Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Fast, highly enantioselective and sustainable fluorination of 4-substituted pyrazolones catalyzed by hybrid amide-based phase transfer catalysts

Yakun Wang,*[a] Shuaifei Wang,[a]Yufeng Wu,[b] Ting Zhao,[c] Jie Liu,[a] Junlin Zheng,[a] Lin Wang,[a] Jieli Lv[a] and Tao Zhang *[a]

[a]School of Pharmacy, Xinxiang Medical University, Xinxiang, Henan 453003, P.R. China. E-mail: 161072@xxmu.edu.cn. zhangtao126@163.com. Fax: (+86)-0373-3029879.

[b] School of Chemical Engineering, Dalian University of Technology, Dalian, Liaoning 116024, P.R. China.

[c] School of Pharmacy, Shenyang Pharmaceutical University, Shenyang, Liaoning 117004, P.R. China.

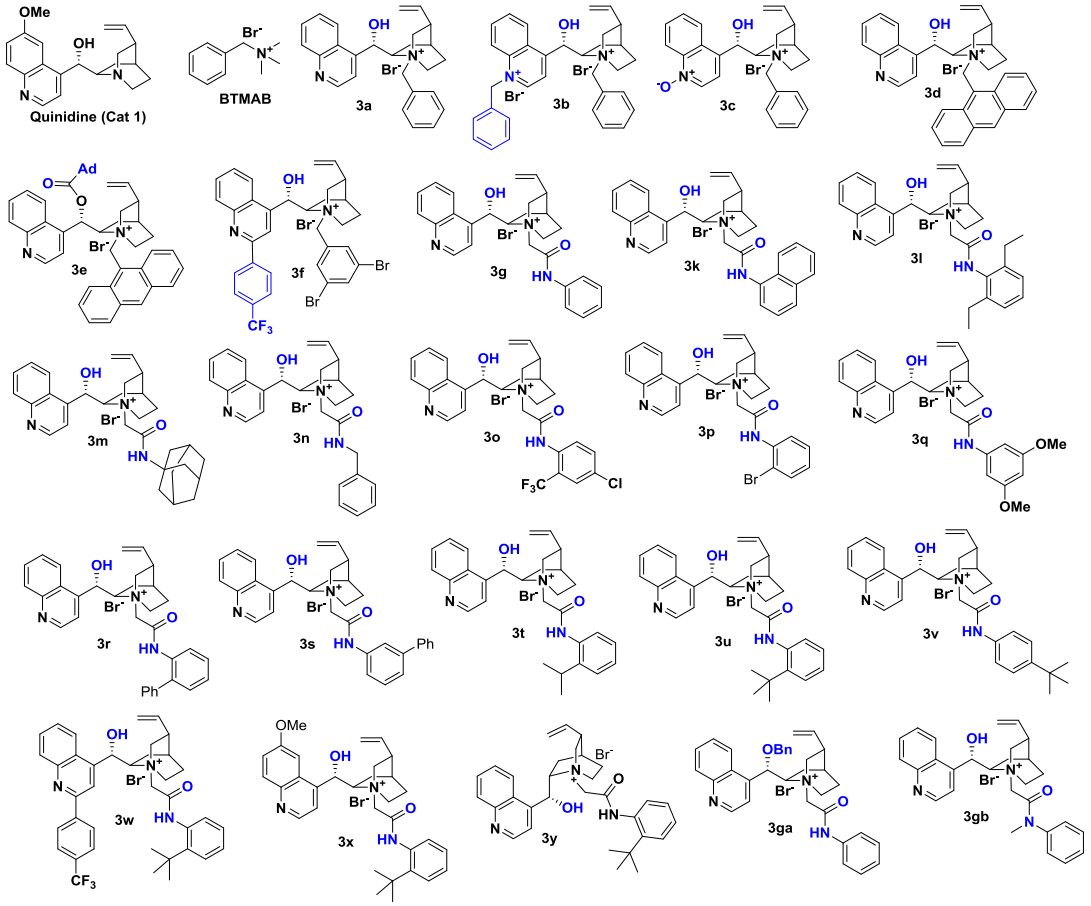
1. General Information:

Unless otherwise stated, all commercial reagents and solvents were used without further additional purification. Analytical TLC was visualized with UV light at 254 nm. Thin layer chromatography was carried out on TLC aluminum sheets with silica gel 60 F_{254}. Purification of reaction products was carried out with chromatography on silica gel 60 (200-300 mesh). ^{1}H NMR (400 MHz) spectra was obtained at 25 ℃; ^{13}C NMR (126 MHz) and ^{19}F NMR (376 MHz) were recorded on a VARIAN INOVA-400M and AVANCE II 400 spectrometer at 25 ℃. Chemical shifts are reported as δ (ppm) values relative to TMS as internal standard and coupling constants (J) in Hz. The enantiomeric excesses (*ee*) were determined by HPLC. HPLC analyses were performed on equipped with Diacel Chiralpak AD-H, AS or OJ-H chiral column (0.46 cm × 25 cm), using mixtures of *n*-hexane/isopropyl alcohol as mobile phase, at 25 ℃. Mass spectra are reported by using electron ionization and electrospray ionization techniques. Melting points were determined with a hot plate apparatus. Optical rotations were measured on a digital polarimeter with a sodium lamp at 25 ^{o}C.

1.1 4-Sustitued pyrazolones

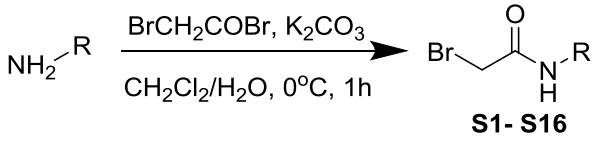
4-Sustitued pyrazolones **1a**-**1ai** were prepared from acetophenone and *β*-keto esters according to the literature: (*Adv. Synth. Catal.*, **2010**, *352*, 827; *Angew. Chem., Int. Ed.*, **2011**, *50*, 4928. *Adv. Synth. Catal.*, **2016**, *358*, 3971.)

1.2 Phase transfer catalysts



Quinidine (**Cat 1**), BTMAB were purchased from **Innochem**. Phase transfer catalysts **3b-3f** were easily prepared according to the previous papers (*Angew. Chem. Int. Ed.*, 2014, **126**, 8375; *J. Org.Chem.* **2016**, *81*, 7042; *Green Chem.*, 2016, **18**, 5493).

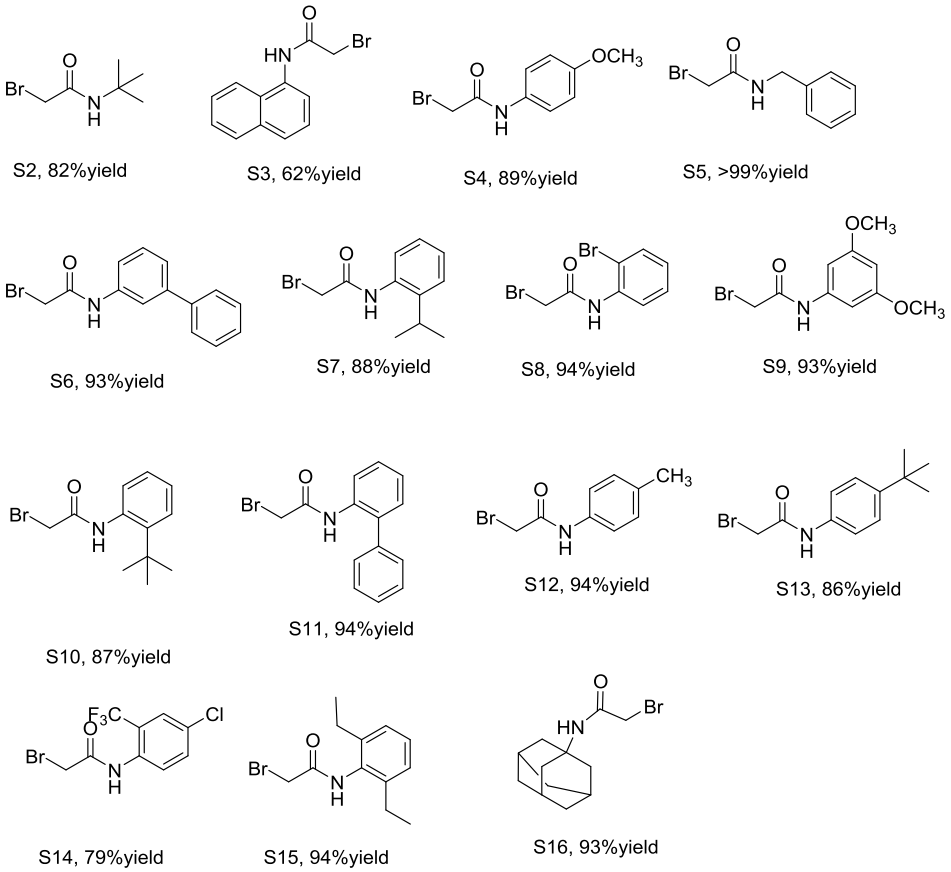
Synthesis of α-bromoamides S1-S16



α-bromoamides **S1-S16** were prepared according to the previous papers (*Org. Lett.* **2019**, *21*, 8085; *Org. Lett.* **2020**, *22*, 8687).

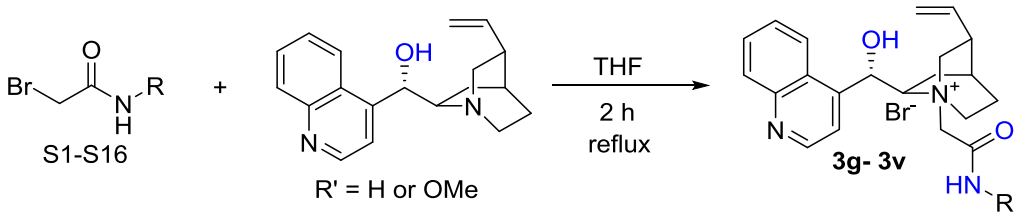
To the solution of corresponding amine (5 mmol) in DCM (10 mL) the aqueous (20 mL) solution of K_2CO_3 (1.1 g, 7.5 mmol) was added. Subsequently the mixture was cooled to 0 ^{0}C and the solution of bromoacetyl bromide (0.6 mL, 7.5 mmol) in DCM (3 mL) was added dropwise. The reaction was controlled using TLC for about 1h. Then the phases were separated and the aqueous phase was extracted with DCM (3 x 15 mL). The combined

organic phases were dried over anhydrous Na_2SO_4 and then evaporated under *vacuum.* **S1-S16** were prepared according to the procedure without further purification.

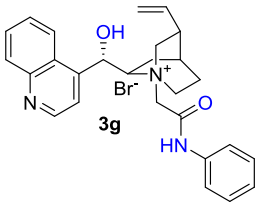


Synthesis of hybrid amide-based PTC 3g – 3v

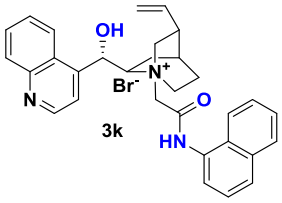
Hybrid amide-based PTC **3g – 3v** were prepared according to the previous papers (*Org. Lett.* **2019**, *21*, 8085; *Org. Lett.* **2020**, *22*, 8687).



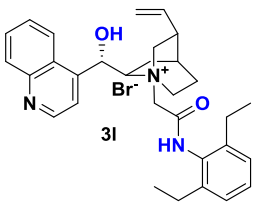
To the solution of cinchonine (1.0 g, 3.4 mmol) in THF (30 mL) the corresponding amide (3.4 mmol) was added. The mixture was refluxed for 2h and the reaction was controlled using TLC. Subsequently the solvent was evaporated under *vacuum* and the solid residue was dissolved in DCM (2 mL). The solution of crude catalyst was added dropwise to diethyl ether (15 mL). Then the precipitate was filtered, washed with diethyl ether (10 mL) and dried. Catalysts **3g-3v** were obtained in a form of solids.



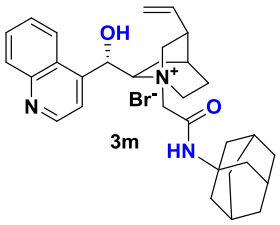
White solid (89% yield). m.p.196-198 °C; $[\alpha]_D^{25}$ +42.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.04 (d, *J* = 5.5 Hz, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 8.25 – 8.02 (m, 2H), 7.87 – 7.70 (m, 4H), 7.60 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.21 (td, *J* = 7.4, 1.2 Hz, 1H), 6.79 (dd, *J* = 15.5, 3.4 Hz, 1H), 6.21 – 5.91 (m, 2H), 5.37 – 5.13 (m, 2H), 4.80 (dd, *J* = 16.1, 12.1 Hz, 1H), 4.66 (d, *J* = 15.9 Hz, 1H), 4.51 – 4.15 (m, 3H), 3.96 – 3.83 (m, 1H), 3.76 – 3.59 (m, 1H), 2.87 (q, *J* = 8.7 Hz, 1H), 2.23 (t, *J* = 11.9 Hz, 1H), 2.02 – 1.85 (m, 3H), 1.20 – 0.98 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.22, 150.65, 148.05, 145.14, 138.24, 137.06, 130.39, 129.89, 129.62, 127.51, 125.14, 124.83, 123.60, 120.63, 120.10, 117.68, 66.01, 65.19, 59.70, 59.59, 57.60, 37.58, 26.62, 23.39, 20.59, 11.76. HRMS Calcd. For $[C_{27}H_{30}N_3O_2]^+$requires m/z 428.2333, found m/z 428.2337.



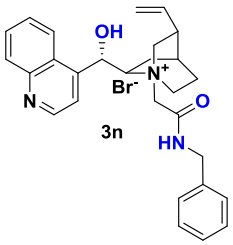
White solid (96% yield). m.p. 88-92 °C; $[\alpha]_D^{25}$ +92.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.95 (d, *J* = 5.5 Hz, 1H), 8.99 (d, *J* = 4.5 Hz, 1H), 8.32 – 8.13 (m, 2H), 8.10 – 7.69 (m, 6H), 7.68 – 7.49 (m, 3H), 7.41 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.20 (q, *J* = 6.5, 4.8 Hz, 1H), 6.05 (ddd, *J* = 17.2, 10.2, 6.7 Hz, 1H), 5.38 – 5.21 (m, 2H), 5.06 (d, *J* = 15.9 Hz, 1H), 4.84 (dd, *J* = 16.1, 12.1 Hz, 1H), 4.58 – 4.21 (m, 3H), 3.98 (t, *J* = 11.4 Hz, 1H), 3.87 – 3.70 (m, 1H), 3.65 – 3.52 (m, 2H), 2.98 – 2.82 (m, 1H), 2.24 (t, *J* = 11.9 Hz, 1H), 1.96 (d, *J* = 8.5 Hz, 3H), 1.87 – 1.68 (m, 2H), 1.06 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.26, 150.65, 148.06, 145.24, 137.11, 134.24, 132.29, 130.32, 129.86, 128.77, 128.28, 127.43, 127.05, 126.84, 126.77, 126.05, 124.87, 123.70, 123.13, 122.91, 120.62, 117.67, 67.48, 66.11, 65.42, 59.57, 57.56, 37.60, 26.64, 25.60, 23.43, 20.68, 11.77. HRMS Calcd. For $[C_{31}H_{32}N_3O_2]^+$requires m/z 478.2489, found m/z 478.2492.



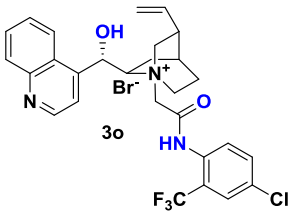
Light yellow solid (94% yield), m.p. 213-215 °C; $[\alpha]_D^{25}$ +74.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.38 (q, *J* = 4.8, 3.6 Hz, 1H), 8.99 (d, *J* = 4.5 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 8.4 Hz, 1H), 7.93 – 7.66 (m, 2H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 6.95 (dd, *J* = 16.5, 3.9 Hz, 1H), 6.20 – 5.95 (m, 2H), 5.29 (dd, *J* = 14.1, 3.3 Hz, 2H), 5.04 (s, 1H), 4.76 (d, *J* = 15.6 Hz, 1H), 4.52 – 4.31 (m, 2H), 4.16 (t, *J* = 11.5 Hz, 1H), 3.97 (t, *J* = 11.7 Hz, 1H), 3.78 (q, *J* = 15.5, 12.4 Hz, 1H), 2.86 (q, *J* = 8.9 Hz, 1H), 2.66 – 2.44 (m, 6H), 2.13 (q, *J* = 11.8 Hz, 1H), 2.01 – 1.88 (m, 4H), 1.31 – 0.81 (m, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.18, 150.65, 148.07, 145.27, 141.72, 137.01, 132.51, 130.28, 129.89, 128.42, 127.50, 126.67, 124.88, 123.92, 120.55, 117.66, 66.21, 65.28, 59.59, 58.86, 57.01, 37.60, 26.65, 24.81, 23.38, 20.80, 15.19, 11.73. HRMS Calcd. For $[C_{31}H_{38}N_3O_2]^+$requires m/z 484.2959, found m/z 484.2956.



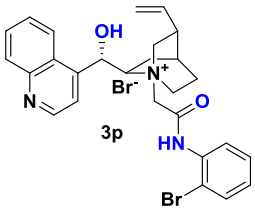
White solid (88% yield). m.p. 196-198 °C; $[\alpha]_D^{25}$ +69.4 (*c* 0.20, $CHCl_3$);^{1}H NMR (400 MHz, DMSO-d_6) δ 8.97 (d, *J* = 4.5 Hz, 1H), 8.47 (d, *J* = 7.4 Hz, 1H), 8.25 (d, *J* = 8.4 Hz, 1H), 8.09 (d, *J* = 8.3 Hz, 1H), 7.90 – 7.73 (m, 2H), 7.71 – 7.55 (m, 1H), 6.78 (dd, *J* = 16.1, 3.7 Hz, 1H), 6.08 – 5.88 (m, 2H), 5.34 – 5.09 (m, 2H), 4.57 (d, *J* = 15.9 Hz, 1H), 4.45 – 4.19 (m, 4H), 3.84 (t, *J* = 11.3 Hz, 1H), 3.69 – 3.52 (m, 1H), 2.81 (q, *J* = 8.8 Hz, 1H), 2.07 (q, *J* = 11.3, 8.1 Hz, 10H), 1.89 (q, *J* = 9.4, 7.6 Hz, 3H), 1.67 (s, 6H), 1.03 – 0.93 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.79, 150.67, 148.04, 145.25, 137.02, 130.30, 129.96, 127.48, 124.83, 123.89, 120.53, 117.60, 66.07, 64.64, 59.48, 59.02, 57.23, 52.69, 49.05, 37.55, 36.33, 29.26, 26.66, 23.36, 20.67, 11.74. HRMS Calcd. For $[C_{31}H_{40}N_3O_2]^+$requires m/z 486.3115, found m/z 486.3116.



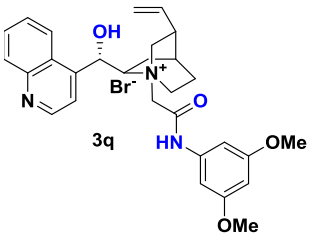
White solid (93% yield). m.p. 190-192 °C; $[\alpha]_D^{25}$ +88.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.44 (t, *J* = 5.8 Hz, 1H), 8.97 (d, *J* = 4.5 Hz, 1H), 8.23 – 8.03 (m, 2H), 7.86 – 7.69 (m, 2H), 7.66 – 7.58 (m, 1H), 7.46 – 7.18 (m, 6H), 6.79 (dd, *J* = 15.4, 3.6 Hz, 1H), 6.07 – 5.90 (m, 2H), 5.34 – 5.16 (m, 2H), 4.64 (d, *J* = 15.9 Hz, 1H), 4.55 – 4.44 (m, 3H), 4.40 – 4.20 (m, 3H), 3.95 – 3.79 (m, 1H), 3.71 – 3.58 (m, 1H), 2.83 (q, *J* = 8.9 Hz, 1H), 2.16 (t, *J* = 11.9 Hz, 1H), 1.91 (q, *J* = 8.7, 7.1 Hz, 3H), 1.04 – 0.82 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.49, 150.58, 148.04, 145.20, 138.57, 137.06, 130.28, 129.84, 128.95, 128.05, 127.70, 127.65, 127.58, 124.84, 123.65, 120.51, 117.61, 66.04, 65.12, 59.59, 59.01, 57.38, 42.94, 37.55, 26.62, 23.37, 20.63, 11.74. HRMS Calcd. For $[C_{28}H_{32}N_3O_2]^+$requires m/z 442.2489, found m/z 442.2485.



Light yellow solid (87% yield), m.p.133-136 °C; $[\alpha]_D^{25}$ +50.0 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.82 (s, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 8.12 (dd, *J* = 27.2, 8.5 Hz, 2H), 8.01 – 7.89 (m, 2H), 7.86 – 7.67 (m, 3H), 7.53 (t, *J* = 7.7 Hz, 1H), 6.86 (dd, *J* = 15.7, 3.4 Hz, 1H), 6.18 – 5.86 (m, 2H), 5.38 – 5.12 (m, 2H), 4.90 (d, *J* = 16.0 Hz, 1H), 4.80 – 4.59 (m, 1H), 4.53 – 4.07 (m, 3H), 3.98 – 3.64(m, 2H), 2.86 (q, *J* = 8.8 Hz, 1H), 2.16 (q, *J* = 11.9 Hz, 1H), 1.93 (d, *J* = 8.4 Hz, 3H), 1.07 – 0.92 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.02, 150.62, 148.07, 145.18, 137.02, 133.95, 132.93 (t, *J* = 9.2 Hz), 130.30, 129.91, 128.19 – 126.33 (m), 124.87, 124.34, 123.75, 121.61, 120.57, 117.67, 66.12, 65.35, 59.60, 59.06, 57.32, 37.56, 26.58, 23.34, 20.71, 11.74. ^{19}F NMR (376 MHz, DMSO-d_6) δ -59.52 (s, 3F). HRMS Calcd. For $[C_{28}H_{28}ClF_3N_3O_2]^+$requires m/z 530.1817, found m/z 530.1814.

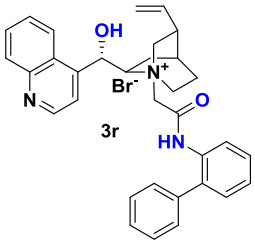


White solid (97% yield). m.p. 172-174 °C; $[\alpha]_D^{25}$ +35.6 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.67 (s, 1H), 8.99 (d, *J* = 4.5 Hz, 1H), 8.27 – 8.05 (m, 2H), 7.85 – 7.65 (m, 4H), 7.57 – 7.41 (m, 2H), 7.31 (td, *J* = 7.7, 1.7 Hz, 1H), 6.87 (d, *J* = 3.2 Hz, 1H), 6.17 (t, *J* = 3.2 Hz, 1H), 6.02 (ddd, *J* = 17.2, 10.1, 6.8 Hz, 1H), 5.38 – 5.15 (m, 2H), 4.88 (d, *J* = 16.0 Hz, 1H), 4.67 (dd, *J* = 16.1, 12.0 Hz, 1H), 4.41 (t, *J* = 10.5 Hz, 1H), 4.28 (t, *J* = 9.6 Hz, 2H), 3.92 (t, *J* = 11.4 Hz, 1H), 3.80 – 3.65 (m, 1H), 2.86 (q, *J* = 8.7 Hz, 1H), 2.33 – 2.14 (m, 1H), 1.95 (s, 3H), 1.10 – 0.94 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.93, 150.63, 148.08, 145.21, 137.05, 135.12, 133.47, 130.32, 129.90, 129.12, 128.85, 128.61, 127.35, 124.87, 123.85, 120.59, 119.64, 117.67, 66.18, 65.34, 60.23, 59.67, 59.27, 57.56, 37.57, 26.60, 23.39, 20.68, 14.57, 11.75. HRMS Calcd. For $[C_{27}H_{29}BrN_3O_2]^+$requires m/z 506.1438, found m/z 506.1442.



White solid (89% yield), m.p.129-131 °C; $[\alpha]_D^{25}$ +66.4 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (d, *J* = 3.6 Hz, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 8.24 (dt, *J* = 8.8, 2.2 Hz, 1H), 8.09 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.81 (ddd, *J* = 9.5, 5.7, 1.7 Hz, 2H), 7.57 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.05 (d, *J* = 2.2 Hz, 2H), 6.80 (dd, *J* = 15.9, 3.6 Hz, 1H), 6.37 (t, *J* = 2.2 Hz, 1H), 6.17 – 5.92

(m, 2H), 5.77 (s, 1H), 5.28 (dd, *J* = 14.9, 3.1 Hz, 2H), 4.95 – 4.80 (m, 1H), 4.69 (d, *J* = 15.9 Hz, 1H), 4.44 – 4.21 (m, 3H), 4.00 – 3.87 (m, 1H), 3.78 (s, 8H), 3.38 (s, 2H), 2.86 (q, *J* = 8.8 Hz, 1H), 2.51 (p, *J* = 1.8 Hz, 1H), 2.22 (t, *J* = 11.9 Hz, 1H), 2.04 – 1.87 (m, 3H), 1.16 – 0.96 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.32, 161.12, 150.66, 148.06, 145.17, 139.90, 137.05, 130.38, 129.90, 127.40, 124.83, 123.72, 120.63, 117.65, 98.43, 96.92, 65.91, 65.35, 59.63, 59.56, 57.54, 55.76, 55.42, 37.56, 26.60, 23.39, 20.63, 11.75. HRMS Calcd. For $[C_{29}H_{34}N_3O_4]^+$requires m/z 488.2544, found m/z 488.2549.



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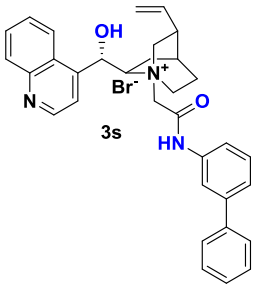
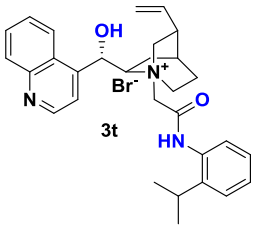
White solid (91% yield), m.p. 172-174 °C; $[\alpha]_D^{25}$ +35.6 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.45 (d, *J* = 6.3 Hz, 1H), 8.97 (d, *J* = 4.5 Hz, 1H), 8.25 – 7.97 (m, 2H), 7.88 – 7.71 (m, 2H), 7.65 – 7.35 (m, 9H), 7.32 – 7.23 (m, 1H), 6.74 (dd, *J* = 15.0, 3.2 Hz, 1H), 6.04 – 5.70 (m, 2H), 5.31 – 4.96 (m, 2H), 4.68 (d, *J* = 15.6 Hz, 1H), 4.44 – 4.07 (m, 3H), 3.93 – 3.70 (m, 2H), 3.54 – 3.40 (m, 1H), 2.77 (q, *J* = 8.8 Hz, 1H), 2.10 (q, *J* = 12.1 Hz, 1H), 1.97 – 1.71 (m, 3H), 0.96 – 0.78 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.59, 150.60, 148.06, 145.18, 139.14, 138.26, 137.01, 133.52, 131.08, 130.28, 129.89, 129.19, 128.99, 128.61, 127.93, 127.80, 127.77, 127.54, 124.87, 123.90, 120.48, 117.63, 66.18, 65.42, 59.41, 57.24, 37.55, 26.53, 23.35, 20.69, 11.72. HRMS Calcd. For $[C_{33}H_{34}N_3O_2]^+$requires m/z 504.2646, found m/z 504.2651.



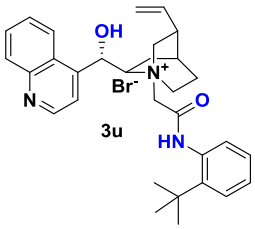
3s

White solid (92% yield), m.p.145-148 °C; $[\alpha]_D^{25}$ +76.4 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.34 (s, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 8.31 (dd, *J* = 8.6, 3.3 Hz, 1H), 8.22 (d, *J* = 2.0 Hz, 1H), 8.08 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.86 – 7.73 (m, 3H), 7.71 – 7.64 (m, 2H), 7.59 – 7.48 (m, 5H), 7.46 – 7.37 (m, 1H), 6.81 (dd, *J* = 15.9, 3.7 Hz, 1H), 6.17 (q, *J* = 5.8, 4.4 Hz, 1H), 6.02 (dd, *J* = 17.3, 10.2 Hz, 1H), 5.33 – 5.20 (m, 2H), 5.00 (d, *J* = 15.8 Hz, 1H), 4.78 (d, *J* = 15.6 Hz, 1H), 4.54 – 4.19 (m, 3H), 4.08 – 3.98 (m, 1H), 3.83 – 3.65 (m, 1H), 2.87 (d, *J* = 8.4 Hz, 1H), 2.29 – 2.14 (m, 1H), 1.92 (d, *J* = 12.0 Hz, 3H), 1.10 – 0.97 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.79, 163.37, 150.67, 148.07, 145.22, 141.47, 140.27, 138.87, 137.04, 130.36, 130.21, 129.83, 129.56, 128.30, 127.43, 127.09, 124.85, 123.83, 123.43, 120.64, 119.15, 118.50, 117.65, 65.88, 65.54, 60.24, 59.71, 59.43, 57.55, 37.57, 26.62, 23.43, 21.25, 20.69, 14.56, 11.75. HRMS Calcd. For $[C_{33}H_{34}N_3O_2]^+$requires m/z 504.2646, found m/z 504.2648.



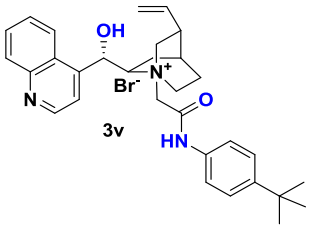
3t

White solid (89% yield), m.p. 216-219 °C; $[\alpha]_D^{25}$ +64.5 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 10.41 (s, 1H), 8.99 (d, *J* = 4.5 Hz, 1H), 8.27 – 8.03 (m, 2H), 7.88 – 7.74 (m, 2H), 7.51 (ddd, *J* = 8.4, 6.8, 1.3 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 2H), 7.31 (dtd, *J* = 21.0, 7.4, 1.6 Hz, 2H), 6.88 (d, *J* = 3.4 Hz, 1H), 6.15 – 5.95 (m, 2H), 5.45 – 5.12 (m, 2H), 5.00 – 4.61 (m, 2H), 4.48 – 4.21 (m, 3H), 3.91 – 3.68 (m, 2H), 3.31 – 3.13 (m, 1H), 2.87 (q, *J* = 8.8 Hz, 1H), 2.17 (q, *J* = 12.3 Hz, 1H), 1.93 (d, *J* = 13.1 Hz, 3H), 1.16 (dd, *J* = 21.0, 6.8 Hz, 6H), 1.04 (dt, *J* = 15.4, 9.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.15, 150.65, 148.07, 145.23, 144.06, 137.08, 133.38, 130.34, 129.91, 127.82, 127.51, 127.47, 126.51, 124.88, 123.76, 120.57, 117.67, 66.21, 65.21, 59.67, 59.26, 57.42, 37.59, 27.74, 26.64, 23.97, 23.84, 23.39, 20.69, 11.75. HRMS Calcd. For $[C_{30}H_{36}N_3O_2]^+$requires m/z 470.2802, found m/z 470.2804.



3u

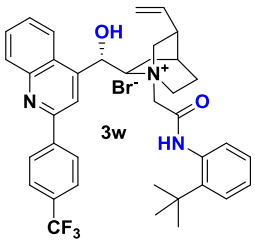
White solid (95% yield), m.p.179-182 °C; $[\alpha]_D^{25}$ +21.5 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 10.34 (d, *J* = 6.3 Hz, 1H), 8.99 (d, *J* = 4.5 Hz, 1H), 8.32 – 8.19 (m, 1H), 8.09 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.86 – 7.73 (m, 2H), 7.62 – 7.46 (m, 2H), 7.36– 7.18 (m, 3H), 6.87 (dd, *J* = 16.1, 3.6 Hz, 1H), 6.19 – 5.93 (m, 2H), 5.37 – 5.20 (m, 2H), 4.93 (d, *J* = 16.2 Hz, 1H), 4.69 (d, *J* = 16.3 Hz, 1H), 4.49 – 4.32 (m, 2H), 4.22 (d, *J* = 9.8 Hz, 1H), 3.95 (t, *J* = 11.4 Hz, 1H), 3.85 – 3.66 (m, 1H), 2.86 (q, *J* = 8.8 Hz, 1H), 2.23 – 2.09 (m, 1H), 1.97 – 1.82 (m, 3H), 1.39 (d, *J* = 1.5 Hz, 10H), 0.99 (d, *J* = 12.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.81, 150.65, 148.09, 147.17, 145.30, 137.05, 134.52, 131.91, 130.31, 129.92, 128.35, 127.51, 127.11, 124.93, 123.94, 120.58, 117.66, 66.29, 65.39, 65.10, 59.66, 59.28, 57.22, 37.61, 35.28, 31.45, 31.40, 26.68, 23.38, 20.76, 15.65, 11.74. HRMS Calcd. For $[C_{31}H_{38}N_3O_2]^+$requires m/z 484.2959, found m/z 484.2963.



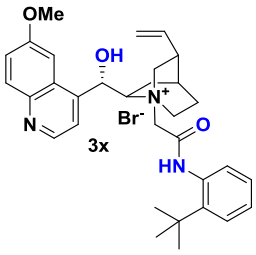
3v

White solid (86% yield), m.p. 181-183°C; $[\alpha]_D^{25}$ +46.3 (*c* 0.20, $CHCl_3$);^1H NMR (400 MHz, DMSO-d_6) δ 11.05 (d, *J* = 3.9 Hz, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 8.26 (d, *J* = 8.3 Hz, 1H), 8.09 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.88 – 7.69 (m, 4H), 7.67 – 7.53 (m, 1H), 7.46 (dd, *J* = 8.7, 1.8 Hz, 2H), 6.80 (dd, *J* = 16.0, 3.6 Hz, 1H), 6.18 – 5.90 (m, 2H), 5.28 (ddd, *J* = 14.6, 3.1, 1.4 Hz, 2H), 4.87 (t, *J* =

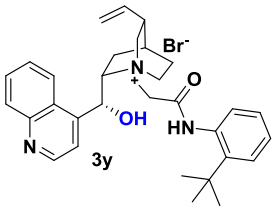
14.3 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 4.43 – 4.21 (m, 3H), 3.95 (d, *J* = 11.1 Hz, 1H), 3.73 (q, *J* = 9.3 Hz, 1H), 2.86 (q, *J* = 8.8 Hz, 1H), 2.51 (p, *J* = 1.8 Hz, 1H), 2.34 – 2.06 (m, 1H), 1.94 (t, *J* = 8.2 Hz, 3H), 1.29 (s, 9H), 1.05 (q, *J* = 8.0, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 170.79, 162.91, 150.63, 148.05, 147.51, 145.24, 145.19, 137.06, 135.70, 130.34, 129.86, 127.57, 126.16, 126.00, 124.83, 123.76, 120.67, 120.60, 119.90, 117.65, 65.91, 65.39, 60.23, 59.63, 59.47, 57.51, 37.57, 34.64, 31.62, 26.61, 23.41, 21.25, 20.65, 14.57, 11.75. HRMS Calcd. For $[C_{31}H_{38}N_3O_2]^+$requires m/z 484.2959, found m/z 484.2965.



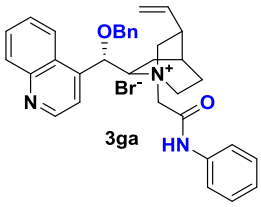
White solid (92% yield), m.p. 247-251°C; $[\alpha]_D^{25}$ +17.6 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.37 (s, 1H), 8.52 (d, *J* = 8.1 Hz, 2H), 8.40 (s, 1H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.19 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.90 – 7.79 (m, 1H), 7.65 – 7.56 (m, 1H), 7.51 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.40 – 7.24 (m, 3H), 7.01 (d, *J* = 3.5 Hz, 1H), 6.26 – 6.05 (m, 2H), 5.35 – 5.20 (m, 2H), 4.98 (d, *J* = 16.3 Hz, 1H), 4.72 (d, *J* = 16.3 Hz, 1H), 4.42 (q, *J* = 8.5 Hz, 2H), 4.27 (d, *J* = 11.8 Hz, 1H), 4.00 (t, *J* = 11.2 Hz, 1H), 3.77 (t, *J* = 10.4 Hz, 1H), 3.35 (s, 1H), 2.86 (d, *J* = 8.8 Hz, 1H), 2.30 (t, *J* = 12.0 Hz, 1H), 1.95 (d, *J* = 8.2 Hz, 3H), 1.40 (s, 9H), 1.09 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 164.82, 154.61, 148.11, 142.84, 147.12 (d, *J* = 9.1 Hz), 137.18, 134.53, 131.93, 130.69 (d, *J* = 6.3 Hz), 130.39, 130.07, 128.55, 128.36, 128.03, 127.50, 127.12, 126.64 – 126.16 (m), 126.09, 124.40, 123.98, 123.38, 66.64, 65.34, 59.68, 59.31, 57.22, 38.06, 35.29, 31.41, 26.78, 23.45, 20.70. HRMS Calcd. For $[C_{31}H_{38}N_3O_2]^+$requires m/z 484.2959, found m/z 484.2965. HRMS Calcd. For $[C_{38}H_{41}F_3N_3O_2]^+$requires m/z 628.3145, found m/z 628.3141.



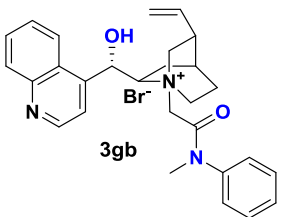
Light yellow solid (93% yield), m.p. 263-265 °C, $[\alpha]_D^{25}$ +26.5 (*c* 0.20, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.32 (s, 1H), 8.80 (d, *J* = 4.5 Hz, 1H), 7.94 (d, *J* = 9.2 Hz, 1H), 7.77 (d, *J* = 4.6 Hz, 1H), 7.54 – 7.18 (m, 6H), 6.87 (d, *J* = 3.3 Hz, 1H), 6.12 – 5.88 (m, 2H), 5.36 – 5.18 (m, 2H), 4.84 (d, *J* = 16.8 Hz, 1H), 4.72 – 4.39 (m, 3H), 4.23 (t, *J* = 11.0 Hz, 1H), 3.83 – 3.67 (m, 2H), 3.42 (s, 3H), 2.85 (q, *J* = 8.7 Hz, 1H), 2.17 – 1.81 (m, 4H), 1.37 (s, 9H), 0.91 (d, *J* = 6.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.16, 158.36, 147.72, 146.80, 144.21, 143.92, 137.02, 134.28, 131.80, 131.72, 128.23, 127.41, 126.92, 126.15, 122.78, 120.82, 117.66, 101.91, 66.59, 64.05, 60.79, 59.52, 57.31, 56.13, 37.73, 35.28, 31.44, 26.83, 23.32, 20.96, 11.75. HRMS Calcd. For $[C_{32}H_{40}N_3O_3]^+$requires m/z 514.3064, found m/z 514.3060.



White solid (88% yield), m.p.215-217 °C; $[\alpha]_D^{25}$ -11.3 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, DMSO-d_6) δ 10.39 (s, 1H), 8.98 (d, *J* = 4.5 Hz, 1H), 8.21 (dd, *J* = 8.6, 1.3 Hz, 1H), 8.08 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.84 – 7.68 (m, 2H), 7.61 – 7.43 (m, 2H), 7.35 – 7.21 (m, 3H), 6.88 (d, *J* = 4.1 Hz, 1H), 6.14 (t, *J* = 3.5 Hz, 1H), 5.72 – 5.61 (m, 1H), 5.34 – 4.98 (m, 2H), 4.96 – 4.64 (m, 2H), 4.47 (q, *J* = 10.6, 9.9 Hz, 2H), 4.30 (dt, *J* = 12.6, 3.2 Hz, 1H), 4.00 (dd, *J* = 12.6, 10.2 Hz, 1H), 3.90 – 3.77 (m, 1H), 2.88 (s, 1H), 2.22 – 1.89 (m, 4H), 1.38 (s, 9H), 1.15 – 0.96 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 164.97, 150.64, 148.05, 147.19, 145.38, 138.58, 134.53, 131.89, 130.35, 129.96, 128.33, 127.48, 127.46, 127.14, 124.72, 123.69, 120.49, 116.17, 65.96, 64.51, 60.40, 59.31, 56.21, 37.29, 35.27, 31.40, 25.76, 25.26, 21.55. HRMS Calcd. For $[C_{31}H_{38}N_3O_2]^+$requires m/z 484.2959, found m/z 484.2955.



White solid (91% yield), m.p.161-164 °C; $[\alpha]_D^{25}$ +31.5 (*c* 0.20, $CHCl_3$); H^1 NMR (400 MHz, Methanol-d_4) δ 8.99 (d, *J* = 4.6 Hz, 1H), 8.35 (d, *J* = 8.5 Hz, 1H), 8.13 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.93 – 7.74 (m, 4H), 7.65 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H), 7.49 – 7.32 (m, 7H), 7.23 (td, *J* = 7.4, 1.3 Hz, 1H), 6.04 (d, *J* = 2.8 Hz, 1H), 5.93 (ddd, *J* = 17.2, 10.6, 6.6 Hz, 1H), 5.28 – 5.03 (m, 2H), 4.75 – 4.53 (m, 3H), 4.52 – 4.33 (m, 4H), 3.79 (t, *J* = 11.3 Hz, 1H), 3.71 – 3.55 (m, 1H), 2.89 (q, *J* = 8.8 Hz, 1H), 2.46 (t, *J* = 12.1 Hz, 1H), 2.11 – 1.89 (m, 3H), 1.21 (ddd, *J* = 13.9, 8.8, 5.0 Hz, 1H).^{13}C NMR (101 MHz, Methanol-d_4) δ 162.13, 149.57, 147.88, 141.11, 137.35, 135.83, 135.43, 130.05, 128.97, 128.87, 128.79, 128.64, 128.58, 127.60, 125.78, 124.97, 123.25, 120.27, 119.95, 116.58, 70.94, 60.83, 59.41, 57.79, 37.58, 26.90, 22.97, 21.00. HRMS Calcd. For $[C_{34}H_{36}N_3O_2]^+$requires m/z 518.2802, found m/z 518.2810.



Light yellow solid (81% yield), m.p.126-129 °C; $[\alpha]_D^{25}$ +24.1 (*c* 0.20, $CHCl_3$); ^1H NMR (400 MHz, Methanol-d_4) δ 8.93 (dd, *J* = 4.6, 2.3 Hz, 1H), 8.33 (dd, *J* = 8.5, 1.5 Hz, 1H), 8.11 (dd, *J* = 8.5, 1.3 Hz, 1H), 7.96 – 7.70 (m, 3H), 7.63 – 7.44 (m, 5H), 6.09 – 5.75 (m, 2H), 5.29 – 5.13 (m, 2H), 4.89 (s, 2H), 4.72 (d, *J* = 9.6 Hz, 2H), 4.44 – 4.20 (m, 3H), 3.48 (d, *J* = 2.4 Hz, 5H), 2.81 (q, *J* = 9.0 Hz, 1H), 2.29 – 2.12 (m, 1H), 2.04 – 1.91 (m, 3H), 1.02 – 0.73 (m, 2H). ^{13}C NMR (101

MHz, MeOD) δ 163.84, 149.63, 147.33, 141.00, 135.50, 130.51, 129.89, 129.23, 128.84, 127.48, 127.10, 124.89, 123.17, 119.72, 116.57, 66.73, 63.71, 61.23, 58.46, 57.33, 37.70, 36.88, 27.03, 23.18, 20.38.HRMS Calcd. For $[C_{28}H_{32}N_3O_2]^+$requires m/z 442.2492, found m/z 442.2497.

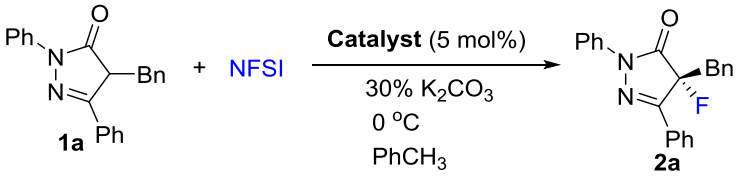
1.3 Commercial grade reagents and solvents

Commercial grade reagents, bases and solvents were purchased from Sinoreagent, Meryer and Energy-Chemical without further purifications.

2. General proceduce for the enantioselective fluorination of 4-substituted pyrazolones

2.1 Optimization of reaction parameters for the asymmetric fluorination

Table S1. Screening of catalysts for asymmetric fluorination of pyrazolone **1a** [a]



Entry	Cat.	Base	Time [h]	Yield [%][b]	*ee* [%][c]
1	-	-	4	77	Nd
2	**Cat 1**	-	4	75	6 (*S*)
3	**Cat 2**	30% K_2CO_3	1	95	Nd
4	**3a**	30% K_2CO_3	1	94	8 (*S*)
5	**3b**	30% K_2CO_3	1	96	6 (*S*)
6	**3c**	30% K_2CO_3	4	78	3 (*S*)
7	**3d**	30% K_2CO_3	1	97	21 (*S*)
8	**3e**	30% K_2CO_3	1	92	3 (*S*)
9	**3f**	30% K_2CO_3	1	95	14 (*S*)
10	**3g**	30% K_2CO_3	0.2	97	37 (*R*)
11	**3k**	30% K_2CO_3	0.2	96	42 (*R*)
12	**3l**	30% K_2CO_3	0.2	98	51 (*R*)
13	**3m**	30% K_2CO_3	0.2	98	48 (*R*)
14	**3n**	30% K_2CO_3	0.2	95	14 (*R*)
15	**3o**	30% K_2CO_3	0.2	97	58 (*R*)
16	**3p**	30% K_2CO_3	0.2	98	56 (*R*)
17	**3q**	30% K_2CO_3	0.2	99	19 (*R*)
18	**3r**	30% K_2CO_3	0.2	99	64 (*R*)
19	**3s**	30% K_2CO_3	0.2	94	27 (*R*)
20	**3t**	30% K_2CO_3	0.2	99	67 (*R*)
21	**3u**	**30% K_2CO_3**	**0.2**	**99**	**75 (*R*)**
22	**3v**	30% K_2CO_3	0.2	99	31 (*R*)

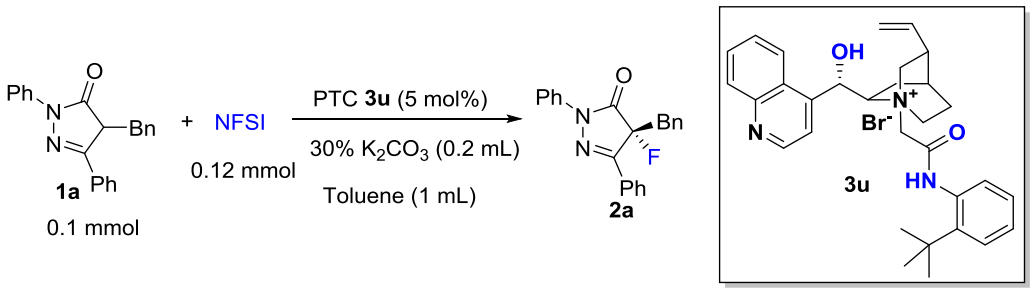
23	**3w**	30% K_2CO_3	0.2	99	74 (*R*)
24	**3x**	30% K_2CO_3	0.2	99	73 (*R*)
25	**3y**	30% K_2CO_3	0.2	99	74 (*S*)

[a] Unless specified otherwise, reactions were carried out with 1a (0.1 mmol), N-fluorobenzenesulfonimide (NFSI) (0.12 mmol), Cat (5 mol %) and 30% K_2CO_3 (0.2 mL) in toluene (1 mL) at 15 ^{o}C.

[b] Isolated yield.

[c] The ee values were determined by using chiral HPLC.

Table S2. Evaluation of different temperatures



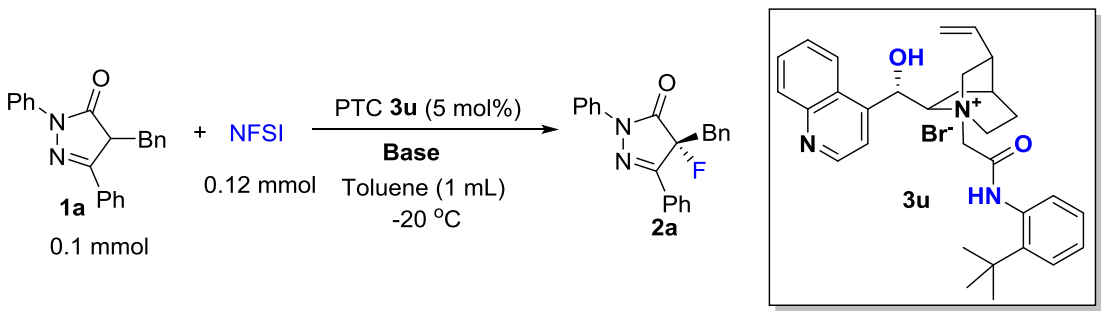
Entry	T [℃]	Time [min]	Yield[b][%]	*ee* [c][%]
1	30	10	99	67
2	15	10	99	72
3	-10	10	99	81
4	**-20**	**30**	**99**	**85**
5	-30	60	78	67
6	-40	120	67	43

[a] Unless specified otherwise, reactions were carried out with **1a** (0.1 mmol), N-fluorobenzenesulfonimide (NFSI) (0.12 mmol), **PTC 3u** (5 mol%) and base (0.2 mL) in toluene (1 mL)

[b] Isolated yield.

[c] The ee values were determined by using chiral HPLC .

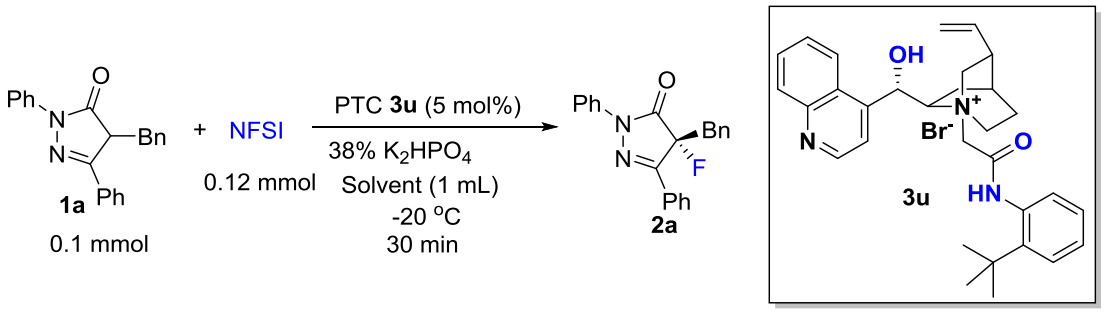
Table S3. Evaluation of different bases



Entry	Base	Time [min]	Yield[b][%]	*ee* [c][%]
1	Solid K_2CO_3 (0.2 equiv.)	10	99	68
2	Solid KOH (0.2 equiv.)	10	99	53
3	30% $C_{S2}CO_3$ (0.2 mL)	10	93	73
4	10% KOH (0.2 mL)	10	99	53
5	50% K_2HPO_4 (0.2 mL)	30	99	90
6	**38% K_2HPO_4** (0.2 mL)	**30**	**99**	**91**
7	10% K_2HPO_4 (0.2 mL)	60	91	85
8	25% KF (0.2 mL)	60	94	87
9	30% CH_3COOK (0.2 mL)	60	96	88
10	30% K_3PO_4(0.2 mL)	60	98	90

[a] Unless specified otherwise, reactions were carried out with **1a** (0.1 mmol), N-fluorobenzenesulfonimide (NFSI) (0.12 mmol), **PTC 3u** (5 mol%) and base (0.2 mL) in toluene (1 mL) at -20 °C
[b] Isolated yield.
[c] The ee values were determined by using chiral HPLC .

Table S4. Evaluation of different solvents



Entry	Solvent	Yield[b] [%]	*ee*[c] [%]
1	$PhCF_3$	92	81
2	p-xylene	99	89
3	mesitylene	99	91
4	m-xylene	99	89
5	Et_2O	99	27
6	$CHCl_3$	87	73
7	CH_2Cl_2	91	72
8	n-hexane	98	79

9	acetone	87	68

[a] Unless specified otherwise, reactions were carried out with **1a** (0.1 mmol), N-fluorobenzenesulfonimide (NFSI) (0.12 mmol), **PTC 3u** (5 mol%) and 38% K_2HPO_4 (0.2 mL) in toluene (1 mL) at -20 ^oC
[b] Isolated yield.
[c] The ee values were determined by using chiral HPLC .

Table S5. Evaluation of the concentration

Entry	**Concentration** (mol/L)	Yield[b] [%]	*ee*[c] [%]
1	0.2	99	86
2	0.1	99	89
3	0.04	99	93
4	**0.02**	**99**	**95**
5	0.01	95	93

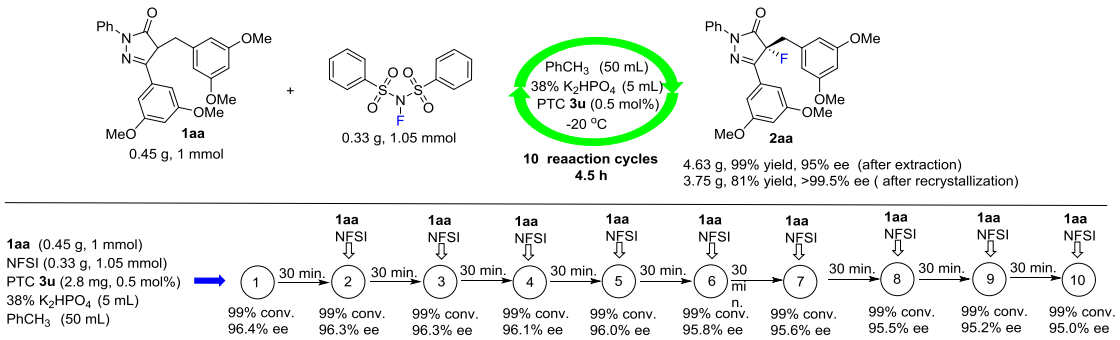
[a] Reactions were carried out with **1a** (0.1 mmol), PTC **3u** (5 mol%) and 38% K_2HPO_4 in toluene at -20 ^oC, then N-fluorobenzenesulfonimide (NFSI) (0.11 mmol in toluene) was dropwise added.
[b] Isolated yield.
[c] The ee values were determined by using chiral HPLC.

Table S6. Evaluation of the catalyst loading

Entry	Catalyst loading [%]	Time [min]	Yield[b] [%]	*ee*[c][%]
1	10	10	99	95
2	2.5	30	99	95
3	**0.5**	**30**	**99**	**94**
4	0.1	120	99	89

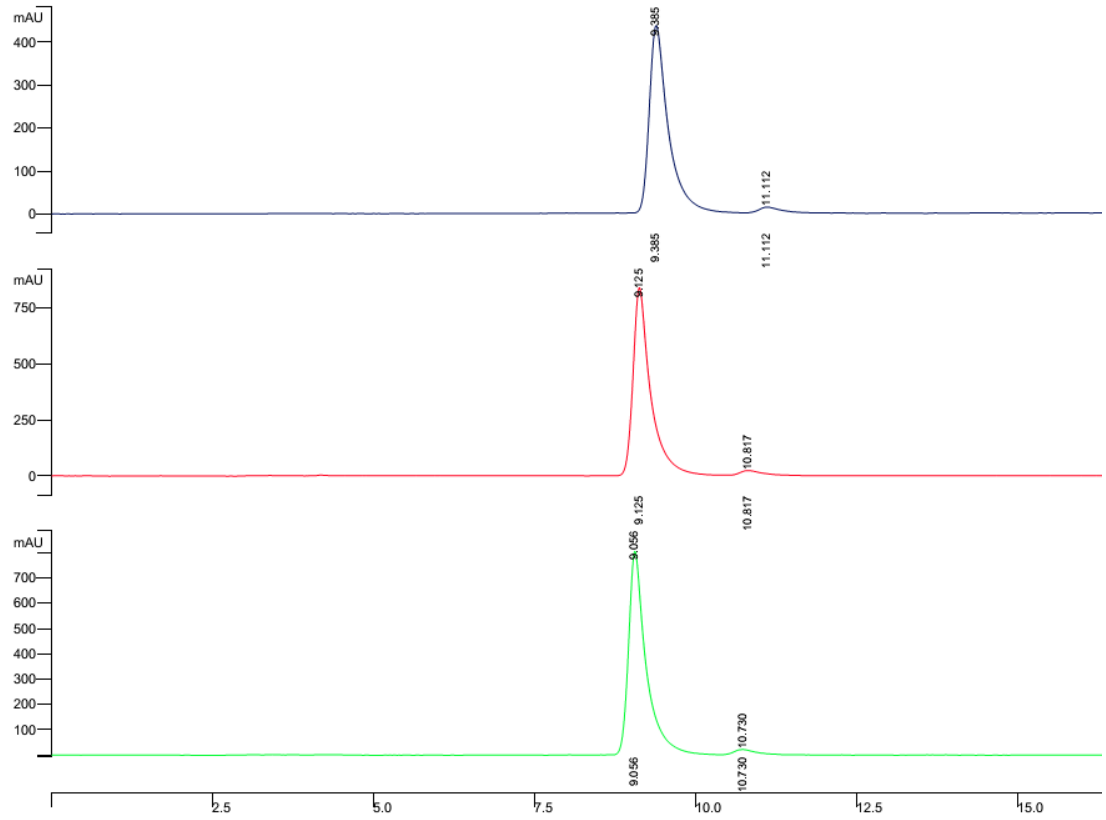
[a] Reactions were carried out with **1a** (0.1 mmol), PTC **3u** (0.1-10 mol%) and 38% K_2HPO_4 (0.2 mL) in toluene (4 mL) at -20 ^oC, then N-fluorobenzenesulfonimide (NFSI) (0.11 mmol in 1 mL toluene) was dropwise added.
[b] Isolated yield.
[c] The *ee* values were determined by using chiral HPLC.

2.2 Multigram synthesis of fluoride product 2aa using subsequent fluorinations

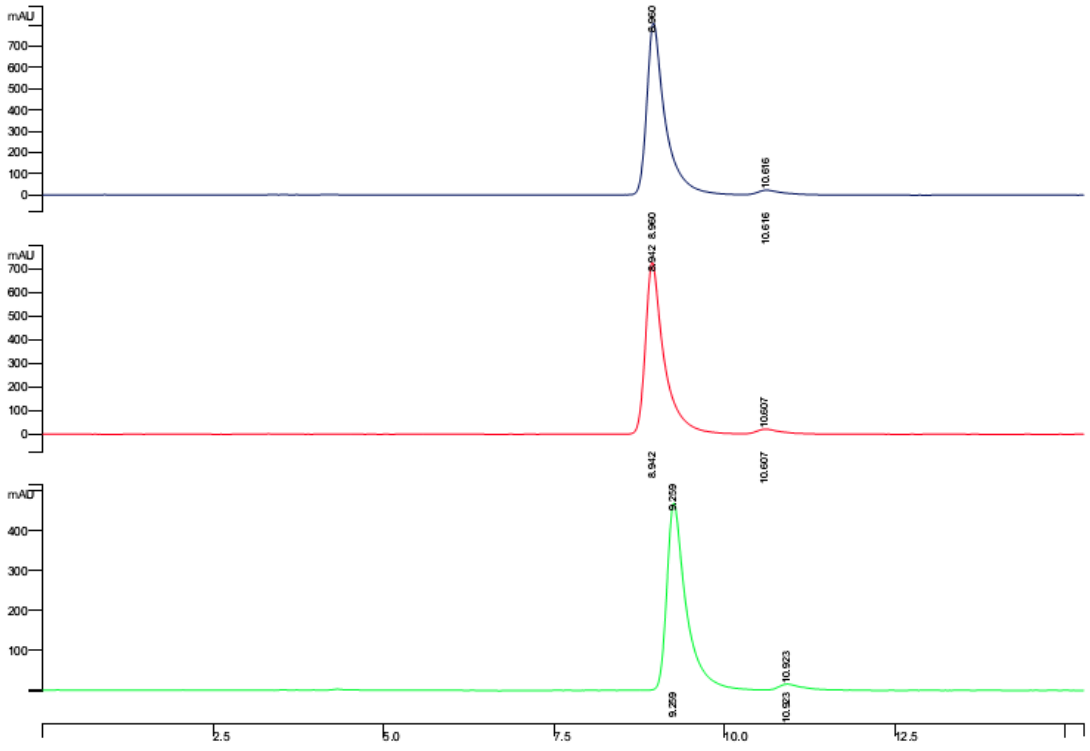


The pyrazolone **1aa** (0.45 g, 1mmol), NFSI (0.33 g, 1.05 mmol), 38% K_2HOP_4 (5mL), $PhCH_3$ (50 mL) in the presence of 0.5 mol % of PTC **3u** were presented for the first reaction cycle. After completion of the reaction, another portion of pyrazolone **1aa** (1 mmol) and **NFSI** (1.05 mmol) were added (the second cycle). After each reaction cycle, conversions and ee values were monitored by HPLC analysis. This procedure was repeated after each reaction cycle in order to maintain full conversion of the reaction. We carried out fluorination of **1aa** on 4.5 g scale after 10 reaction cycles, and the crude product **2aa** was obtained in total with 99% yield and 95% ee in 4.5 h after simple extraction with ethyl acetate and washing with water (>95% purity by ^{1}H-NMR and ^{19}F-NMR). Note that during ten reaction cycles, the model catalytic reaction did not lose efficiency or enantioselectivity distinctly. Moreover, the optically pure product **2aa** (>99.5% ee) could be easily obtained by recrystallization with ethanol.

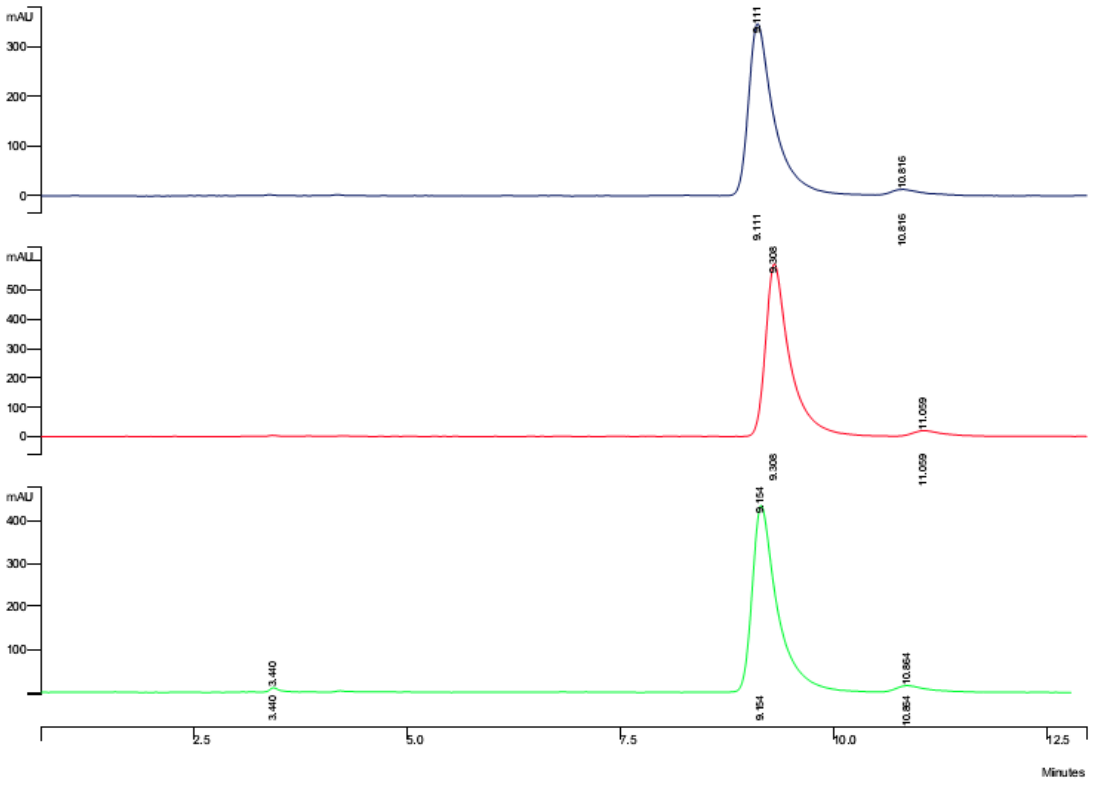
1-3 circles (HPLC data of chiral **2aa**)



4-6 circles (HPLC data of chiral **2aa**)

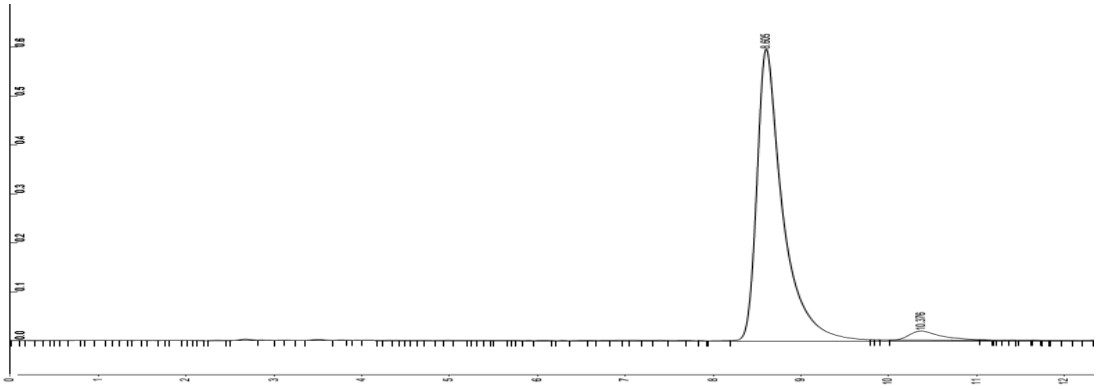


7-9 circles (HPLC data of chiral **2aa**)

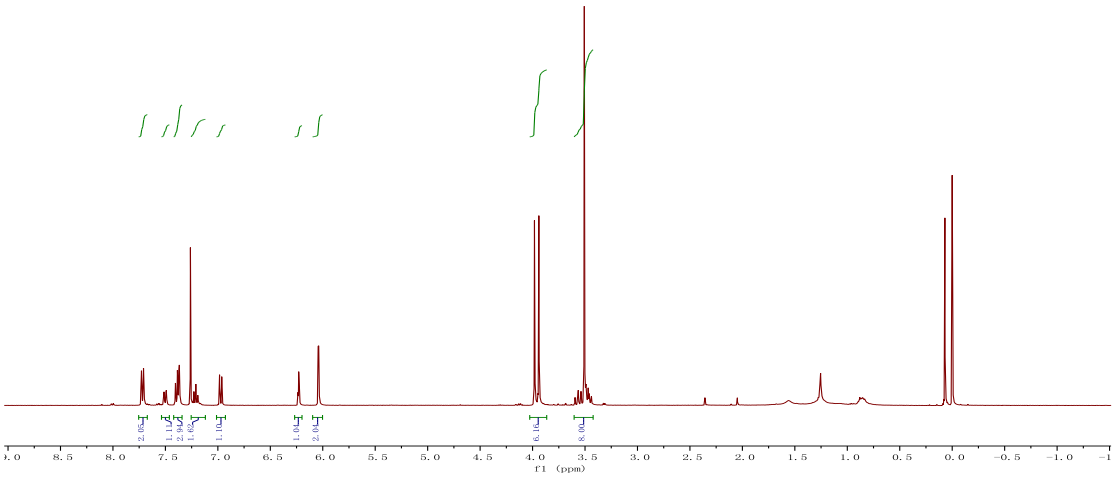


10 circles after single extraction (4.63 g, 99% yield, 95% ee)

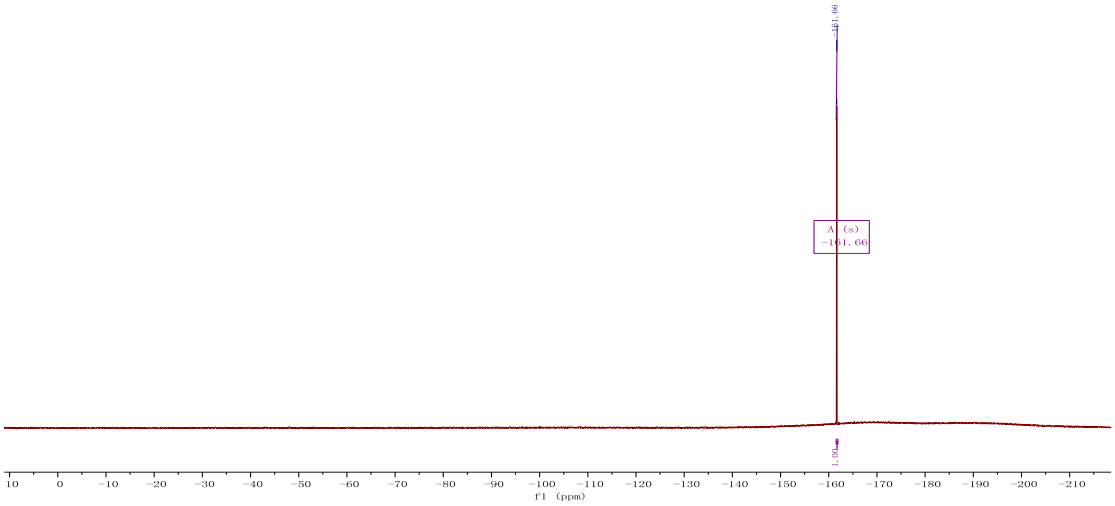
HPLC data of chiral **2aa**



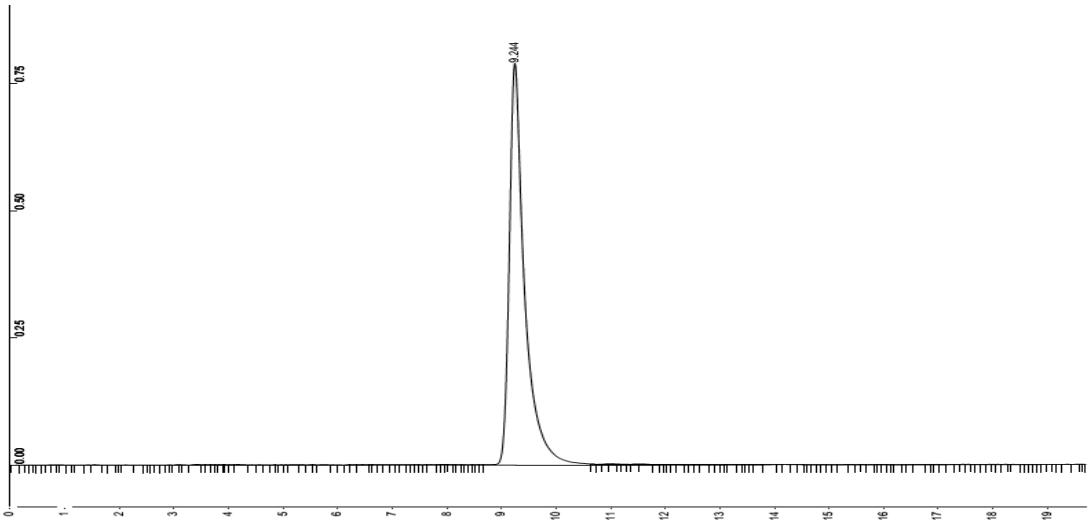
^{1}H NMR of the crude chiral **2aa (>95% purity)**



^{1}F NMR of the crude chiral **2aa (>99% con. and residual NFSI and 1aa was not observed)**

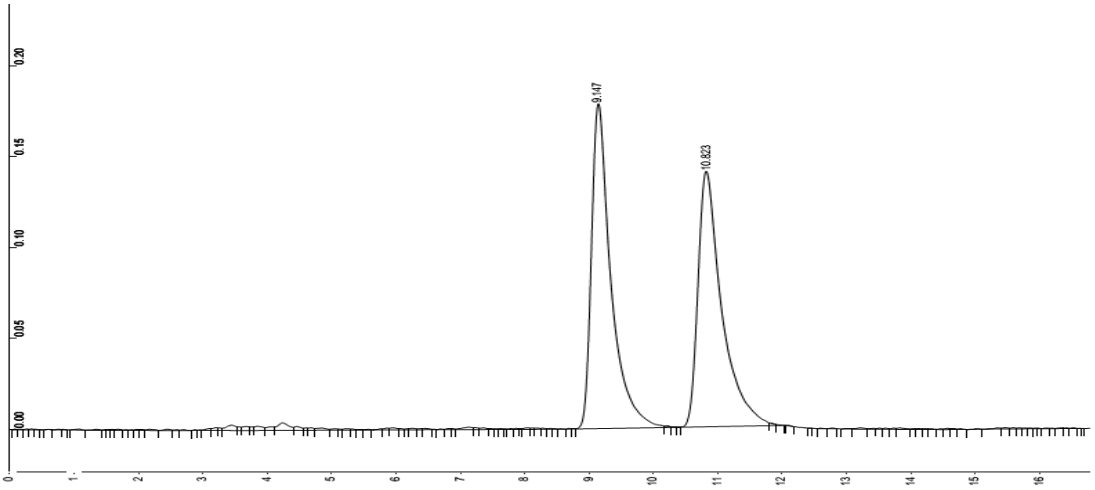


Final chiral product **2aa** after recrystallization with ethanol (3.75 g, 81% yield, >99.5% ee)



9.244	Area	Area%
9.147	**154587584**	**100**

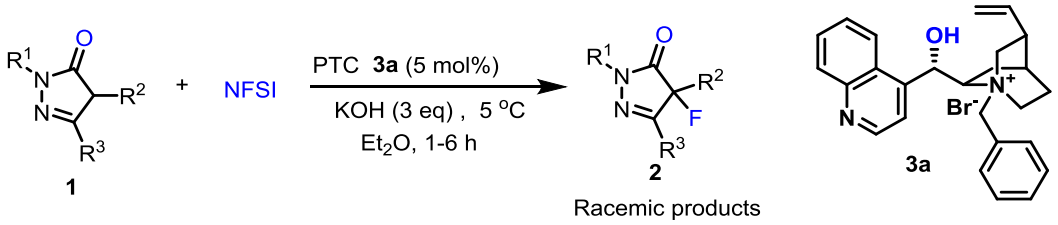
Racemic product:



R.Time	Area	Area%
9.147	**374877804**	**51.0278**
10.823	**35977715**	**48.9722**

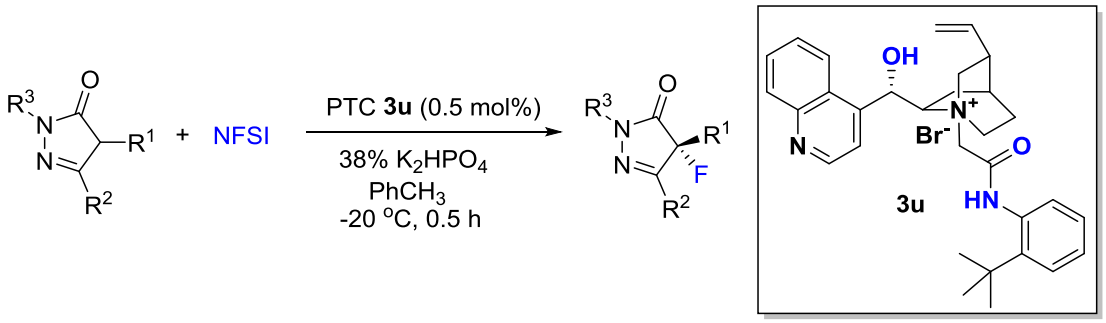
3. Experimental procedures and characterization of products

3.1 Achiral fluorination of pyrazolones

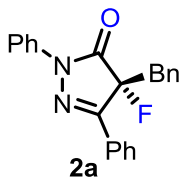


The reaction was conducted with substrate **1** (0.1 mmol) in the presence of PTC **3a** (5 mol%) in Et_2O (2 mL). Then KOH (0.3 mmol) was added slowly, and the reaction was stirred at 5 °C for 1-6 h. After completion of the reaction (confirmed by TLC analysis), the solvent was removed under reduced pressure and the reside was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the corresponding products. The *ee* of the products were determined by chiral HPLC.

