Supporting Information

Photochemical Intermolecular [3σ+2σ]-Cycloaddition for the Construction of Aminobicyclo[3.1.1]heptanes

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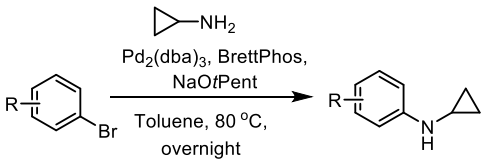
1. General remarks

1.1 General: For purple light irradiation, a Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) was placed 1.5 inches away from the reaction vials. NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K using 400, 500 and 600 MHz spectrometers. Chemical shifts are referenced to residual, nondeuterated $CHCl_3$ (δ 7.26 in the ^{1}H NMR and 77.2 in the ^{13}C NMR. Flash chromatography was carried out using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of leucine enkephalin for ESI-LC/MS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Melting points (°C) are uncorrected. UV/vis studies were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific.

1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Dry DMSO, dioxane, DMA, and DMF were obtained from Acros Organics and used as received. THF and Et_2O were purchased and dried via a solvent delivery system. Data are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J* (Hz) and integration

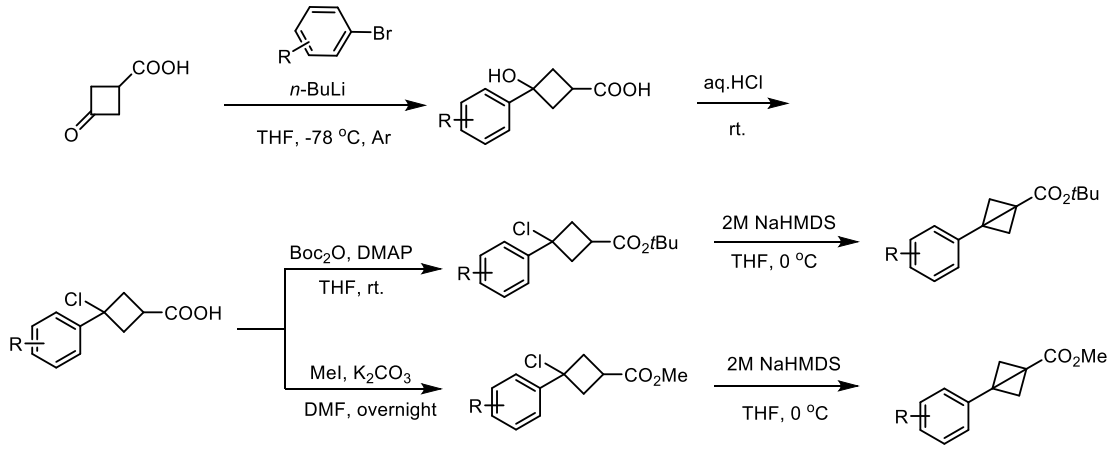
2. Experimental procedure

2.1. Synthesis of Cyclopropylanilines



General procedure A: Following a modified procedure,[1] an oven-dried microwave vial was charged with $Pd_2(dba)_3$ (1 mol %) and BrettPhos (3 mol %). The vial was sealed, evacuated, and back-filled with nitrogen (3 times). Then, toluene (0.5 M), cyclopropylamine (1.6 equiv), the aromatic bromide (1 equiv) and NaO*t*Pent (25% solution in toluene, 1.5 equiv) were added via syringe to the vial, and it was heated at 80 °C overnight. The reaction mixture was then cooled to rt, diluted with Et_2O, and filtered through a short pad of silica. The filtrate was evaporated under reduced pressure, and the obtained crude residue was subjected to column chromatography with the indicated solvents.

2.2. Synthesis of bicyclo[1.1.0]butanes[2]



Step 1, General procedure B: To a solution of aromatic bromide (2.2 equiv) in dry THF (0.7 M) was added *n*-BuLi (2.5 M, 2.2 equiv) dropwise at -78 °C under argon. The mixture was stirred for 1 h at -78 °C, and a soln of 3-oxocyclobutane-1-carboxylic acid (1.0 equiv) in dry THF (2.5 M) was added in one portion (reaction temperature became - 25 °C). The mixture was stirred for 1 h and quenched with a sat soln of NH_4Cl and H_2O (3:2). Then, the mixture was diluted with hexane. The organic layer was separated and washed with H_2O. The combined aq layers were acidified with a 2 M soln of $NaHSO_4$ and extracted with MTBE. The organic layer

[1] Maity, S.; Zhu, M.; Shinabery, R. S.; Zheng, N. *Angew. Chem. Int. Ed*. **2012**, *51*, 222–226.
Muriel, B.; Gagnebin, A.; Waser, J. *Chem. Sci.*, **2019**, *10,* 10716–10722.

[2] (a) Bychek, R. M.; Hutskalova, V.; Bas, Y. P.; Zaporozhets, O. A.; Zozulya, S.; Levterov, V. V.; Mykhailiuk, P. K. *J. Org. Chem.* **2019**, *84*, 15106−15117.
(b) Bychekand, R.; Mykhailiuk, P. K. *Angew. Chem. Int. Ed*. **2022**, doi.org/10.1002/anie.202205103

was washed with brine, dried (Na_2SO_4), filtered, and concentrated under reduced pressure. This material was used directly in the next step without further purification.

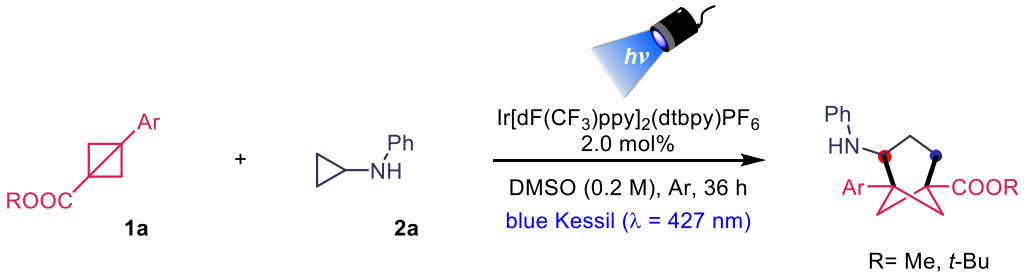
Step 2, General procedure C: To a soln of phenylcyclobutane-1-carboxylic acid (1.0 equiv) in toluene (0.8 M) conc HCl (12 equiv) was added dropwise at rt. The resulting mixture was stirred at rt overnight. The organic phase was separated, washed with H_2O, and brine 2 times, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the title compound. This material was used directly in the next step without further purification.

Step 3, General procedure D: To a soln of 3-chloro-phenylcyclobutane-1-carboxylic acid (1.0 equiv) in THF (0.3 M) were added Boc_2O (1.2 equiv) and DMAP (0.05 equiv). The mixture was stirred at rt overnight and concentrated under reduced pressure. The residue was dissolved in a mixture of MTBE and hexane (1:1). The soln was washed with 1 M $NaHSO_4$, 1 M $NaHCO_3$, and brine, and filtered through SiO_2 and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography eluting with a gradient from hexanes to 10% EtOAc in hexanes.

Step 3, General procedure E: Phenyl-3-chlorocyclobutane-1-carboxylic acid (1.0 equiv) was added in a round-bottomed flask. The reaction vessel was evacuated and backfilled with a balloon of nitrogen three times. DMF (0.5 M) was added into the reaction vessel followed by addition of K_2CO_3 (2.0 equiv) and MeI (1.5 equiv). The reaction mixture was stirred overnight at rt. Afterwards, the product mixture was diluted with EtOAc. The diluted mixture was washed with satd aq NaCl three times. The organic layer was dried (Na_2SO_4). The dried soln was filtered and concentrated to dryness. The obtained residue was purified by flash column chromatography eluting with a gradient from hexanes to 10% EtOAc in hexanes.

Step 4, General procedure F: To a solution of 3-chloro-3-phenylcyclobutane-1-carboxylate (1.0 equiv.) in THF (0.4 M) was added 2 M NaHMDS (1.2 equiv.) at 0-5 °C under argon atmosphere. The resulted mixture was stirred for 1 h at the same temperature and a 25% solution of NH_4Cl and water were added dropwise. The mixture was then diluted with hexane (25 mL). The organic layer was separated and washed with brine, dried over Na_2SO_4, filtered through SiO_2 and concentrated under reduced pressure. The obtained residue was purified by flash column chromatography with flash column chromatography eluting with a gradient from hexanes to 10% EtOAc in hexanes.

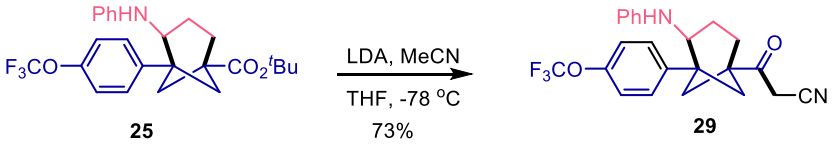
2.3. Synthesis of aminobicyclo[3.1.1]heptanes



General Procedure G

To an 4.0 mL clear borosilicate glass vial with a screw top equipped with a magnetic stir bar was added Ir{dF(CF_3)$_2$ppy}$_2$(dtbbpy)]PF_6 (4.5 mg, 0.02 mmol, 2 mol %), the desired cyclopropylaniline (0.04 mmol, 2.0 equiv), and bicyclo[1.1.0]butane (0.20 mmol, 1.0 equiv). The vial was then sealed with a screw-cap containing a PTFE-lined silicone septum. An inlet needle was inserted, and the atmosphere was exchanged for Ar *via* three evacuation-backfill cycles. The vial was then charged with 1.0 mL of dry DMSO via syringe. The reaction was then sparged for ~2 min with Ar, the cap was sealed with Parafilm®, and the reaction mixture was irradiated with a Kessil® PR160 λ_{max} = 427 nm lamp for 36 h. Upon reaction completion, the product mixture was diluted with EtOAc (10 mL). The diluted product mixture was washed with H_2O and brine. The organic layer was dried (Na_2SO_4). The dried soln was filtered and concentrated to dryness. The obtained residue was purified by flash column chromatography eluting with a gradient from hexanes to 10% EtOAc in hexanes.

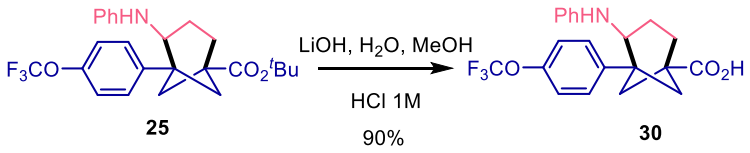
2.4. Synthesis of ***29***



General Procedure H

To a stirred soln of compound **25** (45 mg, 0.1 mmol), MeCN (9 mg, 0.22 mmol) in THF (2 mL) cooled to -78 °C, a freshly prepared soln of LDA (2 M in THF, 0.11 mL, 0.22 mmol) was added over a period of 10 min under nitrogen. The resulting soln was stirred at -78 °C for 20 min and then warmed to rt over 2 h. The reaction mixture was quenched with 2 M HCl (0.5 mL), extracted with EtOAc (3 x 5 mL), and the organic layers were dried ($MgSO_4$), filtered and evaporated to afford a yellow residue. The crude product was purified by flash silica chromatography (elution gradient 0 to 30 % EtOAc in heptane). Pure fractions were evaporated to dryness to afford **29** (30 mg, 73%) as a colorless oil.

2.5. Synthesis of ***30***

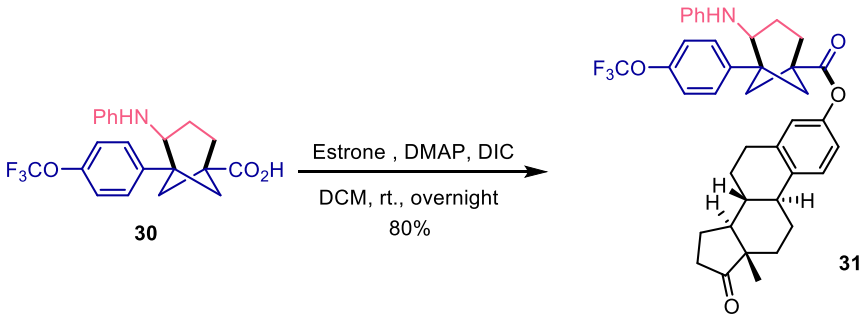


25 **30**

General Procedure I

To a soln of **25** (224 mg, 0.5 mmol) in MeOH (4 mL) was added dropwise a soln of LiOH (48 mg, 2 mmol) in H_2O (4 mL) at rt. The resulting mixture was stirred at rt for 12 h, and the organic solvents were evaporated. H_2O (4 mL) was then added, and the mixture was extracted with Et_2O (3 x 5 mL). The aq layer was acidified with 1 M HCl to pH ~3, and the so-formed cloudy soln was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), filtered, and concentrated under reduced pressure to afford **30** (176 mg, 90%) as a white solid.

2.6. Synthesis of ***31***

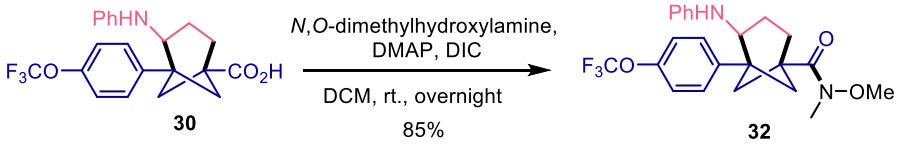


30 **31**

General Procedure J

To a soln of **30** (39 mg, 0.1 mmol), estrone (27 mg, 0.1 mmol), and 4-*N, N*-dimethylaminopyridine (0.6 mg, 0.05 mmol) in CH_2Cl_2 (4 mL), *N*, *N*′-diisopropylcarbodiimide (DIC, 15 mg, 0.12 mmol) was added in one portion. The resulting soln was stirred at rt overnight. The mixture solution was evaporated to afford a yellow residue. The crude product was purified by flash silica chromatography (elution gradient 0 to 50 % EtOAc in heptane). Pure fractions were evaporated to dryness to afford **31** (51 mg, 80 %) as a colorless oil.

2.7. Synthesis of ***32***



30 **32**

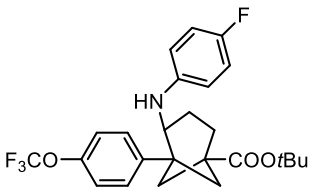
General Procedure K

To a soln of **30** (39 mg, 0.1 mmol), *N, O*-dimethylhydroxylamine (6 mg, 0.1 mmol) and 4-*N, N*-dimethylaminopyridine (0.6 mg, 0.05 mmol) in CH_2Cl_2 (4 mL), *N*, *N*′-

diisopropylcarbodiimide DIC (15 mg, 0.12 mmol) was added in one portion. The resulting soln was stirred at rt overnight. The mixture solution was evaporated to afford a yellow residue. The crude product was purified by flash silica chromatography (elution gradient 0 to 50 % EtOAc in heptane). Pure fractions were evaporated to dryness to afford **32** (37 mg, 85 %) as a colorless oil.

3. Characterization data

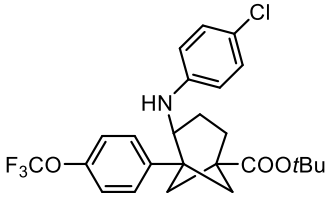
***tert*-Butyl 4-((4-Fluorophenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (3)**



$C_{25}H_{27}F_4NO_3$
MW: 465.19 g mol^{-1}
Colorless oil
70% (65 mg, 0.14 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.7 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.70 (t, *J* = 8.7 Hz, 2H), 6.23 (dd, *J* = 9.0, 4.4 Hz, 2H), 3.79 – 3.75 (m, 1H), 3.42 (s, 1H), 2.42 (m, 1H), 2.37 – 2.31 (m, 2H), 2.29 (dd, *J* = 9.6, 7.0 Hz, 1H), 2.16 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.13 – 2.07 (m, 1H), 2.07 – 1.98 (m, 1H), 1.84 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 155.8(d, J_{C-F} = 233.7 Hz), 147.7, 145.1, 143.9 (d, J_{C-F} = 2.0 Hz), 127.4, 120.9, 120.6 (q, J_{C-F} = 256.9 Hz), 115.4 (d, J_{C-F} = 22.1 Hz), 114.4 (d, J_{C-F} = 7.4 Hz), 80.5, 58.6, 46.2, 43.7, 41.1, 34.5, 28.7, 28.2, 25.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9, -128.1.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}F_4NO_3$ 466.2005; Found 466,1999.
IR (neat): ν = 3401, 2950, 1716, 1507, 1368, 1297, 1252, 1217, 1157, 1101, 845, 817, 776, 508 cm^{-1}.
R_f: 0.34 (hexane/EtOAc 9:1 *v/v*, UV).

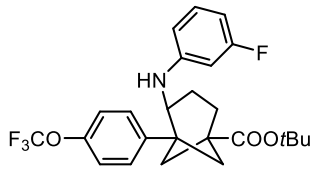
***tert*-Butyl 4-((4-Chlorophenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (4)**



$C_{25}H_{27}ClF_3NO_3$
MW: 481.16 g mol^{-1}
Colorless oil
36% (35 mg, 0.072 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.09 (d, *J* = 8.7 Hz, 2H), 7.07 – 7.04 (m, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 6.22 (d, *J* = 8.9 Hz, 2H), 3.80 (t, *J* = 6.2 Hz, 1H), 3.52 (s, 1H), 2.43 (m, 1H), 2.38 – 2.32 (m, 2H), 2.27 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.18 – 2.14 (m, 1H), 2.13 – 2.02 (m, 2H), 1.87 – 1.78 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.5, 147.8, 146.1, 144.9, 128.9, 127.3, 121.9, 121.0, 120.6 (q, J_{C-F} = 255.0 Hz), 114.4, 80.6, 57.9, 46.2, 43.7, 41.1, 34.5, 28.7, 28.2, 25.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{28}ClF_3NO_3$ 482.1710; Found 482.1722.
IR (neat): ν = 3400, 2975, 1715, 1599, 1496, 1368, 1295, 1253, 1220, 1160, 1103, 840, 813 cm^{-1}.
R_f: 0.29 (hexane/EtOAc 9:1 *v/v*, UV).

***tert*-Butyl 4-((3-Fluorophenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (5)**



$C_{25}H_{27}F_4NO_3$
MW: 465.19 g mol^{-1}
Colorless oil
50% (46 mg, 0.10 mmol)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.12 – 7.05 (m, 4H), 6.90 (q, *J* = 8.1 Hz, 1H), 6.26 – 6.22 (m, 1H), 6.07 (d, *J* = 8.1 Hz, 1H), 5.99 (d, *J* = 11.9 Hz, 1H), 3.83 (q, *J* = 6.5 Hz, 1H), 3.66 (d, *J* = 6.9 Hz, 1H), 2.49 – 2.41 (m, 1H), 2.36 (dd, *J* = 13.9, 9.6 Hz, 2H), 2.28 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.17 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.14 – 2.02 (m, 2H), 1.88 – 1.81 (m, 1H), 1.45 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.5, 163.9 (d, J_{C-F} = 242.6 Hz), 149.3 (d, J_{C-F} = 10.8 Hz), 147.8, 144.8, 130.1 (d, J_{C-F} = 10.3 Hz), 127.4, 120.9, 120.5 (q, J_{C-F} = 257.5 Hz), 109.2 (d, J_{C-F} = 2.3 Hz), 103.7 (d, J_{C-F} = 21.5 Hz), 99.9 (d, J_{C-F} = 25.4 Hz), 80.6, 57.6, 46.1, 43.6, 41.1, 34.5, 28.7, 28.2, 25.8.

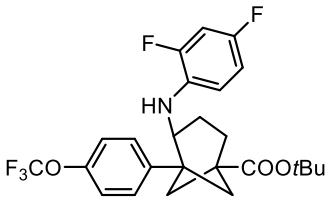
^{19}F NMR (376 MHz, $CDCl_3$) δ= -57.9, -113.3.

HRMS (EI-TOF) m/z: [M] calcd for $C_{25}H_{27}F_4NO_3$ 465.1927; Found 465.1922.

IR (neat): ν = 3400, 2977, 1723, 1620, 1507, 1255, 1221, 1150, 1104 cm^{-1}.

R*f*: 0.40 (hexane/EtOAc 9:1 *v/v*, UV).

***tert*-Butyl 4-((2,4-Difluorophenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (6)**



$C_{25}H_{26}F_5NO_3$
MW: 483.18 g mol^{-1}
Colorless oil
60% (58 mg, 0.120 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.7 Hz, 2H), 7.05 – 7.01 (m, 2H), 6.61 – 6.57 (m, 1H), 6.49 – 6.45 (m, 1H), 6.18 (td, *J* = 9.3, 5.4 Hz, 1H), 3.80 (t, *J* = 6.3 Hz, 1H), 3.63 (s, 1H), 2.46 – 2.37 (m, 2H), 2.35 – 2.28 (m, 2H), 2.18 – 2.10 (m, 2H), 2.06 – 2.01 (m, 1H), 1.88 – 1.80 (m, 1H), 1.44 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.5, 154.2 (dd, J_{C-F} = 237.8, 11.2 Hz), 150.7 (dd, J_{C-F} = 240.5, 11.5 Hz), 147.7 (t, J_{C-F} = 2.1 Hz), 144.8, 132.4 (dd, J_{C-F} = 11.4, 3.1 Hz), 127.4, 120.9, 120.5 (q, J_{C-F} = 255.0 Hz), 110.3 (dd, J_{C-F} = 21.7, 3.6 Hz), 103.3 (dd, J_{C-F} = 26.7, 23.4 Hz), 80.6, 58.3, 46.4, 43.6, 41.2, 34.2, 28.7, 28.1, 26.2.

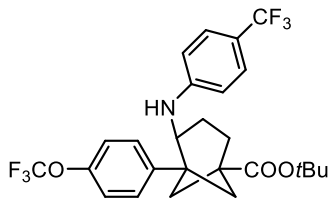
^{19}F NMR (565 MHz, $CDCl_3$) δ= -58.0, -126.1, -132.0.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{27}F_5NO_3$ 484.1988; Found 484.1909.

IR (neat): ν = 3380, 2973, 1718, 1518, 1295, 1219, 1205, 1159, 1101, 844 cm^{-1}.

R*f*: 0.52 (hexane/EtOAc 9:1 *v/v*, UV).

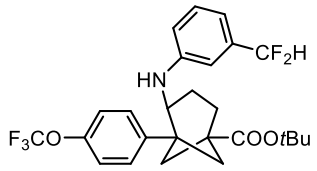
***tert*-Butyl 5-(4-(Trifluoromethoxy)phenyl)-4-((4-(trifluoromethyl)phenyl)amino)bicyclo[3.1.1]heptane-1-carboxylate (7)**



$C_{26}H_{27}F_6NO_3$
MW: 515.19 g mol^{-1}
Colorless oil
63% (65 mg, 0.126 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.20 (d, *J* = 8.4 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.29 (d, *J* = 8.5 Hz, 2H), 3.91 (t, *J* = 6.2 Hz, 1H), 3.86 (s, 1H), 2.50 – 2.44 (m, 1H), 2.40 (m, 1H), 2.37 – 2.33 (m, 1H), 2.28 (m, 1H), 2.17 (m, 1H), 2.14 – 2.03 (m, 2H), 1.83 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.4, 149.9, 147.8, 144.6, 127.3, 126.4 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.9 (q, $J_{C\text{-}F}$ = 268.8 Hz), 121.4, 120.5 (q, $J_{C\text{-}F}$ = 255.6 Hz), 118.8 (q, $J_{C\text{-}F}$ = 33.2 Hz), 112.3, 80.7, 57.2, 46.1, 43.6, 41.2, 34.3, 28.7, 28.2, 25.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -58.1, -61.2.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{28}F_6NO_3$ 516.1973; Found 516.1966.
IR (neat): ν = 3388, 2976, 1616, 1319, 1259, 1161, 1105 cm^{-1}.
R*f*: 0.34 (hexane/EtOAc 9:1 *v/v*, UV).

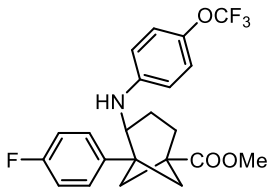
***tert*-Butyl 4-((3-(Difluoromethyl)phenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (8)**



$C_{26}H_{28}F_5NO_3$
MW: 497.20 g mol^{-1}
Colorless oil
65% (65 mg, 0.130 mmol)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 8.8 Hz, 2H), 7.07 – 7.00 (m, 3H), 6.65 (d, *J* = 7.5 Hz, 1H), 6.41 (t, *J* = 56.0 Hz, 1H), 6.41 – 6.35 (m, 2H), 3.94 – 3.86 (m, 1H), 3.68 (d, *J* = 6.7 Hz, 1H), 2.52 – 2.42 (m, 1H), 2.41 – 2.26 (m, 3H), 2.18 (dd, *J* = 9.5, 6.8 Hz, 1H), 2.14 – 2.00 (m, 2H), 1.91 – 1.78 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (101 MHz, $CDCl_3$): δ = 174.5, 147.7, 144.8, 135.2 (t, $J_{C\text{-}F}$ = 21.9 Hz), 129.4, 127.4, 120.9, 120.5 (q, $J_{C\text{-}F}$ = 250.4 Hz), 115.6, 115.0 (t, $J_{C\text{-}F}$ = 239.4 Hz), 114.4 (t, $J_{C\text{-}F}$ = 6.4 Hz), 109.5 (t, $J_{C\text{-}F}$ = 6.1 Hz), 80.6, 57.5, 46.2, 43.7, 41.2, 34.4, 28.7, 28.2, 25.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ= -58.0, -110.9, -110.9.
HRMS (EI-TOF) m/z: [M] calcd for $C_{26}H_{28}F_5NO_3$ 497.1989; Found 497.1987.
IR (neat): ν = 3396, 2952, 1713, 1611, 1296, 1254, 1222, 1160, 1103, 1020 cm^{-1}.
R*f*: 0.26 (hexane/EtOAc 9:1 *v/v*, UV).

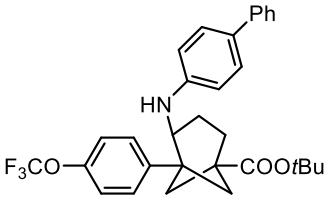
Methyl 5-(4-Fluorophenyl)-4-((4-(trifluoromethoxy)phenyl)amino)bicyclo[3.1.1]heptane-1-carboxylate (9)



$C_{22}H_{21}F_4NO_3$
MW: 423.15 g mol^{-1}
Colorless oil
62% (52 mg, 0.124 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.04 (dd, *J* = 8.7, 5.3 Hz, 2H), 6.91 (t, *J* = 8.7 Hz, 2H), 6.88 – 6.83 (m, 2H), 6.28 (d, *J* = 9.0 Hz, 2H), 3.81 (t, *J* = 6.0 Hz, 1H), 3.69 (s, 3H), 3.58 (s, 1H), 2.52 – 2.40 (m, 3H), 2.31 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.20 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.15 – 2.05 (m, 2H), 1.90 – 1.82 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.4, 162.8, 160.4, 146.4, 141.6 (d, $J_{C\text{-}F}$ = 3.2 Hz), 127.4 (d, $J_{C\text{-}F}$ = 8.0 Hz), 122.3, 120.8 (q, $J_{C\text{-}F}$ = 255.2 Hz), 115.3 (d, $J_{C\text{-}F}$ = 21.3 Hz), 113.6, 58.0, 52.0, 46.4, 42.8, 41.3, 34.6, 28.6, 25.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -58.6, -116.4.
HRMS (EI-TOF) m/z: [M] calcd for $C_{22}H_{21}F_4NO_3$ 423.1458; Found 423.1467.
IR (neat): ν = 3390, 2952, 1723, 1510, 1248, 1215, 1157, 1100, 827 cm^{-1}.
R_f: 0.21 (hexane/EtOAc 9:1 *v/v*, UV).

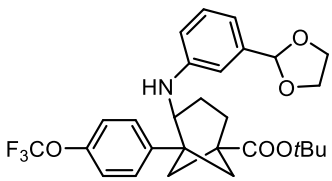
***tert*-Butyl 4-([1,1'-Biphenyl]-4-ylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (10)**



$C_{31}H_{32}F_3NO_3$
MW: 523.23 g mol^{-1}
Colorless oil
57% (60 mg, 0.114 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 – 7.44 (m, 2H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.42 (d, *J* = 8.6 Hz, 2H), 3.91 (dd, *J* = 7.3, 4.5 Hz, 1H), 3.66 (s, 1H), 2.53 – 2.46 (m, 1H), 2.40 – 2.38 (m, 2H), 2.31 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.22 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.16 – 2.06 (m, 2H), 1.95 – 1.89 (m, 1H), 1.46 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 147.8, 146.9, 145.1, 141.3, 130.4, 128.7, 127.8, 127.3, 126.4, 126.2, 120.9, 120.5 (q, $J_{C\text{-}F}$ = 255.0 Hz), 113.6, 80.5, 57.6, 46.1, 43.7, 40.8, 34.9, 28.7, 28.2, 25.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{31}H_{33}F_3NO_3$ 524.2413; Found 524.2424.
IR (neat): ν = 3402, 2952, 1717, 1610, 1296, 1252, 1219, 1158, 1101, 696 cm^{-1}.
R_f: 0.38 (hexane/EtOAc 9:1 *v/v*, UV).

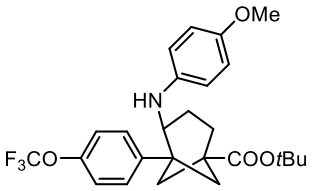
***tert*-Butyl 4-((3-(1,3-Dioxolan-2-yl)phenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (11)**



$C_{28}H_{32}F_3NO_5$
MW: 519.22 g.mol^{-1}
Colorless oil
42% (44 mg, 0.084 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.8 Hz, 1H), 6.69 (d, *J* = 7.6 Hz, 1H), 6.48 (t, *J* = 2.0 Hz, 1H), 6.31 (dd, *J* = 8.1, 1.5 Hz, 1H), 5.65 (s, 1H), 4.08 – 4.02 (m, 2H), 4.02 – 3.96 (m, 2H), 3.88 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.62 (s, 1H), 2.47 – 2.41 (m, 1H), 2.37 – 2.32 (m, 2H), 2.27 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.19 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.89 – 1.83 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 147.7, 147.6, 145.1, 138.9, 129.2, 127.3, 120.9, 120.6 (q, J_{C-F} = 255.0 Hz), 115.5, 114.0, 111.1, 103.8, 80.5, 65.3, 65.3, 57.4, 46.1, 43.7, 40.7, 34.9, 28.7, 28.2, 25.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{33}F_3NO_5$ 520.2311; Found 520.2311.
IR (neat): ν = 3389, 2952, 1717, 1254, 1219, 1158, 1100, 845, 774 cm^{-1}.
R_f: 0.29 (hexane/EtOAc 4:1 *v/v*, UV).

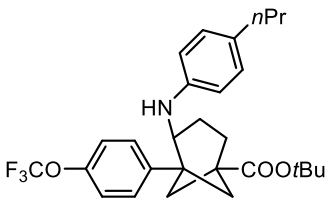
***tert*-Butyl 4-((4-Methoxyphenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (12)**



$C_{26}H_{30}F_3NO_4$
MW: 477.21 g.mol^{-1}
Colorless oil
30% (29 mg, 0.06 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.7 Hz, 2H), 6.62 (d, *J* = 8.9 Hz, 2H), 6.30 (d, *J* = 9.0 Hz, 2H), 3.75 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.68 (s, 3H), 3.27 (s, 1H), 2.45 – 2.37 (m, 1H), 2.35 – 2.28 (m, 3H), 2.17 (dd, *J* = 9.5, 6.8 Hz, 1H), 2.13 – 2.00 (m, 2H), 1.90 – 1.84 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.7, 152.3, 147.7, 145.3, 141.7, 127.4, 120.9, 120.6 (q, J_{C-F} = 255.0 Hz), 115.2, 114.8, 80.4, 58.9, 55.9, 46.2, 43.7, 41.0, 34.7, 28.7, 28.2, 25.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{31}F_3NO_4$ 478.2205; Found 478.2216.
IR (neat): ν = 3390, 2975, 1719, 1510, 1294, 1254, 1161, 1103 cm^{-1}.
R_f: 0.18 (hexane/EtOAc 9:1 *v/v*, UV).

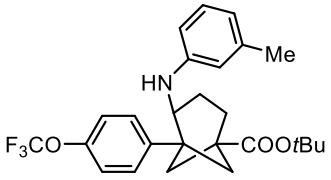
***tert*-Butyl 4-((4-Propylphenyl)amino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (13)**



$C_{28}H_{34}F_3NO_3$
MW: 489.24 g mol^{-1}
Colorless oil
61% (59 mg, 0.122 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ =7.12 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 6.29 (d, *J* = 8.4 Hz, 2H), 3.82 (dd, *J* = 7.2, 4.3 Hz, 1H), 3.45 (s, 1H), 2.46 – 2.42 (m, 1H), 2.41 – 2.38 (m, 2H), 2.36 – 2.32 (m, 2H), 2.29 – 2.28 (m, 1H), 2.20 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.11 – 2.01 (m, 2H), 1.91 – 1.86 (m, 1H), 1.54 – 1.50 (m, 2H), 1.44 (s, 9H), 0.88 (t, *J* = 7.3 Hz, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.7, 147.7, 145.5, 145.3, 131.8, 129.0, 127.4, 120.9, 120.5 (q, J_{C-F} = 255.0 Hz), 113.6, 80.5, 57.9, 46.1, 43.7, 40.7, 37.2, 35.0, 28.7, 28.2, 25.7, 24.9, 13.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{35}F_3NO_3$ 490. 2569; Found 490. 2572.
IR (neat): ν = 3398, 2958, 1719, 1515, 1296, 1253, 1102 cm^{-1}.
R*f*: 0.51 (hexane/EtOAc 9:1 *v/v*, UV).

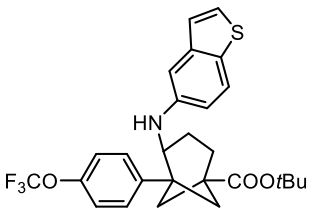
***tert*-Butyl 4-(*m*-Tolylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (14)**



$C_{26}H_{30}F_3NO_3$
MW: 461.21 g mol^{-1}
Colorless oil
57% (53 mg, 0.114 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.13 (d, *J* = 8.7 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 6.91 (t, *J* = 7.7 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.16 (d, *J* = 8.5 Hz, 1H), 6.14 (s, 1H), 3.85 (dd, *J* = 7.3, 4.4 Hz, 1H), 3.51 (s, 1H), 2.48 – 2.40 (m, 1H), 2.37 – 2.33 (m, 2H), 2.28 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.20 (dd, *J* = 9.4, 7.1 Hz, 1H), 2.16 (s, 3H), 2.11 – 2.04 (m, 2H), 1.90 – 1.85 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 147.7, 147.5, 145.2, 138.9, 129.0, 127.4, 120.9, 120.5 (q, J_{C-F} = 255.0 Hz), 118.4, 114.2, 110.5, 80.5, 57.5, 46.1, 43.7, 40.7, 35.0, 28.7, 28.2, 25.8, 21.6.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{31}F_3NO_3$ 462.2256; Found 462.2258.
IR (neat): ν = 3398, 2975, 1716, 1604, 1509, 1254, 1219, 1154, 691 cm^{-1}.
R*f*: 0.45 (hexane/EtOAc 9:1 *v/v*, UV).

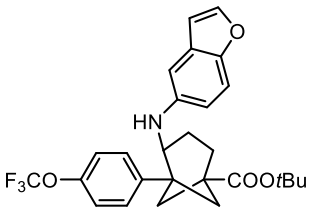
***tert*-Butyl 4-(Benzo[b]thiophen-5-ylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (15)**



$C_{27}H_{28}F_3NO_3S$
MW: 503.17 g mol^{-1}
Colorless oil
51% (51 mg, 0.102 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 5.4 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 2H), 7.09 – 7.04 (m, 3H), 6.73 (d, *J* = 2.3 Hz, 1H), 6.46 (dd, *J* = 8.7, 2.3 Hz, 1H), 3.90 (dd, *J* = 7.1, 4.5 Hz, 1H), 3.58 (s, 1H), 2.54 – 2.46 (m, 1H), 2.41 – 2.34 (m, 2H), 2.32 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.22 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.15 – 2.05 (m, 2H), 1.96 – 1.91 (m, 1H), 1.45 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 147.7, 145.1, 145.0, 140.9, 129.5, 127.3, 127.0, 123.2, 122.8, 120.9, 120.5 (q, J_{C-F} = 256.5 Hz), 114.5, 105.8, 80.5, 58.2, 46.2, 43.8, 40.8, 35.0, 28.7, 28.2, 25.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{29}F_3NO_3S$ 504.1820; Found 504.1808.
IR (neat): ν = 3400, 2975, 1716, 1508, 1295, 1251, 1219, 1156, 1101, 689 cm^{-1}.
R*f*: 0.36 (hexane/EtOAc 9:1 *v/v*, UV).

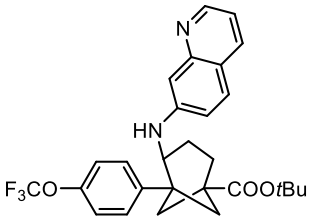
***tert*-Butyl 4-(Benzofuran-5-ylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (16)**



$C_{27}H_{28}F_3NO_4$
MW: 487.19 g mol^{-1}
Colorless oil
47% (46 mg, 0.094 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.47 (d, *J* = 2.2 Hz, 1H), 7.15 (d, *J* = 8.7 Hz, 3H), 7.07 (d, *J* = 7.9 Hz, 2H), 6.52 (dd, *J* = 2.2, 0.9 Hz, 1H), 6.49 (d, *J* = 2.4 Hz, 1H), 6.35 (dd, *J* = 8.8, 2.4 Hz, 1H), 3.84 (dd, *J* = 7.2, 4.4 Hz, 1H), 3.44 (s, 1H), 2.48 – 2.42 (m, 1H), 2.39 – 2.29 (m, 3H), 2.20 (dd, *J* = 9.5, 7.0 Hz, 1H), 2.14 – 2.02 (m, 2H), 1.95 – 1.89 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.7, 149.0, 147.7, 145.3, 145.3, 143.8, 128.1, 127.4, 120.9, 120.6 (q, J_{C-F} = 256.5 Hz), 113.2, 111.6, 106.3, 103.9, 80.5, 59.0, 46.2, 43.8, 40.9, 34.9, 28.7, 28.2, 25.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{29}F_3NO_4$ 488.2049; Found 488.2031.
IR (neat): ν = 3390, 2975, 1716, 1474, 1253, 1206, 1157, 1102, 801 cm^{-1}.
R*f*: 0.34 (hexane/EtOAc 9:1 *v/v*, UV).

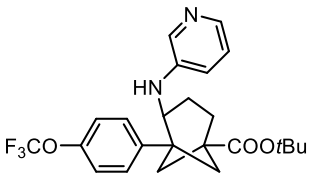
***tert*-Butyl 4-(Quinolin-7-ylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (17)**



$C_{28}H_{29}F_3N_2O_3$
MW: 498.21 g.mol^{-1}
Colorless oil
20% (20 mg, 0.04 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.66 (dd, *J* = 4.5, 1.7 Hz, 1H), 7.85 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 8.8 Hz, 1H), 7.14 (d, *J* = 8.6 Hz, 2H), 7.04 (dd, *J* = 8.0, 4.3 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.83 (s, 1H), 6.62 (dd, *J* = 8.8, 2.0 Hz, 1H), 4.10 – 4.05 (m, 1H), 3.95 (d, *J* = 7.1 Hz, 1H), 2.59 – 2.51 (m, 1H), 2.42 – 2.37 (m, 2H), 2.32 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.21 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.15 – 2.05 (m, 2H), 1.98 – 1.92 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): 174.5, 150.5, 150.2, 148.2, 147.7, 144.6, 135.6, 128.5, 127.3, 121.8, 120.9, 120.4 (q, $J_{C\text{-}F}$ = 255.0 Hz), 118.7, 117.4, 105.7, 80.6, 57.1, 46.0, 43.7, 41.5, 34.3, 28.7, 28.2, 25.5.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -58.0.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{28}H_{30}F_3N_2O_3$ 499.2209; Found 499.2211.
IR (neat): ν =3398, 2972, 1716, 1624, 1366, 1295, 1253, 1218, 1157, 1102, 826, 736 cm^{-1}.
R_f: 0.23 (hexane/EtOAc 3:2 *v/v*, UV).

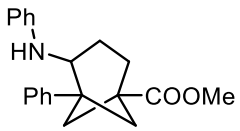
***tert*-Butyl 4-(Pyridin-3-ylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (18)**



$C_{24}H_{27}F_3N_2O_3$
MW: 448.19 g mol^{-1}
Colorless oil
15% (13 mg, 0.03 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 2.9 Hz, 1H), 7.77 (d, *J* = 4.7 Hz, 1H), 7.09 (d, *J* = 8.7 Hz, 2H), 7.04 (d, *J* = 8.3 Hz, 2H), 6.84 (dd, *J* = 8.4, 4.7 Hz, 1H), 6.48 – 6.44 (m, 1H), 3.86 (q, *J* = 7.2 Hz, 1H), 3.76 (s, 1H), 2.48 – 2.42 (m, 1H), 2.40 (d, *J* = 9.5, 1H), 2.32 (d, *J* = 5.0 Hz, 2H), 2.18 – 2.08 (m, 2H), 2.08 – 2.01 (m, 1H), 1.87 – 1.81 (m, 1H), 1.43 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.4, 147.8, 144.7, 143.6, 138.1, 136.1, 127.5, 123.5, 121.0, 120.5 (q, $J_{C\text{-}F}$ = 255.0 Hz), 119.7, 80.6, 57.5, 46.2, 43.6, 41.2, 34.2, 28.7, 28.1, 25.9.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{24}H_{28}F_3N_2O_3$ 449.2052; Found 449.2058.
IR (neat): ν = 2976, 1716, 1582, 1482, 1293, 1254, 1219, 1158, 1102, 708 cm^{-1}.
R_f: 0.20 (hexane/EtOAc 3:2 *v/v*, UV).

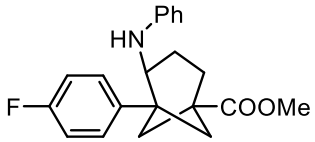
Methyl 5-Phenyl-4-(phenylamino)bicyclo[3.1.1]heptane-1-carboxylate (19)



$C_{21}H_{23}NO_2$
MW: 321.17 g mol^{-1}
Colorless oil
45% (29 mg, 0.09 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.25 (dd, *J* = 8.0, 7.2 Hz, 2H), 7.16 – 7.09 (m, 3H), 7.03 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.6 Hz, 2H), 3.85 (dd, *J* = 7.0, 4.1 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 1H), 2.51 – 2.45 (m, 2H), 2.43 (dd, *J* = 9.6, 1.6 Hz, 1H), 2.36 – 2.32 (m, 1H), 2.25 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.17 – 2.07 (m, 2H), 1.93 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.7, 147.7, 146.0, 129.1, 128.5, 126.5, 125.7, 117.3, 113.5, 57.5, 51.9, 46.7, 42.9, 41.0, 34.9, 28.7, 25.6.
HRMS (EI-TOF) m/z: [M] calcd for $C_{21}H_{23}NO_2$ 321.1729; Found 321.1736.
IR (neat): ν = 3402, 2949, 1727, 1601, 1501, 1312, 1213, 1102, 748, 699 cm^{-1}.
R_f: 0.34 (hexane/EtOAc 9:1 *v/v*, UV).

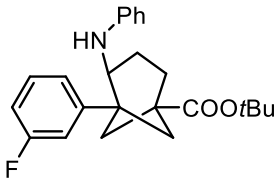
Methyl 5-(4-Fluorophenyl)-4-(phenylamino)bicyclo[3.1.1]heptane-1-carboxylate (20)



$C_{21}H_{22}FNO_2$
MW: 339.16 g mol^{-1}
Colorless oil
52% (35 mg, 0.104 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.09 – 7.05 (m, 2H), 7.03 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.92 (t, *J* = 8.7 Hz, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 2H), 3.84 (dd, *J* = 7.2, 4.5 Hz, 1H), 3.69 (s, 3H), 3.54 (s, 1H), 2.50 – 2.40 (m, 3H), 2.33 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.23 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.17 – 2.06 (m, 2H), 1.91 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.6, 161.5 (d, $J_{C\text{-}F}$ = 243.3 Hz), 147.6, 141.8 (d, $J_{C\text{-}F}$ = 3.2 Hz), 129.2, 127.4 (d, $J_{C\text{-}F}$ = 8.1 Hz), 117.4, 115.2 (d, $J_{C\text{-}F}$ = 21.2 Hz), 113.4, 57.6, 52.0, 46.2, 42.8, 41.1, 35.0, 28.6, 25.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -116.6.
HRMS (EI-TOF) m/z: [M] calcd for $C_{21}H_{22}FNO_2$ 339.1635; Found 339.1648.
IR (neat): ν = 3401, 2950, 1726, 1601, 1509, 1312, 1290, 1215, 1100, 829, 748 cm^{-1}.
R_f: 0.25 (hexane/EtOAc 9:1 *v/v*, UV).

