, J = 35.2 Hz), 149.56, 147.47 (d, J = 289.8 Hz), 138.05 (d, J = 3.2 Hz), 129.84, 127.80, 125.08, 62.29, 55.93, 51.35, 38.56, 34.40, 31.32, 30.69, 25.33, 13.82; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.52; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{27}FO_3$+H^+: 347.2017; Found 347.2005.



3d

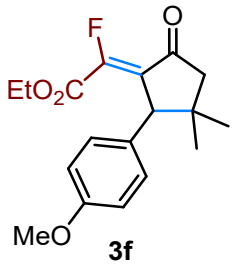
Compound ***3d:*** 48 mg, 62% yield, yellow oil, Z/E > 20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.03 – 6.97 (m, 4H), 4.26 (s, 1H), 4.15 (q, J = 7.2 Hz, 2H), 2.47 (d, J = 18.0 Hz, 1H), 2.21 (d, J = 18.0 Hz, 1H), 1.21 – 1.20 (m, 3H), 1.19 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.83, 162.86, 160.39 (d, J = 6.7 Hz), 160.01, 147.66 (d, J = 292.2 Hz), 137.06 (t, J = 3.4 Hz), 129.58 (d, J = 5.7 Hz), 115.19 (d, J = 21.4

Hz), 62.44, 55.57, 51.20, 38.47, 30.73, 25.29, 13.88; ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.78, -115.74; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{18}F_2O_3$+H^+: 309.1297; Found 309.1290.



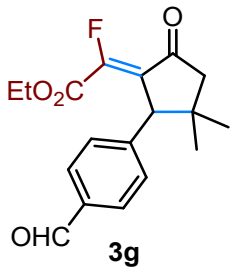
3e

Compound ***3e:*** 53 mg, 81% yield, yellow oil, *Z*/*E* > 20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.26 (d, *J* = 8.5 Hz, 2H), 6.99 (d, *J* = 8.5 Hz, 2H), 4.25 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.46 (d, *J* = 18.0 Hz, 1H), 2.22 (dd, *J* = 18.0, 1.5 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.19 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.63, 160.13 (d, *J* = 34.6 Hz), 147.68 (d, *J* = 292.7 Hz), 139.78 (d, *J* = 3.5 Hz), 132.66, 129.45, 129.30, 128.48, 62.48, 55.72, 51.21, 38.49, 30.78, 25.30, 13.89; ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.56; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{18}ClFO_3$+H^+: 325.1001; Found 325.0995.



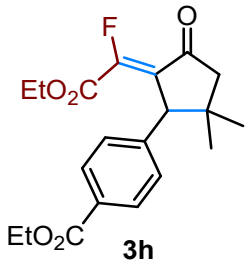
3f

Compound ***3f:*** 51 mg, 80% yield, yellow oil, *Z*/*E* = 12:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 8.6 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.22 (s, 1H), 4.16 – 4.11 (m, 2H), 3.78 (s, 3H), 2.49 (d, *J* = 18.0 Hz, 1H), 2.19 (dd, *J* = 18.0, 1.5 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 1.18 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.35, 160.30 (d, *J* = 35.2 Hz), 158.32, 147.46 (d, *J* = 290.5 Hz), 133.47 (d, *J* = 3.2 Hz), 129.98, 129.12, 113.61, 62.35, 55.58, 55.19, 51.26, 38.55, 30.70, 25.29, 13.89; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.50; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}FO_4$+H^+: 321.1497; Found 321.1501.



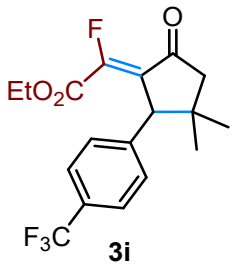
3g

*Compound **3g:*** 45 mg, 70% yield, yellow oil, *Z*/*E* = 16:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 4.36 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.50 (d, *J* = 18.1 Hz, 1H), 2.26 (dd, *J* = 18.1, 1.3 Hz, 1H), 1.23 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.78 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.23, 191.65, 160.07 (d, *J* = 34.4 Hz), 148.35 (d, *J* = 3.5 Hz), 147.87 (d, *J* = 293.6 Hz), 135.10, 129.75, 128.90, 128.87, 62.54, 56.42, 51.31, 38.74, 30.89, 25.32, 13.87; ^{19}F NMR (565 MHz, $CDCl_3$) δ -109.94; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{18}H_{19}FO_4$+H^+: 319.1340; Found 319.1340.



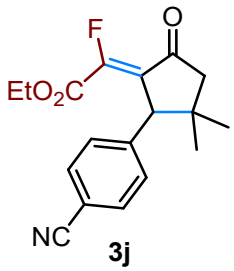
3h

*Compound **3h:*** 43 mg, 60% yield, yellow oil, *Z*/*E* = 11:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 4.32 (s, 1H), 4.15 – 4.09 (m, 2H), 2.49 (d, *J* = 18.0 Hz, 1H), 2.24 (dd, *J* = 18.0, 1.4 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.22 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.49, 166.26, 160.09 (d, *J* = 34.6 Hz), 148.80 (d, *J* = 293.6 Hz), 146.40 (d, *J* = 3.3 Hz), 129.57, 129.14, 129.06 (d, *J* = 3.1 Hz), 128.17, 62.48, 60.98, 56.28, 51.32, 38.62, 30.83, 25.29, 14.32, 13.87; ^{19}F NMR (565 MHz, $CDCl_3$) δ -110.22; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{23}FO_5$+H^+: 363.1602; Found 363.1592.



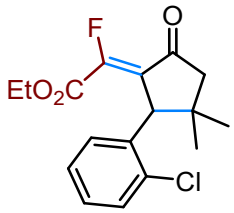
3i

*Compound **3i:*** 49 mg, 69% yield, yellow oil, *Z*/*E* = 11:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.9 Hz, 2H), 4.34 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.48 (d, *J* = 18.1 Hz, 1H), 2.25 (dd, *J* = 18.1, 1.4 Hz, 1H), 1.22 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.38, 160.08 (d, *J* = 34.2 Hz), 147.82 (d, *J* = 293.8 Hz), 145.30, 129.13 (q, *J* = 32.7 Hz)128.99 (d, *J* = 3.3 Hz), 128.48, 125.29 (d, *J* = 3.8 Hz), 124.05 (q, *J* = 272.21 Hz), 62.55, 56.10, 51.22, 38.60, 30.84, 25.33, 13.85; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.50, -110.10; HRMS (ESI) *m*/*z*: [*M* + H]$^{+}$ Calcd for $C_{18}H_{18}F_4O_3$+H^{+}: 359.1265; Found 359.1281.



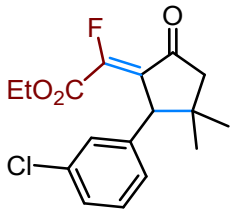
3j

*Compound **3j:*** 45 mg, 71% yield, yellow oil, *Z*/*E* = 10:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 4.32 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.45 (d, *J* = 18.1 Hz, 1H), 2.26 (dd, *J* = 18.1, 1.4 Hz, 1H), 1.22 (s, 3H), 1.20 (d, *J* = 7.1 Hz, 3H), 0.76 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.91, 160.01 (d, *J* = 34.0 Hz), 147.92 (d, *J* = 295.4 Hz), 146.76 (d, *J* = 3.5 Hz), 132.15, 128.94, 128.59, 118.55, 110.88, 62.62, 56.32, 51.23, 38.71, 30.88, 25.33, 13.89; ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.62; HRMS (ESI) *m*/*z*: [*M* + H]$^{+}$ Calcd for $C_{18}H_{18}FNO_3$+H^{+}: 316.1343; Found 316.1333.



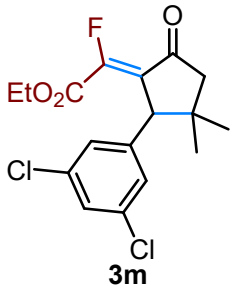
3k

Compound ***3k:*** 47 mg, 73% yield, yellow oil, *Z*/*E* = 14:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 5.8, 3.5 Hz, 1H), 7.17 – 7.15 (m, 2H), 6.84 (dd, *J* = 5.9, 3.5 Hz, 1H), 4.89 (s, 1H), 4.16 (q, *J* = 7.2, 2H), 2.50 (d, *J* = 18.1 Hz, 1H), 2.20 (dd, *J* = 18.1, 1.4 Hz, 1H), 1.25 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.87 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.81, 160.05 (d, *J* = 35.5 Hz), 147.85 (d, *J* = 290.3 Hz), 139.93 (d, *J* = 3.6 Hz), 134.88, 129.70, 129.40 (d, *J* = 3.4 Hz), 127.95, 127.57, 127.07, 62.58, 51.76, 51.52, 39.10, 30.78, 23.85, 13.85; ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.26; HRMS (ESI) *m*/*z*: [*M* + H]$^{+}$ Calcd for $C_{17}H_{18}ClFO_3$+H^{+}: 325.1001; Found 325.0987.



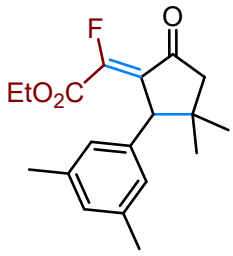
3l

Compound ***3l:*** 40 mg, 65% yield, yellow oil, *Z*/*E* = 12:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 – 7.22 (m, 2H), 7.04 (s, 1H), 6.93 (d, *J* = 6.3 Hz, 1H), 4.24 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 2.49 (d, *J* = 18.1 Hz, 1H), 2.23 (dd, *J* = 18.1, 1.4 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.20 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 203.54, 160.11 (d, *J* = 35.1 Hz), 147.80 (d, *J* = 292.4 Hz), 143.23 (d, *J* = 3.6 Hz), 134.20, 129.56, 128.96, 128.30, 127.07, 126.34, 62.54, 56.00, 51.24, 38.55, 30.82, 25.32, 13.86; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.14; HRMS (ESI) *m*/*z*: [*M* + H]$^{+}$ Calcd for $C_{17}H_{18}ClFO_3$+H^{+}: 325.1001; Found 325.0996.



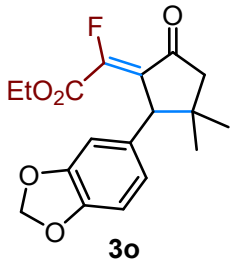
3m

Compound ***3m:*** 43 mg, 60% yield, yellow oil, *Z*/*E* = 10:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, J = 2.2 Hz, 1H), 7.16 (dd, J = 8.4, 2.2 Hz, 1H), 6.77 (d, J = 8.4 Hz, 1H), 4.85 (s, 1H), 4.22 – 4.16 (m, 2H), 2.46 (d, J = 18.2 Hz, 1H), 2.23 (dd, J = 18.1, 1.4 Hz, 1H), 1.25 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H), 0.89 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.97, 160.01 (d, J = 34.2 Hz), 148.02 (d, J = 294.3 Hz), 144.57 (d, J = 3.8 Hz), 134.91, 128.33 (d, J = 3.5 Hz), 127.19, 126.65, 62.69, 55.78, 51.16, 38.61, 30.84, 25.33, 13.87; ^{19}F NMR (377 MHz, $CDCl_3$) δ -109.25; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{17}H_{17}Cl_2FO_3$+H^+: 359.0612; Found 325.0603.



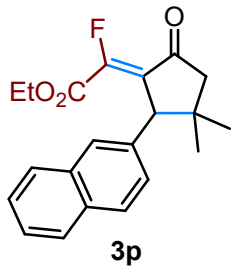
3n

Compound ***3n:*** 46 mg, 72% yield, yellow oil, *Z*/*E* = 12:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.62 (s, 2H), 4.19 (s, 1H), 4.17 – 4.11 (m, 2H), 2.52 (d, J = 18.0 Hz, 1H), 2.27 (s, 6H), 2.18 (dd, J = 18.1, 1.5 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H), 1.18 (s, 3H), 0.77 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.54, 160.34 (d, J = 34.9 Hz), 147.40 (d, J = 289.8 Hz), 141.04 (d, J = 3.2 Hz), 137.57, 129.90, 128.45, 126.09, 62.33, 56.23, 51.30, 38.45, 30.88, 25.33, 21.38, 13.83; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.60; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{19}H_{23}FO_3$+H^+: 319.1704; Found 319.1696.



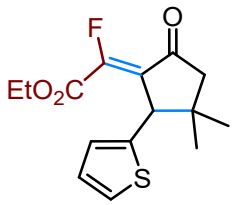
3o

Compound ***3o:*** 51 mg, 77% yield, yellow solid, mp 124-126 °C, *Z*/*E* = 10:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (d, J = 8.0 Hz, 1H), 6.54 (d, J = 1.8 Hz, 1H), 6.49 (dd, J = 8.0, 1.8 Hz, 1H), 5.93 (s, 2H), 4.20 (s, 1H), 4.22 – 4.12 (m, 2H), 2.49 (d, J = 18.1 Hz, 1H), 2.18 (dd, J = 18.0, 1.5 Hz, 1H), 1.23 (t, J = 7.2 Hz, 3H), 1.17 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.11, 160.25 (d, J = 34.9 Hz), 147.54 (d, J = 291.7 Hz), 147.51, 146.44 (d, J = 41.3 Hz), 135.16 (d, J = 4.1 Hz), 129.72, 121.19, 108.77, 108.04, 101.04, 62.40, 55.98, 51.19, 38.57, 30.81, 25.29, 13.93; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.09; HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{19}FO_5$+H^+: 335.1289; Found 335.1278.



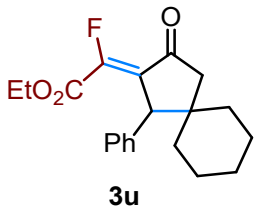
3p

Compound ***3p:*** 27 mg, 40% yield, yellow oil, *Z*/*E* = 10:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 3H), 7.49 – 7.43 (m, 3H), 7.26 – 7.23 (m, 1H), 4.46 (s, 1H), 4.12 – 4.05 (m, 2H), 2.60 (d, J = 18.1 Hz, 1H), 2.25 (dd, J = 18.0, 1.4 Hz, 1H), 1.26 (s, 3H), 1.14 (t, J = 7.1 Hz, 3H), 0.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.24, 160.23 (d, J = 34.9 Hz), 147.70 (d, J = 291.3 Hz), 139.01, 133.21, 132.32, 129.82 (d, J = 2.7 Hz), 127.82, 127.79, 127.60, 127.34, 126.29, 126.16, 125.80, 62.39, 56.42, 51.36, 38.79, 30.95, 25.40, 13.84; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.87. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{21}FO_3$+H^+: 341.1547; Found 341.1547.



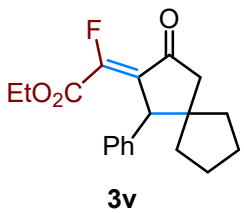
3r

Compound ***3r:*** 30 mg, 51% yield, yellow oil, *Z*/*E* = 10:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.76 (dt, *J* = 3.5, 0.8 Hz, 1H), 4.57 (s, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 2.61 (d, *J* = 18.1 Hz, 1H), 2.21 (dd, *J* = 18.1, 1.6 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.18 (s, 3H), 0.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.26, 160.21 (d, *J* = 34.8 Hz), 147.82 (d, *J* = 292.0 Hz), 143.42 (d, *J* = 4.1 Hz), 129.47 (d, *J* = 3.5 Hz), 126.59, 125.24, 123.59, 62.53, 51.58, 50.89, 38.60, 30.09, 24.92, 13.92; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.12; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{15}H_{17}FO_3S+H^+$: 297.0955; Found 297.0959.



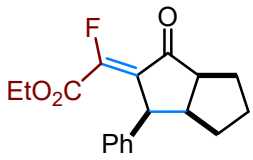
3u

Compound ***3u:*** 41 mg, 62% yield, colorless oil, *Z*/*E* = 8:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.23 – 7.20 (m, 1H), 7.06 (d, *J* = 7.5 Hz, 2H), 4.32 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 2.51 (d, *J* = 18.5Hz, 1H), 2.43 (d, *J* = 18.5 Hz, 1H), 1.59 – 1.39 (m, 5H), 1.31 – 1.19 (m, 6H), 1.15 – 1.11 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.34, 160.31 (d, *J* = 35.0 Hz), 147.45 (d, *J* = 290.5 Hz), 140.55 (d, *J* = 3.6 Hz), 129.86 (d, *J* = 2.7 Hz), 128.58, 128.18, 126.77, 62.33, 56.32, 47.22, 42.11, 38.62, 34.71, 25.60, 23.15, 22.45, 13.90; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.67; HRMS (ESI) *m*/*z*: $[M + H]^+$ Calcd for $C_{20}H_{23}FO_3+H^+$: 331.1704; Found 337.1694.



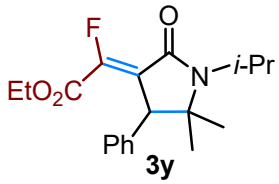
3v

Compound ***3v:*** 38 mg, 60% yield, yellow solid, *Z*/*E* = 8:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.21 (m, 1H), 7.08 – 7.06 (m, 2H), 4.37 (s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 2.63 (d, *J* = 18.2 Hz, 1H), 2.29 (dd, *J* = 18.2, 1.6 Hz, 1H), 1.82 – 1.63 (m, 4H), 1.42 – 1.35 (m, 1H), 1.25 (s, 2H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.11 – 1.04 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.11, 160.29 (d, *J* = 34.8 Hz), 146.87 (d, *J* = 291.3 Hz), 141.81 (d, *J* = 3.5 Hz), 129.88 (d, *J* = 2.4 Hz), 128.29, 128.06, 126.77, 62.36, 54.60, 50.53, 49.01, 40.71, 34.60, 26.92, 23.55 (d, *J* = 5.0 Hz), 13.90; ^{19}F NMR (565 MHz, $CDCl_3$) δ -112.12; HRMS (ESI) *m*/*z*: [*M* + H]$^+$ Calcd for $C_{19}H_{21}FO_3$+H$^+$: 317.1547; Found 317.1537.



3w

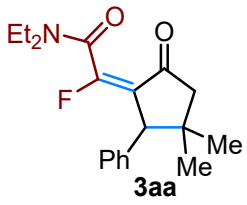
Compound ***3w:*** 23 mg, 38% yield, yellow solid, *Z*/*E* = 11:1; dr = 3:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H), 7.15 – 7.13 (m, 2H), 4.52 (s, 1H), 4.19 – 4.14 (m, 2H), 2.95 – 2.89 (m, 1H), 2.76 – 2.44 (m, 1H), 2.24 – 1.84 (m, 4H), 1.43 – 1.22 (m, 2H), 1.17 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.66, 160.37 (d, *J* = 35.0 Hz), 147.46 (d, *J* = 291.0 Hz), 144.85 (d, *J* = 3.6 Hz), 128.75, 128.18 (d, *J* = 9.1 Hz), 126.69, 126.53, 62.43, 52.06, 49.54, 48.86, 34.37, 29.78, 25.97, 13.84; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -110.41; HRMS (ESI) *m*/*z*: [*M* + H]$^+$ Calcd for $C_{18}H_{19}FO_3$+H$^+$: 303.1391; Found 303.1399.



3y

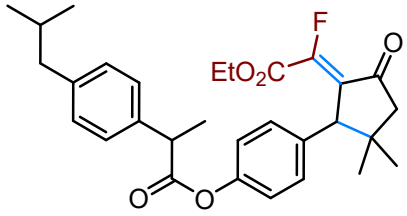
Compound ***3y:*** 31 mg, 46% yield, white solid, mp 121-123 °C, *Z*:*E* = 14:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.21 (m, 3H), 7.11 (d, *J* = 6.7 Hz, 2H), 4.29 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.50 – 3.43 (m, 1H),

1.51 (d, J = 6.8 Hz, 3H), 1.45 (d, J = 6.8 Hz, 3H), 1.37 (s, 3H), 1.19 (t, J = 7.1 Hz, 3H), 0.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.43, 160.43 (d, J = 33.6 Hz), 147.15 (d, J = 281.4 Hz), 140.64 (d, J = 3.6 Hz), 128.31, 128.02, 127.98, 127.15, 63.50, 61.94, 53.87, 45.32, 30.09, 23.85, 20.22, 19.93, 13.94; ^{19}F NMR (377 MHz, $CDCl_3$) δ -121.15; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}FNO_3$+H^+: 334.1813; Found 334.1817.



3aa

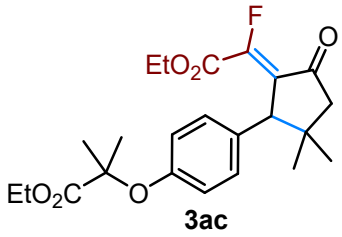
*Compound **3aa:*** 33 mg, 52% yield, yellow oil, Z/E = 1:5; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; ^{1}H NMR (600 MHz, Chloroform-*d*) δ 7.30 (t, J = 7.4 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.10 – 7.09 (m, 2H), 3.92 (d, J = 3.3 Hz, 1H), 3.53 – 3.43 (m, 2H), 3.20 –3.25 (m, 2H), 2.43 (d, J = 17.6 Hz, 1H), 2.25 (d, J = 17.6 Hz, 1H), 1.24 (t, J = 7.2 Hz, 3H), 1.19 (s, 3H), 1.12 (t, J = 7.2 Hz, 3H), 0.73 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 204.23 (d, J = 14.9 Hz), 160.66 (d, J = 29.8 Hz), 157.65 (d, J = 291.5 Hz), 139.08, 128.29, 128.24, 127.04, 121.25 (d, J = 9.1 Hz), 55.12, 52.74, 42.69, 39.16, 38.80, 29.61, 24.96, 14.17, 12.18; ^{19}F NMR (377 MHz, Chloroform-*d*) δ -96.10, -98.87; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}FNO_2$+H^+: 318.1864; Found 318.1866.



3ab

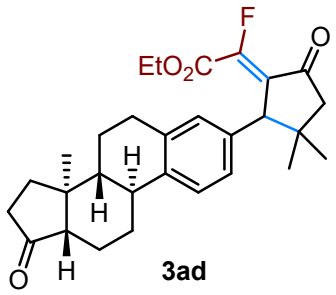
*Compound **3ab:*** 50 mg, 51% yield, yellow oil, Z/E = 11:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 4.26 (s, 1H), 4.16 – 4.08 (m, 2H), 3.92 (q, J = 7.2 Hz, 1H), 2.49 - 2.44 (m, 3H), 2.20 (dd, J = 17.9, 1.4 Hz, 1H), 1.86 (dt, J = 13.5, 6.8 Hz, 1H), 1.59 (d, J = 7.1 Hz, 3H), 1.18 (t, J = 7.2 Hz, 6H), 0.91 (d, J = 6.6 Hz, 6H), 0.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.87, 173.15, 160.15 (d, J = 34.9 Hz), 149.67, 147.70 (d,

J = 291.7 Hz), 140.87, 138.66 (d, *J* = 3.4 Hz), 137.16, 129.53, 129.42 (d, *J* = 2.8 Hz), 128.94, 127.20, 121.25, 62.44, 55.73, 51.25, 45.25, 45.05, 38.51, 30.71, 30.20, 25.29, 22.40, 18.46, 13.88; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.71; HRMS (ESI) *m/z*: [*M* + H]$^+$ Calcd for $C_{30}H_{35}FO_5$+H$^+$: 495.2541; Found 459.2549.



3ac

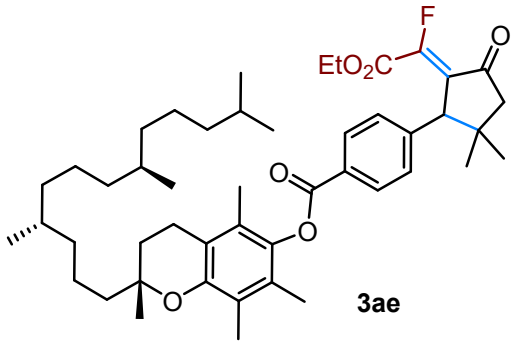
Compound ***3ac:*** 48 mg, 57% yield, yellow oil, *Z*/*E* = 16:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 (d, *J* = 8.6 Hz, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 4.26 - 4.21 (m, 3H), 4.18 - 4.09 (m, 2H), 2.48 (d, *J* = 18.0 Hz, 1H), 2.19 (dd, *J* = 17.9, 1.4 Hz, 1H), 1.58 (s, 6H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 6H), 0.76 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.15, 174.16, 160.25 (d, *J* = 35.3 Hz), 154.22, 147.56 (d, *J* = 290.0 Hz), 135.00, 129.71, 128.81, 118.99, 79.18, 62.31, 61.40, 55.59, 51.28, 38.49, 30.66, 25.37 (d, *J* = 10.1 Hz), 25.24, 13.96 (d, *J* = 19.6 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.09; HRMS (ESI) *m/z*: [*M* + H]$^+$ Calcd for $C_{23}H_{29}FO_6$+H$^+$: 421.2021; Found 421.2023.



3ad

Compound ***3ad:*** 59 mg, 61% yield, yellow oil, *Z*:*E* = 16:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 8.1 Hz, 1H), 6.70 (s, 1H), 4.20 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 2.85 – 2.83 (m, 2H), 2.52 – 2.45 (m, 2H), 2.19 – 1.91 (m, 6H), 1.64 – 1.43 (m, 6H), 1.40 (s, 1H), 1.24 – 1.17 (m, 6H), 0.90 (s, 3H), 0.78 (d, *J* = 1.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.46, 160.35 (d, *J* = 35.0 Hz), 147.31 (d, *J* = 292.2 Hz), 138.56, 138.20, 136.24, 129.99, 128.38, 125.99, 125.09, 125.06,

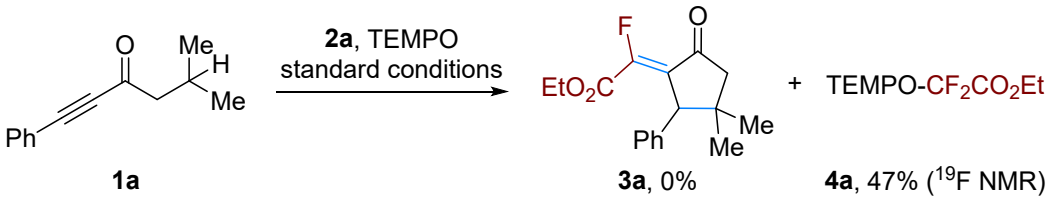
62.33, 55.94, 51.20, 50.54, 47.97, 44.26 (d, J = 1.9 Hz), 38.50, 38.07, 35.84, 31.60, 30.83, 29.44 (d, J = 3.1 Hz), 26.91, 26.51, 25.60, 25.36 (d, J = 2.9 Hz), 21.58, 13.88; ^{19}F NMR (377 MHz, $CDCl_3$) δ -111.76 (d, J = 10.5 Hz); HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{29}H_{35}FNO_4$+H^+: 427.2592; Found 427.2594.



3ae

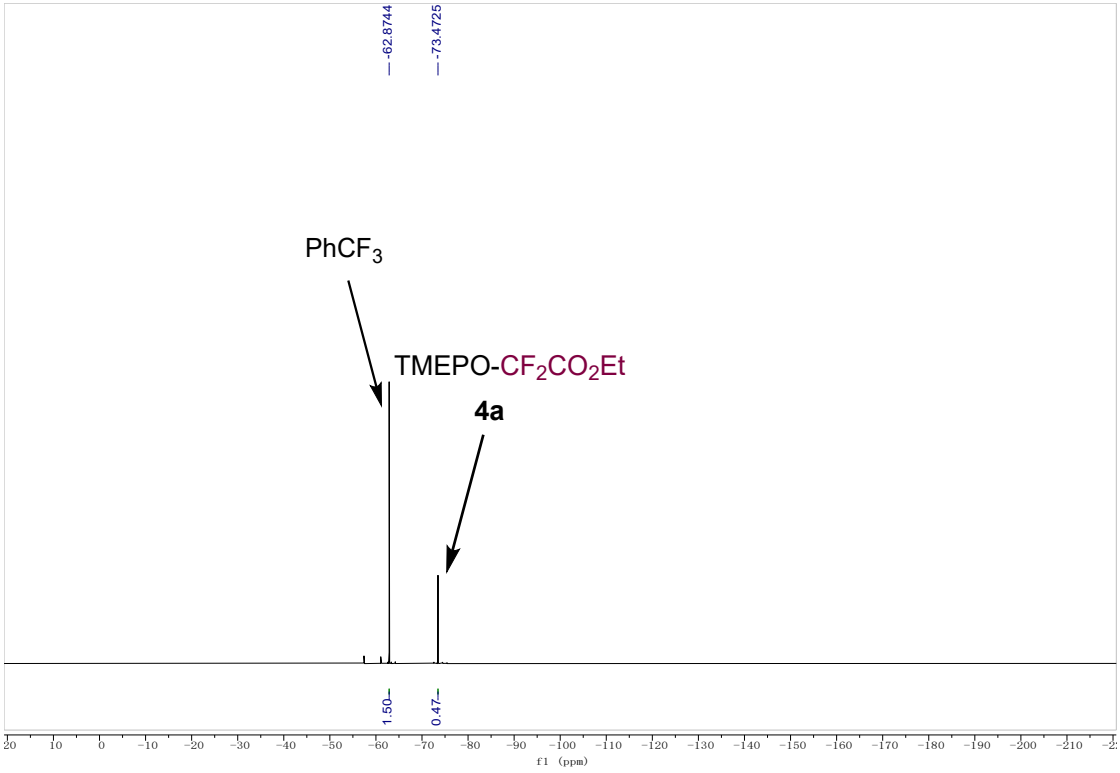
Compound ***3ae:*** 87 mg, 58% yield, yellow oil, Z/E = 8:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 4.39 (s, 1H), 4.18 (q, J = 7.1 Hz, 2H), 2.62 (t, J = 6.8 Hz, 2H), 2.54 (d, J = 18.1 Hz, 1H), 2.27 (dd, J = 18.0, 1.4 Hz, 1H), 2.12 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.60 – 1.03 (m, 35H), 0.87 (d, J = 6.7 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.47, 164.86, 160.18 (d, J = 34.3 Hz), 148.31 (d, J = 242.0 Hz), 146.37, 140.57, 130.20, 129.15, 128.45, 128.28, 126.88, 125.12, 123.16, 117.51, 75.11, 62.56, 56.38, 51.30, 39.39, 38.75, 37.46, 37.30, 32.82, 30.93, 28.00, 25.41, 24.83, 24.47, 22.75, 22.66, 21.05, 20.65, 19.78, 19.69, 13.91, 13.10, 12.26, 11.88; ^{19}F NMR (377 MHz, $CDCl_3$) δ -110.22; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{47}H_{67}FO_6$+H^+: 747.4994; Found 747.5004.

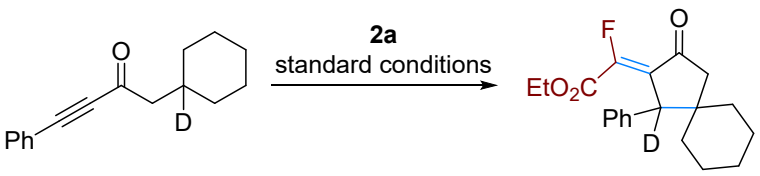
3. Mechanistic Experiments



1a **3a**, 0% **4a**, 47% (^{19}F NMR)

To a mixture of $Cu(MeCN)_4PF_6$ (14.9 mg, 0.04 mmol), **L1** (18.9 mg, 0.08 mmol), **2a** (142.1 mg, 0.7 mmol), TEMPO (125 mg, 0.8 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of DCM was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After stirring at 80 °C for 17 h, the reaction mixture was quenched with water, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4, and concentrated to give **4a** in 47% ^{19}F NMR yield using $PhCF_3$ as the internal standard.

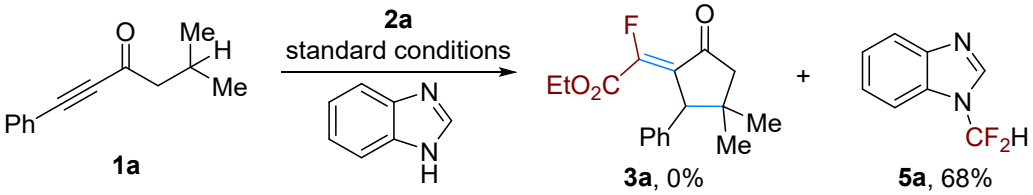




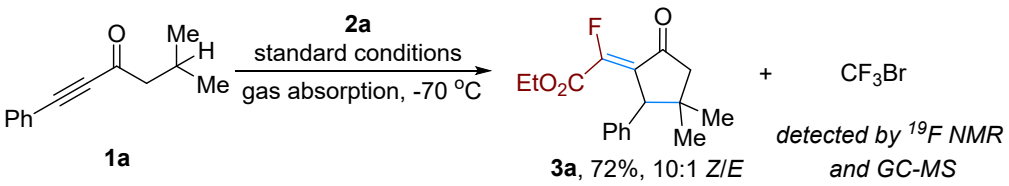
[D]-**1u**, 70% D

[D]-**3u**, 58%,
70% D, 10:1 *Z*/*E*

To a mixture of $Cu(MeCN)_4PF_6$ (14.9 mg, 0.04 mmol), **L1** (18.9 mg, 0.08 mmol), **2a** (142.1 mg, 0.7 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of DCM was added [D]-**1u** (45.4 mg, 0.2 mmol) under nitrogen atmosphere. After stirring at 80 °C for 17 h, the reaction mixture was quenched with water, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4. Column chromatography on silica gel (petroleum ethers/EtOAc = 40:1) gave 38 mg (58% yield) of [D]-**3u**, 70% D, as yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, J = 6.9 Hz, 1H), 7.19 (d, J = 7.2 Hz, 0H), 7.03 (d, J = 7.4 Hz, 1H), 4.29 (s, 0H), 4.12 (q, J = 7.2 Hz, 1H), 2.48 (d, J = 18.6 Hz, 0H), 2.40 (d, J = 18.3 Hz, 0H), 1.53 – 1.31 (m, 4H), 1.22 – 1.09 (m, 3H), 0.89 – 0.84 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 204.32, 160.30 (d, J = 35.1 Hz), 147.42 (d, J = 290.5 Hz), 140.54 (d, J = 3.5 Hz), 129.85 (d, J = 2.7 Hz), 128.57, 128.17, 126.76, 62.33, 56.32, 47.20, 42.10, 38.61, 34.70, 25.60, 23.15, 22.45, 13.91; ^{19}F NMR (565 MHz, $CDCl_3$) δ -111.70; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{22}DFO_3$+H^+: 332.1767; Found 332.1765.



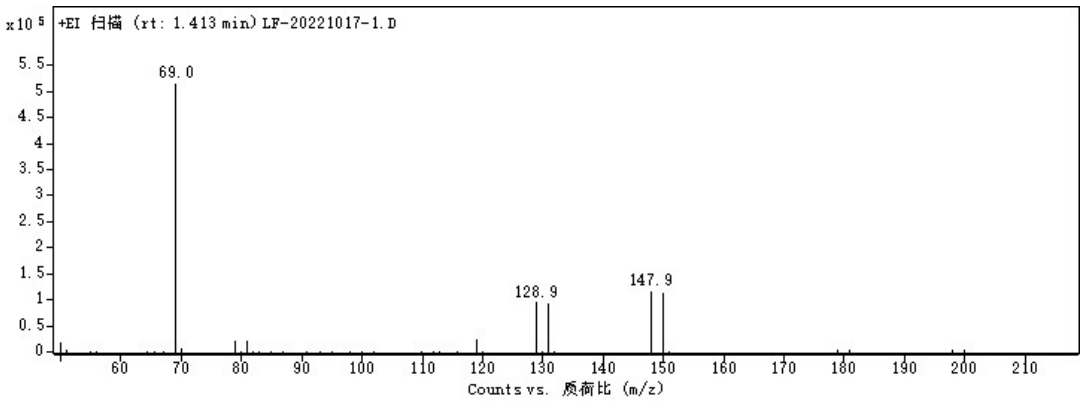
To a mixture of $Cu(MeCN)_4PF_6$ (14.9 mg, 0.04 mmol), **L1** (18.9 mg, 0.08 mmol), **2a** (142.1 mg, 0.7 mmol), benzimidazole (118 mg, 1.0 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of DCM was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After stirring at 80 °C for 17 h, the reaction mixture was quenched with water, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4, Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave 23 mg (68% yield) of **5a**; as yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.86 – 7.83 (m, 1H), 7.62 – 7.60 (m, 1H), 7.44 – 7.34 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.91, 139.07, 130.55, 124.81, 124.17, 120.98, 111.08, 108.97 (t, J = 250.0 Hz); ^{19}F NMR (377 MHz, $CDCl_3$) δ -93.70; HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_8H_6F_2N_2$+H^+: 169.0572; Found 169.0570.