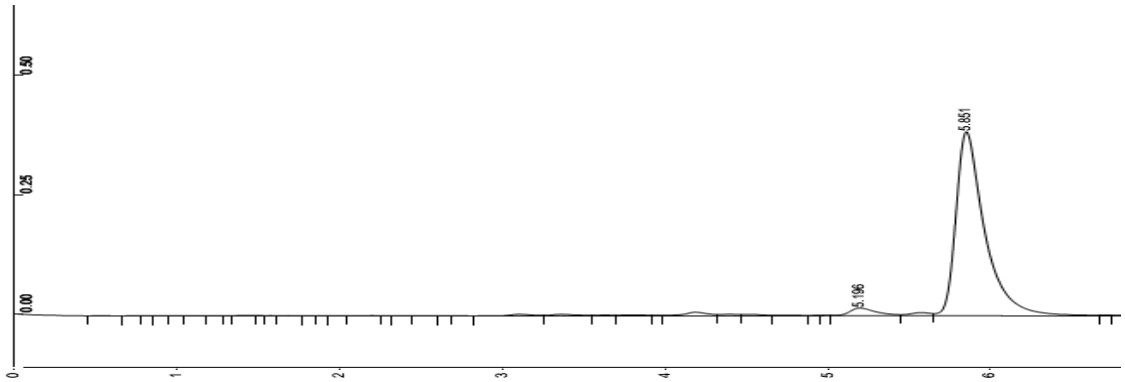
3.2 Asymmetric fluorination of pyrazolones



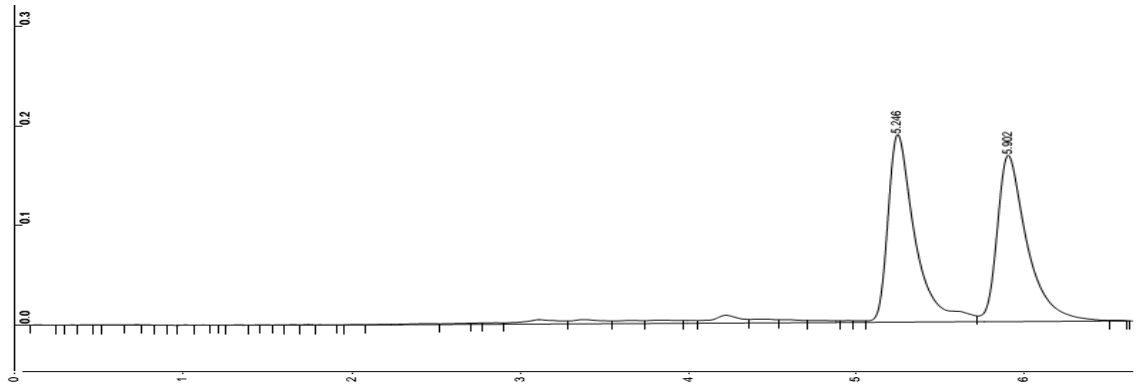
The reaction was conducted with substrate **1** (0.1 mmol) in the presence of PTC **3u** (0.5 mol%) and 38% K_2HPO_4 (0.2 mL) in toluene (4 mL). then N-fluorobenzenesulfonimide (NFSI) (0.11 mmol in 1 mL toluene) was dropwise added slowly, and the reaction was stirred at -20 °C for 0.5 h. After completion of the reaction (confirmed by TLC analysis), the mixture was diluted with EtOAc (20 mL), washed with water (2×10 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo.The reside was purified by column chromatography on silica gel (ethyl acetate/petroleum ether) to provide the corresponding products. The *ee* of the product was determined by chiral HPLC.



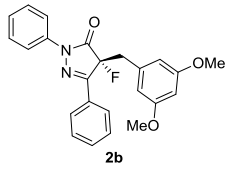
(*R*)-4-benzyl-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2a). White solid, m.p. 58-61 °C, $[\alpha]_D^{25}$ +45.1 (*c* 0.41, $CHCl_3$); 99% yield, 94% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.66 (m, 2H), 7.61 – 7.46 (m, 2H), 7.35 (dq, *J* = 9.3, 2.6, 1.8 Hz, 3H), 7.26 – 7.12 (m, 2H), 7.08 – 6.87 (m, 4H), 6.81 – 6.65 (m, 2H), 3.61 – 3.21 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.88 (d, *J* = 21.5 Hz), 152.99 (d, *J* = 13.9 Hz), 135.78, 130.05, 128.82, 128.72, 128.29, 128.27, 128.01, 127.74, 127.29, 126.84, 125.54, 125.53, 124.80, 118.19, 95.27, 93.28, 40.05 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, Chloroform-d) δ -162.21 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 5.85 min, τR (minor) = 5.19 min. HRMS Calcd. for $[C_{22}H_{17}FN_2O+Na]^+$ requires m/z = 367.1223, found m/z = 367.1221.



R.Time	Area	Area%
5.196	**1525385**	**3.1162**
5.851	**47424796**	**96.8838**

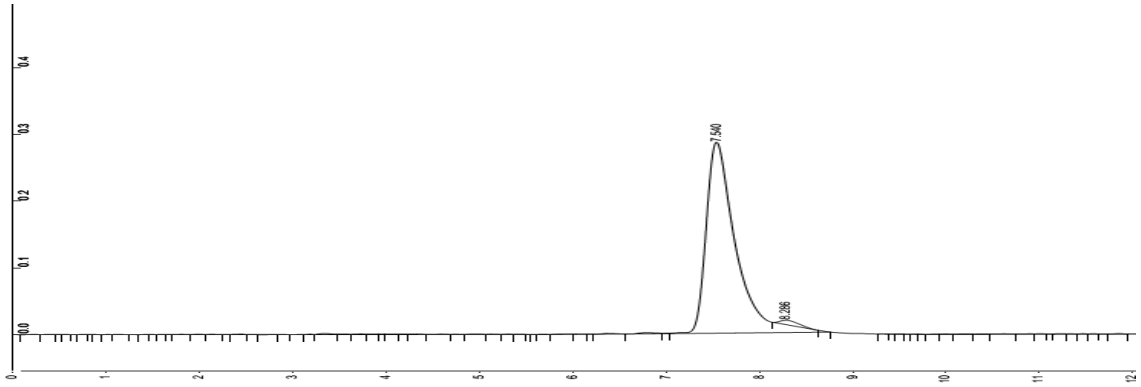


R.Time	Area	Area%
5.246	**21100312**	**50.5611**
5.902	**20632020**	**49.4389**

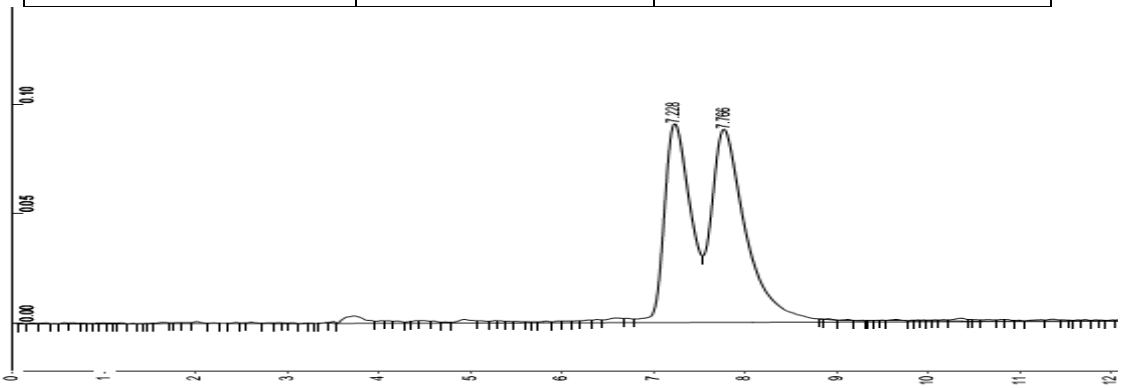


2b

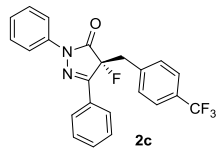
(*R*)-4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*) -one (2b). White solid, m.p. 140-143 °C; $[\alpha]_D^{25}$ +95.1 (*c* 0.43, $CHCl_3$); 95% yield, 94% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.85 (m, 2H), 7.77 – 7.65 (m, 2H), 7.56 – 7.45 (m, 3H), 7.42 – 7.33 (m, 2H), 7.24 – 7.13 (m, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.00 (d, *J* = 2.3 Hz, 2H), 3.68 – 3.37 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.07 (d, *J* = 21.3 Hz), 160.50, 154.21 (d, *J* = 13.7 Hz), 136.96, 131.87 (d, *J* = 12.1 Hz), 131.11, 129.58 (d, *J* = 1.7 Hz), 129.05, 128.87, 126.67, 126.66, 125.88, 119.17, 107.40, 100.87, 96.15, 94.17, 55.03, 41.36 (d, *J* = 26.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -161.82 (s, 1F). HPLC conditions: Chiralcel AS-H column (250 × 4.6 mm), hexane /*i*-PrOH = 95 / 5, 1 mL / min, 254 nm, τR (major) = 7.54 min, τR (minor) = 8.28 min. HRMS Calcd. for $[C_{24}H_{21}FN_2O_3+Na]^+$ requires m/z = 427.1434, found m/z = 427.1431.



R.Time	Area	Area%
7.540	**62948884**	**97.4068**
8.286	**1675848**	**2.5932**

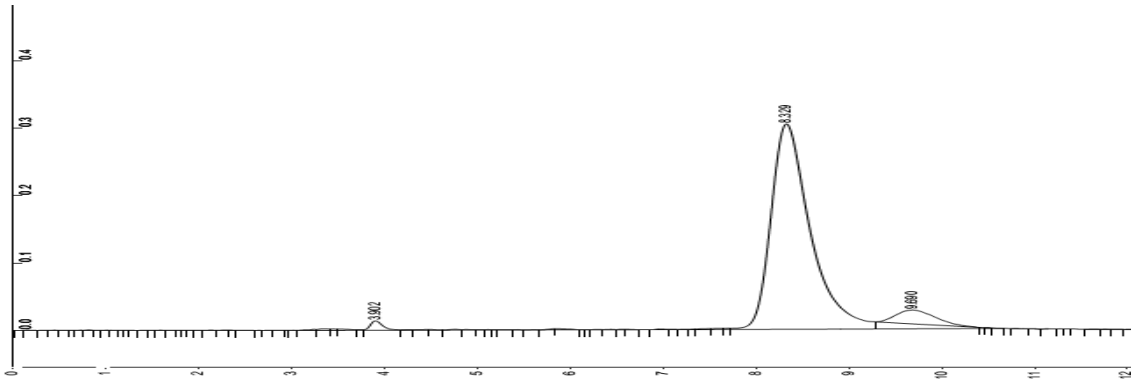


R.Time	Area	Area%
7.228	**17800654**	**46.4521**
7.766	**20519796**	**53.5479**

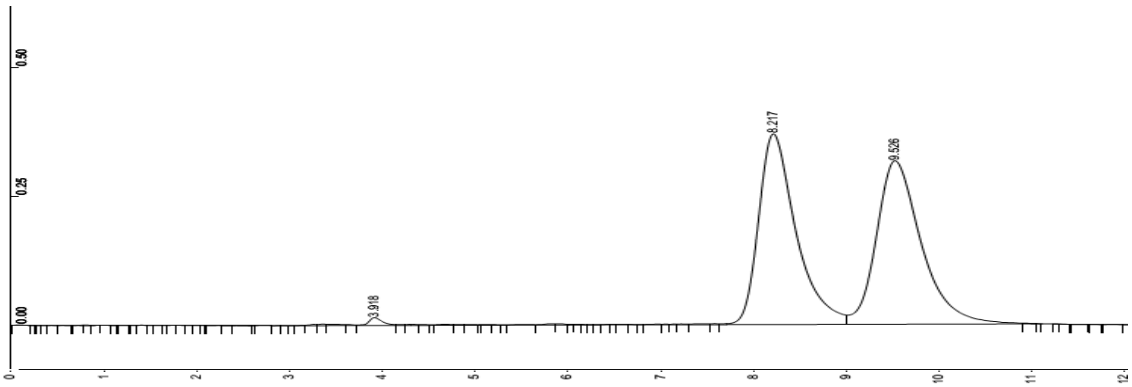


2c

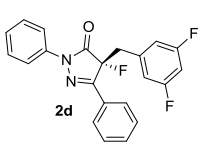
(*R*)-4-(4-trifluoromethyl-benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5 (4*H*)-one (2c). Yellow solid, m.p 102-104 °C; $[\alpha]_D^{25}$ +55.6 (*c* 0.54, $CHCl_3$); 98% yield, 87% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.82 (m, 2H), 7.72 – 7.60 (m, 2H), 7.59 – 7.44 (m, 3H), 7.38 (dd, *J* = 8.7, 7.5 Hz, 4H), 7.26 – 7.16 (m, 2H), 7.02 (d, *J* = 8.0 Hz, 2H), 3.73 – 3.48 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.50 (d, *J* = 21.4 Hz), 152.86 (d, *J* = 13.7 Hz), 135.65, 133.19 (d, *J* = 10.7 Hz), 130.33, 129.38, 128.18, 127.91, 125.58, 125.56, 125.13, 124.30, 124.26, 122.78 (q, *J* = 272.3 Hz), 94.85, 92.85, 39.81 (d, *J* = 26.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.76 (s, 3F), -162.96 (s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 95 / 5, 1 mL / min, 254 nm, τR (major) = 8.32 min, τR (minor) = 7.76 min. HRMS Calcd. for $[C_{23}H_{16}F_4N_2O+Na]^+$ requires m/z = 435.1096, found m/z = 435.1091.



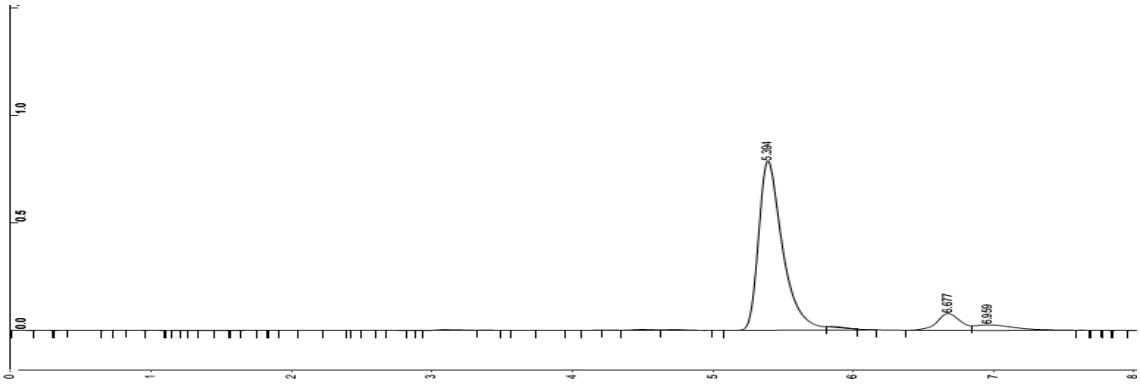
R.Time	Area	Area%
8.329	**93651352**	**93.5294**
7.766	**6488048**	**6.4796**



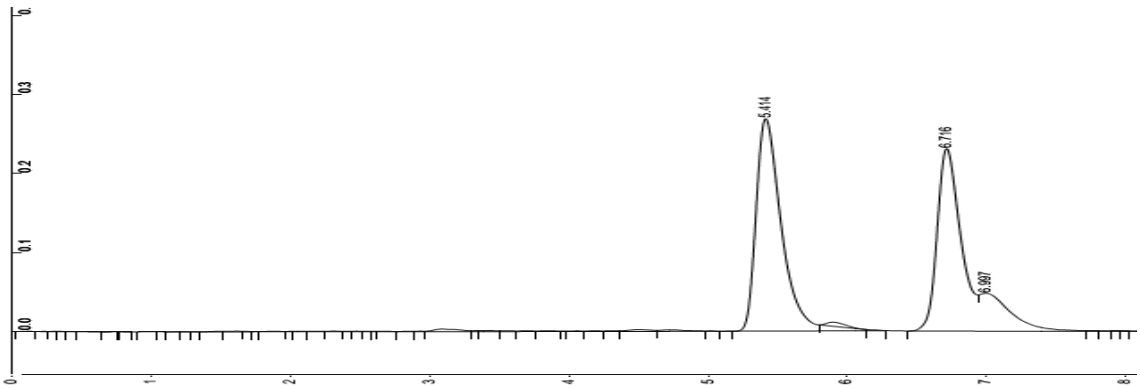
R.Time	Area	Area%
8.217	**103512536**	**49.9800**
9.526	**103595379**	**50.0200**



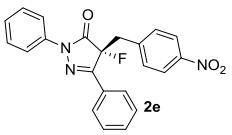
(*R*)-4-(3, 5-bis(fluoro)benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2d). Yellow solid, m.p. 113-115 °C; $[\alpha]_D^{25}$ +65.1 (*c* 0.54, $CHCl_3$); 98% yield, 87% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.83 (m, 2H), 7.80 – 7.66 (m, 2H), 7.61 – 7.48 (m, 3H), 7.45 – 7.33 (m, 2H), 7.25 – 7.17 (m, 1H), 6.61 (tt, *J* = 8.8, 2.3 Hz, 1H), 6.52 – 6.30 (m, 2H), 3.70 – 3.37 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.41 (d, *J* = 21.3 Hz), 163.86 (d, *J* = 12.7 Hz), 161.38 (d, *J* = 12.8 Hz), 153.87 (d, *J* = 13.7 Hz),136.72, 133.83, 131.46, 129.26, 128.99, 126.60, 126.58, 126.15, 119.18, 113.02 (d, *J* = 25.6 Hz), 103.69 (t, *J* = 25.1 Hz), 95.55, 93.55, 40.55 (d, *J* = 27.5 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -109.16 (s, 2F), -162.68 (s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 95 / 5, 1 mL / min, 254 nm, τR (major) = 6.67 min, τR (minor) = 5.39 min. HRMS Calcd. for $[C_{22}H_{15}F_3N_2O+Na]^+$ requires m/z = 403.1034, found m/z = 403.1038.



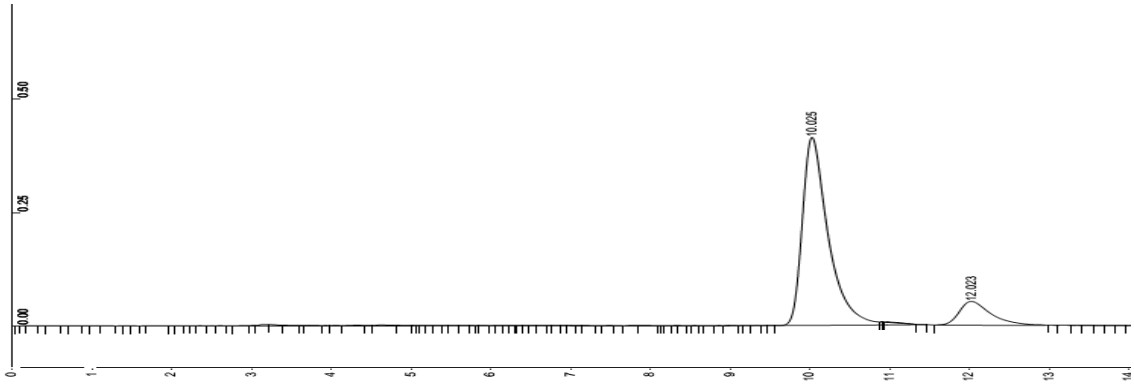
R.Time	Area	Area%
5.394	**94438728**	**93.5120**
6.677	**6552297**	**6.4880**



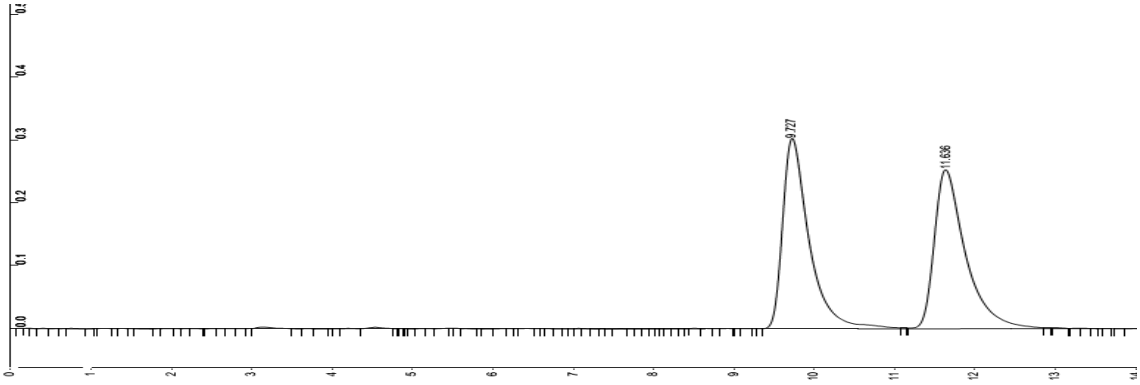
R.Time	Area	Area%
5.414	**27228898**	**49.6595**
6.716	**27602298**	**50.3405**



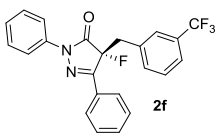
(*R*)-4-(4-(nitryl)benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2e). Light yellow solid, m.p. 117-119 °C; $[\alpha]_D^{25}$ +27.6 (*c* 0.51, $CHCl_3$); 97% yield, 80% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.82 (m, 4H), 7.78 – 7.65 (m, 2H), 7.62 – 7.46 (m, 3H), 7.43 – 7.31 (m, 2H), 7.25 – 7.17 (m, 1H), 7.14 – 6.94 (m, 2H), 3.81 – 3.55 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.24 (d, *J* = 21.3 Hz), 153.70 (d, *J* = 13.8 Hz), 147.62, 137.68, 137.57, 136.61, 131.57, 131.01, 129.32, 129.01, 128.93, 128.92, 126.58, 126.56, 126.22, 123.52, 118.98, 95.55, 93.55, 40.73 (d, *J* = 27.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -162.65 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 10.02 min, τR (minor) = 12.02 min. HRMS Calcd. for $[C_{22}H_{16}FN_3O_3+Na]^+$ requires m/z = 412.1073, found m/z = 412.1069.



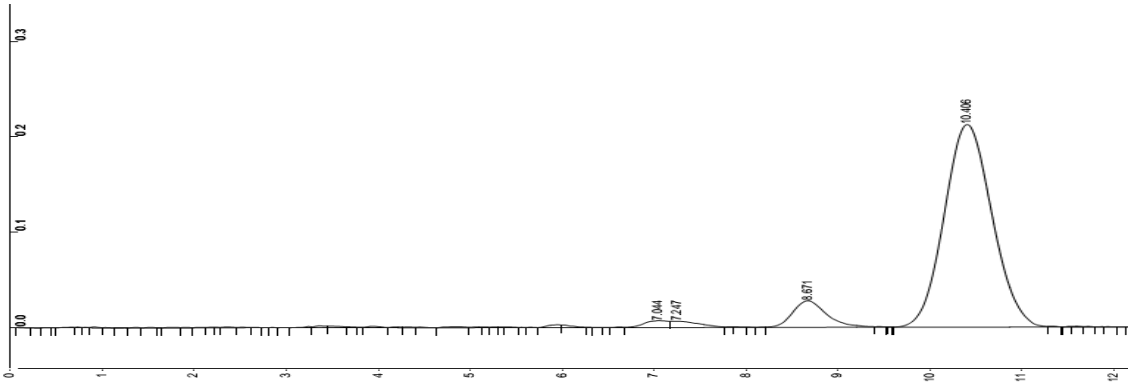
R.Time	Area	Area%
10.025	**94021752**	**89.8744**
12.023	**10592856**	**10.1256**



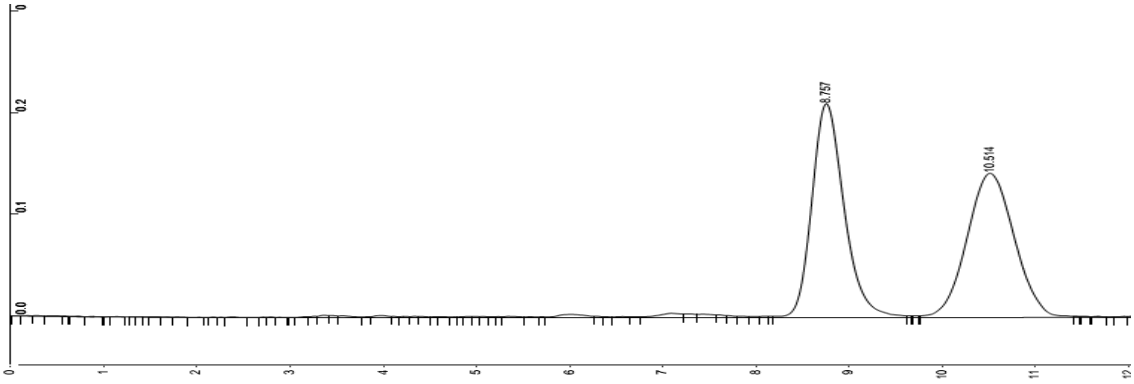
R.Time	Area	Area%
9.727	**69328320**	**50.3525**
11.636	**68357544**	**49.6475**



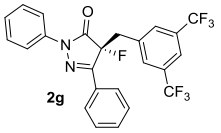
(*R*)-4-(3-trifluoromethyl-benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5 (4*H*)-one (2f). Light yellow oil; $[\alpha]_D^{25}$ +110.7 (*c* 0.58, $CHCl_3$); 95% yield, 84% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 2H), 7.71 – 7.60 (m, 2H), 7.57 – 7.46 (m, 3H), 7.44 – 7.30 (m, 3H), 7.21 (dd, *J* = 8.6, 7.2 Hz, 2H), 7.15 – 7.04 (m, 2H), 3.72 – 3.47 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.58 (d, *J* = 21.5 Hz), 153.93 (d, *J* = 13.7 Hz), 136.65, 133.31, 131.39, 131.29 – 130.81 (m), 129.21, 129.16, 129.14, 128.92, 128.90, 126.88 (q, *J* = 3.8 Hz), 126.63, 126.61, 126.09, 125.23 – 124.39 (m), 95.91, 93.91, 40.81 (d, *J* = 26.8 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.90 (s, 3F), -163.34 (s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 95 / 5, 1 mL / min, 254 nm, τR (major) = 10.40 min, τR (minor) = 8.67 min. HRMS Calcd. for $[C_{23}H_{16}F_4N_2O+Na]^+$ requires m/z = 435.1096, found m/z = 435.1093.



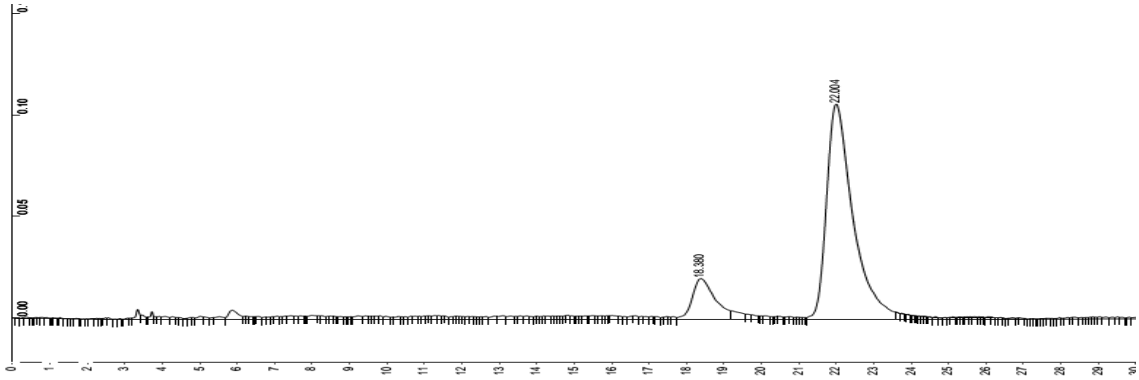
R.Time	Area	Area%
8.671	**7159978**	**8.2310**
10.406	**79827970**	**91.7690**



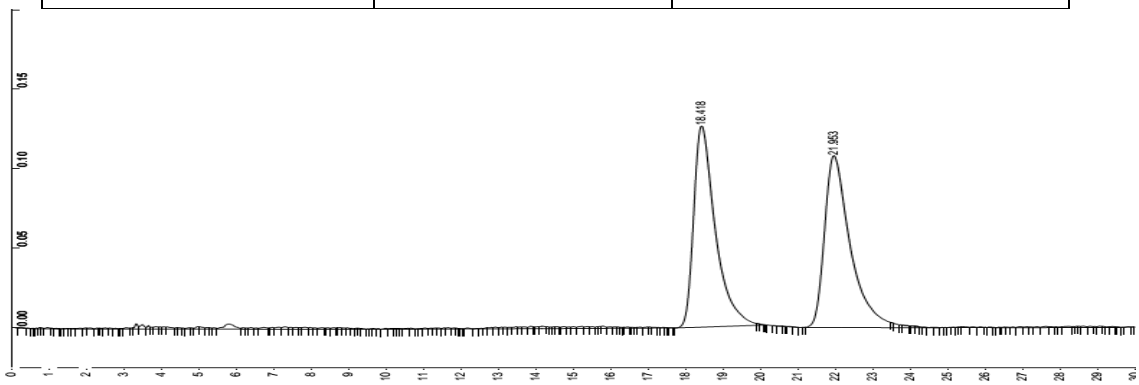
R.Time	Area	Area%
8.757	**50619408**	**49.7025**
10.514	**51225316**	**50.2975**



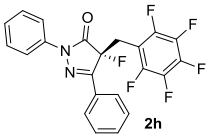
(*R*)-4-(3,5-bis(trifluoromethyl)-benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2g). White solid. m.p. 85-87 °C; $[\alpha]_D^{25}$ +46.5 (*c* 0.42, $CHCl_3$); 96% yield, 83% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (dq, *J* = 6.9, 1.2 Hz, 2H), 7.72 – 7.62 (m, 3H), 7.59 – 7.44 (m, 3H), 7.43 – 7.29 (m, 4H), 7.25 – 7.18 (m, 1H), 3.82 – 3.52 (m, 2H).^{13}C NMR (101 MHz, Chloroform-*d*) δ167.19 (d, *J* = 21.4 Hz), 153.71 (d, *J* = 13.5 Hz), 136.46, 132.86 (d, *J* = 10.6 Hz), 131.73 (q, *J* = 33.6 Hz), 131.65, 130.33, 129.33, 128.98, 126.60, 126.58, 126.28, 122.78 (q, *J* = 272.8 Hz), 122.04, 122.00, 121.96, 95.41, 93.40, 40.61 (d, *J* = 27.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -63.10 (s, 6F) , -164.38 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 98 / 2, 1 mL / min, 254 nm, τR (major) = 22.00 min, τR (minor) = 18.38 min. HRMS Calcd. for $[C_{24}H_{15}F_7N_2O+Na]^+$ requires m/z = 503.0970, found m/z = 503.0968.



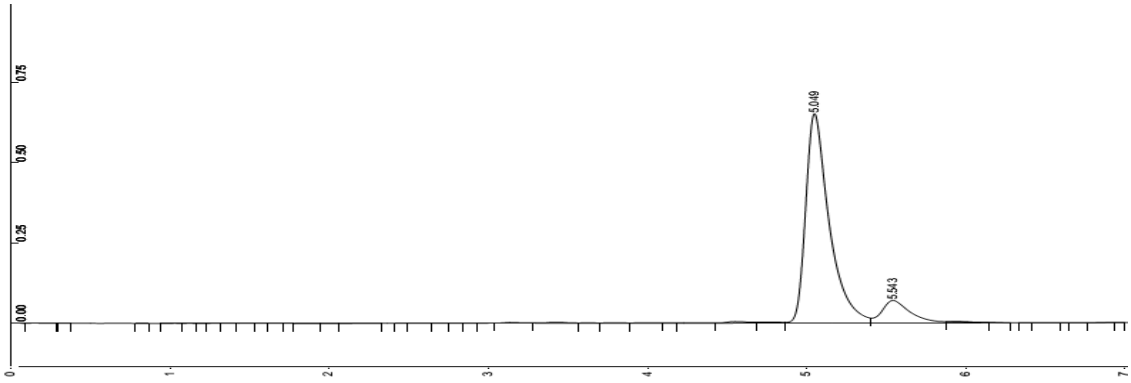
R.Time	Area	Area%
18.380	**10543245**	**8.9165**
22.004	**107700965**	**91.0835**



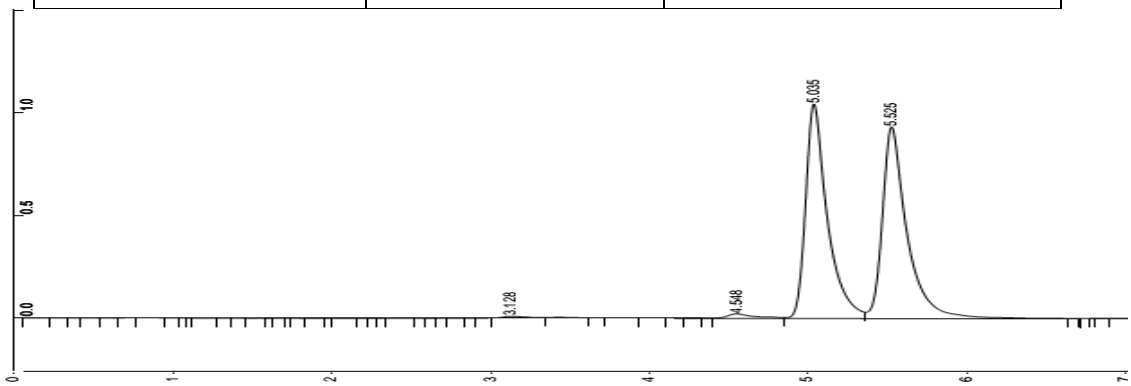
R.Time	Area	Area%
18.418	**50928628**	**49.3875**
21.953	**52191848**	**50.6125**



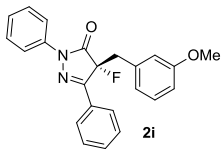
(*R*)-4-(2,3,4,5,6-fluorobenzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2h). Light yellow solid, m.p. 165-167 °C; $[\alpha]_D^{25}$ +56.7 (*c* 0.72, $CHCl_3$); 96% yield, 87% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.73 (m, 4H), 7.48 – 7.30 (m, 5H), 7.23 – 7.17 (m, 1H), 3.57 (tt, *J* = 15.2, 1.8 Hz, 1H), 3.29 (ddt, *J* = 26.9, 15.1, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.72 (d, *J* = 22.6 Hz), 153.29 (d, *J* = 13.7 Hz), 153.22, 146.02, 143.59, 143.55, 141.35, 138.81, 137.60, 135.99, 130.45, 128.06, 127.98, 125.60, 125.58, 125.10, 117.98, 104.31 (t, *J* = 18.1 Hz), 92.43, 90.40, 28.68, 27.29 (d, *J* = 26.7 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -139.19 – -139.75 (m, 2F), -153.43 (t, *J* = 20.8 Hz, 1F), -161.83 (dd, *J* = 21.0, 14.2 Hz, 2F), -170.79 (t, *J* = 10.5 Hz, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 5.04 min, τR (minor) = 5.54 min. HRMS Calcd. for $[C_{22}H_{12}F_6N_2O+H]^+$ requires m/z = 435.0932, found m/z = 435.0931.



R.Time	Area	Area%
5.049	**67048160**	**91.5148**
5.543	**6216667**	**8.4852**

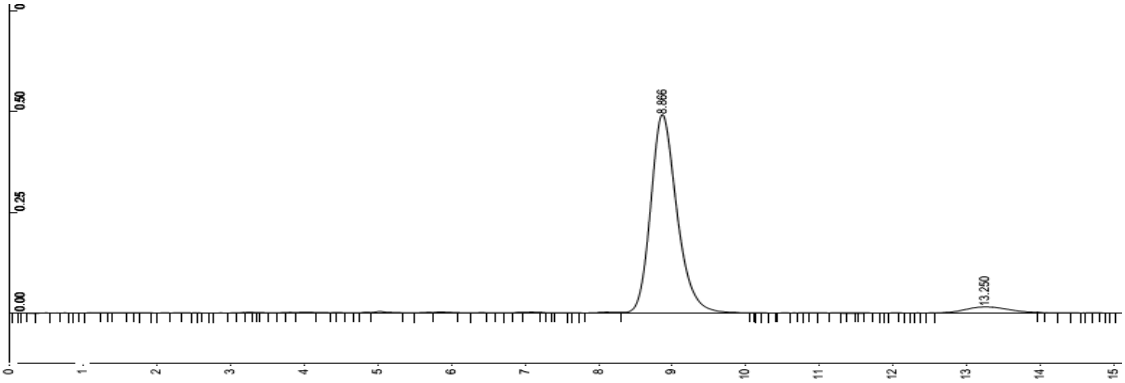


R.Time	Area	Area%
5.035	**993606632**	**49.9252**
5.525	**996583957**	**50.0748**

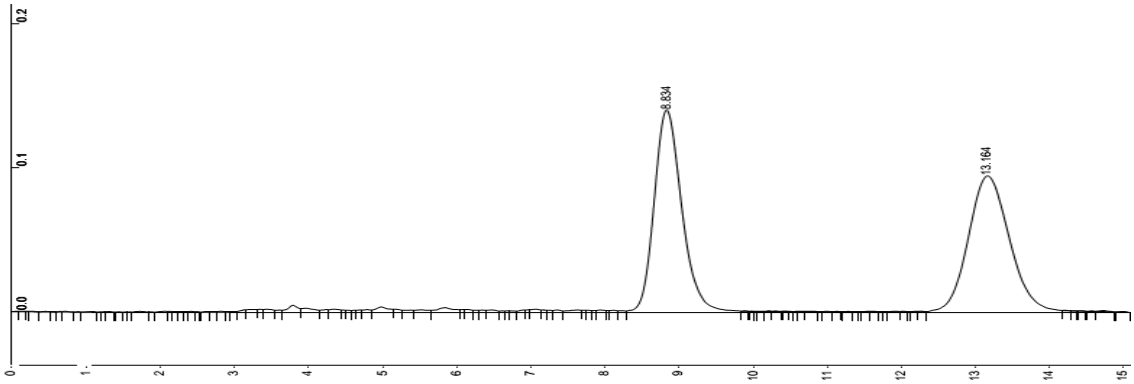


2i

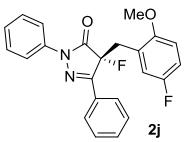
(*R*)-4-(3-methoxyl-benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5 (4*H*)-one (2i). Light yellow wax, $[\alpha]_D^{25}$ +48.2 (*c* 0.41, $CHCl_3$); 99% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.86 (m, 2H), 7.74 – 7.62 (m, 2H), 7.57 – 7.46 (m, 3H), 7.40 – 7.33 (m, 2H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.67 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1H), 6.49 (dt, *J* = 7.5, 1.2 Hz, 1H), 6.38 (t, *J* = 2.1 Hz, 1H), 3.69 – 3.51 (m, 2H), 3.49 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.05 (d, *J* = 21.5 Hz), 159.39, 154.19 (d, *J* = 13.8 Hz), 136.93, 131.32, 131.20, 131.14, 129.53, 129.52, 129.42, 129.10, 128.88, 126.69, 126.68, 125.92, 122.23, 119.30, 114.59, 114.42, 96.28, 94.29, 54.92, 41.21 (d, *J* = 26.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -162.10 (s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = 8.86 min, τR (minor) = 13.25 min. HRMS Calcd. for $[C_{23}H_{19}FN_2O_2+H]^+$ requires m/z = 375.1509, found m/z = 375.1507.



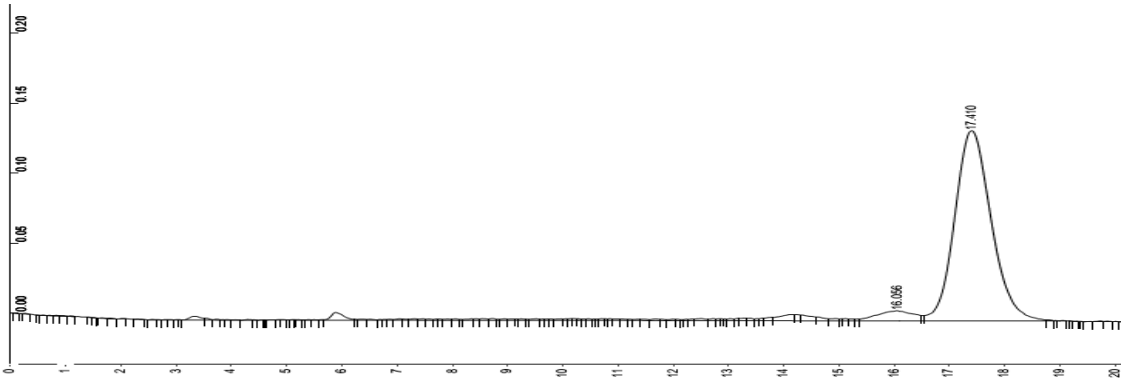
R.Time	Area	Area%
8.866	**122565072**	**96.0405**
13.250	**5053039**	**3.9595**



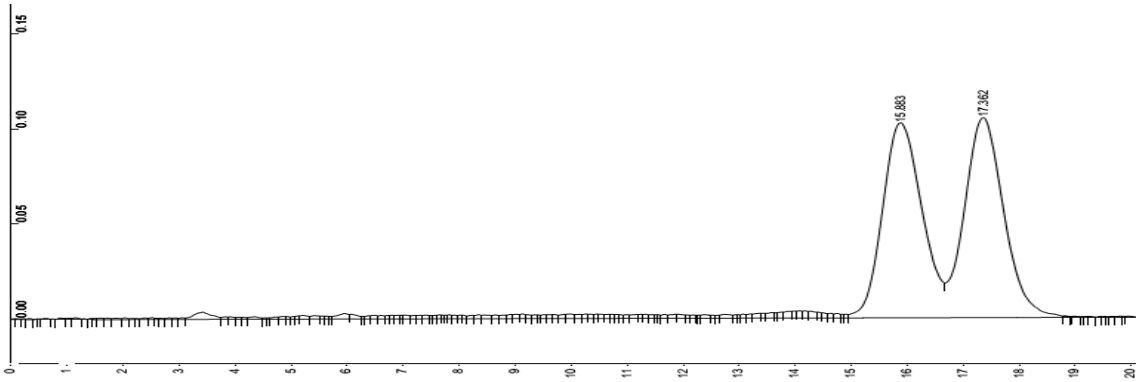
R.Time	Area	Area%
8.834	**37205960**	**50.1683**
13.164	**36956388**	**49.8317**



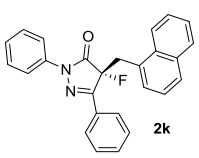
(*R*)-4-(2-methoxyl,5-fluorobenzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2j). White solid, m.p. 86-89 °C; $[\alpha]_D^{25}$ +56.7 (*c* 0.42, $CHCl_3$); 98% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (dq, *J* = 8.4, 1.5 Hz, 4H), 7.40 – 7.24 (m, 5H), 7.17 – 7.06 (m, 1H), 6.89 – 6.63 (m, 2H), 6.38 (dd, *J* = 9.0, 4.4 Hz, 1H), 3.72 – 3.27 (m, 2H), 3.09 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ167.19 (d, *J* = 21.8 Hz), 155.19 – 153.34 (m), 152.72, 152.70, 136.12, 128.70, 128.68, 127.88, 127.44, 125.45, 125.43, 124.73, 119.58, 117.97, 117.64 (d, *J* = 23.6 Hz), 114.14 (d, *J* = 22.7 Hz), 109.48 (d, *J* = 8.4 Hz), 94.88, 92.89, 53.74, 34.19 (d, *J* = 27.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.15 (s, 1F), -164.47(s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 95 / 5, 1 mL / min, 254 nm, τR (major) = 17.41 min, τR (minor) = 16.05 min. HRMS Calcd. for $[C_{23}H_{18}F_2N_2O_2+Na]^+$ requires m/z = 415.1234, found m/z = 415.1231.



R.Time	Area	Area%
16.056	**3236348**	**4.1352**
17.410	**75027049**	**95.8648**

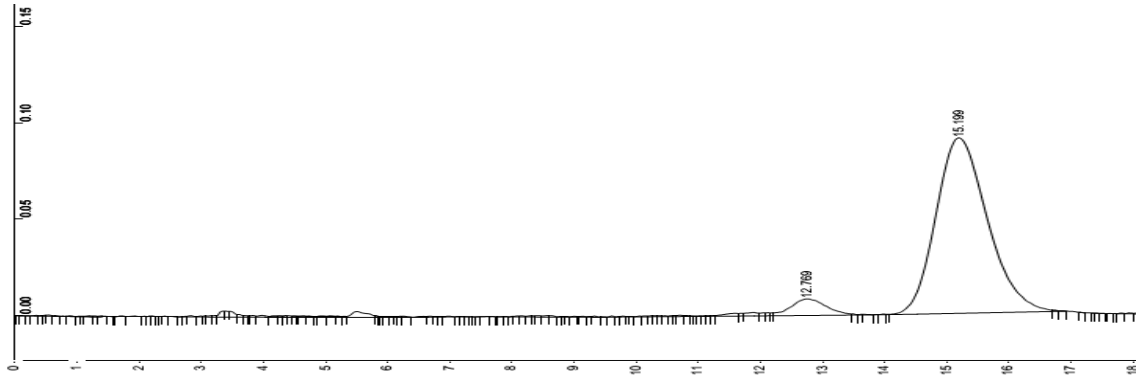


R.Time	Area	Area%
15.883	**50159428**	**49.3827**
17.362	**51413432**	**50.6173**

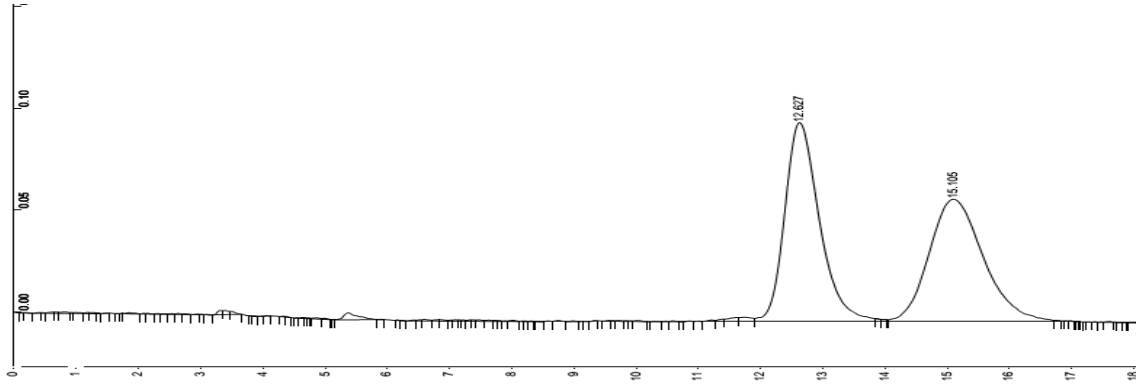


2k

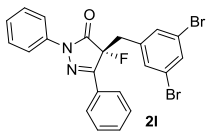
(*R*)-4-(naphthalen-2-methylene)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2k). Colourless oil; $[\alpha]_D^{25}$ +112.3 (*c* 0.42, $CHCl_3$); 99% yield, 90% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.5 Hz, 1H), 7.75 – 7.62 (m, 4H), 7.59 – 7.50 (m, 2H), 7.47 – 7.38 (m, 1H), 7.39 – 7.29 (m, 5H), 7.25 – 7.21 (m, 1H), 7.21 – 7.11 (m, 3H), 4.10 – 3.95 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.52 (d, *J* = 21.8 Hz), 154.84 (d, *J* = 13.9 Hz), 136.85, 133.63, 132.02, 130.92, 129.68, 129.66, 129.20, 128.82, 128.76, 128.53, 126.76, 126.67, 126.65, 125.87, 125.86, 125.60, 124.82, 123.64, 119.24, 96.54, 94.55, 37.30 (d, *J* = 26.4 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -163.17 (s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 15.19 min, τR (minor) = 12.76 min. HRMS Calcd. for $[C_{26}H_{19}FN_2O+Na]^+$ requires m/z = 417.1379, found m/z = 417.1382.



R.Time	Area	Area%
12.769	**3351168**	**5.0038**
15.199	**63621293**	**94.9962**

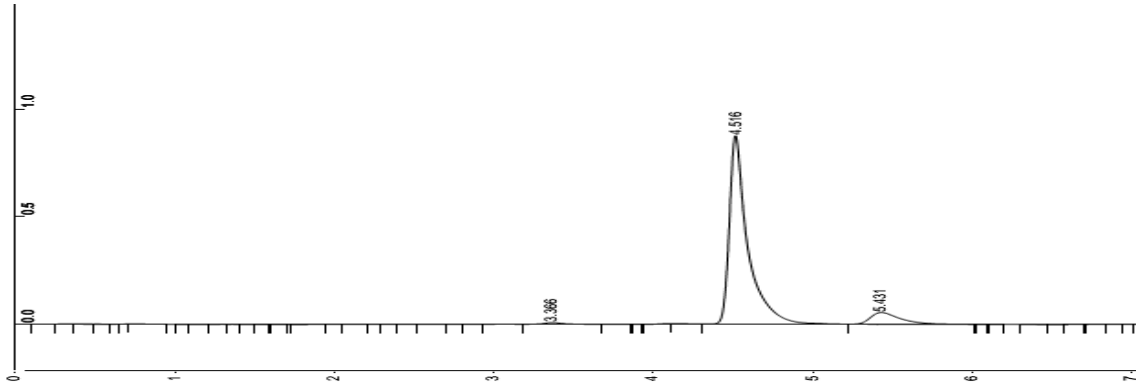


R.Time	Area	Area%
12.627	**33979232**	**50.8720**
15.105	**36677300**	**49.1281**

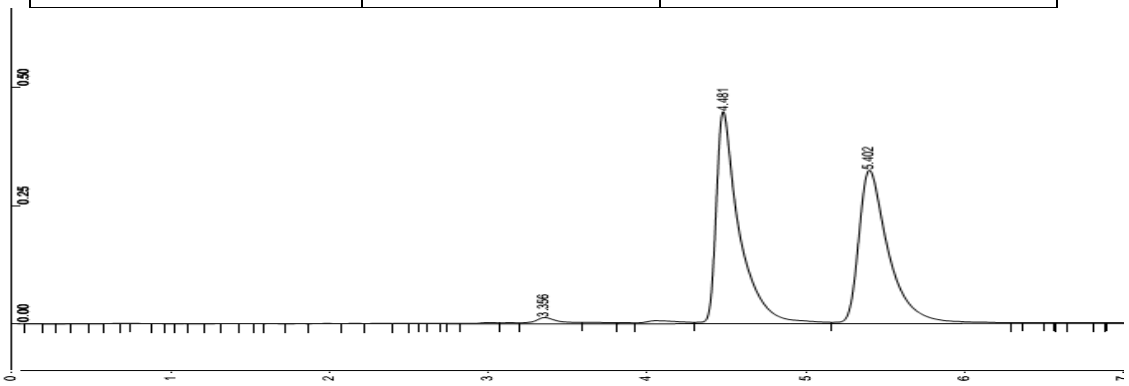


2l

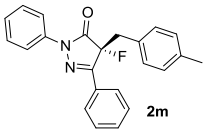
(*R*)-4-(3,5-bis(bromo) benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5 (4*H*)-one (2l). White solid, m.p. 103-105 °C; $[\alpha]_D^{25}$ +53.8 (*c* 0.62, $CHCl_3$); 98% yield, 90% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.70 (m, 2H), 7.67 – 7.58 (m, 2H), 7.51 – 7.40 (m, 3H), 7.39 – 7.26 (m, 3H), 7.18 – 7.12 (m, 1H), 6.90 (d, *J* = 1.7 Hz, 2H), 3.53 – 3.25 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ166.40 (d, *J* = 21.5 Hz), 152.85 (d, *J* = 13.6 Hz), 135.52, 132.91, 132.81, 132.68, 130.78, 130.46, 128.22, 128.07, 128.06, 127.96, 125.60, 125.58, 125.23, 121.68, 118.42, 94.52, 92.51, 39.14 (d, *J* = 27.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -163.81(s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = 4.51 min, τR (minor) = 5.43 min. HRMS Calcd. for $[C_{22}H_{15}Br_2FN_2O+Na]^+$ requires m/z = 522.9433, found m/z = 522.9439.



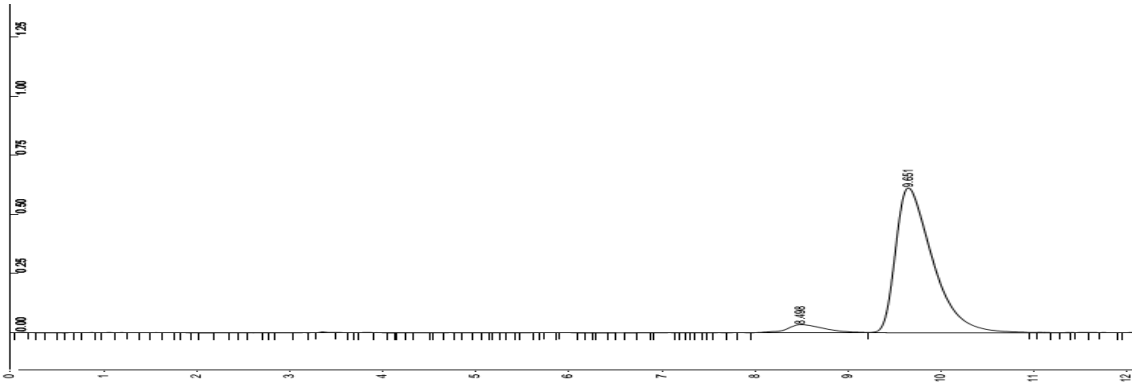
R.Time	Area	Area%
4.516	**71101400**	**94.8205**
5.431	**3883861**	**5.1795**



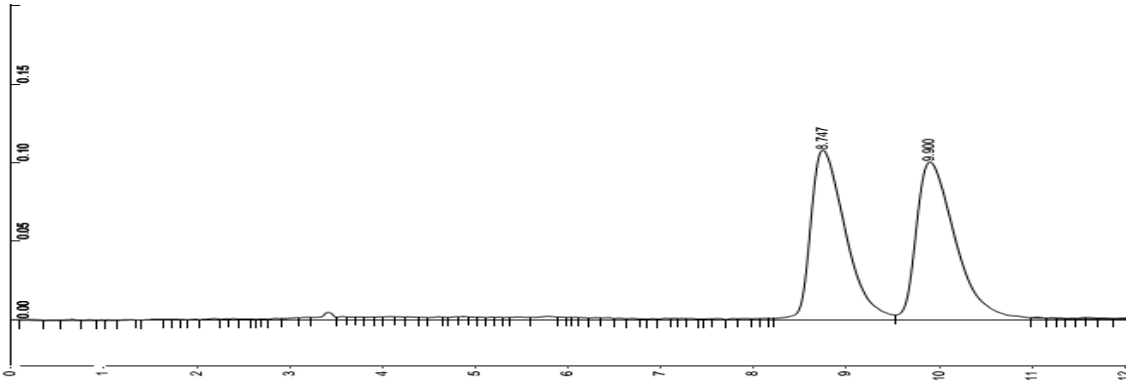
R.Time	Area	Area%
4.481	**45264252**	**50.1031**
5.402	**45077966**	**49.8969**



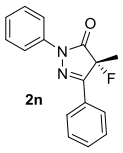
(*R*)-4-(4-methyl benzyl)-4-fluoro-1,3-diphenyl-1*H*-pyrazol-5 (4*H*)-one. Brown solid, m.p. 104-106 °C; $[\alpha]_D^{25}$ +48.2 (*c* 0.40, $CHCl_3$); 98% yield, 90% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.77 (m, 2H), 7.65 – 7.54 (m, 2H), 7.48 – 7.37 (m, 3H), 7.33 – 7.23 (m, 2H), 7.14 – 7.04 (m, 1H), 6.81 (d, *J* = 7.8 Hz, 2H), 6.74 – 6.64 (m, 2H), 3.68 – 3.30 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.14 (d, *J* = 21.5 Hz), 154.24 (d, *J* = 13.9 Hz), 137.63, 136.96, 131.13, 129.80, 129.49, 129.14, 129.11, 128.86, 126.71, 126.69, 126.60, 125.90, 119.39, 96.39, 94.41, 40.71 (d, *J* = 26.0 Hz), 21.07. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -161.89 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 98 / 2, 1 mL / min, 254 nm, τR (major) = 9.65 min, τR (minor) = 8.49 min. HRMS Calcd. for $[C_{23}H_{19}FN_2O+Na]^+$ requires m/z = 381.1379, found m/z = 381.1374.



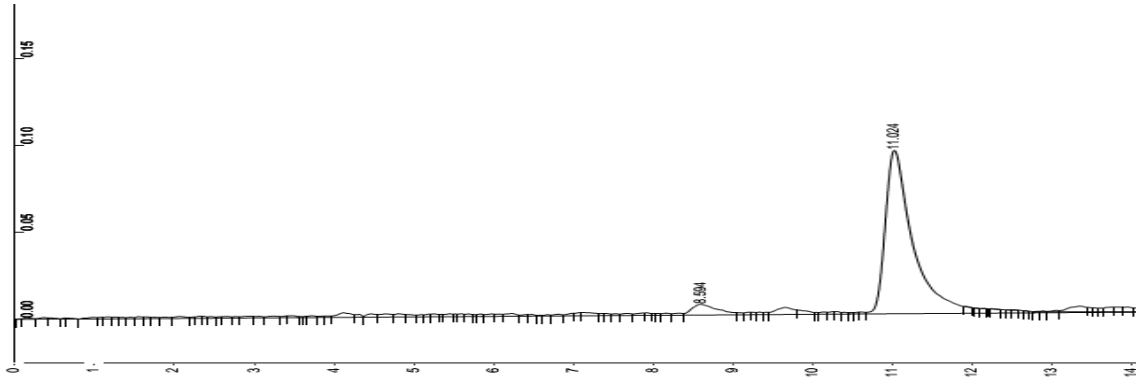
R.Time	Area	Area%
8.498	**6773943**	**4.4512**
9.651	**14466760**	**95.5488**



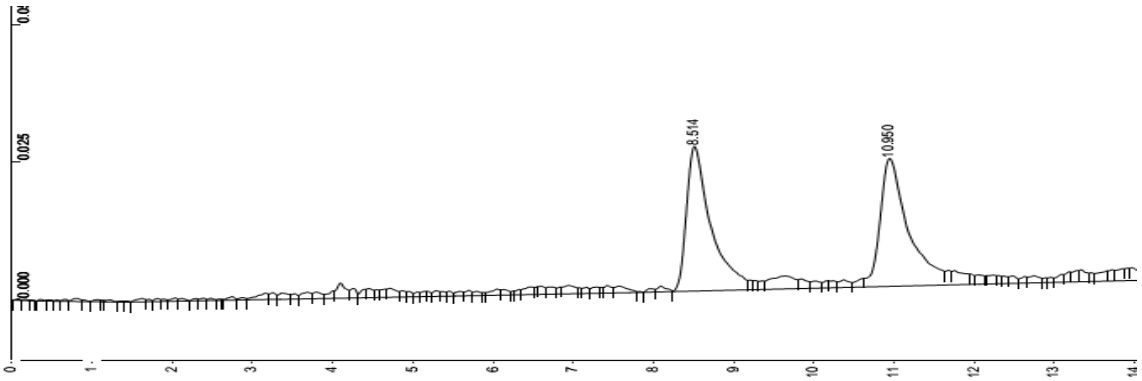
R.Time	Area	Area%
46.1073	**28154166**	**46.1073**
53.8926	**32908040**	**53.8926**



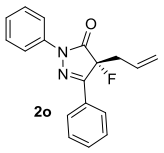
(*R*)-4-fluoro-4-methyl-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2n). Light yellow solid, m.p. 80-82 °C; $[\alpha]_D^{25}$ +27.4 (*c* 0.38, $CHCl_3$); 99% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (tdd, *J* = 6.3, 2.9, 1.1 Hz, 4H), 7.57 – 7.36 (m, 5H), 7.30 – 7.20 (m, 1H), 1.88 (d, *J* = 22.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.65 (d, *J* = 22.0 Hz), 155.61 (d, *J* = 14.5 Hz), 137.42, 131.26, 129.05, 129.01, 128.54, 128.53, 126.69, 126.67, 125.77, 118.80, 93.70, 91.77, 29.70, 21.42 (d, *J* = 26.5 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -163.74 (s, 1H). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 98 / 2, 0.8 mL / min, 254 nm, τR (major) = 11.02 min, τR (minor) = 8.59 min. HRMS Calcd. for $[C_{16}H_{13}FN_2O+Na]^+$ requires m/z = 291.0910, found m/z = 291.0916.



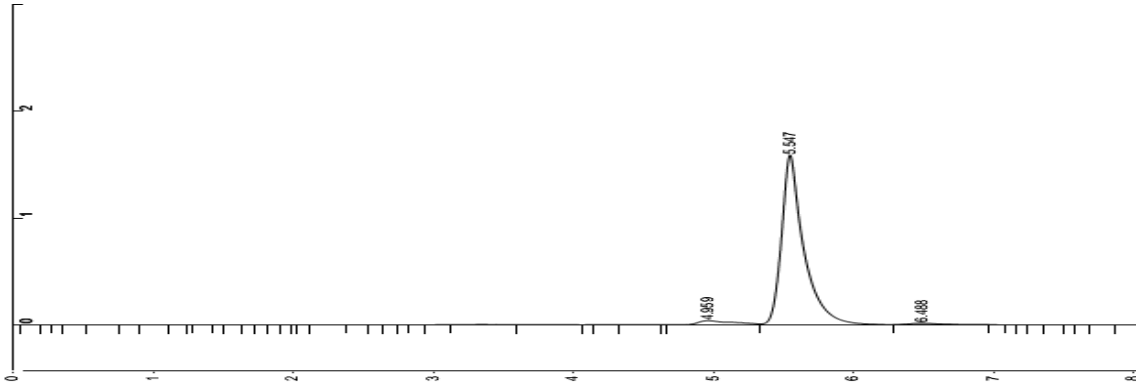
R.Time	Area	Area%
8.594	**1338913**	**4.0330**
11.024	**31860020**	**95.9670**



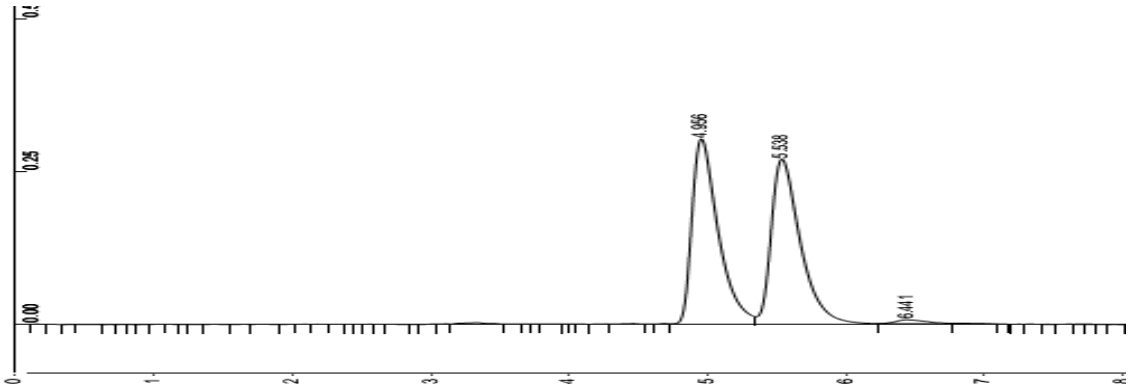
R.Time	Area	Area%
8.514	**5533149**	**49.6385**
10.950	**5613752**	**50.3615**



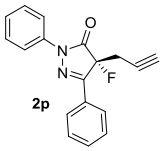
(*R*)-4-fluoro-4-allyl-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2o). Colorless oil; $[\alpha]_D^{25}$ +64.5 (*c* 0.31, $CHCl_3$); 92% yield, 94% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.82 (m, 4H), 7.56 – 7.38 (m, 5H), 7.24 (d, *J* = 7.5 Hz, 1H), 5.54 – 5.32 (m, 1H), 5.22 – 4.92 (m, 2H), 3.18 – 2.89 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.90 (d, *J* = 21.7 Hz), 154.26 (d, *J* = 13.9 Hz), 137.23, 131.23, 129.06, 128.99, 128.94, 126.63, 126.62, 126.37, 126.26, 125.82, 122.71, 118.94, 95.41, 93.43, 39.16 (d, *J* = 26.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -164.30 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 5.54 min, τR (minor) = 4.95 min. HRMS Calcd. for $[C_{18}H_{15}FN_2O+Na]^+$ requires m/z = 317.1066, found m/z = 317.1062.



