

Supporting Information

Chemodivergent Dearomatization of Benzene-linked O-oxime Esters via EnT-Induced Radical Cross-coupling

Guohui Zeng,^a Dongwen Guo,^a Huanfeng Jiang,^a Biaolin Yin^{a*}

^aKey Laboratory of Functional Molecular Engineering of Guangdong Province, School of Chemistry and Chemical Engineering, South China University of Technology (SCUT), Guangzhou 510640, China.

*Corresponding Author: Biaolin Yin: blyin@scut.edu.cn

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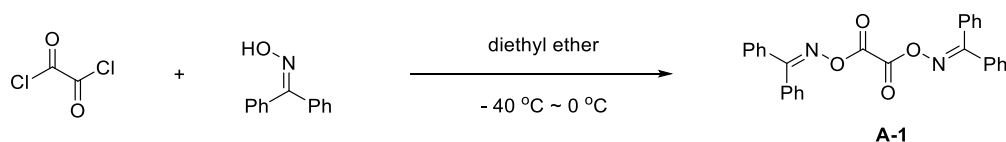
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I. General information

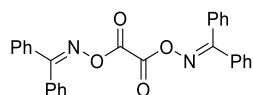
Unless specified otherwise, all experiments were performed under a N₂ atmosphere. All reagents and starting materials were purchased from commercial suppliers and used as received. FT-IR spectra were obtained with thin film samples or KBr pellets on a Bruker Vector 22 spectrometer, and data are expressed in cm⁻¹. ¹H, ¹³C, ¹⁹F NMR spectra were recorded on Bruker AVANCE 400 (400 MHz for ¹H; 100 MHz for ¹³C; 376 MHz for ¹⁹F) or a Bruker AVANCE 500 (500 MHz for ¹H; 126 MHz for ¹³C; 471 MHz for ¹⁹F), ¹H NMR and ¹³C NMR chemical shifts were determined relative to internal standard CDCl₃ at 7.26 and 77.0. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are in Hertz (Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet. The HRMS measurements were recorded on a TOF analyzer using an ESI source in the positive mode. The crystal data was collected on an Agilent Gemini E diffractometer (Mo, 50kV 40mA) and reduced by CrysAlisPro (Rigaku). Melting points were determined using a hot stage apparatus. Column chromatography was performed on silica gel (200–300 mesh) with mixtures of petroleum ether and ethyl acetate as the eluent or other solvents.

II. General procedure for preparing additive and 4-halogenated materials.

II.1 The synthesis of A-1



To a solution of oxalyl dichloride (10 mmol, 1.0 eq) in dry diethyl ether (20 mL), a solution of diphenylmethanone oxime (20 mmol, 2.0 eq) in dry diethyl ether (40 mL) was slowly added at -40 °C for over 10 minutes. After addition, the mixture was carefully warmed to 0 °C and stirred for another 2 hours. The reaction mixture was filtered, and the filter cake washed with diethyl ether to give the product **A-1** which was used directly in the next step without purification.



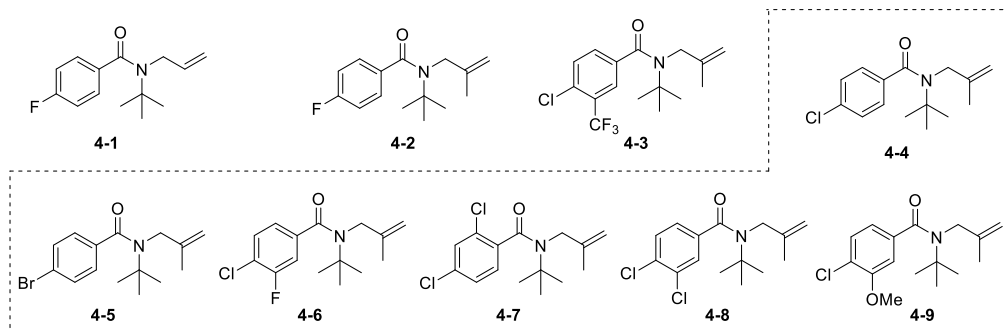
O,O'-oxalylbis(1,1-diphenylbenzophenone oxime) (**A-1**)

The title compound was obtained as a white solid (4.0 g, 89% yield).

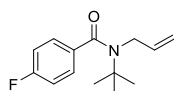
NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.52 – 7.44 (m, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 7.29 (d, *J* = 7.1 Hz, 1H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 133.8, 131.4, 131.1, 130.2, 129.2, 129.1, 128.5, 128.3.

This compound is known.^{1,2}

II.2 The synthesis of 4



The 4-halogenated *N*-allyl benzamide starting materials (**4-1** to **4-9**) are prepared using our previous method.³ **4-1**, **4-2** and **4-3** are new compounds, **4-4** to **4-9** are known compounds.



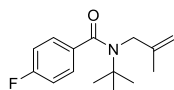
N-allyl-*N*-(tert-butyl)-4-fluorobenzamide (**4-1**)

The title compound was obtained as a colorless oil (500 mg, 86% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.41 – 7.33 (m, 2H), 7.06 – 6.99 (m, 2H), 5.81 – 5.70 (m, 1H), 5.17 – 5.05 (m, 2H), 3.94 – 3.88 (m, 2H), 1.54 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 164.1, 161.6, 137.0, 135.5 (d, *J* = 3.6 Hz), 128.2 (d, *J* = 8.3 Hz), 116.2, 115.1 (d, *J* = 21.7 Hz), 57.6, 49.9, 28.6.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.83.

HRMS (APCI): calcd for C₁₄H₁₉FNO⁺ [*M* + *H*]⁺: 236.1445; found: 236.1441.

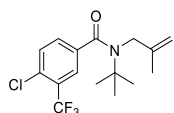


N-(tert-butyl)-4-fluoro-*N*-(2-methylallyl)benzamide (**4-2**)

The title compound was obtained as a white solid (486 mg, 85% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.35 (m, 2H), 7.03 – 6.94 (m, 2H), 5.04 (s, 1H), 4.99 (m, 1H), 3.74 (s, 2H), 1.53 (s, 9H), 1.52 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.7, 162.8 (d, *J* = 248.3 Hz), 144.0, 135.4 (d, *J* = 3.6 Hz), 128.0 (d, *J* = 8.4 Hz), 115.0 (d, *J* = 21.6 Hz), 111.9, 57.9, 53.2, 28.2, 20.0. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.9.

HRMS (APCI): calcd for C₁₅H₂₁FNO⁺ [*M* + *H*]⁺: 250.1602; found: 250.1659.



N-(tert-butyl)-4-chloro-*N*-(2-methylallyl)-3-(trifluoromethyl)benzamide (**4-3**)

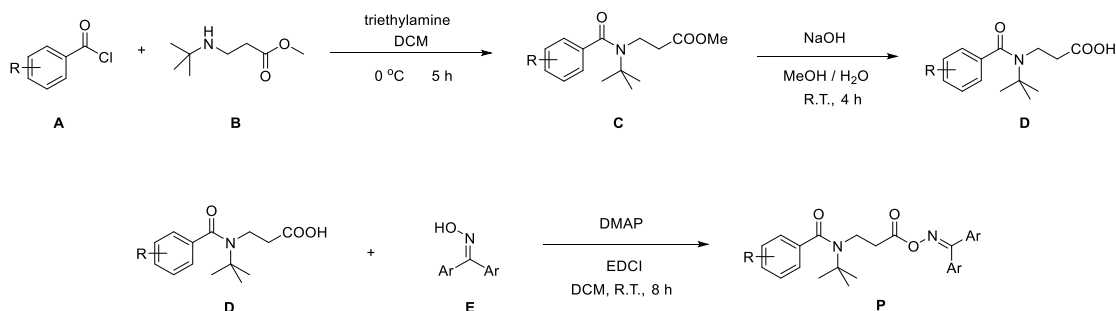
The title compound was obtained as a colorless oil (510 mg, 87% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 5.06 (s, 1H), 5.05 (q, *J* = 1.5 Hz, 1H), 3.68 (s, 2H), 1.53 (s, 9H), 1.52 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 170.9, 143.8, 138.0, 132.7 (d, *J* = 2.0 Hz), 131.2, 130.2, 128.2 (q, *J* = 31.8 Hz), 125.3 (q, *J* = 5.3 Hz), 122.5 (d, *J* = 273.4 Hz), 112.1, 58.2, 53.0, 28.1, 19.9. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.8.

HRMS (APCI): calcd for $C_{16}H_{20}ClF_3NO^+ [M + H]^+$: 334.1180; found: 334.1177.

III. General procedure for preparing O-oxime ester materials.

III.1 Method I



Step 1:

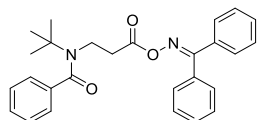
To a solution of methyl 3-(tert-butylamino)propanoate **B** (5 mmol, 1.0 eq) and triethylamine (7.5 mmol, 1.5 eq) in DCM (30 mL) was slowly added the corresponding benzoyl chloride **A** (5 mmol, 1.0 eq) at 0°C, then stirred at 0°C for 5 hours. Then the reaction was quenched with water and extracted with DCM for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and filtered. The solvent was removed under reduced pressure to give crude product **C** which was used directly in the next step without purification.

Step 2:

To a solution of crude product **C** in MeOH and H₂O (30 mL, v/v = 4/1) was added NaOH (7.5 mmol, 1.5 eq). The solution was stirred at room temperature for 4 hours, then the reaction solution was carefully adjusted pH to 3~5 by 1M HCl(aq). After removing MeOH under reduced pressure the reaction mixture was extracted with DCM for three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by recrystallization from petroleum ether and EtOAc to give the corresponding acid **D**.

Step 3:

To a solution of acid **D**, oxime derivatives **E** (4.5 mmol, 0.9 eq) and DMAP (0.25 mmol, 5 mol%) in dry DCM (50 mL), was added EDCI (12.5 mmol, 2.5 eq) in portions at room temperature and stirred for 8 hours.⁴ The reaction mixture was quenched with water and extracted with DCM three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by column chromatography on silica gel (10 : 1 petroleum ether : EtOAc) to give the oximes **P**.



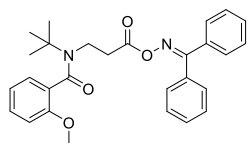
N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)benzamide (**1-1**)

The title compound was obtained as a white solid (1.5 g, 71% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 7.8 Hz, 2H), 7.49 – 7.40 (m, 4H), 7.37 – 7.31 (m, 5H), 7.30 – 7.25 (m, 2H), 7.24 – 7.17 (m, 2H), 3.60 – 3.51 (m, 2H), 2.54 – 2.45 (m, 2H), 1.47 (s,

9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 168.1, 165.2, 138.9, 134.2, 132.2, 130.9, 129.6, 128.9, 128.8, 128.4, 128.4, 128.3, 128.1, 125.8, 57.1, 42.4, 34.9, 28.7.

HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{29}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 429.2173; found: 429.2175.

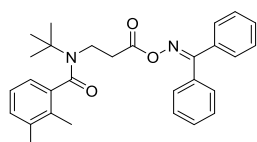


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2-methoxybenzamide (**1-2**)

The title compound was obtained as a colorless oil (1.4 g, 60% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.53 – 7.40 (m, 4H), 7.39 – 7.33 (m, 2H), 7.32 – 7.21 (m, 3H), 7.09 (dd, J = 7.4, 1.7 Hz, 1H), 6.96 – 6.90 (m, 1H), 6.86 (dd, J = 8.4, 0.9 Hz, 1H), 3.75 (s, 3H), 3.60 – 3.38 (m, 2H), 2.63 – 2.36 (m, 2H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.4, 168.4, 165.1, 154.4, 134.3, 132.3, 130.9, 129.6, 129.5, 128.8, 128.5, 128.3, 128.1, 126.7, 120.7, 111.0, 57.2, 55.3, 42.0, 34.7, 28.8.

HRMS (APCI): calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_4^+$ $[\text{M} + \text{H}]^+$: 459.2278; found: 459.2277.

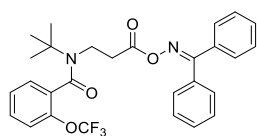


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2,3-dimethylbenzamide (**1-3**)

The title compound was obtained as colorless oil (1.3 g, 58% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.51 (m, 2H), 7.50 – 7.41 (m, 4H), 7.37 – 7.32 (m, 2H), 7.25 – 7.18 (m, 2H), 7.09 (d, J = 6.2 Hz, 1H), 7.04 (t, J = 7.5 Hz, 1H), 6.91 (d, J = 7.5 Hz, 1H), 3.59 – 3.48 (m, 1H), 3.36 – 3.24 (m, 1H), 2.46 (t, J = 8.1 Hz, 2H), 2.25 (s, 3H), 2.14 (s, 3H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 165.3, 137.5, 134.3, 131.3, 131.0, 129.8, 129.6, 128.9, 128.5, 128.3, 128.2, 125.7, 122.7, 57.3, 41.8, 34.7, 28.8, 20.0, 15.8.

HRMS (APCI): calcd for $\text{C}_{29}\text{H}_{33}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 457.2486; found: 457.2488.

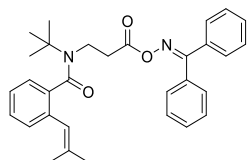


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2-(trifluoromethoxy)benzamide (**1-4**)

The title compound was obtained as a colorless oil (1.3 g, 58% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.50 (m, 2H), 7.51 – 7.40 (m, 4H), 7.40 – 7.30 (m, 3H), 7.30 – 7.26 (m, 2H), 7.25 – 7.19 (m, 3H), 3.59 – 3.47 (m, 1H), 3.43 – 3.31 (m, 1H), 2.61 – 2.49 (m, 1H), 2.48 – 2.36 (m, 1H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 167.7, 165.4, 144.2, 134.3, 132.3, 132.1, 131.0, 130.0, 129.6, 128.9, 128.4, 128.3, 128.2, 127.8, 127.0, 120.1, 57.7, 42.0, 34.8, 28.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.9.

HRMS (APCI): calcd for $\text{C}_{28}\text{H}_{28}\text{F}_3\text{N}_2\text{O}_4^+$ $[\text{M} + \text{H}]^+$: 513.1996; found: 513.1998.

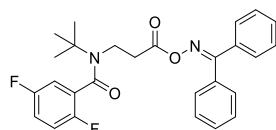


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2-(2-methylprop-1-en-1-yl)benzamide (**1-5**)

The title compound was obtained as a brown oil (1.1 g, 48% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 7.7 Hz, 2H), 7.52 – 7.40 (m, 4H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 5.3 Hz, 1H), 7.25 – 7.12 (m, 5H), 6.23 (s, 1H), 3.53 – 3.40 (m, 1H), 3.39 – 3.26 (m, 1H), 2.52 – 2.33 (m, 2H), 1.84 (s, 3H), 1.73 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 168.0, 138.2, 136.9, 134.2, 134.0, 132.2, 130.9, 129.5, 129.5, 128.7, 128.3, 128.2, 128.1, 127.8, 126.2, 125.1, 122.0, 57.1, 41.6, 34.3, 28.6, 26.0, 19.1.

HRMS (APCI): calcd for $\text{C}_{31}\text{H}_{35}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 483.2642; found: 483.2637.

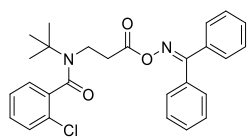


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2,5-difluorobenzamide (**1-6**)

The title compound was obtained as a white solid (1.0 g, 43% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, J = 7.8 Hz, 2H), 7.50 – 7.39 (m, 4H), 7.33 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 7.3 Hz, 2H), 6.99 (t, J = 5.6 Hz, 2H), 6.93 (t, J = 6.4 Hz, 1H), 3.53 (t, J = 7.9 Hz, 2H), 2.51 (d, J = 8.0 Hz, 2H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 166.0 (d, J = 1.5 Hz), 165.3, 158.4 (dd, J = 244.7, 2.3 Hz), 153.3 (dd, J = 242.3, 2.5 Hz), 134.1, 132.1, 131.0, 129.6, 128.8, 128.3, 128.3, 128.1, 117.1 (dd, J = 19.2, 8.4 Hz), 116.9 (dd, J = 18.9, 8.4 Hz), 114.5 (dd, J = 25.2, 4.5 Hz), 57.8, 42.1, 34.6, 28.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.3 (d, J = 17.7 Hz), -122.6 (d, J = 17.6 Hz).

HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{27}\text{F}_2\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 465.1984; found: 465.1988.

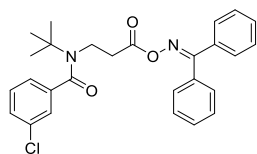


N-(tert-butyl)-2-chloro-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)benzamide (**1-7**)

The title compound was obtained as a white solid (1.2 g, 51% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 2H), 7.50 – 7.41 (m, 4H), 7.34 (t, J = 7.9 Hz, 3H), 7.28 – 7.17 (m, 5H), 3.61 – 3.50 (m, 1H), 3.43 – 3.28 (m, 1H), 2.64 – 2.52 (m, 1H), 2.49 – 2.37 (m, 1H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 167.9, 165.2, 137.8, 134.2, 132.1, 130.9, 129.6, 129.6, 129.4, 128.8, 128.3, 128.2, 128.1, 127.0, 126.9, 57.6, 41.8, 34.7, 28.6.

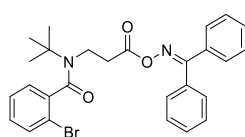
HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{28}\text{ClN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 463.1783; found: 463.1781.



N-(tert-butyl)-3-chloro-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)benzamide (1-8)

The title compound was obtained as a white solid (1.3 g, 56% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 – 7.52 (m, 2H), 7.50 – 7.42 (m, 4H), 7.38 – 7.32 (m, 3H), 7.31 – 7.26 (m, 2H), 7.23 (dd, J = 7.8, 1.7 Hz, 2H), 7.19 – 7.15 (m, 1H), 3.58 – 3.53 (m, 2H), 2.53 – 2.47 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 168.0, 165.4, 140.6, 134.4, 134.2, 132.2, 131.0, 129.9, 129.6, 129.1, 128.9, 128.4, 128.3, 128.2, 126.1, 124.0, 57.4, 42.4, 34.8, 28.7. HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{28}\text{ClN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 463.1783; found: 463.1781.

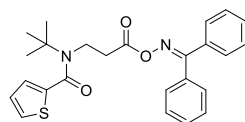


2-bromo-N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)benzamide (1-9)

The title compound was obtained as a white solid (1.3 g, 50% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 – 7.42 (m, 7H), 7.35 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 7.7 Hz, 1H), 7.23 (d, J = 6.2 Hz, 2H), 7.20 – 7.14 (m, 2H), 3.64 – 3.49 (m, 1H), 3.45 – 3.28 (m, 1H), 2.69 – 2.54 (m, 1H), 2.50 – 2.35 (m, 1H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.6, 167.9, 165.3, 134.2, 132.8, 132.2, 131.0, 129.7, 129.6, 128.8, 128.4, 128.3, 128.1, 127.4, 127.1, 118.6, 57.7, 41.9, 34.7, 28.5.

HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{28}\text{BrN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 507.1278; found: 507.1276.

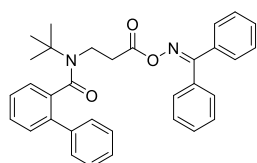


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)thiophene-2-carboxamide (1-11)

The title compound was obtained as a white solid (1.0 g, 46% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.51 – 7.43 (m, 4H), 7.37 (t, J = 7.3 Hz, 3H), 7.30 – 7.25 (m, 2H), 7.21 (d, J = 3.3 Hz, 1H), 7.01 – 6.93 (m, 1H), 3.85 – 3.76 (m, 2H), 2.72 – 2.62 (m, 2H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 166.3, 165.3, 140.0, 134.2, 132.2, 131.0, 129.6, 128.9, 128.5, 128.3, 128.2, 127.7, 127.3, 126.6, 57.9, 42.6, 35.5, 28.6.

HRMS (APCI): calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{O}_3\text{S}^+$ $[\text{M} + \text{H}]^+$: 435.1737; found: 435.1738.

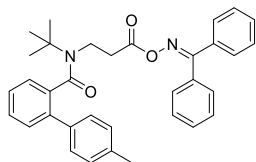


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxamide (1-12)

The title compound was obtained as a colorless oil (1.0 g, 41% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 7.8 Hz, 2H), 7.51 – 7.43 (m, 6H), 7.41 – 7.27 (m, 9H), 7.22 (d, J = 6.7 Hz, 2H), 3.26 – 3.07 (m, 2H), 2.21 (t, J = 8.1 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 168.0, 165.0, 139.6, 137.8, 137.4, 134.3, 132.3, 131.0, 129.6, 129.5, 129.0, 128.8, 128.7, 128.4, 128.3, 128.1, 127.4, 126.5, 57.2, 41.6, 34.3, 28.4.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 505.2486; found: 505.2484.

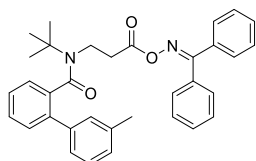


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-4'-methyl-[1,1'-biphenyl]-2-carboxamide (**1-13**)

The title compound was obtained as a colorless oil (1.1 g, 42% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 7.8 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.37 – 7.27 (m, 7H), 7.25 – 7.16 (m, 3H), 7.12 (d, J = 7.7 Hz, 2H), 3.24 – 3.06 (m, 2H), 2.34 (s, 3H), 2.18 (t, J = 8.2 Hz, 2H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.0, 168.1, 165.0, 137.4, 137.1, 136.7, 134.3, 132.3, 131.0, 129.7, 129.6, 128.9, 128.8, 128.6, 128.5, 128.3, 128.1, 127.1, 126.6, 57.2, 41.6, 34.3, 28.4, 21.1.

HRMS (APCI): calcd for $\text{C}_{34}\text{H}_{35}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 519.2642; found: 519.2639.

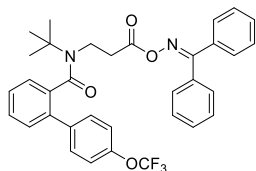


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-3'-methyl-[1,1'-biphenyl]-2-carboxamide (**1-14**)

The title compound was obtained as a white solid (1.0 g, 40% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, J = 7.8 Hz, 2H), 7.49 – 7.41 (m, 4H), 7.38 – 7.29 (m, 6H), 7.26 – 7.18 (m, 5H), 7.13 (t, J = 4.6 Hz, 1H), 3.26 – 3.07 (m, 2H), 2.33 (s, 3H), 2.20 (t, J = 8.2 Hz, 2H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 168.1, 165.0, 139.6, 137.8, 137.6, 137.5, 134.3, 132.3, 131.0, 129.8, 129.6, 129.6, 128.8, 128.6, 128.5, 128.3, 128.1, 127.3, 126.6, 126.0, 57.1, 41.6, 34.3, 28.4, 21.3.

HRMS (APCI): calcd for $\text{C}_{34}\text{H}_{35}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 519.2642; found: 519.2639.



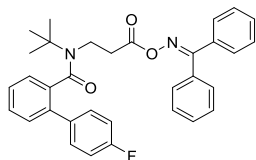
N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-4'-(trifluoromethoxy)-[1,1'-biphenyl]-2-carboxamide (**1-15**)

The title compound was obtained as a colorless oil (1.3 g, 45% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 – 7.50 (m, 2H), 7.49 – 7.43 (m, 5H), 7.42 – 7.37 (m, 2H), 7.36 – 7.31 (m, 3H), 7.30 – 7.26 (m, 2H), 7.23 – 7.17 (m, 4H), 3.21 – 3.06 (m, 2H), 2.30 – 2.15 (m,

2H), 1.27 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 167.8, 165.1, 148.5 (q, $J = 1.8$ Hz), 138.3, 135.9, 134.2, 132.2, 130.9, 130.5, 129.5, 129.5, 128.7, 128.3, 128.2, 128.1, 127.8, 126.4, 120.5, 57.2, 41.6, 34.3, 28.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.8.

HRMS (APCI): calcd for $\text{C}_{34}\text{H}_{32}\text{F}_3\text{N}_2\text{O}_4^+$ $[\text{M} + \text{H}]^+$: 589.2309; found: 589.2305.

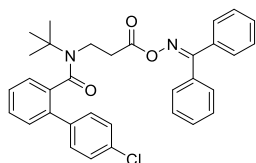


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-4'-fluoro-[1,1'-biphenyl]-2-carboxamide (**1-16**)

The title compound was obtained as a white solid (1.1 g, 42% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, $J = 7.1$ Hz, 2H), 7.49 – 7.39 (m, 6H), 7.39 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.21 (d, $J = 6.1$ Hz, 2H), 7.02 (t, $J = 8.7$ Hz, 2H), 3.16 (t, $J = 8.3$ Hz, 2H), 2.21 (t, $J = 8.1$ Hz, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 168.0, 165.1, 163.5, 161.1, 137.8, 136.3, 135.7 (d, $J = 3.4$ Hz), 134.2, 132.3, 131.0, 130.8, 130.7, 129.7, 129.6, 128.8, 128.7, 128.4, 128.3, 128.2, 127.5, 126.5, 115.1, 114.9, 57.3, 41.6, 34.3, 28.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -114.7.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{32}\text{FN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 523.2391; found: 523.2390.

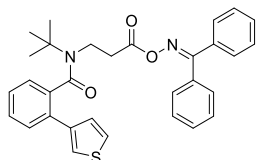


N-(tert-butyl)-4'-chloro-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-[1,1'-biphenyl]-2-carboxamide (**1-17**)

The title compound was obtained as a colorless oil (1.2 g, 46% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.51 (m, 2H), 7.50 – 7.44 (m, 3H), 7.44 – 7.41 (m, 1H), 7.41 – 7.36 (m, 3H), 7.36 – 7.33 (m, 2H), 7.32 – 7.29 (m, 3H), 7.28 – 7.23 (m, 2H), 7.23 – 7.19 (m, 2H), 3.16 (t, $J = 8.0$ Hz, 2H), 2.21 (t, $J = 8.1$ Hz, 2H), 1.30 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.6, 167.9, 165.1, 138.1, 137.7, 136.0, 134.2, 133.6, 132.2, 131.0, 130.4, 129.6, 128.8, 128.8, 128.4, 128.3, 128.1, 127.7, 126.6, 57.3, 41.6, 34.3, 28.4.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{32}\text{ClN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 539.2096; found: 539.2095.



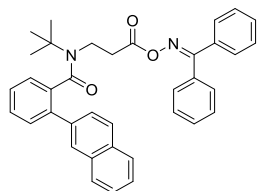
N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2-(thiophen-3-yl)benzamide (**1-18**)

The title compound was obtained as a colorless oil (1.2 g, 46% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, $J = 7.1$ Hz, 2H), 7.50 – 7.44 (m, 3H), 7.43 – 7.39 (m, 2H), 7.38 – 7.31 (m, 4H), 7.31 – 7.27 (m, 1H), 7.26 – 7.24 (m, 1H), 7.23 – 7.18 (m, 4H), 3.21 (t, $J = 8.1$ Hz, 2H), 2.25 – 2.03 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 168.0, 165.0,

140.0, 137.6, 134.2, 132.3, 132.0, 130.9, 129.5, 129.2, 128.8, 128.5, 128.4, 128.4, 128.3, 128.1, 127.3, 126.3, 125.4, 123.6, 57.3, 41.8, 34.1, 28.4.

HRMS (APCI): calcd for $C_{31}H_{31}N_2O_3S^+$ $[M + H]^+$: 511.2050; found: 511.2049.

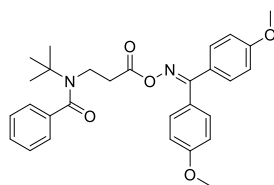


N-(tert-butyl)-N-(3-(((diphenylmethylene)amino)oxy)-3-oxopropyl)-2-(naphthalen-2-yl)benzamide (**1-19**)

The title compound was obtained as a colorless oil (0.97 g, 35% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.88 – 7.80 (m, 3H), 7.61 (dd, J = 8.4, 1.8 Hz, 1H), 7.55 – 7.51 (m, 2H), 7.51 – 7.47 (m, 2H), 7.47 – 7.44 (m, 3H), 7.43 – 7.38 (m, 3H), 7.38 – 7.30 (m, 4H), 7.21 – 7.18 (m, 2H), 3.32 – 3.19 (m, 1H), 3.15 – 3.00 (m, 1H), 2.20 (t, J = 8.1 Hz, 2H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.0, 168.0, 165.1, 138.0, 137.2, 137.0, 134.3, 133.0, 132.4, 132.2, 131.0, 130.0, 129.5, 128.8, 128.8, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.5, 127.5, 127.1, 126.8, 126.1, 126.0, 57.2, 41.6, 34.4, 28.4.

HRMS (APCI): calcd for $C_{37}H_{35}N_2O_3^+$ $[M + H]^+$: 555.2642; found: 555.2638.

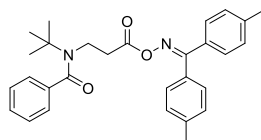


N-(3-(((bis(4-methoxyphenyl)methylene)amino)oxy)-3-oxopropyl)-N-(tert-butyl)benzamide (**1-20**)

The title compound was obtained as a white solid (1.3 g, 53% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, J = 8.8 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.31 – 7.27 (m, 2H), 7.17 (d, J = 8.7 Hz, 2H), 6.94 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.8 Hz, 2H), 3.87 (s, 3H), 3.80 (s, 3H), 3.62 – 3.56 (m, 2H), 2.55 – 2.48 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 168.3, 164.6, 161.7, 160.4, 139.0, 130.6, 130.6, 128.9, 128.4, 127.0, 125.8, 124.4, 113.6, 113.4, 57.1, 55.2, 42.4, 34.9, 28.8.

HRMS (APCI): calcd for $C_{29}H_{33}N_2O_5^+$ $[M + H]^+$: 489.2384; found: 489.2386.



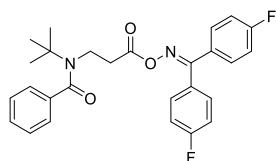
N-(tert-butyl)-N-(3-(((di-p-tolylmethylene)amino)oxy)-3-oxopropyl)benzamide (**1-21**)

The title compound was obtained as a white solid (1.2 g, 54% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.41 (d, J = 8.2 Hz, 2H), 7.36 – 7.31 (m, 3H), 7.30 – 7.26 (m, 2H), 7.24 (d, J = 7.9 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.1 Hz, 2H), 3.59 – 3.53 (m, 2H), 2.52 – 2.47 (m, 2H), 2.44 (s, 3H), 2.35 (s, 3H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.4,

168.3, 141.3, 139.6, 139.0, 131.7, 129.4, 129.0, 128.9, 128.7, 128.6, 128.4, 125.8, 57.1, 42.4, 34.9, 28.8, 21.4, 21.3.

HRMS (APCI): calcd for $C_{29}H_{33}N_2O_3^+$ $[M + H]^+$: 457.2486; found: 457.2483.

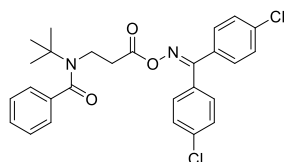


N-(3-(((bis(4-fluorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-(tert-butyl)benzamide (**1-22**)

The title compound was obtained as a colorless oil (1.1 g, 50% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.50 (dd, J = 8.7, 5.5 Hz, 2H), 7.35 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 7.21 – 7.17 (m, 2H), 7.13 (t, J = 8.6 Hz, 2H), 7.02 (t, J = 8.6 Hz, 2H), 3.60 – 3.54 (m, 2H), 2.51 – 2.46 (m, 2H), 1.47 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 167.9, 165.0 (d, J = 132.1 Hz), 163.1, 162.5 (d, J = 130.5 Hz), 138.9, 130.9 (d, J = 8.8 Hz), 130.7 (d, J = 8.4 Hz), 130.3 (d, J = 3.3 Hz), 128.9, 128.3, 127.8 (d, J = 3.6 Hz), 125.8, 115.6 (d, J = 7.2 Hz), 115.4 (d, J = 7.2 Hz), 57.1, 42.4, 34.8, 28.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -108.3, -109.5.

HRMS (APCI): calcd for $C_{27}H_{27}F_2N_2O_3^+$ $[M + H]^+$: 465.1984; found: 465.1979.

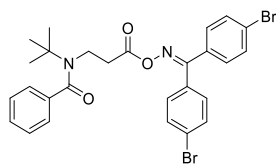


N-(3-(((bis(4-chlorophenyl)methylene)amino)oxy)-3-oxopropyl)-N-(tert-butyl)benzamide (**1-23**)

The title compound was obtained as a white solid (1.2 g, 49% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.42 (m, 4H), 7.38 – 7.32 (m, 5H), 7.31 – 7.26 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 3.62 – 3.55 (m, 2H), 2.56 – 2.46 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 167.8, 163.0, 139.0, 137.5, 136.0, 132.4, 130.0, 129.9, 129.0, 128.7, 128.7, 128.4, 125.9, 57.1, 42.4, 34.8, 28.8.

HRMS (APCI): calcd for $C_{27}H_{27}Cl_2N_2O_3^+$ $[M + H]^+$: 497.1393; found: 497.1386.

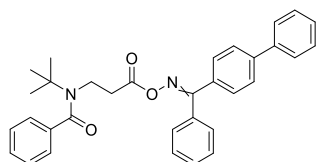


N-(3-(((bis(4-bromophenyl)methylene)amino)oxy)-3-oxopropyl)-N-(tert-butyl)benzamide (**1-24**)

The title compound was obtained as a white solid (1.3 g, 44% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, J = 8.4 Hz, 2H), 7.50 – 7.46 (m, 2H), 7.39 – 7.32 (m, 5H), 7.29 – 7.25 (m, 2H), 7.06 (d, J = 8.8 Hz, 2H), 3.57 (d, J = 7.4 Hz, 2H), 2.48 (d, J = 7.5 Hz, 2H), 1.48 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 167.7, 163.0, 138.9, 132.7, 131.6, 131.6, 130.4, 130.1, 130.0, 128.9, 128.3, 125.9, 125.8, 124.2, 57.1, 42.3, 34.7, 28.8.

HRMS (APCI): calcd for $C_{27}H_{27}Br_2N_2O_3^+$ $[M + H]^+$: 585.0383; found: 585.0376.

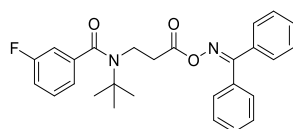


N-(3-(((1,1'-biphenyl]-4-yl(phenyl)methylene)amino)oxy)-3-oxopropyl)-N-(tert-butyl)benzamide (**1-25**)

The title compound was obtained as a colorless oil (1.0 g, 40% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.67 (m, 2H), 7.65 – 7.56 (m, 4H), 7.53 – 7.48 (m, 2H), 7.44 (t, J = 7.9 Hz, 2H), 7.40 – 7.37 (m, 1H), 7.37 – 7.34 (m, 2H), 7.33 – 7.25 (m, 6H), 3.64 – 3.56 (m, 2H), 2.60 – 2.48 (m, 2H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.3, 168.2, 168.0, 164.9, 164.9, 143.7, 142.4, 139.8, 139.8, 139.0, 134.3, 133.0, 132.2, 131.0, 131.0, 129.6, 129.3, 129.2, 128.9, 128.9, 128.8, 128.4, 128.4, 128.3, 128.3, 128.2, 127.9, 127.8, 127.0, 126.9, 126.7, 125.8, 57.1, 42.4, 34.9, 28.8.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{33}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 505.2486; found: 505.2484.

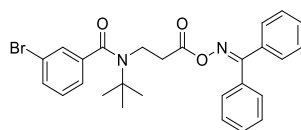


N-(tert-butyl)-N-(3-(((diphenyl)methylene)amino)oxy)-3-oxopropyl)-3-fluorobenzamide (**1-26**)

The title compound was obtained as a white solid (1.1 g, 49% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.53 (m, 2H), 7.52 – 7.42 (m, 4H), 7.40 – 7.30 (m, 3H), 7.26 – 7.21 (m, 2H), 7.10 – 7.04 (m, 2H), 7.03 – 6.99 (m, 1H), 3.61 – 3.54 (m, 2H), 2.55 – 2.48 (m, 2H), 1.49 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.7, 167.9, 165.4, 162.4 (d, J = 248.1 Hz), 140.9 (d, J = 6.9 Hz), 134.2, 132.2, 131.0, 130.3 (d, J = 8.0 Hz), 129.6, 128.8, 128.4, 128.3, 128.1, 121.5 (d, J = 3.1 Hz), 116.0 (d, J = 21.0 Hz), 113.2 (d, J = 22.7 Hz), 57.3, 42.3, 34.8, 28.7. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.5.

HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{28}\text{FN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 447.2078; found: 447.2072.

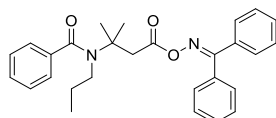


2-bromo-N-(tert-butyl)-N-(3-(((diphenyl)methylene)amino)oxy)-3-oxopropyl)benzamide (**1-27**)

The title compound was obtained as a white solid (1.1 g, 45% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (d, J = 7.1 Hz, 2H), 7.52 – 7.40 (m, 6H), 7.35 (t, J = 7.5 Hz, 2H), 7.22 (t, J = 5.3 Hz, 4H), 3.58 – 3.51 (m, 2H), 2.52 – 2.45 (m, 2H), 1.46 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.5, 168.0, 165.4, 140.8, 134.2, 132.1, 131.0, 130.1, 129.7, 129.0, 128.9, 128.5, 128.4, 128.2, 124.5, 122.5, 57.4, 42.4, 34.8, 28.7.

HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{28}\text{BrN}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 507.1278; found: 507.1273.



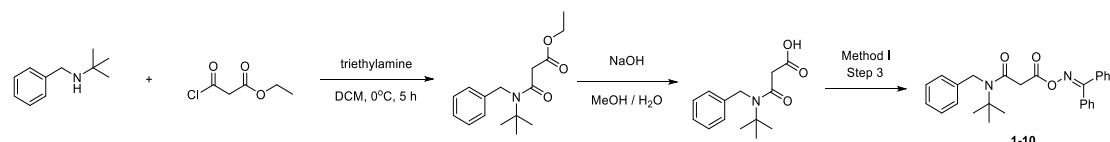
N-(4-(((diphenylmethylene)amino)oxy)-2-methyl-4-oxobutan-2-yl)-N-propylbenzamide (**1-28**)

The title compound was obtained as a colorless oil (930 mg, 42% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.55 (m, 2H), 7.46 – 7.41 (m, 4H), 7.38 – 7.28 (m, 9H), 3.26 – 3.20 (m, 4H), 1.57 (s, 6H), 1.53 – 1.39 (m, 2H), 0.59 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.1, 168.8, 164.8, 139.3, 134.8, 132.5, 130.7, 129.5, 129.0, 128.8, 128.4, 128.2, 128.1, 128.1, 126.0, 57.4, 49.4, 41.3, 27.4, 25.2, 10.9.

HRMS (APCI): calcd for $\text{C}_{28}\text{H}_{31}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 443.2329; found: 443.2325.

III.2 Method II



Step 1:

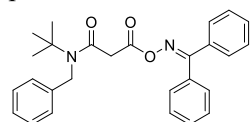
To a solution of N-benzyl-2-methylpropan-2-amine (5.0 mmol, 1.0 eq) and triethylamine (7.5 mmol, 1.5 eq) in dry DCM (30 mL) was slowly added ethyl 3-chloro-3-oxopropanoate (5 mmol, 1.0 eq) at 0 °C. When the addition was complete the reaction mixture was stirred at room temperature for another 8 hours. The reaction mixture was quenched with water and extracted with DCM three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and used for the next step without further purification.

Step 2:

To the solution of crude product from step 1 in MeOH/H₂O (20 mL, v/v=4/1) was added NaOH (7.5 mmol, 1.5 eq) in one portion, and this reaction solution was stirred at room temperature for 4 hours. The reaction solution was carefully adjusted to pH 3~5 by 1M HCl (aq). After removing MeOH under reduced pressure the reaction mixture was extracted with DCM three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by recrystallization from petroleum ether and EtOAc to give 3-(benzyl(tert-butyl)amino)-3-oxopropanoic acid.

Step 3:

To a solution of the acid from step 2, diphenylmethanone oxime (4.5 mmol, 0.9 eq) and DMAP (0.25 mmol, 5 mol%) in dry DCM (30 mL), was added EDCI (12.5 mmol, 2.5 eq) in portions at room temperature and stirred for 8 hours. The reaction mixture was quenched with water and extracted with CH₂Cl₂ three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by column chromatography on silica gel (10 : 1 petroleum ether : EtOAc) to give the starting materials **1-10**.



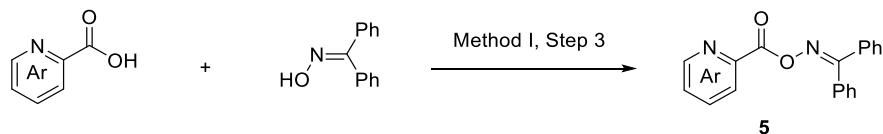
N-benzyl-N-(tert-butyl)-3-(((diphenylmethylene)amino)oxy)-3-oxopropanamide (**1-10**)

The title compound was obtained as a brown-gray solid (1.2 g, 56% yield).

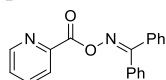
NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.56 (d, $J = 7.1$ Hz, 2H), 7.51 – 7.41 (m, 4H), 7.40 – 7.31 (m, 4H), 7.30 – 7.20 (m, 4H), 7.11 (d, $J = 6.2$ Hz, 2H), 4.47 (s, 2H), 3.46 (s, 2H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.7, 165.8, 164.8, 138.3, 134.6, 132.4, 130.8, 129.6, 129.0, 129.0, 128.8, 128.2, 128.1, 127.1, 125.3, 58.3, 49.0, 42.8, 28.4.

HRMS (APCI): calcd for $C_{27}H_{29}N_2O_3^+ [M + H]^+$: 429.2173; found: 429.2175.

III.3 Method III



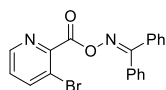
To a solution of picolinic acid (5.0 mmol), diphenylmethanone oxime (4.5 mmol, 0.9 eq) and DMAP (0.25 mmol, 5 mol%) in dry DCM (30 mL), was added EDCI (12.5 mmol, 2.5 eq) in portions at room temperature and stirred for 8 hours. The reaction mixture was quenched with water and extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over sodium sulfate, filtered, concentrated, and purified by column chromatography on silica gel (4 : 1 petroleum ether : EtOAc) to give the starting materials **5**.



diphenylmethanone *O*-picolinoyl oxime (**5-1**)

The title compound was obtained as a white solid (1.2 g, 80% yield), it has been reported.⁵

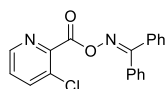
NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, J = 4.1 Hz, 1H), 7.73 – 7.62 (m, 4H), 7.49 – 7.39 (m, 7H), 7.37 (t, J = 7.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 162.1, 150.2, 146.8, 136.8, 134.4, 132.4, 131.0, 129.7, 129.1, 128.9, 128.3, 128.2, 126.9, 125.0.



diphenylmethanone *O*-(3-bromopicolinoyl) oxime (**5-2**)

The title compound was obtained as a yellow solid (1.2 g, 65% yield), it has been reported.⁵

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.49 (dd, J = 4.6, 1.4 Hz, 1H), 7.86 (dd, J = 8.2, 1.4 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.46 – 7.42 (m, 1H), 7.39 (s, 5H), 7.35 (t, J = 7.6 Hz, 2H), 7.19 (dd, J = 8.2, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.3, 163.1, 149.1, 147.6, 141.1, 134.3, 131.9, 131.0, 129.7, 129.1, 129.0, 128.3, 128.0, 126.2, 118.4.

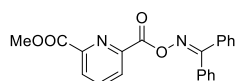


diphenylmethanone *O*-(3-chloropicolinoyl) oxime (**5-3**)

The title compound was obtained as a yellow solid (1.1 g, 68% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.48 (dd, J = 4.6, 1.4 Hz, 1H), 7.70 (dd, J = 8.2, 1.4 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.47 – 7.34 (m, 8H), 7.30 (dd, J = 8.2, 4.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.4, 162.5, 147.3, 138.1, 134.4, 132.1, 131.1, 130.5, 129.7, 129.1, 129.0, 128.3, 128.0, 126.2.

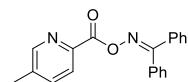
HRMS (APCI): calcd for $C_{19}H_{14}ClN_2O_2^+ [M + H]^+$: 337.0738; found: 337.0733.



methyl 6-((((diphenylmethylene)amino)oxy)carbonyl)picolinate (**5-4**)

The title compound was obtained as a beige solid (1.2 g, 70% yield), it has been reported.⁵

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.48 (s, 5H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 2H), 3.96 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.3, 164.9, 161.5, 148.3, 147.1, 138.2, 134.4, 132.1, 131.0, 129.8, 129.3, 129.2, 128.3, 128.1, 127.8, 127.8, 52.8.



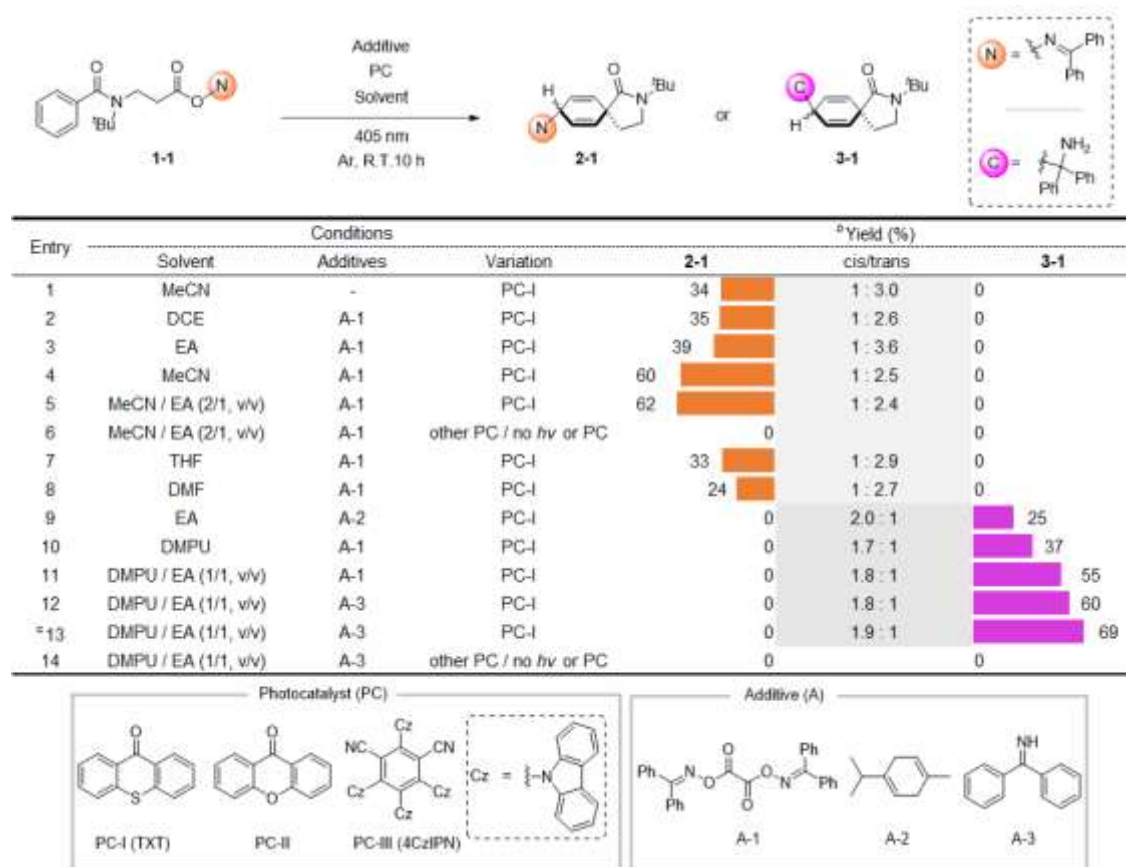
diphenylmethanone *O*-(5-methylpicolinoyl) oxime (**5-5**)

The title compound was obtained as a yellow solid (1.3 g, 82% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.39 (m, 5H), 7.39 – 7.35 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 166.0, 162.0, 150.5, 143.8, 137.3, 136.8, 134.2, 132.2, 130.8, 129.5, 128.9, 128.6, 128.1, 127.9, 124.4, 18.3.

HRMS (APCI): calcd for C₂₀H₁₇N₂O₂⁺ [M + H]⁺: 317.1285; found: 317.1279.

IV. Investigations of reaction conditions



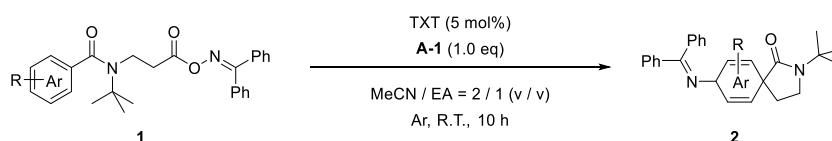
Standard conditions: The reactions were carried out under argon using **1-1** (0.1 mmol), Additive (1.0 equiv), PC (5 mol%), Solvents for **2-1** (0.033 M), Solvents for **3-1** (0.05 M) at room temperature for 10 hours. ^bThe yield of **2-1** and **3-1** were based on ¹H NMR analysis of the crude product using

CH₂Br₂ as the internal standard. ^cAdditive (2.0 equiv). EA = ethyl acetate, DMPU = 1,3-dimethyltetrahydropyrimidin-2(1H)-one.

Notes: For product **3-1**, various potential HAT solvents, including NMP, cyclohexane, 1,4-dioxane, CHCl₃ and 1,3-dimethylimidazolidin-2-one were explored. However, C-C coupling product formation was not observed in any of these solvents.

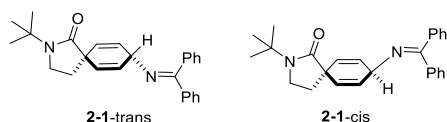
V. General procedure for the chemodivergent reactions.

V.1 Carboamination



Standard Conditions: O-oxime ester **1** (0.2 mmol), **A-1** (0.2 mmol, 1.0 equiv), **TXT** (5 mol%) in 6 mL of MeCN/EA (0.033 M, v/v = 2/1) under an Ar atmosphere at R.T. and irradiated with visible LEDs (2 x 15 W, 405 nm) for 10 h.

Workup: After removing the solvent under reduced pressure, the crude product was purified by column chromatography on pre-basified silica gel using a PE/EtOAc eluent system containing 1% (v/v) triethylamine (TEA) to isolate all isomers of the target product **2**. Isolated yields were reported as the average of four experiments.



2-(tert-butyl)-8-((diphenylmethylene)amino)-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-1**)

2-1-trans was obtained (132 mg, 43% yield) as a brown oil.

2-1-cis was obtained (55 mg, 18% yield) as a brown oil, which can become solid under lower temperature.

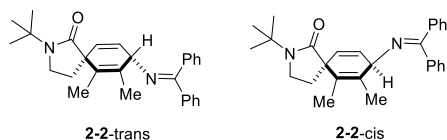
d.r. (cis:trans) = 1:2.4

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.60 (m, 2H), 7.45 – 7.40 (m, 3H), 7.35 – 7.27 (m, 3H), 7.20 – 7.14 (m, 2H), 5.75 (dd, *J* = 10.1, 2.7 Hz, 2H), 5.69 (dd, *J* = 10.1, 1.9 Hz, 2H), 4.70 – 4.66 (m, 1H), 3.48 (t, *J* = 6.8 Hz, 2H), 2.11 (t, *J* = 6.8 Hz, 2H), 1.37 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.7, 169.2, 139.5, 136.5, 130.0, 128.8, 128.6, 128.6, 128.4, 127.8, 127.4, 127.4, 55.4, 54.1, 49.1, 42.1, 32.5, 27.4.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.37 – 7.25 (m, 3H), 7.22 – 7.15 (m, 2H), 5.71 (s, 4H), 4.45 (s, 1H), 3.44 (t, *J* = 6.8 Hz, 2H), 1.90 (t, *J* = 6.8 Hz, 2H), 1.40 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.8, 169.2, 139.1, 136.8, 130.2, 128.8, 128.6, 128.4, 128.3, 128.0, 128.0, 127.5, 55.6, 54.3, 48.6, 42.1, 33.4, 27.6.