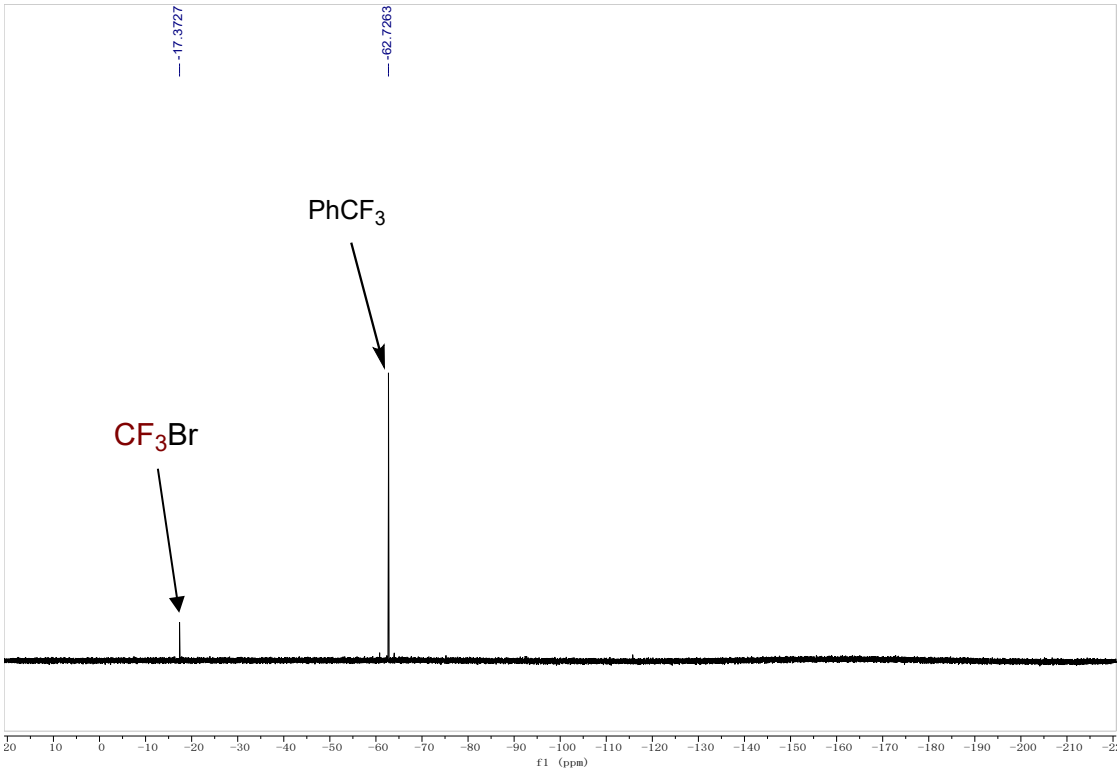


To a mixture of $Cu(MeCN)_4PF_6$ (14.9 mg, 0.04 mmol), **L1** (18.9 mg, 0.08 mmol), **2a** (142.1 mg, 0.7 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of CD_3CN was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After completion of the reaction, the gas in the reaction vessel was bubbled into a sealed tube with $CDCl_3$ cooled to -70 ℃ and then subjected to ^{19}F NMR and analysis using $PhCF_3$ as the internal standard and GC-MS analysis, the signal of CF_3Br was detected at low temperature.

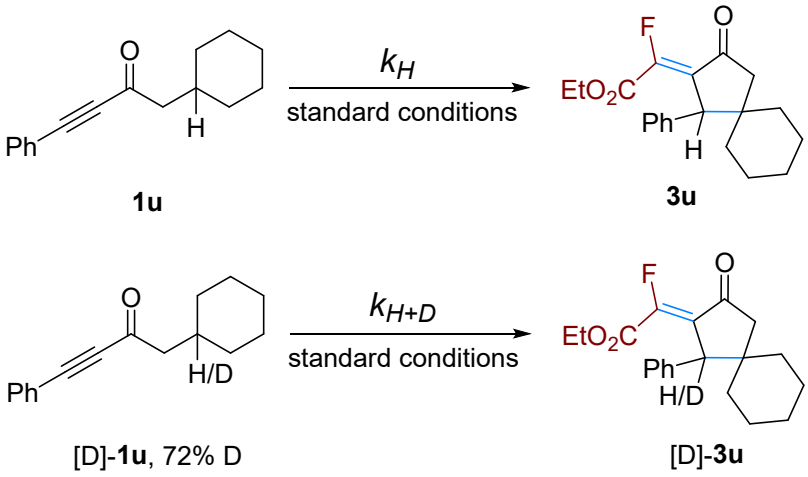

Reaction Bath
郑州长城科工贸有限公司

CF_3Br


x10 5
+EI 扫描 (rt: 1.413 min) LF-20221017-1.D
69.0
128.9
147.9
Counts vs. 质荷比 (m/z)



Determination of the KIE Values



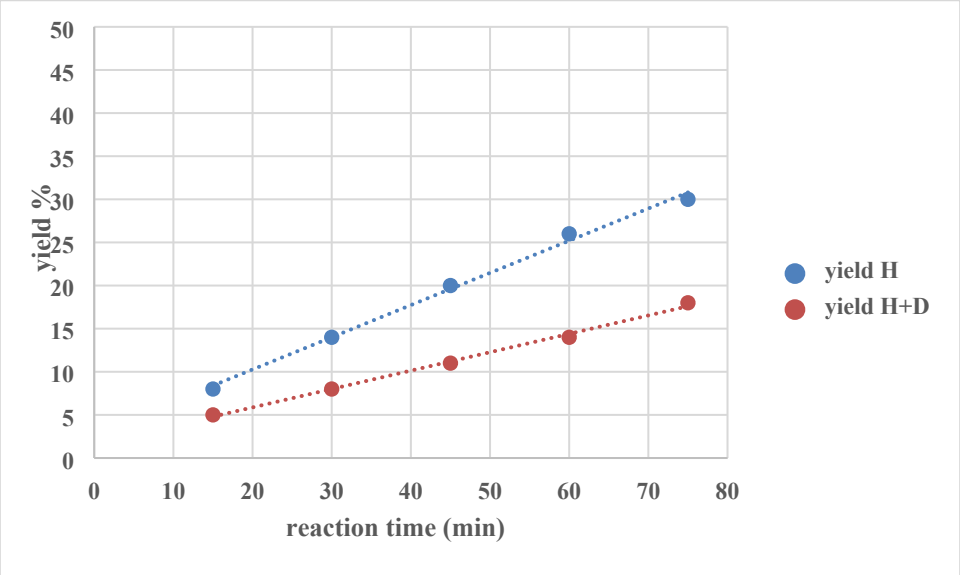
[D]-**1u**, 72% D

[D]-**3u**

The method to calculate KIE is according to the reported method[2] through parallel reactions of **1u** and [D]-**1u** (72% D) using the general produre with *N*,*N*-Dimethyltrifluoroacetamide as the internal standard.

[2] a) X.-H. Yang, R. Davison, S.-Z. Nie, Cruz, F. A., T. M. McGinnis and V. M. Dong, Catalytic hydrothiolation: counterion-controlled regioselectivity. *J. Am. Chem. Soc*. 2019, **141**, 3006; b) C. Obradors, R. M. Martinez and R. A. Shenvi, Ph(*i*-PrO) SiH_2: An exceptional reductant for metal-catalyzed hydrogen atom transfers, *J. Am. Chem. Soc.* **138**, 4962-4971 (2016).

time (min)	15	30	45	60	75
yield of *H*	8%	14%	20%	26%	30%
yield of *H*+*D*	5%	8%	11%	14%	18%



Adjusted initial rates:

k_H=0.3733

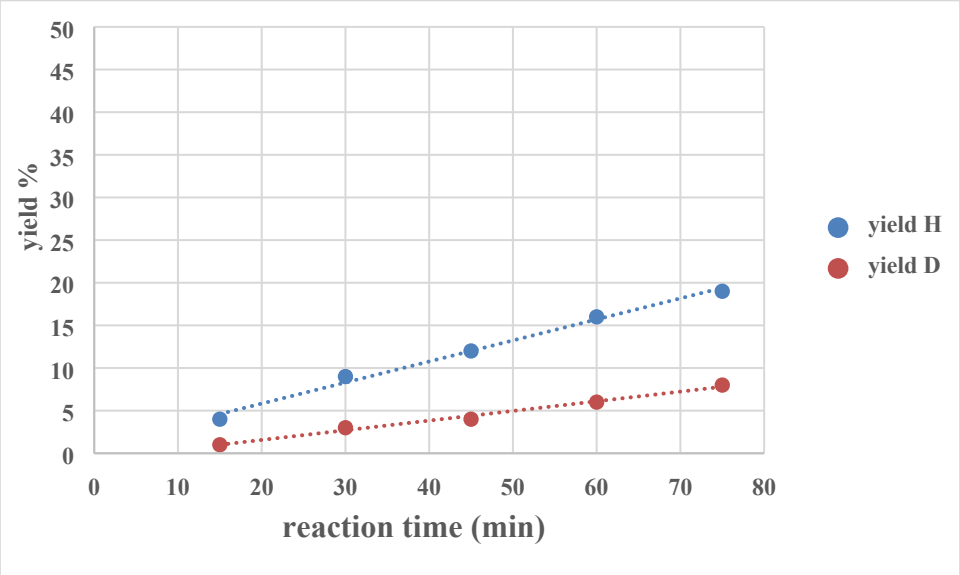
k_H * 28%+k_D * 72% = 0.2133

k_D=0.1511

KIE=k_H/k_D=2.47

Competitive reactions of **1u** and [D]-**1u** (72% D) were conducted under the standard conditions with *N*,*N*-Dimethyltrifluoroacetamide as the internal standard.

time (min)	15	30	45	60	75
yield of *H*	4%	9%	12%	16%	19%
yield of *D*	1%	3%	4%	6%	8%



KIE=k_H/k_D=2.18

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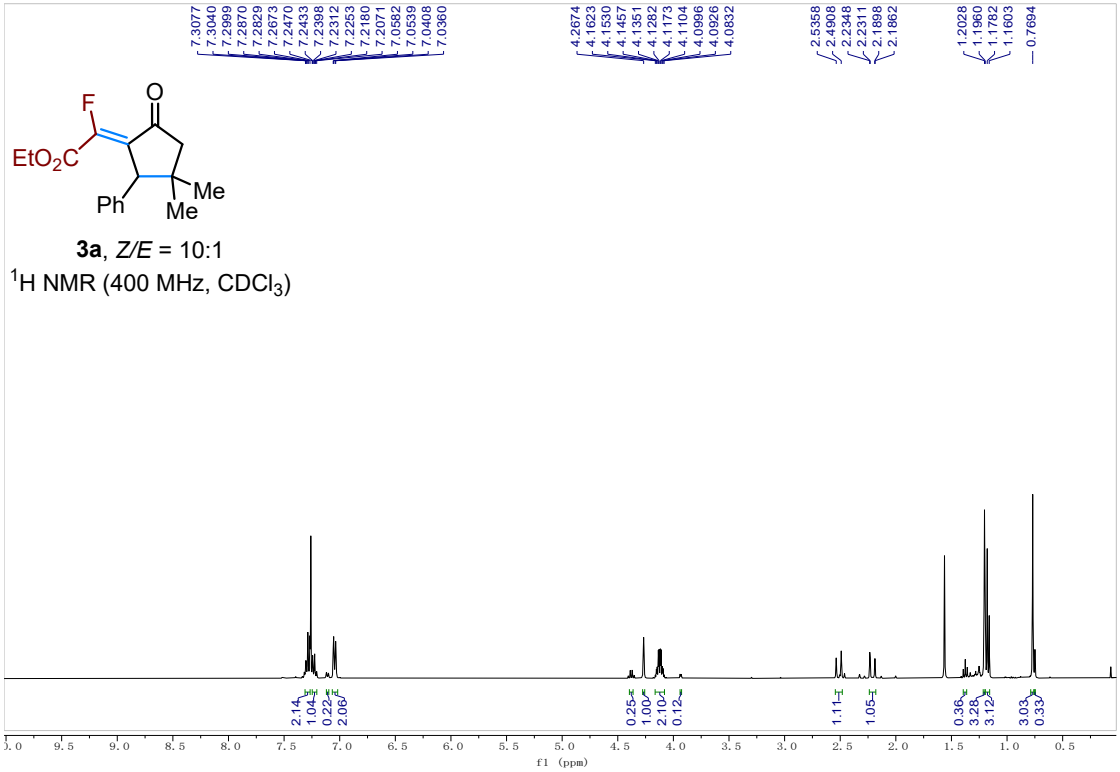
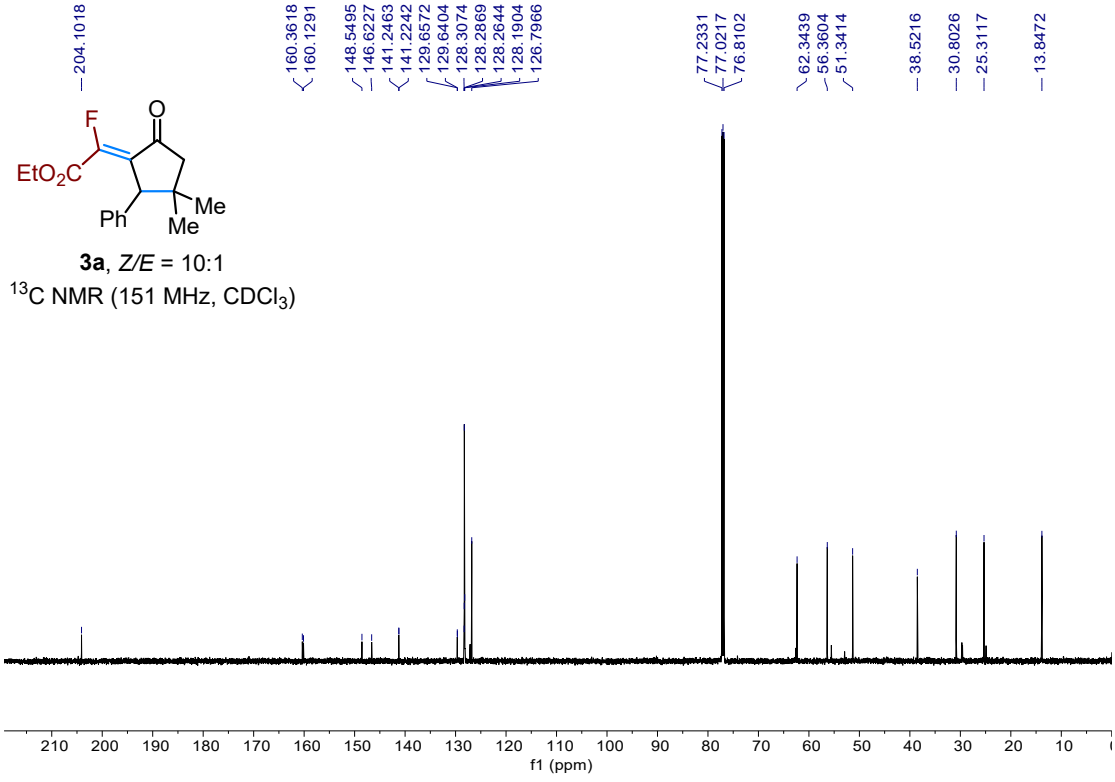
[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F. Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; and Fox, D. J. *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.

4. NMR Spectra



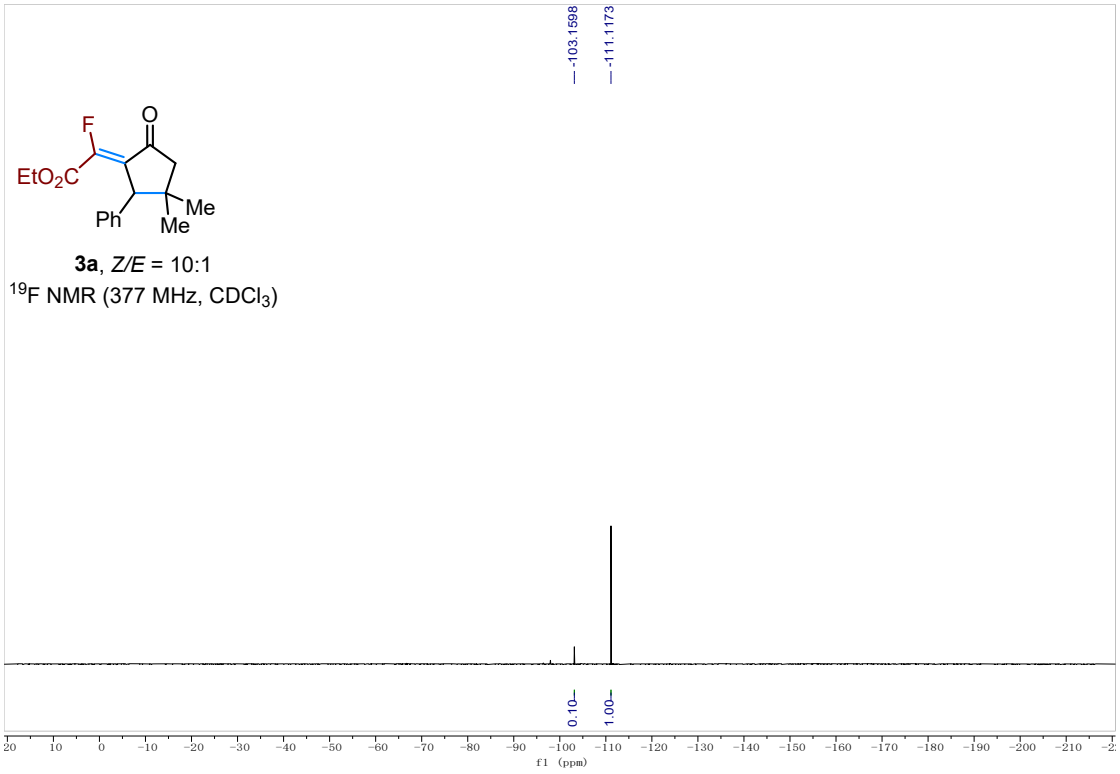
3a, *Z*/*E* = 10:1

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



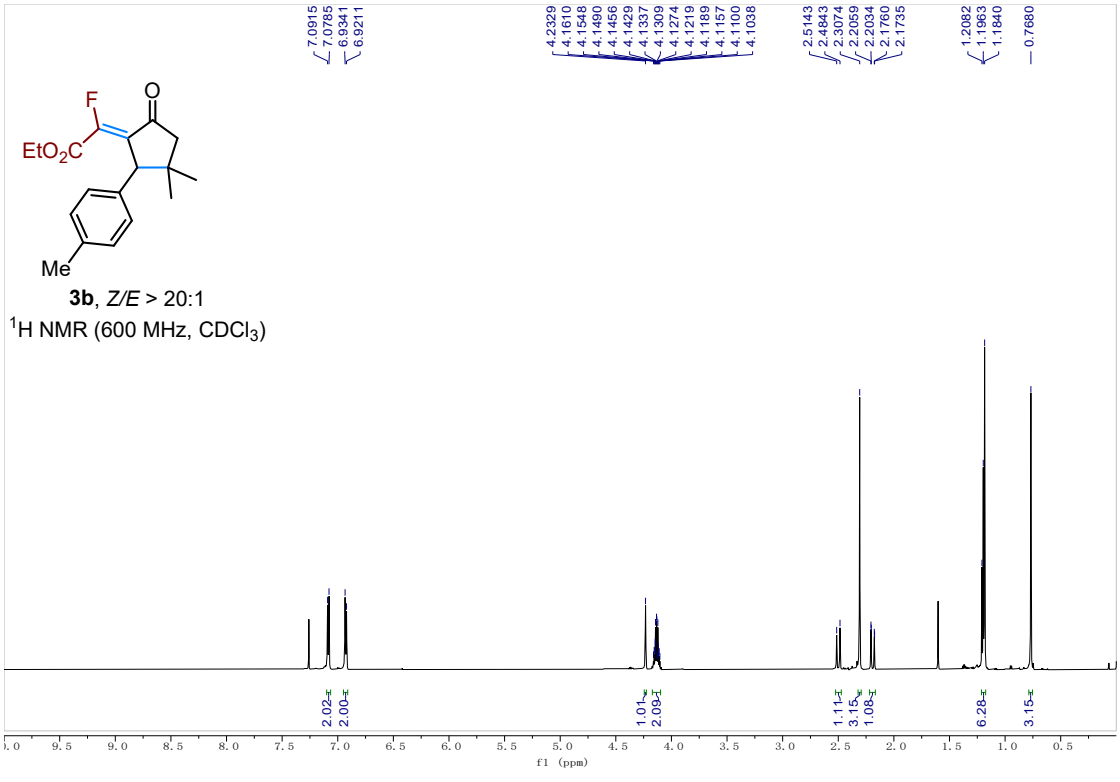
3a, *Z*/*E* = 10:1

^{13}C NMR (151 MHz, $CDCl_3$)



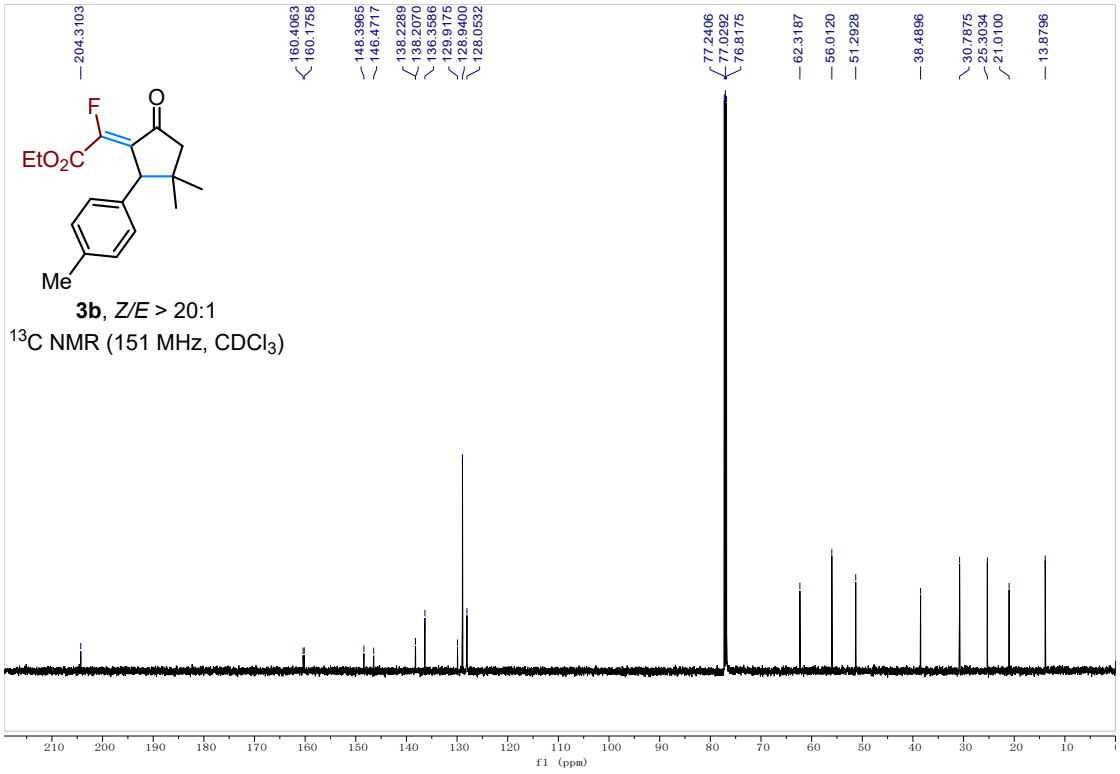
3a, *Z*/*E* = 10:1

^{19}F NMR (377 MHz, $CDCl_3$)



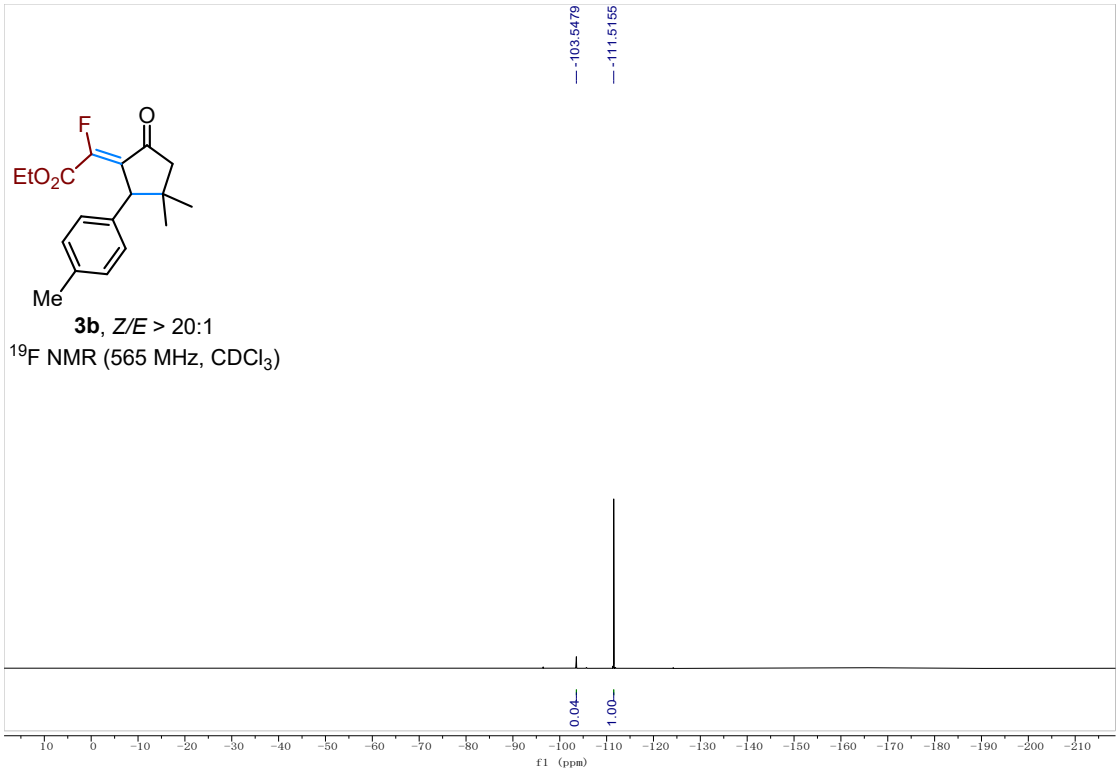
3b, *Z*/*E* > 20:1

^{1}H NMR (600 MHz, $CDCl_3$)



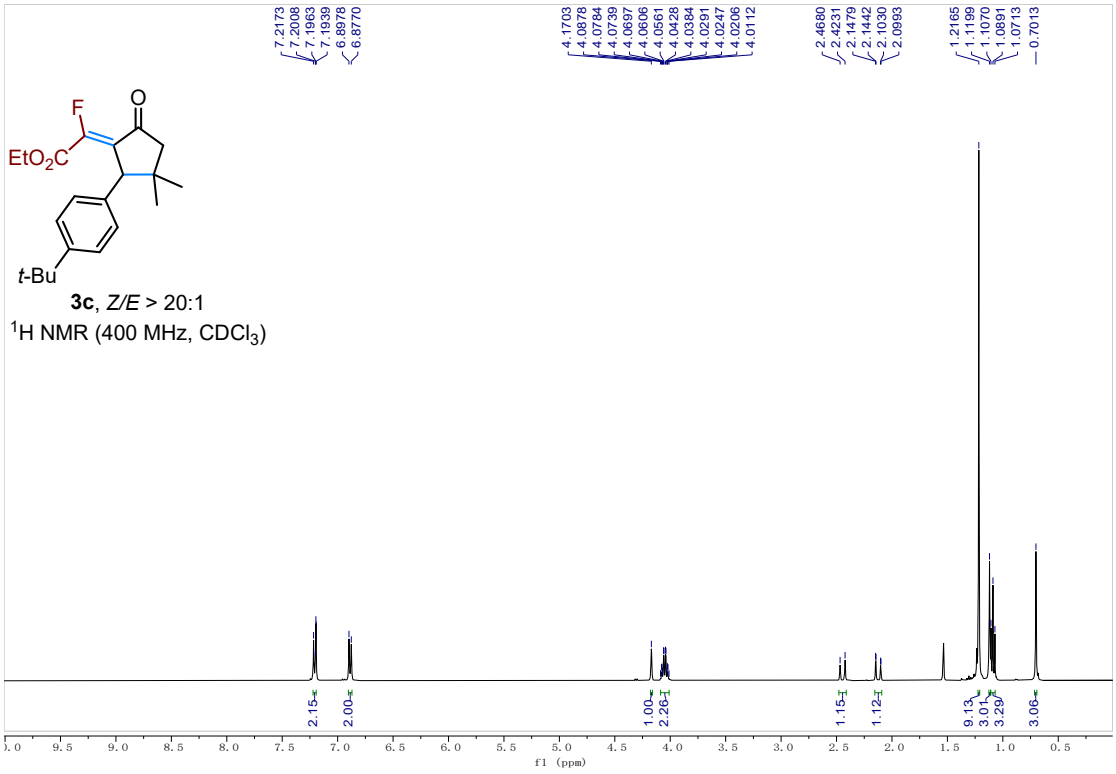
3b, *Z*/*E* > 20:1

^{13}C NMR (151 MHz, $CDCl_3$)



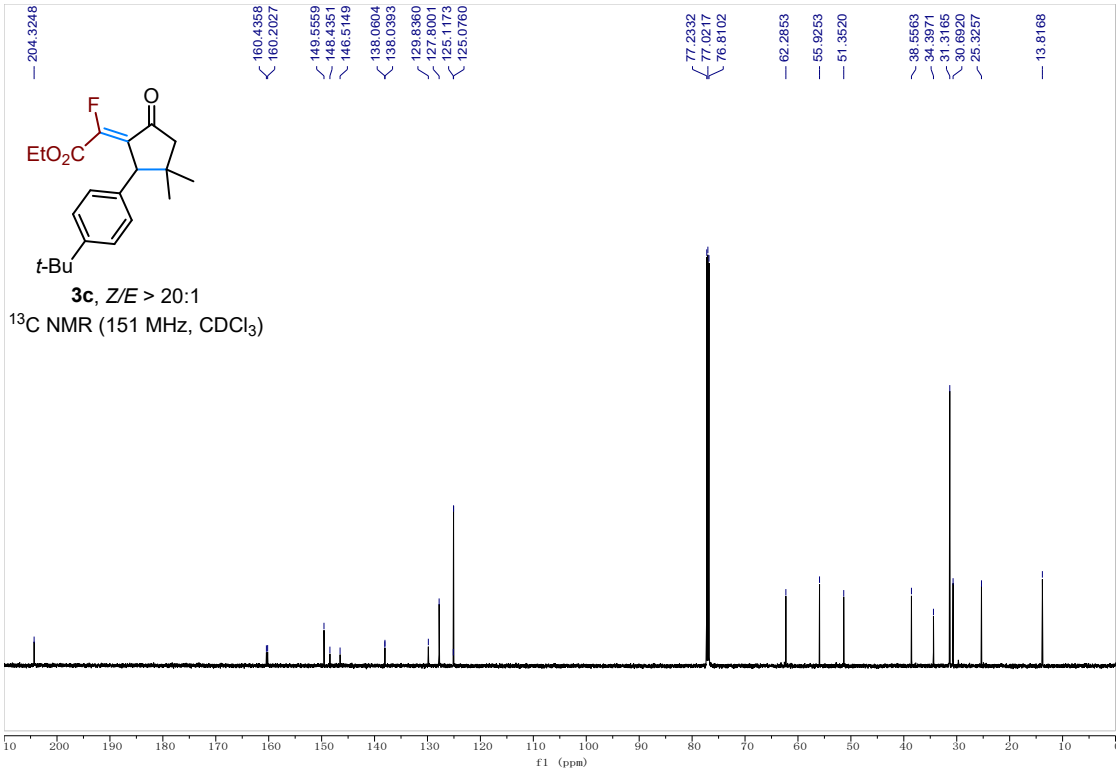
3b, *Z*/*E* > 20:1

^{19}F NMR (565 MHz, $CDCl_3$)



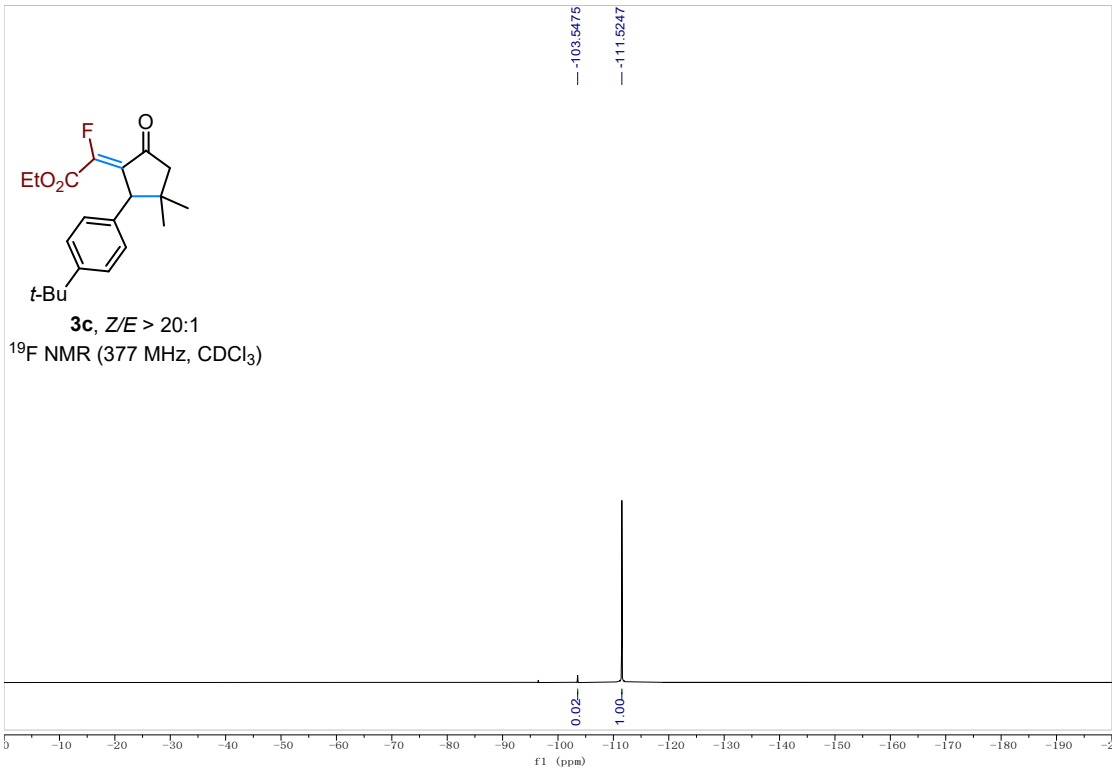
3c, *Z*/*E* > 20:1

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



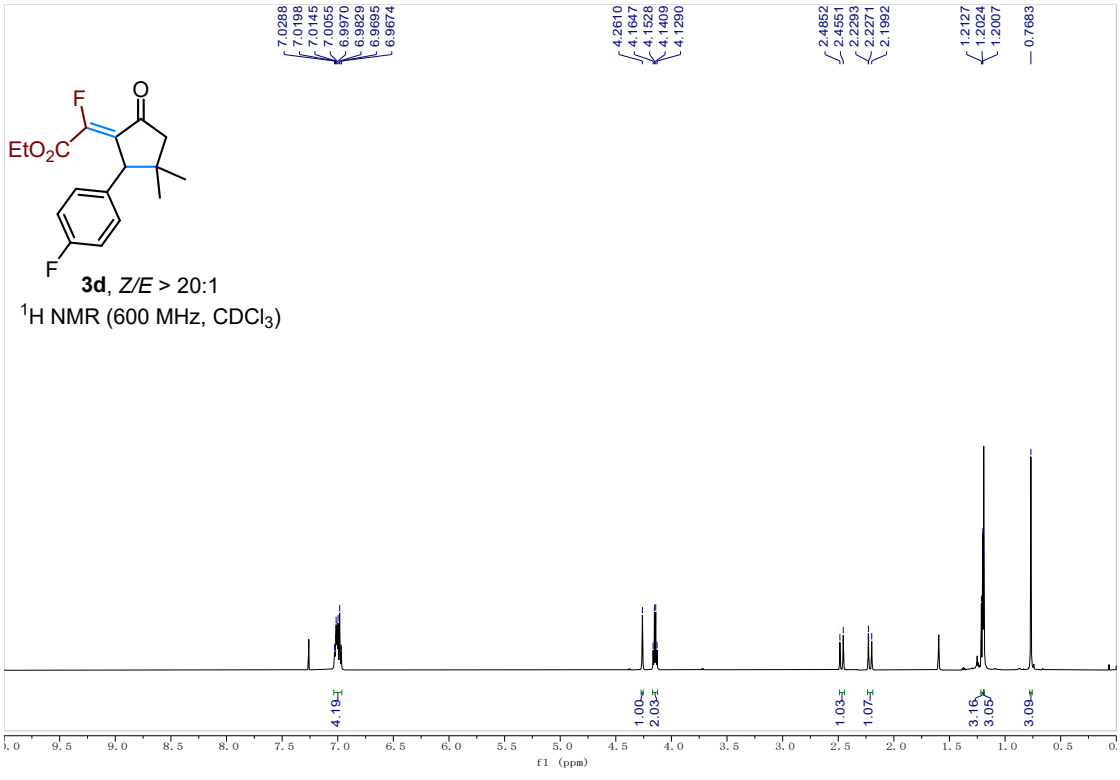
3c, *Z*/*E* > 20:1

^{13}C NMR (151 MHz, $CDCl_3$)



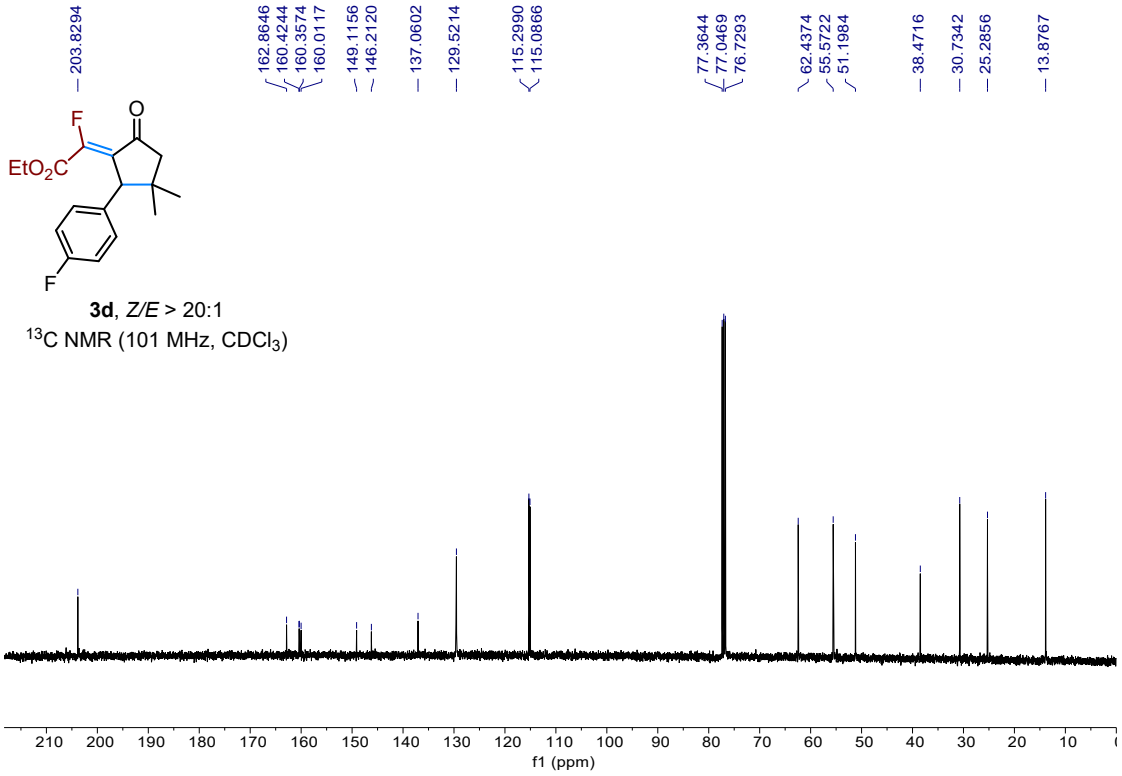
3c, *Z*/*E* > 20:1

^{19}F NMR (377 MHz, $CDCl_3$)