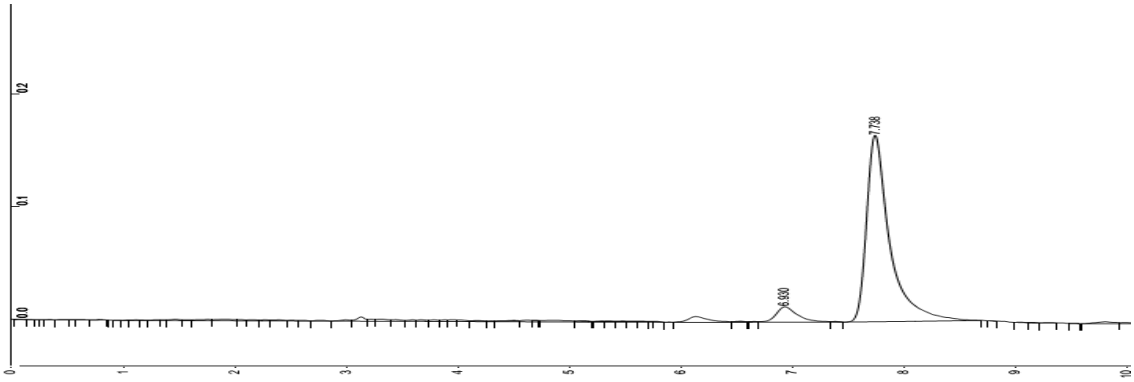
R.Time	Area	Area%
4.959	**7189615**	**3.0152**
5.547	**231256093**	**96.9848**



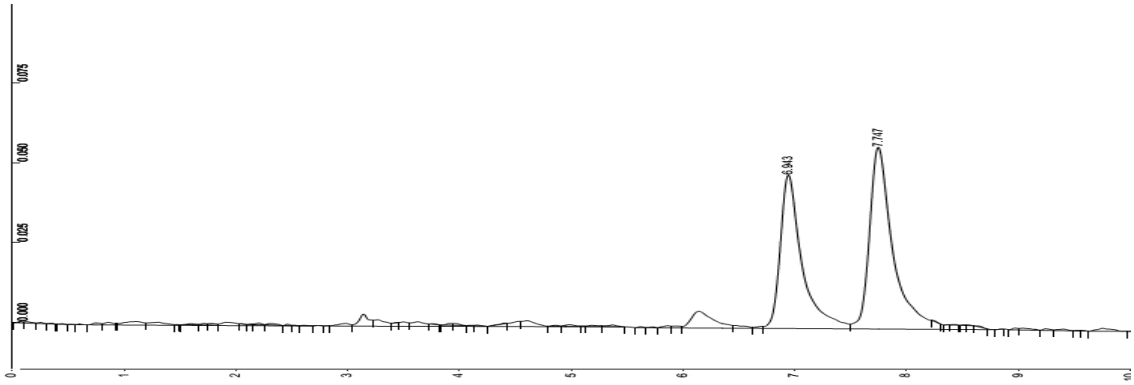
R.Time	Area	Area%
4.956	**40182424**	**49.1460**
5.538	**40569900**	**50.8540**



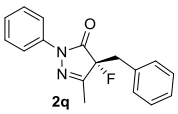
(*R*)-4-fluoro-4-propargyl-1,3-diphenyl-1*H*-pyrazol-5(4*H*)-one (2p). Colorless oil; $[\alpha]_D^{25}$ +57.3 (*c* 0.25, $CHCl_3$); 94% yield, 89% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (ddt, *J* = 15.4, 7.9, 1.2 Hz, 4H), 7.58 – 7.39 (m, 5H), 7.30 – 7.26 (m, 1H), 3.27 (ddd, *J* = 15.8, 8.1, 2.8 Hz, 1H), 3.12 (ddd, *J* = 15.8, 7.5, 2.8 Hz, 1H), 1.93 (t, *J* = 2.7 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ165.82 (d, *J* = 21.0 Hz), 152.35 (d, *J* = 13.4 Hz), 136.08, 130.33, 128.07, 127.99, 127.56, 127.54, 125.56, 125.54, 124.94, 118.04, 92.99, 91.00, 72.12 (d, *J* = 19.0 Hz), 71.90 (d, *J* = 2.6 Hz), 24.30 (d, *J* = 34.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -164.40 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = 7.73 min, τR (minor) = 6.93 min. HRMS Calcd. for $[C_{18}H_{13}FN_2O+Na]^+$ requires m/z = 315.0910, found m/z = 315.0914.



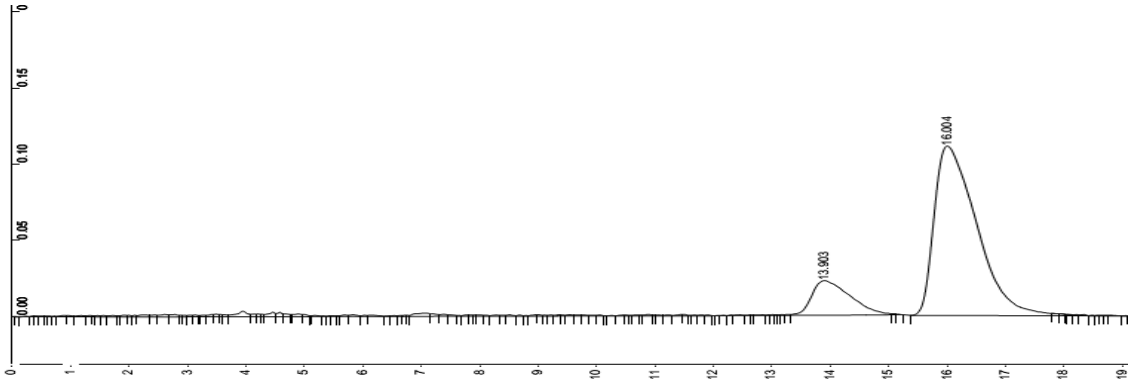
R.Time	Area	Area%
6.930	**1801908**	**5.2195**
7.738	**32720709**	**94.7805**



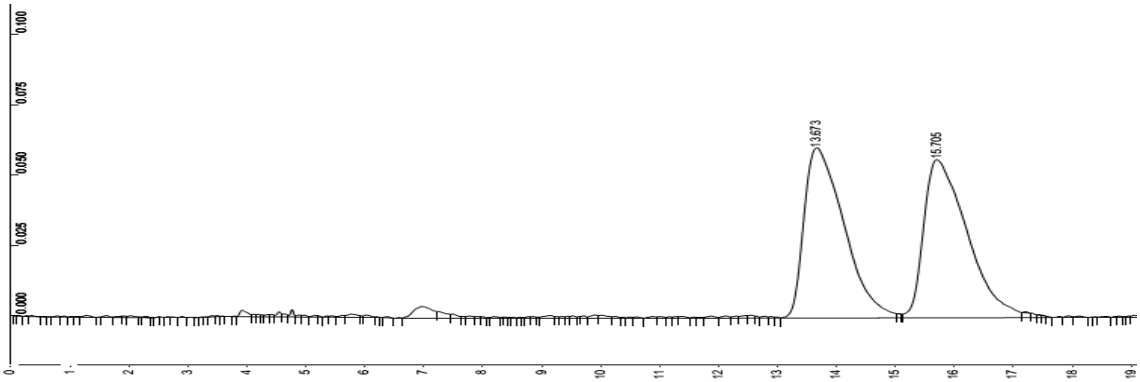
R.Time	Area	Area%
6.943	**6479264**	**48.1015**
7.747	**6990719**	**51.8985**



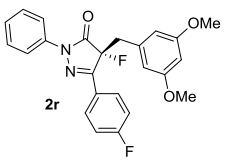
(*R*)-4-benzyl-4-fluoro-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2q). Colorless oil; $[\alpha]_D^{25}$ +29.6 (*c* 0.21, $CHCl_3$); 95% yield, 72% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.59 (m, 2H), 7.40 – 7.30 (m, 2H), 7.29 – 7.23 (m, 3H), 7.21 – 7.12 (m, 3H), 3.65 – 3.10 (m, 2H), 2.14 (d, *J* = 1.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.97, 130.65, 130.55, 129.76, 128.87, 128.77, 128.06, 125.65, 118.96, 95.52, 93.56, 13.83. ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.79 (d, *J* = 21.0 Hz), 157.01 (d, *J* = 16.4 Hz), 39.41 (d, *J* = 26.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -167.08 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 99 / 1, 1 mL / min, 254 nm, τR (major) = =16.00 min, τR (minor) = 13.90 min. HRMS Calcd. for $[C_{17}H_{15}FN_2O+Na]^+$ requires m/z = 305.1066, found m/z = 315. 305.1071.



R.Time	Area	Area%
13.903	**14.0058**	**10334163**
16.004	**85.9942**	**63450719**

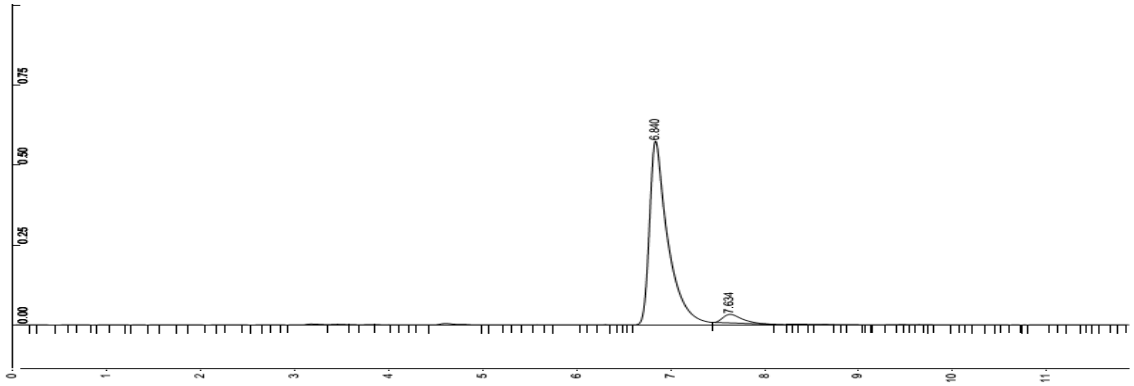


R.Time	Area	Area%
13.673	**28569898**	**49.6354**
15.705	**28989670**	**50.3646**

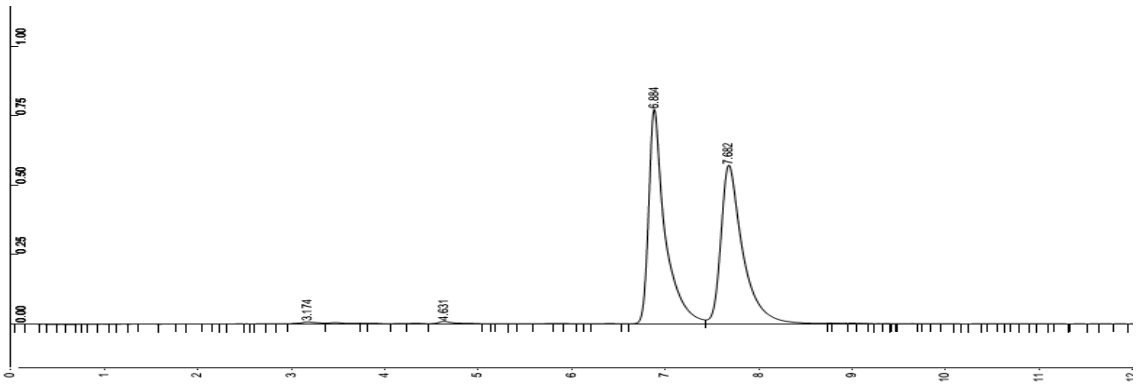


2r

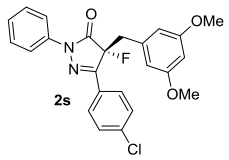
(*R*)-3-(4-fluorophenyl)4-(3,5-bis(methoxyl)benzyl)-4-hydroxy-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2r). White solid, m.p. 131-133 ^{o}C; $[\alpha]_D^{25}$ +79.5 (*c* 0.41, $CHCl_3$); 99% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.65 (m, 3H), 7.59 (dt, *J* = 9.6, 2.1 Hz, 1H), 7.48 (td, *J* = 8.1, 5.7 Hz, 1H), 7.39 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.25 – 7.18 (m, 2H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.3 Hz, 2H), 3.71 – 3.32 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.96 (d, *J* = 21.3 Hz), 164.16, 161.70, 160.57, 153.18 (dd, *J* = 13.9, 3.2 Hz), 136.78, 131.72, 131.60, 131.56, 131.47, 130.82, 130.74, 128.92, 126.07, 122.50, 122.48, 122.45, 119.17, 118.14 (d, *J* = 21.3 Hz), 114.50 – 112.27 (m), 107.43, 100.77, 95.88, 93.89, 55.06, 41.33 (d, *J* = 26.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -110.99 (s, 1F), -162.34 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 ×4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 6.84 min, τR (minor) = 7.63 min. HRMS Calcd. for $[C_{24}H_{20}F_2N_2O_3+H]^+$ requires m/z = 423.1520, found m/z = 423.1523.



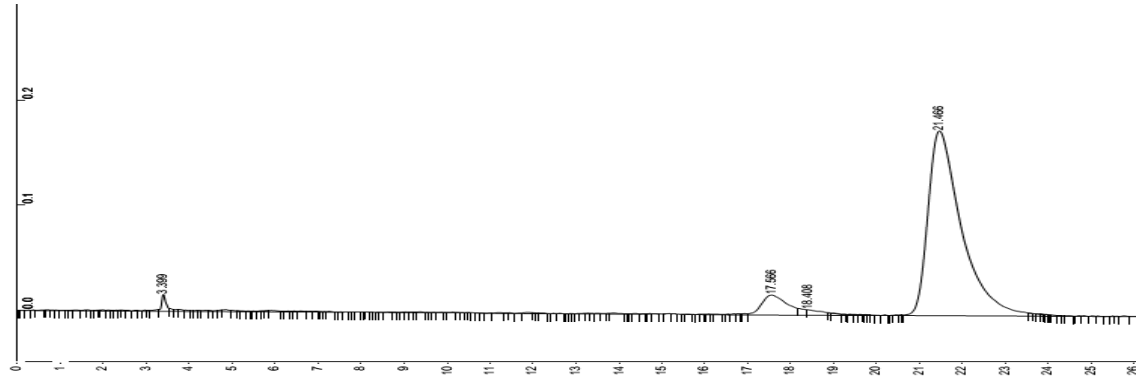
R.Time	Area	Area%
6.840	**81551424**	**96.1530**
7.634	**3262803**	**3.8470**



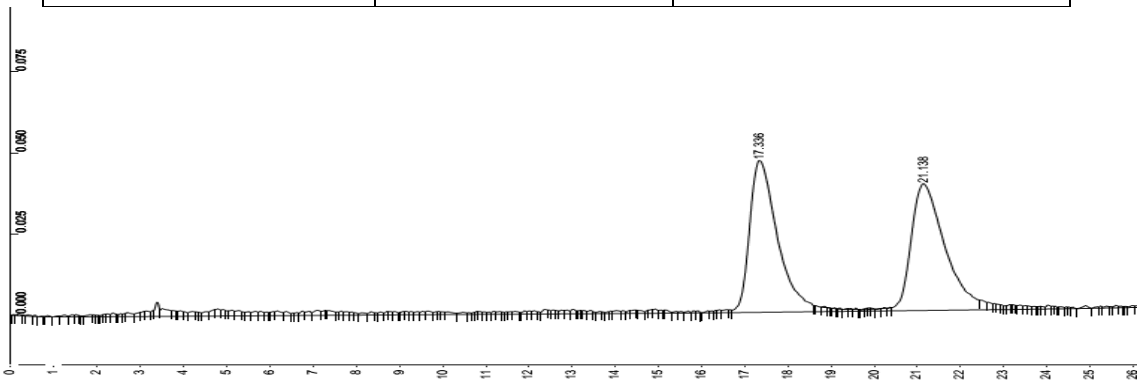
R.Time	Area	Area%
6.884	**94762256**	**50.0017**
7.682	**94755812**	**49.9983**



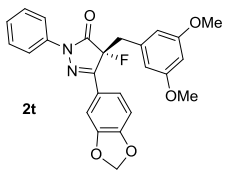
(*R*)-3-(4-chlorophenyl)4-(3,5-bis(methoxyl)benzyl)-4-hydroxy-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2s). White solid, m.p. 122-124°C; $[\alpha]_D^{25}$ +64.3 (*c* 0.40, $CHCl_3$); 97% yield, 86% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.78 (m, 2H), 7.77 – 7.62 (m, 2H), 7.54 – 7.43 (m, 2H), 7.43 – 7.33 (m, 2H), 7.25 – 7.15 (m, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.00 (d, *J* = 2.3 Hz, 2H), 3.65 – 3.33 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.96 (d, *J* = 21.4 Hz), 160.60, 153.32 (d, *J* = 14.0 Hz), 137.26, 136.85, 131.80, 131.69, 129.40, 128.94, 128.04, 128.02, 127.92, 127.90, 126.06, 119.19, 107.52, 100.68, 95.99, 94.01, 55.11, 41.39 (d, *J* = 26.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -162.48 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 98 / 2, 1 mL / min, 254 nm, τR (major) = =21.46 min, τR (minor) = 17.56 min. HRMS Calcd. for $[C_{24}H_{20}FClN_2O_3+H]^+$ requires m/z = 439.1225, found m/z = 439.1221.



R.Time	Area	Area%
17.566	**5635154**	**7.2022**
21.466	**2189058**	**92.7978**

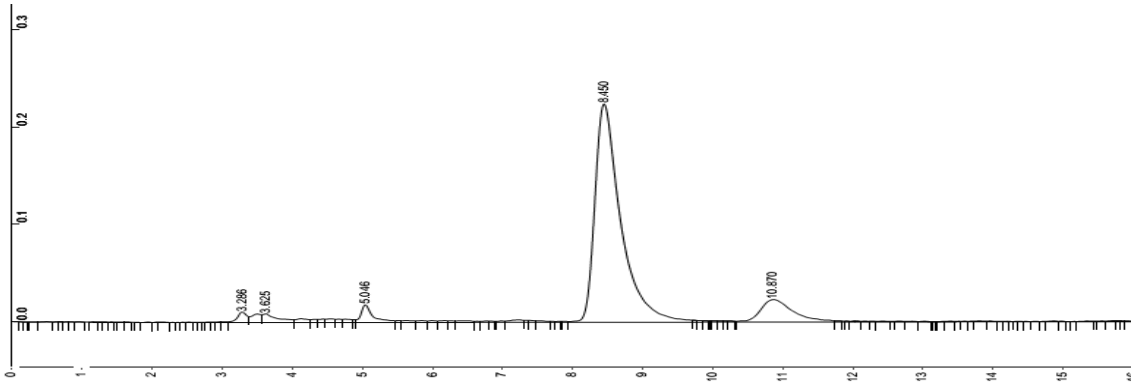


R.Time	Area	Area%
17.336	**21645702**	**50.8739**
21.138	**20902034**	**49.1261**

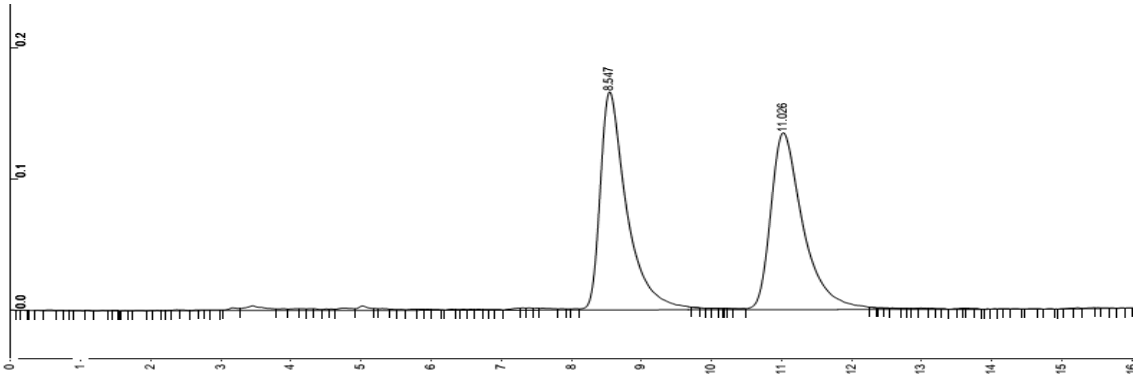


2t

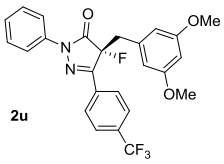
(*R*)-3-(3,4-(methylenedioxy)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2t). Light yellow solid, m.p. 131-133 ^{o}C; $[\alpha]_D^{25}$ +27.5 (*c* 0.57, $CHCl_3$); 98% yield, 86% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.60 (m, 2H), 7.43 (ddd, *J* = 8.2, 1.8, 1.0 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.24 – 7.13 (m, 1H), 6.92 (d, *J* = 8.1 Hz, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.11 – 5.94 (m, 4H), 3.63 – 3.35 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ167.90 (d, *J* = 21.6 Hz), 160.49, 153.86, 153.72, 150.13, 148.43, 136.96, 132.02, 131.90, 128.83, 125.78, 123.71, 123.69, 122.05, 122.02, 119.10, 108.65, 107.53, 106.24, 101.71, 100.61, 96.25, 94.27, 55.09, 41.61 (d, *J* = 26.3 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -161.64 (s, 1F). HPLC conditions: Chiralcel AS-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = =8.45 min, τR (minor) = 10.87 min. HRMS Calcd. for $[C_{25}H_{21}FN_2O_5+Na]^+$ requires m/z = 471.1332, found m/z = 471.1327.



R.Time	Area	Area%
8.450	**58073924**	**93.0720**
10.870	**4355294**	**6.9280**

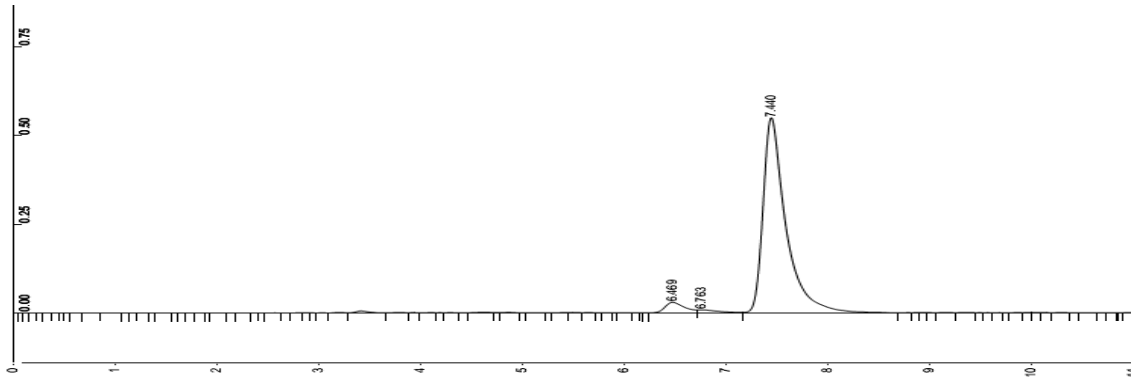


R.Time	Area	Area%
8.547	**44062572**	**50.3372**
11.026	**43472228**	**49.6628**

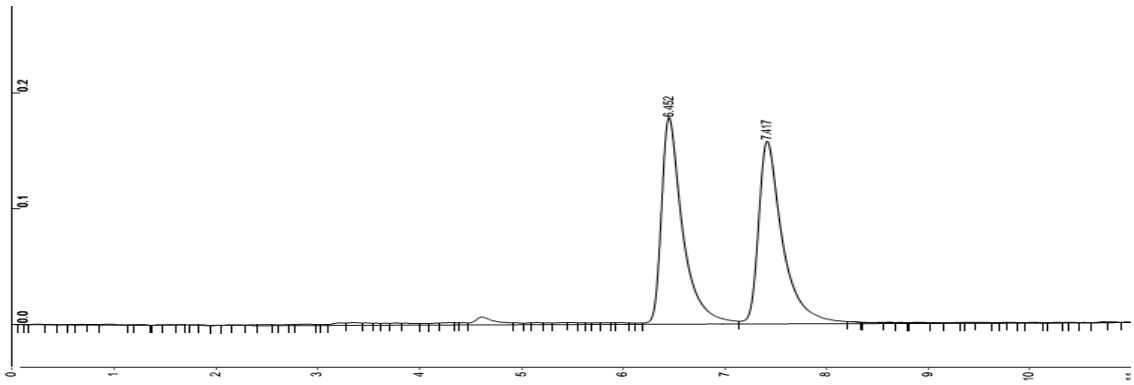


2u

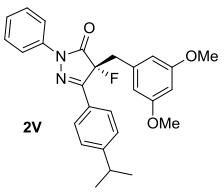
(*R*)-3-(4-trifluoromethylphenyl)4-(3,5-bis(methoxyl)benzyl)-4-hydroxy-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2u).Light yellow solid, m.p. 78-81 ^{o}C; $[\alpha]_D^{25}$ +43.2 (*c* 0.40, $CHCl_3$); 93% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.1 Hz, 2H), 7.73 (dd, *J* = 8.4, 6.9 Hz, 4H), 7.46 – 7.35 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 5.98 (d, *J* = 2.3 Hz, 2H), 3.57 – 3.32 (m, 8H).^{13}C NMR (101 MHz, Chloroform-*d*) δ167.98 (d, *J* = 21.1 Hz), 160.62, 152.98 (d, *J* = 14.1 Hz), 136.73, 132.47 (q, *J* = 32.8 Hz), 128.98, 126.92, 126.91, 126.22, 125.97, 125.93, 123.67 (q, *J* = 1651.3, 817.3 Hz), 119.22, 107.53, 100.64, 95.78, 93.79, 55.04, 41.29 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.99 (s, 3F), -162.75 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = =7.44 min, τR (minor) = 6.46 min. HRMS Calcd. for $[C_{25}H_{20}F_4N_2O_3+Na]^+$ requires m/z = 495.1308, found m/z = 495.1305.



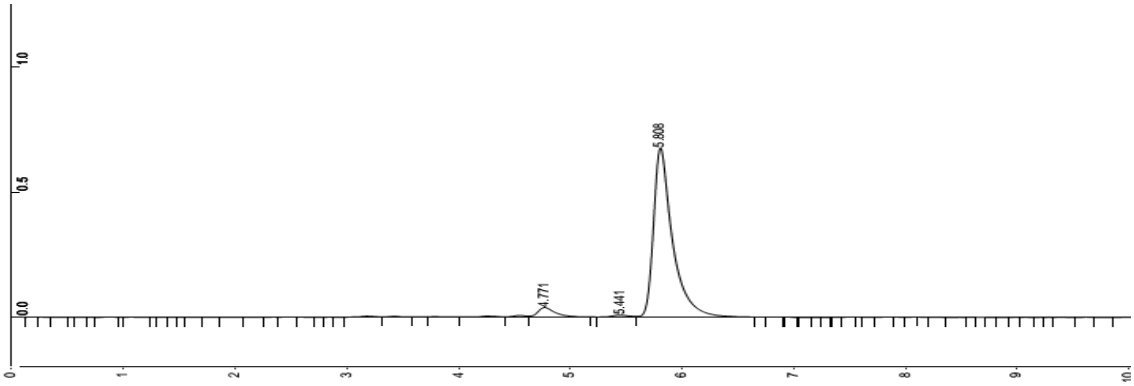
R.Time	Area	Area%
6.469	**4065412**	**4.2335**
7.440	**91964161**	**95.7665**



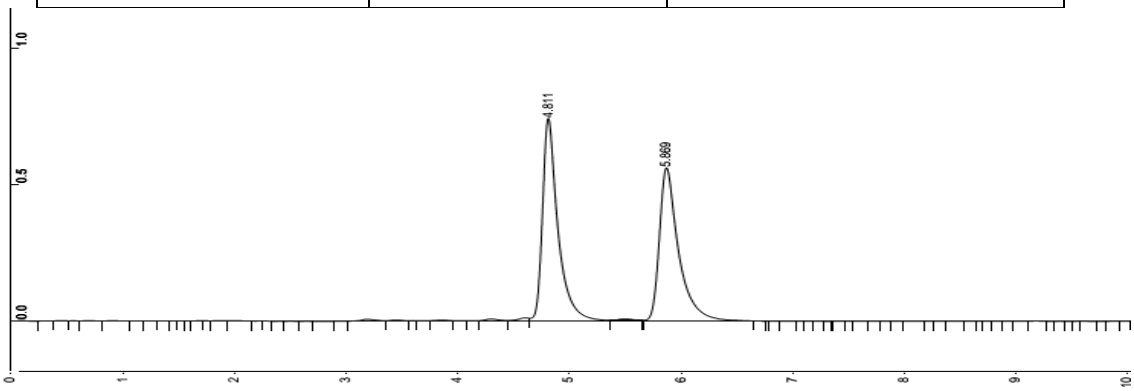
R.Time	Area	Area%
6.452	**25825888**	**49.5009**
7.417	**26346656**	**50.4991**



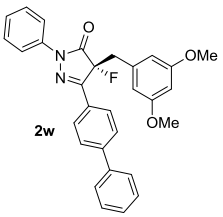
(*R*)-3-(4-isopropylphenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2v). White wax; $[\alpha]_D^{25}$ +52.5 (*c* 0.42, $CHCl_3$); 97% yield, 90% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.78 – 7.66 (m, 2H), 7.45 – 7.30 (m, 4H), 7.24 – 7.09 (m, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.2 Hz, 2H), 3.46 (s, 8H), 3.07 – 2.84 (m, 1H), 1.30 (dd, *J* = 6.9, 1.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.05 (d, *J* = 21.4 Hz), 160.44, 154.31 (d, *J* = 13.8 Hz), 152.41, 137.02, 132.07, 131.95, 128.84, 127.18, 127.12, 126.79, 126.78, 125.78, 119.16, 107.39, 100.93, 96.21, 94.23, 55.00, 41.43 (d, *J* = 26.2 Hz), 34.21, 23.75, 23.74. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -161.86 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) =5.80 min, τR (minor) = 4.77 min. HRMS Calcd. for $[C_{27}H_{27}FN_2O_3+Na]^+$ requires m/z = 469.1903, found m/z = 469.1905.



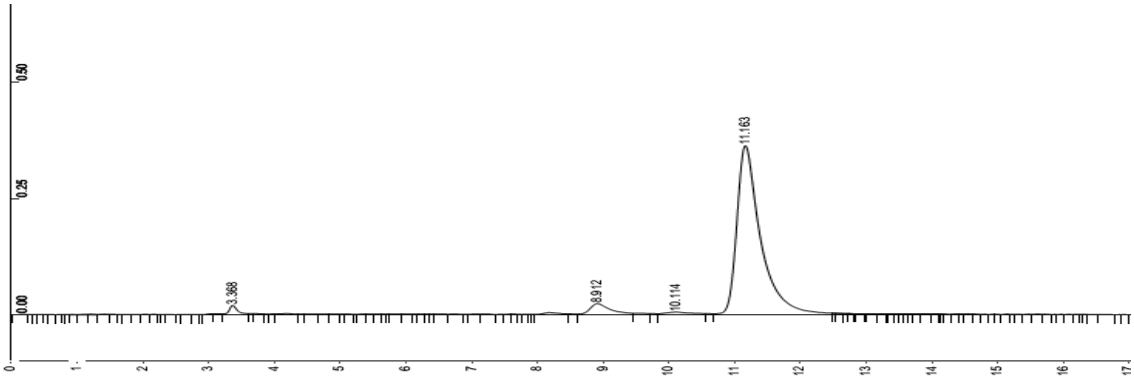
R.Time	Area	Area%
4.771	**4638473**	**4.9705**
5.808	**88681575**	**95.0295**



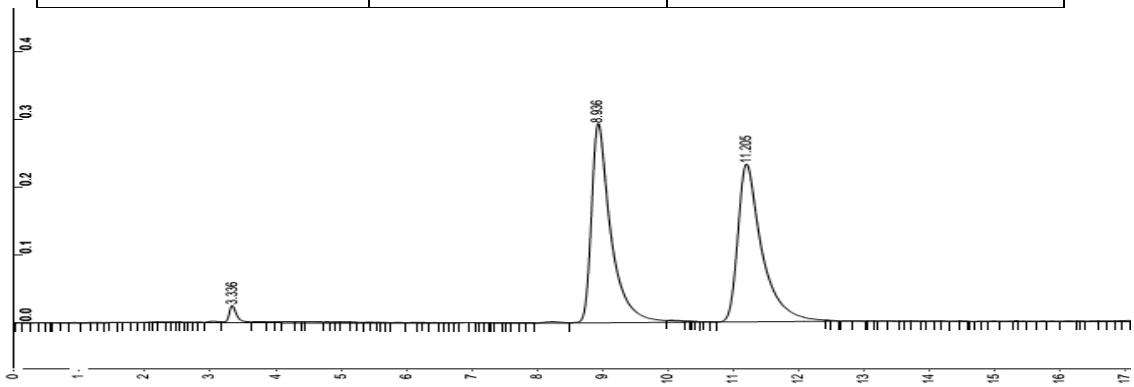
R.Time	Area	Area%
4.811	**72197344**	**51.6427**
5.869	**67604280**	**48.3573**



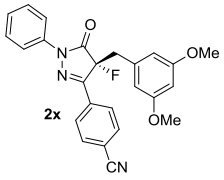
***(R)*-3-(4-(phenyl)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2w).** White solid, m.p. 140-142 ^{o}C; $[\alpha]_D^{25}$ +37.2 (*c* 0.38, $CHCl_3$); 98% yield, 90% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.89 (m, 2H), 7.79 – 7.69 (m, 4H), 7.69 – 7.61 (m, 2H), 7.54 – 7.46 (m, 2H), 7.44 – 7.34 (m, 3H), 7.25 – 7.19 (m, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.05 (d, *J* = 2.3 Hz, 2H), 3.69 – 3.49 (m, 2H), 3.47 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.12 (d, *J* = 21.3 Hz), 160.55, 154.03 (d, *J* = 14.0 Hz), 143.75, 139.90, 137.01, 131.97 (d, *J* = 11.8 Hz), 129.05, 128.92, 128.44, 128.43, 128.18, 127.64, 127.18, 127.16, 127.12, 125.94, 119.23, 107.53, 100.85, 96.22, 94.24, 55.09, 41.52 (d, *J* = 26.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -162.05 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = 11.16 min, τR (minor) = 8.91 min. HRMS Calcd. for $[C_{30}H_{25}FN_2O_3+Na]^+$ requires m/z = 503.1747, found m/z = 503.1743.



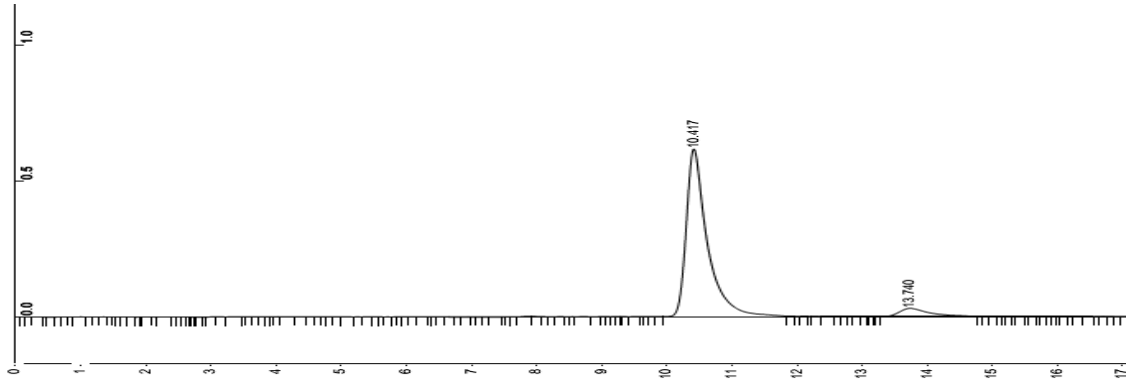
R.Time	Area	Area%
8.912	**1782540**	**5.0578**
11.163	**33460846**	**94.9422**



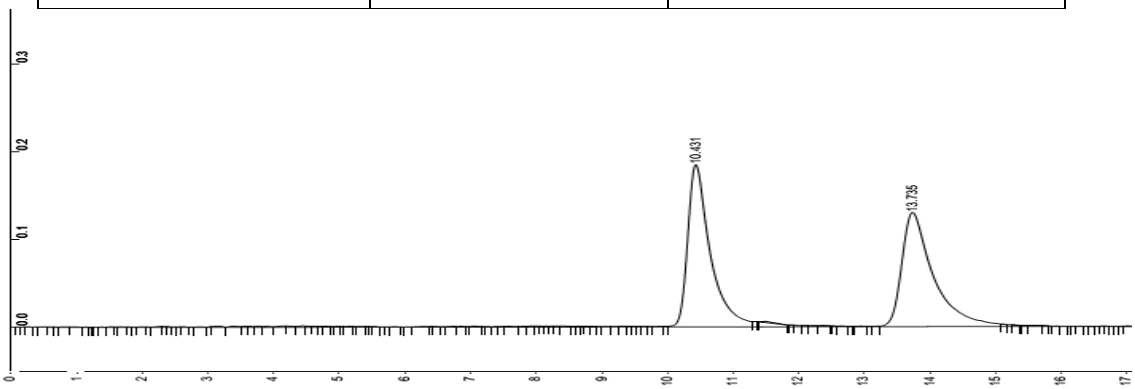
R.Time	Area	Area%
8.936	**60801088**	**50.8094**
11.205	**58863950**	**49.1906**



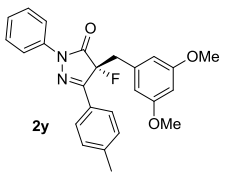
***(R)*-3-(4-(cyano)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2x).** White solid, m.p. 145-147 °C; $[\alpha]_D^{25}$ +38.1 (*c* 0.31, $CHCl_3$); 93% yield, 89% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.82 – 7.64 (m, 4H), 7.46 – 7.35 (m, 2H), 7.31 – 7.18 (m, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 5.97 (d, *J* = 2.3 Hz, 2H), 3.66 – 3.37 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ167.96 (d, *J* = 21.2 Hz), 160.69, 152.52 (d, *J* = 14.1 Hz), 136.63, 133.51, 133.49, 132.71, 131.58, 131.47, 129.04, 127.01, 127.00, 126.39, 119.23, 118.15, 114.22, 107.59, 100.52, 95.64, 93.65, 41.32 (d, *J* = 26.0 Hz), 55.12. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -163.05 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) =10.41 min, τR (minor) = 13.74 min. HRMS Calcd. for $[C_{25}H_{20}FN_3O_3+Na]^+$ requires m/z = 452.1386, found m/z = 452.1389.



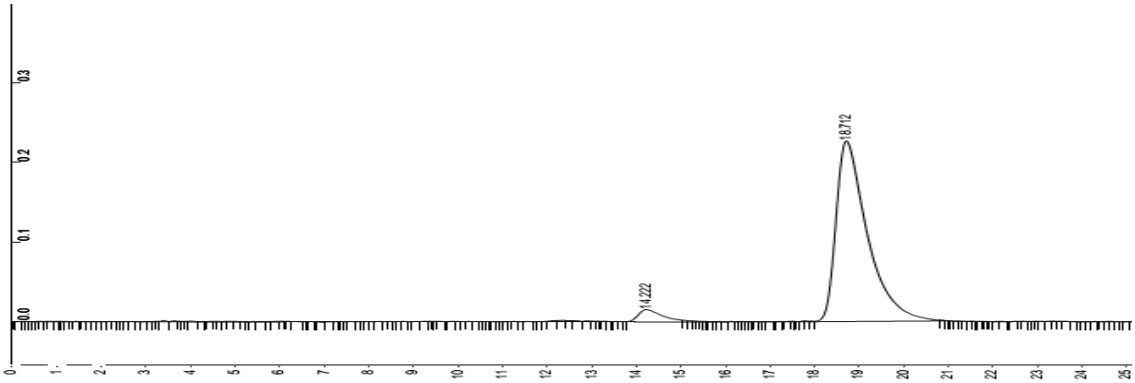
R.Time	Area	Area%
10.417	**142426464**	**94.4466**
13.740	**8374585**	**5.5534**



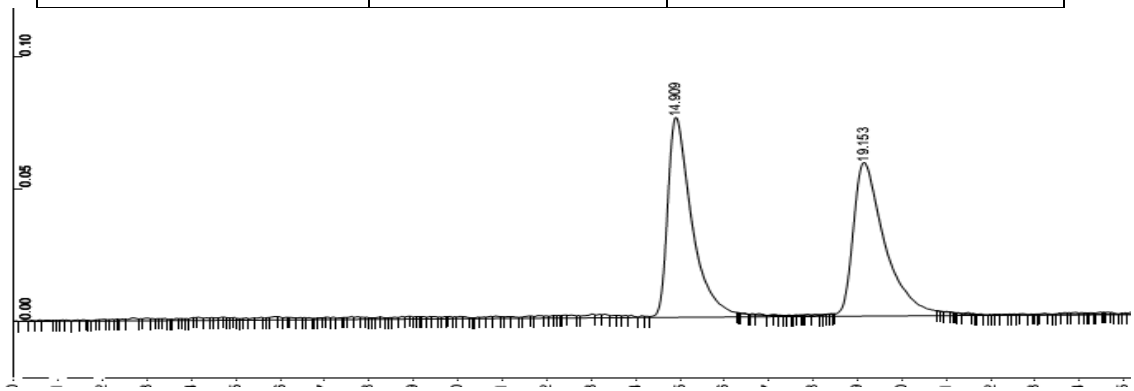
R.Time	Area	Area%
10.431	**45867988**	**51.0201**
13.735	**44033880**	**48.9799**



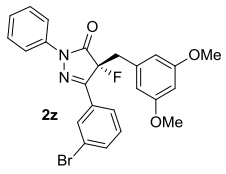
***(R)*-3-(4-(methyl)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2y).** White solid, m.p. 132-135 °C; $[\alpha]_D^{25}$ +42.3 (*c* 0.40, $CHCl_3$); 98% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.57 (m, 2H), 7.35 – 7.26 (m, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.16 – 7.07 (m, 1H), 6.14 (t, *J* = 2.3 Hz, 1H), 5.94 (d, *J* = 2.3 Hz, 2H), 3.55 – 3.32 (m, 8H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.07 (d, *J* = 21.5 Hz), 160.49, 154.33 (d, *J* = 13.9 Hz), 141.63, 137.03, 132.06, 131.93, 129.79, 128.86, 126.81, 126.66, 126.64, 125.82, 119.20, 107.49, 100.79, 96.30, 94.32, 55.08, 41.46 (d, *J* = 26.2 Hz), 21.68. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -161.91 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 98 / 2, 1 mL / min, 254 nm, τR (major) = =18.71 min, τR (minor) = 14.22 min. HRMS Calcd. for $[C_{25}H_{23}FN_2O_3+Na]^+$ requires m/z = 441.1590, found m/z = 441.1587.



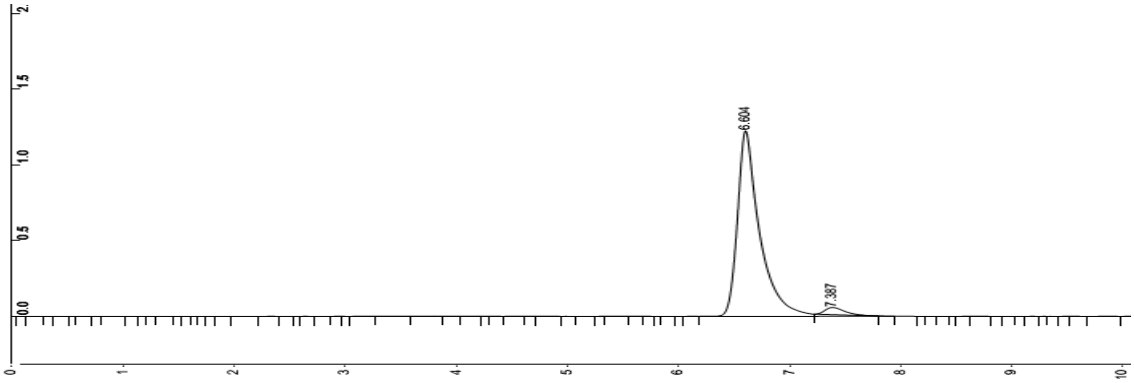
R.Time	Area	Area%
14.222	**5708837**	**4.0023**
18.712	**136930071**	**95.9977**



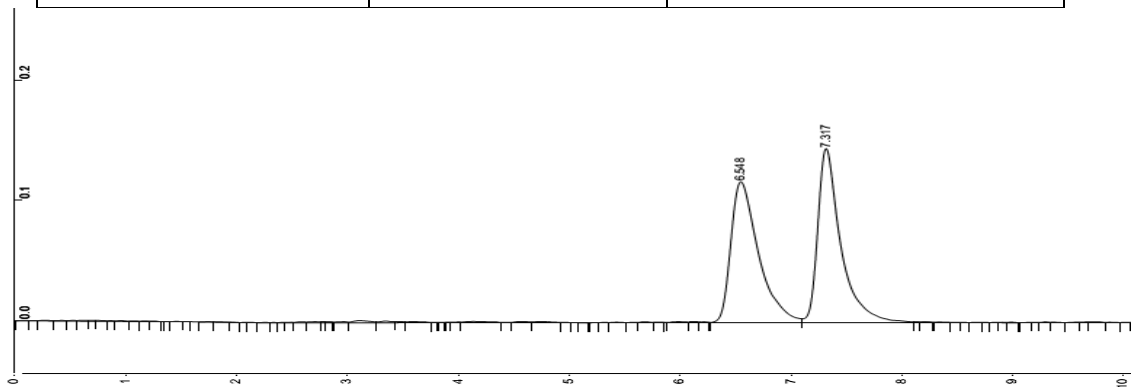
R.Time	Area	Area%
14.909	**29295790**	**50.1869**
19.153	**29077542**	**49.8131**



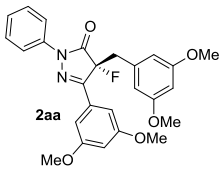
***(R)*-3-(3-(bromo)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2z).** White solid, m.p. 114-117 °C; $[\alpha]_D^{25}$ +51.2 (*c* 0.41, $CHCl_3$); 99% yield, 95% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.60 (m, 2H), 7.59 – 7.50 (m, 1H), 7.30 (dt, *J* = 10.3, 7.7 Hz, 3H), 7.16 (q, *J* = 7.4, 6.2 Hz, 1H), 6.16 (t, *J* = 2.3 Hz, 1H), 5.93 (d, *J* = 2.3 Hz, 2H), 3.55 – 3.31 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ166.91 (d, *J* = 21.3 Hz), 159.55, 151.92 (d, *J* = 13.8 Hz), 135.74, 132.91, 131.02 – 130.16 (m), 129.50, 127.90, 125.06, 124.16 (d, *J* = 2.0 Hz), 122.18, 118.15, 106.44, 99.85, 94.80, 92.82, 54.04, 40.28 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -162.59 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) =6.60 min, τR (minor) = 7.38 min. HRMS Calcd. for $[C_{24}H_{20}BrFN_2O_3+Na]^+$ requires m/z = 505.0539, found m/z = 505.0545.



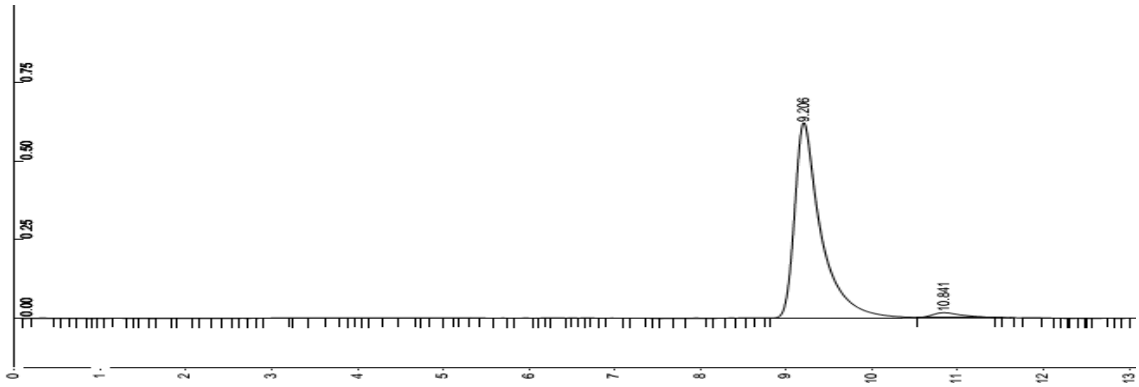
R.Time	Area	Area%
6.604	**171962848**	**97.5073**
7.387	**4396099**	**2.4927**



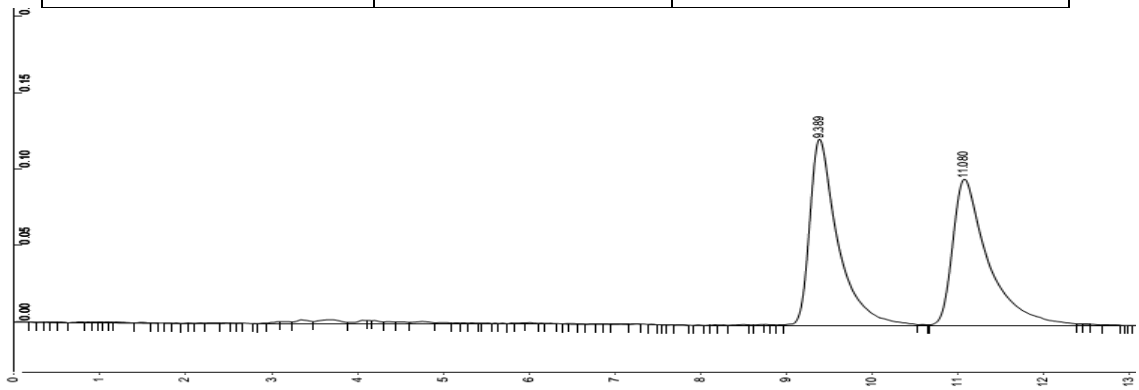
R.Time	Area	Area%
6.548	**20402396**	**49.1906**
7.317	**21073850**	**50.8094**



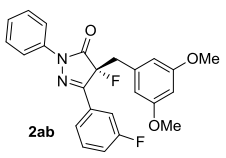
***(R)*-3-(3,5-bis(methoxyl)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2aa).** White solid, m.p. 148-151 °C; $[\alpha]_D^{25}$ +21.2 (*c* 0.40, $CHCl_3$); 98% yield, 96% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.62 (m, 2H), 7.50 (dt, *J* = 8.6, 1.5 Hz, 1H), 7.43 – 7.32 (m, 3H), 7.25 – 7.15 (m, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.04 (d, *J* = 2.3 Hz, 2H), 3.98 (s, 3H), 3.94 (s, 3H), 3.62 – 3.39 (m, 8H). $^{1\ 13}$C NMR (101 MHz, $CDCl_3$) δ168.00 (d, *J* = 21.4 Hz), 160.51, 154.12 (d, *J* = 13.8 Hz), 151.71, 149.52, 136.99, 132.06 (d, *J* = 12.1 Hz), 128.85, 125.86, 122.47, 120.80, 120.77, 119.32, 110.86, 108.54, 107.59, 100.67, 96.35, 94.37, 56.06, 55.09, 41.78. ^{9}F NMR (376 MHz, Chloroform-*d*) δ -161.65 (s, 1F). (d, *J* = 26.2 Hz). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = 9.20 min, τR (minor) = 10.84 min. HRMS Calcd. for $[C_{26}H_{25}FN_2O_5+Na]^+$ requires m/z = 487.1645, found m/z = 487.1641.



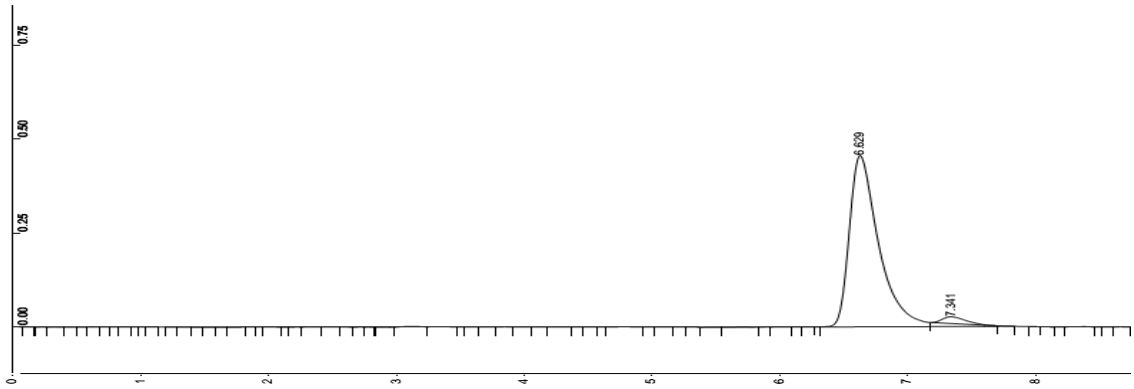
R.Time	Area	Area%
9.206	**133625192**	**98.0071**
10.841	**2717167**	**1.9929**



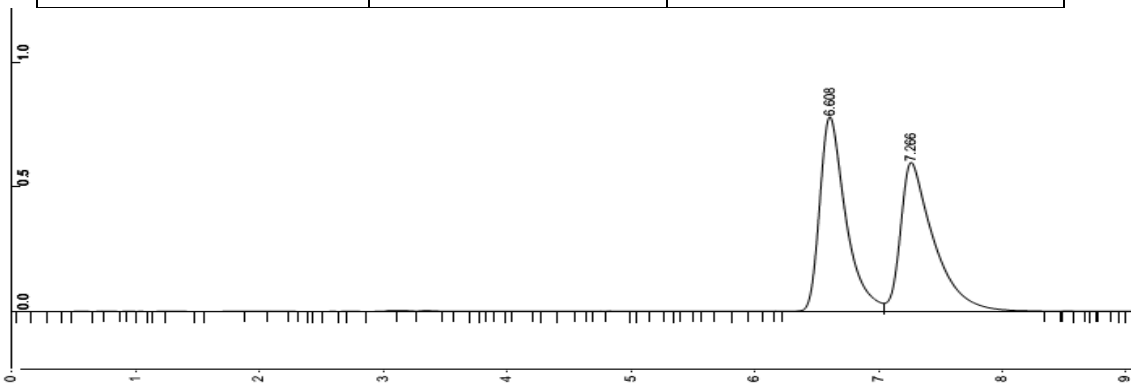
R.Time	Area	Area%
9.389	**29927560**	**50.2301**
11.080	**27671706**	**49.7699**



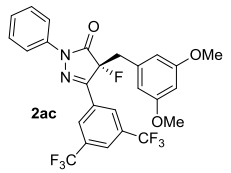
***(R)*-3-(3-(fluoro)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2ab).** White wax; $[\alpha]_D^{25}$ +17.8 (*c* 0.40, $CHCl_3$); 98% yield, 94% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.64 (m, 3H), 7.59 (dt, *J* = 9.7, 2.1 Hz, 1H), 7.48 (td, *J* = 8.1, 5.7 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.25 – 7.17 (m, 2H), 6.23 (t, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.3 Hz, 2H), 3.63 – 3.39 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.99 (d, *J* = 21.2 Hz), 164.19, 161.73, 160.60, 153.20 (d, *J* = 10.9 Hz), 136.81, 132.33 – 131.31 (m), 130.81 (d, *J* = 8.1 Hz), 128.95, 126.10, 122.53, 122.51, 122.49, 119.20, 118.17 (d, *J* = 21.3 Hz), 113.40 (d, *J* = 23.3 Hz), 107.46, 100.80, 95.90, 93.92, 55.08, 41.36 (d, *J* = 26.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.00 (s, 1F) , -162.32 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 6.62 min, τR (minor) = 7.34 min. HRMS Calcd. for $[C_{24}H_{20}F_2N_2O_3+Na]^+$ requires m/z = 445.1340, found m/z = 445.1336.



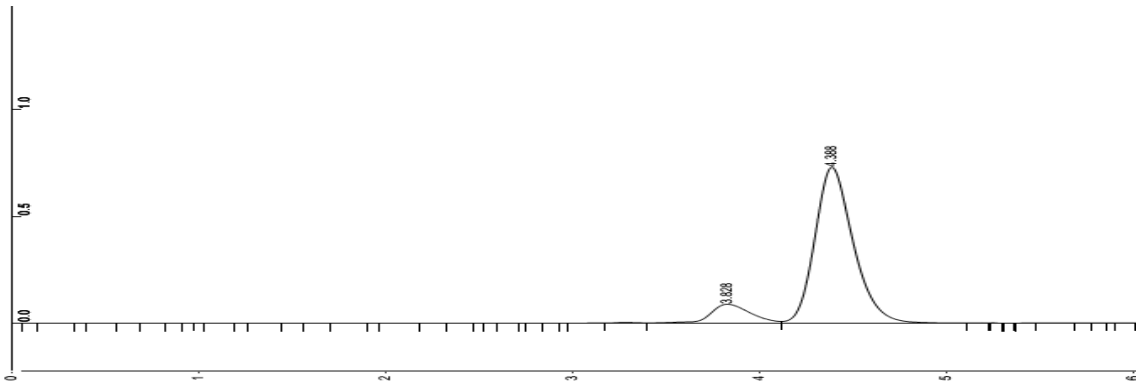
R.Time	Area	Area%
6.629	**74521648**	**97.0382**
7.341	**2274514**	**2.9618**



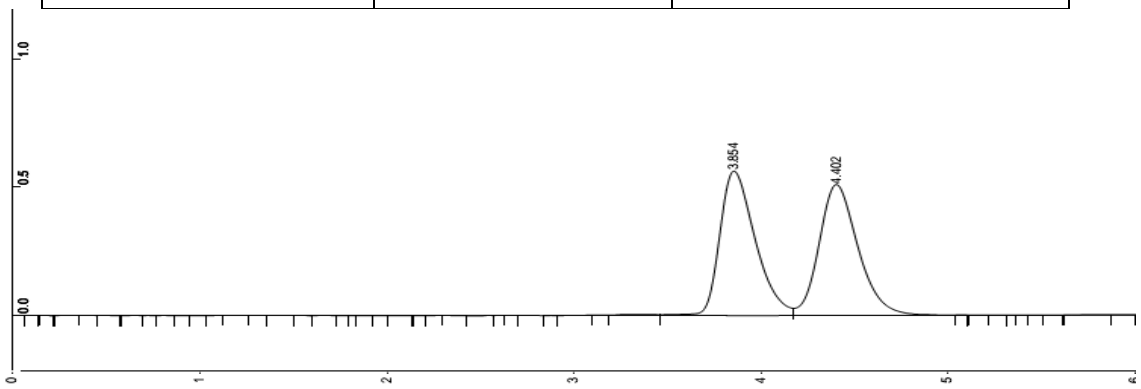
R.Time	Area	Area%
6.608	**114577792**	**50.3311**
7.266	**113070384**	**49.6689**



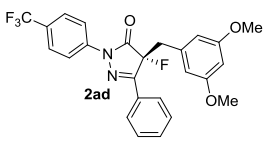
(*R*)-3-(3,5-bis(trifluoromethyl)phenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-1-phenyl-1*H*-pyrazol-5(4*H*)-one (2ac). White solid, m.p. 63-65 ^{o}C; $[\alpha]_D^{25}$ +39.5 (*c* 0.40, $CHCl_3$); 98% yield, 80% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.20 – 8.06 (m, 2H), 7.95 (s, 1H), 7.83 – 7.68 (m, 2H), 7.51 – 7.31 (m, 2H), 7.34 – 7.26 (m, 1H), 6.23 (t, *J* = 2.3 Hz, 1H), 5.99 (d, *J* = 2.3 Hz, 2H), 3.61 – 3.40 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.89 (d, *J* = 21.2 Hz), 160.78, 152.06 (d, *J* = 14.4 Hz), 136.58, 132.48 (q, *J* = 33.9 Hz), 131.91 – 131.45 (m), 129.12, 126.54, 126.35, 124.17, 123.99, 107.78, 100.45, 95.45, 93.46, 55.04, 41.45 (d, *J* = 25.6 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.99 (s, 6F) , -164.91 (s, 1F). HPLC conditions: Chiralcel AS-H column (250 × 4.6 mm), hexane /*i*-PrOH = 95 / 5, 1 mL / min, 254 nm, τR (major) = 4.38 min, τR (minor) = 3.82 min. HRMS Calcd. for $[C_{26}H_{19}F_7N_2O_3+Na]^+$ requires m/z = 563.1182, found m/z = 563.1186.



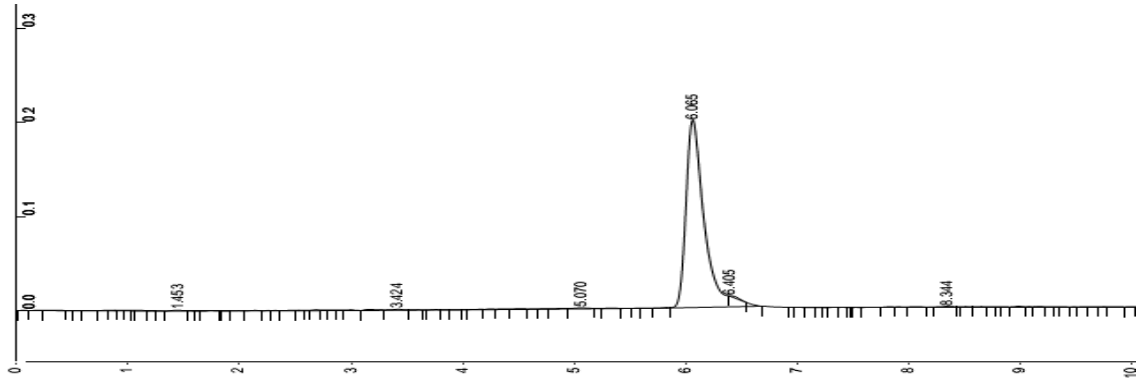
R.Time	Area	Area%
3.828	**13386573**	**10.0049**
4.388	**107033578**	**79.9951**



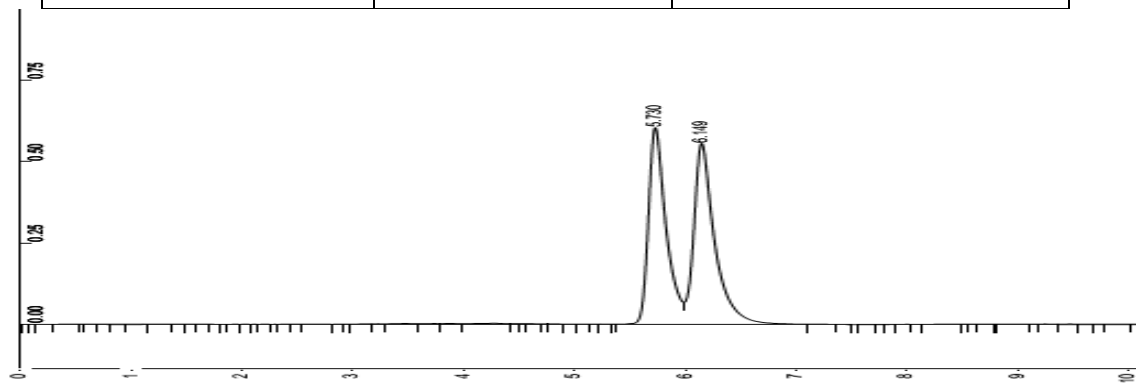
R.Time	Area	Area%
3.854	**73959952**	**50.0547**
4.402	**73798304**	**49.9453**



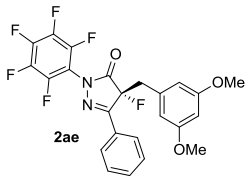
(*R*)-1-(4-trifluoromethylphenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-3-phenyl-1*H*-pyrazol-5(4*H*)-one (2ad). Brown oil, $[\alpha]_D^{25}$ +19.3 (*c* 0.40, $CHCl_3$); 98% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.87 (m, 4H), 7.67 – 7.60 (m, 2H), 7.57 – 7.49 (m, 3H), 6.21 (t, *J* = 2.3 Hz, 1H), 5.98 (d, *J* = 2.3 Hz, 2H), 3.61 – 3.35 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.33 (d, *J* = 21.6 Hz), 160.56, 154.82 (d, *J* = 13.9 Hz), 139.69, 131.52, 131.49, 129.17, 128.23 – 126.91 (m), 126.80, 126.78, 126.15, 126.12, 118.45, 107.42, 100.75, 96.18, 94.19, 55.05, 41.37 (d, *J* = 26.1 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.25 (s, 3F), -161.37 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 80 / 20, 1 mL / min, 254 nm, τR (major) = 6.06min, τR (minor) = 6.40 min. HRMS Calcd. for $[C_{25}H_{20}F_4N_2O_3+Na]^+$ requires m/z = 495.1308, found m/z = 495.1311.



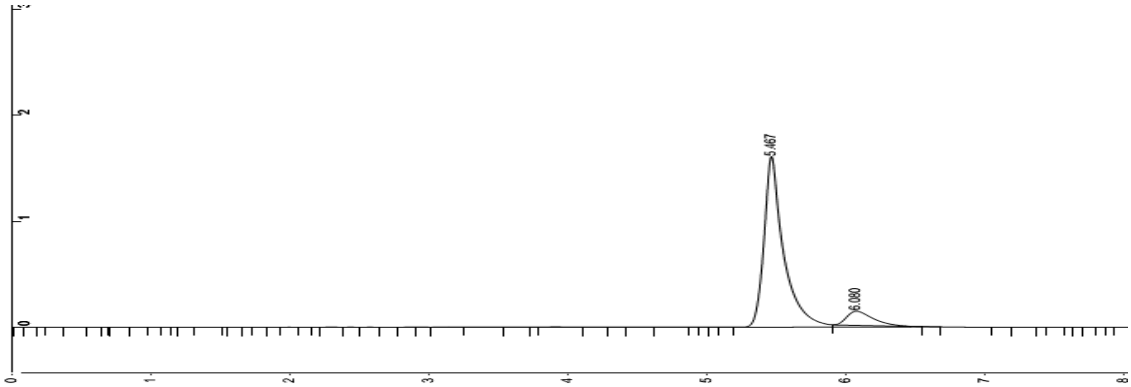
R.Time	Area	Area%
6.065	**22825084**	**96.1051**
6.405	**925043**	**3.8949**



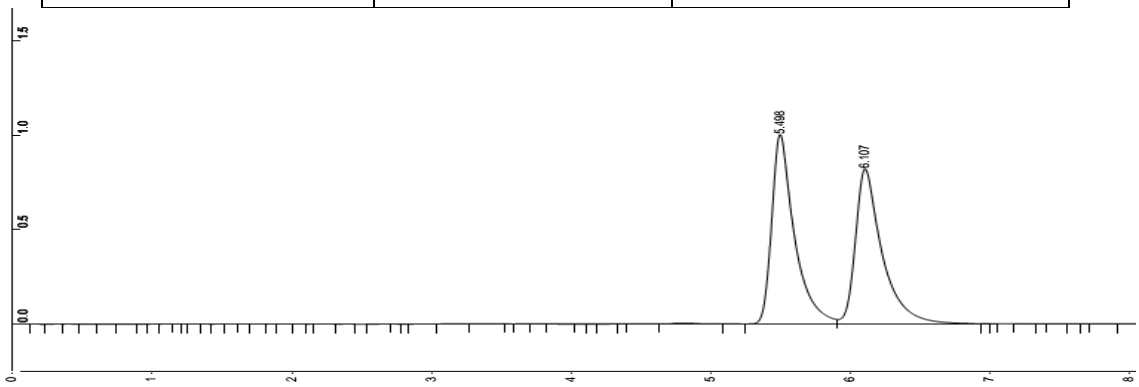
R.Time	Area	Area%
5.730	**66959468**	**47.7232**
6.149	**73348640**	**52.2768**



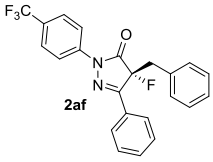
(*R*)-1-(2,3,4,5,6-fluorolphenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-3-phenyl-1*H*-pyrazol-5(4*H*)-one (2ae). White wax, $[\alpha]_D^{25}$ +57.1 (*c* 0.40, $CHCl_3$); 92% yield, 83% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.72 (m, 2H), 7.57 – 7.33 (m, 3H), 6.25 (t, *J* = 2.3 Hz, 1H), 5.96 (d, *J* = 2.2 Hz, 2H), 3.56 – 3.41 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.53 (d, *J* = 21.6 Hz), 159.72, 154.90 (d, *J* = 14.1 Hz), 144.05 (dd, *J* = 12.0, 4.1 Hz), 142.66 – 140.89 (m), 141.46 – 138.89 (m), 138.50 – 137.16 (m), 136.44 – 134.59 (m), 130.55, 128.21, 128.08, 128.07, 125.71, 125.70, 106.75, 99.60, 93.51, 91.53, 54.06, 39.96 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -142.54 – 143.00 (m, 2F), -151.62 – 152.05 (m, 1F), -160.88 (s, 1F) , -160.92 – 161.16 (m, 2F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 90 / 10, 1 mL / min, 254 nm, τR (major) = 5.46 min, τR (minor) = 6.08 min. HRMS Calcd. for $[C_{24}H_{16}F_6N_2O_3+Na]^+$ requires m/z = 517.0963, found m/z = 517.0967.