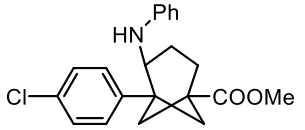
***tert*-Butyl 5-(3-Fluorophenyl)-4-(phenylamino)bicyclo[3.1.1]heptane-1-carboxylate (21)**



$C_{24}H_{28}FNO_2$
MW: 381.21 g mol^{-1}
Colorless oil
64% (49 mg, 0.128 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.23 – 7.17 (m, 1H), 7.06 – 7.02 (m, 2H), 6.91 – 6.88 (m, 1H), 6.86 – 6.80 (m, 2H), 6.62 – 6.58 (m, 1H), 6.40 – 6.37 (m, 2H), 3.90 – 3.82 (m, 1H), 3.59 (s, 1H), 2.49 – 2.41 (m, 1H), 2.36 (t, *J* = 10.1 Hz, 2H), 2.29 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.19 (dd, *J* = 9.5, 7.1 Hz, 1H), 2.13 – 2.04 (m, 2H), 1.92 – 1.87 (m, 1H), 1.45 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 163.0 (d, $J_{C\text{-}F}$ = 246.2 Hz), 149.1 (d, $J_{C\text{-}F}$ = 6.9 Hz), 147.6, 129.9 (d, $J_{C\text{-}F}$ = 8.2 Hz), 129.1, 121.5 (d, $J_{C\text{-}F}$ = 2.7 Hz), 117.4, 113.4, 113.3 (d, $J_{C\text{-}F}$ = 21.1 Hz), 113.0 (d, $J_{C\text{-}F}$ = 21.2 Hz), 80.5, 57.5, 46.3 (d, $J_{C\text{-}F}$ = 1.8 Hz), 43.7, 40.8, 34.8, 28.7, 28.2, 25.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -113.2.
HRMS (EI-TOF) m/z: [M] calcd for $C_{24}H_{28}FNO_2$ 381.2104; Found 381.2100.
IR (neat): ν = 3390, 2972, 1717, 1600, 1499, 1296, 1253, 1154, 1100, 745, 692 cm^{-1}.
R_f: 0.45 (hexane/EtOAc 9:1 *v/v*, UV).

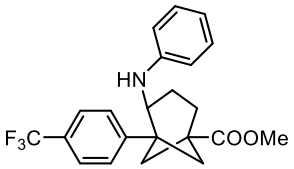
Methyl 5-(4-Chlorophenyl)-4-(phenylamino)bicyclo[3.1.1]heptane-1-carboxylate (22)



$C_{21}H_{22}ClNO_2$
MW: 355.13 g mol^{-1}
Colorless oil
53% (38 mg, 0.106 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.21 (d, *J* = 8.5 Hz, 2H), 7.08 – 6.99 (m, 4H), 6.61 (m, 1H), 6.41 – 6.35 (m, 2H), 3.85 (dd, *J* = 6.9, 4.2 Hz, 1H), 3.69 (s, 3H), 3.56 (s, 1H), 2.50 – 2.42 (m, 2H), 2.40 (dd, *J* = 9.6, 1.7 Hz, 1H), 2.32 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.23 (m, 1H), 2.17 – 2.06 (m, 2H), 1.93 – 1.88 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.5, 147.5 144.6, 132.3, 129.2, 128.6, 127.3, 117.6, 113.5, 57.45, 52.0, 46.4, 42.9, 41.0, 34.9, 28.6, 25.7.
HRMS (EI-TOF) m/z: [M] calcd for $C_{21}H_{22}ClNO_2$ 355.1339; Found 355.1342.
IR (neat): ν = 3388, 2949, 1724, 1600, 1495, 1433, 1313, 1290, 1213, 1090, 747, 692 cm^{-1}.
R_f: 0.25 (hexane/EtOAc 9:1 *v/v*, UV).

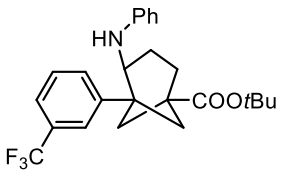
Methyl 4-(Phenylamino)-5-(4-(trifluoromethyl)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (23)



$C_{22}H_{22}F_3NO_2$
MW: 389.16 g mol^{-1}
Colorless oil
66% (51 mg, 0.132 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 – 7.47 (m, 2H), 7.24 – 7.21 (m, 2H), 7.06 – 6.99 (m, 2H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.38 – 6.30 (m, 2H), 3.92 (dd, *J* = 7.2, 4.5 Hz, 1H), 3.70 (s, 3H), 3.54 (s, 1H), 2.52 – 2.43 (m, 3H), 2.39 – 2.34 (m, 1H), 2.28 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.18 – 2.09 (m, 2H), 1.96 – 1.87 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.4, 150.1, 147.3, 129.2, 128.7 (q, J_{C-F} = 32.5 Hz), 126.3, 125.3 (q, J_{C-F} = 3.8 Hz), 124.3 (q, J_{C-F} = 272.0 Hz), 117.6, 113.5, 57.4, 52.0, 46.9, 42.9, 40.9, 34.9, 28.5, 25.7.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -62.4.
HRMS (EI-TOF) m/z: [M] calcd for $C_{22}H_{22}F_3NO_2$ 389.1603; Found 389.1629.
IR (neat): ν = 3400, 2952, 1727, 1325, 1121, 1066 cm^{-1}.
R_f: 0.18 (hexane/EtOAc 9:1 *v/v*, UV).

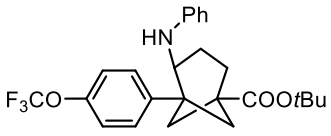
***tert*-Butyl 4-(Phenylamino)-5-(3-(trifluoromethyl)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (24)**



$C_{25}H_{28}F_3NO_2$
MW: 431.20 g.mol^{-1}
Colorless oil
32% (28 mg, 0.064 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38 – 7.33 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 7.9 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.57 – 6.54 (m, 1H), 6.32 (d, *J* = 7.5 Hz, 2H), 3.90 (dd, *J* = 7.2, 4.9 Hz, 1H), 3.54 (s, 1H), 2.49 – 2.41 (m, 1H), 2.41 – 2.30 (m, 3H), 2.22 (dd, *J* = 9.5, 6.5 Hz, 1H), 2.14 – 2.03 (m, 2H), 1.92 – 1.84 (m, 1H), 1.45 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.5, 147.3 (d, J_{C-F} = 3.9 Hz), 130.5 (q, J_{C-F} = 32.0 Hz), 129.4, 129.1, 128.7, 124.3 (q, J_{C-F} = 271.5 Hz),123.2 (q, J_{C-F} = 3.8 Hz), 122.8 (q, J_{C-F} = 3.8 Hz), 117.4, 113.4, 80.6, 57.4, 46.5, 43.8, 40.9, 34.5, 28.7, 28.2, 25.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -62.5.
HRMS (EI-TOF) m/z: [M] calcd for $C_{25}H_{28}F_3NO_2$ 431.2072; Found 431.2059.
IR (neat): ν = 3400, 2952, 1715, 1601, 1304, 1254, 1161, 1120, 1107, 745, 702 cm^{-1}.
R_f: 0.36 (hexane/EtOAc 9:1 *v/v*, UV).

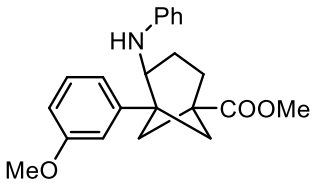
***tert*-Butyl 4-(Phenylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (25)**



$C_{25}H_{28}F_3NO_3$
MW: 447.20 g mol^{-1}
Colorless oil
43% (38 mg, 0.086 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.13 – 7.10 (m, 2H), 7.08 – 7.05 (m, 2H), 7.03 – 6.99 (m, 2H), 6.58 (t, *J* = 7.3 Hz, 1H), 6.33 (dd, *J* = 8.7, 1.1 Hz, 2H), 3.86 (dd, *J* = 7.2, 4.5 Hz, 1H), 3.55 (s, 1H), 2.48 – 2.41 (m, 1H), 2.37 – 2.33 (m, 2H), 2.29 (dd, *J* = 9.6, 7.1 Hz, 1H), 2.22 – 2.17 (m, 1H), 2.11 – 2.02 (m, 2H), 1.90 – 1.83 (m, 1H), 1.44 (s, 9H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.6, 147.7, 147.5, 145.1, 129.1, 127.4, 120.9, 120.6 (q, $J_{C\text{-}F}$ = 256.5 Hz), 117.4, 113.4, 80.5, 57.6, 46.1, 43.7, 40.6, 34.9, 28.7, 28.2, 25.8.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (EI-TOF) m/z: $[M]^+$ calcd for $C_{25}H_{28}F_3NO_3$ 447.2021; Found 447.2025.
IR (neat): ν = 3398, 2976, 1716, 1504, 1252, 1156, 1102, 745 cm^{-1}.
R_f: 0.4 (hexane/EtOAc 9:1 *v/v*, UV).

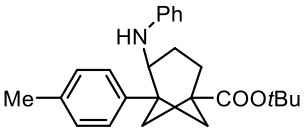
Methyl 5-(3-Methoxyphenyl)-4-(phenylamino)bicyclo[3.1.1]heptane-1-carboxylate (26)



$C_{22}H_{25}NO_3$
MW: 351.18 g mol^{-1}
Colorless oil
40% (28 mg, 0.08 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.18 (t, *J* = 7.9 Hz, 1H), 7.05 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.72 – 6.71 (m, 1H), 6.70 – 6.67 (m, 1H), 6.66 – 6.64 (m, 1H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 2H), 3.84 (dd, *J* = 7.2, 4.3 Hz, 1H), 3.74 (s, 3H), 3.68 (s, 3H), 2.51 – 2.44 (m, 2H), 2.42 (dd, *J* = 9.5, 1.7 Hz, 1H), 2.33 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.22 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.16 – 2.07 (m, 2H), 1.96 – 1.90 (m, 1H) NH not observed.
^{13}C NMR (151 MHz, $CDCl_3$): δ = 175.7, 159.8, 147.7, 129.6, 129.1, 118.1, 117.4, 115.2, 113.6, 112.0, 111.6, 57.6, 55.3, 52.0, 46.8, 42.8, 41.1, 34.9, 28.7, 25.6.
HRMS (EI-TOF) m/z: [M] calcd for $C_{22}H_{25}NO_3$ 351.1834; Found 351.1824.
IR (neat): ν = 3400, 2948, 1724, 1600, 1499, 1287, 1253, 1235, 1200, 1169, 746, 692 cm^{-1}.
R_f: 0.23 (hexane/EtOAc 9:1 *v/v*, UV).

***tert*-Butyl 4-(Phenylamino)-5-(p-tolyl)bicyclo[3.1.1]heptane-1-carboxylate (27)**



$C_{25}H_{31}NO_2$
MW: 377.23 g mol^{-1}
Colorless oil
35% (26 mg, 0.07 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.10 – 6.99 (m, 6H), 6.60 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 2H), 3.81 (dd, *J* = 7.2, 4.0 Hz, 1H), 3.61 (s, 1H), 2.49 – 2.42 (m, 1H), 2.40 (d, *J* = 9.6 Hz, 1H), 2.34 – 2.31 (m, 1H), 2.29 – 2.26 (m, 1H), 2.28 (s, 3H), 2.20 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.08 (m, 2H), 1.92 (m, 1H), 1.44 (s, 9H).

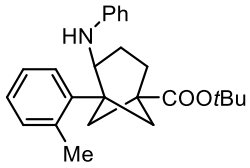
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.9, 147.9, 143.3, 135.9, 129.2, 129.1, 125.6, 117.2, 113.5, 80.3, 57.6, 46.0, 43.8, 40.9, 35.0, 28.9, 28.2, 25.5, 21.1.

HRMS (EI-TOF) m/z: [M] calcd for $C_{25}H_{31}NO_2$ 377.2355; Found 377.2359.

IR (neat): ν = 3380, 2973, 1718, 1600, 1500, 1366, 1341, 1295, 1162, 1140, 1100, 810, 744, 691 cm^{-1}.

R_f: 0.47 (hexane/EtOAc 9:1 *v/v*, UV).

***tert*-Butyl 4-(Phenylamino)-5-(o-tolyl)bicyclo[3.1.1]heptane-1-carboxylate (28)**



$C_{25}H_{31}NO_2$
MW: 377.23 g mol^{-1}
Colorless oil
38% (28 mg, 0.076 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.14 – 7.10 (m, 1H), 7.05 (td, *J* = 7.4, 1.4 Hz, 1H), 7.02 – 6.98 (m, 4H), 6.57 (t, *J* = 7.3 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 2H), 4.01 – 3.93 (m, 1H), 3.55 (s, 1H), 2.49 (dd, *J* = 9.5, 1.9 Hz, 1H), 2.48 – 2.42 (m, 2H), 2.40 (dt, *J* = 9.5, 1.3 Hz, 1H), 2.34 (dd, *J* = 9.5, 7.2 Hz, 1H), 2.29 (s, 3H), 2.13 – 2.08 (m, 1H), 2.06 – 2.01 (m, 1H), 1.94 – 1.87 (m, 1H), 1.44 (s, 9H).

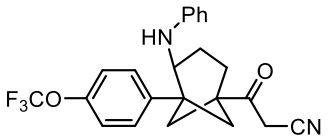
^{13}C NMR (151 MHz, $CDCl_3$): δ = 174.9, 147.9, 143.4, 135.7, 131.4, 129.1, 127.4, 126.8, 125.8, 117.2, 113.4, 80.3, 55.6, 47.5, 43.6, 41.8, 36.2, 28.8, 28.2, 25.9, 20.6.

HRMS (EI-TOF) m/z: [M] calcd for $C_{25}H_{31}NO_2$ 377.2355; Found 377.2346.

IR (neat): ν = 3398, 2973, 1717, 1600, 1499, 1252, 1095, 744, 691 cm^{-1}.

R_f: 0.45 (hexane/EtOAc 9:1 *v/v*, UV).

3-Oxo-3-(4-(Phenylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptan-1-yl)propanenitrile (29)



$C_{23}H_{21}F_3N_2O_2$
MW: 414.16 g mol^{-1}
Colorless oil
73% (30 mg, 0.073 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.13 – 7.09 (m, 2H), 7.07 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.62 – 6.59 (m, 1H), 6.33 (d, *J* = 7.6 Hz, 2H), 3.92 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.52 (s, 1H), 3.51 (s, 2H), 2.56 – 2.50 (m, 1H), 2.44 (dd, *J* = 9.6, 6.9 Hz, 1H), 2.37 (td, *J* = 9.5, 2.0 Hz, 2H), 2.32 (dd, *J* = 9.6, 6.9 Hz, 1H), 2.17 – 2.12 (m, 1H), 2.10 – 2.05 (m, 1H), 2.00 – 1.95 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ = 199.1, 148.0, 147.1, 143.9, 129.2, 127.2, 121.1, 120.5(q, J_{C-F} = 258.2 Hz), 117.9, 113.6, 113.5, 57.4, 49.8, 45.9, 40.4, 34.5, 28.4, 27.8, 25.6.

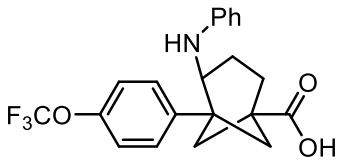
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.

HRMS (EI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{22}F_3N_2O_2$ 415.1633; Found 415.1666.

IR (neat): ν = 3393, 2948, 2190, 1601, 1257, 1223, 1163, 750 cm^{-1}.

R_f: 0.45 (hexane/EtOAc 3:2 *v/v*, UV).

4-(Phenylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylic acid (30)



$C_{21}H_{20}F_3NO_3$
MW: 391.14 gmol^{-1}
white solid
90% (176 mg, 0.45 mmol)
Melting point: 155-156 ℃

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.8 Hz, 2H), 7.07 (d, *J* = 8.3 Hz, 2H), 7.02 (dd, *J* = 8.6, 7.3 Hz, 2H), 6.61 (t, *J* = 7.2 Hz, 1H), 6.36 (d, *J* = 7.6 Hz, 2H), 3.89 (dd, *J* = 7.2, 4.6 Hz, 1H), 2.50 – 2.44 (m, 3H), 2.41 – 2.36 (m, 1H), 2.25 (dd, *J* = 9.6, 7.2 Hz, 1H), 2.20 – 2.09 (m, 2H), 1.97 – 1.89 (m, 1H). COOH and NH H missing

^{13}C NMR (151 MHz, $CDCl_3$): δ = 180.8, 147.8, 147.1, 144.5, 129.2, 127.3, 121.0, 120.6(q, J_{C-F} = 256.7 Hz), 117.9, 113.7, 57.7, 46.5, 42.6, 41.0, 34.8, 28.2, 25.6.

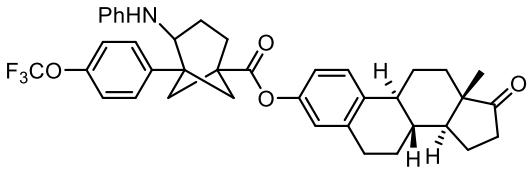
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}F_3NO_3$ 392.1474; Found 392.1468.

IR (neat): ν = 3393, 2950, 2871, 1698, 1601, 1505, 1306, 1254, 1161, 748, 692 cm^{-1}.

R_f: 0.54 (hexane/EtOAc 1:4 *v/v*, UV).

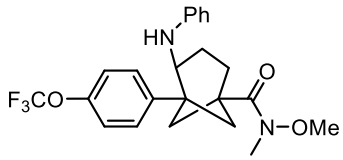
(8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl4-(phenylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxylate (31)



$C_{39}H_{40}F_3NO_4$
MW: 643.29 g mol^{-1}
Colorless oil
80% (51 mg, 0.080 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 8.6 Hz, 1H), 7.16 (d, *J* = 8.7 Hz, 2H), 7.09 (d, *J* = 7.7 Hz, 2H), 7.03 (dd, *J* = 8.6, 7.2 Hz, 2H), 6.83 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.79 (d, *J* = 2.5 Hz, 1H), 6.62 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 2H), 3.94 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.67 (s, 1H), 2.90 (dd, *J* = 7.7, 3.3 Hz, 2H), 2.61 – 2.57 (m, 2H), 2.56 – 2.46 (m, 3H), 2.43 – 2.34 (m, 2H), 2.33 – 2.22 (m, 3H), 2.15 (dt, *J* = 19.0, 9.0 Hz, 1H), 2.09 – 2.05 (m, 1H), 2.03 – 1.95 (m, 3H), 1.63 – 1.56 (m, 3H), 1.54 – 1.47 (m, 3H), 0.91 (s, 3H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 173.7, 148.7, 147.8, 144.6, 138.2, 137.6, 129.2, 127.4, 126.6, 121.5, 120.5(q, J_{C-F} = 256.7 Hz), 121.0, 118.7, 117.9, 113.7, 113.0, 57.7, 50.6, 48.1, 46.5, 44.3, 43.1, 41.1, 38.1, 36.0, 35.0, 31.7, 29.5, 28.6, 26.5, 25.9, 25.7, 21.7, 14.0.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (EI-TOF) m/z: $[M+H]^+$ calcd for $C_{39}H_{41}F_3NO_4$ 644.2988; Found 644.2980.
IR (neat): ν = 3400, 2929, 2868, 1735, 1601, 1494, 1221, 1203, 1178, 1163, 1075, 909, 731 cm^{-1}.
R*f*: 0.58 (hexane/EtOAc 3:2 *v/v*, UV).

***N*-Methoxy-*N*-methyl-4-(phenylamino)-5-(4-(trifluoromethoxy)phenyl)bicyclo[3.1.1]heptane-1-carboxamide (32)**



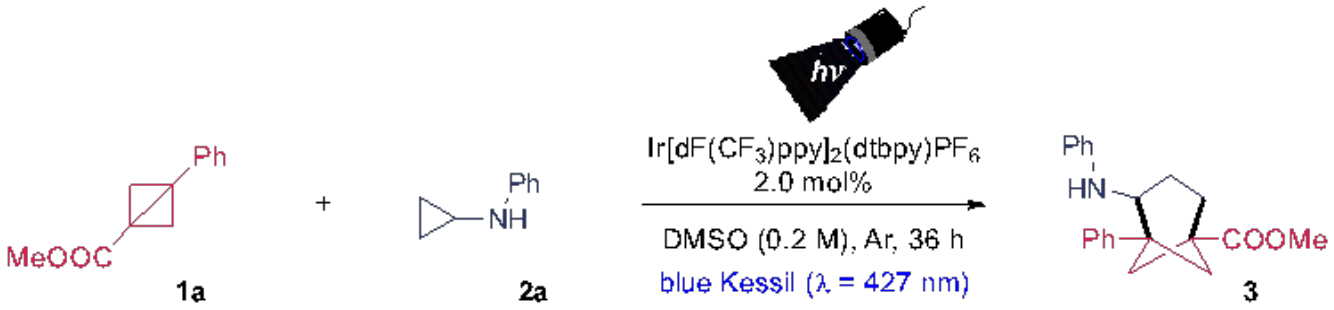
$C_{23}H_{25}F_3N_2O_3$
MW: 434.18 g mol^{-1}
Colorless oil
85% (37 mg, 0.085 mmol)

^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.16 – 7.11 (m, 2H), 7.08 – 7.04 (m, 2H), 7.04 – 7.00 (m, 2H), 6.59 (t, *J* = 7.3 Hz, 1H), 6.38 – 6.34 (m, 2H), 3.89 (dd, *J* = 7.2, 4.6 Hz, 1H), 3.71 (s, 3H), 3.58 (s, 1H), 3.17 (s, 3H), 2.52 – 2.41 (m, 2H), 2.38 – 2.31 (m, 3H), 2.15 – 2.10 (m, 1H), 2.09 – 2.03 (m, 1H), 1.95 – 1.90 (m, 1H).
^{13}C NMR (151 MHz, $CDCl_3$): δ = 176.9, 147.7, 147.4, 145.0, 129.2, 127.4, 120.9, 120.6 (q, J_{C-F} = 256.7 Hz), 117.5, 113.5, 61.2, 57.6, 45.7, 44.3, 41.6, 35.3, 32.8, 29.0, 25.6.
^{19}F NMR (565 MHz, $CDCl_3$) δ= -57.9.
HRMS (EI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{26}F_3N_2O_3$ 435.1896; Found 435.1896.
IR (neat): ν = 3390, 2943, 1639, 1601, 1507, 1312, 1254, 1221, 1161, 747 cm^{-1}.
R*f*: 0.30 (hexane/EtOAc 3:2 *v/v*, UV).

4. Mechanistic Investigations

4.1. Photochemical Quantum Yield (Φ)

The quantum yield of the reaction was determined using the procedure reported previously:[3] Methyl 3-phenylbicyclo[1.1.0]butane-1-carboxylate **1a** and *N*-cyclopropylaniline **2a** were used as model substrates in the presence of $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ as a photocatalyst to determine the quantum yield of this transformation.



The quantum yield of the reaction is defined as:

$$\Phi = \frac{\text{mol of formed product}}{\text{mol of photon flux} \cdot t \cdot f} \qquad (1)$$

where Φ is the quantum yield of the reaction, t is the time of the reaction (s), and f is the incident light absorbed by all the reaction components at 438 nm. The photon flux is calculated by standard ferrioxalate actinometry[4] (see Section *B.3*).

B.1. Incident light absorbed by the reaction mixture

The fraction of light, f, absorbed was determined according to equation 2:

$$F = 1 - 10^{-A} \qquad (2)$$

Where A is the absorbance of the reaction mixture at 438 nm. The wavelength of 438 nm was chosen based on the known absolute $\Phi(Fe^{+2})$[4] value and its proximity to our wavelength irradiation. The absorbance of the reaction mixture was measured (0.2 M **1a**, 0.4 M **2a**, and 4 mM $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$) in DMSO (0.5 mL) in a cuvette equipped with a Teflon-coated magnetic stir bar and stirred for 30 sec. The absorbance was recorded. The absorbance (A) at 438 nm was determined to be >4 (*Figure S1*), thus indicating the fraction of light absorbed is ~1 according to equation 2.

[3] El Khatib, M.; Serafim, R. A. M.; Molander, G. A. *Angew. Chem. Int. Ed.*, **2016**, *55*, 254.

[4] Demas, J. N.; Bowman, W. D.; Zalewski, E. F.; Velapoidl, R. *J. Phys. Chem.*, **1981**, *85*, 2766.

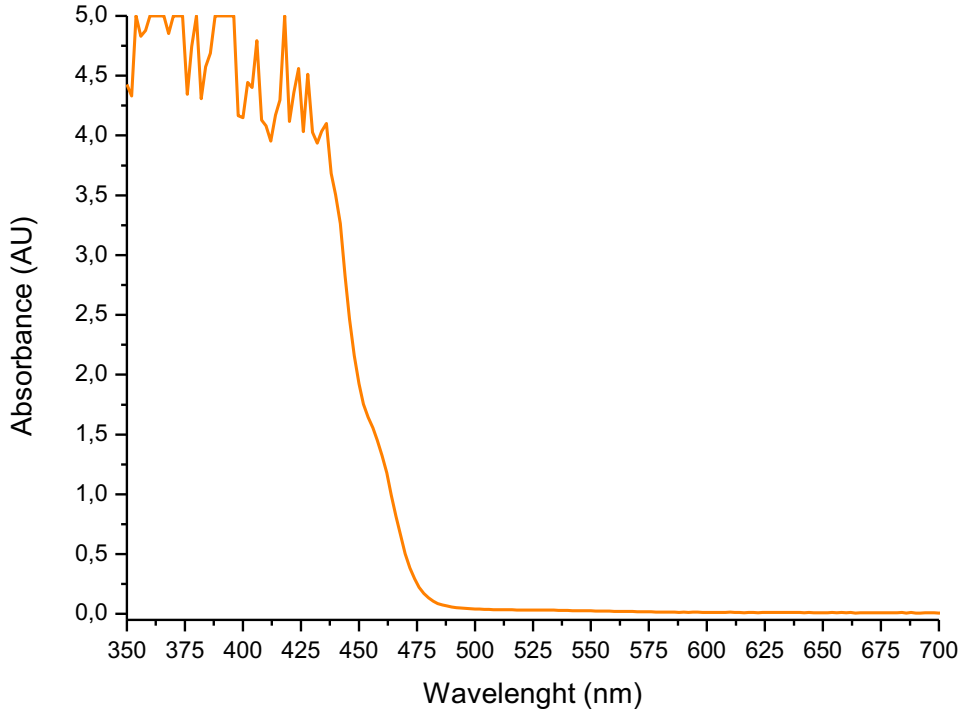


Figure S1. Absorption spectra for reaction mixture in DMSO (0.2 M **1a**, 0.4 M **2a**, and 4 mM $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$).

B.2. The photoredox reaction

The photoredox transformation was developed using the general procedure for 300 min (18000 s). Afterward, 1,3,5-trimethoxybenzene was added as internal standard, and the reaction was worked up. The yield of the reaction was determined by ^1H NMR, where 0.019 mmols (19%, see *Figure S2*) of the desired compound were obtained.

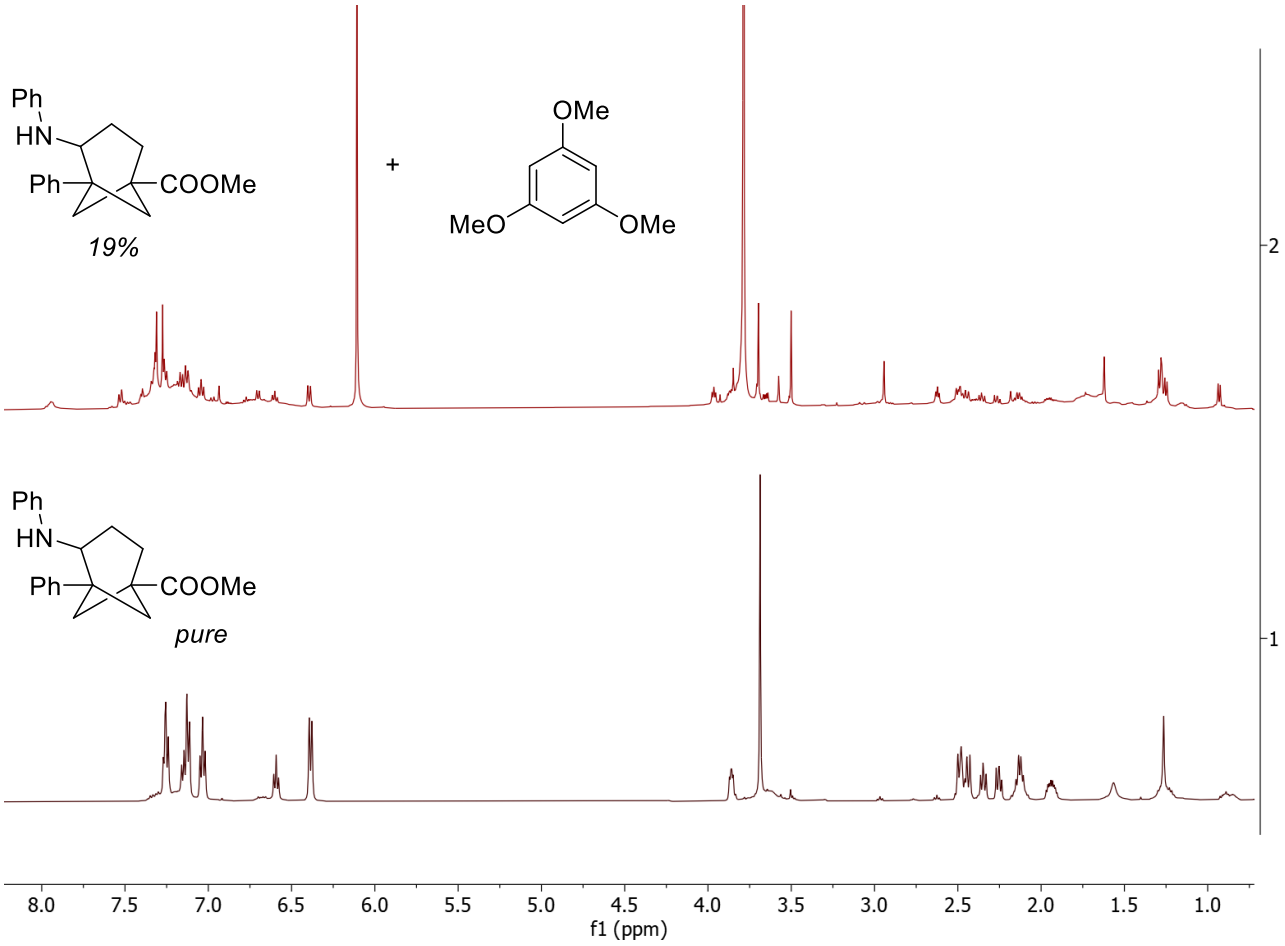


Figure S2. ^{1}H NMR (500 MHz, $CDCl_3$) of the standard reaction after 5 h in presence of 1,3,5-trimethoxybenzene and ^{1}H NMR (500 MHz, $CDCl_3$) of the product **19**.

B.3. Photon flux at 438 nm

Standard ferrioxalate actinometry was used to determine the photon flux of the spectrophotometer using equations 3 and 4. For the ferrioxalate actinometer, the production of iron(II) ions proceeds by the following reactions:[3]

$$[Fe(C_2O_4)n]^{+(3-2n)} \xrightarrow{\text{light}} Fe^{+2} + (n-1)(C_2O_4)^{-2} + C_2O_4^{-}$$

$$[Fe(C_2O_4)n]^{+(3-2n)} + C_2O_4^{-} \longrightarrow Fe^{+2} + n(C_2O_4)^{-2} + 2\,CO_2$$

The moles of Fe^{+2} formed are determined spectrophotometrically by development with 1,10-phenanthroline (phen) to form the red $[Fe(phen)_3]^{+2}$ moiety (λ = 510 nm).[4] The photon flux is defined as shown in equation 3:

$$\text{Photon flux} = \frac{\text{mol } Fe^{+2}}{\Phi(Fe^{+2}) \cdot t \cdot f} \qquad (3)$$

where Φ is the quantum yield for the ferrioxalate actinometer (1.01 at λ = 438 nm),[4] t is the time (s), f ~1, and the mol of Fe^{+2} are calculated according to equation 4.

$$\text{mol}\,(Fe^{+2}) = \frac{V \cdot \Delta A}{l \cdot \epsilon} \qquad (4)$$

where V is the total volume of the solution, ΔA is the difference in absorbance between irradiated and nonirradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11110 L mol^{-1} cm^{-1}).[4]

B.4. Experimental

The following solutions were prepared in the dark (flasks were wrapped in aluminum foil) and stored in the dark at room temperature:

– Ferrioxalate solution (0.15 M): Potassium ferrioxalate hydrate (1.312 g) was added to a flask wrapped in aluminum foil containing H_2SO_4 (20 mL, 0.05 M). The flask was stirred for complete solvation of the green solid in complete darkness. It is noteworthy that the solution should not be exposed to any incident light.

– Developer solution: 1,10-Phenanthroline (50 mg) and NaOAc (11.25 g) was added to a flask containing H_2SO_4 (50 mL, 0.5 M) and sonicated until completely solvated.

The absorbance of the non-irradiated sample. The buffered solution of phen (350 μL) was added to a ferrioxalate solution (2.0 mL) in a vial that had been covered with aluminum foil and with the lights of the laboratory switched off. The vial was capped and allowed to rest for 1 h and then transferred to a cuvette. The absorbance of the non-irradiated solution was measured at 510 nm to be 0.20 (average of two determinations, see *Figure S3*).

The absorbance of the irradiated sample. In a cuvette equipped with a stir bar was added the ferrioxalate solution (2.0 mL), and the stirred solution was irradiated for 90 s at λ = 427 nm. After irradiation, the buffered phen solution (350 μL) was added to the cuvette and allowed to rest for 1 h in the dark to allow the ferrous ions to coordinate completely to phen. The absorbance was measured at 510 nm to be 1.16 (average of two determinations, *Figure S3*).

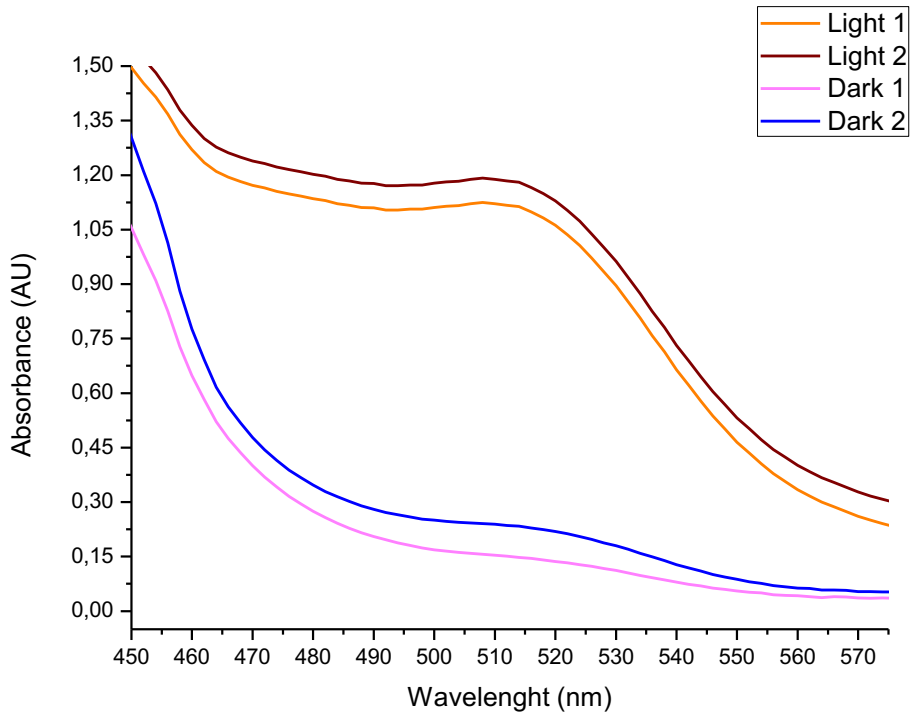


Figure S3. Absorption spectra for irradiated and non-irradiated samples of red $[Fe(phen)_3]^{+2}$

Photon flux sample calculation. Sample calculation:

$$\text{mol } (Fe^{+2}) = \frac{V \cdot \Delta A}{l \cdot \epsilon} \qquad (4)$$

$$\text{mol } (Fe^{+2}) = \frac{0.00235 \text{ L} \cdot 0.96}{1.0 \text{ cm} \cdot 11100 \text{ L} \cdot \text{mol}^{-1}\text{cm}^{-1}} = 2.03\text{x}10^{-7}\text{mol}$$

$$\text{Photon flux} = \frac{\text{mol } Fe^{+2}}{\Phi(Fe^{+2}) \cdot t \cdot f} \qquad (3)$$

$$\text{Photon flux} = \frac{2.03\text{x}10^{-7}\text{mol}}{1.01 \cdot 90 \text{ s} \cdot 1} = 2.24\text{x}10^{-9} \text{ einstein s}^{-1}$$

B.5. Quantum yield of the photoinduced transformation

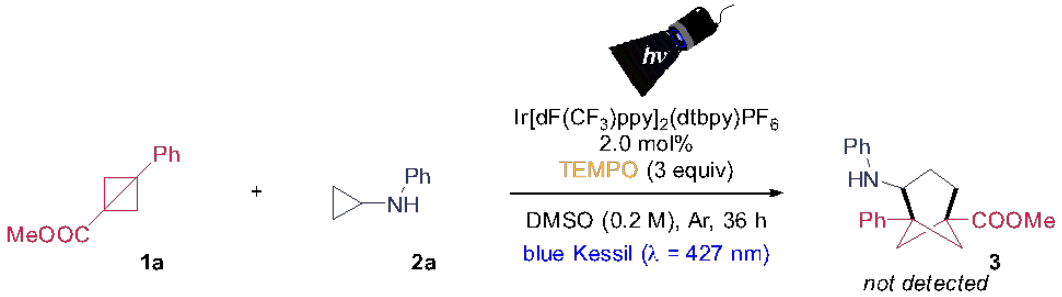
Therefore, the quantum yield of the reaction was determined to be:

$$\Phi = \text{ mol of formed} \frac{\text{product}}{\text{mol of photon flux} \cdot t \cdot f} \qquad (1)$$

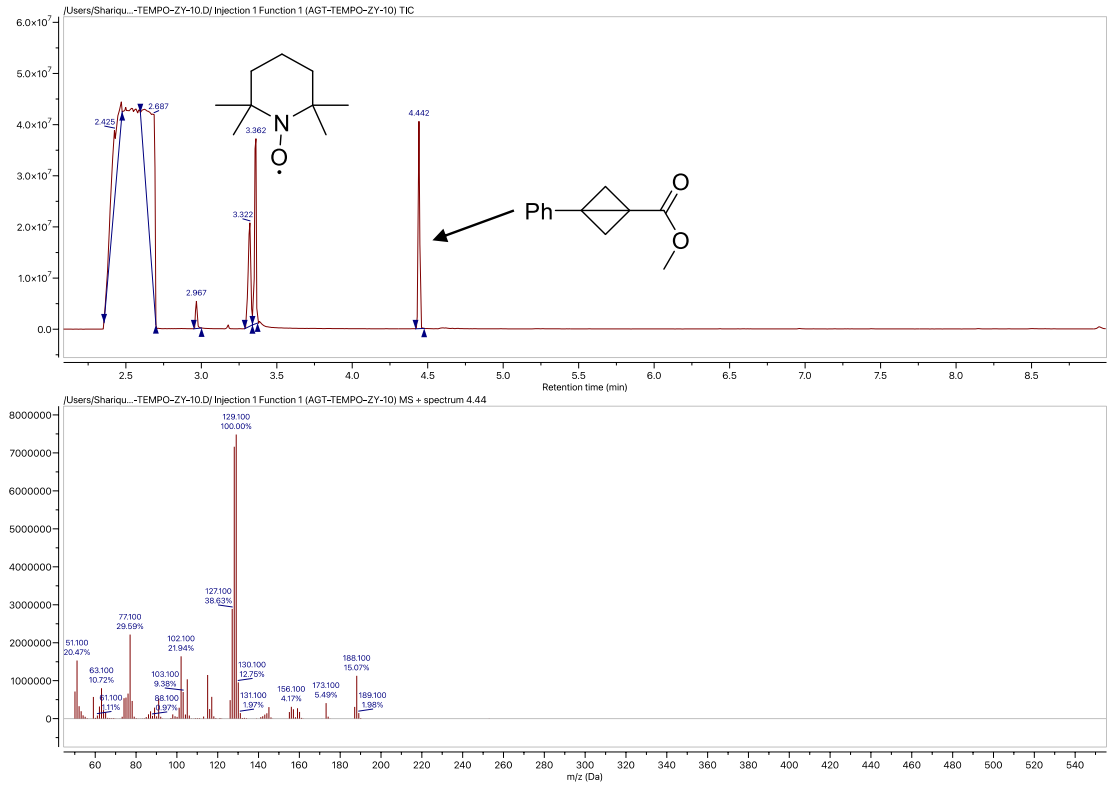
$$\boldsymbol{\Phi} = \frac{1.9\text{x}10^{-5} \text{ mol}}{2.24\text{x}10^{-9} \text{ einstein s}^{-1} \cdot 18000 \text{ s} \cdot 1} = \mathbf{0.47}$$

The photochemical quantum yield study indicates that the mechanism is more likely proceeding through a closed catalytic cycle.

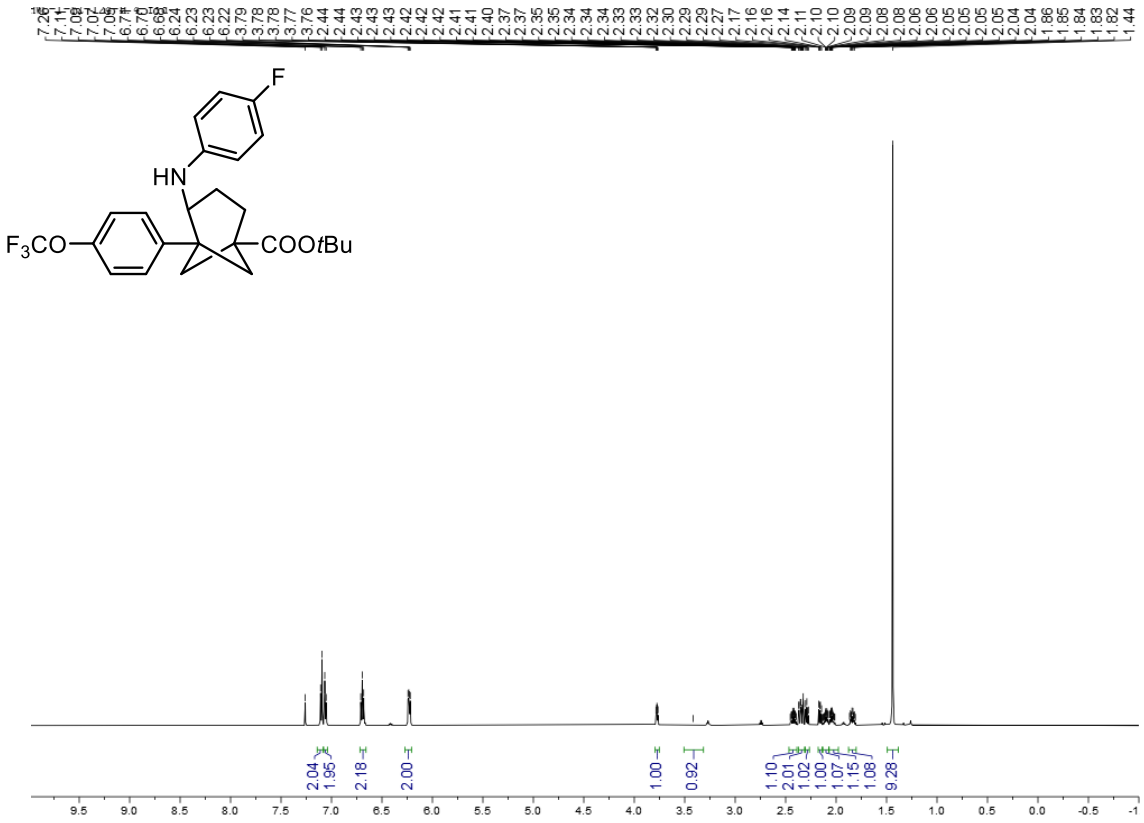
4.2. TEMPO Experiment



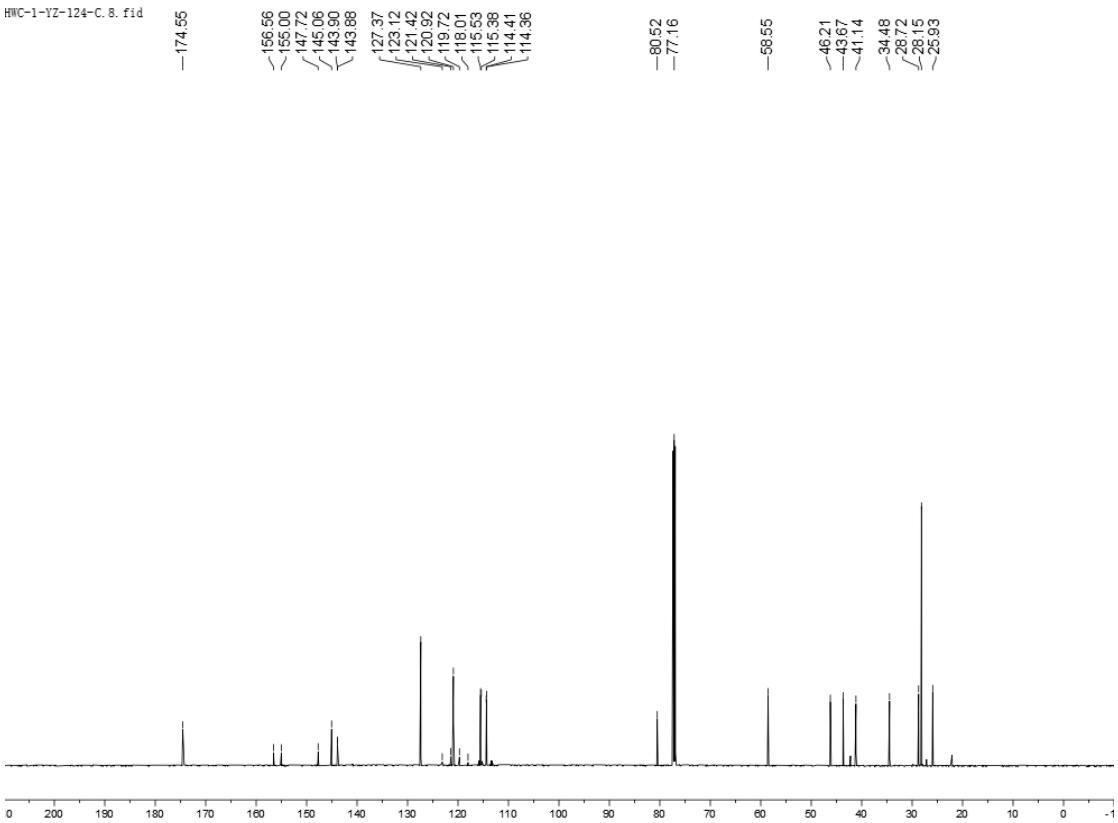
To a flame-dried 4 mL vial equipped with a magnetic stir bar, bicyclobutane **1a** (18.8 mg, 0.1 mmol, 1.0 equiv), aniline **2a** (26.6 mg, 0.2 mmol, 2 equiv), TEMPO (46.8 mg, 0.3 mmol, 3 equiv), and $Ir[dF(CF_3)ppy]_2(dtbpy)PF_6$ (2.2 mg, 2 mol %) were added, and the vial was subjected to 3 cycles of vacuum/argon degassing. Subsequently, 0.5 mL of dry DMSO were added under inert atmosphere. The reaction mixture was irradiated with Kessil PR160L-blue LED lamp (30 W High Luminous DEX 2100 LED, λ_{max} = 427 nm) for 36 h. The temperature of the reaction was maintained at approximately 25 °C via a fan. Then, the reaction mixture was quenched with H_2O (5 mL) and poured into a separatory funnel containing 10 mL of EtOAc. The organic phase was washed with brine (3x5 mL). The organics were dried (anhyd Na_2SO_4) and removed under high vacuum. The crude analysis by GCMS did not show the formation of product **3**, thus the presence of TEMPO totally inhibits the product formation.



