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# Ring Expansion of Unsubstituted Aziridinium Ylide to Trifluoromethylated Dehydropiperidines

Jiaqi Tang,[a,†] Tian Tian,[a,†] Yingyu Wang,[a,†] Dandan Wei,[a,†] Yong Yang,[a] Xinyu Wang,[a] Paramasivam Sivaguru,[a] Yongquan Ning,[a]* Zhaohong Liu[a]* and Valentine Nenajdenko[b*]

[a] Jilin Province Key Laboratory of Organic Functional Molecular Design & Synthesis, Department of Chemistry, Northeast Normal University, Changchun 130024, China

b. Department of Chemistry, Lomonosov Moscow State University, 119899 Moscow, Russia

Email: ningyq508@nenu.edu.cn, liuzh944@nenu.edu.cn, nenajdenko@gmail.com.

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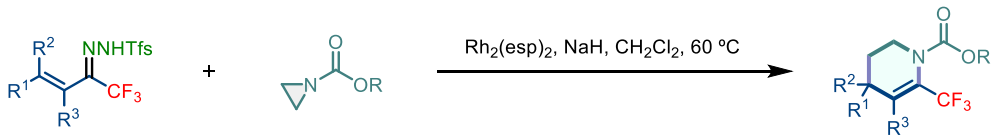
## 1. General Information

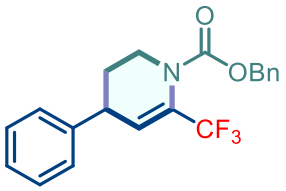
Unless otherwise noted, materials were purchased and used as received from Tokyo Chemical Industry Co., Aldrich Inc., Alfa Aesar, and other commercial suppliers. Dichloromethane ($CH_2Cl_2$) was dried and distilled over $CaH_2$ under an argon atmosphere and stored in a nitrogen-filled glovebox. Aziridines were dried and purified by column chromatography before use. All reactions dealing with air- or moisture-sensitive compounds were carried out in a flame-dried, sealed Schlenk reaction tube under an argon atmosphere. Thin layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230-400 mesh silica gel and visualized under UV light irradiation (254 nm) and/or staining with aqueous $KMnO_4$ stain. Manual column chromatography was carried out on silica gel. NMR spectra were recorded on a Brüker Advance 600 ($^1$H: 600 MHz, $^{13}$C:150 MHz, $^{19}$F: 565 MHz) and Brüker Advance 500 ($^1$H: 500 MHz, $^{13}$C: 125 MHz, $^{19}$F: 470 MHz) at ambient temperature. Data were reported as chemical shifts in ppm relative to TMS (0.00 ppm) for $^1$H and $CDCl_3$ (77.0 ppm) for $^{13}$C. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, qi = quintet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on Magnetic Sector High-Resolution Gas Chromatography-Mass Spectra and Q Exactive Focus (Thermal) by using the ESI method.

## 2. Experimental Procedures and Characterization Data

### 2.1 Rhodium-catalyzed [3 + 3] cyclization reactions




**General procedure A:** Experiments were set up inside a glovebox under an argon atmosphere. An oven-dried glass screw-capped reaction tube was charged with trifluoromethyl vinyl *N*-triftosylhydrazone (0.2 mmol), NaH (16.0 mg, 60 wt% dispersion in mineral oil, 0.4 mmol, 2.0 equiv) in $CH_2Cl_2$ (3.0 mL). Then $Rh_2(esp)_2$ (3.0 mg, 2 mol%) and aziridine (0.4 mmol, 2.0 equiv) were added. The tube was sealed and stirred at 60 °C for 12 h, after which time the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel using ethyl acetate (EA) as an eluent. The volatiles was removed from the collected filtrate under reduced pressure, and the resulting residue was purified via flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain pure products.




(**3**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(p-tolyl)acrylaldehyde (87.2 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **3** (66.5 mg, 92% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 7H), 7.26-7.23 (m, 1H), 7.13 (d, *J* = 7.0 Hz, 2H), 6.08 (d, *J* = 3.5 Hz, 1H), 5.25-5.18 (m, 2H), 3.84-3.77 (m, 1H), 3.64-3.55 (m, 2H), 2.22-2.16 (m, 1H), 1.85-1.77 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.20, 142.66, 135.65, 131.98 (q, *J* = 34.9 Hz), 128.91, 128.54, 128.46, 128.39, 127.49, 127.13, 124.09 (q, *J* = 3.6 Hz), 121.12 (q, *J* = 274.7 Hz), 68.39, 44.36, 39.51, 32.56. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.94 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{18}F_3NNaO_2$ $[M+Na]^+$ 384.1177, found 384.1182.

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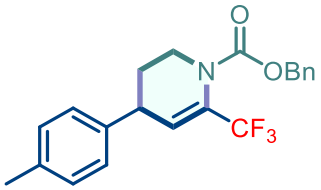


(**5**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(p-tolyl)but-3-en-2-one (87.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **5** (60.8 mg, 81% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 3.5 Hz, 1H), 5.25-5.19 (m, 2H), 3.82-3.77 (m, 1H), 3.61-3.56 (m, 2H), 2.33 (s, 3H), 2.20-2.15 (m, 1H), 1.82-1.78 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.20, 139.64, 136.79, 135.65, 131.75 (q, *J* = 35.0 Hz), 129.55, 128.52, 128.43, 128.36, 127.36, 124.33 (q, *J* = 3.6 Hz), 121.12 (q, *J* = 272.4 Hz), 68.36, 44.32, 39.08, 32.58, 21.01. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.95 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{21}H_{20}F_3NNaO_2$ $[M+Na]^+$ 398.1331, found 398.1338.

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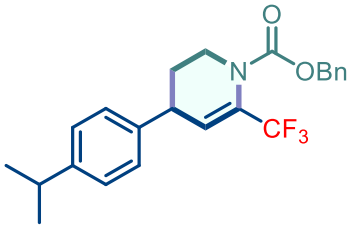

(**6**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(4-isopropylphenyl)but-3-en-2-one (92.9 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **6** (71.1 mg, 84% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.34 (m, 5H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.08 (d, *J* = 3.0 Hz, 1H), 5.24-5.19 (m, 2H), 3.83-3.78 (m, 1H), 3.62-3.57 (m, 2H), 2.91-2.89 (m, 1H), 2.20-2.17 (m, 1H), 1.84-1.82 (m, 1H), 1.24 (d, *J* = 7.0 Hz, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.17, 147.75, 139.92, 135.62, 131.72 (q, *J* = 34.6 Hz), 128.48, 128.39, 128.31, 127.39, 126.87, 124.39 (q, *J* = 3.6 Hz), 121.09 (q, *J* = 272.3 Hz), 68.31, 44.30, 39.05, 33.70, 32.46, 23.94. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.94 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{23}H_{24}F_3NNaO_2$ $[M+Na]^+$ 426.1651, found 426.1651.

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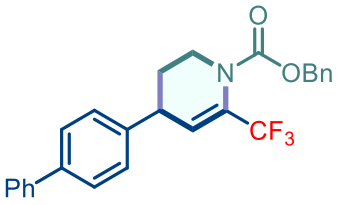


(**7**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-([1,1'-biphenyl]-4-yl)-1,1,1-trifluorobut-3-en-2-one (99.7 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **7** (85.7 mg, 98% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.59-7.55 (m, 4H), 7.47-7.35 (m, 8H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.13 (d, *J* = 3.5 Hz, 1H), 5.28-5.22 (m, 2H), 3.88-3.84 (m, 1H), 3.69-3.60 (m, 2H), 2.24-2.22 (m, 1H), 1.92-1.82 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.22, 141.71, 140.66, 140.20, 135.68, 132.07 (q, *J* = 35.0 Hz), 128.88, 128.58, 128.51, 128.44, 127.96, 127.66, 127.43, 127.10, 124.00 (q, *J* = 3.8 Hz), 121.17 (q, *J* = 275.0 Hz), 68.46, 44.41, 39.20, 32.56. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.89 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{26}H_{22}F_3NNaO_2$ $[M+Na]^+$ 437.1633, found 460.1637.

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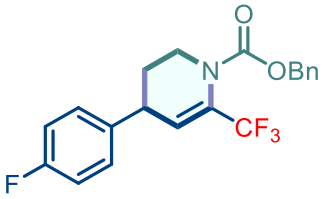


(**8**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(4-fluorophenyl)but-3-en-2-one (88.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **8** (68.3 mg, 90% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 7.11-7.08 (m, 2H), 7.07-6.98 (m, 2H), 6.04 (d, *J* = 3.5 Hz, 1H), 5.25-5.18 (m, 2H), 3.84-3.79 (m, 1H), 3.62-3.55 (m, 2H), 2.22-2.15

(m, 1H), 1.80-1.72 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 161.88 (q, *J* = 245.0 Hz), 154.12, 138.32, 135.58, 132.18 (q, *J* = 35.8 Hz), 128.94 (d, *J* = 7.8 Hz), 128.52, 128.47, 128.40, 123.69 (q, *J* = 3.6 Hz), 121.02 (q, *J* = 278.0 Hz), 115.73 (d, *J* = 21.0 Hz), 68.43, 44.32, 38.81, 32.68. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.03 (s, 3F), (-115.16)-(-115.51) (m, 1F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{17}F_4NNaO_2$ $[M+Na]^+$ 402.1097, found 402.1088.

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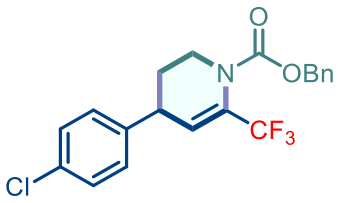


(**9**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-one (91.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **9** (67.3 mg, 85% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.33 (m, 5H), 7.28 (d, *J* = 8.5 Hz, 2H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.03 (d, *J* = 3.5 Hz, 1H), 5.24-5.18 (m, 2H), 3.84-3.78 (m, 1H), 3.61-3.53 (m, 2H), 2.21-2.16(m, 1H), 1.80-1.73 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.08, 141.07, 135.54, 132.99, 132.36 (q, *J* = 34.6 Hz), 129.04, 128.79, 128.53, 128.47, 128.42, 123.29 (q, *J* = 4.0 Hz), 120.90 (d, *J* = 275.0 Hz), 68.46, 44.29, 38.92, 32.50. $^{19}$F NMR (565 MHz, $CDCl_3$) δ -62.04 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{17}ClF_3NNaO_2$ $[M+Na]^+$ 418.0798, found 418.0792.

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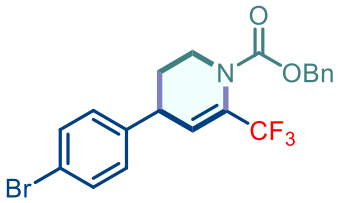


(**10**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(4-bromophenyl)-1,1,1-trifluorobut-3-en-2-one (100.2 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **10** (76.6 mg, 87% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.40-7.33 (m, 5H), 7.01 (d, *J* = 8.5 Hz, 2H), 6.02 (d, *J* = 3.5 Hz, 1H), 5.24-5.18 (m, 2H), 3.83-3.77 (m, 1H), 3.61-3.54 (m, 2H), 2.23-2.15 (m, 1H), 1.79-1.72 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.07, 141.60, 135.54, 132.41(d, *J* = 35.5 Hz), 132.00, 129.16, 128.53, 128.48, 128.42, 123.17, 121.00, 120.97 (q, *J* = 277.0 Hz), 68.46, 44.28, 38.98, 32.44. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.04 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{17}BrF_3NNaO_2$ $[M+Na]^+$ 462.0288, found 462.0287.

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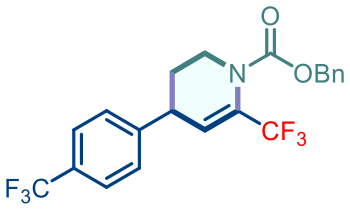


(**11**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one (96.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **11** (67.0 mg, 78% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.40-7.33 (m, 5H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.04 (d, *J* = 3.5 Hz, 1H), 5.26-5.18 (m, 2H), 3.87-3.83 (m, 1H), 3.71-3.69 (m, 1H), 3.60-3.55 (m, 1H), 2.56-2.20 (m, 1H), 1.83-1.76 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.03, 146.59, 135.48, 132.75 (q, *J* = 35.4 Hz), 129.56 (q, *J* = 33.0 Hz), 128.55, 128.52, 128.47, 127.85, 125.88 (q, *J* = 3.6 Hz), 124.02 (q, *J* = 272.0 Hz), 122.72 (q, *J* = 4.0 Hz), 120.94 (q, *J* = 274.0 Hz), 68.53, 44.28, 39.33, 32.37. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.04 (s, 3F), -61.54 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{21}H_{17}F_6NNaO_2$ $[M+H]^+$ 452.1056, found 452.1052.

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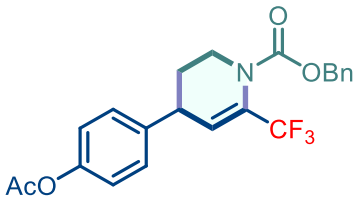


(**12**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(4,4,4-trifluoro-3-oxobut-1-en-1-yl)phenyl acetate (96.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **12** (67.9 mg, 81% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.30 (m, 5H), 7.15 (d, *J* = 8.5 Hz, 2H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.06 (d, *J* = 3.5 Hz, 1H), 5.25-5.18 (m, 2H), 3.84-3.78 (m, 1H), 3.67-3.61 (m, 1H), 3.61-3.55 (m, 1H), 2.30 (s, 3H), 2.26-2.19 (m, 1H), 1.84-1.76 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 169.49, 154.11, 149.66, 140.14, 135.57, 132.15 (q, *J* = 35.3 Hz), 128.53, 128.49, 128.46, 128.40, 123.66 (q, *J* = 3.8 Hz), 122.00, 121.03 (q, *J* = 274.0 Hz), 68.42, 44.28, 38.94, 32.51, 21.11. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.90 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{20}F_3NNaO_4$ $[M+Na]^+$ 442.1237, found 442.1237.

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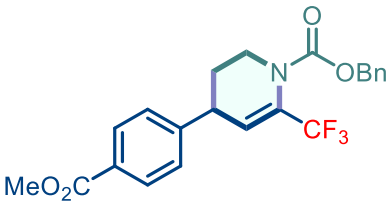


(**13**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from methyl (*E*)-4-(4,4,4-trifluoro-3-oxobut-1-en-1-yl) benzoate (96.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **13** (67.0 mg, 88% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.40-7.32 (m, 5H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.06 (d, *J* = 3.5 Hz, 1H), 5.25-5.19 (m, 2H), 3.90 (s, 3H), 3.87-3.83 (m, 1H), 3.71-3.66 (m, 1H), 3.60-3.54 (m, 1H), 2.24-2.18 (m, 1H), 1.83-1.75 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 166.71, 154.05, 147.76, 135.52, 132.53 (q, *J* = 35.0 Hz), 130.23, 129.13, 128.55, 128.48, 128.45, 127.51, 122.99 (q, *J* = 3.5 Hz), 121.00 (q, *J* = 274.0 Hz), 68.48, 52.15, 44.32, 39.48, 32.32. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.95 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{20}F_3NNaO_4$ $[M+Na]^+$ 442.1237, found 442.1237.

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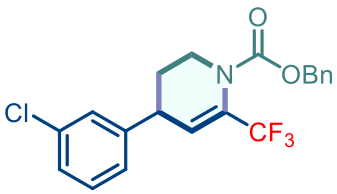


(**14**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(3-chlorophenyl)-1,1,1-trifluorobut-3-en-2-one (91.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **14** (66.1 mg, 88% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.42-7.30 (m, 5H), 7.26-7.22 (m, 2H), 7.13 (s, 1H), 7.05-6.97 (m, 1H), 6.03 (d, *J* = 3.5 Hz, 1H), 5.25-5.18 (m, 2H), 3.85-3.81 (m, 1H), 3.61-3.55 (m, 2H), 2.22-2.16 (m, 1H), 1.82-1.75 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.04, 144.60, 135.51, 134.70, 132.48 (q, *J* = 35.0 Hz), 130.18, 128.55, 128.47, 128.43, 127.67, 127.38, 125.63, 122.95 (q, *J* = 4.0 Hz), 120.97 (q, *J* = 274.0 Hz), 68.49, 44.27, 39.20, 32.35. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.98 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{17}ClF_3NNaO_2$ $[M+Na]^+$418.0792, found 418.0784.

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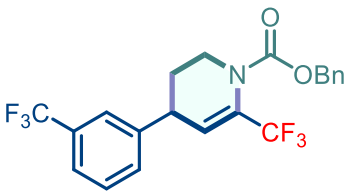

(**15**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(3-(trifluoromethyl)phenyl)but-3-en-2-one (96.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **15** (78.1 mg, 91% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.40-7.31 (m, 7H), 6.05 (d, *J* = 3.5 Hz, 1H), 5.25-5.19 (m, 2H), 3.86-3.84 (m, 1H), 3.72-3.68 (m, 1H), 3.61-3.56 (m, 1H), 2.26-2.20 (m, 1H), 1.84-1.77(m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.02, 143.54, 135.47, 132.73 (q, *J* = 34.0 Hz), 131.28 (q, *J* = 32.0 Hz), 130.75, 129.45, 128.55, 128.48, 128.45, 124.29 (q, *J* = 4.0 Hz), 124.09 (q, *J* = 4.0 Hz), 123.94 (q, *J* = 273.0 Hz), 122.67 (q, *J* = 4.0 Hz), 120.94 (q, *J* = 274.7 Hz), 68.54, 44.29, 39.39, 32.40. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.02 (s, 3F), -62.63 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{21}H_{17}F_6NNaO_2$ $[M+Na]^+$ 452.1055, found 452.1045.

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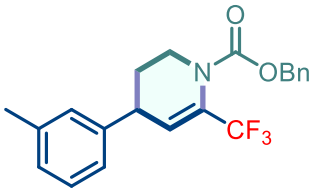


(**16**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(m-tolyl)but-3-en-2-one (87.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **16** (69.1 mg, 91% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 6.98-6.95 (m, 2H), 6.09 (d, *J* = 3.5 Hz, 1H), 5.27-5.21 (m, 2H), 3.84-3.80 (m, 1H), 3.60-3.55 (m, 2H), 2.35 (s, 3H), 2.20-2.14 (m, 1H), 1.84-1.77 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.20, 142.61, 138.62, 135.68, 131.81 (q, *J* = 35.0 Hz), 128.79, 128.54, 128.43, 128.38, 128.20, 127.88, 124.53, 124.26 (q, *J* = 4.0 Hz), 121.15 (q, *J* = 274.0 Hz), 68.37, 44.42, 39.48, 32.53, 21.43.**$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.91 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{21}H_{20}F_3NNaO_2$ $[M+Na]^+$ 398.1329, found 398.1338.

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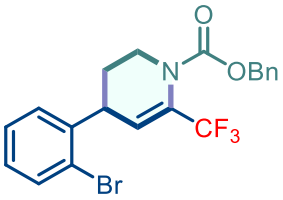


(**17**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(2-bromophenyl)-1,1,1-trifluorobut-3-en-2-one (100.2 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **17** (86.3 mg, 98% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.58-7.56 (m, 1H), 7.41-7.34 (m, 5H),

7.29-7.26 (m, 1H), 7.14-7.09 (m, 2H), 6.04 (d, $J$ = 3.5 Hz, 1H), 5.26-5.20 (m, 2H), 4.11-4.07 (m, 1H), 3.79-3.77 (m, 1H), 3.65-3.60 (m, 1H), 2.35-2.28 (m, 1H), 1.72-1.69 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.08, 141.61, 135.59, 133.26, 132.89 (q, $J$ = 35.5 Hz), 128.74, 128.61, 128.55, 128.48, 128.42, 127.97, 124.07, 123.17 (q, $J$ = 4.0 Hz), 121.08 (q, $J$ = 274.5 Hz), 68.44, 44.23, 38.83, 30.47. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.93 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{17}BrF_3NNaO_2$ $[M+Na]^+$ 464.0374, found 464.0370.

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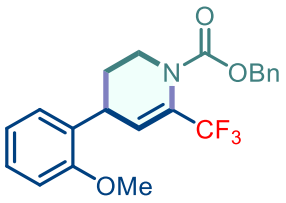


(**18**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(2-methoxyphenyl)but-3-en-2-one (90.5 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **17** (64.1 mg, 82% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H), 7.25-7.22 (m, 1H), 7.03-7.00 (m, 1H), 6.92-6.86 (m, 2H), 6.05 (d, $J$ = 3.5 Hz, 1H), 5.24-5.18 (m, 2H), 4.01-3.97 (m, 1H), 3.80 (s, 3H), 3.77-3.72 (m, 1H), 3.63-3.58 (m, 1H), 2.21-2.15 (m, 1H), 1.79 -1.71 (m, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 156.67, 154.28, 135.73, 131.91 (q, $J$ = 34.0 Hz), 130.71, 128.50, 128.40, 128.31, 128.18, 128.09, 124.64 (q, $J$ = 4.0 Hz), 121.19 (q, $J$ = 276.0 Hz), 120.66, 68.25, 55.30, 44.48, 33.20, 30.30. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.90 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{21}H_{20}F_3NNaO_3$ $[M+Na]^+$ 414.1279, found 414.1287.

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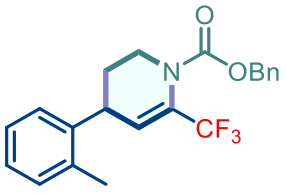


(**19**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(o-tolyl)but-3-en-2-one (87.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **19** (68.3 mg, 91% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.33 (m, 5H), 7.17-7.15 (m, 3H), 7.04-7.00 (m, 1H), 6.06 (d, $J$ = 3.4 Hz, 1H), 5.26-5.20 (m, 2H), 3.84-3.80 (m, 1H), 3.78-3.73 (m, 1H), 3.66-3.61 (m, 1H), 2.33 (s, 3H), 2.23-2.16 (m, 1H), 1.74-1.67 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.22, 140.78, 135.65, 135.26, 132.21 (q, $J$ = 35.0 Hz), 130.83, 128.52, 128.44, 128.37, 127.24, 127.06, 126.52, 124.51 (q, $J$ = 4.4 Hz), 121.14 (q, $J$ = 272.0 Hz), 68.37, 44.12, 35.79, 30.83, 19.23.

**$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.98 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{21}H_{20}F_3NNaO_2$ $[M+Na]^+$ 398.1338, found 398.1336.

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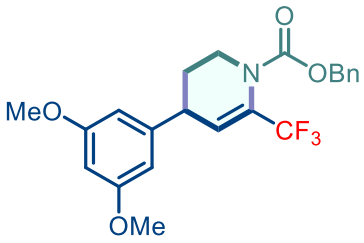


(**20**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(3,5-dimethoxyphenyl)-1,1,1-trifluorobut-3-en-2-one (96.5 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **20** (75.0 mg, 89% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.34 (m, 5H), 6.35 (t, *J* = 2.0 Hz, 1H), 6.29 (d, *J* = 2.0 Hz, 2H), 6.06 (d, *J* = 3.5 Hz, 1H), 5.24-5.19 (m, 2H), 3.81-3.72 (m, 1H), 3.75 (s, 6H), 3.62-3.53 (m, 1H), 2.21-2.14 (m, 1H), 1.85-1.79 (m, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 161.16, 154.13, 145.07, 135.61, 131.96 (q, *J* = 35.0 Hz), 128.52, 128.42, 128.37, 123.80 (q, *J* = 4.0 Hz), 121.08 (q, *J* = 275.0 Hz), 105.73, 98.60, 68.39, 55.32, 44.33, 39.54, 32.28. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.93 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{22}F_3NNaO_4$ $[M+Na]^+$ 444.1401, found 444.1393.

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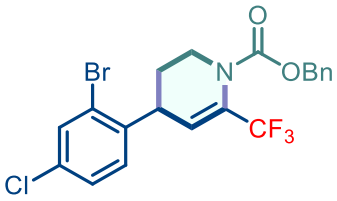


(**21**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(2-bromo-4-chlorophenyl)-1,1,1-trifluorobut-3-en-2-one (107.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **21** (85.4 mg, 90% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.0 Hz, 1H), 7.39-7.32 (m, 5H), 7.25-7.23 (m, 1H), 7.01 (d, *J* = 8.5 Hz, 1H), 5.98 (d, *J* = 3.5 Hz, 1H), 5.24-5.18 (m, 2H), 4.06-4.02 (m, 1H), 3.78-3.76 (m, 1H), 3.63-3.58 (m, 1H), 2.32-2.25 (m, 1H), 1.68-1.61 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.98, 140.20, 135.49, 133.70, 133.25(q, *J* = 35.0 Hz), 132.82, 129.39, 128.55, 128.51, 128.46, 128.18, 124.26, 122.46 (q, *J* = 4.2 Hz), 121.96 (q, *J* = 274.5 Hz), 68.52, 44.18, 38.35, 30.38. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.00 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{16}BrClF_3NNaO_2$ $[M+Na]^+$ 495.9902, found 495.9897.

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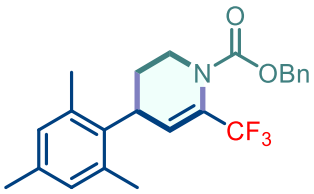


(**22**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-mesitylbut-3-en-2-one (92.9 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **22** (67.0 mg, 83% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H), 6.81 (s, 2H), 6.05 (d, *J* = 3.5 Hz, 1H), 5.27 (d, *J* = 12.0 Hz, 1H), 5.16 (d, *J* = 12.0 Hz, 1H), 4.46-4.42 (m, 1H), 4.04-3.98 (m, 1H), 3.23-3.17 (m, 1H), 2.37-2.07 (m, 9H), 2.05-1.96 (m, 1H), 1.95-1.85 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.31, 136.52, 135.73, 134.10, 130.71 (d, *J* = 35.4 Hz), 128.48, 128.43, 128.32, 126.64 (q, *J* = 3.6 Hz), 121.12 (d, *J* = 275.0 Hz), 68.22, 46.35, 36.64, 28.01, 20.67. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.38 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{23}H_{24}F_3NNaO_2$ $[M+Na]^+$ 426.1651, found 426.1659.

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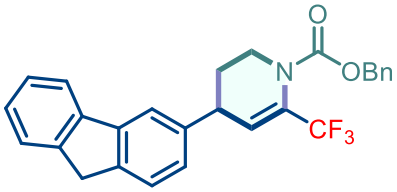


(**23**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(9H-fluoren-3-yl)-1,1,1-trifluorobut-3-en-2-one (100.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **23** (71.9 mg, 80% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.73 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.44-7.29 (m, 8H), 7.16 (d, *J* = 7.5 Hz, 1H), 6.16 (d, *J* = 3.5 Hz, 1H), 5.29-5.23 (m, 2H), 3.93-3.80 (m, 3H), 3.74-3.65 (m, 1H), 3.65-3.58 (m, 1H), 2.29-2.14 (m, 1H), 1.92-1.84 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.23, 144.02, 143.25, 141.25, 140.86, 135.69, 131.89 (q, *J* = 35.0 Hz), 128.60 (q, *J* = 7.5 Hz), 128.44 (q, *J* = 7.5 Hz), 128.22, 126.85, 126.81, 126.25, 125.09, 124.34 (q, *J* = 4.0 Hz), 124.10, 121.20 (q, *J* = 274.5 Hz), 120.18, 119.89, 68.42, 44.49, 39.70, 36.90, 32.82. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.81 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{27}H_{22}F_3NNaO_2$ $[M+Na]^+$ 472.1494, found 472.1495.

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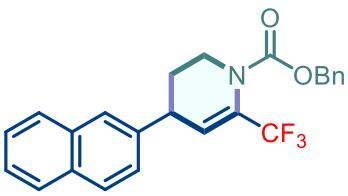

(**24**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(naphthalen-2-yl)but-3-en-2-one (94.5 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **24** (71.6 mg, 87% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83-7.78 (m, 3H), 7.56 (s, 1H), 7.50-7.46 (m, 2H), 7.41-7.32 (m, 5H), 7.27-7.25 (m, 1H), 6.18 (d, *J* = 3.5 Hz, 1H), 5.27-5.21 (m, 2H), 3.88-3.83 (m, 1H), 3.82-3.26 (m, 1H), 3.66-3.60 (m, 1H), 2.29-2.23 (m, 1H), 1.94-1.88 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.18, 139.97, 135.64, 133.46, 132.50, 132.19 (q, *J* = 34.5 Hz), 128.78, 128.53, 128.44, 128.38, 127.68, 127.66, 126.40, 125.96, 125.94, 125.71, 123.89 (q, *J* = 4.0 Hz), 121.12 (q, *J* = 270.6 Hz), 68.42, 44.34, 39.57, 32.42. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.92 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{24}H_{20}F_3NNaO_2$ $[M+Na]^+$ 434.1347, found 434.1338.

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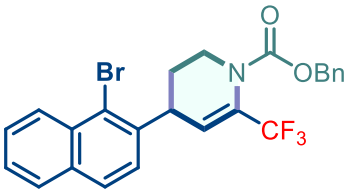


(**25**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(1-bromonaphthalen-2-yl)-1,1,1-trifluorobut-3-en-2-one (110.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **25** (84.3 mg, 86% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.5 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.50-7.27 (m, 5H), 7.20 (d, *J* = 8.5 Hz, 1H), 6.11 (d, *J* = 3.5 Hz, 1H), 5.29-5.22 (m, 2H), 4.51-4.45 (m, 1H), 4.02-4.00 (m, 1H), 3.59-3.53 (m, 1H), 2.42-2.35 (m, 1H), 1.81-1.73 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.14, 139.28, 135.61, 133.71, 132.89 (d, *J* = 35.0 Hz), 132.54, 128.56, 128.48, 128.43, 128.18, 127.83, 127.59, 126.62, 125.33, 123.91, 123.63 (q, *J* = 3.6 Hz), 121.08 (d, *J* = 274.0 Hz), 68.48, 44.90, 40.24, 30.65. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.96 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{24}H_{19}BrF_3NNaO_2$ $[M+Na]^+$ 512.0449, found 512.0451.

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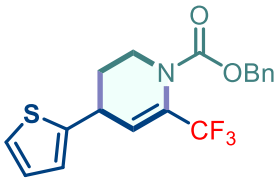


(**26**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(thiophen-2-yl)but-3-en-2-one (85.7 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **26** (59.5 mg, 81% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.41-7.30 (m, 5H), 7.20-7.19 (m, 1H), 6.95-6.93 (m, 1H), 6.81 (d, *J* = 3.5 Hz, 1H), 6.11 (d, *J* = 3.5 Hz, 1H), 5.20 (s, 2H), 3.93-3.86 (m, 1H),

3.82-3.76 (m, 1H), 3.63-3.58 (m, 1H), 2.23-2.16 (m, 1H), 1.97-1.90 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.96, 145.80, 135.50, 131.47 (q, *J* = 35.0 Hz), 128.53, 128.48, 128.41, 127.01, 124.44, 124.32, 122.85 (q, *J* = 3.5 Hz), 121.00 (q, *J* = 274.2 Hz), 68.48, 43.56, 34.22, 32.45. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.88 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{18}H_{16}F_3NNaO_2S$ $[M+Na]^+$ 390.0746, found 390.0741.

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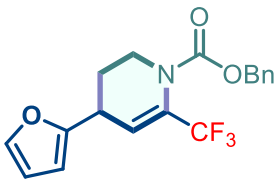


(**27**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-(furan-2-yl)but-3-en-2-one (82.5 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **27** (51.3 mg, 73% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.31 (m, 6H), 6.29 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.09 (d, *J* = 3.5 Hz, 1H), 6.02 (d, *J* = 3.1 Hz, 1H), 5.22-5.17 (m, 2H), 3.85-3.78 (m, 1H), 3.71-3.67 (m, 1H), 3.54-3.50 (m, 1H), 2.14-2.07 (m, 1H), 2.03-1.97 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.73, 153.94, 141.99, 135.48, 132.04 (q, *J* = 35.5 Hz), 128.51, 128.47, 128.39, 120.96 (q, *J* = 274.0 Hz), 120.77 (q, *J* = 4.5 Hz), 110.26, 105.77, 68.45, 43.48, 32.70, 28.51. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.98 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{18}H_{16}F_3NNaO_3$ $[M+Na]^+$ 374.0974, found 374.0973.

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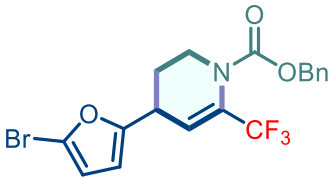


(**28**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(5-bromofuran-2-yl)-1,1,1-trifluorobut-3-en-2-one (98.2 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **29** (74.8 mg, 87% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 6.22 (d, *J* = 3.3 Hz, 1H), 6.05 (d, *J* = 3.5 Hz, 1H), 6.02 (d, *J* = 3.5 Hz, 1H), 5.22-5.17 (m, 2H), 3.84-3.79 (m, 1H), 3.69-3.64 (m, 1H), 3.54-3.49 (m, 1H), 2.15-2.08 (m, 1H), 2.03-1.96 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 156.67, 153.83, 135.41, 132.56 (q, *J* = 35.0 Hz), 128.53, 128.50, 128.44, 121.00, 120.87 (q, *J* = 274.2 Hz), 119.66 (q, *J* = 3.8 Hz), 111.94, 108.71, 68.53, 43.32, 32.79, 28.35. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.94 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{18}H_{15}BrF_3NNaO_3$ $[M+Na]^+$ 452.0080, found 452.0078.

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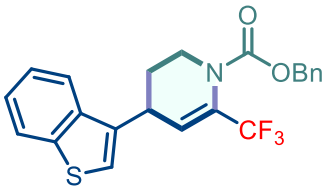


(**29**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(benzo[*b*]thiophen-3-yl)-1,1,1-trifluorobut-3-en-2-one (95.7 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **28** (56.8 mg, 68% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.90-7.86 (m, 1H), 7.73-7.70 (m, 1H), 7.41-7.33 (m, 7H), 7.06 (s, 1H), 6.19 (d, *J* = 3.5 Hz, 1H), 5.26-5.20 (m, 2H), 4.05-3.99 (m, 1H), 3.87-3.82 (m, 1H), 3.57-3.51 (m, 1H), 2.27-2.21 (m, 1H), 1.98-1.92 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.07, 140.88, 137.23, 136.92, 135.54, 132.36 (q, *J* = 35.1 Hz), 128.56, 128.50, 128.44, 124.69, 124.29, 123.26, 122.99, 122.52 (d, *J* = 3.8 Hz), 121.26, 121.08 (d, *J* = 274.0 Hz), 68.49, 43.57, 33.04, 29.75. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.77 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{24}H_{20}F_3NNaO_2$ $[M+Na]^+$ 434.1338, found 434.1333.

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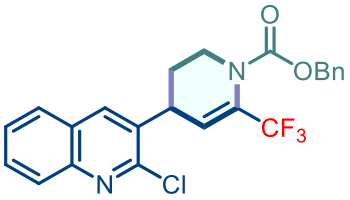


(**30**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-4-(2-chloroquinolin-3-yl)-1,1,1-trifluorobut-3-en-2-one (101.6 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **30** (78.6 mg, 88% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.84 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.75-7.70 (m, 1H), 7.59-7.55 (m, 1H), 7.45-7.29 (m, 5H), 6.11 (d, *J* = 3.5 Hz, 1H), 5.26-5.21 (m, 2H), 4.22-4.16 (m, 1H), 3.76-3.70 (m, 2H), 2.47-2.40 (m, 1H), 1.84-1.77 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.91, 150.25, 146.71, 136.63, 135.41, 134.23, 133.87 (q, *J* = 35.0 Hz), 130.54, 128.58, 128.51, 128.27, 127.50, 127.41, 127.18, 121.47 (q, *J* = 4.0 Hz), 120.96 (q, *J* = 274.0 Hz), 68.60, 43.85, 36.12, 30.22. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.86 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{23}H_{18}ClF_3N_2NaO_2$ $[M+Na]^+$ 469.0901, found 469.0893.

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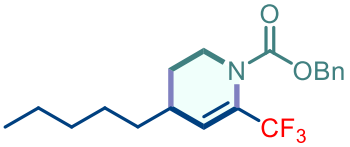

(**31**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluorononon-3-en-2-one (83.3 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **31** (54.7 mg, 77% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.29 (m, 5H), 5.95 (d, *J* = 3.5 Hz, 1H), 5.17 (s, 2H), 3.77-3.72 (m, 1H), 3.48-3.38 (m, 1H), 2.37-2.22 (m, 1H), 1.99-1.83 (m, 1H), 1.53-1.45 (m, 1H), 1.45-1.37 (m, 1H), 1.36-1.22 (m, 7H), 0.89 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.19, 135.73, 130.40 (q, *J* = 35.0 Hz), 128.46, 128.37, 128.38, 126.37 (q, *J* = 4.0 Hz), 121.15 (q, *J* = 274.0 Hz), 68.19, 44.55, 34.89, 33.44, 31.75, 29.36, 26.51, 22.52, 14.01. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.96 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{19}H_{24}F_3NNaO_2$ $[M+Na]^+$ 378.1651, found 378.1641.

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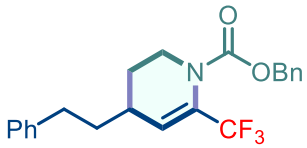


(**32**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-6-phenylhex-3-en-2-one (90.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **32** (61.5 mg, 79% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 5H), 7.30-7.24 (m, 2H), 7.21-7.15 (m, 3H), 5.96 (d, *J* = 3.5 Hz, 1H), 5.20-5.16 (m, 2H), 3.83-3.78 (m, 1H), 3.45-3.39 (m, 1H), 2.72-2.61 (m, 2H), 2.37-2.29 (m, 1H), 1.98-1.95 (m, 1H), 1.81-1.76 (m, 1H), 1.69-1.61 (m, 1H), 1.60-1.53 (m, 1H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ154.14, 141.27, 135.67, 130.79 (q, *J* = 35.0 Hz), 128.54, 128.50, 128.42, 128.33, 126.13, 125.74 (q, *J* = 4.0 Hz), 121.09 (q, *J* = 274.0 Hz), 68.27, 44.54, 36.49, 33.01, 32.80, 29.24. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.96 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{22}F_3NNaO_2$ $[M+Na]^+$ 412.1534, found 412.1538.

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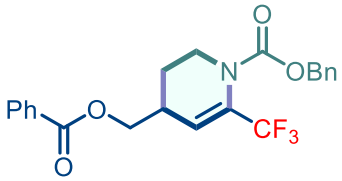


(**33**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-5,5,5-trifluoro-4-oxopent-2-en-1-yl benzoate (96.1 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **33** (67.1 mg, 80% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.04-7.98 (m, 2H), 7.58 (t, *J* = 7.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.38-7.30 (m, 5H), 6.04 (d, *J* = 3.5 Hz, 1H), 5.21-5.15 (m, 2H), 4.32-4.23 (m, 2H), 3.75-7.71 (m, 1H), 3.65-3.60 (m, 1H), 2.89-2.82 (m, 1H), 2.05-1.99 (m, 1H), 1.78-1.72 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 166.29, 153.94, 135.44, 133.28, 132.91 (q, *J* = 35.0 Hz),

129.71, 129.59, 128.52, 128.46, 128.40, 121.31 (q, $J$ = 4.5 Hz), 120.85 (q, $J$ = 274.0 Hz), 68.48, 66.51, 44.00, 33.11, 26.49. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.16 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{20}F_3NNaO_4$ $[M+Na]^+$ 442.1237, found 442.1235.

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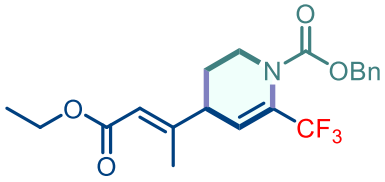


(**34**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from ethyl (2*E*,4*E*)-7,7,7-trifluoro-3-methyl-6-oxohepta-2,4-dienoate (91.7 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **35** (69.9 mg, 88% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.36-7.33 (m, 5H), 5.87 (d, $J$ = 3.5 Hz, 1H), 5.61 (s, 1H), 5.21-5.16 (m, 2H), 4.15 (q, $J$ = 7.0 Hz, 2H), 3.75-3.72 (m, 1H), 3.56-3.47 (m, 1H), 3.07-7.01 (m, 1H), 2.12 (s, 3H), 2.03-1.93 (m, 1H), 1.72-1.68 (m, 1H), 1.28 (t, $J$ = 7.0 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 166.26, 158.08, 153.90, 135.46, 133.02 (q, $J$ = 35.0 Hz), 128.52, 128.44, 128.41, 121.78 (q, $J$ = 4.0 Hz), 120.71 (q, $J$ = 274.5 Hz, 2H), 117.70, 68.47, 59.94, 44.02, 42.87, 28.23, 17.46, 14.27. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.11 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{20}H_{22}F_3NNaO_4$ $[M+Na]^+$ 420.1433, found 420.1439.

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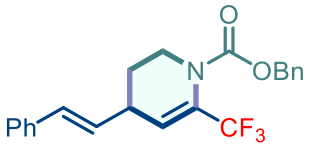


(**35**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (3*E*,5*E*)-1,1,1-trifluoro-6-phenylhexa-3,5-dien-2-one (89.7 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **36** (69.7 mg, 90% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 9H), 7.25-7.21 (m, 1H), 6.40 (d, $J$ = 16.0 Hz, 1H), 6.07 (dd, $J$ = 16.0 Hz, 7.5 Hz, 1H), 5.99 (d, $J$ = 3.5 Hz, 1H), 5.22-5.17 (m, 2H), 3.72-3.68 (m, 1H), 3.66-.61 (m, 1H), 3.23-3.16 (m, 1H), 2.07-2.01 (m, 1H), 1.78-1.72 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.08, 136.65, 135.56, 131.40 (q, $J$ = 34.5 Hz), 131.38, 130.07, 128.64, 128.52, 128.48, 128.38, 127.72, 126.25, 123.38 (q, $J$ = 4.0 Hz), 121.04 (q, $J$ = 274.0 Hz), 68.41, 43.77, 36.51, 29.59 ppm. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.86 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{20}F_3NNaO_2$ $[M+Na]^+$ 410.1338, found 410.1329.

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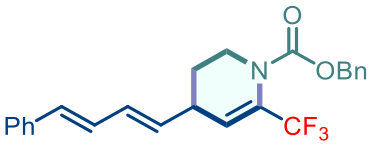


(**36**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (3*E*,5*E*,7*E*)-1,1,1-trifluoro-8-phenylocta-3,5,7-trien-2-one (94.9 mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **37** (69.4 mg, 84% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.28 (m, 9H), 7.24-7.21 (m, 1H), 6.72 (dd, *J* = 15.7, 10.4 Hz, 1H), 6.52 (d, *J* = 15.7 Hz, 1H), 6.20 (dd, *J* = 15.2, 10.4 Hz, 1H), 5.95 (d, *J* = 3.5 Hz, 1H), 5.68 (dd, *J* = 15.2, 7.5 Hz, 1H), 5.19 (s, 2H), 3.64 (t, *J* = 5.4 Hz, 2H), 3.16-3.08 (m, 1H), 2.04-1.97 (m, 1H), 1.73-1.66 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.03, 136.06, 134.54, 133.07, 131.44, 130.72, 130.29 (q, *J* = 35.0 Hz), 127.62, 127.48, 127.43, 127.34, 127.09, 126.61, 125.32, 122.21 (q, *J* = 4.0 Hz), 120.00 (d, *J* = 274.0 Hz), 67.35, 42.67, 35.22, 28.52. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.87 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{24}H_{22}F_3NNaO_2$ $[M+Na]^+$ 436.1495, found 436.1499.

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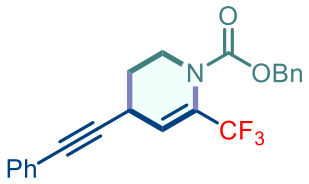


(**37**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-6-phenylhex-3-en-5-yn-2-one (89.3mg, 0.2 mmol) and propyl aziridine-1-carboxylate **2** (70.9 mg, 0.4 mmol) afforded **38** (54.7 mg, 71% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.32 (m, 7H), 7.31-7.27 (m, 3H), 6.04 (d, *J* = 3.5 Hz, 1H), 5.23-5.15 (m, 2H), 3.85-3.80 (m, 1H), 3.68-3.63 (m, 1H), 3.53-3.48 (s, 1H), 2.13-2.02 (m, 2H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.84, 135.42, 131.67, 131.22 (q, *J* = 35.0 Hz), 128.53, 128.43, 128.31, 122.77, 120.89 (q, *J* = 274.0 Hz), 120.57 (q, *J* = 4.0 Hz), 88.20, 82.43, 68.53, 43.66, 29.93, 26.01. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.02 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{18}F_3NNaO_2$ $[M+Na]^+$ 408.1182, found 408.1184.

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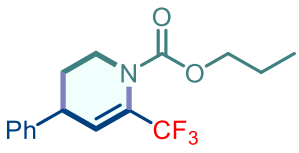


(**38**) Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (51.7 mg, 0.4 mmol) afforded **42** (59.5 mg, 95% yield) as a colorless oil. **$^1$H NMR**

(500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.07 (d, *J* = 3.5 Hz, 1H), 4.14 (t, *J* = 7.0 Hz, 2H), 3.82-3.78 (m, 1H), 3.66-3.55 (m, 2H), 2.24-2.18 (m, 1H), 1.88-1.79 (m, 1H), 1.76-1.66 (m, 2H), 0.97 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.50, 142.78, 132.10 (q, *J* = 34.7 Hz), 128.88, 127.47, 127.09, 123.62 (q, *J* = 4.0 Hz), 121.18 (q, *J* = 272.5 Hz), 68.40, 44.12, 39.52, 32.54, 21.97, 10.23. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.03 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{16}H_{18}F_3NNaO_2$ $[M+Na]^+$ 336.1183, found 336.1182.

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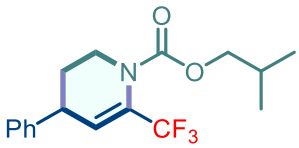


**(39)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (57.3 mg, 0.4 mmol) afforded **43** (46.5 mg, 71% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.34 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.09 (d, *J* = 3.5 Hz, 1H), 4.02-3.93 (m, 2H), 3.84-3.80 (m, 1H), 3.68-3.55 (m, 2H), 2.26-2.17 (m, 1H), 2.04-1.96 (m 1H), 1.97-1.80 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.56, 142.75, 132.19 (q, *J* = 35.0 Hz), 128.88, 127.45, 127.09, 123.83 (q, *J* = 4.0 Hz), 121.14 (q, *J* = 272.0 Hz), 72.95, 44.29, 39.55, 32.59, 27.80, 18.97, 18.96. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.07 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{17}H_{20}F_3NNaO_2$ $[M+Na]^+$ 350.1344, found 350.1338.

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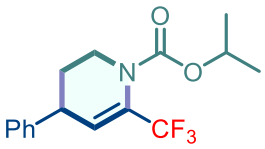


**(40)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (51.7 mg, 0.4 mmol) afforded **44** (60.8 mg, 97% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.05 (d, *J* = 3.5 Hz, 1H), 5.05-4.96 (m, 1H), 3.81-3.74 (m, 1H), 3.66-3.54 (m, 2H), 2.24-2.16 (m, 1H), 1.86-1.77 (m 1H), 1.30 (d, *J* = 6.0 Hz, 3H), 1.29 (d, *J* = 6.0 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.99, 142.88, 132.17 (q, *J* = 35.0 Hz), 128.87, 127.47, 127.06, 123.33 (q, *J* = 3.6 Hz), 121.22 (q, *J* = 274.0 Hz), 70.65, 43.90, 39.49, 32.53, 21.74, 21.67. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.70 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{16}H_{18}F_3NNaO_2$ $[M+Na]^+$ 336.1183, found 336.1182.

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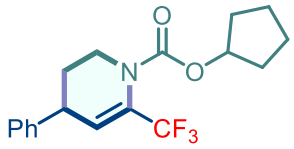

**(41)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (62.1 mg, 0.4 mmol) afforded **45** (60.8 mg, 97% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.16 (d, *J* = 7.5 Hz, 2H), 6.05 (d, *J* = 3.5 Hz, 1H), 5.24-5.16 (m, 1H), 3.79-3.75 (m, 1H), 3.67-3.61 (m, 1H), 3.60-3.51 (m, 1H), 2.24-2.15 (m, 1H), 1.93-1.70 (m, 7H), 1.66-1.53 (m, 2H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.27, 142.83, 132.13 (q, *J* = 34.8 Hz), 128.85, 127.44, 127.04, 123.44 (q, *J* = 4.0 Hz), 121.16 (q, *J* = 274.0 Hz), 79.91, 44.01, 39.47, 32.59, 32.52, 32.49, 23.60. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.85 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{18}H_{20}F_3NNaO_2$ $[M+Na]^+$ 362.1338, found 362.1319.

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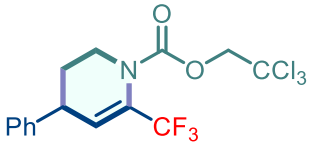

**(42)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (87.4 mg, 0.4 mmol) afforded **46** (66.8 mg, 83% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.20-7.06 (m, 2H), 6.20 (d, *J* = 3.5 Hz, 1H), 4.89 (d, *J* = 12.0 Hz, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 3.95-3.91 (m, 1H), 3.70-3.61 (m, 2H), 2.30-2.24 (m, 1H), 1.92-1.85 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 152.53, 142.23, 131.61 (q, *J* = 35.0 Hz), 128.99, 127.45, 127.27, 125.51 (q, *J* = 3.5 Hz), 120.88 (q, *J* = 274.0 Hz), 94.93, 75.48, 45.03, 39.55, 32.68. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.06 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{15}H_{13}Cl_3F_3NNaO_2$ $[M+Na]^+$ 423.9856, found 423.9851.

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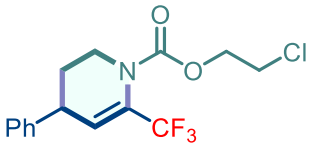

**(43)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (59.8 mg, 0.4 mmol) afforded **47** (62.1 mg, 93% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.12 (d, *J* = 3.5 Hz, 1H), 4.47-4.39 (m, 2H), 3.86-3.81 (m, 1H), 3.72 (t, *J* = 6.0, 2H), 3.67-3.63 (m, 1H), 3.62-3.57 (m, 1H), 2.27-2.21(m, 1H), 1.89-1.75 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ

153.65, 142.51, 131.67 (q, $J$ = 35.0 Hz), 128.93, 127.47, 127.17, 124.41 (q, $J$ = 4.2 Hz), 121.06 (q, $J$ = 274.0 Hz), 65.92, 44.40, 41.28, 39.50, 32.50. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.07 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{15}H_{15}ClF_3NNaO_2$ $[M+Na]^+$ 356.0636, found 356.0629.

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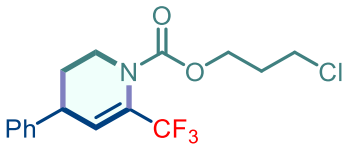


**(44)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (65.4 mg, 0.4 mmol) afforded **48** (61.9 mg, 89% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.34 (t, $J$ = 7.5 Hz, 2H), 7.26 (t, $J$ = 6.0 Hz, 1H), 7.16 (d, $J$ = 7.0 Hz, 2H), 6.09 (d, $J$ = 3.5 Hz, 1H), 4.35 (t, $J$ = 6.0 Hz, 2H), 3.84-3.80 (m, 1H), 3.68-3.61 (m, 3H), 3.61-3.54 (m, 1H), 2.27-2.21 (m, 1H), 2.18-2.10 (m, 2H), 1.88-1.79 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.11, 142.58, 131.73 (q, $J$ = 35.0 Hz), 128.93, 127.45, 127.16, 124.18 (q, $J$ = 4.0 Hz), 121.15 (q, $J$ = 274.0 Hz), 63.54, 44.25, 41.08, 39.51, 32.49, 31.61. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.99 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{16}H_{17}ClF_3NNaO_2$ $[M+Na]^+$ 370.0792, found 370.0789.

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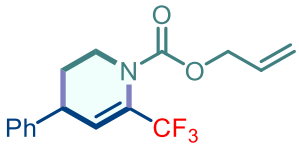


**(45)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (50.8 mg, 0.4 mmol) afforded **49** (56.0 mg, 90% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, $J$ = 7.5 Hz, 2H), 7.26 (t, $J$ = 7.5 Hz, 1H), 7.17 (d, $J$ = 7.5 Hz, 2H), 6.09 (d, $J$ = 3.5 Hz, 1H), 6.00-5.92 (m, 1H), 5.37-5.33 (m, 1H), 5.28-5.25 (m, 1H), 4.69 (d, $J$ = 6.0 Hz, 2H), 3.83-3.79 (m, 1H), 3.67-3.54 (m, 2H), 2.25-2.19 (m, 1H), 1.89-1.75 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.01, 142.68, 131.98, 131.95 (q, $J$ = 34.5 Hz), 128.90, 127.48, 127.12, 123.88 (q, $J$ = 3.8 Hz), 121.13 (q, $J$ = 273.6 Hz), 118.55, 67.32, 44.21, 39.49, 32.54. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.01 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{16}H_{16}F_3NNaO_2$ $[M+Na]^+$ 334.1035, found 334.1025.

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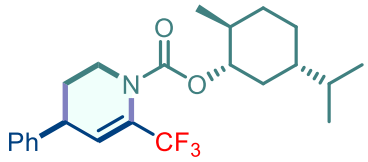
**2.2 Mild functionalization of biomolecules**



**(46)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (95.7 mg, 0.4 mmol) afforded **46** (62.7 mg, 74% yield) major:minor = 3:1, as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.33 (m, major, 4H, minor, 4H), 7.31-7.26 (m, major, 1H, minor, 1H), 6.02 (s, minor,1H), 5.99 (s, major, 1H), 4.72-4.69 (m, minor,1H), 4.68-4.62 (m, major, 1H), 4.32-4.28 (m, major, 1H), 4.19-4.15 (m, minor, 1H), 3.39-3.34 (m, minor, 1H), 3.28-3.23 (m, major, 1H), 2.19-2.16 (m, minor, 2H), 2.18-2.13 (m, major, 2H), 2.08-2.01 (m, major, 1H, minor, 1H), 2.00-1.84 (m, major, 2H, minor, 2H), 1.71-1.64 (m, major, 2H, minor, 2H), 1.48-1.40 (m, major, 2H, minor, 2H), 1.08-1.00 (m, major, 2H, minor, 2H), 0.93-0.90 (m, minor, 7H), 0.88-0.84 (m, major, 7H), 0.79-0.77 (m, major, 3H), 0.76-0.74 (m, minor, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.68, 144.66, 128.66, 127.86, 124.82, 124.69, 123.96, 123.94, 70.50, 46.88, 43.51, 43.41, 40.94, 40.47, 40.44, 34.17, 34.12, 31.44, 31.38, 26.78, 26.00, 23.79, 23.19, 21.98, 20.86, 20.67, 16.70, 16.13. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.03 (s, major, 3F), -62.13 (s, minor, 3F). **HRMS** (ESI) *m/z* calculated $C_{23}H_{30}F_3NNaO_2$ $[M+Na]^+$ 432.2121, found 432.2129.

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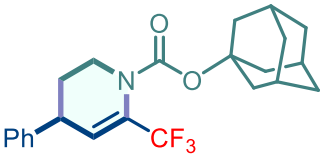
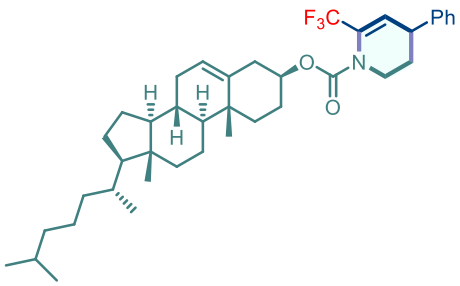


**(47)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (88.5 mg, 0.4 mmol) afforded **47** (72.2 mg, 89% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.34-7.31 (m, 2H), 7.27-7.23 (m, 1H), 7.16 (d, $J$ = 7.5 Hz, 2H), 6.00 (d, $J$ = 3.5 Hz, 1H), 3.71-3.66 (m, 1H), 3.63-3.60 (m, 1H), 3.57-3.52 (m, 1H), 2.20-2.14 (m, 10H), 1.84-1.78 (m, 1H), 1.71-1.62 (m, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) $^{13}$C NMR (150 MHz, $CDCl_3$) δ 152.97, 143.08, 132.51 (q, $J$ = 34.5 Hz), 128.84, 127.51, 127.00, 122.86 (q, $J$ = 3.5 Hz), 121.29 (q, $J$ = 274.0 Hz), 82.34, 43.72, 41.19, 39.45, 36.16, 32.53, 30.96. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.19 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{23}H_{26}F_3NNaO_2$ $[M+Na]^+$ 428.5116, found 428.5118.




**(48)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (85.0 mg, 0.2 mmol) and aziridine (182.3 mg, 0.4 mmol) afforded **48** (92.1 mg, 72% yield) as a green oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.05 (d, *J* = 3.5 Hz, 1H), 5.41-5.37 (m, 1H), 4.65-4.57 (m, 1H), 3.82-3.75 (m, 1H), 3.66-3.57 (m, 2H), 2.47-2.34 (m, 2H), 2.24-2.16 (m, 1H), 2.07-1.92 (m, 3H), 1.91-1.78 (m, 3H), 1.72-1.62 (m, 1H), 1.62-1.43 (m, 6H), 1.41-1.30 (m, 3H), 1.30-1.22 (m, 1H), 1.21-1.09 (m, 6H), 1.04-0.93 (m, 7H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.88-0.86 (m, 6H), 0.68 (s, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.84, 142.87, 139.60, 132.11 (q, *J* = 35.0 Hz), 128.88, 127.50, 127.07, 123.35 (q, *J* = 3.5 Hz), 122.76, 121.22 (q, *J* = 274.0 Hz), 56.72, 56.16, 50.03, 43.90, 42.34, 39.76, 39.54, 39.47, 38.05, 37.98, 36.96, 36.60, 36.21, 35.83, 32.52, 31.94, 31.88, 28.27, 28.04, 27.70, 27.62, 24.31, 23.87, 22.85, 22.59, 21.08, 19.35, 18.74, 11.89. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.55 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{40}H_{56}F_3NNaO_2$ $[M+Na]^+$ 662.4155, found 662.4150.

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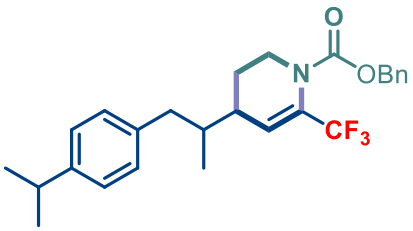
**2.3 Late-stage modification of molecules containing an aldehyde moiety**




**(49)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from cyclamen aldehyde (100.8 mg, 0.2 mmol) and aziridine **2** (70.9 mg, 0.4 mmol) afforded **49** (65.0 mg, 73% yield), major : minor = 1:1 as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.37-7.31 (m, 10H), 7.14 (d, *J* = 8.0 Hz, 4H), 7.05 (d, *J* = 8.0 Hz, 4H), 6.02 (d, *J* = 3.5 Hz, 1H), 5.91 (d, *J* = 3.5 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 2H), 5.18-5.15 (m, 2H), 4.03-3.97 (m, 2H), 3.26-3.20 (m, 2H), 2.93-2.84 (m, 2H), 2.67-2.63 (m, 1H), 2.59-2.55 (m, 1H), 2.47-2.43 (m, 1H), 2.41-2.36 (m, 3H), 1.99-1.96 (m, 1H), 1.91-1.79 (m, 3H), 1.71-1.62 (m, 2H), 1.24 (d, *J* = 7.0 Hz, 12H), 0.85-0.81 (m, 6H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.27, 146.71, 146.66, 137.65, 137.63, 135.79, 135.77, 132.05 (q, *J* = 34.0 Hz), 131.80 (q, *J* = 34.0 Hz), 128.92, 128.78, 128.47, 128.33, 128.30, 128.27, 128.26, 126.55 (q, *J* = 3.5 Hz), 126.46, 126.43, 124.47 (q, *J* = 4.0 Hz), 121.07 (d, *J* = 274.0 Hz), 121.05 (d, *J* = 274.0 Hz), 68.17, 68.14, 45.51, 45,49, 40.08,

39.93, 38.86, 38.39, 37.98, 37.15, 33.70, 27.40, 24.44, 24.05, 16.24, 15.57. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.10 (s, 3F), -62.22 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{26}H_{30}F_3NNaO_2$ $[M+Na]^+$ 468.2121, found 468.2114.

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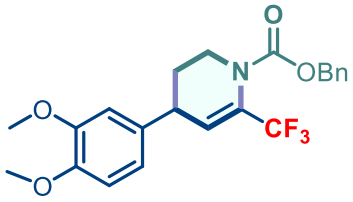


**(50)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from Veratraldehyde (96.5 mg, 0.2 mmol) and aziridine **2** (70.9 mg, 0.4 mmol) afforded **50** (66.6 mg, 79% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.40-7.33 (m, 5H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.67 (dd, *J* = 8.0 Hz, 2.0 Hz 1H), 6.64 (d, *J* = 2.0 Hz, 1H), 6.07 (d, *J* = 3.5 Hz, 1H), 5.22 (ABq, *J* = 12.0 Hz, 2H), 3.86 (s, 3H), 3.83 (s, 3H), 3.81-3.76 (m, 1H), 3.63-3.57 (m, 2H), 2.21-2.15 (m, 1H), 1.84-1.78 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 154.17, 149.23, 148.13, 135.60, 135.19, 131.75 (q, *J* = 35.0 Hz), 128.53, 128.45, 128.39, 124.21 (q, *J* = 4.0 Hz), 121.11 (q, *J* = 274.0 Hz), 119.47, 111.38, 110.64, 68.38, 55.97, 55.89, 44.30, 39.00, 32.64. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.92 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{22}H_{22}F_3NNaO_4$ $[M+Na]^+$ 444.4701, found 444.4705.

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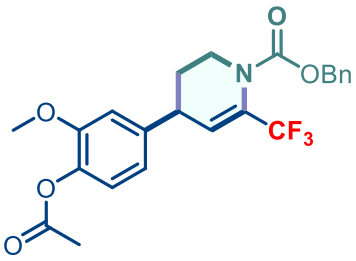
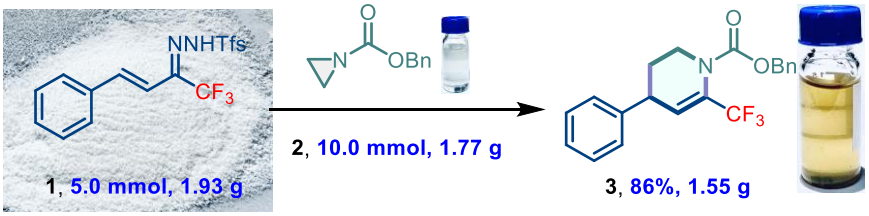
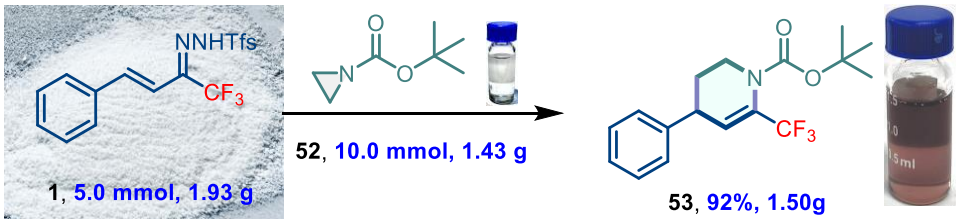



**(51)** Prepared according to **General Procedure A** using trifluoromethyl vinyl *N*-triftosylhydrazone derived from Vanillin acetate (102.1 mg, 0.2 mmol) and aziridine **2** (70.9 mg, 0.4 mmol) afforded **51** (71.9 mg, 80% yield) as a colorless oil. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ 7.43-7.28 (m, 5H), 6.96 (d, *J* = 8.5 Hz, 1H), 6.72-6.67 (m, 2H), 6.06 (d, *J* = 3.5 Hz, 1H), 5.21 (ABq, *J* = 12.0 Hz, 2H), 3.83-3.78 (m, 1H), 3.77 (s, 3H), 3.63-3.56 (m, 2H), 2.30 (s, 3H), 2.22-2.16 (m, 1H), 1.86-1.79 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 169.11, 154.11, 151.27, 141.50, 138.74, 135.55, 132.13 (q, *J* = 35.0 Hz), 128.54, 128.46, 128.42, 123.66 (q, *J* = 4.0 Hz), 123.05, 121.04 (q, *J* = 274.0 Hz), 119.63, 111.57, 68.43, 55.86, 44.33, 39.33, 32.48, 20.67. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -62.00 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{23}H_{22}F_3NNaO_5$ $[M+Na]^+$ 472.1478, found 472.1478.

## 2.4 Gram-scale experiments




An oven-dried screwcap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with trifluoromethyl vinyl *N*-triftosylhydrazone (1.93 g, 5.0 mmol), NaH (400.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CH_2Cl_2$ (50.0 mL) inside a glove box under nitrogen atmosphere. Then $Rh_2(esp)_2$ (75.6 mg, 2 mol%) and aziridine (10.0 mmol, 2.0 equiv) were added. The tube was sealed and stirred at 60 °C for 12 h, after which time the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel using ethyl acetate (EA) as an eluent. The volatiles was removed from the collected filtrate under reduced pressure, and the resulting residue was purified via flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **3** (1.55 g, 86% yield) as a colorless oil.

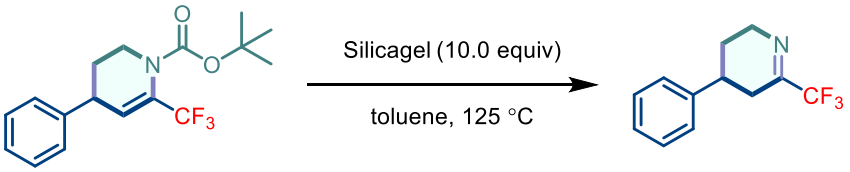



An oven-dried screwcap reaction tube equipped with a Teflon-coated magnetic stir bar was charged with trifluoromethyl vinyl *N*-triftosylhydrazone (1.93 g, 5.0 mmol), NaH (400.0 mg, 60 wt% dispersion in mineral oil, 0.6 mmol, 2.0 equiv) and dry $CH_2Cl_2$ (50.0 mL) inside a glove box with nitrogen atmosphere. Then $Rh_2(esp)_2$ (75.6 mg, 2 mol%) and aziridine (10.0 mmol, 2.0 equiv) were added. The tube was sealed and stirred at 60 °C for 12 h, after which time the reaction mixture was cooled to room temperature and filtered through a short pad of silica gel using ethyl acetate (EA) as an eluent. The volatiles was removed from the collected filtrate under reduced pressure, and the resulting residue was purified via flash chromatography on silica gel (using petroleum ether / EtOAc as eluent) to obtain **53** (1.50 g, 92% yield) as a colorless oil.

**(53)** Prepared according to the above-mentioned procedure using trifluoromethyl vinyl *N*-triftosylhydrazone derived from (*E*)-1,1,1-trifluoro-4-phenylbut-3-en-2-one (1.93 g, 5 mmol) and aziridine **52** (1.43g, 10.0 mmol) afforded **53** (1.50 g, 92% yield) as a colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.27-7.24 (m, 1H), 7.17 (d, *J* = 7.5 Hz, 2H), 6.01 (d, *J* = 3.5 Hz, 1H), 3.73-3.68 (m, 1H), 3.65-3.60 (m, 1H), 3.59-3.54 (m, 1H), 2.23-2.16 (m, 1H), 1.86-1.78 (m, 1H), 1.51 (s, 9H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 153.44, 143.06, 132.49 (q, *J* = 34.5 Hz), 128.86, 127.50, 127.02, 122.88 (q, *J* = 3.6 Hz), 121.29 (q, *J* = 274.0 Hz), 82.37, 43.72, 39.45,

32.57, 28.00. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -61.37 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{17}H_{20}F_3NNaO_2$ $[M+Na]^+$ 350.1520, found 350.1514.

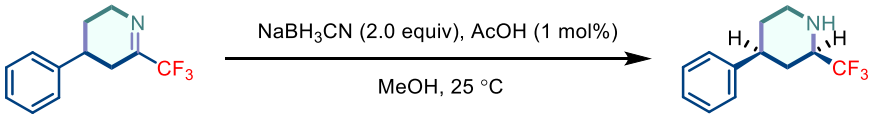
**2.5 Synthetic applications**




**53** **54**, **95%, 1.0g**

**54** were prepared according to the literature procedure[1]. To a stirred solution of **53** (1.6g, 4.9 mmol, 1.0 equiv) in toluene (10 mL) was added silica gel (49.0 mmol, 10.0 equiv) and the mixture was stirred at 125 °C for 12 h. After completion, the reaction mixture was cooled to room temperature, and the solvent was evaporated under reduced pressure. The resulting crude was purified by flash column chromatography on silica gel (PE/$Et_2O$) to obtain **54 (**1.0g, 95**%)** as a colorless oil.

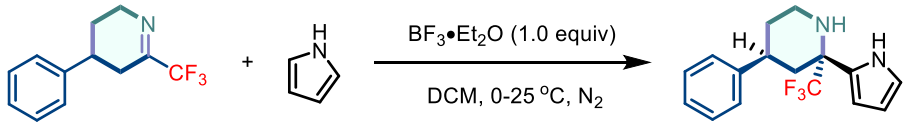
**(54)** Prepared according to the above-mentioned procedure. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.5 Hz, 2H), 7.28-7.24 (m, 1H), 7.19 (d, *J* = 7.5 Hz, 2H), 4.14-4.08 (m, 1H), 3.86-3.72 (m, 1H), 2.98-2.90 (m, 1H), 2.75-2.70 (m, 1H), 2.40-2.29 (m, 1H), 2.01-1.96 (m, 1H), 1.81-1.72 (m, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 158.60 (q, *J* = 33.5 Hz), 143.75, 128.87, 127.02, 126.60, 119.70 (q, *J* = 278.0 Hz), 50.07, 35.83, 31.34, 28.60. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -74.61 (s, 3F). **HRMS** (ESI) *m/z* calculated $C_{12}H_{12}F_3NNa$ $[M+Na]^+$ 250.4122, found 250.4125.




**54**, 0.2 mmol **55**, 75 %, dr > 20:1

**55** were prepared according to the literature procedure[2]. To a 25 mL round-bottomed flask with a magnetic stirrer bar containing imine **54** (45.4 mg, 0.2 mmol, 1.0 equiv) in methanol (2.0 mL) were added sodium cyanide borohydride (25.1 mg, 0.4 mmol, 2.0 equiv) and glacial acetic acid at 0 °C. The reaction mixture was stirred at room temperature for 8-10 hours and quenched with saturated $NaHCO_3$ solution (10 mL). Then the mixture was extracted by DCM (20 mL × 3), dried over anhydrous $Na_2SO_4$, and evaporated under reduced pressure. The residue was purified by flash column chromatography to afford **55** (34.4 mg, 75%) as a yellow oil.

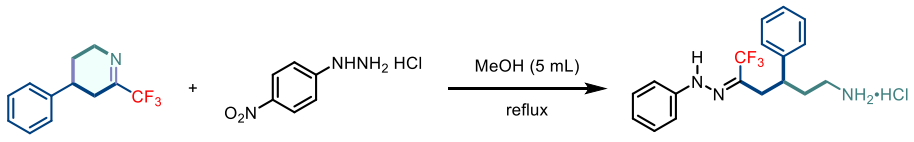
**(55)** Prepared according to the above-mentioned procedure. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.26 (m, 2H), 7.26-7.19 (m, 3H), 3.34-3.24 (m, 2H), 2.86-2.78 (m, 1H), 2.70-2.62 (m, 1H), 2.08-2.02 (m, 1H), 1.89-1.78 (m, 2H), 1.74-1.61 (m, 2H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 145.08, 128.65, 126.75, 126.65, 125.66 (q, *J* = 279.0 Hz), 58.45 (q, *J* = 28.6 Hz), 46.20, 41.62, 33.16, 32.40. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -77.73 (d, *J* = 6.5 Hz, 3F). **HRMS** (ESI) *m/z* calculated $C_{12}H_{14}F_3NNa$ $[M+Na]^+$ 252.4278, found 252.4280.




**54**, 0.2 mmol  2.0 equiv  **56**, 71 %, d.r. = 10:1

**56** were prepared according to the literature procedure[4]. An oven-dried screw-capped reaction tube equipped with a Teflon-coated magnetic stir bar was charged with imine **54** (45.4 mg, 0.2 mmol, 1.0 equiv) and anhydrous DCM (1.0 mL) inside a glove box with nitrogen atmosphere. Then, pyrrole (0.4 mmol, 2.0 equiv) was added and the vial was sealed. After transferred out of the glove box, boron trifluoride diethyl etherate was added at 0 °C. After stirring at room temperature for 12 hours, the reaction was quenched with saturated $NaHCO_3$ solution (10 mL) and then extracted by DCM (20 mL × 3), dried over anhydrous $Na_2SO_4$. The residue was purified by flash column chromatography to afford **56** (41.8 mg, 71%) as a yellow oil.

**(56)** Prepared according to the above-mentioned procedure. major:minor = 10:1, yellow oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.38 (s, minor, 1H), 8.20 (s, major, 1H), 7.35-7.28 (m, major, 2H, minor, 2H), 7.28-7.19 (m, major, 3H, minor, 3H), 6.88-6.85 (m, minor, 1H), 6.84-6.80 (m, major, 1H, minor, 1H), 6.76-6.72 (m, major, 1H), 6.31-6.25 (m, major, 1H, minor, 1H), 3.34-3.25 (m, major, 1H), 3.19-3.05 (m, major, 2H, minor, 1H), 3.02-2.96 (m, minor, 1H), 2.86-2.78 (m, minor, 1H), 2.63-2.57 (m, major, 1H), 2.41-2.36 (m, minor, 1H), 1.97 (s, major, 1H, minor, 1H), 1.92-1.84 (m, major, 2H, minor, 2H), 1.74-1.63 (m, major, 1H, minor, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 145.03, 144.66, 128.24, 127.57, 127.54, 126.32, 125.94, 125.76, 125.45, 125.43, 124.72, 117.47, 116.84, 116.75, 114.32, 107.43, 105.71, 59.46 (q, $J$ = 26.81), 56.87 (q, $J$ = 25.0 Hz), 41.33, 40.54, 38.60, 37.06, 36.64, 35.06, 32.38, 31.47. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -70.69 (s, major, 3F), -81.54 (s, minor, 3F). **HRMS** (ESI) m/z calculated$C_{16}H_{17}F_3NNaO_2$ $[M+Na]^+$ 317.4544, found 317.4540.




**54**, 0.2 mmol  1.0 eq  **57**, 91%

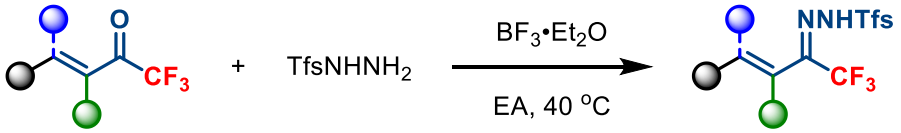
**57** were prepared according to the literature procedure[5]. To a 25 mL round-bottomed flask with a magnetic stirrer bar containing imine **54** (45.4 mg, 0.2 mmol, 1.0 equiv) dissolved in methanol (5.0 mL) was added arylhydrazine hydrochlorides (37.9 mg, 0.2 mmol, 1.0 equiv). Then the reaction mixture was refluxed for 2 hours. After evaporation of the solvent under reduced pressure, the resultant residue was purified by flash column chromatography to afford **57** (75.9 mg, 91%) as a yellow solid.

**(57)** Prepared according to the above-mentioned procedure. **$^1$H NMR** (500 MHz, DMSO) δ 11.52-11.46 (m, 1H), 8.40-8.01 (m, 4H), 7.51-7.23 (m, 5H), 3.34-3.12 (m, 3H), 2.77-2.61 (m, 1H),

2.51-2.40 (m, 1H), 2.28-1.84 (m, 2H). **$^{13}$C NMR** (150 MHz, DMSO) δ 150.59, 142.12, 140.65, 128.73, 128.29, 127.43, 126.06, 125.85, 122.09 (q, *J* = 274.0 Hz), 113.48, 113.26, 55.41, 37.57, 32.95, 32.54. **$^{19}$F NMR** (565 MHz, DMSO) δ -65.55 (S, 1H). **HRMS** (ESI) *m/z* calculated $C_{18}H_{20}ClF_3N_4NaO_2$ $[M+Na]^+$ 439.4427, found 439.4423.

## 3. Synthesis of starting materials

### 3.1 General procedures for the synthesis of *N*-triftosylhydrazones




To a stirred solution of $TfsNHNH_2$ (2.2 mmol, 1.1 equiv) in ethyl acetate (2.0 mL) were added carbonyl compounds (2.2 mmol, 1.1 equiv) and boron trifluoride etherate. The mixture was stirred at 40 ℃ for 5 h. After the complete consumption of ketones, the solvent was removed under reduced pressure, and the resultant residue was purified by flash chromatography on silica gel to obtain the trifluoromethyl vinyl-*N*- sulfonylhydrazones.

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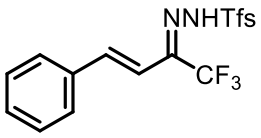


Yield 86 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.77 (s, 1H), 8.13 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.99-7.91 (m, 2H), 7.80-7.73 (m, 2H), 7.51-7.40 (m, 4H), 7.20-7.13 (m, 1H); **$^{13}$C NMR** (150 MHz, DMSO) δ 138.87, 137.75 (q, *J* = 32.0 Hz), 135.56, 134.51, 133.85, 132.16, 130.68, 129.32, 129.00 (q, *J* = 6.0 Hz) 128.53, 126.95 (q, *J* = 32.0 Hz), 125.99, 123.10 (q, *J* = 274.5 Hz), 120.93 (q, *J* = 274.5 Hz), 112.60. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.46 (s, 3F), -64.20 (s, 3F). HRMS (ESI) m/z calculated $C_{17}H_{12}F_6N_2NaO_2S$ $[M+Na]^+$ 445.0416, found 445.0411.

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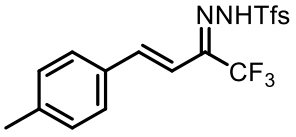


Yeild 80 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.76 (s, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.99 (t, *J* = 7.5 Hz, 1H), 7.94 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 16.5 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 16.5 Hz, 1H), 2.37 (s, 3H). **$^{13}$C NMR** (150 MHz, DMSO) δ 140.96, 139.13, 138.22 (q, *J* = 33.0 Hz ), 137.61, 134.67, 134.01, 132.99, 132.28, 130.13, 129.16 (q, *J* = 5.5 Hz), 128.70, 127.12 (q, *J* = 32.8 Hz), 123.27 (q, *J* = 275.0 Hz), 121.11 (q, *J* = 275.5 Hz), 111.70, 60.34, 21.55, 14.60. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.46 (s, 3F), -64.18 (s, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{14}F_6N_2NaO_2S$ $[M+Na]^+$ 459.0572, found 459.0566.

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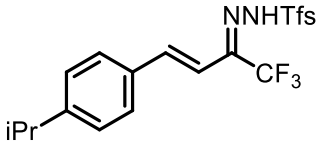


Yeild 83 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.76 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.99-7.92 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 16.5 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 16.5 Hz, 1H), 2.96-2.91 (m, 1H), 1.22 (d, *J* = 7.0 Hz, 6H). **$^{13}$C NMR** (150 MHz, DMSO) δ 151.54, 138.89, 137.94 (q, *J* = 32.5Hz), 134.53, 133.88, 132.14, 129.03 (q, *J* = 5.5Hz), 128.67, 127.47, 127.32, 126.90 (q, *J* = 32.5Hz), 126.06, 123.11 (q, *J* = 274.5Hz), 120.97 (q, *J* = 274.5Hz), 111.69, 33.83, 24.02. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.41 (s, 3F), -64.10 (s, 3F). **HRMS** (ESI) m/z calculated $C_{20}H_{18}F_6N_2NaO_2S$ $[M+Na]^+$ 487.0885, found 487.0878.

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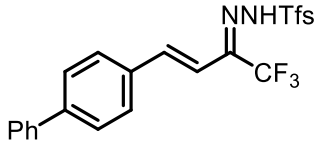


Yeild 90 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.84 (s, 1H), 8.17 (d, *J* = 7.5 Hz, 1H), 8.07 (d, *J* = 7.5 Hz, 1H), 7.99 (t, *J* = 7.5 Hz, 1H), 7.94 (t, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.77 (d, *J* = 7.5 Hz, 2H), 7.54-7.50 (m, 3H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 142.20, 139.60, 138.37, 137.76 (q, *J* = 32.0 Hz), 137.44, 134.73, 134.58, 133.92, 132.17, 129.47, 129.22, 129.06 (q, *J* = 6.5 Hz), 128.45, 127.51, 127.17, 126.92 (q, *J* = 32.5 Hz), 123.12 (q, *J* = 274.0 Hz), 120.97 (q, *J* = 274.0 Hz), 112.49. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.43 (s, 3F), -64.15 (s, 3F). **HRMS** (ESI) m/z calculated $C_{23}H_{16}F_6N_2NaO_2S$ $[M+Na]^+$ 521.0729, found 521.0722.

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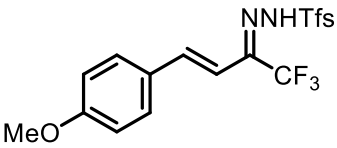


Yeild 82 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.63 (s, 1H), 8.11 (d, *J* = 7.5 Hz, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 16.5 Hz, 1H), 7.11 (d, *J* = 16.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H). **$^{13}$C NMR** (150 MHz, DMSO) δ 161.56, 138.73, 138.26 (q, *J* = 32.0 Hz), 134.52, 133.91, 132.05, 130.34, 129.05 (q, *J* = 6.5 Hz), 128.16, 127.48, 126.90 (q, *J* = 33.0 Hz), 123.12 (q, *J* = 274.0 Hz), 121.00 (q, *J* = 274.0 Hz), 114.90, 110.12, 55.84. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.37 (s, 3F), -64.02 (s, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{14}F_6N_2NaO_3S$ $[M+Na]^+$ 475.0521, found 475.0529.

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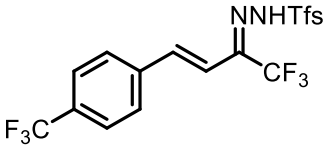


Yeild 83 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.99 (s, 1H), 8.18 (d, *J* = 7.5 Hz, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 7.96-8.03 (m, 4H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 16.5 Hz, 1H), 7.30 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 148.44, 142.88, 133.93, 132.35, 129.42 (q, *J* = 32.0 Hz), 129.05, 127.21, 126.82 (q, *J* = 5.5 Hz), 126.66, 126.54, 126.20, 125.88 (q, *J* = 33.0 Hz), 124.51 (d, *J* = 274.5 Hz), 124.41, 124.22 (d, *J* = 274.5 Hz), 102.84. **$^{19}$F NMR** (565 MHz, DMSO) δ -55.82 (s, 3F), -60.52(s, 3F), -61.22 (s, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{11}F_9N_2NaO_3S$ $[M+Na]^+$ 513.0290, found 513.0284.

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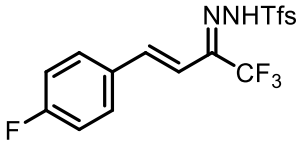


Yeild 80 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.64 (s, 1H), 8.07 (d, *J* = 7.5 Hz, 1H),7.90 (d, *J* = 7.5 Hz, 1H), 7.84 (t, *J* = 7.5 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.74-7.67 (m, 2H), 7.30 (d, *J* = 16.5 Hz, 1H), 7.17 (t, *J* = 8.5 Hz, 2H), 7.05 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 163.65 (d, *J* = 248.0 Hz), 137.68 (q, *J* = 32.0 Hz), 137.57, 137.35, 134.42, 133.75, 132.19, 130.72 (d, *J* = 8.5 Hz), 128.91 (q, *J* = 6.0 Hz), 128.21 (d, *J* = 8.6 Hz), 126.99 (q, *J* = 33.0 Hz), 123.08 (q, *J* = 274.0 Hz), 120.89 (q, *J* = 275.0 Hz), 116.31 (d, *J* = 22.0 Hz), 112.47. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.57 (s, 3F), -64.33 (s, 3F), -110.27-(-110.32) (m, 1F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}F_7N_2NaO_2S$ $[M+Na]^+$ 463.0322, found 463.0329.