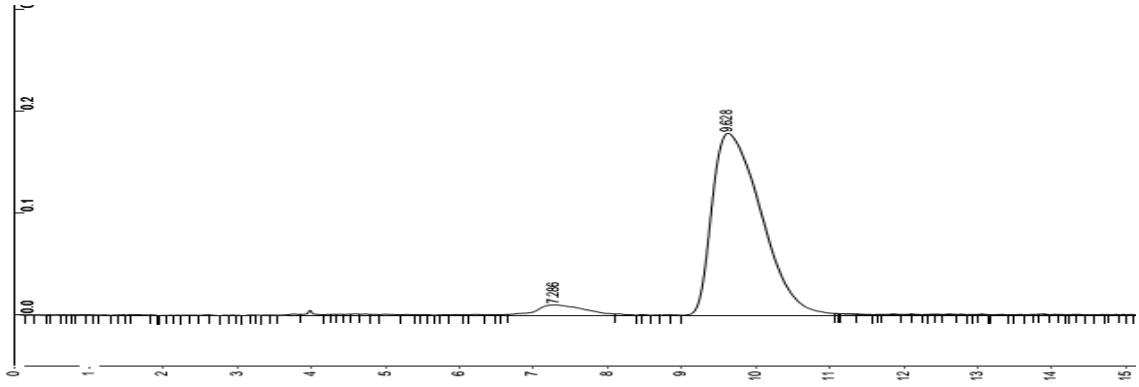
R.Time	Area	Area%
5.467	**161875480**	**91.5702**
6.080	**14901987**	**8.4298**



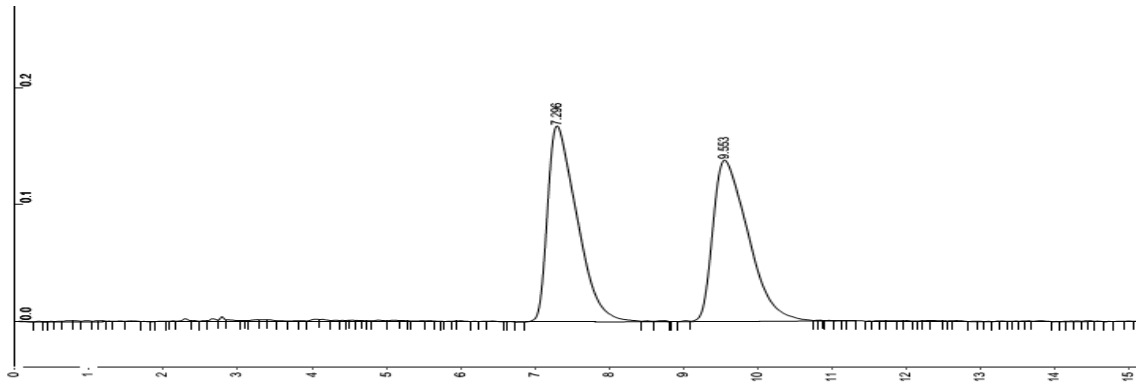
R.Time	Area	Area%
5.498	**113450080**	**50.9616**
6.107	**109168544**	**49.0384**



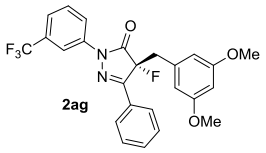
(*R*)-1-(4-trifluoromethylphenyl)4-benzyl-4-fluoro-3-phenyl-1*H*-pyrazol-5(4*H*)-one (2af). Brown oil, $[\alpha]_D^{25}$ +43.2 (*c* 0.40, $CHCl_3$); 97% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.71 (m, 4H), 7.58 – 7.37 (m, 5H), 7.10 – 6.94 (m, 3H), 6.86 – 6.71 (m, 2H), 3.64 – 3.39 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.21 (d, *J* = 21.7 Hz), 153.70 (d, *J* = 14.0 Hz), 138.56, 130.47, 128.81, 128.62, 128.50, 128.17, 128.04 (d, *J* = 1.8 Hz), 127.43, 127.04, 125.75 (d, *J* = 1.8 Hz), 125.07 (q, *J* = 3.8 Hz), 117.49, 95.38, 93.38, 40.16 (d, *J* = 26.0 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.27 (s, 3F), -162.06 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 99 / 1, 1 mL / min, 254 nm, τR (major) = 9.62 min, τR (minor) = 7.28 min. HRMS Calcd. for $[C_{23}H_{16}F_4N_2O+Na]^+$ requires m/z = 435.1096, found m/z = 435.1091.



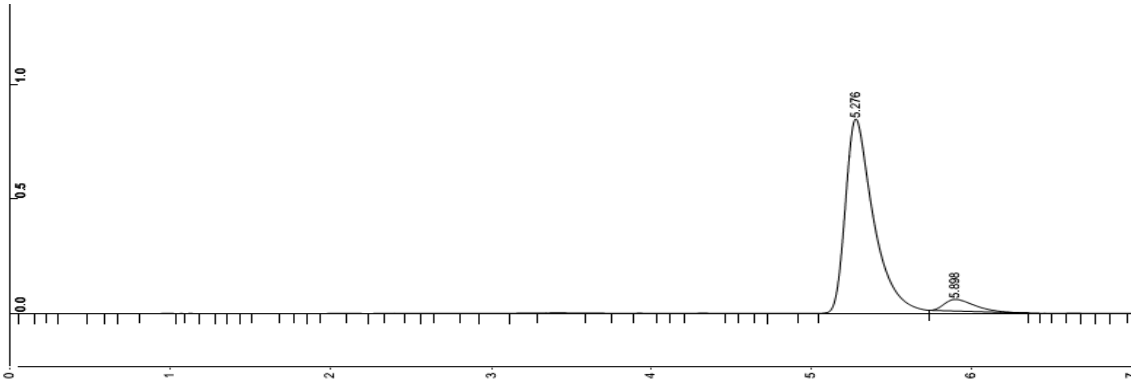
R.Time	Area	Area%
7.286	**4611572**	**4.1560**
9.628	**106350218**	**95.8440**



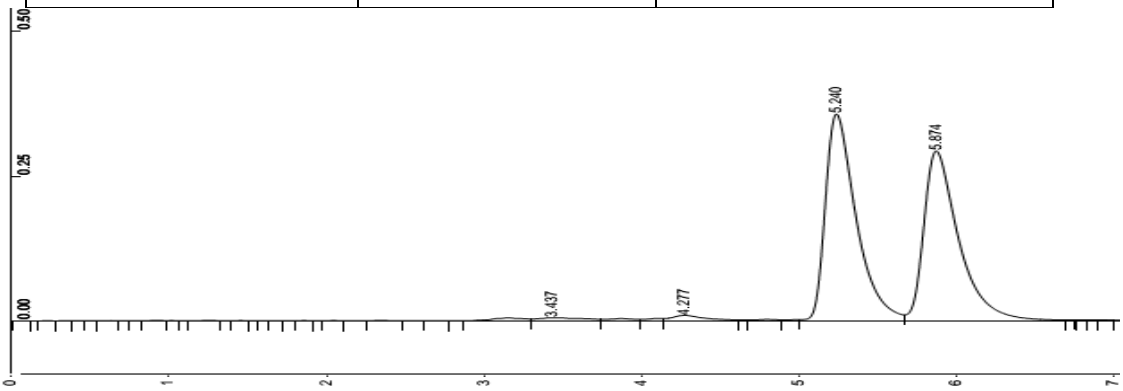
R.Time	Area	Area%
7.296	**46053968**	**50.3926**
9.553	**45336320**	**49.6074**



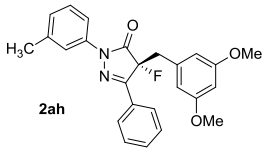
(*R*)-1-(3-trifluoromethylphenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-3-phenyl-1*H*-pyrazol-5(4*H*)-one (2ag). White solid, m.p. 73-75 °C; $[\alpha]_D^{25}$ +58.1 (*c* 0.40, $CHCl_3$); 97% yield, 90% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.76 (m, 4H), 7.54 – 7.33 (m, 5H), 6.13 (t, *J* = 2.3 Hz, 1H), 5.92 (d, *J* = 2.3 Hz, 2H), 3.55 – 3.42 (m, 2H), 3.40 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.23 (d, *J* = 21.6 Hz), 160.59, 154.76 (d, *J* = 14.1 Hz), 137.40, 131.69, 131.56, 131.48, 131.21, 129.54, 129.24, 129.18, 126.82, 126.80, 123.02 – 121.87 (m), 121.84, 115.94 – 115.33 (m), 107.44, 100.78, 96.26, 94.27, 55.05, 41.43 (d, *J* = 26.2 Hz). ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.71 (s, 3F) , -161.76 (s, 1F). HPLC conditions: Chiralcel AD-H column (250 × 4.6 mm), hexane /*i*-PrOH = 93 / 7, 1 mL / min, 254 nm, τR (major) = 5.27 min, τR (minor) = 5.89 min. HRMS Calcd. for $[C_{25}H_{20}F_4N_2O_3+Na]^+$ requires m/z = 495.1308, found m/z = 495.1303.



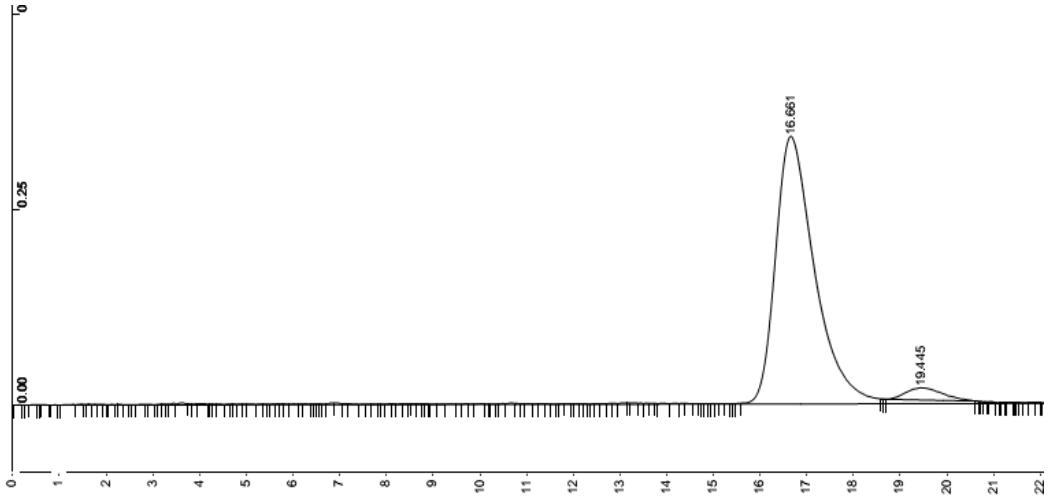
R.Time	Area	Area%
5.276	**107602176**	**95.1845**
5.898	**5443725**	**4.8155**



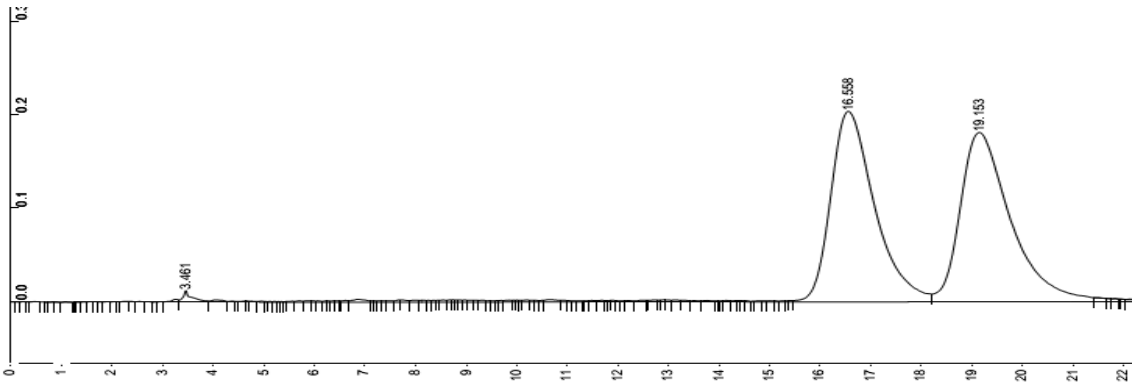
R.Time	Area	Area%
5.240	**48472348**	**50.1599**
5.874	**48163307**	**49.8401**



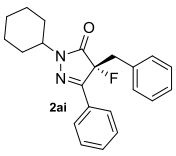
(*R*)-1-(3-methylphenyl)4-(3,5-bis(methoxyl)benzyl)-4-fluoro-3-phenyl-1*H*-pyrazol-5(4*H*)-one (2ah). Brown oil; $[\alpha]_D^{25}$ +31.2 (*c* 0.40, $CHCl_3$); 97% yield, 92% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.82 (m, 2H), 7.57 – 7.44 (m, 5H), 7.32 – 7.20 (m, 1H), 7.03 (ddt, *J* = 7.5, 1.7, 0.9 Hz, 1H), 6.22 (t, *J* = 2.3 Hz, 1H), 6.01 (d, *J* = 2.3 Hz, 2H), 3.65 – 3.34 (m, 8H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.08 (d, *J* = 21.3 Hz), 160.53, 154.14 (d, *J* = 13.8 Hz), 138.87, 136.88, 132.00, 131.88, 131.08, 129.67, 129.65, 129.06, 128.72, 126.79, 126.70, 126.68, 119.94, 116.57, 107.45, 100.89, 96.15, 94.17, 55.06, 41.39 (d, *J* = 26.3 Hz), 21.55. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -161.88 (s, 1F). HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 98 / 2, 1 mL / min, 254 nm, τR (major) = 16.66 min, τR (minor) = 19.44 min. HRMS Calcd. for $[C_{25}H_{23}FN_2O_3+Na]^+$ requires m/z = 441.1590, found m/z = 441.1584.



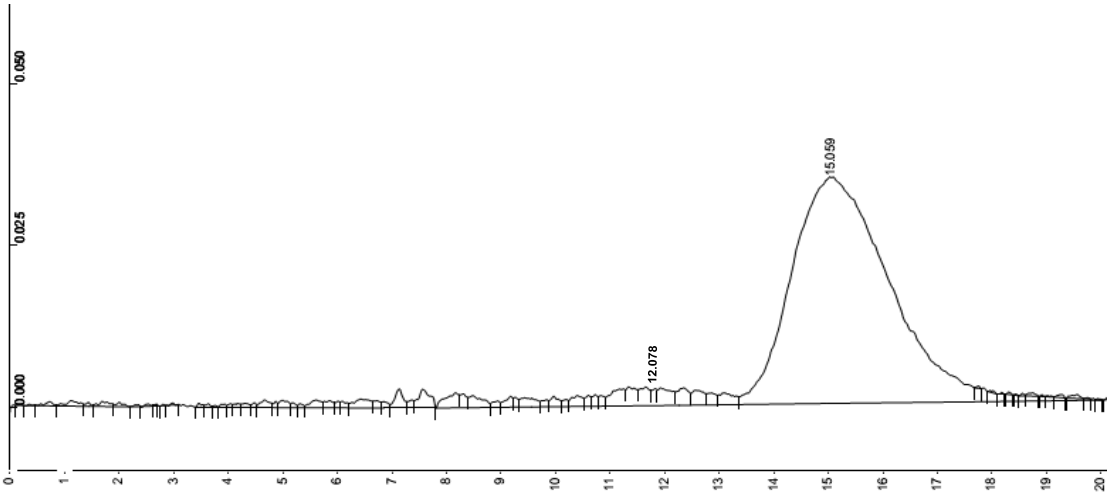
R.Time	Area	Area%
16.661	**205245264**	**96.1042**
19.445	**8320151**	**3.8958**



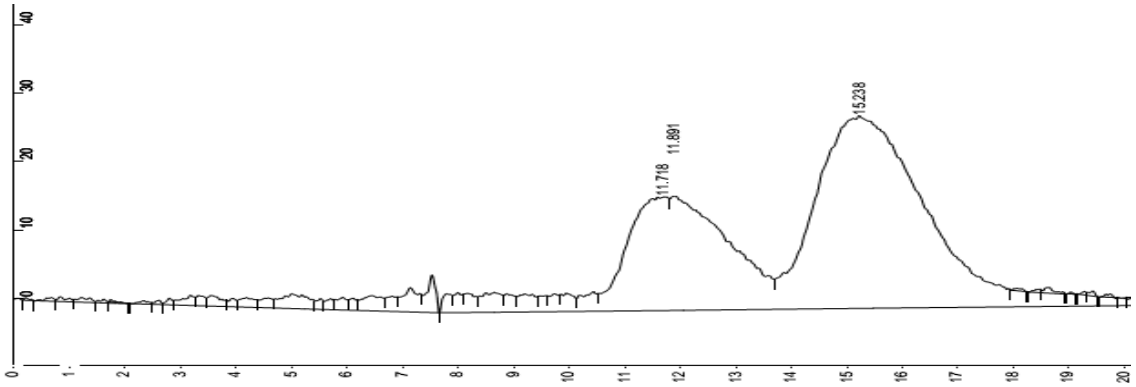
R.Time	Area	Area%
16.558	**122398784**	**49.9655**
19.153	**122567811**	**50.0345**



(*R*)-1-cyclohexyl-4-benzyl-4-fluoro-3-phenyl-1*H*-pyrazol-5(4*H*)-one (2ai). White solid, m.p. 81-83 °C; $[\alpha]_D^{25}$ +49.1 (*c* 0.40, $CHCl_3$); 96% yield, 98% ee. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.57 – 7.37 (m, 3H), 7.24 – 7.03 (m, 3H), 6.95 – 6.74 (m, 2H), 3.84 (ddd, *J* = 11.2, 6.9, 4.2 Hz, 1H), 3.61 – 3.31 (m, 2H), 1.86 – 1.72 (m, 1H), 1.72 – 1.52 (m, 4H), 1.31 – 0.98 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ168.54 (d, *J* = 20.8 Hz), 152.91 (d, *J* = 13.7 Hz), 130.54, 130.13, 129.02, 128.25, 127.71, 126.30, 126.29, 96.54, 94.56, 52.84, 40.76 (d, *J* = 26.1 Hz), 30.13, 30.00, 25.22, 25.08. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -165.69 (s, 1F) .HPLC conditions: Chiralcel OJ-H column (250 × 4.6 mm), hexane /*i*-PrOH = 99 / 1, 0.5 mL / min, 254 nm, τR (major) = 15.05 min, τR (minor) = 12.07 min. HRMS Calcd. for $[C_{22}H_{23}FN_2O+Na]^+$ requires m/z = 373.1692, found m/z = 373.1687.



R.Time	Area	Area%
12.078	**374675**	**0.8470**
15.059	**43860816**	**99.1530**



R.Time	Area	Area%
11.718	**8231438**	**34.4801**
15.238	**15641573**	**65.5199**

3.3 Crystallographic data

CCDC 2159180 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Crystal Data for $C_{25}H_{20}F_4N_2O_3$ (*M*=472.43 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a*= 8.5752(4)Å, *b*= 12.4172(6)Å, *c*= 20.9749(10)Å, *V*= 2233.40(17)Å^3, *Z*=4, *T*= 293(2) K, μ(CuKα) = 0.987 mm^{-1}, *Dcalc*= 1.405 g/cm^3, 22488 reflections measured (8.274° ≤ 2Θ ≤ 142.708°), 4307 unique (R_{int} = 0.0412, R_{sigma} = 0.0294) which were used in all calculations. The final R_1 was 0.0425 (I > 2σ(I)) and wR_2 was 0.1179 (all data).

Table 1 Crystal data and structure refinement for CCDC 2159180.

Identification code	202110
Empirical formula	$C_{25}H_{20}F_4N_2O_3$
Formula weight	472.43
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.5752(4)
b/Å	12.4172(6)
c/Å	20.9749(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2233.40(17)
Z	4
ρ_{calc}g/cm^3	1.405
μ/mm^{-1}	0.987
F(000)	976.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.274 to 142.708
Index ranges	-10 ≤ h ≤ 10, -15 ≤ k ≤ 14, -25 ≤ l ≤ 24
Reflections collected	22488
Independent reflections	4307 [R_{int} = 0.0412, R_{sigma}= 0.0294]
Data/restraints/parameters	4307/0/309
Goodness-of-fit on F^2	1.052

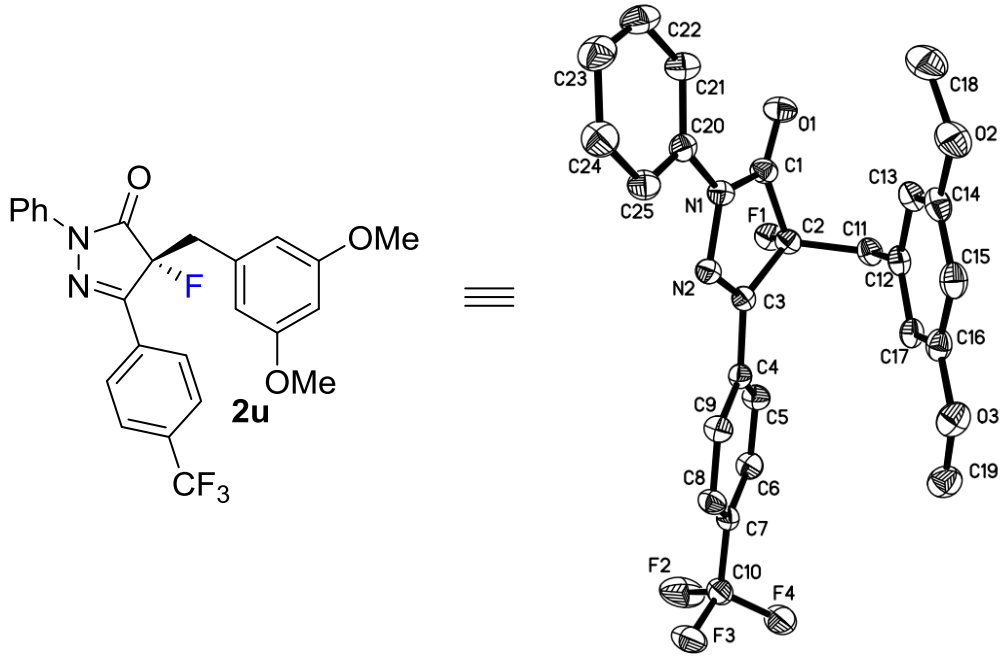
Final R indexes [I>=2σ (I)]	R_1 = 0.0425, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0493, wR_2 = 0.1179
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.20
Flack parameter	0.01(9)

Table 2 Bond Lengths for CCDC 2159180.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	C2	1.391(3)	C5	C6	1.370(5)
F2	C10	1.327(5)	C6	C7	1.381(5)
F3	C10	1.325(4)	C7	C8	1.379(4)
F4	C10	1.316(4)	C7	C10	1.489(4)
O1	C1	1.206(4)	C8	C9	1.381(4)
O2	C14	1.370(5)	C11	C12	1.514(4)
O2	C18	1.410(7)	C12	C13	1.392(5)
O3	C16	1.369(4)	C12	C17	1.382(5)
O3	C19	1.402(5)	C13	C14	1.389(5)
N1	N2	1.403(3)	C14	C15	1.378(6)
N1	C1	1.373(4)	C15	C16	1.379(5)
N1	C20	1.419(4)	C16	C17	1.393(4)
N2	C3	1.279(4)	C20	C21	1.386(5)
C1	C2	1.534(4)	C20	C25	1.386(5)
C2	C3	1.513(4)	C21	C22	1.391(6)
C2	C11	1.524(4)	C22	C23	1.367(7)
C3	C4	1.469(4)	C23	C24	1.380(7)
C4	C5	1.394(4)	C24	C25	1.381(5)
C4	C9	1.385(4)			

Table 3 Bond Angles for CCDC 2159180.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C14	O2	C18	118.0(4)	F2	C10	C7	112.5(3)
C16	O3	C19	117.4(3)	F3	C10	F2	106.2(3)
N2	N1	C20	118.1(2)	F3	C10	C7	114.0(3)
C1	N1	N2	112.2(2)	F4	C10	F2	104.7(4)
C1	N1	C20	129.6(3)	F4	C10	F3	105.6(3)
C3	N2	N1	109.5(2)	F4	C10	C7	113.1(3)
O1	C1	N1	128.5(3)	C12	C11	C2	112.3(2)
O1	C1	C2	126.4(3)	C13	C12	C11	119.9(3)
N1	C1	C2	105.0(2)	C17	C12	C11	119.4(3)
F1	C2	C1	109.1(2)	C17	C12	C13	120.7(3)
F1	C2	C3	112.9(2)	C14	C13	C12	118.9(3)
F1	C2	C11	108.7(2)	O2	C14	C13	123.3(4)
C3	C2	C1	100.9(2)	O2	C14	C15	115.9(3)
C3	C2	C11	114.1(2)	C15	C14	C13	120.9(3)
C11	C2	C1	110.8(3)	C14	C15	C16	119.7(3)
N2	C3	C2	111.6(2)	O3	C16	C15	116.2(3)
N2	C3	C4	121.5(2)	O3	C16	C17	123.3(3)
C4	C3	C2	126.8(2)	C15	C16	C17	120.5(3)
C5	C4	C3	121.0(3)	C12	C17	C16	119.3(3)
C9	C4	C3	119.7(3)	C21	C20	N1	121.0(3)
C9	C4	C5	119.2(3)	C21	C20	C25	120.0(3)
C6	C5	C4	120.2(3)	C25	C20	N1	119.0(3)
C5	C6	C7	120.3(3)	C20	C21	C22	118.7(4)
C6	C7	C10	119.2(3)	C23	C22	C21	121.7(4)
C8	C7	C6	120.0(3)	C22	C23	C24	119.1(4)
C8	C7	C10	120.7(3)	C23	C24	C25	120.6(4)
C7	C8	C9	120.0(3)	C24	C25	C20	119.9(4)
C8	C9	C4	120.2(3)				

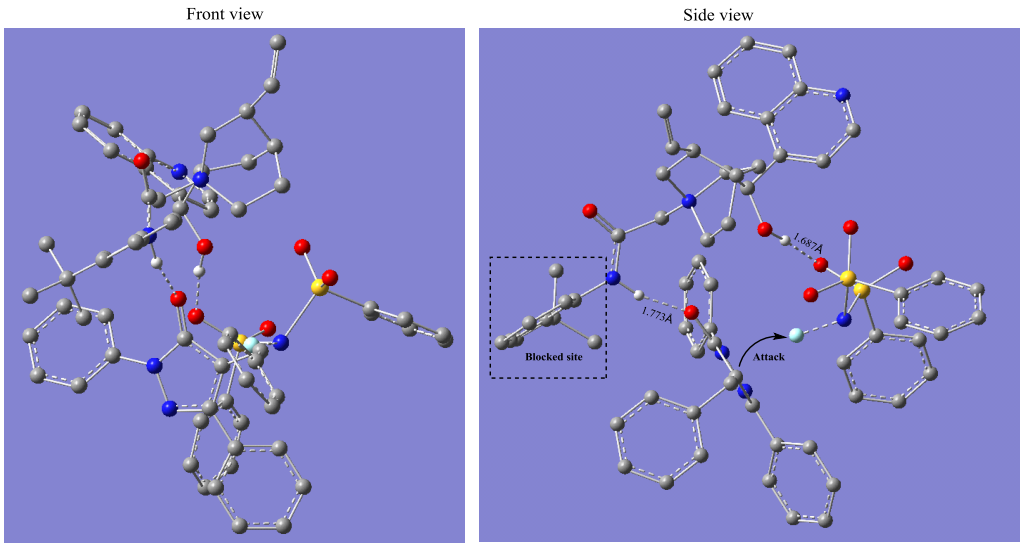


CCDC: 2159180

X-ray crystal structures of **2u**; the thermal ellipsoids at the 30% probability level for the crystal structure.Single crystals of **2u** was obtained for X-ray crystallographic analysis, whose absolute configuration was unambiguously determined to be R [30]. On this basis, the other fluoride products from this reaction were assumed to have the same (R)-configuration

4. Computation details

The presented models were generated on the basis of calculations using the density functional theory (DFT) method, combined with the 6-31G* basis set. Only one imaginary frequency (268.69*i*) corresponding to the reaction coordinates was found for the transition state. Plausible transition state depicted in Scheme 5 was proposed on the basis of calculations using the density functional theory (DFT) method, combined with the 6-31G* basis set. Only one imaginary frequency (268.69*i*) corresponding to the reaction coordinates was found for the transition state (Scheme 5). Based on the calculation results, two different types of interactions could exist: (1) an ion-pair interaction between the substrate and the PTC; (2) multiple hydrogen bonding interactions among catalyst, pyrazolone and NFSI. Our proposed model of the transition state (Scheme 5) posits that the pyrazolone substrate is stabilized by the hydrogen bond from the amide function of the catalyst. Moreover, the hydroxyl group of the catalyst forms an hydrogen-bond interaction with the oxygen of NFSI. Consequently, the fluorine can reach the α-carbon atom of pyrazolone exclusively from above to afford the *R*-product. A key element determining the high enantioselective manner is the ortho-*t*-Bu-phenyl group which blocks the *Si*-face of the enolate. This transition state can be supported by the results with a series of 9-OH and amide modified Cinchona alkaloids



Scheme A. Proposed transition-state model of *R*-Product for **PTC 3u,** pyrazolone **1a** and NFSI

Optimized Cartesian Coordinates (Å) *R*-Product for catalyst PTC 3u, pyrazolone 1a and NFSI **(These results could be seen in the supporting information).**

C -1.92561400 -0.13902700 4.88263600

C -1.88036800 -0.32946300 3.48582000

C -0.62621600 -0.09090700 2.86379200

C 0.48253400 0.33190000 3.61391900

C 0.39775800 0.52212700 4.99201500

C -0.81994000 0.27777300 5.62861100

N -0.39896500 -0.27020200 1.44857400

C -0.09855900 0.76987700 0.62584100

O -0.05776900 1.97479200 0.97670200

C 0.13810900 0.38110900 -0.84085800

C -1.64430300 2.48183200 -5.82597300

C -1.50586300 2.57496600 -7.23377700

C -0.63633100 1.73344000 -7.89680100

C 0.12957700 0.77397500 -7.18388000

C 0.00351400 0.67706500 -5.75559200

C -0.90992200 1.55828800 -5.10580100

N 0.97308400 -0.03777100 -7.91064000

C 1.68976900 -0.93998600 -7.24913000

C 1.64384900 -1.10662200 -5.84147700
C 0.80807800 -0.30656300 -5.08433000
C 0.74472800 -0.47040500 -3.56532800
C 1.64418600 0.59439800 -2.89162300
O 1.18807100 -1.74604400 -3.09025300
N 1.57179900 0.60960200 -1.32019200
C 2.11709400 1.98717100 -0.88368500
C 3.46083300 2.29371400 -1.59815400
C 4.02833300 0.93844900 -2.11696300
C 3.13588500 0.47238400 -3.28650100
C 3.96641100 -0.12501800 -0.99838800
C 2.49242500 -0.48767500 -0.72703200
C 4.39349000 3.04320400 -0.67687900
C 4.89144300 4.25892900 -0.92893100
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H 1.41745700 0.51127400 3.09511400
H 1.26587600 0.85037000 5.55358900
H -0.08198200 -0.67251100 -1.01825200
H -0.50486800 1.02535300 -1.44585300
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H -2.08974700 3.30526600 -7.78410700
H -0.50561800 1.76727100 -8.97222500
H -1.04757200 1.50480800 -4.03105700
H 2.34116000 -1.57427200 -7.84143100
H 2.27259800 -1.85571100 -5.37581900
H -0.29725500 -0.30841500 -3.25846800
H 1.24760500 1.57811100 -3.16571300
H 0.84373900 -2.53182600 -3.60282000
H 1.34308200 2.72786200 -1.08638500
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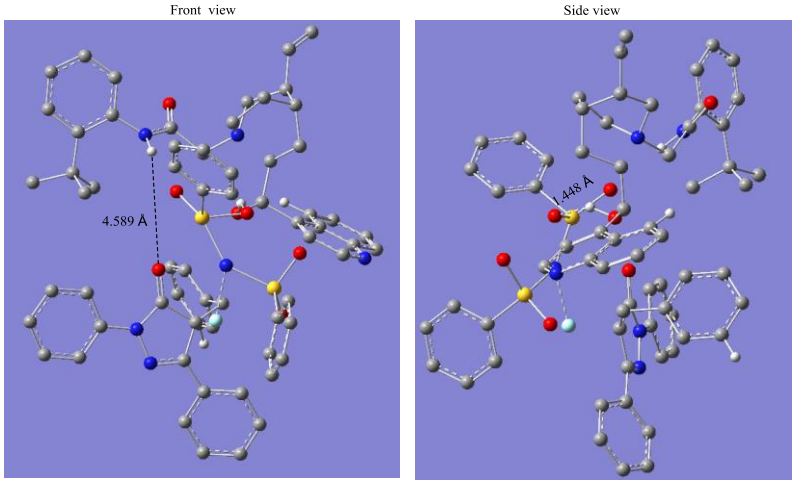
H 3.26898100 2.93136500 -2.47163100
H 5.05851900 1.07408100 -2.45851300
H 3.31132700 1.08896700 -4.17413100
H 3.37147400 -0.56368900 -3.54616500
H 4.49315300 -1.03425300 -1.30281900
H 4.45323000 0.24532500 -0.08884100
H 2.25436600 -0.53544700 0.33703300
H 2.18526900 -1.41699800 -1.20362800
H 4.66817000 2.53263200 0.24686800
H 5.57129200 4.75325200 -0.24224800
H 4.63819300 4.80663100 -1.83375400
H -0.35916700 -1.22287500 1.05789400
H -0.91702700 0.41315500 6.70126800
C -4.38545200 -0.87015800 3.65831300
H -4.61624100 0.09000000 4.13383300
H -5.25725000 -1.16596600 3.06478700
H -4.24927500 -1.62540700 4.44047600
C -3.15426100 -0.77395000 2.72043800
C -2.94682500 -2.18155600 2.09773100
H -2.16246800 -2.19466100 1.33974800
H -2.68643800 -2.91213700 2.87245400
H -3.87231000 -2.51338400 1.61241700
C -3.51453500 0.25359100 1.61167400
H -2.74275100 0.31377800 0.84351300
H -4.45005900 -0.04674700 1.12452400
H -3.65331500 1.25345700 2.03819900
N -1.18463000 -4.59115700 -0.55967000
N -1.04415800 -5.98427400 -0.42743300
C 0.16556100 -6.17726700 0.13388300
C 0.84578800 -4.94369100 0.36704100
C -0.07476500 -3.91019300 -0.04771200
O 0.02240500 -2.63500700 0.05680800
C -2.35851600 -4.06088100 -1.14820900
C 2.09989600 -4.66589700 1.14730000

C 0.63461500 -7.55251900 0.37400500
C 1.88980700 -4.69610300 2.66047800
C 1.31414200 -3.59884200 3.32406400
C 1.11163900 -3.62292100 4.70771600
C 1.48211000 -4.75038500 5.45164200
C 2.05565900 -5.84915400 4.80179900
C 2.25776200 -5.82104300 3.41681400
C -0.24470900 -8.52010600 0.89630500
C 0.18762000 -9.83182000 1.10893800
C 1.50422900 -10.19877200 0.80303300
C 2.38186800 -9.24707400 0.26947800
C 1.95103200 -7.93507200 0.05062000
C -3.59354400 -4.68230300 -0.90714100
C -4.75251700 -4.16904100 -1.49475300
C -4.68993200 -3.03576000 -2.31557600
C -3.45242000 -2.42888600 -2.56134500
C -2.28374600 -2.94001500 -1.98970300
H 2.87823800 -5.38498200 0.87999200
H 2.47121000 -3.68125500 0.84422100
H 1.02298100 -2.72537800 2.74996900
H 0.66922300 -2.76254900 5.20052600
H 1.32663300 -4.77125900 6.52609900
H 2.34690900 -6.72722100 5.37076700
H 2.69967200 -6.67842500 2.91767500
H -1.26018900 -8.22728800 1.13925000
H -0.49935800 -10.56541900 1.51988700
H 1.84114100 -11.21651500 0.97439300
H 3.39802400 -9.52904200 0.01097100
H 2.61629400 -7.21179100 -0.40711000
H -3.62518000 -5.55958600 -0.27296700
H -5.70586300 -4.65364000 -1.30838800
H -5.59263700 -2.63842000 -2.76834900
H -3.39272400 -1.56794400 -3.22015200
H -1.31554500 -2.51099600 -2.21181600
C -0.56432400 -9.26604700 -4.38897400
C 0.33627400 -8.97590400 -5.42351900
C 0.98031500 -7.73423200 -5.46660500
C 0.67956200 -6.82117500 -4.45933600
C -0.20722900 -7.06732100 -3.41993900
C -0.83382300 -8.31947900 -3.39271100
S 1.54748100 -5.16625400 -4.54313000
O 2.47415400 -5.14794800 -5.89918500
O 0.41344300 -3.98834800 -4.33716400
S 4.34287900 -3.85656200 -3.20728100
O 4.10592200 -2.68377000 -4.33146000
O 4.71989100 -3.39938300 -1.67741900
C 5.70531000 -4.97852500 -3.83348000
C 5.70117000 -5.32184800 -5.18226900
C 6.72960500 -6.15703000 -5.63557300
C 7.70961300 -6.61852300 -4.74590400
C 7.67413500 -6.25377200 -3.39338800
C 6.65435900 -5.42068600 -2.91743100
H -1.05323700 -10.23420500 -4.35813300
H 0.53887700 -9.71056300 -6.19540800
H 1.68042200 -7.47178200 -6.25078800
H -0.41437200 -6.34610400 -2.63798300
H -1.51901200 -8.53961700 -2.58235800
H 4.91813100 -4.96572200 -5.84254700
H 6.76108600 -6.44542400 -6.68059700
H 8.50169700 -7.26604000 -5.10736500
H 8.43659700 -6.61188300 -2.71004100
H 6.59879500 -5.11039200 -1.88048300
N 2.76686600 -5.21274500 -2.98149700
F 1.87153300 -4.87041700 -1.707875

Next, we also calculated the Proposed transition-state model of *S*-Product for **PTC 3u,** pyrazolone **1a** and NFSI. As we can see, Because of the distance (O atom of pyrazolone with N-H of the catalyst) is relatively far (4.589 Å). It's hard to form effective hydrogen bond between O and N-H. Moreover, the ortho-*t*-Bu-phenyl group could not block the *Re*-face of the enolate effectively. This transition state can be supported by the results with a series of 9-OH and amide modified Cinchona alkaloids (Scheme 4) in manuscript.



Scheme B. Proposed transition-state model of *S*-Product for **PTC 3u,** pyrazolone **1a** and NFSI

Optimized Cartesian Coordinates (Å) *S*-Product for catalyst PTC 3u, pyrazolone 1a and NFSI

C 0.41200700 -1.37339000 -0.28950300
C 0.64004600 -0.86801800 1.00743100
C 1.63702500 -1.53373000 1.77105900
C 2.32059300 -2.64452400 1.25143600
C 2.05717500 -3.12398500 -0.02991200
C 1.09759000 -2.47499100 -0.80725200
N 2.00855000 -1.10611900 3.09566600
C 1.98333100 -1.93445200 4.17430400
O 1.64308900 -3.14556100 4.16109400
C 2.35515200 -1.26278300 5.49815800
C 1.97298500 -1.39856000 11.74368100
C 2.57537900 -0.92024800 12.93457600
C 3.51978300 0.08416800 12.87288600
C 3.90671600 0.64248400 11.62598900
C 3.31917900 0.14838100 10.41105100
C 2.33488100 -0.87821800 10.51508700
N 4.84093500 1.65562500 11.64158200
C 5.19202600 2.19655400 10.47843500
C 4.68020300 1.76413400 9.22665200
C 3.75932100 0.73490000 9.17467600
C 3.23948300 0.23723000 7.82222300
C 3.93049900 -1.14092500 7.51056700
O 3.30238800 1.22219500 6.79848400
N 3.69014700 -1.73675700 6.07219100
C 3.74999800 -3.26529600 6.25128800
C 5.00561700 -3.64408000 7.09086200
C 6.01594800 -2.45540400 6.98965200
C 5.44663000 -1.24805400 7.77788400
C 6.14101000 -2.02673600 5.51461500
C 4.83342900 -1.32355100 5.11082800
C 5.57409100 -4.96639000 6.63323100
C 5.71123200 -6.04192600 7.41681400
H -0.33091600 -0.90185000 -0.91760800
H 3.05972400 -3.13320700 1.87411000
H 2.59588900 -3.98471300 -0.41231200
H 2.43923400 -0.17803100 5.42453100
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H 5.02019200 2.26218800 8.32666500
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H 4.22042600 1.44980500 6.33474600
H 2.81725900 -3.58189400 6.72141900
H 3.77034200 -3.69723700 5.25092600
H 4.71744700 -3.75309600 8.14477600
H 6.98434400 -2.76009800 7.39642300
H 5.59743500 -1.37098100 8.85436900
H 5.96130500 -0.32773200 7.47901500
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H 6.13667500 -6.96938900 7.04687200
H 5.40360600 -6.03552500 8.45996500
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C -1.33494600 0.70852500 0.54524300
H -2.02277000 -0.13270900 0.40074300
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H -0.96803800 1.03267800 -0.43479100
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C 0.73562200 1.60657600 1.61583300
H 1.57851500 1.48163500 2.30014800
H 1.14465600 1.85362800 0.62818000
H 0.14358200 2.46365100 1.96197200
C -0.83636800 0.05410000 2.89087900
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H -1.47252000 0.89998500 3.17922000
H -1.46345500 -0.84352800 2.83482000
N 0.60258000 6.13483400 4.78325400
N 0.18529100 6.95997200 5.84126900
C 0.66514100 6.50877200 6.98867200
C 1.48635100 5.30052600 6.75859500
C 1.36227400 5.06905500 5.24800100
O 1.85429200 4.13288300 4.60683900
C 0.21260900 6.45835000 3.45021000
C 1.71462500 4.13881900 7.65073700
C 0.32214500 7.17170600 8.25032200
C 0.38936600 3.35719300 7.72918400
C 0.11351700 2.34465100 6.79347600
C -1.08131400 1.62118700 6.87529500
C -2.00971400 1.90357000 7.88540400
C -1.73814400 2.91163100 8.81835200
C -0.54741200 3.64141800 8.73747000
C -0.86925100 7.92489800 8.32790000
C -1.21388200 8.57890000 9.50973800
C -0.37972600 8.49035500 10.63351600
C 0.80436700 7.74883300 10.56169300
C 1.16235200 7.09205100 9.37906300
C -0.63861200 7.55421300 3.23600700
C -1.02530700 7.87940500 1.93445000
C -0.57324400 7.12411700 0.84605000
C 0.27578400 6.03584600 1.07170200
C 0.67699800 5.69369700 2.36678400
H 2.48939500 3.49624000 7.21492300
H 2.04597600 4.45911200 8.63983300
H 0.84472100 2.12286500 6.02446100
H -1.28777600 0.84179200 6.14824400
H -2.93727400 1.34282500 7.94490700
H -2.44995300 3.13011700 9.60801200
H -0.33862700 4.41957000 9.46436900
H -1.51666500 7.97971400 7.46028900
H -2.13541100 9.14986000 9.55932600
H -0.65332400 8.99392600 11.55522200
H 1.46070600 7.67980800 11.42280500
H 2.10375300 6.55225600 9.34030200
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H 1.33327100 4.85142100 2.53298100
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C 7.23536700 7.45651700 7.79411800
C 5.91921300 7.36966500 8.23644900
C 5.14717400 8.47709500 8.57097400
C 5.73244300 9.74366300 8.45045800
S 5.15166600 5.66600100 8.34936800
O 6.39328500 4.59419700 8.49613000
O 3.99304900 5.76202400 9.51715100
S 4.58855400 2.26375100 3.91795300
O 5.31171200 1.69238100 5.39034400
O 3.68610100 1.02510400 3.18997300
C 6.13845000 2.21910500 2.85608700
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C 8.48102900 2.67962700 2.58843600
C 8.40652800 2.22513400 1.26453200

C 7.19133100 1.75958800 0.74580100
C 6.04197600 1.75382300 1.54714100
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H 8.83250300 8.83031200 7.34580500
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H 4.13341800 8.35232500 8.93197400
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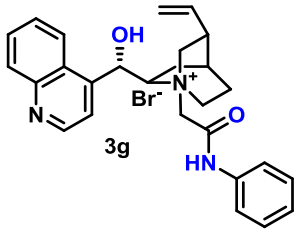
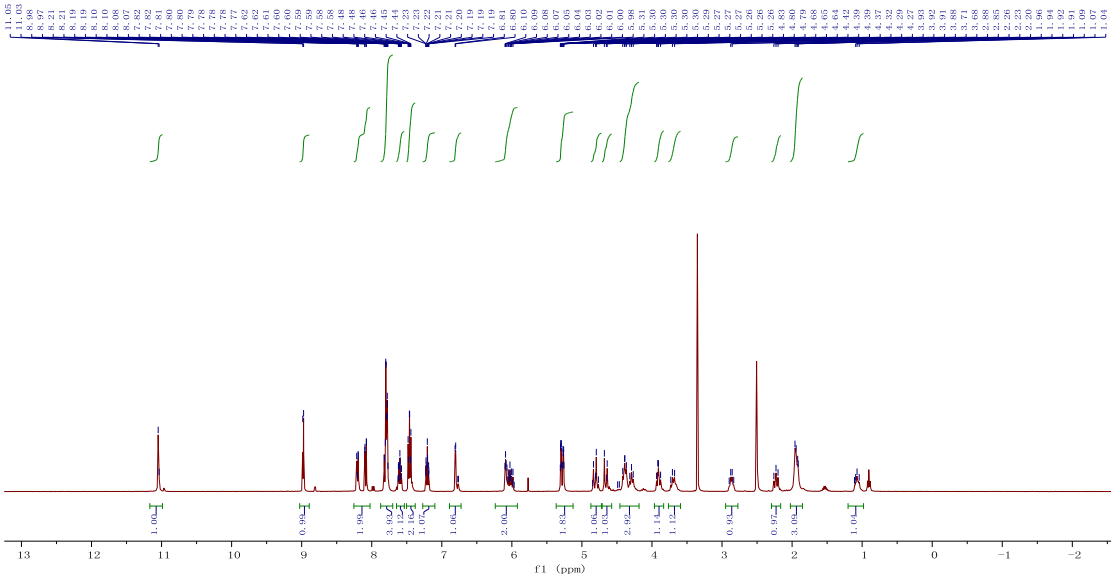
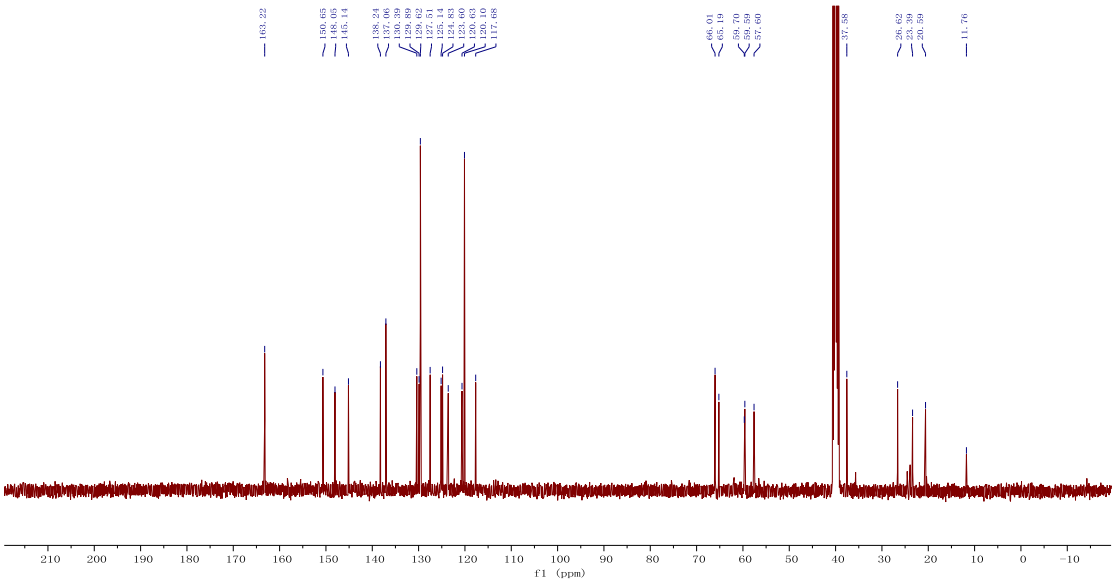
H 7.37437100 2.99634900 4.43384900
H 9.42651200 3.02852800 2.99197000
H 9.29489400 2.23031300 0.64036500
H 7.13830800 1.39745500 -0.27631300
H 5.09033900 1.37736500 1.18857700
N 4.45810500 5.17586500 6.67515900
F 3.13827400 6.11002200 6.62204100

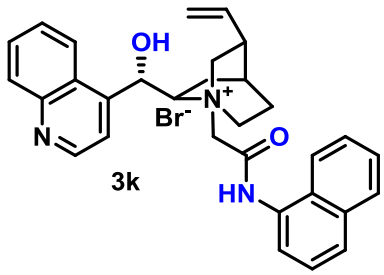
5. NMR spectra for compounds

5.1 **NMR spectra for catalysts**









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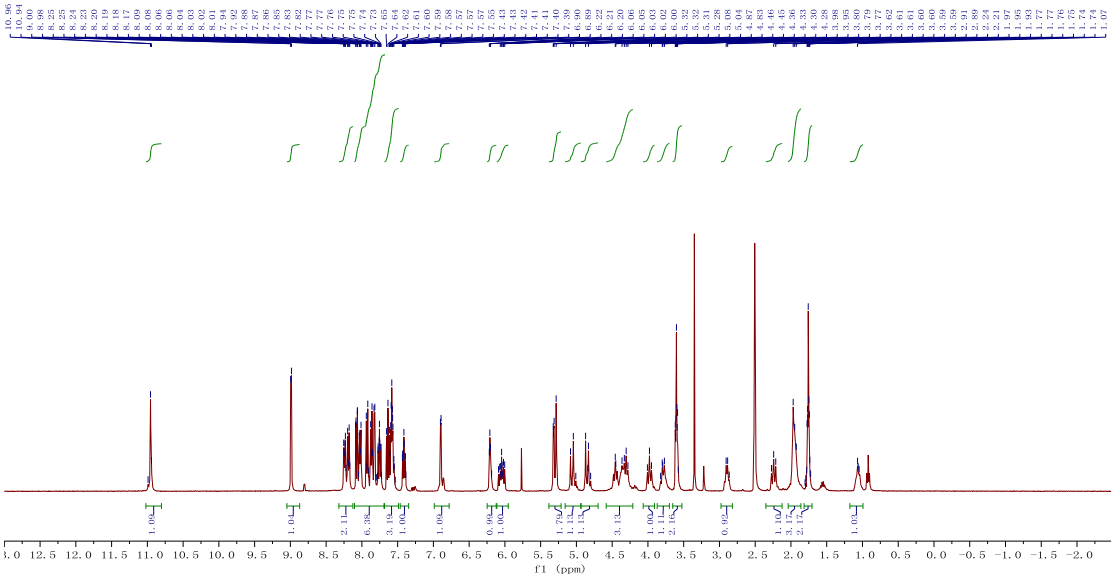

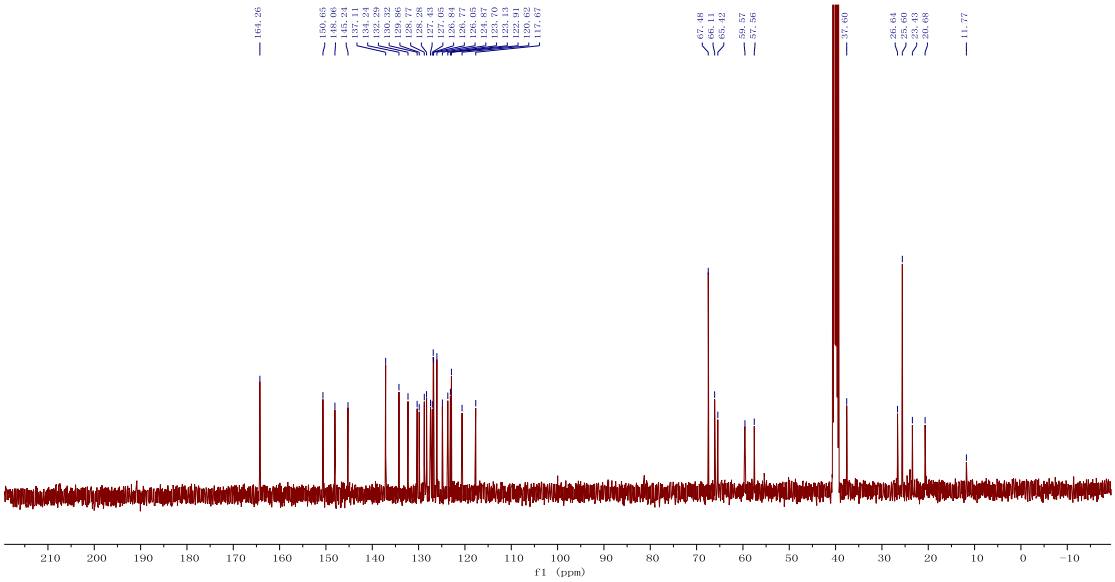

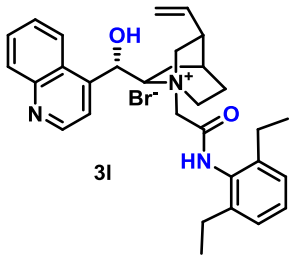

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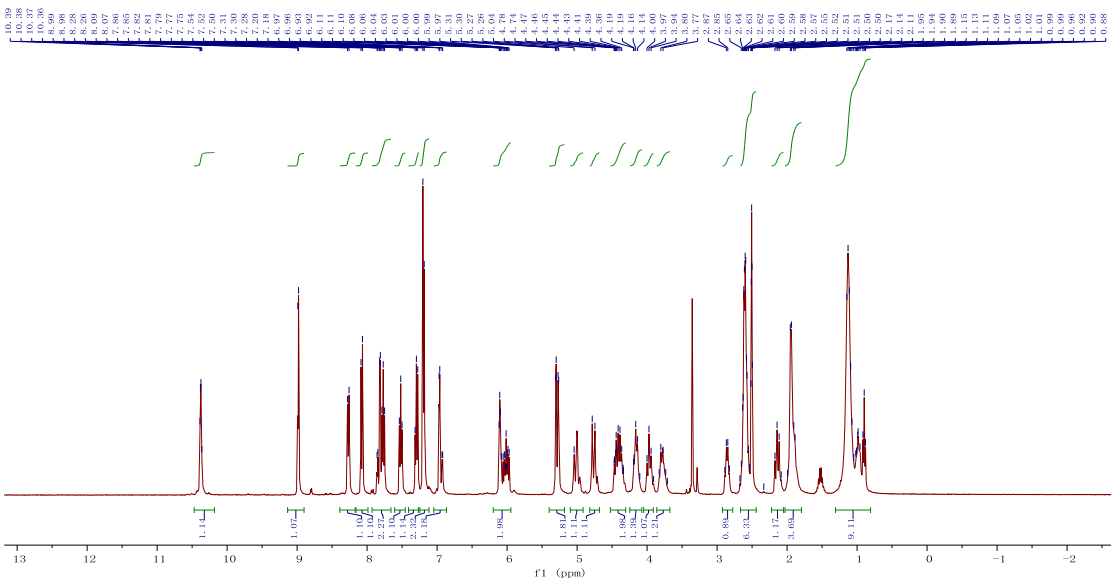
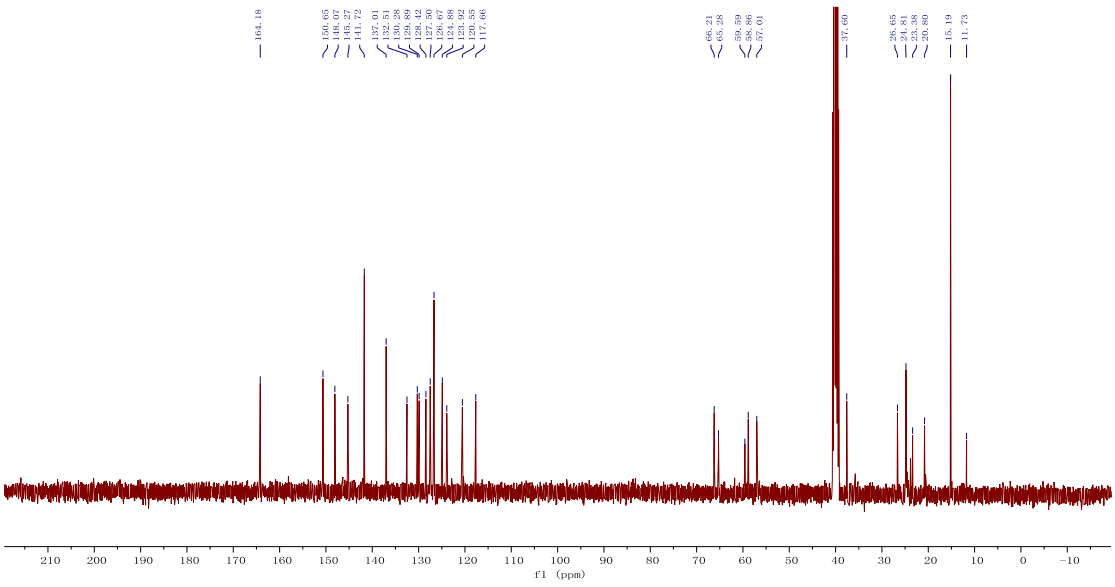
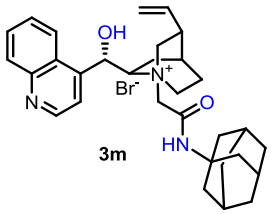
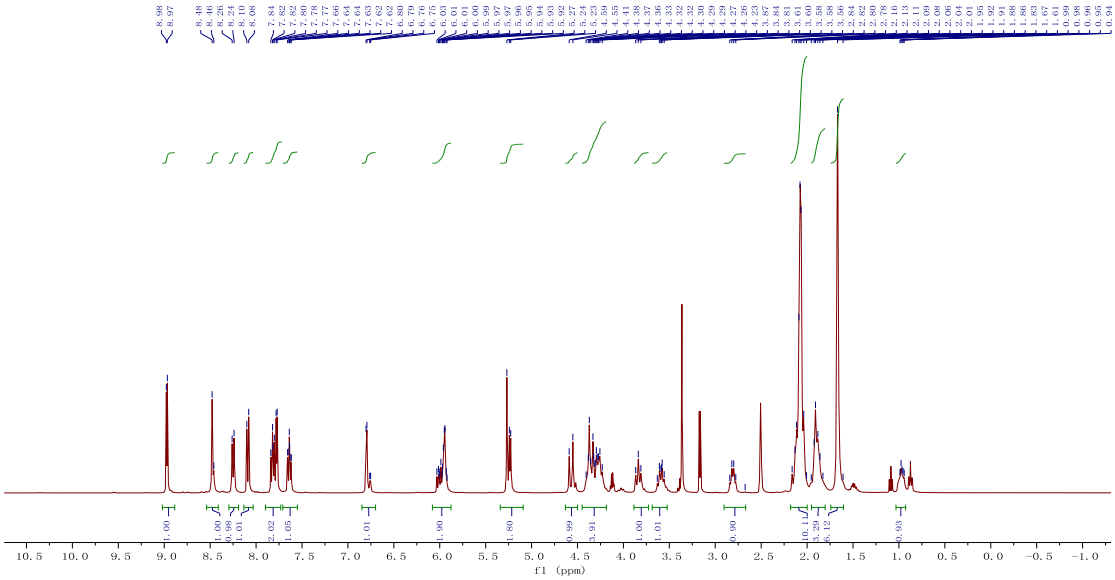
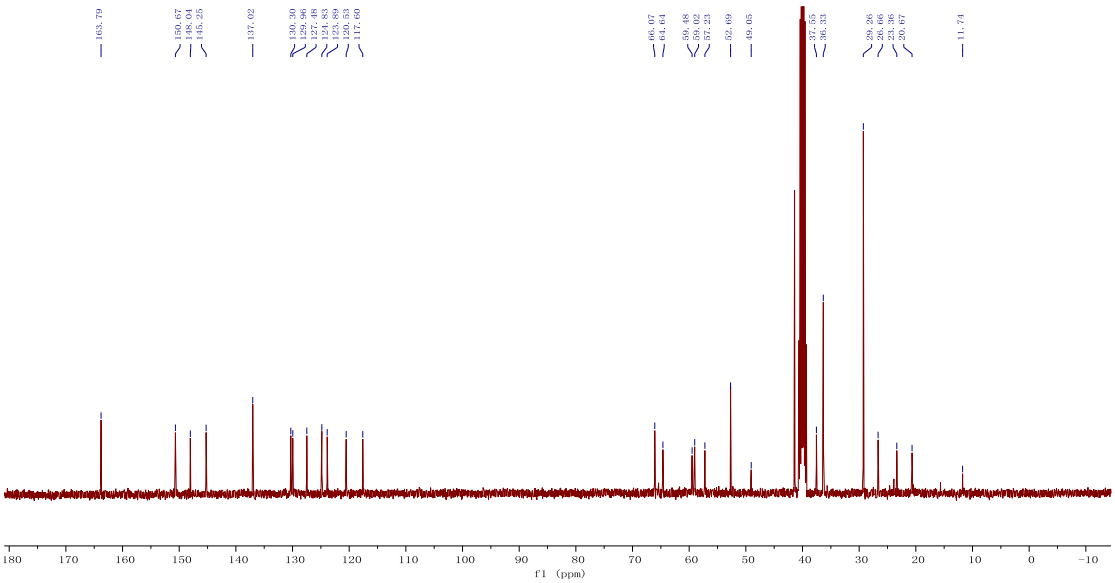


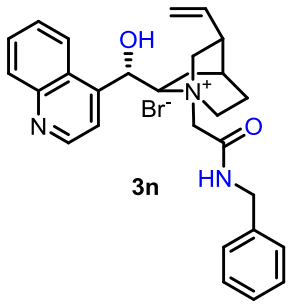




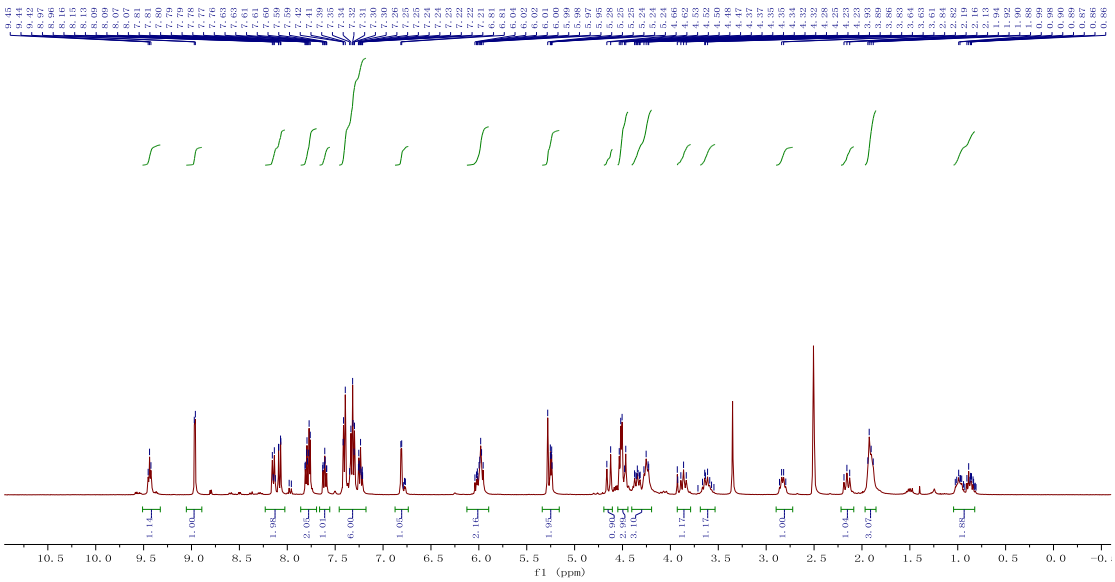
3m

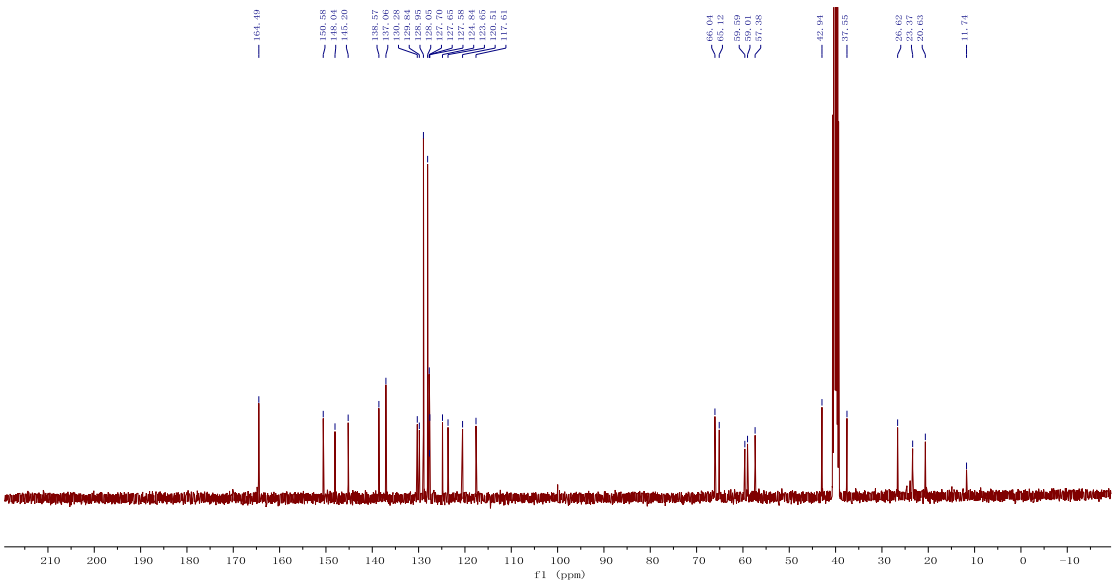


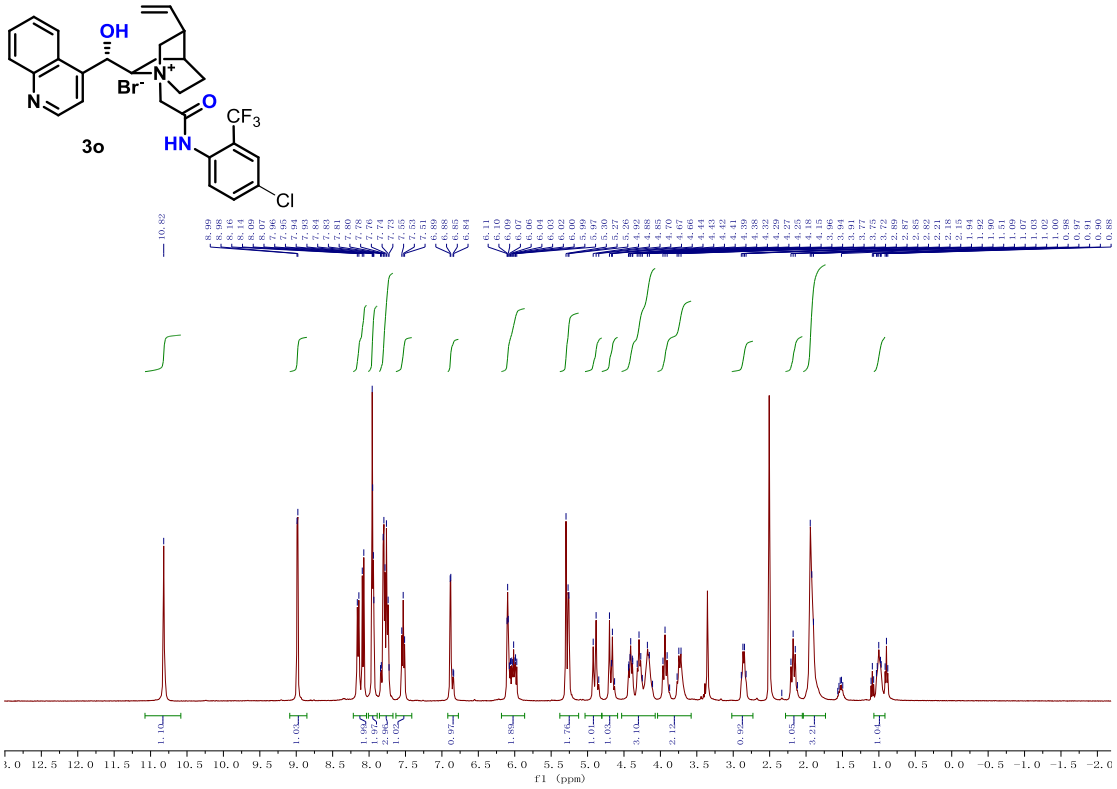


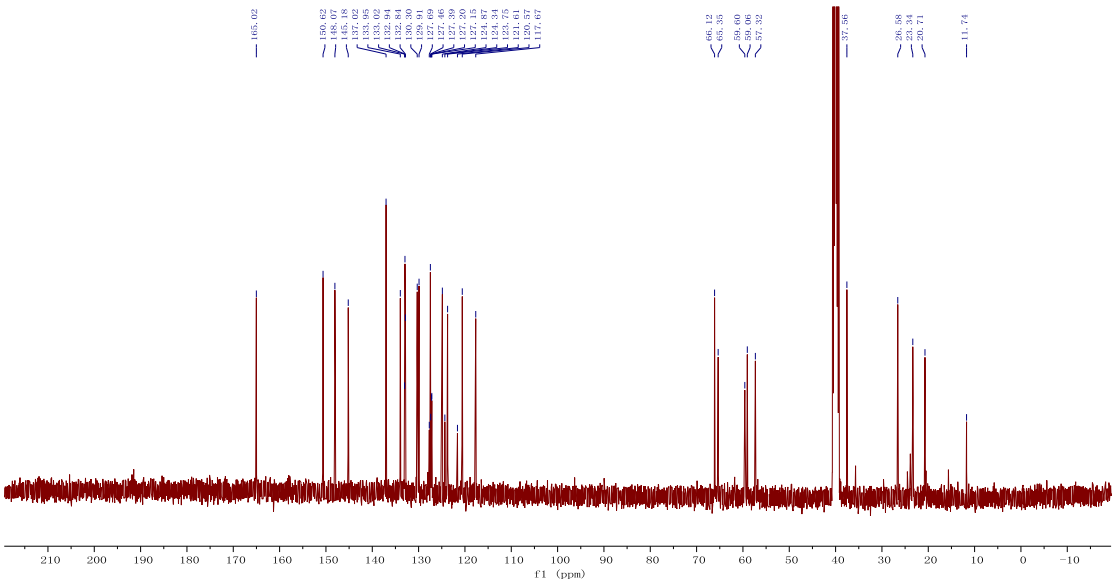


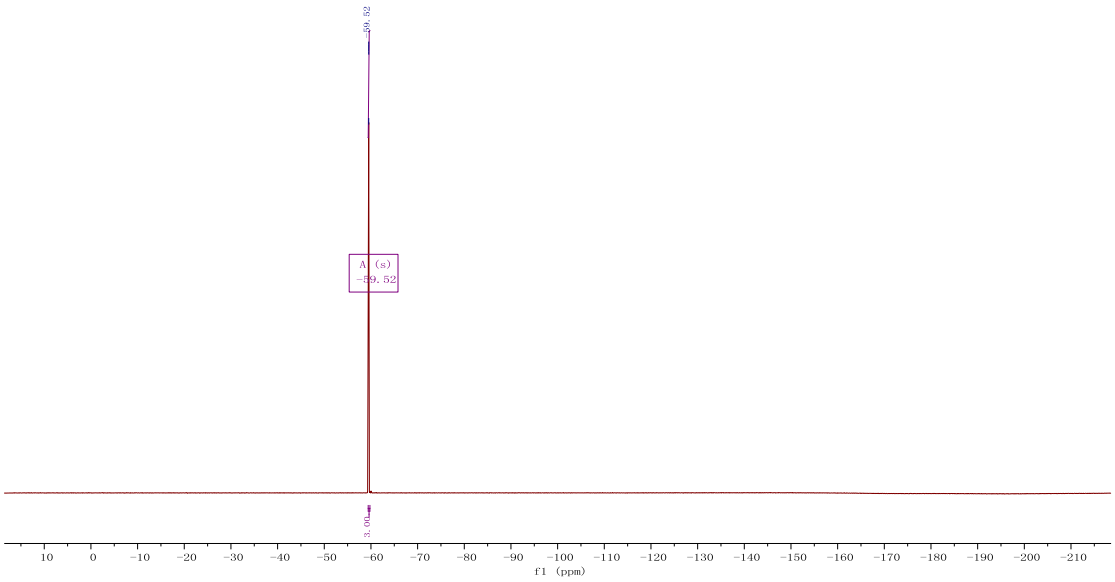
3n

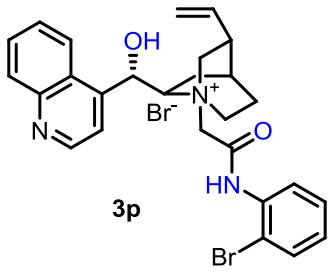




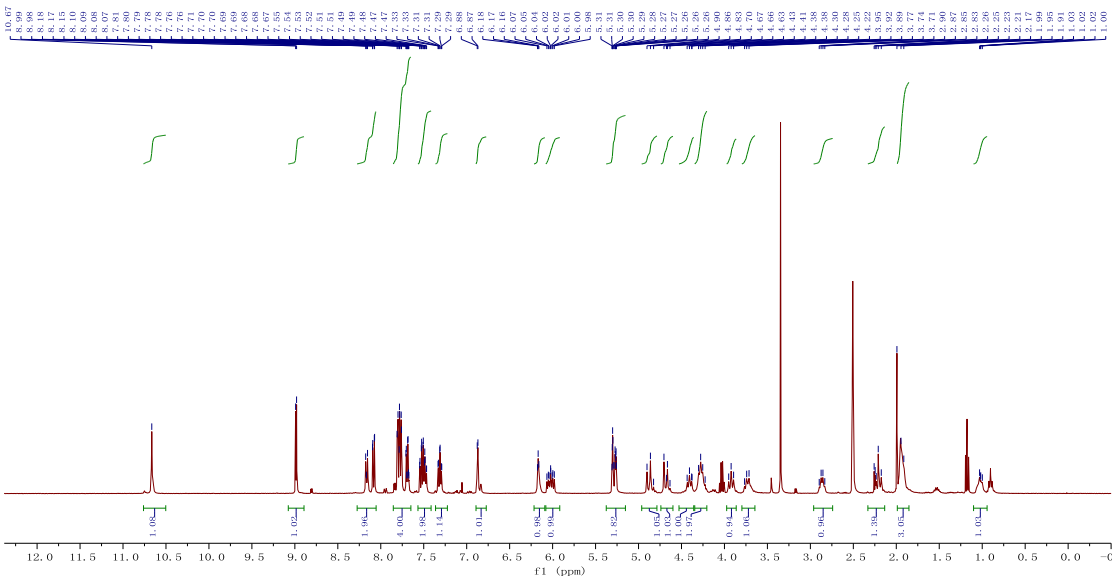

OH
N
Br-
N+
O
HN
CF3
Cl
3o
f1 (ppm)