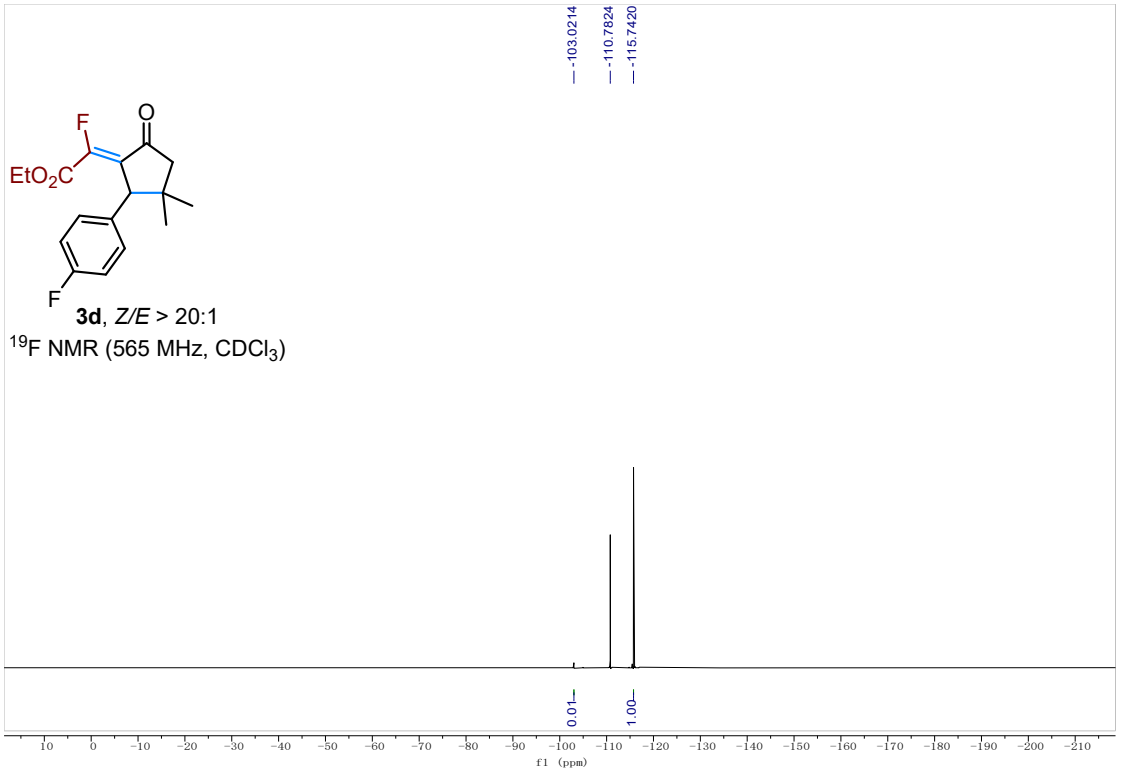
3d, *Z*/*E* > 20:1

^{1}H NMR (600 MHz, $CDCl_3$)



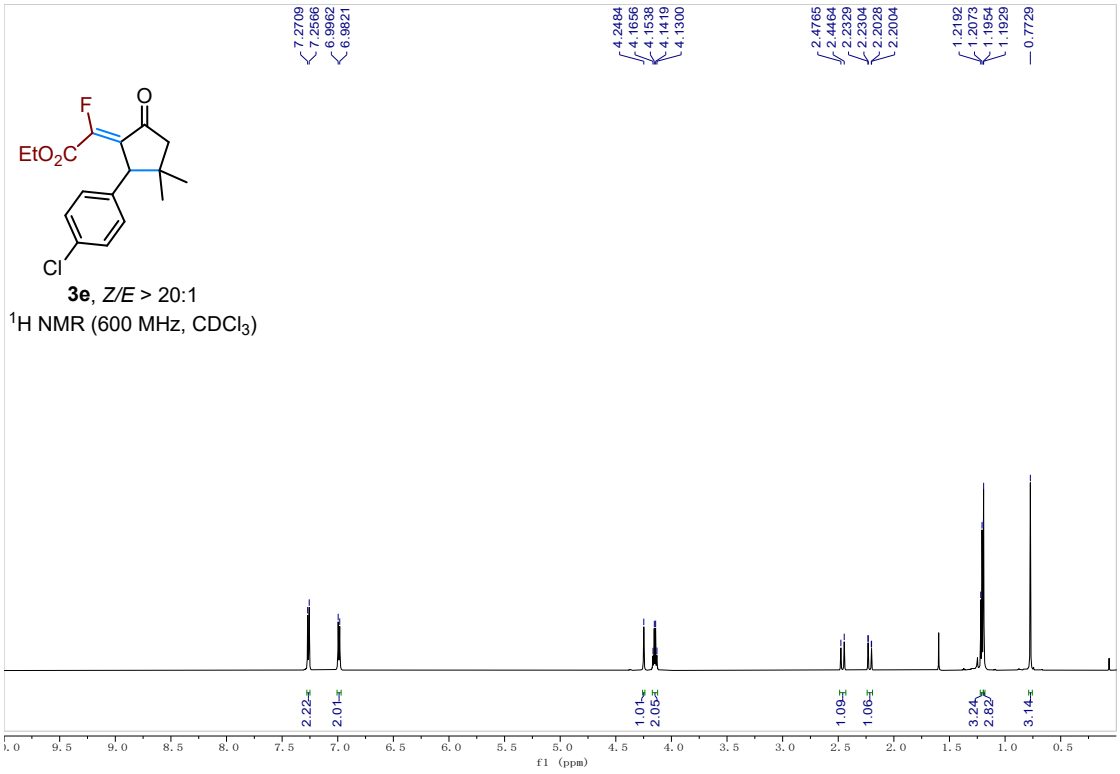
3d, *Z*/*E* > 20:1

^{13}C NMR (101 MHz, $CDCl_3$)



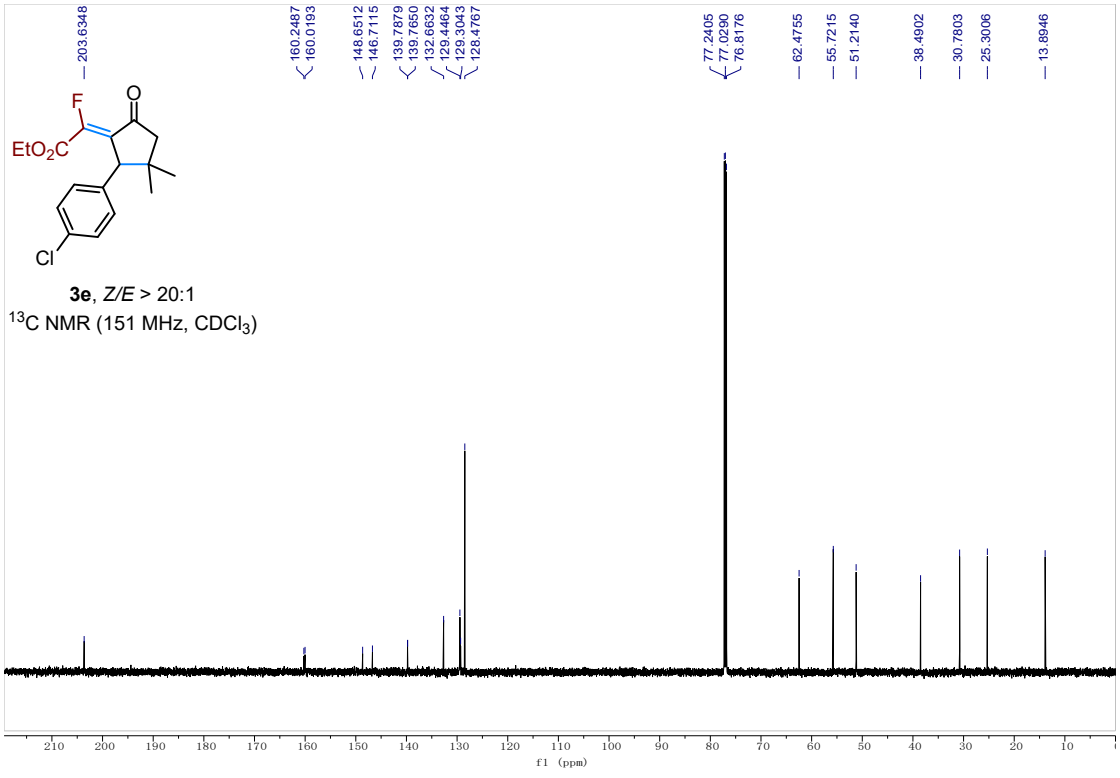
3d, *Z*/*E* > 20:1

^{19}F NMR (565 MHz, $CDCl_3$)



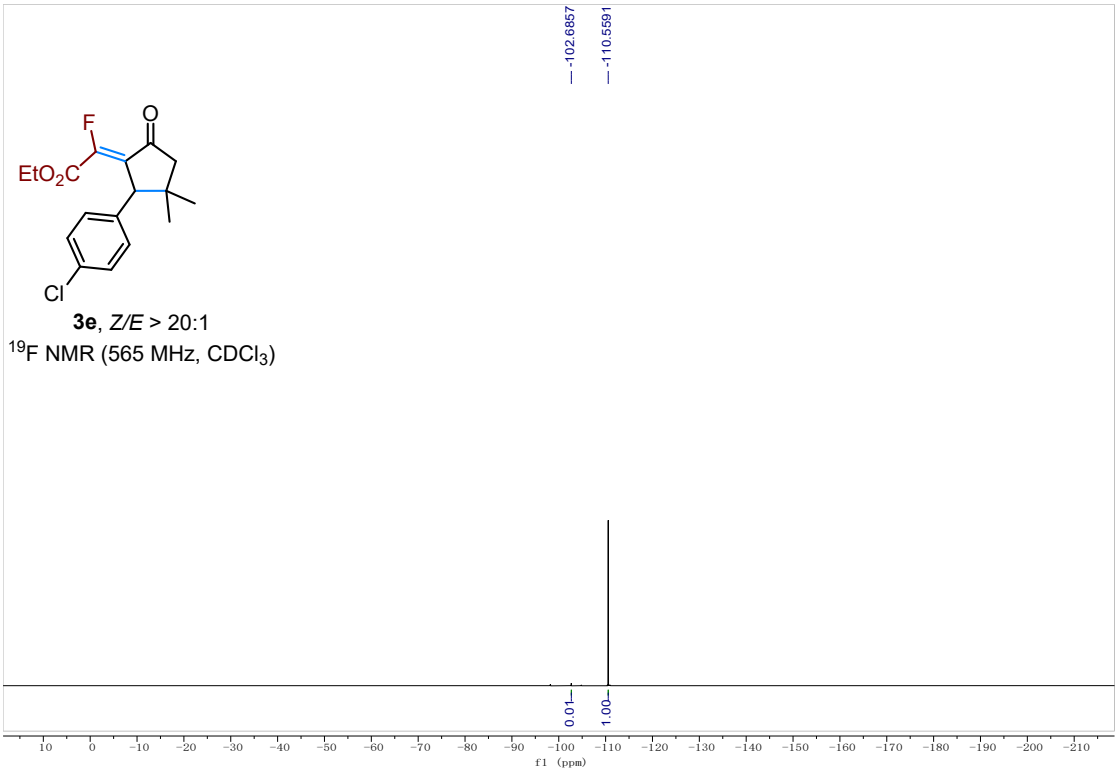
3e, *Z*/*E* > 20:1

^{1}H NMR (600 MHz, $CDCl_3$)



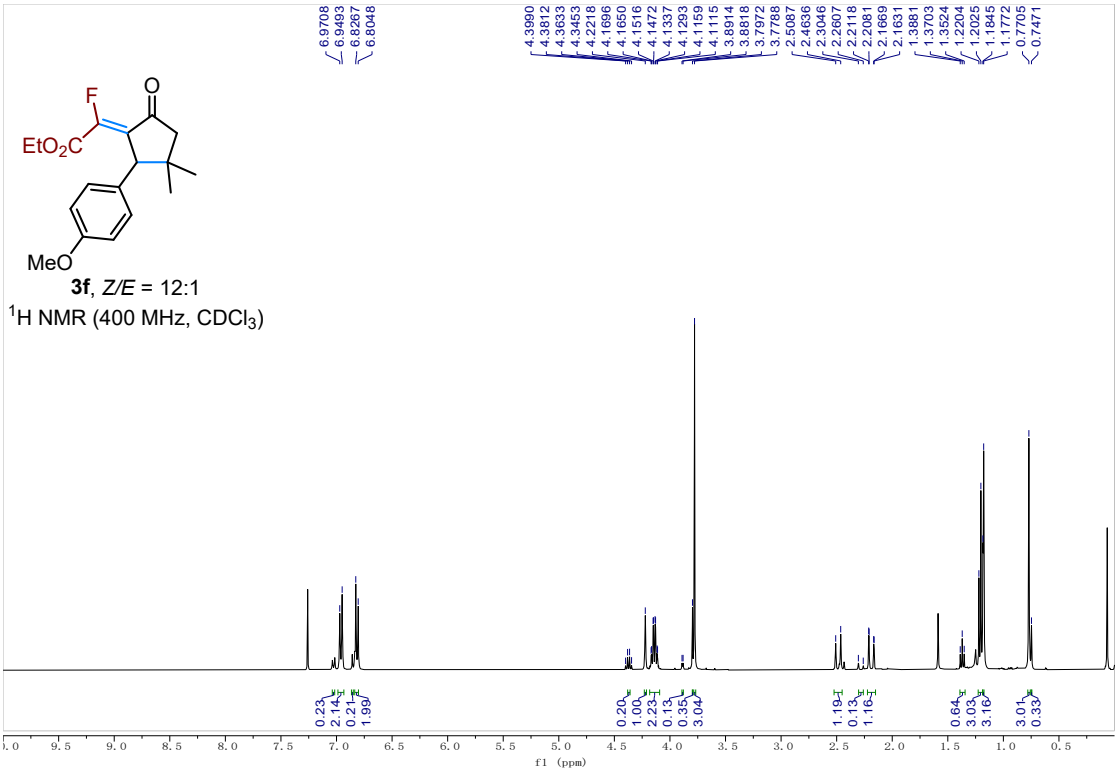
3e, *Z*/*E* > 20:1

^{13}C NMR (151 MHz, $CDCl_3$)



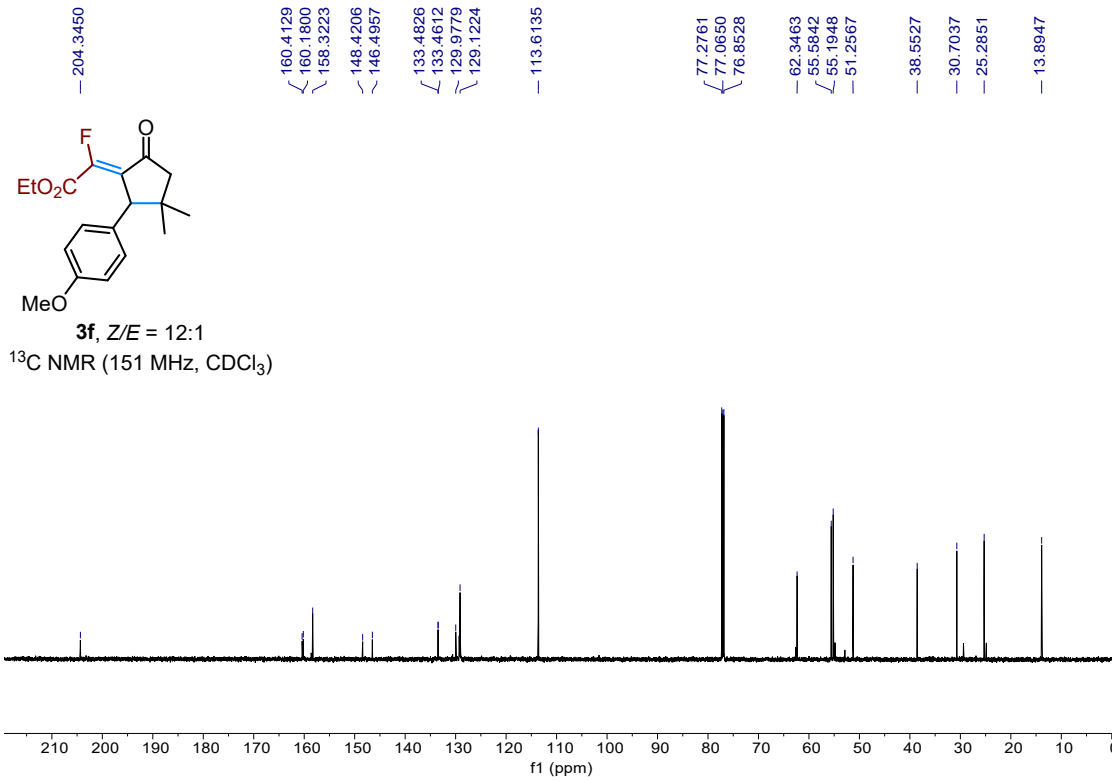
3e, *Z*/*E* > 20:1

^{19}F NMR (565 MHz, $CDCl_3$)



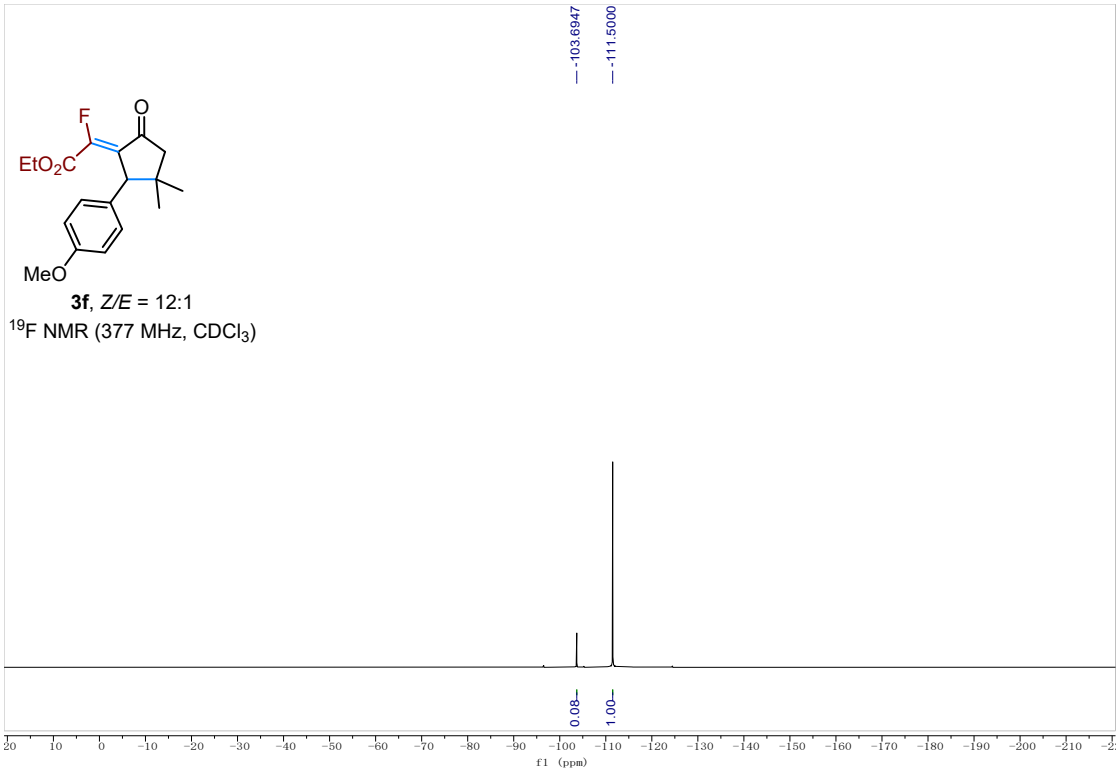
3f, *Z*/*E* = 12:1

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



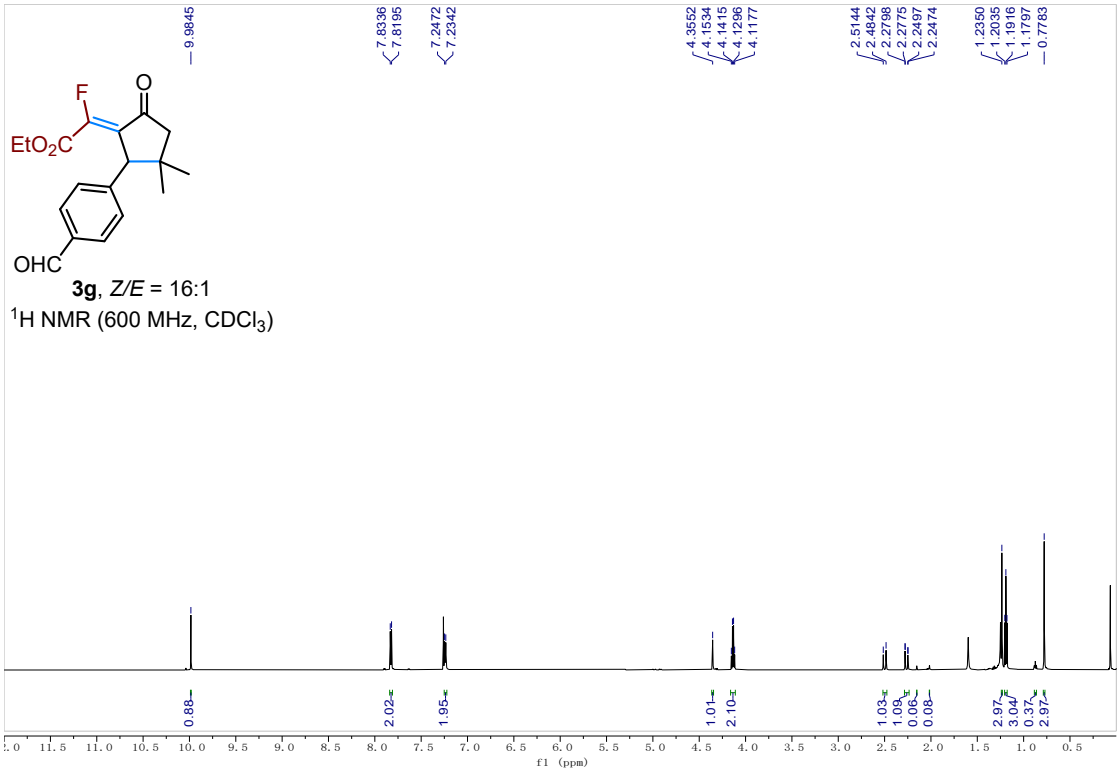
3f, *Z*/*E* = 12:1

^{13}C NMR (151 MHz, $CDCl_3$)



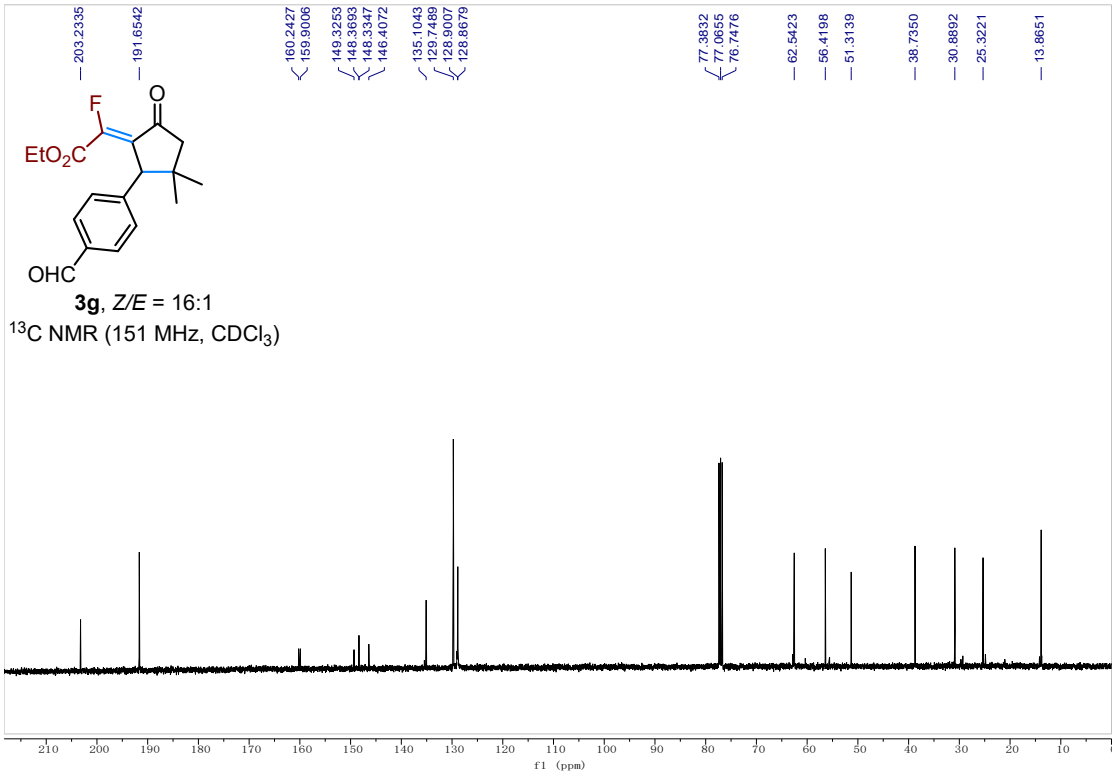
3f, *Z*/*E* = 12:1

^{19}F NMR (377 MHz, $CDCl_3$)



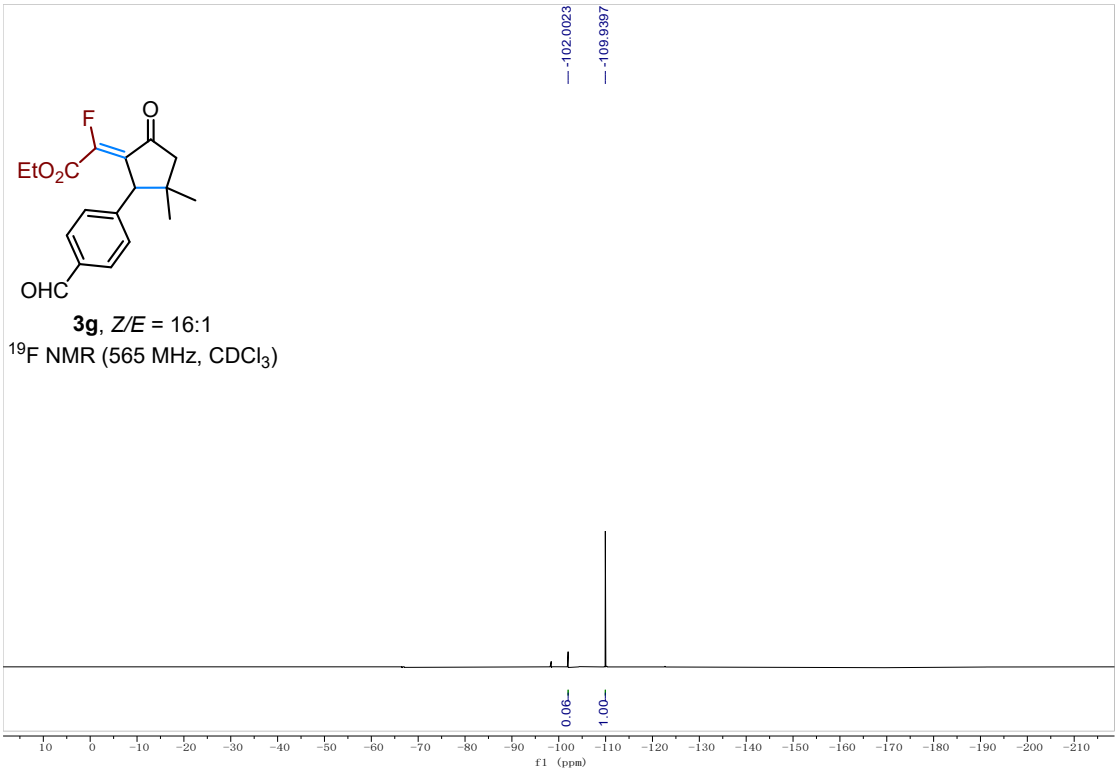
3g, *Z*/*E* = 16:1

^{1}H NMR (600 MHz, $CDCl_3$)



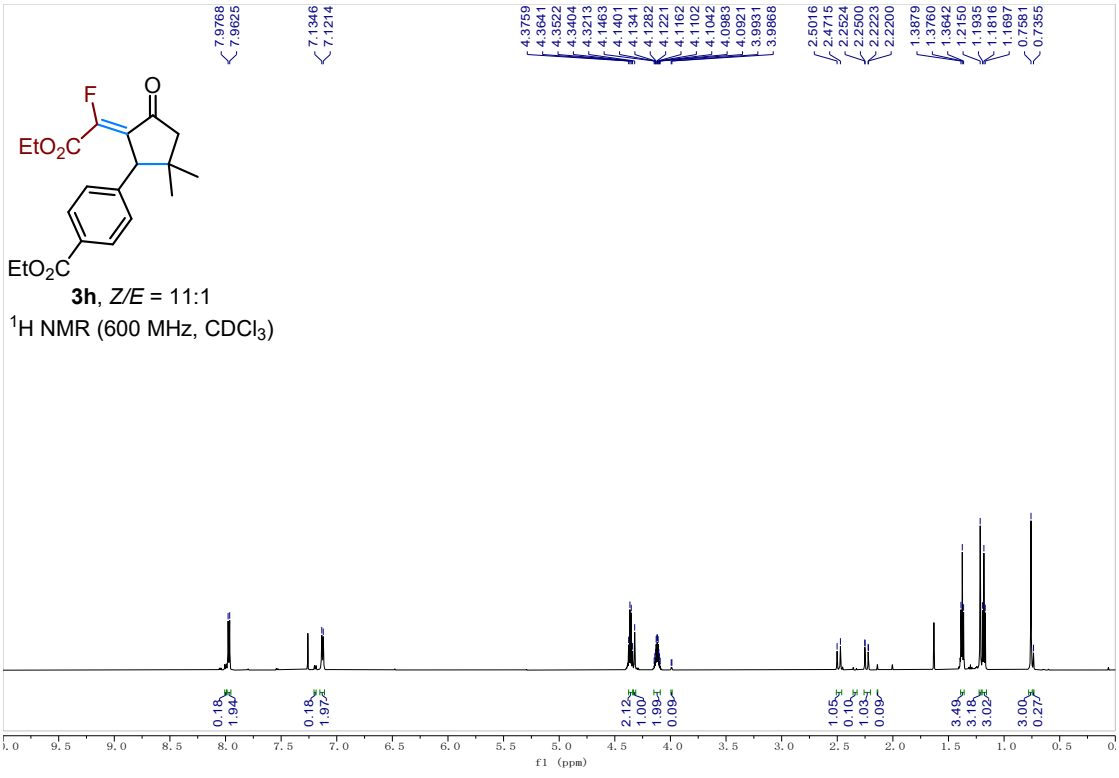
3g, *Z*/*E* = 16:1

^{13}C NMR (151 MHz, $CDCl_3$)



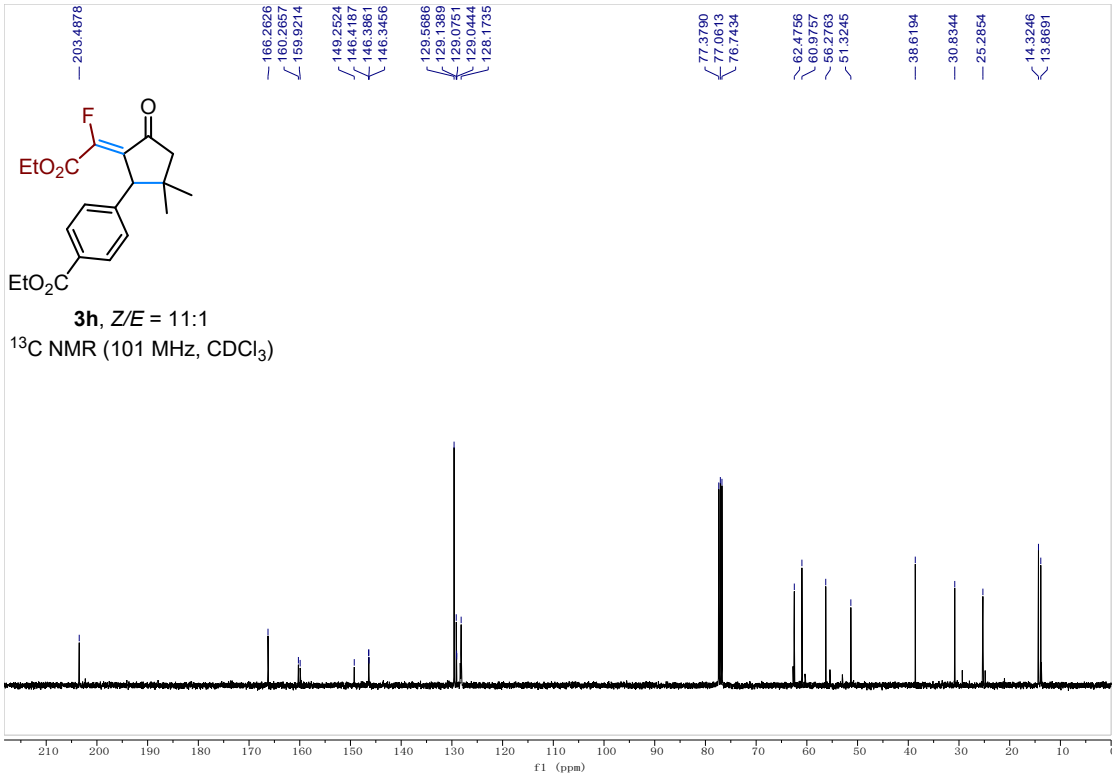
3g, *Z*/*E* = 16:1

^{19}F NMR (565 MHz, $CDCl_3$)



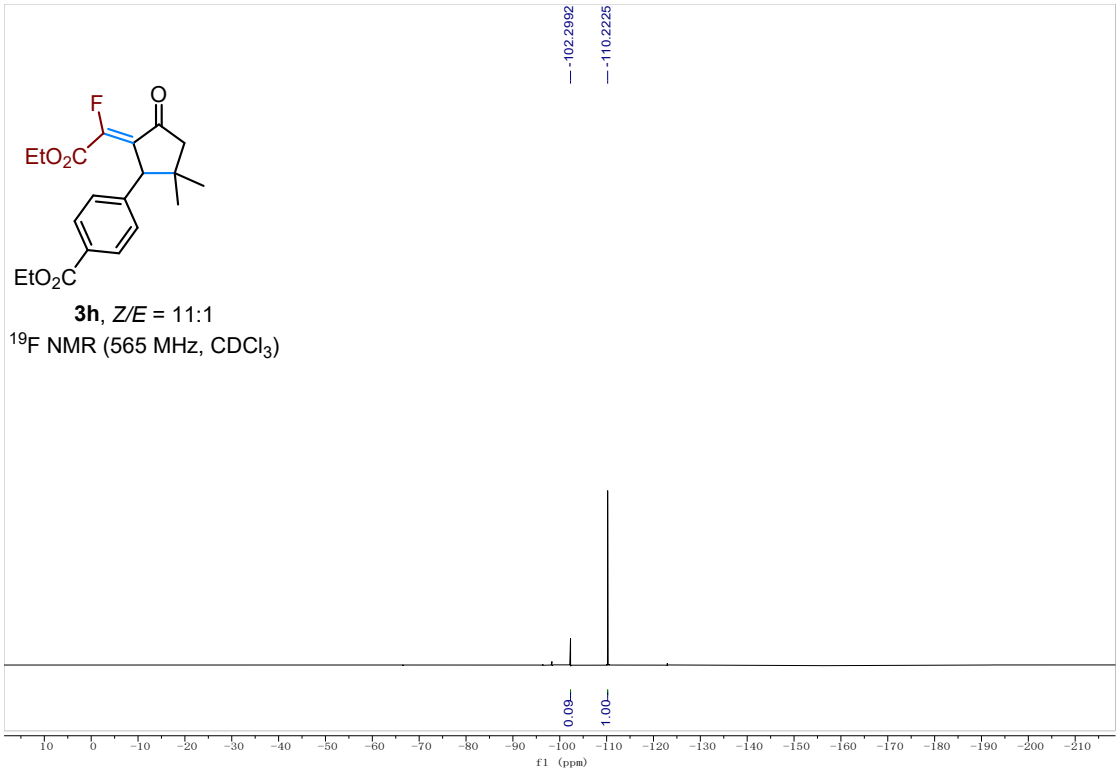
3h, *Z*/*E* = 11:1

^{1}H NMR (600 MHz, $CDCl_3$)



