Electronic Supplementary Information to

A diastereoselective synthesis of cyclopentanones via photocatalytic reductive alkyltrifluoromethylation of ynones

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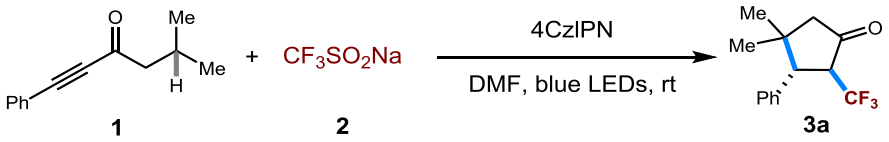
Contents

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 APCI or ESI source. Flash column chromatography was carried out on the silica gel (200-300 mesh).

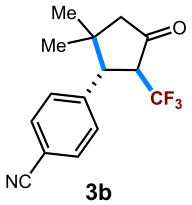
2. General Procedures for Experiments and Analytical Data



To a mixture of CF_3SO_2Na (62.4 mg, 0.4 mmol) and 4CzIPN (3.2 mg, 2 mol%) in 2 mL of DMF was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After 20 h of irradiation at a distance of ~5 cm from 30 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity), 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 = 100:1) gave 42 mg (82% yield) of **3a** as a white solid, mp 88-90 ^{o}C, dr >20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.37 (m, 2H), 7.36-7.32 (m, 1H), 7.22 (d, J = 7.2 Hz, 2H), 3.48 (dq, J = 12.2, 8.9 Hz, 1H), 3.39 (d, J = 12.4 Hz, 1H), 2.48 (s, 2H), 1.19 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.17, 135.71, 128.31, 127.52, 125.60, 124.64 (q, J = 279.5 Hz), 55.05 (q, J = 1.2 Hz), 54.22 (q, J = 26.3 Hz), 53.76 (q, J = 0.9 Hz), 38.15, 27.00, 22.85. ^{19}F NMR

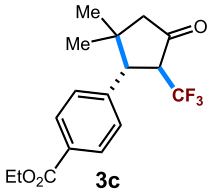
[1] (a) Q.-X. Wang and J. A. May, *Org. Lett.*, 2020, **22**, 9579; (b) T. P. Reddy, J. Gujral, P. Roy and D. B. Ramachary, *Org. Lett*., 2020, **22**, 9653.

(565 MHz, $CDCl_3$) δ -66.23. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{15}F_3O+H^+$: 257.1148; Found 257.1138.



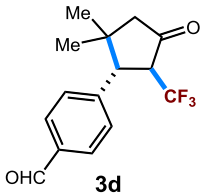
3b

Compound ***3b:*** 34 mg, 60% yield, white solid, mp 175-178 ^oC, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^1H NMR (600 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.34 (d, J = 8.3 Hz, 2H), 3.51-3.36 (m, 2H), 2.49 (s, 2H), 1.18 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 205.60, 141.34, 132.19, 129.10, 124.35 (q, J = 279.4 Hz), 118.42, 111.74, 54.78 (q, J = 0.9 Hz), 54.10 (q, J = 26.7 Hz), 53.80 (q, J = 0.8 Hz), 38.39, 26.92, 22.76. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.22. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{14}F_3NO+H^+$: 282.1100; Found 282.1072.



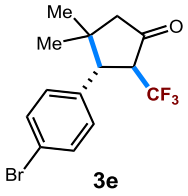
3c

Compound ***3c:*** 46 mg, 70% yield, white solid, mp 123-125 ^oC, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^1H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 4.39 (q, J = 7.1 Hz, 2H), 3.49 (dq, J = 12.2, 8.6 Hz, 1H), 3.43 (d, J = 12.4 Hz, 1H), 2.48 (s, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.18 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.38, 166.21, 140.89, 129.93, 129.57, 128.32, 124.49 (q, J = 279.7 Hz), 98.89, 54.93, 54.19 (q, J = 26.6 Hz), 53.71, 38.29, 26.98, 22.82, 14.36. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.24. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{19}F_3O_3+H^+$: 329.1359; Found 329.1360.



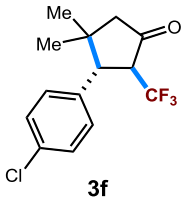
3d

Compound ***3d:*** 46 mg, 81% yield, white solid, mp 89-91 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.04 (s, 1H), 7.91 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.2 Hz, 2H), 3.54-3.44 (m, 2H), 2.49 (s, 2H), 1.20 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.02, 191.60, 142.83, 135.80, 129.70, 129.02, 124.43 (q, J = 279.6 Hz), 54.89 (q, J = 1.2 Hz), 54.22 (q, J = 26.6 Hz), 53.89 (q, J = 0.9 Hz), 38.40, 27.01, 22.85. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.23. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{15}F_3O_2$+H^+ 285.1097; Found 285.1095.



3e

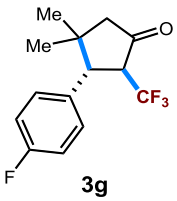
Compound ***3e:*** 48 mg, 72% yield, white solid, mp 127-129 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.38 (dq, J = 12.2, 8.6 Hz, 1H), 3.33 (d, J = 12.4 Hz, 1H), 2.45 (s, 2H), 1.16 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.51, 134.27, 133.44, 129.58, 128.57, 124.51 (q, J = 279.4 Hz), 54.88 (q, J = 0.9 Hz), 54.18 (q, J = 26.3 Hz), 53.21, 38.13, 26.90, 22.73. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.23. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}BrF_3O$+H^+: 335.0253; Found 335.0255.



3f

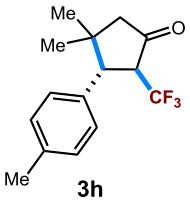
Compound ***3f:*** 42 mg, 72% yield, white solid, mp 108-110 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52-7.49 (m, 2H), 7.12-7.06 (m, 2H), 3.41-3.31 (m, 2H), 2.45 (s, 2H), 1.16 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.49, 134.27, 133.45, 129.58, 128.57, 124.51 (q, J = 279.5 Hz),

54.88 (q, J = 1.0 Hz), 54.24 (q, J = 26.4 Hz), 53.21 (q, J = 0.9 Hz), 38.13, 26.91, 22.73. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.22. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}ClF_3O+H^+$: 291.0758; Found 291.0760.



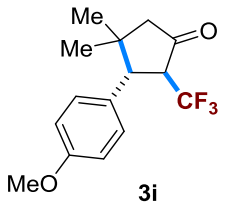
3g

Compound ***3g:*** 41 mg, 75% yield, white solid, mp 86-88 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (dd, J = 8.6, 5.3 Hz, 2H), 7.07 (dd, J = 11.9, 5.3 Hz, 2H), 3.42-3.33 (m, 2H), 2.45 (s, 2H), 1.16 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.72, 162.17 (d, J = 246.2 Hz), 131.46 (d, J = 3.3 Hz), 129.76 (d, J = 7.9 Hz), 124.58 (q, J = 279.4 Hz), 115.32 (d, J = 21.4 Hz), 54.89 (q, J = 1.4 Hz), 54.39 (q, J = 26.3 Hz), 53.09 (q, J = 1.2 Hz), 38.10 (q, J = 1.0 Hz), 26.90, 22.72. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.24, -115.01. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}F_4O+H^+$: 275.1054; Found 275.1055.



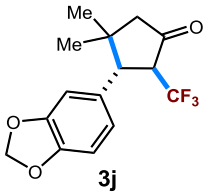
3h

Compound ***3h:*** 42 mg, 78% yield, white solid, mp 83-85 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.17 (d, J = 7.9 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 3.42 (dq, J = 12.2, 9.0 Hz, 1H), 3.33 (d, J = 12.4 Hz, 1H), 2.44 (s, 2H), 2.36 (s, 3H), 1.15 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.37, 137.16, 132.65, 129.01, 128.17, 124.68 (q, J = 279.6 Hz), 55.06 (q, J = 1.2 Hz), 54.24 (q, J = 26.2 Hz), 53.41, 38.11, 27.00, 22.84, 21.06. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.22. HRMS (ESI) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{17}F_3O+Na^+$: 293.1124; Found 293.1123.



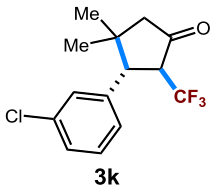
3i

Compound ***3i:*** 40 mg, 70% yield, white solid, mp 80-83 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.09 (m, 2H), 6.92–6.88 (m, 2H), 3.82 (s, 3H), 3.43–3.26 (m, 2H), 2.43 (s, 2H), 1.15 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.26 (q, J = 1.6 Hz), 158.88, 129.25, 127.69, 124,67 (q, J = 280.5 Hz), 113.67, 55.20, 54.96 (q, J = 1.3 Hz), 54.31 (q, J = 26.2 Hz), 53.03 (q, J = 1.2 Hz), 38.12, 26.94, 22.75. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.24. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{15}H_{17}F_3O_2$+Na^{+}: 309.1073; Found 309.1078.



3j

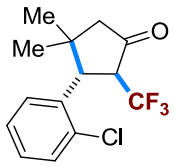
Compound ***3j:*** 45 mg, 75% yield, white solid, mp 92-94 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 60:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 (d, J = 7.9 Hz, 1H), 6.68-6.64 (m, 2H), 5.99 (s, 2H), 3.36-3.27 (m, 2H), 2.43 (d, J = 3.1 Hz, 2H), 1.16 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.98, 147.68, 146.97, 124.62 (q, J = 279.4 Hz), 121.84, 121.77 (q, J = 0.9 Hz), 108.46, 108.12, 101.21, 54.97 (q, J = 2.8 Hz), 54.48 (q, J = 26.1 Hz), 53.56 (q, J = 1.4 Hz), 38.17, 27.05, 22.90. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.24. HRMS (ESI) *m/z*: [M + Na]$^{+}$ Calcd for $C_{15}H_{15}F_3O_3$+Na^{+}: 323.0866; Found 323.0870.



3k

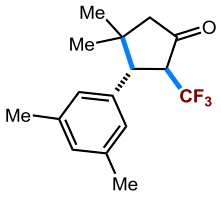
Compound ***3k:*** 40 mg, 69% yield, white solid, mp 95-97 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.30 (m, 2H), 7.20 (s, 1H), 7.11-7.08 (m, 1H), 3.41 (dq, J = 12.2, 8.8 Hz, 1H), 3.34 (d, J =

12.4 Hz, 1H), 2.46 (s, 2H), 1.18 (s, 3H), 0.80 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.34, 137.90, 134.33, 129.60, 128.49, 127.81, 126.07, 124.48 (q, J = 279.7 Hz), 54.90, 54.20 (q, J = 26.4 Hz), 53.45 (q, J = 0.8 Hz), 38.19, 26.98, 22.82. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.21. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}ClF_3O+H^+$: 291.0758; Found 291.0760.



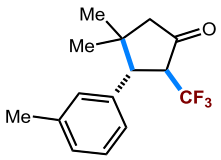
3l

Compound ***3l:*** 32 mg, 55% yield, colorless oil, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.45 (m, 1H), 7.31-7.27 (m, 1H), 7.26–7.19 (m, 2H), 4.24 (d, J = 12.3 Hz, 1H), 3.37–3.27 (m, 1H), 2.57–2.44 (m, 2H), 1.21 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 206.71 (q, J = 1.7 Hz), 135.38, 134.10, 130.25, 128.53, 128.36, 126.49, 124.46 (q, J = 280.6 Hz), 55.52 (q, J = 26.4 Hz) 55.22 (q, J = 1.6 Hz), 47.60 (q, J = 1.5 Hz), 39.29, 27.22, 23.39. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.65. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{14}ClF_3O+H^+$: 291.0758; Found 291.0760.



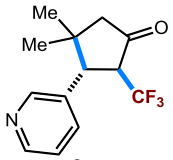
3m

Compound ***3m:*** 41 mg, 72% yield, white solid, mp 88-90 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.96 (s, 1H), 6.81 (s, 2H), 3.45 (dq, J = 12.2, 9.0 Hz, 1H), 3.31 (d, J = 12.3 Hz, 1H), 2.46 (s, 2H), 2.35 (s, 6H), 1.18 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.46, 137.64, 135.62, 129.17, 126.18, 123.77 (q, J = 279.6 Hz), 55.15, 54.26 (q, J = 26.2 Hz), 53.62, 38.04, 27.12, 22.98, 21.42. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.21. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{16}H_{19}F_3O+H^+$: 285.1461; Found 285.1456.



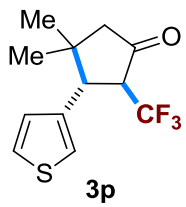
3n

Compound ***3n:*** 40 mg, 74% yield, white solid, mp 83-85 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.27-7.23 (m, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.00-6.95 (m, 2H), 3.44 (dq, J = 12.3, 9.0 Hz, 1H), 3.33 (d, J = 12.3 Hz, 1H), 2.45 (s, 2H), 2.37 (s, 3H), 1.16 (s, 3H), 0.78 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.35, 137.86, 135.66, 129.18, 128.27, 128.13, 125.27, 124.68 (q, J = 279.6 Hz), 55.09 (q, J = 0.9 Hz), 54.23 (q, J = 26.1 Hz), 53.68, 38.10, 27.06, 22.91, 21.55. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.21. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{17}F_3O+H^+$: 271.1304; Found 271.1309.



3o

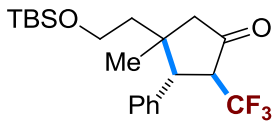
Compound ***3o:*** 34 mg, 66% yield, black oil, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, J = 4.4 Hz, 1H), 8.54 (s, 1H), 7.55 (d, J = 7.9 Hz, 1H), 7.35 (dd, J = 7.8, 4.8 Hz, 1H), 3.45 (dq, J = 12.2, 8.6 Hz, 1H), 3.38 (d, J = 12.4 Hz, 1H), 2.49 (s, 2H), 1.19 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.33, 158.89, 129.28, 127.70, 124.68 (q, J = 279.6 Hz), 121.91, 55.23, 54.33 (q, J = 26.1 Hz), 53.05, 38.15, 26.96, 22.78. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.23. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{13}H_{14}F_3NO+H^+$: 258.1100; Found 258.1106.



3p

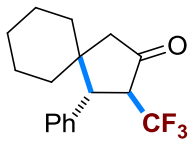
Compound ***3p:*** 28 mg, 53% yield, yellow solid, mp 86-88 ^{o}C, dr = 15:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.32 (m, 1H), 7.07 (d, J = 2.7 Hz, 1H), 6.97 (d, J = 5.0 Hz, 1H), 3.48 (d, J = 12.1 Hz, 1H),

3.33 (dq, J = 12.0, 9.1 Hz, 1H), 2.42 (s, 2H), 1.21 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.86, 137.11, 127.37, 125.68, 124.60 (q, J = 279.4 Hz), 122.27, 55.23 (q, J = 26.4 Hz), 54.77 (q, J = 1.1 Hz), 49.30, 38.03, 27.11, 23.03. ^{19}F NMR (377 MHz, $CDCl_3$) δ -66.40 (d, J = 8.8 Hz). HRMS (ESI) *m/z*: $[M + NH_4]^+$ Calcd for $C_{12}H_{13}F_3OS+NH_4^+$: 280.0977; Found 280.0971.



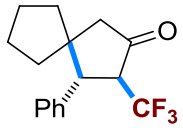
3q

Compound ***3q:*** 54 mg, 68% yield, colorless oil, dr >5:1:1:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 40:1; ^{1}H NMR (600 MHz, $CDCl_3$) data of major isomer δ 7.39-7.34 (m, 2H), 7.34-7.30 (m, 1H), 7.21 (d, J = 7.2 Hz, 2H), 3.75-3.70 (m, 1H), 3.66-3.62 (m, 1H), 3.48 (d, J = 12.3 Hz, 1H), 3.44-3.37 (m, 1H), 2.62 (d, J = 17.9 Hz, 1H), 2.52 (d, J = 17.9 Hz, 1H), 1.74-1.69 (m, 1H), 1.66-1.61 (m, 1H), 0.89 (s, 9H), 0.81 (s, 3H), 0.04 (s, 3H), 0.03 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) data of major isomer δ 207.77, 135.93, 128.63, 128.30, 127.52, 124.73 (q, J = 270.3 Hz), 59.71, 53.52 (q, J = 26.0 Hz), 53.36, 53.22, 41.63, 40.24, 25.92, 20.75, 18.21, -5.47, -5.46. ^{19}F NMR (565 MHz, $CDCl_3$) data of major isomer δ -66.14. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{21}H_{31}F_3O_2Si+H^+$: 401.2118; Found 401.2121.



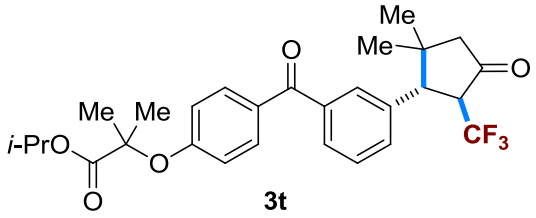
3r

Compound ***3r:*** 44 mg, 74% yield, white solid, mp 84-86 ^{o}C; dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.34-7.30 (m, 1H), 7.17 (d, J = 7.3 Hz, 2H), 3.46 (dq, J = 12.6, 8.9 Hz, 1H), 3.30 (d, J = 12.5 Hz, 1H), 2.90-2.87 (m, 1H), 2.25-2.20 (m, 1H), 1.65-1.57 (m, 4H), 1.53-1.47 (m, 2H), 1.02-0.97 (m, 1H), 0.91-0.86 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.34, 135.57, 128.91, 128.19, 127.47, 124.74 (q, J = 279.7 Hz), 54.82, 53.93 (q, J = 26.1 Hz), 49.46 (q, J = 0.9 Hz), 41.88, 36.72, 29.82, 25.43, 23.69, 21.91. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.18. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{17}H_{19}F_3O+H^+$: 297.1461; Found 297.1460.



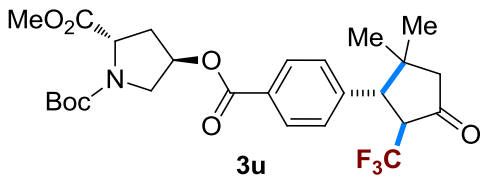
3s

Compound ***3s:*** 41 mg, 73% yield, white solid, mp 80-82 ^{o}C, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 100:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41-7.38 (m, 2H), 7.35-7.32 (m, 1H), 7.25-7.21 (m, 2H), 3.63 (d, J = 12.3 Hz, 1H), 3.47-3.40 (m, 1H), 2.65-2.60 (m, 1H), 2.40-2.34 (m, 1H), 1.77-1.72 (m, 1H), 1.61-1.54 (m, 3H), 1.50-1.43 (m, 2H), 1.38-1.32 (m, 1H), 1.27-1.23 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.10, 136.01, 128.89, 128.31, 127.45, 124.51 (q, J = 279.6 Hz), 55.31 (q, J = 26.2 Hz), 52.82 (q, J = 0.7 Hz), 51.05, 49.40, 36.04, 31.25, 23.24, 22.88. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.19. HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{16}H_{17}F_3O$+H^{+}: 283.1304; Found 283.1301.



3t

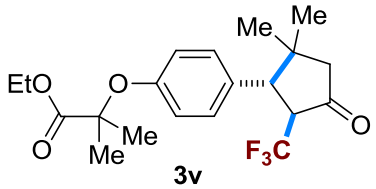
Compound ***3t:*** 51 mg, 51% yield, yellow oil, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81-7.75 (m, 4H), 7.32 (d, J = 8.2 Hz, 2H), 6.89-6.86 (m, 2H), 5.13-5.06 (m, 1H), 3.52 (dq, J = 12.5, 8.5 Hz, 1H), 3.47 (d, J = 12.4 Hz, 1H), 2.49 (s, 2H), 1.67 (s, 6H), 1.22 (d, J = 6.2 Hz, 6H), 1.22 (s, 3H), 0.82 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.40, 194.91, 173.13, 159.69, 140.13, 137.43, 132.02, 130.40, 129.83, 128.22, 125.43 (q, J = 271.7 Hz), 117.24, 79.42, 69.33, 58.45, 54.96, 54.24 (q, J = 26.5 Hz), 53.74 (q, J = 0.7 Hz), 53.43, 38.34, 27.01, 25.38, 25.37, 22.86, 21.52, 18.42. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.15. HRMS (ESI) *m/z*: [M + H]$^{+}$ Calcd for $C_{28}H_{31}F_3O_5$+H^{+}: 505.2196; Found 505.2198.



3u

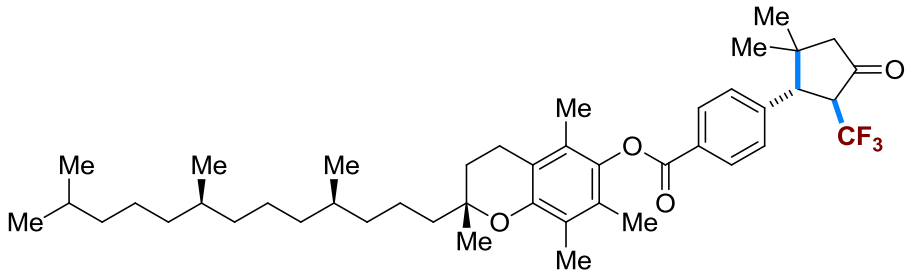
Compound ***3u:*** 64 mg, 61% yield, white solid, mp 138-140 ^{o}C, as a 1.3:1 mixture of two rotamers;

Flash column chromatography conditions: petroleum ethers/EtOAc = 5:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, J = 7.9 Hz, 2H), 7.32 (d, J = 7.8 Hz, 2H), 5.59-5.53 (m, 1H), 4.55 (t, J = 7.8 Hz, 0.45H, minor rotamer), 4.45 (t, J = 7.9 Hz, 0.55H, major rotamer), 3.88-3.85 (m, 1H), 3.79 (s, 1.30H, minor rotamer), 3.78 (s, 1.70H, major rotamer), 3.73-3.71 (m, 1H), 3.54-3.44 (m, 2H), 2.59-2.50 (m, 3H), 2.39-2.31 (m, 1H), 1.48 (s, 3.90H, minor rotamer), 1.45 (s, 5.10H, major rotamer), 1.20 (s, 3H), 0.81 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 199.95, 183.70, 172.80, 165.19, 154.31, 130.16, 129.47, 127.67 (q, J = 279.4 Hz), 80.75, 73.69, 58.00, 57.62, 52.37 (q, J = 29.6 Hz), 52.27, 50.87, 43.04, 36.72, 33.93, 29.71, 28.25, 26.62. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.23. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{26}H_{32}F_3NO_7$+Na^+: 550.2023; Found 550.2031.



3v

Compound ***3v:*** 43 mg, 56% yellow oil, dr >20:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 10:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.05 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.23 (q, J = 7.1 Hz, 2H), 3.36 (dq, J = 12.4, 8.8 Hz, 1H), 3.29 (d, J = 12.4 Hz, 1H), 2.42 (s, 2H), 1.61 (s, 6H), 1.21 (t, J = 7.1 Hz, 3H), 1.13 (s, 3H), 0.76 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.15, 174.16, 154.89, 129.11, 128.94, 124.63 (q, J = 279.2 Hz), 118.63, 79.19, 61.41, 54.95, 54.32 (q, J = 26.3 Hz), 53.06, 38.10, 26.97, 25.45, 25.43, 22.78, 14.00. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.24. HRMS (ESI) *m/z*: $[M + Na]^+$ Calcd for $C_{20}H_{25}F_3O_4$+Na^+: 409.1597; Found 409.1599.

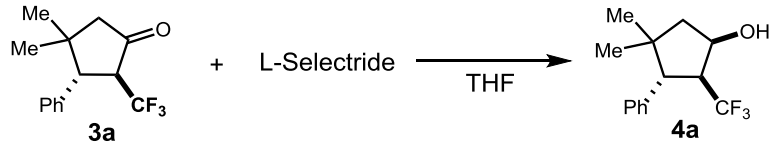


3w

Compound ***3w:*** 92 mg, 65% yellow oil, dr >19:1; Flash column chromatography conditions: petroleum ethers/EtOAc = 50:1; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.25 (d, J = 8.2 Hz, 2H), 7.36 (d, J

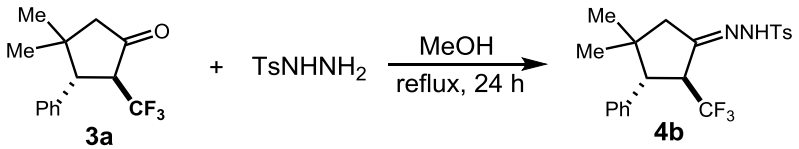
= 8.2 Hz, 2H), 3.55-3.46 (m, 2H), 2.63 (t, *J* = 6.6 Hz, 2H), 2.50 (s, 2H), 2.14-2.03 (m, 9H), 1.86-1.74 (m, 2H), 1.55-1.38 (m, 6H), 1.31-1.20 (m, 15H), 1.16-1.04 (m, 6H), 0.87-0.84 (m, 15H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 206.30, 164.77, 149.53, 141.58, 140.54, 130.16, 129.06, 128.59, 126.87, 125.12, 124.51 (q, *J* = 279.8 Hz), 123.18, 117.51, 75.12, 54.97, 54.24 (q, *J* = 26.2 Hz), 53.80, 39.38, 38.40, 37.46, 37.30, 32.82, 32.77 (q, *J* = 1.0 Hz), 32.73, 32.69, 28.00, 27.02, 24.82, 24.47, 22.88, 22.74, 22.65, 21.05, 20.66, 19.77, 19.68, 13.13, 12.28, 11.88. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.17. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{44}H_{63}F_3O_4$+H^+: 713.4751; Found 713.4769.

