Supporting Information

Copper-catalyzed trifluoromethylazidation and rearrangement of aniline-linked 1,7-enynes: access to CF_3-substituted azaspirocyclic dihydroquinolin-2-ones and furoindolines

Liu-Zhu Yu,[a] Yin Wei,[c] and Min Shi[a,b,c]

[a]*Key Laboratory for Advanced Materials and Institute of Fine Chemicals, School of Chemistry & Molecular Engineering, East China University of Science and Technology, Meilong Road No. 130 Shanghai, 200237 (China).*

[b]*State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, Tianjin 300071, P. R. China.*

[c]*State Key Laboratory of Organometallic Chemistry, University of Chinese Academy of Science, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032 (China).*

Mshi@mail.sioc.ac.cn. Fax: 86-21-64166128

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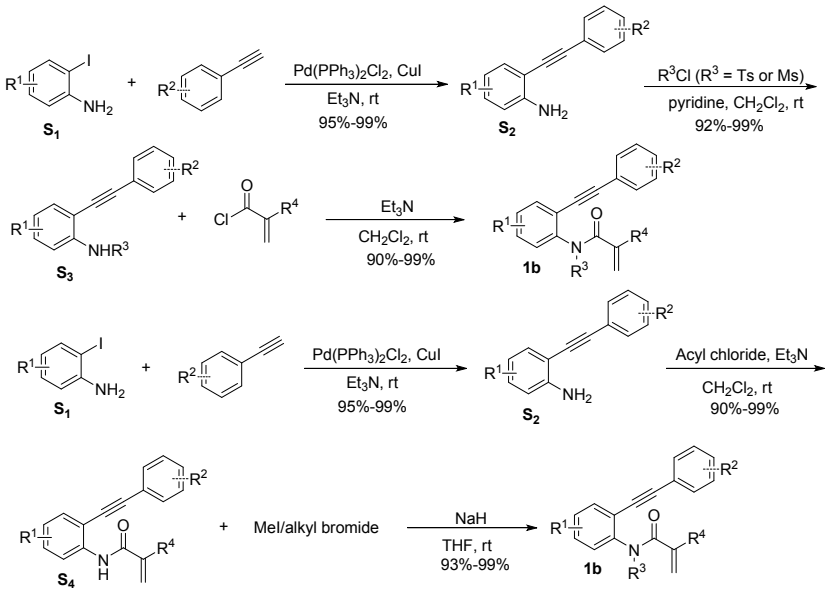
General remarks

Unless otherwise indicated, all reactions (for the synthesis of new products) were performed under an atmosphere of argon. THF was distilled from sodium (Na) under argon (Ar) atmosphere. MeCN was purified and dried according to standard methods prior to use. All other solvents were purchased from Adamas and used without further purification. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. All NMR spectra were recorded on an AM-300 or AM-400 spectrophotometers in $CDCl_3$, NMR chemical shifts are reported in ppm referenced to the solvent peaks of $CDCl_3$ (7.26 ppm for ^1H and 77.0 ppm for ^{13}C, respectively). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by ESI, and HRMS were measured on a HP-5989 instrument.

General procedure for the synthesis of substrate 1b

Compounds **1b** were partially prepared according to the previously reported work and the corresponding spectroscopic data were consistent with those reported in the literature.[1]



General procedure for synthesis of $\mathbf{S_2}$: To a 150 mL flask charged with $\mathbf{S_1}$ (2 mmol, 1.0 equiv), $Pd(PPh_3)_2Cl_2$ (0.04 mmol, 2 mol%), and CuI (0.08 mmol, 4 mol%) in degassed Et_3N (5 mL) was added aryl alkynes (2.4 mmol, 1.2 equiv), and the resulting solution was stirred at room temperature for 2 h. Upon completion, the solvent was removed under reduced pressure, and the residue was extracted with EtOAc (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford $\mathbf{S_2}$ in good yields ranging from 95% to 99%.

General procedure for synthesis of $\mathbf{S_3}$: To a stirred solution of $\mathbf{S_2}$ (1.0 equiv) in CH_2Cl_2 (5 mL) was added R^3Cl (1.5 equiv) and pyridine (1.5 equiv). The resulted mixture was stirred at room temperature for 12 h. Then the reaction was quenched by saturated $CuSO_4$ solution and the reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated for the next step without further purification.

General procedure for synthesis of **1b**: To a stirred solution of $\mathbf{S_2}$ (1.0 equiv) in CH_2Cl_2 (5 mL) was added acyl chloride (1.5 equiv) and Et_3N (2.0 equiv). The resulted mixture was stirred at room

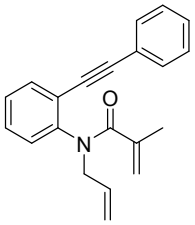
temperature for 6 h. Then the reaction was quenched by saturated $NaHCO_3$ solution and the reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford **1b** in good yields ranging from 90% to 99%.

When R^3 was substituted by Me, Bn, or allyl group, the synthesized procedure was as follows:

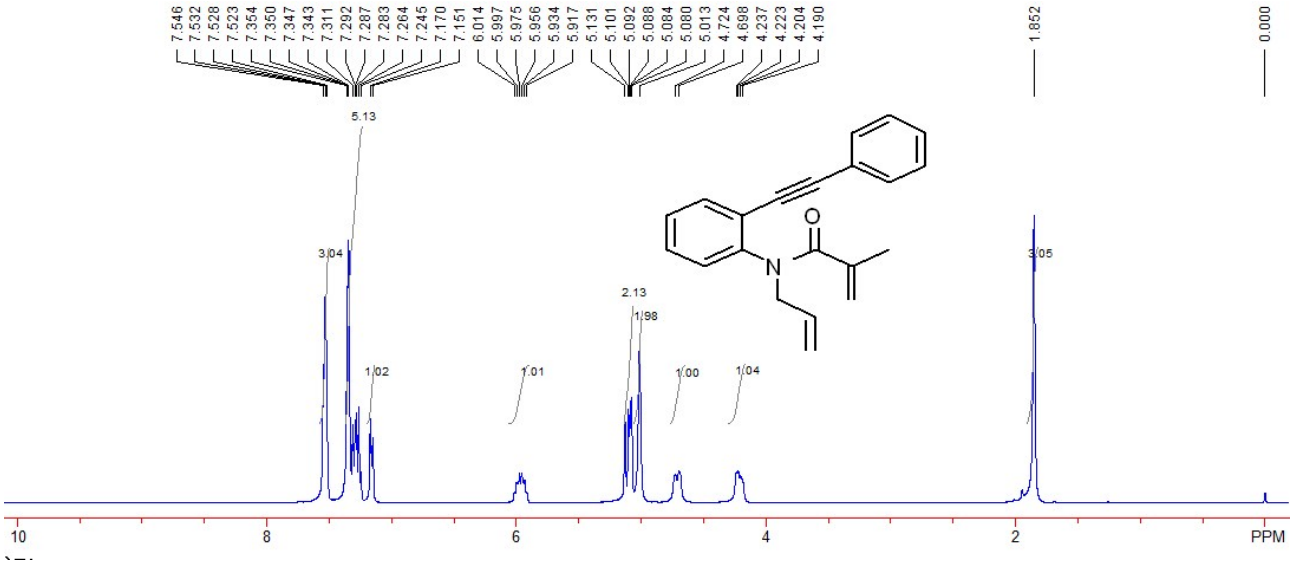
General procedure for synthesis of $\mathbf{S_4}$: To a stirred solution of $\mathbf{S_3}$ (1.0 equiv) in CH_2Cl_2 (5 mL) was added acyl chloride (1.5 equiv) and Et_3N (2.0 equiv). The resulted mixture was stirred at room temperature for 6 h. Then the reaction was quenched by saturated $NaHCO_3$ solution and the reaction mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated for the next step without further purification.

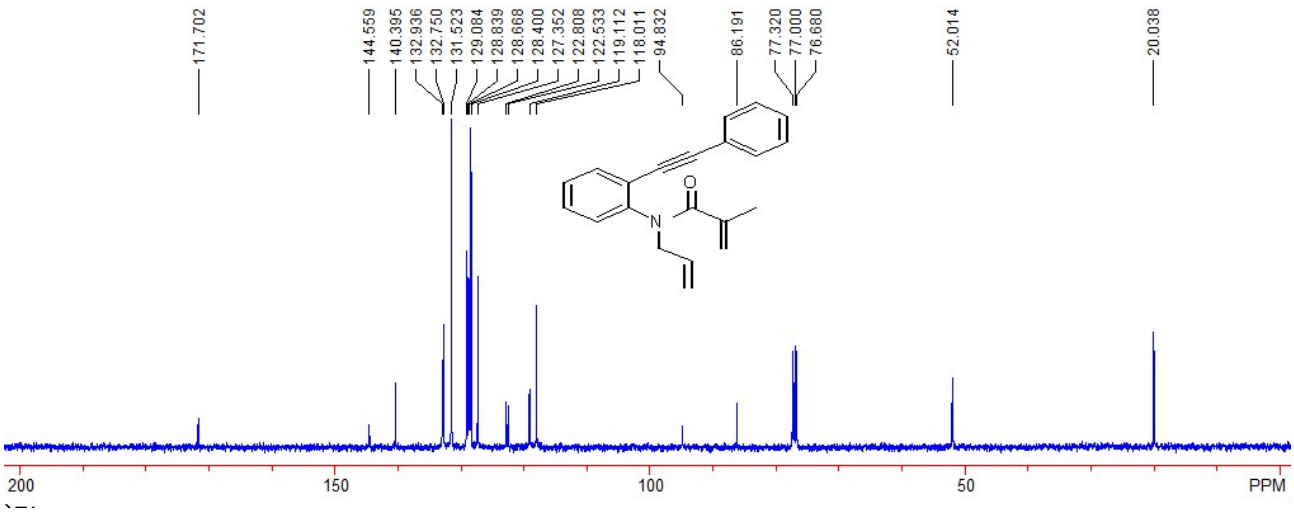
General procedure for synthesis of **1b**: To a solution of NaH (2.0 equiv) in THF (5.0 mL) at 0 ^oC was added a solution of $\mathbf{S_4}$ (1.0 equiv) in THF (5 mL) dropwise and the reaction mixture was stirred for 30 min. Afterwards iodomethane or alkyl bromide (1.5 equiv) was added and the reaction mixture was stirred overnight at room temperature. The reaction was quenched by water and the reaction mixture was extracted with DCM for 3 times. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under vacuum and the residue was purified by a flash column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the product **1b** in good yields ranging from 93% to 99%.

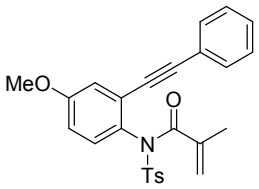
Spectroscopic data for substrates 1



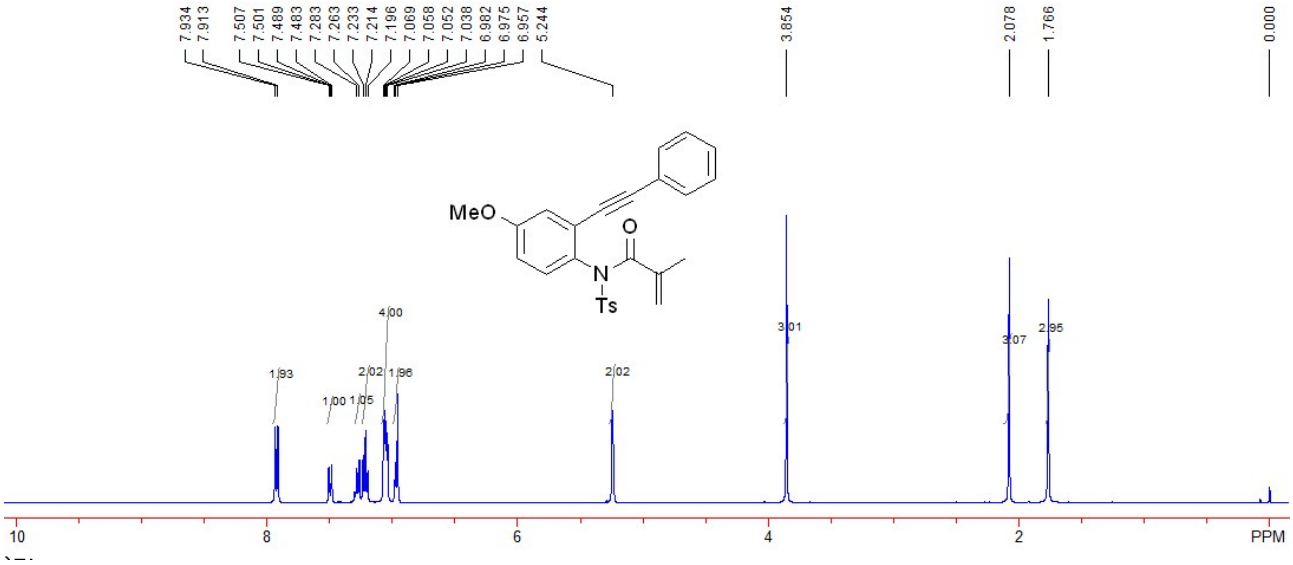
Compound 1be: 482 mg, 80%, A white solid, m.p. 150-152 ^{o}C; IR (EtOH): ν 3062, 2920, 1719, 1648, 1623, 1494, 1389, 1215, 1134, 915, 771, 755, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.85 (s, 3H), 4.21 (dd, 1H, J_1 = 13.2 Hz, J_2 = 5.6 Hz), 4.71 (dd, 1H, J_1 = 13.2 Hz, J_2 = 5.6 Hz), 5.01 (s, 2H), 5.08-5.13 (m, 2H), 5.92-6.01 (m, 1H), 7.16 (d, 1H, J = 7.6 Hz), 7.25-7.35 (m, 5H), 7.52-7.55 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 20.0, 52.0, 86.2, 94.8, 118.0, 119.1, 122.5, 122.8, 127.4, 128.4, 128.7, 128.8, 129.1, 131.5, 132.8, 132.9, 140.4, 144.6, 171.7; MS (ESI) *m/z*: 302.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{20}NO^+$ requires: 302.1539, Found: 302.1537.

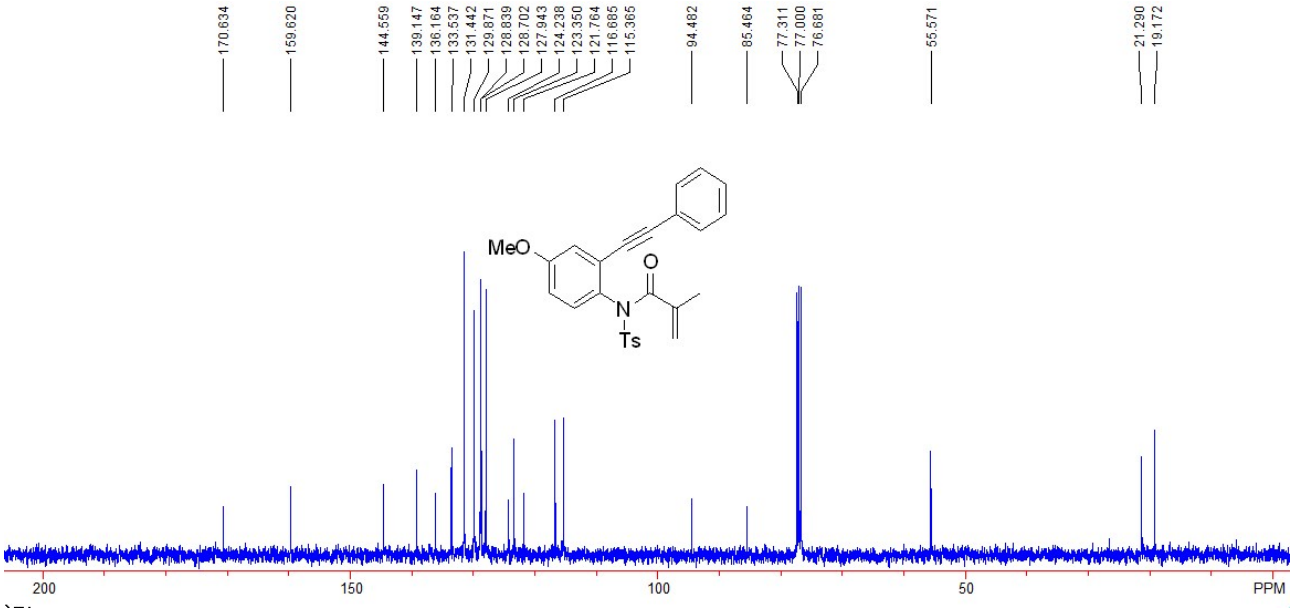


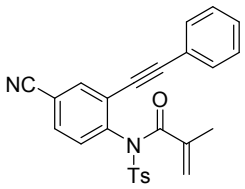




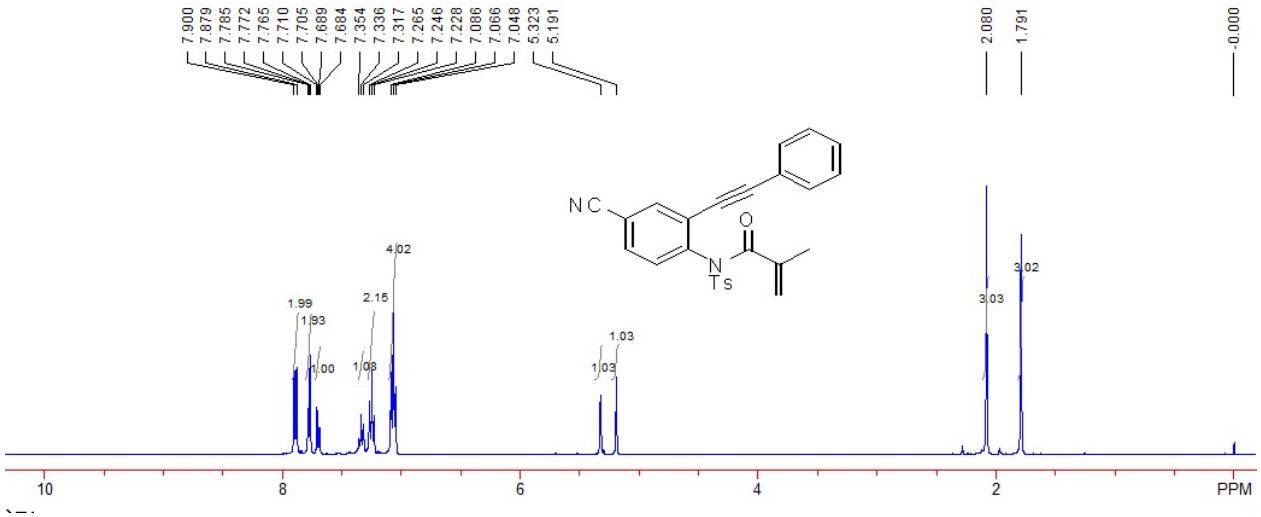
Compound 1bh: 703 mg, 79%, A white solid, m.p. 191-193 ^{o}C; IR (EtOH): ν 3059, 1691, 1564, 1477, 1419, 1353, 1216, 1188, 1181, 1132, 1086, 940, 753, 688 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.77 (s, 3H), 2.08 (s, 3H), 3.85 (s, 3H), 5.24 (s, 2H), 6.96-6.98 (m, 2H), 7.04-7.07 (m, 4H), 7.20-7.23 (m, 2H), 7.27 (d, 1H, J = 8.0 Hz), 7.49 (dd, 1H, J_1 = 7.2 Hz, J_2 = 2.4 Hz), 7.92 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 21.3, 55.6, 85.5, 94.5, 115.4, 116.7, 121.8, 123.4, 124.2, 127.9, 128.7, 128.8, 129.9, 131.4, 133.5, 136.2, 139.1, 144.6, 159.6, 170.6; MS (ESI) *m/z*: 446.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}NO_4S^{+}$ requires: 446.1421, Found: 446.1417.

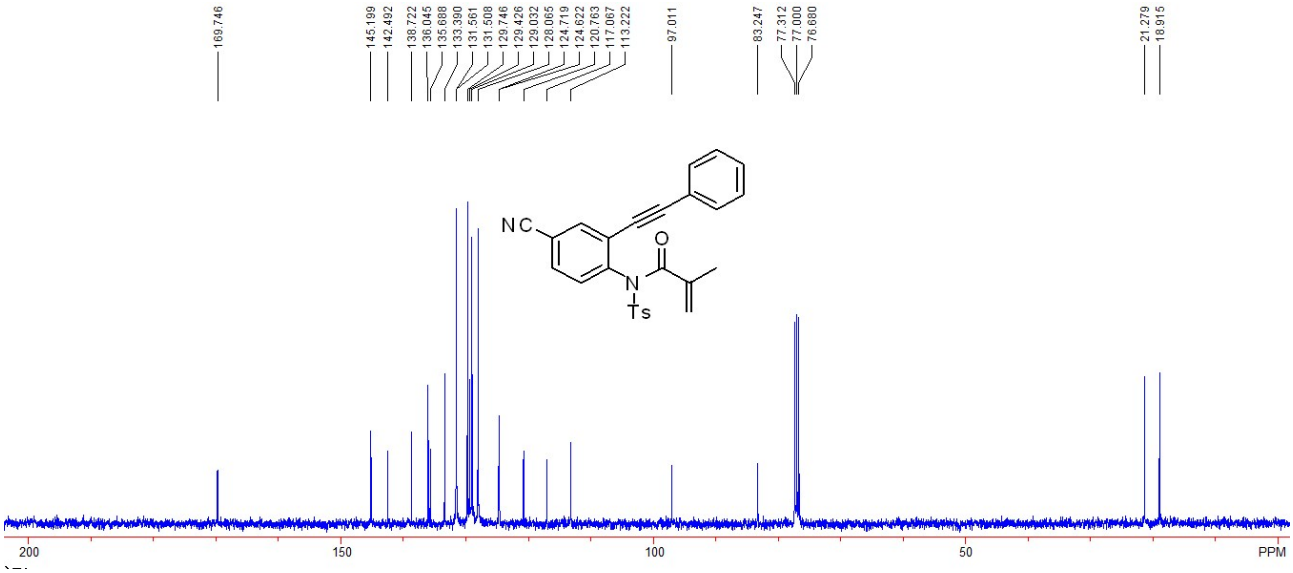


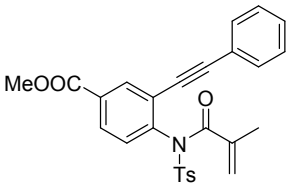




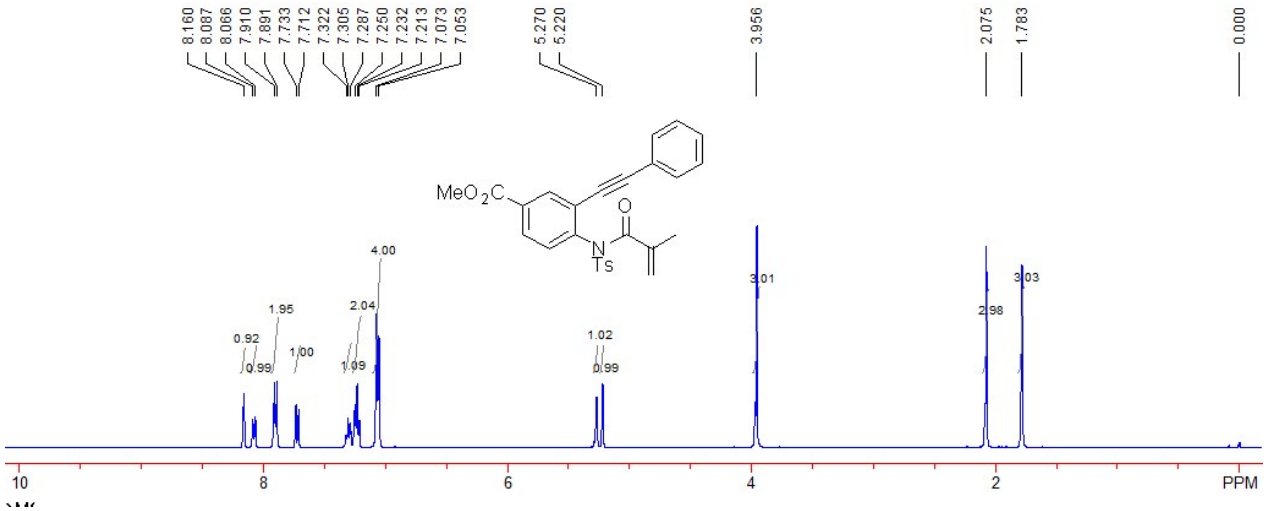
Compound 1bi: 730 mg, 83%, A white solid, m.p. 186-188 ^{o}C; IR (EtOH): ν 3029, 1701, 1495, 1364, 1172, 1128, 1084, 814, 762, 753, 692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.79 (s, 3H), 2.08 (s, 3H), 5.19 (s, 1H), 5.32 (s, 1H), 7.05-7.09 (m, 4H), 7.23-7.27 (m, 2H), 7.33 (d, 1H, J = 7.6 Hz), 7.70 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.0 Hz), 7.77-7.79 (m, 2H), 7.89 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 21.3, 83.2, 97.0, 113.2, 117.1, 120.8, 124.6, 124.7, 128.1, 129.0, 129.4, 129.7, 131.5, 131.6, 133.4, 135.7, 136.0, 138.7, 142.5, 145.2, 169.7; MS (ESI) *m/z*: 458.2 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}N_3O_3S^+$ requires: 458.1533, Found: 458.1530.

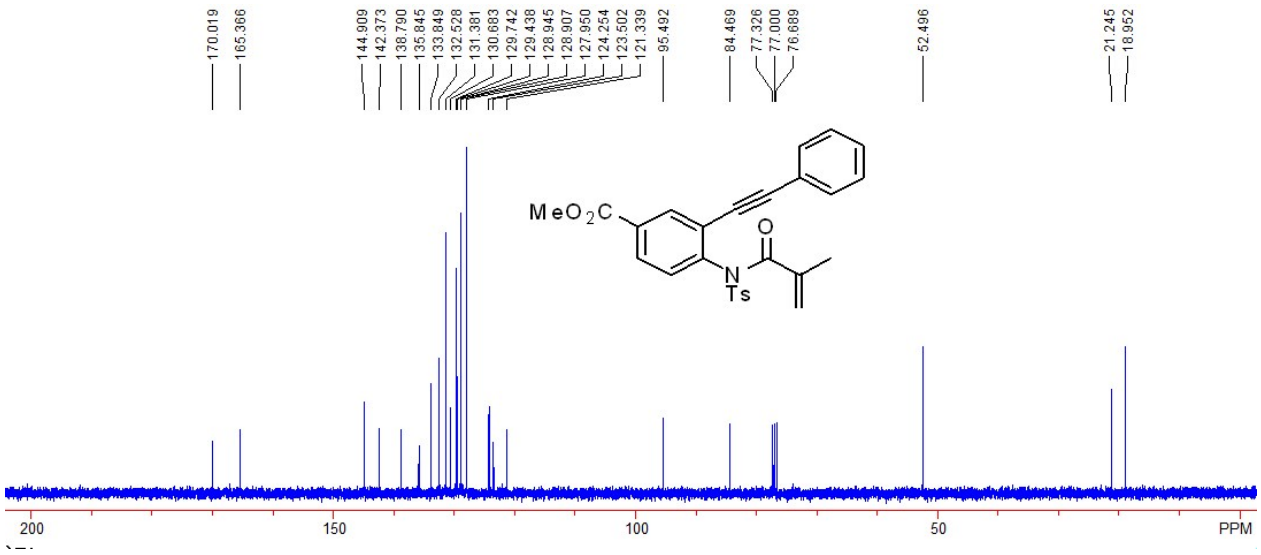


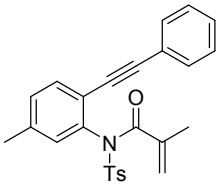




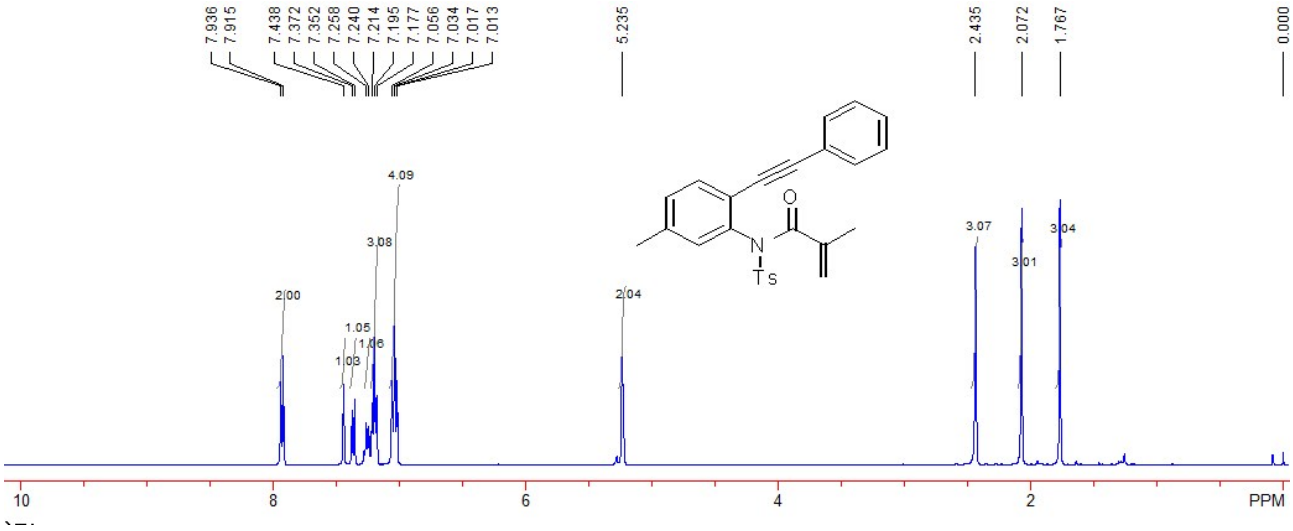
Compound 1bj: 719 mg, 76%, A white solid, m.p. 174-176 ^{o}C; IR (EtOH): ν 3062, 2984, 1727, 1624, 1495, 1363, 1260, 1173, 1133, 1085, 759, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.78 (s, 3H), 2.08 (s, 3H), 3.96 (s, 3H), 5.22 (s, 1H), 5.27 (s, 1H), 7.05-7.07 (m, 4H), 7.21-7.25 (m, 2H), 7.30 (d, 1H, J = 7.2 Hz), 7.72 (d, 1H, J = 8.4 Hz), 7.90 (d, 2H, J = 7.6 Hz), 8.08 (d, 1H, J = 8.4 Hz), 8.16 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.2, 52.5, 84.5, 95.5, 121.3, 123.5, 124.3, 128.0, 128.91, 128.95, 129.4, 129.7, 130.7, 131.4, 132.5, 133.8, 135.8, 138.8, 142.4, 144.9, 165.4, 170.0; MS (ESI) *m/z*: 474.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{27}H_{24}NO_5S^{+}$ requires: 474.1370, Found: 474.1365.

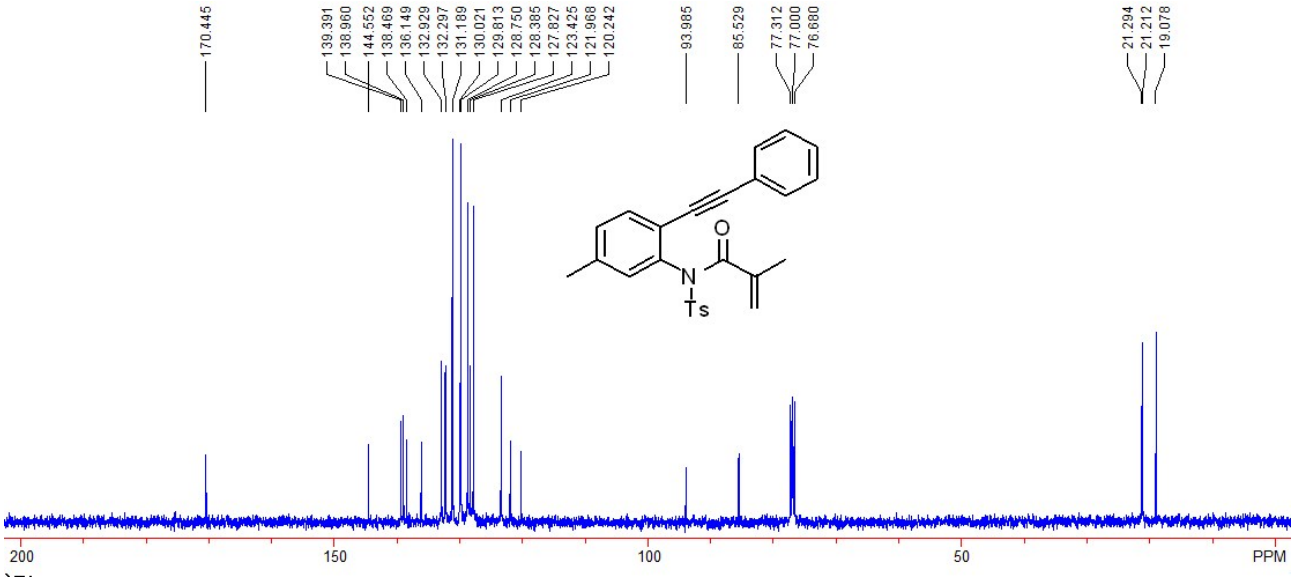


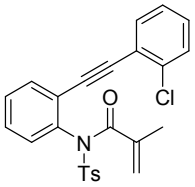




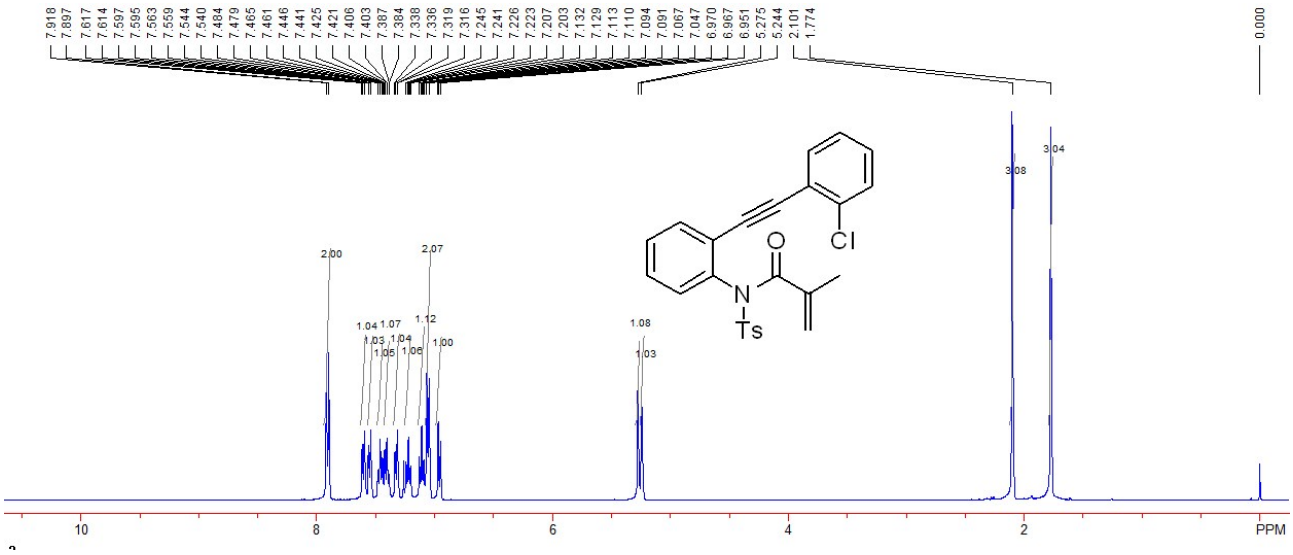
Compound 1bk: 721 mg, 84%, A white solid, m.p. 172-174 ^{o}C; IR (EtOH): ν 2923, 2845, 1686, 1505, 1363, 1305, 1170, 1138, 951, 809, 771, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.78 (s, 3H), 2.07 (s, 3H), 2.44 (s, 3H), 5.24 (s, 2H), 7.01-7.06 (m, 4H), 7.18-7.21 (m, 3H), 7.25 (d, 1H, *J* = 7.2 Hz), 7.36 (d, 1H, *J* = 8.0 Hz), 7.44 (s, 1H), 7.93 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 21.2, 21.3, 85.5, 94.0, 120.2, 122.0, 123.4, 127.8, 128.4, 128.8, 129.8, 130.0, 131.2, 132.3, 132.9, 136.1, 138.5, 139.0, 139.4, 144.6, 170.4; MS (ESI) *m/z*: 430.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}NO_3S^{+}$ requires: 430.1471, Found: 430.1468.

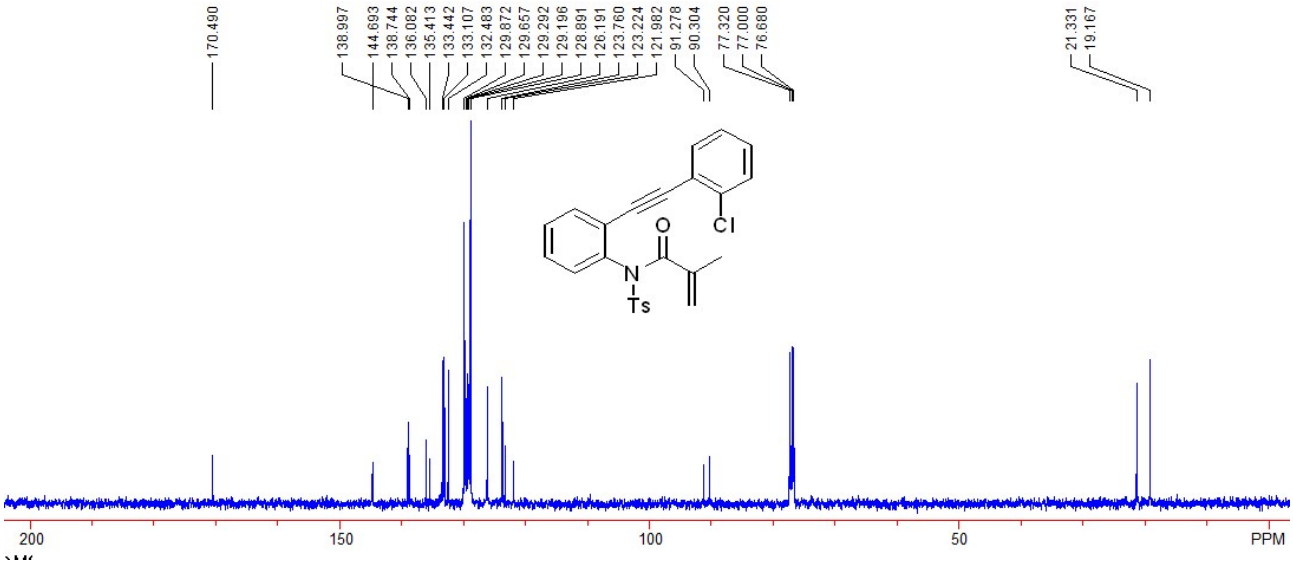


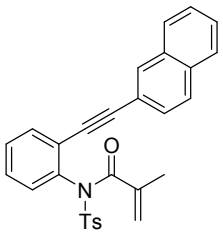




Compound 1bq: 772 mg, 86%, A white solid, m.p. 195-197 ^{o}C; IR (EtOH): ν 2951, 2920, 1683, 1489, 1363, 1174, 1138, 1086, 954, 811, 770, 725, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.77 (s, 3H), 2.10 (s, 3H), 5.24 (s, 1H), 5.28 (s, 1H), 6.97 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.06 (d, 2H, J = 8.0 Hz), 7.11 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.22 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.33 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.38-7.48 (m, 2H), 7.55 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.60 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.91 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 21.3, 90.3, 91.3, 121.9, 123.2, 123.8, 126.2, 128.9, 129.2, 129.3, 129.6, 129.9, 132.5, 133.1, 133.4, 135.4, 136.1, 138.7, 139.0, 144.7, 170.5; MS (ESI) *m/z*: 450.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{25}H_{21}ClNO_3S^{+}$ requires: 450.0925, Found: 450.0923.

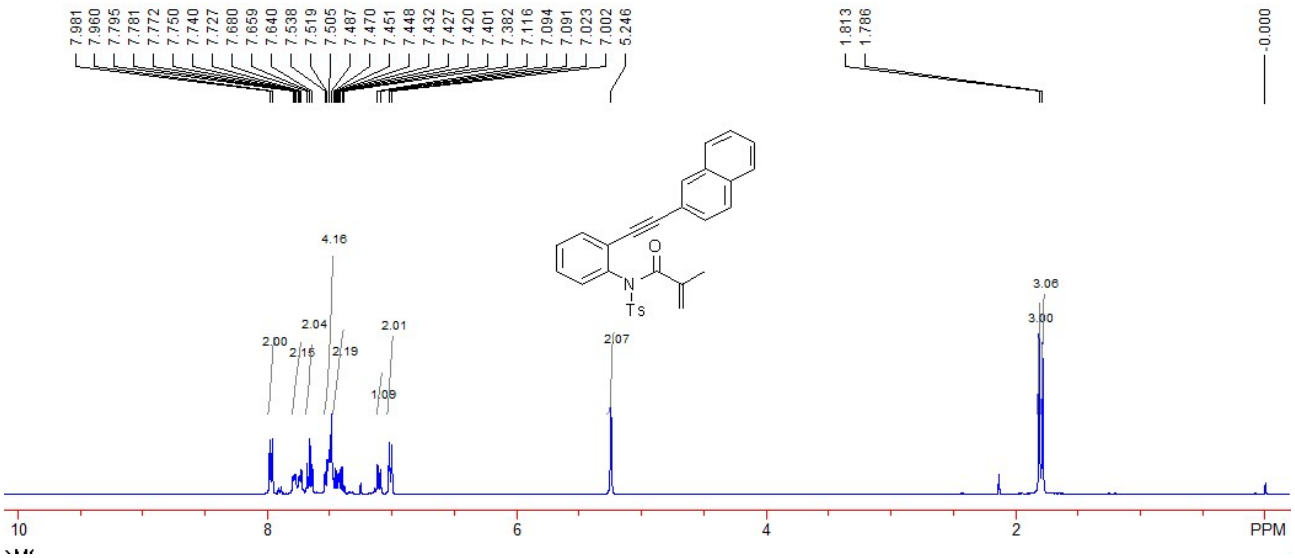


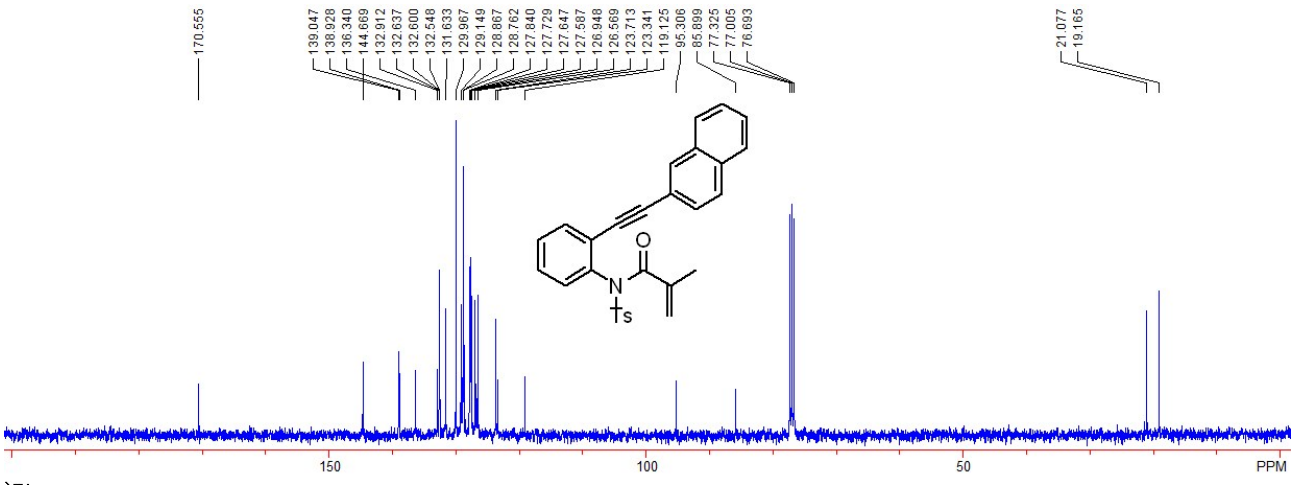


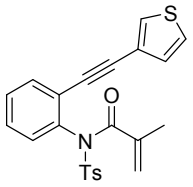


Compound 1br: 679 mg, 73%, A white solid, m.p. 200-202 ^{o}C; IR (EtOH): ν 3056, 1688, 1370, 1362, 1173, 1143, 1086, 867, 810, 769, 701, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.79 (s, 3H), 1.81 (s, 3H), 5.25 (s, 2H), 7.01 (d, 2H, J = 8.4 Hz), 7.10 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.38-7.54 (m, 6H), 7.64-7.68 (m, 2H), 7.73-7.80 (m, 2H), 7.97 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 21.1, 85.9, 95.3, 119.1, 123.3, 123.7, 126.6, 126.9, 127.59, 127.65, 127.7, 127.8, 128.8, 128.9, 129.1, 130.0, 131.6, 132.5, 132.60, 132.64, 132.9, 136.3, 138.9, 139.0,

144.7, 170.6; MS (ESI) *m/z*: 466.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{29}H_{24}NO_3S^+$ requires: 466.1471, Found: 466.1468.

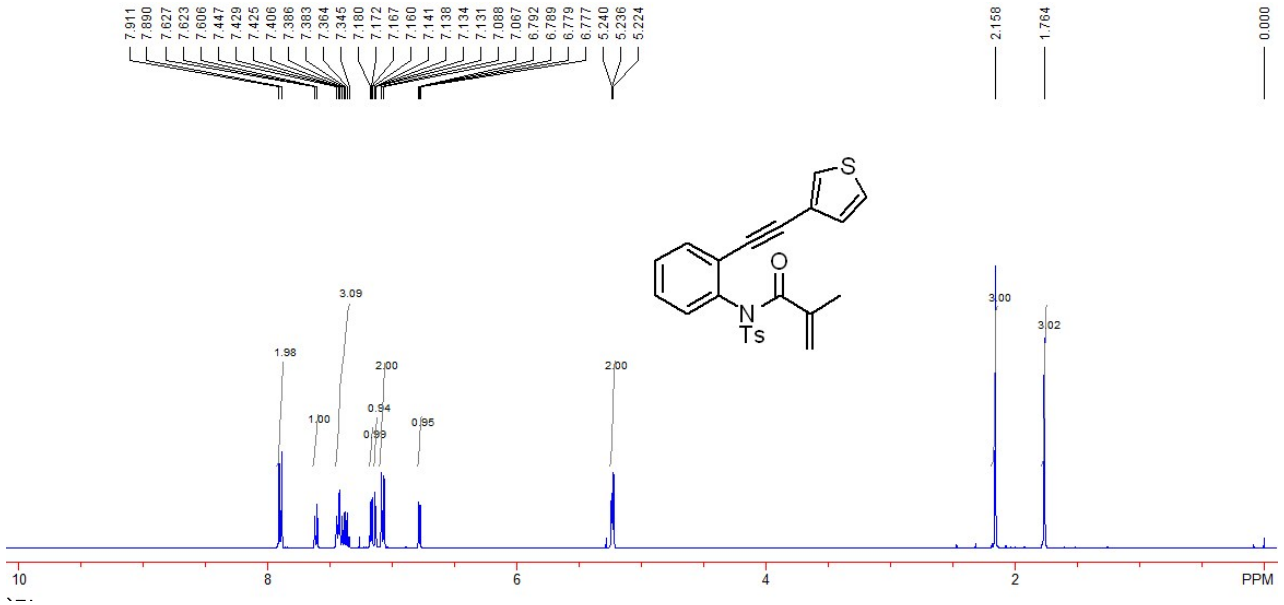


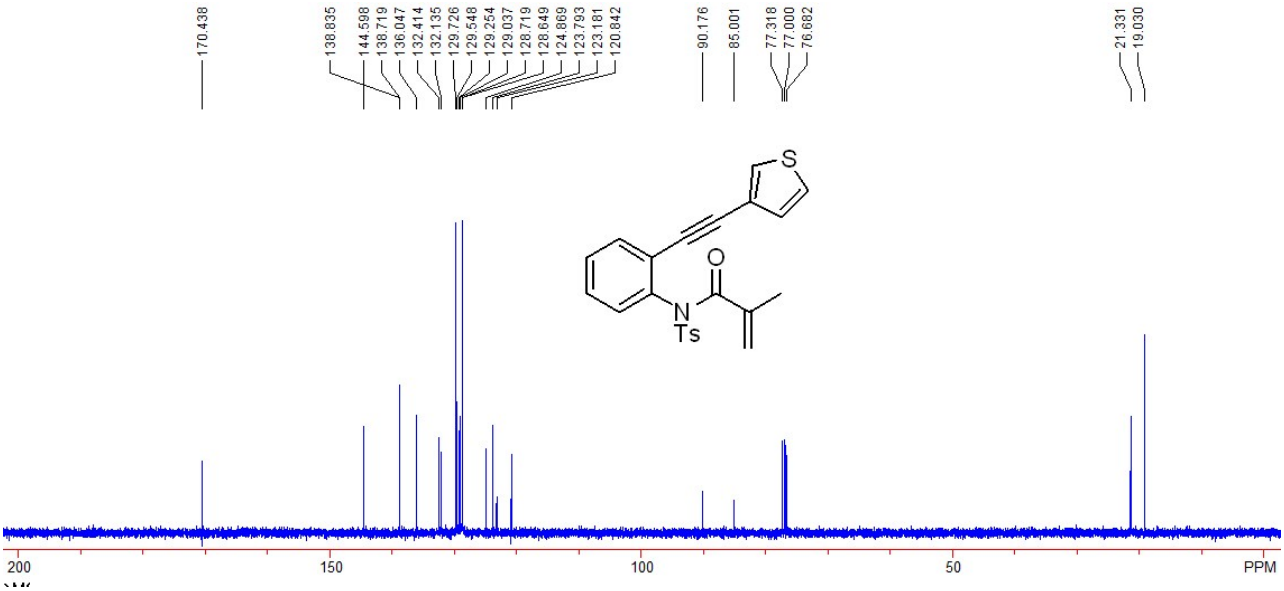


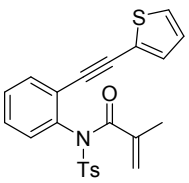


Compound 1bt: 699 mg, 83%, A white solid, m.p. 177-179 ^oC; IR (EtOH): ν 2984, 1682, 1360, 1173, 1133, 1086, 934, 799, 769, 692 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.76 (s, 3H), 2.16 (s, 3H), 5.22 (s, 1H), 5.24 (s, 1H), 6.78 (dd, 1H, J_1 = 8.8 Hz, J_2 = 1.2 Hz), 7.08 (d, 2H, J = 8.4 Hz), 7.14 (dd, 1H, J_1 = 2.8 Hz, J_2 = 1.2 Hz), 7.17 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.8 Hz), 7.35-7.45 (m, 3H), 7.62 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.90 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.3, 85.0, 90.2, 120.8, 123.2, 123.8, 124.9, 128.6, 128.7, 129.0, 129.3, 129.5, 129.7,

132.1, 132.4, 136.0, 138.7, 138.8, 144.6, 170.4; MS (ESI) *m/z*: 422.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{20}NO_3S_2^+$ requires: 422.0879, Found: 422.0875.

