Supporting Information to

Access to cyclopentenones via copper-catalyzed 5-*endo* trifluoromethylcarbocyclization of ynones

Siya Le,[§] Yihui Bai,[§] Jiayan Qiu, Zuxiao Zhang, Hanliang Zheng,* and Gangguo Zhu*

Key Laboratory of the Ministry of Education for Advanced Catalysis Materials, Department of Chemistry, Zhejiang Normal University, 688 Yingbin Road, Jinhua 321004, P. R. China.

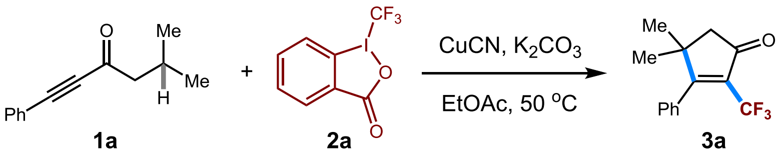
**email: hanliang@zjnu.edu.cn, gangguo@zjnu.cn*

Contents

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 were 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. General procedures for experiments and analytical data

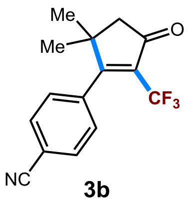


To a mixture of CuCN (1.8 mg, 0.02 mmol), **2a** (94.8 mg, 0.3 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of EtOAc was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After being heated in an oil bath at 50 ^{o}C for 10 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 40 mg (79% yield) of **3a** as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.45 (m, 3H), 7.15 (dd, J = 6.5, 3.0 Hz, 2H), 2.60 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.62, 185.51, 132.45, 129.83 (q, J = 31.1 Hz), 128.90, 128.07, 126.17 (q, J = 0.8 Hz), 120.90 (q, J = 273.4 Hz), 51.01, 43.02, 26.65. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.39. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{13}F_3O+H^+$: 255.0991; Found 255.0991.

[1] (a) Q.-X. Wang and J. A. May, *Org. Lett.*, 2020, **22**, 9579; (b) T. P. Reddy, J. Gujral, P. Roy and D. B. Ramachary, *Org. Lett*., 2020, **22**, 9653.

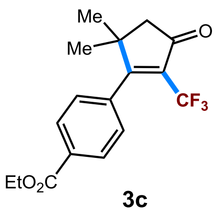
Scale-up experiments.

To a mixture of CuCN (17.9 mg, 0.2 mmol), **2a** (948 mg, 3.0 mmol) and K_2CO_3 (553 mg, 4.0 mmol) in 20 mL of EtOAc was added **1a** (372 mg, 2.0 mmol) under nitrogen atmosphere. After being heated in an oil bath at 50 °C for 16 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 422 mg (83% yield) of **3a** as a yellow oil.



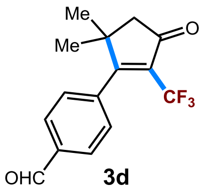
3b

*Compound **3b:*** 46 mg, 82% yield, white solid, mp 168-170 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 7.9 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 2.63 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.52, 182.29, 137.14, 131.95, 130.60 (q, J = 31.0 Hz), 127.18, 120.53 (q, J = 273.6 Hz), 118.01, 113.19, 50.77, 43.05, 26.56. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.36. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{12}F_3NO+H^+$: 280.0944; Found 280.0942.



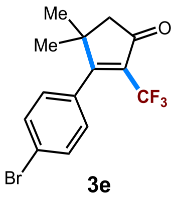
3c

*Compound **3c:*** 53 mg, 81% yield, white solid, mp 105-107 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 20:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.2 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H), 2.62 (s, 2H), 1.43 (t, J = 7.1 Hz, 3H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.98, 183.97, 165.85, 136.90, 131.09, 130.20 (q, J = 31.3 Hz), 129.27, 126.34, 120.69 (q, J = 273.5 Hz), 61.32, 50.90, 43.02, 26.62, 14.32. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.40. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}F_3O_3+H^+$: 327.1203; Found 327.1202.



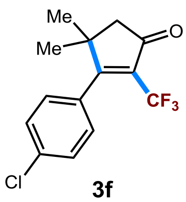
3d

*Compound **3d:*** 48 mg, 85% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.08 (s, 1H), 7.98 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.62 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.81, 191.41, 183.32, 138.52, 136.46, 130.34 (q, J = 31.2 Hz), 129.33, 127.07, 120.63 (q, J = 273.5 Hz), 50.86, 43.08, 26.63. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.38. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}F_3O_2$+H^+: 283.0940; Found 283.0945.



3e

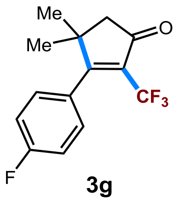
*Compound **3e:*** 52 mg, 78% yield, white solid, mp 136-137 ^{o}C; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 2.60 (s, 2H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.09, 183.90, 131.44, 131.24, 130.23 (q, J = 31.1 Hz), 127.86 (q, J = 0.9 Hz), 123.41, 120.74 (q, J = 273.5 Hz), 50.90, 42.94, 26.60. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.35. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{12}BrF_3O$+H^+: 333.0096; Found 333.0097.



3f

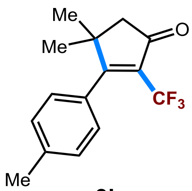
*Compound **3f:*** 48 mg, 83% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, J = 8.4 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.60 (s, 2H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.11, 183.96, 135.28, 130.75, 130.27 (q, J = 31.2 Hz), 128.51, 127.64, 120.75 (q, J = 273.6 Hz), 50.91, 42.99, 26.61. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.36. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{12}ClF_3O$+H^+: 289.0602;

Found: 289.0601.



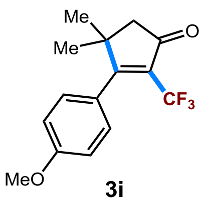
3g

*Compound **3g:*** 43 mg, 79% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.21-7.11 (m, 4H), 2.60 (s, 2H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.24, 184.42 (d, J = 2.9 Hz), 163.05 (d, J = 249.3 Hz), 130.28 (q, J = 31.0 Hz), 128.25 (d, J = 4.2 Hz), 128.18 (d, J = 1.5 Hz), 120.81 (q, J = 273.5 Hz), 115.45 (d, J = 21.8 Hz), 50.94, 43.01, 26.62. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.38, -112.09. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{12}F_4O+H^+$: 273.0897; Found 273.0888.



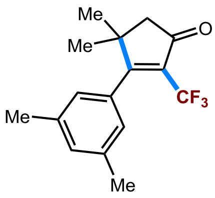
3h

*Compound **3h:*** 42 mg, 78% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (d, J = 7.9 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 2.56 (s, 2H), 2.41 (s, 3H), 1.25 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.69, 185.99, 138.93, 129.70 (q, J = 30.9 Hz), 129.50, 128.75, 126.14, 120.96 (q, J = 273.5 Hz), 51.07, 43.03, 26.70, 21.31. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.35. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}F_3O+H^+$: 269.1148; Found 269.1150.



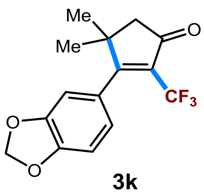
3i

*Compound **3i:*** 43 mg, 76% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.10 (d, J = 8.7 Hz, 2H), 6.98 (d, J = 8.7 Hz, 2H), 3.87 (s, 3H), 2.58 (s, 2H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.73, 185.85, 160.16, 129.65 (q, *J* = 30.4 Hz), 127.80, 124.59, 121.03 (q, *J* = 273.5 Hz), 113.62, 55.28, 51.17, 43.14, 26.78. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.28. HRMS (ESI) *m/z*: [*M* + H]$^+$ Calcd for $C_{15}H_{15}F_3O_2$+H$^+$: 285.1097; Found 285.1099.



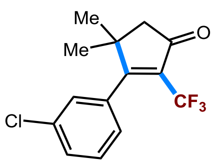
3j

*Compound **3j:*** 40 mg, 71% yield, white solid, mp 77-79 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.07 (s, 1H), 6.73 (s, 2H), 2.58 (s, 2H), 2.38 (s, 6H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.85, 186.16, 137.62, 132.41, 130.52, 129.51 (q, *J* = 30.8 Hz), 123.79, 120.96 (q, *J* = 273.3 Hz), 51.08, 42.97, 26.77, 21.37. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.41. HRMS (ESI) *m/z*: [*M* + H]$^+$ Calcd for $C_{16}H_{17}F_3O$+H$^+$: 283.1304; Found 283.1305.



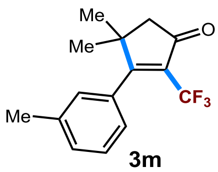
3k

*Compound **3k:*** 47 mg, 79% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 30:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.89 (d, *J* = 7.9 Hz, 1H), 6.64 (s, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.06 (s, 2H), 2.57 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.55, 185.35, 148.28, 147.57, 129.94 (q, *J* = 30.8 Hz), 125.72, 120.92 (q, *J* = 273.5 Hz), 120.24 (q, *J* = 1.5 Hz), 108.24, 107.09 (q, *J* = 1.4 Hz), 101.50, 51.11, 43.12, 26.83. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.37. HRMS (ESI) *m/z*: [*M* + H]$^+$ Calcd for $C_{15}H_{13}F_3O_3$+H$^+$: 299.0890; Found 299.0888.



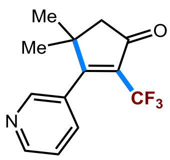
3l

*Compound **3l:*** 45 mg, 78% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.39 (m, 2H), 7.18-7.14 (m, 1H), 7.03 (d, J = 7.4 Hz, 1H), 2.60 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.01, 183.25, 134.32, 134.04, 130.32 (q, J = 31.2 Hz), 129.52, 129.12, 126.15, 124.56, 120.68 (q, J = 273.5 Hz), 50.90, 42.99, 26.63. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.42. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{12}ClF_3O+H^+$: 289.0602; Found 289.0599.



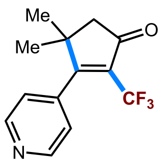
3m

*Compound **3m:*** 34 mg, 63% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36-7.32 (m, 1H), 7.26 (d, J = 7.7 Hz, 1H), 6.96-6.91 (m, 2H), 2.59 (s, 2H), 2.42 (s, 3H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.70, 185.83, 137.78, 132.41, 129.64, 129.45 (q, J = 31.0 Hz), 127.92, 126.60, 123.30, 120.92 (q, J = 273.5 Hz), 51.03, 42.99, 26.71, 21.50. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.40. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{15}H_{15}F_3O+H^+$: 269.1148; Found 269.1150.



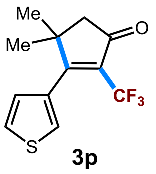
3n

*Compound **3n:*** 42 mg, 82% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.81-8.69 (m, 1H), 8.54-8.42 (m, 1H), 7.57-7.40 (m, 2H), 2.63 (s, 2H), 1.29 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.74, 181.05, 150.22, 146.14, 133.93, 131.20 (q, J = 31.0 Hz), 123.13, 120.64 (q, J = 273.5 Hz), 99.98, 50.81, 43.02, 26.41. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.25. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}F_3NO+H^+$: 256.0944; Found 256.0942.



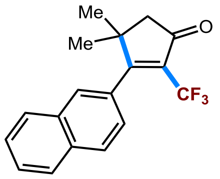
3o

Compound ***3o:*** 38 mg, 75% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.78-8.68 (m, 2H), 7.08 (d, J = 5.5 Hz, 2H), 2.61 (s, 2H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.52, 181.09, 149.56, 140.65, 130.37 (q, J = 31.5 Hz), 121.02, 120.49 (q, J = 273.6 Hz), 50.74, 42.81, 26.48. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.41. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{12}F_3NO+H^+$: 256.0944; Found 256.0943.



3p

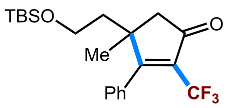
Compound ***3p:*** 33 mg, 63% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.43 (m, 1H), 7.30-7.27 (m, 1H), 7.04-7.01 (m, 1H), 2.56 (s, 2H), 1.29 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.26, 181.41, 131.88, 129.70 (q, J = 31.0 Hz), 126.99 (q, J = 1.1 Hz), 126.16, 124.15 (q, J = 1.5 Hz), 120.98 (q, J = 273.4 Hz), 51.27, 42.93, 26.97. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.51. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{12}H_{11}F_3OS+Na^+$: 283.0375; Found 283.0362.



3q

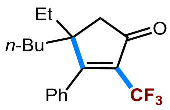
Compound ***3q:*** 40 mg, 66% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95-7.89 (m, 3H), 7.64-7.57 (m, 3H), 7.26 (dd, J = 8.4, 1.6 Hz, 1H), 2.65 (s, 2H), 1.34 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.60, 185.51, 133.03, 132.38, 130.12 (q, J = 31.0 Hz), 129.97, 128.26, 127.88, 127.84, 127.01, 126.91, 125.38 (q, J = 0.8 Hz), 124.04 (q, J = 0.8 Hz), 120.93 (q, J = 273.5 Hz), 51.11, 43.34, 26.82. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.32. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for

$C_{18}H_{15}F_3O+H^+$: 305.1148; Found 305.1148.



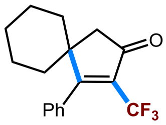
3r

*Compound **3r:*** 54 mg, 68% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.41 (m, 3H), 7.19-7.15 (m, 2H), 3.74-3.68 (m, 2H), 3.00 (d, J = 19.0 Hz, 1H), 2.43 (d, J = 19.0 Hz, 1H), 1.83-1.77 (m, 1H), 1.74-1.70 (m, 1H), 1.25 (s, 3H), 0.88 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.82, 184.65, 132.60, 130.61 (q, J = 31.0 Hz), 128.95, 128.05, 126.56, 120.95 (q, J = 273.6 Hz), 59.73, 48.58, 45.48, 39.80, 25.90, 25.34, 18.23, -5.55, -5.56. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.12. HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{21}H_{29}F_3O_2Si+NH_4^+$: 416.2227; Found 416.2196.



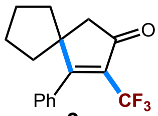
3s

*Compound **3s:*** 44 mg, 71% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49-7.43 (m, 3H), 7.14 (dd, J = 6.6, 2.9 Hz, 2H), 2.52 (s, 2H), 1.64-1.55 (m, 3H), 1.51-1.45 (m, 1H), 1.34-1.28 (m, 3H), 1.26-1.22 (m, 1H), 0.94-0.90 (m, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.99, 183.22, 132.71, 131.93 (q, J = 30.8 Hz), 129.11, 128.19, 126.15, 120.84 (q, J = 273.5 Hz), 50.72, 44.74, 36.49, 29.67, 26.51, 23.02, 13.93, 8.70. ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.71. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{18}H_{21}F_3O+H^+$: 311.1617; Found 311.1615.



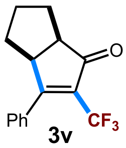
3t

*Compound **3t:*** 47 mg, 80% yield, yellow solid, mp 86-88 ^{o}C; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.75-7.42 (m, 3H), 7.10 (dd, J = 6.5, 2.9 Hz, 2H), 2.59 (s, 2H), 1.78-1.74 (m, 2H), 1.69-1.66 (m, 1H), 1.57-1.48 (m, 4H), 1.41-1.31 (m, 2H), 1.06-0.98 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.83, 185.98, 132.63, 130.25 (q, J = 31.1 Hz), 128.70, 127.89, 126.34, 120.94 (q, J = 273.5 Hz), 47.81, 46.48, 33.96, 24.68, 22.97. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.13. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{17}F_3O$+H^+: 295.1304; Found 295.1305.



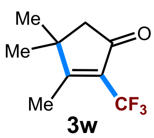
3u

Compound ***3u:*** 43 mg, 77% yield, white solid, mp 83-85 ^{o}C; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.47-7.42 (m, 3H), 7.14-7.10 (m, 2H), 2.51 (s, 2H), 1.82-1.78 (m, 2H), 1.73-1.67 (m, 4H), 1.60-1.57 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.64, 183.95 (d, J = 2.8 Hz), 132.39, 131.04 (q, J = 30.9 Hz), 128.74, 127.97, 126.59 (d, J = 0.8 Hz), 120.82 (q, J = 273.4 Hz), 54.16, 49.85, 36.99, 23.86. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.19. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{15}F_3O$+H^+: 281.1148; Found 281.1146.



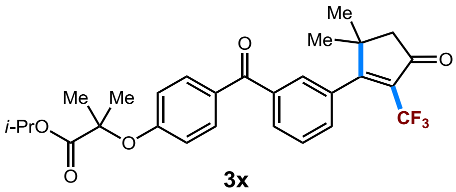
3v

Compound ***3v:*** 35 mg, 66% yield, yellow oil; *cis*/*trans* >20:1. The *cis*-stereochemistry was determined by NOE. Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50-7.44 (m, 3H), 7.38-7.35 (m, 2H), 3.77-3.69 (m, 1H), 3.05-3.01 (m, 1H), 2.09-2.04 (m, 1H), 1.88-1.81 (m, 1H), 1.72-1.62 (m, 3H), 1.51-1.46 (m, 1H), 1.35-1.26 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.10, 180.33, 133.79, 130.46, 130.23 (q, J = 31.3 Hz), 128.50, 127.44 (q, J = 1.5 Hz), 121.12 (q, J = 273.2 Hz), 50.75, 49.30, 29.93, 29.30, 23.97. ^{19}F NMR (565 MHz, $CDCl_3$) δ -59.95. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}F_3O$+H^+: 267.0991; Found 267.0989.



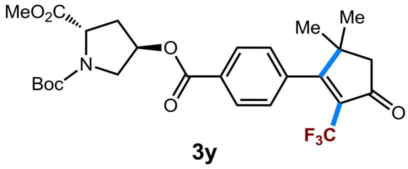
3w

*Compound **3w:*** 15 mg, 39% yield, colorless oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 2.42 (s, 2H), 2.24-2.21 (m, 3H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.30, 186.37, 128.67 (q, J = 30.9 Hz), 121.82 (q, J = 273.0 Hz), 50.79, 42.29, 26.32, 12.79. ^{19}F NMR (565 MHz, $CDCl_3$) δ -61.13. HRMS (ESI) *m/z*: $[2M + H]^+$ Calcd for $C_{18}H_{22}F_6O_2$+H^+: 385.1597; Found 385.1592.



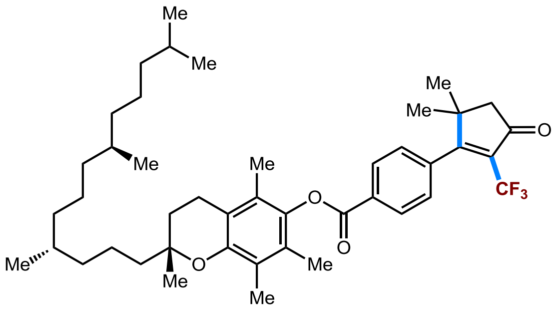
3x

*Compound **3x:*** 56 mg, 56% yield, white solid, mp 109-111 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 8.8 Hz, 2H), 7.27-7.23 (m, 2H), 6.91-6.87 (m, 2H), 5.13-5.06 (m, 1H), 2.62 (s, 2H), 1.68 (s, 6H), 1.29 (s, 6H), 1.21 (d, J = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.07, 194.61, 173.07, 159.92, 138.55, 136.05, 132.09, 130.25 (q, J = 31.2 Hz), 130.01, 129.77, 129.39, 129.37, 126.25, 126.24, 120.75 (q, J = 273.5 Hz), 117.29, 79.48, 69.36, 50.94, 43.10, 26.67, 25.38, 21.54. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.30. HRMS (ESI) *m/z*: $[M + H - H_2O]^+$ Calcd for $C_{28}H_{29}F_3O_5$+H^+-H_2O: 485.1934; Found 485.1955.



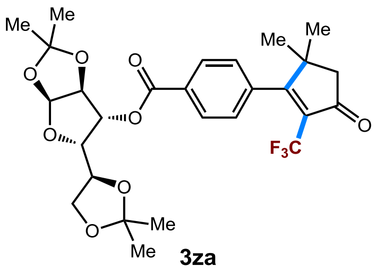
3y

*Compound **3y:*** 84 mg, 80% yield, white solid, mp 127-129 °C, as a 1.3:1 mixture of two rotamers; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, J = 8.2 Hz, 2H), 7.27-7.23 (m, 2H), 5.60-5.56 (m, 1H), 4.55 (t, J = 7.9 Hz, 0.43H, minor rotamer), 4.45 (t, J = 8.0 Hz, 0.57H, major rotamer), 3.87 (d, J = 3.1 Hz, 1H), 3.80 (s, 1.29H, minor rotamer), 3.79 (s, 1.71H, major rotamer), 3.75-3.73 (m, 1H), 2.62 (s, 1 H), 2.60-2.53 (m, 2H), 2.40-2.35 (m, 1H), 1.48 (s, 3.90H, minor rotamer), 1.46 (s, 5.10H, major rotamer), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.87, 183.63, 173.01, 165.11, 153.60, 137.47, 130.29 (q, J = 31.5 Hz), 130.16, 129.44, 120.66 (q, J = 273.4 Hz), 80.73, 72.98, 57.99, 53.37, 52.05, 50.87, 43.02, 36.70, 28.24, 26.60. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.38. HRMS (ESI) *m/z*: [*M* + Na]$^+$ Calcd for $C_{26}H_{30}F_3NO_7$+Na$^+$: 548.1867; Found 548.1814.



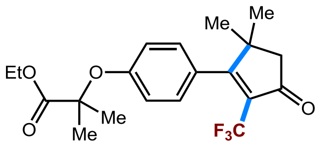
3z

*Compound **3z:*** 110 mg, 77% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 2.69-2.63 (m, 4H), 2.16 (s, 3H), 2.11 (s, 3H), 2.07 (s, 3H), 1.61-1.16 (m, 32H), 0.90-0.87 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.95, 183.81, 164.45, 149.62, 140.50, 137.53, 130.28 (q, *J* = 31.5 Hz), 130.21, 126.80, 126.64, 125.07, 123.25, 120.73 (q, *J* = 273.5 Hz), 117.58, 77.25, 77.04, 76.83, 75.16, 50.92, 43.12, 39.39, 37.47, 37.31, 32.82, 28.00, 26.65, 24.83, 24.47, 22.74, 22.65, 21.05, 20.67, 19.78, 19.69, 13.15, 12.30, 11.89. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.28. HRMS (ESI) *m/z*: [M + H]$^+$ Calcd for $C_{44}H_{61}F_3O_4$+H$^+$: 711.4595; Found 711.4622.



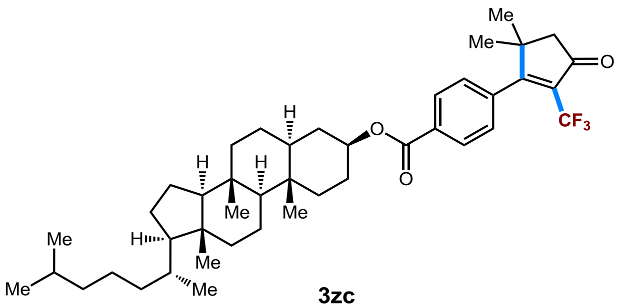
3za

*Compound **3za:*** 76 mg, 70% yield, white solid, mp 184-186 ^{o}C; Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.3 Hz, 2H), 5.96 (d, *J* = 3.7 Hz, 1H), 5.52 (d, *J* = 2.8 Hz, 1H), 4.65 (d, *J* = 3.7 Hz, 1H), 4.40-4.36 (m, 1H), 4.34 (dd, *J* = 8.1, 2.8 Hz, 1H), 4.16-4.09 (m, 2H), 2.61 (s, 2H), 1.57 (s, 3H), 1.43 (s, 3H), 1.33 (s, 3H), 1.29 (s, 3H), 1.27 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.85, 183.50, 164.51, 137.62, 130.32 (q, *J* = 31.2 Hz), 130.12, 129.45, 126.60, 120.65 (q, *J* = 273.6 Hz), 112.46, 109.52, 105.11, 83.33, 79.85, 72.55, 67.34, 50.85, 43.04, 26.90, 26.72, 26.64, 26.60, 26.21, 25.25. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.36. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{27}H_{31}F_3O_8$+Na^+: 563.1863; Found 563.1865.



3zb

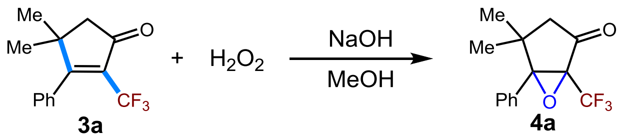
*Compound **3zb:*** 62 mg, 81% yield, yellow oil; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.02 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.55 (s, 2H), 1.64 (s, 6H), 1.24 (s, 6H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.58, 185.51, 173.91, 156.31, 129.77 (q, *J* = 30.7 Hz), 127.44, 125.69, 120.95 (q, *J* = 273.4 Hz), 118.02, 79.34, 61.55, 51.13, 43.07, 26.75, 25.44, 13.97. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.35. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{23}F_3O_4$+H^+: 385.1621; Found 385.1626.



3zc

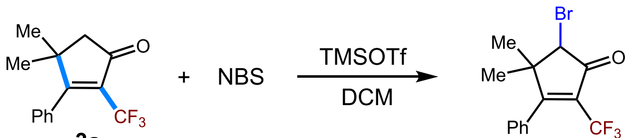
*Compound **3zc:*** 88 mg, 65% yield, white solid, mp 65-66 °C; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 5.02-4.92 (m, 1H), 2.59 (s, 2H), 2.01-1.00 (m, 38H), 0.92-0.85 (m, 12H), 0.73-0.64 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.01, 184.06, 165.34, 136.75, 131.52, 130.16 (q, *J* = 31.3 Hz), 129.26, 126.28, 120.70 (q, *J* = 273.5 Hz), 74.86, 56.43, 56.28, 54.24, 50.89, 44.71, 43.01, 42.61, 39.99, 39.52, 36.79, 36.18, 35.81, 35.53, 35.50, 34.12, 32.01, 28.65, 28.26, 28.02, 27.58, 26.61, 24.22, 23.85, 22.83, 22.57, 21.24, 18.68, 12.30, 12.09. ^{19}F NMR (377 MHz, $CDCl_3$) δ -60.37. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{43}H_{61}F_3O_3$+H^+: 683.4646 Found 683.4660.

Experimental procedure for the transformation of 3a to 4a



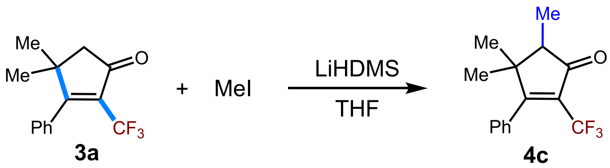
To a solution of **3a** (50.8 mg, 0.2 mmol) and NaOH (8.0 mg, 0.2 mmol) in 2 mL of MeOH was added H_2O_2 (30 wt%, 226.7 mg, 2 mmol) at 0 °C. After stirring at 25 °C for 10 h, the reaction mixture was quenched with water, extracted with DCM, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 46 mg (85% yield) of **4a** as a white solid, mp 83-85 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46-7.33 (m, 5H), 2.56 (d, J = 17.3 Hz, 1H), 2.13 (d, J = 17.2 Hz, 1H), 1.22 (s, 3H), 1.12 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.64, 129.34, 128.85, 128.55, 128.08, 120.72 (q, J = 276.9 Hz), 79.11, 64.48 (q, J = 38.2 Hz), 47.43, 39.23, 26.20, 21.85. ^{19}F NMR (565 MHz, $CDCl_3$) δ -67.58. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}F_3O_2+H^+$: 271.0940; Found 271.0948.

Experimental procedure for the transformation of 3a to 4b



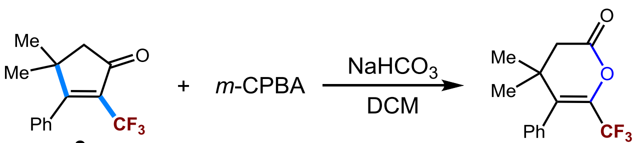
To a solution of **3a** (50.8 mg, 0.2 mmol) in 5 mL of DCM was added NBS (42.7 mg, 0.24 mmol) and TMSOTf (8.9 mg, 0.04 mmol) at 0 °C. After stirring at reflux for 4 h, the reaction mixture was quenched by water, extracted with DCM, washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Mg_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 46 mg (69% yield) of **4b** as a white solid, mp 113-115 ℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53-7.46 (m, 3H), 7.18 (dd, J = 6.4, 3.1 Hz, 2H), 4.59 (s, 1H), 1.36 (s, 3H), 1.31 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.29, 182.56 (q, J = 2.9 Hz), 131.72, 131.65, 129.49, 128.26, 127.63 (q, J = 32.2 Hz), 126.28, 120.53 (q, J = 273.8 Hz), 59.18 (q, J = 1.4 Hz), 47.12, 26.06, 24.89. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.17. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{12}BrF_3O+H^+$: 333.0096; Found 333.0097.

Experimental procedure for the transformation of 3a to 4c



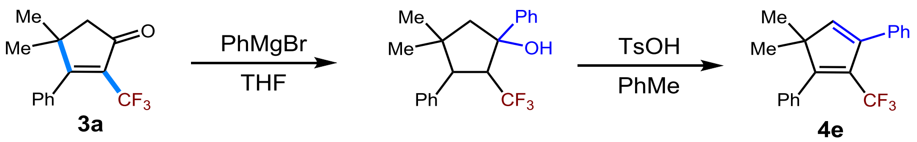
To a solution of **3a** (50.8 mg, 0.2 mmol) in 1 mL of dry THF was added LiHDMS (0.24 mmol, 1.0 M solution in THF) at -78 ℃. After stirring at -78 ℃ for 1 h, a solution of MeI (0.22 mmol) in 1 mL of THF was added. Upon warming to 25 ℃ over 2 h, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with EtOAc, dried over anhydrous $MgSO_4$, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 44 mg (82% yield) of **4c** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.48-7.44 (m, 3H), 7.17-7.14 (m, 2H), 2.48 (q, J = 7.3 Hz, 1H), 1.22 (s, 3H), 1.21 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.81, 183.83, 132.67, 128.80, 128.45 (q, J = 28.8 Hz), 128.00, 126.35, 121.09 (d, J = 273.3 Hz), 53.13, 46.48, 25.49, 23.02, 9.80. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.13. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}F_3O+H^+$: 269.1148; Found 269.1153.

Experimental procedure for the transformation of 3a to 4d



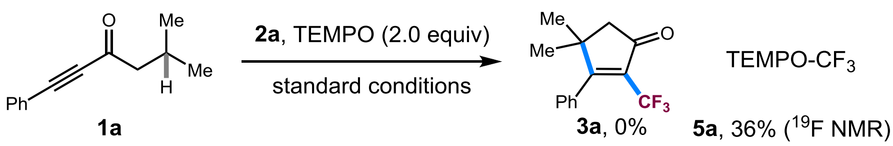
To a mixture of *m*-CPBA (69.0 mg, 0.4 mmol) and $NaHCO_3$ (42 mg, 0.5 mmol) in 2 mL of DCM was added **3a** (50.8 mg, 0.2 mmol) at 0 ℃. After stirring at 25 ℃ overnight, the reaction mixture was quenched with aqueous Na_2SO_3 solution, extracted with DCM, washed with brine, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 40:1) gave 39 mg (72% yield) of **4d** as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 7.49-7.43 (m, 3H), 7.15 (dd, J = 6.5, 3.1 Hz, 2H), 2.60 (s, 2H), 1.28 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.58, 185.50, 132.44, 129.81 (q, J = 31.1 Hz), 128.88, 128.05, 126.16, 120.89 (q, J = 273.6 Hz), 51.00, 43.02, 26.65. ^{19}F NMR (565 MHz, $CDCl_3$) δ -60.39. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{13}F_3O_2+H^+$: 271.0940; Found 271.0948.

Experimental procedure for the transformation of 3a to 4e



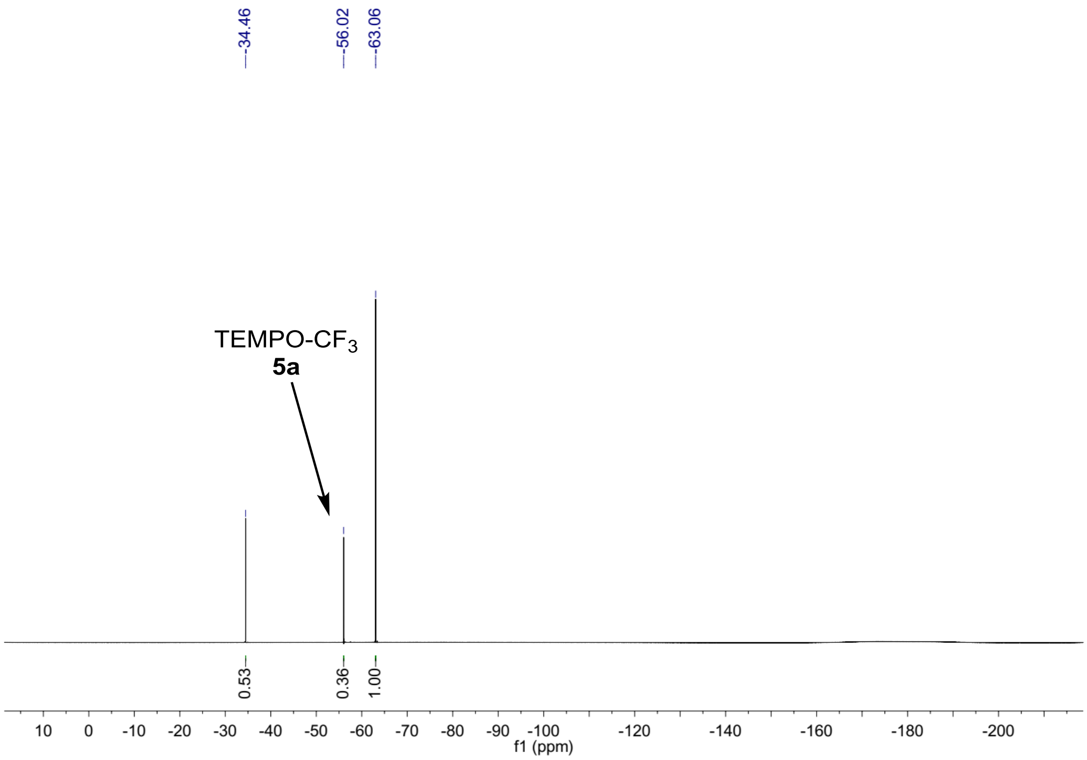
To a solution of **3a** (50.8 mg, 0.2 mmol) in 1 mL of dry THF was added PhMgBr (0.4 mmol, 2.5 M in THF) at 0 °C. After stirring at 0 ℃ for 2 h, the reaction mixture was quenched with saturated NH_4Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous $MgSO_4$ and concentrated to give the crude alcohol. To a solution of the crude alcohol obtained above in 2 mL of PhMe was added TsOH (6.7 mg, 0.04 mmol) at 25 ℃. After stirring at reflux for 2 h, the reaction mixture was quenched with saturated K_2CO_3 solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4 and concentrated. Column chromatography on silica gel using petroleum ethers as the eluent gave 49 mg (78% yield) of **4e** as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44-7.33 (m, 8H), 7.18-7.15 (m, 2H), 6.30 (s, 1H), 1.22 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.15 (q, J = 4.5 Hz), 145.10, 139.77, 135.80, 134.75, 128.19 (q, J = 1.7 Hz), 128.17 (q, J = 1.4 Hz), 128.00, 127.98, 127.67, 127.49, 125.96, 122.57 (q, J = 272.4 Hz), 54.19, 21.09. ^{19}F NMR (565 MHz, $CDCl_3$) δ -55.69. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{20}H_{17}F_3+H^+$: 315.1355; Found 315.1349.

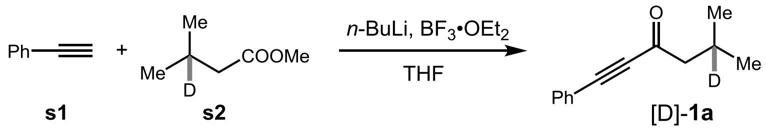
3. Mechanistic experiments



To a mixture of CuCN (1.8 mg, 0.02 mmol), **2a** (94.8 mg, 0.3 mmol), TEMPO (62.5 mg, 0.4 mmol) and K_2CO_3 (55.3 mg, 0.4 mmol) in 2 mL of EtOAc was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After stirring at 50 °C for 16 h, the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated to give **5a**[2] in 36% ^{19}F NMR yield using $PhCF_3$ as the internal standard.

[2] Z. Xiong, F. Zhang, Y. Yu, Z. Tan and G. Zhu, *Org. Lett.*, 2020, **22**, 4088.



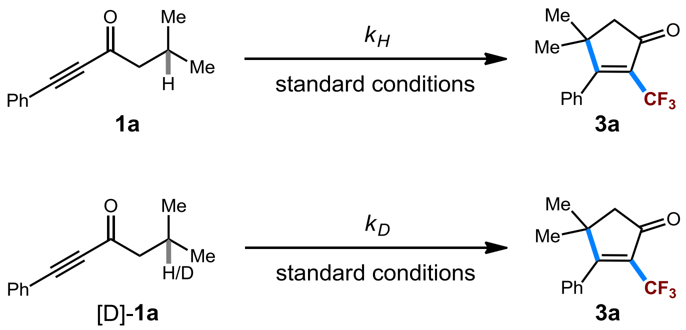


To a solution of phenylacetylene (**s1**, 612 mg, 6.0 mmol) in 15 mL of dry THF was added *n*-BuLi (2.5 M in hexanes, 2.4 mL, 6.0 mmol) at -78 ^{o}C under nitrogen atmosphere. After stirring at -78 ^{o}C for 1 h, BF_3•Et_2O (1.7 g, 12 mmol) and **s2** (585 mg, 5 mmol, 75% D), prepared from methyl 3-methylbut-2-enoate using $NaBD_4$ and $CoSO_4$•$7H_2O$ using the known method,[3] was added. After stirring at 25 ^{o}C for 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 486 mg (52% yield) of [D]-**1a** with 75% deuterium incorporation as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58-7.57 (m, 2H), 7.47-7.44 (m, 1H), 7.40-7.37 (m, 2H), 2.55-2.52 (m, 2H), 2.37-2.30 (m, 0.25H), 1.01 (d, J = 7.9 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.0, 133.0, 130.7, 128.6, 120.1, 90.5, 88.1, 54.4, 25.0, 24.9, 24.7, 22.4. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for

[3] F. J. Lundevall, V. Elumalai, A. Drageset, C. Totland and H.-R. Bjørsvik, *Eur. J. Org. Chem.*, 2018, 3416.

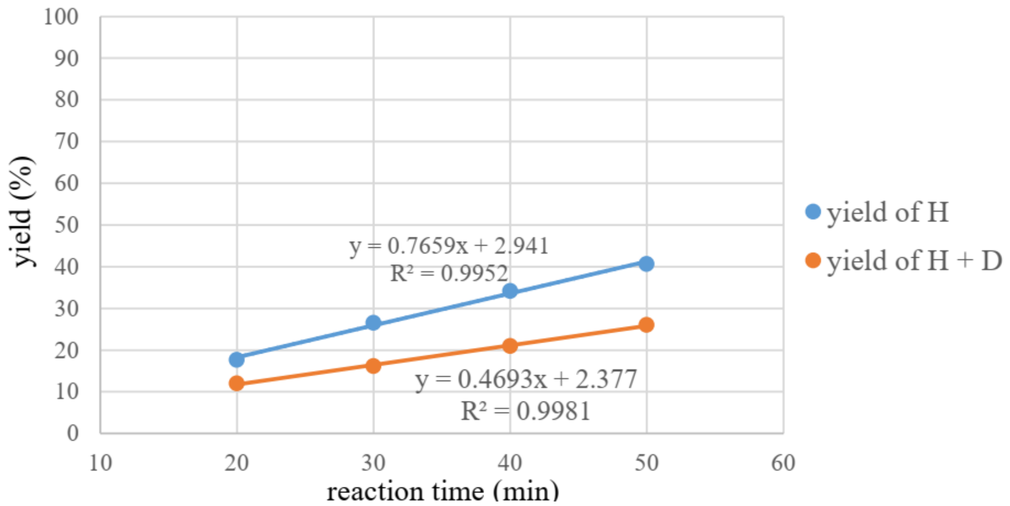
$C_{13}H_{13}DO+H^+$: 188.1180; Found 188.1166.

Determination of the KIE values



The method to calculate KIE is according to the reported method[4] through parallel reactions of **1a** and [D]-**1a** (75% D) using the general produre with *n*-dodecane as the internal standard.

time (min)	20	30	40	50
yield of *H*	0.1766	0.2653	0.3415	0.4065
yield of *H+D*	0.1201	0.1615	0.2102	0.2603



Adjusted initial rates:

k_H=0.7659

0.4693=k_Hx25%+k_Dx75%

k_D=0.3704

KIE=k_H/k_D=2.07

[4] (a) X.-H. Yang, R. Davison, S.-Z. Nie, F. A. Cruz, T. M. McGinnis and V. M. Dong, *J. Am. Chem. Soc.*, 2019, **141**, 3006; (b) C. Obradors, R. M. Martinez and R. A. Shenvi, *J. Am. Chem. Soc.*, 2016, **138**, 4962.

4. Computational data

Computational details: All density functional theory (DFT) calculations were performed using Gaussian 16.[5] Geometry optimizations and frequencies were calculated at the B3LYP-D3(BJ)/6-31G(d)-SDD(Cu,I)-SMD(EtOAc) level of theory.[6] 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 B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc) level of theory with the optimized structures. Structures were generated using CYLview.[7] Grimme's quasi-RRHO correction[8] 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.[9]

The Gibbs free energy profile for the mechanism of Cu-catalyzed trifluoromethylative *endo*-carbocyclization of ynones is shown in Figure S1. The reaction is initiated by electron transfer from Cu(I) to **2a**, producing CF_3 radical and Cu(II) species **Int1**. Coordination of **Int1** with **1a** leads to a stable carbonyl-coordinated Cu(II) complex **Int2**, which is exergonic by 6.1 kcal/mol. Addition of CF_3 radical to **Int2** at the alkynyl carbon atom α to the carbonyl group proceeds via transition state $\mathbf{TS_{2\text{-}3a}}$ to give vinyl radical intermediate **Int3a**, which is highly exergonic by 21.9 kcal/mol. Subsequently, 1,5-HAT occurs to form a more stable tertiary alkyl radical intermediate **Int4a**, through transition state $\mathbf{TS_{3a\text{-}4a}}$ that requires a Gibbs free energy barrier of 10.8 kcal/mol. This step is calculated to be the rate-determining step, which is consistent with the observed significant KIE value (2.1). Then, 5-*endo-trig* cyclization of **Int4a** results in the formation of α-carbonyl radical **Int5a**, with an activation free energy of 5.6 kcal/mol. Combined with K_2CO_3, an adduct **Int5b** that lies 24.8 kcal/mol lower in energy than **Int5a** is formed.

---

5 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, J. 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.; Fox, D. J. *Gaussian 16, Revision A.03*, Gaussian, Inc., Wallingford CT, 2016.

6 (a) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter Mater. Phys.* 1988, **37**, 785; (b) D. Andrae, U. Haußermann, M. Dolg, H. Stoll and H. Preuß, *Theor. Chim. Acta*. 1990, **77**, 123.

7 C. Y. Legault, CYL view 1.0b; Université de Sherbrooke, Sherbrooke, Canada, 2009; http://www.cylview.org.

8 S. Grimme, *Chem. Eur. J*. 2012, **18**, 9955.

9 G. Luchini, J. Alegre-Requena, I. Funes, J. Rodríguez-Guerra, J. Chen and R. S. Paton, 2019, GoodVibes: GoodVibes 3.0.0 http://doi.org/10.5281/zenodo.595246.

Afterward, proton transfer takes place with an activation free energy of only 3.8 kcal/mol to afford radical anion **Int6**. Electron transfer from this radical anion to Cu(II) via **MECP1** would deliver **3a** as well as regenerate Cu(I). Notably, the SET oxidation of α-carbonyl radical **Int5a** by Cu(II) followed by deprotonation is also a possible pathway leading to **3a**. However, calculations indicate that the SET oxidation via **MECP2** has an electronic barrier of 15.2 kcal/mol, which is much less favored than the above mentioned pathway.

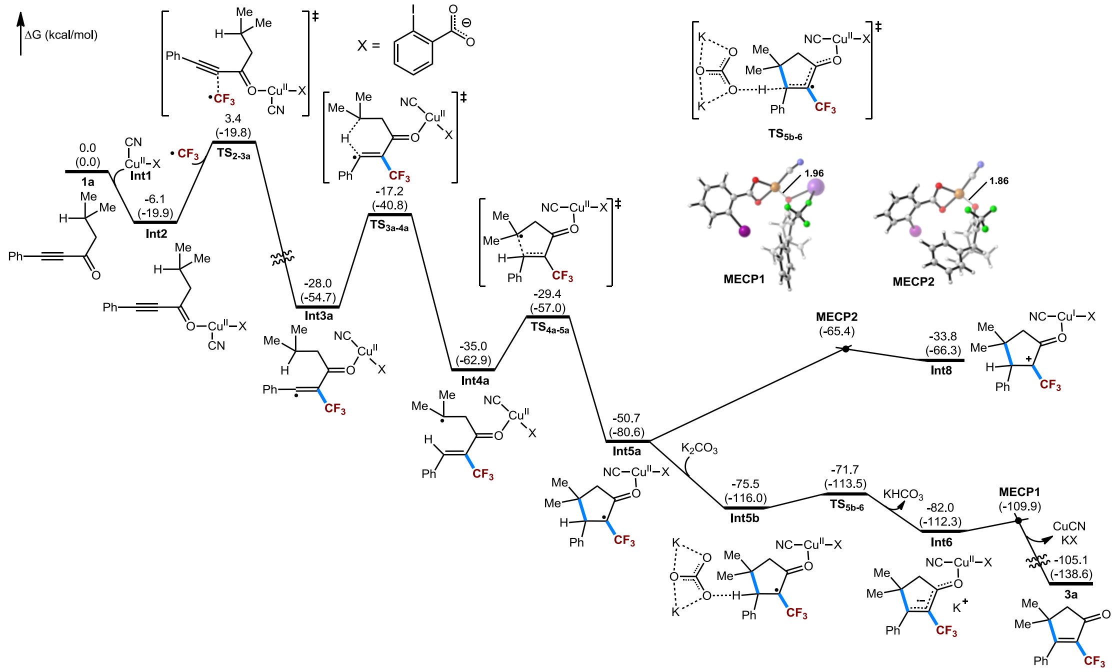


Figure S1. The relative free energies (ΔG) and relative electronic energies (ΔE, in parentheses) of intermediates and transition-states for the model reaction at the B3LYP-D3(BJ)/6-311+G(d,p) -SDD(Cu,I)-SMD(EtOAc)//B3LYP-D3(BJ)/6-31G(d)-SDD(Cu,I)-SMD(EtOAc) level of theory at 298.15 K. All energies are in kcal/mol.

The calculated Cartesian coordinates and energies of structures.