HRMS (APCI): calcd for C₂₆H₂₉N₂O⁺ [*M* + *H*]⁺: 385.2274; found: 385.2270.



2-(tert-butyl)-8-((diphenylmethylene)amino)-6,7-dimethyl-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-2**)

2-2-trans was obtained (149 mg, 45% yield) as a brown oil.

2-2-cis was obtained (79 mg, 24% yield) as a brown oil.

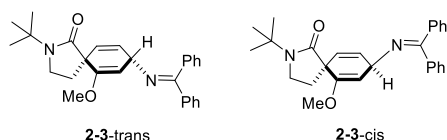
d.r. (cis:trans) = 1:1.9

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.60 (m, 2H), 7.44 – 7.39 (m, 3H), 7.35 – 7.27 (m, 3H), 7.21 – 7.15 (m, 2H), 5.70 (dd, *J* = 9.8, 1.7 Hz, 1H), 5.57 (dd, *J* = 9.8, 3.4 Hz, 1H), 4.50 (s, 1H), 3.52 – 3.45 (m, 2H), 2.37 – 2.27 (m, 1H), 2.02 – 1.95 (m, 1H), 1.68 (s, 3H), 1.61 (s, 3H), 1.39 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.4, 169.2, 139.7, 136.9, 129.9, 129.5, 129.1, 128.5, 128.5, 128.3, 127.8, 127.5, 126.8, 126.3, 60.7, 54.2, 53.3, 42.8, 30.3, 27.4, 16.7, 14.6.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 7.5 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.37 – 7.26 (m, 3H), 7.20 (d, *J* = 7.2 Hz, 2H), 5.70 (d, *J* = 9.9 Hz, 1H), 5.51 (dd, *J* = 9.9, 3.4 Hz, 1H), 4.29 (s, 1H), 3.50 – 3.40 (m, 2H), 2.19 – 2.09 (m, 1H), 1.78 – 1.71 (m, 1H), 1.67 (s, 3H), 1.58 (s, 3H), 1.42 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.0, 167.9, 139.5, 137.2, 129.8, 129.1, 128.8, 128.5, 128.1, 127.8, 127.6, 126.5, 126.2, 60.5, 54.2, 53.0, 42.6, 30.7, 27.5, 16.6, 14.6.

HRMS (APCI): calcd for C₂₈H₃₃N₂O⁺ [M + H]⁺: 413.2587; found: 413.2582.



2-(tert-butyl)-8-((diphenylmethylene)amino)-6-methoxy-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-3**)

2-3-trans was obtained (159 mg, 48% yield) as a brown oil.

2-3-cis was obtained (64 mg, 19% yield) as a brown oil.

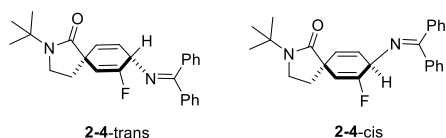
d.r. (cis:trans) = 1:2.5

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.58 (m, 2H), 7.44 – 7.38 (m, 3H), 7.35 – 7.27 (m, 3H), 7.19 – 7.15 (m, 2H), 5.69 – 5.63 (m, 1H), 5.58 (dd, *J* = 9.6, 1.7 Hz, 1H), 4.89 – 4.84 (m, 1H), 4.65 (dd, *J* = 3.6, 1.4 Hz, 1H), 3.55 (s, 3H), 3.53 – 3.46 (m, 1H), 3.45 – 3.38 (m, 1H), 2.52 – 2.44 (m, 1H), 2.01 – 1.92 (m, 1H), 1.36 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.2, 168.5, 155.7, 139.7, 136.7, 129.9, 128.6, 128.5, 128.3, 128.3, 128.2, 127.8, 127.4, 96.3, 57.4, 54.2, 54.2, 51.5, 43.4, 29.9, 27.3.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 6.9 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.34 – 7.27 (m, 3H), 7.19 (d, *J* = 6.6 Hz, 2H), 5.65 – 5.56 (m, 2H), 4.65 – 4.59 (m, 2H), 3.54 (s, 3H), 3.50 – 3.44 (m, 1H), 3.42 – 3.36 (m, 1H), 2.26 – 2.18 (m, 1H), 1.83 – 1.75 (m, 1H), 1.39 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.0, 168.3, 156.5, 139.4, 137.1, 130.2, 128.9, 128.6, 128.6, 128.4, 128.0, 127.6, 127.6, 96.3, 57.5, 54.5, 54.5, 51.3, 43.4, 31.0, 27.5.

HRMS (APCI): calcd for C₂₇H₃₁N₂O₂⁺ [M + H]⁺: 415.2380; found: 415.2374.



2-(tert-butyl)-8-((diphenylmethylene)amino)-7-fluoro-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-4**)

2-4-trans was obtained (116 mg, 36% yield) as a brown oil.

2-4-cis was obtained (74 mg, 23% yield) as a brown oil.

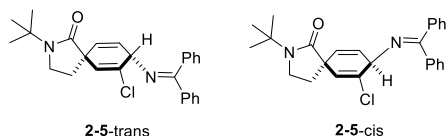
d.r. (cis:trans) = 1:1.5

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.39 (m, 3H), 7.35 (d, *J* = 7.1 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 7.6 Hz, 2H), 5.67 – 5.60 (m, 1H), 5.60 – 5.52 (m, 1H), 5.25 (d, *J* = 15.6 Hz, 1H), 4.86 (s, 1H), 3.45 (t, *J* = 6.8 Hz, 2H), 2.19 – 2.06 (m, 2H), 1.36 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.1 (d, *J* = 3.1 Hz), 171.7, 159.1 (d, *J* = 259.4 Hz), 139.2, 136.1, 130.2, 128.7, 128.5, 128.5, 127.9, 127.7 (d, *J* = 2.4 Hz), 127.6, 127.0 (d, *J* = 7.2 Hz), 104.5 (d, *J* = 17.0 Hz), 56.2 (d, *J* = 24.1 Hz), 54.2, 51.1 (d, *J* = 6.9 Hz), 42.1, 32.4, 27.4. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.4.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.36 – 7.32 (m, 1H), 7.31 – 7.25 (m, 2H), 7.20 (d, *J* = 7.8 Hz, 2H), 5.67 – 5.61 (m, 1H), 5.54 – 5.48 (m, 1H), 5.26 (d, *J* = 15.7 Hz, 1H), 4.65 (s, 1H), 3.42 (t, *J* = 6.7 Hz, 2H), 1.97 – 1.90 (m, 2H), 1.39 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.8 (d, *J* = 2.0 Hz), 171.4, 159.2 (d, *J* = 259.8 Hz), 138.9, 136.3, 130.3, 128.9, 128.5, 128.4, 128.2 (d, *J* = 2.2 Hz), 127.8, 127.7, 126.4 (d, *J* = 7.7 Hz), 104.9 (d, *J* = 17.2 Hz), 56.2 (d, *J* = 24.4 Hz), 54.3, 50.8 (d, *J* = 6.9 Hz), 41.9, 33.2, 27.5. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -111.7.

HRMS (APCI): calcd for C₂₆H₂₈FN₂O⁺ [M + H]⁺: 403.2180; found: 403.2184.



2-(tert-butyl)-7-chloro-8-((diphenylmethylene)amino)-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-5**)

2-5-trans was obtained (107 mg, 32% yield) as a brown oil.

2-5-cis was obtained (77 mg, 23% yield) as a brown oil.

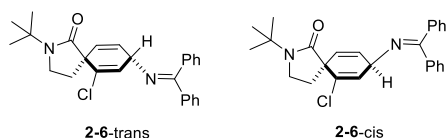
d.r. (cis:trans) = 1:1.4

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.47 – 7.41 (m, 3H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 2H), 5.83 (s, 1H), 5.67 (dd, *J* = 9.9, 2.0 Hz, 1H), 5.60 (dd, *J* = 9.8, 3.2 Hz, 1H), 4.73 (s, 1H), 3.47 (t, *J* = 6.8 Hz, 2H), 2.19 – 2.10 (m, 2H), 1.38 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.6, 171.2, 139.4, 136.3, 134.5, 130.3, 128.8, 128.6, 128.6, 128.0, 127.7, 127.6, 127.3, 125.0, 59.8, 54.4, 52.2, 42.2, 32.2, 27.5.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.53 – 7.42 (m, 3H), 7.39 – 7.36 (m, 1H), 7.35 – 7.30 (m, 2H), 7.27 (d, *J* = 7.2 Hz, 2H), 5.86 (s, 1H), 5.70 (d, *J* = 9.9 Hz, 1H), 5.58 (dd, *J* = 9.8, 3.6 Hz, 1H), 4.56 (s, 1H), 3.47 (t, *J* = 6.8 Hz, 2H), 1.98 (t, *J* = 6.7 Hz, 2H), 1.43 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.1, 170.7, 139.0, 136.5, 134.4, 130.3, 129.0, 128.5, 128.4, 127.9, 127.7, 127.7, 127.1, 125.4, 60.1, 54.5, 51.9, 41.9, 33.1, 27.6.

HRMS (APCI): calcd for $C_{26}H_{28}ClN_2O^+$ $[M + H]^+$: 419.1885; found: 419.1880.



2-(tert-butyl)-8-((diphenylmethylene)amino)-7-fluoro-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-6**)

2-6-trans was obtained (116 mg, 36% yield) as a brown oil.

2-6-cis was obtained (74 mg, 23% yield) as a brown oil.

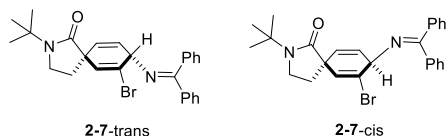
d.r. (cis:trans) = 1:1.4

NMR:

[trans]: 1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, $J = 7.2$ Hz, 2H), 7.43 – 7.39 (m, 3H), 7.36 – 7.34 (m, 1H), 7.31 – 7.28 (m, 2H), 7.14 (d, $J = 7.5$ Hz, 2H), 5.85 (d, $J = 3.7$ Hz, 1H), 5.66 (s, 2H), 4.81 (d, $J = 3.1$ Hz, 1H), 3.61 – 3.55 (m, 1H), 3.51 – 3.45 (m, 1H), 2.61 – 2.53 (m, 1H), 2.10 – 2.03 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.2, 170.0, 139.2, 136.2, 133.9, 130.2, 128.7, 128.6, 128.5, 128.3, 127.9, 127.2, 127.0, 57.9, 54.5, 53.9, 43.1, 29.7, 27.2.

[cis]: 1H NMR (400 MHz, Chloroform-*d*) δ 7.6 (d, $J = 7.2$ Hz, 2H), 7.5 – 7.4 (m, 3H), 7.4 – 7.3 (m, 1H), 7.3 – 7.3 (m, 2H), 7.2 (d, $J = 7.9$ Hz, 2H), 5.8 – 5.8 (m, 1H), 5.7 – 5.7 (m, 1H), 5.7 – 5.6 (m, 1H), 4.6 (t, $J = 3.5$ Hz, 1H), 3.6 – 3.5 (m, 1H), 3.5 – 3.4 (m, 1H), 2.4 – 2.3 (m, 1H), 1.9 – 1.8 (m, 1H), 1.4 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.9, 169.6, 138.9, 136.4, 134.2, 130.3, 128.8, 128.7, 128.5, 128.5, 127.9, 127.3, 127.1, 126.6, 57.9, 54.7, 53.6, 42.9, 30.5, 27.3.

HRMS (APCI): calcd for $C_{26}H_{28}ClN_2O^+$ $[M + H]^+$: 419.1885; found: 419.1880.



2-(tert-butyl)-8-((diphenylmethylene)amino)-7-fluoro-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-7**)

2-7-trans was obtained (141 mg, 38% yield) as a brown oil.

2-7-cis was obtained (82 mg, 22% yield) as a brown oil.

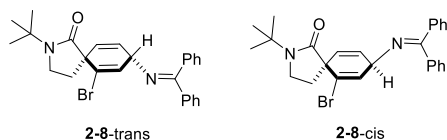
d.r. (cis:trans) = 1:1.7

NMR:

[trans]: 1H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, $J = 7.0$ Hz, 2H), 7.47 – 7.36 (m, 3H), 7.37 – 7.33 (m, 1H), 7.33 – 7.25 (m, 3H), 7.22 (d, $J = 5.7$ Hz, 2H), 6.07 (s, 1H), 5.71 – 5.65 (m, 1H), 5.59 (dd, $J = 9.7, 3.3$ Hz, 1H), 4.80 – 4.74 (m, 1H), 3.43 (t, $J = 6.8$ Hz, 2H), 2.16 – 2.04 (m, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 170.6, 139.2, 136.1, 130.1, 128.7, 128.6, 128.4, 127.8, 127.4, 127.3, 127.1, 125.8, 60.5, 54.2, 52.7, 41.9, 31.8, 27.3.

[cis]: 1H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, $J = 7.3$ Hz, 2H), 7.47 – 7.41 (m, 3H), 7.35 – 7.32 (m, 1H), 7.29 (d, $J = 7.9$ Hz, 2H), 7.24 (d, $J = 8.0$ Hz, 2H), 6.07 (s, 1H), 5.71 – 5.67 (m, 1H), 5.53 (dd, $J = 9.8, 3.6$ Hz, 1H), 4.60 – 4.57 (m, 1H), 3.43 (t, $J = 6.8$ Hz, 2H), 1.94 (t, $J = 6.5$ Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.8, 170.6, 138.9, 136.3, 130.3, 129.3, 128.9, 128.4, 128.4, 127.8, 127.6, 127.5, 127.0, 125.6, 61.0, 54.4, 52.5, 41.8, 32.7, 27.5.

HRMS (APCI): calcd for $C_{26}H_{28}BrN_2O^+$ $[M + H]^+$: 463.1380; found: 463.1374.



6-bromo-2-(tert-butyl)-8-((diphenylmethylene)amino)-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-4**)

2-4-trans was obtained (163 mg, 44% yield) as a brown oil.

2-4-cis was obtained (78 mg, 21% yield) as a brown oil.

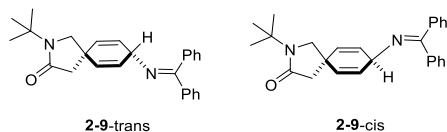
d.r. (cis:trans) = 1:2.1

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.42 (d, *J* = 7.1 Hz, 3H), 7.30 (t, *J* = 7.4 Hz, 3H), 7.14 (dd, *J* = 7.5, 1.9 Hz, 2H), 6.11 (d, *J* = 3.6 Hz, 1H), 5.69 (s, 2H), 4.76 (dd, *J* = 3.6, 1.3 Hz, 1H), 3.63 – 3.57 (m, 1H), 3.50 – 3.44 (m, 1H), 2.61 – 2.53 (m, 1H), 2.10 – 2.03 (m, 1H), 1.39 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.3, 170.2, 139.2, 136.1, 131.4, 130.3, 128.7, 128.6, 128.2, 127.9, 127.2, 126.8, 125.7, 58.5, 54.6, 43.0, 30.6, 27.2.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 7.2 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.37 – 7.33 (m, 1H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.17 (d, *J* = 6.1 Hz, 2H), 6.07 (d, *J* = 2.1 Hz, 1H), 5.71 (d, *J* = 10.1 Hz, 1H), 5.65 (d, *J* = 11.1 Hz, 1H), 4.52 (t, *J* = 3.7 Hz, 1H), 3.59 – 3.53 (m, 1H), 3.48 – 3.42 (m, 1H), 2.39 – 2.32 (m, 1H), 1.91 – 1.83 (m, 1H), 1.43 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 172.0, 169.3, 139.0, 136.5, 131.4, 130.3, 128.8, 128.7, 128.4, 128.4, 127.9, 127.3, 126.5, 125.7, 58.5, 54.6, 54.3, 42.8, 31.3, 27.4.

HRMS (APCI): calcd for C₂₆H₂₈BrN₂O⁺ [M + H]⁺: 463.1380; found: 463.1374.



2-(tert-butyl)-8-((diphenylmethylene)amino)-2-azaspiro[4.5]deca-6,9-dien-3-one (**2-9**)

2-9-trans was obtained (46 mg, 15% yield) as a brown oil.

2-9-cis was obtained (46 mg, 15% yield) as a brown oil.

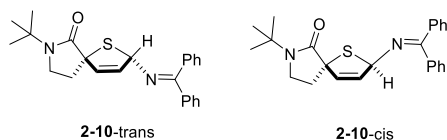
d.r. (cis:trans) = 1:1

NMR:

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.40 – 7.35 (m, 1H), 7.33 – 7.28 (m, 2H), 7.19 (d, *J* = 6.0 Hz, 2H), 5.86 (dd, *J* = 10.1, 1.8 Hz, 2H), 5.60 (dd, *J* = 10.0, 3.2 Hz, 2H), 4.49 – 4.41 (m, 1H), 3.43 (s, 2H), 2.28 (s, 2H), 1.40 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.0, 169.4, 139.5, 136.7, 131.3, 130.2, 128.7, 128.6, 128.5, 128.0, 127.5, 127.1, 57.3, 55.9, 54.0, 46.7, 36.6, 27.7.

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 7.6 Hz, 2H), 7.50 – 7.43 (m, 3H), 7.39 – 7.34 (m, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.0 Hz, 2H), 5.85 (d, *J* = 9.8 Hz, 2H), 5.61 (dd, *J* = 10.0, 3.2 Hz, 2H), 4.44 (s, 1H), 3.24 (s, 2H), 2.46 (s, 2H), 1.36 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 173.3, 169.3, 139.4, 136.7, 131.4, 130.2, 128.6, 128.4, 128.0, 127.5, 127.2, 57.5, 55.7, 53.9, 46.4, 36.6, 27.6.

HRMS (APCI): calcd for C₂₆H₂₉N₂O⁺ [M + H]⁺: 385.2274; found: 385.2270.



7-(tert-butyl)-2-((diphenylmethylene)amino)-1-thia-7-azaspiro[4.4]non-3-en-6-one (**2-10**)

2-10-trans was obtained (91 mg, 29% yield) as a brown oil.

2-10-cis was obtained (82 mg, 26% yield) as a brown oil.

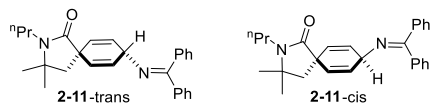
d.r. (cis:trans) = 1:1.1

NMR:

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, J = 7.6 Hz, 2H), 7.44 – 7.33 (m, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.12 (d, J = 6.8 Hz, 2H), 6.05 (s, 1H), 5.89 (dd, J = 6.1, 2.5 Hz, 1H), 5.73 (d, J = 6.0 Hz, 1H), 3.45 – 3.32 (m, 2H), 2.54 – 2.40 (m, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.6, 170.1, 139.1, 135.8, 134.3, 133.3, 130.4, 128.9, 128.7, 128.6, 127.9, 127.6, 75.1, 69.6, 54.4, 42.8, 35.3, 27.3.

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, J = 7.1 Hz, 2H), 7.49 – 7.39 (m, 3H), 7.34 (t, J = 7.2 Hz, 1H), 7.30 – 7.24 (m, 2H), 7.14 (d, J = 6.5 Hz, 2H), 5.92 (s, 1H), 5.88 (dd, J = 6.1, 2.4 Hz, 1H), 5.73 (d, J = 5.6 Hz, 1H), 3.41 – 3.35 (m, 1H), 3.35 – 3.28 (m, 1H), 2.32 – 2.25 (m, 1H), 2.21 – 2.14 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.2, 170.3, 138.7, 136.1, 134.0, 133.2, 130.5, 129.0, 128.6, 128.5, 127.8, 127.7, 74.7, 69.2, 54.5, 42.7, 35.2, 27.4.

HRMS (APCI): calcd for $\text{C}_{24}\text{H}_{27}\text{N}_2\text{OS}^+ [\text{M} + \text{H}]^+$: 391.1839; found: 391.1833.



8-((diphenylmethylene)amino)-3,3-dimethyl-2-propyl-2-azaspiro[4.5]deca-6,9-dien-1-one (**2-11**)

2-11-trans was obtained (118 mg, 38% yield) as a yellow solid.

2-11-cis was obtained (49 mg, 16% yield) as a yellow solid.

d.r. (cis:trans) = 1:2.4

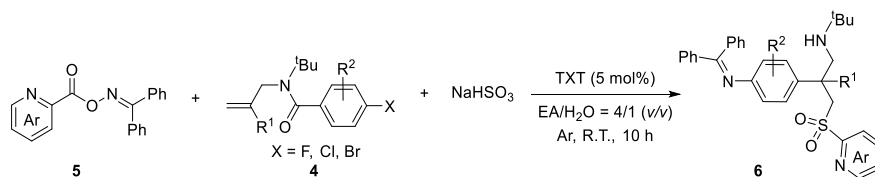
NMR:

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.58 (m, 2H), 7.44 – 7.37 (m, 3H), 7.37 – 7.27 (m, 3H), 7.18 – 7.12 (m, 2H), 5.73 (dd, J = 10.2, 2.6 Hz, 2H), 5.68 (dd, J = 10.1, 1.7 Hz, 2H), 4.66 (p, J = 2.1 Hz, 1H), 3.10 – 3.03 (m, 2H), 2.11 (s, 2H), 1.62 – 1.51 (m, 2H), 1.30 (s, 6H), 0.86 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 169.3, 139.5, 136.4, 130.0, 129.4, 128.6, 128.5, 128.5, 128.4, 127.8, 127.4, 58.0, 54.9, 48.4, 47.3, 41.9, 29.2, 22.4, 11.5.

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.61 (m, 2H), 7.49 – 7.42 (m, 3H), 7.36 – 7.27 (m, 3H), 7.21 – 7.17 (m, 2H), 5.75 – 5.67 (m, 4H), 4.43 (q, J = 1.8 Hz, 1H), 3.14 – 3.10 (m, 2H), 1.92 (s, 2H), 1.66 – 1.59 (m, 2H), 1.29 (s, 6H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 169.4, 139.1, 136.8, 130.3, 129.7, 128.8, 128.6, 128.4, 128.0, 128.0, 127.5, 58.1, 55.1, 49.2, 46.9, 42.0, 29.3, 22.5, 11.6.

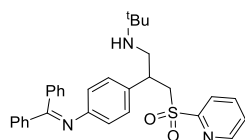
HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{31}\text{N}_2\text{O}^+ [\text{M} + \text{H}]^+$: 399.2431; found: 399.2426.

V.2 Rearomatization



Standard Conditions: N-allyl-N-(tert-butyl)benzamide **4** (0.2 mmol), O-oxime ester **5** (0.34 mmol, 1.7 equiv), NaHSO₃ (0.6 mmol, 3.0 equiv.), TXT (5 mol%) in 5 mL of EA/H₂O (v/v = 4/1) under Ar atmosphere at R.T. and irradiated with visible LEDs (2 x 15 W, 405 nm) for 10h.

Workup: The reaction mixture was washed with brine (saturated NaCl(aq)) and extracted with EA multiple times. The combined organic layers were then dried over Na₂SO₄, concentrated under reduced pressure, and purified by column chromatography to isolate all isomers of target product **6**. Isolated yields were reported as the average of two parallel experiments.

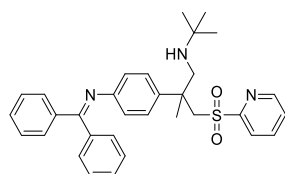


N-(tert-butyl)-2-(4-((diphenylmethylene)amino)phenyl)-3-(pyridin-2-ylsulfonyl)propan-1-amine (**6-1**)

The title compound was obtained as a beige solid (131 mg, 64% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.57 (d, *J* = 4.7 Hz, 1H), 7.78 (dd, *J* = 6.8, 1.7 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.27 – 7.18 (m, 3H), 7.04 (dd, *J* = 7.4, 2.0 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.49 (d, *J* = 8.0 Hz, 2H), 3.79 (d, *J* = 6.7 Hz, 2H), 3.19 (p, *J* = 6.8 Hz, 1H), 2.80 – 2.67 (m, 2H), 0.92 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.3, 157.1, 150.1, 149.8, 139.2, 137.7, 135.9, 134.4, 130.6, 129.2, 129.1, 128.4, 128.0, 127.7, 127.7, 126.8, 122.0, 120.9, 55.4, 49.8, 47.3, 40.6, 28.7. HRMS (APCI): calcd for C₁₉H₁₄ClN₂O₂⁺ [M + H]⁺: 337.0738; found: 337.0733.

HRMS (APCI): calcd for C₃₁H₃₄N₃O₂S⁺ [M + H]⁺: 512.2366; found: 512.2361.

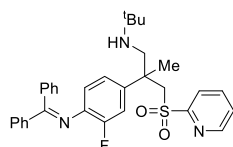


N-(tert-butyl)-2-(4-((diphenylmethylene)amino)phenyl)-2-methyl-3-(pyridin-2-ylsulfonyl)propan-1-amine (**6-2**)

The title compound was obtained as a brown oil (126 mg, 60% yield).

NMR: ¹H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 4.7 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.48 – 7.45 (m, 1H), 7.44 – 7.36 (m, 3H), 7.22 (q, *J* = 6.7 Hz, 3H), 7.04 (d, *J* = 6.4 Hz, 2H), 6.92 (d, *J* = 8.2 Hz, 2H), 6.44 (d, *J* = 8.2 Hz, 2H), 4.00 (d, *J* = 14.9 Hz, 1H), 3.81 (d, *J* = 15.0 Hz, 1H), 2.83 – 2.74 (m, 2H), 1.57 (s, 3H), 0.94 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 168.3, 158.2, 149.7, 149.5, 139.4, 137.9, 137.2, 136.0, 130.7, 129.4, 129.2, 128.5, 128.1, 127.8, 126.6, 126.5, 121.7, 120.5, 60.2, 52.6, 50.2, 41.0, 28.8, 22.7.

HRMS (APCI): calcd for $C_{32}H_{36}N_3O_2S^+$ $[M + H]^+$: 526.2523; found: 526.2521.

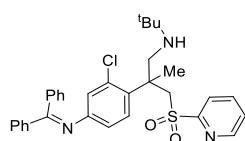


N-(tert-butyl)-2-(4-((diphenylmethylene)amino)-3-fluorophenyl)-2-methyl-3-(pyridin-2-ylsulfonyl)propan-1-amine (**6-3**)

The title compound was obtained as a brown oil (126 mg, 58% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, $J = 4.0$ Hz, 1H), 7.81 – 7.76 (m, 1H), 7.75 – 7.70 (m, 2H), 7.65 (d, $J = 7.8$ Hz, 1H), 7.49 – 7.43 (m, 2H), 7.39 (t, $J = 7.4$ Hz, 2H), 7.26 – 7.19 (m, 3H), 7.11 – 7.04 (m, 2H), 6.74 (dd, $J = 8.3, 2.1$ Hz, 1H), 6.66 (dd, $J = 12.4, 2.0$ Hz, 1H), 6.48 (t, $J = 8.4$ Hz, 1H), 3.98 (d, $J = 14.9$ Hz, 1H), 3.78 (d, $J = 14.9$ Hz, 1H), 2.77 – 2.70 (m, 2H), 1.54 (s, 3H), 0.93 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.2, 157.9, 151.4 (d, $J = 244.4$ Hz), 149.8, 139.4 (d, $J = 5.9$ Hz), 138.7, 137.8, 137.6 (d, $J = 12.7$ Hz), 136.1, 131.0, 129.3, 128.8, 128.5, 128.1, 127.8, 126.7, 121.9, 121.9, 121.6, 114.0 (d, $J = 21.1$ Hz), 59.9, 52.6, 50.2, 40.9, 28.7, 22.6. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -124.8.

HRMS (APCI): calcd for $C_{32}H_{34}FN_3O_2S^+$ $[M + H]^+$: 543.2350; found: 543.2347.

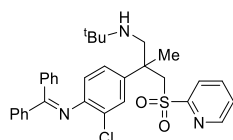


N-(tert-butyl)-2-(2-chloro-4-((diphenylmethylene)amino)phenyl)-2-methyl-3-(pyridin-2-ylsulfonyl)propan-1-amine (**6-4**)

The title compound was obtained as a brown oil (90 mg, 40% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, $J = 3.3$ Hz, 1H), 7.74 – 7.67 (m, 3H), 7.49 (dd, $J = 18.4, 7.5$ Hz, 2H), 7.44 – 7.37 (m, 3H), 7.29 – 7.25 (m, 3H), 7.14 (d, $J = 8.5$ Hz, 1H), 7.07 (dd, $J = 7.6, 2.0$ Hz, 2H), 6.50 (dd, $J = 8.5, 2.3$ Hz, 1H), 6.37 (d, $J = 2.3$ Hz, 1H), 4.50 (d, $J = 15.1$ Hz, 1H), 3.89 (d, $J = 15.1$ Hz, 1H), 3.07 (d, $J = 11.7$ Hz, 1H), 2.98 (d, $J = 11.7$ Hz, 1H), 1.68 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.6, 151.0, 149.9, 139.0, 137.6, 135.5, 132.8, 132.5, 131.0, 130.6, 129.3, 128.9, 128.2, 128.0, 126.6, 123.7, 121.8, 119.1, 57.6, 50.3, 49.7, 42.2, 29.0, 24.2.

HRMS (APCI): calcd for $C_{32}H_{35}ClN_3O_2S^+$ $[M + H]^+$: 560.2133; found: 560.2128.



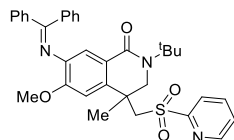
N-(tert-butyl)-2-(3-chloro-4-((diphenylmethylene)amino)phenyl)-2-methyl-3-(pyridin-2-ylsulfonyl)propan-1-amine (**6-5**)

The title compound was obtained as a brown oil (122 mg, 55% yield).

NMR: 1H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, $J = 4.7$ Hz, 1H), 7.78 – 7.72 (m, 3H), 7.61 (d, $J = 7.8$ Hz, 1H), 7.50 – 7.36 (m, 5H), 7.22 (d, $J = 7.0$ Hz, 2H), 7.08 (d, $J = 5.3$ Hz, 2H), 6.97 (d, $J = 2.1$ Hz, 1H), 6.80 (dd, $J = 8.3, 2.1$ Hz, 1H), 6.29 (d, $J = 8.3$ Hz, 1H), 3.99 (d, $J = 15.0$ Hz, 1H), 3.76 (d, $J = 14.9$

Hz, 1H), 2.73 (s, 2H), 1.54 (s, 3H), 0.93 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.9, 157.7, 149.8, 147.1, 138.5, 138.5, 137.7, 135.9, 131.0, 129.4, 128.8, 128.5, 128.1, 127.7, 127.6, 126.8, 125.0, 124.2, 121.6, 120.6, 59.9, 52.5, 50.2, 40.8, 28.8, 22.5.

HRMS (APCI): calcd for $\text{C}_{32}\text{H}_{34}\text{ClN}_3\text{O}_2\text{S}^+$ $[\text{M} + \text{H}]^+$: 559.2055; found: 559.2051.

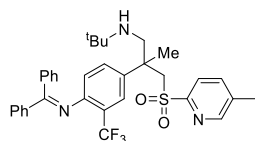


2-((tert-butyl)-7-((diphenylmethylene)amino)-6-methoxy-4-methyl-4-((pyridin-2-ylsulfonyl)-methyl)-3,4-dihydroisoquinolin-1(2H)-one (6-6)

The title compound was obtained as a brown oil (145 mg, 62% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 8.60 (d, $J = 4.7$ Hz, 1H), 7.89 – 7.83 (m, 2H), 7.66 (d, $J = 7.2$ Hz, 2H), 7.47 – 7.44 (m, 1H), 7.40 (d, $J = 7.0$ Hz, 1H), 7.34 (d, $J = 7.6$ Hz, 2H), 7.21 – 7.14 (m, 4H), 7.11 – 7.04 (m, 2H), 6.57 (s, 1H), 4.07 (d, $J = 13.0$ Hz, 1H), 3.69 (s, 3H), 3.64 (d, $J = 14.4$ Hz, 1H), 3.58 (d, $J = 14.4$ Hz, 1H), 3.22 (d, $J = 12.9$ Hz, 1H), 1.67 (s, 3H), 1.53 (s, 9H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.1, 164.5, 157.7, 151.9, 150.0, 140.4, 139.1, 138.9, 138.0, 136.4, 130.6, 129.3, 128.5, 128.4, 127.9, 127.5, 127.1, 123.0, 120.8, 120.8, 105.5, 57.3, 55.7, 55.4, 51.3, 37.1, 28.5, 21.6.

HRMS (APCI): calcd for $\text{C}_{34}\text{H}_{36}\text{N}_3\text{O}_4\text{S}^+$ $[\text{M} + \text{H}]^+$: 582.2421; found: 582.2416.

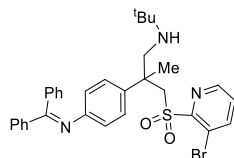


N-(tert-butyl)-2-(4-((diphenylmethylene)amino)-3-(trifluoromethyl)phenyl)-2-methyl-3-((5-methylpyridin-2-yl)sulfonyl)propan-1-amine (6-7)

The title compound was obtained as a brown oil (115 mg, 48% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 7.75 (d, $J = 7.7$ Hz, 2H), 7.48 – 7.38 (m, 5H), 7.27 – 7.22 (m, 4H), 7.14 – 7.06 (m, 2H), 7.01 (d, $J = 8.5$ Hz, 1H), 6.20 (d, $J = 8.4$ Hz, 1H), 4.02 (d, $J = 15.0$ Hz, 1H), 3.74 (d, $J = 15.0$ Hz, 1H), 2.72 (s, 2H), 2.39 (s, 3H), 1.56 (s, 3H), 0.93 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 154.9, 150.3, 147.5, 138.6, 137.8, 137.7, 137.2, 135.5, 131.0, 130.2, 129.3, 128.8, 128.1, 127.8, 124.1 (q, $J = 5.4$ Hz), 123.8 (d, $J = 273.4$ Hz), 121.5, 120.6, 120.0 (q, $J = 29.7$ Hz), 60.1, 52.7, 50.1, 40.8, 28.8, 22.5, 18.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -61.3.

HRMS (APCI): calcd for $\text{C}_{34}\text{H}_{37}\text{F}_3\text{N}_3\text{O}_2\text{S}^+$ $[\text{M} + \text{H}]^+$: 608.2553; found: 608.2548.



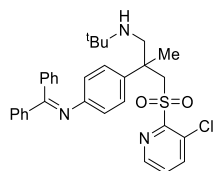
3-((3-bromopyridin-2-yl)sulfonyl)-N-(tert-butyl)-2-(4-((diphenylmethylene)amino)phenyl)-2-methylpropan-1-amine (6-8)

The title compound was obtained as a brown oil (72 mg, 30% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 8.51 (d, $J = 4.6$ Hz, 1H), 7.94 (d, $J = 8.1$ Hz, 1H), 7.71 (d, $J = 7.7$ Hz, 2H), 7.46 (t, $J = 7.1$ Hz, 1H), 7.39 (t, $J = 7.5$ Hz, 2H), 7.31 – 7.22 (m, 4H), 7.06 (t, $J = 6.7$

Hz, 4H), 6.53 (d, J = 8.1 Hz, 2H), 4.09 (d, J = 14.9 Hz, 1H), 4.04 (d, J = 14.6 Hz, 1H), 2.85 (s, 2H), 1.61 (s, 3H), 0.96 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.4, 155.2, 149.5, 147.1, 143.9, 139.5, 137.7, 136.0, 130.7, 129.4, 129.2, 128.6, 128.1, 127.8, 127.4, 126.3, 120.7, 117.6, 60.0, 52.5, 50.4, 41.2, 28.8, 22.7.

HRMS (APCI): calcd for $\text{C}_{32}\text{H}_{35}\text{BrN}_3\text{O}_2\text{S}^+$ $[\text{M} + \text{H}]^+$: 604.1628; found: 604.1624.

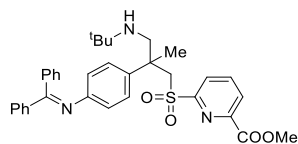


N-(tert-butyl)-3-((3-chloropyridin-2-yl)sulfonyl)-2-(4-((diphenylmethylene)amino)phenyl)-2-methylpropan-1-amine (**6-9**)

The title compound was obtained as a brown oil (67 mg, 30% yield).

NMR: ^1H NMR (400 MHz, Chloroform- d) δ 8.51 (d, J = 4.5 Hz, 1H), 7.74 (t, J = 8.1 Hz, 3H), 7.48 (t, J = 7.3 Hz, 1H), 7.44 – 7.39 (m, 3H), 7.27 – 7.22 (m, 3H), 7.11 – 7.02 (m, 4H), 6.53 (d, J = 8.1 Hz, 2H), 4.10 – 4.01 (m, 2H), 2.86 (s, 2H), 1.63 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.4, 153.8, 149.5, 146.7, 140.4, 139.5, 137.6, 136.0, 130.7, 130.2, 129.4, 129.2, 128.6, 128.1, 127.8, 127.6, 126.3, 120.7, 60.5, 52.5, 50.4, 41.2, 28.8, 22.7.

HRMS (APCI): calcd for $\text{C}_{32}\text{H}_{35}\text{ClN}_3\text{O}_2\text{S}^+$ $[\text{M} + \text{H}]^+$: 560.2133; found: 560.2128.



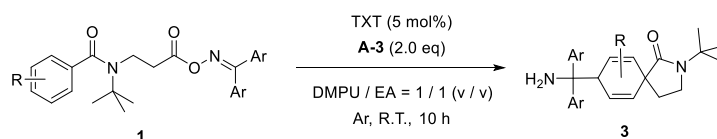
methyl 6-((3-(tert-butylamino)-2-(4-((diphenylmethylene)amino)phenyl)-2-methylpropyl)sulfonyl)picolinate (**6-10**)

The title compound was obtained as a brown oil (112 mg, 48% yield).

NMR: ^1H NMR (400 MHz, Chloroform- d) δ 8.18 (dd, J = 7.8, 1.1 Hz, 1H), 7.89 (t, J = 7.9 Hz, 1H), 7.73 (dd, J = 7.8, 1.1 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.47 – 7.43 (m, 1H), 7.39 (t, J = 7.4 Hz, 2H), 7.23 – 7.17 (m, 3H), 7.02 (dd, J = 7.9, 1.7 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 6.35 (d, J = 8.5 Hz, 2H), 4.11 (d, J = 15.0 Hz, 1H), 3.99 (s, 3H), 3.86 (d, J = 15.1 Hz, 1H), 2.75 (s, 2H), 1.56 (s, 3H), 0.94 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 168.3, 164.3, 158.2, 149.5, 148.0, 139.4, 139.1, 136.8, 136.0, 130.7, 129.4, 129.2, 128.5, 128.1, 127.8, 127.4, 126.7, 124.3, 120.3, 60.1, 53.0, 52.6, 50.0, 40.9, 28.9, 22.7.

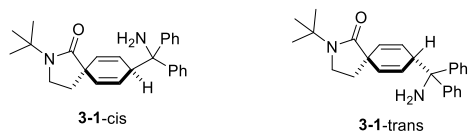
HRMS (APCI): calcd for $\text{C}_{34}\text{H}_{38}\text{N}_3\text{O}_4\text{S}^+$ $[\text{M} + \text{H}]^+$: 584.2578; found: 584.2573.

V.3 Carbo-aminoalkylation



Standard Conditions: O-oxime ester **1** (0.2 mmol), **A-3** (0.4 mmol, 2.0 equiv), **TXT** (5 mol%) in 4 mL of DMPU/EA (0.05 M, v/v = 1/1) under Ar atmosphere at R.T. and irradiated with visible LEDs (2 x 15 W, 405 nm) for 10 h.

Workup: The reaction mixture was washed with brine (saturated NaCl(aq)) and extracted with EA multiple times. The combined organic layers were then dried over Na₂SO₄, concentrated under reduced pressure, and purified by column chromatography to isolate all isomers of target product **3**. Isolated yields were reported as the average of four experiments.



8-(aminodiphenylmethyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-1**)

3-1-cis was obtained (132 mg, 43% yield) as a brown oil, which can slowly solidify.

3-1-trans was obtained (78 mg, 25% yield) as a brown oil.

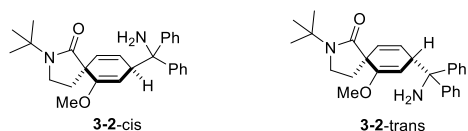
d.r. (cis:trans) = 1.7:1

NMR:

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.8 Hz, 4H), 7.27 (t, *J* = 7.5 Hz, 4H), 7.13 (t, *J* = 7.3 Hz, 2H), 5.64 (d, *J* = 10.1 Hz, 2H), 5.56 (dd, *J* = 10.3, 3.4 Hz, 2H), 4.24 (s, 1H), 3.43 (t, *J* = 6.7 Hz, 2H), 2.13 (s, 2H), 1.95 (t, *J* = 6.7 Hz, 2H), 1.38 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.9, 146.7, 130.5, 128.2, 126.9, 126.2, 125.9, 62.3, 54.2, 49.4, 44.7, 42.0, 33.7, 27.6.

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 6.9 Hz, 4H), 7.28 (t, *J* = 7.6 Hz, 4H), 7.15 (t, *J* = 7.3 Hz, 2H), 5.73 – 5.66 (m, 4H), 4.33 (s, 1H), 3.42 (t, *J* = 6.8 Hz, 2H), 1.92 (t, *J* = 6.8 Hz, 2H), 1.80 (s, 2H), 1.38 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 175.1, 146.3, 130.4, 128.3, 127.5, 126.3, 126.2, 62.8, 54.3, 49.4, 44.1, 42.2, 33.5, 27.6.

HRMS (APCI): calcd for C₂₆H₃₁N₂O⁺ [M + H]⁺: 387.2431; found: 387.2430.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-methoxy-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-2**)

3-2-cis was obtained (150 mg, 45% yield) as a brown solid.

3-2-trans was obtained (73 mg, 22% yield) as a brown oil.

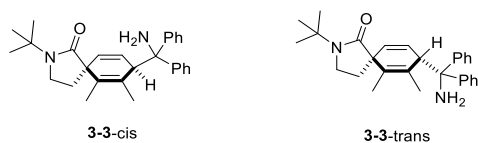
d.r. (cis:trans) = 2.1:1

NMR:

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 (dd, *J* = 12.9, 7.8 Hz, 4H), 7.26 (t, *J* = 15.0 Hz, 4H), 7.12 (t, *J* = 7.5 Hz, 2H), 5.57 – 5.48 (m, 2H), 4.36 (s, 2H), 3.49 – 3.35 (m, 2H), 3.30 (s, 3H), 2.42 – 2.29 (m, 1H), 1.87 – 1.72 (m, 1H), 1.37 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.4, 157.7, 147.1, 146.9, 130.9, 128.2, 128.1, 126.4, 126.2, 125.9, 125.8, 93.5, 62.6, 54.4, 54.2, 51.8, 45.8, 43.3, 30.7, 27.5.

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.59 (t, *J* = 8.5 Hz, 4H), 7.29 (t, *J* = 7.6 Hz, 4H), 7.15 (t, *J* = 7.4 Hz, 2H), 5.68 – 5.61 (m, 1H), 5.61 – 5.54 (m, 1H), 4.53 – 4.44 (m, 2H), 3.51 – 3.40 (m, 1H), 3.41 – 3.36 (m, 1H), 3.35 (s, 3H), 2.27 – 2.17 (m, 1H), 1.84 – 1.77 (m, 1H), 1.37 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.3, 157.8, 146.6, 146.3, 131.0, 128.2, 128.2, 126.9, 126.2, 126.1, 126.1, 93.5, 63.0, 54.4, 54.2, 51.6, 45.5, 43.4, 31.1, 27.4.

HRMS (APCI): calcd for C₂₇H₃₃N₂O₂⁺ [M + H]⁺: 417.2537; found: 417.2539.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6,7-dimethyl-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-3**)

3-3-cis was obtained (63 mg, 19% yield) as a beige solid.

3-3-trans was obtained (93 mg, 28% yield) as an off-white solid.

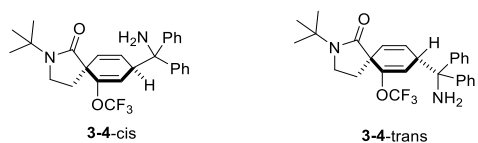
d.r. (cis:trans) = 1:1.5

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, J = 7.2 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.7 Hz, 2H), 7.22 (t, J = 7.7 Hz, 2H), 7.16 (t, J = 7.3 Hz, 2H), 7.11 (t, J = 7.3 Hz, 1H), 5.91 (dd, J = 10.1, 4.3 Hz, 1H), 5.67 (d, J = 10.0 Hz, 1H), 4.19 (d, J = 4.3 Hz, 1H), 3.47 – 3.41 (m, 2H), 2.20 – 2.11 (m, 1H), 1.83 (s, 2H), 1.79 – 1.75 (m, 1H), 1.58 (s, 3H), 1.39 (s, 9H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.3, 146.9, 146.7, 132.3, 130.8, 128.3, 128.2, 127.8, 126.6, 126.4, 126.2, 126.0, 63.4, 54.3, 53.4, 52.0, 42.5, 31.5, 27.4, 20.4, 15.5.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, J = 7.9 Hz, 2H), 7.69 (d, J = 7.8 Hz, 2H), 7.27 (t, J = 7.8 Hz, 2H), 7.20 (t, J = 7.6 Hz, 2H), 7.16 – 7.04 (m, 2H), 5.69 (dd, J = 10.1, 4.1 Hz, 1H), 5.58 (d, J = 10.1 Hz, 1H), 4.22 (d, J = 4.2 Hz, 1H), 3.49 – 3.39 (m, 2H), 2.32 – 2.19 (m, 3H), 1.76 – 1.68 (m, 1H), 1.56 (s, 3H), 1.39 (s, 9H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.4, 147.9, 147.8, 131.2, 129.5, 129.1, 128.1, 127.7, 126.8, 126.8, 126.7, 125.8, 125.7, 62.8, 54.3, 53.8, 51.5, 42.4, 31.0, 27.6, 20.4, 16.2.

HRMS (APCI): calcd for $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 415.2744; found: 415.2742.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(trifluoromethoxy)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-4**)

3-4-cis was obtained (75 mg, 20% yield) as a brown oil.

3-4-trans was obtained (94 mg, 25% yield) as a brown oil.

d.r. (cis:trans) = 1:1.2

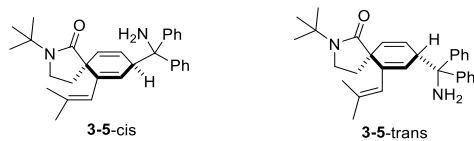
NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, J = 7.4 Hz, 2H), 7.59 (d, J = 7.2 Hz, 2H), 7.31 – 7.24 (m, 4H), 7.17 – 7.12 (m, 2H), 5.55 (s, 2H), 5.24 (s, 1H), 4.42 (dd, J = 4.0, 1.9 Hz, 1H), 3.49 – 3.40 (m, 2H), 2.38 – 2.30 (m, 1H), 2.12 (s, 2H), 1.96 – 1.88 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.1, 148.7, 146.2 (d, J = 14.1 Hz), 130.8, 128.3 (d, J = 2.6 Hz), 126.2, 126.2, 125.9, 125.9, 110.2, 62.6, 54.8, 51.4, 46.5, 43.0, 30.1, 27.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -56.4.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, J = 7.1 Hz, 2H), 7.49 (d, J = 7.4 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.20 – 7.14 (m, 2H), 5.76 – 5.70 (m, 1H), 5.57 (dd, J = 10.1, 1.8 Hz, 1H), 5.50 – 5.44 (m, 1H), 4.50 – 4.44 (m, 1H), 3.44 – 3.36 (m, 2H), 2.16 – 2.07 (m, 1H), 1.85 – 1.77 (m, 1H), 1.71 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.0, 148.4, 145.7, 145.5, 130.4, 128.2 (d, J = 11.0

Hz), 126.5 (d, $J = 1.3$ Hz), 126.2, 126.1 (d, $J = 38.1$ Hz), 110.4 (d, $J = 2.1$ Hz), 63.3, 54.7, 51.2, 46.0, 42.9, 30.1, 27.2. ^{19}F NMR (376 MHz, Chloroform- d) δ -56.3.

HRMS (APCI): calcd for $\text{C}_{27}\text{H}_{30}\text{F}_3\text{N}_2\text{O}_2^+ [\text{M} + \text{H}]^+$: 471.2254; found: 471.2259.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(2-methylprop-1-en-1-yl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-5**)

3-5-cis was obtained (134 mg, 38% yield) as a beige solid.

3-5-trans was obtained (99 mg, 28% yield) as a yellow solid.

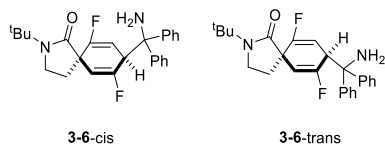
d.r. (cis:trans) = 1.4:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform- d) δ 7.72 – 7.67 (m, 4H), 7.31 – 7.26 (m, 3H), 7.25 (d, $J = 1.6$ Hz, 1H), 7.15 – 7.10 (m, 2H), 5.64 (dd, $J = 10.2, 1.6$ Hz, 1H), 5.58 – 5.52 (m, 1H), 5.51 – 5.47 (m, 1H), 5.27 – 5.22 (m, 1H), 4.38 – 4.32 (m, 1H), 3.46 – 3.39 (m, 1H), 3.37 – 3.30 (m, 1H), 2.21 (s, 2H), 2.17 – 2.11 (m, 1H), 1.88 – 1.81 (m, 1H), 1.68 (s, 3H), 1.56 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 174.8, 147.0, 146.9, 138.9, 136.3, 132.3, 128.1, 128.1, 126.1, 126.1, 125.8, 125.8, 124.9, 122.9, 62.4, 54.2, 51.6, 45.2, 43.2, 31.4, 27.4, 25.9, 19.3.

[trans]: ^1H NMR (400 MHz, Chloroform- d) δ 7.61 (dd, $J = 13.5, 7.8$ Hz, 4H), 7.27 (q, $J = 7.6$ Hz, 4H), 7.14 (q, $J = 7.1$ Hz, 2H), 5.69 (s, 2H), 5.45 (s, 1H), 5.33 (s, 1H), 4.43 (t, $J = 2.7$ Hz, 1H), 3.43 – 3.37 (m, 1H), 3.37 – 3.30 (m, 1H), 2.08 – 1.99 (m, 1H), 1.86 – 1.77 (m, 3H), 1.67 (s, 3H), 1.50 (s, 3H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 174.7, 146.5, 146.2, 138.6, 136.3, 131.8, 128.2, 128.1, 126.1, 126.1, 126.0, 125.9, 125.3, 123.1, 62.8, 54.2, 51.5, 45.2, 42.9, 31.5, 27.4, 26.0, 19.5.

HRMS (APCI): calcd for $\text{C}_{30}\text{H}_{37}\text{N}_2\text{O}^+ [\text{M} + \text{H}]^+$: 441.2900; found: 441.2896.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6,9-difluoro-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-6**)

3-6-cis was obtained (110 mg, 32.5% yield) as a white solid.

3-6-trans was obtained (110 mg, 32.5% yield) as a white solid.

