Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

A $NaSO_2CF_3$/$NaBrO_3$-Mediated Bromotrifluoromethylation of Enyne via Free-Radical Cascade Processes

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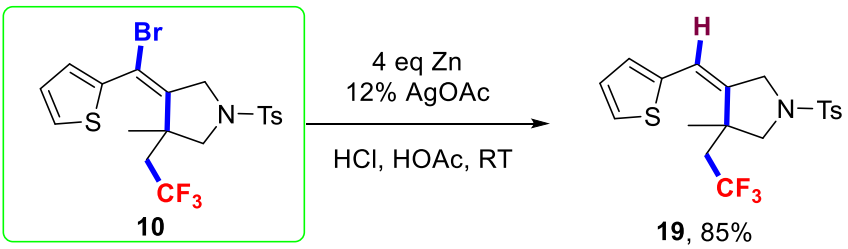
General Information

^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on a Bruker advance III 400 spectrometer in $CDCl_3$ with TMS as internal standard. Mass spectra were determined on a Hewlett Packard 5988A spectrometer by direct inlet at 70 eV. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker Apex II. Element analysis (EA) data were measured on a Vario EL. All products were identified by ^{1}H, ^{19}F and ^{13}C NMR, MS, HRMS, and Element Analysis. The starting materials were purchased from Aldrich, Acros Organics, J&K Chemicals or TCI and used without further purification.

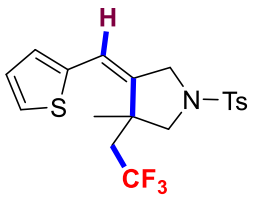
Typical procedure

A mixture of enyne (1 equiv., 0.2 mmol), $NaSO_2CF_3$ (5 equiv., 1.0 mmol), $NaBrO_3$ (2.5 equiv., 0.5 mmol) and CH_2Cl_2/H_2O (4/1, 10 ml) was heated in a sealed tube at 110^0C (measured temperature of the oil bath) for 24 hours. After the reaction finished, it was abstracted by CH_2Cl_2 (3 × 5 mL). The organic layer was dried with anhydrous Na_2SO_4, the filtrate was evaporated under vacuum and purified by column chromatography to afford the desired product.

Confirming the configuration of product:



19.(*E*)-3-methyl-4-(thiophen-2-ylmethylene)-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine:



^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.28 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.98 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.84 (d, *J* = 3.5 Hz, 1H),

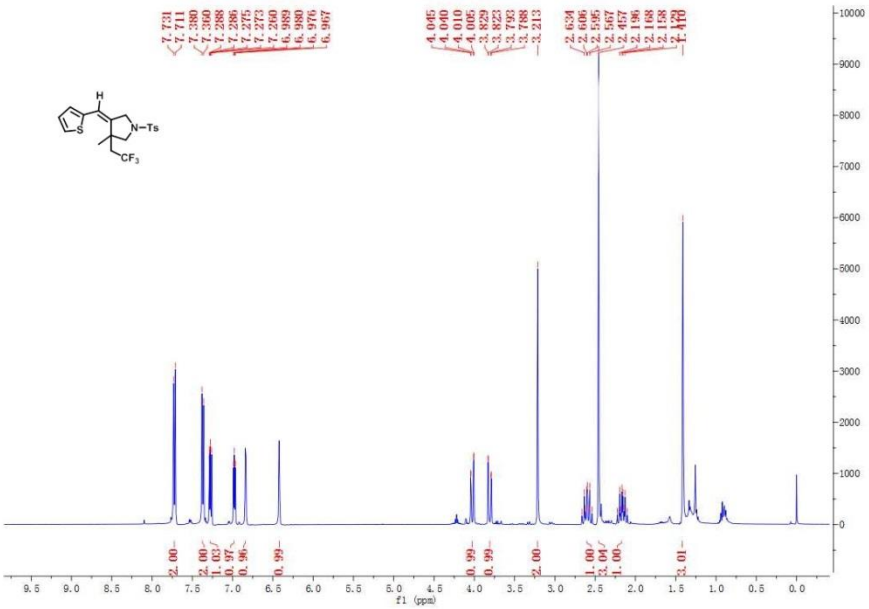
6.42 (s, 3H), 4.03 (dd, *J* = 14.1, 2.0 Hz, 1H), 3.81 (dd, *J* = 14.1, 2.1 Hz, 1H), 3.21 (s, 2H), 2.60 (dq, *J* = 15.5, 11.4 Hz, 1H), 2.46 (s, 3H), 2.16 (dq, *J* = 15.5, 11.5 Hz, 1H), 1.41 (s, 3H).

^{19}F NMR (376 MHz, $CDCl_3$): δ -60.25 (t, *J* = 11.4 Hz, 3F), -60.37 (t, *J* = 11.2 Hz, 0.12F).

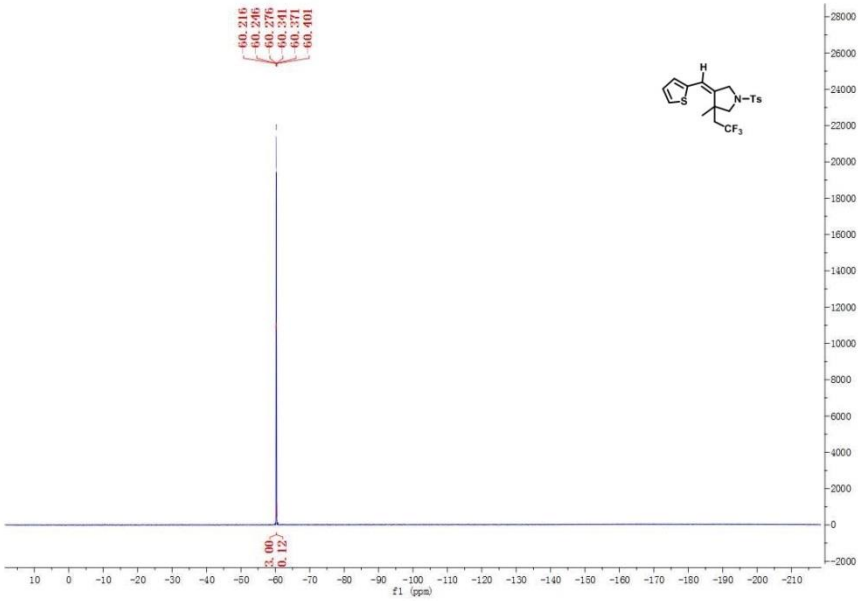
^{13}C NMR (101 MHz, $CDCl_3$): δ 144.9, 144.0 136.9, 131.8, 129.8, 128.0 127.9, 127.2, 126.2, 123.4 (q, *J* = 278.4 Hz), 116.4, 60.5 (q, *J* = 2.3 Hz), 53.8, 42.6, 39.3 (q, *J* = 27.2 Hz), 23.3, 21.6.

HRMS (ESI, m/z): Calculated for $C_{19}H_{21}F_3N_1O_2S_2$ $(M+H)^+$ 416.0960, found 416.0961.

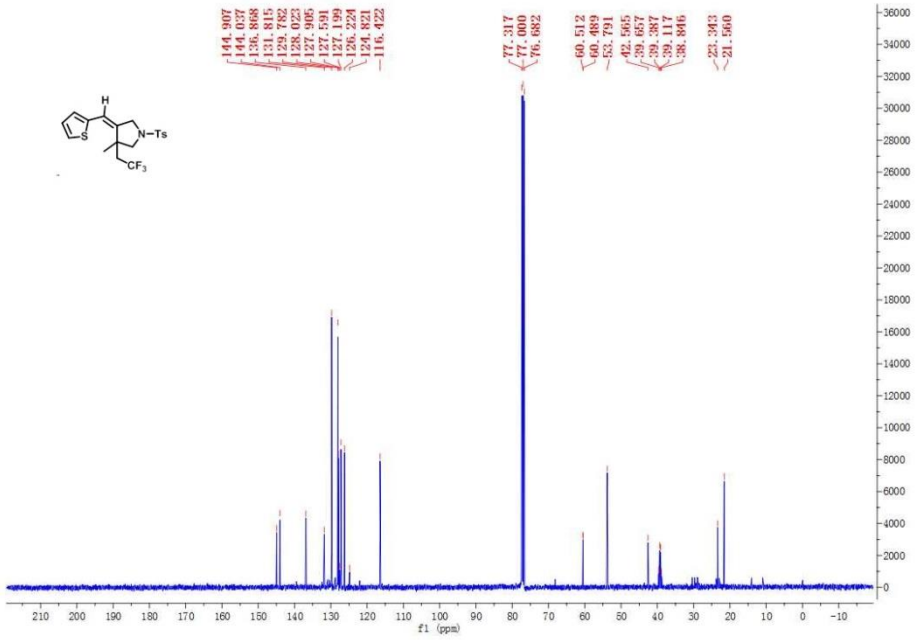
19. ^{1}H NMR



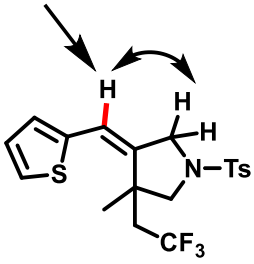
19. ^{19}F NMR

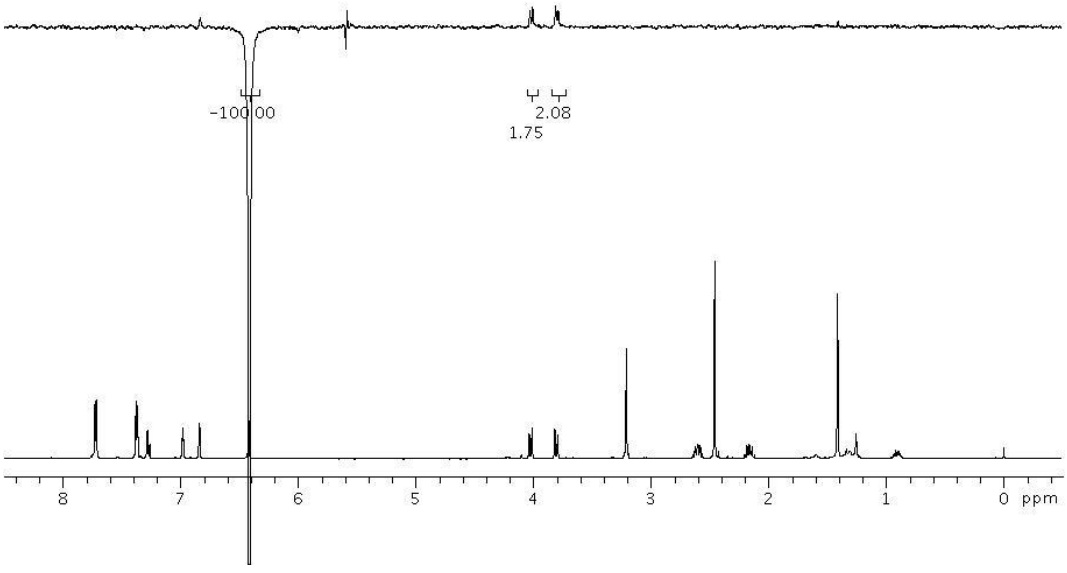


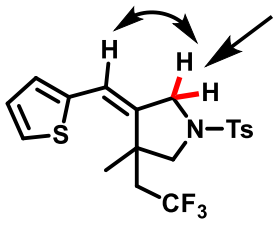
19. ^{13}C NMR

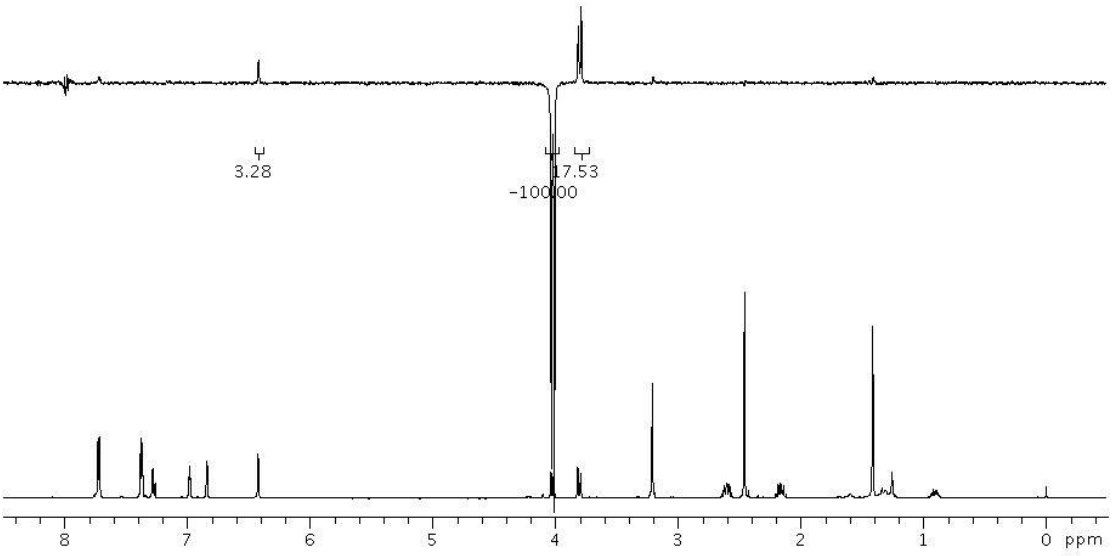


19. NOE









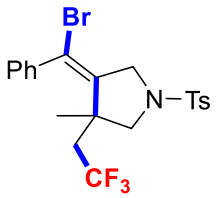
Physical data for the products:

All known compounds are determined by ^{1}H NMR, ^{13}C NMR and ^{31}P NMR, MS analysis and compared with which were cited in the following references, and the new compounds were further confirmed by HRMS and/or element analysis.

References:

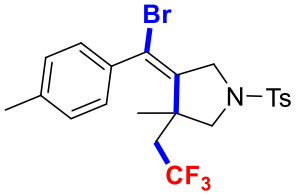
1. L. Zhang, Z. Li and Z.-Q. Liu, *Org. Lett.*, 2014, **16**, 3688.
2. P. Gao, X.-B. Yan, T. Tao, F. Yang, T. He, X.-R. Song, X.-Y. Liu and Y.-M. Liang, *Chem. Eur. J.* 2013, **19**, 14420;
3. Y.-F. Qiu, X.-Y. Zhu, Y.-X. Li, Y.-T. He, F. Yang, J. Wang, H.-L. Hua, L. Zheng, L.-C. Wang, X.-Y. Liu and Y.-M. Liang, *Org. Lett.* 2015, **17**, 3694;
4. Y.-Q. Wang, Y.-T. He, L.-L. Zhang, X.-X Wu, X.-Y. Liu and Y.-M. Liang, *Org. Lett.* 2015, **17**, 4280;
5. M. Li, C.-T. Wang, Y.-F. Qiu, X.-Y. Zhu, Y.-P. Han, Y. Xia, X.-S. Li and Y.-M. Liang, *Chem. Commun.* 2018, **54**, 5334.

(1).(*E*)-4-(bromo(phenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



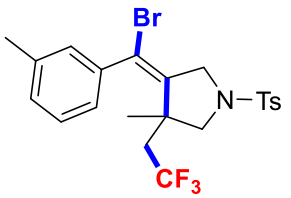
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 70%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.35 (m, 3H), 7.21 – 7.19 (m, 2H), 4.09 (d, *J* = 15.6 Hz, 1H), 3.85 (d, *J* = 15.6 Hz, 1H), 3.24 (s, 2H), 2.47 (s, 3H), 2.07 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.85 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.15 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.32 (t, *J* = 11.3 Hz, 3F). **^{13}C NMR (151 MHz, $CDCl_3$):** δ 144.1, 143.0, 138.7, 129.9, 129.3, 128.64, 128.60, 128.0, 125.6 (q, *J* = 278.7 Hz), 60.0, 55.8, 44.2, 40.3 (q, *J* = 27.6 Hz), 24.3, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{21}H_{22}Br_1F_3N_1O_2S_1$ $(M+H)^+$ 488.0501, found 488.0508.

(2).(*E*)-4-(bromo(p-tolyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 66%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 7.8 Hz, 2H), 4.09 (d, *J* = 15.4 Hz, 1H), 3.85 (d, *J* = 15.4 Hz, 1H), 3.25 (s, 2H), 2.47 (s, 3H), 2.35 (s, 3H), 2.08 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.90 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.16 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.26 (t, *J* = 11.3 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.1, 142.8, 139.4, 135.9, 131.8, 129.8, 129.3, 128.5, 128.0, 125.7 (q, *J* = 278.8 Hz), 117.9, 60.0 (d, *J* = 2.2 Hz), 55.8, 44.2 (d, *J* = 1.5 Hz), 40.3 (q, *J* = 27.4 Hz), 24.3, 21.6, 21.3. **HRMS (ESI, m/z):** Calculated for $C_{22}H_{24}Br_1F_3N_1O_2S_1$ $(M+H)^+$ 502.0658, found 502.0662.

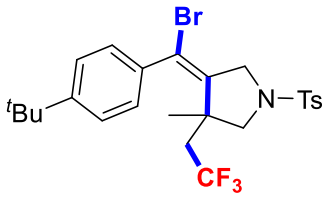
(3).(*E*)-4-(bromo(m-tolyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 65%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* =

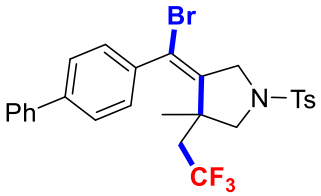
8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.6 Hz, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.01 – 6.98 (m, 2H), 4.10 (d, *J* = 15.8 Hz, 1H), 3.85 (d, *J* = 15.8 Hz, 1H), 3.24 (s, 2H), 2.47 (s, 3H), 2.33 (s, 3H), 2.10 – 2.04 (m, 1H), 1.91 – 1.84 (m, 1H), 1.16 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.31 (t, *J* = 11.3 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.1, 142.7, 138.7, 138.5, 131.8, 130.1, 129.9, 129.2, 128.5, 128.0, 125.7 (q, *J* = 278.9 Hz), 125.7, 117.7, 60.0, 55.8, 44.3 (d, *J* = 1.6 Hz), 40.3 (q, *J* = 27.4 Hz), 24.3, 21.6, 21.3. **HRMS (ESI, m/z):** Calculated for $C_{22}H_{24}Br_1F_3O_2N_1S_1$ $(M+H)^+$ 502.0658, found 502.0663.

(4).(*E*)-4-(bromo(4-(tert-butyl)phenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



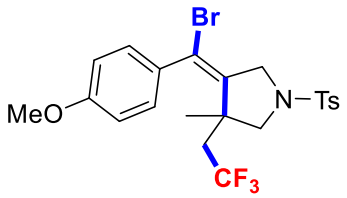
A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 66%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.29 (s, 2H), 4.08 (d, *J* = 15.2 Hz, 1H), 3.84 (d, *J* = 15.2 Hz, 1H), 3.23 (s, 2H), 2.47 (s, 3H), 2.06 (dq, *J* = 15.2, 11.4 Hz, 1H), 1.84 (dq, *J* = 15.2, 11.3 Hz, 1H), 1.30 (s, 9H), 1.16 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.37 (s, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 152.6, 144.1, 142.8, 135.8, 131.6, 129.9, 128.3, 128.1, 125.7 (q, *J* = 278.7 Hz), 125.5, 117.9, 59.9, 55.8, 53.4, 44.2, 40.3 (q, *J* = 27.4 Hz), 34.8, 31.1, 24.3, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{25}H_{30}Br_1F_3N_1O_2S_1$ $(M+H)^+$ 544.1127, found 544.1135.

(5).(*E*)-4-([1,1'-biphenyl]-4-ylbromomethylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



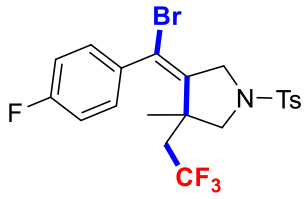
A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 65%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.62 – 7.59 (m, 4H), 7.47 – 7.38 (m, 5H), 7.28 (d, *J* = 8.4 Hz, 1H), 4.12 (d, *J* = 15.2 Hz, 1H), 3.90 (d, *J* = 15.2 Hz, 1H), 3.27 (q, *J* = 9.6 Hz, 2H), 2.49 (s, 3H), 2.18 – 2.11 (m, 1H), 1.99 – 1.93 (m, 1H), 1.20 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.24 (t, *J* = 11.3 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.1, 143.3, 142.1, 139.7, 137.6, 131.8, 129.9, 129.1, 128.9, 128.1, 128.0, 127.3, 127.1, 125.7 (q, *J* = 278.7 Hz), 117.4, 60.0, 55.9, 44.4, 40.5 (q, *J* = 27.5 Hz), 24.4, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{27}H_{25}Br_1F_3N_1O_2S_1Na_1$ $(M+Na)^+$ 586.0634, found 586.0629.

(6).(*E*)-4-(bromo(4-methoxyphenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoro ethyl)pyrrolidine



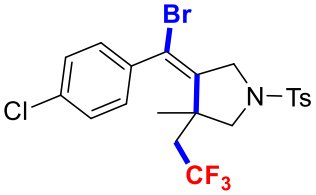
A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 62%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.07 (d, *J* = 15.4 Hz, 1H), 3.83 (d, *J* = 15.4 Hz, 1H), 3.81 (s, 3H), 3.23 (s, 2H), 2.47 (s, 3H), 2.08 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.90 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.17 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -58.46 (s, 0.23F), -60.24 (t, *J* = 11.3 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 160.0, 144.1, 143.0, 131.5, 131.0, 130.0, 129.8, 128.0, 125.7 (q, *J* = 278.8 Hz), 117.9, 114.0, 60.0, 55.8, 55.3, 44.2, 40.3 (q, *J* = 27.4 Hz), 24.3, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{22}H_{23}Br_1F_3N_1O_3S_1Na_1$ $(M+Na)^+$ 540.0426, found 540.0421.

(7).(*E*)-4-(bromo(4-fluorophenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroet hyl)pyrrolidine



A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 60%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.21 – 7.17 (m, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 4.06 (d, *J* = 15.4 Hz, 1H), 3.84 (d, *J* = 15.4 Hz, 1H), 3.23 (dd, *J* = 22.4, 9.4 Hz, 2H), 2.47 (s, 3H), 2.09 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.86 (dq, *J* = 15.0, 11.2 Hz, 1H), 1.14 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.27 (t, *J* = 10.6 Hz, 3F), -110.36 (d, *J* = 3.3 Hz, 1F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.0, 161.5, 144.2, 143.7, 134.8 (d, *J* = 3.7 Hz), 131.5, 130.6 (d, *J* = 8.4 Hz), 129.9, 128.0, 125.5 (q, *J* = 278.8 Hz), 116.4, 116.0, 115.8, 59.9, 55.8, 44.3, 40.4 (q, *J* = 27.5 Hz), 24.3, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{21}H_{20}Br_1F_4N_1O_2S_1Na_1$ $(M+Na)^+$ 528.0226, found 528.0220.

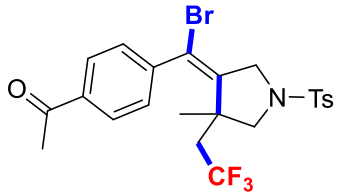
(8).(*E*)-4-(bromo(4-chlorophenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroet hyl)pyrrolidine



A slight yellow solid after purification by flash column chromatography (petroleum

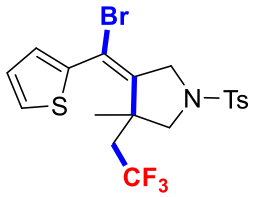
ether/ethyl acetate = 10/1, Yield: 71%). **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 4.06 (d, *J* = 15.6 Hz, 1H), 3.85 (d, *J* = 15.6 Hz, 1H), 3.24 (dd, *J* = 43.3, 9.6 Hz, 2H), 2.47 (s, 3H), 2.11 (dq, *J* = 22.6, 11.4 Hz, 1H), 1.89 (dq, *J* = 22.6, 11.4 Hz, 1H), 1.14 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.23 (t, *J* = 11.1 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.2, 143.9, 137.2, 135.4, 131.8, 130.1, 129.9, 129.0, 128.1, 125.6 (q, *J* = 278.9 Hz), 116.1, 59.9, 55.9, 44.6, 40.5 (q, *J* = 27.3 Hz), 24.3, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{21}H_{21}Br_1Cl_1F_3N_1O_2S_1$ $(M+H)^+$ 522.0112, found 522.0115.

(9).(*E*)-1-(4-(bromo(4-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)pyrrolidin-3-ylidene) methyl)phenyl)ethan-1-one



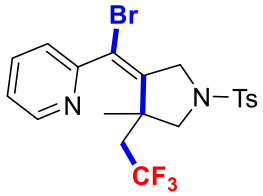
A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 64%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.09 (d, *J* = 15.6 Hz, 1H), 3.90 (d, *J* = 15.6 Hz, 1H), 3.26 (dd, *J* = 37.4, 9.6 Hz, 2H), 2.62 (s, 3H), 2.48 (s, 3H), 2.15 – 2.09 (m, 1H), 1.91 – 1.84 (m, 1H), 1.14 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.24 (t, *J* = 11.1 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 196.9, 144.2, 143.9, 143.2, 137.4, 131.8, 129.9, 129.1, 128.6, 128.1, 125.5 (q, *J* = 278.9 Hz), 115.8, 59.9, 55.9, 44.4, 40.5 (q, *J* = 27.6 Hz), 26.6, 24.3, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{23}H_{24}Br_1F_3N_1O_3S_1$ $(M+H)^+$ 530.0607, found 530.0602.

(10).(*E*)-4-(bromo(thiophen-2-yl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroet hyl)pyrrolidine



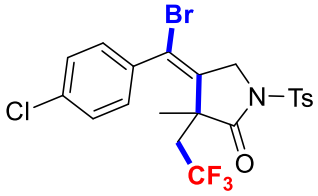
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 75%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 6.8 Hz, 3H), 6.99 – 6.96(m, 2H), 4.07 (d, *J* = 15.8 Hz, 1H), 3.81 (d, *J* = 15.8 Hz, 1H), 3.25 (q, *J* = 2.8 Hz, 2H), 2.47 (s, 3H), 2.22 – 2.00 (m, 2H), 1.26 (s, 3H).**^{19}F NMR (376 MHz, $CDCl_3$):** δ -59.76 (s, 0.09F), -60.21 (t, *J* = 11.2 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 147.3, 144.2, 139.4, 131.4, 129.9, 129.0, 128.1, 128.0, 126.8,125.7 (q, *J* = 278.7 Hz), 109.5, 60.0 (d, *J* = 2.3 Hz), 56.1, 44.6, 39.7 (q, *J* = 27.6 Hz), 23.9, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{19}H_{20}Br_1F_3N_1O_2S_2$ $(M+H)^+$ 494.0065, found 494.0060.