Experimental Procedure for the Transformation of 3a to 4a



To a solution of **3a** (51.2 mg, 0.2 mmol) in 1 mL of dry THF was added L-Selectride (1.0 M in THF, 0.25 mL, 0.25 mmol) at -78 ℃. Upon warming to 25 ℃ over 2 h, the reaction mixture was quenched with saturated aqueous NH_4Cl solution, extracted with EtOAc, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 10:1) gave 39 mg (76% yield) of **4a** as a colorless oil, dr >20:1. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37-7.31 (m, 2H), 7.30-7.27 (m, 1H), 7.21-7.14 (m, 2H), 4.74-4.67 (m, 1H), 3.32 (d, *J* = 12.3 Hz, 1H), 3.21-3.15 (m, 1H), 2.15 (dd, *J* = 13.8, 6.5 Hz, 1H), 1.88 (d, *J* = 3.6 Hz, 1H), 1.79 (dd, *J* = 13.8, 5.0 Hz, 1H), 1.12 (s, 3H), 0.68 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 137.37, 128.78, 127.88, 126.97 (q, *J* = 279.9 Hz), 126.89, 70.41 (q, *J* = 1.7 Hz), 54.10 (q, *J* = 1.6 Hz), 50.63 (q, *J* = 23.7 Hz), 50.11, 40.58, 29.12, 25.18. ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.69. HRMS (ESI) *m/z*: $[M + H]^+$ Calcd for $C_{14}H_{17}F_3O$+H^+: 259.1304; Found 259.1304.

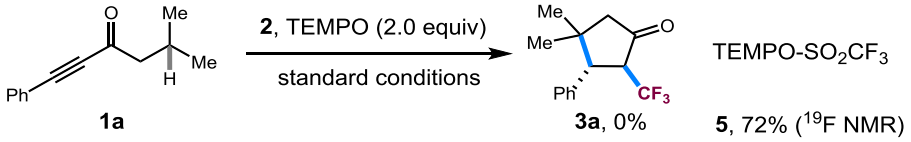
Experimental Procedure for the Transformation of 3a to 4b



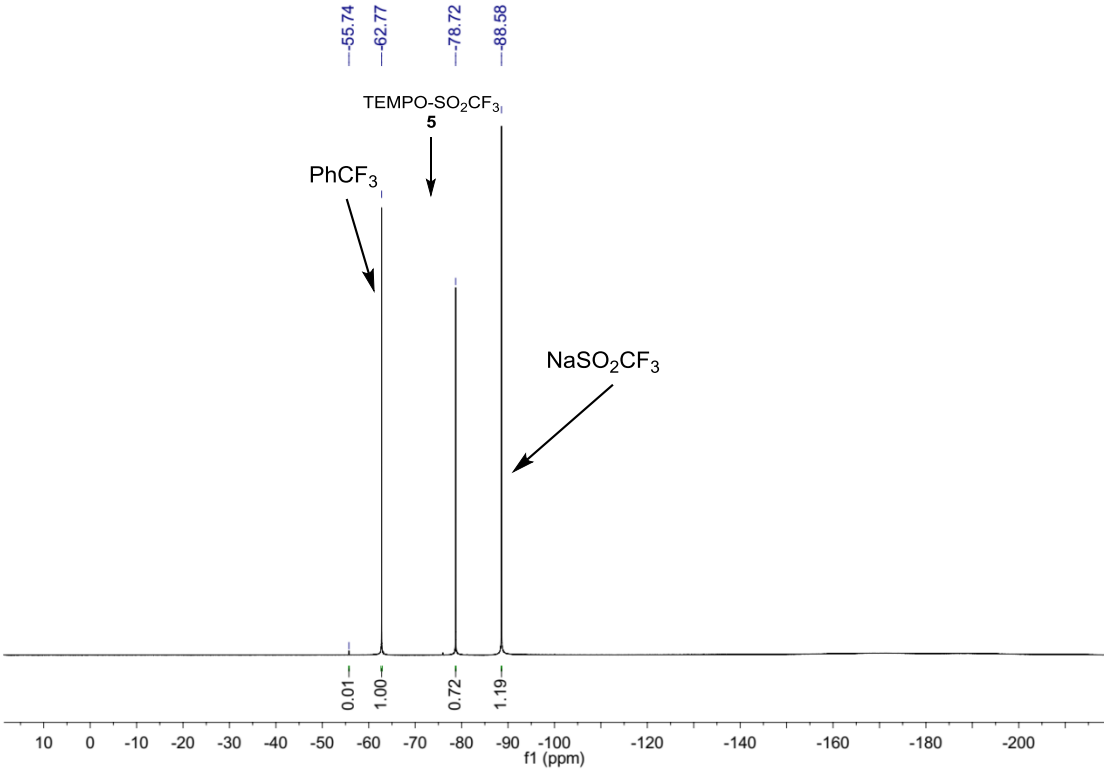
To a solution of **3a** (25.6 mg, 0.1 mmol) in 1 mL of dry MeOH was added $TsNHNH_2$ (22.3 mg,

0.12 mmol) and HOAc (1.2 mg, 0.02 mmol) at room temperature. After being refluxed for 18 h, the reaction mixture was quenched with water, extracted with EtOAc, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 5:1) gave 34 mg (80% yield) of **4b** as a white solid, mp 158-160 ^oC, dr >20:1. ^1H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, J = 8.3 Hz, 2H), 7.46 (s, 1H), 7.34-7.27 (m, 5H), 7.13 (d, J = 7.2 Hz, 2H), 3.87-3.79 (m, 1H), 3.06 (d, J = 11.6 Hz, 1H), 2.48 (d, J = 16.5 Hz, 1H), 2.43 (s, 3H), 2.14 (d, J = 15.4 Hz, 1H), 1.06 (s, 3H), 0.69 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 156.40, 144.30, 136.06, 134.92, 129.48, 128.37, 128.09 (d, J = 28.2 Hz), 127.34, 125.64 (q, J = 279.7 Hz), 54.74, 50.67 (q, J = 27.2 Hz), 43.81, 40.75, 26.75, 22.90, 21.60. ^{19}F NMR (565 MHz, $CDCl_3$) δ -67.63. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}F_3N_2O_2S+H^+$: 425.1505; Found 425.1497.

3. Mechanistic Experiments

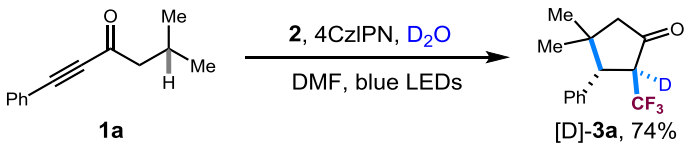


To a mixture of CF_3SO_2Na (62.4 mg, 0.4 mmol), 4CzIPN (3.2 mg, 2 mol%) and TEMPO (62.5 mg, 0.4 mmol) in 2 mL of DMF was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After 20 h of irradiation at a distance of ~5 cm from 30 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity), the reaction mixture was quenched with water, extracted with EtOAc, washed with brine, dried over anhydrous Na_2SO_4, and concentrated to give **5** in 72% ^{19}F NMR yield using $PhCF_3$ as the internal standard.



1a **3a**, 76%

To a mixture of CF_3SO_2Na (62.4 mg, 0.4 mmol) and 4CzIPN (3.2 mg, 2 mol%) in 2 mL of [D_7]-DMF (98% D) was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After 20 h of irradiation at a distance of ~5 cm from 30 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity), 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 39 mg (76% yield) of **3a** as a white solid.

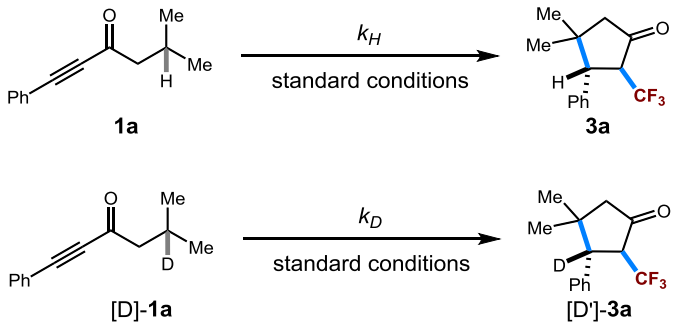


1a [D]-**3a**, 74%

To a mixture of CF_3SO_2Na (62.4 mg, 0.4 mmol), D_2O (98% D, 12.0 mg, 0.6 mmol), and 4CzIPN (3.2 mg, 2 mol%) in 2 mL of DMF was added **1a** (37.2 mg, 0.2 mmol) under nitrogen atmosphere. After 20 h of irradiation at a distance of ~5 cm from 30 W blue LEDs (BESTLLON® lamps, 450 nm, 100% light intensity), the reaction mixture was quenched with water, extracted with EtOAc,

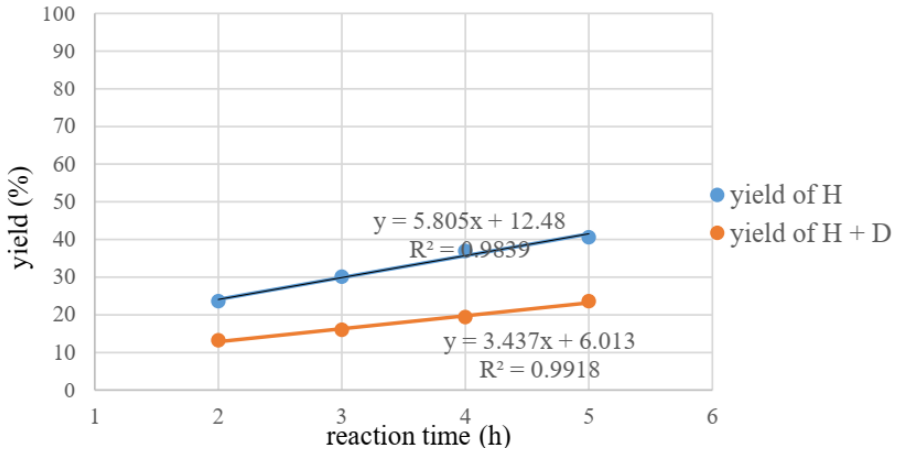
washed with brine, dried over anhydrous Na_2SO_4, and concentrated. Column chromatography on silica gel (petroleum ethers/EtOAc = 50:1) gave 38 mg (74% yield) of [D]-**3a** with 69% deuterium incorporation as a white solid, mp 89-90 ^oC. ^1H NMR (600 MHz, $CDCl_3$) δ 7.41-7.35 (m, 2H), 7.33-7.30 (m, 1H), 7.20 (d, J = 7.8 Hz, 2H), 3.49-3.43 (m, 0.31H), 3.42-3.36 (m, 1H), 2.45 (s, 2H), 1.17 (s, 3H), 0.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 207.19, 135.71, 128.31, 127.52, 124.64 (q, J = 279.4 Hz), 55.06, 54.22 (q, J = 26.4 Hz), 53.71 (d, J = 14.1 Hz), 38.16, 27.00, 22.85. ^{19}F NMR (565 MHz, $CDCl_3$) δ -66.23 (D), -66.32. MS (EI) m/z: $[M]^+$ Calcd for $C_{14}H_{14}DF_3O^+$: 257.1; Found 257.1.

Determination of the KIE Values



The method to calculate KIE is according to the reported method[2] through parallel reactions of **1a** and [D]-**1a** (75% D) using the general produre with *n*-dodecane as the internal standard.

time (h)	2	3	4	5
yield of *H*	0.2355	0.3007	0.3697	0.406
yield of *H*+*D*	0.1322	0.1602	0.1937	0.2356



[2] (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.

Adjusted initial rates:

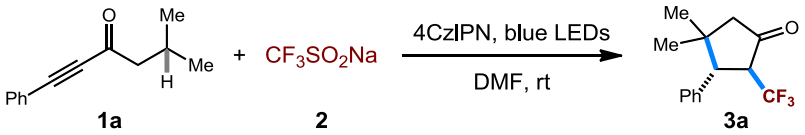
k_H =5.805

3.437=k_H×25%+k_D×75%

k_D=2.648

KIE=k_H/k_D=2.19

Table S1. The dr value of **3a** at different time[a]

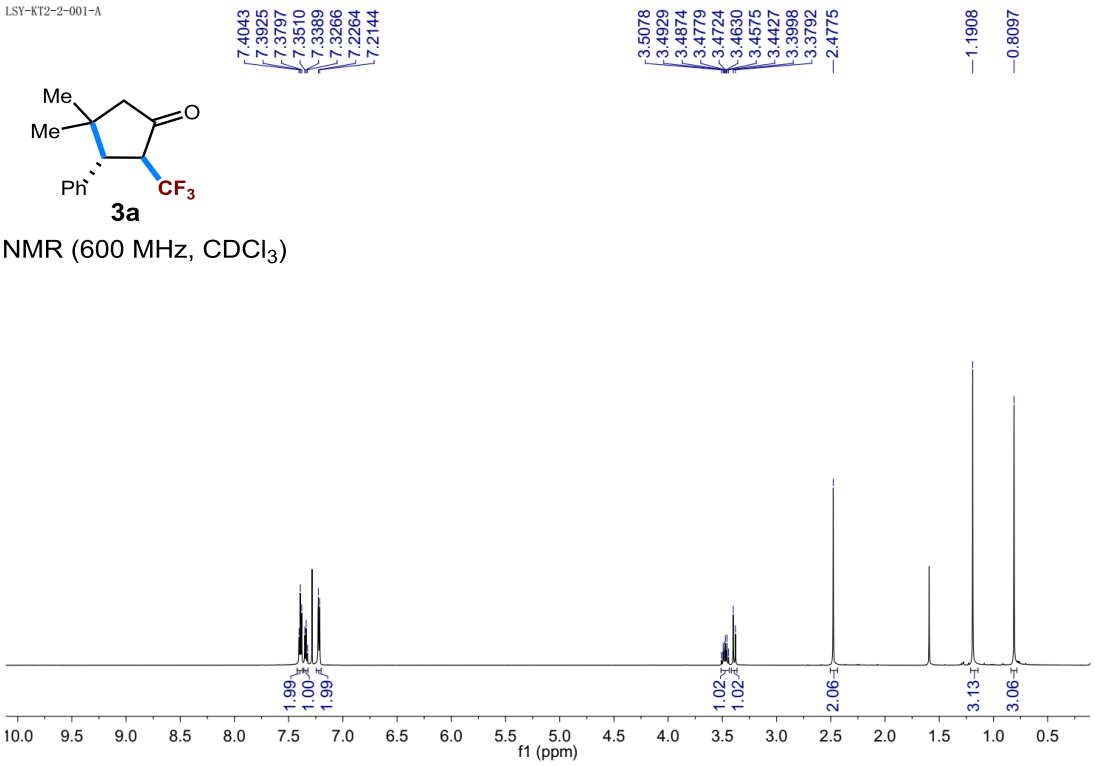


1a **2** **3a**

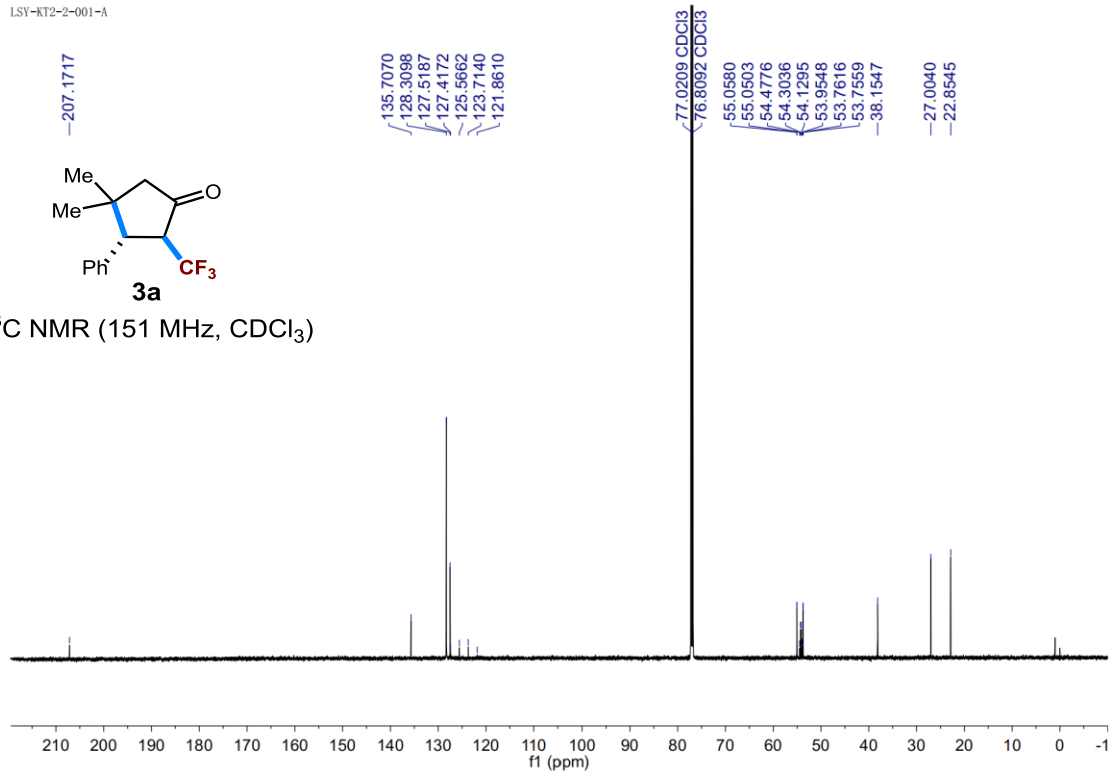
Entry	Time (h)	Conversion of **1a** (%)	Dr of **3a**
1	1	58	7:1
2	2	90	8:1
3	4	95	14:1
4	8	>99	20:1
5	20	>99	25:1

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), 4CzIPN (2 mol%), DMF (2 mL), 30 W blue LEDs, 25 °C. [b] Determined by ^{19}F NMR.

4. NMR Spectra

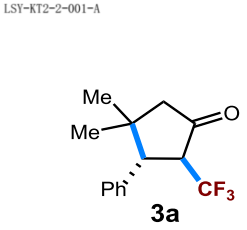


^{1}H NMR (600 MHz, $CDCl_3$)



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

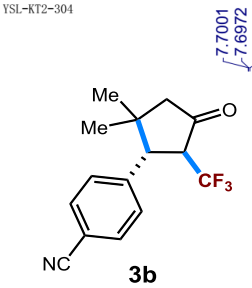
LSY-KT2-2-001-A



3a

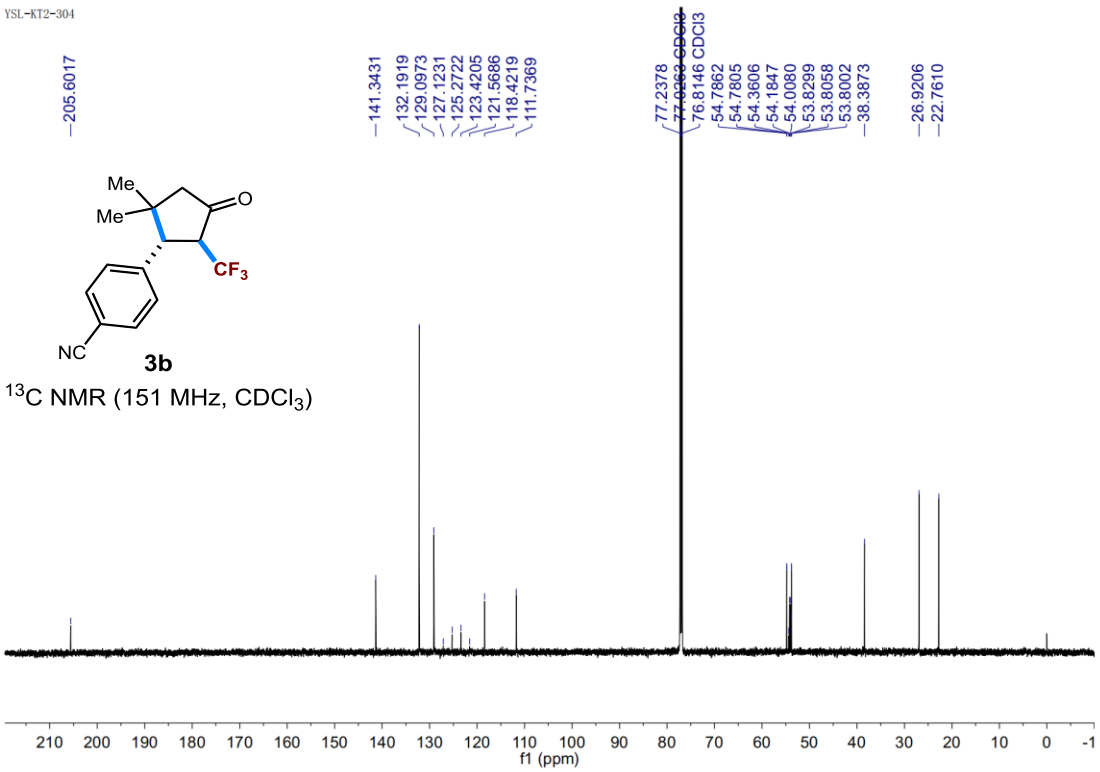
^{19}F NMR (565 MHz, $CDCl_3$)