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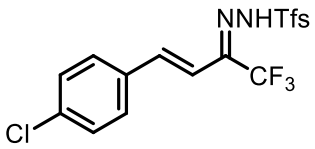


Yeild 88 %. 189-190 ºC. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.72 (s, 1H), 8.13 (d, *J* = 7.5 Hz, 1H), 8.01 (d, *J* = 7.5 Hz, 1H), 7.96-7.88 (m, 2H), 7.76 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 16.5 Hz, 1H), 7.12 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (125 MHz, DMSO) δ 141.5, 141.4 (q, *J* = 33.0 Hz) 141.3, 138.8, 138.5, 137.8, 136.3, 136.2, 134.4, 133.0 (q, *J* = 6.5 Hz), 131.0 (q, *J* = 33.0 Hz), 128.1, 126.4 (q, *J* = 272.5 Hz), 125.9, 117.3. **$^{19}$F NMR** (470 MHz, DMSO) δ -56.47 (s, 3F), -64.25 (s, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}ClF_6N_2NaO_2S$ $[M+Na]^+$ 479.0026, found

479.0021.

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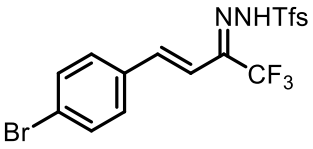


Yeild 85 %, m.p. 187-188 ºC. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.75 (s, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 7.5 Hz, 1H), 7.95-7.87 (m, 2H), 7.72-7.64 (m, 4H), 7.44 (d, *J* = 16.5 Hz, 1H), 7.10 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (125 MHz, DMSO) δ 141.6, 141.5 (q, *J* = 32.7 Hz) 141.4, 138.9, 138.6, 137.9, 136.4, 136.3, 134.5, 133.1 (q, *J* = 6.5 Hz), 131.0 (q, *J* = 32.7 Hz), 128.2, 126.5 (q, *J* = 272.5 Hz), 126.0, 117.4. **$^{19}$F NMR** (470 MHz, DMSO) δ -56.48 (s, 3F), -64.25 (s, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}BrF_6N_2NaO_2S$ $[M+Na]^+$ 522.9503, found 522.9521.

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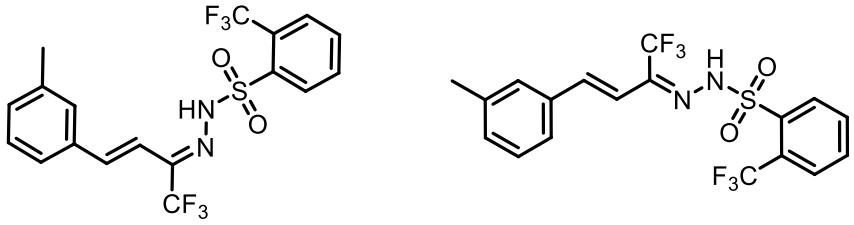


**major** **minor**

**major + minor** = 85 %, **major/minor** = 3 : 2

Yeild 85%, major: minor = 3: 2, **$^{1}$H NMR** (500 MHz, DMSO) δ 12.70 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.87 (t, *J* = 7.5 Hz, 1H), 7.82 (t, *J* = 7.5 Hz, 1H), 7.49-7.43 (m, 2H), 7.33 (d, *J* = 16.5 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 16.5 Hz, 1H), 2.26 (s, 3H). **$^{13}$C NMR** (150 MHz, DMSO) $^{13}$C NMR (151 MHz, DMSO) δ 148.44, 144.70, 139.09, 138.85, 138.65, 137.85 (q, *J* = 32.0 Hz), 137.46, 135.46, 134.52, 133.87, 132.30, 132.11, 131.45, 130.00, 129.43, 129.23, 129.01 (q, *J* = 6.0 Hz), 128.92, 128.51, 126.78 (q, *J* = 6.0 Hz), 126.62, 126.57, 125.92 (d, *J* = 32.5 Hz) 125.87, 125.82, 124.41, 124.22 (d, *J* = 274.0 Hz), 123.12, 123.10 (q, *J* = 274.0 Hz), 122.20 (q, *J* = 276.0 Hz),, 120.94 (d, *J* = 276.0 Hz), 112.33, 101.32, 21.39, 21.33. **$^{19}$F NMR** (470 MHz, DMSO) δ -55.88 (s, minor, 3F), -56.42 (s, major, 3F), -60.52 (s, minor, 3F), -64.14 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{14}F_6N_2NaO_2S$ $[M+Na]^+$ 459.0572, found 459.0579.

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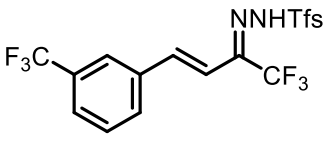

Yeild 78 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.76 (s, 1H), 8.06-8.03 (m, 2H), 7.97 (t, *J* = 8.0 Hz, 2H), 7.89-7.82 (m, 2H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.43 (d, *J* = 16.5 Hz, 1H), 7.20 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (125 MHz, DMSO) δ 148.44, 133.91, 132.33, 130.73, 130.48 (q, *J* = 32.0 Hz), 129.91, 126.80 (q, *J* = 5.0 Hz), 126.01, 125.79 (q, *J* = 3.5 Hz), 125.77, 125.75, 125.44 (q, *J* = 272.44 Hz), 124.40, 123.36, 124.21 (q, *J* = 3.5 Hz), 122.53 (d, *J* = 3.5 Hz), 120.07 (q, *J* = 279.0 Hz), 102.58. **$^{19}$F NMR** (470 MHz, DMSO) δ -55.86 (s, 3F), -60.56 (s, 3F), -61.30 (s, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{11}F_9N_2NaO_3S$ $[M+Na]^+$ 513.0290, found 513.0299.

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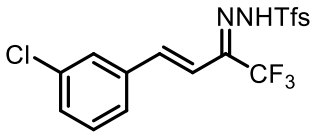


Yeild 83 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.75 (s, 1H), 8.05 (d, *J* = 7.5 Hz, 1H), 7.96 (d, *J* = 7.5 Hz, 1H), 7.91-7.78 (m, 3H), 7.64-7.58 (m, 1H), 7.45-7.32 (m, 3H), 7.06 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (125 MHz, DMSO) δ 148.35, 137.78, 137.25, 137.22 (q, *J* = 32.5 Hz), 134.65, 134.30, 133.96, 133.92, 132.14, 131.16, 130.29, 129.10 (q, *J* = 5.5 Hz), 127.68, 127.45, 123.10 (q, *J* = 276.0 Hz), 120.83 (q, *J* = 275.5 Hz), 113.94. **$^{19}$F NMR** (470 MHz, DMSO) δ -55.95 (s, 3F), -61.20 (s, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}ClF_6N_2NaO_2S$ $[M+Na]^+$ 479.0026, found 479.0018.

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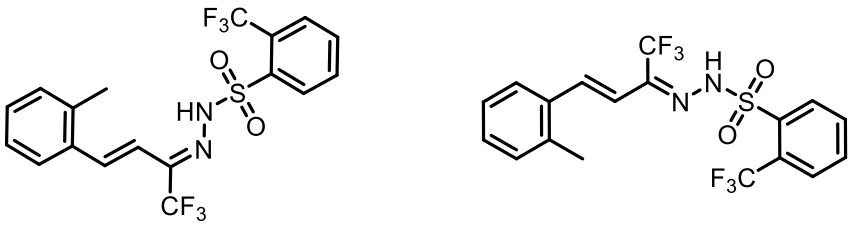


**major** **minor**

**major + minor** = 74 %, **major/minor** = 3 : 1

Yeild 74 %, major: minor = 3: 1. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.82 (s, 1H), 8.13 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.91 (t, J = 7.5 Hz, 1H), 7.88-7.82 (m, 1H), 7.37-7.31 (m, 4H), 7.26 (d, *J* = 2.5 Hz, 1H), 2.33 (s, 3H). **$^{13}$C NMR** (125 MHz, DMSO) δ 148.47, 143.78, 137.57, 137.83 (q, *J* = 32.8 Hz), 137.46, 136.30, 136.05, 134.54, 134.20, 133.89, 132.31, 132.12, 131.29, 131.17, 130.51, 129.64, 129.52, 129.03 (q, *J* = 6.0 Hz), 128.71, 126.79 (q, *J* = 6.0 Hz), 126.59, 126.47, 125.90 (q, *J* = 32.8 Hz), 124.40, 124.22 (q, *J* = 275.0 Hz), 122.30 (q, *J* = 268.0 Hz), 120.95, 119.91, 113.49, 104.01, 20.69, 19.40. **$^{19}$F NMR** (471 MHz, DMSO) δ -55.86 (s, minor, 3F), -56.41 (s, major, 3F), -60.23 (s, minor, 3F), -64.16 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{14}F_6N_2NaO_2S$ $[M+Na]^+$ 459.0572, found 459.0579.

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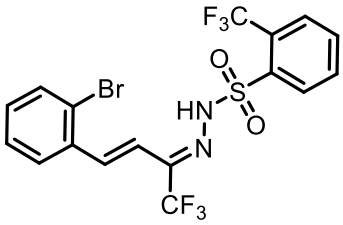
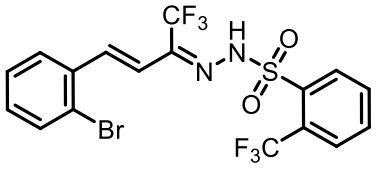



**major**




**minor**

**major + minor** = 75 %, **major/minor** = 3 : 2

Yeild 75 %, major: minor = 3: 2. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.86 (s, 1H), 8.15 (d, *J* = 7.5 Hz, 1H), 8.09-8.06 (m, 2H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.46-7.39 (m, 2H), 7.37-7.33 (m, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 148.39, 142.94, 137.10 (q, *J* = 32.0 Hz), 136.37, 134.80, 134.59, 133.89, 133.85, 133.68, 132.29, 132.26, 132.19, 131.91, 131.48, 130.12, 129.03 (q, *J* = 6.0 Hz), 128.62, 128.47, 128.36, 127.06, 126.83 (q, *J* = 3.0 Hz), 126.77 (q, *J* = 5.5 Hz), 125.94 (q, *J* = 32.0 Hz), 125.11, 125.07, 124.41, 123.29, 123.08 (q, *J* = 274.0 Hz), 123.02, 122.26, 122.17, 120.91 (d, *J* = 276.0 Hz), 115.33, 104.77. **$^{19}$F NMR** (565 MHz, DMSO) δ -55.90 (s, minor, 3F), -56.46 (s, major, 3F), -60.30 (s, minor, 3F), -64.38 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}BrF_6N_2NaO_2S$ $[M+Na]^+$ 522.9521, found 522.9515.

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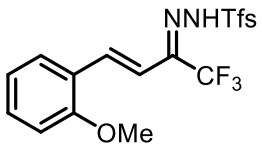


Yeild 72 %. **$^{1}$H NMR** (600 MHz, DMSO) δ 12.72 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.96 (t, *J* = 7.5 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 16.5 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 7.37 (d, *J* = 16.5 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 3.85 (s, 3H). **$^{13}$C NMR** (150 MHz, DMSO) δ 157.85, 138.23 (q, *J* = 32.0 Hz), 137.47, 134.55, 133.92, 132.80, 132.49, 132.07, 129.05 (q, *J* = 6.5 Hz), 126.90 (q, *J* = 32.0 Hz) 127.17, 123.74, 123.11 (q, *J* = 274.0 Hz), 121.14, 121.01 (q, *J* = 276.0 Hz), 112.25, 112.07, 56.26. **$^{19}$F NMR** (564 MHz, DMSO) δ -56.38 (s, 3F), -64.08 (s, 3F). **HRMS** (ESI) m/z calculated $C_{18}H_{14}F_6N_2NaO_3S$ $[M+Na]^+$ 475.0521, found 475.0526.

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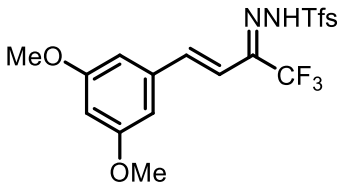

Yeild 84 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.66 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.90-7.81 (m, 2H), 7.84 (d, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 16.5 Hz, 1H), 7.02 (d, *J* = 16.5 Hz, 1H), 6.87 (d, *J* = 1.5 Hz, 2H), 6.51 (d, *J* = 1.5 Hz, 1H), 3.72 (s, 6H). **$^{13}$C NMR** (150 MHz, DMSO) δ 161.46, 161.27, 138.98, 137.45, 133.92, 132.06, 126.91 (d, *J* = 33.0 Hz), 126.80, 125.89 (d, *J* = 33.0 Hz), 124.41, 123.11 (d, *J* = 274.0 Hz), 120.92 (d, *J* = 276.0 Hz), 112.94, 106.72, 104.09, 55.90. **$^{19}$F NMR** (564 MHz, DMSO) δ -56.37 (s, 3F), -64.10 (s, 3F). **HRMS** (ESI) m/z calculated $C_{19}H_{16}F_6N_2NaO_4S$ $[M+Na]^+$ 505.0627, found 505.0627.

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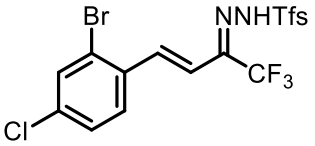


Yeild 80 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 13.97 (s, 1H), 8.04 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.89-7.94(m, 2H), 7.76 (s, 1H), 7.52 (s, 1H), 7.34 (d, *J* = 16.5 Hz, 1H), 7.24 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 148.41, 141.83, 135.25, 133.91, 133.19, 133.00, 132.34, 129.11, 128.64, 126.81 (q, *J* = 5.5 Hz), 125.89 (q, *J* = 32.5 Hz), 124.41, 124.22 (d, *J* = 273.0 Hz), 123.03, 105.06. **$^{19}$F NMR** (564 MHz, DMSO) δ -55.84 (s, 3F), -60.29 (s, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{10}BrClF_6N_2NaO_2S$ $[M+Na]^+$ 556.9131, found 556.9125.

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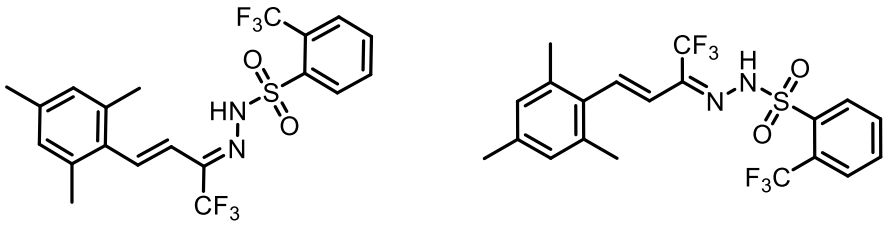


**major** **minor**

**major + minor** = 85 %, **major/minor** = 3 : 1

Yeild 85 %, major: minor = 3: 1. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.55 (s, 1H), 8.02 (d, *J* = 7.5 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.89-7.82 (m, 2H), 7.12 (d, *J* = 17.0 Hz, 1H), 6.85 (s, 2H), 6.74 (d, *J* = 17.0 Hz, 1H), 2.09-2.18 (m, 9H). **$^{13}$C NMR** (150 MHz, DMSO) δ 138.89, 138.18, 137.95, 137.68, 137.47, 136.42, 136.19, 135.48, 134.56, 134.53, 133.95, 133.90, 133.85, 132.38, 132.16, 132.05, 131.81, 129.34, 129.24, 129.06 (q, *J* = 5.0 Hz), 128.60, 126.87 (q, *J* = 33.0 Hz), 125.87 (q, *J* = 32.0 Hz), 124.41, 123.09 (q, *J* = 274.0 Hz), 121.02 (q, *J* = 276.0 Hz), 117.41, 104.16, 21.14, 21.12, 20.90, 20.85, 20.42, 19.54. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.28 (s, minor, 3F), -56.43 (s,

major, 3F), -64.01 (s, major, 3F), -67.76 (s, minor, 3F). **HRMS** (ESI) m/z calculated $C_{20}H_{18}F_6N_2NaO_2S$ $[M+Na]^+$ 487.0791, found 487.0787.

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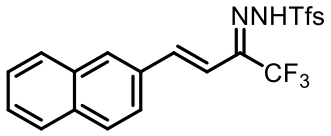


Yeild 90 %. **$^1$H NMR** (500 MHz, DMSO) δ 12.71 (s, 1H), 8.12 (s, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.94-7.90 (m, 2H), 7.90-7.82 (m, 4H), 7.50-7.46 (m, 3H), 7.24 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 138.89, 137.77 (q, *J* = 32.0 Hz), 137.51, 134.56, 134.16, 133.93, 133.41, 133.23, 132.12, 130.47, 129.07 (q, *J* = 6.5 Hz), 128.96, 128.92, 128.19, 127.87, 127.35, 126.94 (q, *J* = 33.0 Hz), 123.87, 123.14 (q, *J* = 274.0 Hz), 121.02 (d, *J* = 276.0 Hz), 112.85. **$^{19}$F NMR** (564 MHz, DMSO) δ -56.33 (s, 3F), -64.00 (s, 3F). **HRMS** (ESI) m/z calculated $C_{21}H_{14}F_6N_2NaO_2S$ $[M+Na]^+$ 495.0564, found 495.0572.

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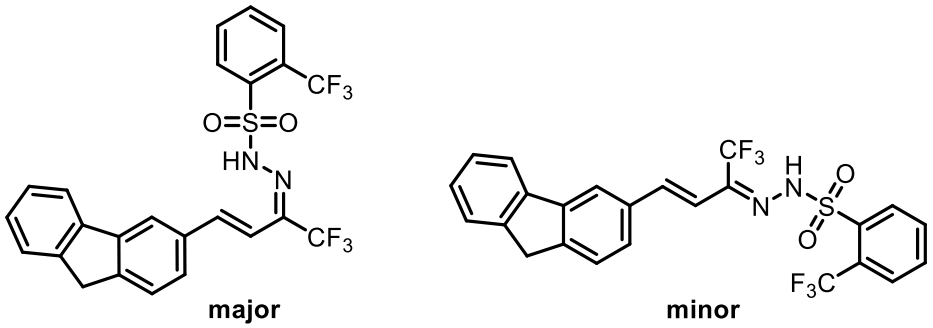


**major + minor = 87%, major/minor = 3:1**

Yeild 87%, major: minor = 3: 1. **$^1$H NMR** (500 MHz, DMSO) δ 12.71 (s, major, 1H), 12.03 (s, minor, 1H), 8.11-8.02 (m, major, 1H, minor, 1H), 7.99-7.92 (m, major, 2H, minor, 2H), 7.91-7.71 (m, major, 4H, minor, 4H), 7.67 (d, *J* = 7.5 Hz, major, 1H, minor, 1H), 7.53 (d, *J* = 7.5 Hz, major, 1H, minor, 1H), 7.41 (d, *J* = 16.5 Hz, major, 1H, minor, 1H), 7.35-7.23 (m, major, 2H, minor, 2H), 7.15 (d, *J* = 16.0 Hz, major, 1H, minor, 1H), 3.91 (s, major, 2H), 3.71 (s, minor, 2H). **$^{13}$C NMR** (150 MHz, DMSO) δ 148.44, 144.31, 144.27, 144.18, 143.85, 143.80, 143.56, 142.70, 142.26, 141.50, 140.88, 140.83, 139.29, 137.79, 137.51, 134.56, 134.21, 133.94, 133.68, 132.36, 132.11, 131.54, 129.06, 128.50, 128.03, 127.84, 127.72, 127.44, 127.38, 126.81, 125.74, 125.69, 125.33, 124.88, 124.55, 124.41, 122.69, 122.23, 121.10, 120.93, 120.89, 120.42, 120.11, 112.74, 111.65, 36.90, 36.77. **$^{19}$F NMR** (564 MHz, DMSO) δ -55.81(s, minor, 3F), -55.35 (s, major, 3F), -60.44(s, minor, 3F) -63.95 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{24}H_{16}F_6N_2NaO_2S$ $[M+Na]^+$ 533.0729, found 533.0725.

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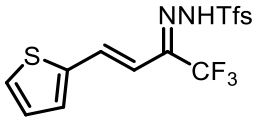


Yeild 80 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.73 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.95 (t, *J* = 7.5 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 7.75 (d, *J* = 5.0 Hz, 1H), 7.54 (d, *J* = 3.5 Hz, 1H), 7.36 (d, *J* = 16.5 Hz, 1H), 7.18-7.07 (m, 2H). **$^{13}$C NMR** (150 MHz, DMSO) δ 140.75, 137.81 (q, *J* = 32.0 Hz), 137.52 , 134.48, 133.89, 132.49, 132.14, 131.98, 130.59, 129.01 (q, *J* = 6.0 Hz), 128.98, 126.94 (q, *J* = 33.0 Hz), 123.11 (q, *J* = 274.0 Hz), 120.91 (q, *J* = 276.0 Hz), 110.99. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.36 (s, 3F), -64.10 (s, 3F). **HRMS** (ESI) m/z calculated $C_{15}H_{10}F_6N_2NaO_2S_2$ $[M+Na]^+$ 528.0423, found 528.0419.

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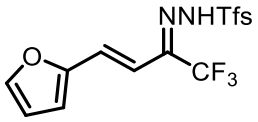


Yeild 78 %. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.74 (s, 1H), 8.10 (d, *J* = 8.0 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.97-7.83 (m, 3H), 7.17 (d, *J* = 16.5 Hz, 1H), 7.00 (d, *J* = 16.5 Hz, 1H), 6.95 (d, *J* = 3.0 Hz, 1H), 6.66 (dd, *J* = 3.0, 1.7 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 154.73, 149.78, 141.54 (q, *J* = 32.0 Hz), 140.96, 137.74, 137.16, 135.29, 132.28 (q, *J* = 6.0 Hz), 130.35 (q, *J* = 33.0 Hz), 129.05, 126.43 (q, *J* = 274.0 Hz), 124.27 (q, *J* = 276.0 Hz), 119.66, 116.85, 112.87. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.35 (s, 3F), -64.31 (s, 3F). **HRMS** (ESI) m/z calculated $C_{15}H_{10}F_6N_2NaO_3S$ $[M+Na]^+$ 435.0208, found 435.0214.

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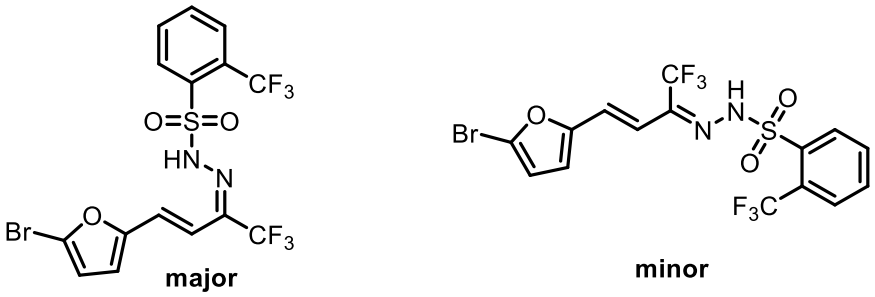


**major + minor = 80%, major/minor = 6:1**

Yeild 80 %, major: minor = 6: 1. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.81 (s, 1H), 8.08 (d, *J* = 7.5 Hz, 1H), 8.03 (d, *J* = 7.5 Hz, 1H), 7.98-7.88 (m, 2H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.11 (d, *J* = 16.5 Hz, 1H), 7.01-6.89 (m, 2H), 6.78 (d, *J* = 2.5 Hz, 1H). **$^{13}$C NMR** (125 MHz, DMSO) δ 153.44, 148.38, 137.65 (q, *J* = 32.2 Hz), 137.58, 134.45, 133.91, 133.87, 132.35, 131.94, 128.98 (q, *J* = 6.0 Hz), 126.95 (q, *J* = 275.0 Hz), 126.82 (q, *J* = 6.0 Hz), 125.99, 125.77, 124.55, 124.41, 123.10, 122.96, 120.80 (q, *J* = 275.0 Hz), 118.74, 115.63, 114.46, 111.33, 109.83, 100.86. **$^{19}$F NMR** (565 MHz,

DMSO) δ -55.84(s, minor, 3F), -56.31 (s, major, 3F), -60.55(s, minor, 3F) -64.23 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{15}H_9BrF_6N_2NaO_3S$ $[M+Na]^+$ 512.9314, found 512.9319.

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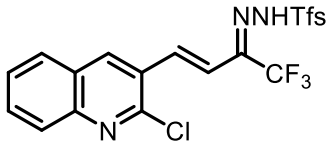


Yeild 70 %. **$^1$H NMR** (500 MHz, DMSO) δ 14.24 (s, 1H), 8.94 (s, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.97-7.91 (m, 2H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.90-7.86 (m, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 16.5 Hz, 1H), 7.47 (d, *J* = 16.5 Hz, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 148.41, 147.87, 147.09 , 140.71, 133.94, 132.41, 132.37, 128.80, 128.59, 128.20, 126.95, 126.83 (q, *J* = 5.5 Hz), 125.87 (q, *J* = 33.0 Hz), 124.41, 123.22 (q, *J* = 273.0 Hz), 122.95, 122.43, 122.06 (q, *J* = 269.5 Hz), 121.49, 105.84. **$^{19}$F NMR** (565 MHz, DMSO) δ -55.80 (s, 3F), -60.29 (s, 3F). **HRMS** (ESI) m/z calculated $C_{20}H_{12}ClF_6N_3NaO_2S$ $[M+Na]^+$ 530.0135, found 530.0161.

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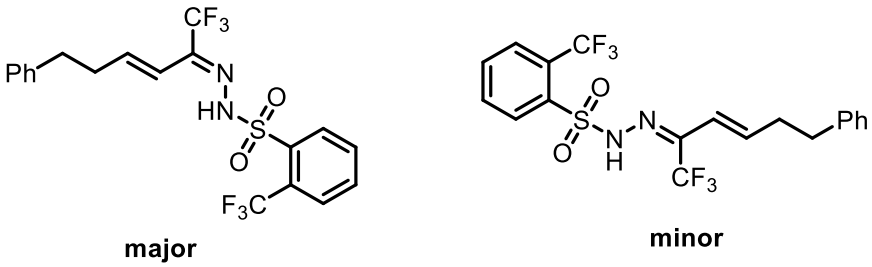


**major + minor = 66%, major/minor = 6:1**

Yeild 66%, major: minor = 6: 1. **$^1$H NMR** (500 MHz, DMSO) δ 12.48 (s, major, 1H, minor, 1H), 8.23-8.20 (m, minor, 1H), 8.11-8.07 (m, major, 2H), 8.03-8.01 (m, minor, 1H), 8.00-7.97 (m, major, 1H), 7.96-7.93 (m, major, 1H), 7.92-7.89 (m, minor, 1H), 7.84-7.79 (m, minor, 1H), 7.35-7.31 (m, major, 2H, minor, 2H), 7.28-7.25 (m, major, 2H, minor, 2H), 7.24-7.20 (m, major, 1H, minor, 1H), 6.72-6.69 (m, major, 1H, minor, 1H), 6.51-6.46 (m, major, 1H, minor, 1H), 2.84-2.82 (m, major, 1H, minor, 1H), 2.61-2.57 (m, major, 2H, minor, 2H), 2.55-2.54 (m, major, 1H, minor 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 143.86, 143.55, 142.24, 141.31, 138.17 (q, *J* = 32.0 Hz), 137.52, 134.48, 133.94, 133.86, 133.81, 133.42, 132.37, 131.89, 129.00 (q, *J* = 6.0 Hz), 128.80, 128.78, 128.73, 128.68, 126.94 (q, *J* = 33.0 Hz), 126.47, 126.20, 125.30, 124.41, 123.08 (q, *J* = 274.0 Hz), 120.80 (d, *J* = 276.0 Hz), 115.53, 35.42, 35.17, 34.08, 30.98. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.34 (s, major, 3F), -56.32 (s, minor, 3F), -64.59 (s, major, 3F), -68.37 (s, minor, 3F). **HRMS** (ESI) m/z calculated $C_{19}H_{16}F_6N_2NaO_2S$ $[M+Na]^+$ 473.0729, found 473.0722.

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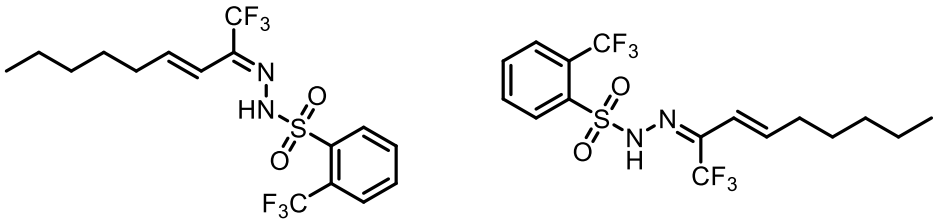

**major** **minor**

**major + minor = 63%, major/minor = 10:1**

Yeild 63%, major: minor = 10: 1. **$^{1}$H NMR** (500 MHz, DMSO) δ 13.34 (s, minor, 1H), 12.49 (s, major, 1H), 8.12 (d, *J* = 7.5 Hz, major, 1H, minor, 1H), 8.04 (d, *J* = 7.5 Hz, major, 1H, minor, 1H), 7.97 (t, *J* = 7.5 Hz, major, 1H, minor, 1H), 7.92 (t, *J* = 7.5 Hz, major, 1H, minor, 1H), 6.67 (d, *J* = 16.0 Hz, major, 1H, minor, 1H), 6.46-6.38 (m, major, 1H, minor, 1H), 2.65 (t, *J* = 7.5 Hz, minor, 2H), 2.32-2.21 (m, major, 2H), 1.69-1.55 (m, minor, 2H), 1.54-1.41 (m, major, 2H), 1.37-1.22 (m, major, 4H, minor, 4H), 0.88 (t, *J* = 6.5 Hz, major, 3H, minor, 3H). **$^{13}$C NMR** (150 MHz, DMSO) δ 145.78, 144.32, 138.32 (q, *J* = 32.0 Hz), 137.56, 134.34, 133.81, 133.72, 132.24, 131.97, 128.87 (q, *J* = 6.0 Hz), 127.03 (q, *J* = 32.0 Hz), 124.40, 123.05 (d, *J* = 274.0 Hz), 120.80 (d, *J* = 276.0 Hz), 115.23, 101.63, 33.47, 31.20, 31.10, 28.65 , 27.60, 25.01, 22.26, 22.14, 14.15, 14.12. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.00 (s, minor, 3F), -56.52 (s, major, 3F), -60.47 (s, minor, 3F), -64.76 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{16}H_{18}F_6N_2NaO_2S$ $[M+Na]^+$ 439.0885, found 439.0880.

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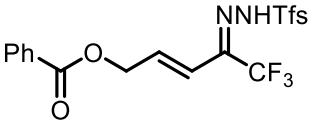

Yeild 75 %. **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 8.69 (s, 1H), 8.41-8.34 (m, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 7.91-7.85 (m, 1H), 7.81-7.73 (m, 2H), 7.60 (t, *J* = 7.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 6.57 (dt, *J* = 16.5, 4.0 Hz, 1H), 6.26 (d, *J* = 16.5 Hz, 1H), 5.00 (d, *J* = 4.0 Hz, 2H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 165.90, 138.97 (q, *J* = 35.0 Hz), 138.74, 135.75, 133.96, 133.88, 133.56, 132.59, 129.75, 129.21, 128.59, 128.42 (q, *J* = 6.5 Hz), 127.75 (q, *J* = 36.0 Hz), 122.69 (q, *J* = 274.0 Hz), 119.73 (q, *J* = 275.4 Hz), 114.23, 63.52. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -58.11 (s, 3F), -67.48 (s, 3F). **HRMS** (ESI) m/z calculated $C_{19}H_{14}F_6N_2NaO_4S$ $[M+Na]^+$ 503.0471, found 503.0450.

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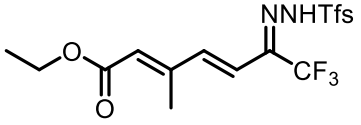

Yeild 72 %. **$^{1}$H NMR** (600 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.43-8.38 (m, 1H), 7.93-7.89 (m, 1H), 7.82-7.78 (m, 2H), 6.83 (d, *J* = 16.5 Hz, 1H), 6.35 (d, *J* = 16.5 Hz, 1H), 6.02 (s, 1H), 4.20 (q, *J* =

7.0 Hz, 2H), 2.28 (s, 3H), 1.30 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 165.82, 148.47, 144.50, 139.42 (q, *J* = 34.5 Hz), 135.58, 134.08, 134.04, 132.62, 128.45 (q, *J* = 6.5 Hz), 127.78 (q, *J* = 33.0 Hz), 126.72, 122.69 (q, *J* = 274.0 Hz), 119.80 (q, *J* = 276.0 Hz), 113.98, 60.46, 14.20, 13.06. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -58.07 (s, 3F), -66.78 (s, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{16}F_6N_2NaO_4S$ $[M+Na]^+$ 481.0627, found 481.0600.

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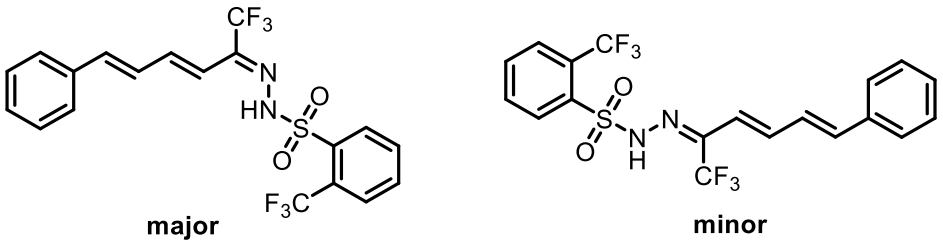


**major + minor = 78%, major/minor = 3:1**

Yeild 78 %, major: minor = 3: 1. **$^{1}$H NMR** (500 MHz, DMSO) δ 12.59 (s, 1H), 8.10 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.97 (t, *J* = 7.5 Hz, 1H), 7.92 (t, *J* = 7.5 Hz, 1H), 7.59 (d, *J* = 7.5 Hz, 2H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 15.0 Hz, 1H), 7.09-6.98 (m, 2H), 6.90 (d, *J* = 15.0 Hz, 1H). **$^{13}$C NMR** (125 MHz, DMSO) δ 148.43, 143.26, 140.48, 139.59, 137.62, 136.42, 136.39, 134.59, 134.43, 133.92, 133.84, 132.35, 132.25, 131.90, 129.55, 129.40, 129.37, 128.93, 128.37, 127.64, 127.14, 127.03, 126.82 (q, *J* = 5.5 Hz), 125.88 (q, *J* = 33.0 Hz), 124.41, 124.22 (q, *J* = 275.0 Hz), 122.20 (q, *J* = 269.0 Hz), 115.72, 115.00, 101.91. **$^{19}$F NMR** (565 MHz, DMSO) δ -55.83(s, major, 3F), -55.28 (s, minor, 3F), -60.50 (s, major, 3F) -64.32 (s, minor, 3F). **HRMS** (ESI) m/z calculated $C_{19}H_{14}F_6N_2NaO_2S$ $[M+Na]^+$ 471.0572, found 471.0578.

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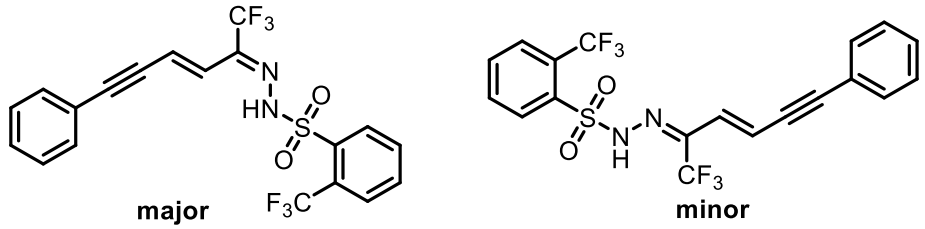


**major + minor = 68%, major/minor = 3:1**

Yeild 68 %, major: minor = 3: 1. **$^{1}$H NMR** (600 MHz, DMSO) δ 14.40 (s, major, 1H, minor, 1H), 8.18 (d, *J* = 7.5 Hz, minor, 1H), 8.12 (d, *J* = 7.5 Hz, major, 1H), 8.03 (d, *J* = 7.5 Hz, major, 1H), 7.96-7.88 (m, major, 2H, minor, 1H), 7.85 (d, *J* = 7.5 Hz, minor, 1H), 7.77 (t, *J* = 7.5 Hz, minor, 1H), 7.59 (d, *J* = 6.0 Hz, minor, 1H), 7.53 (d, *J* = 6.0 Hz, major, 1H), 7.50-7.31 (m, major, 4H, minor, 4H), 7.28-7.17 (m, major, 1H), 7.12-7.07 (m, minor, 1H), 6.61-6.48 (m, major, 1H, minor, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 148.39, 141.92, 134.33, 133.90, 133.80, 132.34, 132.09, 132.03, 131.93, 131.20, 130.24, 130.13, 129.42, 129.28, 129.16, 128.91 (q, *J* = 6.0 Hz), 126.81 (q, *J* = 5.5 Hz), 125.90 (q, *J* = 33.0 Hz), 124.73, 124.41, 124.34, 124.21 (q, *J* = 275.0 Hz), 122.19,

121.96, 121.67 (q, *J* = 269.0 Hz), 121.18, 120.78, 108.32, 94.35, 88.52, 84.88, 77.25. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -55.87 (s, major, 3F), -56.35 (s, minor, 3F), -60.55 (s, minor, 3F), -64.24 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{19}H_{12}F_6N_2NaO_2S$ $[M+Na]^+$ 469.0416, found 469.0460.

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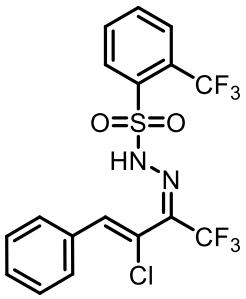
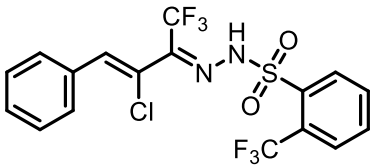



major




minor

**major + minor = 66%, major/minor = 3 : 1**

Yeild 66%, major: minor = 3: 1. **$^1$H NMR** (500 MHz, DMSO) δ 13.16 (s, 1H), 8.11-8.04 (m, 2H), 7.98 (t, *J* = 7.5 Hz, 1H), 7.93 (t, *J* = 7.5 Hz, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.52-7.43 (m, 3H), 7.27 (s, 1H). **$^{13}$C NMR** (150 MHz, DMSO) δ 149.41, 148.40, 140.25, 137.49, 136.14, 135.73 (q, *J* = 35.0 Hz), 134.65, 133.94, 133.89, 133.23, 132.33, 131.80, 130.48, 130.25, 130.13, 129.53, 129.11 (q, *J* = 5.5 Hz), 128.88, 128.76, 128.57, 127.77, 127.32, 127.04 (q, *J* = 33.0 Hz), 126.79 (q, *J* = 5.5 Hz), 125.91 (q, *J* = 32.0 Hz), 124.43, 123.04 (q, *J* = 274.0 Hz), 120.20 (q, *J* = 275.0 Hz), 114.80 (q, *J* = 35.0 Hz), 113.20. **$^{19}$F NMR** (565 MHz, DMSO) δ -55.88 (s, minor, 3F), -56.38 (s, major, 3F), -57.75(s, minor, 3F), -66.06 (s, major, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}ClF_6N_2NaO_2S$ $[M+Na]^+$ 479.0026, found 479.0026.

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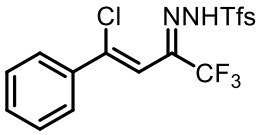


Yeild 83 %. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 8.41-8.37 (m, 2H), 7.93-7.89 (m, 1H), 7.80-7.78 (m, 2H), 7.68-7.64 (m, 2H), 7.52-7.42 (m, 3H), 6.34 (s, 1H). **$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 145.70, 137.47 (q, *J* = 37.0 Hz), 135.97, 134.60, 133.97, 133.64, 132.63, 131.38, 128.94, 128.37 (q, *J* = 6.0 Hz), 127.89 (q, *J* = 33.0 Hz), 127.01, 122.66 (q, *J* = 274.0 Hz), 119.60 (q, *J* = 278.0 Hz), 109.53. **$^{19}$F NMR** (565 MHz, $CDCl_3$) δ -57.92 (s, 3F), -68.83 (s, 3F). **HRMS** (ESI) m/z calculated $C_{17}H_{11}ClF_6N_2NaO_2S$ $[M+Na]^+$ 479.0026, found 479.0006.

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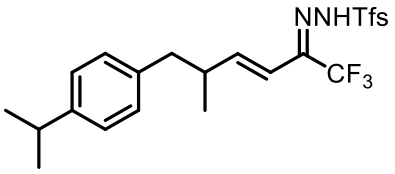

Yeild 72 %. **$^1$H NMR** (600 MHz, DMSO) δ 8.91 (s, 1H), 8.43-8.38 (m, 1H), 7.93-7.89 (m, 1H), 7.78-7.73 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.46 (dd, *J* = 16.5, 6.0 Hz, 1H), 5.97 (d, *J* = 16.5 Hz, 1H), 2.98-2.88 (m, 1H), 2.72-2.63 (m, 3H), 1.29 (d, *J* = 7.0 Hz, 6H), 1.11 (d, *J* = 5.8 Hz, 3H). **$^{13}$C NMR** (125 MHz, DMSO) δ 148.83, 146.46, 138.19 (q, *J* = 32.0 Hz), 137.52, 137.25, 134.45, 133.82, 131.92, 129.40, 128.98 (q, *J* = 6.0 Hz), 126.96 (q, *J* = 33.0 Hz), 126.50, 123.07 (d, *J* = 274.0 Hz), 120.81 (d, *J* = 276.0 Hz), 113.65, 41.67, 33.46, 24.34, 18.76. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.37 (s, 3F), -64.46 (s, 3F). **HRMS** (ESI) m/z calculated $C_{23}H_{24}F_6N_2NaO_2S$ $[M+Na]^+$ 529.1355, found 529.1362.

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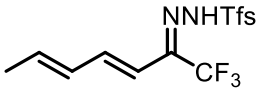


Yeild 75 %. **$^1$H NMR** (600 MHz, DMSO) δ 12.43 (s, 1H), 8.08-8.00 (m, 2H), 7.94 (t, *J* = 7.5 Hz, 1H), 7.90 (t, *J* = 7.5 Hz, 1H), 6.80-6.72 (m, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 6.31-6.19 (m, 2H), 1.89-1.79 (m, 3H). **$^{13}$C NMR** (125 MHz, DMSO) δ 140.07, 139.92, 138.91 (q, *J* = 32.0 Hz), 137.52, 134.47, 133.86, 131.89, 131.57, 129.00 (q, *J* = 6.0 Hz), 126.96 (q, *J* = 33.0 Hz), 123.08 (d, *J* = 274.0 Hz), 120.86 (d, *J* = 276.0 Hz), 113.44, 19.00. **$^{19}$F NMR** (565 MHz, DMSO) δ -56.33 (s, 3F), -64.41 (s, 3F). **HRMS** (ESI) m/z calculated $C_{14}H_{12}F_6N_2NaO_2S$ $[M+Na]^+$ 409.0416, found 409.0422.

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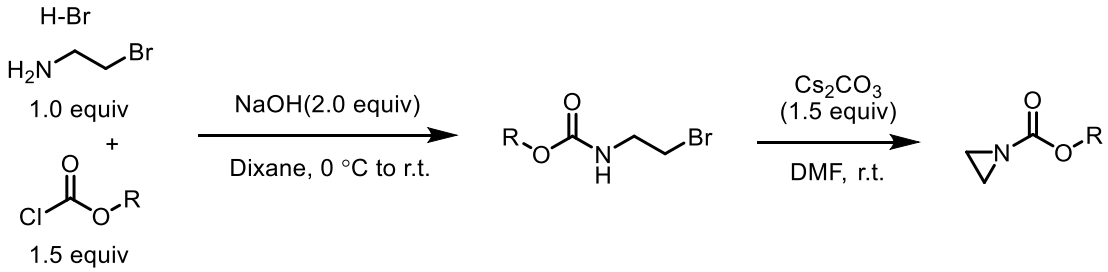
**3.2 General procedure for the synthesis of aziridines**




To an oven-dried 50 mL round-bottomed flask with a magnetic stir bar containing 2-bromoethylamine hydrobromide (10 mmol, 1.0 equiv) was slowly added sodium hydroxide solution (1 M, 15 mL) and chloroacetate (15 mmol, 1.5 equiv) at 0 ℃. After stirring overnight at room temperature, the reaction mixture was extracted with dichloromethane (3 × 20 mL), dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The crude mixture was purified by rapid silica gel column chromatography to afford the amide product.

Under nitrogen atmosphere, a clean and oven-dried nitrogen-filled 100 ml eggplant bottle with a magnetic stir bar was charged with cesium carbonate (1.5 equiv). Then the amide (10 mmol, 1.0 equiv) obtained in the previous step was dissolved in DMF (90 ml) and injected into the

eggplant bottle. After stirring for 5-6 hours at 40 ℃, the suspension was extracted with DCM (3 × 20 mL), dried over anhydrous sodium, and concentrated under reduced pressure. The resultant residue was purified by silica gel column chromatography to obtain pure aziridine.

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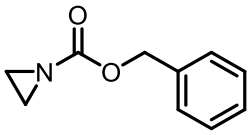

Benzyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.38-7.34 (m, 5H), 5.13 (s, 2H), 2.22 (s, 4H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.61, 135.81, 128.60, 128.37, 128.20, 68.21, 25.86. **HRMS** (ESI) *m/z* calculated $C_{10}H_{11}NNaO_2$ $[M+Na]^+$ 200.0682, found 200.0678.

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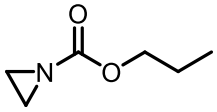

Propyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.06 (t, *J* = 7.0 Hz, 2H), 2.21 (s, 4H), 1.72-1.64 (m, 1H), 0.96 (t, *J* = 7.5 Hz, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.99, 68.19, 25.74, 22.04, 10.21. **HRMS** (ESI) *m/z* calculated $C_6H_{11}NNaO_2$ $[M+Na]^+$ 152.0682, found 152.0688.

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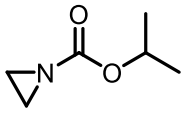

Isopropyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.94-4.87 (m, 1H), 2.19 (s, 4H), 1.27 (d, *J* = 6.5 Hz, 6H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.42, 70.04, 53.42, 25.72, 21.74. **HRMS** (ESI) *m/z* calculated $C_6H_{11}NNaO_2$ $[M+Na]^+$ 152.0682, found 152.0682.

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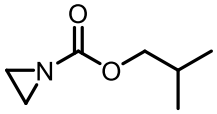

Isobutyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 3.86 (d, *J* = 7.0 Hz, 2H), 2.19 (s, 4H), 1.98-1.90 (m, 1H), 0.92 (d, *J* = 7.0 Hz, 6H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 164.0, 77.30, 77.05, 76.79, 72.66, 27.80, 25.74, 18.94. **HRMS** (ESI) *m/z* calculated $C_7H_{13}NNaO_2$ $[M+Na]^+$ 166.0838, found 166.0830.

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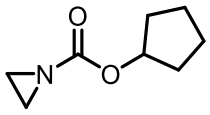

Cyclopentylmethyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.09 (s, 1H), 2.18 (s, 4H), 1.89-1.83 (m, 2H), 1.77-1.70 (m, 4H), 1.63-1.55 (m, 2H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.76, 76.79, 32.63, 25.80, 23.66. **HRMS** (ESI) *m/z* calculated $C_8H_{13}NNaO_2$ $[M+Na]^+$ 178.0838, found 178.0833.

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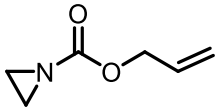

Allyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 5.99-5.86 (m, 1H), 5.36-5.31 (m, 1H), 5.27-5.24 (m, 1H), 4.62-4.57 (m, 2H), 2.23 (s, 4H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.4, 131.97, 118.44, 67.06, 25.77. **HRMS** (ESI) *m/z* calculated $C_6H_9NNaO_2$ $[M+Na]^+$ 150.0525, found 150.0517.

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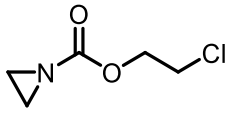

2-Chloroethyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.36 (t, $J$ = 6.0 Hz, 2H), 3.70 (t, $J$ = 6.0 Hz, 2H), 2.26 (s, 4H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.27, 65.80, 41.57, 25.96. **HRMS** (ESI) *m/z* calculated $C_5H_8ClNNaO_2$ $[M+Na]^+$ 172.0136, found 172.0132.

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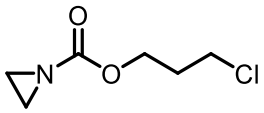

3-Chloroethyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.26 (t, $J$ = 6.0 Hz, 2H), 3.64 (t, $J$ = 6.5 Hz, 2H), 2.22 (s, 4H), 2.16-2.10 (m, 2H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.58, 63.25, 41.08, 31.61, 25.82. **HRMS** (ESI) *m/z* calculated $C_6H_{10}ClNNaO_2$ $[M+Na]^+$ 186.0292, found 186.0283.

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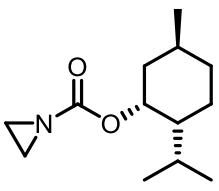

(1*R*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl aziridine-1-carboxylate, colorless oil. **$^1$H NMR** (500 MHz, $CDCl_3$) δ 4.54 (td, *J* = 11.0, 4.5 Hz, 1H), 2.17 (s, 3H), 1.99 (d, *J* = 12.0 Hz, 1H), 1.95-1.85 (m, 1H), 1.66 (d, *J* = 12.0 Hz, 2H), 1.53-1.43 (m, 1H), 1.39 (t, *J* = 12.0 Hz, 1H), 1.25-0.91 (m, 3H), 0.88 (d, *J* = 7.0 Hz, 7H), 0.75 (d, *J* = 7.0 Hz, 2H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.64, 47.09, 40.83, 34.20, 31.37, 26.23, 25.79, 23.40, 21.99, 20.76, 16.29. **HRMS** (ESI) *m/z* calculated $C_{13}H_{23}NNaO_2$ $[M+Na]^+$ 248.1621, found 248.1627.

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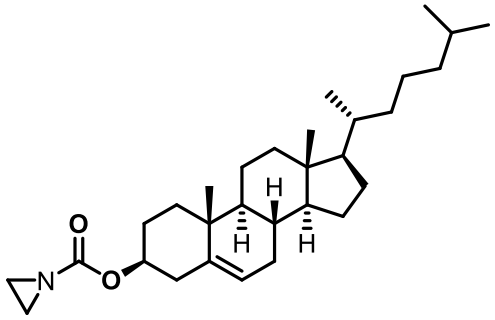


(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl aziridine-1-carboxylate, white solid. **$^1$H NMR** (600 MHz, $CDCl_3$) δ 5.38 (d, J = 4.0 Hz, 1H), 4.55-4.47 (m, 1H), 2.38-2.31 (m, 2H), 2.19 (s, 4H), 2.03-1.94 (m, 2H), 1.91-1.80 (m, 3H), 1.70-1.40 (m, 8H), 1.40-1.30 (m, 3H), 1.27-1.22 (m, 1H), 1.19-1.06 (m, 7H), 1.03-0.94 (m, 6H), 0.91 (d, J = 6.6 Hz, 3H), 0.86 (dd, J = 6.6, 2.8 Hz, 6H), 0.68 (s, 3H). **$^{13}$C NMR** (125 MHz, $CDCl_3$) δ 163.35, 139.50, 122.80, 76.20, 56.70, 56.16, 50.02, 42.33, 39.74, 39.53, 38.08, 36.94, 36.57, 36.20, 35.80, 31.89 (d, *J* = 6.0 Hz), 28.23, 28.02, 27.74, 25.84, 24.29, 23.84, 22.82, 22.57, 21.05, 19.31, 18.73, 11.87. **HRMS** (ESI) *m/z* calculated $C_{30}H_{49}NNaO_2$ $[M+Na]^+$ 478.3655, found 478.3652.

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## 4. Mechanistic Studies

### 4.1 DFT calculations

All DFT calculations described in this work were carried out with the Gaussian16 suite of programs[6]. All geometry optimizations and single point calculations were presented by using the B3LYP functional[7,8] and GD3BJ empirical dispersion[9] and def2-SVP basis set[10] for all atoms by using the SMD solvent model[11] for dichloromethane. The nature of the local minima was established with analytical frequency calculations and geometry optimizations were computed without any symmetry constraints. Intrinsic reaction coordinate (IRC)[12,13] calculations were carried out to ascertain the true nature of the transition states. 3D structures of optimized geometries were generated using CYLview visualization software.

### 4.2 Carbene formation process

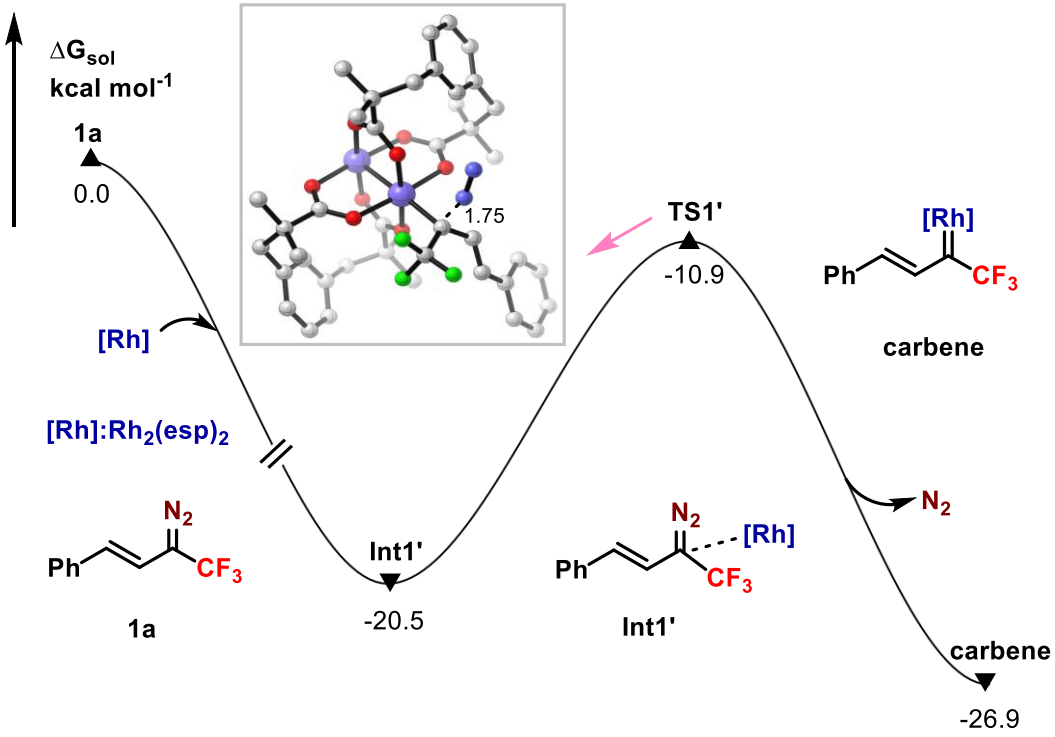


**Figure S1**. Gibbs free energy profile (in kcal $mol^{-1}$) of the generation for trifluoromethyl vinyl rhodium carbene

### 4.3 Gibbs free energy profile (in kcal mol$^{-1}$) of one carbon insertion into C–N bond

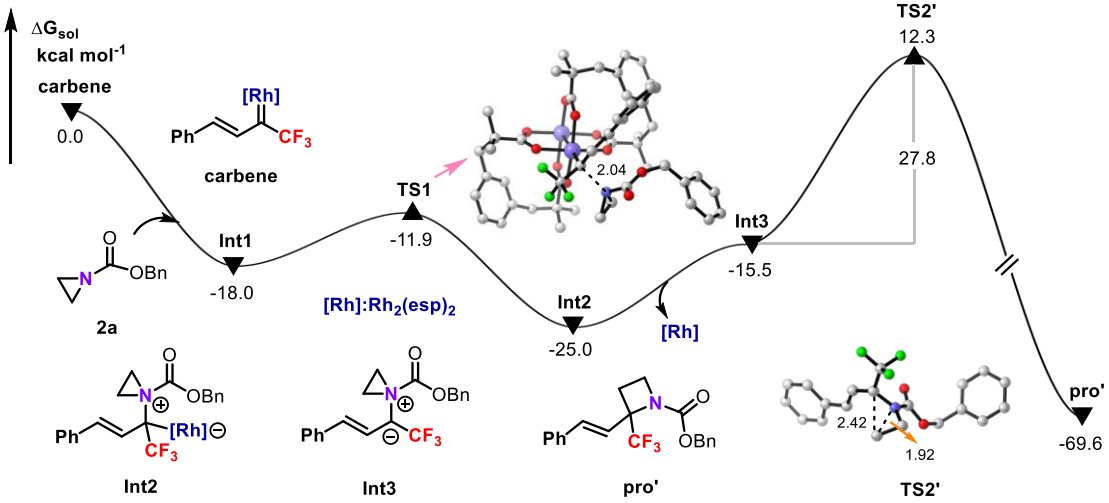


**Figure S2**. Gibbs free energy profile (in kcal mol$^{-1}$) of one carbon insertion into C–N bond.

### 4.4 Cartesian coordinates of all optimized structures

**1a**

| | |
|---|---|
| Zero-point correction= | 0.153775 (Hartree/Particle) |
| Thermal correction to Energy= | 0.166696 |
| Thermal correction to Enthalpy= | 0.167640 |
| Thermal correction to Gibbs Free Energy= | 0.112227 |
| Sum of electronic and zero-point Energies= | -793.558845 |
| Sum of electronic and thermal Energies= | -793.545924 |
| Sum of electronic and thermal Enthalpies= | -793.544980 |
| Sum of electronic and thermal Free Energies= | -793.600393 |

| | | | |
|---|---|---|---|
| N | -2.63356000 | 1.61125900 | 0.00003100 |
| N | -3.30484600 | 2.52781900 | 0.00004800 |
| C | -2.52788100 | -0.76711200 | -0.00007700 |
| F | -3.86273400 | -0.63078100 | -0.00046300 |
| F | -2.19322600 | -1.50508200 | -1.07681000 |
| F | -2.19388700 | -1.50489800 | 1.07701200 |
| C | 4.17392300 | -1.12510000 | -0.00007100 |
| C | 2.78141300 | -1.22360100 | 0.00011100 |
| C | 1.96710200 | -0.07213900 | 0.00018600 |
| C | 2.60490800 | 1.18729900 | 0.00008000 |
| C | 3.99500500 | 1.28445900 | -0.00010400 |
| C | 4.78908500 | 0.13008700 | -0.00017700 |
| H | 4.78139000 | -2.03379300 | -0.00013400 |
| H | 2.30548700 | -2.20796000 | 0.00019600 |
| H | 2.00952800 | 2.10269000 | 0.00014200 |

| | | | |
|---|---|---|---|
| H | 4.46618200 | 2.27079600 | -0.00017700 |
| C | 0.51224100 | -0.24335000 | 0.00035000 |
| C | -0.40505500 | 0.75122200 | -0.00000100 |
| H | 0.17699400 | -1.28379600 | 0.00072300 |
| H | -0.08713900 | 1.79690600 | -0.00035500 |
| C | -1.84303400 | 0.56774600 | -0.00001300 |
| H | 5.87878200 | 0.21139700 | -0.00030700 |

**Int1'**

Zero-point correction= 0.827789 (Hartree/Particle)
Thermal correction to Energy= 0.883141
Thermal correction to Enthalpy= 0.884085
Thermal correction to Gibbs Free Energy= 0.741297
Sum of electronic and zero-point Energies= -2858.586034
Sum of electronic and thermal Energies= -2858.530683
Sum of electronic and thermal Enthalpies= -2858.529738
Sum of electronic and thermal Free Energies= -2858.672527

| | | | |
|---|---|---|---|
| N | -0.77719100 | -0.79359800 | -3.09301200 |
| N | -1.85455700 | -0.87212600 | -3.40179000 |
| C | 1.25231400 | 0.40558200 | -3.33938000 |
| F | 0.46544500 | 1.45967000 | -3.60323500 |
| F | 2.29943900 | 0.81647000 | -2.62133200 |
| F | 1.74111900 | -0.02127500 | -4.52552900 |
| Rh | -0.88362400 | 0.92322600 | 1.76666700 |
| O | 0.91440300 | 0.23096100 | 2.48602500 |
| O | -0.07597400 | 2.76169700 | 1.29824000 |
| O | 1.55601600 | -0.45060200 | 0.44468300 |
| O | 0.56616200 | 2.02645600 | -0.72382000 |
| C | 1.74101600 | -0.30835000 | 1.68861500 |
| C | 3.05529700 | -0.82261100 | 2.28831000 |
| C | 2.70585200 | -1.85051000 | 3.38026500 |
| H | 2.08750300 | -1.40010800 | 4.16970400 |
| H | 3.62942000 | -2.23798700 | 3.83839800 |
| H | 2.15516400 | -2.70332900 | 2.95187600 |
| C | 3.91957000 | -1.48821500 | 1.21433500 |
| H | 3.40806400 | -2.36044400 | 0.78791500 |
| H | 4.86648800 | -1.83034300 | 1.66048800 |
| H | 4.15137500 | -0.80290700 | 0.38869400 |
| C | 3.79865600 | 0.37942600 | 2.94738200 |
| H | 3.20639100 | 0.71302500 | 3.81180800 |
| H | 4.75592300 | -0.00583400 | 3.33205100 |
| C | 4.04059700 | 1.55120100 | 2.02636000 |
| C | 5.20190600 | 1.64961600 | 1.24466500 |

| | | | |
|---|---|---|---|
| H | 5.97683400 | 0.88353400 | 1.32864600 |
| C | 5.37585200 | 2.72584000 | 0.37001900 |
| H | 6.28852000 | 2.79815700 | -0.22748000 |
| C | 4.39127800 | 3.71139400 | 0.25629400 |
| H | 4.53523500 | 4.54985000 | -0.42983100 |
| C | 3.22081600 | 3.63748400 | 1.02702000 |
| C | 3.07242900 | 2.55908100 | 1.91110300 |
| H | 2.17092700 | 2.49698000 | 2.52135400 |
| C | 2.11702900 | 4.65984000 | 0.89678200 |
| H | 2.53651600 | 5.63926500 | 0.61826000 |
| H | 1.61642700 | 4.78021200 | 1.86850600 |
| C | 1.02904500 | 4.31056200 | -0.16451000 |
| C | 1.61268600 | 4.33416700 | -1.58115000 |
| H | 2.41031600 | 3.59068000 | -1.70772900 |
| H | 2.02654400 | 5.33247800 | -1.79320400 |
| H | 0.83670400 | 4.11613700 | -2.32889400 |
| C | -0.11939300 | 5.32995600 | -0.05426200 |
| H | -0.92092700 | 5.09596400 | -0.77318500 |
| H | 0.25458600 | 6.34145800 | -0.27785200 |
| H | -0.55244500 | 5.33430000 | 0.95623600 |
| C | 0.46218900 | 2.92443800 | 0.16129800 |
| Rh | -0.20495900 | 0.16414300 | -0.41026600 |
| O | -1.99897200 | 0.86203400 | -1.11710100 |
| O | -1.02960600 | -1.66700300 | 0.04536700 |
| O | -2.64816700 | 1.54349000 | 0.92036600 |
| O | -1.66870500 | -0.94670000 | 2.07321600 |
| C | -2.82931100 | 1.40567800 | -0.32259000 |
| C | -4.13136400 | 1.92810200 | -0.93774600 |
| C | -3.75854900 | 2.97461000 | -2.00464100 |
| H | -3.13001000 | 2.53331300 | -2.79126200 |
| H | -4.67217200 | 3.37506100 | -2.47126000 |
| H | -3.20829300 | 3.81586000 | -1.55369000 |
| C | -5.01658200 | 2.56924400 | 0.13502700 |
| H | -4.50803700 | 3.42475500 | 0.60317400 |
| H | -5.94916800 | 2.93243700 | -0.32438900 |
| H | -5.27596300 | 1.85774200 | 0.93046700 |
| C | -4.86360500 | 0.74073500 | -1.63587000 |
| H | -4.25380600 | 0.42453900 | -2.49423000 |
| H | -5.81189300 | 1.13618100 | -2.03202200 |
| C | -5.12779700 | -0.44982600 | -0.74527600 |
| C | -6.31421100 | -0.57221900 | -0.00568800 |
| H | -7.09253700 | 0.18903200 | -0.10200600 |
| C | -6.50849200 | -1.66561900 | 0.84318400 |
| H | -7.44030100 | -1.75589600 | 1.40770200 |

| | | | |
|---|---|---|---|
| C | -5.52007700 | -2.64552100 | 0.97324800 |
| H | -5.68007900 | -3.49715400 | 1.63932700 |
| C | -4.32538100 | -2.54844000 | 0.24355900 |
| C | -4.15675900 | -1.45298000 | -0.61500700 |
| H | -3.23672400 | -1.37398300 | -1.19220900 |
| C | -3.21825100 | -3.56510100 | 0.38746400 |
| H | -3.63805100 | -4.55016500 | 0.64439500 |
| H | -2.69661100 | -3.67185900 | -0.57488300 |
| C | -2.15452200 | -3.22507600 | 1.47582400 |
| C | -2.76872200 | -3.26686800 | 2.87831300 |
| H | -3.57052200 | -2.52556700 | 2.99584800 |
| H | -3.18889700 | -4.26698100 | 3.06766400 |
| H | -2.00782000 | -3.06282700 | 3.64569400 |
| C | -1.00502600 | -4.24487400 | 1.37685000 |
| H | -0.20212000 | -4.00642600 | 2.09235200 |
| H | -1.37954400 | -5.25475000 | 1.60573100 |
| H | -0.57281000 | -4.25629000 | 0.36681600 |
| C | -1.57628100 | -1.83639500 | 1.18072200 |
| C | 5.12705400 | -4.67575700 | -1.32048800 |
| C | 4.46415300 | -3.56161700 | -1.83854700 |
| C | 3.07154900 | -3.40963000 | -1.68974800 |
| C | 2.36450500 | -4.41382600 | -0.99675000 |
| C | 3.02636000 | -5.52563900 | -0.47953900 |
| C | 4.41149700 | -5.66382300 | -0.63782800 |
| H | 6.20863400 | -4.77019600 | -1.44628400 |
| H | 5.02944400 | -2.78560800 | -2.36134400 |
| H | 1.29011300 | -4.31263200 | -0.83767600 |
| H | 2.45917200 | -6.28792400 | 0.06080600 |
| C | 2.43511900 | -2.19882300 | -2.21554600 |
| C | 1.11081000 | -1.95460600 | -2.22502900 |
| H | 3.12991600 | -1.44248300 | -2.58613000 |
| H | 0.40088000 | -2.69390800 | -1.85031600 |
| C | 0.48050700 | -0.68718800 | -2.62234000 |
| H | 4.92824800 | -6.53397600 | -0.22565700 |

**TS1'**

| | |
|---|---|
| Zero-point correction= | 0.825248 (Hartree/Particle) |
| Thermal correction to Energy= | 0.880691 |
| Thermal correction to Enthalpy= | 0.881635 |
| Thermal correction to Gibbs Free Energy= | 0.738537 |
| Sum of electronic and zero-point Energies= | -2858.570508 |
| Sum of electronic and thermal Energies= | -2858.515066 |
| Sum of electronic and thermal Enthalpies= | -2858.514122 |
| Sum of electronic and thermal Free Energies= | -2858.657220 |

| | | | |
|---|---|---|---|
| N | 0.81150500 | 0.94656300 | -3.20657700 |
| N | 1.89354700 | 1.17471600 | -3.28563200 |
| C | -1.35251800 | -0.28532000 | -3.16013700 |
| F | -0.57954600 | -1.31618900 | -3.52946600 |
| F | -2.43888300 | -0.76412800 | -2.54146600 |
| F | -1.77456400 | 0.29530200 | -4.30860300 |
| Rh | 0.94843100 | -1.01290800 | 1.71463700 |
| O | -0.84530000 | -0.37358400 | 2.51400400 |
| O | 0.14577300 | -2.83574600 | 1.17185700 |
| O | -1.54559800 | 0.38032300 | 0.51685800 |
| O | -0.55396200 | -2.01978800 | -0.80212200 |
| C | -1.69459900 | 0.18389500 | 1.75979800 |
| C | -3.00578900 | 0.66061500 | 2.39822200 |
| C | -2.65070200 | 1.65765600 | 3.51628900 |
| H | -2.00997700 | 1.19086000 | 4.27791000 |
| H | -3.57014000 | 2.01614100 | 4.00541100 |
| H | -2.12031600 | 2.53230200 | 3.10638400 |
| C | -3.89977000 | 1.34563200 | 1.36002200 |
| H | -3.40780600 | 2.23570700 | 0.94490700 |
| H | -4.84092700 | 1.66446900 | 1.83498200 |
| H | -4.14153500 | 0.67908400 | 0.52174600 |
| C | -3.72018800 | -0.57281300 | 3.03023700 |
| H | -3.10343300 | -0.92960400 | 3.86790000 |
| H | -4.67276800 | -0.21413000 | 3.45077000 |
| C | -3.97044900 | -1.71346100 | 2.07275600 |
| C | -5.15613200 | -1.80514200 | 1.32769100 |
| H | -5.94174200 | -1.05823300 | 1.46741600 |
| C | -5.34061100 | -2.85058500 | 0.41850600 |
| H | -6.27206000 | -2.91835300 | -0.14986500 |
| C | -4.34259300 | -3.81142300 | 0.23359700 |
| H | -4.49490400 | -4.62622300 | -0.47876300 |
| C | -3.14698400 | -3.74315200 | 0.96537800 |
| C | -2.98763600 | -2.69611800 | 1.88470900 |
| H | -2.06623200 | -2.63920600 | 2.46482700 |
| C | -2.03042700 | -4.73848200 | 0.75657600 |
| H | -2.44296600 | -5.71373200 | 0.45380400 |
| H | -1.49407900 | -4.88765600 | 1.70488500 |
| C | -0.98613100 | -4.32775900 | -0.32607000 |
| C | -1.62054000 | -4.29618500 | -1.72041700 |
| H | -2.43033400 | -3.55805800 | -1.78543200 |
| H | -2.03105900 | -5.28930100 | -1.96196100 |
| H | -0.87461400 | -4.03602000 | -2.48489400 |
| C | 0.17600400 | -5.33736900 | -0.30353800 |

| | | | |
|---|---|---|---|
| H | 0.94887500 | -5.06084900 | -1.03861900 |
| H | -0.19444200 | -6.34237800 | -0.56032500 |
| H | 0.64500300 | -5.38220700 | 0.68978000 |
| C | -0.41937900 | -2.95137300 | 0.04523200 |
| Rh | 0.19406600 | -0.15139300 | -0.43617300 |
| O | 1.98986300 | -0.76283500 | -1.21529000 |
| O | 1.00965000 | 1.66555700 | 0.10872000 |
| O | 2.68876700 | -1.55900000 | 0.76467700 |
| O | 1.70728400 | 0.85897500 | 2.08659700 |
| C | 2.84253000 | -1.34286100 | -0.46752800 |
| C | 4.14134300 | -1.80735200 | -1.13687500 |
| C | 3.76627300 | -2.76470200 | -2.28310600 |
| H | 3.12746400 | -2.26504400 | -3.02525400 |
| H | 4.67790800 | -3.11928600 | -2.78920500 |
| H | 3.22512200 | -3.64402700 | -1.89863400 |
| C | 5.03746900 | -2.52902700 | -0.12583600 |
| H | 4.53535100 | -3.42083400 | 0.27688900 |
| H | 5.96716700 | -2.85124800 | -0.62041000 |
| H | 5.30117400 | -1.88222300 | 0.72166900 |
| C | 4.86764900 | -0.56546500 | -1.73915100 |
| H | 4.26124900 | -0.18934700 | -2.57553700 |
| H | 5.82060200 | -0.92324300 | -2.15941900 |
| C | 5.11934100 | 0.55916000 | -0.76321300 |
| C | 6.30034100 | 0.64025500 | -0.00937700 |
| H | 7.08456600 | -0.10801600 | -0.14959900 |
| C | 6.48256900 | 1.67853200 | 0.90893900 |
| H | 7.41024100 | 1.73723700 | 1.48435400 |
| C | 5.48891600 | 2.64464100 | 1.09369200 |
| H | 5.64129900 | 3.45447200 | 1.81175300 |
| C | 4.29914700 | 2.58692300 | 0.35209900 |
| C | 4.14166000 | 1.54518700 | -0.57221600 |
| H | 3.22443900 | 1.49864100 | -1.15634300 |
| C | 3.18363400 | 3.58630500 | 0.54420100 |
| H | 3.59301100 | 4.55915200 | 0.85828500 |
| H | 2.66987300 | 3.74149500 | -0.41587100 |
| C | 2.11269000 | 3.17852900 | 1.60181500 |
| C | 2.70908000 | 3.17641900 | 3.01261900 |
| H | 3.52979700 | 2.45294300 | 3.10784000 |
| H | 3.09873900 | 4.17854500 | 3.25065600 |
| H | 1.94571500 | 2.91730400 | 3.76079800 |
| C | 0.94336100 | 4.17758900 | 1.52902100 |
| H | 0.13620500 | 3.89282000 | 2.22262900 |
| H | 1.29255300 | 5.18468300 | 1.80555500 |
| H | 0.52535400 | 4.22413100 | 0.51372300 |

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|---|---|---|---|
| C | 1.57128800 | 1.78806200 | 1.24532400 |
| C | -5.14489000 | 4.89100100 | -1.59752000 |
| C | -4.45863100 | 3.77795500 | -2.08346900 |
| C | -3.13649900 | 3.50799300 | -1.67483600 |
| C | -2.52752700 | 4.38057000 | -0.74673200 |
| C | -3.21445400 | 5.49038000 | -0.26265500 |
| C | -4.52470000 | 5.75149300 | -0.68635700 |
| H | -6.16852200 | 5.08548600 | -1.92633300 |
| H | -4.94402900 | 3.10055100 | -2.79074200 |
| H | -1.51968100 | 4.17532700 | -0.38437400 |
| H | -2.73131900 | 6.15317600 | 0.45929300 |
| C | -2.46891300 | 2.32559700 | -2.20827000 |
| C | -1.17893700 | 1.97644500 | -1.97171900 |
| H | -3.11145800 | 1.66851400 | -2.79821300 |
| H | -0.53493500 | 2.62979500 | -1.37940600 |
| C | -0.61477000 | 0.66848700 | -2.22902500 |
| H | -5.06216900 | 6.62050900 | -0.29906500 |

**carbene**

| | |
|---|---|
| Zero-point correction= | 0.817941 (Hartree/Particle) |
| Thermal correction to Energy= | 0.871221 |
| Thermal correction to Enthalpy= | 0.872165 |
| Thermal correction to Gibbs Free Energy= | 0.731840 |
| Sum of electronic and zero-point Energies= | -2749.163699 |
| Sum of electronic and thermal Energies= | -2749.110419 |
| Sum of electronic and thermal Enthalpies= | -2749.109475 |
| Sum of electronic and thermal Free Energies= | -2749.249801 |

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|---|---|---|---|
| C | 1.06688800 | 0.42118100 | 3.15154300 |
| F | 0.20050000 | -0.53699000 | 3.50725000 |
| F | 2.29926800 | -0.12917700 | 3.15064900 |
| F | 1.03967500 | 1.32754300 | 4.16279600 |
| Rh | -0.96210600 | -1.43699300 | -1.48052500 |
| O | 0.74713600 | -0.94390000 | -2.53437900 |
| O | -0.04346600 | -3.07059100 | -0.59789500 |
| O | 1.54316300 | 0.27306200 | -0.82000000 |
| O | 0.78451000 | -1.80909000 | 1.06963600 |
| C | 1.61206400 | -0.19691400 | -1.99750400 |
| C | 2.84943800 | 0.17216500 | -2.82584400 |
| C | 2.36814400 | 0.84677600 | -4.12295900 |
| H | 1.71321800 | 0.17828400 | -4.69954300 |
| H | 3.23311400 | 1.11439000 | -4.75011800 |
| H | 1.80939000 | 1.77023700 | -3.90085300 |
| C | 3.76078300 | 1.12891600 | -2.05007400 |

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|---|---|---|---|
| H | 3.23719700 | 2.06797500 | -1.81749300 |
| H | 4.64636300 | 1.37133500 | -2.65832000 |
| H | 4.09937300 | 0.69361600 | -1.10064700 |
| C | 3.59910200 | -1.14576200 | -3.19241800 |
| H | 2.95961500 | -1.71727600 | -3.88066600 |
| H | 4.50604300 | -0.85790500 | -3.74690300 |
| C | 3.96298600 | -2.01543700 | -2.01248500 |
| C | 5.18532400 | -1.87127600 | -1.33814200 |
| H | 5.91627700 | -1.14068300 | -1.69381400 |
| C | 5.47567900 | -2.66393200 | -0.22410800 |
| H | 6.43471100 | -2.55039600 | 0.28830900 |
| C | 4.54924800 | -3.60374500 | 0.23625800 |
| H | 4.78516800 | -4.22126300 | 1.10658800 |
| C | 3.31980000 | -3.76925100 | -0.42015500 |
| C | 3.05299400 | -2.97478900 | -1.54461200 |
| H | 2.10382700 | -3.10117600 | -2.06651100 |
| C | 2.27924100 | -4.74514600 | 0.07522800 |
| H | 2.76592600 | -5.60462300 | 0.56255100 |
| H | 1.70755600 | -5.13180600 | -0.78095300 |
| C | 1.26508400 | -4.15142800 | 1.10018200 |
| C | 1.95885300 | -3.78633100 | 2.41687700 |
| H | 2.74056400 | -3.02921900 | 2.27231300 |
| H | 2.41911900 | -4.68623700 | 2.85453900 |
| H | 1.23703800 | -3.37930100 | 3.13956700 |
| C | 0.15822100 | -5.18820900 | 1.36270400 |
| H | -0.59053300 | -4.79121600 | 2.06680100 |
| H | 0.59347200 | -6.09822700 | 1.80502200 |
| H | -0.35640800 | -5.46498300 | 0.43156300 |
| C | 0.61370900 | -2.91372500 | 0.46982000 |
| Rh | -0.08242900 | -0.09416500 | 0.37591400 |
| O | -1.79673600 | -0.58418900 | 1.39509300 |
| O | -0.98619500 | 1.53323600 | -0.49716400 |
| O | -2.61068400 | -1.80373200 | -0.30954700 |
| O | -1.81978500 | 0.30250700 | -2.18359200 |
| C | -2.67793100 | -1.32622900 | 0.85518000 |
| C | -3.90807800 | -1.64570200 | 1.71381600 |
| C | -3.42281000 | -2.38970700 | 2.97184600 |
| H | -2.71524100 | -1.77627800 | 3.54752300 |
| H | -4.28070600 | -2.63405900 | 3.61800300 |
| H | -2.92072900 | -3.33223500 | 2.70057800 |
| C | -4.89530100 | -2.52118100 | 0.93649600 |
| H | -4.43175900 | -3.47650900 | 0.65029700 |
| H | -5.77223500 | -2.73858800 | 1.56641900 |
| H | -5.24180500 | -2.02909300 | 0.01757200 |

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|---|---|---|---|
| C | -4.57351300 | -0.30425500 | 2.15055300 |
| H | -3.88103300 | 0.21382000 | 2.82982700 |
| H | -5.47158700 | -0.56570900 | 2.73185800 |
| C | -4.94332500 | 0.61951600 | 1.01437500 |
| C | -6.20186200 | 0.56156000 | 0.39593800 |
| H | -6.95439600 | -0.13947500 | 0.76608100 |
| C | -6.49905000 | 1.39917200 | -0.68277300 |
| H | -7.48513600 | 1.35068600 | -1.15233000 |
| C | -5.54310500 | 2.29717000 | -1.16611000 |
| H | -5.78306800 | 2.94664100 | -2.01190600 |
| C | -4.27707700 | 2.37637600 | -0.56590900 |
| C | -4.00472600 | 1.54139600 | 0.52801400 |
| H | -3.02775900 | 1.60274500 | 1.00762000 |
| C | -3.20458400 | 3.30141600 | -1.09114200 |
| H | -3.66384700 | 4.19060200 | -1.55073400 |
| H | -2.58209700 | 3.64802300 | -0.25346000 |
| C | -2.26301600 | 2.66972200 | -2.16234400 |
| C | -3.02827900 | 2.35534600 | -3.45097900 |
| H | -3.83555300 | 1.63066300 | -3.27917700 |
| H | -3.47049600 | 3.27993600 | -3.85413300 |
| H | -2.35671500 | 1.93386500 | -4.21319800 |
| C | -1.11882100 | 3.65688900 | -2.45931200 |
| H | -0.40938000 | 3.22961900 | -3.18608400 |
| H | -1.52615400 | 4.58647100 | -2.88681300 |
| H | -0.56552100 | 3.91026000 | -1.54350200 |
| C | -1.64550500 | 1.39279500 | -1.57840900 |
| C | 4.05067600 | 6.27555100 | 2.22120500 |
| C | 3.50058000 | 5.05328700 | 2.59361600 |
| C | 2.63075000 | 4.35488200 | 1.72062100 |
| C | 2.33186700 | 4.92520300 | 0.45682900 |
| C | 2.88409300 | 6.14548600 | 0.09119000 |
| C | 3.74330800 | 6.82326500 | 0.97011600 |
| H | 4.72006600 | 6.80512800 | 2.90240500 |
| H | 3.73475400 | 4.61597200 | 3.56724100 |
| H | 1.66690500 | 4.40787500 | -0.23555100 |
| H | 2.64934900 | 6.57849200 | -0.88356300 |
| C | 2.09492300 | 3.09448700 | 2.16112400 |
| C | 1.25020000 | 2.27567800 | 1.42916100 |
| H | 2.41660500 | 2.77852600 | 3.15524800 |
| H | 0.95514100 | 2.60539000 | 0.43119900 |
| C | 0.76008500 | 1.01547300 | 1.79528700 |
| H | 4.17458800 | 7.78287900 | 0.67495300 |

**Int1**

| | |
|---|---|
| Zero-point correction= | 1.014652 (Hartree/Particle) |
| Thermal correction to Energy= | 1.081190 |
| Thermal correction to Enthalpy= | 1.082134 |
| Thermal correction to Gibbs Free Energy= | 0.911100 |
| Sum of electronic and zero-point Energies= | -3341.481826 |
| Sum of electronic and thermal Energies= | -3341.415288 |
| Sum of electronic and thermal Enthalpies= | -3341.414344 |
| Sum of electronic and thermal Free Energies= | -3341.585378 |

| | | | |
|---|---|---|---|
| C | -0.05542800 | -0.73232300 | 1.90482700 |
| C | 1.11091400 | -0.37189000 | 2.59657700 |
| H | 1.32616800 | -0.85098000 | 3.55609600 |
| C | 2.03201100 | 0.51744900 | 2.08422200 |
| H | 1.80387600 | 0.95635000 | 1.11647700 |
| C | 3.28043300 | 0.89967300 | 2.69432000 |
| C | 4.08112700 | 1.87153100 | 2.04833900 |
| C | 3.75770300 | 0.31522200 | 3.89279700 |
| C | 5.31043600 | 2.24976500 | 2.58033700 |
| H | 3.72529400 | 2.32168000 | 1.12154500 |
| C | 4.98886900 | 0.69112600 | 4.41580200 |
| H | 3.17031800 | -0.45027100 | 4.40040500 |
| C | 5.76766000 | 1.65868600 | 3.76335900 |
| H | 5.91681400 | 3.00208300 | 2.07144900 |
| H | 5.35274500 | 0.22779500 | 5.33542700 |
| H | 6.73555300 | 1.94828600 | 4.17967100 |
| Rh | -1.97803500 | 1.25454400 | -1.63011300 |
| O | -2.58269300 | -0.60270800 | -2.28318100 |
| O | -3.64614600 | 1.44366300 | -0.42812100 |
| O | -1.50626400 | -1.63288800 | -0.60199400 |
| O | -2.65392600 | 0.31838900 | 1.24627300 |
| C | -2.24166900 | -1.63241300 | -1.63590000 |
| C | -2.74538400 | -2.98674800 | -2.16116800 |
| C | -2.07991400 | -3.22188700 | -3.53080300 |
| H | -2.34580100 | -2.42778400 | -4.24355200 |
| H | -2.40839900 | -4.18749700 | -3.94677100 |
| H | -0.98255200 | -3.24802600 | -3.43654200 |
| C | -2.38460100 | -4.12742100 | -1.20482000 |
| H | -1.29744200 | -4.25598700 | -1.13557600 |
| H | -2.81377500 | -5.07021600 | -1.57880400 |
| H | -2.76783300 | -3.94951800 | -0.19170200 |
| C | -4.28848500 | -2.90522100 | -2.36431800 |
| H | -4.49202700 | -2.13846000 | -3.12512500 |
| H | -4.60909400 | -3.87463800 | -2.77693700 |
| C | -5.06903500 | -2.59296600 | -1.11010400 |