1a

C	-0.61385	0.60934	-0.18605
C	2.90434	-0.92414	0.142
C	2.9143	0.31691	-0.77617
C	1.92789	1.39046	-0.36322
C	0.54387	0.97463	-0.27081
H	3.9094	0.77496	-0.79325
H	2.6628	0.00758	-1.80043
O	2.25698	2.54553	-0.11893
C	-1.96671	0.18208	-0.086
C	-2.30314	-1.16387	-0.33238
C	-2.97861	1.09878	0.26143
C	-3.62698	-1.57964	-0.23142
H	-1.52031	-1.86666	-0.59925
C	-4.2994	0.67207	0.35872
H	-2.71531	2.13448	0.45051
C	-4.62575	-0.66465	0.11341
H	-3.8815	-2.61814	-0.42143
H	-5.07627	1.38201	0.62652
H	-5.65811	-0.99335	0.19097

C	3.86846	-1.98369	-0.39973
H	3.60758	-2.27618	-1.42391
H	4.89932	-1.60695	-0.40995
H	3.84867	-2.8848	0.22464
C	3.24847	-0.54756	1.58704
H	4.24607	-0.09342	1.64484
H	2.53033	0.16894	2.0028
H	3.24498	-1.43399	2.23199
H	1.88919	-1.34304	0.12643

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -579.210640381 hartree

Corrected Gibbs Free Energy = -579.01657 hartree

3a

C	-0.11456	0.54423	0.08445
C	-0.52424	2.01552	-0.08917
C	-2.06587	1.96945	0.01032
C	-2.44861	0.49857	-0.0276
C	-1.19114	-0.27329	0.11732
H	-2.42018	2.38553	0.96151
H	-2.56846	2.51843	-0.79133
O	-3.57224	0.04482	-0.15751
C	-1.20876	-1.76553	0.18976
F	-0.07203	-2.28896	0.70036
F	-1.37945	-2.31874	-1.03929
F	-2.22232	-2.21128	0.96285
C	1.30315	0.12557	0.05083
C	2.20547	0.48133	1.06395
C	1.76312	-0.63046	-1.03983
C	3.54068	0.0857	0.98581
H	1.85919	1.03942	1.92651
C	3.10143	-1.00864	-1.12184
H	1.06385	-0.91905	-1.81867
C	3.99416	-0.65164	-0.10911
H	4.22622	0.35464	1.78432
H	3.44462	-1.58792	-1.97424
H	5.03636	-0.95169	-0.17028
C	0.08734	2.94315	0.97116
H	-0.31901	3.95264	0.84254
H	-0.15488	2.60754	1.98567
H	1.17475	3.00659	0.87395
C	-0.07583	2.47148	-1.49338
H	1.01167	2.40649	-1.59973
H	-0.53491	1.85447	-2.27398
H	-0.37523	3.5125	-1.65732

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -916.416875676 hartree

Corrected Gibbs Free Energy = -916.217277 hartree

CF_3•

C	0.00004	0.00025	0.32887
F	1.0608	-0.68858	-0.07307
F	-1.12676	-0.57438	-0.07306
F	0.06593	1.2628	-0.07312

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -337.670228227 hartree

Corrected Gibbs Free Energy = -337.681950 hartree

Int1

Cu	2.8856	-0.35776	-0.01454
C	0.75829	0.65467	-0.01797
O	0.95854	-0.614	-0.02503
O	1.81666	1.37728	-0.01707
C	-0.57768	1.27694	-0.00863
C	-0.59979	2.68665	-0.00779
C	-1.80537	0.5875	0.00234
C	-1.79504	3.39117	0.00366
H	0.34756	3.21349	-0.01596
C	-3.00726	1.2955	0.01431
C	-3.00185	2.69079	0.01504
H	-1.78593	4.47626	0.00412
H	-3.94945	0.75992	0.02312
H	-3.94726	3.22496	0.02459
C	4.77801	-0.11485	0.02551
N	5.93606	0.01826	0.05175
I	-2.01127	-1.55366	0.00381

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -721.439621570 hartree

Corrected Gibbs Free Energy = --721.377300 hartree

Int2

C	-1.26498	1.25445	0.65013
C	-5.11055	0.91903	-0.69535
C	-3.98122	0.45333	-1.65593

C	-2.85053	-0.1689	-0.89894
C	-2.04061	0.64542	-0.06789
H	-4.36839	-0.28226	-2.36779
H	-3.59787	1.32	-2.20791
O	-2.64009	-1.40501	-0.95654
C	-0.33408	1.93045	1.47205
C	-0.3586	3.33661	1.57098
C	0.64668	1.19037	2.16623
C	0.5912	3.98831	2.34983
H	-1.11799	3.89598	1.03446
C	1.59013	1.85549	2.94035
H	0.65797	0.109	2.08852
C	1.56522	3.25094	3.03139
H	0.57483	5.07099	2.42722
H	2.34626	1.2866	3.47255
H	2.30567	3.76547	3.63682
C	-6.20365	1.62202	-1.5053
H	-5.80342	2.47701	-2.06278
H	-6.66206	0.93213	-2.22489
H	-6.99504	1.98949	-0.84194
C	-5.67644	-0.25446	0.1111
H	-6.07917	-1.02755	-0.55561
H	-4.91975	-0.72415	0.74984
H	-6.49081	0.08682	0.76015
Cu	-1.20426	-2.07492	0.33847
C	1.14583	-1.77631	0.10024
O	0.32575	-1.62006	-0.8646
O	0.68573	-2.22531	1.20407
C	2.59036	-1.46112	-0.02653
C	3.4813	-2.30825	0.65654
C	3.11654	-0.3867	-0.76164
C	4.85578	-2.11405	0.58502
H	3.06978	-3.12888	1.23442
C	4.49402	-0.17649	-0.82091
C	5.36111	-1.04611	-0.15718
H	5.52685	-2.78798	1.10796
H	4.89126	0.66443	-1.3779
H	6.43216	-0.87693	-0.21839
C	-2.44294	-2.51991	1.75288
N	-3.2119	-2.74214	2.60205
H	-4.67214	1.64503	0.00214
I	1.89227	1.08587	-1.7459

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1300.68201570 hartree

Corrected Gibbs Free Energy = -1300.403585 hartree

Int3a

C	-3.20134	-0.89523	-0.75795
C	-4.23468	1.73568	1.22232
C	-3.094	0.76058	1.63415
C	-1.99291	0.74145	0.6153
C	-2.17898	-0.07216	-0.61996
H	-2.66266	1.08696	2.58491
H	-3.50433	-0.2445	1.76059
O	-0.98035	1.42662	0.81717
C	-1.18715	0.05986	-1.75603
F	-1.47492	-0.77342	-2.76792
F	0.08212	-0.21478	-1.36038
F	-1.17622	1.31735	-2.25296
C	-4.35726	-1.56755	-0.4224
C	-5.63339	-1.0447	-0.79382
C	-4.29278	-2.80829	0.28205
C	-6.78524	-1.7299	-0.44491
H	-5.68293	-0.11017	-1.34155
C	-5.46236	-3.47068	0.61577
H	-3.32353	-3.21105	0.55582
C	-6.71107	-2.94058	0.2595
H	-7.75262	-1.32188	-0.72183
H	-5.40727	-4.40842	1.16046
H	-7.62072	-3.46923	0.52659
C	-5.41222	1.55685	2.18477
H	-5.79002	0.52808	2.1645
H	-5.11647	1.79208	3.21489
H	-6.23581	2.22629	1.91086
C	-3.74997	3.18804	1.18453
H	-3.38004	3.50166	2.16888
H	-2.9428	3.34138	0.4601
H	-4.57403	3.85545	0.90745
Cu	0.74319	2.11759	-0.00891
C	2.88532	1.10903	0.15231
O	1.86203	0.65277	0.76192
O	2.73458	2.17566	-0.53383
C	4.2194	0.46957	0.25417
C	5.32917	1.33306	0.27501
C	4.44325	-0.91281	0.35075
C	6.62082	0.83983	0.41938
H	5.15191	2.39981	0.18936

C	5.73786	-1.41405	0.4797
C	6.8229	-0.53644	0.52517
H	7.46289	1.52414	0.4459
H	5.90333	-2.48368	0.54003
H	7.82603	-0.93787	0.63524
C	-0.02659	3.74606	-0.70679
N	-0.52042	4.7247	-1.10654
H	-4.57077	1.45529	0.2169
I	2.86922	-2.37539	0.18823

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.40767619 hartree
Corrected Gibbs Free Energy = -1638.120434 hartree

Int4a

C	-1.63692	1.70888	-0.72857
C	-4.71202	-0.35311	-1.3906
C	-3.45705	-0.26178	-2.21949
C	-2.42071	-0.56236	-1.16413
C	-2.01134	0.50856	-0.22219
H	-3.4131	-1.03027	-2.99568
H	-3.3394	0.73094	-2.65837
O	-2.06595	-1.75386	-1.01262
C	-2.07044	0.17323	1.24552
F	-2.56264	1.19564	1.97428
F	-0.85865	-0.1473	1.78162
F	-2.8789	-0.88622	1.4731
C	-1.07834	2.91824	-0.13368
C	-1.12367	4.08168	-0.93037
C	-0.45333	2.9938	1.12851
C	-0.60223	5.28735	-0.47179
H	-1.57865	4.0289	-1.91579
C	0.08028	4.19787	1.57693
H	-0.34488	2.11391	1.74536
C	0.00215	5.34837	0.78594
H	-0.65598	6.17318	-1.09738
H	0.56869	4.23556	2.54593
H	0.42152	6.28384	1.14446
C	-5.22804	0.85628	-0.68293
H	-6.32587	0.84878	-0.66162
H	-4.90103	0.88362	0.36959
H	-4.89363	1.78622	-1.15404
C	-5.23894	-1.69838	-1.01903
H	-5.02981	-2.44952	-1.78806
H	-4.78684	-2.06296	-0.08137
H	-6.32156	-1.65716	-0.84831
Cu	-0.59484	-2.57166	0.10053
C	1.70513	-1.96423	-0.00258
O	0.79521	-1.383	-0.68705
O	1.34776	-2.89947	0.78428
C	3.14128	-1.62249	-0.16017
C	4.04572	-2.69843	-0.16527
C	3.64048	-0.32293	-0.33628
C	5.40474	-2.49089	-0.37512
H	3.6565	-3.70019	-0.01691
C	5.00401	-0.10758	-0.53003
C	5.88186	-1.19329	-0.56221
H	6.0861	-3.33571	-0.38955
H	5.38359	0.90096	-0.6496
H	6.94095	-1.01575	-0.72473
C	-1.66004	-3.94541	0.94476
N	-2.31286	-4.7723	1.44606
I	2.38752	1.41821	-0.1758
H	-1.75474	1.79602	-1.80581

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.42083735 hartree
Corrected Gibbs Free Energy = -1638.131533 hartree

Int5a

C	3.43679	-0.21385	0.38578
C	4.31002	0.32767	-0.8096
C	3.27891	1.02077	-1.73324
C	2.13557	1.42196	-0.83277
C	2.27221	0.71796	0.41991
H	4.00556	-0.13952	1.31848
H	3.67643	1.88949	-2.26671
H	2.88055	0.33156	-2.49038
O	1.24234	2.22221	-1.18055
C	1.37278	0.81437	1.6113
F	2.0504	0.59001	2.75095
F	0.36411	-0.0752	1.55283
F	0.8081	2.04803	1.71939
C	2.92969	-1.65573	0.29674
C	3.33726	-2.5808	1.26578
C	2.05803	-2.07655	-0.72007
C	2.90835	-3.90708	1.20788
H	3.99917	-2.25956	2.0654

C	1.63755	-3.40572	-0.78333
H	1.7006	-1.37805	-1.46905
C	2.05895	-4.32442	0.18058
H	3.24126	-4.6136	1.96274
H	0.97784	-3.72065	-1.58688
H	1.72776	-5.35758	0.13103
C	5.26629	1.38974	-0.24194
H	5.84123	1.85705	-1.04897
H	4.72059	2.1835	0.28415
H	5.9722	0.93956	0.46511
C	5.10579	-0.76074	-1.52761
H	5.78503	-1.26823	-0.83313
H	4.45396	-1.51591	-1.97599
H	5.71096	-0.31593	-2.32579
Cu	-0.54855	2.74703	-0.36858
C	-2.40473	1.28026	-0.14193
O	-1.33799	0.96887	-0.77541
O	-2.44713	2.44346	0.38306
C	-3.57556	0.37475	-0.0478
C	-4.8239	0.99784	0.13938
C	-3.53756	-1.02685	-0.15427
C	-5.99923	0.25938	0.19839
H	-4.84742	2.07843	0.22572
C	-4.71491	-1.77187	-0.0841
C	-5.94267	-1.12969	0.08357
H	-6.95072	0.76362	0.33398
H	-4.67583	-2.85292	-0.15637
H	-6.85116	-1.72319	0.12853
C	-0.12034	4.59615	-0.01048
N	0.15209	5.71117	0.19801
I	-1.71928	-2.16542	-0.32637

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.44906459 hartree

Corrected Gibbs Free Energy = -1638.156616 hartree

Int5b

C	2.06139	1.28171	0.69147
C	1.69663	1.26632	2.23093
C	1.57242	-0.24876	2.52189
C	1.13568	-0.8559	1.20695
C	1.39146	0.01271	0.18007
H	3.15342	1.14987	0.66011
H	2.54539	-0.68216	2.7942
H	0.86652	-0.47936	3.32713
O	0.69372	-2.0896	1.17452
C	1.21021	-0.32265	-1.23765
F	1.98598	0.45847	-2.06538
F	-0.06018	-0.19022	-1.72188
F	1.55168	-1.61754	-1.55293
C	1.75744	2.58016	-0.02607
C	2.73813	3.58331	-0.08695
C	0.51916	2.82327	-0.63625
C	2.48706	4.79748	-0.73438
H	3.70198	3.41763	0.39253
C	0.26458	4.0329	-1.2824
H	-0.24404	2.05453	-0.61398
C	1.24715	5.02626	-1.33436
H	3.25952	5.56137	-0.7668
H	-0.70214	4.19648	-1.75173
H	1.04869	5.96717	-1.83987
C	2.79131	1.93408	3.06417
H	2.56415	1.85594	4.13431
H	3.76529	1.46297	2.88757
H	2.87625	2.99996	2.82071
C	0.34466	1.93993	2.49904
H	0.37186	3.00778	2.25925
H	-0.45739	1.47965	1.9139
H	0.08719	1.83874	3.56
Cu	-0.84611	-2.59762	0.08667
C	-2.98819	-1.55543	-0.08837
O	-2.0798	-1.1012	0.68036
O	-2.71565	-2.58007	-0.79866
C	-4.35962	-0.97896	-0.12432
C	-5.41411	-1.8946	-0.29159
C	-4.67619	0.37949	0.02875
C	-6.74066	-1.47864	-0.27725
H	-5.16614	-2.94269	-0.41982
C	-6.00415	0.80595	0.02826
C	-7.03475	-0.12488	-0.11356
H	-7.53813	-2.20562	-0.39515
H	-6.23632	1.85965	0.13423
H	-8.06549	0.21717	-0.10239
C	0.0113	-4.22994	-0.57843
N	0.72845	-5.09609	-0.89866
I	-3.18104	1.92173	0.16284
C	4.94634	-1.01726	0.46728
O	5.41754	0.15149	0.64738

O	4.65927	-1.4493	-0.69484
O	4.74299	-1.75407	1.49212
K	4.5791	1.03247	-1.8415
K	2.86392	-3.42303	0.13434

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -3102.43162934 hartree
Corrected Gibbs Free Energy = 3102.136319 hartree

Int6

C	1.94105	1.59079	0.5329
C	2.06466	1.53405	2.06992
C	1.66908	0.06383	2.39335
C	1.79631	-0.67392	1.09017
C	1.94554	0.23634	0.05235
H	2.28875	-0.38496	3.17897
H	0.62331	-0.00528	2.72547
O	1.73803	-1.98936	1.03172
C	2.13861	-0.21395	-1.34921
F	2.73186	0.69311	-2.14502
F	0.97705	-0.58595	-1.97103
F	2.94217	-1.33559	-1.42833
C	1.70703	2.78991	-0.23268
C	2.18906	4.05929	0.18467
C	0.93467	2.76604	-1.42682
C	1.91907	5.21494	-0.54039
H	2.80801	4.13276	1.07062
C	0.66688	3.92527	-2.14503
H	0.51112	1.83068	-1.76882
C	1.15511	5.16322	-1.71137
H	2.31589	6.16538	-0.19245
H	0.06177	3.86305	-3.04605
H	0.94447	6.06799	-2.27421
C	3.53106	1.75704	2.50106
H	3.62908	1.63862	3.58773
H	4.18951	1.02554	2.01691
H	3.88944	2.75673	2.23712
C	1.1312	2.50399	2.80913
H	1.40904	3.55025	2.6572
H	0.09633	2.37641	2.47302
H	1.16621	2.30298	3.88692
Cu	0.16421	-2.7044	0.06452
C	-2.05927	-1.83666	0.09129
O	-1.11066	-1.33321	0.77921
O	-1.80862	-2.88139	-0.59521
C	-3.42568	-1.25493	0.11211
C	-4.50094	-2.15965	0.11462
C	-3.70275	0.12147	0.14843
C	-5.81567	-1.71162	0.18441
H	-4.28079	-3.2213	0.07412
C	-5.02048	0.57538	0.1999
C	-6.07339	-0.34119	0.23018
H	-6.63267	-2.42624	0.19858
H	-5.22747	1.63971	0.21105
H	-7.09493	0.02438	0.28005
C	1.14574	-4.18471	-0.75255
N	1.93069	-4.96274	-1.13323
I	-2.16564	1.61939	-0.01896
K	3.86181	-3.3084	0.13606

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -2237.89238729 hartree
Corrected Gibbs Free Energy = -2237.614148 hartree

Int7

C	0.36894	-0.47837	0.94692
C	-1.3286	1.40975	-0.00654
C	-2.67732	1.1888	0.75922
C	-2.12076	-0.1063	1.30633
C	-0.93163	-0.12428	0.29605
H	0.26877	-0.98988	1.90082
H	-2.96938	1.94037	1.499
H	-3.52104	0.99898	0.0861
O	-2.36629	-0.81348	2.24952
C	-1.26678	-1.10607	-0.82526
F	-1.11246	-2.38129	-0.40919
F	-0.49141	-0.94917	-1.9208
F	-2.55636	-0.99416	-1.24405
C	1.68191	-0.24262	0.47869
C	2.77756	-0.63669	1.30341
C	1.99397	0.37593	-0.76657
C	4.08887	-0.42047	0.91248
H	2.56424	-1.11234	2.2571
C	3.31126	0.58928	-1.14551
H	1.19479	0.67057	-1.43384
C	4.36917	0.19708	-0.31466
H	4.90256	-0.73098	1.56231

H	3.52128	1.06337	-2.10055
H	5.39736	0.36753	-0.61984
C	-0.43097	2.37277	0.77261
H	-0.87559	3.37443	0.75136
H	-0.32393	2.0739	1.82119
H	0.56964	2.43406	0.33583
C	-1.47239	1.8679	-1.45512
H	-0.49981	1.93876	-1.95275
H	-2.11594	1.21139	-2.04447
H	-1.91998	2.86893	-1.46432

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -916.958139716 hartree
Corrected Gibbs Free Energy = -916.749894 hartree

Int8

C	2.26777	-2.00617	0.00878
C	2.08651	-2.19931	-1.55586
C	1.72985	-0.77919	-2.08109
C	2.2677	0.15308	-1.02702
C	2.52383	-0.54227	0.14325
H	3.15596	-2.56277	0.33644
H	2.16441	-0.5662	-3.06311
H	0.64492	-0.63427	-2.15958
O	2.46458	1.42567	-1.20028
C	2.87864	0.1274	1.43122
F	3.19579	-0.75806	2.39118
F	1.82393	0.86358	1.89758
F	3.91181	0.98102	1.29677
C	1.12484	-2.47703	0.90413
C	1.26634	-3.66722	1.62887
C	-0.07361	-1.75836	1.00483
C	0.22197	-4.14227	2.42199
H	2.197	-4.22521	1.5642
C	-1.1179	-2.23091	1.8005
H	-0.19547	-0.83537	0.45279
C	-0.97401	-3.42412	2.51092
H	0.34244	-5.07179	2.97147
H	-2.04257	-1.66415	1.86231
H	-1.78564	-3.79161	3.13259
C	3.44522	-2.62569	-2.13296
H	3.39495	-2.69911	-3.22525
H	4.22976	-1.90234	-1.87896
H	3.74568	-3.60377	-1.73936
C	1.01672	-3.22667	-1.92443
H	1.25876	-4.2142	-1.5155
H	0.0306	-2.93744	-1.54912
H	0.95223	-3.32047	-3.01499
Cu	1.12228	2.51897	-0.39397
C	-1.07607	1.91885	0.2302
O	-0.28633	1.19108	-0.47937
O	-0.62205	3.067	0.54855
C	-2.38431	1.43696	0.69907
C	-2.88237	2.03103	1.87422
C	-3.12906	0.41033	0.08925
C	-4.07717	1.60559	2.44024
H	-2.30085	2.81953	2.3394
C	-4.33211	-0.01154	0.6522
C	-4.79883	0.57992	1.82852
H	-4.44108	2.06837	3.3516
H	-4.90748	-0.79789	0.17741
H	-5.73383	0.2346	2.25942
C	2.26594	4.02024	-0.25046
N	2.96119	4.95149	-0.15419
I	-2.57202	-0.53606	-1.75842

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.42623790 hartree
Corrected Gibbs Free Energy = -1638.129723 hartree

TS$_{2\text{-}3a}$

C	-3.52081	-0.26274	0.46023
C	-3.96163	3.27828	-0.11014
C	-2.58098	3.06044	0.56594
C	-1.94661	1.77308	0.13289
C	-2.59839	0.55099	0.49257
H	-1.89898	3.87683	0.30853
H	-2.71178	3.03462	1.6547
O	-0.90625	1.78286	-0.55621
C	-0.85494	-0.5122	1.85415
F	-1.57477	-1.00603	2.85543
F	0.06539	0.33267	2.30875
F	-0.28136	-1.51014	1.17237
C	-4.47654	-1.29486	0.45366
C	-4.36007	-2.35135	-0.47798
C	-5.54866	-1.27685	1.3737
C	-5.3034	-3.37147	-0.47727
H	-3.54369	-2.34149	-1.1922

C	-6.47768	-2.30954	1.3661
H	-5.62895	-0.45905	2.08234
C	-6.35711	-3.35481	0.44328
H	-5.21908	-4.18263	-1.19381
H	-7.29884	-2.30229	2.07627
H	-7.08833	-4.15787	0.44046
C	-4.54577	4.6139	0.35823
H	-4.63547	4.65284	1.45026
H	-3.91251	5.45151	0.03993
H	-5.54318	4.76617	-0.06993
C	-3.85314	3.21709	-1.63751
H	-3.14091	3.96406	-2.01064
H	-3.5245	2.23215	-1.98886
H	-4.82648	3.42212	-2.0974
Cu	-0.08933	0.12186	-1.39286
C	2.05626	-0.77389	-0.90175
O	1.61727	0.31352	-0.39524
O	1.30793	-1.36629	-1.75091
C	3.3539	-1.3755	-0.50734
C	3.49462	-2.75539	-0.74869
C	4.4234	-0.69353	0.09789
C	4.64797	-3.44038	-0.38823
H	2.66814	-3.27591	-1.21913
C	5.58857	-1.37514	0.45109
C	5.69702	-2.74617	0.21481
H	4.72809	-4.5061	-0.57764
H	6.41225	-0.83903	0.90843
H	6.60749	-3.26437	0.5014
C	-1.58649	-0.29298	-2.54293
N	-2.51429	-0.53755	-3.2078
H	-4.62412	2.47034	0.22523
I	4.44527	1.42747	0.47667

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.35229620 hartree
Corrected Gibbs Free Energy = -1638.070334 hartree

TS$_{3a\text{-}4a}$

C	-3.67439	-0.29508	0.20604
C	-4.41465	1.90298	1.3907
C	-3.04546	1.79653	2.06493
C	-1.99509	1.16022	1.18172
C	-2.36681	-0.02786	0.38779
H	-2.66603	2.77518	2.37958
H	-3.12501	1.1621	2.95868
O	-0.84399	1.63087	1.18917
C	-1.24022	-0.84901	-0.1952
F	-1.66326	-1.95487	-0.82319
F	-0.36289	-1.22723	0.7561
F	-0.52311	-0.14192	-1.1249
C	-4.50225	-1.29621	-0.4007
C	-5.58596	-0.87825	-1.20476
C	-4.33352	-2.67326	-0.1356
C	-6.43921	-1.81671	-1.7738
H	-5.73213	0.1819	-1.38873
C	-5.21523	-3.59955	-0.68187
H	-3.5224	-3.0005	0.50445
C	-6.26047	-3.17852	-1.51011
H	-7.25434	-1.48669	-2.41088
H	-5.08273	-4.65586	-0.46704
H	-6.93899	-3.90863	-1.94134
C	-5.59386	1.81984	2.3338
H	-5.5491	0.91824	2.95555
H	-5.6092	2.68943	3.00848
H	-6.53944	1.81457	1.78069
C	-4.49716	2.98777	0.33615
H	-4.45479	3.9794	0.81104
H	-3.669	2.9343	-0.3793
H	-5.43978	2.92788	-0.21904
Cu	0.5484	1.9589	-0.26225
C	2.79588	1.21476	-0.37092
O	2.03713	0.97434	0.62639
O	2.31722	1.92795	-1.31544
C	4.19696	0.73312	-0.43722
C	5.14059	1.6182	-0.98776
C	4.6366	-0.51908	0.01892
C	6.48798	1.28137	-1.05225
H	4.79434	2.58033	-1.35015
C	5.9839	-0.8688	-0.0592
C	6.90858	0.03639	-0.58372
H	7.20316	1.98374	-1.46846
H	6.3129	-1.84373	0.28222
H	7.95701	-0.24299	-0.63108
C	-0.65205	3.04163	-1.3253
N	-1.42167	3.66826	-1.93911
H	-4.36438	0.78189	0.75078
I	3.29403	-2.03714	0.74567

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SM

D(EtOAc): E = -1638.38554492 hartree
Corrected Gibbs Free Energy = -1638.103171 hartree

TS$_{4\text{-}7}$

C	0.42036	0.60468	0.75758
C	-1.95535	1.26434	-0.82926
C	-2.42982	1.73749	0.53979
C	-1.98918	0.50379	1.30616
C	-0.80761	-0.02097	0.48691
H	0.32749	1.49889	1.3712
H	-1.88331	2.62491	0.88022
H	-3.5037	1.93268	0.62752
O	-2.51715	-0.05266	2.24123
C	-0.90601	-1.44698	0.01074
F	-0.07015	-2.29135	0.66088
F	-0.61641	-1.56811	-1.31625
F	-2.15352	-1.9448	0.16354
C	1.78205	0.34867	0.34864
C	2.78296	1.16254	0.93982
C	2.20805	-0.62426	-0.58793
C	4.12748	1.00441	0.63144
H	2.48145	1.92238	1.65637
C	3.55599	-0.7748	-0.8944
H	1.48915	-1.24946	-1.09592
C	4.52602	0.02969	-0.28876
H	4.86751	1.64241	1.10683
H	3.85276	-1.52714	-1.6202
H	5.57628	-0.09719	-0.53494
C	-0.98254	2.09732	-1.60391
H	-1.51406	2.92837	-2.09523
H	-0.2097	2.53164	-0.96312
H	-0.49367	1.50989	-2.38915
C	-2.94214	0.46613	-1.63182
H	-2.45098	-0.11556	-2.41739
H	-3.53788	-0.21233	-1.01443
H	-3.64509	1.15784	-2.12518

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -916.932729439 hartree
Corrected Gibbs Free Energy = -916.728062 hartree

TS$_{4a\text{-}5a}$

C	-3.17364	0.54548	0.15894
C	-2.39454	0.54765	2.72755
C	-2.21031	1.99257	2.33388
C	-1.53591	2.13488	0.97441
C	-2.08208	1.36271	-0.11429
H	-3.85746	0.88744	0.92592
H	-3.17987	2.50819	2.31374
H	-1.57215	2.52455	3.05409
O	-0.49839	2.83791	0.91041
C	-1.42645	1.43845	-1.46373
F	-2.20662	0.96076	-2.45099
F	-0.23812	0.76658	-1.54678
F	-1.14472	2.72377	-1.78605
C	-3.59321	-0.68237	-0.47802
C	-4.9235	-1.11181	-0.27994
C	-2.70618	-1.51947	-1.19085
C	-5.36731	-2.31463	-0.81689
H	-5.60058	-0.48533	0.29421
C	-3.15019	-2.72856	-1.70982
H	-1.66772	-1.23735	-1.30658
C	-4.48138	-3.12479	-1.53369
H	-6.39633	-2.62782	-0.66961
H	-2.4578	-3.36842	-2.24857
H	-4.82319	-4.07058	-1.94374
C	-3.59425	0.16495	3.52498
H	-3.44562	0.39279	4.59544
H	-4.49143	0.71141	3.20857
H	-3.78995	-0.91166	3.45558
C	-1.19042	-0.32913	2.75278
H	-1.46574	-1.38947	2.74247
H	-0.50799	-0.13264	1.91998
H	-0.6084	-0.15665	3.67656
Cu	1.24954	2.59481	-0.0458
C	2.59658	0.63063	0.06273
O	1.50878	0.73983	0.71855
O	2.9771	1.63746	-0.62326
C	3.44092	-0.5908	0.10761
C	4.83235	-0.38554	0.10041
C	2.96055	-1.90861	0.16469
C	5.71867	-1.45355	0.17969
H	5.20039	0.63309	0.04167
C	3.84501	-2.98496	0.22872
C	5.22193	-2.75531	0.24707
H	6.78852	-1.27073	0.1838
H	3.46461	-3.99975	0.25734

H	5.90092	-3.60104	0.3043
C	1.4591	4.37687	-0.77045
N	1.59288	5.45591	-1.19369
I	0.86894	-2.40484	0.03119

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.41137878 hartree
Corrected Gibbs Free Energy = -1638.122661 hartree

TS_{5b-6}

C	-2.05182	-1.18831	0.82669
C	-1.82768	-1.30893	2.37816
C	-1.54566	0.15868	2.77407
C	-0.98356	0.80247	1.52945
C	-1.26577	-0.0182	0.4192
H	-3.19712	-0.82806	0.72122
H	-2.4765	0.68632	3.00793
H	-0.85716	0.2596	3.61936
O	-0.39863	1.93422	1.58577
C	-1.0391	0.38676	-0.98532
F	-1.82938	-0.29507	-1.86773
F	0.23451	0.21372	-1.42785
F	-1.31223	1.71228	-1.21405
C	-1.98899	-2.45593	0.01844
C	-3.12854	-3.26883	-0.10196
C	-0.80705	-2.862	-0.62129
C	-3.08617	-4.45336	-0.84237
H	-4.05214	-2.96305	0.38043
C	-0.76295	-4.04545	-1.35765
H	0.08086	-2.24416	-0.54281
C	-1.90279	-4.84609	-1.47303
H	-3.97831	-5.06875	-0.92382
H	0.16373	-4.34075	-1.84284
H	-1.86868	-5.76755	-2.04752
C	-3.05135	-1.88082	3.09538
H	-2.89673	-1.86898	4.181
H	-3.94766	-1.29656	2.86534
H	-3.23106	-2.92032	2.79725
C	-0.58868	-2.17026	2.67383
H	-0.72961	-3.2016	2.33478
H	0.30311	-1.76665	2.18073
H	-0.39953	-2.19091	3.75365
Cu	1.015	2.60381	0.39257
C	3.08562	1.51135	-0.05517
O	2.26879	1.09527	0.83097
O	2.78067	2.5748	-0.69182
C	4.37528	0.8254	-0.32193
C	5.45142	1.64398	-0.70916
C	4.59881	-0.55483	-0.1911
C	6.7169	1.11398	-0.93226
H	5.27139	2.70806	-0.81763
C	5.86275	-1.09424	-0.4286
C	6.92166	-0.25838	-0.78801
H	7.53597	1.76649	-1.21779
H	6.02339	-2.16251	-0.33689
H	7.90369	-0.68922	-0.96009
C	0.07179	4.21743	-0.1652
N	-0.65348	5.07834	-0.47918
I	3.04043	-1.9693	0.26685
C	-4.38076	0.97884	0.23102
O	-4.52873	-0.35283	0.27529
O	-4.71625	1.54913	-0.87273
O	-3.88804	1.58542	1.22543
K	-4.48523	-0.64873	-2.2982
K	-3.07634	3.59804	-0.19662

B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -3102.42767379 hartree
Corrected Gibbs Free Energy = -3102.130248

MECP1

C	1.922902	1.625477	0.530531
C	2.060364	1.561988	2.066903
C	1.700431	0.081852	2.387560
C	1.805788	-0.646520	1.078173
C	1.933903	0.258426	0.045032
H	2.350472	-0.362096	3.151449
H	0.666446	-0.012878	2.749462
O	1.754650	-1.973948	1.036494
C	2.124622	-0.183550	-1.358040
F	2.708227	0.731259	-2.152647
F	0.963872	-0.563127	-1.980525
F	2.933706	-1.302143	-1.449650
C	1.645874	2.818746	-0.224009
C	2.084251	4.102633	0.204618
C	0.880911	2.786655	-1.424666
C	1.781223	5.255876	-0.510762
H	2.696072	4.189377	1.093929
C	0.582196	3.944172	-2.133720

H	0.488152	1.843583	-1.781481
C	1.026757	5.194105	-1.687462
H	2.147149	6.214193	-0.150851
H	-0.012652	3.871370	-3.040801
H	0.794531	6.097039	-2.245154
C	3.521948	1.817871	2.494752
H	3.629795	1.693448	3.580056
H	4.196116	1.106715	2.001470
H	3.855148	2.828420	2.238037
C	1.102972	2.500905	2.817668
H	1.348643	3.556397	2.673334
H	0.070298	2.346548	2.484164
H	1.148948	2.292985	3.893802
Cu	0.217738	-2.693139	0.061734
C	-2.000301	-1.860178	0.081251
O	-1.052365	-1.308101	0.729643
O	-1.721748	-2.925248	-0.569455
C	-3.380415	-1.321733	0.112440
C	-4.427812	-2.258846	0.133021
C	-3.694126	0.047221	0.157818
C	-5.753220	-1.848735	0.228543
H	-4.177975	-3.313702	0.089343
C	-5.022945	0.460932	0.239189
C	-6.048039	-0.486310	0.286434
H	-6.549418	-2.586410	0.256747
H	-5.259340	1.519069	0.261620
H	-7.077938	-0.149584	0.359979
C	1.222509	-4.162673	-0.756572
N	2.019153	-4.925001	-1.142667
I	-2.208617	1.592163	-0.039549
K	3.925182	-3.221498	0.144688

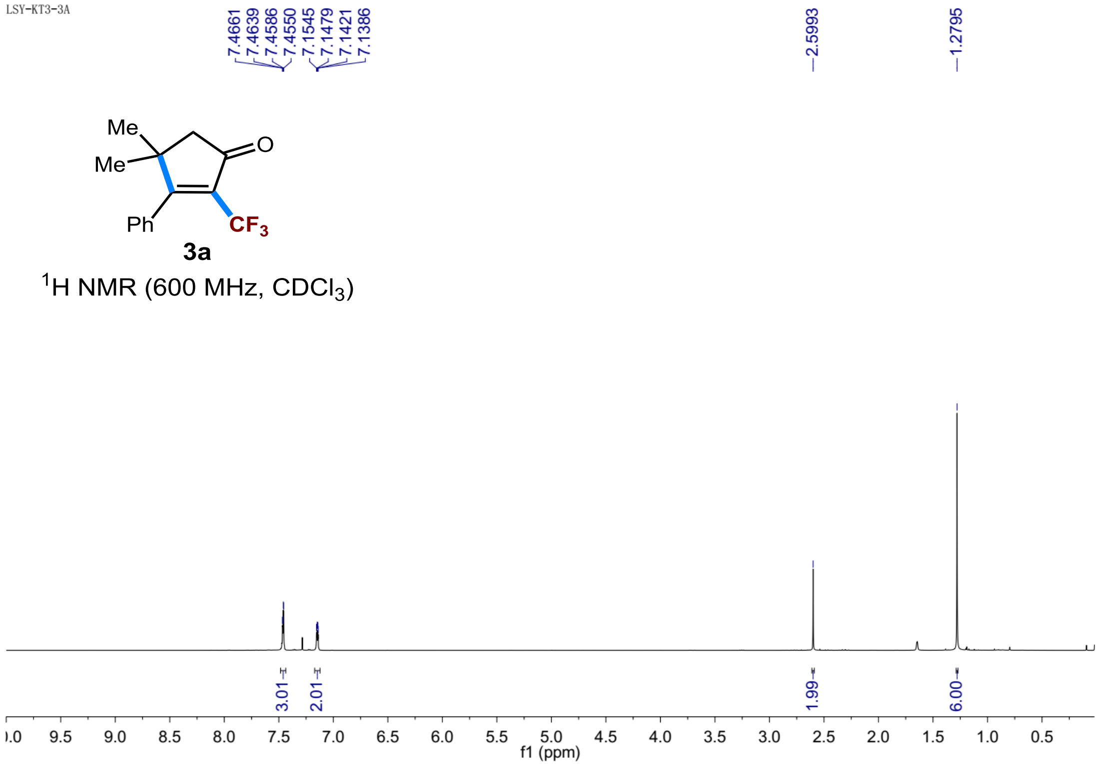
B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -2237.8913894 hartree

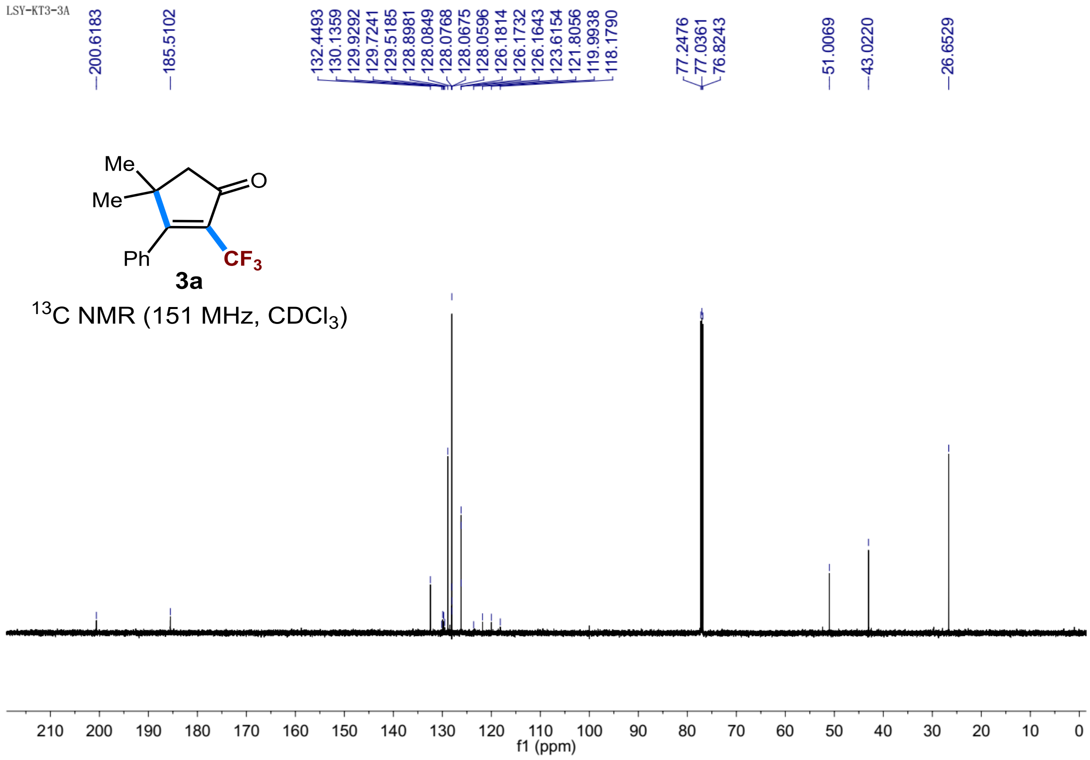
MECP2

C	2.265611	-1.993103	0.016928
C	2.078260	-2.176250	-1.549401
C	1.716143	-0.753294	-2.067845
C	2.255275	0.166070	-1.000997
C	2.522160	-0.523401	0.149850
H	3.155143	-2.551284	0.335334
H	2.161225	-0.537317	-3.044685
H	0.632428	-0.612578	-2.157191
O	2.445940	1.459762	-1.173162
C	2.871638	0.142641	1.439223
F	3.189426	-0.743148	2.399479
F	1.810443	0.873576	1.909445
F	3.899306	1.006130	1.318270
C	1.122675	-2.472900	0.906618
C	1.264387	-3.665947	1.625809
C	-0.078805	-1.761098	1.009749
C	0.222754	-4.145343	2.421152
H	2.195597	-4.223079	1.558253
C	-1.121609	-2.237313	1.805053
H	-0.203764	-0.837805	0.459636
C	-0.974295	-3.430868	2.514399
H	0.347306	-5.075219	2.969571
H	-2.047799	-1.672682	1.868422
H	-1.783598	-3.800031	3.138367
C	3.435658	-2.594968	-2.135645
H	3.379753	-2.663948	-3.228066
H	4.218684	-1.869910	-1.882659
H	3.742194	-3.573948	-1.748724
C	1.010656	-3.204873	-1.921750
H	1.254907	-4.193677	-1.516727
H	0.023832	-2.920211	-1.544568
H	0.945694	-3.295015	-3.012704
Cu	1.088144	2.465818	-0.387159
C	-1.097698	1.896468	0.233115
O	-0.326249	1.158927	-0.485803
O	-0.602579	3.033131	0.550566
C	-2.410493	1.448856	0.708695
C	-2.896206	2.063008	1.879002
C	-3.170218	0.426310	0.108861
C	-4.093619	1.656557	2.453289
H	-2.304455	2.848813	2.335896
C	-4.374239	0.023457	0.682296
C	-4.827181	0.630834	1.855933
H	-4.449667	2.132357	3.360963
H	-4.961146	-0.760027	0.217159
H	-5.762048	0.297329	2.296495
C	2.214688	3.963190	-0.230718
N	2.895635	4.903899	-0.130492
I	-2.633509	-0.534329	-1.735612

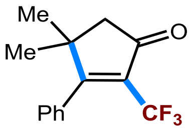
B3LYP-D3(BJ)/6-311+G(d,p)-SDD(Cu,I)-SMD(EtOAc): E = -1638.424815 hartree