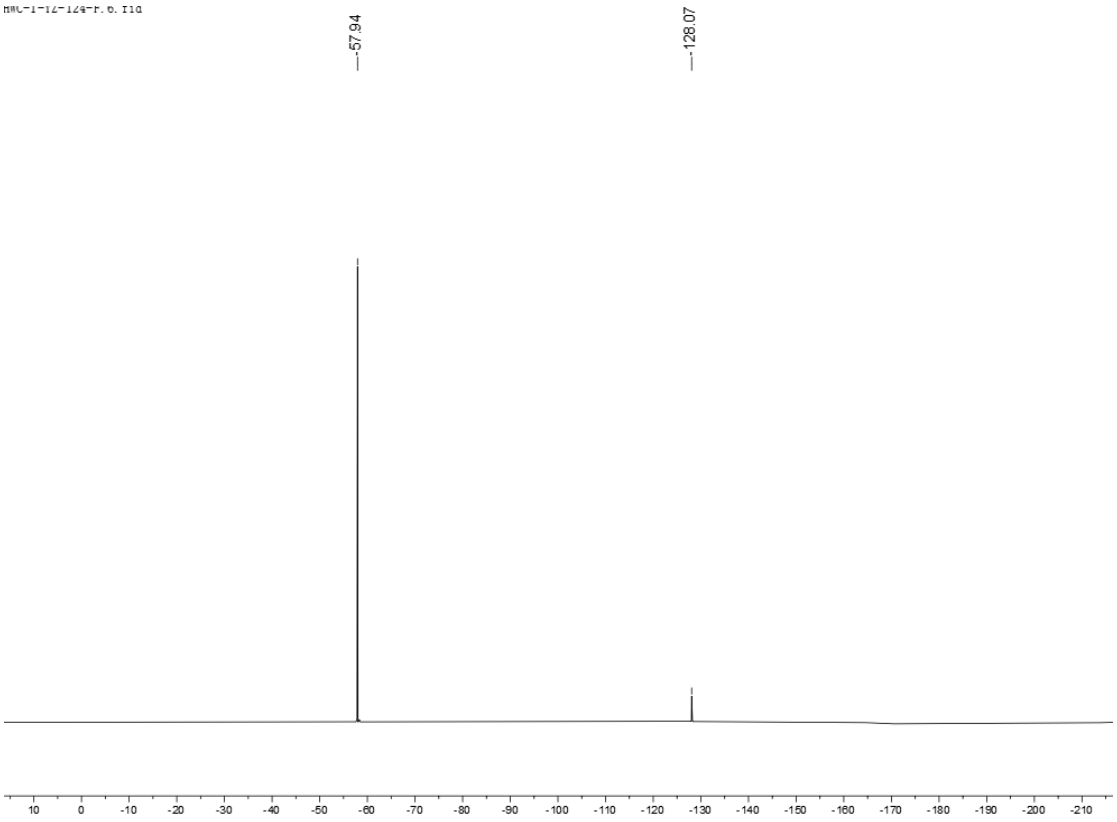
5. NMR Data



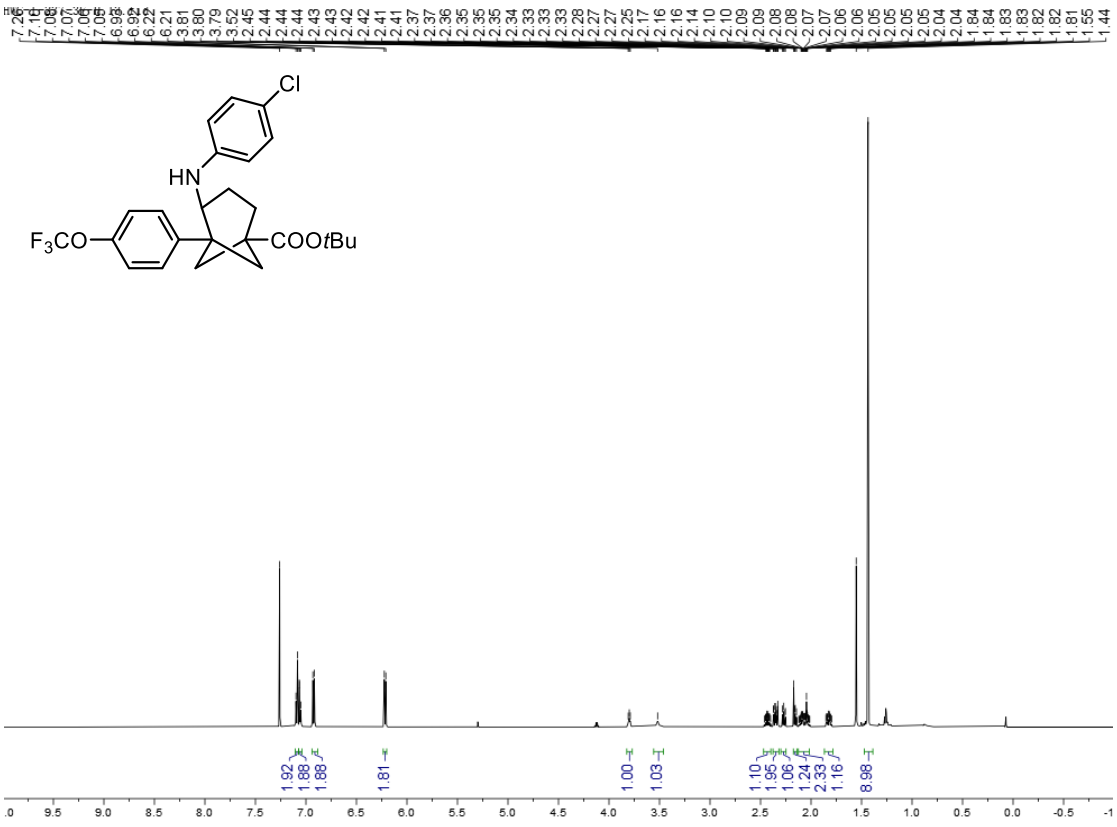
^{1}H NMR (600 MHz, $CDCl_3$) of 3



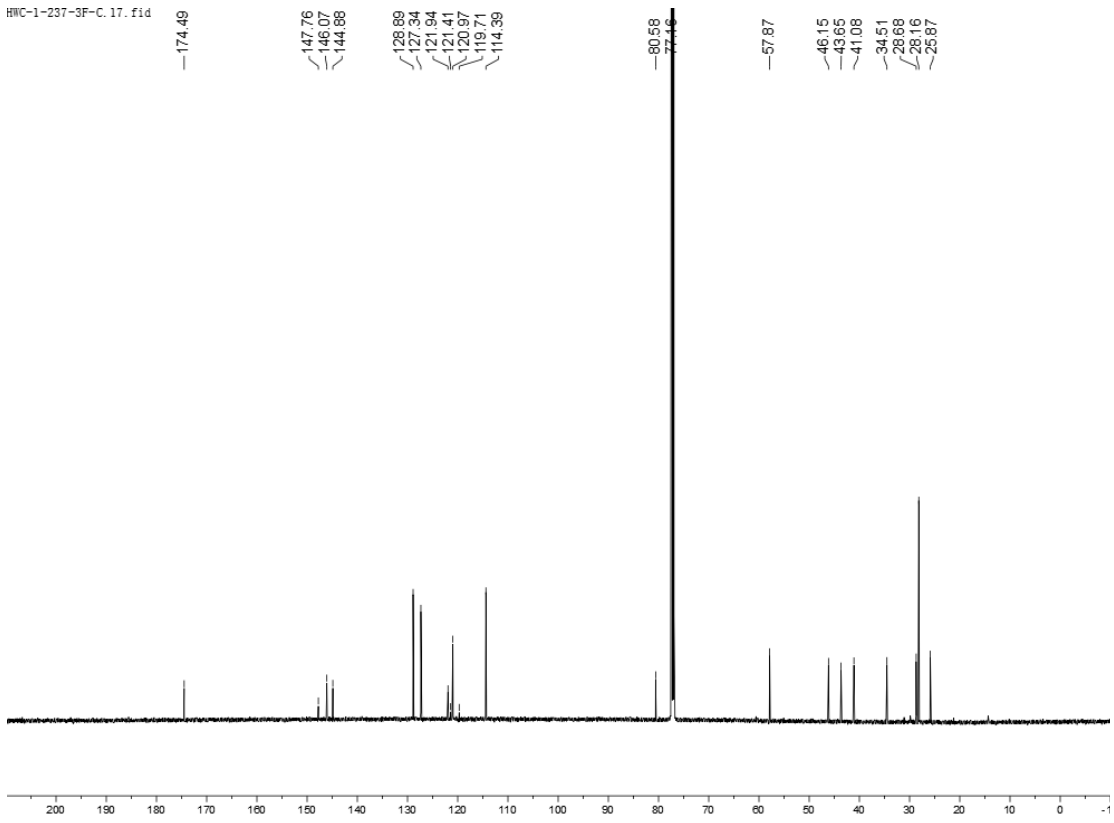
^{13}C NMR (151 MHz, $CDCl_3$) of 3



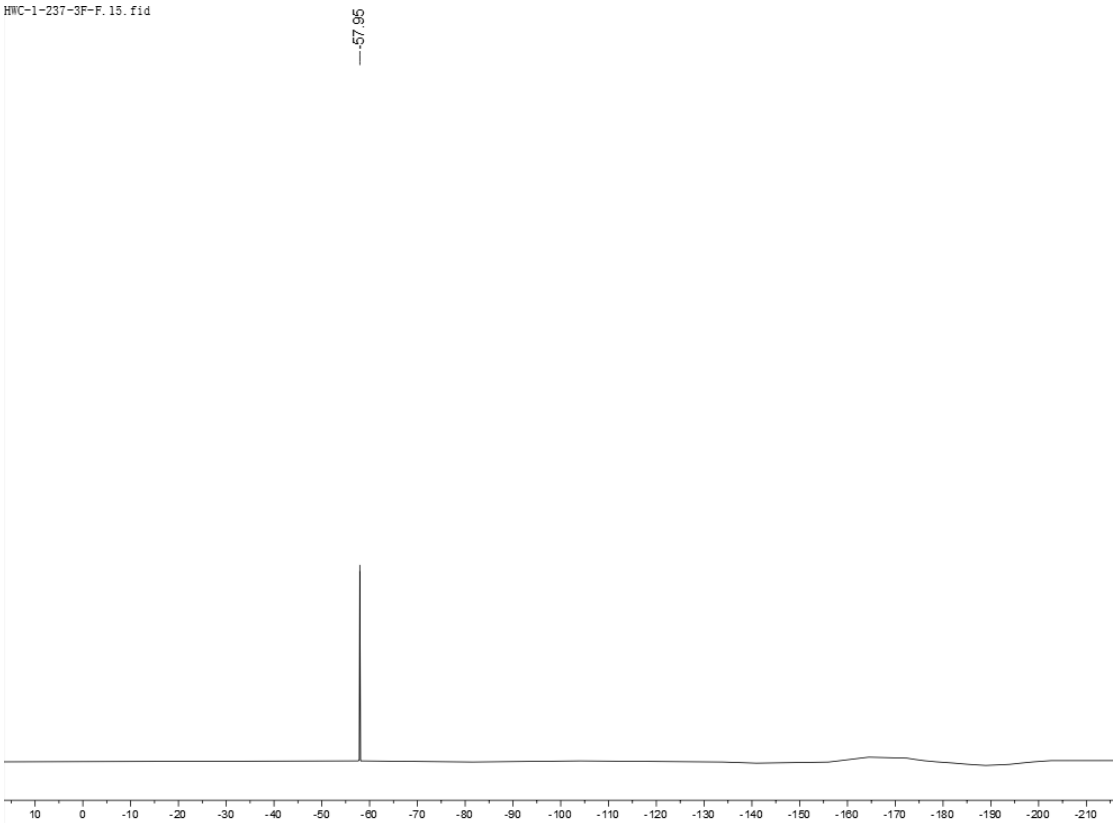
^{19}F NMR (565 MHz, $CDCl_3$) of 3



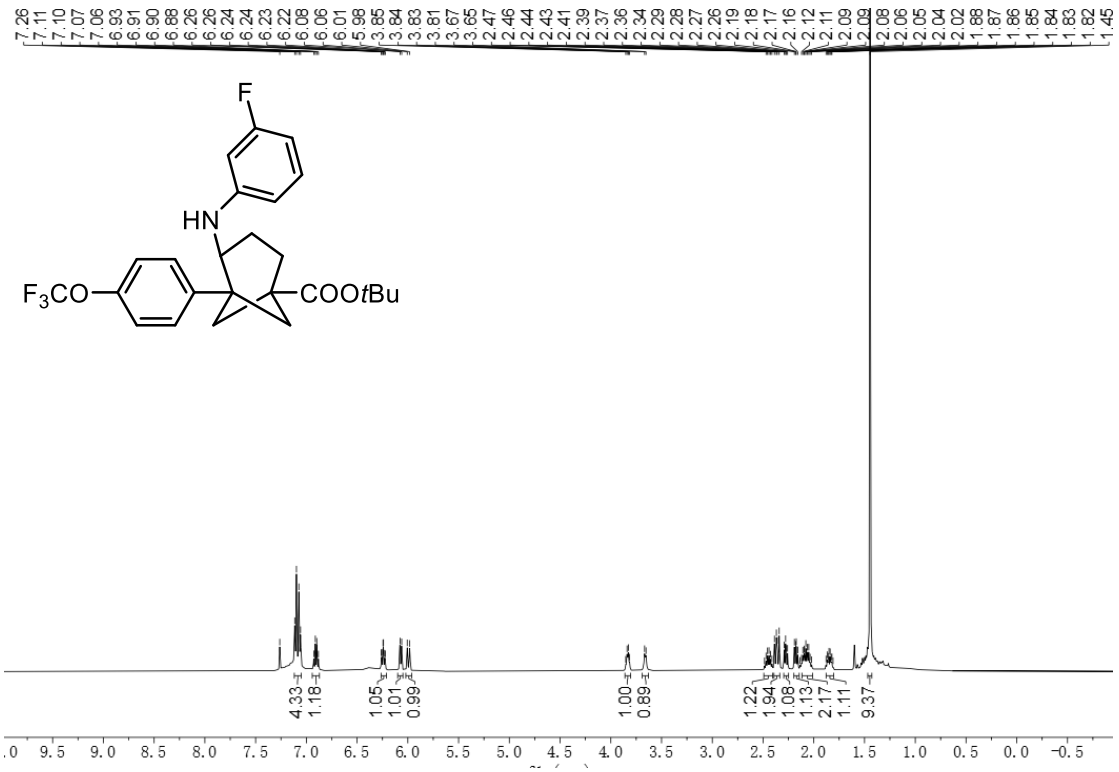
^{1}H NMR (600 MHz, $CDCl_3$) of 4



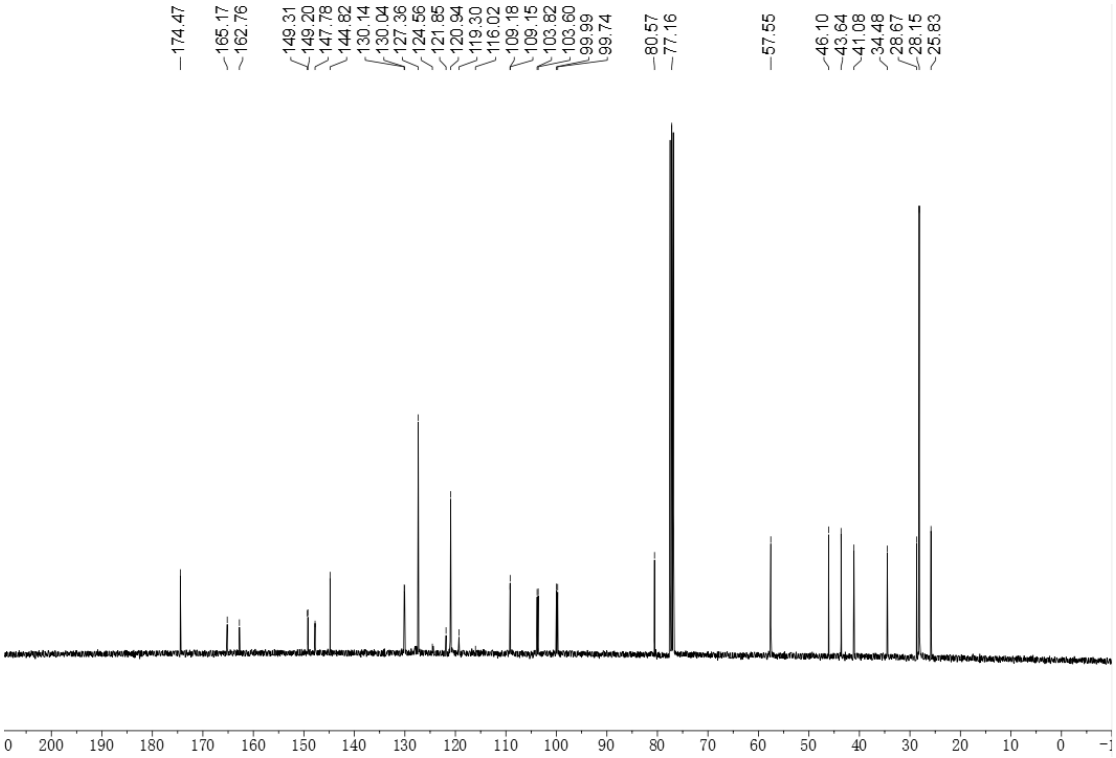
^{13}C NMR (151 MHz, $CDCl_3$) of 4



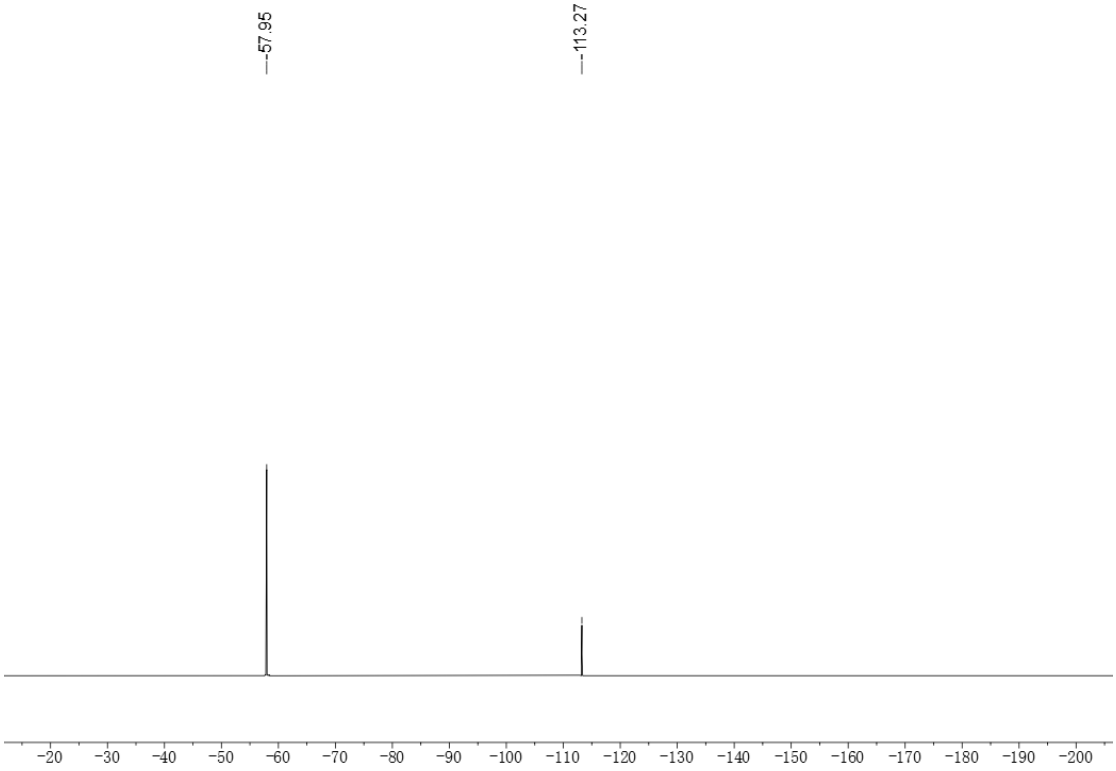
^{19}F NMR (565 MHz, $CDCl_3$) of 4



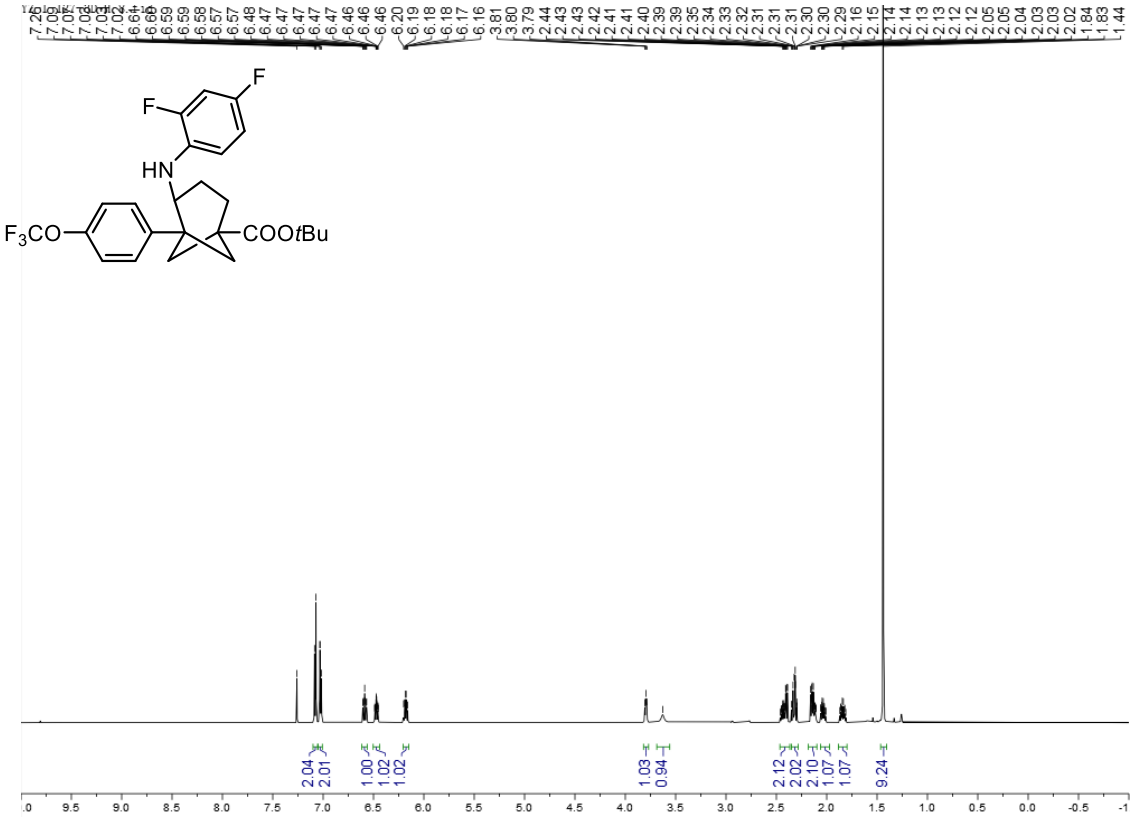
^{1}H NMR (500 MHz, $CDCl_3$) of 5



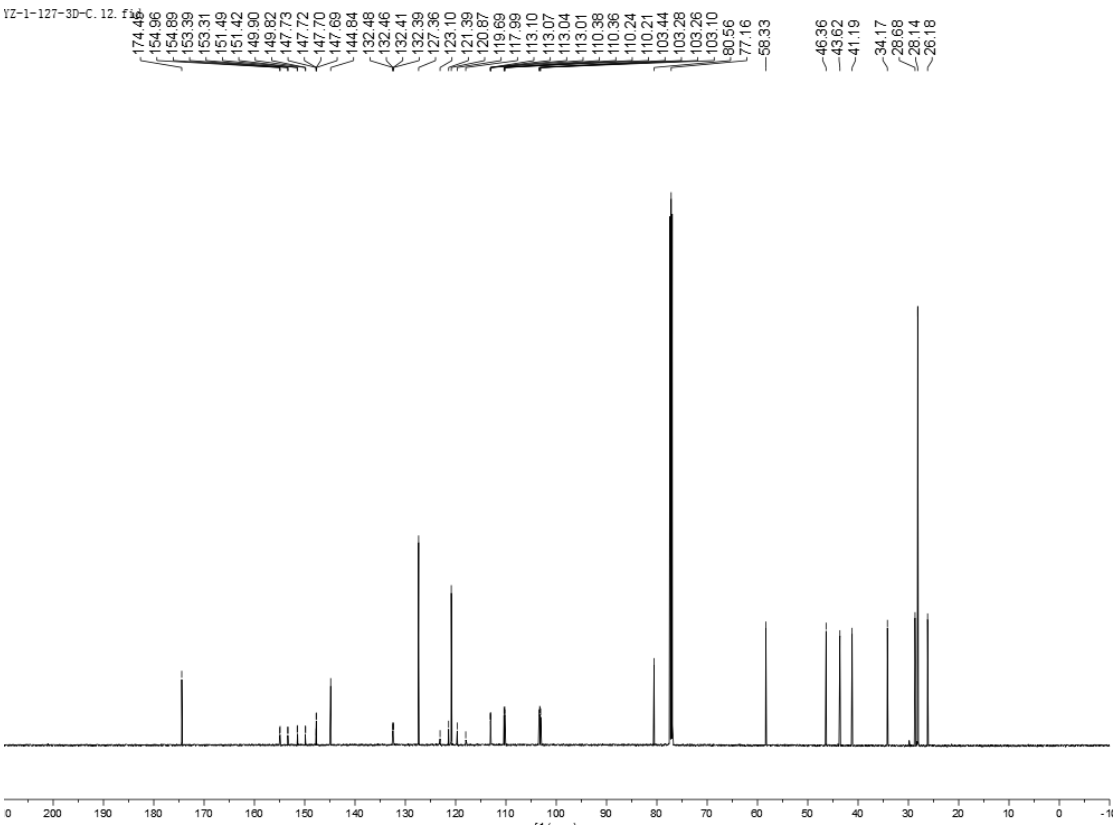
^{13}C NMR (101 MHz, $CDCl_3$) of 5



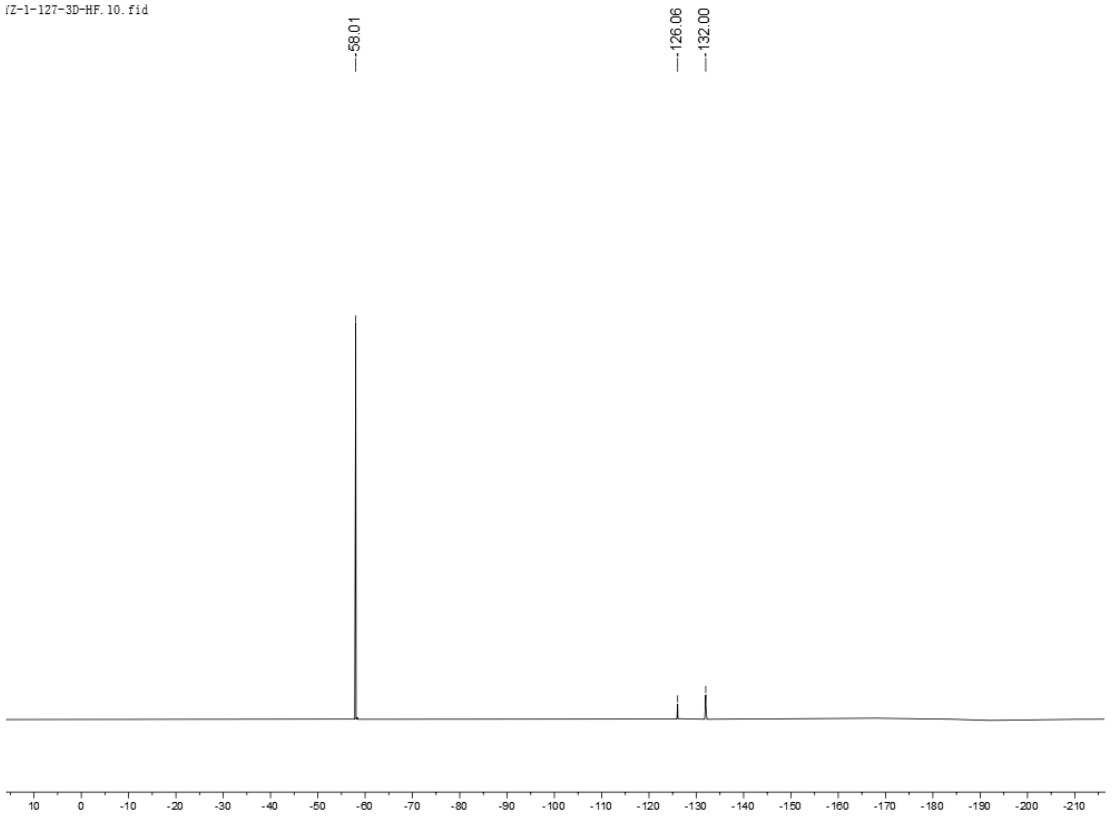
^{19}F NMR (376 MHz, $CDCl_3$) of 5



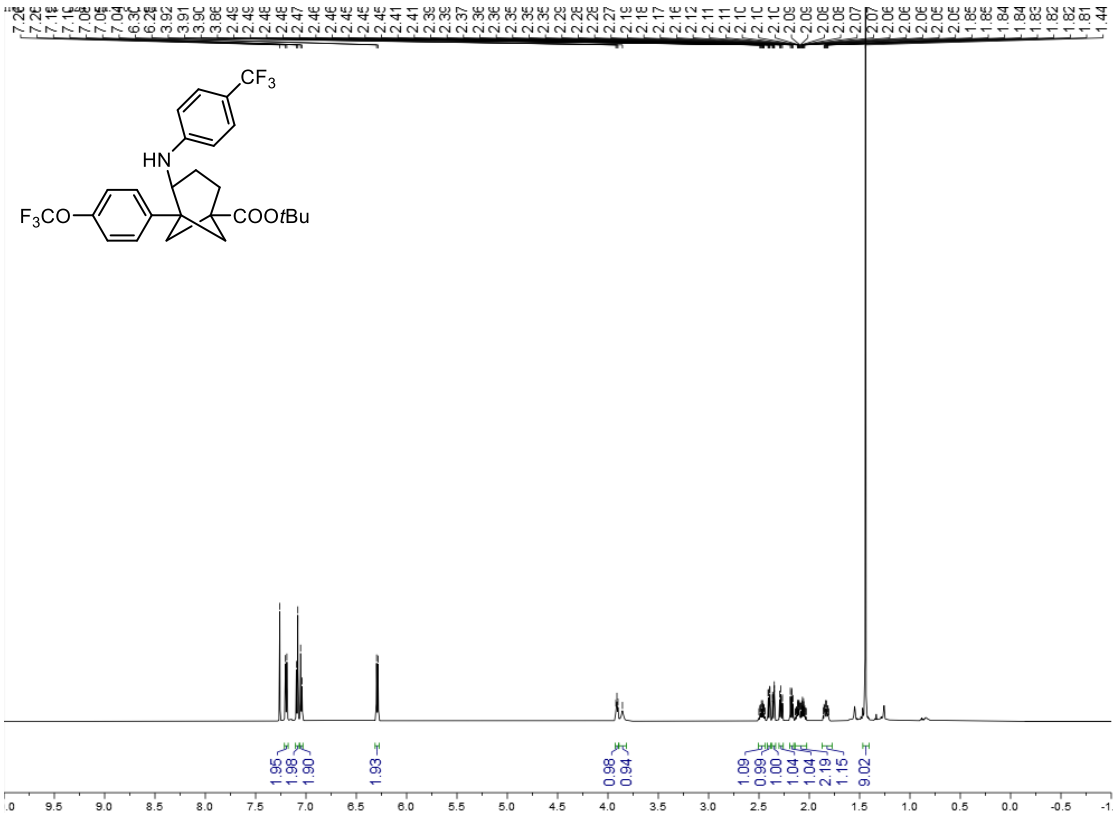
^{1}H NMR (600 MHz, $CDCl_3$) of 6



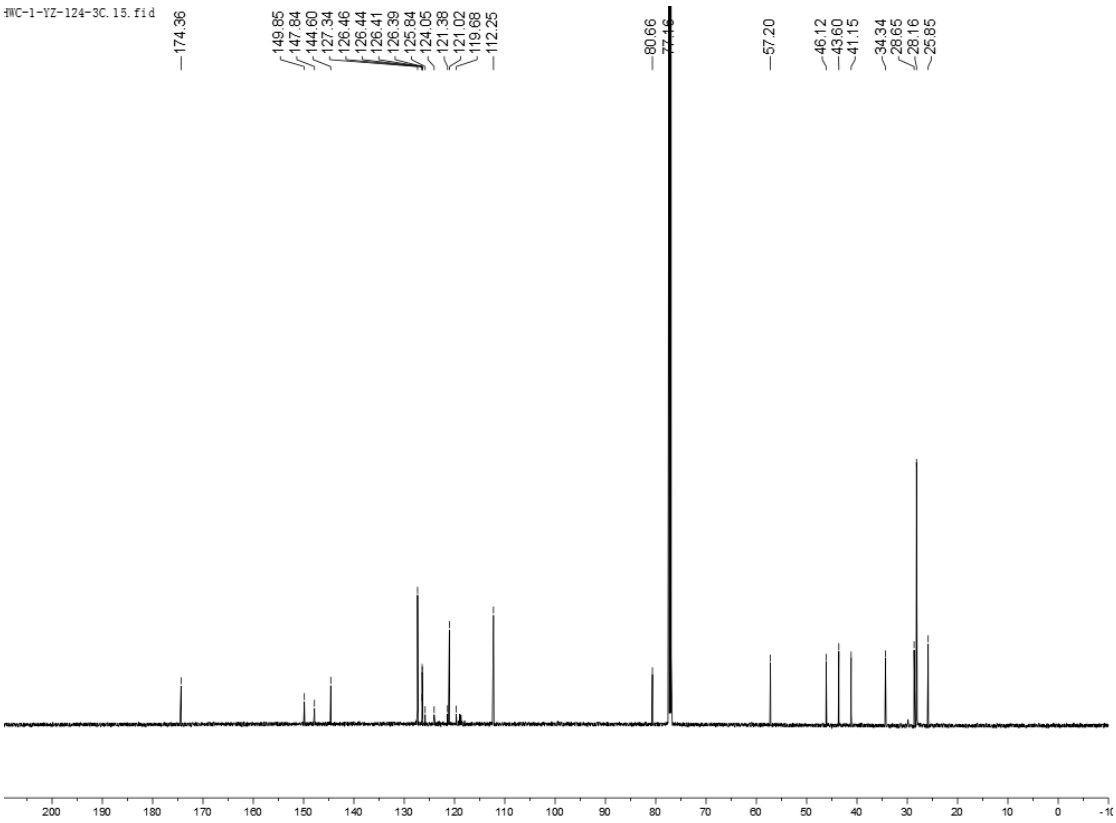
^{13}C NMR (151 MHz, $CDCl_3$) of 6



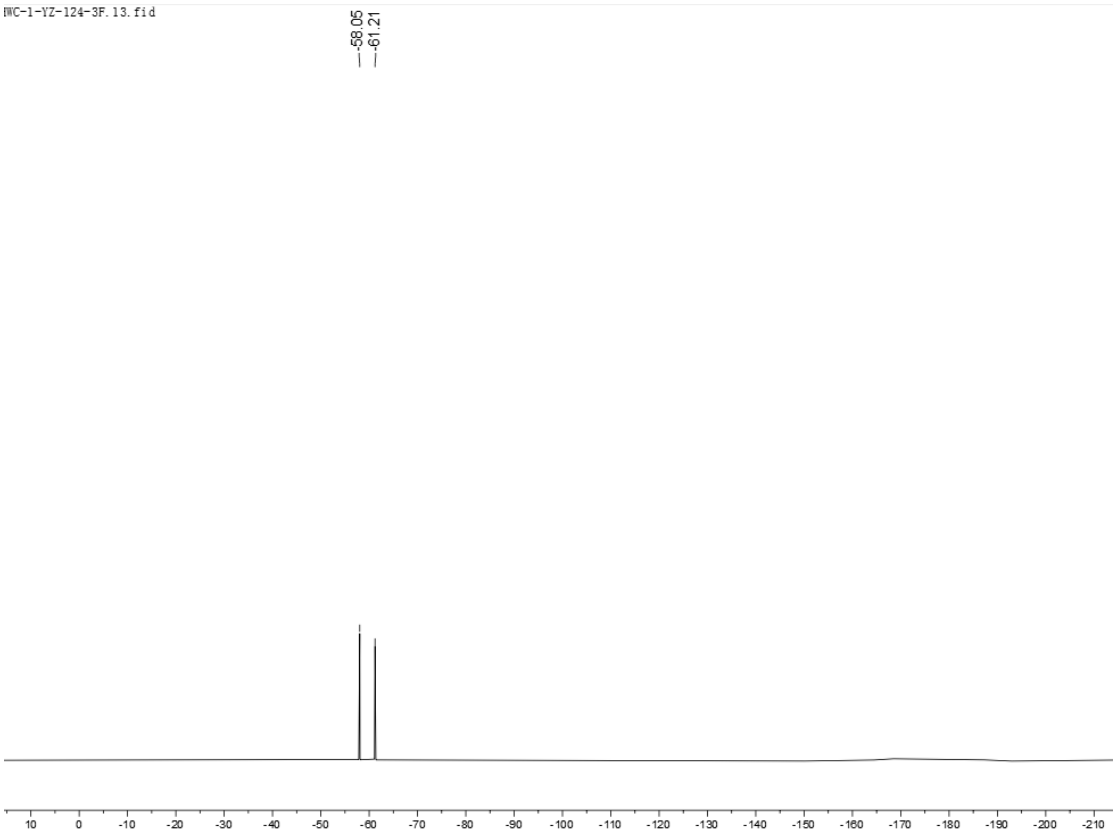
^{19}F NMR (565 MHz, $CDCl_3$) of 6