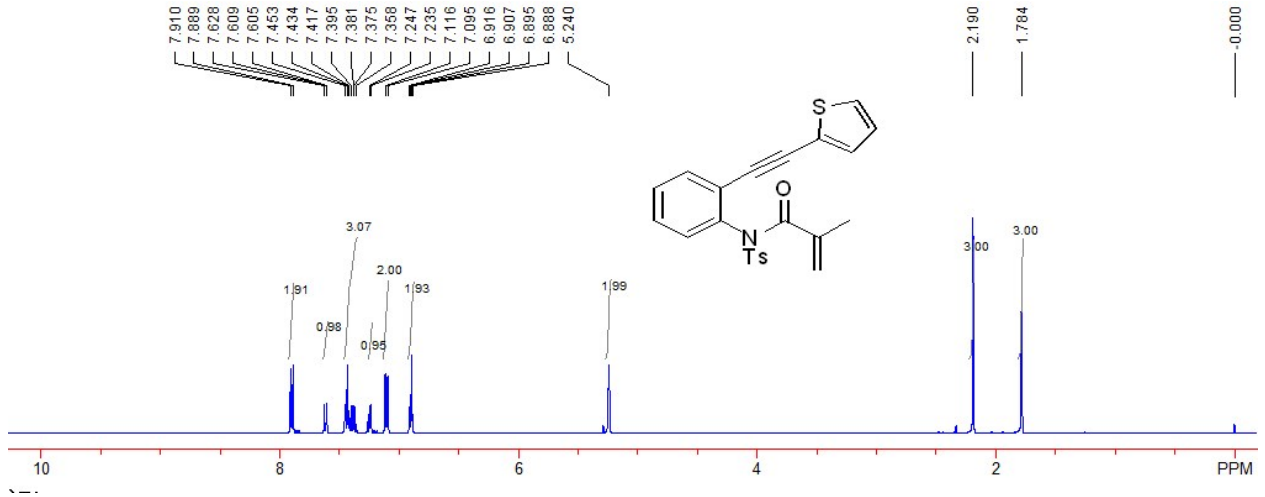


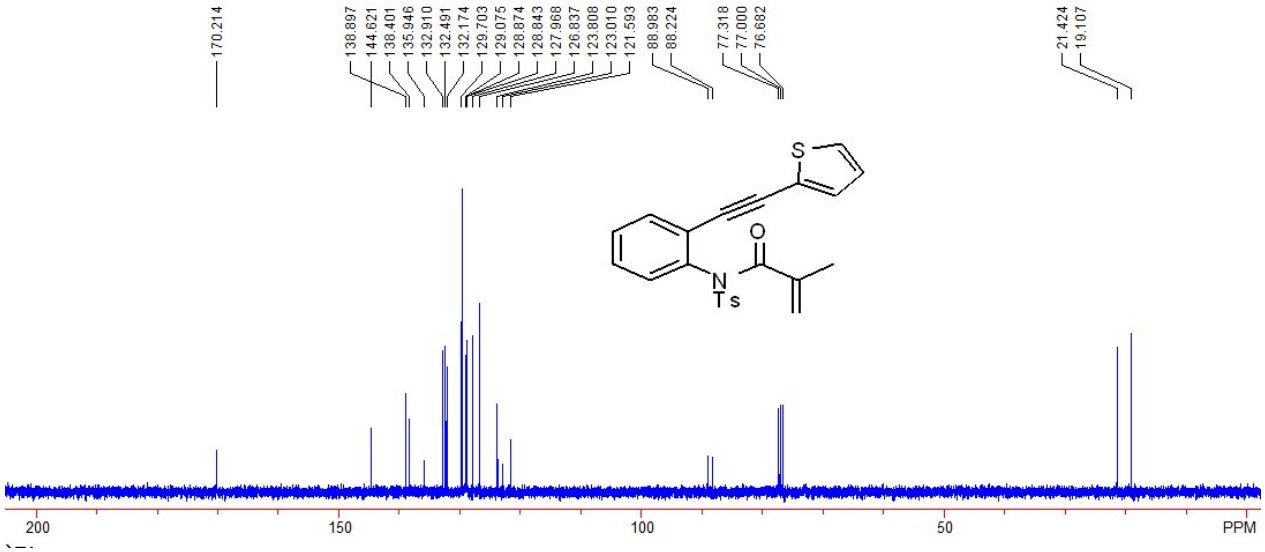


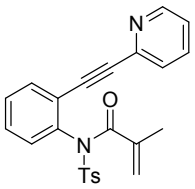


Compound 1bu: 690 mg, 82%, A white solid, m.p. 175-177 ^oC; IR (EtOH): ν 2976, 2918, 1697, 1363, 1173, 1086, 703, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.78 (s, 3H), 2.19 (s, 3H), 5.24 (s, 2H), 6.89-6.92 (m, 2H), 7.10 (d, 2H, J = 8.4 Hz), 7.23-7.25 (m, 1H), 7.36-7.45 (m, 3H), 7.62 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.90 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$,

TMS): δ 19.1, 21.4, 88.2, 89.0, 121.6, 123.0, 123.8, 126.8, 128.0, 128.8, 128.9, 129.1, 129.7, 132.2, 132.5, 132.9, 135.9, 138.4, 138.9, 144.6, 170.2; MS (ESI) *m/z*: 422.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{20}NO_3S_2^+$ requires: 422.0879, Found: 422.0875.

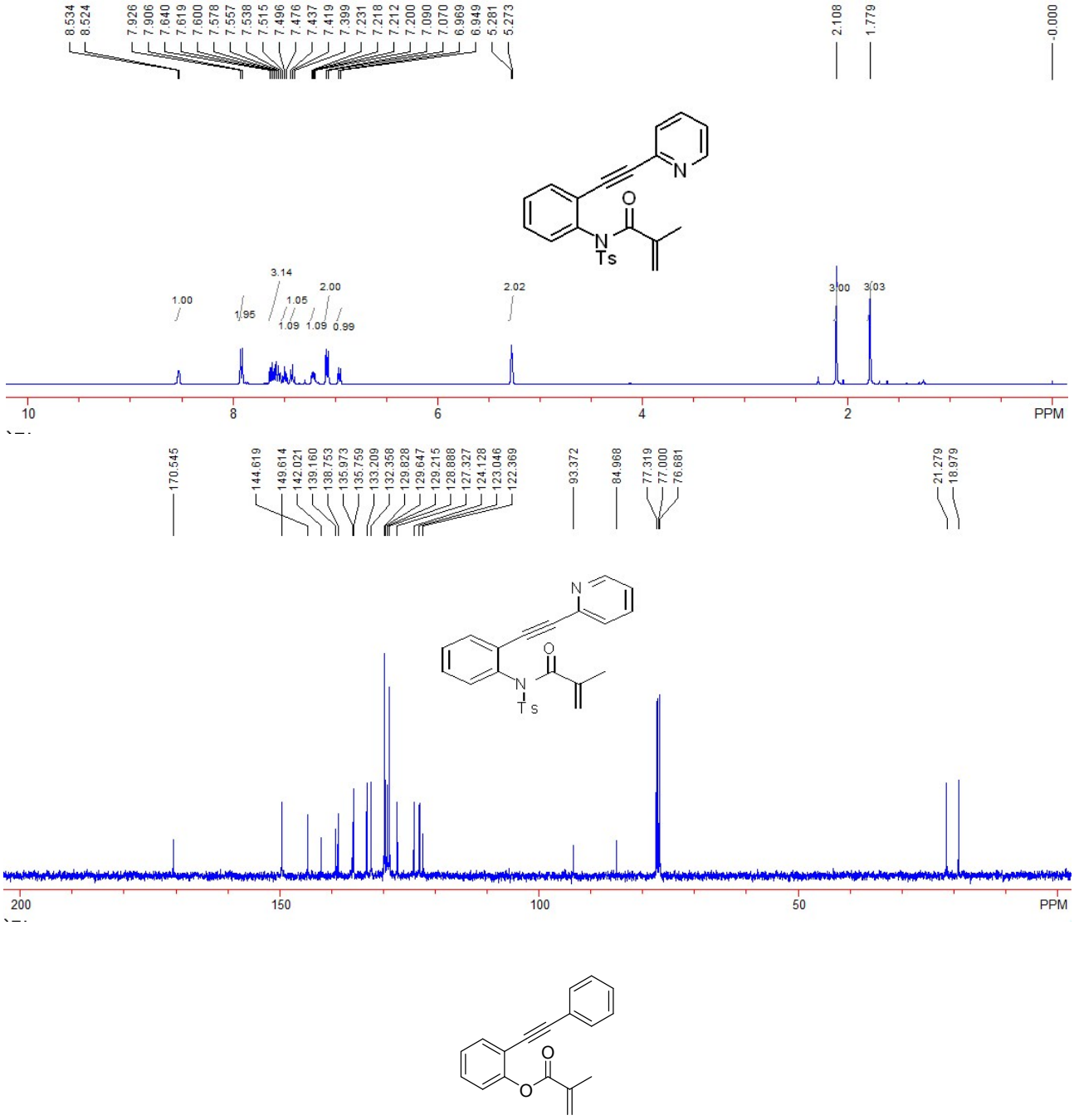






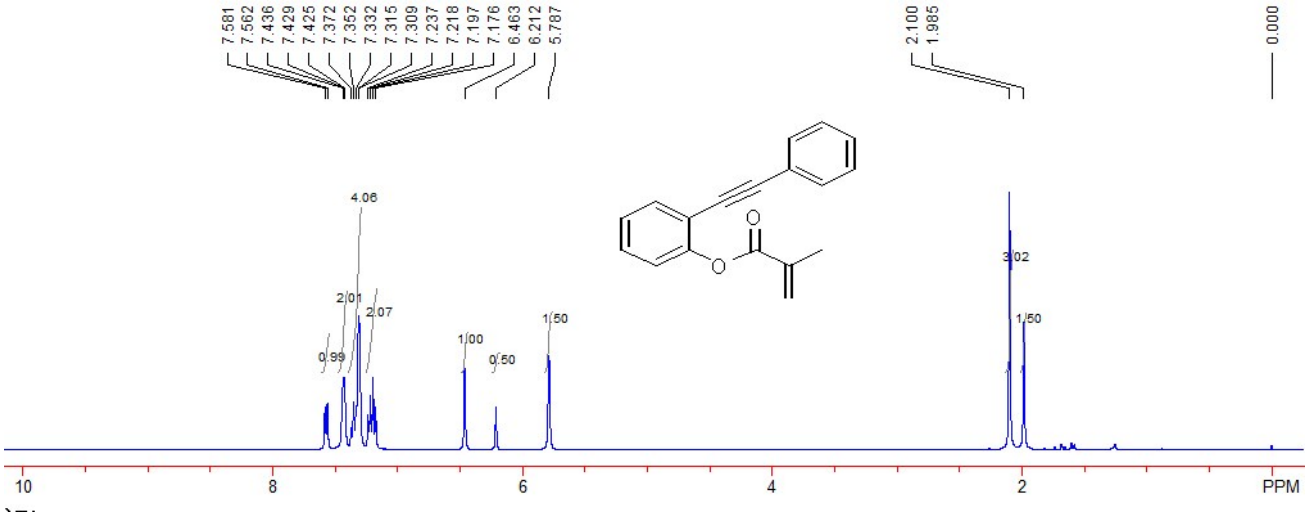
Compound 1bv: 532 mg, 64%, A white solid, m.p. 181-183 °C; IR (EtOH): ν 2967, 2922, 1698, 1489, 1364, 1174, 1144, 777, 668 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.78 (s, 3H), 2.11 (s, 3H), 5.27 (s, 1H), 5.28 (s, 1H), 6.96 (d, 1H, *J* = 8.0 Hz), 7.08 (d, 2H, *J* = 8.0 Hz), 7.20-7.23 (m, 1H), 7.40-7.44 (m, 1H), 7.50 (t, 1H, *J* = 8.0 Hz), 7.54-7.64 (m, 3H), 7.92 (d, 2H, *J* = 8.0 Hz), 8.53 (d, 1H, *J* = 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.3, 85.0, 93.4, 122.4, 123.0, 124.1, 127.3, 128.9, 129.2, 129.6, 129.8, 132.4, 133.2, 135.8, 136.0, 138.8, 139.2, 142.0, 144.6, 149.6, 170.5; MS

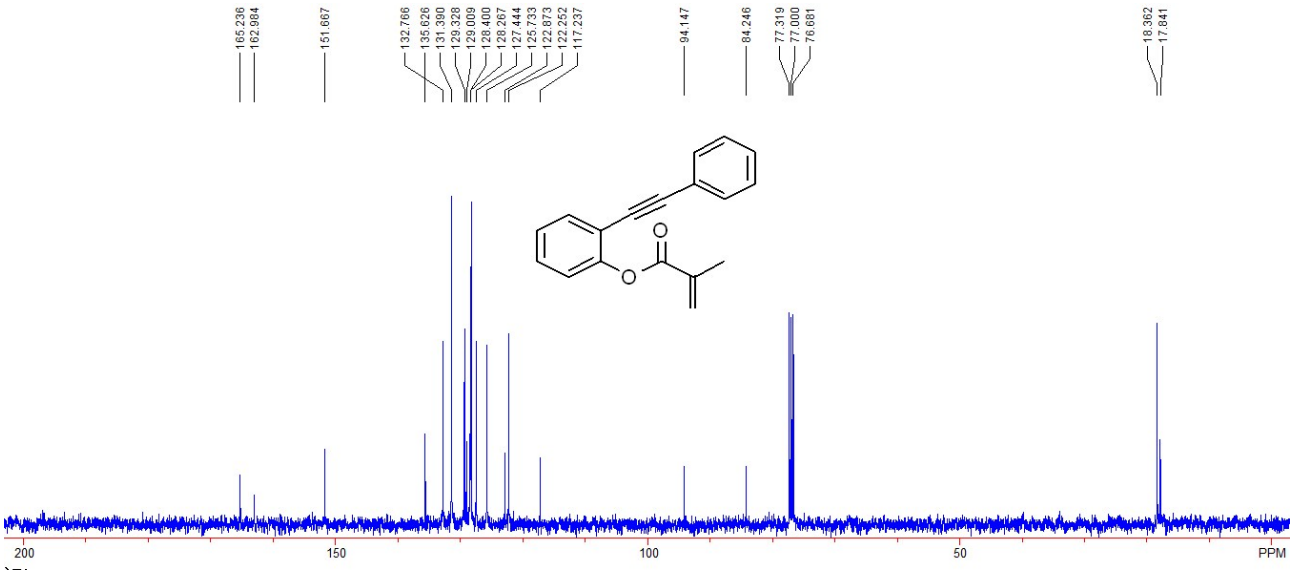
(ESI) *m/z*: 417.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{21}N_2O_3S^+$ requires: 417.1267, Found: 417.1263.

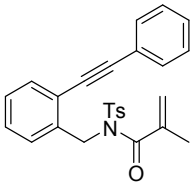


Compound 1bx: 461 mg, 88%, A colorless oil, obtained as 2:1 mixture of rotamers; IR (EtOH): ν 2979, 2923, 1737, 1496, 1445, 1319, 1294, 1198, 1117, 947, 752, 689 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.99 (s, 1.5H), 2.10 (s, 3H), 5.79 (s, 1.5H), 6.21 (s, 0.5H), 6.46 (s, 1H), 7.18-7.24 (m, 2H), 7.31-7.37 (m, 4H), 7.43-7.44 (m, 2H), 7.57 (d, 1H, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.8, 18.4, 84.2, 94.1, 117.2, 122.3, 122.9, 125.7, 127.4, 128.3, 128.4, 129.0, 129.3,

131.4, 132.8, 135.6, 151.7, 163.0, 165.2; MS (ESI) *m/z*: 280.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{18}H_{18}NO_2^+$ requires: 280.1332, Found: 280.1332.

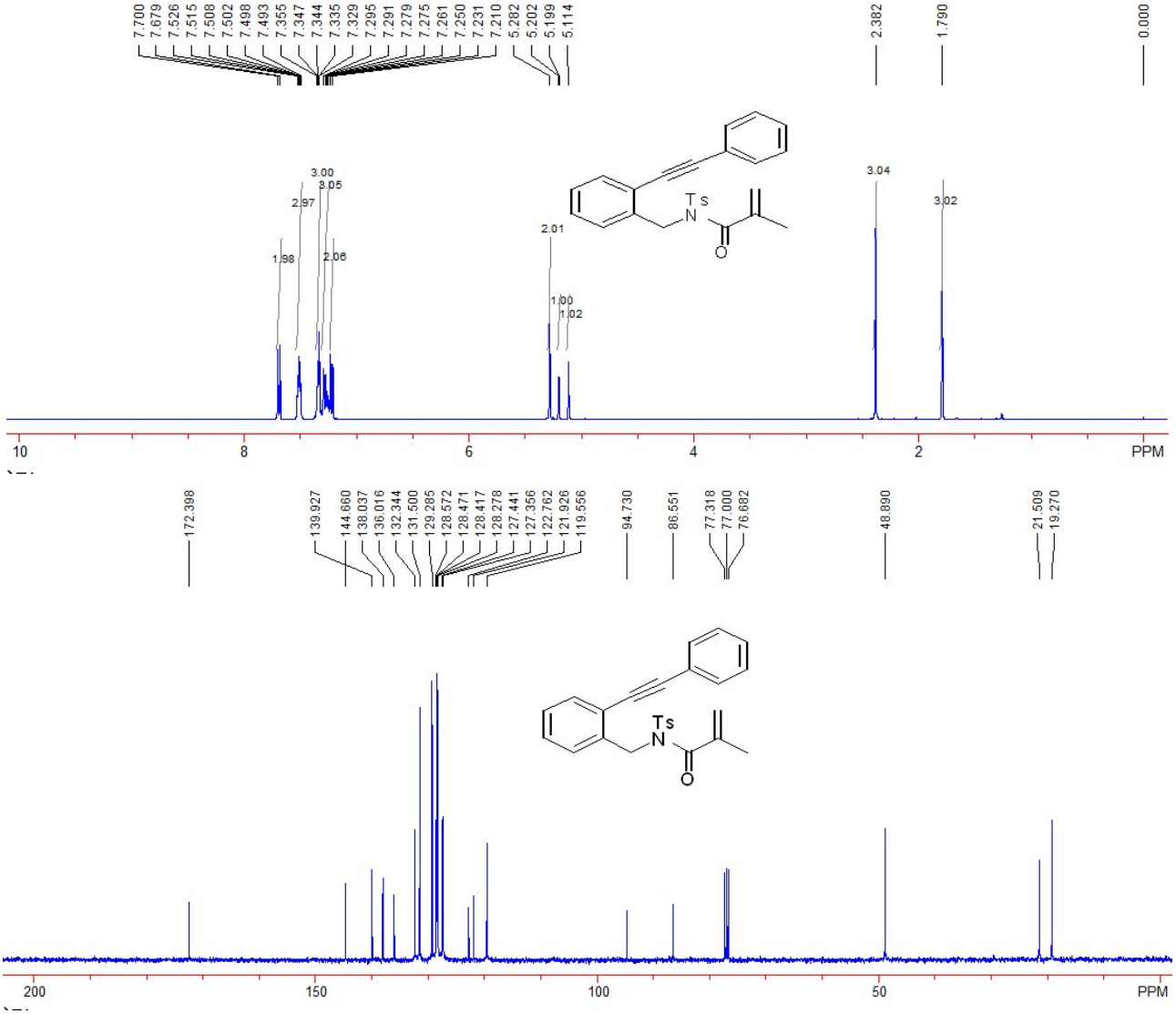






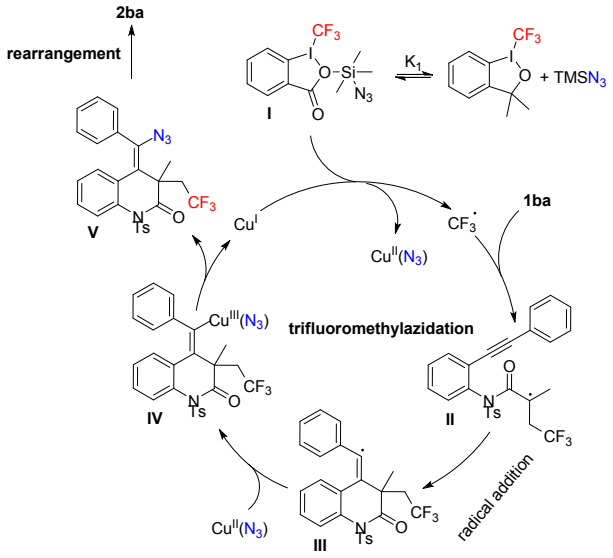
Compound 6: 463 mg, 54%, A white solid, m.p. 186-188 ^oC; IR (EtOH): ν 2970, 2918, 1690, 1494, 1355, 1308, 1167, 1087, 757, 705, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.79 (s, 3H), 2.38 (s, 3H), 5.11 (s, 1H), 5.20 (s, 1H), 5.28 (s, 2H), 7.22 (d, 2H, *J* = 8.4 Hz), 7.25-7.30 (m, 3H), 7.33-7.36 (m, 3H), 7.49-7.53 (m, 3H), 7.69 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.3, 21.5, 48.9, 86.6, 94.7, 119.6, 121.9, 122.8, 127.36, 127.44, 128.3, 128.4, 128.5, 128.6,

129.3, 131.5, 132.3, 136.0, 138.0, 139.9, 144.7, 172.4; MS (ESI) *m/z*: 447.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{27}N_2O_3S_2^+$ requires: 447.1737, Found: 447.1733.



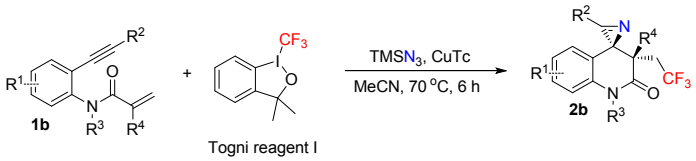
The proposed mechanism for the formation of 2ba

According to our previous work and Liang's work,[2] we proposed the reaction might undergo consecutive trifluoromethylazidation of enynes and thermally induced rearrangement of corresponding vinyl azides, herein we use **1ba** as an example to explain the detailed mechanism: Initially, The trifluoromethyl radical is released accompanied by the formation of $Cu^{II}(N_3)$ complex when Togni reagent **I** is activated by a TMS group,[3] followed by a single-electron transfer (SET) process in the presence of copper catalyst. Afterwards, the chemoselective attack of trifluoromethyl radical on alkene moiety forms the radical intermediate **II**, which induces radical attack on the alkyne moiety to form radical intermediate **III**. Then the activated radical intermediate **III** is combined with the released N_3-coordinated Cu^{II} complex $Cu^{II}(N_3)$ to produce Cu^{III} intermediate **IV**. Finally, reductive elimination of Cu^{III} occurs to form vinyl azide **V** and regenerate Cu^{I} catalyst to complete the whole trifluoromethylazidation process. The formed vinyl azide **V** is not stable under thermal conditions, and a consecutive rearrangement process occurs to deliver the final product **2ba**.



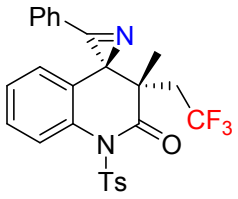
Scheme S1 Proposed mechanism for the synthesis of **2ba**.

General procedure for the synthesis of products 2b and 5

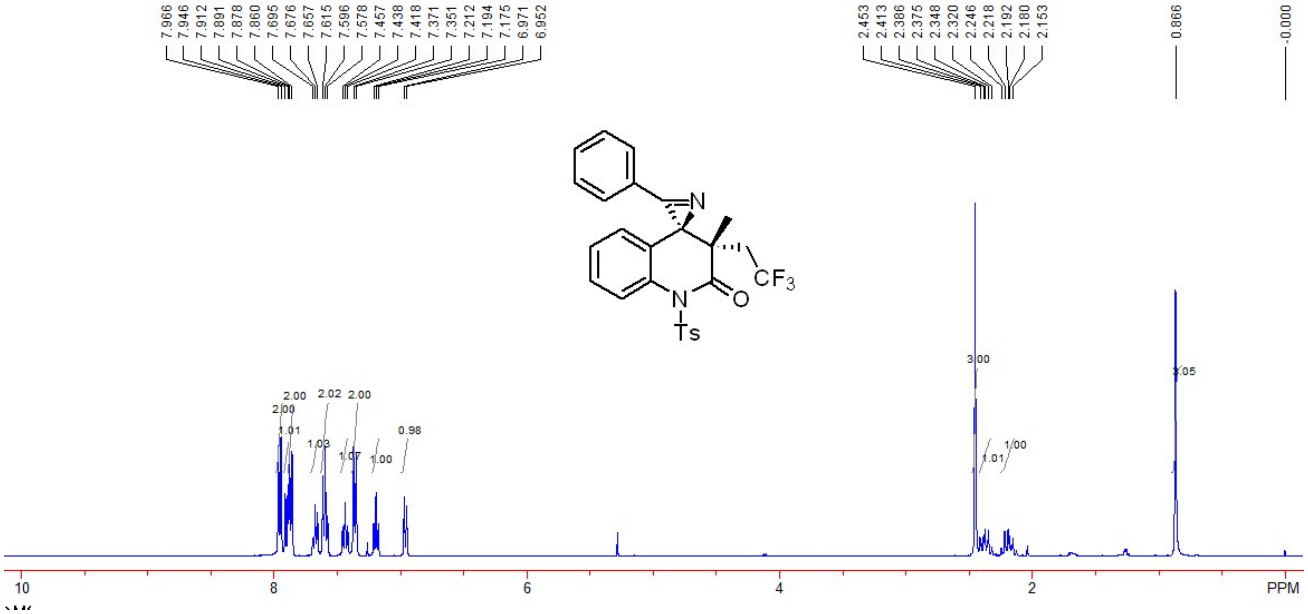


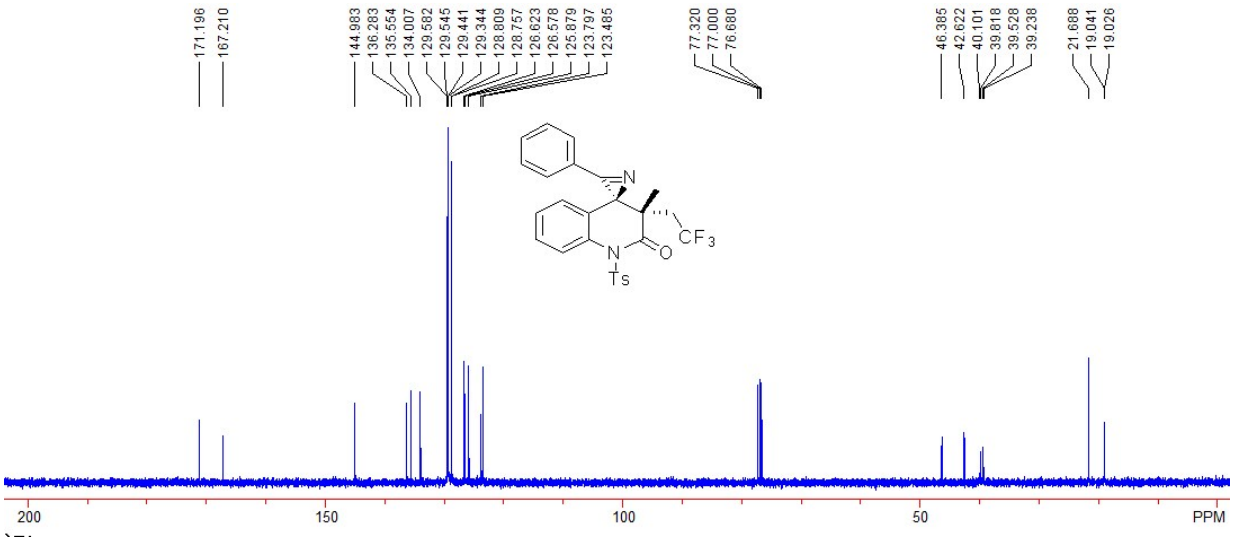
1b or **4** (0.2 mmol, 1.0 equiv), Togni reagent I (0.30 mmol, 1.5 equiv), CuTc (copper(I) thiophene-2-carboxylate, 0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then $TMSN_3$ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 70 °C oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **2b** and **5** in good yield.

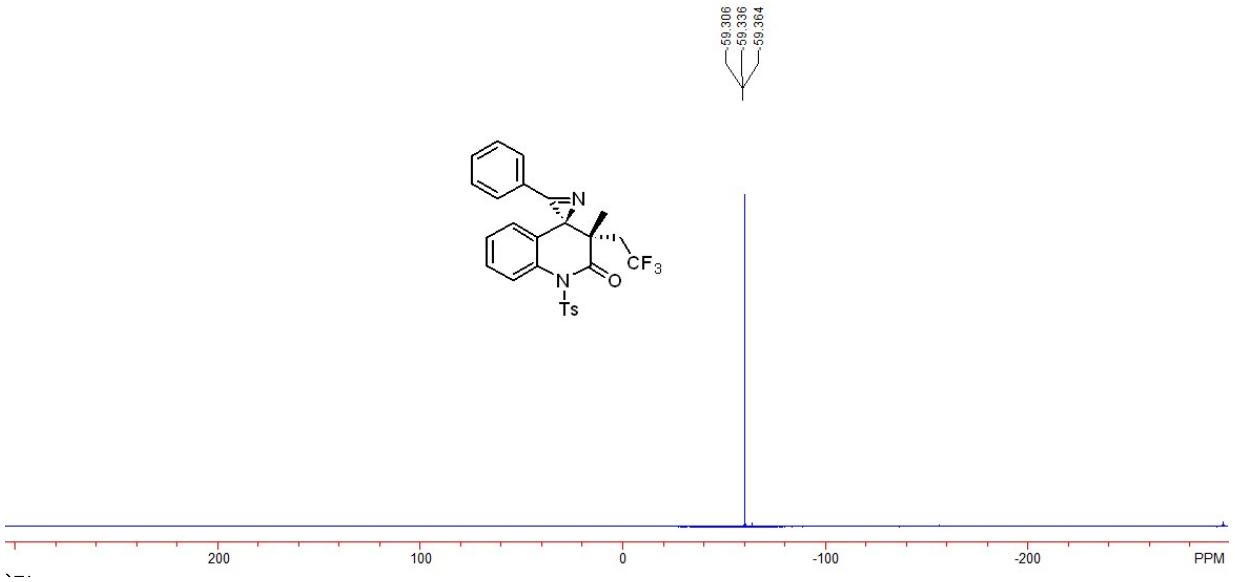
Spectroscopic data for products 2b and 5

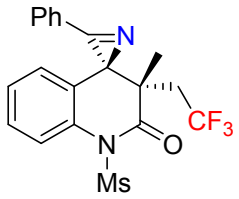


Compound 2ba: 82 mg, 82%, A white solid, m.p. 175-177 ^{o}C; IR (EtOH): ν 2926, 2856, 1715, 1451, 1368, 1263, 1153, 1133, 1118, 1087, 763, 754, 657 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (s, 3H), 2.15-2.25 (m, 1H), 2.32-2.41 (m, 1H), 2.45 (s, 3H), 6.96 (d, 1H, J = 7.6 Hz), 7.21 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.44 (t, 1H, J = 8.0 Hz), 7.60 (t, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.86-7.91 (m, 3H), 7.96 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0 (q, $J_{C\text{-}F}$ = 1.5 Hz), 21.7, 39.7 (q, $J_{C\text{-}F}$ = 29.0 Hz), 42.6, 46.4, 123.5, 123.8, 125.9, 126.6, 128.0 (q, $J_{C\text{-}F}$ = 277.1 Hz), 128.76, 128.81, 129.3, 129.4, 129.5, 129.6, 134.0, 135.6, 136.3, 145.0, 167.2, 171.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.3 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 516.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{25}F_3N_3O_3S^+$ requires: 516.1563, Found: 516.1558.



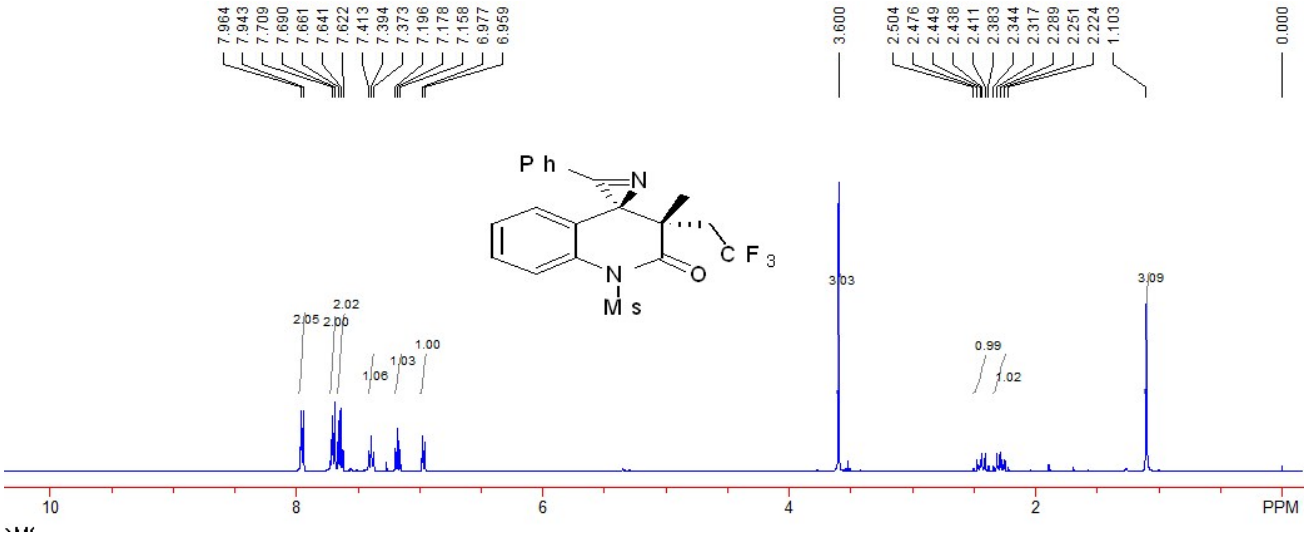


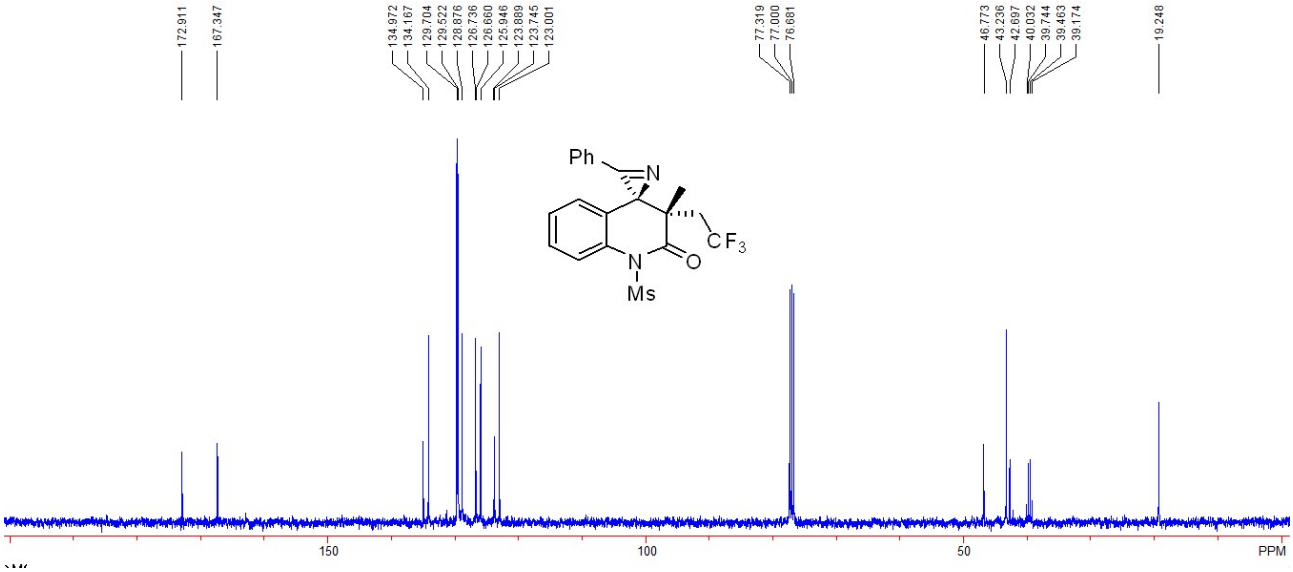


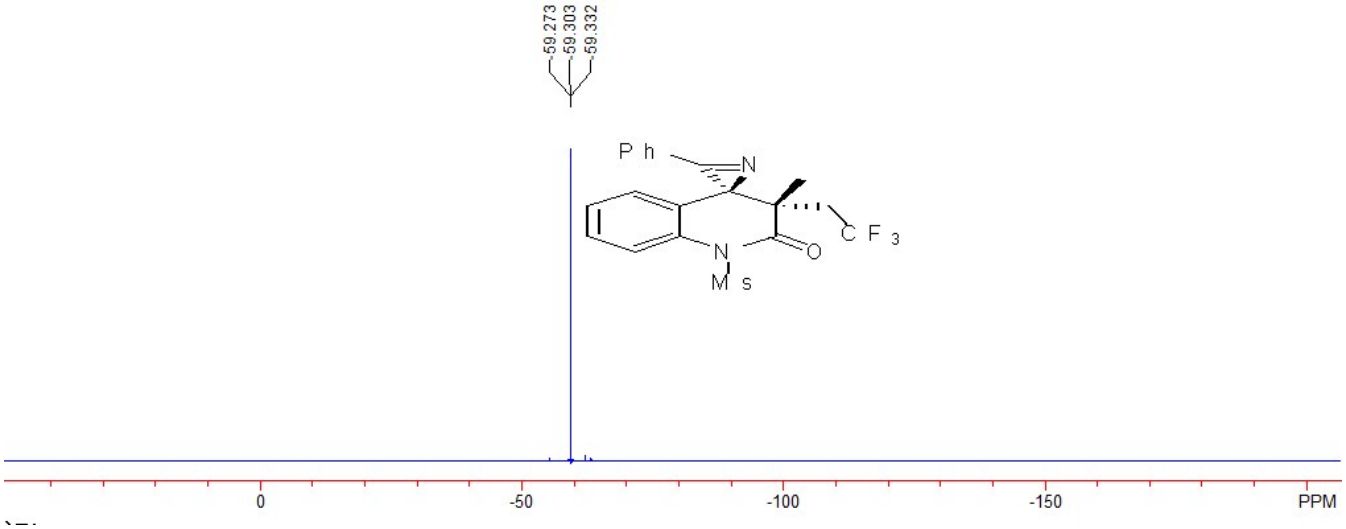


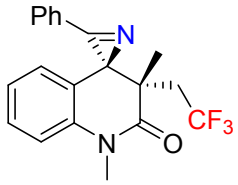
Compound 2bb: 71 mg, 84%, A white solid, m.p. 160-162 ^{o}C; IR (EtOH): ν 2923, 2848, 1713, 1361, 1257, 1174, 1149, 1129, 1110, 971, 962, 769, 760, 695 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.10 (s, 3H), 2.22-2.34 (m, 1H), 2.38-2.50 (m, 1H), 3.60 (s, 3H), 6.97 (d, 1H, J = 7.2 Hz), 7.18 (t, 1H, J = 7.2 Hz), 7.39 (t, 1H, J = 8.4 Hz), 7.62-7.71 (m, 4H), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 39.6 (q, $J_{C\text{-}F}$ = 28.9 Hz), 42.7, 43.2, 46.8 (q, $J_{C\text{-}F}$ = 1.5 Hz), 123.0, 123.7, 125.3 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.9, 126.7, 128.9, 129.5, 129.67, 129.70, 134.2, 135.0, 167.3, 172.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.3 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*:

440.1 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{20}H_{21}F_3N_3O_3S^+$ requires: 440.1250, Found: 440.1246.

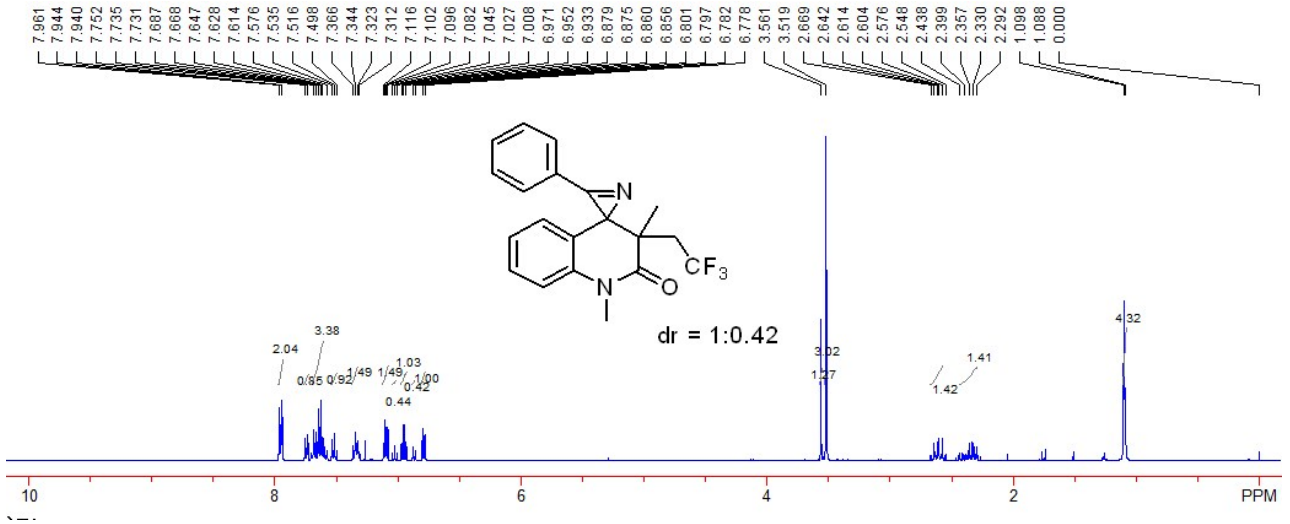


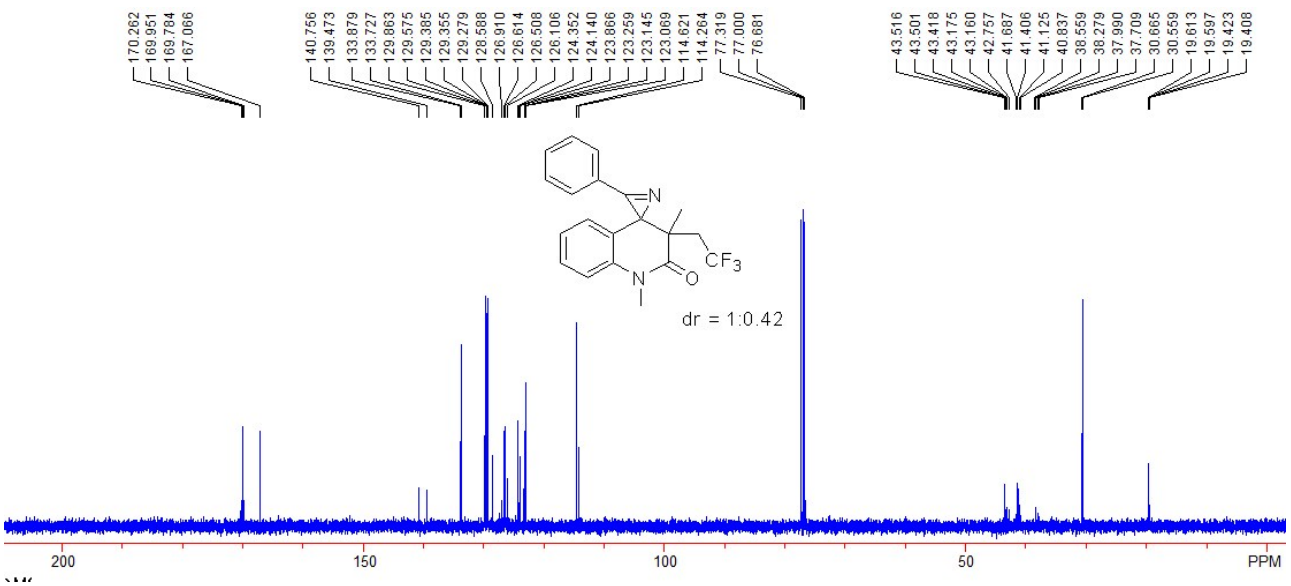


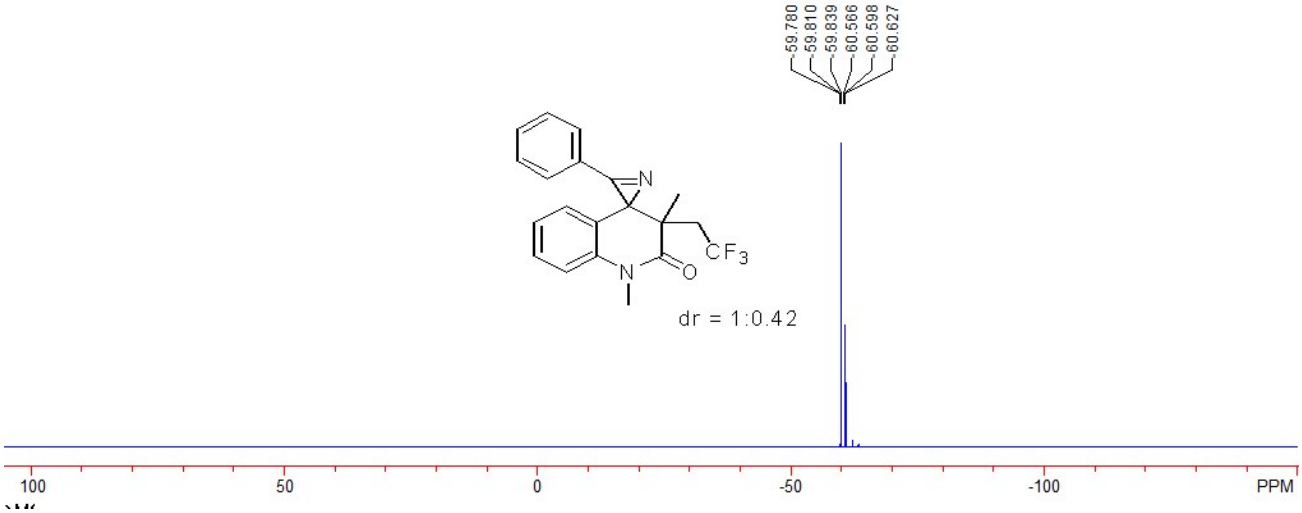


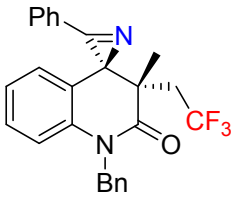


Compound 2bc: 64 mg, 90%, A white solid, m.p. 164-166 °C, dr = 1:0.42; IR (EtOH): ν 2979, 2937, 1677, 1603, 1471, 1356, 1260, 1139, 1112, 762, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.09 (s, 1.26H), 1.10 (s, 3H), 2.29-2.44 (m, 1.42H), 2.55-2.67 (m, 1.42H), 3.52 (s, 3H), 3.56 (s, 1.26H), 6.79 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 6.87 (dd, 0.42H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 6.95 (t, 1H, J = 7.6 Hz), 7.03 (t, 0.42H, J = 7.6 Hz), 7.08-7.12 (m, 1.42H), 7.31-7.37 (m, 1.42H), 7.52 (t, 0.84H, J = 7.6 Hz), 7.58-7.69 (m, 3.42H), 7.74 (dd, 0.84H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.95 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.4 (q, $J_{C\text{-}F}$ = 1.6 Hz), 19.6 (q, $J_{C\text{-}F}$ = 1.6 Hz), 30.56, 30.67, 38.1 (q, $J_{C\text{-}F}$ = 28.1 Hz), 41.3 (q, $J_{C\text{-}F}$ = 28.1 Hz), 42.8, 43.2 (q, $J_{C\text{-}F}$ = 1.5 Hz), 43.4, 43.5 (q, $J_{C\text{-}F}$ = 1.5 Hz), 123.07, 123.15, 123.3, 123.9, 124.4, 125.5 (q, $J_{C\text{-}F}$ = 277.0 Hz), 125.9 (q, $J_{C\text{-}F}$ = 277.0 Hz), 126.1, 126.5, 126.6, 128.6, 129.3, 129.36, 129.39, 129.6, 129.9, 133.7, 133.9, 139.5, 140.8, 167.1, 169.8, 170.0, 170.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.8 (t, 3F, J = 10.9 Hz), -60.6 (t, 1.26F, J = 10.9 Hz); MS (ESI) *m/z*: 359.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{20}H_{18}F_3N_2O^+$ requires: 359.1366, Found: 359.1363.