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|---|---|---|---|
| C | -5.53870500 | -3.60870600 | -0.26257700 |
| H | -5.38212500 | -4.65555100 | -0.53460800 |
| C | -6.20880000 | -3.28863200 | 0.92117900 |
| H | -6.57730100 | -4.08759400 | 1.57014100 |
| C | -6.40959000 | -1.95293000 | 1.28097700 |
| H | -6.92967500 | -1.70988200 | 2.21113100 |
| C | -5.95385900 | -0.91849000 | 0.44975900 |
| C | -5.30142300 | -1.25999600 | -0.74391300 |
| H | -4.95158800 | -0.46453100 | -1.40137300 |
| C | -6.10474800 | 0.53346900 | 0.83488600 |
| H | -6.98747700 | 0.66577400 | 1.47989100 |
| H | -6.26300700 | 1.13827500 | -0.06978800 |
| C | -4.88315100 | 1.12486300 | 1.60084600 |
| C | -4.70584000 | 0.44702900 | 2.96313900 |
| H | -4.49478000 | -0.62569500 | 2.86290300 |
| H | -5.62427500 | 0.56940600 | 3.55873800 |
| H | -3.87165200 | 0.89808200 | 3.51915800 |
| C | -5.10121600 | 2.63711100 | 1.79414400 |
| H | -4.23770800 | 3.09556200 | 2.30241000 |
| H | -5.99393600 | 2.81148500 | 2.41533700 |
| H | -5.24337800 | 3.14534500 | 0.82962600 |
| C | -3.62916700 | 0.94705300 | 0.73360200 |
| Rh | -0.86792100 | 0.13137400 | 0.25786800 |
| O | -0.36604200 | 2.02955200 | 0.91742000 |
| O | 0.82764200 | 0.06109400 | -0.92596100 |
| O | -1.33108800 | 3.03338300 | -0.84833400 |
| O | -0.22741400 | 1.01048000 | -2.67036500 |
| C | -0.71310800 | 3.05807700 | 0.24847100 |
| C | -0.33862400 | 4.42878900 | 0.83135600 |
| C | -0.80218900 | 4.47919200 | 2.29705800 |
| H | -0.33167700 | 3.68193200 | 2.88944100 |
| H | -0.53556300 | 5.45037800 | 2.74276000 |
| H | -1.89523600 | 4.36008100 | 2.36687700 |
| C | -1.01024800 | 5.54849300 | 0.02940600 |
| H | -2.10533100 | 5.44623500 | 0.05063900 |
| H | -0.74631400 | 6.52390900 | 0.46750000 |
| H | -0.69363800 | 5.54311600 | -1.02217300 |
| C | 1.21221800 | 4.58686700 | 0.79146100 |
| H | 1.64247000 | 3.90115700 | 1.53663300 |
| H | 1.44021800 | 5.61163600 | 1.12351800 |
| C | 1.85772500 | 4.31793000 | -0.54699200 |
| C | 2.13167000 | 5.32721000 | -1.48192600 |
| H | 1.88191700 | 6.36573800 | -1.24997300 |
| C | 2.73728900 | 5.00907400 | -2.70264400 |

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|---|---|---|---|
| H | 2.95095100 | 5.80347100 | -3.42262800 |
| C | 3.08709700 | 3.68855100 | -3.00575600 |
| H | 3.57811200 | 3.45732500 | -3.95455300 |
| C | 2.82485000 | 2.66151100 | -2.08684400 |
| C | 2.20387800 | 3.00355500 | -0.88053800 |
| H | 1.98374400 | 2.21235800 | -0.17201400 |
| C | 3.18314200 | 1.21673400 | -2.33915200 |
| H | 4.05336200 | 1.15399800 | -3.01108200 |
| H | 3.47263600 | 0.75094300 | -1.38588700 |
| C | 2.05741500 | 0.34256400 | -2.97014400 |
| C | 1.79143000 | 0.77309500 | -4.41588500 |
| H | 1.46675100 | 1.82065200 | -4.47689600 |
| H | 2.71248200 | 0.65869900 | -5.00900300 |
| H | 1.00756800 | 0.15238900 | -4.87428000 |
| C | 2.50805000 | -1.12745700 | -2.92493000 |
| H | 1.73151200 | -1.78912000 | -3.34057800 |
| H | 3.42174500 | -1.25790700 | -3.52587400 |
| H | 2.71912600 | -1.43739800 | -1.89389300 |
| C | 0.78069700 | 0.48476500 | -2.12609700 |
| C | -0.90415300 | -1.71296500 | 2.70122300 |
| F | -1.60768400 | -1.02461700 | 3.63063400 |
| F | -0.17112400 | -2.62796000 | 3.38124400 |
| F | -1.78171800 | -2.41194300 | 1.97495700 |
| C | 1.23195400 | -3.40867500 | -0.45935400 |
| C | 0.98388200 | -4.25076500 | 0.75831300 |
| H | 0.40354700 | -2.89022500 | -0.94346800 |
| H | 2.07307600 | -3.68948500 | -1.10086300 |
| H | 1.65246700 | -5.09936100 | 0.93995800 |
| H | -0.03315400 | -4.35770500 | 1.14566900 |
| N | 1.55328100 | -2.93095500 | 0.86637000 |
| C | 2.82249200 | -2.66033800 | 1.32440600 |
| O | 3.31878300 | -3.13302900 | 2.32545900 |
| O | 3.40844400 | -1.73488000 | 0.53933300 |
| C | 4.79655200 | -1.42291300 | 0.77760300 |
| H | 4.89406400 | -0.35168400 | 0.56789000 |
| H | 5.02811900 | -1.60895200 | 1.83351500 |
| C | 5.66983400 | -2.23325400 | -0.14249600 |
| C | 6.11833900 | -1.68687400 | -1.35333200 |
| C | 5.99837600 | -3.56169800 | 0.17128100 |
| C | 6.88347400 | -2.45223200 | -2.23828100 |
| H | 5.86151800 | -0.65405700 | -1.60286100 |
| C | 6.76025100 | -4.32877700 | -0.71350700 |
| H | 5.64760800 | -3.99178600 | 1.11238100 |
| C | 7.20412500 | -3.77556400 | -1.91997800 |

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|---|---|---|---|
| H | 7.22920000 | -2.01510100 | -3.17844300 |
| H | 7.01208700 | -5.36170400 | -0.46004200 |
| H | 7.80179100 | -4.37591100 | -2.61058200 |

**TS1**

| | |
|---|---|
| Zero-point correction= | 1.015336 (Hartree/Particle) |
| Thermal correction to Energy= | 1.080262 |
| Thermal correction to Enthalpy= | 1.081206 |
| Thermal correction to Gibbs Free Energy= | 0.915812 |
| Sum of electronic and zero-point Energies= | -3341.476106 |
| Sum of electronic and thermal Energies= | -3341.411180 |
| Sum of electronic and thermal Enthalpies= | -3341.410236 |
| Sum of electronic and thermal Free Energies= | -3341.575630 |

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|---|---|---|---|
| C | 0.16335900 | -0.89307800 | 1.78816500 |
| C | 1.21046200 | -0.23548900 | 2.54936400 |
| H | 1.26316900 | -0.42477500 | 3.62646900 |
| C | 2.15762400 | 0.54748100 | 1.97584600 |
| H | 2.10536800 | 0.68099900 | 0.89758400 |
| C | 3.28259600 | 1.18895800 | 2.64627600 |
| C | 4.22314900 | 1.89072100 | 1.86370100 |
| C | 3.48195600 | 1.13120300 | 4.04273700 |
| C | 5.32263200 | 2.51633800 | 2.45161700 |
| H | 4.08024900 | 1.94364700 | 0.78355300 |
| C | 4.57854300 | 1.75839000 | 4.62823600 |
| H | 2.77263400 | 0.59210200 | 4.67313800 |
| C | 5.50353500 | 2.45287700 | 3.83634900 |
| H | 6.03904400 | 3.05563100 | 1.82738800 |
| H | 4.71790400 | 1.70626300 | 5.71072000 |
| H | 6.36311200 | 2.94195900 | 4.30114500 |
| Rh | -1.91173900 | 1.25762200 | -1.68790000 |
| O | -2.70299800 | -0.56087600 | -2.25848900 |
| O | -3.47248200 | 1.59767800 | -0.38280000 |
| O | -1.67254900 | -1.62839900 | -0.57220400 |
| O | -2.43853300 | 0.47667000 | 1.27032700 |
| C | -2.43311500 | -1.59556500 | -1.58764200 |
| C | -3.06452500 | -2.91803500 | -2.05080200 |
| C | -2.53899200 | -3.21078500 | -3.46879300 |
| H | -2.81361400 | -2.40807500 | -4.16807800 |
| H | -2.96406900 | -4.15689200 | -3.83963200 |
| H | -1.44128600 | -3.30779000 | -3.46962200 |
| C | -2.69120400 | -4.06921400 | -1.11177400 |
| H | -1.60853000 | -4.25465300 | -1.12649000 |
| H | -3.19658900 | -4.99129300 | -1.43933200 |

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|---|---|---|---|
| H | -2.98456800 | -3.86234500 | -0.07433100 |
| C | -4.61115100 | -2.73656500 | -2.11887600 |
| H | -4.83016800 | -1.98129300 | -2.88719000 |
| H | -5.03354200 | -3.69299700 | -2.46504900 |
| C | -5.25112400 | -2.32744800 | -0.81399600 |
| C | -5.71336400 | -3.27688100 | 0.11063000 |
| H | -5.65707900 | -4.34100200 | -0.13245900 |
| C | -6.25099900 | -2.86836300 | 1.33425200 |
| H | -6.61639500 | -3.61536400 | 2.04402200 |
| C | -6.32421000 | -1.51012200 | 1.65596700 |
| H | -6.74254900 | -1.19842900 | 2.61645300 |
| C | -5.87161400 | -0.54013300 | 0.74848300 |
| C | -5.35296800 | -0.96921000 | -0.48190000 |
| H | -5.00501300 | -0.22389400 | -1.19691500 |
| C | -5.88821500 | 0.93149200 | 1.08583900 |
| H | -6.71036000 | 1.15115800 | 1.78497500 |
| H | -6.06862300 | 1.51404800 | 0.17087400 |
| C | -4.57514700 | 1.45828100 | 1.73961400 |
| C | -4.35227700 | 0.82438400 | 3.11616400 |
| H | -4.22803900 | -0.26436600 | 3.05080100 |
| H | -5.21469600 | 1.04065700 | 3.76655400 |
| H | -3.44982000 | 1.23182400 | 3.59312500 |
| C | -4.66949900 | 2.98906900 | 1.87944300 |
| H | -3.74198500 | 3.40062900 | 2.30908700 |
| H | -5.50266300 | 3.25541600 | 2.54905800 |
| H | -4.83956200 | 3.46782000 | 0.90437700 |
| C | -3.40145600 | 1.15076900 | 0.79841400 |
| Rh | -0.76732500 | 0.08332700 | 0.14818600 |
| O | -0.05456400 | 1.94795800 | 0.70830300 |
| O | 0.81964100 | -0.18643300 | -1.16091200 |
| O | -1.07395900 | 2.99381400 | -1.00188500 |
| O | -0.25517000 | 0.85593500 | -2.83979300 |
| C | -0.37443800 | 2.98615000 | 0.04725900 |
| C | 0.14418500 | 4.33337500 | 0.57142600 |
| C | -0.22324900 | 4.45071600 | 2.06054800 |
| H | 0.21444400 | 3.62722900 | 2.64204600 |
| H | 0.15060100 | 5.40383500 | 2.46681700 |
| H | -1.31620100 | 4.42628400 | 2.19808700 |
| C | -0.48064100 | 5.48901000 | -0.21664500 |
| H | -1.57698800 | 5.47978900 | -0.12644500 |
| H | -0.11004500 | 6.44831700 | 0.17786100 |
| H | -0.23285800 | 5.43411800 | -1.28524100 |
| C | 1.69735100 | 4.35721300 | 0.43784500 |
| H | 2.11082400 | 3.65564200 | 1.17602800 |

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|---|---|---|---|
| H | 2.03174000 | 5.36639300 | 0.72516400 |
| C | 2.23493500 | 4.00077900 | -0.92727700 |
| C | 2.52980700 | 4.96404100 | -1.90368700 |
| H | 2.38190300 | 6.02417000 | -1.68207600 |
| C | 3.02545600 | 4.57327700 | -3.15236000 |
| H | 3.25680400 | 5.33257300 | -3.90409900 |
| C | 3.24120100 | 3.22214200 | -3.44382700 |
| H | 3.64547200 | 2.93036900 | -4.41657800 |
| C | 2.95522200 | 2.23971300 | -2.48390200 |
| C | 2.44900200 | 2.65407500 | -1.24643800 |
| H | 2.21491800 | 1.89784700 | -0.50317300 |
| C | 3.17046700 | 0.76596400 | -2.73053400 |
| H | 3.99081500 | 0.61782900 | -3.45041400 |
| H | 3.47458900 | 0.28904100 | -1.78730400 |
| C | 1.93783000 | -0.01570100 | -3.27808200 |
| C | 1.61718100 | 0.41963500 | -4.71119000 |
| H | 1.37722000 | 1.48984100 | -4.76787100 |
| H | 2.48505300 | 0.22253000 | -5.36021000 |
| H | 0.75622400 | -0.13776200 | -5.10883600 |
| C | 2.27021300 | -1.51709400 | -3.24186800 |
| H | 1.41208900 | -2.12148100 | -3.57685700 |
| H | 3.11852800 | -1.73085500 | -3.91104500 |
| H | 2.54239400 | -1.83080700 | -2.22606000 |
| C | 0.73361200 | 0.24126500 | -2.35654100 |
| C | -0.77406000 | -1.62141700 | 2.74416100 |
| F | -1.34259900 | -0.71741200 | 3.56768000 |
| F | -0.14887900 | -2.51705900 | 3.55104300 |
| F | -1.76927300 | -2.29374000 | 2.14582100 |
| C | 0.89473200 | -3.14040200 | -0.23464600 |
| C | 0.53153100 | -3.88645800 | 0.99427900 |
| H | 0.11136900 | -2.64623200 | -0.80224000 |
| H | 1.79269500 | -3.43199500 | -0.78211500 |
| H | 1.16421700 | -4.70961600 | 1.33575900 |
| H | -0.51545600 | -3.93744700 | 1.28864600 |
| N | 1.13960500 | -2.54889400 | 1.08851700 |
| C | 2.49996500 | -2.47736700 | 1.52927800 |
| O | 2.88992500 | -2.95965600 | 2.55949800 |
| O | 3.20952400 | -1.78481800 | 0.65175500 |
| C | 4.63983200 | -1.64600500 | 0.87412600 |
| H | 4.87849200 | -0.64159700 | 0.50676400 |
| H | 4.83793900 | -1.70183000 | 1.95092500 |
| C | 5.37065700 | -2.70790200 | 0.10179900 |
| C | 5.69364100 | -2.49674900 | -1.24739000 |
| C | 5.68179800 | -3.93920800 | 0.69770700 |

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|---|---|---|---|
| C | 6.31898400 | -3.50077000 | -1.99050300 |
| H | 5.45019400 | -1.53918600 | -1.71494700 |
| C | 6.30894300 | -4.94341900 | -0.04490600 |
| H | 5.42631800 | -4.10825600 | 1.74644700 |
| C | 6.62726600 | -4.72605200 | -1.38953300 |
| H | 6.56847400 | -3.32669200 | -3.04012500 |
| H | 6.55141500 | -5.89840900 | 0.42786100 |
| H | 7.11868100 | -5.51145400 | -1.96926300 |

**Int2**

Zero-point correction= 1.017289 (Hartree/Particle)
Thermal correction to Energy= 1.081911
Thermal correction to Enthalpy= 1.082855
Thermal correction to Gibbs Free Energy= 0.920237
Sum of electronic and zero-point Energies= -3341.499487
Sum of electronic and thermal Energies= -3341.434866
Sum of electronic and thermal Enthalpies= -3341.433921
Sum of electronic and thermal Free Energies= -3341.596539

| | | | |
|---|---|---|---|
| C | 0.61407500 | -1.80081300 | 0.59895400 |
| C | 1.84274400 | -1.05055100 | 0.84951000 |
| H | 1.86376600 | -0.54637300 | 1.81564800 |
| C | 2.87576000 | -0.88139100 | -0.00602900 |
| H | 2.83583100 | -1.33522100 | -1.00011700 |
| C | 4.08907700 | -0.10781800 | 0.25265200 |
| C | 4.97686900 | 0.15226800 | -0.81044500 |
| C | 4.42594000 | 0.40083500 | 1.52511600 |
| C | 6.13051900 | 0.91453200 | -0.62355300 |
| H | 4.74889800 | -0.25218100 | -1.79965300 |
| C | 5.57827600 | 1.16134400 | 1.71310700 |
| H | 3.77929800 | 0.19139800 | 2.37911700 |
| C | 6.43700700 | 1.42979000 | 0.63936900 |
| H | 6.79593300 | 1.10571800 | -1.46953100 |
| H | 5.81157800 | 1.54821100 | 2.70867800 |
| H | 7.33840200 | 2.02891100 | 0.78945100 |
| Rh | -2.16803800 | 2.02959700 | -0.46323900 |
| O | -3.19658000 | 0.88659800 | -1.83854900 |
| O | -3.44714100 | 1.49133200 | 1.06015900 |
| O | -2.00695900 | -0.94545900 | -1.32361100 |
| O | -2.23962500 | -0.35293500 | 1.50045100 |
| C | -2.90295200 | -0.33372600 | -1.97982000 |
| C | -3.69292000 | -1.12652100 | -3.03050400 |
| C | -3.49251300 | -0.43366500 | -4.39080400 |
| H | -3.84441400 | 0.60720000 | -4.36220000 |

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|---|---|---|---|
| H | -4.05242100 | -0.97055300 | -5.17270000 |
| H | -2.42789100 | -0.42991800 | -4.67555500 |
| C | -3.20359900 | -2.57523400 | -3.11324100 |
| H | -2.14558600 | -2.61638300 | -3.41040000 |
| H | -3.79066300 | -3.12084500 | -3.86843000 |
| H | -3.30777600 | -3.09852400 | -2.15370000 |
| C | -5.20515500 | -1.06912700 | -2.65415300 |
| H | -5.54052700 | -0.02761000 | -2.76240700 |
| H | -5.74808500 | -1.67012800 | -3.40045800 |
| C | -5.52531000 | -1.55457800 | -1.26041400 |
| C | -5.82877400 | -2.89961900 | -0.99804200 |
| H | -5.87992000 | -3.61387000 | -1.82385100 |
| C | -6.07770500 | -3.32576700 | 0.30974300 |
| H | -6.32297200 | -4.37362000 | 0.50247400 |
| C | -6.01880400 | -2.41948300 | 1.37223800 |
| H | -6.21595900 | -2.76035200 | 2.39178000 |
| C | -5.71904600 | -1.06859900 | 1.13759400 |
| C | -5.48685800 | -0.65770900 | -0.18298800 |
| H | -5.25917100 | 0.39075400 | -0.37665700 |
| C | -5.60319900 | -0.07215300 | 2.26624500 |
| H | -6.26754500 | -0.35978600 | 3.09628400 |
| H | -5.92766000 | 0.91710100 | 1.91212900 |
| C | -4.16766400 | 0.07600800 | 2.85590300 |
| C | -3.72434100 | -1.21244100 | 3.55619800 |
| H | -3.68746200 | -2.06304800 | 2.86340700 |
| H | -4.42786400 | -1.45271000 | 4.36910900 |
| H | -2.72051000 | -1.09769400 | 3.98887600 |
| C | -4.16083900 | 1.24347600 | 3.85925400 |
| H | -3.15200900 | 1.39470500 | 4.27584300 |
| H | -4.84559100 | 1.02669600 | 4.69448800 |
| H | -4.48015600 | 2.18060000 | 3.38134100 |
| C | -3.20616400 | 0.43206300 | 1.71338600 |
| Rh | -0.83643300 | 0.04639000 | 0.05866700 |
| O | 0.15547300 | 1.23427100 | 1.43351100 |
| O | 0.41138100 | 0.62003500 | -1.49172400 |
| O | -1.05250800 | 3.05675500 | 0.91546800 |
| O | -0.79485600 | 2.46538900 | -1.92581800 |
| C | -0.15677600 | 2.45562900 | 1.57272500 |
| C | 0.62441300 | 3.25420300 | 2.62461500 |
| C | 0.43558900 | 2.55846400 | 3.98479700 |
| H | 0.80104600 | 1.52214500 | 3.95510500 |
| H | 0.98967300 | 3.10208600 | 4.76637100 |
| H | -0.62822200 | 2.53919700 | 4.27135700 |
| C | 0.11368400 | 4.69598300 | 2.70033500 |

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|---|---|---|---|
| H | -0.94855800 | 4.72333800 | 2.98431800 |
| H | 0.68741100 | 5.25245600 | 3.45838700 |
| H | 0.21631500 | 5.21574700 | 1.73812300 |
| C | 2.13579500 | 3.21821500 | 2.24918800 |
| H | 2.48516200 | 2.18255600 | 2.35529900 |
| H | 2.67185100 | 3.82398900 | 2.99677300 |
| C | 2.46270100 | 3.70428100 | 0.85759400 |
| C | 2.81920400 | 5.03702200 | 0.60103100 |
| H | 2.88669000 | 5.74799300 | 1.42874200 |
| C | 3.10065600 | 5.45509000 | -0.70311800 |
| H | 3.38509900 | 6.49388200 | -0.89125500 |
| C | 3.02905000 | 4.55056100 | -1.76680200 |
| H | 3.25996100 | 4.88217000 | -2.78262600 |
| C | 2.67515000 | 3.21246400 | -1.53635500 |
| C | 2.40017200 | 2.81151000 | -0.22154300 |
| H | 2.13438500 | 1.77349600 | -0.03393300 |
| C | 2.57290100 | 2.20707800 | -2.65803000 |
| H | 3.24992000 | 2.48707300 | -3.48038300 |
| H | 2.89676000 | 1.22655600 | -2.28521700 |
| C | 1.15072600 | 2.03766000 | -3.27103000 |
| C | 0.70812600 | 3.31347400 | -3.99286300 |
| H | 0.65963400 | 4.17142500 | -3.30880400 |
| H | 1.42236600 | 3.55058800 | -4.79711800 |
| H | -0.28747400 | 3.18664900 | -4.44304500 |
| C | 1.17947700 | 0.85768200 | -4.25943000 |
| H | 0.17876900 | 0.67272000 | -4.68219900 |
| H | 1.86478100 | 1.08093300 | -5.09219700 |
| H | 1.52318000 | -0.06351500 | -3.76760500 |
| C | 0.17358100 | 1.68687500 | -2.14220600 |
| C | -0.03248000 | -2.41654200 | 1.82132800 |
| F | -0.14417700 | -1.50938200 | 2.80564100 |
| F | 0.62285400 | -3.46925900 | 2.39118900 |
| F | -1.26304800 | -2.91205400 | 1.55221200 |
| C | 0.49682600 | -2.46731800 | -1.90939400 |
| C | -0.40203700 | -3.37761100 | -1.20889300 |
| H | 0.23101400 | -1.41808100 | -2.01409700 |
| H | 1.22343800 | -2.87900500 | -2.60908200 |
| H | -0.33610500 | -4.44925200 | -1.40035700 |
| H | -1.33541000 | -2.98211900 | -0.81892800 |
| N | 0.80801900 | -2.83722500 | -0.46803300 |
| C | 1.92814300 | -3.83776200 | -0.39813900 |
| O | 2.15512000 | -4.55041800 | -1.33686300 |
| O | 2.52745100 | -3.79647700 | 0.74867000 |
| C | 3.69570500 | -4.65572800 | 0.95878000 |

| | | | |
|---|---|---|---|
| H | 3.66886100 | -4.86049900 | 2.03487200 |
| H | 3.54388200 | -5.58419400 | 0.39513900 |
| C | 4.95235700 | -3.93989700 | 0.55557800 |
| C | 5.61369900 | -3.11164300 | 1.47415400 |
| C | 5.45624000 | -4.05924100 | -0.74877100 |
| C | 6.76594500 | -2.41858500 | 1.09917500 |
| H | 5.21734100 | -3.00745300 | 2.48740500 |
| C | 6.60798300 | -3.36348100 | -1.12471600 |
| H | 4.94007200 | -4.69819700 | -1.46892900 |
| C | 7.26431700 | -2.54364800 | -0.20098000 |
| H | 7.26875600 | -1.76861500 | 1.81828600 |
| H | 6.99507000 | -3.46200800 | -2.14188400 |
| H | 8.16175000 | -1.99499500 | -0.49628000 |

**Int3**

Zero-point correction= 0.341389 (Hartree/Particle)
Thermal correction to Energy= 0.364234
Thermal correction to Enthalpy= 0.365178
Thermal correction to Gibbs Free Energy= 0.284832
Sum of electronic and zero-point Energies= -1276.445929
Sum of electronic and thermal Energies= -1276.423084
Sum of electronic and thermal Enthalpies= -1276.422140
Sum of electronic and thermal Free Energies= -1276.502487

| | | | |
|---|---|---|---|
| C | 0.76125100 | -1.43571600 | -0.26606400 |
| N | -0.18072300 | -0.57087100 | -0.93621000 |
| C | -0.98648100 | -1.11252900 | -2.10607700 |
| C | 0.11325900 | -0.18979100 | -2.38051400 |
| H | -0.84329400 | -2.18377200 | -2.24544100 |
| O | -1.53021000 | 1.29418700 | -0.82677200 |
| C | -0.87077000 | 0.44153800 | -0.07709100 |
| O | -0.78253900 | 0.39952400 | 1.11008300 |
| H | 1.07767100 | -0.58141400 | -2.70365100 |
| C | 2.04336500 | -0.94038100 | 0.02566500 |
| C | 2.56516400 | 0.29719500 | -0.27497300 |
| H | 2.68051200 | -1.65331100 | 0.55684700 |
| H | -0.10992600 | 0.84930000 | -2.62035600 |
| C | 0.21944700 | -2.70187000 | 0.21726600 |
| F | 0.97987300 | -3.25512700 | 1.18070200 |
| F | -1.05354200 | -2.59361400 | 0.69933300 |
| F | 0.09633800 | -3.69939400 | -0.74381400 |
| H | -2.01256300 | -0.74266900 | -2.12967200 |
| C | -2.38444400 | 2.27693500 | -0.14681700 |
| H | -1.84631600 | 2.64288600 | 0.73609400 |

| | | | |
|---|---|---|---|
| H | -2.48293700 | 3.08061500 | -0.88522100 |
| C | -3.70966500 | 1.66579000 | 0.20423600 |
| C | -3.95902000 | 1.19122200 | 1.50035700 |
| C | -4.69915000 | 1.52639900 | -0.78208500 |
| C | -5.18196900 | 0.58828200 | 1.80641700 |
| H | -3.18833900 | 1.29150800 | 2.26749600 |
| C | -5.91926300 | 0.91993400 | -0.47716000 |
| H | -4.50990000 | 1.89976700 | -1.79229300 |
| C | -6.16176900 | 0.45006100 | 0.81854400 |
| H | -5.36934500 | 0.22383700 | 2.81935200 |
| H | -6.68554100 | 0.81754900 | -1.24949400 |
| H | -7.11764600 | -0.02224300 | 1.05861800 |
| H | 1.93099700 | 1.03992000 | -0.76982700 |
| C | 3.91525900 | 0.74701200 | 0.02280900 |
| C | 4.29943800 | 2.07190900 | -0.30509300 |
| C | 4.90464200 | -0.06605400 | 0.63356600 |
| C | 5.58070200 | 2.55452200 | -0.03901100 |
| H | 3.56375700 | 2.72948300 | -0.77832900 |
| C | 6.18330200 | 0.41976100 | 0.89997600 |
| H | 4.66677800 | -1.09810400 | 0.90146000 |
| C | 6.53904300 | 1.73443100 | 0.56823200 |
| H | 5.83421900 | 3.58412400 | -0.30840200 |
| H | 6.91720200 | -0.23951100 | 1.37296800 |
| H | 7.54365800 | 2.10976400 | 0.77774200 |

**TS2**

| | |
|---|---|
| Zero-point correction= | 0.339587 (Hartree/Particle) |
| Thermal correction to Energy= | 0.362209 |
| Thermal correction to Enthalpy= | 0.363153 |
| Thermal correction to Gibbs Free Energy= | 0.283847 |
| Sum of electronic and zero-point Energies= | -1276.412954 |
| Sum of electronic and thermal Energies= | -1276.390333 |
| Sum of electronic and thermal Enthalpies= | -1276.389389 |
| Sum of electronic and thermal Free Energies= | -1276.468694 |

| | | | |
|---|---|---|---|
| C | 0.66150400 | -0.27544400 | 0.08779500 |
| N | -0.04903600 | 0.95086100 | 0.11214900 |
| C | 0.35981300 | 2.11916500 | -0.65190300 |
| C | 0.66628900 | 2.59493300 | 0.71493800 |
| H | 1.20057100 | 1.89342700 | -1.31028300 |
| O | -2.19484800 | 1.71230000 | 0.01137300 |
| C | -1.36818900 | 0.99659700 | 0.74651900 |
| O | -1.59679500 | 0.45343900 | 1.78871500 |
| H | 1.63725800 | 2.41172200 | 1.17158400 |

| | | | |
|---|---|---|---|
| C | 2.06132700 | -0.39611500 | -0.05756000 |
| C | 3.09185400 | 0.51269500 | -0.13477100 |
| H | 2.36249300 | -1.44508200 | -0.09333000 |
| H | -0.08871600 | 3.14290700 | 1.28148900 |
| C | -0.11461000 | -1.52680400 | 0.32394200 |
| F | 0.46484300 | -2.57346400 | -0.30944000 |
| F | -0.23548400 | -1.93319300 | 1.61694000 |
| F | -1.38601600 | -1.45367800 | -0.15604400 |
| H | -0.46442400 | 2.59673700 | -1.18658400 |
| C | -3.56957200 | 1.85462700 | 0.49301500 |
| H | -3.54649600 | 1.89324600 | 1.58919100 |
| H | -3.89030400 | 2.82270400 | 0.09148200 |
| C | -4.42536400 | 0.72975300 | -0.01766100 |
| C | -4.54000400 | -0.46911200 | 0.70362900 |
| C | -5.08965900 | 0.85681500 | -1.24671000 |
| C | -5.30711600 | -1.52250600 | 0.20103000 |
| H | -4.01570800 | -0.57625900 | 1.65492300 |
| C | -5.85788300 | -0.19639900 | -1.74879700 |
| H | -5.00409000 | 1.78950000 | -1.81089200 |
| C | -5.96674300 | -1.38825500 | -1.02513200 |
| H | -5.39043200 | -2.45236900 | 0.76894000 |
| H | -6.37401600 | -0.08656200 | -2.70575100 |
| H | -6.56777900 | -2.21300600 | -1.41633800 |
| H | 2.90738700 | 1.58618600 | -0.13458900 |
| C | 4.50345100 | 0.16386100 | -0.23350300 |
| C | 5.46007700 | 1.20380700 | -0.33538800 |
| C | 4.99999600 | -1.16346500 | -0.23151900 |
| C | 6.82572200 | 0.93803900 | -0.43178600 |
| H | 5.11053700 | 2.24047300 | -0.34026500 |
| C | 6.36502500 | -1.42619300 | -0.32905500 |
| H | 4.30881200 | -2.00492300 | -0.14901700 |
| C | 7.29319300 | -0.38101200 | -0.43035800 |
| H | 7.53249400 | 1.76904400 | -0.50960400 |
| H | 6.71164800 | -2.46349600 | -0.32424000 |
| H | 8.36243000 | -0.59309000 | -0.50592100 |

**pro**

| | |
|---|---|
| Zero-point correction= | 0.345871 (Hartree/Particle) |
| Thermal correction to Energy= | 0.367654 |
| Thermal correction to Enthalpy= | 0.368599 |
| Thermal correction to Gibbs Free Energy= | 0.290744 |
| Sum of electronic and zero-point Energies= | -1276.554047 |
| Sum of electronic and thermal Energies= | -1276.532263 |
| Sum of electronic and thermal Enthalpies= | -1276.531319 |

Sum of electronic and thermal Free Energies= -1276.609174

| | | | |
|---|---|---|---|
| C | 0.84378800 | -1.17184800 | 0.41454700 |
| N | 0.03393400 | -0.02294300 | 0.55883600 |
| C | 0.76293000 | 1.25191200 | 0.49452800 |
| C | 1.91513200 | 1.22008000 | 1.49381000 |
| H | 1.14087800 | 1.38629600 | -0.53165200 |
| O | -1.86121800 | 1.06360500 | 1.10634600 |
| C | -1.23835100 | -0.12661000 | 1.07825700 |
| O | -1.73635600 | -1.17113800 | 1.44944600 |
| H | 1.49905800 | 1.05991200 | 2.50168400 |
| C | 2.16687300 | -1.13290000 | 0.64831200 |
| C | 2.90038300 | 0.07954900 | 1.14855100 |
| H | 2.76624400 | -2.00882500 | 0.39610900 |
| H | 2.44013600 | 2.18621300 | 1.50144700 |
| C | 0.23422100 | -2.42388700 | -0.19285200 |
| F | 1.14455600 | -3.06226500 | -0.96394200 |
| F | -0.17161400 | -3.32758500 | 0.71192100 |
| F | -0.80780100 | -2.13789200 | -0.99032300 |
| H | 0.06374900 | 2.06311700 | 0.71098700 |
| C | -3.23938000 | 1.08103000 | 1.54189700 |
| H | -3.39221800 | 0.26054700 | 2.25529400 |
| H | -3.36367200 | 2.04167600 | 2.05743300 |
| C | -4.18198200 | 0.97468100 | 0.37035300 |
| C | -4.35465800 | -0.24765900 | -0.30159100 |
| C | -4.88421800 | 2.10210500 | -0.07751000 |
| C | -5.21208400 | -0.33403400 | -1.40023400 |
| H | -3.80592400 | -1.12764500 | 0.03979400 |
| C | -5.74861600 | 2.01452200 | -1.17336500 |
| H | -4.75326000 | 3.05707700 | 0.43891800 |
| C | -5.91289800 | 0.79594200 | -1.83771100 |
| H | -5.33845800 | -1.28953200 | -1.91575300 |
| H | -6.29265000 | 2.90081300 | -1.50971400 |
| H | -6.58671200 | 0.72532800 | -2.69541300 |
| H | 3.42831200 | -0.20658100 | 2.07372800 |
| C | 3.96991200 | 0.53118600 | 0.15911300 |
| C | 5.12187900 | 1.17774100 | 0.63631600 |
| C | 3.82066600 | 0.36665300 | -1.22617400 |
| C | 6.09501600 | 1.65310000 | -0.24508200 |
| H | 5.25453900 | 1.30886900 | 1.71414500 |
| C | 4.79401200 | 0.84209200 | -2.11195900 |
| H | 2.93911500 | -0.14451700 | -1.61870600 |
| C | 5.93353700 | 1.48746000 | -1.62542100 |
| H | 6.98582500 | 2.15116200 | 0.14653000 |

| | | | |
|---|---|---|---|
| H | 4.65974100 | 0.70312600 | -3.18786000 |
| H | 6.69512000 | 1.85684100 | -2.31678600 |

**TS2'**

| | |
|---|---|
| Zero-point correction= | 0.338643 (Hartree/Particle) |
| Thermal correction to Energy= | 0.361594 |
| Thermal correction to Enthalpy= | 0.362538 |
| Thermal correction to Gibbs Free Energy= | 0.281782 |
| Sum of electronic and zero-point Energies= | -1276.401363 |
| Sum of electronic and thermal Energies= | -1276.378412 |
| Sum of electronic and thermal Enthalpies= | -1276.377468 |
| Sum of electronic and thermal Free Energies= | -1276.458224 |

| | | | |
|---|---|---|---|
| C | -0.80034300 | 1.61361000 | 0.31427100 |
| C | -2.01261700 | 0.95308700 | -0.00420100 |
| H | -2.65089800 | 1.54173700 | -0.66892100 |
| C | -2.47359600 | -0.27544600 | 0.39279700 |
| H | -1.85569300 | -0.88945700 | 1.05580700 |
| C | -3.74342700 | -0.87489000 | 0.01507700 |
| C | -4.07613800 | -2.16223500 | 0.50555600 |
| C | -4.69713800 | -0.24886000 | -0.82748800 |
| C | -5.28108500 | -2.78441900 | 0.17941500 |
| H | -3.36259900 | -2.67614500 | 1.15663400 |
| C | -5.90005600 | -0.87273800 | -1.15137500 |
| H | -4.49151500 | 0.74346800 | -1.23500100 |
| C | -6.20788100 | -2.14632300 | -0.65287800 |
| H | -5.49911300 | -3.77900200 | 0.57917400 |
| H | -6.61066600 | -0.35769400 | -1.80434100 |
| H | -7.15261500 | -2.63121900 | -0.91048100 |
| C | -0.31983200 | 2.74505700 | -0.50790900 |
| F | -1.30211300 | 3.33801100 | -1.21078400 |
| F | 0.65773100 | 2.41003600 | -1.40076100 |
| F | 0.25896000 | 3.73633000 | 0.24491100 |
| C | -0.55618200 | 1.16799700 | 2.67949000 |
| C | 0.80483000 | 1.47675300 | 2.24813700 |
| H | -1.34418700 | 1.91622300 | 2.76322100 |
| H | -0.78019000 | 0.13599600 | 2.95706100 |
| H | 1.59872900 | 0.85923100 | 2.67618900 |
| H | 1.07746700 | 2.53281600 | 2.16308700 |
| N | 0.30830900 | 0.91624600 | 0.98368300 |
| C | 0.87965400 | -0.22578300 | 0.37617600 |
| O | 0.59073600 | -0.57070700 | -0.74181500 |
| O | 1.69285800 | -0.86216400 | 1.22012700 |
| C | 2.38938800 | -2.03409200 | 0.71244600 |

| | | | |
|---|---|---|---|
| H | 2.57886100 | -2.64019900 | 1.60655200 |
| H | 1.71456000 | -2.57364600 | 0.03583700 |
| C | 3.67321500 | -1.64696800 | 0.02982100 |
| C | 4.84799200 | -1.48807500 | 0.78070300 |
| C | 3.70592200 | -1.40305800 | -1.35184900 |
| C | 6.03666200 | -1.09258700 | 0.16243900 |
| H | 4.82882500 | -1.68020800 | 1.85711400 |
| C | 4.89467900 | -1.00837800 | -1.97098700 |
| H | 2.79126300 | -1.51565400 | -1.93721100 |
| C | 6.06116600 | -0.85170600 | -1.21533600 |
| H | 6.94706600 | -0.97521900 | 0.75556800 |
| H | 4.91047200 | -0.82255100 | -3.04779900 |
| H | 6.99084900 | -0.54430400 | -1.70090300 |

**pro'**

Zero-point correction= 0.343488 (Hartree/Particle)
Thermal correction to Energy= 0.366248
Thermal correction to Enthalpy= 0.367192
Thermal correction to Gibbs Free Energy= 0.286060
Sum of electronic and zero-point Energies= -1276.531302
Sum of electronic and thermal Energies= -1276.508543
Sum of electronic and thermal Enthalpies= -1276.507599
Sum of electronic and thermal Free Energies= -1276.588731

| | | | |
|---|---|---|---|
| C | -0.73107300 | 1.34652700 | 0.65146200 |
| C | -2.13397200 | 0.98363600 | 0.25916500 |
| H | -2.75708400 | 1.83119200 | -0.04088400 |
| C | -2.62128500 | -0.26443700 | 0.30530800 |
| H | -1.94662600 | -1.06799800 | 0.61578600 |
| C | -3.98819800 | -0.69186900 | -0.02448300 |
| C | -4.30765300 | -2.06034000 | 0.06417800 |
| C | -5.00082200 | 0.20254500 | -0.42771200 |
| C | -5.59023900 | -2.52319200 | -0.23804400 |
| H | -3.53256600 | -2.76638600 | 0.37409400 |
| C | -6.28080700 | -0.25902700 | -0.72960900 |
| H | -4.78541600 | 1.27021000 | -0.50642200 |
| C | -6.58291100 | -1.62391800 | -0.63648800 |
| H | -5.81437000 | -3.59024900 | -0.16257700 |
| H | -7.05163800 | 0.45053000 | -1.04103800 |
| H | -7.58779700 | -1.98163000 | -0.87417400 |
| C | -0.10708100 | 2.27113200 | -0.41006700 |
| F | -0.70241200 | 3.48083200 | -0.37517700 |
| F | -0.23580100 | 1.80731100 | -1.65861200 |
| F | 1.20524100 | 2.46209700 | -0.18415800 |

| | | | |
|---|---|---|---|
| C | -0.54195500 | 1.93968300 | 2.09516000 |
| C | 0.46067900 | 0.79652200 | 2.37681700 |
| H | -0.12659200 | 2.95373400 | 2.12987600 |
| H | -1.46507000 | 1.89239100 | 2.68378300 |
| H | 0.19637900 | 0.11745100 | 3.20111100 |
| H | 1.50947100 | 1.11320000 | 2.48364900 |
| N | 0.15704900 | 0.25860700 | 1.04921100 |
| C | 0.81912700 | -0.64601200 | 0.28197500 |
| O | 0.59704500 | -0.85729200 | -0.89508400 |
| O | 1.75017500 | -1.27991600 | 1.02500400 |
| C | 2.63297000 | -2.19219900 | 0.33830100 |
| H | 2.85801000 | -2.98165200 | 1.06671100 |
| H | 2.09470800 | -2.62643500 | -0.51509800 |
| C | 3.89480500 | -1.49604700 | -0.10520000 |
| C | 5.10344500 | -1.72209800 | 0.56753000 |
| C | 3.87261800 | -0.59263100 | -1.18181200 |
| C | 6.27259400 | -1.06297300 | 0.17411900 |
| H | 5.12754800 | -2.42213800 | 1.40735600 |
| C | 5.03791300 | 0.07111800 | -1.57063500 |
| H | 2.93329500 | -0.41055400 | -1.70795400 |
| C | 6.24128100 | -0.16341900 | -0.89501400 |
| H | 7.20884500 | -1.25105300 | 0.70586800 |
| H | 5.00886000 | 0.77200900 | -2.40890100 |
| H | 7.15306100 | 0.35461700 | -1.20319500 |

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## 6. NMR Spectra of Products