5. NMR spectra



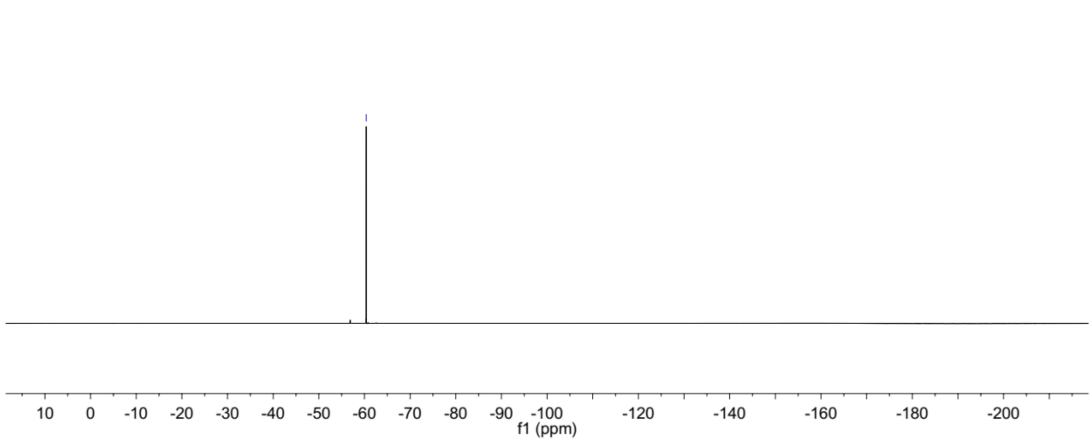


LSY-KT3-3A

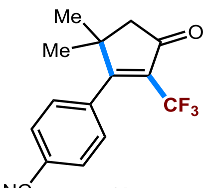


3a

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

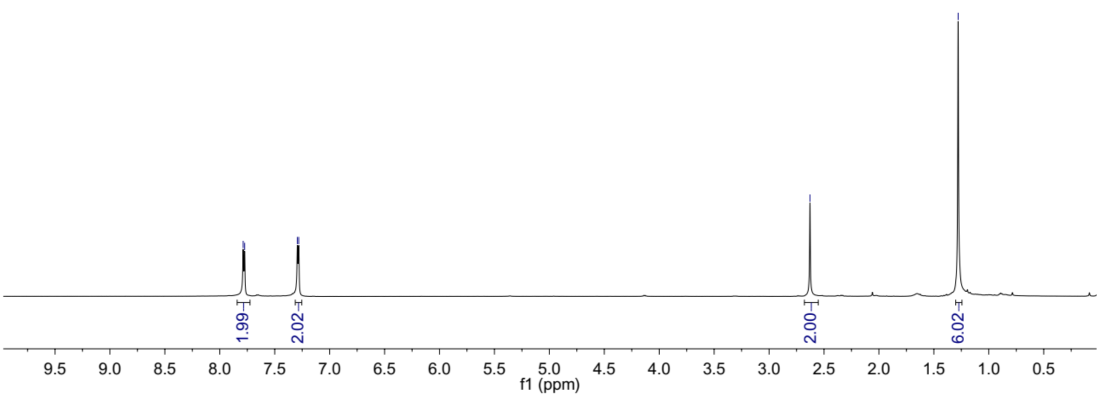


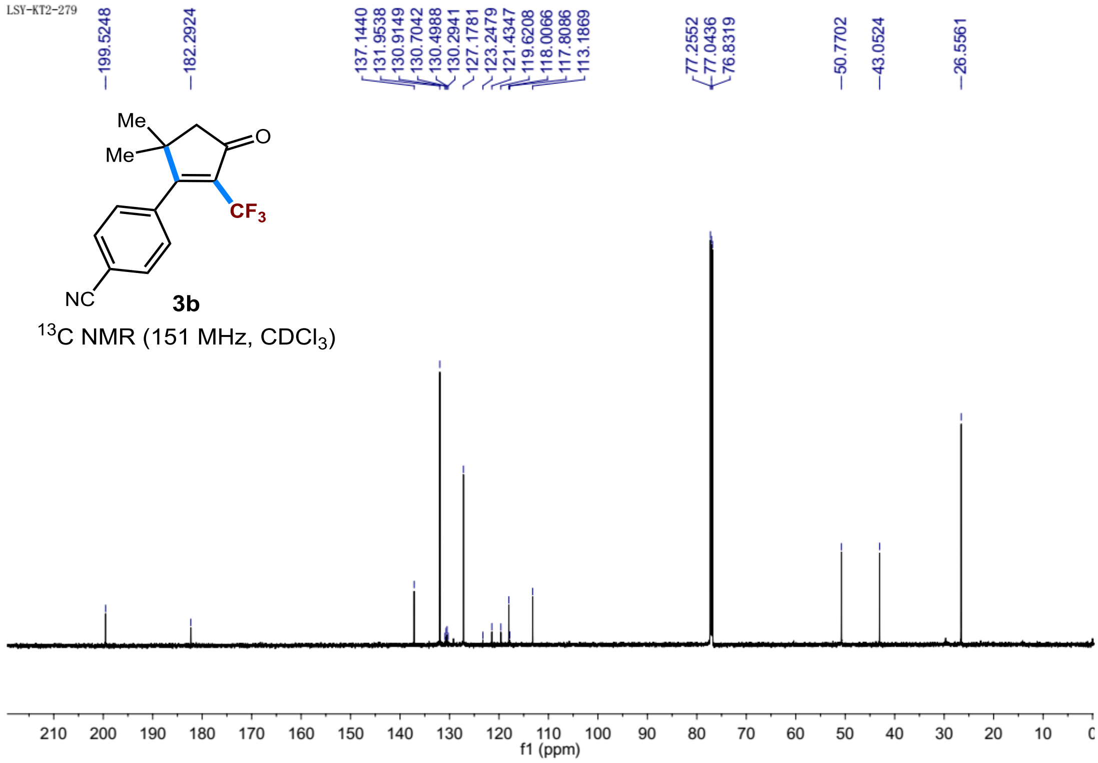
LSY-KT2-279

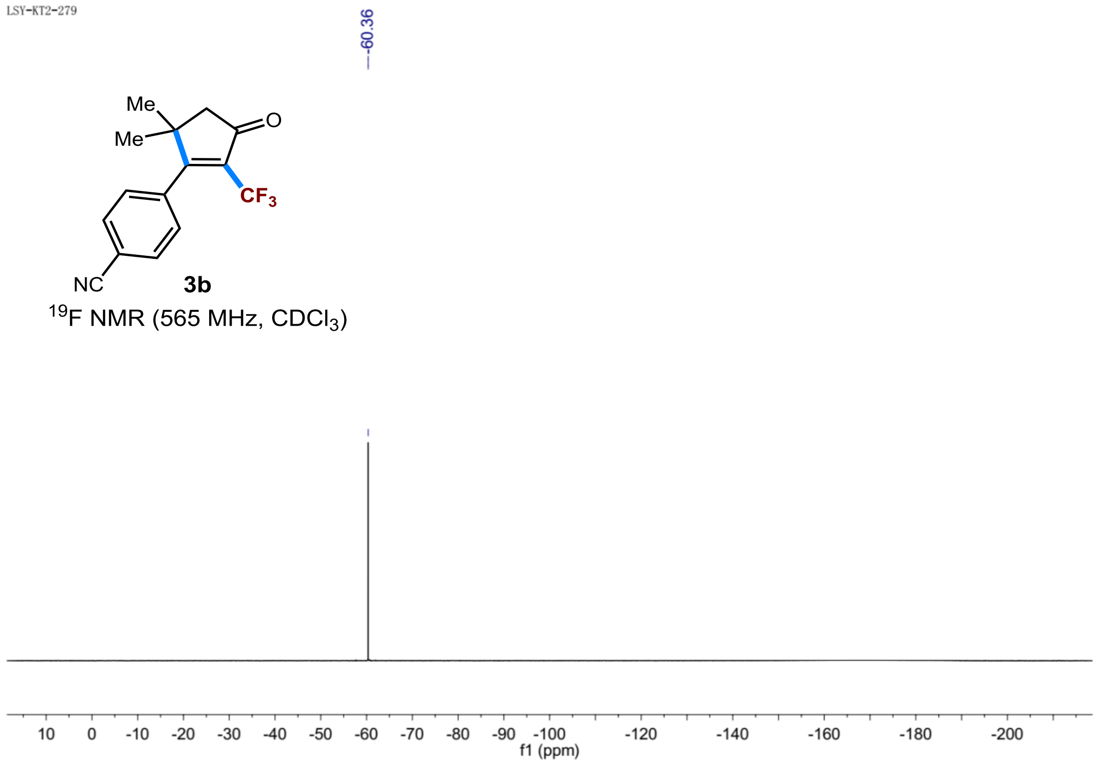


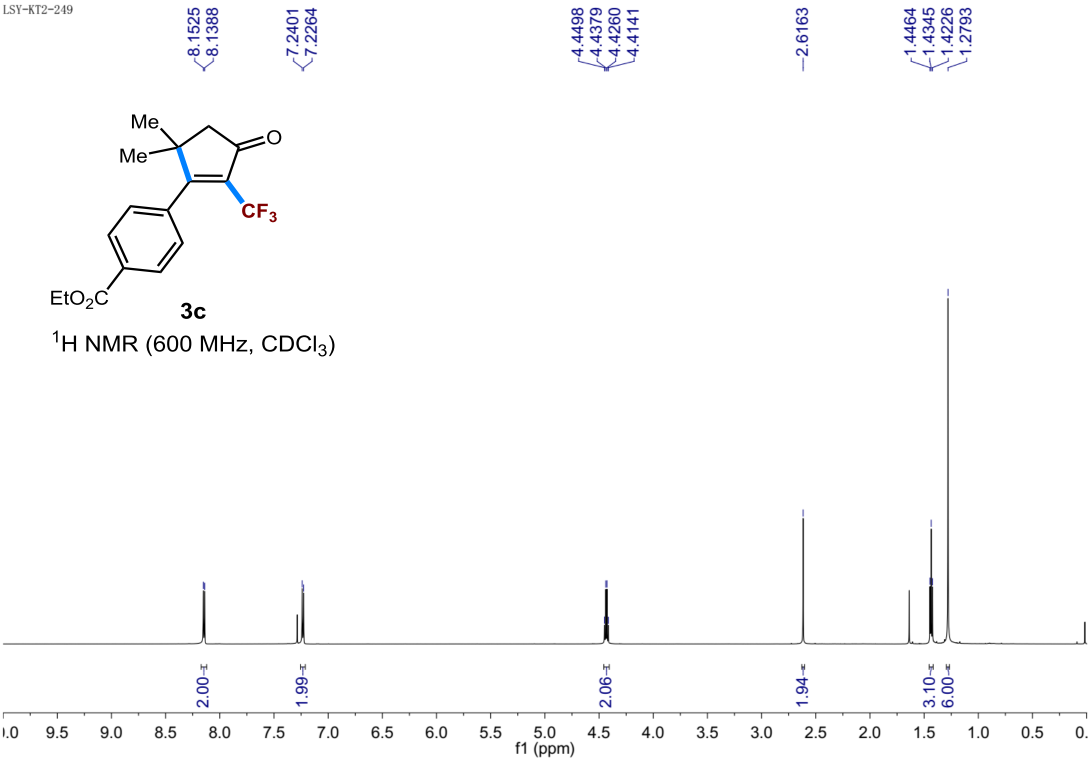
3b

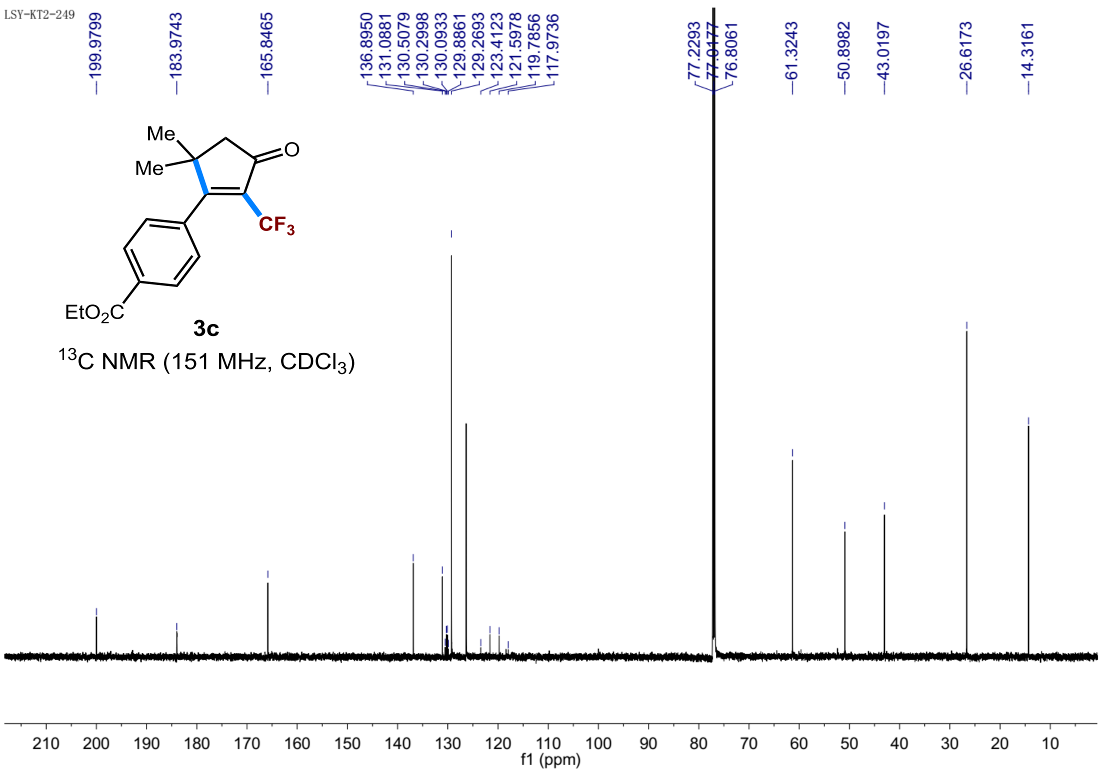
^{1}H NMR (600 MHz, $CDCl_3$)



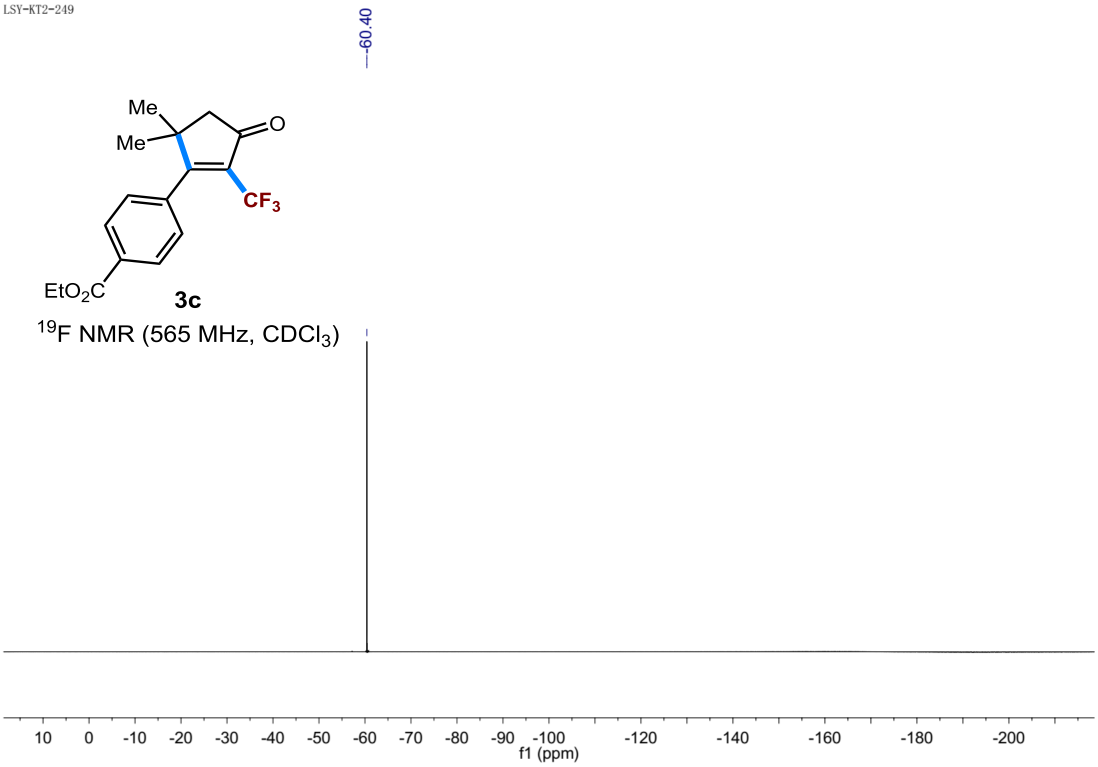

LSY-KT2-279
199.5248
182.2924
137.1440
131.9538
130.9149
130.7042
130.4988
130.2941
127.1781
123.2479
121.4347
119.6208
118.0066
117.8086
113.1869
77.2552
77.0436
76.8319
50.7702
43.0524
26.5561
Me
Me
O
CF3
NC
3b
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


LSY-KT2-279
-60.36
Me
Me
O
CF3
NC
3b
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


LSY-KT2-249
8.1525
8.1388
7.2401
7.2264
4.4498
4.4379
4.4260
4.4141
2.6163
1.4464
1.4345
1.4226
1.2793
Me
Me
O
CF3
EtO2C
3c
1H NMR (600 MHz, CDCl3)
2.00
1.99
2.06
1.94
3.10
6.00
f1 (ppm)

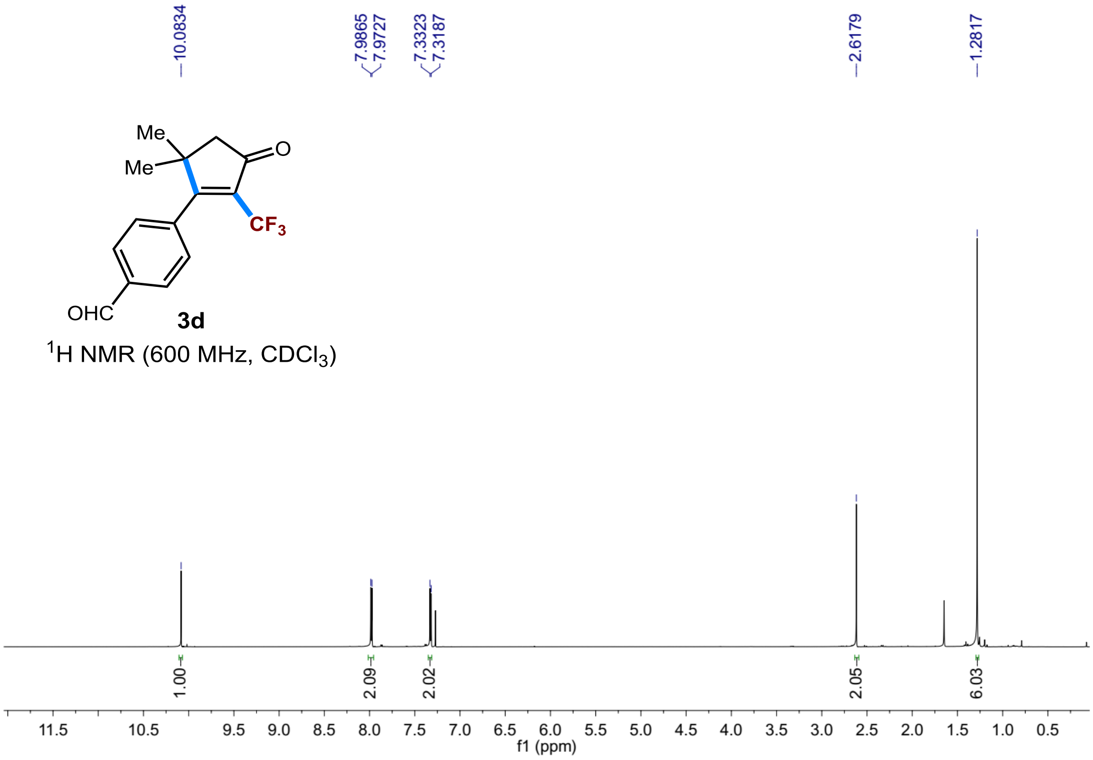

LSY-KT2-249
199.9799
183.9743
165.8465
136.8950
131.0881
130.5079
130.2998
130.0933
129.8861
129.2693
123.4123
121.5978
119.7856
117.9736
77.2293
77.0177
76.8061
61.3243
50.8982
43.0197
26.6173
14.3161
Me
Me
O
CF3
EtO2C
3c
13C NMR (151 MHz, CDCl3)
f1 (ppm)

LSY-KT2-249



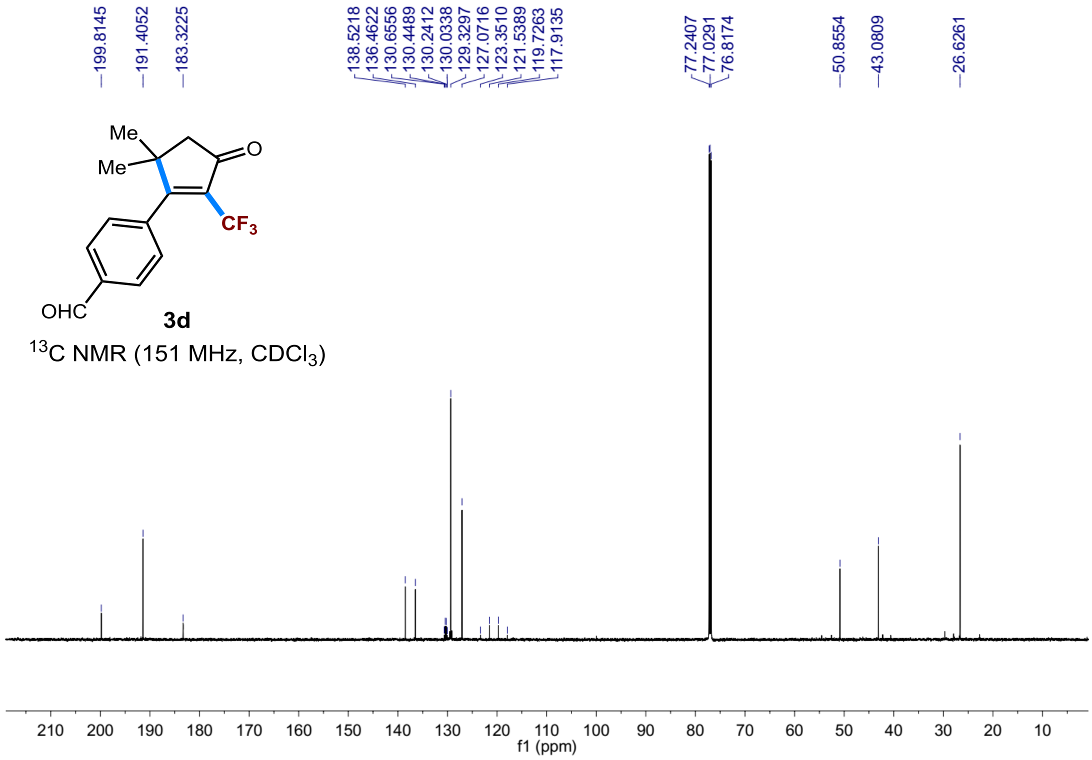
3c

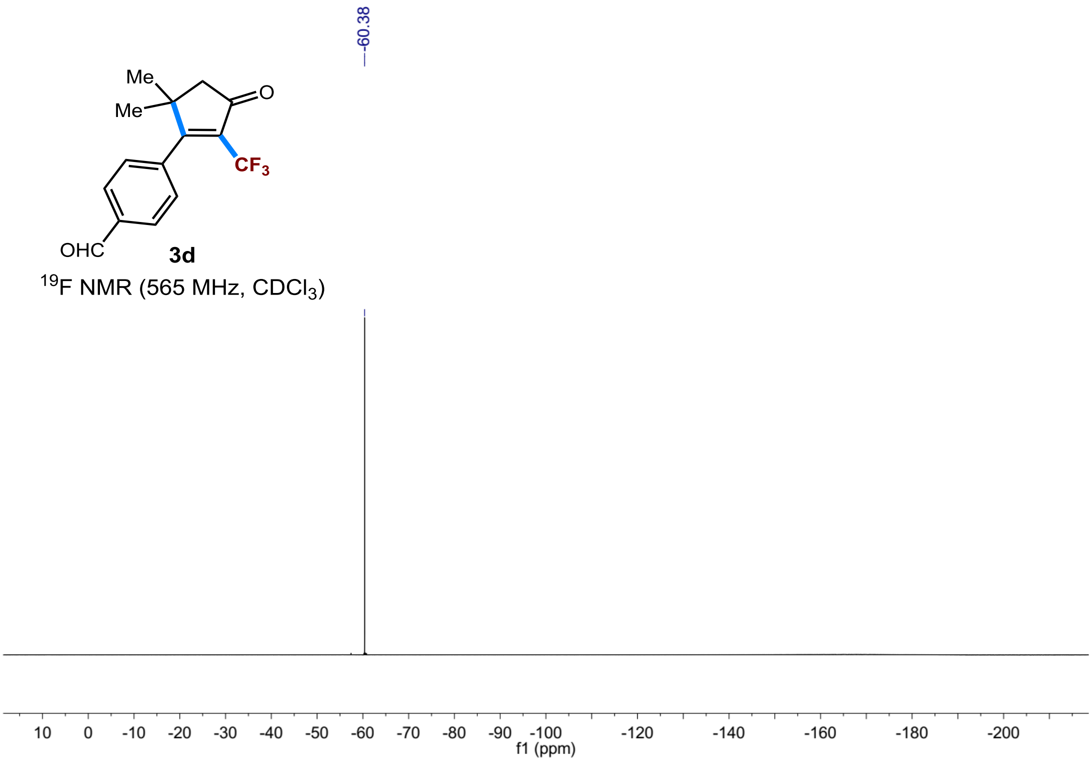
^{19}F NMR (565 MHz, $CDCl_3$)

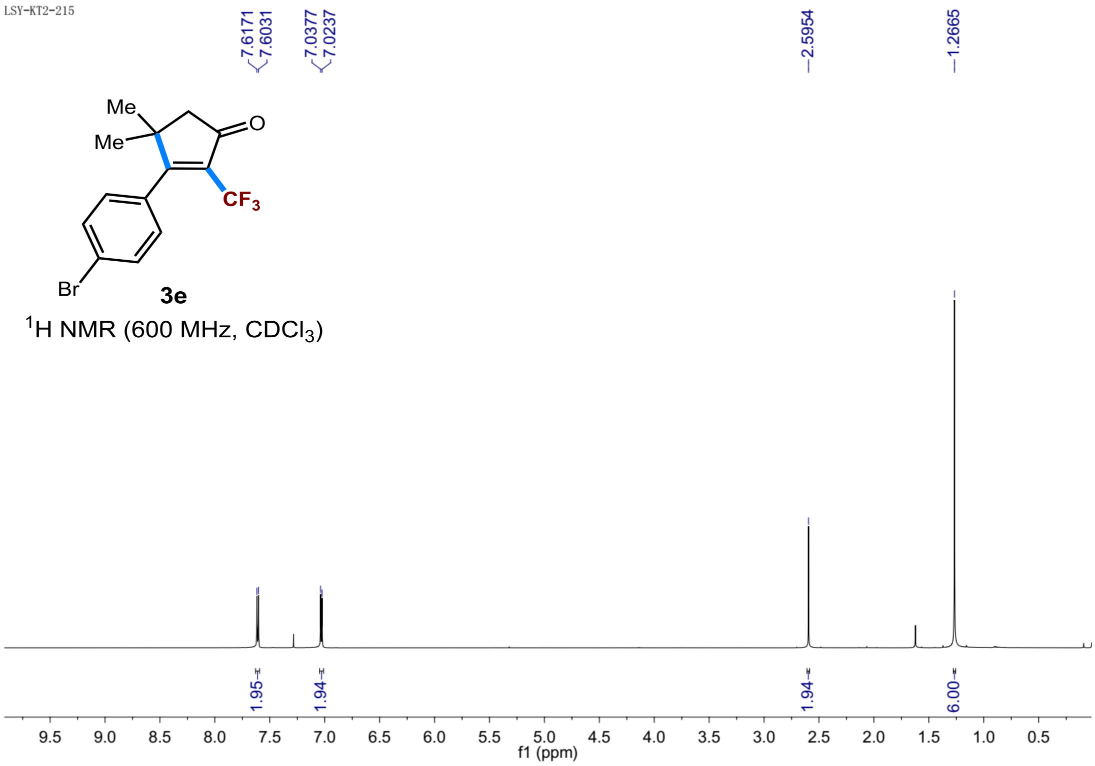


3d

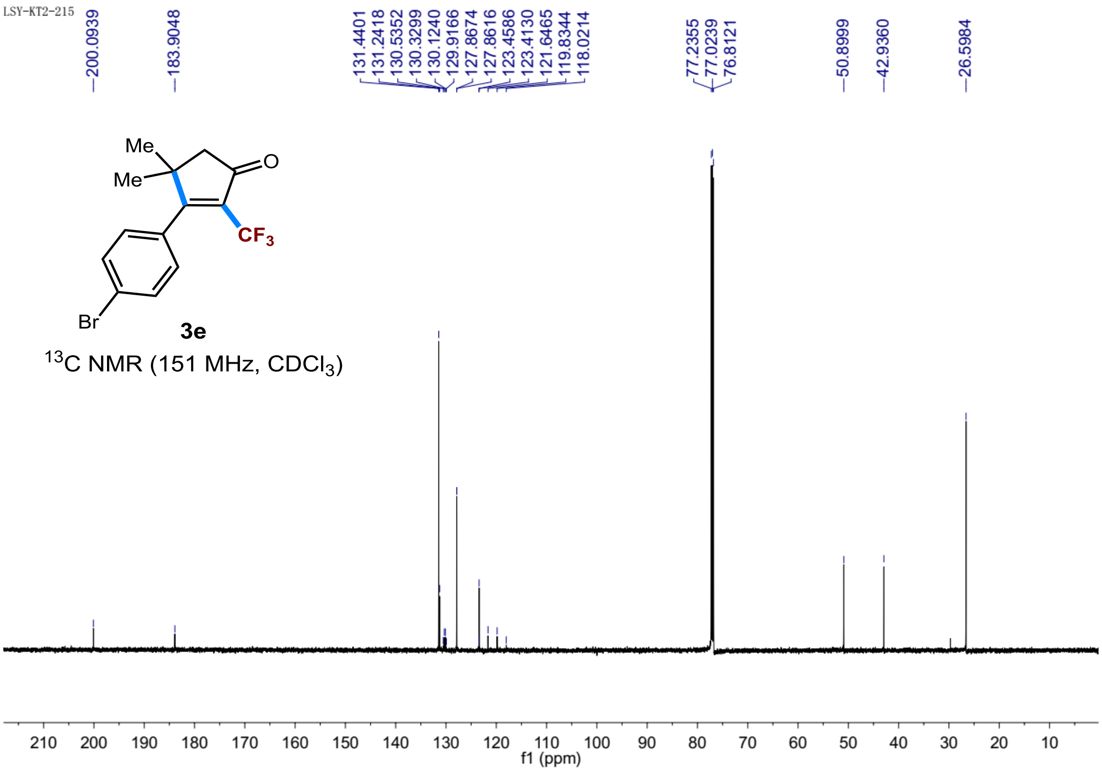
^{1}H NMR (600 MHz, $CDCl_3$)


199.8145
191.4052
183.3225
138.5218
136.4622
130.6556
130.4489
130.2412
130.0338
129.3297
127.0716
123.3510
121.5389
119.7263
117.9135
77.2407
77.0291
76.8174
50.8554
43.0809
26.6261
Me
Me
O
CF3
OHC
3d
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


-60.38
Me
Me
O
CF3
OHC
3d
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

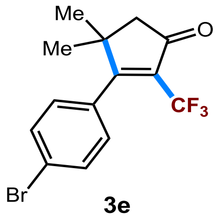


LSY-KT2-215
7.6171
7.6031
7.0377
7.0237
2.5954
1.2665
Me
Me
O
CF3
Br
3e
1H NMR (600 MHz, CDCl3)
1.95
1.94
1.94
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)



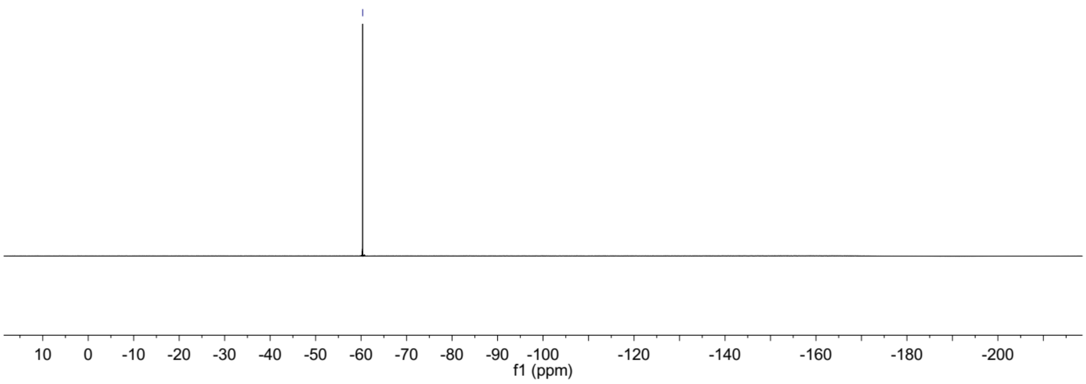
LSY-KT2-215
200.0939
183.9048
131.4401
131.2418
130.5352
130.3299
130.1240
129.9166
127.8674
127.8616
123.4586
123.4130
121.6465
119.8344
118.0214
77.2355
77.0239
76.8121
50.8999
42.9360
26.5984
Me
Me
O
CF3
Br
3e
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

LSY-KT2-215

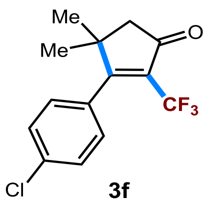


3e

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

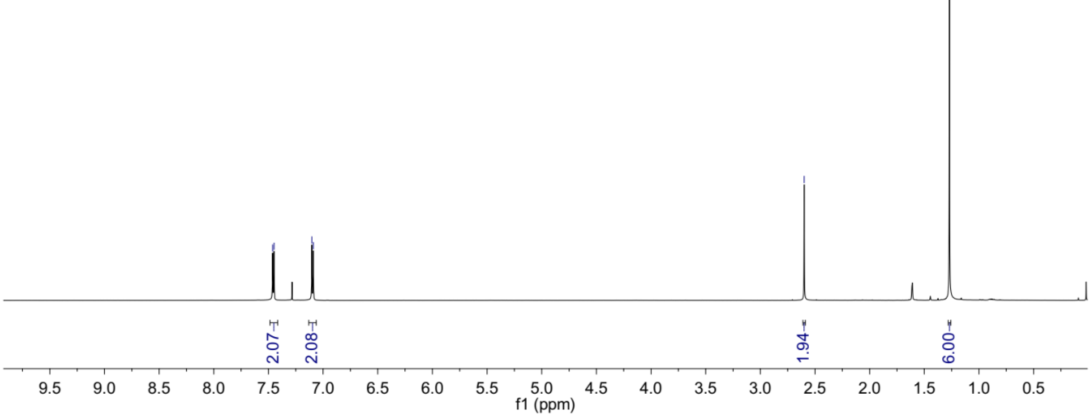


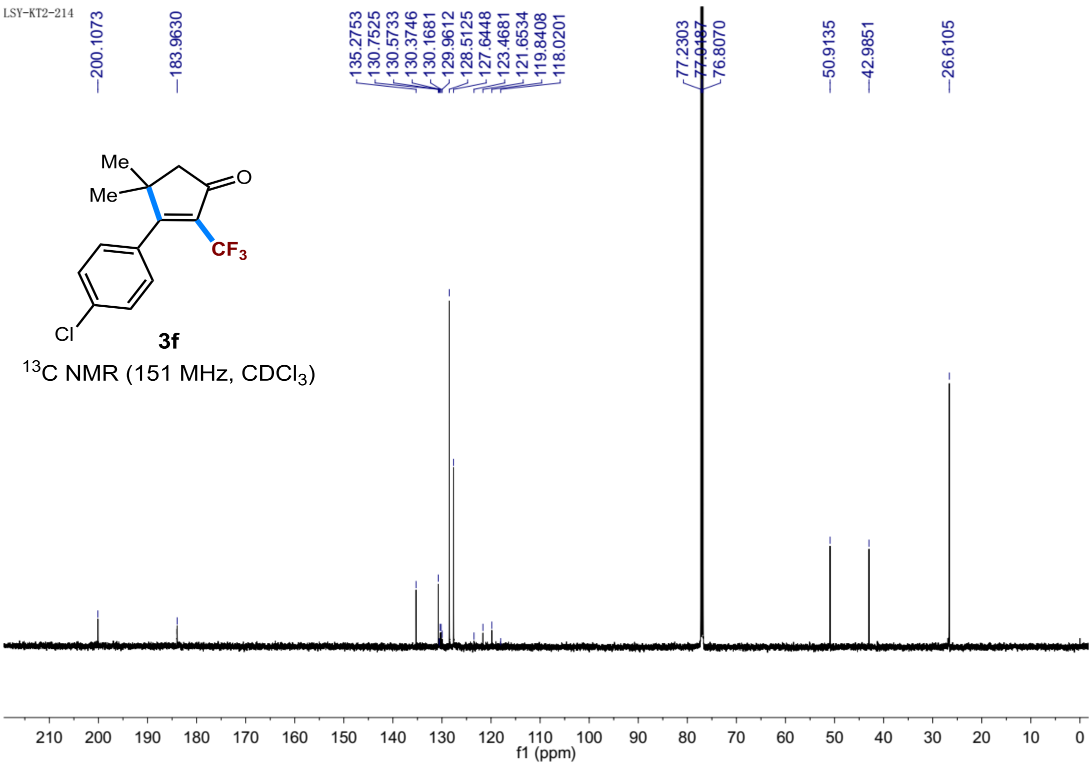
LSY-KT2-214



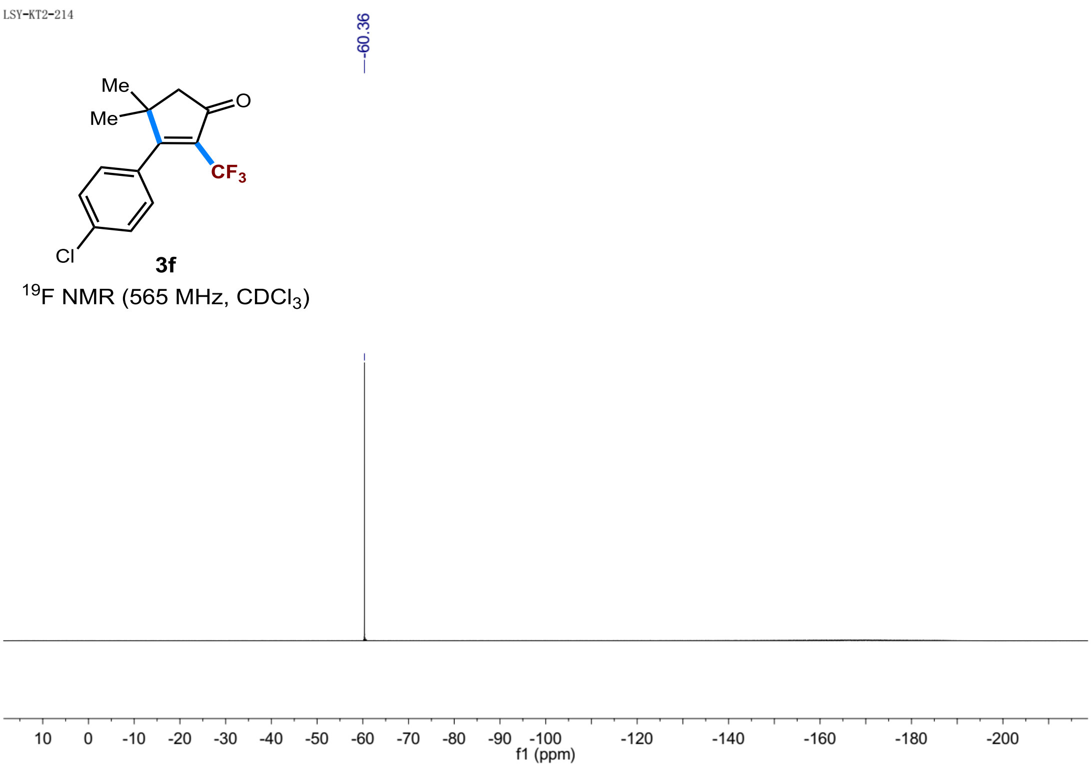
3f

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

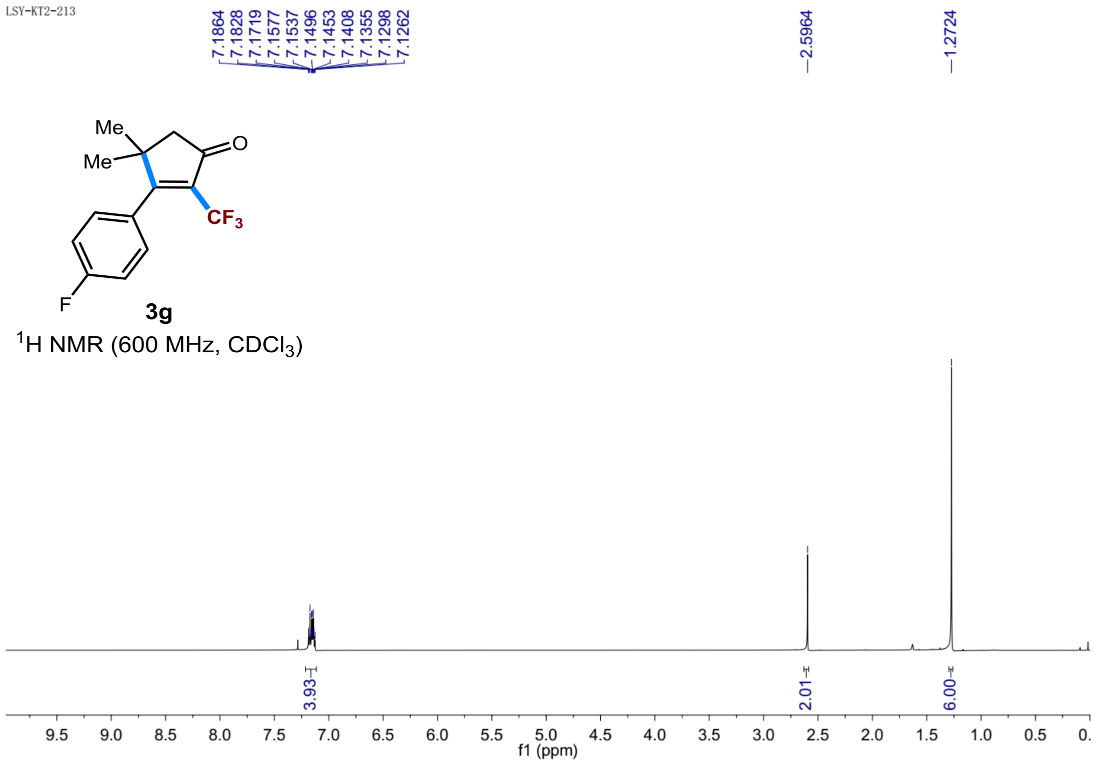


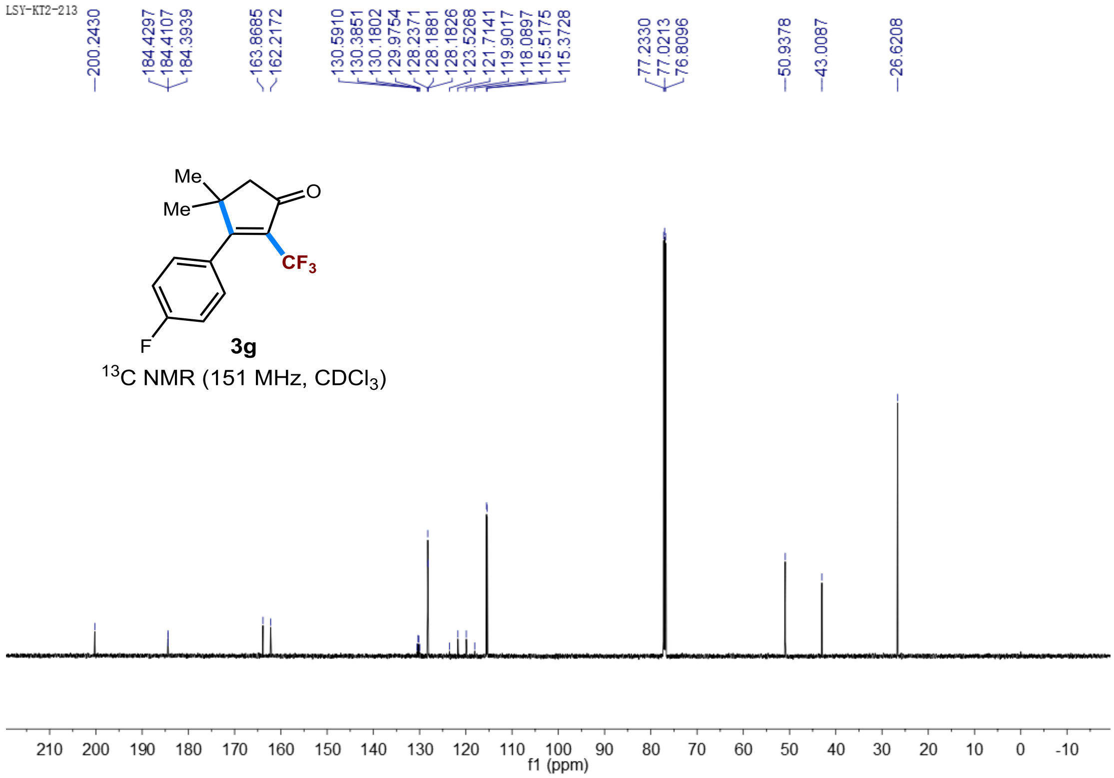


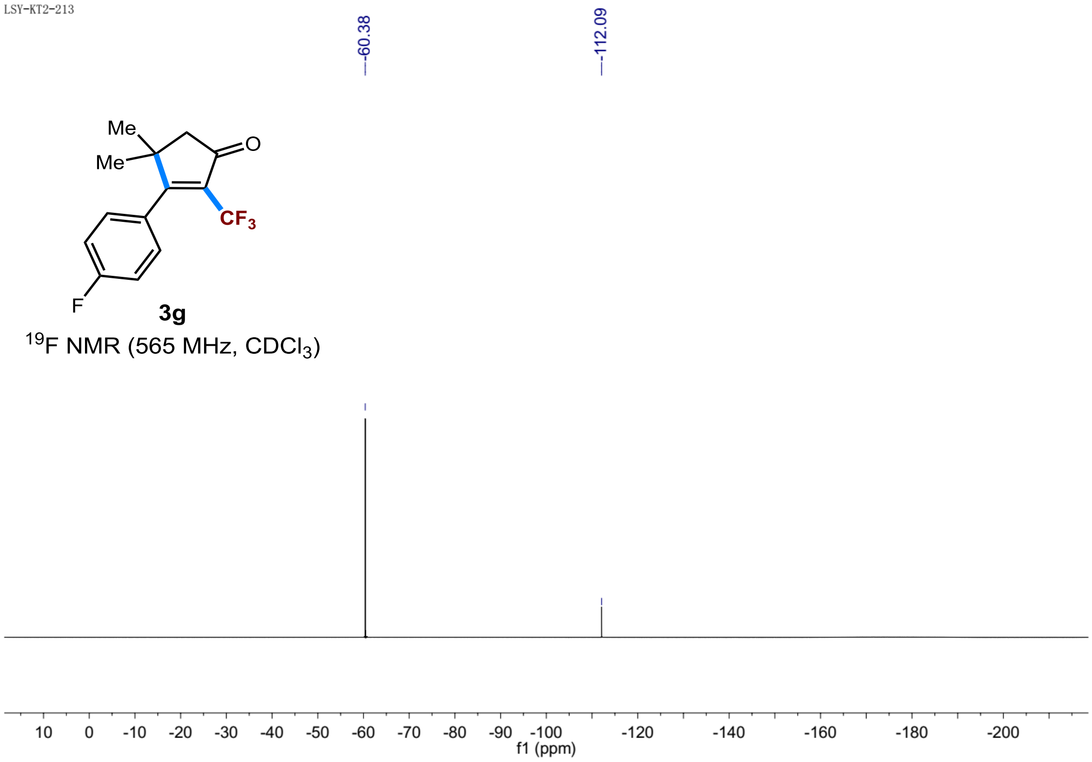
LSY-KT2-214
200.1073
183.9630
135.2753
130.7525
130.5733
130.3746
130.1681
129.9612
128.5125
127.6448
123.4681
121.6534
119.8408
118.0201
77.2303
77.0187
76.8070
50.9135
42.9851
26.6105
Me
Me
O
CF3
Cl
3f
13C NMR (151 MHz, CDCl3)
f1 (ppm)

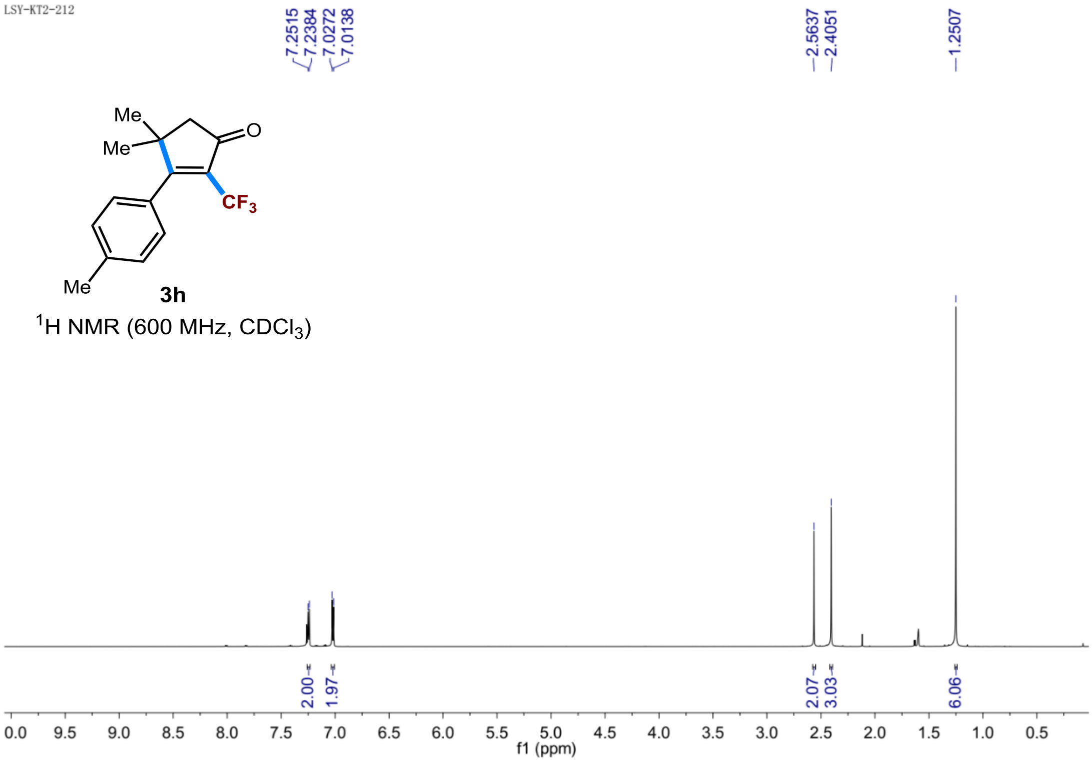


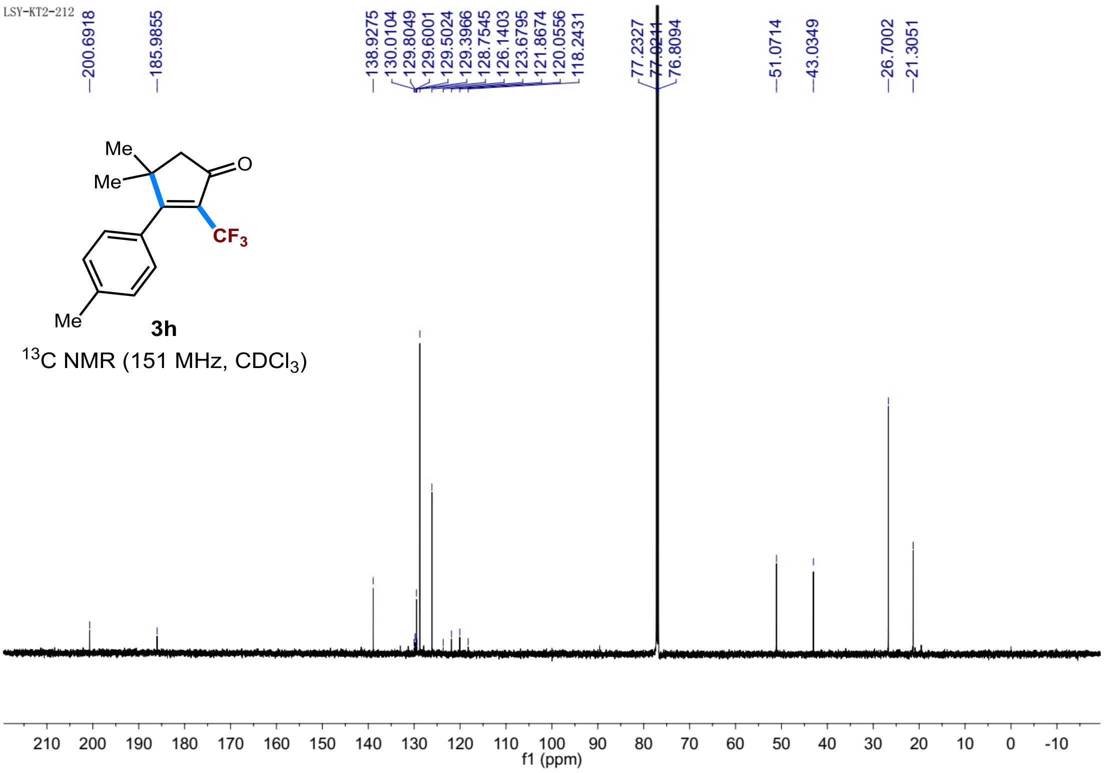
LSY-KT2-214
-60.36
Me
Me
O
CF3
Cl
3f
19F NMR (565 MHz, CDCl3)
f1 (ppm)