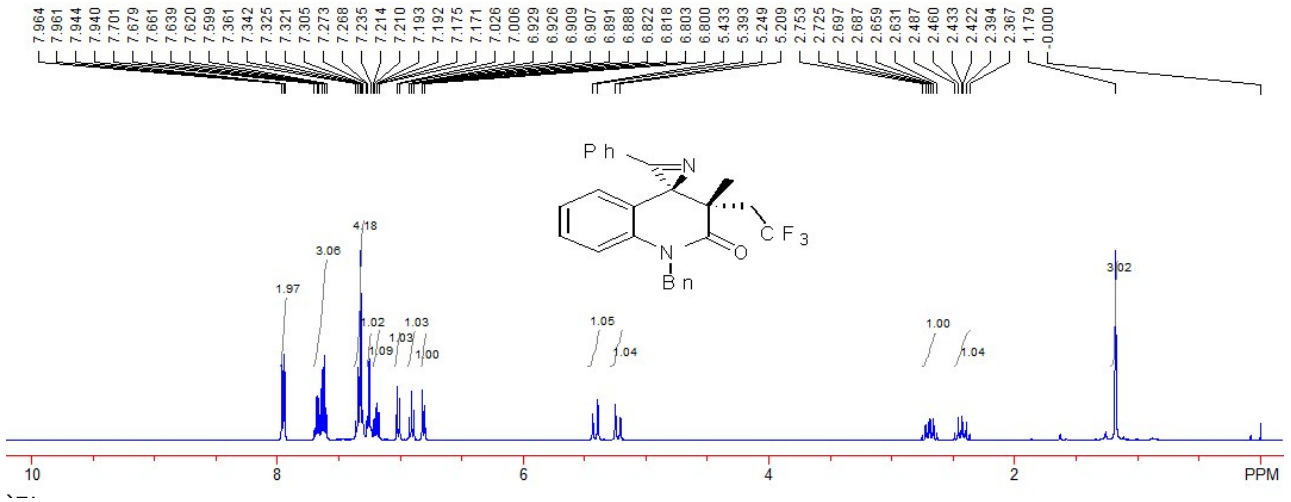


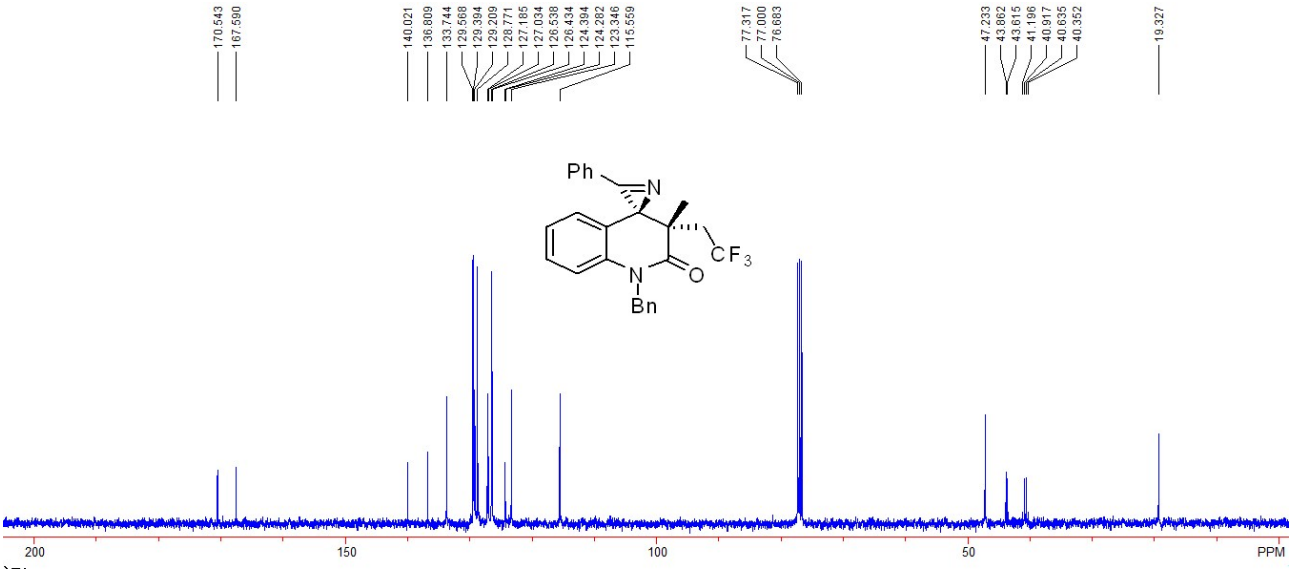


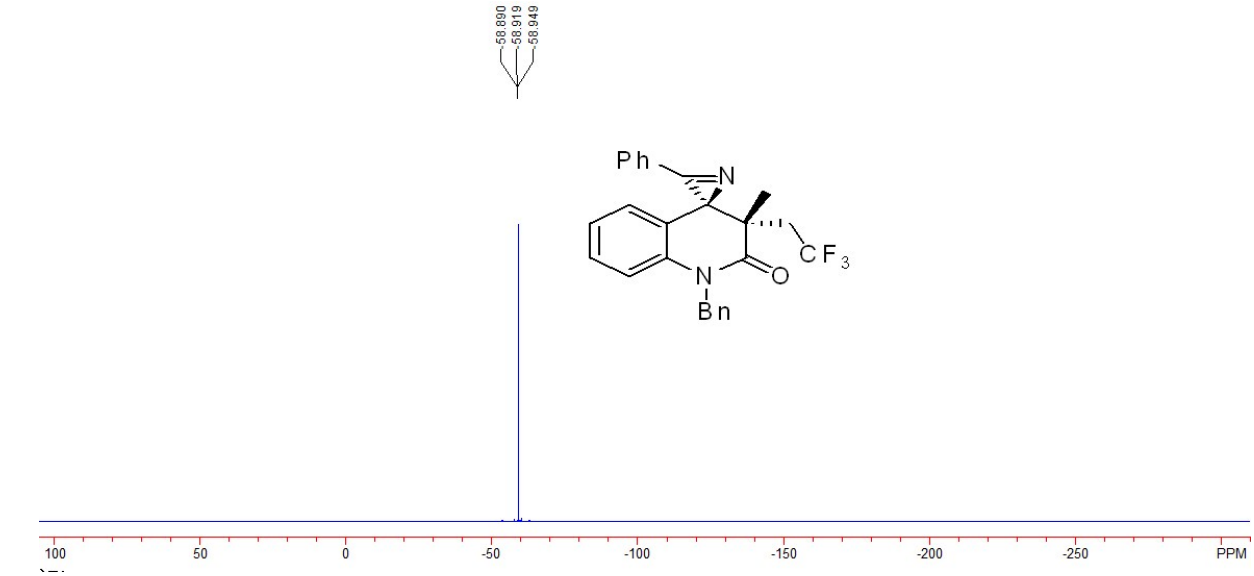


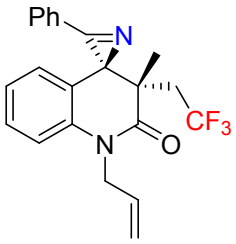
Compound 2bd: 65 mg, 75%, A white solid, m.p. 175-177 ^{o}C; IR (EtOH): ν 2926, 2848, 1679, 1602, 1495, 1459, 1368, 1322, 1261, 1179, 1134, 1119, 1068, 763, 760, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.18 (s, 3H), 2.37-2.49 (m, 1H), 2.63-2.75 (m, 1H), 5.23 (d, 1H, J = 16.0 Hz), 5.41 (d, 1H, J = 16.0 Hz), 6.81 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 6.91 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.02 (d, 1H, J = 8.0 Hz), 7.17-7.21 (m, 1H), 7.24-7.27 (m, 1H), 7.31-7.36 (m, 4H), 7.60-7.70 (m, 3H), 7.95 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.3, 40.8 (q, $J_{C\text{-}F}$ = 28.1 Hz), 43.6, 43.9 (q, $J_{C\text{-}F}$ = 1.6 Hz), 47.2, 115.6, 123.3, 124.4, 125.7 (q, $J_{C\text{-}F}$ = 277.1 Hz), 126.4, 126.5, 127.0, 127.2, 128.8, 129.2, 129.4, 129.6, 133.7, 136.8, 140.0, 167.6, 170.5;

^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.9 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 435.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{22}F_3N_2O^+$ requires: 435.1679, Found: 435.1674.

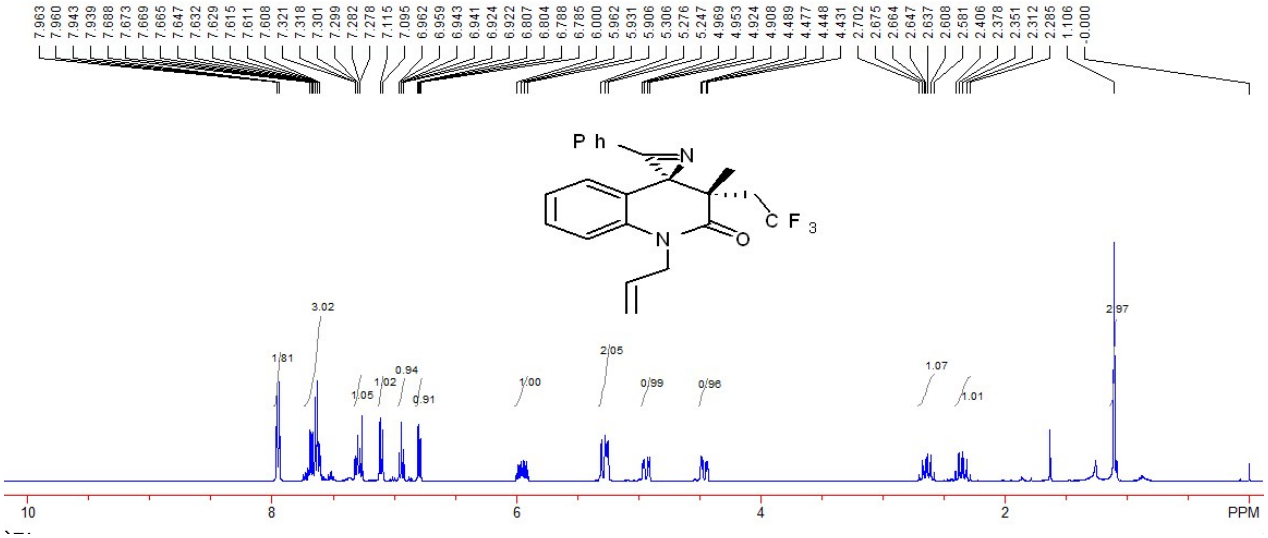


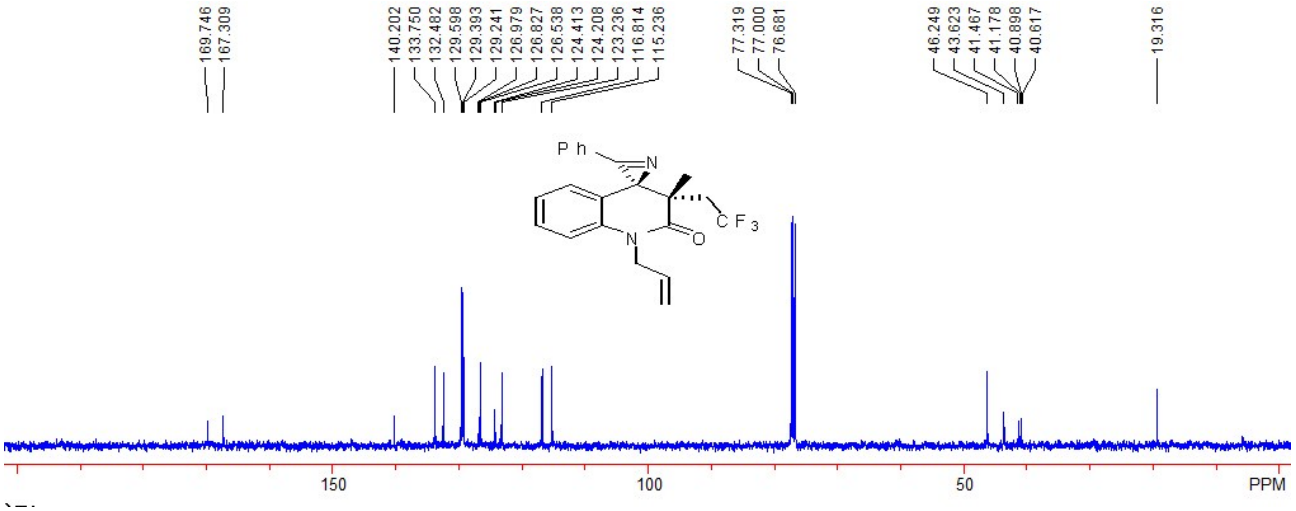


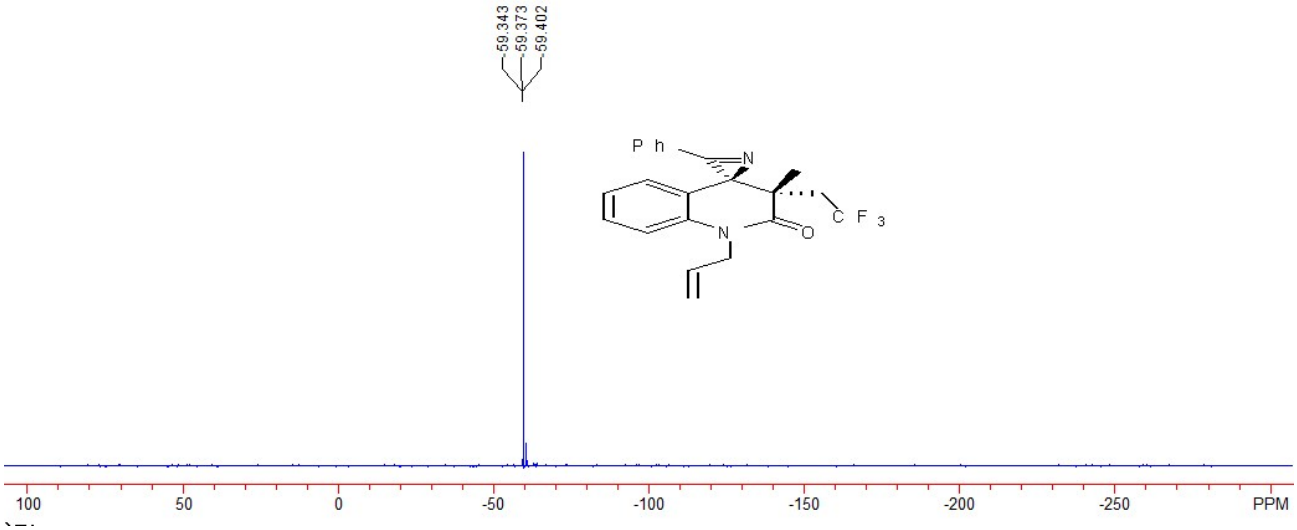


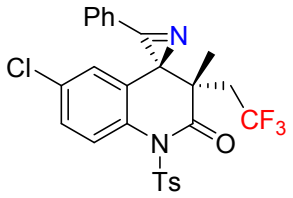


Compound 2be: 48 mg, 63%, A white solid, m.p. 163-165 ^{o}C; IR (EtOH): ν 2937, 2854, 1677, 1603, 1460, 1451, 1367, 1259, 1184, 1133, 1118, 754, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.11 (s, 3H), 2.29-2.41 (m, 1H), 2.61-2.70 (m, 1H), 4.46 (dd, 1H, J_1 = 18.0 Hz, J_2 = 6.4 Hz), 4.93 (dd, 1H, J_1 = 18.0 Hz, J_2 = 6.4 Hz), 5.28-5.31 (m, 2H), 5.91-6.00 (m, 1H), 6.80 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 6.92-6.96 (m, 1H), 7.11 (d, 1H, J = 8.0 Hz), 7.28-7.32 (m, 1H), 7.61-7.69 (m, 3H), 7.95 (dd, 2H, J_1 = 8.0 Hz, J_2 = 1.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.3, 41.0 (q, $J_{C\text{-}F}$ = 28.1 Hz), 43.6, 46.2, 115.2, 116.8, 123.2, 124.4, 125.6 (q, $J_{C\text{-}F}$ = 277.1 Hz), 126.5, 126.8, 129.2, 129.4, 129.6, 132.5, 133.8, 140.2, 167.3, 169.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 385.2 (M+H$^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{20}F_3N_2O^+$ requires: 385.1522, Found: 385.1519.

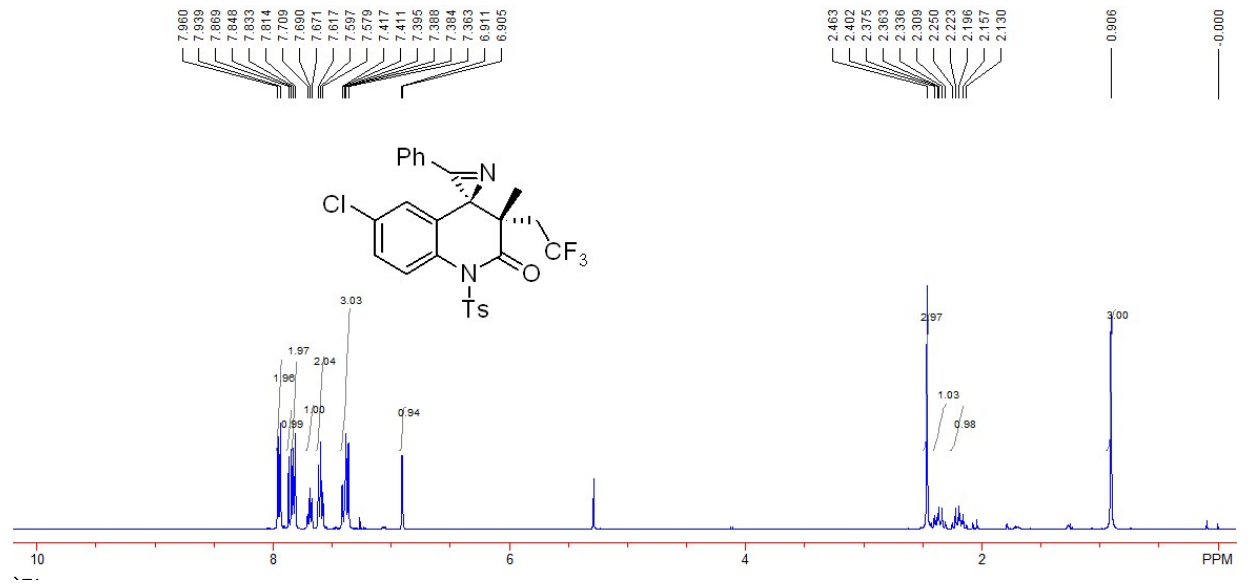








Compound 2bf: 83 mg, 78%, A white solid, m.p. 210-212 ^{o}C; IR (EtOH): ν 3051, 1719, 1396, 1359, 1175, 1153, 1132, 1086, 811, 768, 750, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.91 (s, 3H), 2.13-2.25 (m, 1H), 2.31-2.40 (m, 1H), 2.46 (s, 3H), 6.91 (s, 1H), 7.36-7.42 (m, 3H), 7.58-7.62 (m, 2H), 7.69 (t, 1H, J = 7.6 Hz), 7.81-7.87 (m, 3H), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0 (q, $J_{C\text{-}F}$ = 1.5 Hz), 21.7, 39.4 (q, $J_{C\text{-}F}$ = 29.0 Hz), 42.1, 46.3 (q, $J_{C\text{-}F}$ = 1.5 Hz), 123.2, 124.7, 125.1 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.5, 128.8, 128.9, 129.4, 129.6, 129.7, 131.6, 132.3, 134.0, 134.3, 135.9, 145.3, 166.9, 170.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.0 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 550.1 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}ClF_3N_3O_3S^+$ requires: 550.1174, Found: 550.1170.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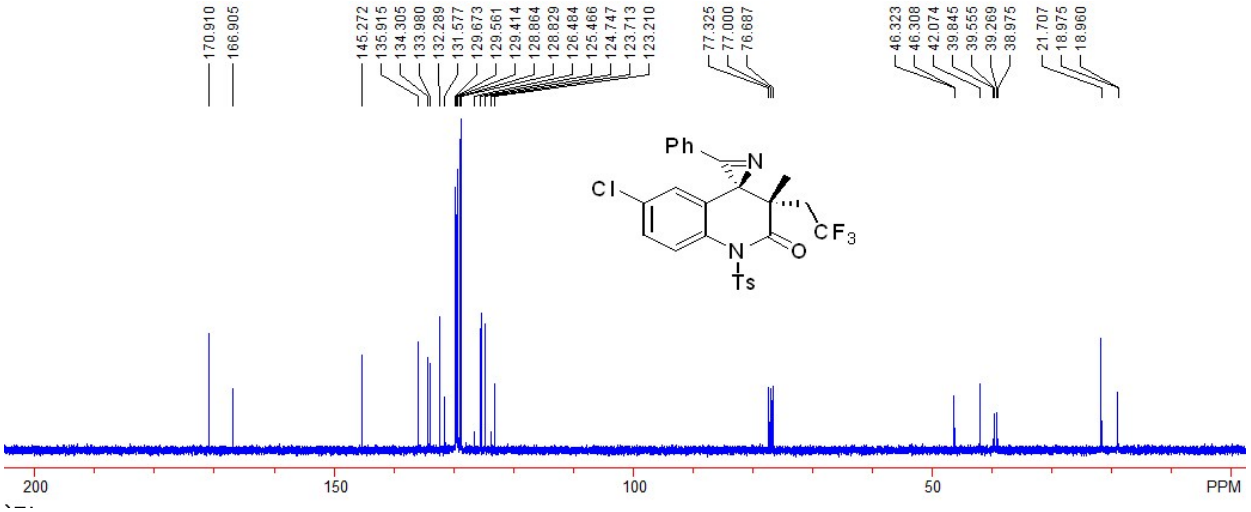
7.869
7.848
7.833
7.814
7.709
7.690
7.671
7.617
7.597
7.579
7.417
7.411
7.395
7.388
7.384
7.363
6.911
6.905
2.463
2.402
2.375
2.363
2.336
2.309
2.250
2.223
2.196
2.157
2.130
0.906
-0.000
Ph
N
Cl
CF3
N
O
Ts
3.03
1.97
1.96
2.04
1.00
0.99
0.94
2.97
3.00
1.03
0.98
10
8
6
4
2
PPM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166.905
145.272
135.915
134.305
133.980
132.289
131.577
129.673
129.561
129.414
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126.484
125.466
124.747
123.713
123.210
77.325
77.000
76.687
46.323
46.308
42.074
39.845
39.555
39.269
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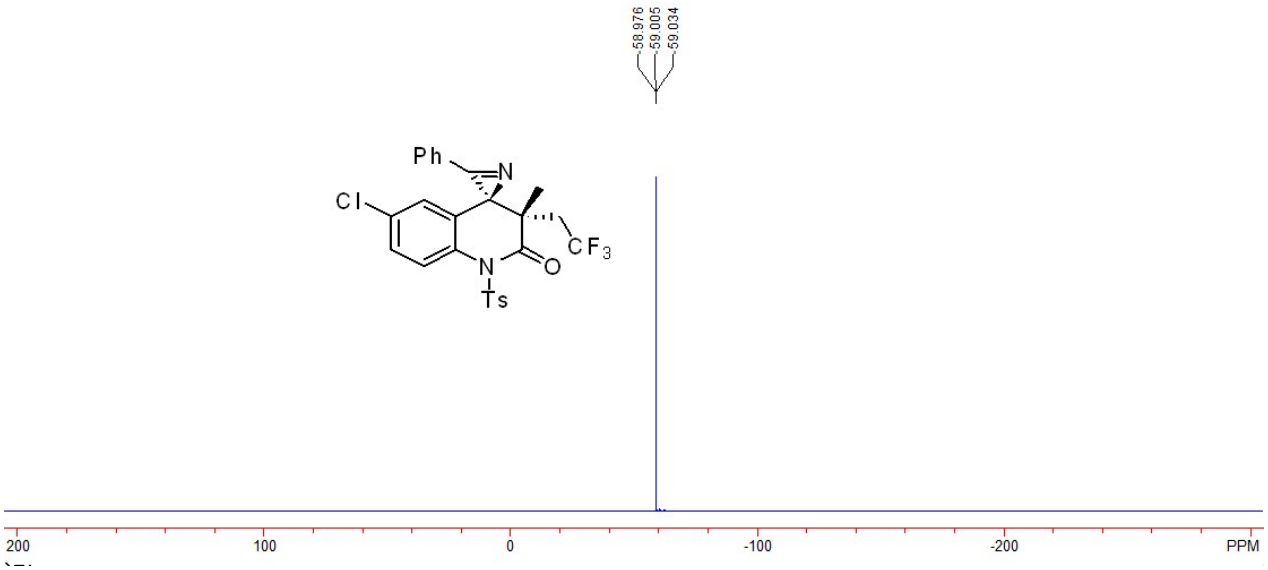
CF3
N
O
Ts
200
150
100
50
PPM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59.034
Ph
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Cl
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N
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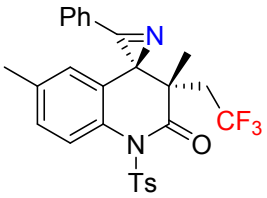
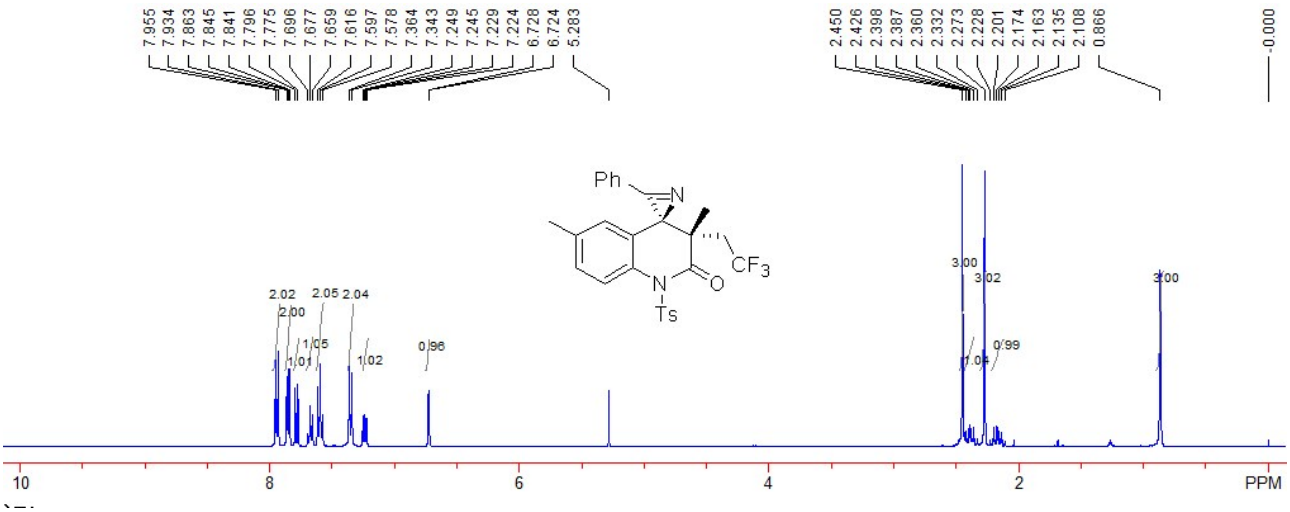
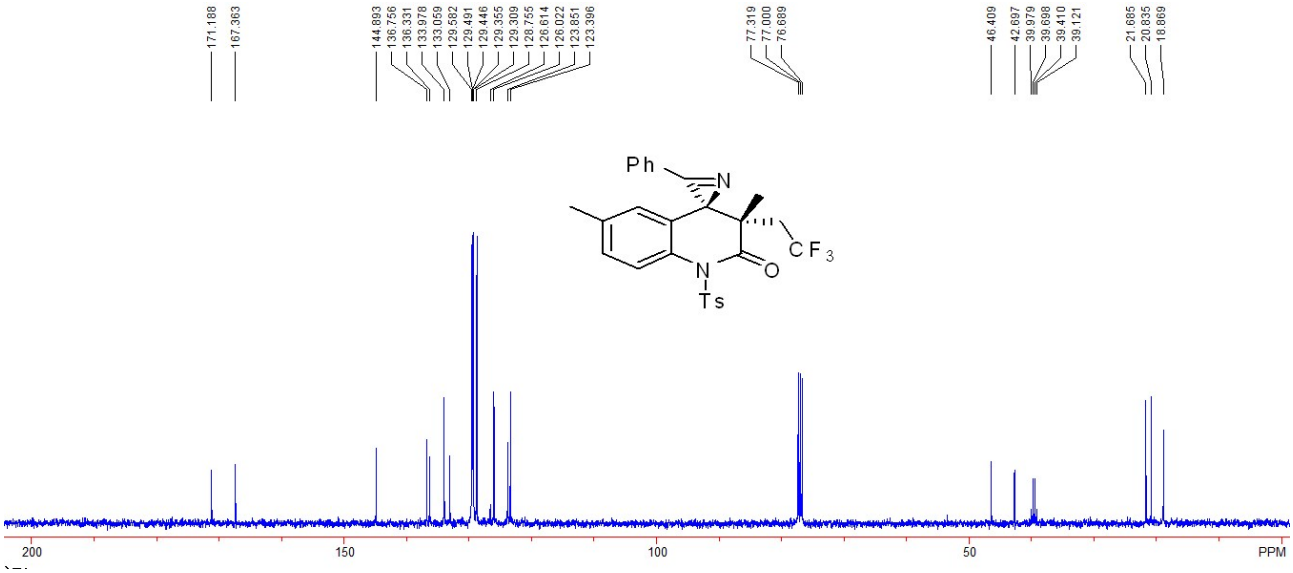
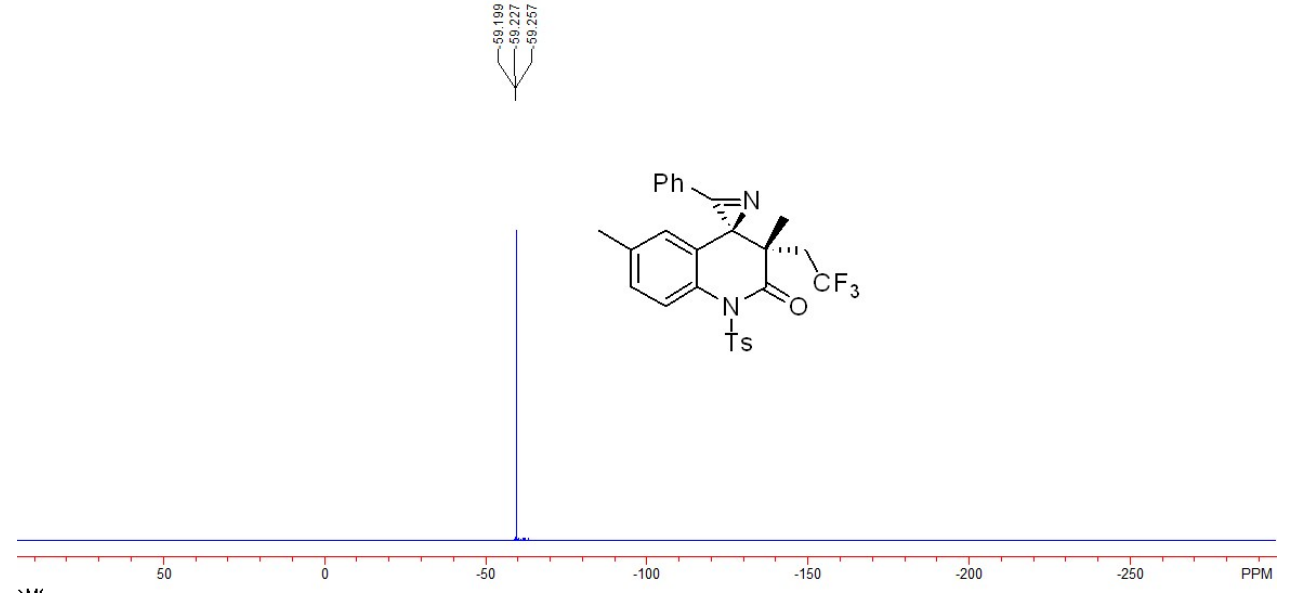
Ts
200
100
0
-100
-200
PPM

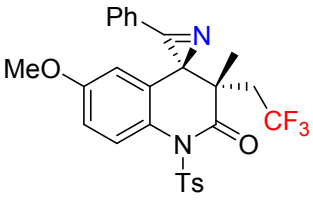


Compound 2bg: 82 mg, 80%, A white solid, m.p. 184-186 ^{o}C; IR (EtOH): ν 2922, 2851, 1719, 1367, 1262, 1173, 1134, 1087, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (s, 3H), 2.11-2.23 (m, 1H), 2.27 (s, 3H), 2.33-2.43 (m, 1H), 2.45 (s, 3H), 6.73 (d, 1H, J = 1.6 Hz), 7.24 (dd, 1H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.35 (d, 2H, J = 8.4 Hz), 7.60 (t, 2H, J = 7.6 Hz), 7.68 (t, 1H, J = 7.6 Hz), 7.79 (d, 1H, J = 8.4 Hz), 7.85 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.94 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 20.8, 21.7, 39.5 (q, $J_{C\text{-}F}$ = 28.9 Hz), 42.7, 46.4 (q, $J_{C\text{-}F}$ = 1.6 Hz), 123.4, 123.8, 126.0, 128.0 (q, $J_{C\text{-}F}$ = 277.1 Hz), 128.7, 129.30, 129.35, 129.4, 129.5, 129.6, 133.1, 134.0, 136.3, 136.7, 144.9, 167.4, 171.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.2 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 530.1 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}F_3N_3O_3S^+$ requires: 530.1720, Found: 530.1714.



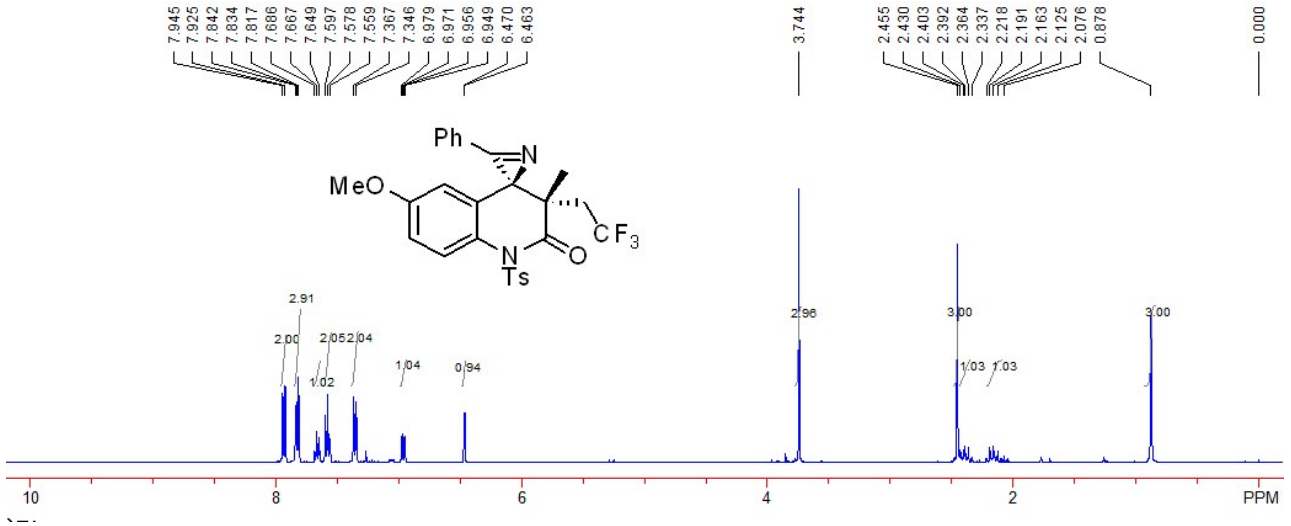


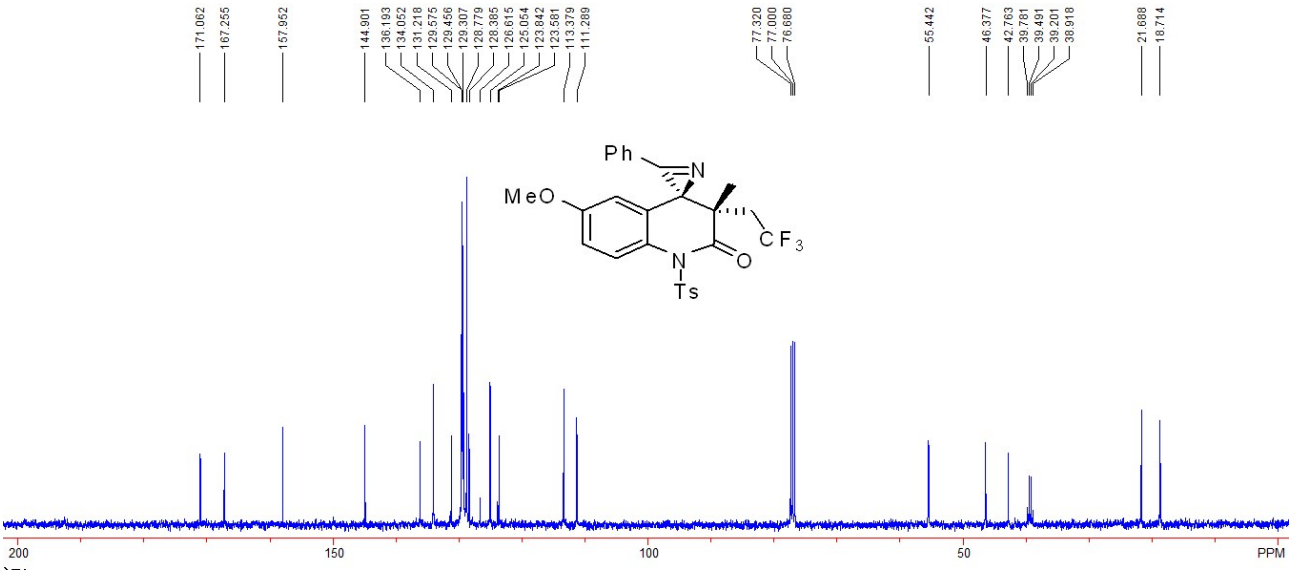


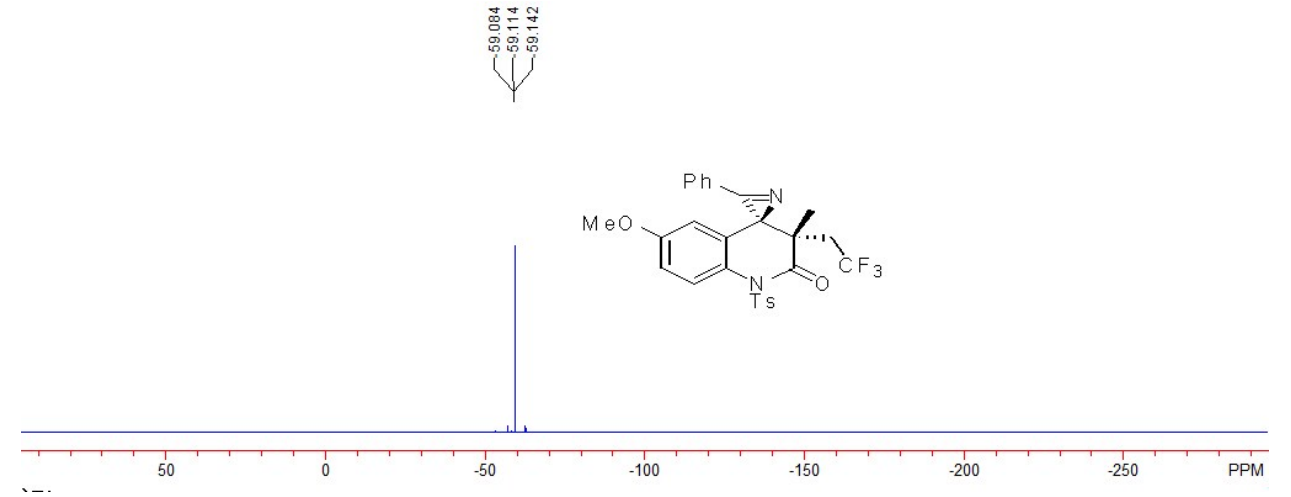


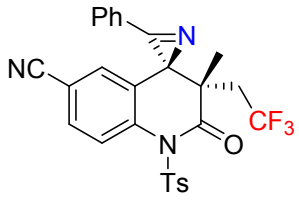
Compound 2bh: 83 mg, 79%, A white solid, m.p. 189-191 ^{o}C; IR (EtOH): ν 2962, 2919, 1729, 1488, 1371, 1263, 1176, 1127, 1085, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (s, 3H), 2.08-2.22 (m, 1H), 2.34-2.43 (m, 1H), 2.46 (s, 3H), 3.74 (s, 3H), 6.47 (d, 1H, J = 2.8 Hz), 6.96 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.8 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.58 (t, 2H, J = 7.6 Hz), 7.67 (t, 1H, J = 7.6 Hz), 7.82-7.84 (m, 3H), 7.94 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.7, 21.7, 39.3 (q, $J_{C\text{-}F}$ = 29.0 Hz), 42.8, 46.4 (q, $J_{C\text{-}F}$ = 1.5 Hz), 55.4, 111.3, 113.4, 123.6, 125.1, 125.2 (q, $J_{C\text{-}F}$ = 277.3 Hz), 128.4, 128.8, 129.3, 129.5, 129.6, 131.2, 134.1, 136.2, 144.9, 158.0, 167.3, 171.1; ^{19}F

NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.1 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 546.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}F_3N_3O_4S^+$ requires: 546.1669, Found: 546.1664.

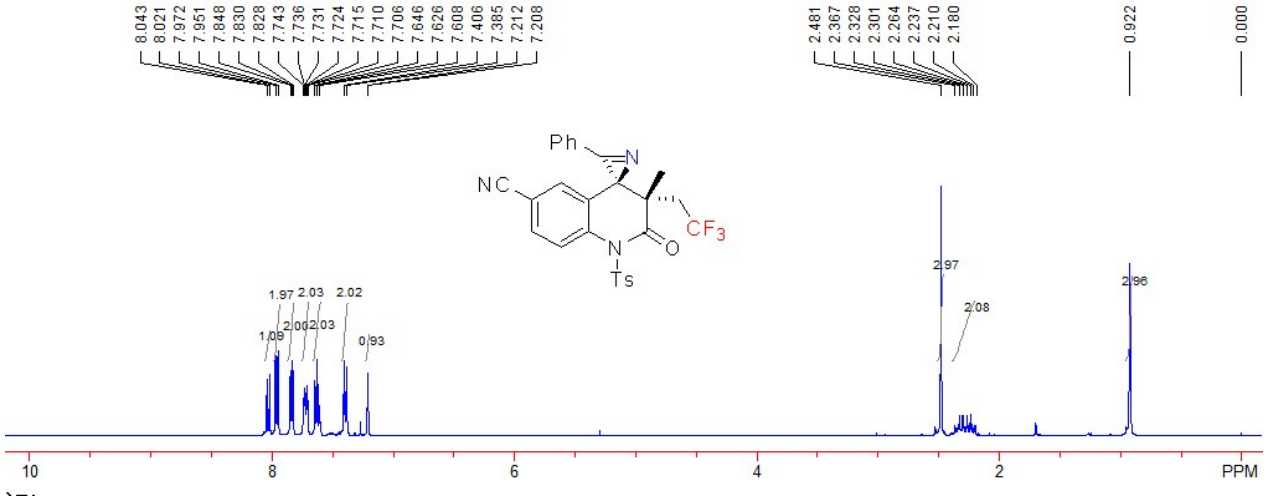


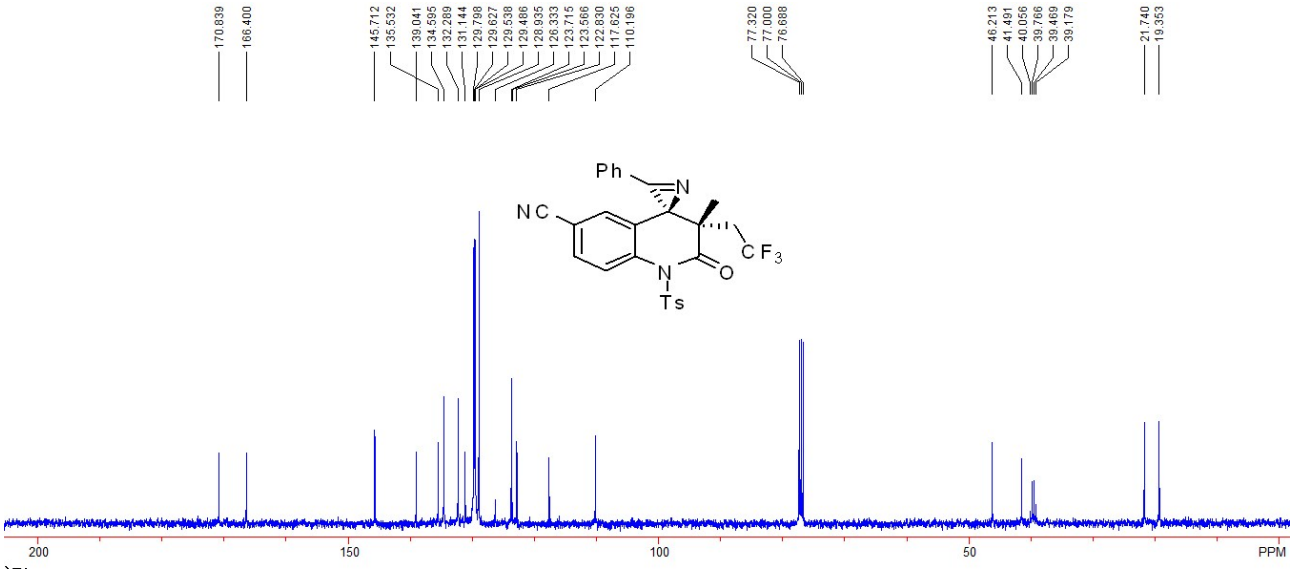


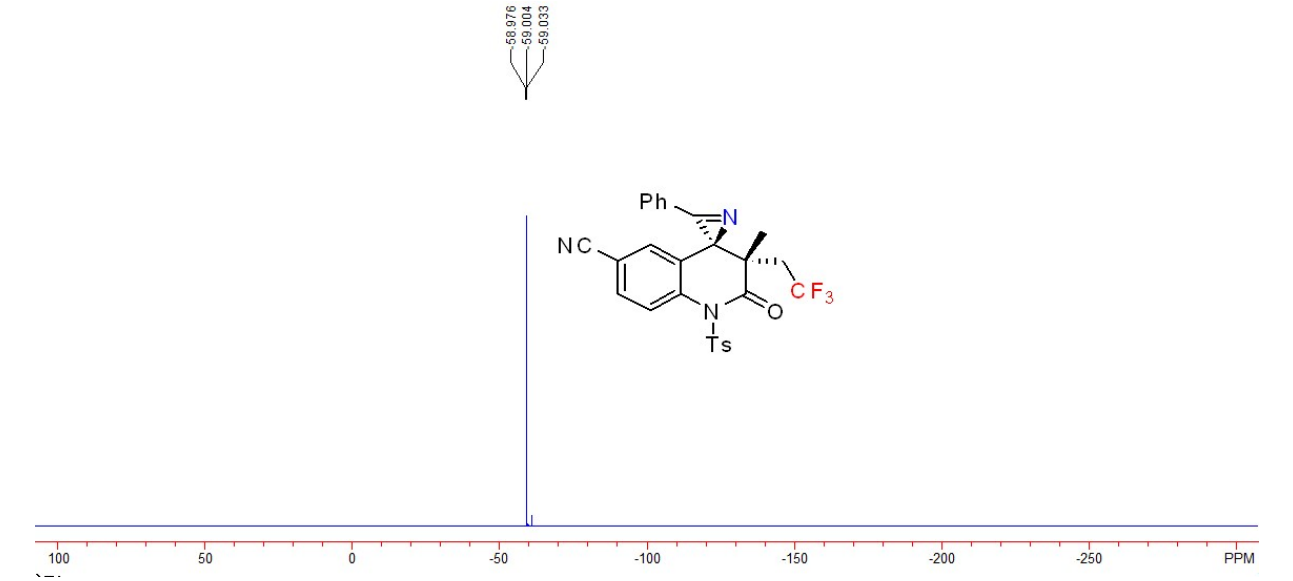


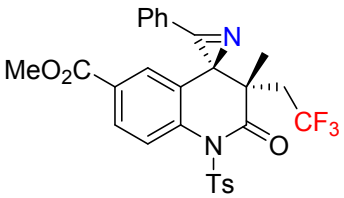


Compound 2bi: 74 mg, 71%, A white solid, m.p. 198-200 ^{o}C; IR (EtOH): ν 2973, 2893, 1719, 1369, 1262, 1175, 1149, 1128, 1086, 1046, 879, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (s, 3H), 2.18-2.37 (m, 2H), 2.48 (s, 3H), 7.21 (d, 1H, J = 1.6 Hz), 7.40 (d, 2H, J = 8.4 Hz), 7.61-7.65 (m, 2H), 7.71-7.74 (m, 2H), 7.85 (dd, 2H, J_1 = 7.2 Hz, J_2 = 0.8 Hz), 7.96 (d, 2H, J = 8.4 Hz), 8.03 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.3, 21.7, 39.6 (q, $J_{C\text{-}F}$ = 29.0 Hz), 41.5, 46.2 (q, $J_{C\text{-}F}$ = 1.5 Hz), 110.2, 117.6, 122.8, 123.7, 124.9 (q, $J_{C\text{-}F}$ = 276.6 Hz), 128.9, 129.48, 129.53, 129.6, 129.8, 131.1, 132.3, 134.6, 135.5, 139.0, 145.7, 166.4, 170.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.0 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 541.2 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{27}H_{24}F_3N_4O_3S^+$ requires: 541.1516, Found: 541.1511.