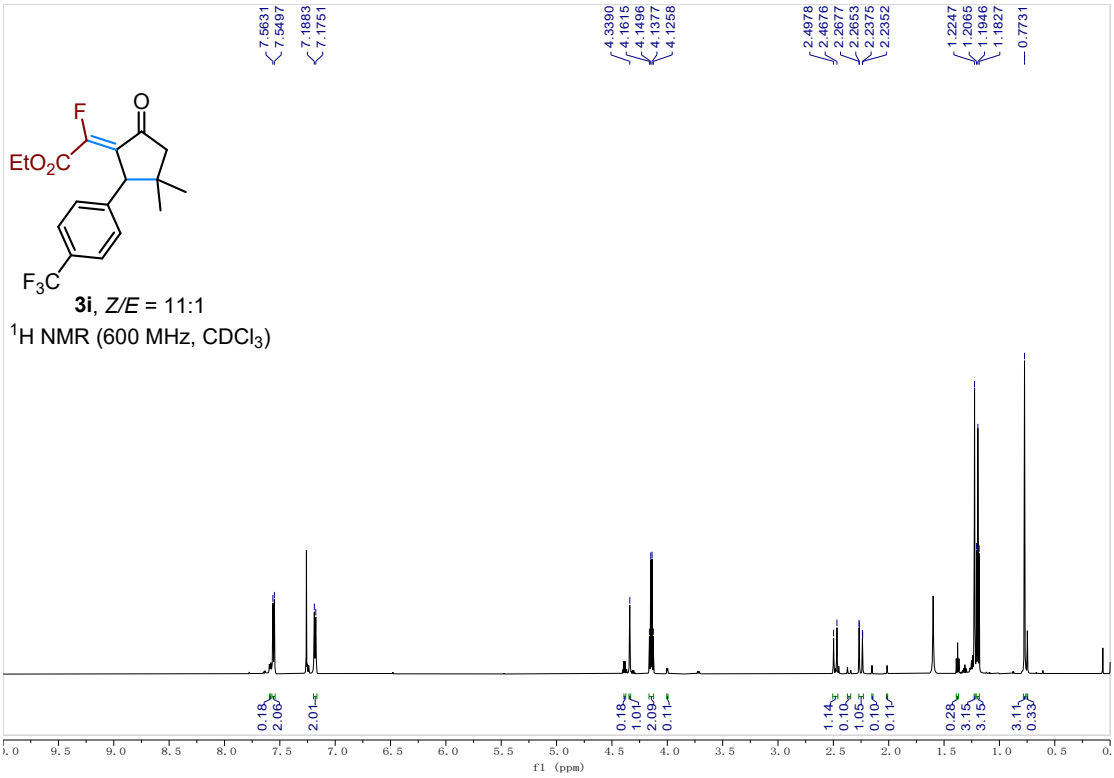
3h, *Z*/*E* = 11:1

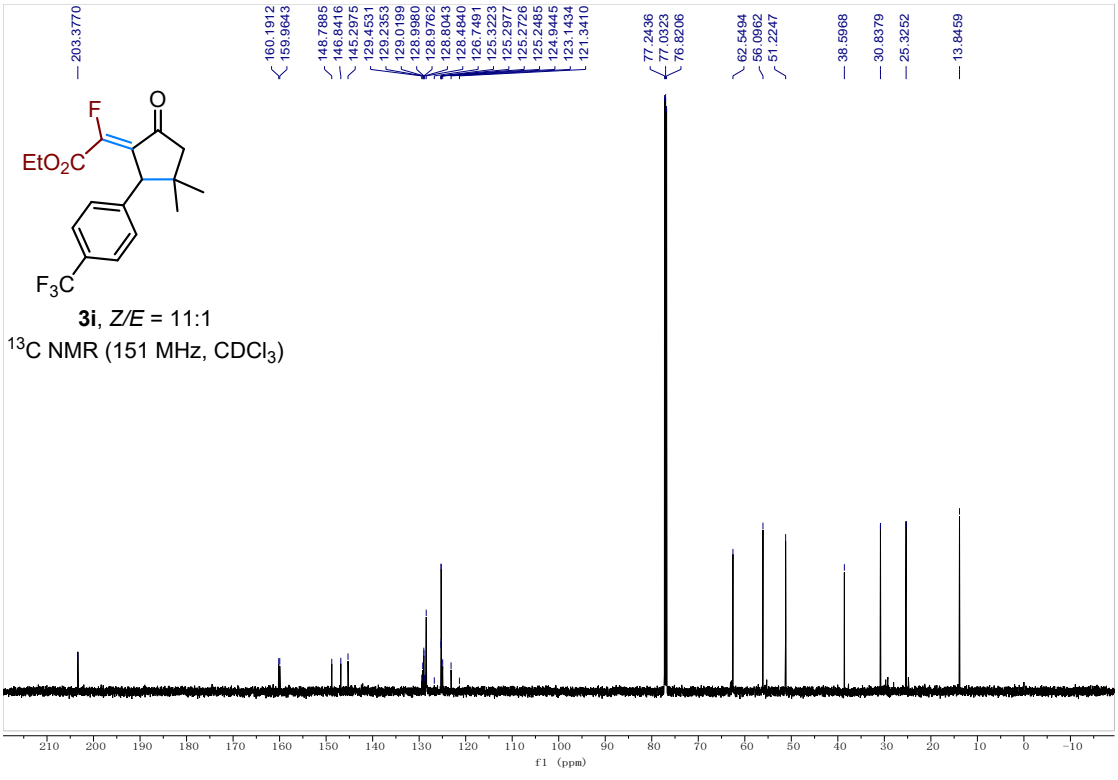
^{13}C NMR (101 MHz, $CDCl_3$)

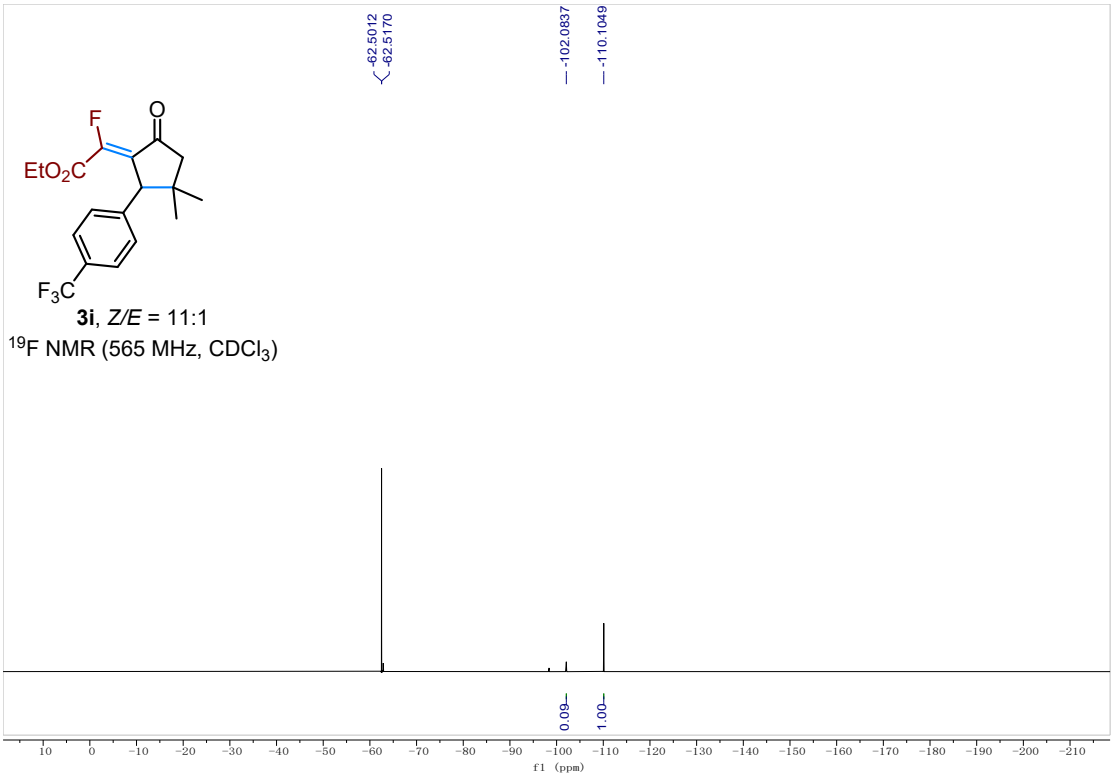


3h, *Z*/*E* = 11:1

^{19}F NMR (565 MHz, $CDCl_3$)

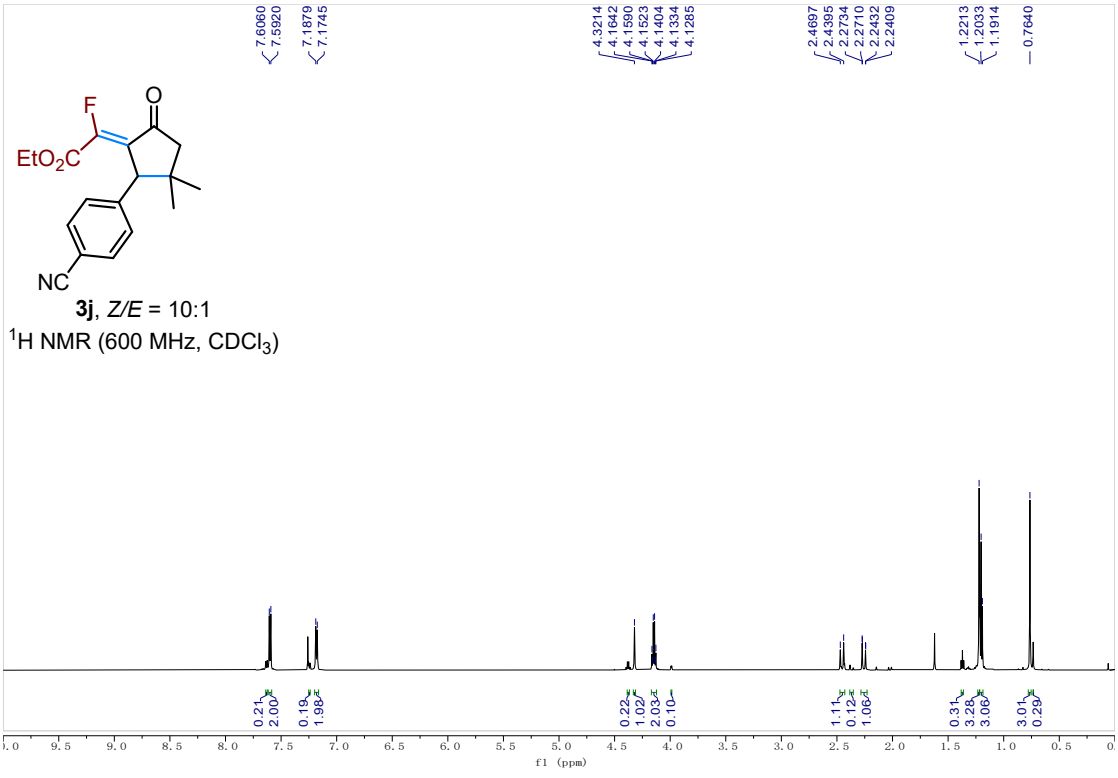

F
O
EtO2C
F3C
3i, Z/E = 11:1
1H NMR (600 MHz, CDCl3)
f1 (ppm)


F
O
EtO2C
F3C
3i, Z/E = 11:1
13C NMR (151 MHz, CDCl3)
f1 (ppm)



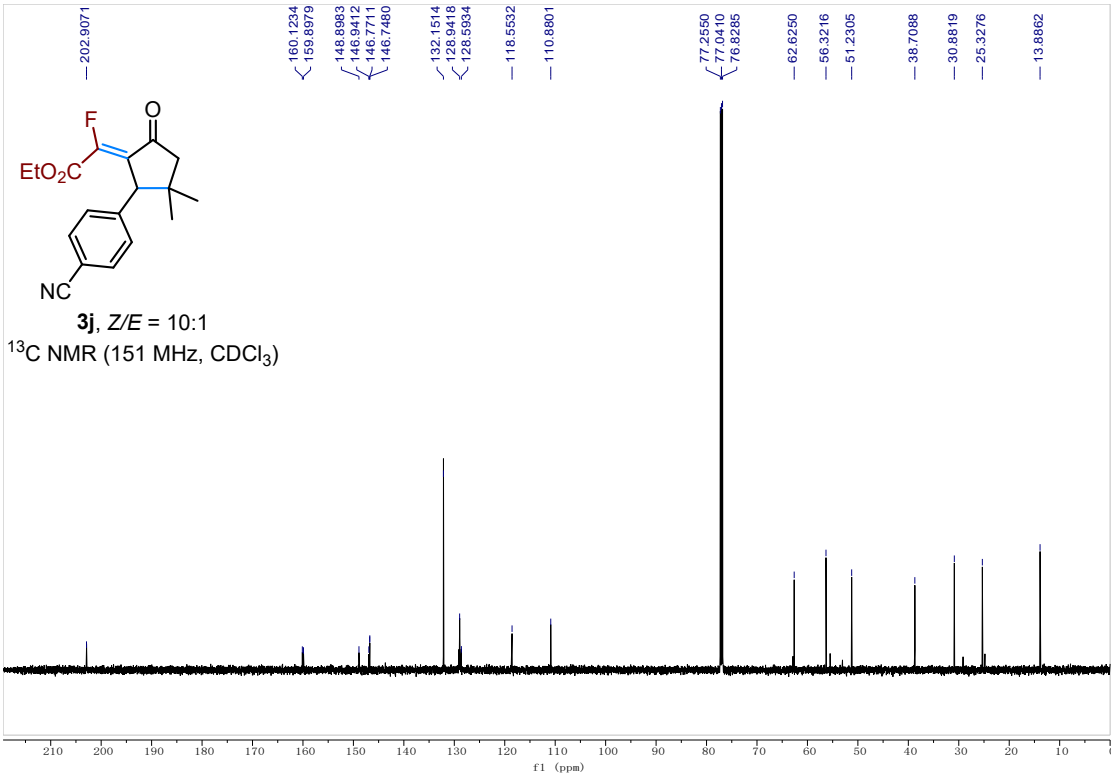
3i, *Z*/*E* = 11:1

^{19}F NMR (565 MHz, $CDCl_3$)



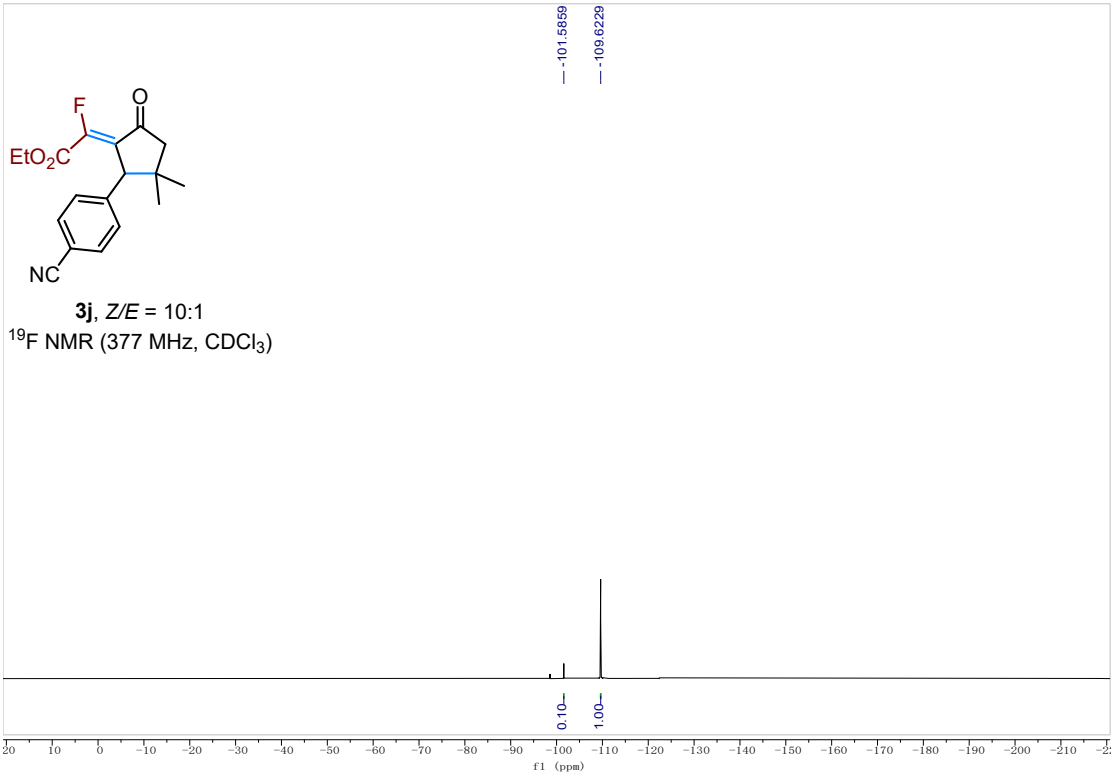
3j, *Z*/*E* = 10:1

^{1}H NMR (600 MHz, $CDCl_3$)



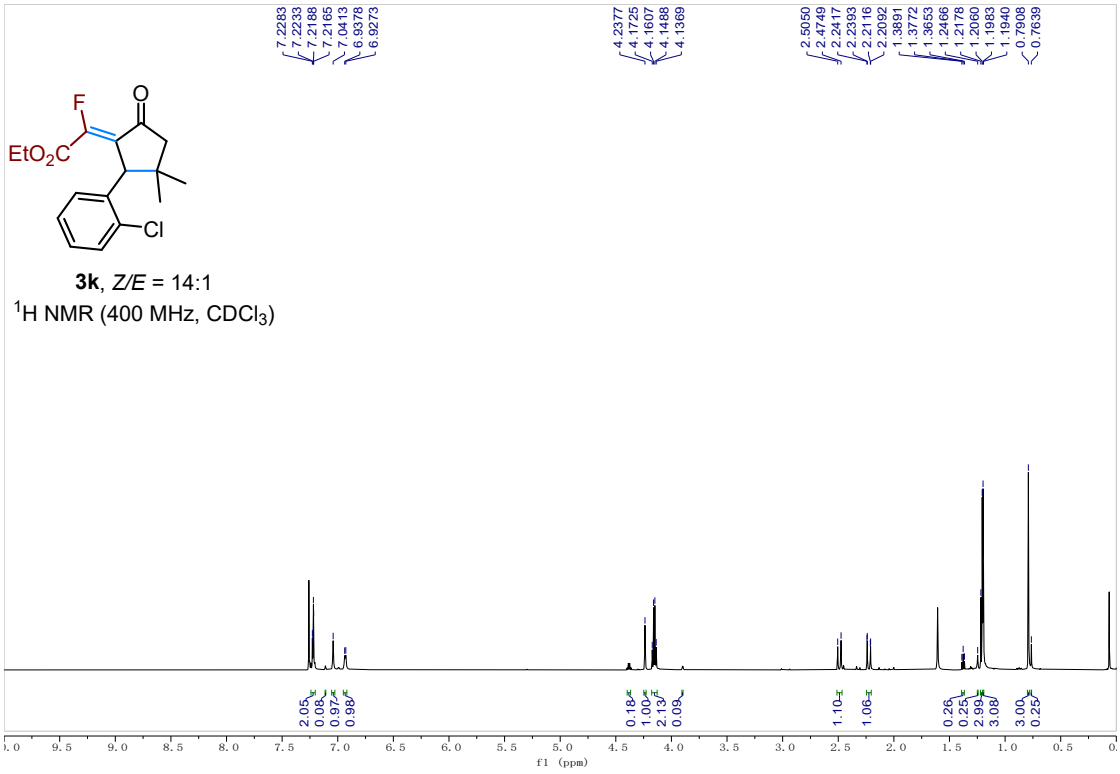
3j, *Z*/*E* = 10:1

^{13}C NMR (151 MHz, $CDCl_3$)



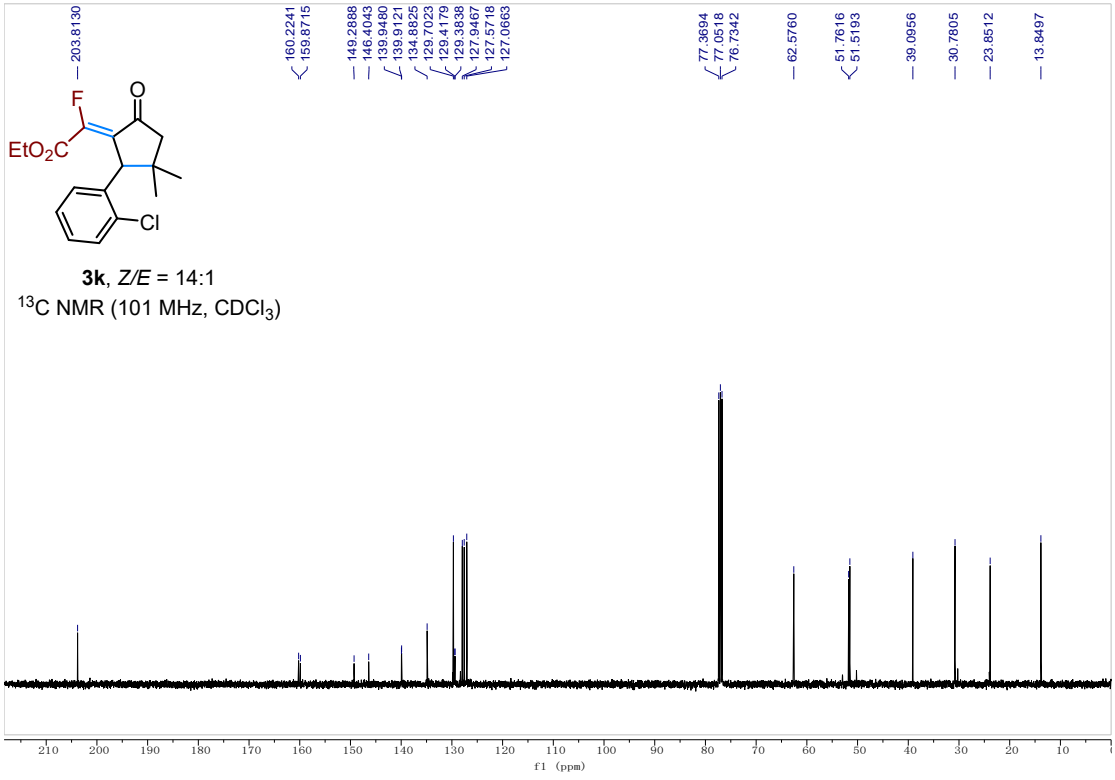
3j, *Z*/*E* = 10:1

^{19}F NMR (377 MHz, $CDCl_3$)



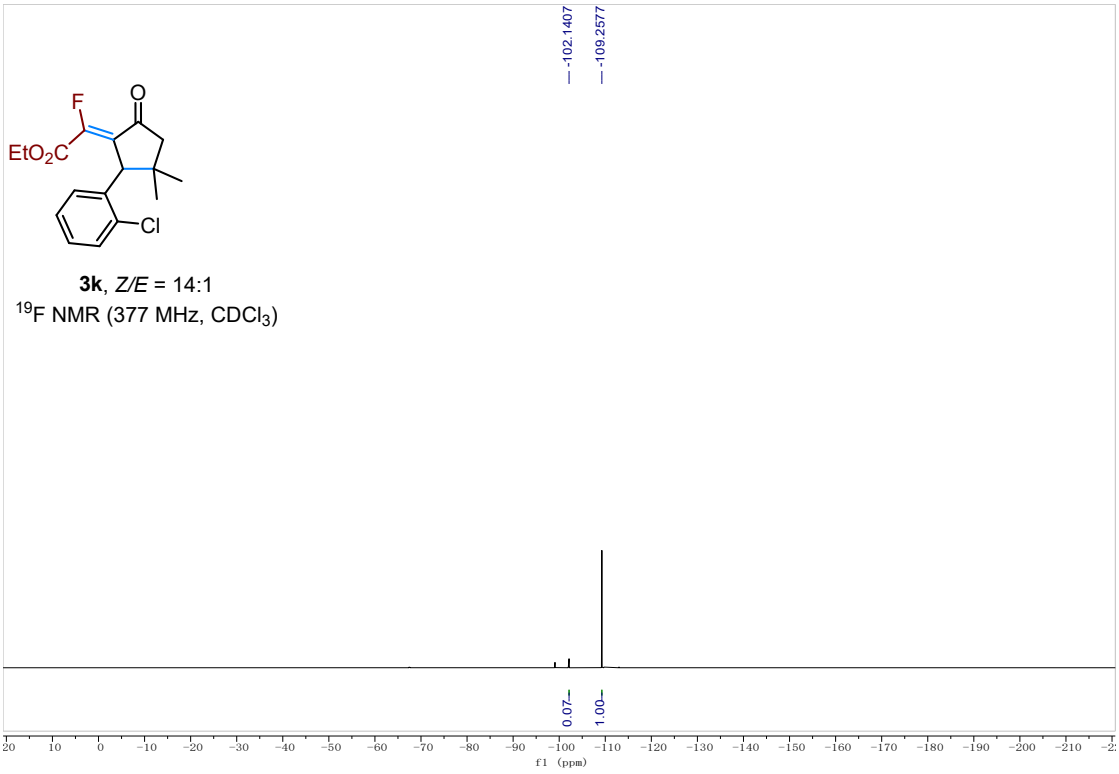
3k, *Z*/*E* = 14:1

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



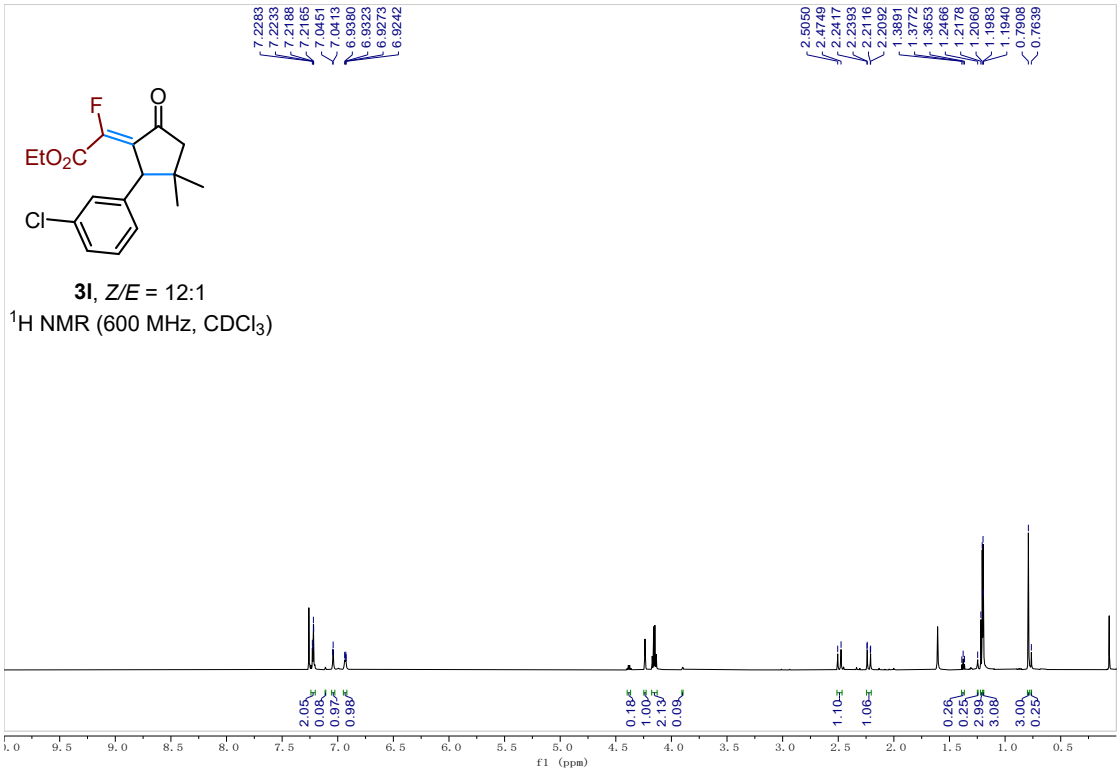
3k, *Z*/*E* = 14:1

^{13}C NMR (101 MHz, $CDCl_3$)



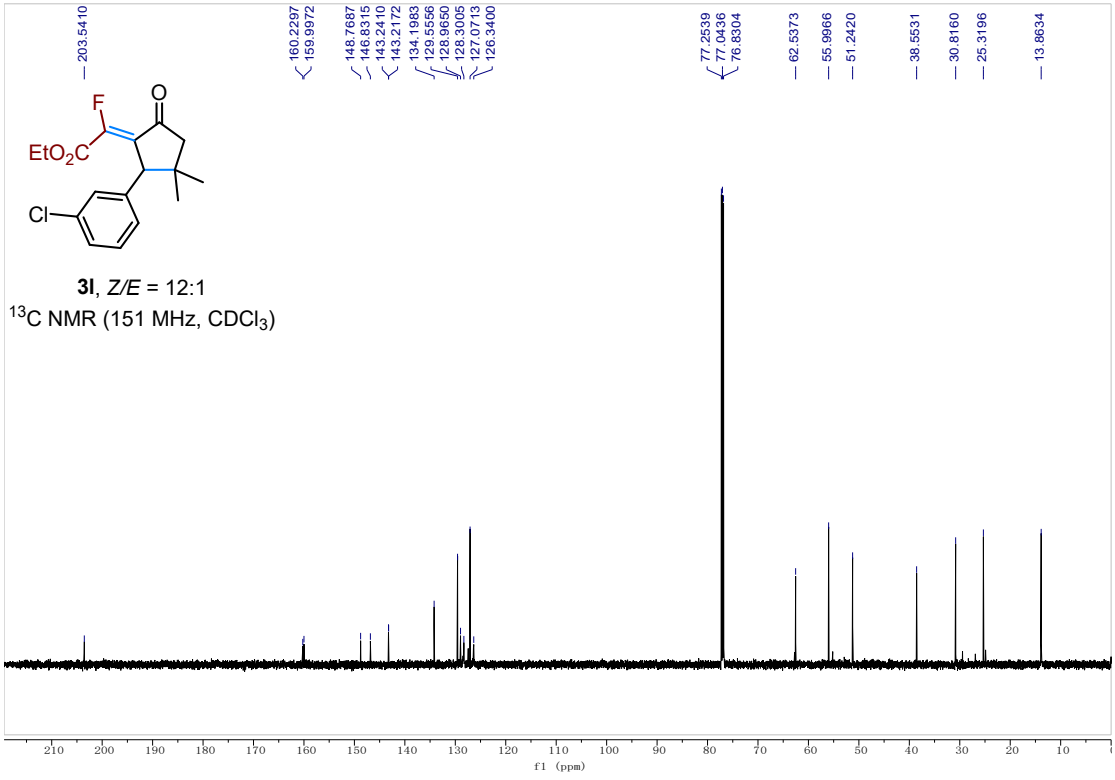
3k, *Z*/*E* = 14:1

^{19}F NMR (377 MHz, $CDCl_3$)



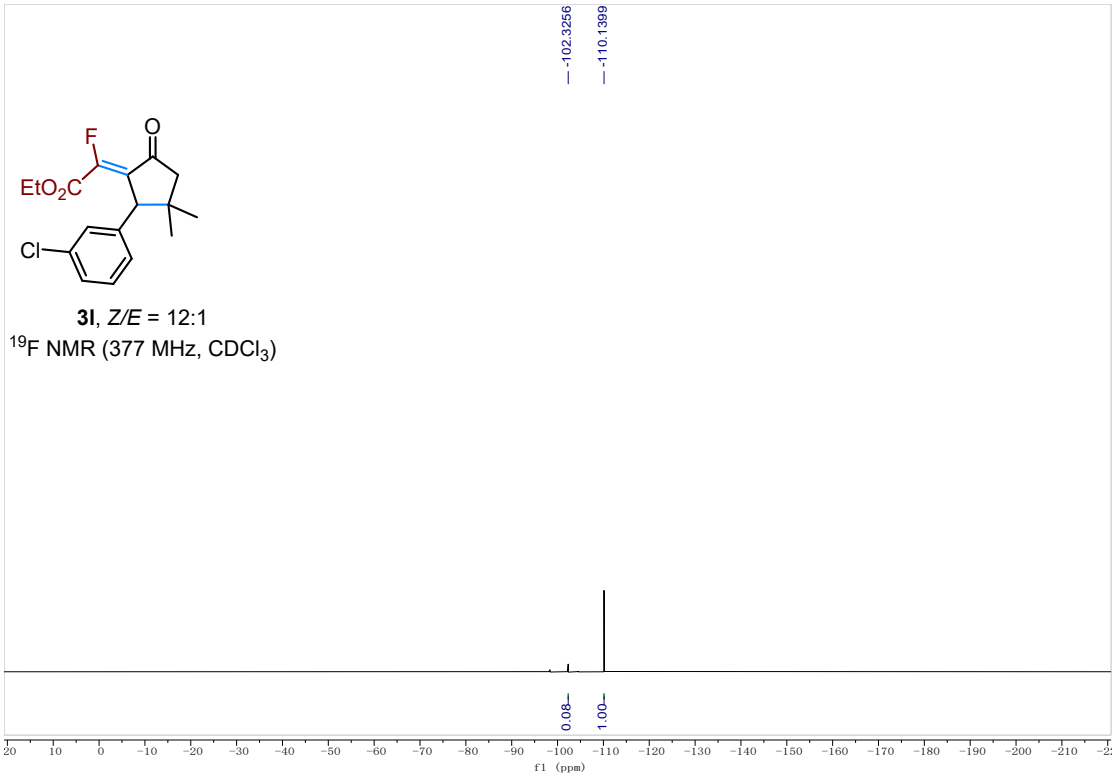
3l, *Z*/*E* = 12:1

^{1}H NMR (600 MHz, $CDCl_3$)



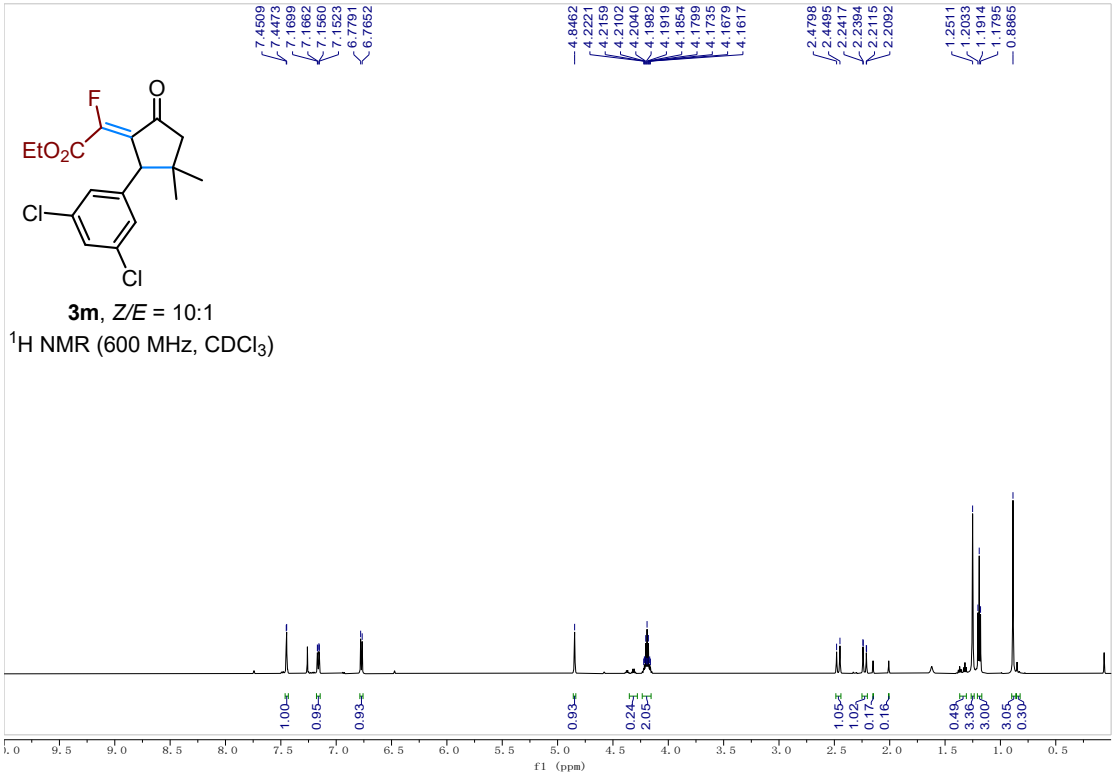
3l, *Z*/*E* = 12:1

^{13}C NMR (151 MHz, $CDCl_3$)



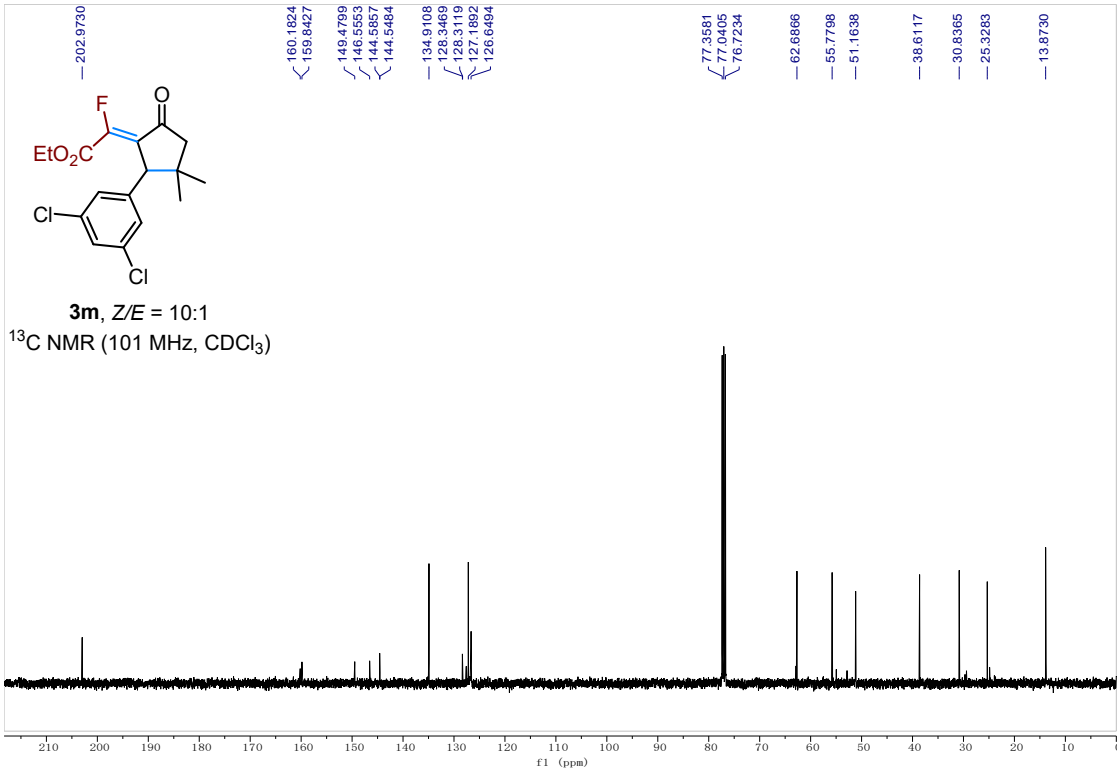
3l, *Z*/*E* = 12:1

^{19}F NMR (377 MHz, $CDCl_3$)