(11).(*E*)-2-(bromo(4-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)pyrrolidin-3-ylidene)methyl)pyridine



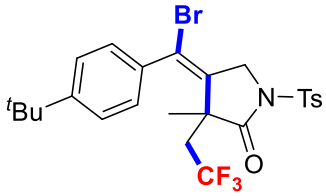
A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 5/1, Yield: 61%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.56 (d, *J* = 4.4 Hz, 1H), 7.75 – 7.71 (m, 3H), 7.40 – 7.36 (m, 3H), 7.28 – 7.25 (m, 1H), 4.04 (d, *J* = 15.6 Hz, 1H), 3.93 (d, *J* = 15.6 Hz, 1H), 3.49 (d, *J* = 9.6 Hz, 1H), 2.98 (d, *J* = 9.6 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.47 (s, 3H), 2.39 – 2.29 (m, 1H), 0.98 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.23 (s, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 156.3, 148.8, 145.4, 144.2, 136.9, 131.3, 129.9, 128.0, 125.8 (q, *J* = 278.9 Hz), 124.5, 123.8, 116.0, 59.7, 55.9, 44.7, 39.6 (q, *J* = 27.3 Hz), 21.9, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{20}H_{21}Br_1F_3N_2O_2S_1$ $(M+H)^+$ 489.0454, found 489.0461.

(12).(*E*)-4-(bromo(4-chlorophenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidin-2-one



A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 67%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 9.2 Hz, 4H), 7.21 (d, *J* = 8.4 Hz, 2H), 4.72 (d, *J* = 15.5 Hz, 1H), 4.37 (d, *J* = 15.5 Hz, 1H), 2.46 (s, 3H), 2.39 – 2.30 (m, 1H), 1.99 – 1.88 (m, 1H), 1.13 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.30 (t, *J* = 10.2 Hz, 3F), -63.20 (t, *J* = 10.4 Hz, 0.22F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 173.7, 145.8, 136.6, 135.8, 134.0, 133.7, 130.2, 130.0, 129.1, 128.4, 124.7 (q, *J* = 278.6 Hz), 120.2, 52.8, 47.4, 41.2 (q, *J* = 27.6 Hz), 25.7, 21.8. **HRMS (ESI, m/z):** Calculated for $C_{21}H_{19}Br_1Cl_1F_3N_1O_3S_1$ $(M+H)^+$ 535.9904, found 535.9904.

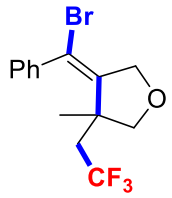
(13).(*E*)-4-(bromo(4-(tert-butyl)phenyl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidin-2-one



A slight yellow solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 65%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.96 (d, *J* = 8.4 Hz, 2H), 7.37 (dd, *J* = 14.6, 8.3 Hz, 4H), 7.19 (d, *J* = 8.4 Hz, 2H), 4.73 (d, *J* =

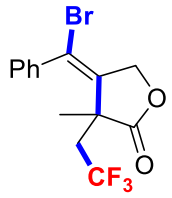
15.2 Hz, 1H), 4.38 (d, *J* = 15.2 Hz, 1H), 2.45 (s, 3H), 2.35 – 2.27 (m, 1H), 2.07 – 1.95 (m, 1H), 1.32 (s, 9H), 1.11 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.25 (t, *J* = 10.2 Hz, 3F), -63.19 (t, *J* = 10.4 Hz, 0.31F). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 174.1, 152.9, 145.7, 135.2, 134.1, 132.5, 129.6, 128.4 (q, *J* = 3.5 Hz), 125.5, 124.9 (q, *J* = 278.6 Hz), 122.0, 52.9, 47.5, 41.3 (q, *J* = 27.3 Hz), 34.8, 31.2, 25.6, 21.7. **HRMS (ESI, m/z):** Calculated for $C_{25}H_{28}Br_1F_3N_1O_3S_1$ $(M+H)^+$ 558.0920, found 558.0922.

(14).(*E*)-4-(bromo(phenyl)methylene)-3-methyl-3-(2,2,2-trifluoroethyl)tetrahydrofuran



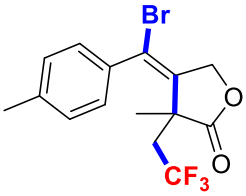
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 55%). **^{1}H NMR (400 MHz, CDCl$_3$):** δ7.42 – 7.37 (m, 3H), 7.30 – 7.28 (m, 2H), 4.59 (d, *J* = 14.8 Hz, 1H), 4.50 (d, *J* = 14.8 Hz, 1H), 3.96 (d, *J* = 8.8 Hz, 1H), 3.79 (d, *J* = 8.8 Hz, 1H), 2.21 – 2.08 (m, 1H), 1.96 – 1.84 (m, 1H), 1.14 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -60.23 (t, *J* = 11.5 Hz, 0.11F), -60.61 (t, *J* = 11.5 Hz,3F). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 146.4, 139.0, 129.1, 128.8, 128.6, 126.0 (q, *J* = 278.7 Hz), 114.3, 80.2 (d, *J* = 2.4 Hz), 75.3, 45.2, 39.8 (q, *J* = 27.3 Hz), 23.2. **HRMS (ESI, m/z):** Calculated for $C_{14}H_{15}Br_1F_3O_1$ $(M+H)^+$ 335.0253, found 335.0250.

(15).(*E*)-4-(bromo(phenyl)methylene)-3-methyl-3-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one



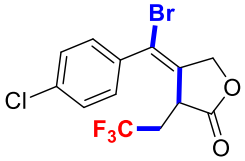
A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 40%). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.45 – 7.43 (m, 3H), 7.33 – 7.30 (m, 2H), 4.98 (d, *J* = 15.4 Hz, 1H), 4.88 (d, *J* = 15.4 Hz, 1H), 2.50 (dq, *J* = 15.1, 10.2 Hz, 1H), 2.13 (dq, *J* = 15.2, 10.0 Hz, 1H), 1.21 (s, 3H). **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.13 (t, *J* = 10.2 Hz, 3F), -62.94 (t, *J* = 10.2 Hz, 0.15F). **^{13}C NMR (101 MHz, CDCl$_3$):** δ 178.8, 137.7, 136.1, 129.7, 128.7, 127.5, 124.9 (q, *J* = 278.3 Hz), 119.4, 72.0, 44.32 – 44.27 (m), 41.6 (q, *J* = 27.8 Hz), 25.7. **HRMS (ESI, m/z):** Calculated for $C_{14}H_{16}Br_1F_3O_2N_1$ $(M+NH_4)^+$ 366.0311, found 366.0316.

(16).(*E*)-3-(bromo(p-tolyl)methylene)-4-methyl-4-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one



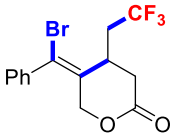
A colorless oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 40%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.23 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 2H), 4.97 (d, *J* = 14.7 Hz, 1H), 4.87 (d, *J* = 14.7 Hz, 1H), 2.52 – 2.46 (m, 1H), 2.39 (s, 3H), 2.19 – 2.12 (m, 1H), 1.23 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.13 (t, *J* = 10.1 Hz, 3F), -62.96 (t, *J* = 10.3 Hz, 0.30F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 178.9, 139.8, 135.8, 134.8, 129.4, 128.6, 124.9 (q, *J* = 278.4 Hz), 119.7, 72.0, 44.3 (q, *J* = 2.4 Hz), 41.5 (q, *J* = 27.7 Hz), 25.7, 21.3. **HRMS (ESI, m/z):** Calculated for $C_{15}H_{14}Br_1F_3O_2Na_1$ $(M+Na)^+$ 385.0021, found 385.0019.

(17).(*E*)-3-(bromo(4-chlorophenyl)methylene)-4-(2,2,2-trifluoroethyl)dihydrofuran-2(3H)-one



A slight yellow oil after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 45%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 9.0 Hz, 2H), 7.34 (d, *J* = 9.0 Hz, 2H), 4.89 – 4.40 (m, 2H), 3.71 – 3.66 (m, 1H), 2.82 – 2.70 (m, 1H), 2.54 – 2.40 (m, 1H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -64.61 (t, *J* = 10.4 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 164.2, 139.4, 136.6, 135.1, 130.2, 128.5, 128.4, 125.9 (q, *J* = 277.8 Hz), 68.1 (d, *J* = 1.8 Hz), 39.4 (d, *J* = 2.8 Hz), 35.8 (q, *J* = 28.1 Hz). **HRMS (ESI, m/z):** Calculated for $C_{13}H_9Br_1Cl_1F_3O_2Na_1$ $(M+Na)^+$ 390.9319, found 390.9315.

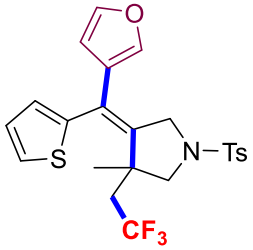
(18).(*E*)-5-(bromo(phenyl)methylene)-4-(2,2,2-trifluoroethyl)tetrahydro-2H-pyran-2-one



A colorless liquid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1, Yield: 40%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.46 – 7.44 (m, 2H), 7.35 – 7.30 (m, 3H), 4.98 (s, 2H), 4.55 – 4.48 (m, 1H), 3.13 (dd, *J* = 16.7, 8.1 Hz, 1H), 3.04 (dd, *J* = 16.7, 8.1 Hz, 1H), 2.91 – 2.82 (m, 2H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -63.84 (t, *J* = 10.1 Hz ,3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 168.7, 131.9, 128.9, 128.3, 125.0 (q, *J* = 278.1 Hz), 121.9, 87.09, 82.2, 53.5, 43.0, 42.1 (q, *J* = 29.0 Hz), 36.8 (q, *J* = 3.3 Hz). **HRMS (ESI, m/z):** Calculated for $C_{14}H_{12}Br_1F_3O_2Na_1$ $(M+Na)^+$ 370.9865, found 370.9863.

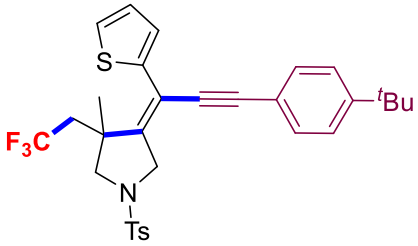
(20)

(*E*)-4-(furan-3-yl(thiophen-2-yl)methylene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 82%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.12 (s, 1H), 6.99 (dd, *J* = 5.2, 3.6 Hz, 1H), 6.85 (dd, *J* = 3.6, 1.2 Hz, 1H), 6.14 (d, *J* = 1.0 Hz, 1H), 4.11 (d, *J* = 14.8 Hz, 1H), 3.90 (d, *J* = 14.8 Hz, 1H), 3.19 (dd, *J* = 21.1, 9.5 Hz, 1H), 2.46 (s, 3H), 2.26 – 2.10 (m, 2H), 1.27 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -59.93 (t, *J* = 11.4 Hz, 0.15F), -60.05 (t, *J* = 11.5 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 144.2, 143.2, 142.9, 140.8, 139.5, 131.4, 129.9, 128.0, 127.8, 127.0, 126.6, 126.2, 126.0 (q, *J* = 274.7 Hz), 121.0, 110.0, 59.3, 53.1, 44.0, 40.1 (q, *J* = 27.2 Hz), 24.6, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{23}H_{23}F_3N_1O_3S_2$ $(M+H)^+$ 482.1066, found 482.1064.

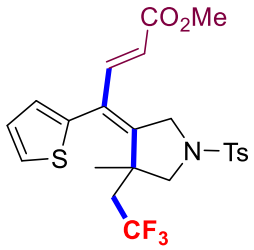
(21).(*E*)-4-(3-(4-(tert-butyl)phenyl)-1-(thiophen-2-yl)prop-2-yn-1-ylidene)-3-methyl-1-tosyl-3-(2,2,2-trifluoroethyl)pyrrolidine



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 74%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.32 (m, 4H), 7.02 – 6.96 (m, 2H), 4.33 (d, *J* = 16.4 Hz, 1H), 4.05 (d, *J* = 16.4 Hz, 1H), 3.24 (dd, *J* = 25.9, 9.5 Hz, 2H), 2.47 (s, 3H), 2.30 – 2.10 (m, 2H), 1.35 (s, 3H), 1.33 (s, 9H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.10 (t, *J* = 11.4 Hz, 3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 152.5, 152.2, 144.1, 137.2, 131.8, 131.2, 129.8, 128.0, 127.8, 126.9, 126.6, 126.0 (d, *J* = 279.0 Hz), 125.4, 119.4, 111.9, 96.5, 87.2, 60.1, 53.9, 43.7, 39.5 (q, *J* = 27.2 Hz), 34.8, 31.1, 26.9, 24.1,

21.6. **HRMS (ESI, m/z):** Calculated for $C_{31}H_{33}F_3N_1O_2S_2$ $(M+H)^+$ 572.1899, found 572.1907.

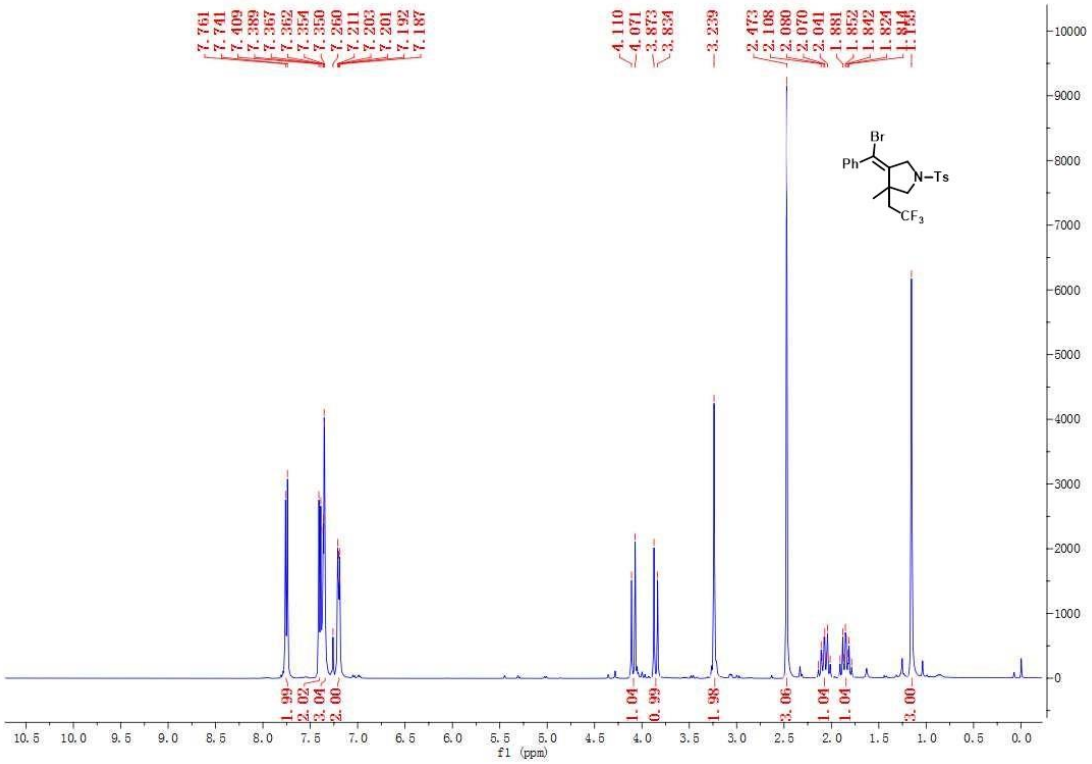
(22).methyl(5*E*)-5-(4-methyl-1-tosyl-4-(2,2,2-trifluoroethyl)pyrrolidin-3-ylidene)-5-(thiophen-2-yl)pent-2-enoate



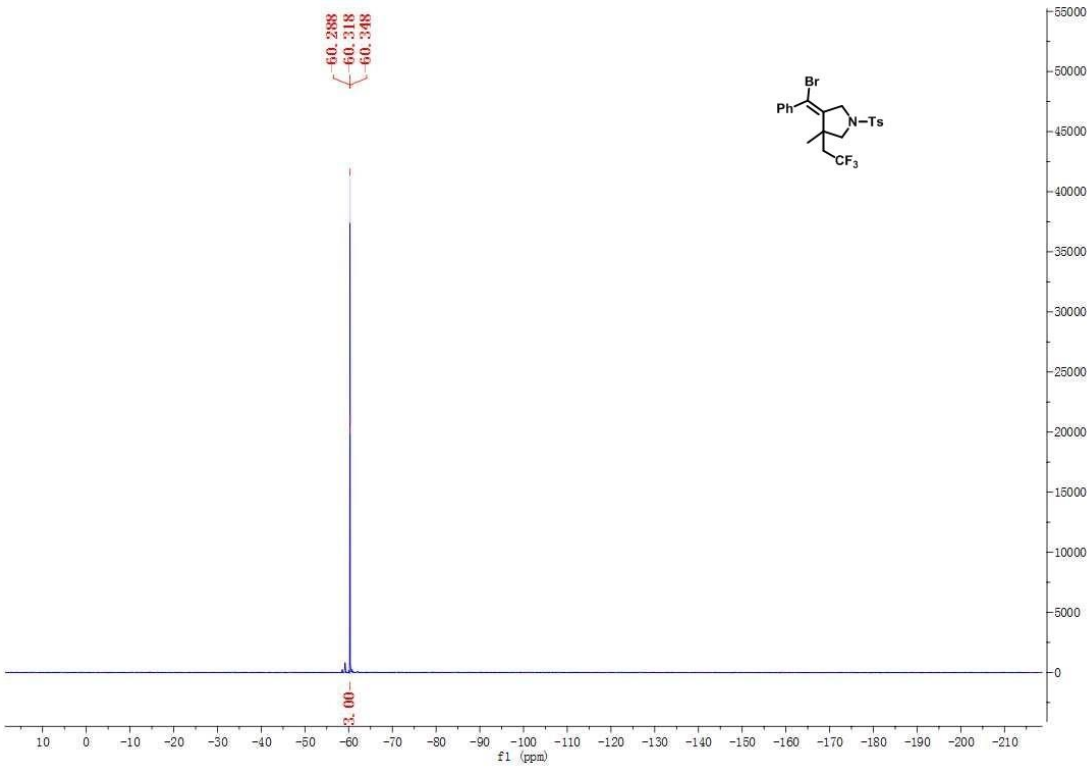
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1, Yield: 70%). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 (d, *J* = 8.2 Hz, 2H), δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 5.3 Hz, 1H), 7.03 – 7.01 (m, 1H), 6.81 (d, *J* = 3.3 Hz, 1H), 6.19 (s, 1H), 5.84 (t, *J* = 7.2 Hz, 1H), 3.67 (s, 3H), 3.63 (d, *J* = 10.7 Hz, 1H), 3.30 (d, *J* = 10.7 Hz, 1H), 3.11 (d, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 2.49 – 2.36 (m, 1H), 2.11 – 1.99 (m, 1H), 1.26 (s, 3H). **^{19}F NMR (376 MHz, $CDCl_3$):** δ -60.23 (t, *J* = 11.3 Hz, 3F), -60.33 (t, *J* = 11.2 Hz, 0.3F). **^{13}C NMR (101 MHz, $CDCl_3$):** δ 171.7, 144.4, 139.0, 132.4 (q, *J* = 6.9 Hz), 130.7, 129.8, 129.6, 127.7, 127.0, 126.3, 122.5, 60.4, 52.0, 45.3, 40.3 (q, *J* = 26.6 Hz), 34.7, 24.4, 21.6. **HRMS (ESI, m/z):** Calculated for $C_{23}H_{25}F_3N_1O_4S_2$ $(M+H)^+$ 500.1172, found 500.1179.