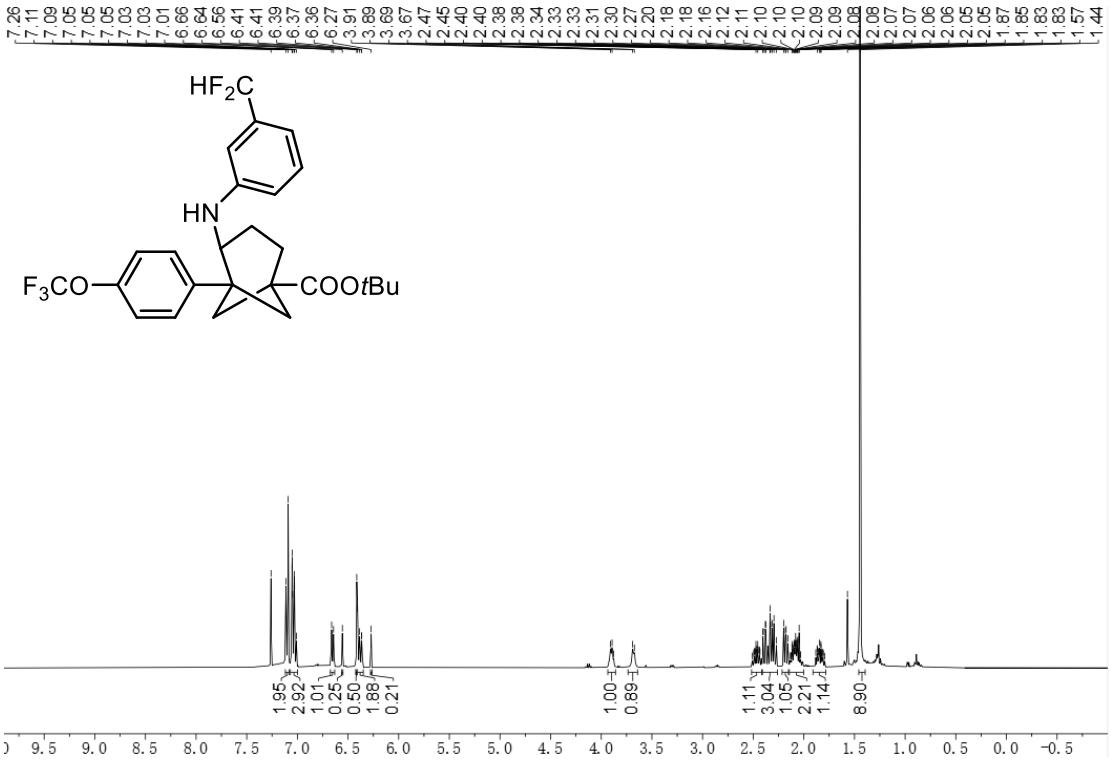
^{1}H NMR (600 MHz, $CDCl_3$) of 7



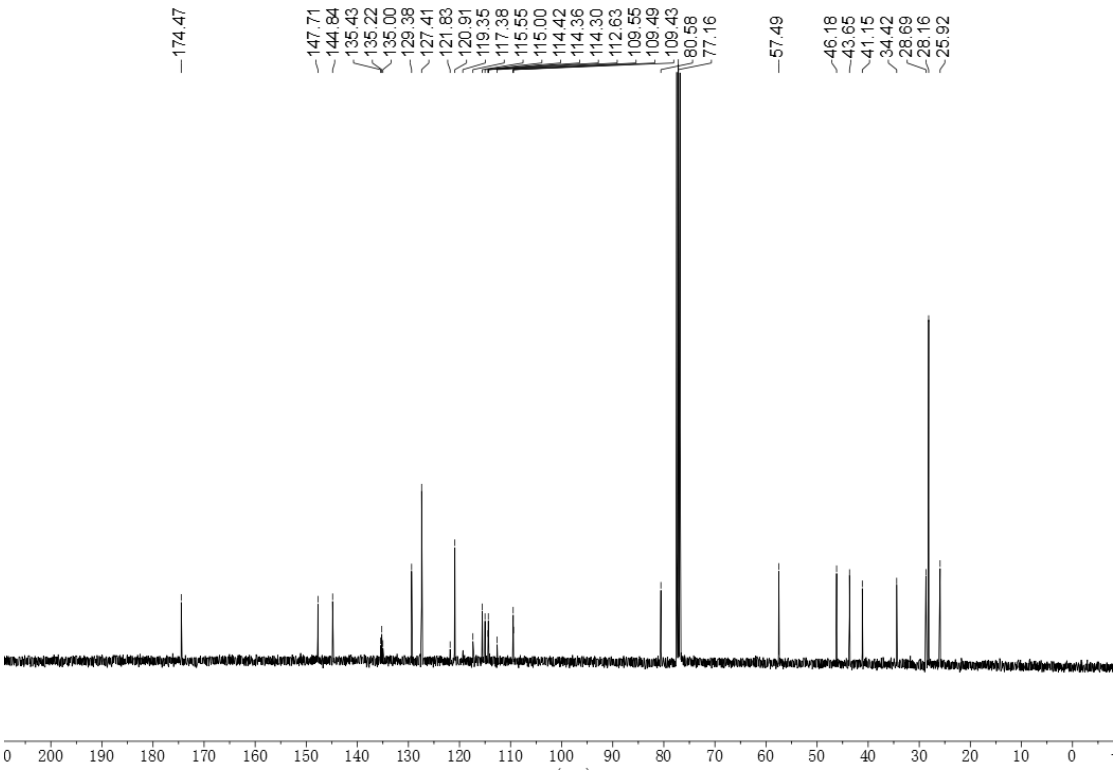
^{13}C NMR (151 MHz, $CDCl_3$) of 7



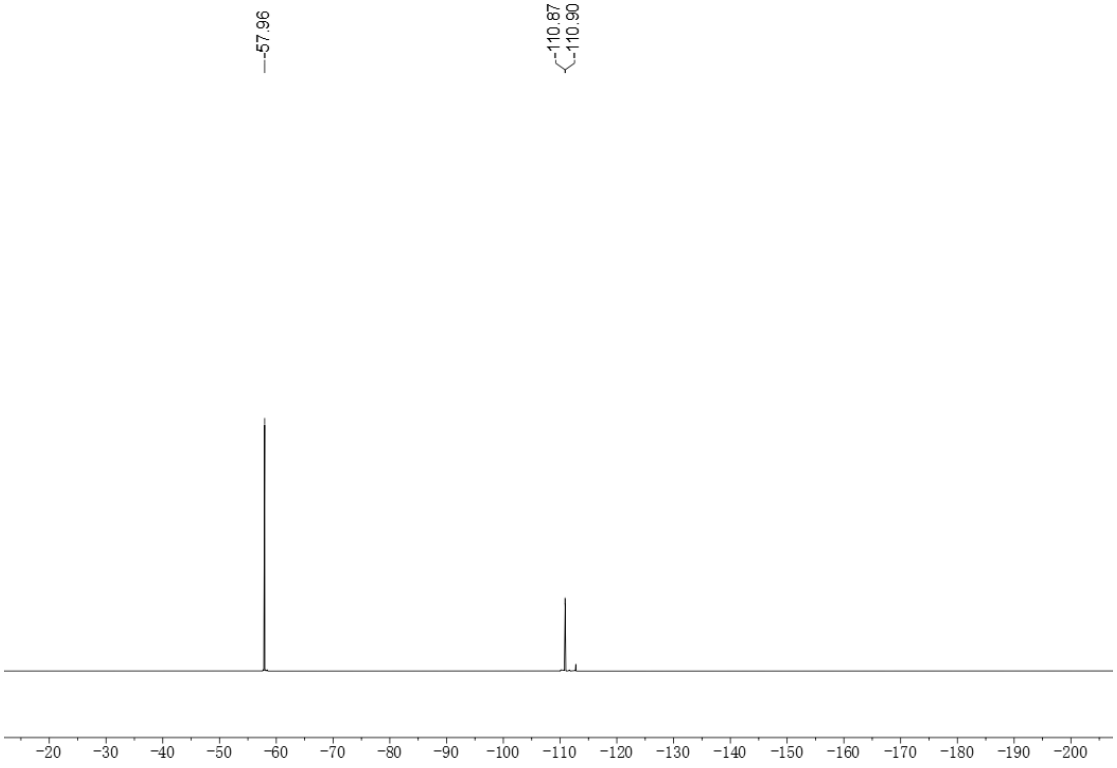
^{19}F NMR (565 MHz, $CDCl_3$) of 7



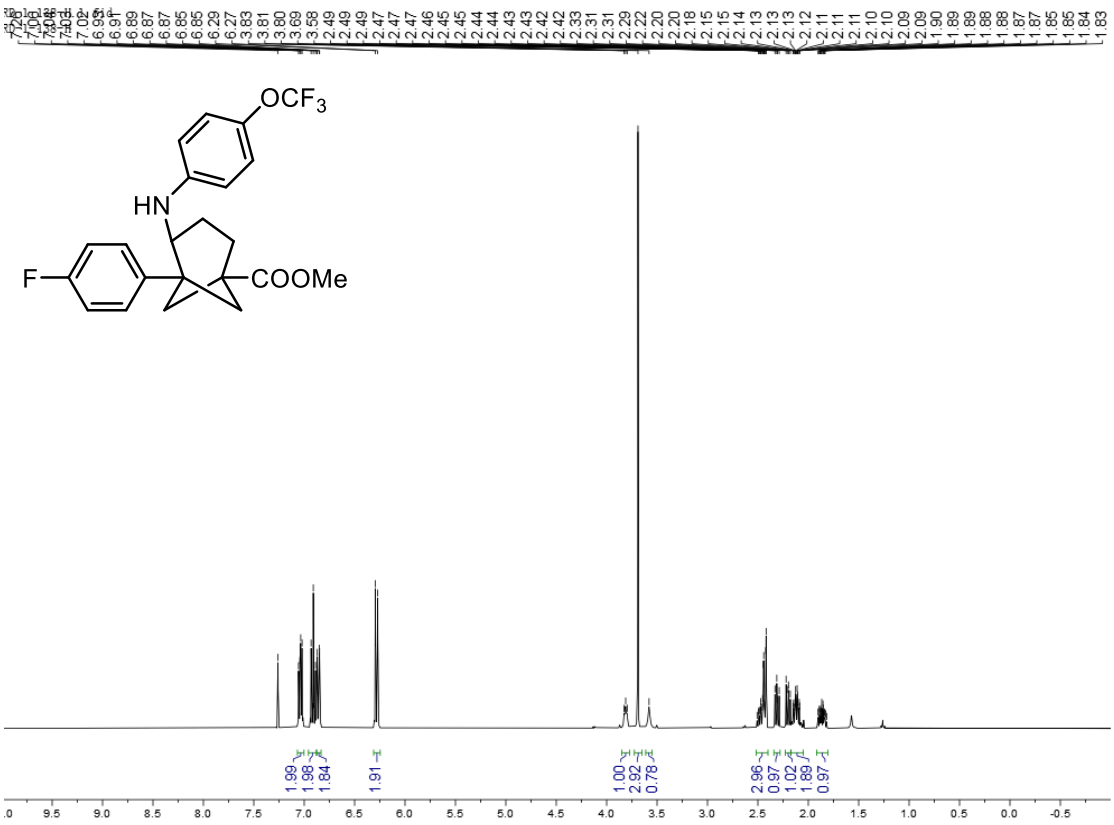
^{1}H NMR (400 MHz, $CDCl_3$) of 8



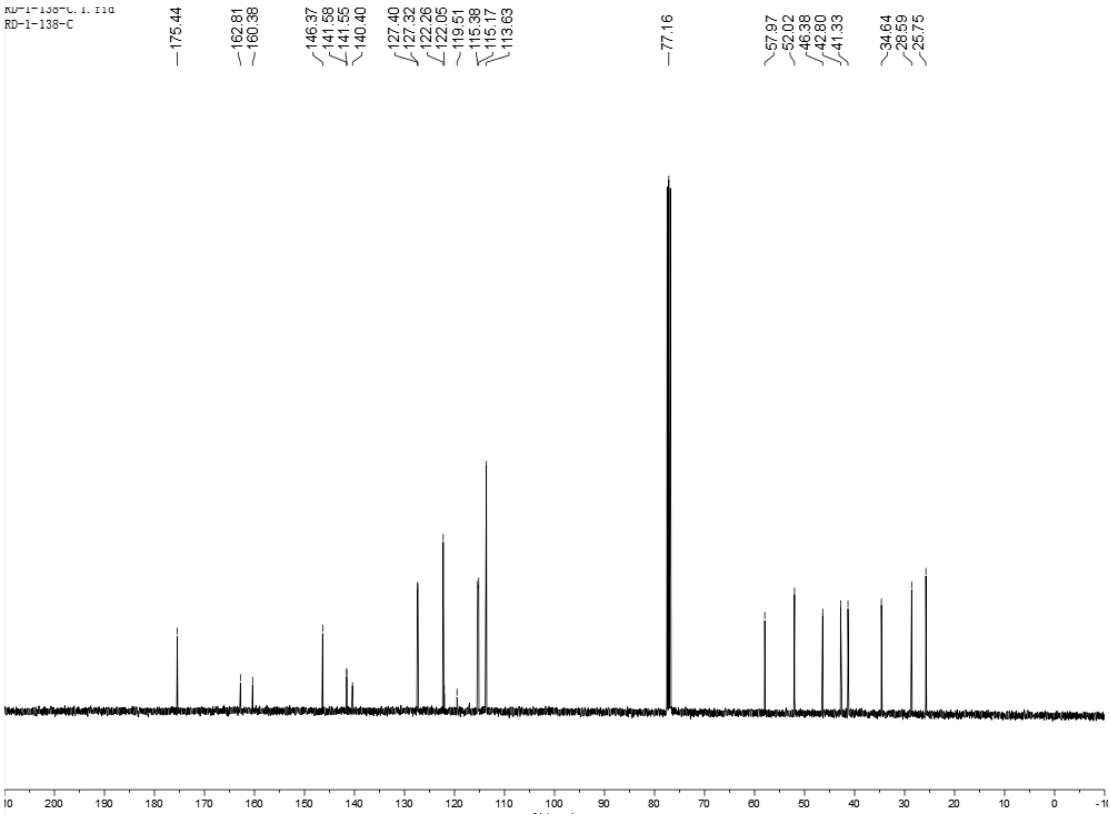
^{13}C NMR (101 MHz, $CDCl_3$) of 8



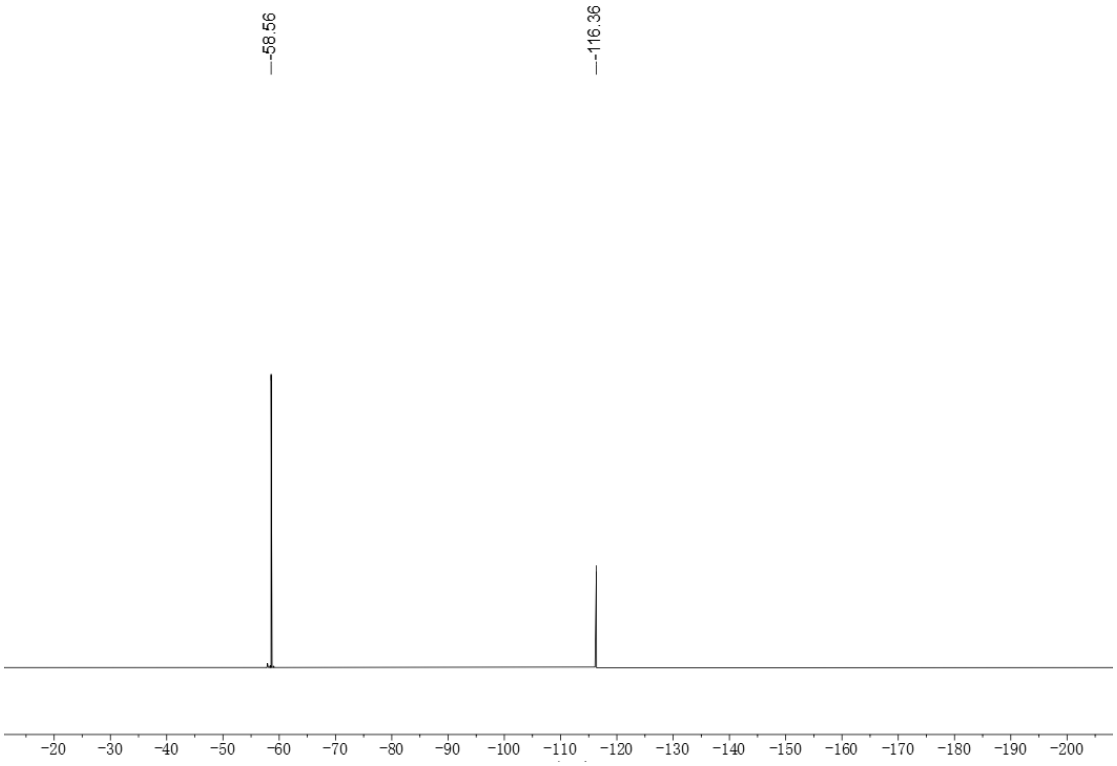
^{19}F NMR (376 MHz, $CDCl_3$) of 8



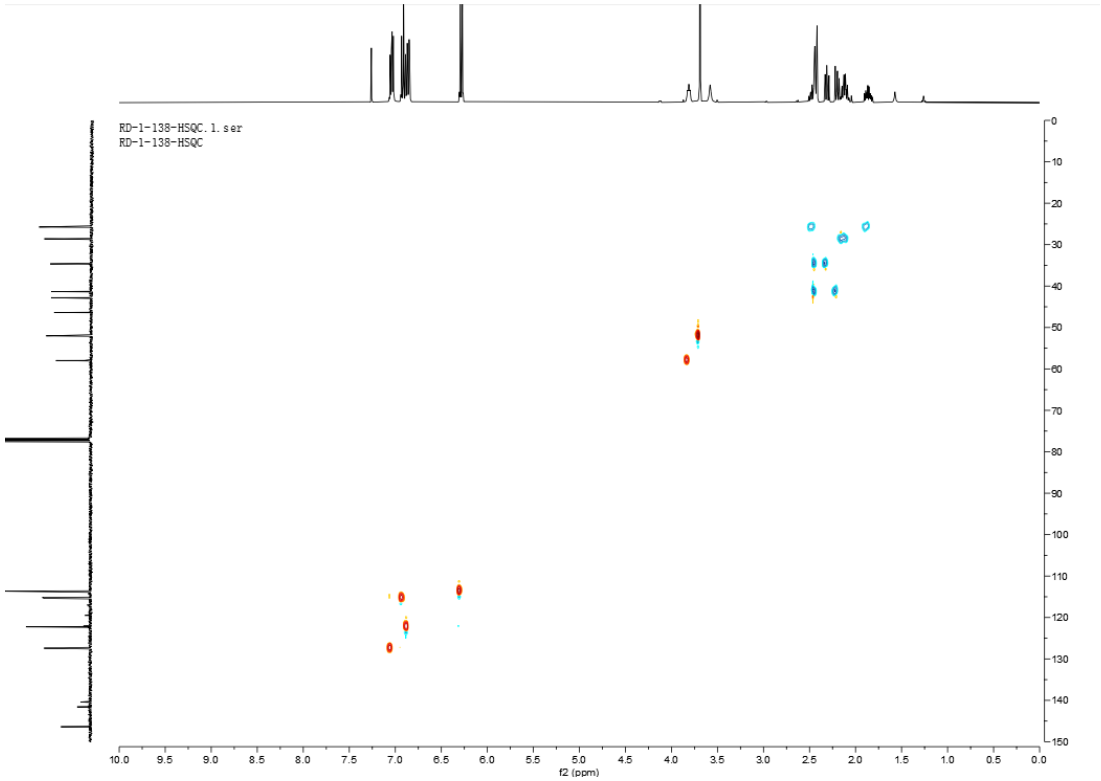
^{1}H NMR (600 MHz, $CDCl_3$) of 9



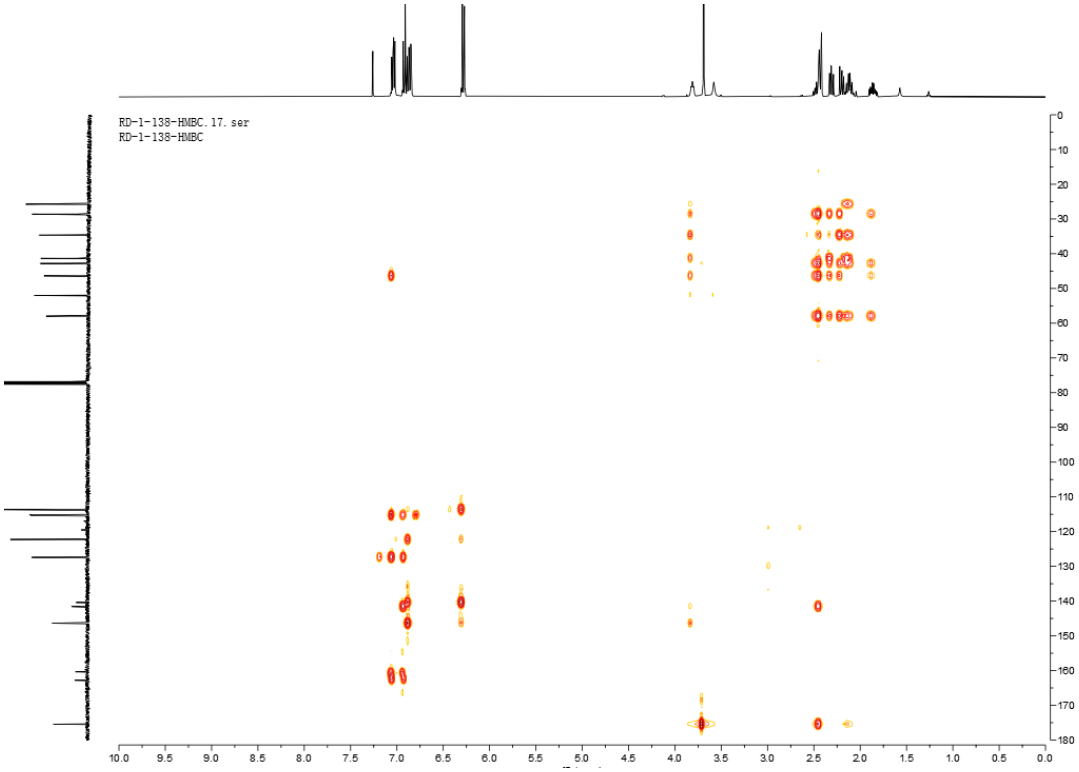
^{13}C NMR (151 MHz, $CDCl_3$) of 9



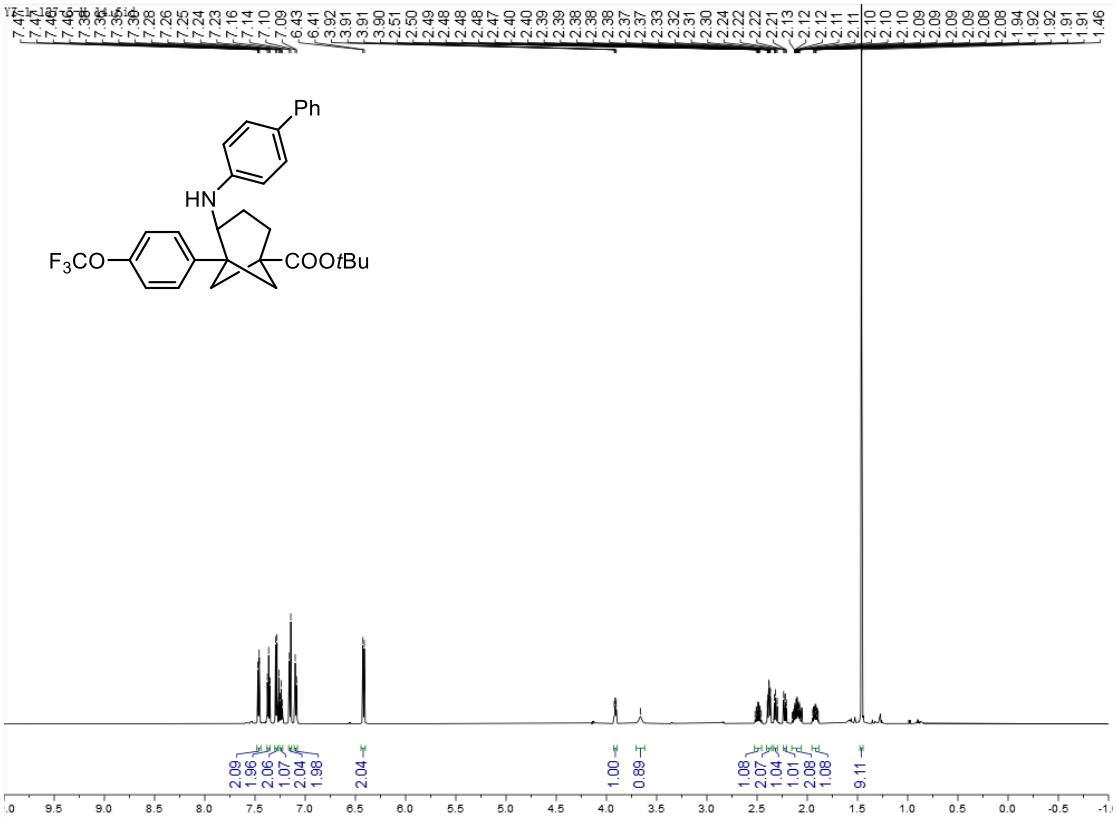
^{19}F NMR (565 MHz, $CDCl_3$) of 9



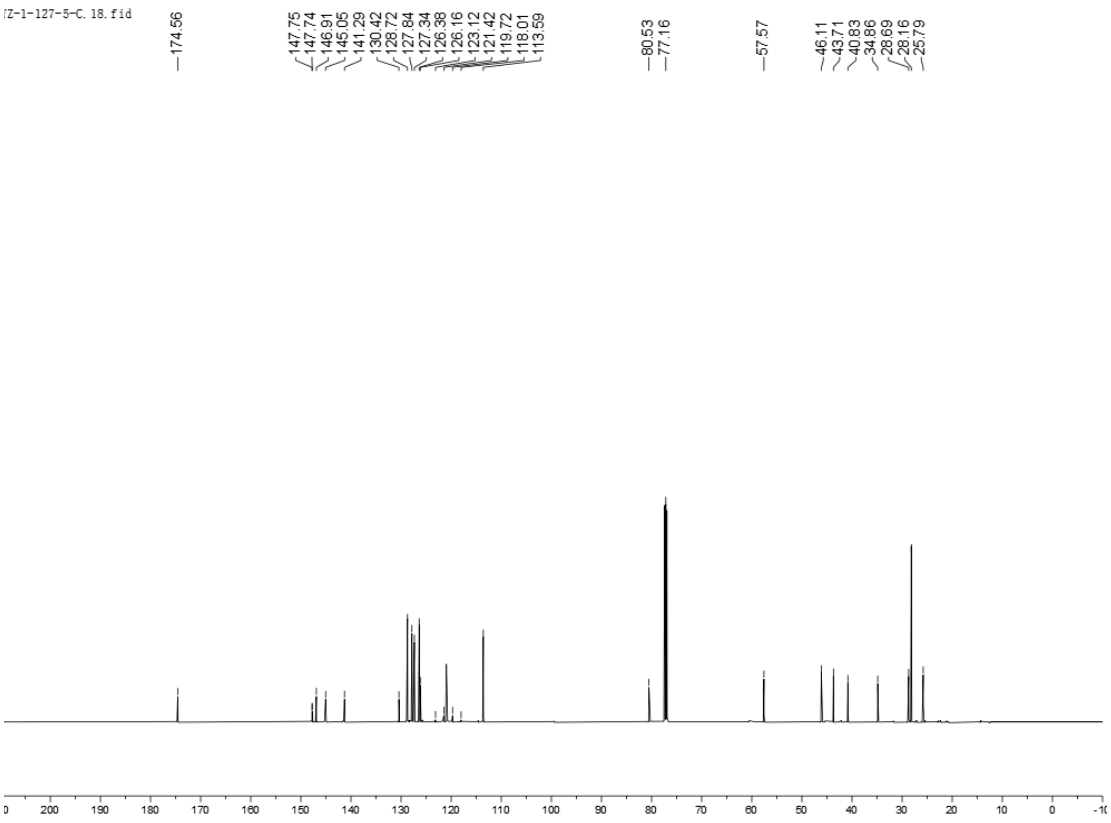
HSQC of 9



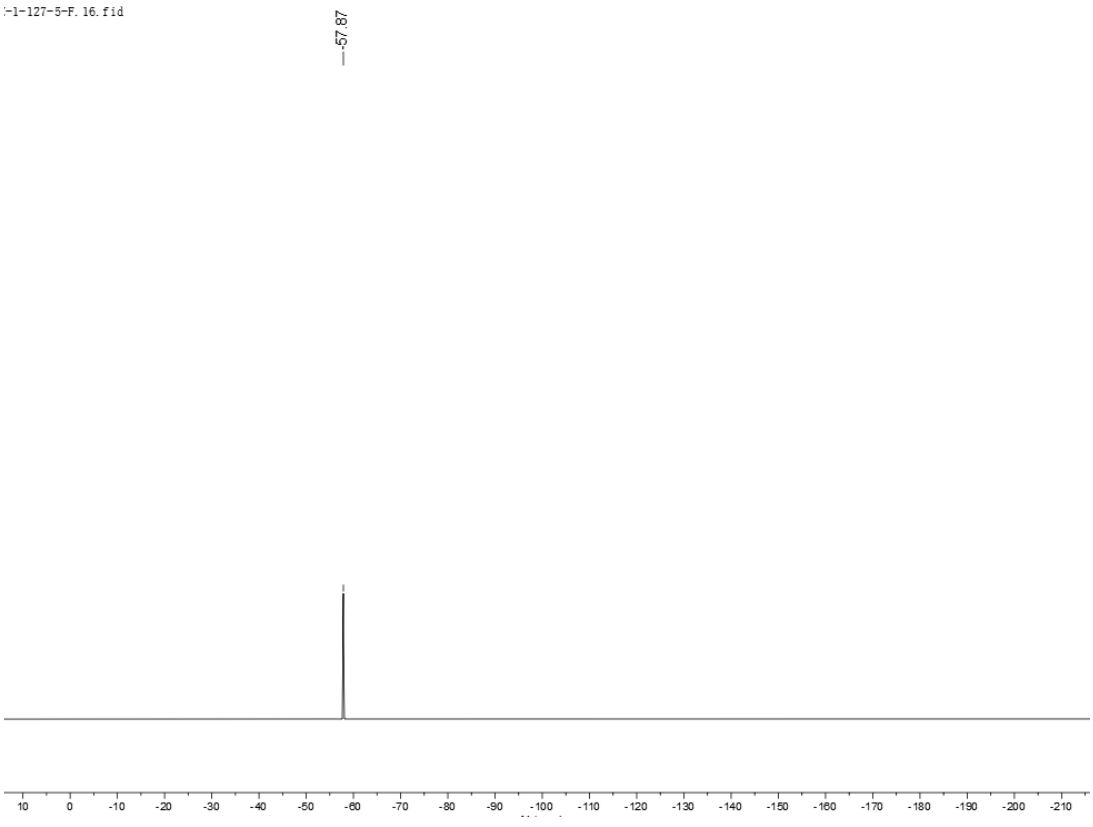
HMBC of 9



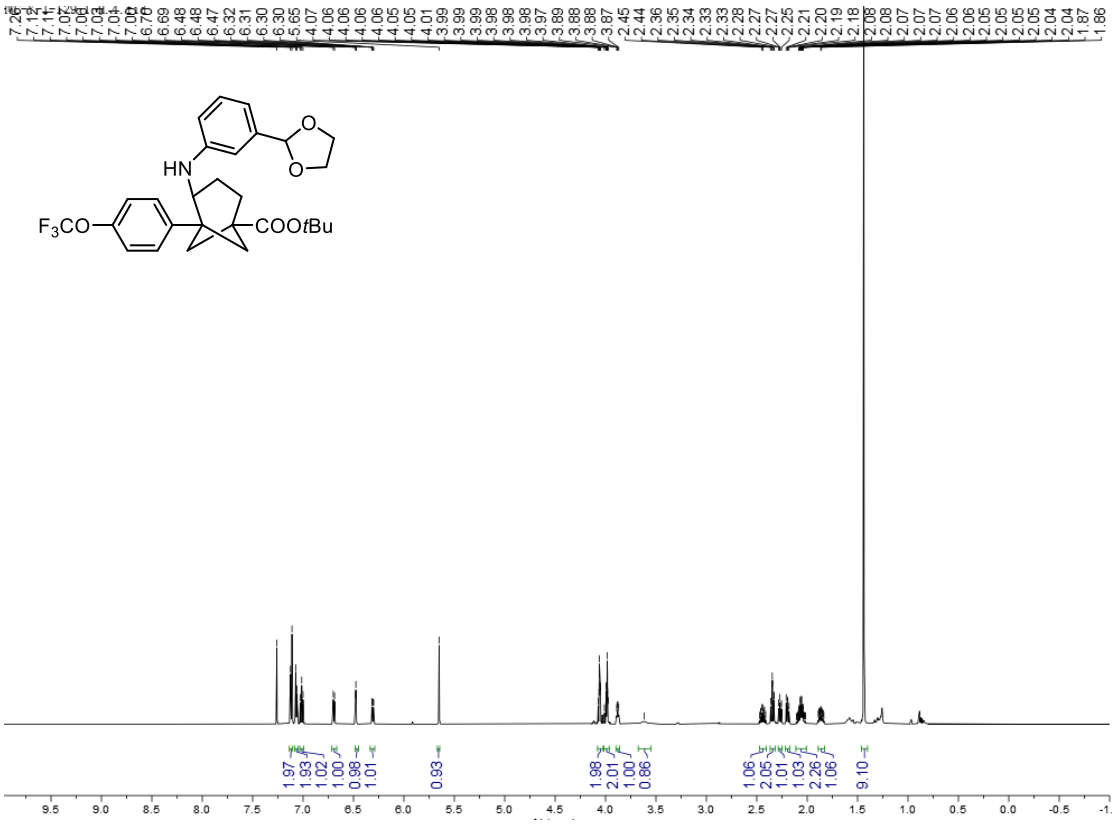
^{1}H NMR (600 MHz, $CDCl_3$) of 10



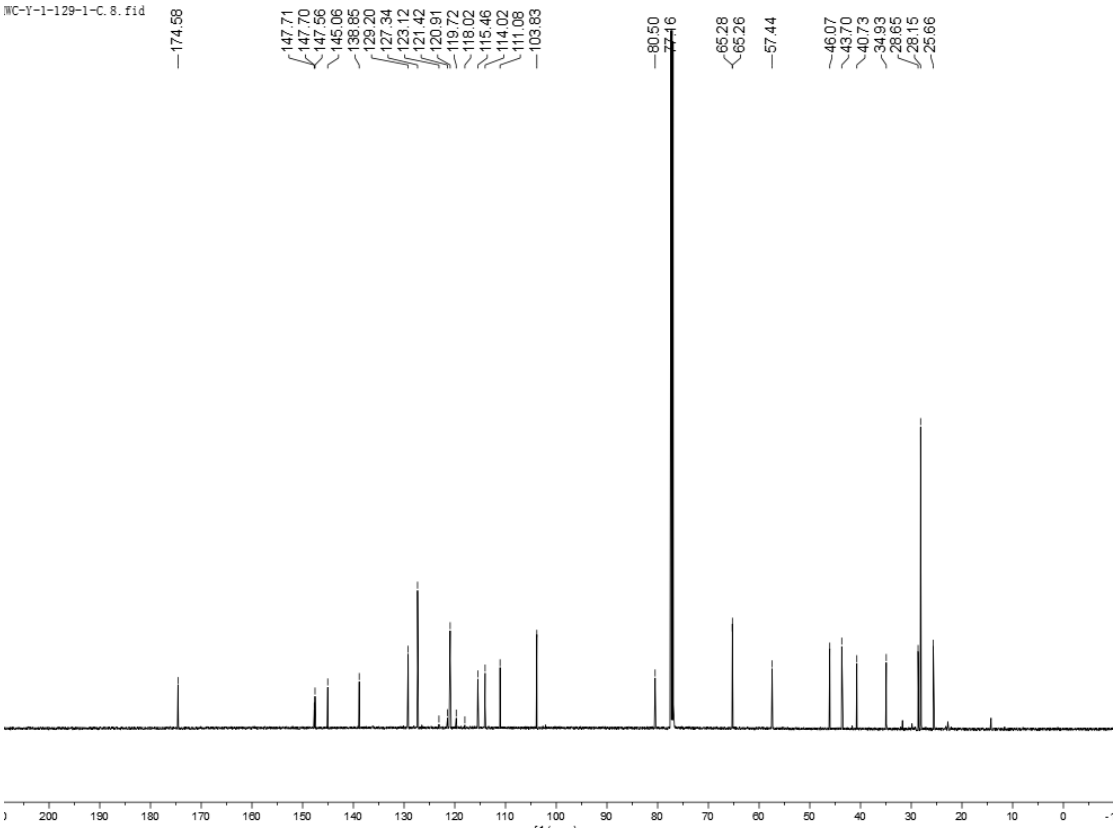
^{13}C NMR (151 MHz, $CDCl_3$) of 10



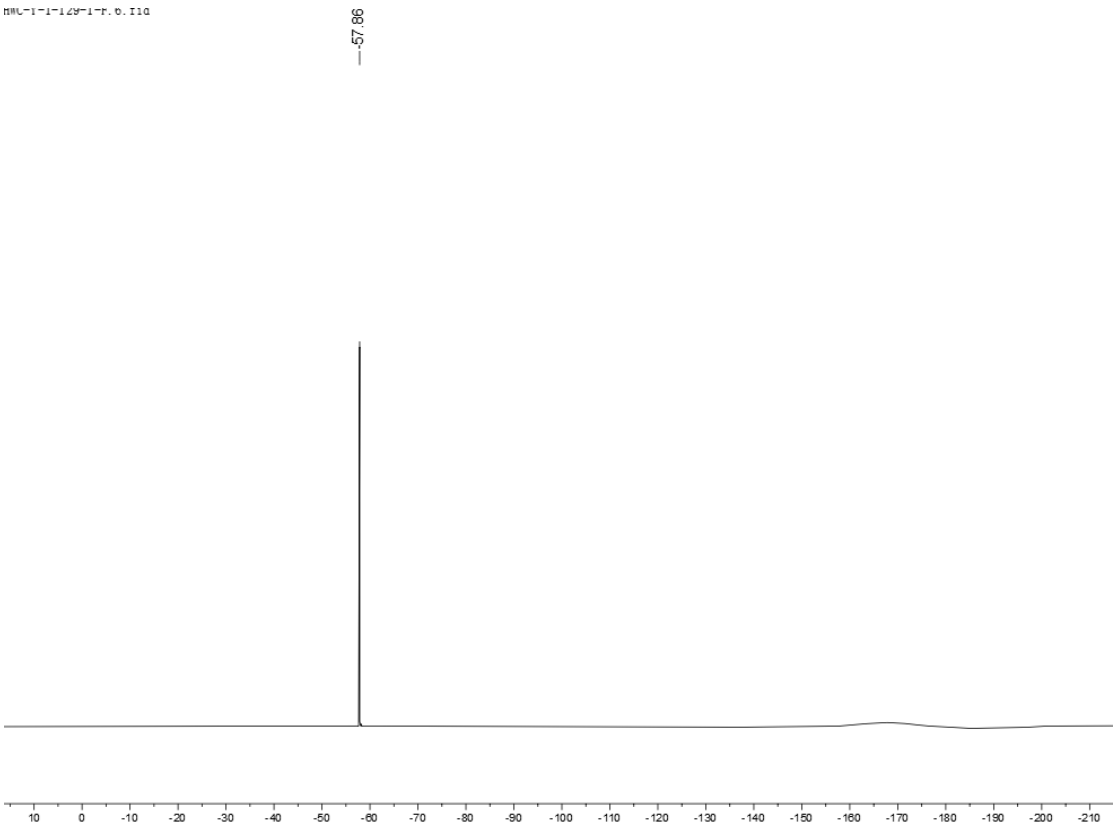