LSY-KT2-213
7.1864
7.1828
7.1719
7.1577
7.1537
7.1496
7.1453
7.1408
7.1355
7.1298
7.1262
2.5964
1.2724
Me
Me
O
CF3
F
3g
1H NMR (600 MHz, CDCl3)
3.93
2.01
6.00
f1 (ppm)


LSY-KT2-213
200.2430
184.4297
184.4107
184.3939
163.8685
162.2172
130.5910
130.3851
130.1802
129.9754
128.2371
128.1881
128.1826
123.5268
121.7141
119.9017
118.0897
115.5175
115.3728
77.2330
77.0213
76.8096
50.9378
43.0087
26.6208
Me
Me
O
CF3
F
3g
13C NMR (151 MHz, CDCl3)
f1 (ppm)

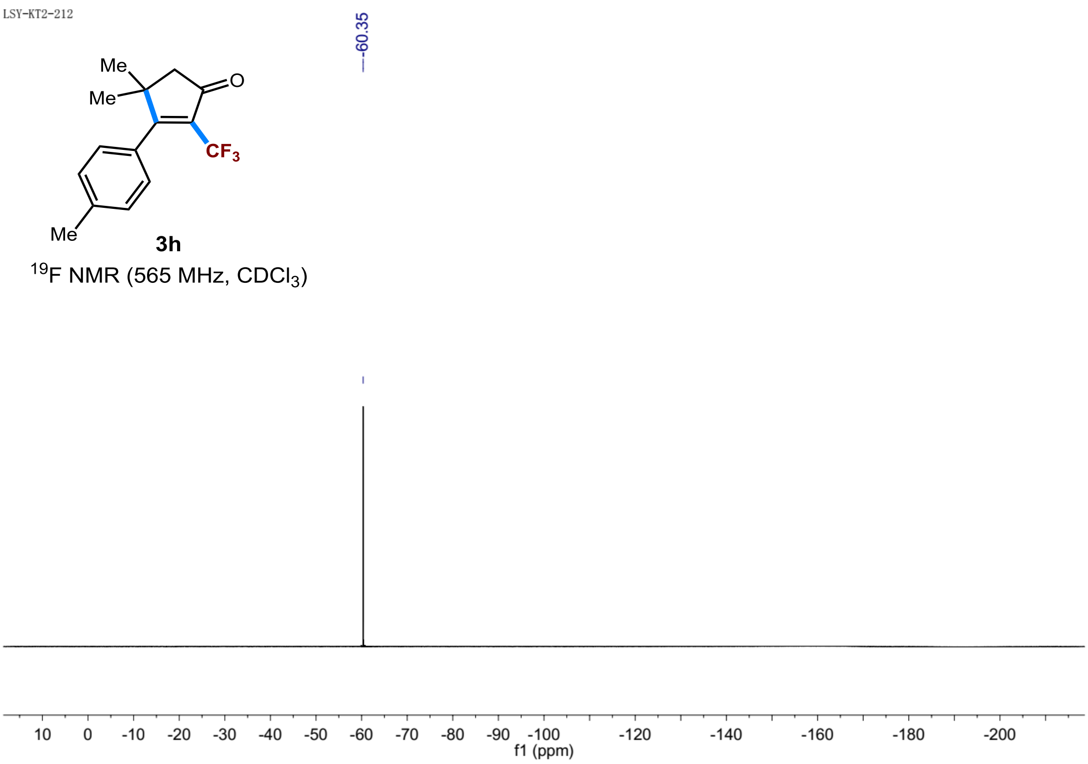

LSY-KT2-213
-60.38
-112.09
Me
Me
O
CF3
F
3g
19F NMR (565 MHz, CDCl3)
f1 (ppm)


LSY-KT2-212
7.2515
7.2384
7.0272
7.0138
2.5637
2.4051
1.2507
Me
Me
O
CF3
Me
3h
1H NMR (600 MHz, CDCl3)
2.00
1.97
2.07
3.03
6.06
f1 (ppm)



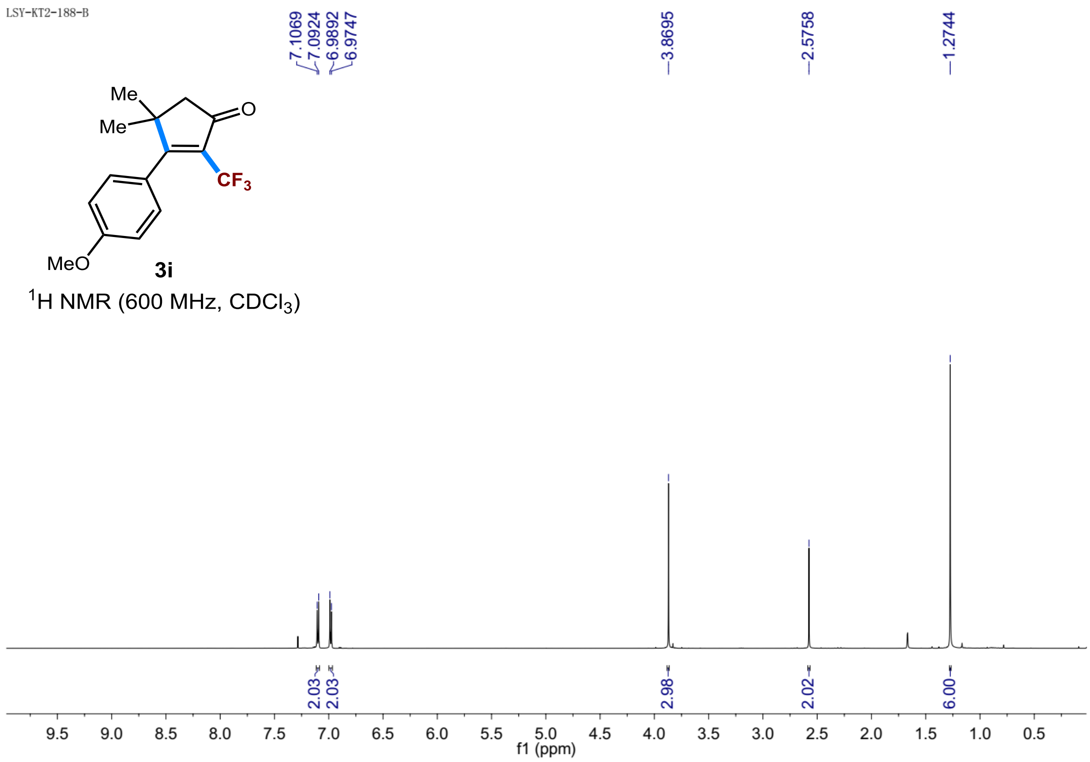
3h

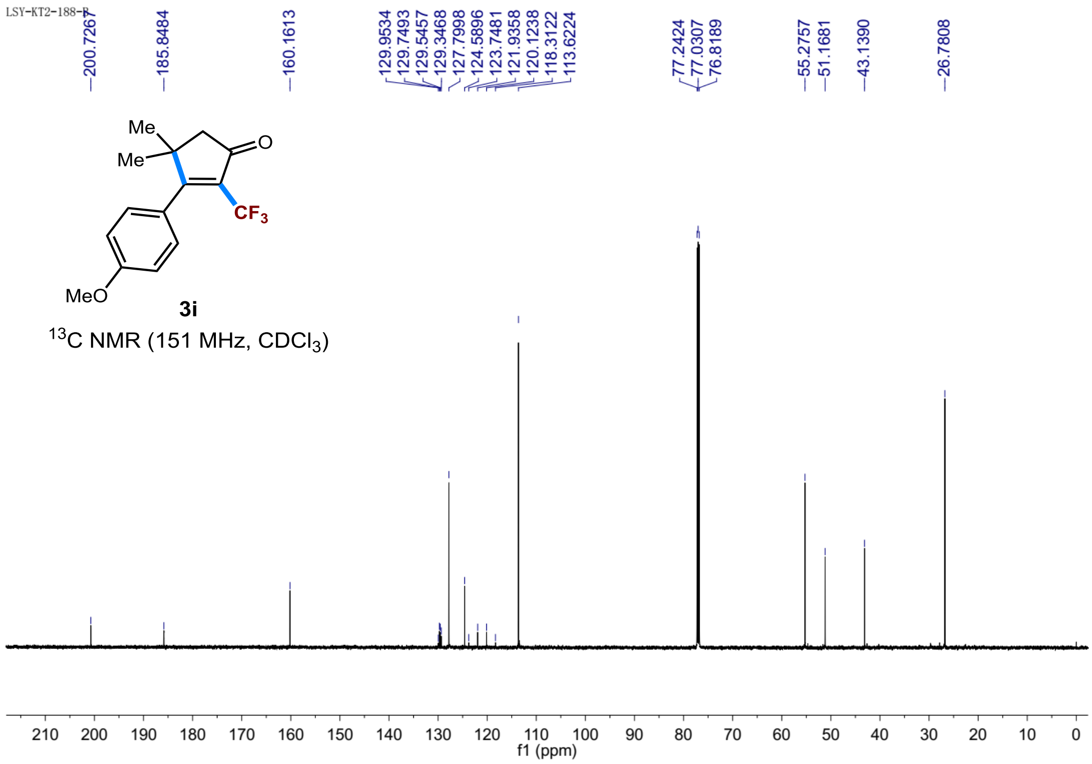
^{13}C NMR (151 MHz, $CDCl_3$)

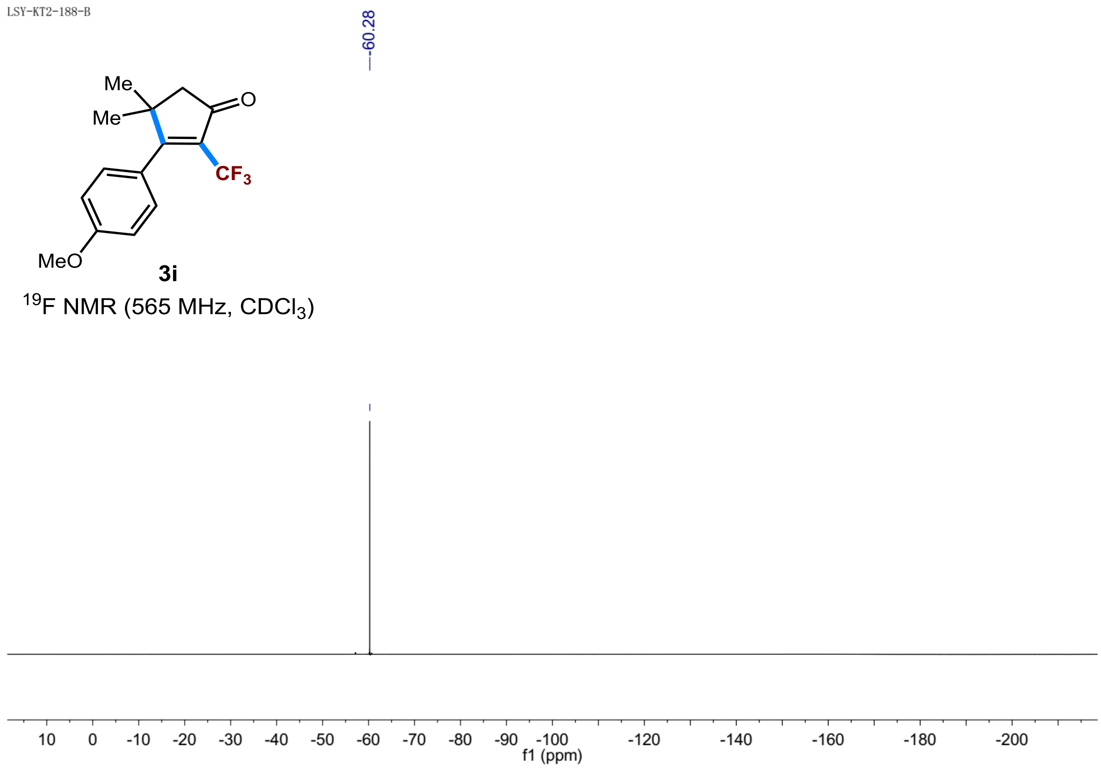


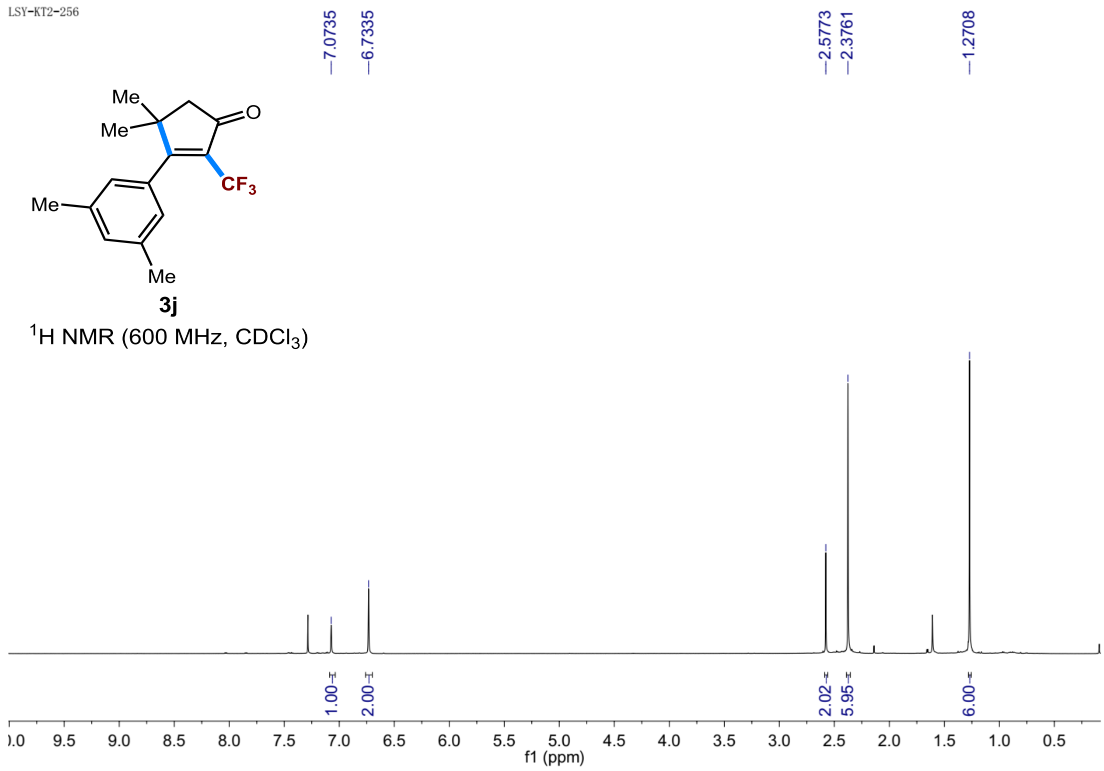
3h

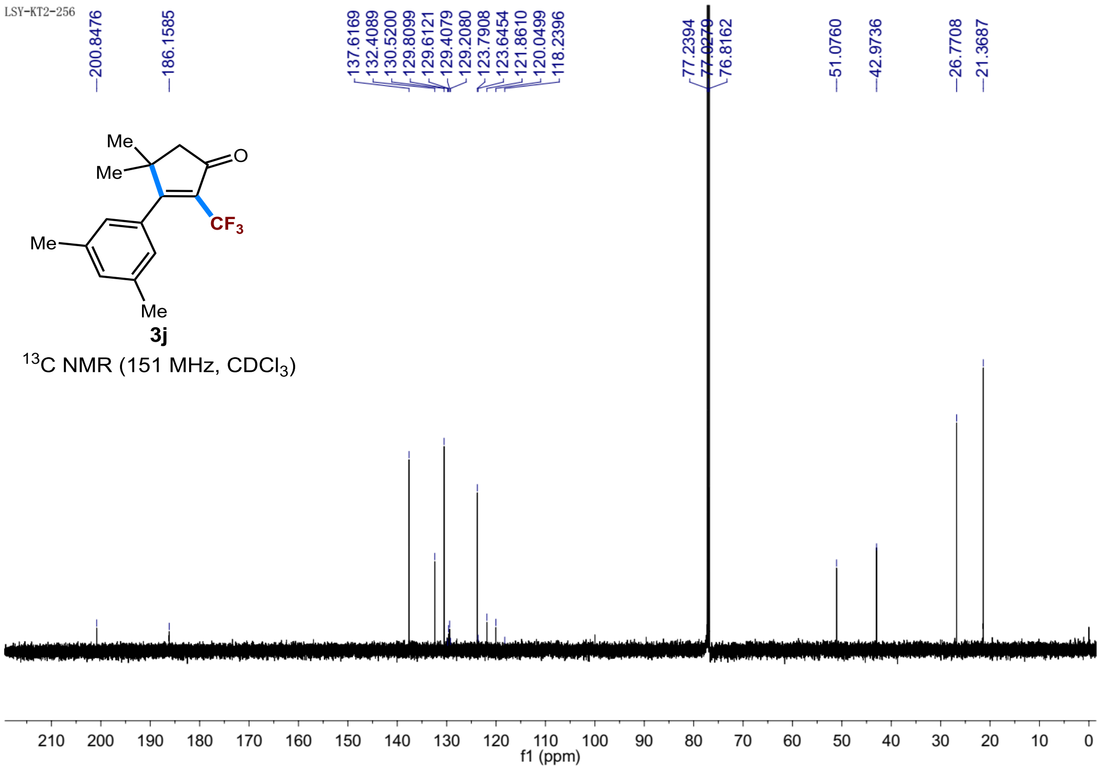
^{19}F NMR (565 MHz, $CDCl_3$)

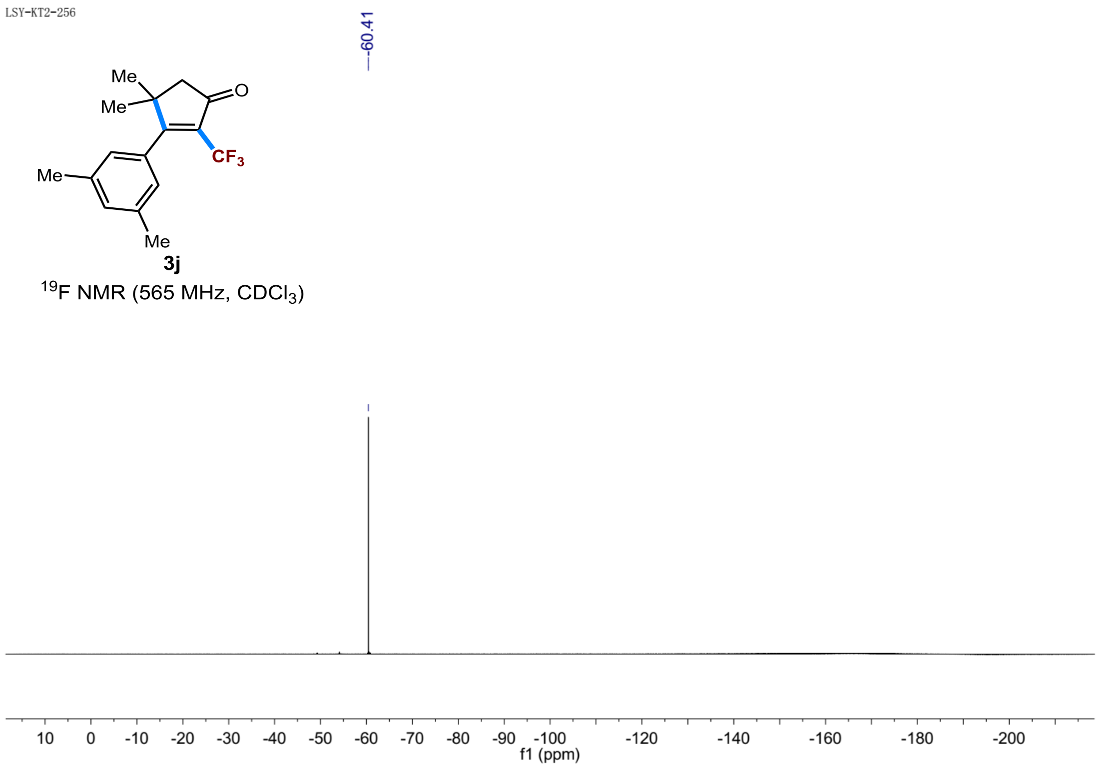

LSY-KT2-188-B
7.1069
7.0924
6.9892
6.9747
3.8695
2.5758
1.2744
Me
Me
O
CF3
MeO
3i
1H NMR (600 MHz, CDCl3)
2.03
2.03
2.98
2.02
6.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

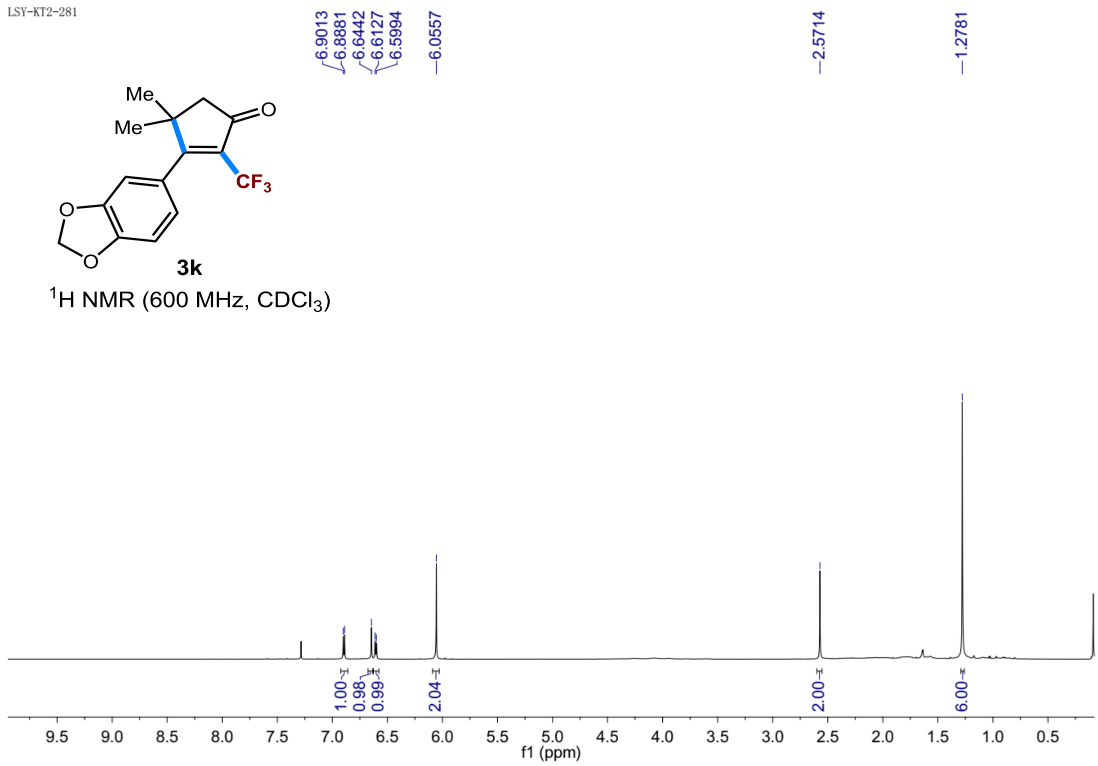

LSY-KT2-188-B
200.7267
185.8484
160.1613
129.9534
129.7493
129.5457
129.3468
127.7998
124.5896
123.7481
121.9358
120.1238
118.3122
113.6224
77.2424
77.0307
76.8189
55.2757
51.1681
43.1390
26.7808
Me
Me
O
CF3
MeO
3i
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

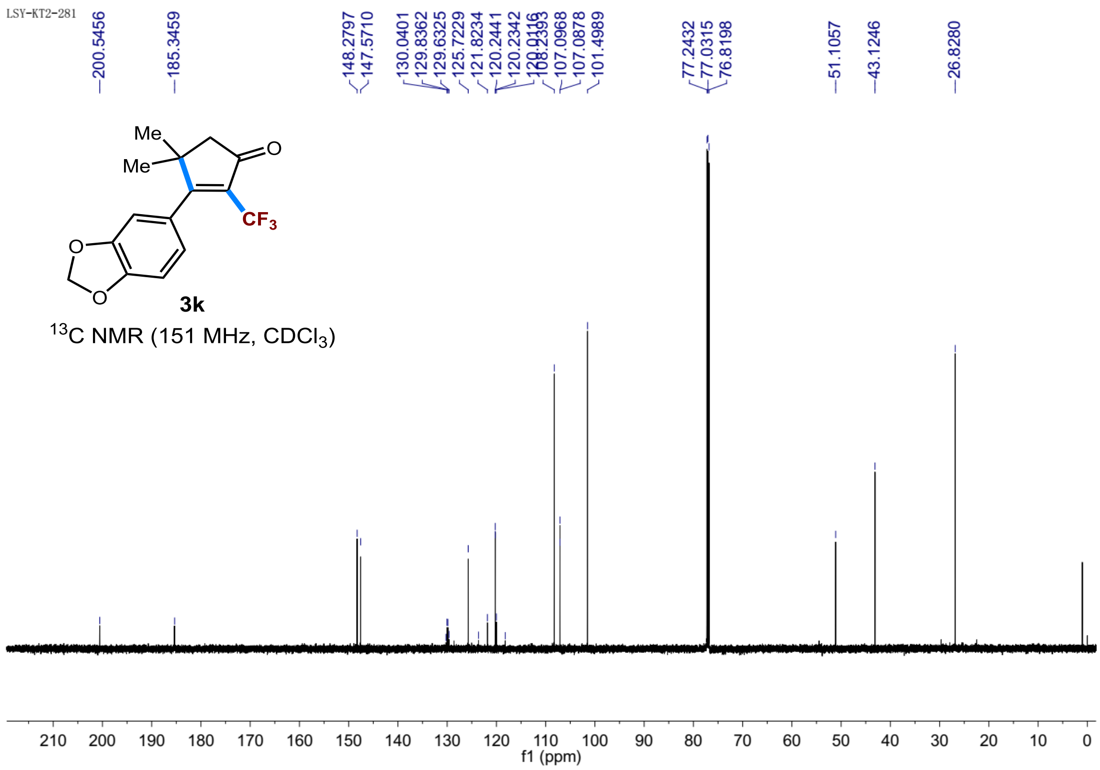

LSY-KT2-188-B
-60.28
Me
Me
O
CF3
MeO
3i
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

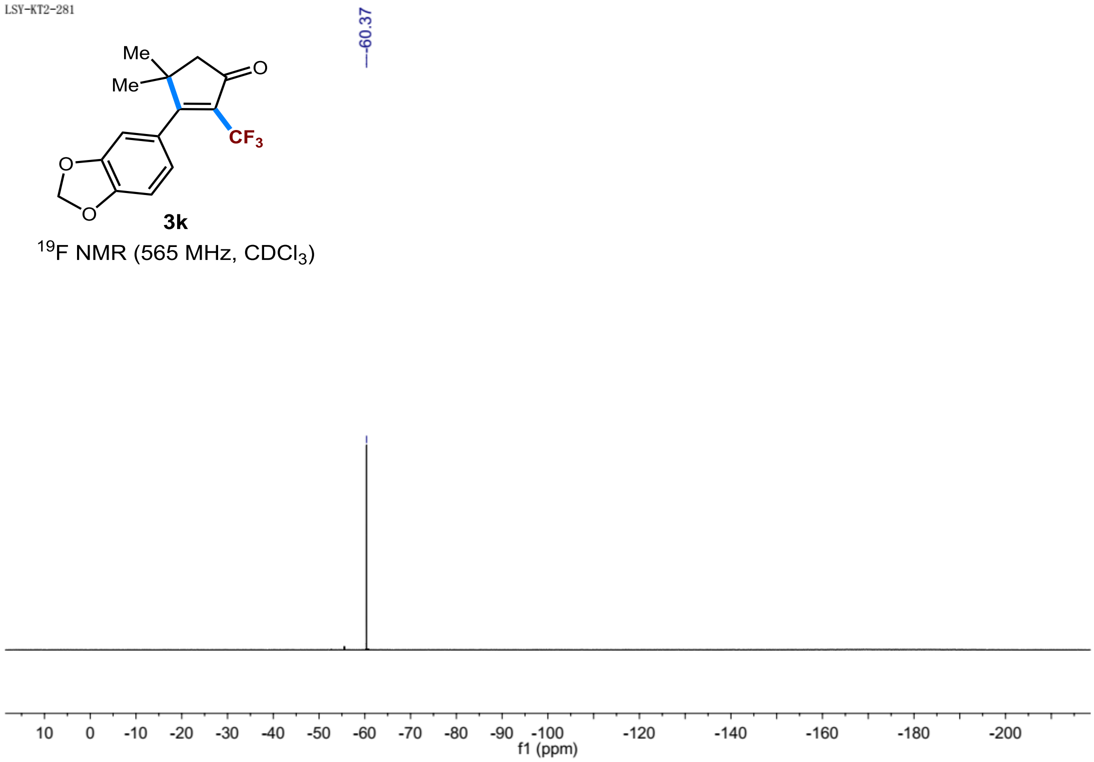

LSY-KT2-256
7.0735
6.7335
2.5773
2.3761
1.2708
Me
Me
O
CF3
Me
Me
3j
1H NMR (600 MHz, CDCl3)
1.00
2.00
2.02
5.95
6.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

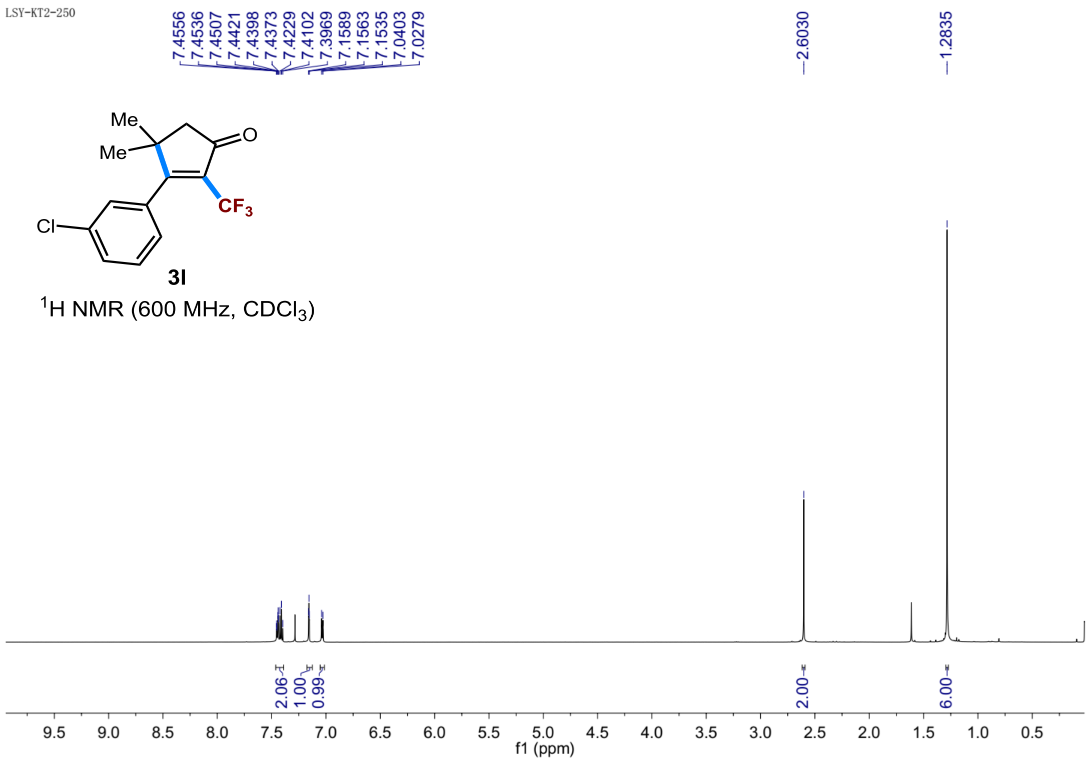

LSY-KT2-256
200.8476
186.1585
137.6169
132.4089
130.5200
129.8099
129.6121
129.4079
129.2080
123.7908
123.6454
121.8610
120.0499
118.2396
77.2394
77.0270
76.8162
51.0760
42.9736
26.7708
21.3687
Me
Me
O
CF3
Me
Me
3j
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

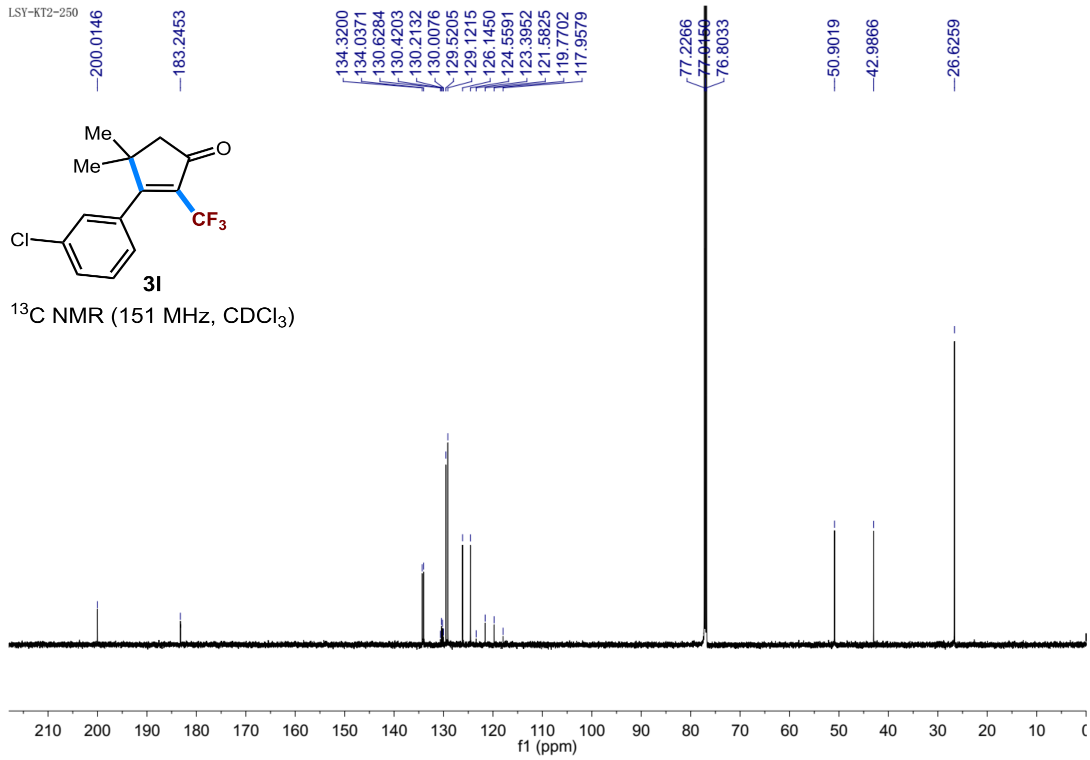

LSY-KT2-256
-60.41
Me
Me
O
CF3
Me
Me
3j
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


LSY-KT2-281
6.9013
6.8881
6.6442
6.6127
6.5994
6.0557
2.5714
1.2781
Me
Me
O
CF3
O
O
3k
1H NMR (600 MHz, CDCl3)
1.00
0.98
0.99
2.04
2.00
6.00
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
f1 (ppm)


LSY-KT2-281
200.5456
185.3459
148.2797
147.5710
130.0401
129.8362
129.6325
125.7229
121.8234
120.2441
120.2342
108.2393
107.0968
107.0878
101.4989
77.2432
77.0315
76.8198
51.1057
43.1246
26.8280
Me
Me
O
CF3
O
O
3k
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

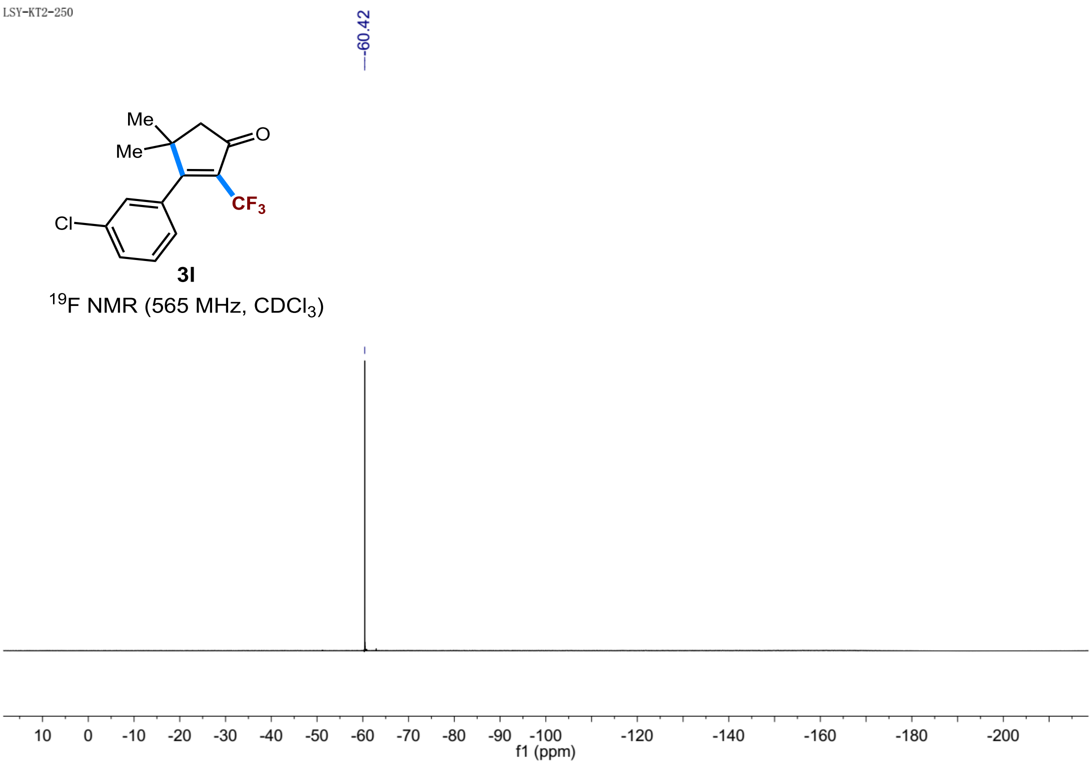

LSY-KT2-281
Me
Me
O
CF3
O
O
3k
19F NMR (565 MHz, CDCl3)
-60.37
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-120
-140
-160
-180
-200
f1 (ppm)


LSY-KT2-250
7.4556
7.4536
7.4507
7.4421
7.4398
7.4373
7.4229
7.4102
7.3969
7.1589
7.1563
7.1535
7.0403
7.0279
2.6030
1.2835
Me
Me
O
CF3
Cl
3l
1H NMR (600 MHz, CDCl3)
2.06
1.00
0.99
2.00
6.00
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
f1 (ppm)



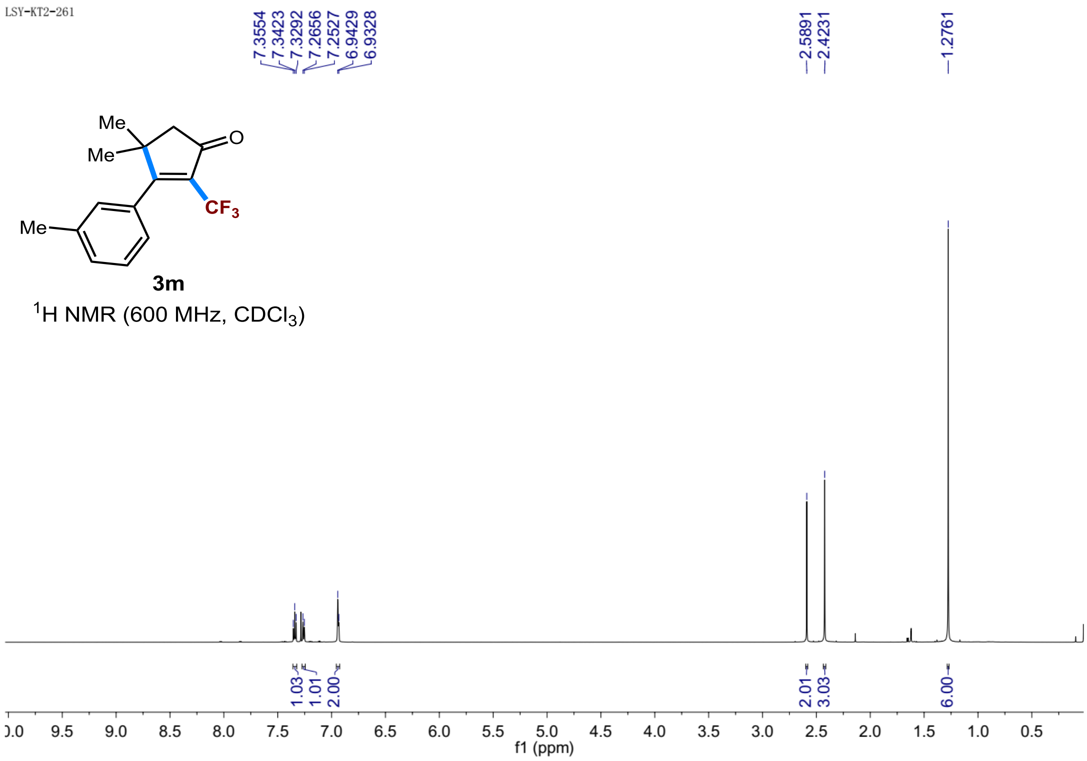
3l

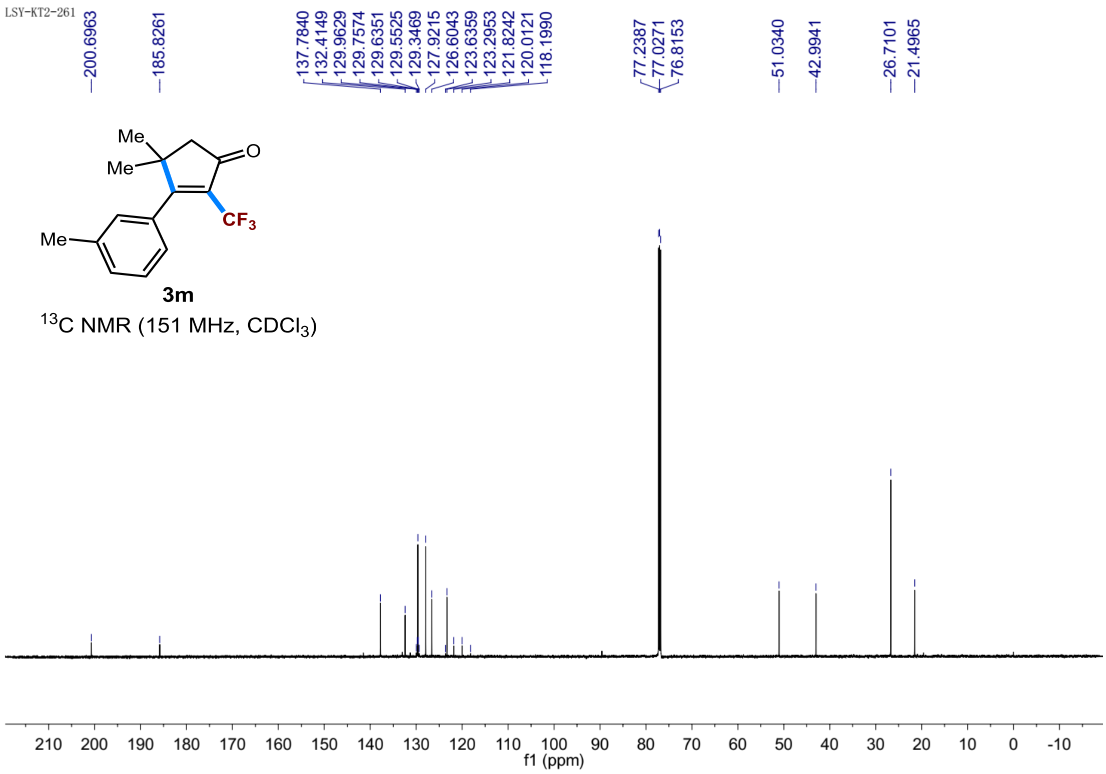
^{13}C NMR (151 MHz, $CDCl_3$)



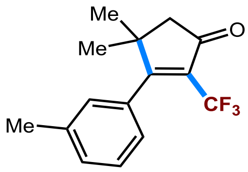
3l

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


LSY-KT2-261
7.3554
7.3423
7.3292
7.2656
7.2527
6.9429
6.9328
2.5891
2.4231
1.2761
Me
Me
O
CF3
Me
3m
1H NMR (600 MHz, CDCl3)
1.03
1.01
2.00
2.01
3.03
6.00
f1 (ppm)