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

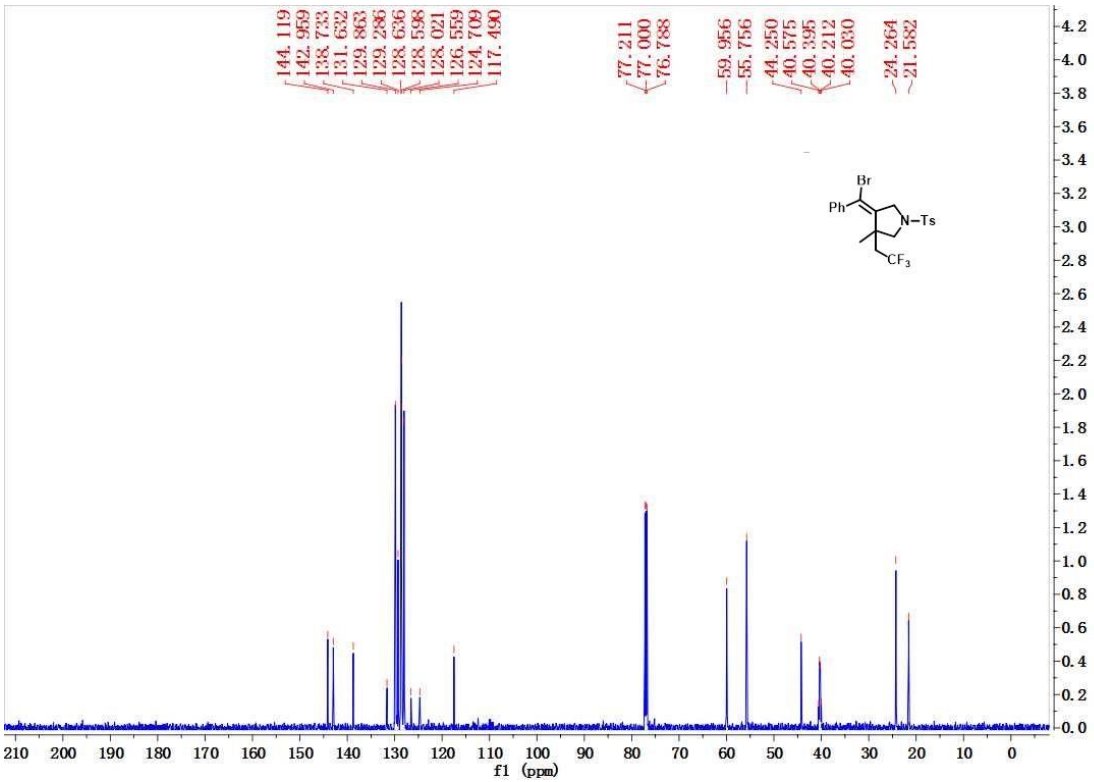
1. ^{1}H NMR



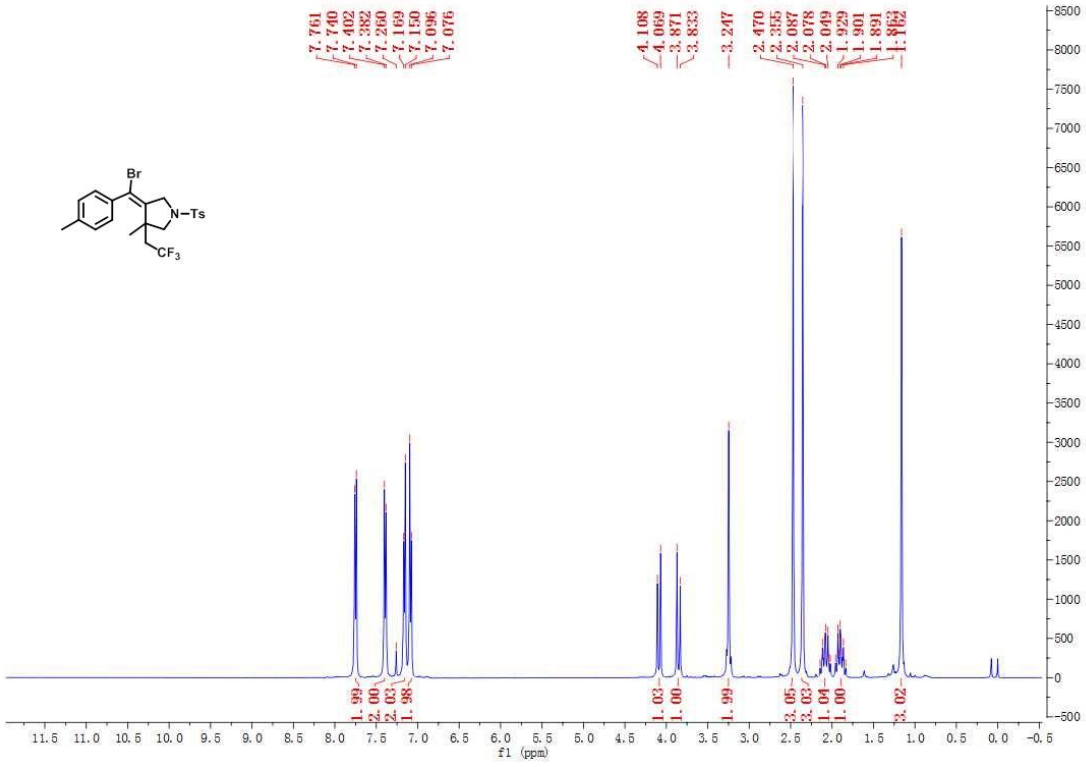
1. ^{19}F NMR



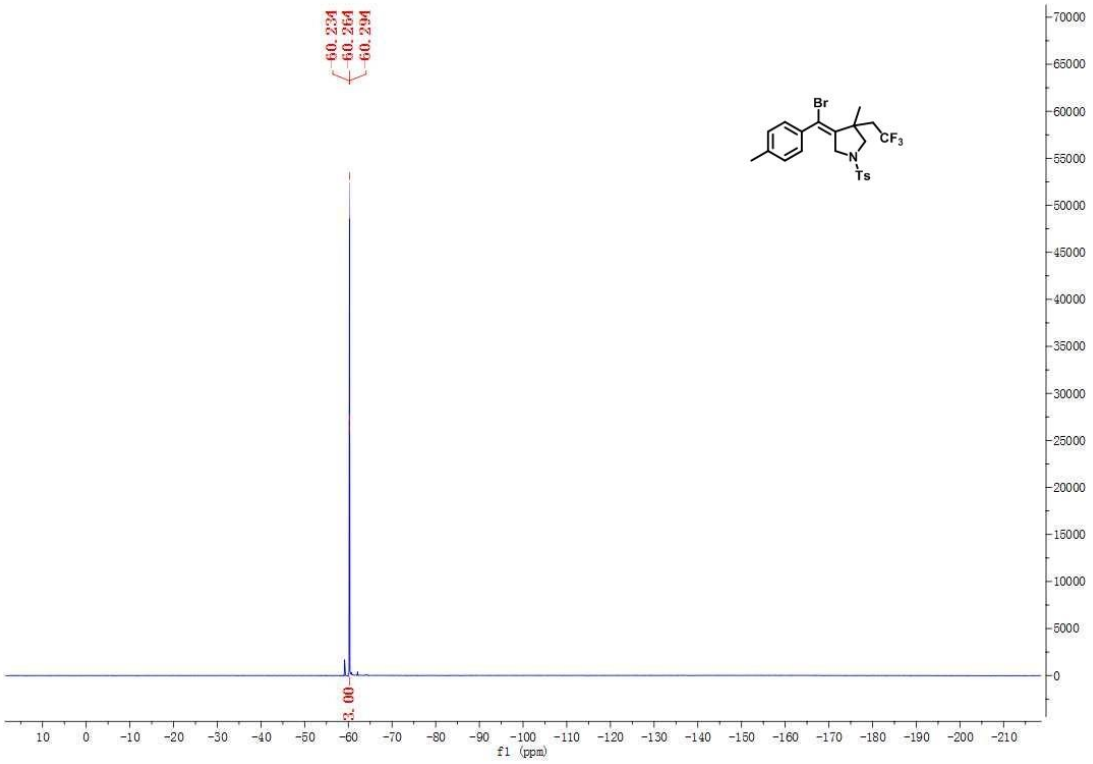
1. ^{13}C NMR



2. ^{1}H NMR



2. ^{19}F NMR



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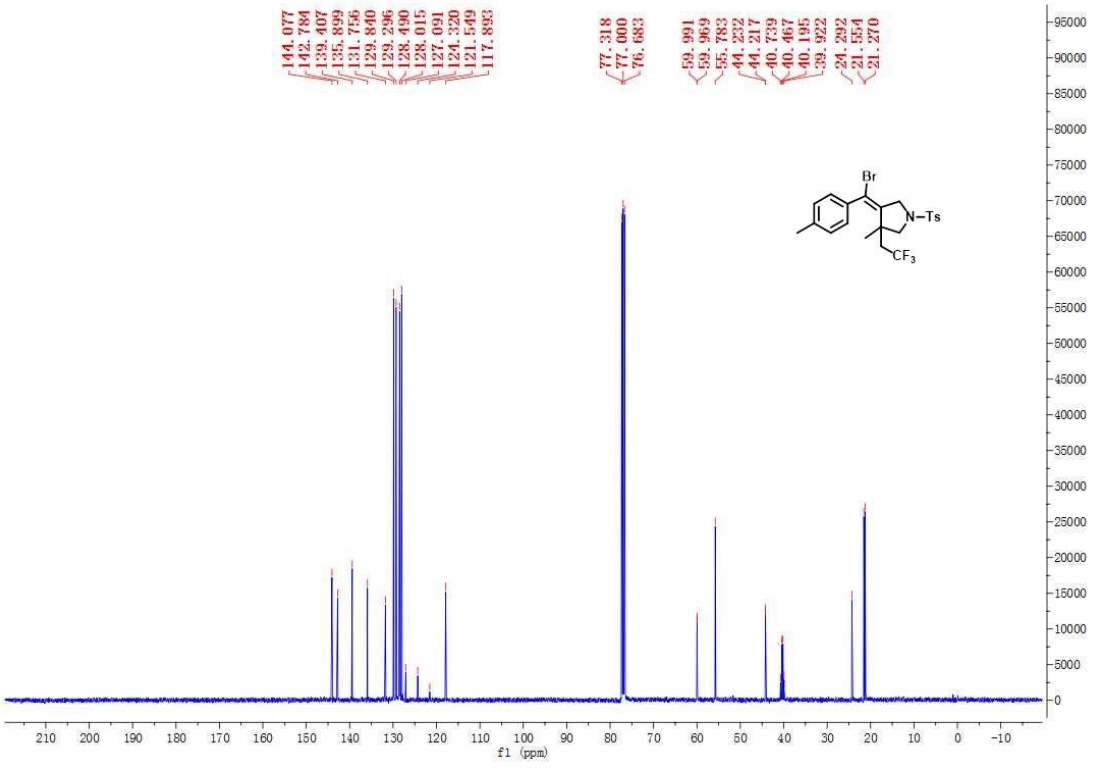

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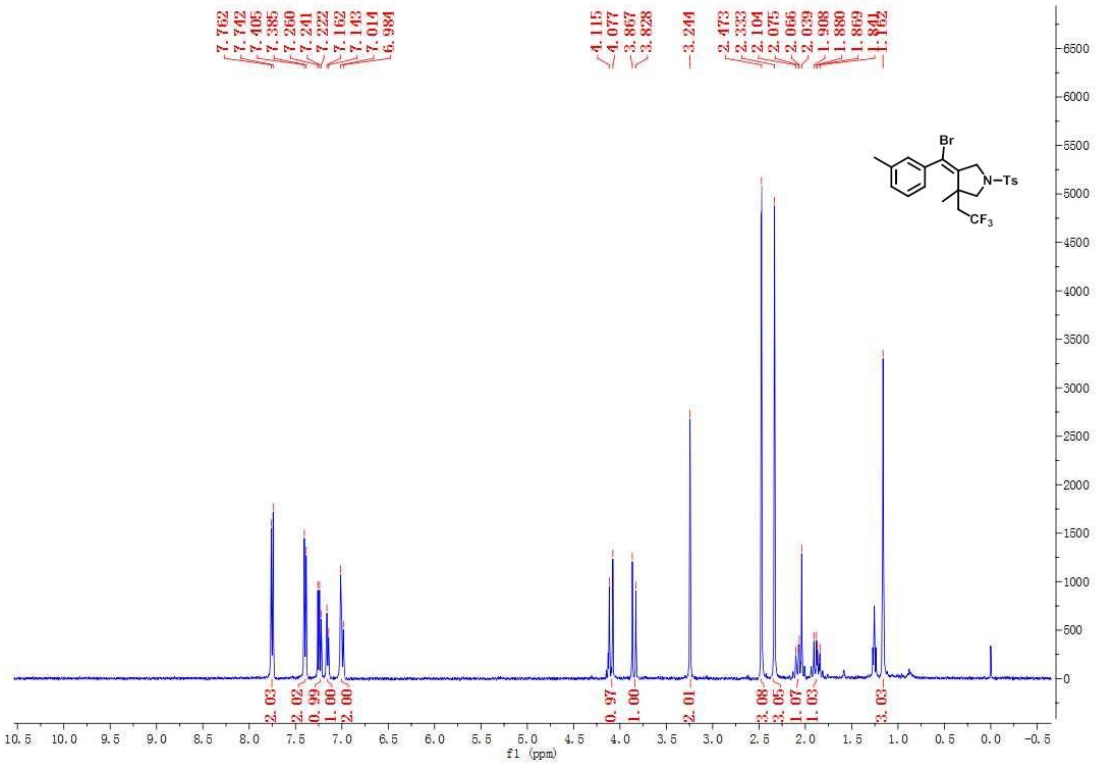

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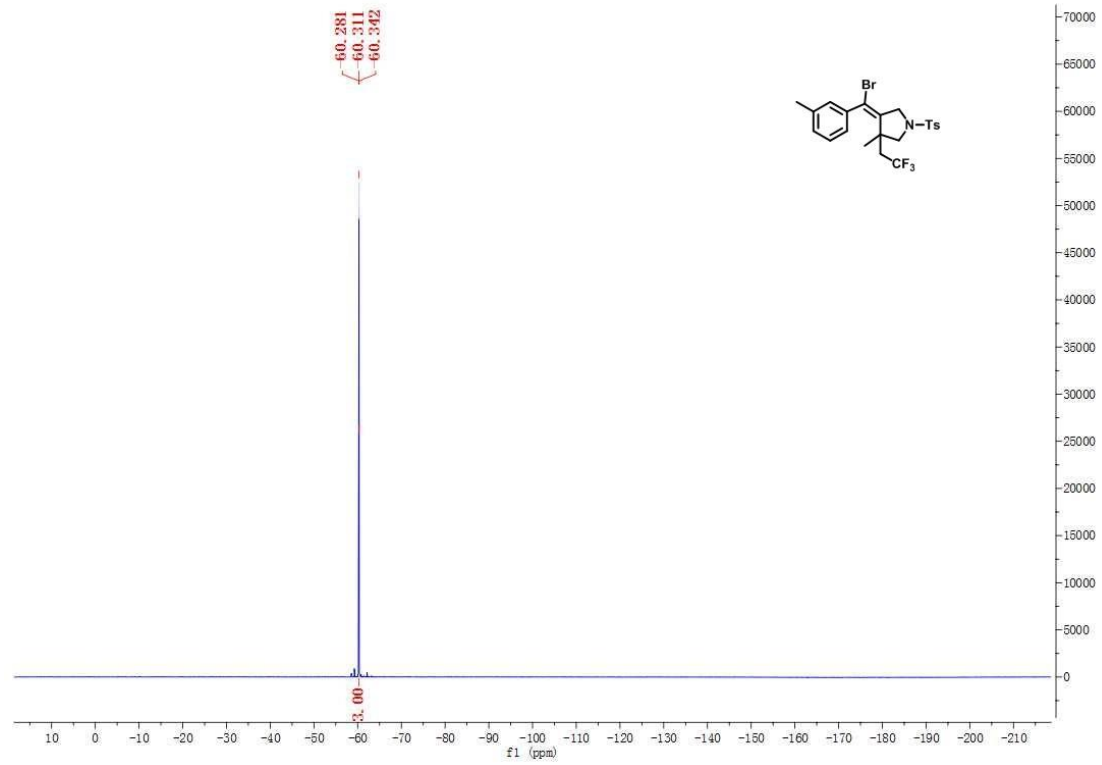

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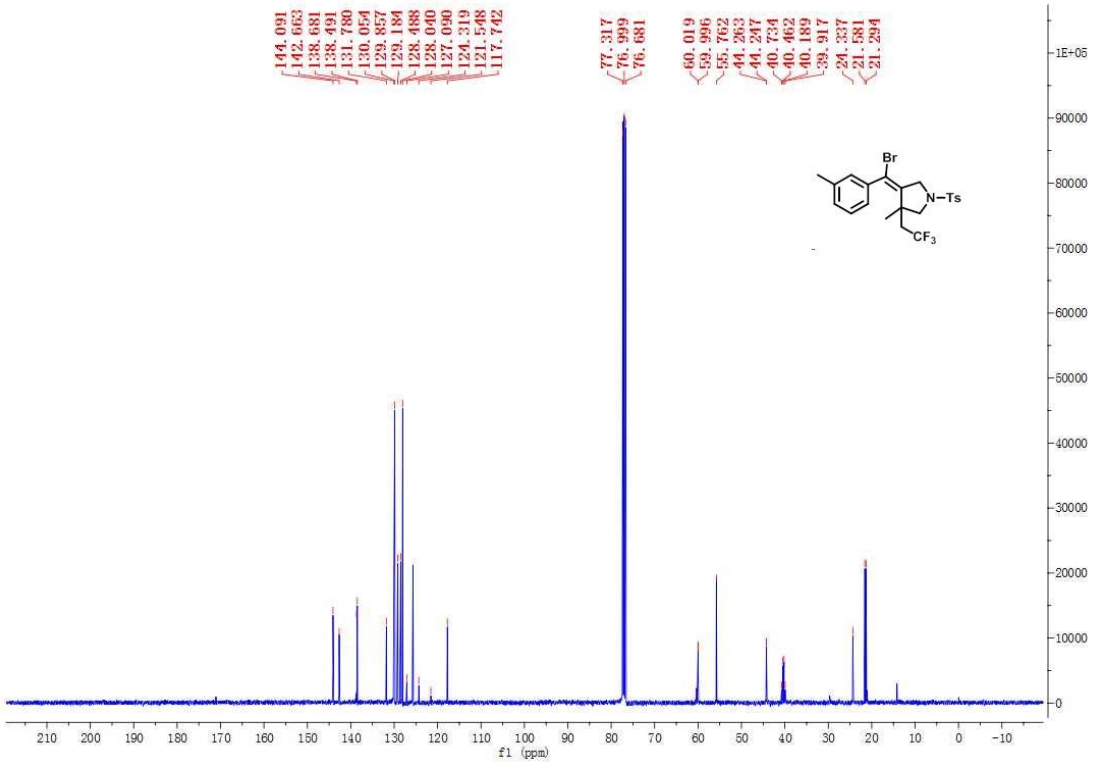

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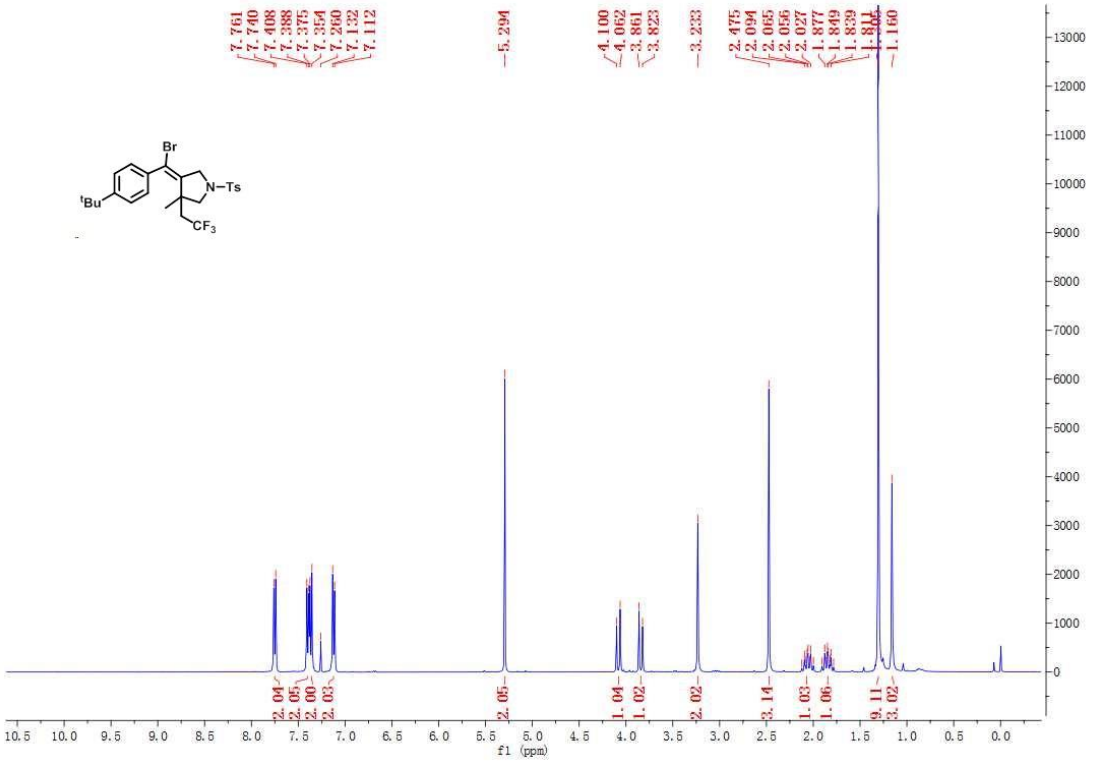

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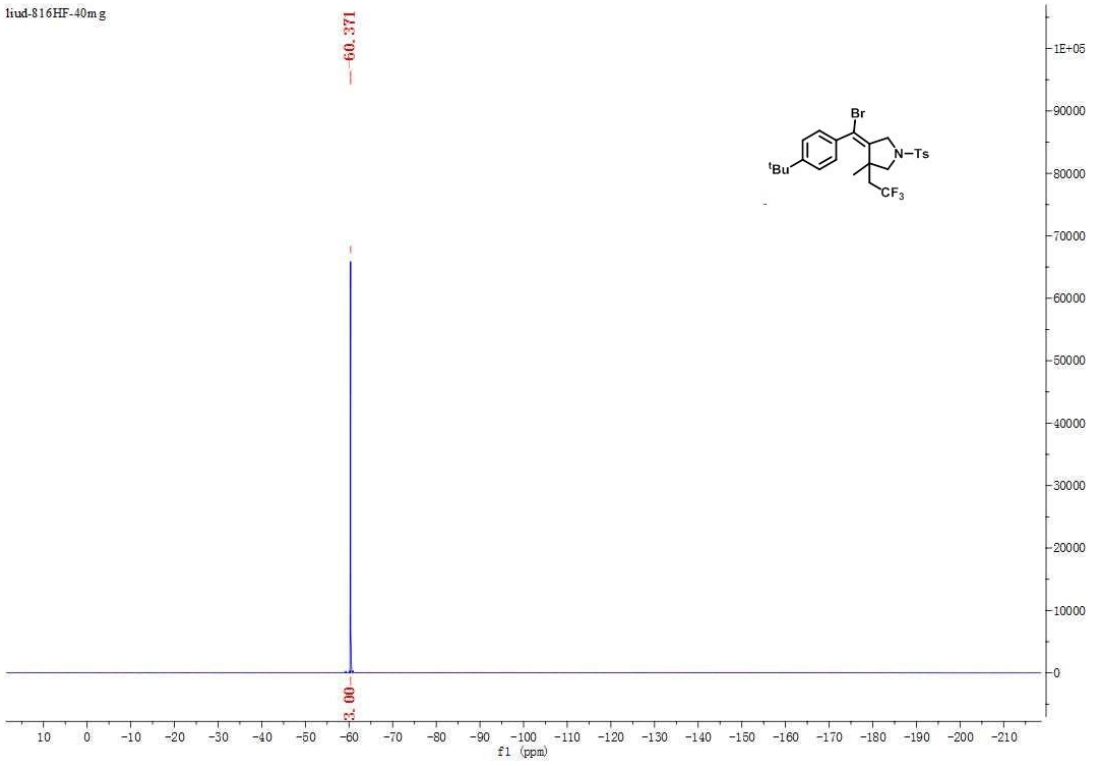

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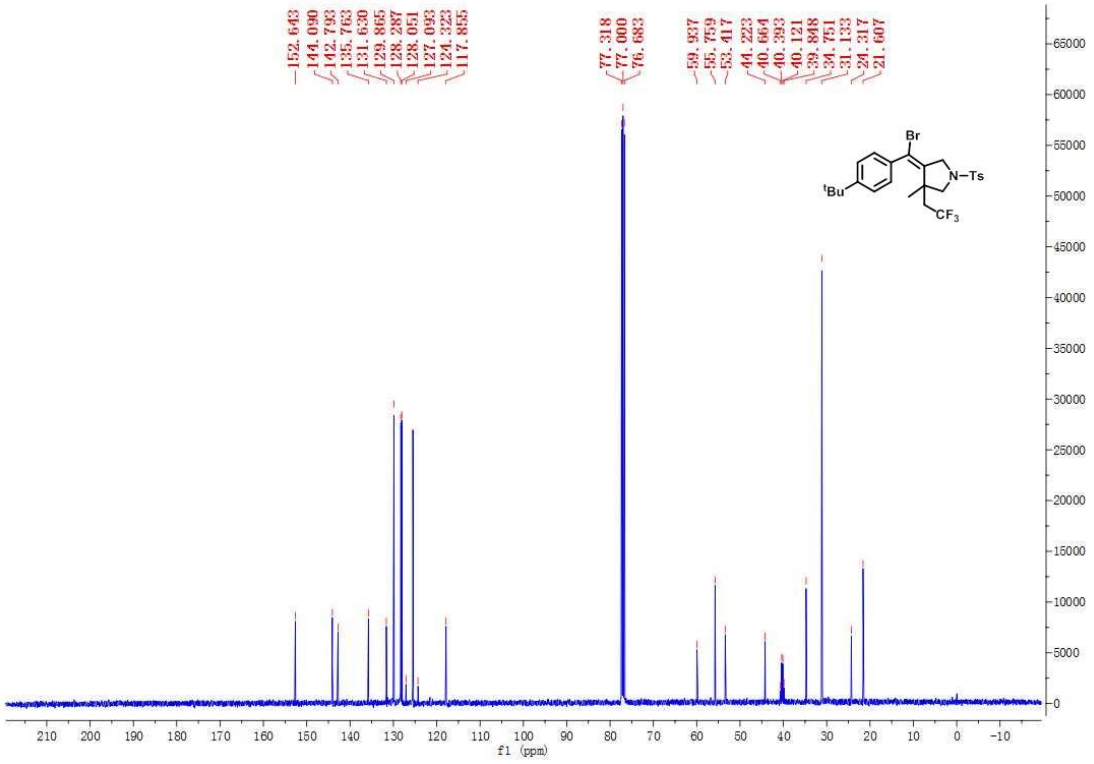

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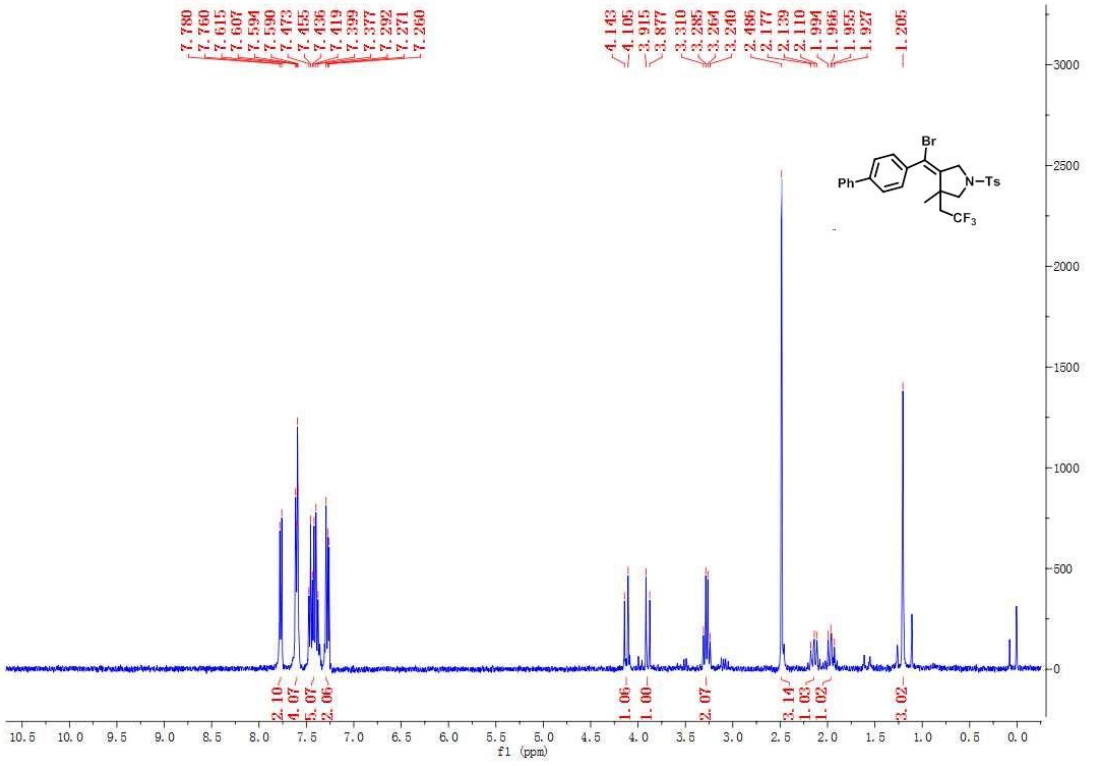

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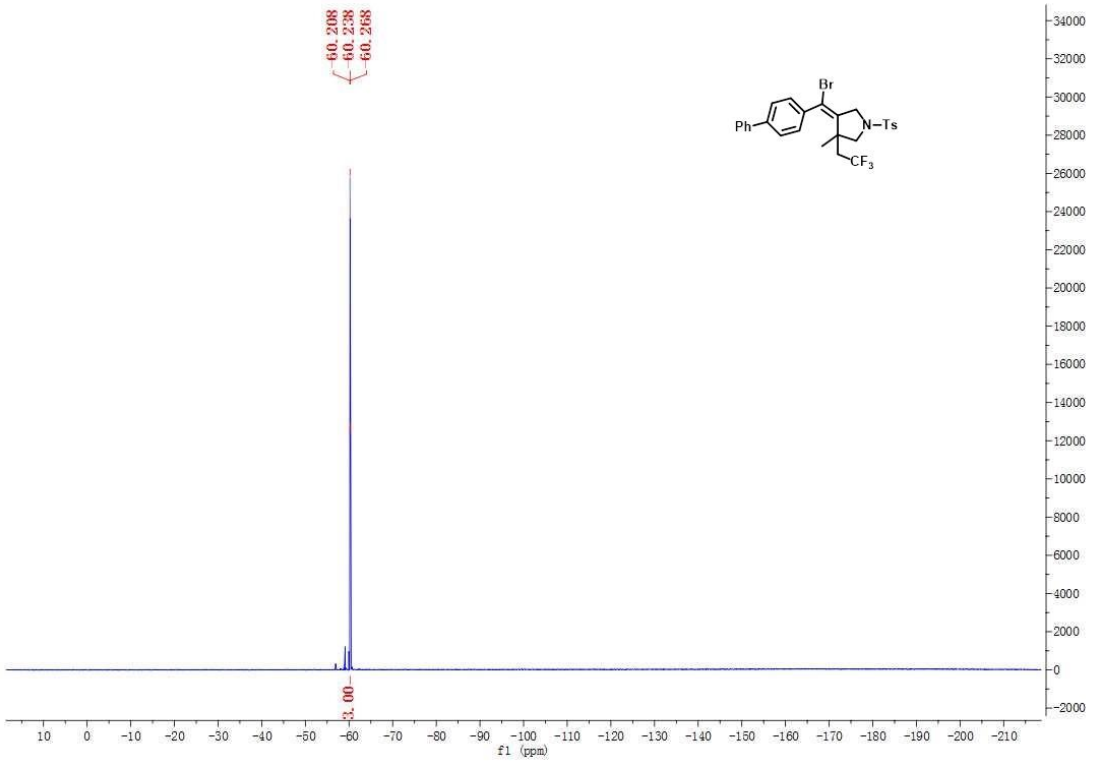