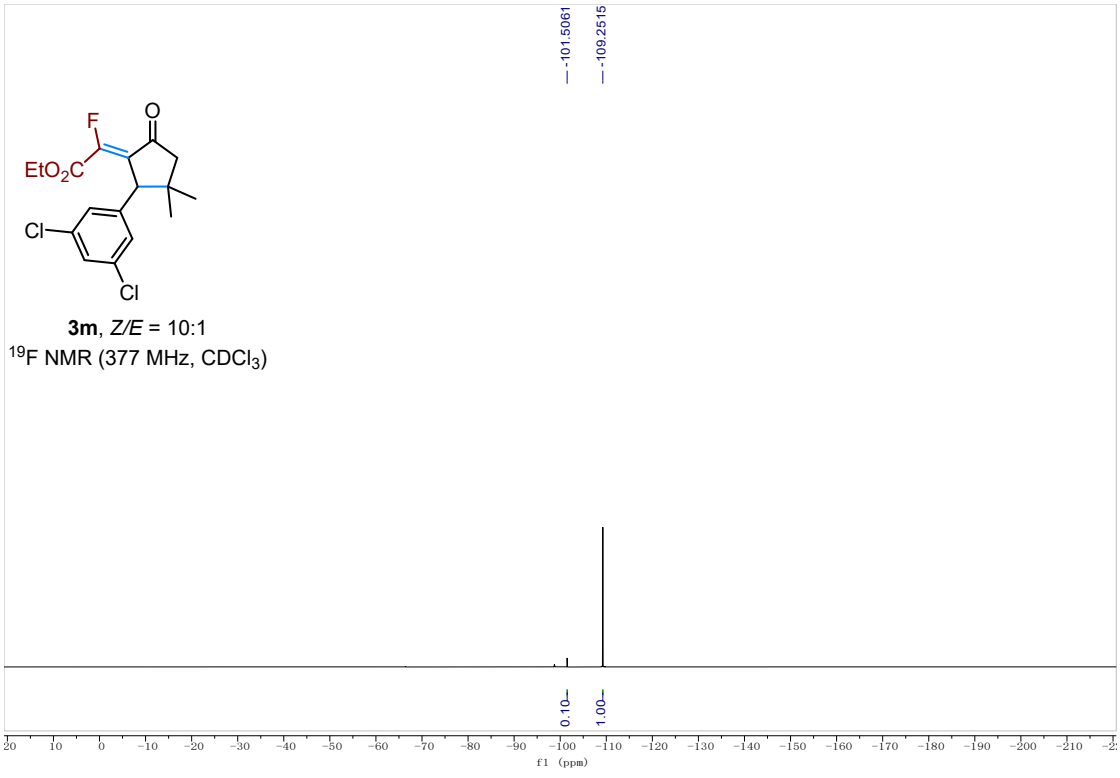
3m, *Z*/*E* = 10:1

^{1}H NMR (600 MHz, $CDCl_3$)



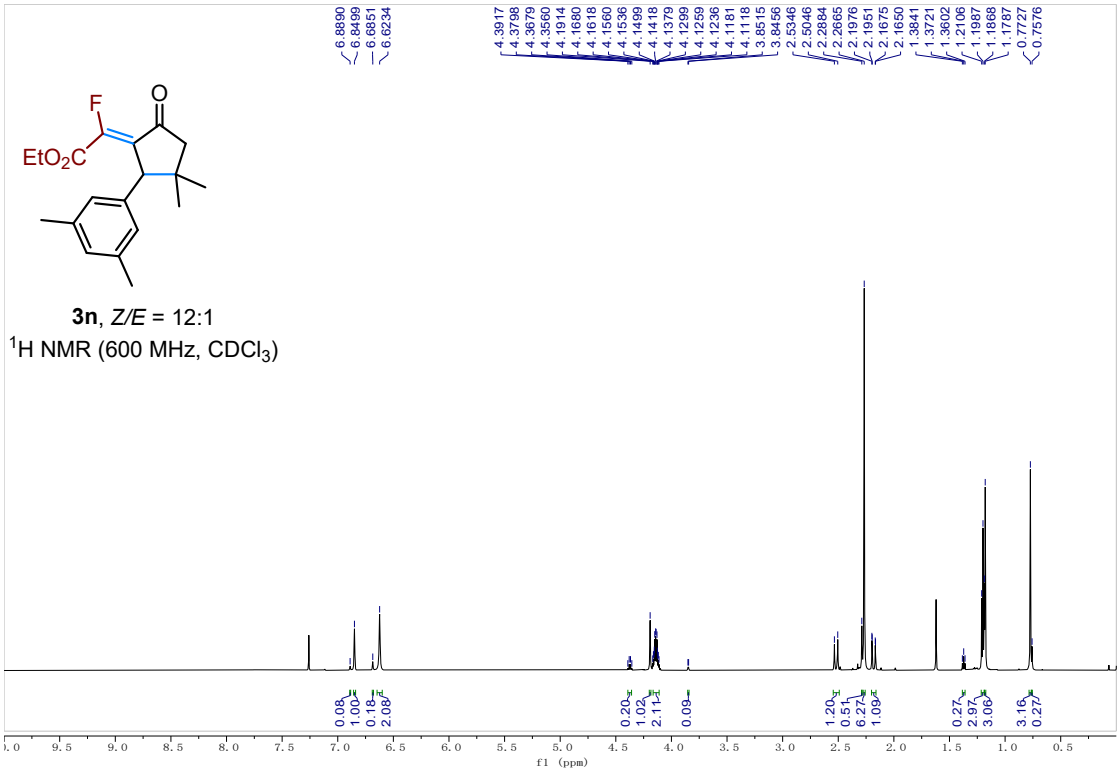
3m, *Z*/*E* = 10:1

^{13}C NMR (101 MHz, $CDCl_3$)



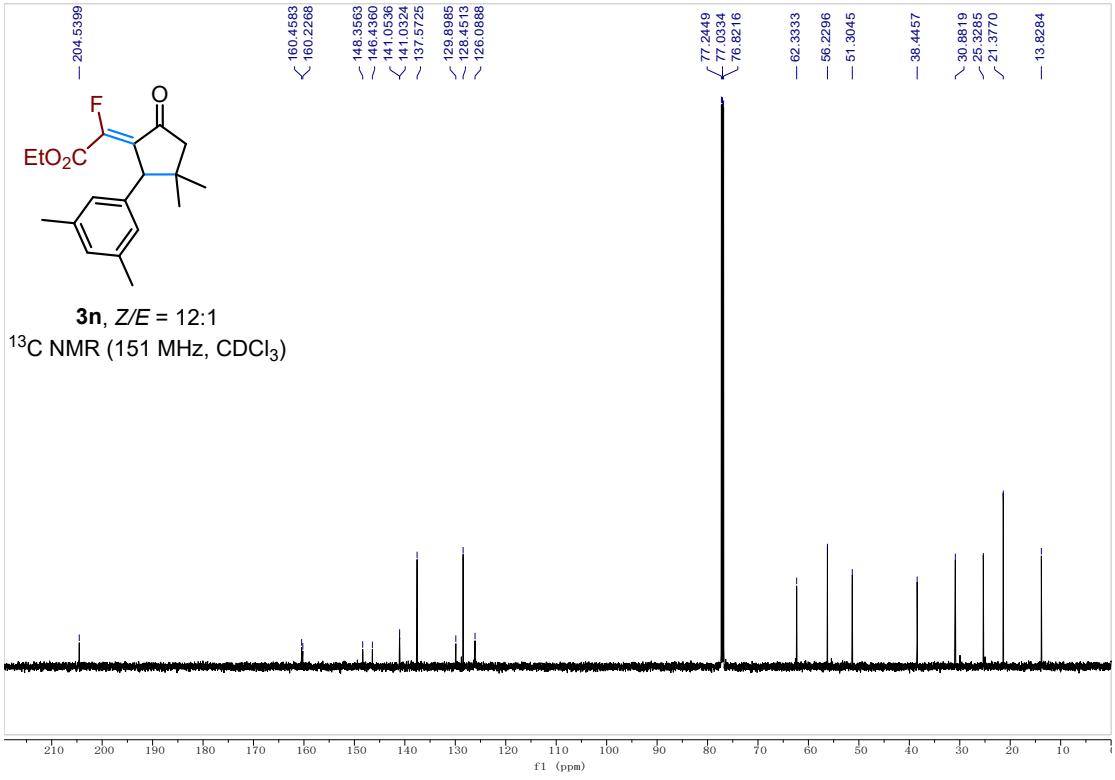
3m, *Z*/*E* = 10:1

^{19}F NMR (377 MHz, $CDCl_3$)



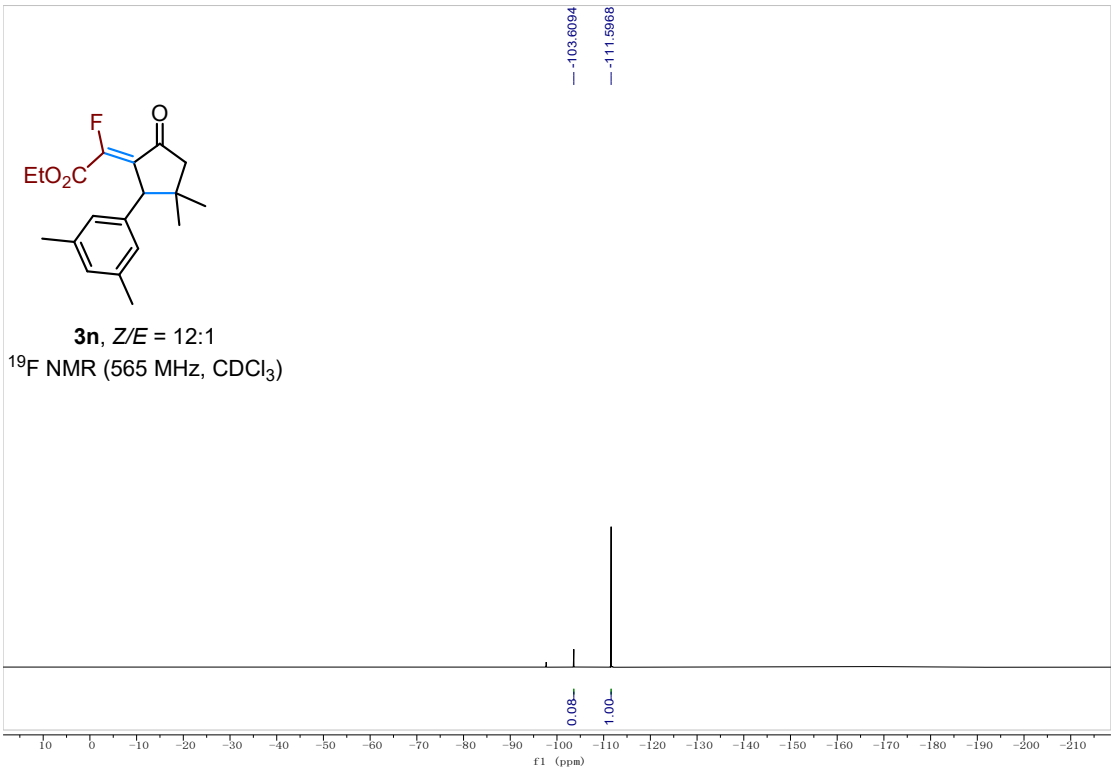
3n, *Z*/*E* = 12:1

^{1}H NMR (600 MHz, $CDCl_3$)



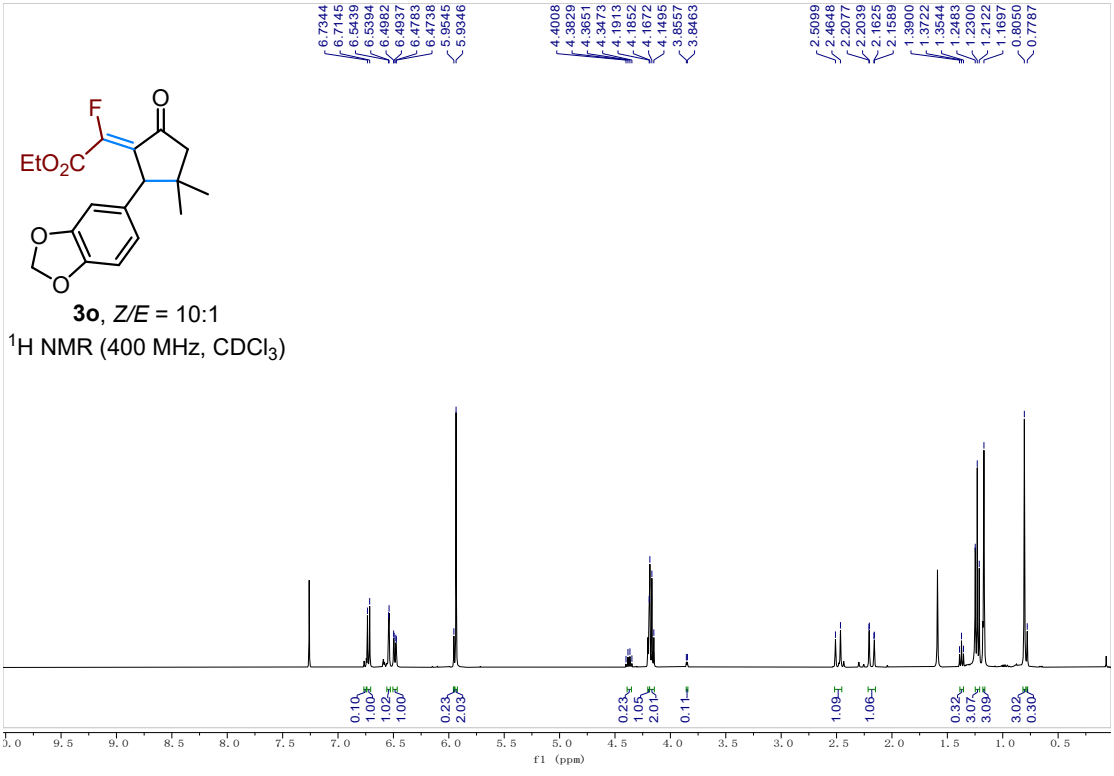
3n, *Z*/*E* = 12:1

^{13}C NMR (151 MHz, $CDCl_3$)



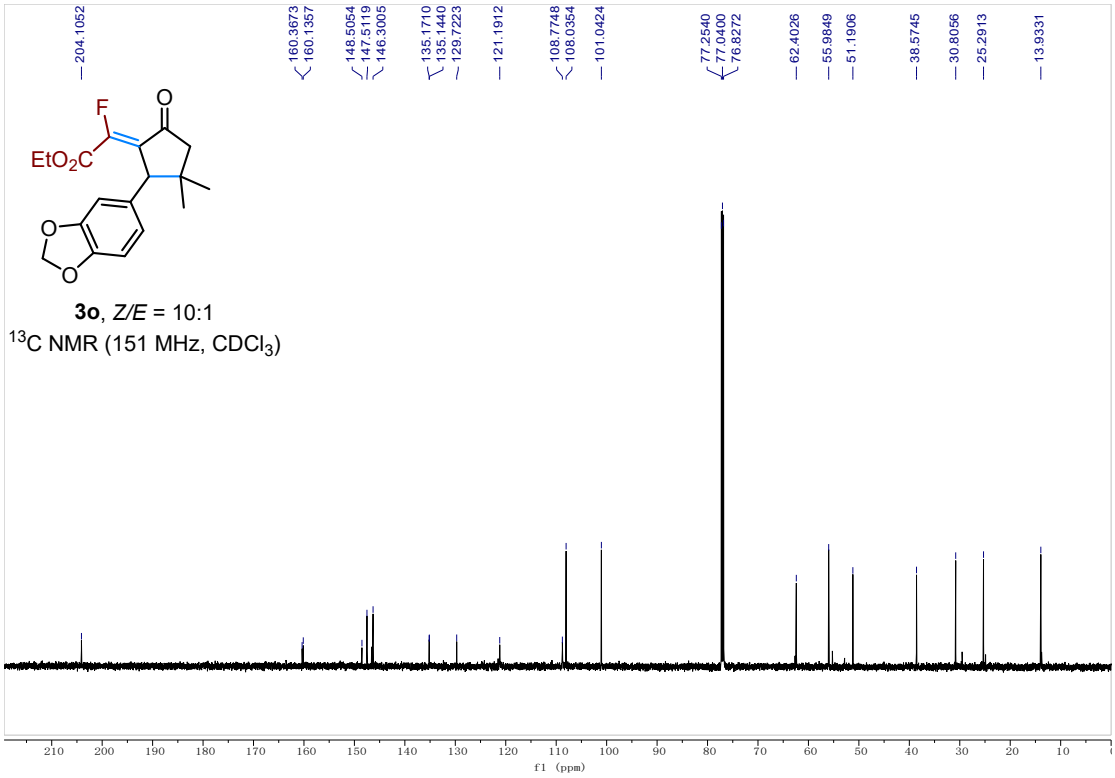
3n, *Z*/*E* = 12:1

^{19}F NMR (565 MHz, $CDCl_3$)



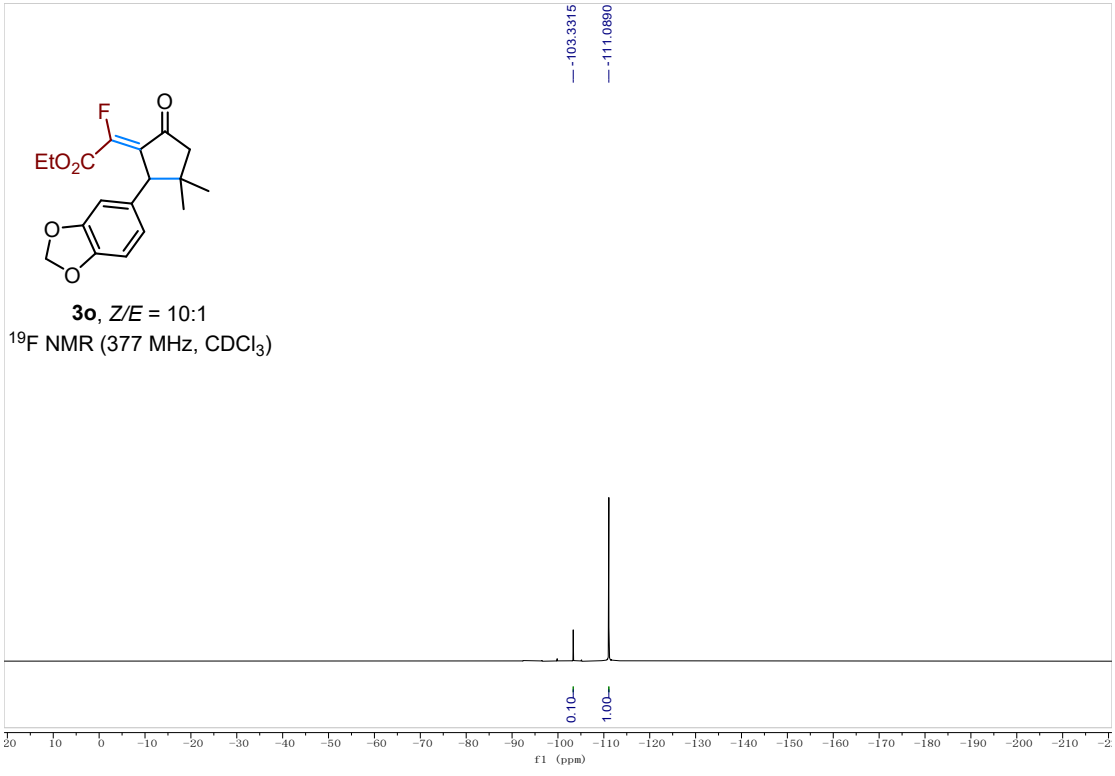
3o, *Z*/*E* = 10:1

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



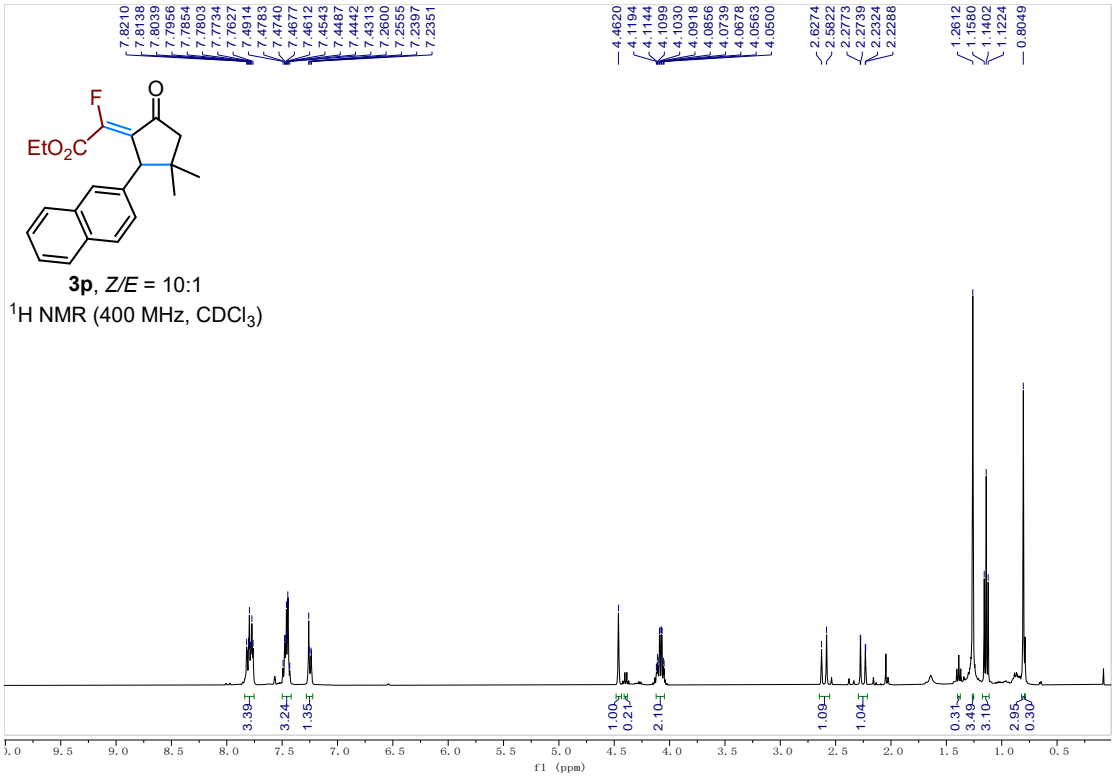
3o, *Z*/*E* = 10:1

^{13}C NMR (151 MHz, $CDCl_3$)



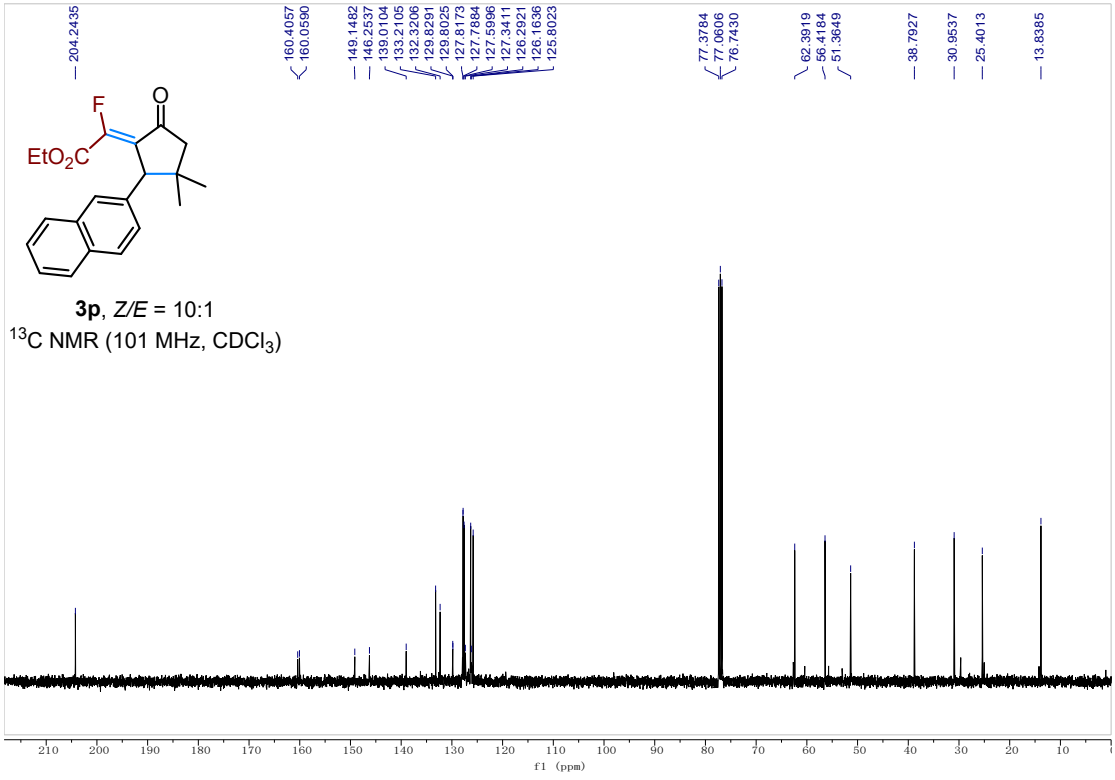
3o, *Z*/*E* = 10:1

^{19}F NMR (377 MHz, $CDCl_3$)



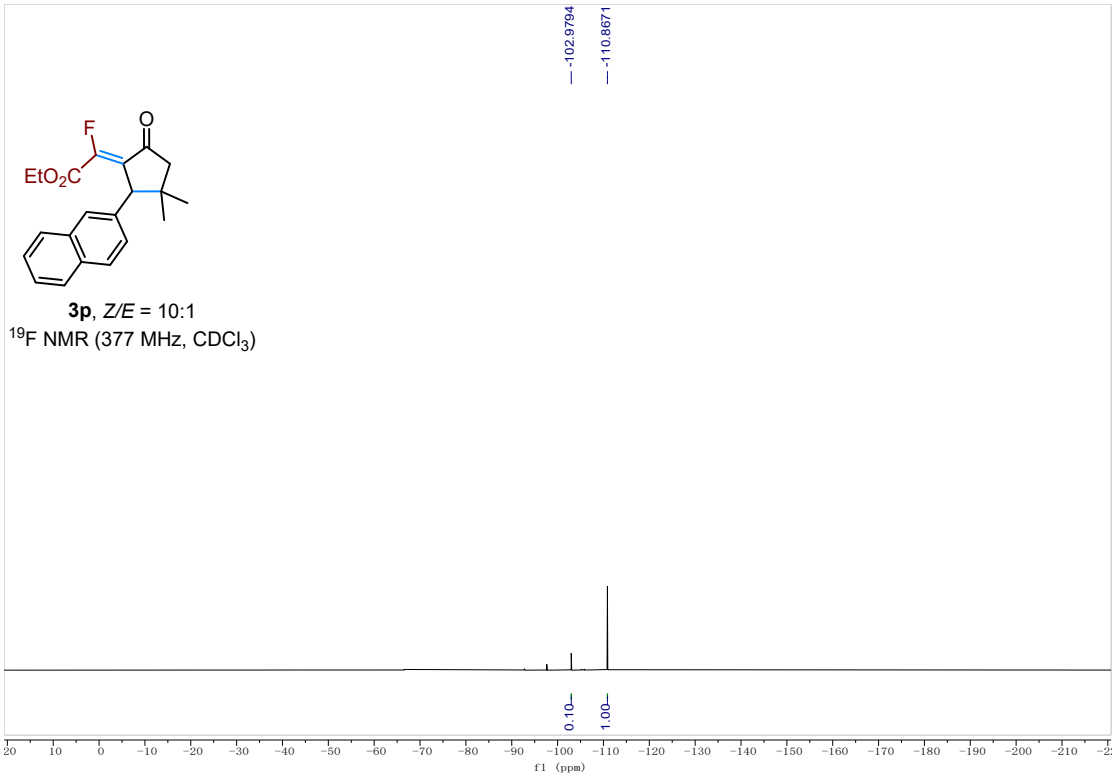
3p, *Z*/*E* = 10:1

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



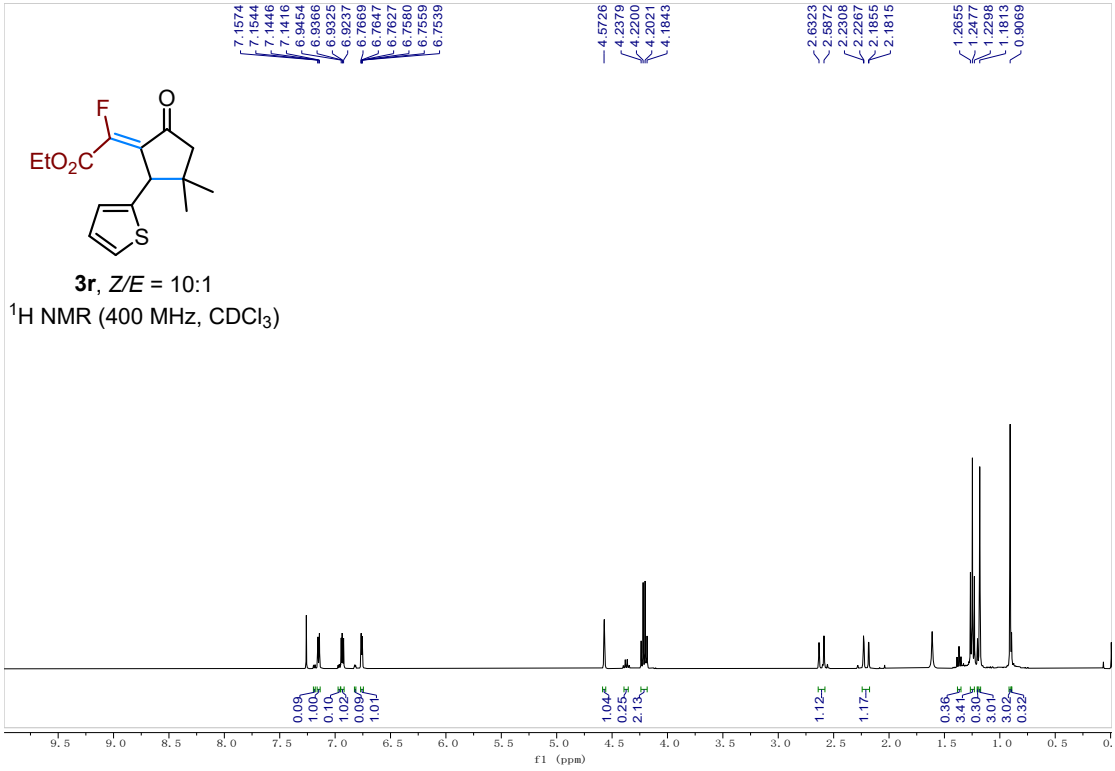
3p, *Z*/*E* = 10:1

^{13}C NMR (101 MHz, $CDCl_3$)



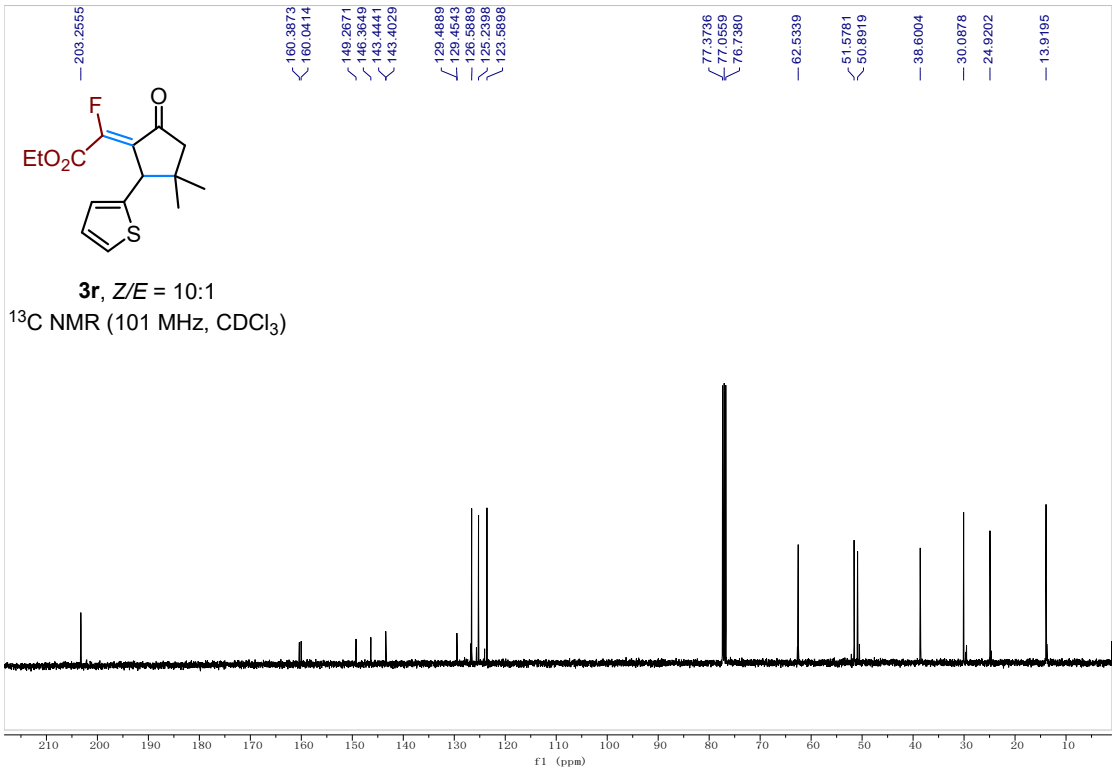
3p, *Z*/*E* = 10:1

^{19}F NMR (377 MHz, $CDCl_3$)



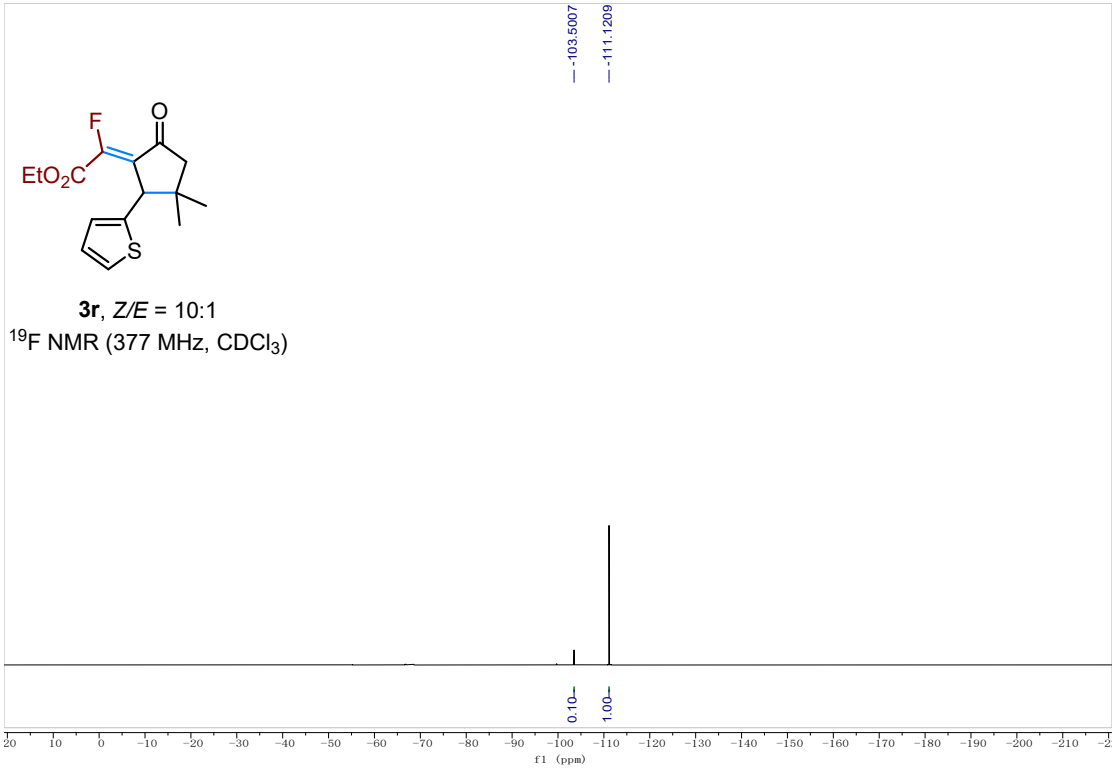
3r, *Z*/*E* = 10:1

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



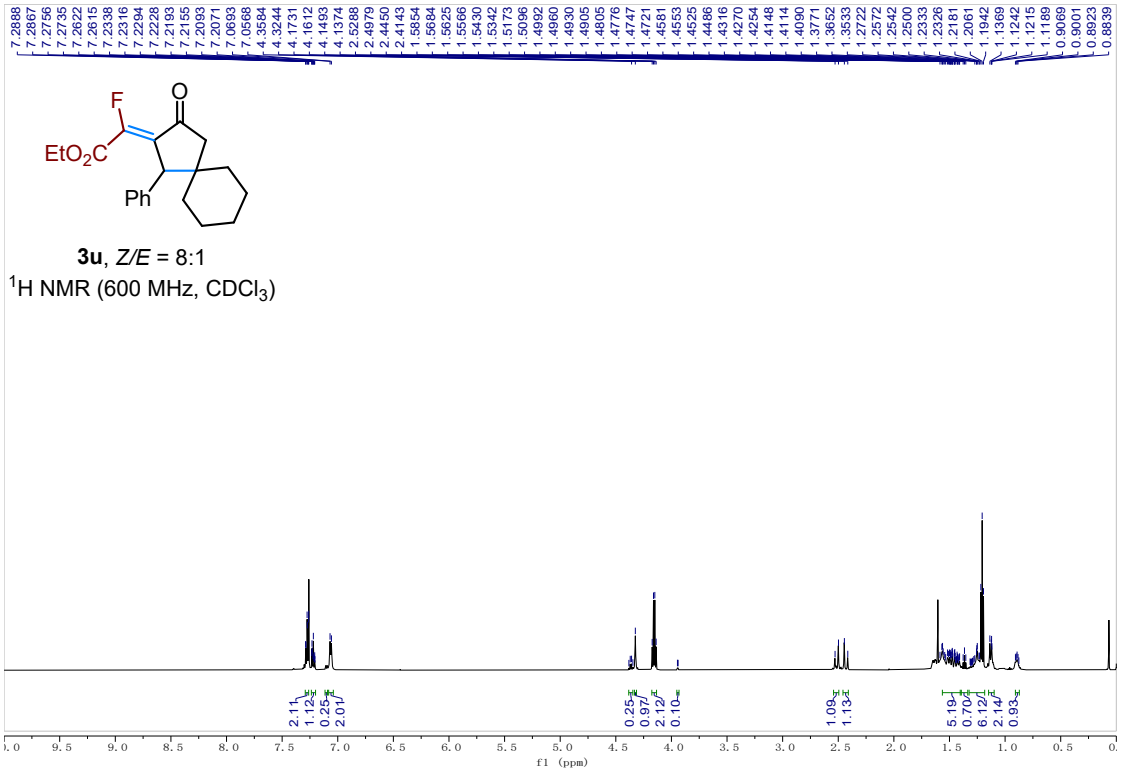
3r, *Z/E* = 10:1

^{13}C NMR (101 MHz, $CDCl_3$)