^{19}F NMR (565 MHz, $CDCl_3$) of 10



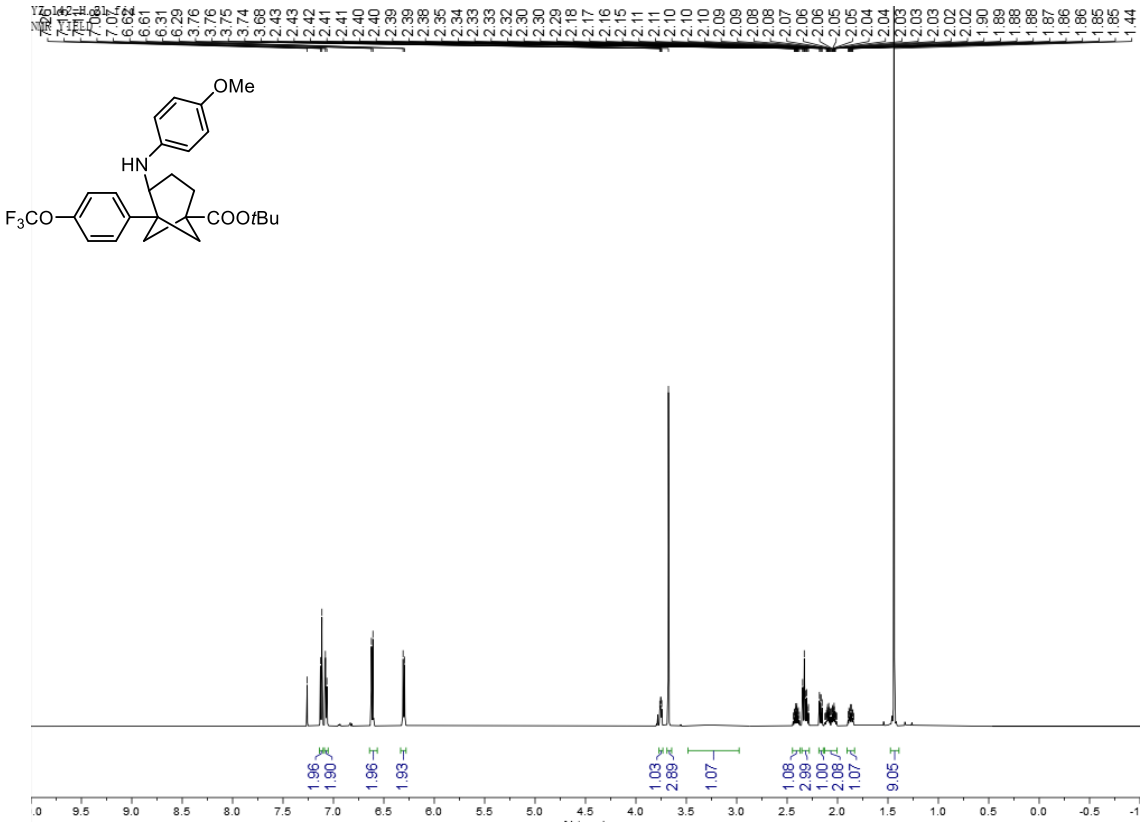
^{1}H NMR (600 MHz, $CDCl_3$) of 11



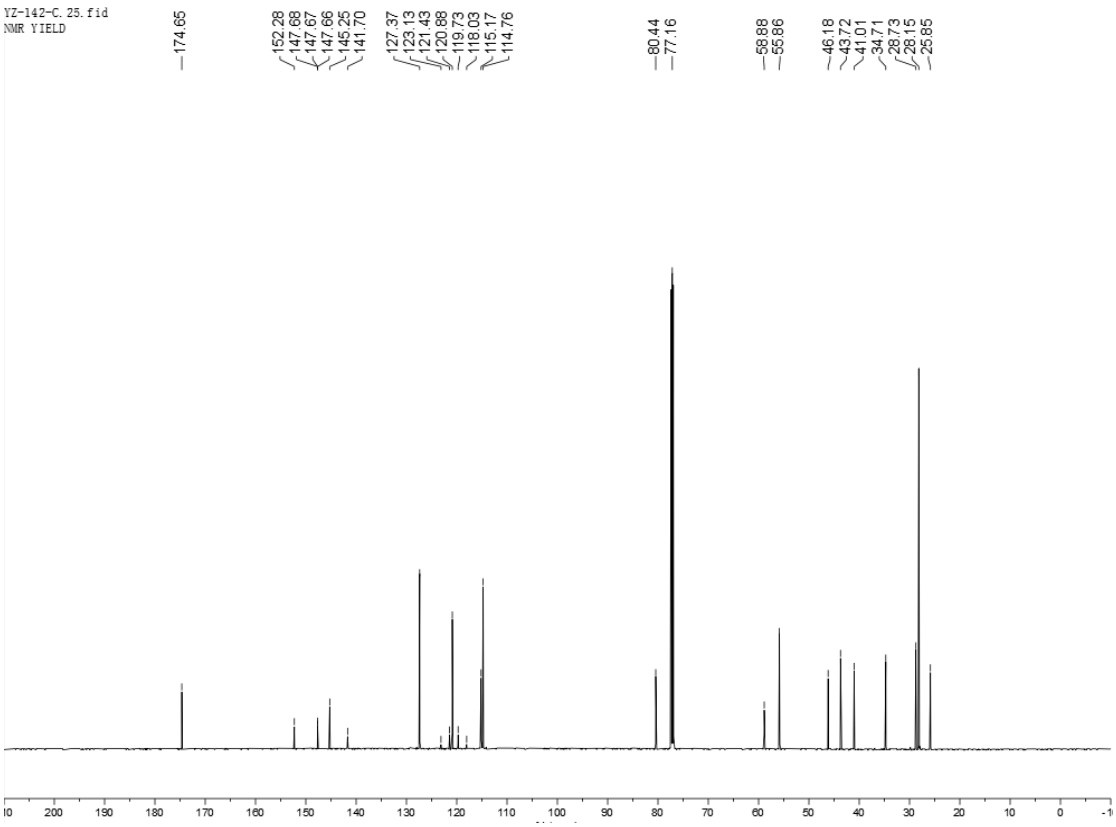
^{13}C NMR (151 MHz, $CDCl_3$) of 11



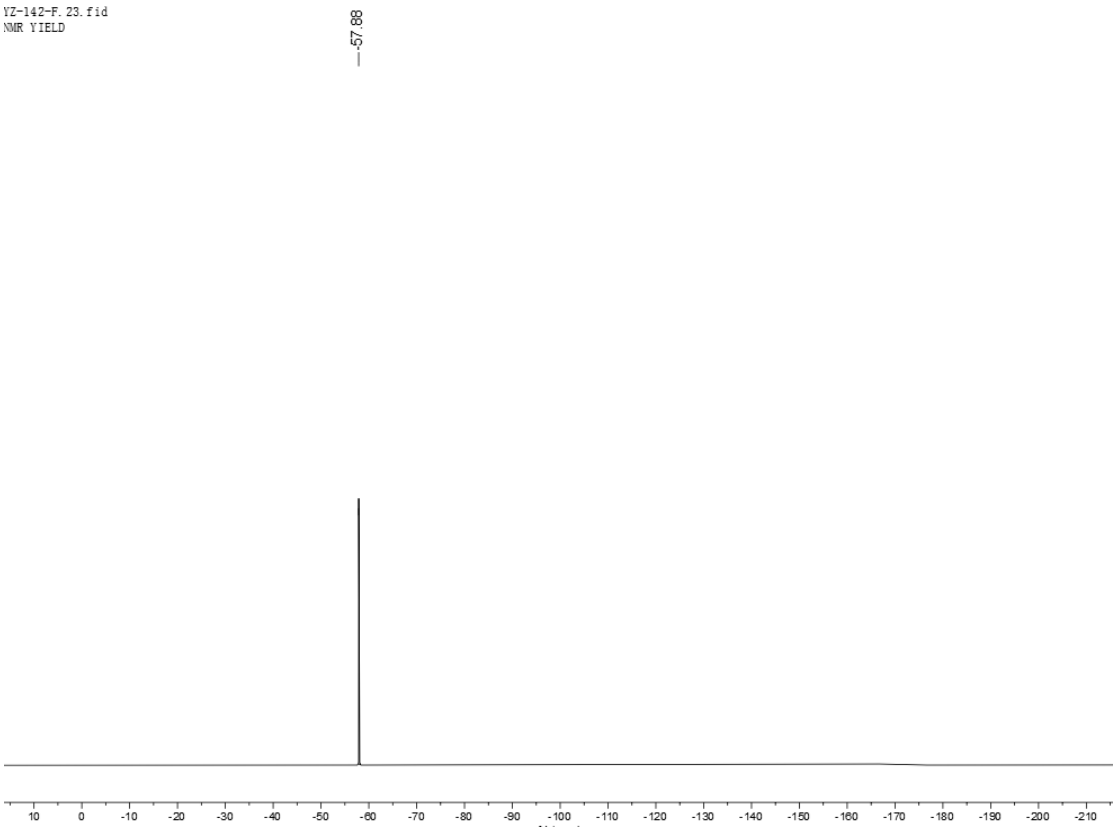
^{19}F NMR (565 MHz, $CDCl_3$) of 11



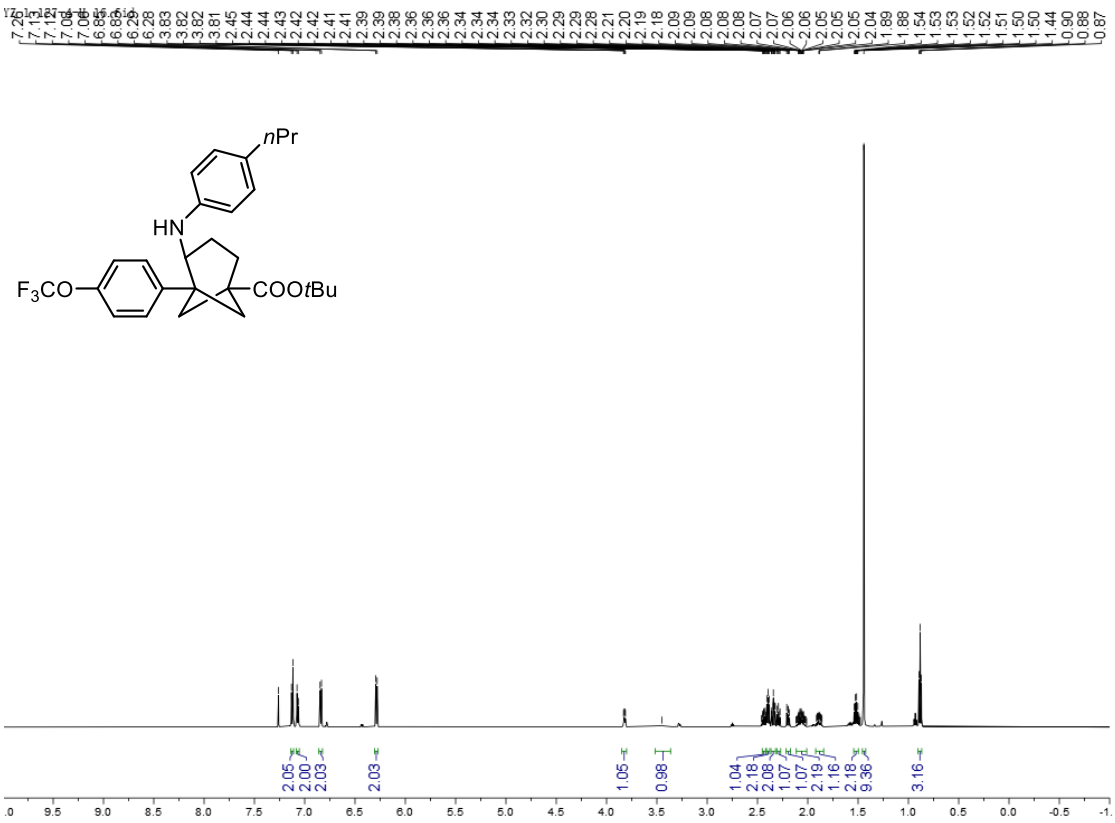
^{1}H NMR (600 MHz, $CDCl_3$) of 12



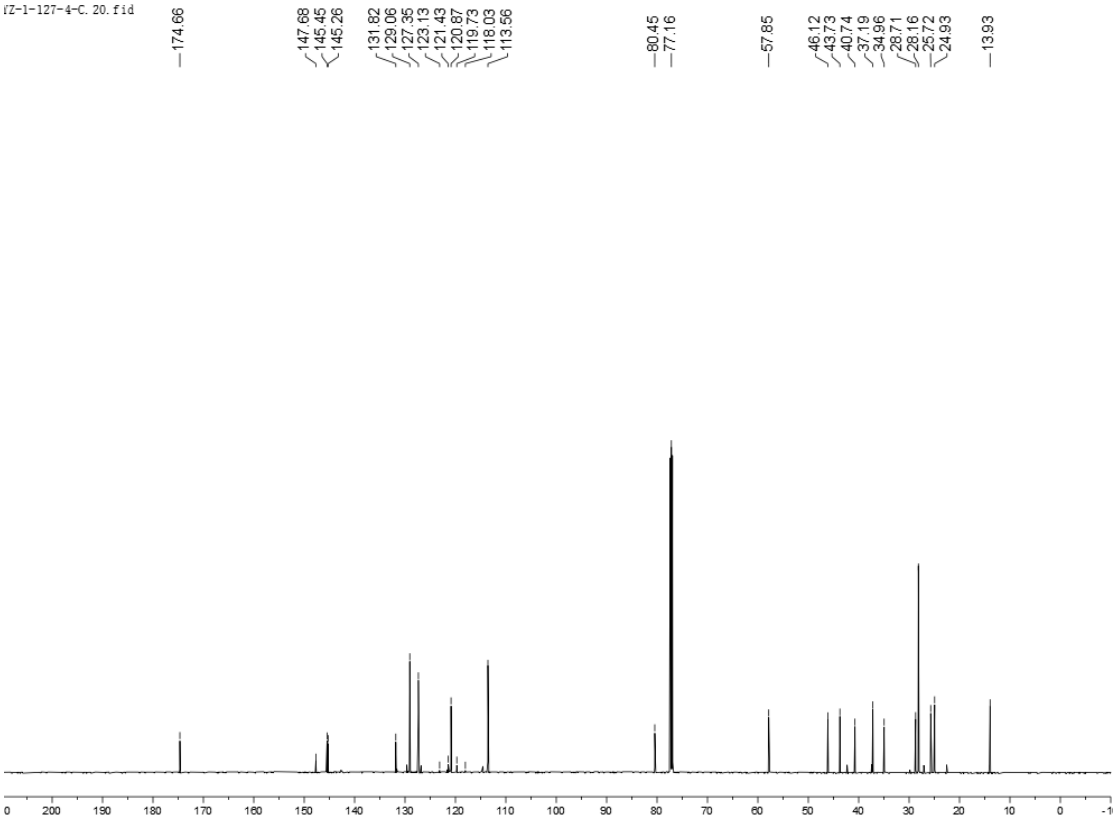
^{13}C NMR (151 MHz, $CDCl_3$) of 12



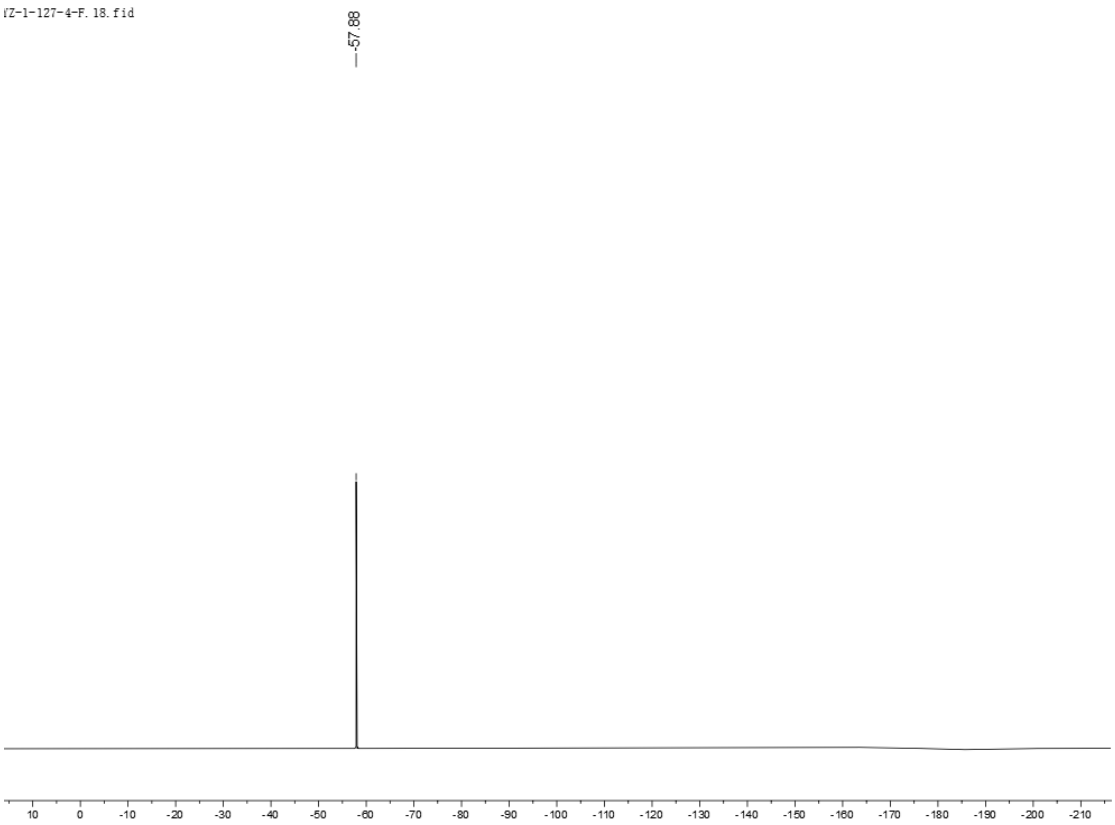
^{19}F NMR (565 MHz, $CDCl_3$) of 12



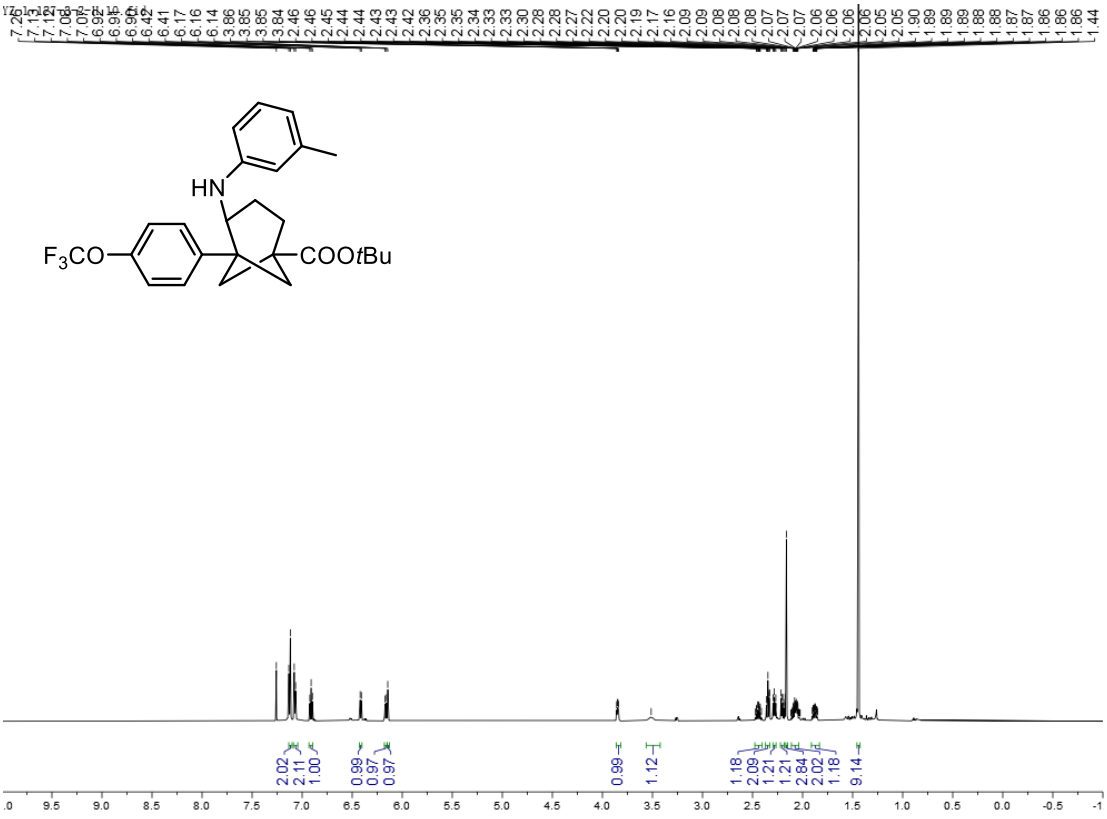
^{1}H NMR (600 MHz, $CDCl_3$) of 13



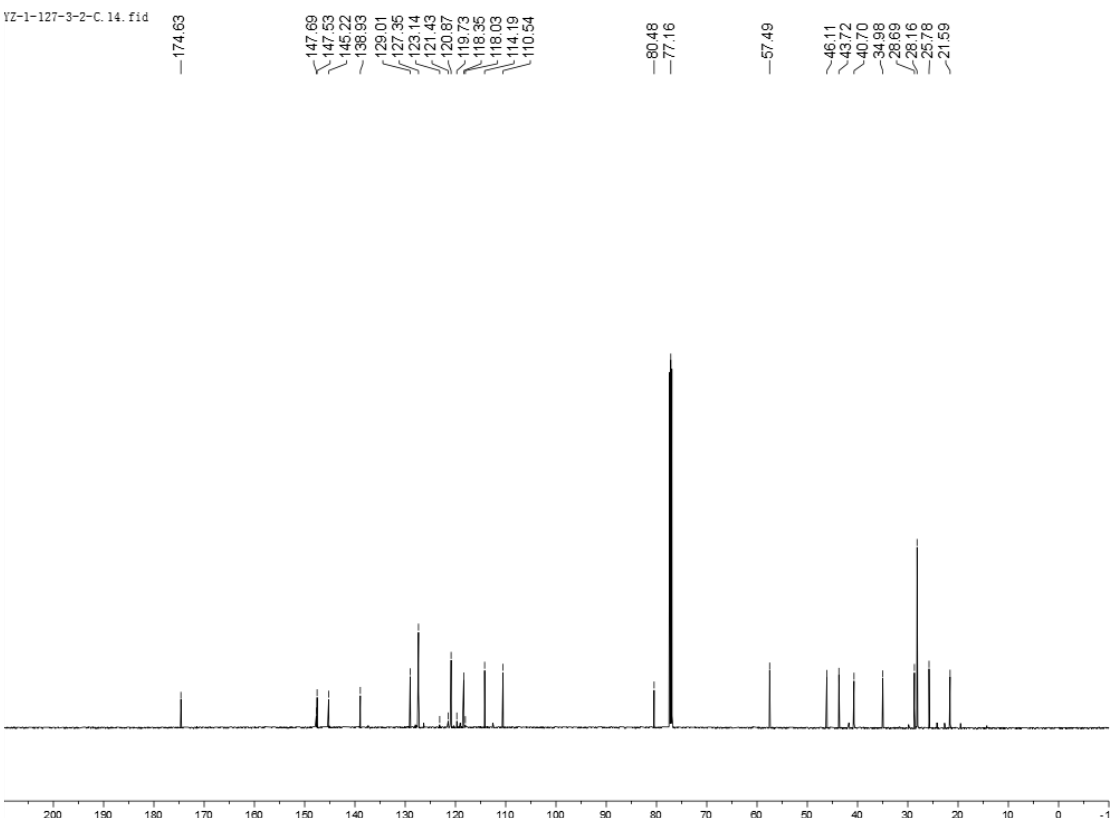
^{13}C NMR (151 MHz, $CDCl_3$) of 13



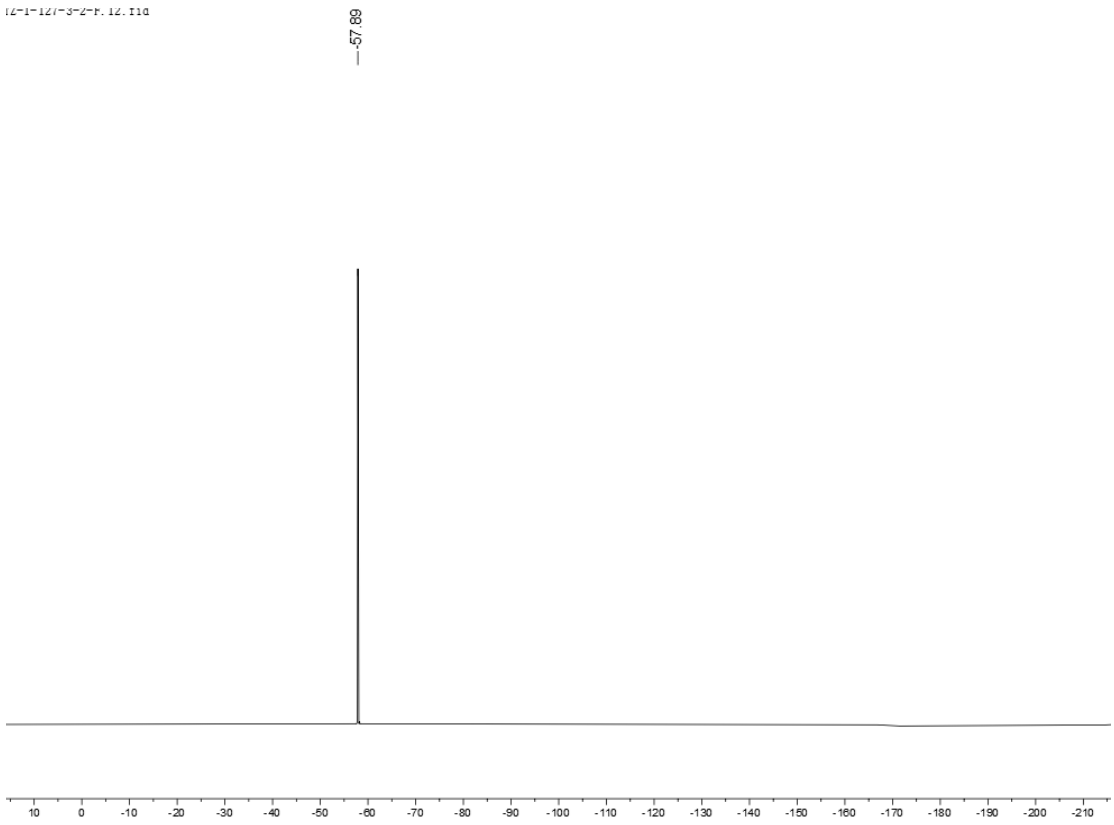
^{19}F NMR (565 MHz, $CDCl_3$) of 13



^{1}H NMR (600 MHz, $CDCl_3$) of 14



^{13}C NMR (151 MHz, $CDCl_3$) of 14



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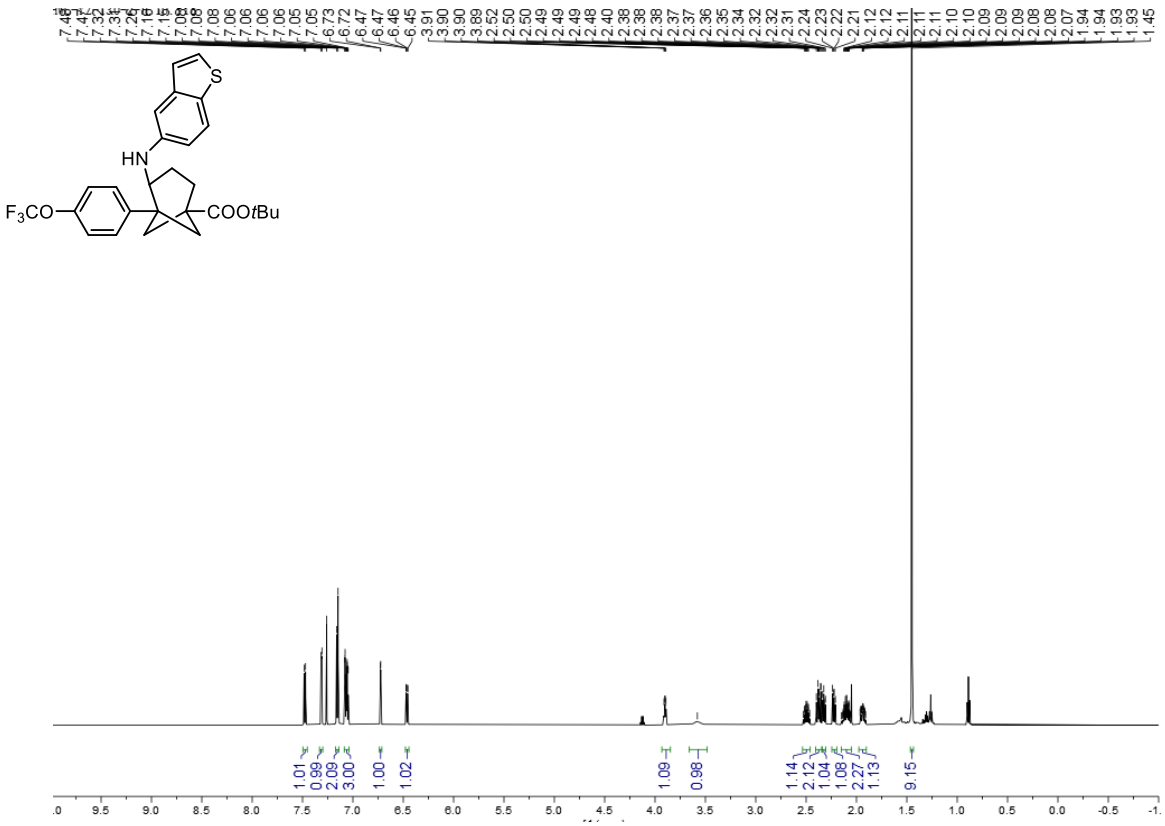
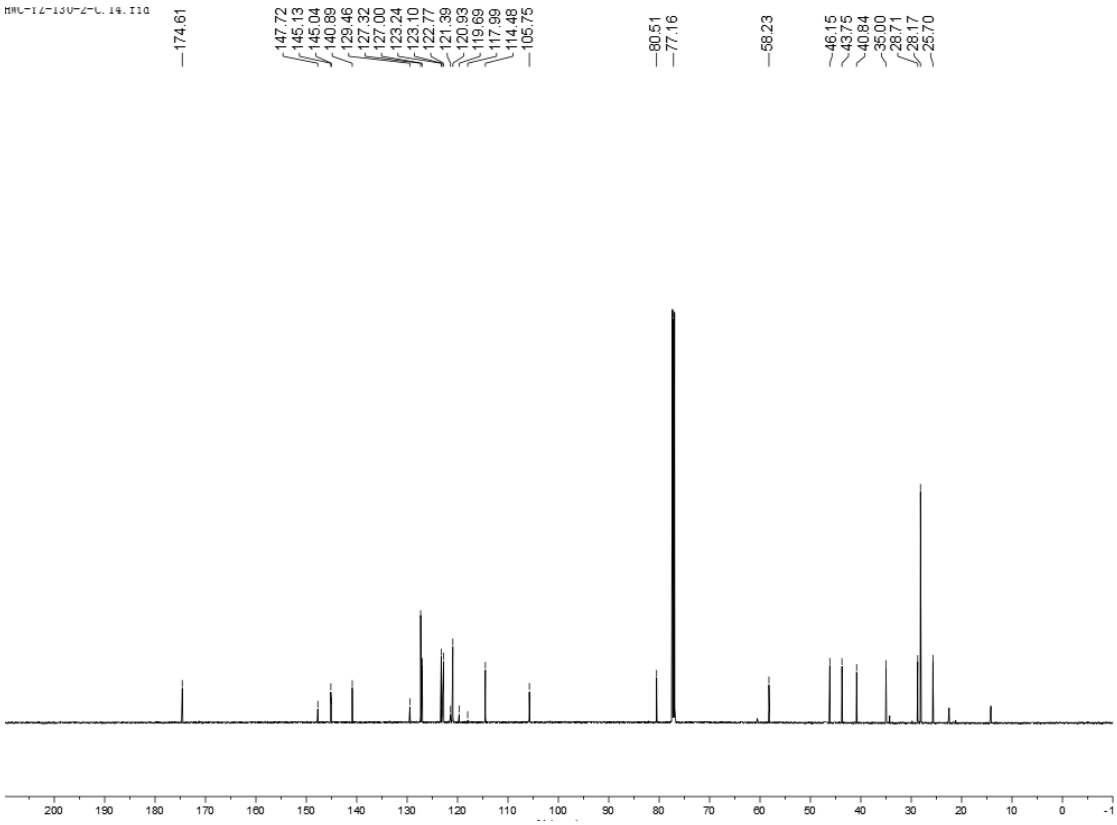
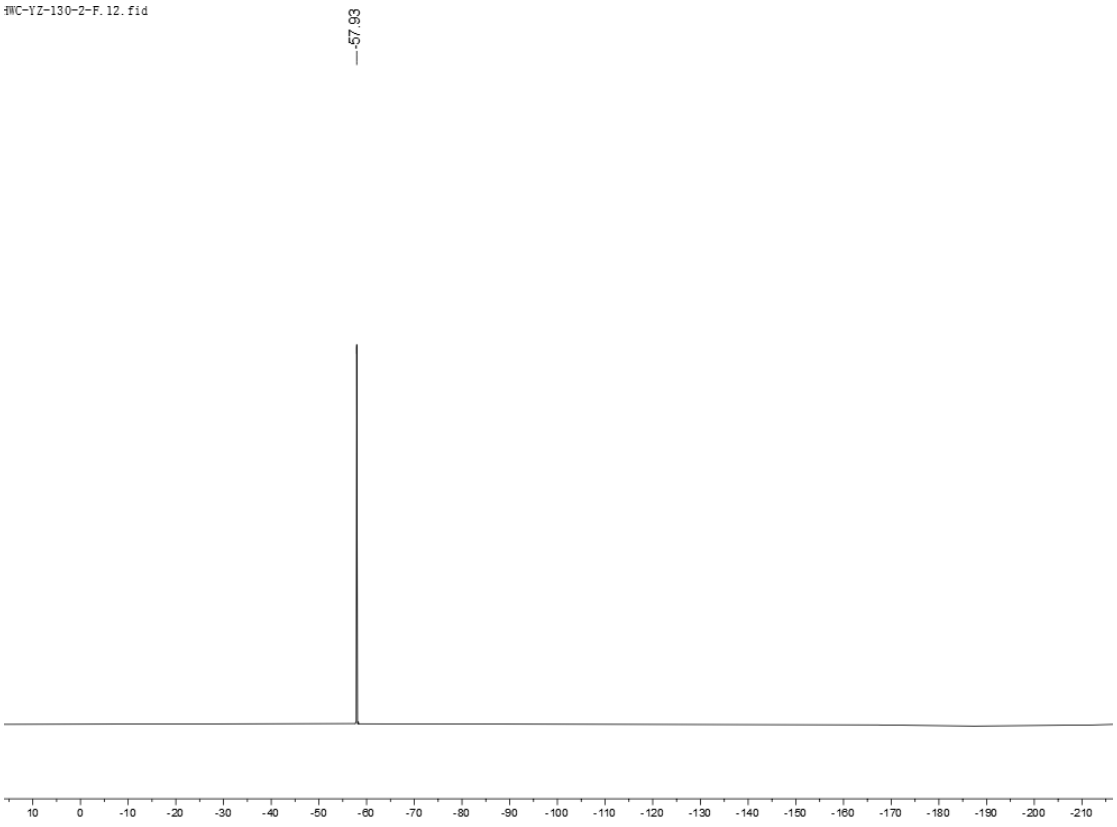