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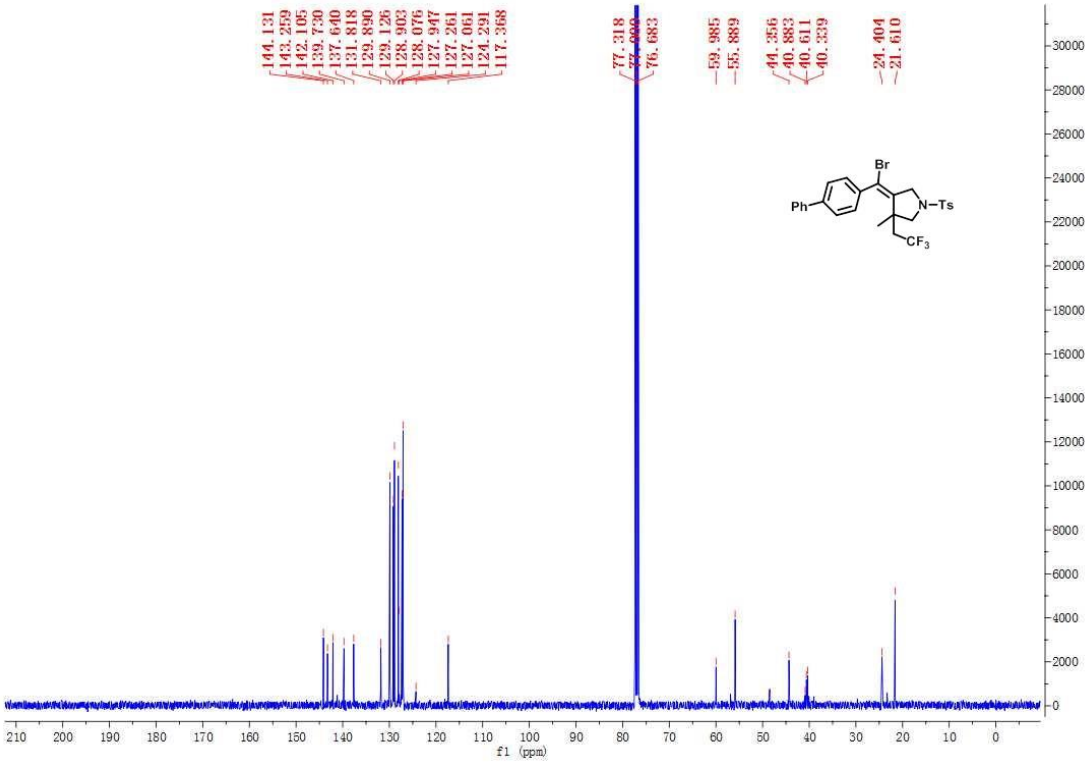

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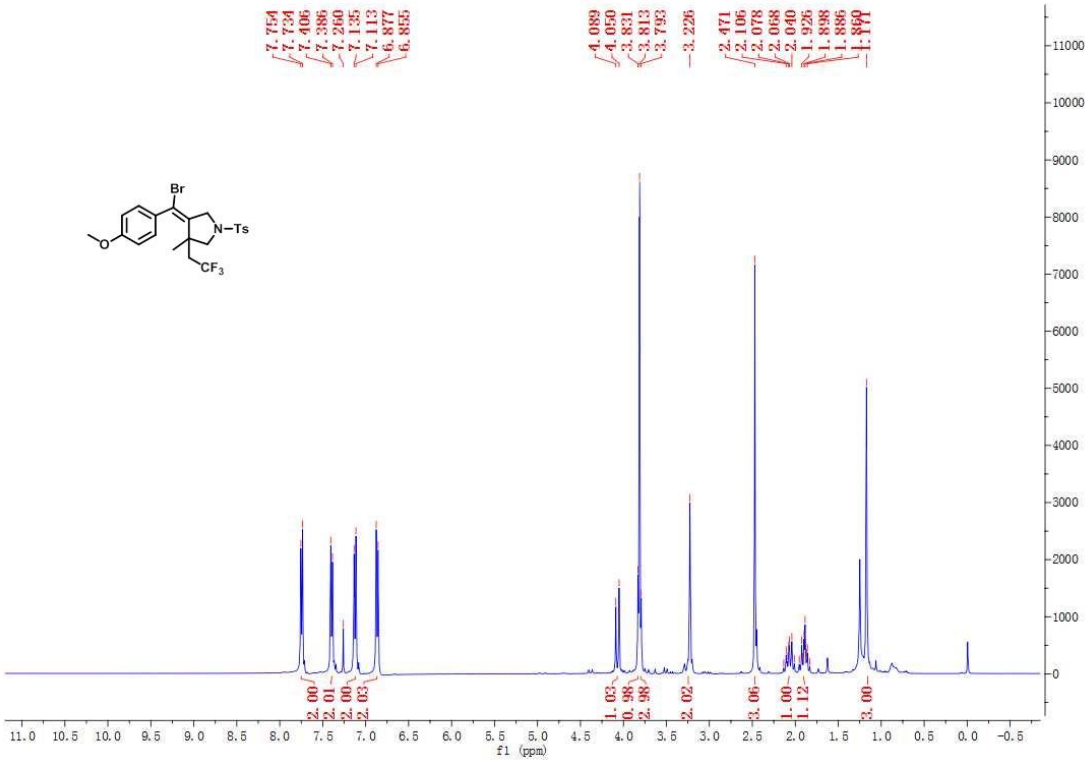

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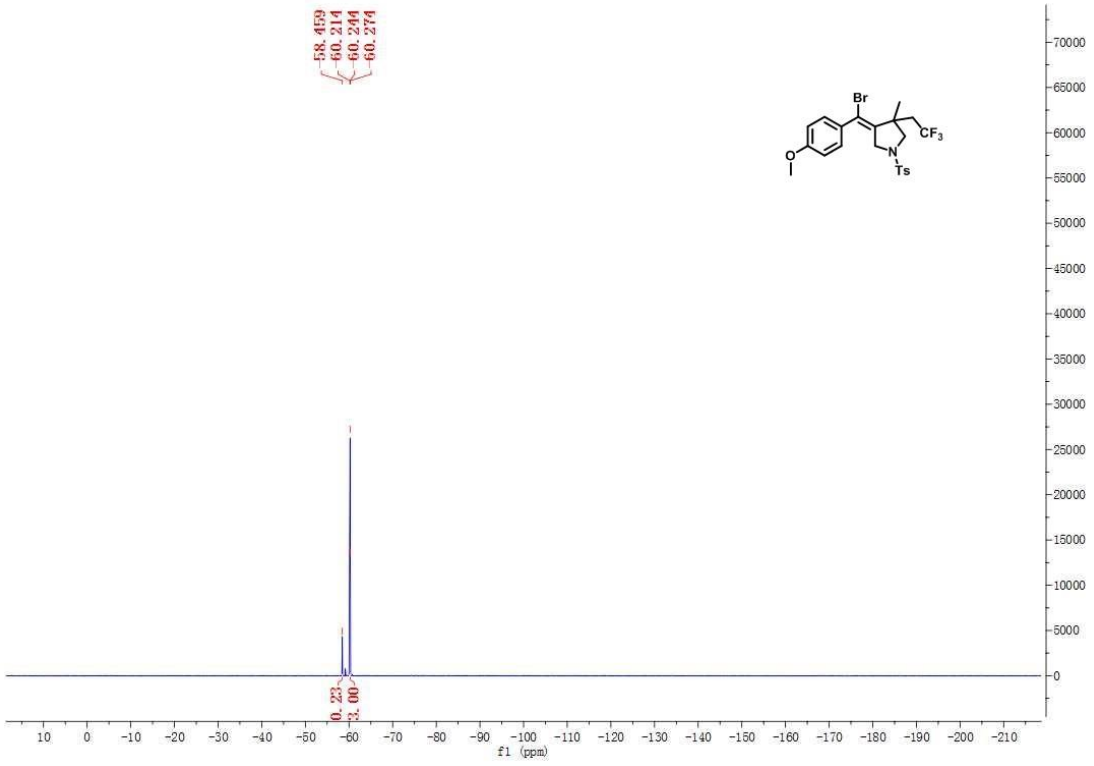

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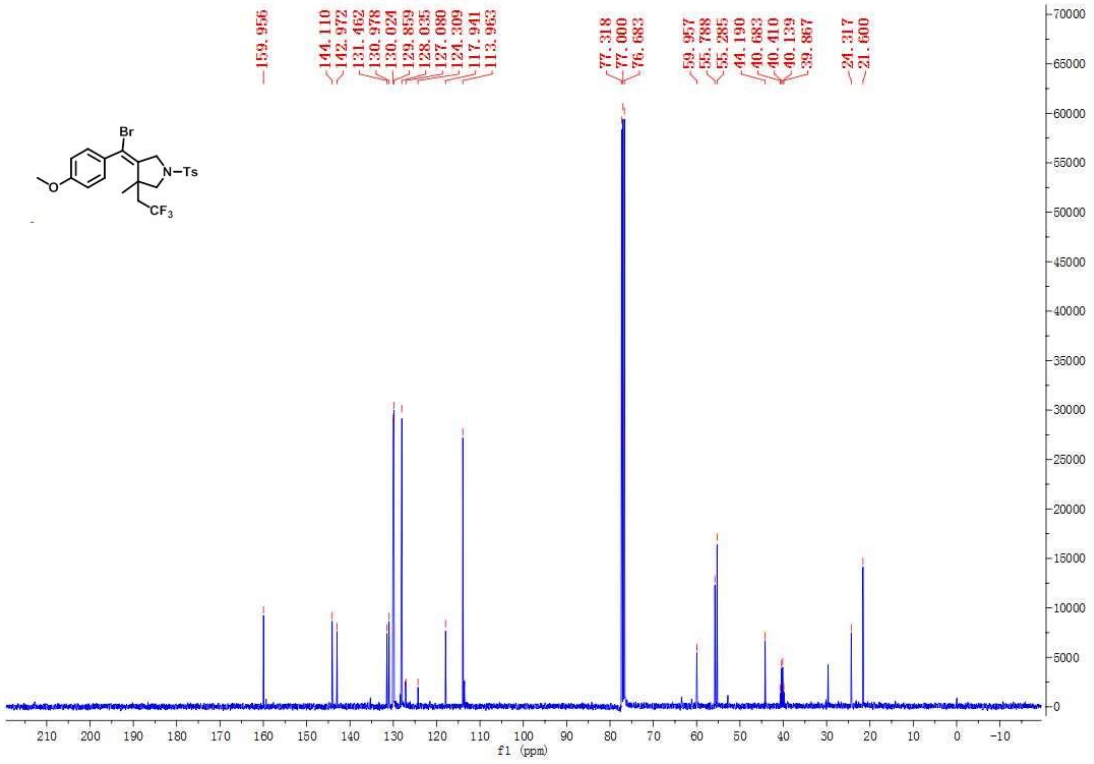

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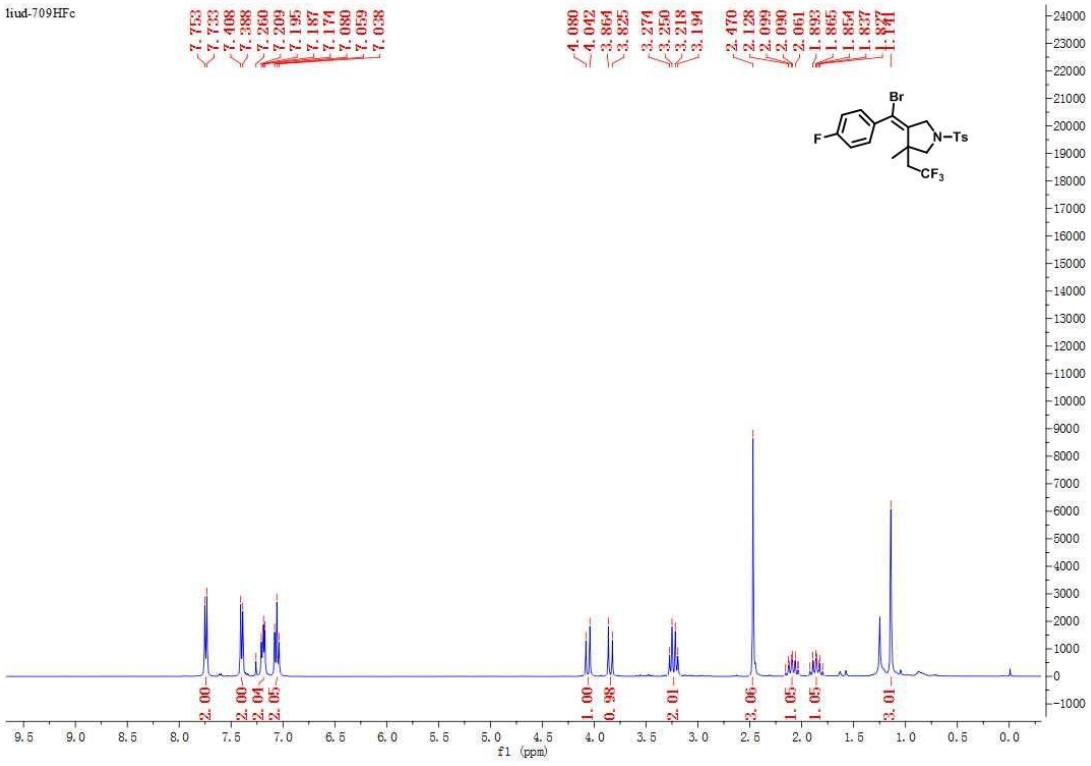

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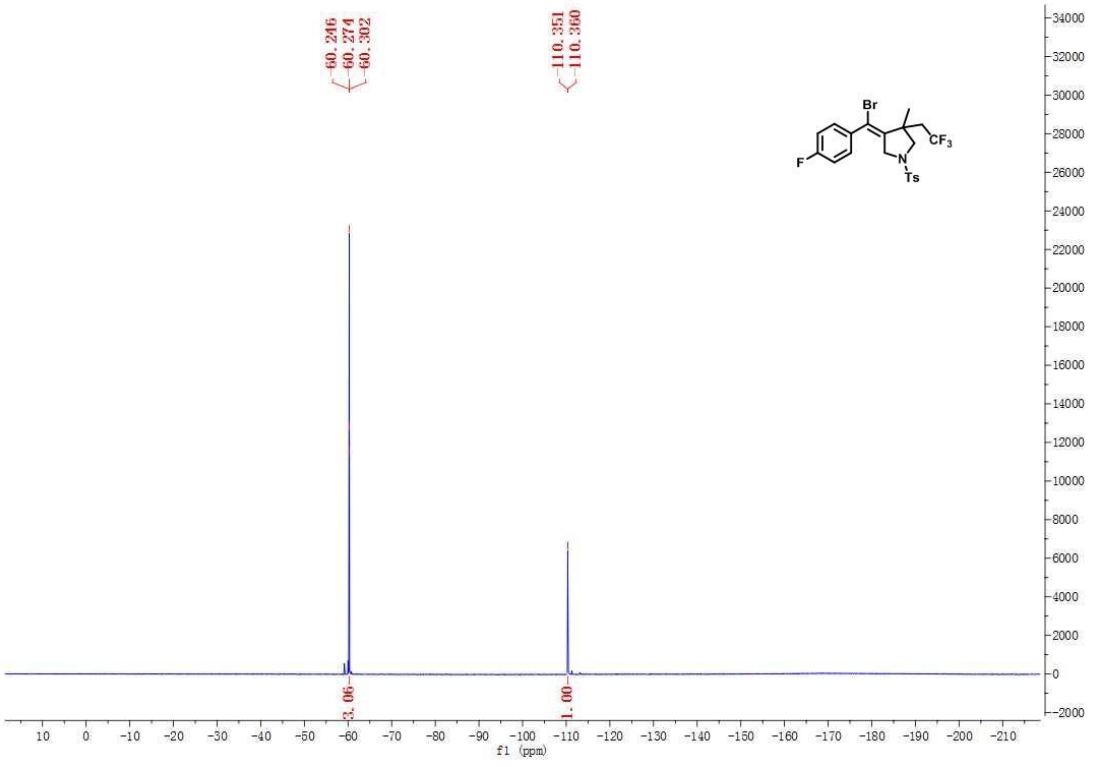

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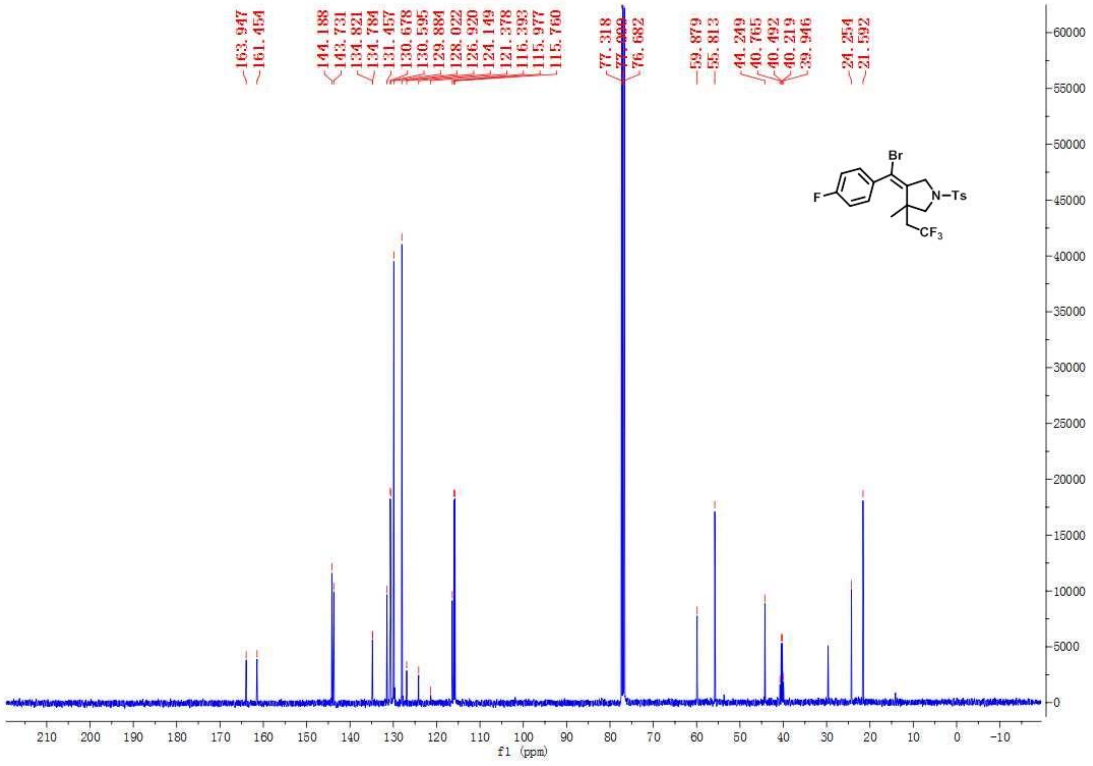
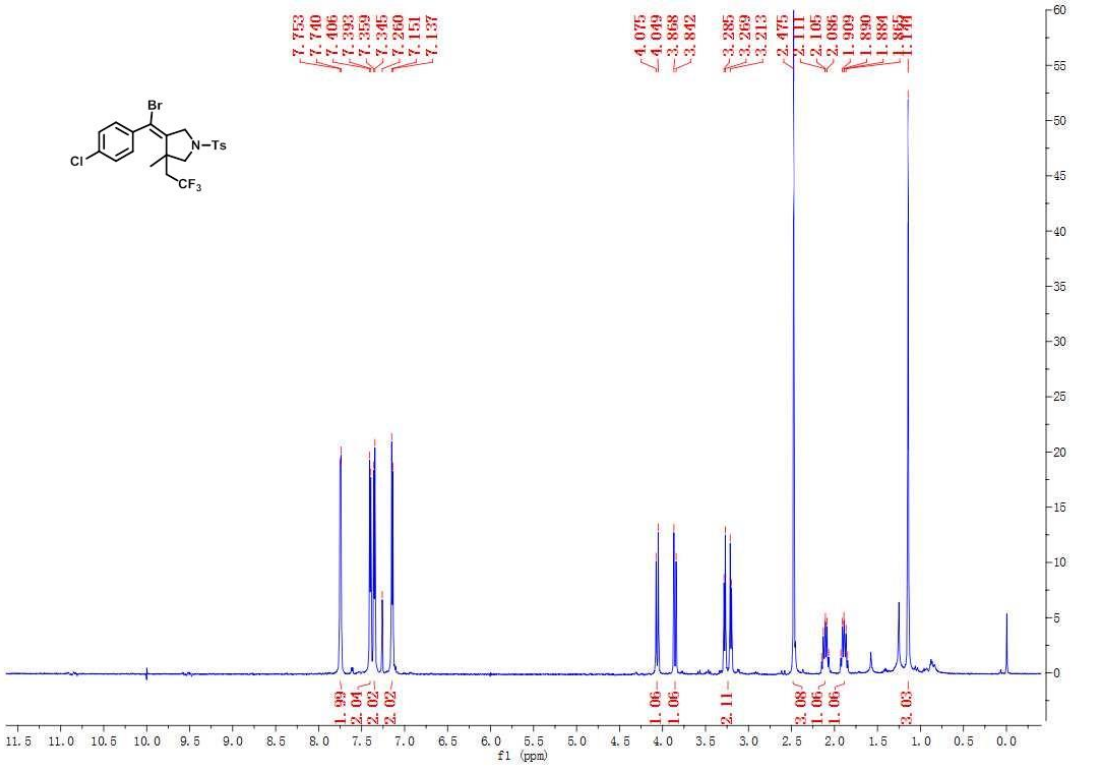


8. ^{1}H NMR



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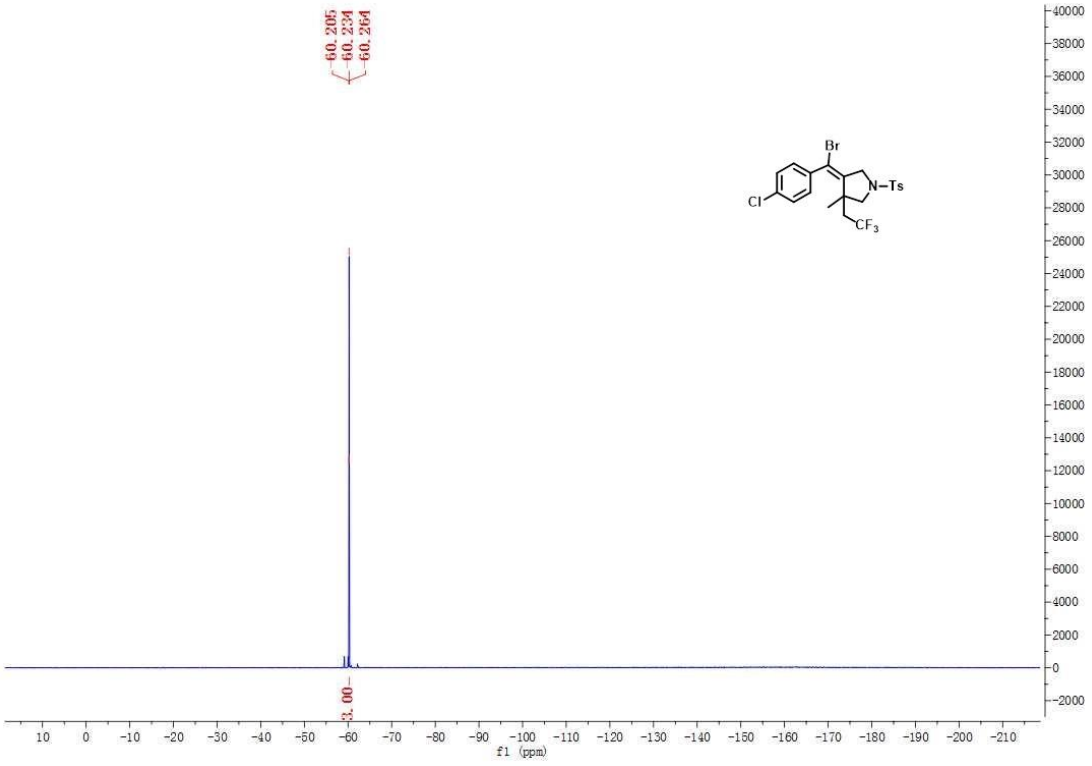

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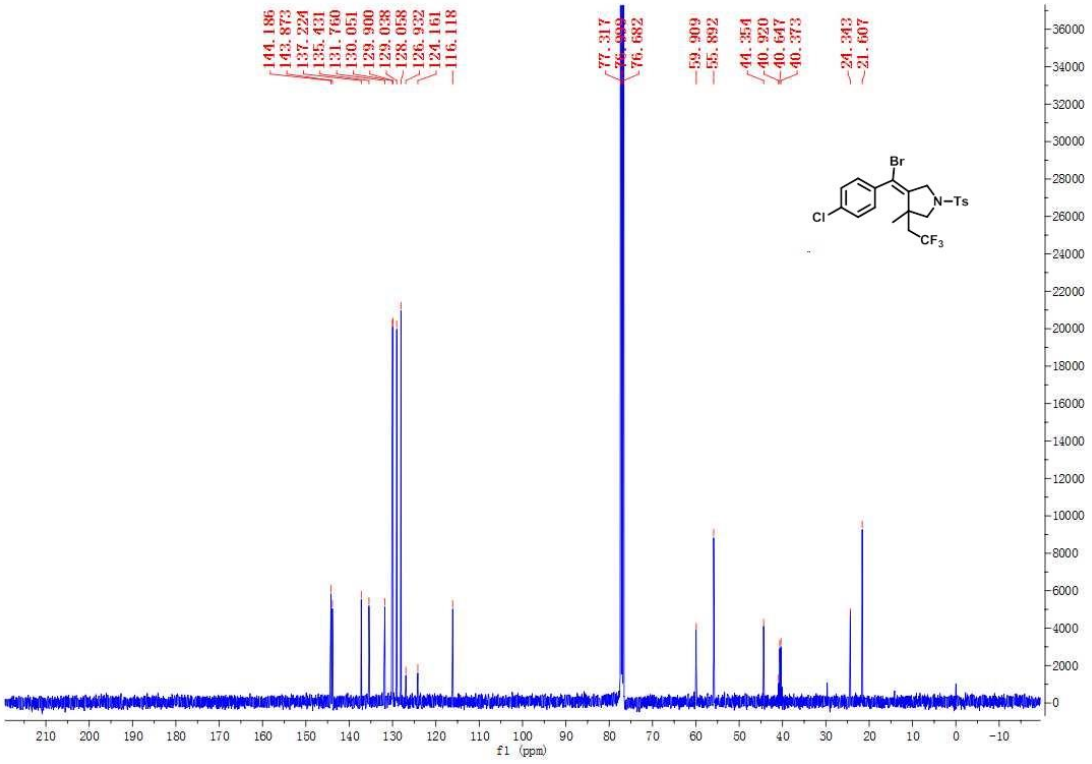