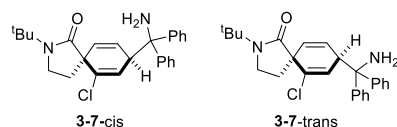
d.r. (cis:trans) = 1:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform- d) δ 7.74 (d, $J = 7.8$ Hz, 2H), 7.68 (d, $J = 7.8$ Hz, 2H), 7.35 – 7.25 (m, 4H), 7.21 – 7.12 (m, 2H), 5.22 (dd, $J = 15.9, 7.1$ Hz, 1H), 5.06 – 4.94 (m, 1H), 4.69 (q, $J = 3.8$ Hz, 1H), 3.55 – 3.38 (m, 2H), 2.49 – 2.38 (m, 1H), 2.28 (s, 2H), 2.00 – 1.88 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 171.6, 146.4, 146.3, 128.4, 127.7, 126.2, 126.1, 126.0, 125.9, 125.9, 108.1 (dd, $J = 22.1, 8.0$ Hz), 102.7 (dd, $J = 21.2, 9.5$ Hz), 62.2, 54.9, 51.0 (dd, $J = 28.0, 8.5$ Hz), 46.6 (dd, $J = 21.8, 7.4$ Hz), 42.6, 29.7, 27.4. ^{19}F NMR (376 MHz, Chloroform- d) δ -102.3 (d, $J = 7.1$ Hz), -117.7 (d, $J = 6.8$ Hz).

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.48 (t, J = 6.7 Hz, 4H), 7.28 (q, J = 7.7 Hz, 4H), 7.20 (t, J = 7.1 Hz, 2H), 5.29 – 5.20 (m, 1H), 5.10 (dd, J = 16.6, 7.1 Hz, 1H), 4.58 (s, 1H), 3.41 – 3.24 (m, 2H), 2.07 – 2.00 (m, 1H), 1.96 (s, 2H), 1.65 – 1.55 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.4, 145.6, 144.8, 127.9, 127.8, 126.7, 126.6, 126.5, 107.5 (dd, J = 22.4, 8.4 Hz), 103.4 (dd, J = 21.5, 9.3 Hz), 64.0, 54.7, 50.7 (dd, J = 27.9, 8.5 Hz), 46.7 (dd, J = 21.6, 7.1 Hz), 42.4, 29.4, 27.3. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -103.0 (d, J = 7.3 Hz), -117.7 (d, J = 7.2 Hz).

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{29}\text{F}_2\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 423.2242; found: 423.2245.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-chloro-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-7**)

3-7-cis was obtained (123 mg, 37% yield) as a white solid.

3-7-trans was obtained (112 mg, 33% yield) as a white solid.

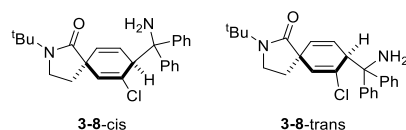
d.r. (cis:trans) = 1.1:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, J = 7.7, 4.1 Hz, 4H), 7.31 (q, J = 7.9 Hz, 4H), 7.17 (q, J = 7.5 Hz, 2H), 5.74 (dd, J = 3.7, 1.7 Hz, 1H), 5.65 (d, J = 10.1 Hz, 1H), 5.54 – 5.47 (m, 1H), 4.42 (t, J = 3.9 Hz, 1H), 3.61 – 3.54 (m, 1H), 3.52 – 3.44 (m, 1H), 2.54 – 2.46 (m, 1H), 2.05 (s, 2H), 1.98 – 1.90 (m, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 146.4, 146.2, 135.4, 131.2, 128.4, 128.3, 126.2, 126.1, 126.0, 125.9, 125.2, 62.5, 54.7, 54.2, 47.5, 43.0, 30.8, 27.4.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (dd, J = 7.2, 3.4 Hz, 4H), 7.31 (q, J = 7.7 Hz, 4H), 7.20 (q, J = 7.1 Hz, 2H), 5.89 (d, J = 3.4 Hz, 1H), 5.67 (s, 2H), 4.50 (d, J = 3.5 Hz, 1H), 3.59 – 3.52 (m, 1H), 3.49 – 3.42 (m, 1H), 2.39 – 2.31 (m, 1H), 1.89 – 1.81 (m, 1H), 1.68 (s, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 145.8, 145.6, 135.3, 131.0, 128.4, 128.3, 126.5, 126.4, 126.1, 126.0, 125.7, 63.1, 54.7, 54.1, 47.2, 43.0, 30.7, 27.3.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{30}\text{ClN}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 421.2041; found: 421.2044.



8-(aminodiphenylmethyl)-2-(tert-butyl)-7-chloro-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-8**)

3-8-cis was obtained (116.5 mg, 34.5% yield) as a white solid.

3-8-trans was obtained (116.5 mg, 34.5% yield) as a white solid.

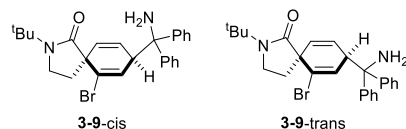
d.r. (cis:trans) = 1:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 7.2 Hz, 2H), 7.72 (d, J = 7.3 Hz, 2H), 7.27 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 8.0 Hz, 2H), 7.16 – 7.07 (m, 2H), 5.83 (d, J = 1.8 Hz, 1H), 5.57 (dd, J = 10.0, 3.9 Hz, 1H), 5.52 (dd, J = 10.3, 1.8 Hz, 1H), 4.54 (d, J = 3.9 Hz, 1H), 3.43 (t, J = 6.7 Hz, 2H), 2.27 (s, 2H), 1.98 (t, J = 6.7 Hz, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.5, 146.8, 146.6, 133.0, 129.9, 128.7, 128.2, 127.6, 126.6, 126.4, 126.0, 126.0, 62.7, 54.6, 52.4, 51.3, 41.9, 33.7, 27.6.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.70 – 7.46 (m, 4H), 7.36 – 7.24 (m, 4H), 7.23 – 7.17 (m, 2H), 5.86 (s, 2H), 5.62 (d, J = 10.1 Hz, 1H), 4.47 (s, 1H), 3.38 (t, J = 7.0 Hz, 2H), 1.97 (s, 2H), 1.78 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.0, 145.9, 145.5, 133.0, 129.8, 128.9, 128.5, 127.9, 127.8, 126.7, 126.4, 64.3, 54.3, 51.8, 51.1, 42.0, 32.6, 27.5.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{30}\text{ClN}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 421.2041; found: 421.2044.



8-(aminodiphenylmethyl)-6-bromo-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-9**)

3-9-cis was obtained (112 mg, 30% yield) as a white solid.

3-9-trans was obtained (112 mg, 30% yield) as a white solid.

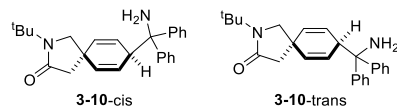
d.r. (cis:trans) = 1:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.64 (t, J = 6.6 Hz, 4H), 7.32 – 7.21 (m, 4H), 7.13 (q, J = 7.7 Hz, 2H), 5.95 (s, 1H), 5.63 (d, J = 10.0 Hz, 1H), 5.49 (d, J = 10.3 Hz, 1H), 4.33 (s, 1H), 3.62 – 3.50 (m, 1H), 3.48 – 3.37 (m, 1H), 2.52 – 2.40 (m, 1H), 2.05 (s, 2H), 1.95 – 1.85 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.4, 146.3, 146.1, 131.1, 130.2, 128.4, 128.2, 127.1, 126.2, 126.1, 126.0, 126.0, 124.9, 62.3, 54.9, 54.7, 48.3, 42.9, 31.7, 27.4.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, J = 7.7, 4.8 Hz, 4H), 7.29 (q, J = 7.4 Hz, 4H), 7.17 (q, J = 6.9 Hz, 2H), 6.11 (d, J = 3.5 Hz, 1H), 5.72 – 5.61 (m, 2H), 4.42 (s, 1H), 3.59 – 3.50 (m, 1H), 3.45 – 3.36 (m, 1H), 2.36 – 2.27 (m, 1H), 1.87 – 1.73 (m, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.5, 145.7, 145.5, 130.8, 130.5, 128.3, 128.3, 126.8, 126.5, 126.4, 126.0, 125.4, 63.0, 54.8, 54.7, 47.9, 42.9, 31.4, 27.3.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{30}\text{BrN}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 465.1536; found: 465.1530.



8-(aminodiphenylmethyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-10**)

3-10-cis was obtained (101 mg, 30% yield) as a brown oil.

3-10-trans was obtained (101 mg, 30% yield) as a brown oil.

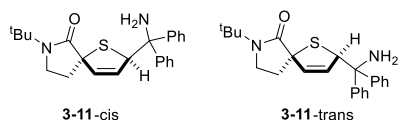
d.r. (cis:trans) = 1:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, J = 7.8 Hz, 4H), 7.29 (t, J = 7.6 Hz, 4H), 7.17 (t, J = 7.3 Hz, 2H), 5.80 (d, J = 10.2 Hz, 2H), 5.61 (dd, J = 10.3, 3.1 Hz, 2H), 4.12 (s, 1H), 3.10 (s, 2H), 2.29 (s, 2H), 1.83 (s, 2H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.0, 146.0, 133.7, 128.2, 126.3, 126.3, 125.6, 63.0, 57.8, 53.9, 47.1, 44.4, 36.8, 27.6.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, J = 7.2 Hz, 4H), 7.28 (t, J = 7.7 Hz, 4H), 7.16 (t, J = 7.3 Hz, 2H), 5.82 (dd, J = 10.4, 1.9 Hz, 2H), 5.57 (dd, J = 10.3, 3.1 Hz, 2H), 4.15 – 4.11 (m, 1H), 3.27 (s, 2H), 2.23 (s, 2H), 1.86 (s, 2H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.9, 146.0, 133.7, 128.2, 126.3, 126.1, 125.7, 62.9, 57.8, 53.9, 47.1, 44.6, 36.9, 27.6.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 387.2431; found: 387.2430.



2-(aminodiphenylmethyl)-7-(tert-butyl)-1-thia-7-azaspiro[4.4]non-3-en-6-one (**3-11**)

3-11-cis was obtained (140 mg, 44.5% yield) as a brown oil.

3-11-trans was obtained (140 mg, 44.5% yield) as a brown oil.

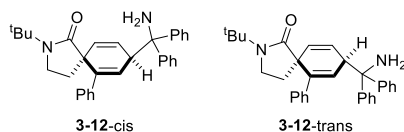
d.r. (cis:trans) = 1:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.53 (d, $J = 7.3$ Hz, 4H), 7.30 – 7.23 (m, 5H), 7.15 (t, $J = 7.3$ Hz, 2H), 5.76 (t, $J = 2.2$ Hz, 1H), 5.62 (dd, $J = 6.3, 2.0$ Hz, 1H), 5.41 (dd, $J = 6.3, 2.4$ Hz, 1H), 3.41 – 3.27 (m, 2H), 2.38 – 2.32 (m, 3H), 2.29 – 2.21 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.9, 147.9, 146.4, 134.6, 132.0, 128.2, 128.0, 126.4, 126.4, 126.3, 126.1, 68.2, 67.9, 63.6, 54.4, 42.7, 35.5, 27.4.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.51 (dd, $J = 15.8, 7.1$ Hz, 4H), 7.30 – 7.24 (m, 4H), 7.16 (t, $J = 7.3$ Hz, 2H), 5.88 (t, $J = 2.2$ Hz, 1H), 5.65 (dd, $J = 6.3, 2.0$ Hz, 1H), 5.51 (dd, $J = 6.3, 2.3$ Hz, 1H), 3.40 – 3.28 (m, 2H), 2.40 – 2.32 (m, 1H), 2.20 – 2.13 (m, 1H), 2.03 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.8, 147.1, 145.7, 134.4, 132.3, 128.3, 128.1, 126.7, 126.6, 126.4, 126.0, 68.6, 67.8, 63.2, 54.5, 42.7, 35.4, 27.4.

HRMS (APCI): calcd for $\text{C}_{24}\text{H}_{29}\text{N}_2\text{OS}^+$ [$\text{M} + \text{H}$] $^+$: 393.1995; found: 393.1997.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-phenyl-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-12**)

3-12-cis was obtained (66 mg, 18% yield) as a brown oil.

3-12-trans was obtained (138 mg, 37% yield) as a brown oil.

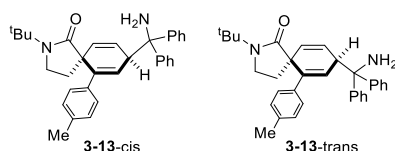
d.r. (cis:trans) = 1:2.1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.74 (d, $J = 8.0$ Hz, 4H), 7.38 – 7.26 (m, 6H), 7.24 – 7.08 (m, 5H), 5.75 (d, $J = 10.0$ Hz, 1H), 5.65 – 5.55 (m, 2H), 4.49 (s, 1H), 3.32 (q, $J = 8.0$ Hz, 1H), 2.93 – 2.80 (m, 1H), 2.39 (s, 2H), 2.16 – 2.06 (m, 1H), 1.88 – 1.77 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.4, 147.0, 146.7, 142.5, 141.3, 131.8, 128.6, 128.2, 128.2, 127.9, 127.1, 127.0, 126.2, 126.2, 125.9, 125.9, 125.3, 62.5, 54.3, 52.4, 45.7, 42.4, 31.1, 27.4.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, $J = 7.8$ Hz, 4H), 7.33 – 7.27 (m, 4H), 7.24 – 7.11 (m, 7H), 5.81 – 5.69 (m, 3H), 4.48 (s, 1H), 3.31 – 3.23 (m, 1H), 2.87 – 2.79 (m, 1H), 2.04 – 1.94 (m, 1H), 1.82 (s, 2H), 1.77 – 1.70 (m, 1H), 1.35 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 146.3, 146.2, 141.9, 131.6, 128.6, 128.2, 128.1, 127.8, 127.5, 127.0, 126.2, 126.2, 125.8, 63.2, 54.3, 52.3, 44.6, 42.4, 30.8, 27.3.

HRMS (APCI): calcd for $\text{C}_{32}\text{H}_{35}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 463.2744; found: 463.2735.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(p-tolyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-13**)

3-13-cis was obtained (60 mg, 16% yield) as a brown oil.

3-13-trans was obtained (143 mg, 37% yield) as a brown oil.

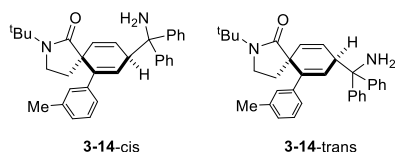
d.r. (cis:trans) = 1:2.4

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 (t, J = 6.5 Hz, 4H), 7.30 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.7 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.11 – 7.03 (m, 5H), 5.73 (d, J = 10.1 Hz, 1H), 5.63 – 5.51 (m, 2H), 4.45 (s, 1H), 3.31 (q, J = 8.1 Hz, 1H), 2.95 – 2.84 (m, 1H), 2.48 (s, 2H), 2.32 (s, 3H), 2.16 – 2.04 (m, 1H), 1.84 – 1.73 (m, 1H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 146.9, 142.4, 138.4, 136.6, 131.8, 128.5, 128.4, 128.2, 128.1, 126.9, 126.2, 126.1, 125.9, 125.8, 125.3, 62.5, 54.3, 52.4, 45.7, 42.4, 31.1, 27.5, 21.0.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.57 (d, J = 7.8 Hz, 4H), 7.25 – 7.18 (m, 4H), 7.11 (t, J = 7.2 Hz, 1H), 7.06 (t, J = 7.3 Hz, 1H), 7.03 – 6.94 (m, 4H), 5.74 – 5.67 (m, 2H), 5.64 (s, 1H), 4.43 (s, 1H), 3.25 – 3.17 (m, 1H), 2.85 – 2.76 (m, 1H), 2.24 (s, 3H), 1.99 – 1.91 (m, 1H), 1.86 (s, 2H), 1.70 – 1.62 (m, 1H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 146.2, 141.8, 138.2, 136.5, 131.5, 128.4, 128.3, 128.1, 128.0, 127.2, 126.1, 126.1, 125.7, 63.1, 54.1, 52.2, 44.6, 42.3, 30.7, 27.2, 20.9.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{37}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 477.2900; found: 477.2895.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(m-tolyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-14**)

3-14-cis was obtained (67 mg, 17.5% yield) as a brown oil.

3-14-trans was obtained (147 mg, 38.5% yield) as a brown oil.

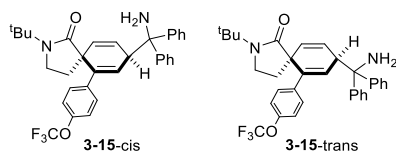
d.r. (cis:trans) = 1:2.2

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 7.8 Hz, 4H), 7.34 (t, J = 7.6 Hz, 2H), 7.29 (d, J = 5.3 Hz, 2H), 7.21 – 7.16 (m, 2H), 7.13 (d, J = 7.0 Hz, 1H), 7.09 (d, J = 8.1 Hz, 1H), 7.06 – 7.00 (m, 2H), 5.77 (d, J = 10.1 Hz, 1H), 5.66 – 5.56 (m, 2H), 4.50 (t, J = 3.7 Hz, 1H), 3.38 – 3.29 (m, 1H), 2.92 – 2.85 (m, 1H), 2.55 (s, 2H), 2.33 (s, 3H), 2.19 – 2.09 (m, 1H), 1.87 – 1.79 (m, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.4, 147.0, 146.7, 142.6, 141.3, 137.3, 131.8, 129.2, 128.2, 128.1, 127.8, 127.7, 126.8, 126.1, 125.8, 125.8, 125.7, 125.2, 62.5, 54.3, 52.3, 45.6, 42.3, 31.1, 27.5, 21.3.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, J = 7.9 Hz, 4H), 7.33 – 7.26 (m, 4H), 7.19 (d, J = 7.3 Hz, 1H), 7.15 – 7.10 (m, 2H), 7.04 (d, J = 7.5 Hz, 1H), 6.96 (s, 1H), 6.92 (d, J = 7.5 Hz, 1H), 5.79 – 5.72 (m, 2H), 5.69 (s, 1H), 4.48 (s, 1H), 3.30 – 3.23 (m, 1H), 2.87 – 2.79 (m, 1H), 2.28 (s, 3H), 2.11 (s, 2H), 2.04 – 1.96 (m, 1H), 1.78 – 1.70 (m, 1H), 1.36 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 146.2, 142.0, 141.1, 137.2, 131.7, 129.2, 128.1, 128.1, 127.7, 127.7, 127.2, 126.2, 126.2, 126.1, 125.8, 125.7, 63.2, 54.2, 52.3, 44.5, 42.4, 30.8, 27.3, 21.2.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{37}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 477.2900; found: 477.2895.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(4-(trifluoromethoxy)phenyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-15**)

3-15-cis was obtained (74 mg, 17% yield) as a brown oil.

3-15-trans was obtained (154 mg, 35% yield) as a brown oil.

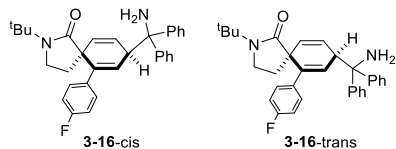
d.r. (cis:trans) = 1:2.1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, $J = 7.9$ Hz, 4H), 7.35 – 7.27 (m, 3H), 7.25 – 7.15 (m, 4H), 7.13 – 7.05 (m, 3H), 5.74 (d, $J = 10.2$ Hz, 1H), 5.64 – 5.54 (m, 2H), 4.46 (s, 1H), 3.35 (q, $J = 8.2$ Hz, 1H), 3.00 – 2.87 (m, 1H), 2.39 (s, 2H), 2.09 – 2.00 (m, 1H), 1.86 – 1.75 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.2, 148.3 (d, $J = 2.7$ Hz), 146.8, 146.7, 141.3, 140.0, 131.2, 130.0, 128.3, 128.2, 126.2, 126.1, 126.0, 126.0, 125.3, 120.4, 62.6, 54.4, 52.4, 45.7, 42.3, 30.9, 27.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.8.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, $J = 7.2$ Hz, 4H), 7.29 (q, $J = 7.7$ Hz, 4H), 7.22 – 7.13 (m, 4H), 7.08 (d, $J = 8.3$ Hz, 2H), 5.82 – 5.77 (m, 1H), 5.76 – 5.71 (m, 2H), 4.45 (q, $J = 2.6$ Hz, 1H), 3.34 – 3.24 (m, 1H), 2.93 – 2.85 (m, 1H), 1.95 – 1.88 (m, 1H), 1.82 (s, 2H), 1.74 – 1.66 (m, 1H), 1.34 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.1, 148.2 (d, $J = 1.8$ Hz), 146.2, 146.0, 140.5, 139.8, 131.0, 130.0, 128.6, 128.2, 128.1, 126.3, 126.2, 126.2, 125.7, 120.3 (d, $J = 257.2$ Hz), 120.3, 63.3, 54.3, 52.2, 44.7, 42.3, 30.7, 27.2. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -57.8.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{34}\text{F}_3\text{N}_2\text{O}_2^+$ [$\text{M} + \text{H}$] $^+$: 547.2567; found: 547.2561.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(4-fluorophenyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-16**)

3-16-cis was obtained (63 mg, 17% yield) as a brown oil.

3-16-trans was obtained (121 mg, 31% yield) as a brown oil.

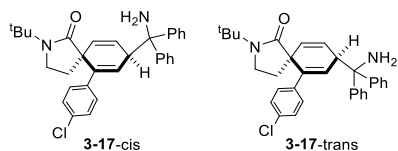
d.r. (cis:trans) = 1:1.9

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 – 7.68 (m, 4H), 7.30 (t, $J = 7.6$ Hz, 2H), 7.25 (t, $J = 7.7$ Hz, 2H), 7.18 – 7.13 (m, 3H), 7.09 (t, $J = 7.2$ Hz, 1H), 6.93 (t, $J = 8.7$ Hz, 2H), 5.74 (d, $J = 10.0$ Hz, 1H), 5.63 – 5.54 (m, 2H), 4.50 – 4.42 (m, 1H), 3.38 – 3.27 (m, 1H), 2.94 – 2.87 (m, 1H), 2.24 (s, 2H), 2.10 – 2.02 (m, 1H), 1.84 – 1.76 (m, 1H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 161.9 (d, $J = 246.2$ Hz), 146.8 (d, $J = 14.1$ Hz), 141.5, 137.2 (d, $J = 3.1$ Hz), 131.4, 130.2, 130.1, 128.2, 128.1, 127.7, 126.1, 126.1, 125.9, 125.2, 114.8, 114.6, 62.4, 54.3, 52.4, 45.7, 42.3, 30.9, 27.4. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.3.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.58 (m, 4H), 7.32 – 7.24 (m, 4H), 7.20 – 7.06 (m, 4H), 6.91 (t, $J = 8.7$ Hz, 2H), 5.81 – 5.76 (m, 1H), 5.75 – 5.70 (m, 2H), 4.45 (q, $J = 2.5$ Hz, 1H), 3.30 –

3.22 (m, 1H), 2.89 – 2.81 (m, 1H), 1.97 – 1.88 (m, 1H), 1.82 (s, 2H), 1.74 – 1.65 (m, 1H), 1.34 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.1, 161.7 (d, *J* = 246.0 Hz), 146.1 (d, *J* = 17.3 Hz), 140.7, 137.0 (d, *J* = 3.4 Hz), 131.1, 130.1, 130.1, 128.0, 128.0, 127.9, 126.1, 126.1, 126.0, 125.6, 114.6, 114.4, 63.2, 54.1, 52.2, 44.5, 42.2, 30.6, 27.2. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -115.2. HRMS (APCI): calcd for C₃₂H₃₄FN₂O⁺ [*M* + *H*]⁺: 481.2650; found: 481.2645.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(4-chlorophenyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (3-17)

3-17-cis was obtained (67 mg, 17% yield) as a brown oil.

3-17-trans was obtained (148 mg, 37% yield) as a brown oil.

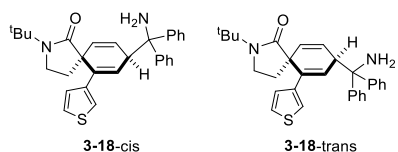
d.r. (cis:trans) = 1:2.2

NMR:

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (t, *J* = 7.9 Hz, 4H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.21 (m, 4H), 7.19 – 7.08 (m, 4H), 5.75 (d, *J* = 10.1 Hz, 1H), 5.66 – 5.53 (m, 2H), 4.47 (s, 1H), 3.36 (q, *J* = 8.0 Hz, 1H), 3.02 – 2.94 (m, 1H), 2.23 (s, 2H), 2.11 – 1.99 (m, 1H), 1.85 – 1.77 (m, 1H), 1.41 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 146.8, 146.7, 141.4, 139.8, 131.2, 129.9, 128.2, 128.2, 128.0, 126.1, 126.1, 125.9, 125.2, 62.5, 54.4, 52.3, 45.7, 42.2, 30.9, 27.4.

[trans]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.53 (m, 4H), 7.27 (q, *J* = 8.0 Hz, 4H), 7.21 – 7.10 (m, 4H), 7.04 (d, *J* = 8.1 Hz, 2H), 5.77 (d, *J* = 10.3 Hz, 1H), 5.71 (d, *J* = 10.4 Hz, 2H), 4.43 (s, 1H), 3.28 (q, *J* = 8.2 Hz, 1H), 2.96 – 2.84 (m, 1H), 1.96 – 1.84 (m, 1H), 1.77 – 1.62 (m, 3H), 1.34 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.1, 146.2, 146.0, 140.7, 139.6, 132.9, 131.0, 129.9, 128.4, 128.2, 128.1, 128.0, 126.3, 126.2, 126.1, 125.7, 63.3, 54.3, 52.2, 44.6, 42.3, 30.6, 27.3.

HRMS (APCI): calcd for C₃₂H₃₄ClN₂O⁺ [*M* + *H*]⁺: 497.2354; found: 497.2349.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(thiophen-3-yl)-2-azaspiro[4.5]deca-6,9-dien-1-one (3-18)

3-18-cis was obtained (51 mg, 14% yield) as a brown oil.

3-18-trans was obtained (148 mg, 39% yield) as a brown oil.

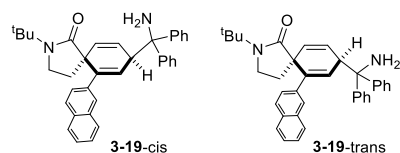
d.r. (cis:trans) = 1:2.9

NMR:

[cis]: ¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.3 Hz, 4H), 7.36 – 7.25 (m, 4H), 7.21 – 7.12 (m, 3H), 7.03 (dd, *J* = 3.0, 1.3 Hz, 1H), 6.95 (dd, *J* = 5.0, 1.3 Hz, 1H), 5.80 – 5.74 (m, 2H), 5.62 – 5.55 (m, 1H), 4.46 (t, *J* = 4.1 Hz, 1H), 3.48 – 3.37 (m, 1H), 3.22 – 3.15 (m, 1H), 2.27 – 2.18 (m, 3H), 1.85 – 1.77 (m, 1H), 1.45 (s, 9H). ¹³C NMR (101 MHz, Chloroform-*d*) δ 174.6, 146.9, 146.7, 141.5, 137.3, 130.8, 128.2, 128.2, 127.9, 127.2, 126.1, 125.9, 125.9, 125.0, 124.8, 121.7, 62.6, 54.3, 52.2, 45.7, 42.2, 31.0, 27.4.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.62 (dd, $J = 7.9, 4.9$ Hz, 4H), 7.35 – 7.25 (m, 4H), 7.20 – 7.13 (m, 3H), 6.99 (d, $J = 3.5$ Hz, 1H), 6.89 (d, $J = 4.9$ Hz, 1H), 5.90 (d, $J = 3.2$ Hz, 1H), 5.77 (s, 2H), 4.47 (d, $J = 3.3$ Hz, 1H), 3.37 (q, $J = 8.4$ Hz, 1H), 3.20 – 3.11 (m, 1H), 2.16 – 2.06 (m, 1H), 1.79 (s, 2H), 1.71 – 1.63 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 146.1, 146.0, 141.0, 136.5, 130.5, 128.0, 128.0, 127.7, 127.4, 126.6, 126.1, 126.1, 126.0, 125.3, 124.6, 121.5, 63.2, 54.1, 51.9, 44.7, 42.1, 30.8, 27.2.

HRMS (APCI): calcd for $\text{C}_{30}\text{H}_{33}\text{N}_2\text{OS}^+$ $[\text{M} + \text{H}]^+$: 469.2308; found: 469.2303.



8-(aminodiphenylmethyl)-2-(tert-butyl)-6-(naphthalen-2-yl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**3-19**)

3-19-cis was obtained (33 mg, 8% yield) as a brown oil.

3-19-trans was obtained (111 mg, 27% yield) as a brown oil.

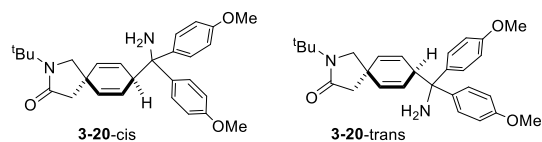
d.r. (cis:trans) = 1:3.4

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.78 (m, 1H), 7.75 (d, $J = 8.8$ Hz, 3H), 7.73 – 7.69 (m, 3H), 7.66 (s, 1H), 7.47 – 7.43 (m, 2H), 7.36 – 7.33 (m, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.22 (t, $J = 7.6$ Hz, 2H), 7.17 (t, $J = 7.3$ Hz, 1H), 7.06 (t, $J = 7.3$ Hz, 1H), 5.78 (d, $J = 10.1$ Hz, 1H), 5.68 (dd, $J = 3.8, 1.8$ Hz, 1H), 5.66 – 5.60 (m, 1H), 4.54 – 4.48 (m, 1H), 3.36 – 3.25 (m, 1H), 2.89 – 2.82 (m, 1H), 2.31 (s, 2H), 2.16 – 2.08 (m, 1H), 1.85 – 1.78 (m, 1H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.5, 147.0, 146.7, 142.5, 138.9, 132.9, 132.3, 131.6, 128.2, 128.2, 127.9, 127.8, 127.4, 127.4, 127.1, 127.1, 126.2, 126.1, 126.1, 125.9, 125.7, 125.3, 62.5, 54.4, 52.6, 45.9, 42.4, 31.1, 27.5.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.75 (m, 2H), 7.73 (d, $J = 8.5$ Hz, 1H), 7.67 (d, $J = 7.8$ Hz, 4H), 7.62 (s, 1H), 7.48 – 7.40 (m, 2H), 7.38 – 7.25 (m, 5H), 7.21 (t, $J = 7.3$ Hz, 1H), 7.14 (t, $J = 7.3$ Hz, 1H), 5.84 (d, $J = 12.9$ Hz, 2H), 5.80 (d, $J = 10.1$ Hz, 1H), 4.54 (s, 1H), 3.30 – 3.24 (m, 1H), 2.87 – 2.79 (m, 1H), 2.11 – 1.99 (m, 1H), 1.97 (s, 2H), 1.80 – 1.71 (m, 1H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.4, 146.2, 146.2, 141.8, 138.7, 132.8, 132.2, 131.4, 128.2, 128.2, 128.1, 127.8, 127.4, 127.1, 127.0, 126.2, 126.2, 126.2, 126.0, 125.8, 125.7, 63.3, 54.3, 52.5, 44.7, 42.4, 30.8, 27.3.

HRMS (APCI): calcd for $\text{C}_{36}\text{H}_{37}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 513.2900; found: 513.2896.



8-(aminobis(4-methoxyphenyl)methyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-20**)

3-20-cis was obtained (72 mg, 19% yield) as a brown oil.

3-20-trans was obtained (72 mg, 19% yield) as a brown oil.

d.r. (cis:trans) = 1:1

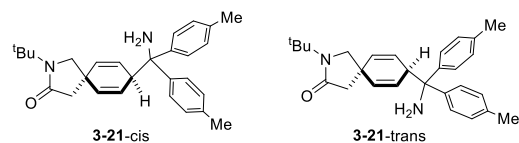
NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.55 (d, $J = 8.9$ Hz, 4H), 6.80 (d, $J = 8.8$ Hz, 4H), 5.63 (d, $J = 10.4$ Hz, 2H), 5.56 (dd, $J = 10.4, 3.3$ Hz, 2H), 4.18 – 4.11 (m, 1H), 3.74 (s, 6H), 3.43 (t, $J = 6.7$ Hz,

2H), 2.14 (s, 2H), 1.95 (t, $J = 6.8$ Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 175.0, 157.6, 139.4, 130.3, 127.2, 127.1, 113.5, 61.4, 55.1, 54.2, 49.4, 44.8, 41.9, 33.7, 27.6.

[trans]: ^1H NMR (400 MHz, Chloroform- d) δ 7.47 (d, $J = 8.9$ Hz, 4H), 6.81 (d, $J = 8.9$ Hz, 4H), 5.75 – 5.64 (m, 4H), 4.23 (s, 1H), 3.74 (s, 6H), 3.42 (t, $J = 6.8$ Hz, 2H), 1.91 (t, $J = 6.8$ Hz, 2H), 1.85 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 175.0, 157.7, 138.8, 130.1, 127.5, 127.0, 113.5, 61.9, 55.1, 54.2, 49.3, 44.1, 42.0, 33.4, 27.5.

HRMS (APCI): calcd for $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}_3^+$ $[\text{M} + \text{H}]^+$: 447.2642; found: 447.2638.



8-(aminodi-p-tolylmethyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-21**)

3-21-cis was obtained (77 mg, 23% yield) as a brown oil.

3-21-trans was obtained (59 mg, 18% yield) as a brown oil.

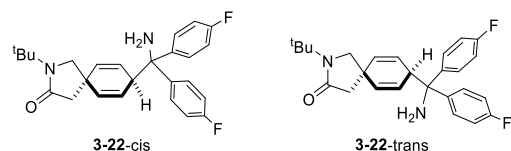
d.r. (cis:trans) = 1.3:1

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform- d) δ 7.55 (d, $J = 7.9$ Hz, 4H), 7.08 (d, $J = 7.9$ Hz, 4H), 5.64 (d, $J = 10.4$ Hz, 2H), 5.61 – 5.56 (m, 2H), 4.21 (s, 1H), 3.43 (t, $J = 6.8$ Hz, 2H), 2.27 (s, 6H), 1.95 (t, $J = 6.8$ Hz, 2H), 1.41 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 174.9, 144.0, 135.2, 130.2, 128.8, 127.0, 125.9, 61.8, 54.1, 49.3, 44.6, 41.8, 33.7, 27.5, 20.8.

[trans]: ^1H NMR (400 MHz, Chloroform- d) δ 7.46 (d, $J = 8.0$ Hz, 4H), 7.08 (d, $J = 7.9$ Hz, 4H), 5.75 – 5.64 (m, 4H), 4.29 (s, 1H), 3.43 (t, $J = 6.8$ Hz, 2H), 2.27 (s, 6H), 1.93 (t, $J = 6.9$ Hz, 2H), 1.75 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 175.1, 143.6, 135.6, 130.1, 129.0, 127.7, 125.8, 62.3, 54.2, 49.3, 44.0, 42.1, 33.5, 27.6, 20.8.

HRMS (APCI): calcd for $\text{C}_{28}\text{H}_{35}\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 415.2744; found: 415.2737.



8-(aminobis(4-fluorophenyl)methyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-22**)

3-22-cis was obtained (97 mg, 29% yield) as a white solid.

3-22-trans was obtained (89 mg, 26% yield) as a white solid.

d.r. (cis:trans) = 1.1:1

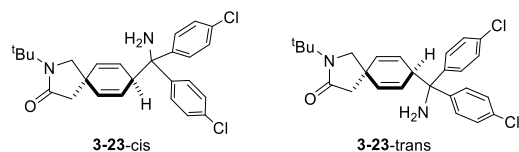
NMR:

[cis]: ^1H NMR (400 MHz, Chloroform- d) δ 7.65 – 7.56 (m, 4H), 6.94 (t, $J = 8.7$ Hz, 4H), 5.66 (d, $J = 10.3$ Hz, 2H), 5.51 (dd, $J = 10.3, 3.5$ Hz, 2H), 4.20 – 4.14 (m, 1H), 3.43 (t, $J = 6.7$ Hz, 2H), 2.07 (s, 2H), 1.95 (t, $J = 6.7$ Hz, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 174.7, 162.3, 159.8, 142.5, 142.5, 130.8, 127.7, 127.7, 126.3, 115.0, 114.7, 61.5, 54.2, 49.4, 44.6, 41.9, 33.5, 27.5. ^{19}F NMR (376 MHz, Chloroform- d) δ -117.2.

[trans]: ^1H NMR (400 MHz, Chloroform- d) δ 7.56 – 7.48 (m, 4H), 6.95 (t, $J = 8.7$ Hz, 4H), 5.70 (dd, $J = 10.2, 1.7$ Hz, 2H), 5.65 (dd, $J = 10.5, 2.5$ Hz, 2H), 4.28 – 4.20 (m, 1H), 3.42 (t, $J = 6.8$ Hz, 2H), 1.90 (t, $J = 6.7$ Hz, 2H), 1.62 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform- d) δ 174.7, 162.4, 159.9,

141.9, 141.9, 130.7, 127.7, 127.6, 126.8, 115.1, 114.9, 62.1, 54.2, 49.3, 44.0, 42.0, 33.3, 27.5. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -116.7.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{29}\text{F}_2\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 423.2242; found: 423.2237.



8-(aminobis(4-chlorophenyl)methyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-23**)

3-23-cis was obtained (100 mg, 28% yield) as a white solid.

3-23-trans was obtained (151 mg, 41% yield) as a white solid.

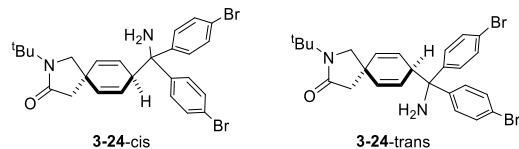
d.r. (cis:trans) = 1:1.5

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.58 (d, J = 8.7 Hz, 4H), 7.24 (d, J = 8.7 Hz, 4H), 5.66 (dd, J = 10.3, 1.5 Hz, 2H), 5.51 (dd, J = 10.2, 3.5 Hz, 2H), 4.18 – 4.14 (m, 1H), 3.44 (t, J = 6.8 Hz, 2H), 2.04 (s, 2H), 1.96 (t, J = 6.8 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 145.0, 132.0, 131.0, 128.4, 127.6, 126.1, 61.7, 54.3, 49.4, 44.3, 42.0, 33.5, 27.6.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, J = 8.2 Hz, 4H), 7.24 (d, J = 8.1 Hz, 4H), 5.71 (d, J = 10.0 Hz, 2H), 5.63 (dd, J = 10.5, 2.7 Hz, 2H), 4.24 (s, 1H), 3.43 (t, J = 6.8 Hz, 2H), 1.91 (t, J = 6.8 Hz, 2H), 1.62 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 144.5, 132.2, 130.9, 128.4, 127.5, 126.6, 62.2, 54.2, 49.3, 43.6, 42.0, 33.2, 27.5.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{29}\text{Cl}_2\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 455.1651; found: 455.1646.



8-(aminobis(4-bromophenyl)methyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-24**)

3-24-cis was obtained (141 mg, 32% yield) as an off-white solid.

3-24-trans was obtained (169 mg, 39% yield) as an off-white solid.

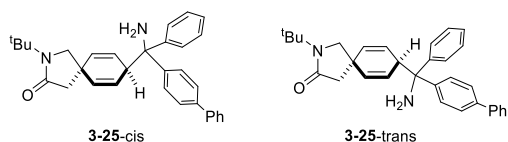
d.r. (cis:trans) = 1:1.2

NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.52 (d, J = 8.4 Hz, 4H), 7.39 (d, J = 8.3 Hz, 4H), 5.66 (d, J = 10.2 Hz, 2H), 5.50 (dd, J = 10.3, 3.5 Hz, 2H), 4.16 (s, 1H), 3.44 (t, J = 6.7 Hz, 2H), 2.01 (s, 2H), 1.96 (t, J = 6.8 Hz, 2H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.7, 145.5, 131.3, 131.1, 128.0, 126.1, 120.2, 61.8, 54.3, 49.4, 44.2, 42.0, 33.5, 27.6.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, J = 8.8 Hz, 4H), 7.38 (d, J = 8.9 Hz, 4H), 5.70 (dd, J = 10.3, 1.9 Hz, 2H), 5.62 (dd, J = 10.3, 2.7 Hz, 2H), 4.24 – 4.20 (m, 1H), 3.42 (t, J = 6.8 Hz, 2H), 1.90 (t, J = 6.8 Hz, 2H), 1.62 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.6, 144.9, 131.5, 131.4, 130.9, 128.4, 127.8, 126.5, 120.4, 62.3, 54.2, 49.3, 43.5, 42.0, 33.2, 27.5.

HRMS (APCI): calcd for $\text{C}_{26}\text{H}_{29}\text{Br}_2\text{N}_2\text{O}^+$ $[\text{M} + \text{H}]^+$: 543.0641; found: 543.0638.



8-([1,1'-biphenyl]-4-yl(amino)(phenyl)methyl)-2-(tert-butyl)-2-azaspiro[4.5]deca-6,9-dien-3-one (**3-25**)

3-25-cis was obtained (80 mg, 21% yield) as a brown oil.

3-25-trans was obtained (72 mg, 20% yield) as a brown oil.

d.r. (cis:trans) = 1.1:1

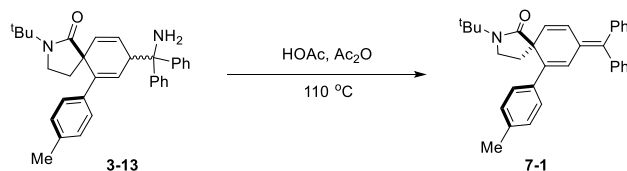
NMR:

[cis]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.78 (dd, J = 11.6, 8.0 Hz, 4H), 7.57 (dd, J = 14.4, 7.9 Hz, 4H), 7.43 (t, J = 7.5 Hz, 2H), 7.34 (t, J = 7.7 Hz, 3H), 7.19 (t, J = 7.3 Hz, 1H), 5.75 – 5.58 (m, 4H), 4.37 – 4.28 (m, 1H), 3.47 (t, J = 6.7 Hz, 2H), 2.18 (s, 2H), 2.00 (t, J = 6.7 Hz, 2H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.9, 146.7, 145.9, 140.7, 138.6, 130.6, 130.5, 128.6, 128.2, 126.9, 126.8, 126.8, 126.6, 126.1, 126.0, 62.1, 54.2, 49.4, 44.7, 41.9, 33.7, 27.6.

[trans]: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.67 (dd, J = 13.0, 8.0 Hz, 4H), 7.54 (dd, J = 12.2, 7.9 Hz, 4H), 7.40 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.0 Hz, 3H), 7.18 (t, J = 7.3 Hz, 1H), 5.82 – 5.69 (m, 4H), 4.38 (s, 1H), 3.43 (t, J = 6.7 Hz, 2H), 1.93 (t, J = 6.8 Hz, 2H), 1.72 (s, 2H), 1.39 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.9, 146.2, 145.3, 140.5, 138.8, 130.4, 130.3, 128.6, 128.3, 127.3, 127.3, 127.0, 126.9, 126.8, 126.5, 126.2, 126.0, 62.6, 54.2, 49.3, 44.0, 42.0, 33.4, 27.5.

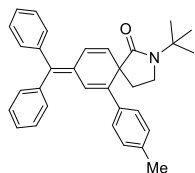
HRMS (APCI): calcd for $\text{C}_{32}\text{H}_{35}\text{N}_2\text{O}^+$ [$\text{M} + \text{H}$] $^+$: 463.2744; found: 463.2737.

V.4 The synthesis of 7-1



Standard Conditions: **3-13** (0.3 mmol), in 3 mL of HOAc/Ac₂O (v/v = 1/2) under Ar atmosphere at 110 °C for 20 h.

Workup: The reaction mixture was carefully adjusted pH value to about 7 with K₂CO₃ (aq), then it was washed with brine (saturated NaCl(aq)) and extracted with EA multiple times. The combined organic layers were then dried over Na₂SO₄, concentrated under reduced pressure, and purified by column chromatography to isolate target product **7-1**.



2-(tert-butyl)-8-(diphenylmethylene)-6-(p-tolyl)-2-azaspiro[4.5]deca-6,9-dien-1-one (**7-1**)

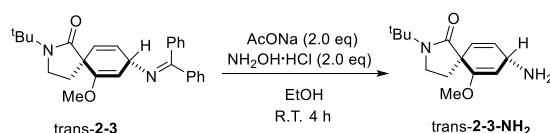
The title compound was obtained as a beige solid (69 mg, 50% yield).

NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.21 (m, 10H), 7.19 (d, J = 7.7 Hz, 2H), 7.10 (d, J = 7.8 Hz, 2H), 6.69 (s, 1H), 6.65 (d, J = 9.9 Hz, 1H), 5.76 (d, J = 9.9 Hz, 1H), 3.39 (q, J = 8.2 Hz, 1H),

3.09 – 3.00 (m, 1H), 2.34 (s, 3H), 2.26 – 2.14 (m, 1H), 1.95 – 1.86 (m, 1H), 1.44 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.8, 141.5, 140.7, 139.8, 138.1, 136.7, 130.6, 130.6, 128.6, 128.2, 128.1, 127.8, 127.7, 126.9, 126.9, 125.8, 54.9, 54.4, 42.3, 31.3, 27.4, 21.0.

HRMS (APCI): calcd for $\text{C}_{33}\text{H}_{34}\text{NO}^+ [\text{M} + \text{H}]^+$: 460.2635; found: 460.2632.

V.5 The synthesis of cyclohexadienyl amine

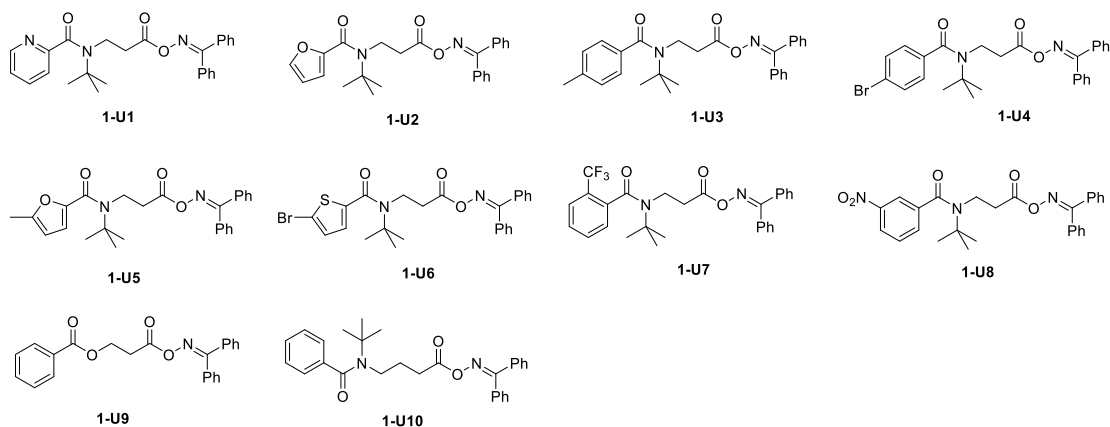


To a solution of **trans-2-3** (125 mg, 0.3 mmol) in EtOH (10 mL), AcONa (50 mg, 2.0 equiv) and $\text{NH}_2\text{OH}\cdot\text{HCl}$ (42 mg, 2.0 equiv) were added. The reaction mixture was stirred at R. T. for 4 hours, then the solvent was removed under reduced pressure, and 10 mL of water was added. The mixture was adjusted to pH about 10 with 1 M NaOH, extracted with DCM three times, The combined organic layers was dried over Na_2SO_4 , concentrated under reduced pressure, and purified by column chromatography to isolate the target product, **trans-2-3-NH₂** (59 mg, 78% yield).

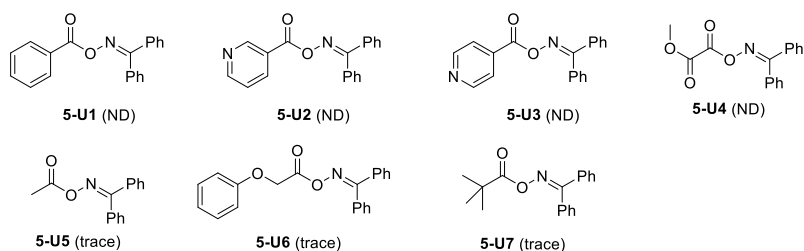
NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 5.80 – 5.72 (m, 1H), 5.36 (dd, $J = 9.8, 1.6$ Hz, 1H), 4.77 (dd, $J = 3.8, 1.5$ Hz, 1H), 4.06 – 4.01 (m, 1H), 3.42 (s, 3H), 3.39 – 3.33 (m, 1H), 3.31 – 3.26 (m, 1H), 3.16 – 3.04 (m, 2H), 2.25 – 2.15 (m, 1H), 1.80 – 1.72 (m, 1H), 1.24 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.7, 155.5, 130.0, 127.4, 98.0, 54.1, 51.1 (spiro C), 51.1 (OMe), 46.6, 43.1, 29.9, 27.1.

VI. Unsuccessful substrates for chemodivergent reactions

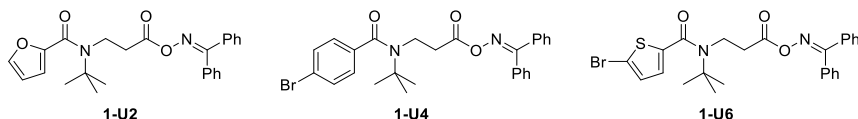
VI. 1 The following compounds were used in carboamination under the corresponding standard conditions, but no desired products were formed.



VI. 2 The following compounds were used in rearomatization with compound **4-1** under the corresponding standard conditions, but no desired products were formed.

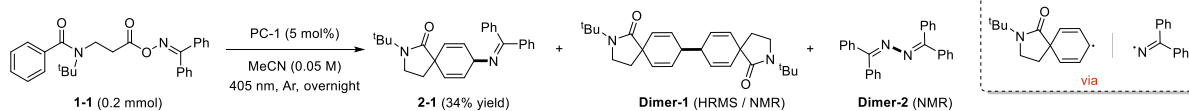


VI. 3 The following compounds were used in carbo-aminoalkylation under the corresponding standard conditions, but no desired products were formed.