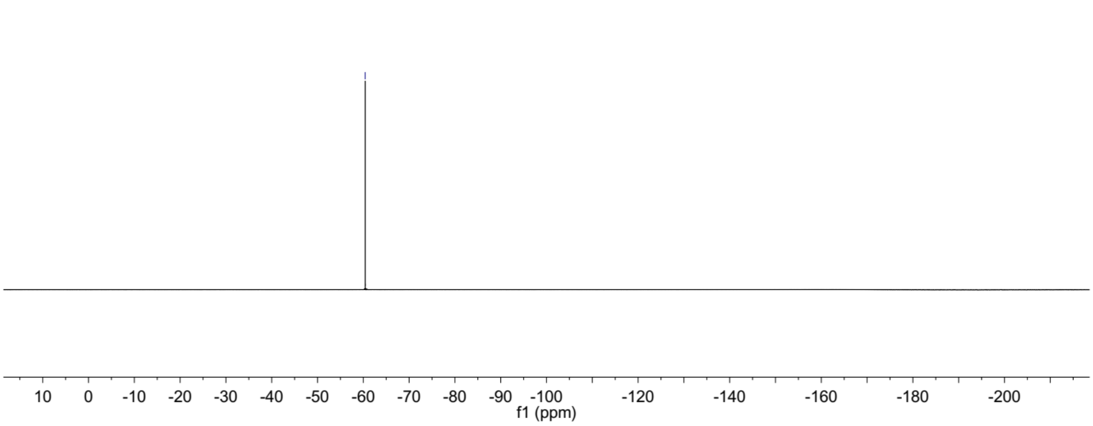

LSY-KT2-261
200.6963
185.8261
137.7840
132.4149
129.9629
129.7574
129.6351
129.5525
129.3469
127.9215
126.6043
123.6359
123.2953
121.8242
120.0121
118.1990
77.2387
77.0271
76.8153
51.0340
42.9941
26.7101
21.4965
Me
Me
O
CF3
Me
3m
13C NMR (151 MHz, CDCl3)
f1 (ppm)

LSY-KT2-243

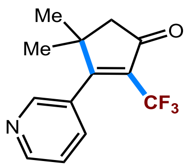


3m

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

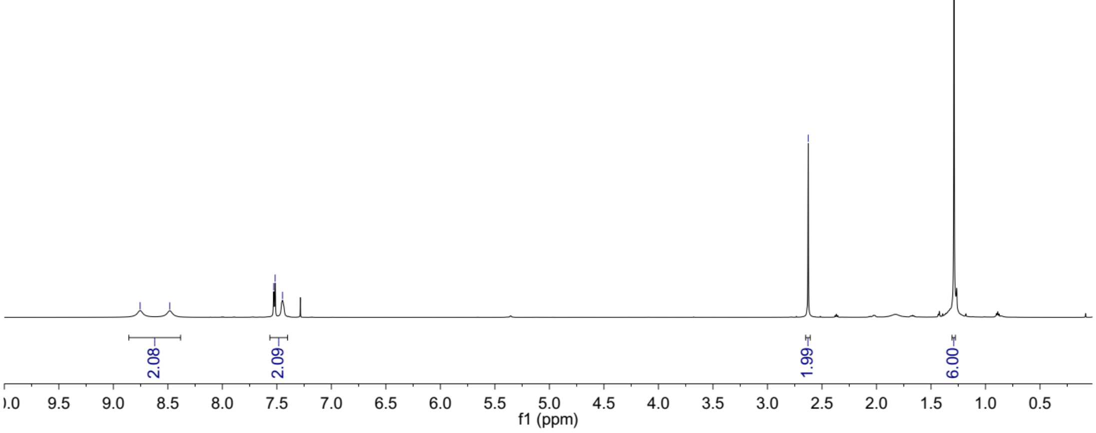


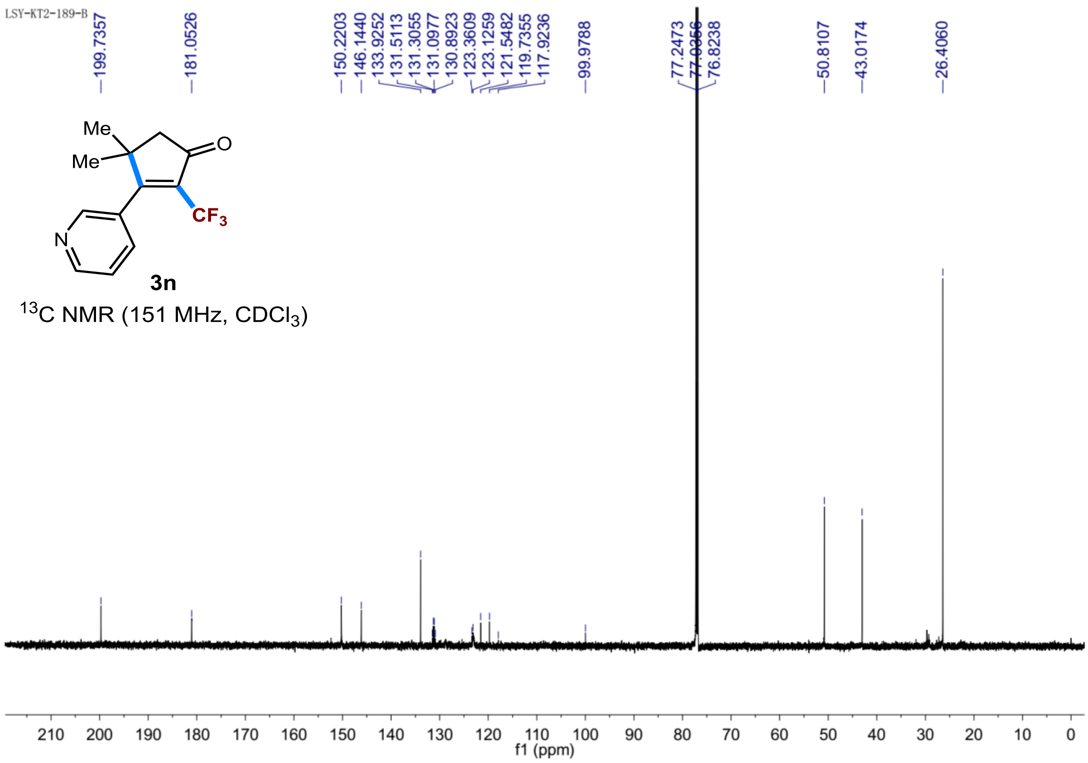
LSY-KT2-189-B

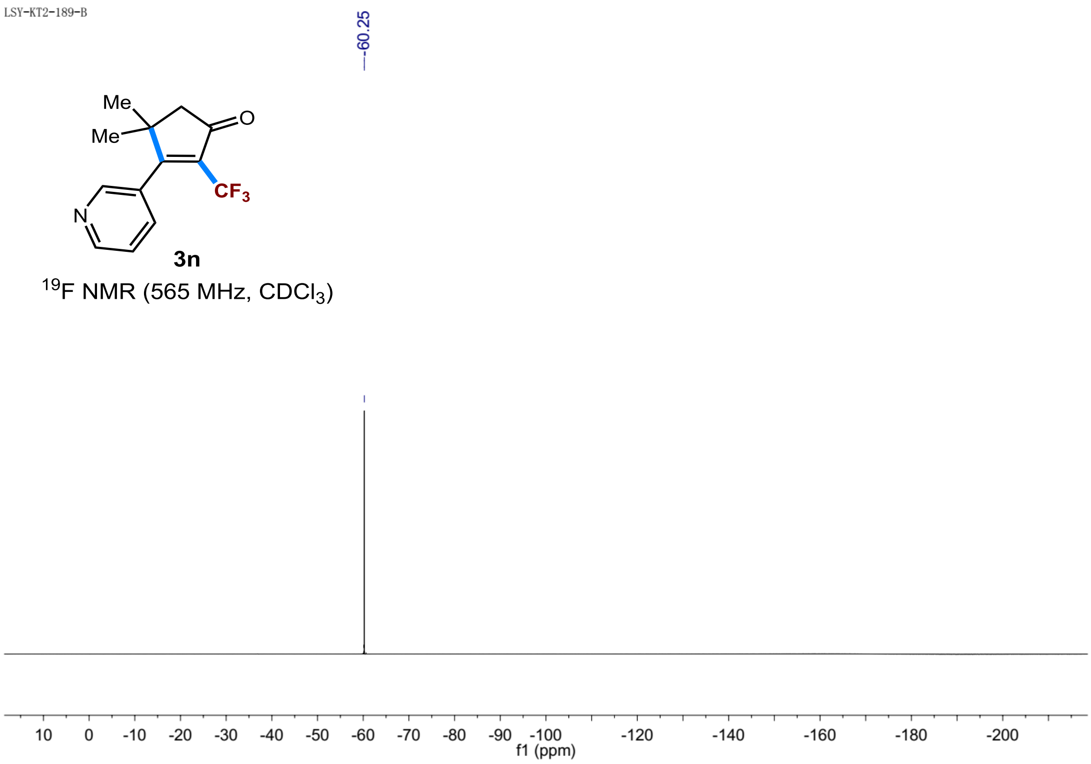


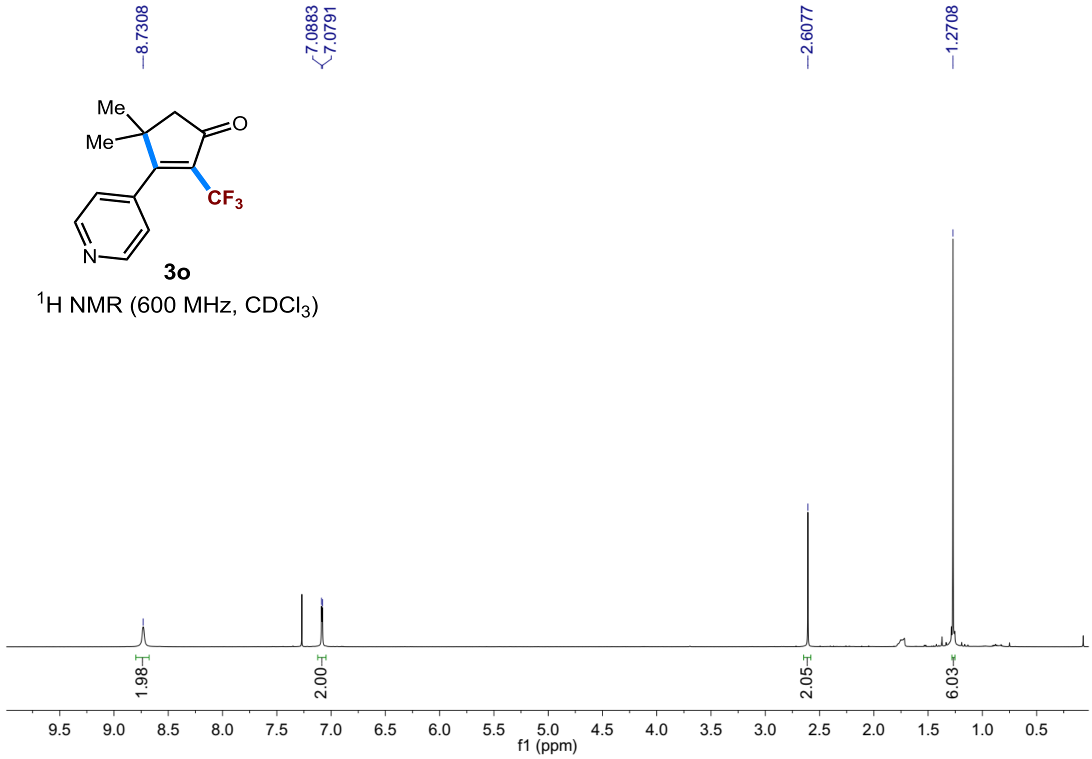
3n

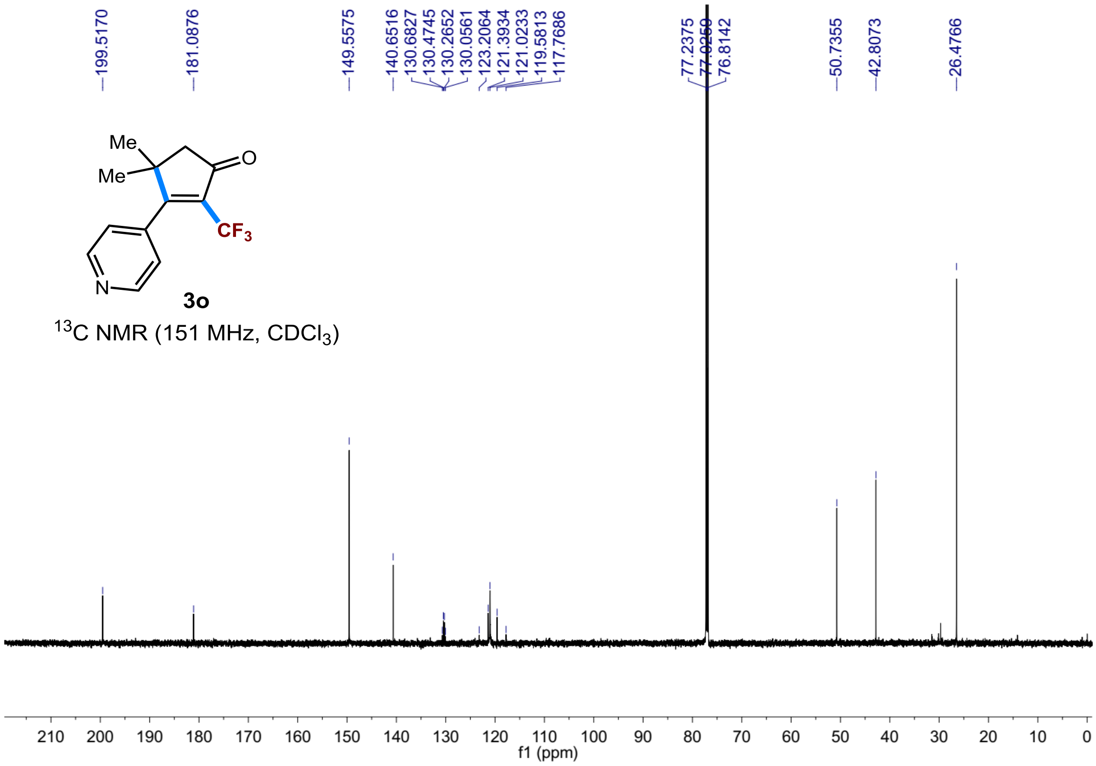
^{1}H NMR (600 MHz, $CDCl_3$)

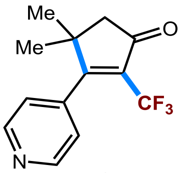



LSY-KT2-189-B
199.7357
181.0526
150.2203
146.1440
133.9252
131.5113
131.3055
131.0977
130.8923
123.3609
123.1259
121.5482
119.7355
117.9236
99.9788
77.2473
77.0356
76.8238
50.8107
43.0174
26.4060
Me
Me
O
CF3
N
3n
13C NMR (151 MHz, CDCl3)
f1 (ppm)


LSY-KT2-189-B
-60.25
Me
Me
O
CF3
N
3n
19F NMR (565 MHz, CDCl3)
f1 (ppm)

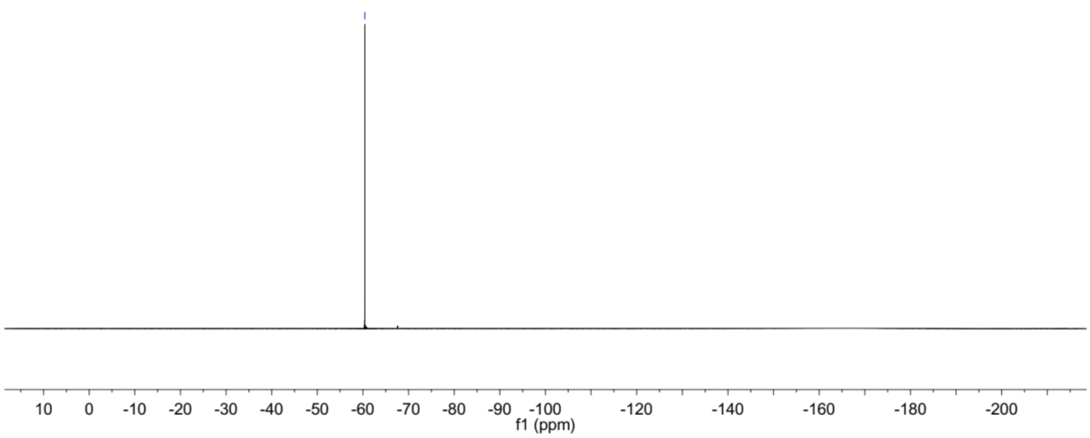

8.7308
7.0883
7.0791
2.6077
1.2708
Me
Me
O
CF3
N
3o
1H NMR (600 MHz, CDCl3)
1.98
2.00
2.05
6.03
f1 (ppm)

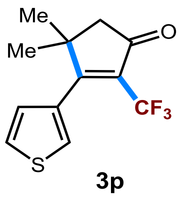

199.5170
181.0876
149.5575
140.6516
130.6827
130.4745
130.2652
130.0561
123.2064
121.3934
121.0233
119.5813
117.7686
77.2375
77.0259
76.8142
50.7355
42.8073
26.4766
Me
Me
O
CF3
N
3o
13C NMR (151 MHz, CDCl3)
f1 (ppm)



3o

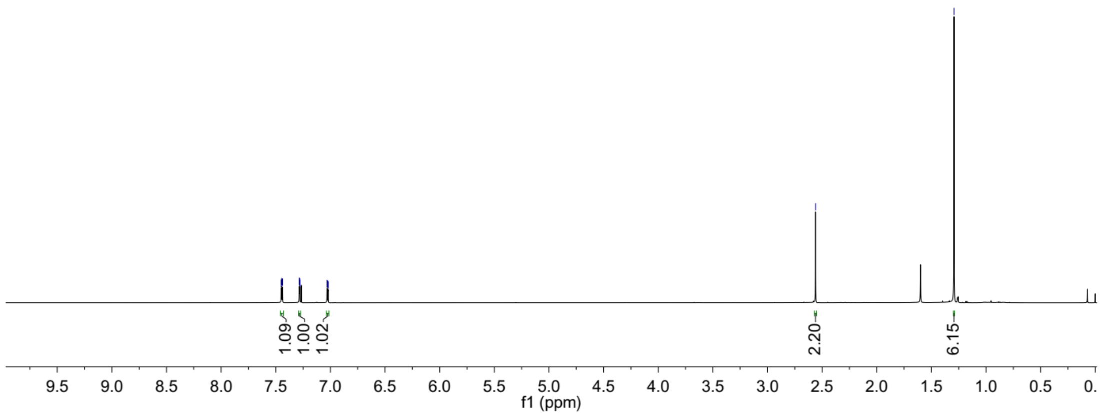
^{19}F NMR (565 MHz, $CDCl_3$)

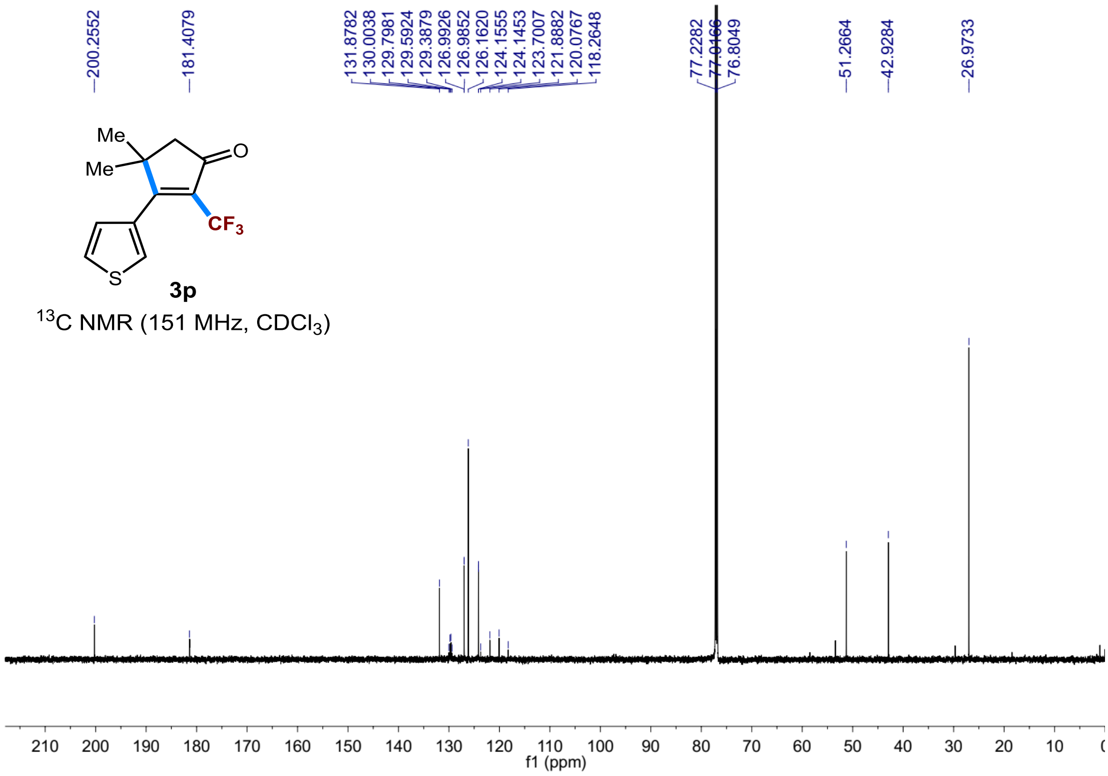


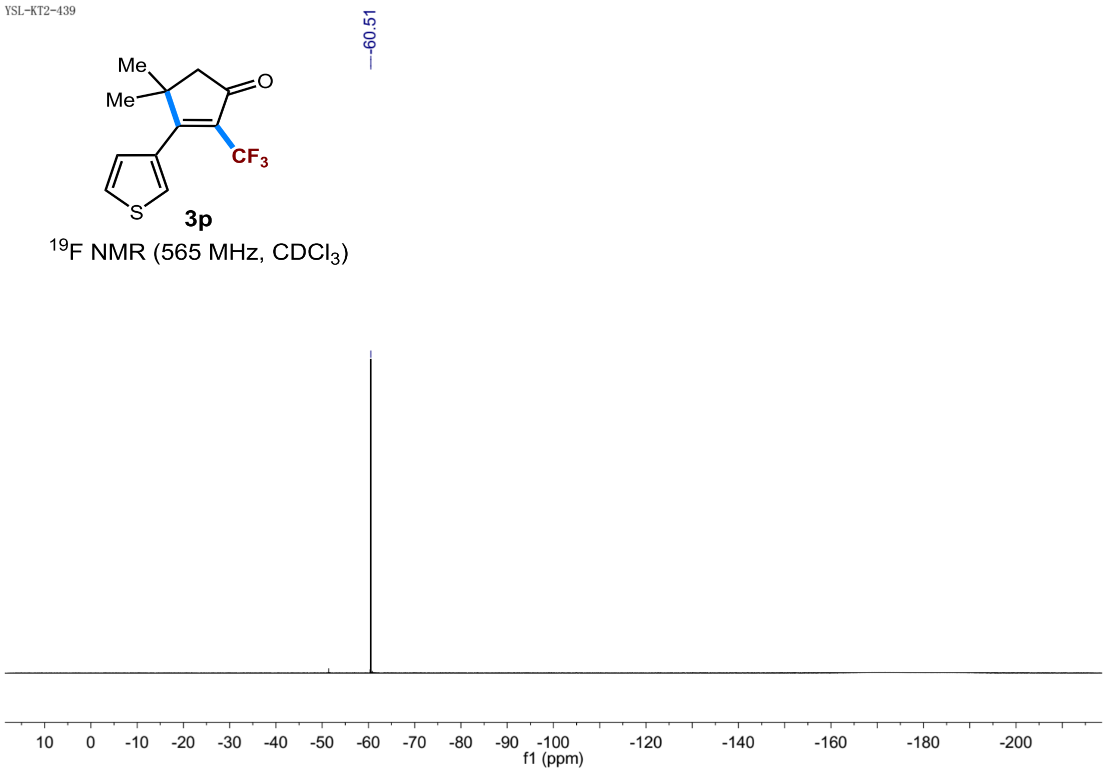


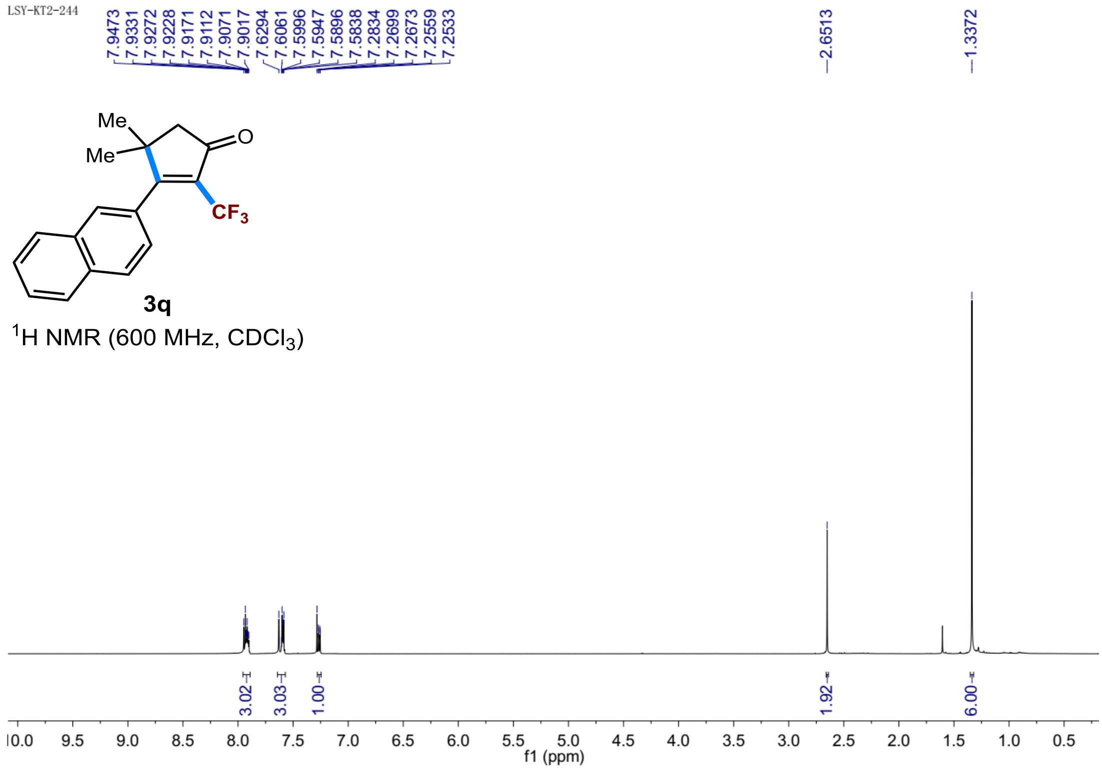
3p

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



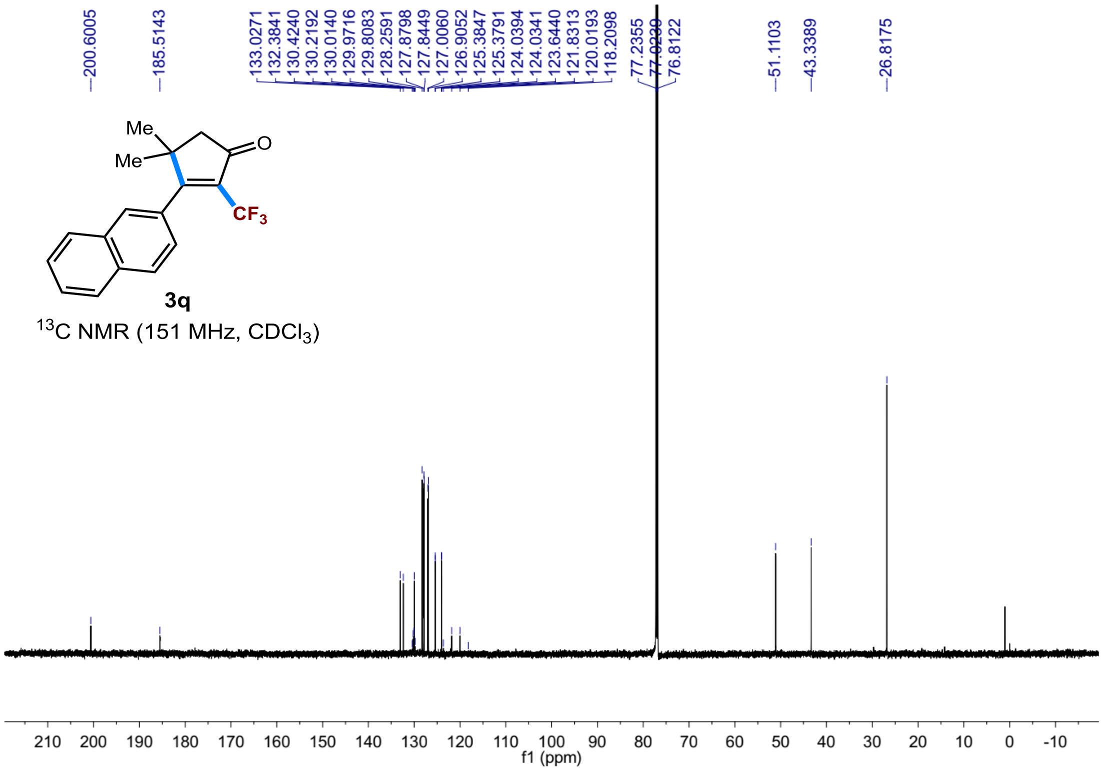

200.2552
181.4079
131.8782
130.0038
129.7981
129.5924
129.3879
126.9926
126.9852
126.1620
124.1555
124.1453
123.7007
121.8882
120.0767
118.2648
77.2282
77.0166
76.8049
51.2664
42.9284
26.9733
Me
Me
O
CF3
S
3p
13C NMR (151 MHz, CDCl3)
f1 (ppm)


YSL-KT2-439
-60.51
Me
Me
O
CF3
S
3p
19F NMR (565 MHz, CDCl3)
f1 (ppm)



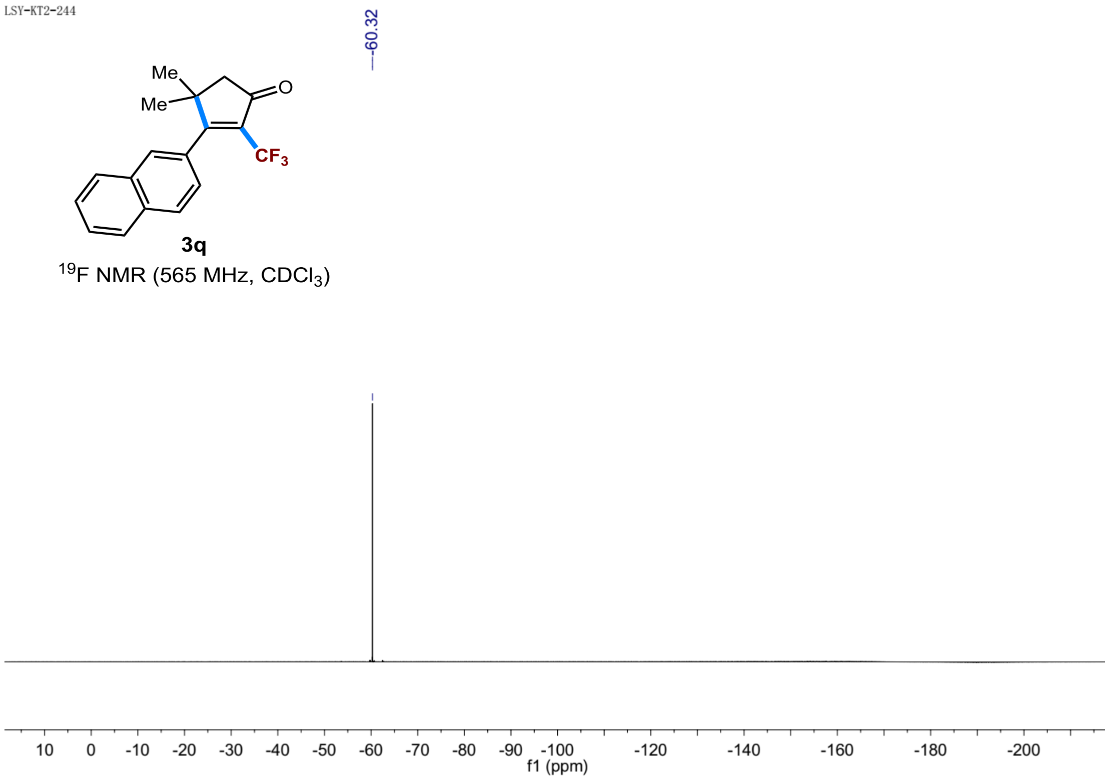
3q

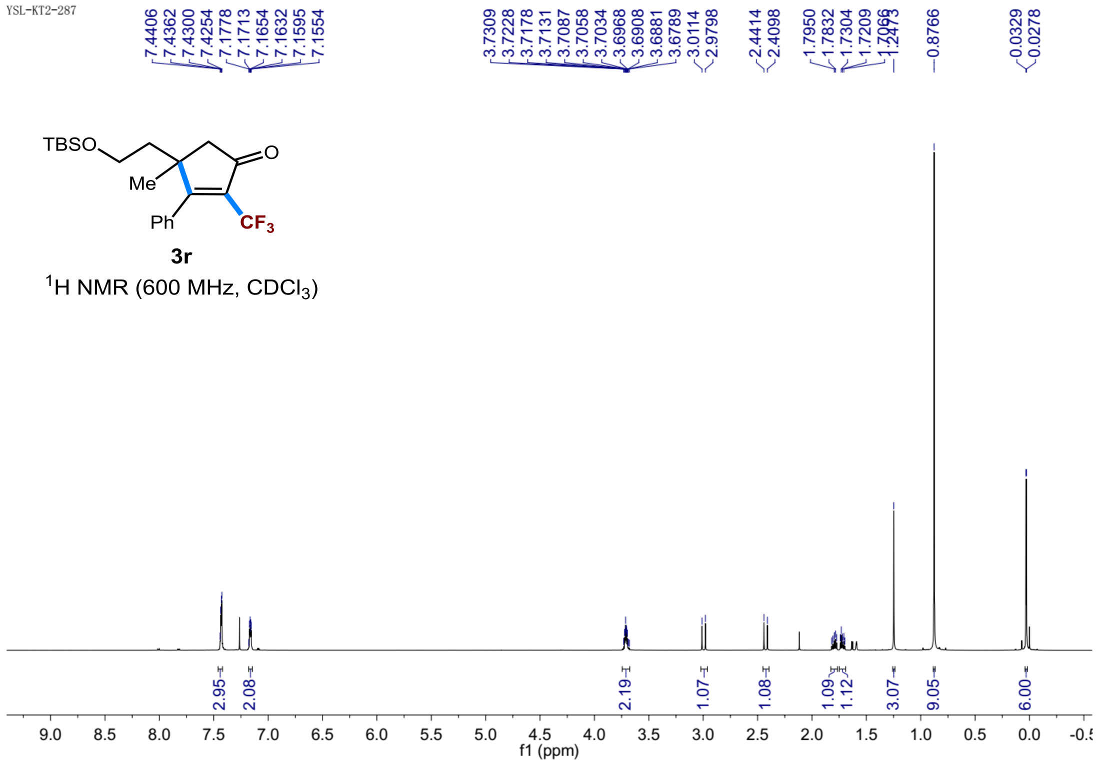
^{1}H NMR (600 MHz, $CDCl_3$)

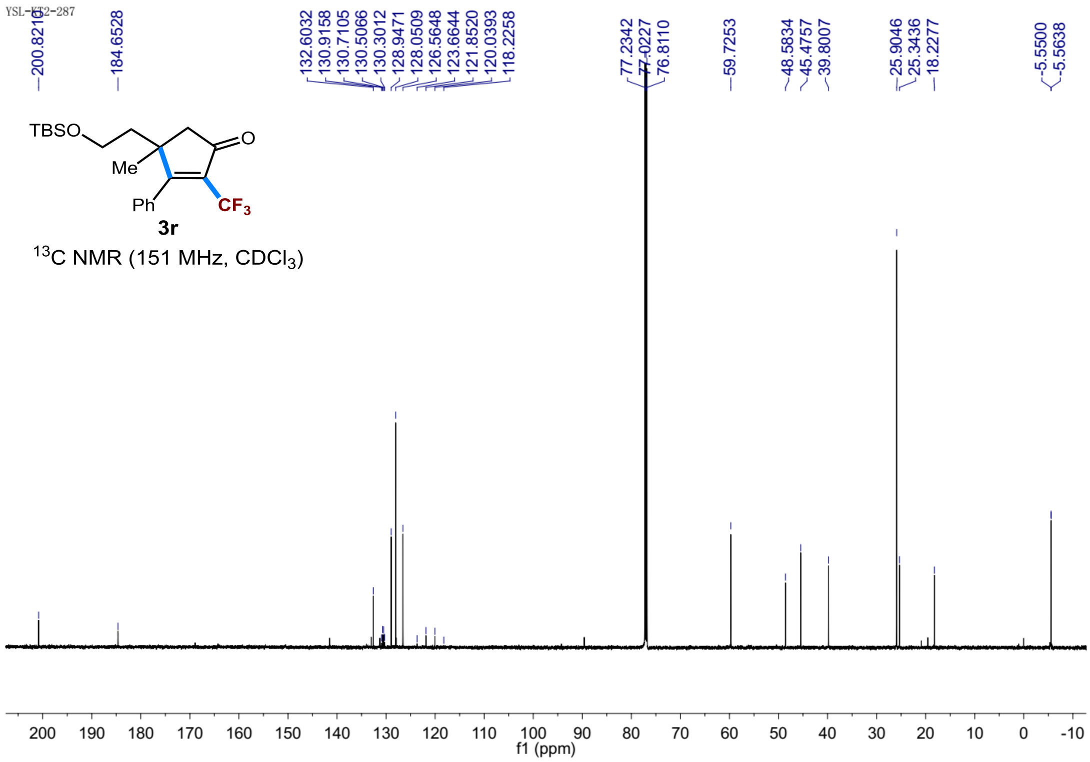


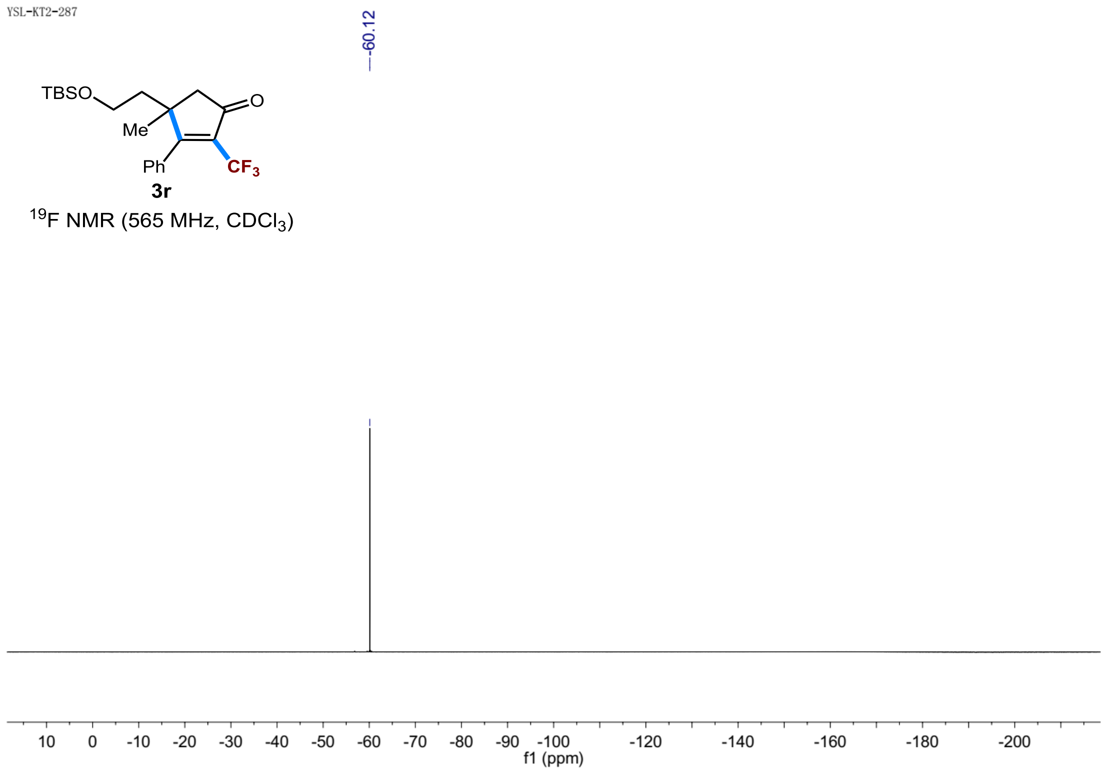
3q

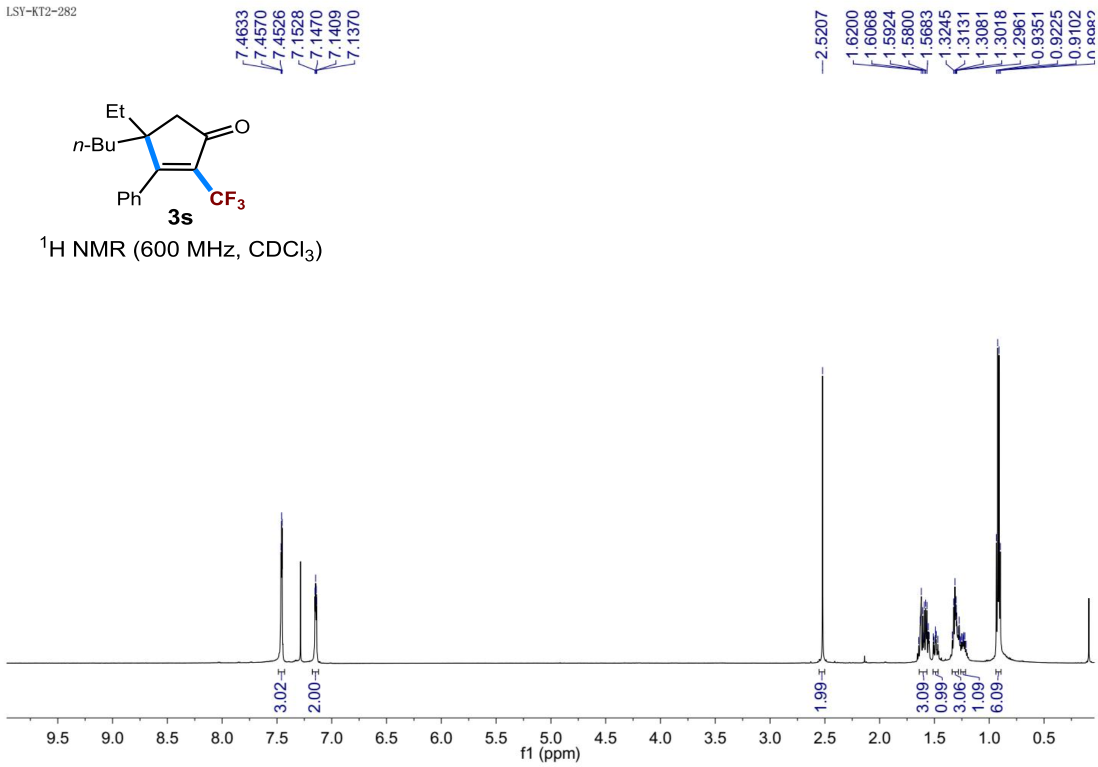
^{13}C NMR (151 MHz, $CDCl_3$)

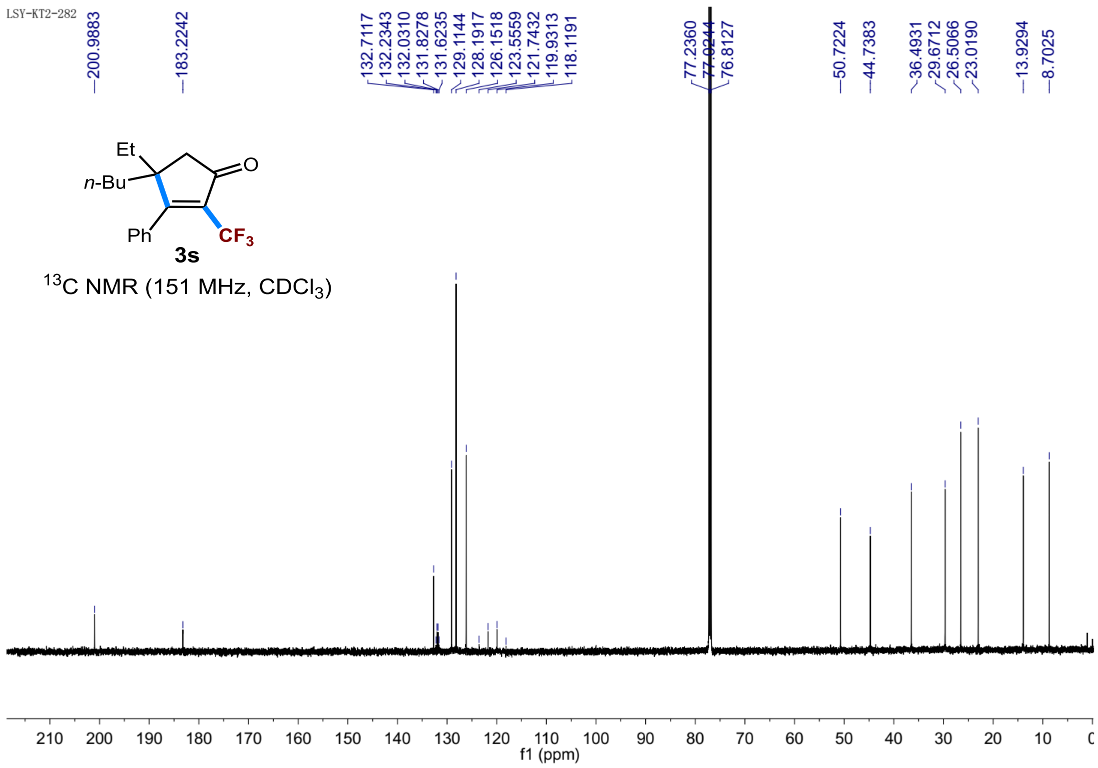

LSY-KT2-244
Me
Me
O
CF3
3q
19F NMR (565 MHz, CDCl3)
-60.32
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