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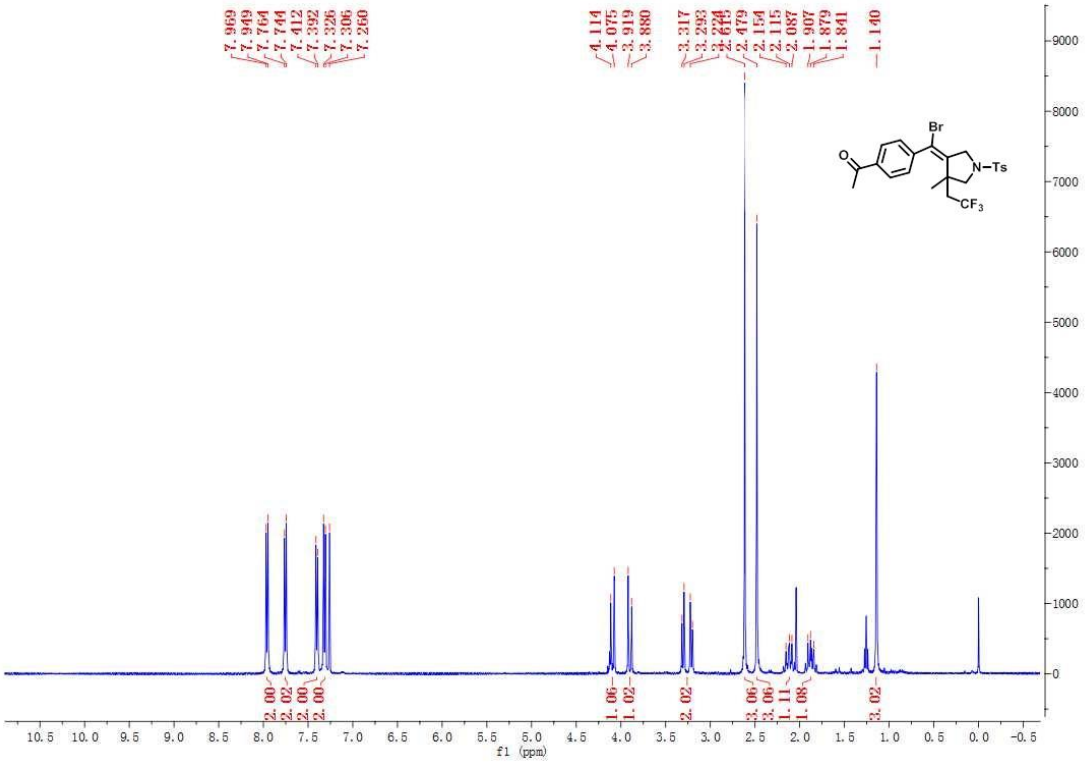

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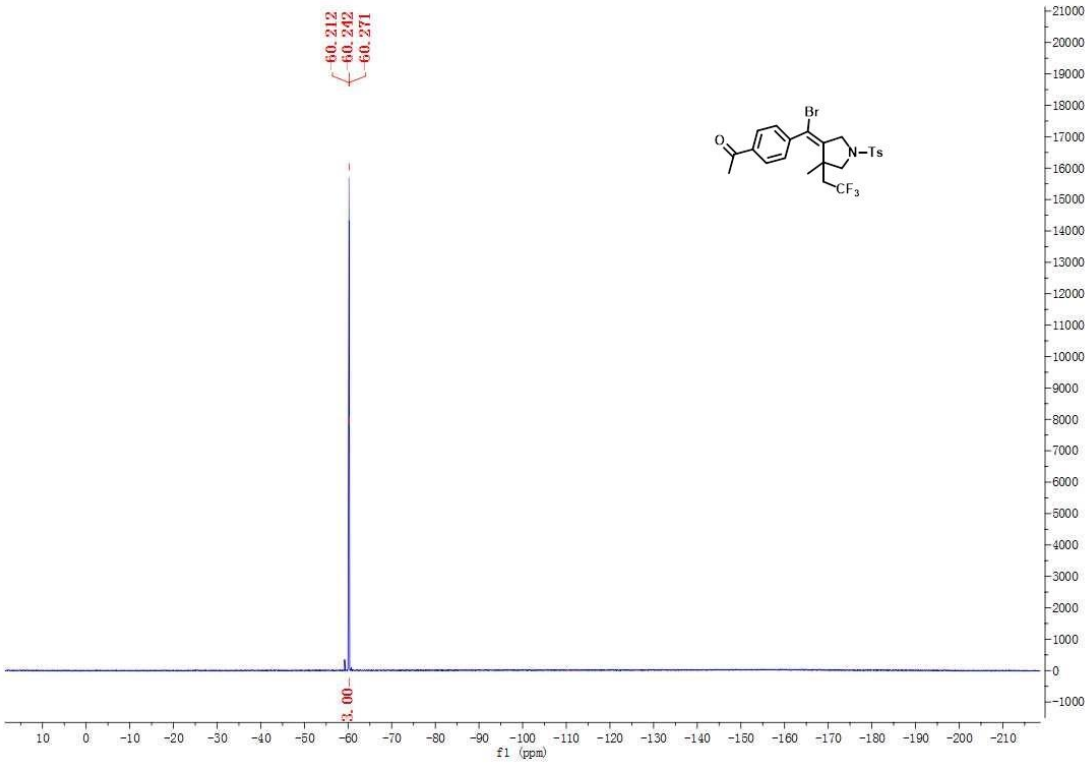

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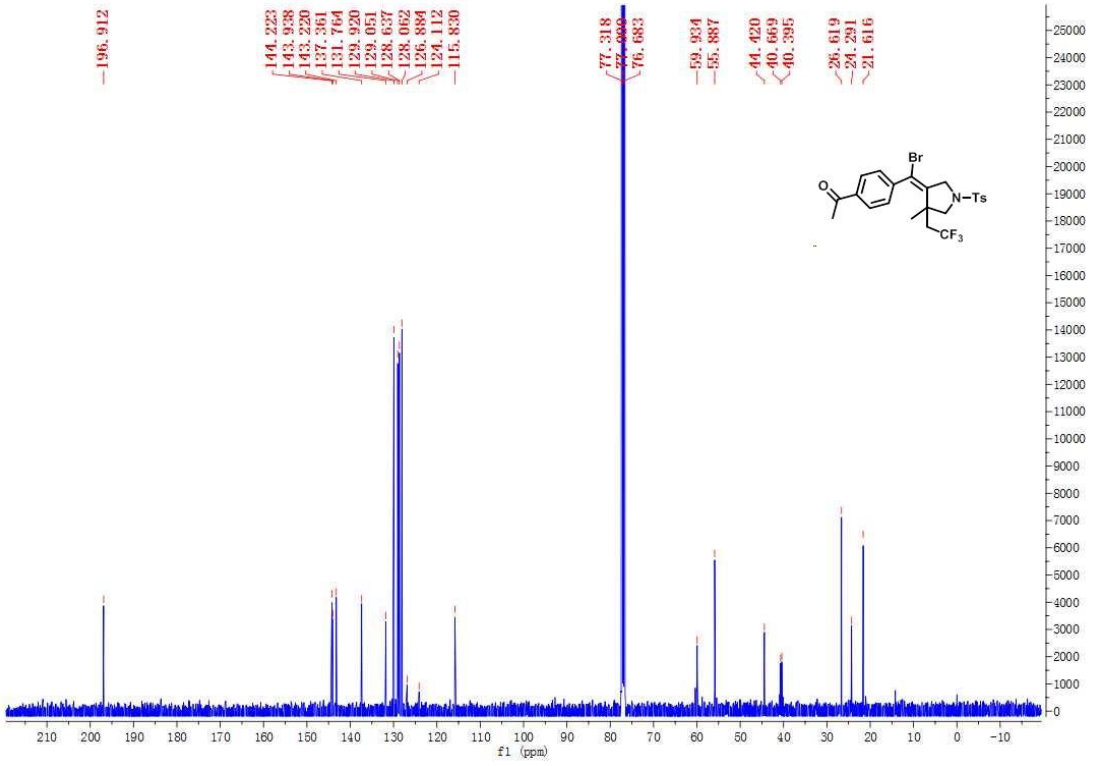

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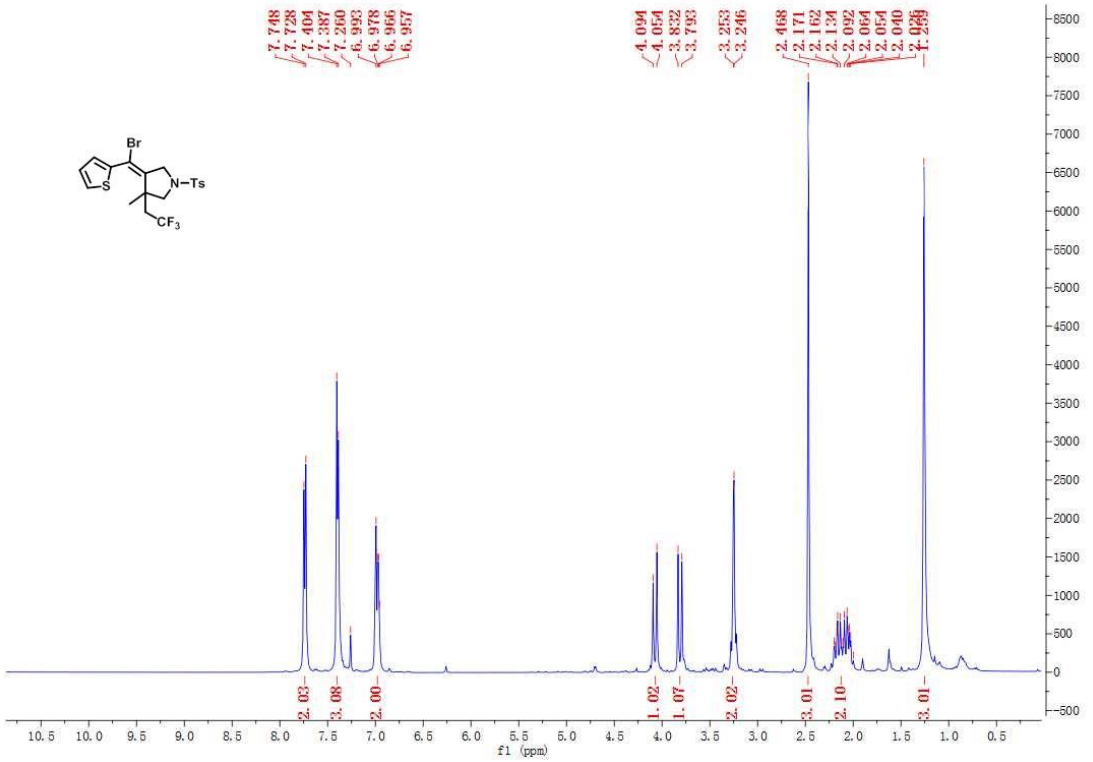

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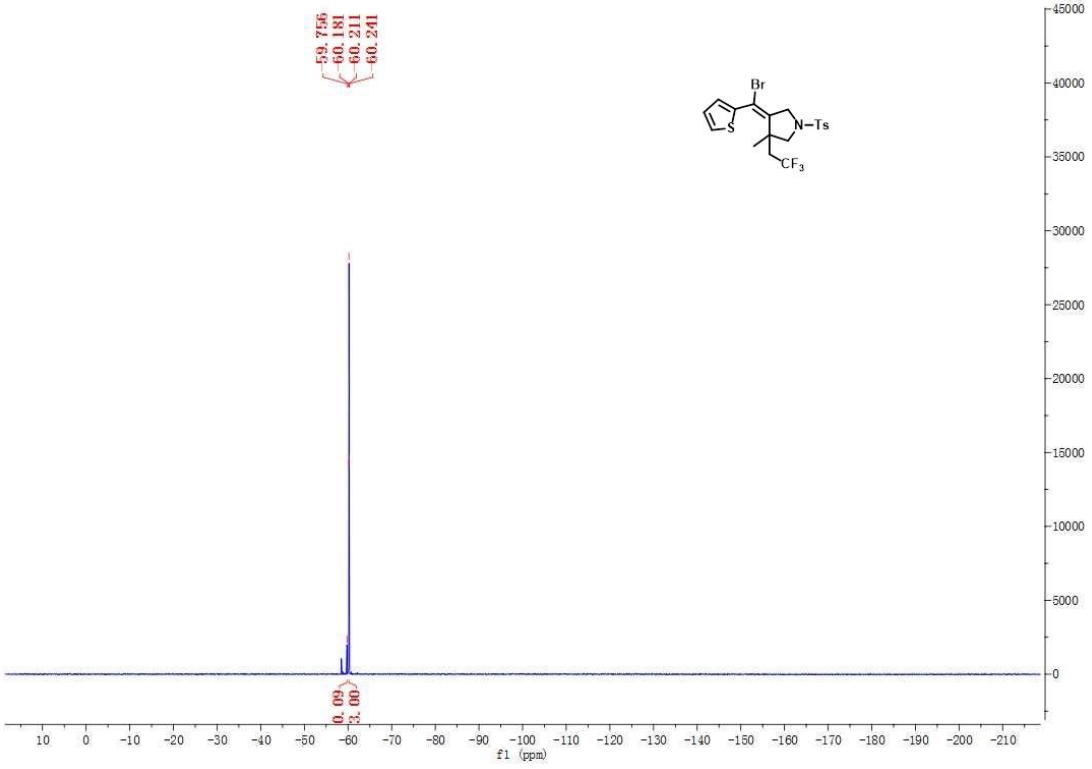

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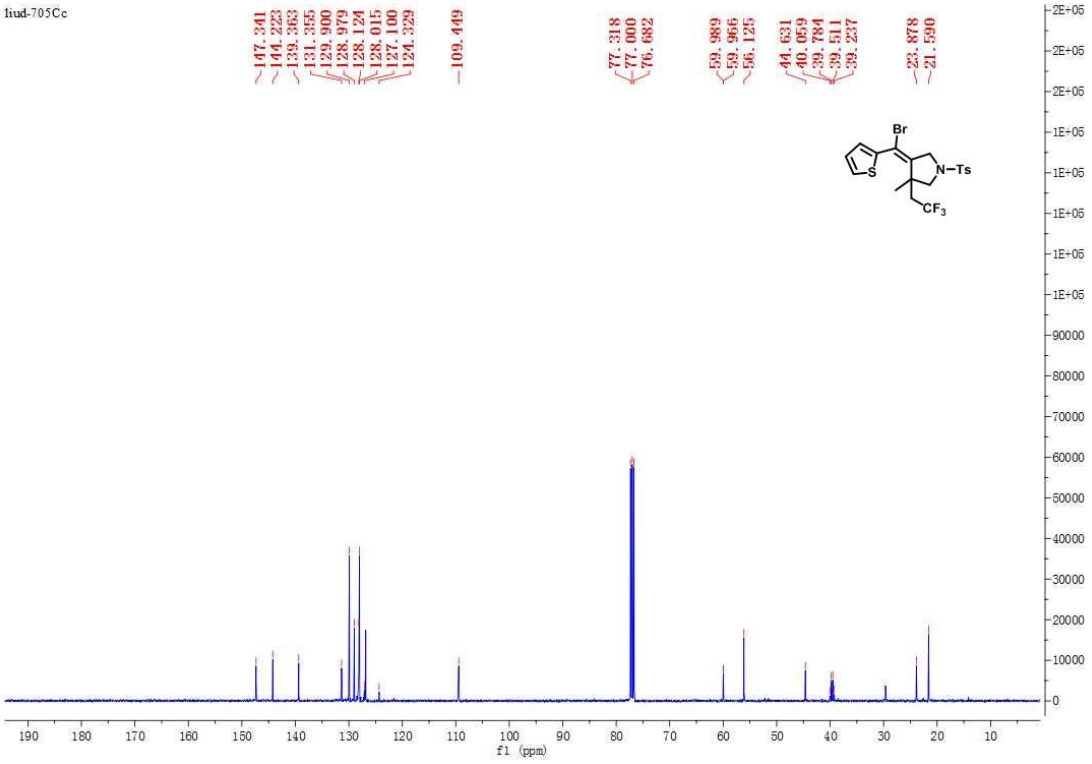
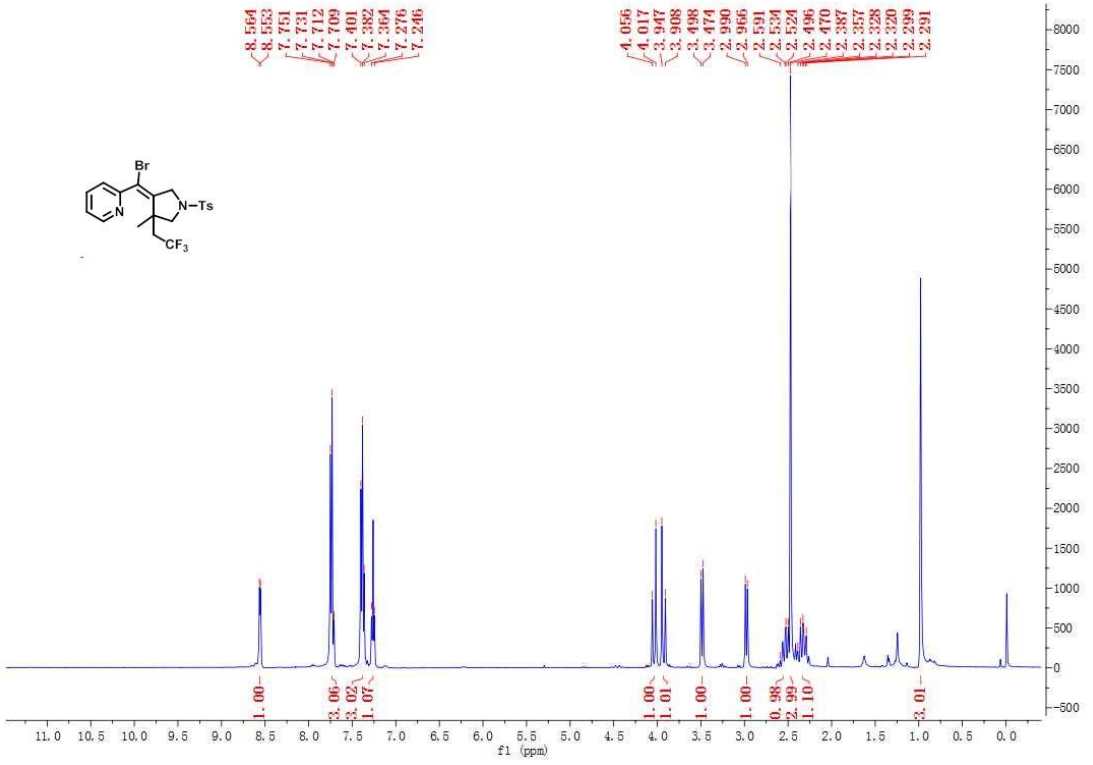


11. ^{1}H NMR



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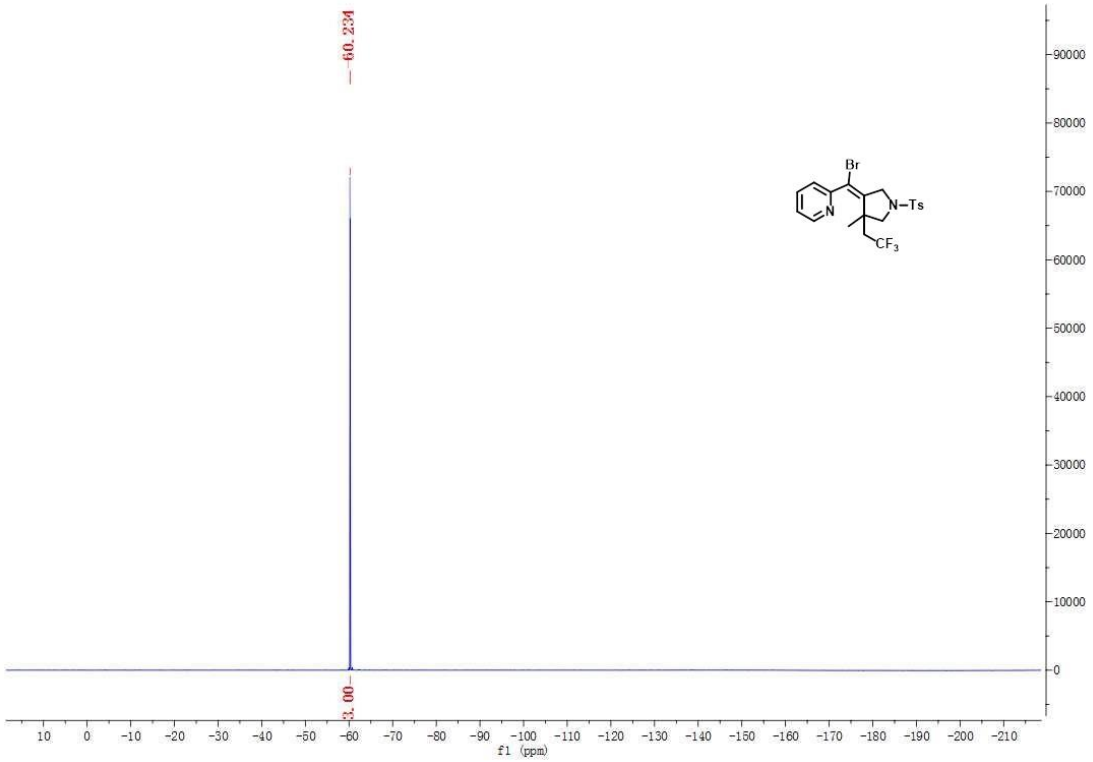

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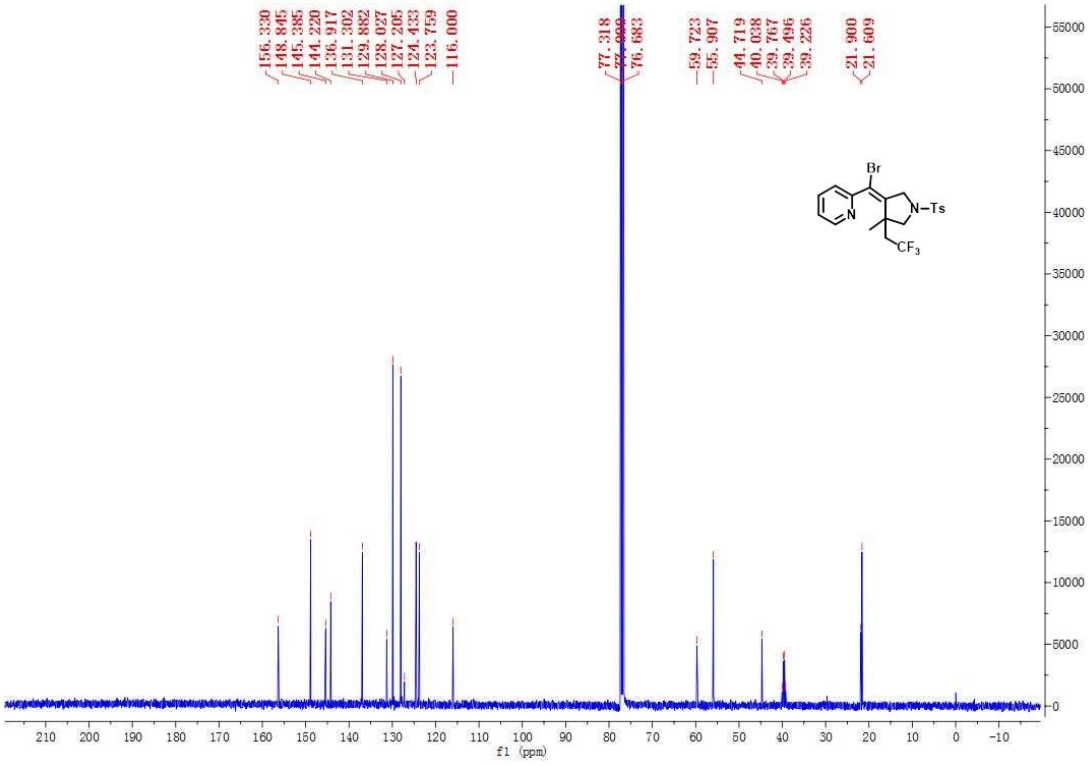

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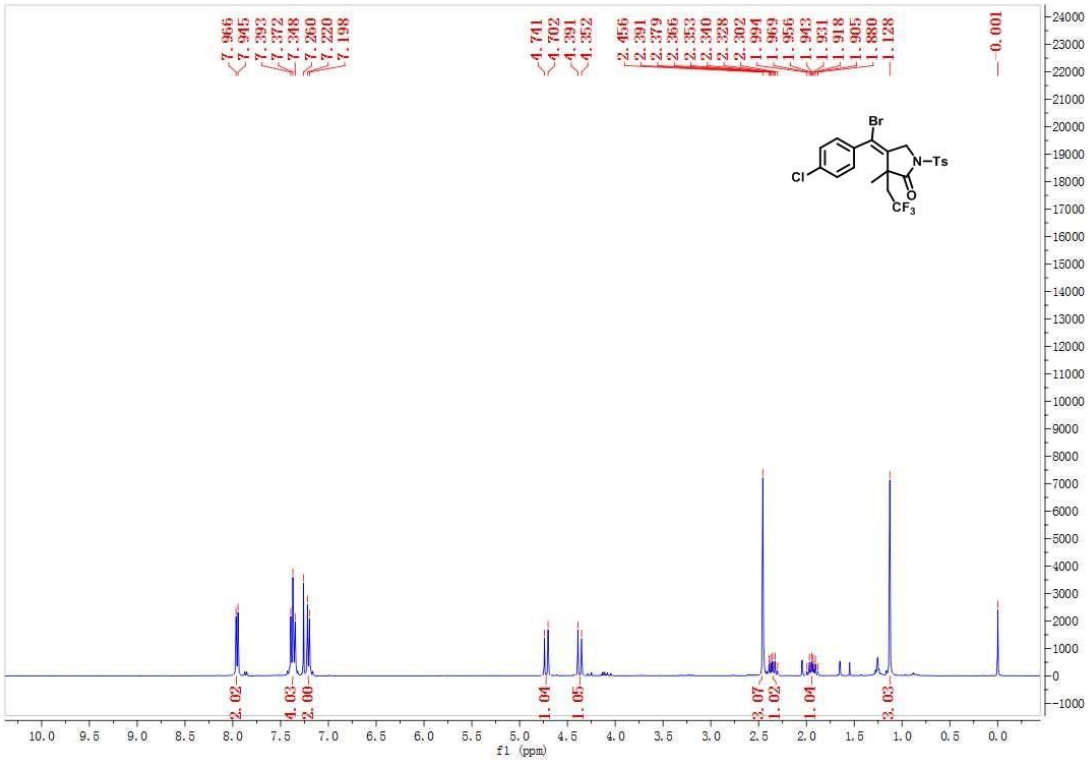