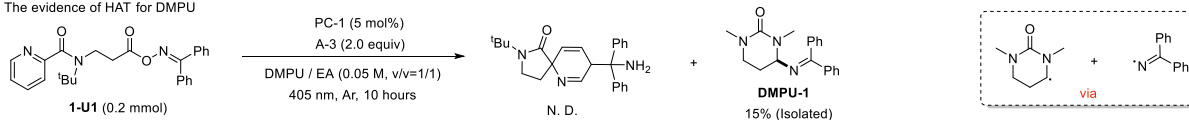


VII. Control experiments

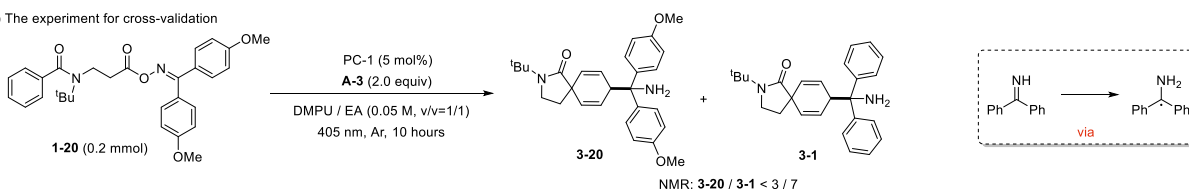
(A) The composition analysis of the reaction mixture for carboamination



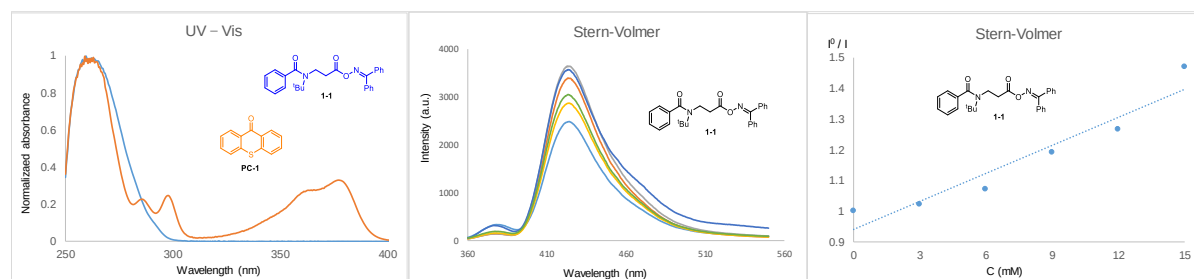
(B) The evidence of HAT for DMPU



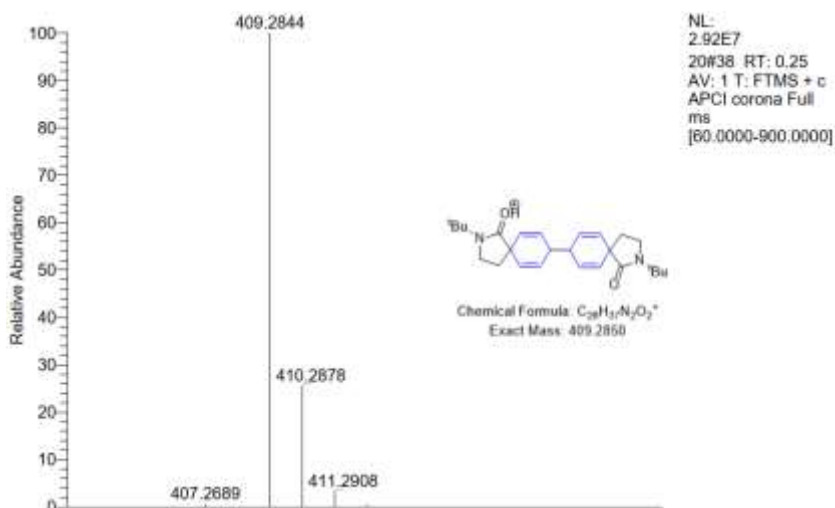
(C) The experiment for cross-validation



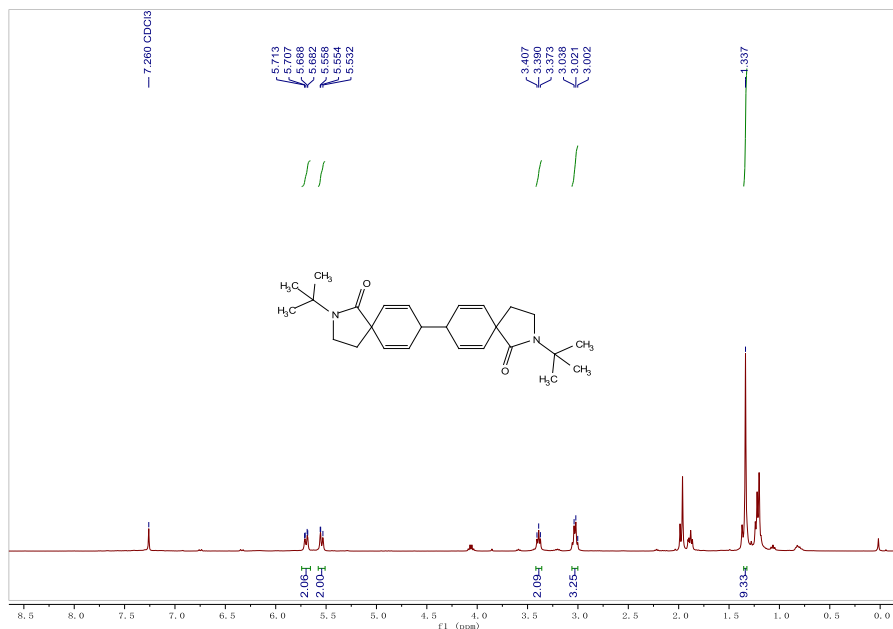
(D) UV-vis absorption spectra and Stern-Volmer experiments



The corresponding experimental data is listed below.

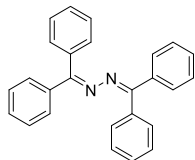


HRMS for **Dimer-1**



^1H -NMR for **Dimer-1**

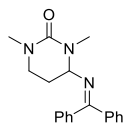
NMR: ^1H NMR (400 MHz, Chloroform- d) δ 5.70 (dd, J = 10.1, 2.3 Hz, 2H), 5.58 – 5.51 (m, 2H), 3.39 (t, J = 6.8 Hz, 2H), 3.04 – 3.00 (m, 3H), 1.34 (s, 9H).



1,2-bis(diphenylmethylene)hydrazine (**dimer-2**)

The title compound was obtained as a yellow solid. This compound is known.⁶

NMR: ^1H NMR (400 MHz, Chloroform- d) δ 7.52 – 7.45 (m, 2H), 7.45 – 7.38 (m, 3H), 7.37 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H). ^{13}C NMR (101 MHz, Chloroform- d) δ 158.9, 138.2, 135.5, 129.6, 129.3, 128.6, 128.6, 128.0, 127.8.

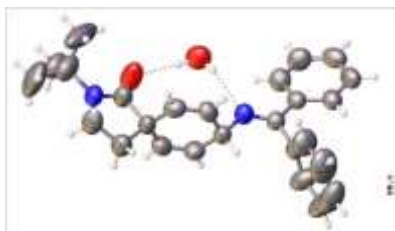


4-((diphenylmethylene)amino)-1,3-dimethyltetrahydropyrimidin-2(1*H*)-one (**DMPU-1**)

The title compound was obtained as a brown oil (34 mg, 15% yield).

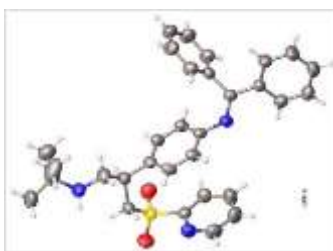
NMR: ^1H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, $J = 7.0$ Hz, 2H), 7.54 – 7.44 (m, 3H), 7.40 (t, $J = 7.3$ Hz, 1H), 7.33 (t, $J = 7.4$ Hz, 2H), 7.16 (dd, $J = 7.3, 2.1$ Hz, 2H), 4.61 (t, $J = 3.6$ Hz, 1H), 3.89 – 3.79 (m, 1H), 3.14 – 3.08 (m, 1H), 3.03 (s, 3H), 2.72 (s, 3H), 2.17 – 2.07 (m, 1H), 1.81 – 1.73 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.8, 156.6, 138.8, 136.0, 130.4, 128.6, 128.6, 127.9, 127.3, 72.7, 44.2, 35.7, 33.4, 29.0.

VIII. Crystallographic data



cis-**2-1** (CCDC: 2343819)

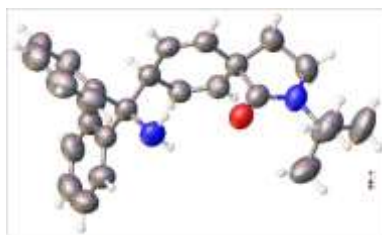
Identification code	exp_13627_autored
Empirical formula	C ₂₆ H ₃₀ N ₂ O ₂
Formula weight	402.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.8065(7)
b/Å	16.1017(12)
c/Å	15.4868(15)
α/°	90
β/°	100.404(8)
γ/°	90
Volume/Å ³	2405.2(3)
Z	4
ρ _{calc} /cm ³	1.112
μ/mm ⁻¹	0.551
F(000)	864.0
Crystal size/mm ³	0.18 × 0.12 × 0.09
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.99 to 129.992
Index ranges	-11 ≤ h ≤ 11, -17 ≤ k ≤ 18, -18 ≤ l ≤ 16
Reflections collected	15383
Independent reflections	3943 [R _{int} = 0.1557, R _{sigma} = 0.0940]
Data/restraints/parameters	3943/0/271
Goodness-of-fit on F ²	1.040
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.1017, wR ₂ = 0.2718
Final R indexes [all data]	R ₁ = 0.1382, wR ₂ = 0.3232
Largest diff. peak/hole / e Å ⁻³	0.35/-0.44



6-1 (CCDC: 2360015)

Crystal data and structure refinement

Identification code	exp_14260_auto
Empirical formula	C ₃₁ H ₃₄ N ₃ O ₂ S
Formula weight	512.67
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	9.0152(4)
b/Å	19.9619(10)
c/Å	15.0973(7)
α /°	90
β /°	92.014(5)
γ /°	90
Volume/Å ³	2715.2(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.254
μ/mm^{-1}	0.152
F(000)	1092.0
Crystal size/mm ³	0.25 × 0.12 × 0.11
Radiation	Mo K α (λ = 0.71073)
2 θ range for data collection/°	4.894 to 53.99
Index ranges	-11 ≤ h ≤ 11, -25 ≤ k ≤ 25, -19 ≤ l ≤ 19
Reflections collected	21642
Independent reflections	5895 [R_{int} = 0.0439, R_{sigma} = 0.0502]
Data/restraints/parameters	5895/0/337
Goodness-of-fit on F ²	1.032
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0545, wR_2 = 0.1173
Final R indexes [all data]	R_1 = 0.0907, wR_2 = 0.1370
Largest diff. peak/hole / e Å ⁻³	0.22/-0.34



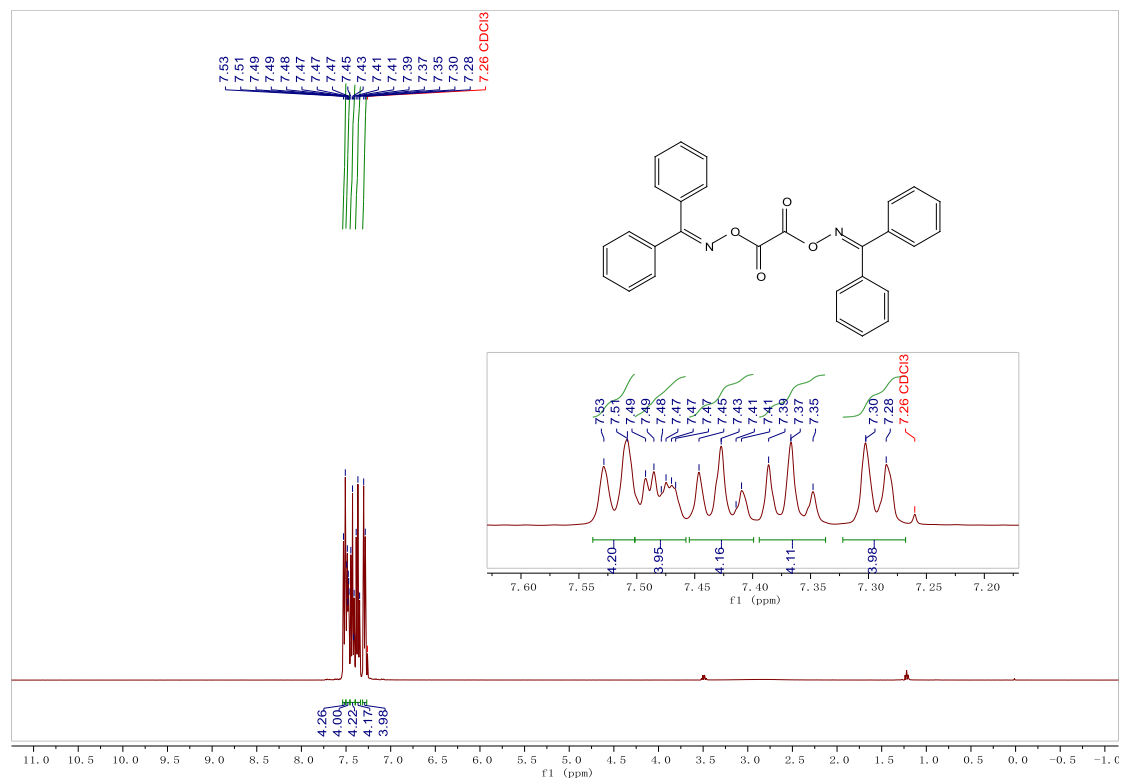
cis-3-1 (CCDC: 2343822)

Identification code	exp_13658_auto
Empirical formula	C ₂₆ H ₃₀ N ₂ O
Formula weight	386.52
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	11.3911(5)
b/Å	9.5082(4)
c/Å	20.4932(10)
α/°	90
β/°	99.690(5)
γ/°	90
Volume/Å ³	2187.93(17)
Z	4
ρ _{calc} /cm ³	1.173
μ/mm ⁻¹	0.550
F(000)	832.0
Crystal size/mm ³	0.25 × 0.17 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	8.34 to 132.996
Index ranges	-13 ≤ h ≤ 13, -8 ≤ k ≤ 11, -24 ≤ l ≤ 24
Reflections collected	14319
Independent reflections	3836 [R _{int} = 0.0610, R _{sigma} = 0.0531]
Data/restraints/parameters	3836/0/272
Goodness-of-fit on F ²	1.024
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0653, wR ₂ = 0.1592
Final R indexes [all data]	R ₁ = 0.1015, wR ₂ = 0.2004
Largest diff. peak/hole / e Å ⁻³	0.17/-0.22

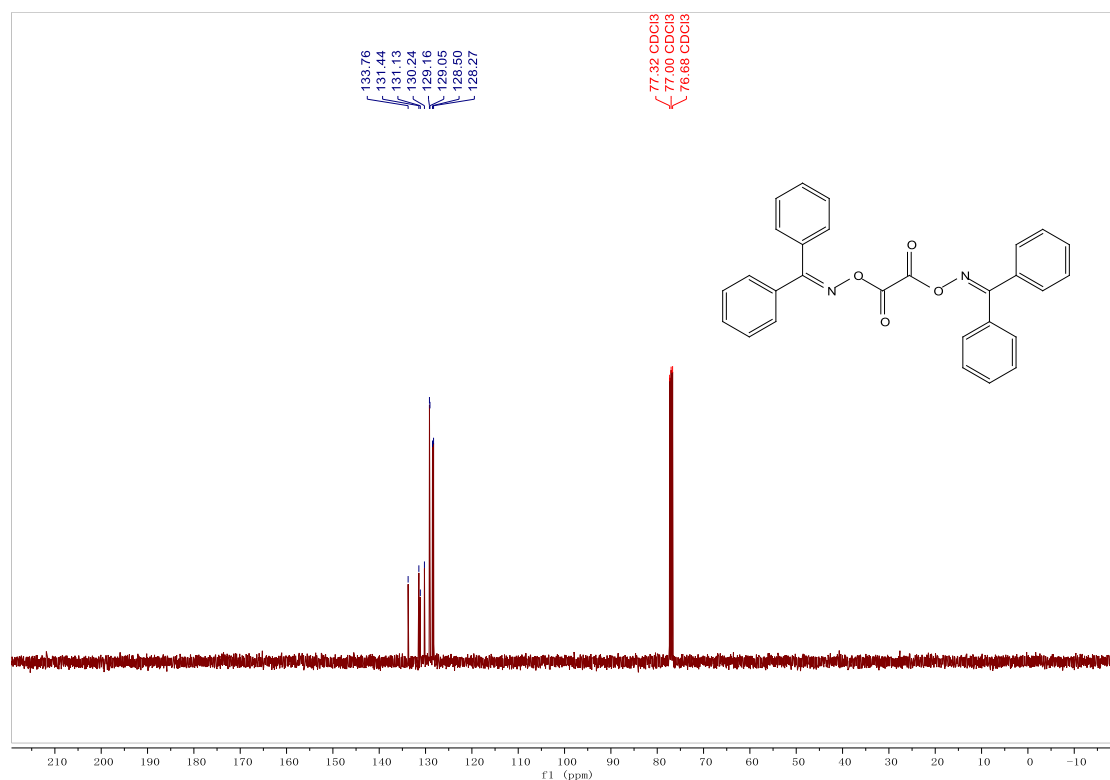
IX. References

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- (6) Xu Y.; Wang B.; Wang J.; Zhou X.; Chen J.; Guo X.; Deng G.-J.; Shao W. Regioselective synthesis of unsymmetrical vicinal diamines via azidoimination of alkenes with TMSN₃ and ketimines. *Org. Lett.* **2023**, 25 (48), 8716-8721.

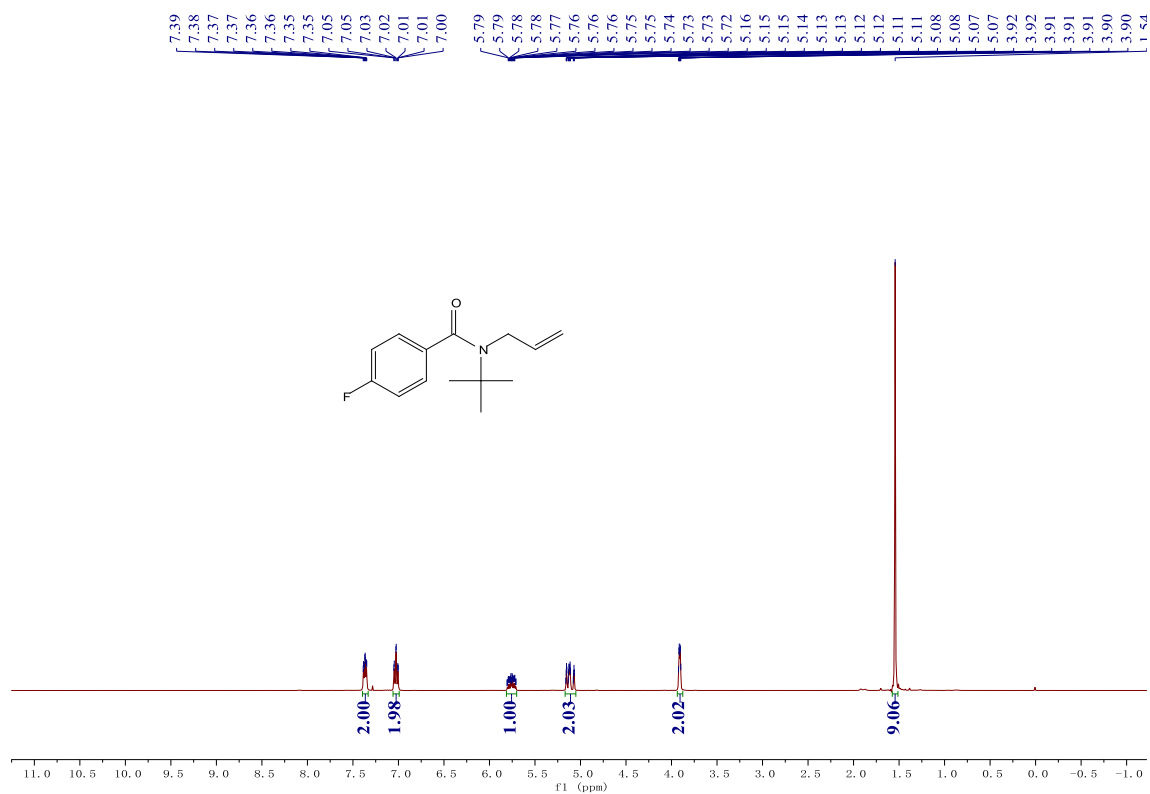
X. NMR Spectra



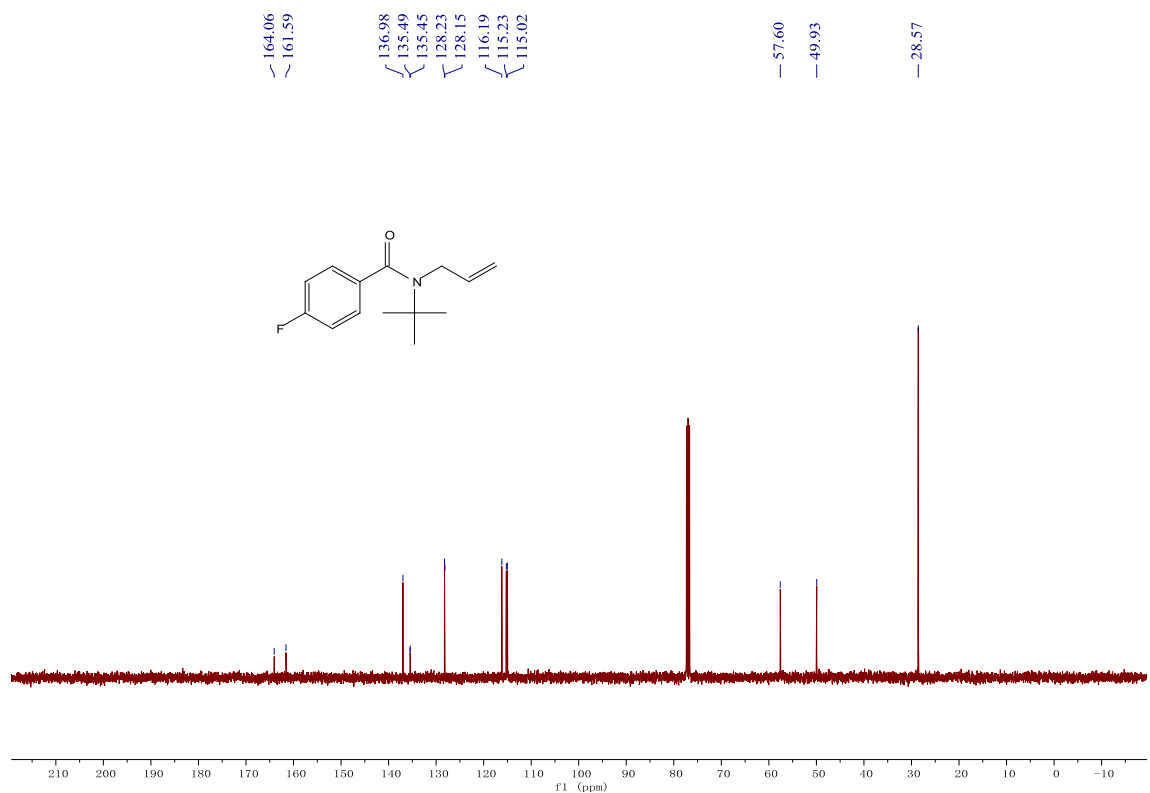
¹H NMR of A-1



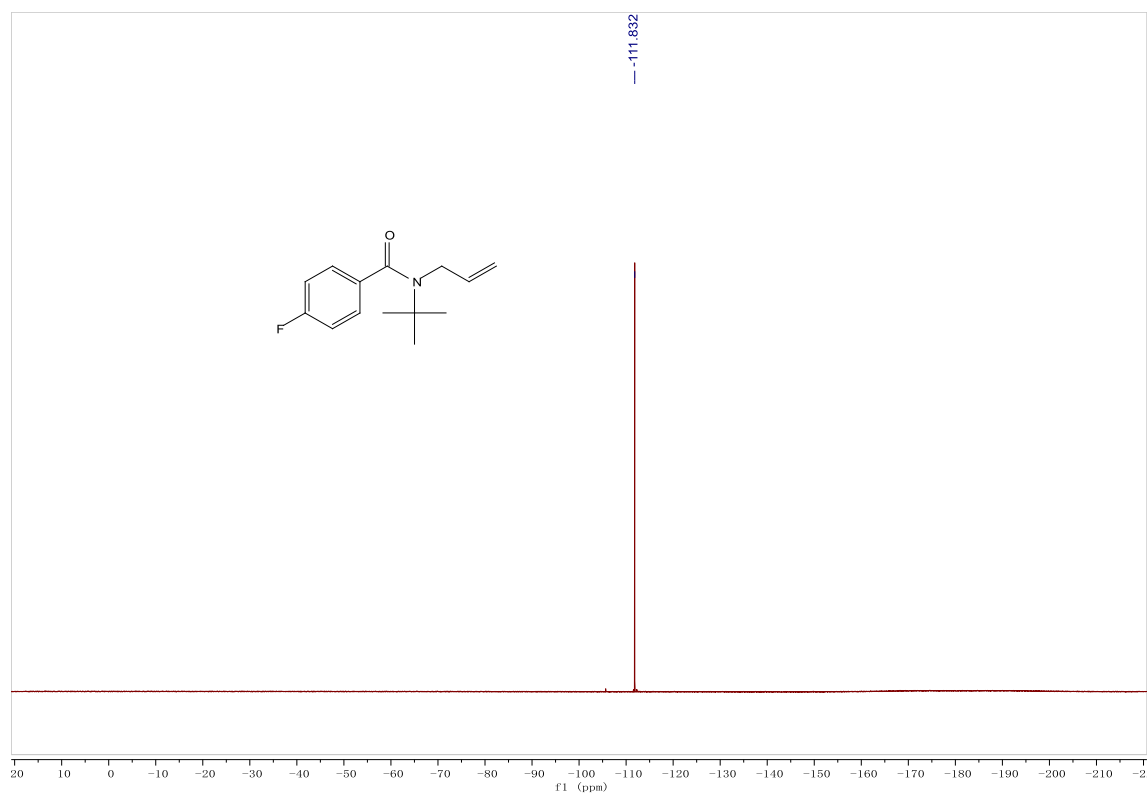
¹³C NMR of A-1



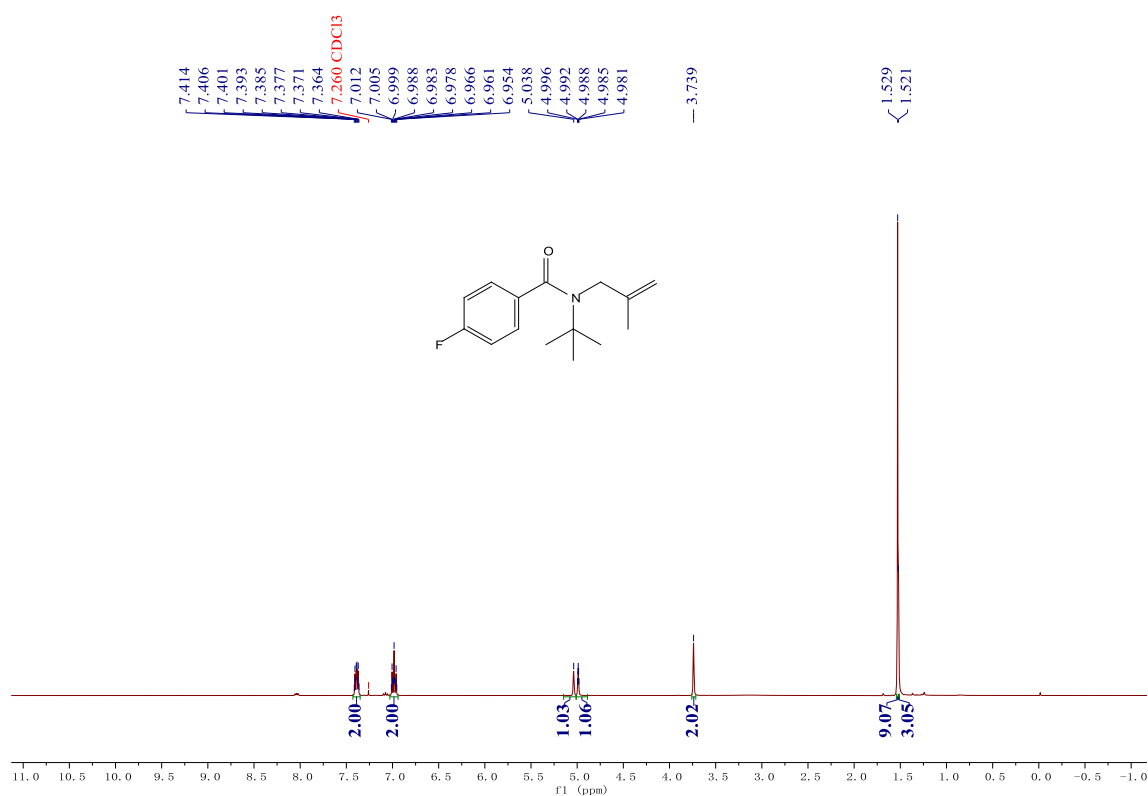
¹H-NMR for 4-1



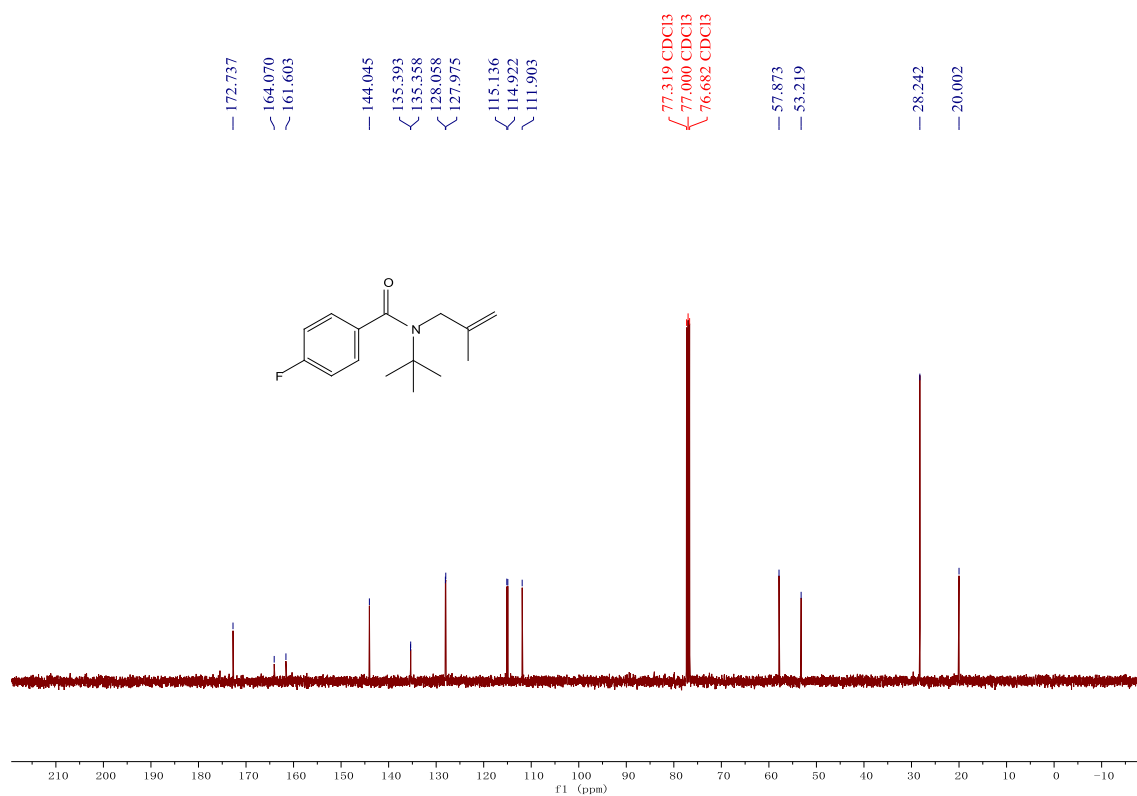
¹³C-NMR for 4-1



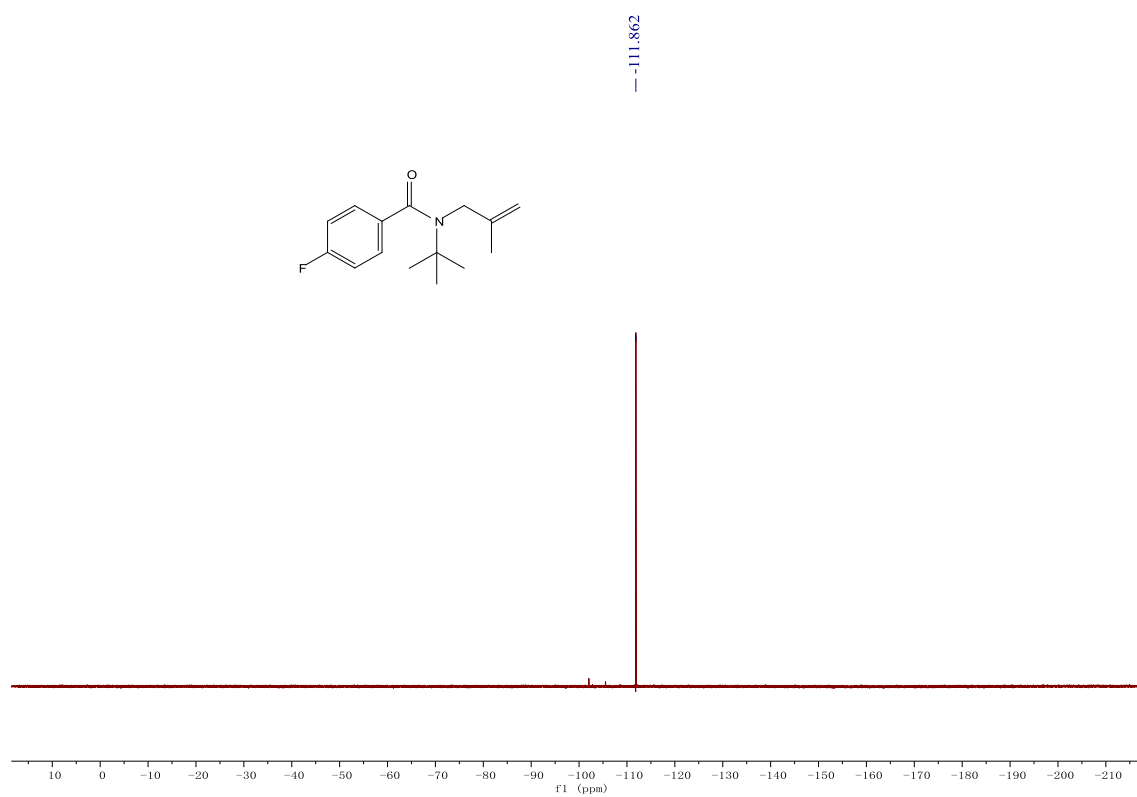
¹⁹F-NMR for 4-1



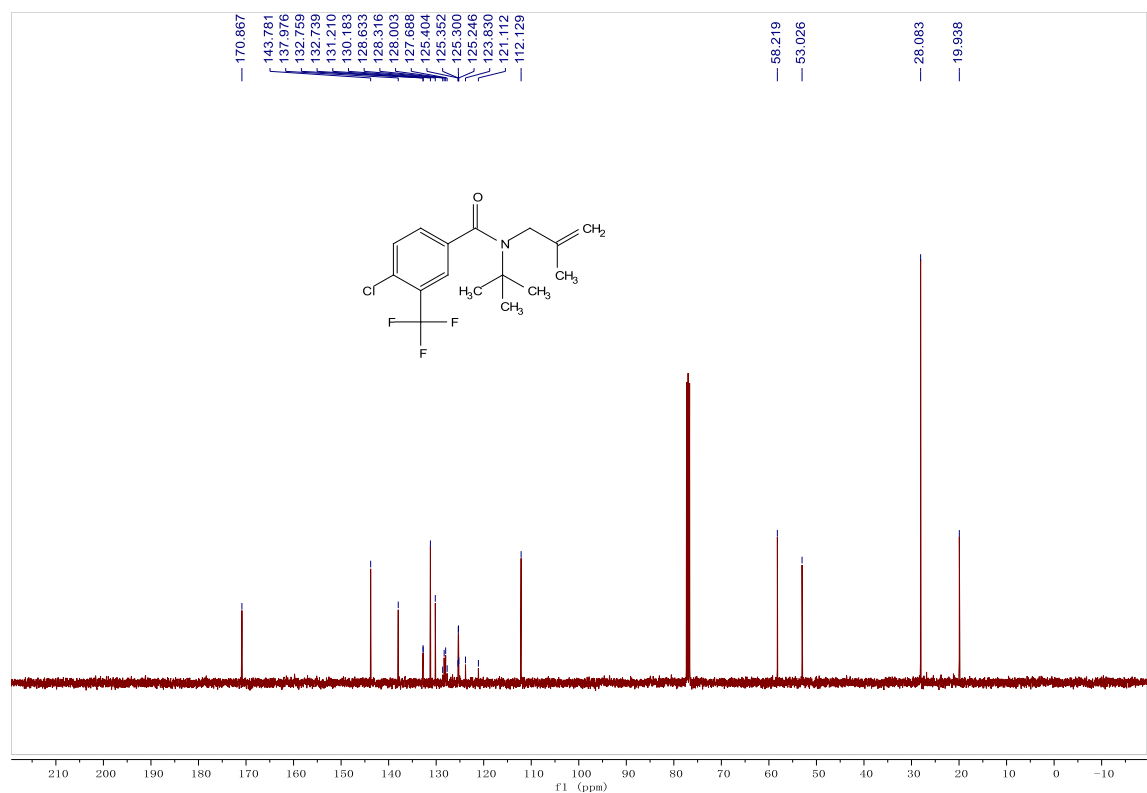
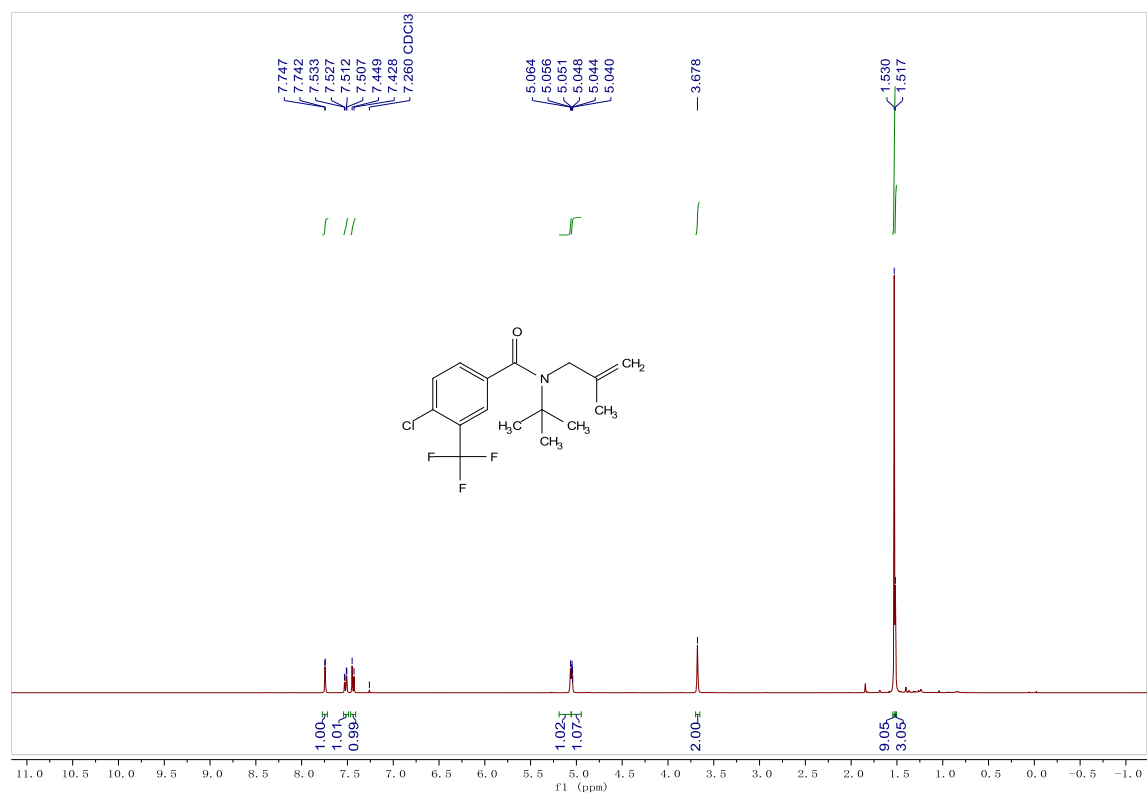
¹H-NMR for 4-2