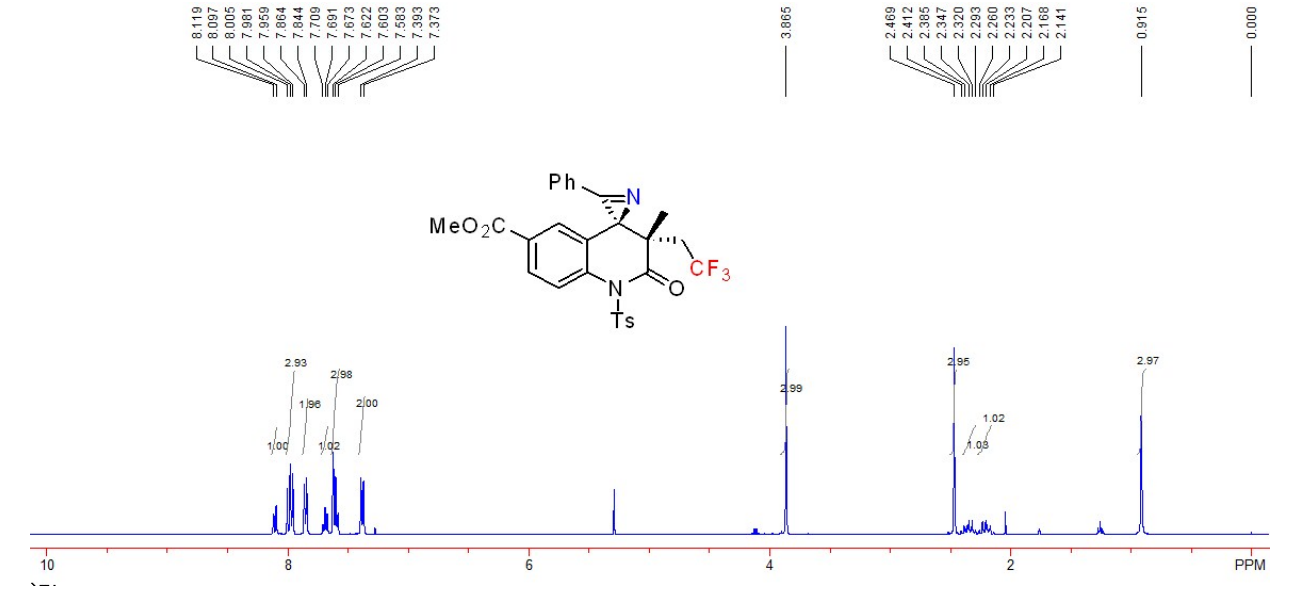


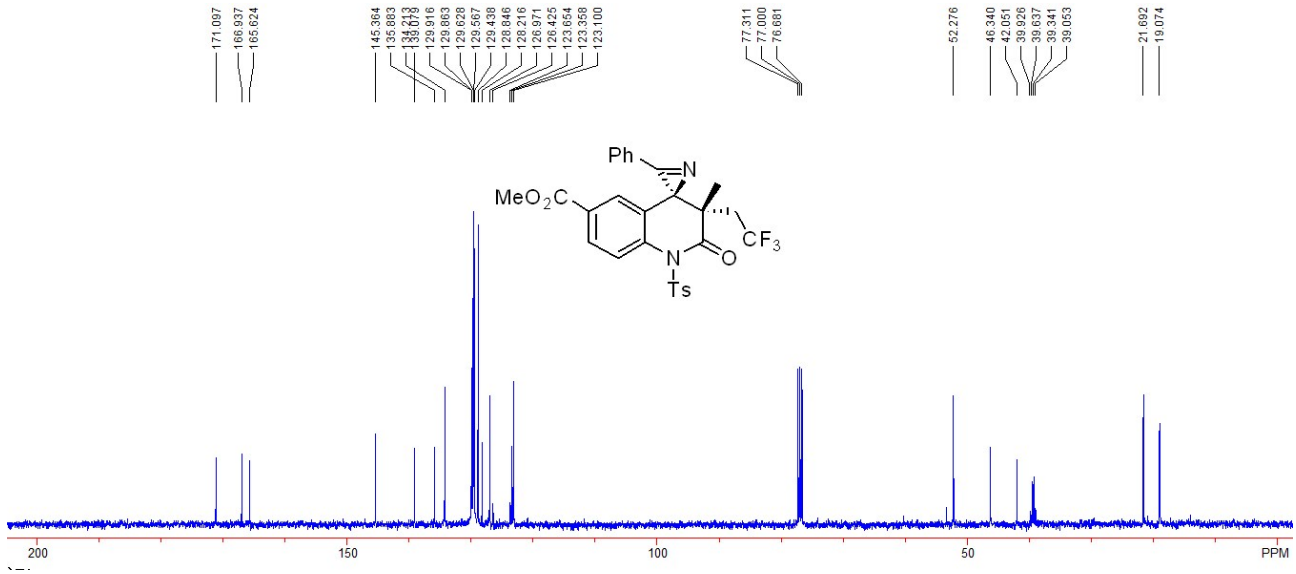


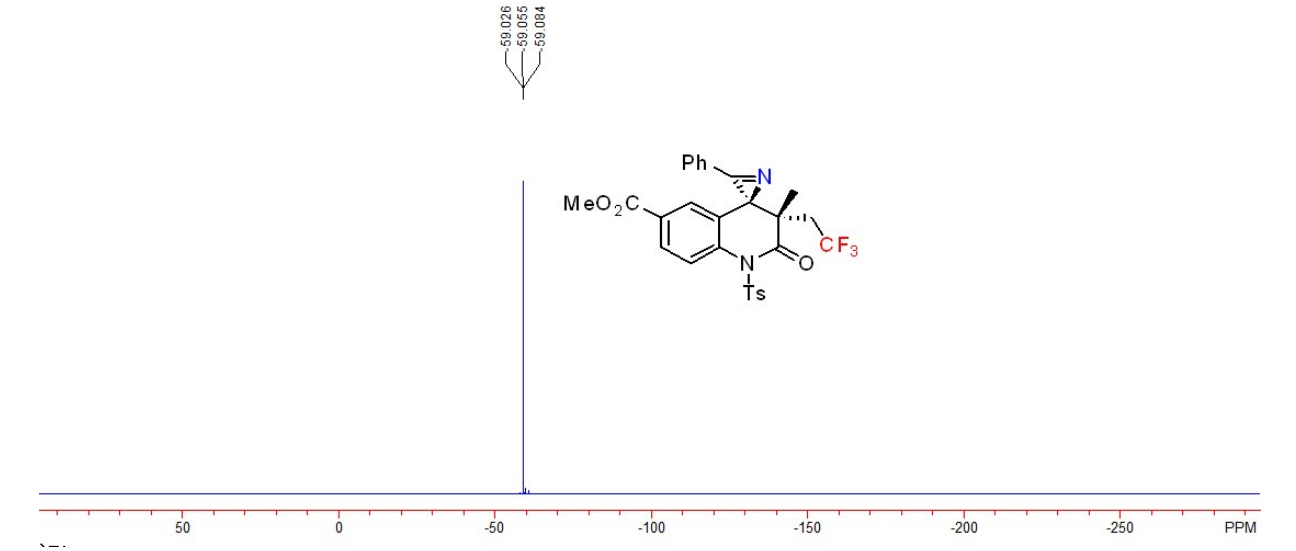


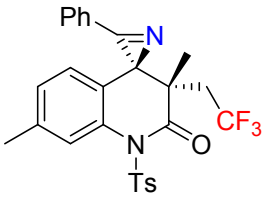
Compound 2bj: 91 mg, 82%, A white solid, m.p. 177-179 ^{o}C; IR (EtOH): ν 2920, 2848, 1722, 1370, 1264, 1176, 1130, 1086, 765, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (s, 3H), 2.14-2.26 (m, 1H), 2.29-2.41 (m, 1H), 2.47 (s, 3H), 3.87 (s, 3H), 7.38 (d, 2H, J = 8.0 Hz), 7.58-7.62 (m, 3H), 7.69 (t, 1H, J = 7.2 Hz), 7.85 (d, 2H, J = 8.0 Hz), 7.96-8.01 (m, 3H), 8.11 (d, 1H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1 (q, $J_{C\text{-}F}$ = 1.5 Hz), 21.7, 39.5 (q, $J_{C\text{-}F}$ = 28.8 Hz), 42.1, 46.3 (q, $J_{C\text{-}F}$ = 1.5 Hz), 52.3, 123.1, 123.4, 125.0 (q, $J_{C\text{-}F}$ = 277.3 Hz), 127.0, 128.2, 128.8, 129.4, 129.57, 129.63, 129.86, 129.92, 134.2, 135.9, 139.1, 145.4, 165.6, 166.9, 171.1; ^{19}F NMR

(376 MHz, $CDCl_3$, $CFCl_3$): δ -59.1 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 574.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{28}H_{27}F_3N_3O_5S^+$ requires: 574.1618, Found: 574.1613.

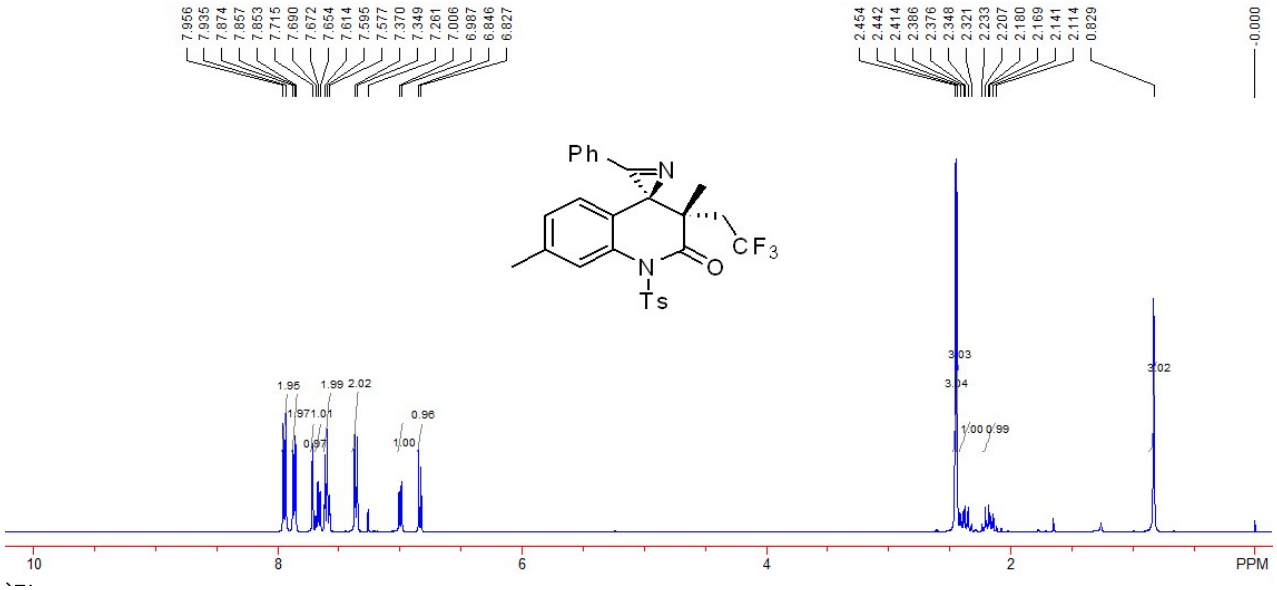


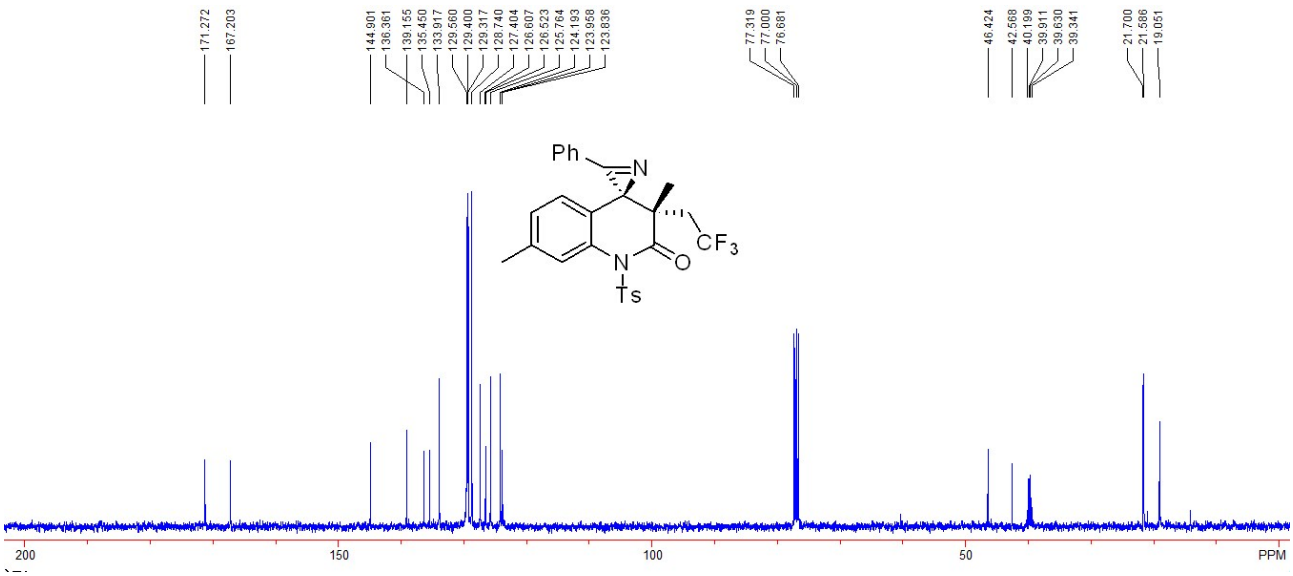


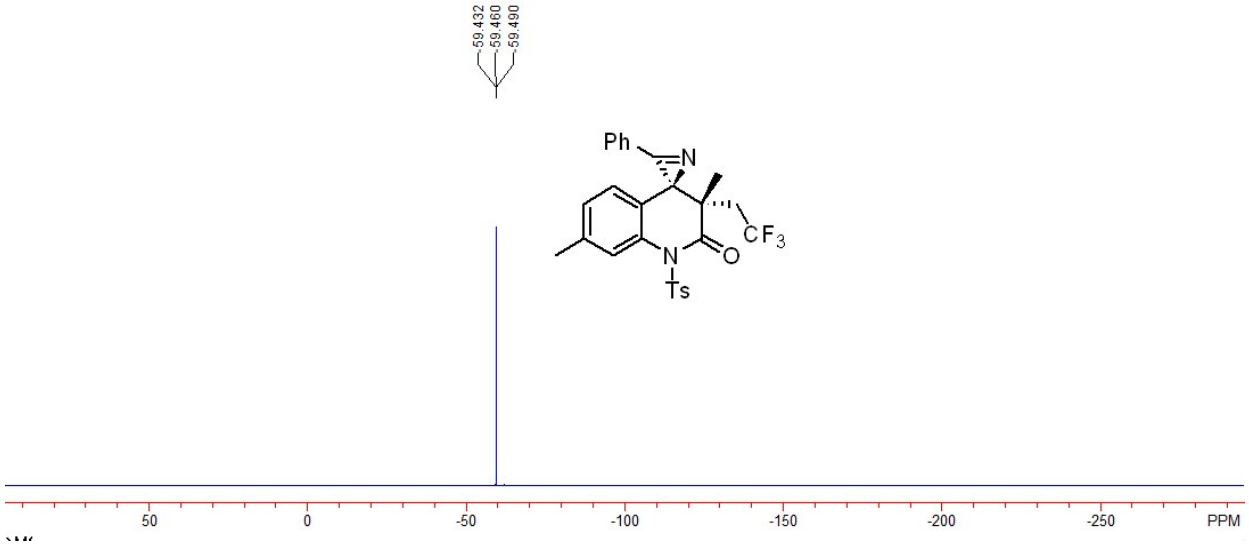


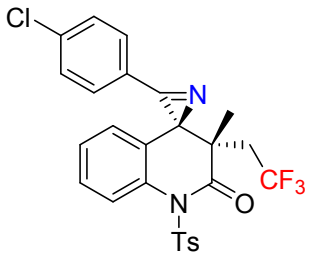


Compound 2bk: 85 mg, 83%, A white solid, m.p. 171-173 °C; IR (EtOH): ν 2959, 2920, 2850, 1717, 1367, 1264, 1175, 1133, 1087, 762, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.83 (s, 3H), 2.11-2.23 (m, 1H), 2.32-2.41 (m, 1H), 2.44 (s, 3H), 2.45 (s, 3H), 6.84 (d, 1H, J = 7.6 Hz), 7.00 (d, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.60 (t, 2H, J = 7.6 Hz), 7.65-7.69 (m, 1H), 7.72 (s, 1 H), 7.86 (dd, 2H, J_1 = 8.4 Hz, J_2 = 1.6 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.6 (q, $J_{C\text{-}F}$ = 1.4 Hz), 39.8 (q, $J_{C\text{-}F}$ = 28.9 Hz), 42.6, 46.4 (q, $J_{C\text{-}F}$ = 1.5 Hz), 124.0, 124.2, 125.2 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.8, 126.5, 127.4, 128.7, 129.3, 129.4, 129.6, 133.9, 135.5, 136.4, 139.2, 144.9, 167.2, 171.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.5 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 530.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}F_3N_3O_3S^+$ requires: 530.1720, Found: 530.1715.



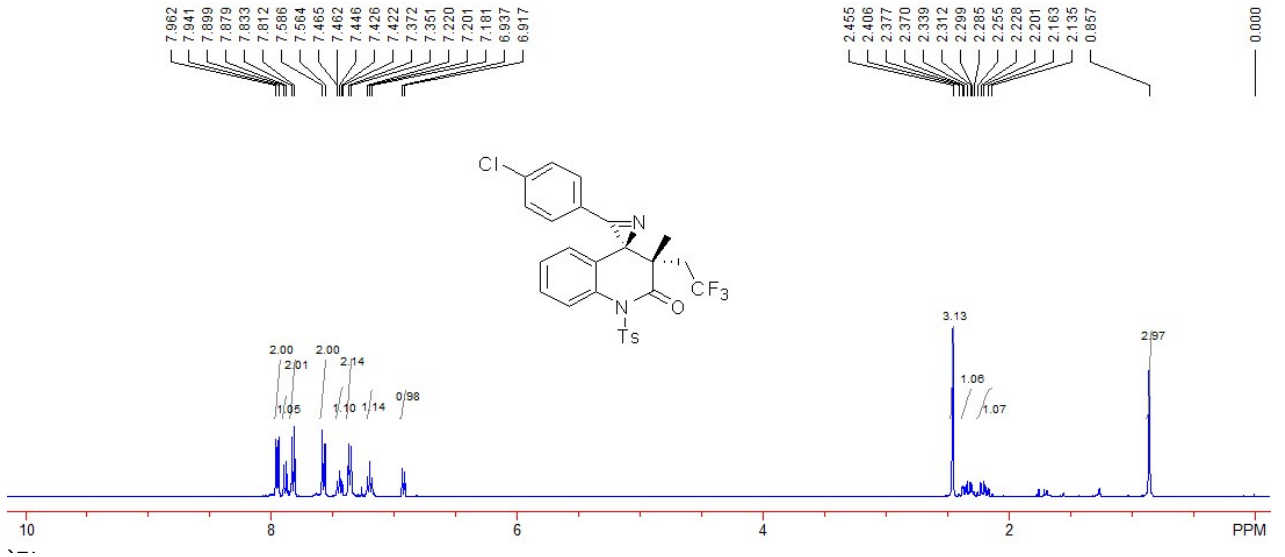


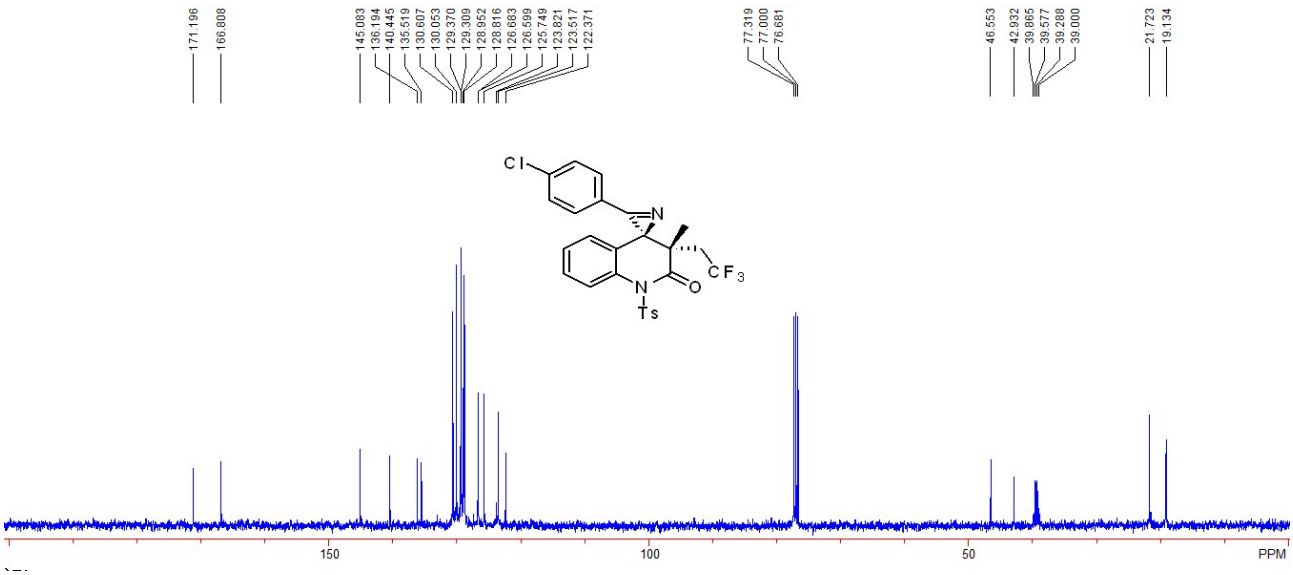


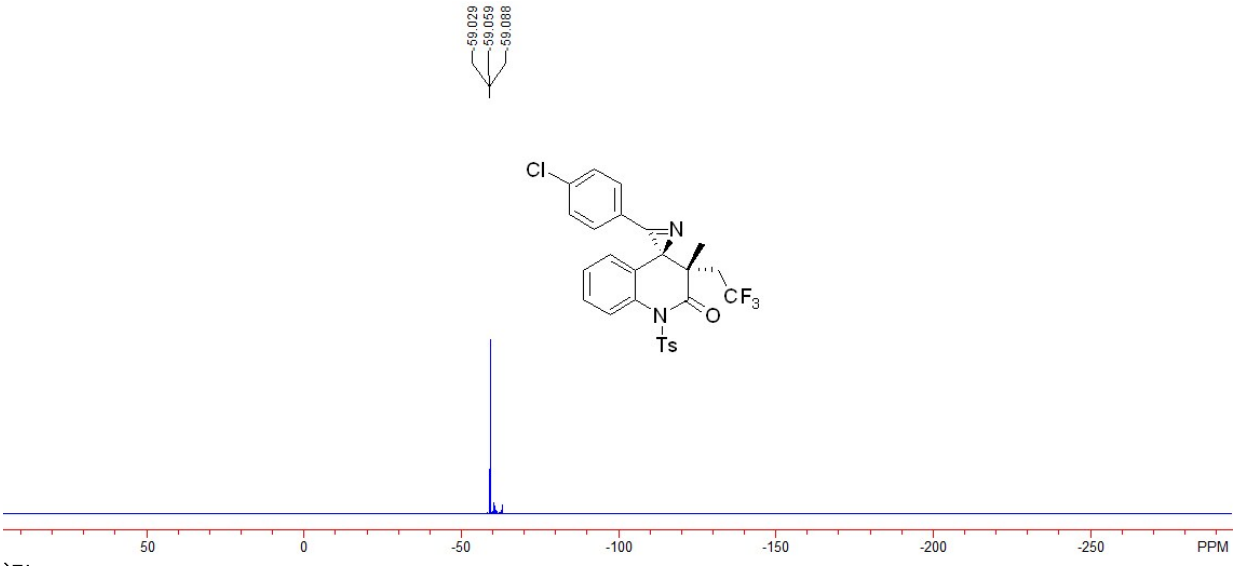


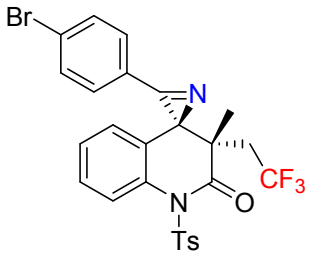
Compound 2bl: 83 mg, 78%, A white solid, m.p. 232-234 ^{o}C; IR (EtOH): ν 2959, 2927, 1718, 1670, 1368, 1261, 1168, 1088, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (s, 3H), 2.14-2.26 (m, 1H), 2.29-2.41 (m, 1H), 2.46 (s, 3H), 6.93 (d, 1H, J = 8.0 Hz), 7.22 (t, 1H, J = 8.0 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.45 (dd, 1H, J_1 = 8.0 Hz, J_2 = 1.2 Hz), 7.57 (d, 2H, J = 8.4 Hz), 7.82 (d, 2H, J = 8.4 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 21.7, 39.4 (q, $J_{C\text{-}F}$ = 28.9 Hz), 42.9, 46.6 (q, $J_{C\text{-}F}$ = 1.5 Hz), 122.4, 123.5, 125.4 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.7, 126.7, 128.8, 129.0, 129.3, 129.4, 130.1, 130.6, 135.5, 136.2, 140.4, 145.1,

166.8, 171.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.1 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 550.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}ClF_3N_3O_3S^+$ requires: 550.1174, Found: 550.1170.

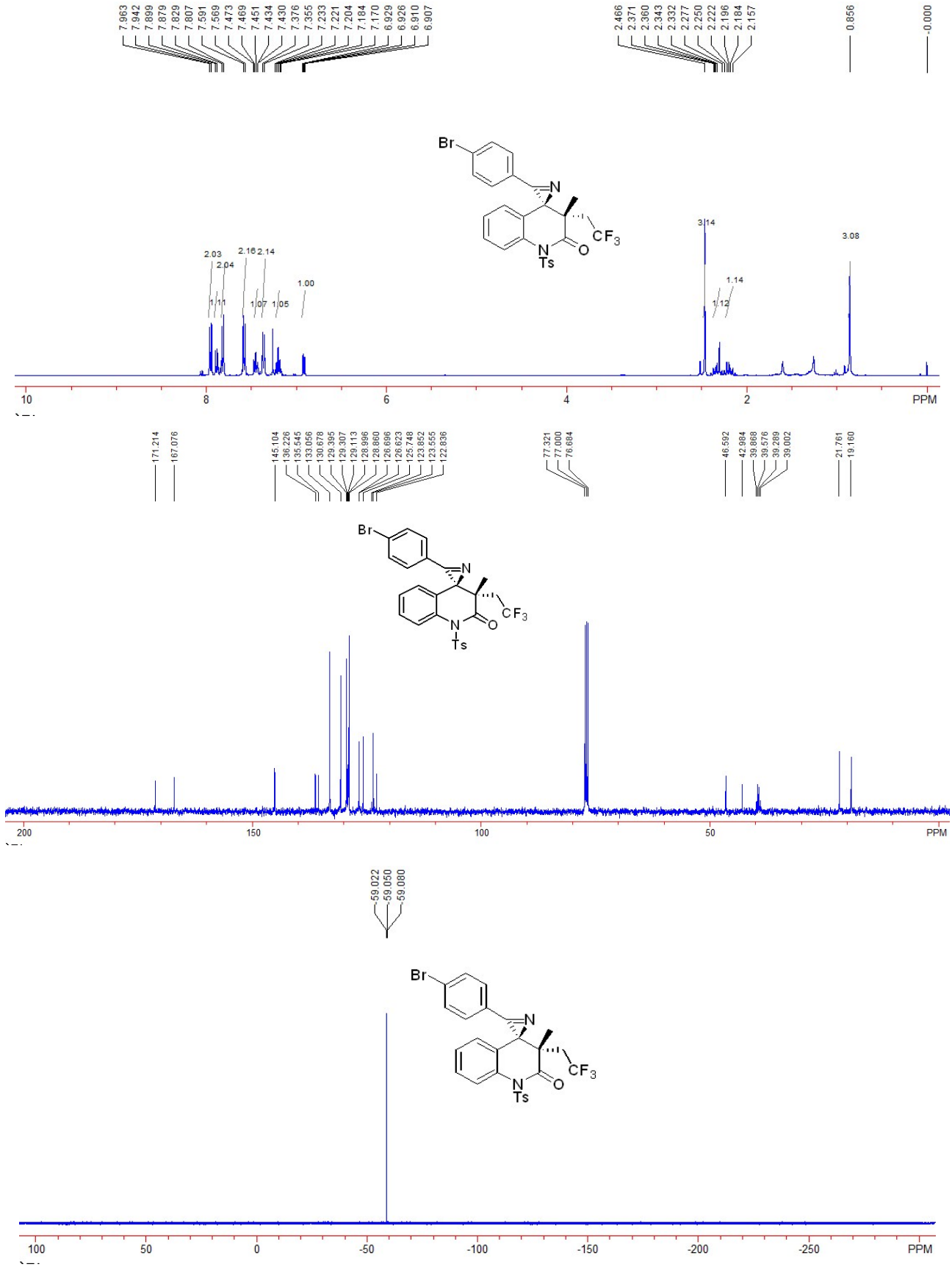


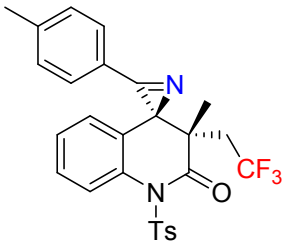




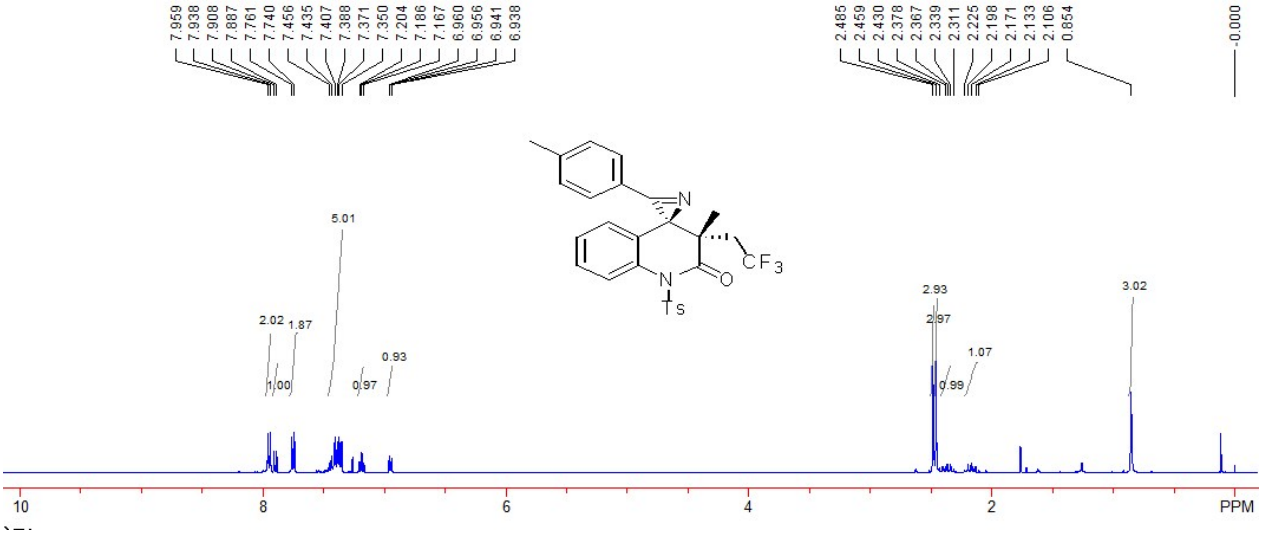


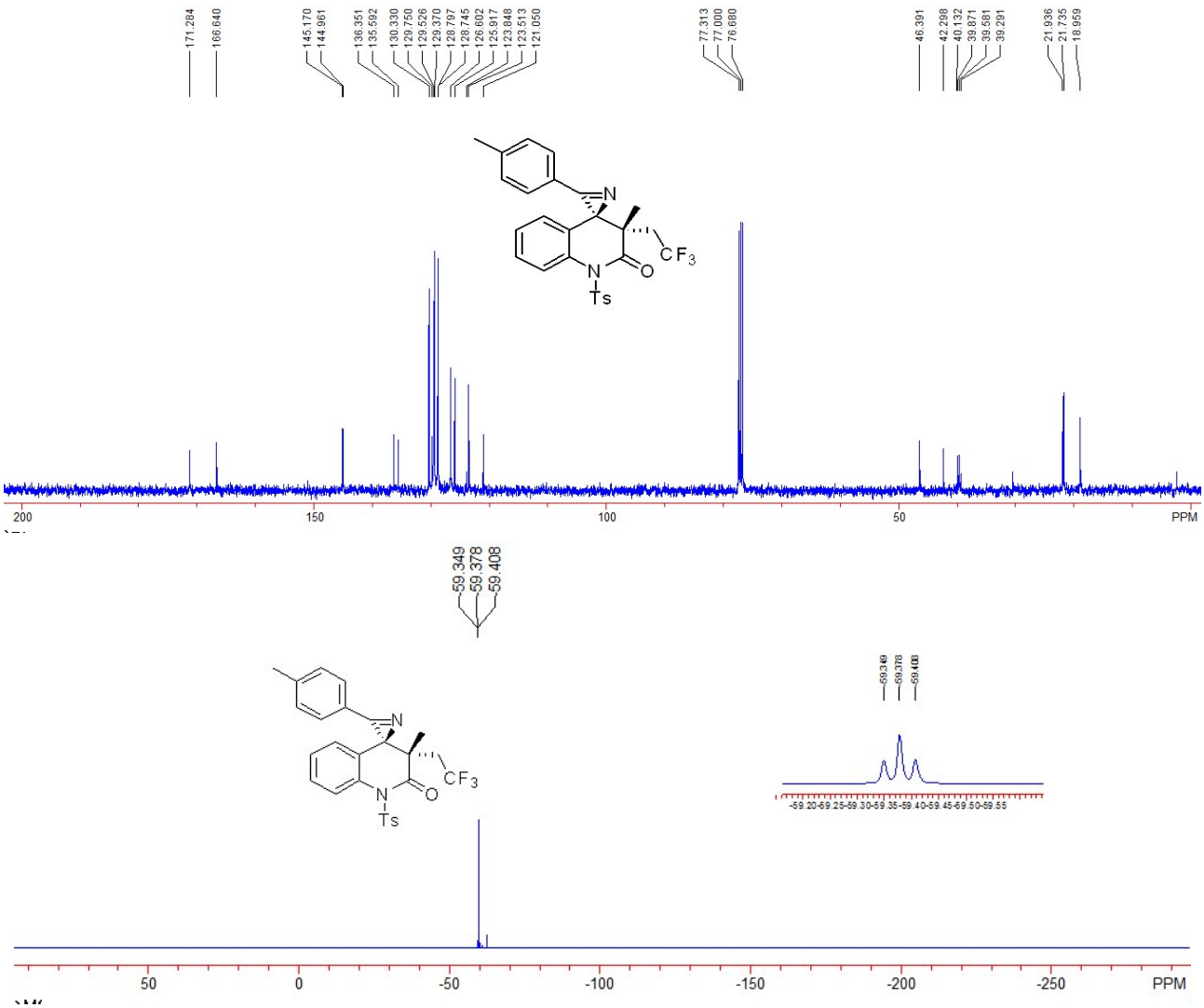
Compound 2bm: 83 mg, 72%, A white solid, m.p. 240-242 ^{o}C; IR (EtOH): ν 2956, 2920, 1719, 1356, 1261, 1154, 1131, 1087, 797, 668 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (s, 3H), 2.16-2.28 (m, 1H), 2.33-2.37 (m, 1H), 2.47 (s, 3H), 6.92 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.17-7.23 (m, 1H), 7.37 (d, 2H, J = 8.4 Hz), 7.45 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.58 (d, 2H, J = 8.8 Hz), 7.82 (d, 2H, J = 8.8 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1 (q, $J_{C\text{-}F}$ = 1.4 Hz), 21.8, 39.4 (q, $J_{C\text{-}F}$ = 28.9 Hz), 43.0, 46.6 (q, $J_{C\text{-}F}$ = 1.5 Hz), 122.8, 123.6, 125.2 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.7, 126.7, 128.9, 129.0, 129.1, 129.3, 129.4, 130.7, 132.0, 133.1, 135.5, 136.2, 145.1, 167.0, 171.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.1 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 594.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}BrF_3N_3O_3S^+$ requires: 594.0668, Found: 594.0665.

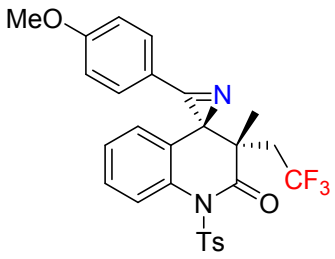

7.963
7.942
7.899
7.879
7.829
7.807
7.591
7.569
7.473
7.469
7.451
7.434
7.430
7.376
7.355
7.233
7.221
7.204
7.184
7.170
6.929
6.926
6.910
6.907
2.466
2.371
2.360
2.343
2.332
2.277
2.250
2.222
2.196
2.184
2.157
0.856
-0.000
Br
N
CF3
O
N
Ts
2.03
2.04
2.16
2.14
1.00
1.11
1.07
1.05
3.14
1.14
1.12
3.08
10
8
6
4
2
PPM
171.214
167.076
145.104
136.226
135.545
133.056
130.678
129.395
129.307
129.113
128.996
128.860
126.696
126.623
125.748
123.852
123.555
122.836
77.321
77.000
76.684
46.592
42.984
39.868
39.576
39.289
39.002
21.761
19.160
200
150
100
50
PPM
59.022
59.050
59.080
100
50
0
-50
-100
-150
-200
-250
PPM



Compound 2bn: 72 mg, 70%, A white solid, m.p. 179-181 ^{o}C; IR (EtOH): ν 2976, 2923, 1718, 1367, 1357, 1262, 1177, 1151, 1129, 1086, 1045, 670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (s, 3H), 2.11-2.23 (m, 1H), 2.32-2.43 (m, 1H), 2.46 (s, 3H), 2.49 (s, 3H), 6.95 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.35-7.46 (m, 5H), 7.75 (d, 2H, J = 8.4 Hz), 7.90 (d, 1H, J = 8.4 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.7, 21.9, 39.7 (q, $J_{C\text{-}F}$ = 29.1 Hz), 42.3, 46.4 (q, $J_{C\text{-}F}$ = 1.5 Hz), 121.1, 123.5, 125.2 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.9, 126.6, 128.7, 128.8, 129.4, 129.5, 129.8, 130.3, 135.6, 136.4, 145.0, 145.2, 166.6, 171.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 530.2 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}F_3N_3O_3S^+$ requires: 530.1720, Found: 530.1715.

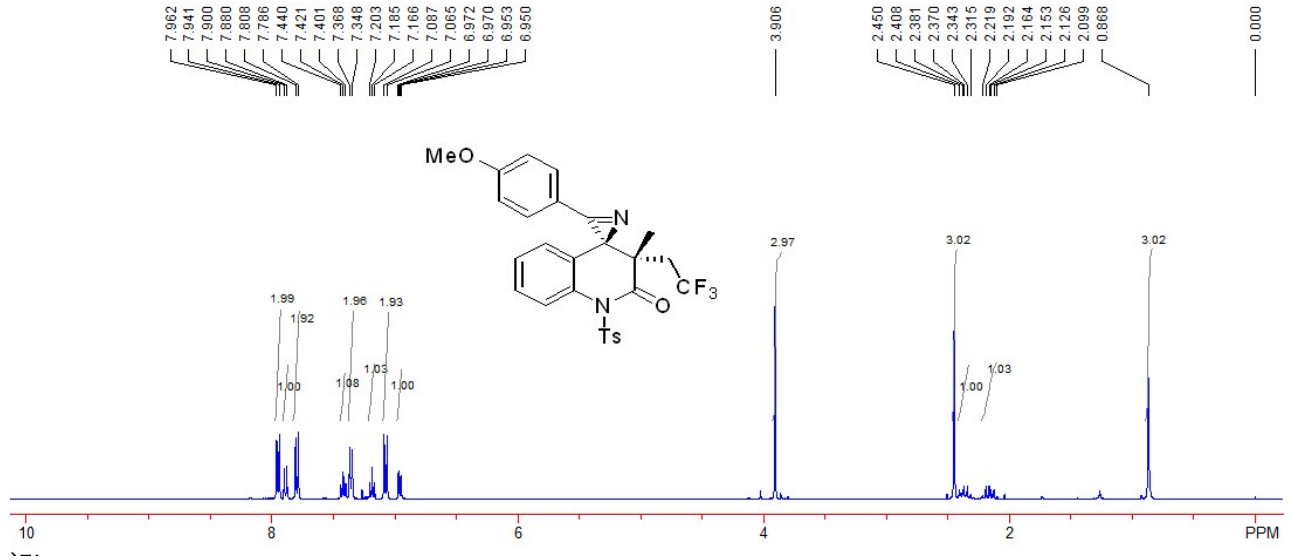


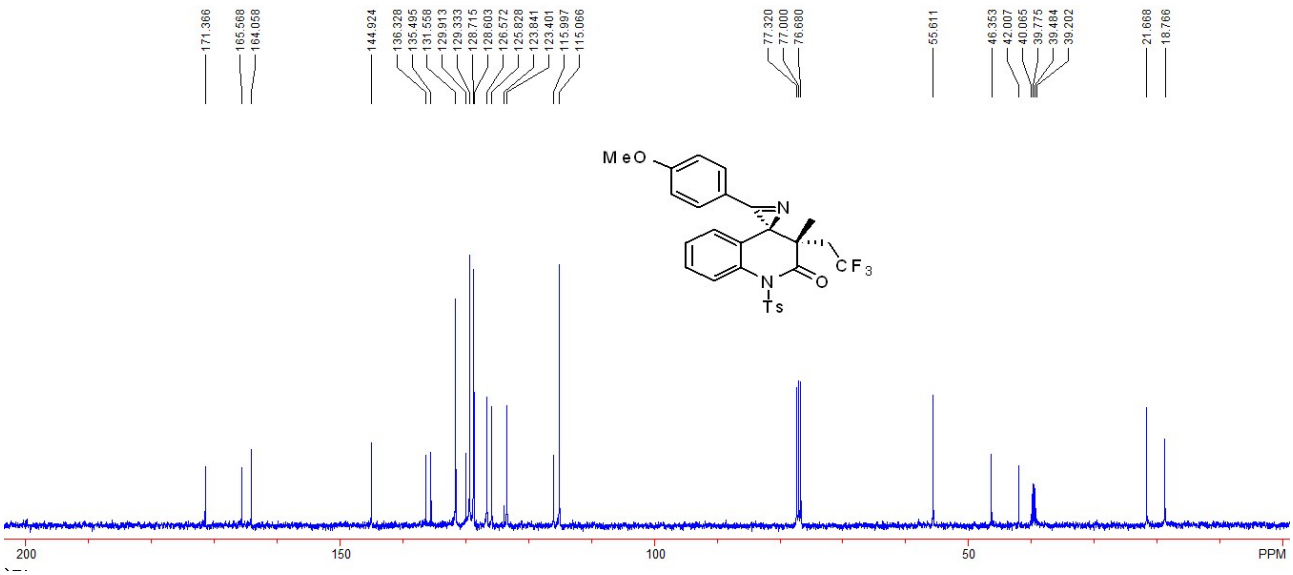


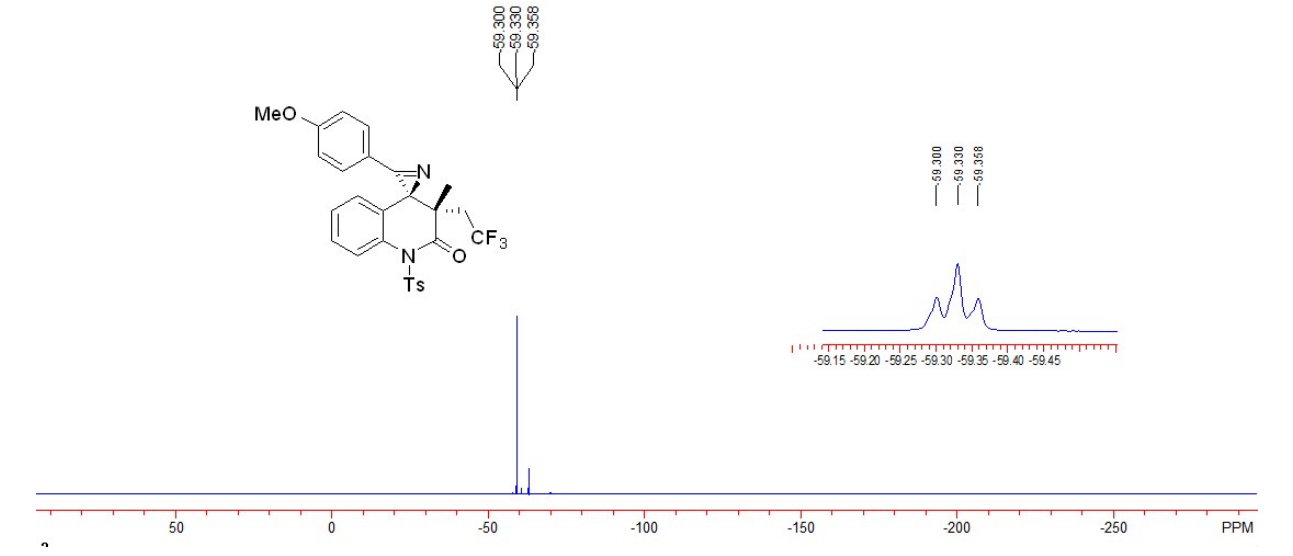


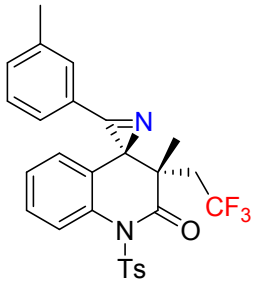
Compound 2bo: 91 mg, 86%, A white solid, m.p. 186-188 ^{o}C; IR (EtOH): ν 2962, 2922, 2851, 1718, 1507, 1261, 1175, 1151, 1132, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (s, 3H), 2.10-2.22 (m, 1H), 2.32-2.41 (m, 1H), 2.45 (s, 3H), 3.91 (s, 3H), 6.96 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.08 (d, 2H, J = 8.4 Hz), 7.19 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.42 (t, 1H, J = 8.0 Hz), 7.79 (d, 2H, J = 8.4 Hz), 7.89 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.8, 21.7, 39.6 (q, $J_{C\text{-}F}$ = 29.0 Hz), 42.0, 46.4 (q, $J_{C\text{-}F}$ = 1.5 Hz), 55.6, 115.1, 116.0, 123.4, 125.2 (q, $J_{C\text{-}F}$ = 277.5 Hz), 125.8, 126.6, 128.6, 128.7, 129.3, 129.9, 131.6, 135.5, 136.3, 144.9, 164.1, 165.6, 171.4; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.3 (t, 3F, J = 10.9 Hz);

MS (ESI) *m/z*: 546.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}F_3N_3O_4S^+$ requires: 546.1669, Found: 546.1664.