YSL-KT2-304



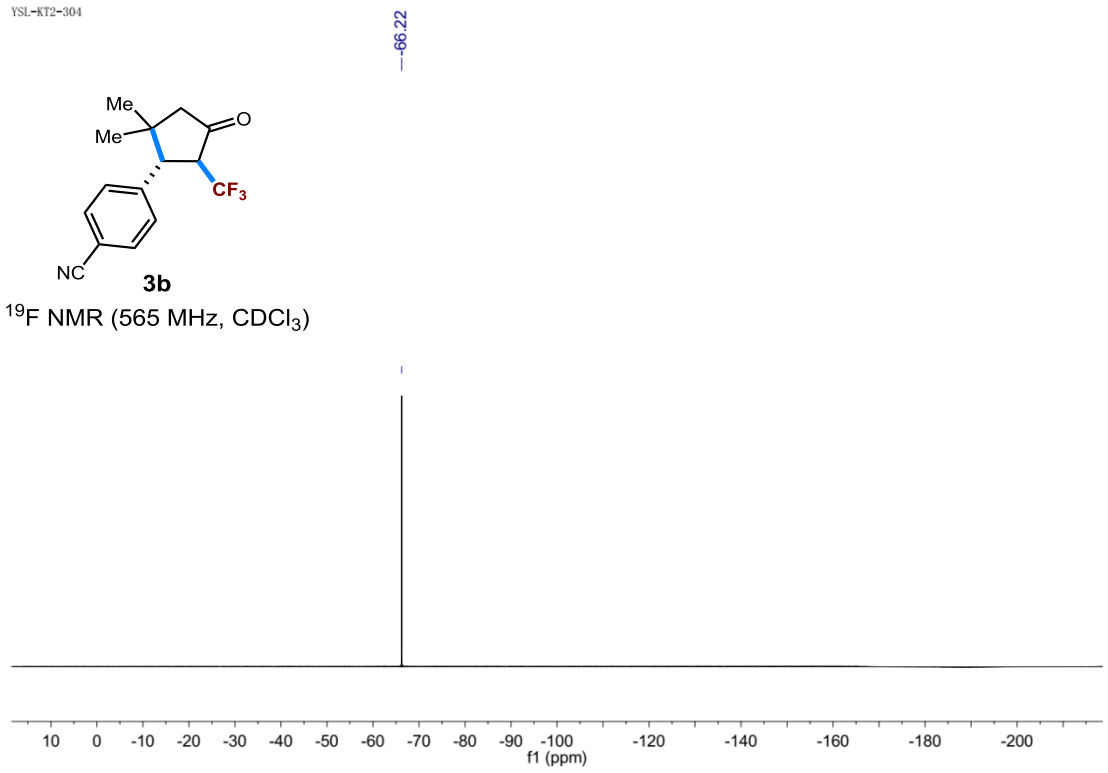
3b

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



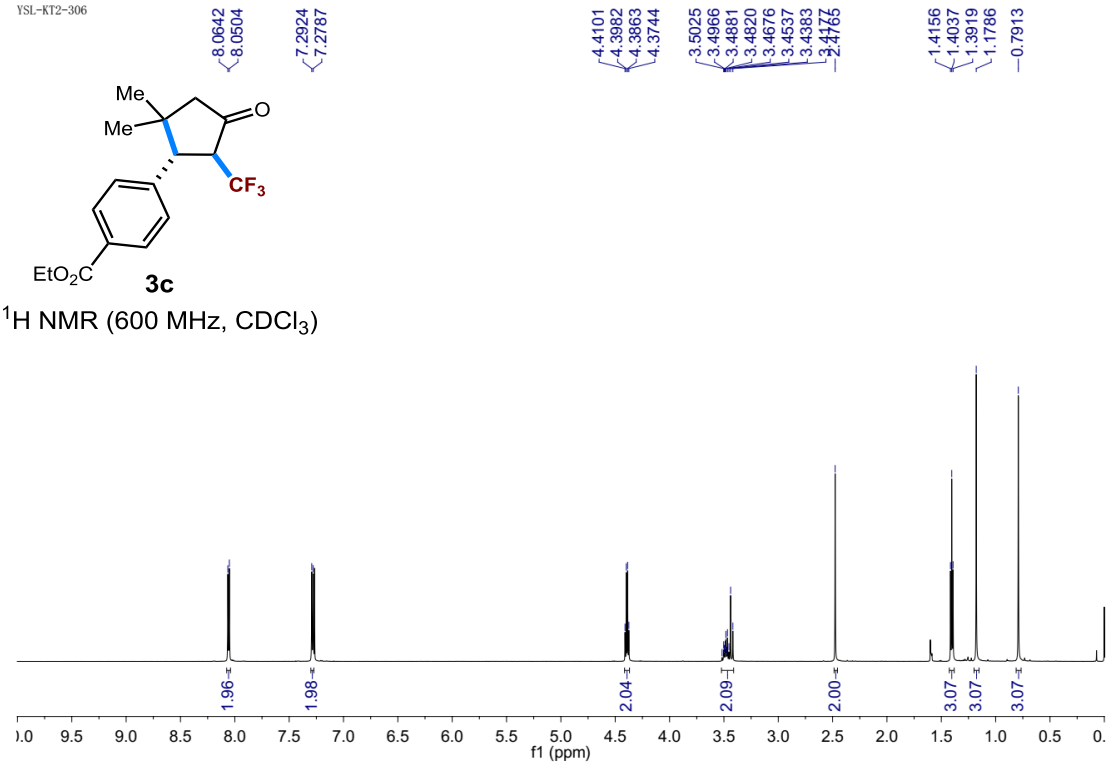
3b

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



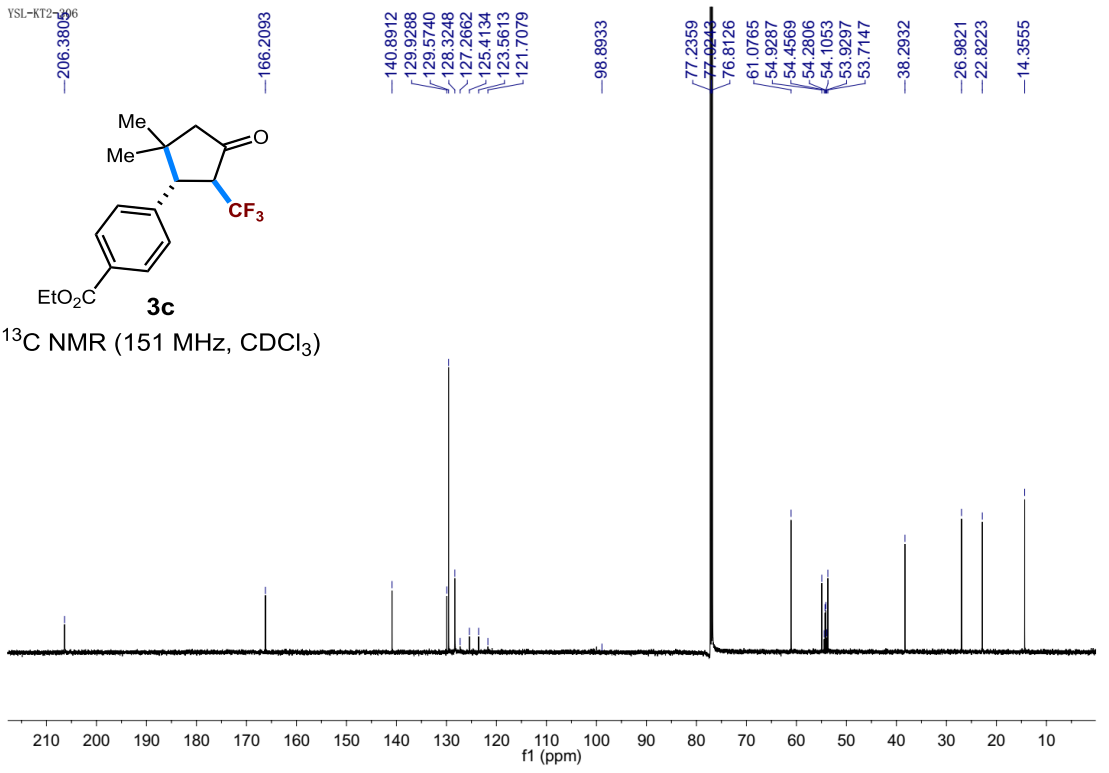
3b

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



3c

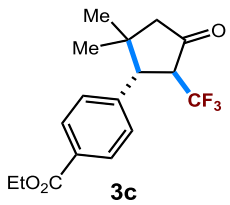
^{1}H NMR (600 MHz, $CDCl_3$)



3c

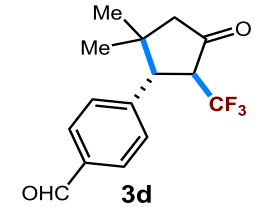
^{13}C NMR (151 MHz, $CDCl_3$)

YSL-KT2-306



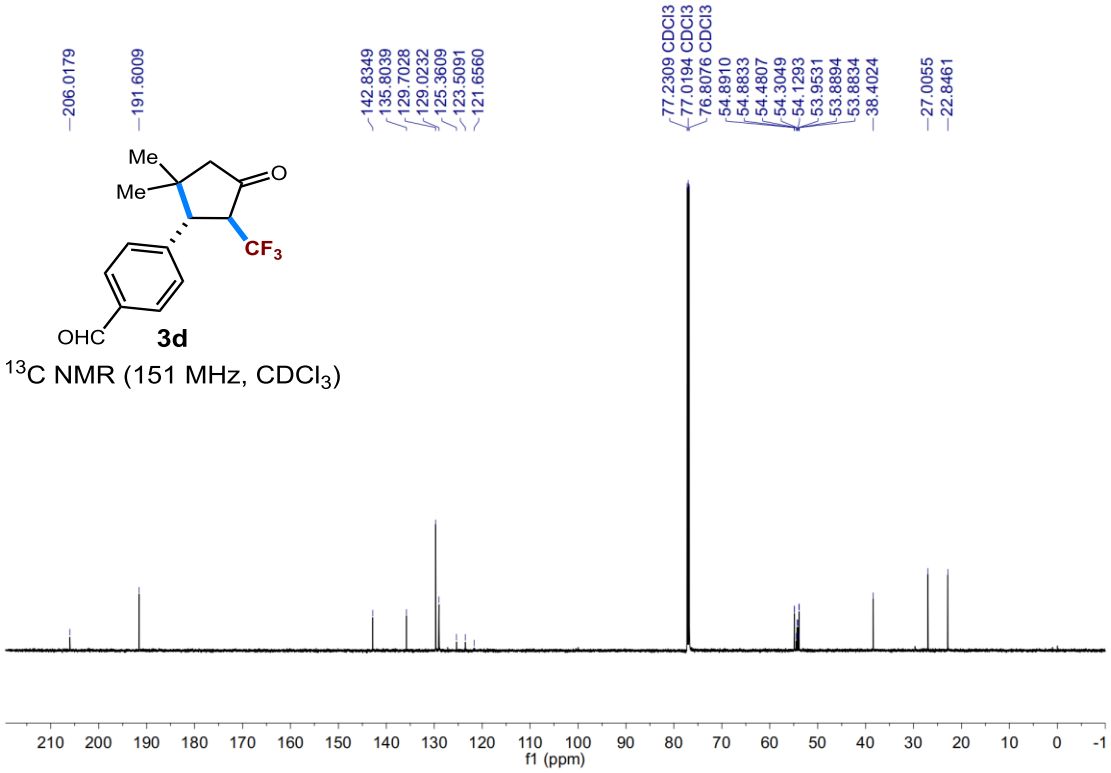
3c

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

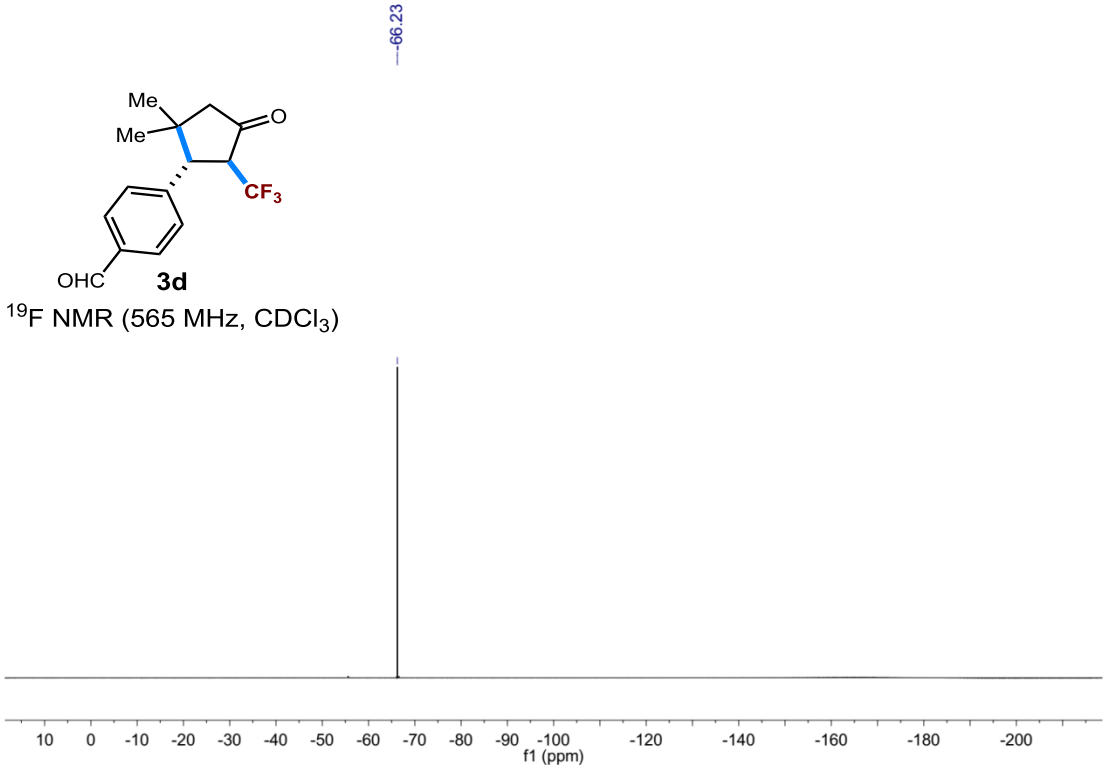


3d

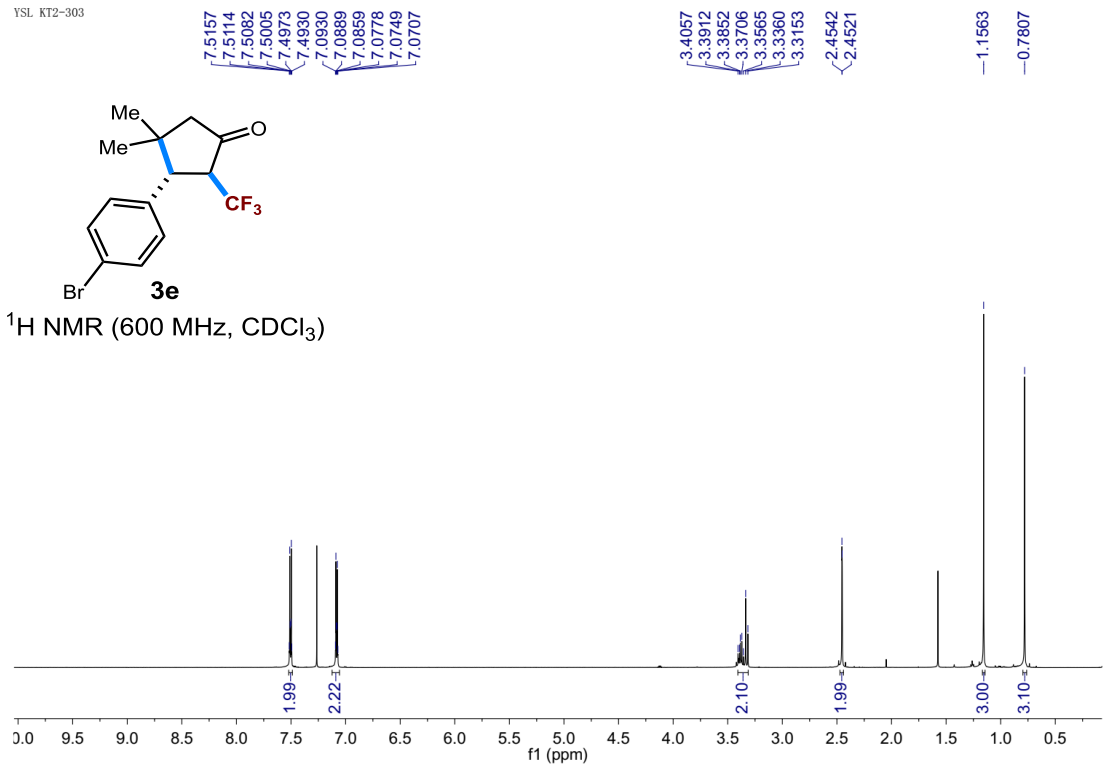
^{1}H NMR (600 MHz, $CDCl_3$)

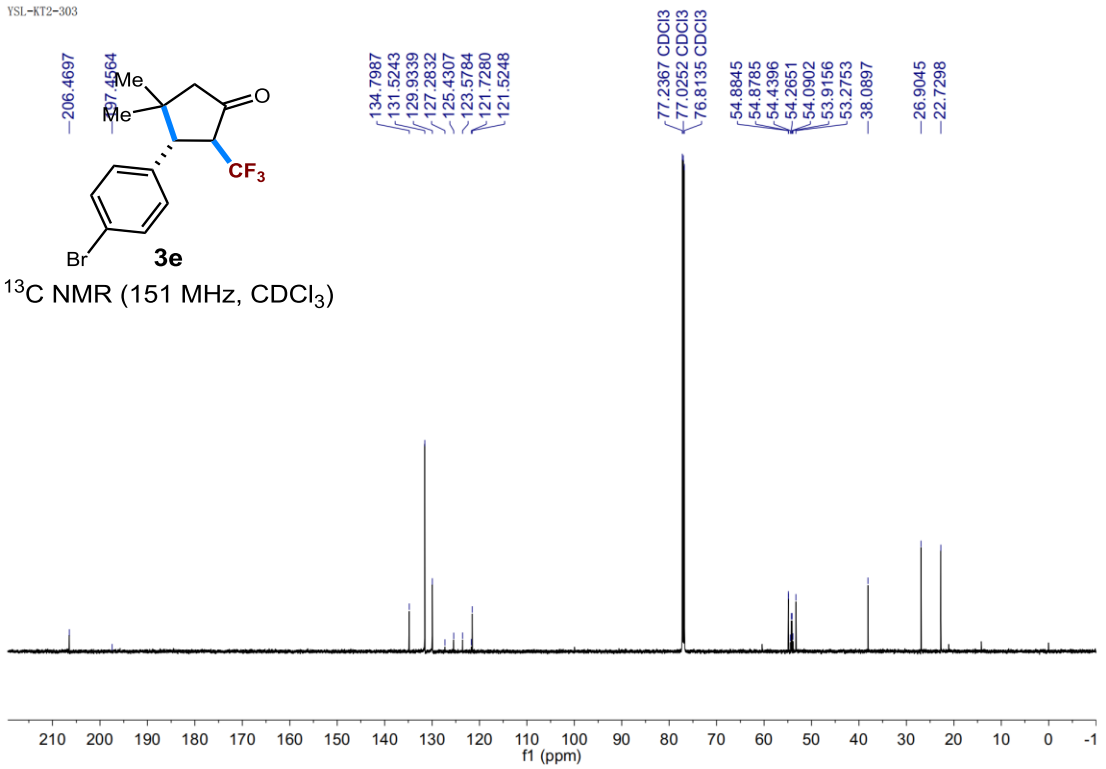


^{13}C NMR (151 MHz, $CDCl_3$)

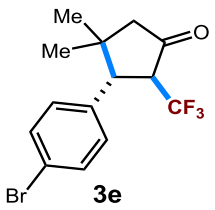


^{19}F NMR (565 MHz, $CDCl_3$)


YSL KT2-303
7.5157
7.5114
7.5082
7.5005
7.4973
7.4930
7.0930
7.0889
7.0859
7.0778
7.0749
7.0707
3.4057
3.3912
3.3852
3.3706
3.3565
3.3360
3.3153
2.4542
2.4521
1.1563
0.7807
Me
Me
O
CF3
Br
3e
1H NMR (600 MHz, CDCl3)
1.99
2.22
2.10
1.99
3.00
3.10
f1 (ppm)


YSL-KT2-303
206.4697
137.4564
134.7987
131.5243
129.9339
127.2832
125.4307
123.5784
121.7280
121.5248
77.2367 CDCl3
77.0252 CDCl3
76.8135 CDCl3
54.8845
54.8785
54.4396
54.2651
54.0902
53.9156
53.2753
38.0897
26.9045
22.7298
Me
Me
O
CF3
Br
3e
13C NMR (151 MHz, CDCl3)
f1 (ppm)

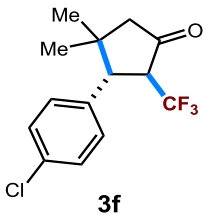
YSL KT2-303



3e

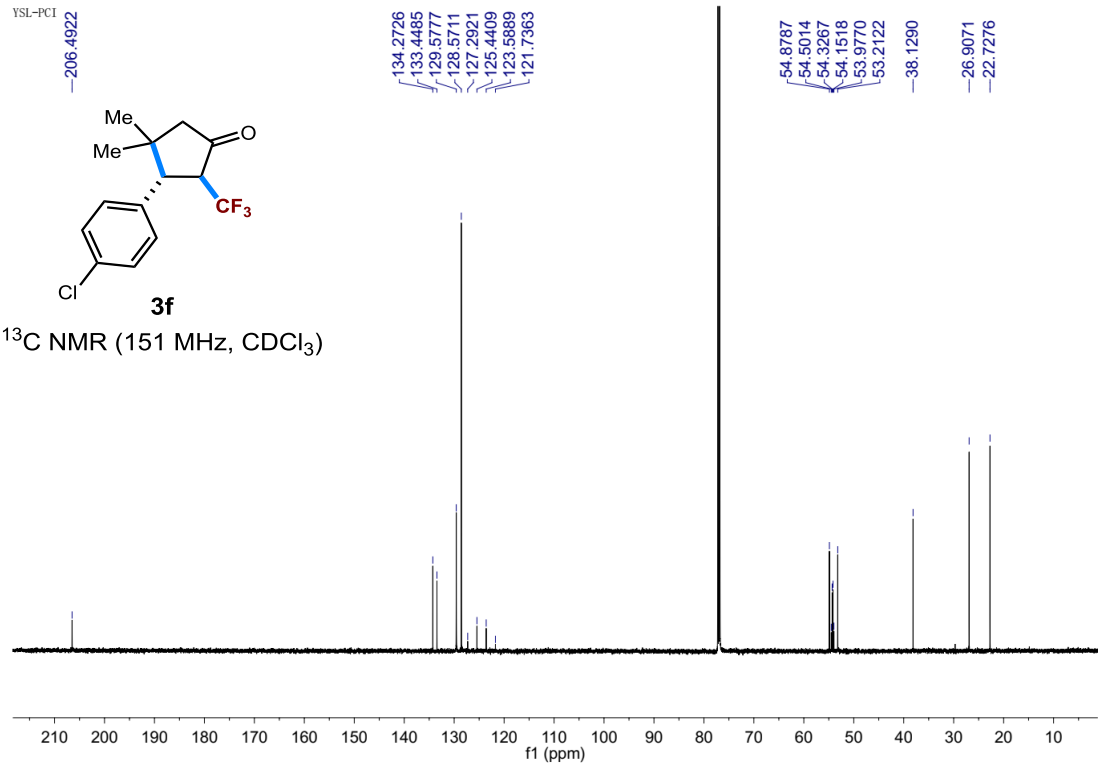
^{19}F NMR (565 MHz, $CDCl_3$)