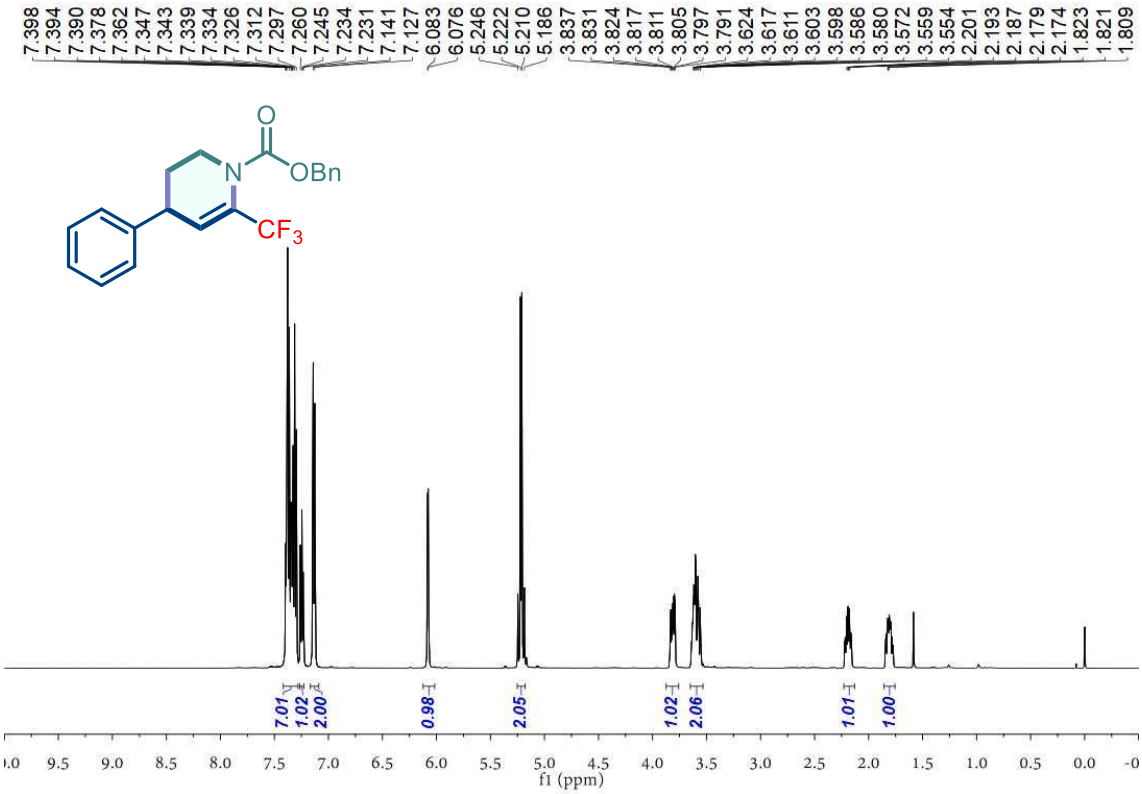


**Figure S3.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **3**.

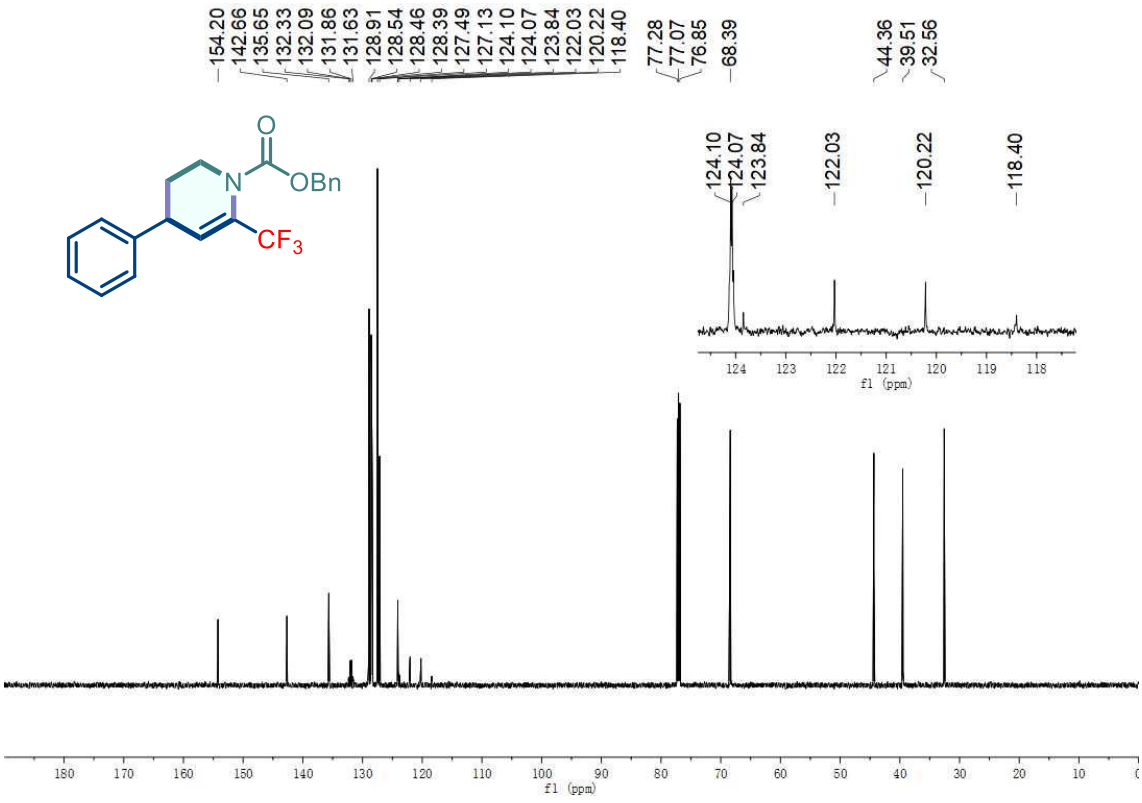


**Figure S4.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **3**.

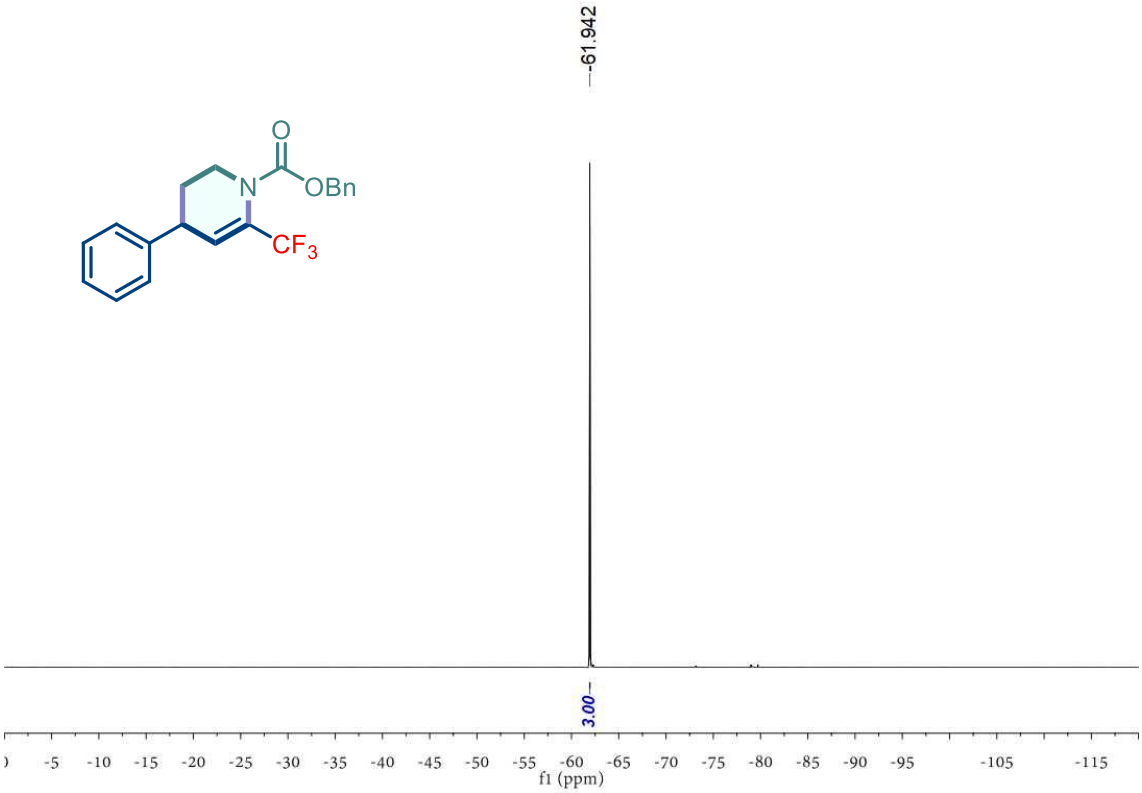


**Figure S5.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **3**.

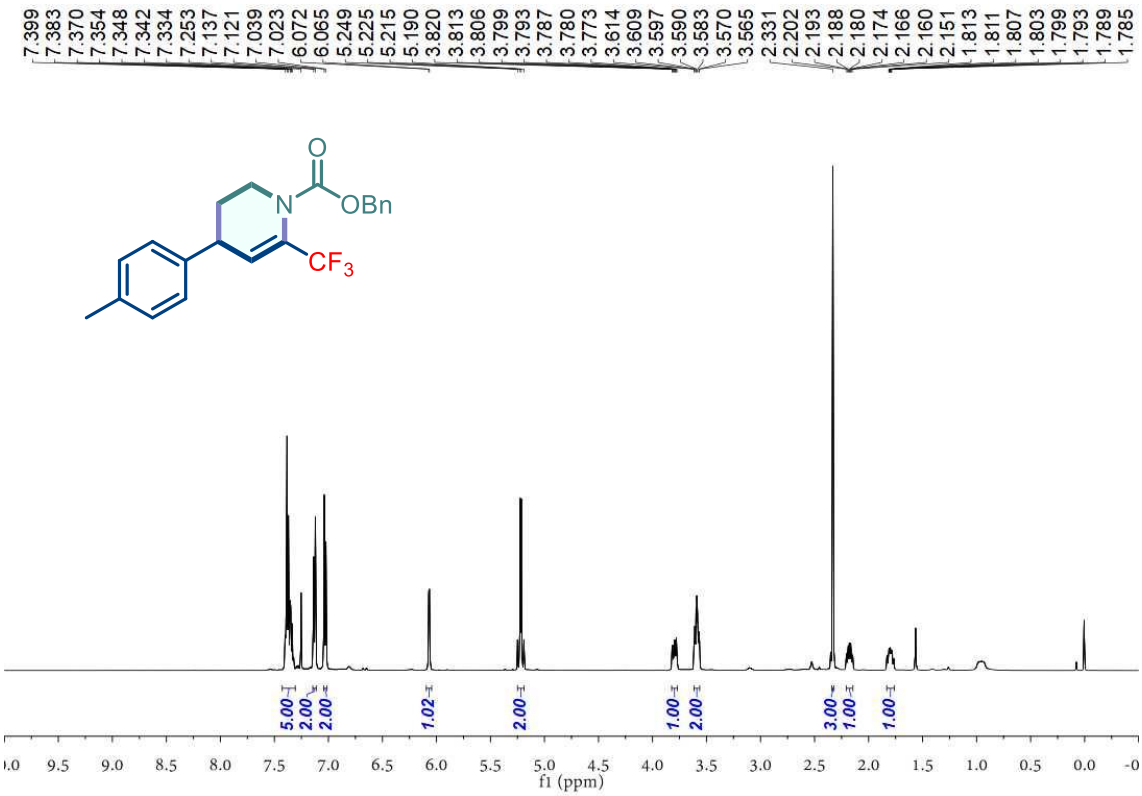


**Figure S6.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **5**.

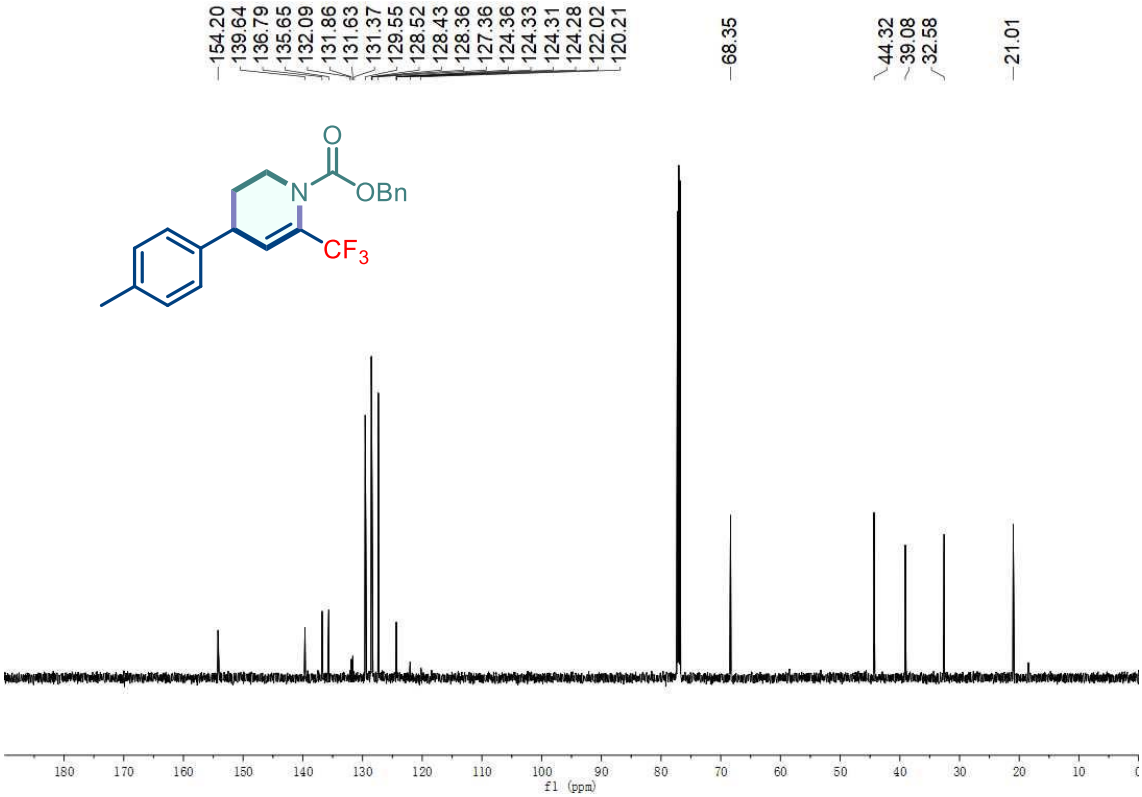


**Figure S7.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **5**.

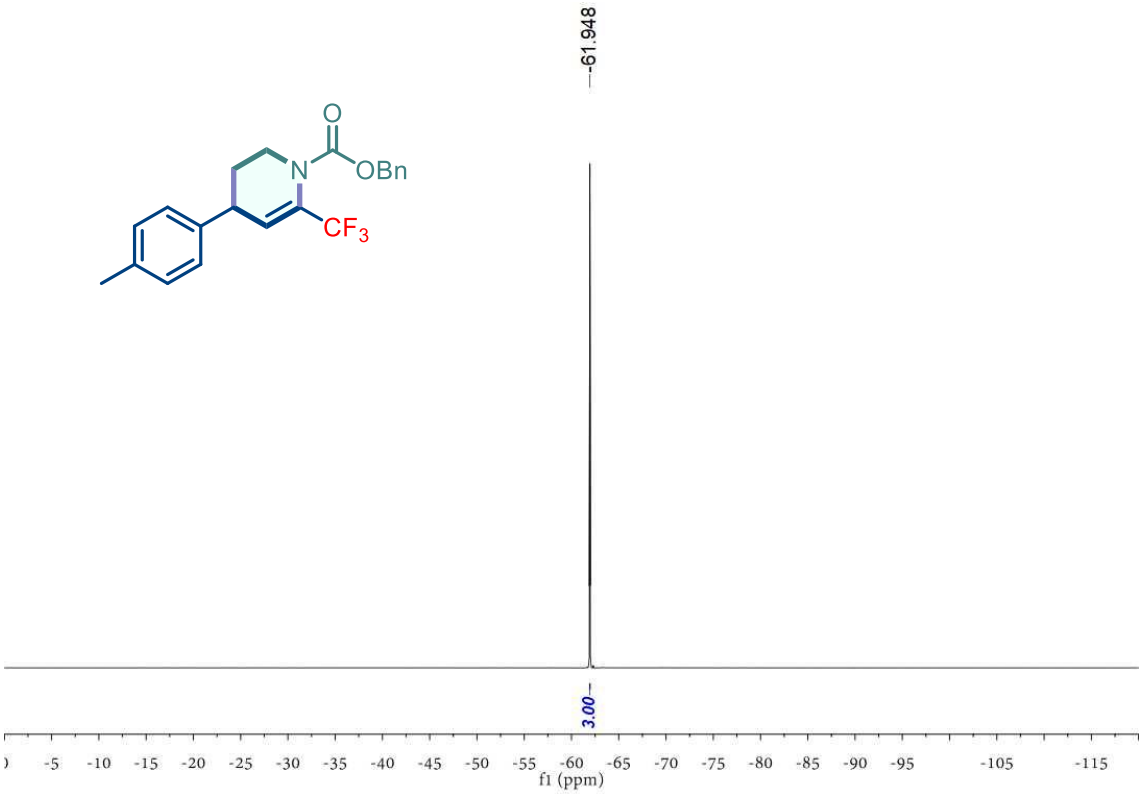


**Figure S8.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **5**.

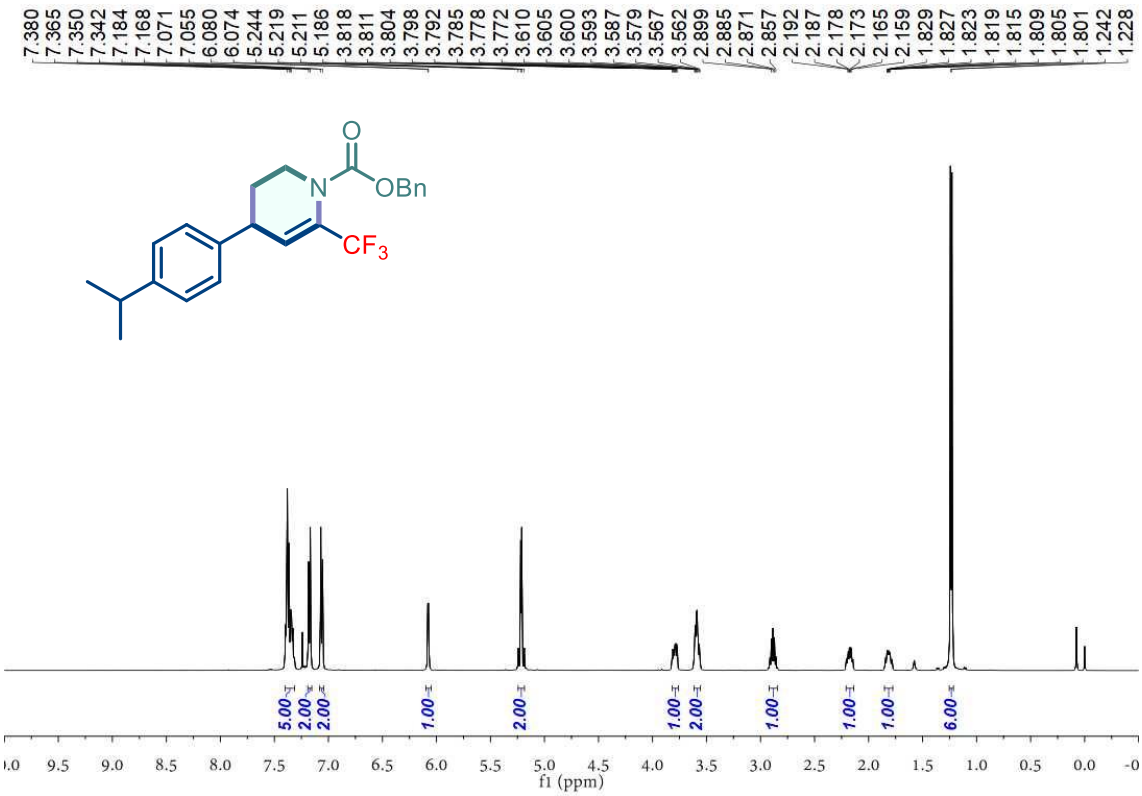


**Figure S9.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **6**.

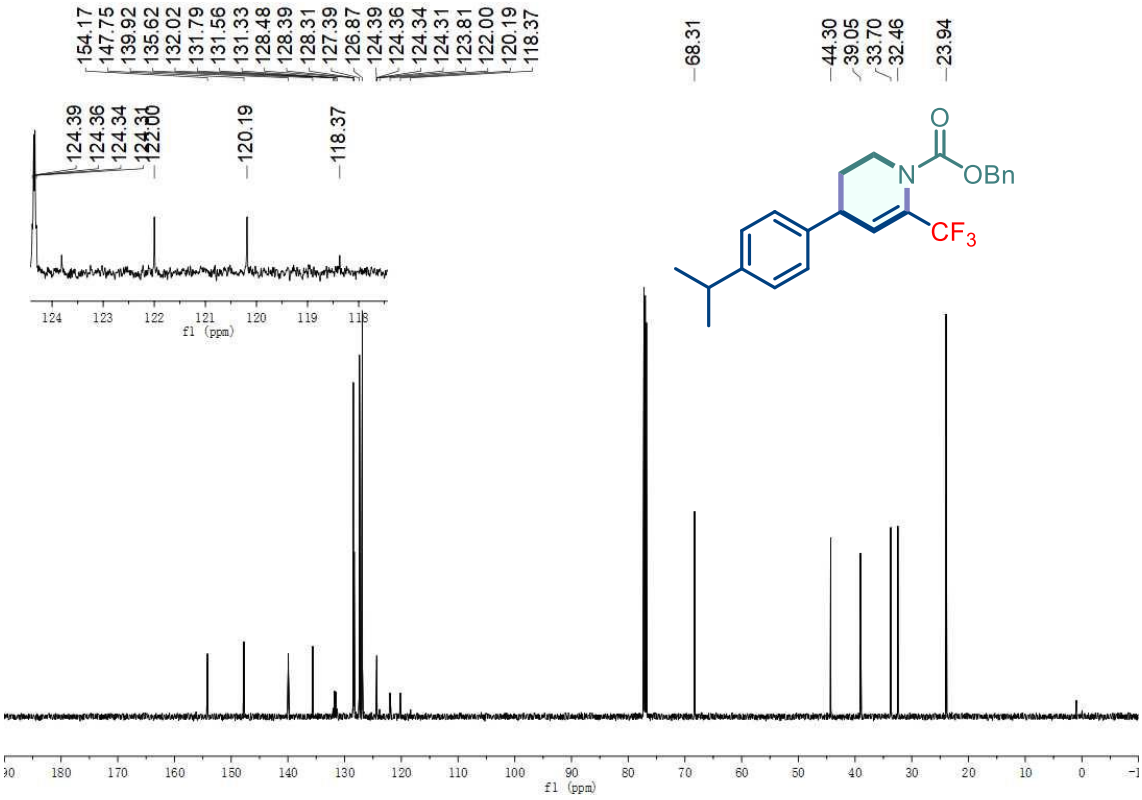


**Figure S10.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **6**.

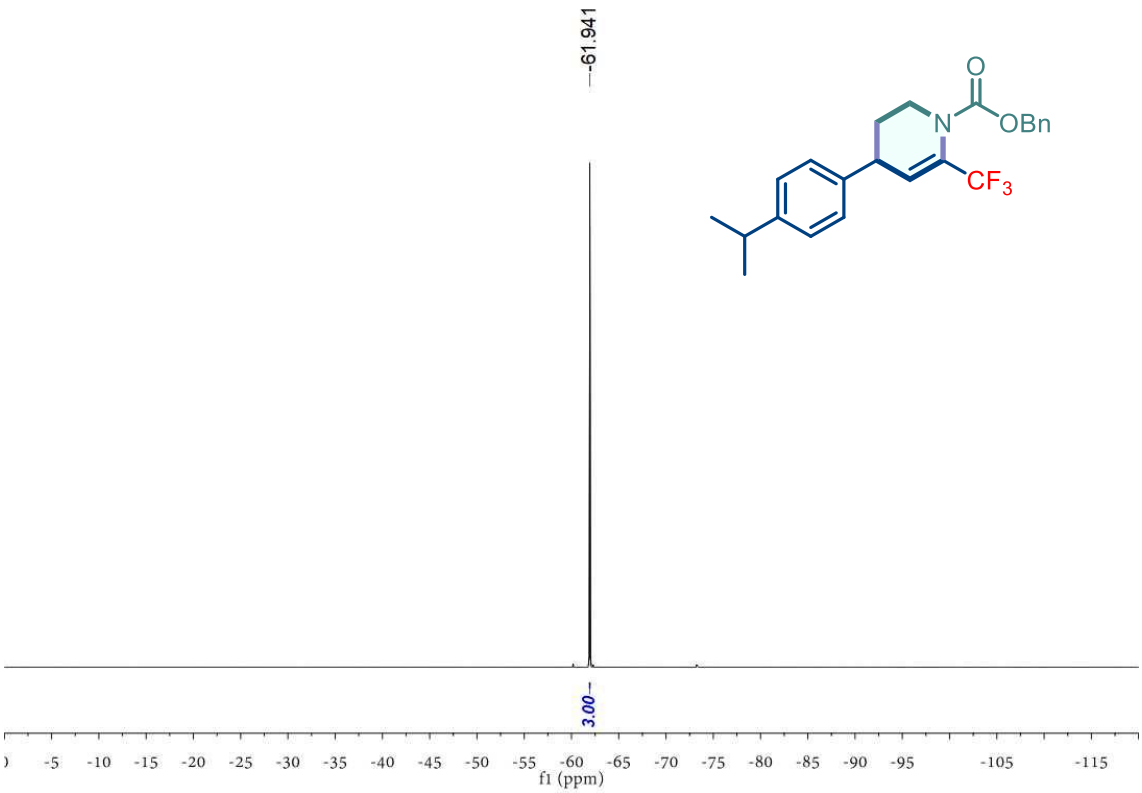


**Figure S11.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **6**.

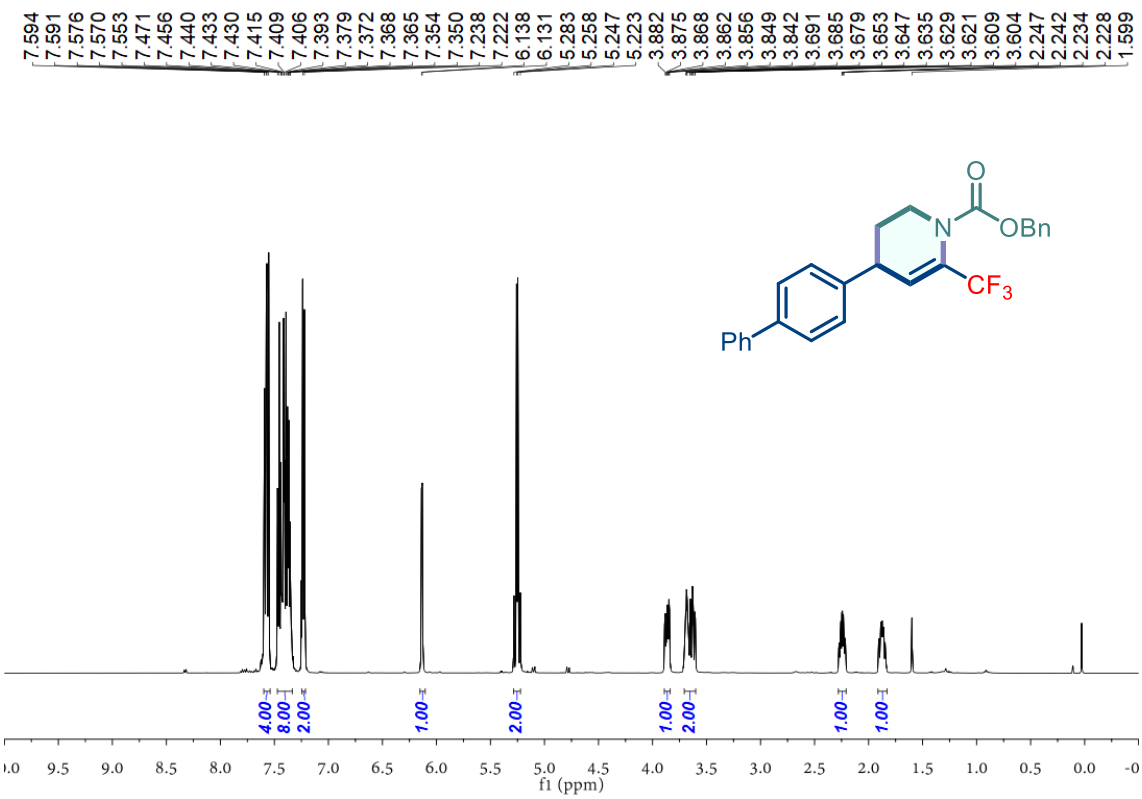


**Figure S12.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **7**.

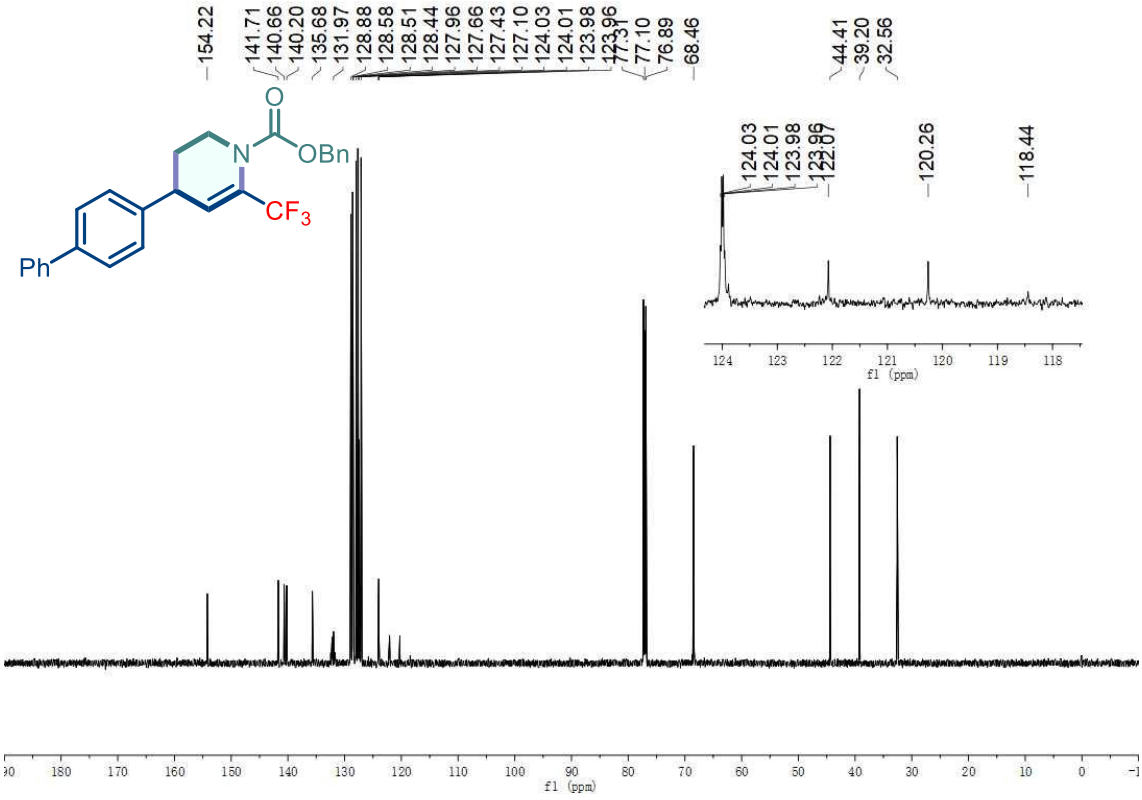


**Figure S13.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **7**.

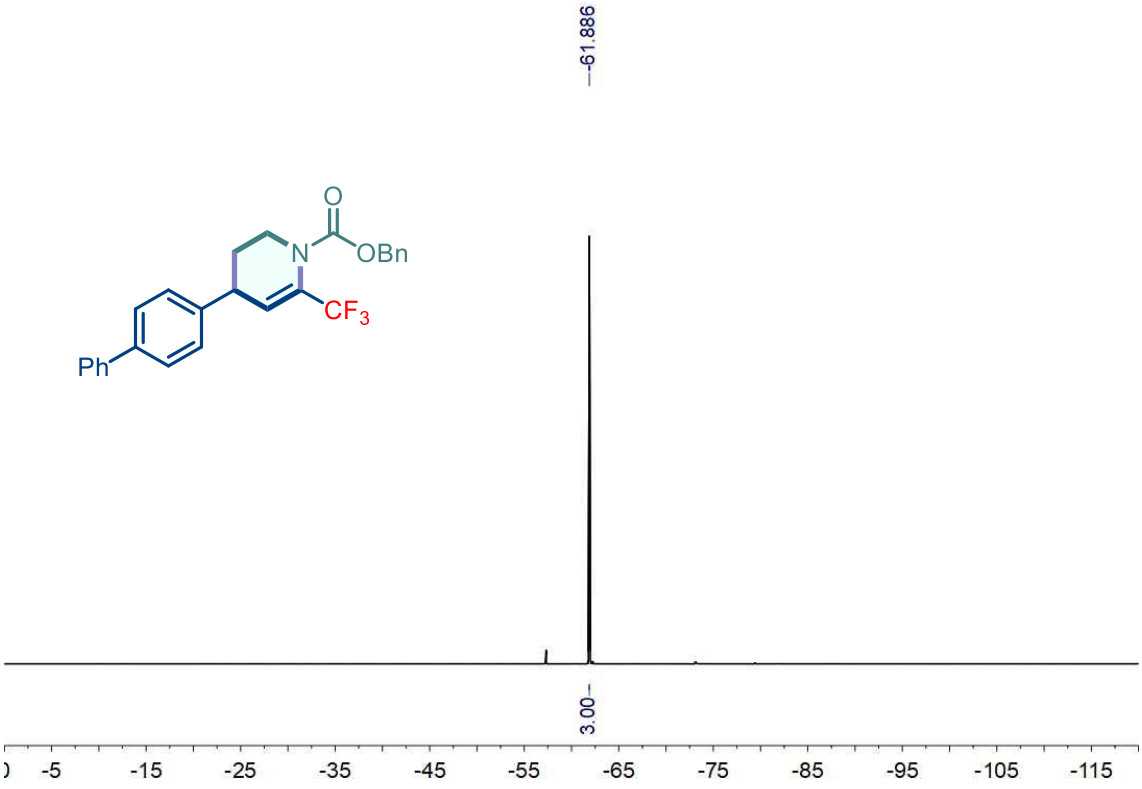


**Figure S14.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **7**.

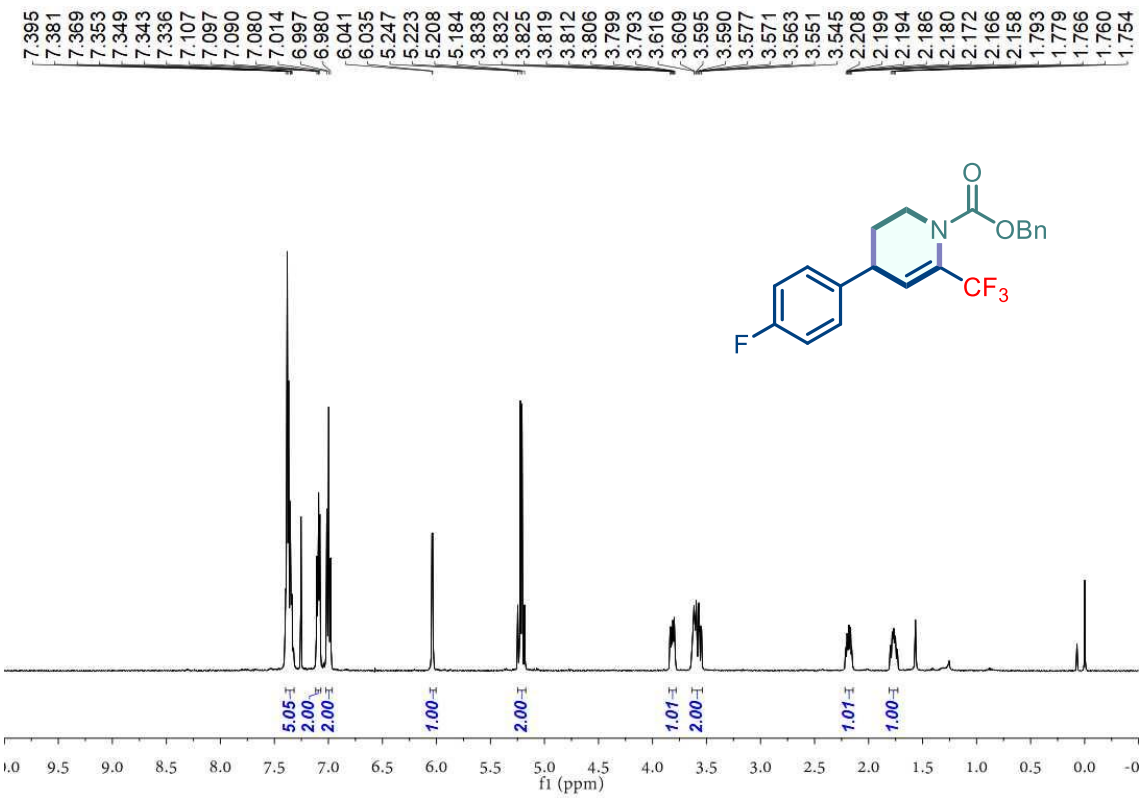


**Figure S15.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **8**.

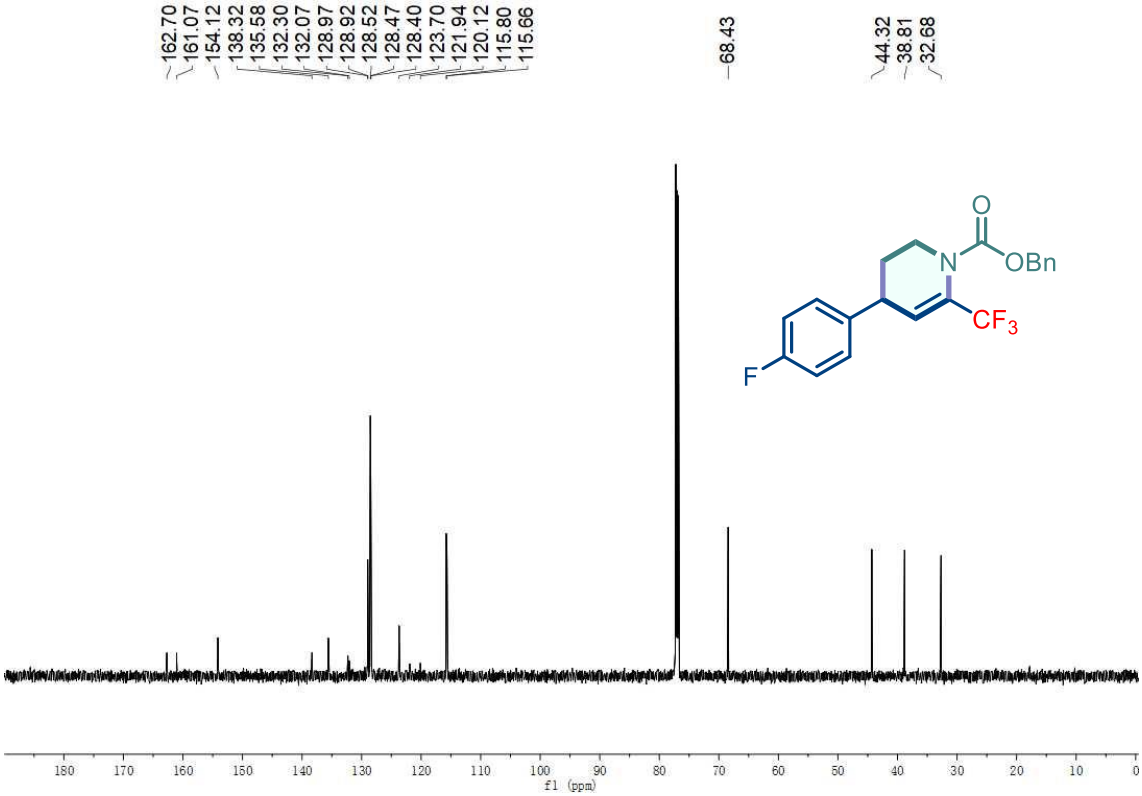


**Figure S16.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **8**.

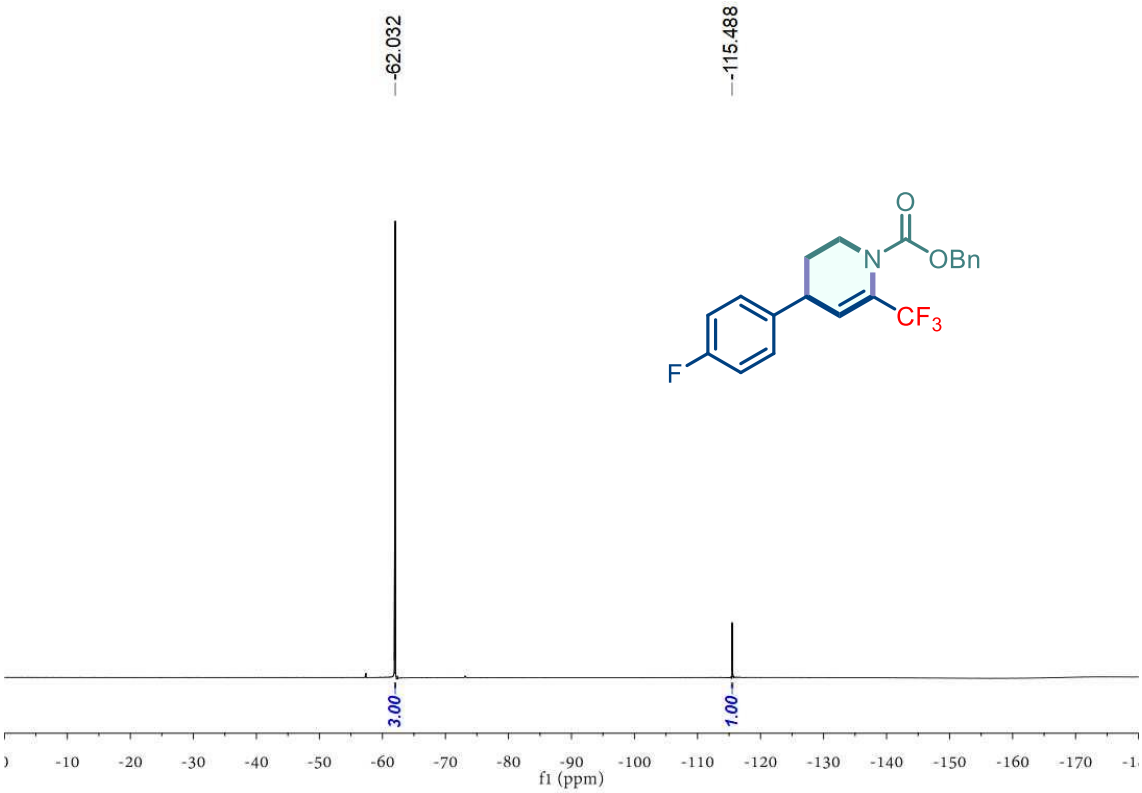


**Figure S17.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **8**.

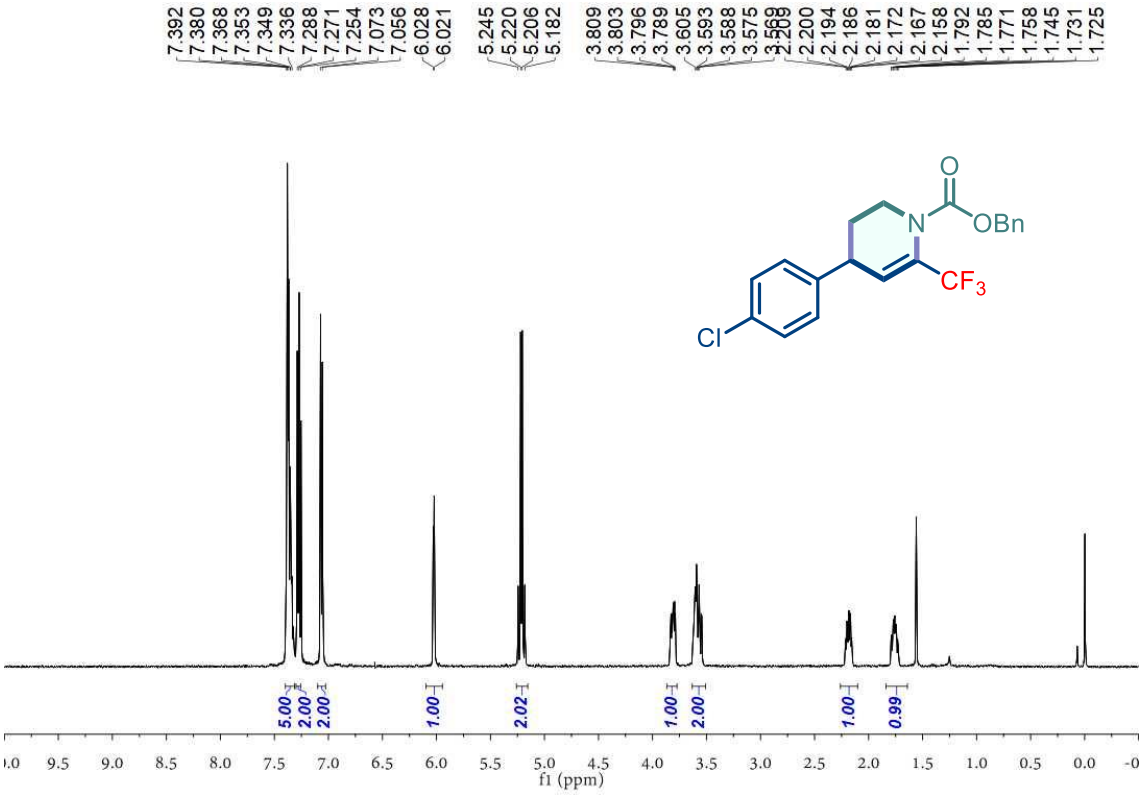


**Figure S18.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **9**.

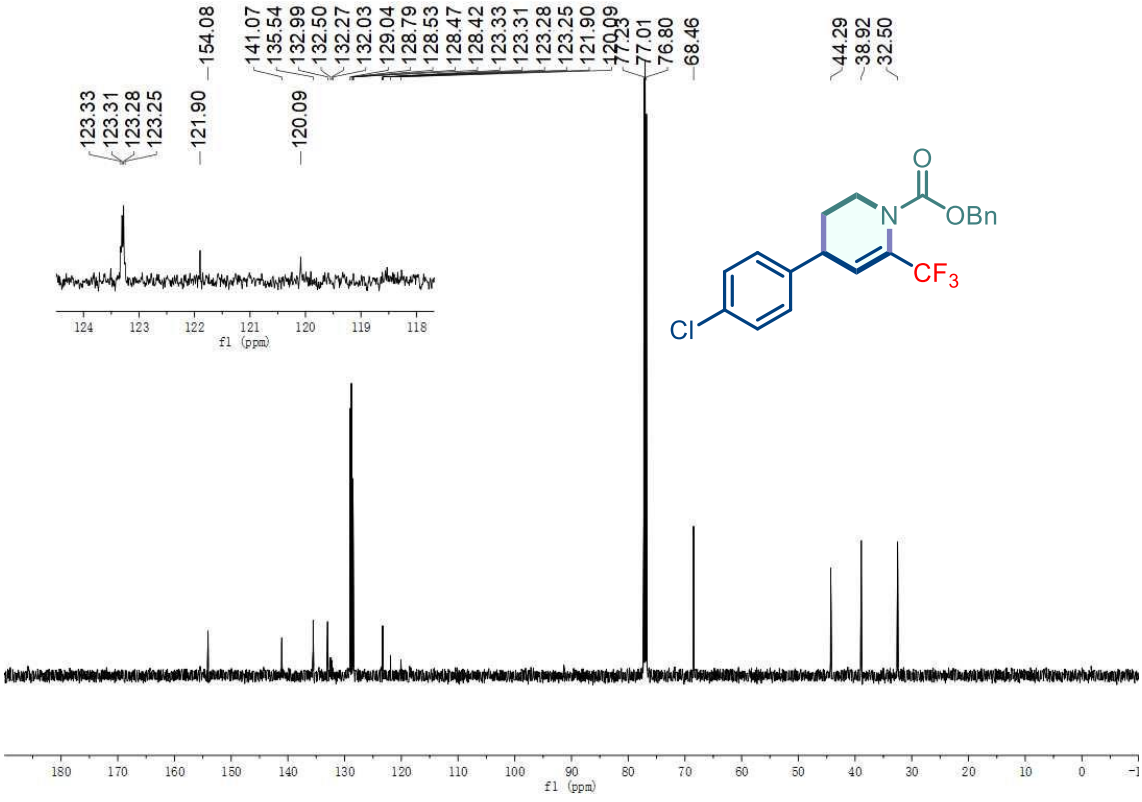


**Figure S19.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **9**.

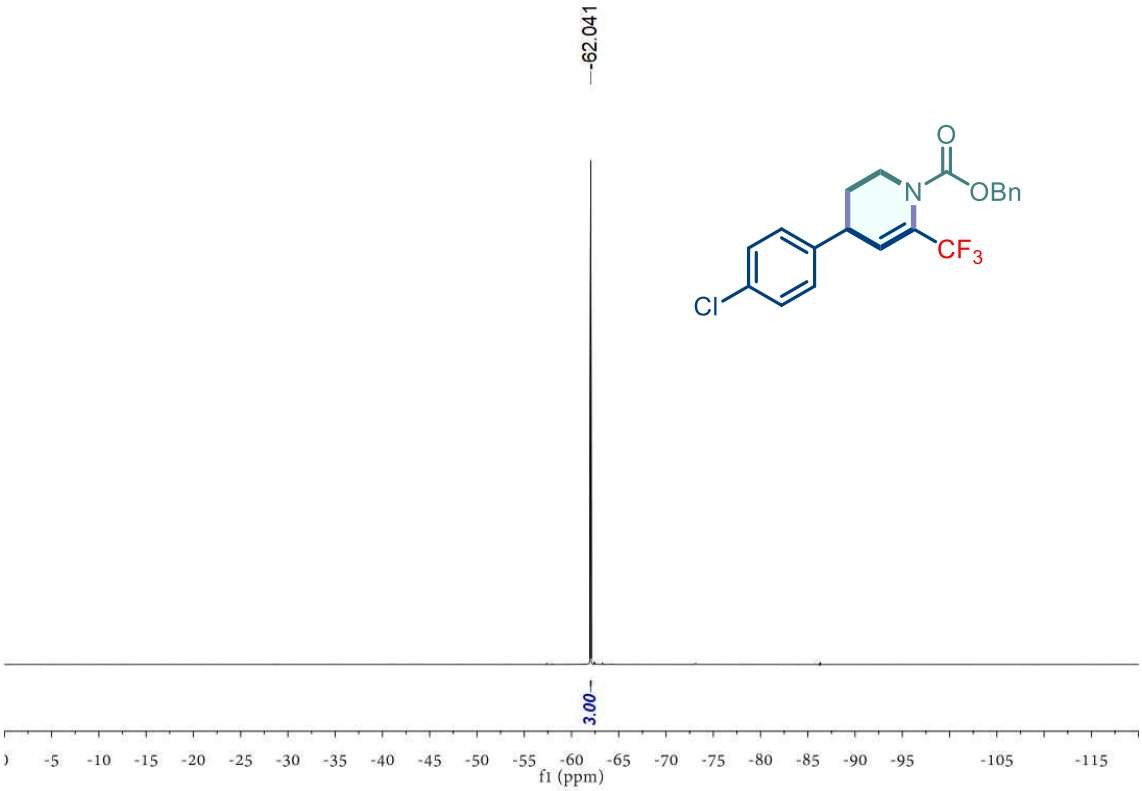


**Figure S20.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **9**.

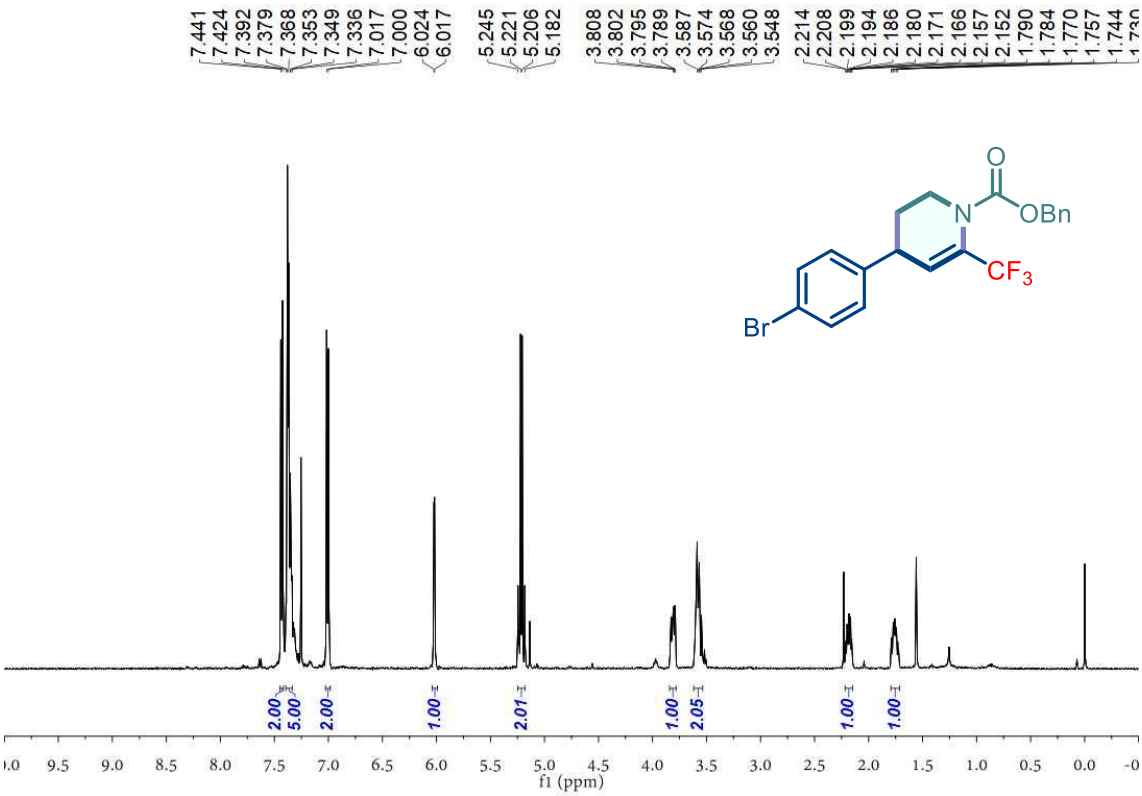


**Figure S21.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **10**.

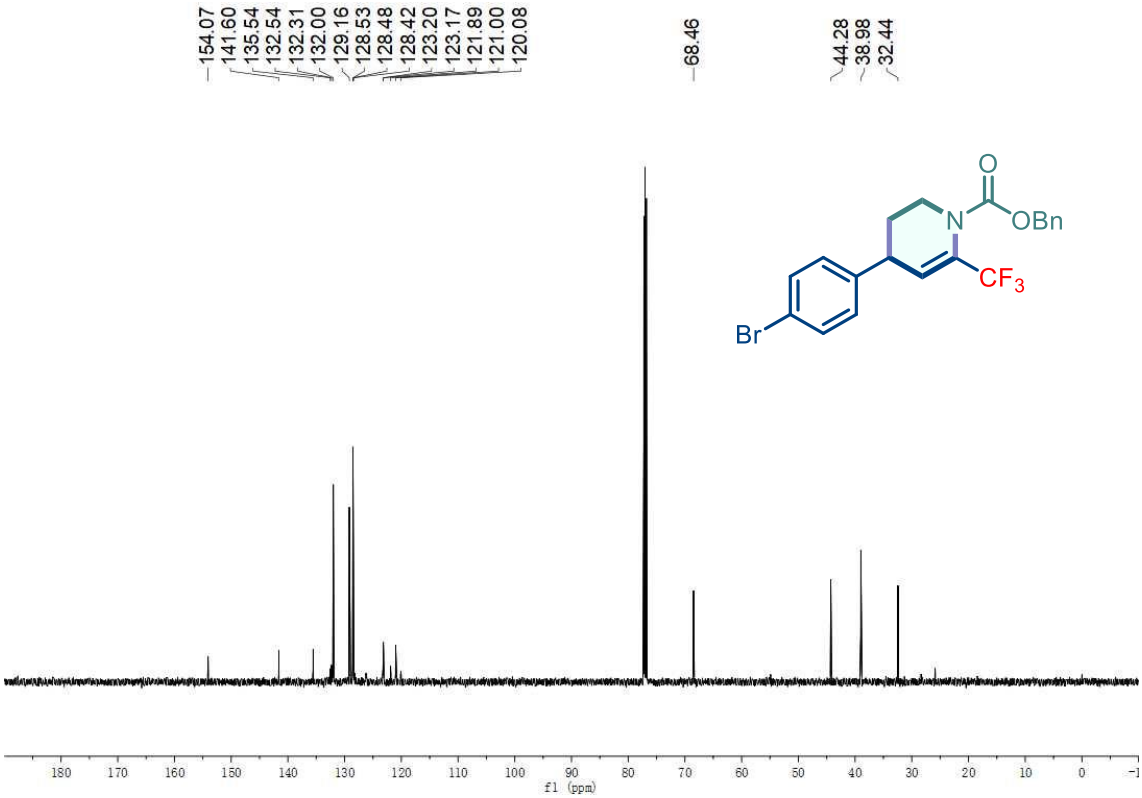


**Figure S22.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **10**.

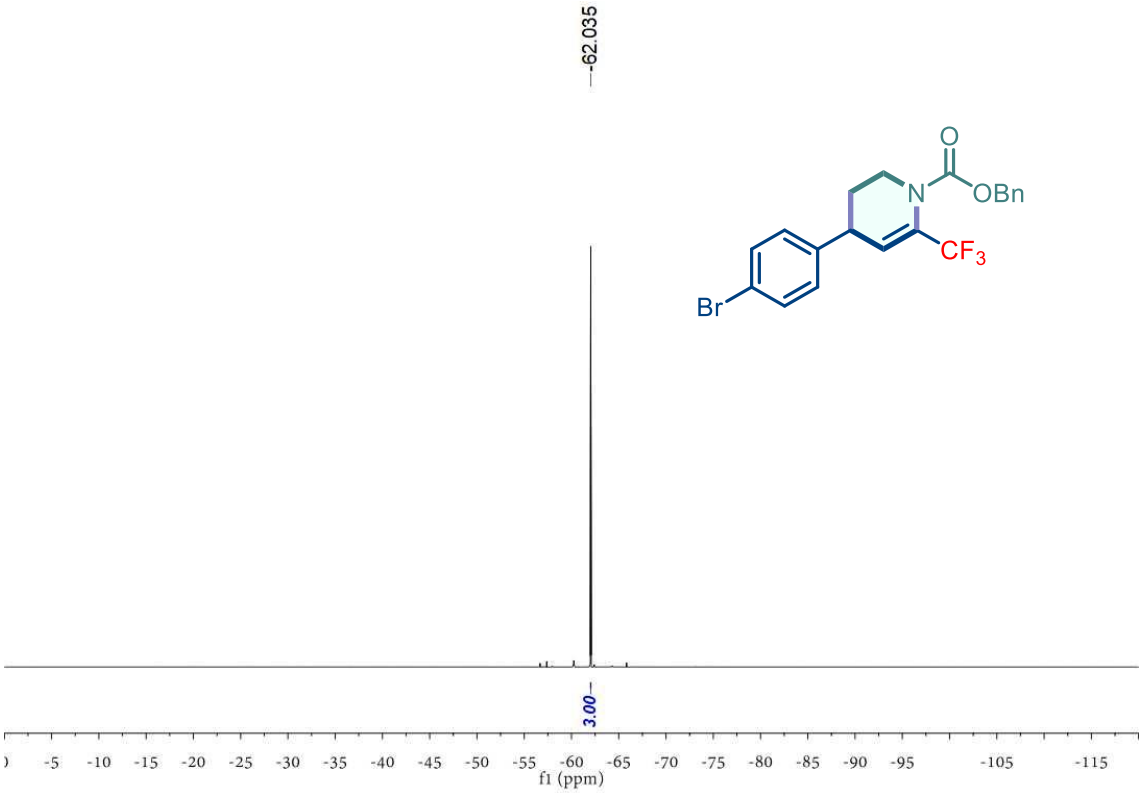


**Figure S23.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **10**.

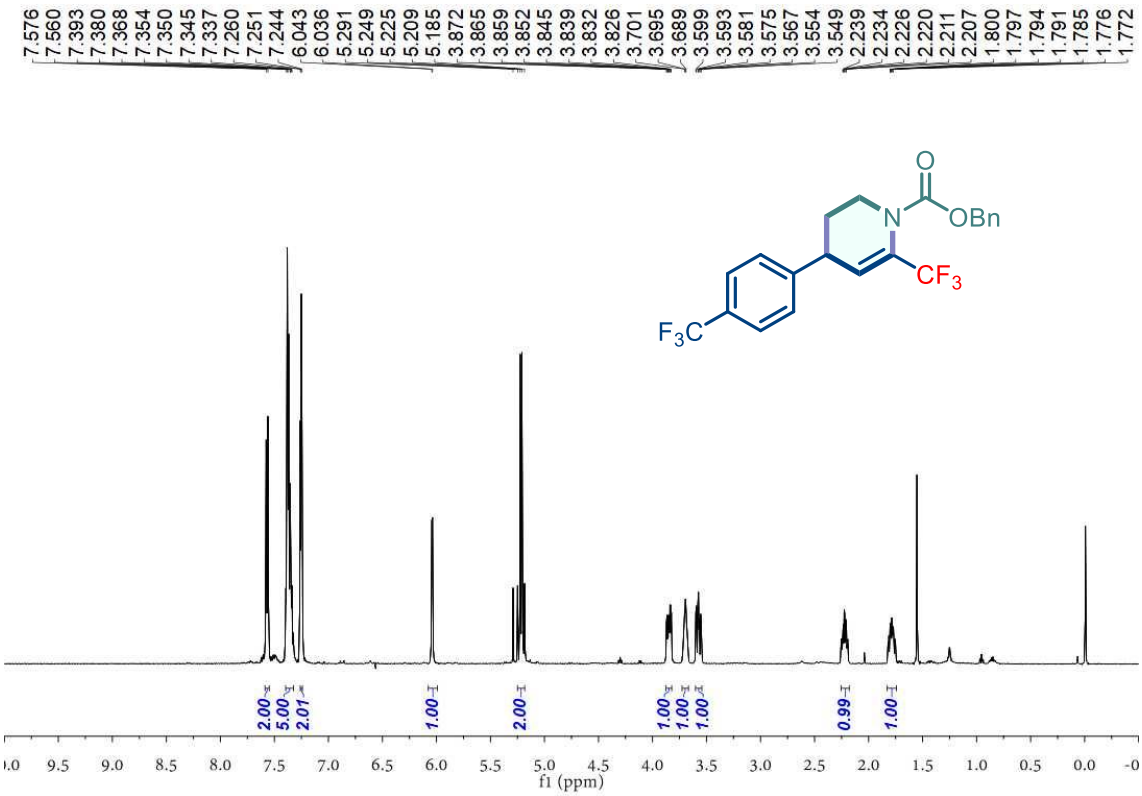


**Figure S24.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **11**.

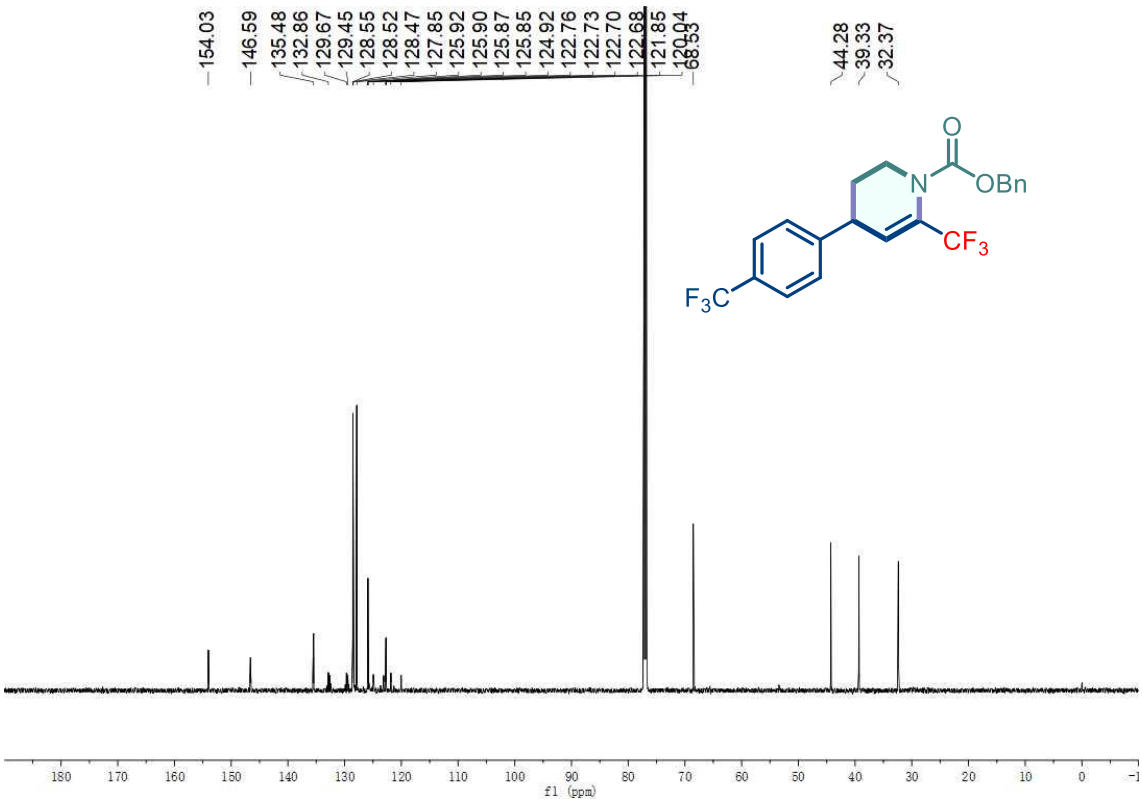


**Figure S25.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **11**.

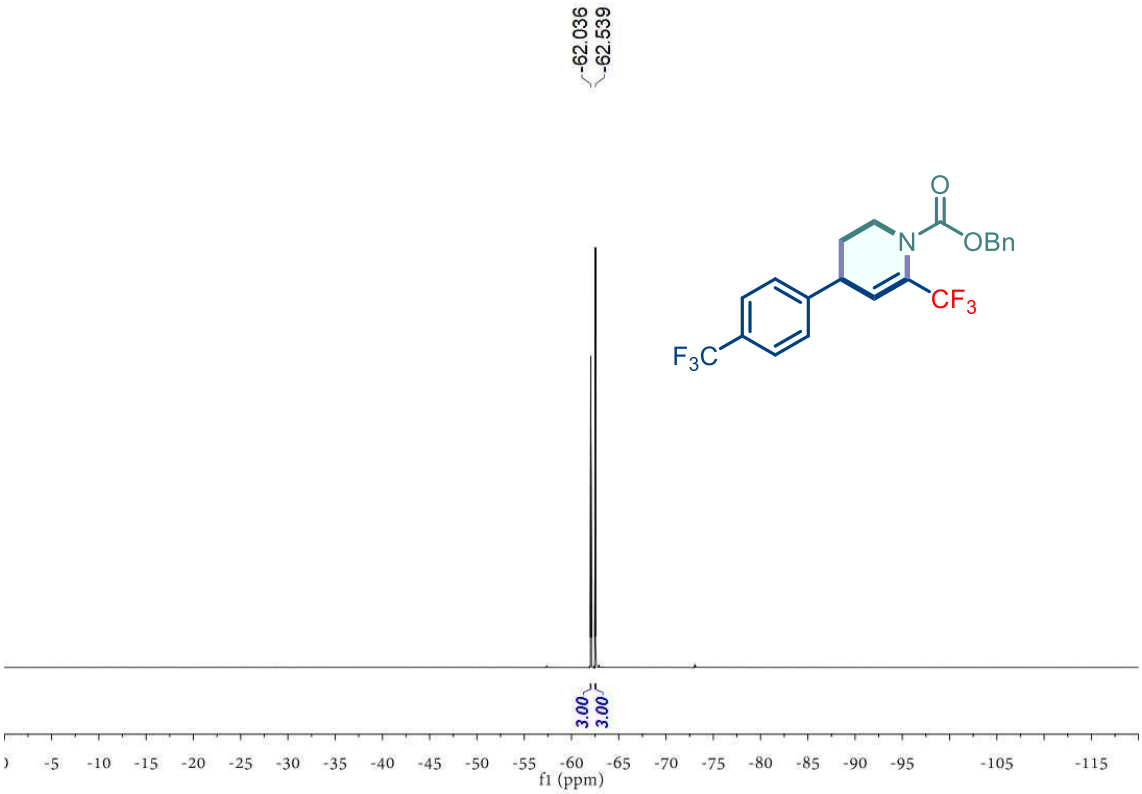


**Figure S26.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **11**.

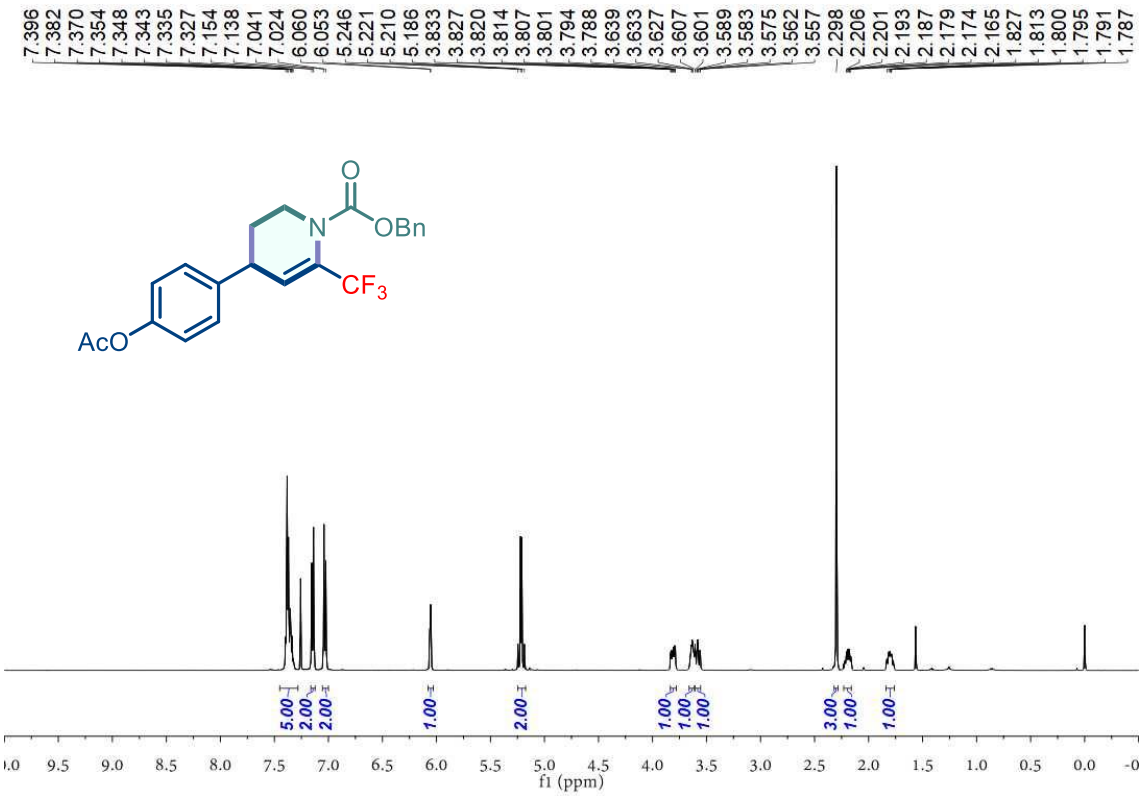


**Figure S27.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **12**.

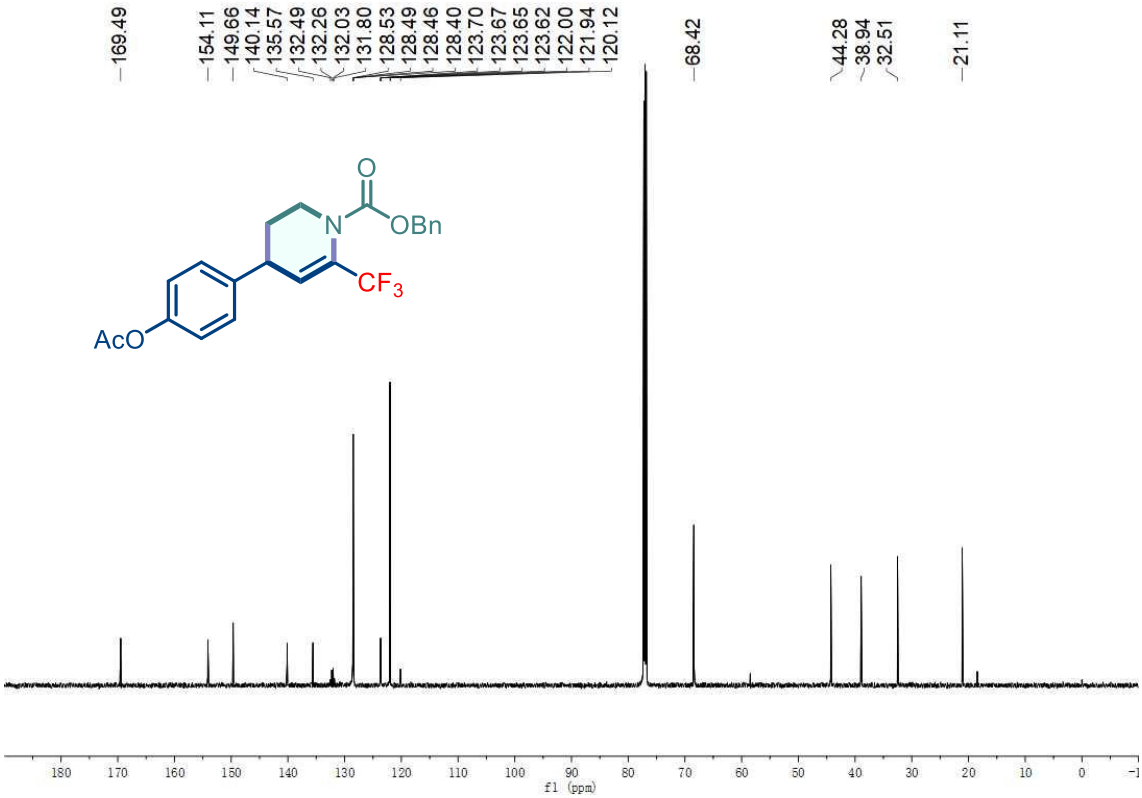


**Figure S28.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **12**.

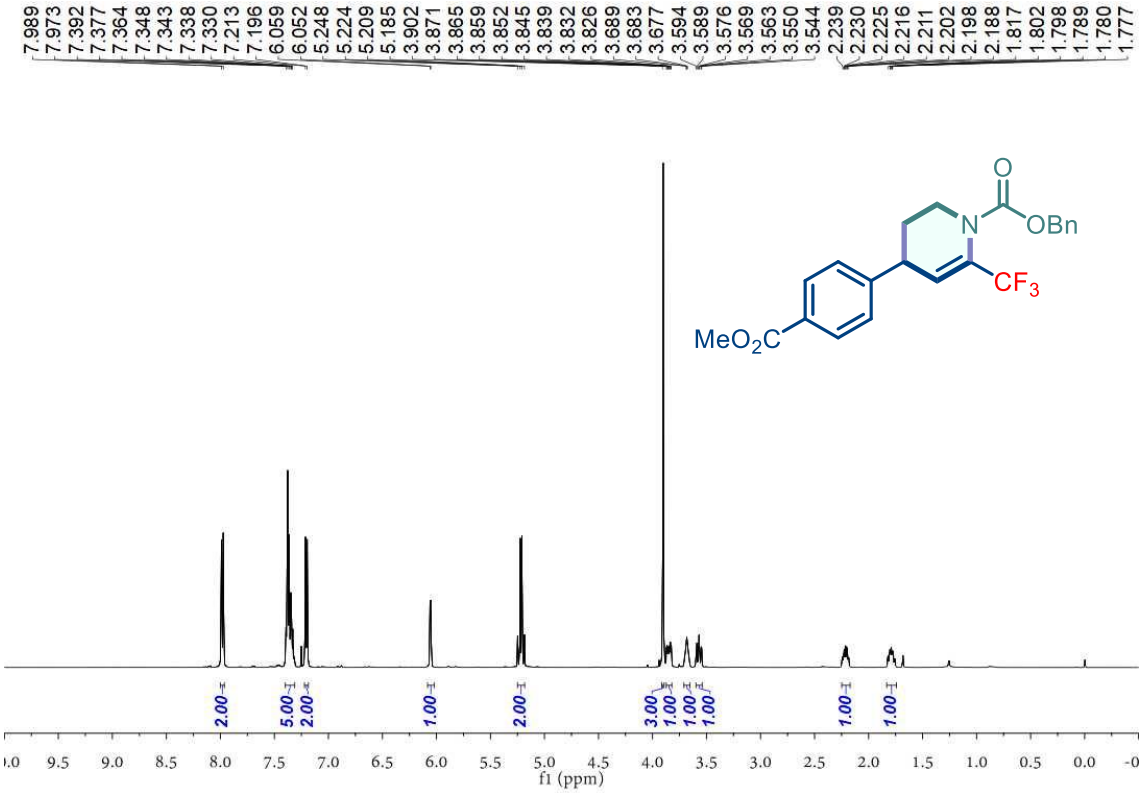


**Figure S29.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **13**.

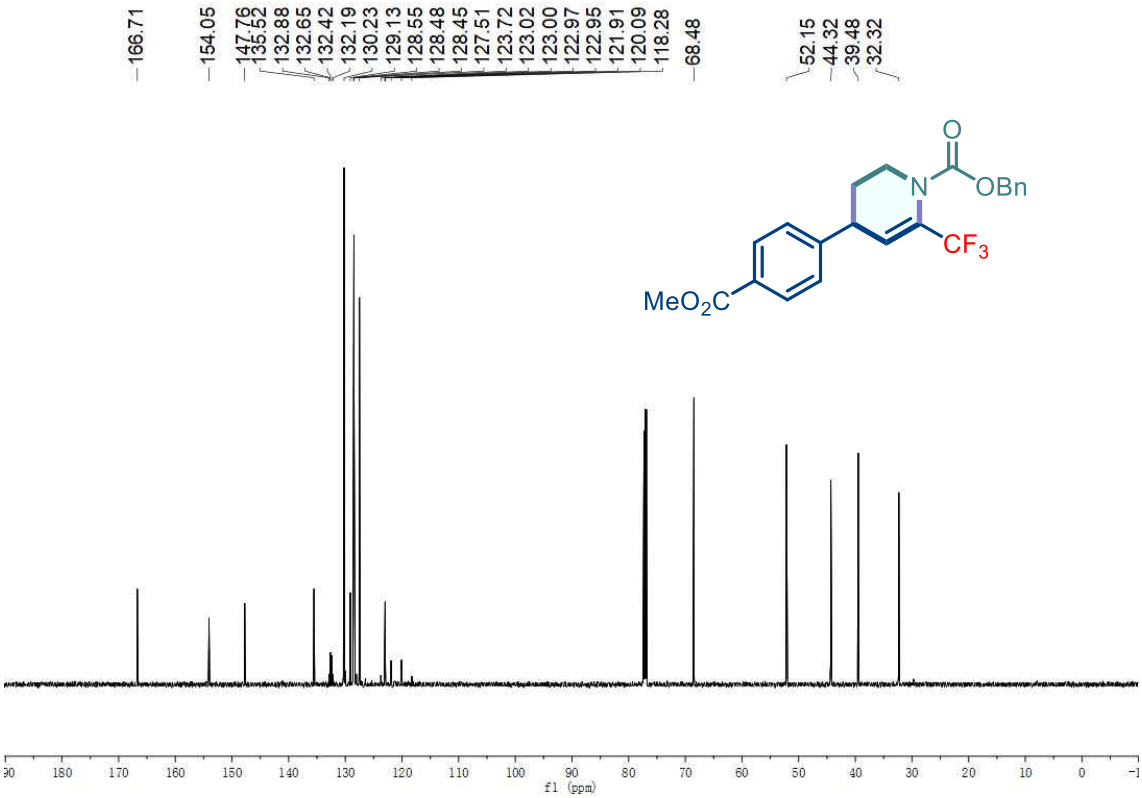


**Figure S30.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **13**.

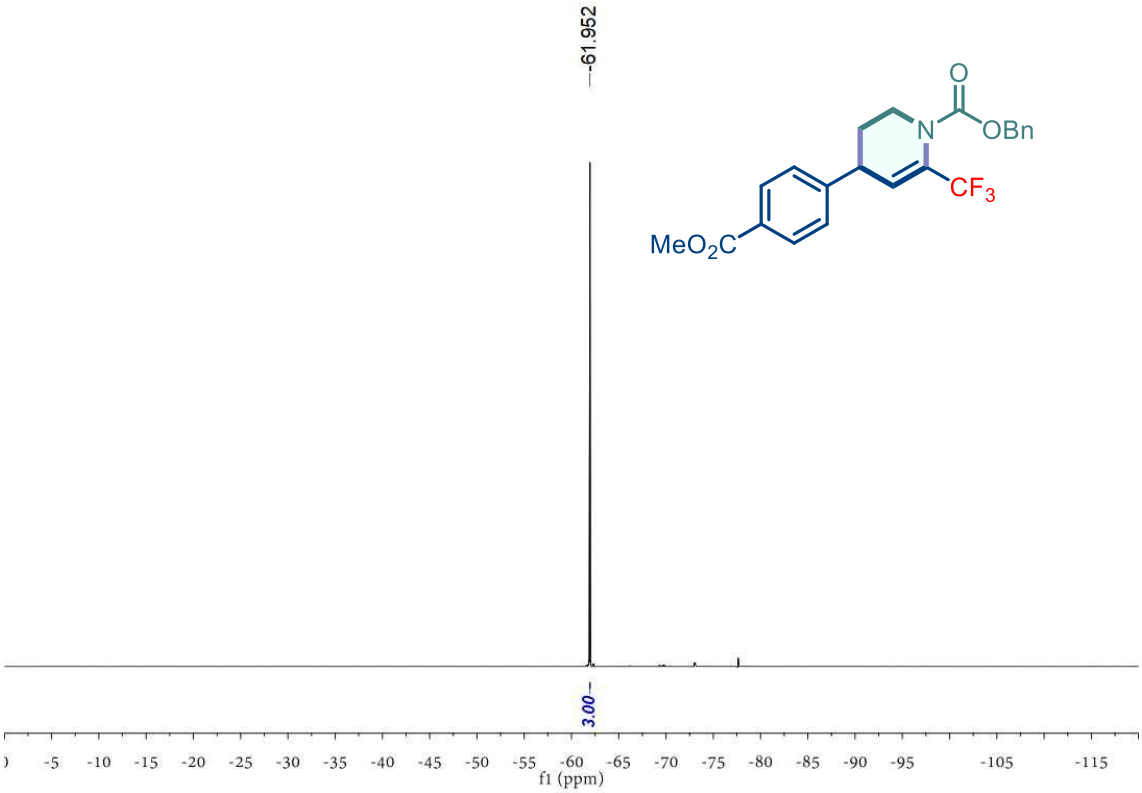


**Figure S31.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **13**.

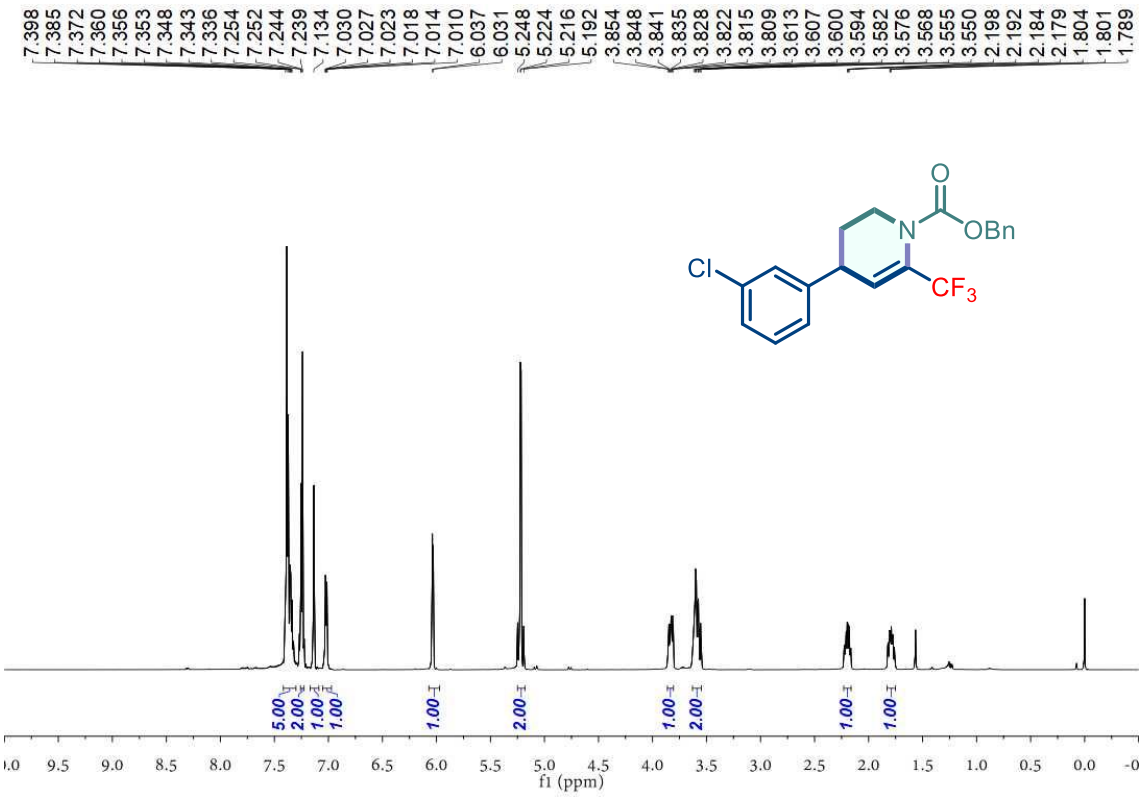


**Figure S32.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **14**.

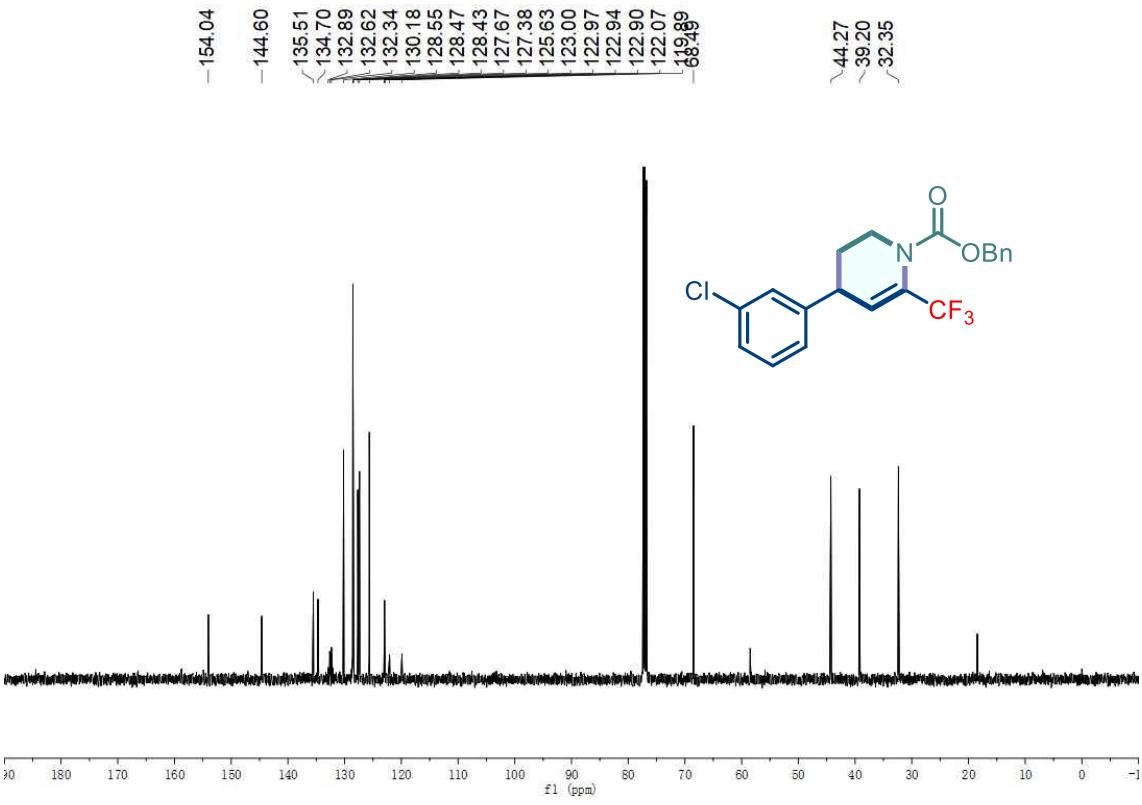


**Figure S33.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **14**.

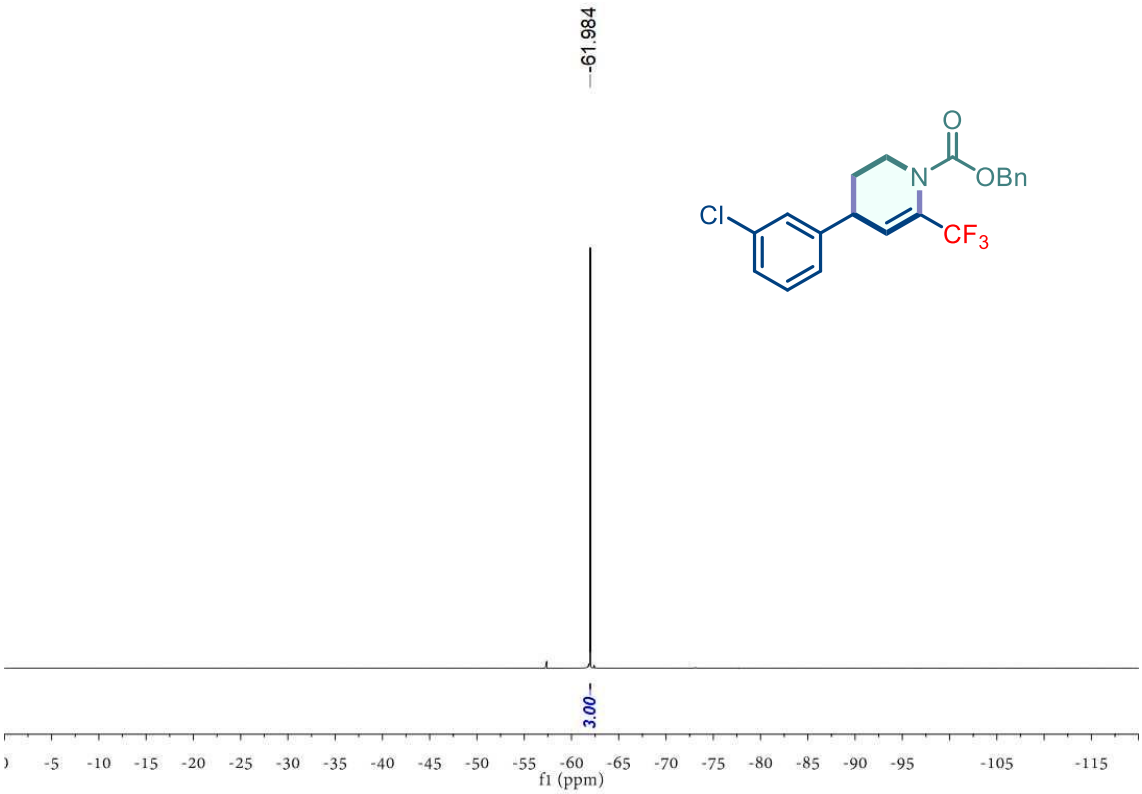


**Figure S34.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **14**.

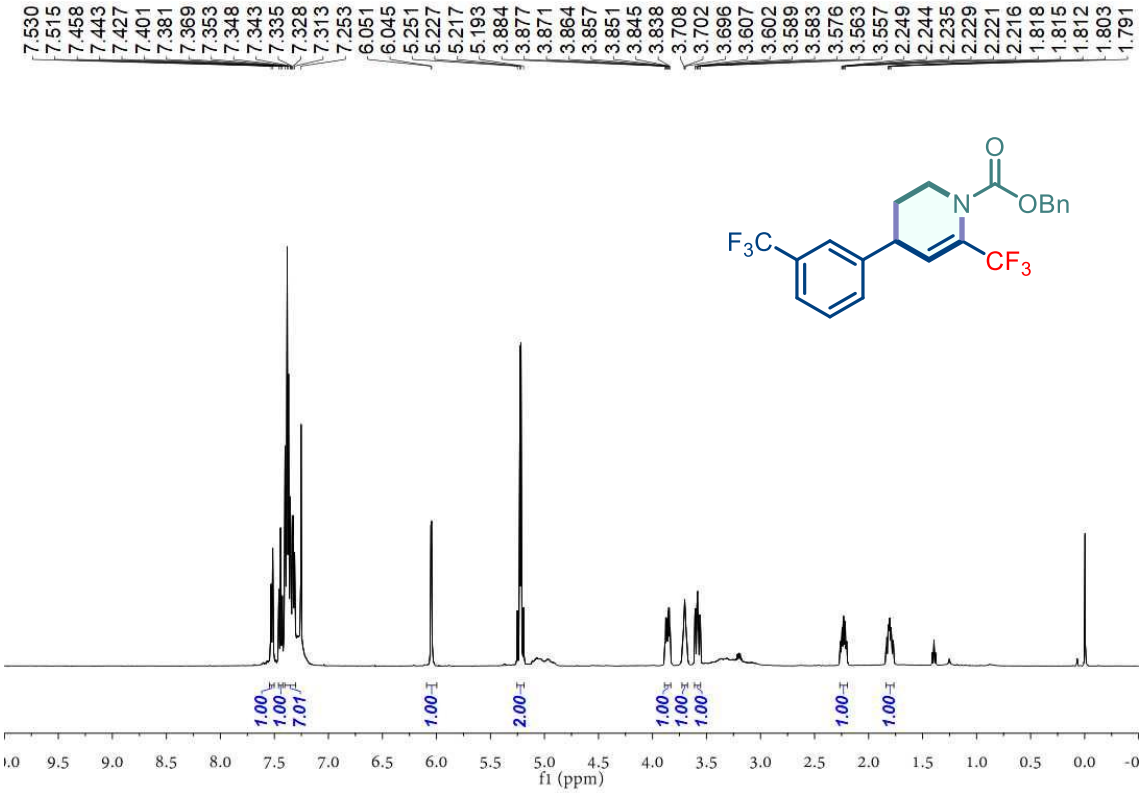