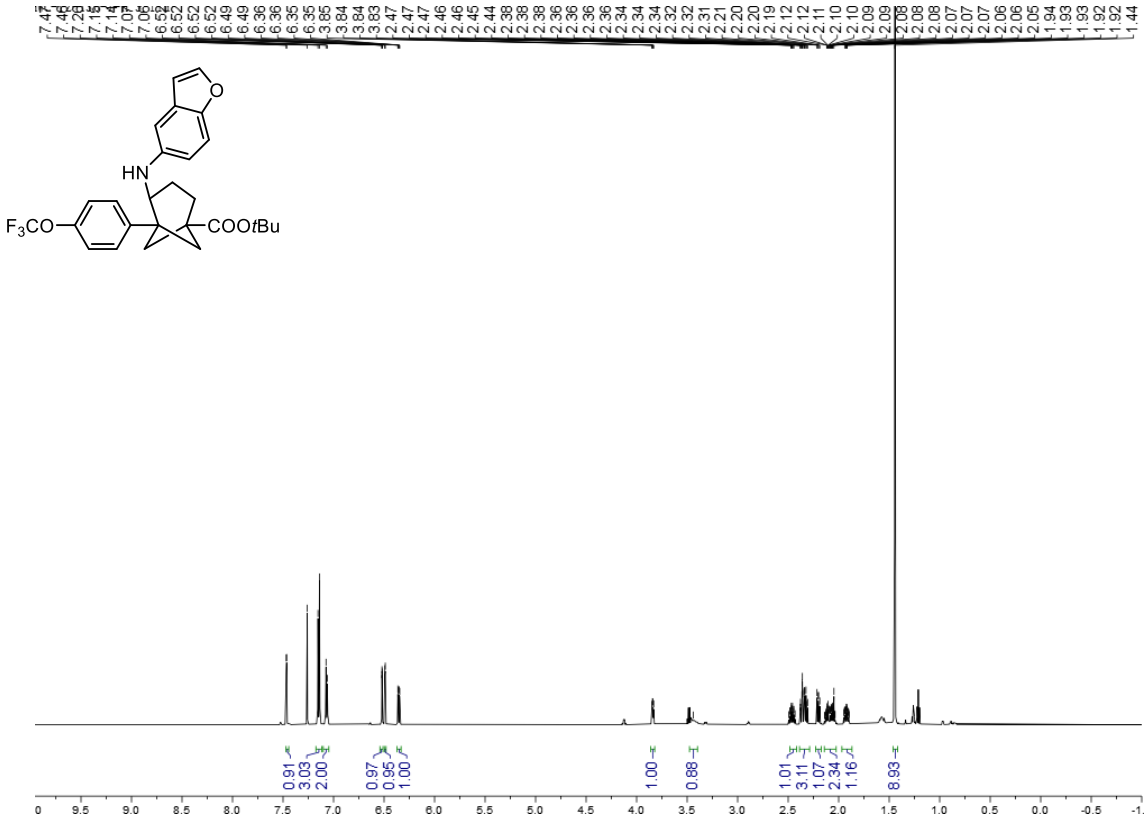
^{1}H NMR (600 MHz, $CDCl_3$) of 15



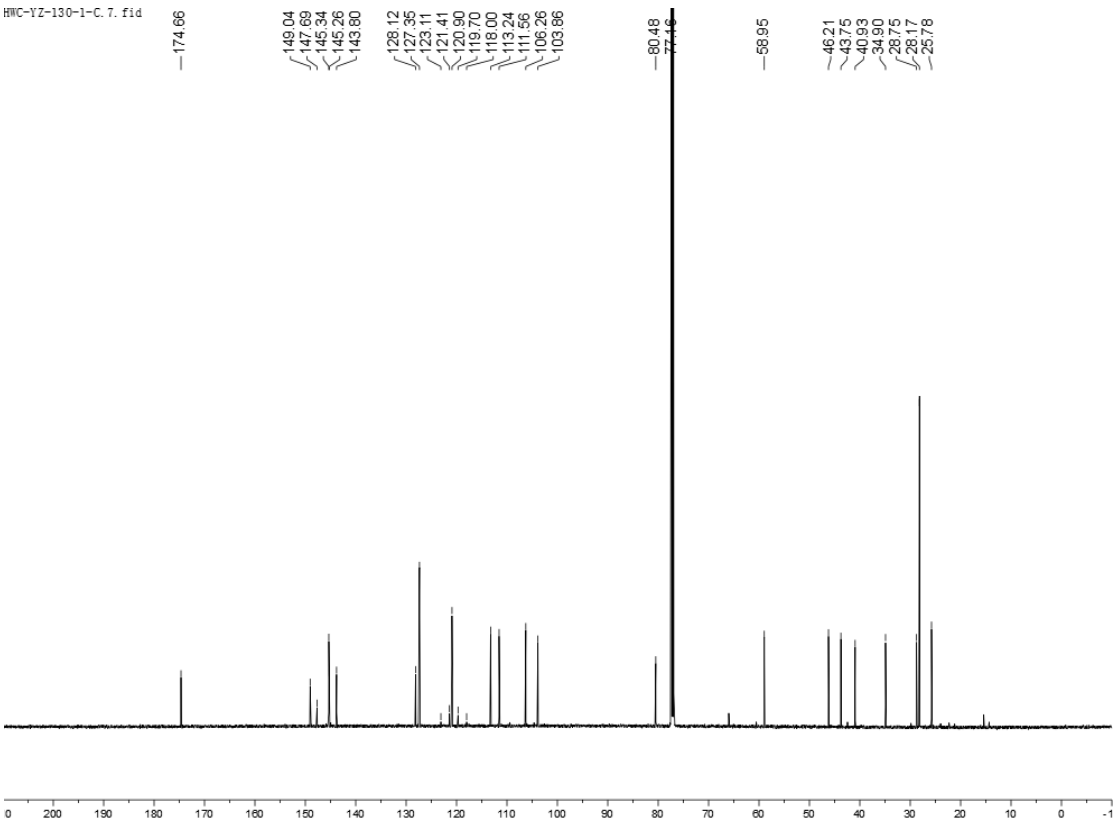
^{13}C NMR (151 MHz, $CDCl_3$) of 15



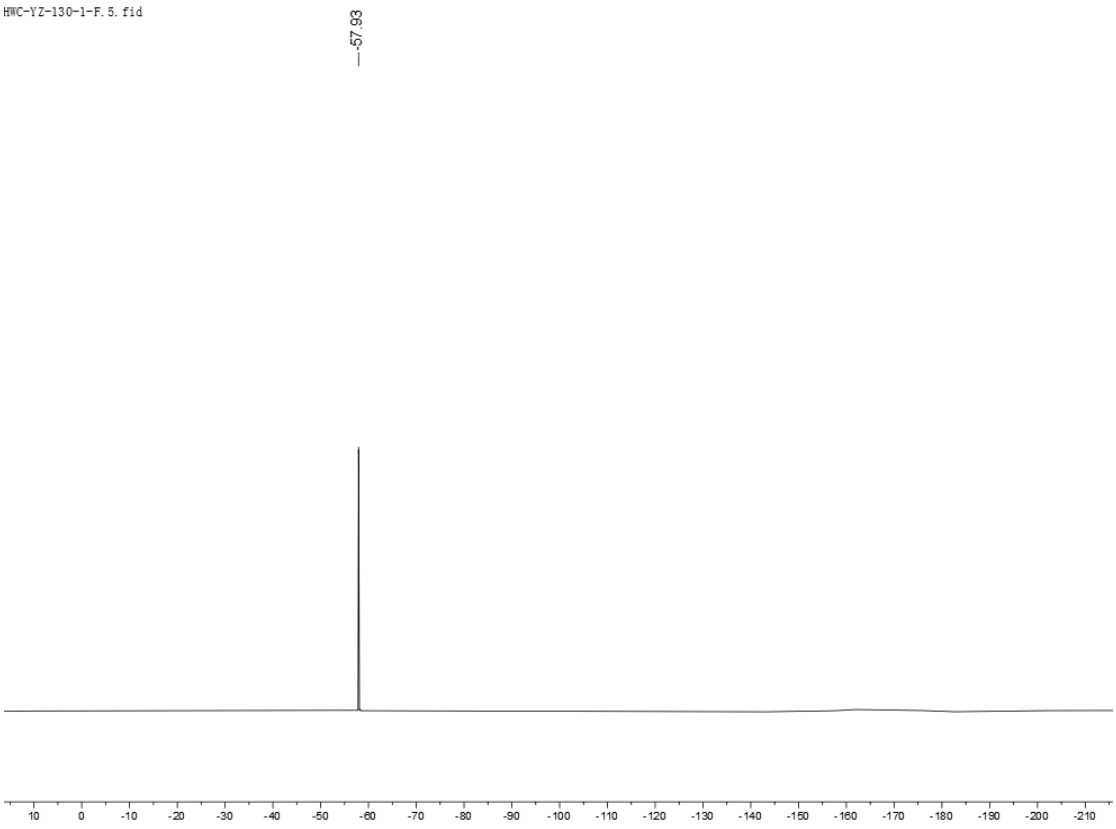
^{19}F NMR (565 MHz, $CDCl_3$) of 15



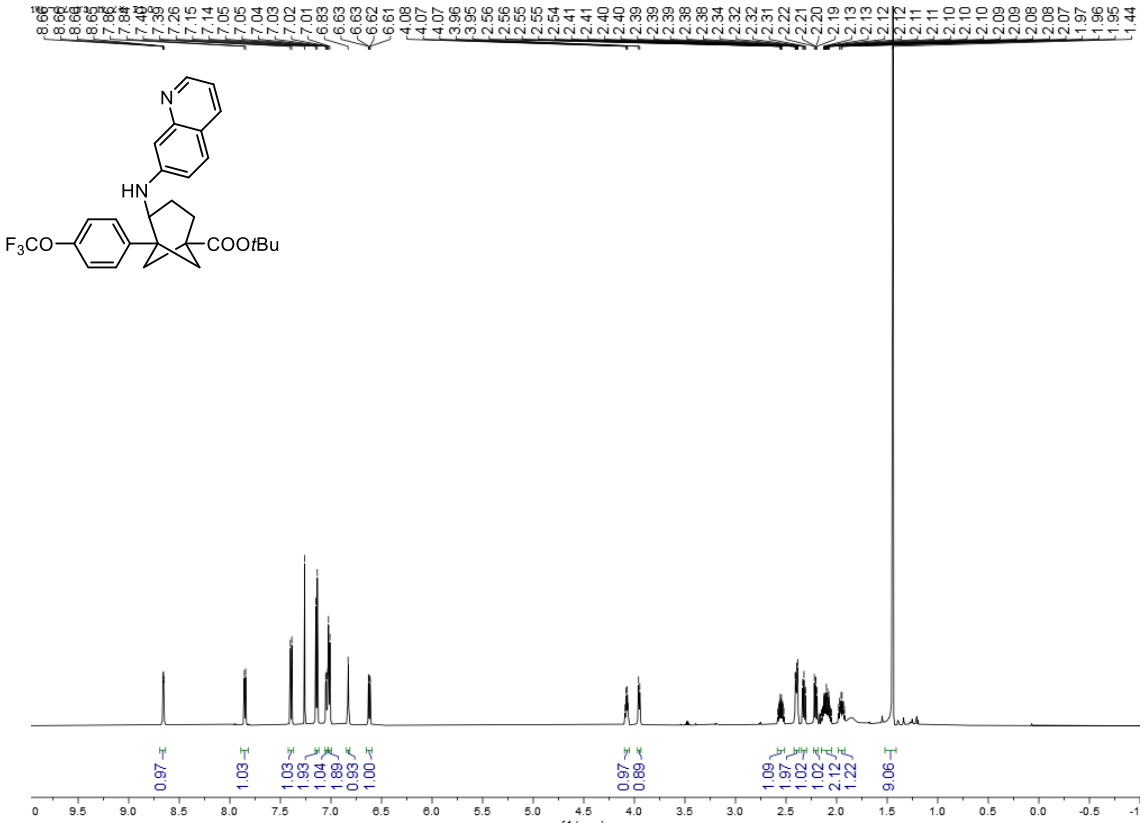
^{1}H NMR (600 MHz, $CDCl_3$) of 16



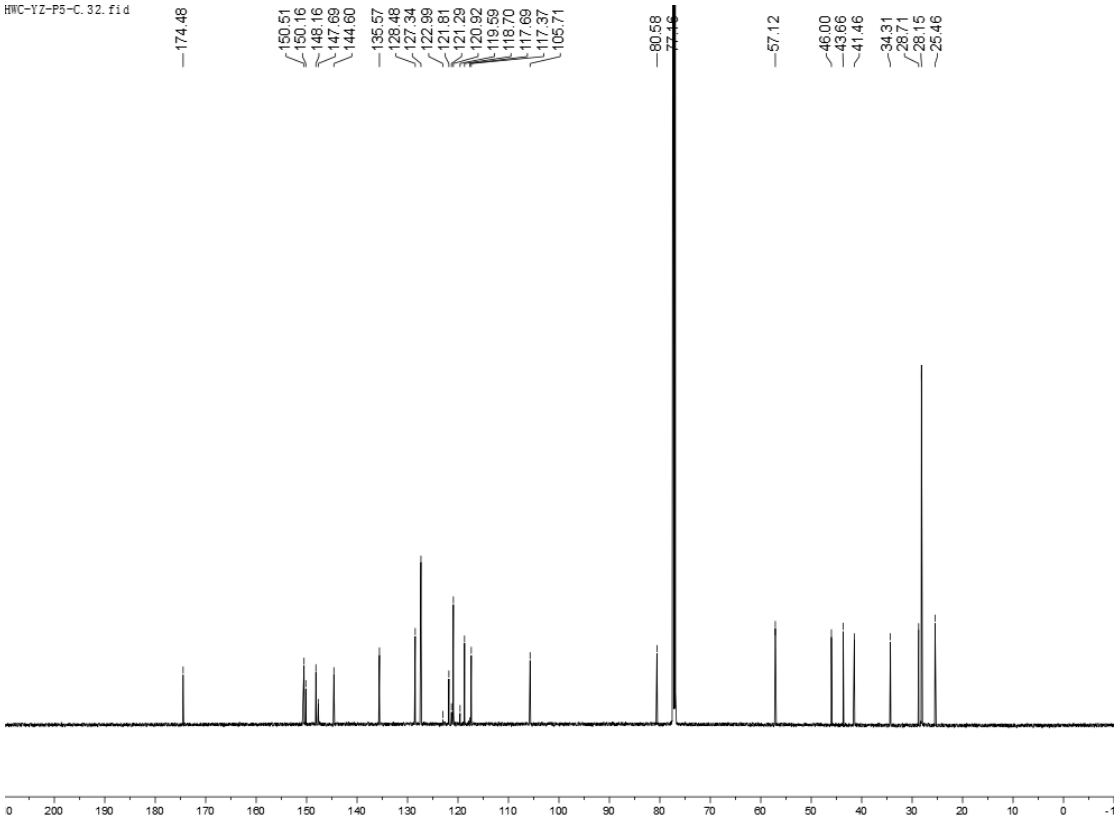
^{13}C NMR (151 MHz, $CDCl_3$) of 16



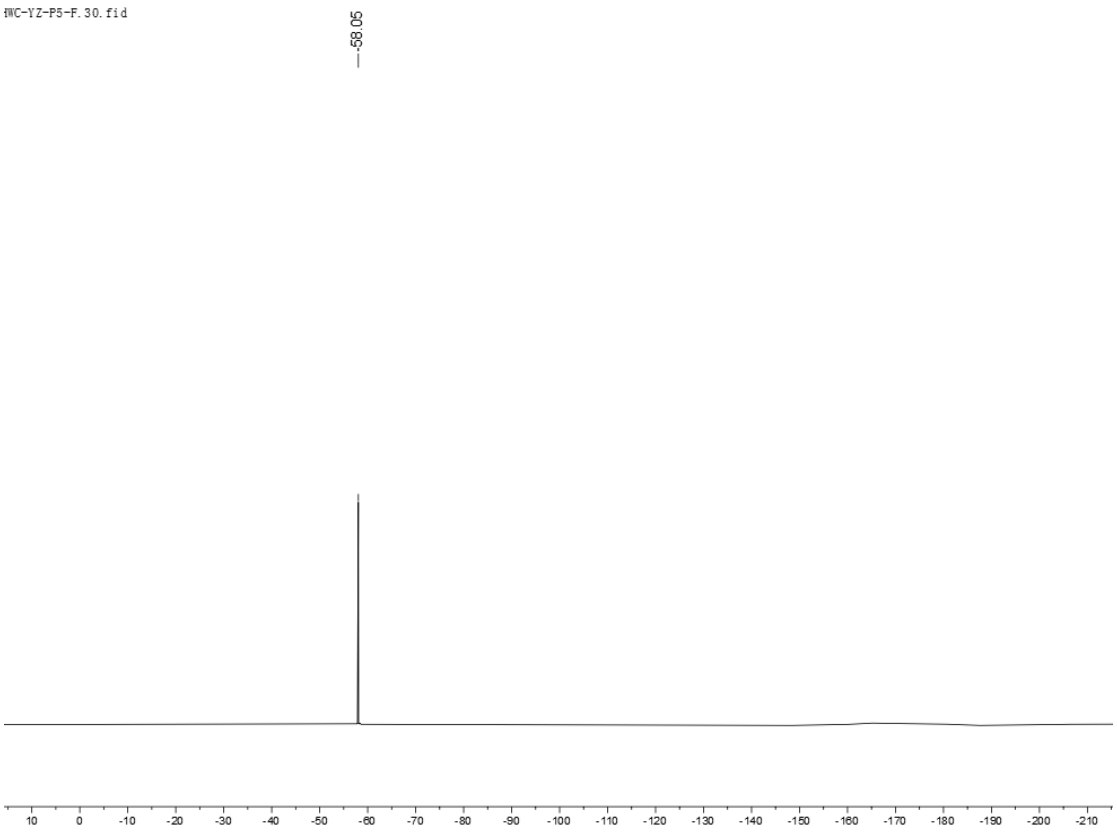
^{19}F NMR (565 MHz, $CDCl_3$) of 16



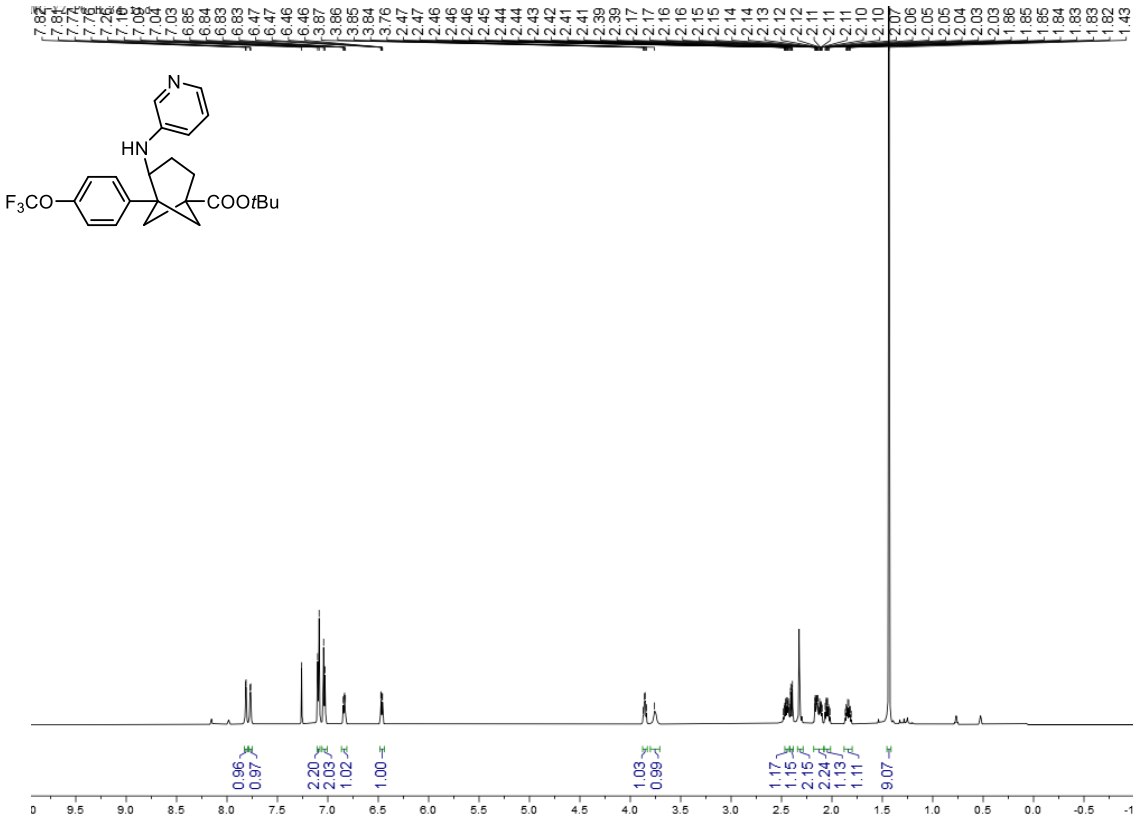
^{1}H NMR (600 MHz, $CDCl_3$) of 17



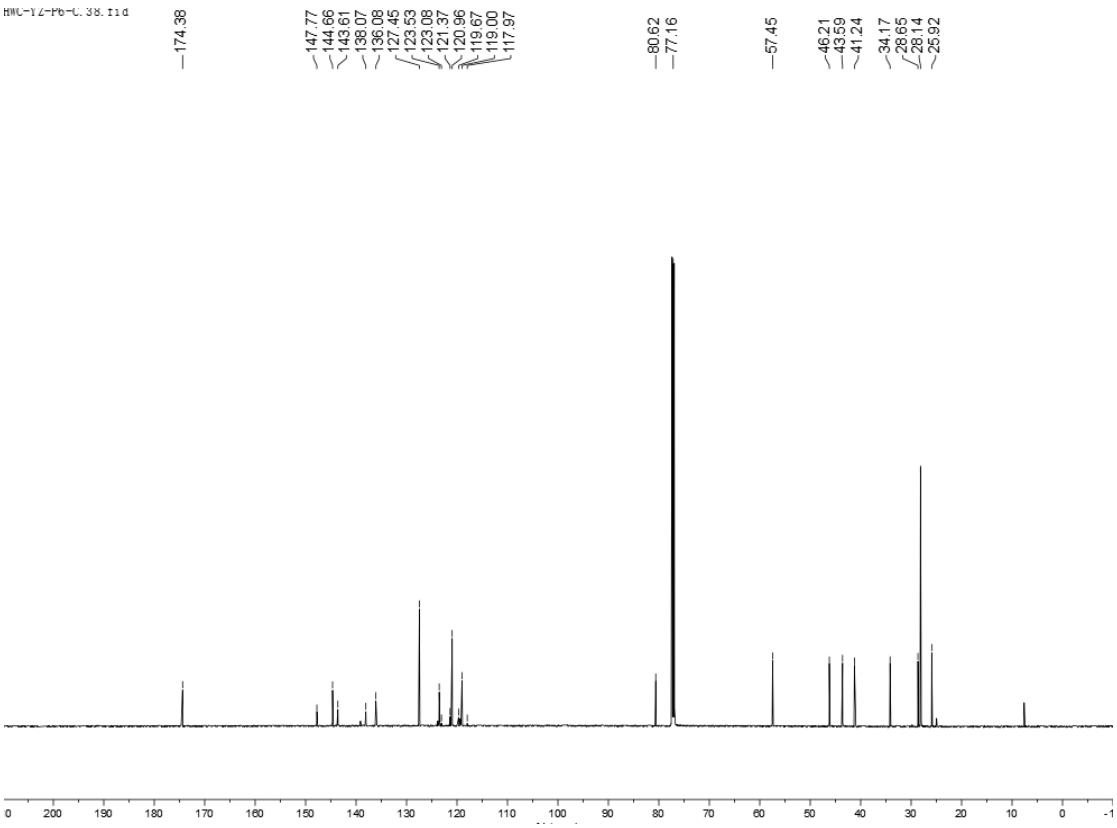
^{13}C NMR (151 MHz, $CDCl_3$) of 17



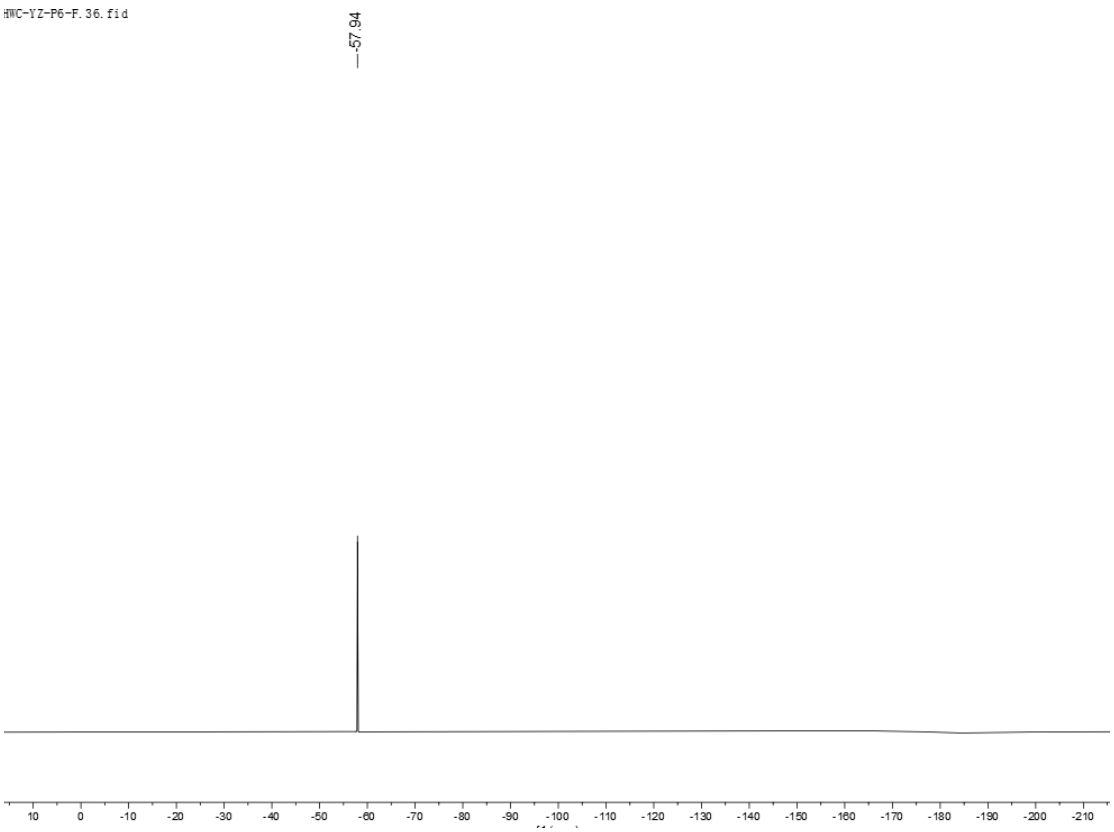
^{19}F NMR (565 MHz, $CDCl_3$) of 17



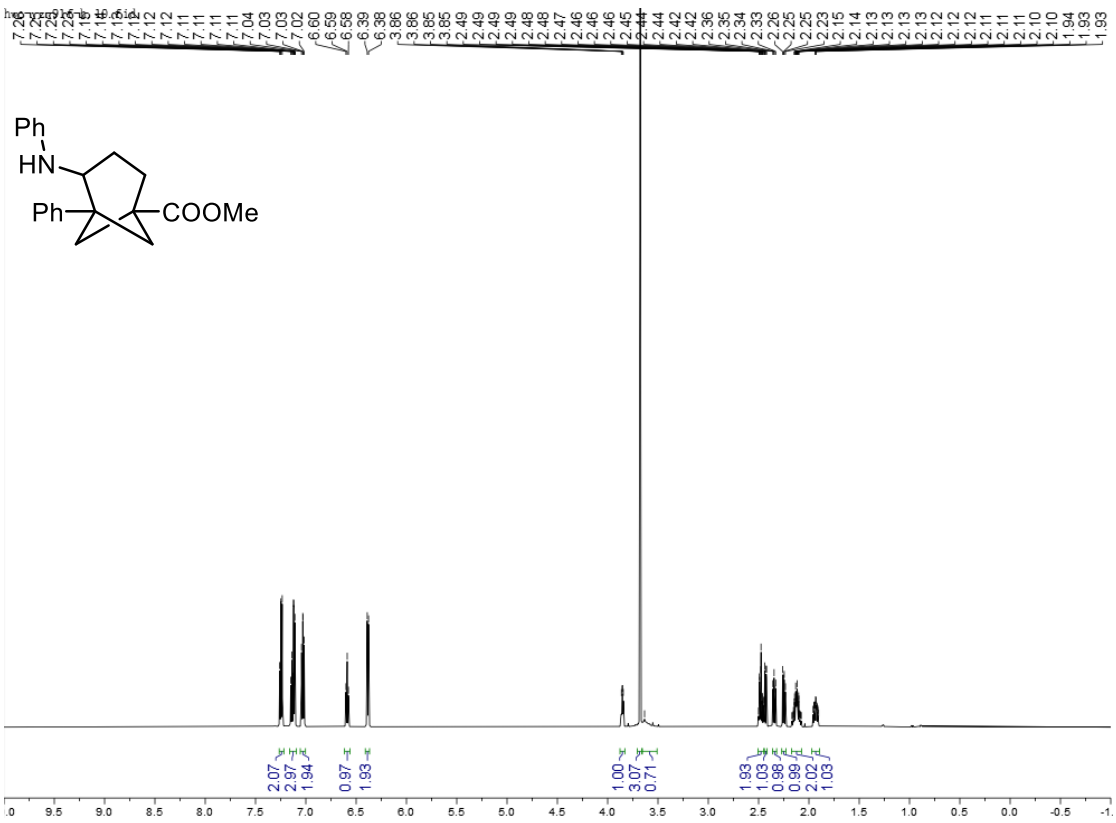
^{1}H NMR (600 MHz, $CDCl_3$) of 18



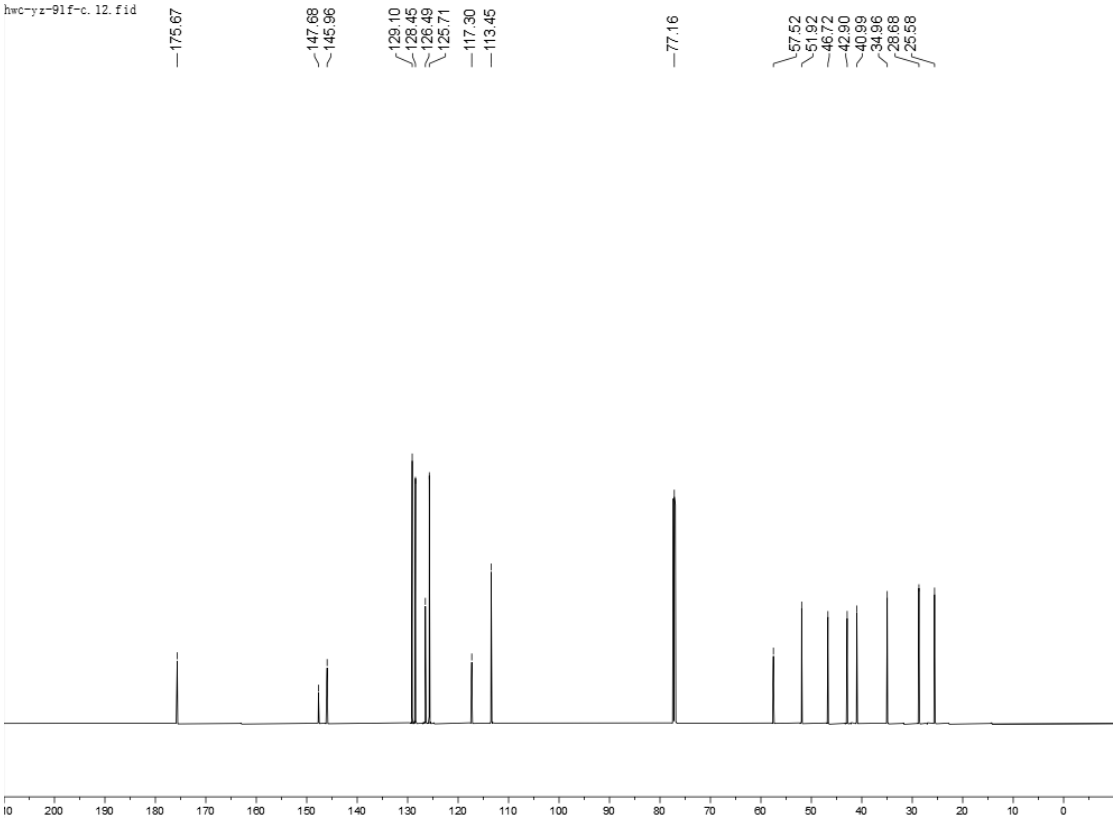
^{13}C NMR (151 MHz, $CDCl_3$) of 18



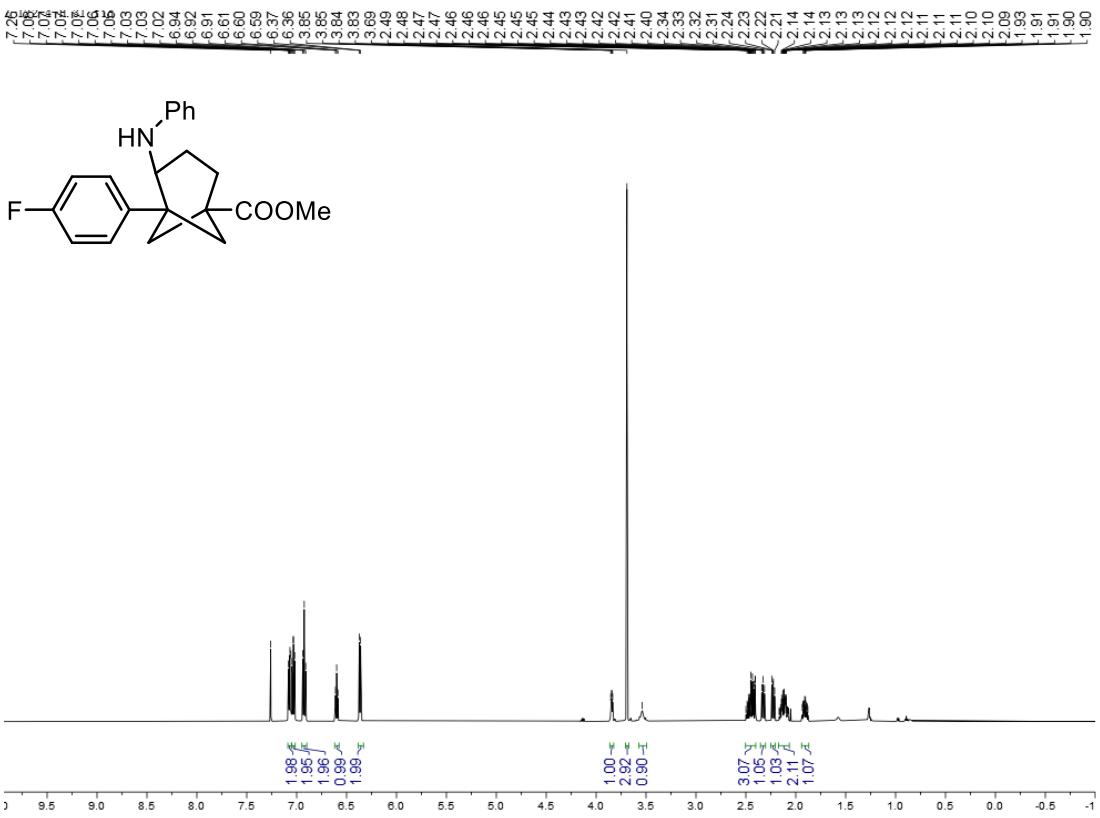
^{19}F NMR (565 MHz, $CDCl_3$) of 18



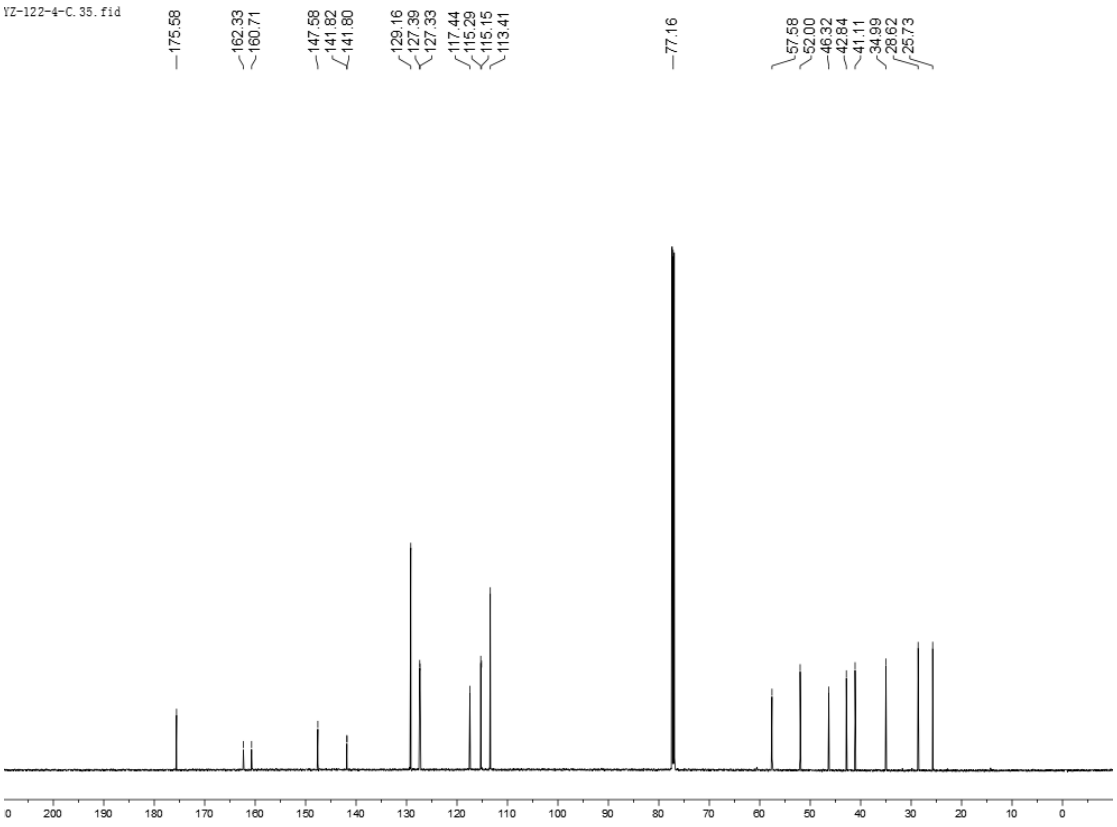
^{1}H NMR (600 MHz, $CDCl_3$) of 19



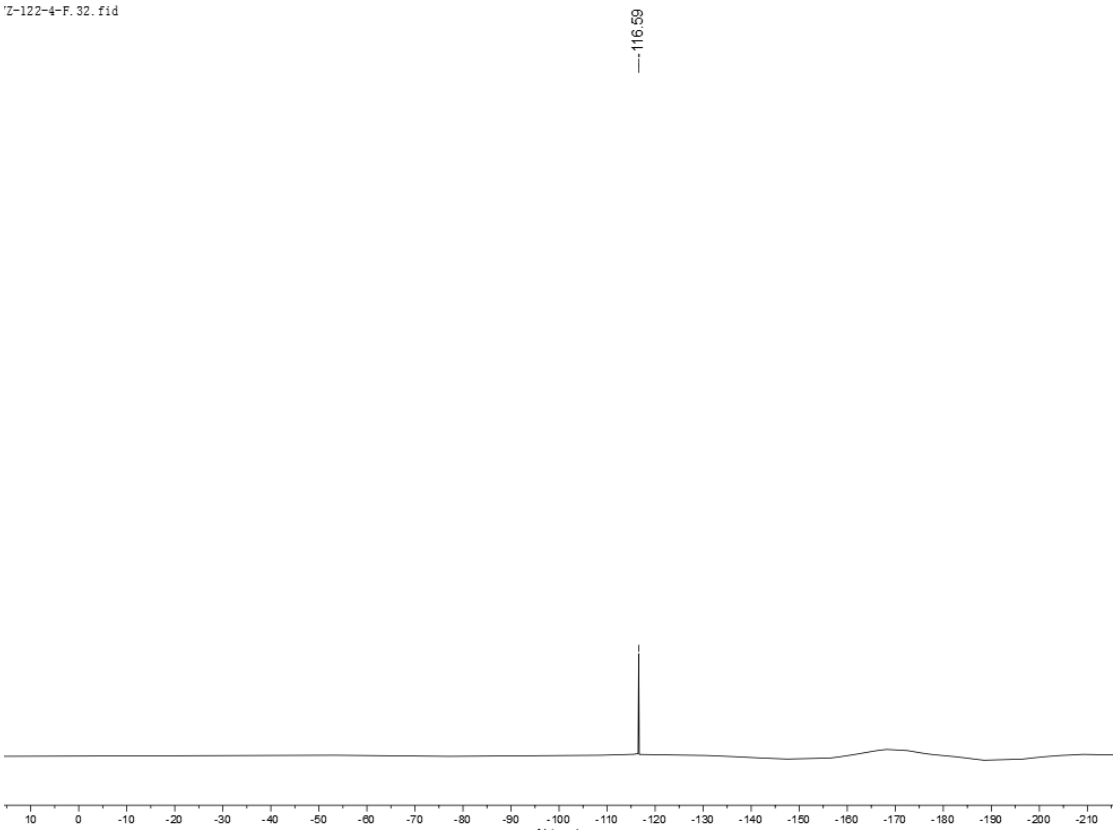
^{13}C NMR (151 MHz, $CDCl_3$) of 19



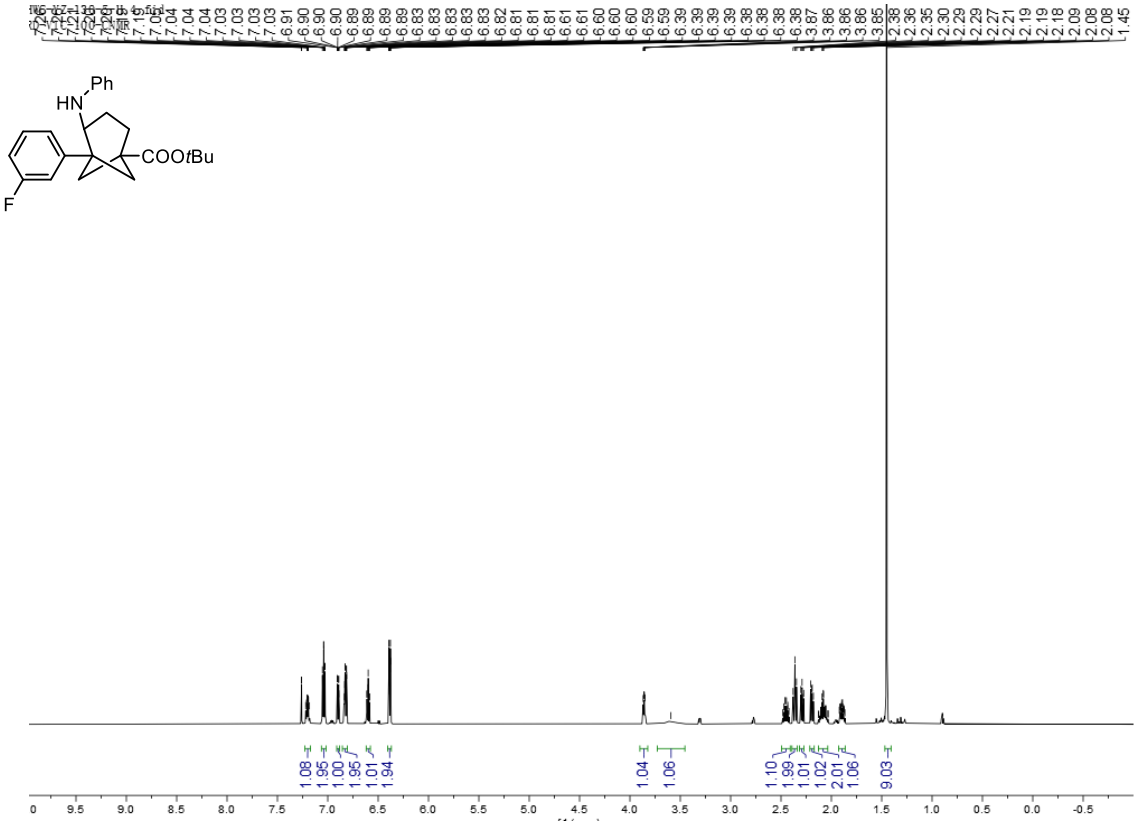
^{1}H NMR (600 MHz, $CDCl_3$) of 20



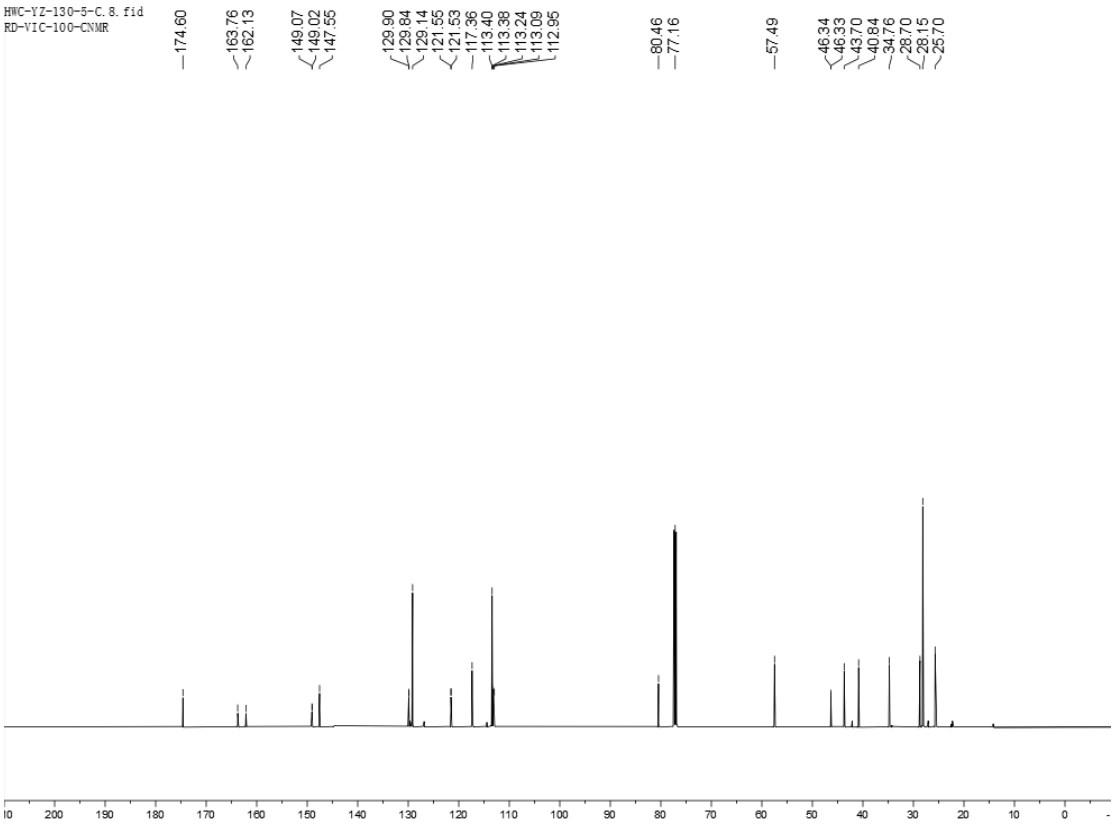
^{13}C NMR (151 MHz, $CDCl_3$) of 20



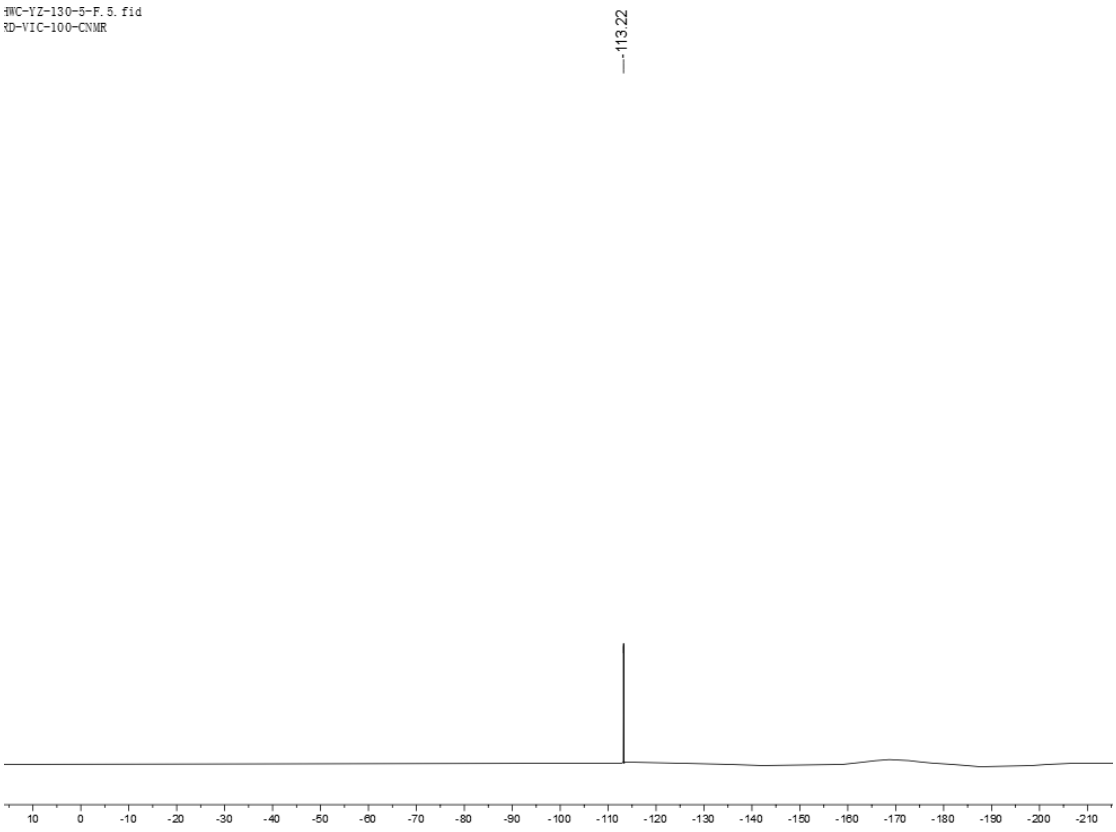