YSL KT2-302



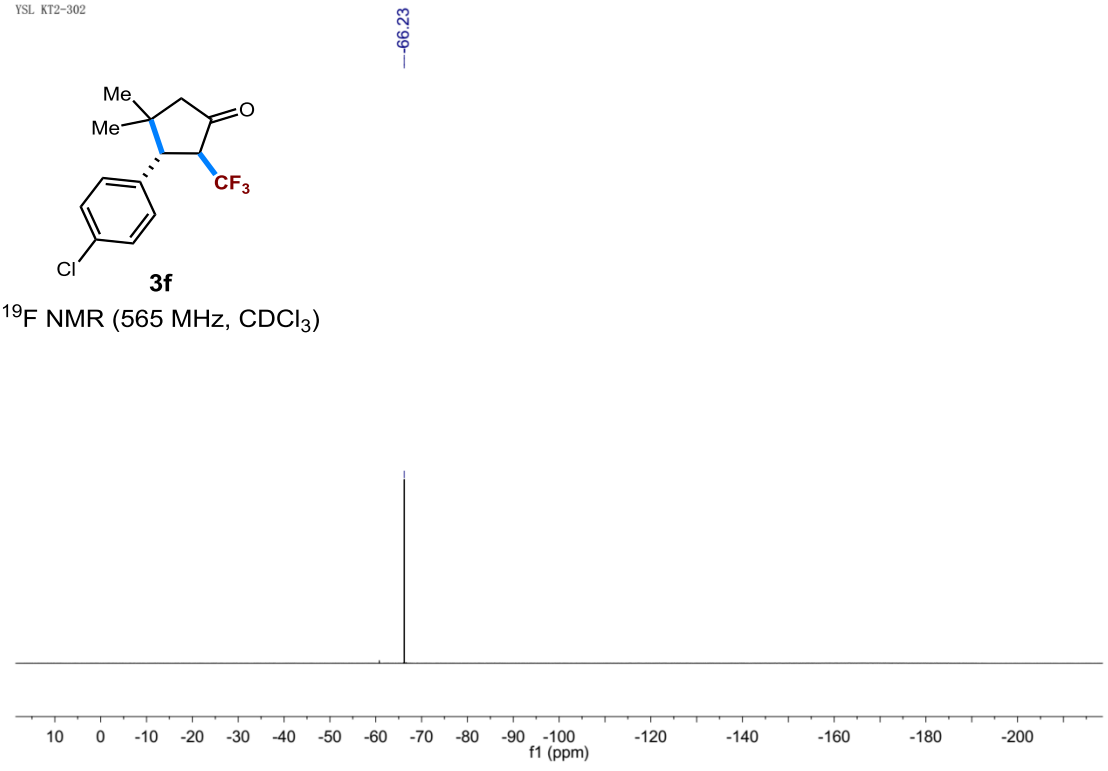
3f

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



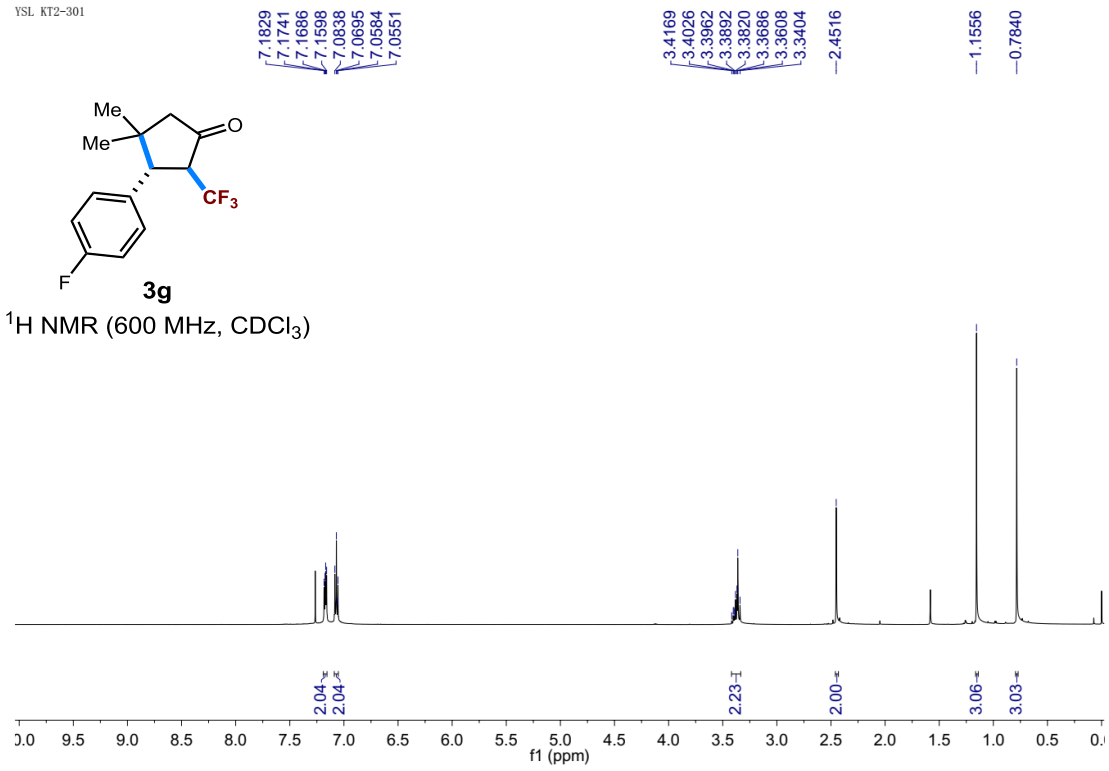
3f

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



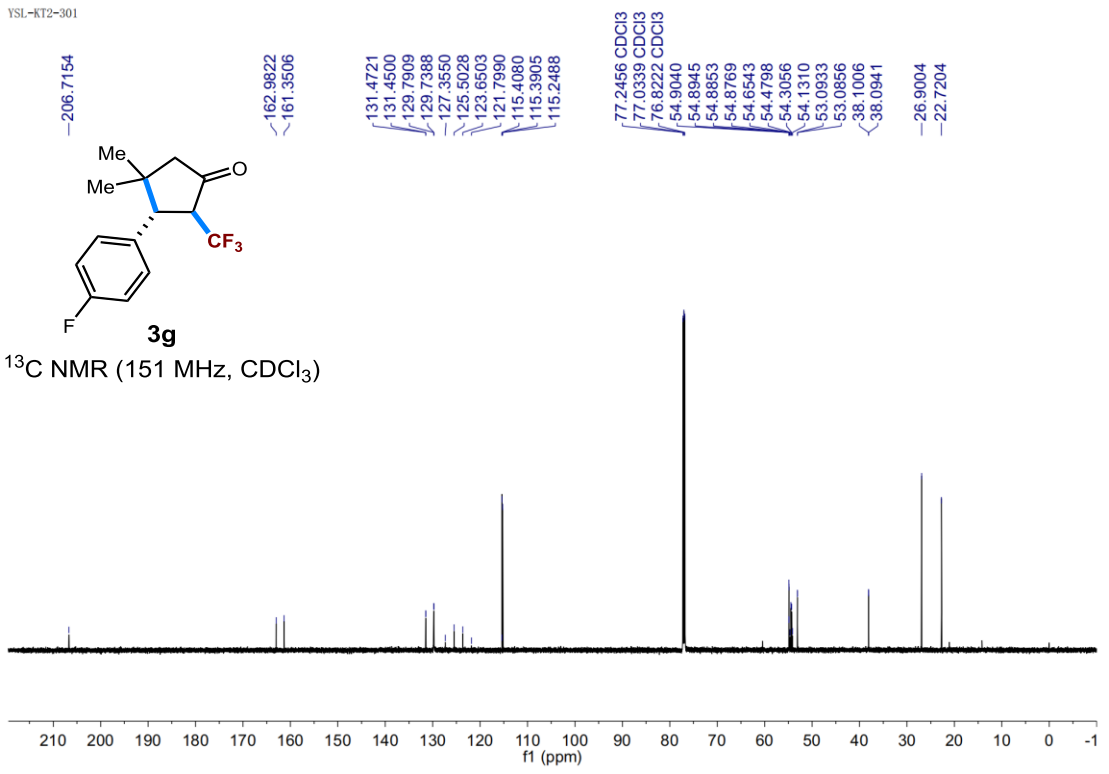
3f

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



3g

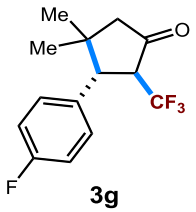
^{1}H NMR (600 MHz, $CDCl_3$)



3g

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

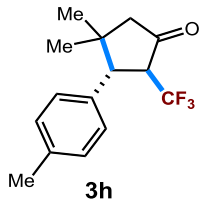
YSL KT2-301



3g

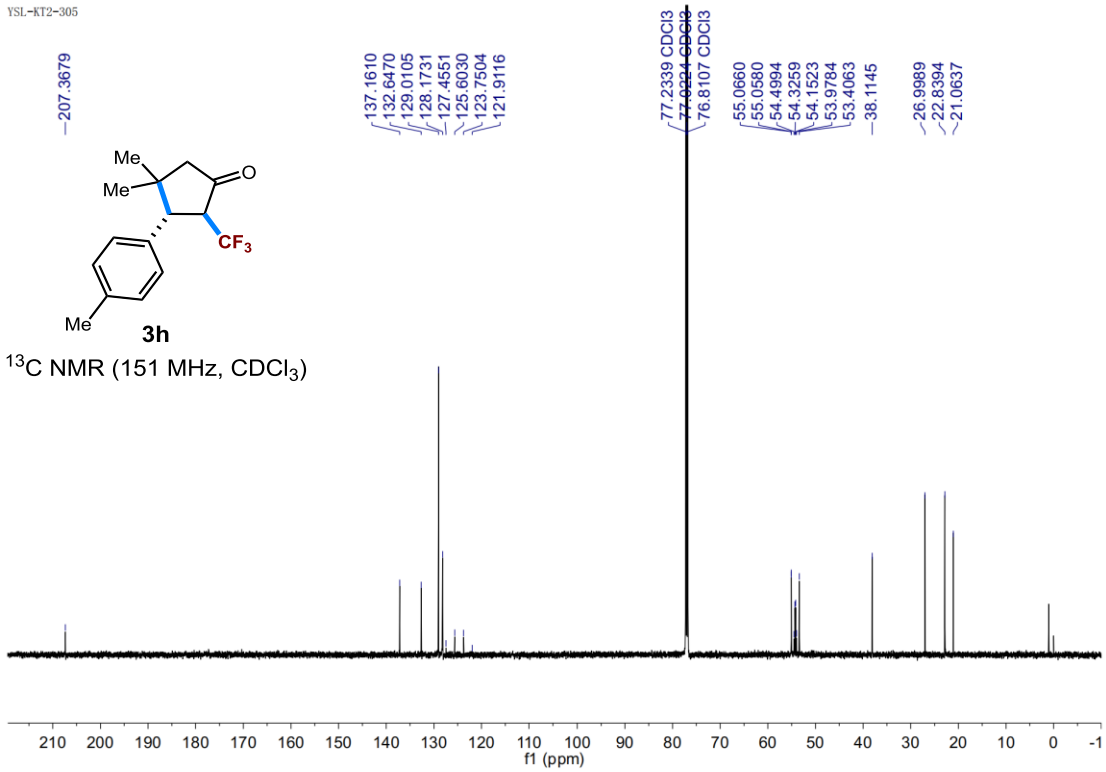
^{19}F NMR (565 MHz, $CDCl_3$)