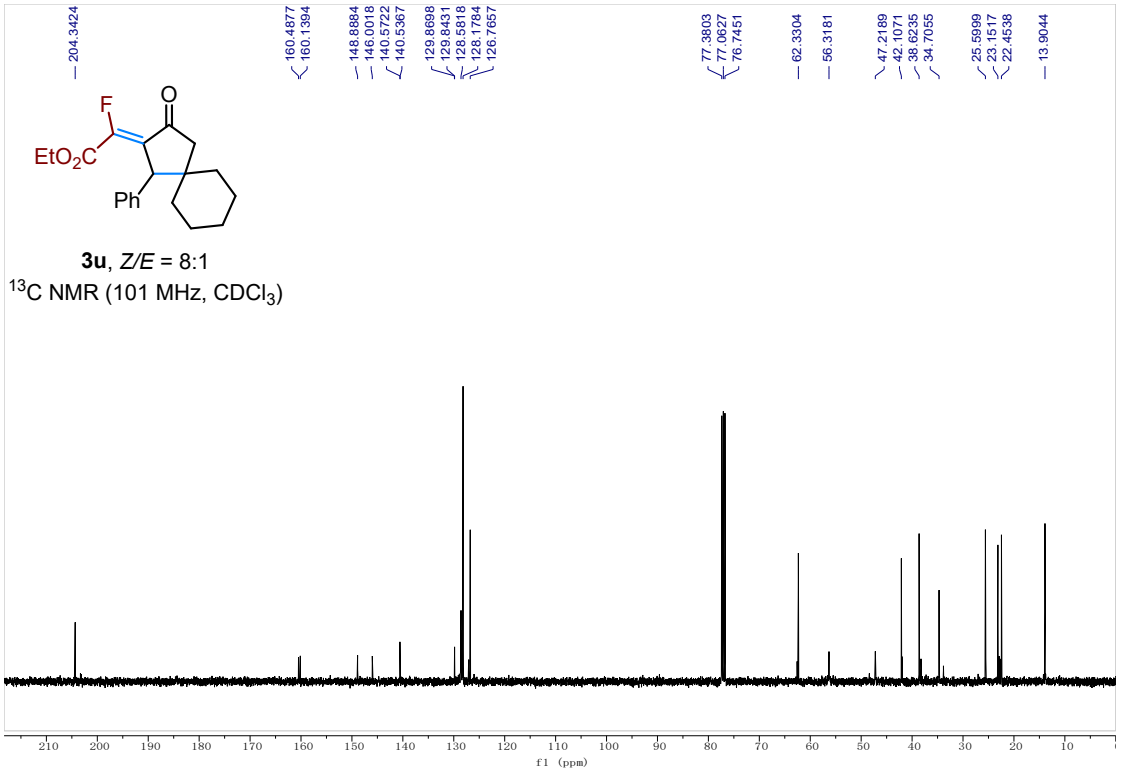
3r, *Z/E* = 10:1

^{19}F NMR (377 MHz, $CDCl_3$)



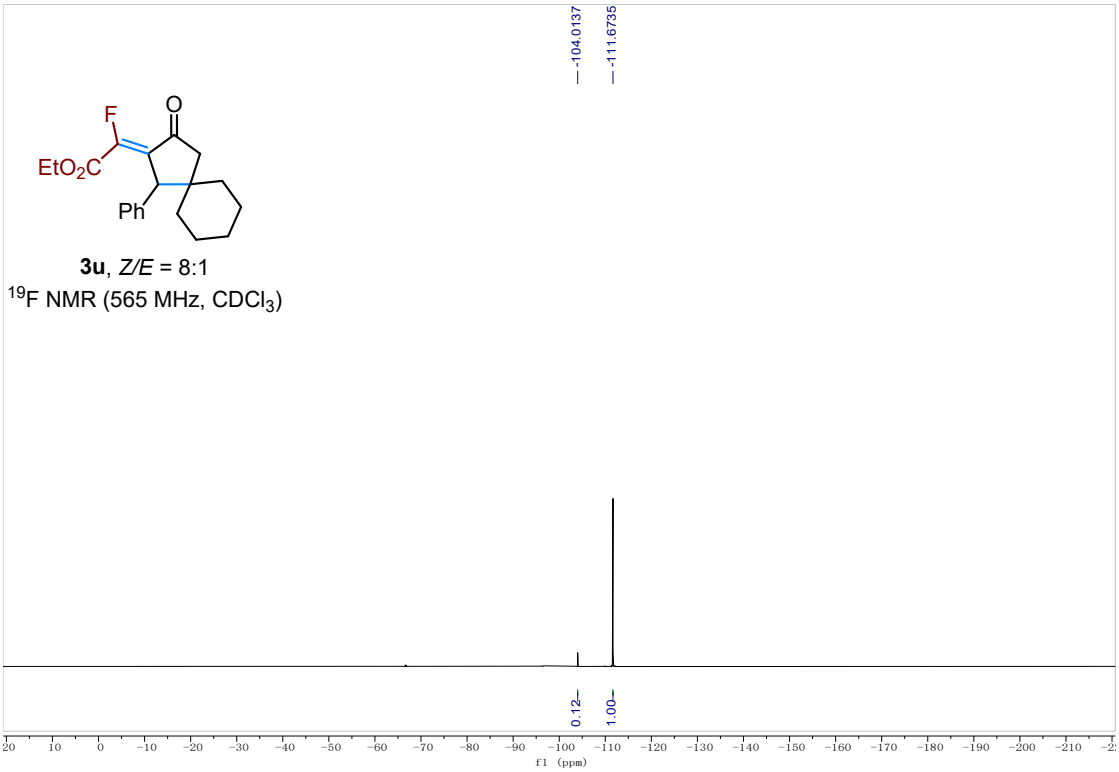
3u, *Z/E* = 8:1

^{1}H NMR (600 MHz, $CDCl_3$)



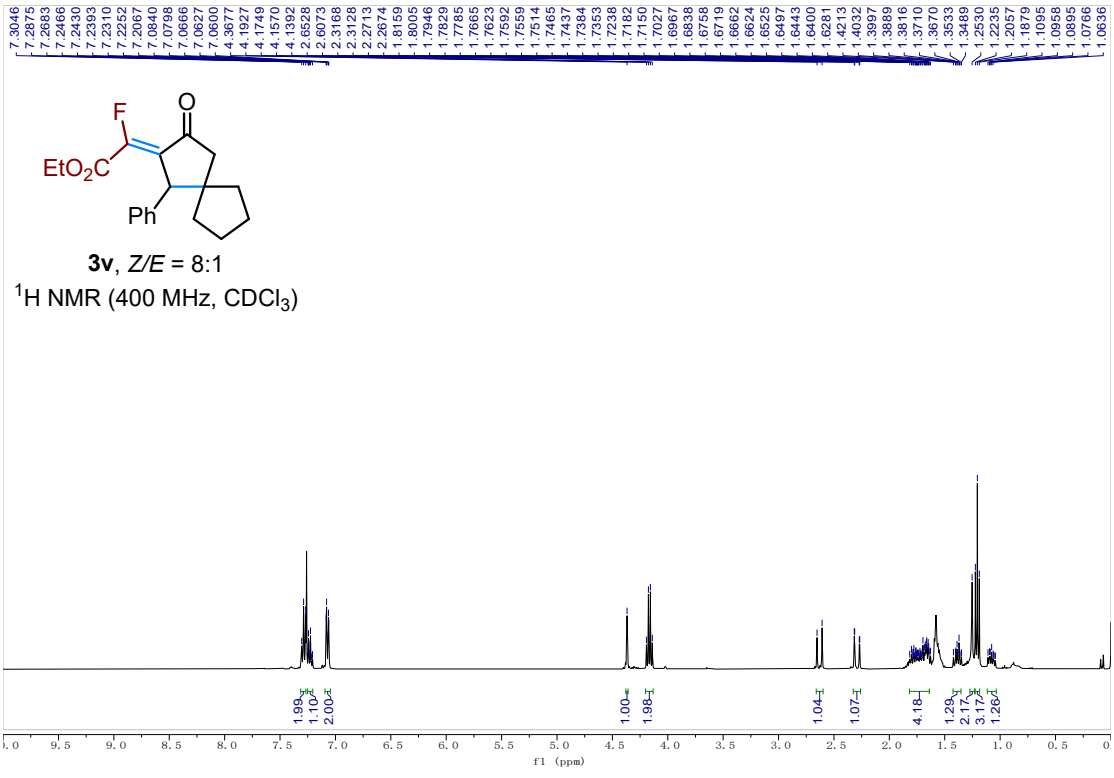
3u, *Z/E* = 8:1

^{13}C NMR (101 MHz, $CDCl_3$)



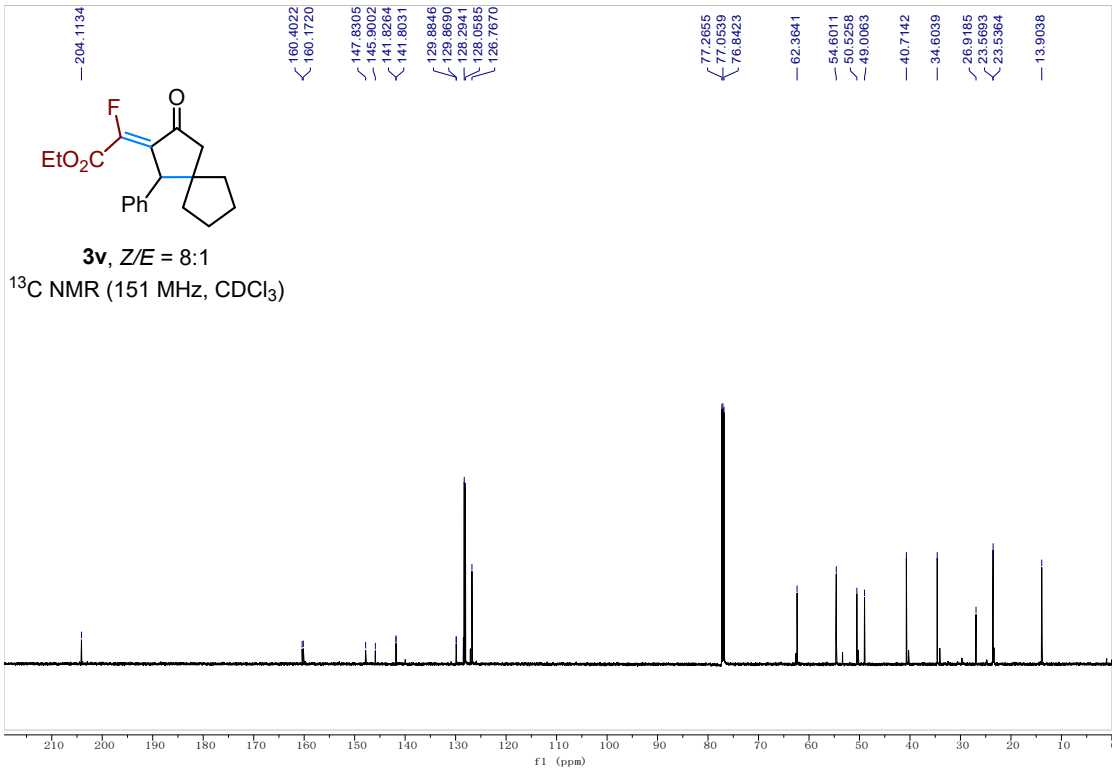
3u, *Z/E* = 8:1

^{19}F NMR (565 MHz, $CDCl_3$)



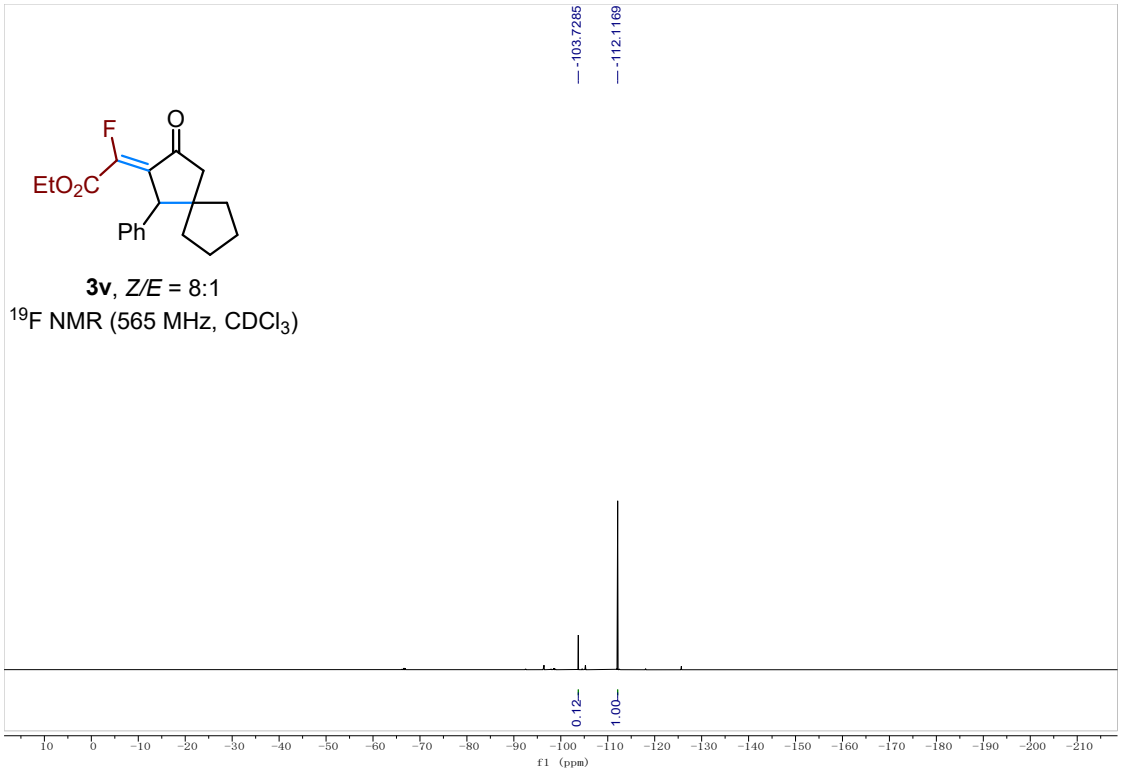
3v, *Z/E* = 8:1

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



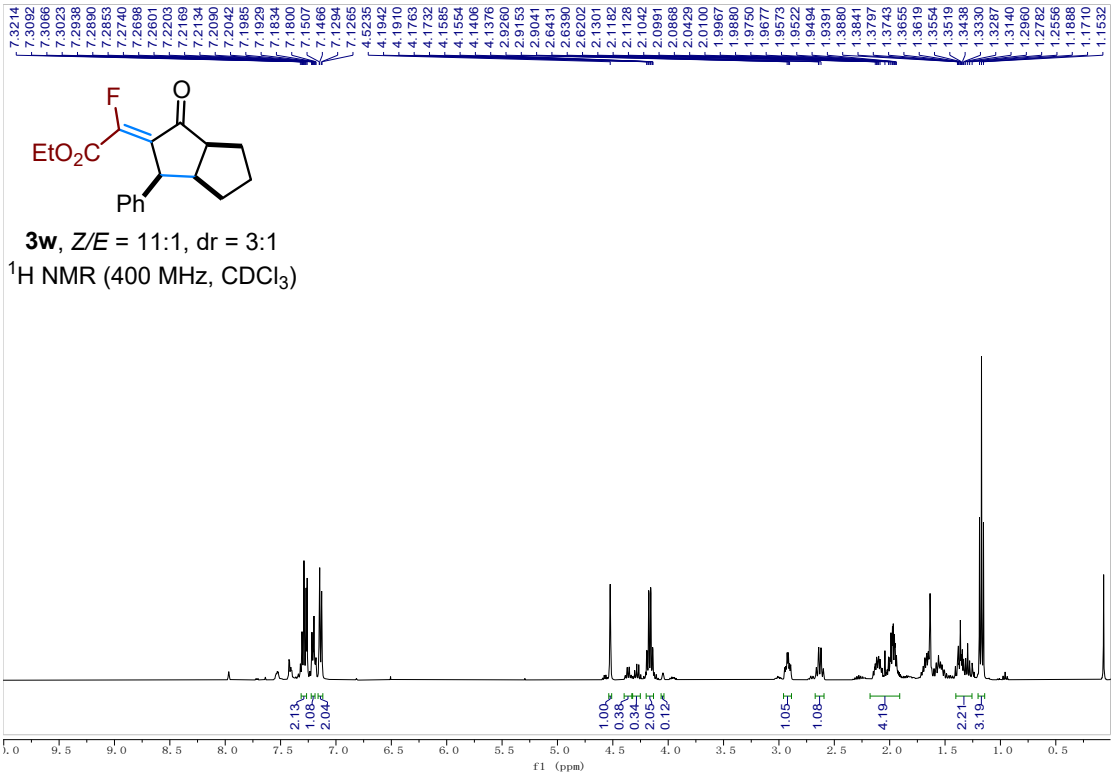
3v, *Z*/*E* = 8:1

^{13}C NMR (151 MHz, $CDCl_3$)



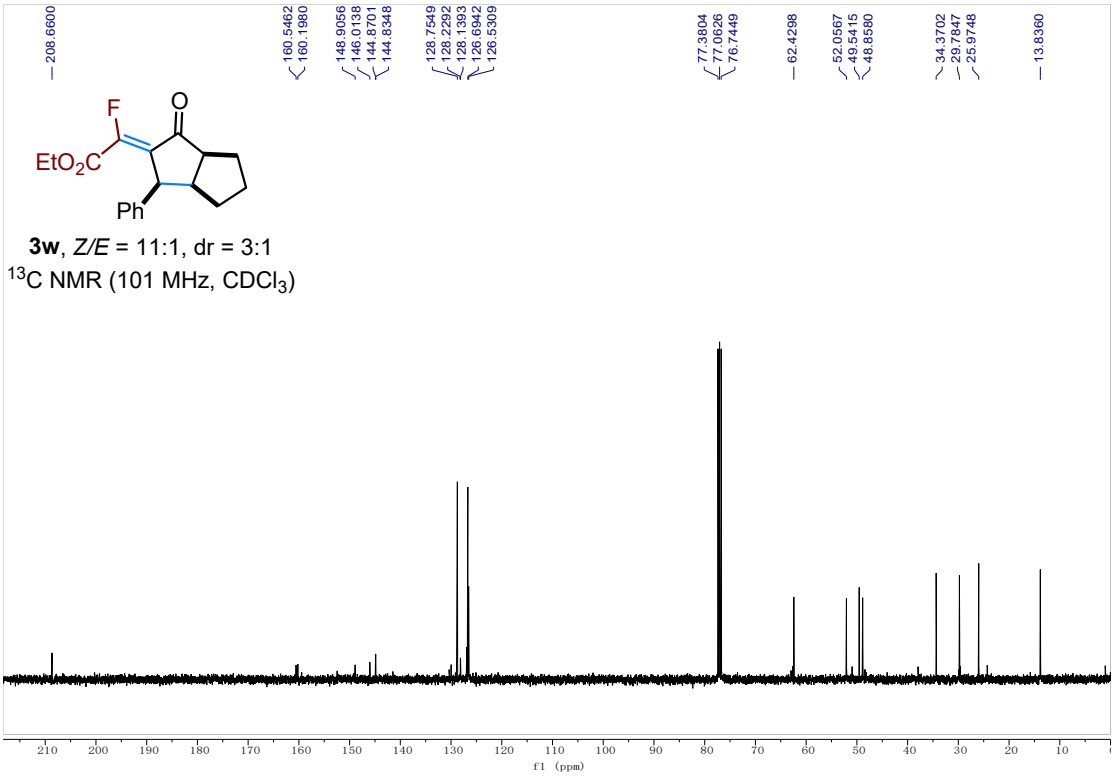
3v, *Z*/*E* = 8:1

^{19}F NMR (565 MHz, $CDCl_3$)



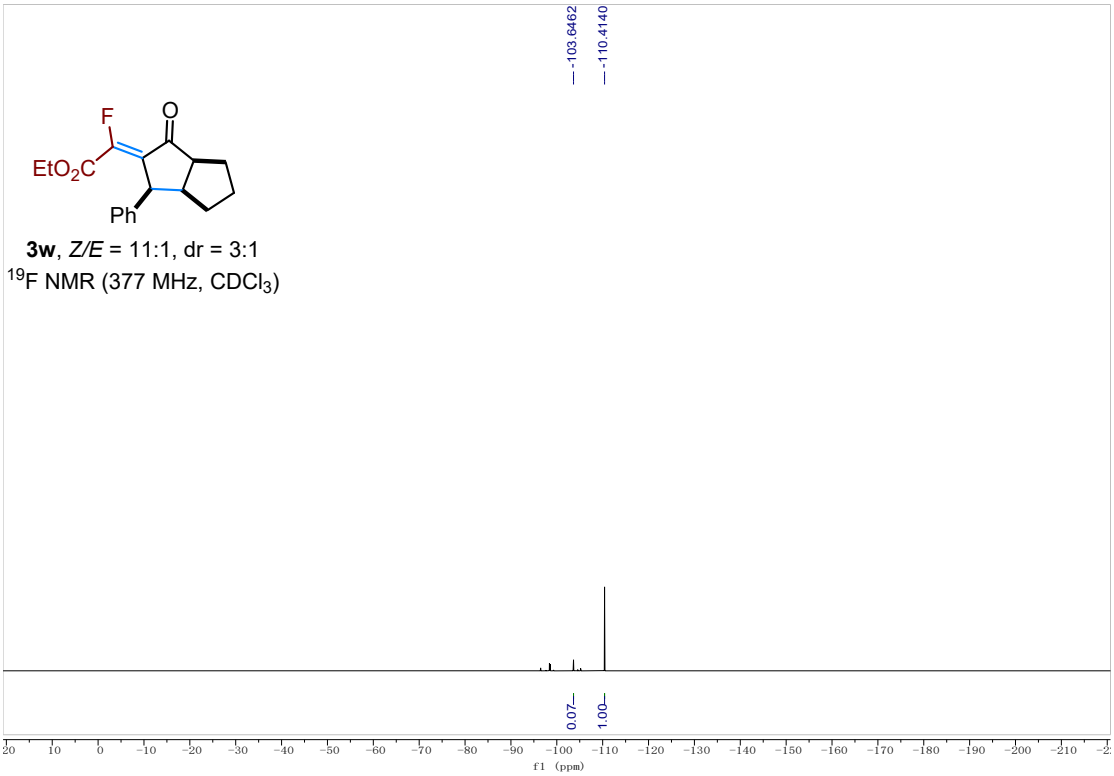
3w, *Z/E* = 11:1, dr = 3:1

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



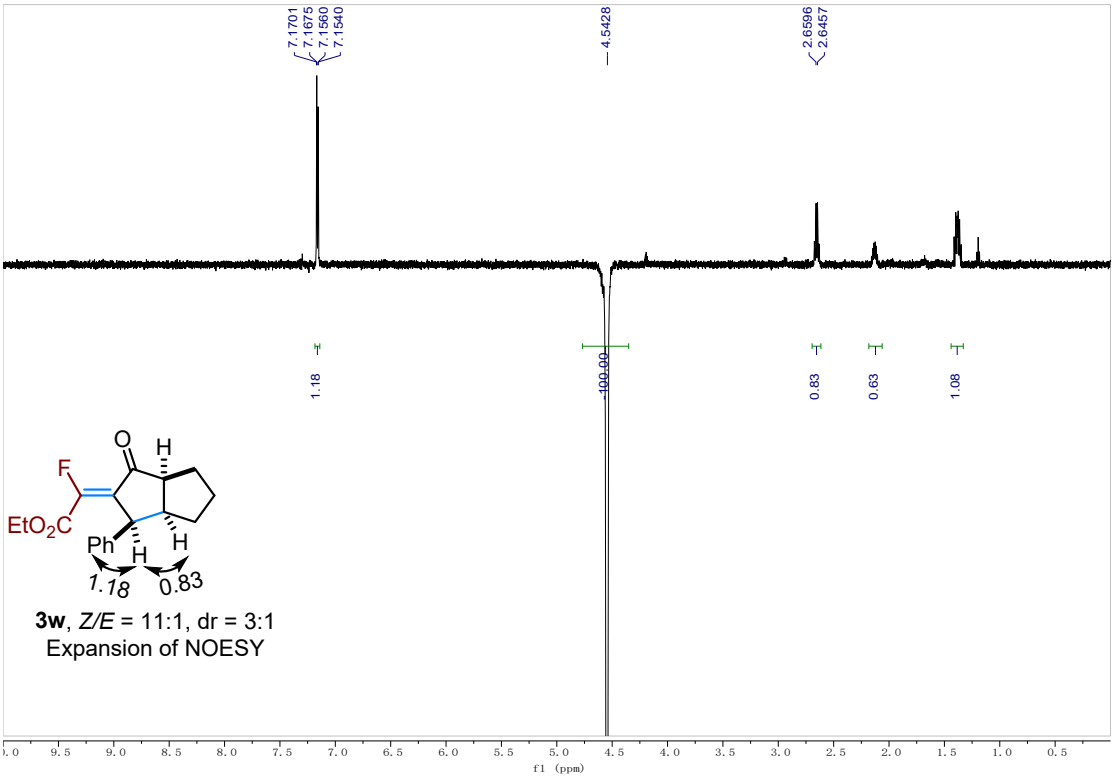
3w, *Z/E* = 11:1, dr = 3:1

^{13}C NMR (101 MHz, $CDCl_3$)



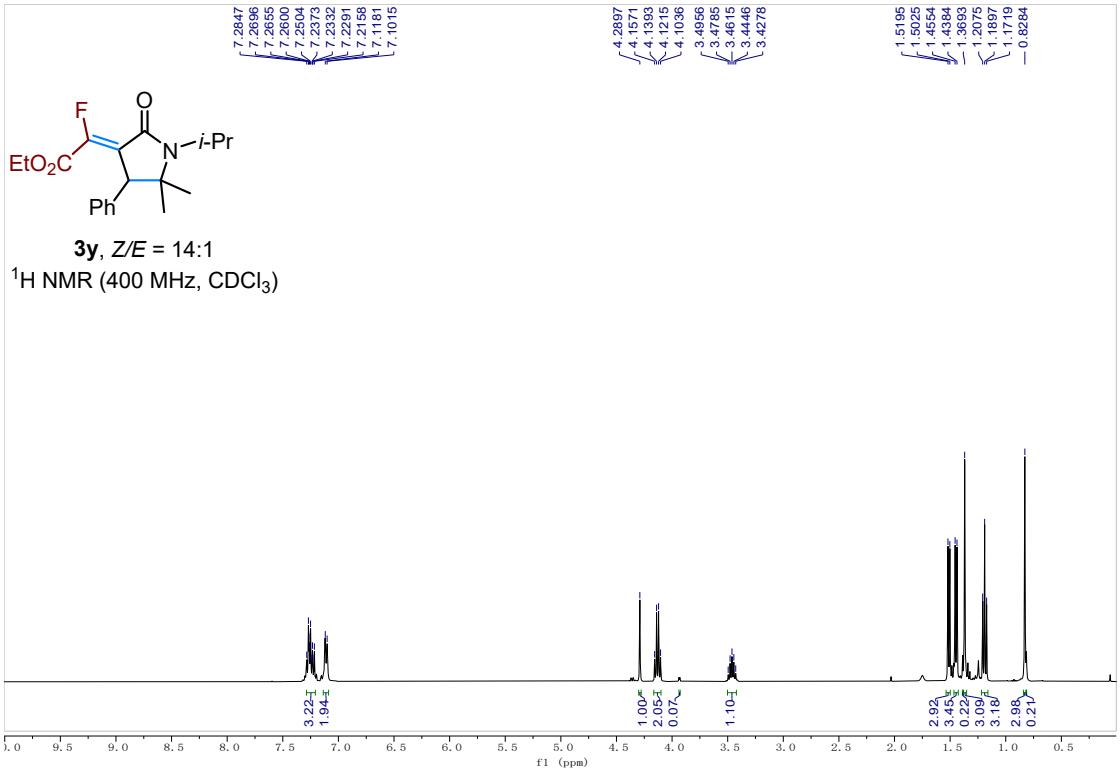
3w, *Z/E* = 11:1, dr = 3:1

^{19}F NMR (377 MHz, $CDCl_3$)



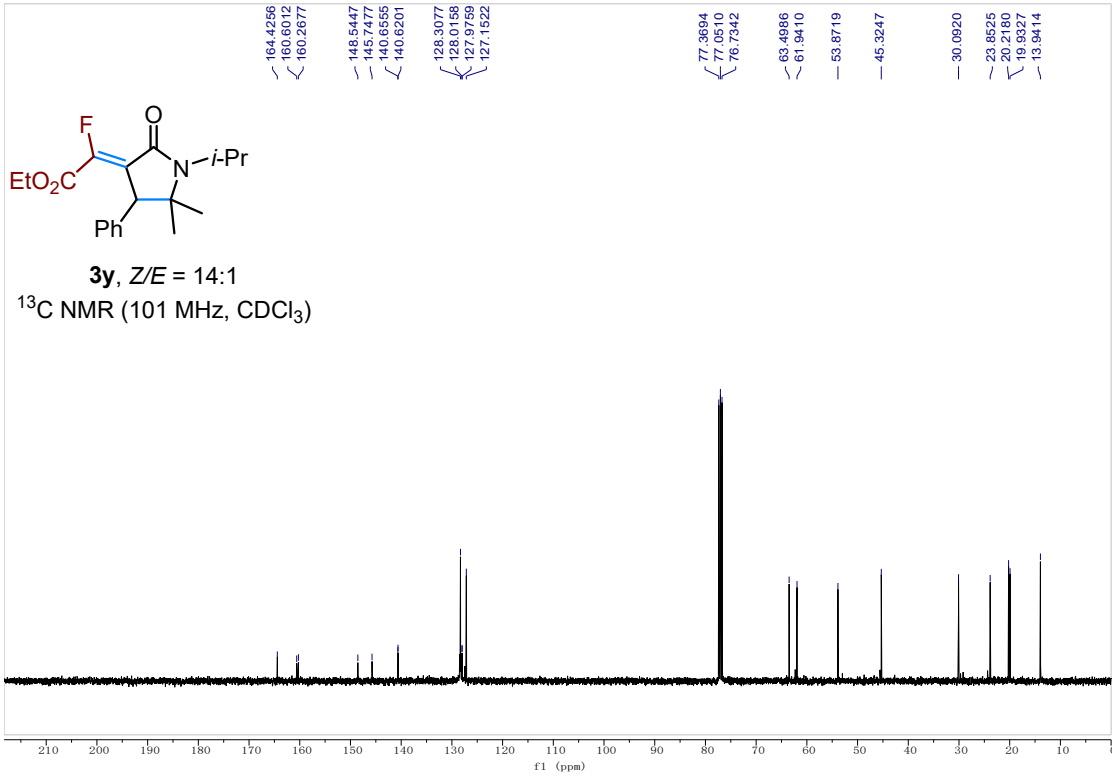
3w, *Z/E* = 11:1, dr = 3:1

Expansion of NOESY



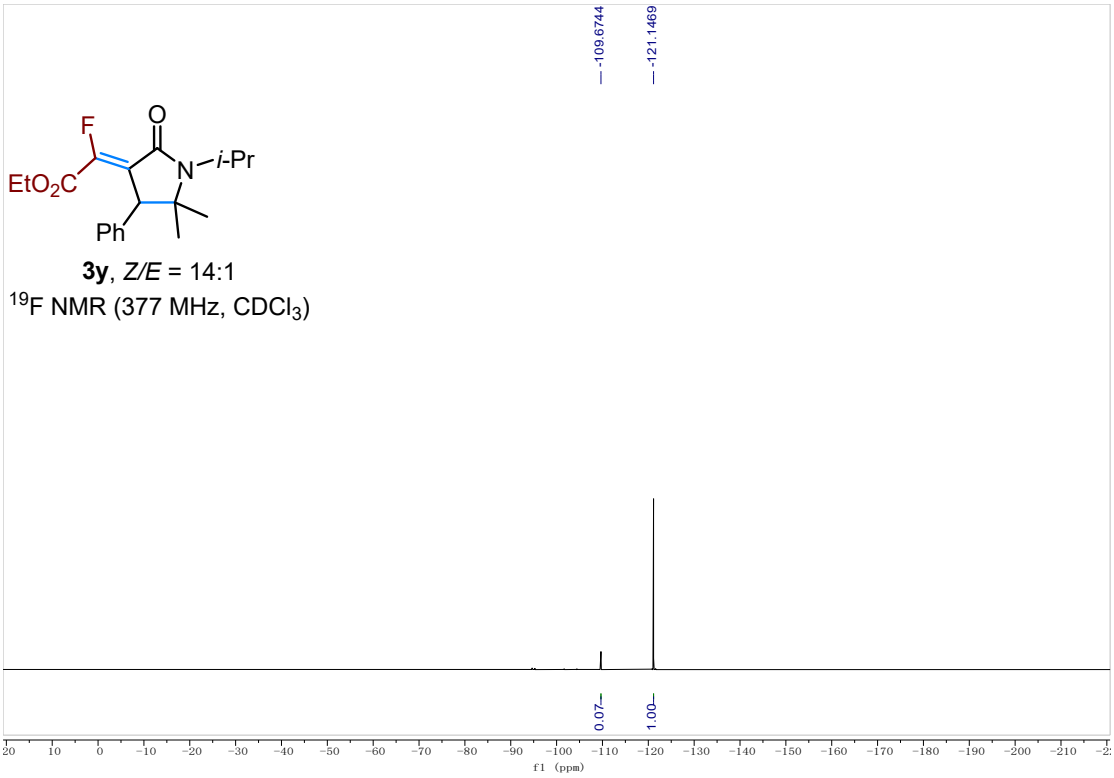
3y, *Z*/*E* = 14:1

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



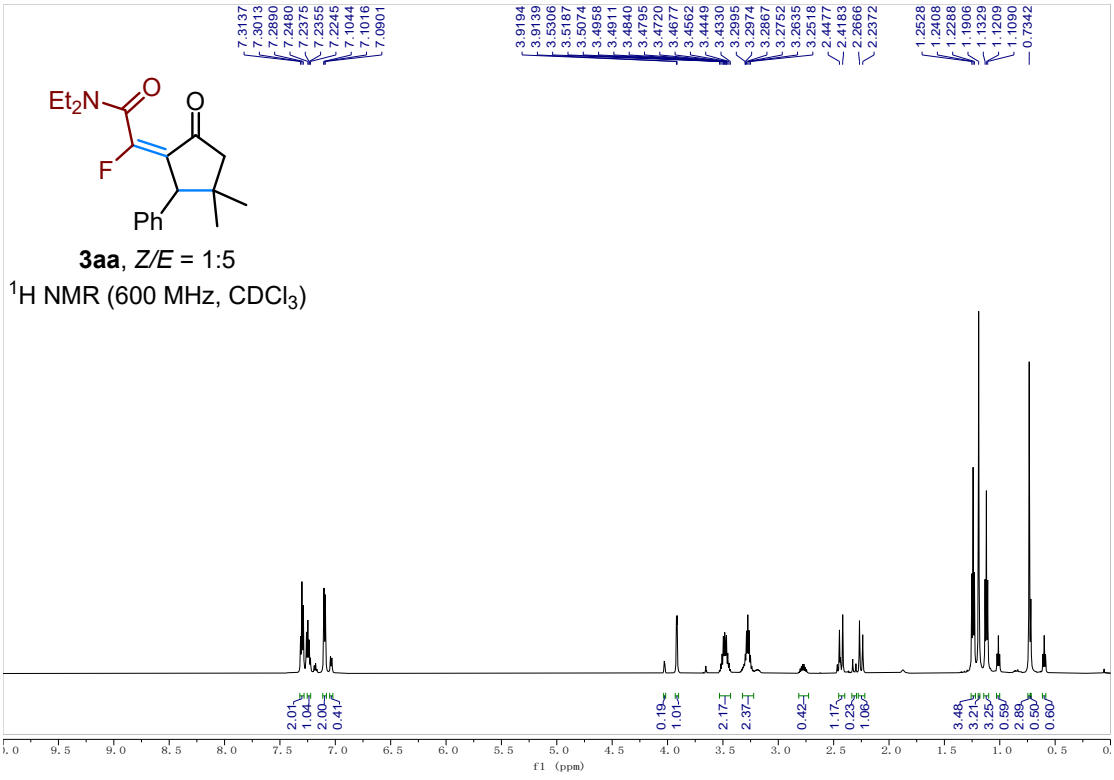
3y, *Z*/*E* = 14:1

^{13}C NMR (101 MHz, $CDCl_3$)