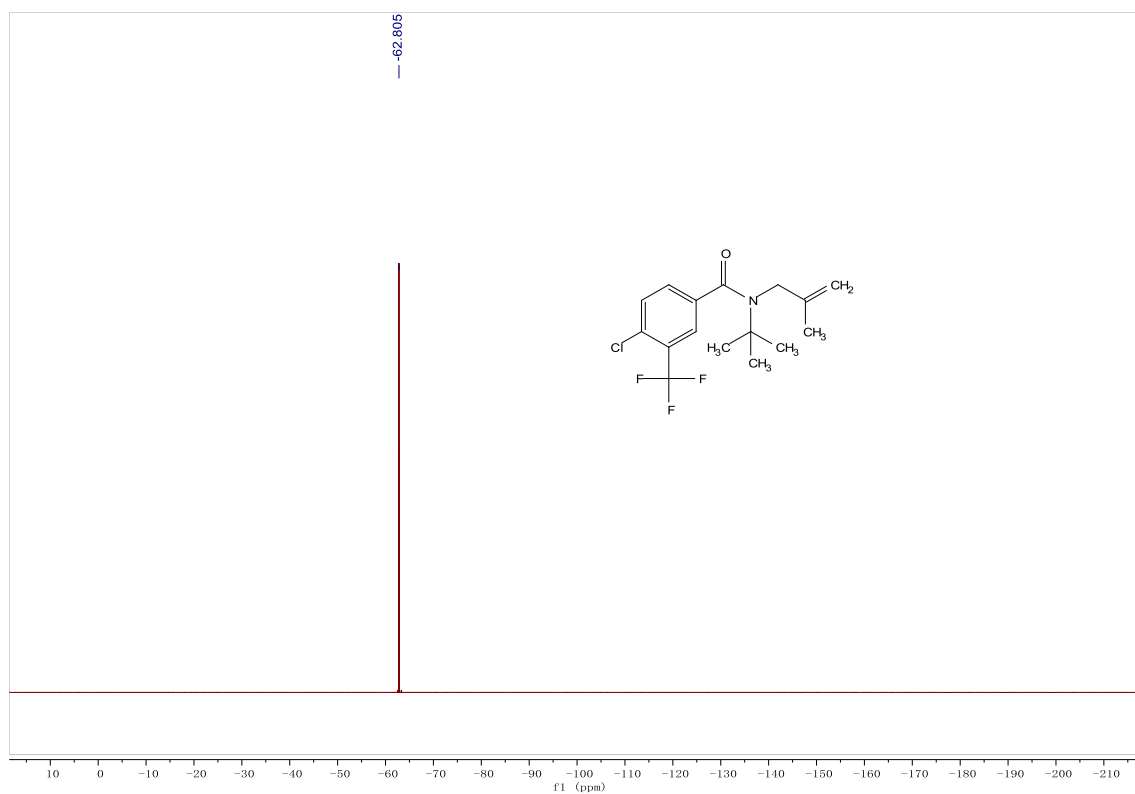


¹³C-NMR for 4-2

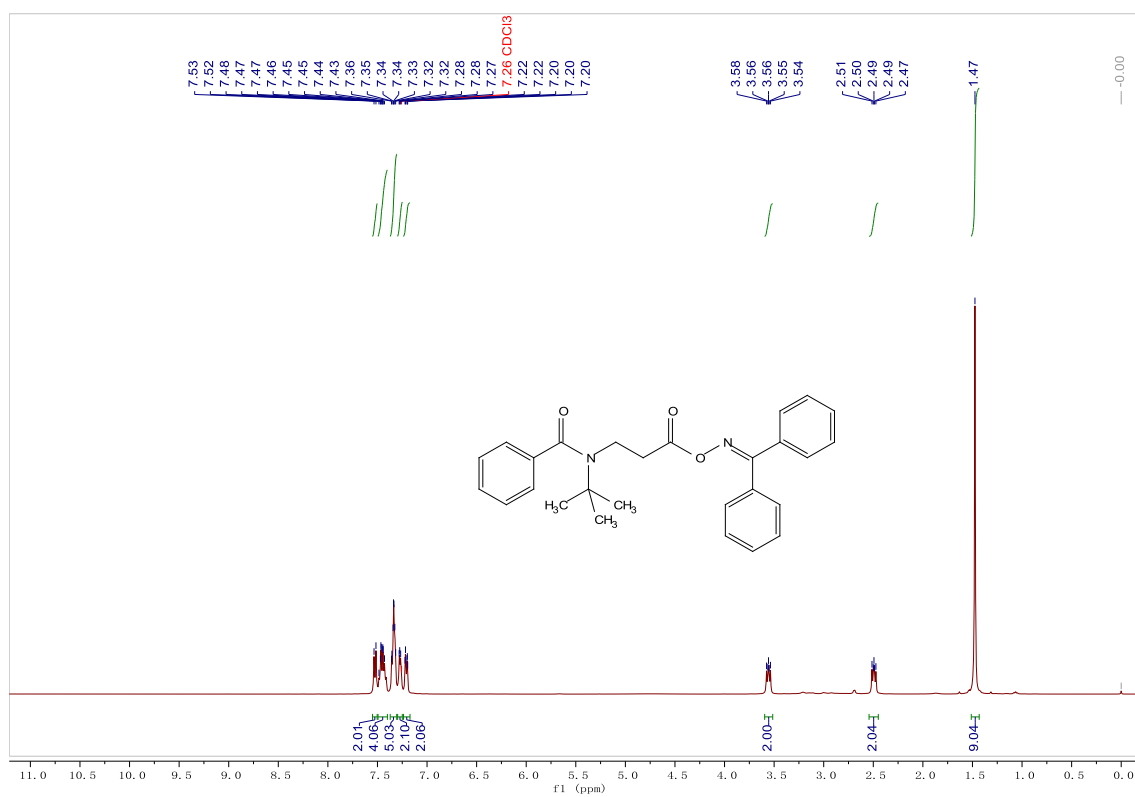


¹⁹F-NMR for 4-2

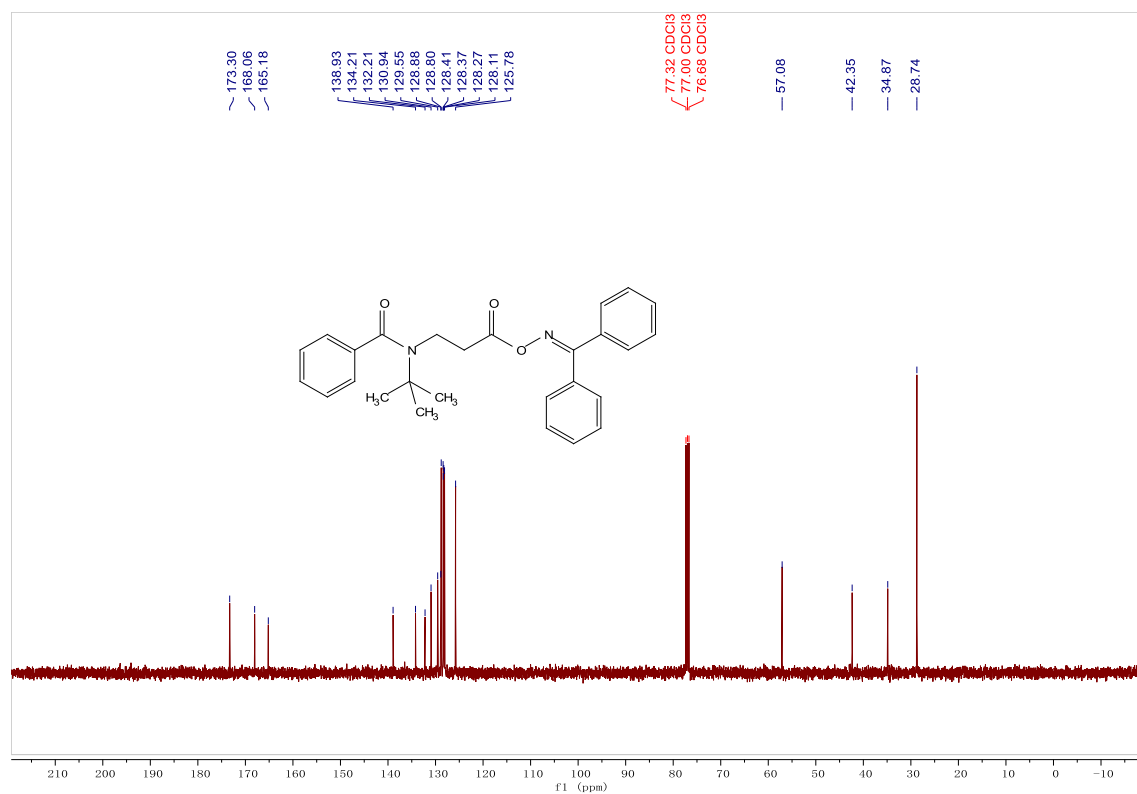




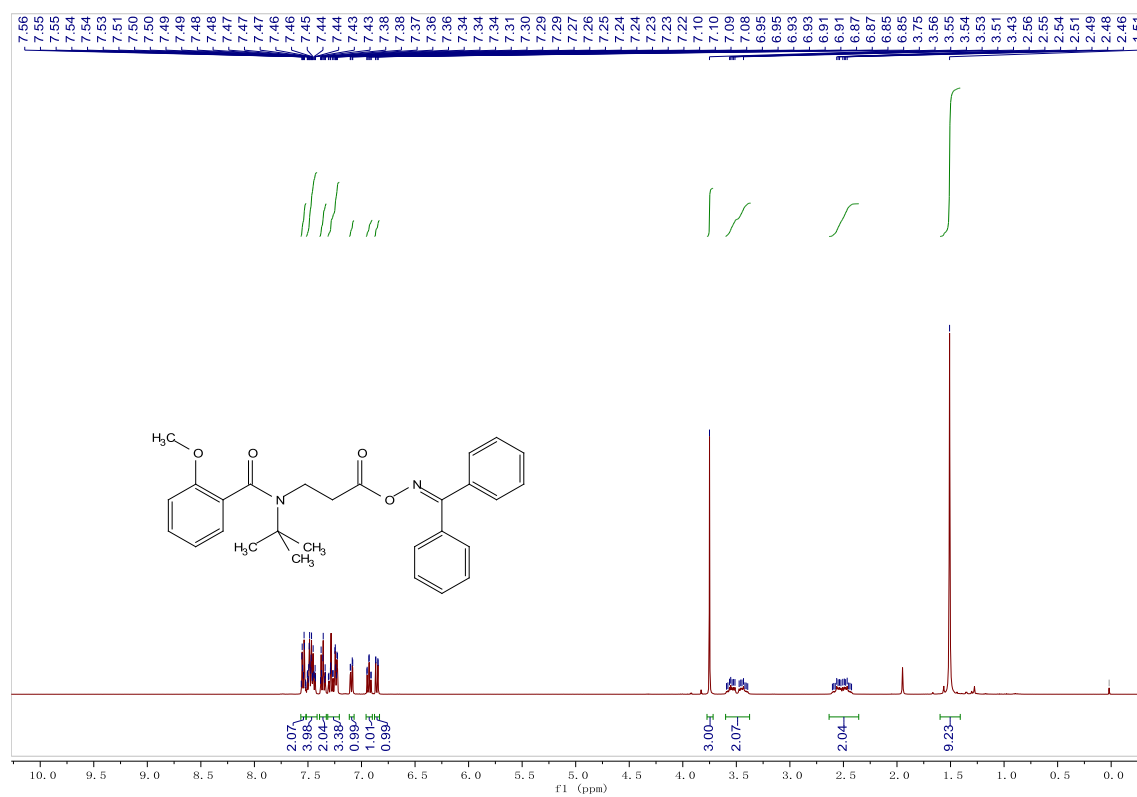
¹⁹C-NMR for 4-3



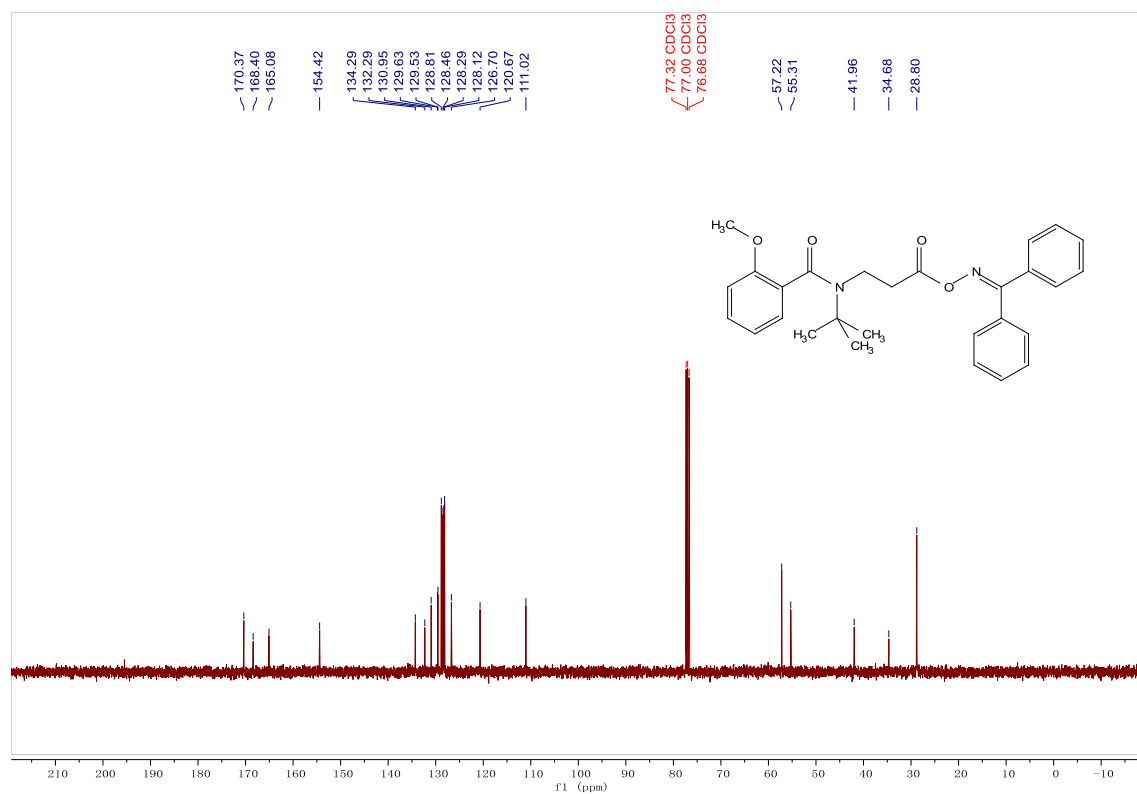
¹H-NMR for 1-1



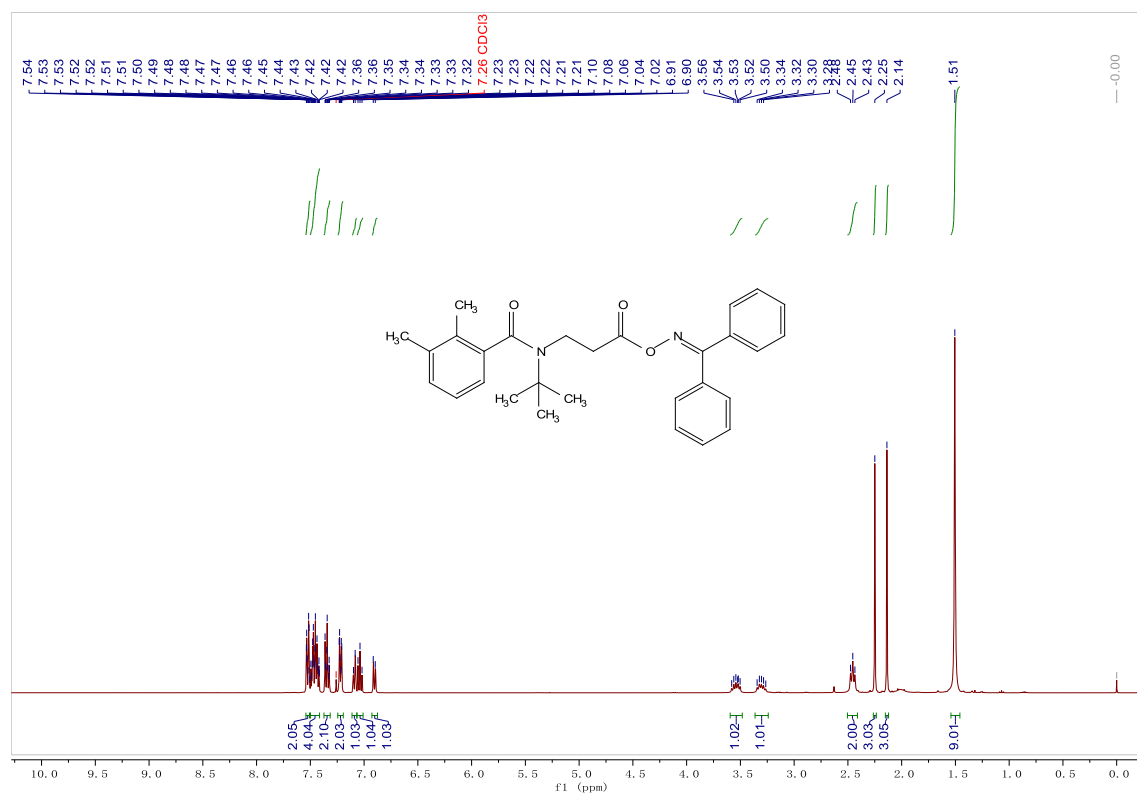
¹³C-NMR for 1-1



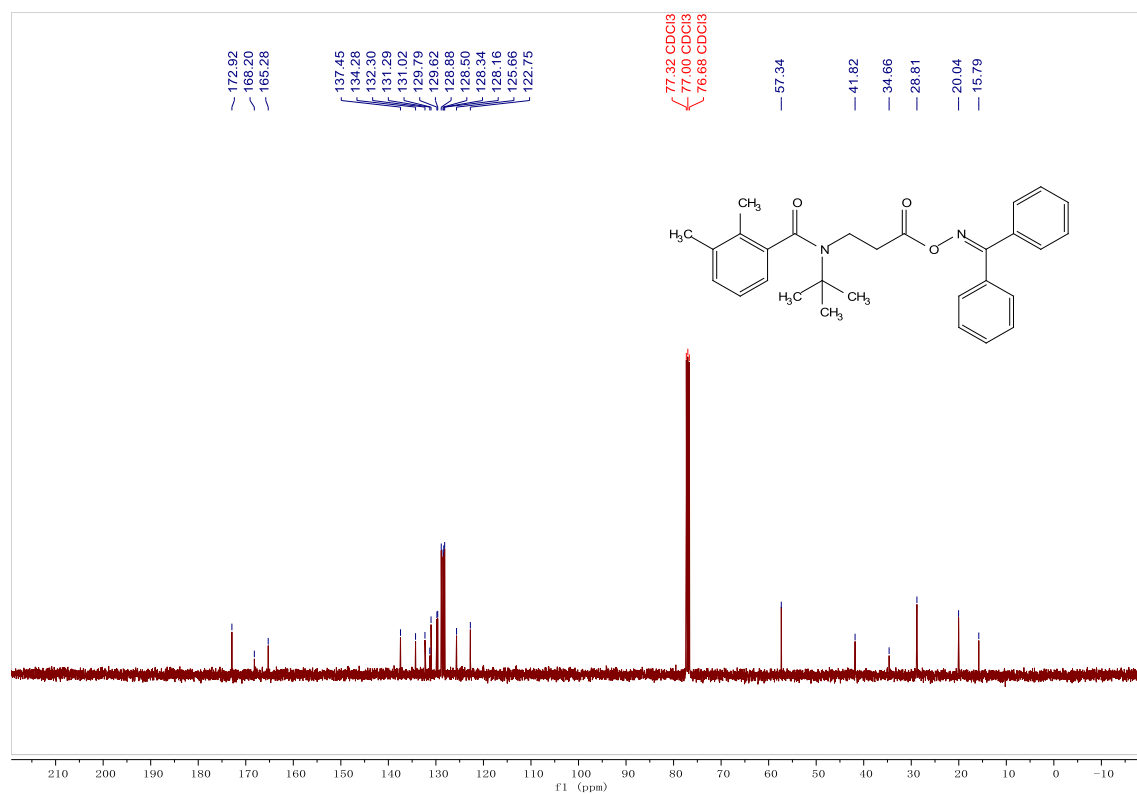
¹H-NMR for 1-2



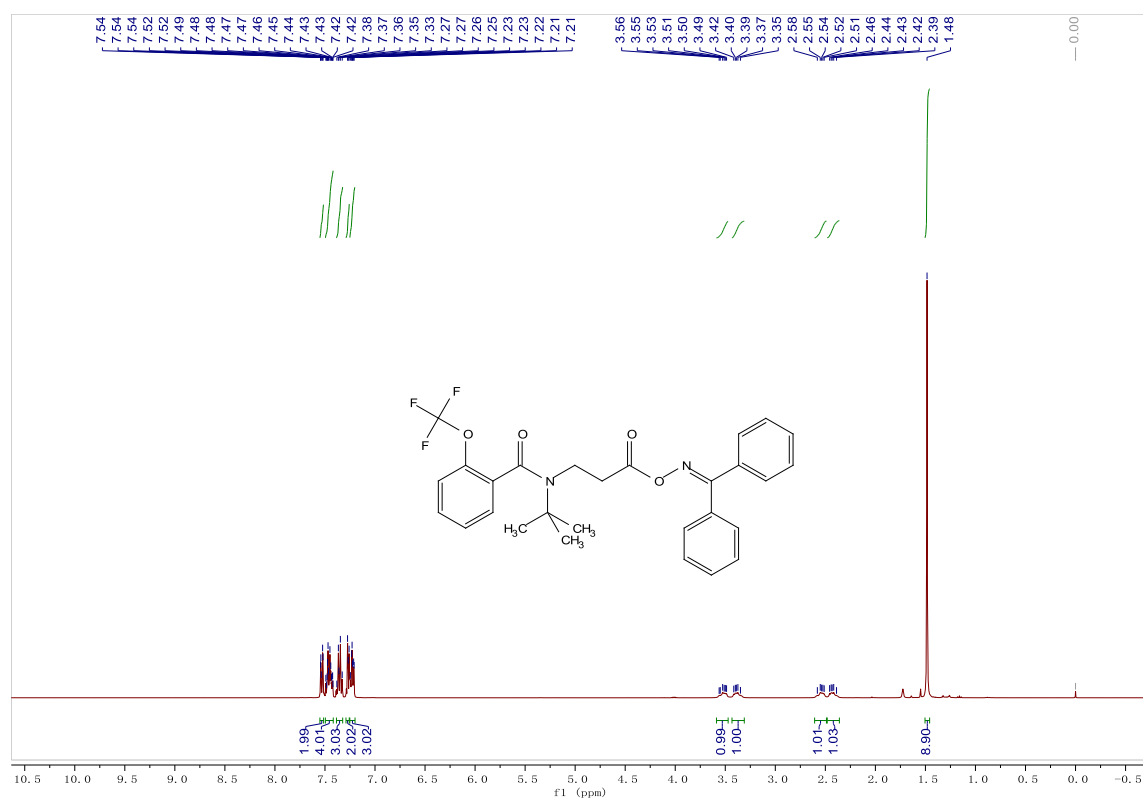
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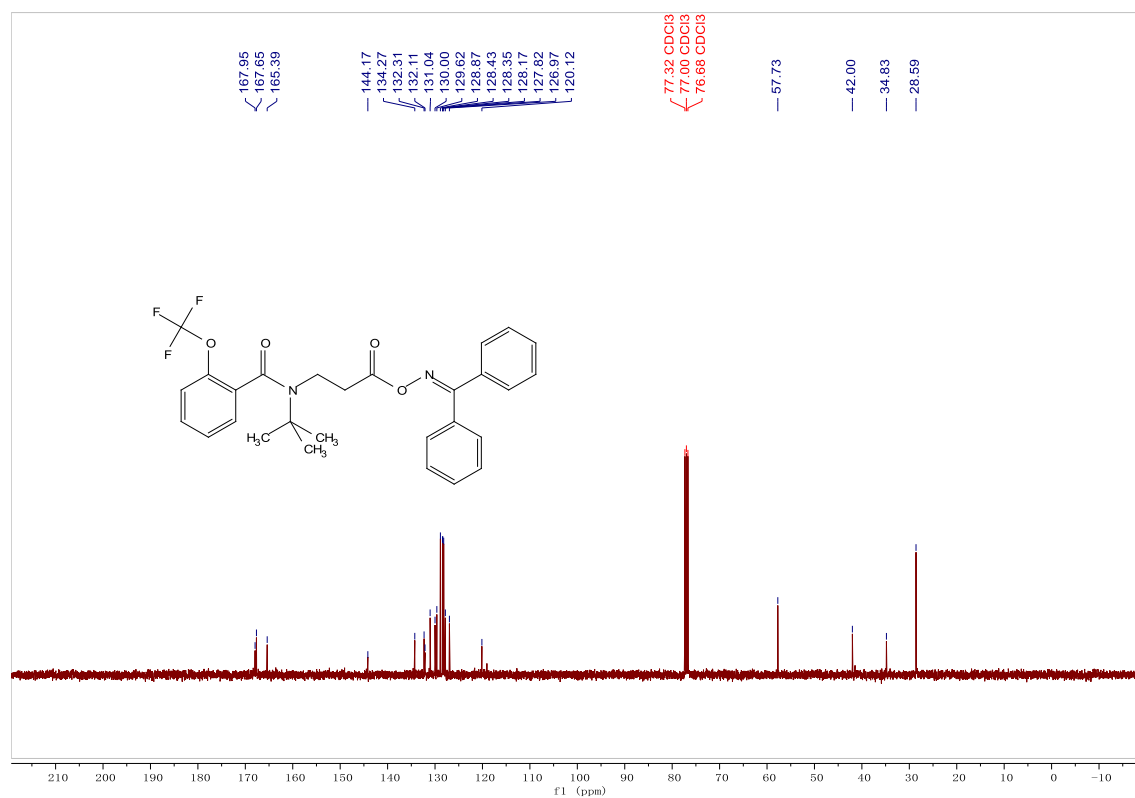
¹H-NMR for 1-3