**Figure S35.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **15**.

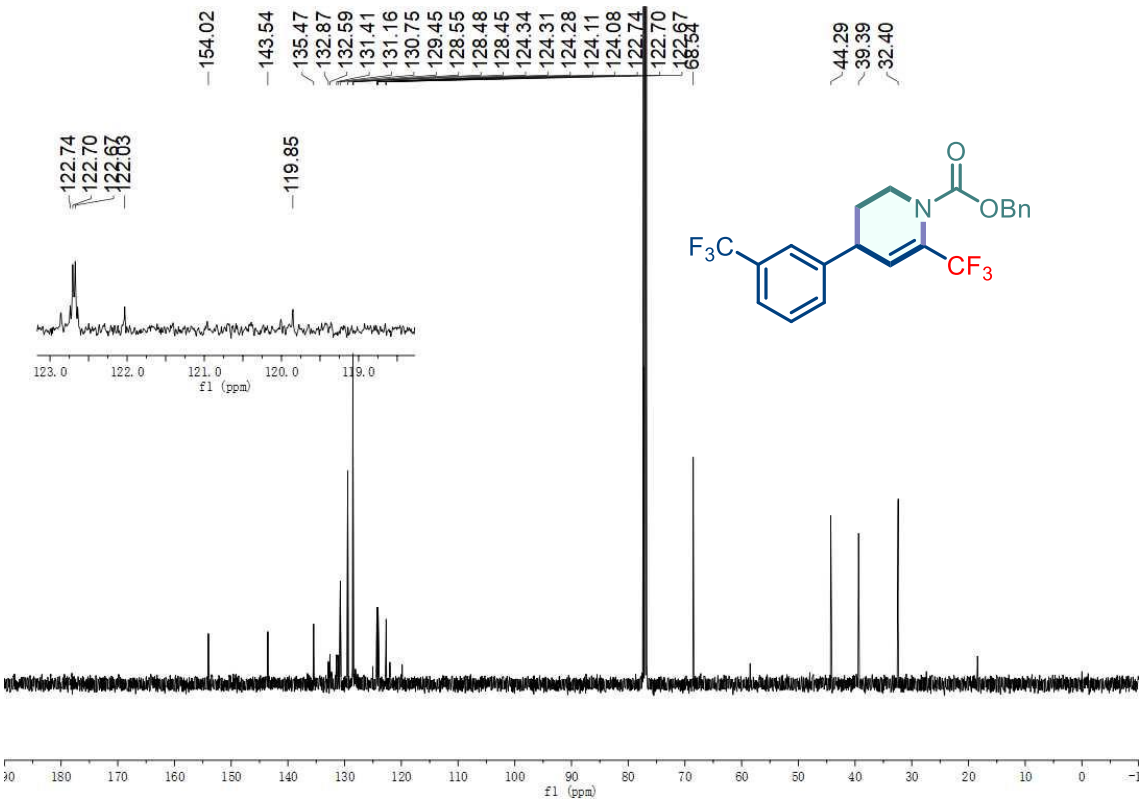


**Figure S36.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **15**.

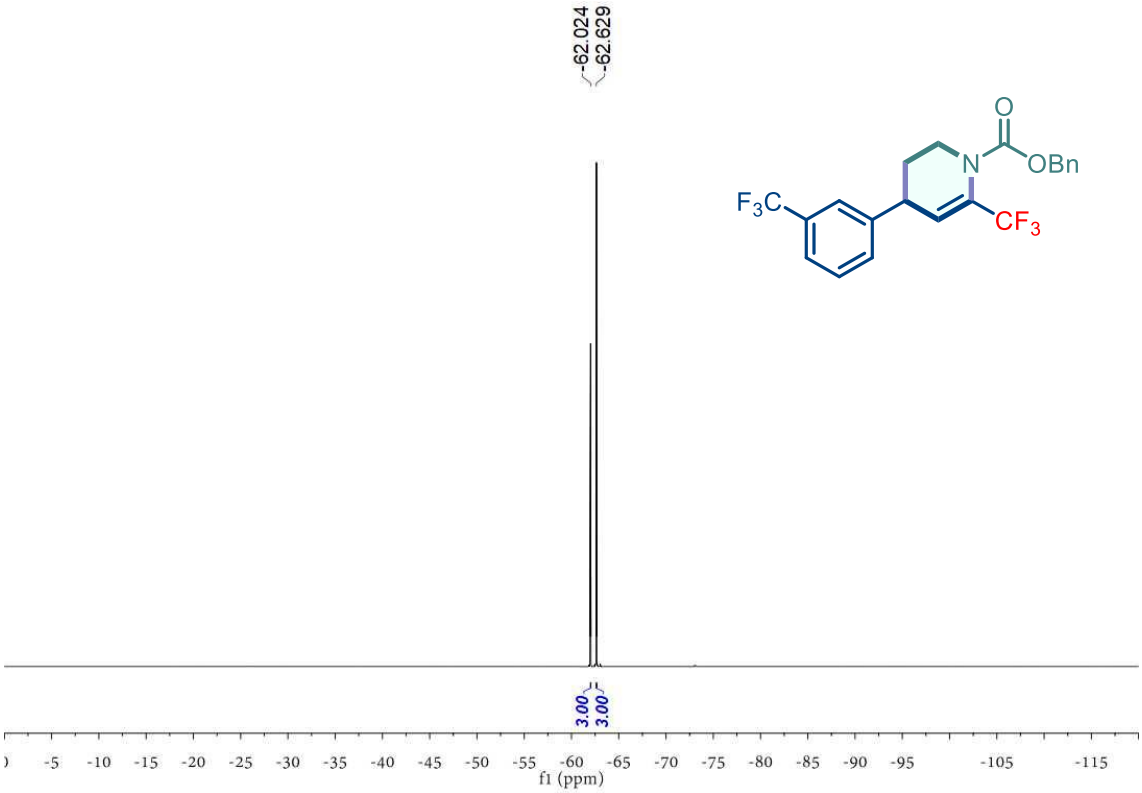


**Figure S37.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **15**.

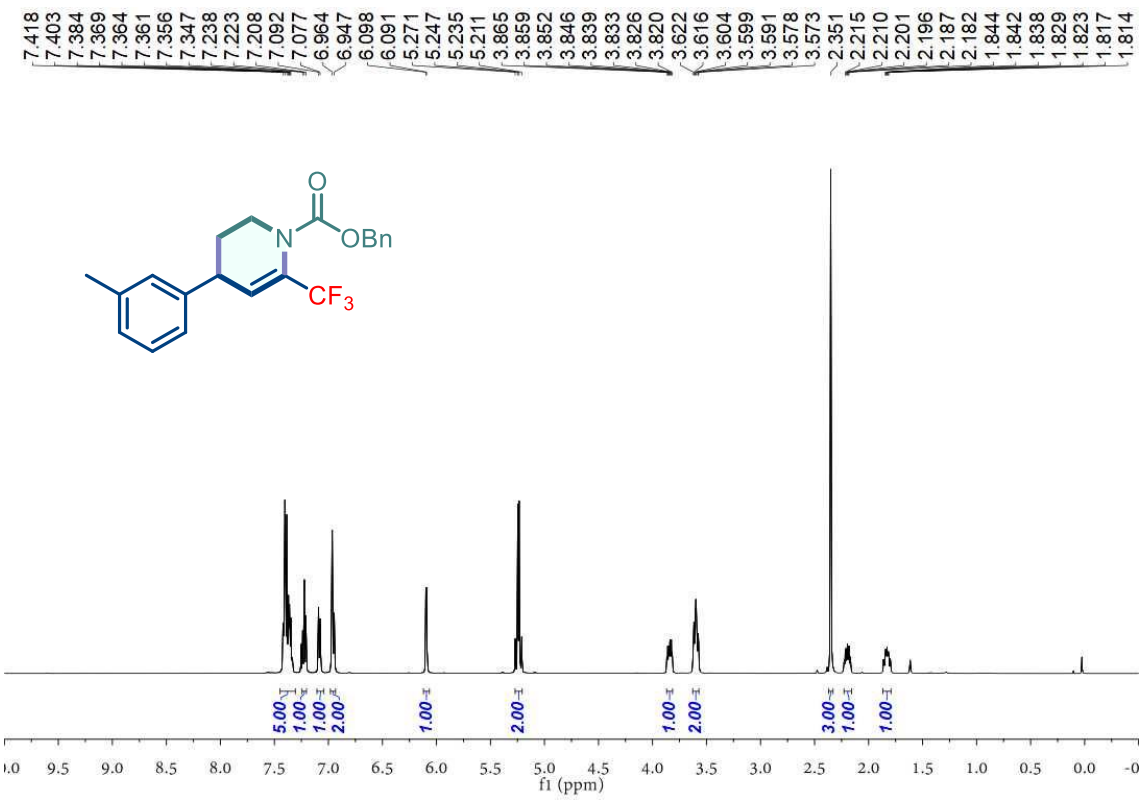


**Figure S38.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **16**.

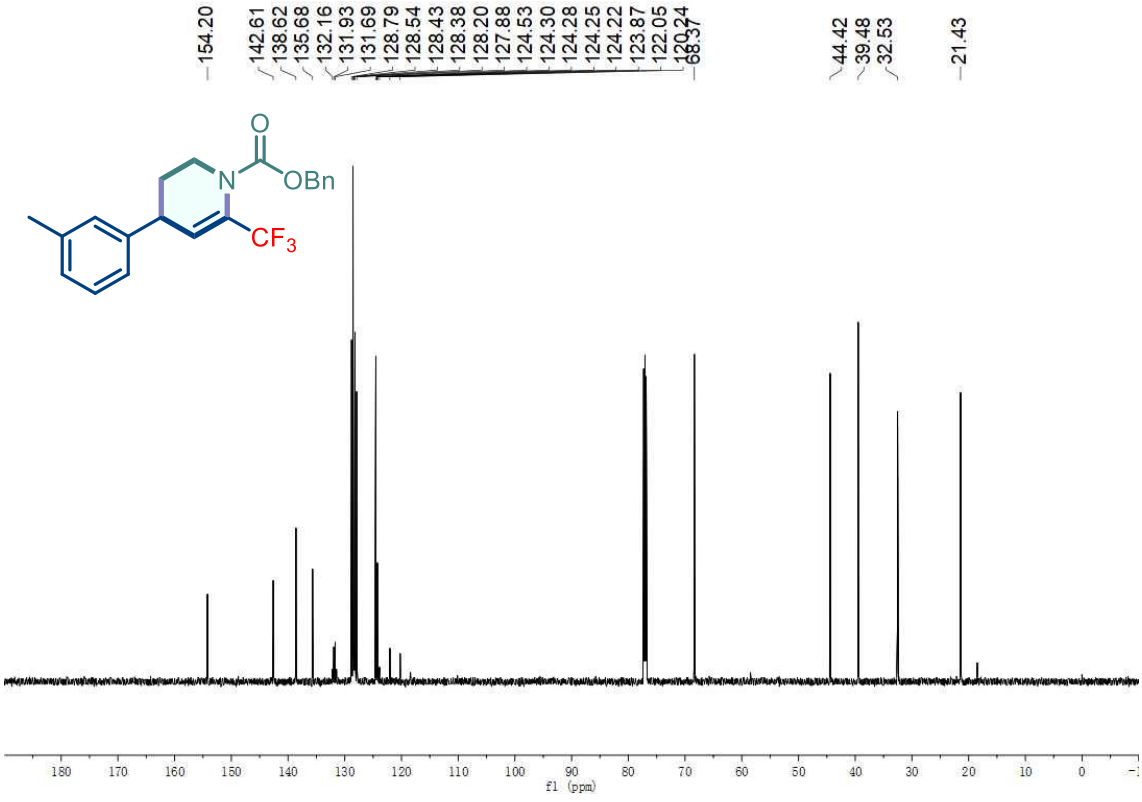


**Figure S39.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **16**.

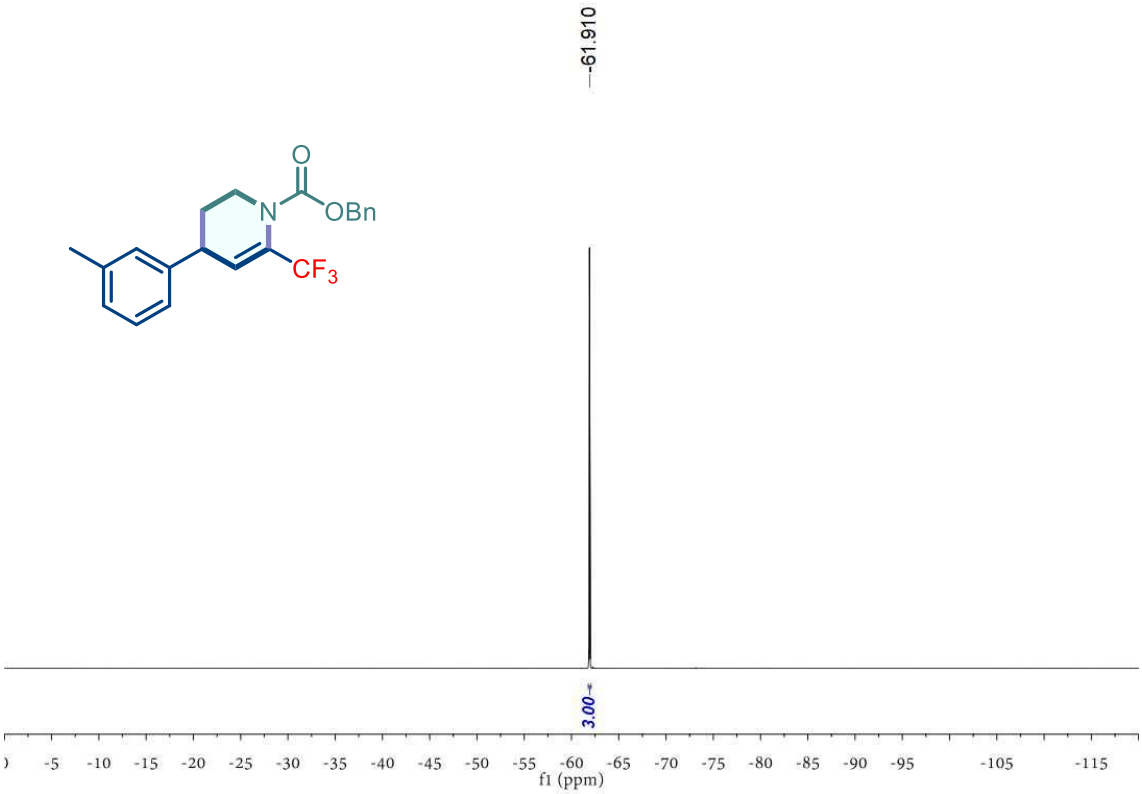


**Figure S40.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **16**.

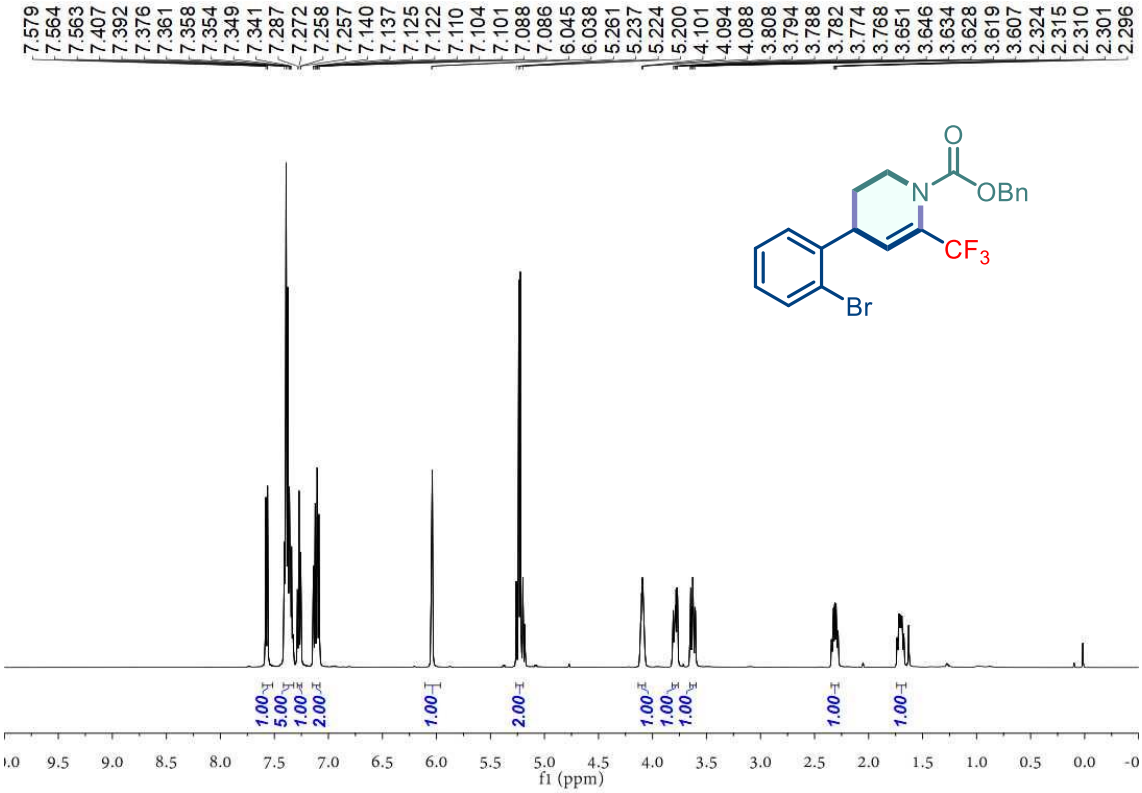


**Figure S41.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **17**.

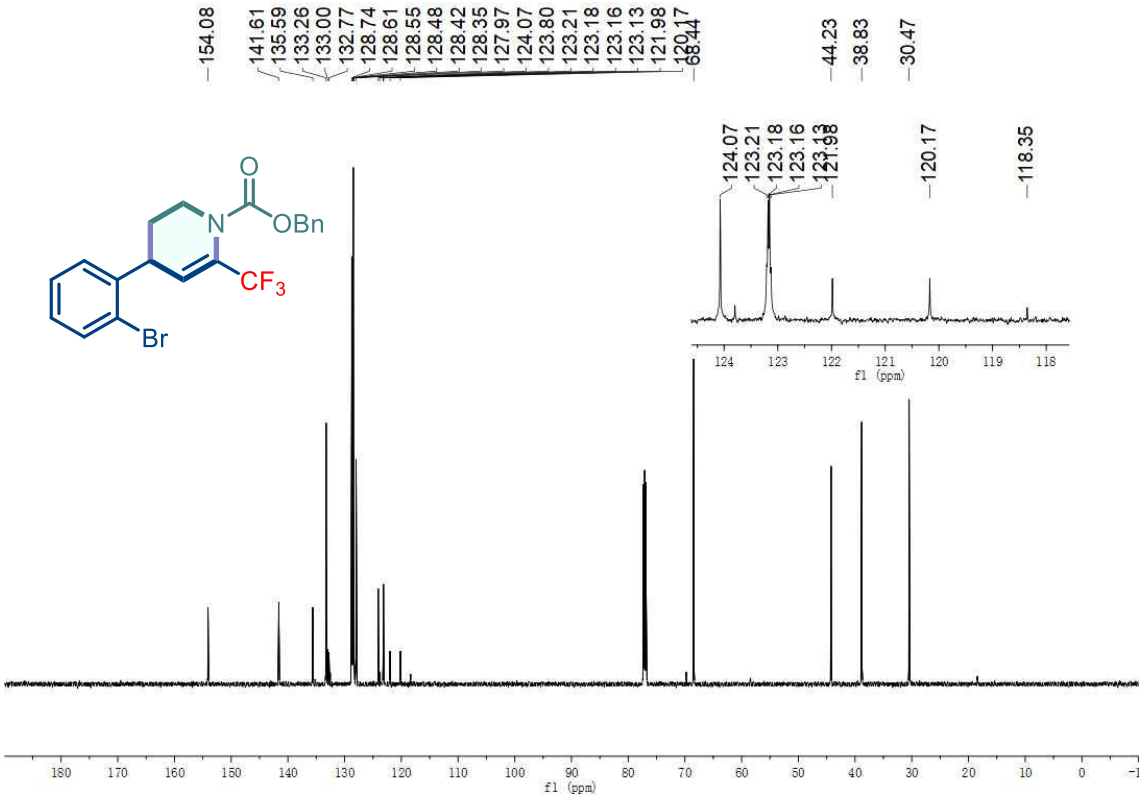


**Figure S42.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **17**.

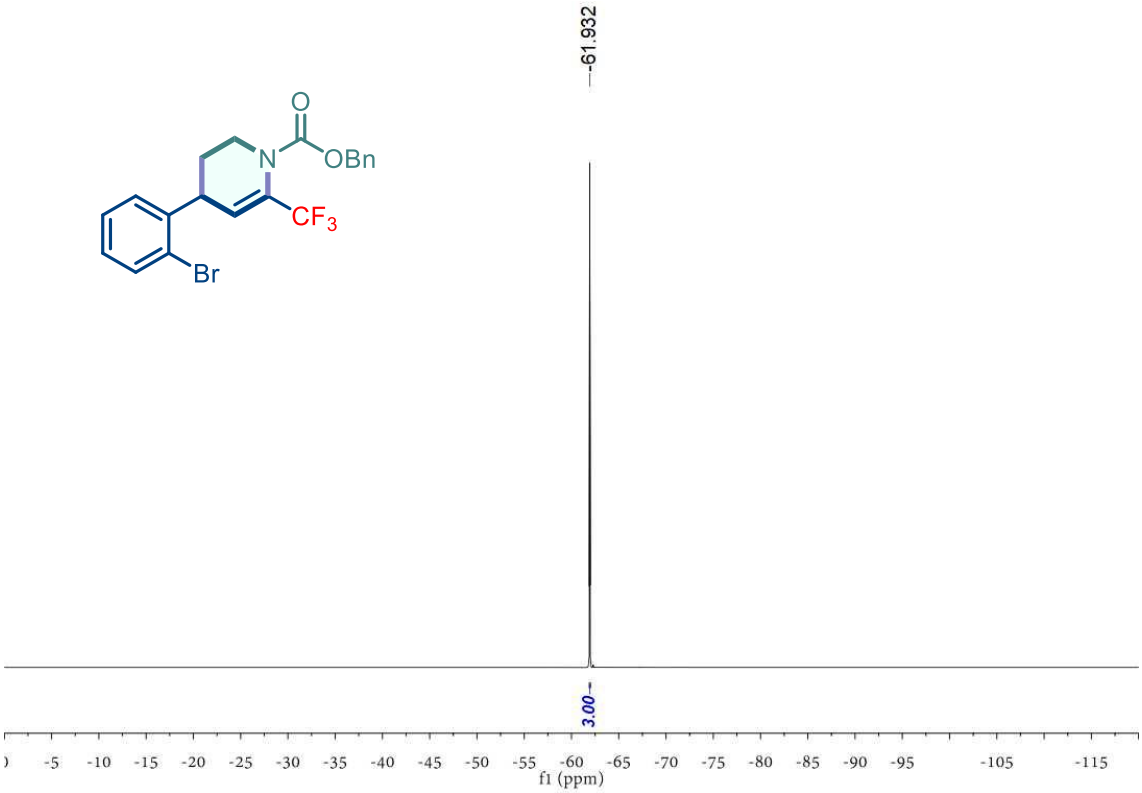


**Figure S43.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **17**.

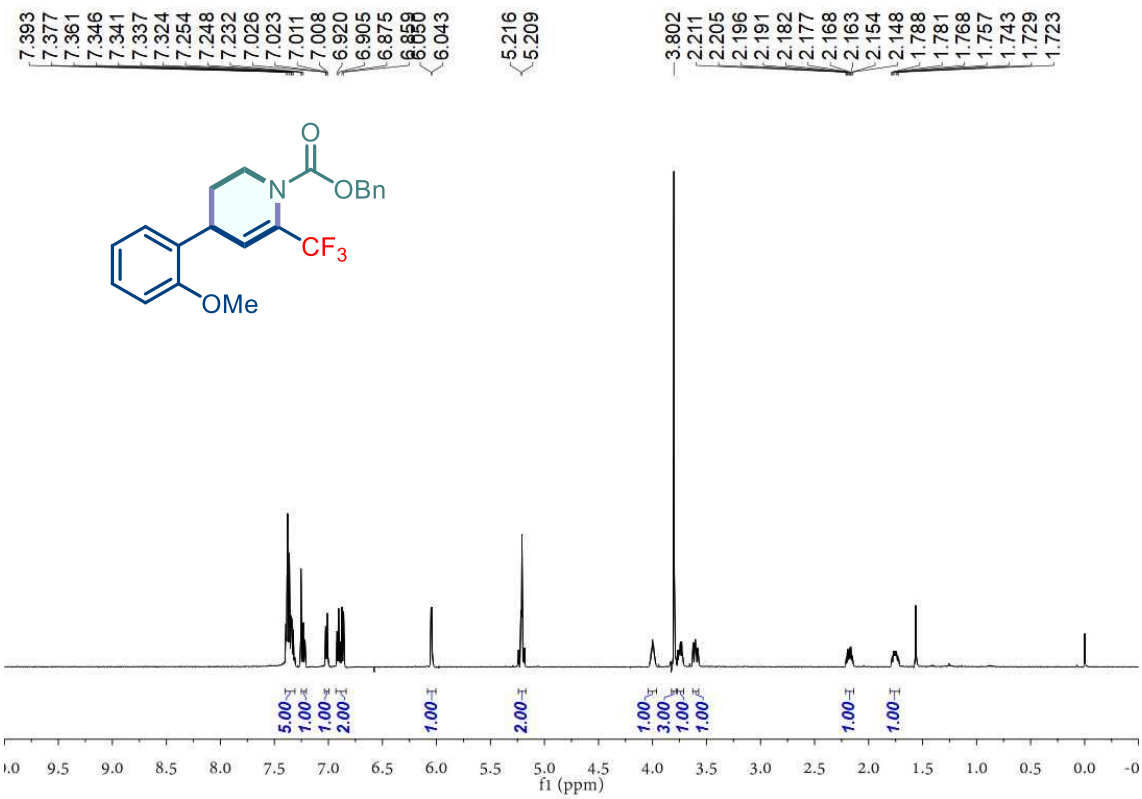


**Figure S44.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **18**.

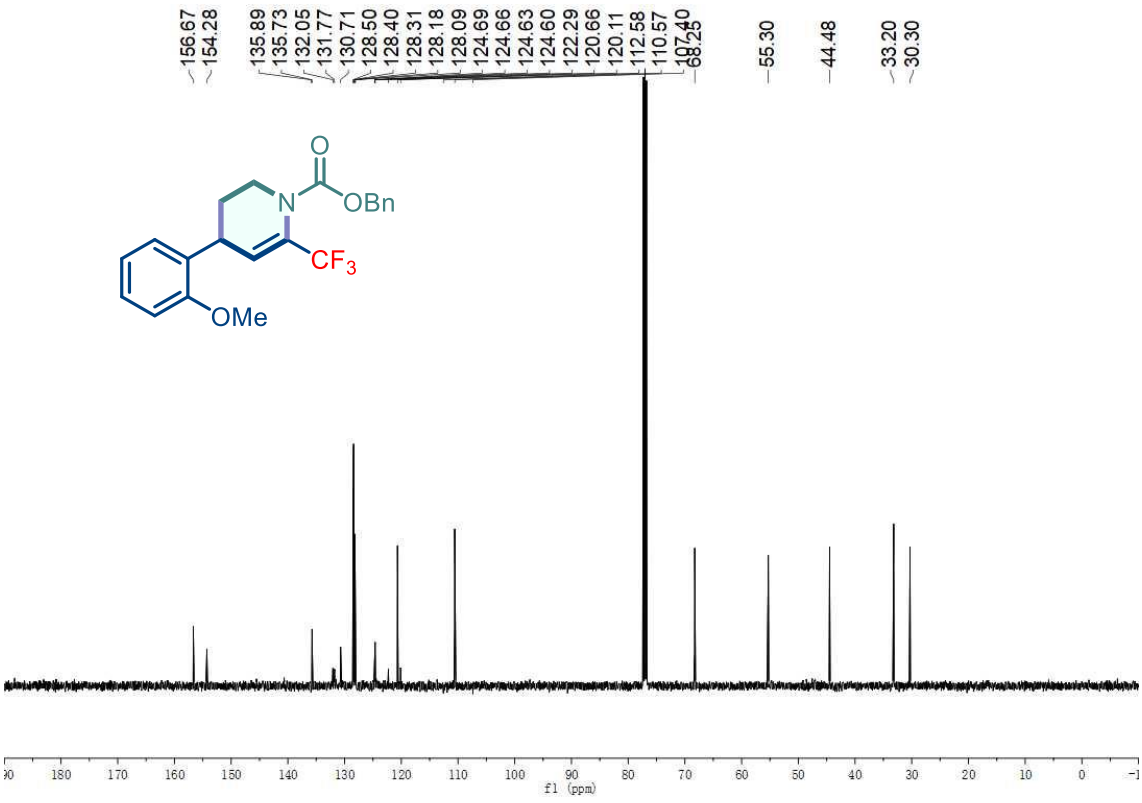


**Figure S45.** $^{13}C$ NMR (125 MHz, $CDCl_3$) Spectrum of **18**.

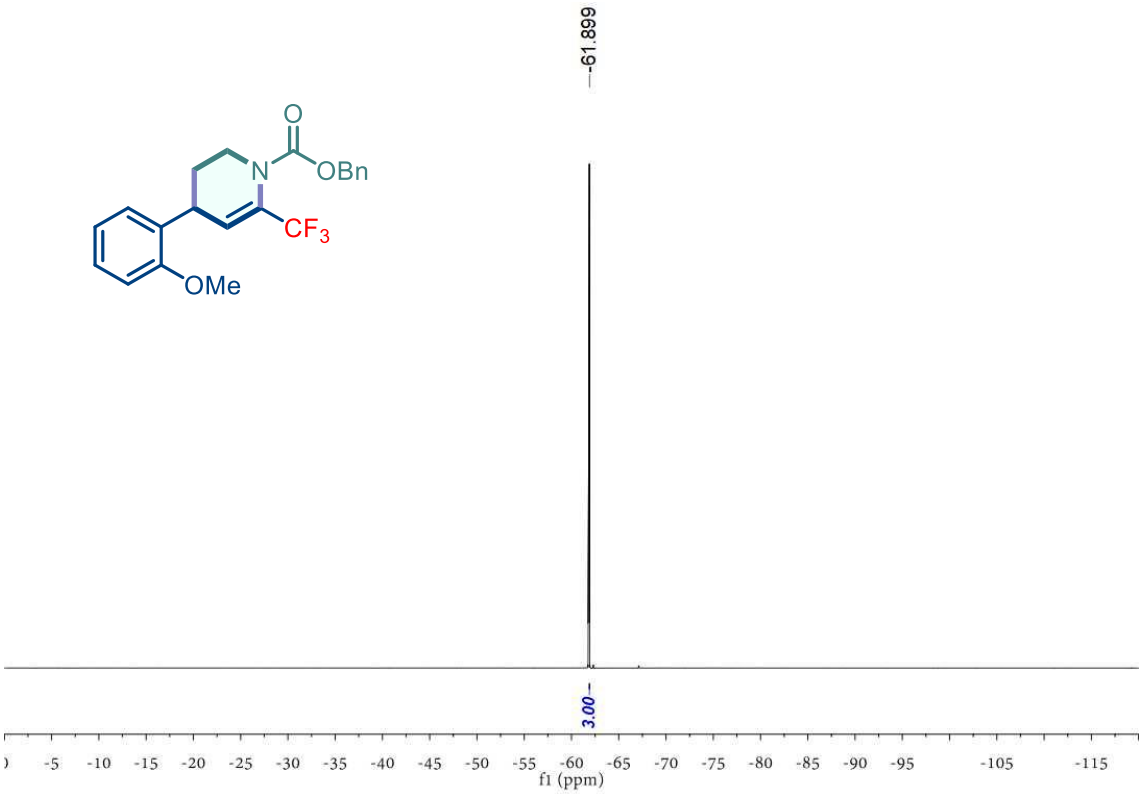


**Figure S46.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **18**.

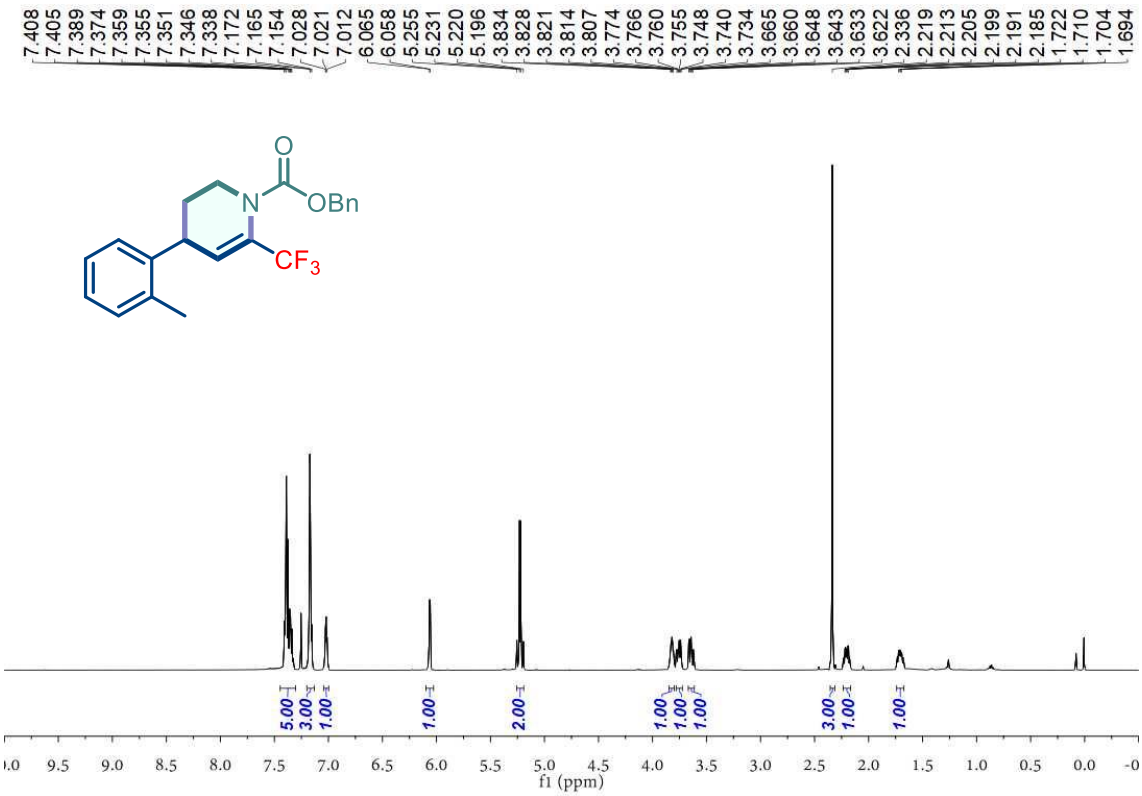


**Figure S47.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **19**.

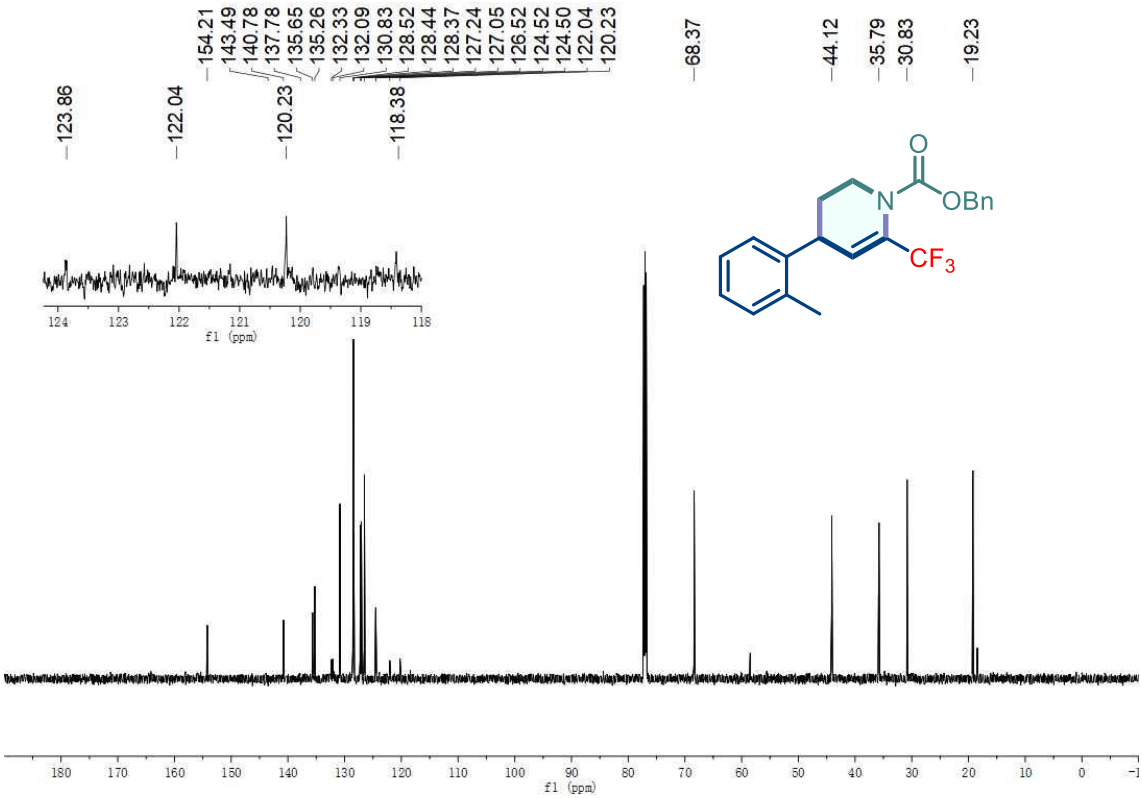


**Figure S48.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **19**.

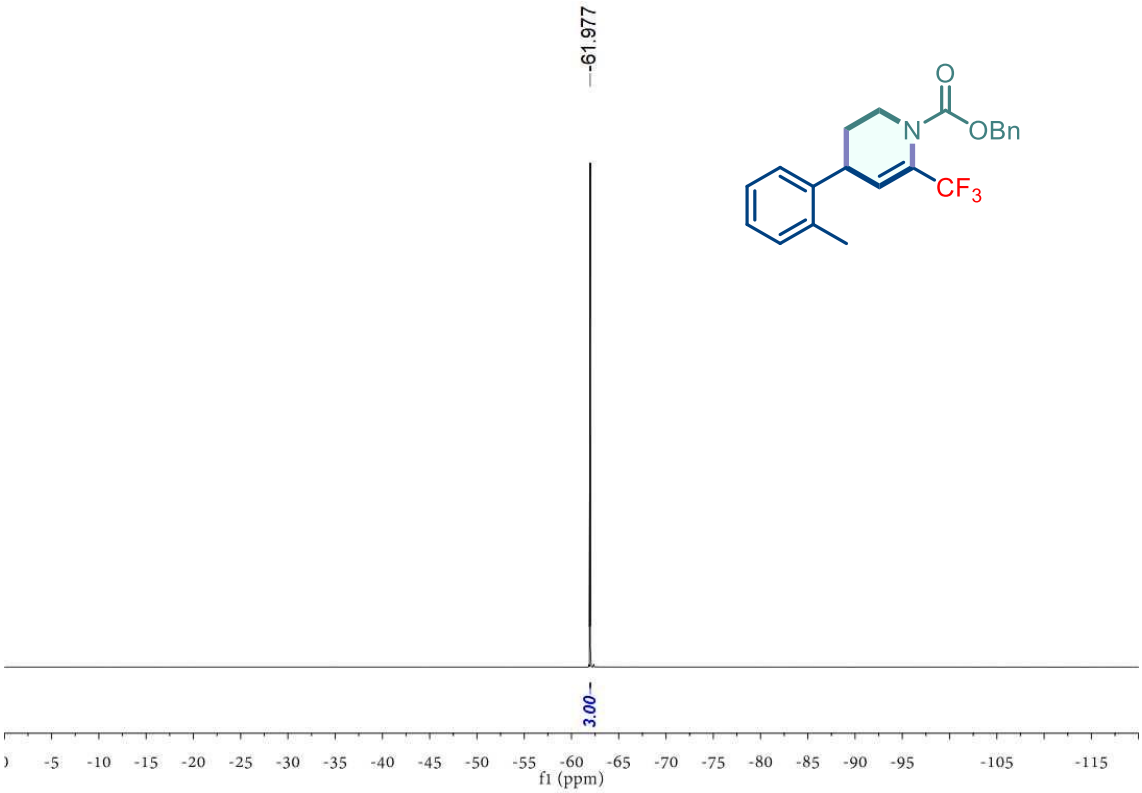


**Figure S49.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **19**.

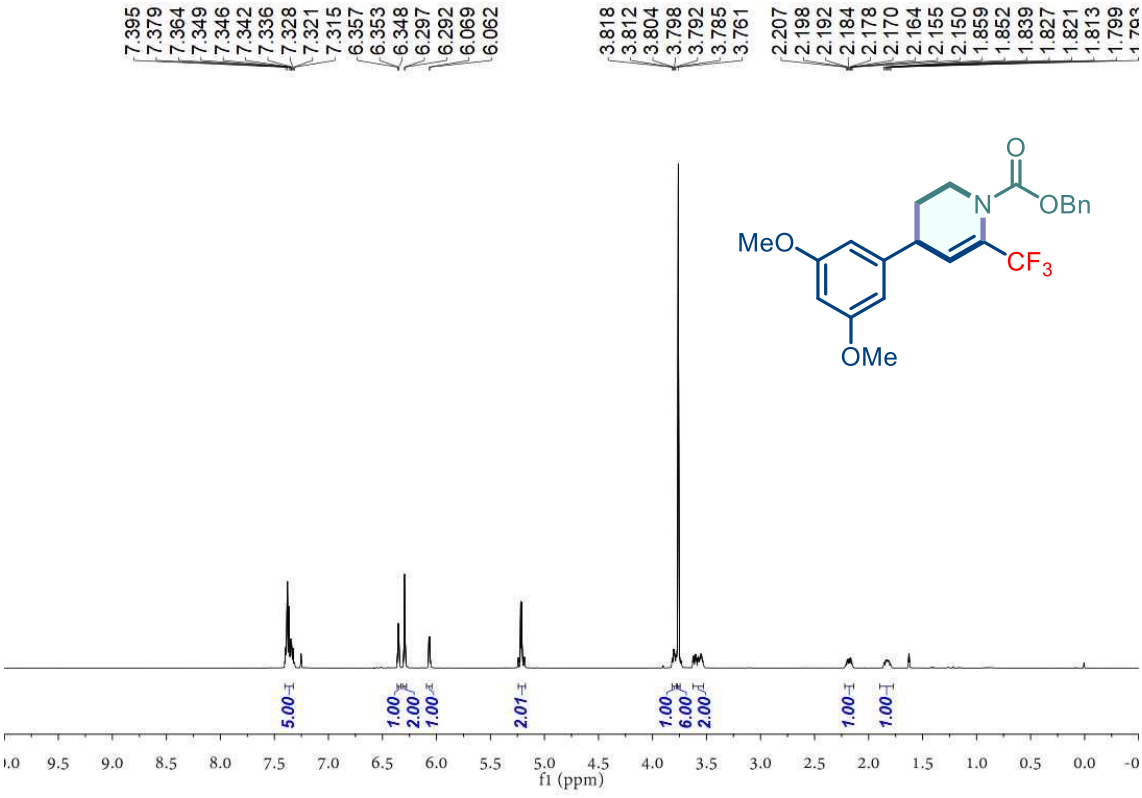


**Figure S50.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **20**.

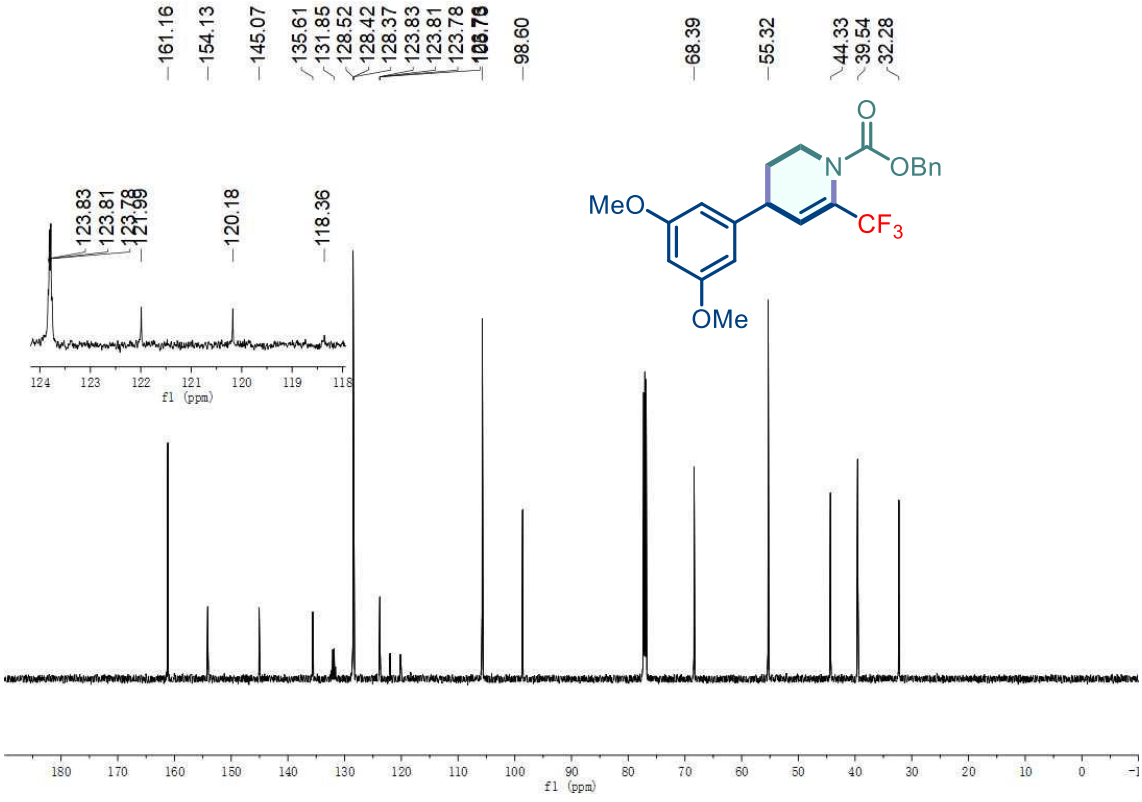


**Figure S51.** $^{13}C$ NMR (125 MHz, $CDCl_3$) Spectrum of **20**.

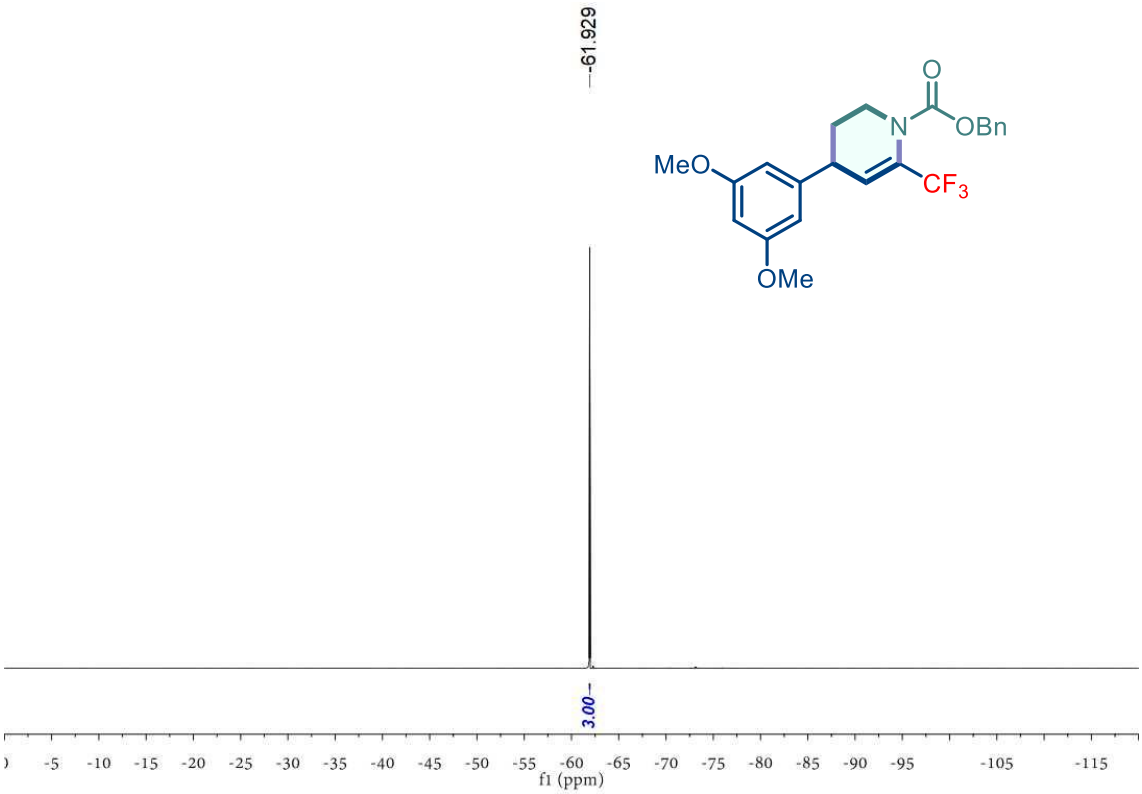


**Figure S52.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **20**.

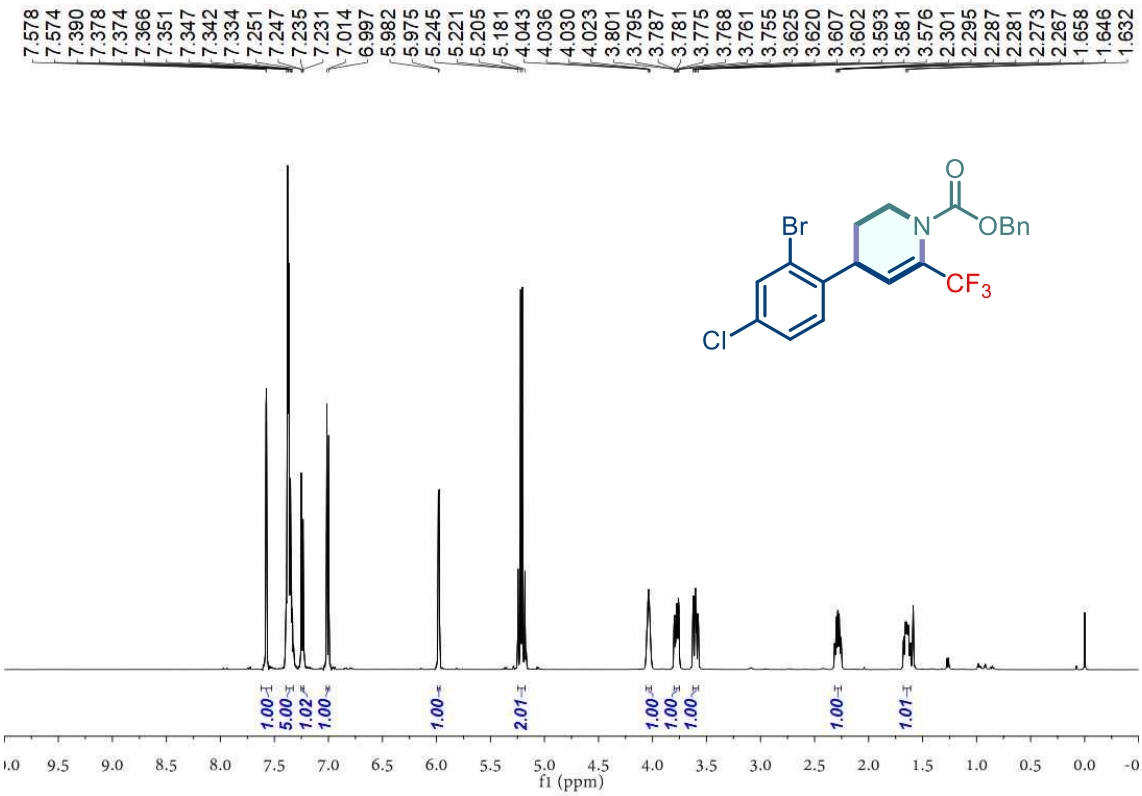


**Figure S53.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **21**.

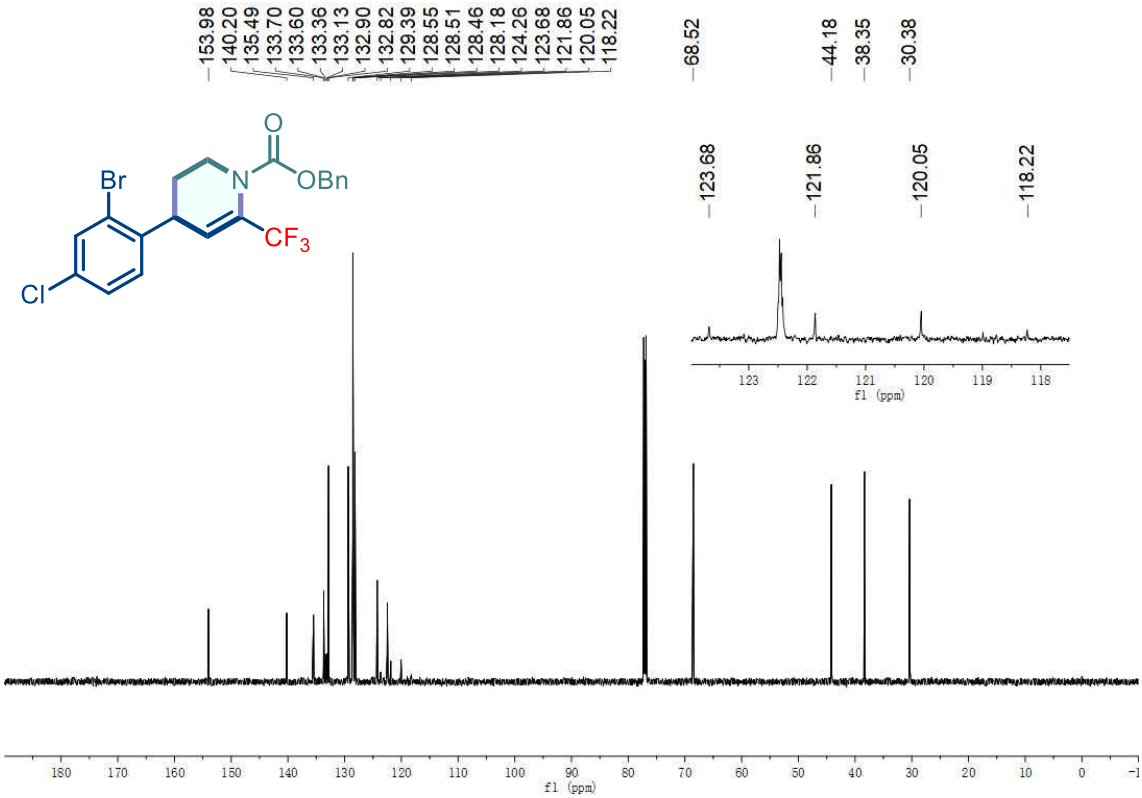


**Figure S54** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **21**.

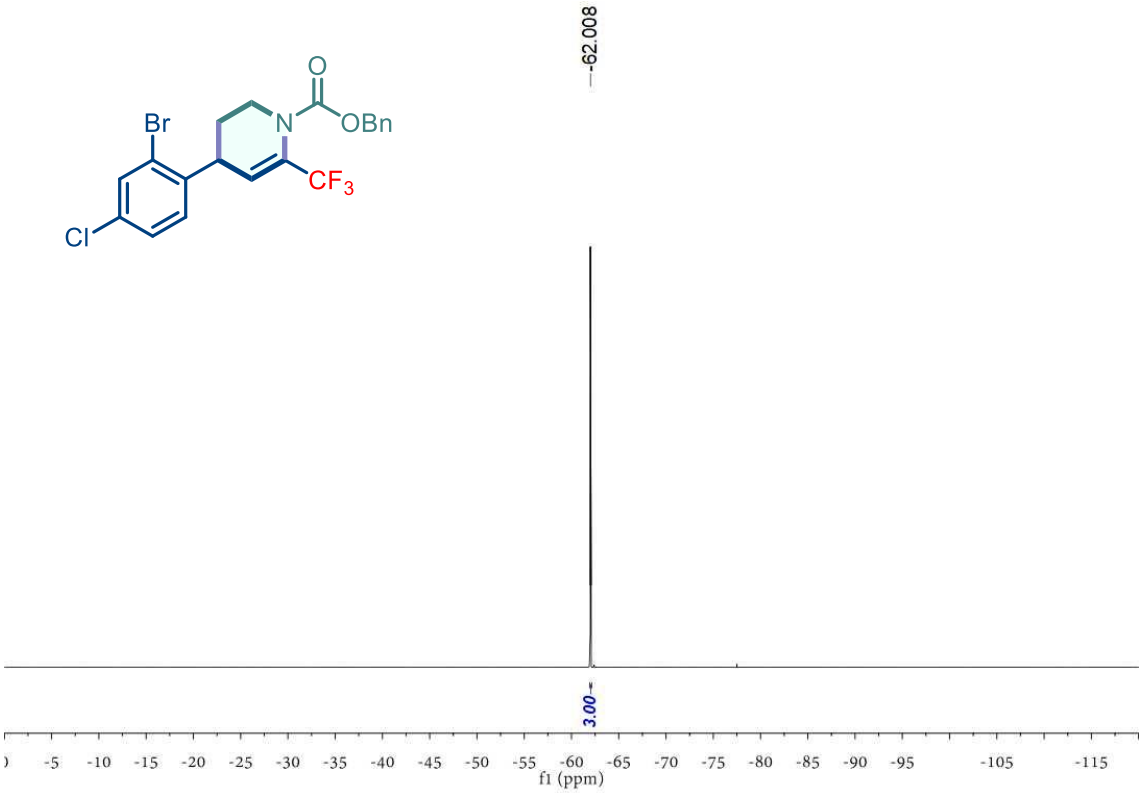


**Figure S55.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **21**.

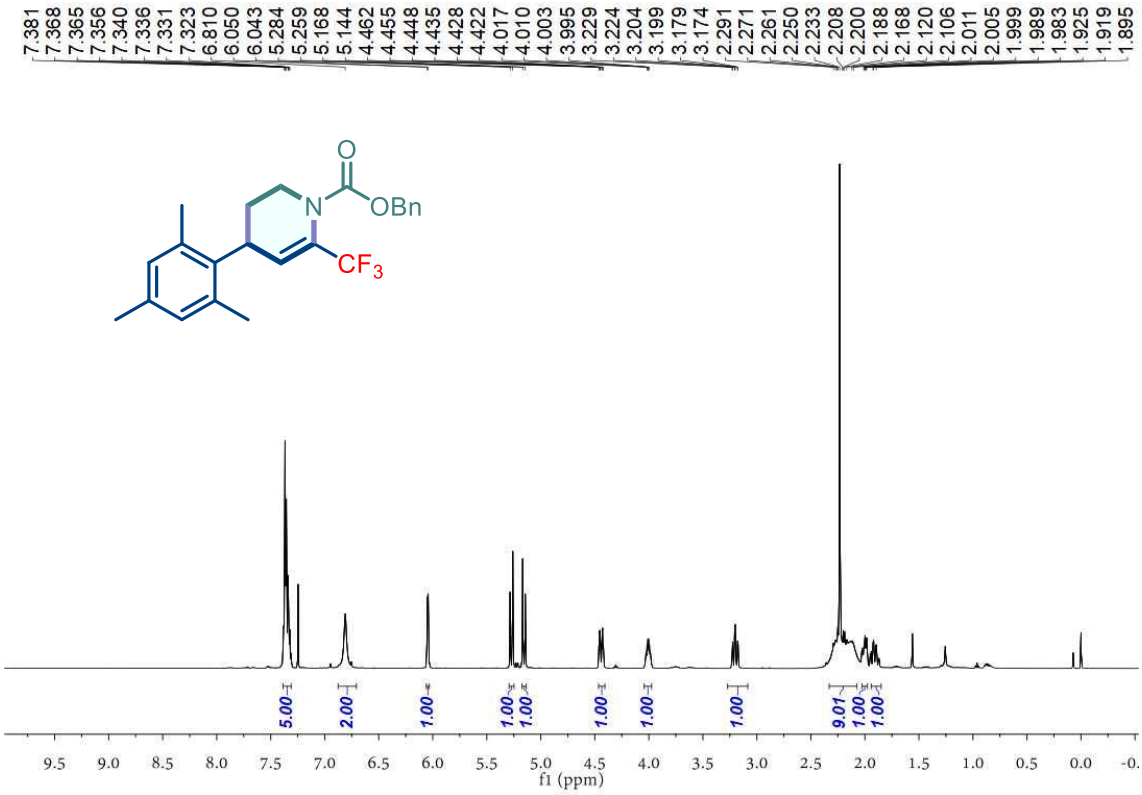


**Figure S56.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **22**.

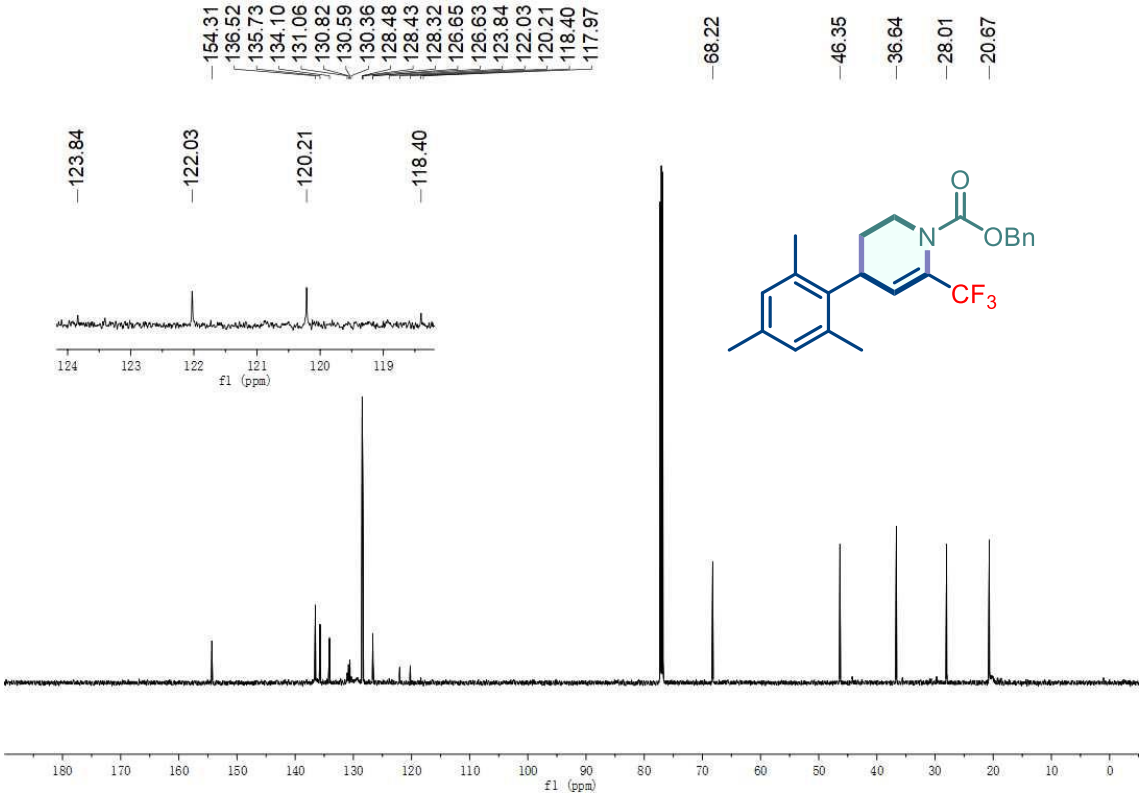


**Figure S57.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **22**.

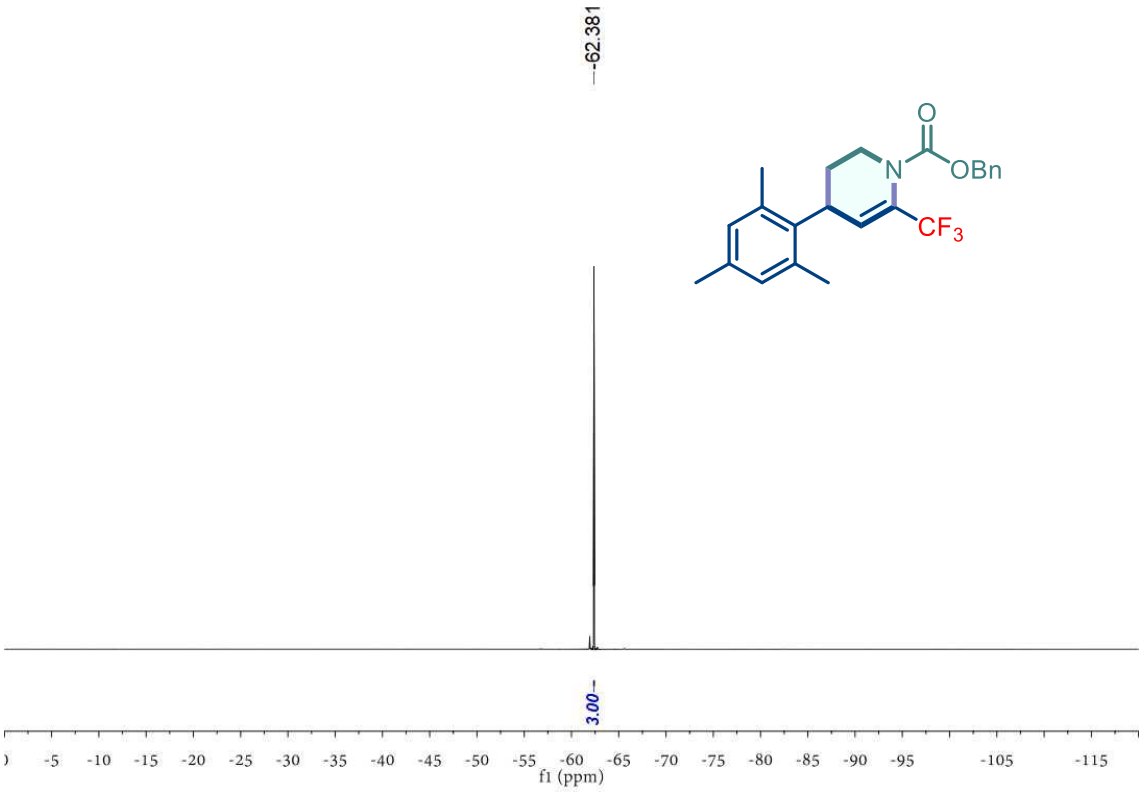


**Figure S58.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **22**.

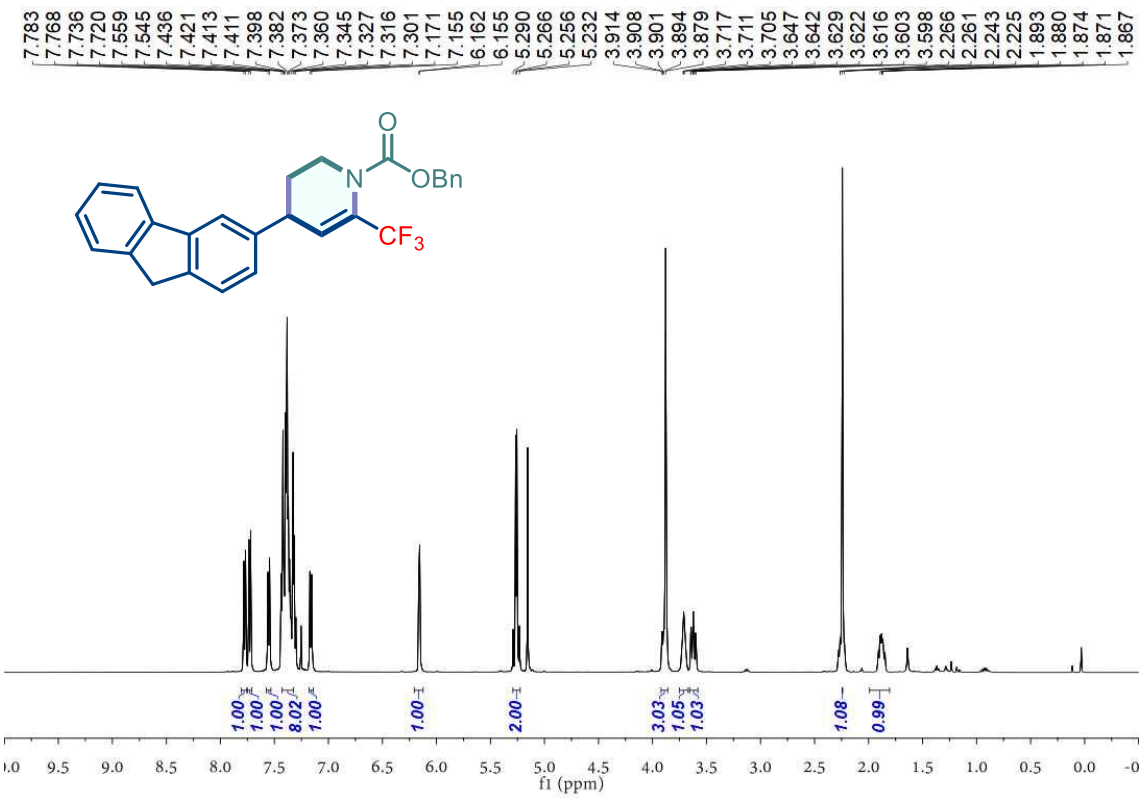


**Figure S59.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **23**.

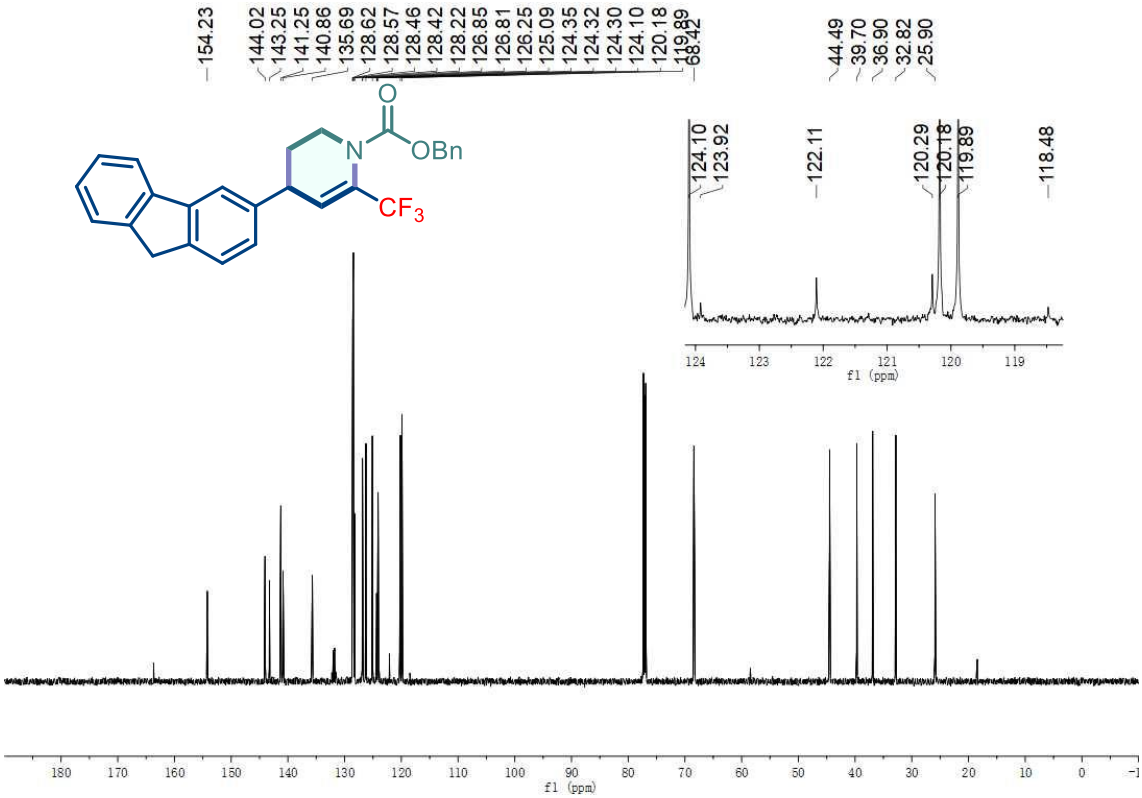


**Figure S60.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **23**.

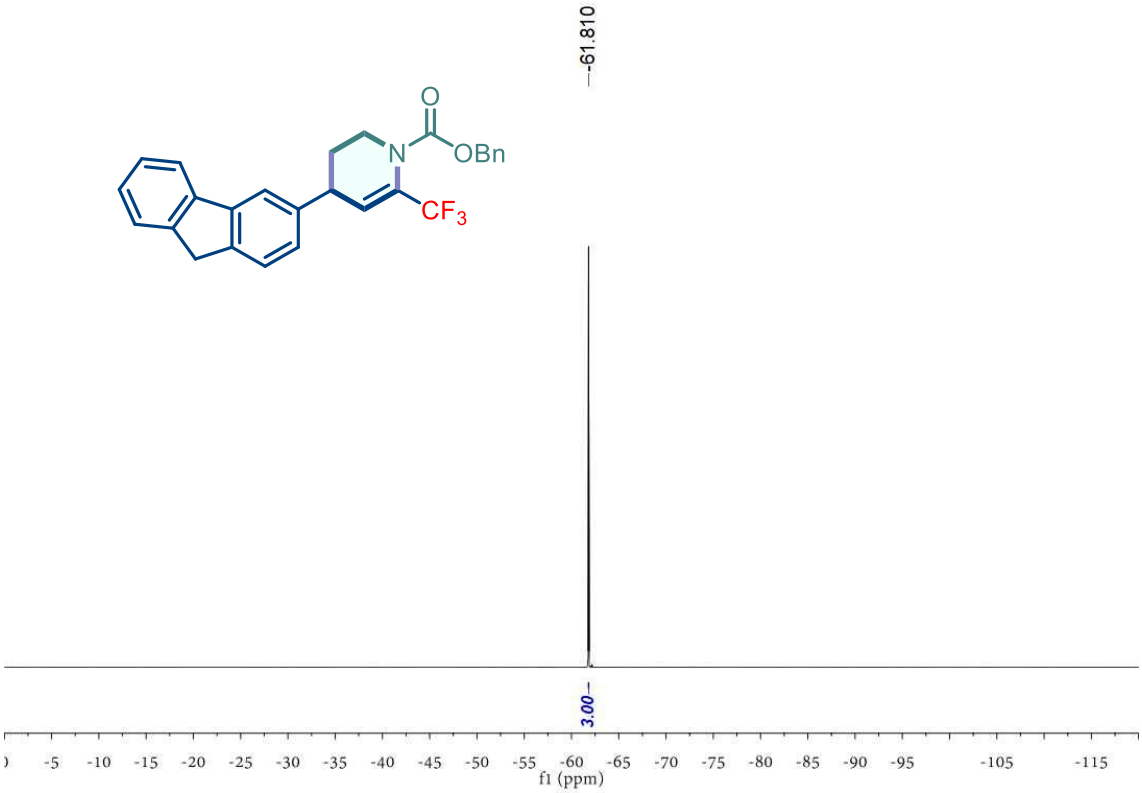


**Figure S61.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **23**.

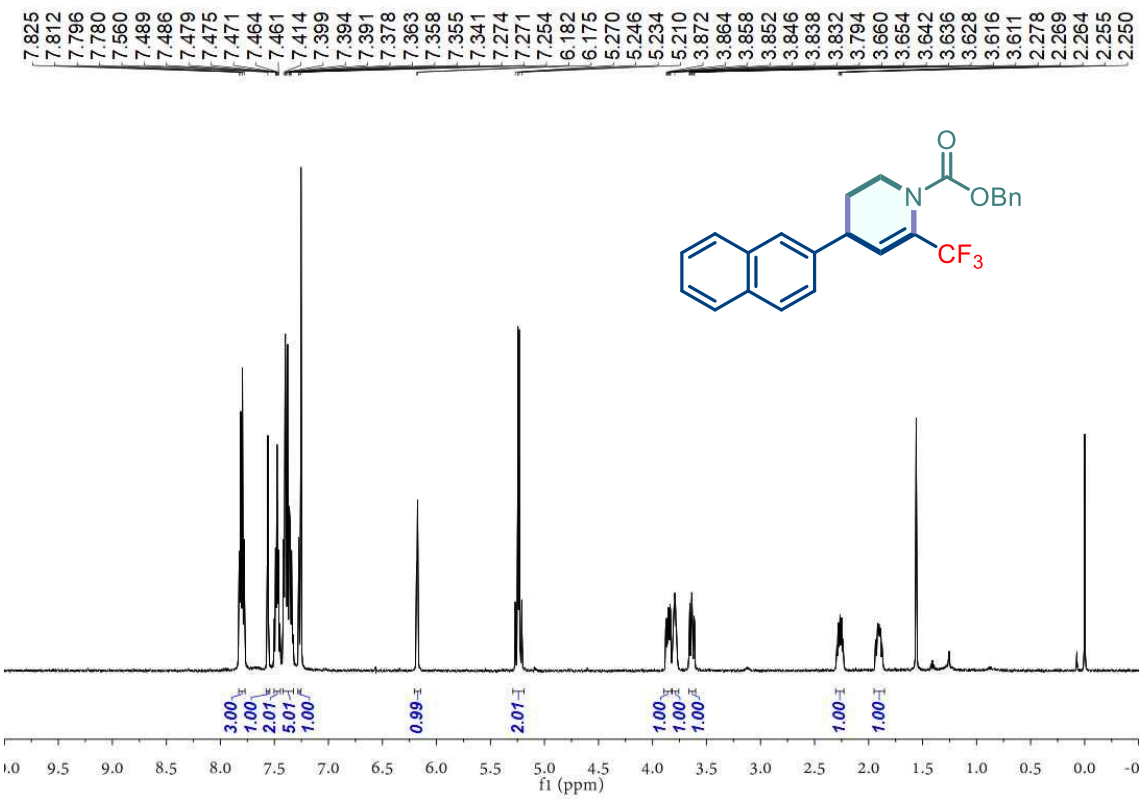


**Figure S62.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **24**.

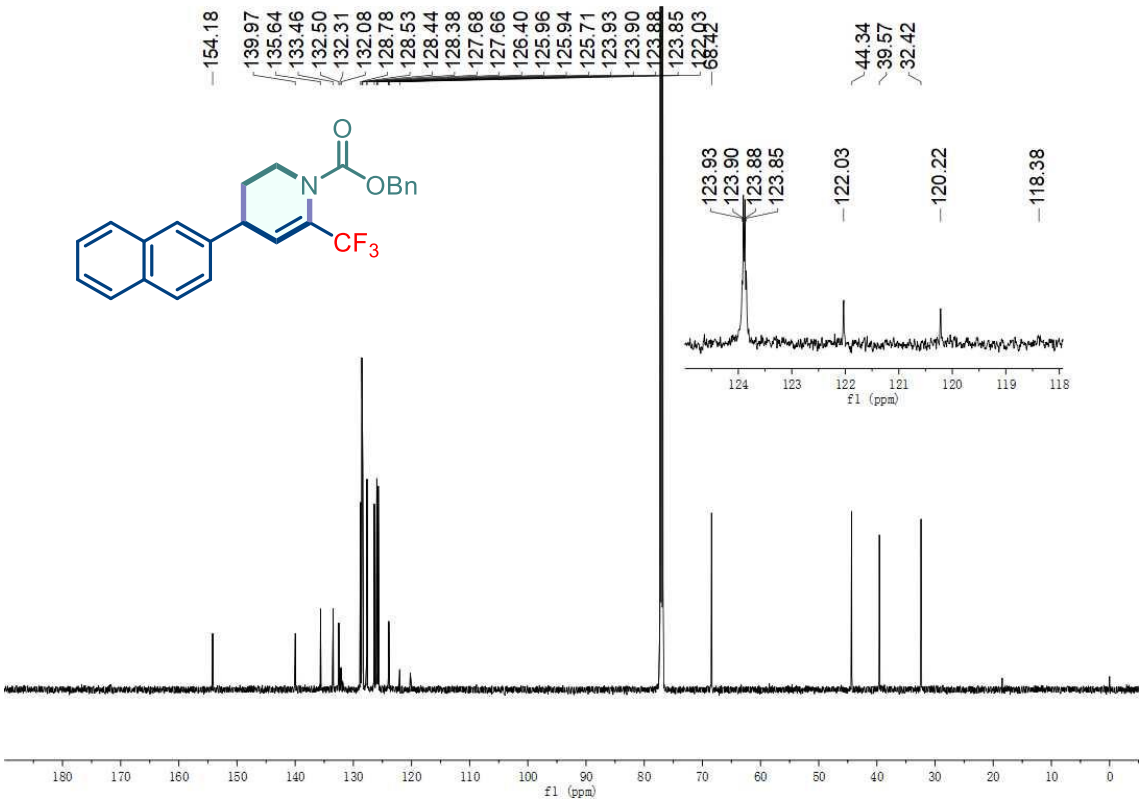


**Figure S63.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **24**.

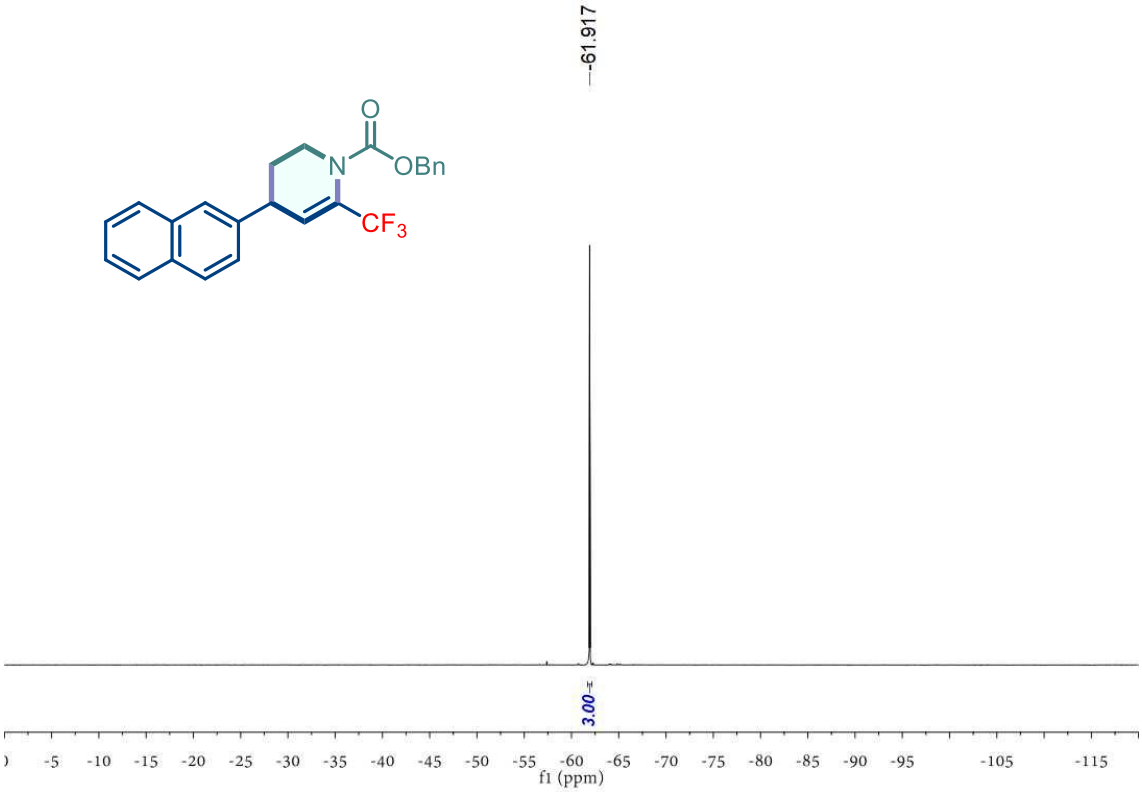


**Figure S64.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **24**.

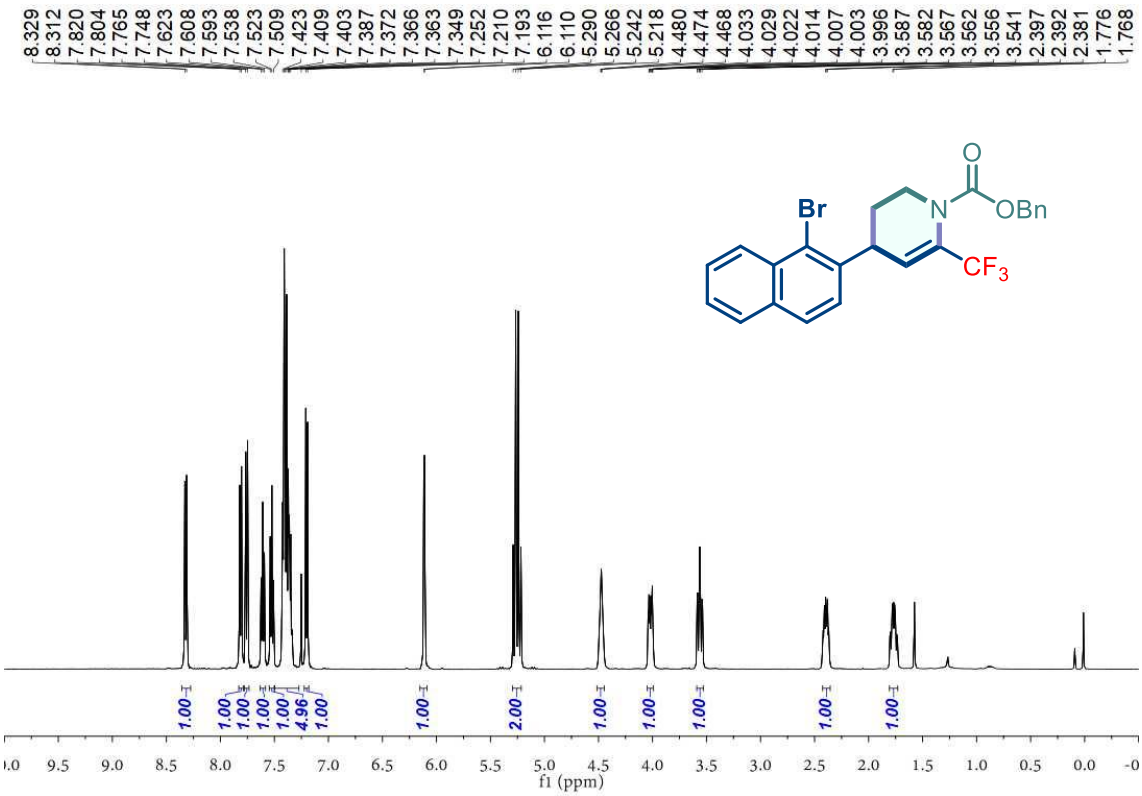


**Figure S65.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **25**.

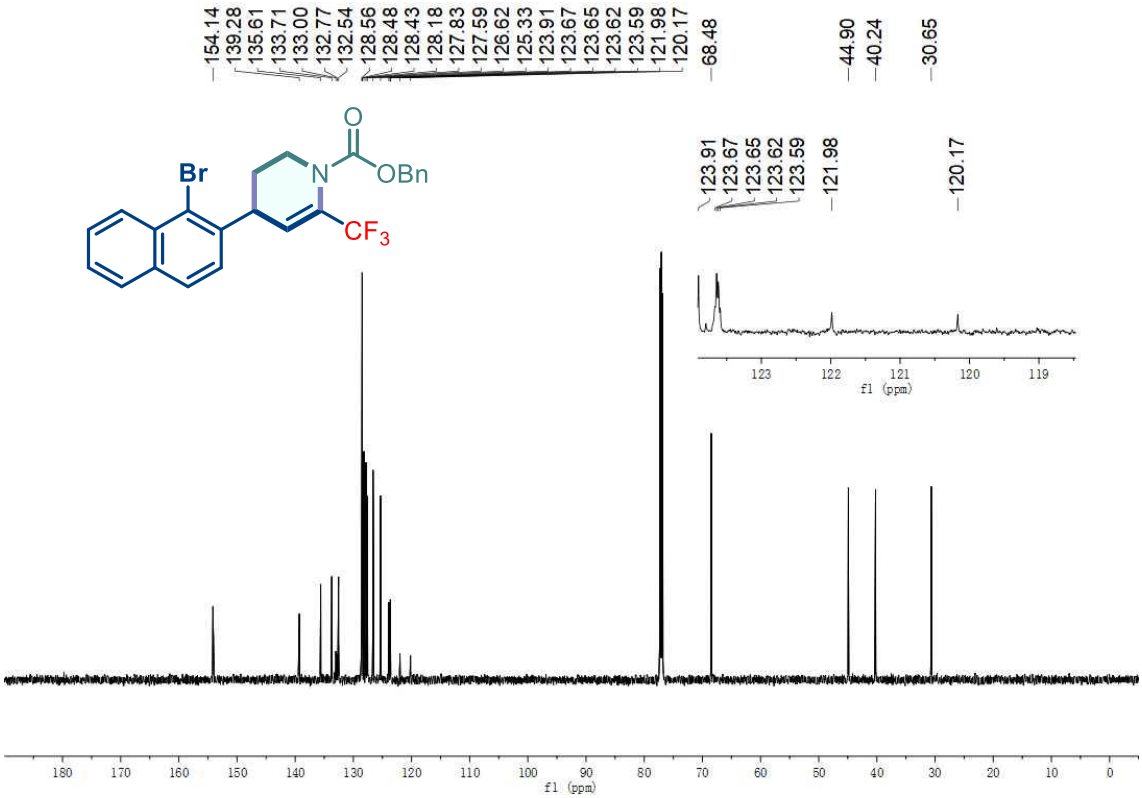


**Figure S66.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **25**.

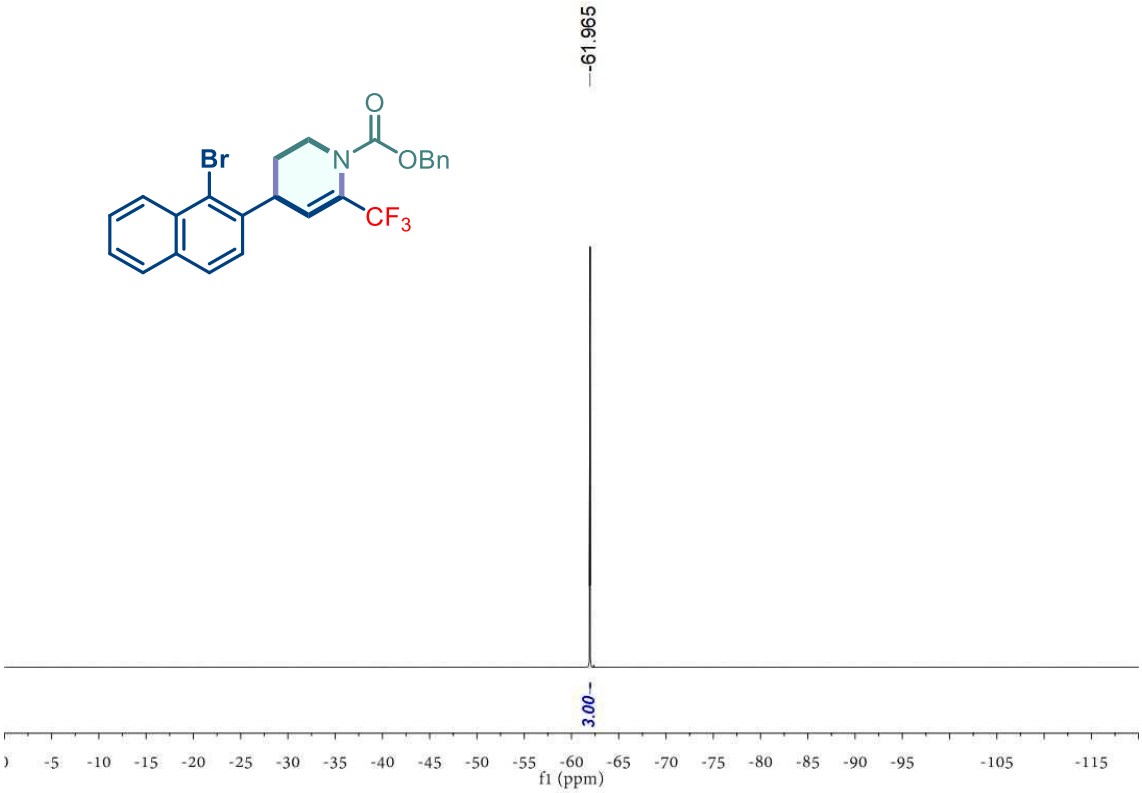