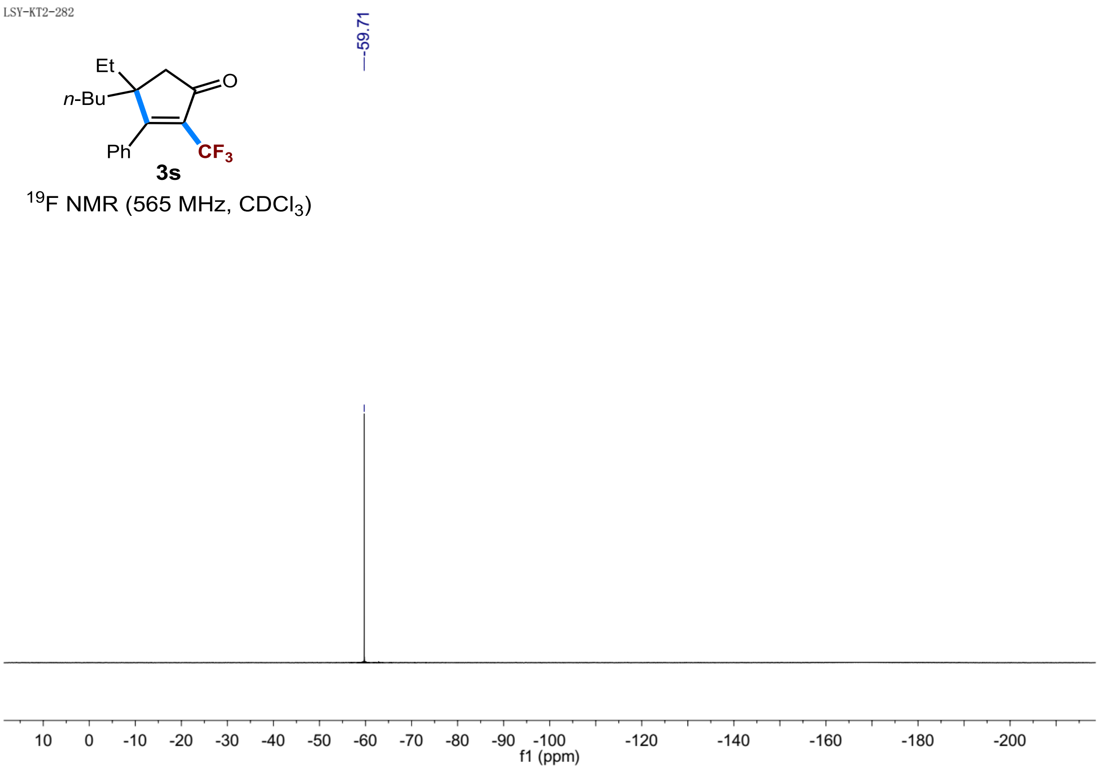

YSL-KT2-287
7.4406
7.4362
7.4300
7.4254
7.1778
7.1713
7.1654
7.1632
7.1595
7.1554
3.7309
3.7228
3.7178
3.7131
3.7087
3.7058
3.7034
3.6968
3.6908
3.6881
3.6789
3.0114
2.9798
2.4414
2.4098
1.7950
1.7832
1.7304
1.7209
1.2473
0.8766
0.0329
0.0278
TBSO
Me
O
Ph
CF3
3r
1H NMR (600 MHz, CDCl3)
2.95
2.08
2.19
1.07
1.08
1.09
1.12
3.07
9.05
6.00
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)


YSL-KT2-287
200.8210
184.6528
132.6032
130.9158
130.7105
130.5066
130.3012
128.9471
128.0509
126.5648
123.6644
121.8520
120.0393
118.2258
77.2342
77.0227
76.8110
59.7253
48.5834
45.4757
39.8007
25.9046
25.3436
18.2277
-5.5500
-5.5638
TBSO
O
Me
Ph
CF3
3r
13C NMR (151 MHz, CDCl3)
f1 (ppm)


YSL-KT2-287
-60.12
TBSO
O
Me
Ph
CF3
3r
19F NMR (565 MHz, CDCl3)
f1 (ppm)

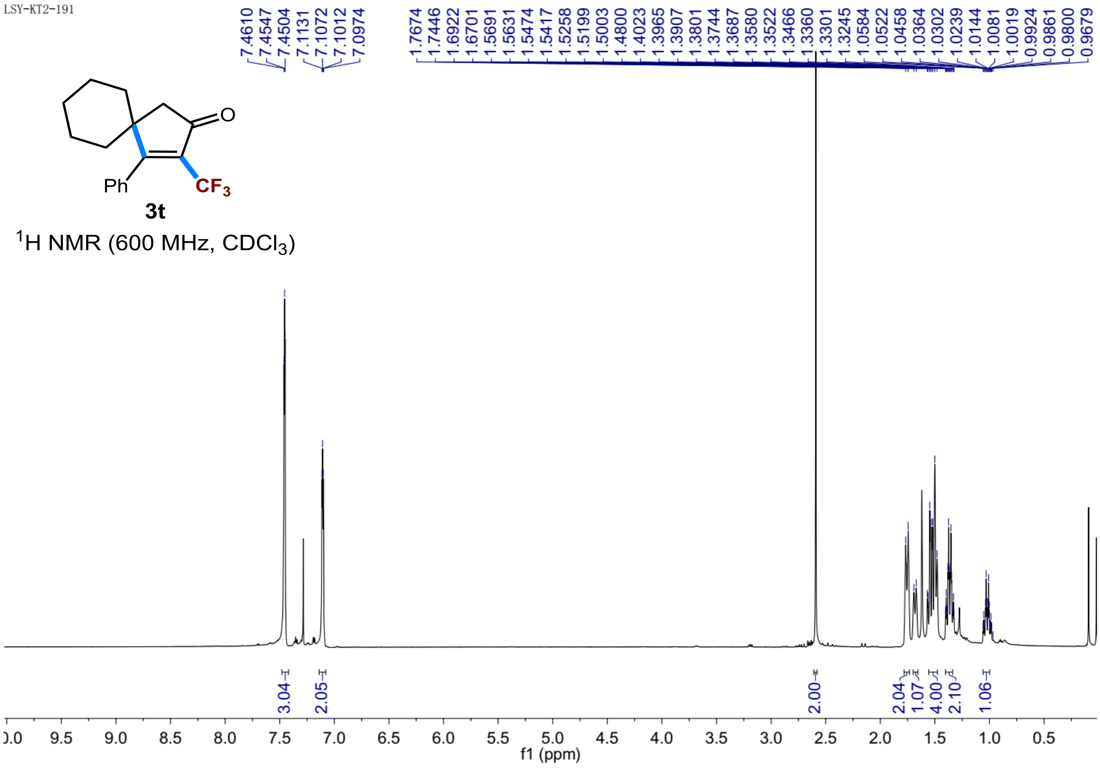

LSY-KT2-282
Et
n-Bu
O
Ph
CF3
3s
1H NMR (600 MHz, CDCl3)
f1 (ppm)


LSY-KT2-282
Et
n-Bu
O
Ph
CF3
3s
13C NMR (151 MHz, CDCl3)
f1 (ppm)



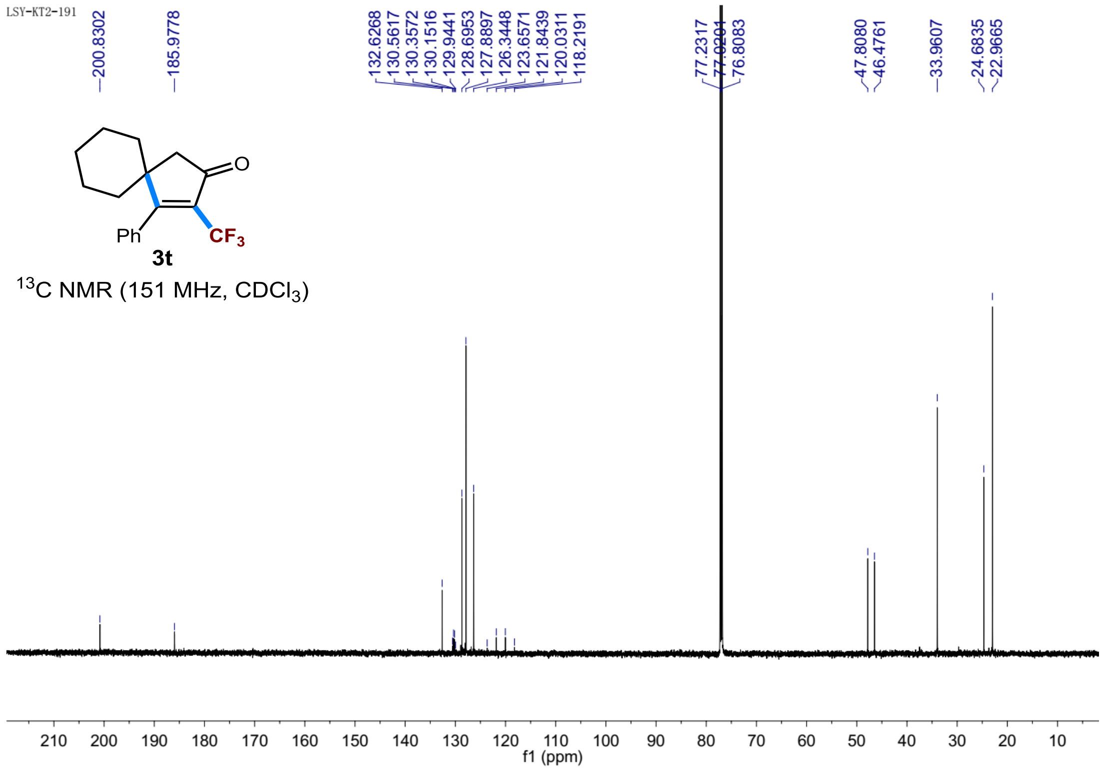
3s

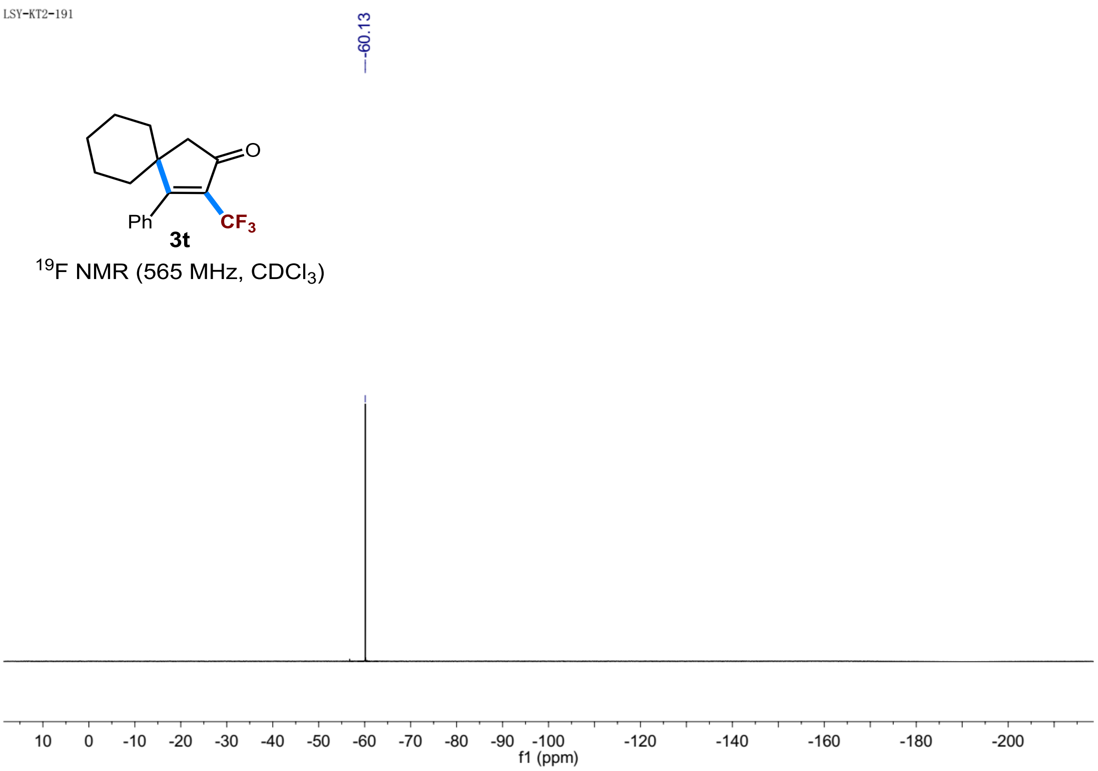
^{19}F NMR (565 MHz, $CDCl_3$)

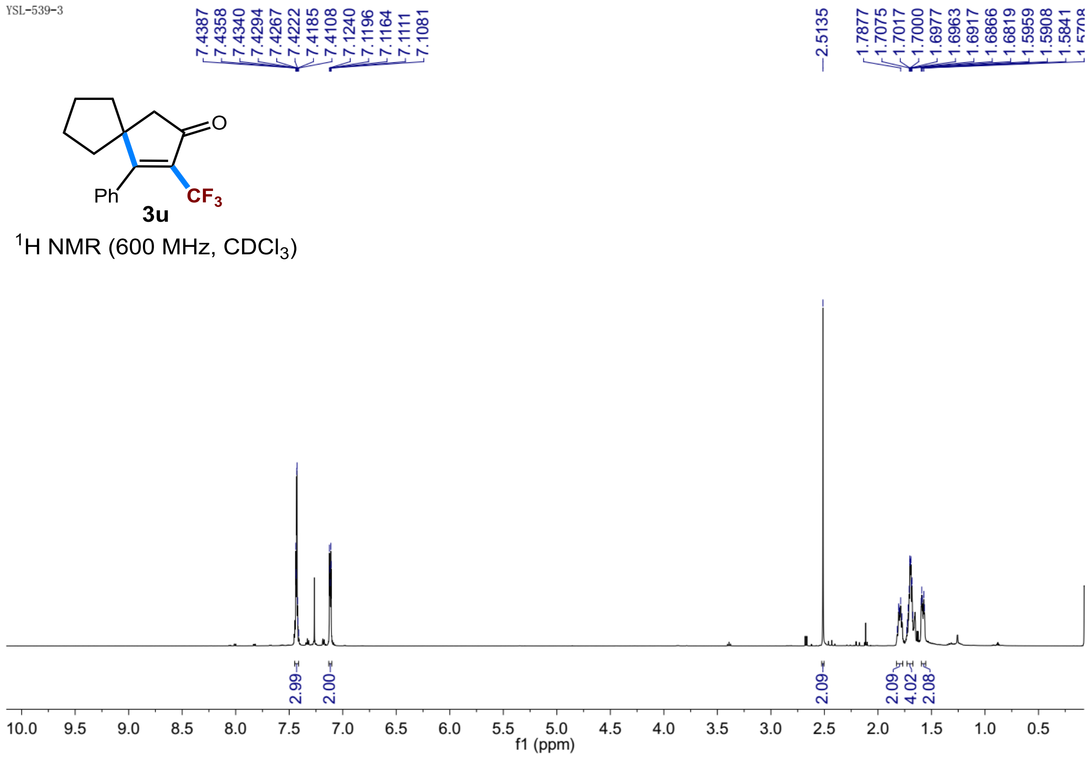


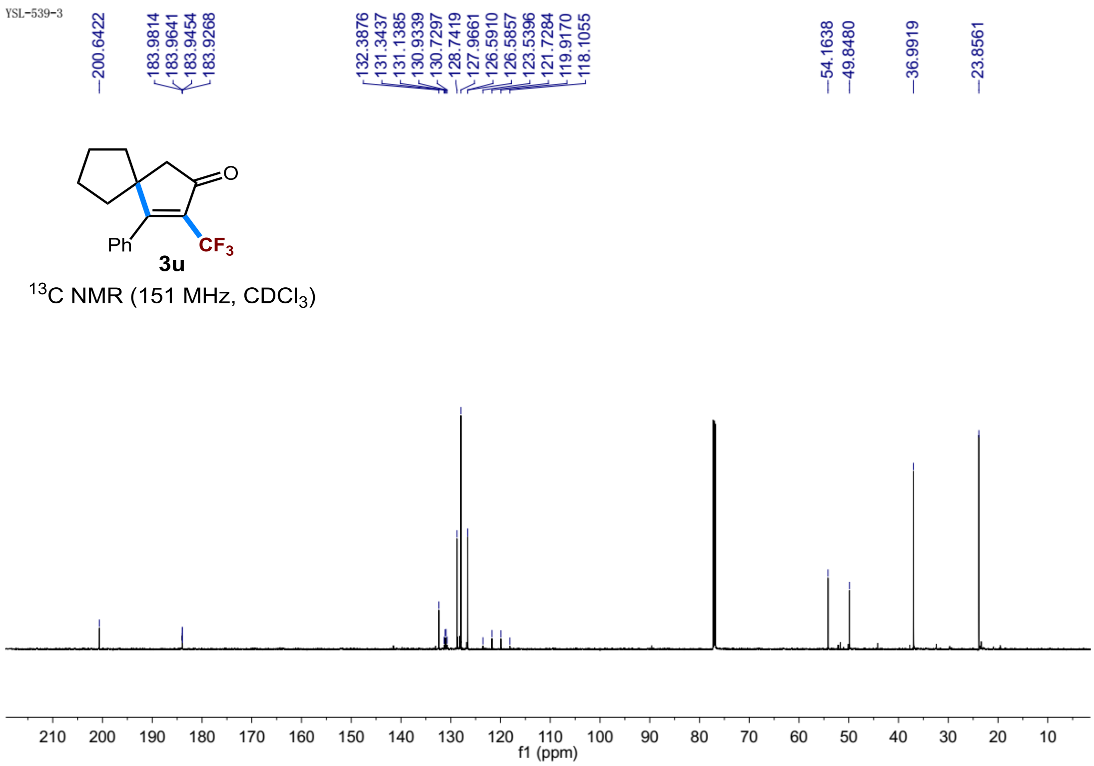
3t

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

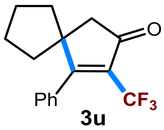

LSY-KT2-191
200.8302
185.9778
132.6268
130.5617
130.3572
130.1516
129.9441
128.6953
127.8897
126.3448
123.6571
121.8439
120.0311
118.2191
77.2317
76.8083
47.8080
46.4761
33.9607
24.6835
22.9665
O
Ph
CF3
3t
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


LSY-KT2-191
-60.13
O
Ph
CF3
3t
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


YSL-539-3
7.4387
7.4358
7.4340
7.4294
7.4267
7.4222
7.4185
7.4108
7.1240
7.1196
7.1164
7.1111
7.1081
2.5135
1.7877
1.7075
1.7017
1.7000
1.6977
1.6963
1.6917
1.6866
1.6819
1.5959
1.5908
1.5841
O
Ph
CF3
3u
1H NMR (600 MHz, CDCl3)
2.99
2.00
2.09
2.09
4.02
2.08
10.0 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
f1 (ppm)

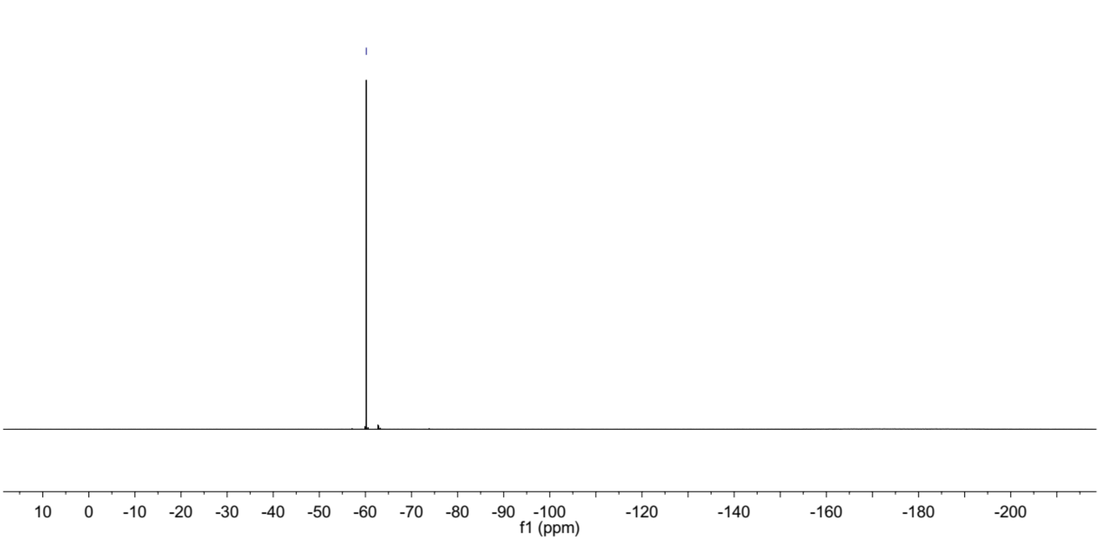

YSL-539-3
200.6422
183.9814
183.9641
183.9454
183.9268
132.3876
131.3437
131.1385
130.9339
130.7297
128.7419
127.9661
126.5910
126.5857
123.5396
121.7284
119.9170
118.1055
54.1638
49.8480
36.9919
23.8561
O
Ph
CF3
3u
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

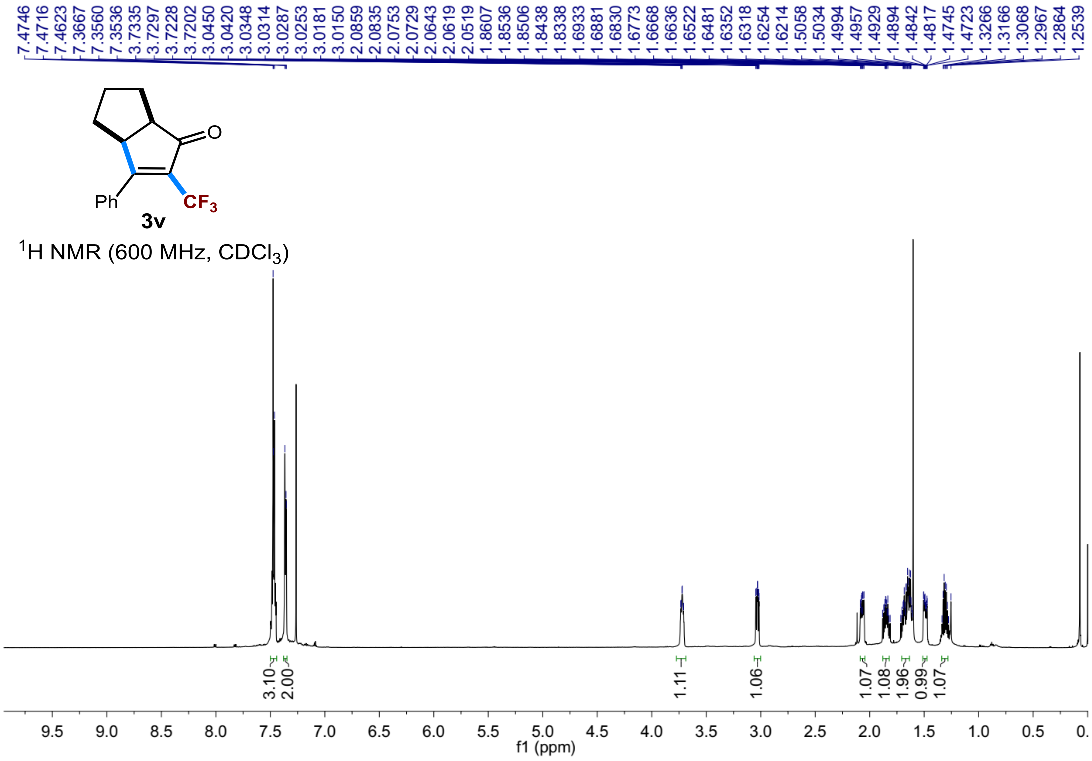
YSL-539-N

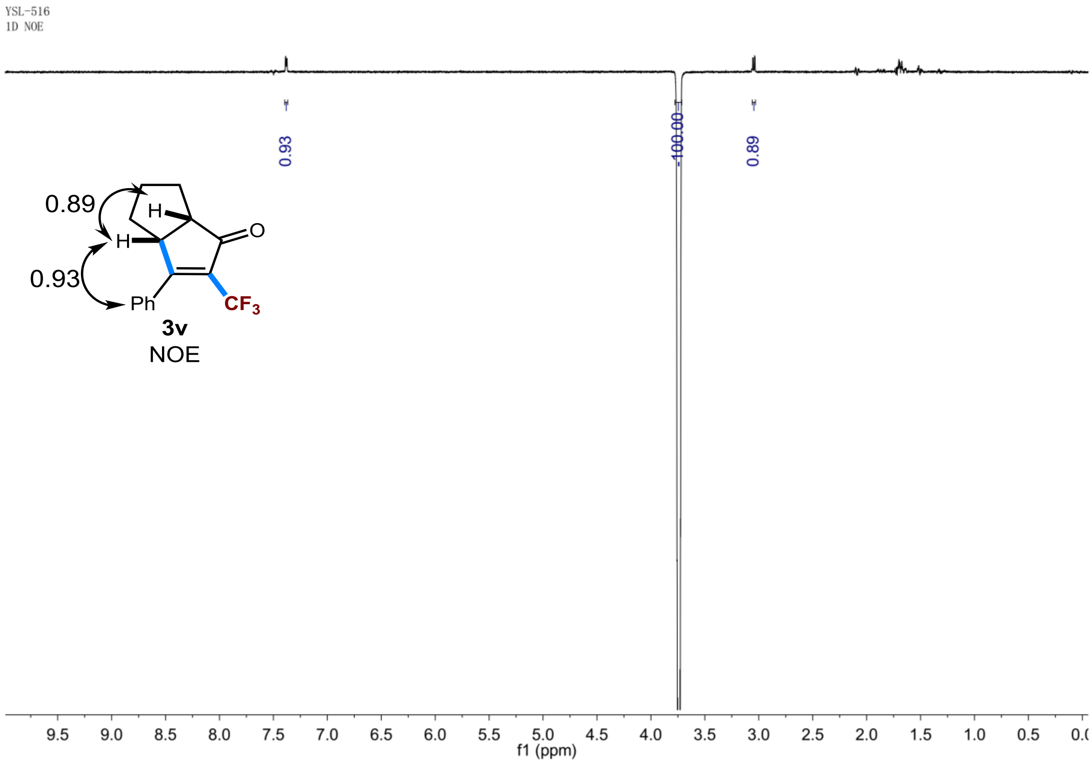


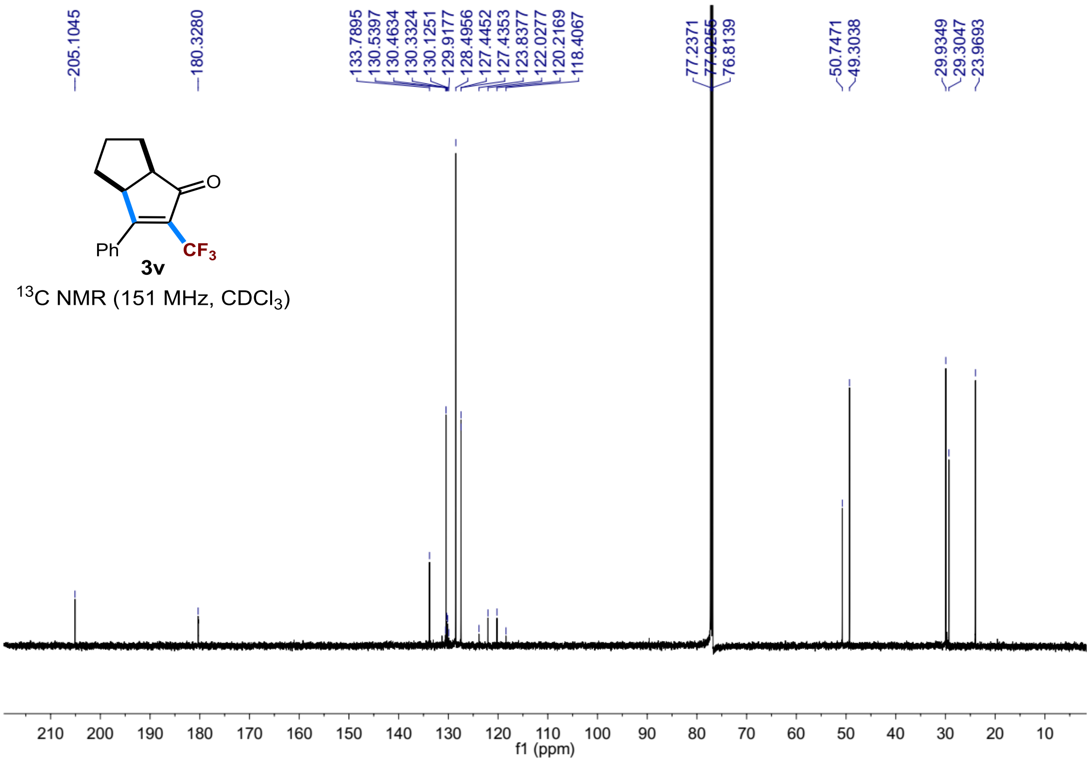
3u

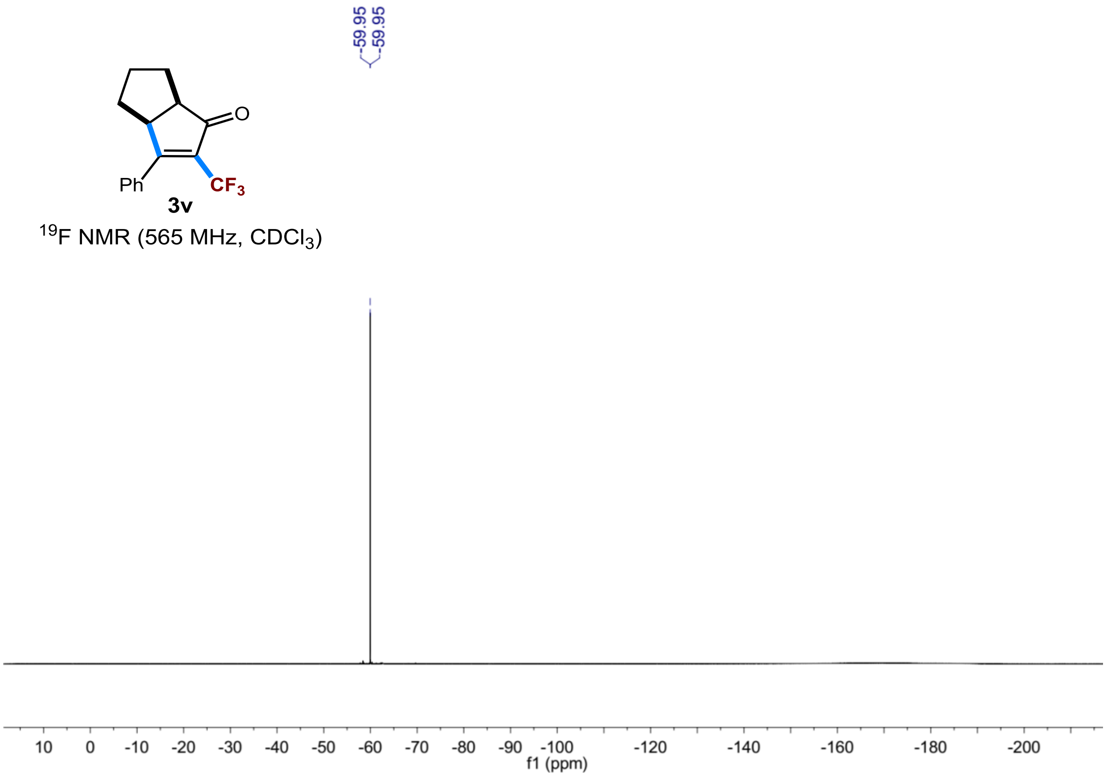
^{19}F NMR (565 MHz, $CDCl_3$)

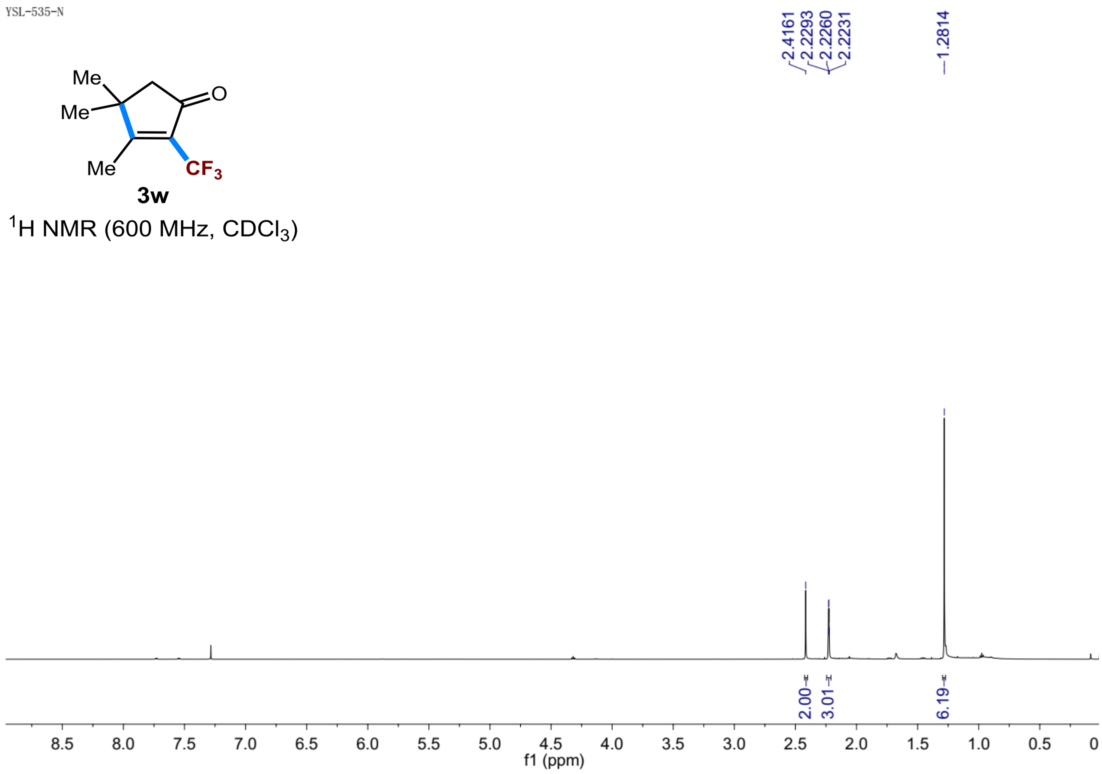



7.4746 7.4716 7.4623 7.3667 7.3560 7.3536 7.3335 3.7297 3.7228 3.7202 3.0450 3.0420 3.0348 3.0314 3.0287 3.0253 3.0181 3.0150 2.0859 2.0835 2.0753 2.0729 2.0643 2.0619 2.0519 1.8607 1.8536 1.8506 1.8438 1.8338 1.6933 1.6881 1.6830 1.6773 1.6668 1.6636 1.6522 1.6481 1.6352 1.6318 1.6254 1.6214 1.5058 1.5034 1.4994 1.4957 1.4929 1.4894 1.4842 1.4817 1.4745 1.4723 1.3266 1.3166 1.3068 1.2967 1.2864 1.2539
O
Ph
CF3
3v
1H NMR (600 MHz, CDCl3)
3.10
2.00
1.11
1.06
1.07
1.08
1.96
0.99
1.07
f1 (ppm)


YSL-516
1D NOE
0.93
-100.00
0.89
0.89
0.93
H
H
O
Ph
CF3
3v
NOE
f1 (ppm)

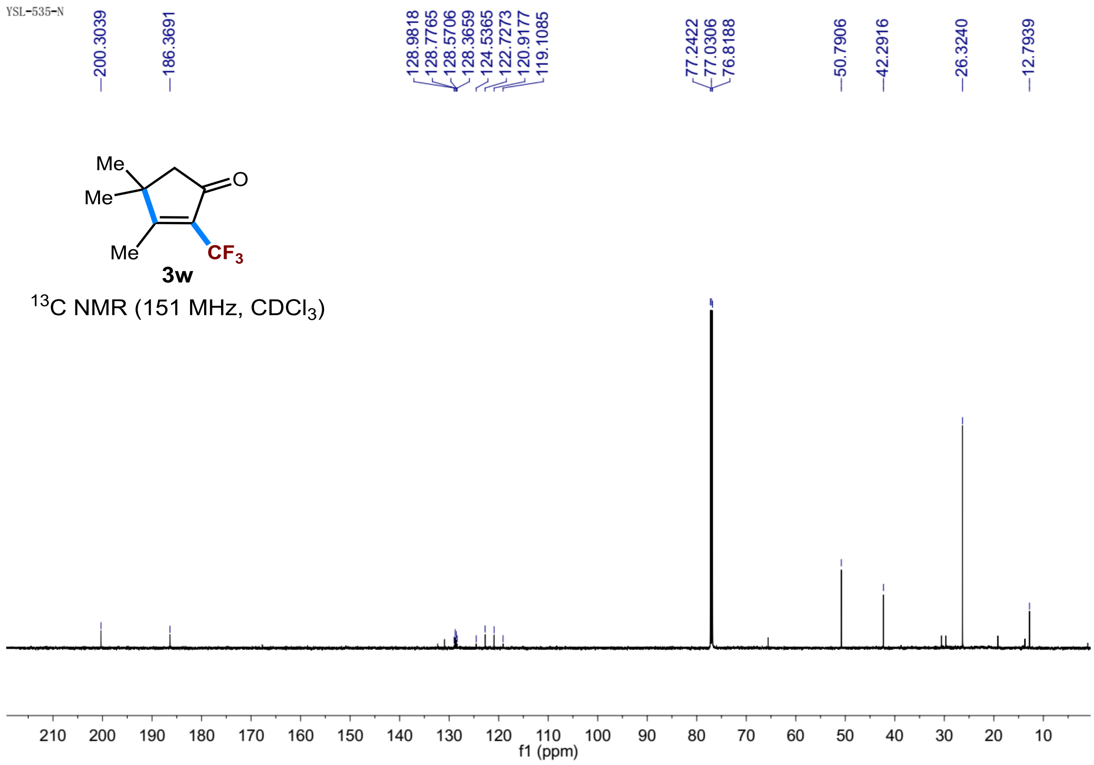

205.1045
180.3280
133.7895
130.5397
130.4634
130.3324
130.1251
129.9177
128.4956
127.4452
127.4353
123.8377
122.0277
120.2169
118.4067
77.2371
77.0255
76.8139
50.7471
49.3038
29.9349
29.3047
23.9693
O
Ph
CF3
3v
13C NMR (151 MHz, CDCl3)
f1 (ppm)


-59.95
-59.95
O
Ph
CF3
3v
19F NMR (565 MHz, CDCl3)
f1 (ppm)



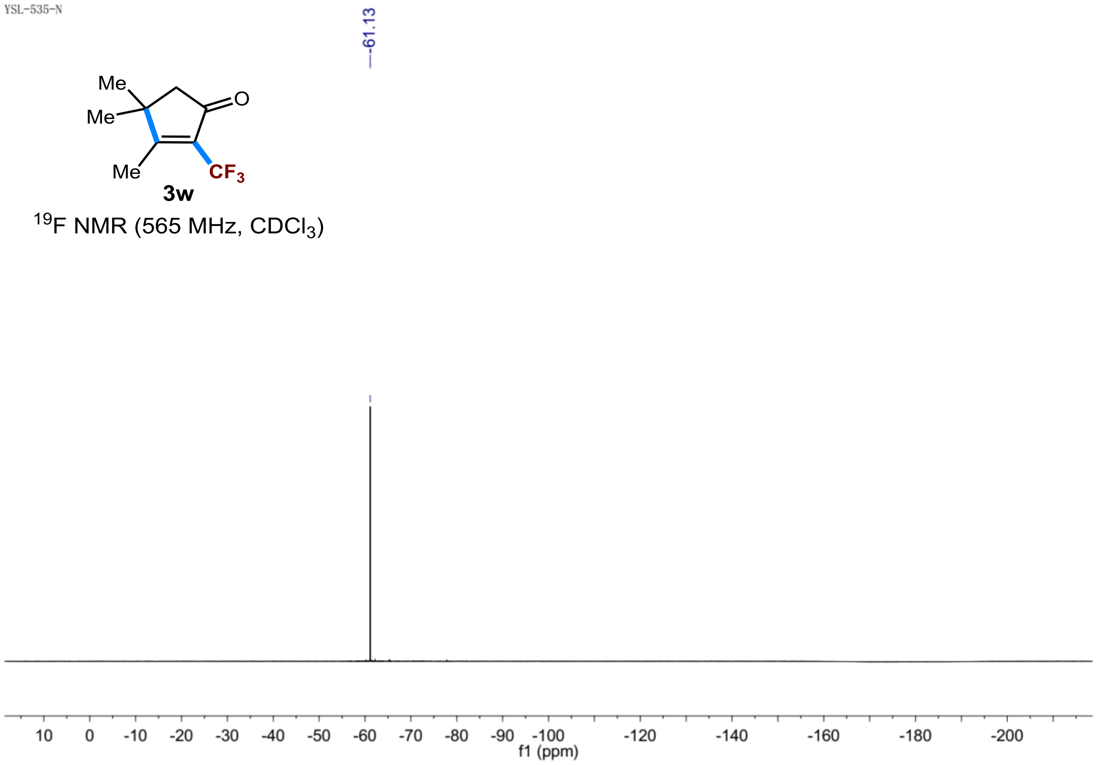
3w

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



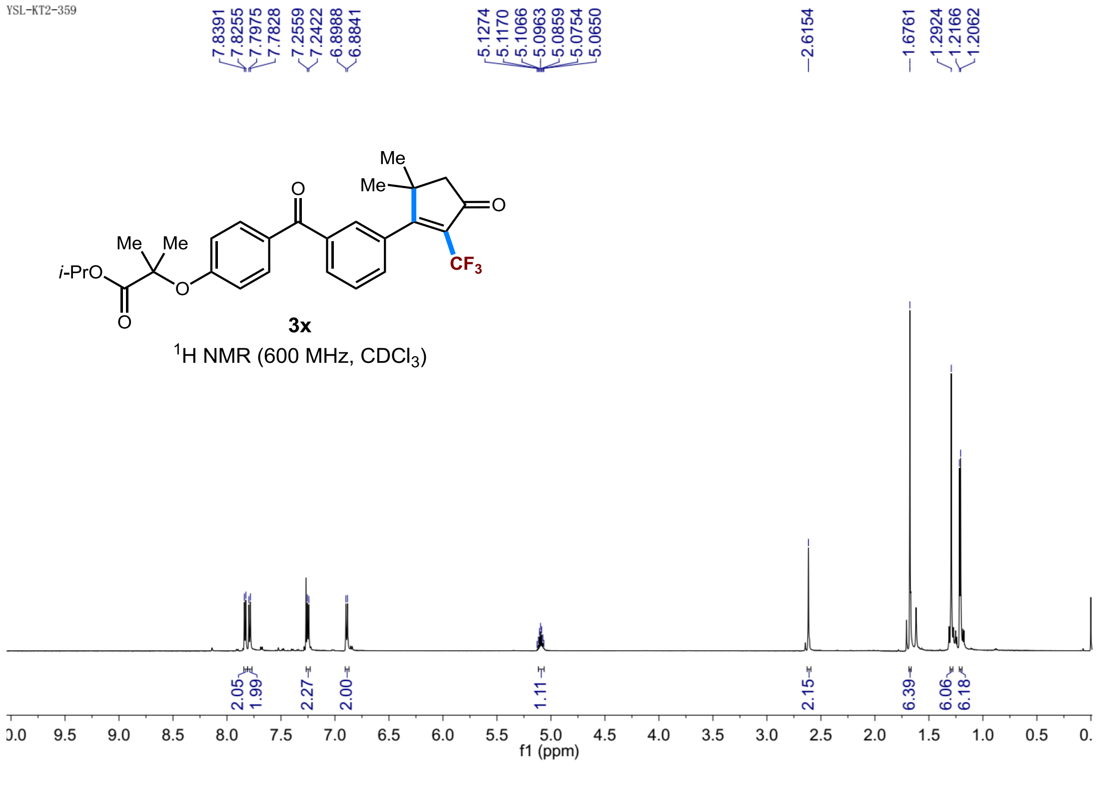
3w

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



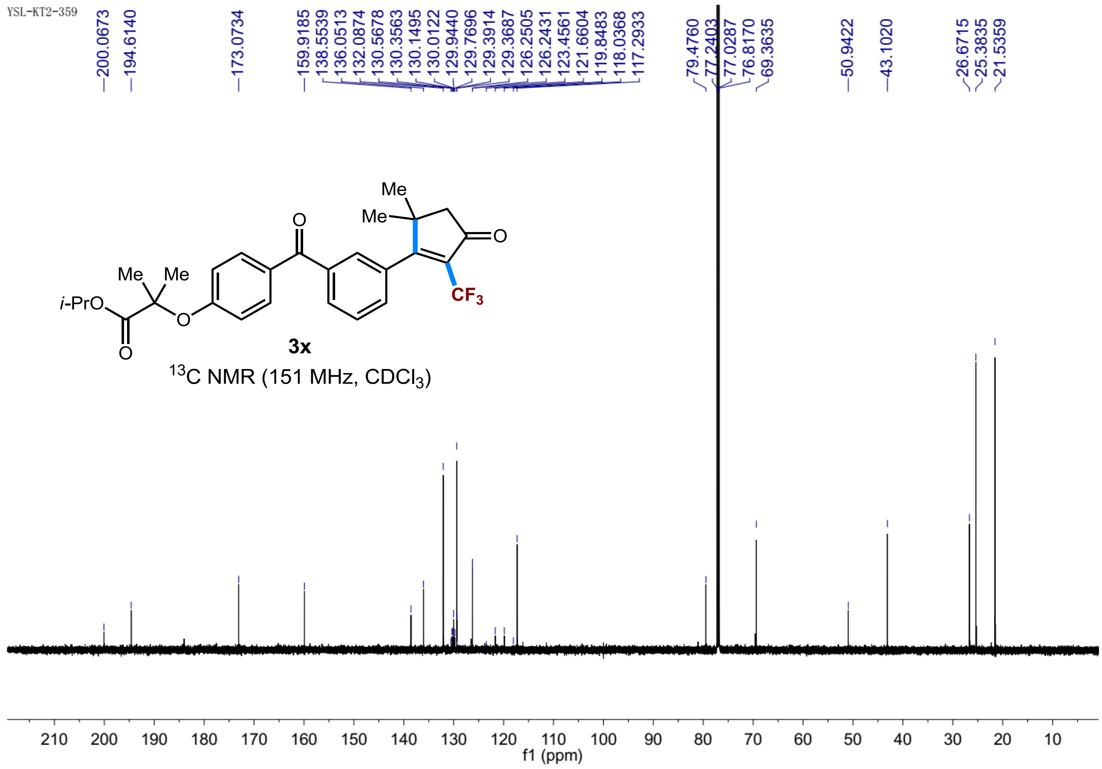
3w

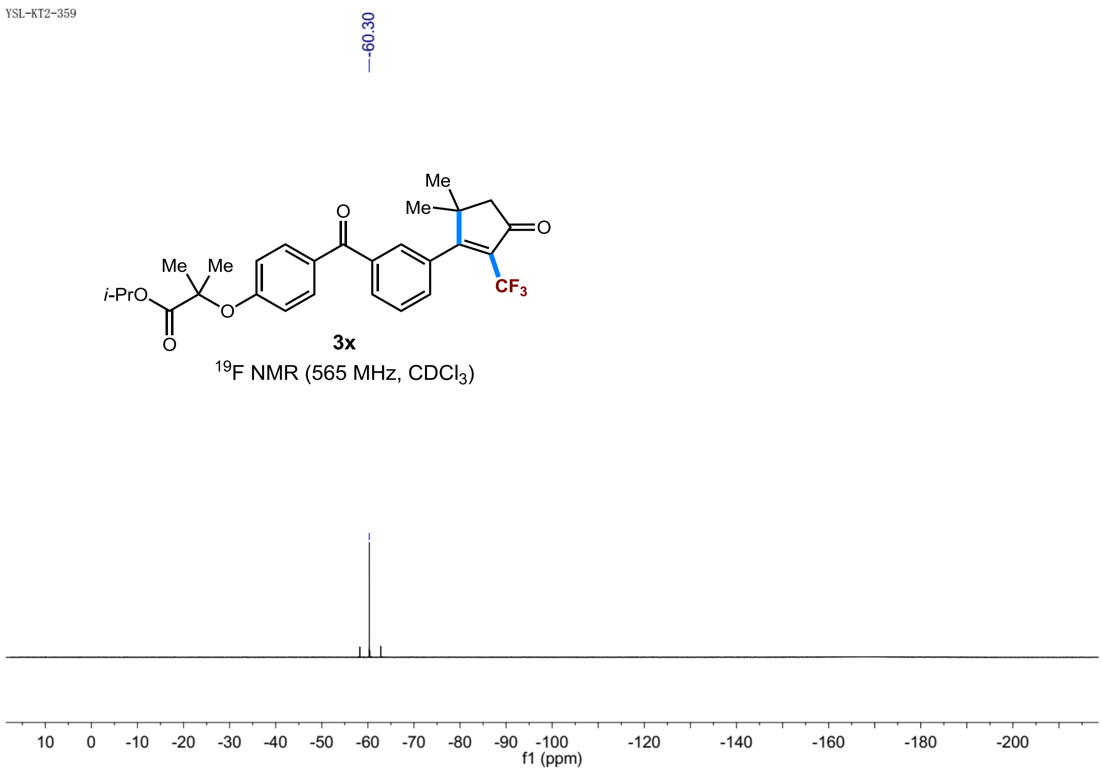
^{19}F NMR (565 MHz, $CDCl_3$)