YSL-KT2-305



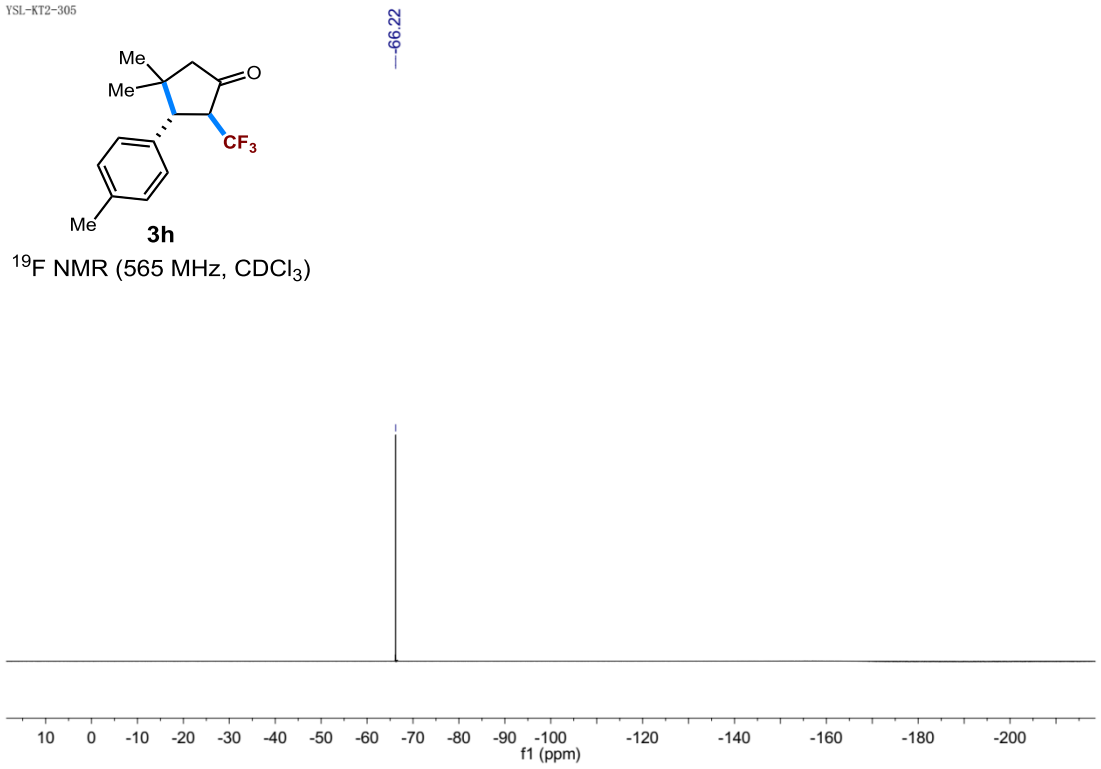
3h

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



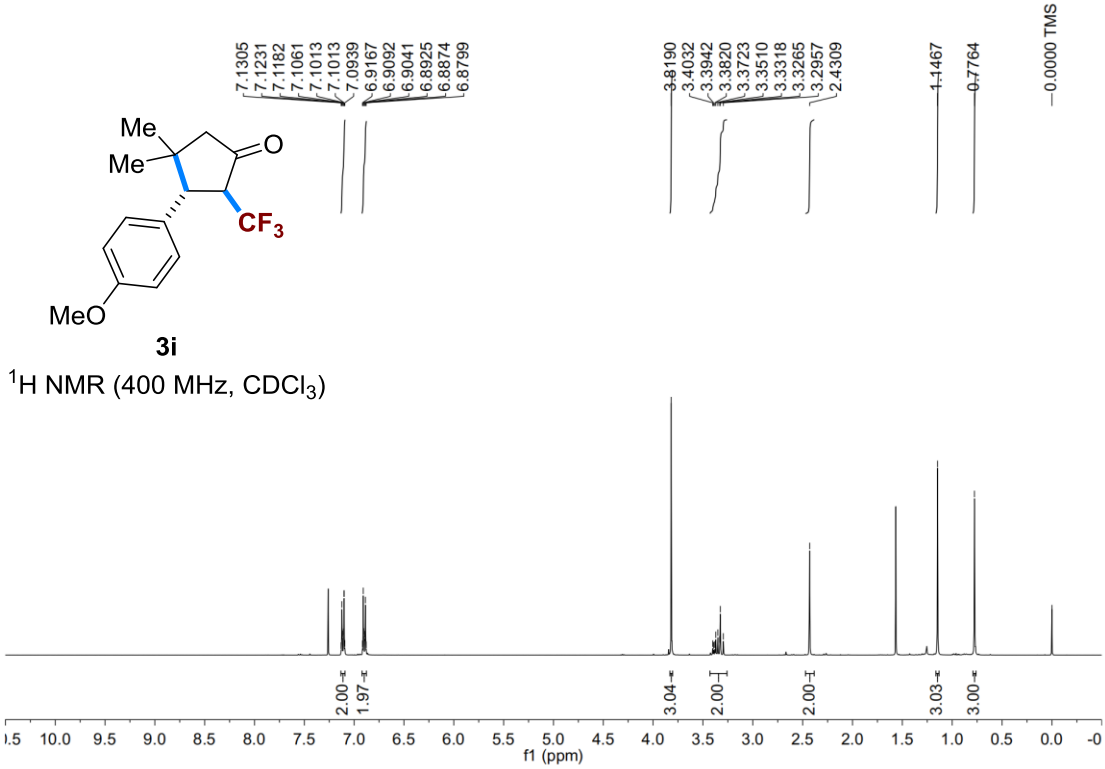
3h

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



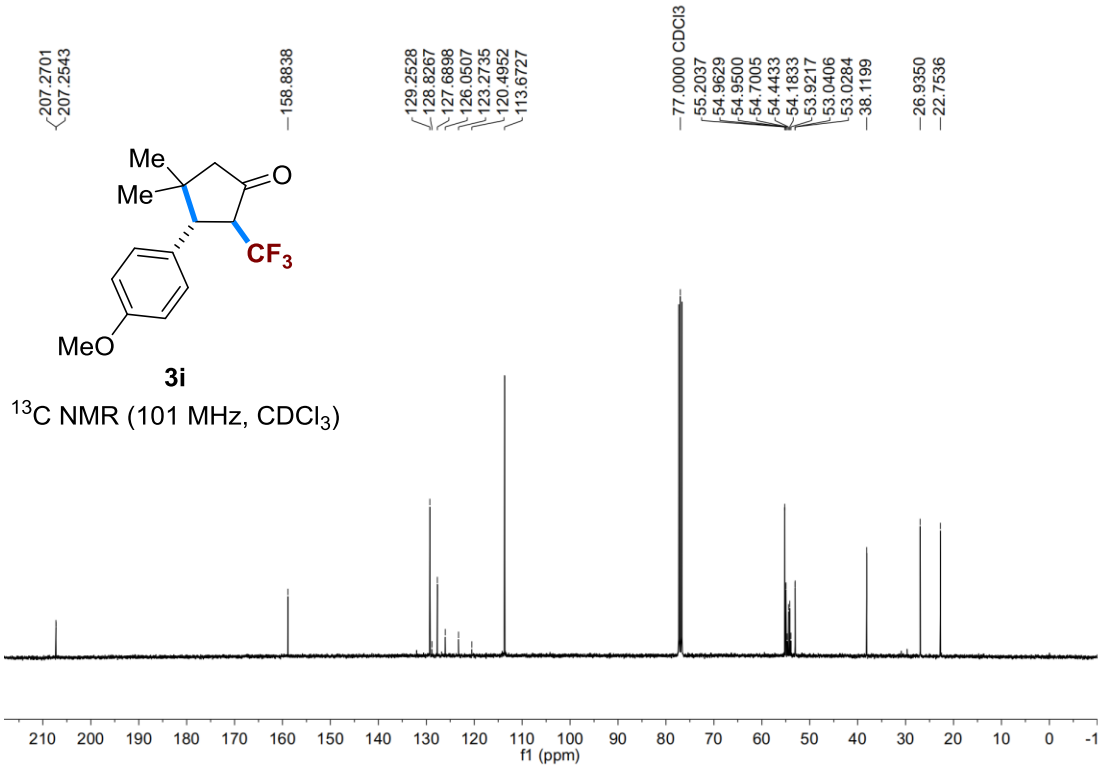
3h

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



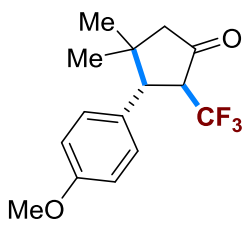
3i

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



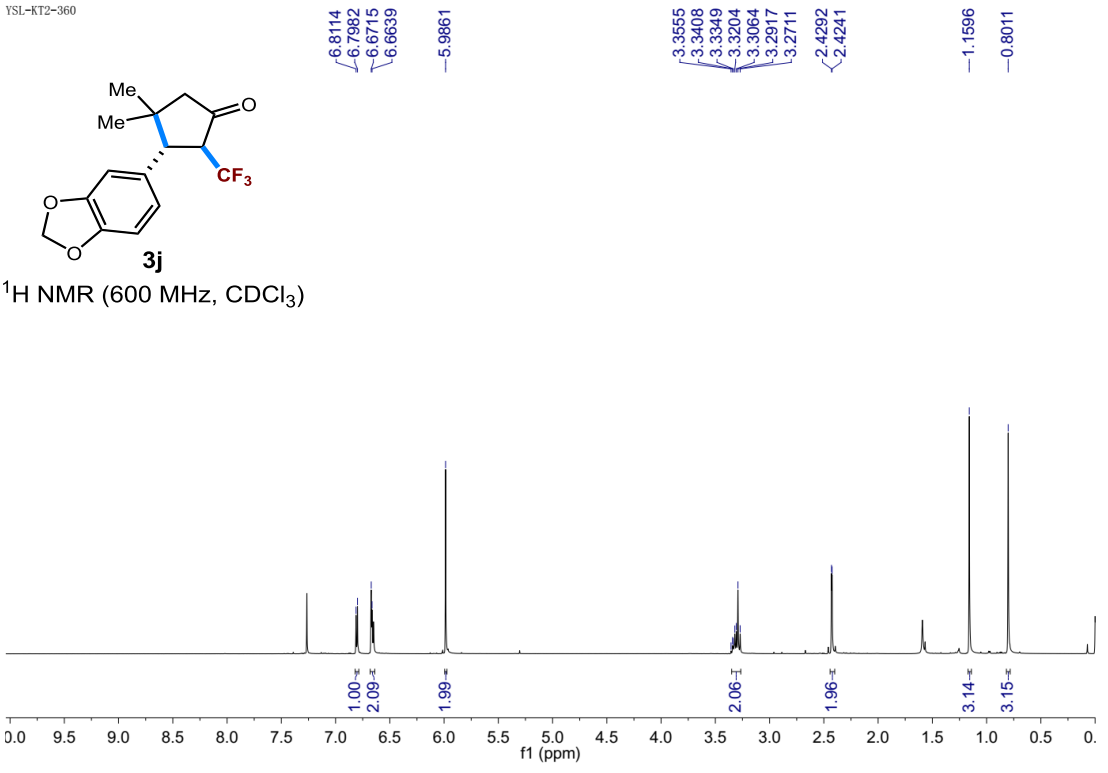
3i

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



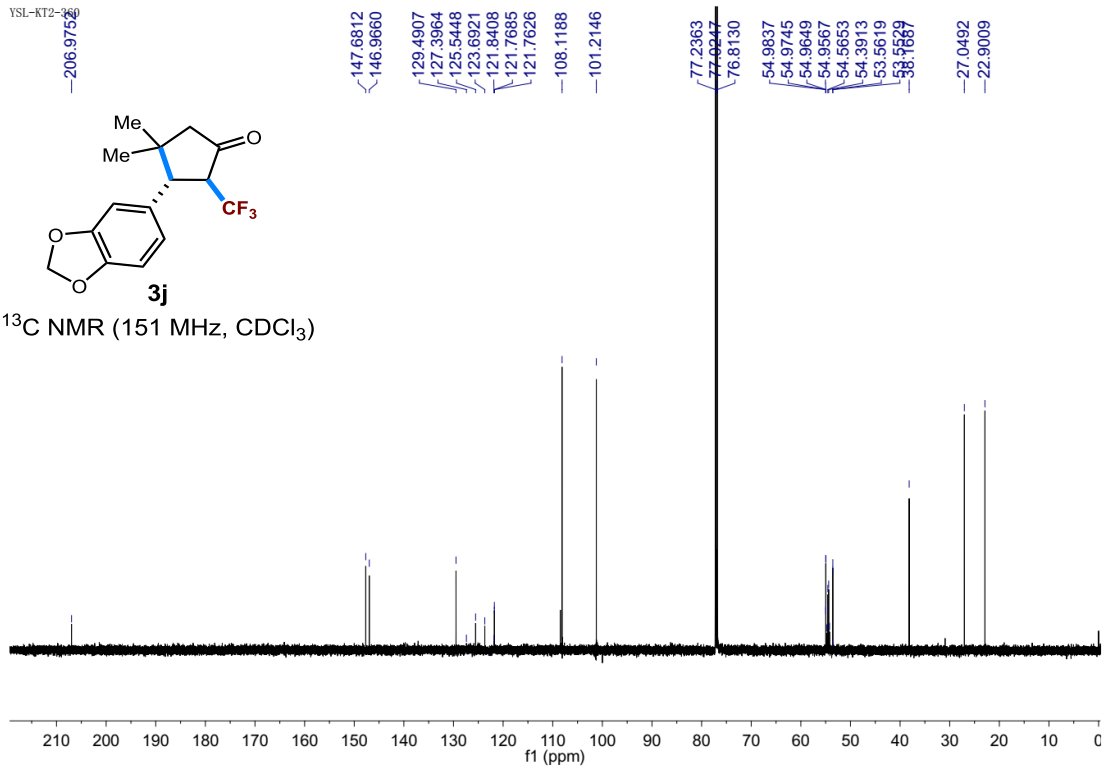
3i

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



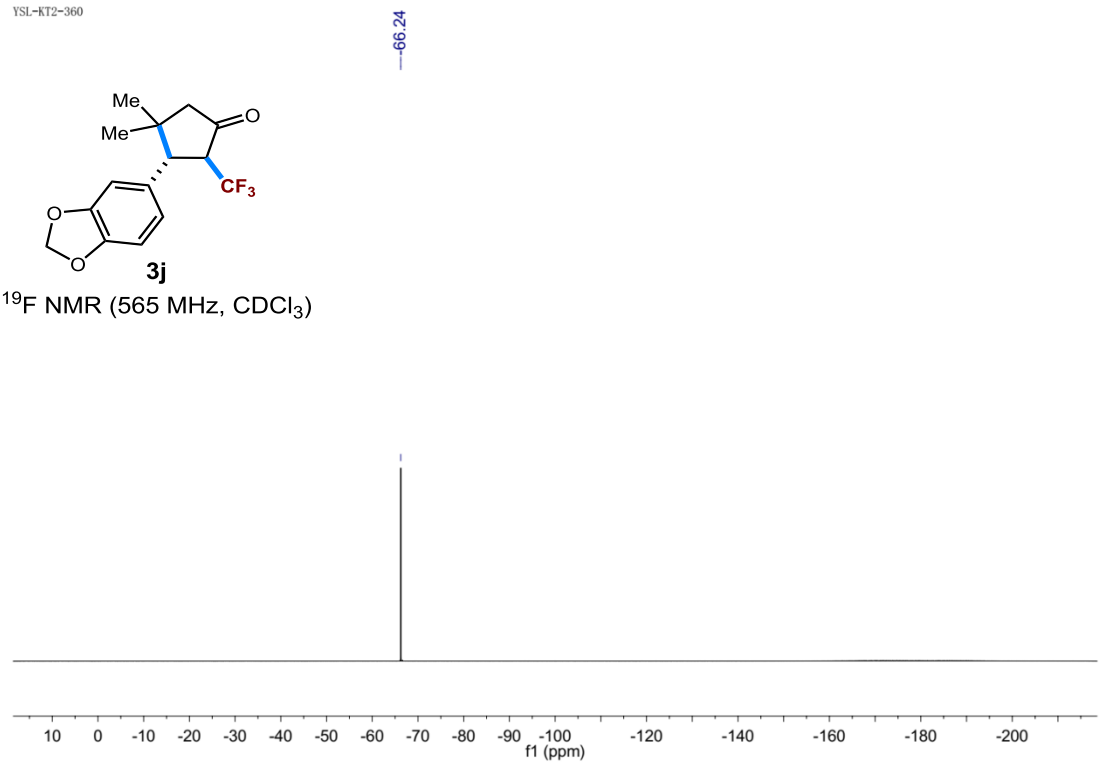
3j

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



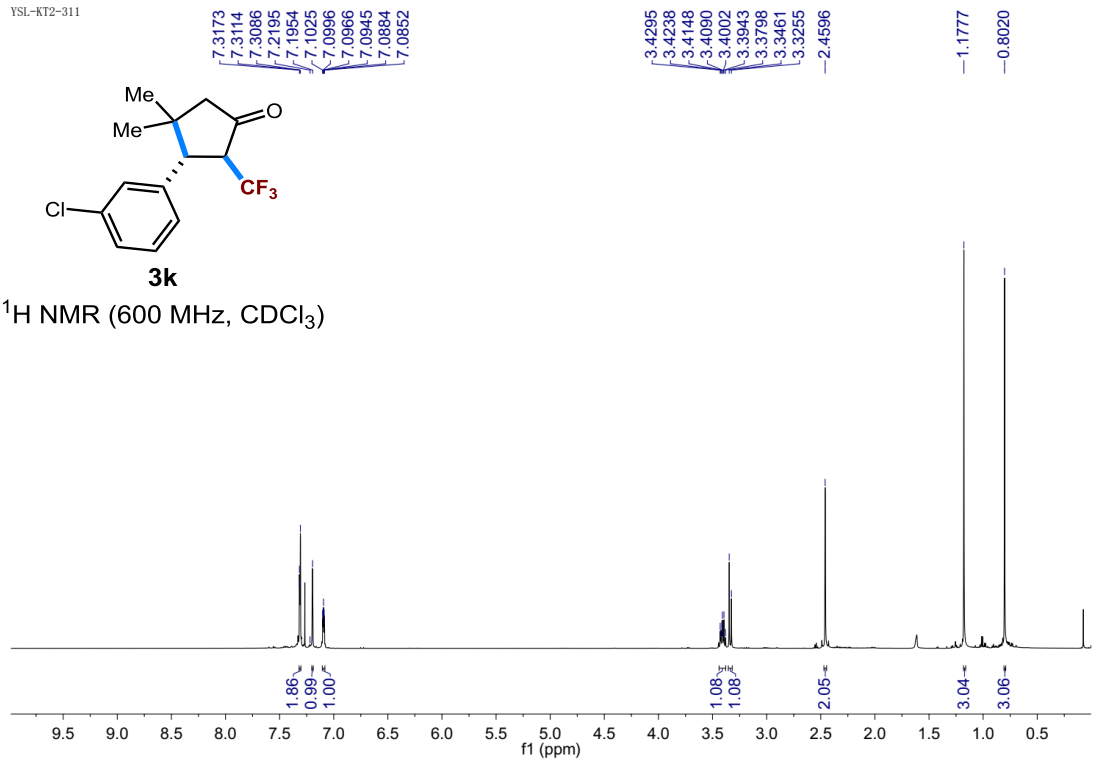
3j

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



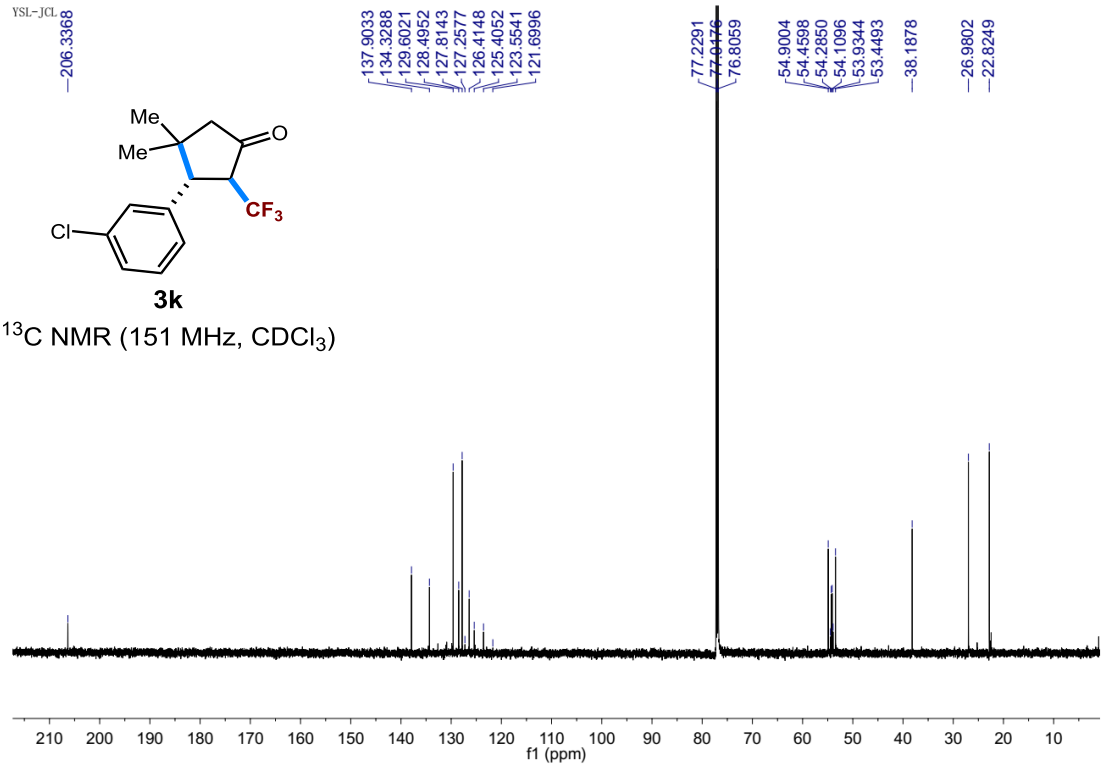
3j

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



3k

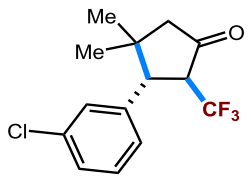
^{1}H NMR (600 MHz, $CDCl_3$)



3k

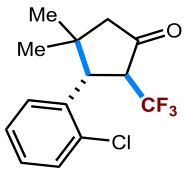
^{13}C NMR (151 MHz, $CDCl_3$)

YSL-KT2-311



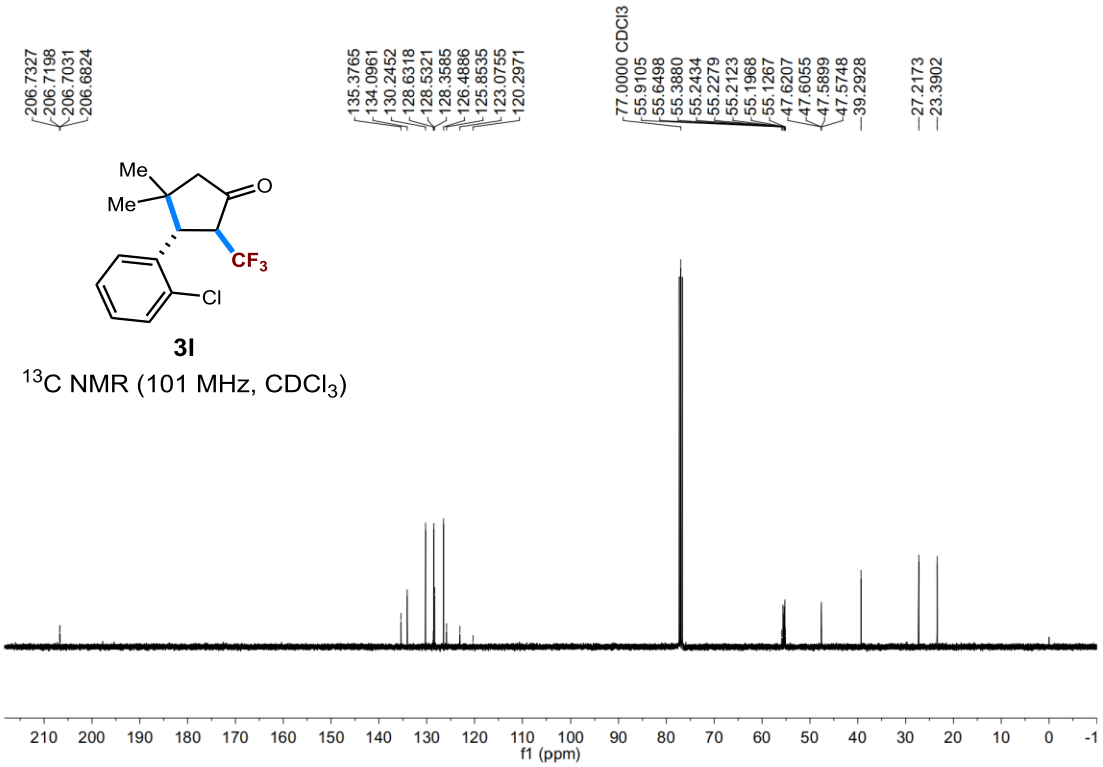
3k

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



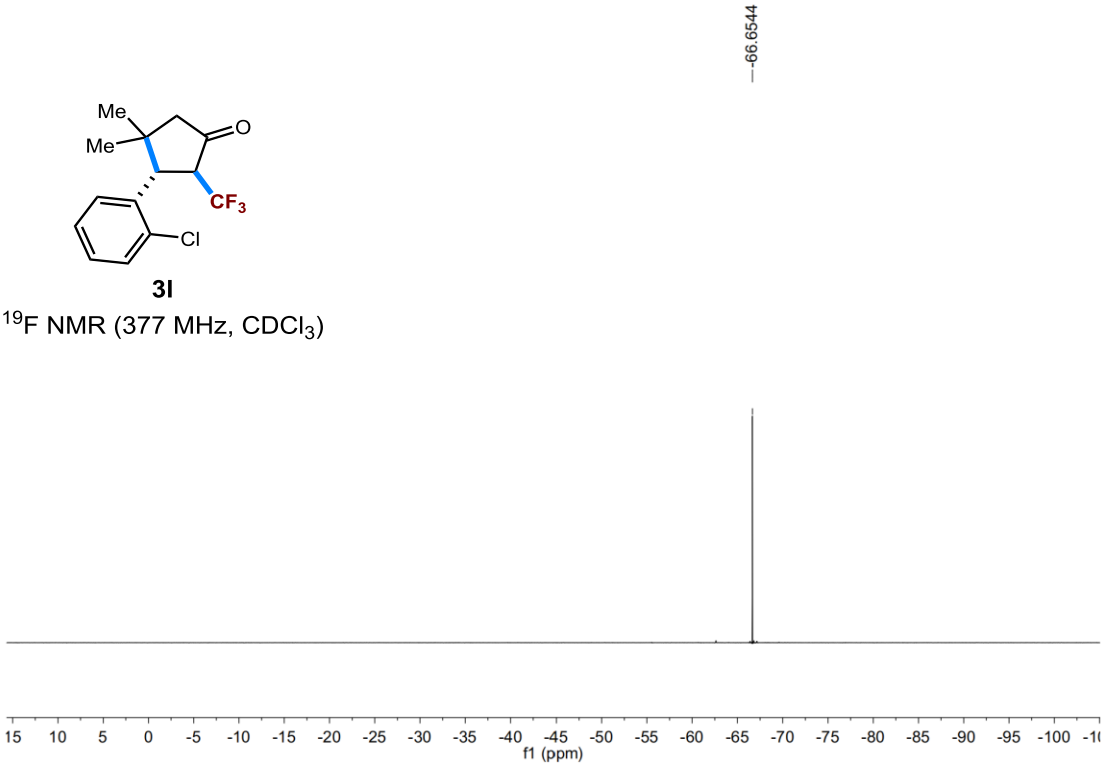
3l

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



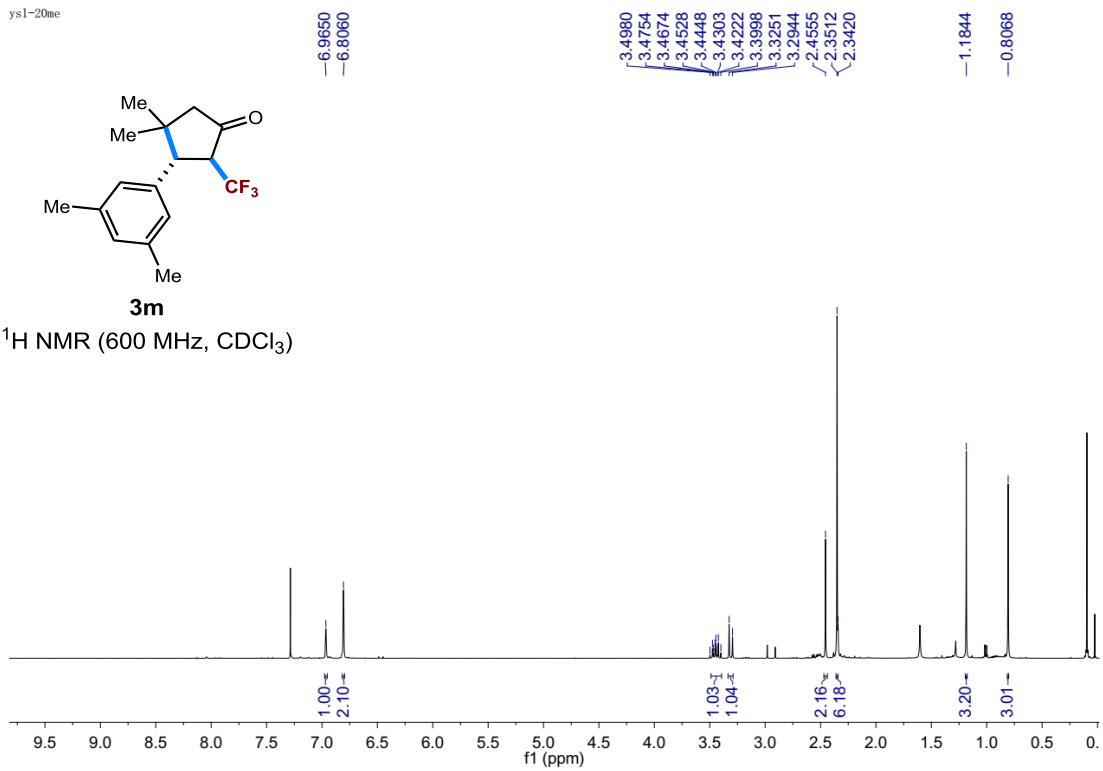
3l

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



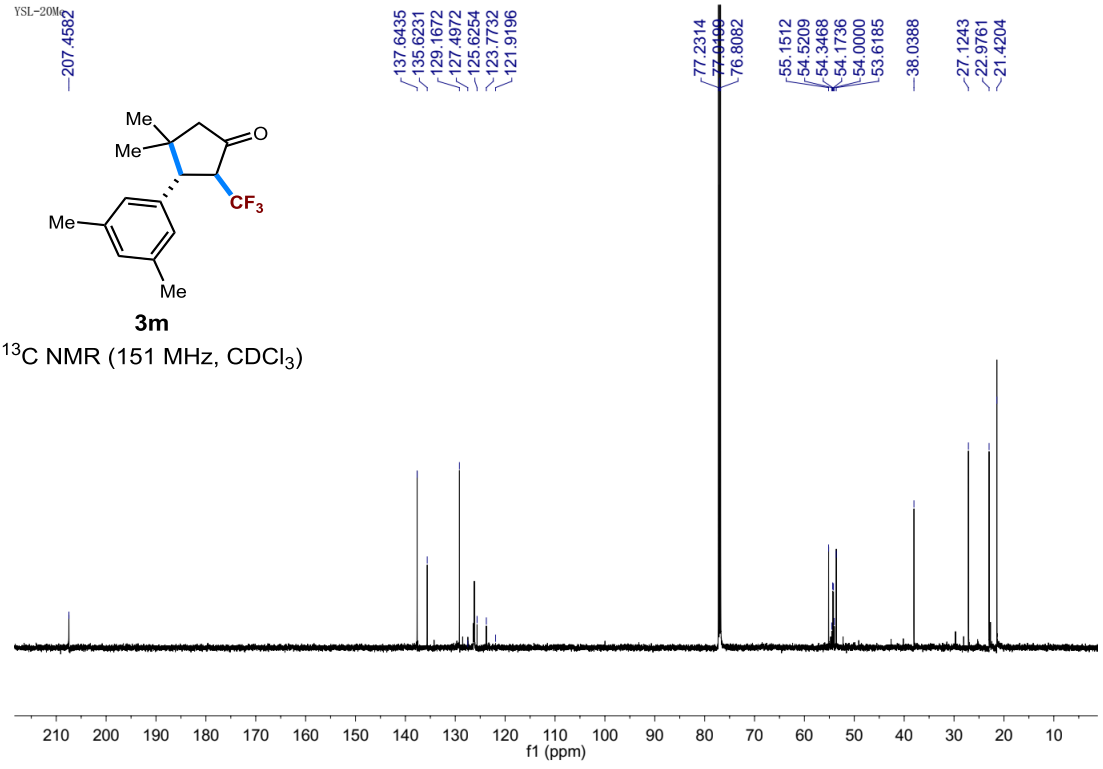
3l

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



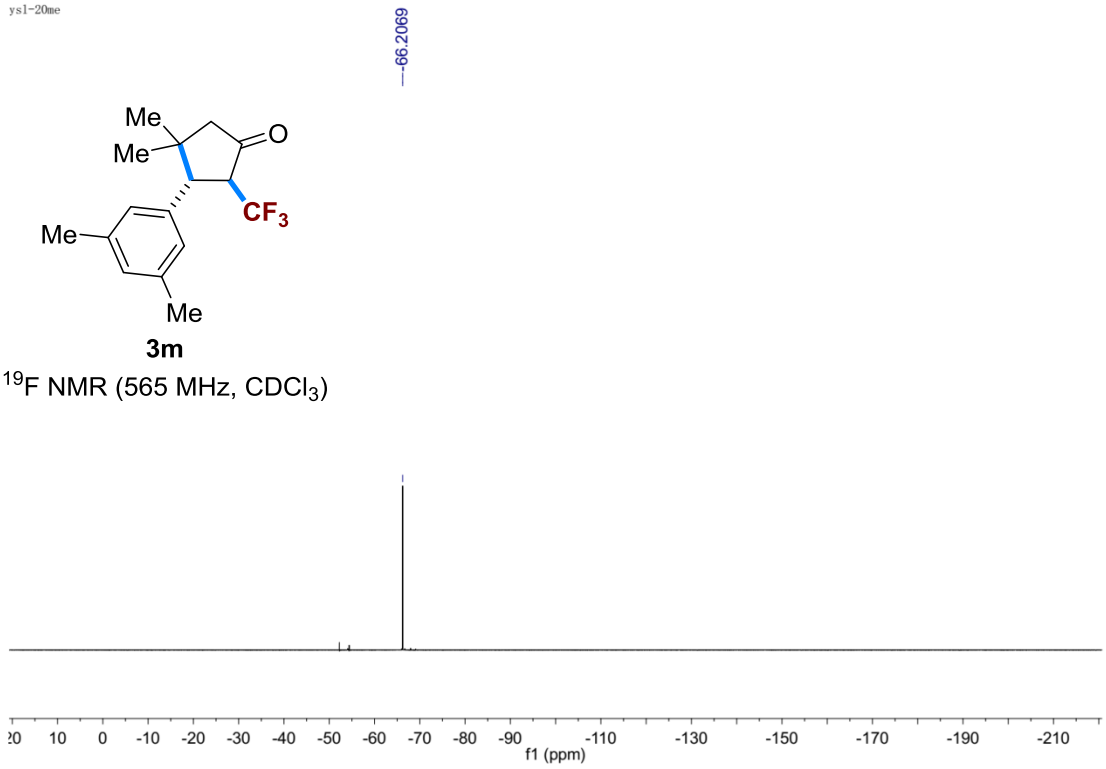
3m

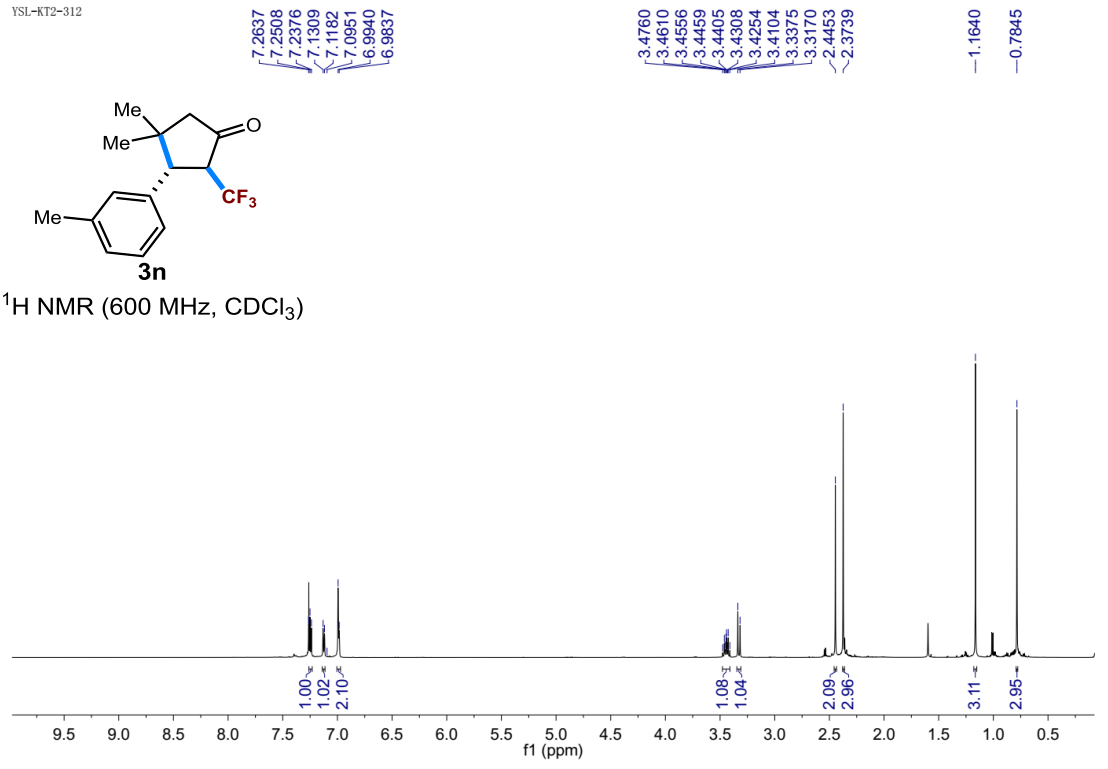
^{1}H NMR (600 MHz, $CDCl_3$)

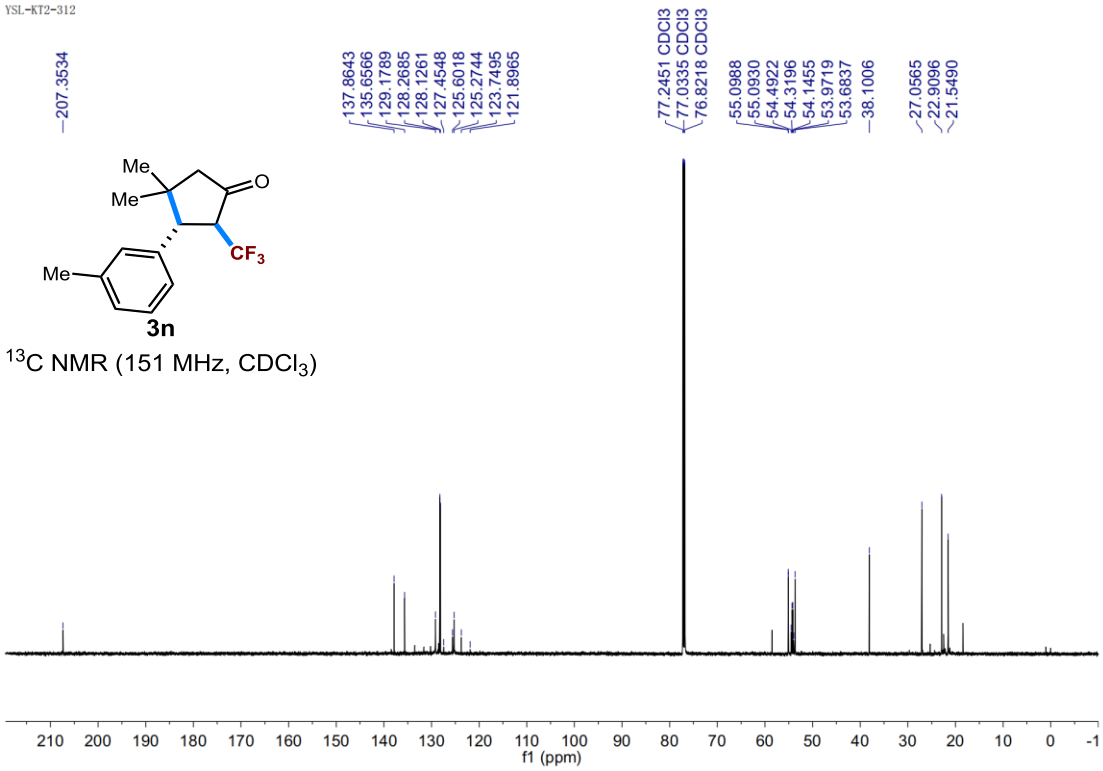


3m

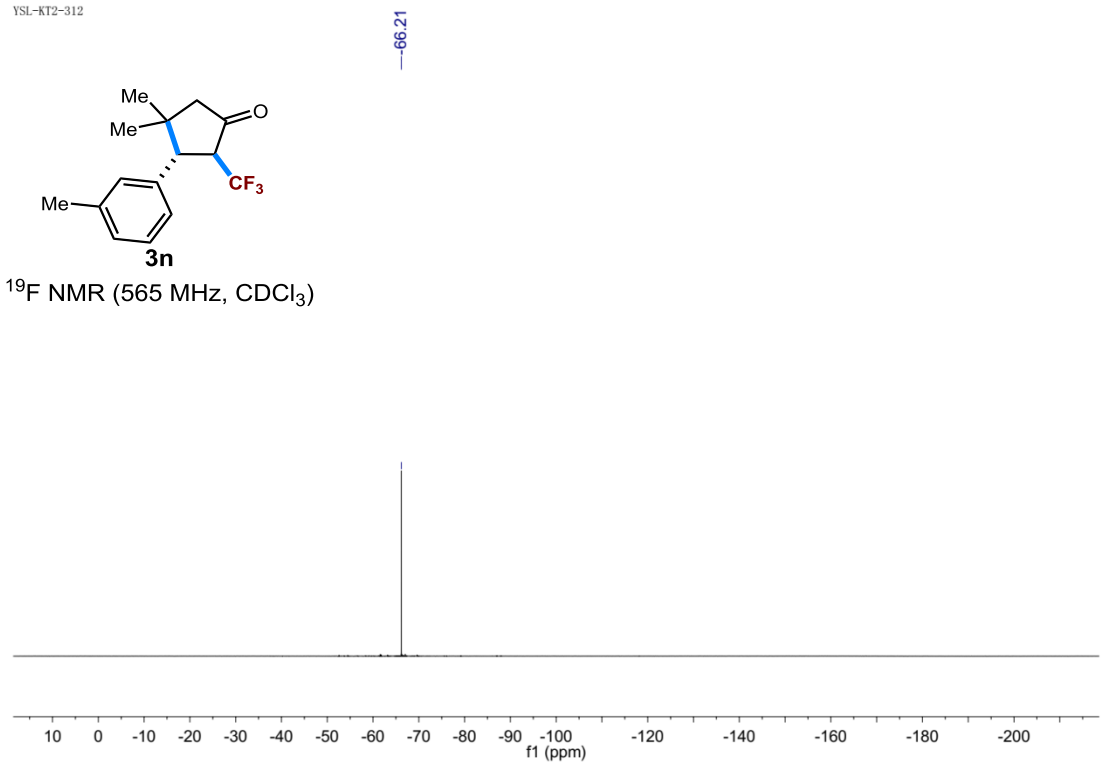
^{13}C NMR (151 MHz, $CDCl_3$)


ys1-20me
-66.2069
Me
Me
O
CF3
Me
Me
3m
19F NMR (565 MHz, CDCl3)
f1 (ppm)