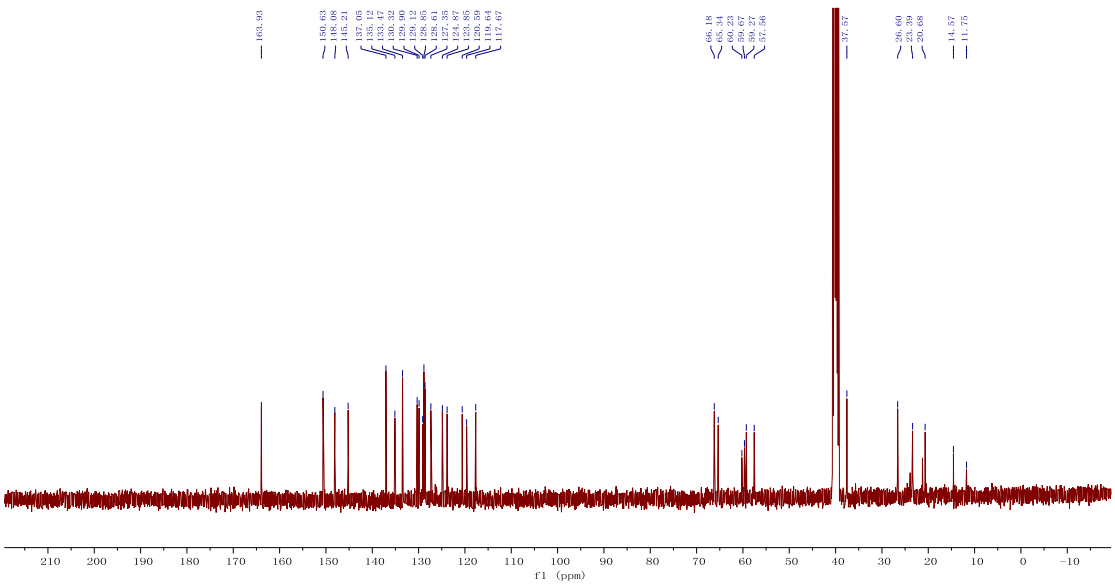

f1 (ppm)

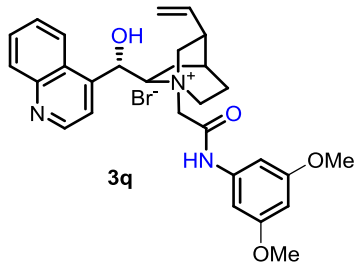

-59.52
A (s)
-59.52
3.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)



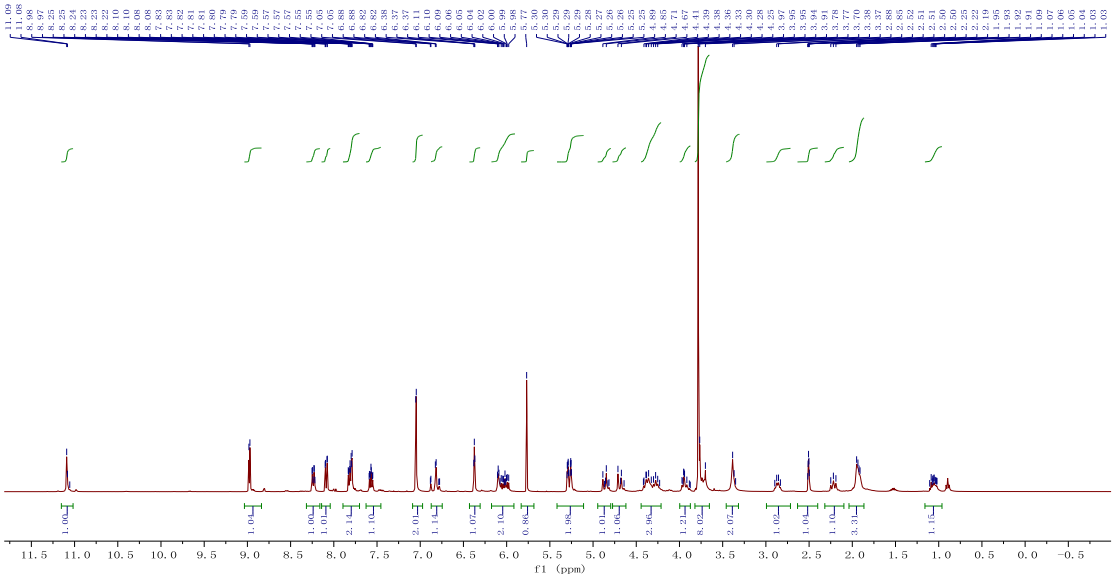
3p

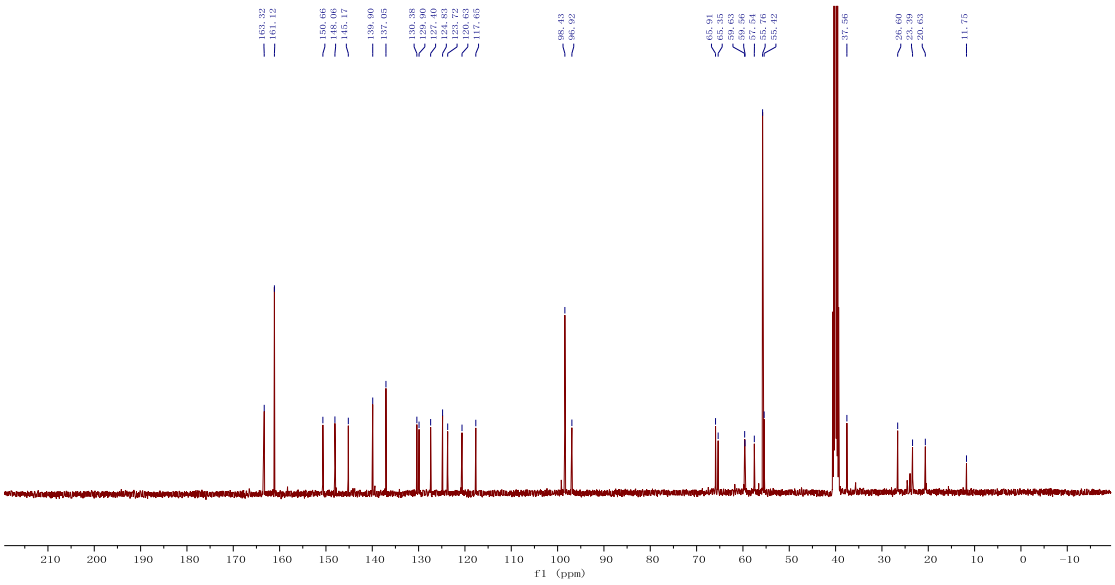


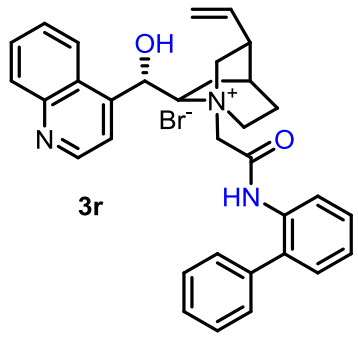




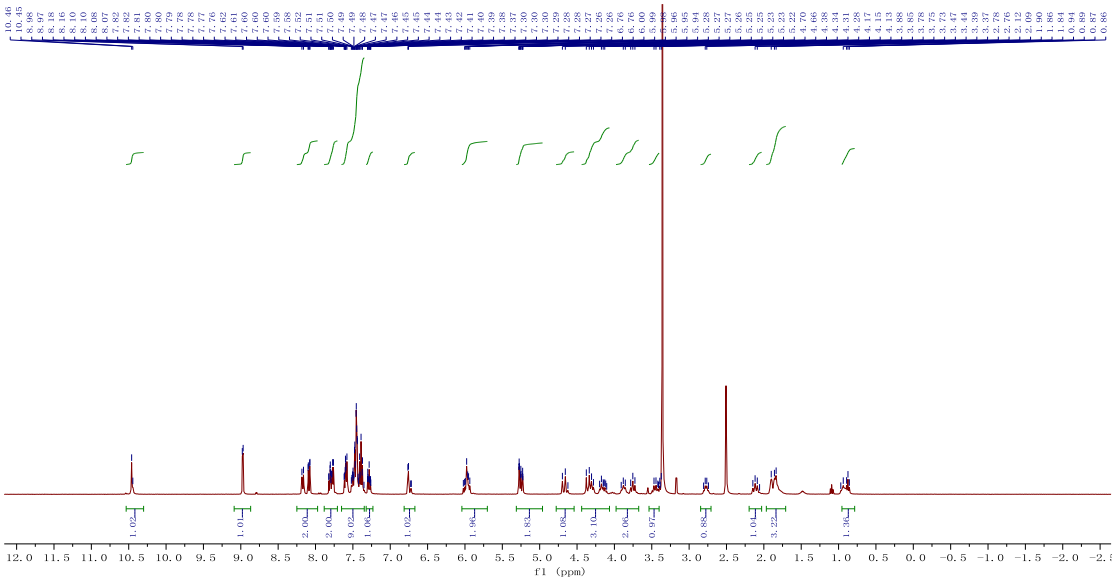
3q

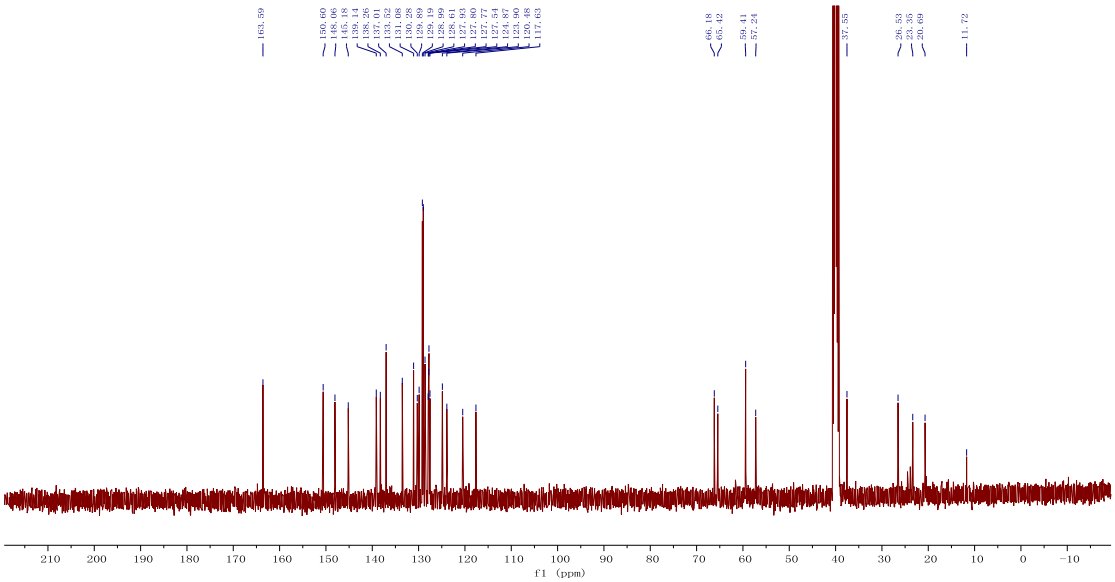


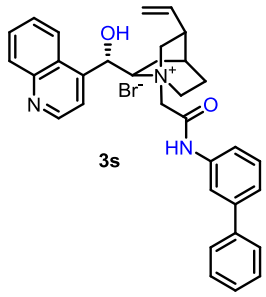




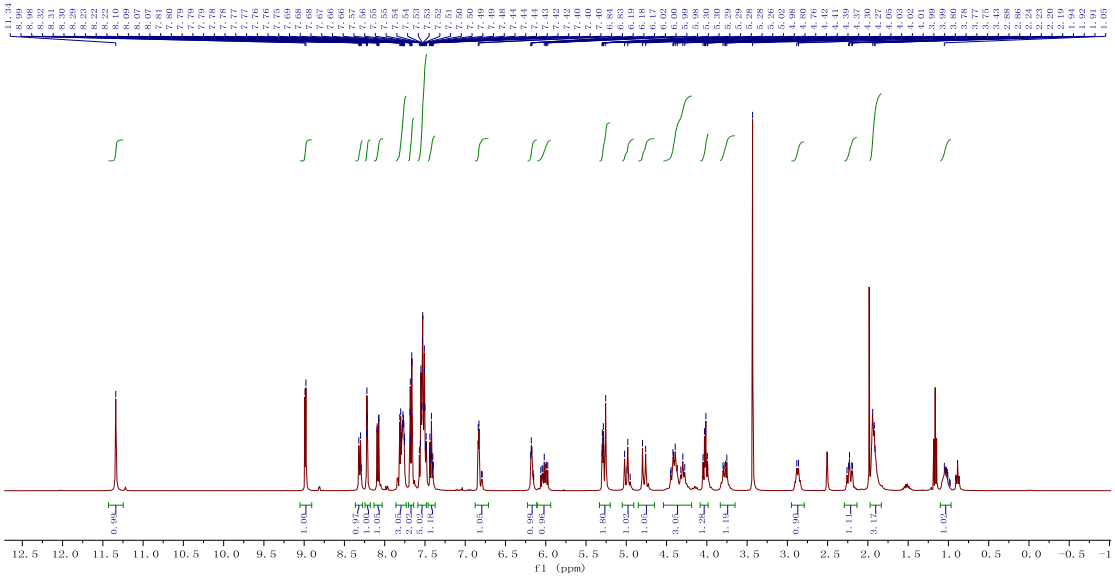
3r

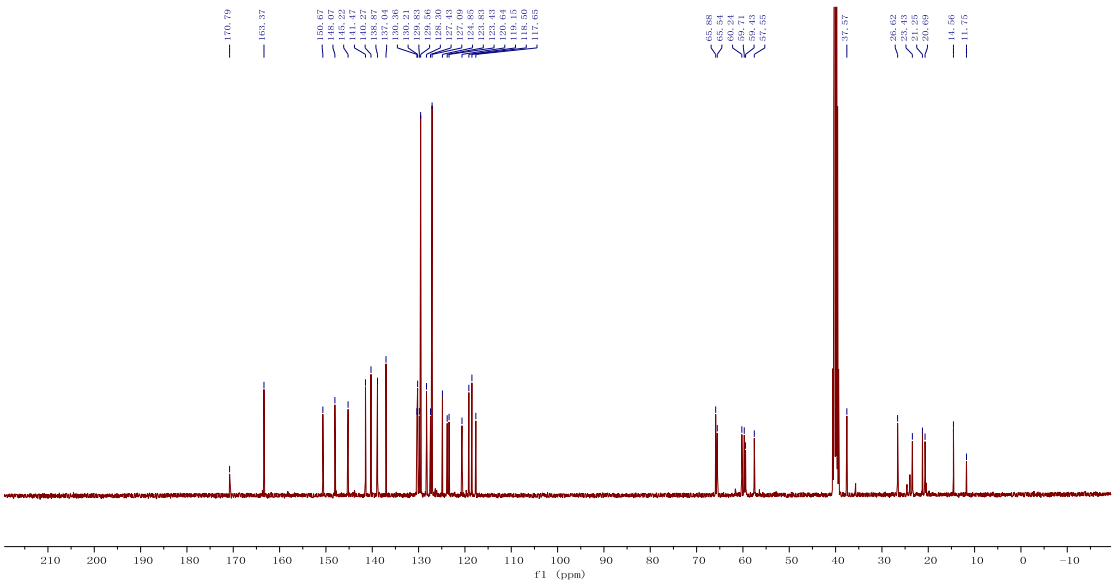


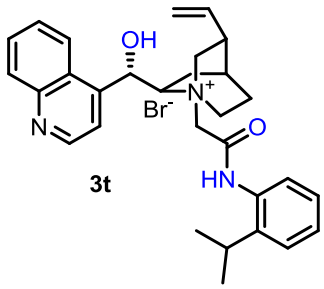




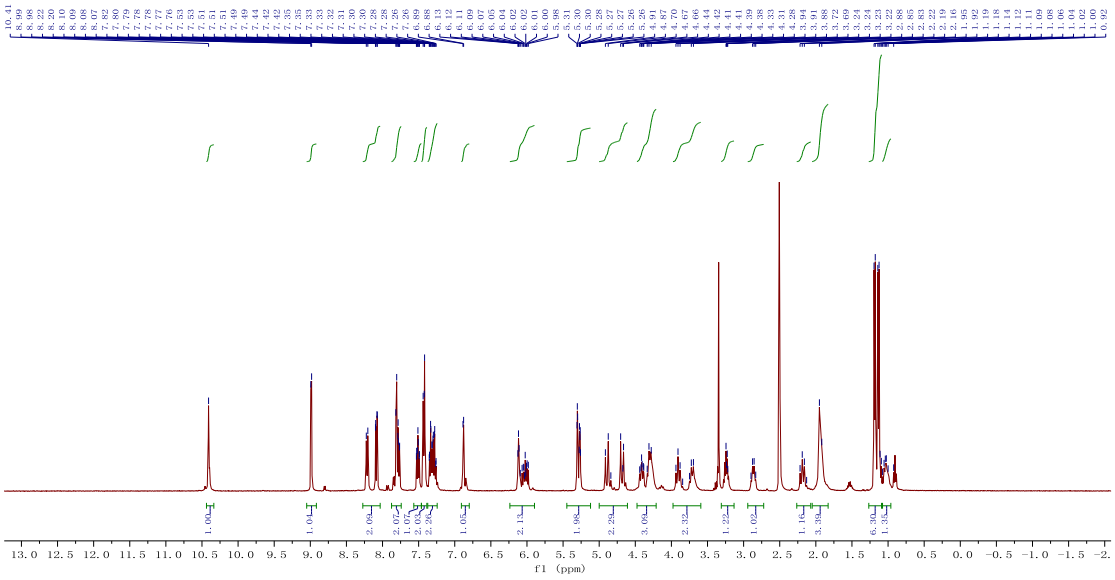
3s

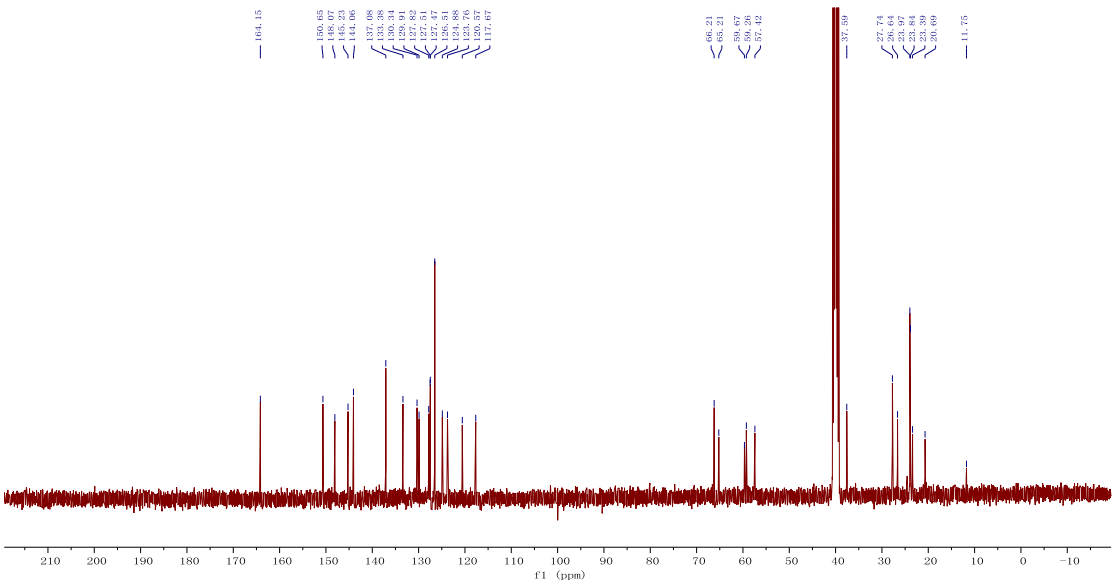


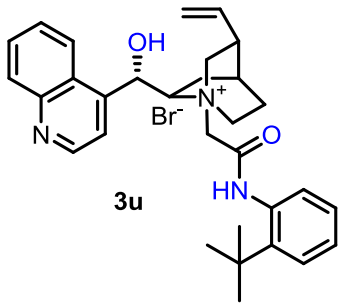




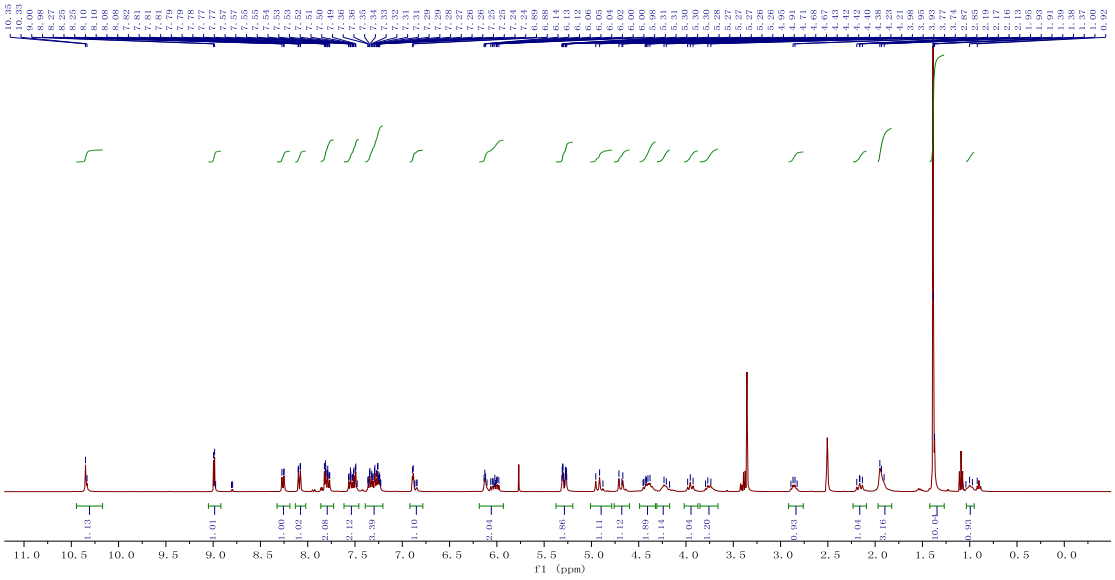
3t

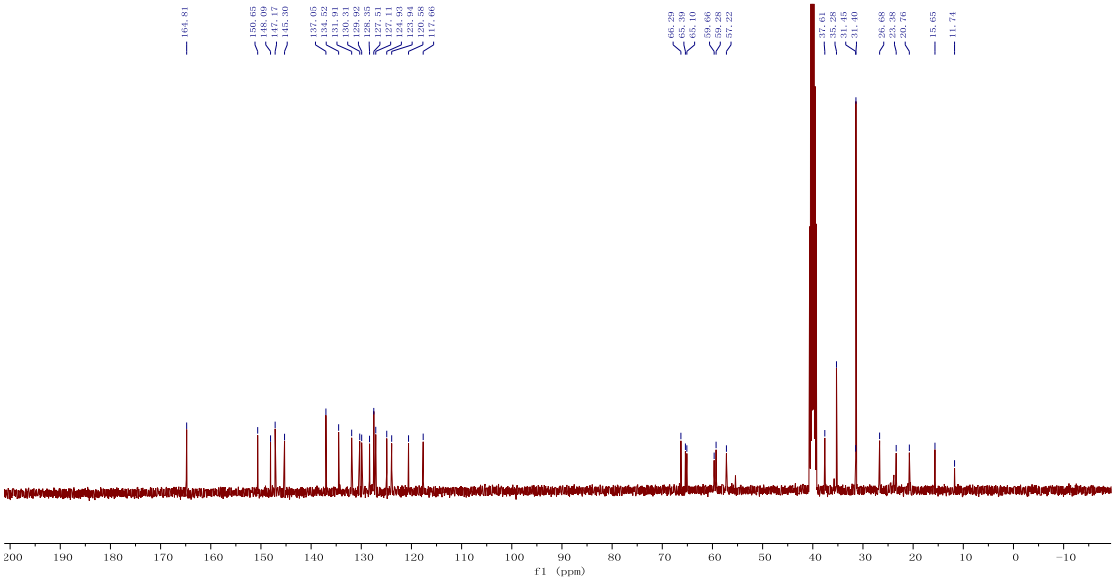


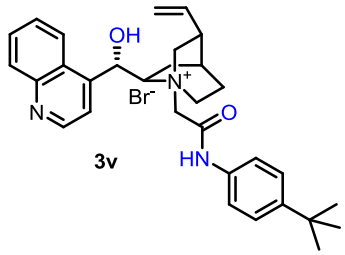




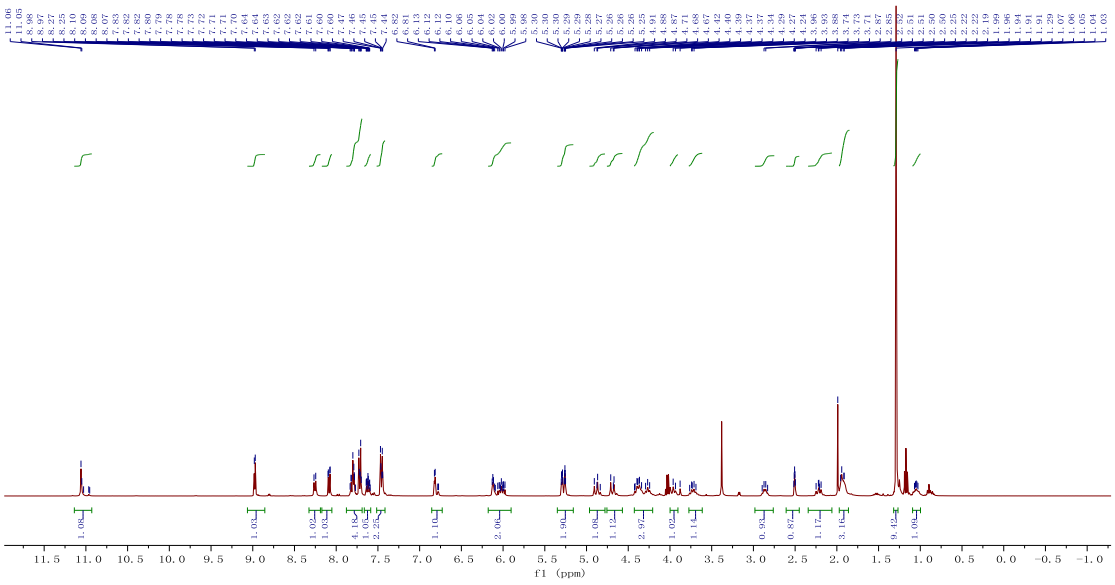
3u

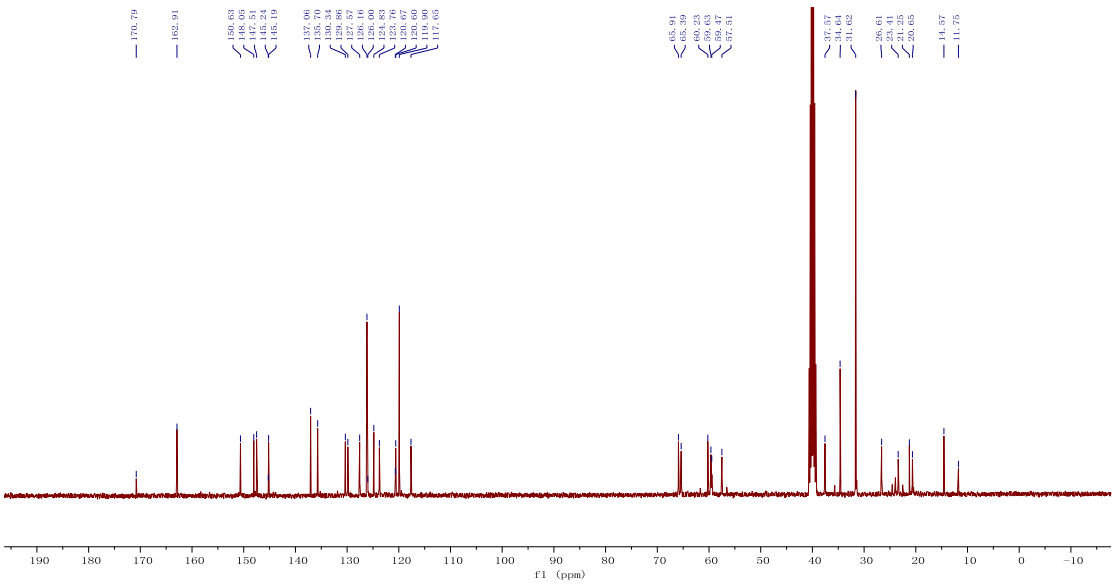


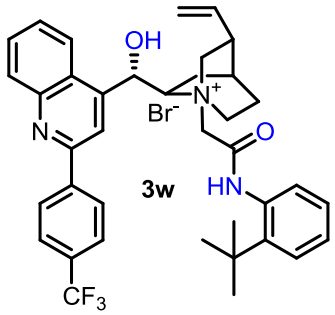


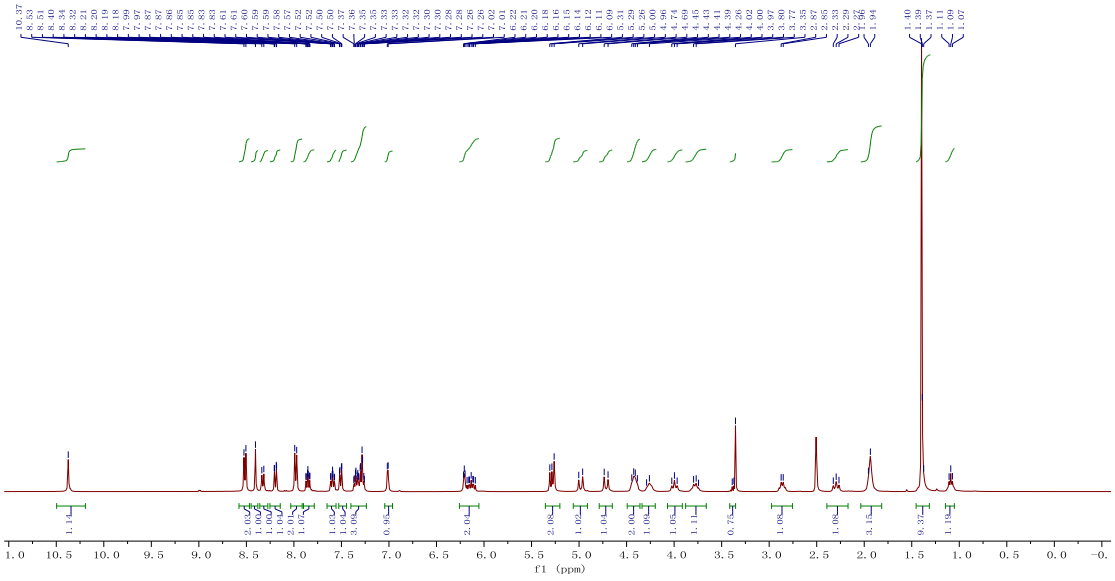


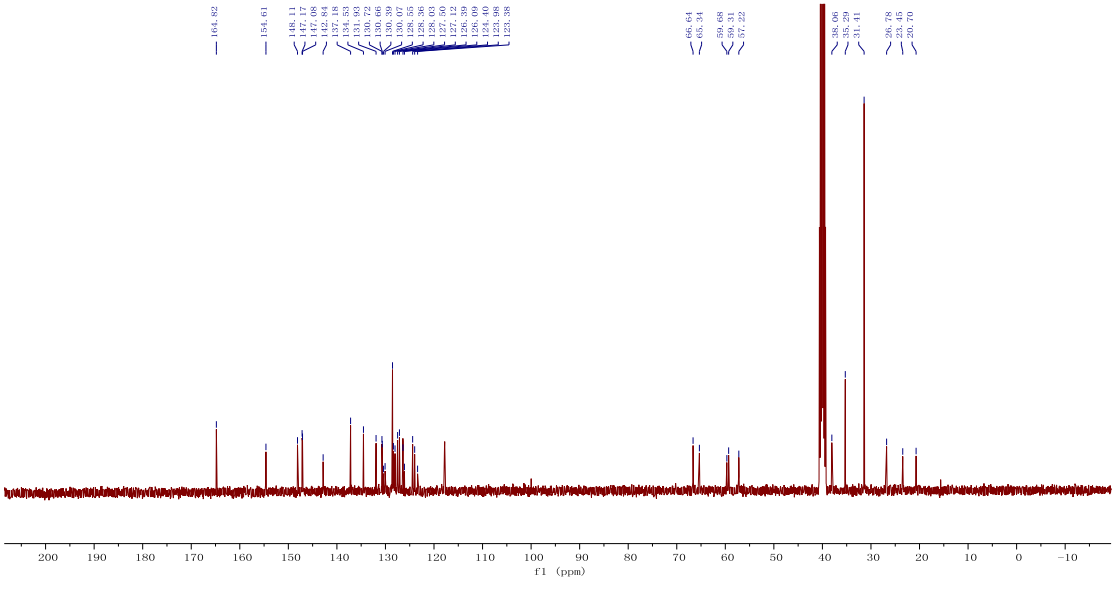
3v

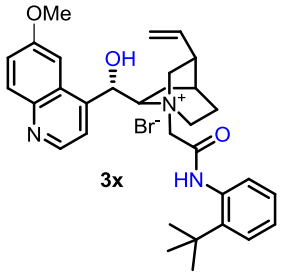


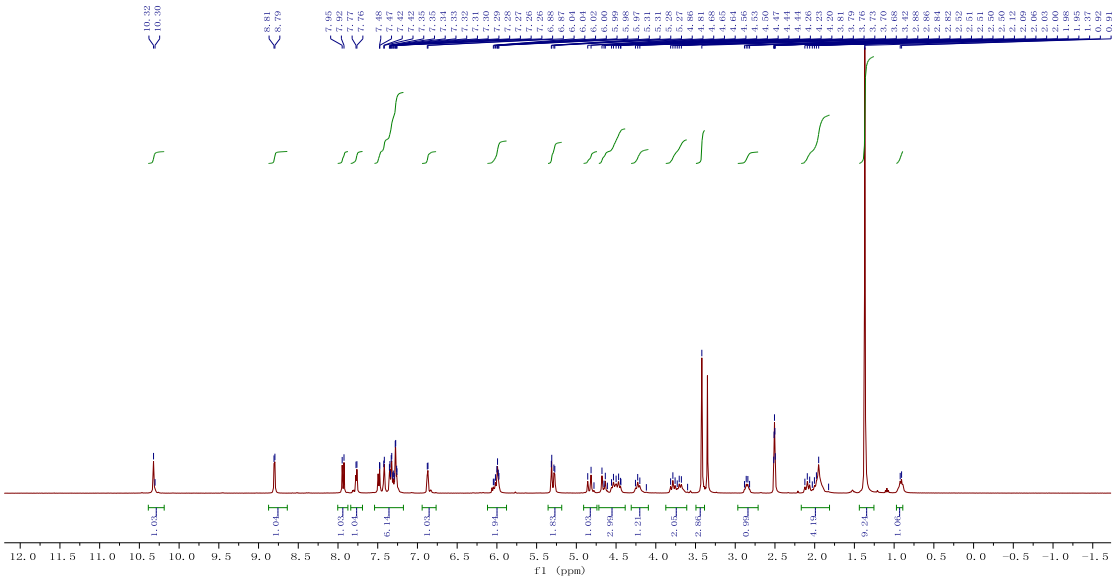


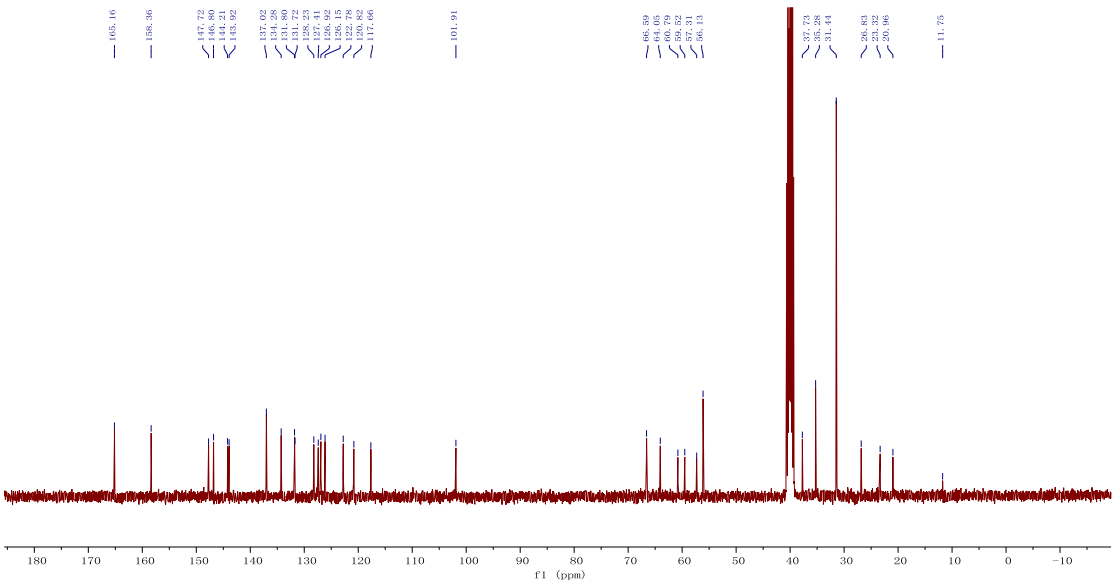

OH
N
Br-
N+
O
HN
3w
CF3

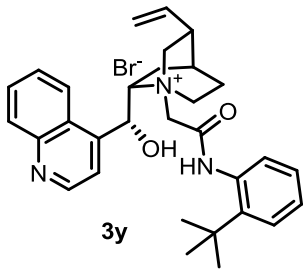




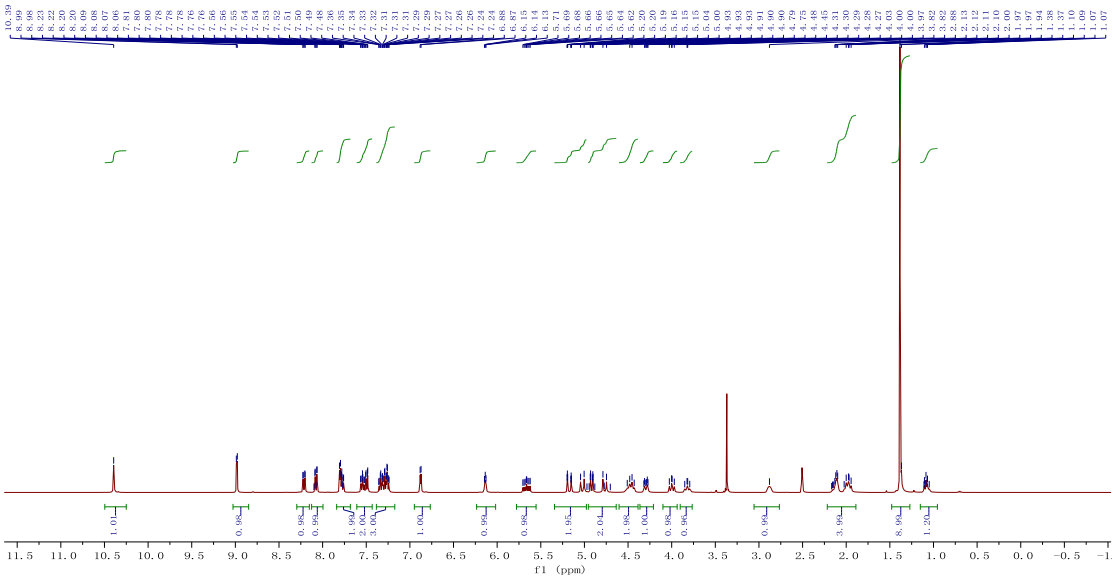

OMe
OH
N
N+
Br-
O
HN
3x

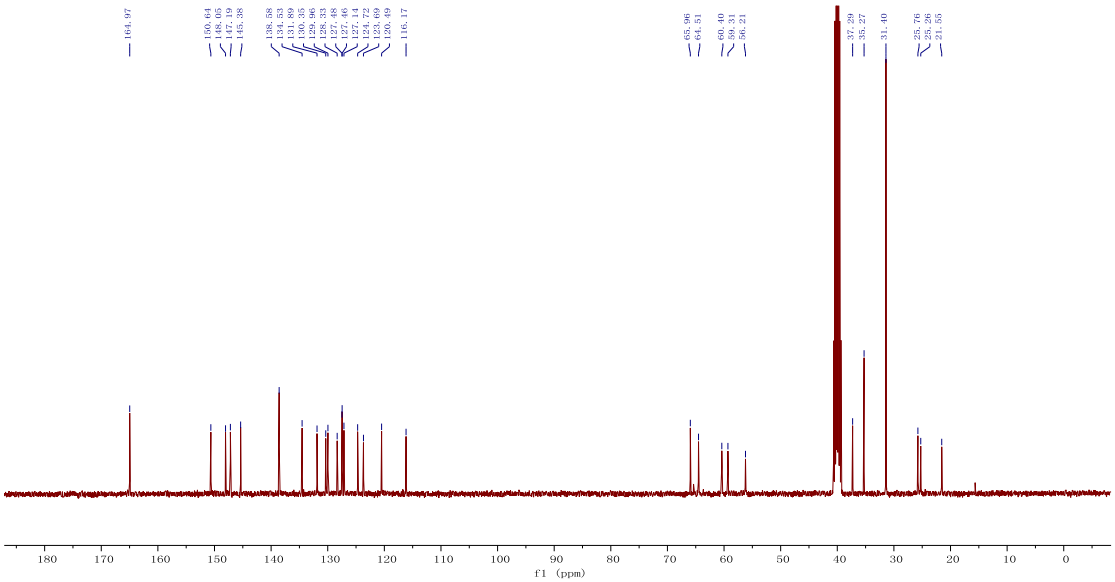


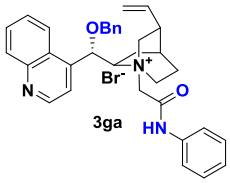


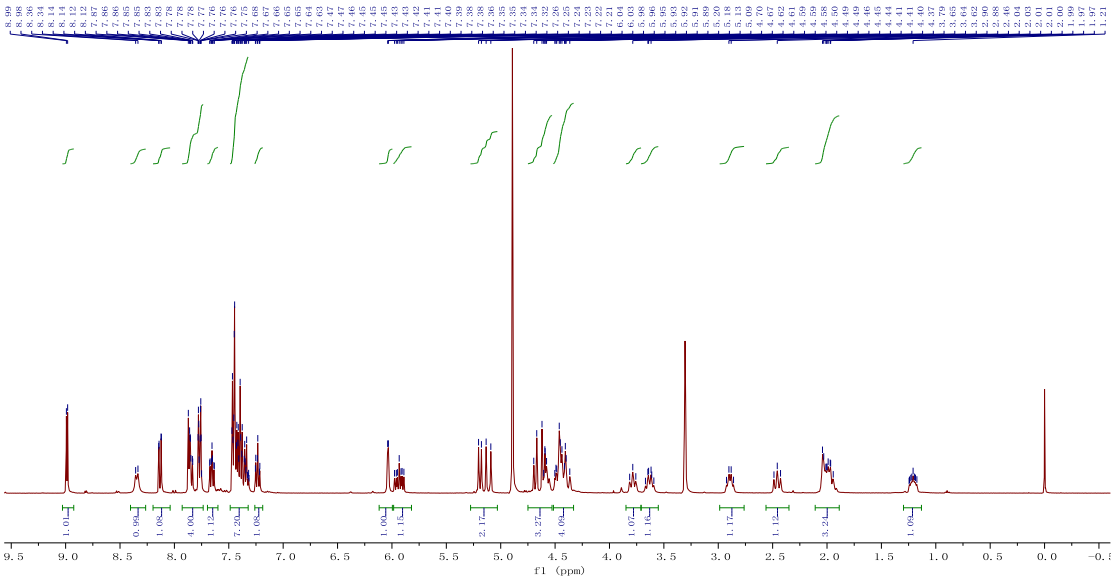


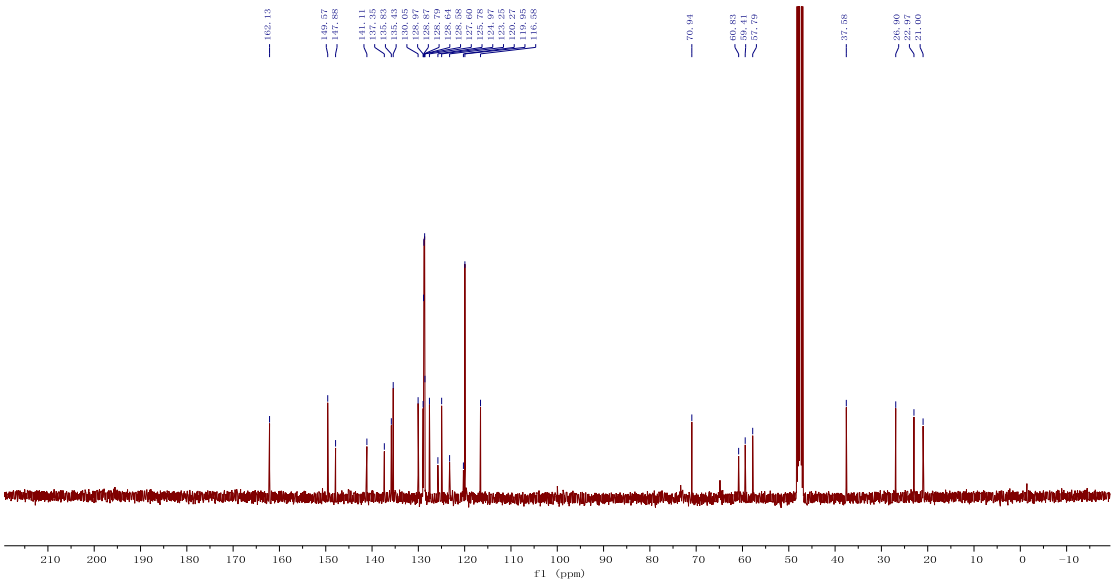
3y

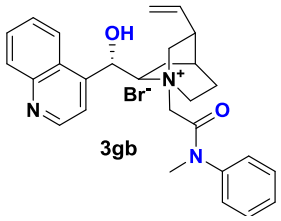


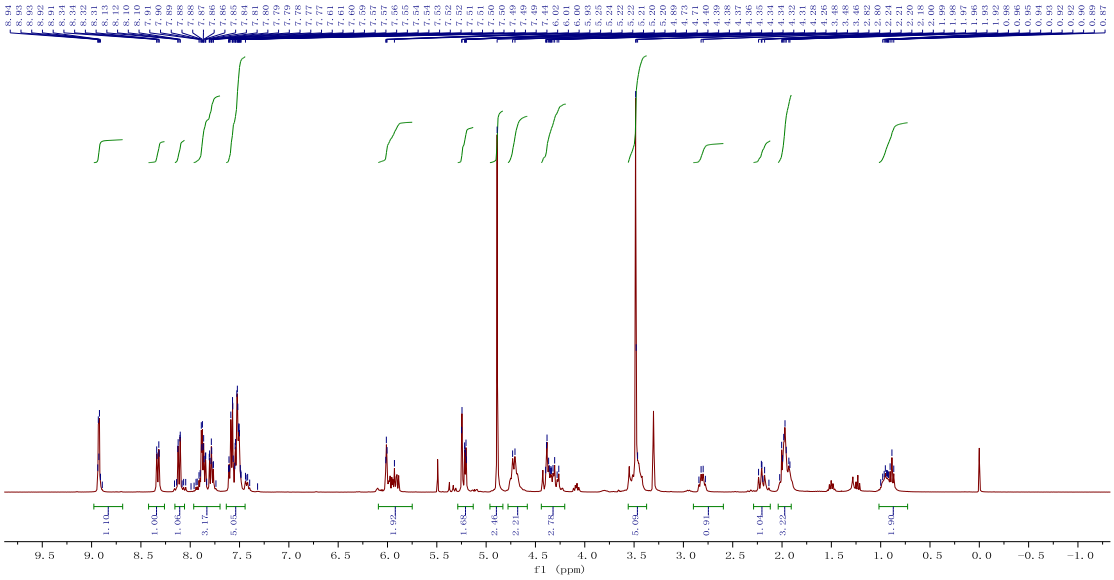


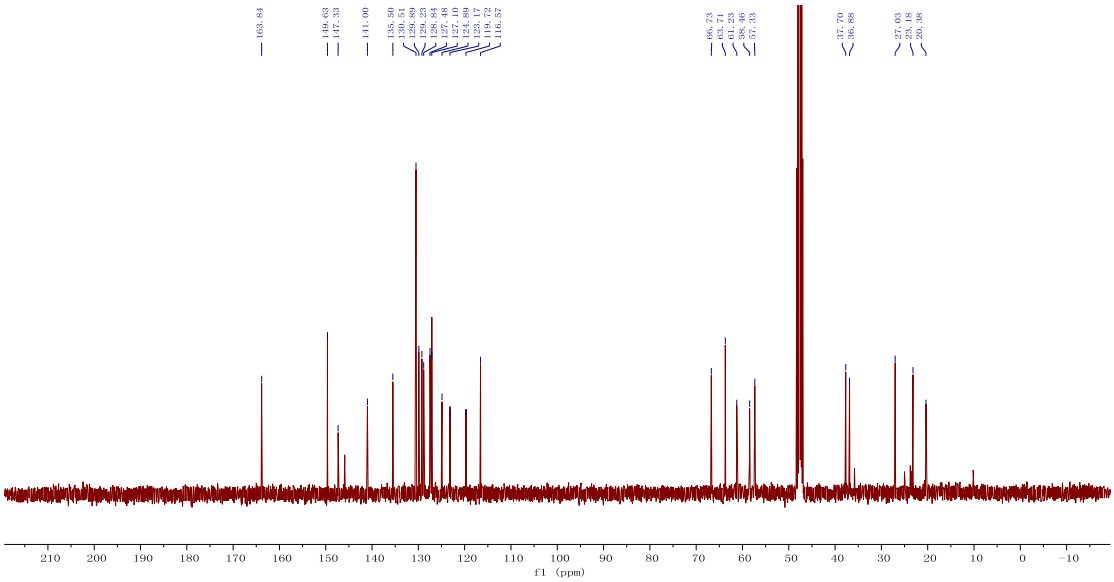

OBn
Br-
N+
N
O
HN
3ga



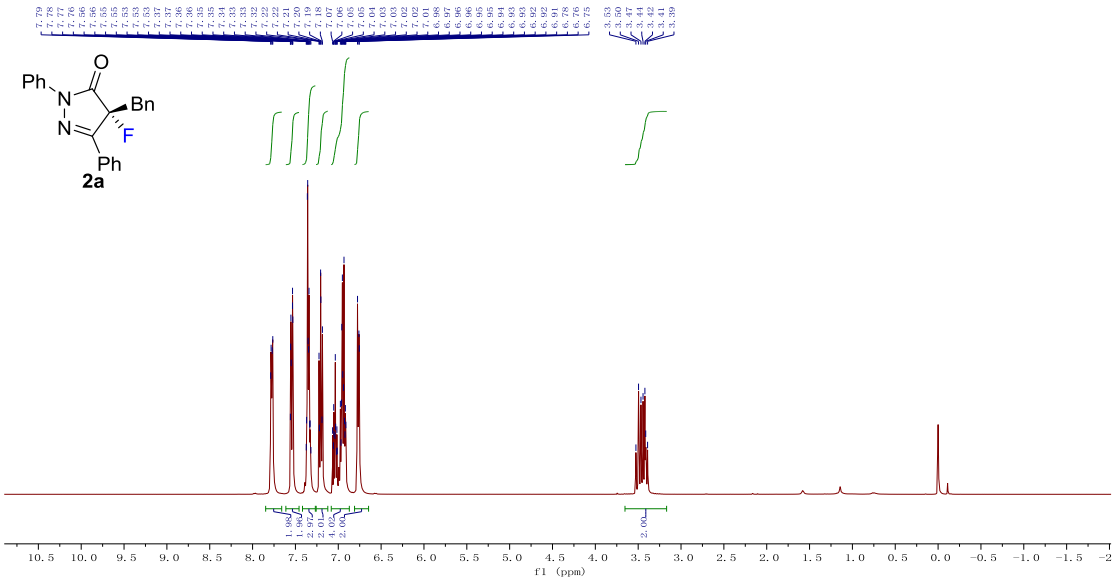


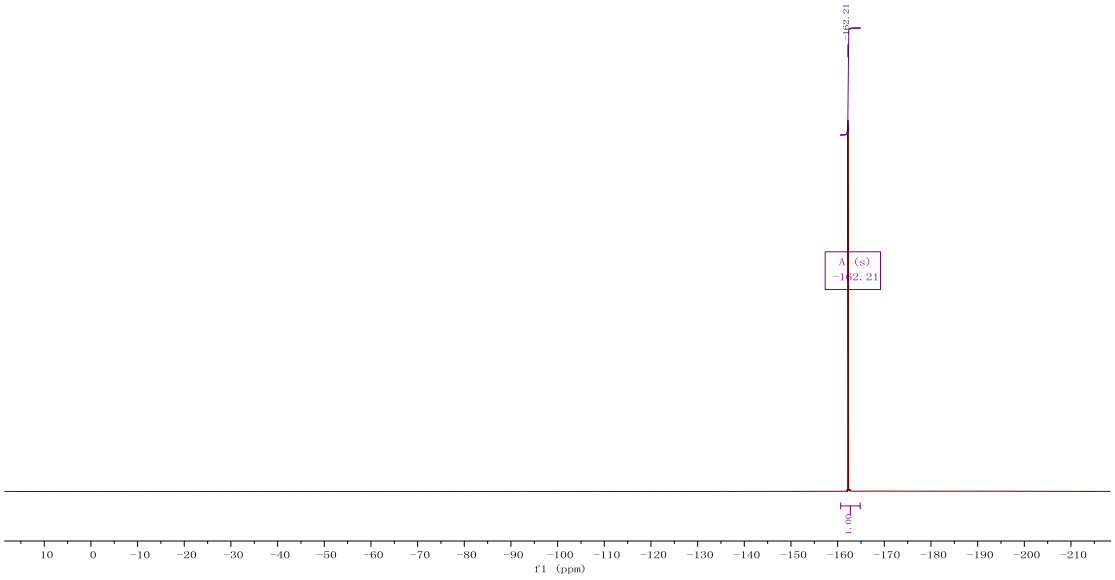

OH
N+
Br-
N
O
N
3gb

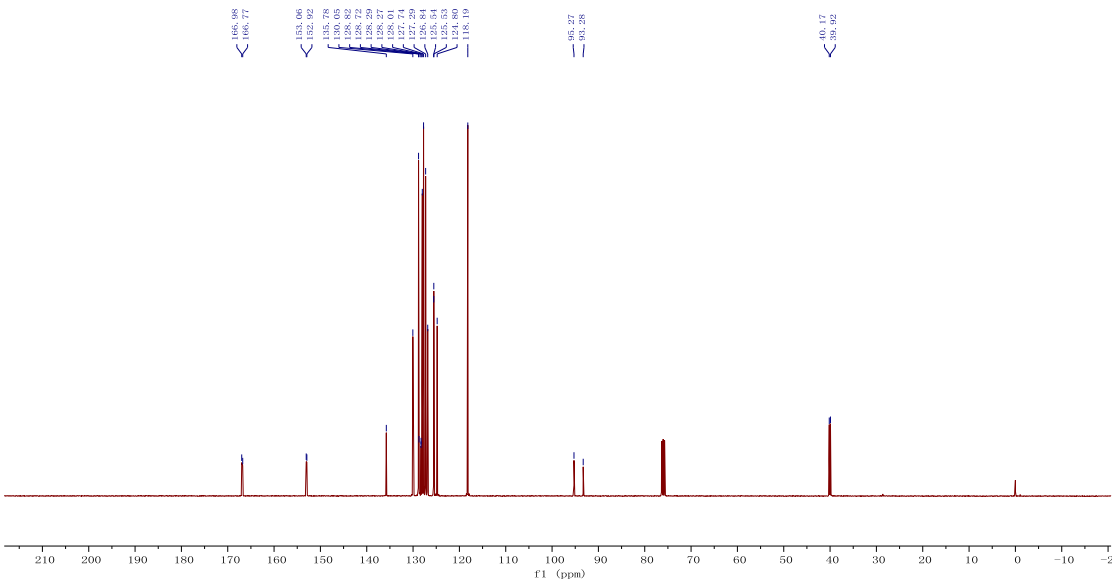

f1 (ppm)

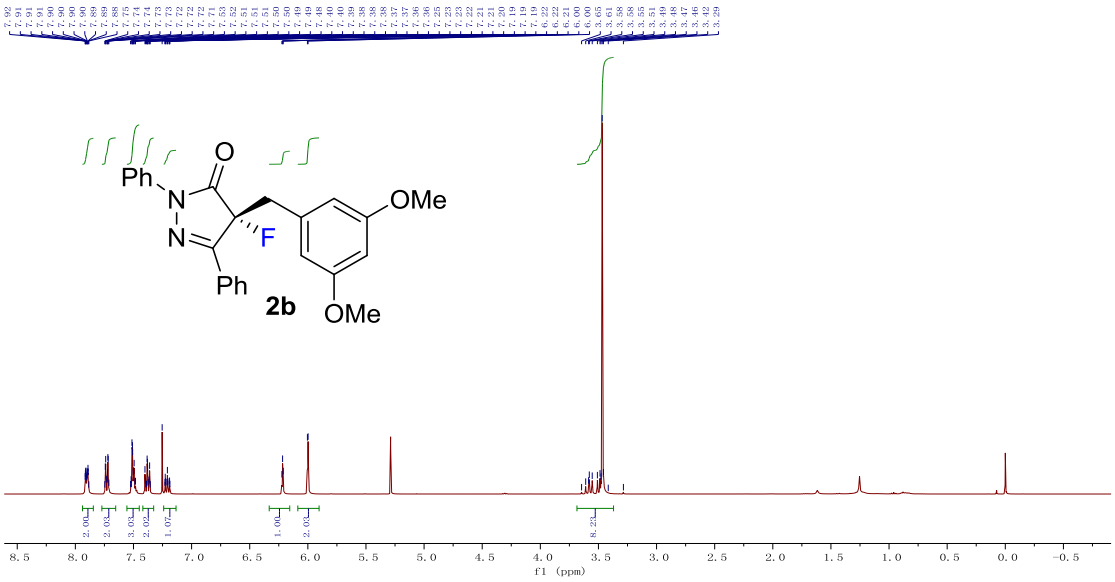

f1 (ppm)

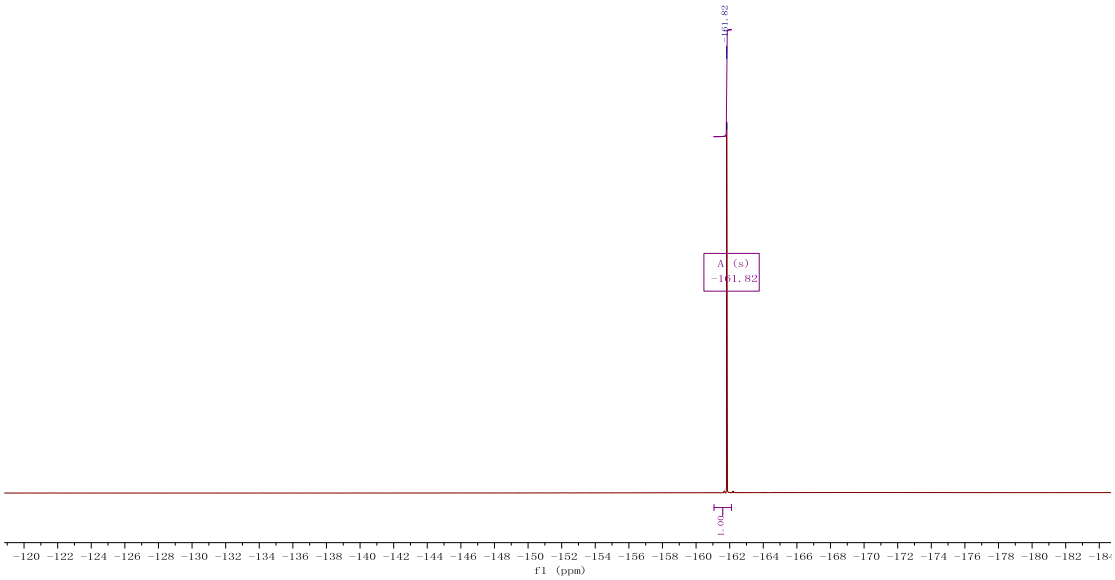
5.2 **NMR spectra for fluorination products**