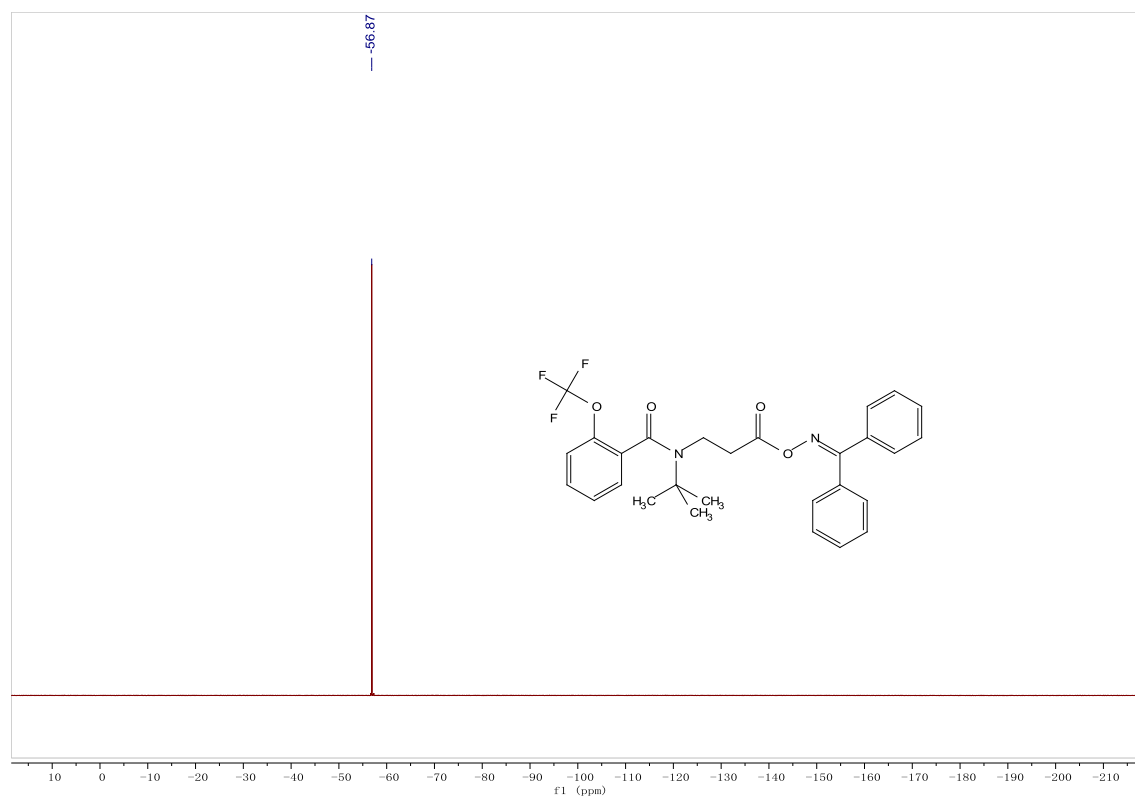
¹³C-NMR for 1-3



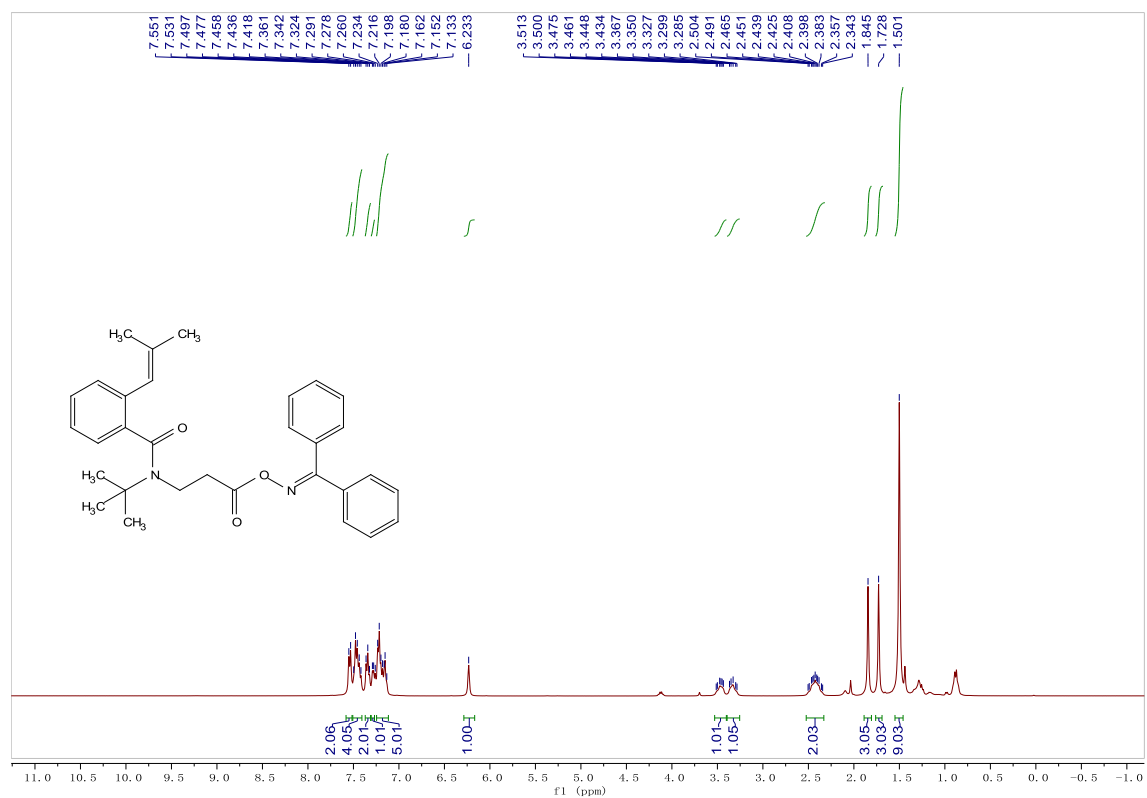
¹H-NMR for 1-4



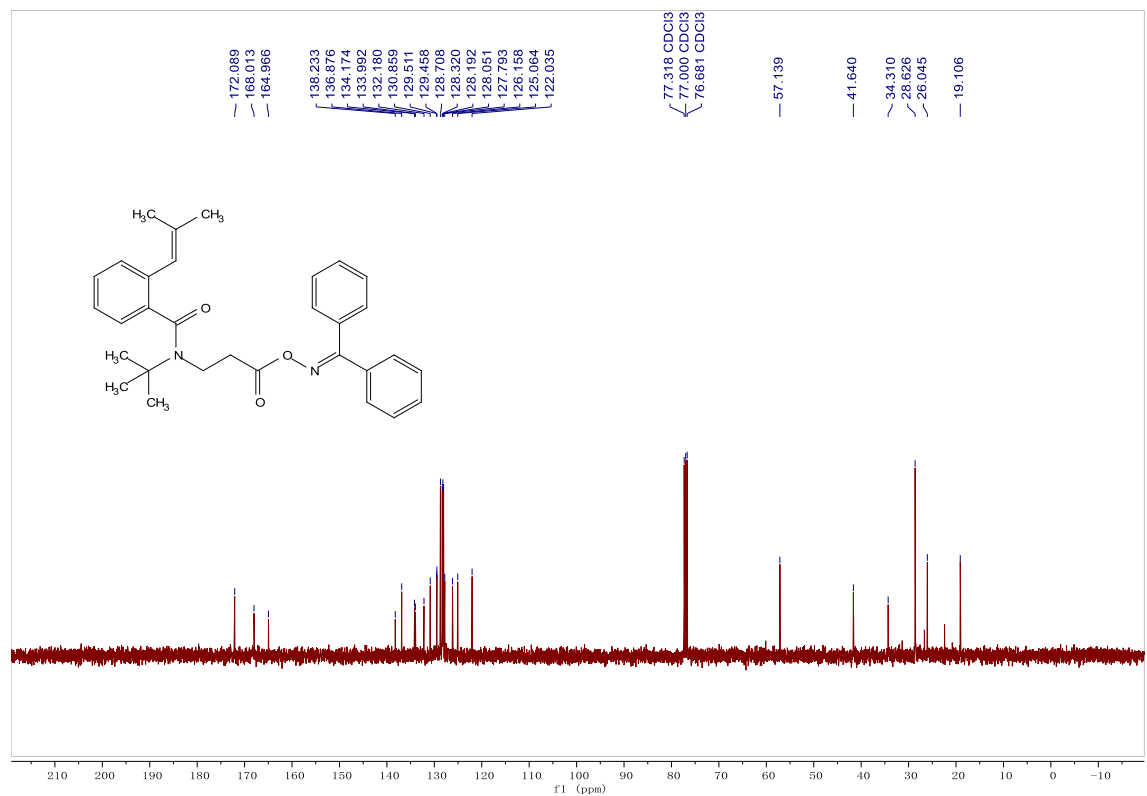
¹³C-NMR for 1-4



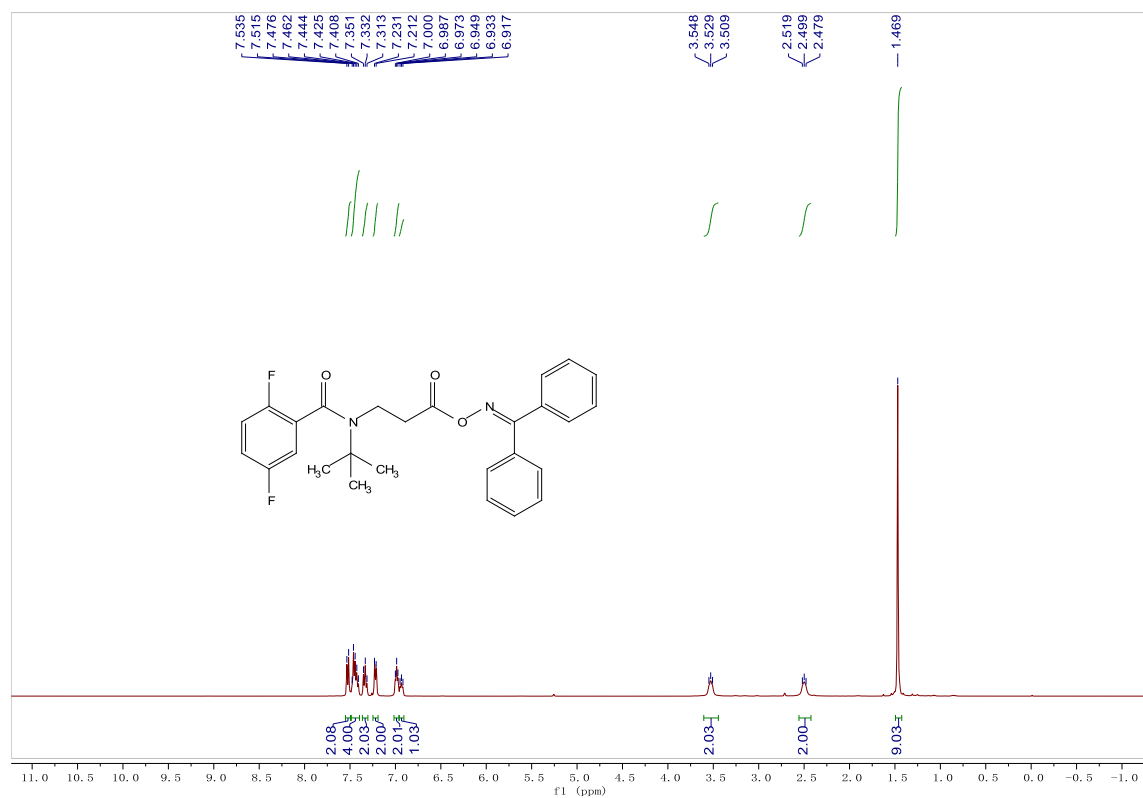
¹⁹F-NMR for 1-4



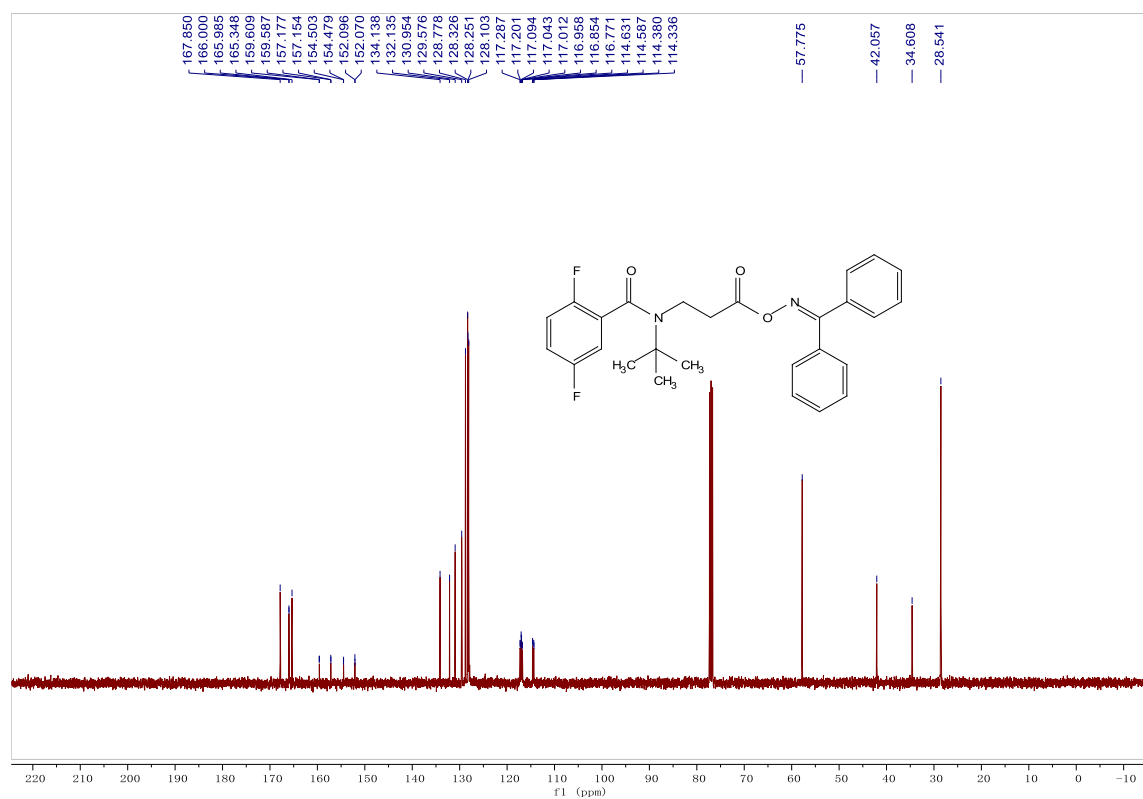
¹H-NMR for 1-5



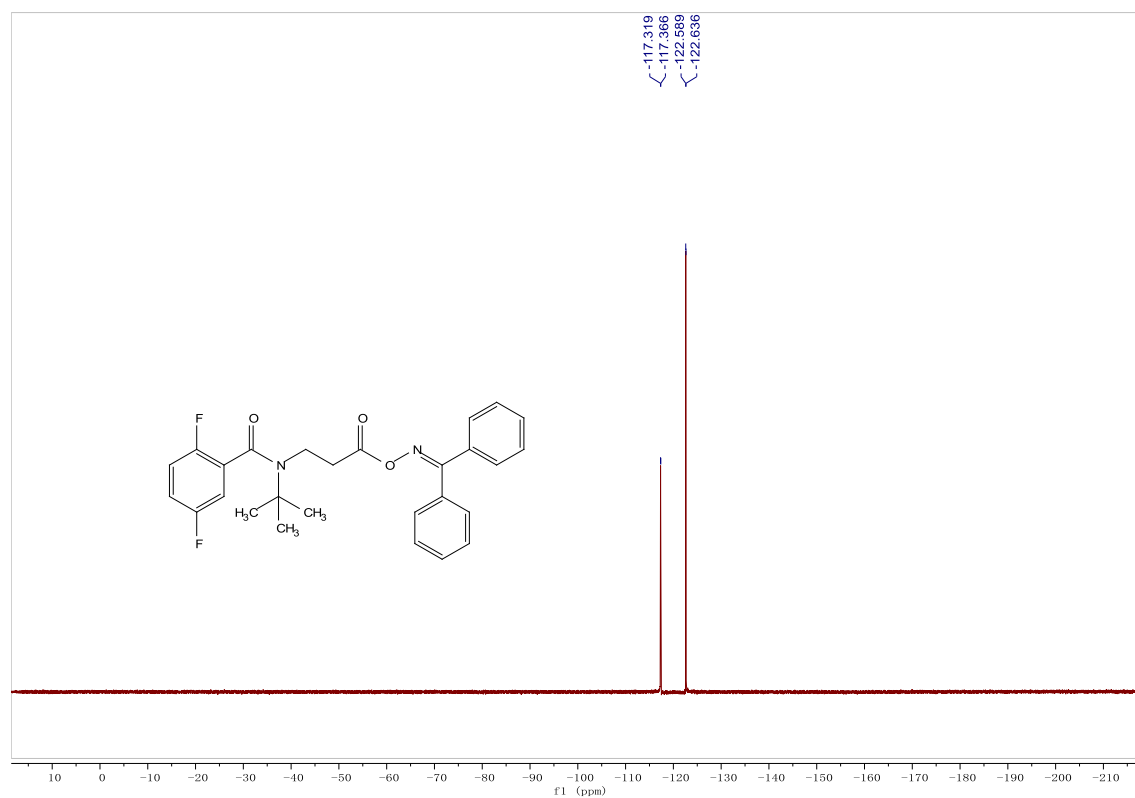
¹³C-NMR for 1-5



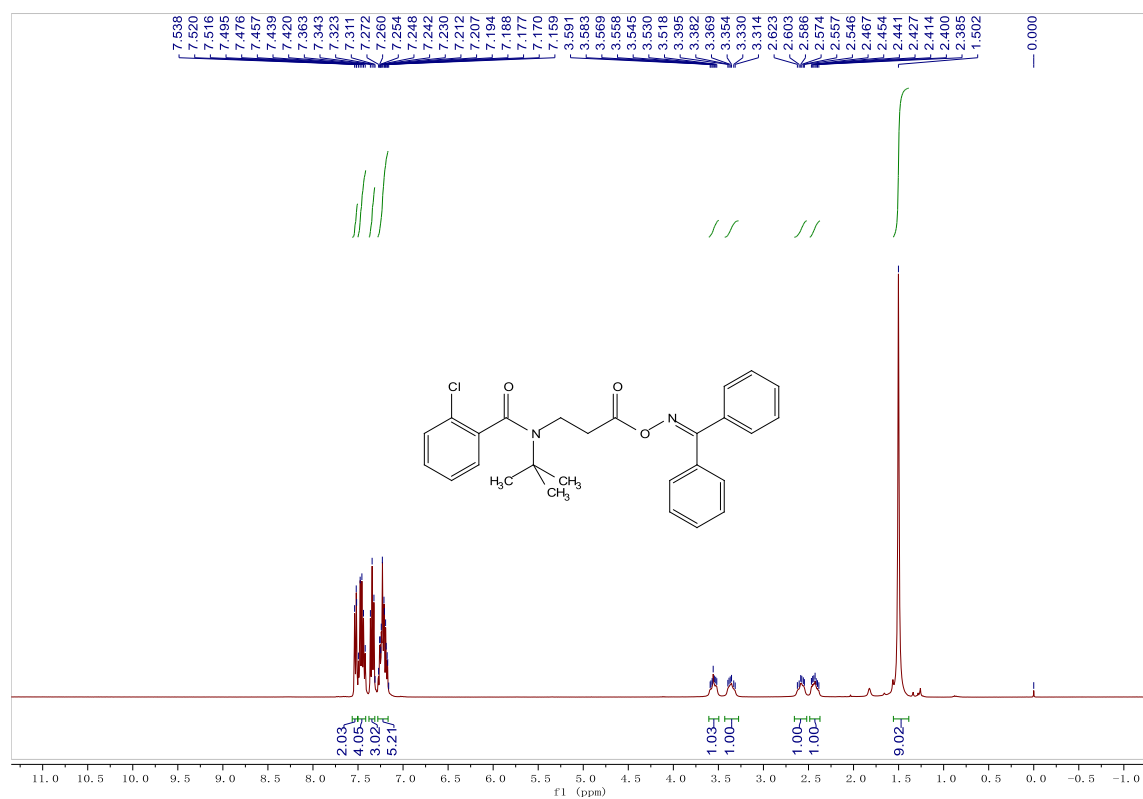
¹H-NMR for 1-6



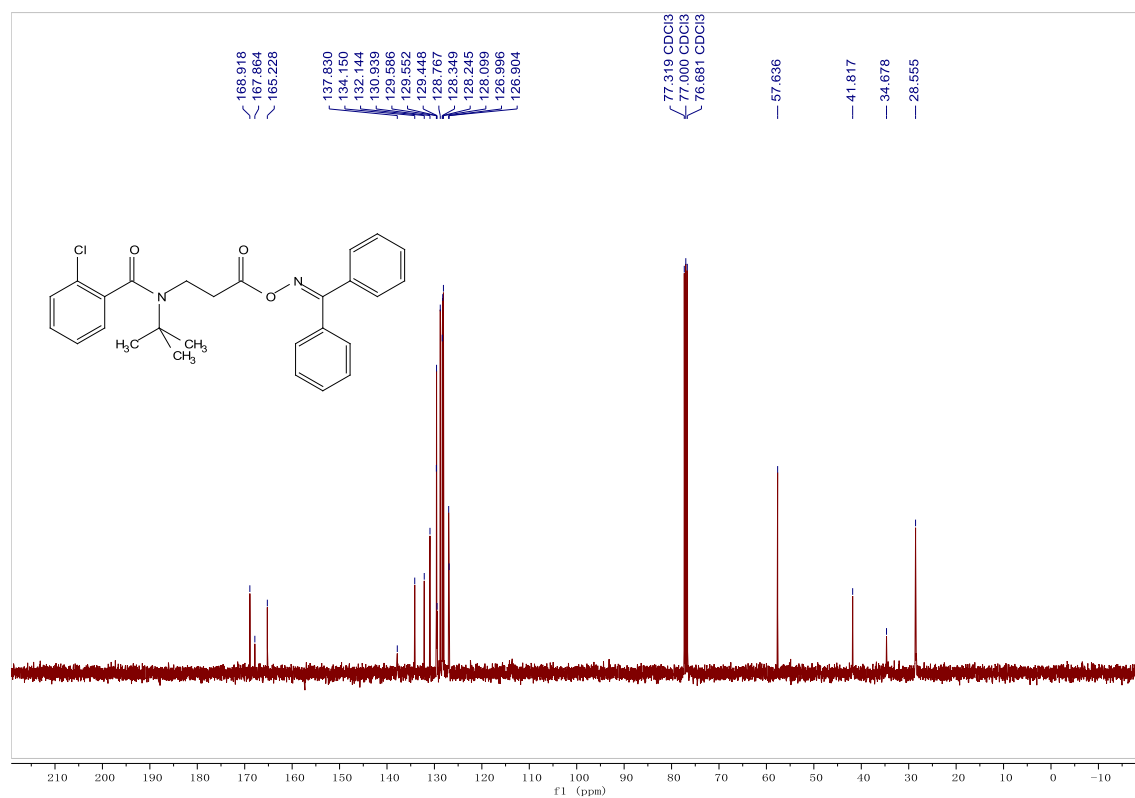
¹³C-NMR for 1-6



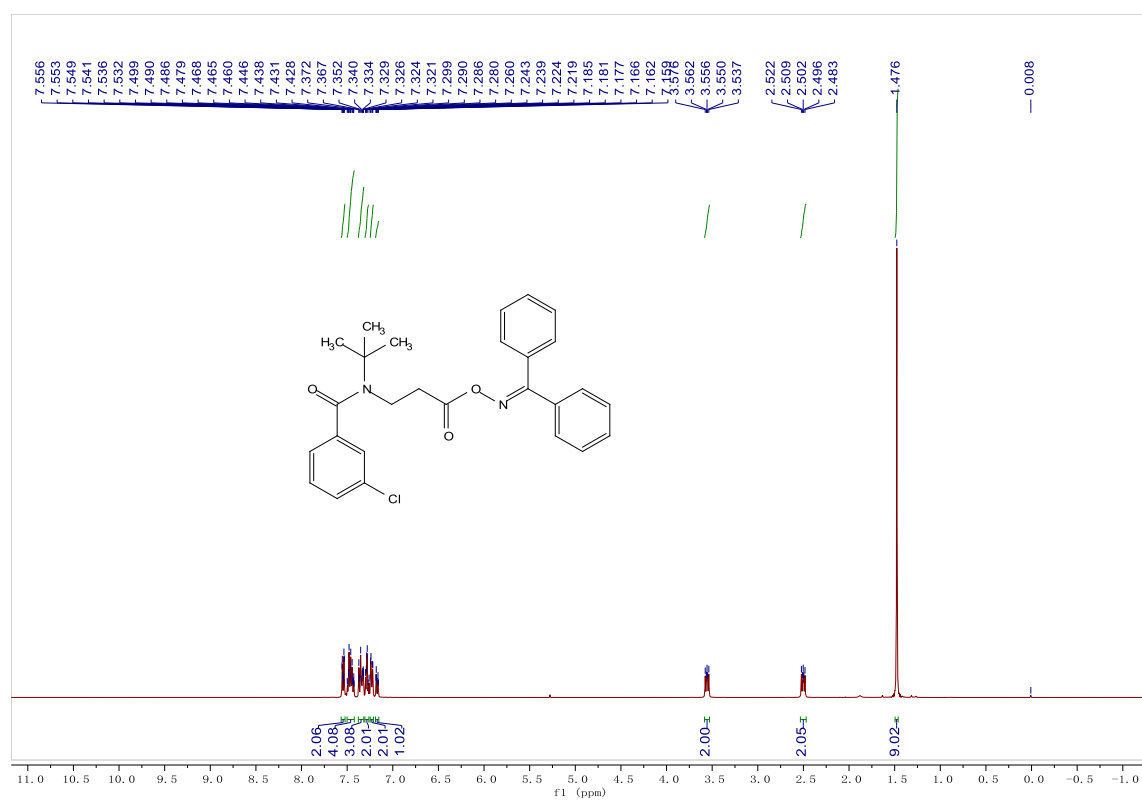
¹⁹F-NMR for 1-6



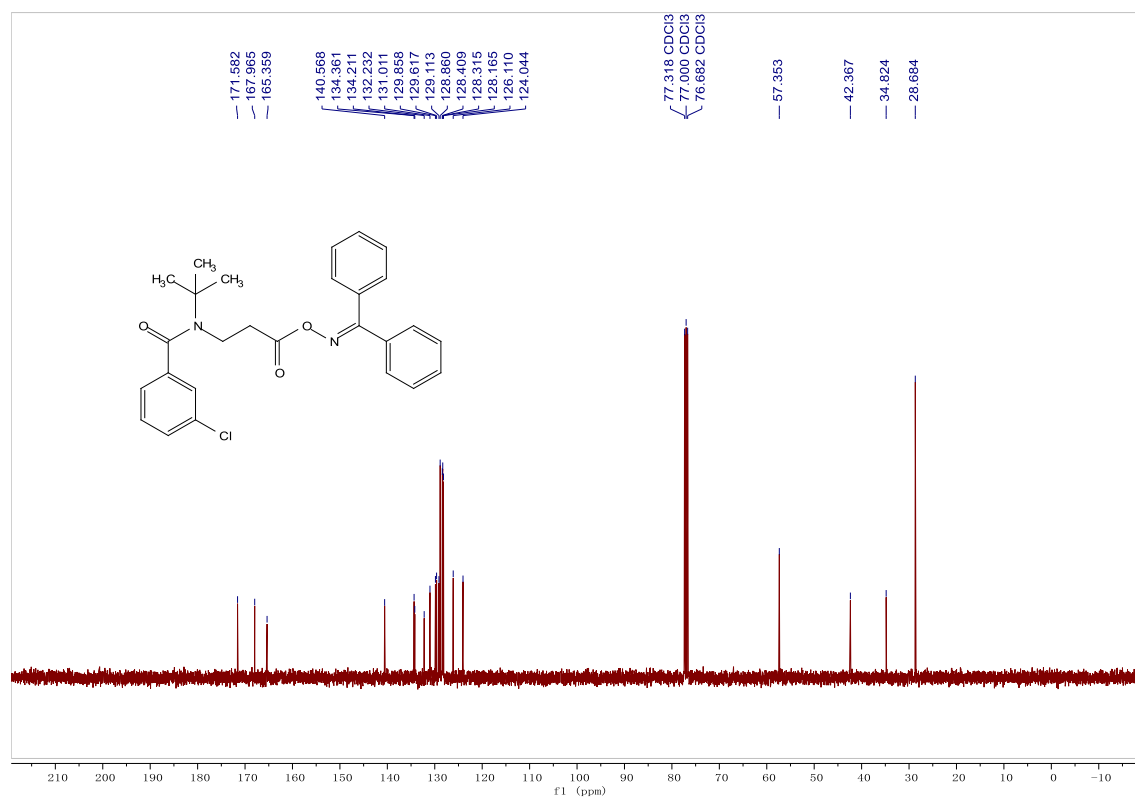
¹H-NMR for 1-7



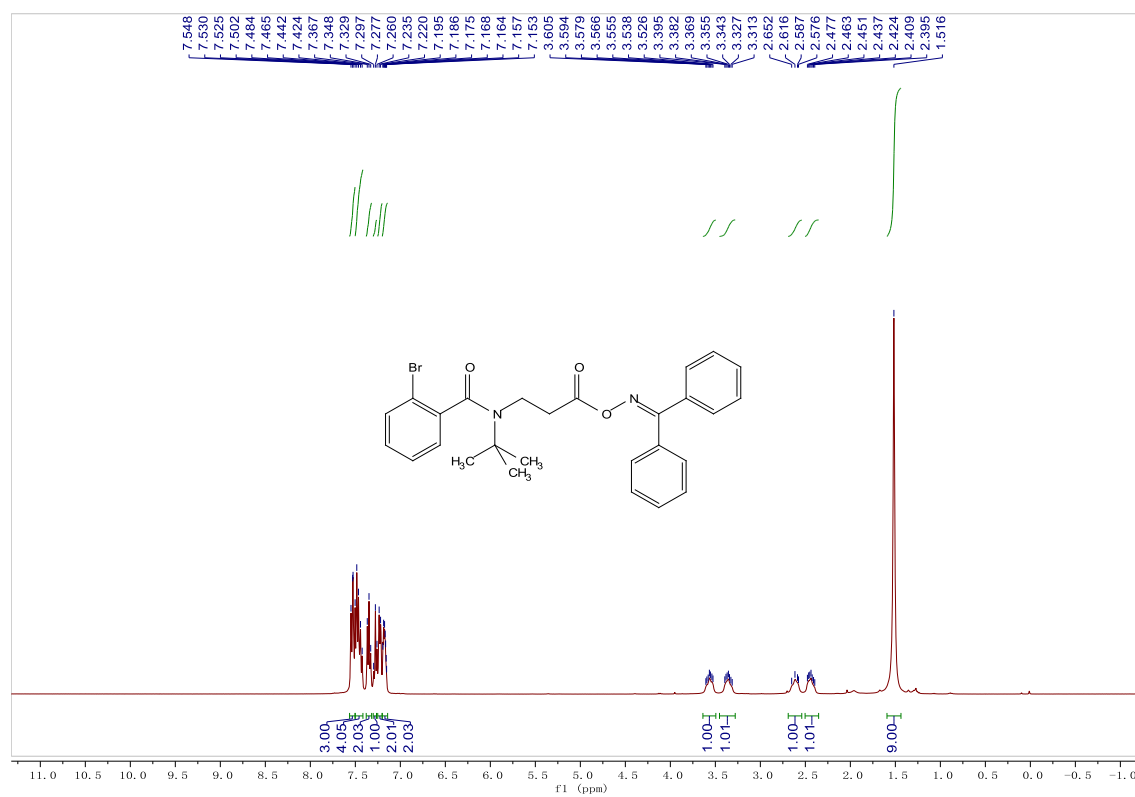
¹³C-NMR for 1-7



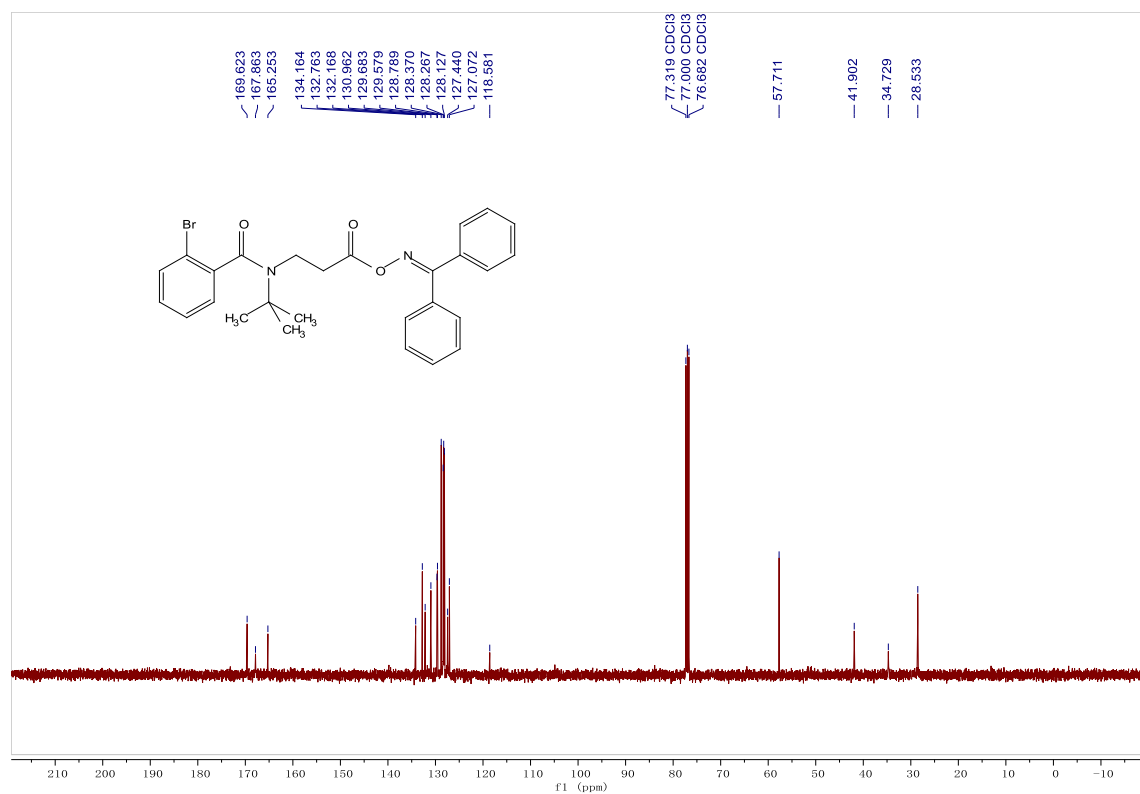
¹H-NMR for 1-8



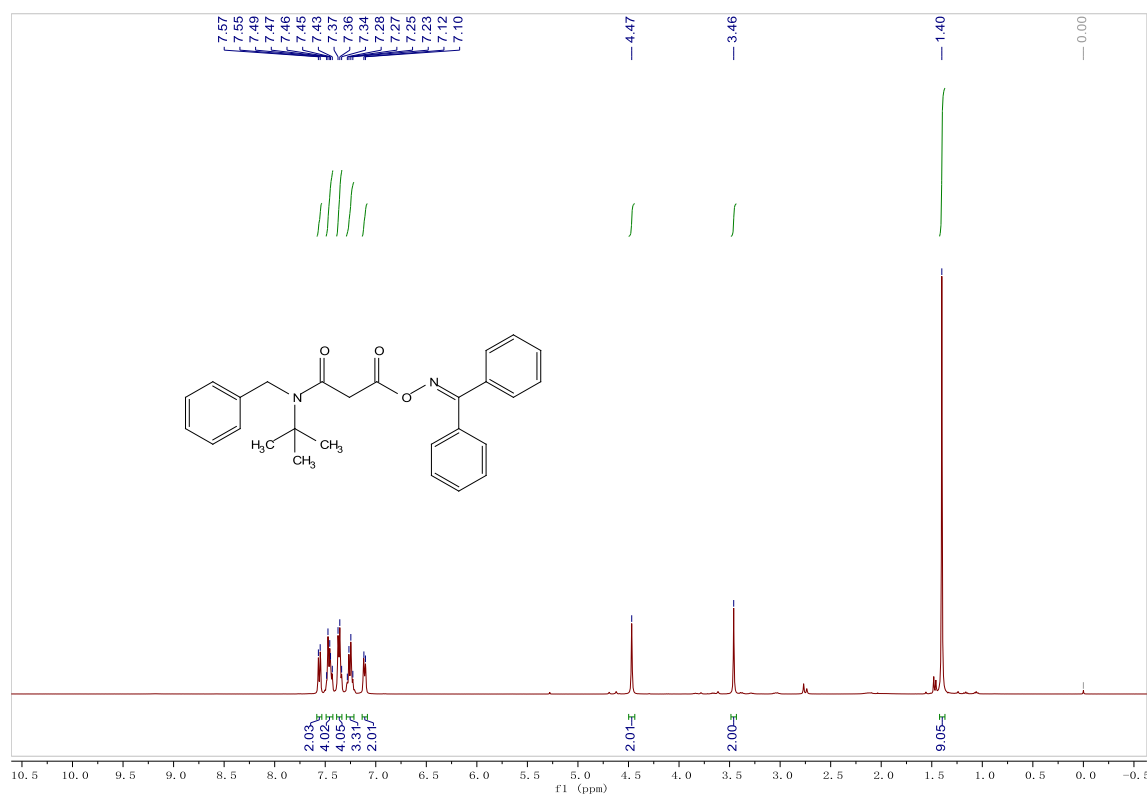
¹³C-NMR for 1-8



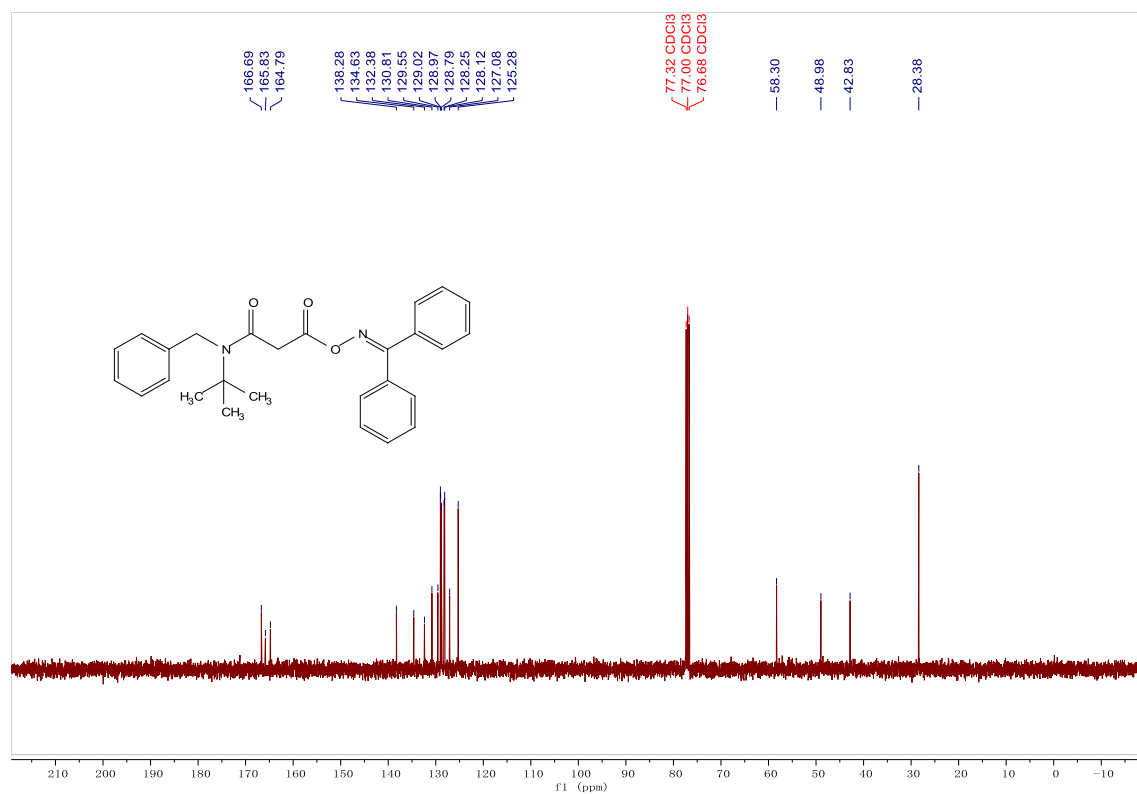
¹H-NMR for 1-9



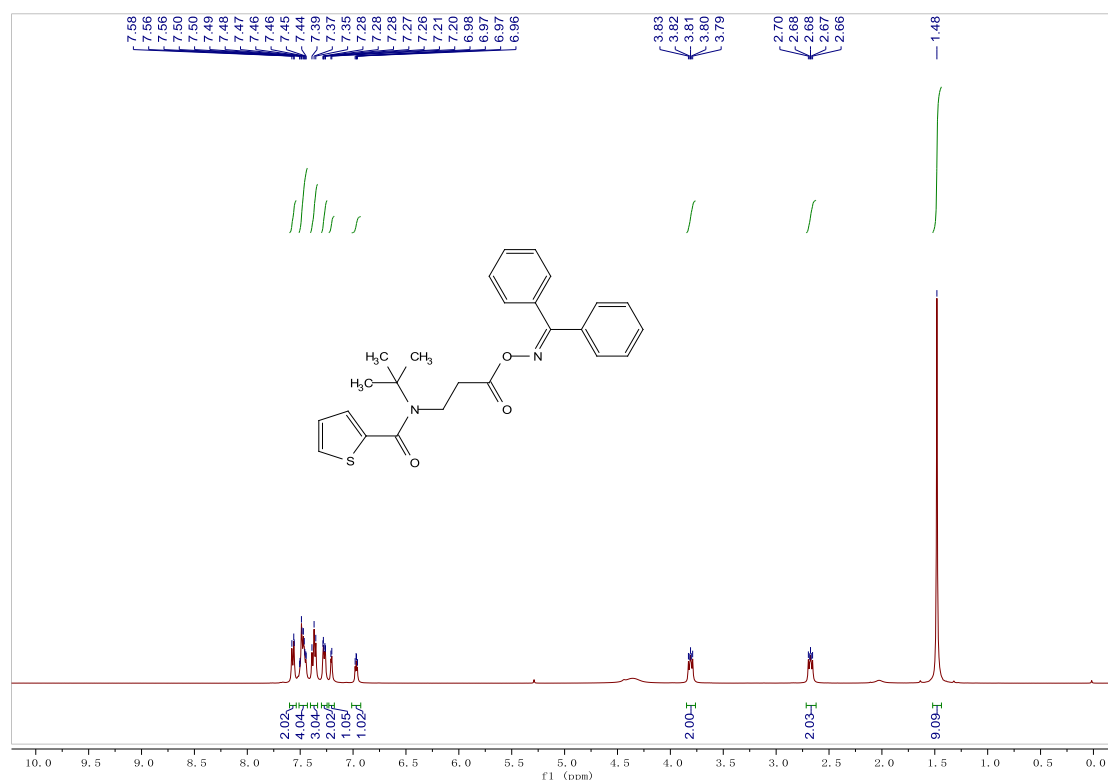
¹³C-NMR for 1-9



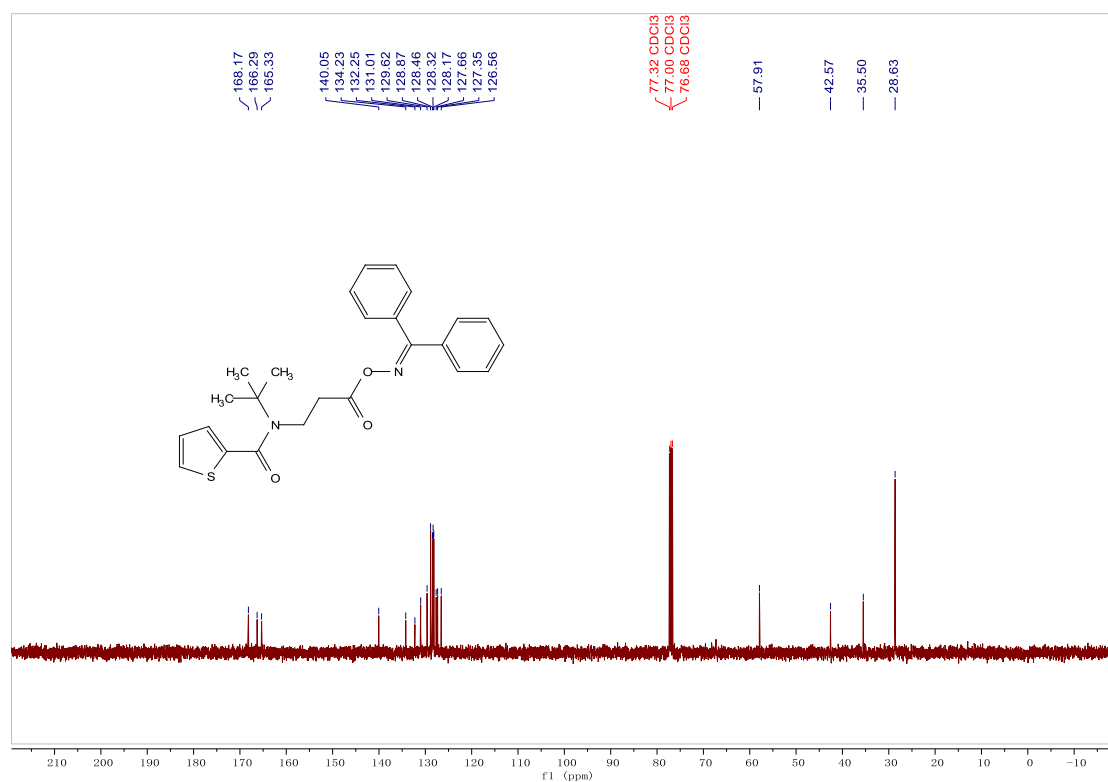
¹H-NMR for 1-10



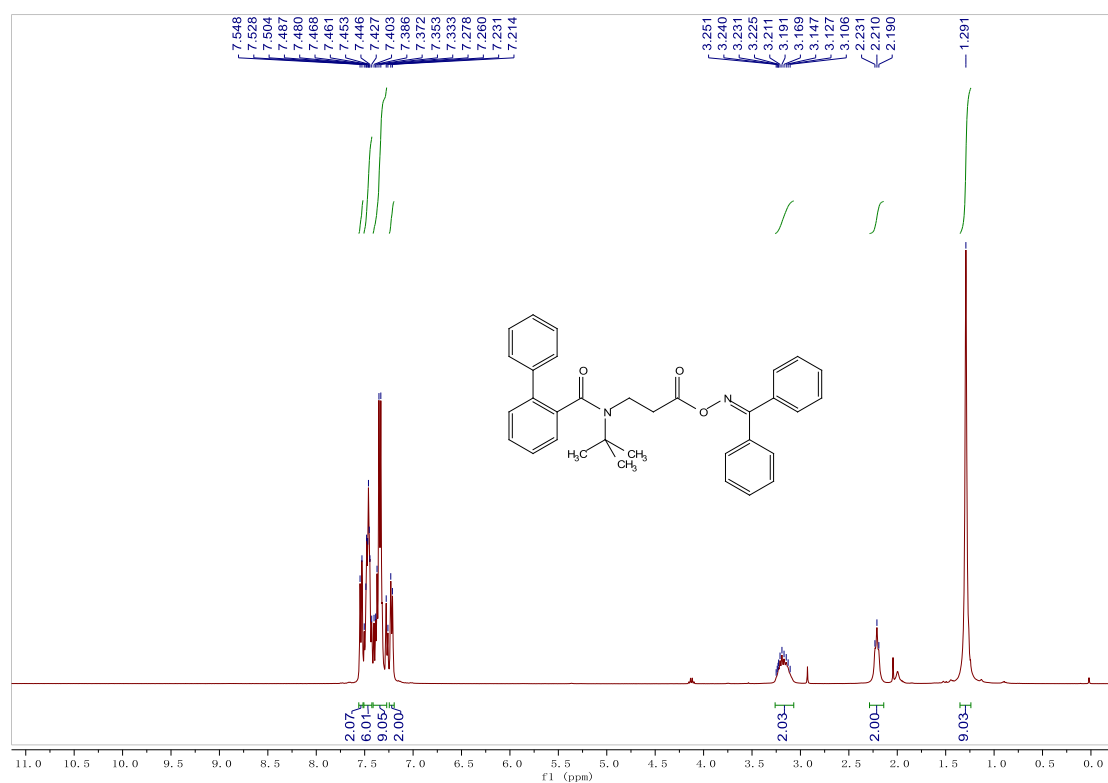
¹³C-NMR for 1-10



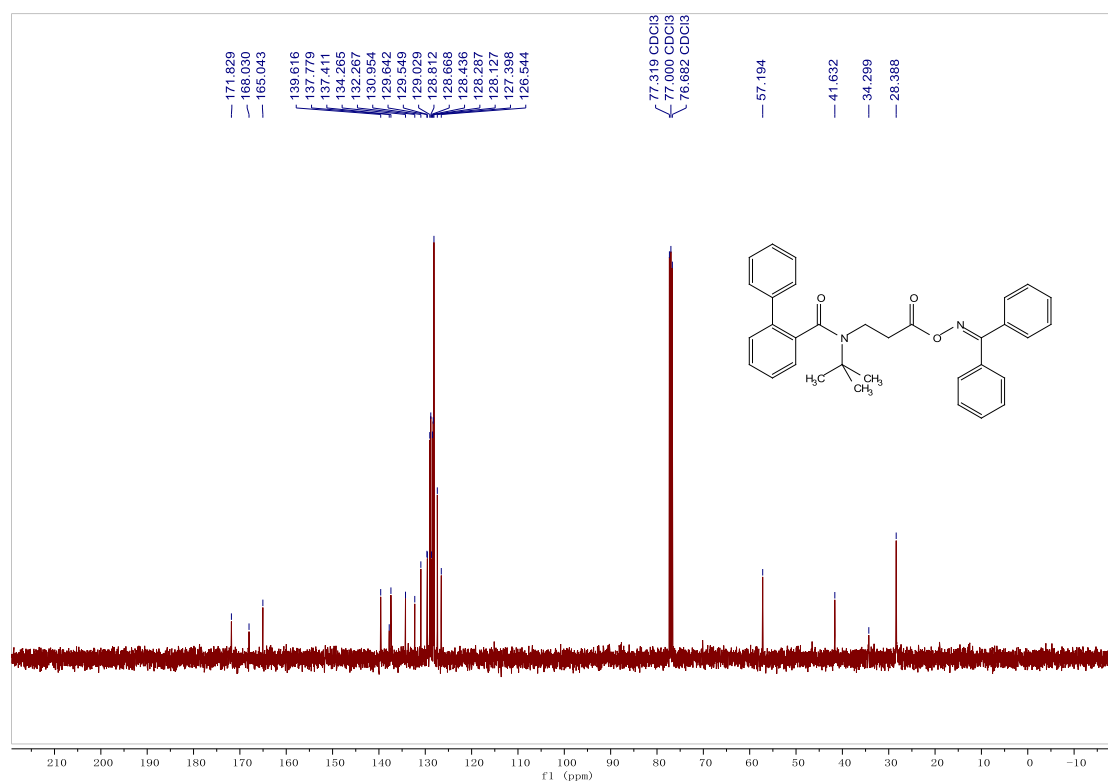
¹H NMR of 1-11



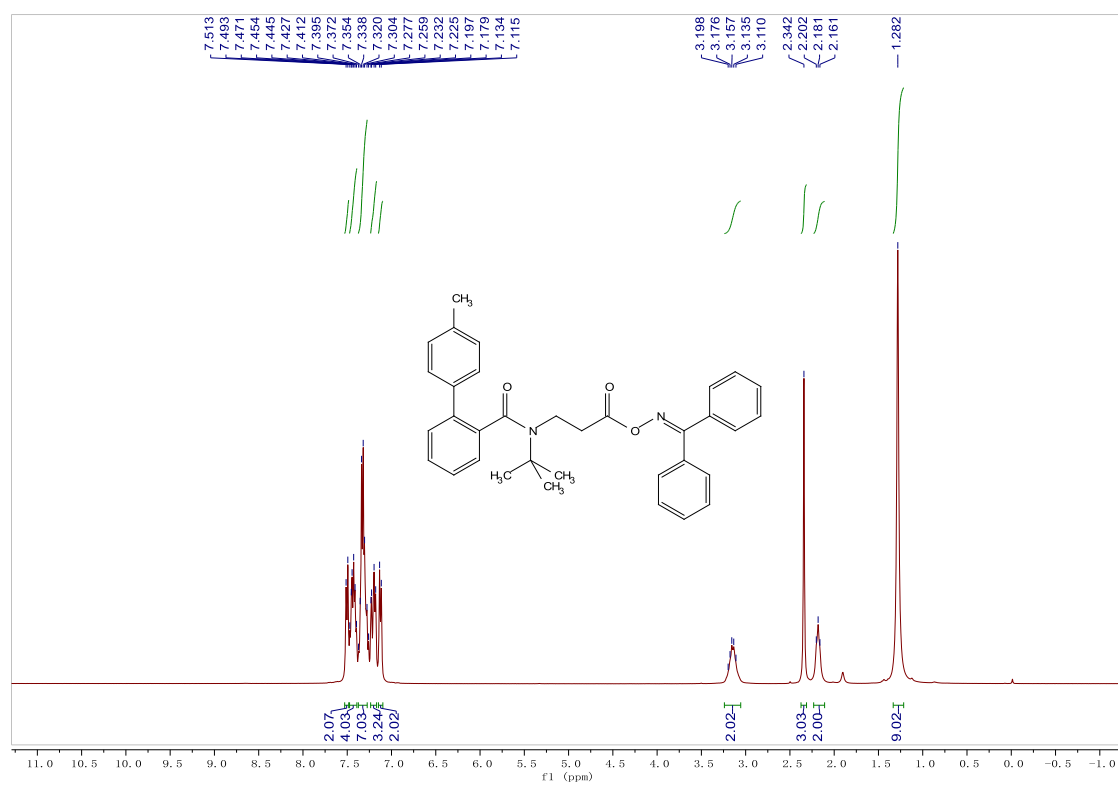
¹³C NMR of 1-11



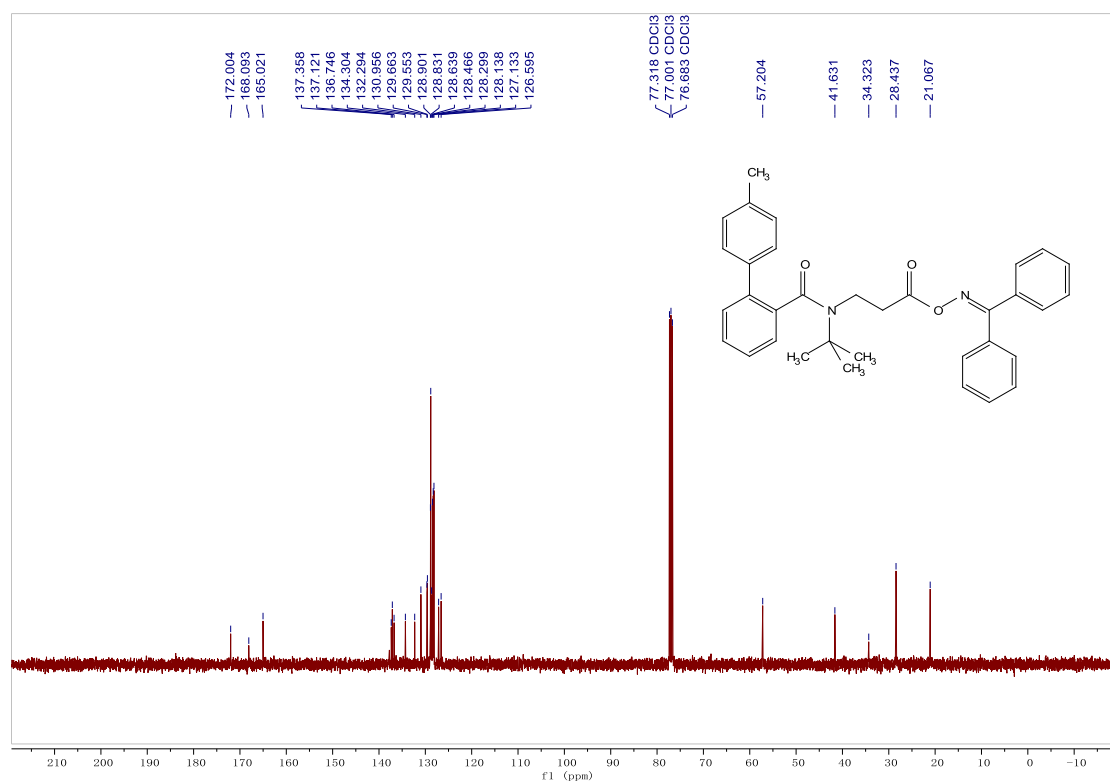
¹H NMR of 1-12



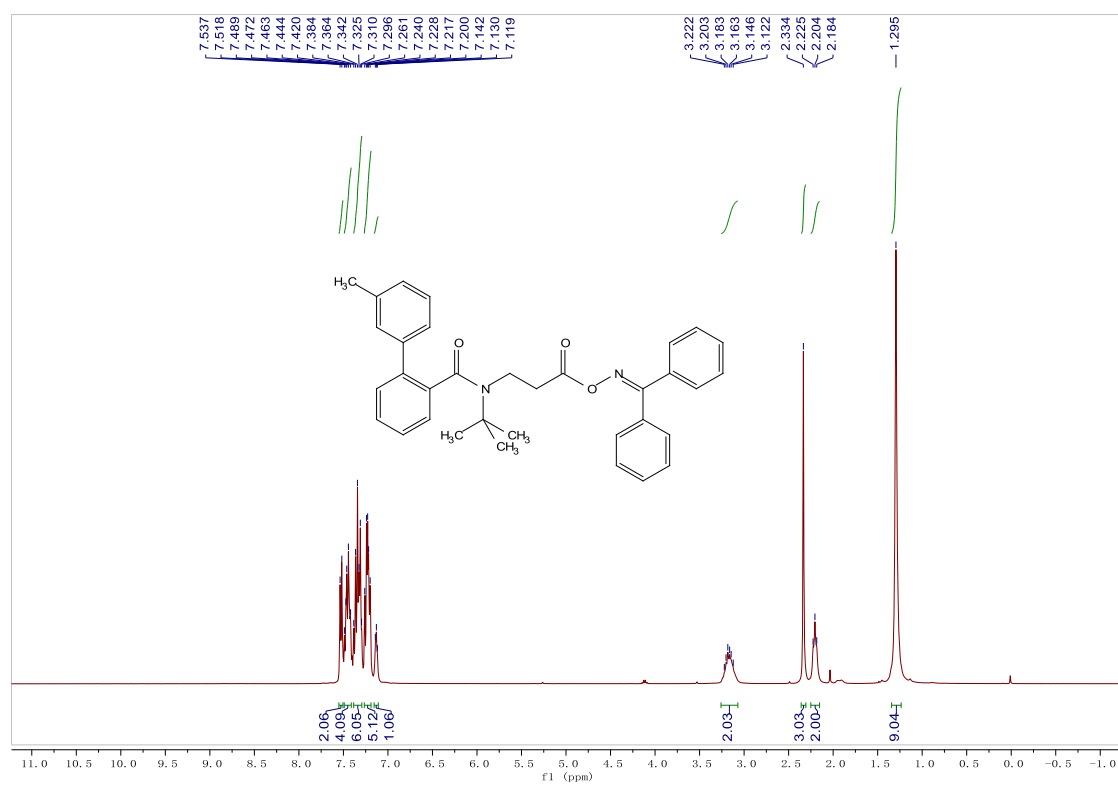
¹³C NMR of 1-12



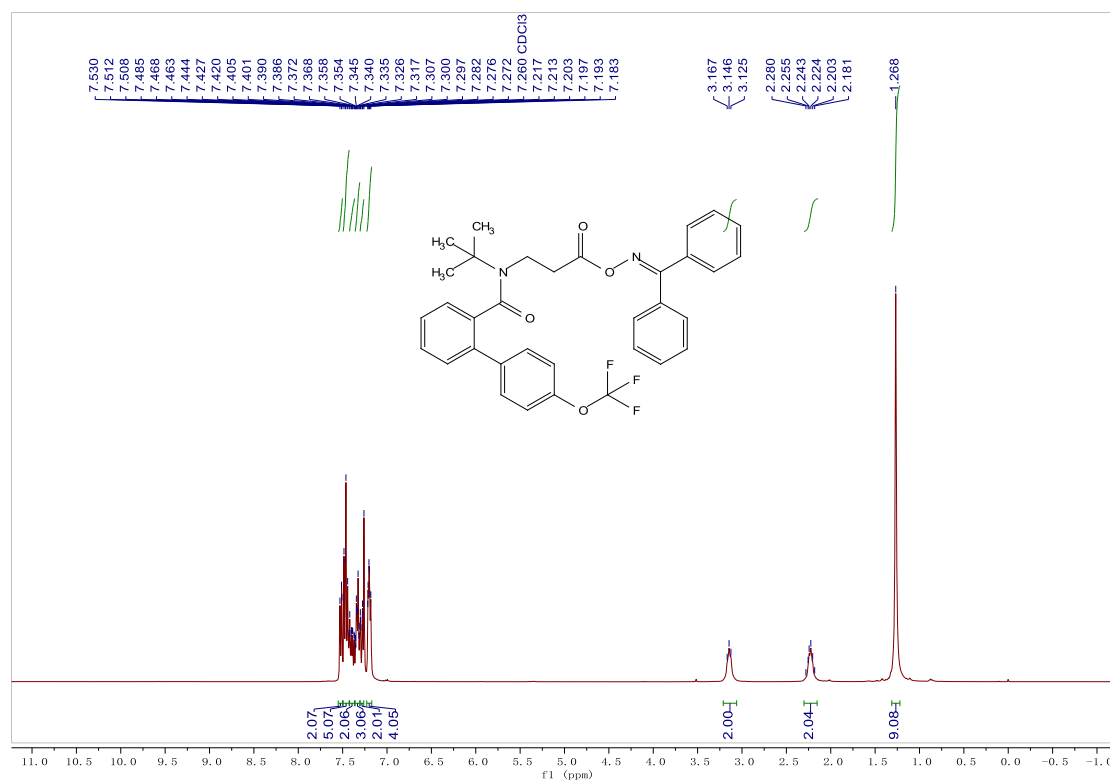
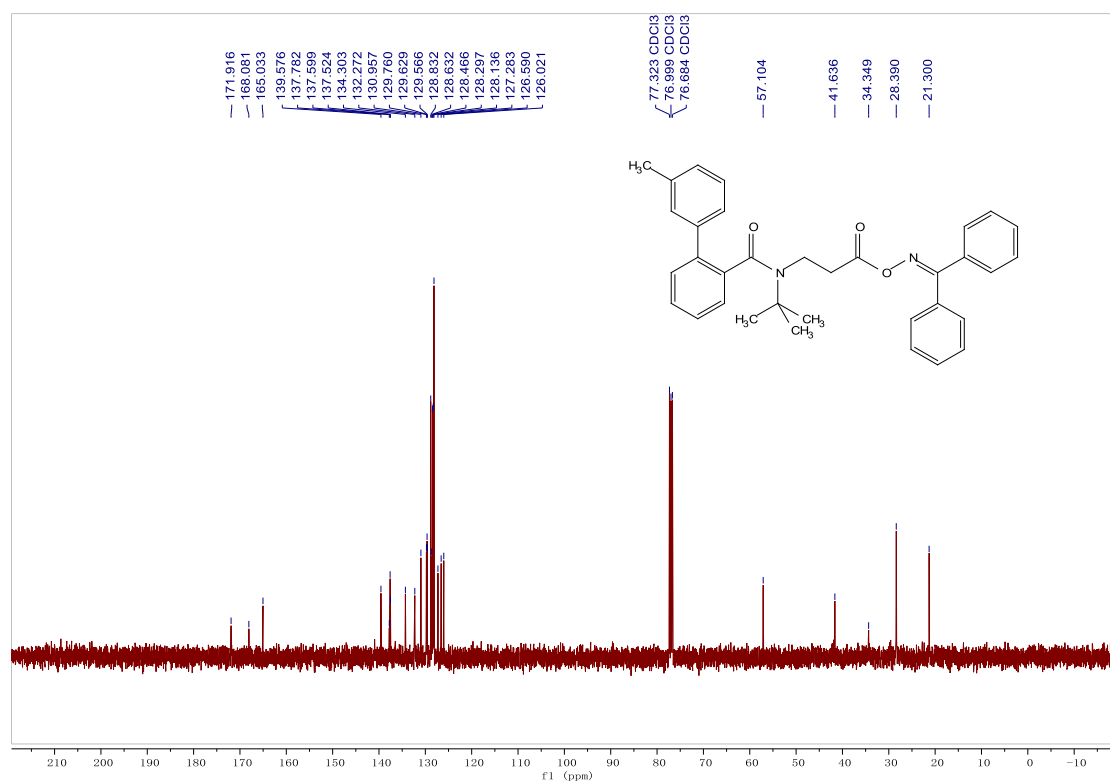
¹H NMR of 1-13