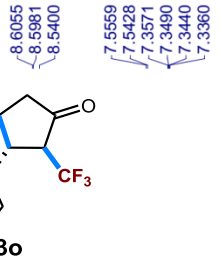

YSL-KT2-312
7.2637
7.2508
7.2376
7.1309
7.1182
7.0951
6.9940
6.9837
3.4760
3.4610
3.4556
3.4459
3.4405
3.4308
3.4254
3.4104
3.3375
3.3170
2.4453
2.3739
1.1640
0.7845
Me
Me
O
CF3
Me
3n
1H NMR (600 MHz, CDCl3)
1.00
1.02
2.10
1.08
1.04
2.09
2.96
3.11
2.95
f1 (ppm)



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

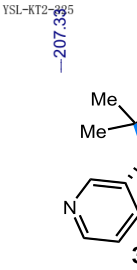


^{19}F NMR (565 MHz, $CDCl_3$)



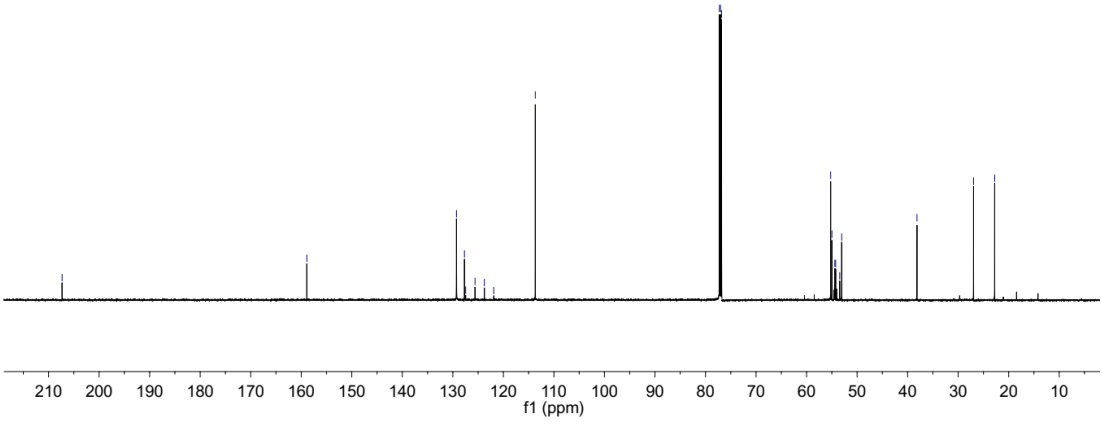
3o

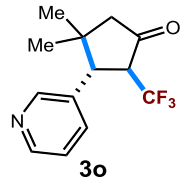
^{1}H NMR (600 MHz, $CDCl_3$)



3o

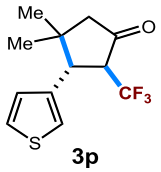
^{13}C NMR (151 MHz, $CDCl_3$)





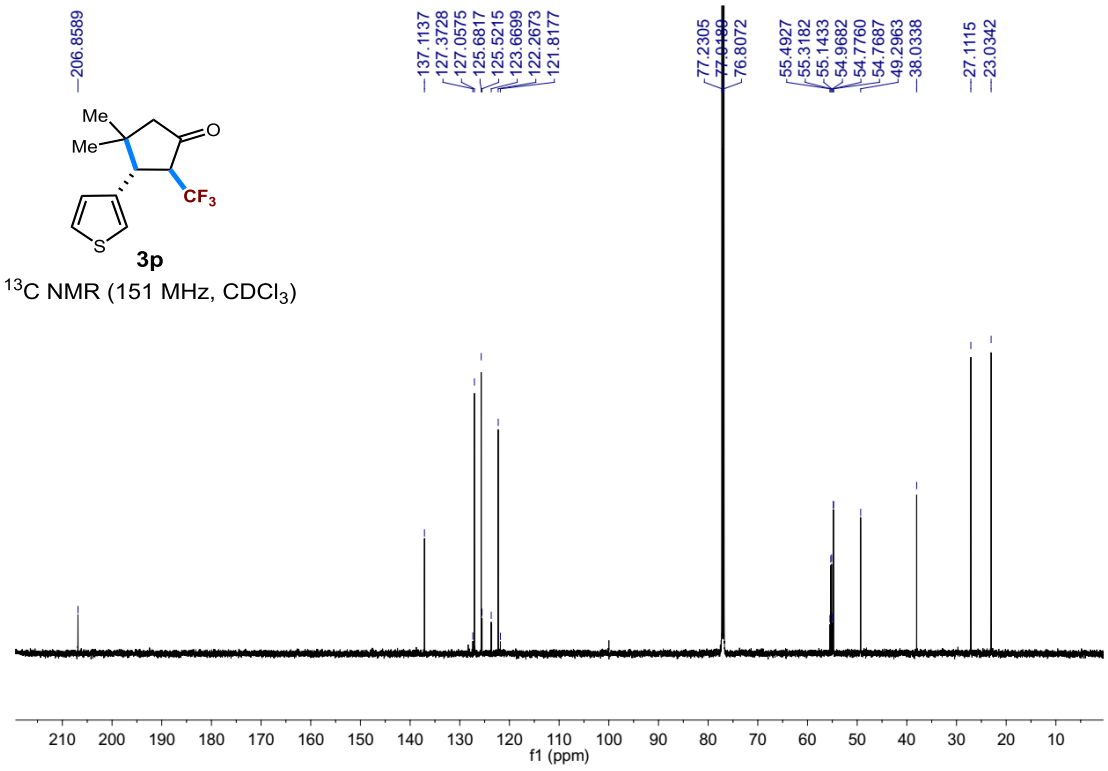
3o

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



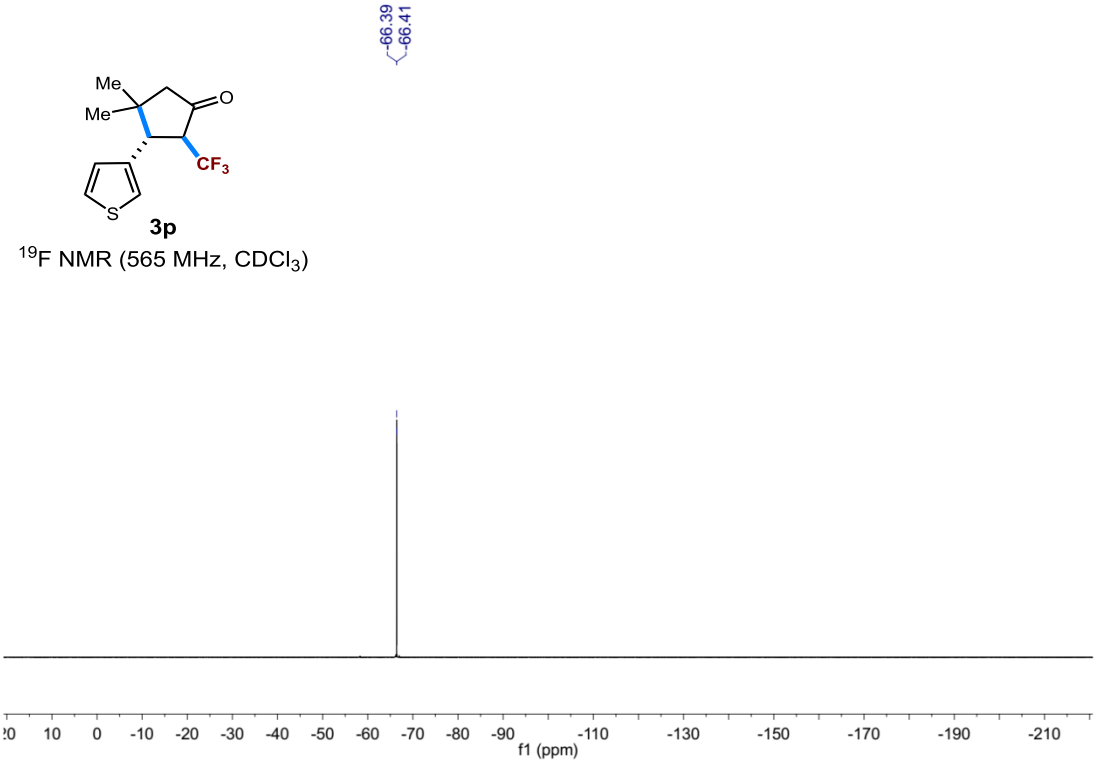
3p

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



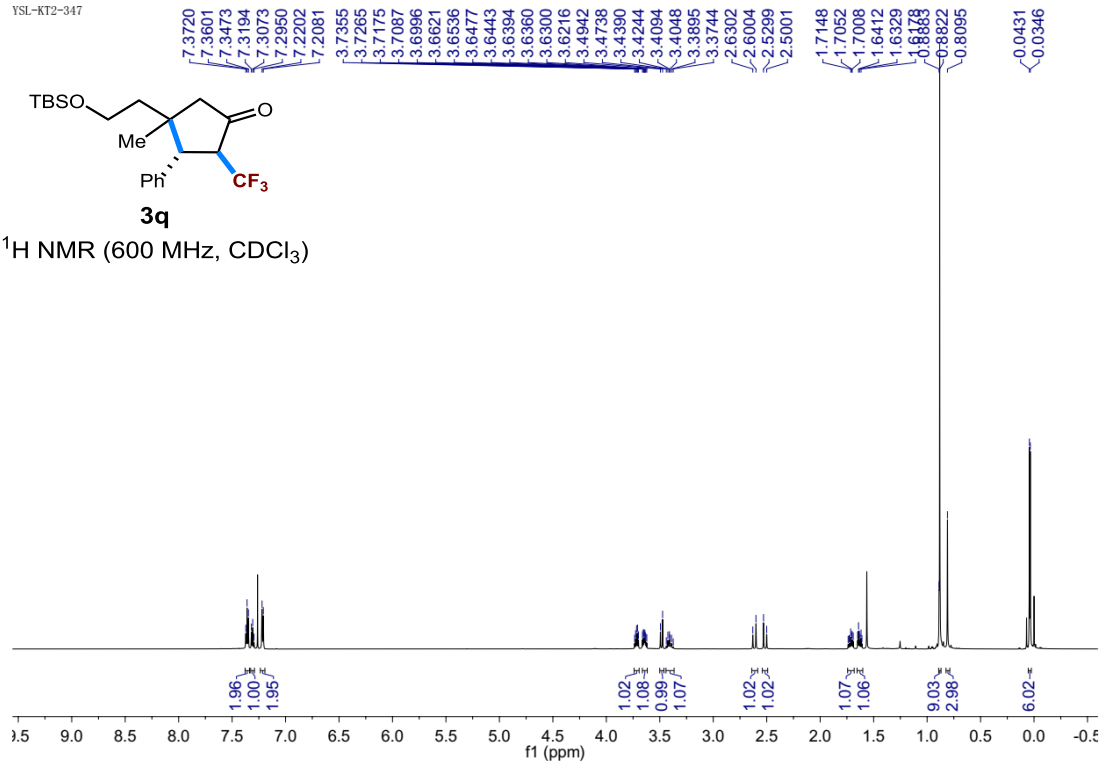
3p

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



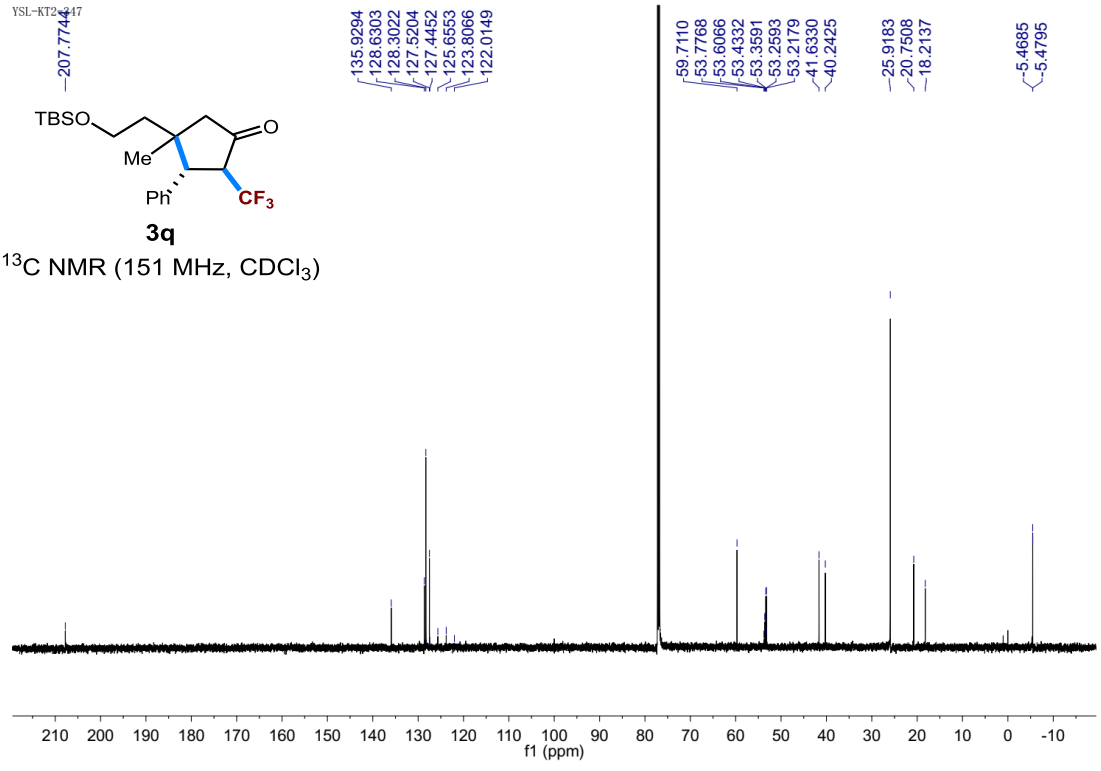
3p

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



3q

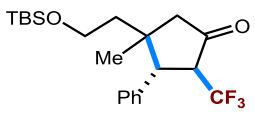
^{1}H NMR (600 MHz, $CDCl_3$)



3q

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

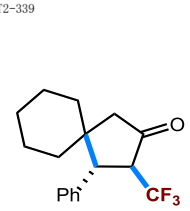
YSL-KT2-347



3q

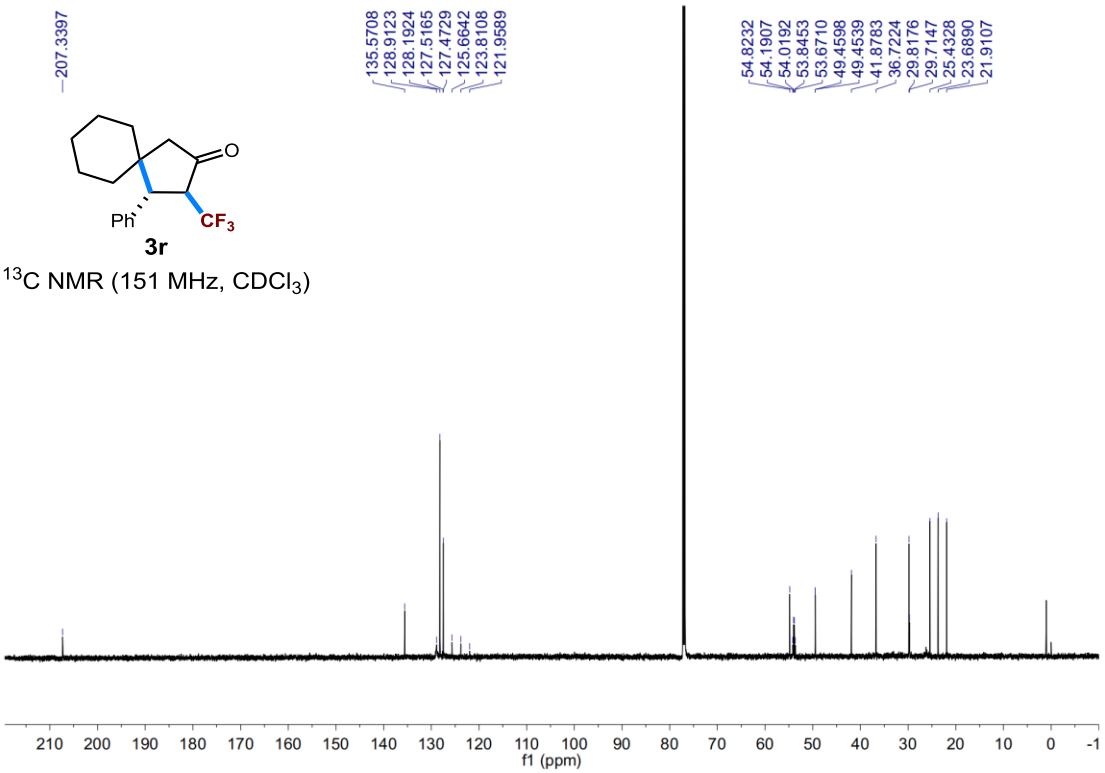
^{19}F NMR (565 MHz, $CDCl_3$)

YSL-KT2-339



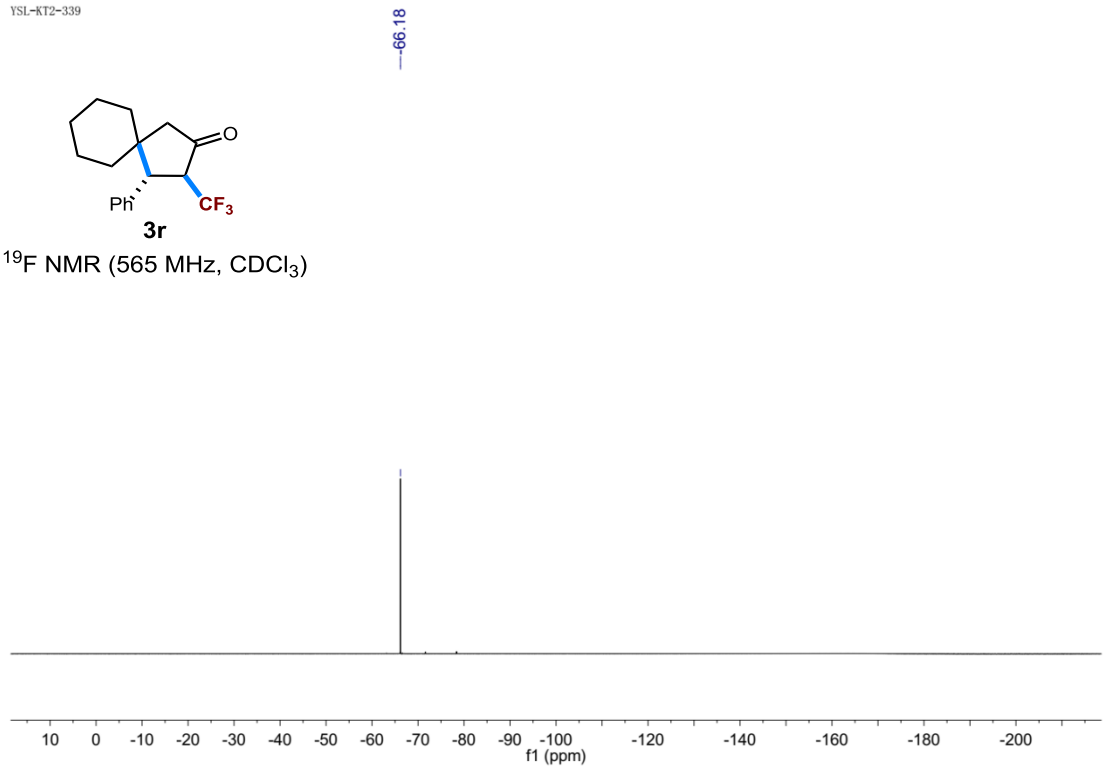
3r

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



3r

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

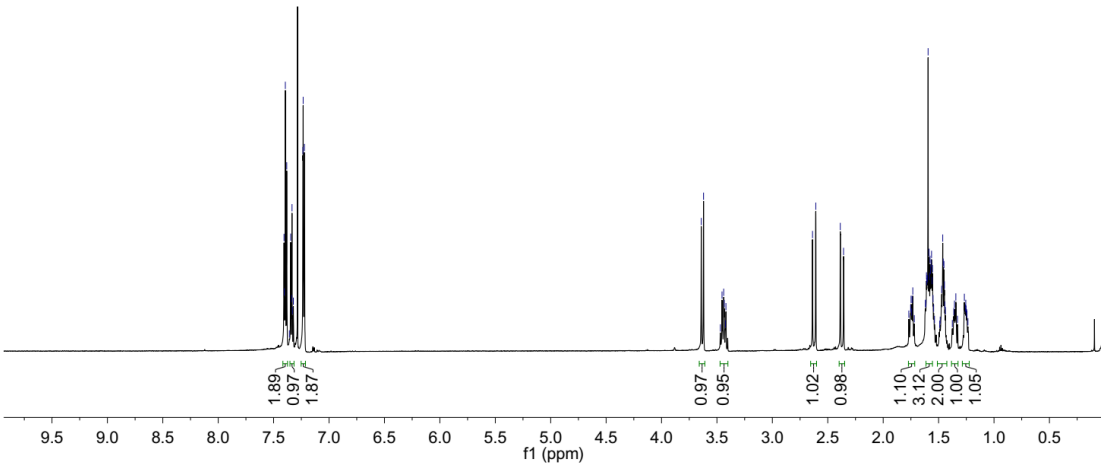


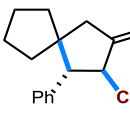
3r

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

3s

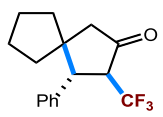
^{1}H NMR (600 MHz, $CDCl_3$)