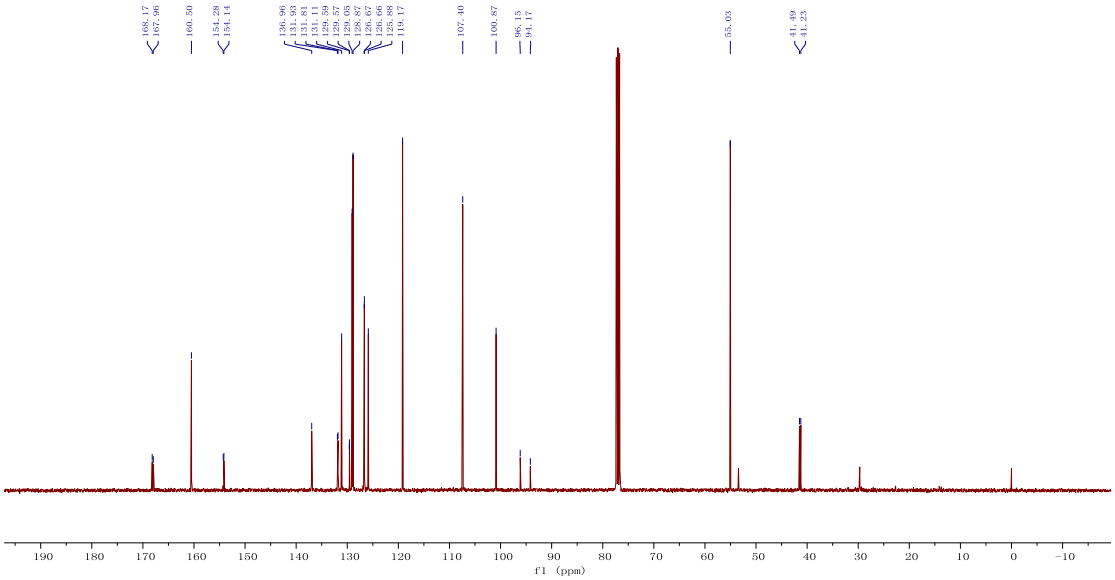


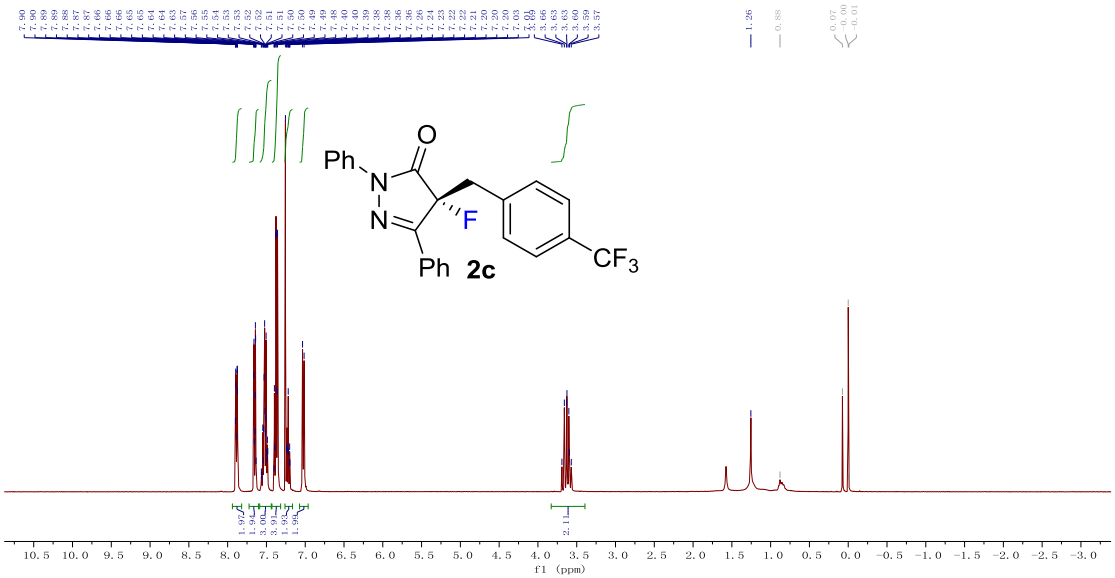


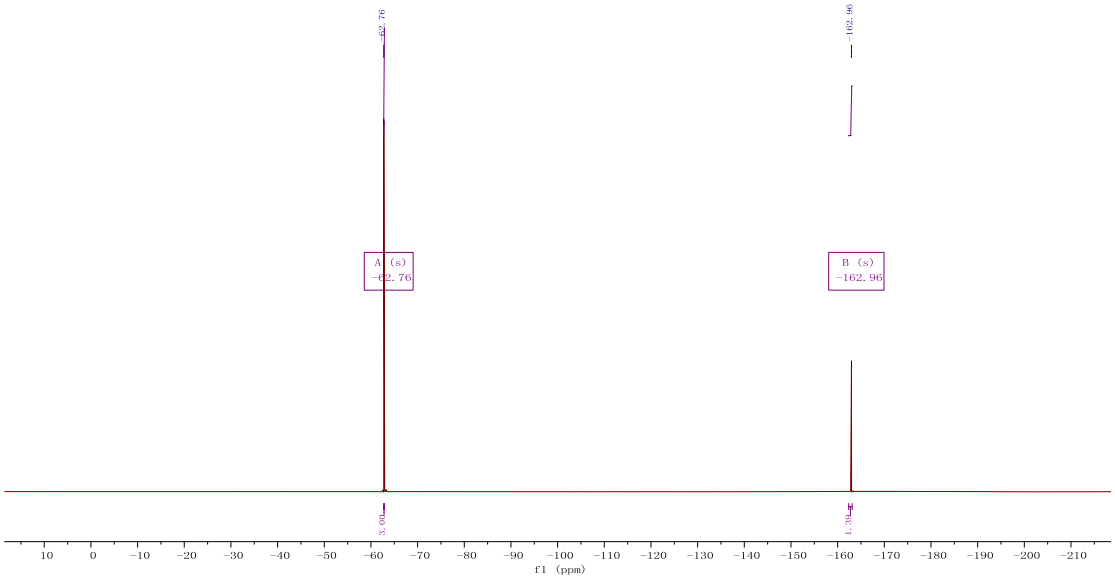


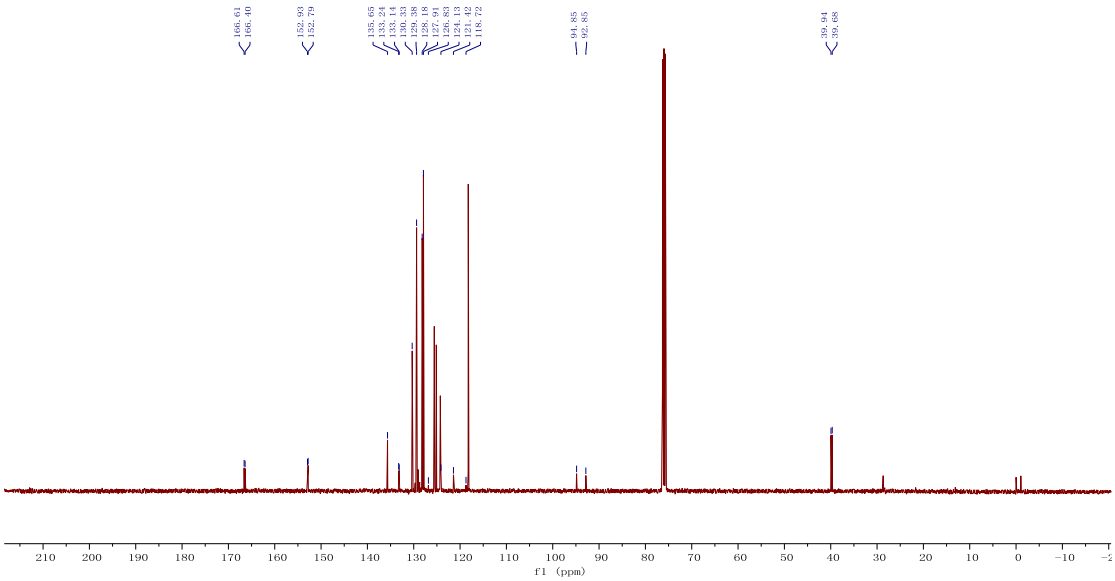

O
Ph
N
N
F
OMe
Ph
OMe
2b

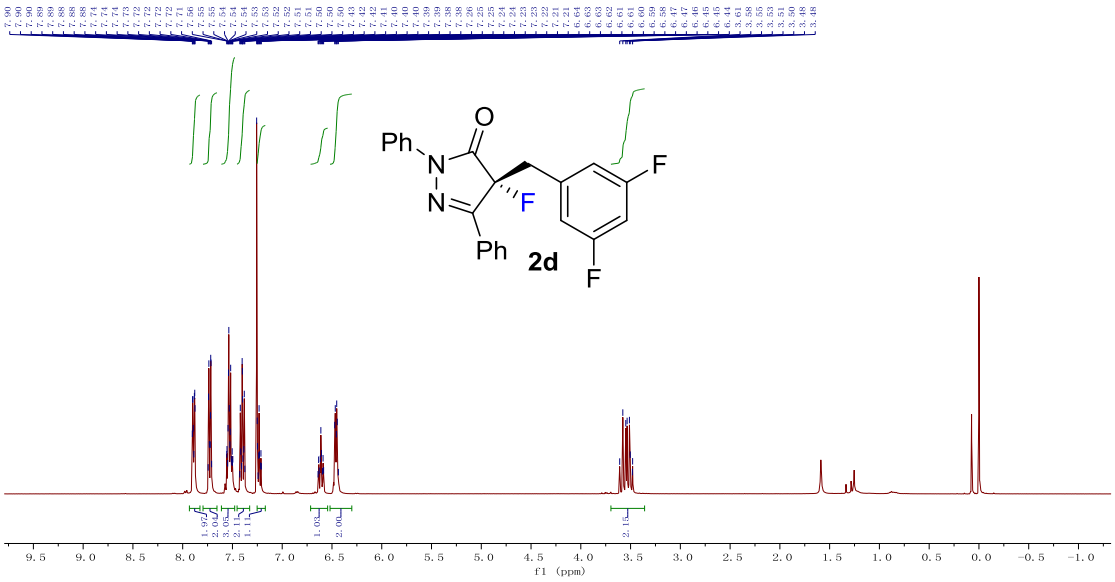

A (s)
-161.82
f1 (ppm)

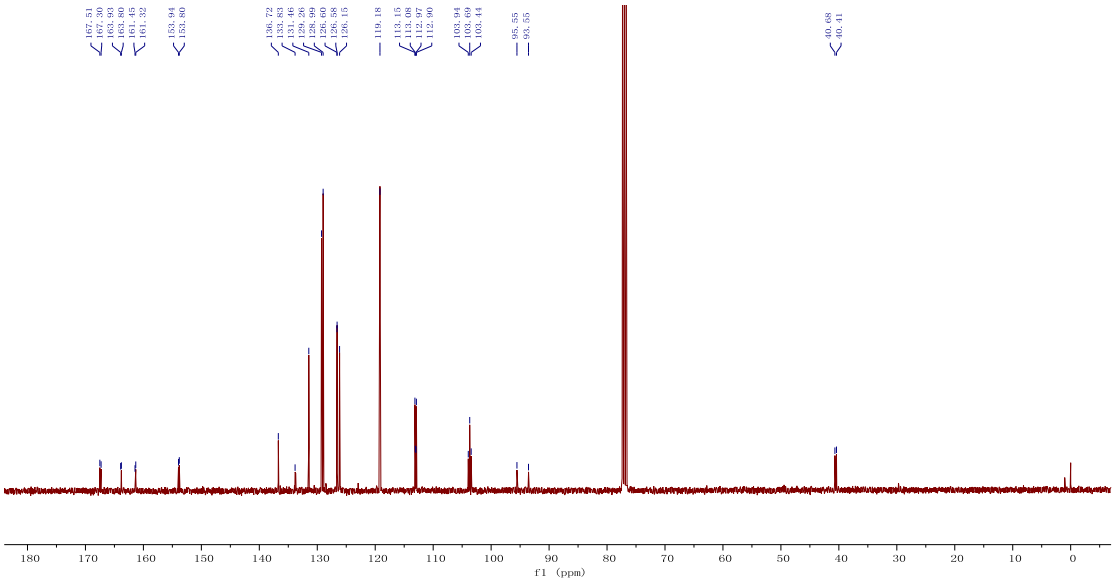

f1 (ppm)

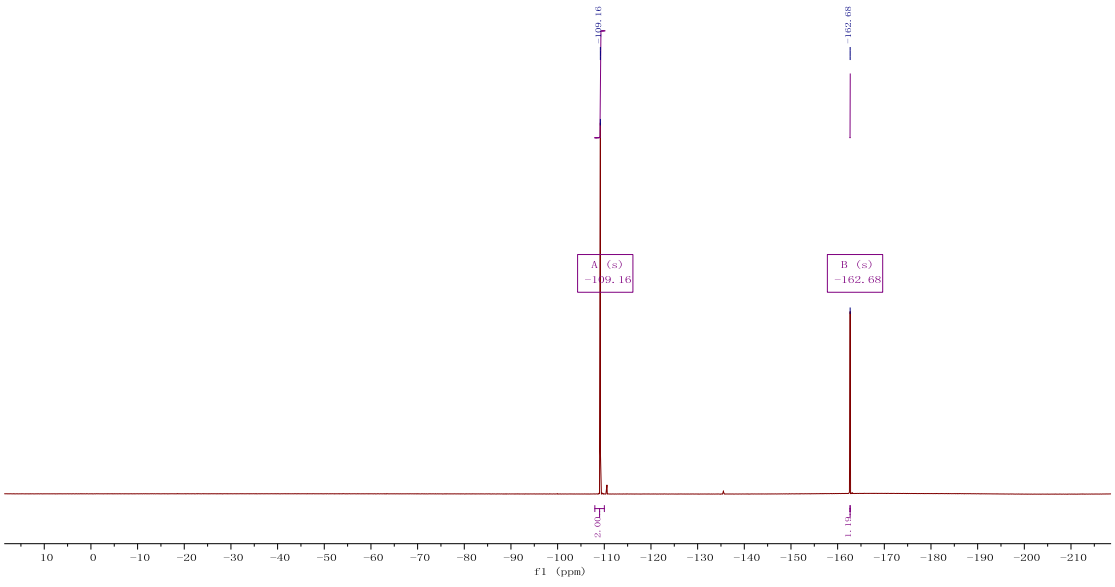

Ph
N
N
O
F
Ph
CF3
2c
f1 (ppm)

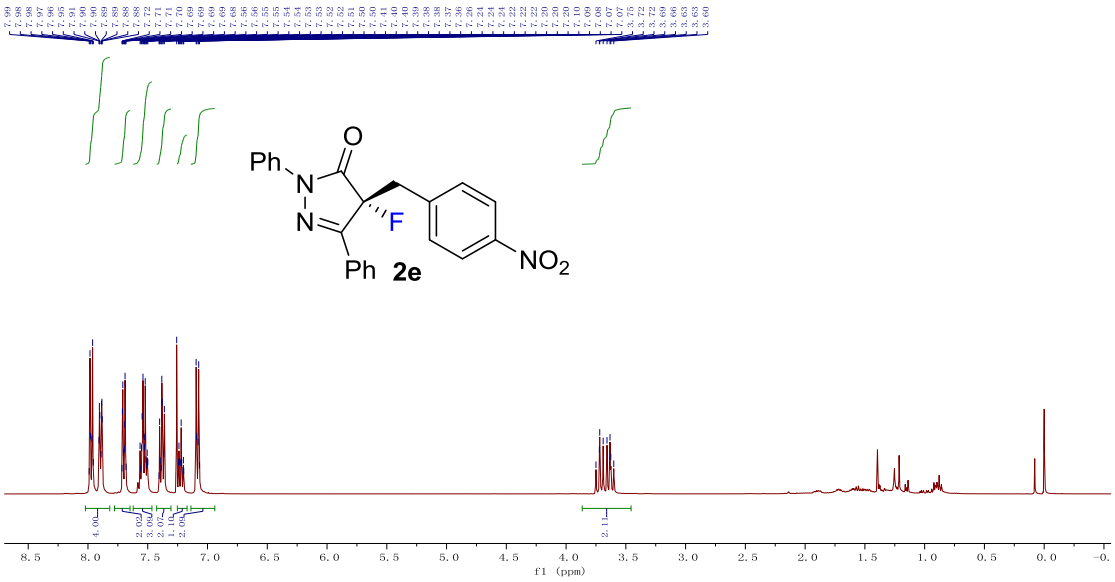

-62.76
-162.96
A (s)
-62.76
B (s)
-162.96
f1 (ppm)


166.61
166.40
152.93
152.79
135.65
133.24
130.33
129.38
128.18
127.84
126.83
124.13
121.42
118.72
94.85
92.85
39.94
39.68
f1 (ppm)

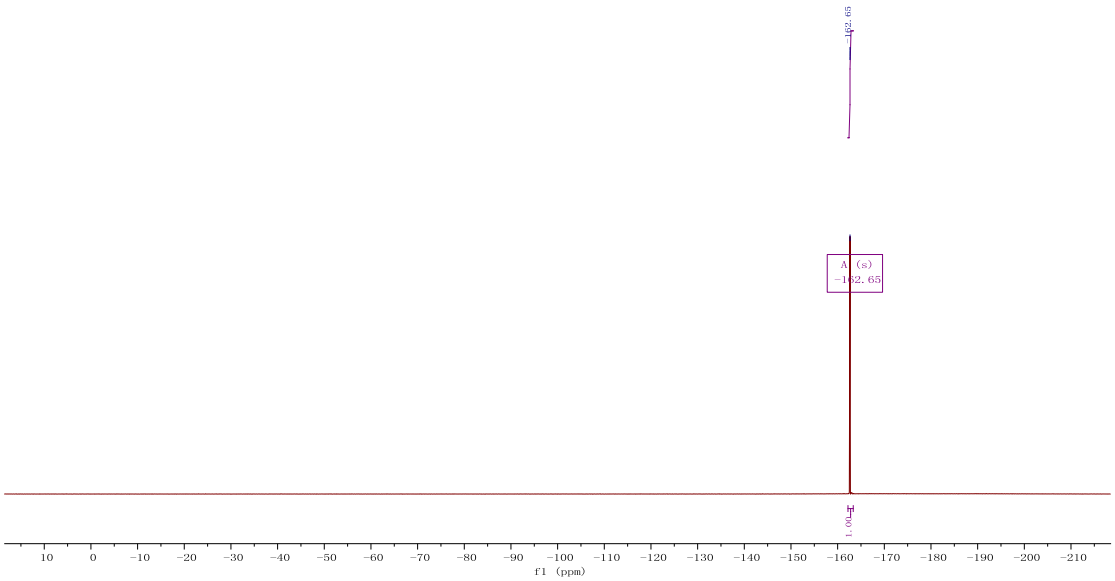

Ph
N
N
O
F
Ph
F
F
2d

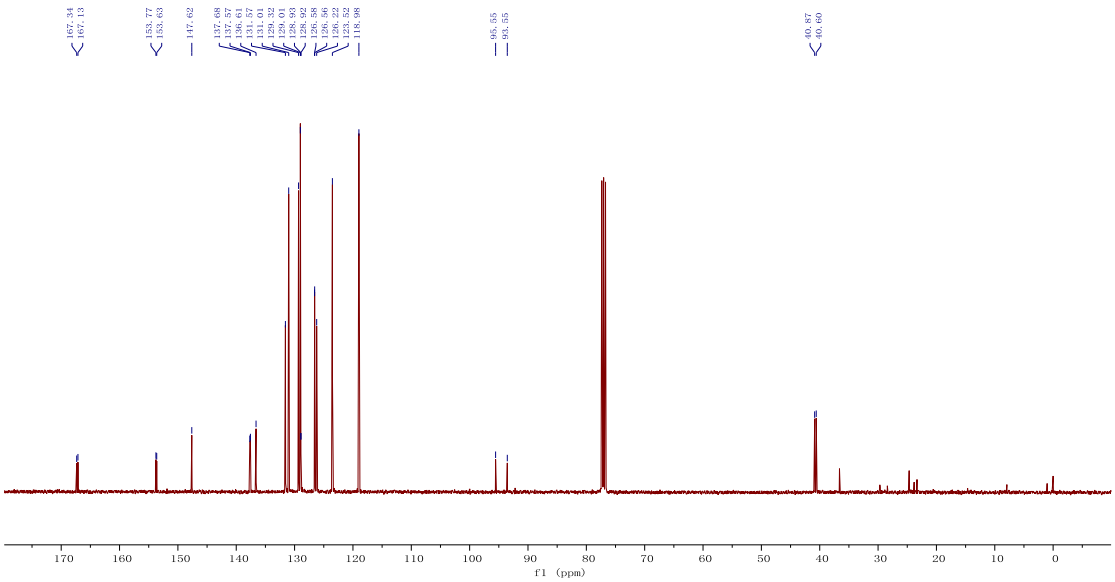


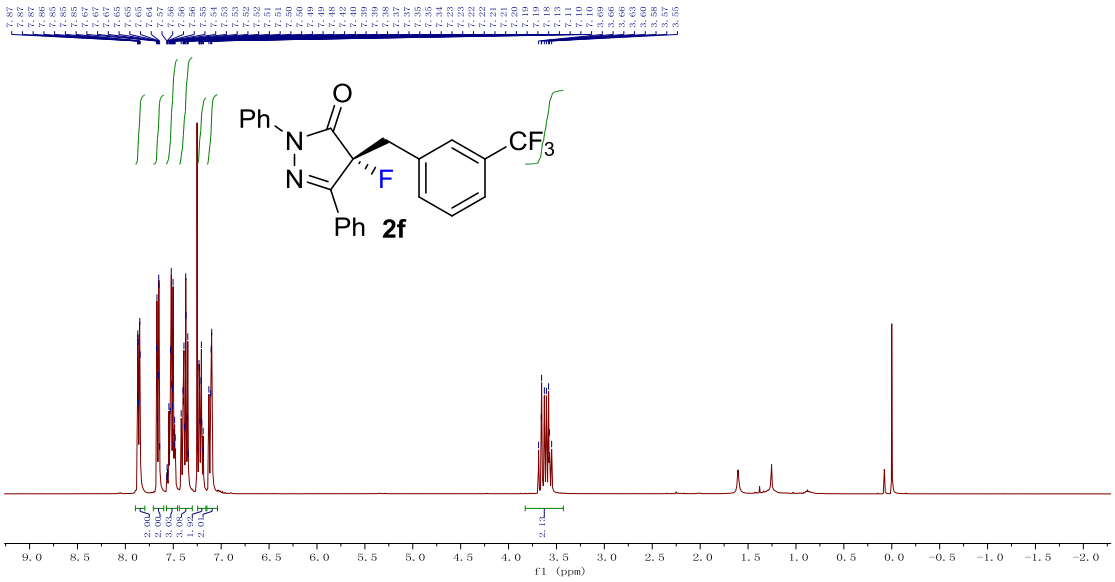

A (s)
-109.16
B (s)
-162.68

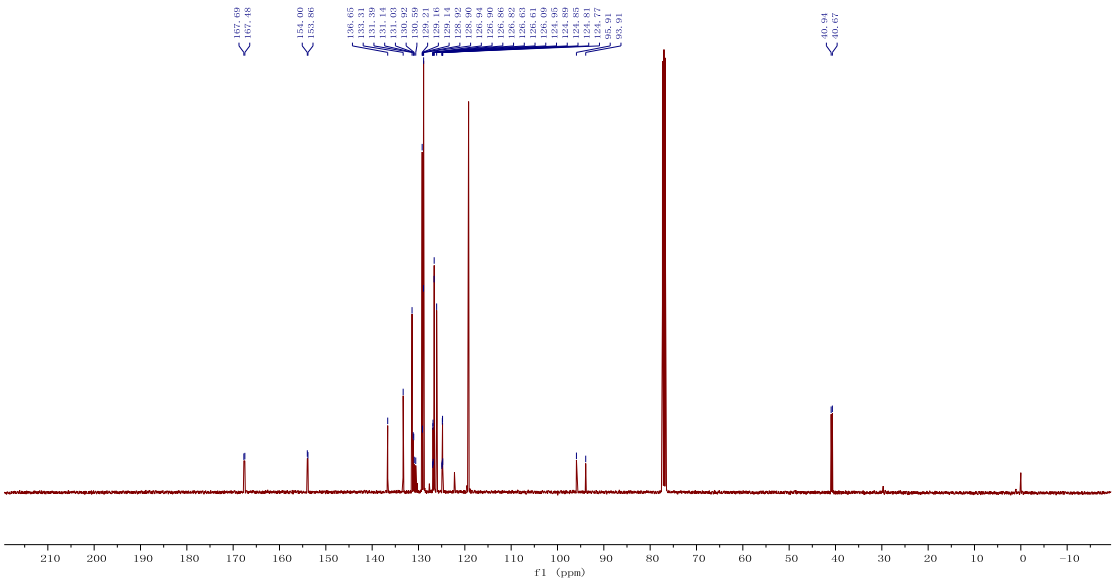

O
Ph
N
N
F
Ph
NO2
2e

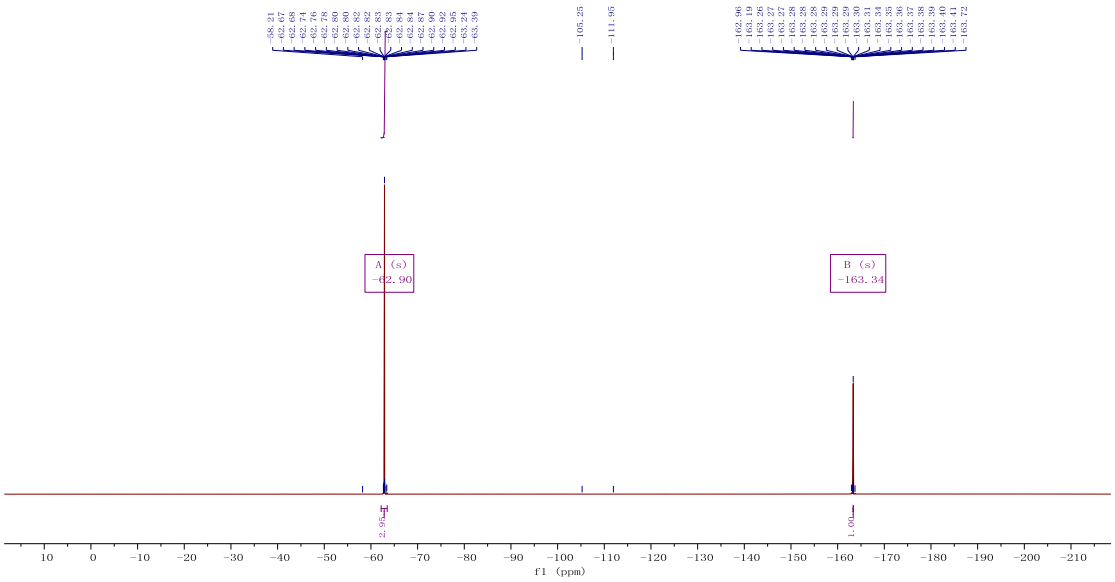
f1 (ppm)

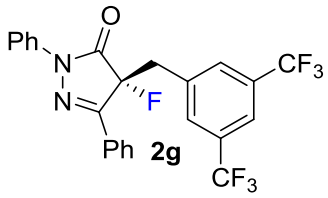

A (s)
-162.65
f1 (ppm)

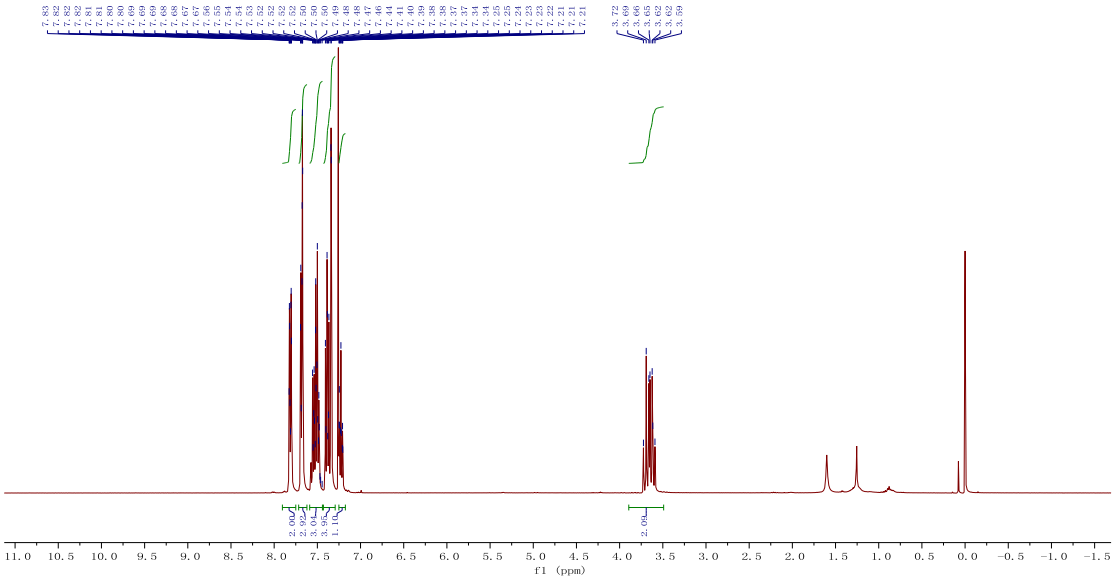

f1 (ppm)

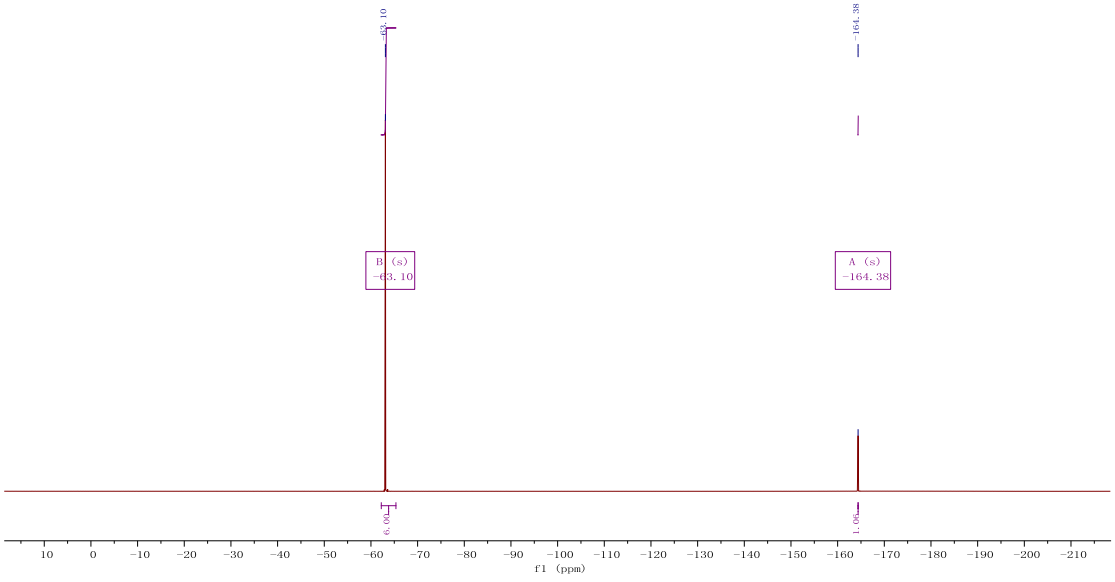

Ph
N
N
O
F
CF3
Ph
2f

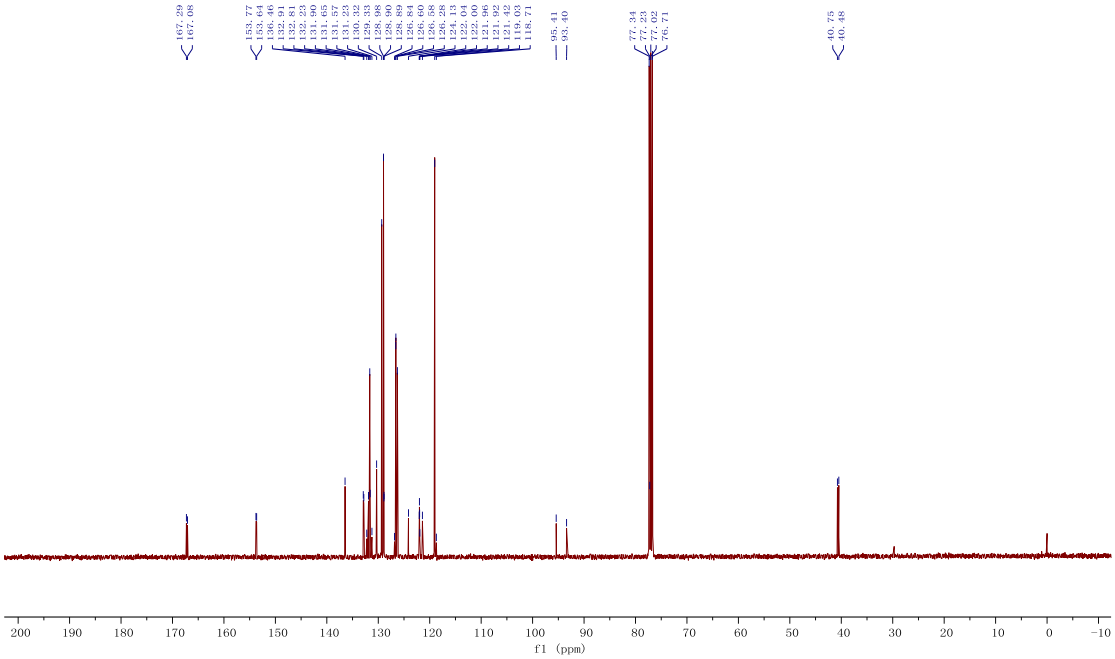


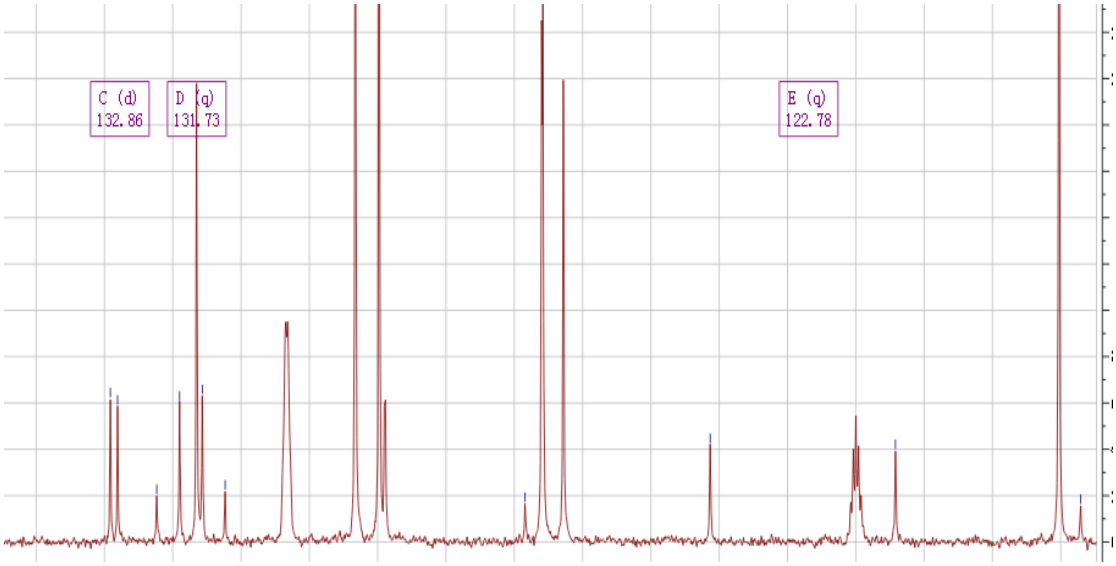

A (s)
-62.90
B (s)
-163.34

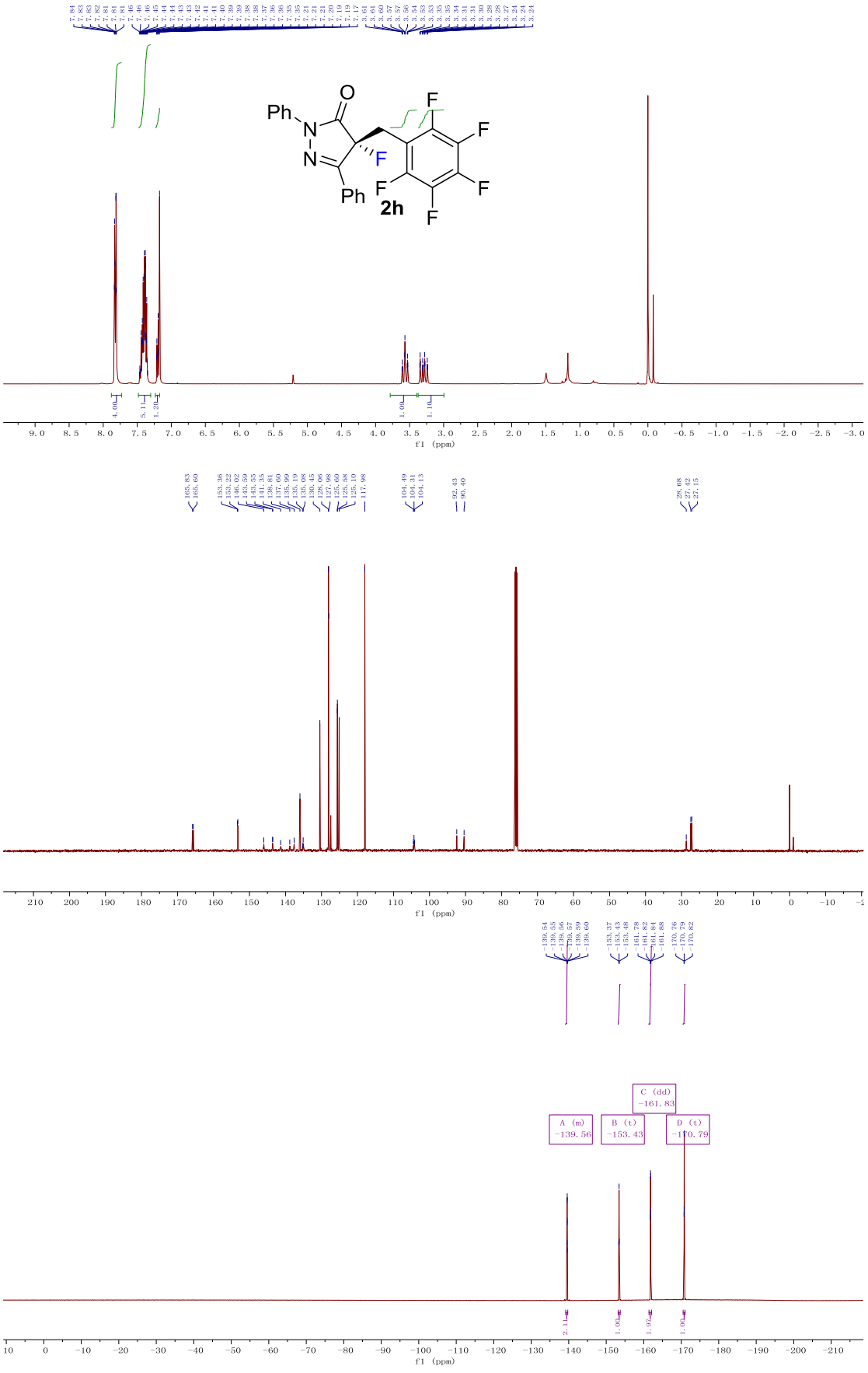

O
Ph
N
N
F
Ph
2g
CF3
CF3

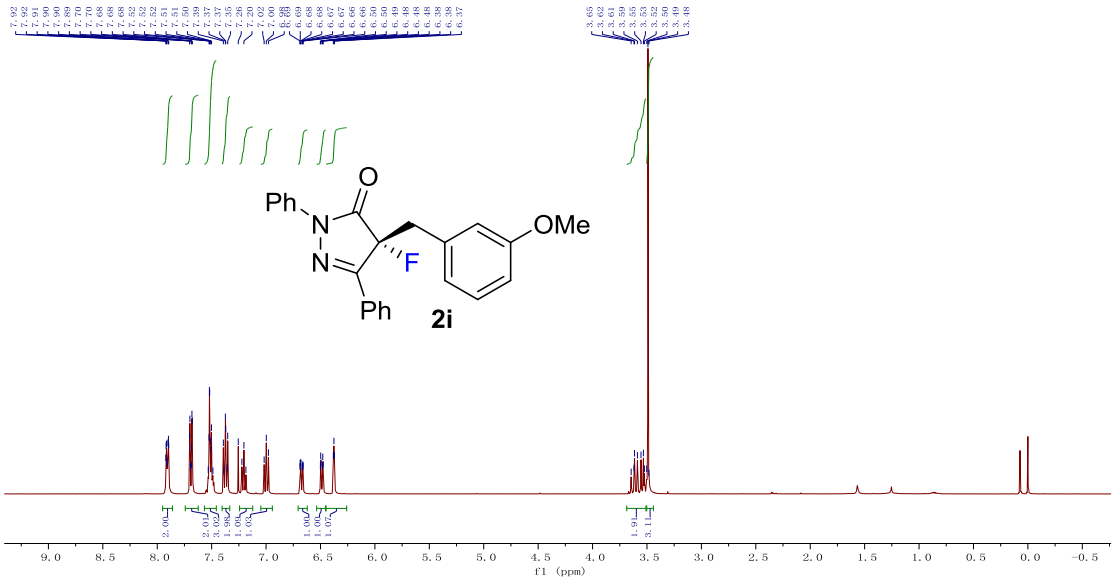

f1 (ppm)

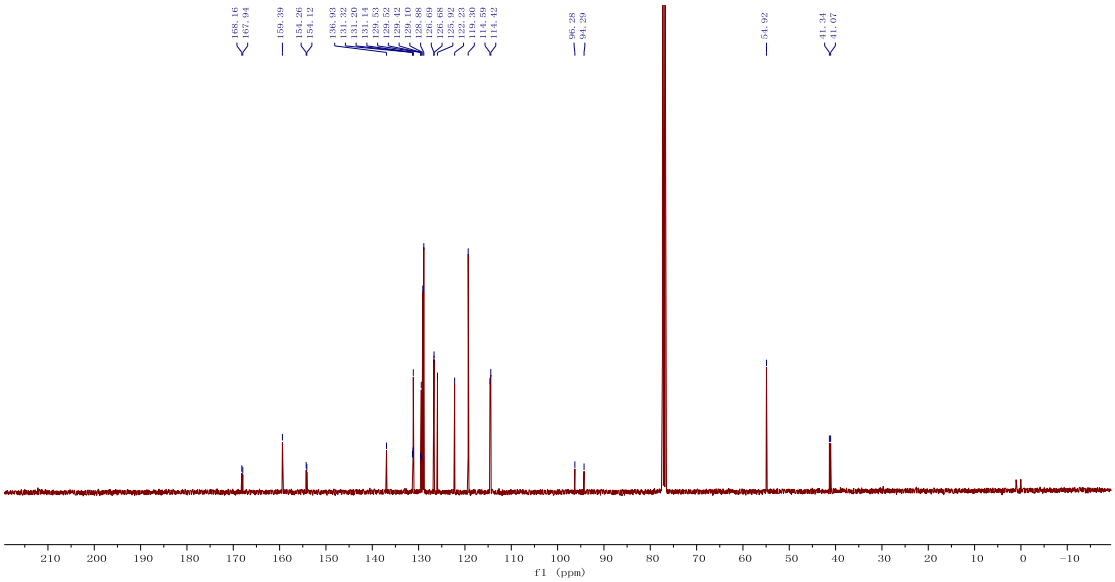

B (s)
-63.10
A (s)
-164.38
f1 (ppm)

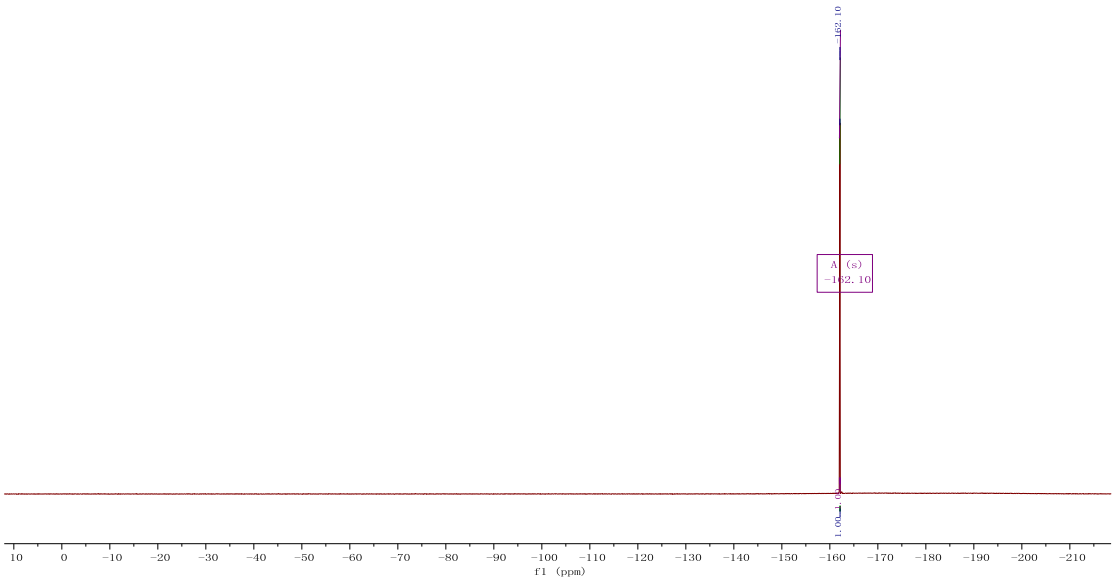

167.29
167.08
153.77
153.64
136.46
132.91
132.81
132.23
131.90
131.65
131.57
131.23
130.32
129.33
128.98
128.90
128.89
126.84
126.60
126.58
126.28
124.13
122.64
122.00
121.96
121.92
121.62
114.63
114.56
118.71
95.41
93.40
77.34
77.23
77.02
76.71
40.75
40.48
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

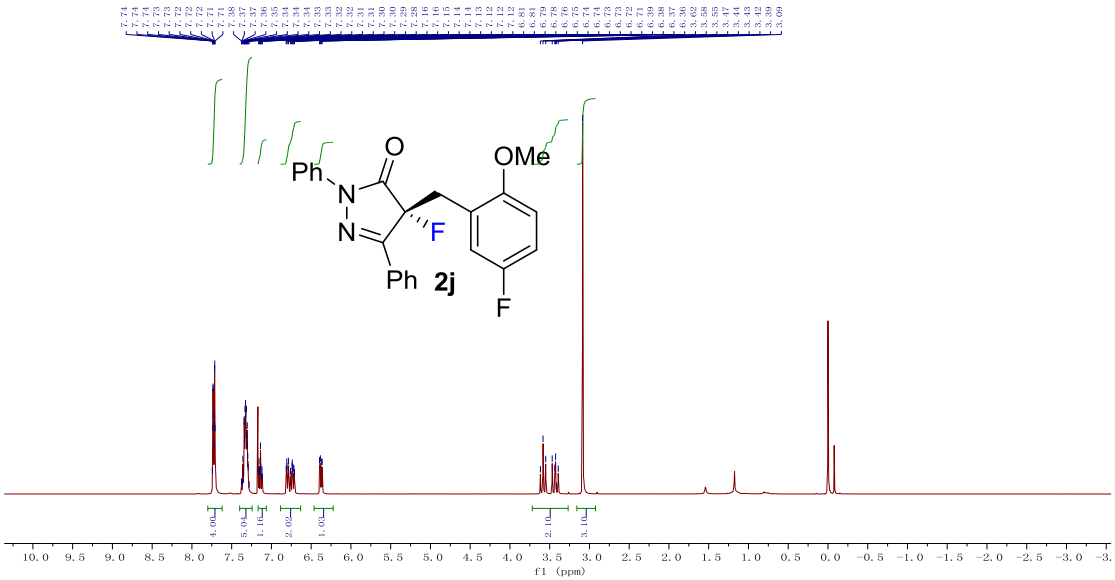

C (d)
132.86
D (q)
131.73
E (q)
122.78

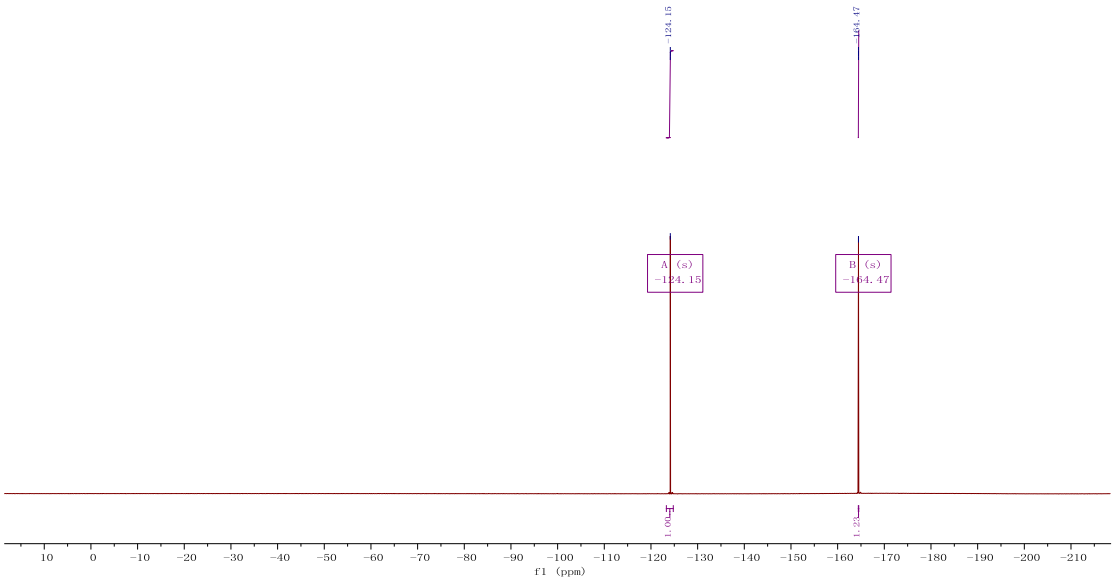

Ph
N
N
O
F
F
F
F
F
Ph
F
2h
f1 (ppm)
f1 (ppm)
A (m)
−139.56
B (t)
−153.43
C (dd)
−161.83
D (t)
−170.79
f1 (ppm)

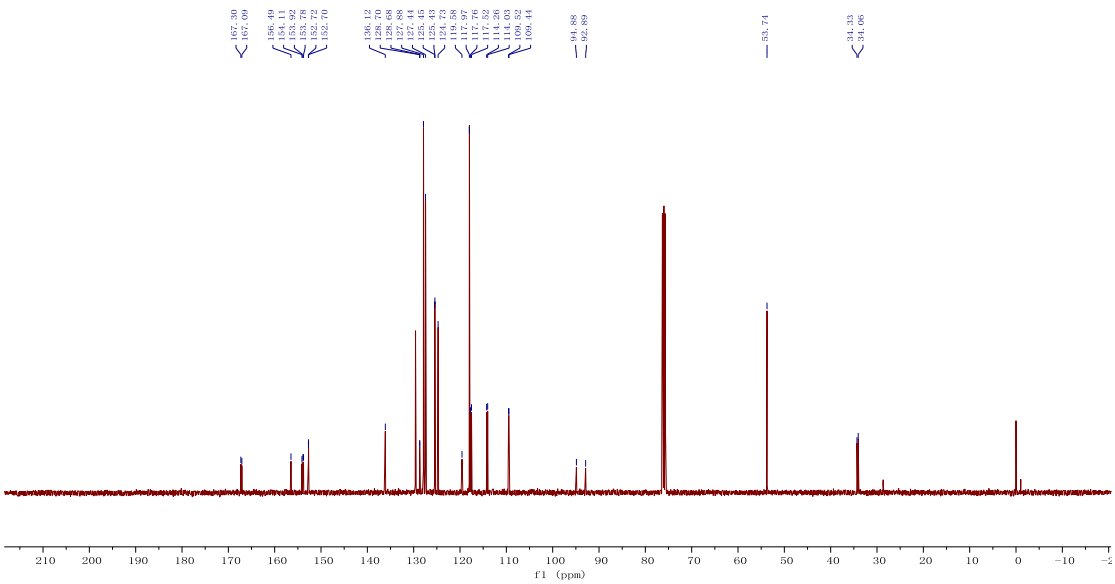

O
Ph
N
N
F
OMe
Ph
2i

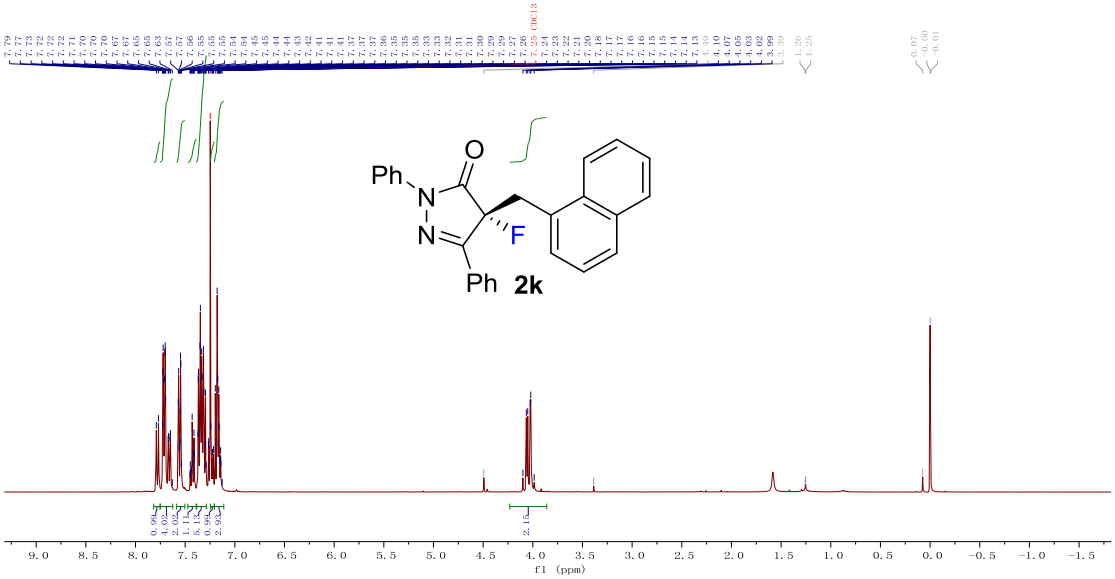


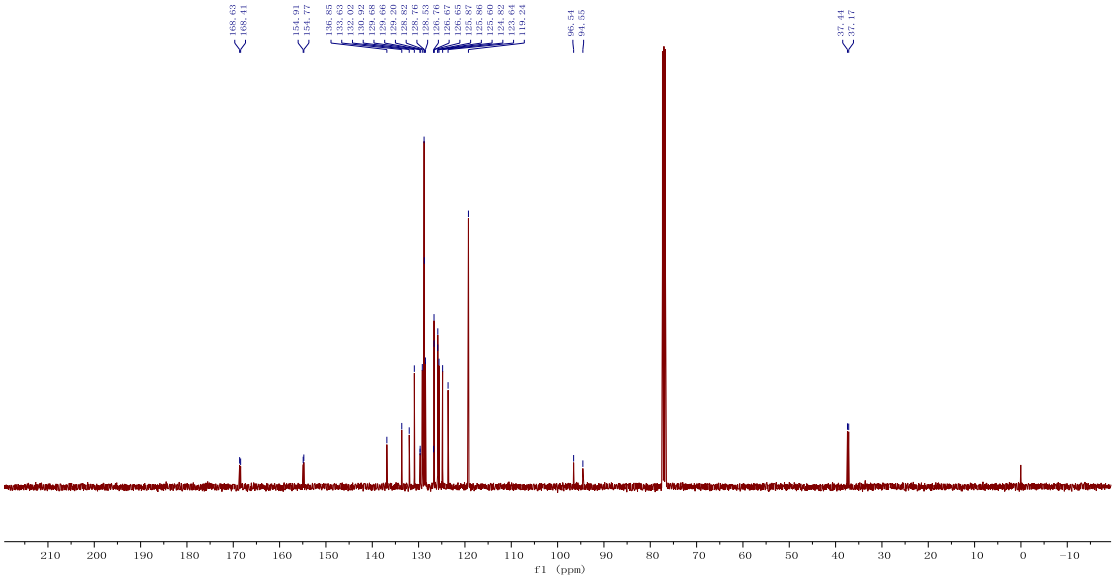

A (s)
-162.10

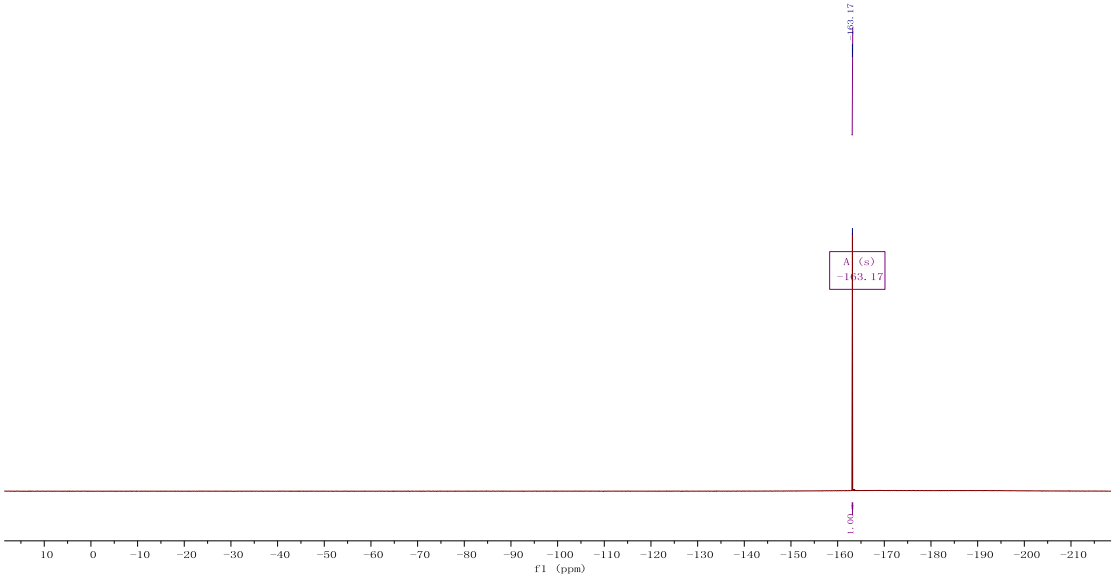

Ph
N
N
O
F
Ph
OMe
F
2j
f1 (ppm)

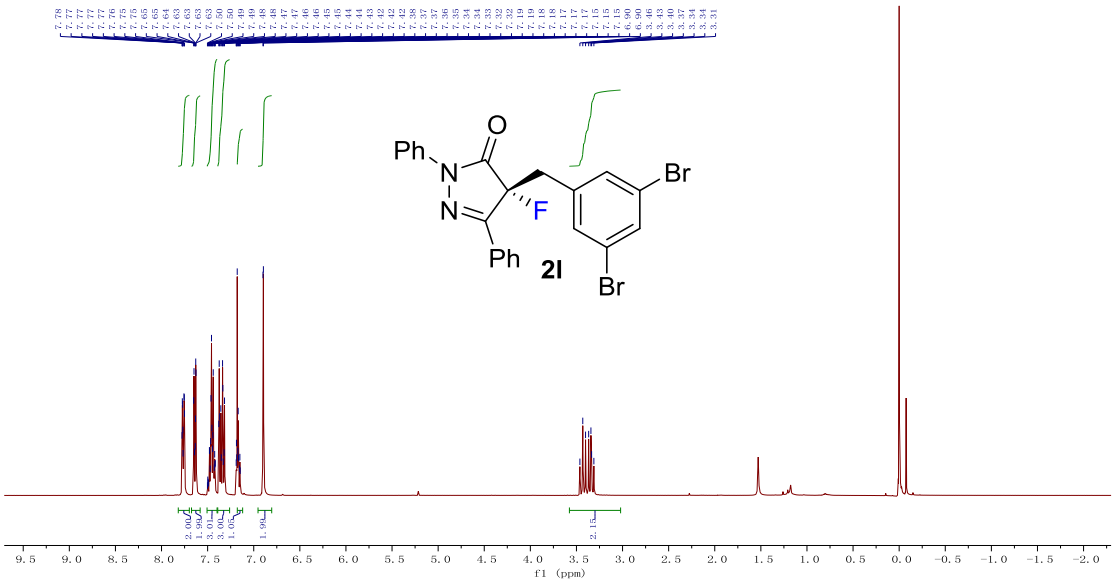

124.15
164.47
A (s)
-124.15
B (s)
-164.47
f1 (ppm)

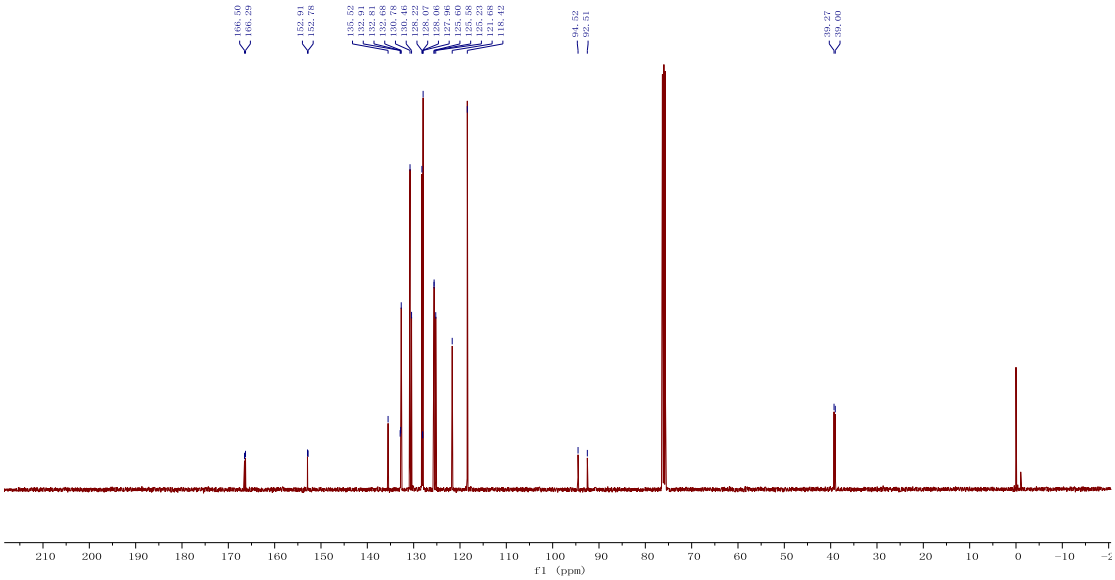

167.30
167.09
156.49
154.11
153.92
153.78
152.72
152.70
130.12
128.70
128.68
127.88
127.44
125.45
125.43
124.73
119.58
117.97
117.76
117.52
114.26
114.03
109.52
109.44
94.88
92.89
53.74
34.33
34.06
f1 (ppm)

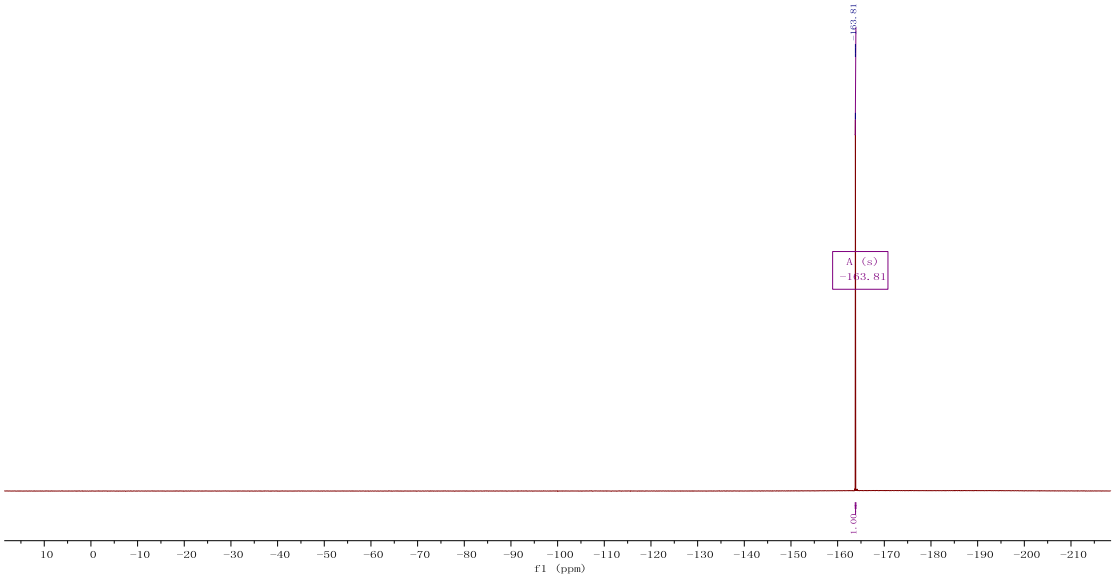

Ph
N
N
O
F
Ph
2k

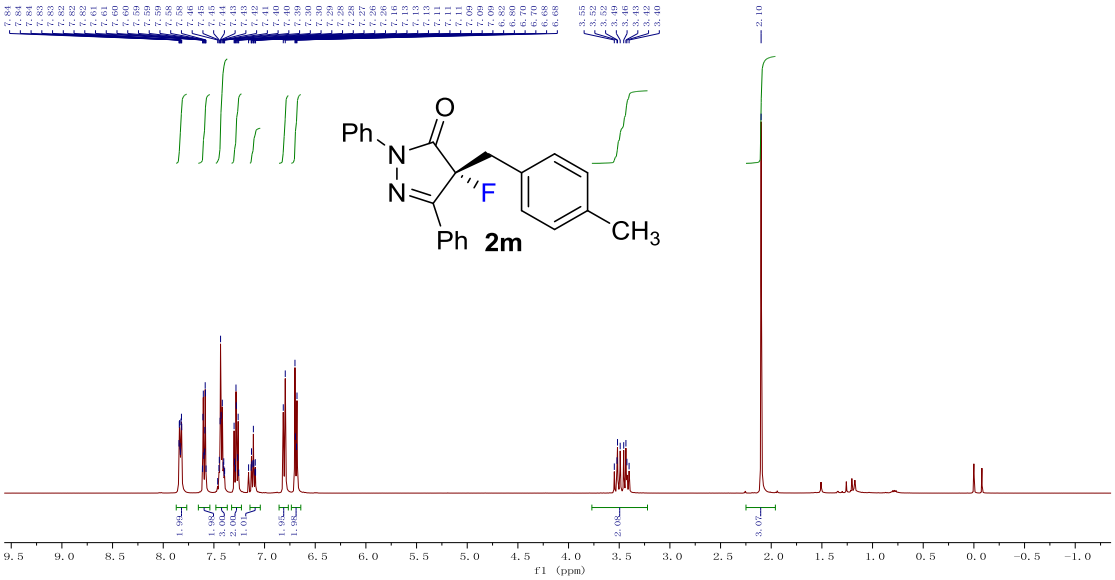


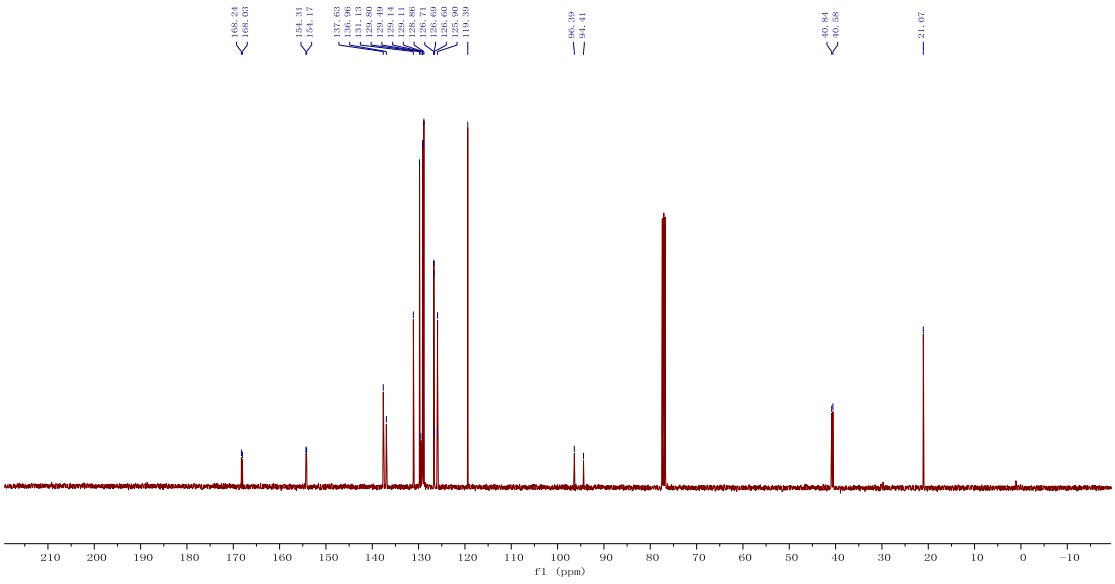

A (s)
-163.17

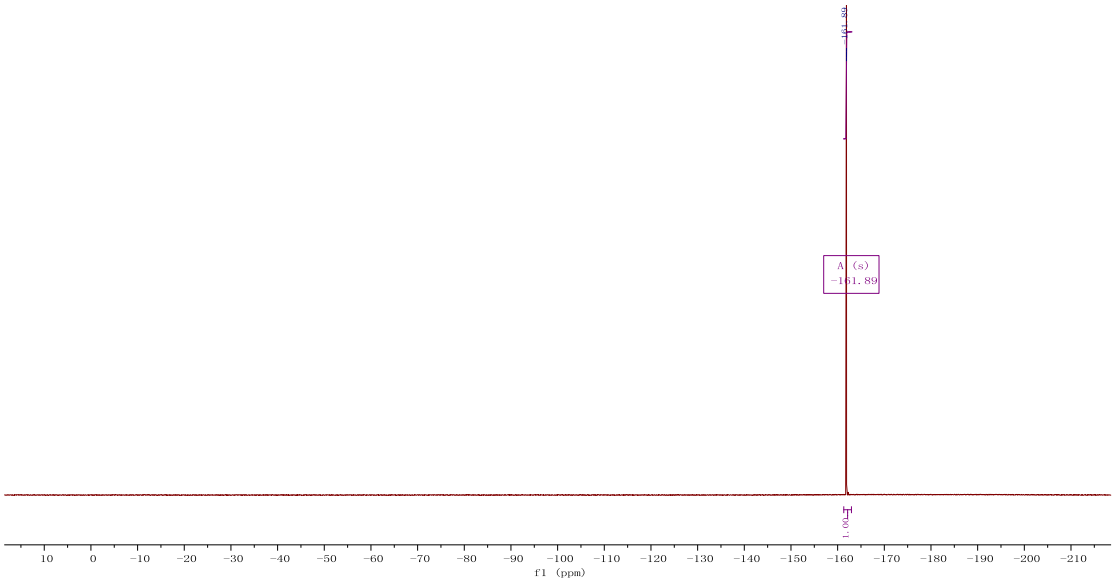

Ph
N
N
O
F
Ph
Br
Br
2l
f1 (ppm)