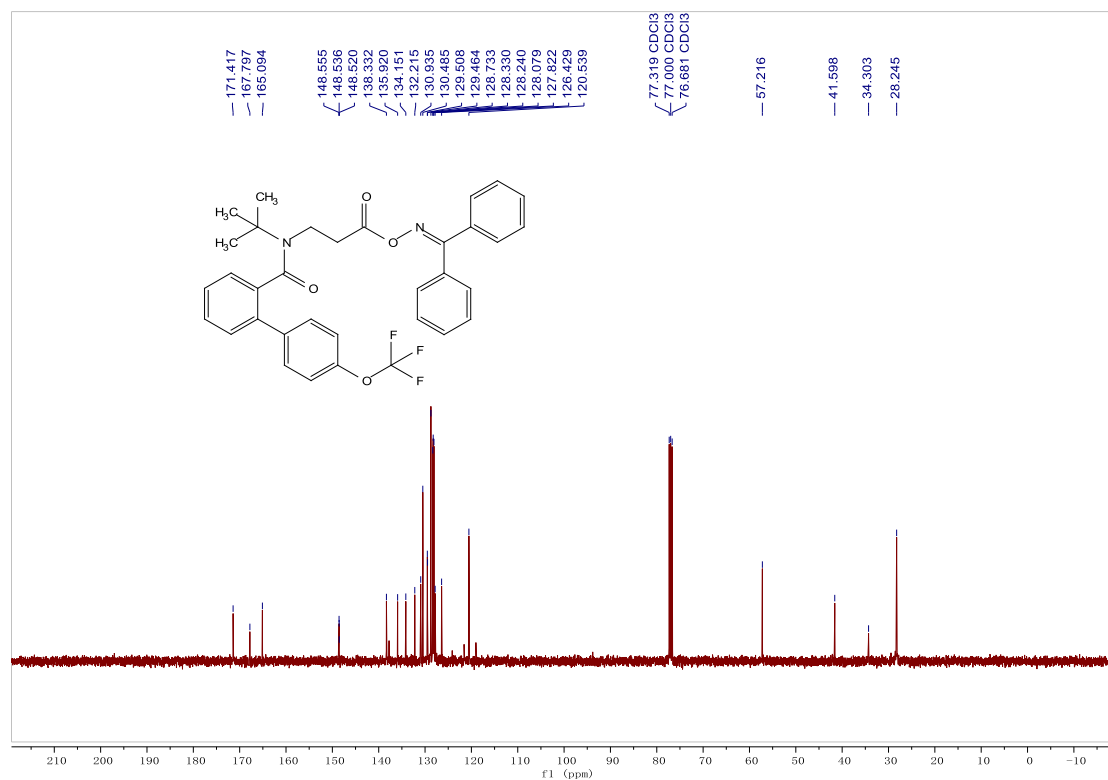


¹³C NMR of 1-13

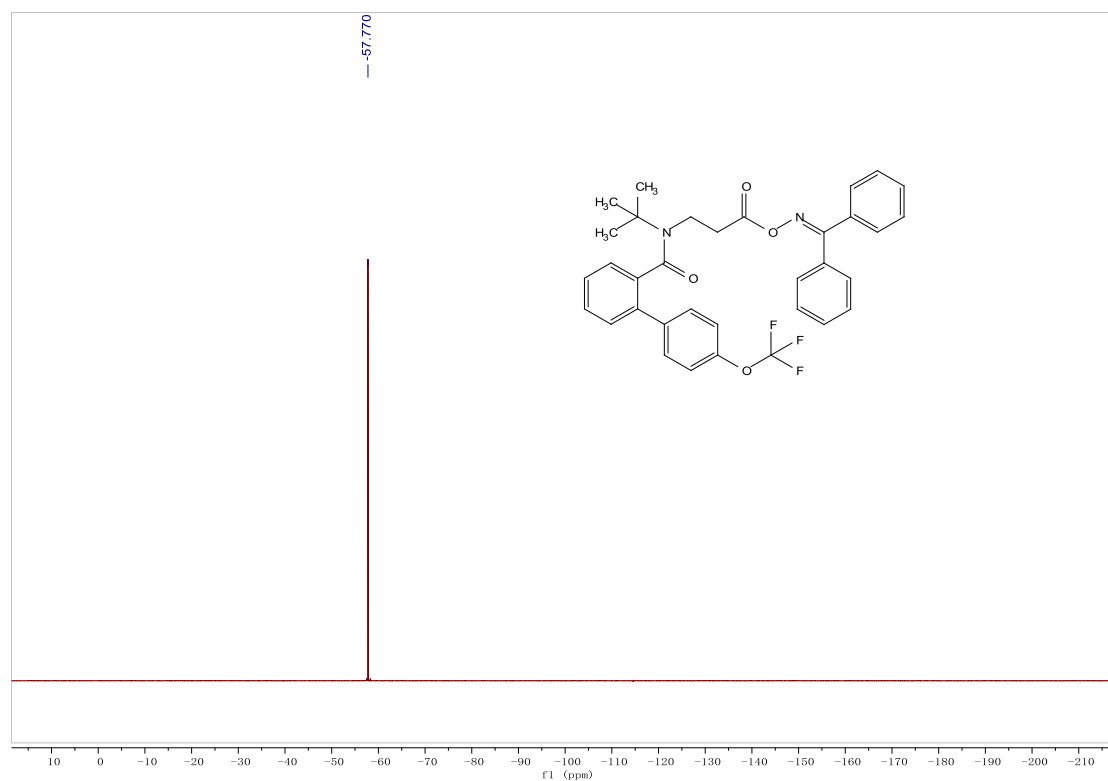


¹H NMR of 1-14

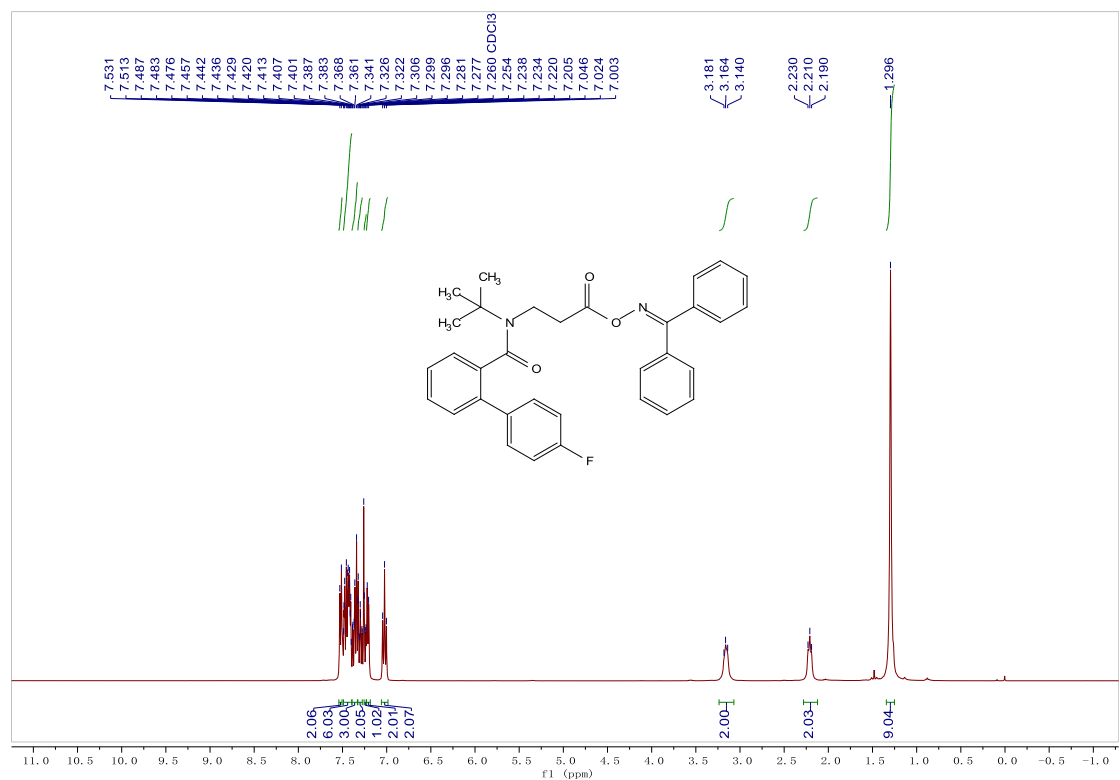




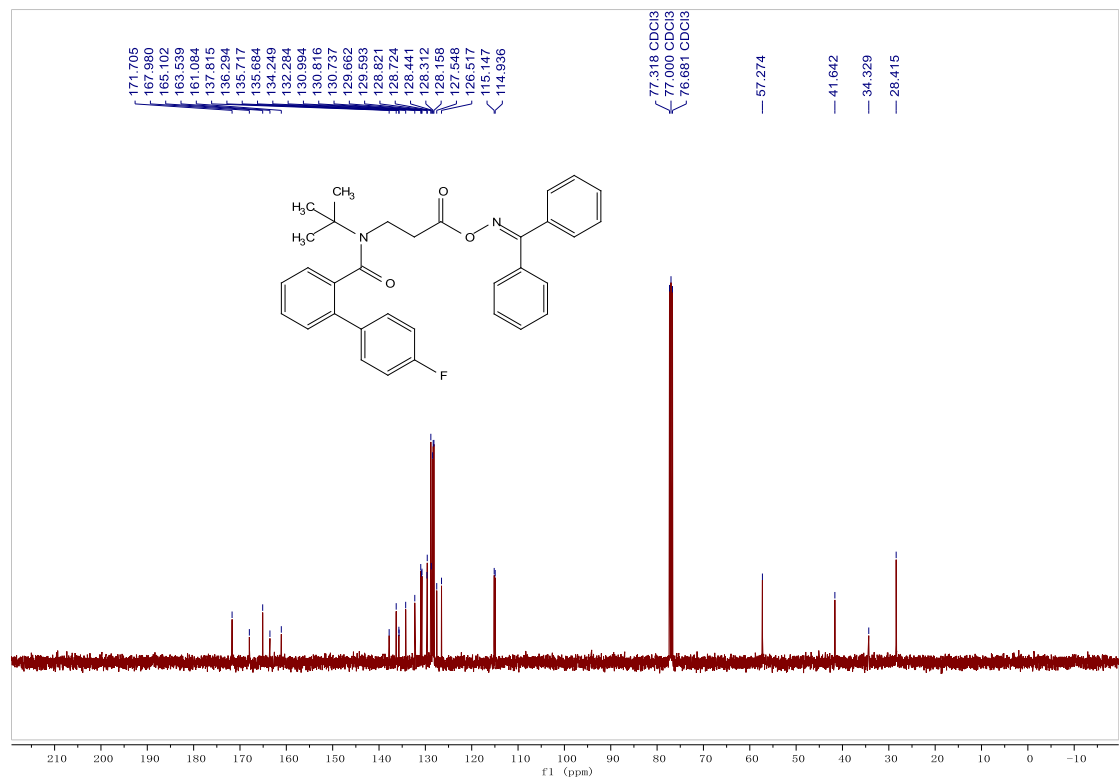
¹³C NMR of 1-15



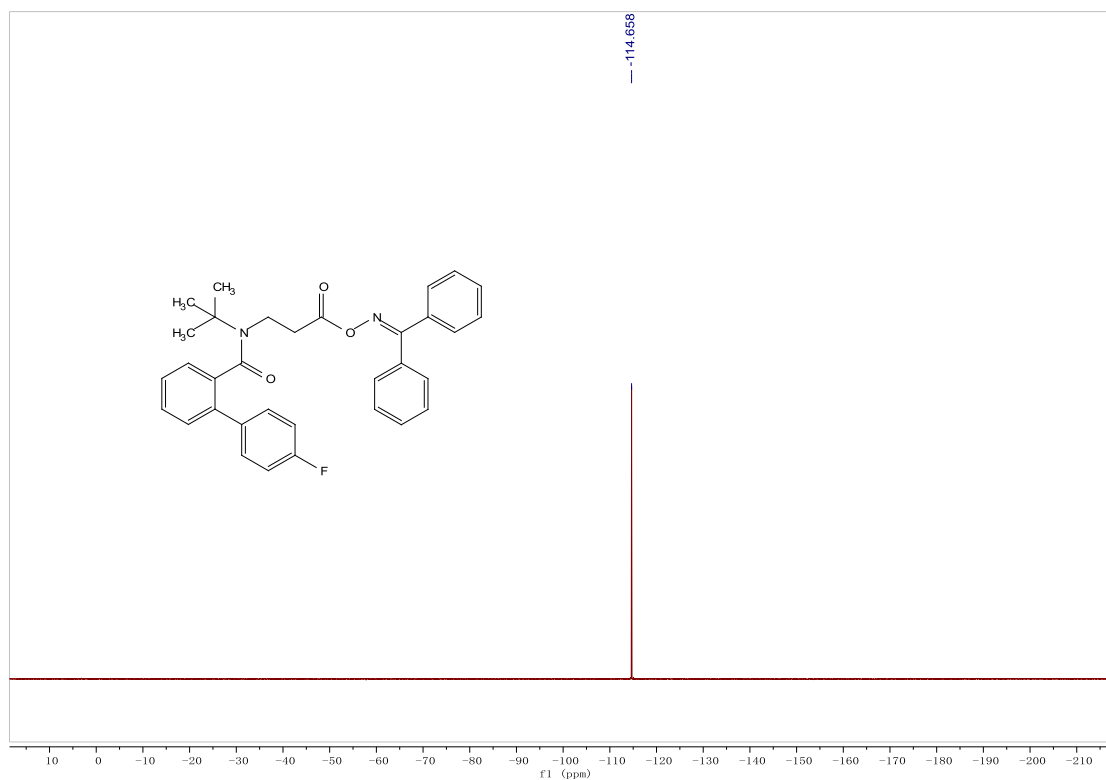
¹⁹F NMR of 1-15



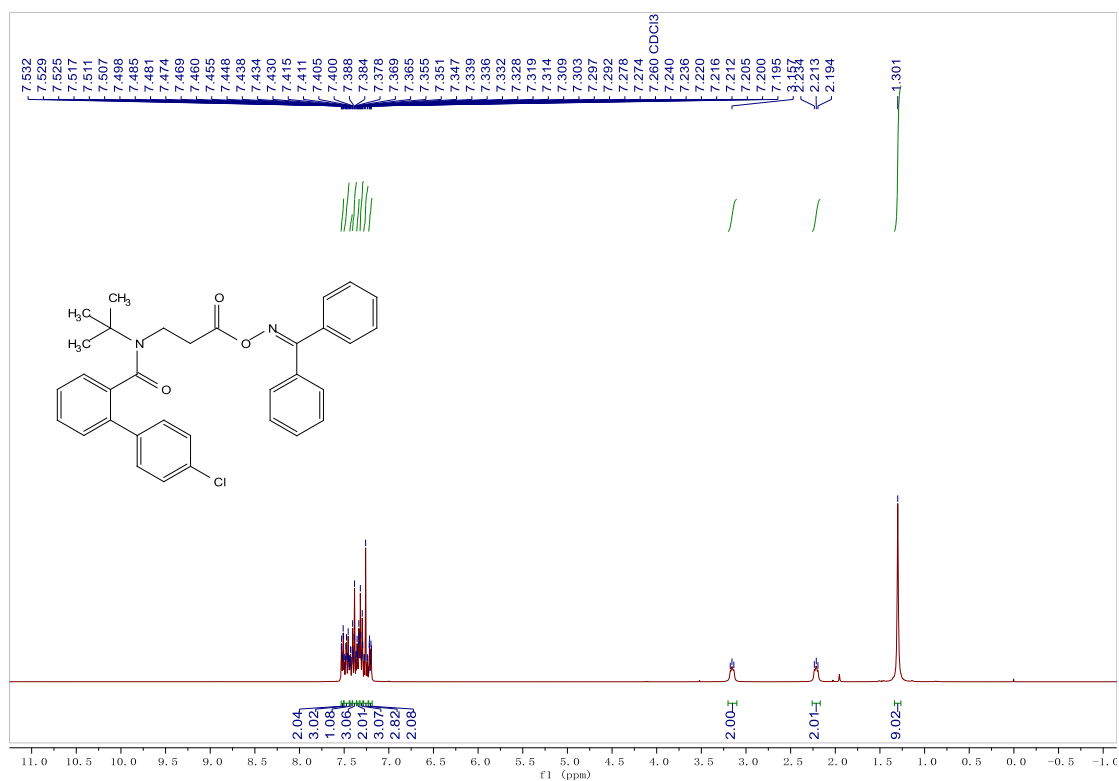
¹H NMR of 1-16



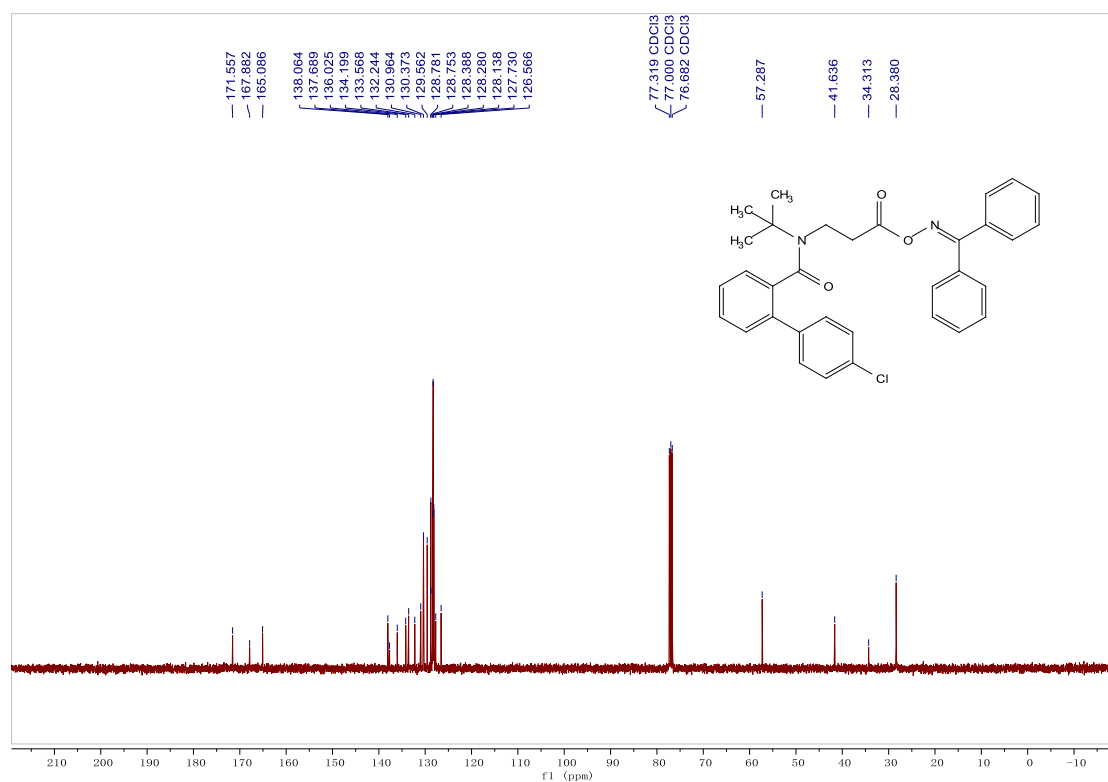
¹³C NMR of 1-16



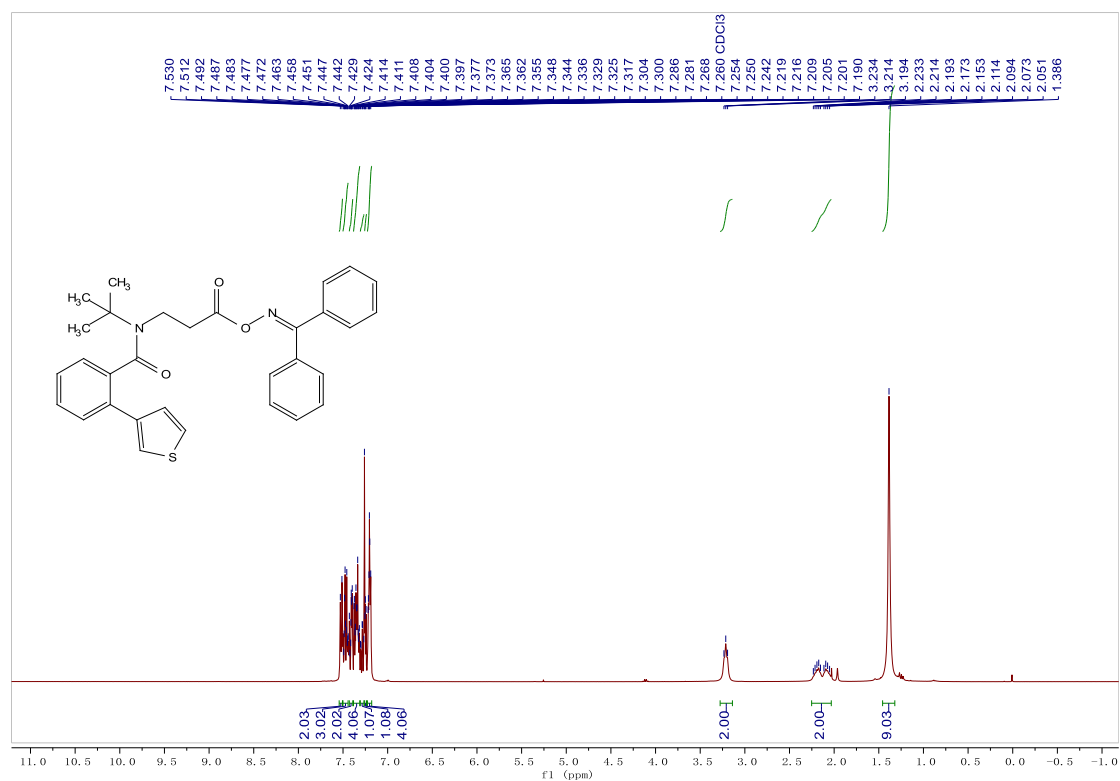
¹⁹F NMR of 1-16



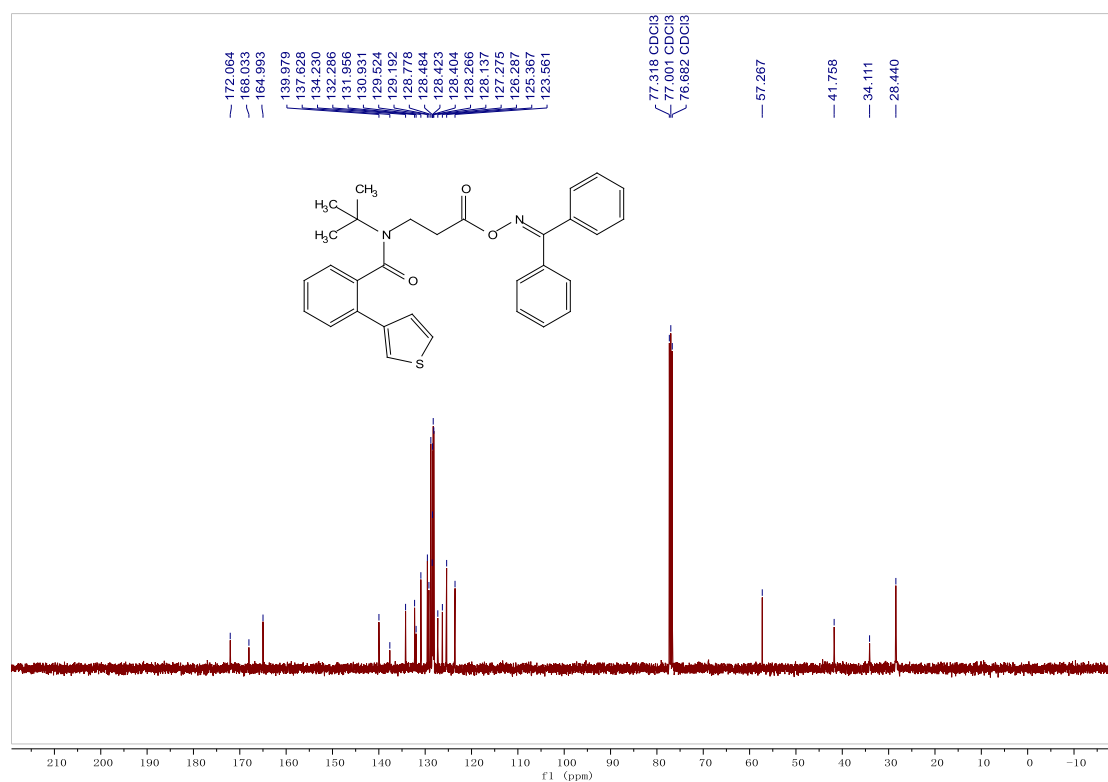
¹H NMR of 1-17



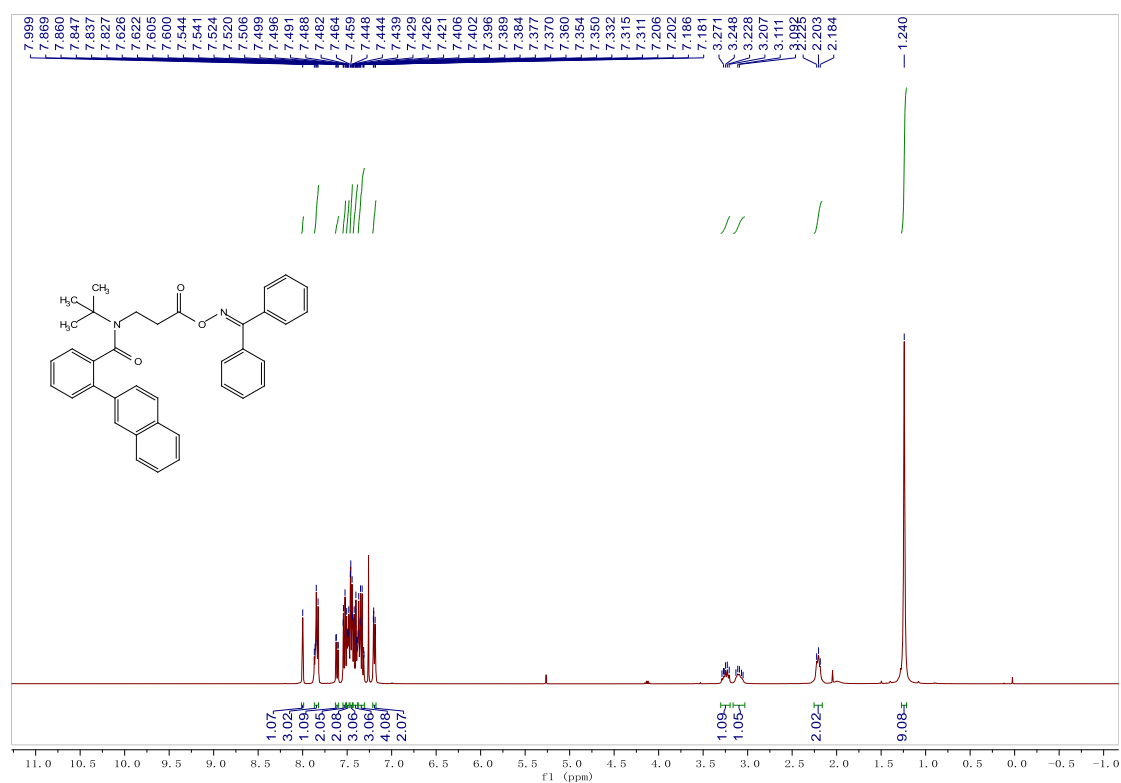
¹³C NMR of 1-17



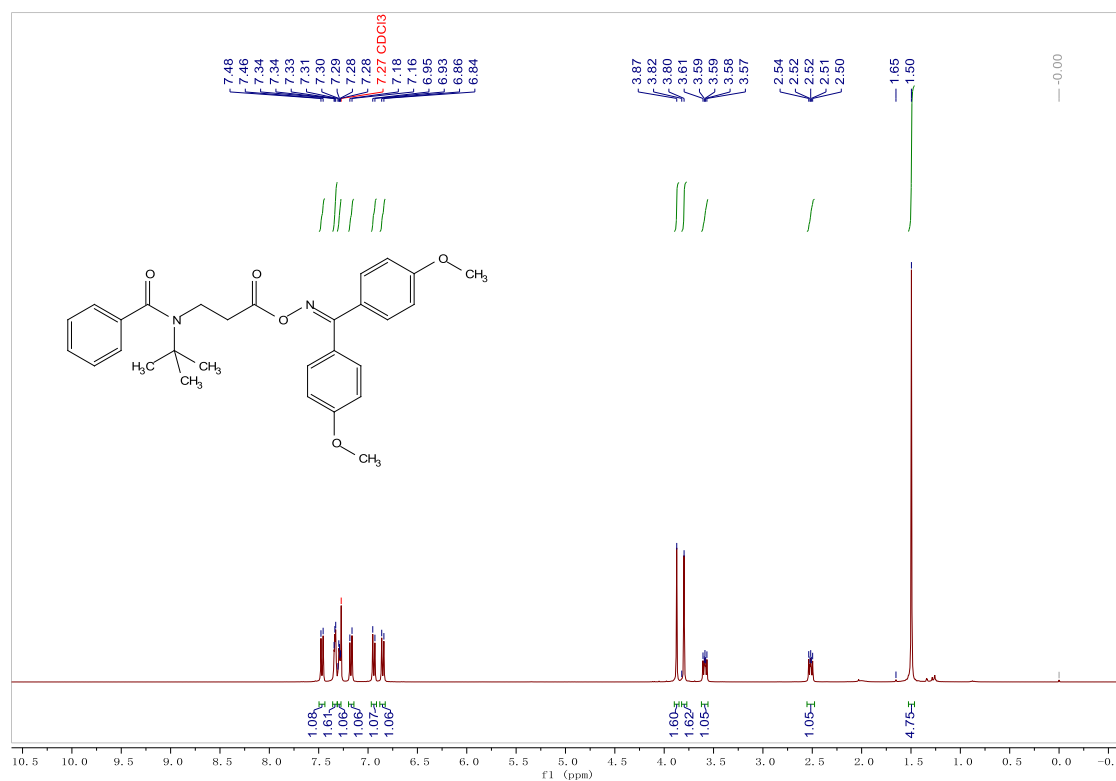
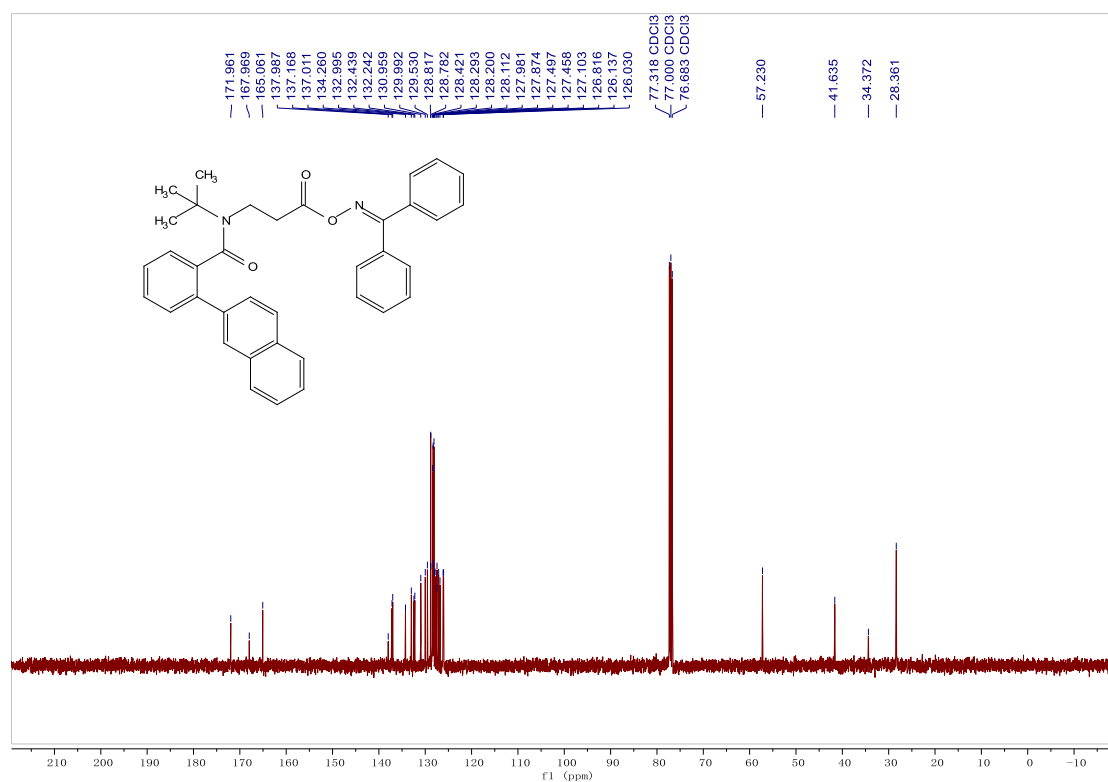
¹H NMR of 1-18