^{19}F NMR (565 MHz, $CDCl_3$) of 20



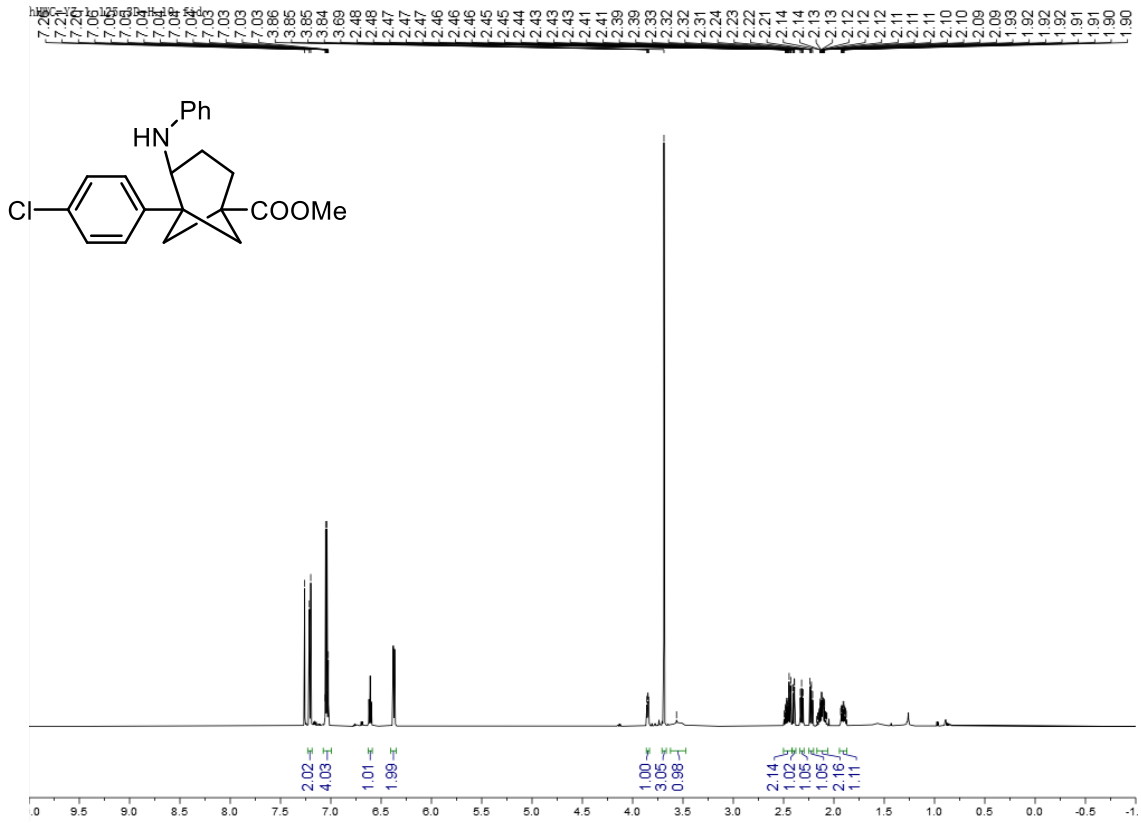
^{1}H NMR (600 MHz, $CDCl_3$) of 21



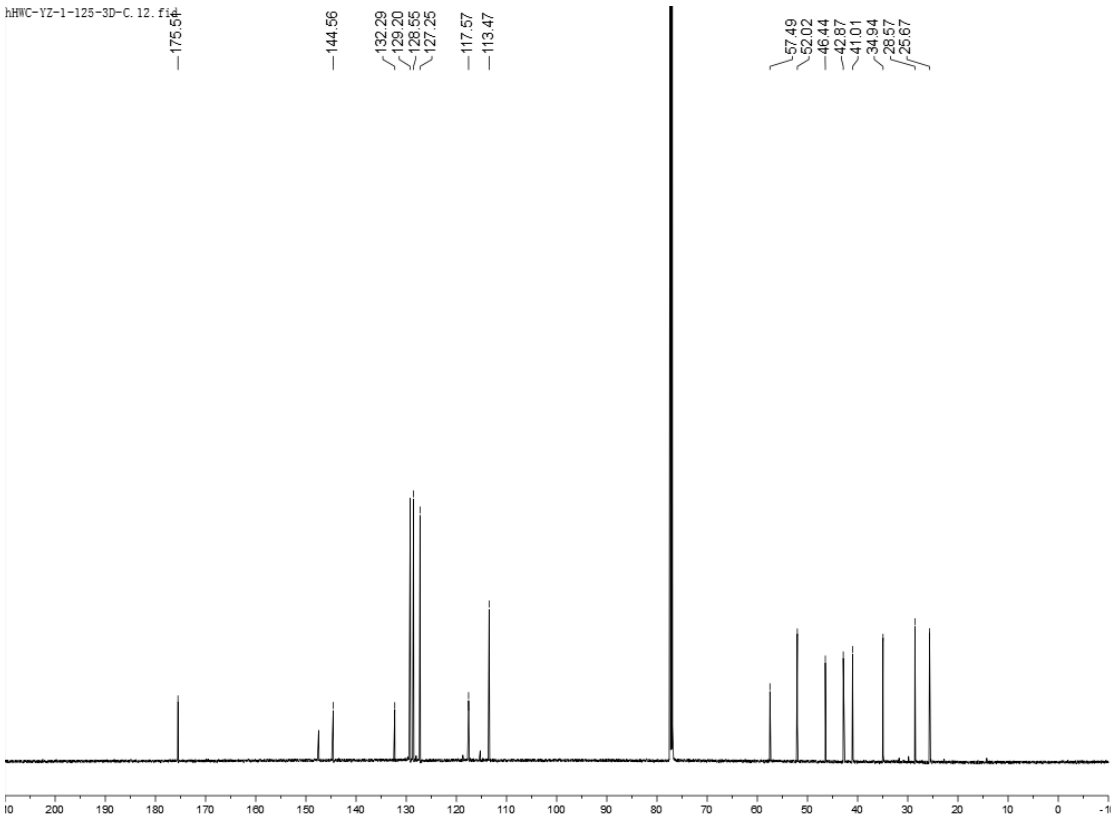
^{13}C NMR (151 MHz, $CDCl_3$) of 21



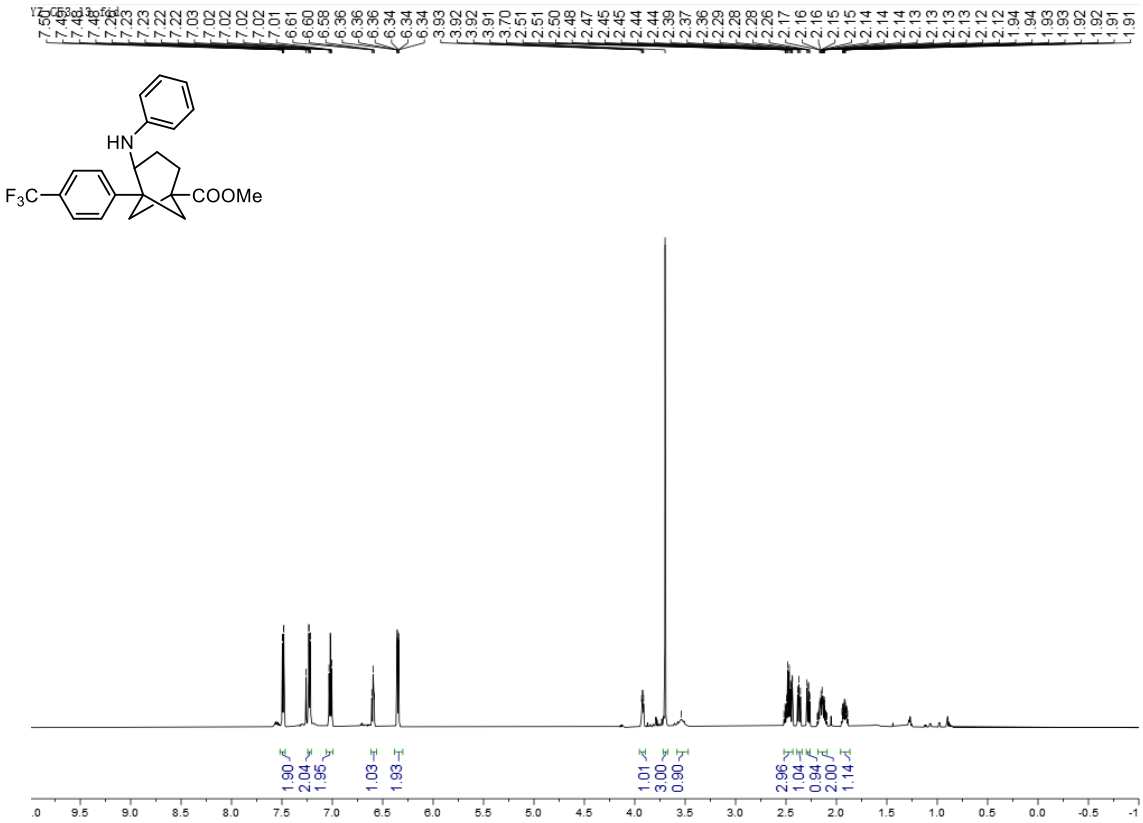
^{19}F NMR (565 MHz, $CDCl_3$) of 21



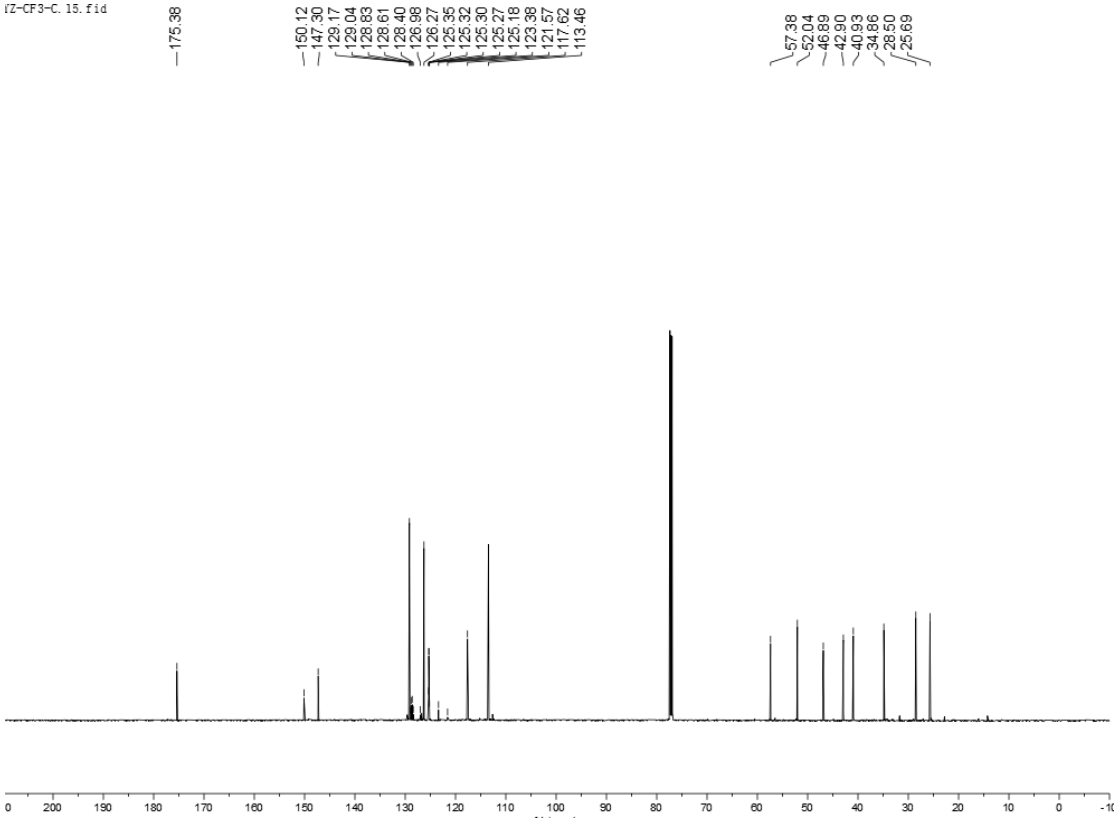
^{1}H NMR (600 MHz, $CDCl_3$) of 22



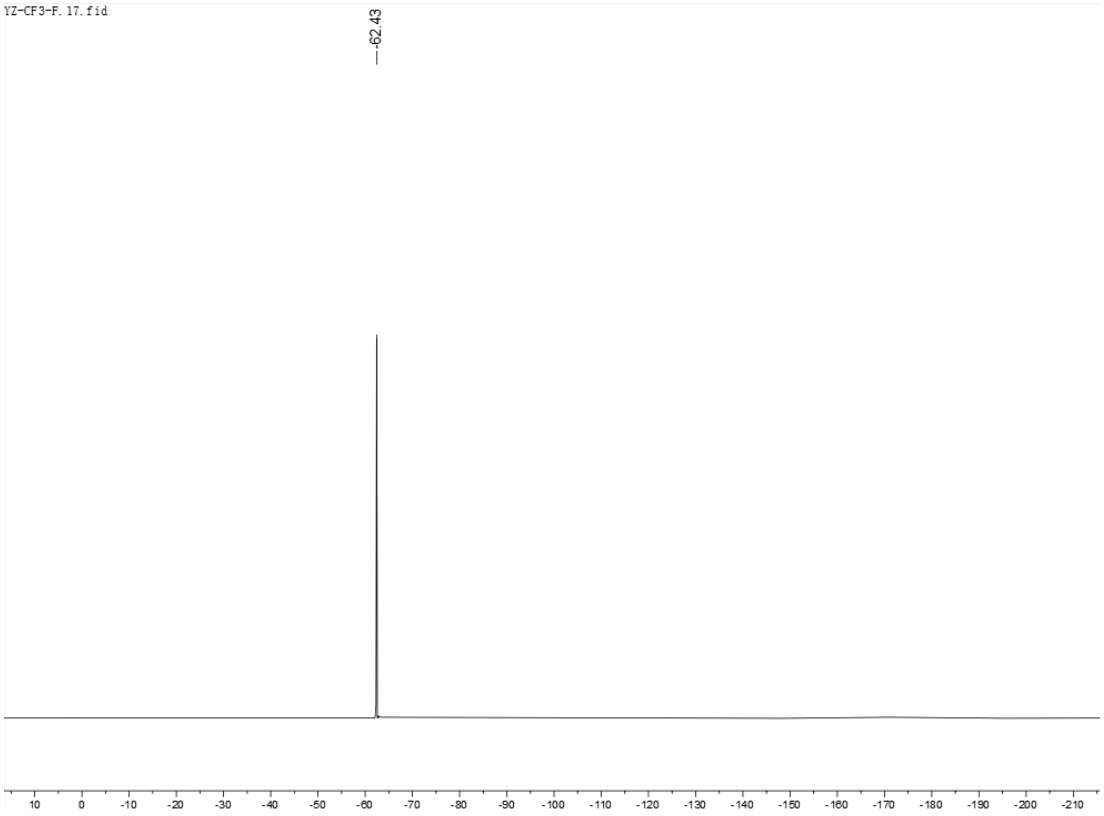
^{13}C NMR (151 MHz, $CDCl_3$) of 22



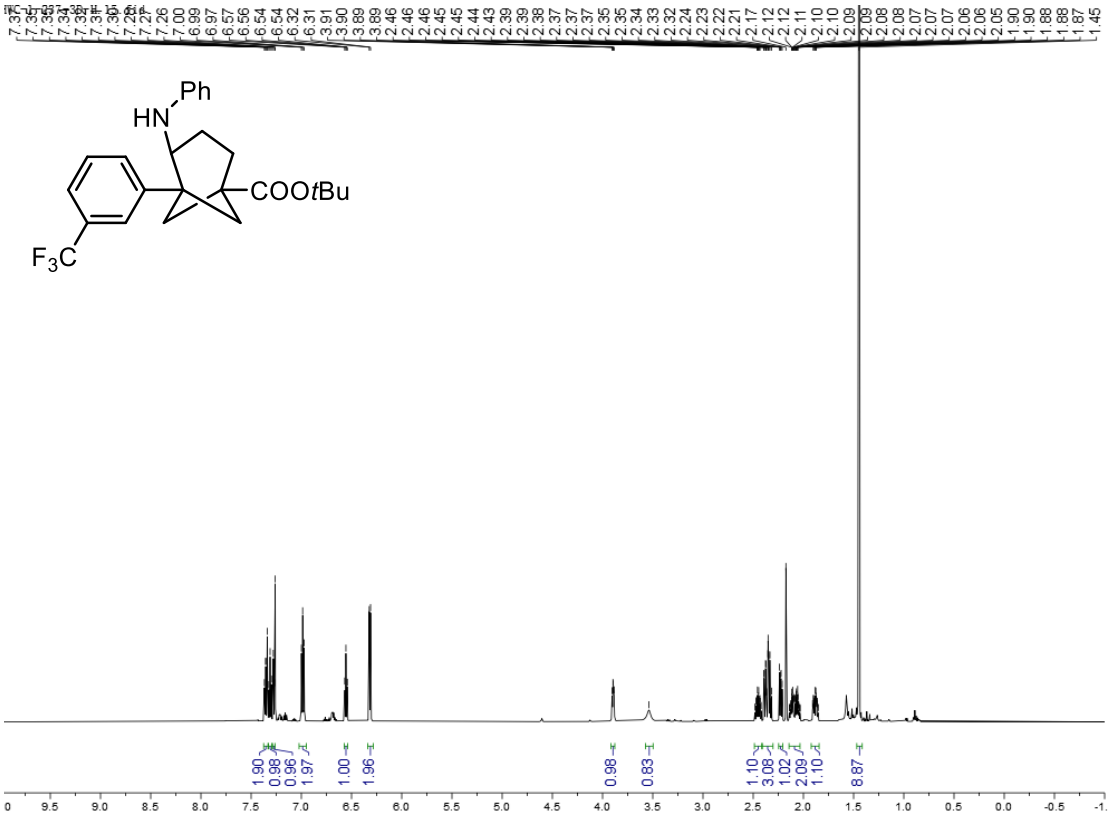
^{1}H NMR (600 MHz, $CDCl_3$) of 23



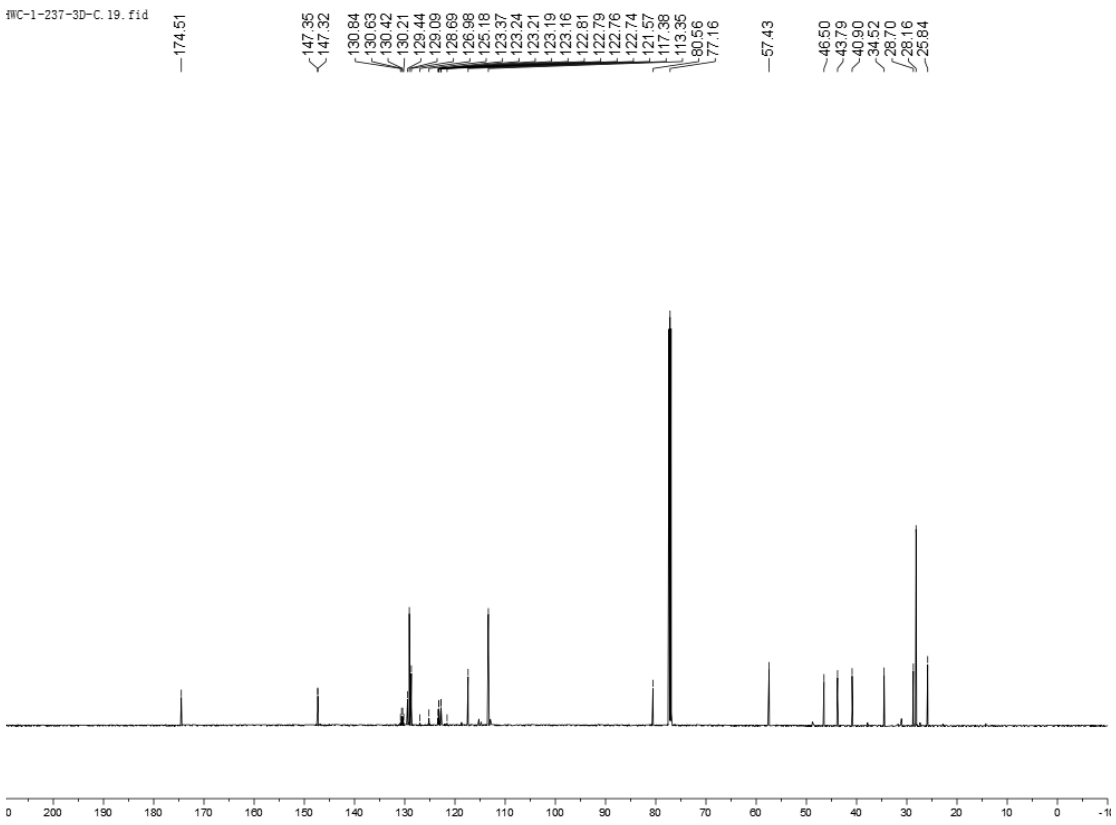
^{13}C NMR (151 MHz, $CDCl_3$) of 23



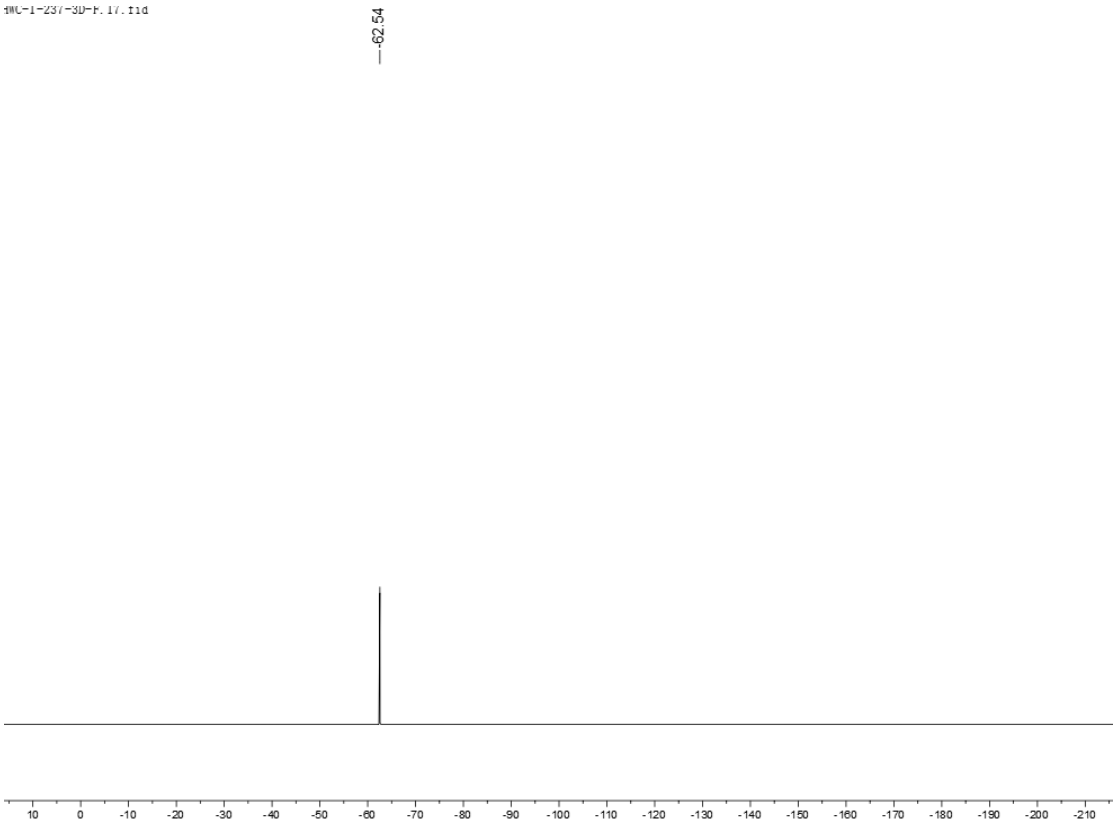
^{19}F NMR (565 MHz, $CDCl_3$) of 23



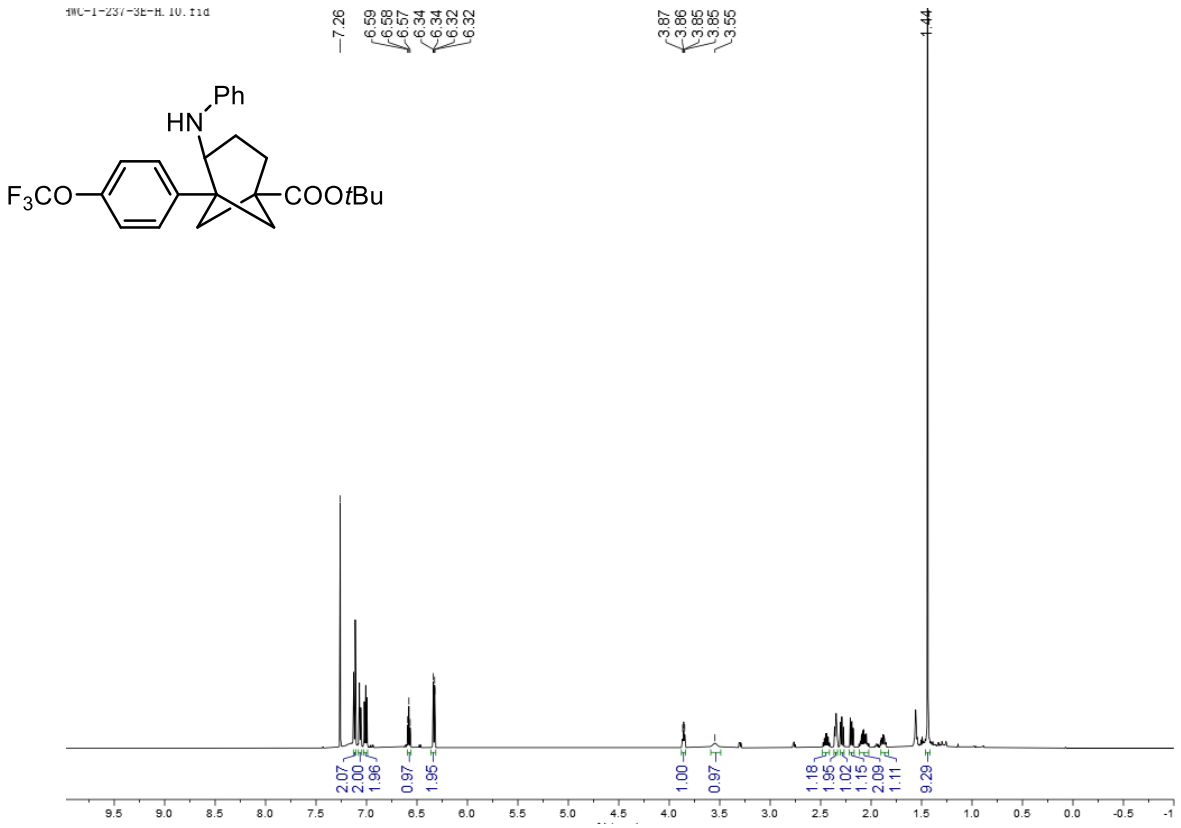
^{1}H NMR (600 MHz, $CDCl_3$) of 24



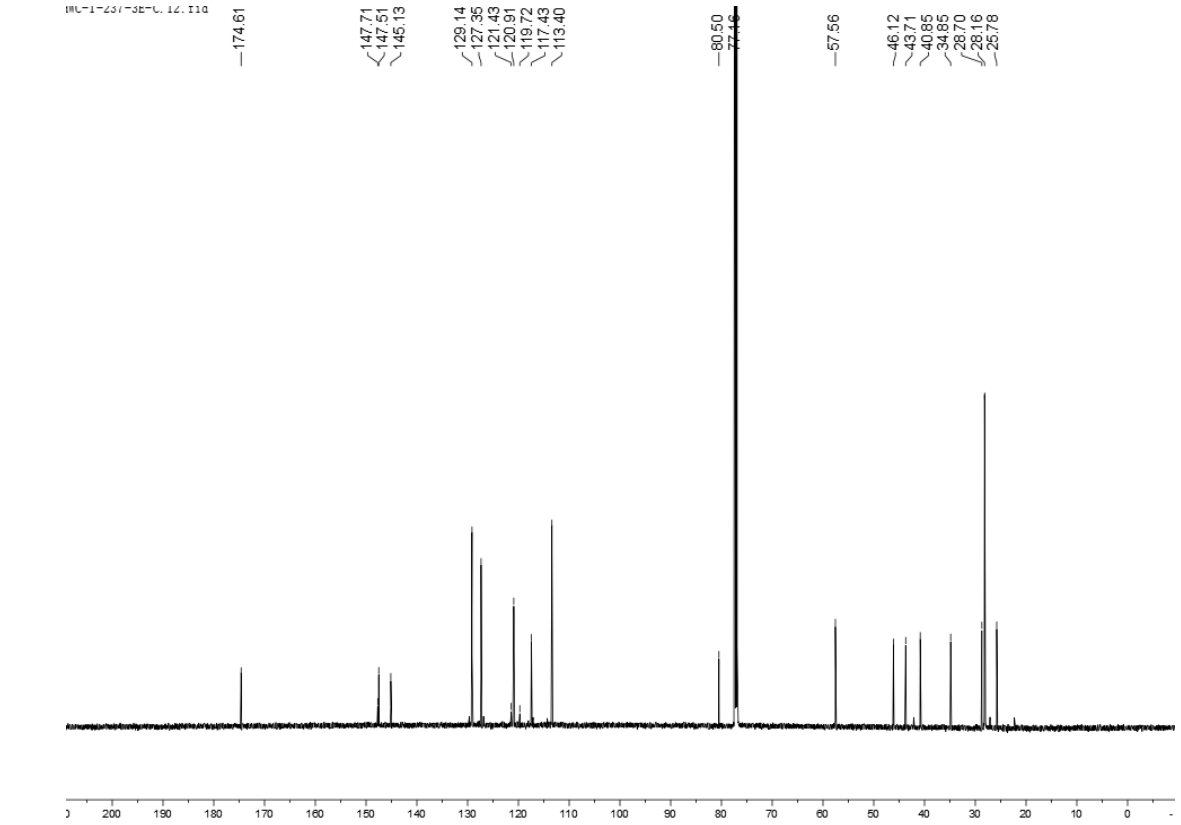
^{13}C NMR (151 MHz, $CDCl_3$) of 24



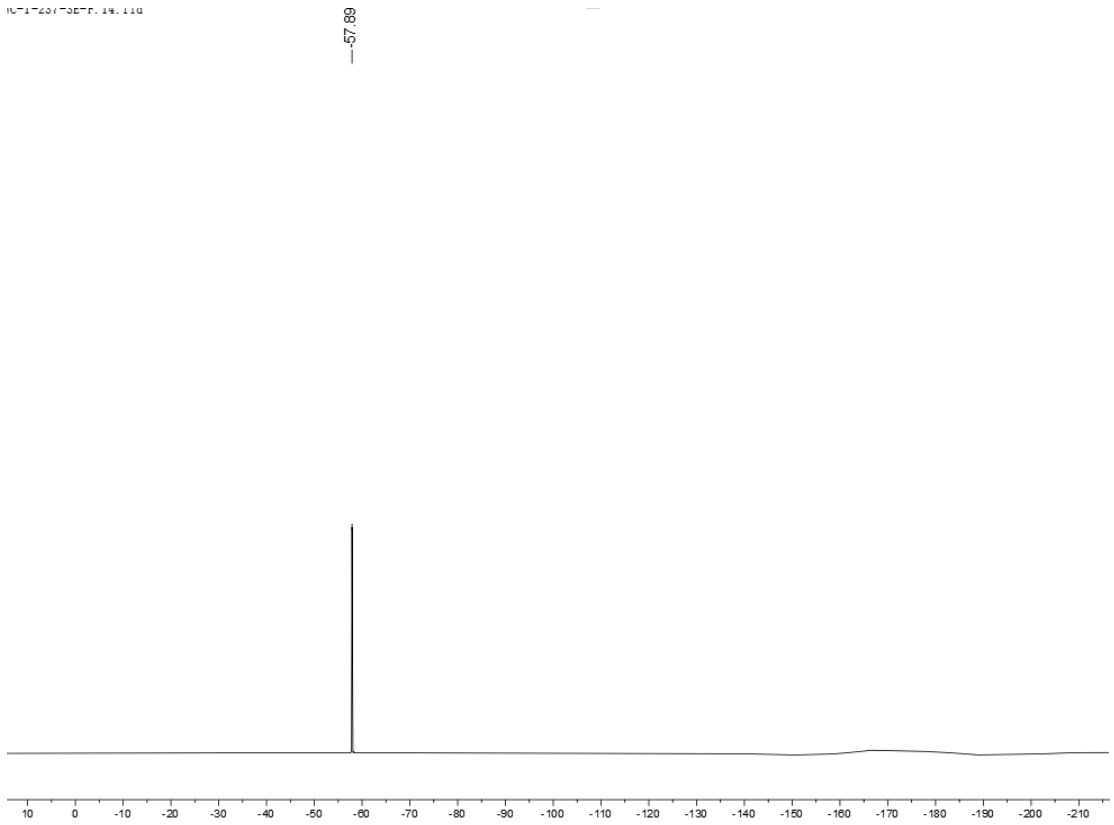
^{19}F NMR (565 MHz, $CDCl_3$) of 24



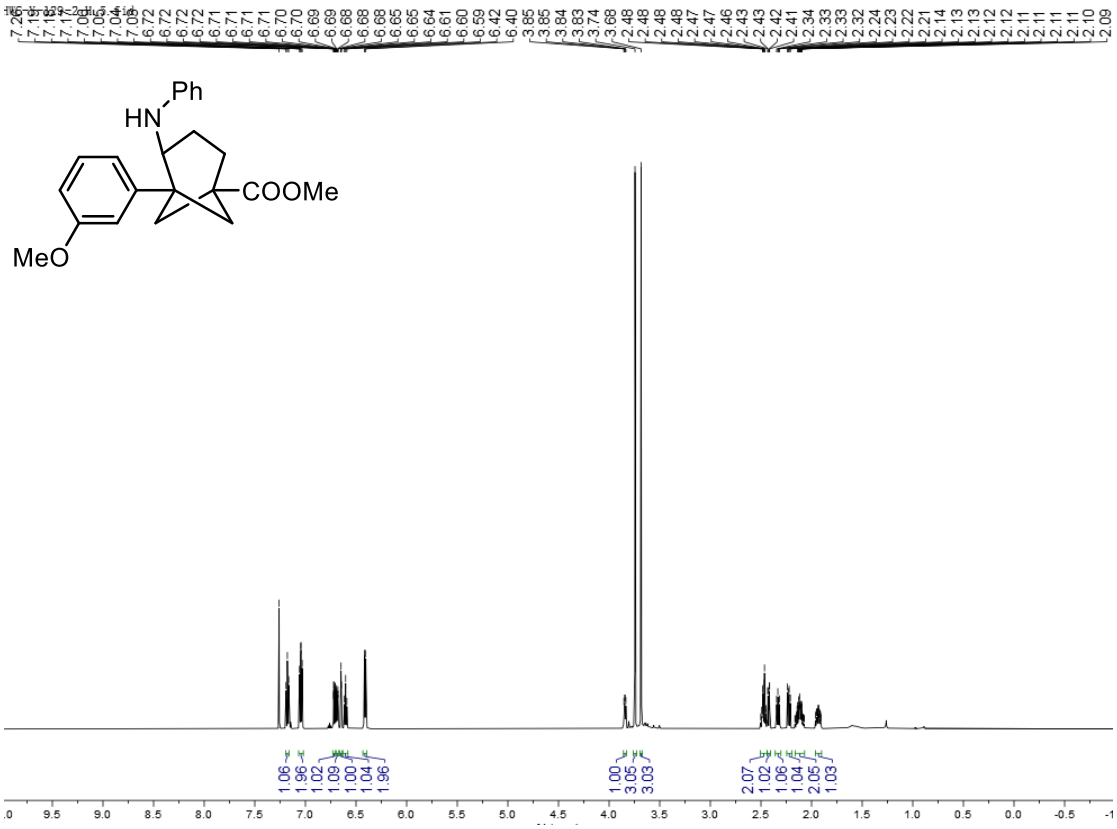
^{1}H NMR (600 MHz, $CDCl_3$) of 25



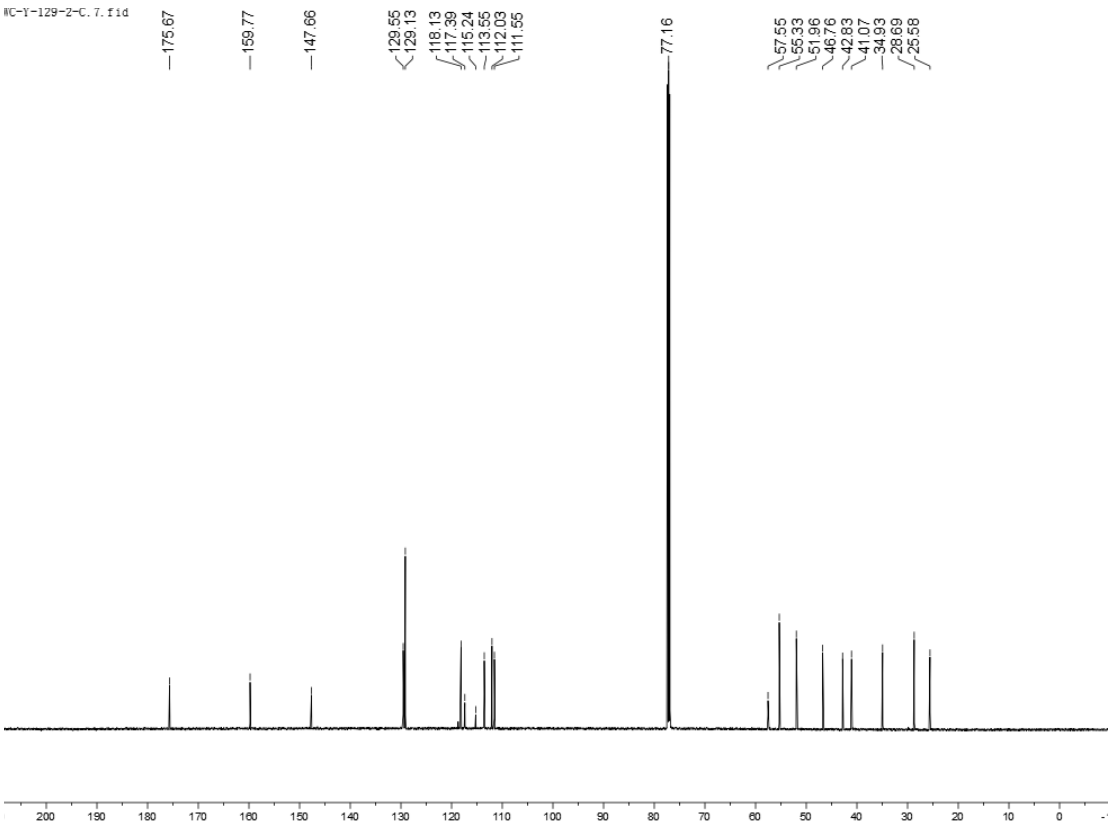
^{13}C NMR (151 MHz, $CDCl_3$) of 25



^{19}F NMR (565 MHz, $CDCl_3$) of 25



^{1}H NMR (600 MHz, $CDCl_3$) of 26



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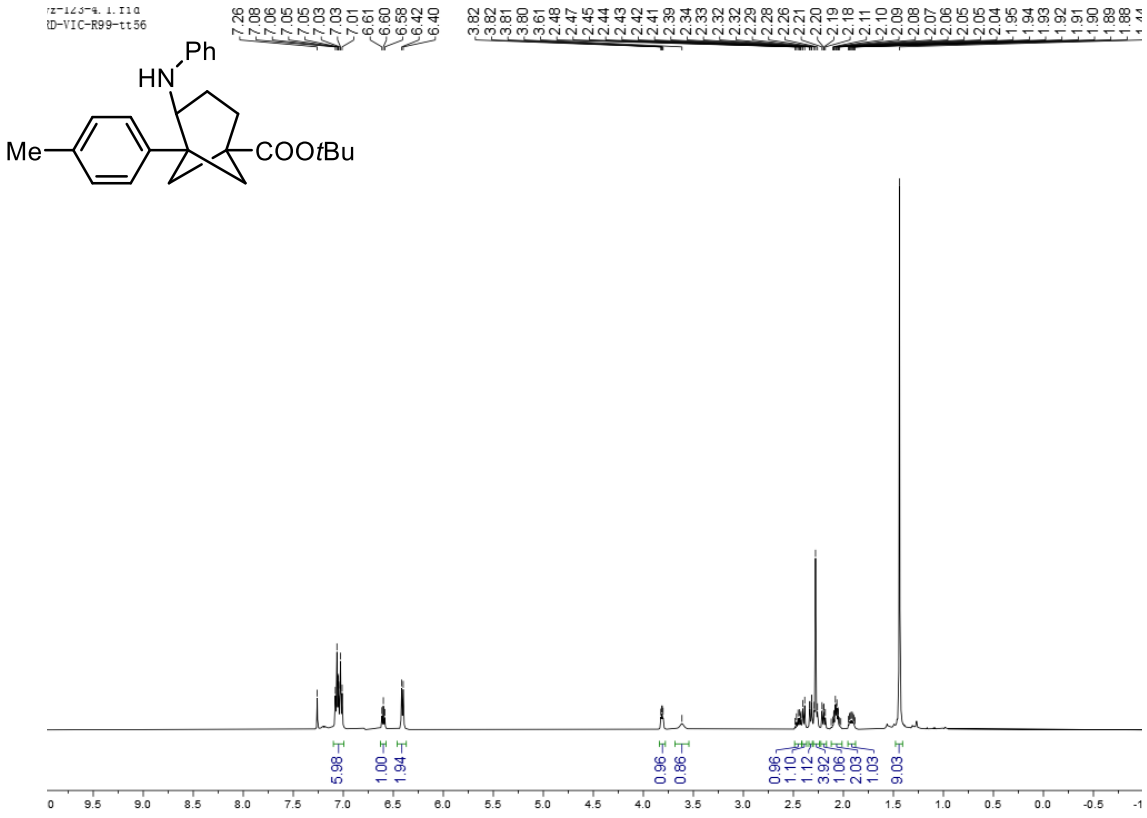
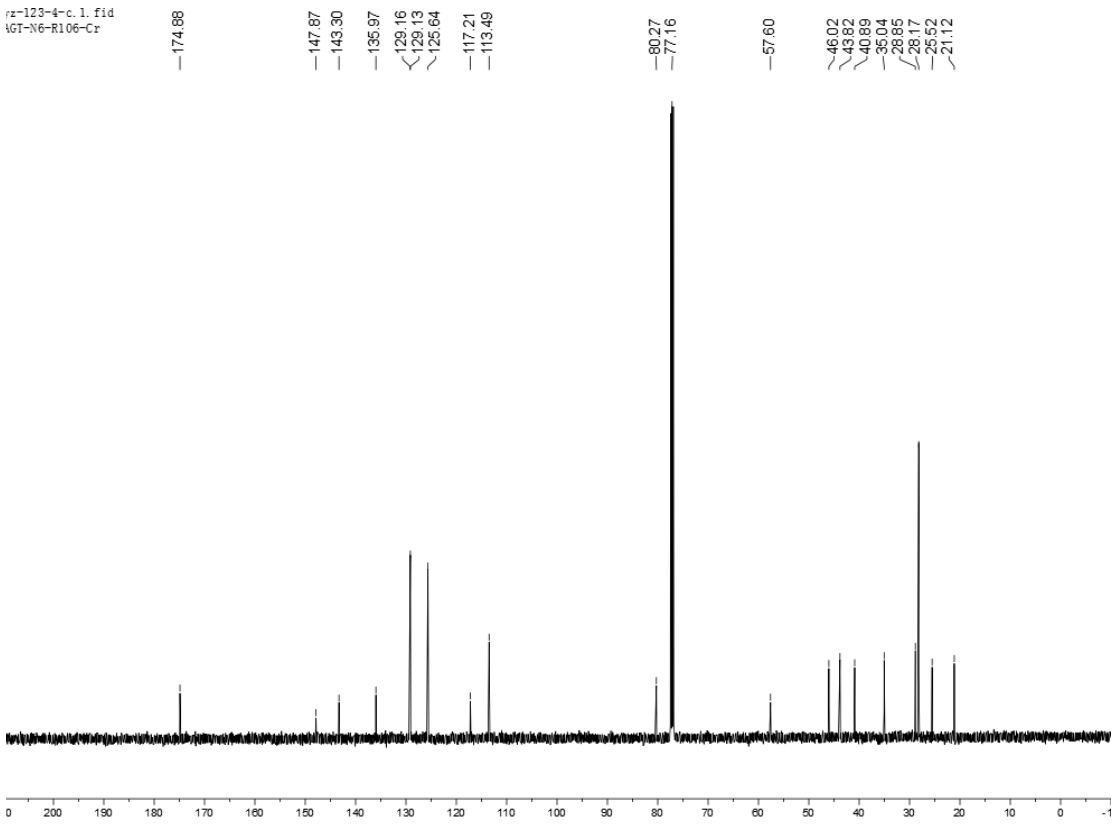
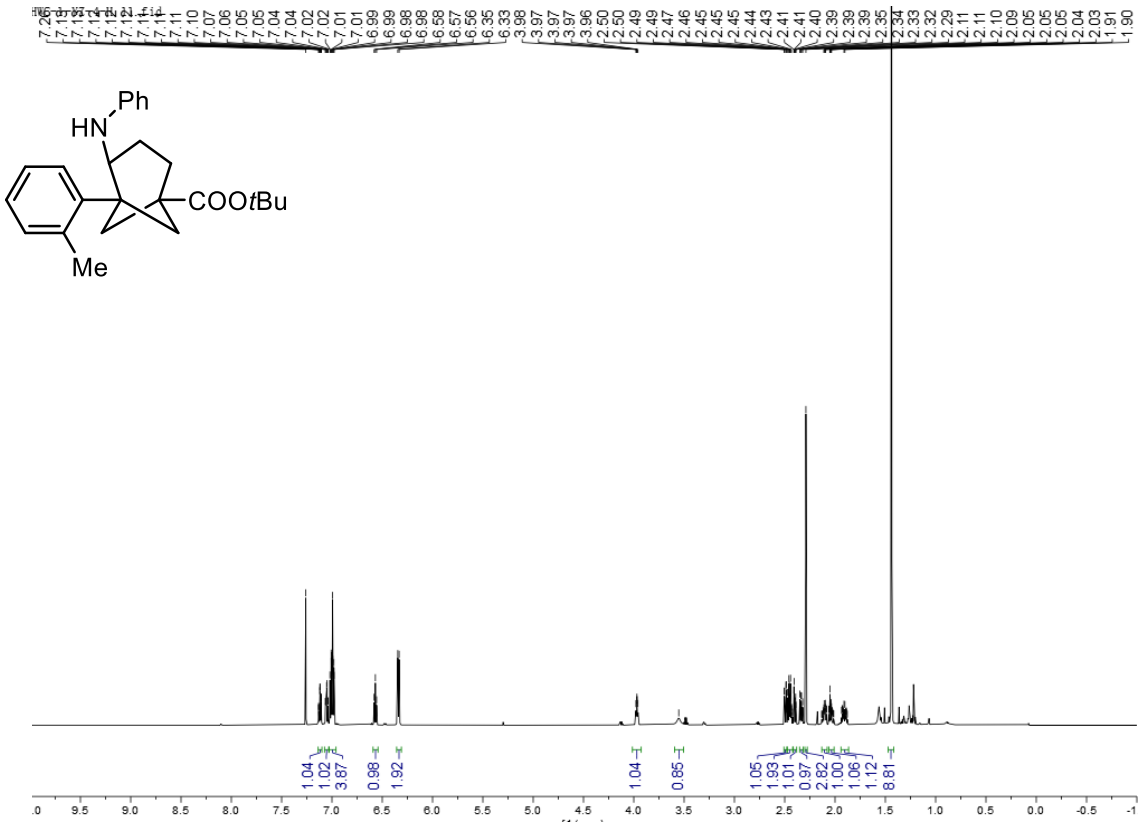