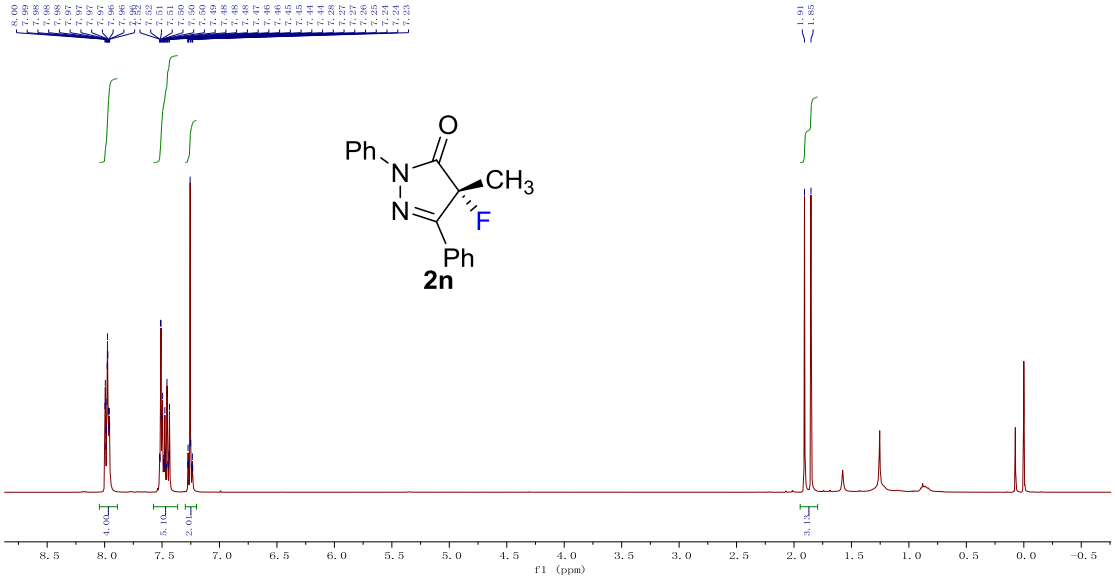

f1 (ppm)

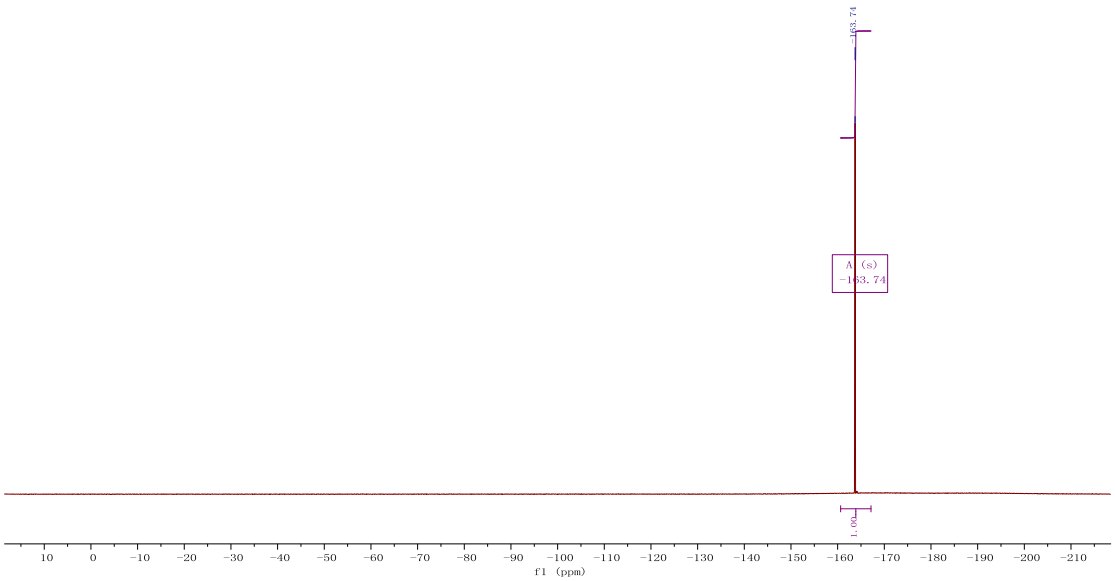

A (s)
-163.81
f1 (ppm)

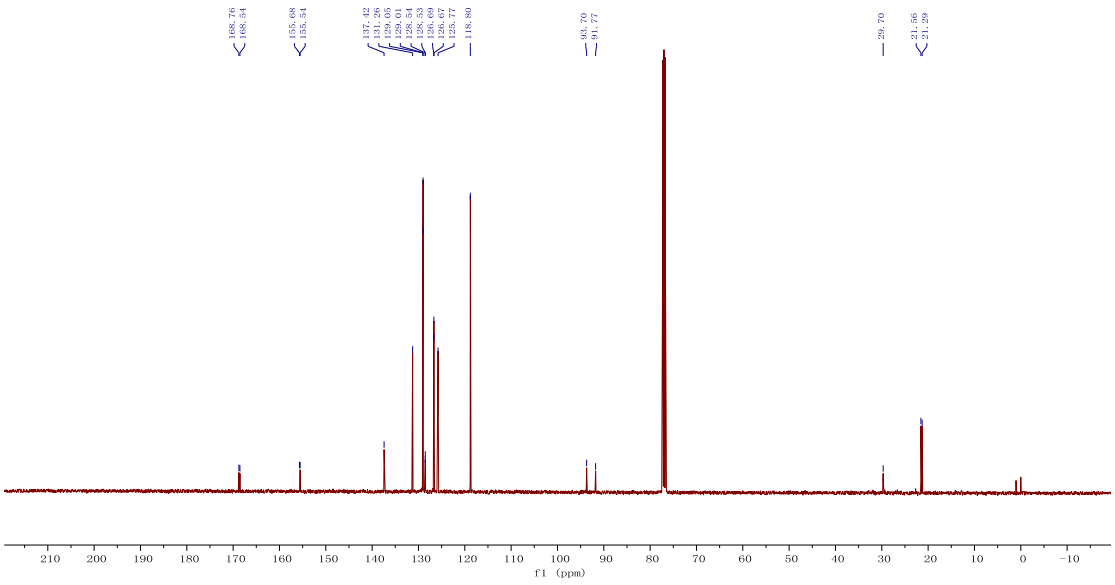

Ph
N
N
O
F
Ph
CH3
2m

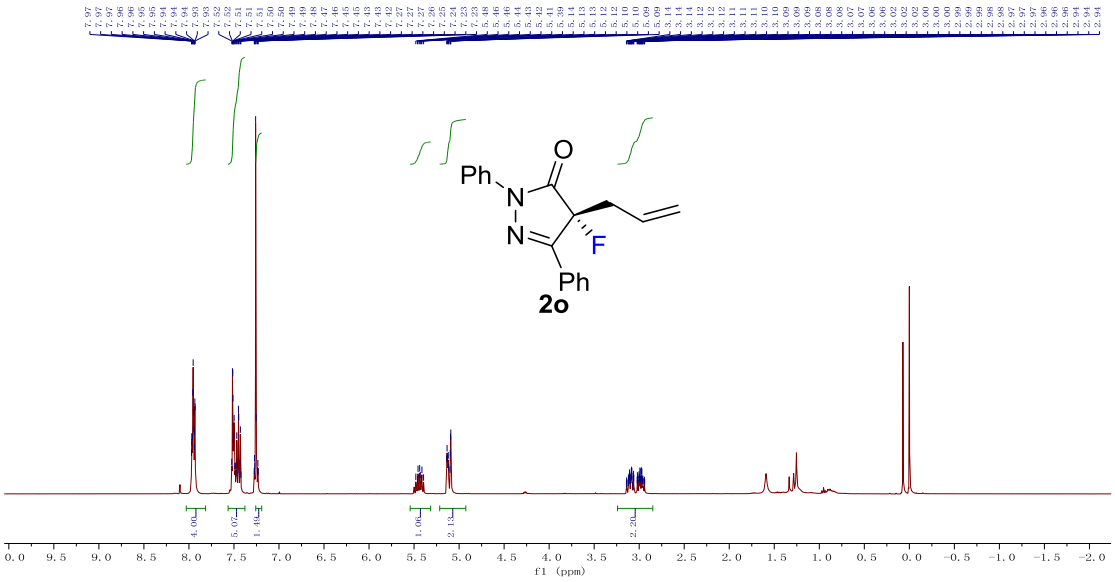


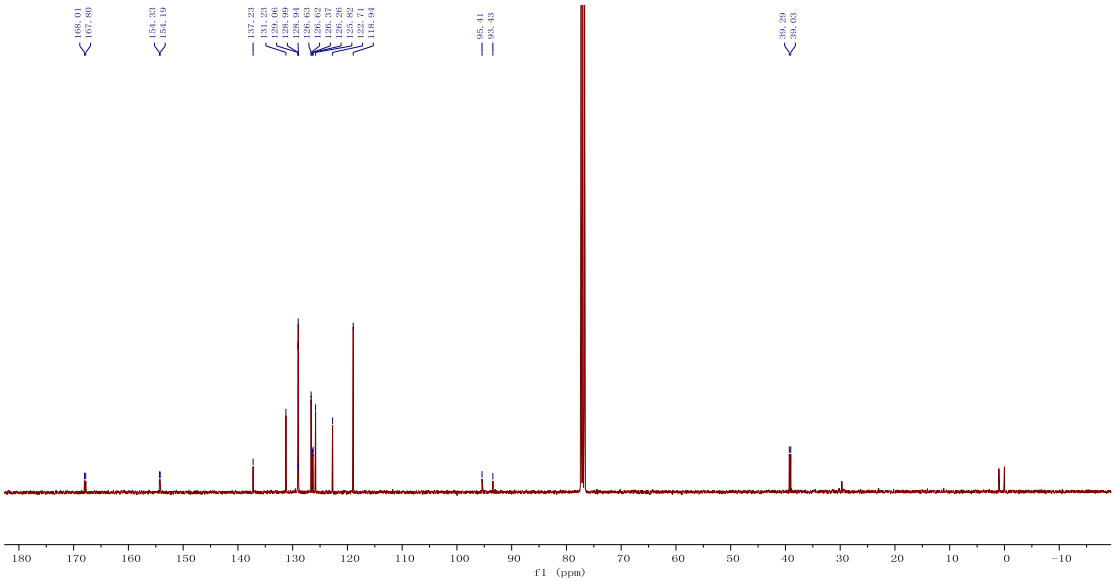

A (s)
-161.89

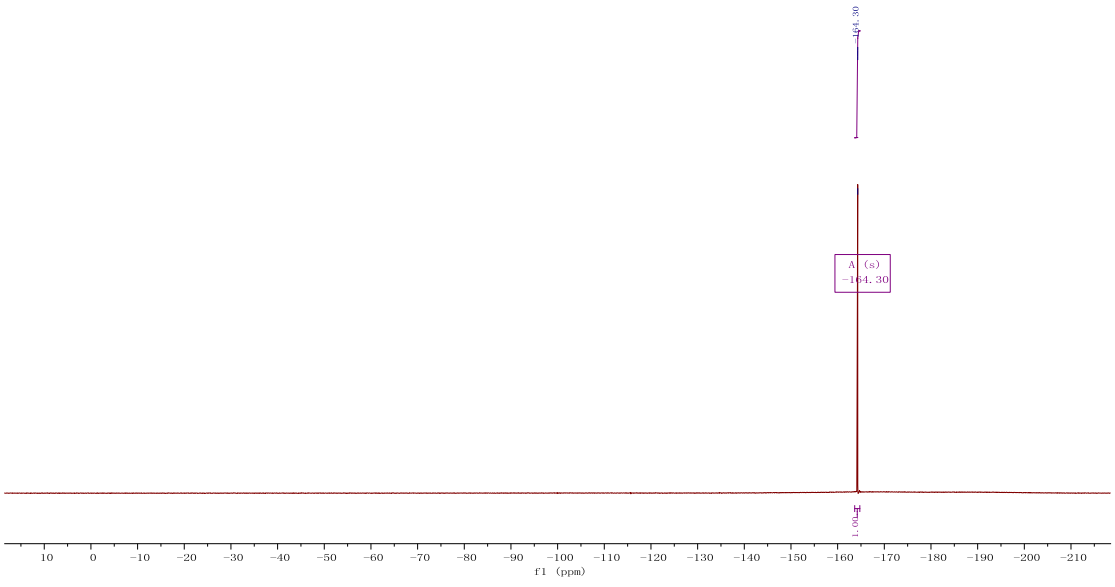

Ph
N
N
O
CH3
F
Ph
2n

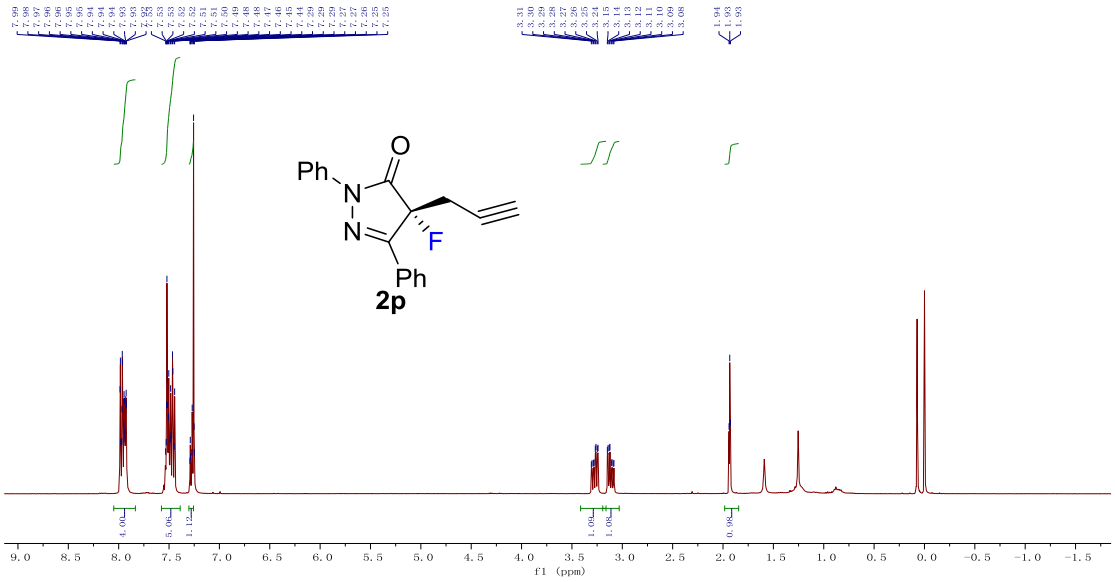

-163.74
A (s)
-163.74
f1 (ppm)

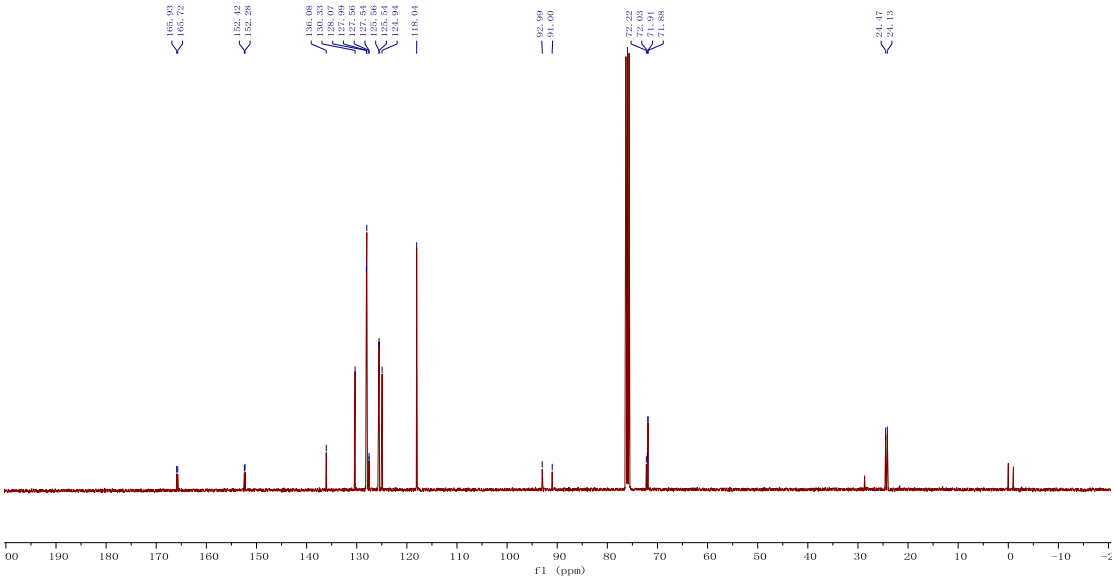

f1 (ppm)

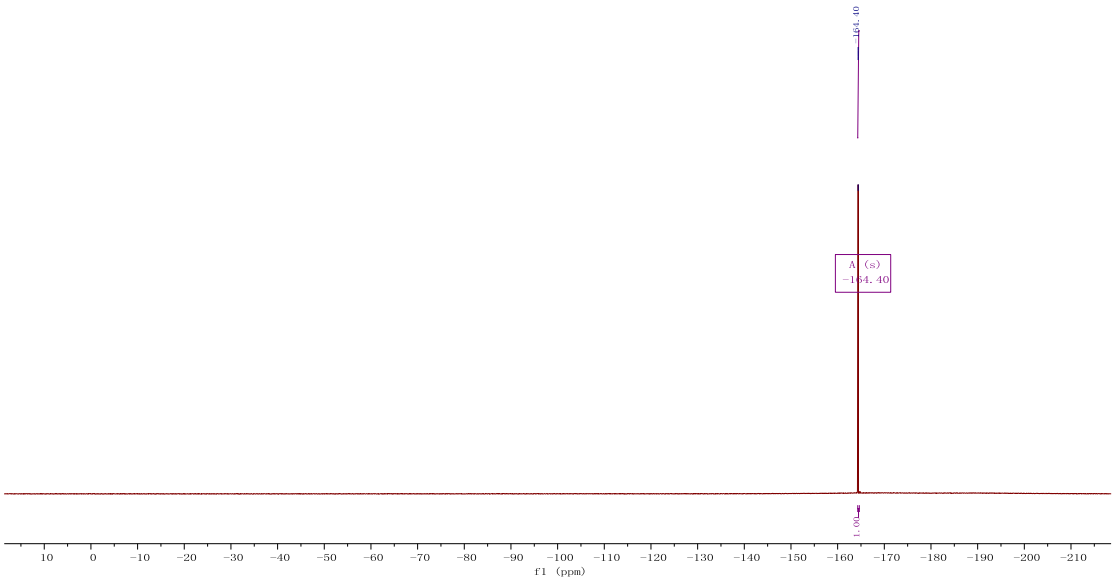

O
Ph
N
N
F
Ph
2o

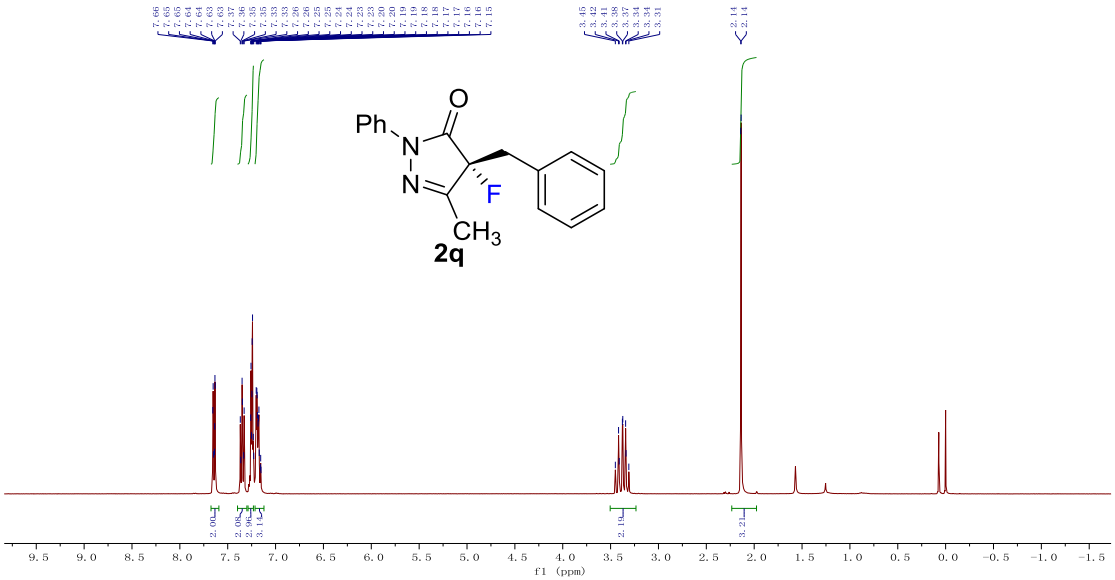


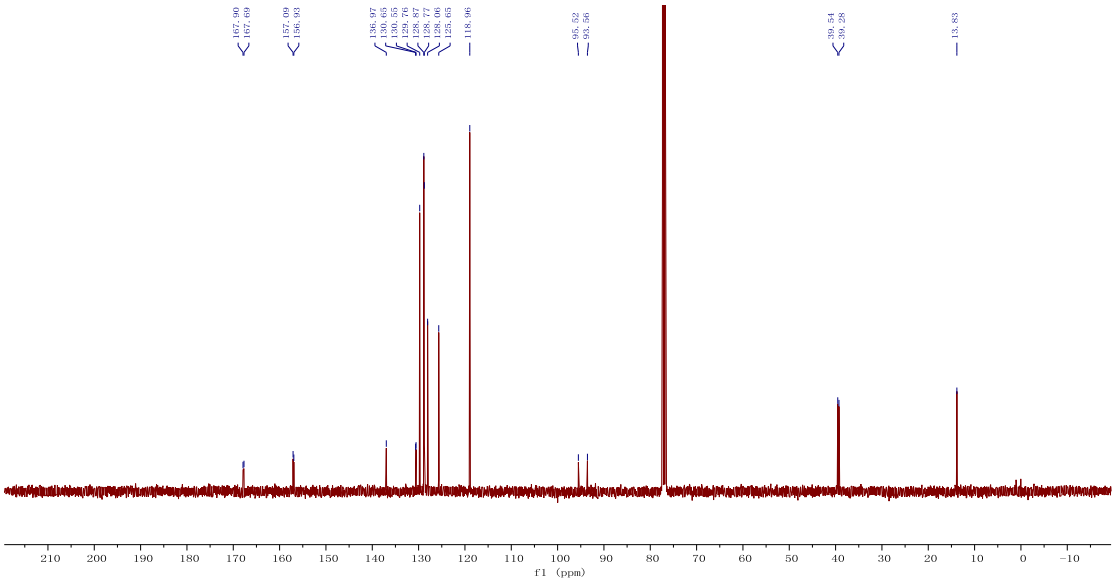

A (s)
-164.30

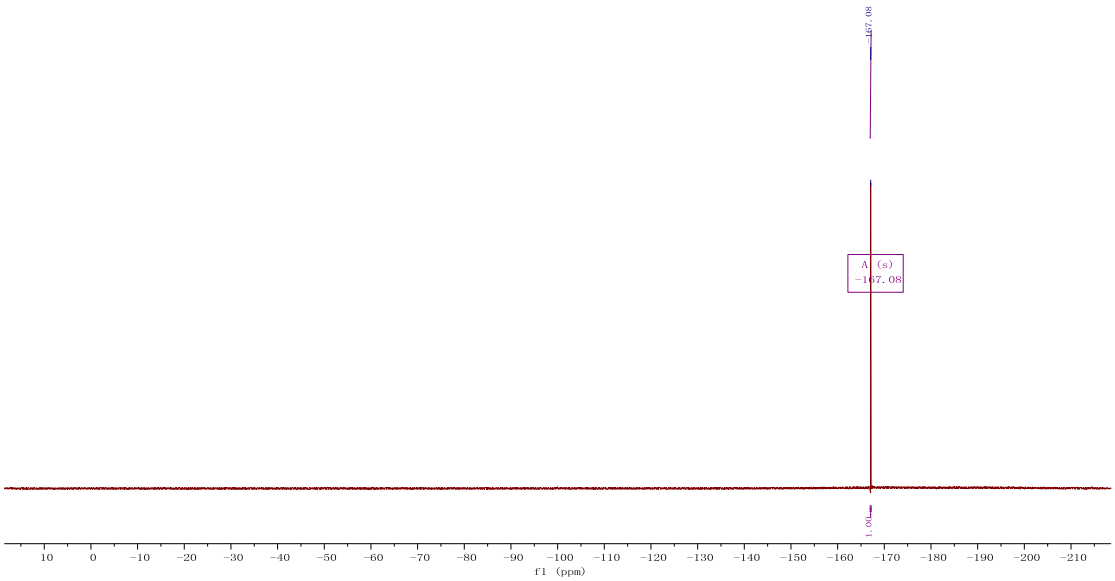

O
Ph
N
N
F
Ph
2p
f1 (ppm)

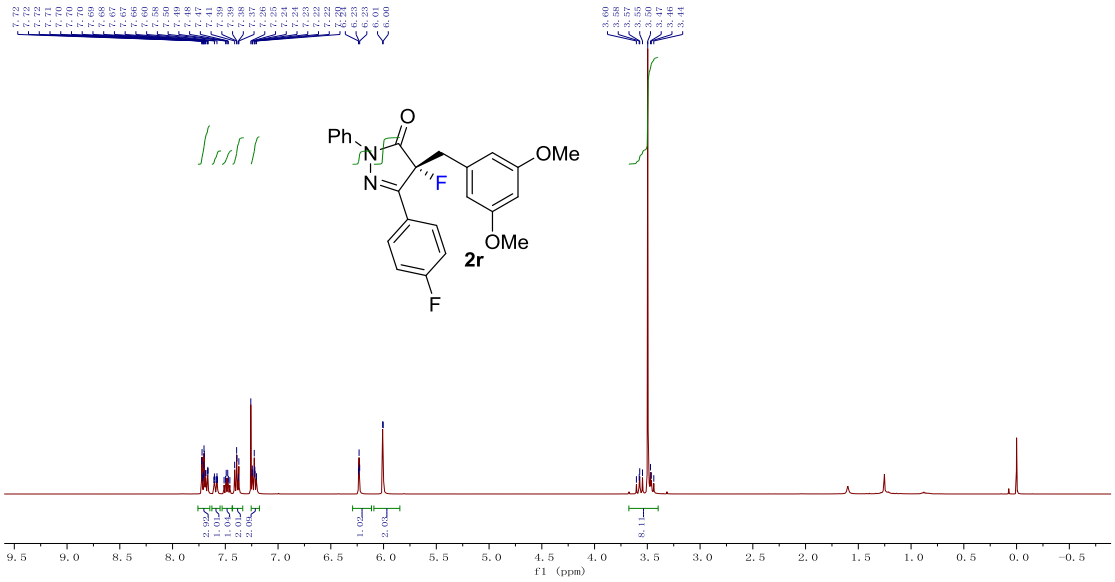

f1 (ppm)

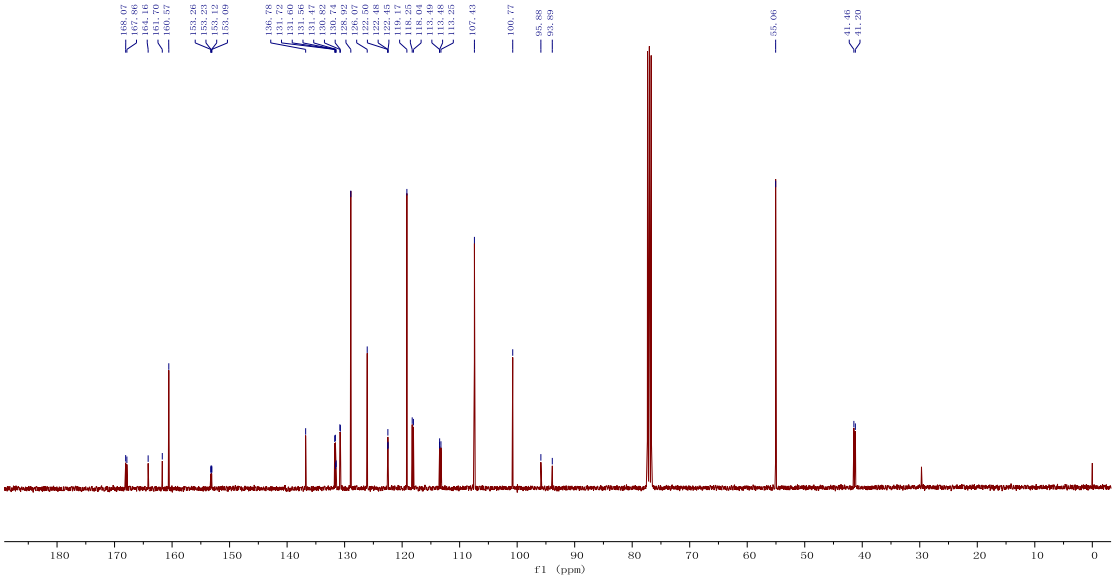

-164.40
A (s)
-164.40
f1 (ppm)

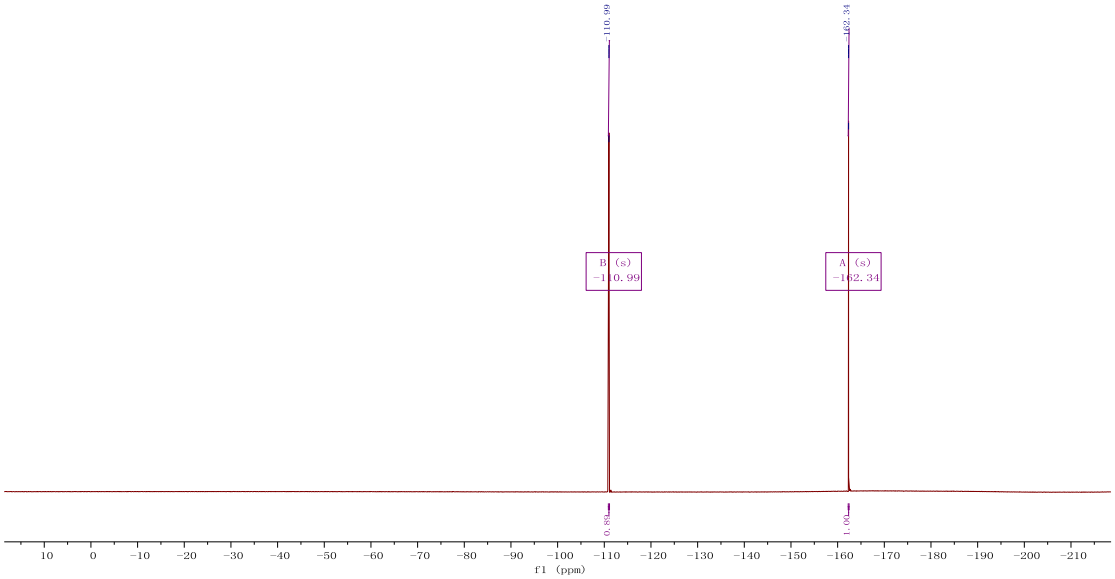

Ph
N
N
O
F
CH3
2q
f1 (ppm)

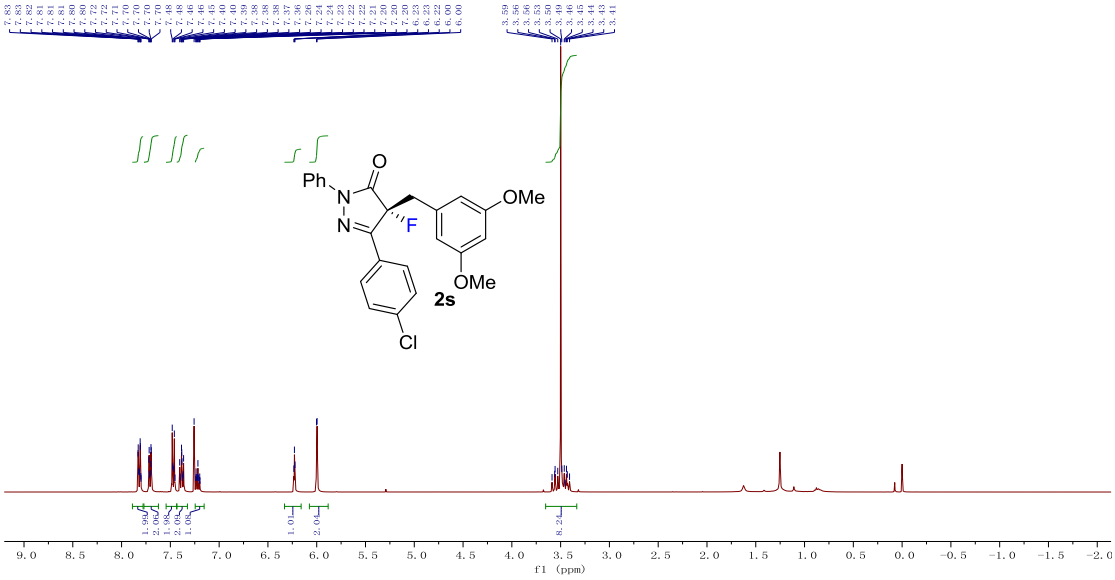

f1 (ppm)

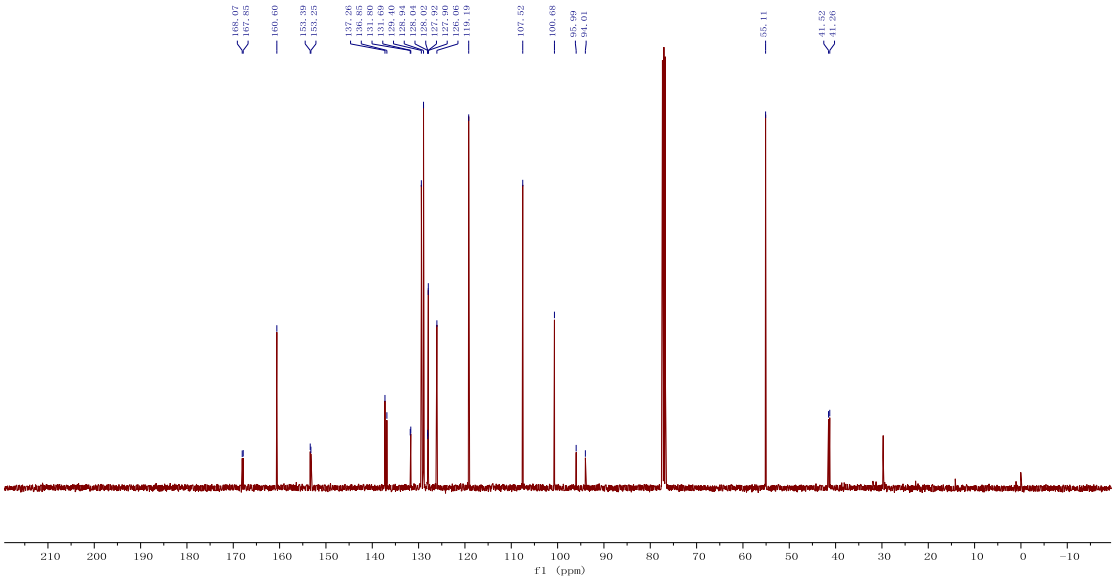

A (s)
-167.08
f1 (ppm)

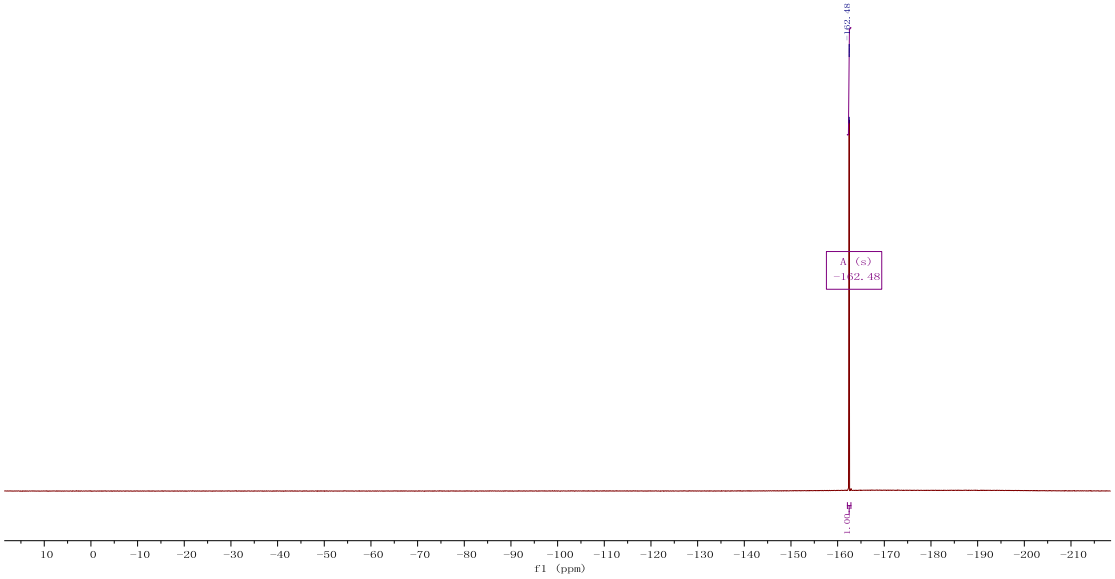

Ph
N
N
O
F
OMe
OMe
F
2r

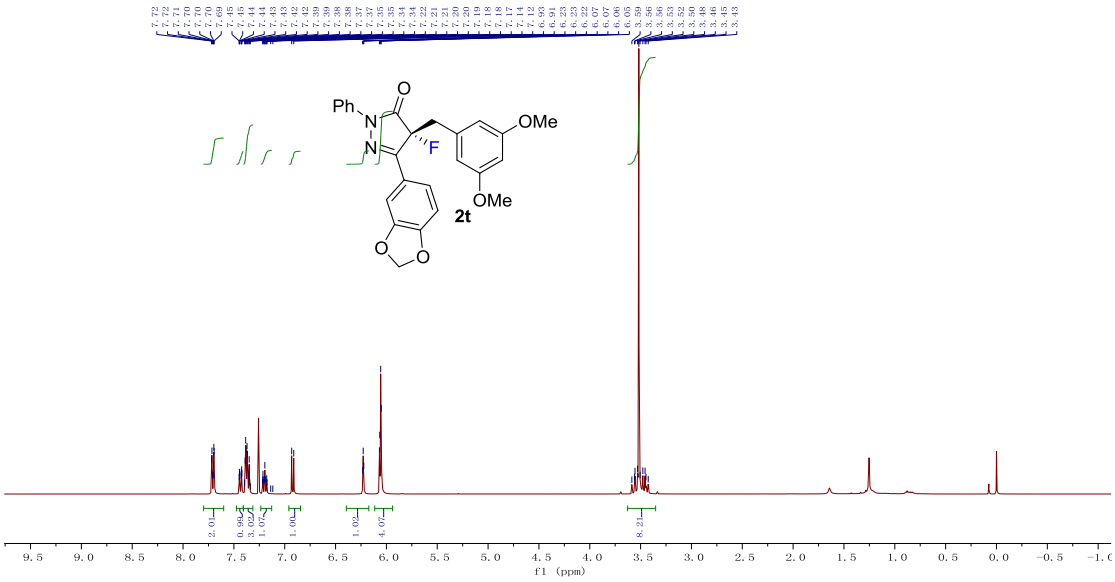


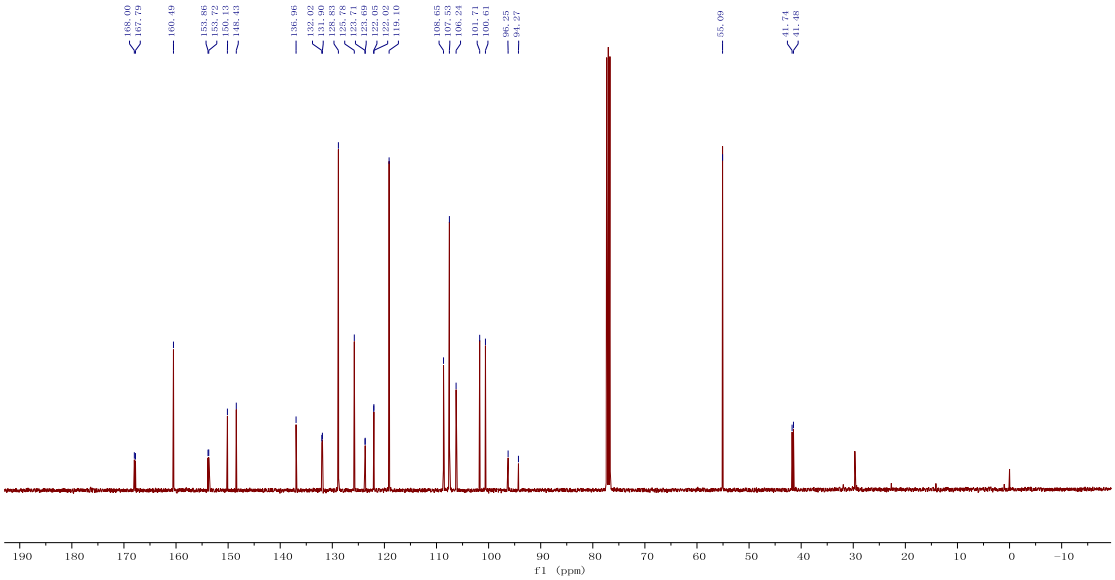

B (s)
-110.99
A (s)
-162.34

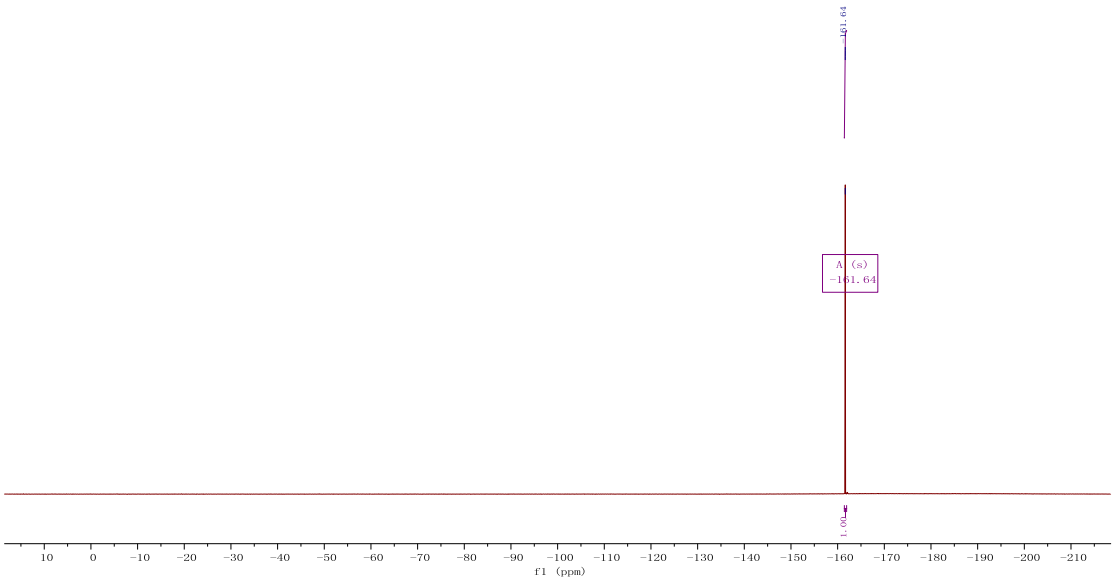

Ph
N
N
O
F
OMe
OMe
Cl
2s

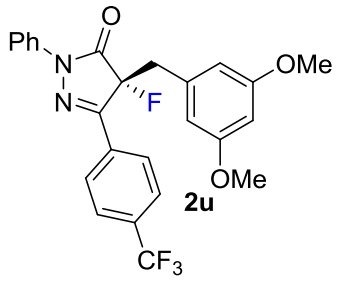


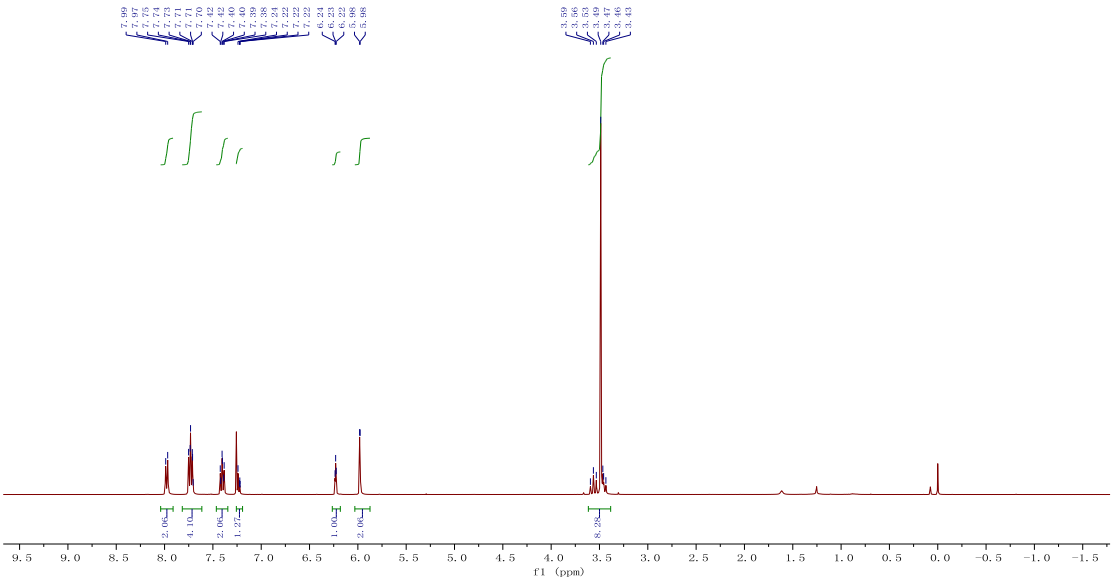

A (s)
-162.48

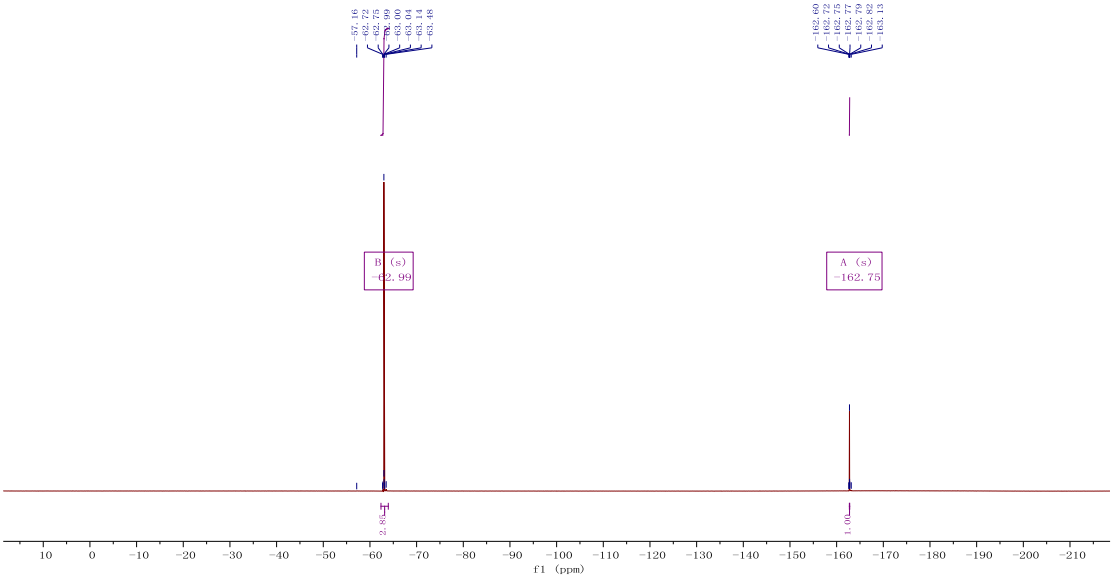

Ph
N
N
O
F
OMe
OMe
O
O
O
2t
f1 (ppm)

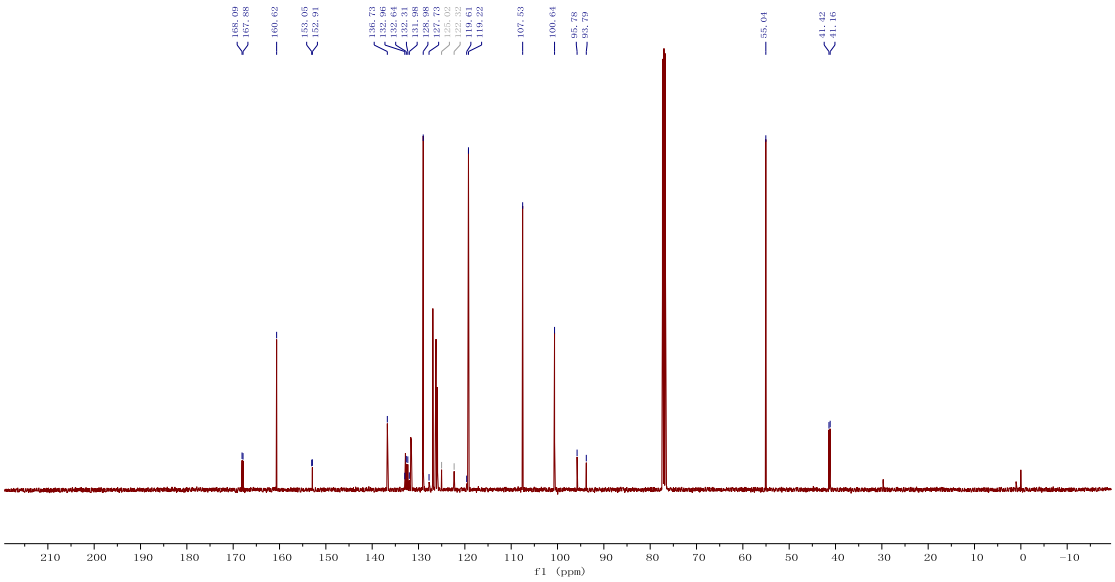

f1 (ppm)

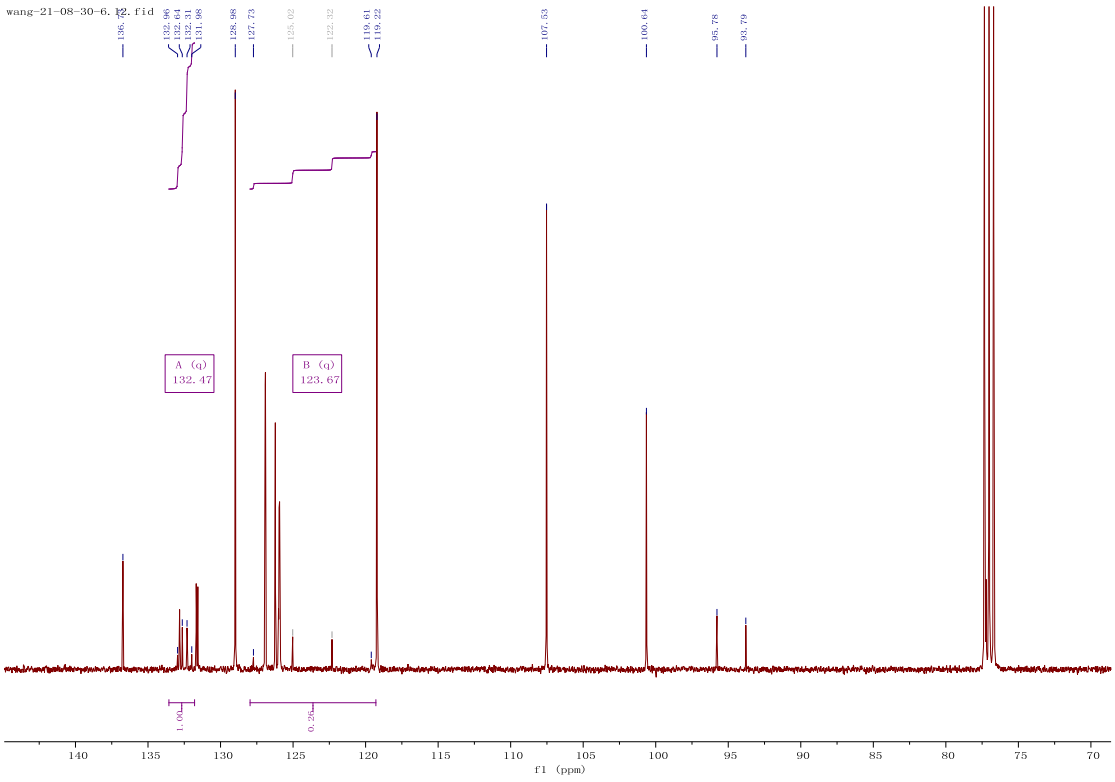

A (s)
-161.64
f1 (ppm)

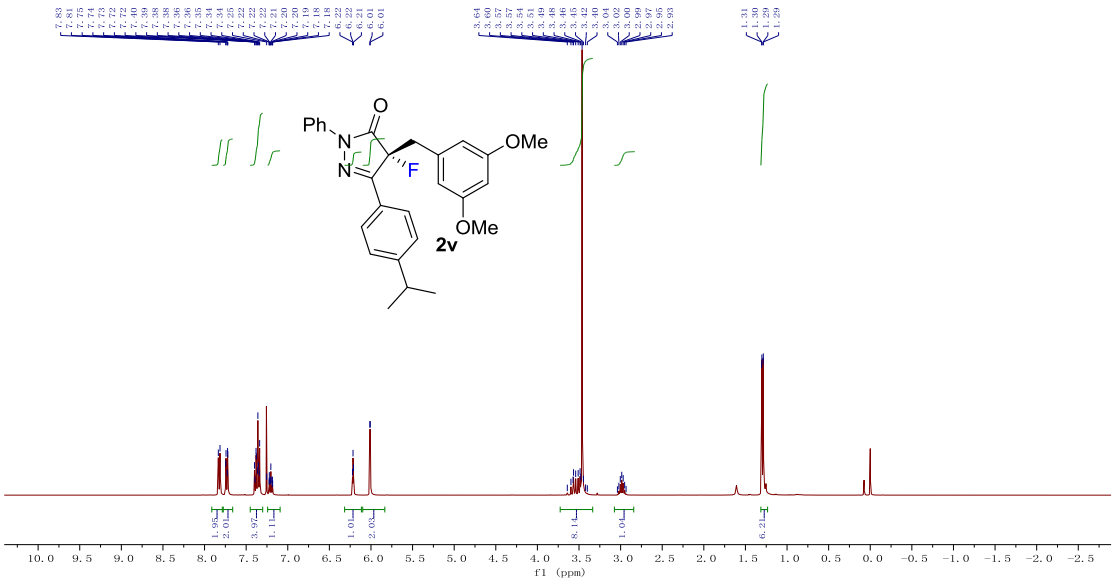

O
Ph
N
N
F
OMe
OMe
2u
CF3

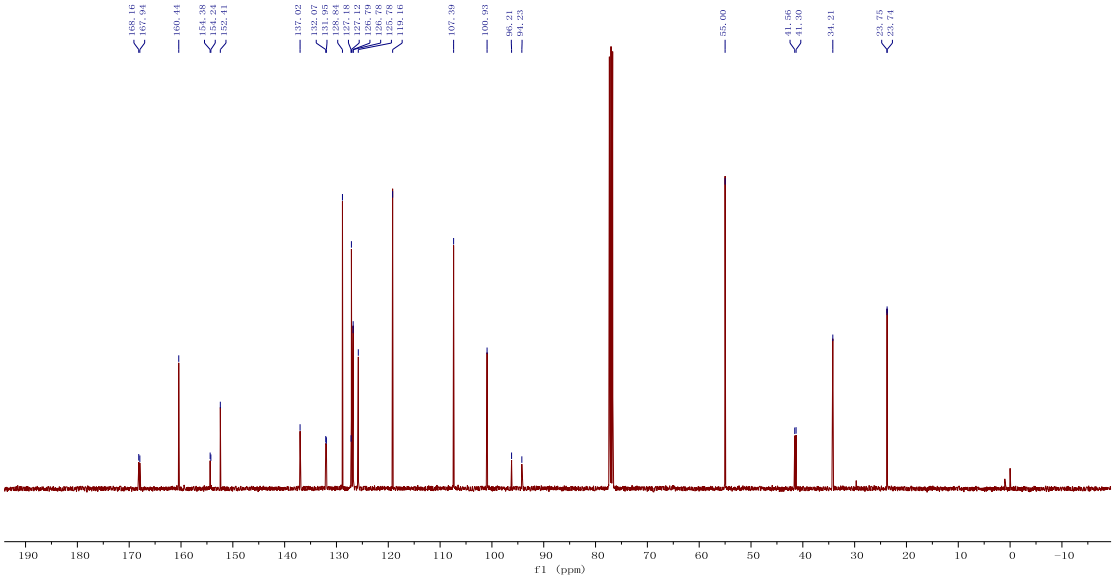

f1 (ppm)

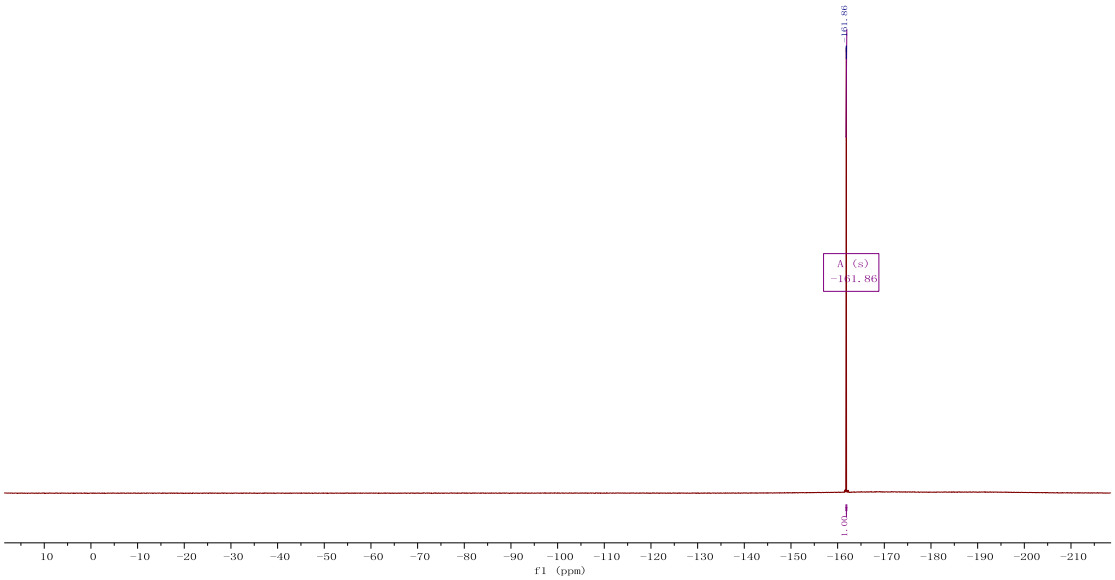

B (s)
-62.99
A (s)
-162.75
f1 (ppm)

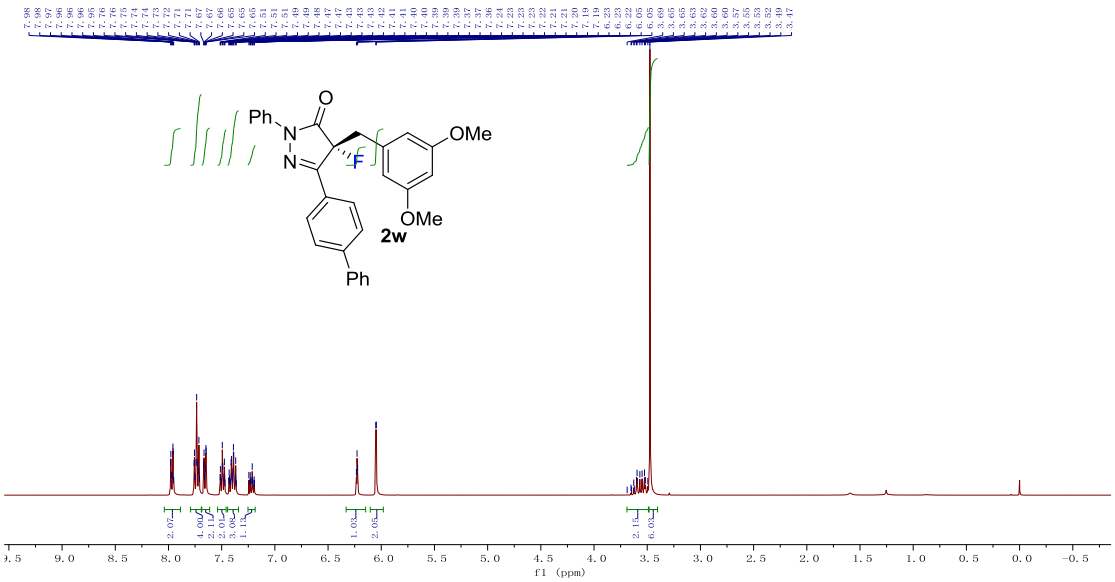

168.09
167.88
160.62
153.05
152.91
136.73
132.96
132.64
132.31
131.98
128.98
127.73
125.02
122.32
119.61
119.22
107.53
100.64
95.78
93.79
55.04
41.42
41.16
f1 (ppm)

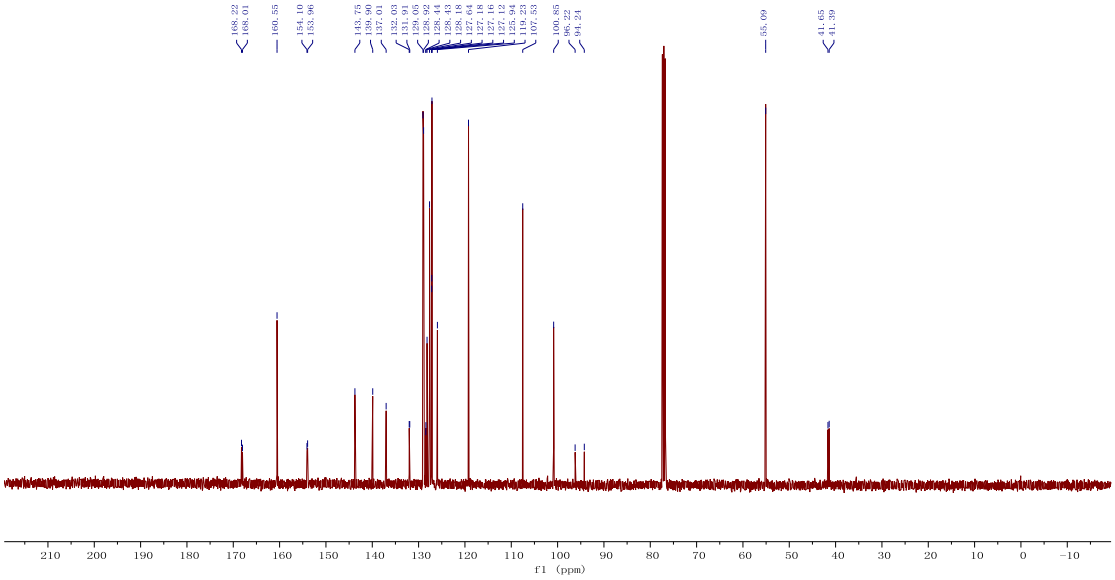

wang-21-08-30-6.22.fid
136.73
132.96
132.64
132.31
131.98
128.98
127.73
125.02
122.32
119.61
119.22
107.53
100.64
95.78
93.79
A (q)
132.47
B (q)
123.67
1.00
0.26
f1 (ppm)