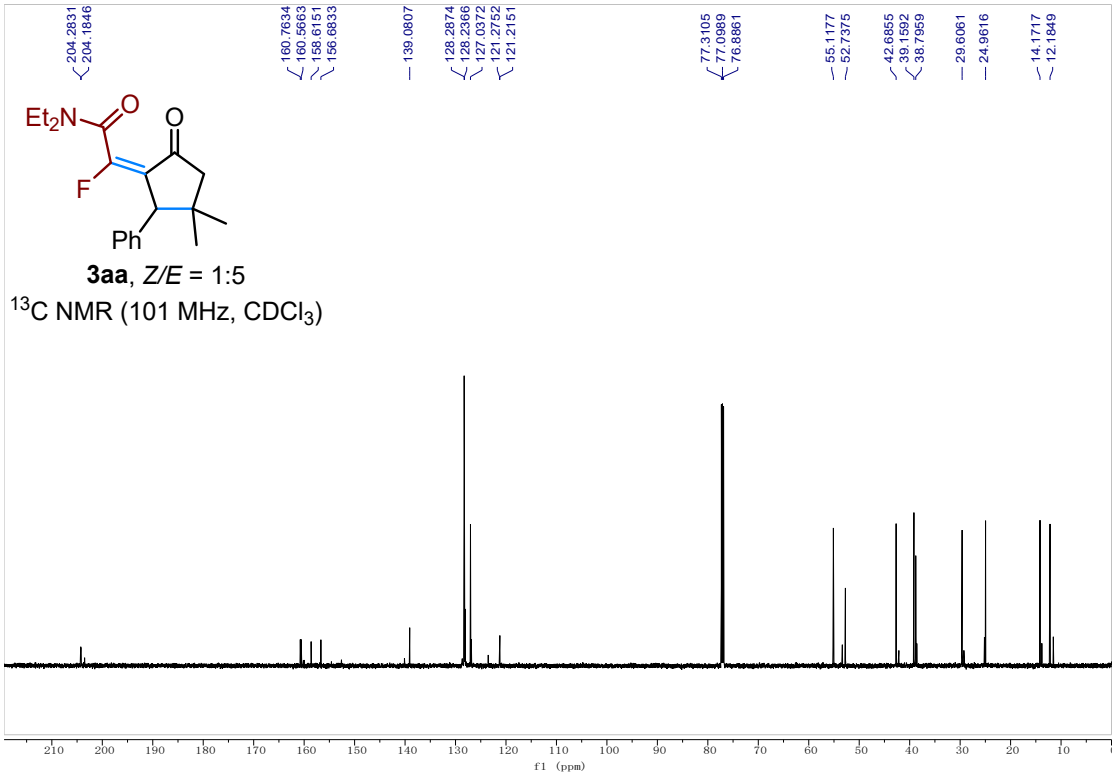
3y, *Z*/*E* = 14:1

^{19}F NMR (377 MHz, $CDCl_3$)



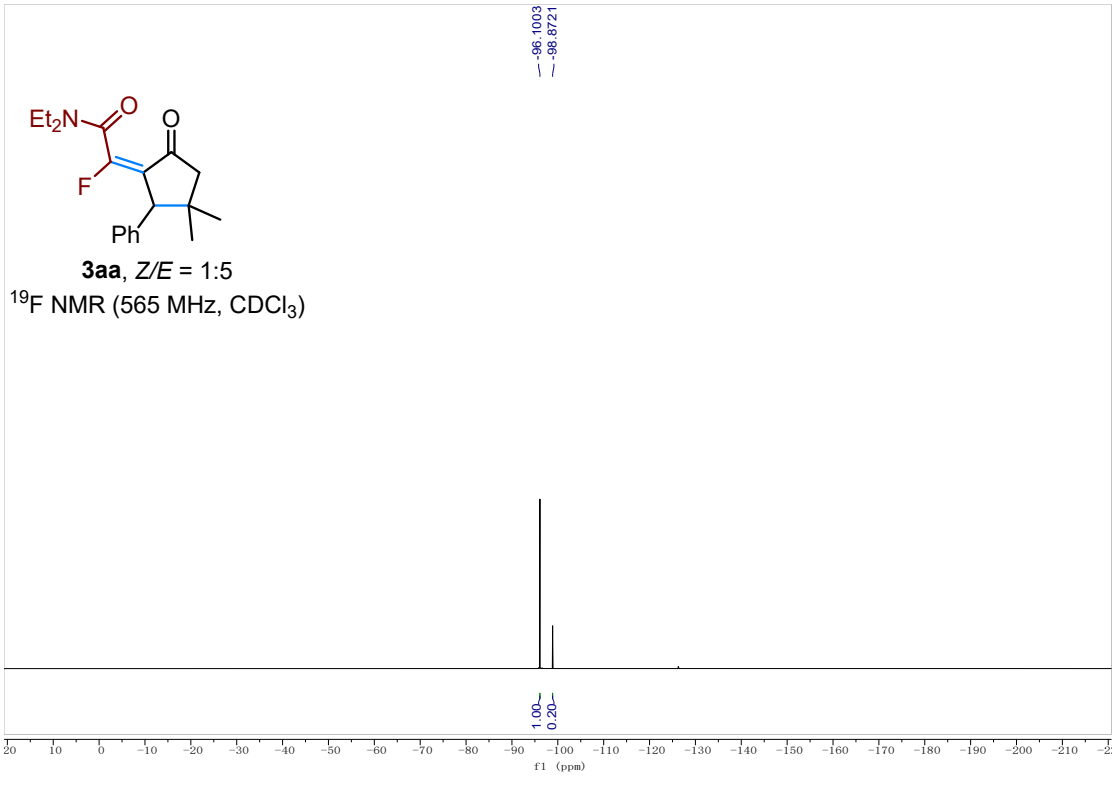
3aa, *Z*/*E* = 1:5

^{1}H NMR (600 MHz, $CDCl_3$)



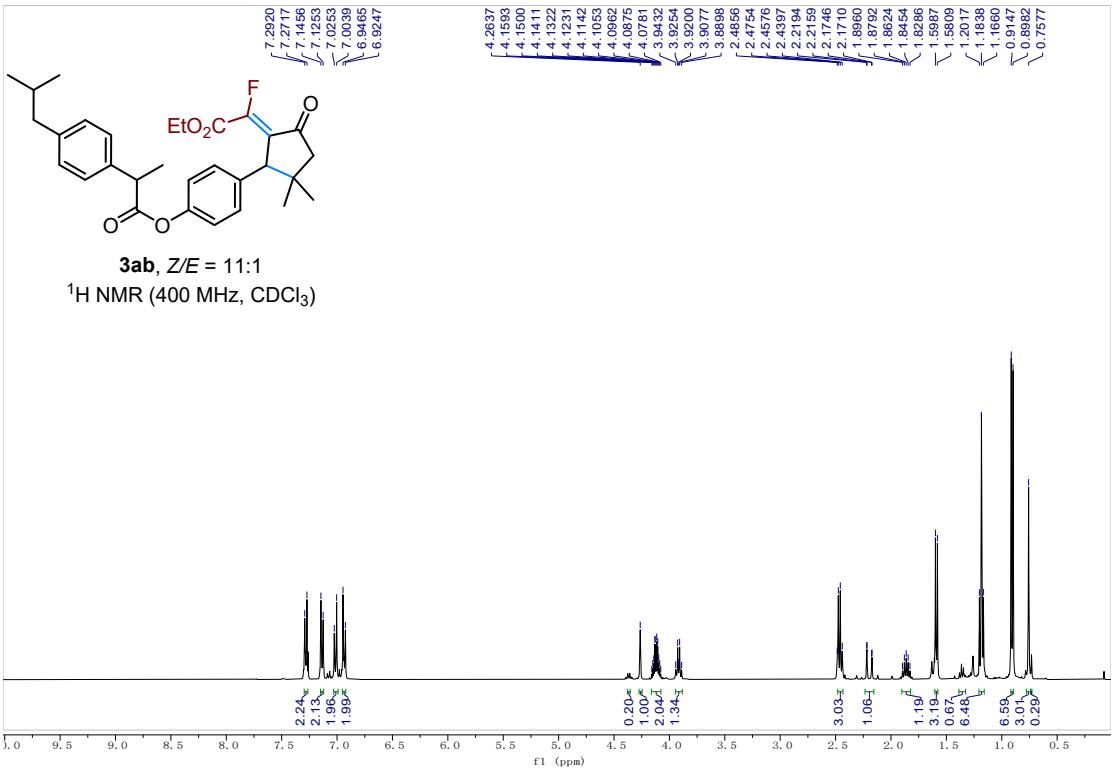
3aa, *Z*/*E* = 1:5

^{13}C NMR (101 MHz, $CDCl_3$)



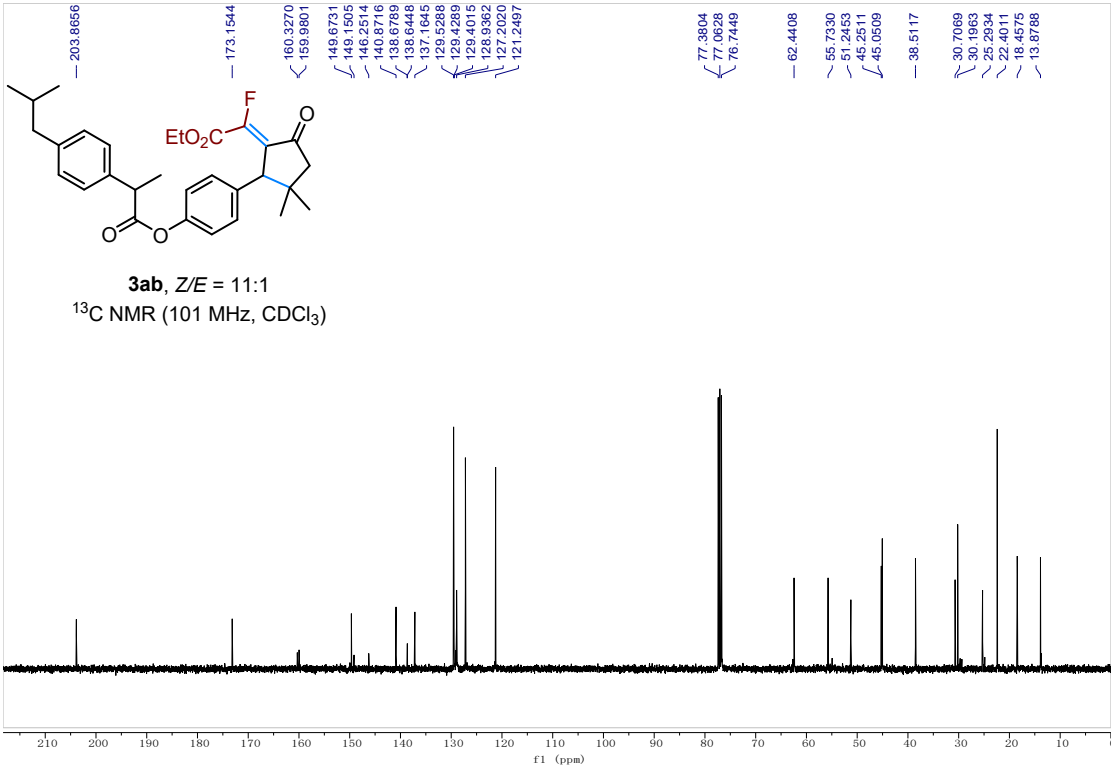
3aa, *Z*/*E* = 1:5

^{19}F NMR (565 MHz, $CDCl_3$)



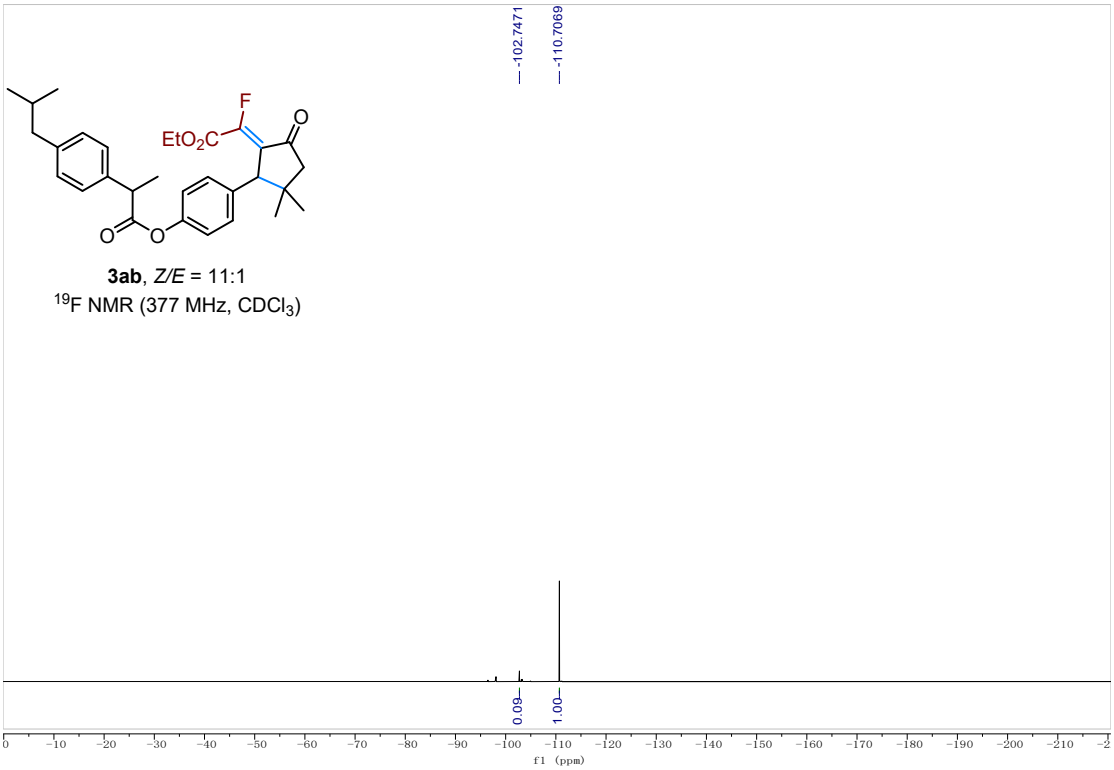
3ab, *Z/E* = 11:1

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



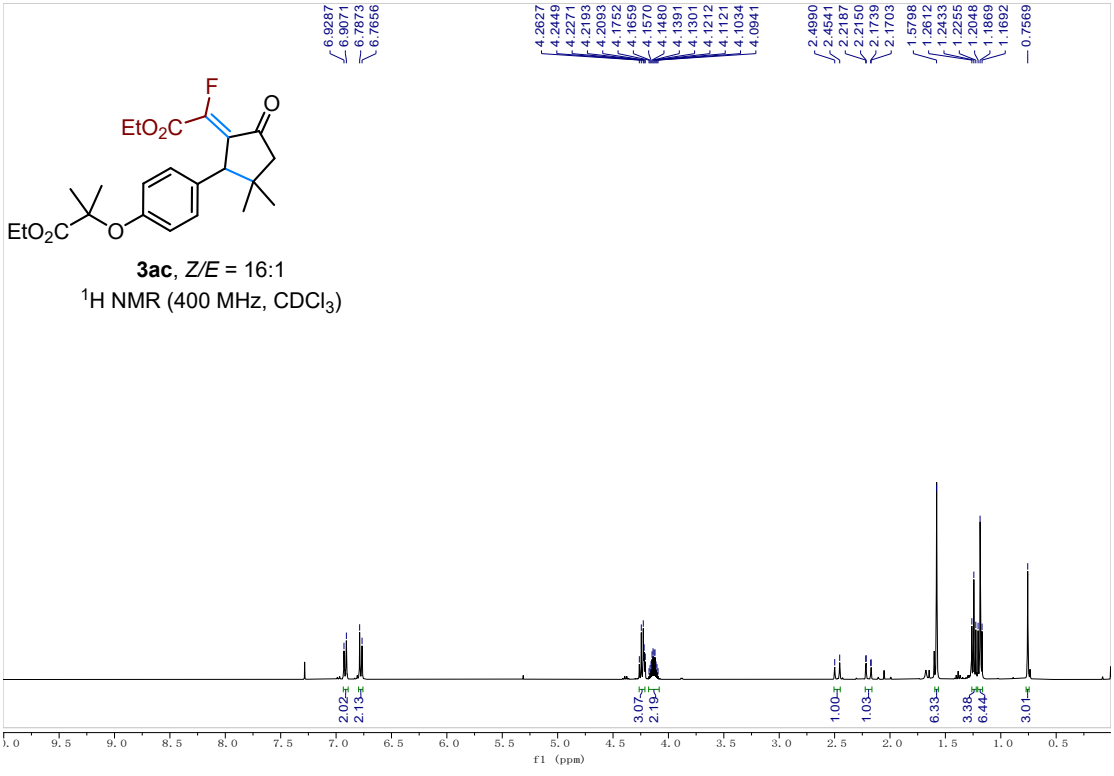
3ab, *Z/E* = 11:1

^{13}C NMR (101 MHz, $CDCl_3$)



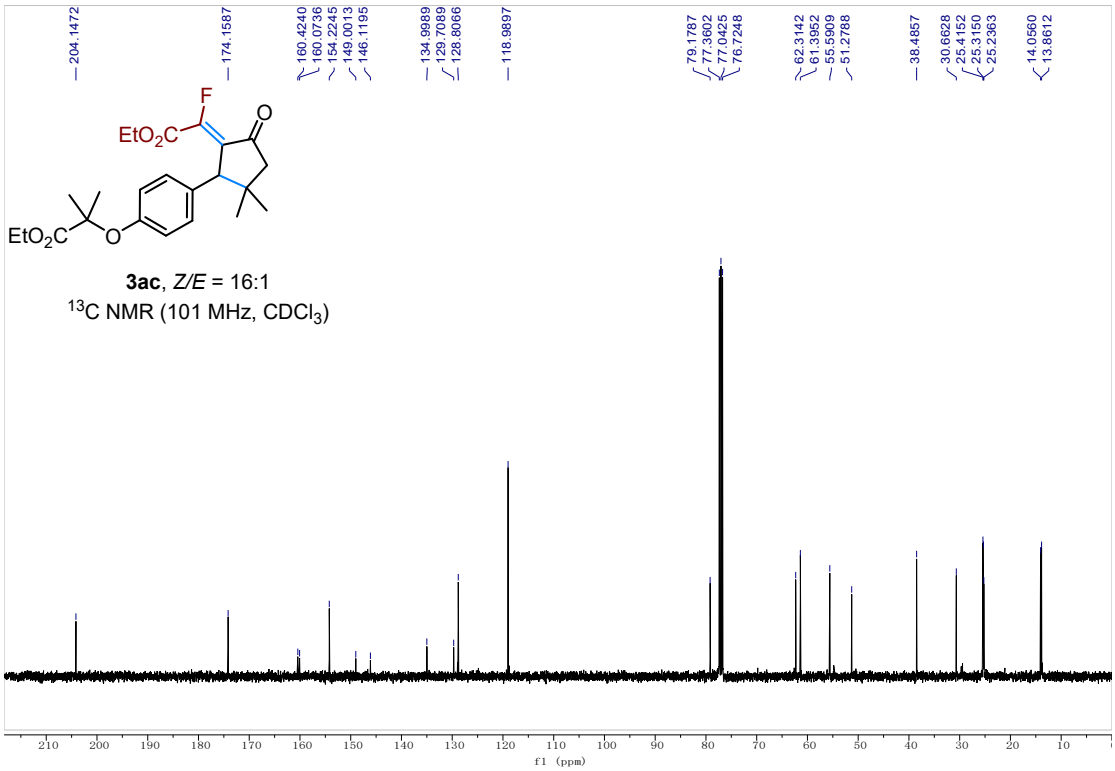
3ab, *Z*/*E* = 11:1

^{19}F NMR (377 MHz, $CDCl_3$)



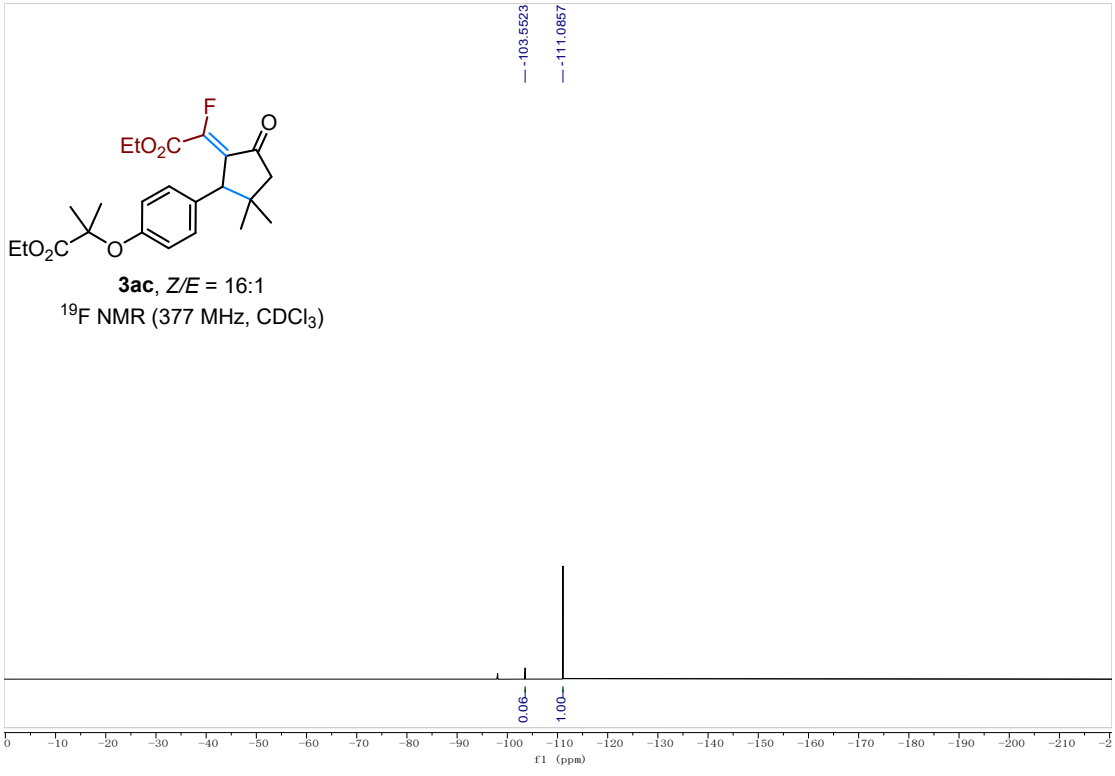
3ac, *Z*/*E* = 16:1

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



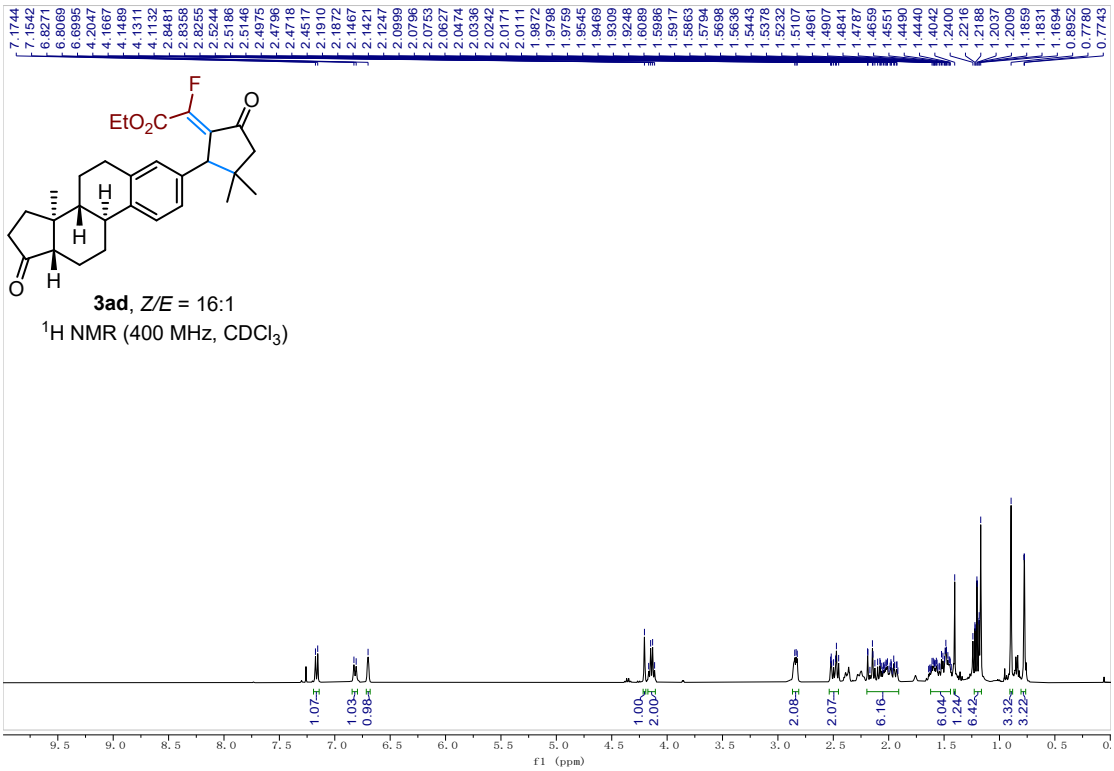
3ac, *Z/E* = 16:1

^{13}C NMR (101 MHz, $CDCl_3$)



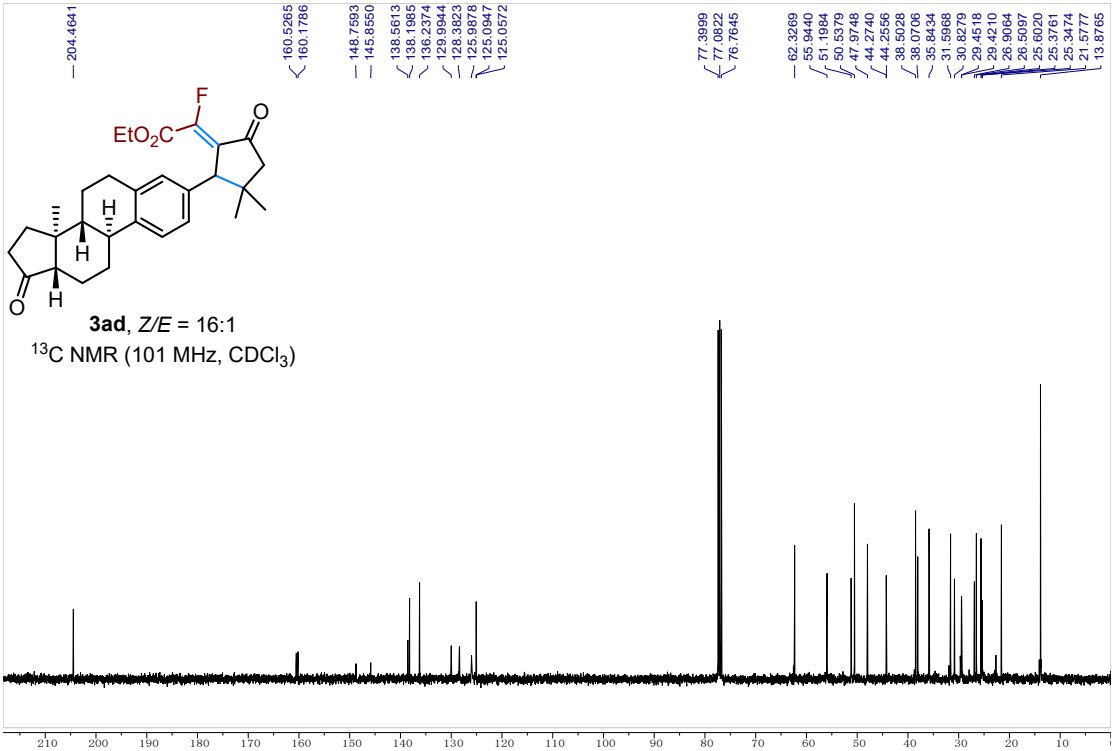
3ac, *Z/E* = 16:1

^{19}F NMR (377 MHz, $CDCl_3$)



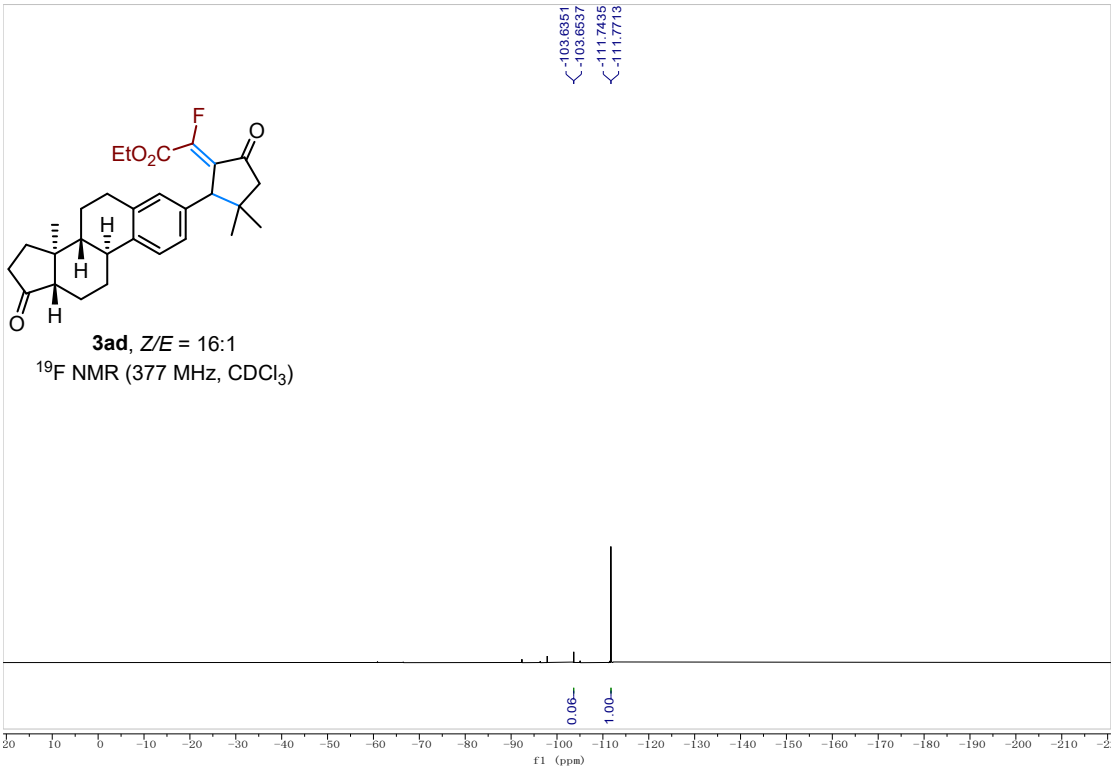
3ad, *Z*/*E* = 16:1

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



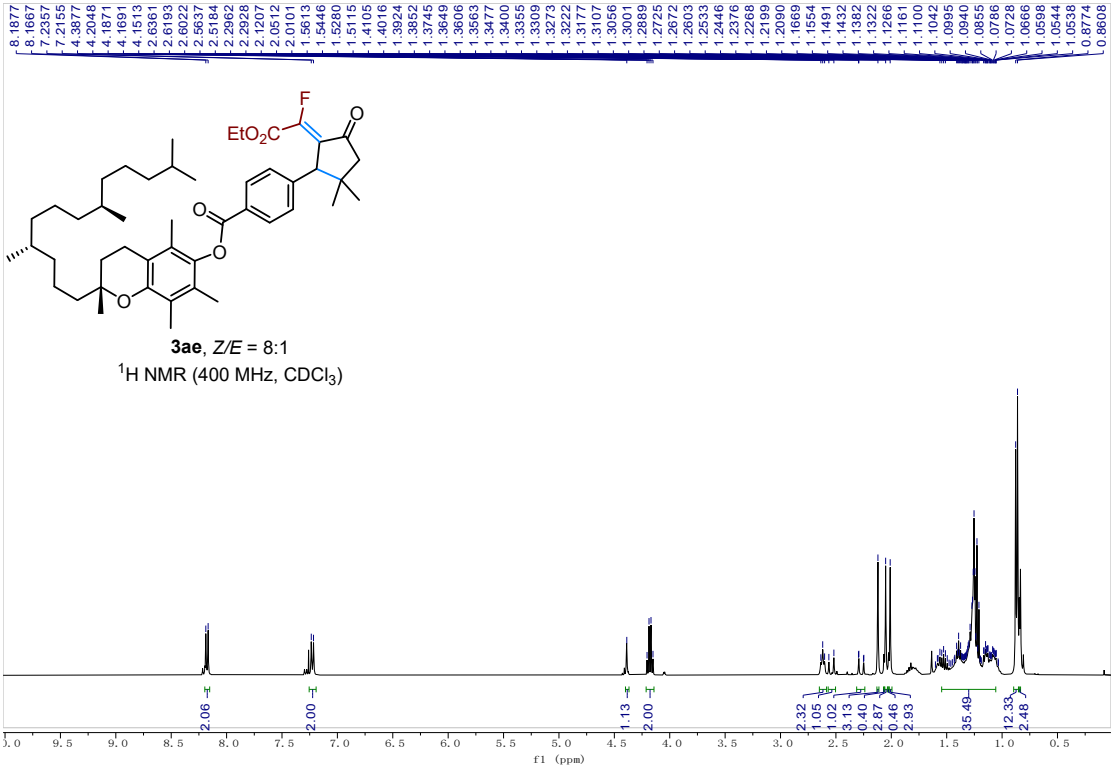
3ad, *Z*/*E* = 16:1

^{13}C NMR (101 MHz, $CDCl_3$)



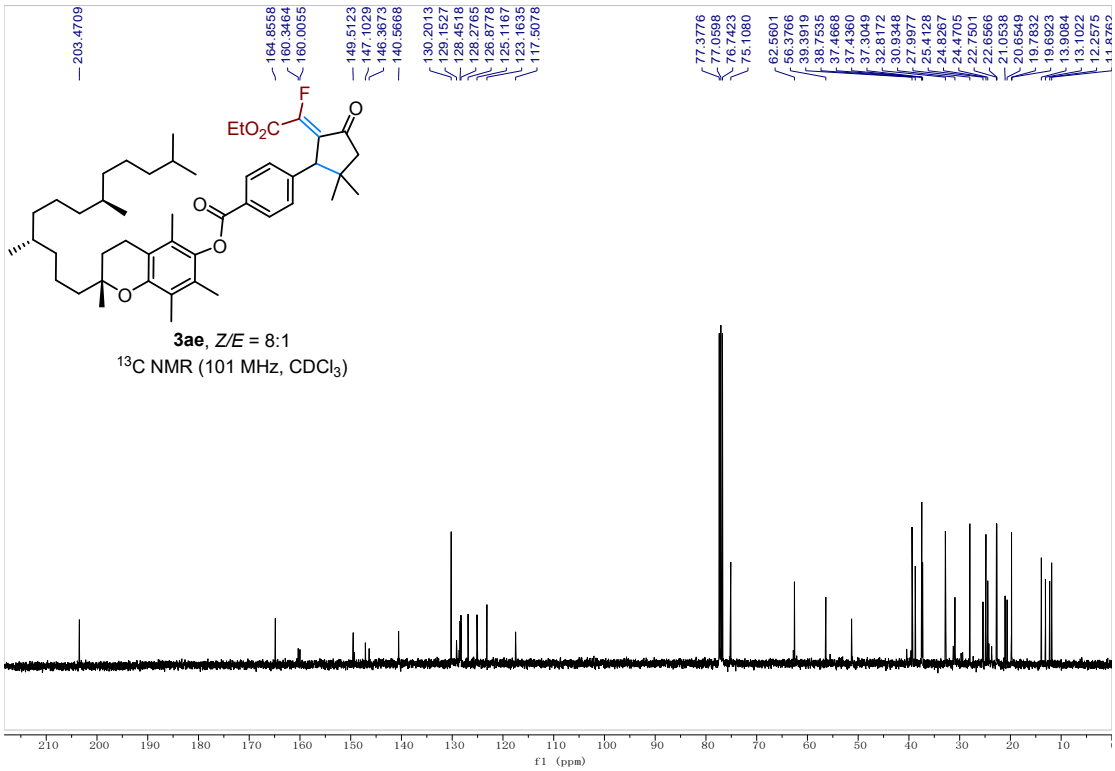
3ad, *Z*/*E* = 16:1

^{19}F NMR (377 MHz, $CDCl_3$)