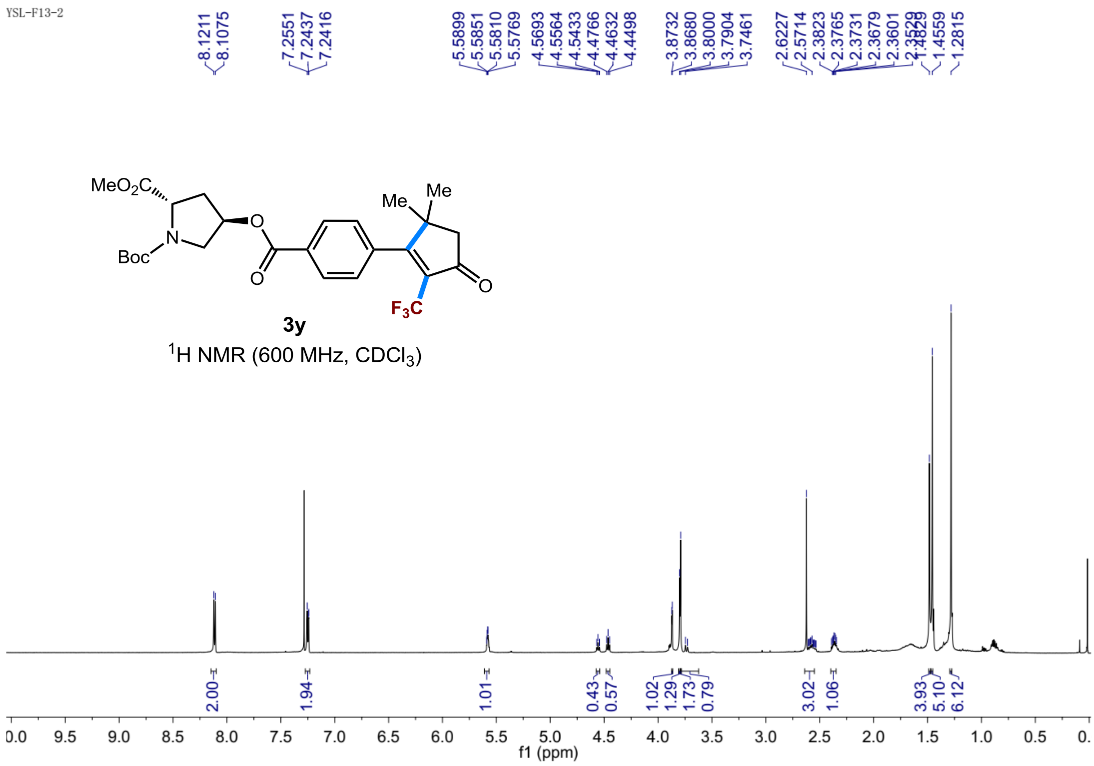


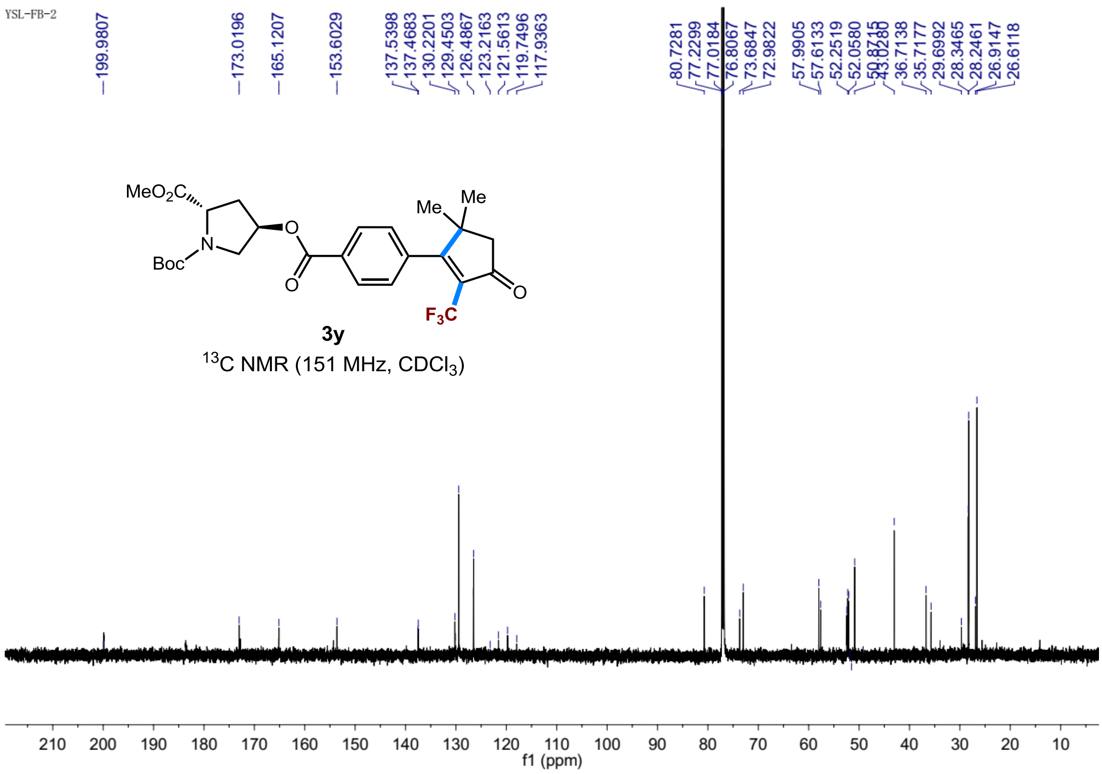
3x

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

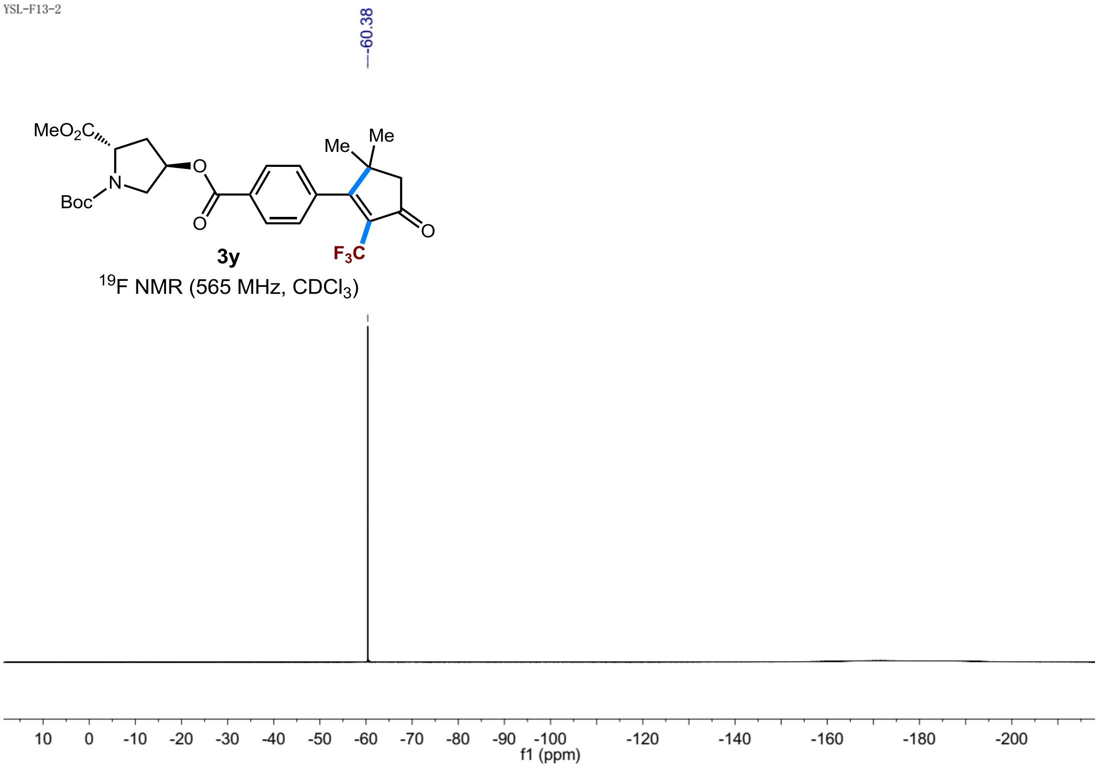

YSL-KT2-359
200.0673
194.6140
173.0734
159.9185
138.5539
136.0513
132.0874
130.5678
130.3563
130.1495
130.0122
129.9440
129.7696
129.3914
129.3687
126.2505
126.2431
123.4561
121.6604
119.8483
118.0368
117.2933
79.4760
77.2403
77.0287
76.8170
69.3635
50.9422
43.1020
26.6715
25.3835
21.5359
Me
Me
O
O
Me
Me
i-PrO
O
O
CF3
3x
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


YSL-KT2-359
-60.30
Me
Me
O
O
Me
Me
i-PrO
O
O
CF3
3x
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


YSL-F13-2
8.1211
8.1075
7.2551
7.2437
7.2416
5.5899
5.5851
5.5810
5.5769
4.5693
4.5564
4.5433
4.4766
4.4632
4.4498
3.8732
3.8680
3.8000
3.7904
3.7461
2.6227
2.5714
2.3823
2.3765
2.3731
2.3679
2.3601
1.4559
1.2815
MeO$_2$C
N
Boc
O
O
Me
Me
O
F$_3$C
3y
^{1}H NMR (600 MHz, CDCl$_3$)
2.00
1.94
1.01
0.43
0.57
1.02
1.29
1.73
0.79
3.02
1.06
3.93
5.10
6.12
f1 (ppm)

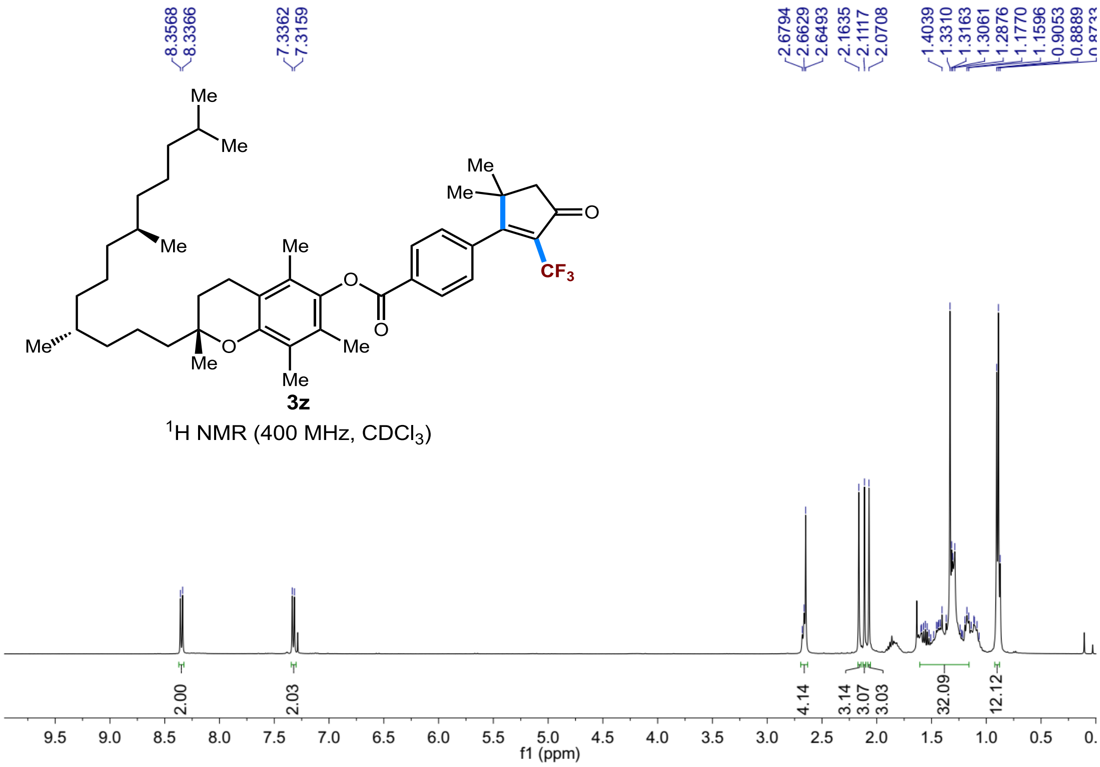

YSL-FB-2
199.9807
173.0196
165.1207
153.6029
137.5398
137.4683
130.2201
129.4503
126.4867
123.2163
121.5613
119.7496
117.9363
80.7281
77.2299
77.0184
76.8067
73.6847
72.9822
57.9905
57.6133
52.2519
52.0580
36.7138
35.7177
29.6992
28.3465
28.2461
26.9147
26.6118
MeO$_2$C
N
Boc
O
O
Me
Me
O
F$_3$C
3y
^{13}C NMR (151 MHz, CDCl$_3$)
f1 (ppm)

YSL-F13-2



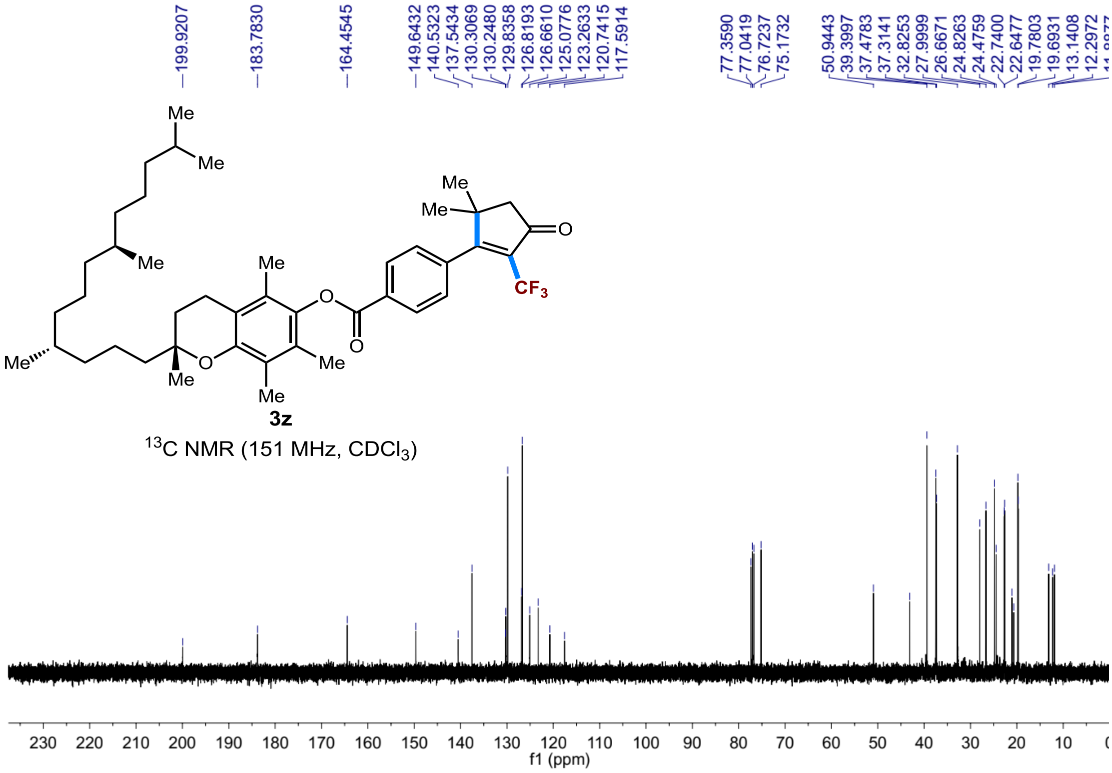
3y

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



3z

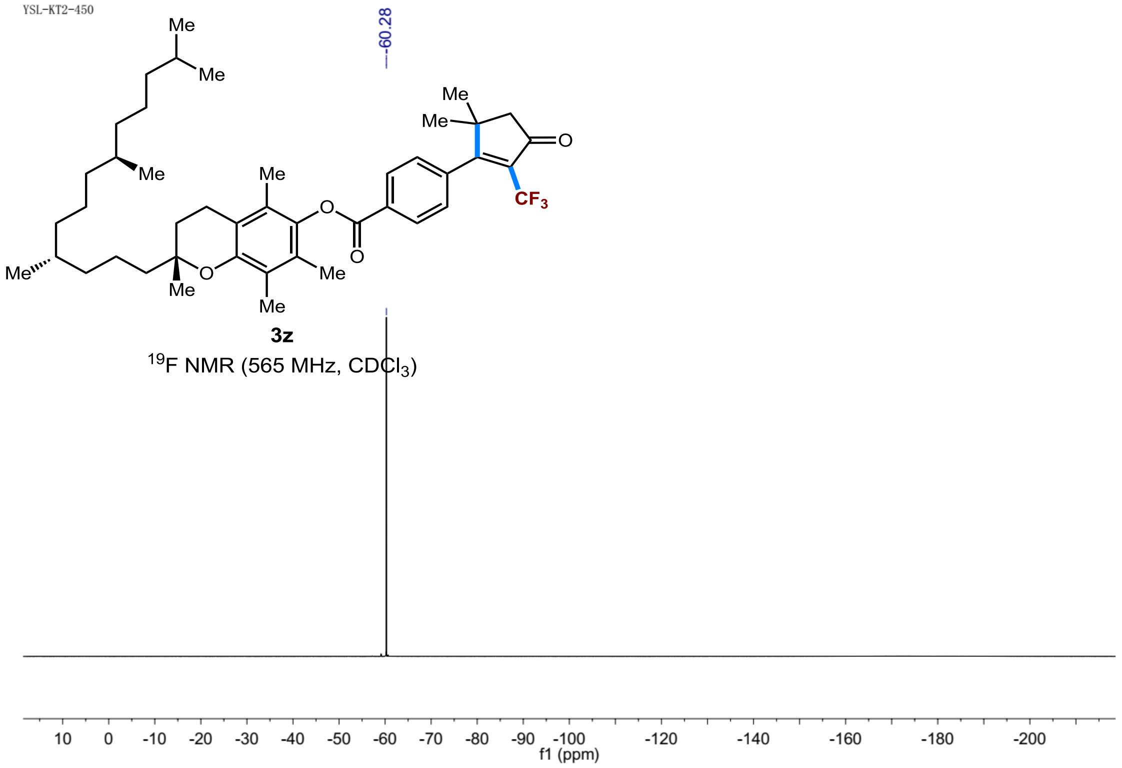
^{1}H NMR (400 MHz, $CDCl_3$)



3z

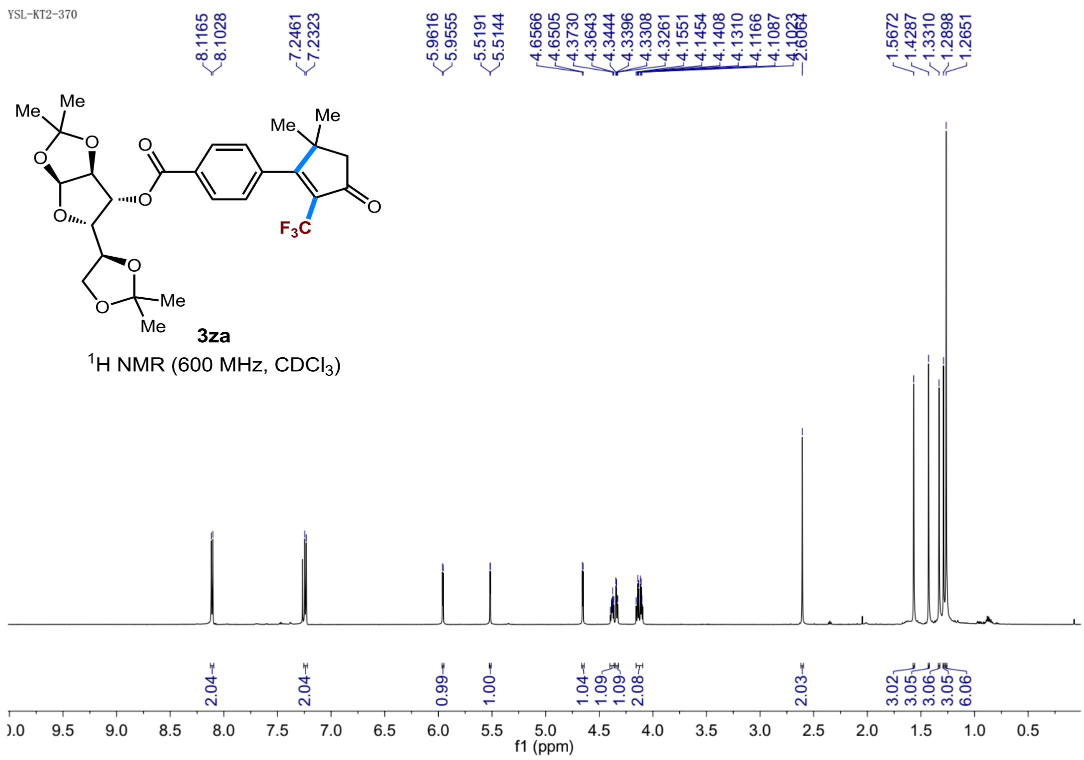
^{13}C NMR (151 MHz, $CDCl_3$)

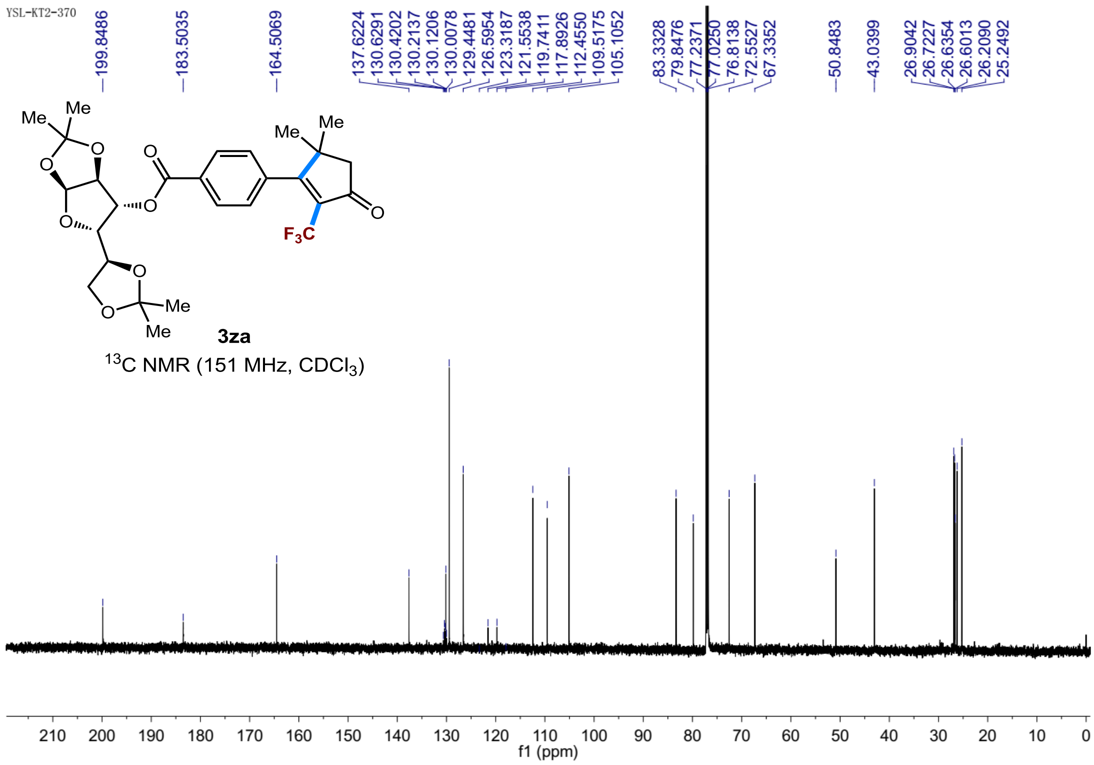
YSL-KT2-450



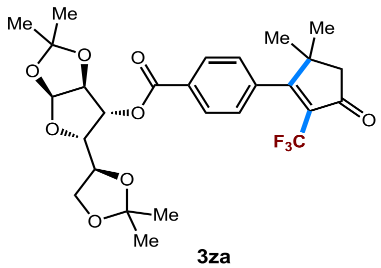
3z

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


YSL-KT2-370
8.1165
8.1028
7.2461
7.2323
5.9616
5.9555
5.5191
5.5144
4.6566
4.6505
4.3730
4.3643
4.3444
4.3396
4.3308
4.3261
4.1551
4.1454
4.1408
4.1310
4.1166
4.1087
4.1023
2.6064
1.5672
1.4287
1.3310
1.2898
1.2651
Me
Me
O
O
O
O
O
O
Me
Me
O
O
Me
Me
F3C
O
3za
1H NMR (600 MHz, CDCl3)
2.04
2.04
0.99
1.00
1.04
1.09
1.09
2.08
2.03
3.02
3.05
3.06
3.05
6.06
f1 (ppm)

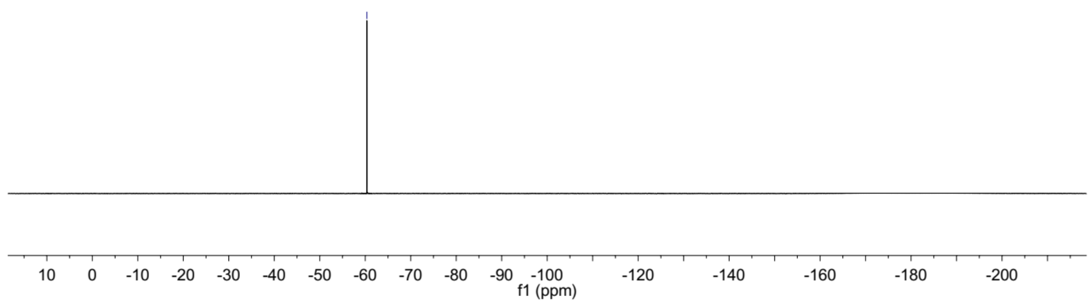

YSL-KT2-370
199.8486
183.5035
164.5069
137.6224
130.6291
130.4202
130.2137
130.1206
130.0078
129.4481
126.5954
123.3187
121.5538
119.7411
117.8926
112.4550
109.5175
105.1052
83.3328
79.8476
77.2371
77.0250
76.8138
72.5527
67.3352
50.8483
43.0399
26.9042
26.7227
26.6354
26.6013
26.2090
25.2492
3za
13C NMR (151 MHz, CDCl3)
f1 (ppm)

YSL-KT2-370

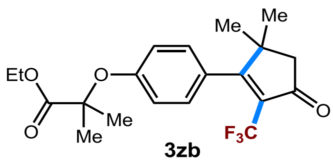


3za

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

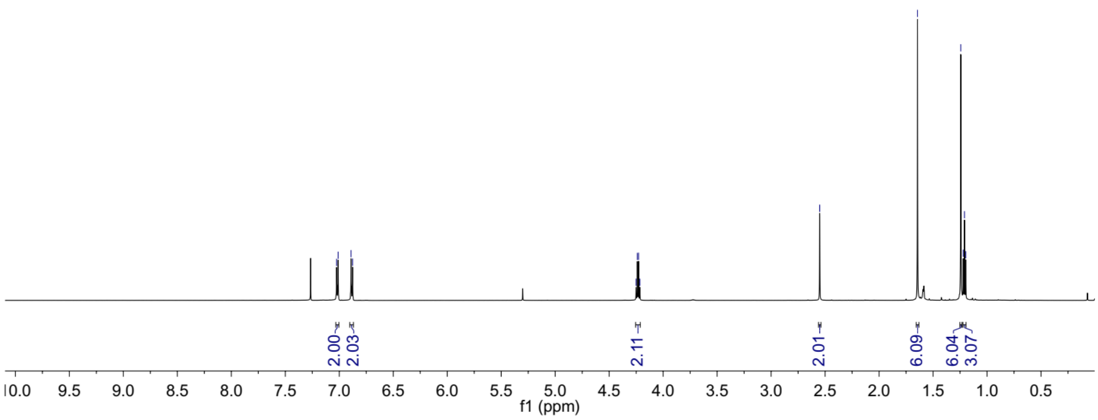


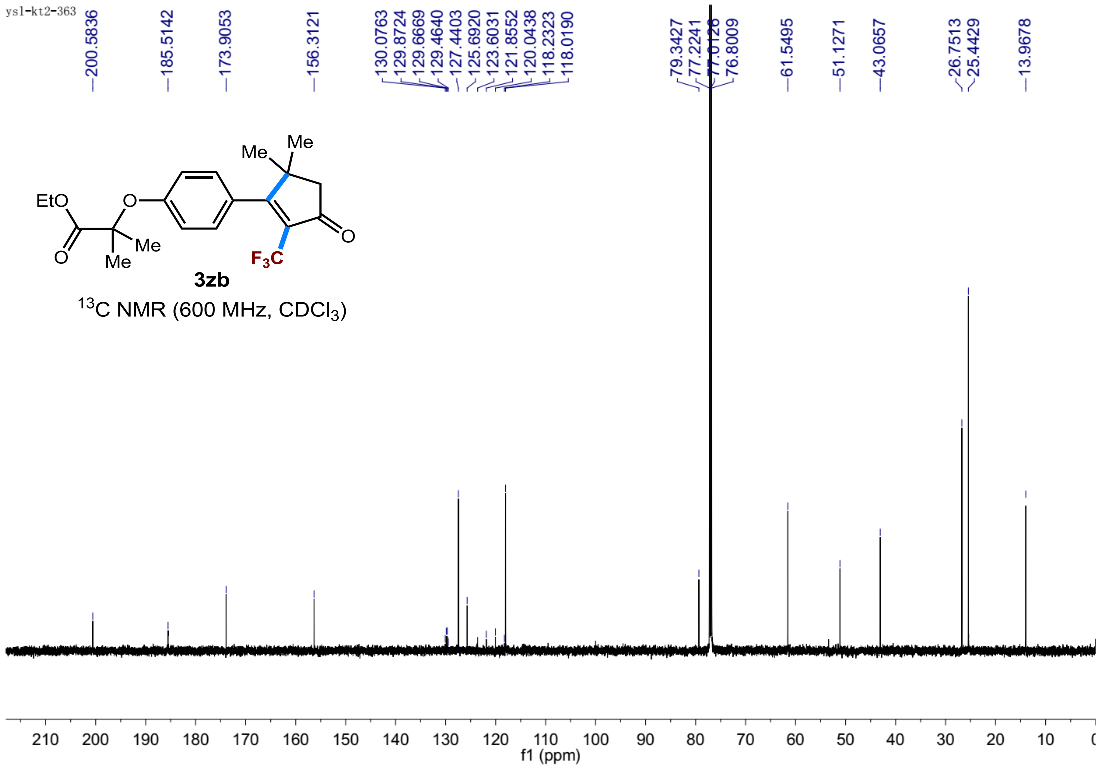
ysl-kt2-363

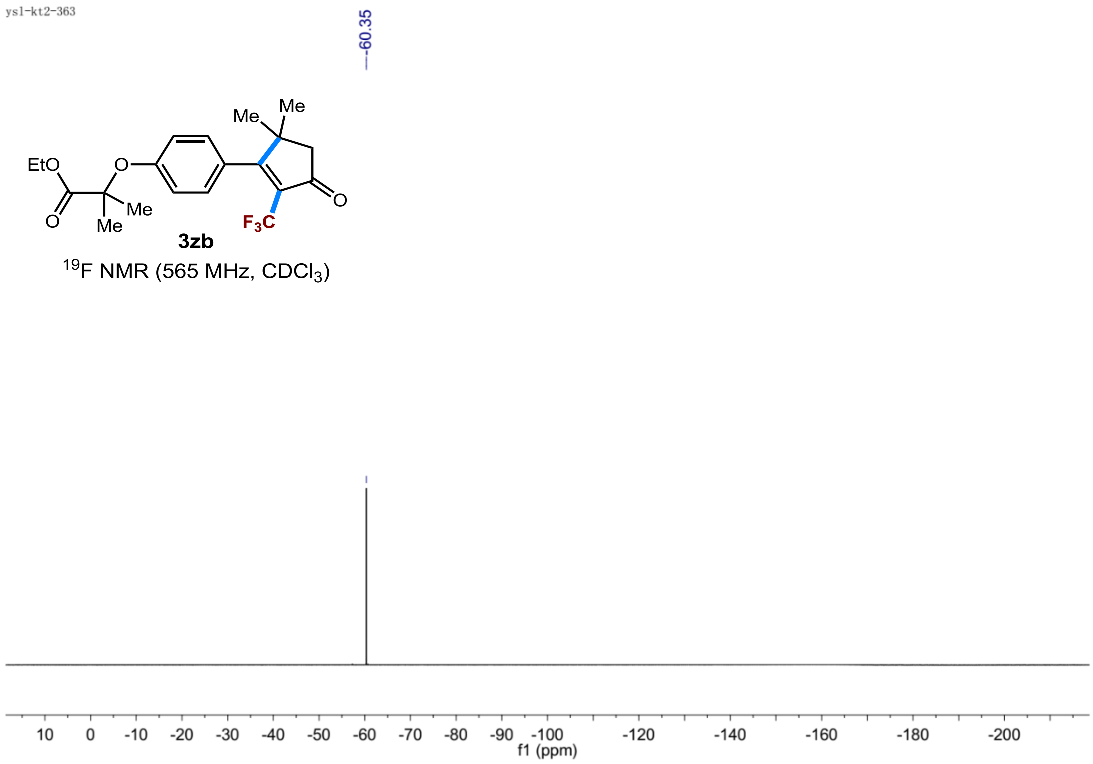


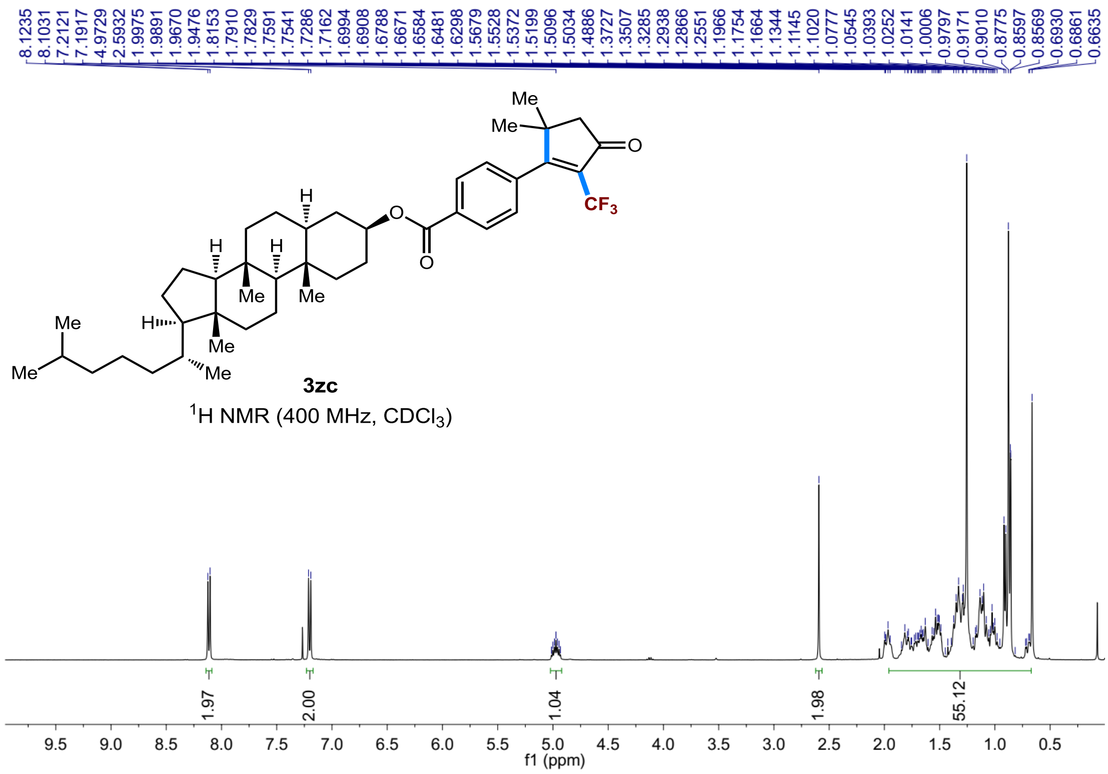
3zb

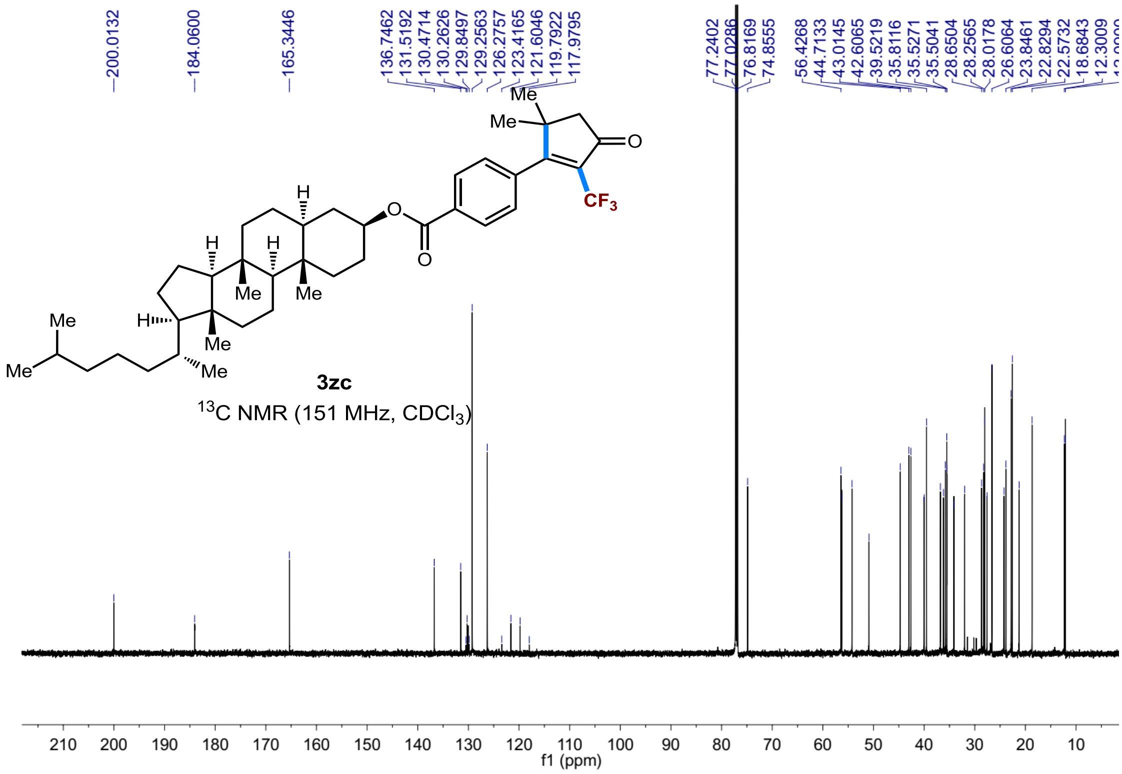
^{1}H NMR (600 MHz, $CDCl_3$)

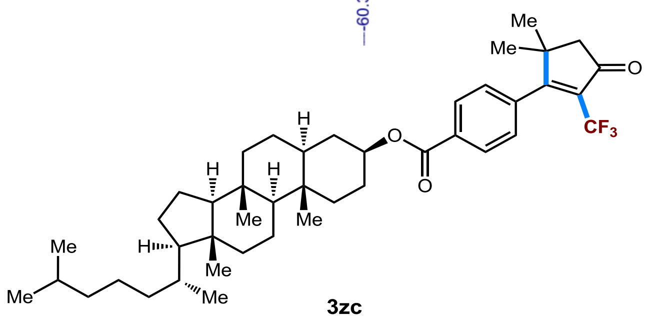



ysl-kt2-363
200.5836
185.5142
173.9053
156.3121
130.0763
129.8724
129.6669
129.4640
127.4403
125.6920
123.6031
121.8552
120.0438
118.2323
118.0190
79.3427
77.2241
77.0126
76.8009
61.5495
51.1271
43.0657
26.7513
25.4429
13.9678
EtO
O
Me
Me
Me
Me
F3C
O
O
3zb
13C NMR (600 MHz, CDCl3)
f1 (ppm)


ysl-kt2-363
-60.35
EtO
O
Me
Me
Me
Me
F3C
O
O
3zb
19F NMR (565 MHz, CDCl3)
f1 (ppm)

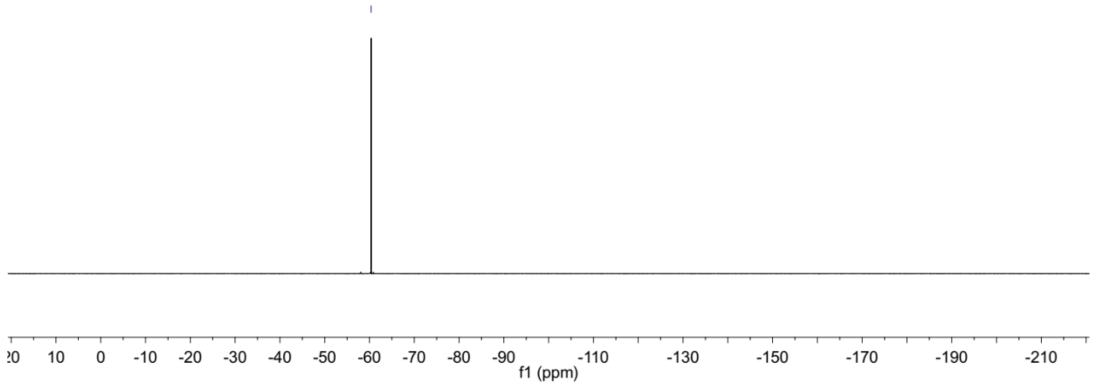

8.1235
8.1031
7.2121
7.1917
4.9729
2.5932
1.9975
1.9891
1.9670
1.9476
1.8153
1.7910
1.7829
1.7591
1.7541
1.7286
1.7162
1.6994
1.6908
1.6788
1.6671
1.6584
1.6481
1.6298
1.5679
1.5528
1.5372
1.5199
1.5096
1.5034
1.4886
1.3727
1.3507
1.3285
1.2938
1.2866
1.2551
1.1966
1.1754
1.1664
1.1344
1.1145
1.1020
1.0777
1.0545
1.0393
1.0252
1.0141
1.0006
0.9797
0.9171
0.9010
0.8775
0.8597
0.8569
0.6930
0.6861
0.6635
Me
Me
O
CF3
H
O
O
H
H
Me
Me
Me
H
Me
Me
Me
3zc
1H NMR (400 MHz, CDCl3)
1.97
2.00
1.04
1.98
55.12
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
f1 (ppm)

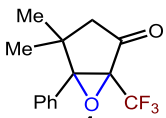

200.0132
184.0600
165.3446
136.7462
131.5192
130.4714
130.2626
129.8497
129.2563
126.2757
123.4165
121.6046
119.7922
117.9795
77.2402
77.0286
76.8169
74.8555
56.4268
44.7133
43.0145
42.6065
39.5219
35.8116
35.5271
35.5041
28.6504
28.2565
28.0178
26.6064
23.8461
22.8294
22.5732
18.6843
12.3009
Me
Me
O
CF3
H
O
O
H
H
Me
Me
Me
H
Me
Me
Me
3zc
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



3zc

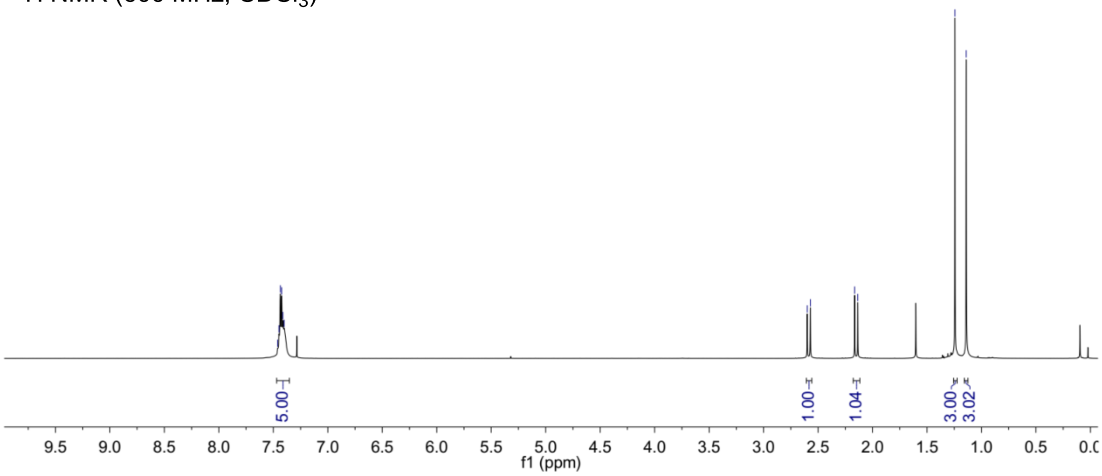
^{19}F NMR (377 MHz, $CDCl_3$)