**Figure S67.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **25**.

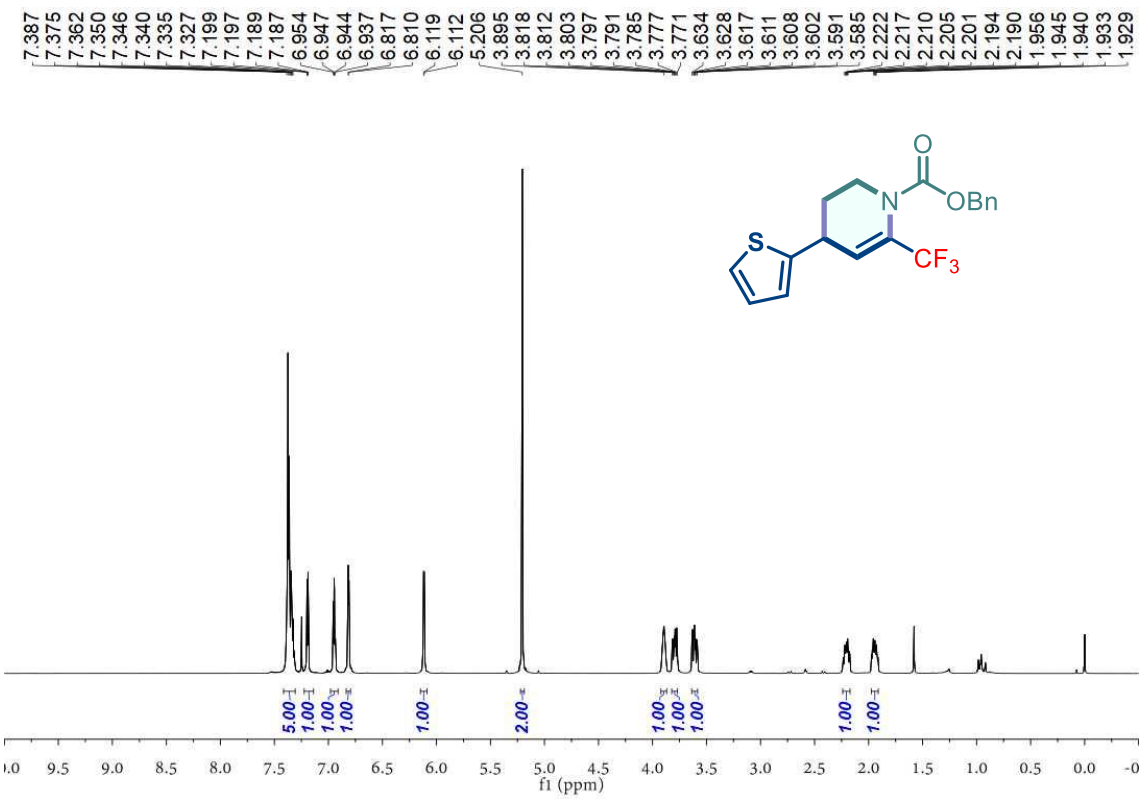


**Figure S68.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **26**.

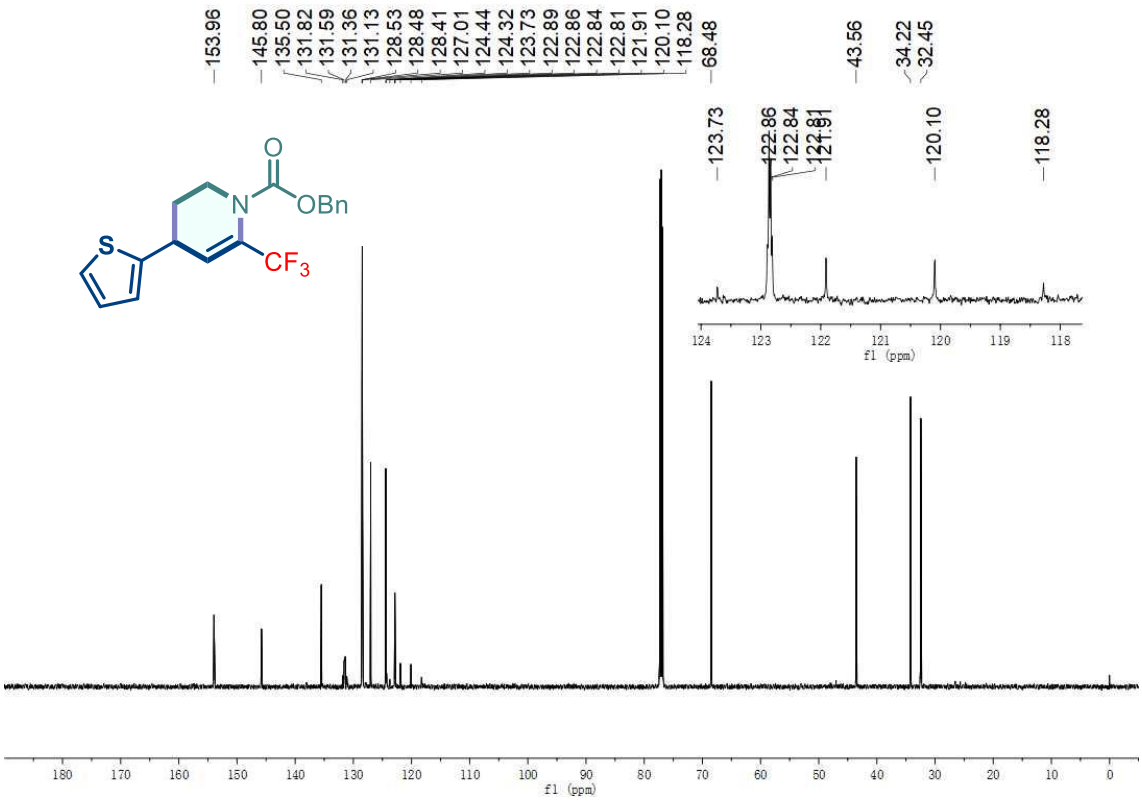


**Figure S69.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **26**.

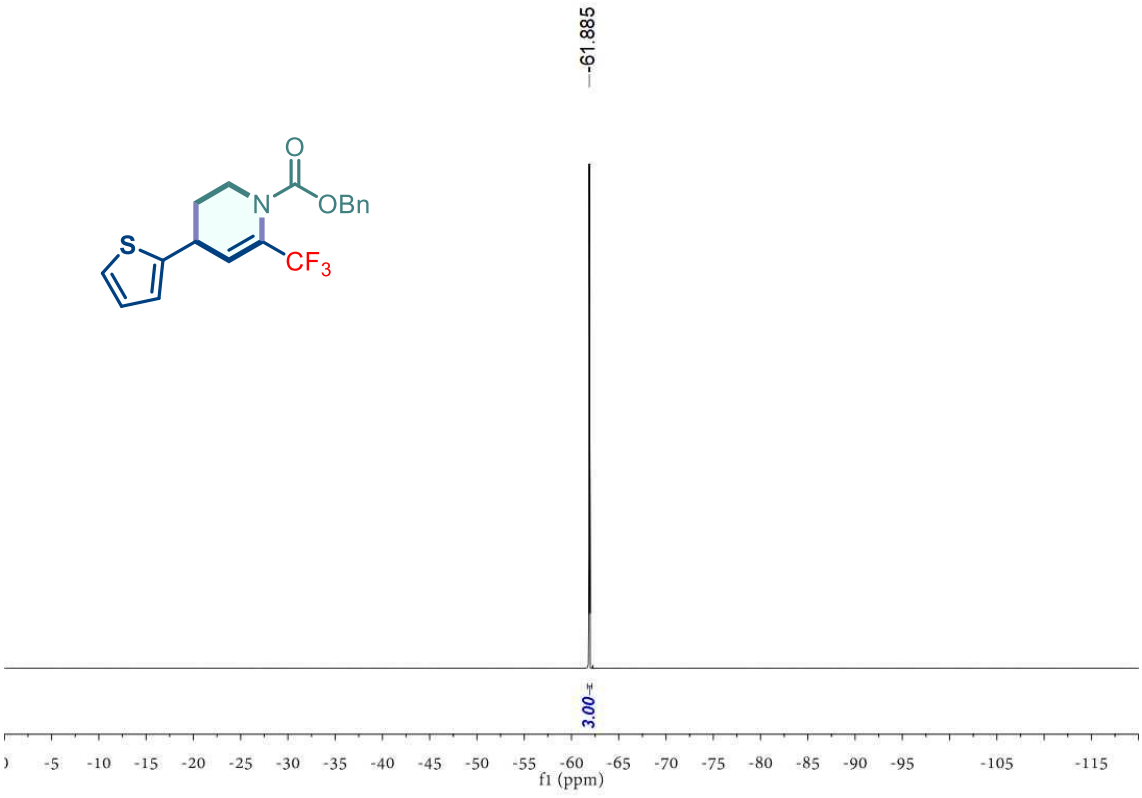


**Figure S70.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **26**.

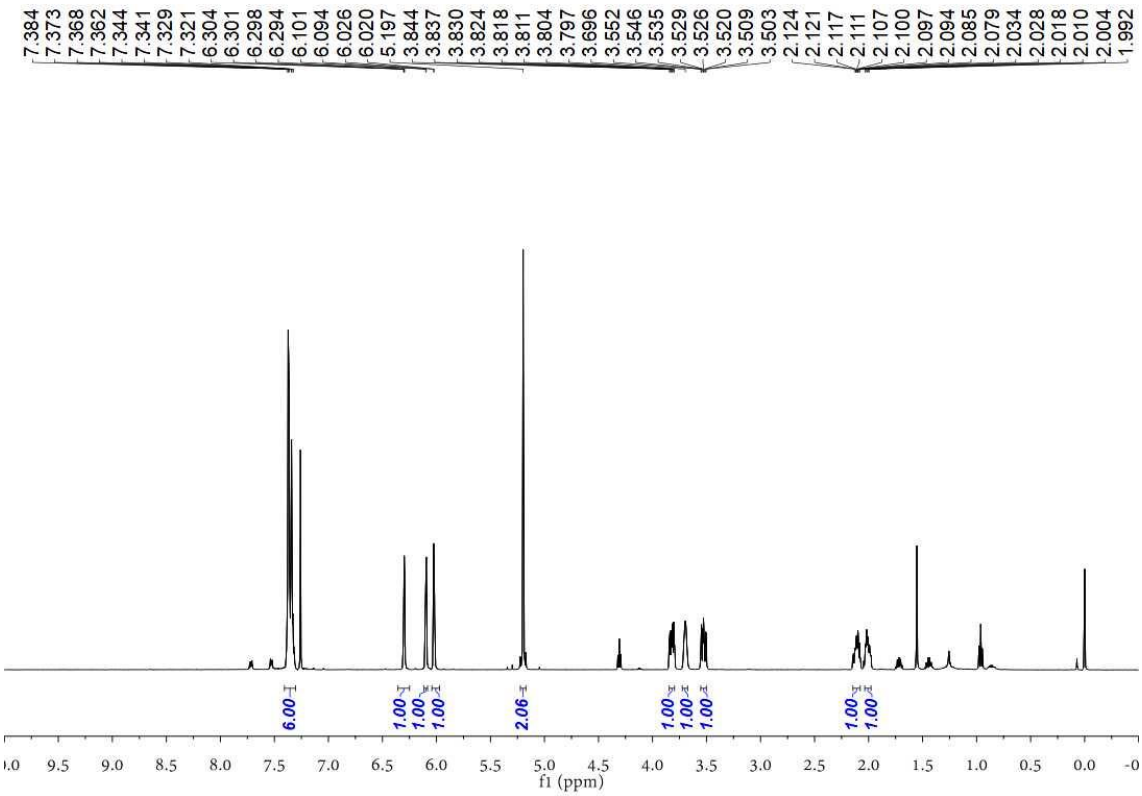


**Figure S71.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **27**.

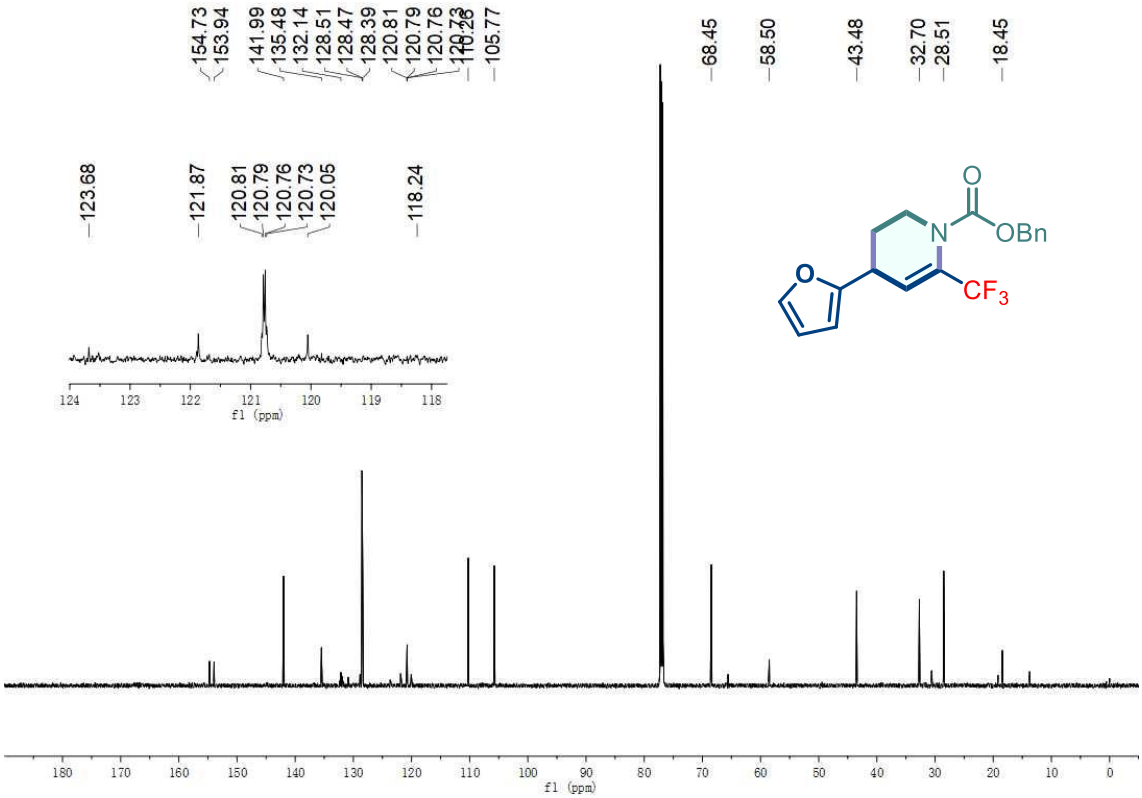


**Figure S72.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **27**.

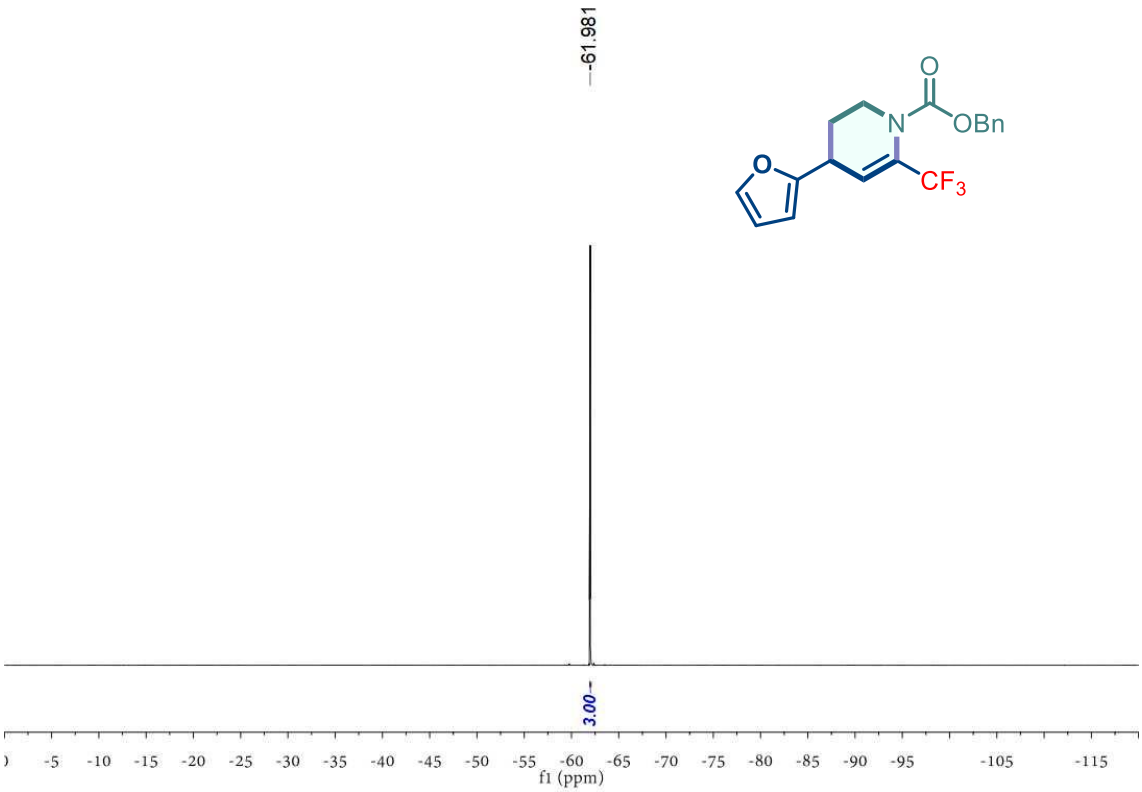


**Figure S73.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **27**.

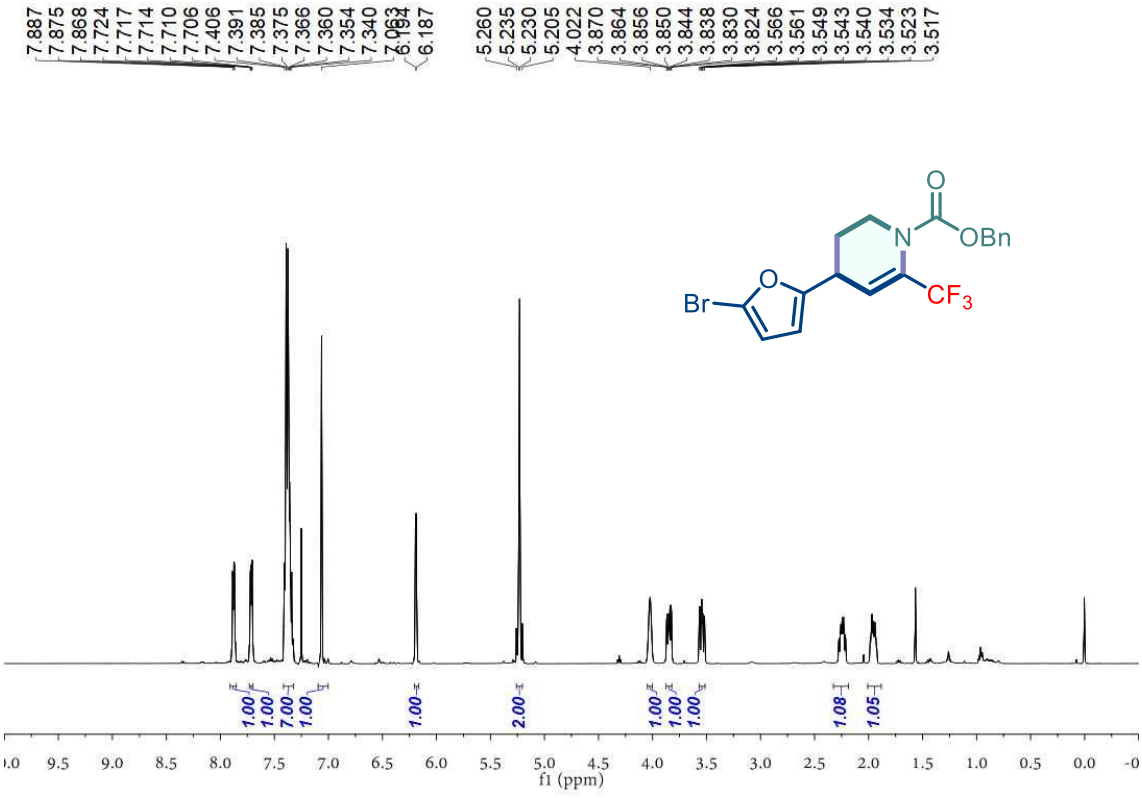


**Figure S74.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **28**.

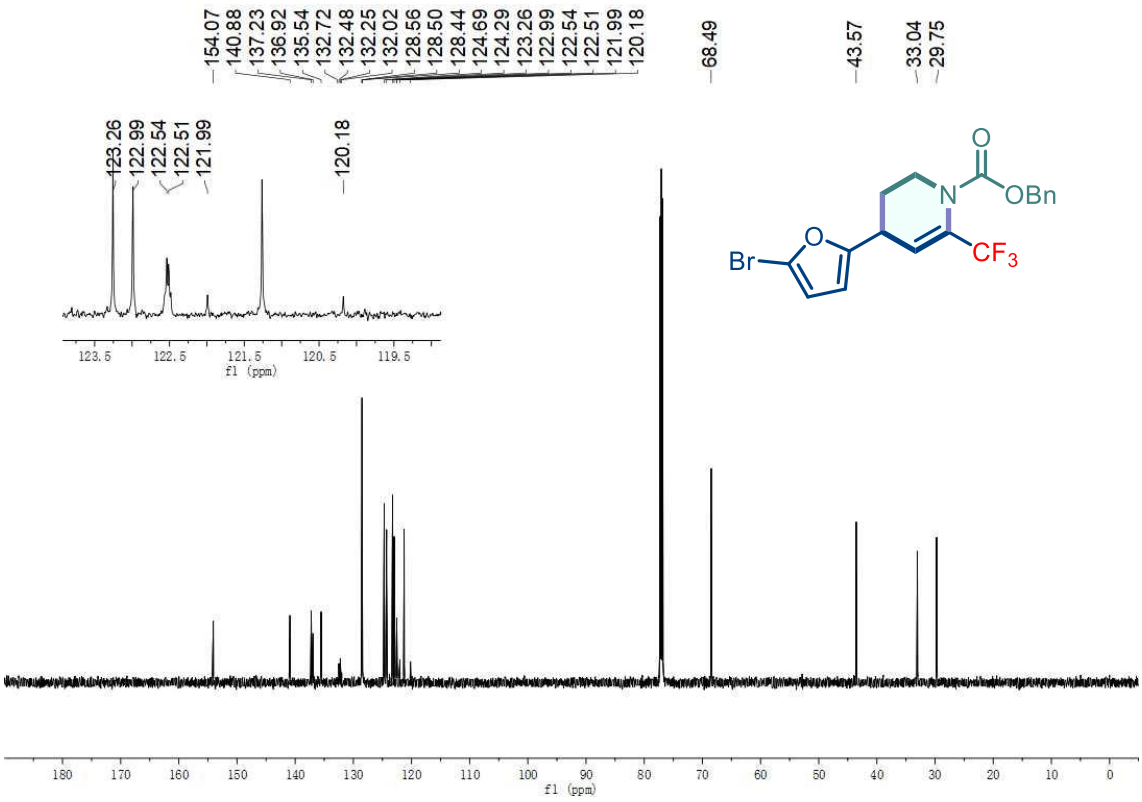


**Figure S75.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **28**.

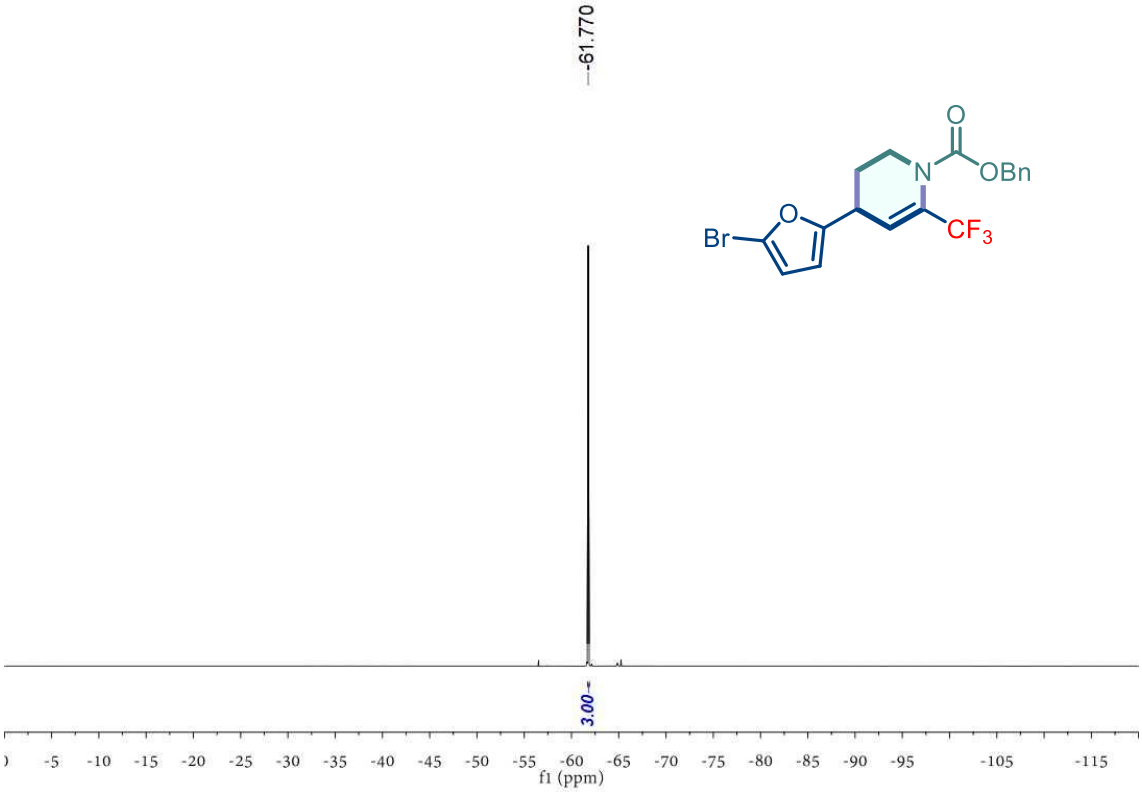


**Figure S76.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **28**.

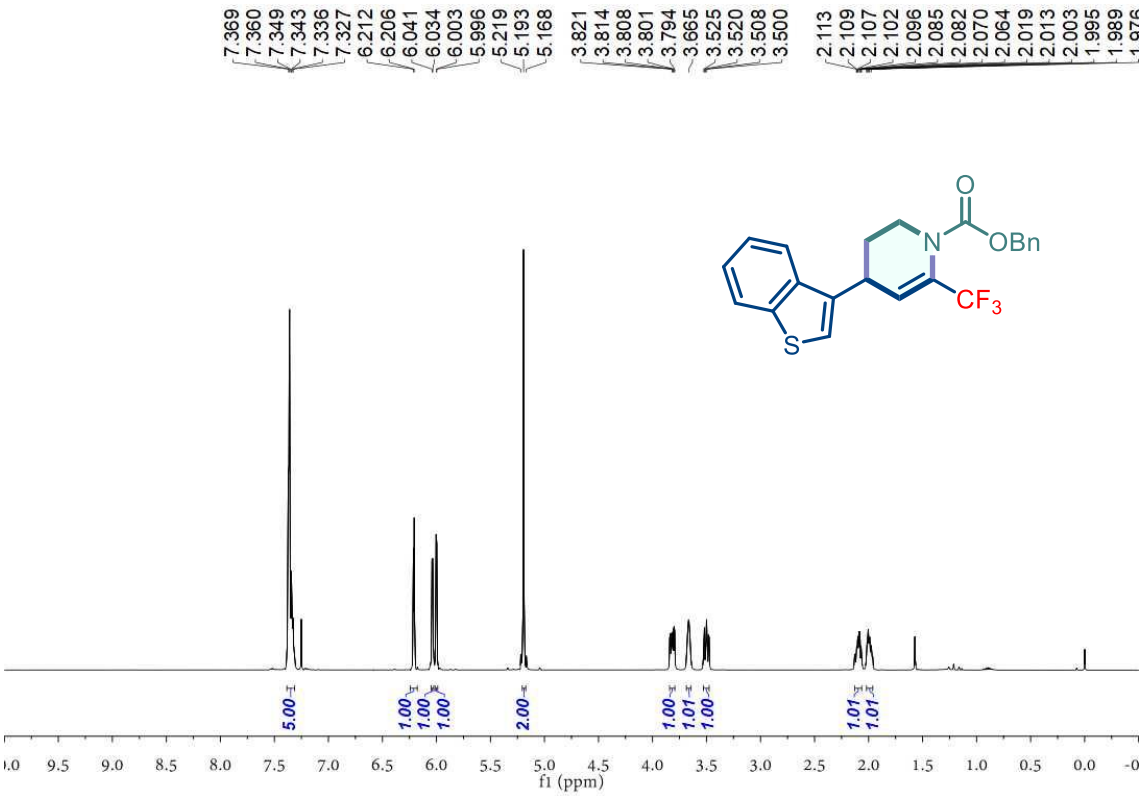


**Figure S77.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **29**.

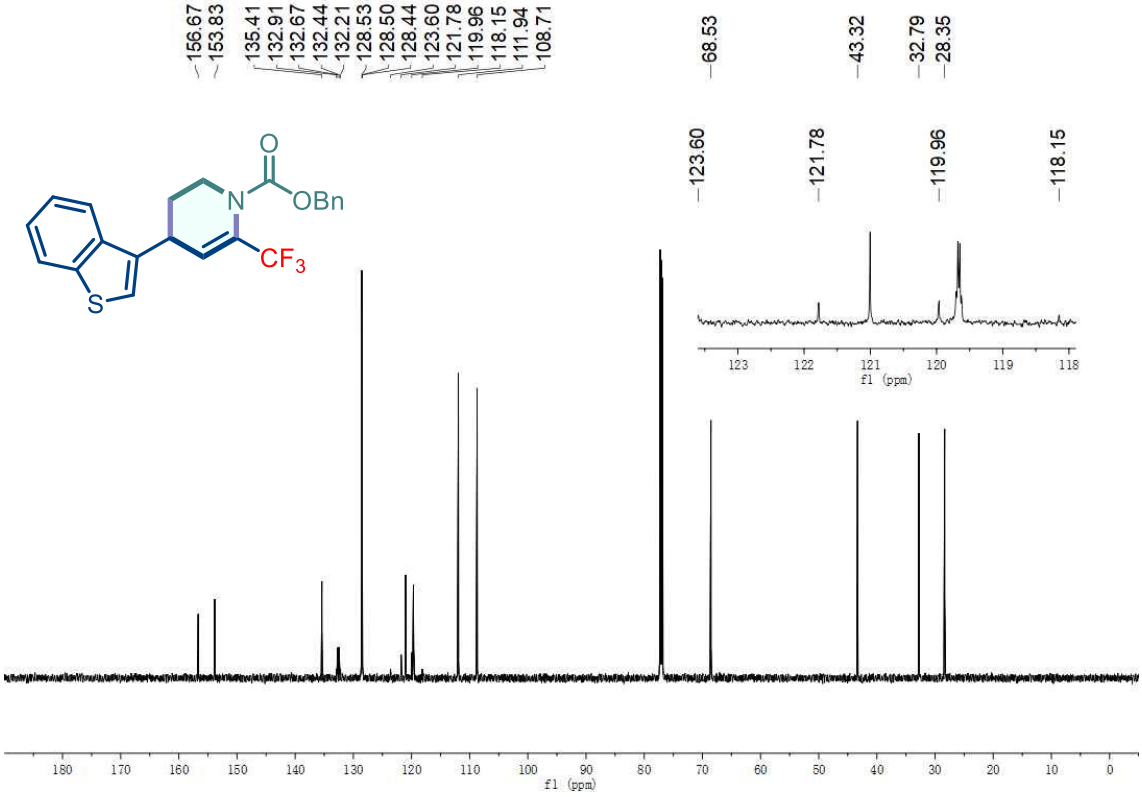


**Figure S78.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **29**.

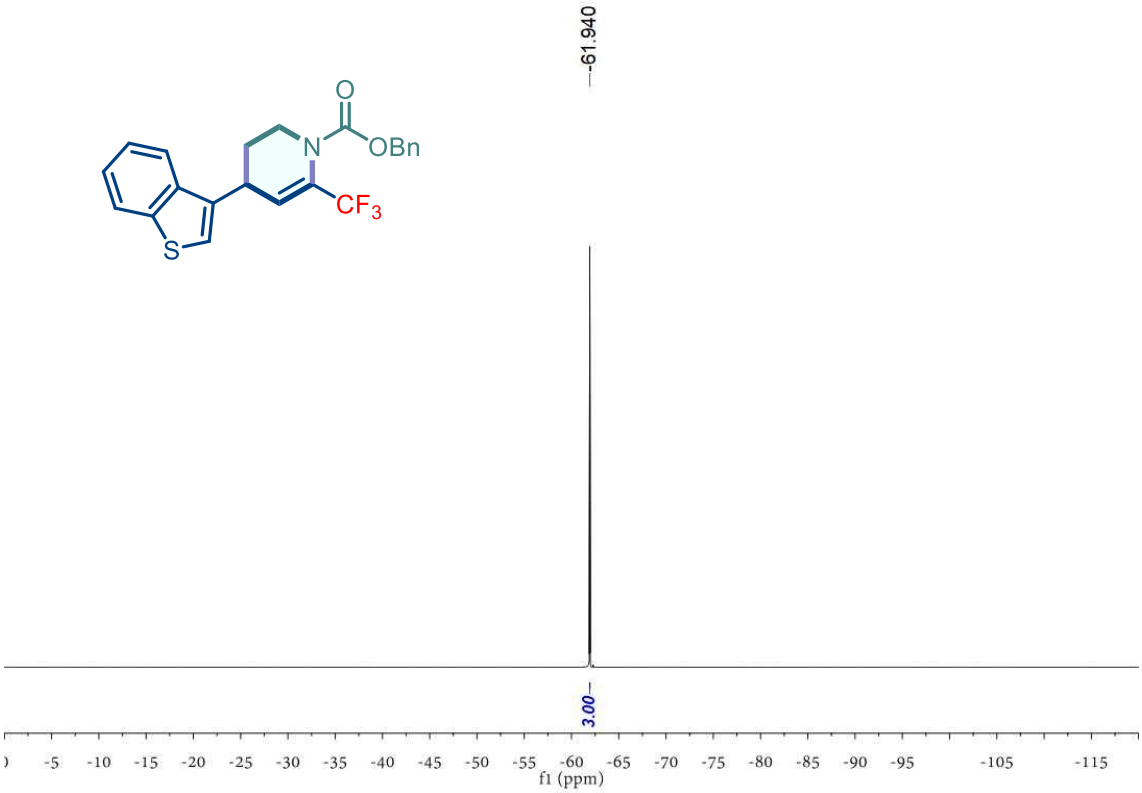


**Figure S79.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **29**.

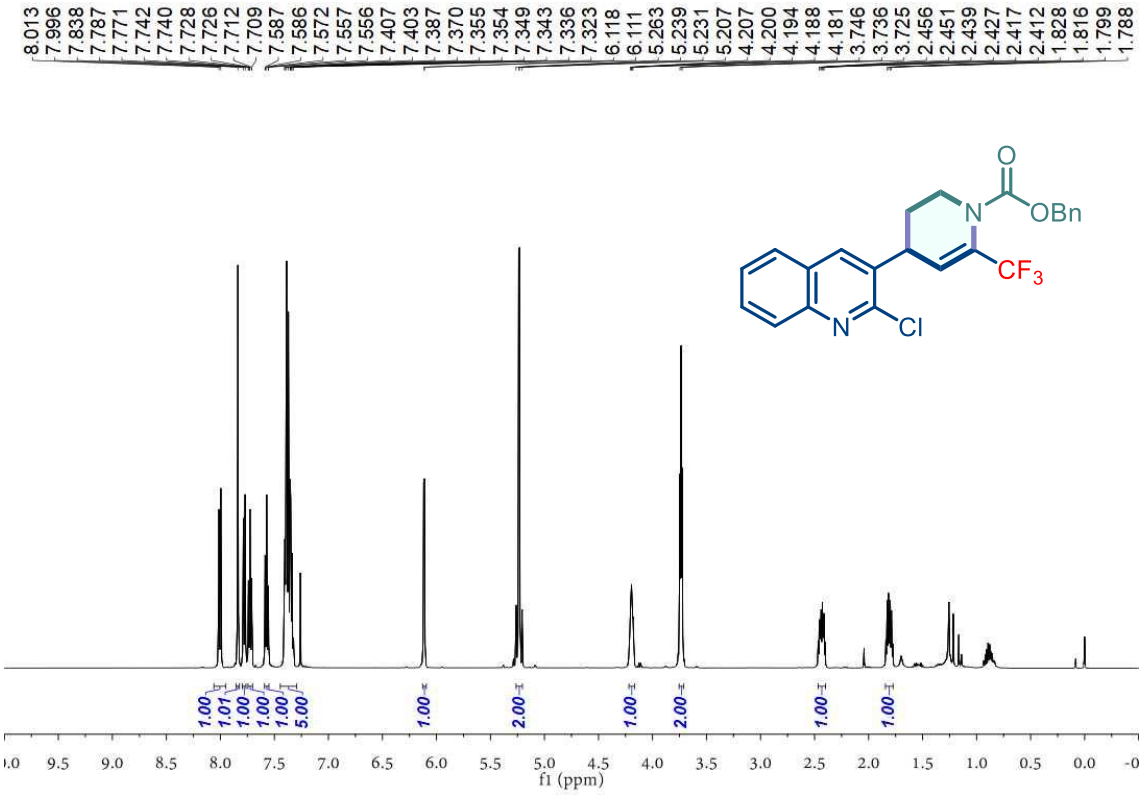


**Figure S80.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **30**.

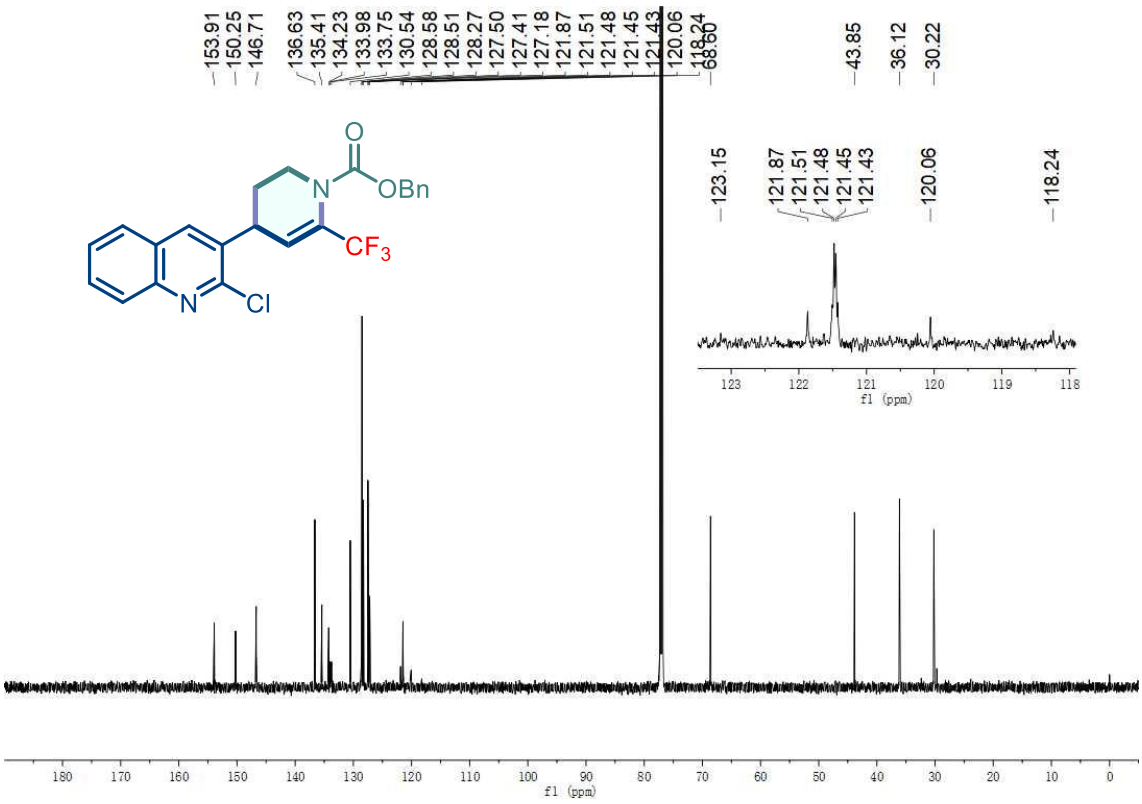


**Figure S81.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **30**.

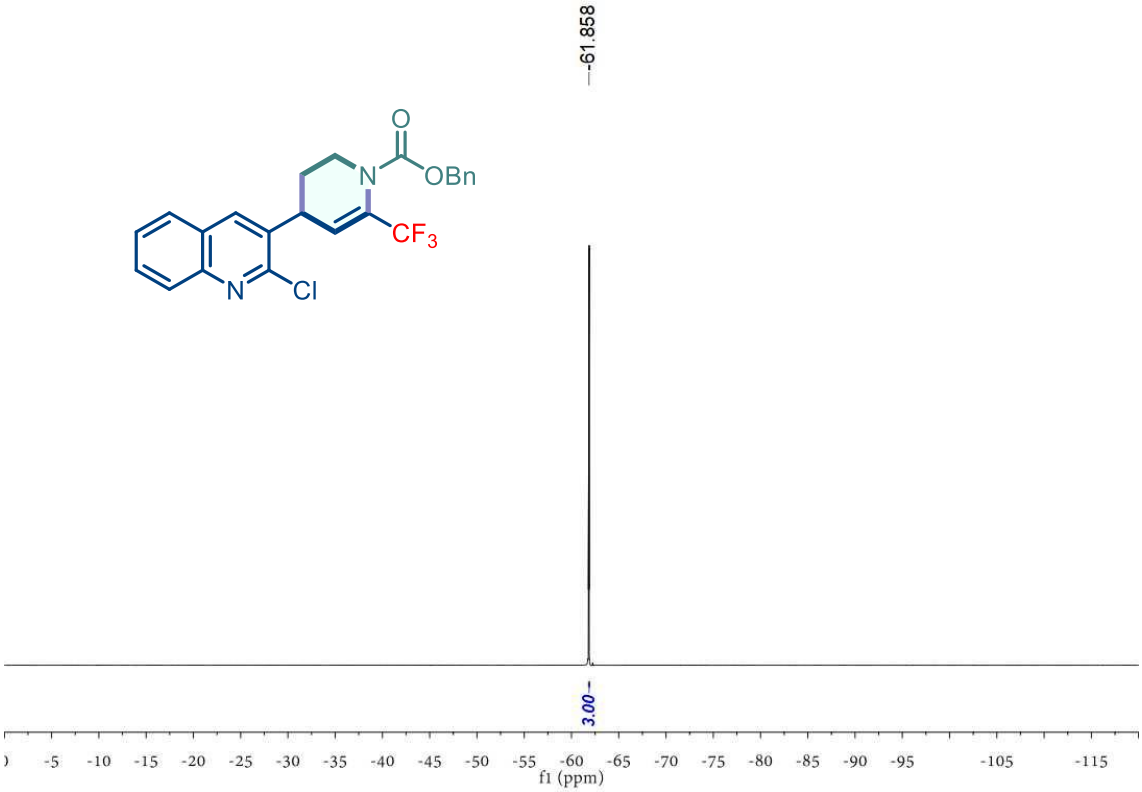


**Figure S82.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **30**.

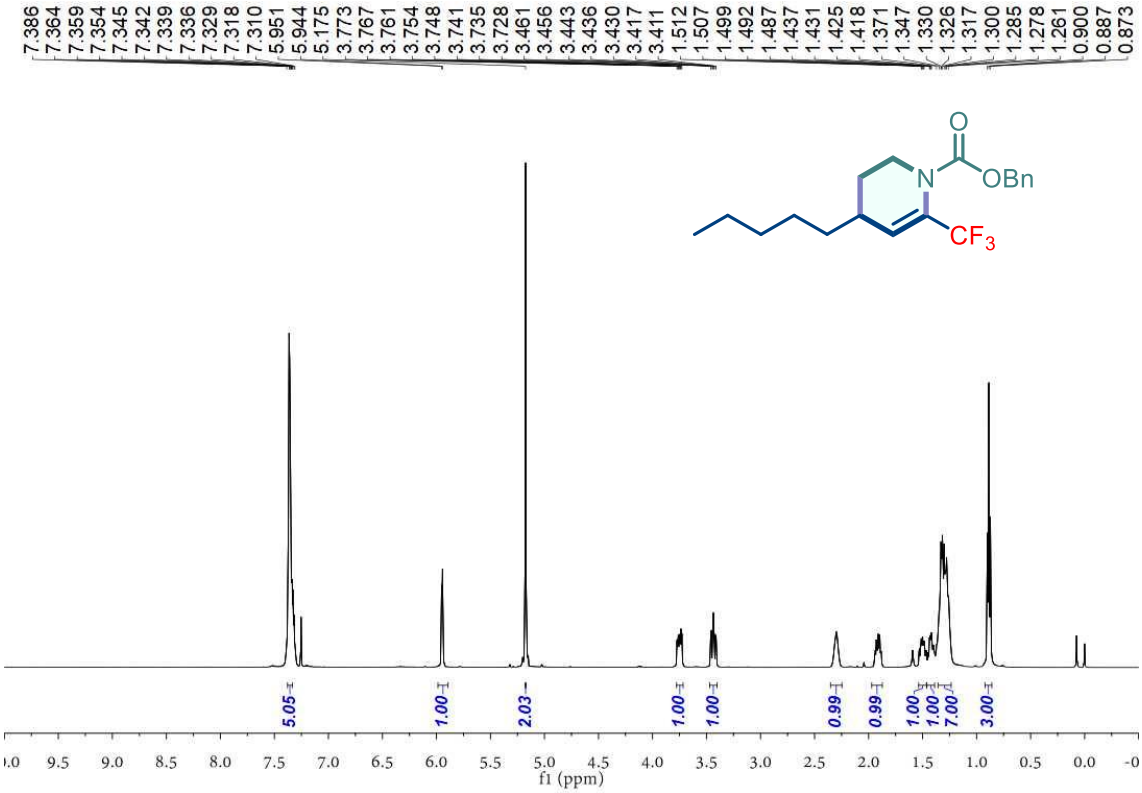


**Figure S83.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **31**.

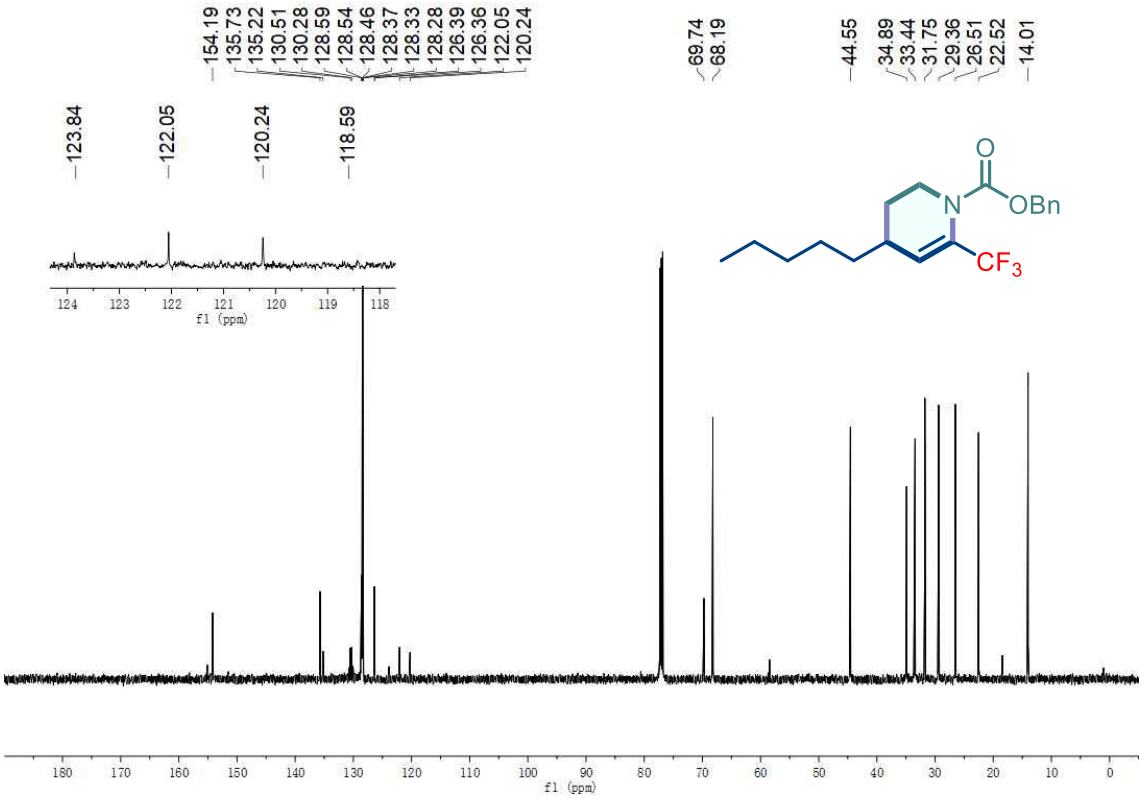


**Figure S84.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **31**.

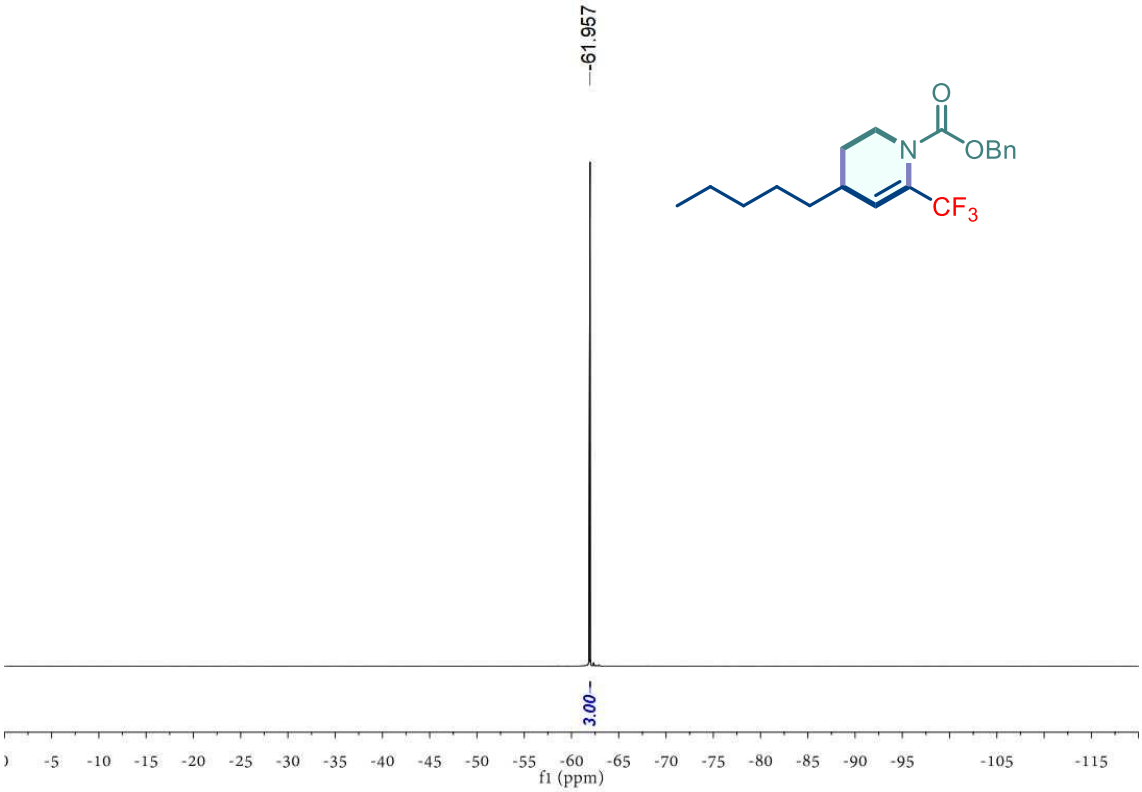


**Figure S85.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **31**.

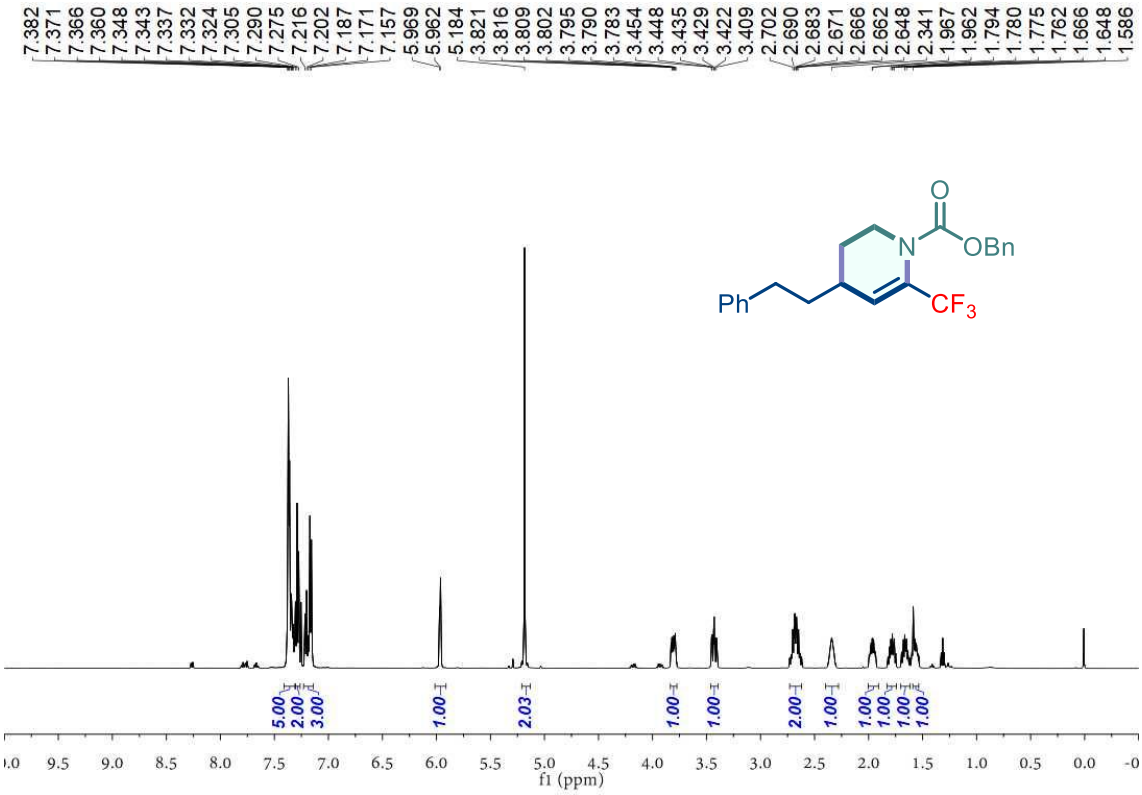


**Figure S86.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **32**.

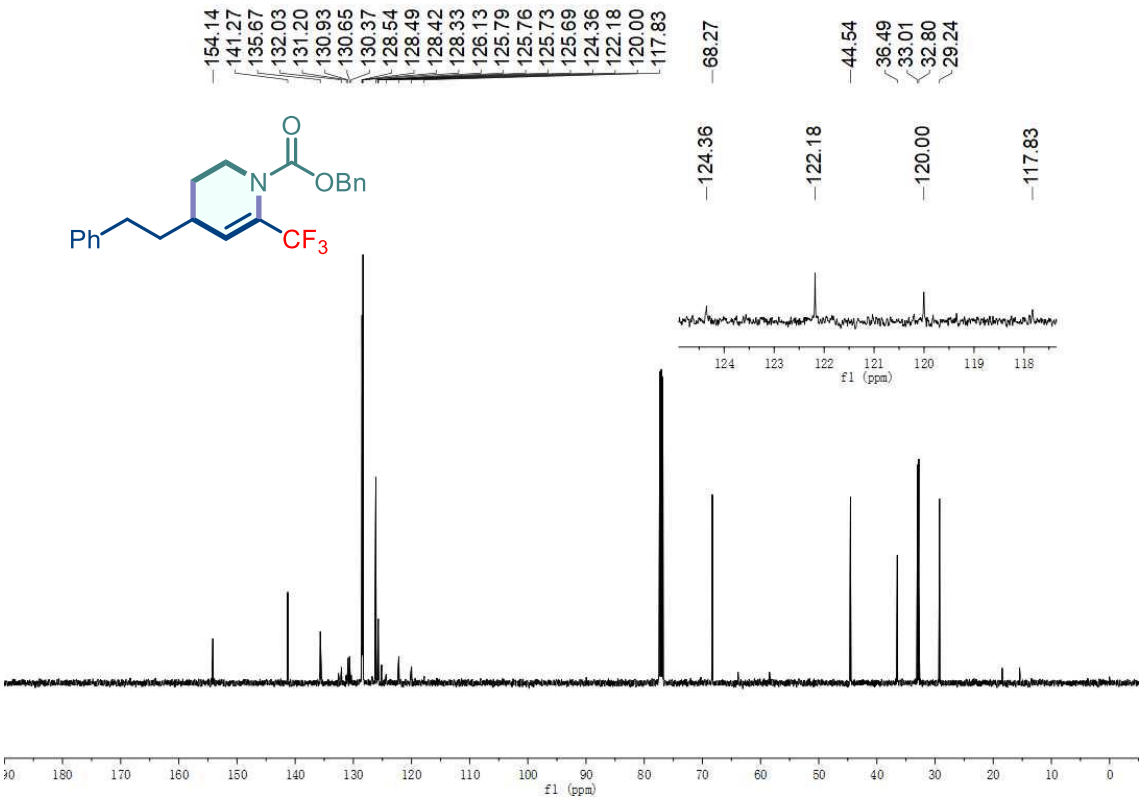


**Figure S87.** $^{13}C$ NMR (125 MHz, $CDCl_3$) Spectrum of **32**.

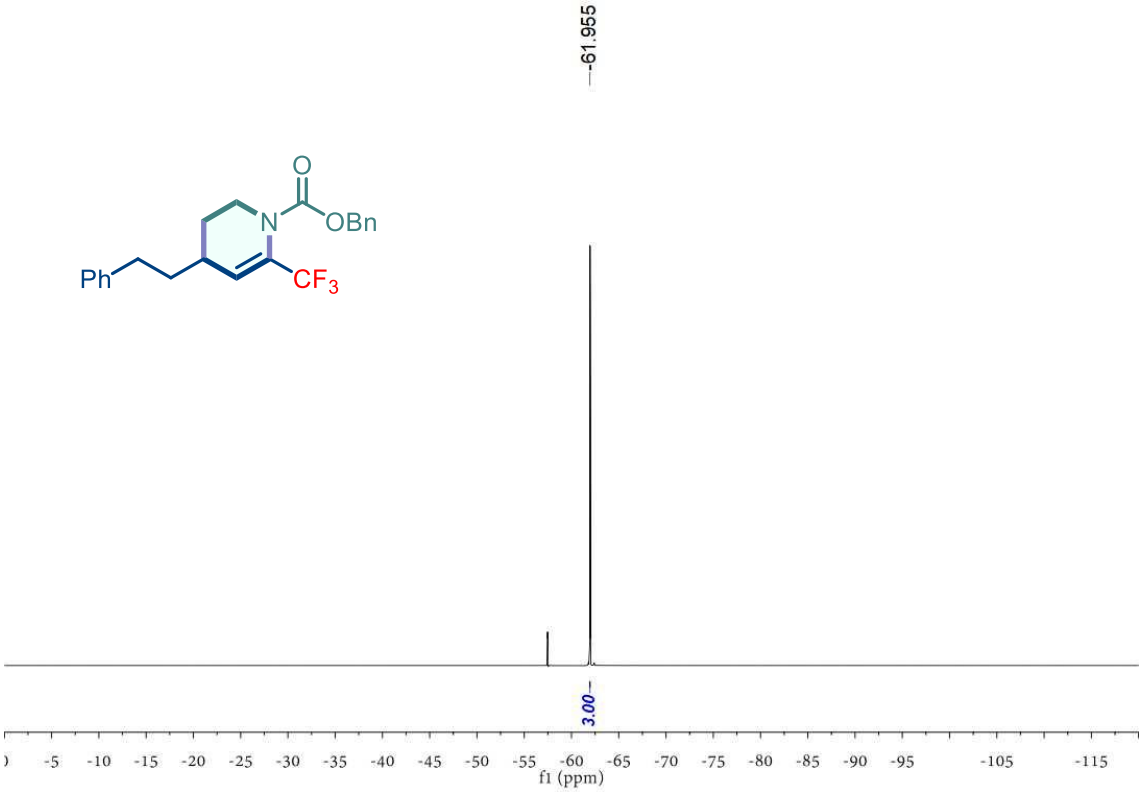


**Figure S88.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **32**.

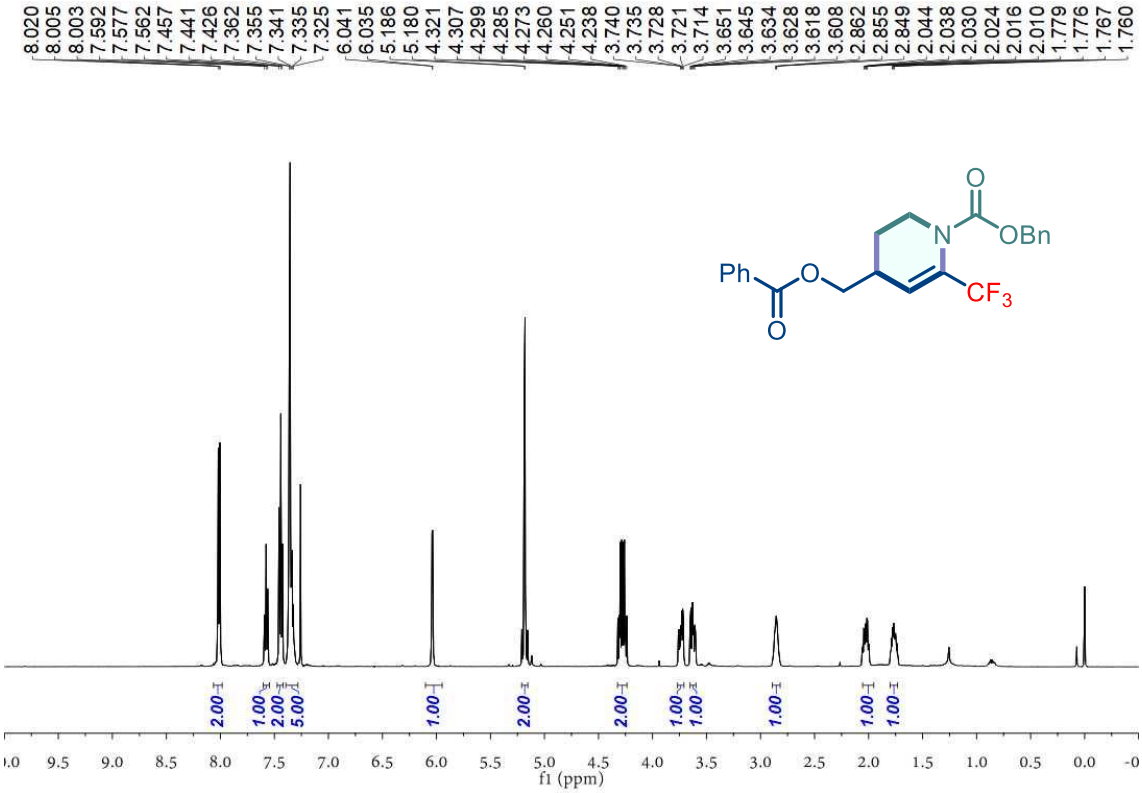


**Figure S89.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **33**.

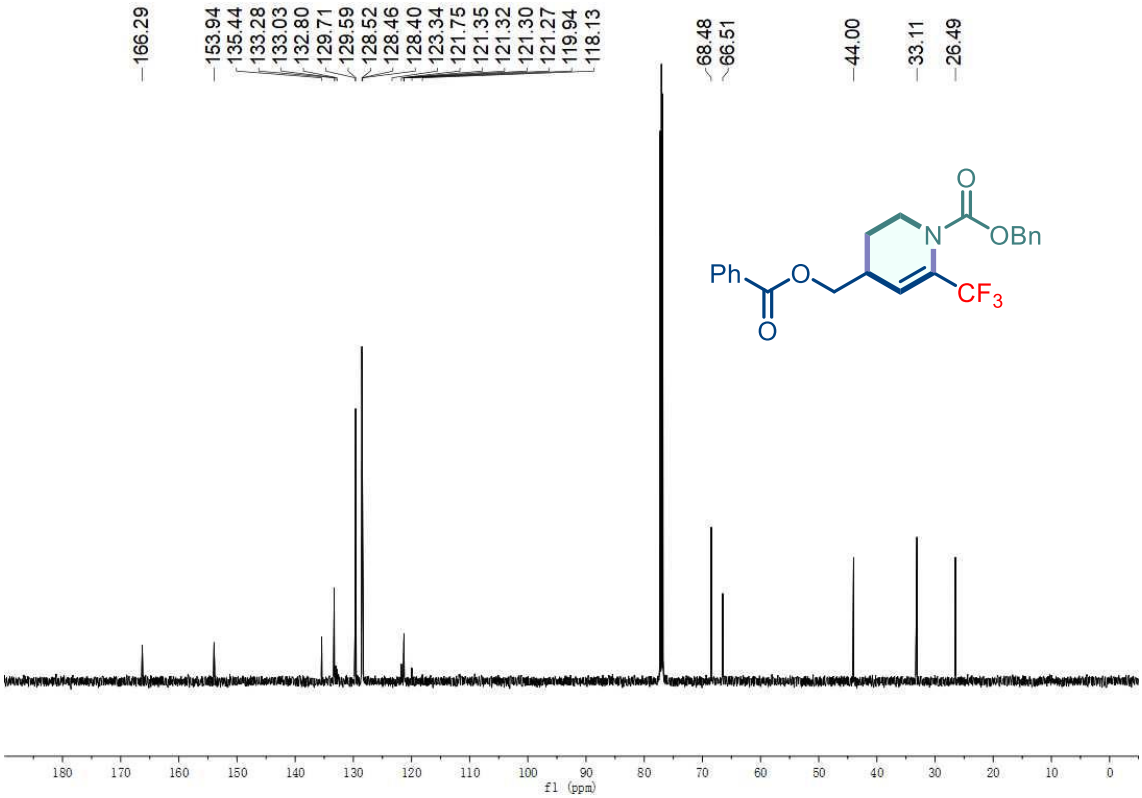


**Figure S90.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **33**.

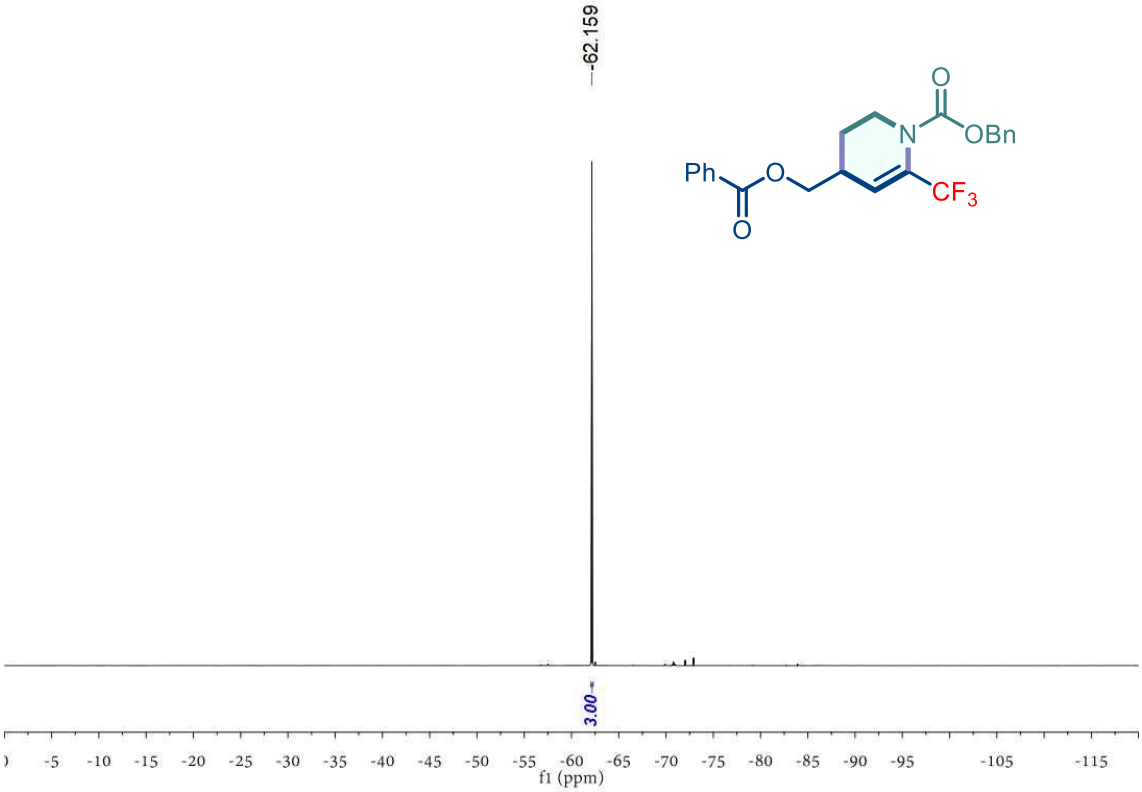


**Figure S91.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **33**.

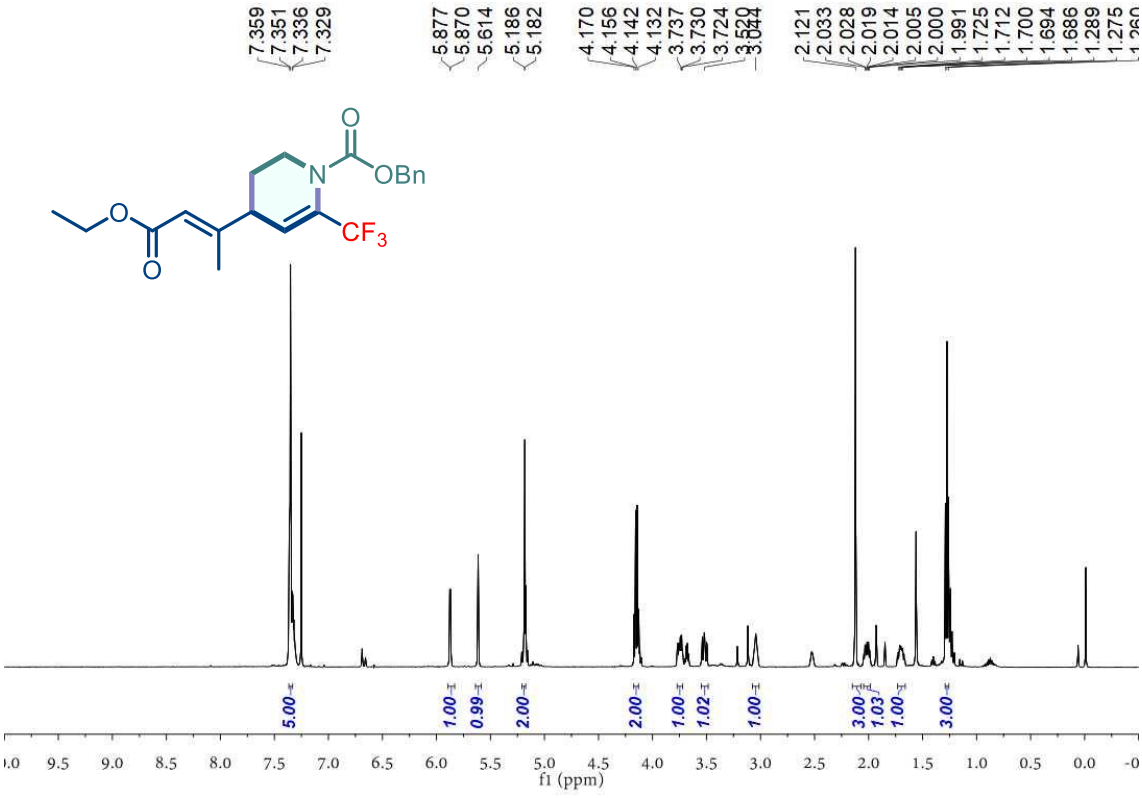


**Figure S92.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **34**.

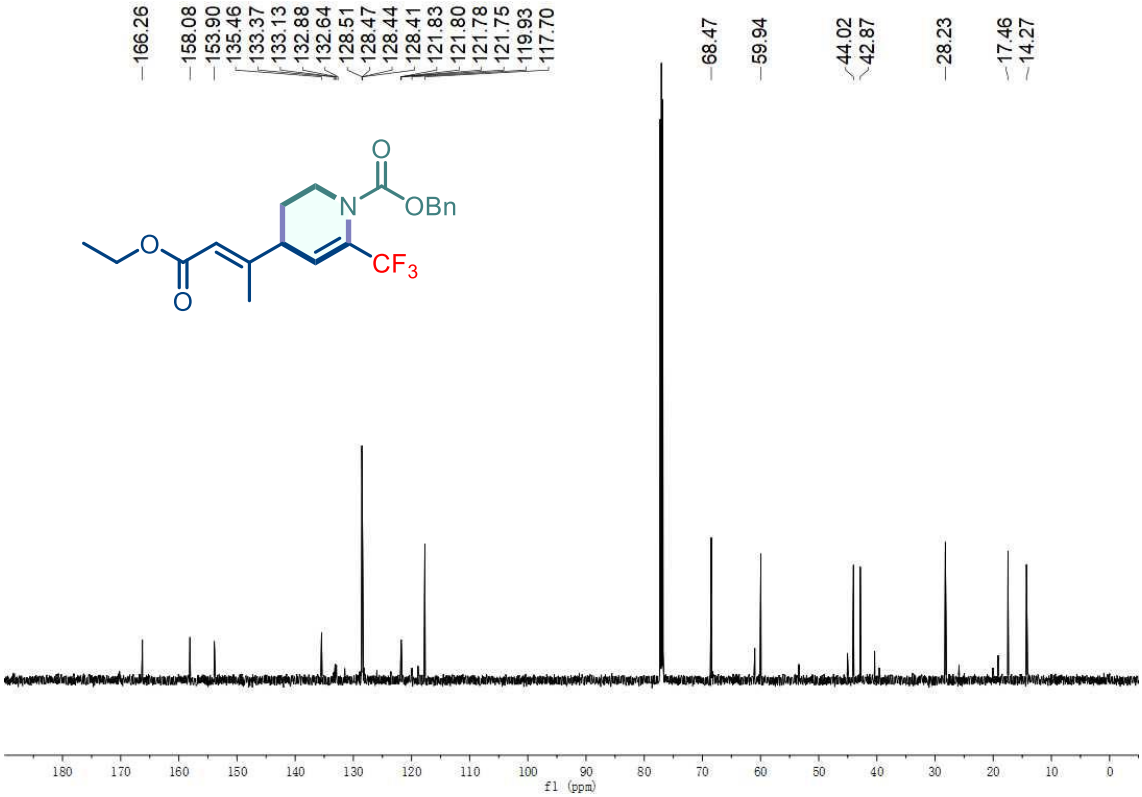


**Figure S93.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **34**.

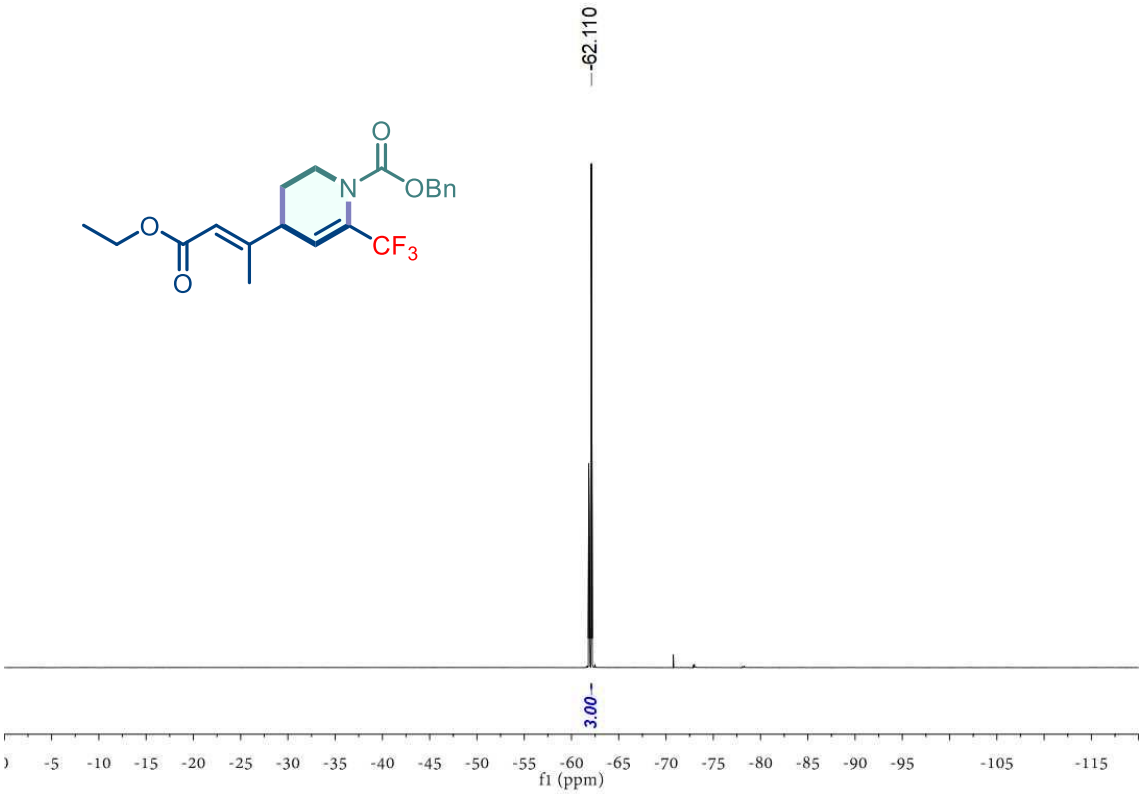


**Figure S94.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **34**.

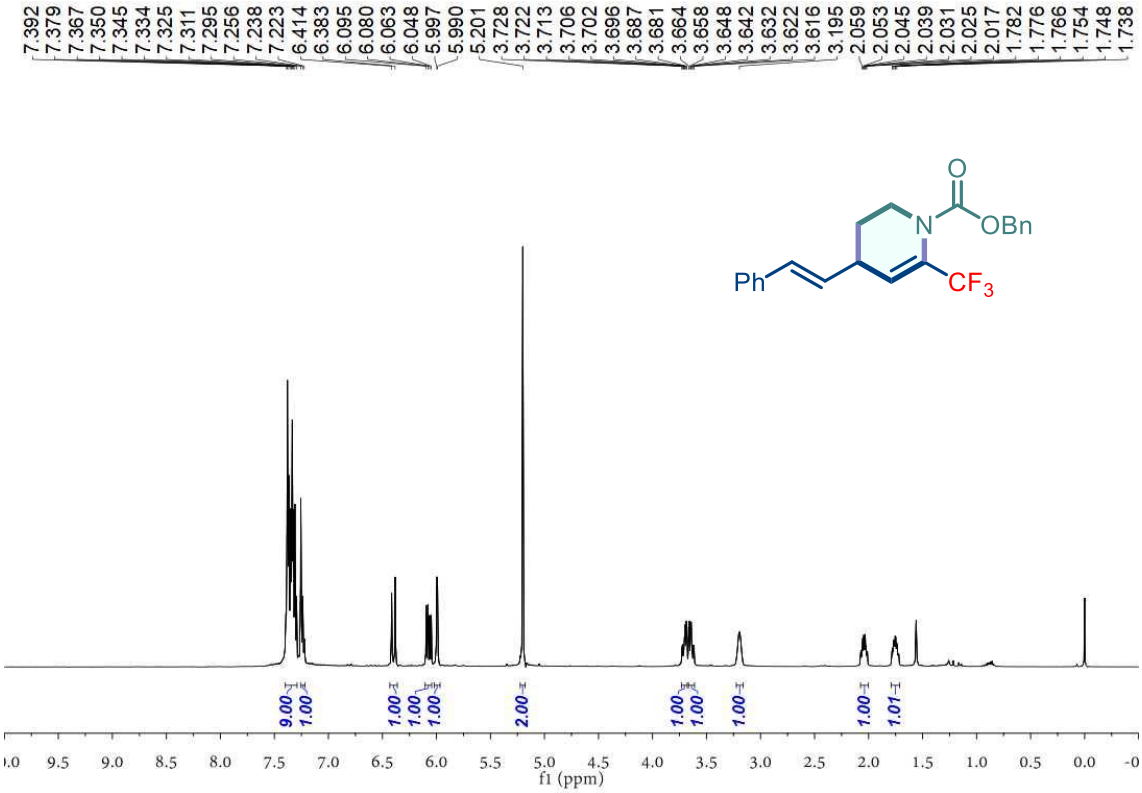


**Figure S95.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **35**.

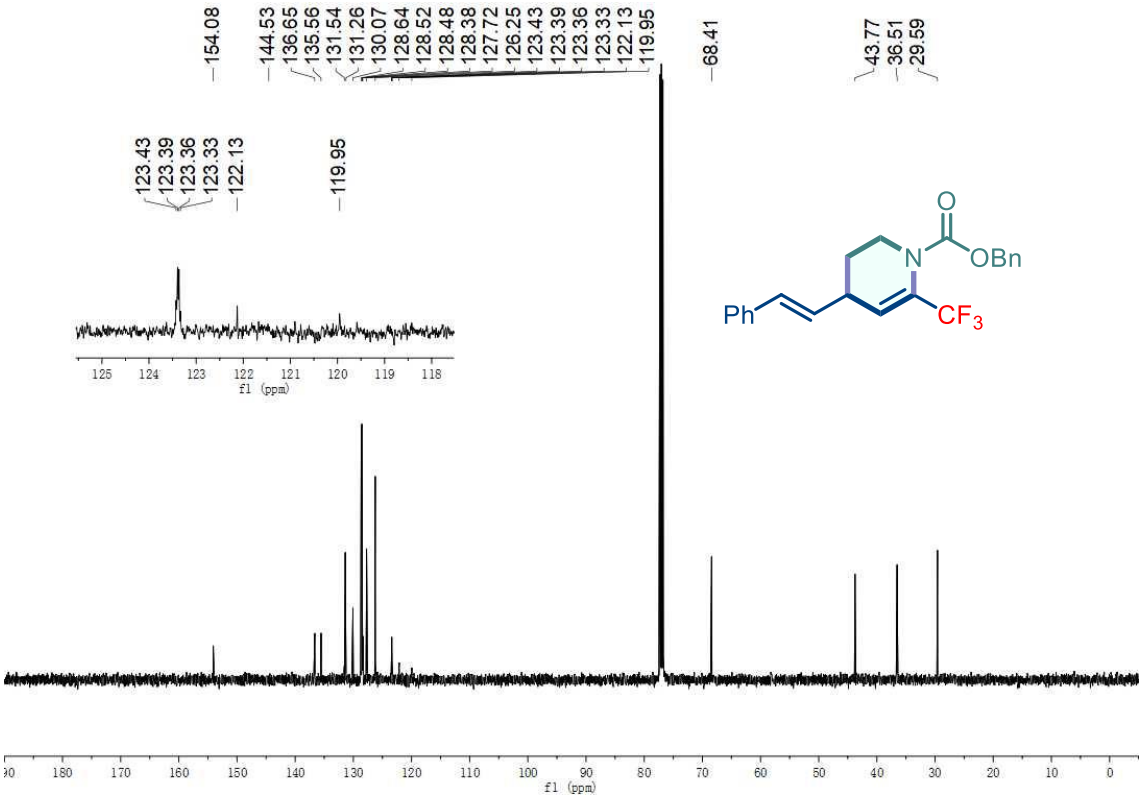


**Figure S96.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **35**.

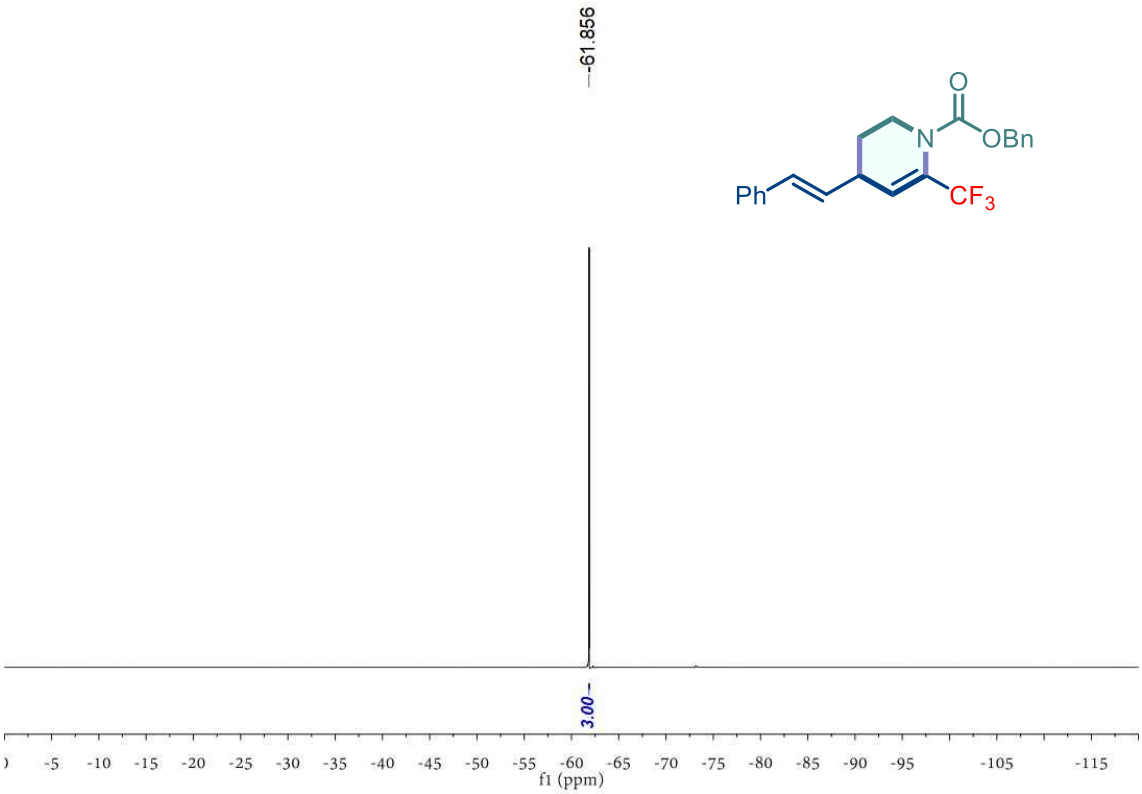


**Figure S97.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **35**.

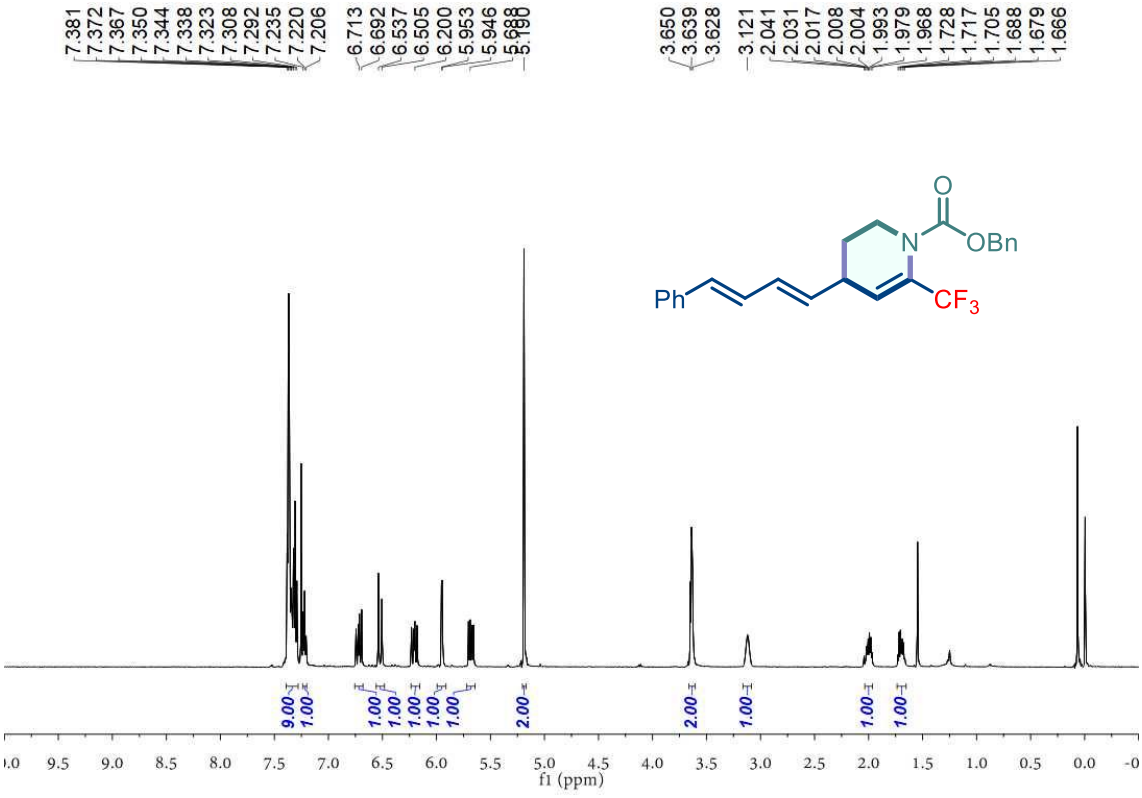