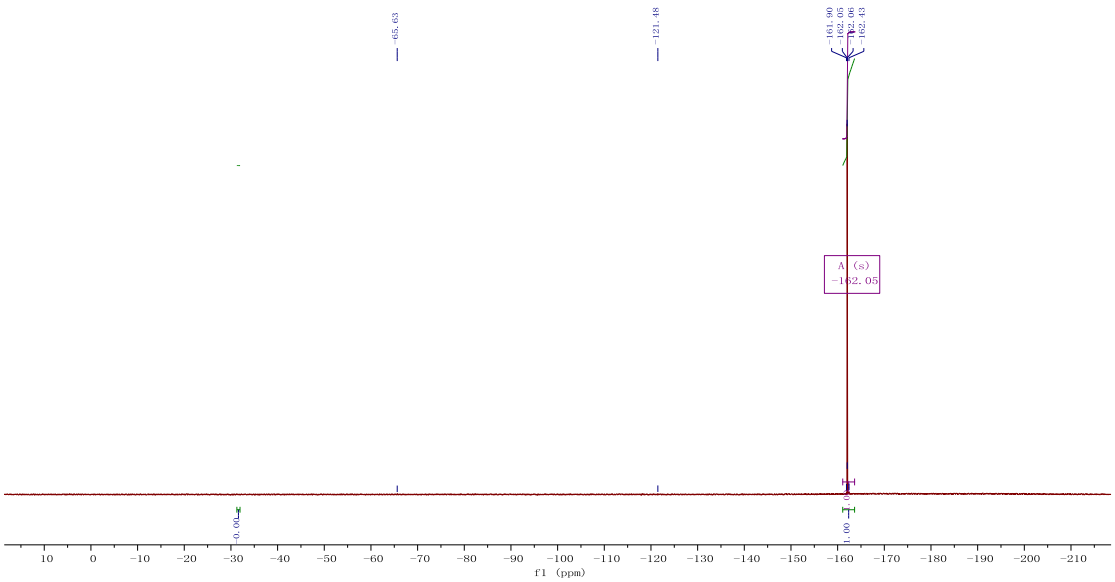

Ph
N
N
O
F
OMe
OMe
2v

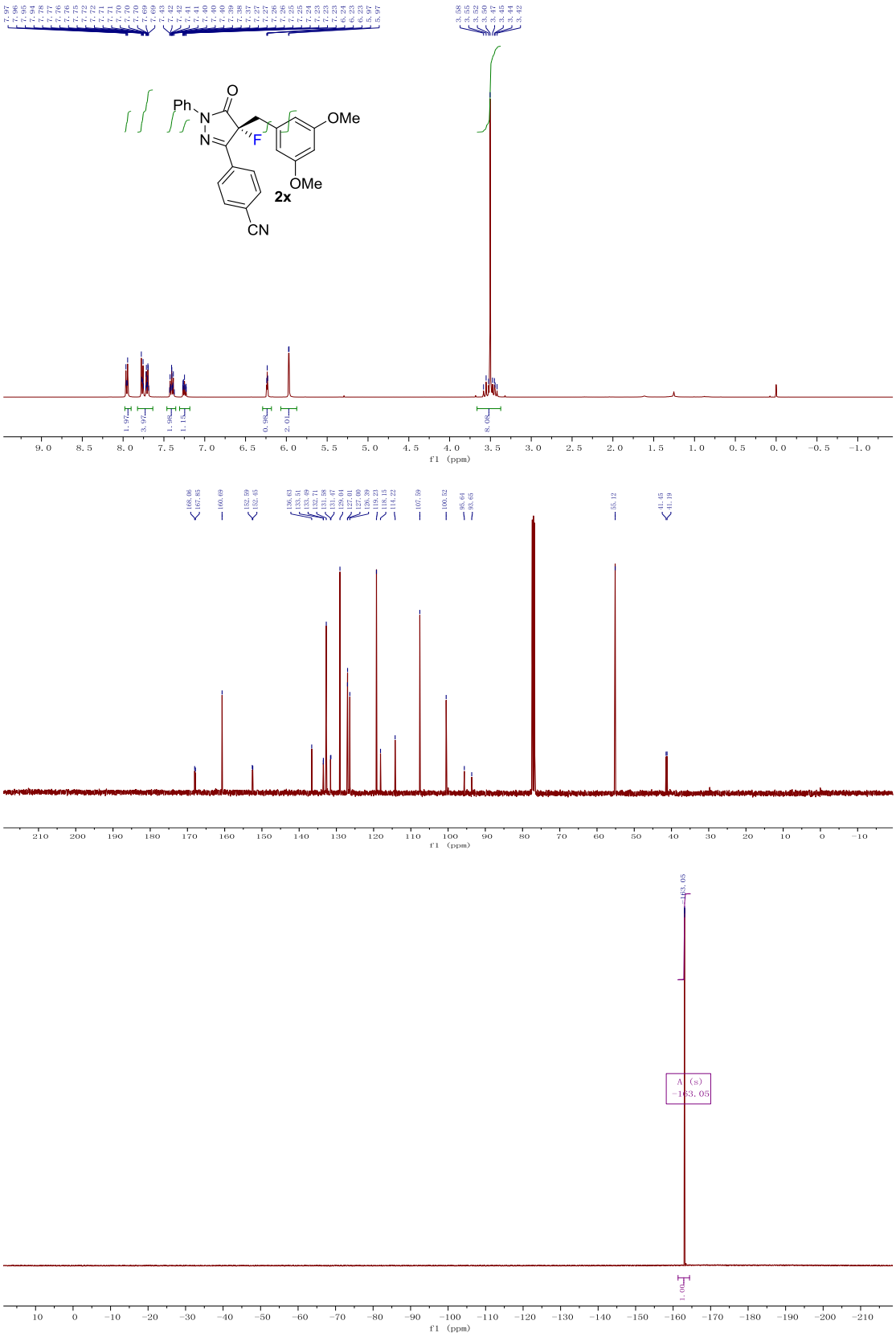


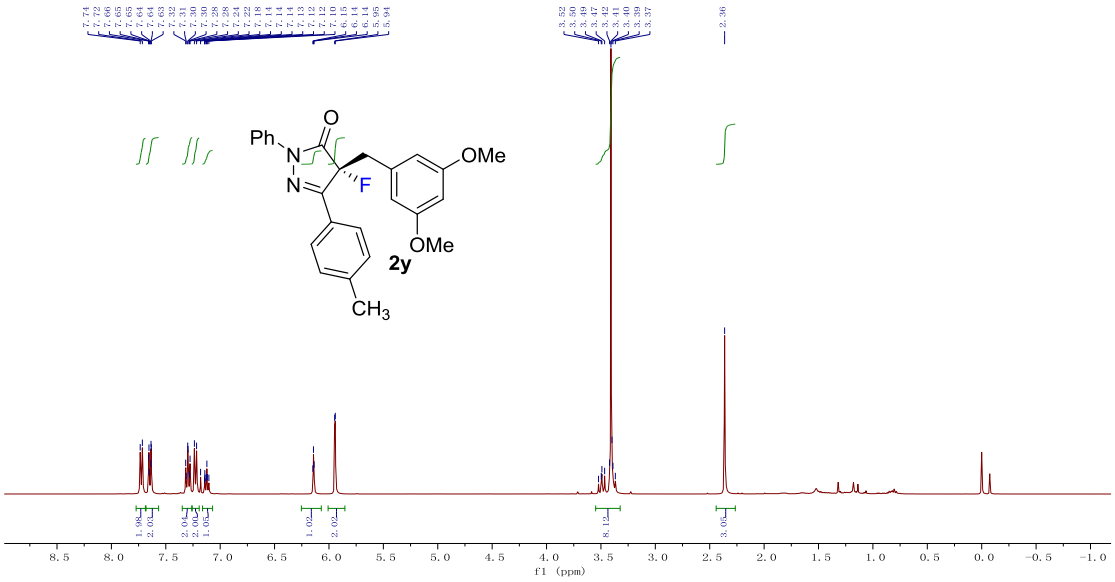

A (s)
-161.86

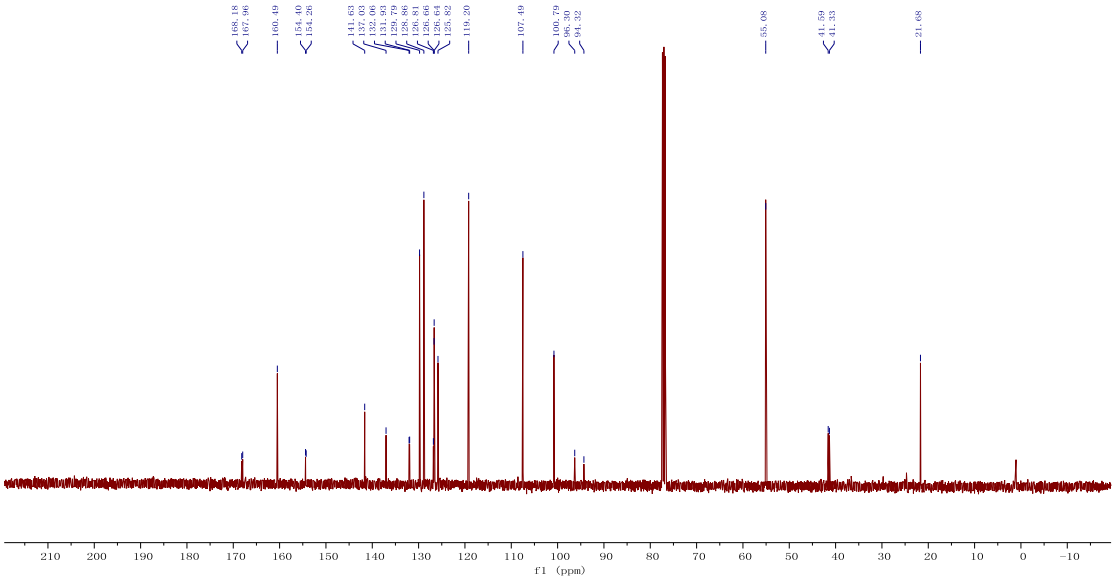

Ph
N
N
O
F
OMe
OMe
Ph
2w

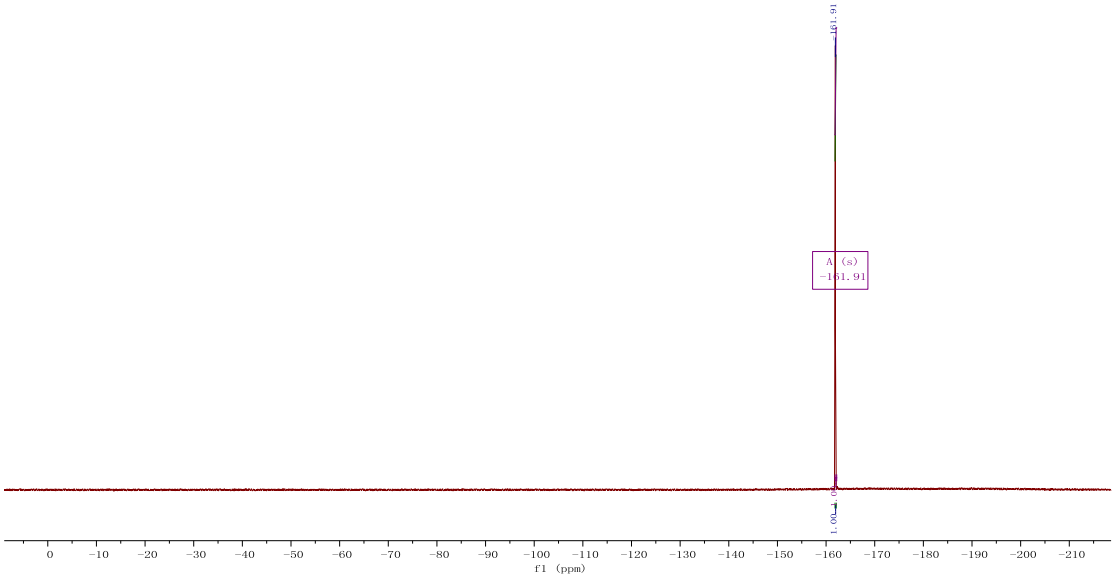


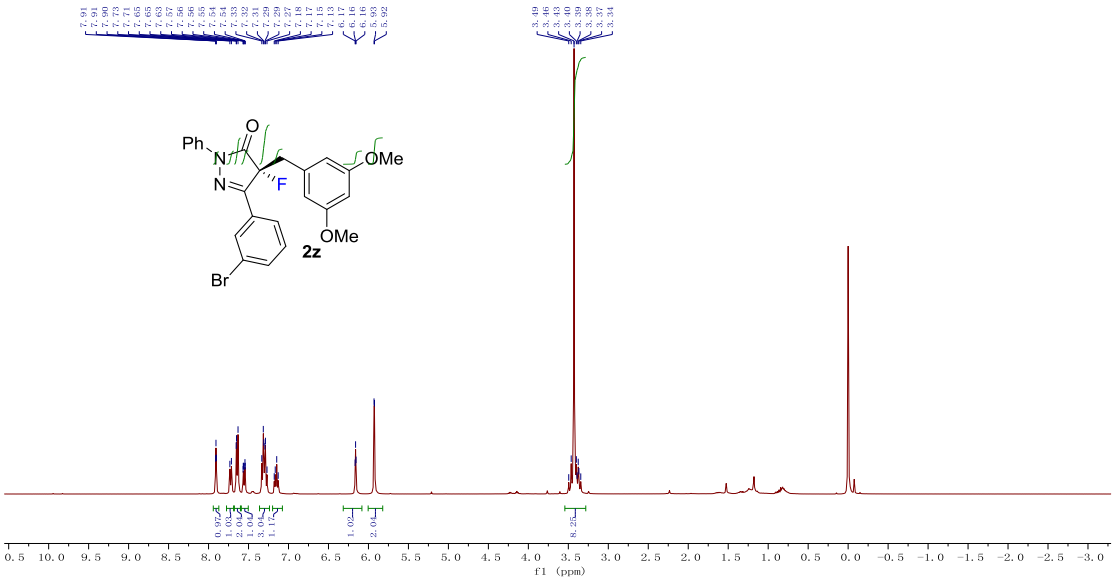

A (s)
-162.05

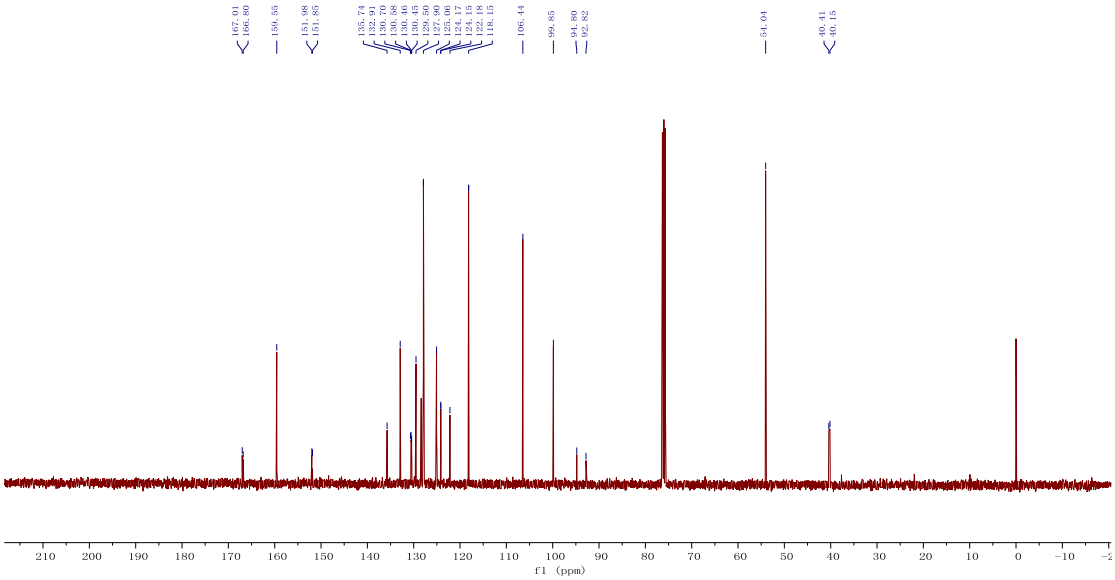

Ph
N
N
O
F
OMe
OMe
2x
CN
f1 (ppm)
A (s)
-163.05

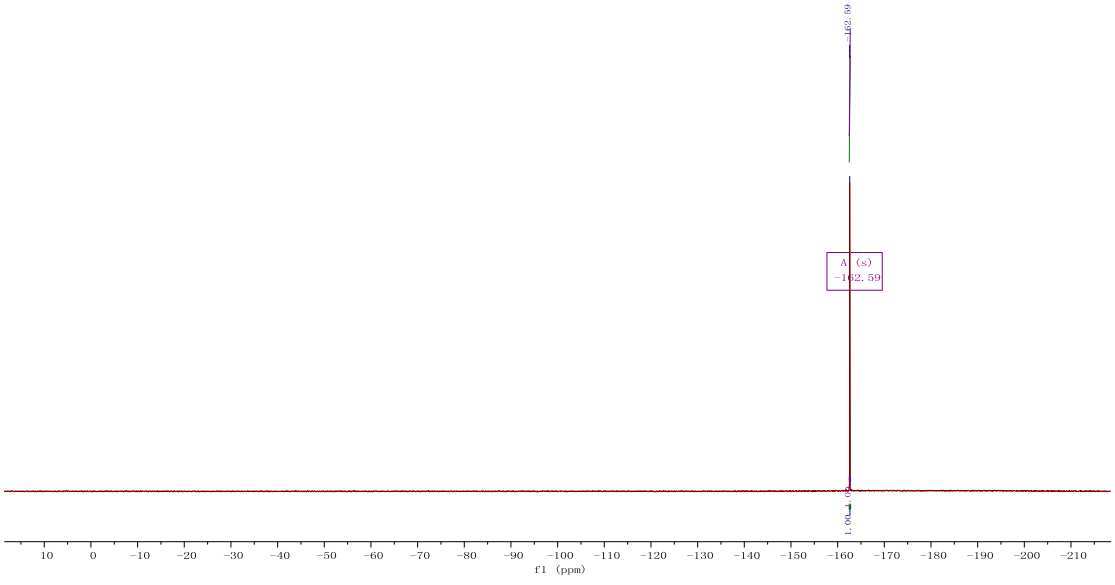

Ph
N
N
O
F
OMe
OMe
CH3
2y
f1 (ppm)

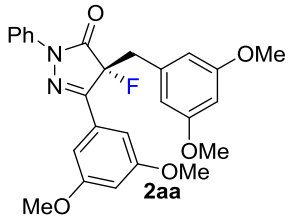

f1 (ppm)

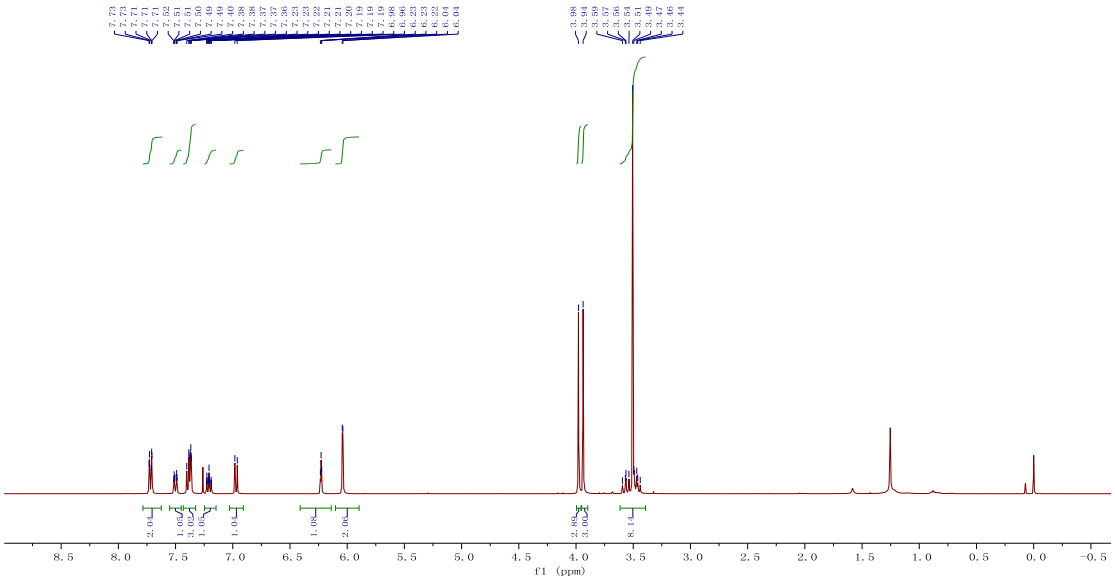

A (s)
-151.91
f1 (ppm)

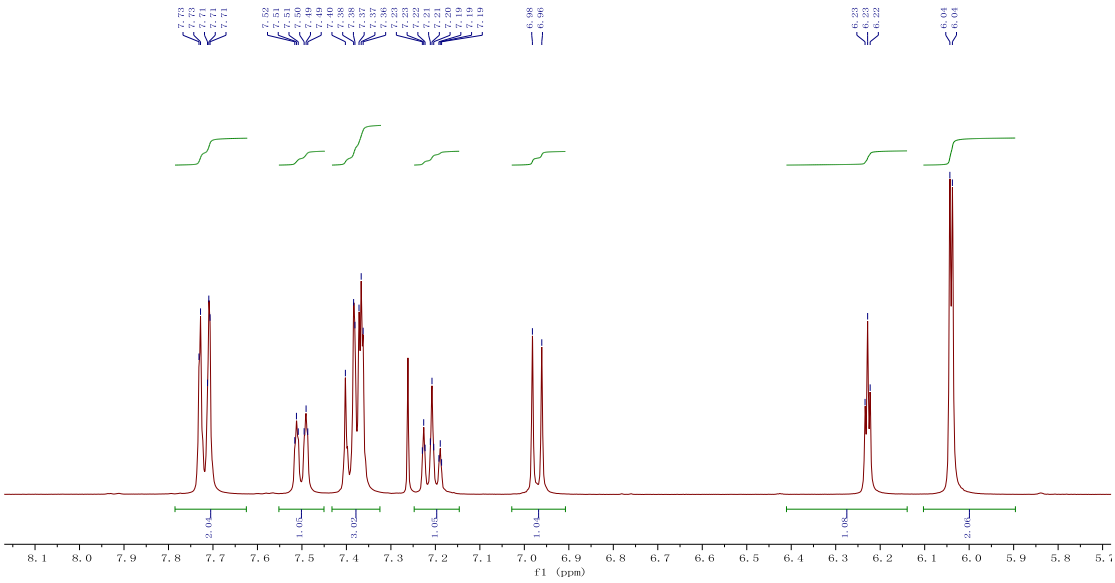

Ph
N
N
O
F
OMe
OMe
Br
2z
f1 (ppm)

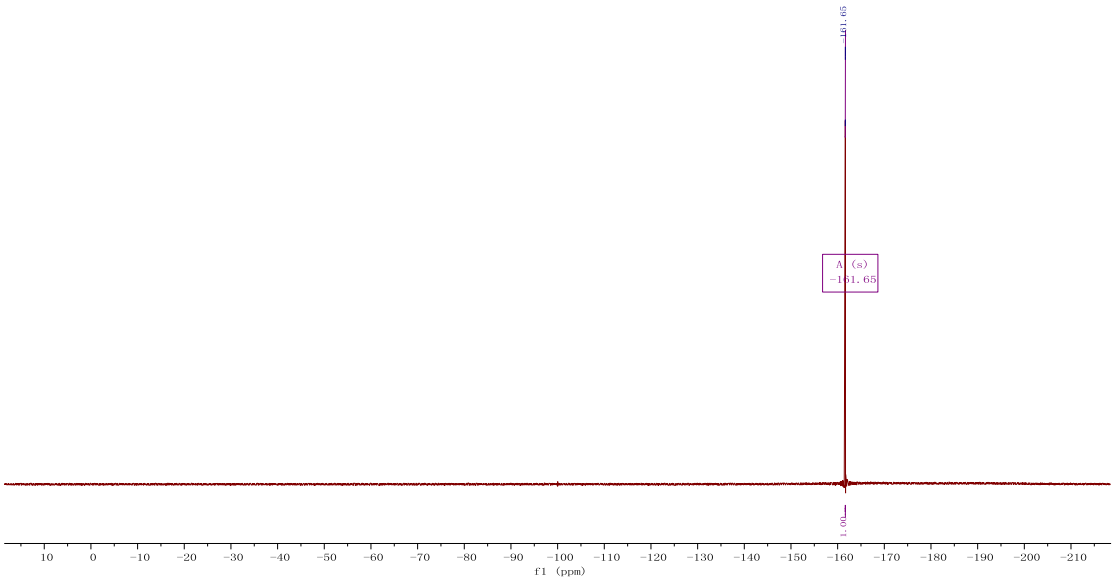

f1 (ppm)

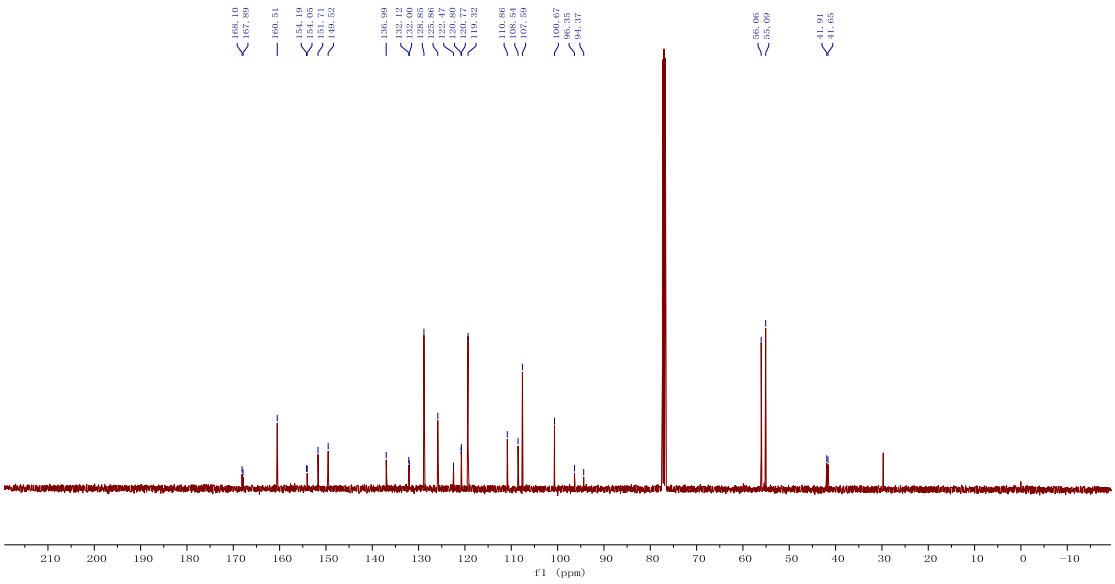

A (s)
-162.59
f1 (ppm)

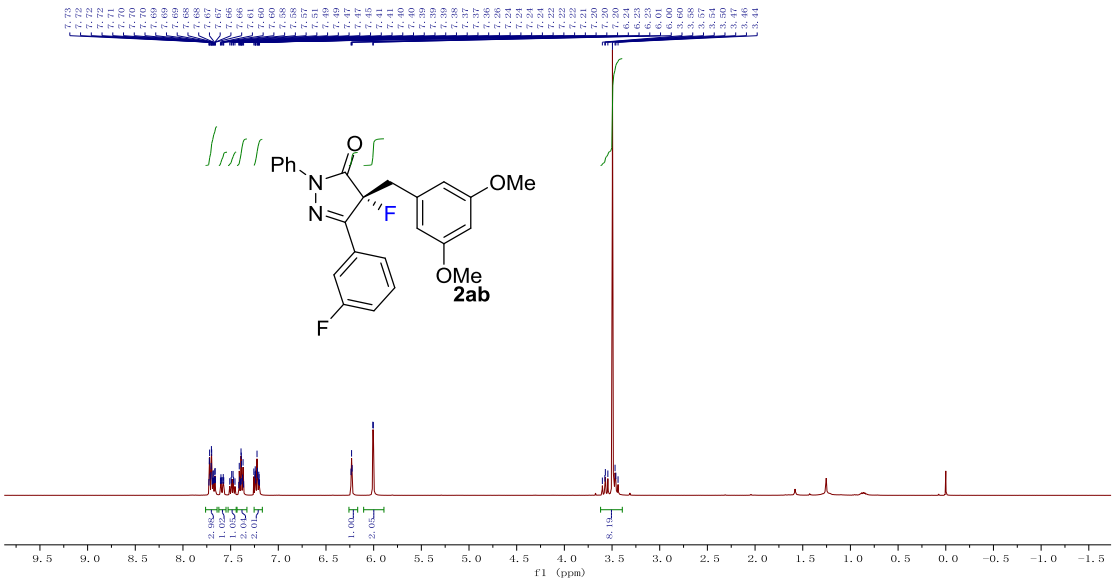

Ph
N
N
O
F
OMe
OMe
OMe
MeO
2aa

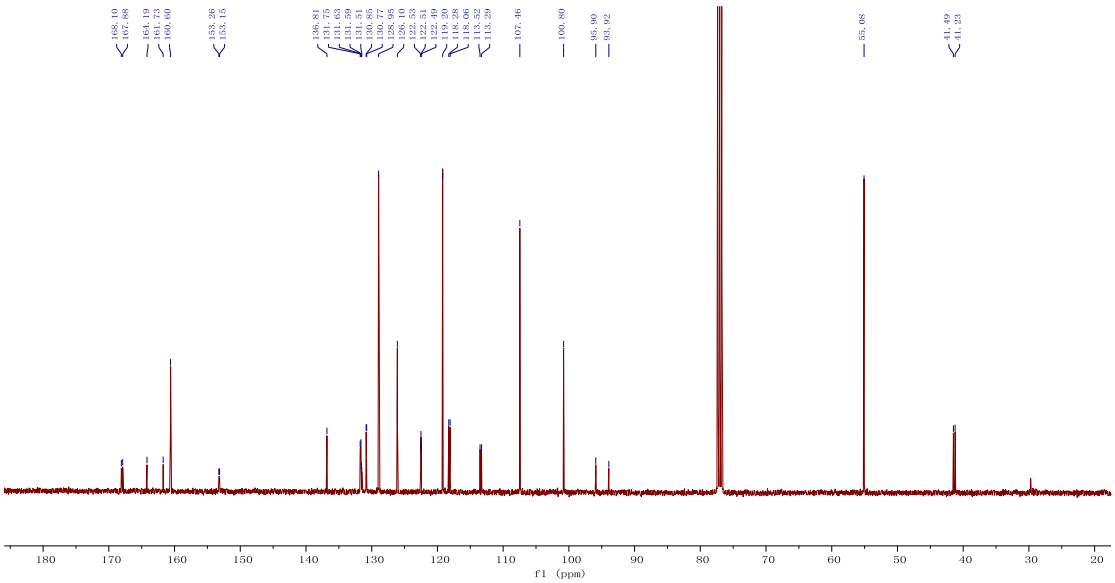


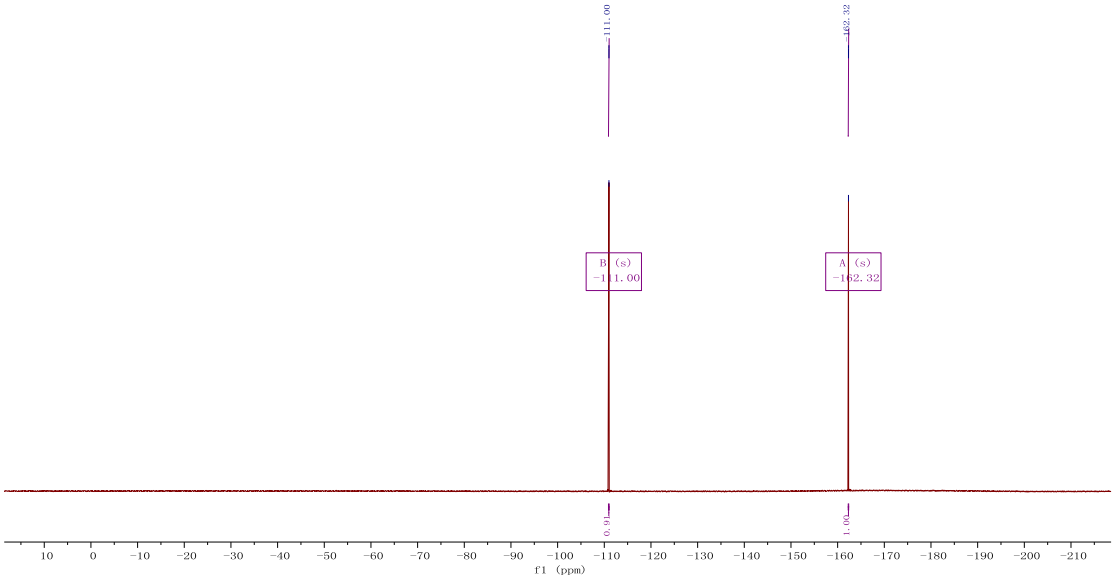


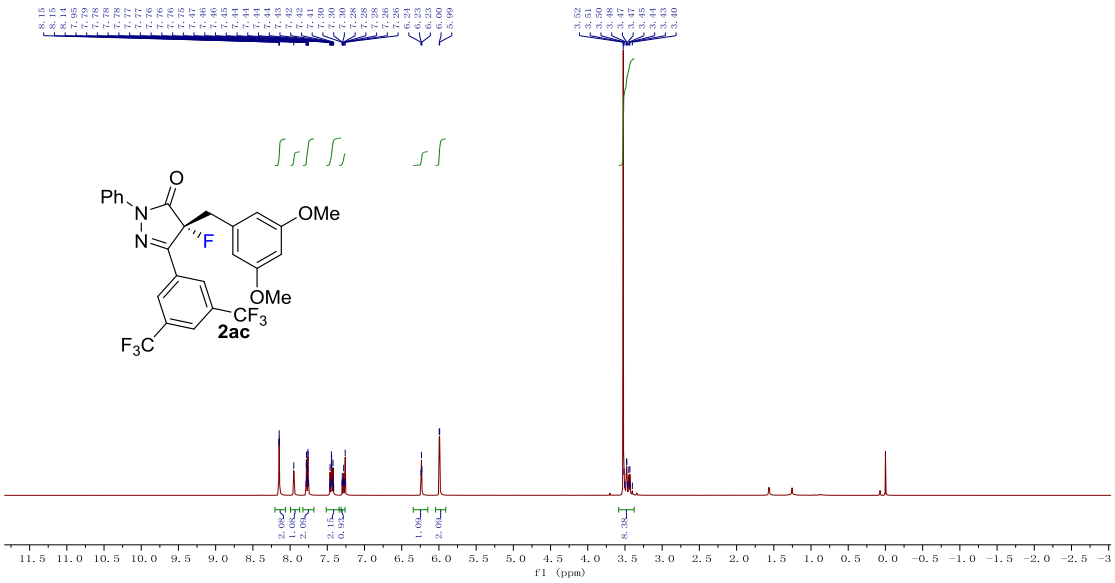

-161.65
A (s)
-161.65
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

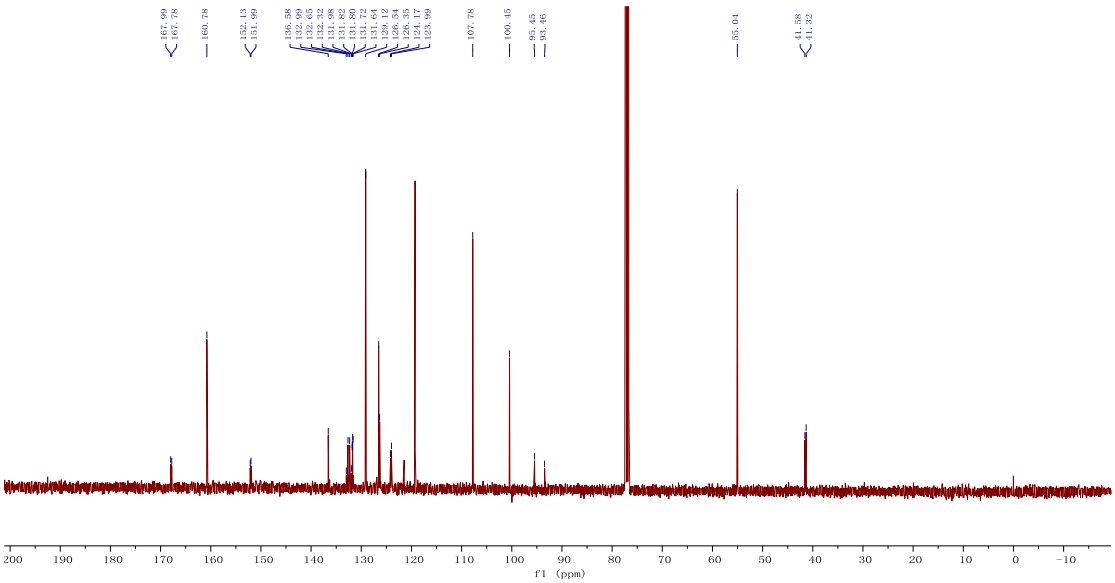

168.10
167.89
160.51
154.19
154.05
151.71
149.52
136.99
132.12
132.00
128.85
125.86
122.47
120.80
119.77
119.32
110.86
108.54
107.59
100.67
96.35
94.37
56.06
55.09
41.91
41.65
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

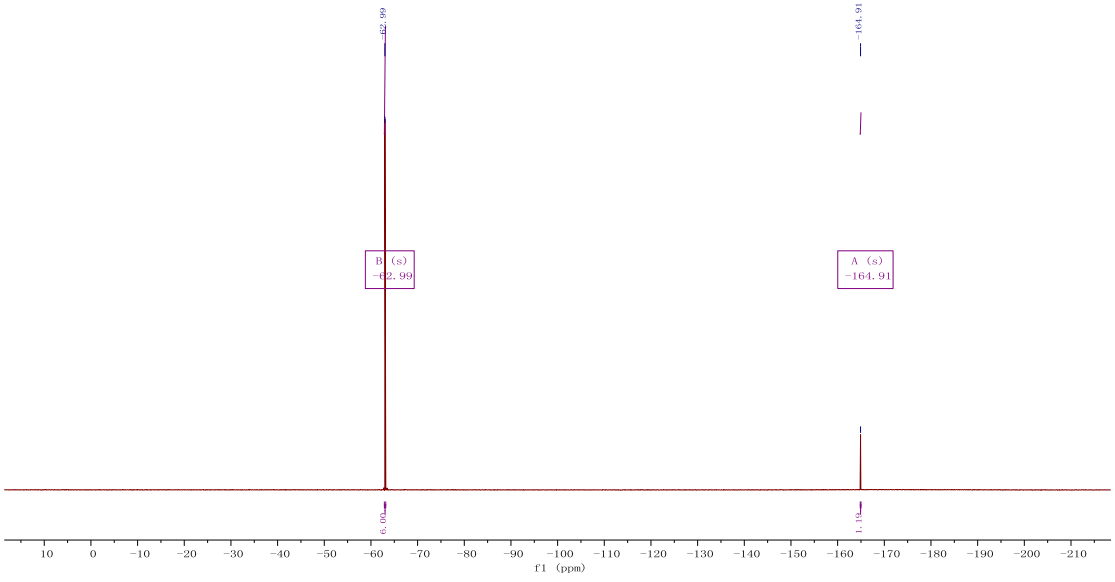

Ph
N
N
O
F
OMe
OMe
2ab
F
f1 (ppm)

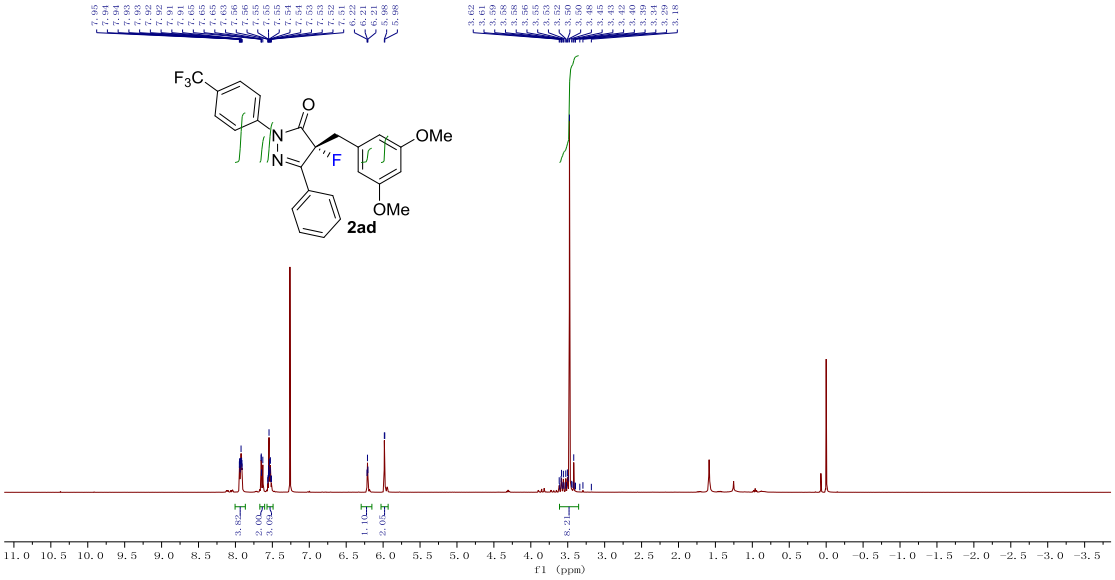

f1 (ppm)

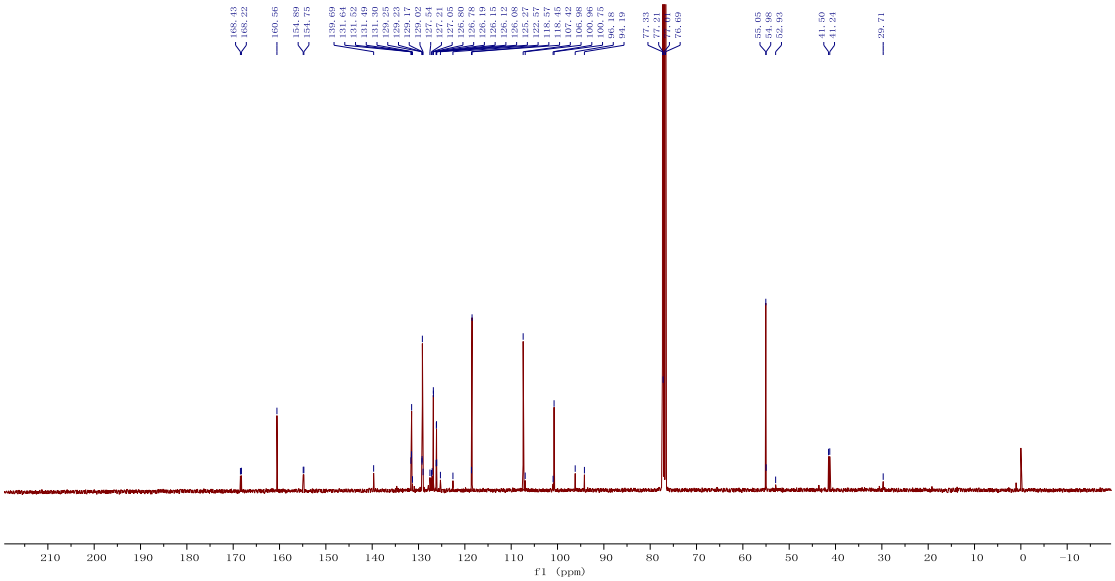

B (s)
-111.00
A (s)
-162.32
f1 (ppm)

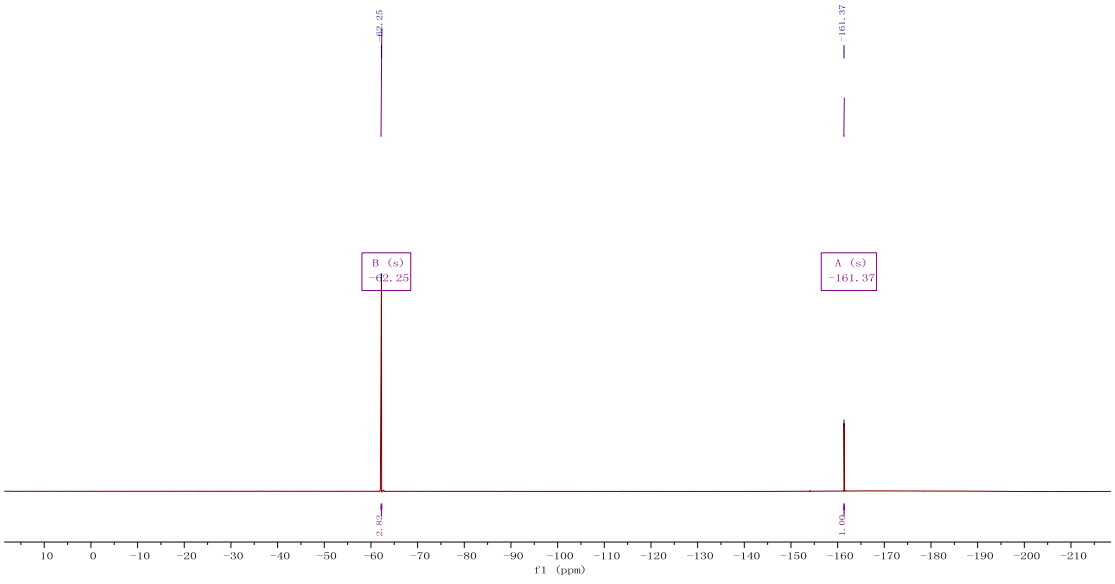

Ph
N
N
O
F
OMe
OMe
CF3
F3C
2ac

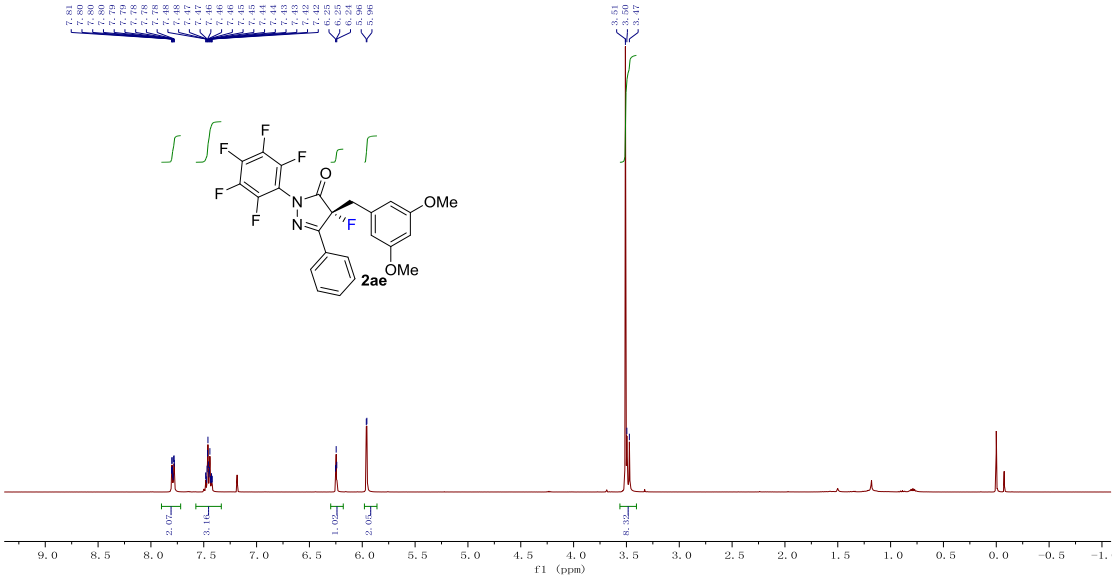


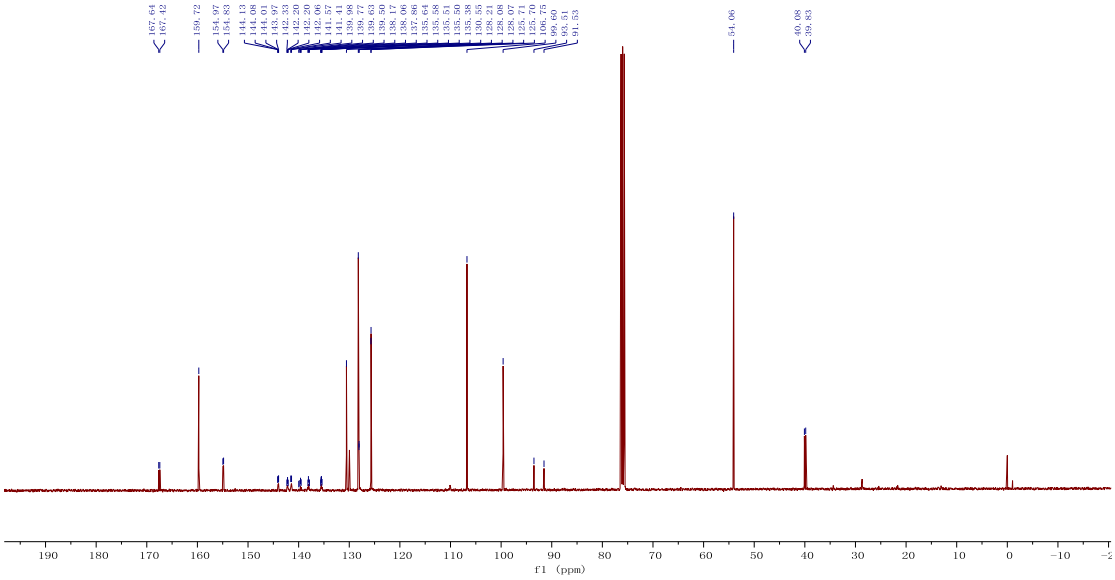

B (s)
-62.99
A (s)
-164.91

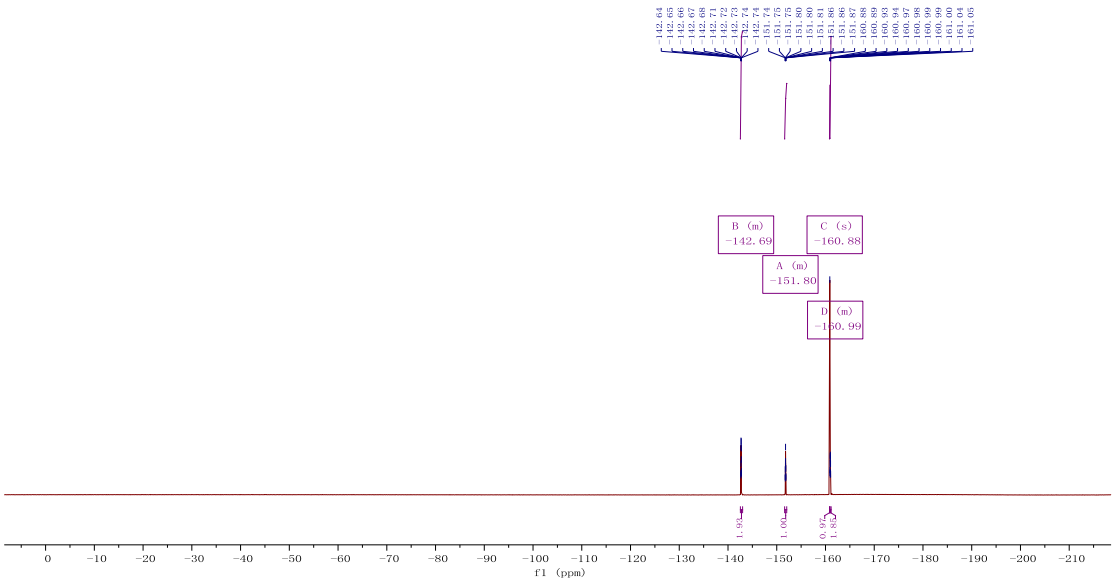

F3C
O
N
N
F
OMe
OMe
2ad

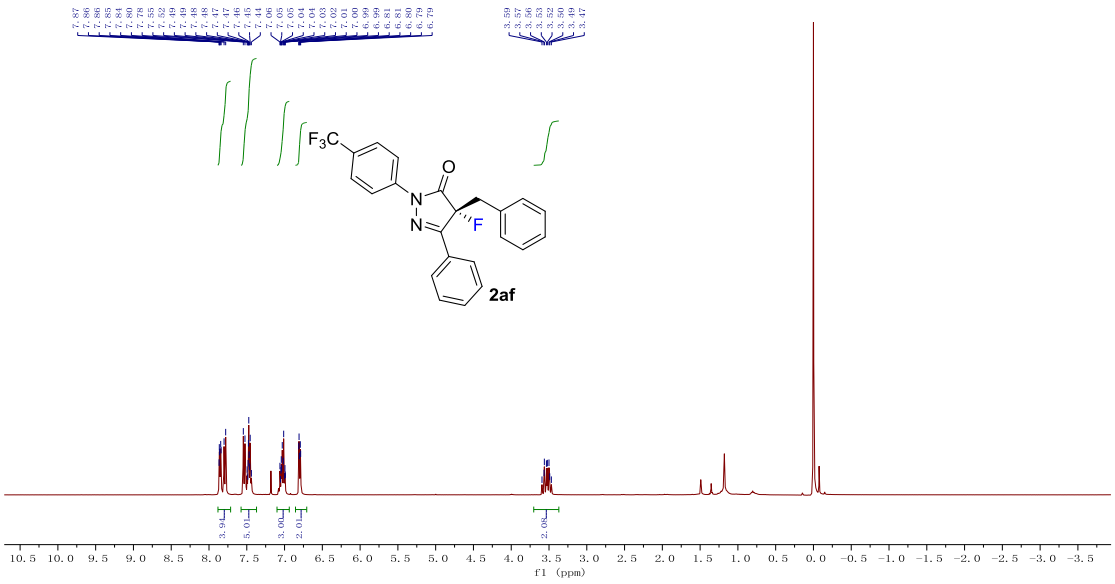


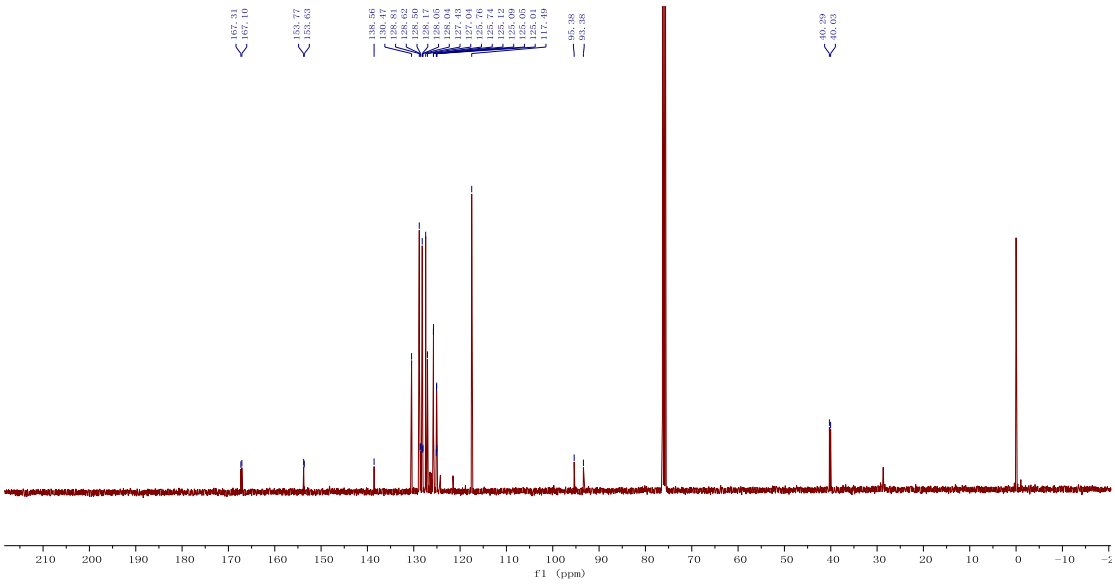

B (s)
-62.25
A (s)
-161.37

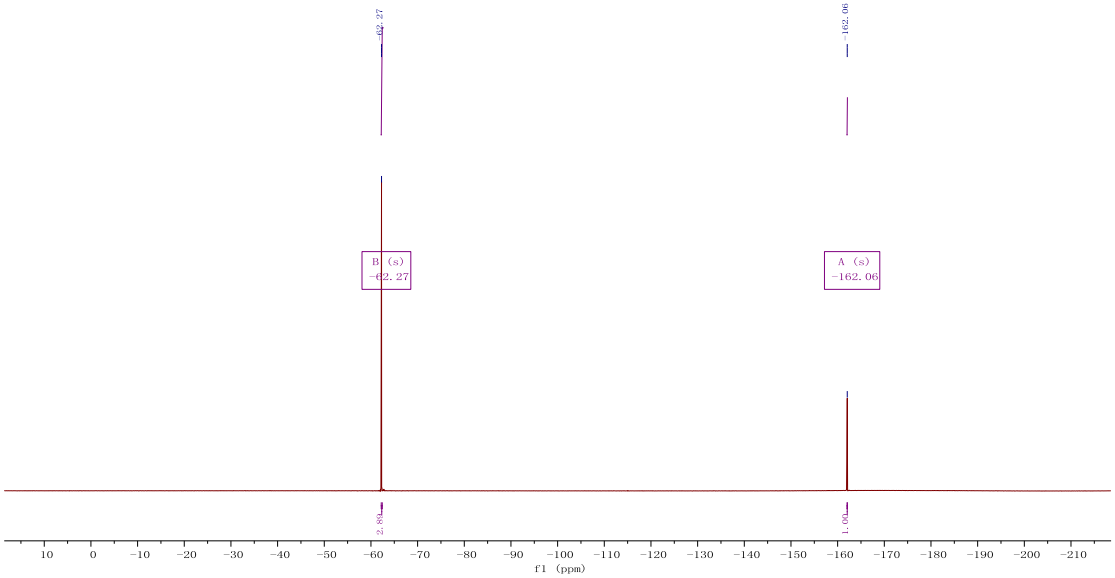

F
F
F
F
F
O
N
N
F
OMe
OMe
2ae
f1 (ppm)

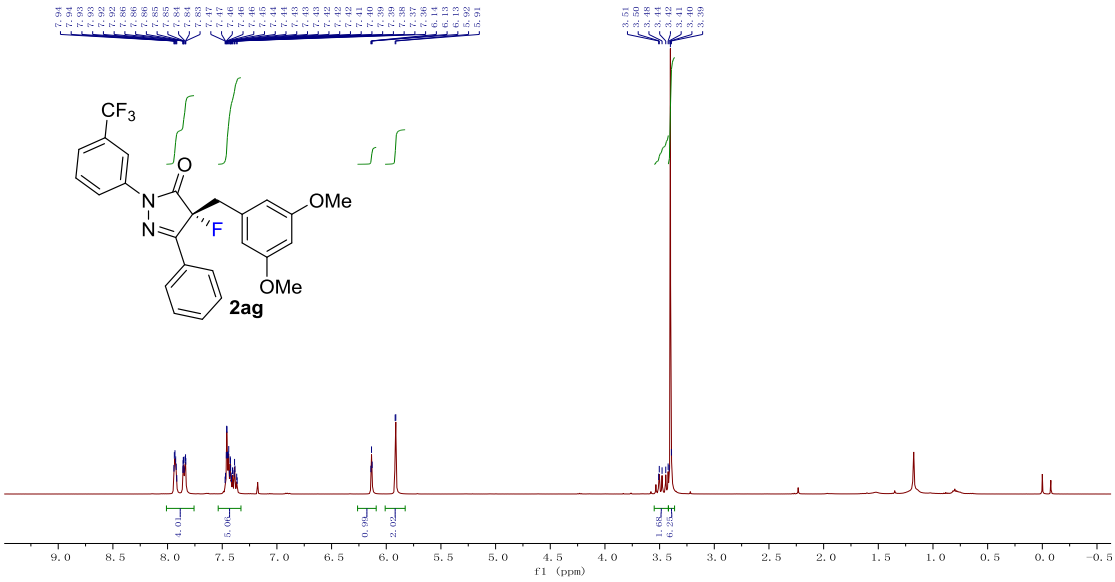

f1 (ppm)

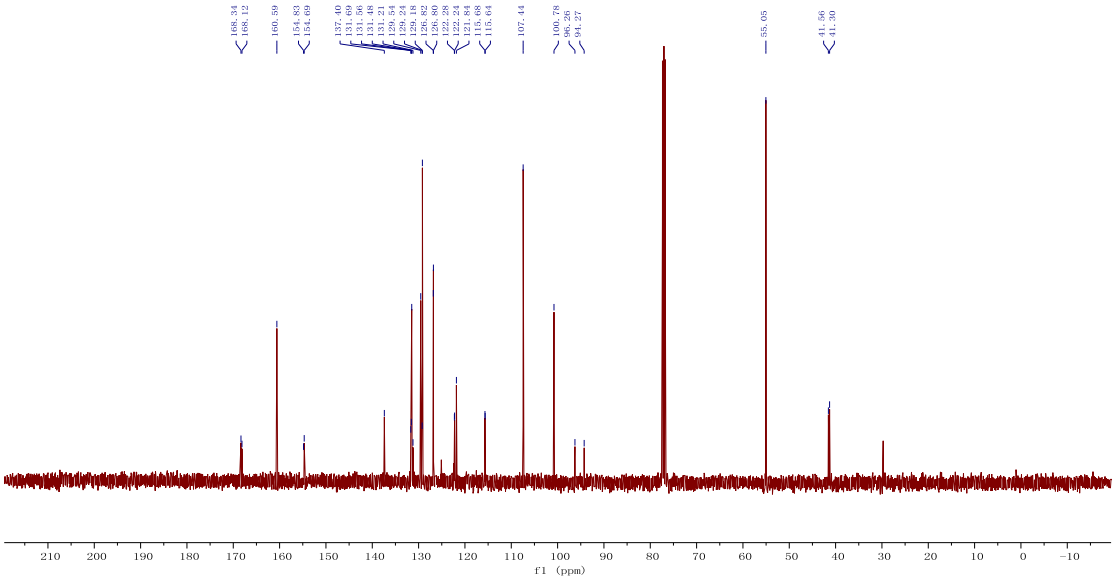

B (m)
-142.69
C (s)
-160.88
A (m)
-151.80
D (m)
-150.99
f1 (ppm)

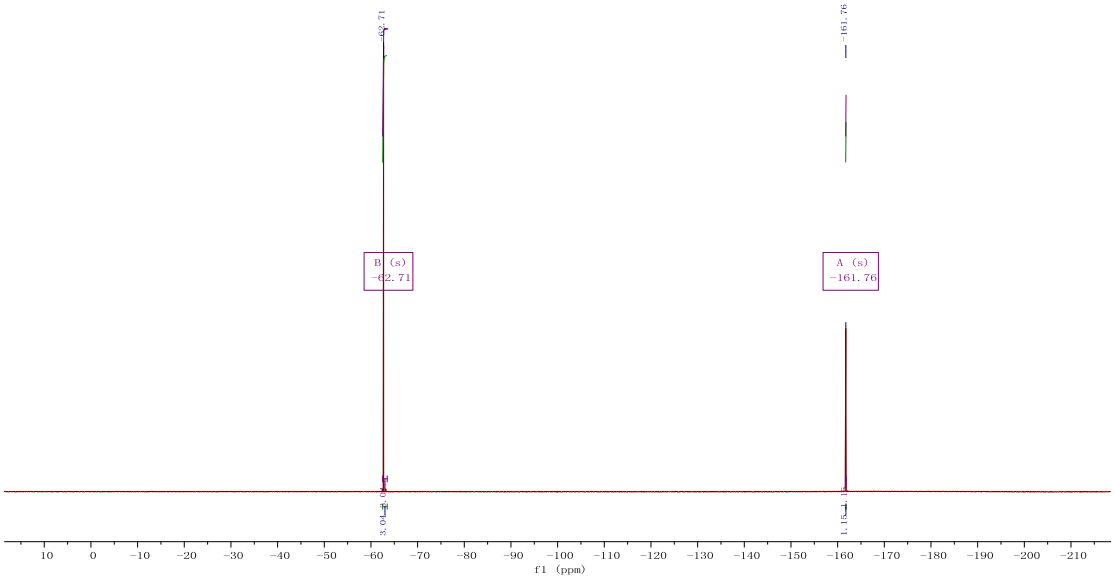

F3C
O
N
N
F
2af

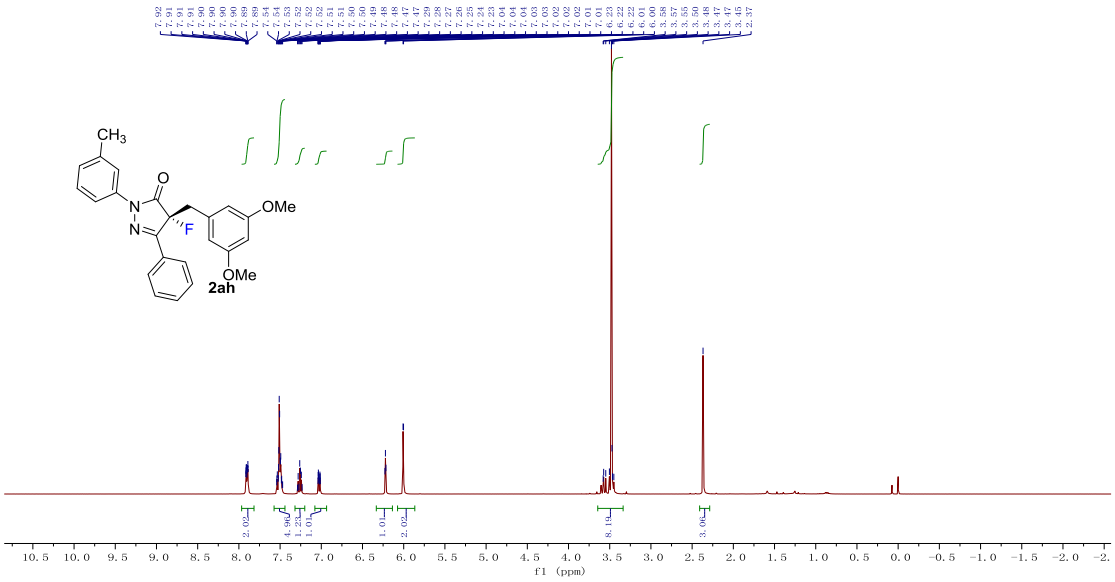


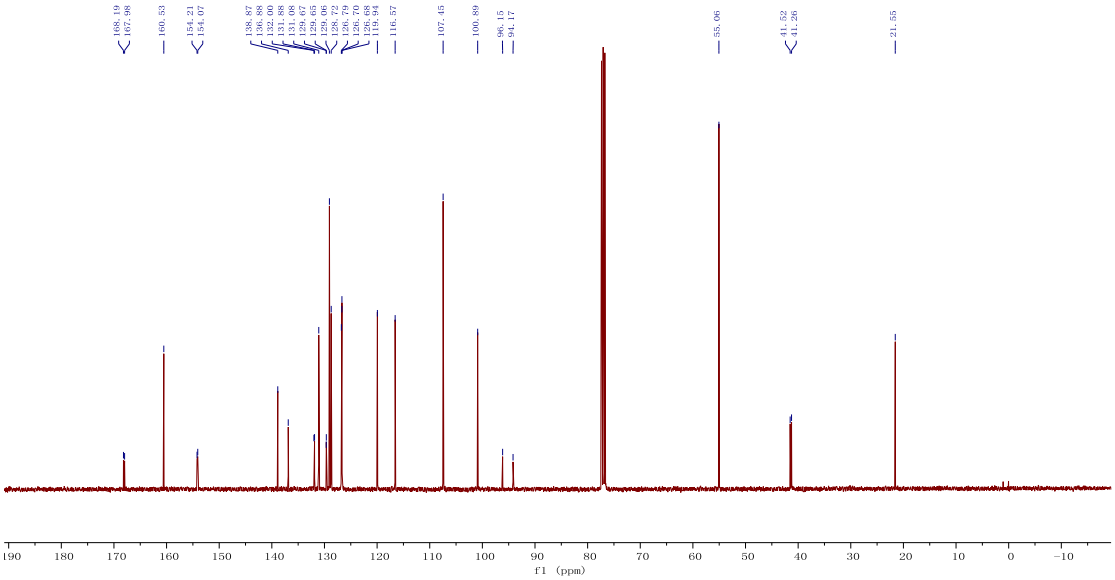

B (s)
-62.27
A (s)
-162.06

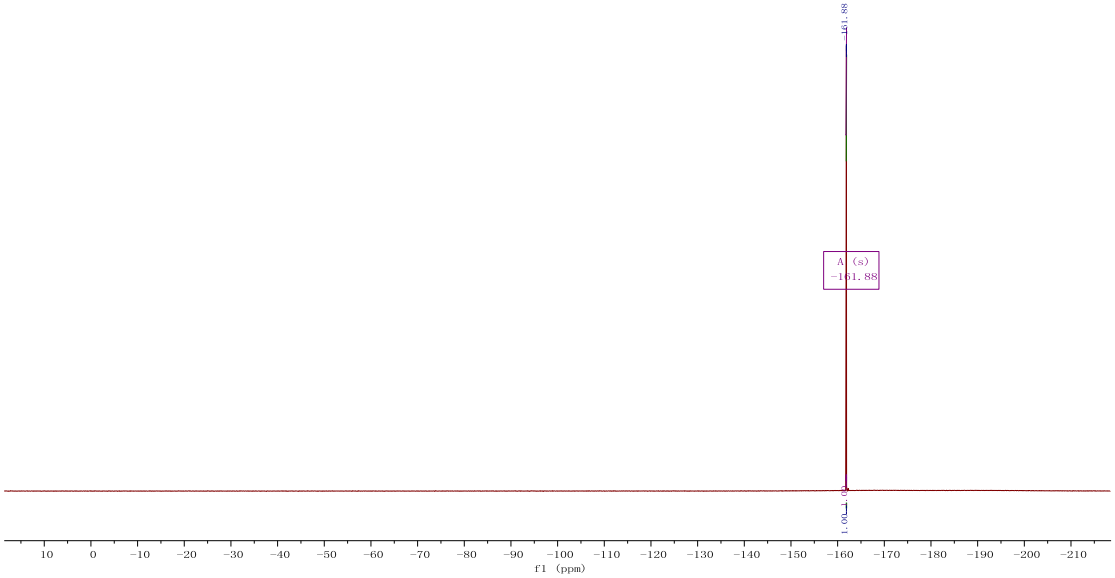

CF3
O
N
N
F
OMe
OMe
2ag
f1 (ppm)

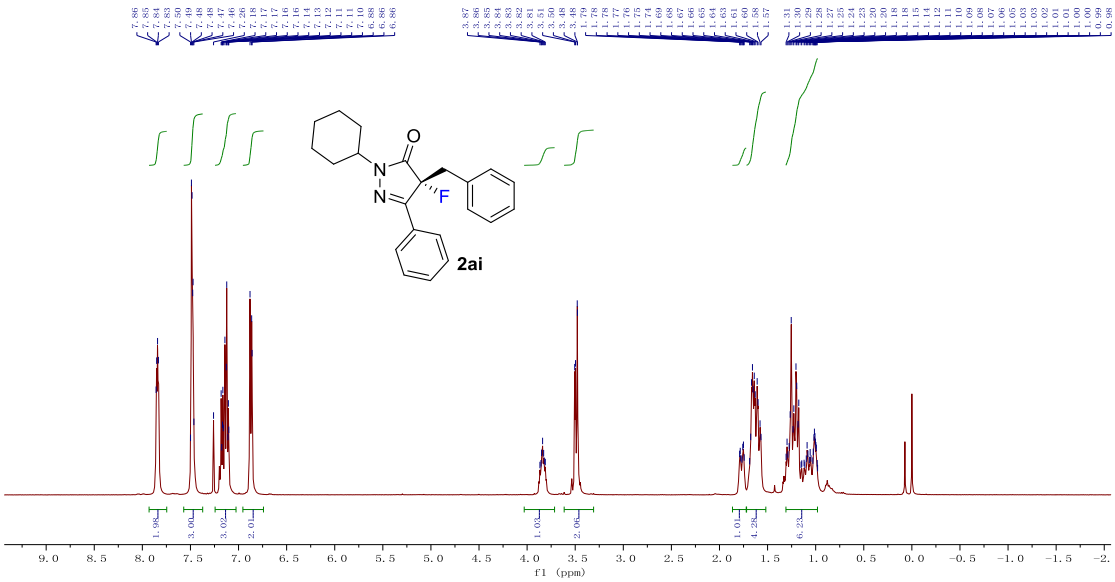

f1 (ppm)

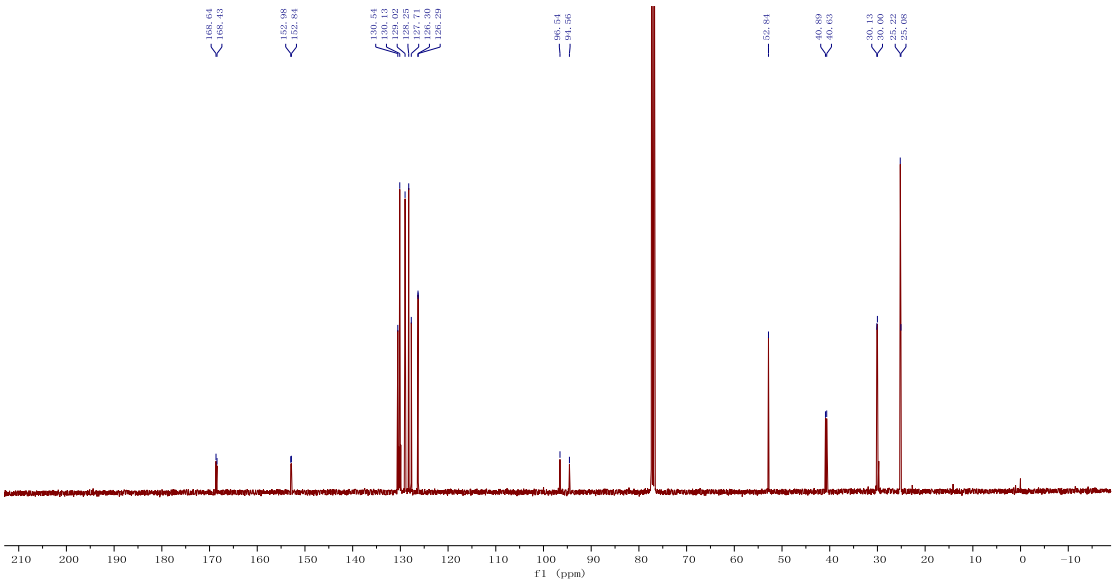

B (s)
-62.71
A (s)
-161.76
f1 (ppm)

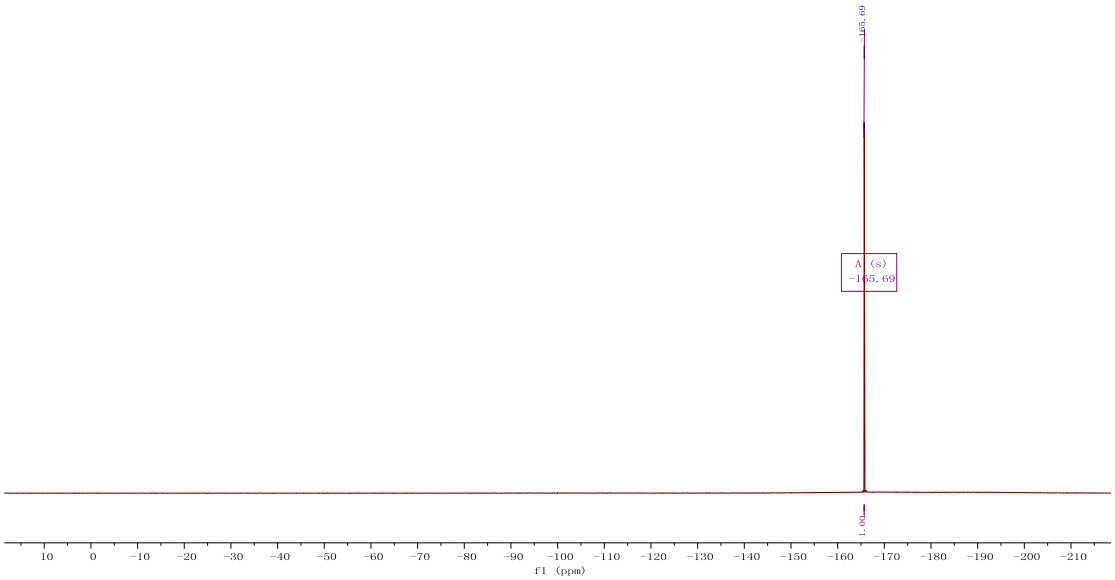

CH3
O
N
N
F
OMe
OMe
2ah
f1 (ppm)


f1 (ppm)


A (s)
-161.88
f1 (ppm)


2ai


f1 (ppm)


A (s)
-165.69
f1 (ppm)