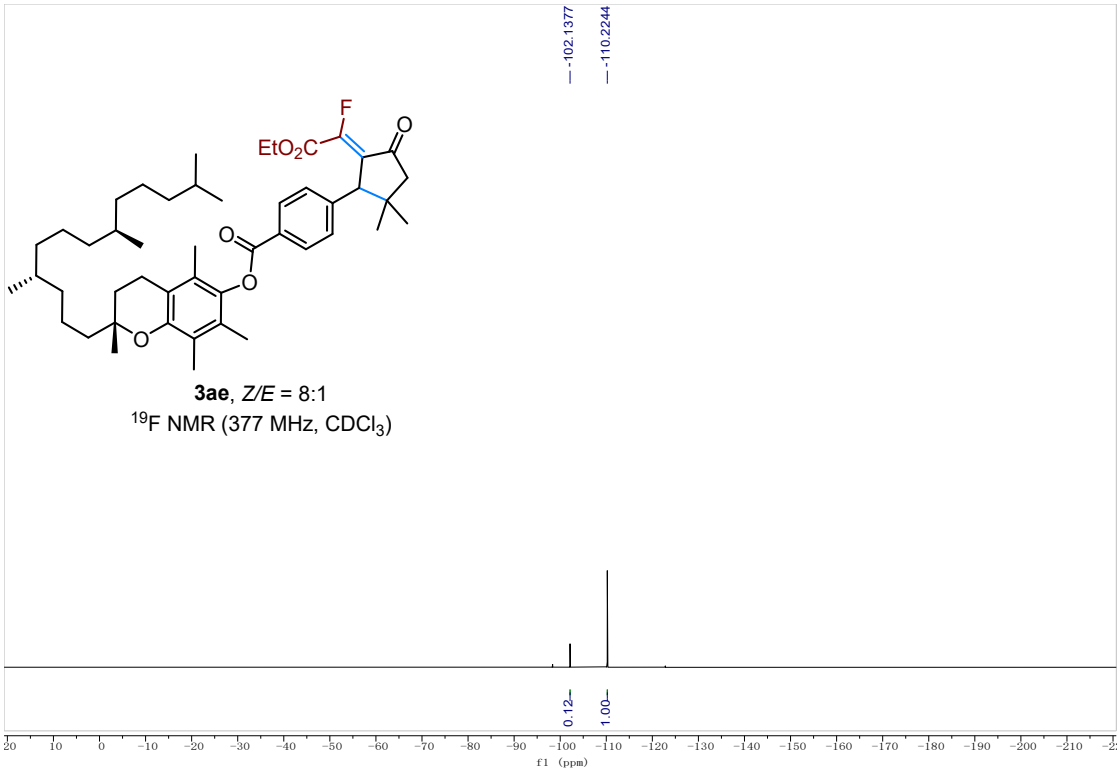
3ae, *Z*/*E* = 8:1

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



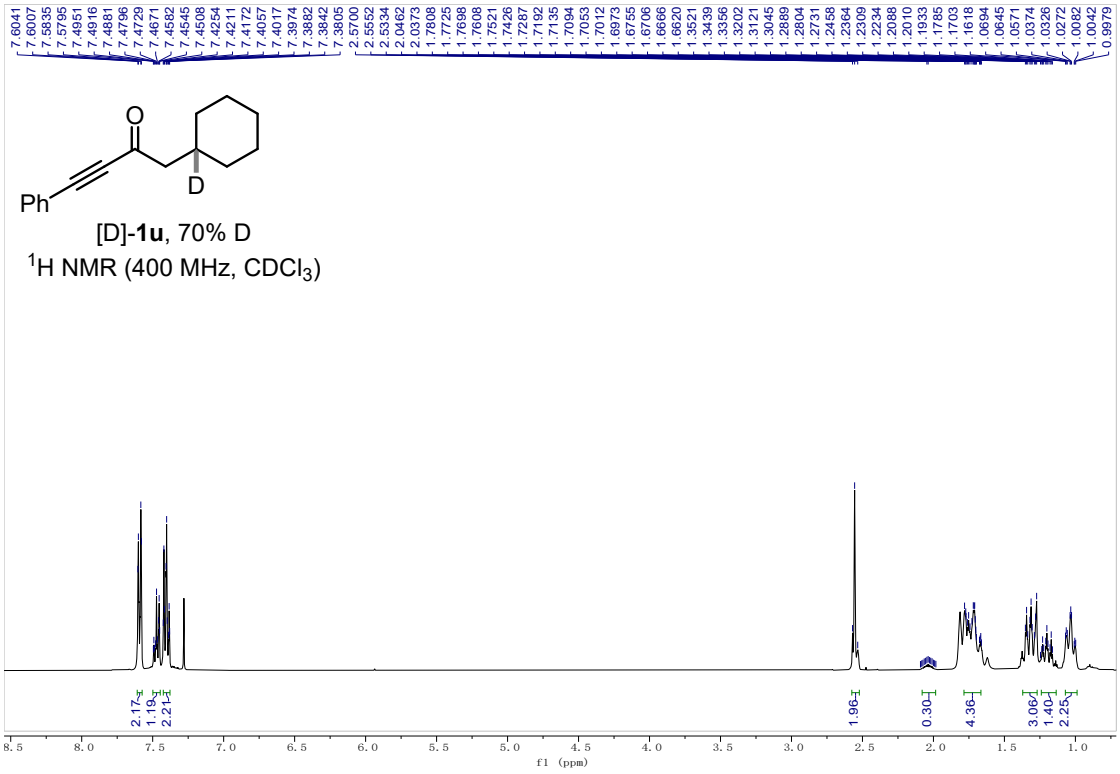
3ae, *Z*/*E* = 8:1

^{13}C NMR (101 MHz, $CDCl_3$)



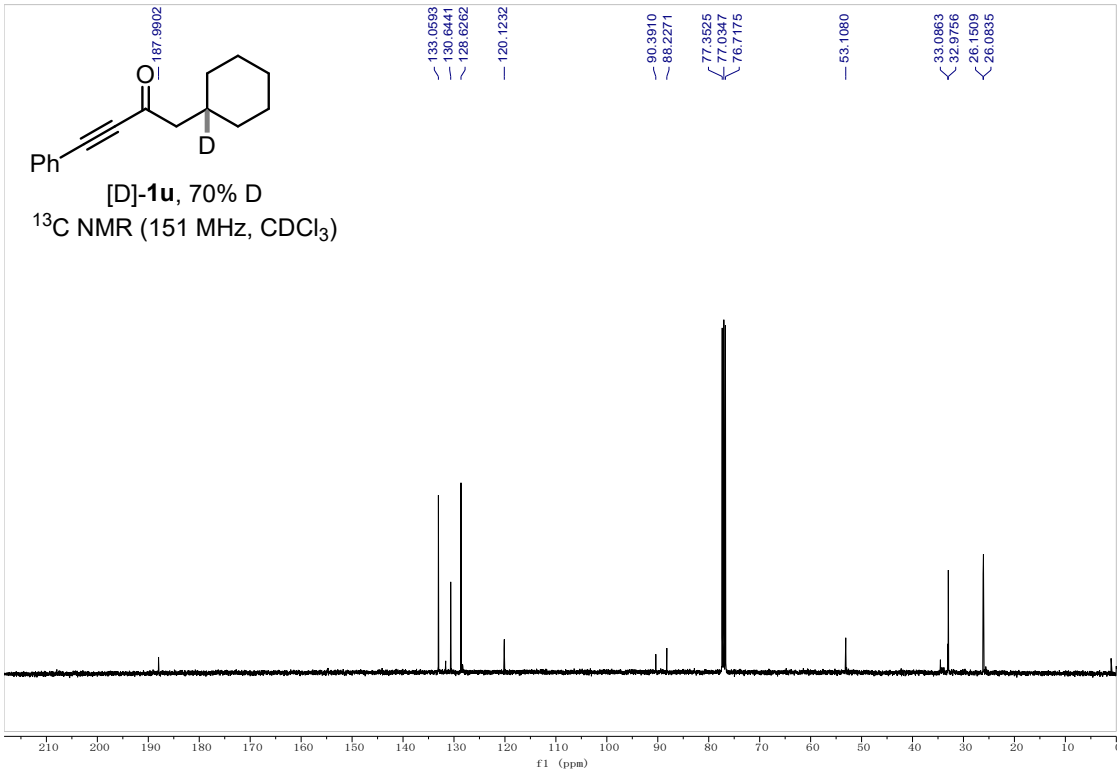
3ae, *Z*/*E* = 8:1

^{19}F NMR (377 MHz, $CDCl_3$)



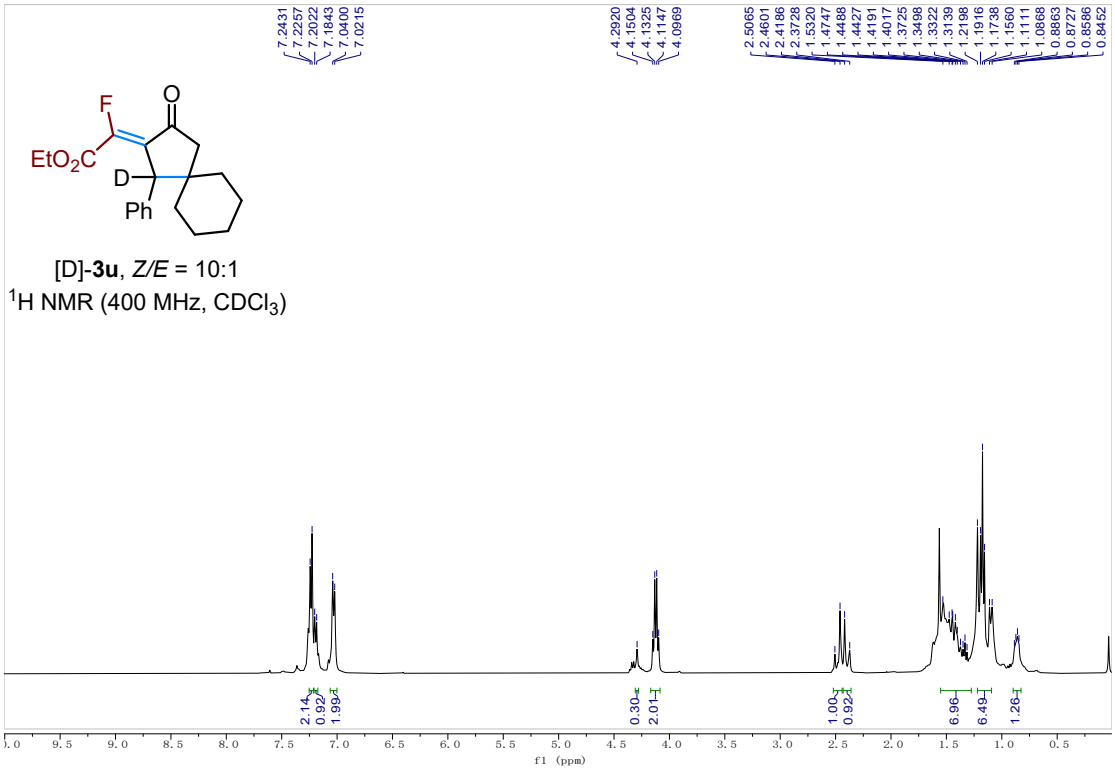
[D]-**1u**, 70% D

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



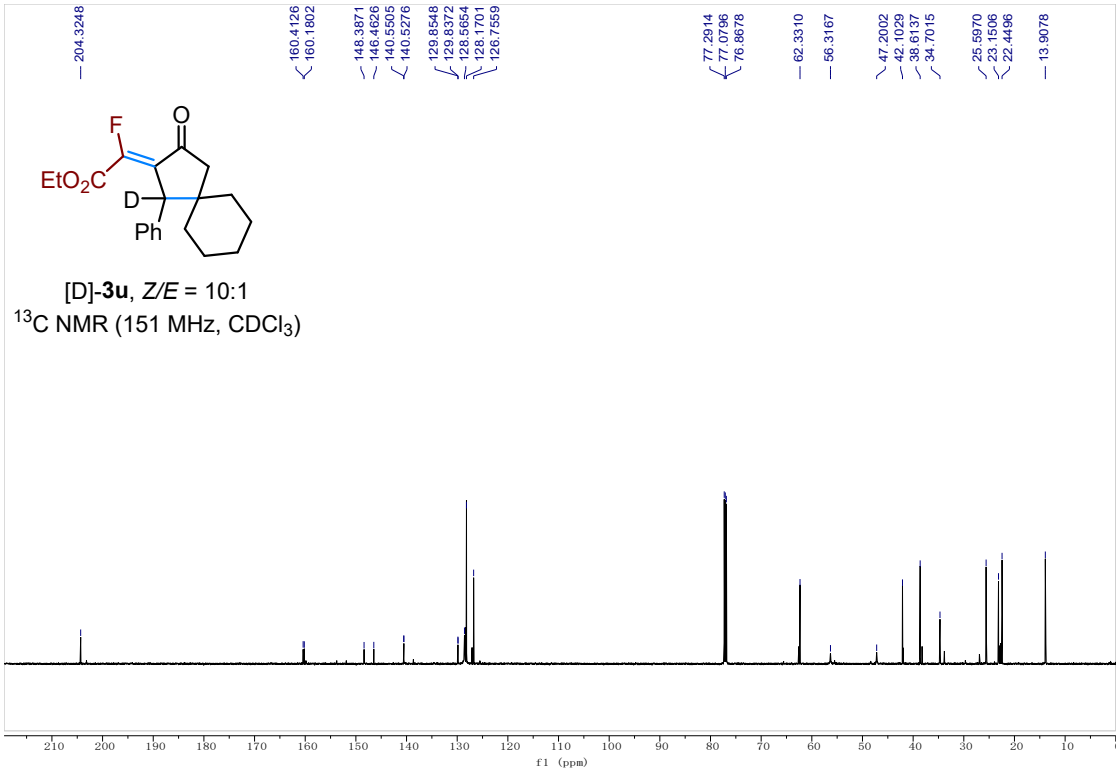
[D]-**1u**, 70% D

^{13}C NMR (151 MHz, $CDCl_3$)



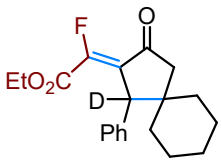
[D]-**3u**, *Z*/*E* = 10:1

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



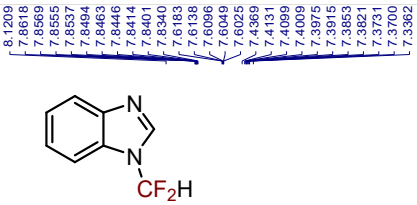
[D]-**3u**, *Z*/*E* = 10:1

^{13}C NMR (151 MHz, $CDCl_3$)



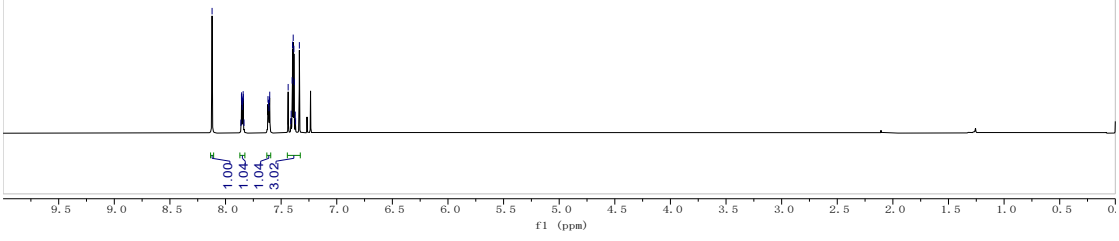
[D]-**3u**, *Z*/*E* = 10:1

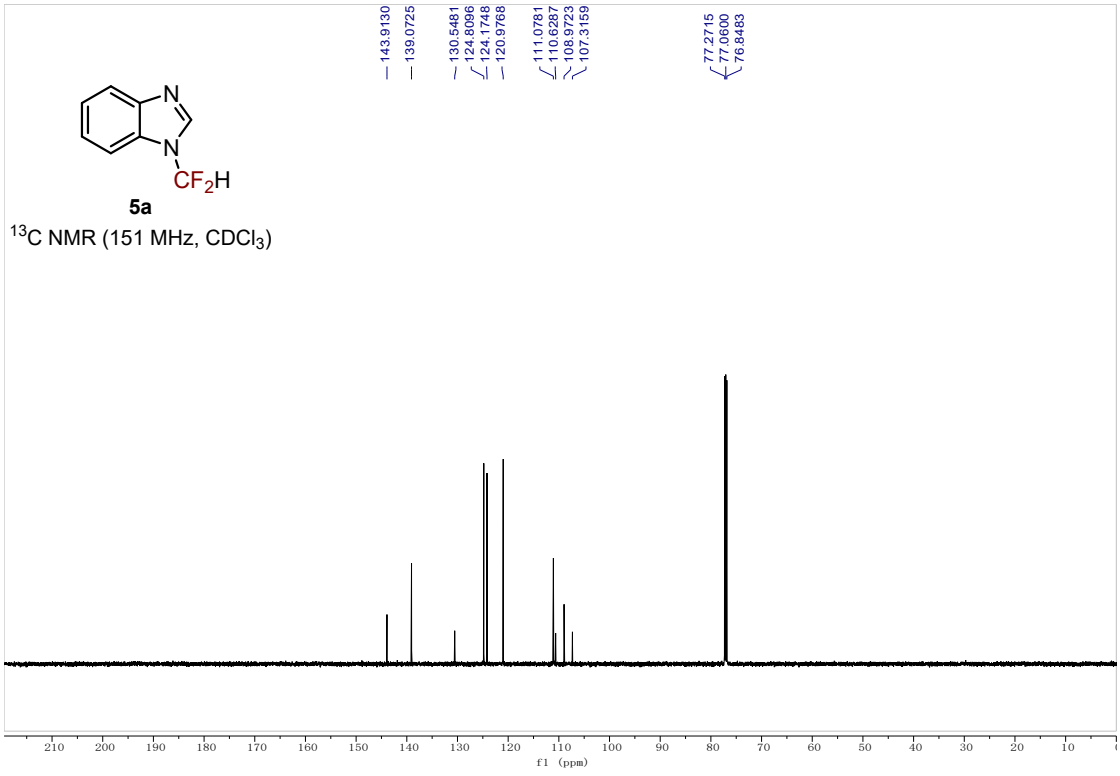
^{19}F NMR (377 MHz, $CDCl_3$)



5a

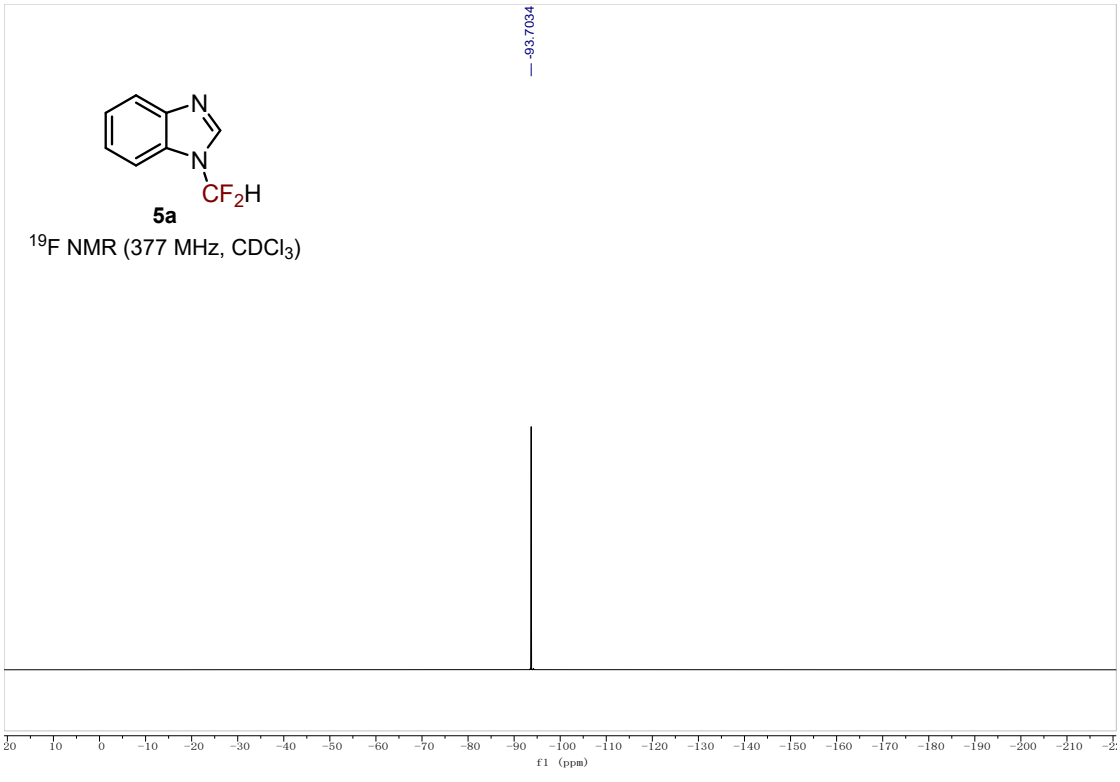
^{1}H NMR (600 MHz, $CDCl_3$)





5a

^{13}C NMR (151 MHz, $CDCl_3$)



5a

^{19}F NMR (377 MHz, $CDCl_3$)

5. X-Ray Crystallographic Data

The crystal of (*Z*)-**3o** (major isomer) was recrystallized in ethyl acetate/petroleum ethers via slow evaporation at room temperature. Crystal data for (*Z*)-**3o** ($C_{18}H_{19}FO_5$, 334.33): triclinic, space group P -1, a = 7.0823(8) Å, b = 8.7728(10) Å, c = 13.8942(15) Å, α = 92.044(4), β = 102.990(4), γ = 94.510(4), U = 837.31(16) Å^3, Z = 2, T = 298(2) K, absorption coefficient 0.103 mm^{-1}, reflections collected 3827, independent reflections1889 [R(int) = 0.0760], refinement by full-matrix least-squares on F^2, data/restraints/parameters 1889/1/228, goodness-of-fit on F^2 = 1.023, final R indices [I>2s(I)] R_1 = 0.0758, wR_2 = 0.2113, largest diff peak and hole 0.231 and -0.196 e.Å^{-3}. Crystallographic data for the structure (*Z*)-**3o** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2215733.

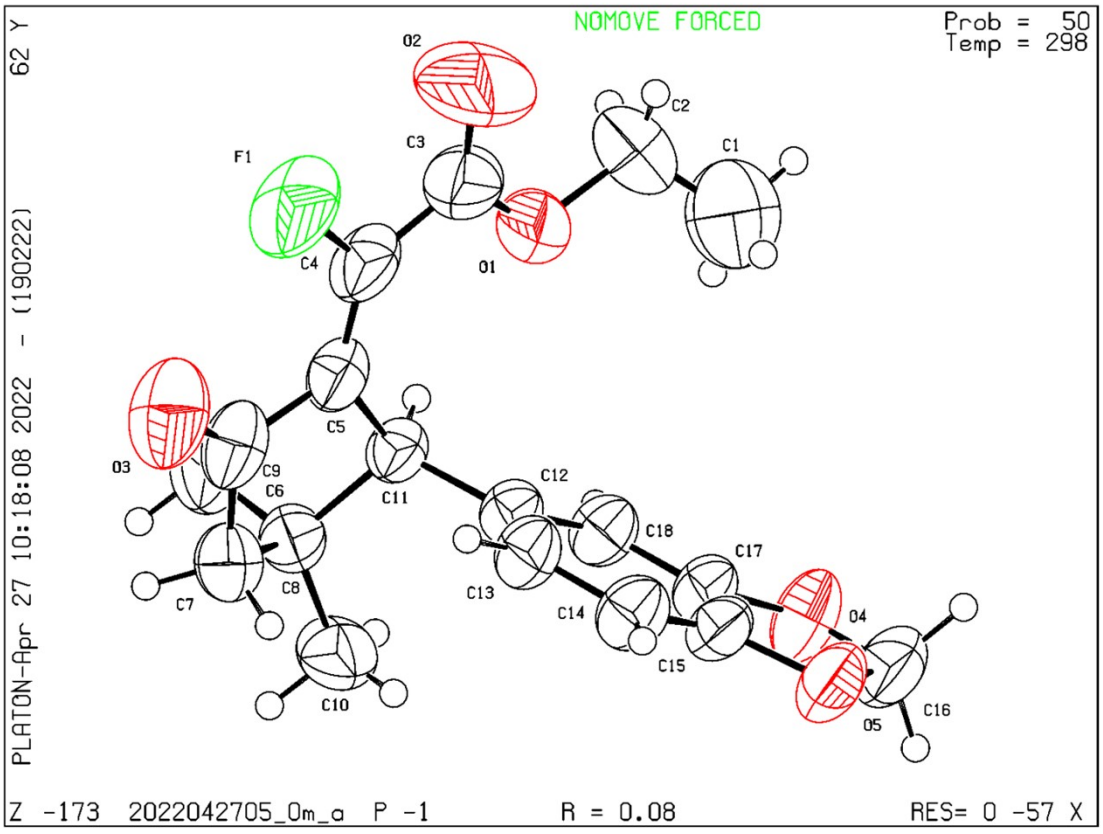


Figure S1. X-Ray crystal structure of (*Z*)-**3o** with the ellipsoid contour at 50% probability levels.

The crystal of (*Z*)-**3aa** (minor isomer) was recrystallized in ethyl acetate/petroleum ethers via slow evaporation at room temperature. Crystal data for (*Z*)-**3aa** ($C_{19}H_{24}FNO_2$, 317.18): triclinic, space group P -1, a = 6.2396(2) Å, b = 9.9099(4) Å, c = 14.5635(6) Å, α = 98.240(2), β = 98.468(2), γ = 91.823(2), U = 880.22(6) Å^3, Z = 2, T = 298 K, absorption coefficient 0.682 mm^{-1}, reflections

collected 3199, independent reflections 2453 [R(int) = 0.1314], refinement by full-matrix least-squares on F^2, data/restraints/parameters 2453/0/213, goodness-of-fit on F^2 = 1.048, final R indices [I>2s(I)] R_1 = 0.0682, wR_2 = 0.2032, largest diff peak and hole 0.391 and -0.244 e.Å^{-3}. Crystallographic data for the structure (*Z*)-**3aa** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2215372.

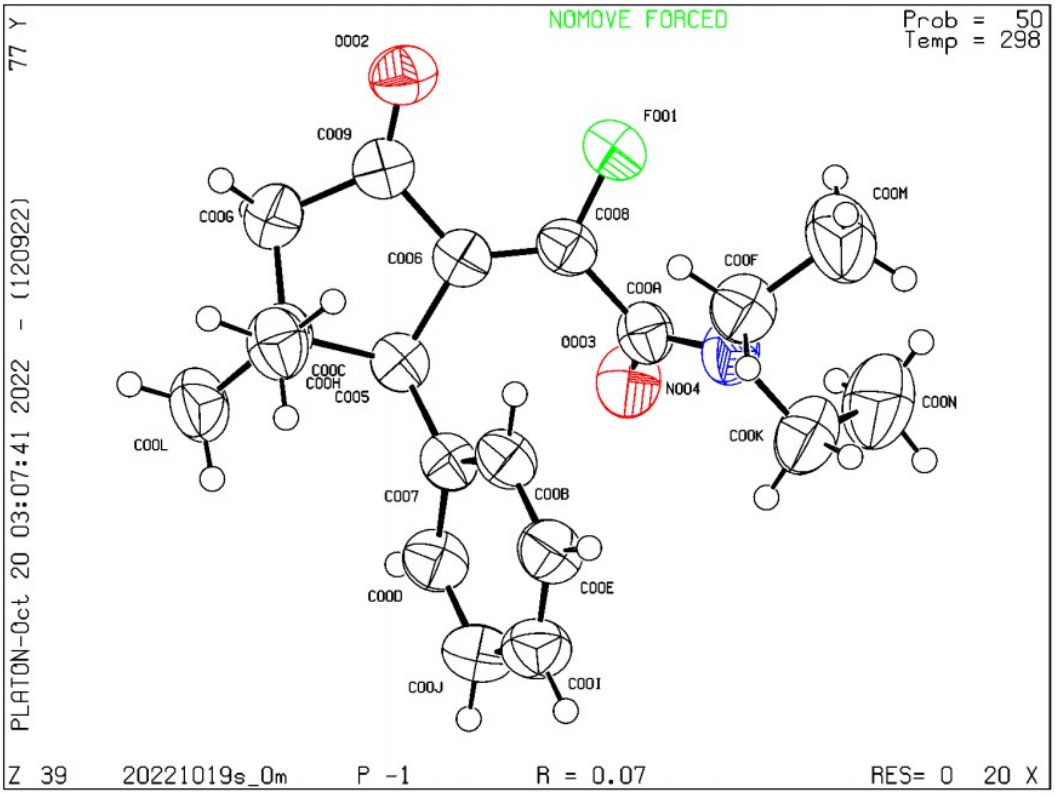


Figure S2. X-Ray crystal structure of (*Z*)-**3aa** with the ellipsoid contour at 50% probability levels.

6. Computational Data

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[2] Geometry optimizations and frequencies were calculated at the B3LYP-D3(BJ)/6-31g(d,p)-SMD(dichloromethane) level of theory.[3,4] Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). To obtain more accurate electronic energies, single-point energy calculations were performed at the ωB97XD/def2-TZVP-SMD(dichloromethane) level of theory with the optimized structures. Grimme's quasi-RRHO correction[5] for the frequencies that are below 100 cm^{-1} and concentration correction for all species (from 1 atm to 1 mol/L) are implemented by the GoodVibes program.[6]

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[3] (a) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys*. 1988, **37**, 785. (b) Becke, A. D. Density-functional thermochemistry. III. The Role of Exact Exchange. *J. Chem. Phys*. 1993, **98**, 5648; (c) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys*. 2010, **132**, 154104.

[4] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* 2009, **113**, 6378.

[5] Grimme, S. Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. Eur. J*. 2012, **18**, 9955.

[6] Luchini, G.; Alegre-Requena J. V.; Guan, Y.; Funes-Ardoiz, I.; Paton, R. S. 2019, GoodVibes: GoodVibes 3.0.1 http://doi.org/10.5281/zenodo.595246

Table S1. The Gibbs free energies of (*Z*)-**3a**, (*E*)-**3a**, (*Z*)-**3aa** and (*E*)-**3aa**.

Entry	structure	Calcd. G (hartree)	Calcd. ΔG (kcal/mol)
1	(*Z*)-**3a**	-984.58201	-1.1
2	(*E*)-**3a**	-984.58033	
3	(*Z*)-**3aa**	-1043.282793	+0.9
4	(*E*)-**3aa**	-1043.284176	

The calculated Cartesian coordinates of optimized structures

(*Z*)-3a

C	-0.79992	0.29611	-0.62188
C	-2.27721	0.83163	-0.8154
C	-3.00389	0.33484	0.44731
C	-2.36284	-1.00117	0.77325
C	-1.00051	-1.00283	0.13713
H	-2.80992	1.00649	1.29495
H	-4.08699	0.24127	0.33654
O	-2.85799	-1.89403	1.43751
C	-0.12642	-2.01176	0.287
F	-0.45921	-3.10008	0.99742
C	-2.36784	2.34775	-0.97937
H	-3.41228	2.64447	-1.12389
H	-1.98381	2.87421	-0.10195
H	-1.80078	2.68681	-1.85264
C	-2.87276	0.14113	-2.05369
H	-2.33865	0.44505	-2.96013
H	-2.81108	-0.95067	-1.98019
H	-3.92802	0.40767	-2.17373
C	1.28472	-2.1207	-0.19551
O	2.01128	-3.03511	0.13961
O	1.62243	-1.11164	-1.00121
C	3.01633	-1.03661	-1.41677
H	2.98802	-0.41532	-2.31284
H	3.35522	-2.04025	-1.68139
C	3.87179	-0.41669	-0.32898
H	4.89939	-0.31615	-0.69334
H	3.49983	0.57541	-0.06047
H	3.88563	-1.04554	0.56478
C	0.1372	1.26619	0.07992
C	0.22607	1.35393	1.47452
C	0.92977	2.12345	-0.69455
C	1.07988	2.27903	2.07825
H	-0.36199	0.68927	2.09937
C	1.7829	3.0498	-0.09579
H	0.88094	2.0548	-1.77759
C	1.86111	3.1313	1.29664
H	1.13637	2.32912	3.1617
H	2.39174	3.70162	-0.71558
H	2.5279	3.84784	1.76665
H	-0.37468	0.09835	-1.60683

(*E*)-3a

C	1.25966	-0.62981	0.62967
C	1.80378	-1.92349	-0.10692
C	0.83903	-2.09088	-1.30181
C	-0.50575	-1.61292	-0.78807
C	-0.2217	-0.65922	0.32346
H	1.13074	-1.42665	-2.12714
H	0.78339	-3.10952	-1.69272
O	-1.60663	-1.9705	-1.17415
C	-1.15988	0.04601	0.95723
F	-0.83365	0.8227	2.00866
C	3.2613	-1.81335	-0.55051
H	3.57517	-2.74342	-1.03649
H	3.40845	-0.99395	-1.25877
H	3.92289	-1.64328	0.30543
C	1.64095	-3.11712	0.84815
H	2.28662	-3.00109	1.72494
H	0.60894	-3.21599	1.20355
H	1.91159	-4.05209	0.34648
C	-2.63866	0.05967	0.69326
O	-3.4457	-0.28102	1.53376
O	-2.90943	0.52324	-0.5232
C	-4.30676	0.49645	-0.93917
H	-4.76588	-0.41399	-0.54896

H	-4.25519	0.43707	-2.02739
C	-5.03484	1.74225	-0.47493
H	-6.05821	1.72976	-0.86382
H	-5.08165	1.78489	0.61615
H	-4.53745	2.64399	-0.84429
C	1.92077	0.67179	0.20615
C	1.5508	1.35358	-0.96131
C	2.9611	1.19484	0.98405
C	2.2125	2.52062	-1.34448
H	0.73471	0.98049	-1.57193
C	3.62366	2.36269	0.60485
H	3.25021	0.68082	1.89657
C	3.25276	3.02917	-0.56412
H	1.91127	3.03537	-2.25221
H	4.42505	2.75345	1.22511
H	3.76471	3.93957	-0.86101
H	1.42926	-0.7451	1.70443

(*Z*)-**3aa**

C	0.80078	-0.43728	0.57298
C	1.77851	-1.51136	1.20435
C	2.117	-2.43243	0.0151
C	0.86185	-2.4559	-0.84411
C	0.08748	-1.22936	-0.50911
H	2.92318	-2.00068	-0.59348
H	2.4228	-3.44104	0.30488
O	0.56023	-3.31508	-1.65658
C	-1.06156	-0.85698	-1.08236
F	-1.64844	-1.59946	-2.0405
C	3.02408	-0.90442	1.84703
H	3.64822	-1.69615	2.27536
H	3.62637	-0.35376	1.11988
H	2.75689	-0.21526	2.65531
C	0.98807	-2.30958	2.25429
H	0.68352	-1.66424	3.08508
H	0.08352	-2.75684	1.82623
H	1.59875	-3.12265	2.66068
C	-1.75743	0.47035	-0.8959
O	-1.5785	1.32766	-1.76518
C	1.47534	0.82152	0.05622
C	2.09167	0.88122	-1.20057
C	1.50598	1.9614	0.86974
C	2.731	2.04578	-1.62585
H	2.0605	0.01973	-1.85989
C	2.14056	3.1298	0.446
H	1.02291	1.93175	1.84242
C	2.75882	3.17472	-0.80448
H	3.20106	2.07314	-2.60454
H	2.1472	4.00415	1.09035
H	3.25086	4.08277	-1.13975
H	0.09952	-0.12426	1.35194
N	-2.517	0.63911	0.20778
C	-3.15836	1.94356	0.41609
H	-3.36748	2.37606	-0.56393
H	-4.11229	1.76579	0.91942
C	-2.85787	-0.45118	1.13067
H	-2.00409	-1.12404	1.22084
H	-3.01638	-0.00191	2.11459
C	-4.09296	-1.22499	0.67591
H	-4.34017	-2.00582	1.40235
H	-4.95947	-0.5639	0.57497
H	-3.90768	-1.69962	-0.2928
C	-2.27515	2.88119	1.23565
H	-2.78493	3.83671	1.39697
H	-2.0435	2.4491	2.21484
H	-1.33487	3.07532	0.7125

(*E*)-**3aa**

C	1.51258	-0.81396	0.61303
C	2.01287	-2.07326	-0.20717
C	1.01826	-2.15996	-1.38582
C	-0.29764	-1.62284	-0.84819
C	0.02206	-0.8191	0.35668
H	1.32706	-1.49959	-2.20769
H	0.90267	-3.16585	-1.79781
O	-1.40702	-1.79517	-1.33337
C	-0.89583	-0.1665	1.0723
F	-0.50347	0.55777	2.1458
C	3.46239	-1.96237	-0.67658
H	3.75128	-2.86836	-1.22026
H	3.60809	-1.10707	-1.34166
H	4.14484	-1.85	0.17268
C	1.84869	-3.31353	0.6862
H	2.51161	-3.25565	1.55593
H	0.82119	-3.41338	1.05366
H	2.09465	-4.22432	0.13011
C	-2.40143	-0.18809	0.95478

O	-3.01893	-0.92205	1.7316
C	2.16192	0.50593	0.22982
C	1.76252	1.23359	-0.90036
C	3.20784	1.01148	1.0113
C	2.39567	2.42914	-1.24098
H	0.94701	0.87149	-1.51773
C	3.84327	2.20751	0.67469
H	3.52088	0.46316	1.89555
C	3.4397	2.92107	-0.45487
H	2.06988	2.97813	-2.11973
H	4.64899	2.58366	1.29838
H	3.92966	3.8539	-0.7172
H	1.72157	-0.98331	1.67325
N	-2.97128	0.65872	0.07403
C	-4.43488	0.69184	-0.01286
H	-4.83075	0.46385	0.97821
H	-4.72464	1.71527	-0.26768
C	-2.2004	1.49245	-0.85886
H	-1.36174	0.91554	-1.24807
H	-2.85558	1.70154	-1.70769
C	-1.71581	2.79368	-0.22478
H	-1.17231	3.39316	-0.96215
H	-2.55878	3.38565	0.14592
H	-1.04309	2.59554	0.61428
C	-4.97222	-0.2998	-1.04248
H	-6.06373	-0.23243	-1.09797
H	-4.56648	-0.09554	-2.0385
H	-4.70186	-1.32224	-0.76501