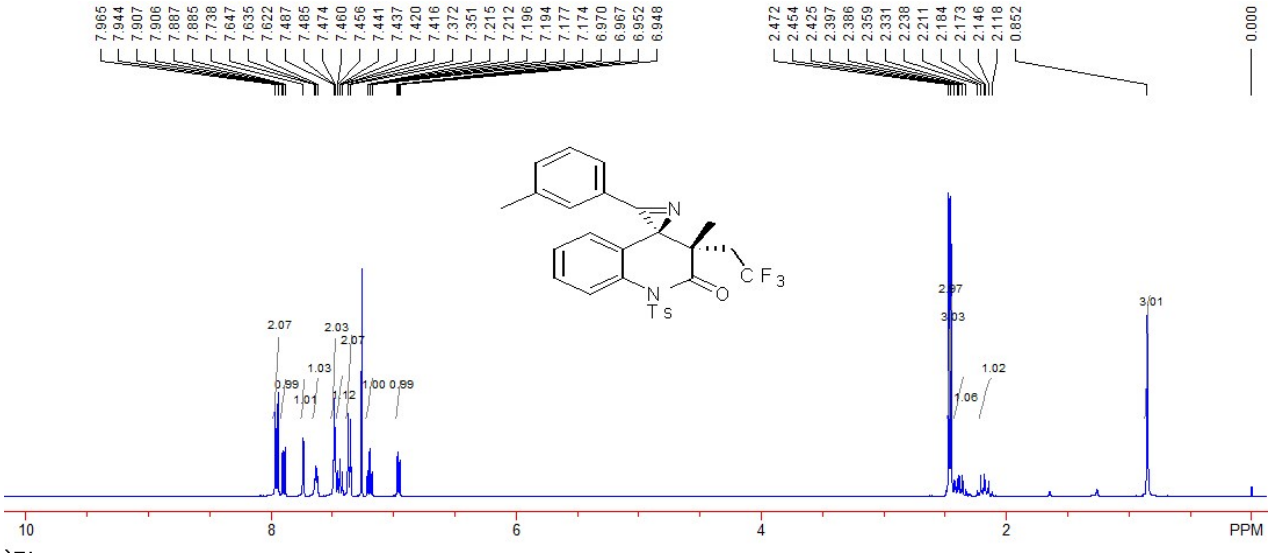


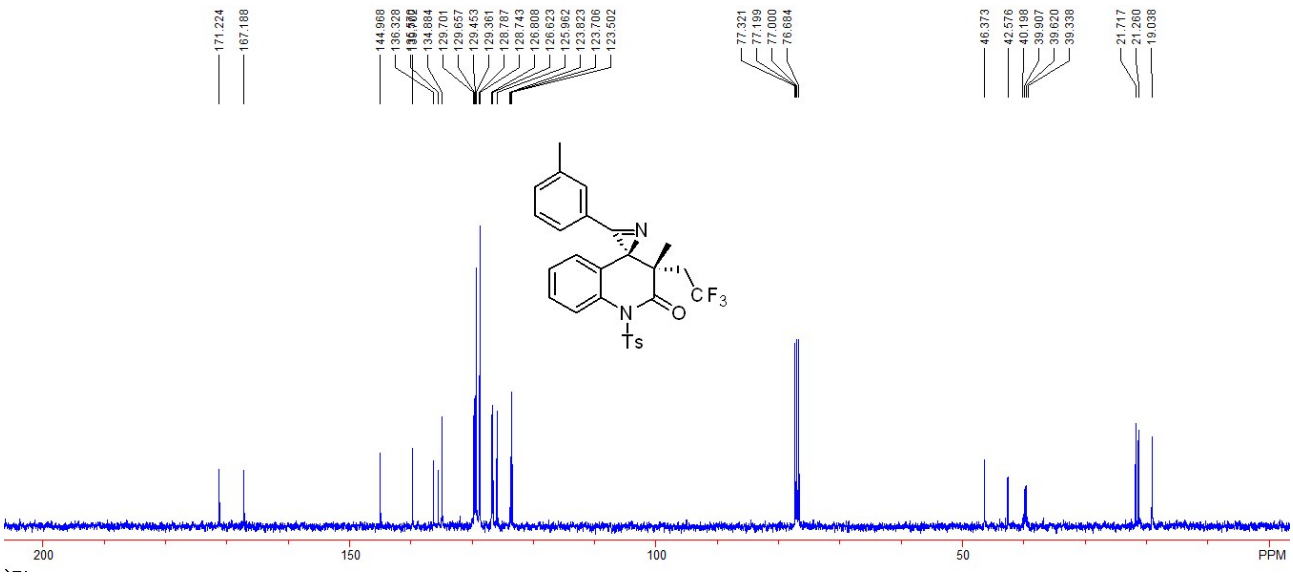


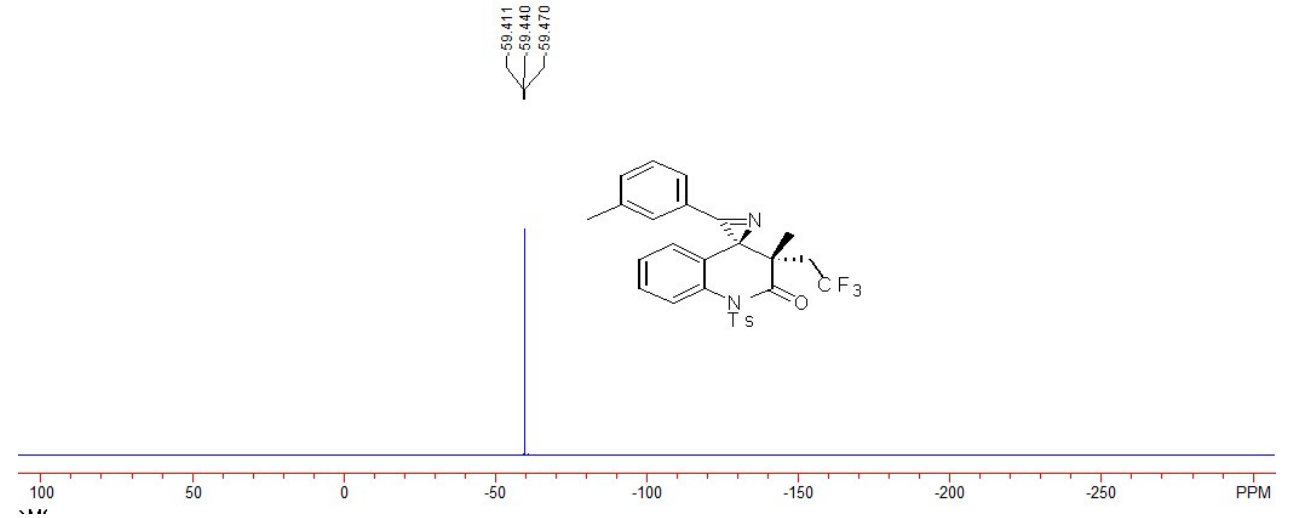


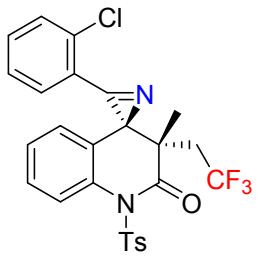


Compound 2bp: 86 mg, 84%, A white solid, m.p. 177-179 °C; IR (EtOH): ν 3031, 1735, 1725, 1374, 1365, 1177, 1138, 1122, 1111, 1085, 789, 756, 658 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 0.85 (s, 3H), 2.12-2.24 (m, 1H), 2.33-2.43 (m, 1H), 2.45 (s, 3H), 2.47 (s, 3H), 6.96 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.20 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.36 (d, 2H, J = 8.4 Hz), 7.42-7.49 (m, 3H), 7.62-7.65 (m, 1H), 7.74 (s, 1H), 7.90 (dd, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.95 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.0, 21.3, 21.7, 39.8 (q, $J_{C\text{-}F}$ = 28.7 Hz), 42.6, 46.4 (q, $J_{C\text{-}F}$ = 1.5 Hz), 123.5, 123.7, 125.2 (q, $J_{C\text{-}F}$ = 276.6 Hz), 126.0, 126.6, 126.8, 128.7, 128.8, 129.4, 129.5, 129.66, 129.70, 134.9, 135.6, 136.3, 139.7, 145.0, 167.2, 171.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 530.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{27}F_3N_3O_3S^+$ requires: 530.1720, Found: 530.1714.



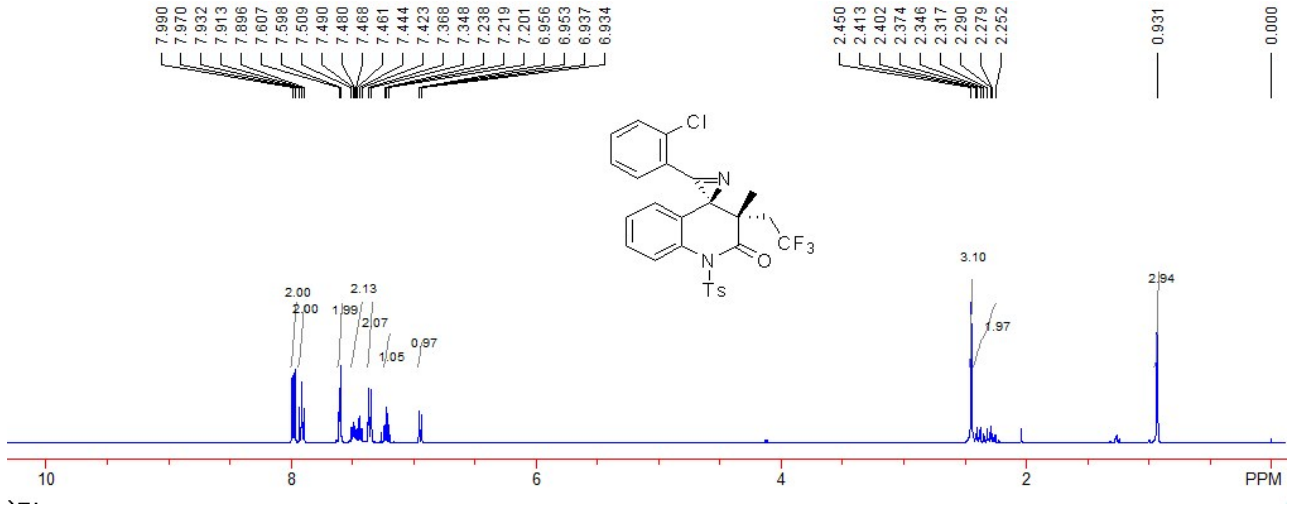


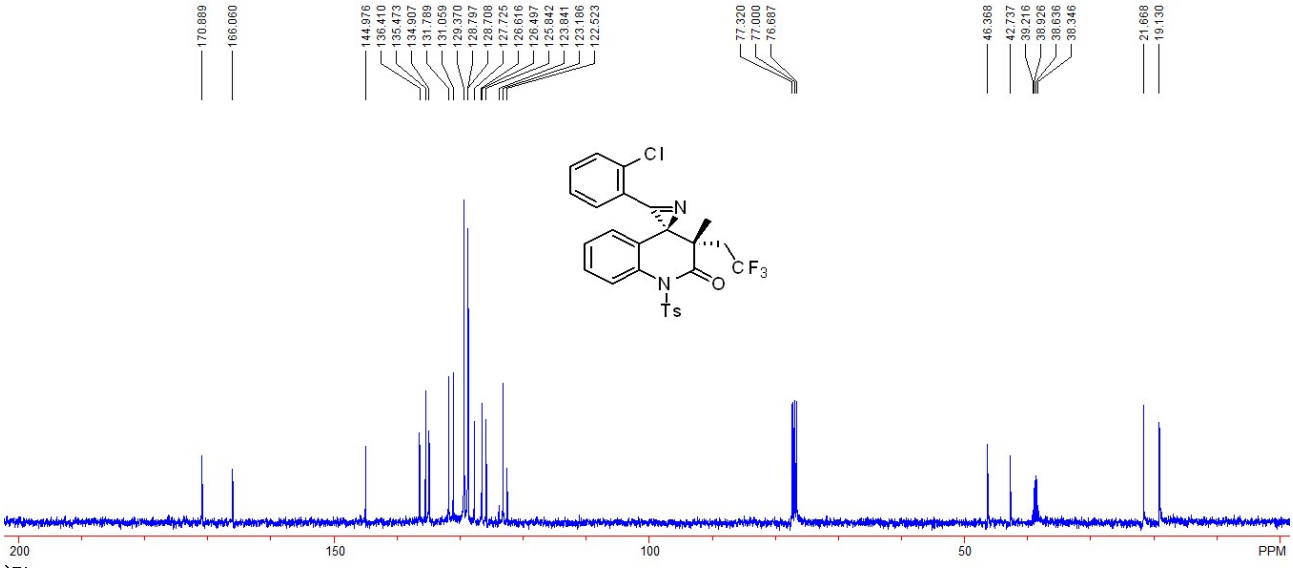


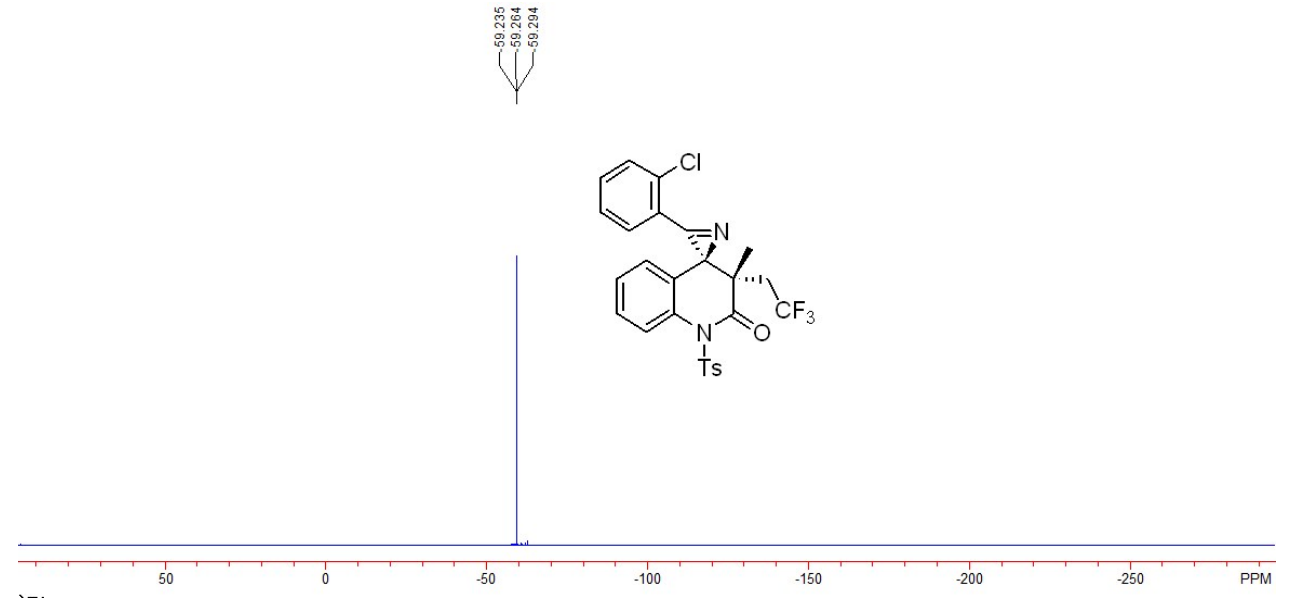


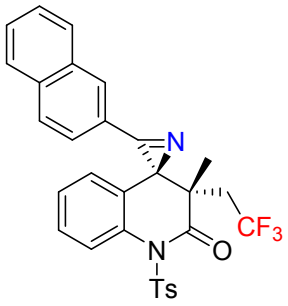
Compound 2bq: 92 mg, 86%, A white solid, m.p. 203-205 ^{o}C; IR (EtOH): ν 2931, 1718, 1455, 1366, 1261, 1175, 1127, 1086, 812, 801, 758, 665 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.93 (s, 3H), 2.25-2.41 (m, 2H), 2.45 (s, 3H), 6.94 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.20 (t, 1H, J = 7.6 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.42-7.51 (m, 2H), 7.60-7.61 (m, 2H), 7.90-7.93 (m, 2H), 7.98 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 21.7, 38.8 (q, $J_{C\text{-}F}$ = 29.0 Hz), 42.7, 46.4 (q, $J_{C\text{-}F}$ = 1.5 Hz), 122.5, 123.2, 125.2 (q, $J_{C\text{-}F}$ = 277.5 Hz), 125.8, 126.5, 127.7, 128.7, 128.8, 129.3, 129.4, 131.1, 131.8, 134.9, 135.5, 136.4, 145.0, 166.1, 170.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$):

δ -59.3 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 550.1 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}ClF_3N_3O_3S^+$ requires: 550.1174, Found: 550.1168.

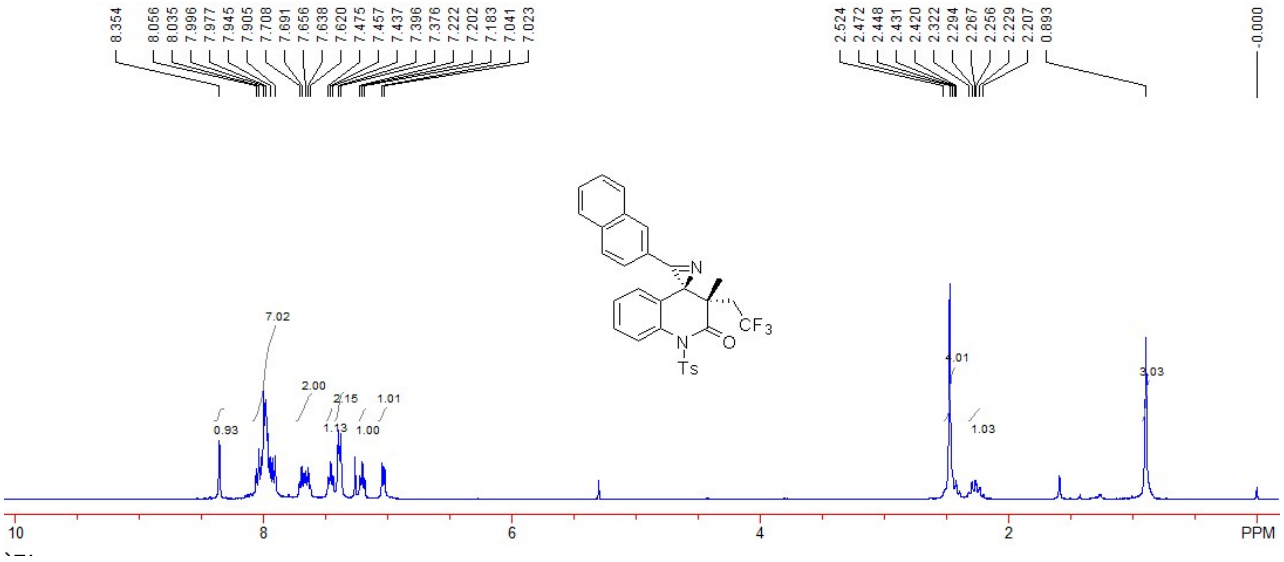


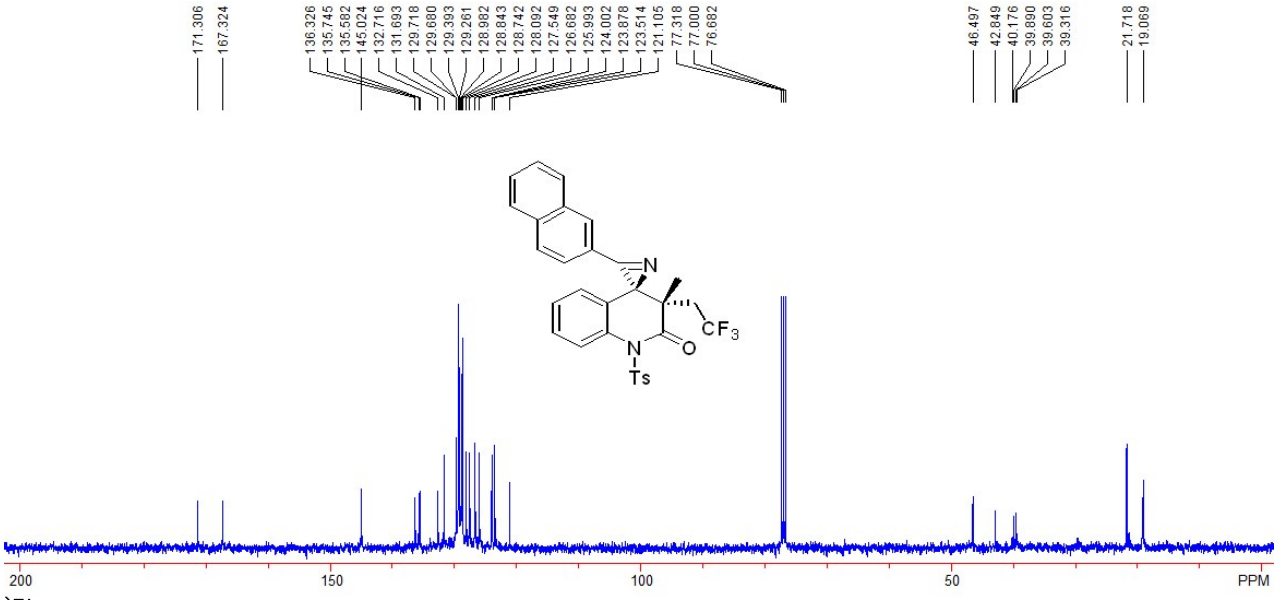


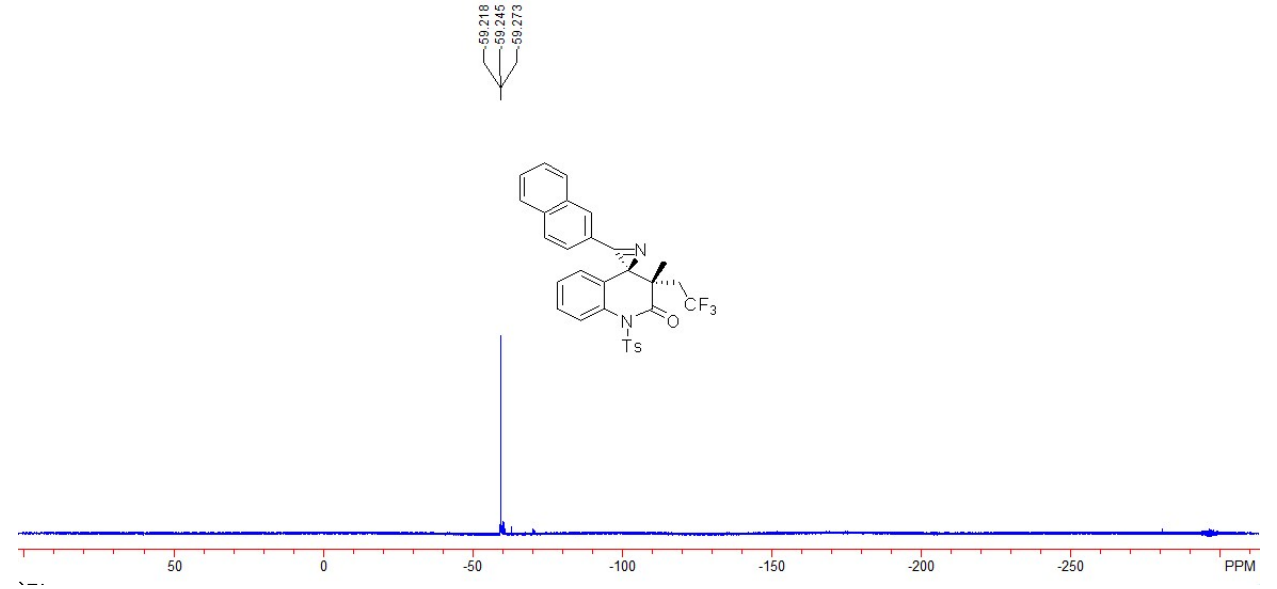


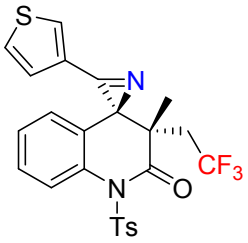


Compound 2br: 78 mg, 71%, A white solid, m.p. 272-274 ^{o}C; IR (EtOH): ν 3051, 1719, 1356, 1263, 1176, 1151, 1133, 1118, 1085, 750, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.89 (s, 3H), 2.21-2.32 (m, 1H), 2.42-2.52 (m, 1H), 2.47 (s, 3H), 7.03 (d, 1H, J = 7.6 Hz), 7.20 (t, 1H, J = 7.6 Hz), 7.39 (d, 2H, J = 8.0 Hz), 7.46 (t, 1H, J = 8.0 Hz), 7.62-7.71 (m, 2H), 7.91-8.06 (m, 7H), 8.35 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1, 21.7, 39.7 (q, J_{C-F} = 28.7 Hz), 42.8, 46.5, 121.1, 123.5, 124.0, 125.3 (q, J_{C-F} = 277.1 Hz), 126.0, 126.7, 127.5, 128.1, 128.7, 128.8, 129.3, 129.4, 129.68, 129.72, 131.7, 132.7, 135.6, 135.7, 136.3, 145.0, 167.3, 171.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.2 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 566.2 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{30}H_{27}F_3N_3O_3S^+$ requires: 566.1720, Found: 566.1715.



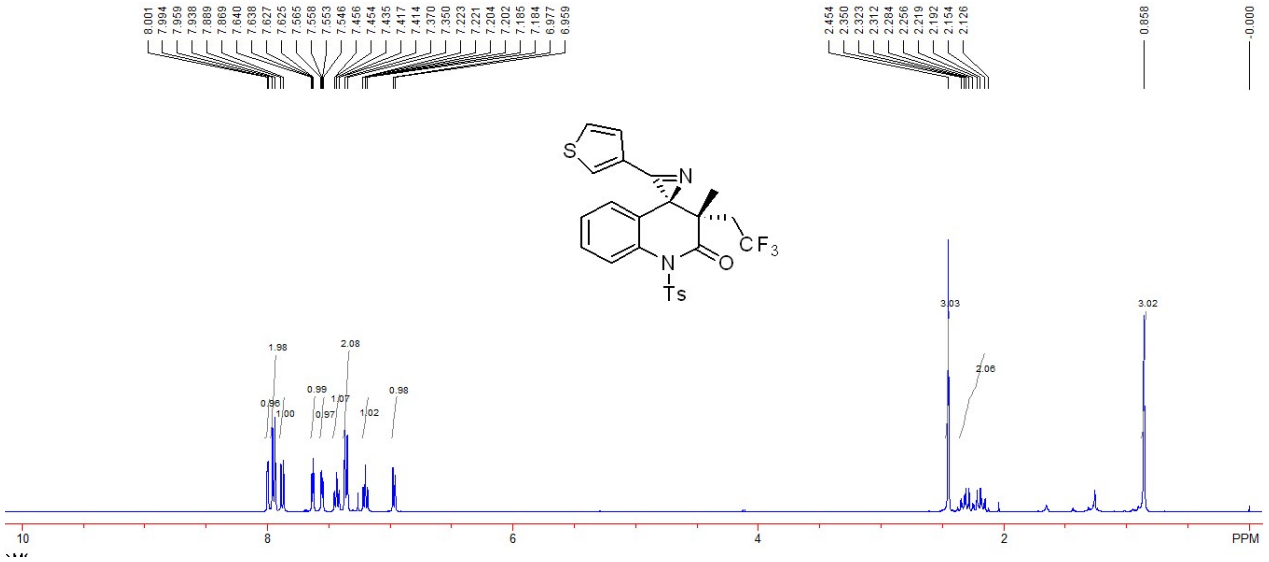


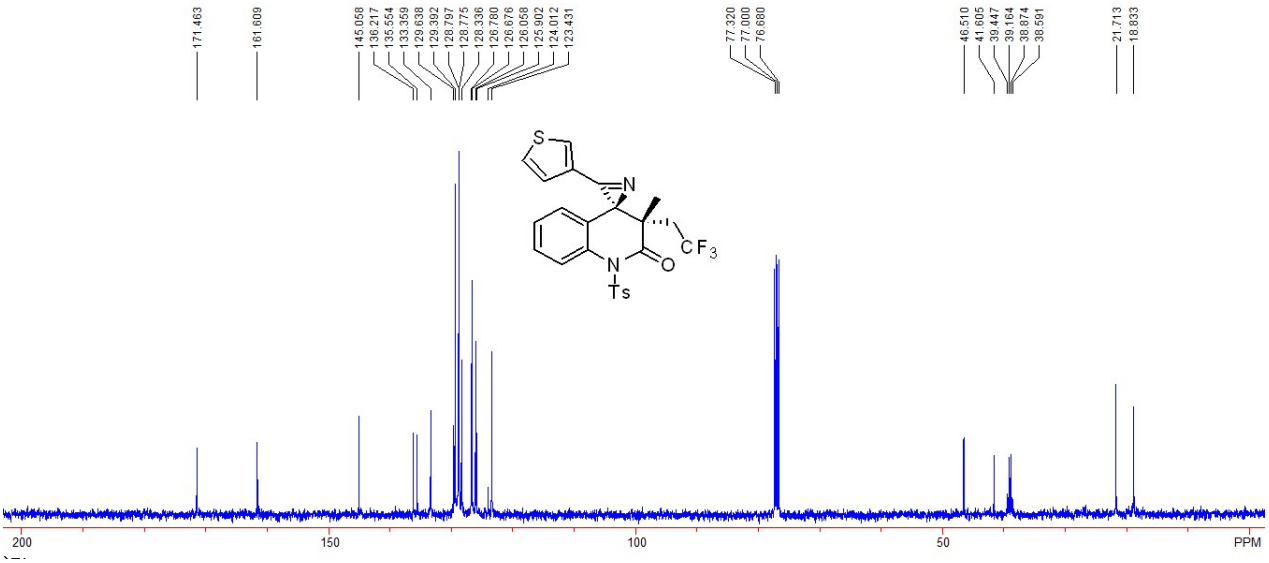


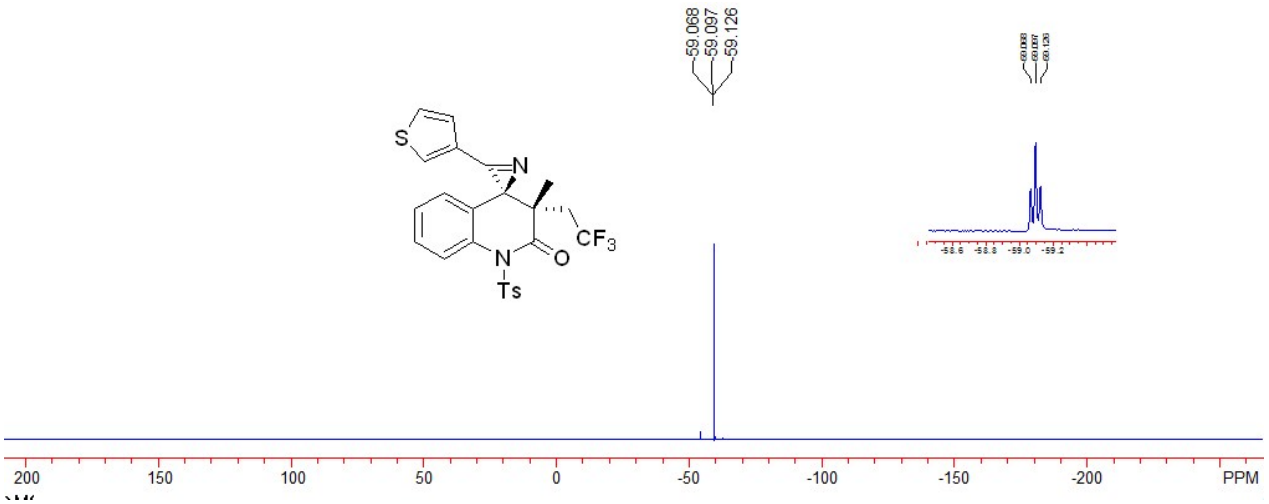


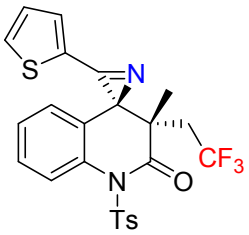
Compound 2bt: 71 mg, 70%, A white solid, m.p. 184-186 ^{o}C; IR (EtOH): ν 2959, 2923, 2856, 1723, 1365, 1264, 1176, 1149, 1122, 1085, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (s, 3H), 2.13-2.35 (m, 2H), 2.45 (s, 3H), 6.97 (d, 1H, J = 7.6 Hz), 7.20 (td, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.36 (d, 2H, J = 8.0 Hz), 7.44 (td, 1H, J_1 = 8.0 Hz, J_2 = 0.8 Hz), 7.55-7.57 (m, 1H), 7.63 (dd, 1H, J_1 = 8.4 Hz, J_2 = 0.8 Hz), 7.88 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.4 Hz), 8.00 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.8, 21.7, 39.0 (q, $J_{C\text{-}F}$ = 29.0 Hz), 41.6, 46.5 (q, $J_{C\text{-}F}$ = 1.5 Hz),

123.4, 125.4 (q, $J_{C\text{-}F}$ = 276.8 Hz), 125.9, 126.1, 126.66, 126.68, 128.3, 128.8, 129.4, 129.6, 133.4, 135.6, 136.2, 145.1, 161.6, 171.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.1 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 522.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{23}F_3N_3O_3S_2^+$ requires: 522.1127, Found: 522.1121.

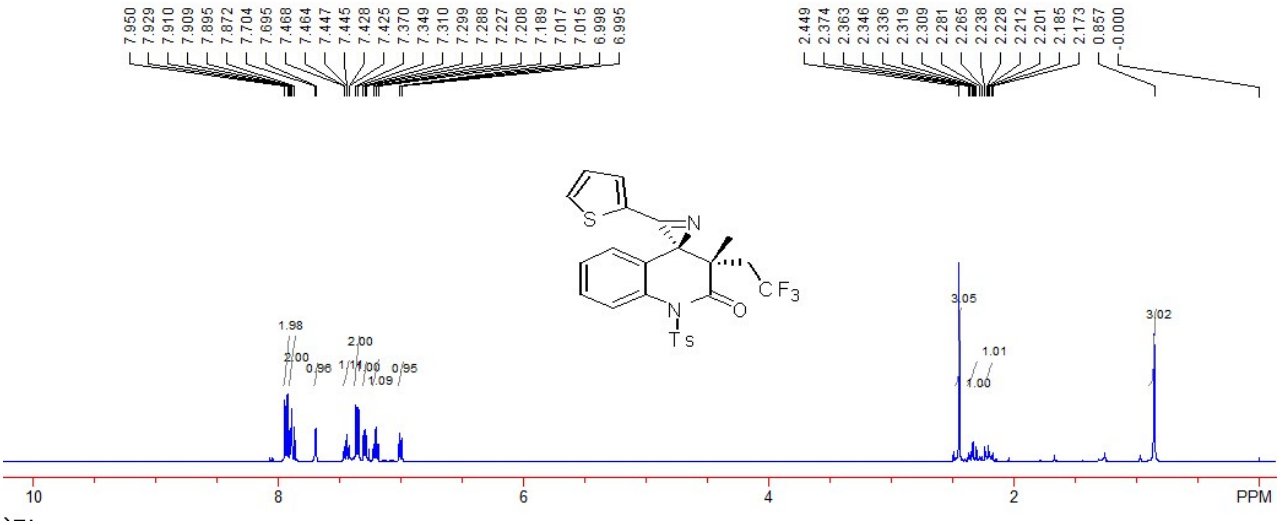


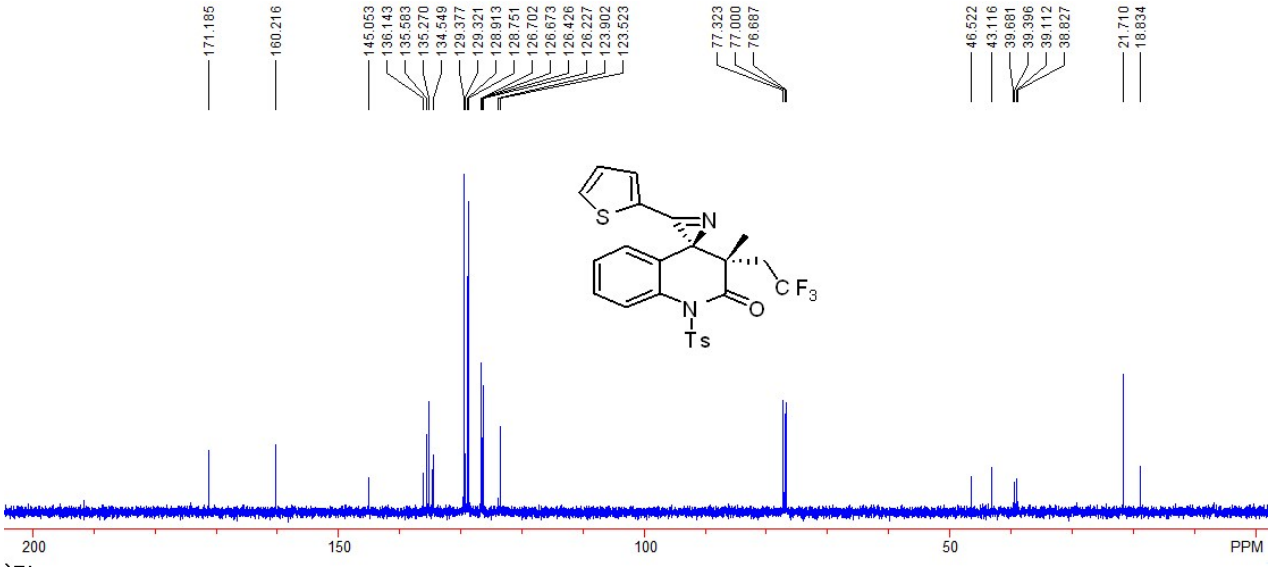


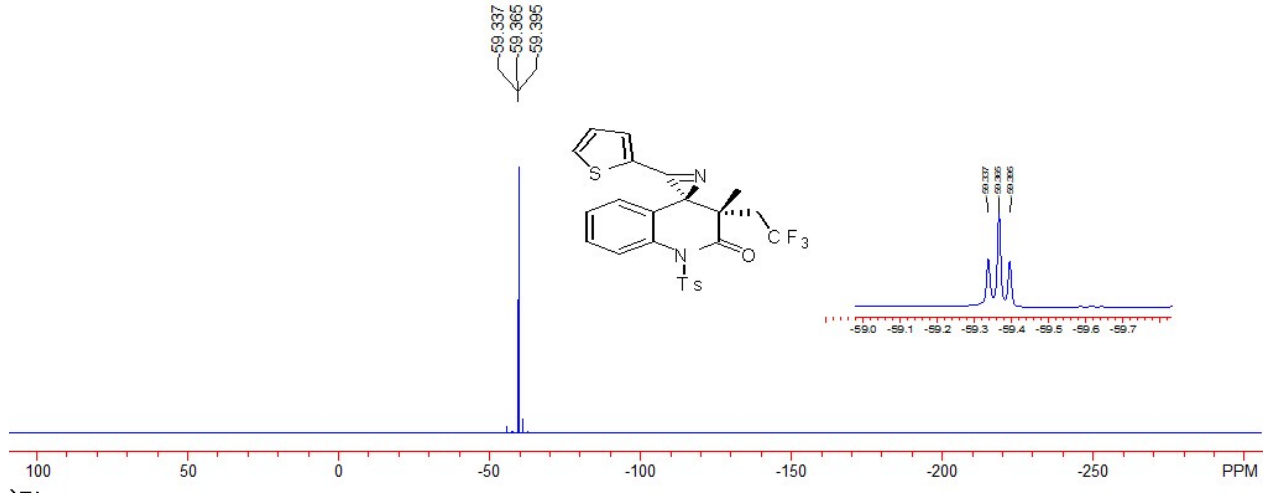


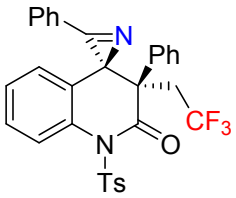


Compound 2bu: 78 mg, 77%, A white solid, m.p. 188-190 ^{o}C; IR (EtOH): ν 2956, 2923, 2854, 1721, 1367, 1262, 1174, 1147, 1124, 1086, 661 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (s, 3H), 2.17-2.27 (m, 1H), 2.28-2.37 (m, 1H), 2.45 (s, 3H), 7.01 (dd, 1H, J = 7.6 Hz, J_2 = 1.2 Hz), 7.21 (t, 1H, J = 7.6 Hz), 7.29-7.31 (m, 1H), 7.36 (d, 2H, J = 8.4 Hz), 7.45 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.70 (d, 1H, J = 3.6 Hz), 7.87-7.91 (m, 2H), 7.94 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.8, 21.7, 39.3 (q, $J_{C\text{-}F}$ = 28.5 Hz), 43.1, 46.5, 123.5, 125.3 (q, $J_{C\text{-}F}$ = 277.1 Hz), 126.2, 126.4, 126.7, 128.8, 128.9, 129.3, 129.4, 134.5, 135.3, 135.6, 136.1, 145.1, 160.2, 171.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.4 (t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 522.1 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{24}H_{23}F_3N_3O_3S_2^+$ requires: 522.1127, Found: 522.1122.



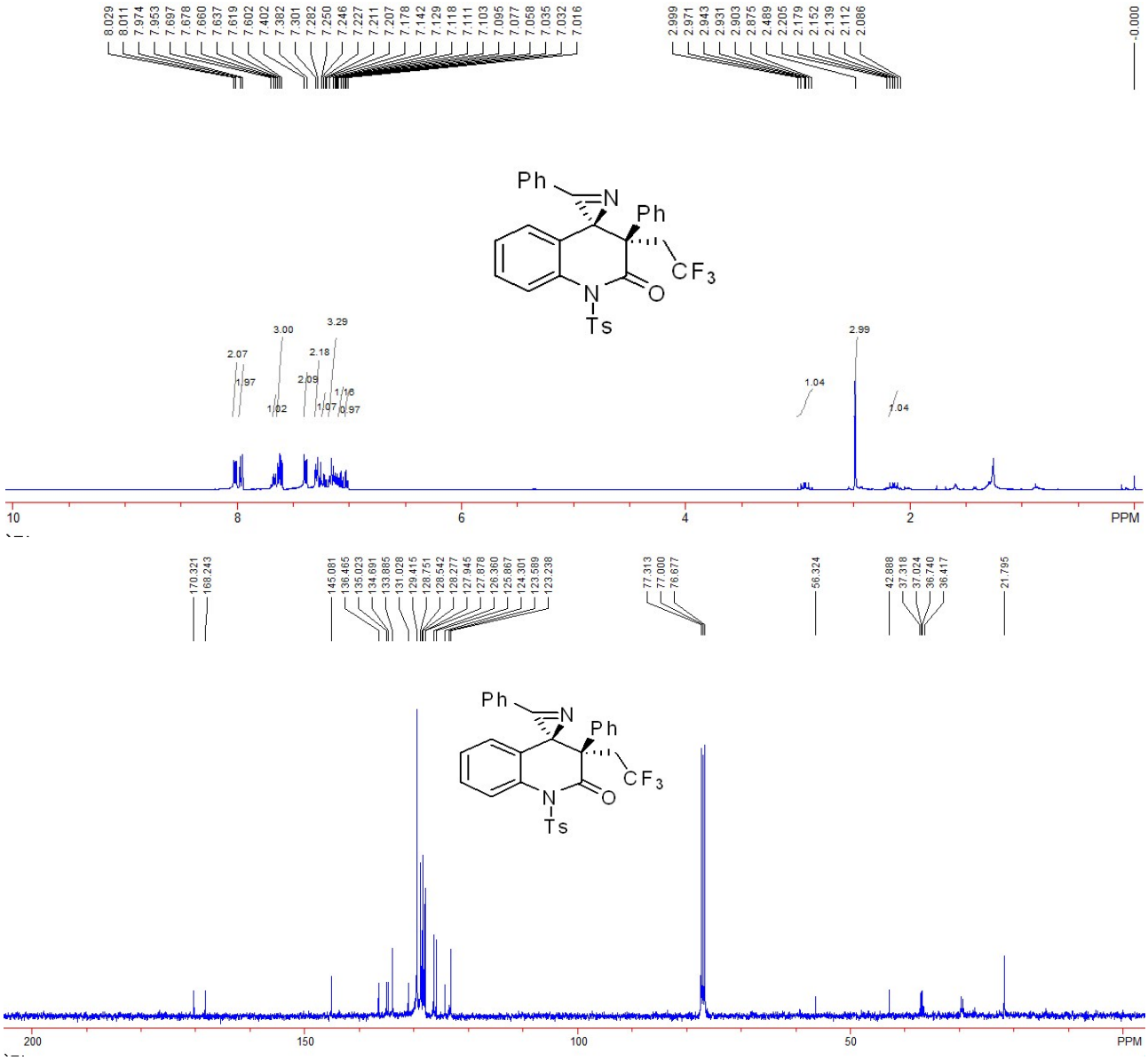


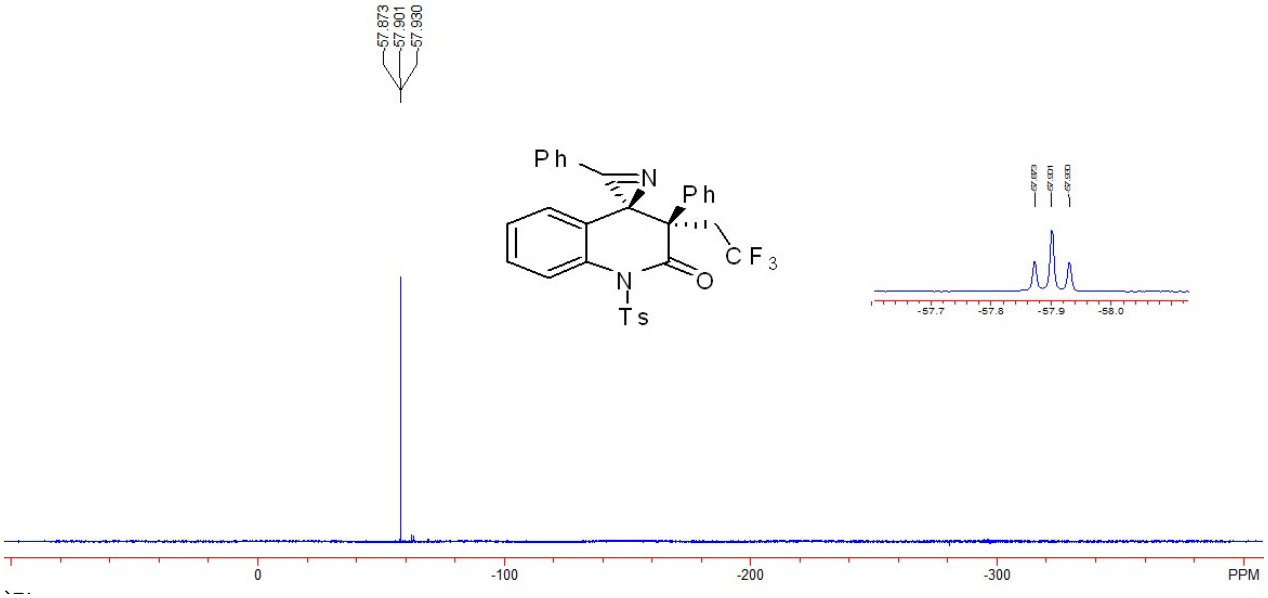


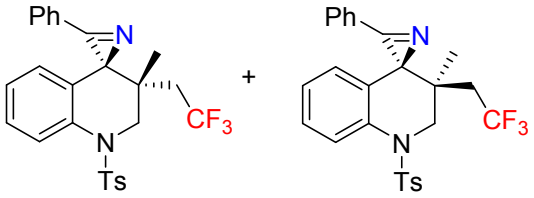


Compound 2bw: 37 mg, 33%, A white solid, m.p. 250-252 ^{o}C; IR (EtOH): ν 2973, 2929, 2887, 1718, 1374, 1173, 1087, 1046, 880, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.09-2.21 (m, 1H), 2.49 (s, 3H), 2.88-3.00 (m, 1H), 7.02 (dd, 1H, J = 7.6 Hz, J_2 = 1.6 Hz), 7.08 (t, 1H, J = 7.6 Hz), 7.11-7.18 (m, 3H), 7.23 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz), 7.29 (d, 2H, J = 7.6 Hz), 7.39 (d, 2H, J = 8.0 Hz), 7.60-7.64 (m, 3H), 7.66-7.70 (m, 1H), 7.96 (d, 2H, J = 8.4 Hz), 8.02 (d, 2H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.8, 36.9 (q, $J_{C\text{-}F}$ = 28.4 Hz), 42.9, 56.3 (q, $J_{C\text{-}F}$ = 1.9 Hz), 123.2, 124.3, 125.0 (q, $J_{C\text{-}F}$ = 277.1 Hz), 125.9, 127.9, 128.0, 128.3, 128.5, 128.8, 129.42, 129.43, 131.0, 133.9, 134.7, 135.0, 136.5, 145.1, 168.2, 170.3; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -57.9

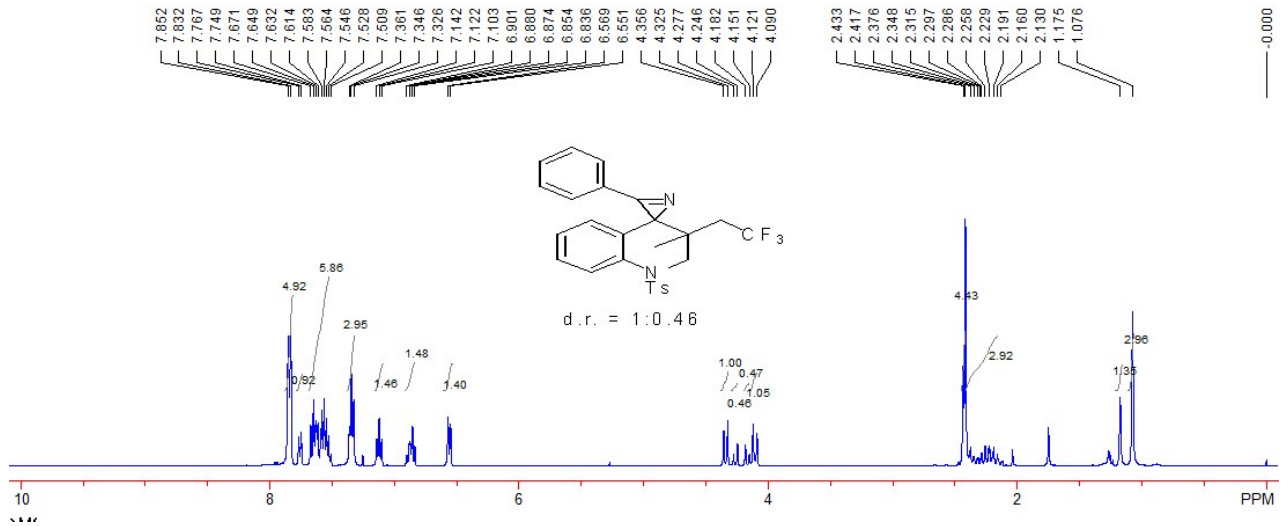
(t, 3F, J = 10.9 Hz); MS (ESI) *m/z*: 578.2 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{31}H_{27}F_3N_3O_3S^+$ requires: 578.1720, Found: 578.1714.