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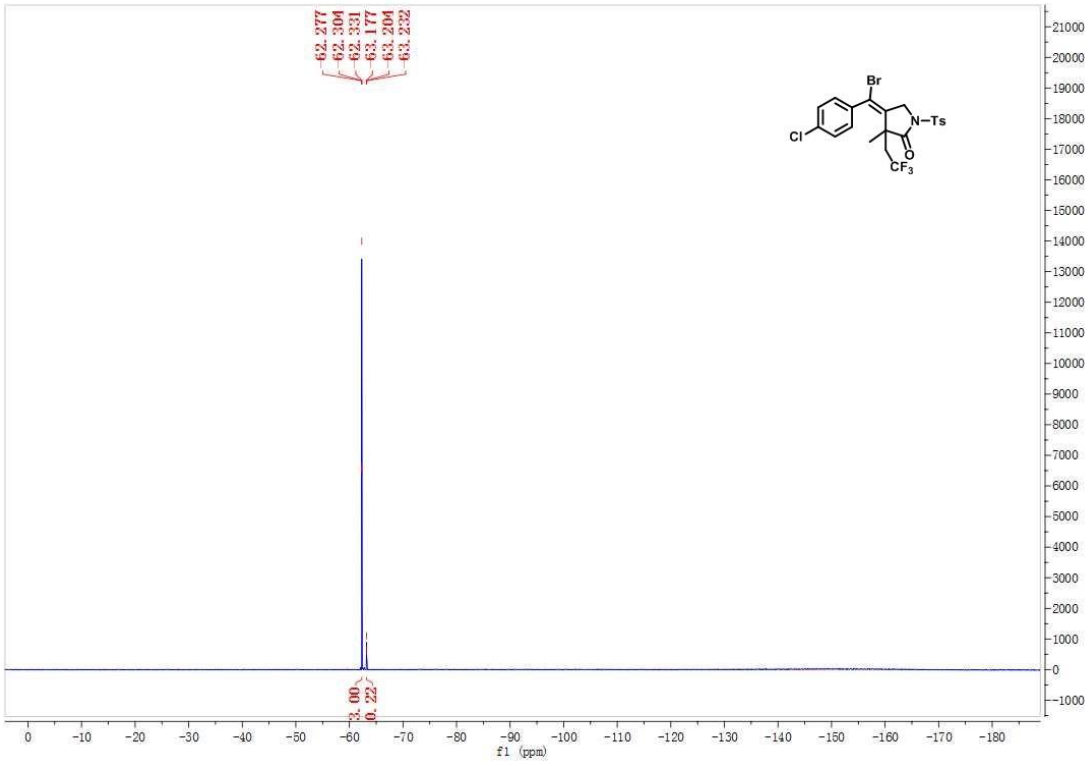

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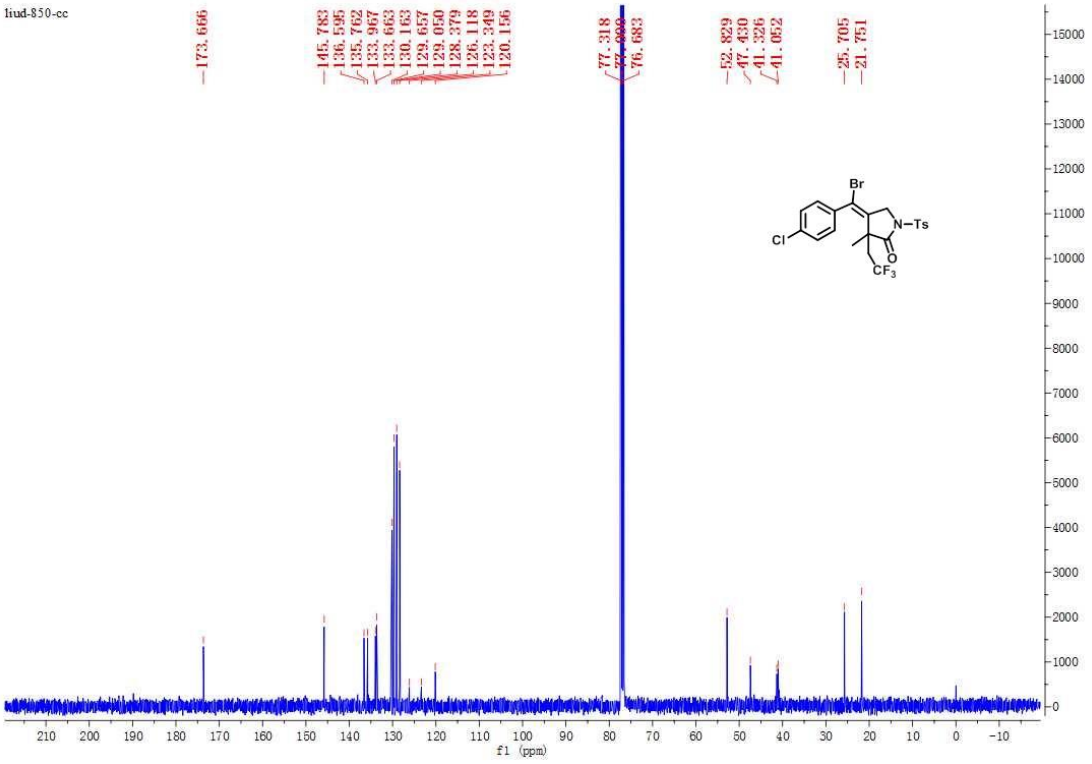

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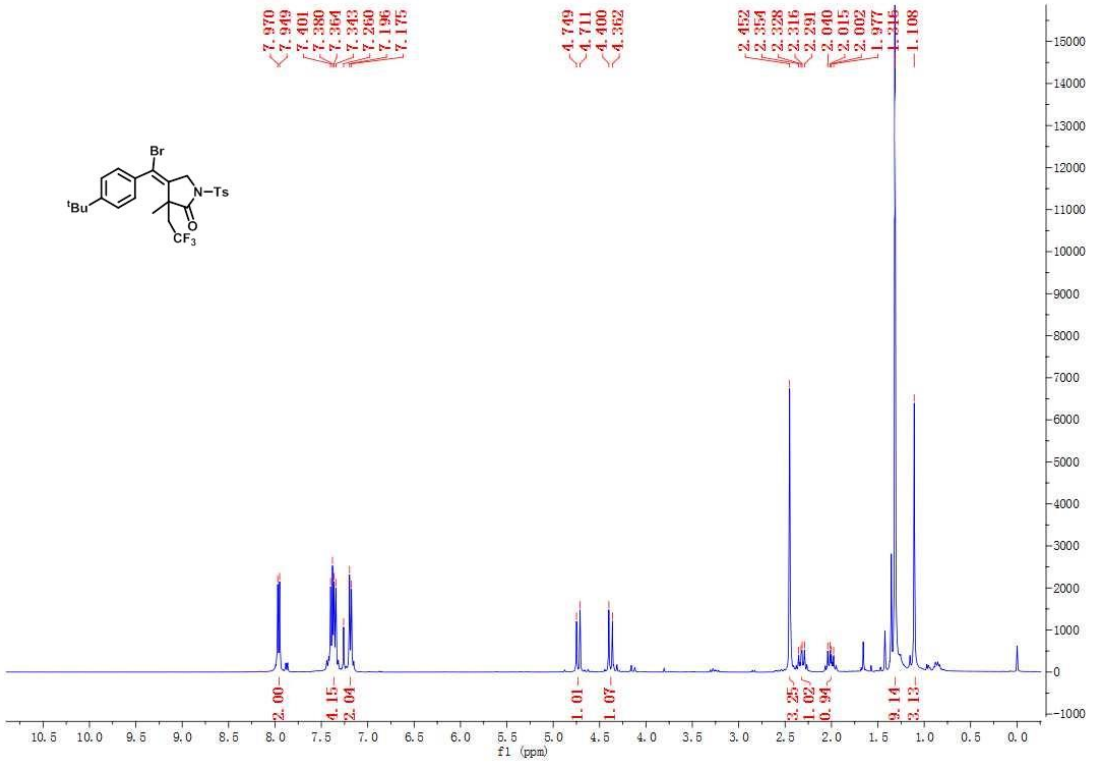

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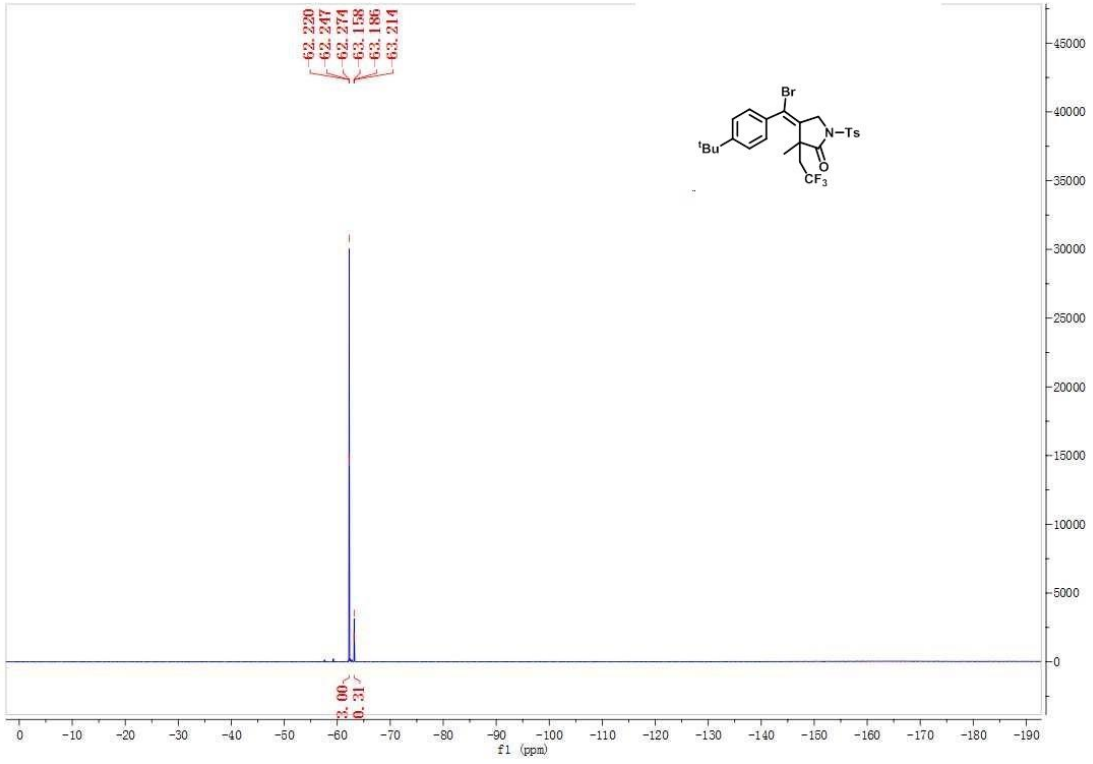

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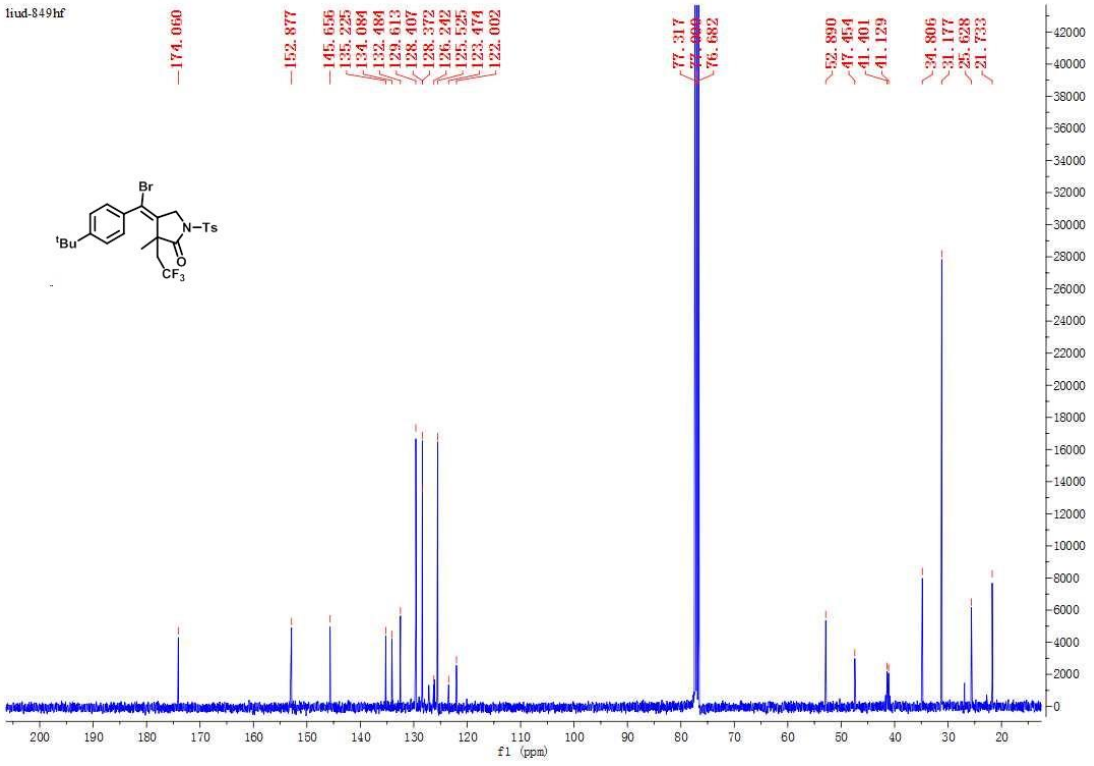

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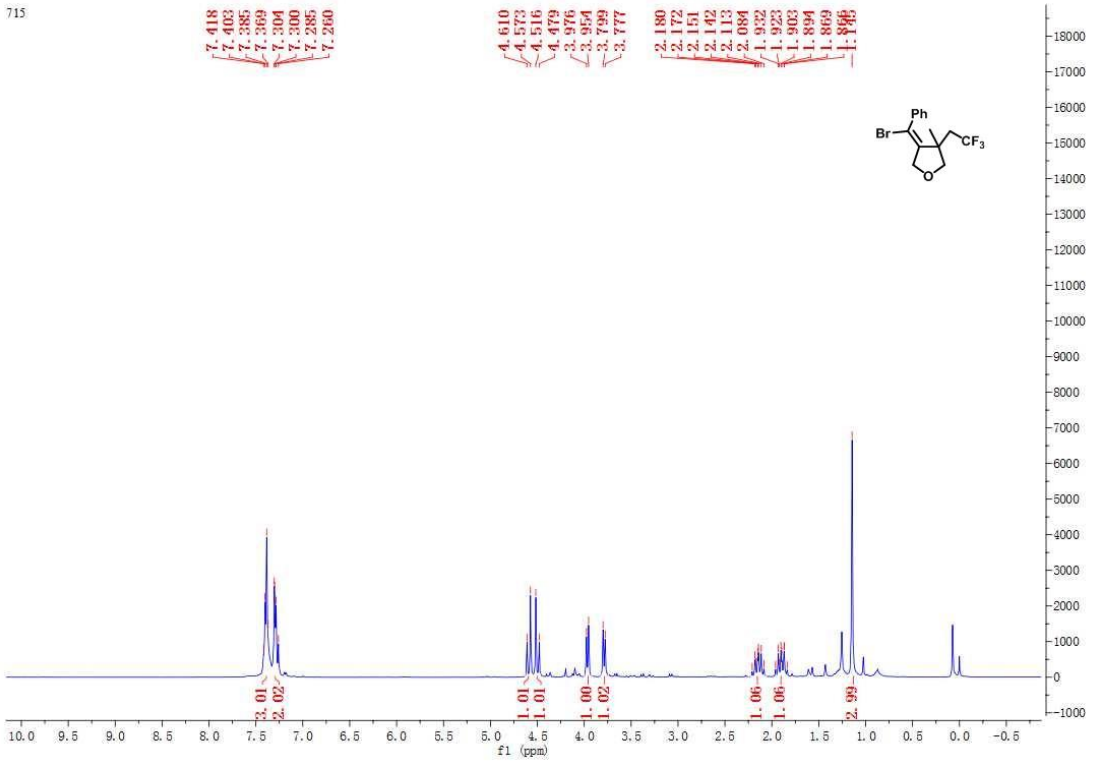

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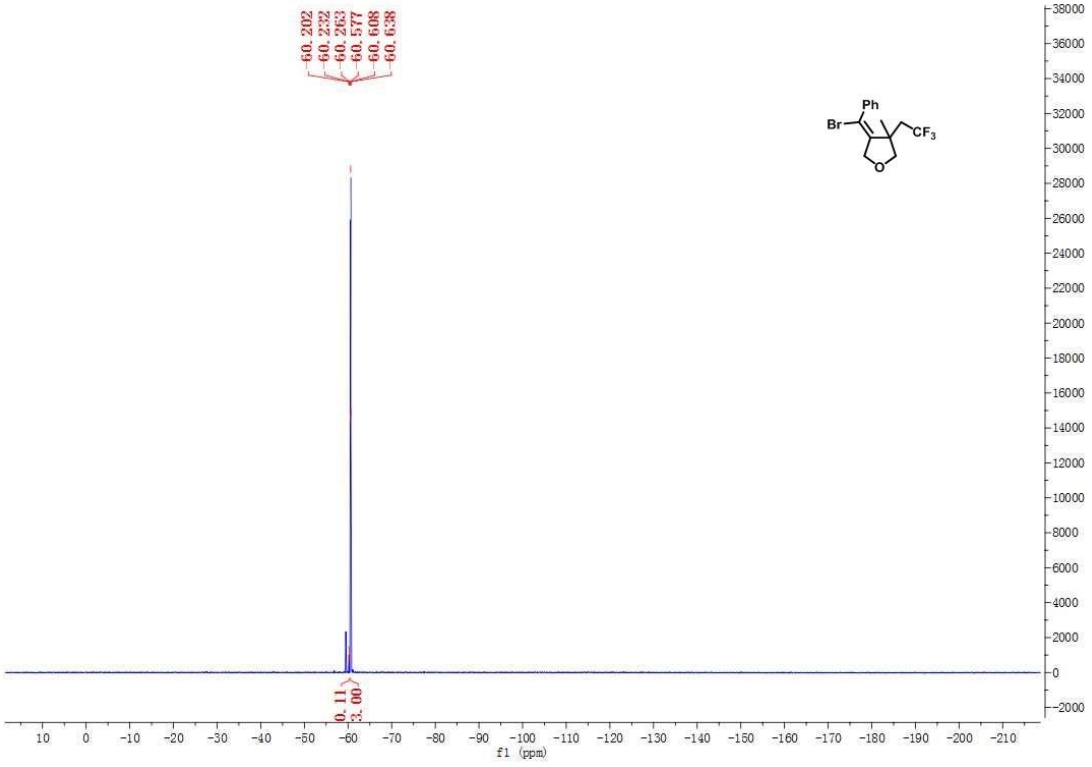

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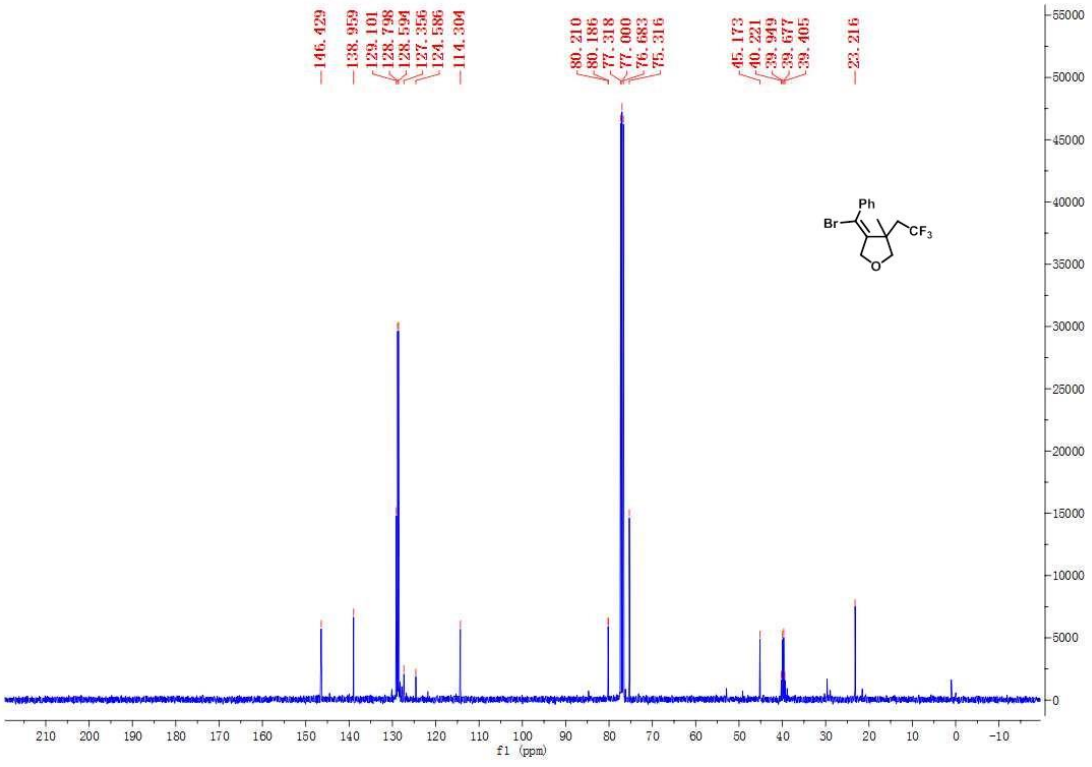

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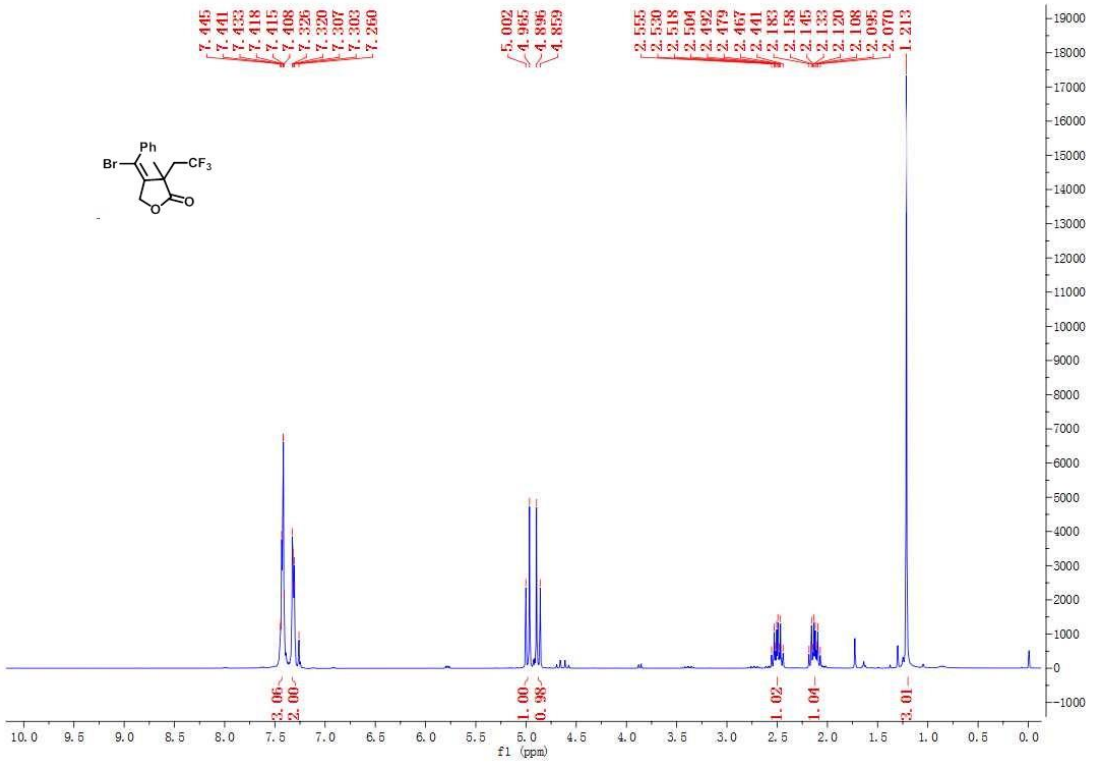