**Figure S98.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **36**.

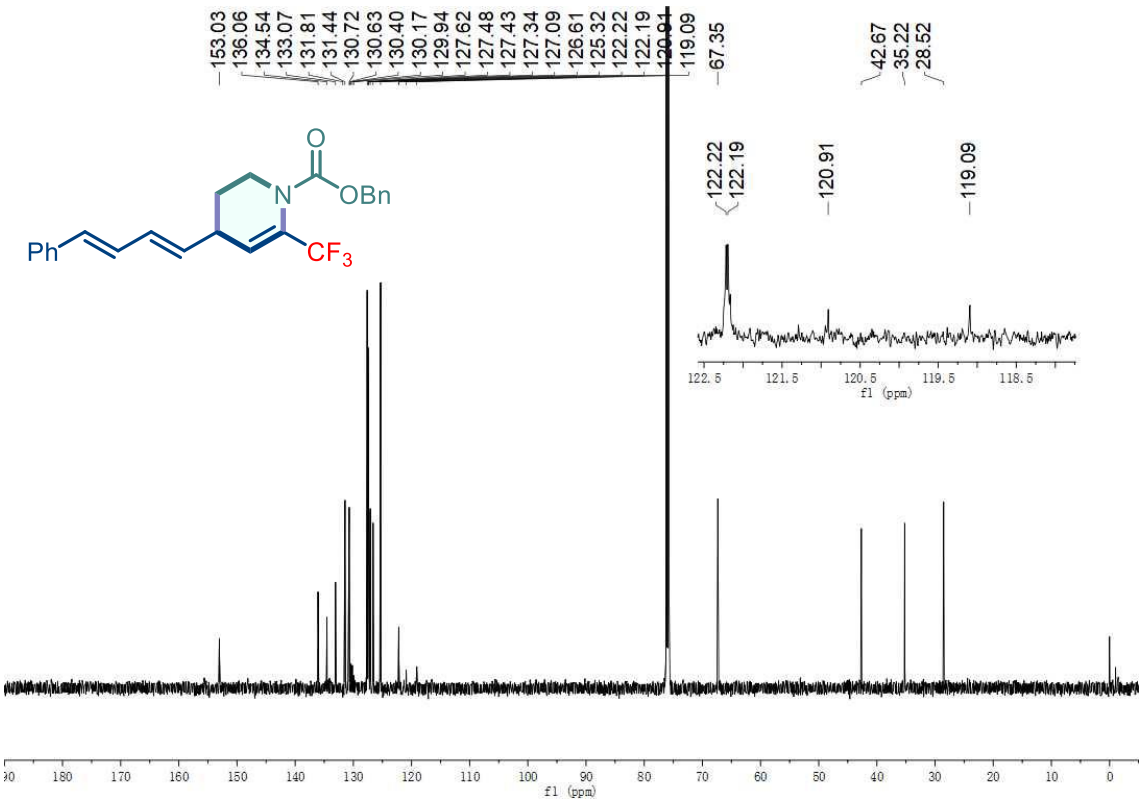


**Figure S99.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **36**.

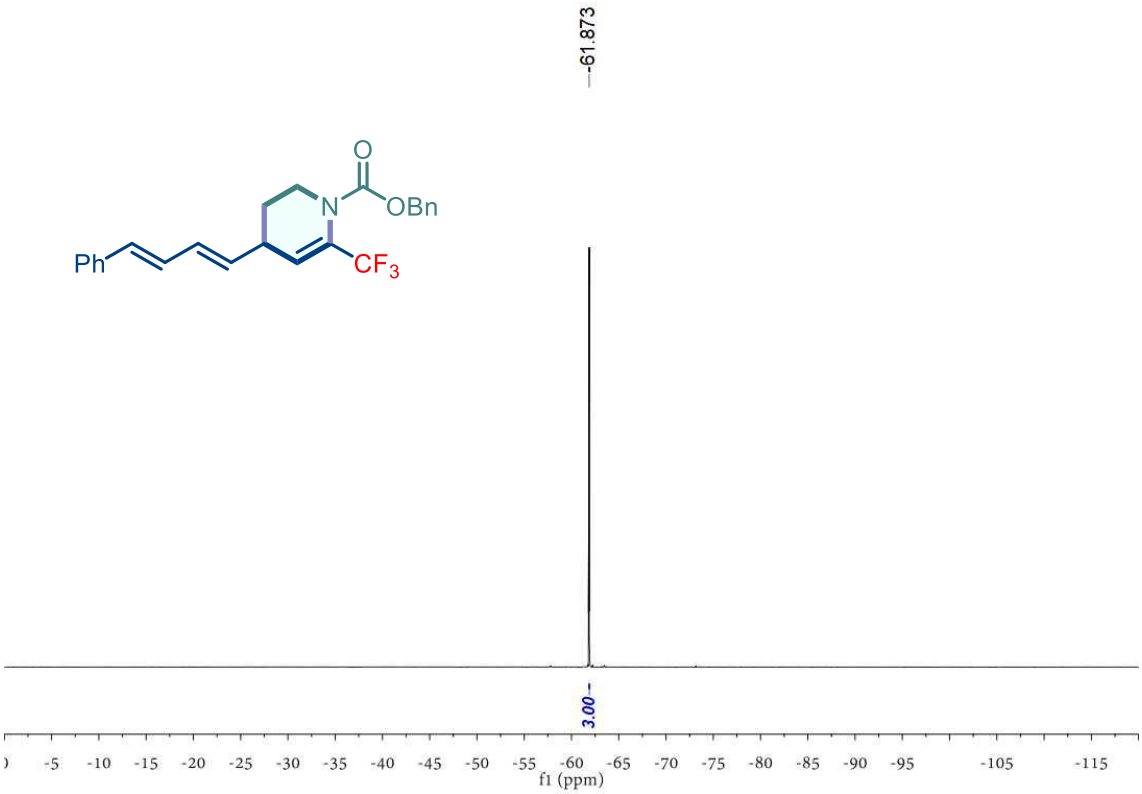


**Figure S100.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **36**.

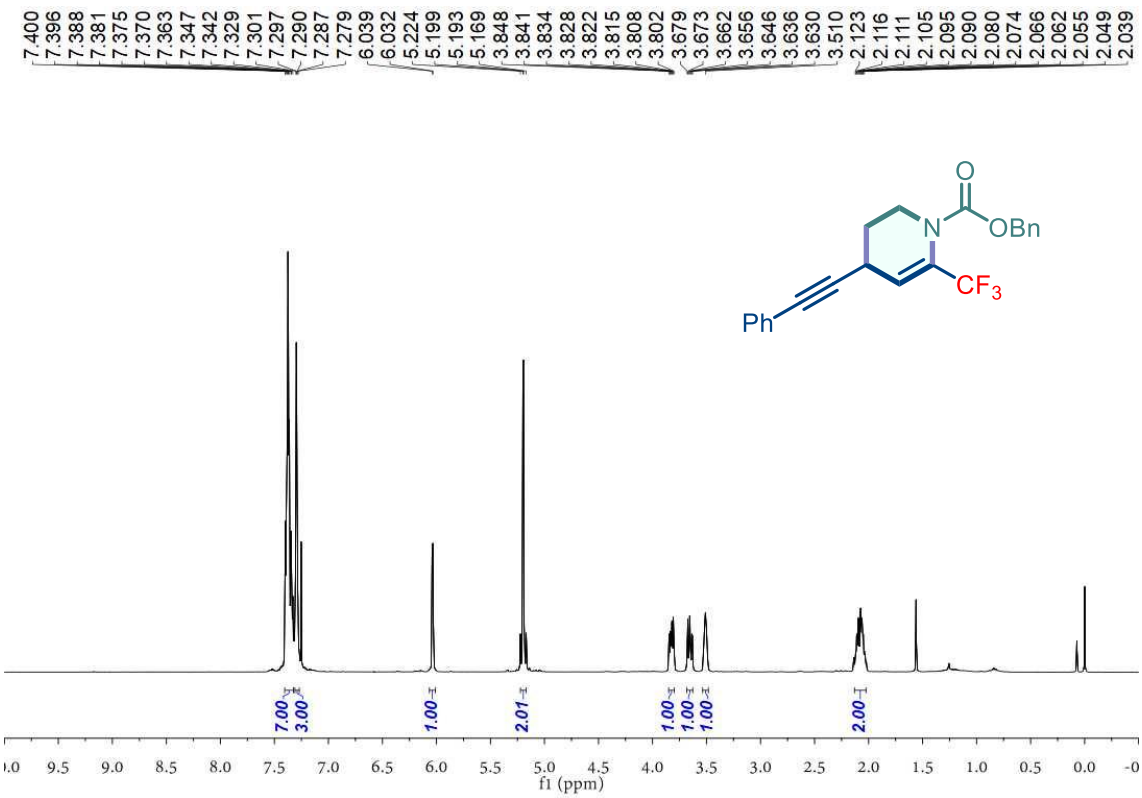


**Figure S101.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **37**.

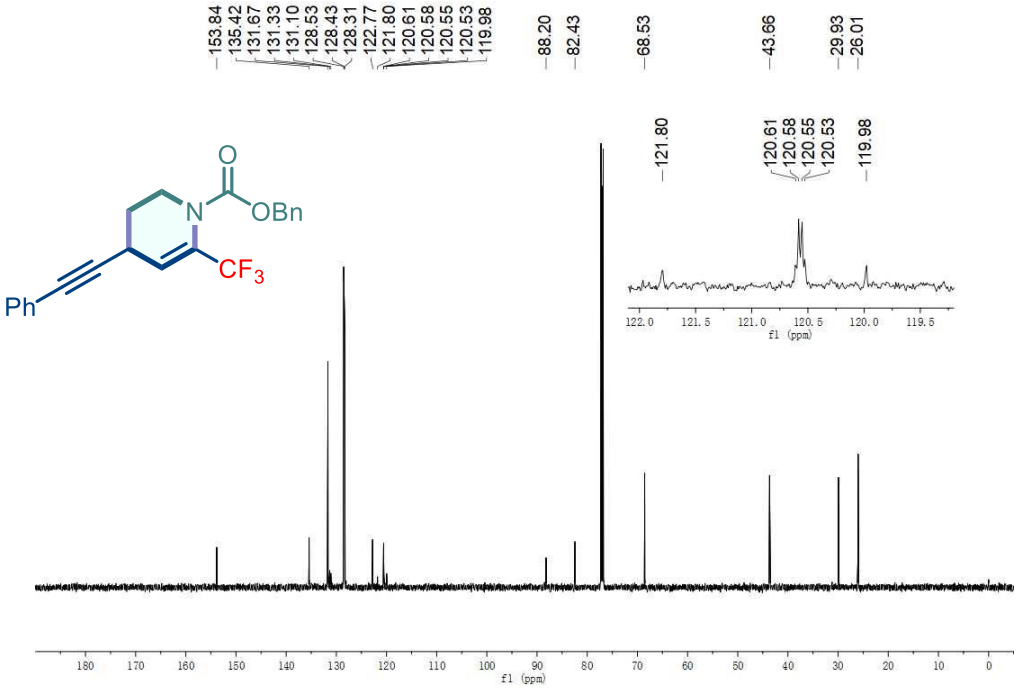


**Figure S102.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **37**.

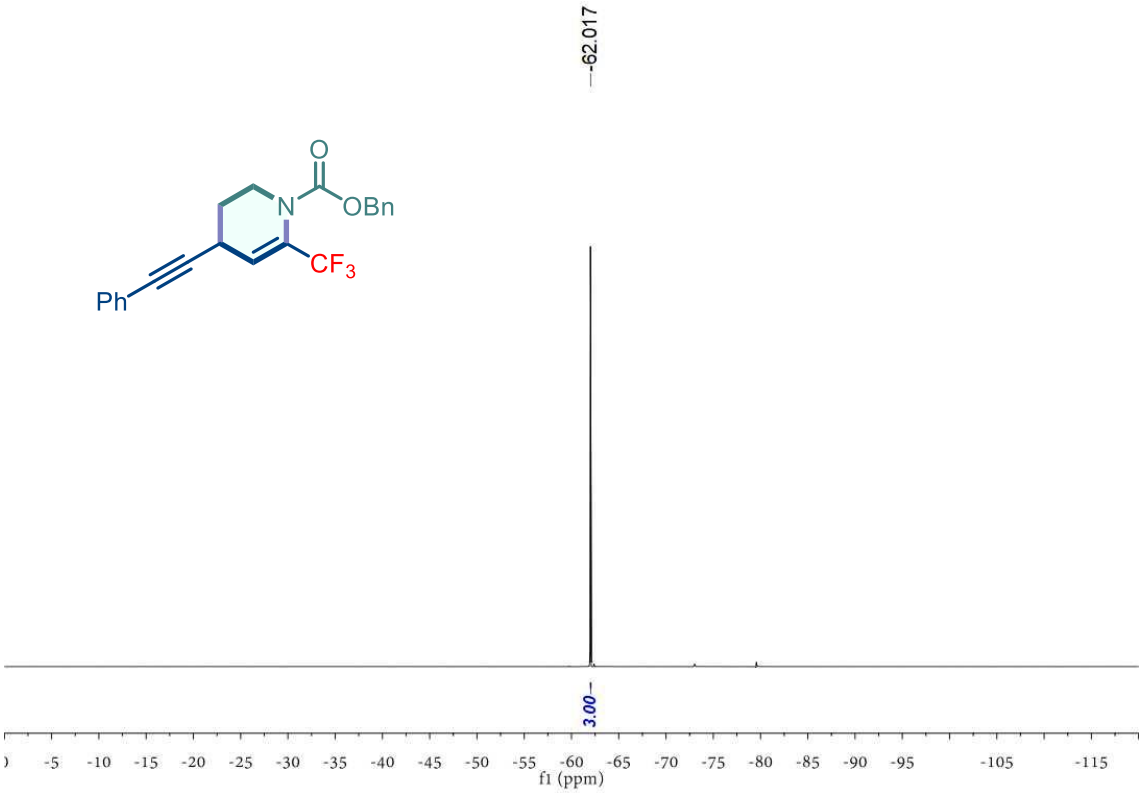


**Figure S103.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **37**.

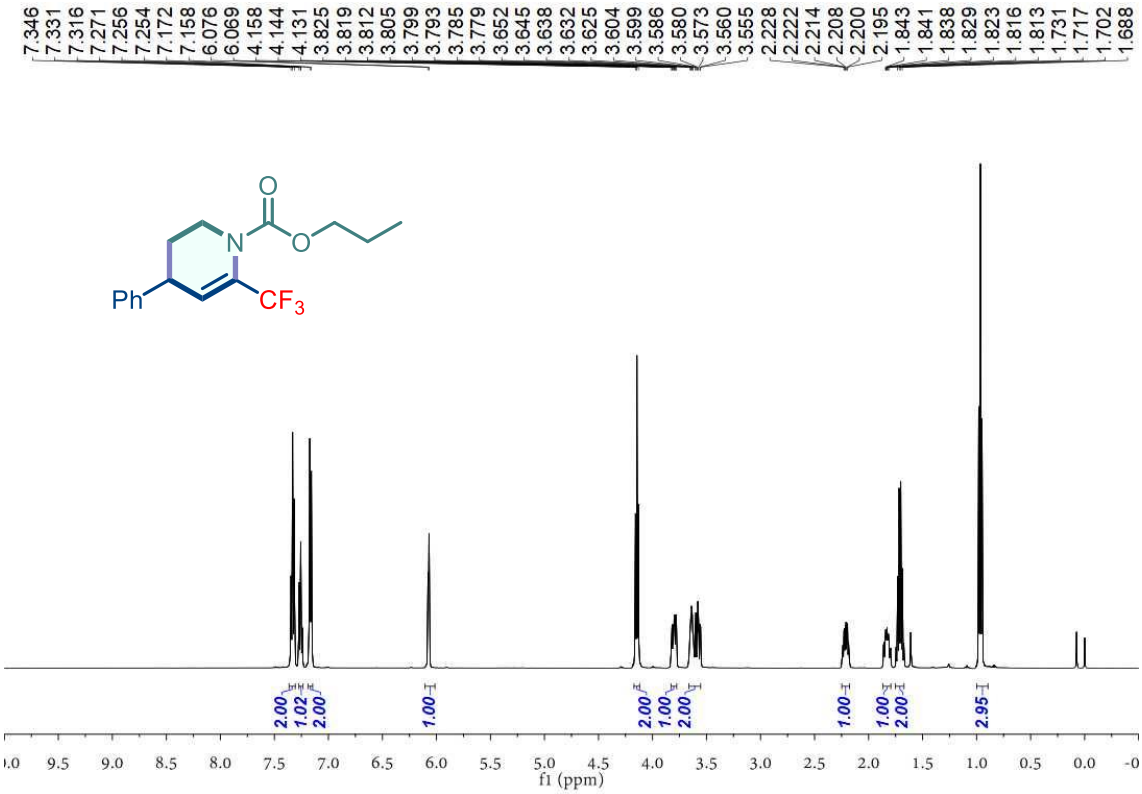


**Figure S104.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **38**.

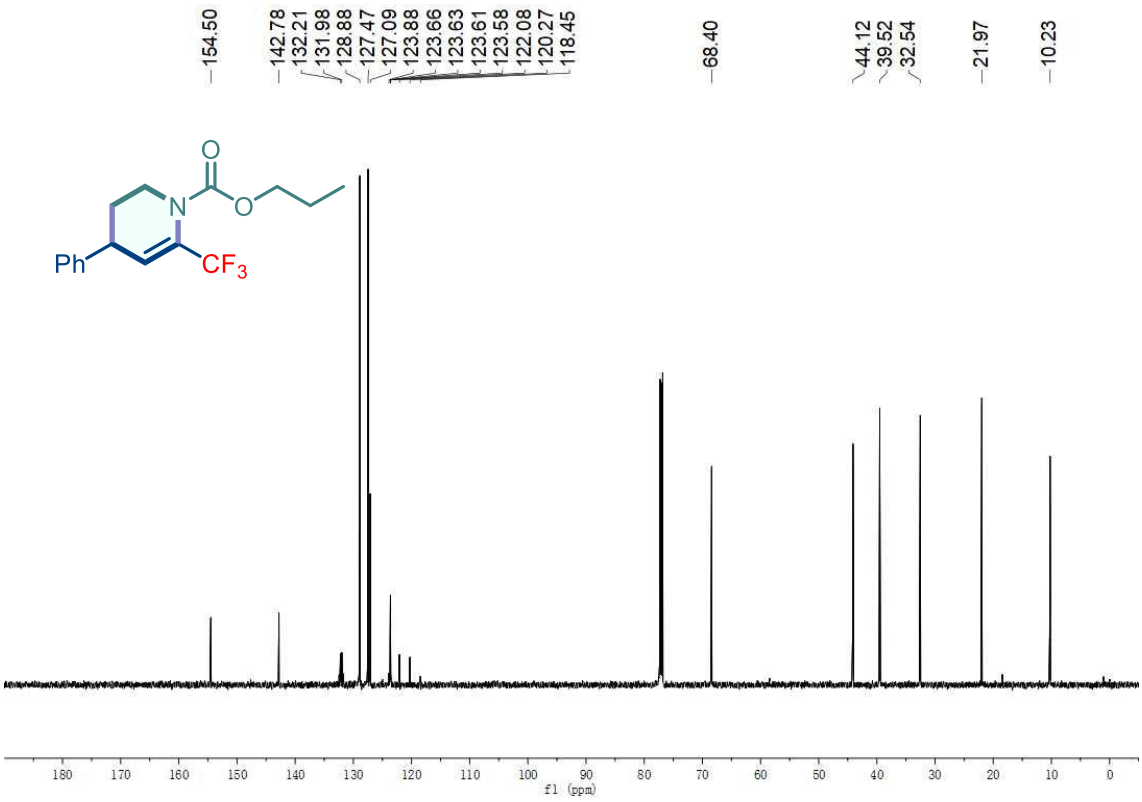


**Figure S105.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **38**.

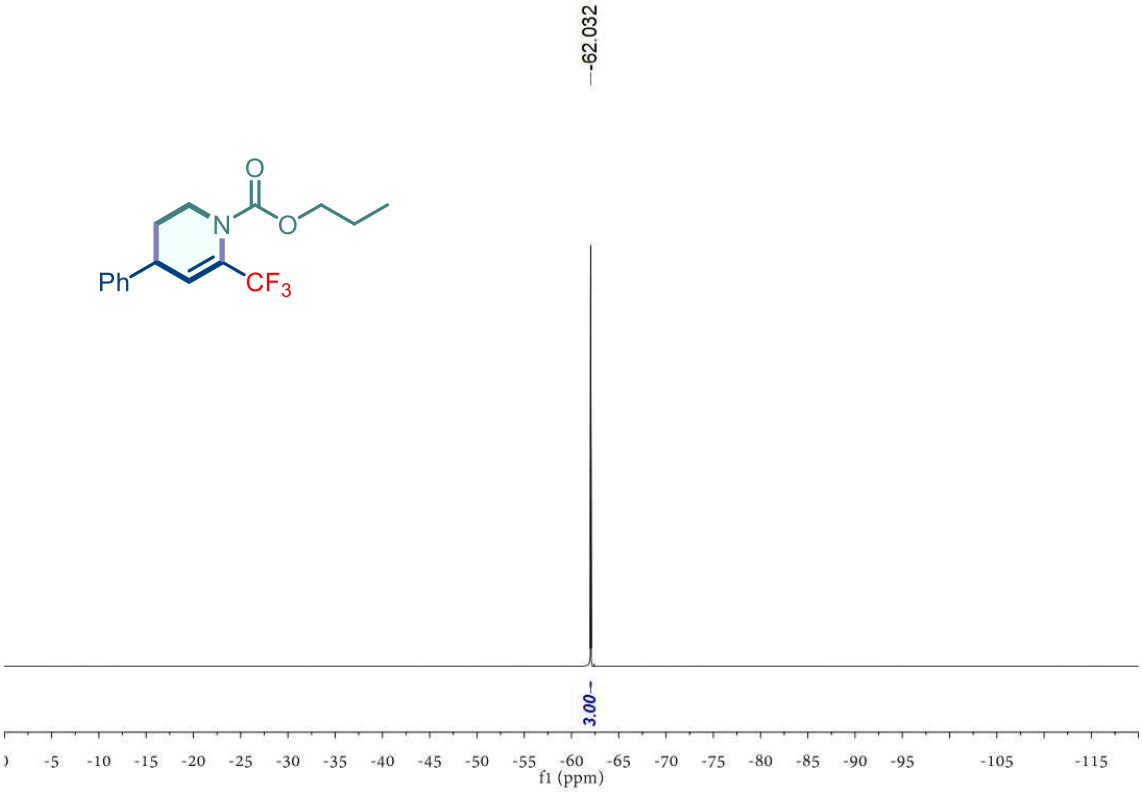


**Figure S106.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **38**.

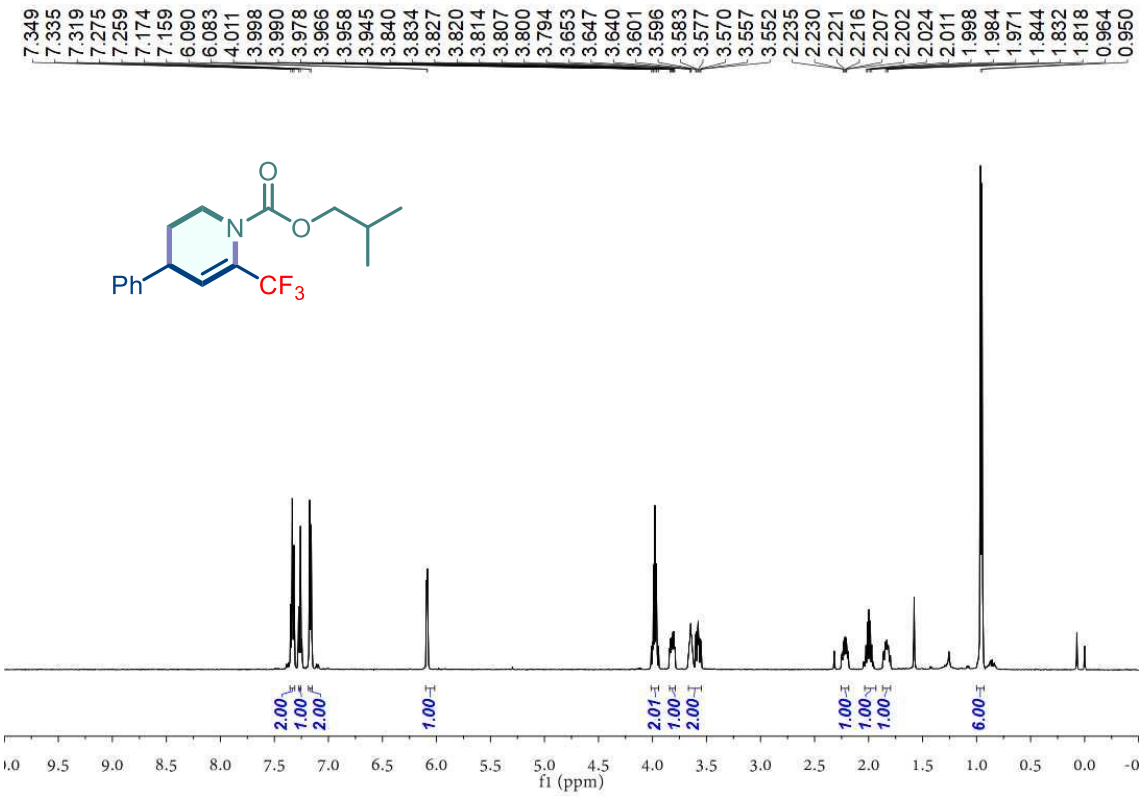


**Figure S107.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **39**.

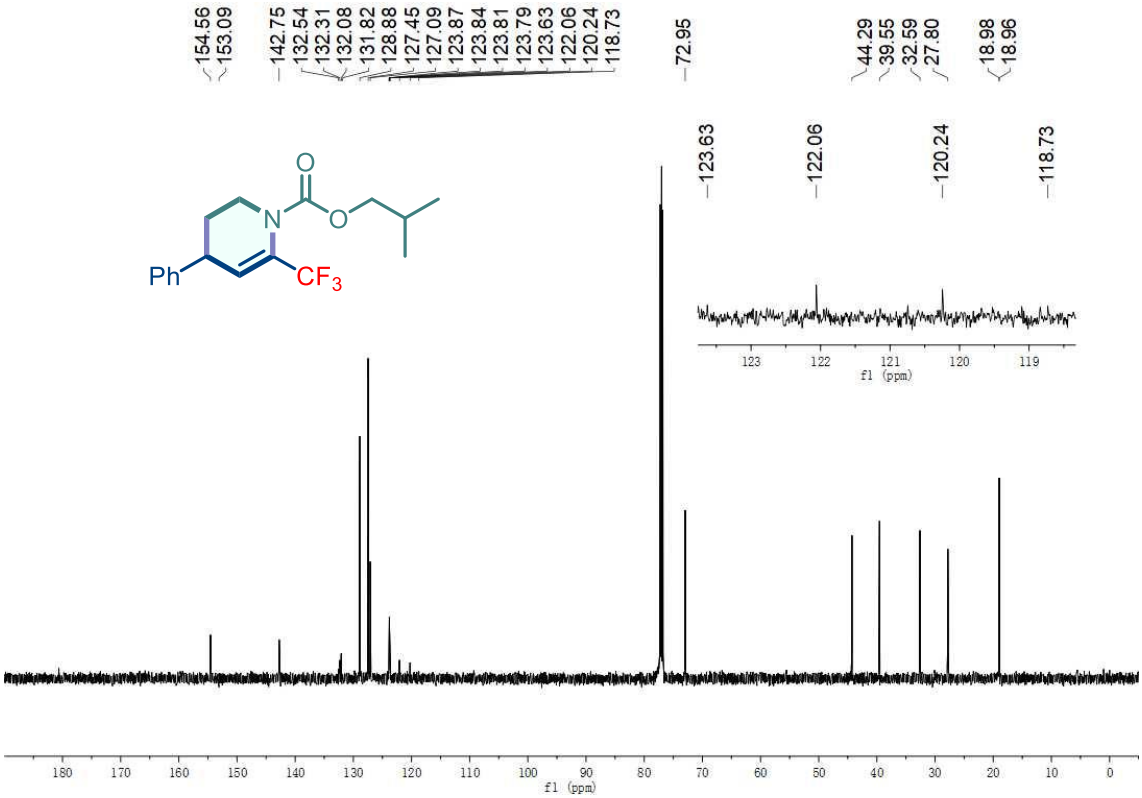


**Figure S108.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **39**.

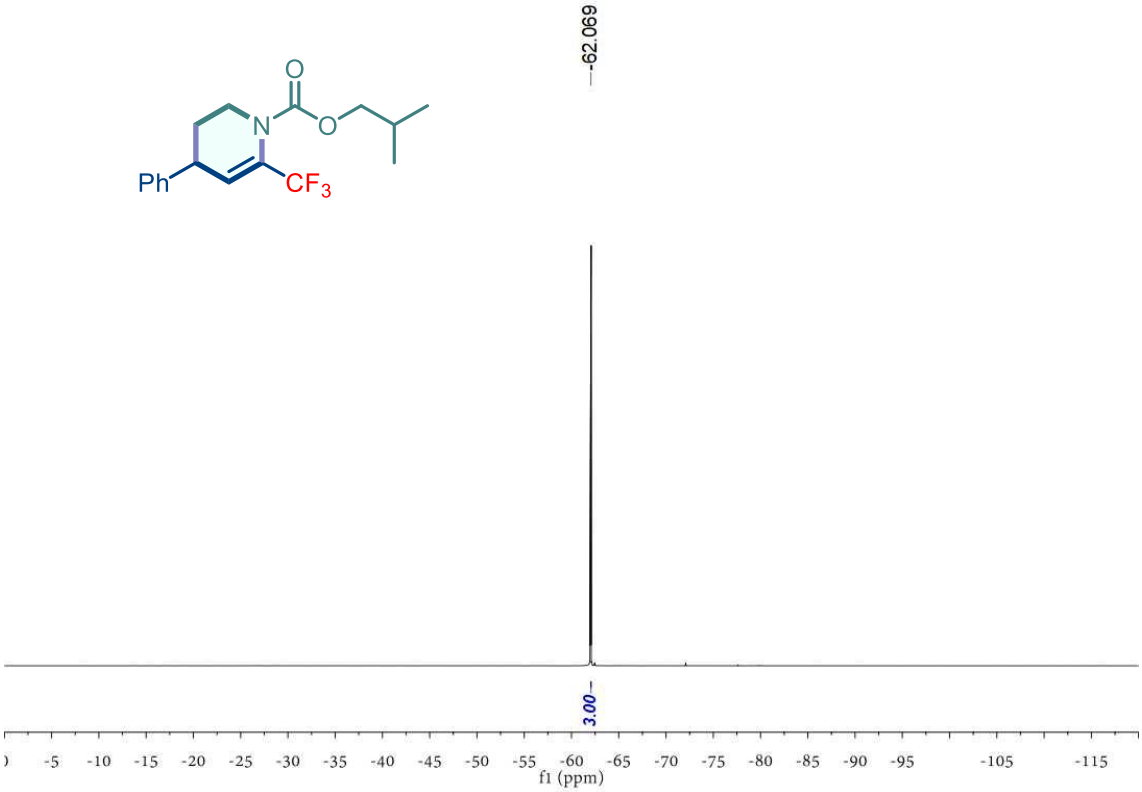


**Figure S109.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **39**.

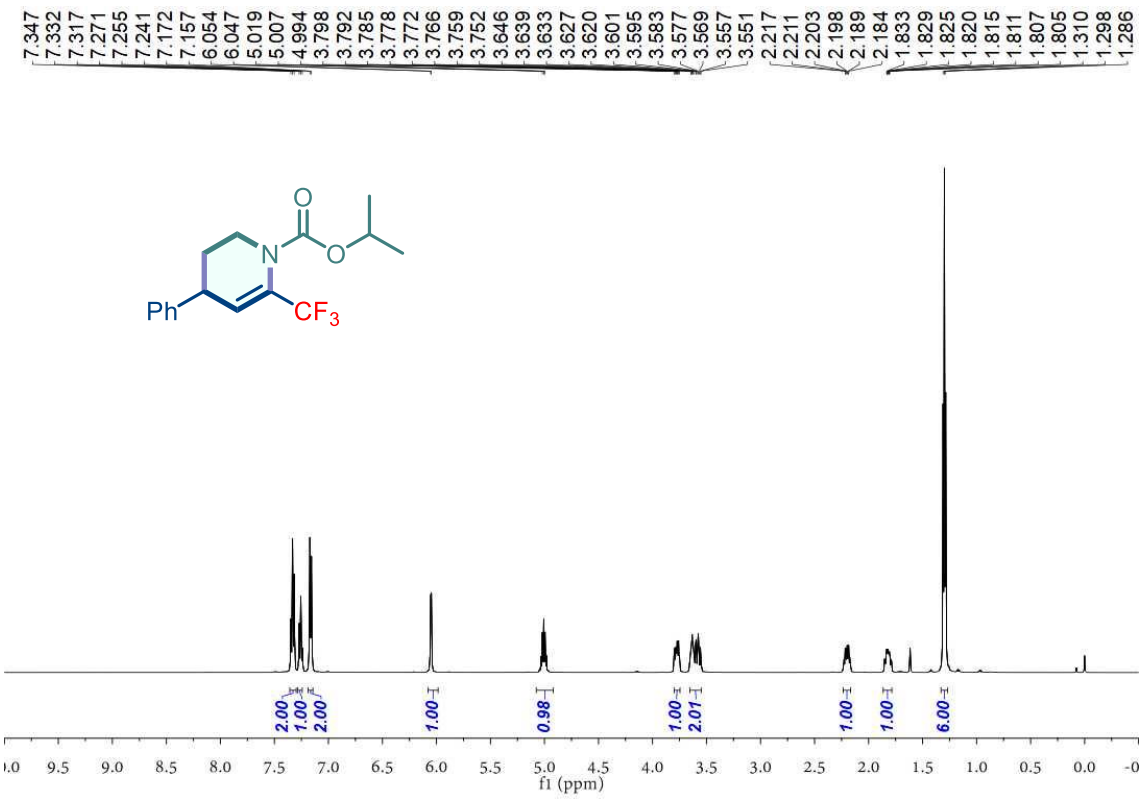


**Figure S110.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **40**.

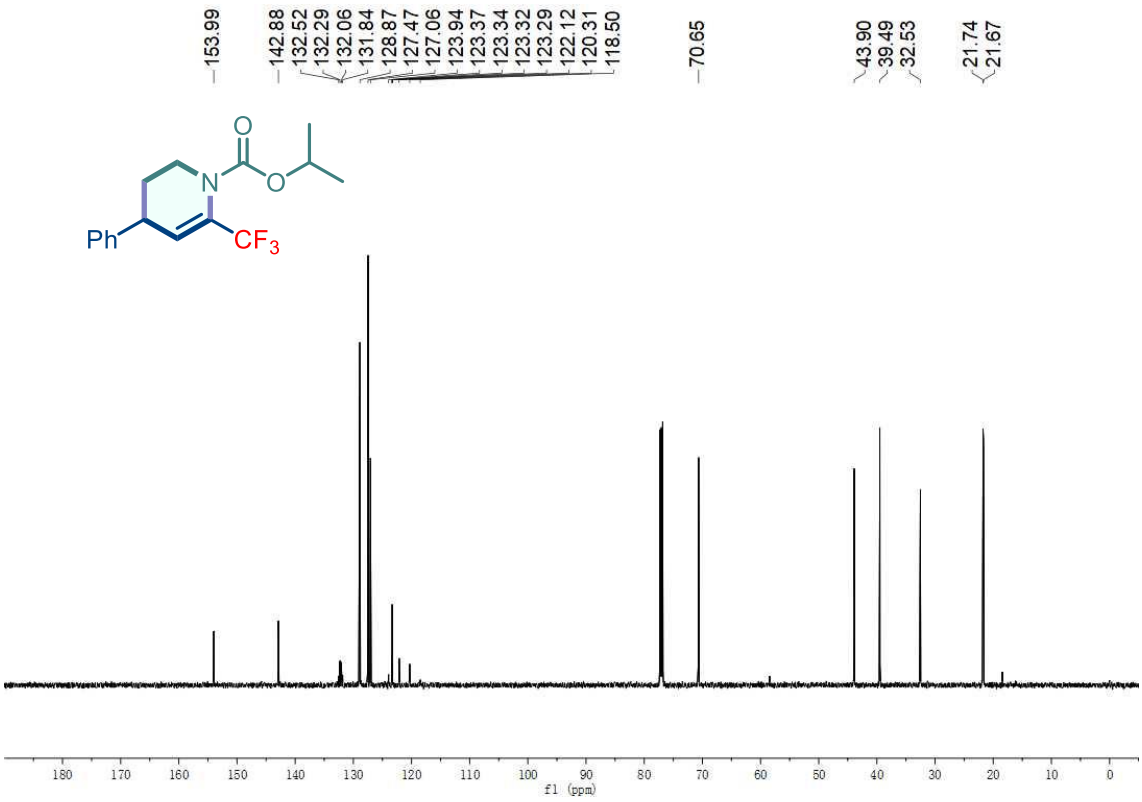


**Figure S111.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **40**.

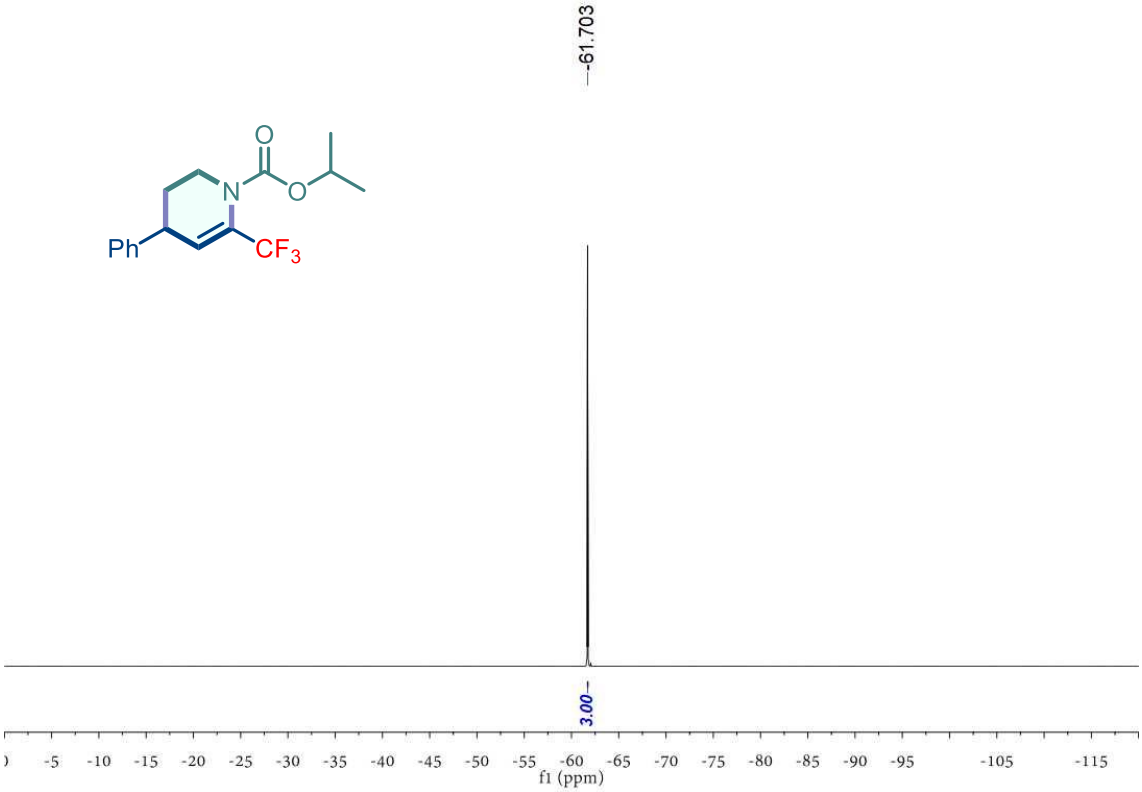


**Figure S112.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **40**.

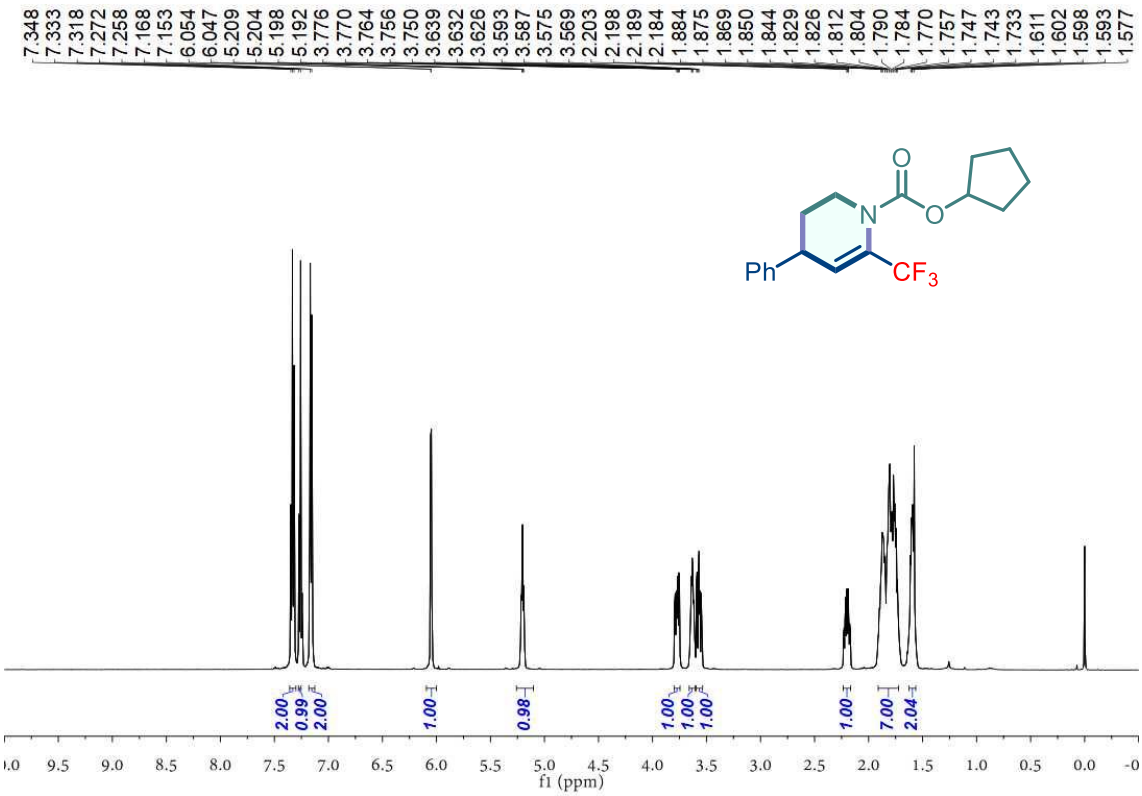


**Figure S113.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **41**.

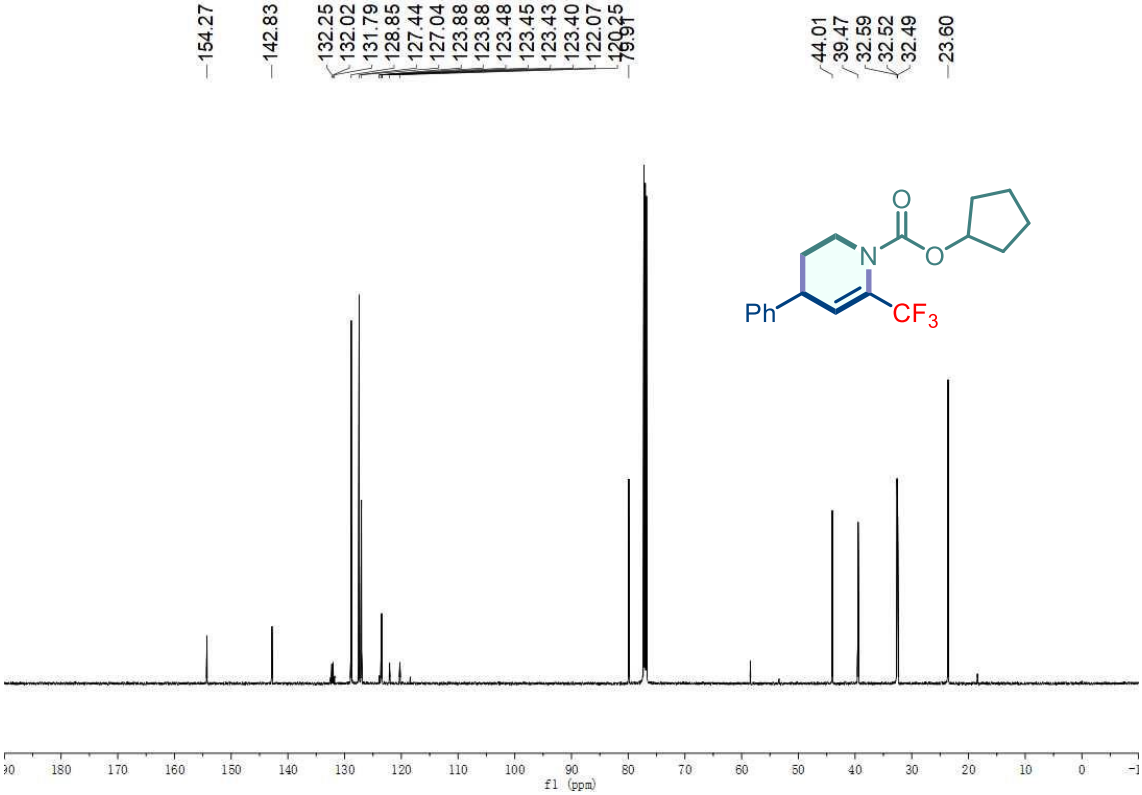


**Figure S114.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **41**.

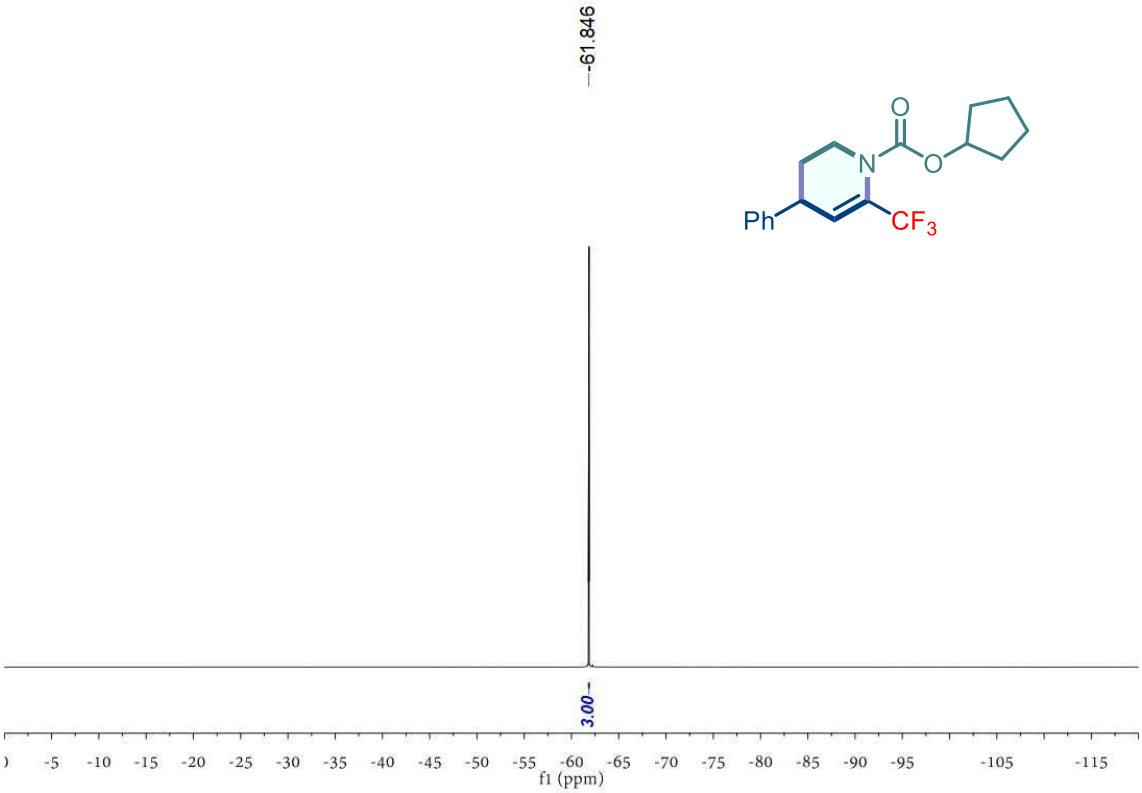


**Figure S115.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **41**.

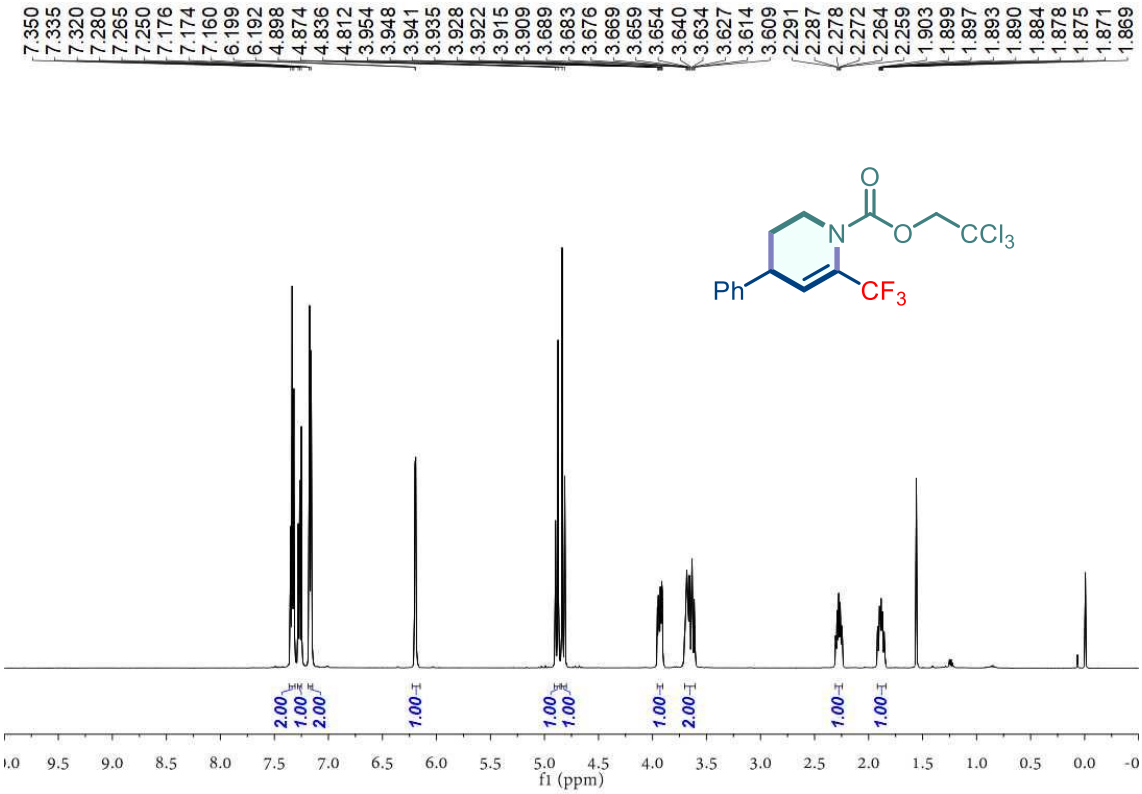


**Figure S116.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **42**.

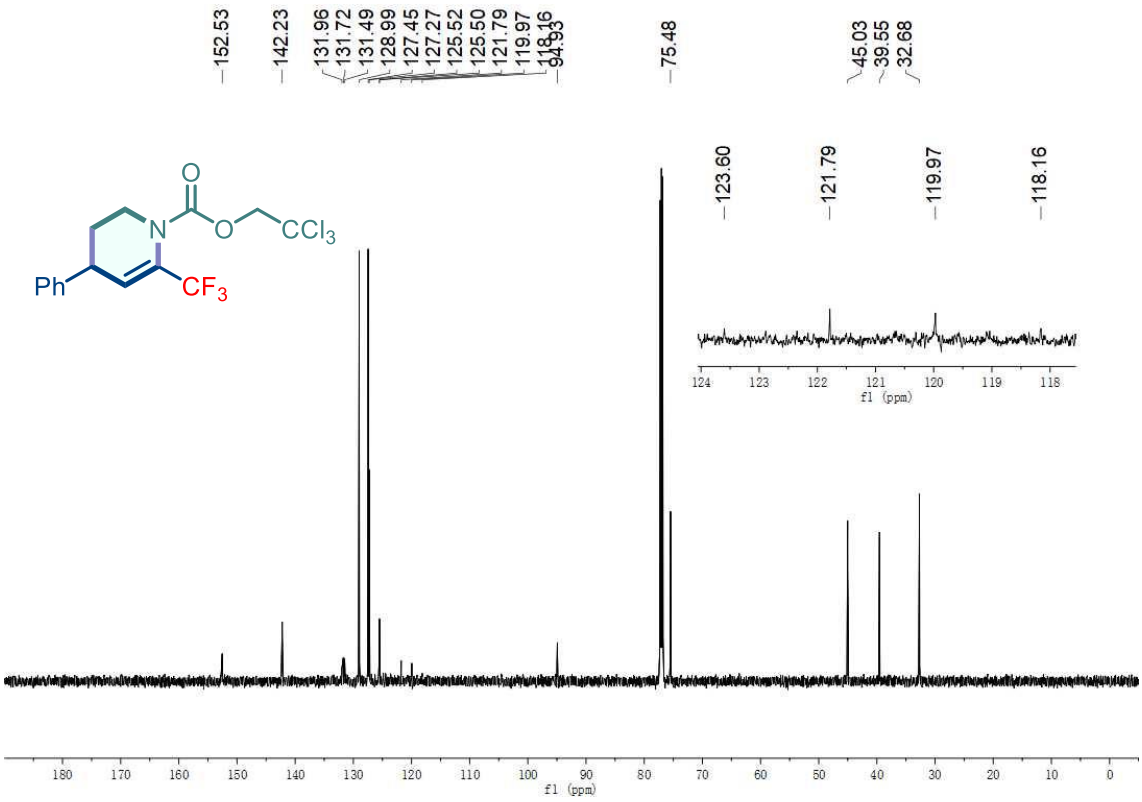


**Figure S117.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **42**.

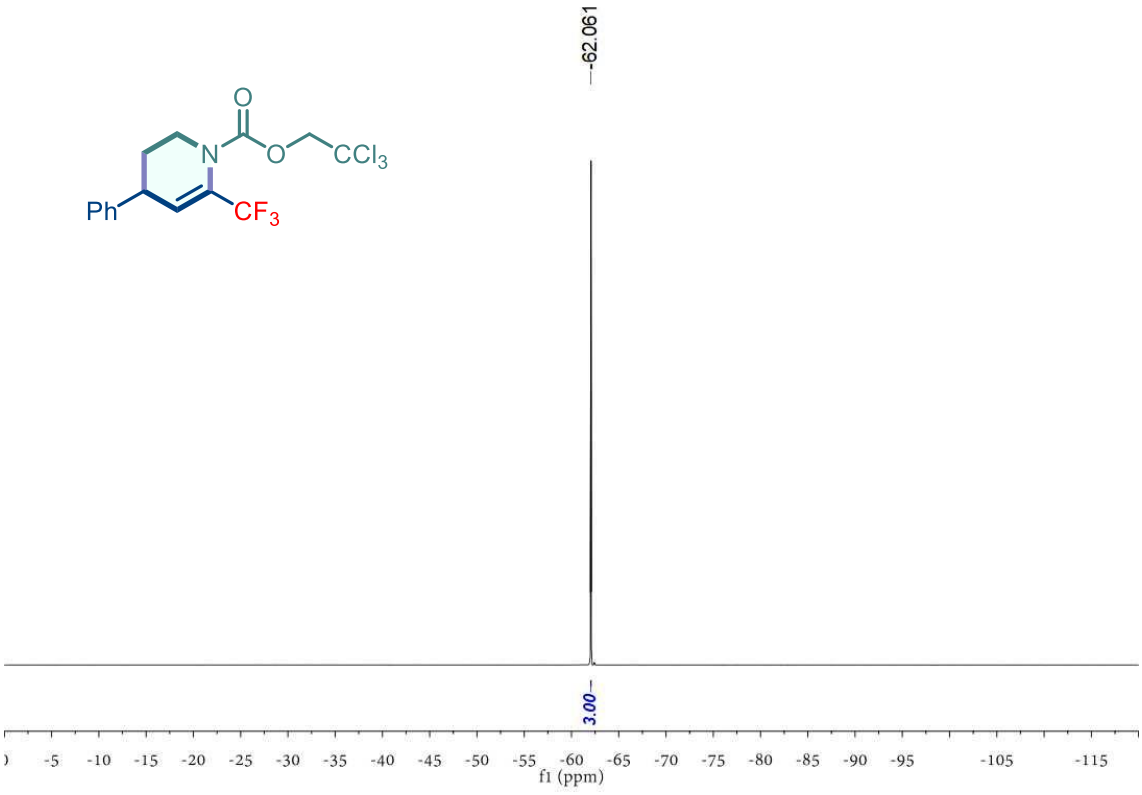


**Figure S118.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **42**.

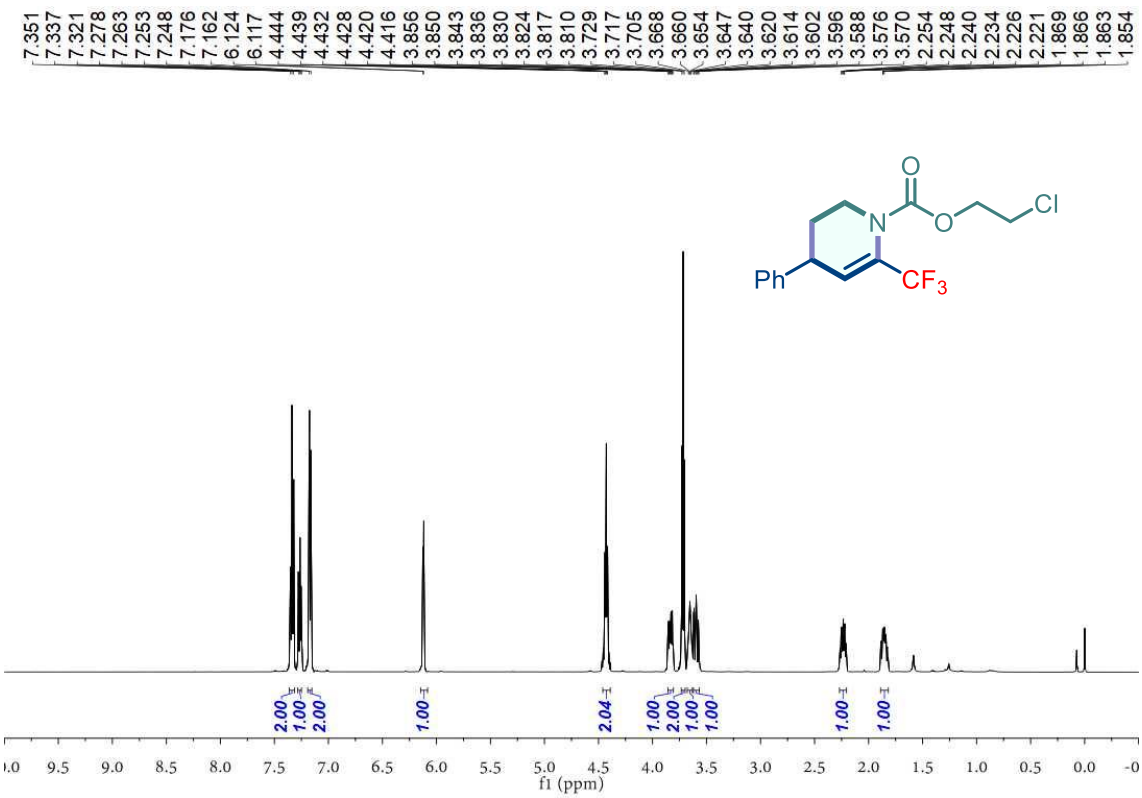


**Figure S119.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of 4**3**.

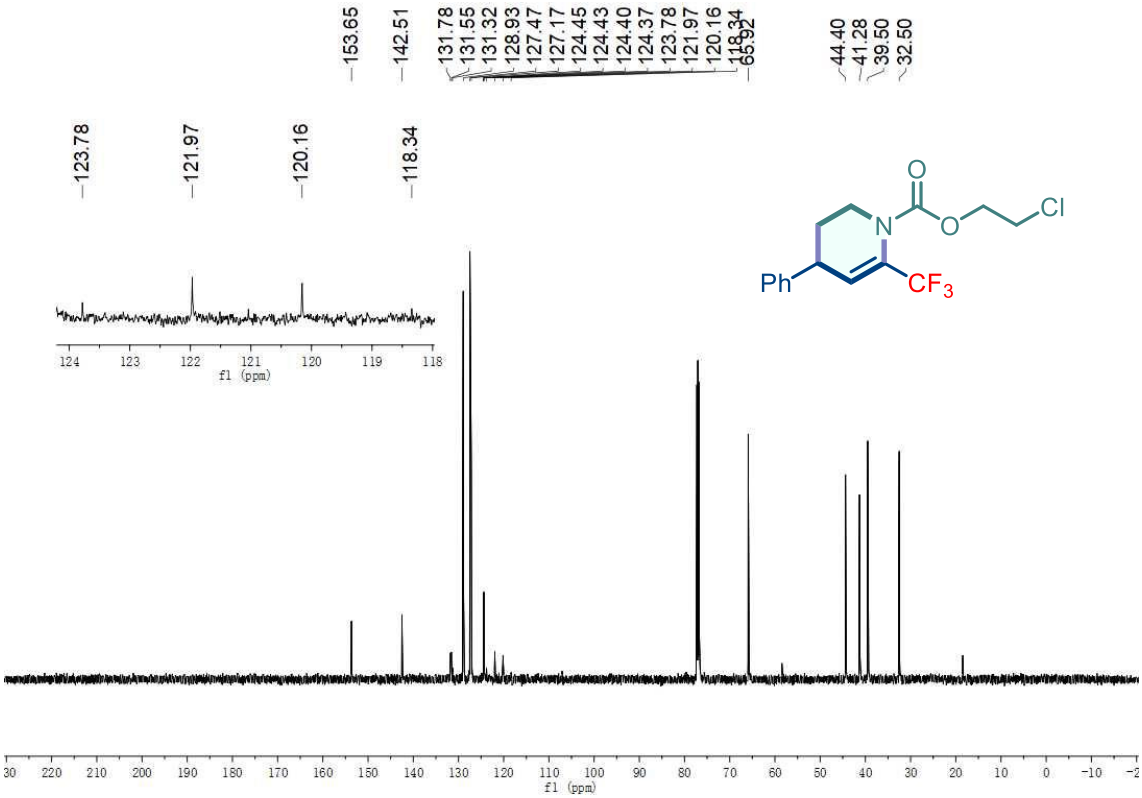


**Figure S120.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of 4**3**.

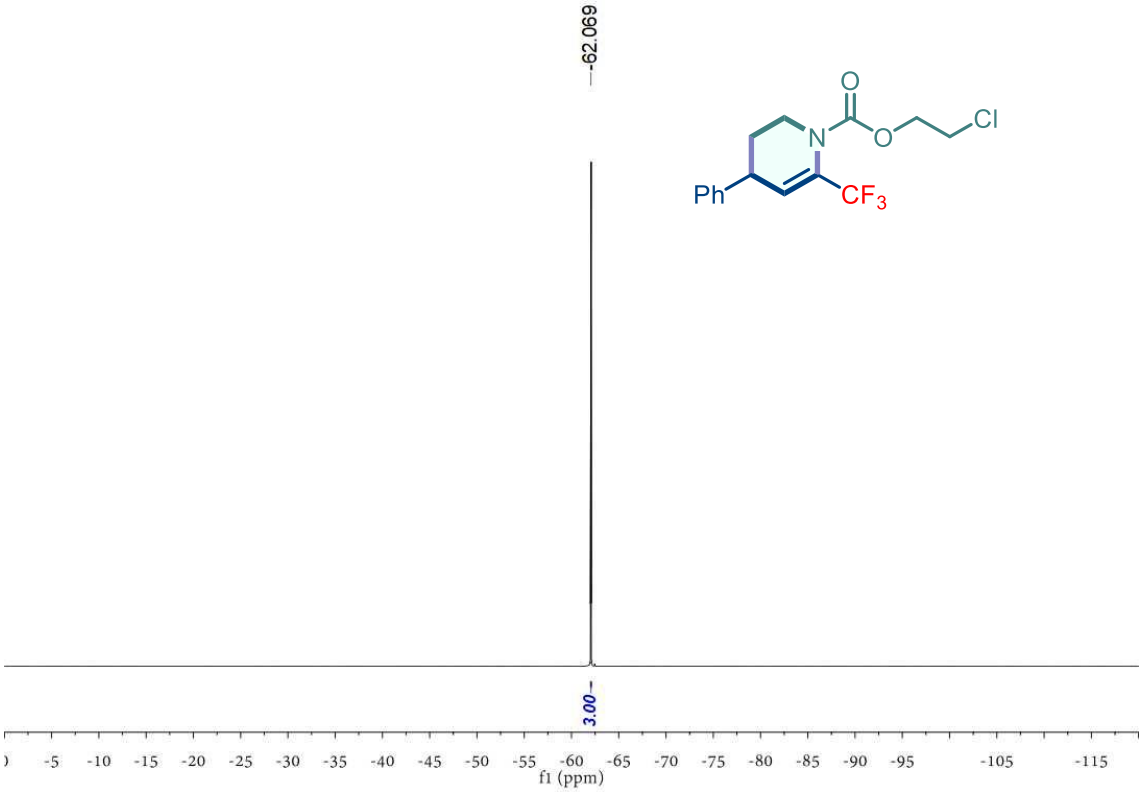


**Figure S121.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of 4**3**.

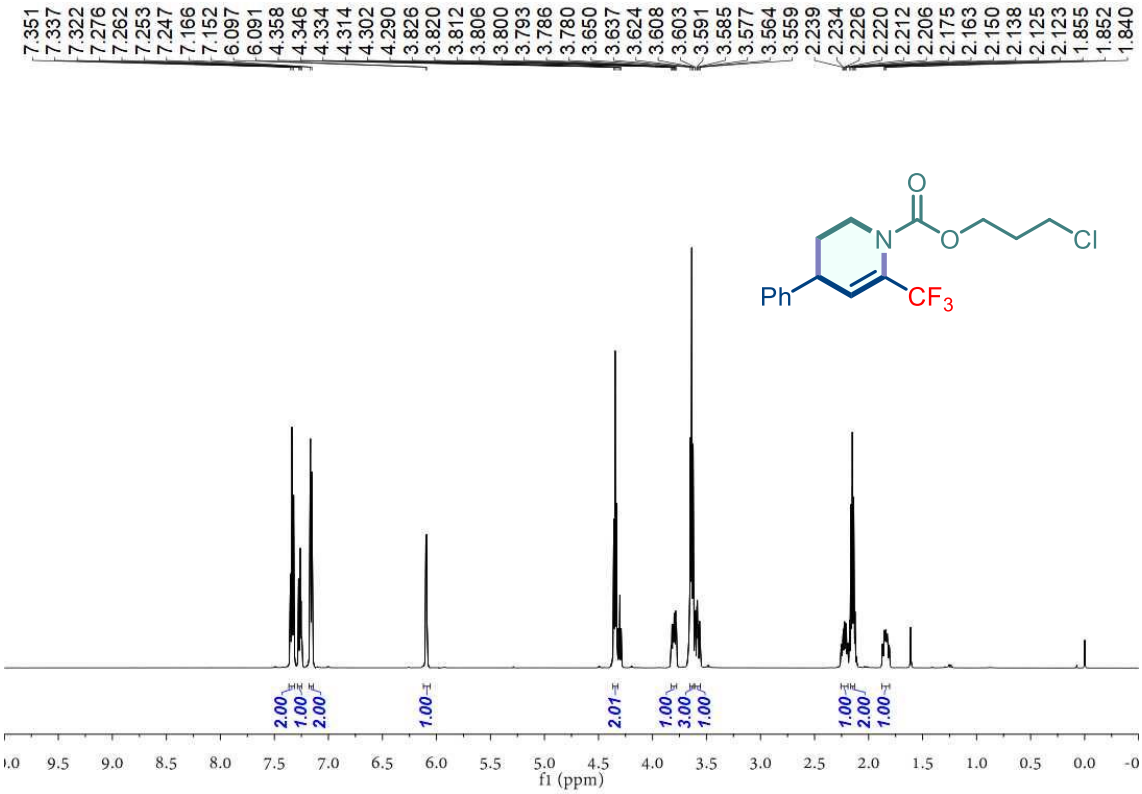


**Figure S122.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **44**.

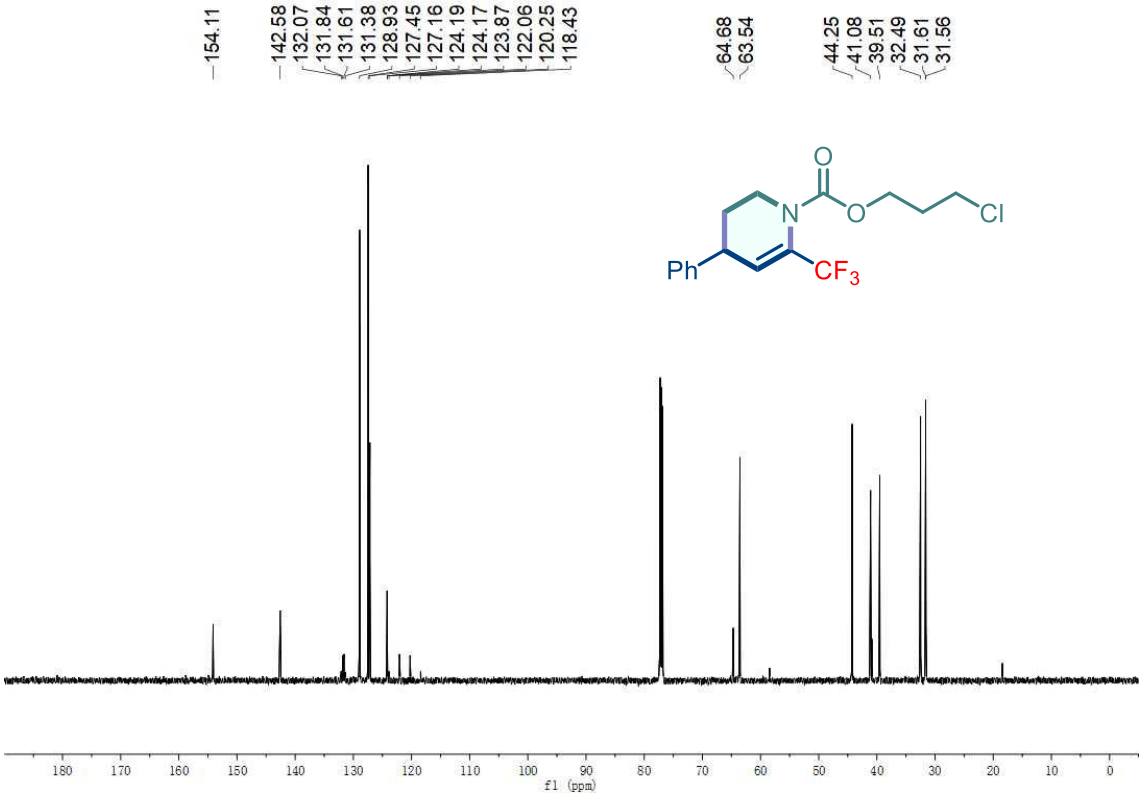


**Figure S123.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **44**.

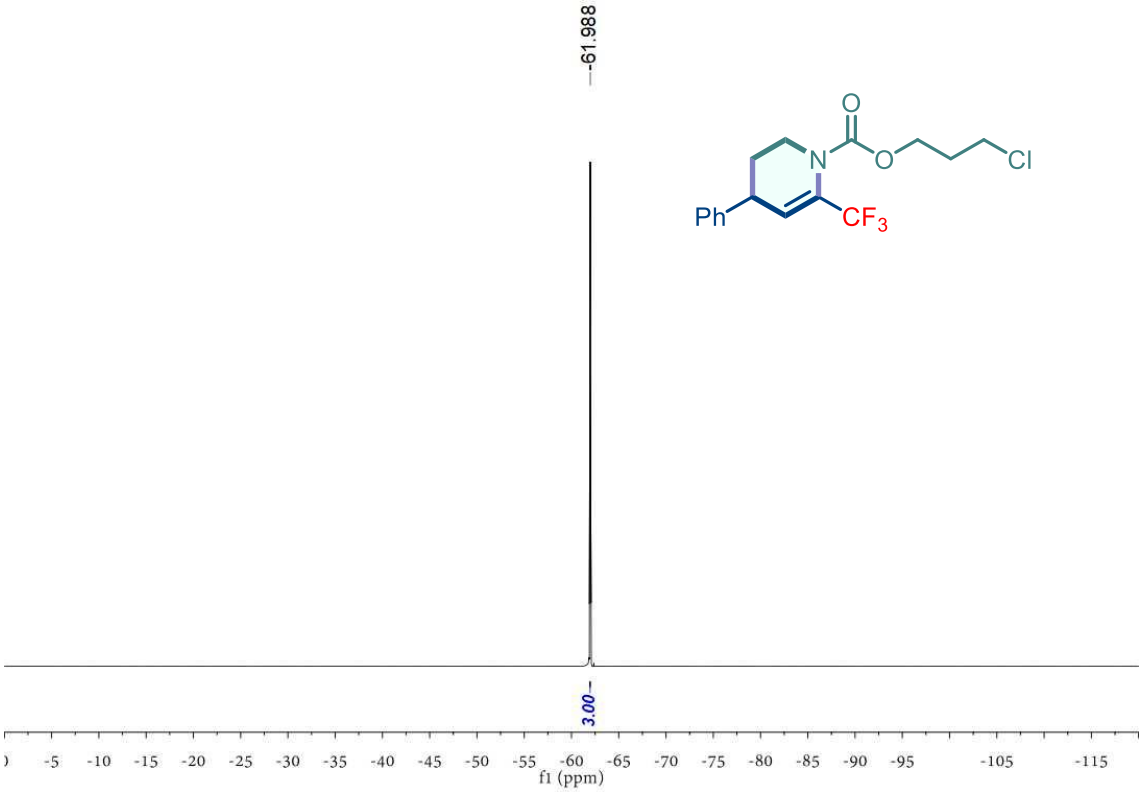


**Figure S124.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **44**.

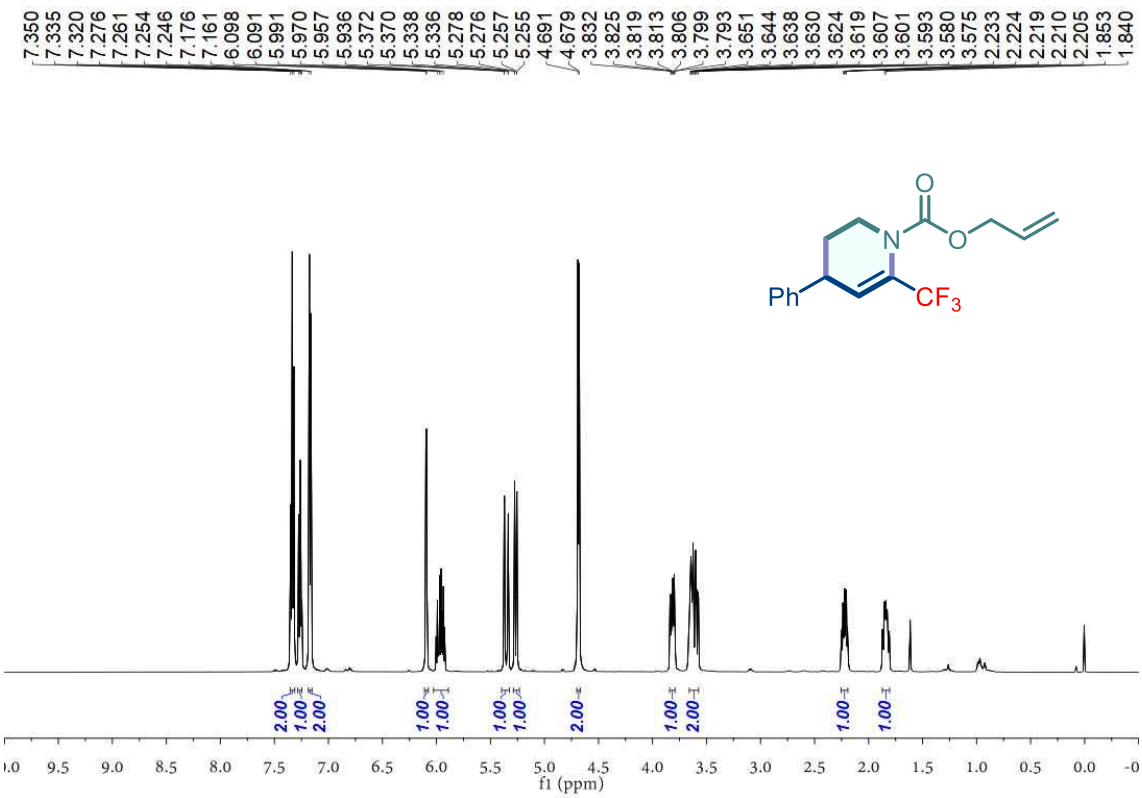


**Figure S125.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **45**.

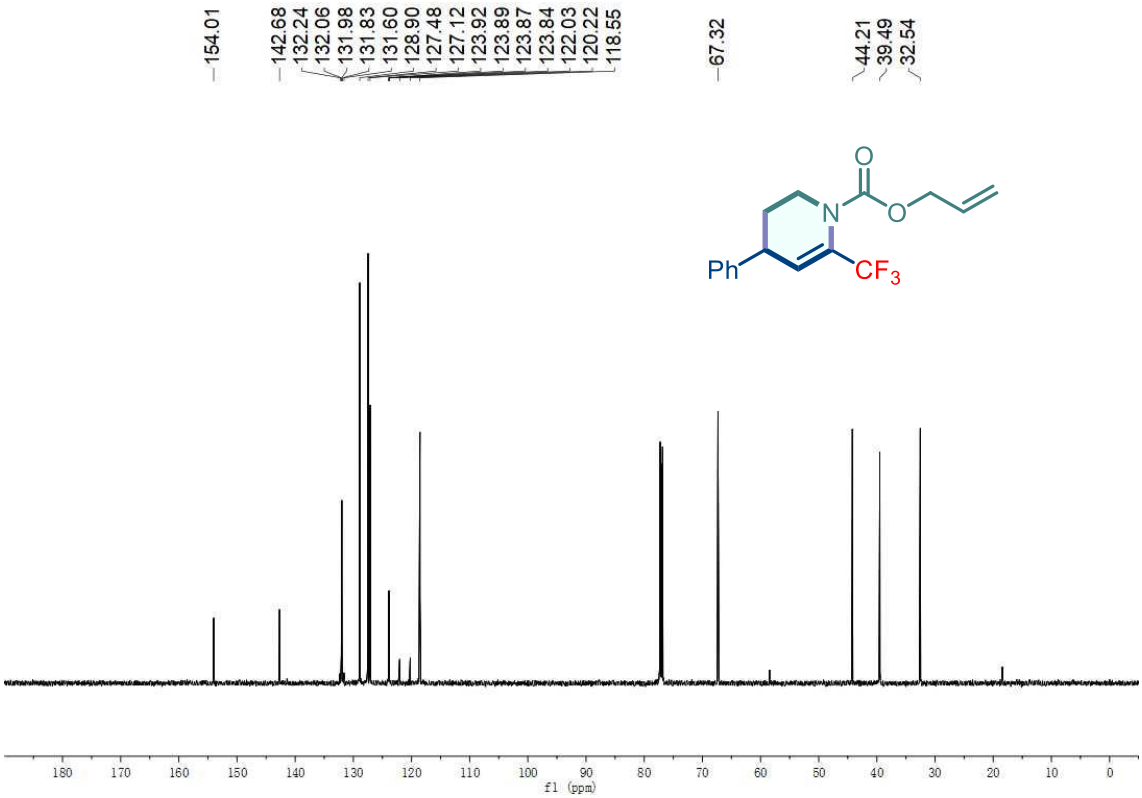


**Figure S126.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **45**.

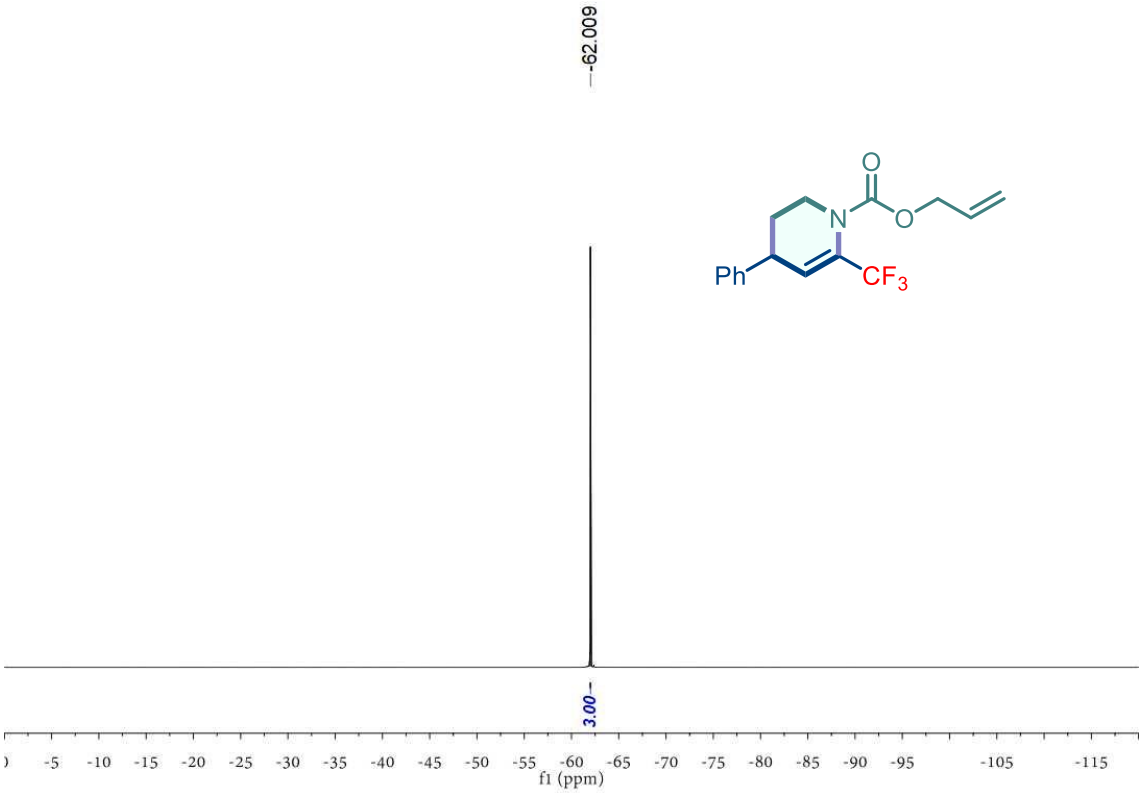


**Figure S127.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **45**.

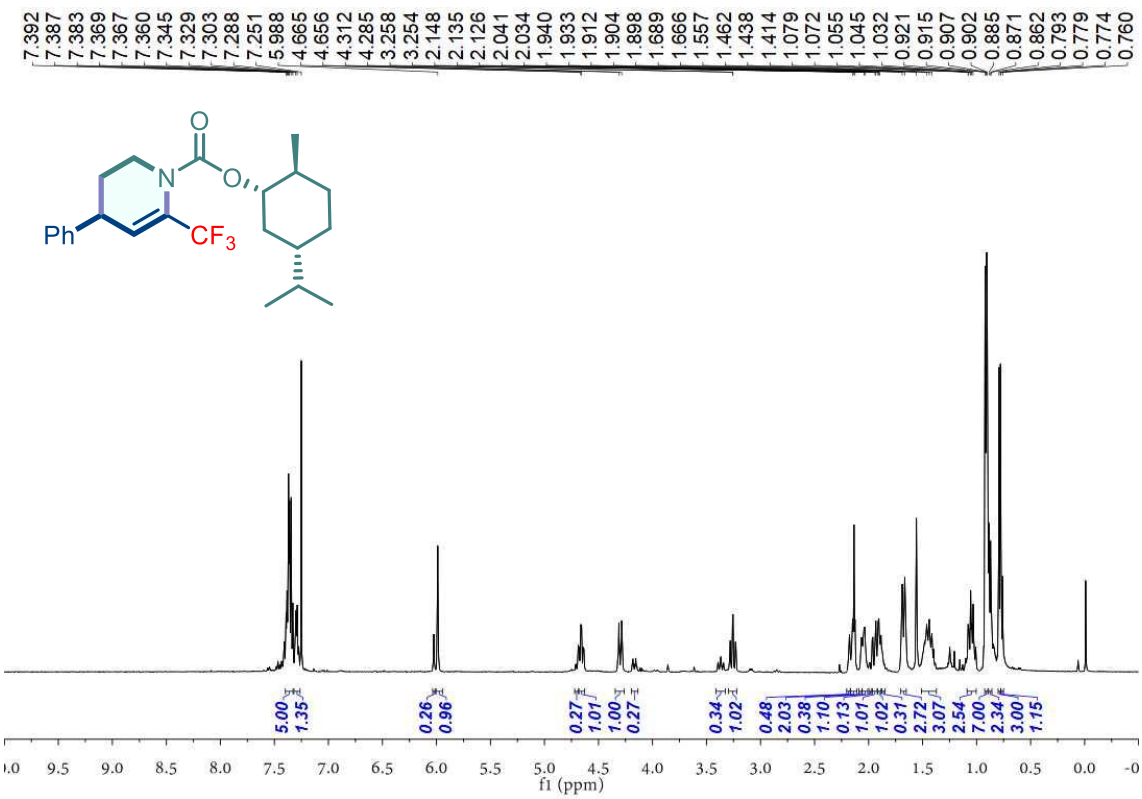


**Figure S128.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **46**.

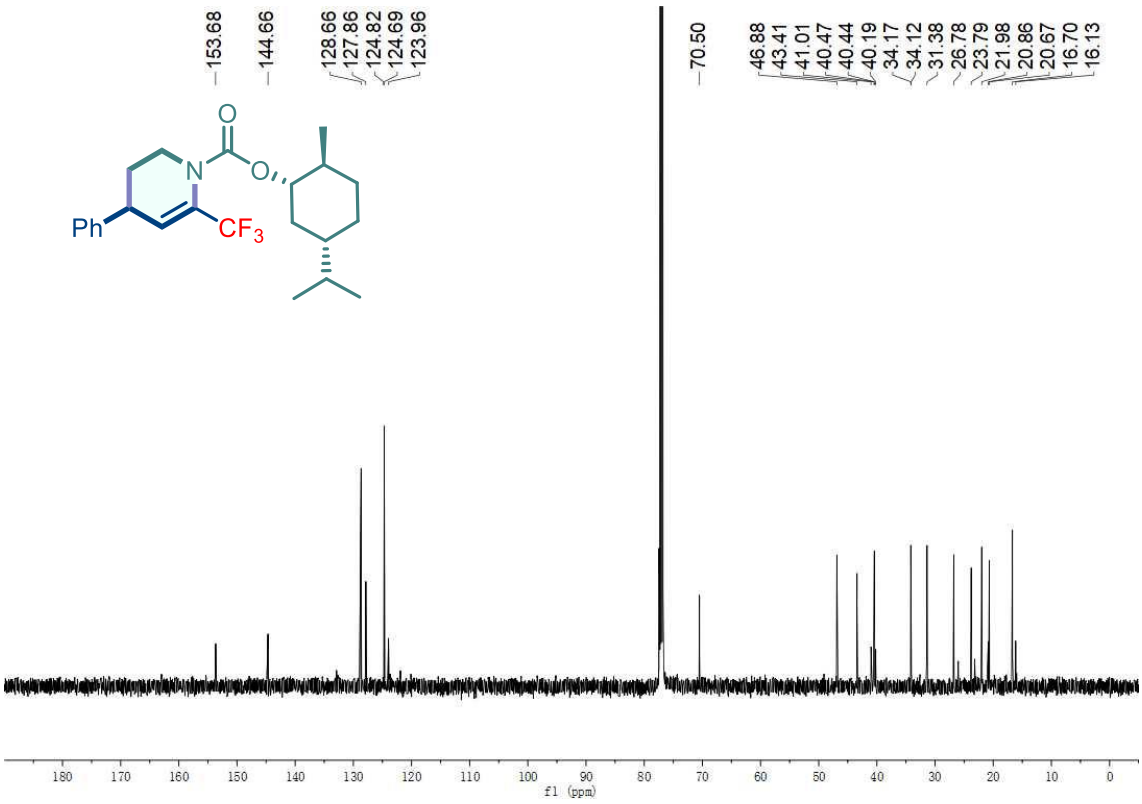


**Figure S129.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **46**.

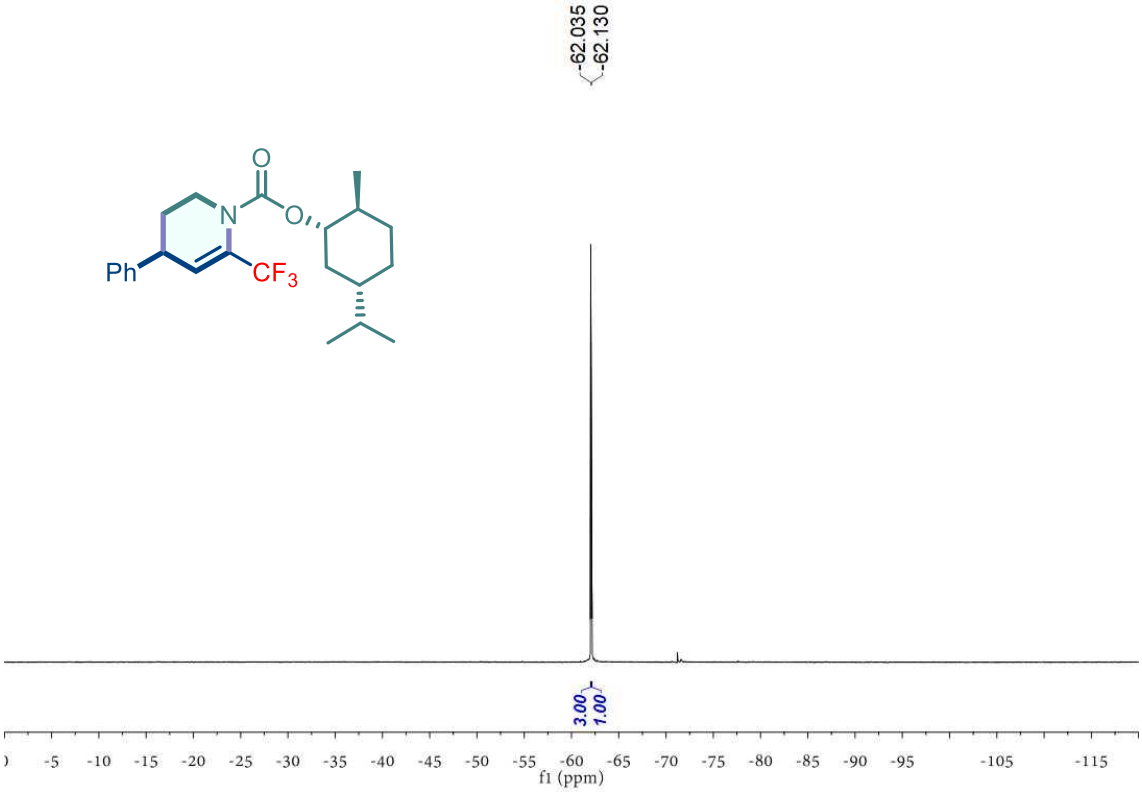