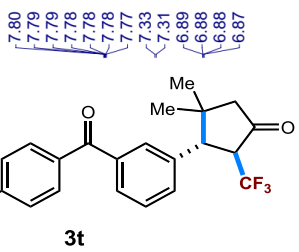
3s

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



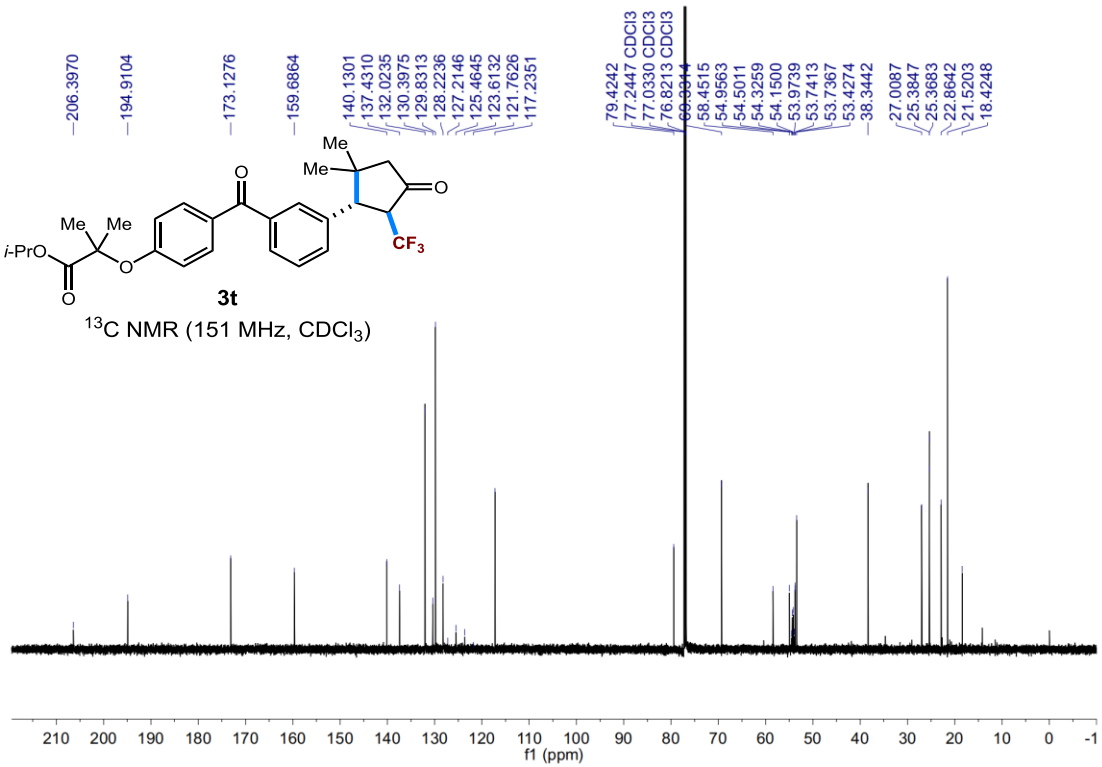
3s

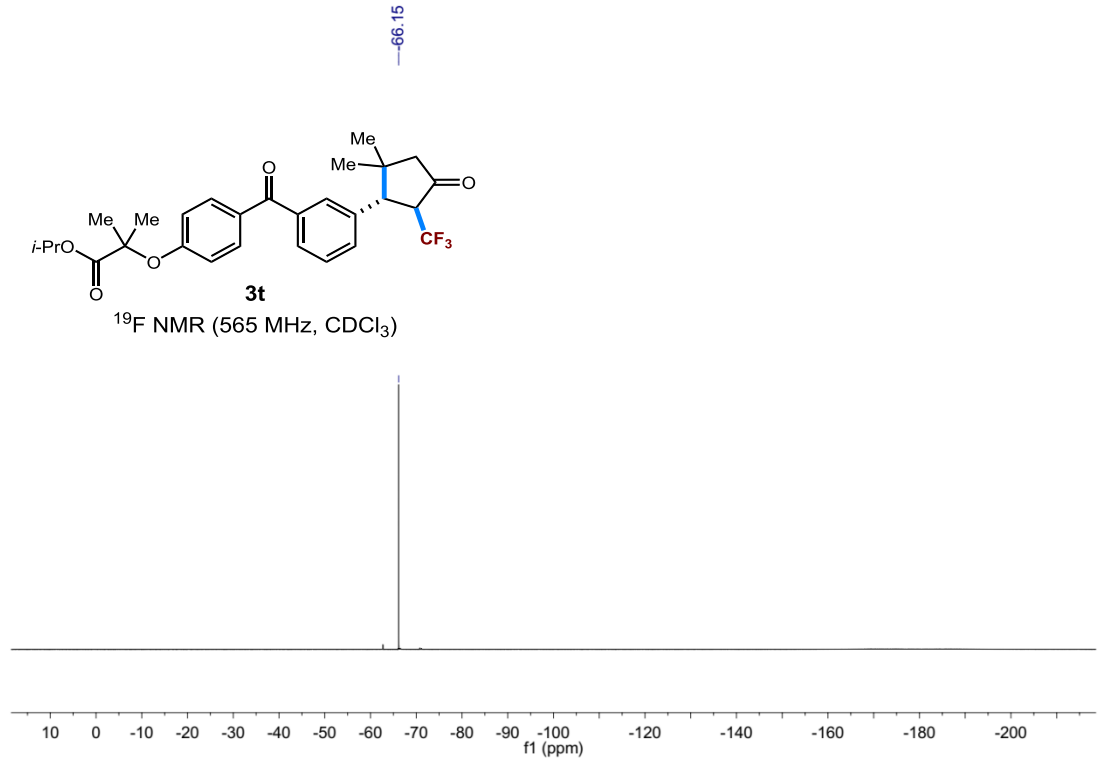
^{19}F NMR (565 MHz, $CDCl_3$)

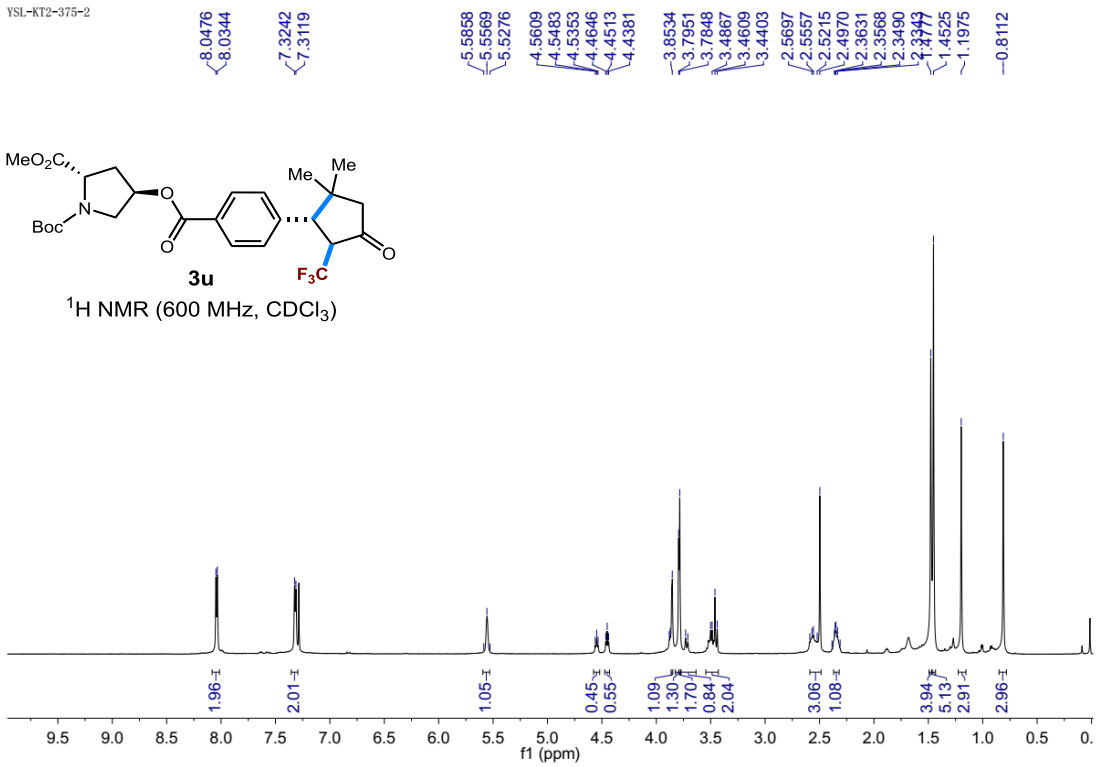


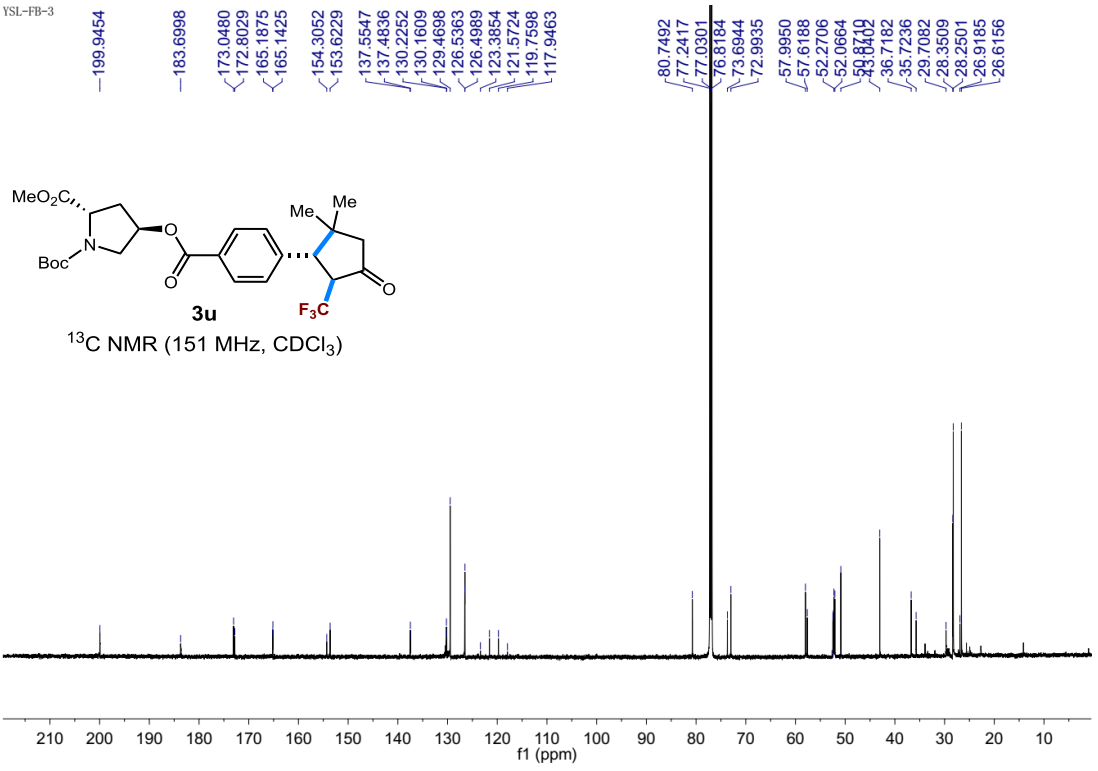
3t

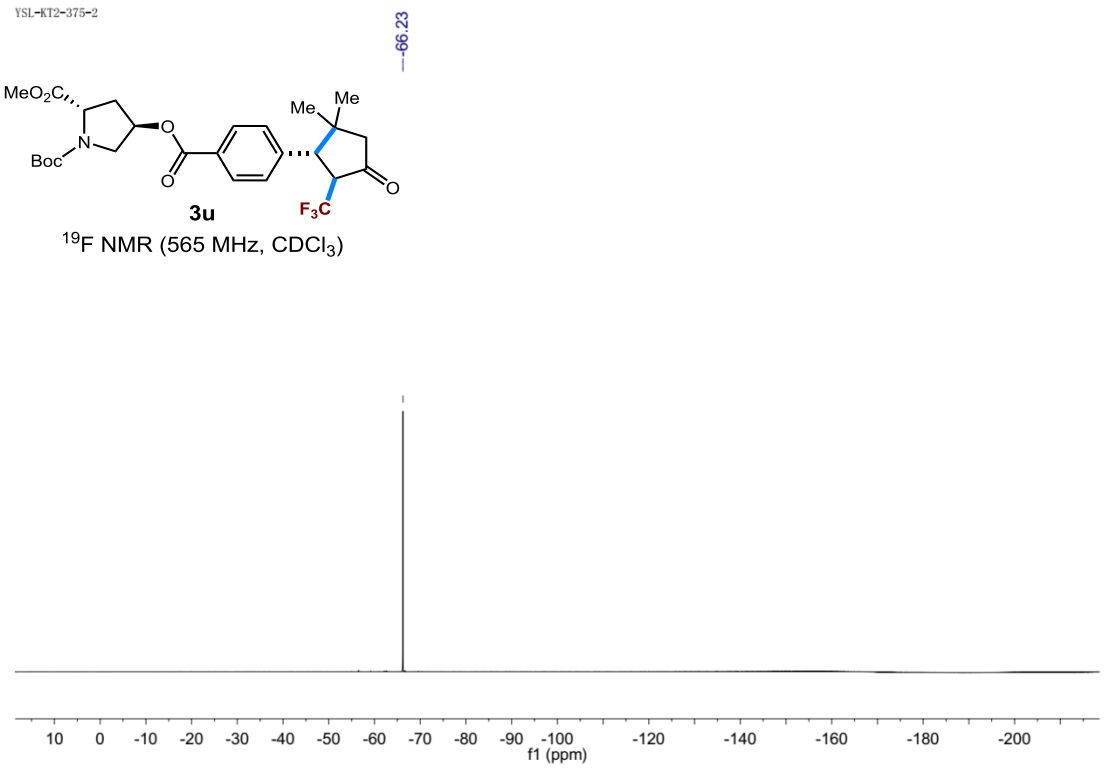
^{1}H NMR (600 MHz, $CDCl_3$)

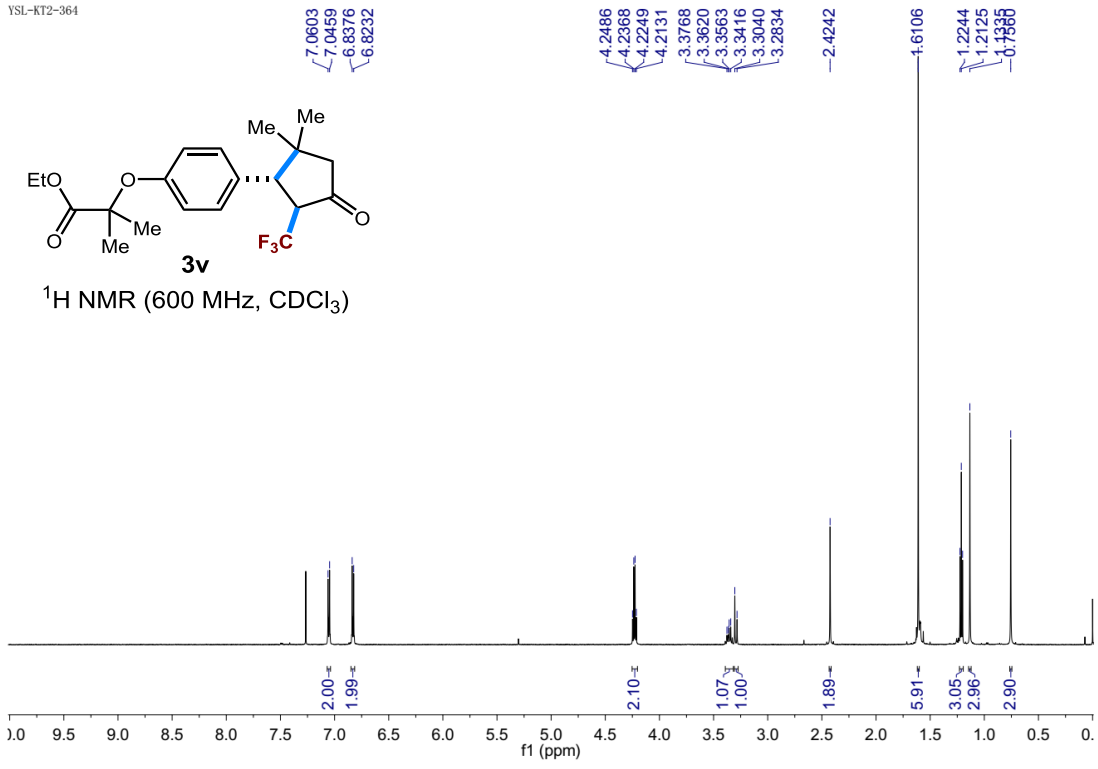

206.3970
194.9104
173.1276
159.6864
140.1301
137.4310
132.0235
130.3975
129.8313
128.2236
127.2146
125.4645
123.6132
121.7626
117.2351
79.4242
77.2447 CDCl3
77.0330 CDCl3
76.8213 CDCl3
68.9314
58.4515
54.9563
54.5011
54.3259
54.1500
53.9739
53.7413
53.7367
53.4274
38.3442
27.0087
25.3847
25.3683
22.8642
21.5203
18.4248
Me
Me
O
O
Me
Me
i-PrO
O
O
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 0 -1
f1 (ppm)

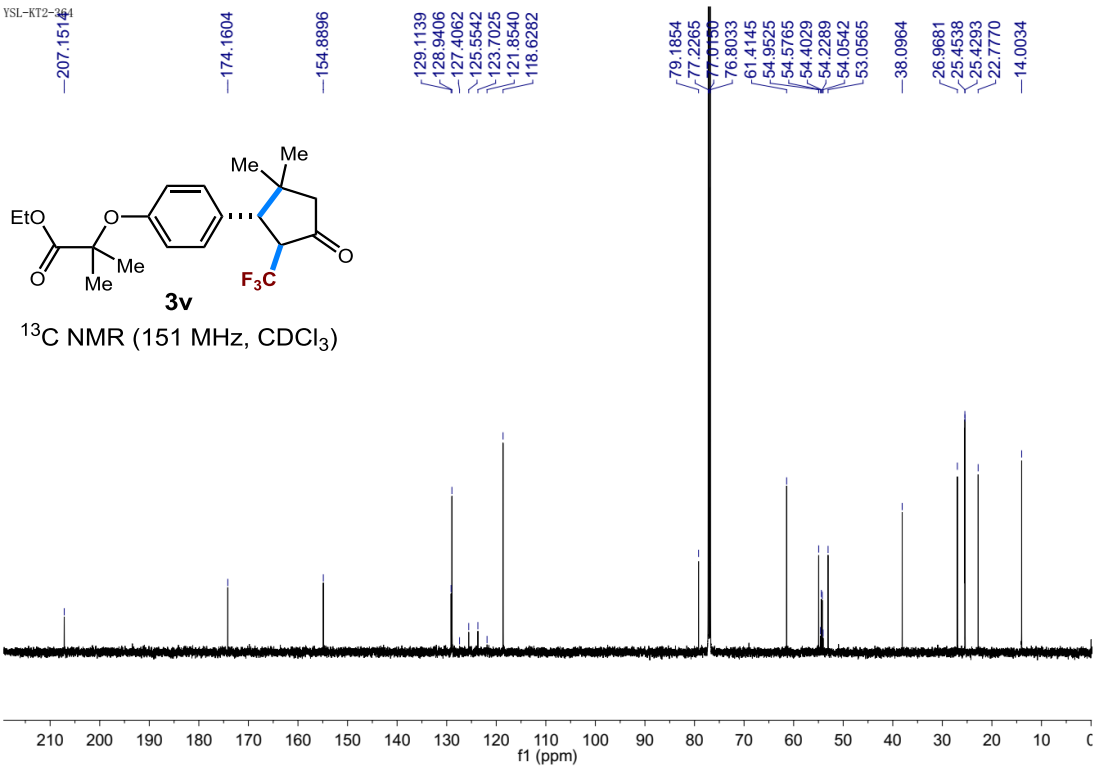

66.15
Me
Me
O
O
Me
Me
i-PrO
O
O
CF3
3t
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)

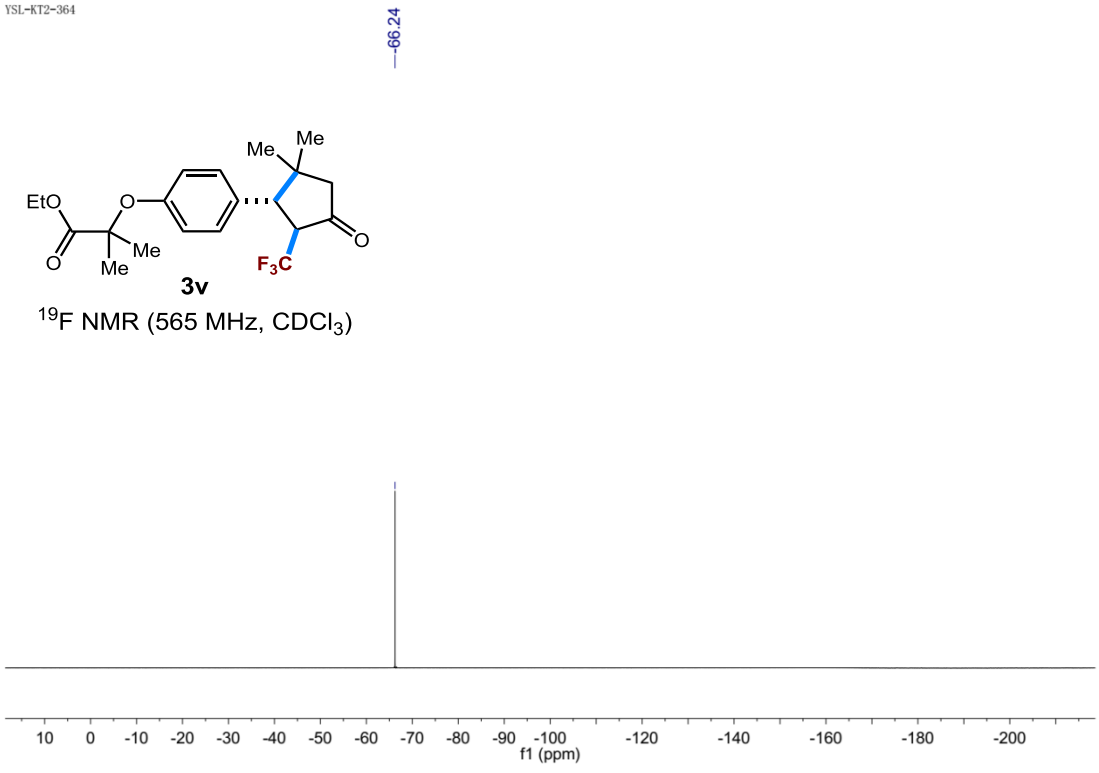

YSL-KT2-375-2
8.0476
8.0344
7.3242
7.3119
5.5858
5.5569
5.5276
4.5609
4.5483
4.5353
4.4646
4.4513
4.4381
3.8534
3.7951
3.7848
3.4867
3.4609
3.4403
2.5697
2.5557
2.5215
2.4970
2.3631
2.3568
2.3490
1.4525
1.1975
0.8112
MeO2C
Boc
N
O
Me
Me
O
O
O
F3C
3u
1H NMR (600 MHz, CDCl3)
1.96
2.01
1.05
0.45
0.55
1.09
1.30
1.70
0.84
2.04
3.06
1.08
3.94
5.13
2.91
2.96
f1 (ppm)

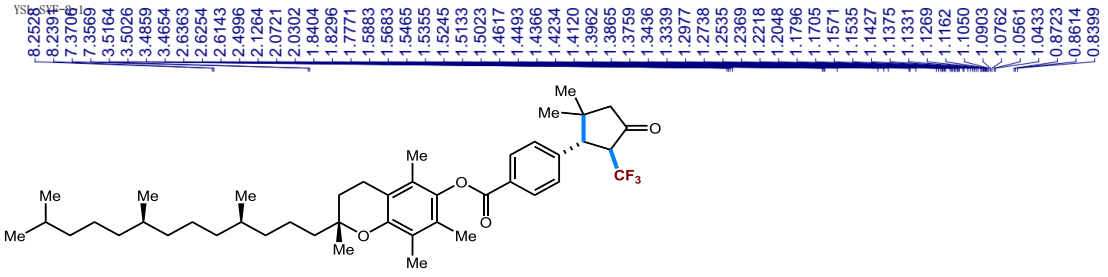

YSL-FB-3
199.9454
183.6998
173.0480
172.8029
165.1875
165.1425
154.3052
153.6229
137.5547
137.4836
130.2252
130.1609
129.4698
126.5363
126.4989
123.3854
121.5724
119.7598
117.9463
80.7492
77.2417
77.0301
76.8184
73.6944
72.9935
57.9950
57.6188
52.2706
52.0664
36.7182
35.7236
29.7082
28.3509
28.2501
26.9185
26.6156
MeO2C
Boc
N
O
Me
Me
O
O
O
F3C
3u
13C NMR (151 MHz, CDCl3)
f1 (ppm)