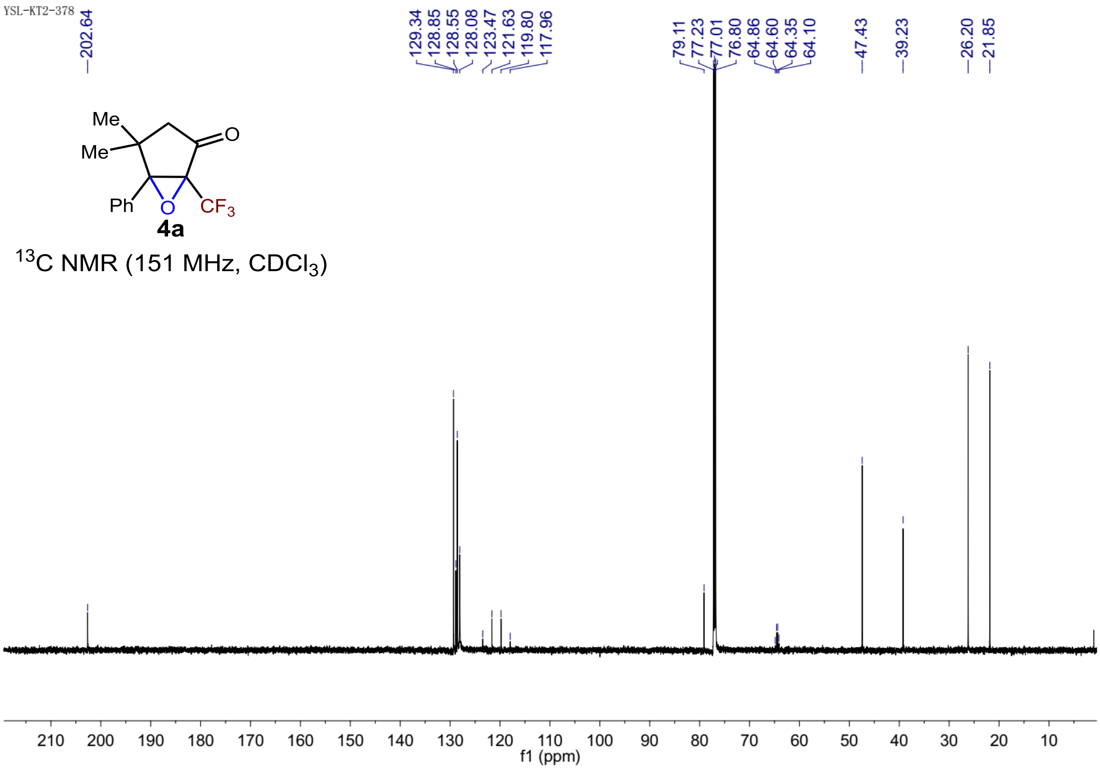


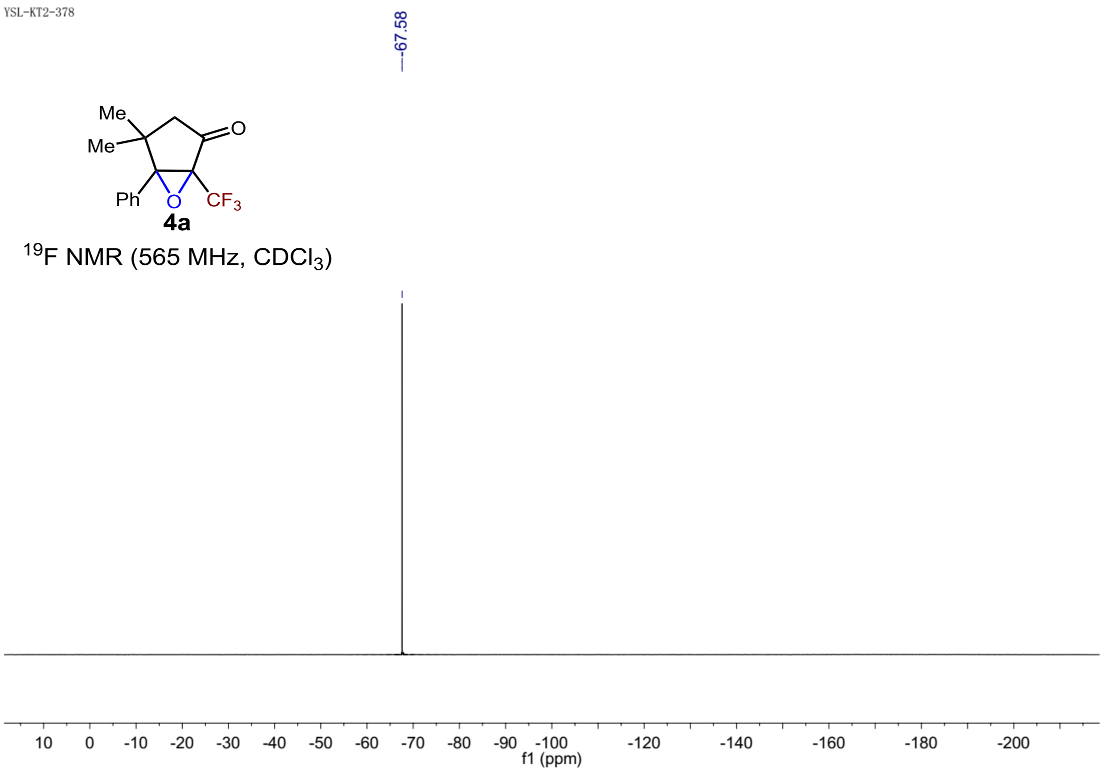


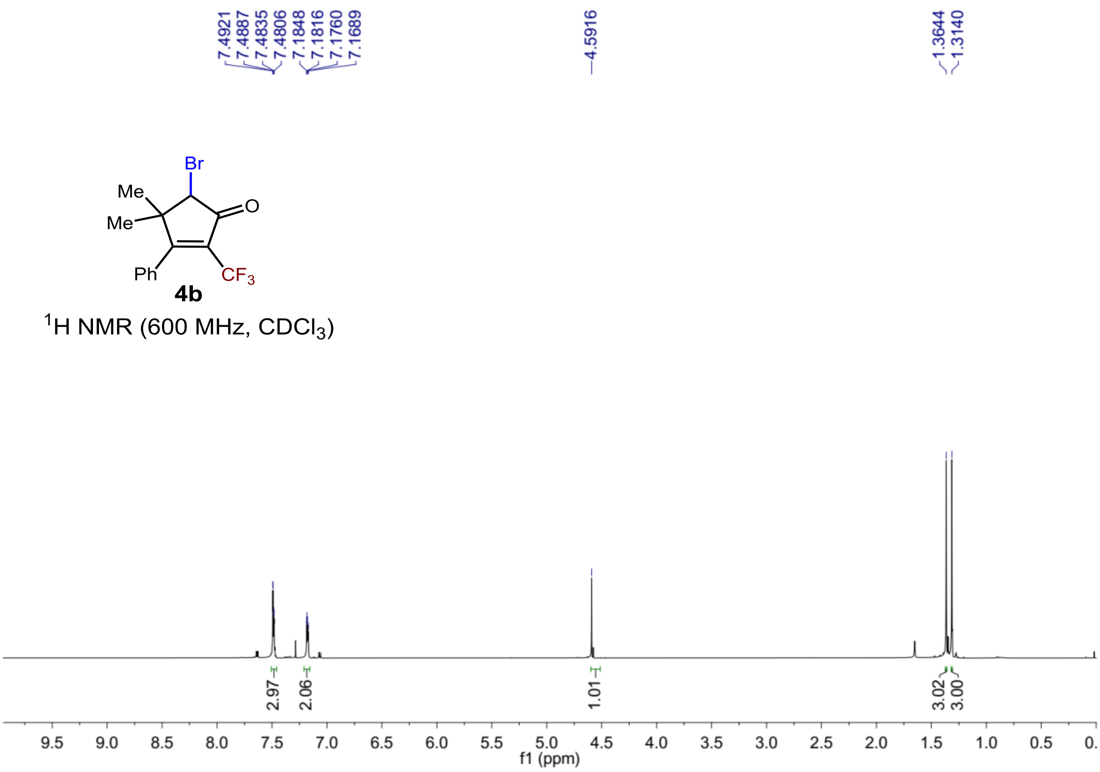
4a

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



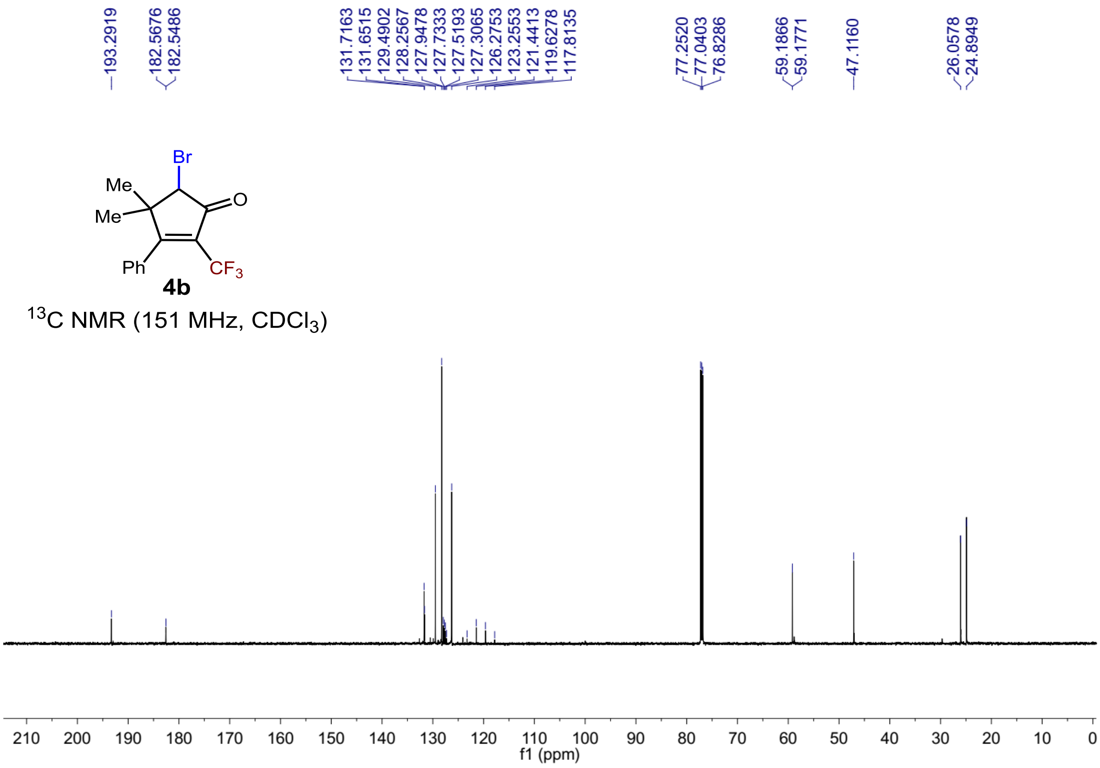

YSL-KT2-378
202.64
129.34
128.85
128.55
128.08
123.47
121.63
119.80
117.96
79.11
77.23
77.01
76.80
64.86
64.60
64.35
64.10
47.43
39.23
26.20
21.85
Me
Me
O
Ph
O
CF3
4a
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


YSL-KT2-378
-67.58
Me
Me
O
Ph
O
CF3
4a
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



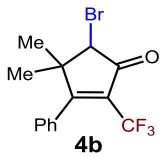
4b

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



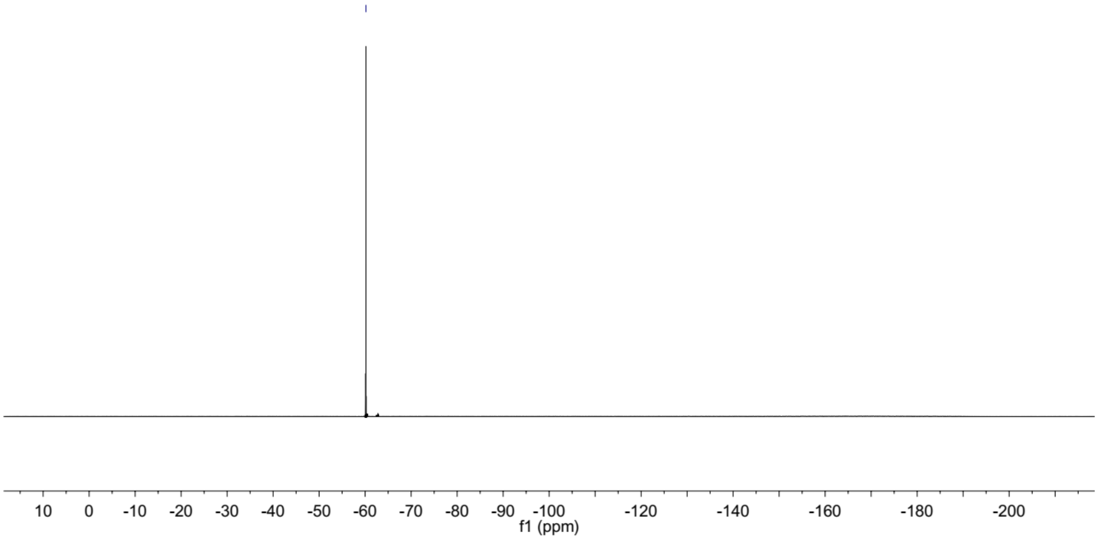
4b

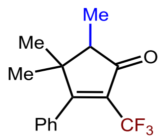
^{13}C NMR (151 MHz, $CDCl_3$)



4b

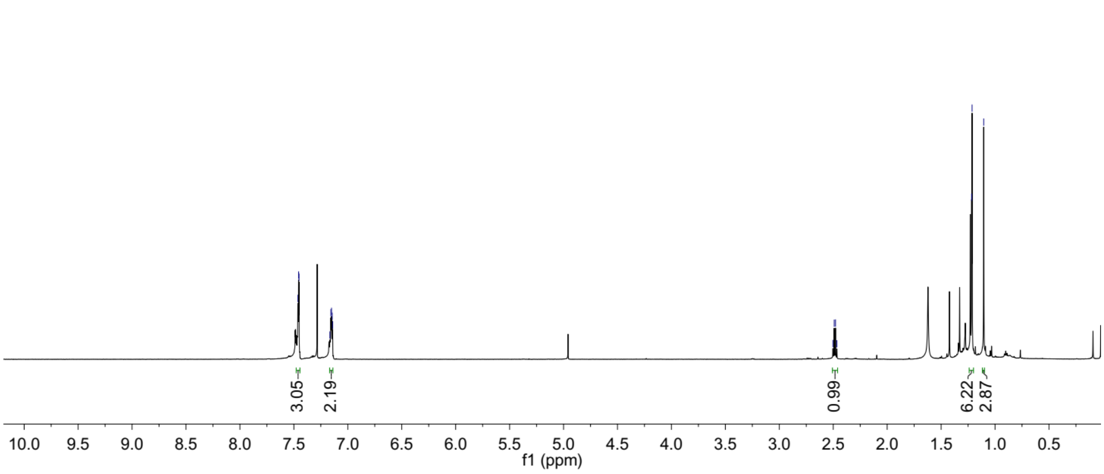
^{19}F NMR (565 MHz, $CDCl_3$)

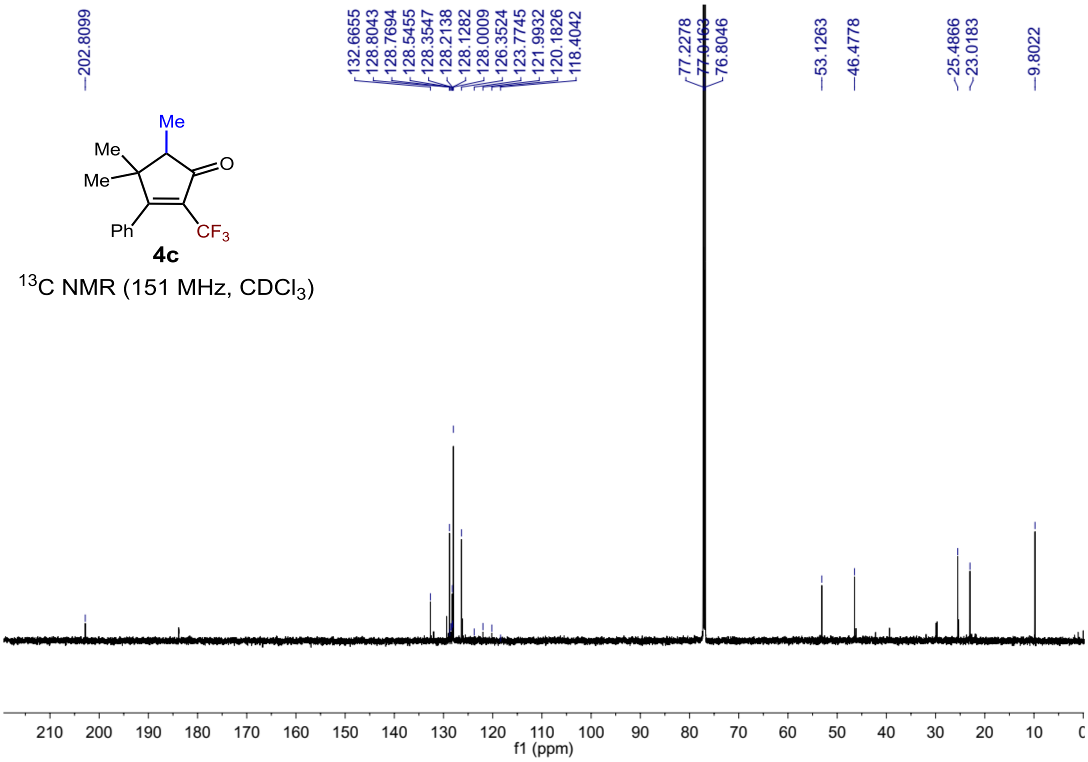


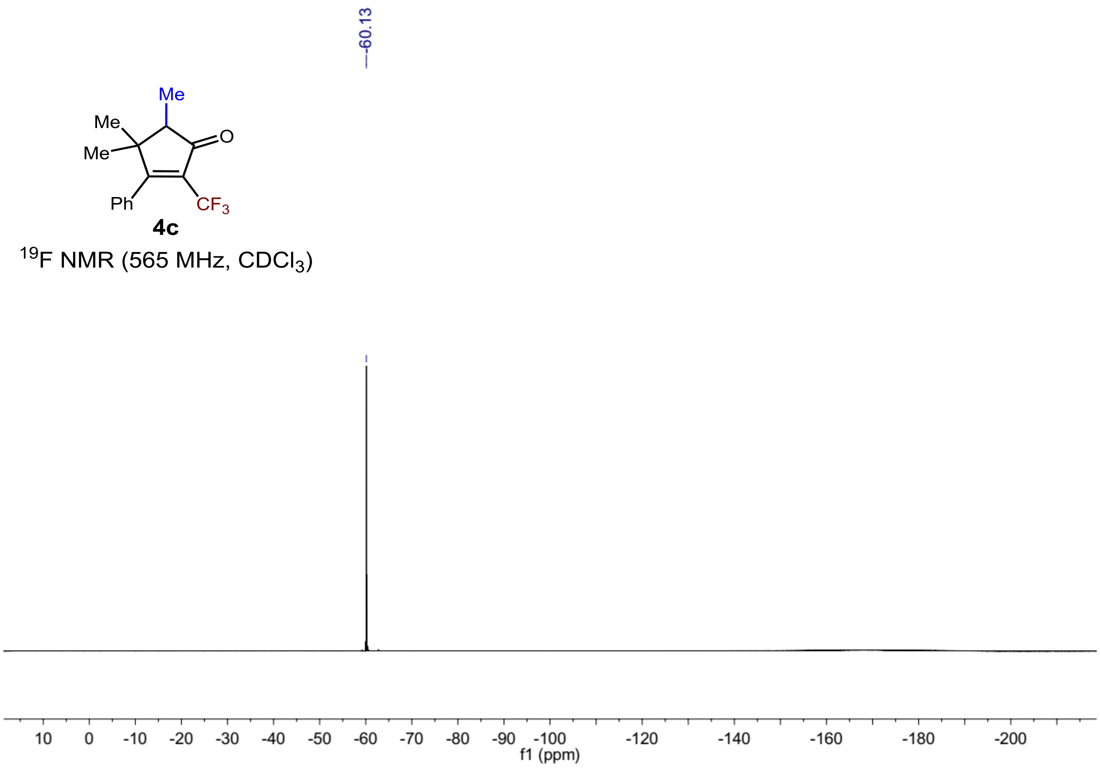


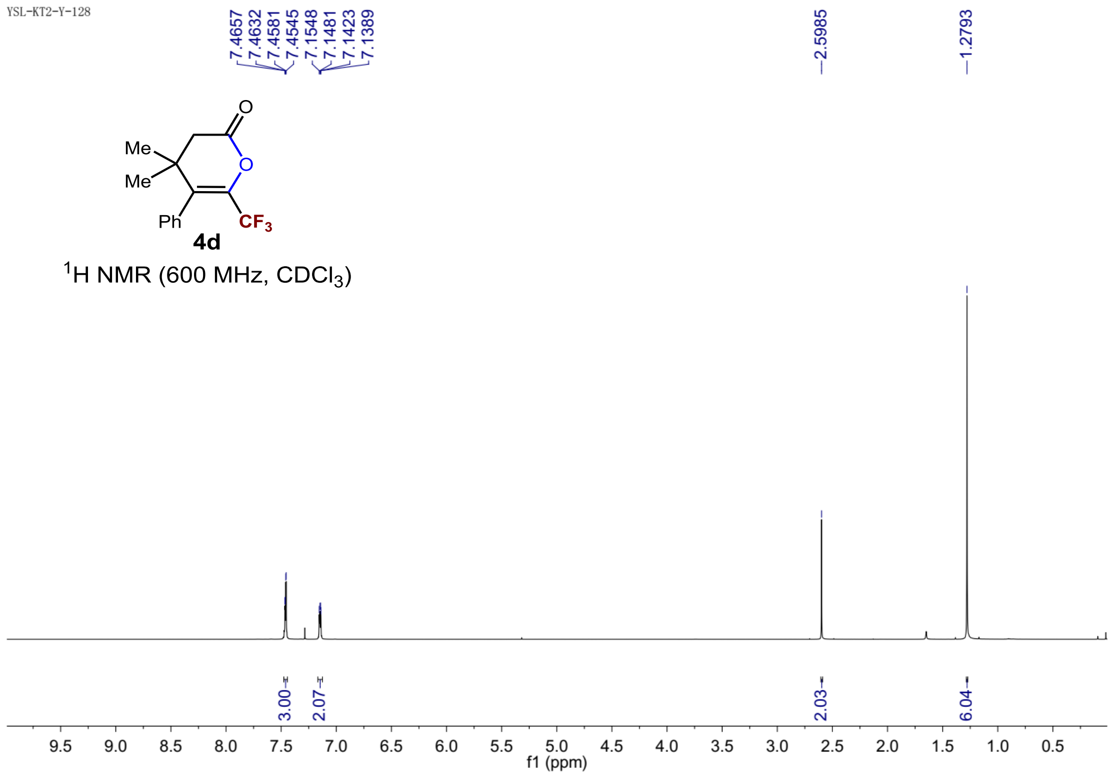
4c

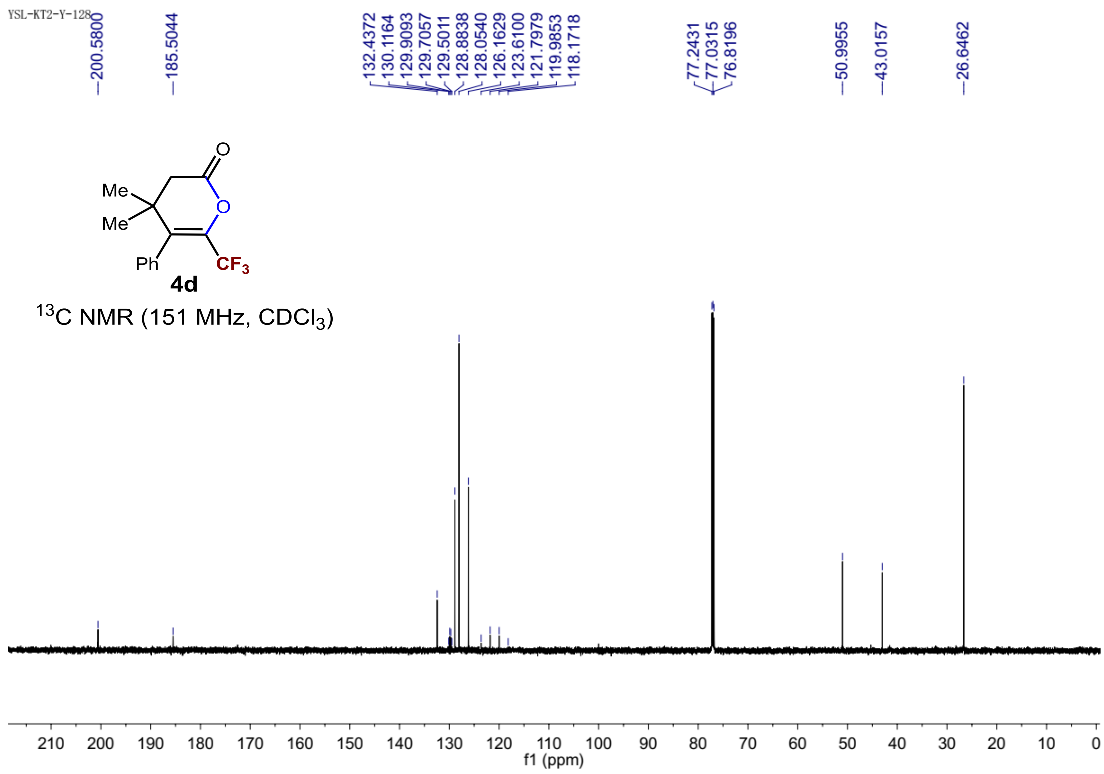
^{1}H NMR (600 MHz, $CDCl_3$)



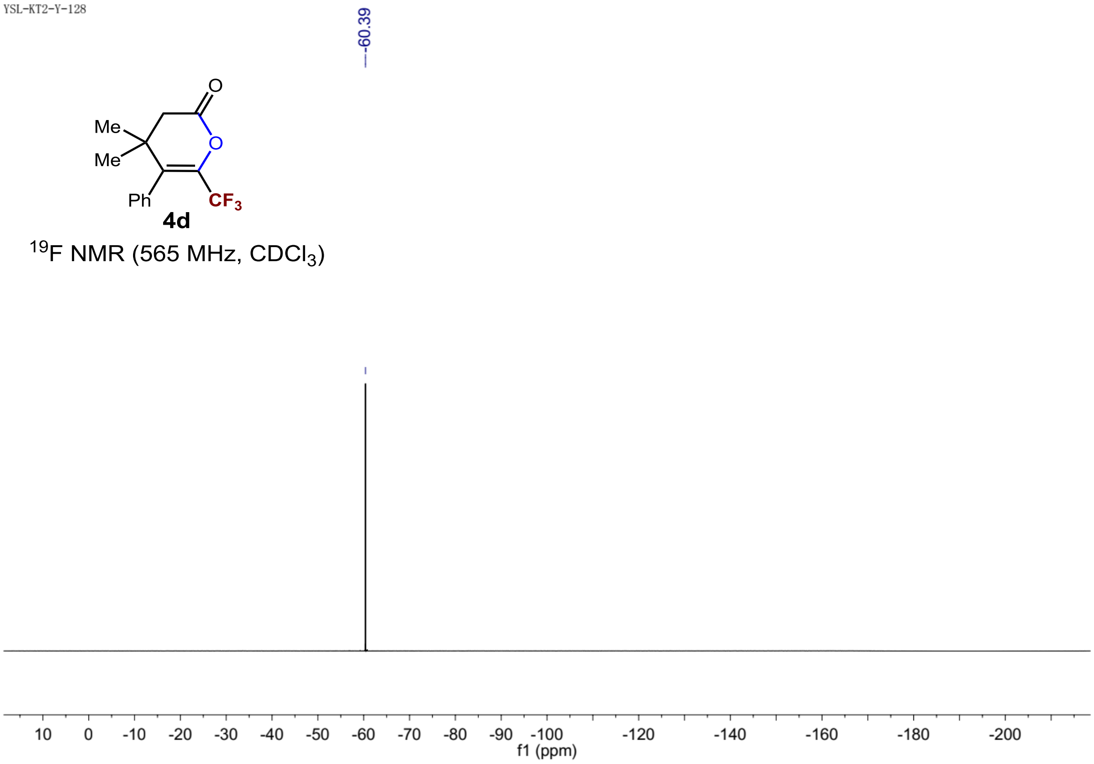

202.8099
132.6655
128.8043
128.7694
128.5455
128.3547
128.2138
128.1282
128.0009
126.3524
123.7745
121.9932
120.1826
118.4042
77.2278
77.0163
76.8046
53.1263
46.4778
25.4866
23.0183
9.8022
Me
Me
Me
O
Ph
CF3
4c
13C NMR (151 MHz, CDCl3)
f1 (ppm)

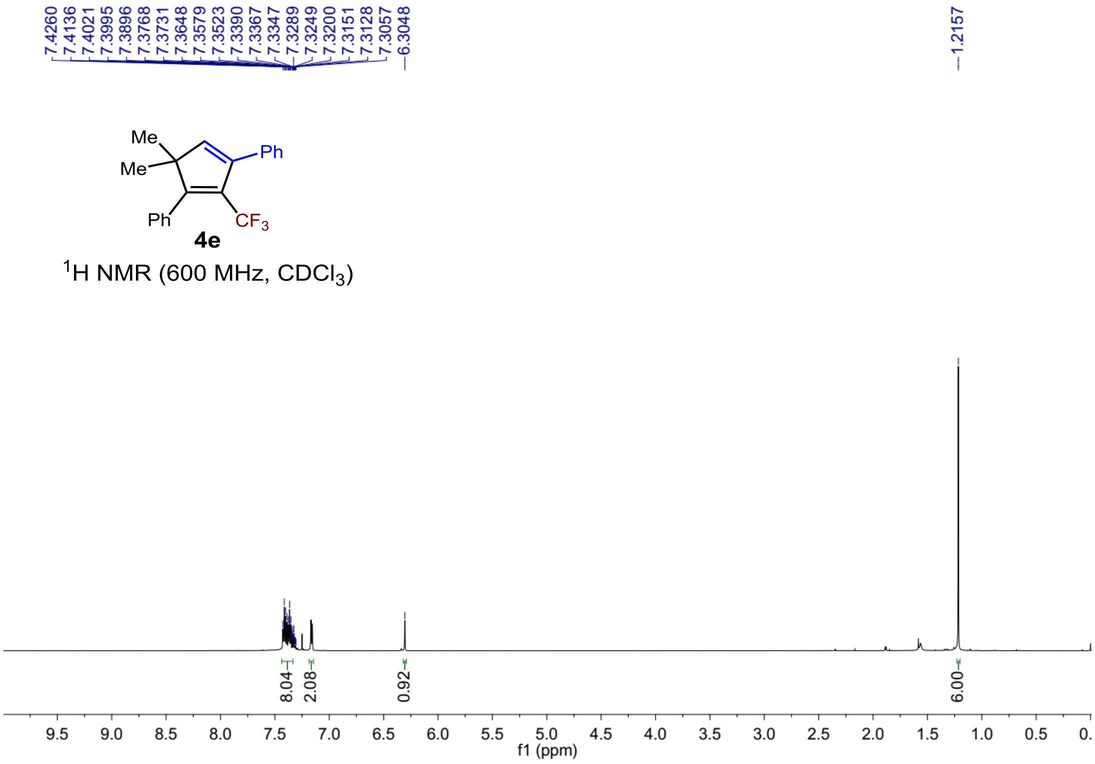

-60.13
Me
Me
Me
O
Ph
CF3
4c
19F NMR (565 MHz, CDCl3)
f1 (ppm)

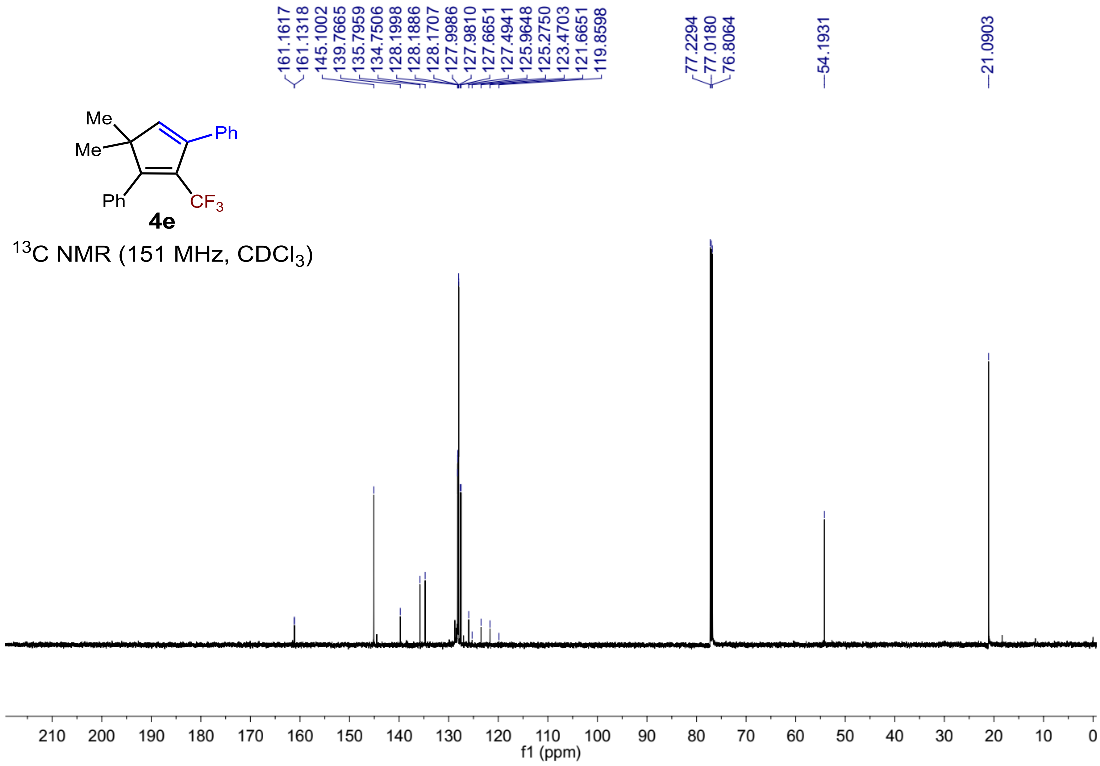

YSL-KT2-Y-128
7.4657
7.4632
7.4581
7.4545
7.1548
7.1481
7.1423
7.1389
2.5985
1.2793
Me
Me
O
O
Ph
CF3
4d
1H NMR (600 MHz, CDCl3)
3.00
2.07
2.03
6.04
f1 (ppm)


YSL-KT2-Y-128
200.5800
185.5044
132.4372
130.1164
129.9093
129.7057
129.5011
128.8838
128.0540
126.1629
123.6100
121.7979
119.9853
118.1718
77.2431
77.0315
76.8196
50.9955
43.0157
26.6462
Me
Me
O
O
Ph
CF3
4d
13C NMR (151 MHz, CDCl3)
f1 (ppm)

YSL-KT2-Y-128

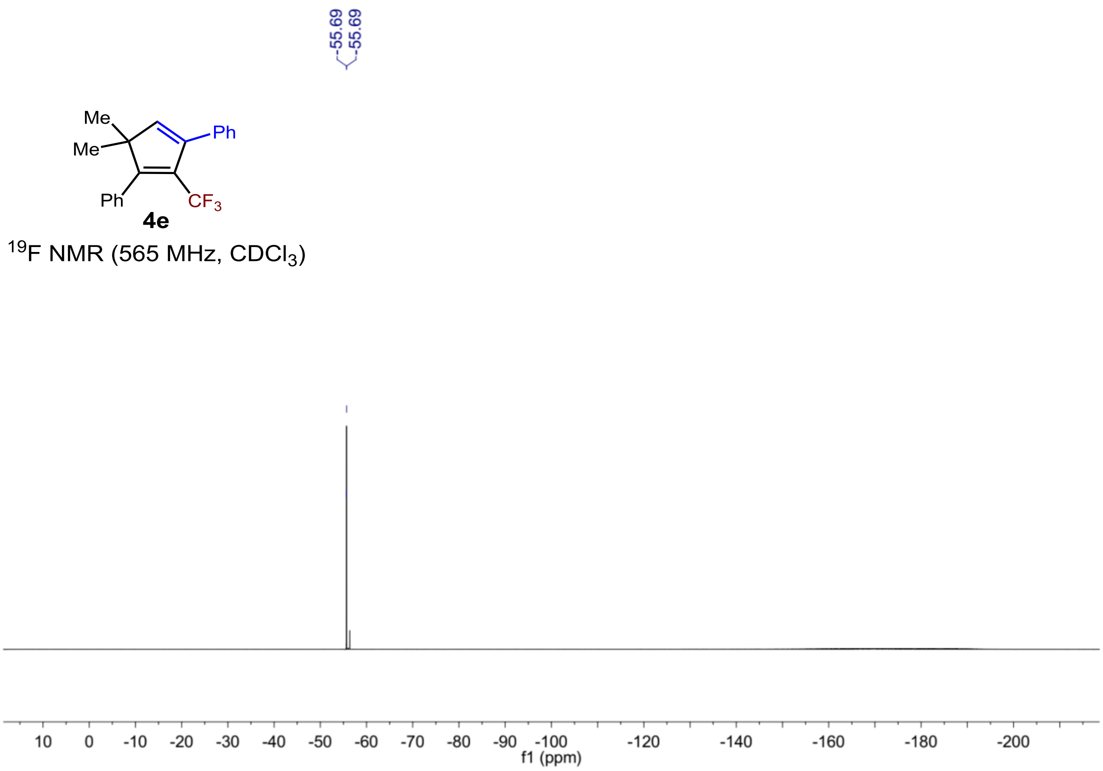

-60.39
Me
Me
Ph
O
O
CF3
4d
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)


7.4260
7.4136
7.4021
7.3995
7.3896
7.3768
7.3731
7.3648
7.3579
7.3523
7.3390
7.3367
7.3347
7.3289
7.3249
7.3200
7.3151
7.3128
7.3057
6.3048
1.2157
Me
Me
Ph
Ph
CF3
4e
1H NMR (600 MHz, CDCl3)
8.04
2.08
0.92
6.00
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.
f1 (ppm)



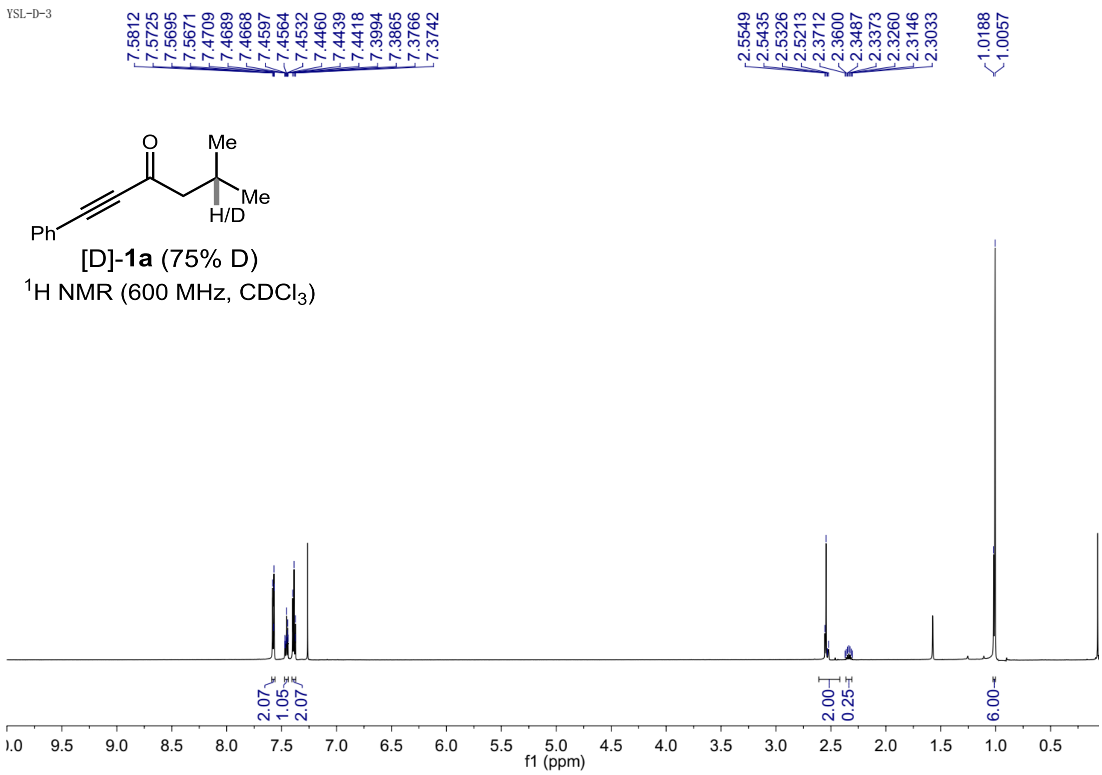
4e

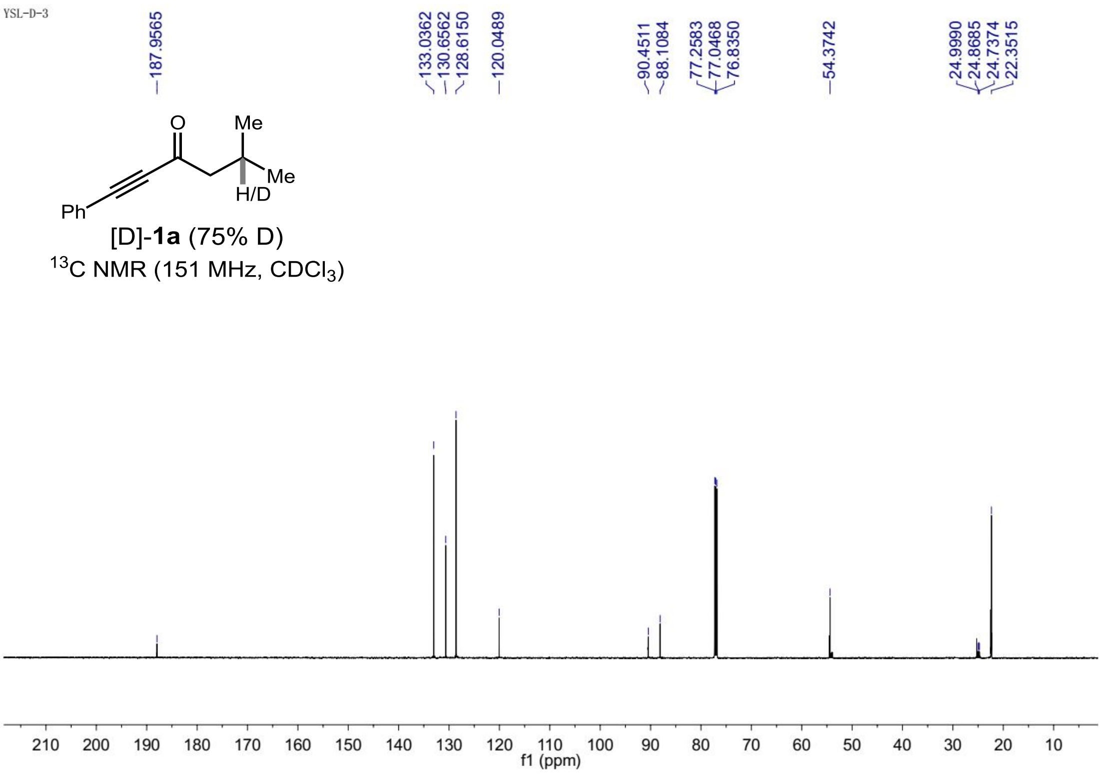
^{13}C NMR (151 MHz, $CDCl_3$)



4e

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


YSL-D-3
[D]-**1a** (75% D)
^{1}H NMR (600 MHz, $CDCl_3$)
f1 (ppm)


YSL-D-3
[D]-**1a** (75% D)
^{13}C NMR (151 MHz, $CDCl_3$)
f1 (ppm)

6. X-Ray crystallographic data

The crystal of **3b** was recrystallized in acetone/petroleum ethers via slow evaporation at room temperature. Crystal data for **3b** ($C_{15}H_{12}F_3NO$, 279.26): monoclinic, space group P2(1)/c, a = 12.1015(19) Å, b = 9.7752(13) Å, c = 22.586(4) Å, β = 92.403(4), U = 2669.5(7) Å^3, Z = 8, T = 297(2) K, absorption coefficient 0.116 mm^{-1}, reflections collected 6094, independent reflections 4325 [R(int) = 0.0250], refinement by full-matrix least-squares on F^2, data/restraints/parameters 4325/0/381, goodness-of-fit on F^2 = 1.029, final R indices [I>2s(I)] R_1 = 0.0559, wR_2 = 0.1863, largest diff peak and hole 0.309 and -0.463 e.Å^{-3}. Crystallographic data for the structure **3b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2114640.

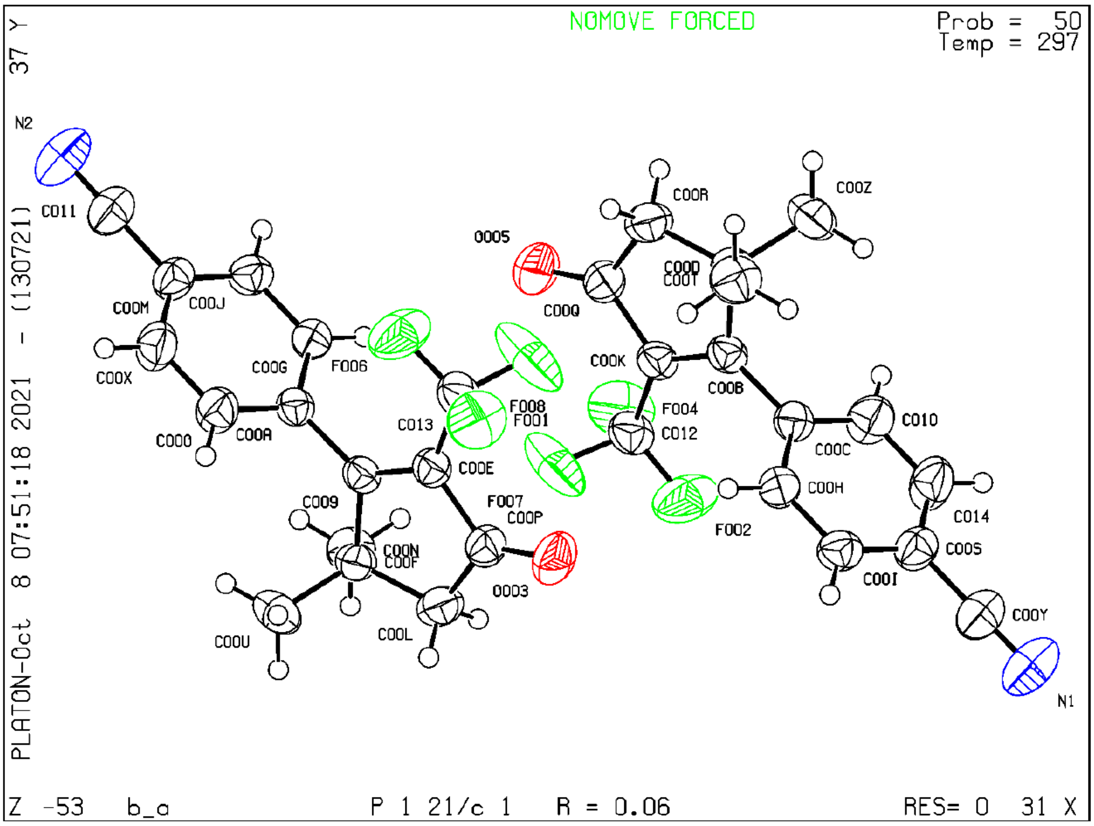


Figure S2. X-Ray crystal structure of **3b** with the ellipsoid contour at 50% probability levels