Compound 2aa+3aa: 85 mg, 88%, A white solid, m.p. 160-162 ^{o}C, dr = 1:0.46; IR (EtOH): ν 2973, 2923, 1596, 1488, 1450, 1352, 1263, 1163, 1119, 1089, 1063, 867, 762, 659 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.08 (s, 3H), 1.18 (s, 1.38H), 2.13-2.38 (m, 2.92H), 2.42 (s, 3H), 2.43 (s, 1.38H), 4.11 (d, 1H, J = 12.4 Hz), 4.17 (d, 0.46H, J = 12.4 Hz), 4.26 (d, 0.46H, J = 12.4 Hz), 4.34 (d, 1H, J = 12.4 Hz), 6.56 (d, 1.46H, J = 7.2 Hz), 6.84-6.90 (m, 1.46H), 7.12 (t, 1.46H, J = 7.6 Hz), 7.33-7.36 (m, 2.92H), 7.51-7.67 (m, 5.84H), 7.76 (d, 0.92H, J = 7.2 Hz), 7.84 (d, 4.92H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.1 (q, $J_{C\text{-}F}$ = 1.5 Hz), 21.1 (q, $J_{C\text{-}F}$ = 1.5 Hz), 21.47, 21.50, 35.6, 36.0, 37.0 (q, $J_{C\text{-}F}$ = 28.9 Hz), 39.1 (q, $J_{C\text{-}F}$ = 28.3 Hz), 45.0, 45.7, 55.1, 55.2, 118.2, 118.5, 123.2, 123.3, 123.4, 123.7, 126.2, 126.3 (q, $J_{C\text{-}F}$ = 277.1 Hz), 126.87, 126.91, 127.1 (q, $J_{C\text{-}F}$ = 277.0 Hz), 127.3, 127.4, 127.6, 127.75, 127.81, 129.42, 129.44, 129.5, 129.7, 129.9, 133.6, 133.7, 137.0, 137.2, 138.19, 138.21, 144.0, 144.1, 165.0, 165.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.5 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 485.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}F_3N_2O_2S^{+}$ requires: 485.1505, Found: 485.1499.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CF3
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1.46
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0.92
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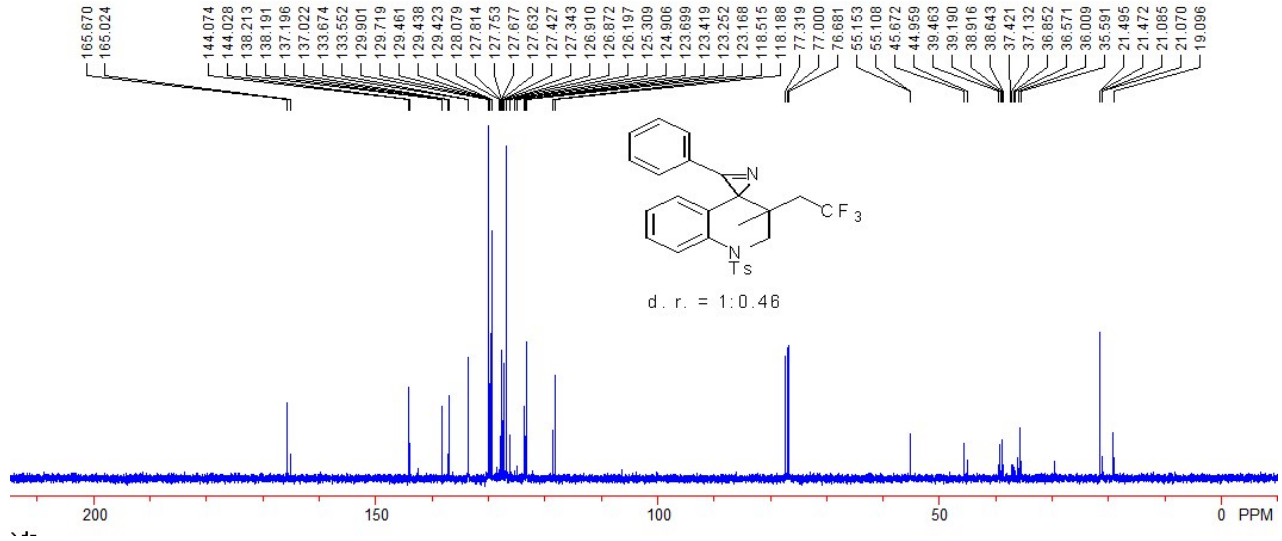
1.96
10
8
6
4
2
PPM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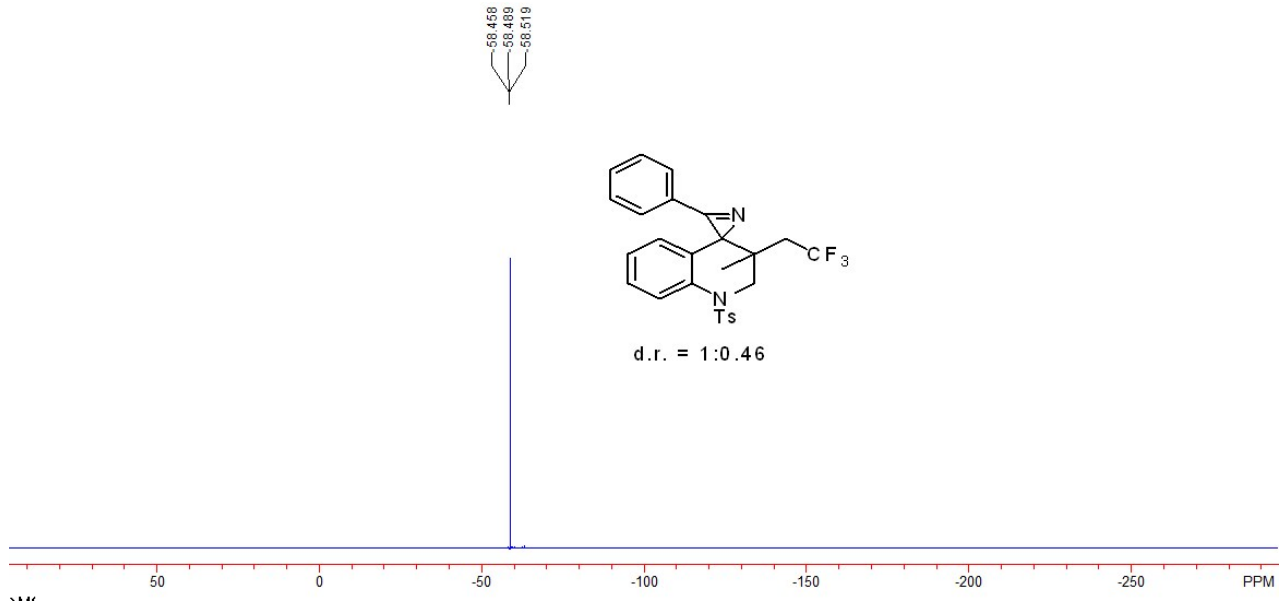
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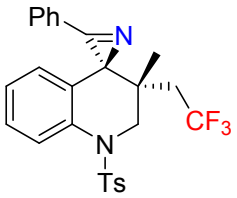
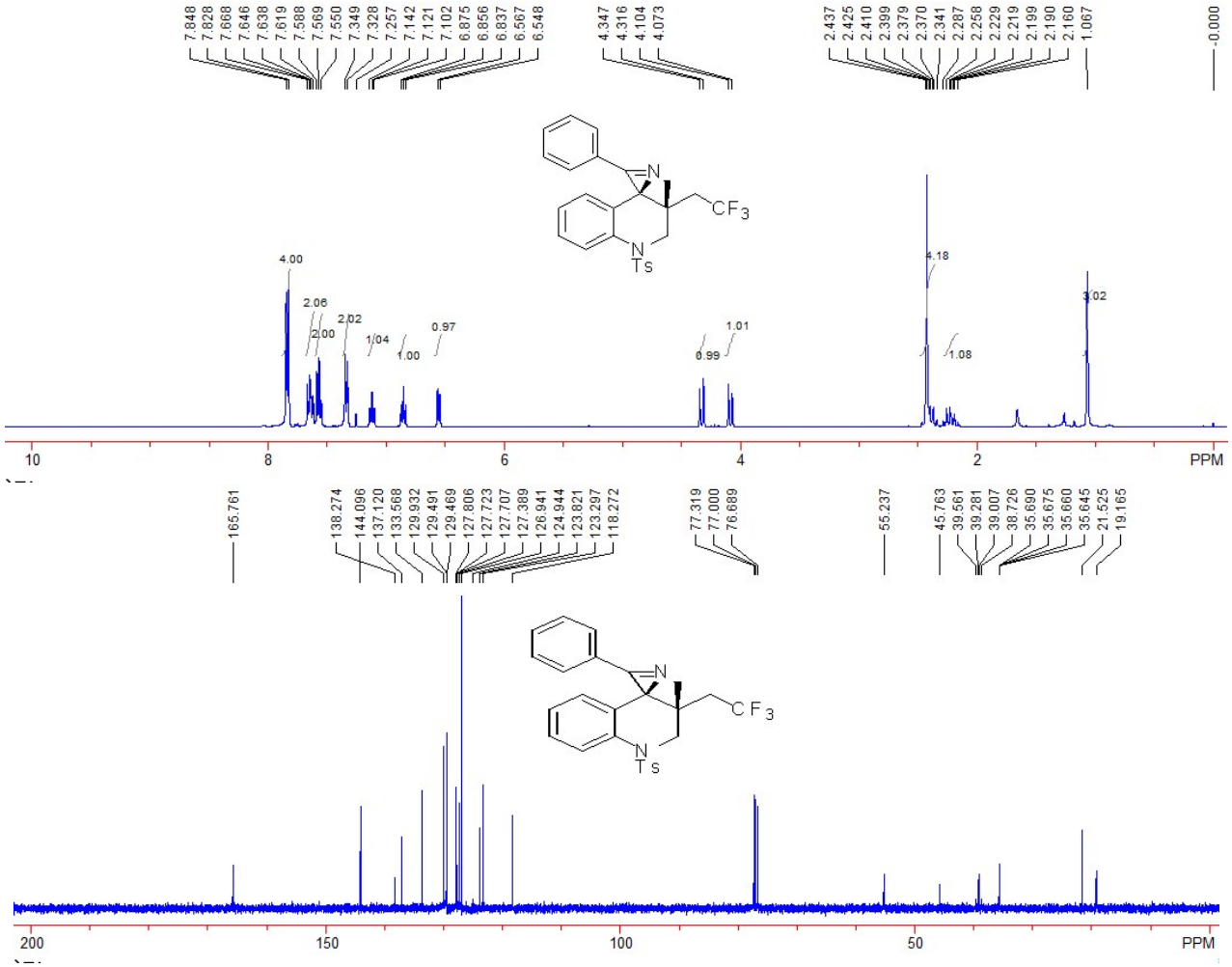
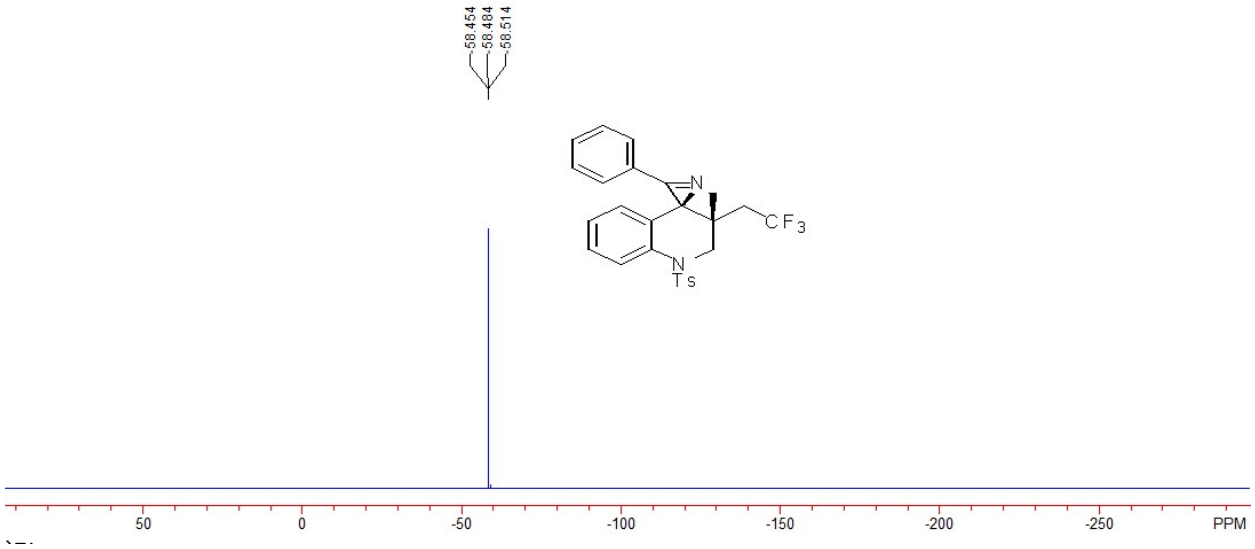
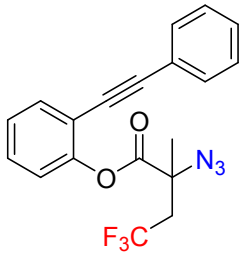
PPM



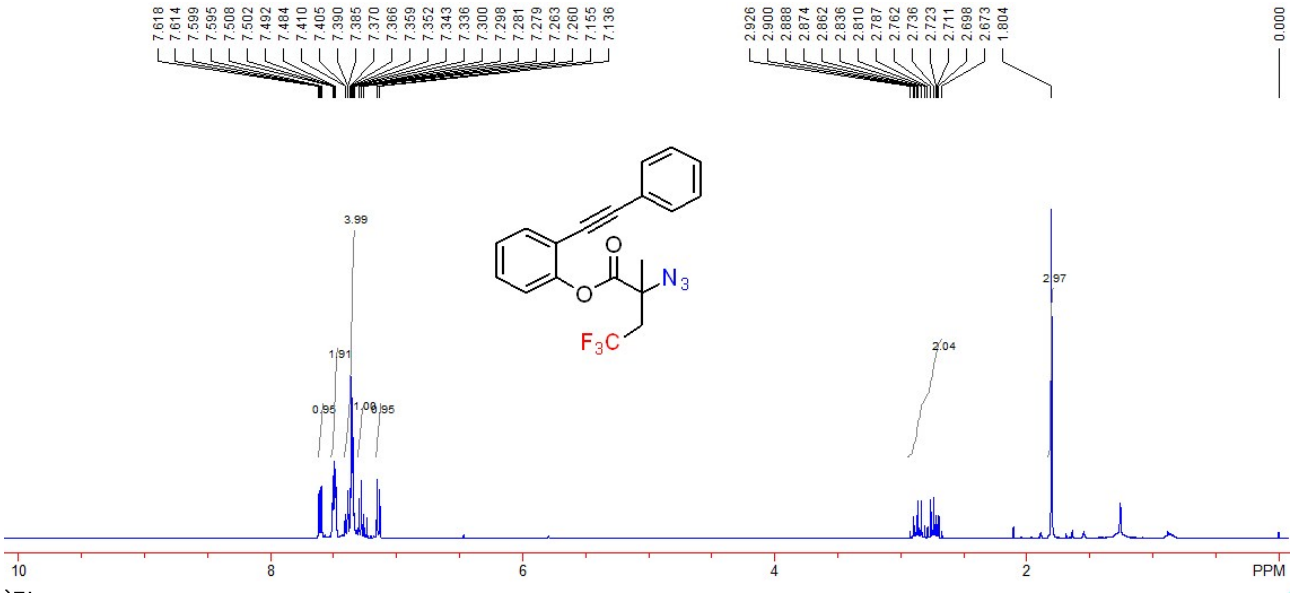
Compound 2aa: 58 mg, 60%, A white solid, m.p. 172-174 °C; IR (EtOH): ν 2973, 2923, 1596, 1488, 1450, 1352, 1263, 1163, 1119, 1089, 1063, 867, 762, 659 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.07 (s, 3H), 2.16-2.29 (m, 1H), 2.34-2.44 (m, 1H), 2.43 (s, 3H), 4.09 (d, 1H, J = 12.4 Hz), 4.33 (d, 1H, J = 12.4 Hz), 6.56 (d, 1H, J = 7.6 Hz), 6.86 (t, 1H, J = 7.6 Hz), 7.12 (t, 1H, J = 7.6 Hz), 7.34 (d, 2H, J = 8.0 Hz), 7.57 (t, 2H, J = 7.6 Hz), 7.62-7.67 (m, 2H), 7.84 (d, 4H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.2, 21.5, 35.7 (q, J_{C-F} = 1.5 Hz), 39.1 (q, J_{C-F} = 28.0 Hz), 45.8, 55.2, 118.3, 123.3, 123.8, 126.3 (q, J_{C-F} = 277.1 Hz), 126.9, 127.4, 127.7, 127.8, 129.47, 129.49, 129.9, 133.6, 137.1, 138.3, 144.1, 165.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.5 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 485.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{24}F_3N_2O_2S^+$ requires: 485.1505, Found: 485.1499.







Compound 2bx: 62 mg, 83%, A colorless oil; IR (EtOH): ν 2990, 2926, 2123, 1768, 1497, 1371, 1262, 1126, 753, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.80 (s, 3H), 2.67-2.93 (m, 2H), 7.15 (d, 1H, J = 7.6 Hz), 7.28 (td, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.34-7.41 (m, 4H), 7.48-7.51 (m, 2H), 7.61 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 22.8, 41.0 (q, $J_{C\text{-}F}$ = 29.0 Hz), 62.3 (q, $J_{C\text{-}F}$ = 2.2 Hz), 83.5, 94.4, 117.0, 121.8, 122.4, 124.8 (q, $J_{C\text{-}F}$ = 276.9 Hz), 126.6, 128.5, 128.8, 129.6, 131.5, 133.5, 150.2, 168.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -60.7 (t, 3F, J = 10.2 Hz); MS (ESI) *m/z*: 391.1 ($M+NH_4^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{18}F_3N_4O_2^+$ requires: 391.1377, Found: 391.1374.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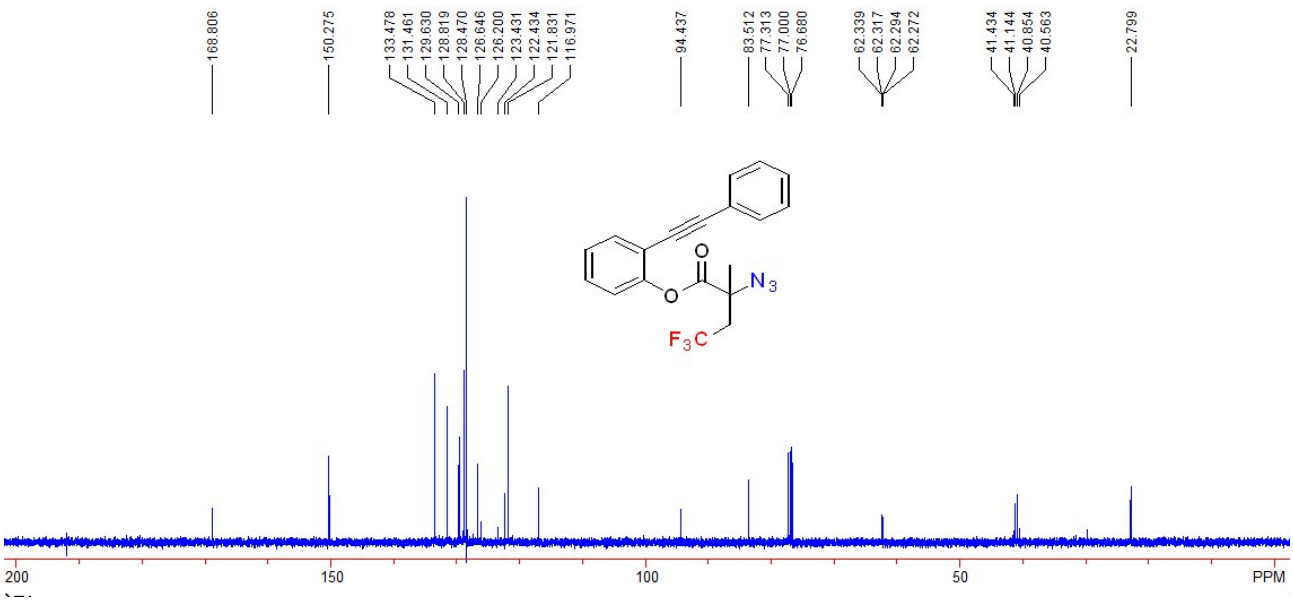
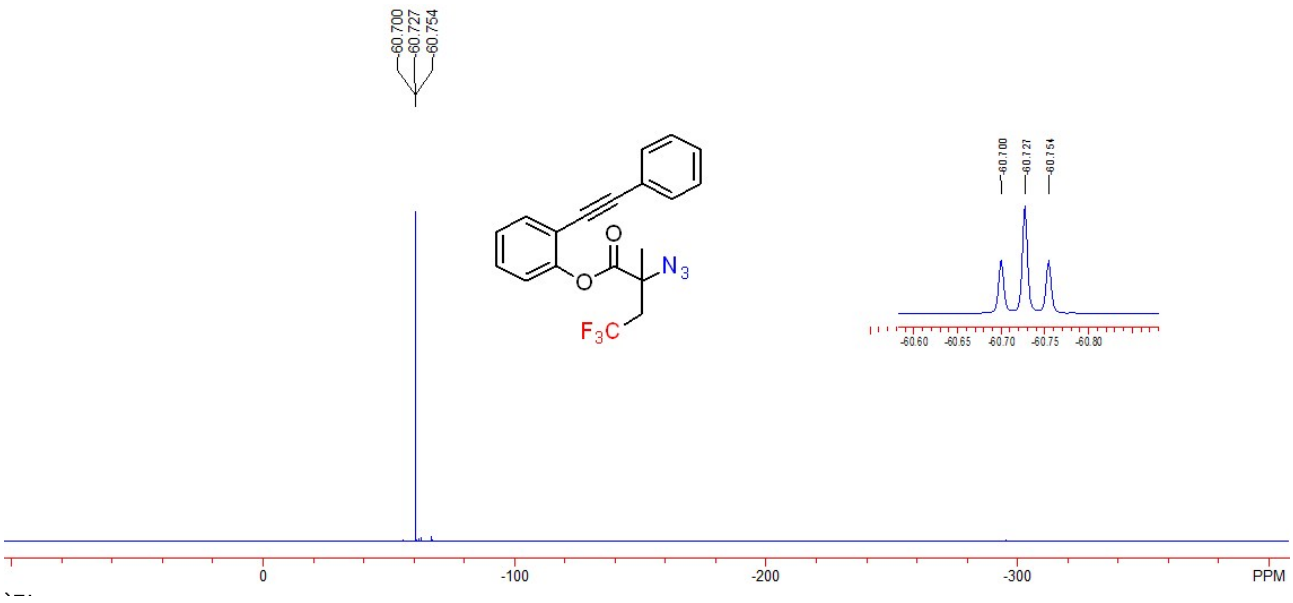
1.08
0.95
2.04
2.97
N3
F3C
10
8
6
4
2
PPM


168.806
150.275
133.478
131.461
129.630
128.819
128.470
126.646
126.200
123.431
122.434
121.831
116.971
94.437
83.512
77.313
77.000
76.680
62.339
62.317
62.294
62.272
41.434
41.144
40.854
40.563
22.799
N3
F3C
200
150
100
50
PPM


-60.700
-60.727
-60.754
N3
F3C
-60.60
-60.65
-60.70
-60.75
-60.80
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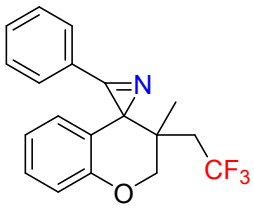
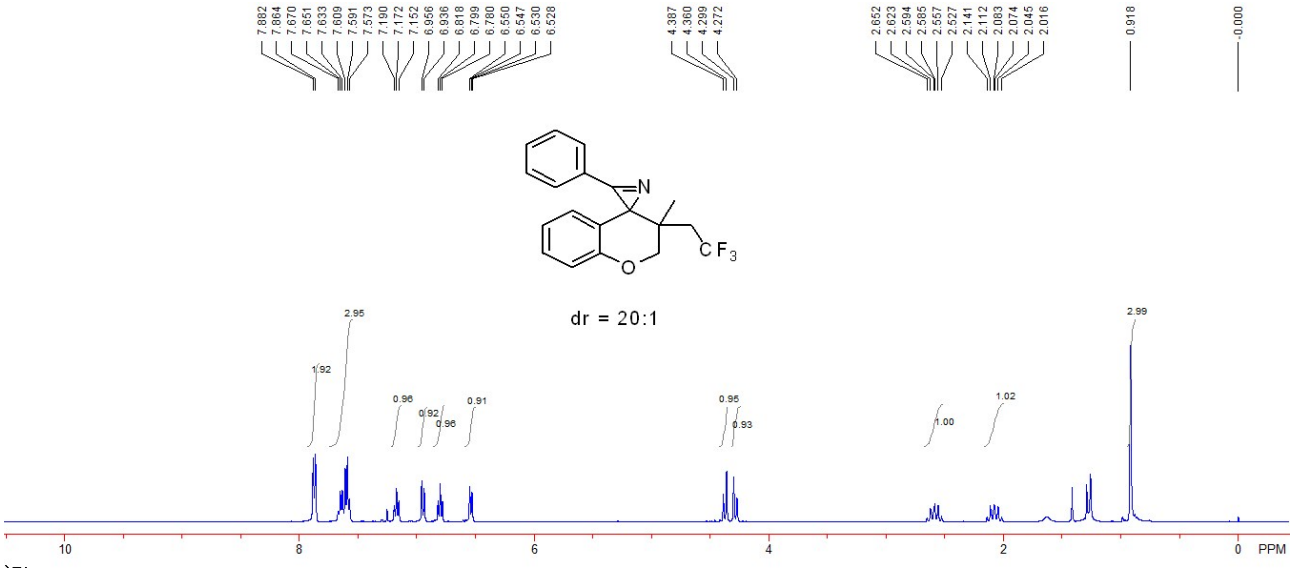
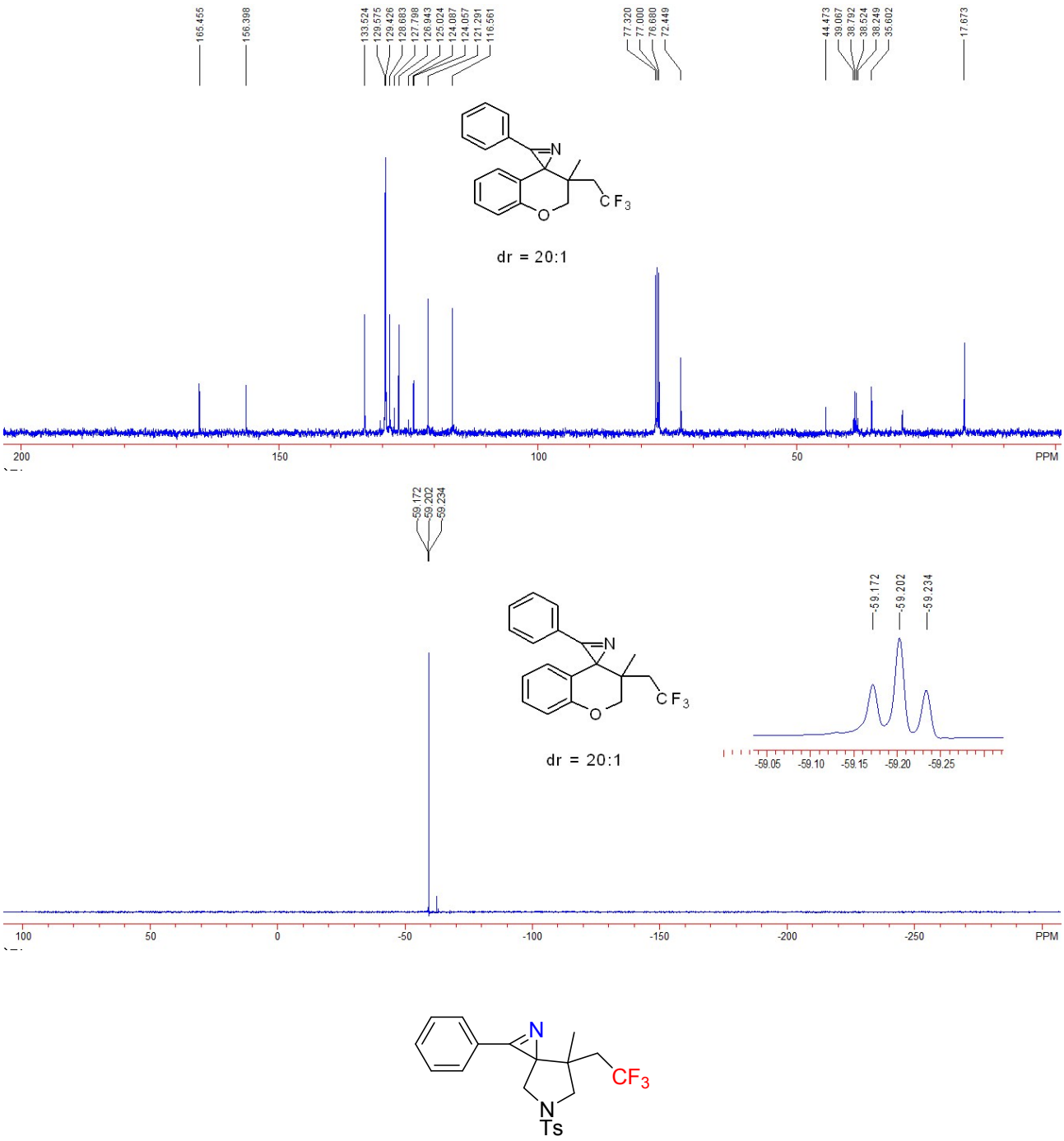
-100
-200
-300
PPM

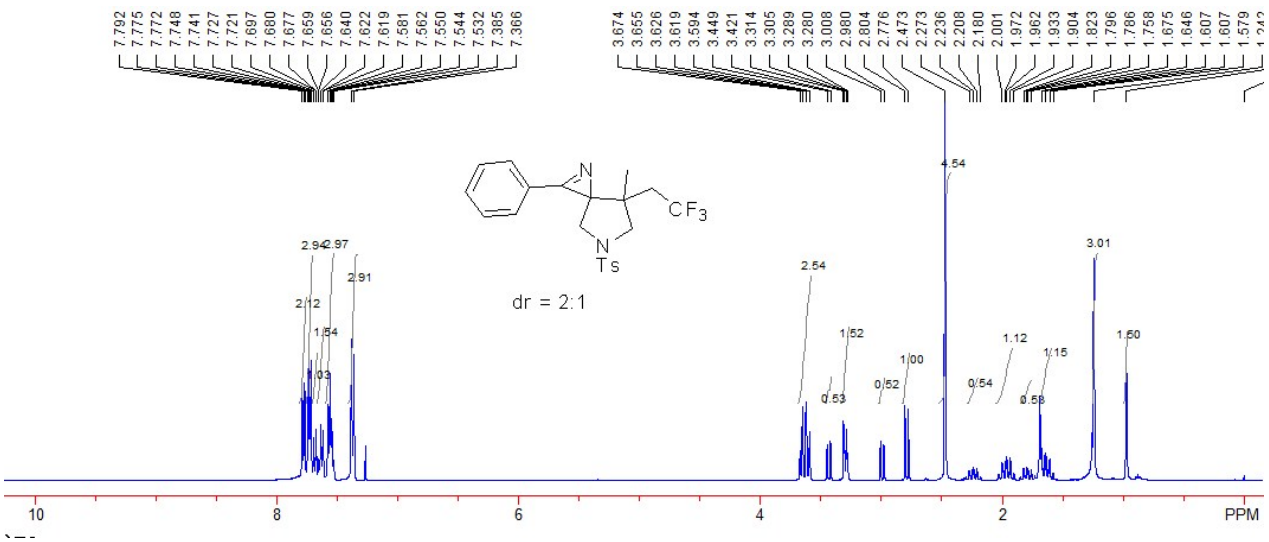


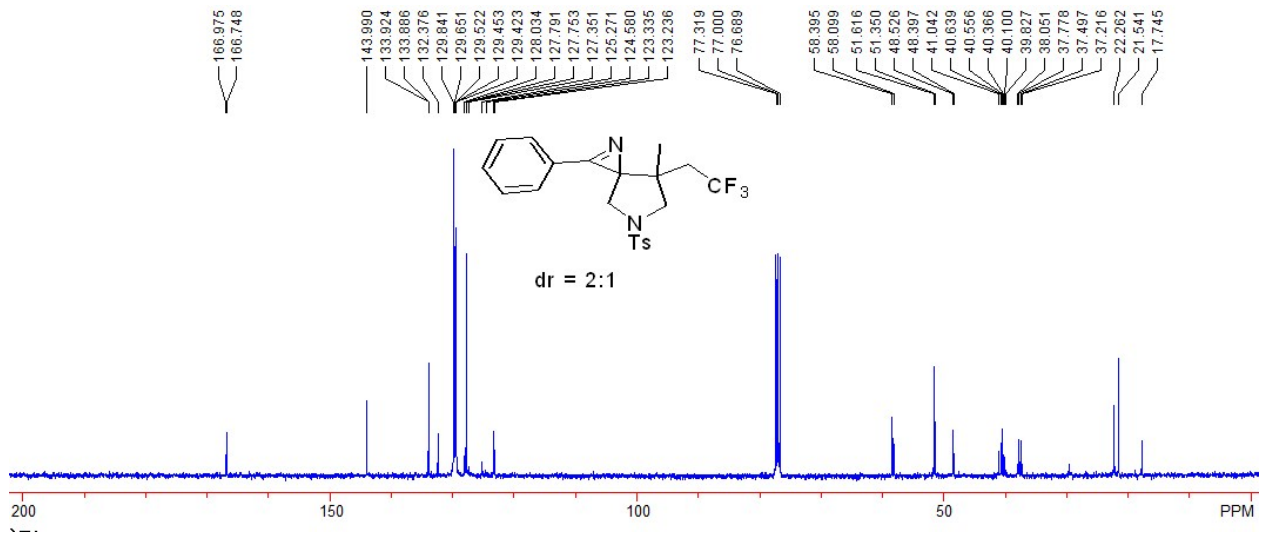
Compound 2by (major product): 54 mg, 81%, A colorless oil, dr = 20:1; IR (EtOH): ν 2931, 2879, 1488, 1451, 1369, 1259, 1115, 1066, 761, 752, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.92 (s, 3H), 2.02-2.14 (m, 1H), 2.53-2.65 (m, 1H), 4.29 (d, 1H, J = 10.8 Hz), 4.37 (d, 1H, J = 10.8 Hz), 6.54 (dd, 1H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 6.80 (t, 1H, J = 7.6 Hz), 6.95 (d, 1H, J = 8.0 Hz), 7.17 (t, 1H, J = 8.0 Hz), 7.57-7.67 (m, 3H), 7.87 (d, 2H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.7, 35.6, 38.7 (q, J_{C-F} = 26.8 Hz), 44.5, 72.4, 116.6, 121.3, 124.06, 124.09, 126.4 (q, J_{C-F} = 277.4 Hz), 126.9, 128.7, 129.4, 129.6, 133.5, 156.4, 165.5; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.2 (t, 3F, J = 11.7 Hz); MS (ESI) *m/z*: 332.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{17}F_3NO^+$ requires: 332.1257, Found: 332.1251.

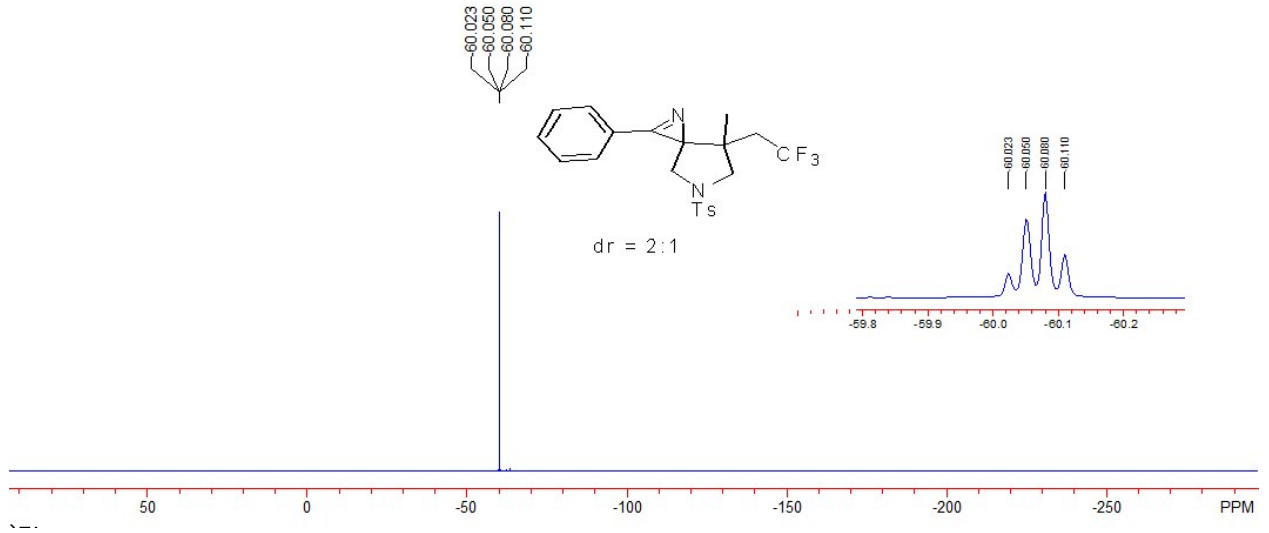




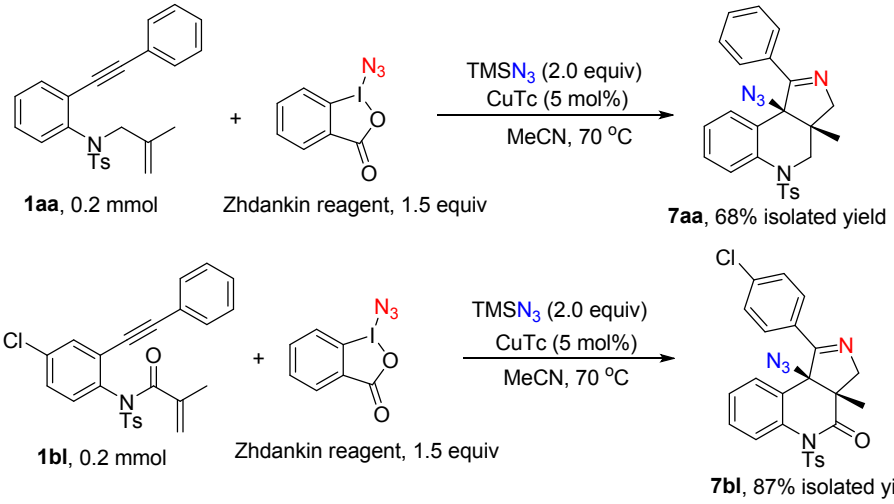
Compound 5: 66 mg, 78%, dr = 2:1. This is a reported compound by Liang's group and spectroscopic data is consistent with reported literature.[2c]


dr = 2:1
Ts
CF3
PPM


dr = 2:1
Ts
CF3
PPM


dr = 2:1
Ts
CF3
PPM

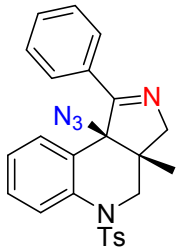
General procedure for diazidation of 1aa and 1bl



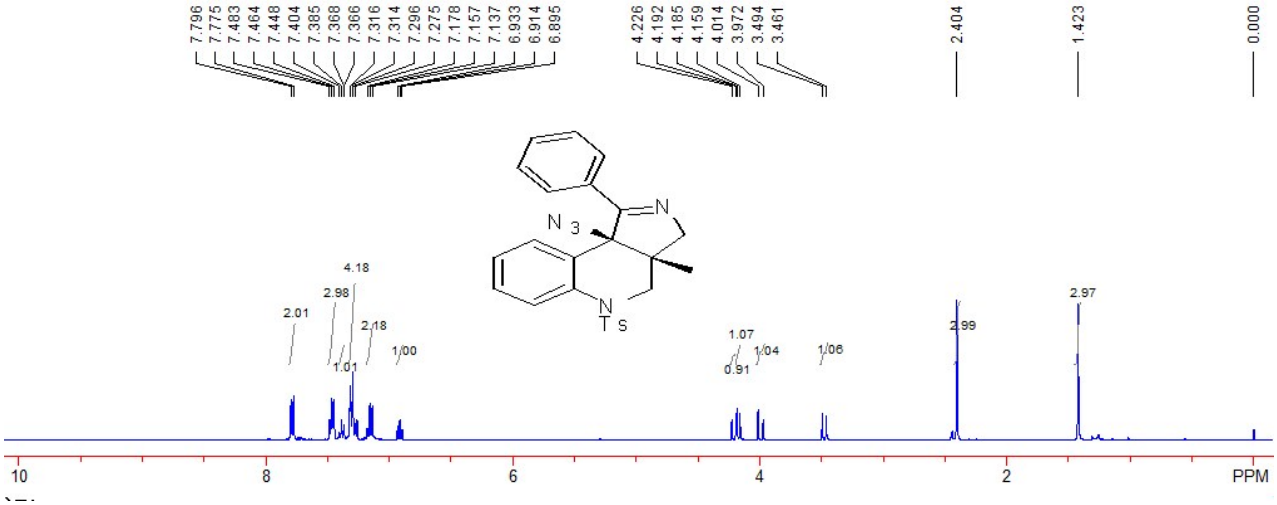
1aa or **1bl** (0.2 mmol, 1.0 equiv), Zhdankin reagent (0.30 mmol, 1.5 equiv), CuTc (0.010 mmol, 0.05 equiv) were dissolved in MeCN (2.0 mL), then $TMSN_3$ (0.40 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 70 °C oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 5 / 1) to afford the products **7aa** or **7bl** in good yield.

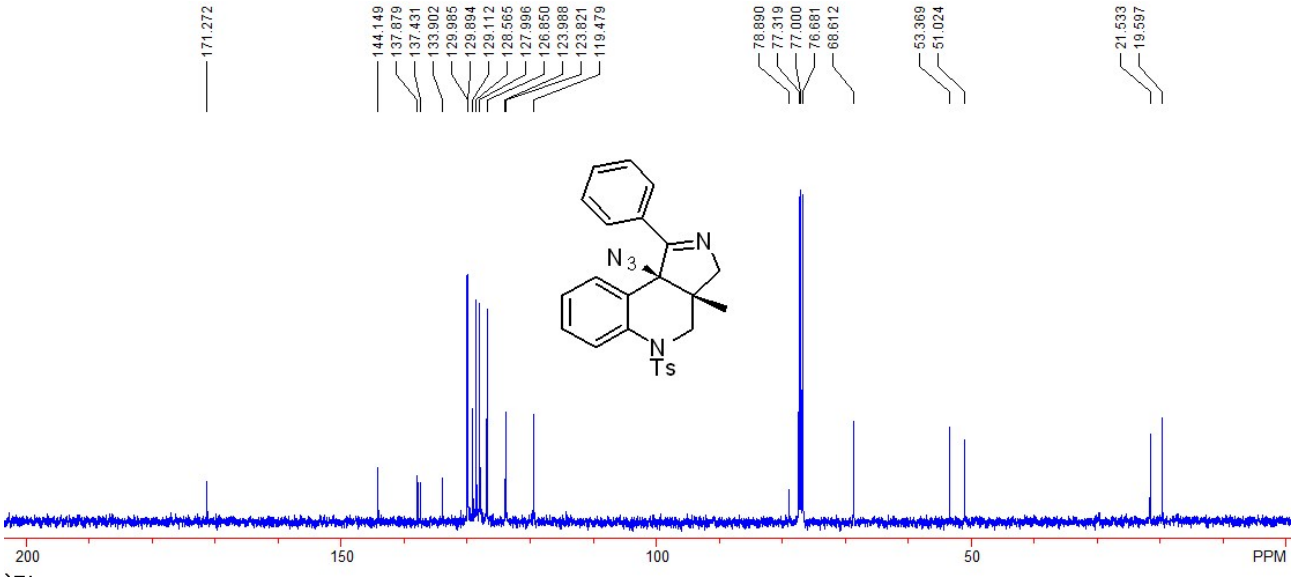
Spectroscopic data for product 7aa

Note: *The spectroscopic data for product **7bl** is consistent with those reported in the literature of Wan's work,[1a] However, our reaction for the formation **7bl** could improve the yield to 87%.*



Compound 7aa: 62 mg, 68%, A white solid, m.p. 191-193 ^{o}C; IR (EtOH): ν 2976, 2934, 2105, 1714, 1455, 1367, 1252, 1170, 1086, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.42 (s, 3H), 2.40 (s, 3H), 3.48 (d, 1H, J = 13.2 Hz), 3.98 (d, 1H, J = 16.8 Hz), 4.18 (d, 1H, J = 13.2 Hz), 4.21 (d, 1H, J = 16.8 Hz), 6.91 (t, 1H, J = 7.6 Hz), 7.15 (d, 2H, J = 8.0 Hz), 7.28-7.32 (m, 4H), 7.39 (td, 1H, J_1 = 7.6 Hz, J_2 = 0.8 Hz), 7.45-7.48 (m, 3H), 7.79 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 19.6, 21.5, 51.0, 53.4, 68.6, 78.9, 119.5, 123.8, 124.0, 126.9, 128.0, 128.6, 129.1, 129.9, 130.0, 133.9, 137.4, 137.9, 144.1, 171.3; MS (ESI) *m/z*: 475.2 (M+NH_4^+, 100); HRMS (ESI) Calcd. for $C_{25}H_{27}N_6O_2S^+$ requires: 475.1911, Found: 475.1908.