YSL-KT2-375-2
-66.23
MeO2C
Me
Me
N
Boc
O
O
O
O
F3C
3u
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-KT2-364
7.0603
7.0459
6.8376
6.8232
4.2486
4.2368
4.2249
4.2131
3.3768
3.3620
3.3563
3.3416
3.3040
3.2834
2.4242
1.6106
1.2244
1.2125
Me
Me
EtO
O
O
Me
Me
O
F3C
O
3v
1H NMR (600 MHz, CDCl3)
2.00
1.99
2.10
1.07
1.00
1.89
5.91
3.05
2.96
2.90
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)

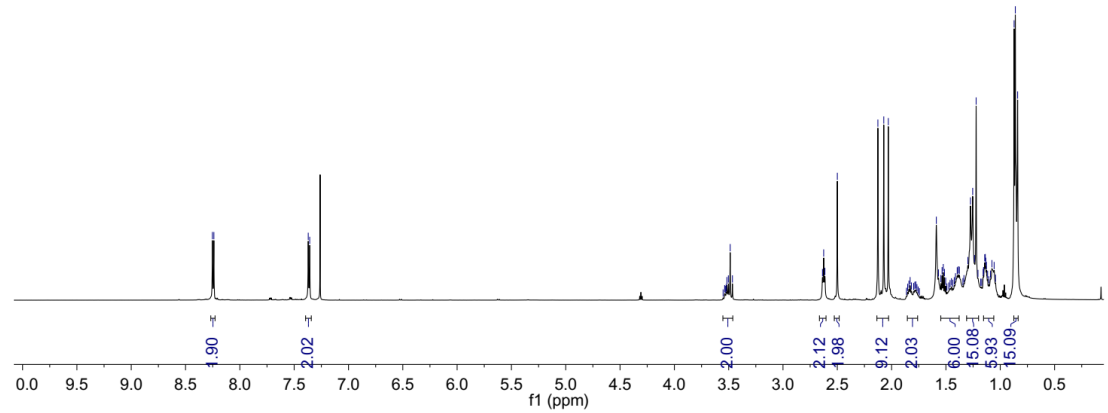

YSL-KT2-364
207.1514
174.1604
154.8896
129.1139
128.9406
127.4062
125.5542
123.7025
121.8540
118.6282
79.1854
77.2265
77.0150
76.8033
61.4145
54.9525
54.5765
54.4029
54.2289
54.0542
53.0565
38.0964
26.9681
25.4538
25.4293
22.7770
14.0034
Me
Me
EtO
O
Me
Me
O
F3C
O
3v
13C NMR (151 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

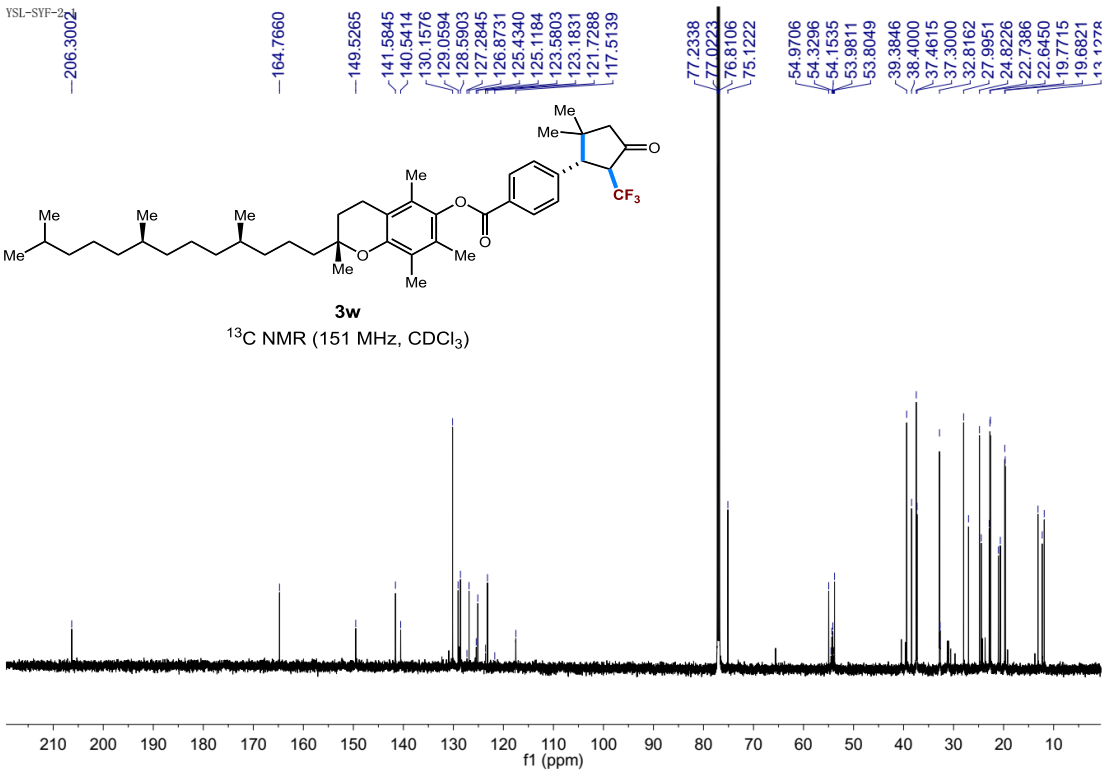

YSL-KT2-364
66.24
Me
Me
EtO
O
Me
Me
O
F3C
O
3v
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)



3w

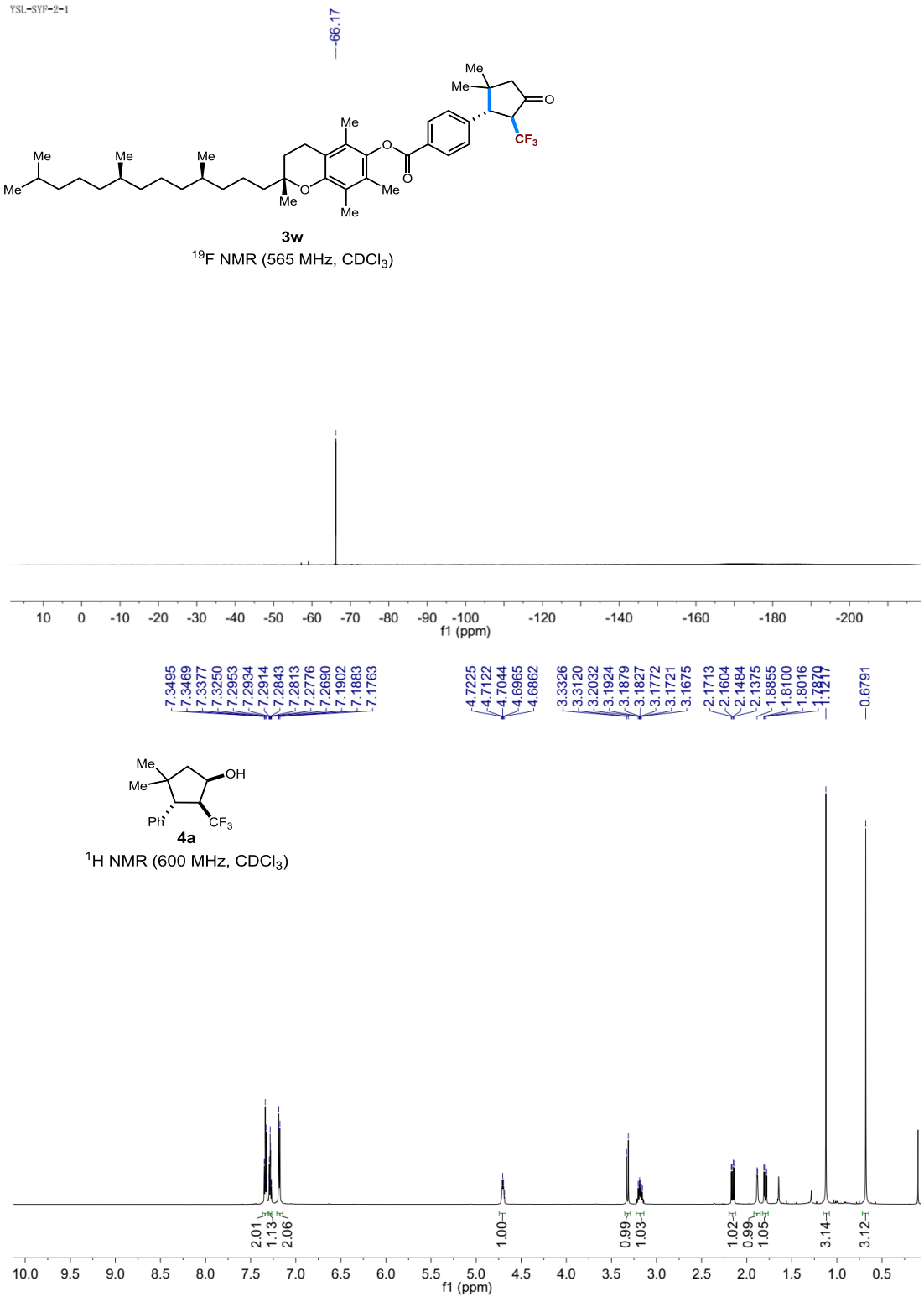
^{1}H NMR (600 MHz, $CDCl_3$)

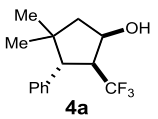




3w

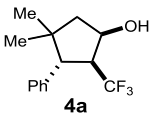
^{13}C NMR (151 MHz, $CDCl_3$)


YSL-SYF-2-1
-66.17
Me
Me
O
CF3
Me
O
O
Me
Me
Me
Me
Me
Me
O
Me
Me
3w
19F NMR (565 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -120 -140 -160 -180 -200
f1 (ppm)
7.3495
7.3469
7.3377
7.3250
7.2953
7.2934
7.2914
7.2843
7.2813
7.2776
7.2690
7.1902
7.1883
7.1763
4.7225
4.7122
4.7044
4.6965
4.6862
3.3326
3.3120
3.2032
3.1924
3.1879
3.1827
3.1772
3.1721
3.1675
2.1713
2.1604
2.1484
2.1375
1.8855
1.8100
1.8016
1.7870
1.7217
0.6791
Me
Me
OH
Ph
CF3
4a
1H NMR (600 MHz, CDCl3)
2.01
1.13
2.06
1.00
0.99
1.03
1.02
0.99
1.05
3.14
3.12
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)



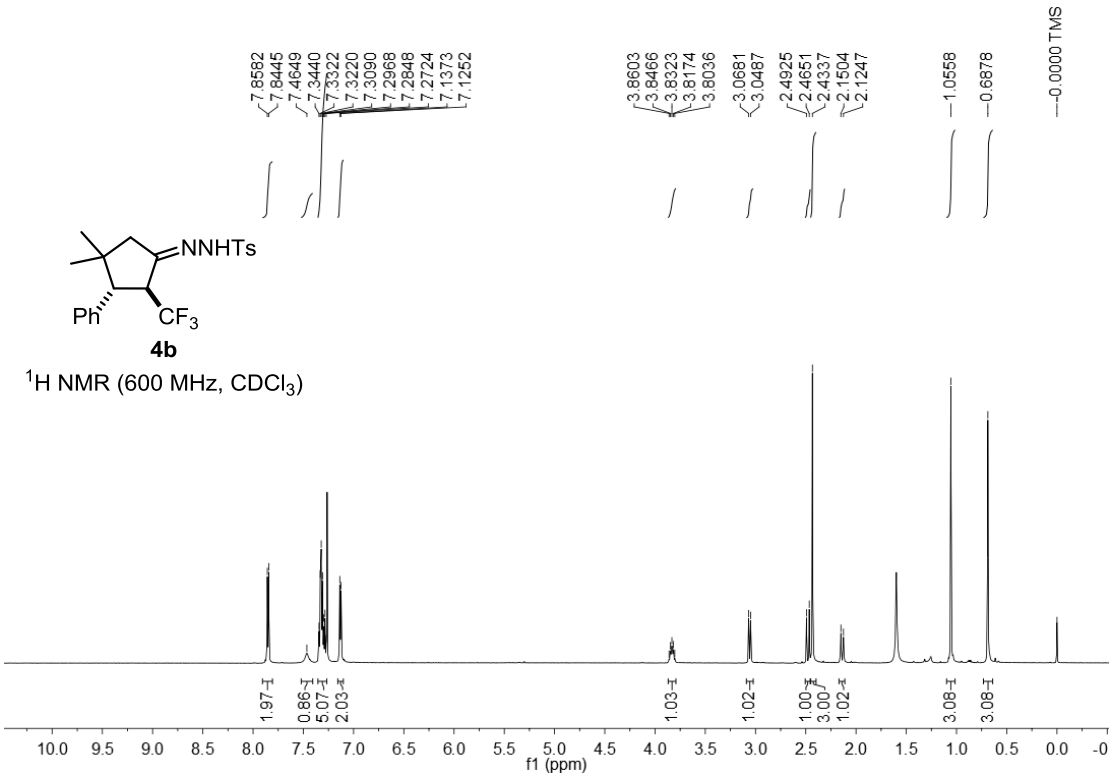
4a

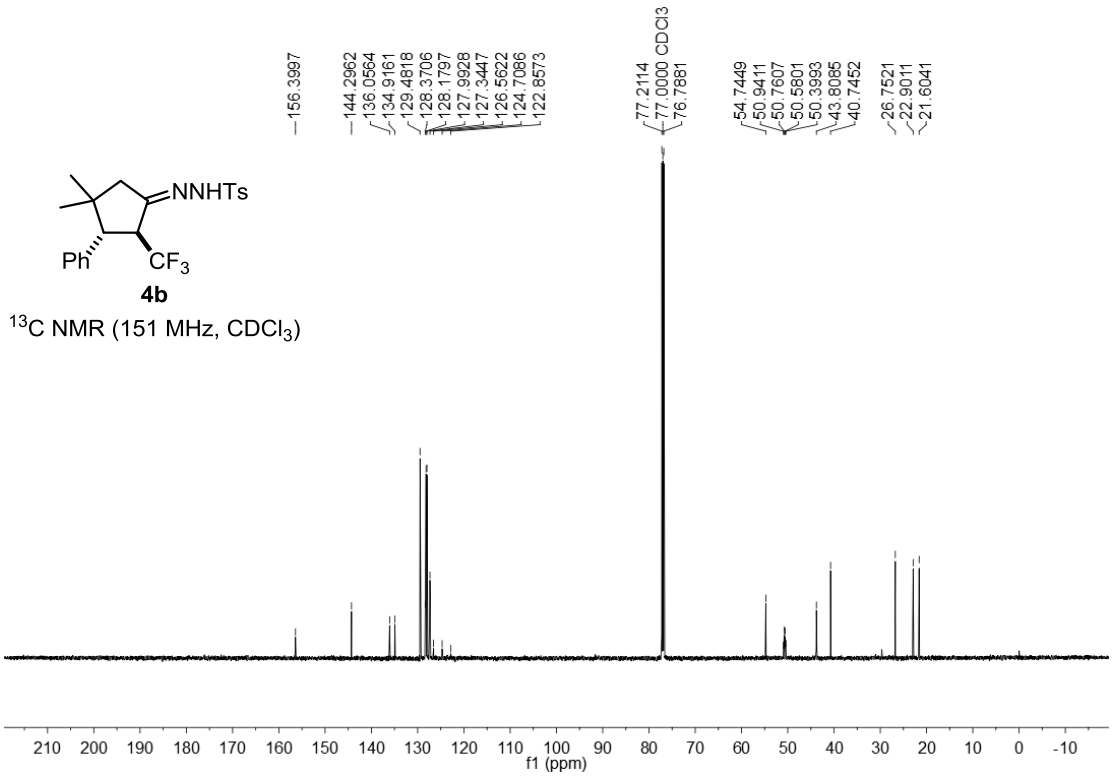
^{13}C NMR (151 MHz, $CDCl_3$)

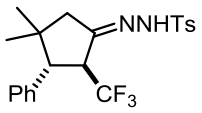


4a

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

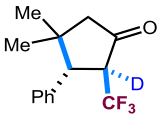

7.8582
7.8445
7.4649
7.3440
7.3322
7.3220
7.3090
7.2968
7.2848
7.2724
7.1373
7.1252
3.8603
3.8466
3.8323
3.8174
3.8036
3.0681
3.0487
2.4925
2.4651
2.4337
2.1504
2.1247
1.0558
0.6878
0.0000 TMS
NNHTs
Ph
CF3
4b
1H NMR (600 MHz, CDCl3)
1.97
0.86
5.07
2.03
1.03
1.02
1.00
3.00
1.02
3.08
3.08
f1 (ppm)


156.3997
144.2962
136.0564
134.9161
129.4818
128.3706
128.1797
127.9928
127.3447
126.5622
124.7086
122.8573
77.2114
77.0000 CDCl3
76.7881
54.7449
50.9411
50.7607
50.5801
50.3993
43.8085
40.7452
26.7521
22.9011
21.6041
NNHTs
Ph
CF3
4b
13C NMR (151 MHz, CDCl3)
f1 (ppm)



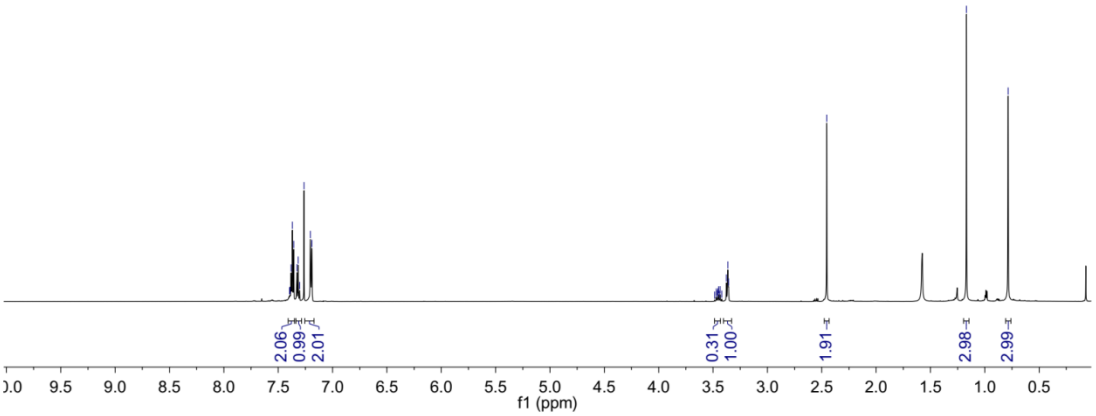
4b

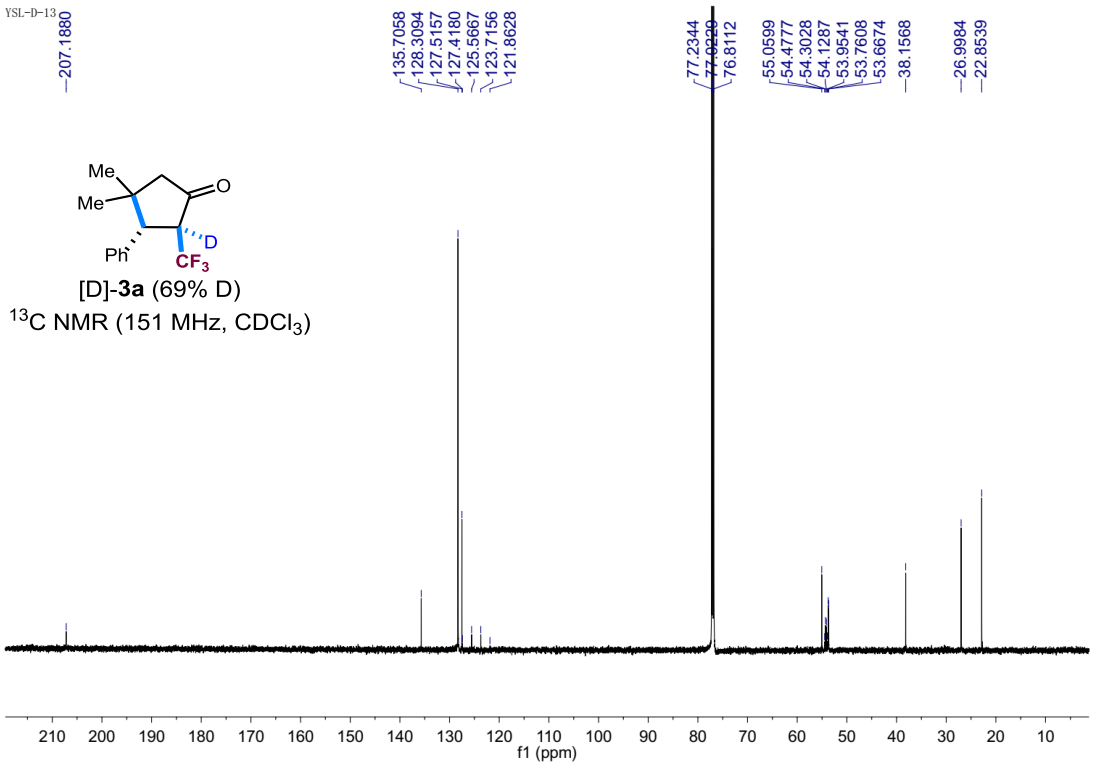
^{19}F NMR (565 MHz, $CDCl_3$)



[D]-**3a** (69% D)

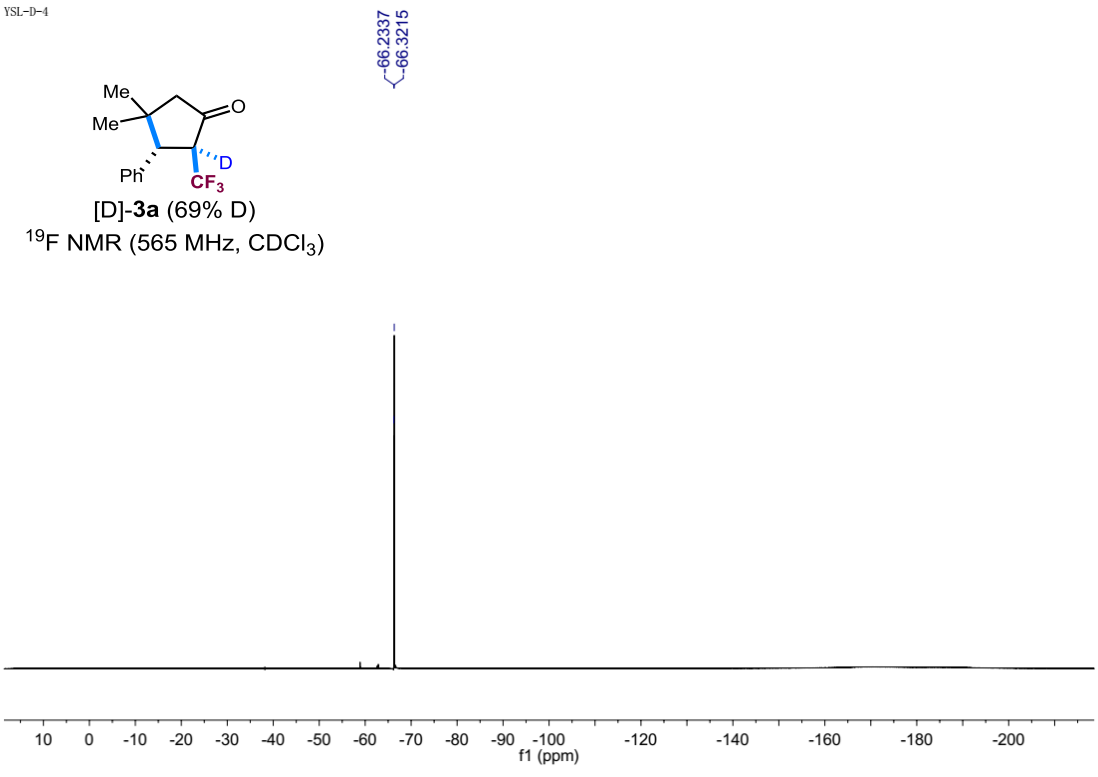
^{1}H NMR (600 MHz, $CDCl_3$)





[D]-**3a** (69% D)

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



[D]-**3a** (69% D)

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

5. X-Ray Crystallographic Data

The crystal of **3a** was recrystallized in ethyl acetate/petroleum ethers via slow evaporation at room temperature. Cystal data for **3a** ($C_{14}H_{15}F_3O$, 256.26): monoclinic, space group P2(1), a = 6.1123(5) Å, b = 7.4620(5) Å, c = 13.8843(11) Å, β = 96.134(3), U = 629.64(8) Å^3, Z = 2, T = 250 K, absorption coefficient 0.114 mm^{-1}, reflections collected 2811, independent reflections 2560 [R(int) = 0.0215], refinement by full-matrix least-squares on F^2, data/restraints/parameters 2560/1/165, goodness-of-fit on F^2 = 1.027, final R indices [I>2s(I)] R_1 = 0.0334, wR_2 = 0.0805, largest diff peak and hole 0.152 and -0.097 e.Å^{-3}. Crystallographic data for the structure **3a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2114641.