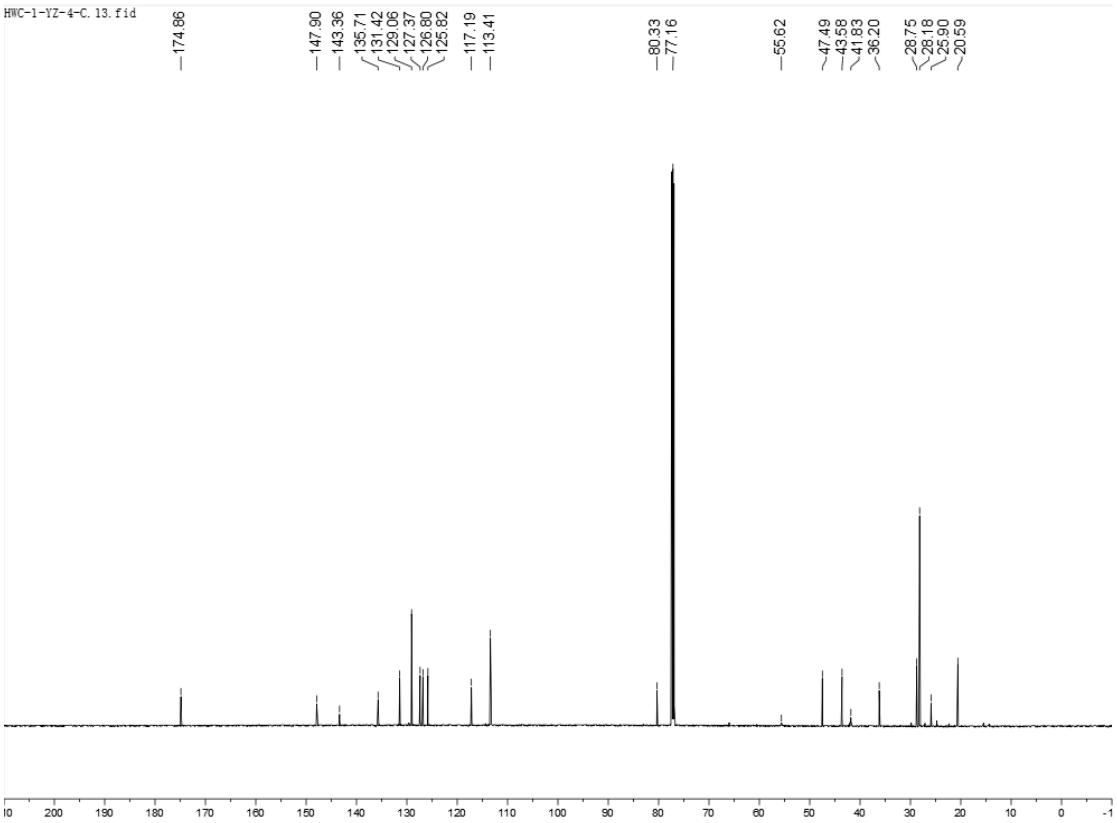
^{1}H NMR (600 MHz, $CDCl_3$) of 27



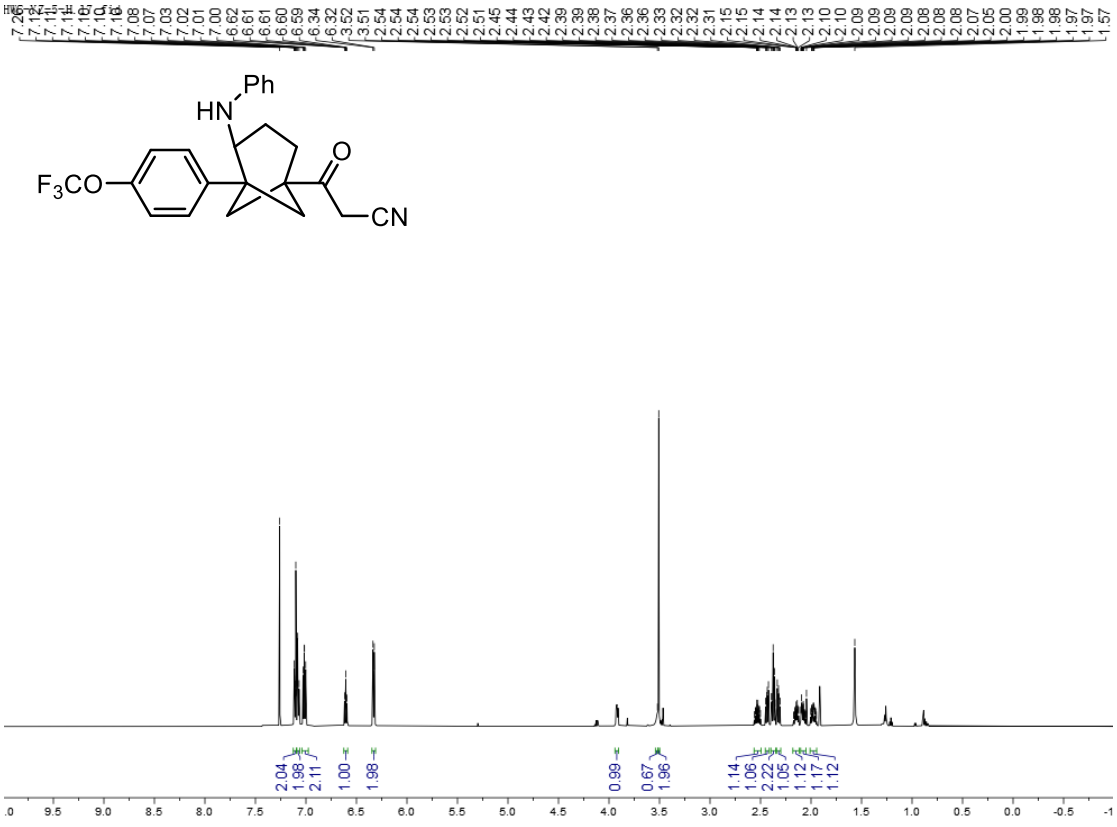
^{13}C NMR (151 MHz, $CDCl_3$) of 27



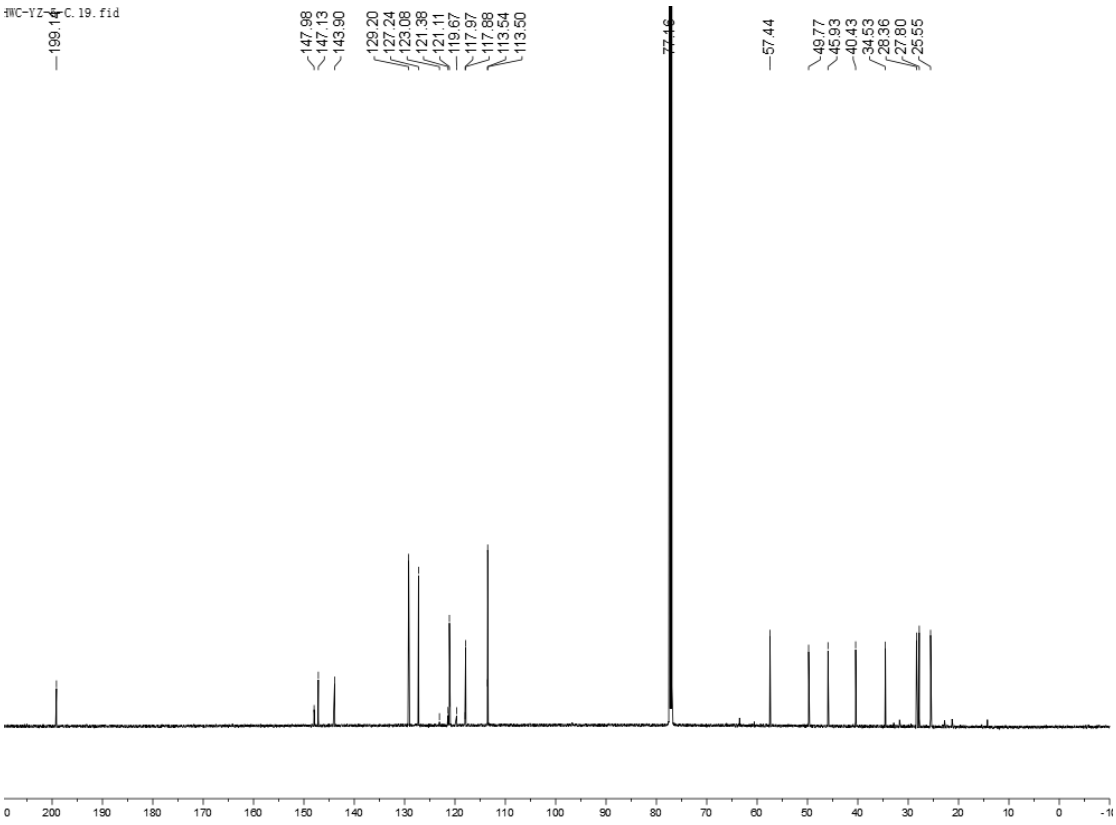
^{1}H NMR (600 MHz, $CDCl_3$) of 28



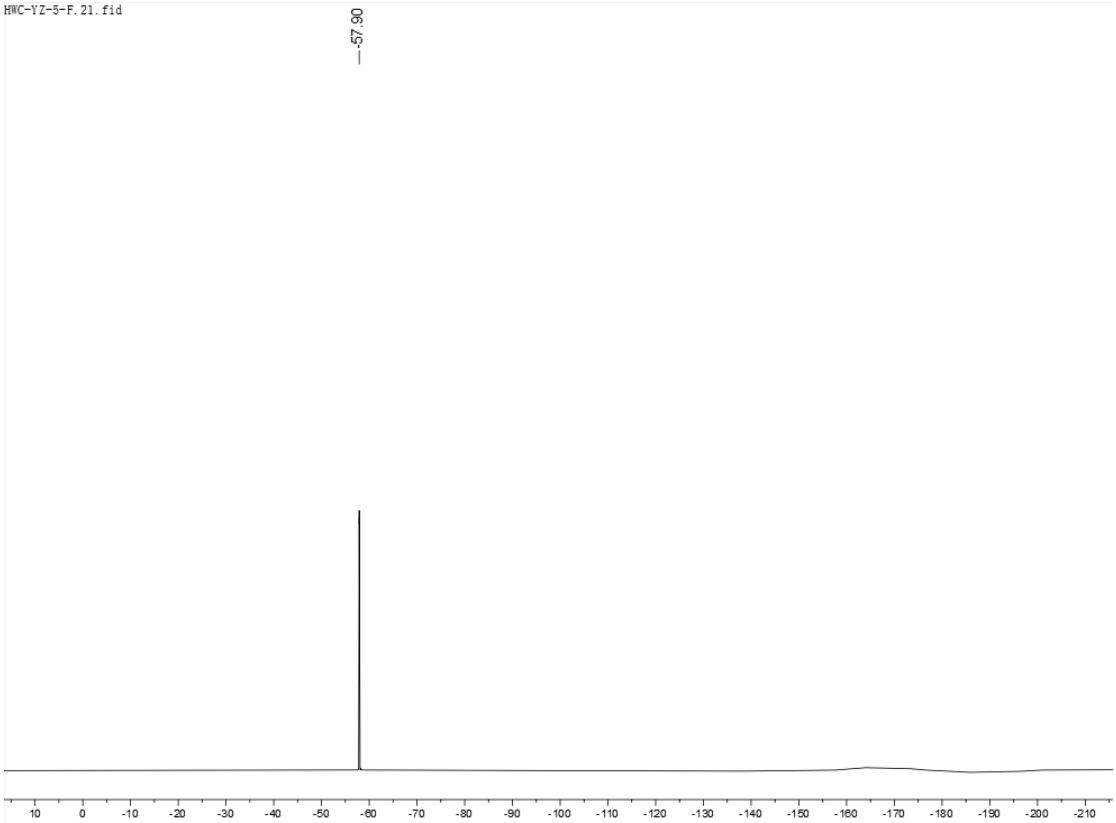
^{13}C NMR (151 MHz, $CDCl_3$) of 28



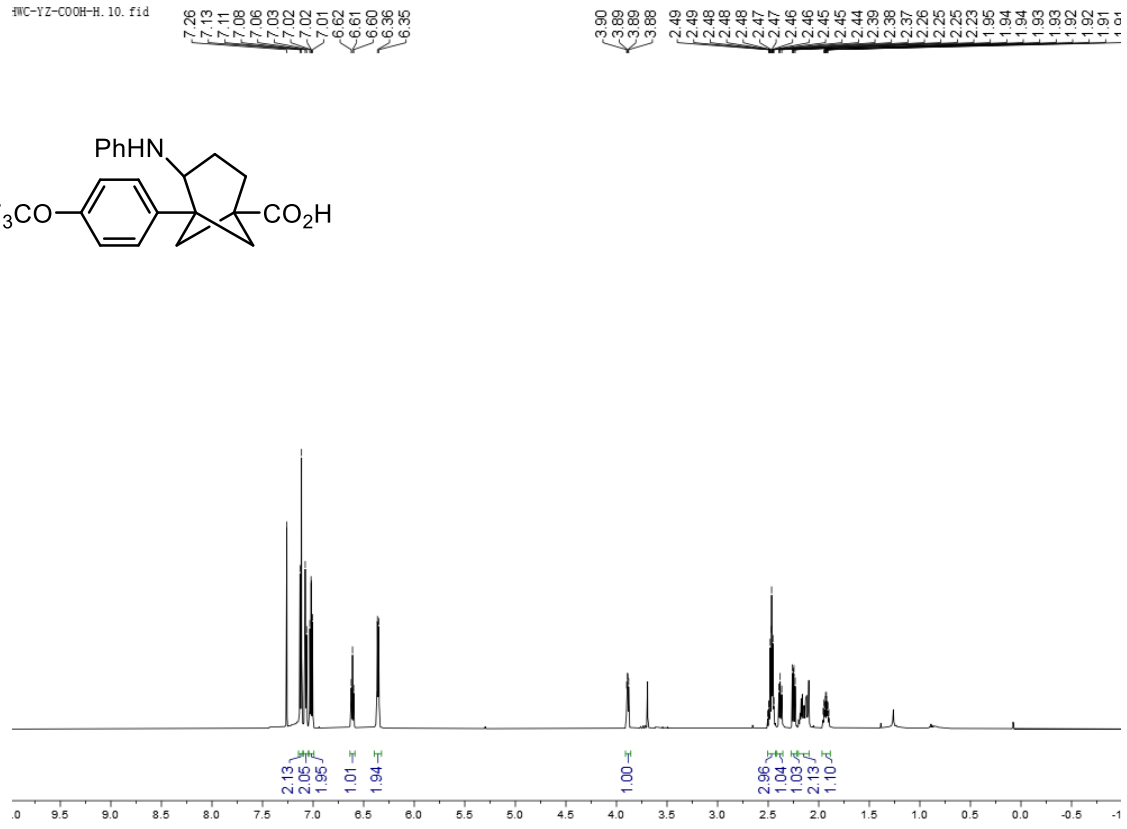
^{1}H NMR (600 MHz, $CDCl_3$) of 29



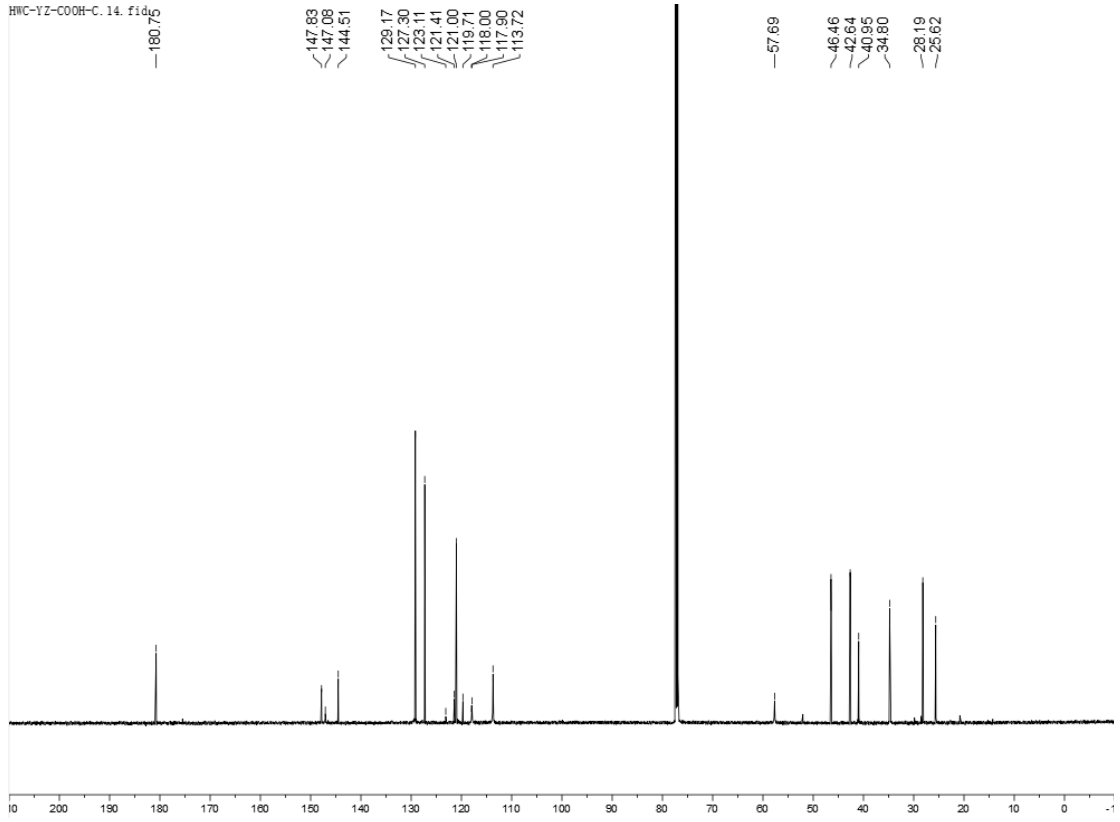
^{13}C NMR (151 MHz, $CDCl_3$) of 29



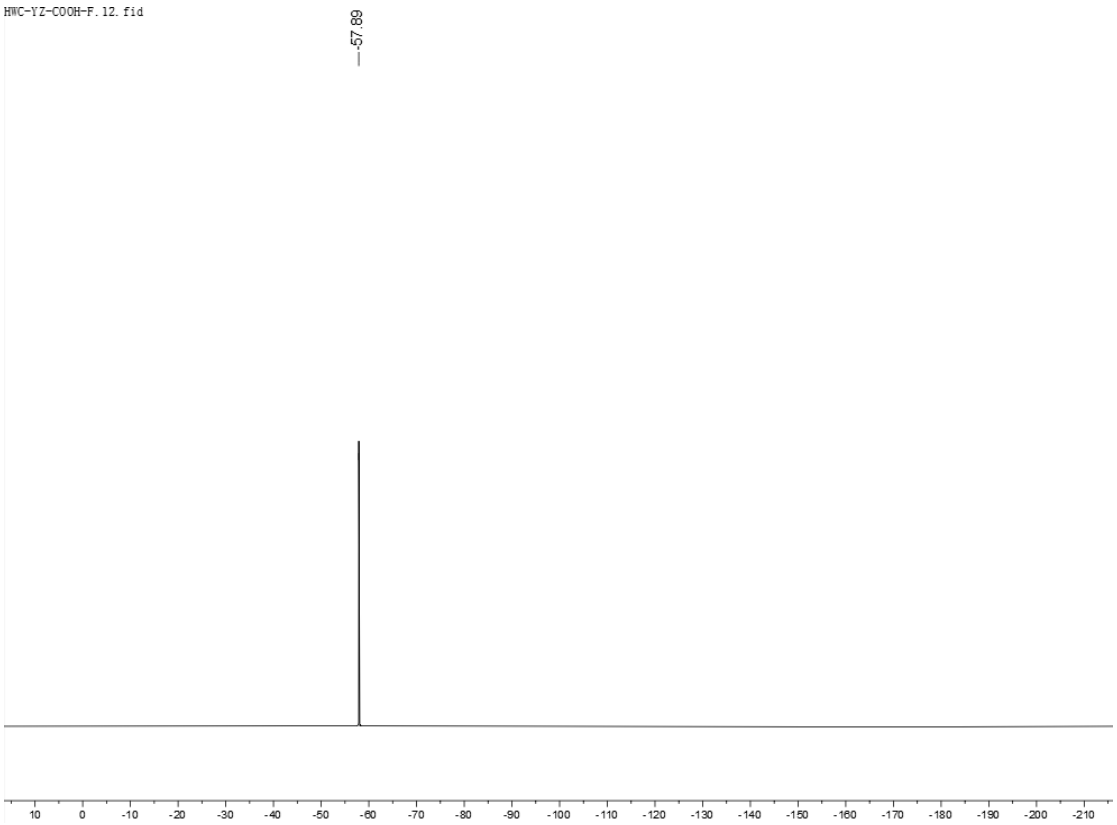
^{19}F NMR (565 MHz, $CDCl_3$) of 29



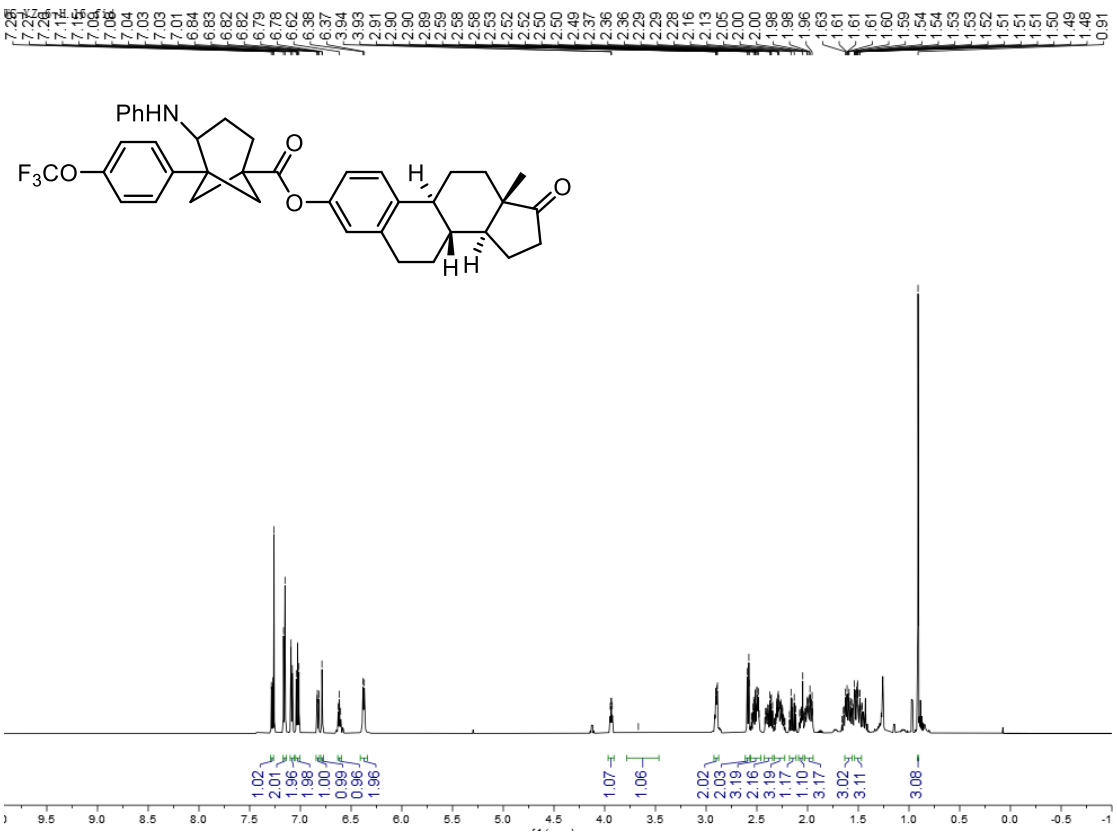
^{1}H NMR (600 MHz, $CDCl_3$) of 30



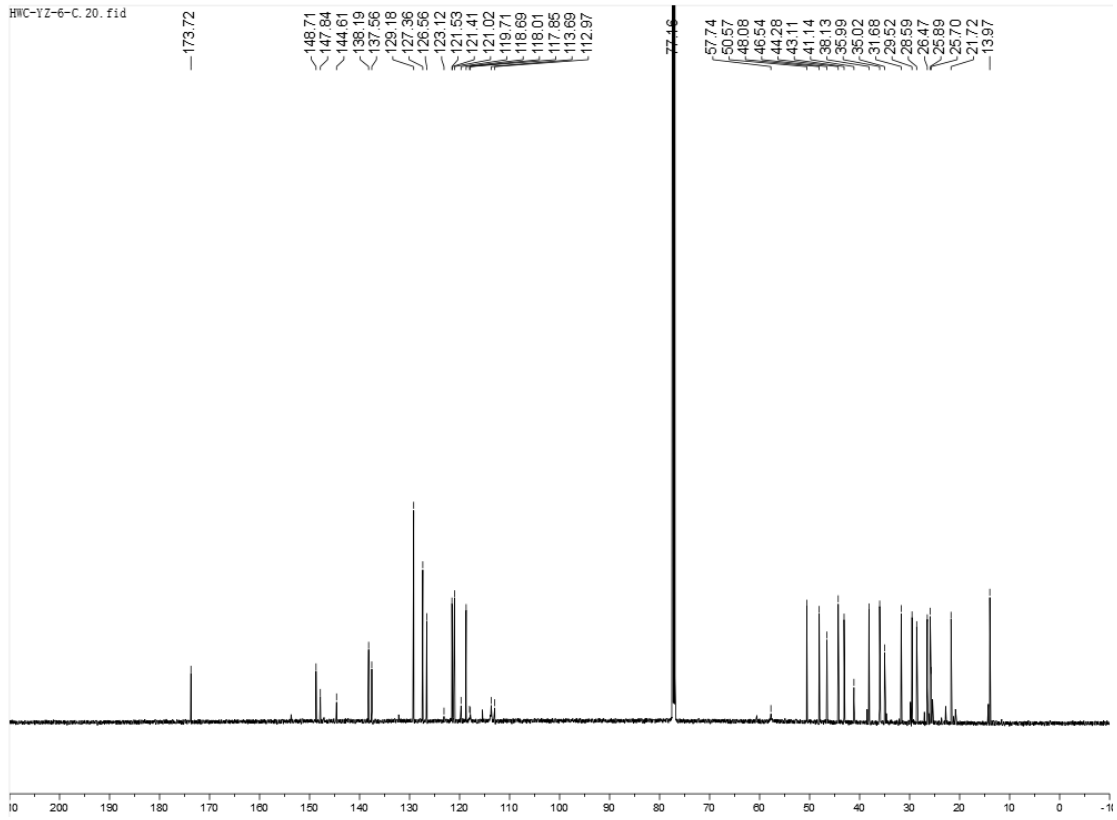
^{13}C NMR (151 MHz, $CDCl_3$) of 30



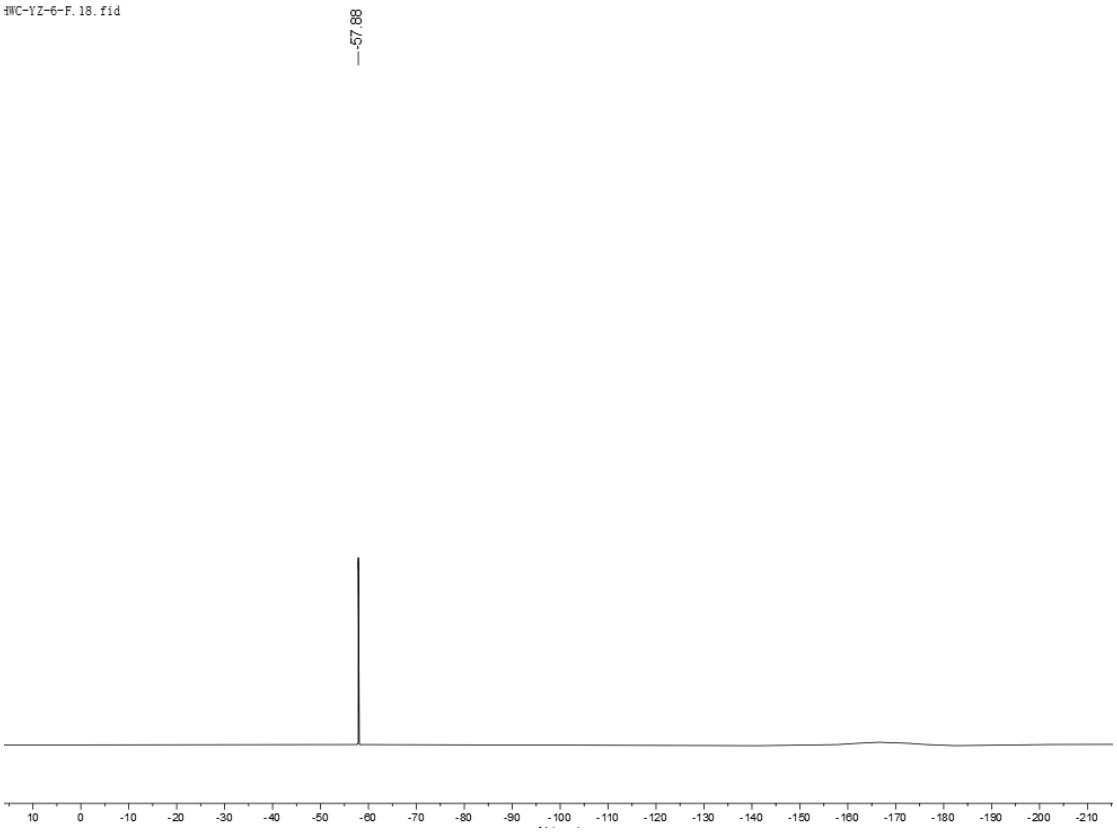
^{19}F NMR (565 MHz, $CDCl_3$) of 30



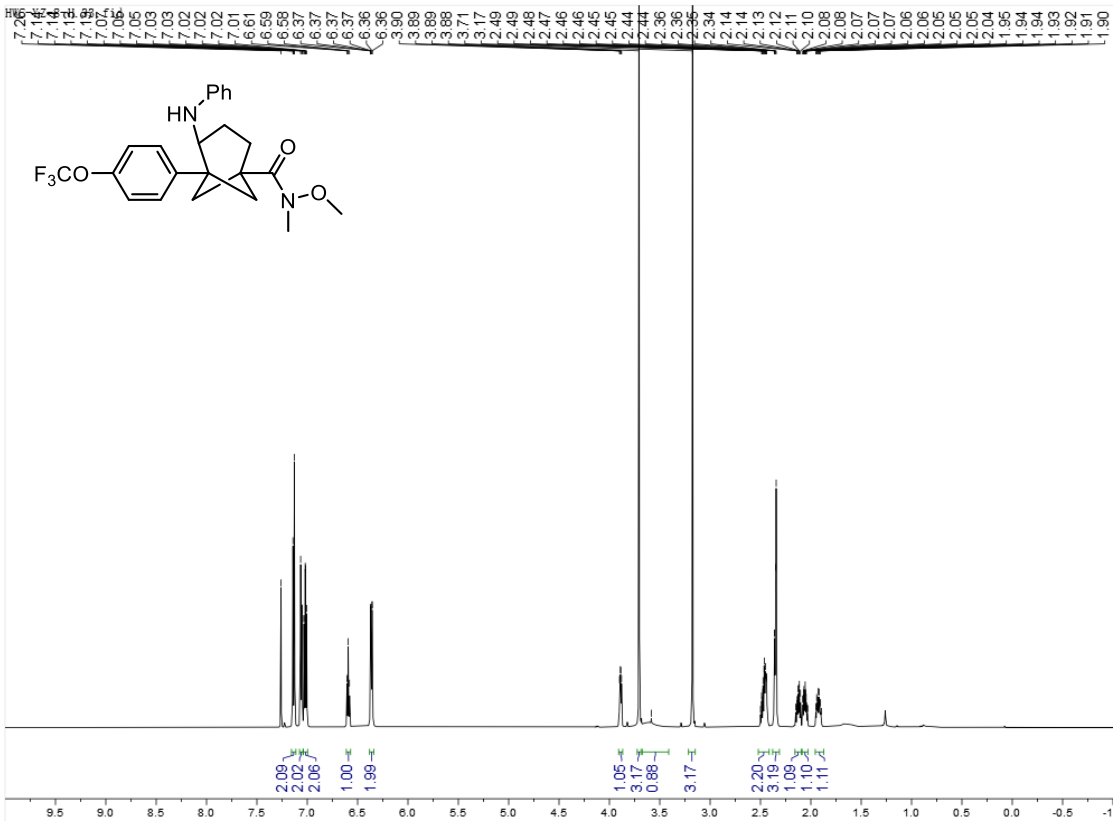
^{1}H NMR (600 MHz, $CDCl_3$) of 31



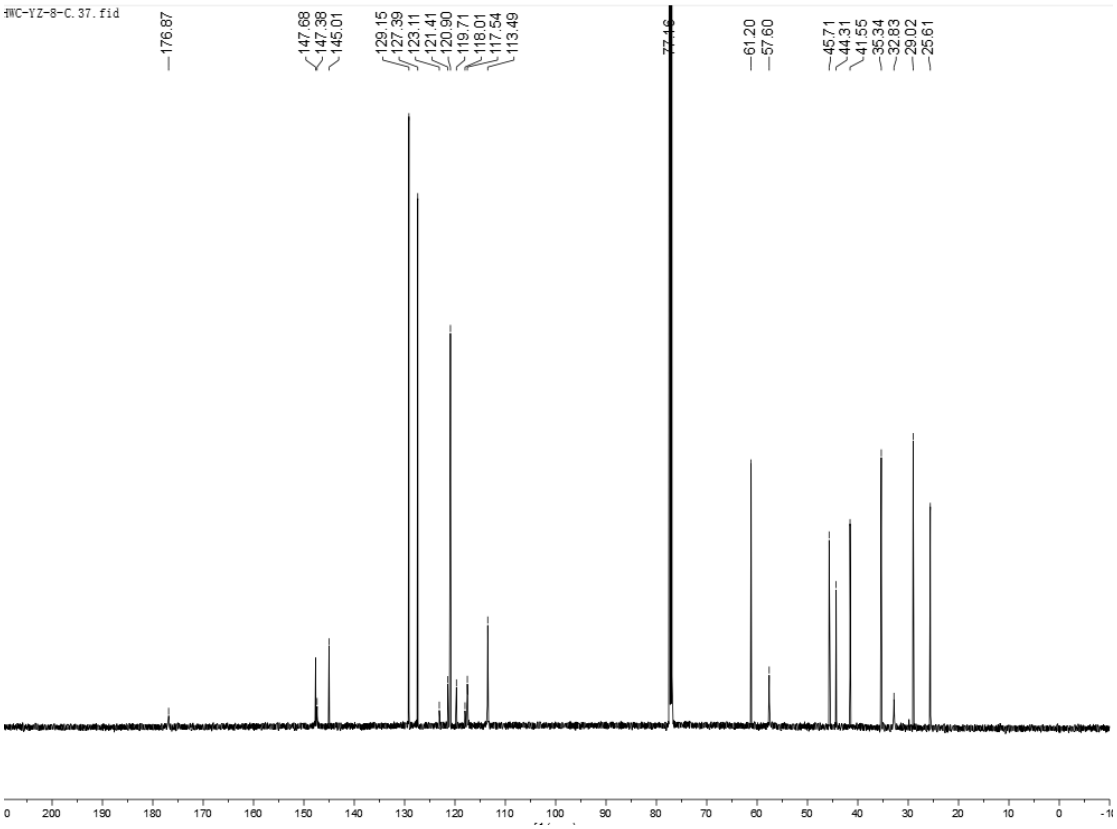
^{13}C NMR (151 MHz, $CDCl_3$) of 31



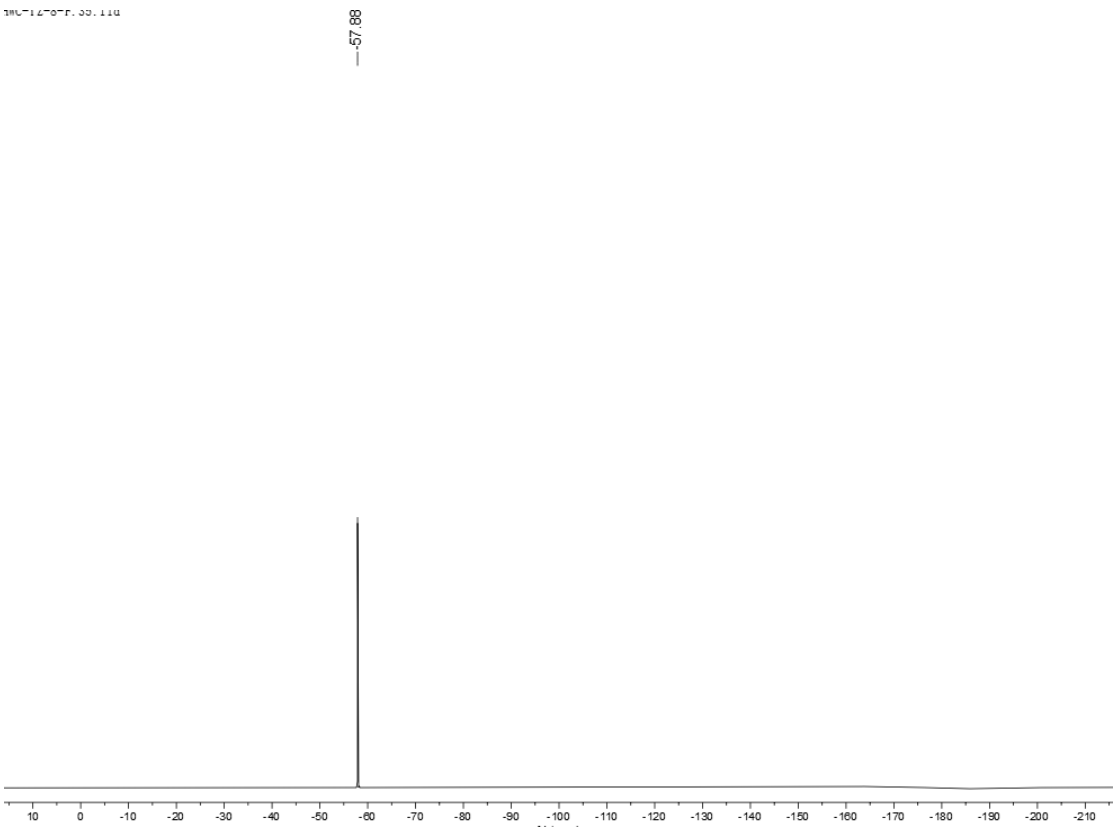
^{19}F NMR (565 MHz, $CDCl_3$) of 31



^{1}H NMR (600 MHz, $CDCl_3$) of 32

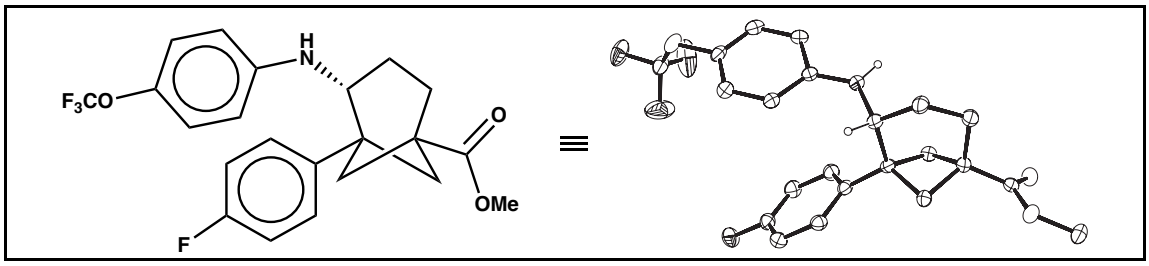


^{13}C NMR (151 MHz, $CDCl_3$) of 32



^{19}F NMR (565 MHz, $CDCl_3$) of 32

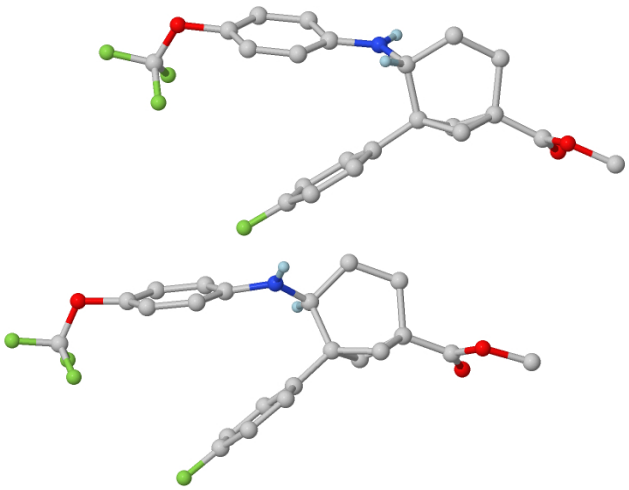
6. X-Ray Structure of Compound 9



Compound **9**, $C_{22}H_{21}F_4NO_3$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences h00: h=odd, 0k0: k=odd, and 0l: l=odd) with a=9.57270(10)Å, b=9.74940(10)Å, c=20.51770(10)Å, V=1914.88(3)Å^3, Z=4, and d_{calc}=1.469 g/cm^3. X-ray intensity data were collected on a Rigaku XtaLAB Synergy-S diffractometer [1] equipped with an HPC area detector (HyPix-6000HE) and employing confocal multilayer optic-monochromated Cu-Kα radiation (λ=1.54184 Å) at a temperature of 100K. Preliminary indexing was performed from a series of sixty 0.5° rotation frames with exposures of 0.25 seconds for θ = ±47.290° and 1 second for θ = 113.25°. A total of 9502 frames (134 runs) were collected employing ω scans with a crystal to detector distance of 34.0 mm, rotation widths of 0.5° and exposures of 0.25 seconds.

Rotation frames were integrated using CrysAlisPro [2], producing a listing of unaveraged F^2 and $\sigma(F^2)$ values. A total of 63877 reflections were measured over the ranges $8.62 \leq 2\theta \leq 148.998°$, $-11 \leq h \leq 11$, $-12 \leq k \leq 12$, $-25 \leq l \leq 25$ yielding 3907 unique reflections (R_{int} = 0.0303). The intensity data were corrected for Lorentz and polarization effects and for absorption using SCALE3 ABSPACK [3] (minimum and maximum transmission 0.7299, 1.0000). The structure was solved by dual space methods - SHELXT [4]. The moiety (C1, C2,

N1, C8-C13) was disordered due to contamination of about 8% of the compound with the opposite stereochemistry at C1, as shown by these two graphics:



92% 8%

Refinement was by full-matrix least squares based on F^2 using SHELXL [5]. All reflections were used during refinement. The weighting scheme used was $w=1/[\sigma^2(F_o^2)+(0.0334P)^2 + 0.6443P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. Refinement converged to R1=0.0295 and wR2=0.0725 for 3891 observed reflections for which $F > 4\sigma(F)$ and R1=0.0297 and wR2=0.0727 and GOF =1.087 for all 3907 unique, non-zero reflections and 342 variables. The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.18 and -0.23 e/Å^3.

Table 1. lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Tables 2. and 3. Anisotropic thermal parameters are in Table 4. Tables 5. and 6. list bond distances and bond angles. Figure 1. is an ORTEP representation of the molecule with 50% probability thermal ellipsoids displayed.

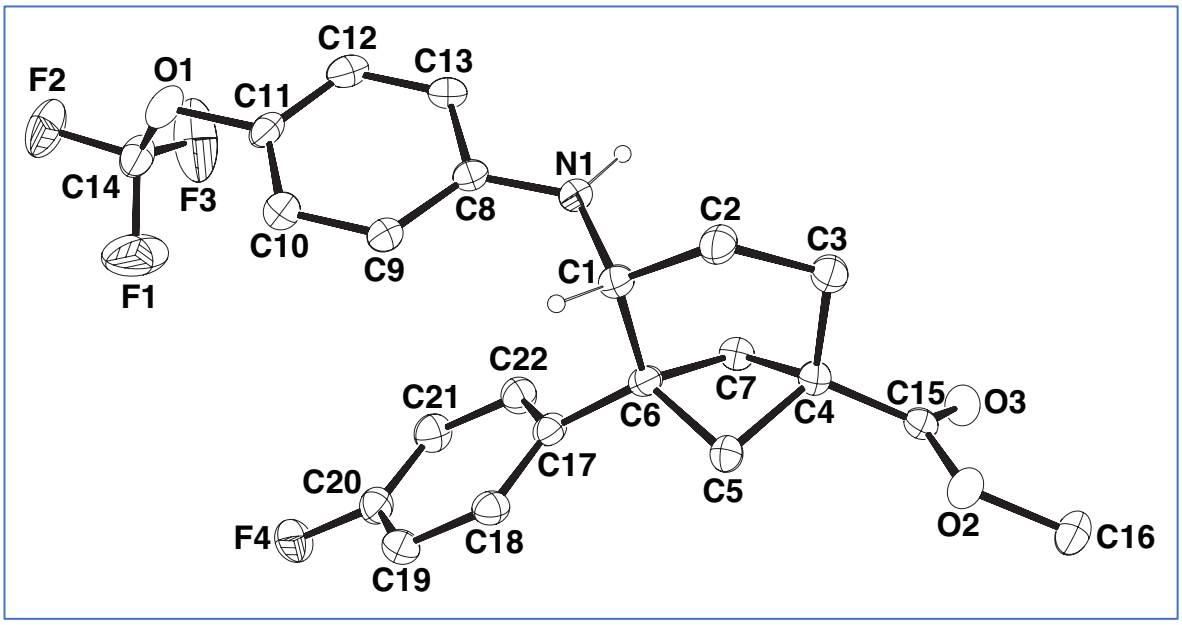


Figure 1. ORTEP drawing of the major component, with 50% thermal ellipsoids.

Table 1. Summary of Structure Determination of Compound 9260

Empirical formula	$C_{22}H_{21}F_4NO_3$
Formula weight	423.40
Diffractometer	Rigaku XtaLAB Synergy-S (HyPix-6000HE)
Temperature/K	100
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a	9.57270(10)Å
b	9.74940(10)Å
c	20.51770(10)Å
Volume	1914.88(3)Å^3
Z	4
d_{calc}	1.469 g/cm^3
μ	1.059 mm^{-1}
F(000)	880.0
Crystal size, mm	0.28 × 0.25 × 0.13
2θ range for data collection	8.62 - 148.998°
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -25 ≤ l ≤ 25
Reflections collected	63877
Independent reflections	3907[R(int) = 0.0303]
Data/restraints/parameters	3907/267/342
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R_1 = 0.0295, wR_2 = 0.0725
Final R indexes [all data]	R_1 = 0.0297, wR_2 = 0.0727
Largest diff. peak/hole	0.18/-0.23 eÅ^{-3}
Flack parameter	0.38(14)

Table 2 . Refined Positional Parameters for Compound 9260

Atom	*x*	*y*	*z*	U(eq)
F1	0.4054(3)	-0.11319(17)	0.43195(8)	0.0709(6)
F2	0.37638(18)	-0.32847(15)	0.42612(7)	0.0450(4)
F3	0.20828(17)	-0.1975(2)	0.45336(8)	0.0677(6)
F4	0.44252(14)	0.32829(14)	0.40238(5)	0.0312(3)
O1	0.38343(17)	-0.23678(14)	0.52164(7)	0.0285(3)
O2	0.26410(14)	0.78455(14)	0.78618(7)	0.0238(3)
O3	0.04609(14)	0.72714(14)	0.75449(7)	0.0248(3)
N1	0.2669(2)	0.19392(18)	0.69344(9)	0.0235(4)
N1*	0.401(2)	0.208(2)	0.6934(10)	0.0213(17)
C1	0.3547(3)	0.3115(2)	0.70790(11)	0.0208(4)
C1*	0.296(3)	0.3006(18)	0.7031(10)	0.0225(19)
C2	0.3492(3)	0.3506(2)	0.78132(12)	0.0251(5)
C2*	0.300(3)	0.3275(19)	0.7774(12)	0.023(2)
C3	0.2451(2)	0.4674(2)	0.79781(10)	0.0255(4)
C4	0.23430(19)	0.56678(19)	0.73952(9)	0.0198(4)
C5	0.3729(2)	0.56862(19)	0.69982(9)	0.0197(4)
C6	0.3152(2)	0.43833(19)	0.66494(9)	0.0197(4)
C7	0.1667(2)	0.4898(2)	0.68202(9)	0.0212(4)
C8	0.2994(2)	0.0891(2)	0.65068(10)	0.0205(4)
C8*	0.384(2)	0.0983(16)	0.6463(9)	0.0208(17)
C13*	0.266(2)	0.016(2)	0.6418(9)	0.0219(17)
C12*	0.263(2)	-0.093(2)	0.5984(12)	0.0236(19)
C11*	0.379(3)	-0.120(2)	0.5594(13)	0.0234(19)
C10*	0.497(2)	-0.038(2)	0.5639(12)	0.0234(19)
C9*	0.500(2)	0.0712(19)	0.6073(10)	0.024(2)
C9	0.4255(3)	0.0834(2)	0.61583(11)	0.0238(4)
C10	0.4528(3)	-0.0244(2)	0.57333(12)	0.0252(5)
C11	0.3541(3)	-0.1261(3)	0.56511(14)	0.0229(5)
C12	0.2303(3)	-0.1254(2)	0.59936(13)	0.0246(5)
C13	0.2029(2)	-0.0183(2)	0.64185(10)	0.0226(4)
C14	0.3433(2)	-0.2188(2)	0.46043(10)	0.0294(4)
C15	0.16923(19)	0.69959(19)	0.75987(9)	0.0192(4)
C16	0.2114(2)	0.9136(2)	0.81068(10)	0.0272(4)

C17	0.3480(2)	0.41495(19)	0.59401(9)	0.0199(4)
C18	0.4795(2)	0.4444(2)	0.56908(9)	0.0217(4)
C19	0.5129(2)	0.4155(2)	0.50445(9)	0.0240(4)
C20	0.4118(2)	0.3578(2)	0.46590(9)	0.0243(4)
C21	0.2789(2)	0.3298(2)	0.48784(10)	0.0259(4)
C22	0.2474(2)	0.3594(2)	0.55254(10)	0.0245(4)

Table 3 . Positional Parameters for Hydrogens in Compound 9260

Atom	*x*	*y*	*z*	U(eq)
H1	0.18593	0.188986	0.713646	0.028
H1*	0.478677	0.214122	0.715872	0.026
H1a	0.453263	0.285779	0.697323	0.025
H1*a	0.204534	0.258324	0.691112	0.027
H2a	0.323129	0.268131	0.806733	0.03
H2b	0.443807	0.378808	0.795417	0.03
H2*a	0.243858	0.255936	0.79949	0.028
H2*b	0.397506	0.318285	0.792715	0.028
H3a	0.152055	0.428138	0.807502	0.031
H3b	0.277747	0.517678	0.836878	0.031
H3c	0.308365	0.507064	0.831024	0.031
H3d	0.151762	0.456471	0.81789	0.031
H5a	0.457856	0.552402	0.72622	0.024
H5b	0.383895	0.649395	0.671032	0.024
H7a	0.124719	0.550362	0.648627	0.025
H7b	0.101166	0.416276	0.695214	0.025
H13*	0.186849	0.03459	0.668452	0.026
H12*	0.182305	-0.149524	0.595317	0.028
H10*	0.575779	-0.056699	0.537231	0.028
H9*	0.580326	0.127416	0.610365	0.029
H9	0.492848	0.154058	0.621328	0.029
H10	0.538631	-0.027982	0.550167	0.03
H12	0.164504	-0.197521	0.593905	0.029
H13	0.117486	-0.017272	0.665443	0.027
H16a	0.145135	0.952425	0.779284	0.041
H16b	0.28929	0.97752	0.81694	0.041

H16c	0.16407	0.898426	0.852409	0.041
H18	0.547864	0.484961	0.596579	0.026
H19	0.603087	0.435296	0.487568	0.029
H21	0.210711	0.291388	0.459603	0.031
H22	0.156116	0.341556	0.568661	0.029

Table 4 . Refined Thermal Parameters (U's) for Compound 9260

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F1	0.137(2)	0.0443(9)	0.0311(7)	0.0037(7)	0.0119(10)	-0.0241(11)
F2	0.0652(10)	0.0359(7)	0.0338(7)	-0.0153(6)	-0.0116(7)	0.0169(7)
F3	0.0446(9)	0.1107(16)	0.0478(9)	-0.0326(10)	-0.0209(7)	0.0348(10)
F4	0.0394(7)	0.0372(7)	0.0169(5)	-0.0036(5)	0.0023(5)	-0.0010(6)
O1	0.0424(9)	0.0178(7)	0.0253(7)	-0.0040(5)	-0.0078(6)	0.0073(6)
O2	0.0229(7)	0.0197(7)	0.0289(7)	-0.0048(6)	-0.0005(5)	0.0011(6)
O3	0.0224(6)	0.0254(7)	0.0267(7)	-0.0026(6)	0.0005(6)	0.0038(6)
N1	0.0266(9)	0.0170(8)	0.0268(9)	-0.0004(7)	0.0073(7)	-0.0009(7)
N1*	0.026(3)	0.017(3)	0.021(3)	0.001(3)	0.003(3)	-0.001(3)
C1	0.0244(10)	0.0173(9)	0.0209(10)	0.0018(8)	0.0010(8)	0.0010(9)
C1*	0.029(3)	0.017(3)	0.021(3)	0.001(3)	0.001(3)	0.002(3)
C2	0.0359(13)	0.0198(10)	0.0194(10)	0.0018(8)	-0.0004(10)	0.0051(10)
C2*	0.032(4)	0.017(4)	0.021(4)	0.001(4)	0.000(4)	0.000(4)
C3	0.0342(11)	0.0221(9)	0.0203(9)	0.0019(7)	0.0030(8)	0.0034(8)
C4	0.0212(8)	0.0186(8)	0.0196(8)	-0.0004(7)	0.0017(7)	0.0012(7)
C5	0.0211(9)	0.0197(9)	0.0184(8)	-0.0021(7)	-0.0001(7)	0.0007(7)
C6	0.0245(9)	0.0147(8)	0.0197(9)	0.0008(7)	0.0008(7)	-0.0014(7)
C7	0.0216(9)	0.0205(9)	0.0215(9)	0.0007(7)	0.0017(7)	-0.0012(8)
C8	0.0238(11)	0.0168(10)	0.0210(9)	0.0036(8)	0.0007(8)	0.0018(8)
C8*	0.025(3)	0.015(3)	0.023(3)	0.002(3)	0.005(3)	0.000(3)
C13*	0.026(3)	0.018(3)	0.023(3)	0.003(3)	0.001(3)	-0.003(3)
C12*	0.029(3)	0.018(3)	0.024(3)	0.003(3)	-0.005(3)	-0.004(3)
C11*	0.029(3)	0.019(3)	0.023(3)	0.001(3)	-0.001(3)	0.002(3)
C10*	0.028(3)	0.018(3)	0.024(3)	-0.002(3)	-0.001(3)	0.001(3)
C9*	0.028(4)	0.019(4)	0.026(4)	-0.001(4)	0.000(4)	0.001(4)
C9	0.0257(11)	0.0175(9)	0.0282(11)	-0.0004(8)	0.0041(9)	-0.0015(9)
C10	0.0276(12)	0.0222(10)	0.0259(11)	-0.0002(8)	0.0015(10)	0.0011(10)
C11	0.0333(13)	0.0147(9)	0.0206(10)	-0.0002(8)	-0.0035(9)	0.0035(9)
C12	0.0307(12)	0.019(1)	0.0239(10)	0.0035(8)	-0.0054(9)	-0.0035(9)
C13	0.0246(11)	0.021(1)	0.0221(10)	0.0047(8)	-0.0001(8)	-0.0020(8)
C14	0.0384(12)	0.0238(10)	0.026(1)	-0.0024(8)	-0.0025(9)	0.0084(9)
C15	0.0221(9)	0.0195(9)	0.0160(8)	0.0023(7)	0.0019(7)	-0.0001(7)
C16	0.0325(11)	0.0204(9)	0.0287(10)	-0.0055(8)	-0.0009(8)	0.0035(8)

C17	0.0250(9)	0.0154(8)	0.0192(9)	0.0008(7)	-0.0013(7)	0.0012(7)
C18	0.025(1)	0.0201(9)	0.0198(9)	0.0012(7)	-0.0015(7)	-0.0019(7)
C19	0.0267(10)	0.0244(9)	0.0210(9)	0.0028(8)	0.0022(7)	-0.0007(8)
C20	0.0334(11)	0.0224(9)	0.0172(9)	-0.0001(7)	0.0014(8)	0.0027(8)
C21	0.0282(10)	0.0266(10)	0.0229(9)	-0.0031(8)	-0.0040(8)	-0.0025(8)
C22	0.0237(10)	0.0246(9)	0.025(1)	-0.0025(8)	0.0003(8)	-0.0018(8)

Table 5 . Bond Distances in Compound 9260, Å

F1-C14	1.325(3)	F2-C14	1.319(2)	F3-C14	1.318(3)
F4-C20	1.367(2)	O1-C11*	1.374(15)	O1-C11	1.428(3)
O1-C14	1.325(3)	O2-C15	1.342(2)	O2-C16	1.446(2)
O3-C15	1.214(2)	N1-C1	1.452(3)	N1-C8	1.383(3)
N1*-C1*	1.37(3)	N1*-C8*	1.45(2)	C1-C2	1.555(3)
C1-C6	1.565(3)	C1*-C2*	1.547(14)	C1*-C6	1.565(13)
C2-C3	1.550(3)	C2*-C3	1.520(13)	C3-C4	1.543(3)
C4-C5	1.557(3)	C4-C7	1.541(3)	C4-C15	1.496(3)
C5-C6	1.559(3)	C6-C7	1.548(3)	C6-C17	1.506(3)
C8-C9	1.404(3)	C8-C13	1.408(3)	C8*-C13*	1.3900
C8*-C9*	1.3900	C13*-C12*	1.3900	C12*-C11*	1.3900
C11*-C10*	1.3900	C10*-C9*	1.3900	C9-C10	1.390(3)
C10-C11	1.380(3)	C11-C12	1.378(3)	C12-C13	1.386(3)
C17-C18	1.389(3)	C17-C22	1.395(3)	C18-C19	1.393(3)
C19-C20	1.370(3)	C20-C21	1.377(3)	C21-C22	1.392(3)

Table 6 . Bond Angles in Compound 9260, °

C14-O1-C11*	114.5(14)	C14-O1-C11	115.80(19)	C15-O2-C16	116.15(15)
C8-N1-C1	125.65(19)	C1*-N1*-C8*	120(2)	N1-C1-C2	111.81(19)
N1-C1-C6	111.64(18)	C2-C1-C6	110.11(17)	N1*-C1*-C2*	103.9(19)
N1*-C1*-C6	114.3(19)	C2*-C1*-C6	110.2(18)	C3-C2-C1	114.42(19)
C3-C2*-C1*	114.6(18)	C2*-C3-C4	111.9(10)	C4-C3-C2	109.60(16)
C3-C4-C5	110.83(15)	C7-C4-C3	108.41(15)	C7-C4-C5	87.88(14)
C15-C4-C3	110.80(15)	C15-C4-C5	119.39(16)	C15-C4-C7	117.43(16)
C4-C5-C6	85.92(14)	C5-C6-C1	107.44(16)	C5-C6-C1*	120.7(10)
C7-C6-C1	110.52(16)	C7-C6-C1*	93.3(12)	C7-C6-C5	87.56(14)
C17-C6-C1	111.98(16)	C17-C6-C1*	112.2(9)	C17-C6-C5	119.54(16)
C17-C6-C7	117.34(16)	C4-C7-C6	86.87(14)	N1-C8-C9	123.1(2)
N1-C8-C13	118.91(19)	C9-C8-C13	118.0(2)	C13*-C8*-N1*	124.0(17)
C13*-C8*-C9*	120.0	C9*-C8*-N1*	115.9(17)	C12*-C13*-C8*	120.0
C11*-C12*-C13*	120.0	O1-C11*-C12*	120.5(16)	O1-C11*-C10*	119.1(16)
C12*-C11*-C10*	120.0	C9*-C10*-C11*	120.0	C10*-C9*-C8*	120.0
C10-C9-C8	120.7(2)	C11-C10-C9	119.4(2)	C10-C11-O1	119.0(2)
C12-C11-O1	119.4(2)	C12-C11-C10	121.5(2)	C11-C12-C13	119.1(2)
C12-C13-C8	121.1(2)	F1-C14-O1	113.0(2)	F2-C14-F1	106.69(18)
F2-C14-O1	109.23(17)	F3-C14-F1	105.6(2)	F3-C14-F2	107.7(2)
F3-C14-O1	114.2(2)	O2-C15-C4	111.38(15)	O3-C15-O2	123.84(17)
O3-C15-C4	124.77(17)	C18-C17-C6	120.89(17)	C18-C17-C22	118.80(17)
C22-C17-C6	120.29(17)	C17-C18-C19	121.11(18)	C20-C19-C18	118.07(19)
F4-C20-C19	119.02(18)	F4-C20-C21	117.95(18)	C19-C20-C21	123.03(18)
C20-C21-C22	118.13(19)	C21-C22-C17	120.82(19)		

This report has been created with Olex2 [6], compiled on 2021.08.20 svn.r13c46975 for OlexSys.

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