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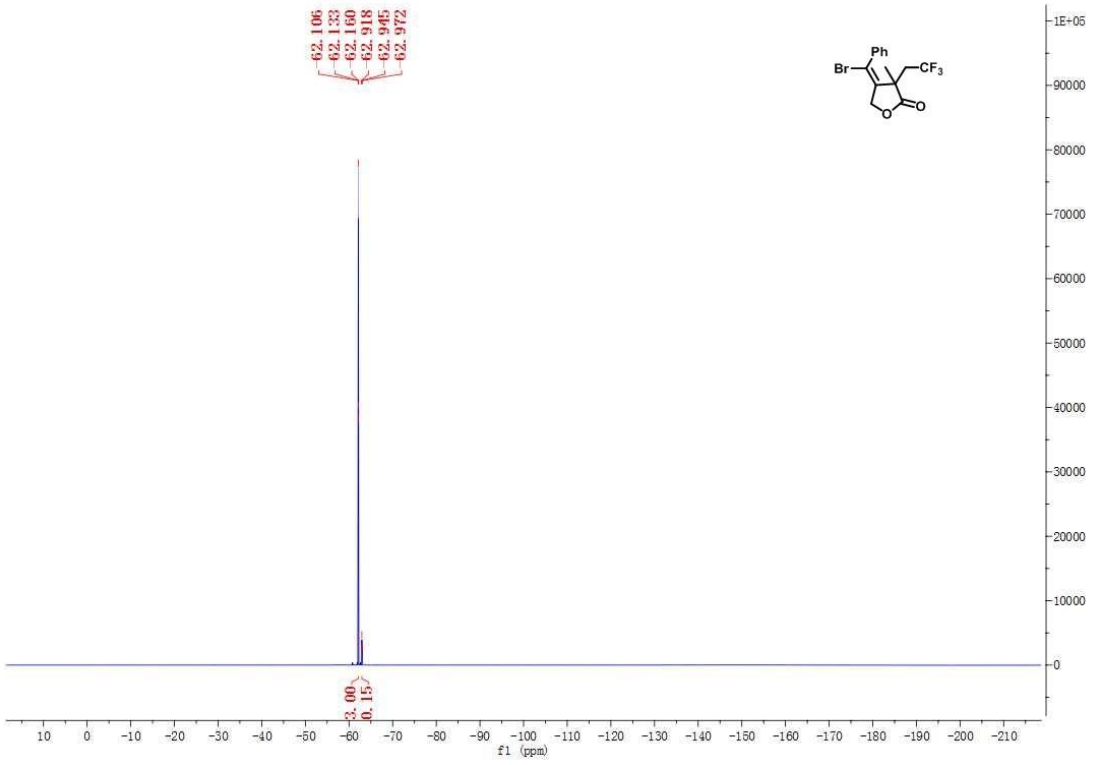

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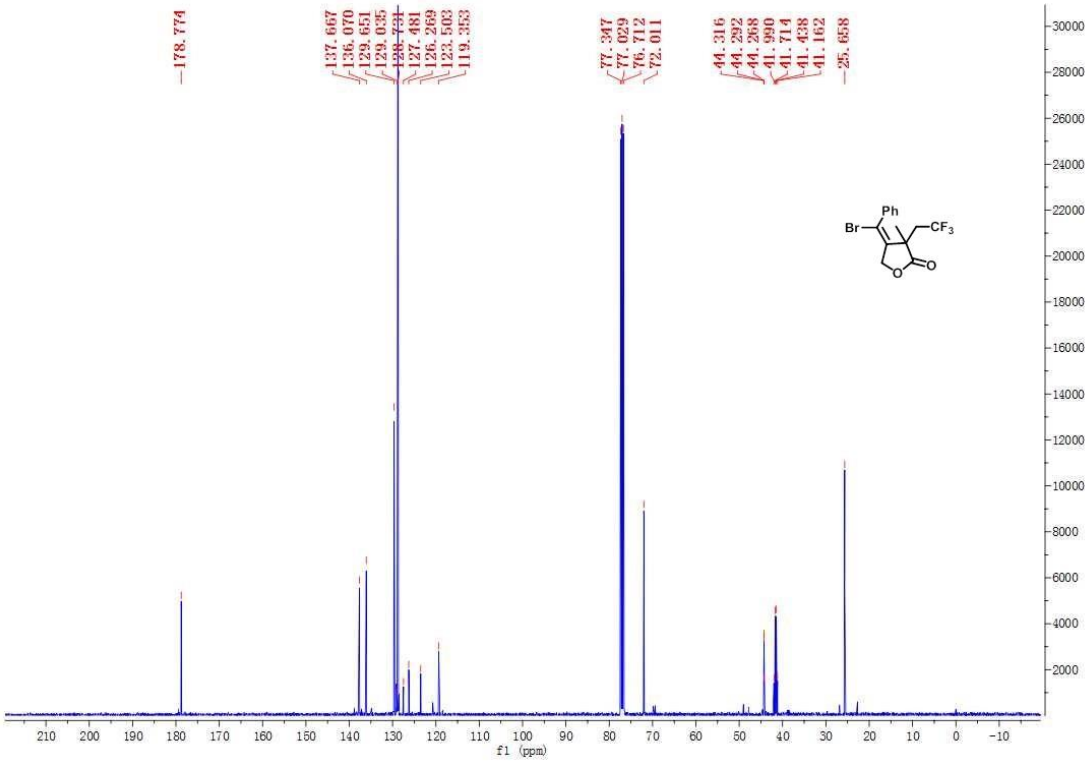

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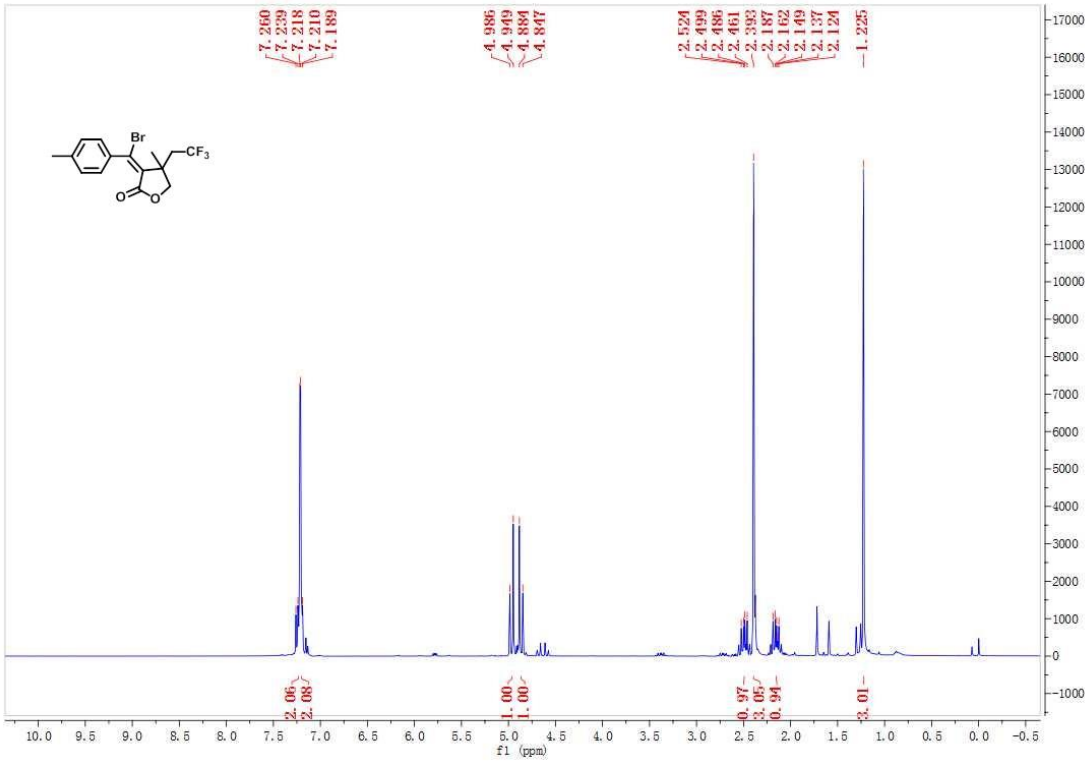

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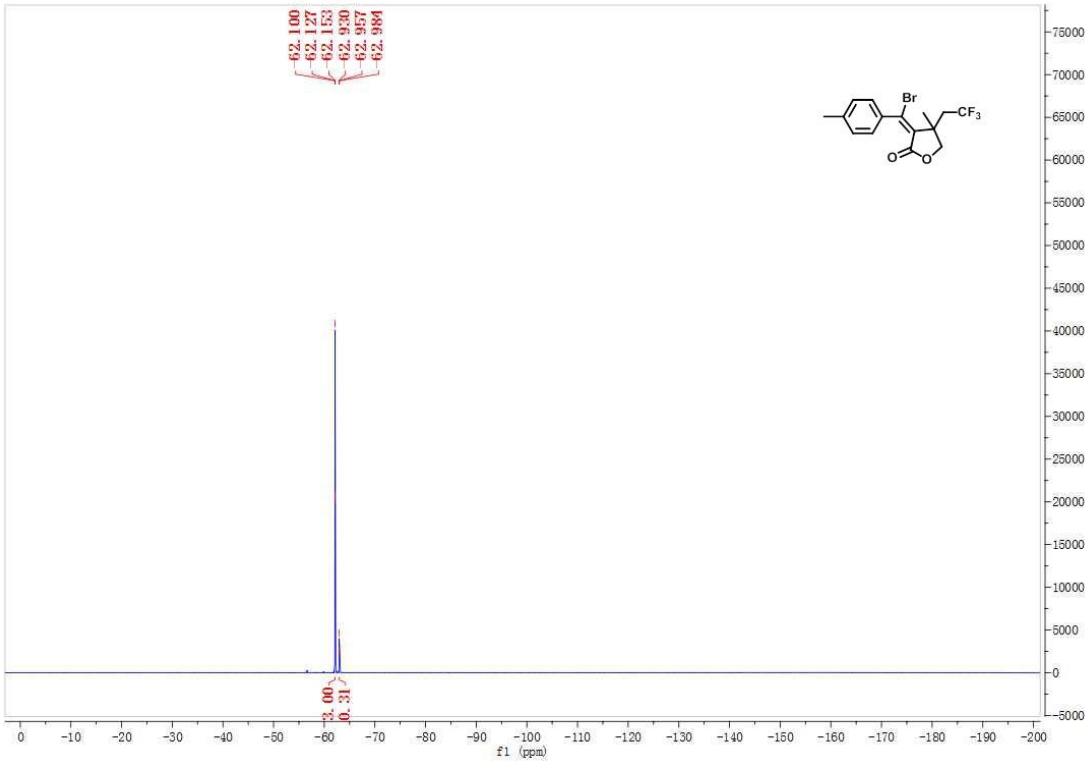

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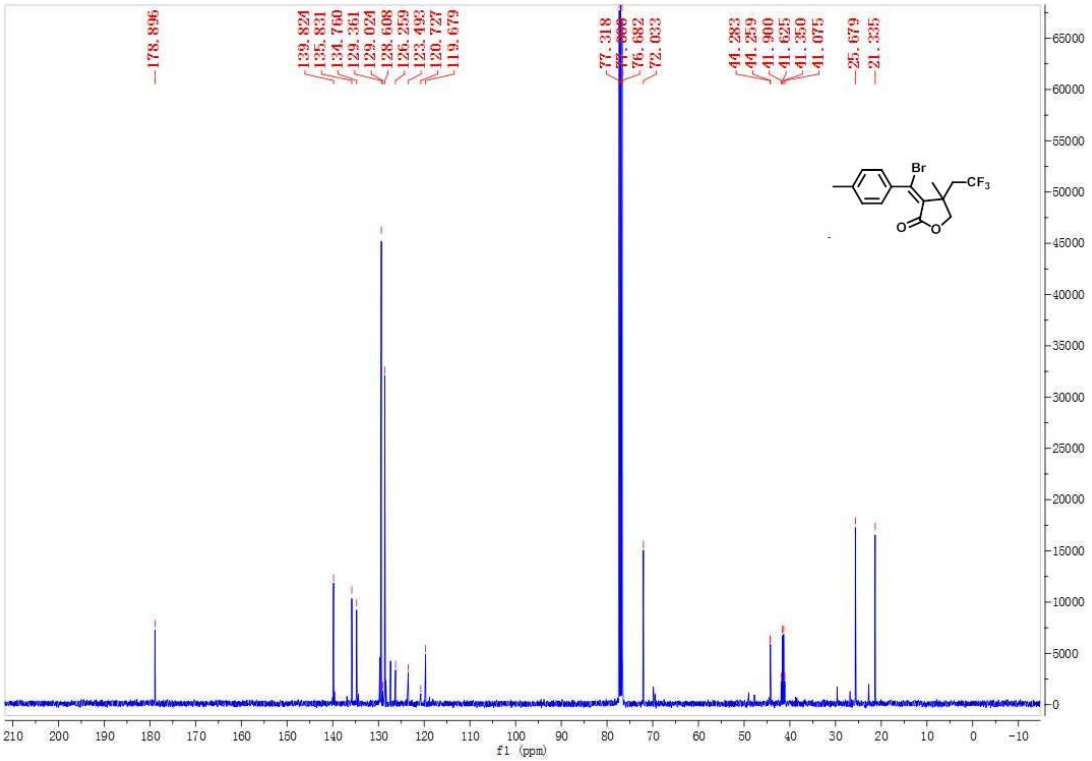
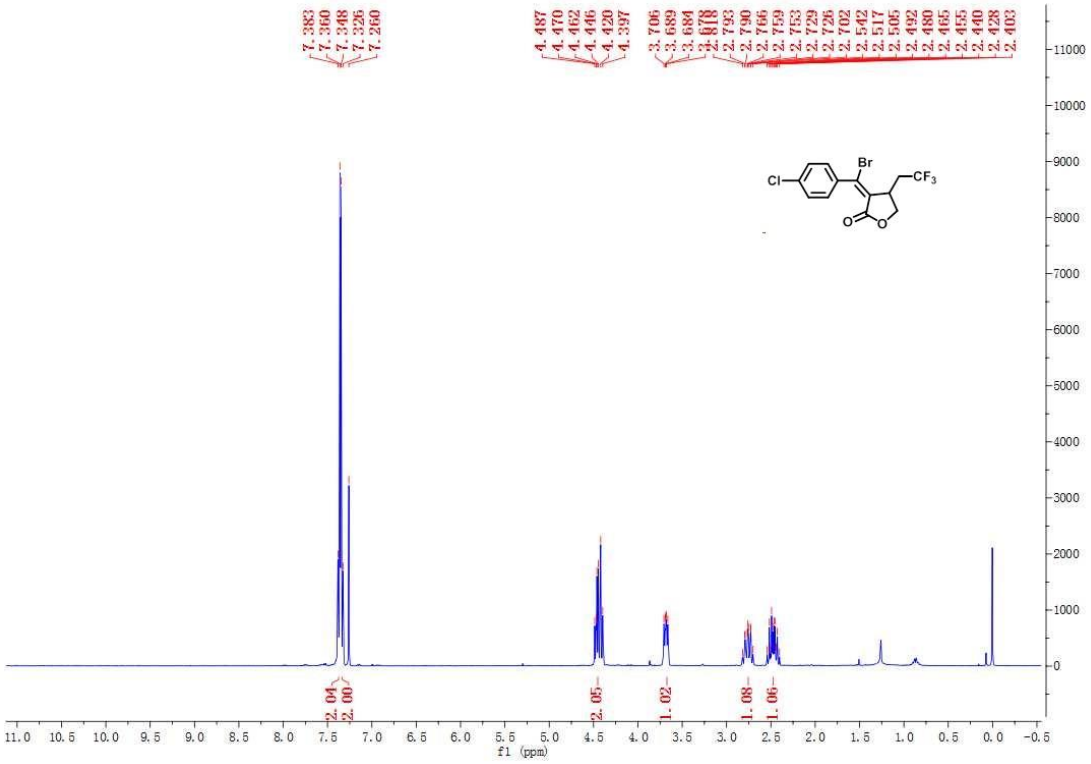


17 ^{1}H NMR



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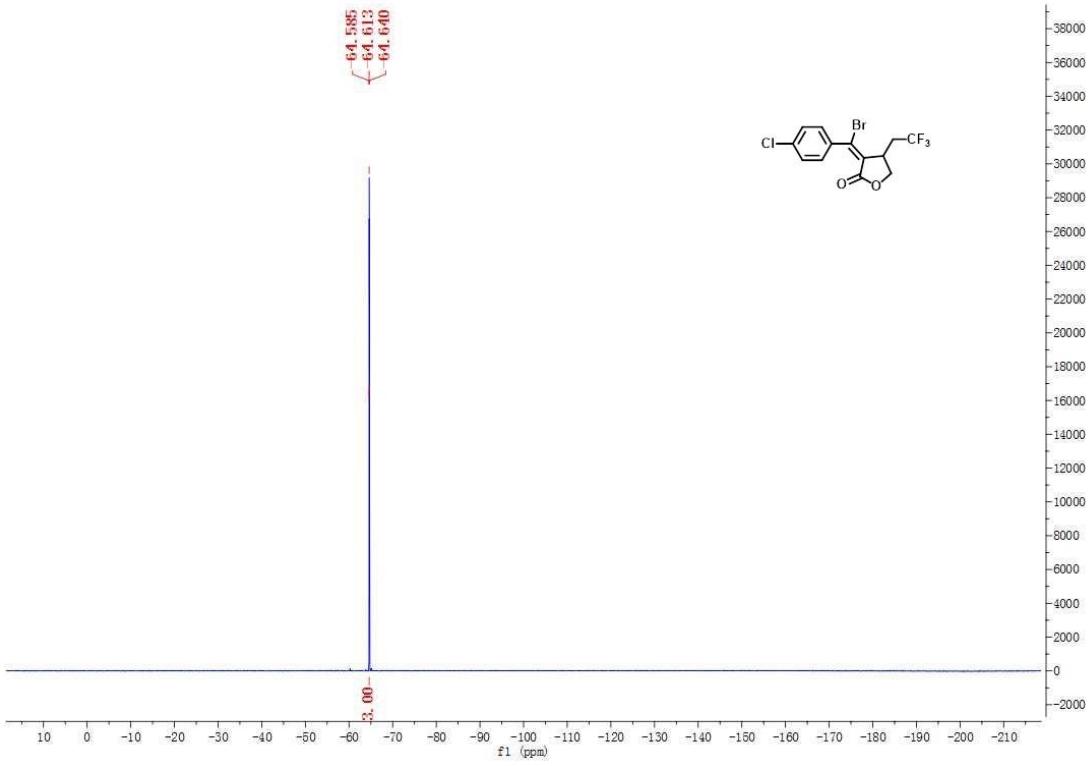

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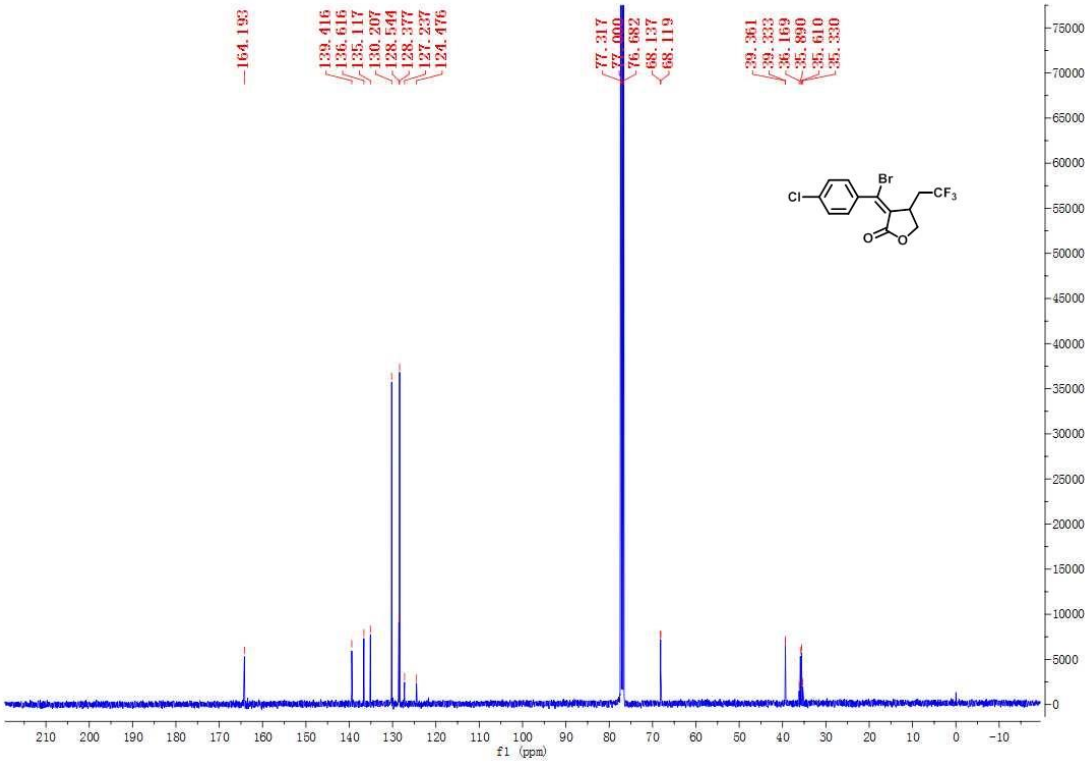

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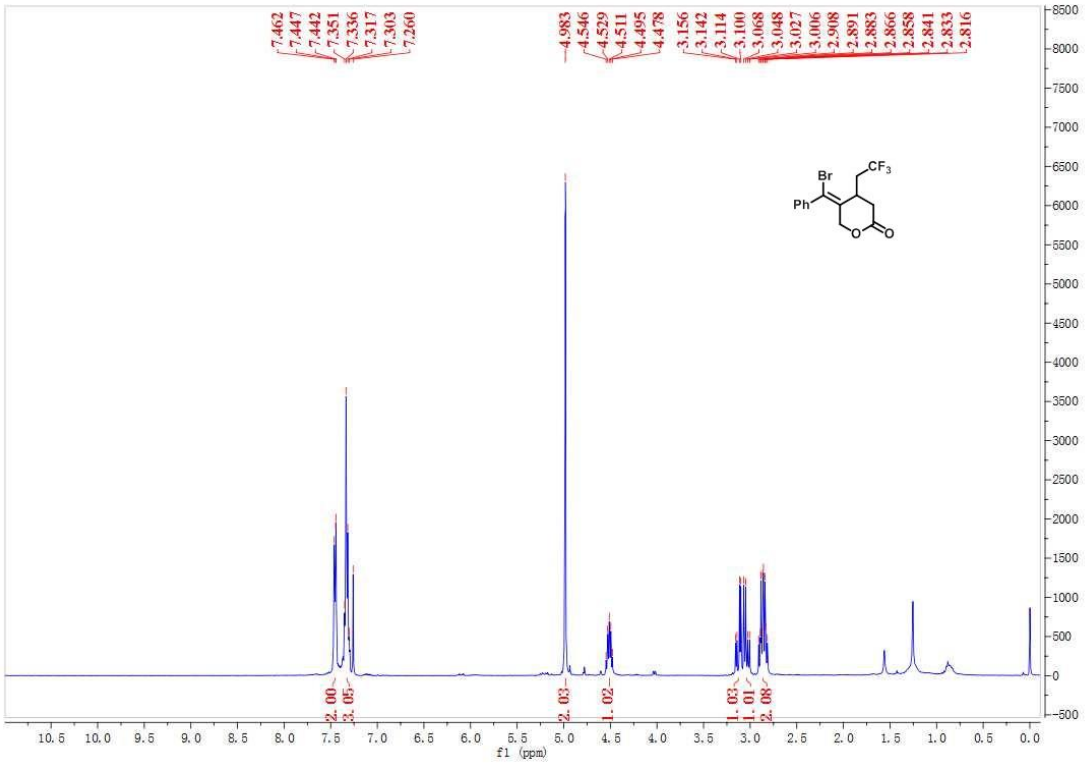

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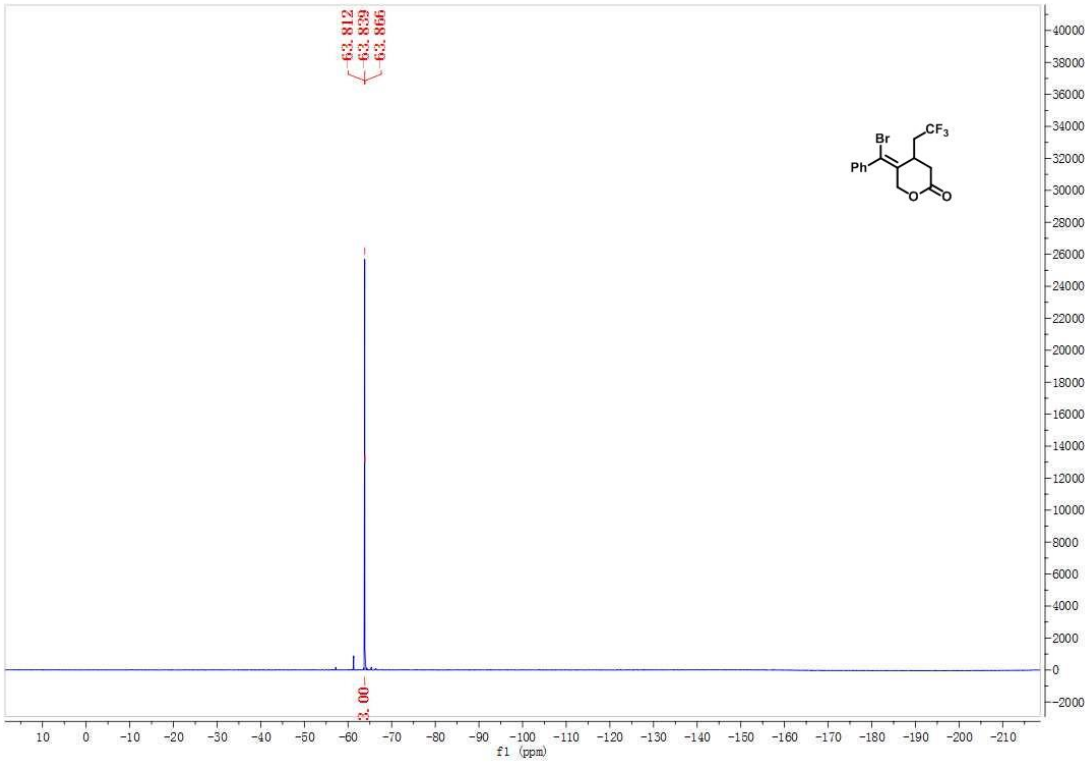