**Figure S130.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **46**.

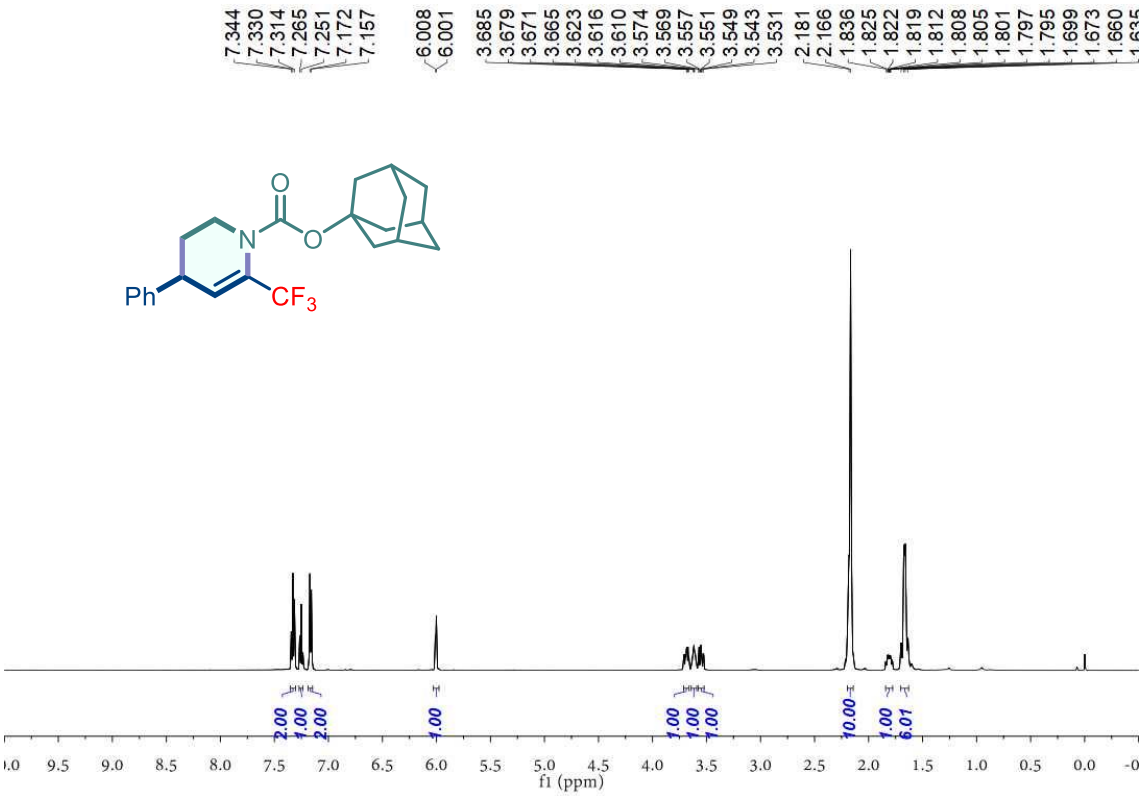


**Figure S131.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **47**.

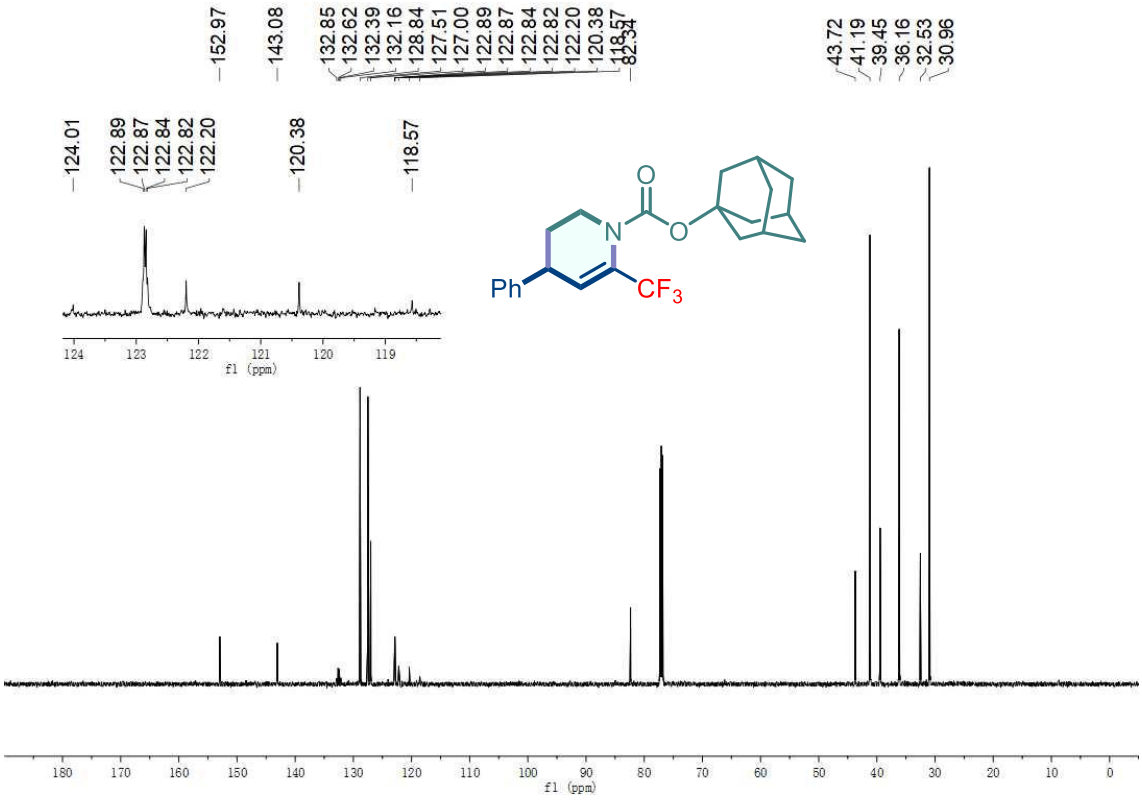


**Figure S132.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **47**.

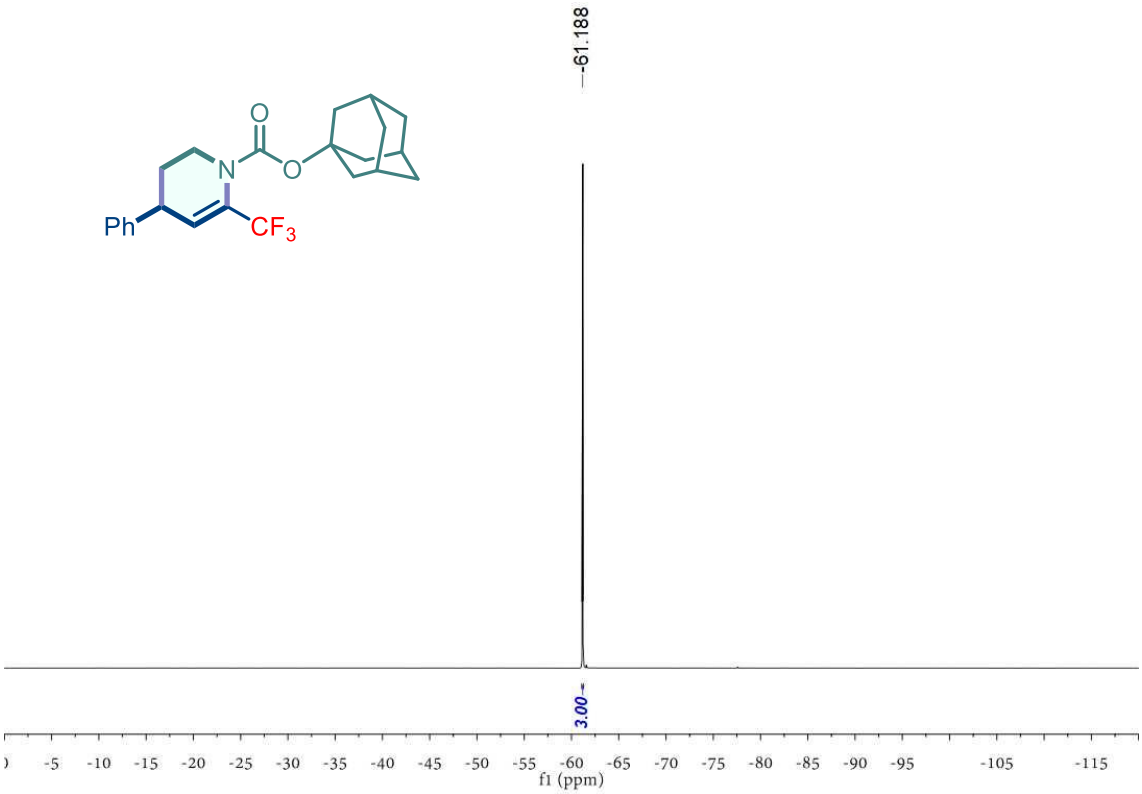


**Figure S133.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **47**.

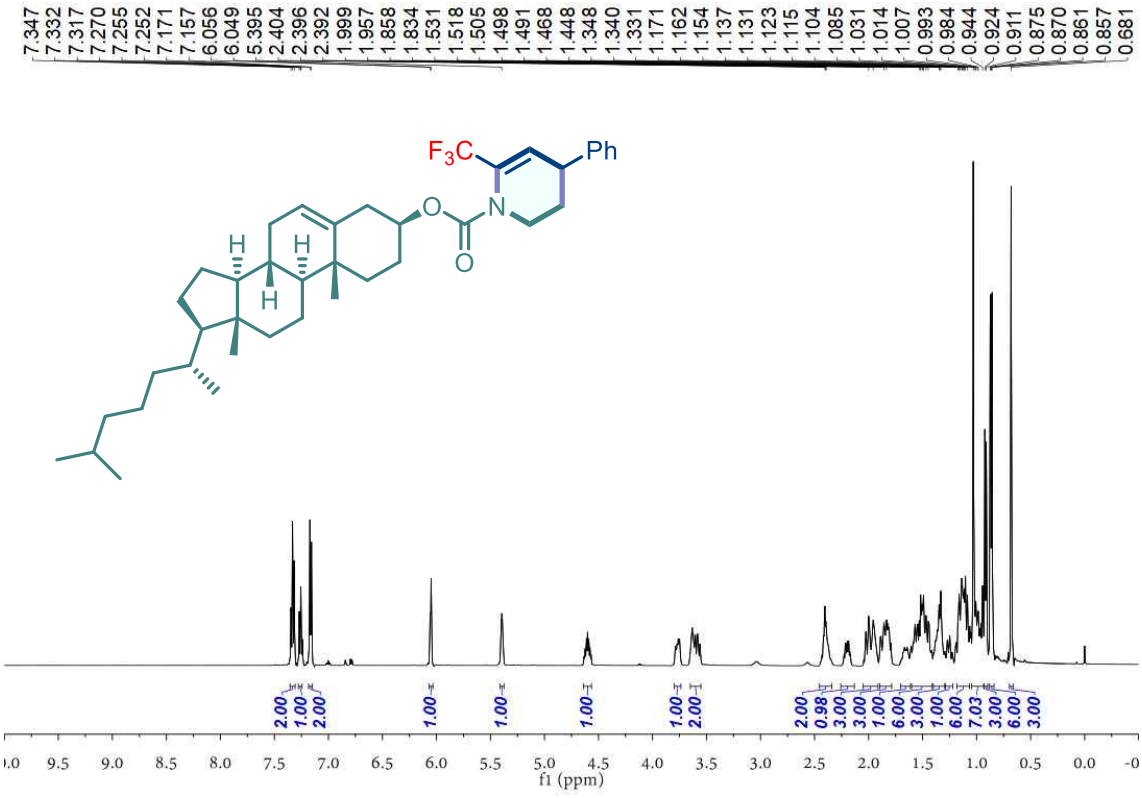


**Figure S134.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **48**.

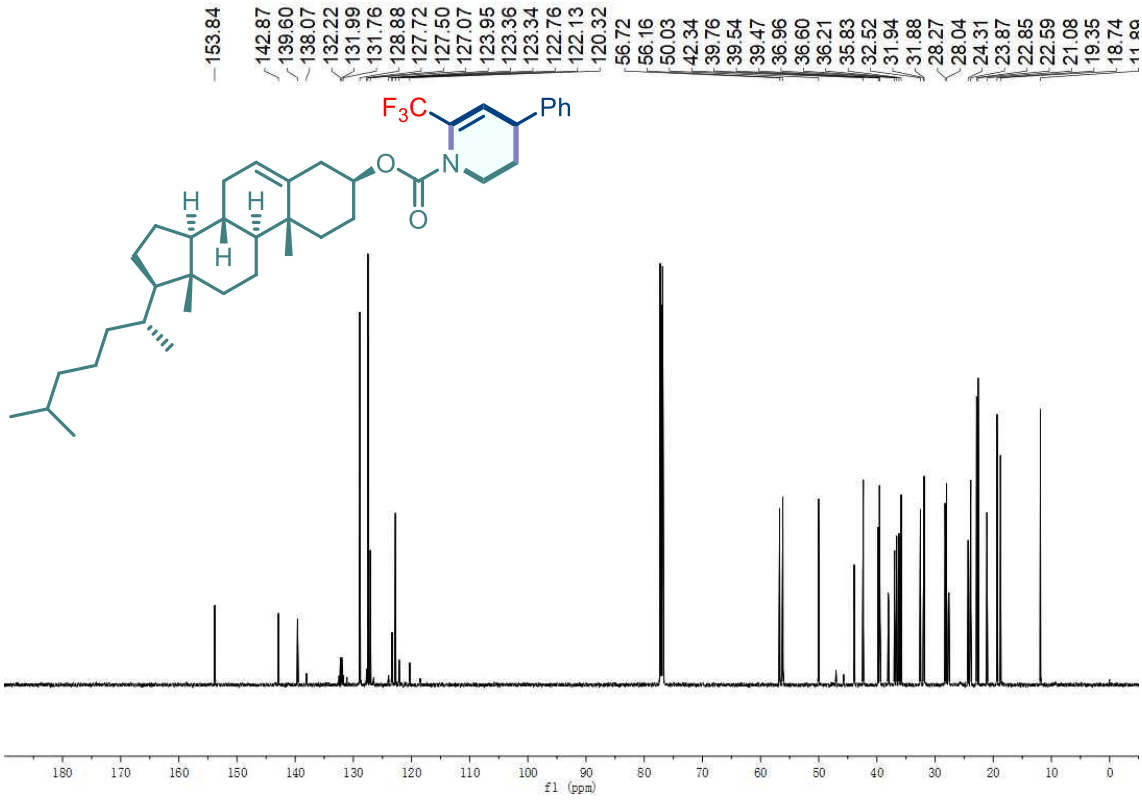


**Figure S135.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **48**.

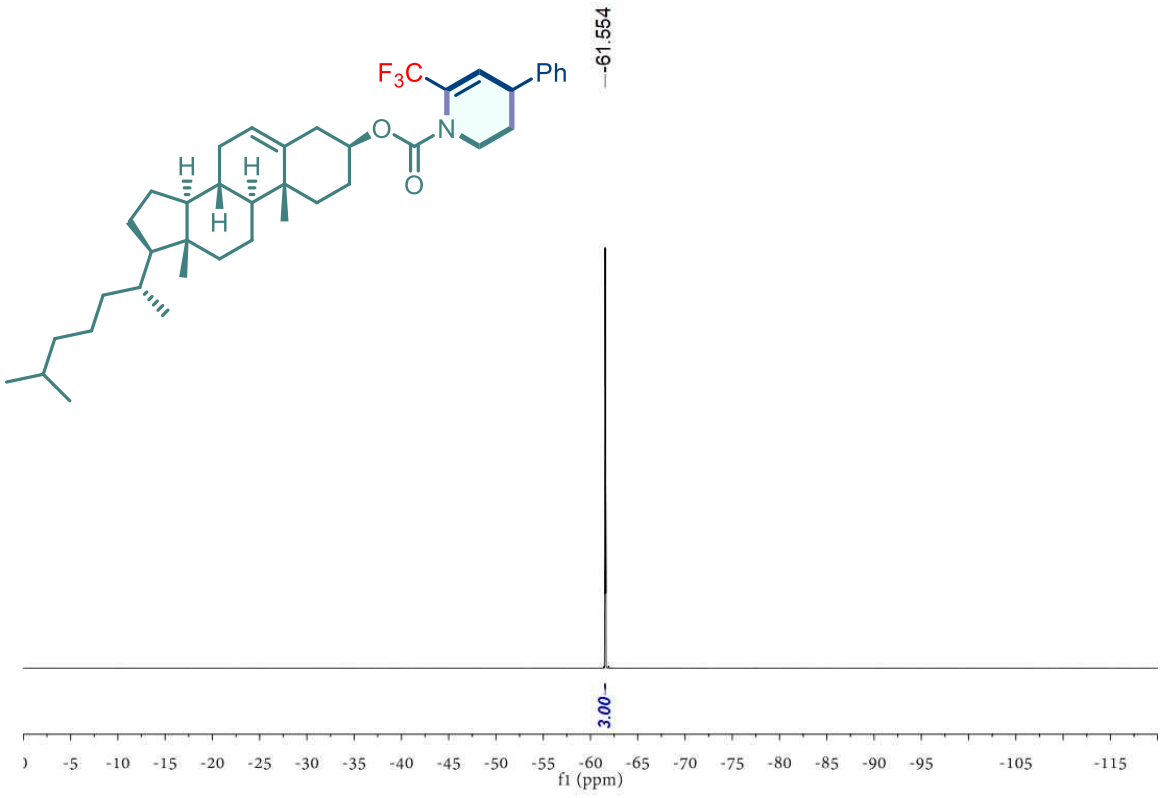


**Figure S136.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **48**.

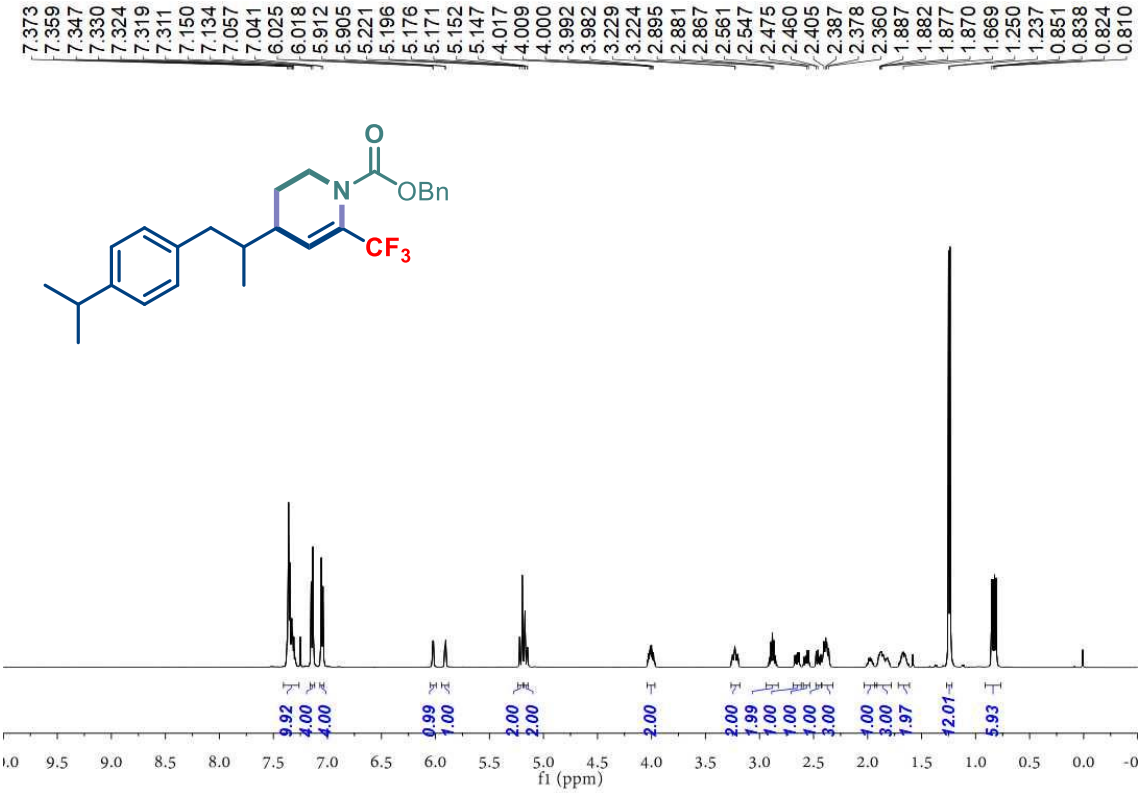


**Figure S137.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **49**.

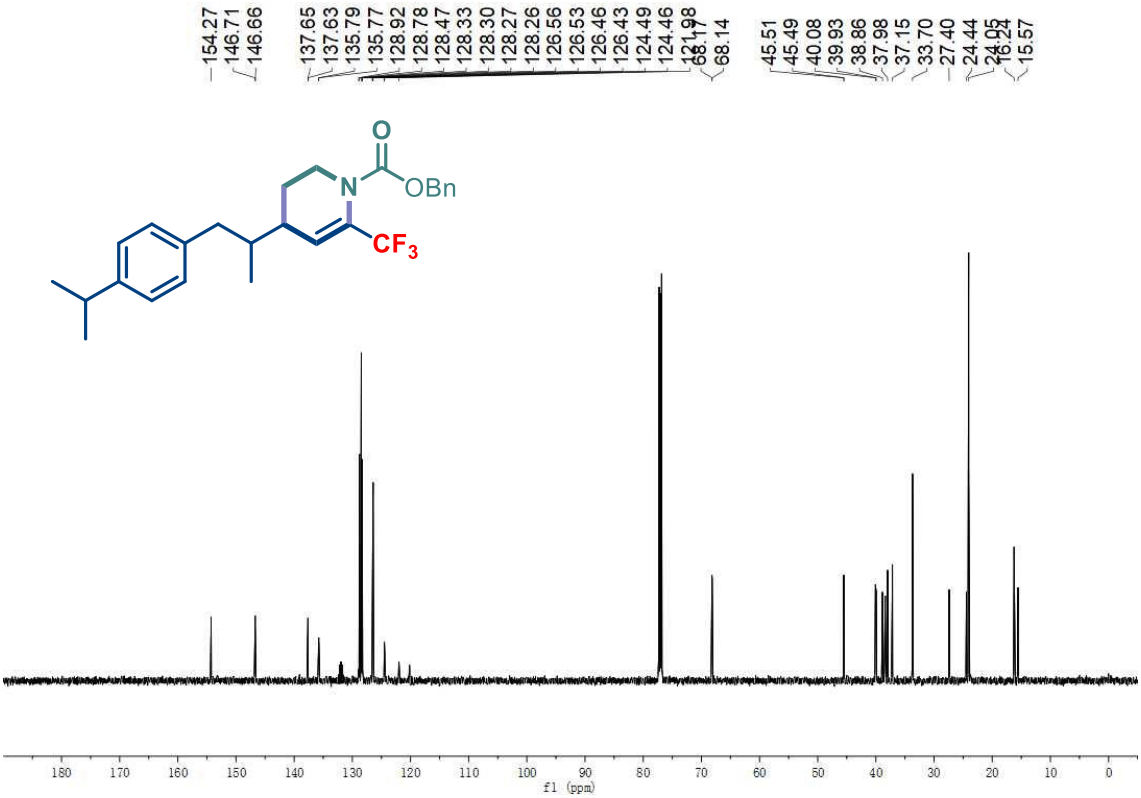


**Figure S138.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **49**.

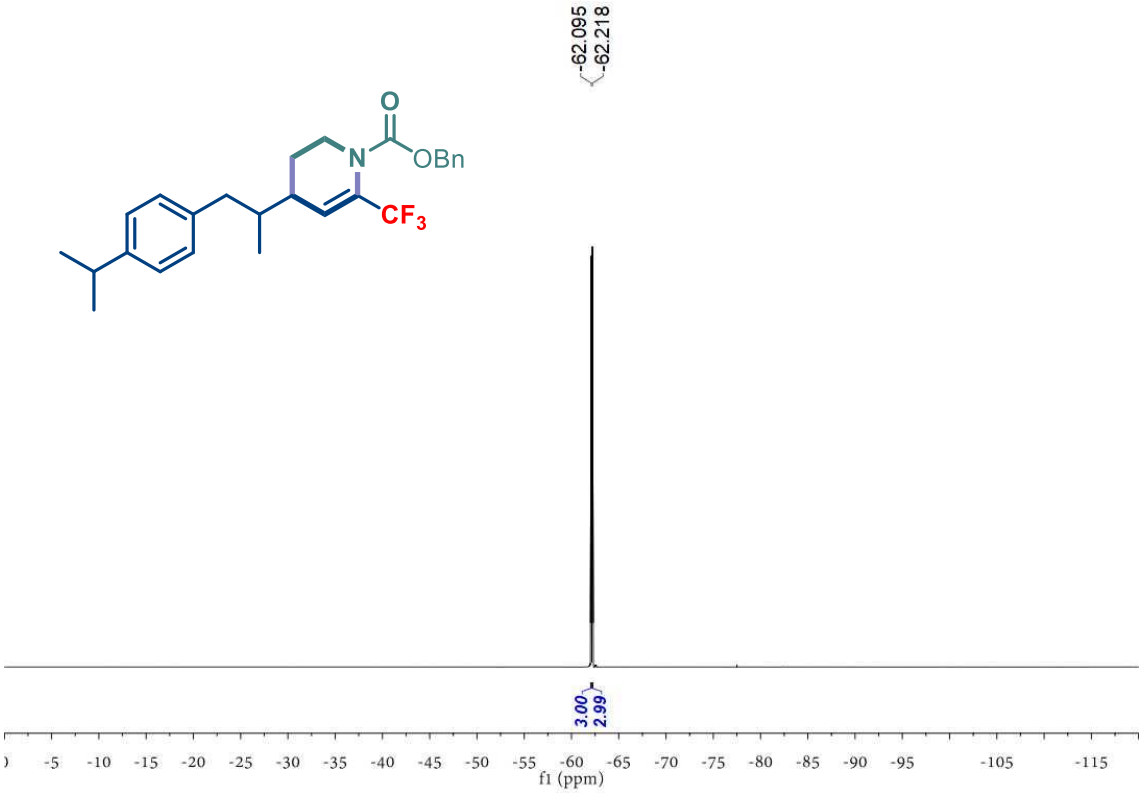


**Figure S139.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **49**.

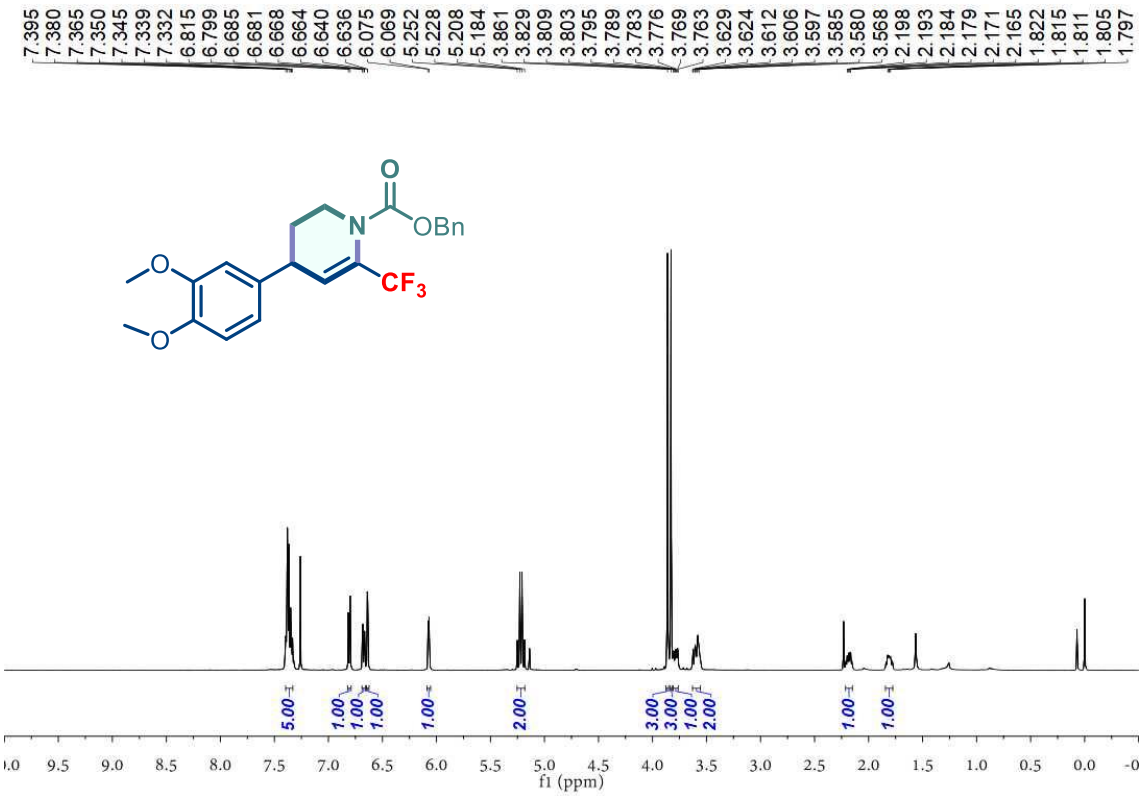


**Figure S140.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **50**.

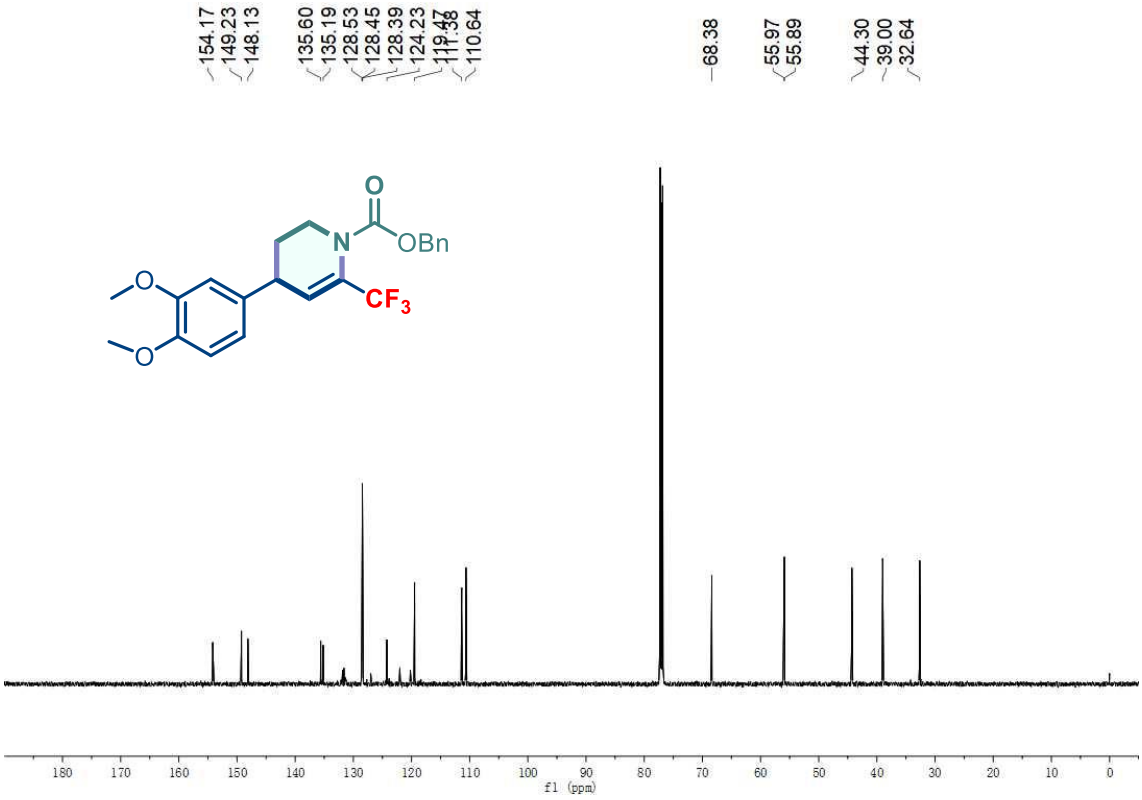


**Figure S141.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **50**.

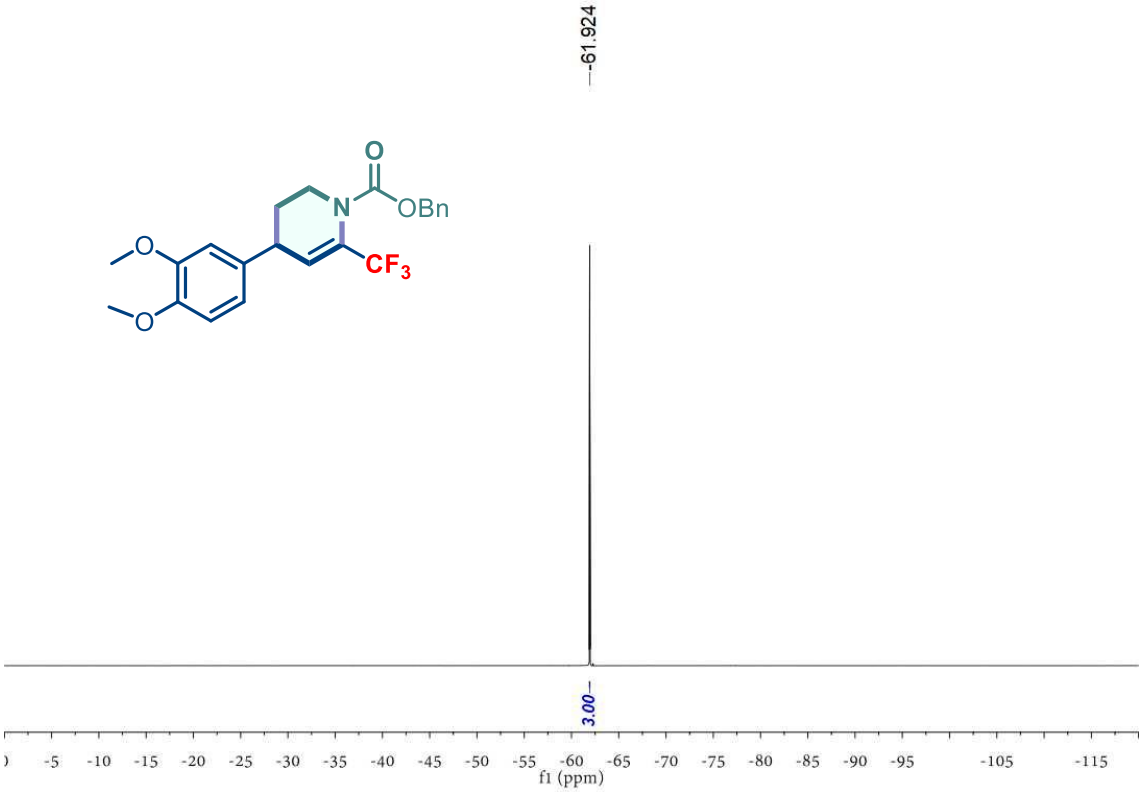


**Figure S142.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **50**.

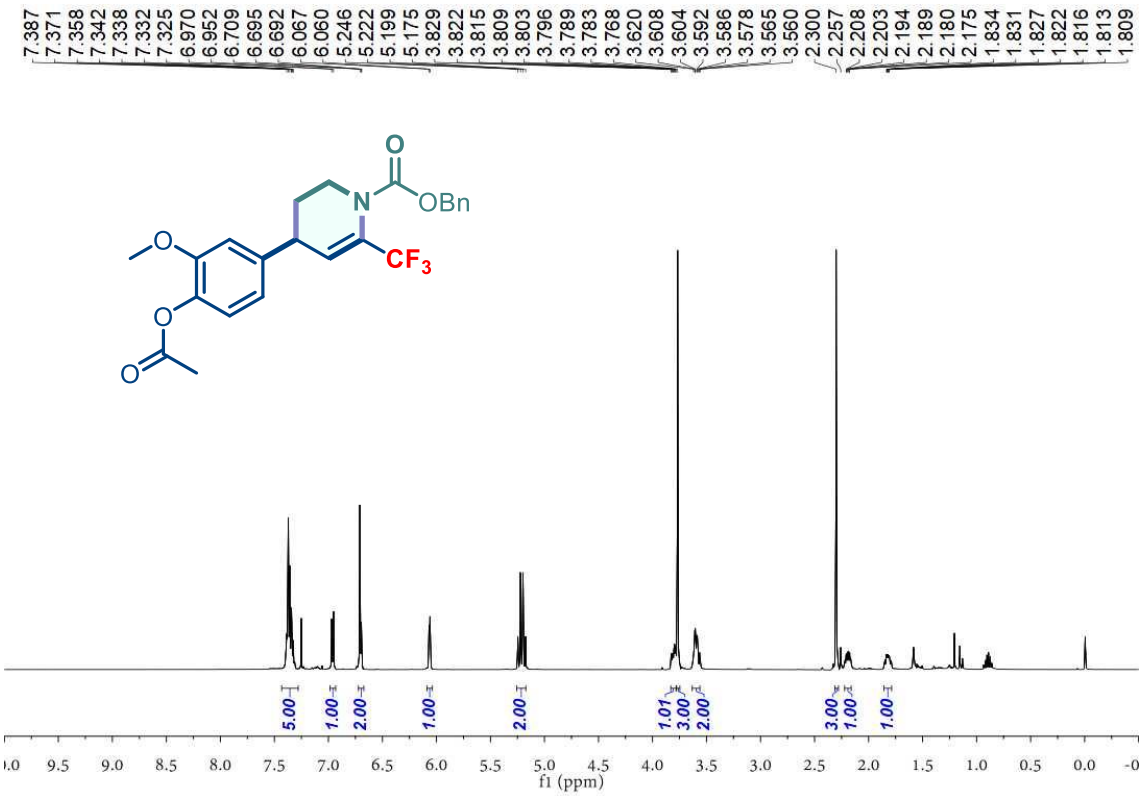


**Figure S143.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **51**.

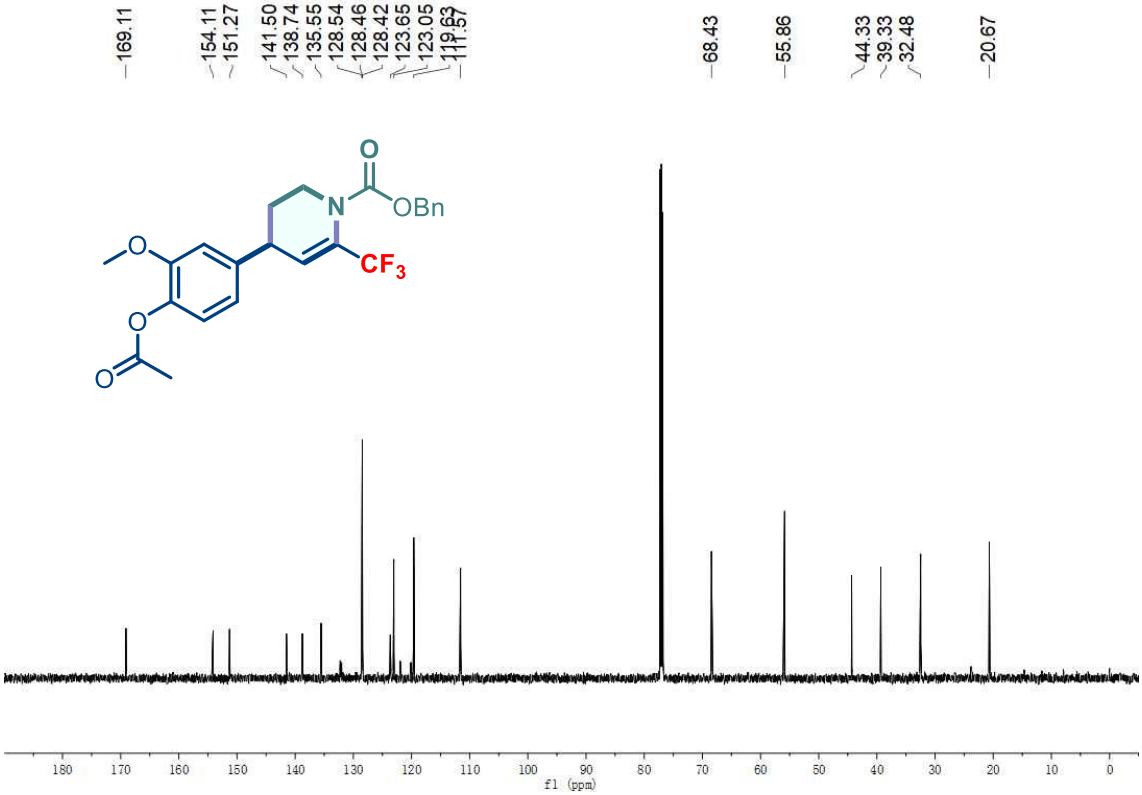


**Figure S144.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **51**.

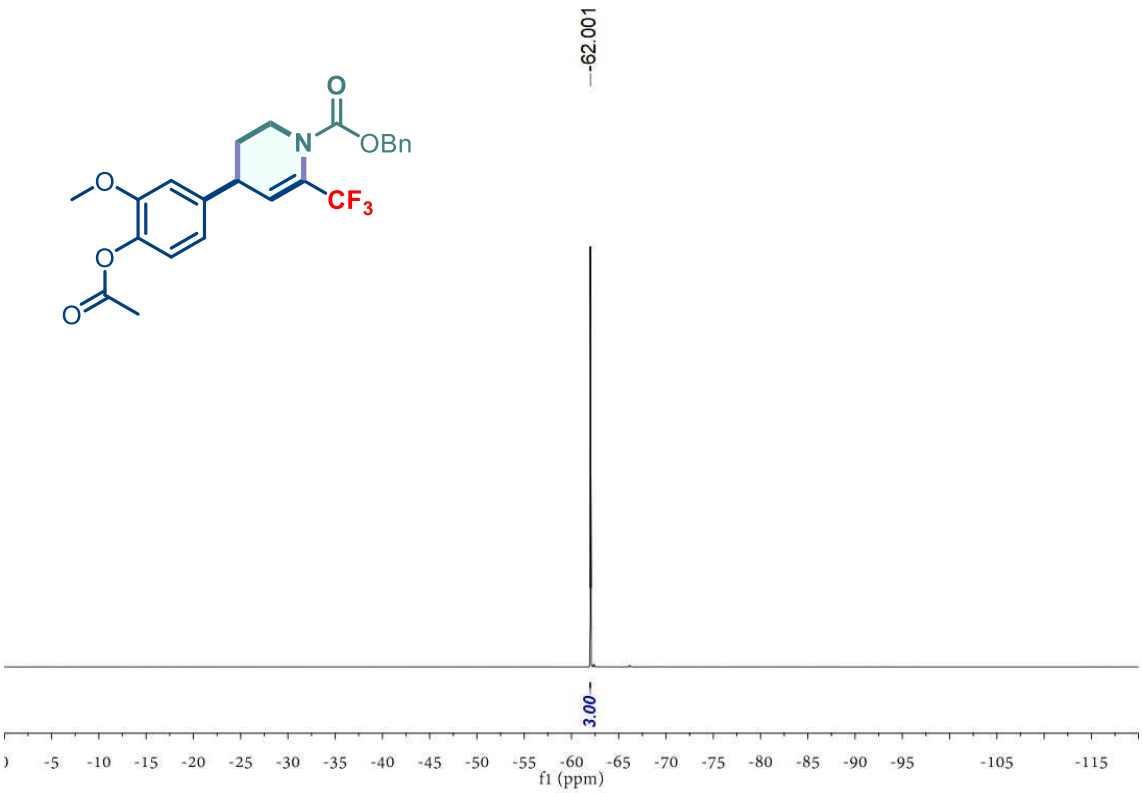


**Figure S145.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **51**.

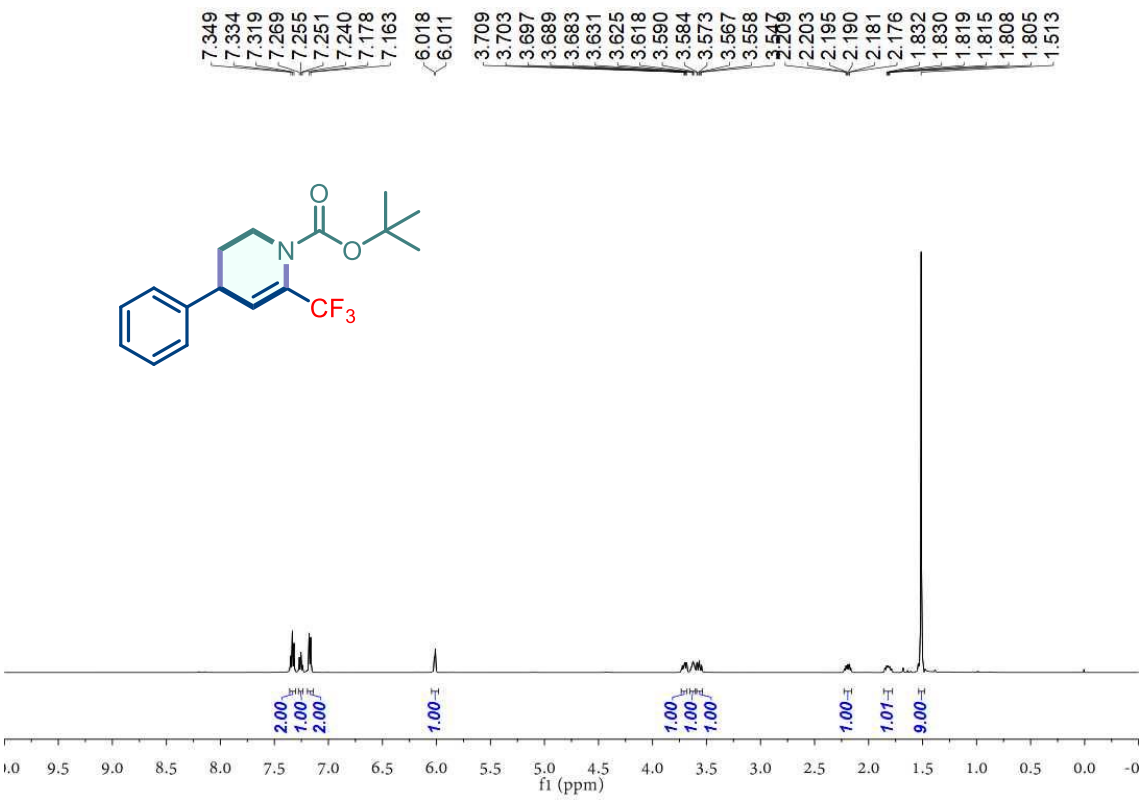


**Figure S146.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **53**.

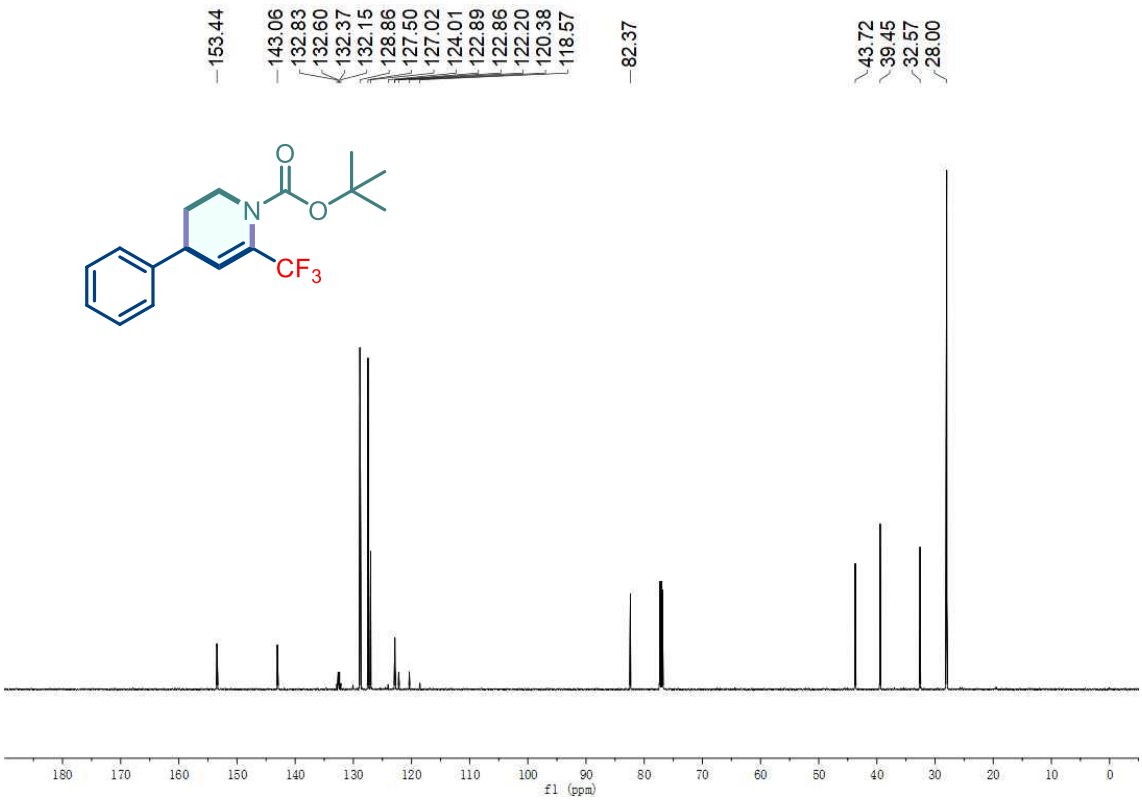


**Figure S147.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **53**.

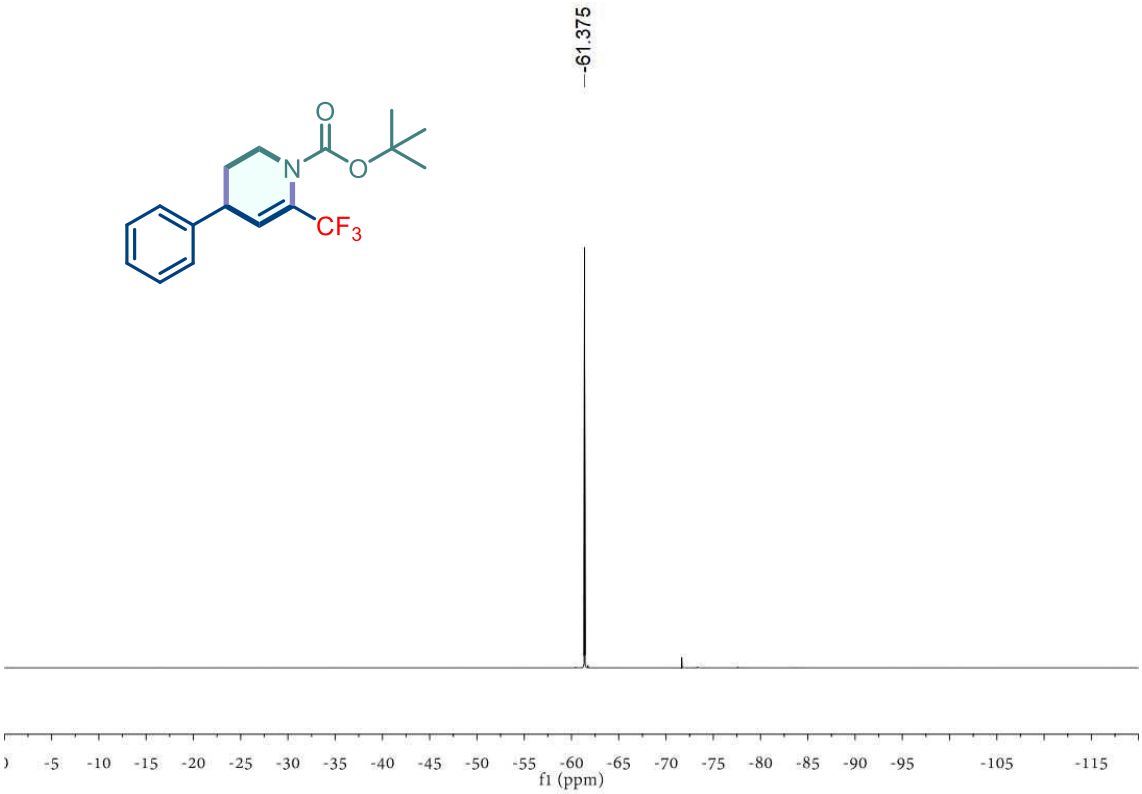


**Figure S148.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **53**.

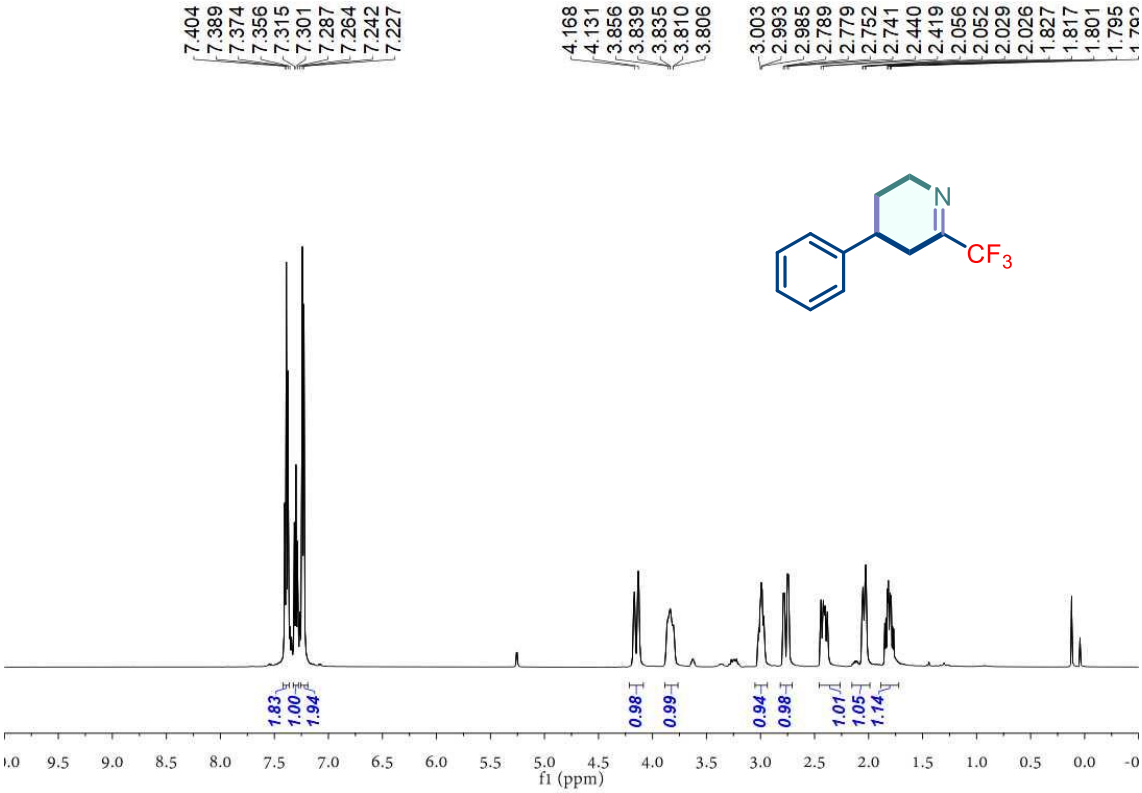


**Figure S149.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **54**.

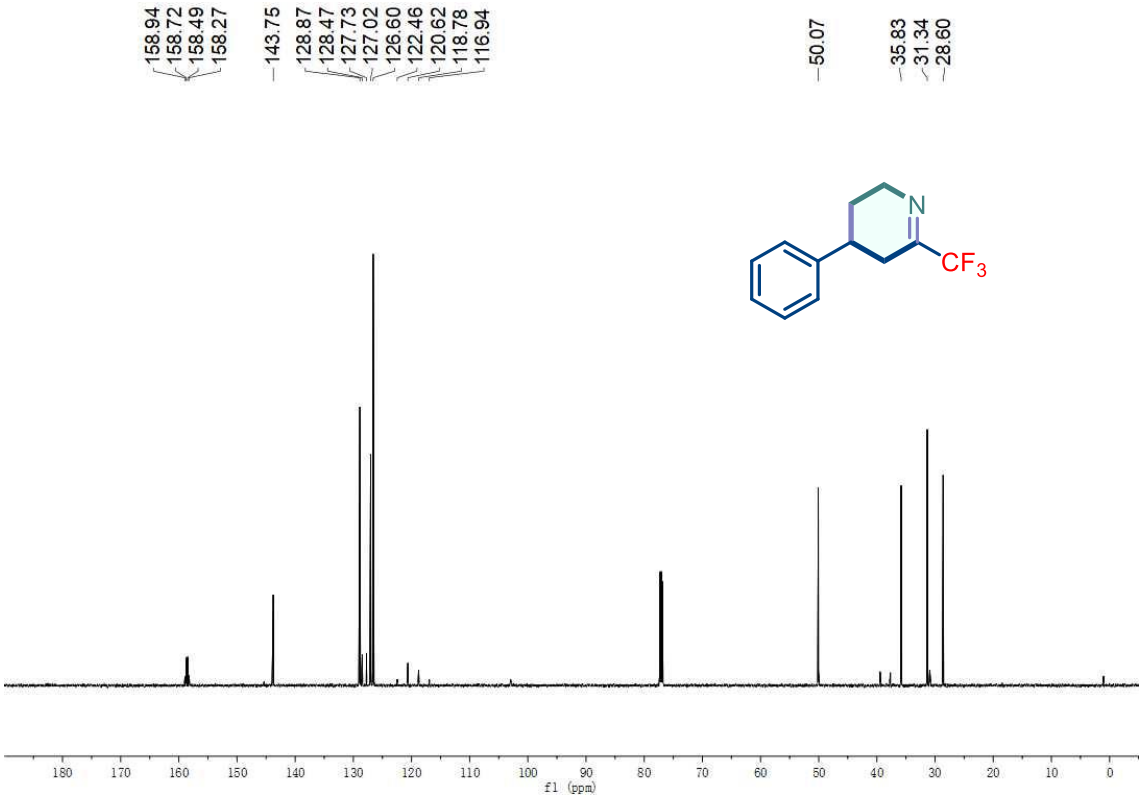


**Figure S150.** $^{13}$C NMR (150 MHz, $CDCl_3$) Spectrum of **54**.

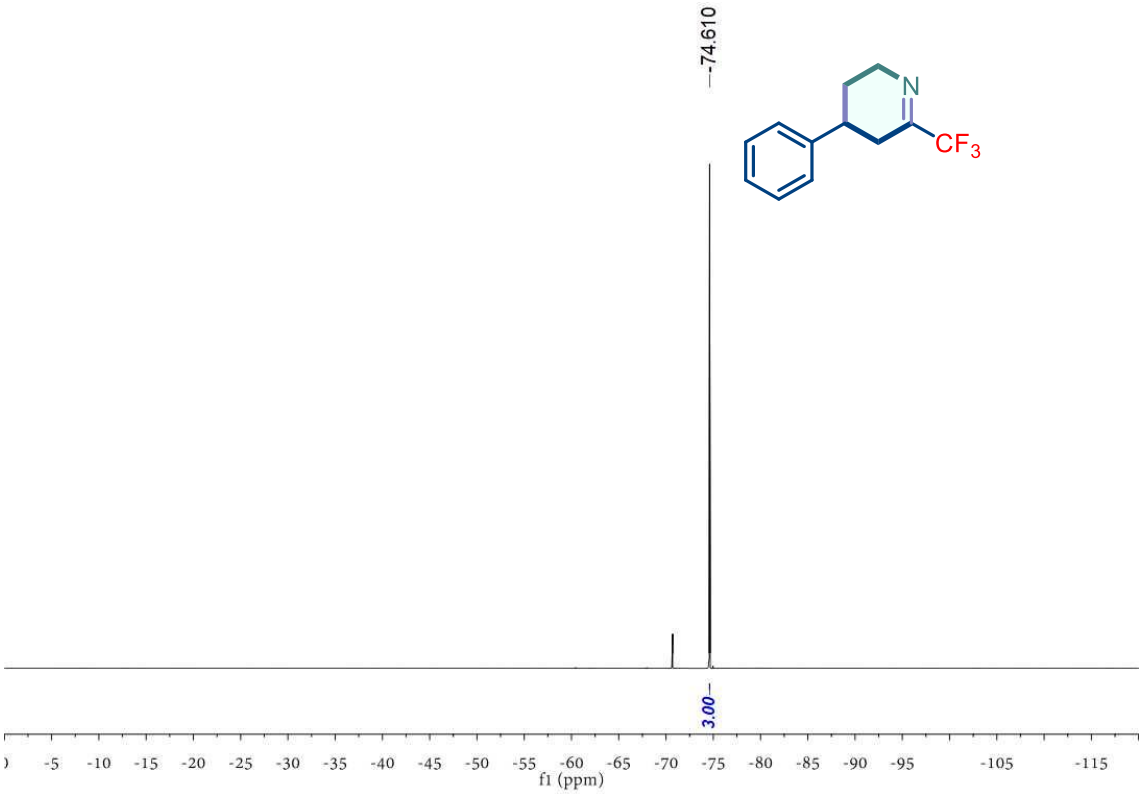


**Figure S151.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **54**.

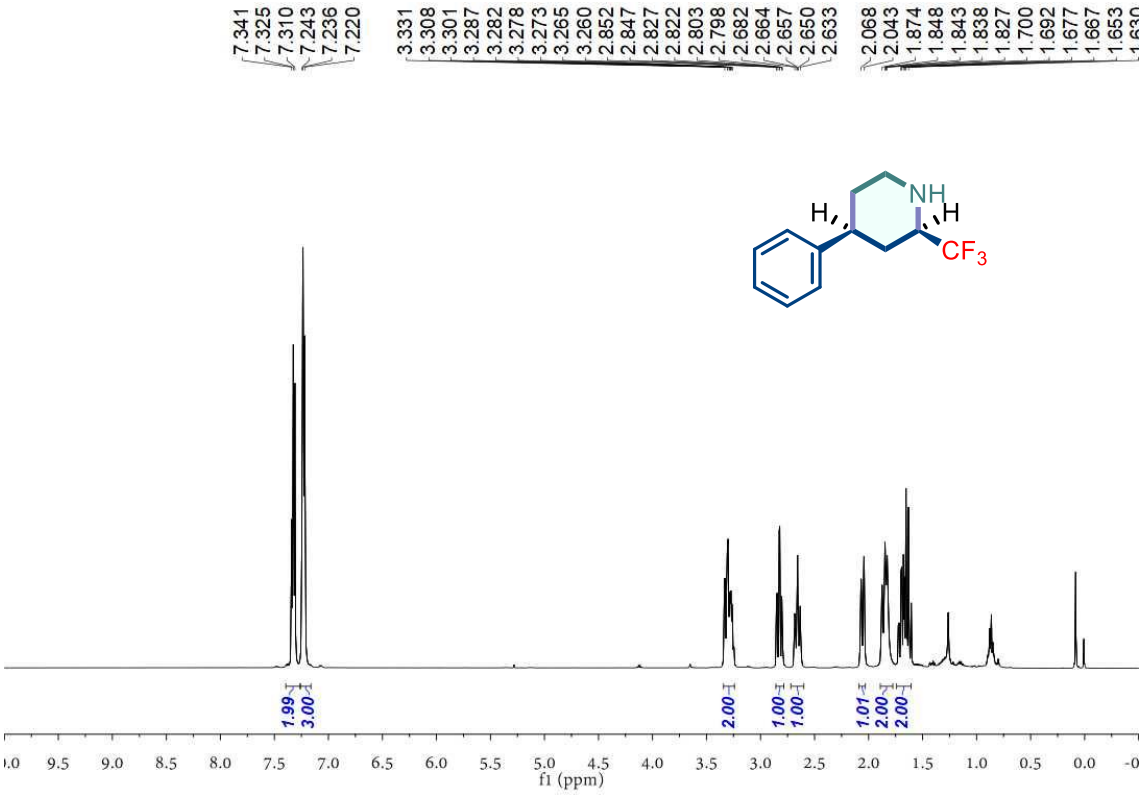


**Figure S152.** $^{1}H$ NMR (500 MHz, $CDCl_3$) Spectrum of **55**.

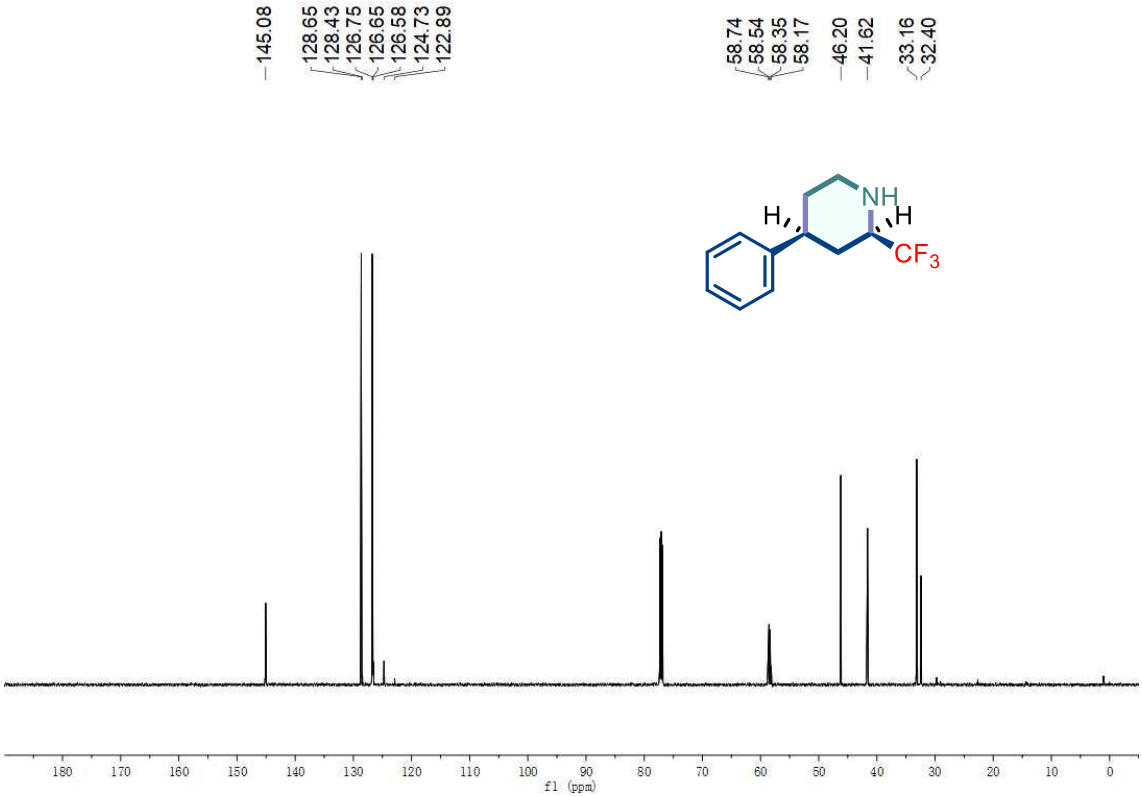


**Figure S153.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **55**.

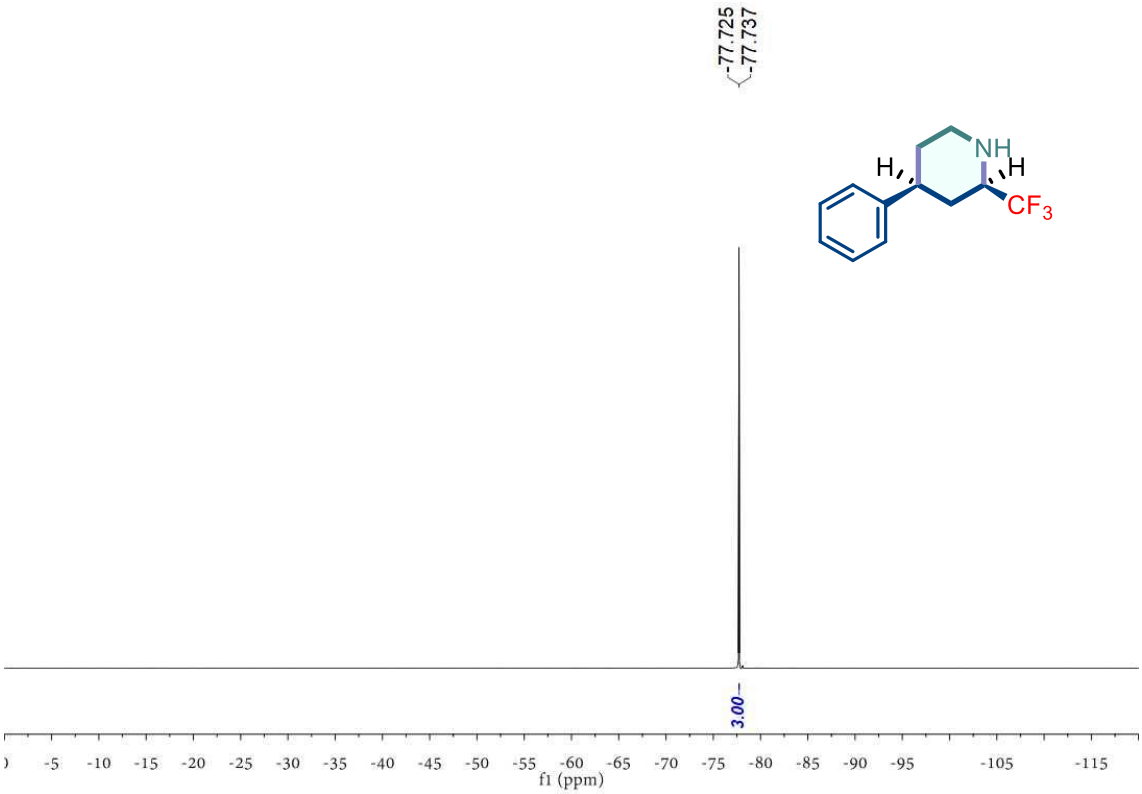


**Figure S154.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **55**.

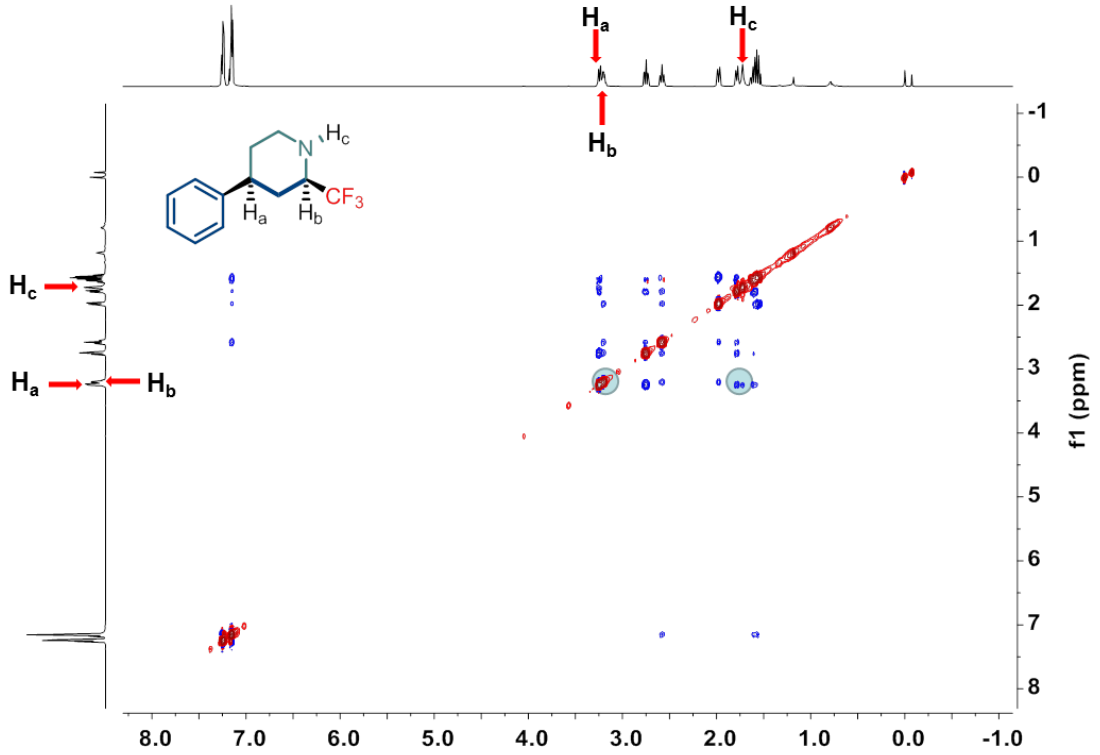


**Figure S155.** NOE of **55**.

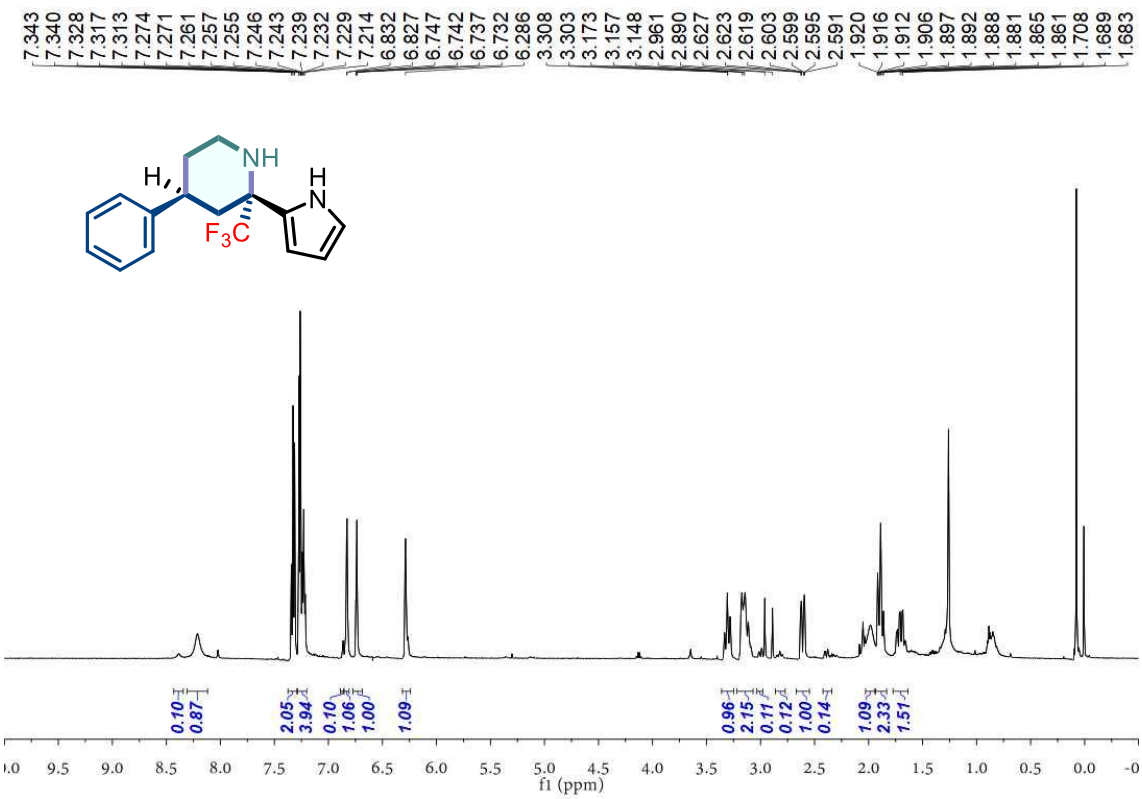


**Figure S156.** $^{1}$H NMR (500 MHz, $CDCl_3$) Spectrum of **56**.

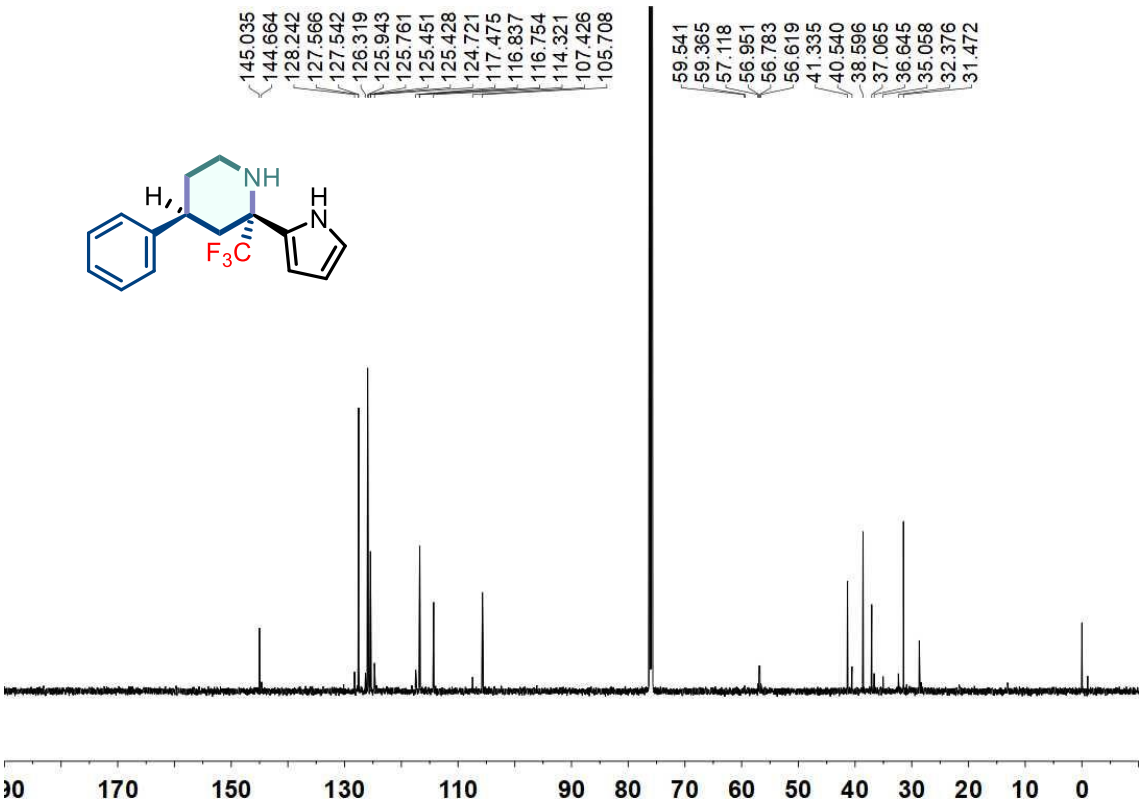


**Figure S157.** $^{13}C$ NMR (150 MHz, $CDCl_3$) Spectrum of **56**.

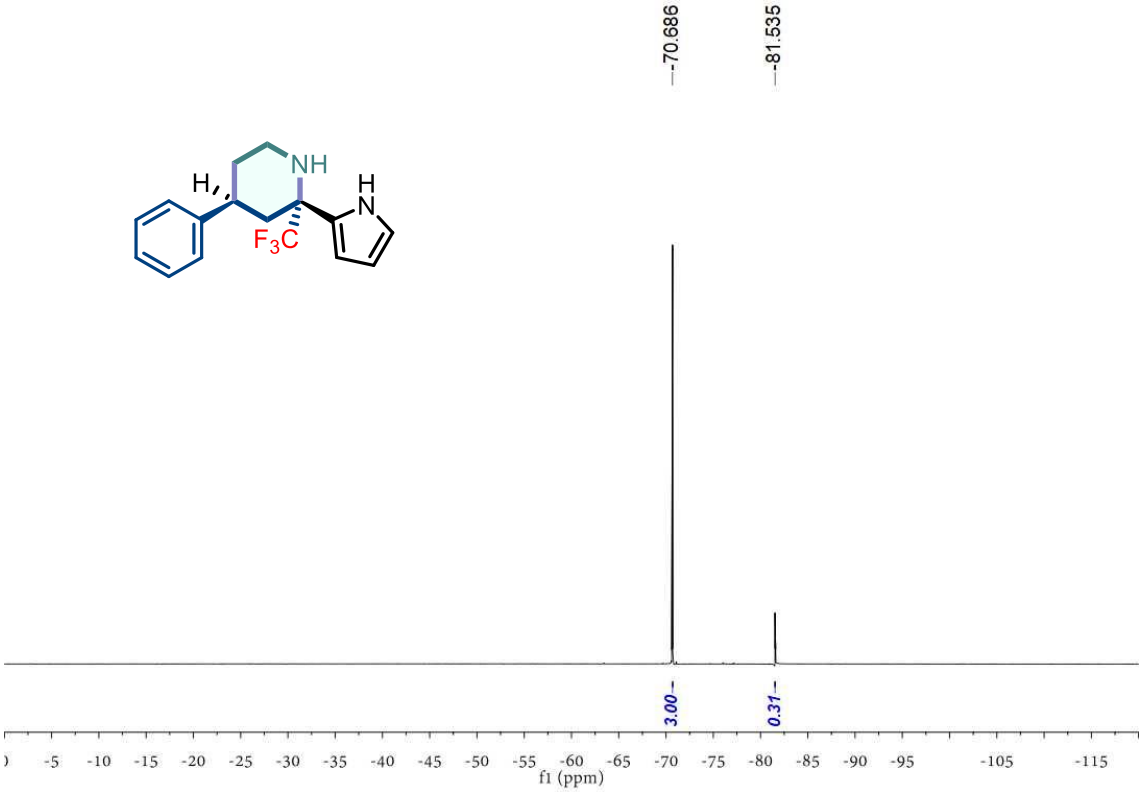


**Figure S158.** $^{19}F$ NMR (565 MHz, $CDCl_3$) Spectrum of **56**.

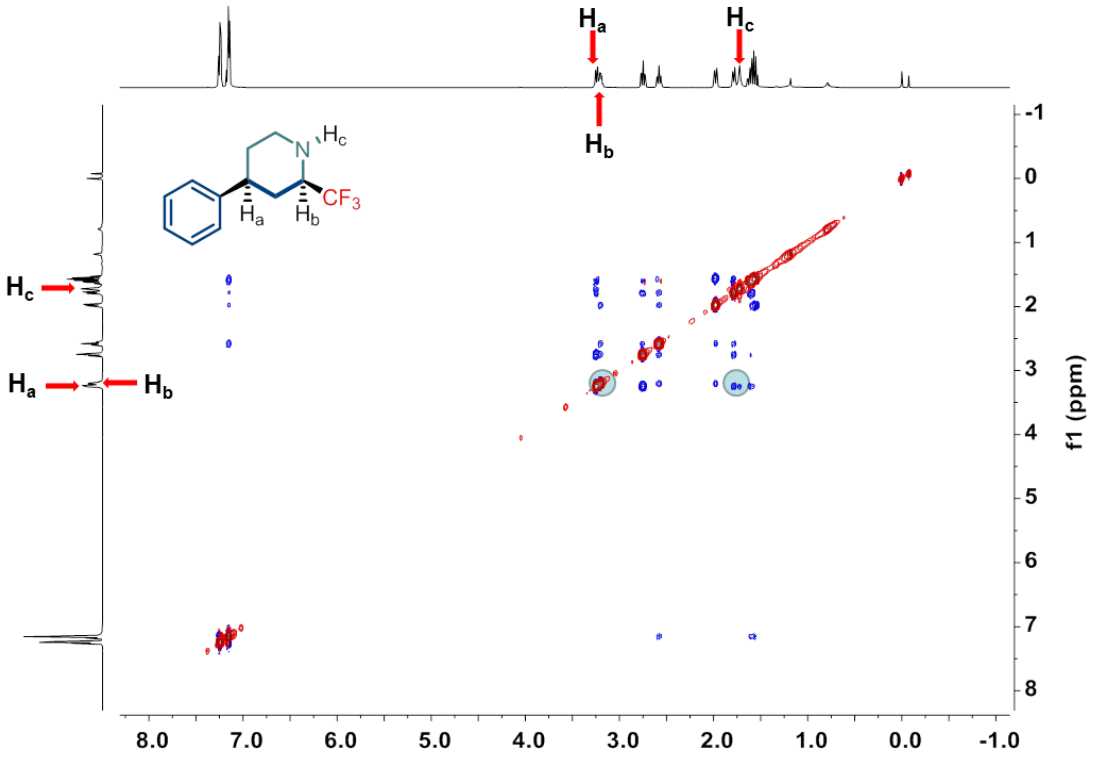


**Figure S159.** NOE of **56**.

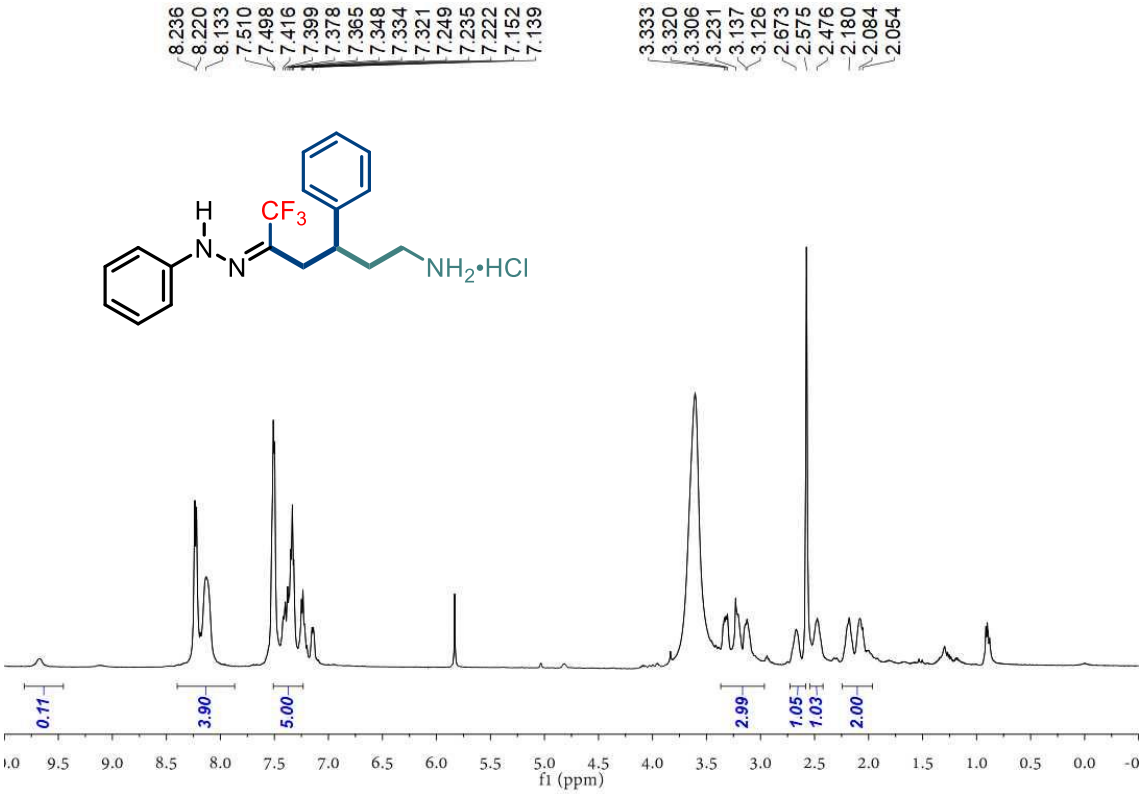


**Figure S160.** $^{1}$H NMR (500 MHz, DMSO) Spectrum of **57**.

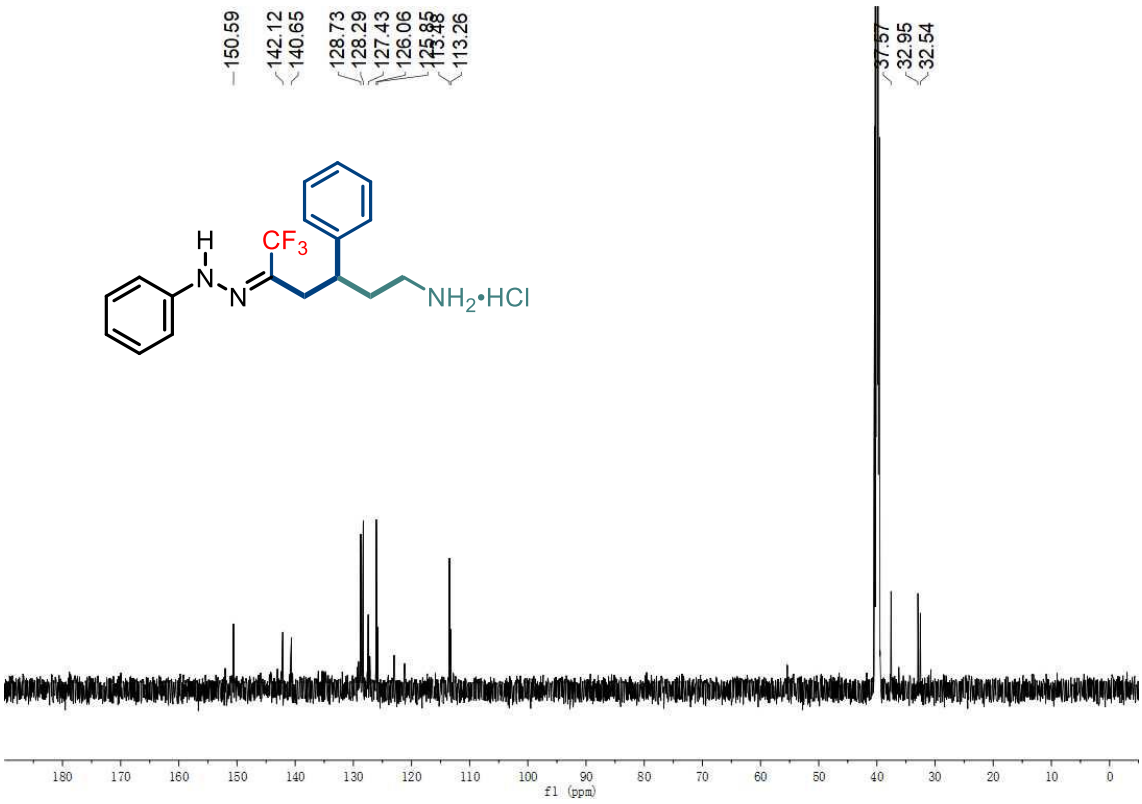


**Figure S161.** $^{13}$C NMR (150 MHz, DMSO) Spectrum of **57**.

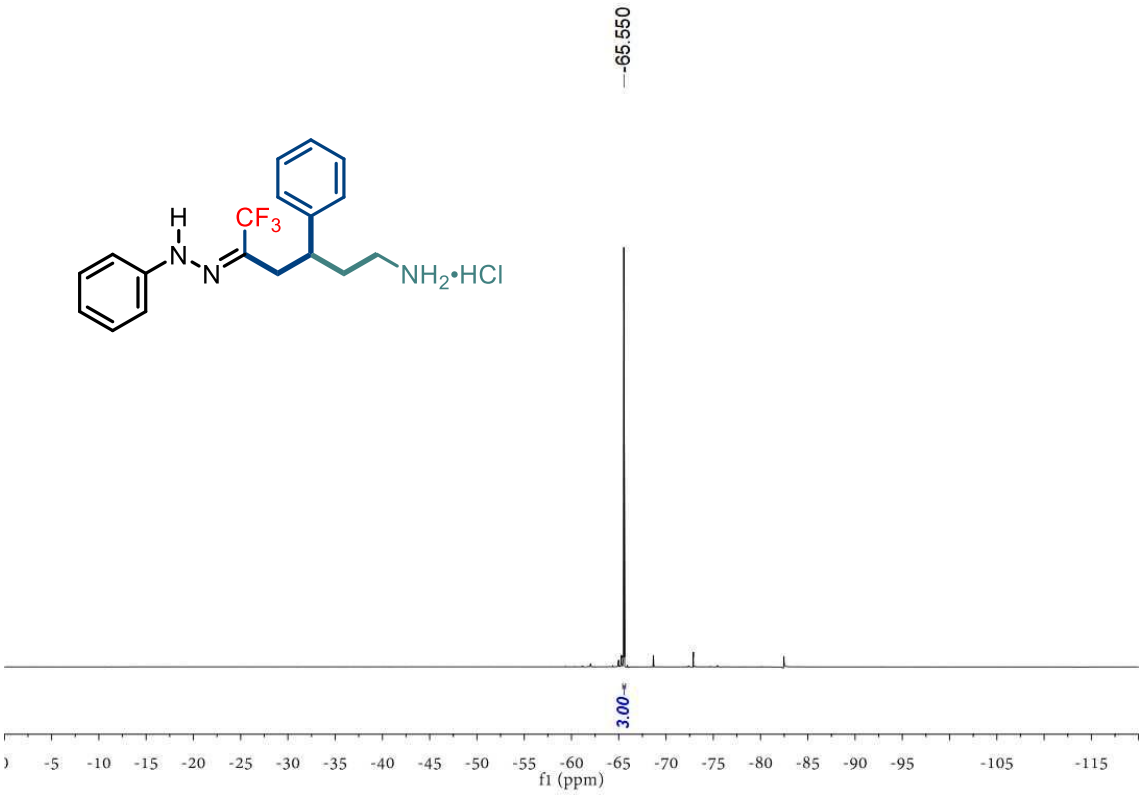


**Figure S162.** $^{19}$F NMR (565 MHz, DMSO) Spectrum of **57**.