171.272
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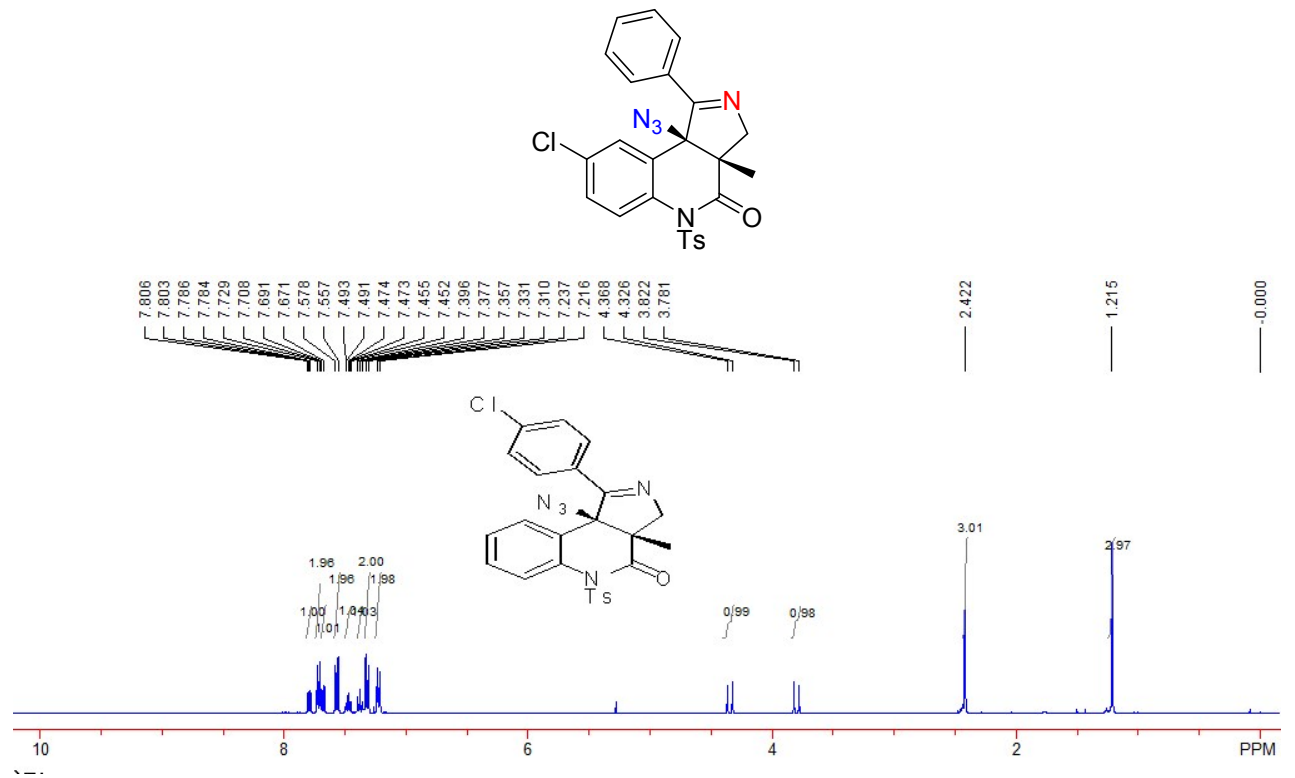
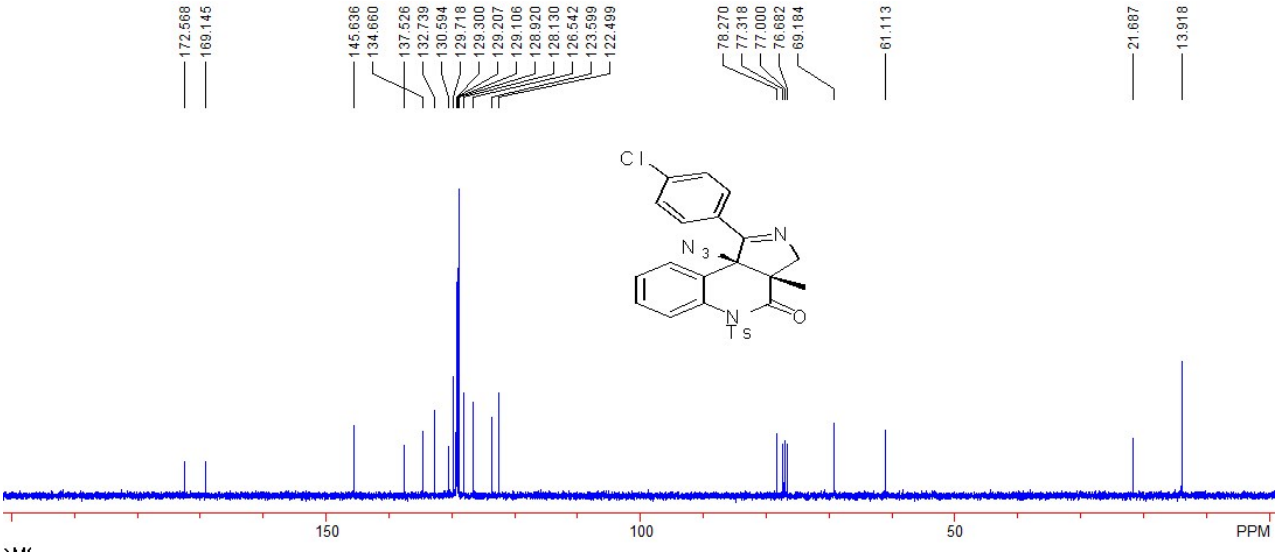
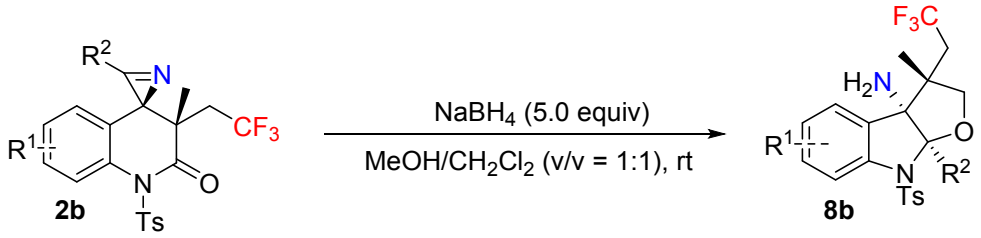
137.879
137.431
133.902
129.985
129.894
129.112
128.565
127.996
126.850
123.988
123.821
119.479
78.890
77.319
77.000
76.681
68.612
53.369
51.024
21.533
19.597
N
N3
N
Ts
200
150
100
50
PPM


N
N3
Cl
N
O
Ts
7.806
7.803
7.786
7.784
7.729
7.708
7.691
7.671
7.578
7.557
7.493
7.491
7.474
7.473
7.455
7.452
7.396
7.377
7.357
7.331
7.310
7.237
7.216
4.368
4.326
3.822
3.781
2.422
1.215
-0.000
Cl
N
N3
N
O
Ts
1.96
2.00
1.96
1.98
1.00
1.01
1.04
1.03
0.99
0.98
3.01
2.97
10
8
6
4
2
PPM

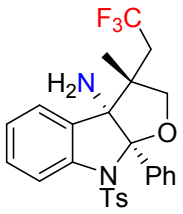

172.568
169.145
145.636
134.660
137.526
132.739
130.594
129.718
129.300
129.207
129.106
128.920
128.130
126.542
123.599
122.499
78.270
77.318
77.000
76.682
69.184
61.113
21.687
13.918
Cl
N
N 3
N
Ts
O
150
100
50
PPM

General procedure for the synthesis of products 8b by $NaBH_4$-reduction

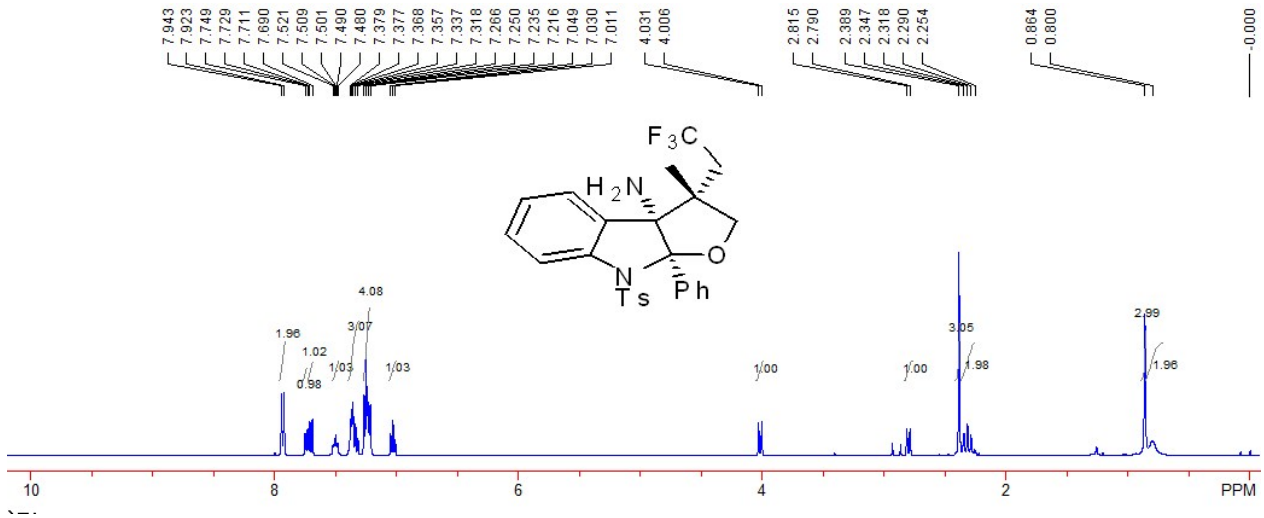


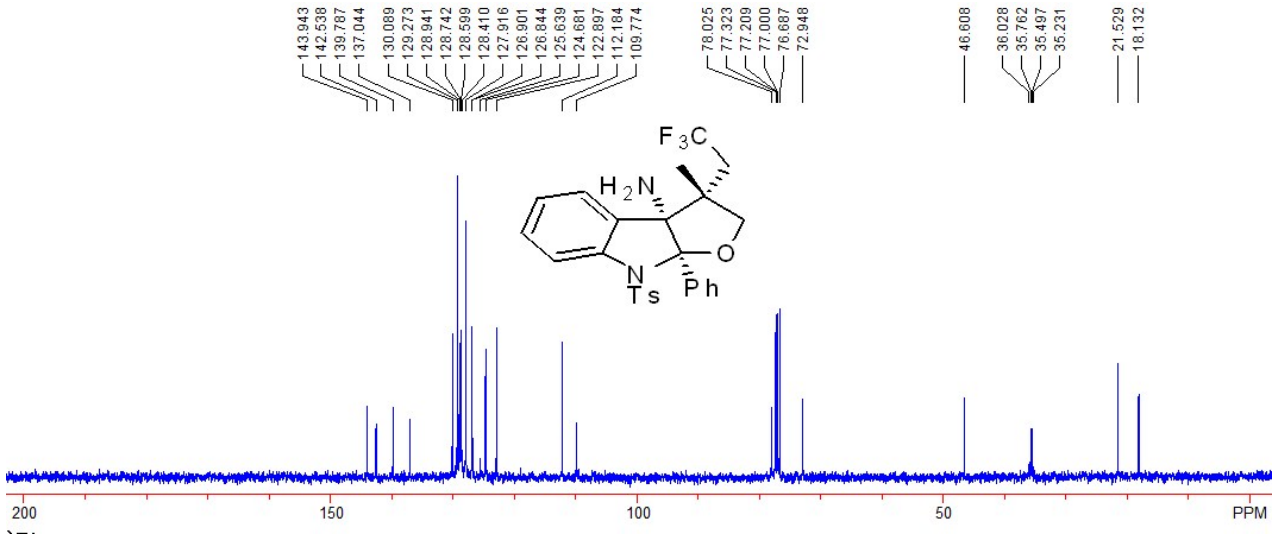
To a stirred solution of **2b** (0.10 mmol. 1.0 equiv) in mixed solvents of MeOH and CH_2Cl_2 (v/v = 1:1, 2.0 mL) at 0 °C was added $NaBH_4$ (0.50 mmol, 5.0 equiv) in one portion. Then the reaction mixture was stirred at room temperature for 15 min. Afterwards, the reaction was quenched by H_2O and the mixture was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford **8b** in good yields ranging from 70% to 89%.

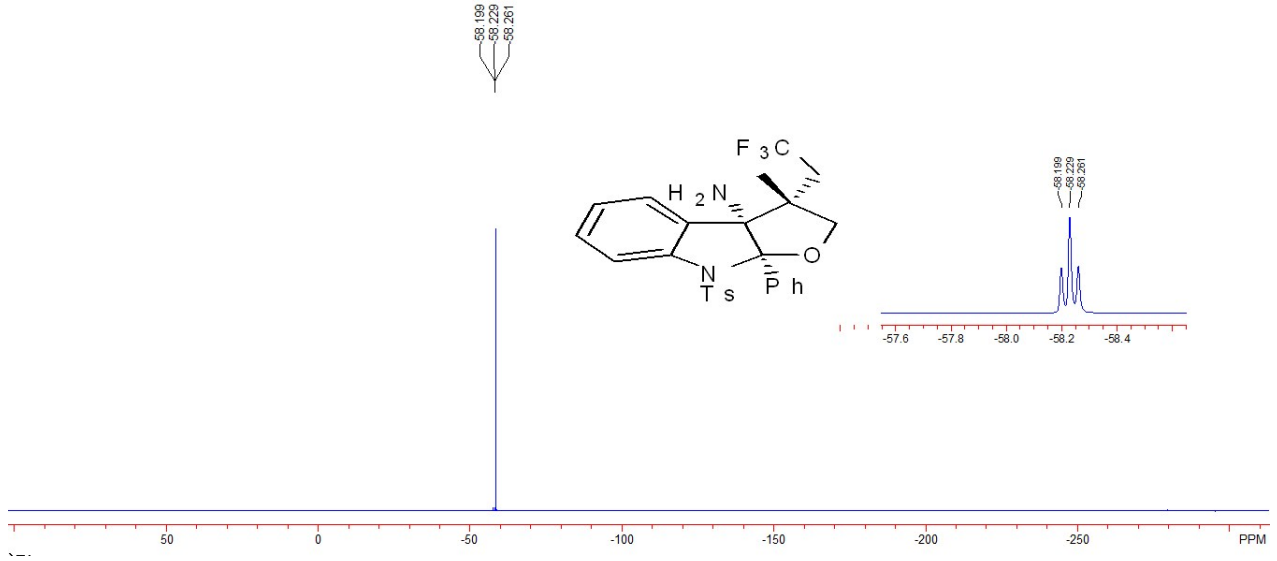
Spectroscopic data for products 8b

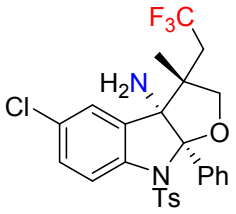


Compound 8ba: 45 mg, 89%, A white solid, m.p. 201-203 ^{o}C; IR (EtOH): ν 2987, 2951, 2873, 1479, 1460, 1364, 1258, 1168, 1107, 1069, 751, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.80 (s, 2H), 0.86 (s, 3H), 2.25-2.35 (m, 2H), 2.39 (s, 3H), 2.80 (d, 1H, J = 10.0 Hz), 4.02 (d, 1H, J = 10.0 Hz), 7.03 (t, 1H, J = 7.6 Hz), 7.22-7.27 (m, 4H), 7.32-7.38 (m, 3H), 7.48-7.52 (m, 1H), 7.70 (d, 1H, J = 8.4 Hz), 7.74 (d, 1H, J = 8.0 Hz), 7.93 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.1, 21.5, 35.6 (q, $J_{C\text{-}F}$ = 26.6 Hz), 46.6, 72.9, 78.0, 109.8, 112.2, 122.9, 124.7, 126.8, 126.9, 127.0 (q, $J_{C\text{-}F}$ = 277.1 Hz), 127.9, 128.6, 128.7, 128.9, 129.3, 130.1, 137.0, 139.8, 142.5, 143.9; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.2 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 503.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{26}F_3N_2O_3S^+$ requires: 503.1611, Found: 503.1604.



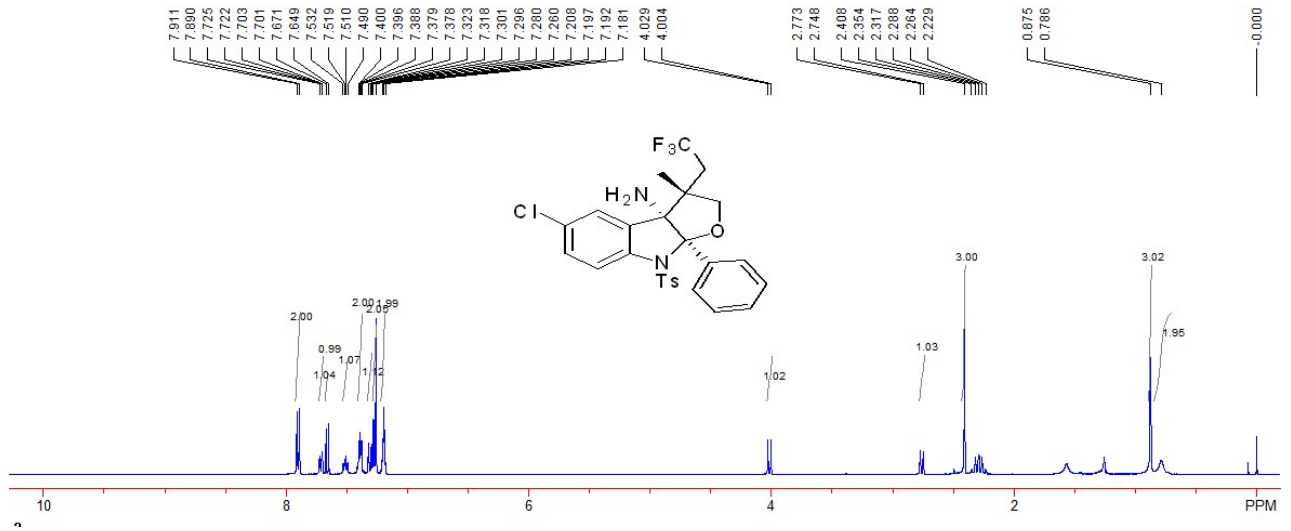


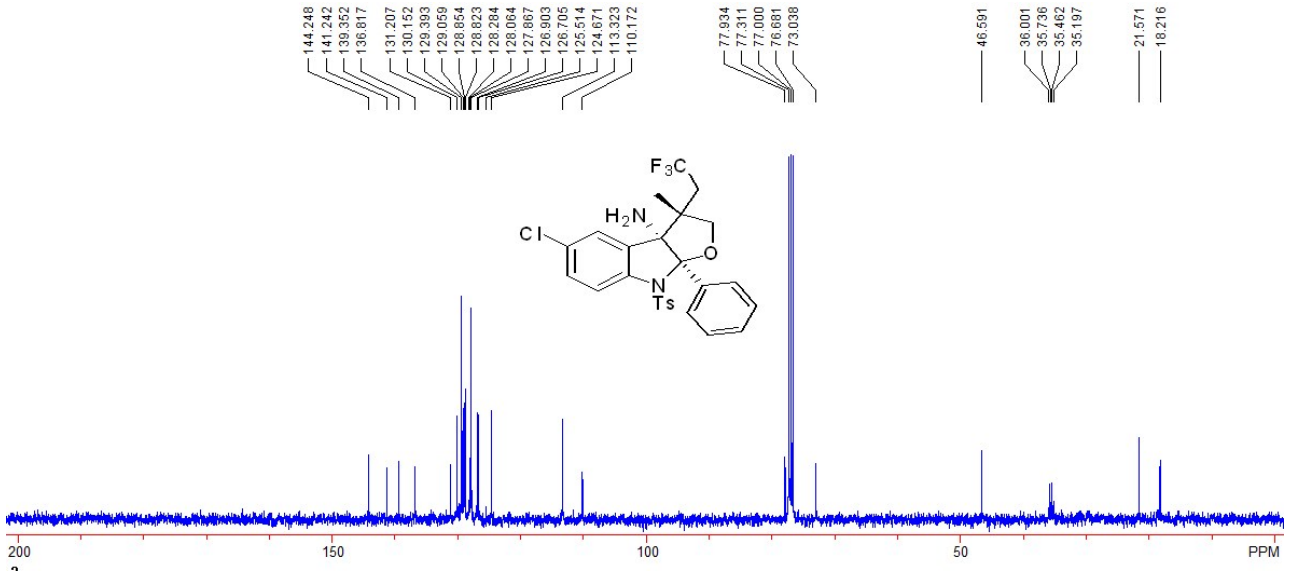


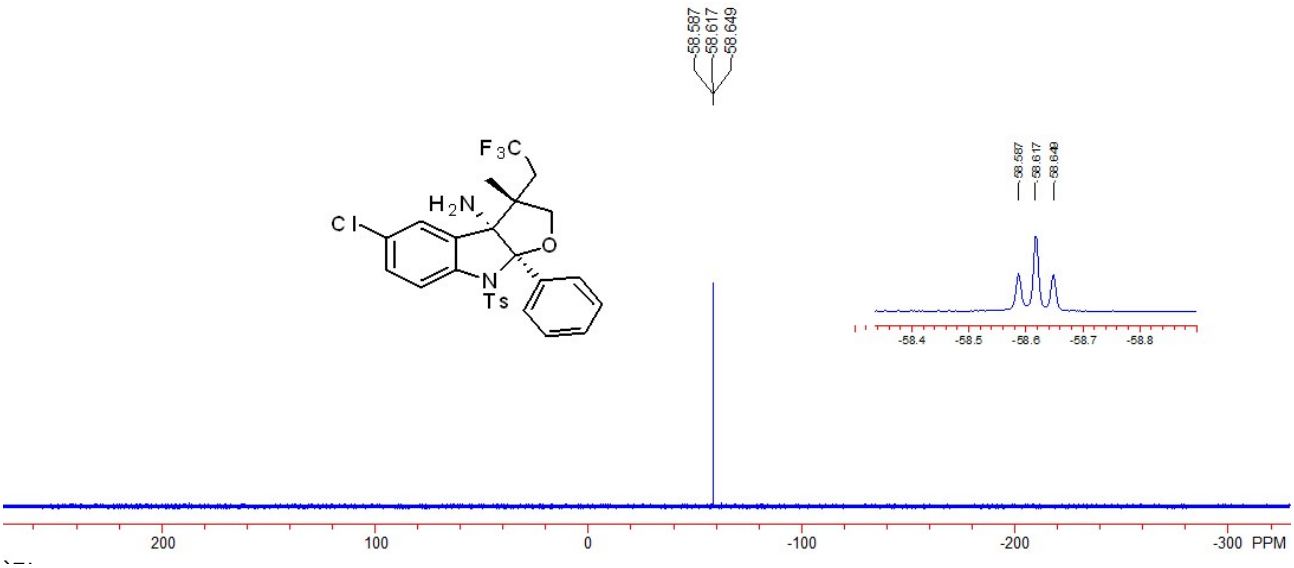


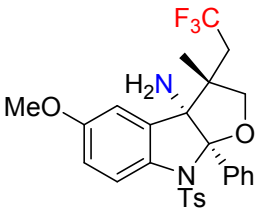
Compound 8bf: 43 mg, 81%, A white solid, m.p. 222-224 ^{o}C; IR (EtOH): ν 2956, 2924, 2854, 1471, 1365, 1258, 1167, 1098, 1070, 814, 663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.79 (s, 2H), 0.88 (s, 3H), 2.23-2.35 (m, 2H), 2.41 (s, 3H), 2.76 (d, 1H, J = 10.0 Hz), 4.02 (d, 1H, J = 10.0 Hz), 7.18-7.21 (m, 2H), 7.26-7.32 (m, 3H), 7.38-7.40 (m, 2H), 7.49-7.53 (m, 1H), 7.66 (d, 1H, J = 8.8 Hz), 7.71 (dd, 1H, J_1 = 8.8 Hz, J_2 = 1.2 Hz), 7.90 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.2, 21.6, 35.6 (q, $J_{C\text{-}F}$ = 27.5 Hz), 46.6, 73.0, 77.9, 110.1, 113.3, 124.7, 126.7, 126.89 (q, $J_{C\text{-}F}$ = 277.0 Hz), 126.90, 127.9, 128.1, 128.8, 128.9, 129.1, 129.4, 130.2, 131.2, 136.8, 139.4, 141.2, 144.2; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI)

m/z: 537.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{25}ClF_3N_2O_3S^+$ requires: 537.1221, Found: 537.1209.

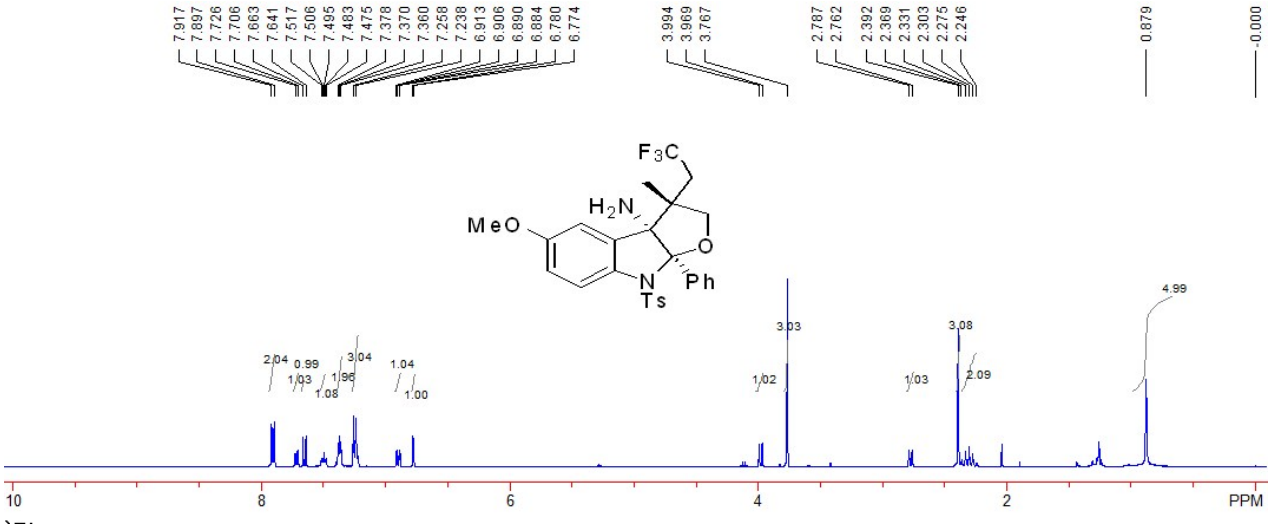


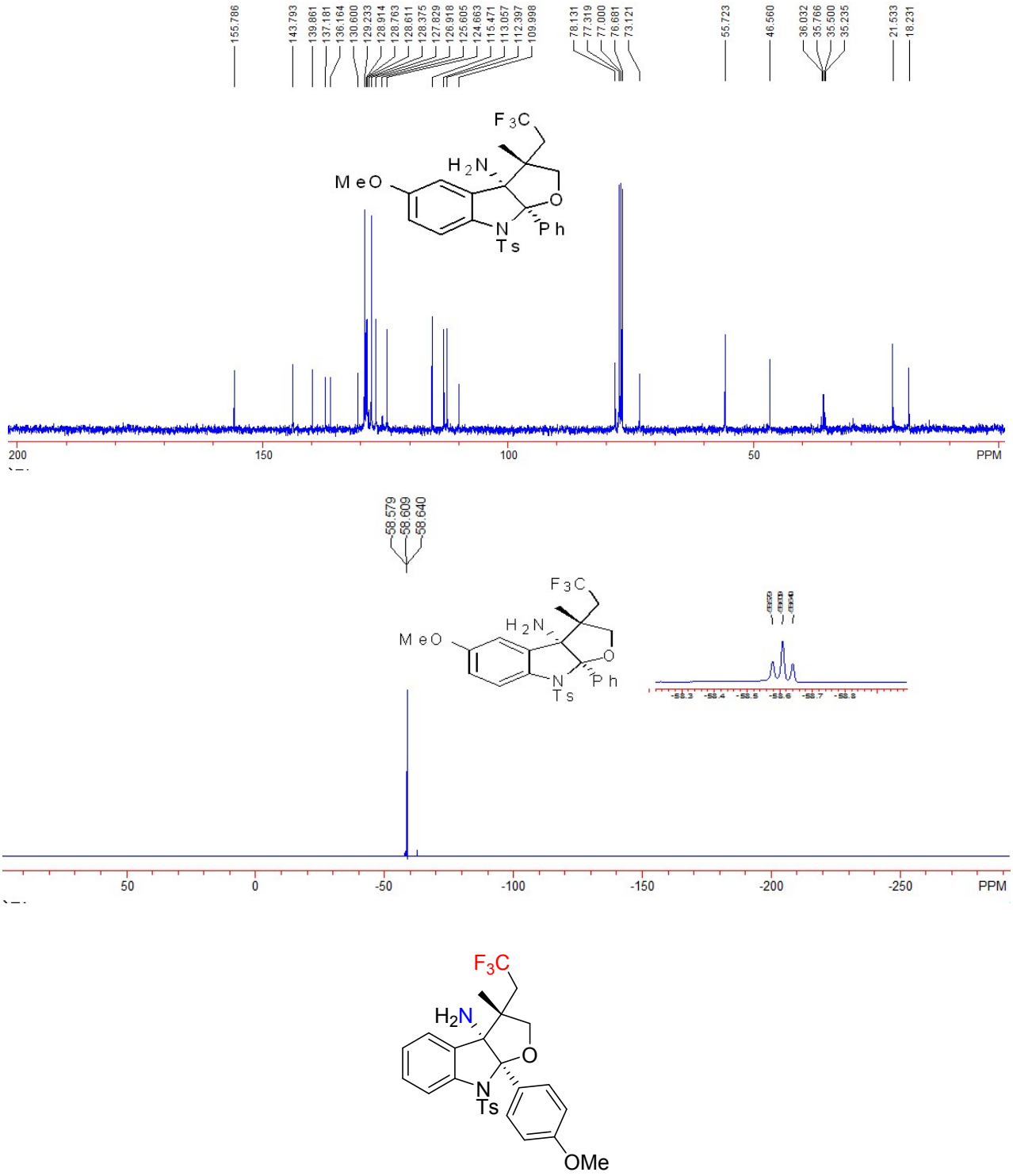






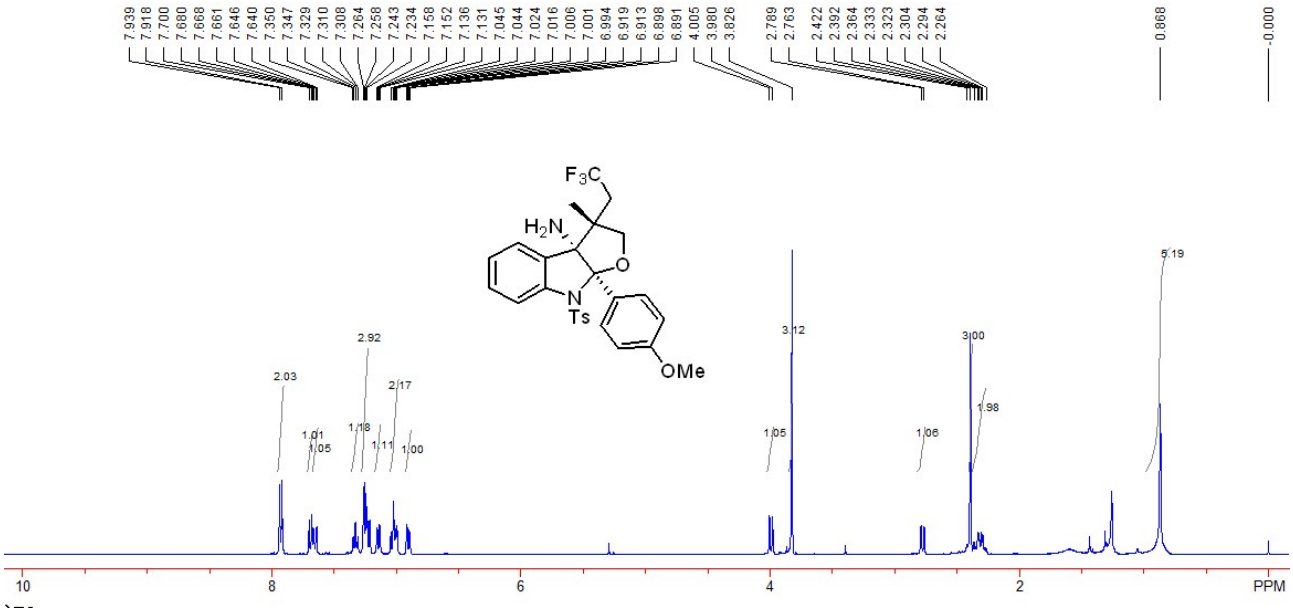
Compound 8bh: 40 mg, 75%, A white solid, m.p. 210-212 °C; IR (EtOH): ν 2948, 2831, 1486, 1363, 1227, 1166, 1025, 814, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (s, 5H), 2.25-2.37 (m, 2H), 2.39 (s, 3H), 2.77 (d, 1H, J = 10.0 Hz), 3.77 (s, 3H), 3.98 (d, 1H, J = 10.0 Hz), 6.78 (d, 1H, J = 2.4 Hz), 6.90 (dd, 1H, J_1 = 8.8 Hz, J_2 = 2.4 Hz), 7.24-7.26 (m, 3H), 7.36-7.38 (m, 2H), 7.48-7.52 (m, 1H), 7.65 (d, 1H, J = 8.8 Hz), 7.72 (d, 1H, J = 8.0 Hz), 7.91 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.2, 21.5, 35.7 (q, $J_{C\text{-}F}$ = 26.6 Hz), 46.6, 55.7, 73.1, 78.1, 110.0, 112.4, 113.1, 115.5, 124.7, 126.9, 127.0 (q, $J_{C\text{-}F}$ = 277.0 Hz), 127.8, 128.6, 128.8, 128.9, 129.2, 130.6, 136.2, 137.2, 139.9, 143.8, 155.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 533.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{28}F_3N_2O_4S^+$ requires: 533.1716, Found: 533.1710.

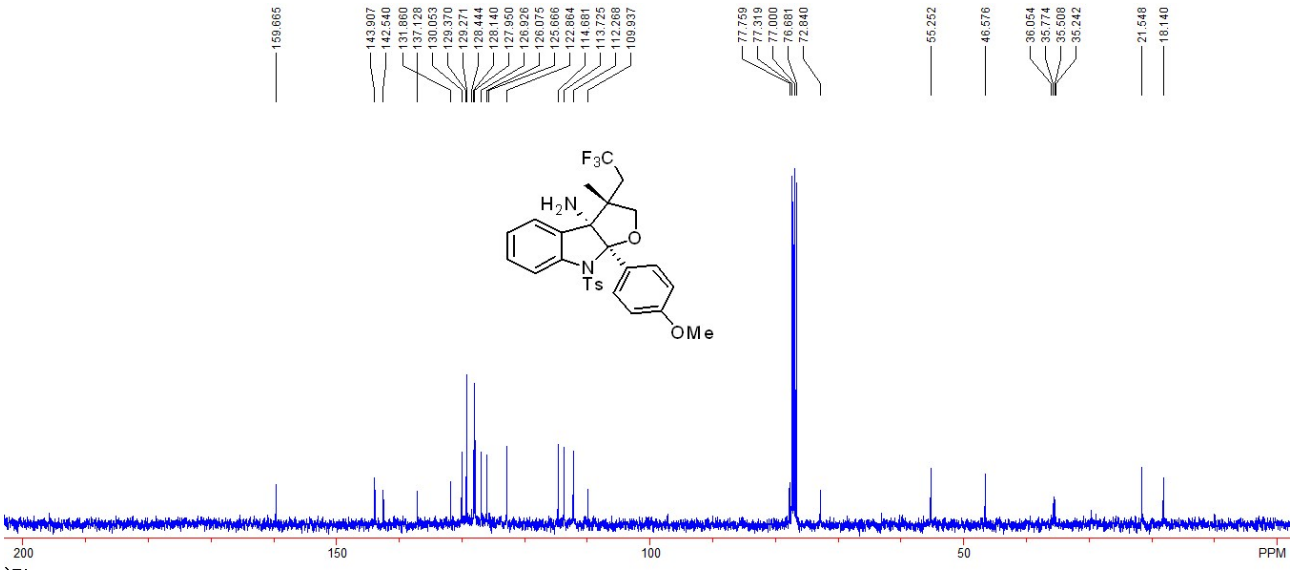


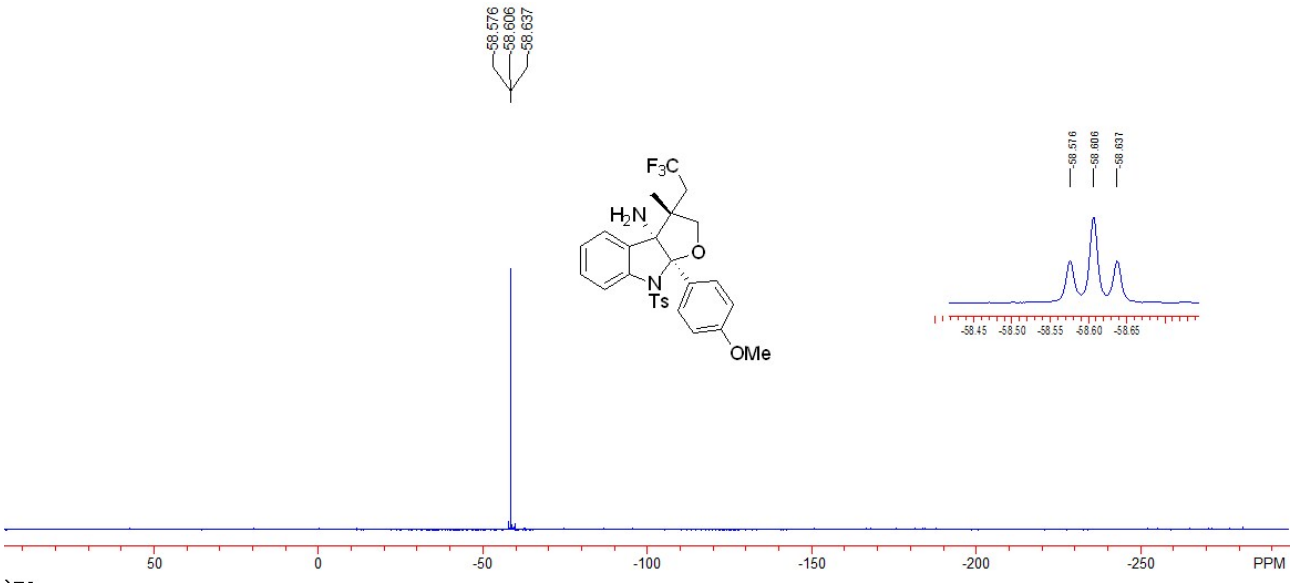


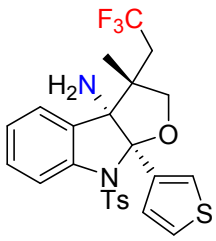
Compound 8bo: 43 mg, 80%, A white solid, m.p. 212-214 ^{o}C; IR (EtOH): ν 2945, 2831, 1487, 1364, 1228, 1164, 1025, 816, 667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.87 (s, 5H), 2.26-2.42 (m, 2H), 2.39 (s, 3H), 2.78 (d, 1H, J = 10.0 Hz), 3.83 (s, 3H), 3.99 (d, 1H, J = 10.0 Hz), 6.90 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 6.99-7.05 (m, 2H), 7.14 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 7.23-7.26 (m, 3H), 7.33 (td, 1H, J_1 = 8.4 Hz, J_2 = 1.2 Hz), 7.65 (dd, 1H, J_1 = 8.4 Hz, J_2 = 2.4 Hz), 7.69 (d, 1H, J = 8.0 Hz), 7.93 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.1, 21.5, 35.6 (q,

$J_{C\text{-}F}$ = 26.6 Hz), 46.6, 55.3, 72.8, 77.8, 109.9, 112.3, 113.7, 114.7, 122.9, 126.1, 126.9, 127.1 (q, $J_{C\text{-}F}$ = 277.8 Hz), 128.0, 128.1, 129.3, 129.4, 130.1, 131.9, 137.1, 142.5, 143.9, 159.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 533.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{27}H_{28}F_3N_2O_4S^+$ requires: 533.1716, Found: 533.1712.

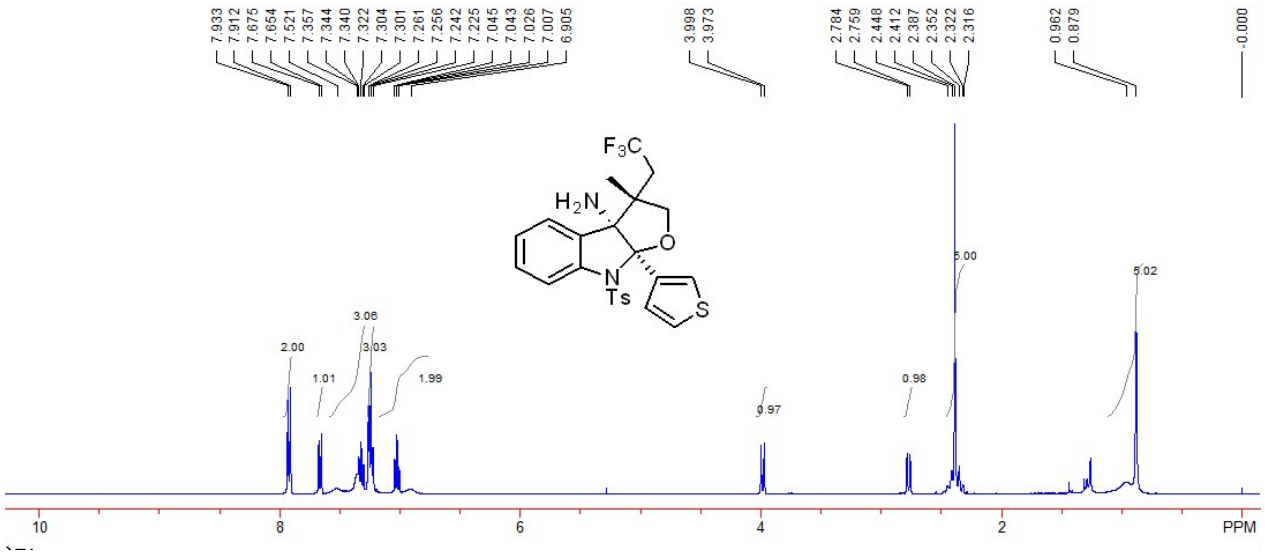








Compound 8bt: 42 mg, 83%, A white solid, m.p. 195-197 ^{o}C; IR (EtOH): ν 2956, 2929, 2870, 1597, 1480, 1363, 1259, 1171, 1089, 1073, 756, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.88 (s, 3H), 0.96 (s, 2H), 2.32-2.45 (m, 2H), 2.39 (s, 3H), 2.77 (d, 1H, J = 10.0 Hz), 3.99 (d, 1H, J = 10.0 Hz), 6.91-7.05 (m, 2H), 7.23-7.26 (m, 3H), 7.30-7.52 (m, 3H), 7.66 (d, 1H, J = 8.4 Hz), 7.92 (d, 2H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.0, 21.5, 35.6 (q, $J_{C\text{-}F}$ = 26.6 Hz), 46.8, 72.9, 108.3, 112.4, 122.2, 122.9, 126.0, 126.9, 127.01 (q, $J_{C\text{-}F}$ = 277.1 Hz), 127.02, 127.9, 129.1, 129.3, 130.1, 136.9, 141.8, 142.1, 144.0; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -58.6 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 509.1 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{24}H_{24}F_3N_2O_3S_2^{+}$ requires: 509.1175, Found: 509.1168.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7.242
7.225
7.045
7.043
7.026
7.007
6.905
3.998
3.973
2.784
2.759
2.448
2.412
2.387
2.352
2.322
2.316
0.962
0.879
-0.000
F3C
H2N
O
N
Ts
S
2.00
1.01
3.06
3.03
1.99
0.97
0.98
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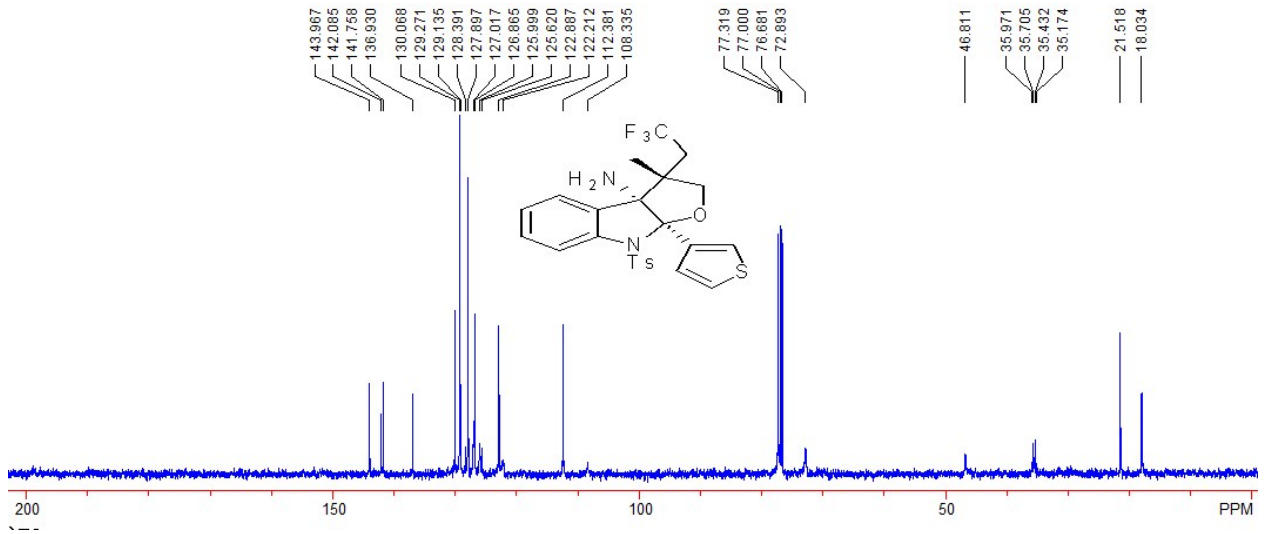
5.02
10
8
6
4
2
PPM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127.017
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76.681
72.893
46.811
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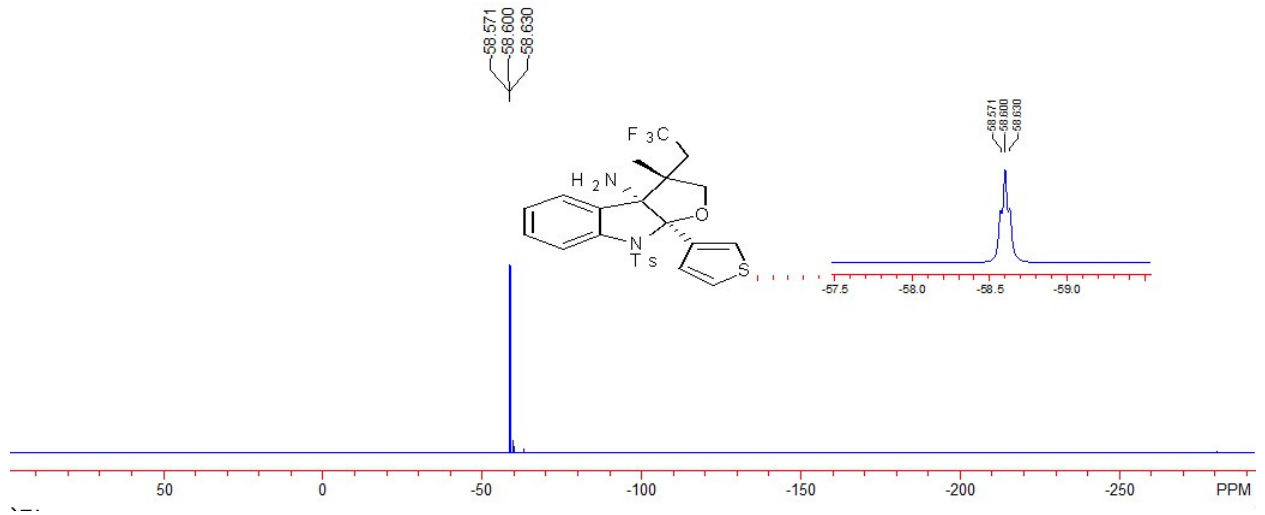
O
N
Ts
S
200
150
100
50
PPM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58.630
F3C
H2N
O
N
Ts
S
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-58.0
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-150
-200
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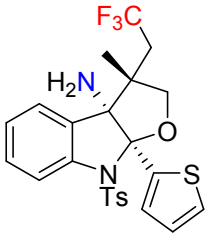
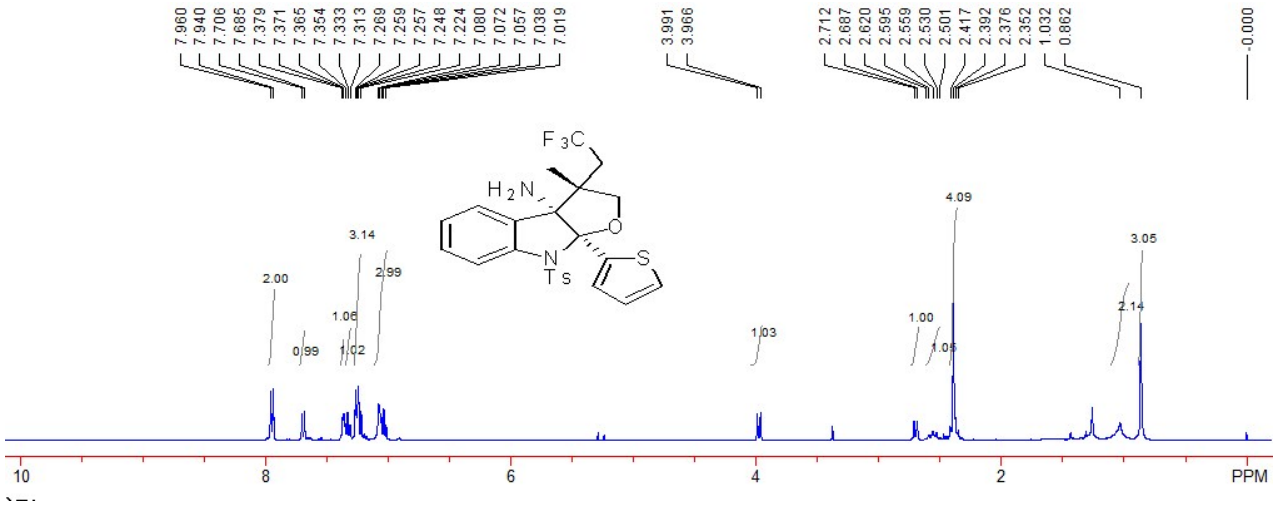
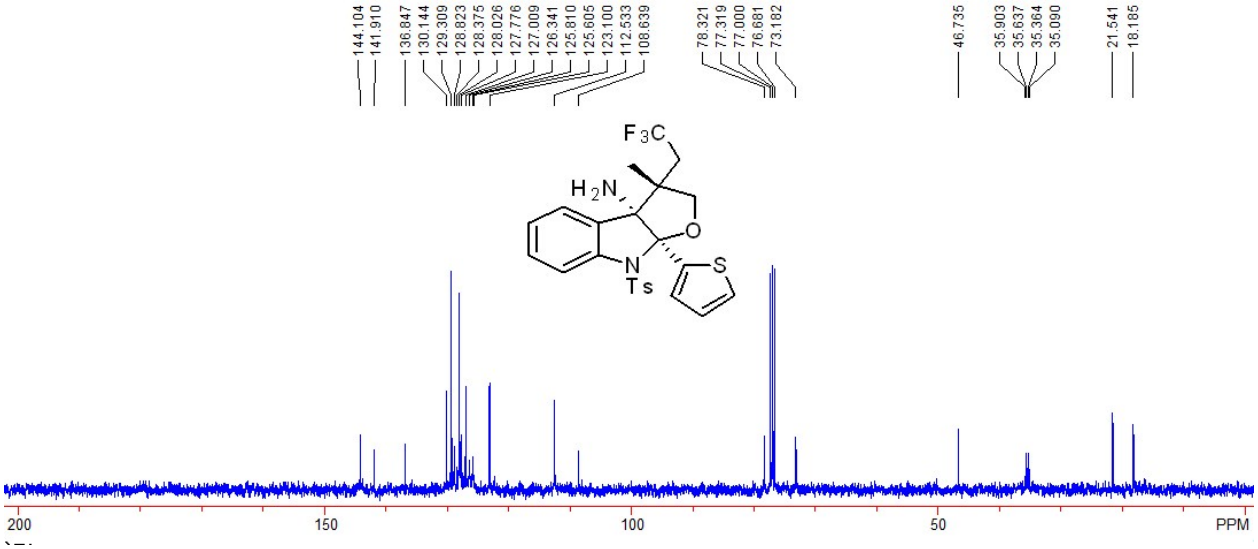
PPM



Compound 8bu: 43 mg, 84%, A white solid, m.p. 188-190 °C; IR (EtOH): ν 2954, 2924, 2856, 1597, 1459, 1364, 1260, 1167, 1106, 1089, 1069, 760, 669 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.86 (s, 3H), 1.03 (s, 2H), 2.35-2.42 (m, 1H), 2.39 (s, 3H), 2.50-2.62 (m, 1H), 2.70 (d, 1H, J = 10.0 Hz), 3.98 (d, 1H, J = 10.0 Hz), 7.02-7.08 (m, 3H), 7.22-7.27 (m, 3H), 7.31-7.38 (m, 2H), 7.70 (d, 1H, J = 8.0 Hz), 7.95 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.2, 21.5, 35.5 (q, J_{C-F} = 26.6 Hz), 46.7, 73.2, 78.3, 108.6, 112.5, 123.1, 125.8, 126.3, 127.00 (q, J_{C-F} = 277.0 Hz), 127.01, 127.8, 128.0, 128.8, 129.3, 130.1, 136.8, 141.9, 144.1; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -170.0 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 509.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{24}F_3N_2O_3S_2^+$ requires: 509.1175, Found: 509.1169.