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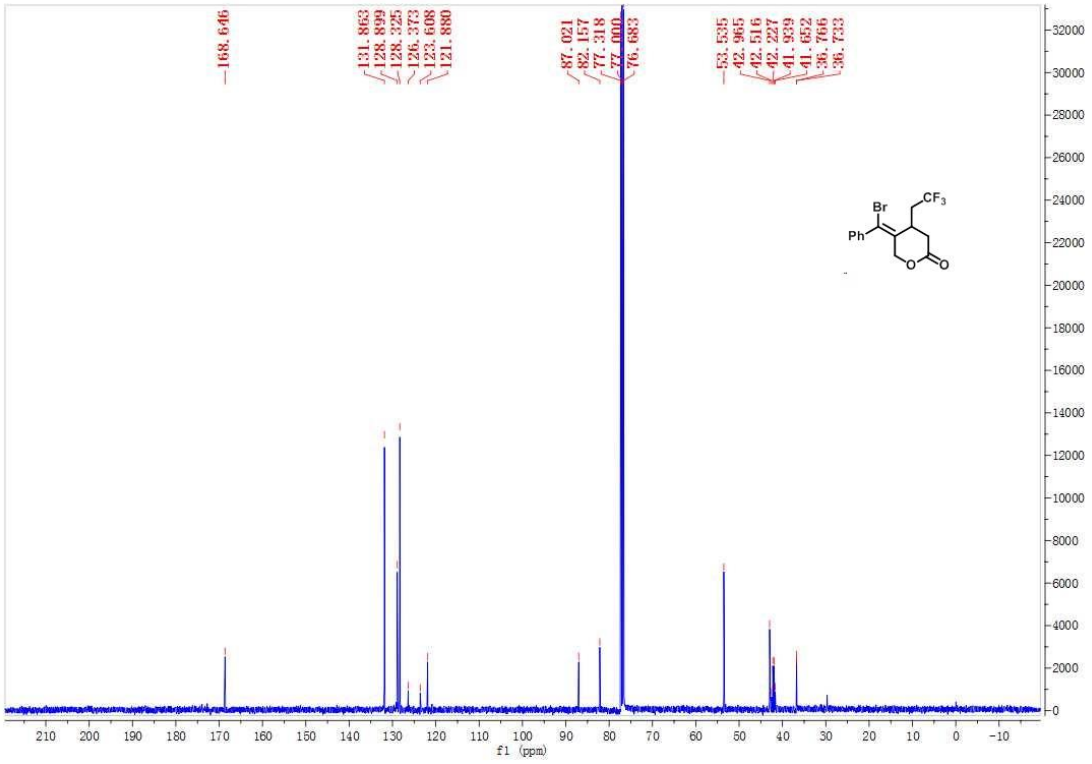

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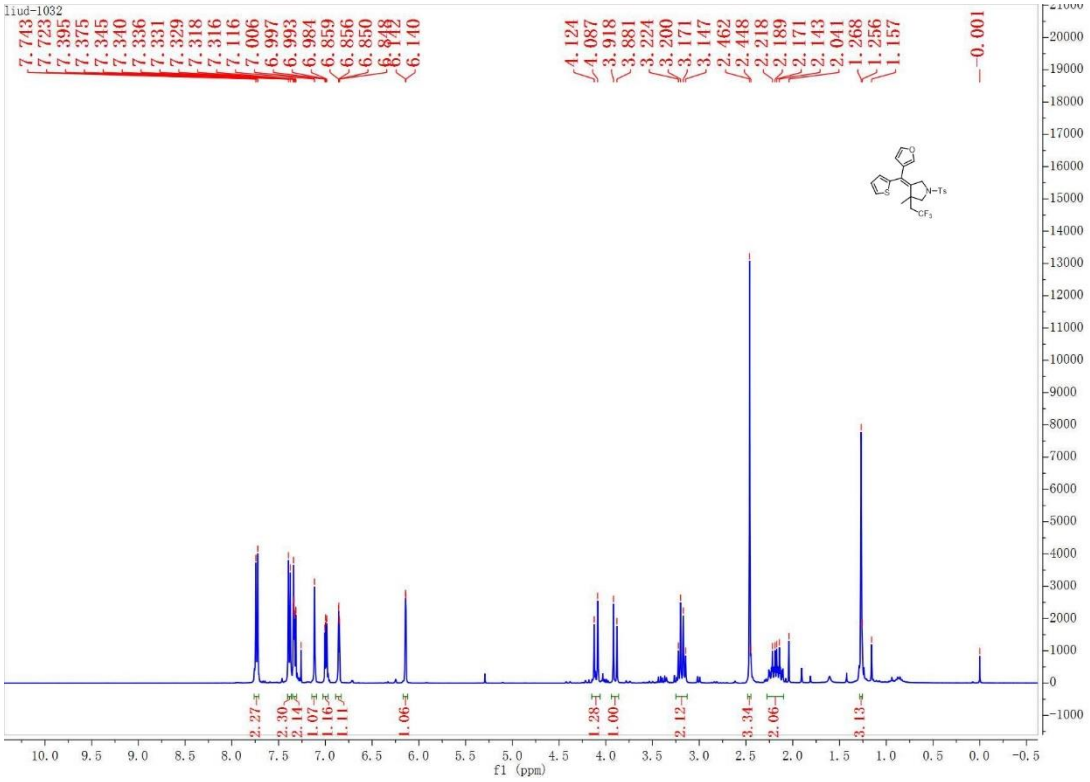

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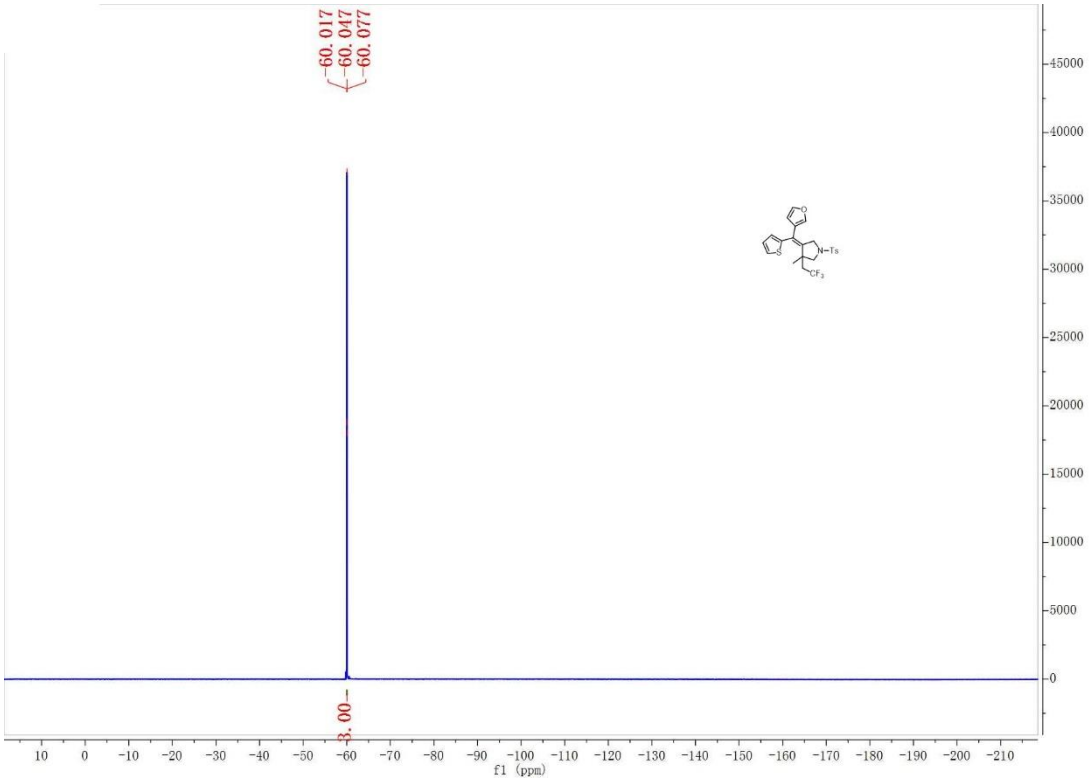

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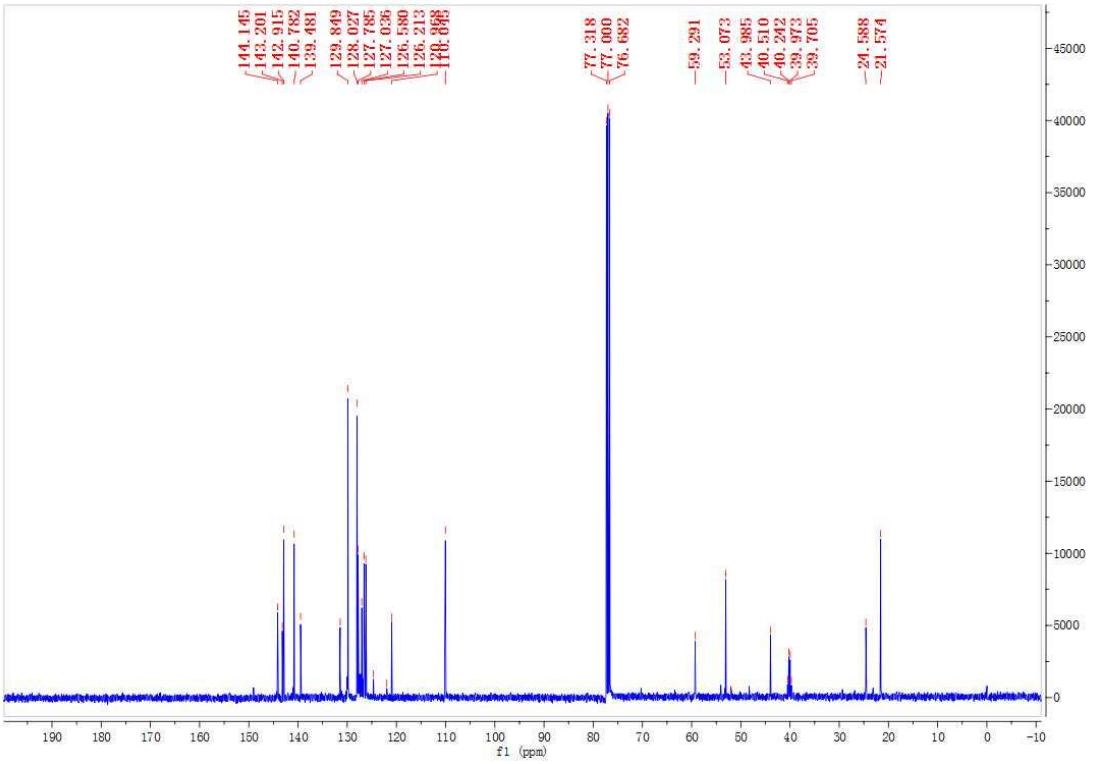

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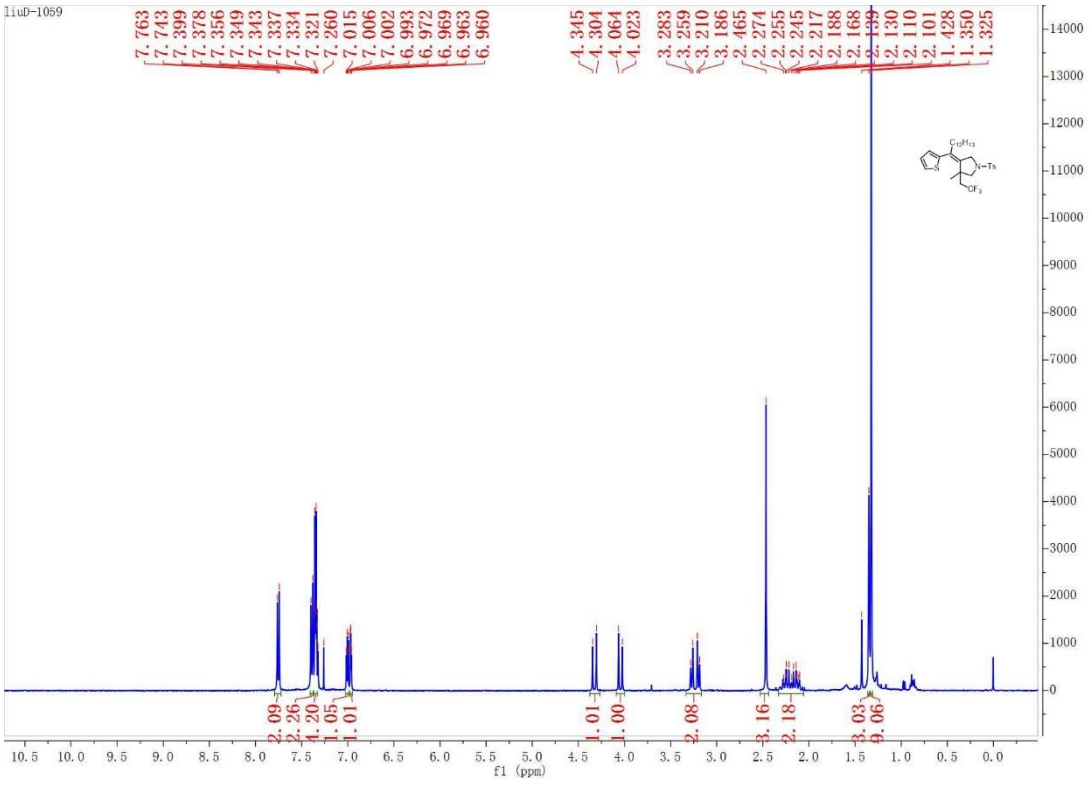

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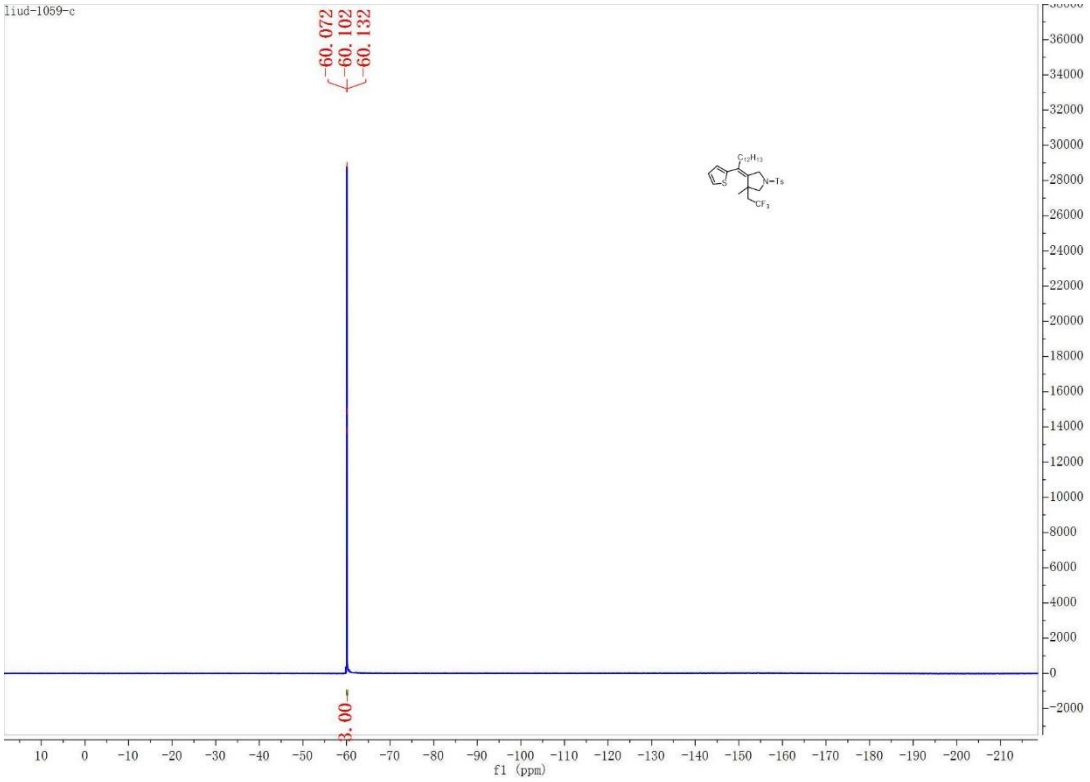

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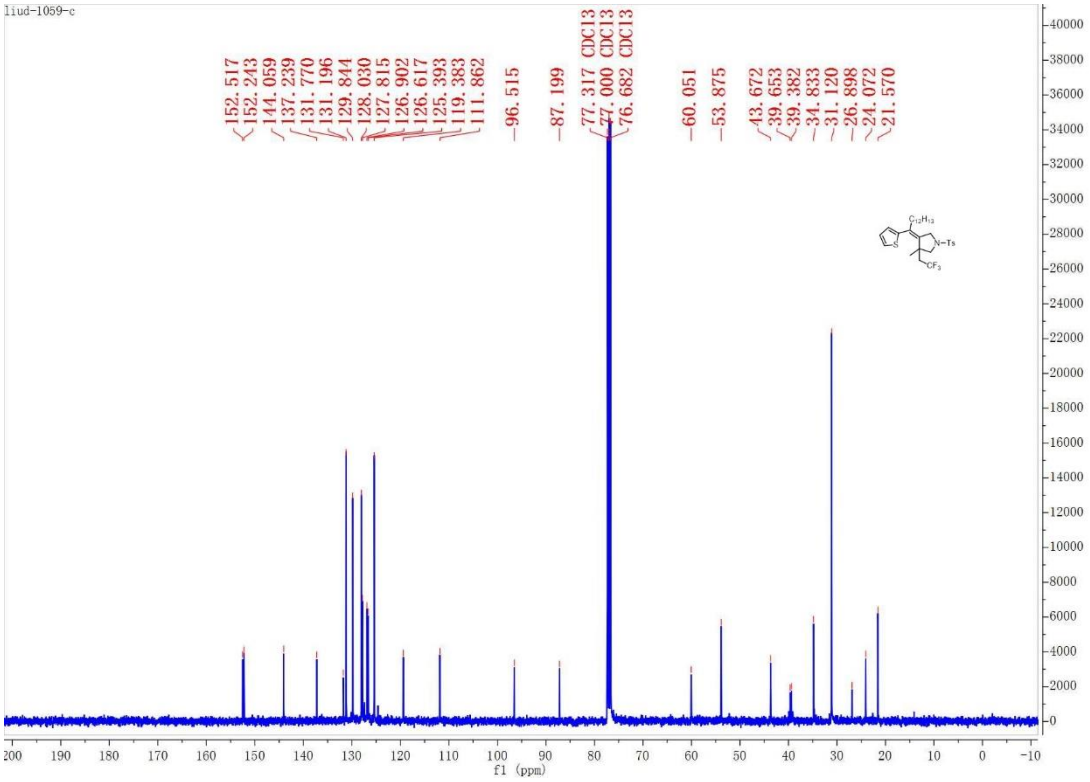

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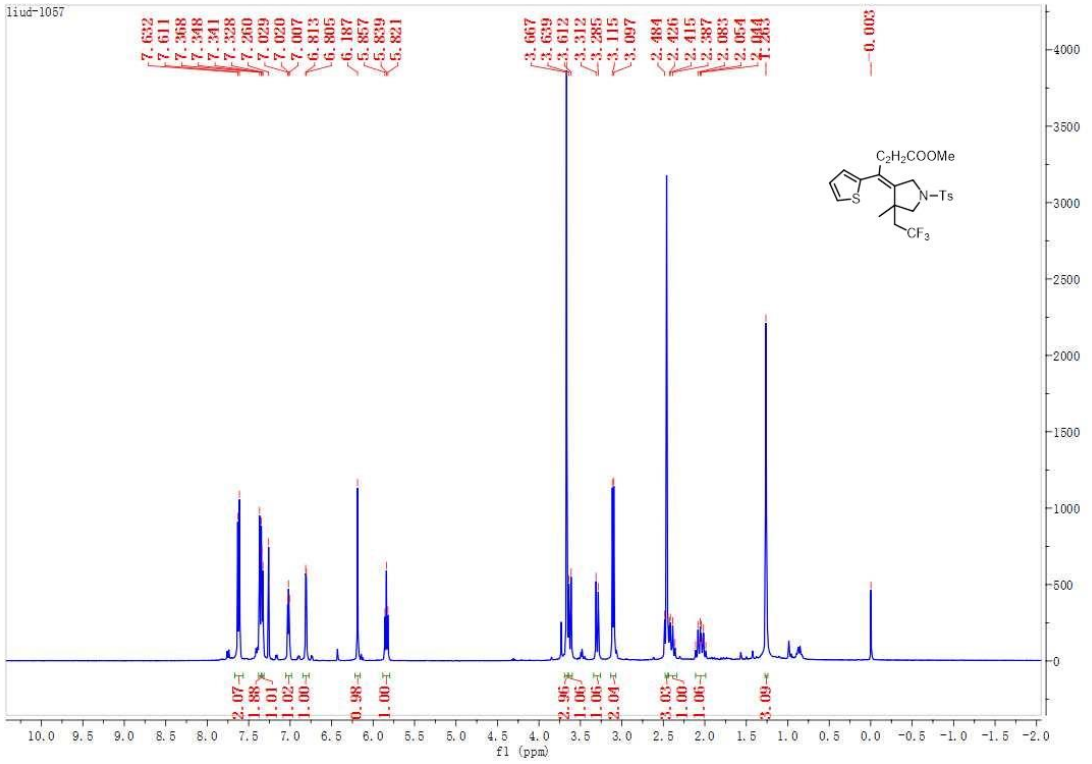
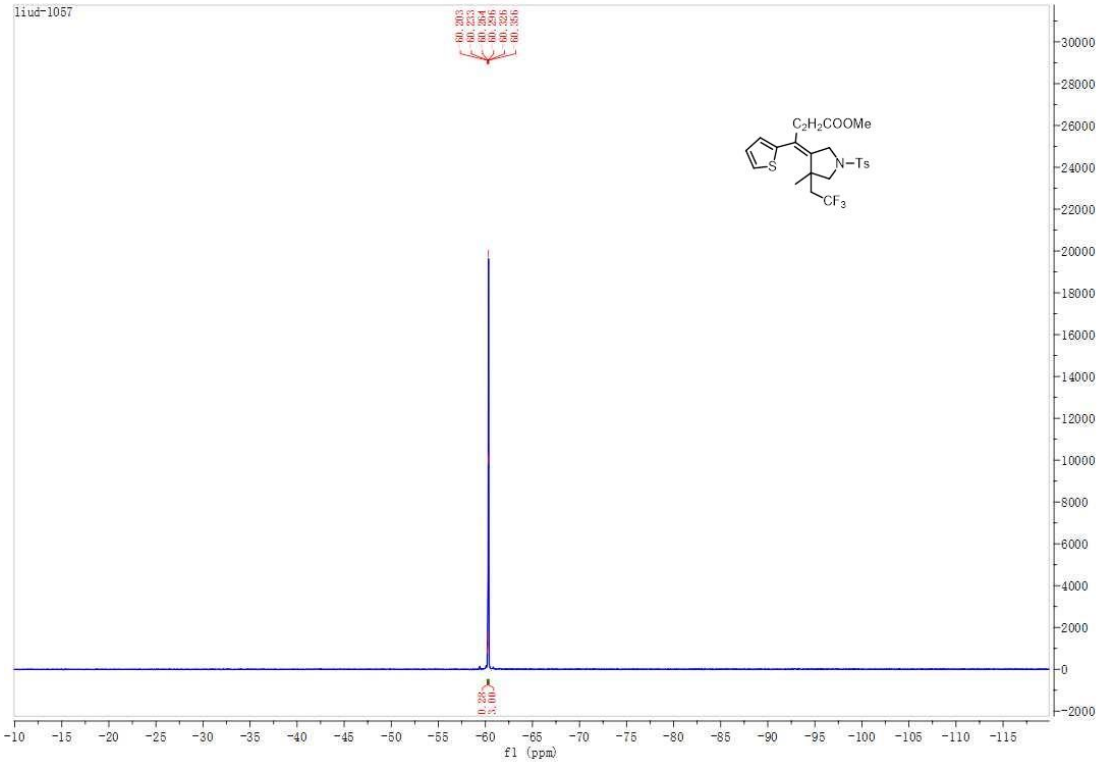
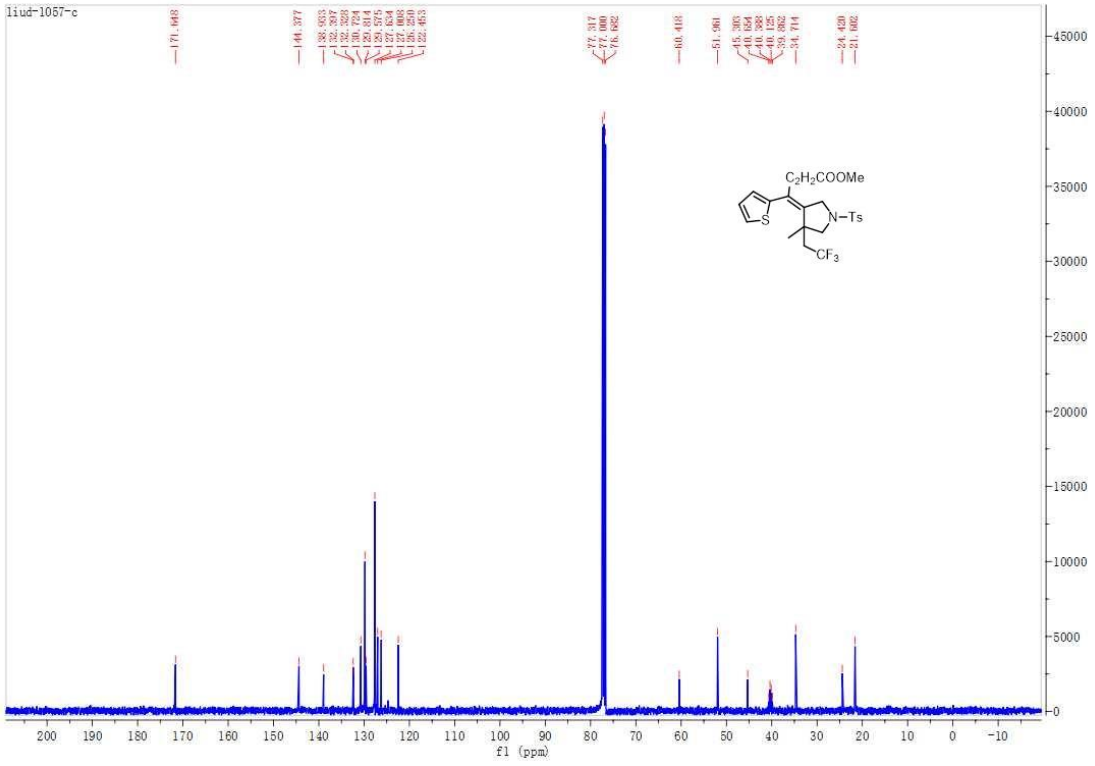


22. ^{19}F NMR



22. ^{13}C NMR


liud-1057-c
171.648
144.377
138.953
132.397
132.293
131.724
130.814
129.575
127.634
127.466
125.255
122.453
77.317
77.000
76.682
60.418
51.961
45.393
41.654
41.388
40.125
39.882
34.714
24.429
21.662
C2H2COOMe
S
N–Ts
CF3
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)