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112.533
108.639
78.321
77.319
77.000
76.681
73.182
46.735
35.903
35.637
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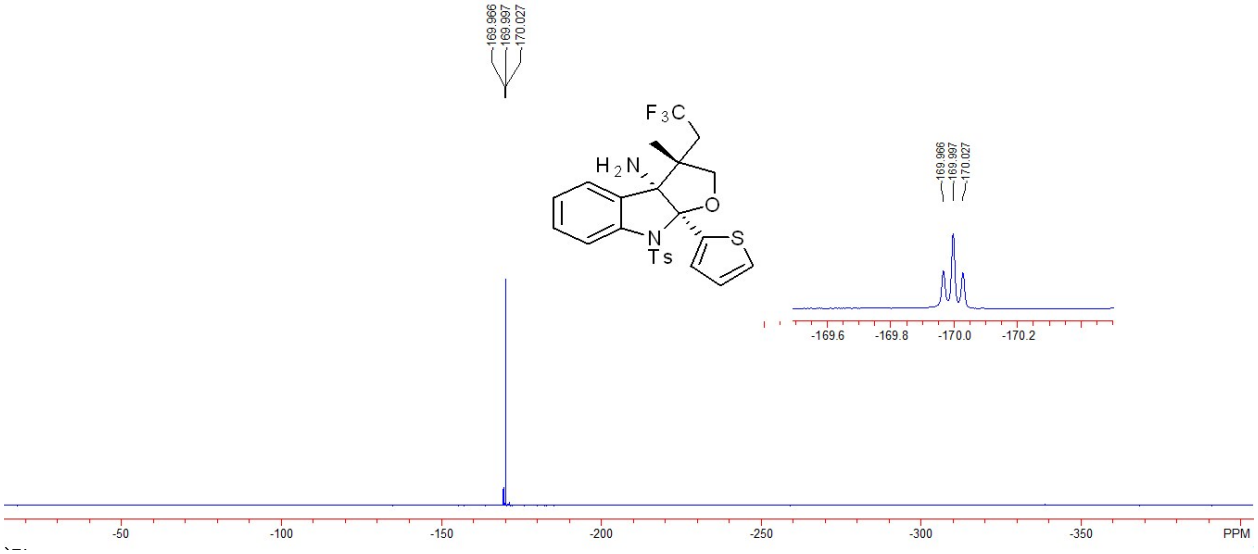
O
N
Ts
S
200
150
100
50
PPM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F3C
H2N
O
N
Ts
S
-169.6
-169.8
-170.0
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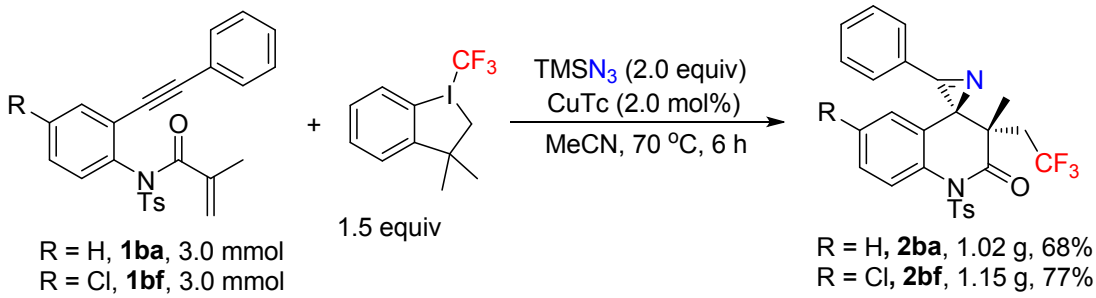
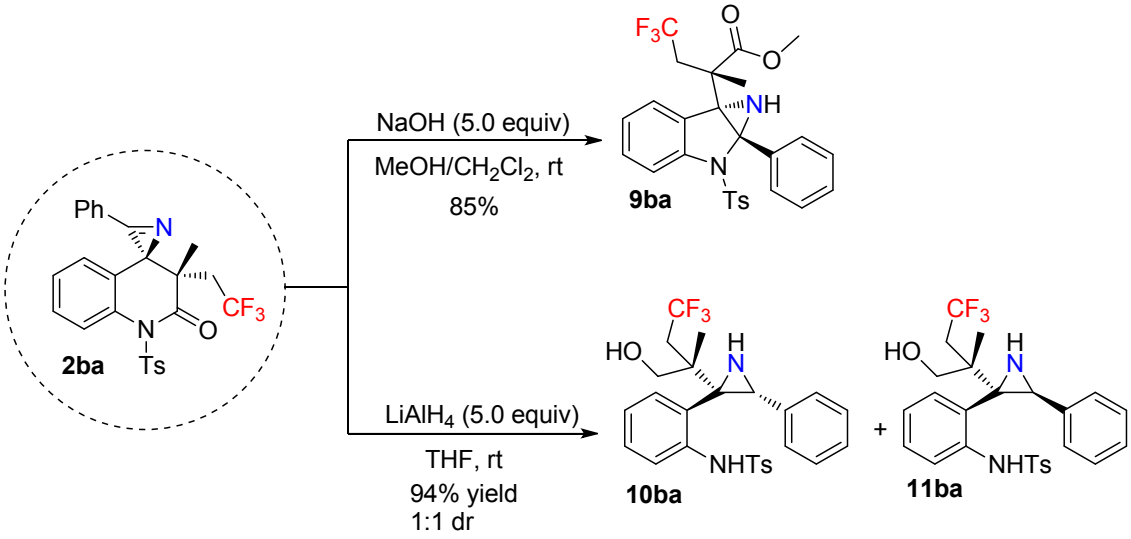
-50
-100
-150
-200
-250
-300
-350
PPM

General procedure for the scalable synthesis and the synthesis of products 9ba, 10ba, and 11ba



Scheme S2 Scalable synthesis of **2ba** and **2bf**.

1ba or **1bf** (3.0 mmol, 1.0 equiv), Togni reagent I (4.5 mmol, 1.5 equiv), CuTc (0.06 mmol, 0.02 equiv) were dissolved in MeCN (2.0 mL), then $TMSN_3$ (6.0 mmol, 2.0 equiv) was added dropwise and the reaction tube was placed in a pre-heated 70 °C oil bath. The reaction was stopped after 6 h and the reaction mixture was filtered through a celite. The filtrate was concentrated under reduced pressure and the residue was purified by a silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 10 / 1) to afford the products **2ba** and **2bf** in 68% and 77% yields, respectively



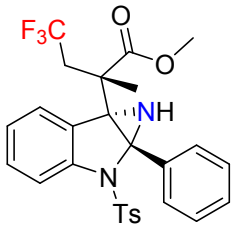
Scheme S3 Alcoholysis and $LiAlH_4$-reduction

Alcoholysis: The solution of **2ba** (0.2 mmol, 1.0 equiv) and NaOH fragment (1.0 mmol, 5.0 equiv) in mixed solvents of MeOH and CH_2Cl_2 (v/v = 1:1, 4.0 mL) was stirred at room temperature for 6 h.

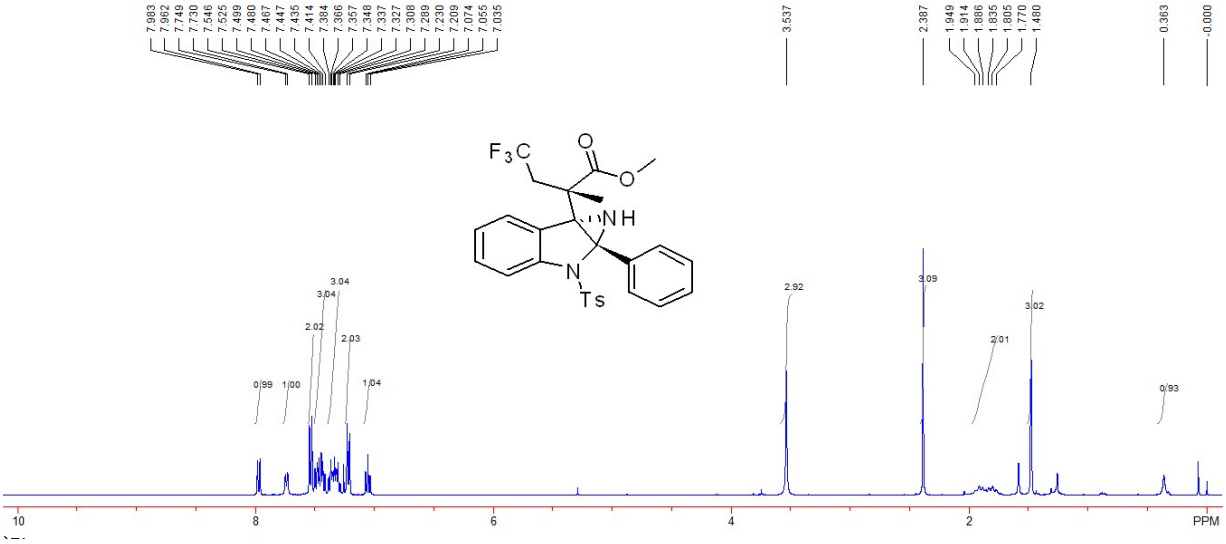
Upon completion, the reaction was quenched by HCl solution (1N) until the pH value of the solution was about 7. Then the solution was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford **9ba** in 85% yield.

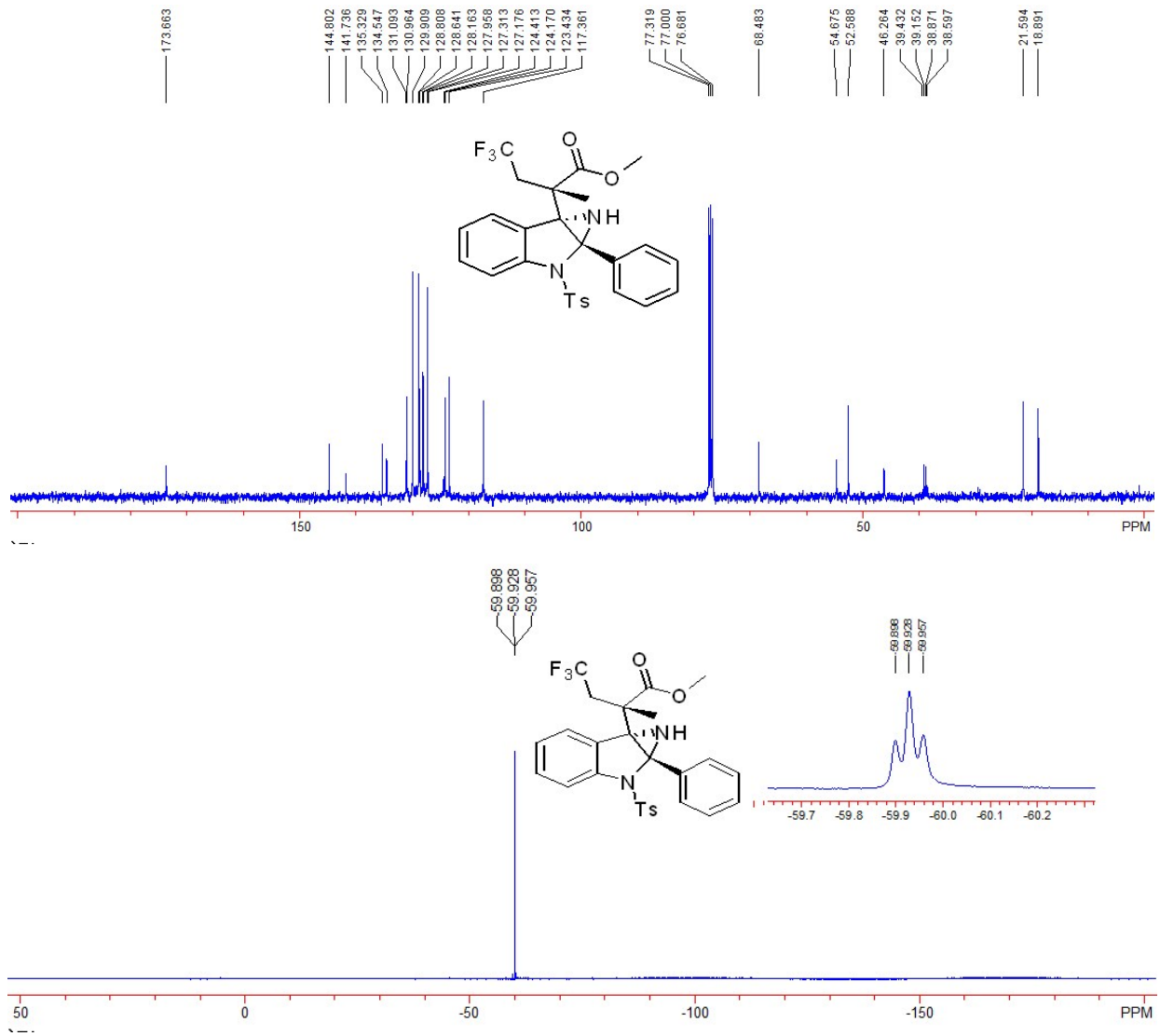
$LiAlH_4$-reduction: To a solution of **2ba** (0.20 mmol, 1.0 equiv) in dry THF (4.0 mL) was added $LiAlH_4$ (1.0 mmol, 5.0 equiv) in one portion, and the resulting solution was stirred at room temperature for 2 h. Upon completion, the reaction was quenched by saturated NH_4Cl solution. Then the solution was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by a silica gel flash chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford **10ba** and **11ba** in 94% yield and 1:1 dr value.

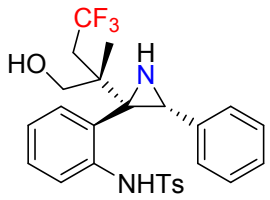
Spectroscopic data for products 9ba, 10ba, and 11ba



Compound 9ba: 90 mg, 85%, A white solid, m.p. 230-232 ^{o}C; IR (EtOH): ν 2956, 2923, 2851, 1748, 1460, 1370, 1268, 1170, 1149, 1093, 702, 662 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.36 (s, 1H), 1.48 (s, 3H), 1.77-1.95 (m, 2H), 2.39 (s, 3H), 3.54 (s, 3H), 7.06 (t, 1H, J = 8.0 Hz), 7.22 (d, 2H, J = 8.4 Hz), 7.29-7.38 (m, 3H), 7.41-7.50 (m, 3H), 7.54 (d, 2H, J = 8.4 Hz), 7.74 (d, 1H, J = 7.6 Hz), 7.97 (d, 1H, J = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 18.9, 21.6, 39.0 (q, $J_{C\text{-}F}$ = 28.1 Hz), 46.3, 52.6, .54.7, 68.5, 117.4, 123.4, 124.2, 125.8 (q, $J_{C\text{-}F}$ = 276.3 Hz), 127.3, 128.0, 128.2, 128.6, 128.8, 129.9, 131.0, 131.1, 134.5, 135.3, 141.7, 144.8, 173.7; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -59.9 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 531.2 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{27}H_{26}F_3N_2O_4S^{+}$ requires: 531.1560, Found: 531.1553.

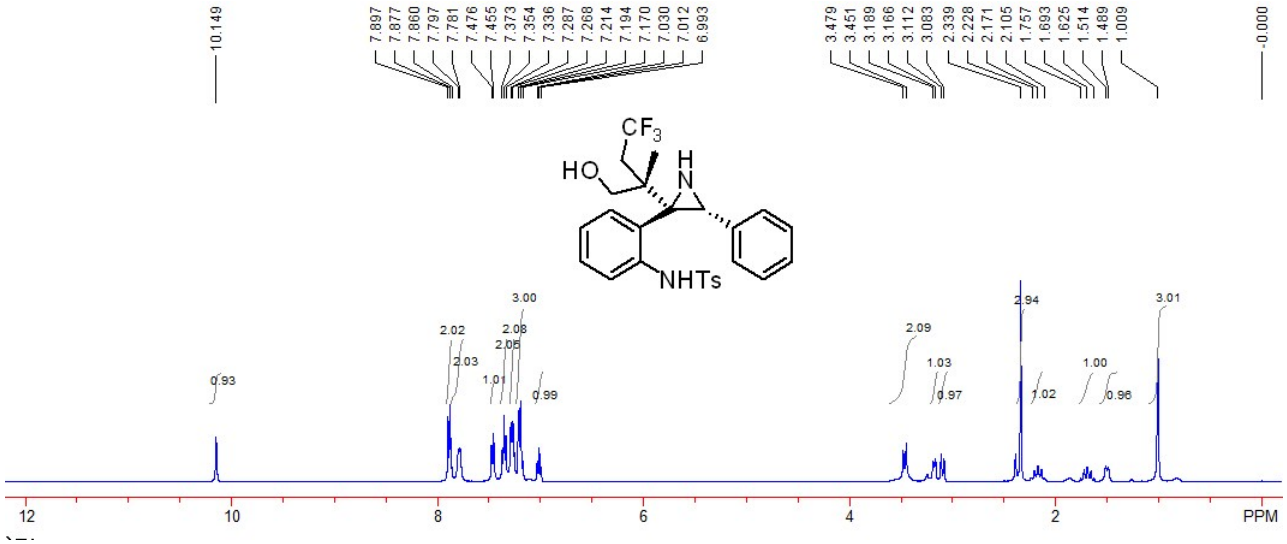


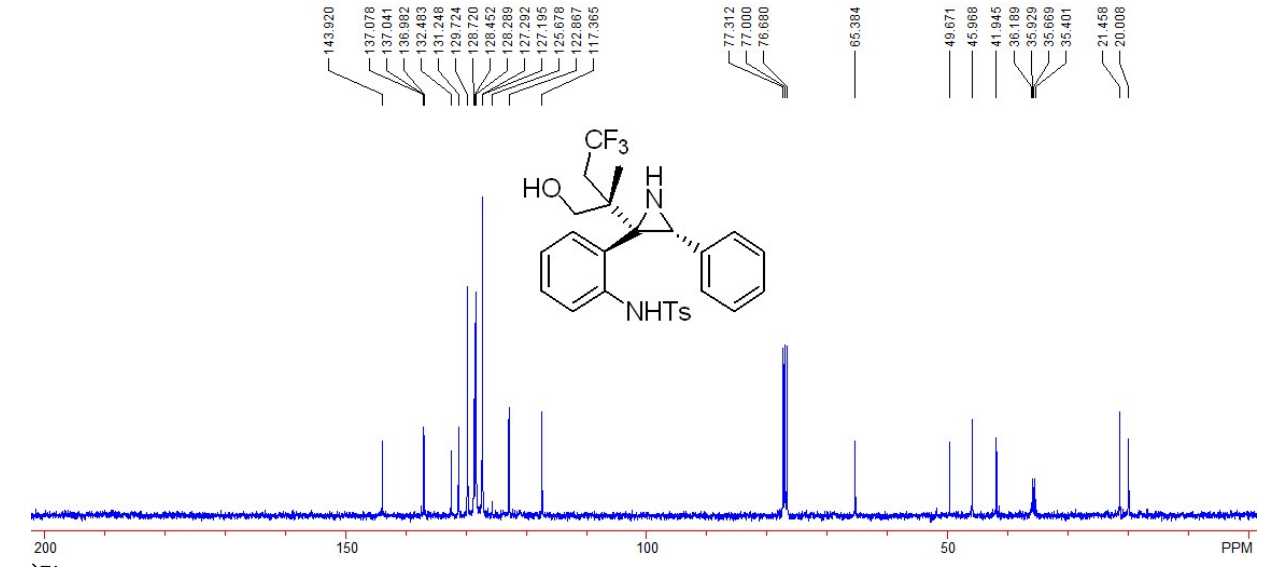


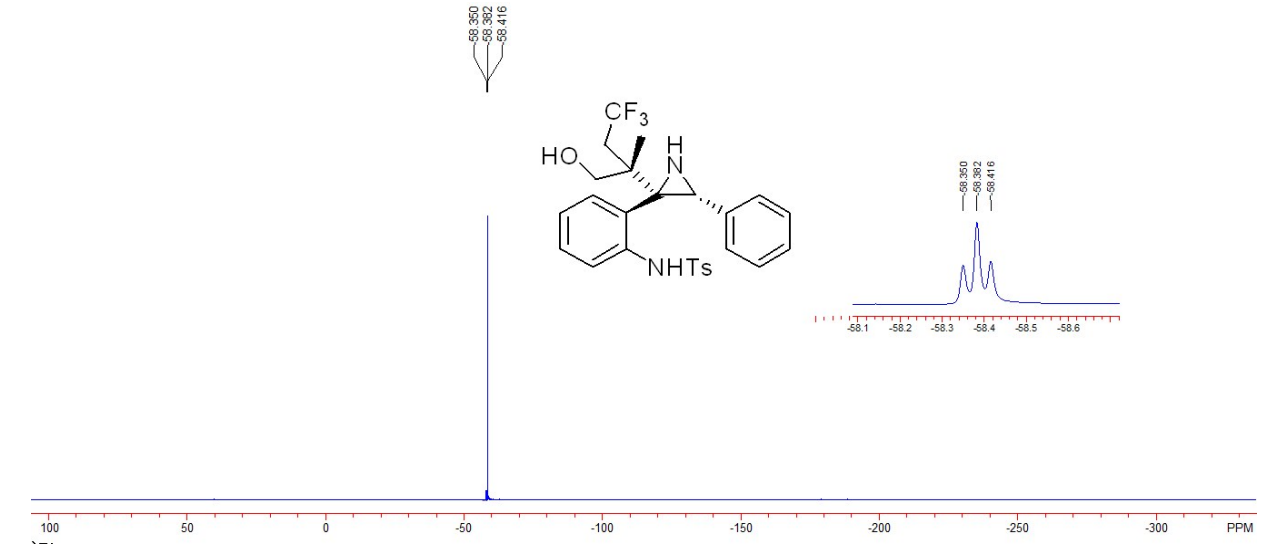


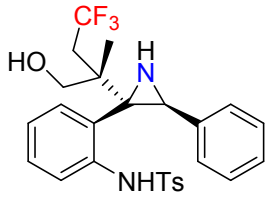
Compound 10ba: 47 mg, 47%, A white solid, m.p. 185-187 ^{o}C; IR (EtOH): ν 2954, 2923, 2887, 1497, 1258, 1155, 1108, 1090, 1062, 933, 758, 660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.01 (s, 3H), 1.50 (d, 1H, J = 10.0 Hz), 1.63-1.76 (m, 1H), 2.11-2.23 (m, 1H), 2.34 (s, 3H), 3.10 (d, 1H, J = 11.6 Hz), 3.18 (d, 1H, J = 10.0 Hz), 3.47 (d, 1H, J = 11.6 Hz), 3.48 (s, 1H), 7.01 (t, 1H, J = 7.6 Hz), 7.17-7.21 (m, 3H), 7.28 (d, 2H, J = 7.6 Hz), 7.35 (t, 2H, J = 7.2 Hz), 7.46 (d, 1H, J = 8.4 Hz), 7.79 (d, 2H, J = 6.4 Hz), 7.86-7.90 (m, 2H), 10.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 20.0, 21.5, 35.8 (q, $J_{C\text{-}F}$ = 26.0 Hz), 41.9, 46.0, 49.7, 65.4, 117.4, 122.9, 127.1 (q, $J_{C\text{-}F}$ = 277.4 Hz), 127.2, 127.3, 128.3, 128.7, 129.7, 131.2, 132.5, 136.98, 137.04, 137.1, 143.9; ^{19}F NMR (376 MHz,

$CDCl_3$, $CFCl_3$): δ -58.4 (t, 3F, J = 12.4 Hz); MS (ESI) *m/z*: 505.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{26}H_{28}F_3N_2O_3S^+$ requires: 505.1767, Found: 505.1762.

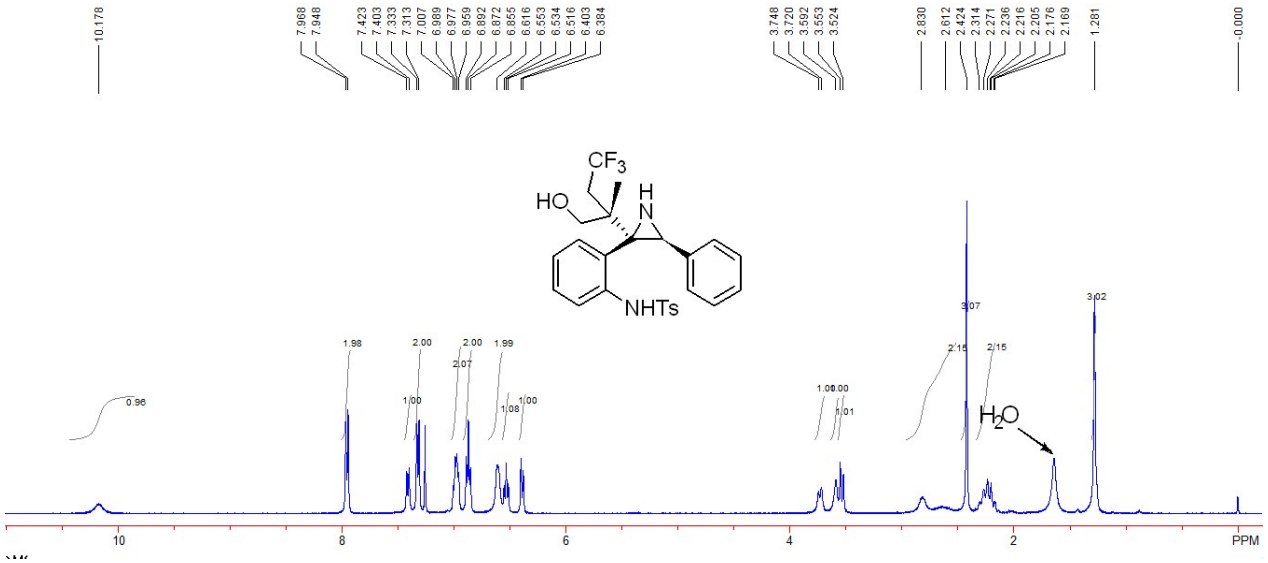


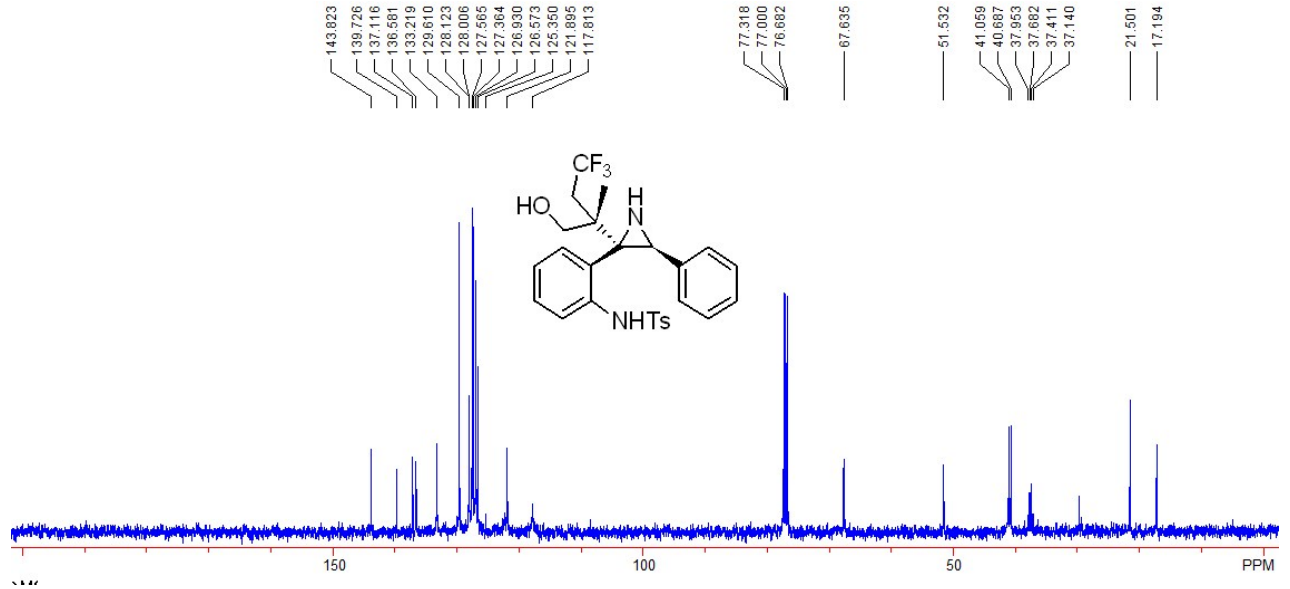






Compound 11ba: 47 mg, 47%, A white solid, m.p. 187-189 ^{o}C; IR (EtOH): ν 2929, 2851, 1497, 1441, 1328, 1257, 1156, 1075, 1021, 812, 746, 699, 658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.28 (s, 3H), 2.17-2.31 (m, 2H), 2.42 (s, 3H), 2.61 (s, 1H), 2.83 (s, 1H), 3.54 (d, 1H, J = 11.2 Hz), 3.59 (s, 1H), 3.74 (d, 1H, J = 11.2 Hz), 6.39 (d, 1H, J = 7.2 Hz), 6.53 (t, 1H, J = 7.2 Hz), 6.62 (brs, 2H), 6.86-6.89 (m, 2H), 6.98-7.01 (m, 2H), 7.32 (d, 2H, J = 8.0 Hz), 7.41 (d, 1H, J = 8.0 Hz), 7.96 (d, 2H, J = 8.0 Hz), 10.18 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 17.2, 21.5, 37.5 (q, $J_{C\text{-}F}$ = 27.1 Hz), 40.7, 41.1, 51.5, 67.6, 117.8, 121.9, 126.6, 126.7 (q, $J_{C\text{-}F}$ = 277.3 Hz), 126.9, 127.4, 127.6, 128.0, 129.6, 133.2, 136.6, 137.1, 139.7, 143.8; ^{19}F NMR (376 MHz, $CDCl_3$, $CFCl_3$): δ -57.7 (t, 3F, J = 11.3 Hz); MS (ESI) *m/z*: 505.2 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{26}H_{28}F_3N_2O_3S^{+}$ requires: 505.1767, Found: 505.1762.

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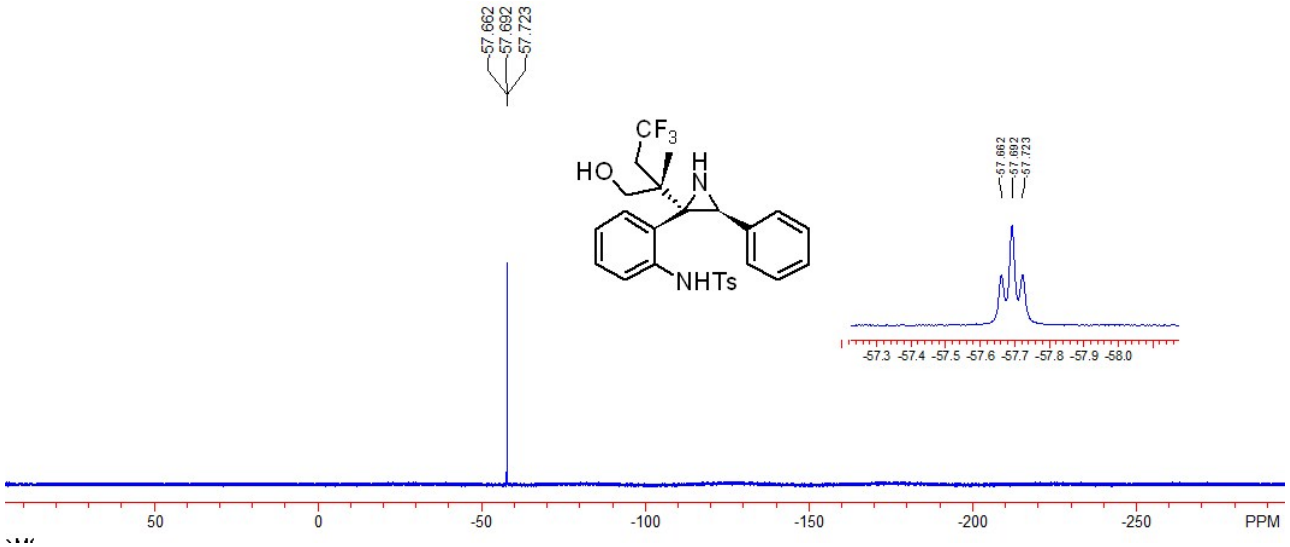
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57.692
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CF3
HO
H
N
NHTs
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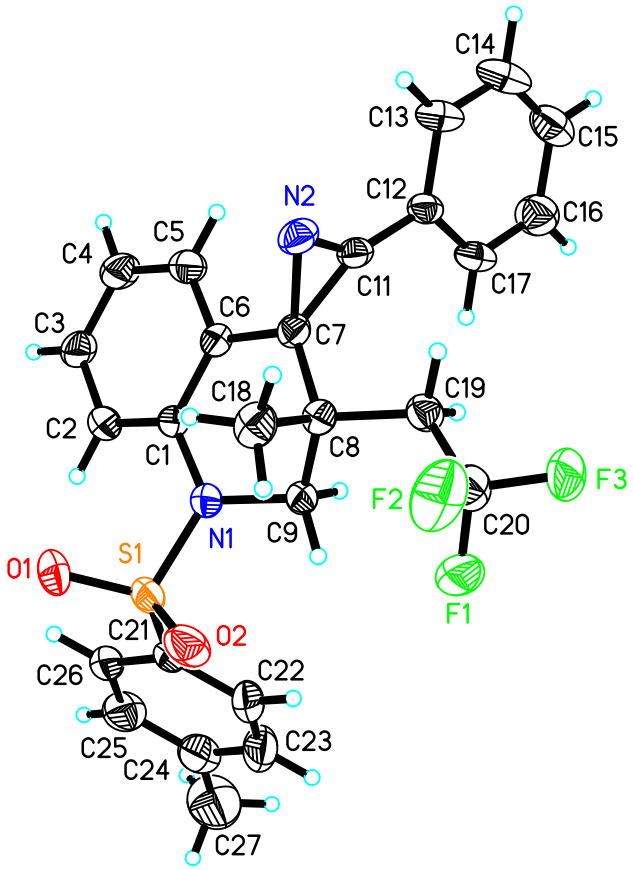
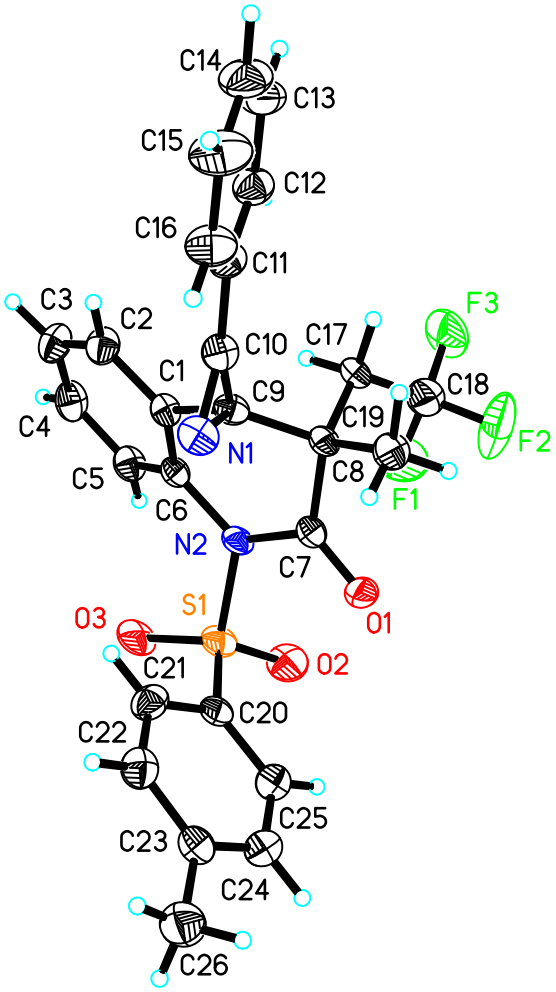
-100
-150
-200
-250
PPM

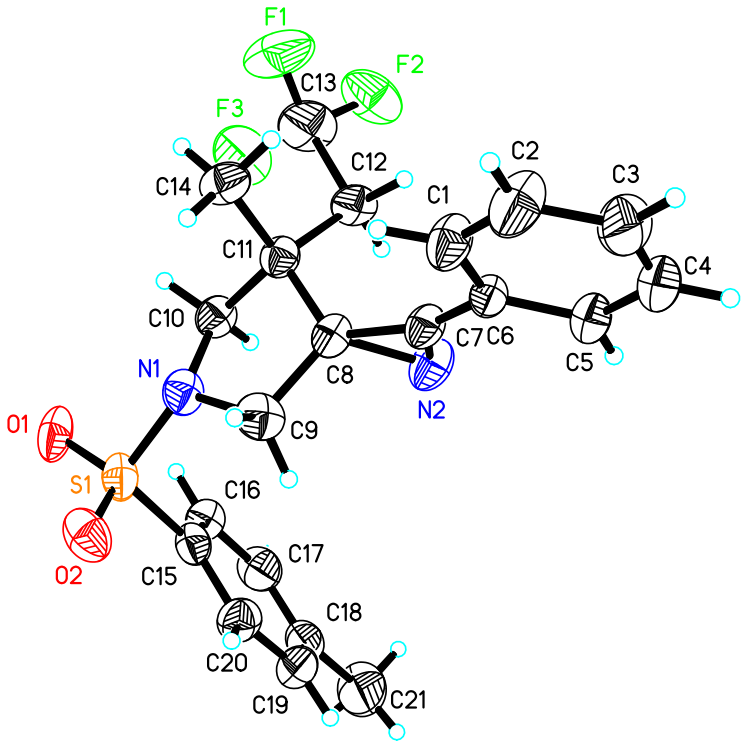
The crystal data of 2aa, 2ba, 5, 7aa, 8bf, 9ba, 10ba and 11ba



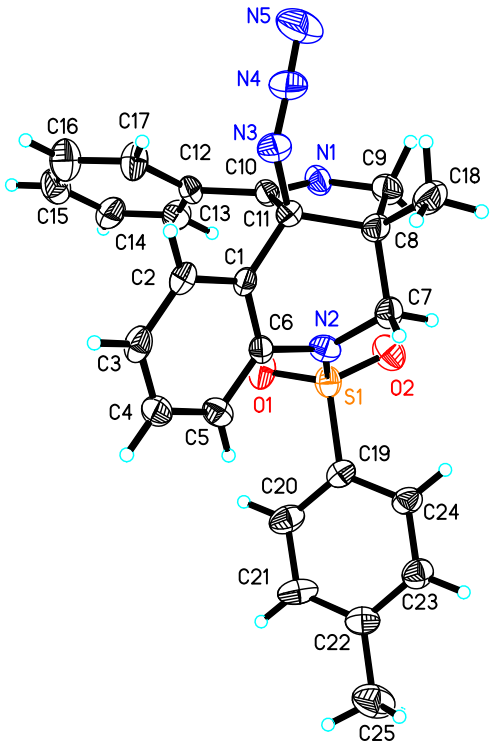
The crystal data of **2aa** have been deposited in CCDC with number 1494648. Empirical Formula: $C_{26}H_{23}F_3N_2O_2S$; Formula Weight: 484.52; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.100 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 12.394(3)Å, b = 26.081(7)Å, c = 8.658(3)Å, α = 90°, β = 122.750(5)°, γ = 90°, V = 2353.8(11)$Å^3$; Space group: C c; Z = 4; D_{calc}= 1.367 g/cm^3; F_{000} = 1008; Final R indices [I>2sigma(I)] R1 = 0.0455, wR2 = 0.1010.



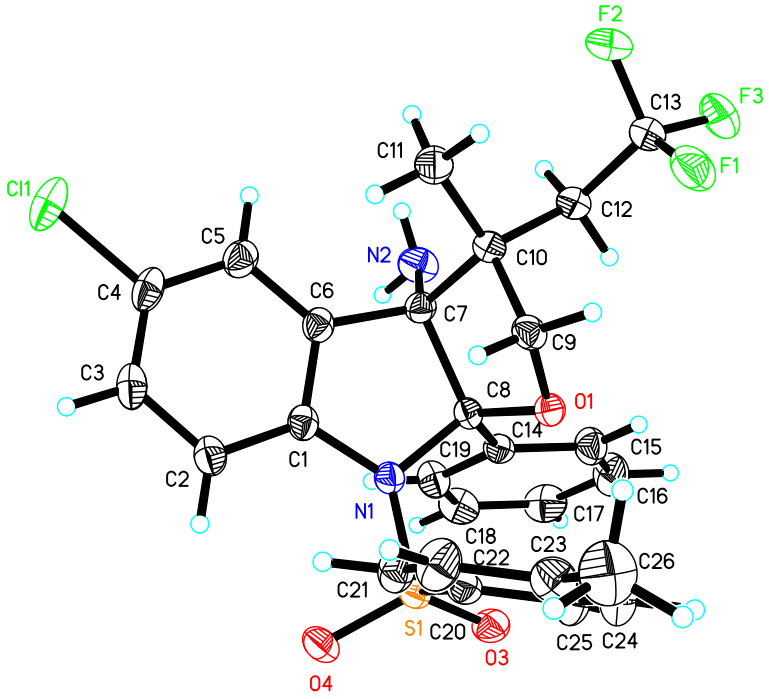
The crystal data of **2ba** have been deposited in CCDC with number 1535602. Empirical Formula: $C_{26}H_{21}F_3N_2O_3S$; Formula Weight: 498.51; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.170 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 8.8511(15)Å, b = 17.643(3)Å, c = 15.334(3)Å, α = 90°, β = 93.701(4)°, γ = 90°, V = 2389.5(7) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.386 g/cm^3; F_{000} = 1032; Final R indices [I>2sigma(I)] R1 = 0.0594, wR2 = 0.1263.



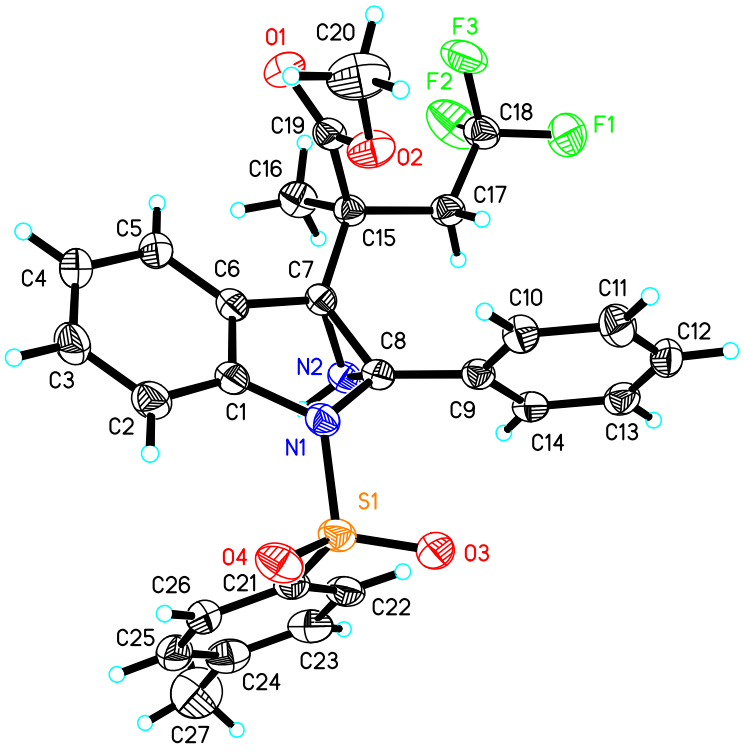
The crystal data of **5** have been deposited in CCDC with number 1501511. Empirical Formula: $C_{21}H_{21}F_3N_2O_2S$; Formula Weight: 422.46; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.110 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 10.439(4)Å, b = 10.668(4)Å, c = 11.232(4)Å, α = 72.878(8)°, β = 74.118(8)°, γ = 65.951(7)°, V = 1074.5(7) $Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.306 g/cm^3; F_{000} = 440; Final R indices [I>2sigma(I)] R1 = 0.0707, wR2 = 0.2067.



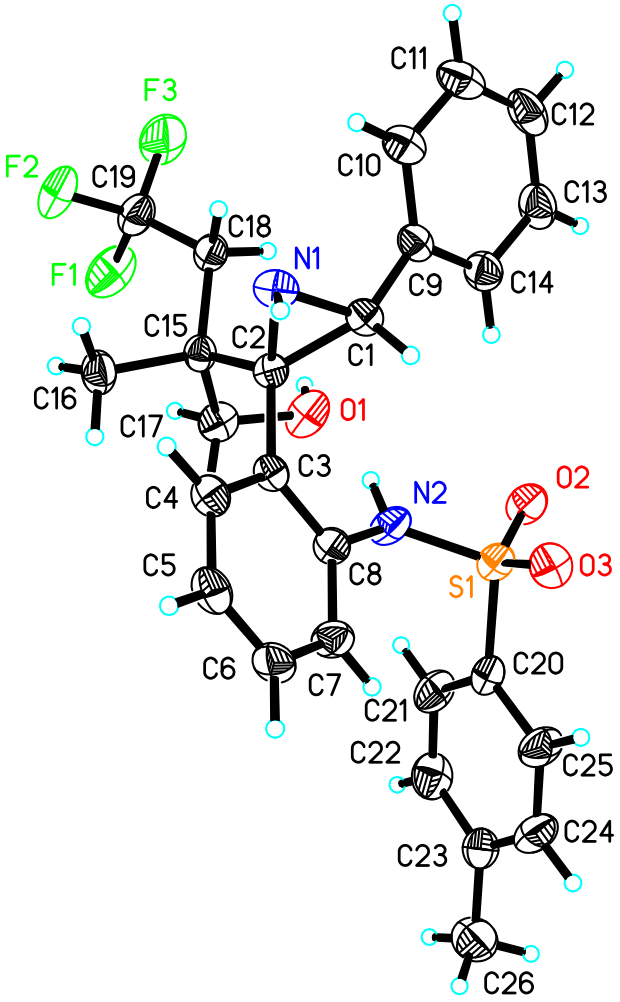
The crystal data of **7aa** have been deposited in CCDC with number 1535603. Empirical Formula: C25H23N5O2S; Formula Weight: 457.54; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.180 x 0.120 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 13.9067(15)Å, b = 18.439(2)Å, c = 8.8970(10)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 2281.4(4) $Å^3$; Space group: P n a 21; Z = 4; D_{calc} = 1.332 g/cm^3; F_{000} = 960; Final R indices [I>2sigma(I)] R1 = 0.0445, wR2 = 0.0981.



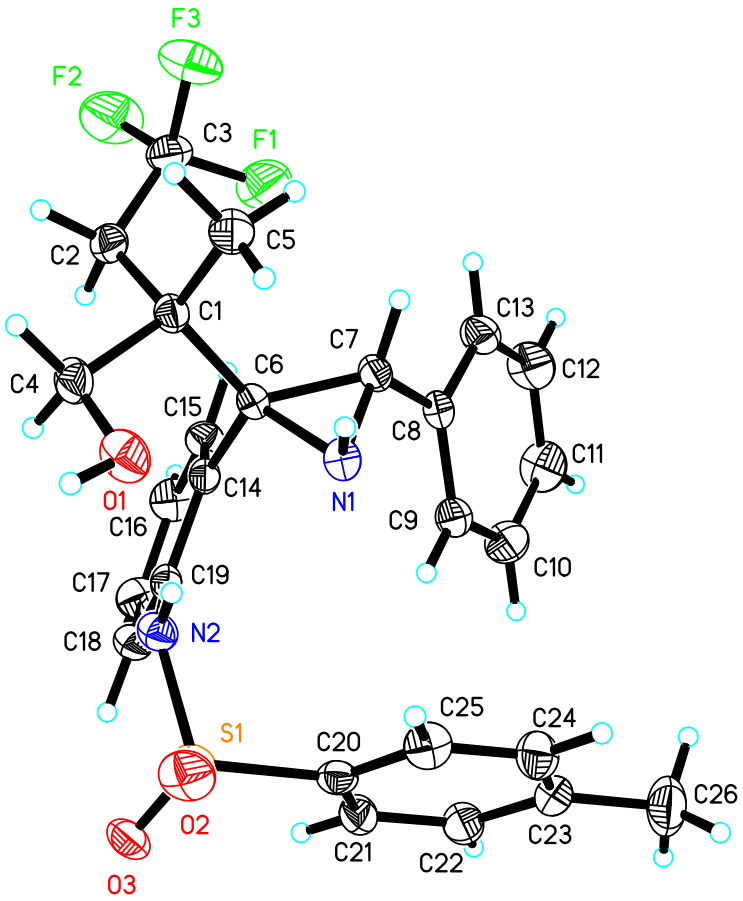
The crystal data of **8bf** have been deposited in CCDC with number 1549550. Empirical Formula: $C_{26}H_{24}ClF_3N_2O_3S$; Formula Weight: 536.98; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.170 x 0.130 mm^3; Crystal System: Triclinic; Lattice Parameters: a = 10.4716(15)Å, b = 10.9609(17)Å, c = 11.0858(17)Å, α = 80.892(3)°, β = 71.645(3)°, γ = 82.468(3)°, V = 1188.0(3) $Å^3$; Space group: P -1; Z = 2; D_{calc} = 1.501 g/cm^3; F_{000} = 556; Final R indices [I>2sigma(I)] R1 = 0.0477, wR2 = 0.1164.



The crystal data of **9ba** have been deposited in CCDC with number 1553802. Empirical Formula: $C_{27}H_{25}F_3N_2O_4S$; Formula Weight: 530.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.1898(16) Å, b = 21.424(3) Å, c = 11.0005(16) Å, $\alpha = 90^o$, $\beta = 105.012(3)^o$, $\gamma = 90^o$, V = 2547.2(6) $Å^3$; Space group: P 21/c; Z = 4; D_{calc} = 1.383 g/cm^3; F_{000} = 1104; Final R indices [I>2sigma(I)] R1 = 0.0492, wR2 = 0.1222.



The crystal data of **10ba** have been deposited in CCDC with number 1552058. Empirical Formula: $C_{26}H_{27}F_3N_2O_3S$; Formula Weight: 504.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.200 x 0.160 x 0.120 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 11.6099(13) Å, b = 10.1840(11) Å, c = 20.888(2) Å, α = 90°, β = 95.677(2)°, γ = 90°, V = 2457.6(5) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.364 g/cm^3; F_{000} = 1056; Final R indices [I>2sigma(I)] R1 = 0.0467, wR2 = 0.1187.



The crystal data of **11ba** have been deposited in CCDC with number 1554196. Empirical Formula: $C_{26}H_{27}F_3N_2O_3S$; Formula Weight: 504.55; Crystal Color, Habit: colorless, Crystal Dimensions: 0.220 x 0.170 x 0.130 mm^3; Crystal System: Monoclinic; Lattice Parameters: a = 13.7278(17) Å, b = 14.2768(18) Å, c = 14.0025(18) Å, $\alpha = 90^o$, $\beta = 118.039(3)^o$, $\gamma = 90^o$, V = 2422.2(5) $Å^3$; Space group: P 21/n; Z = 4; D_{calc} = 1.384 g/cm^3; F_{000} = 1056; Final R indices [I>2sigma(I)] R1 = 0.0585, wR2 = 0.1315.

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