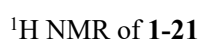


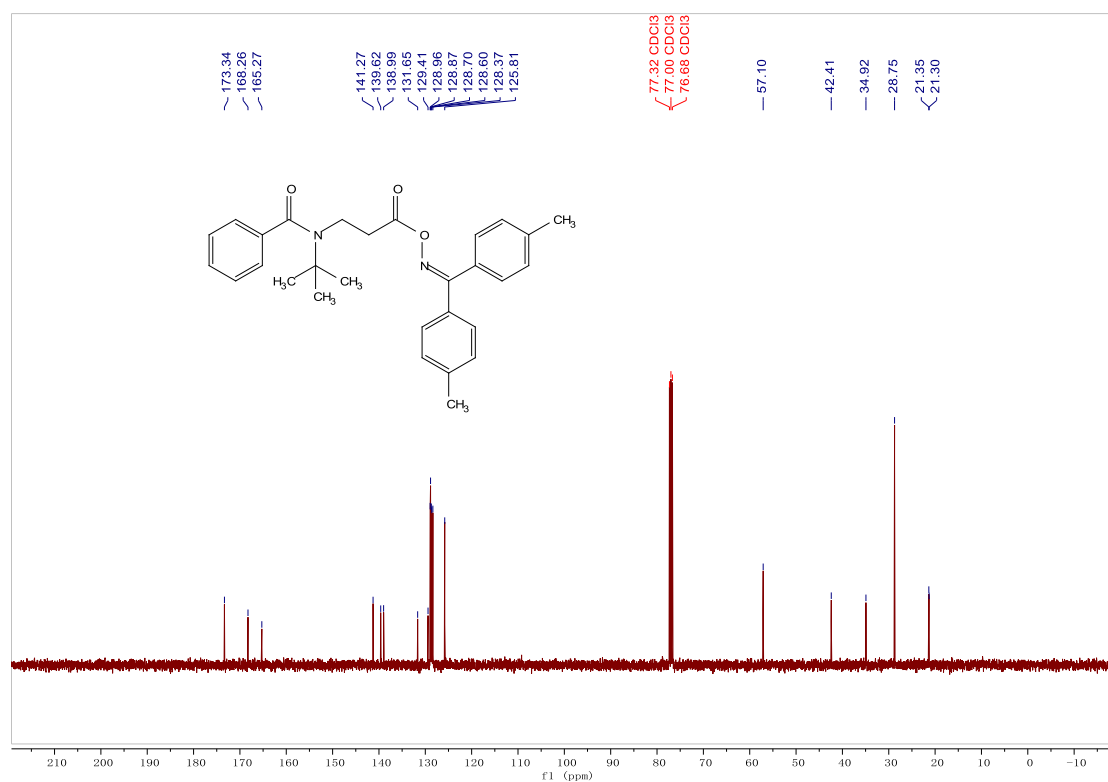
¹³C NMR of 1-18



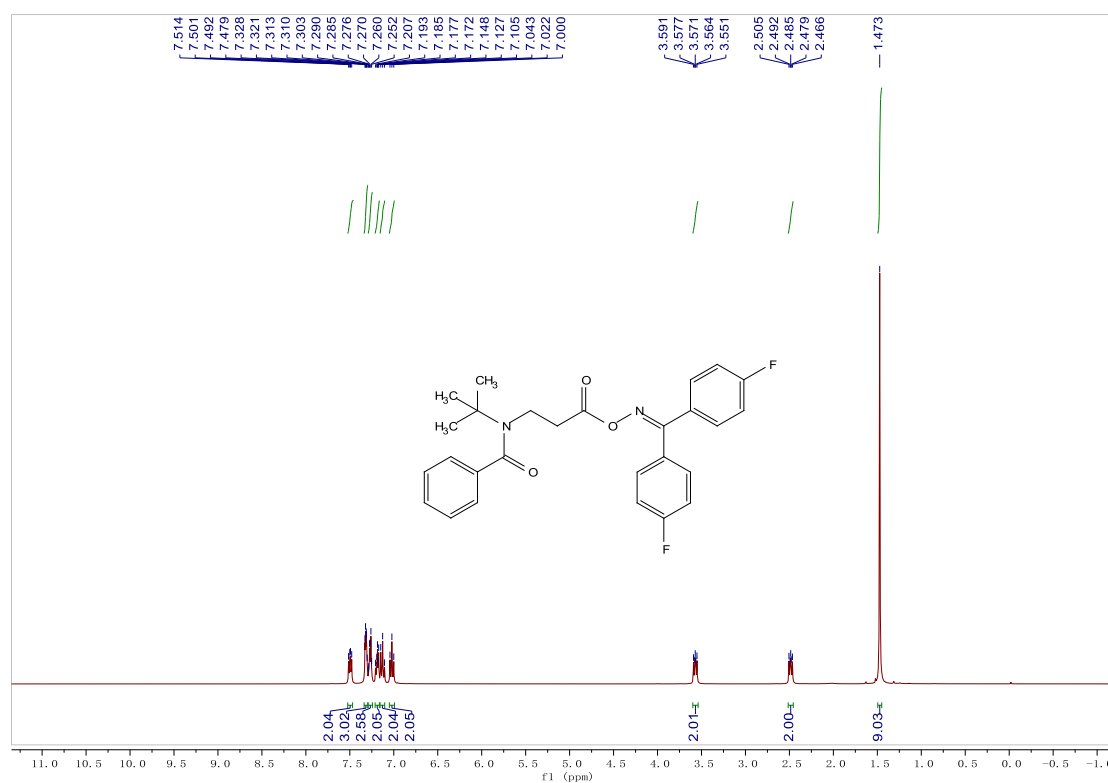
¹H NMR of 1-19



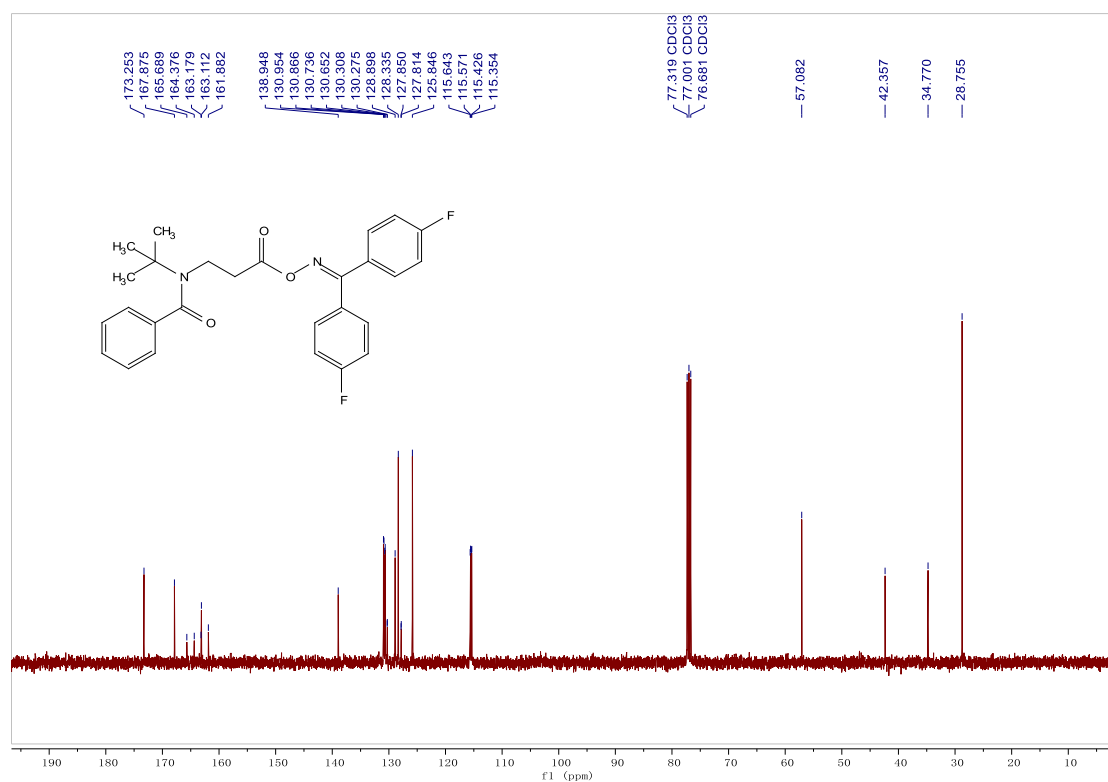




¹³C NMR of 1-21



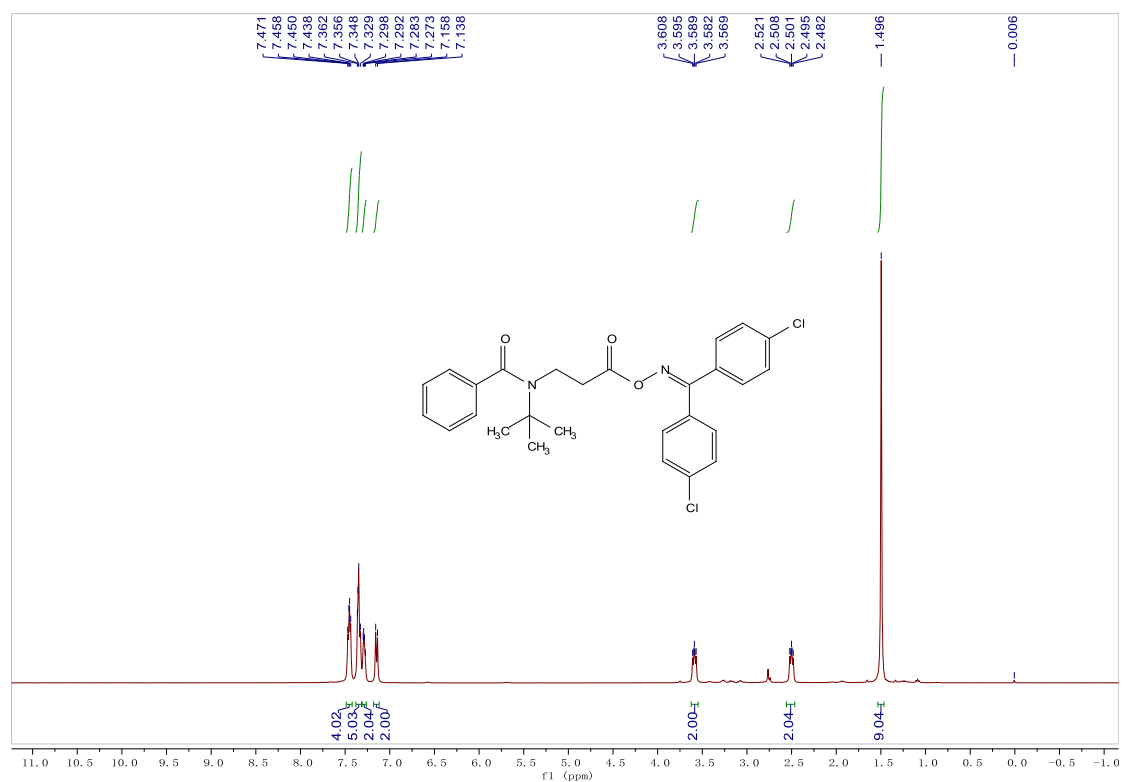
¹H NMR of 1-22



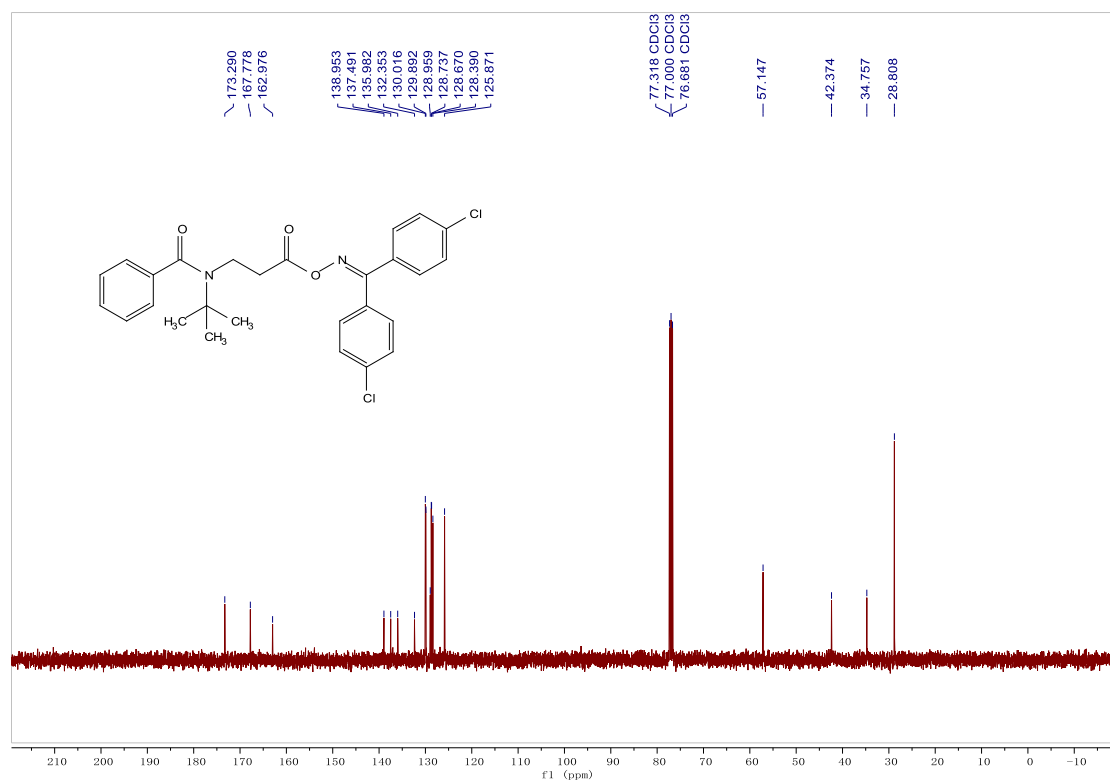
¹³C NMR of 1-22



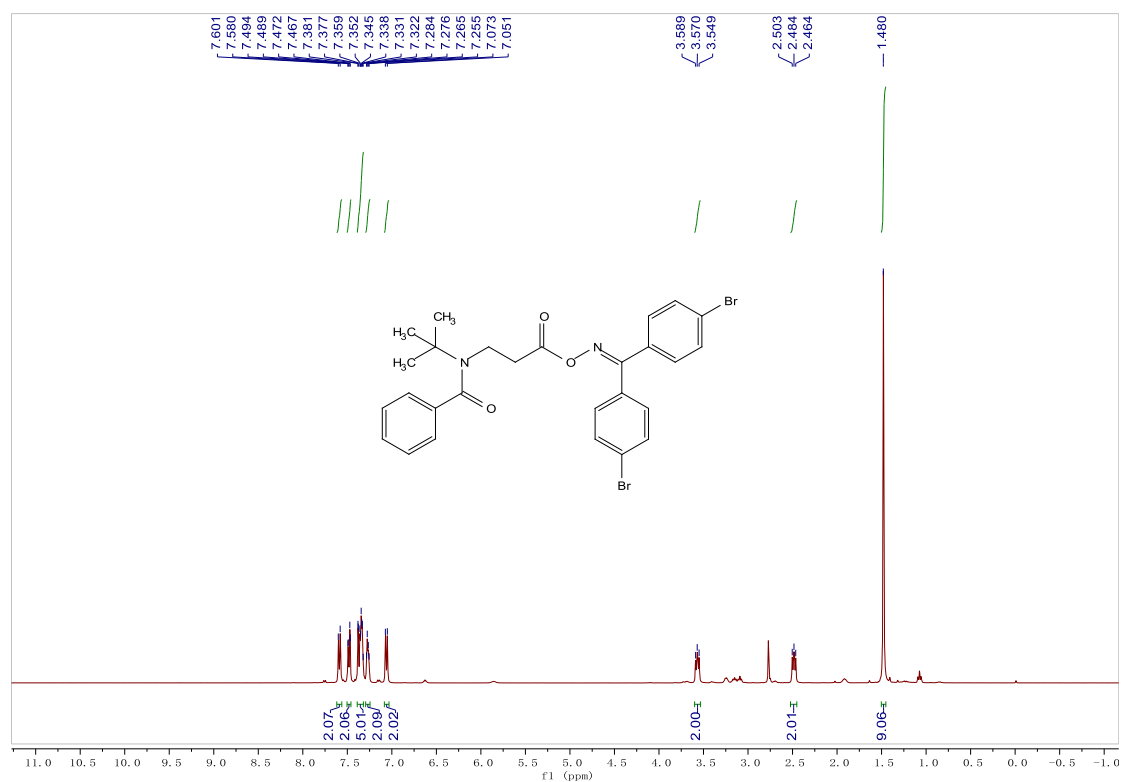
¹⁹F NMR of 1-22



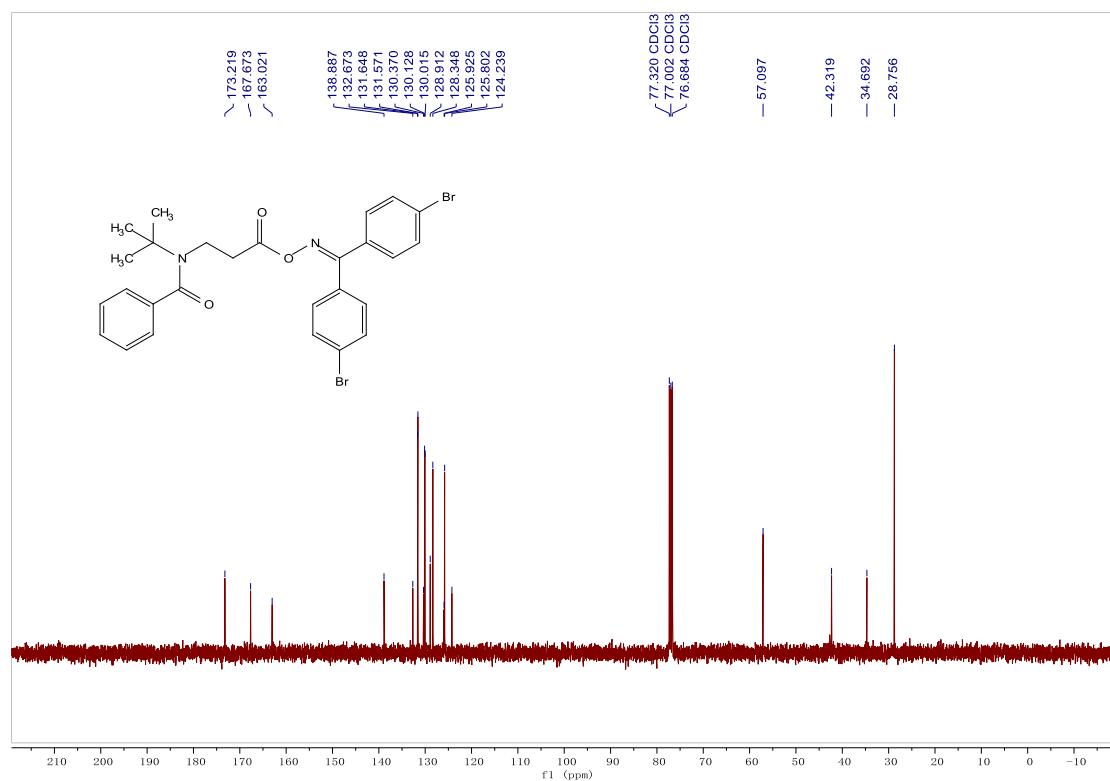
¹H NMR of 1-23



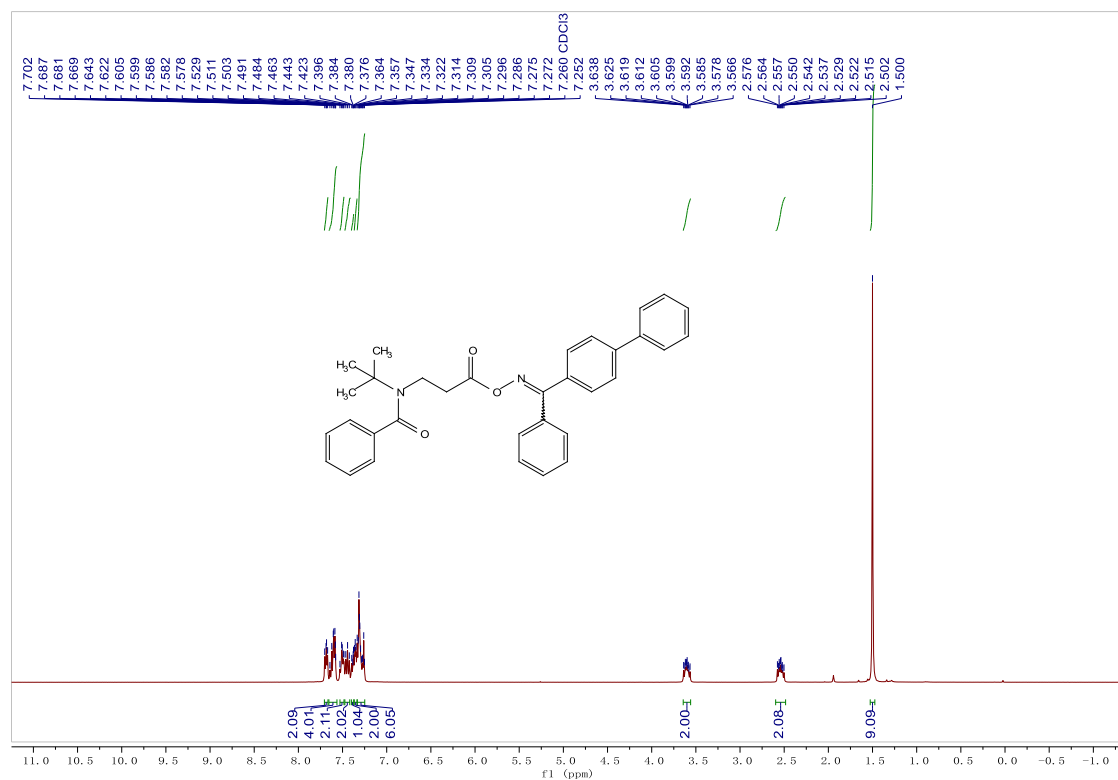
¹³C NMR of 1-23



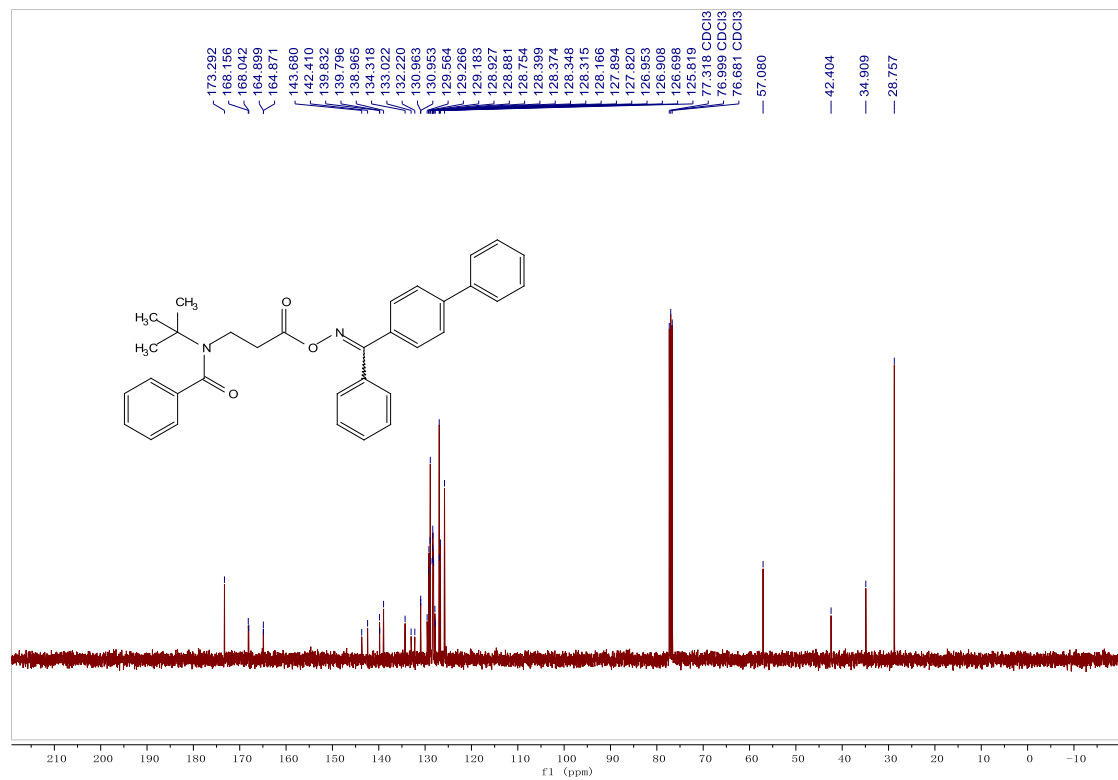
¹H NMR of 1-24



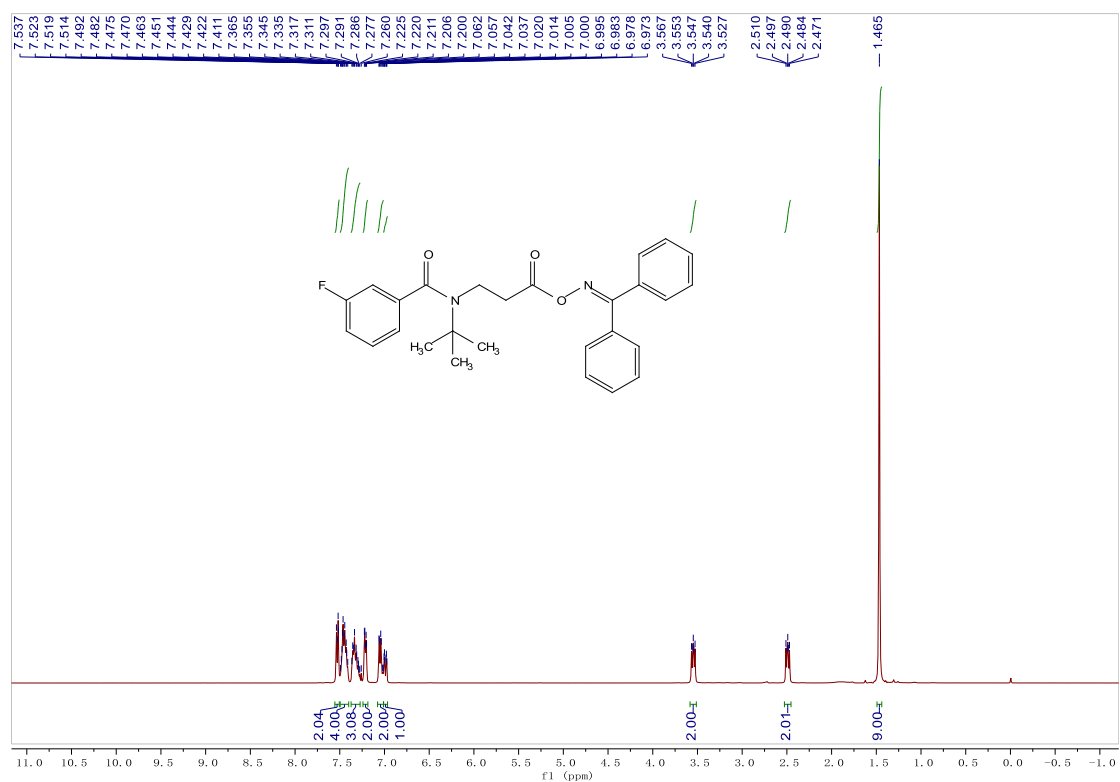
¹³C NMR of 1-24



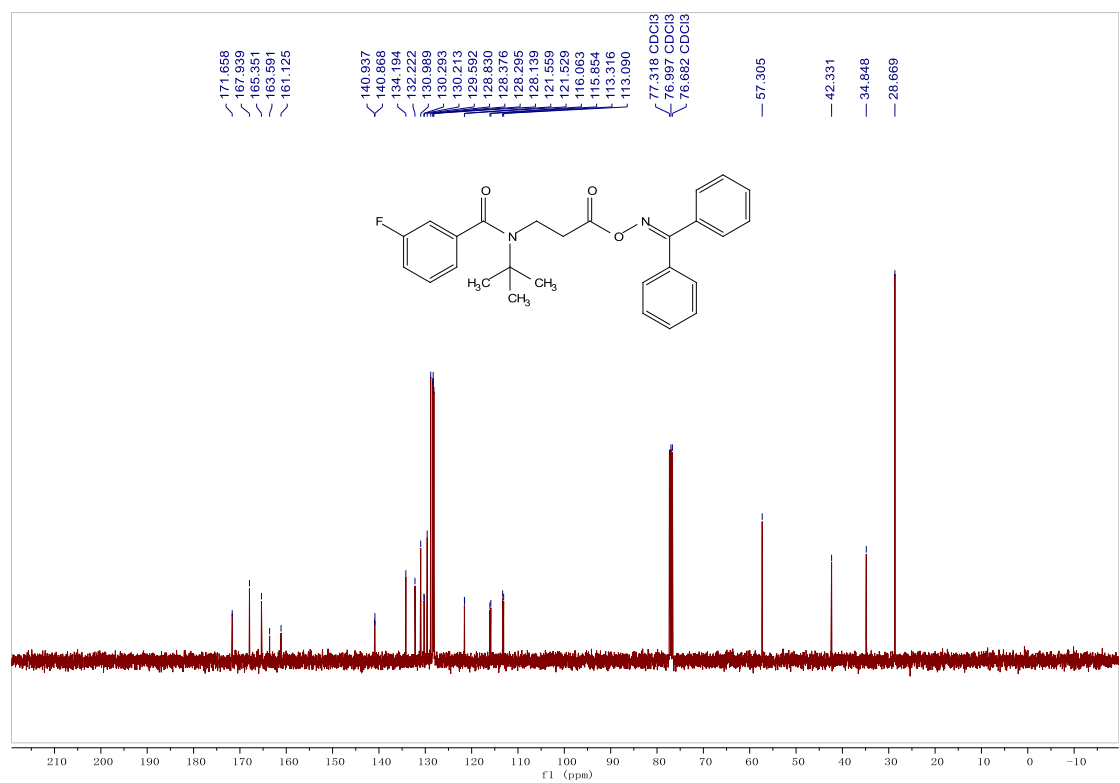
¹H NMR of 1-25



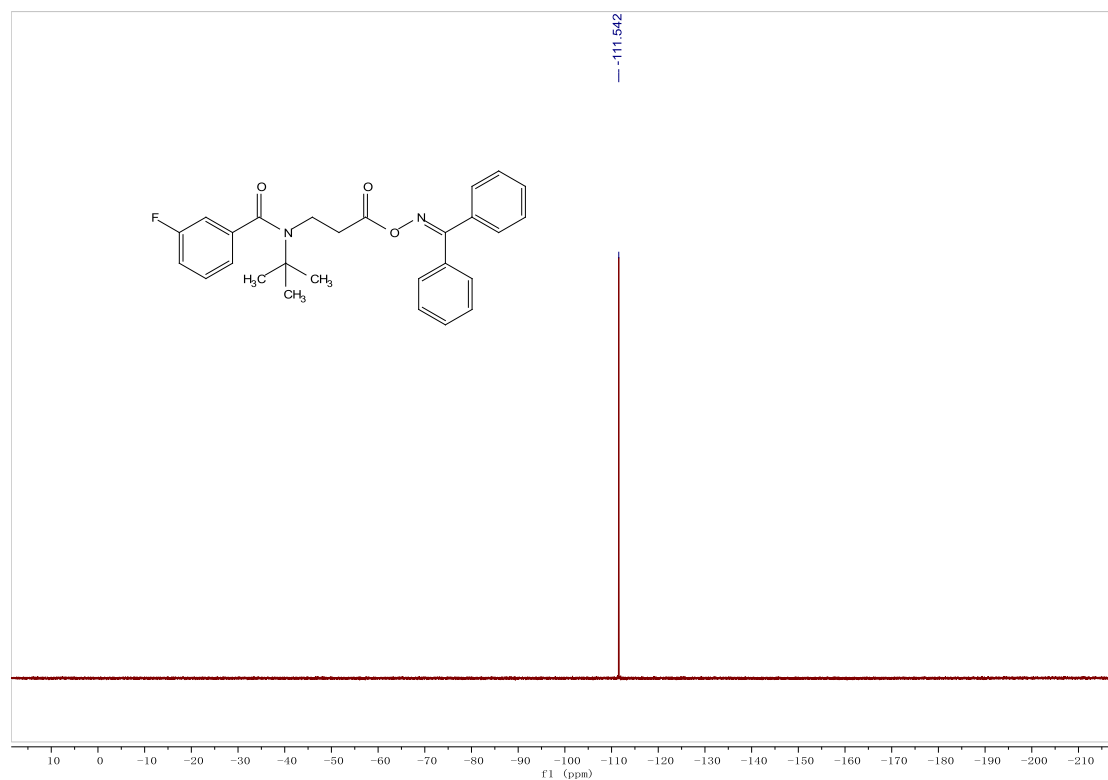
¹³C NMR of 1-25



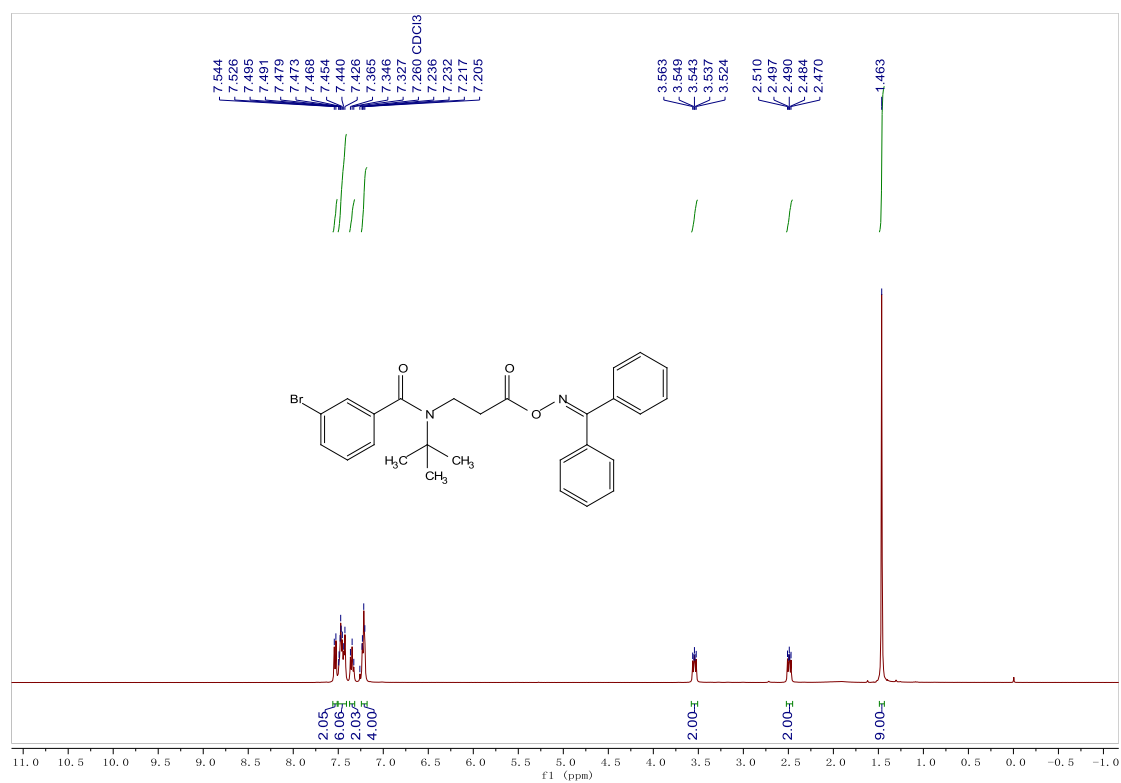
¹H-NMR for 1-26



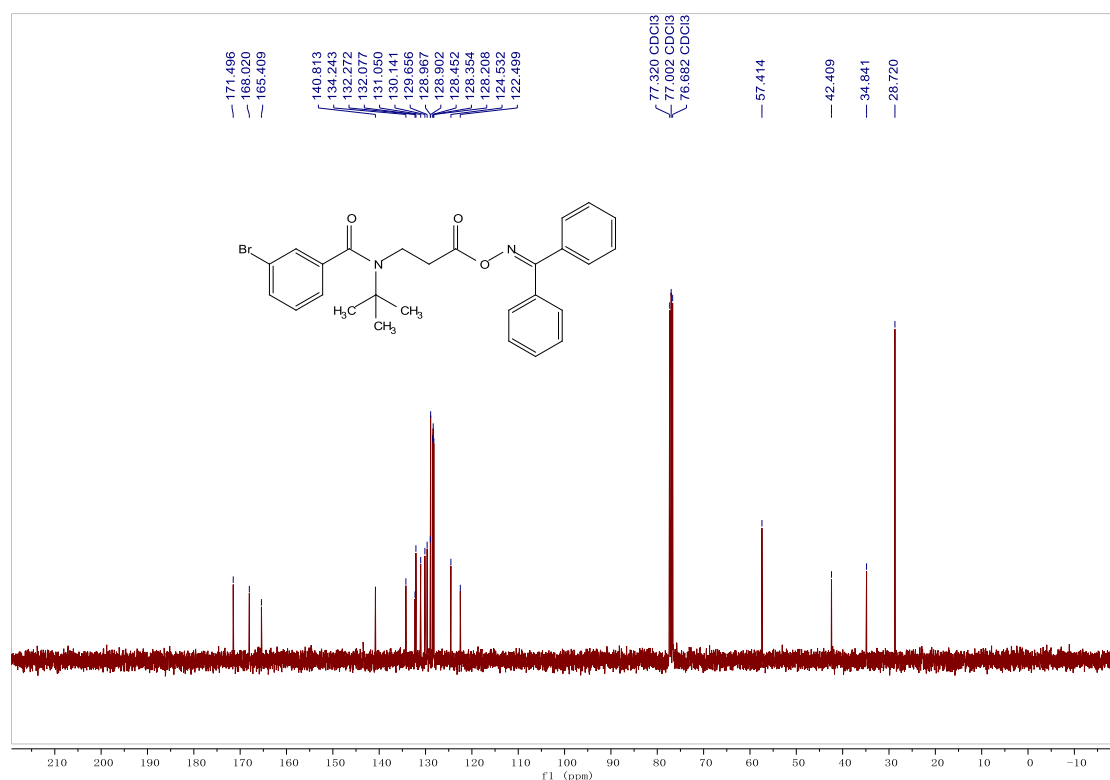
¹³C-NMR for 1-26



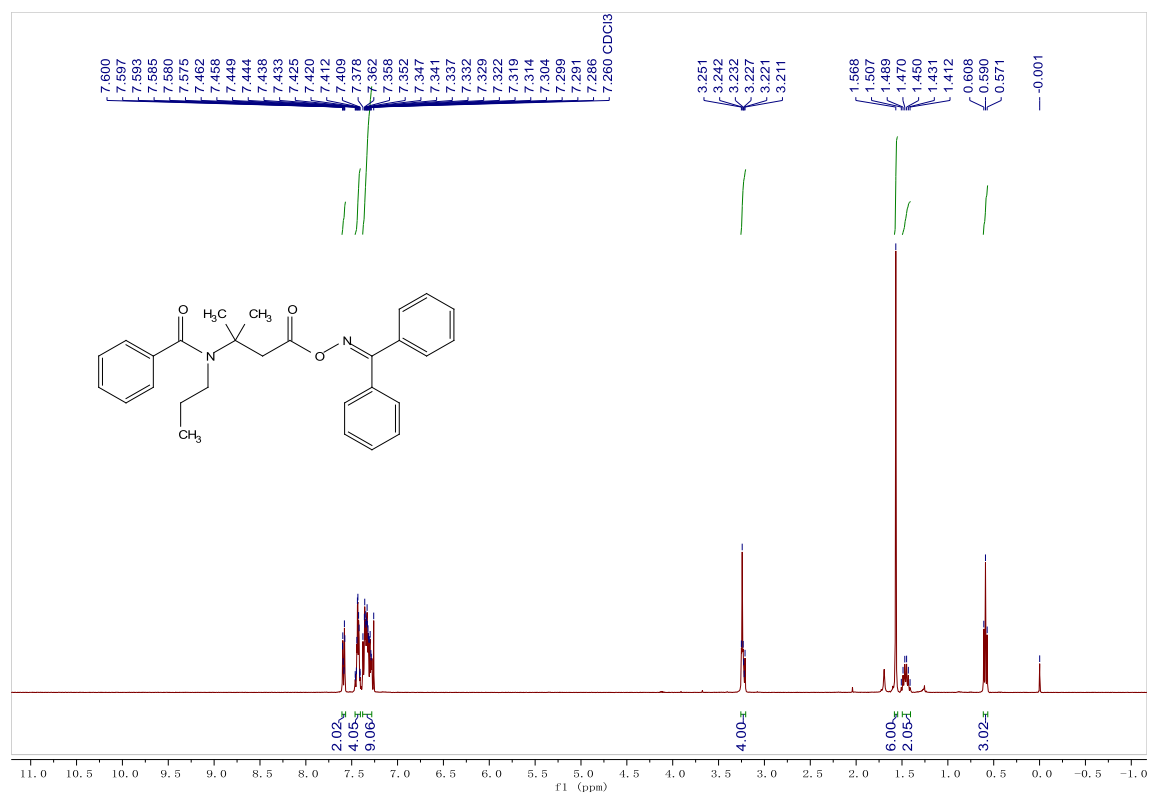
^{19}F -NMR for **1-26**



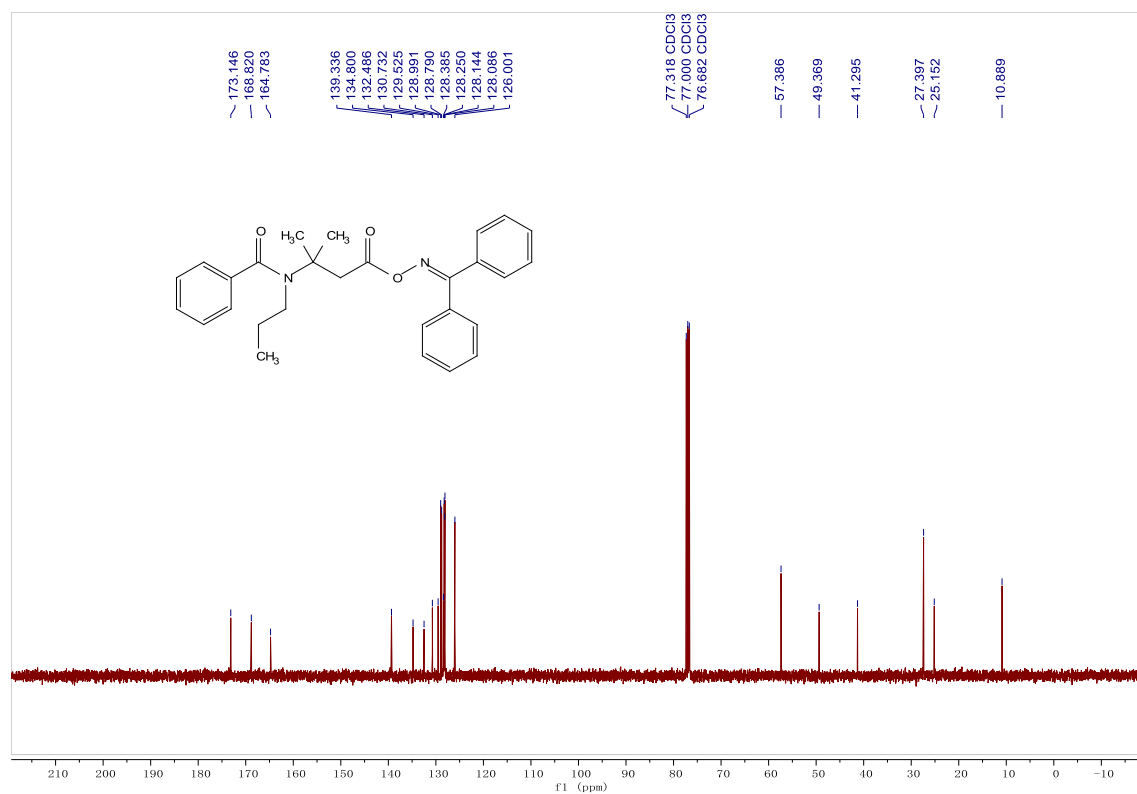
^1H -NMR for **1-27**



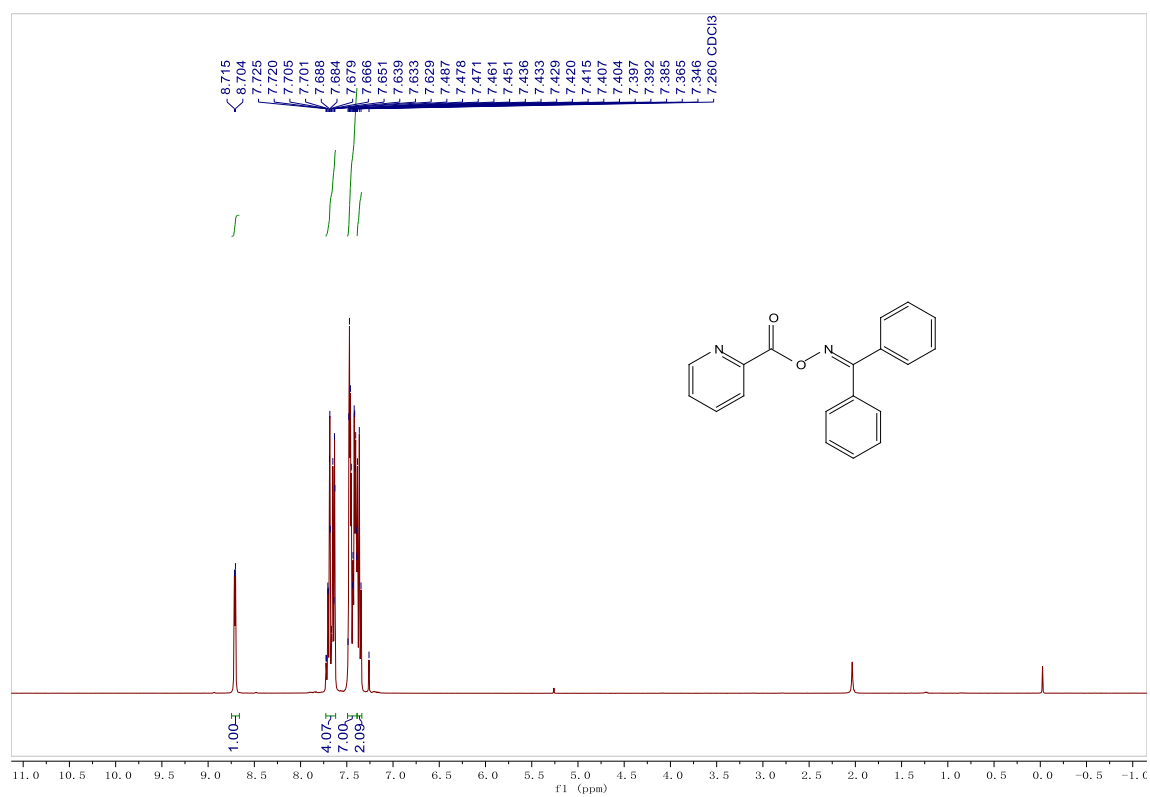
¹³C-NMR for 1-27



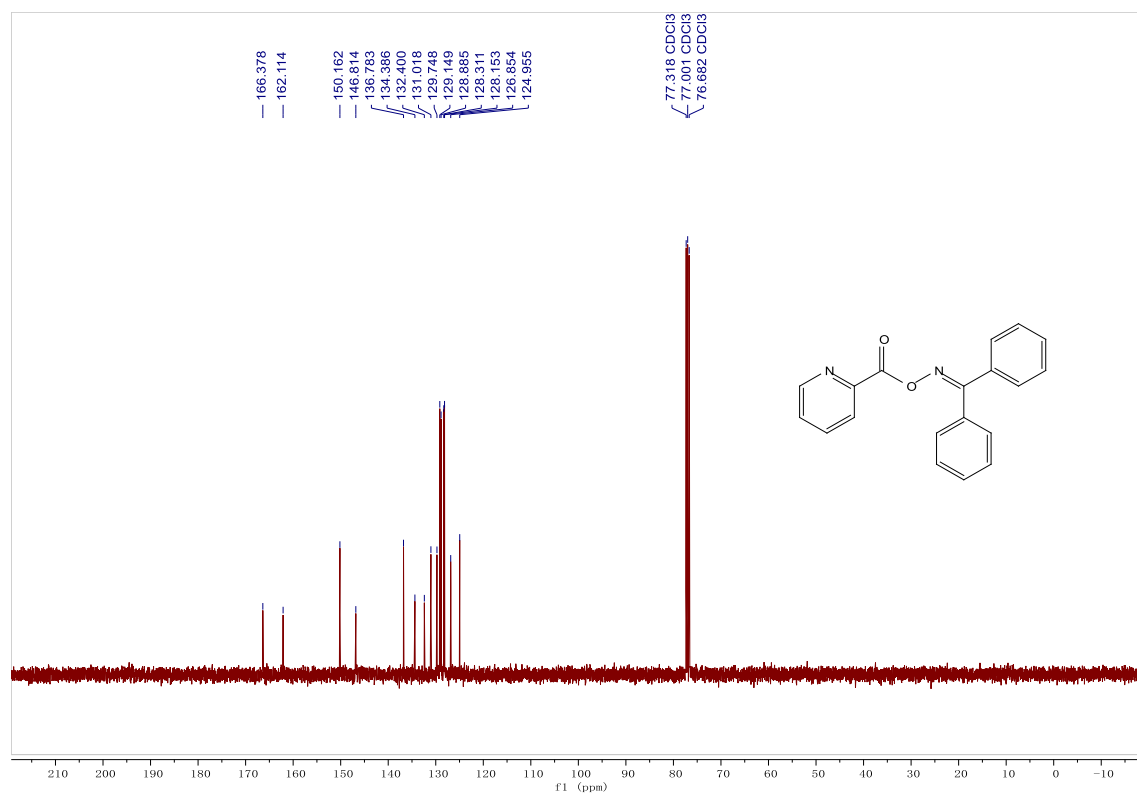
¹H-NMR for 1-28



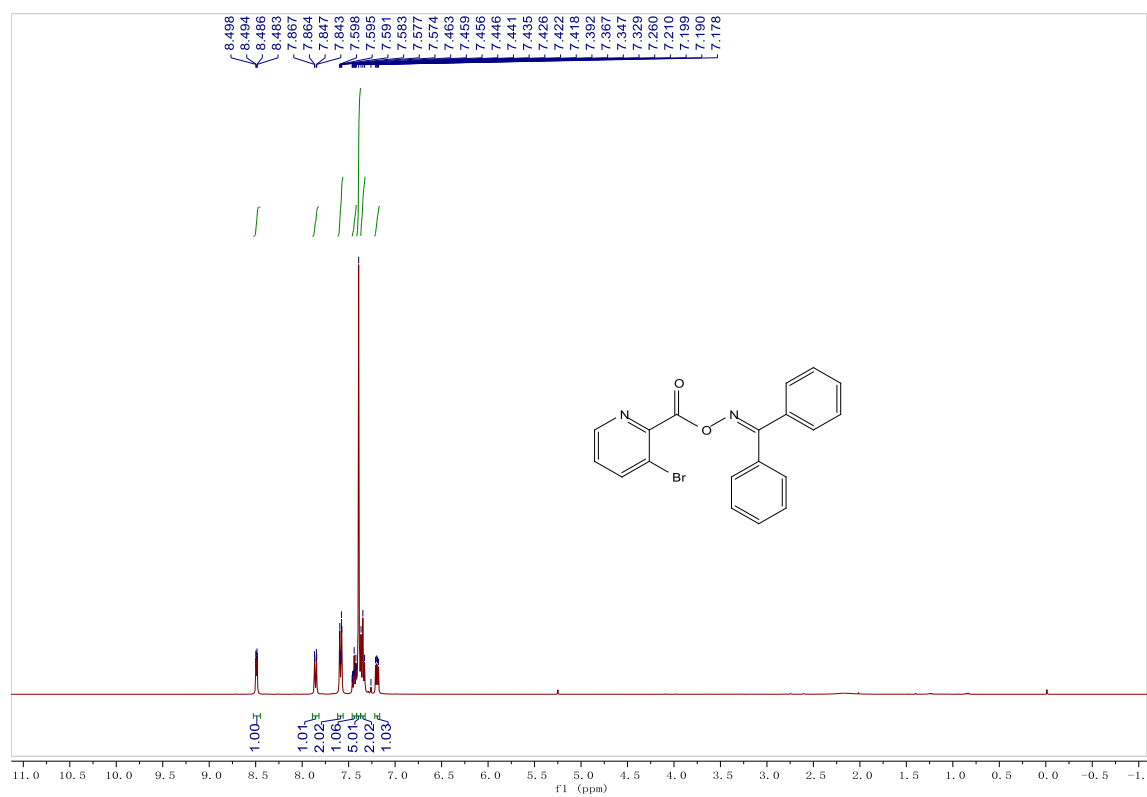
¹³C-NMR for 1-28



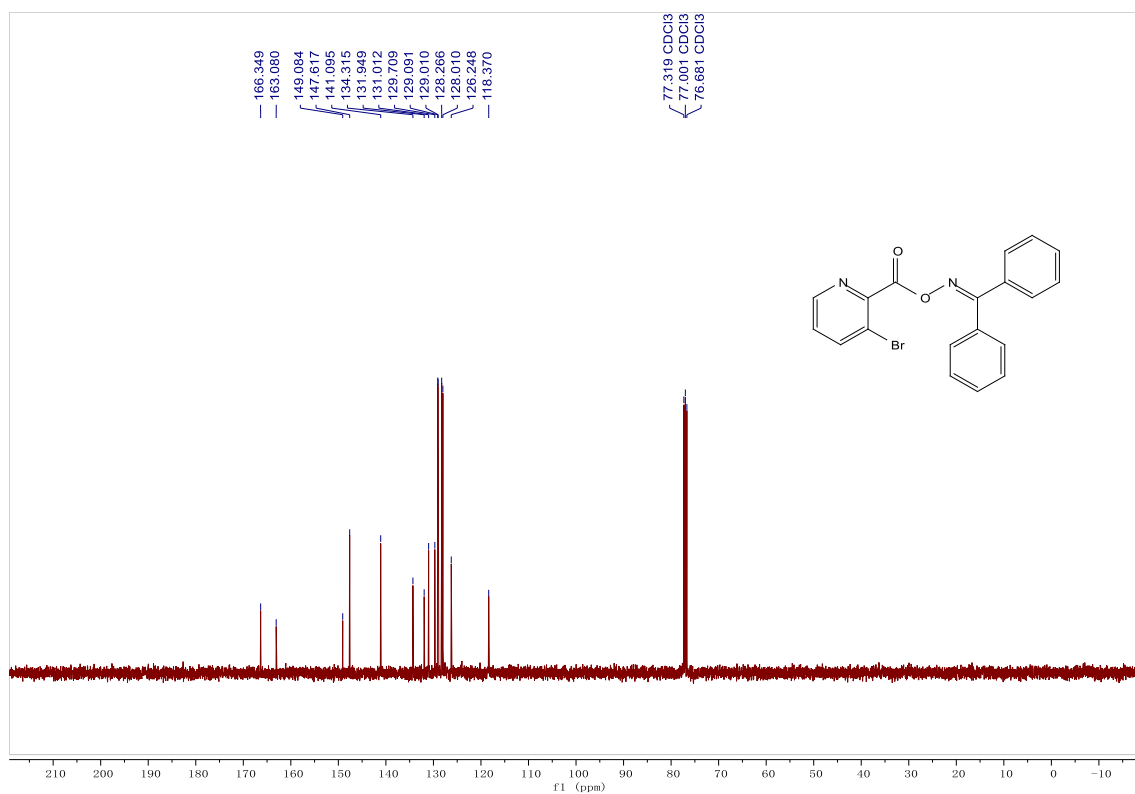
¹H-NMR for 5-1



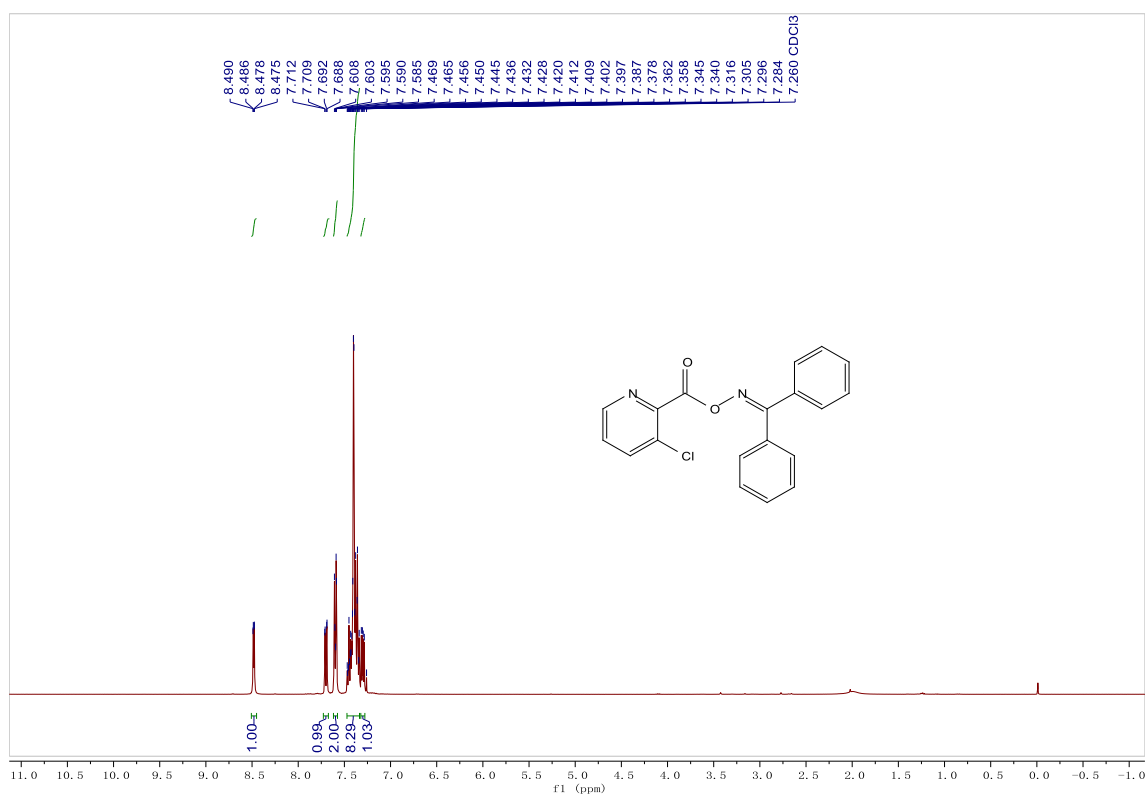
¹³C-NMR for 5-1



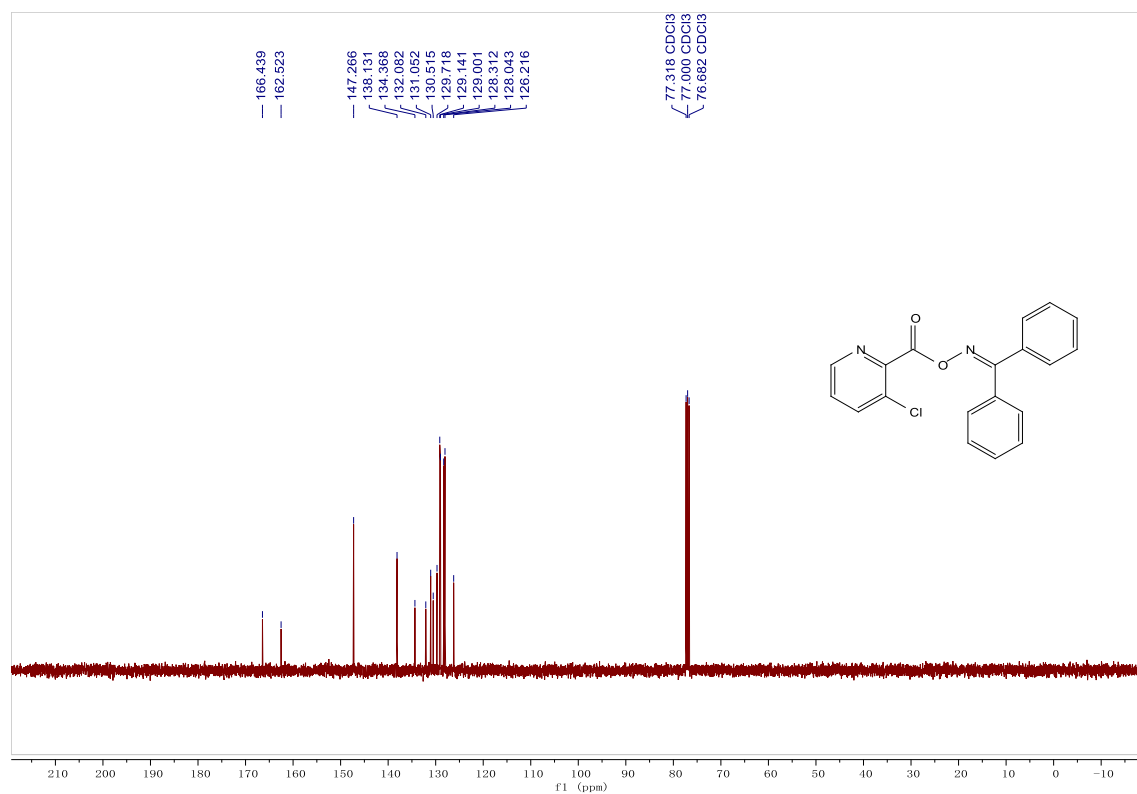
¹H-NMR for 5-2



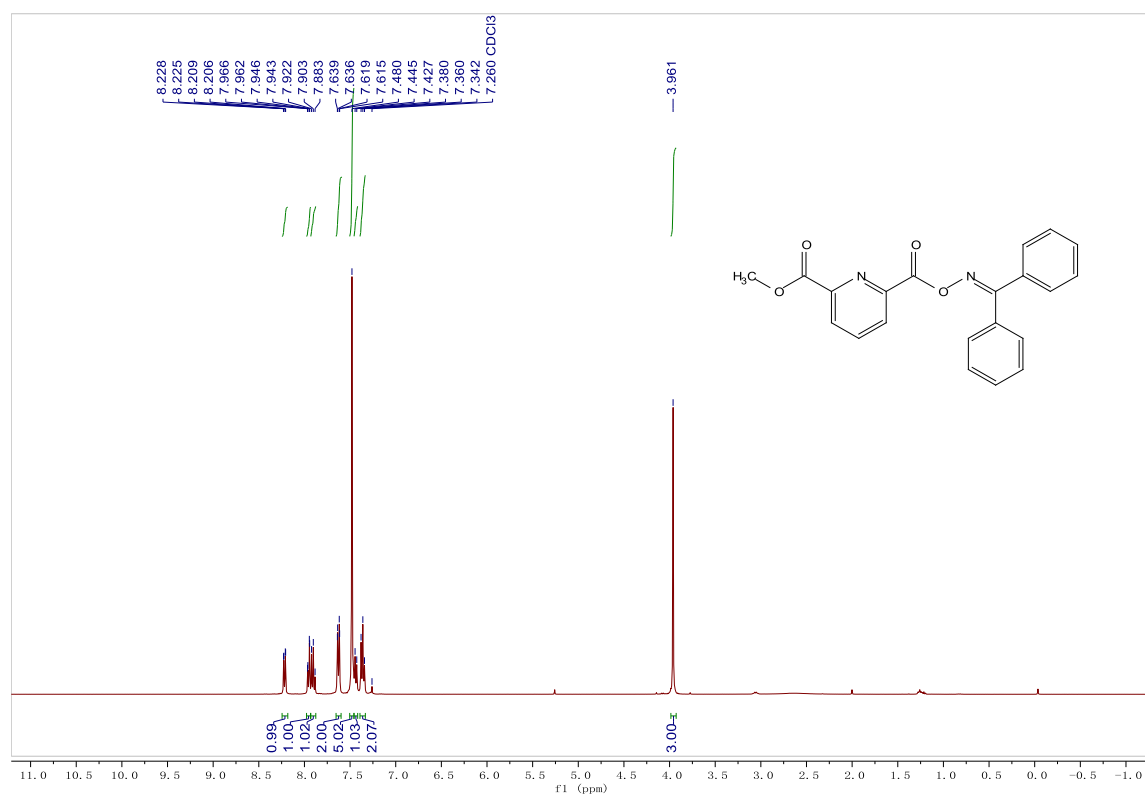
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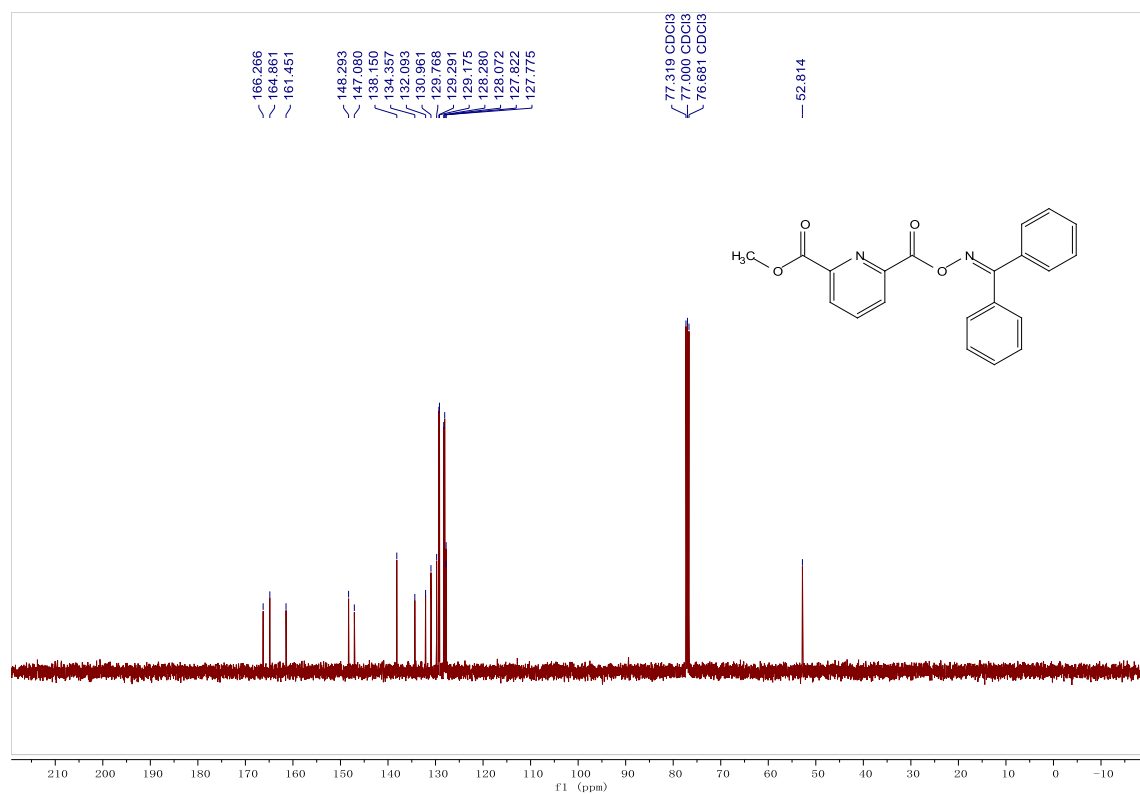
¹H-NMR for 5-3



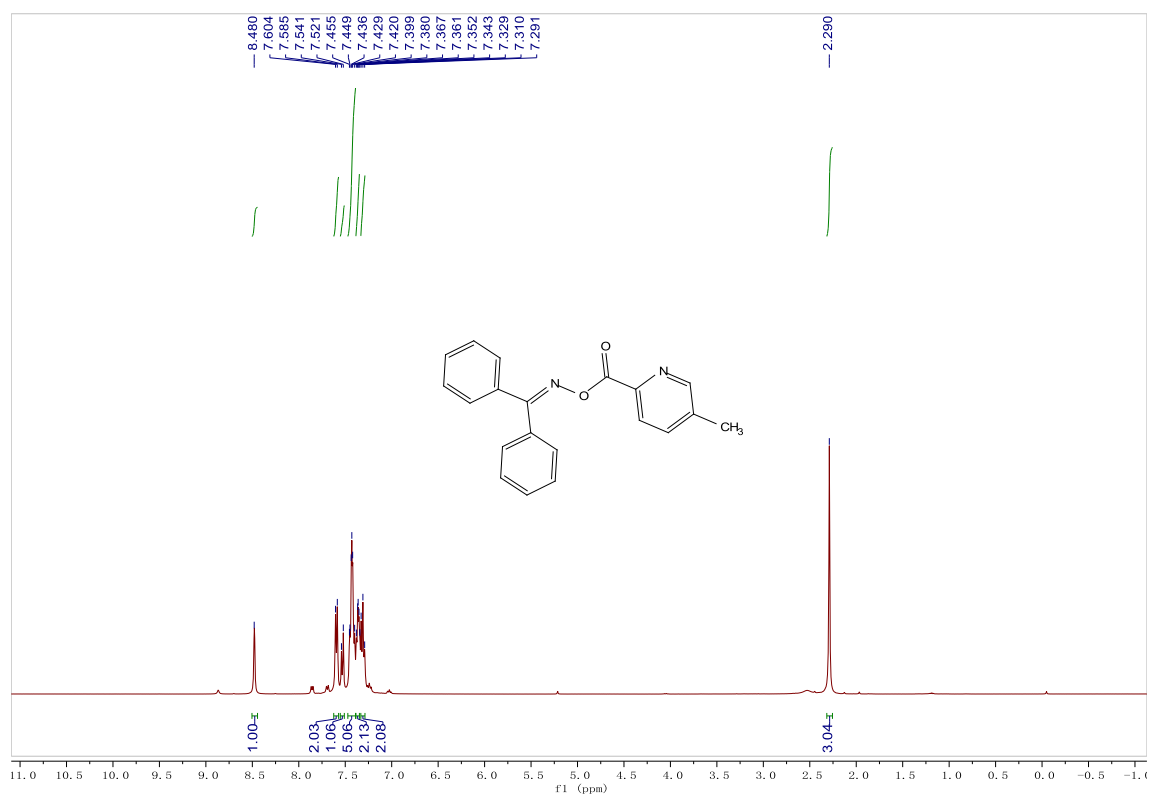
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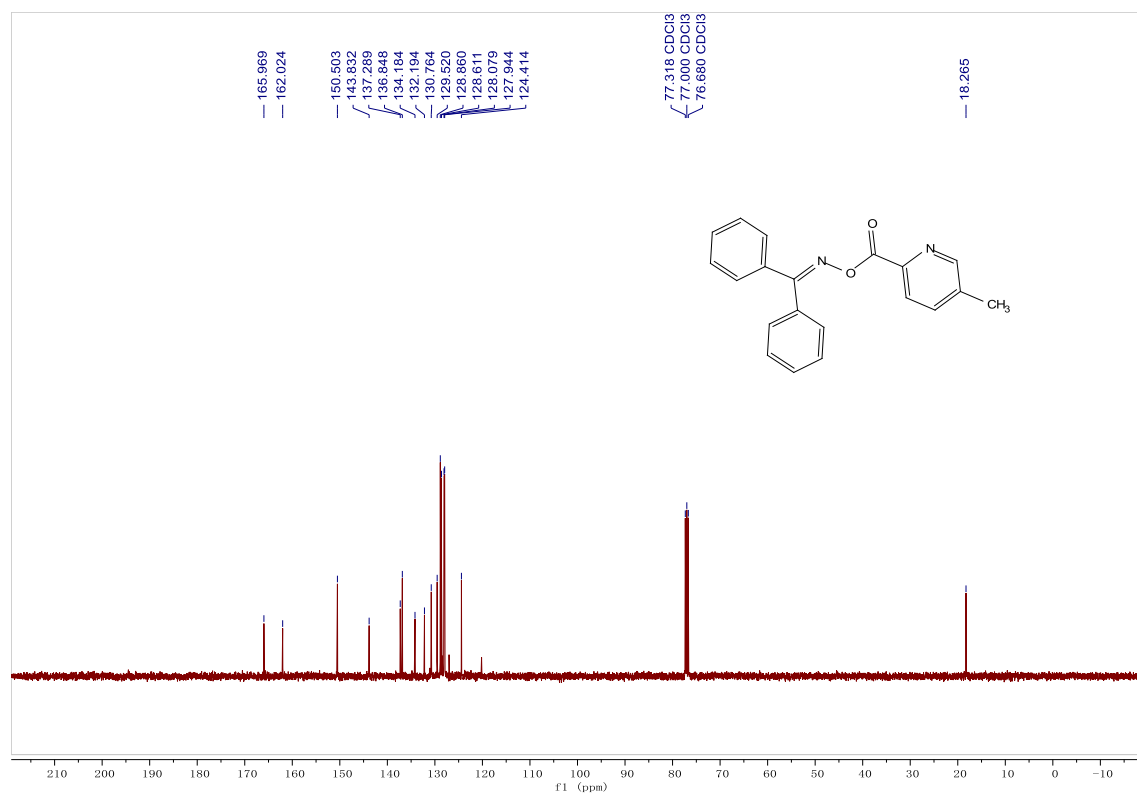
¹H-NMR for 5-4



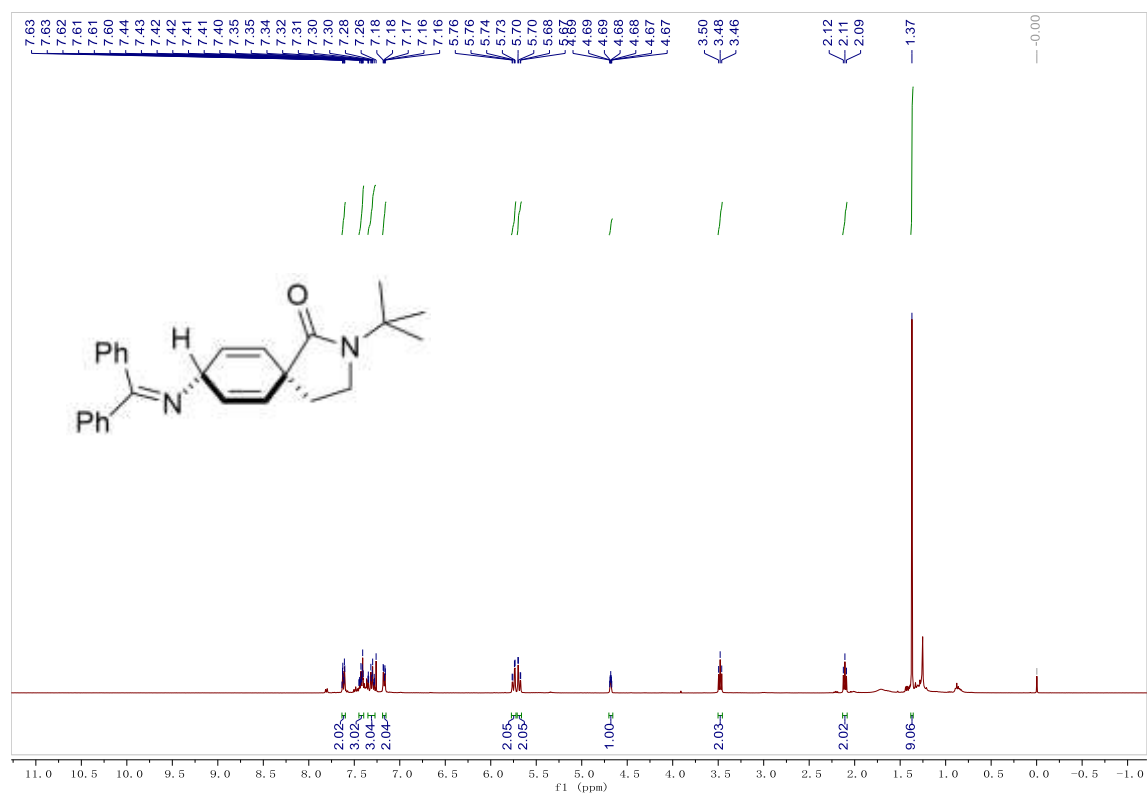
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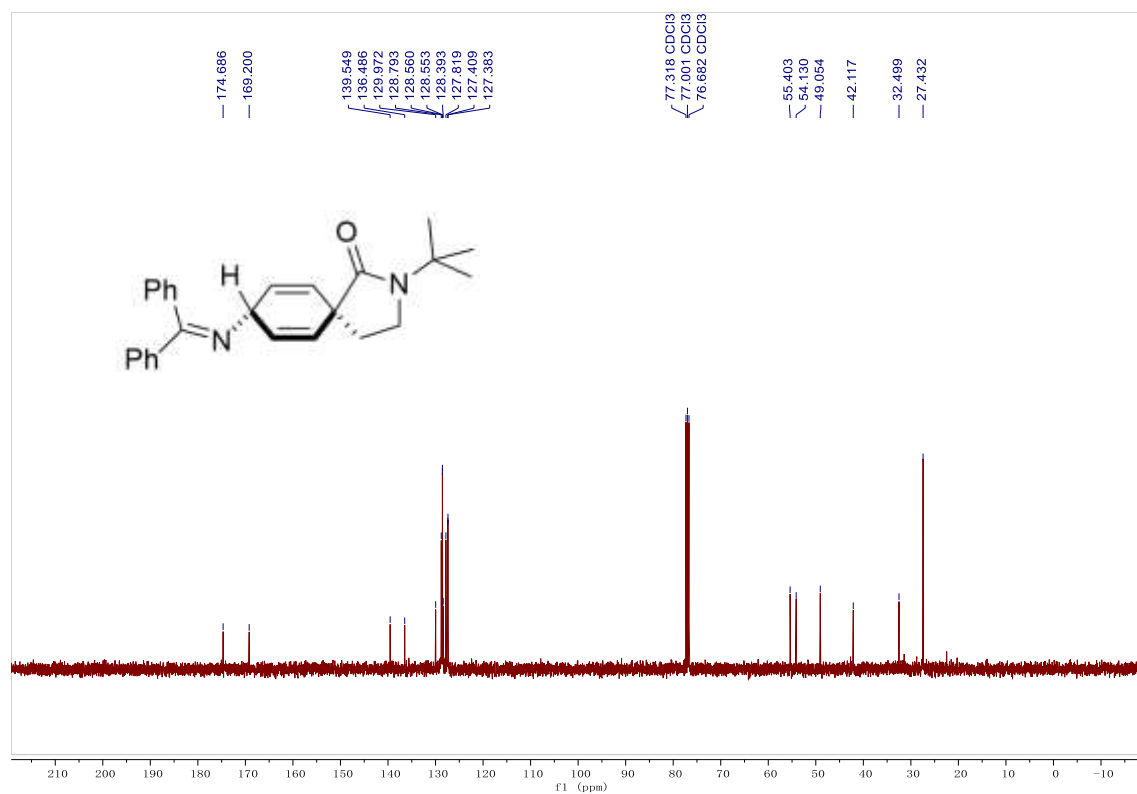
¹H-NMR for 5-5



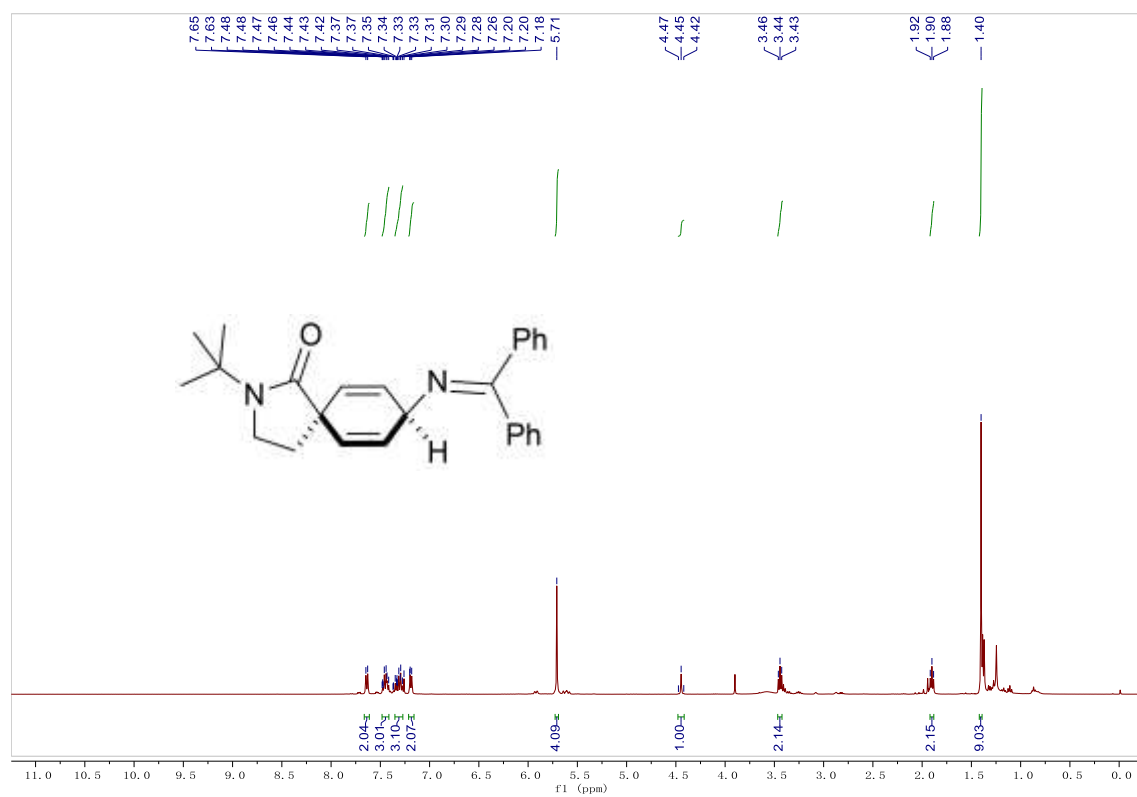
¹³C-NMR for 5-5



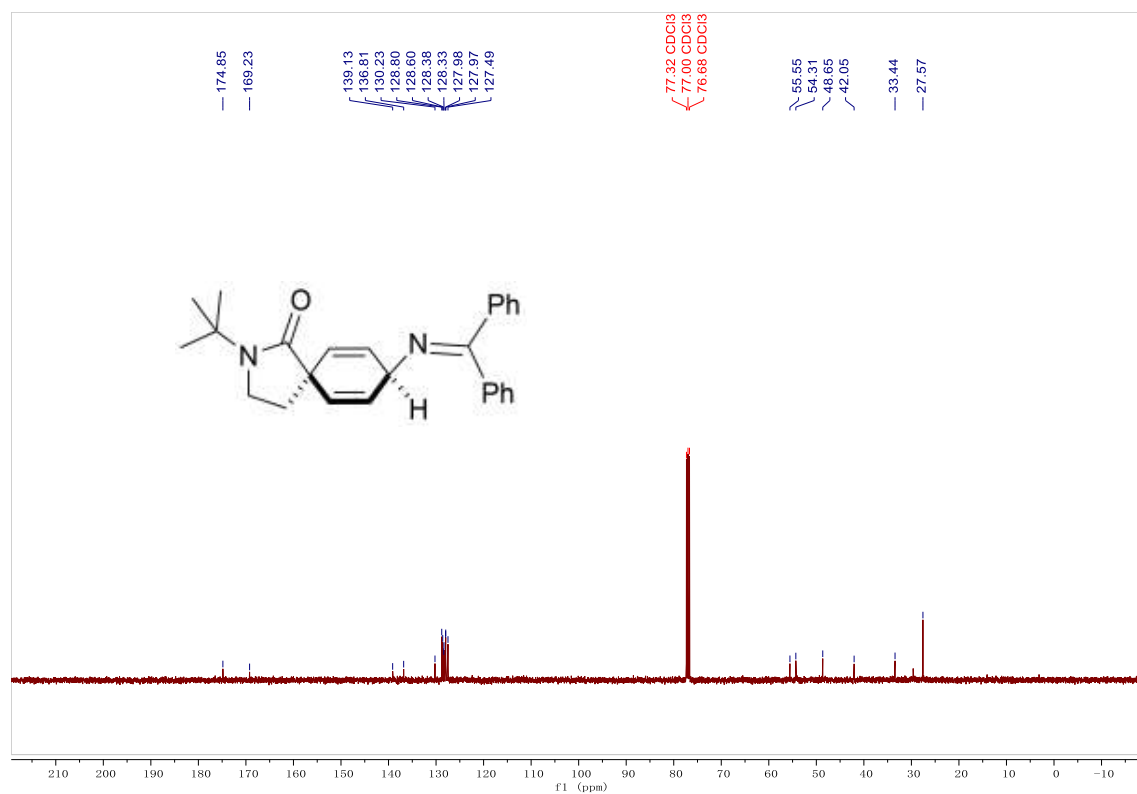
¹H-NMR for trans-2-1



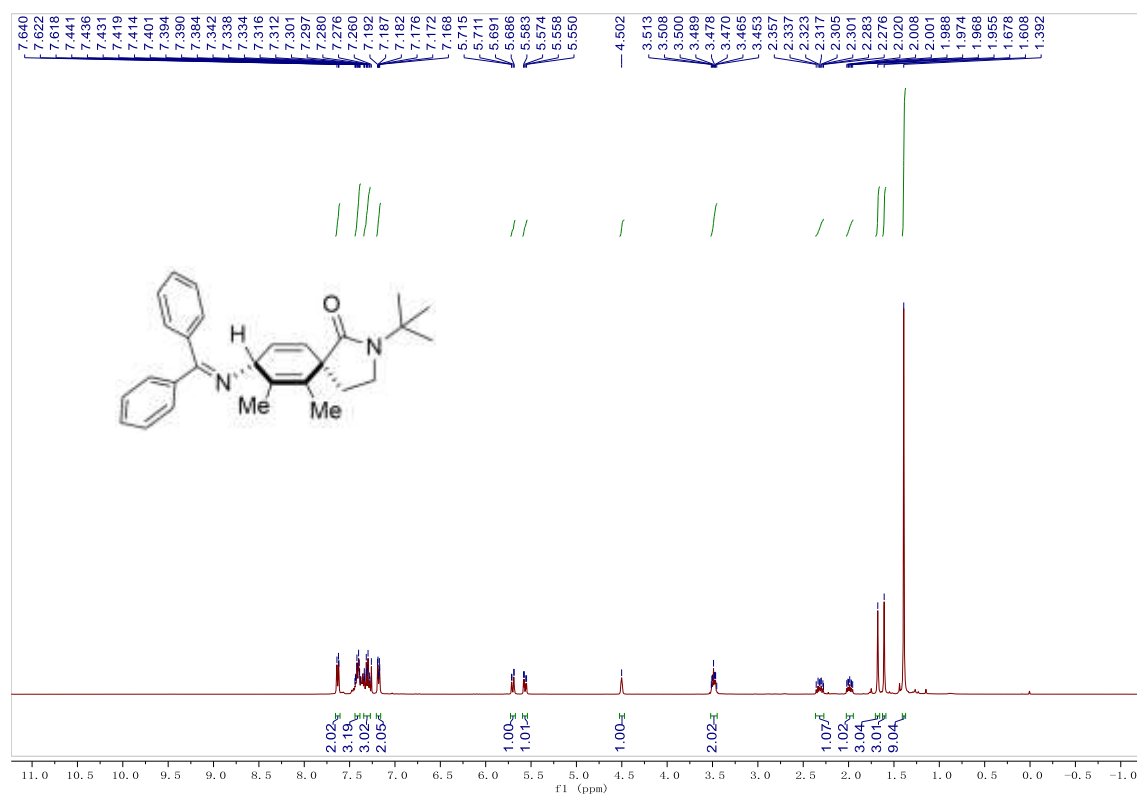
¹³C-NMR for **trans-2-1**



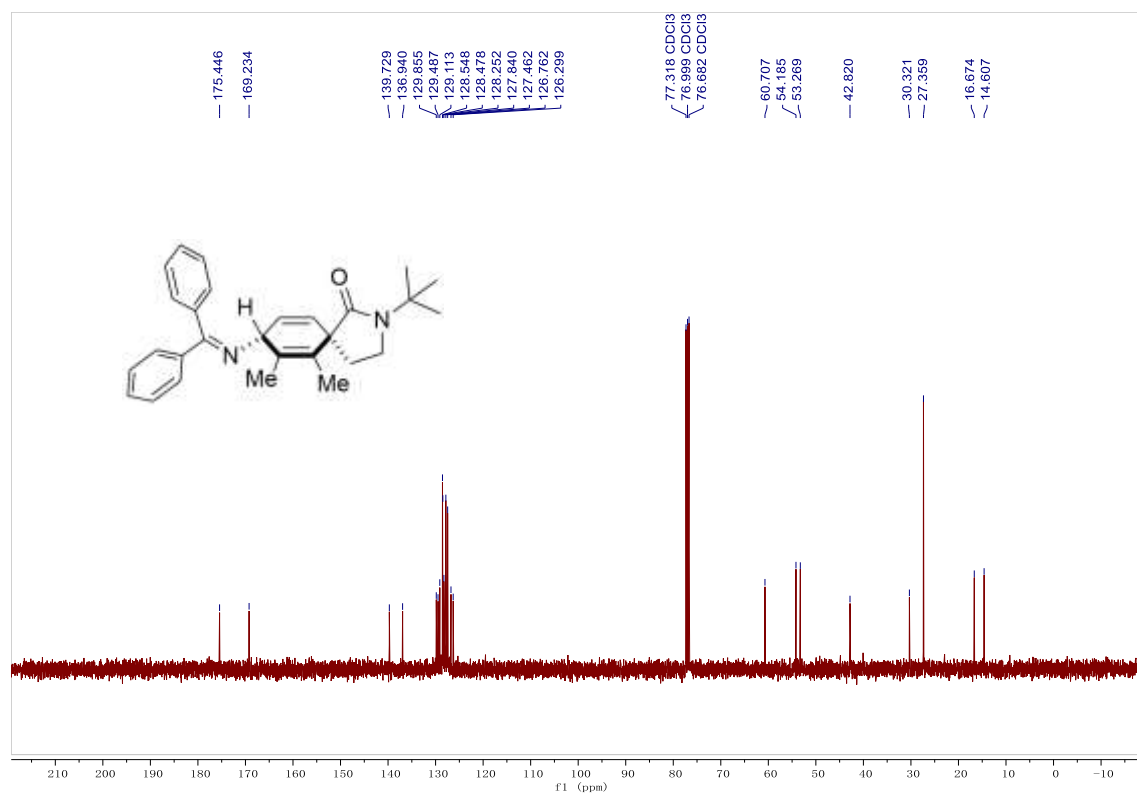
¹H-NMR for **cis-2-1**



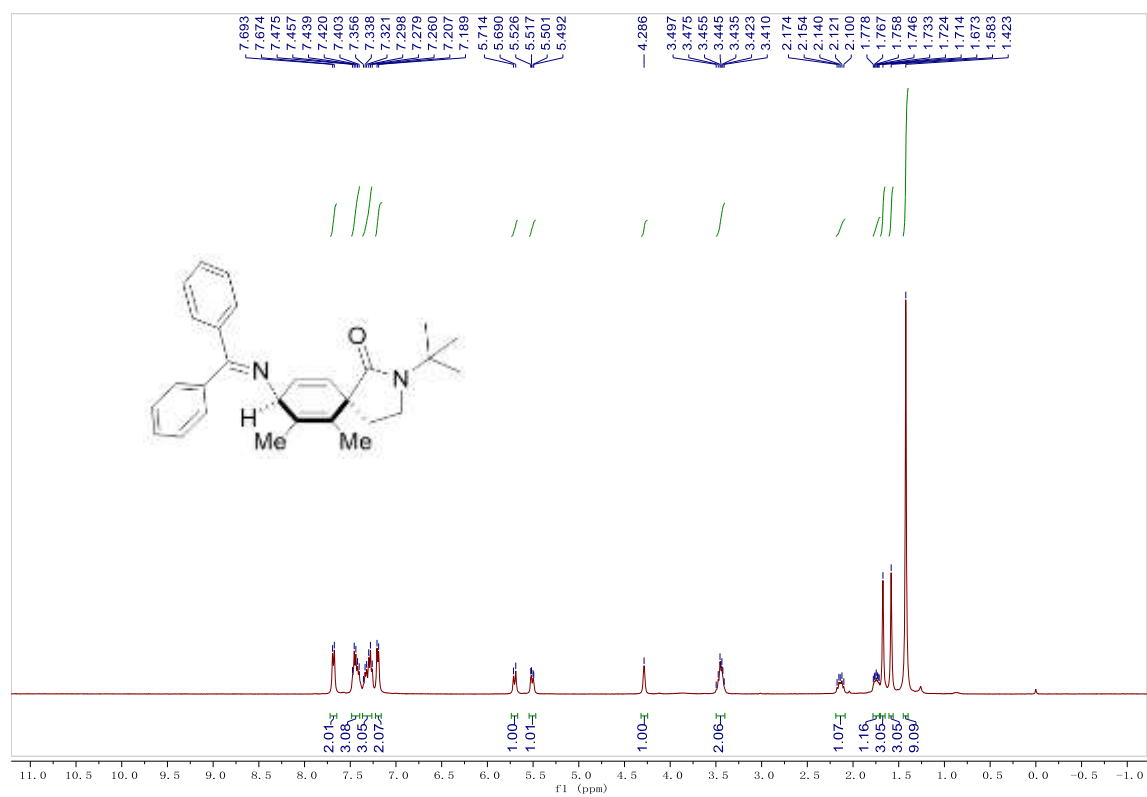
¹³C-NMR for cis-2-1



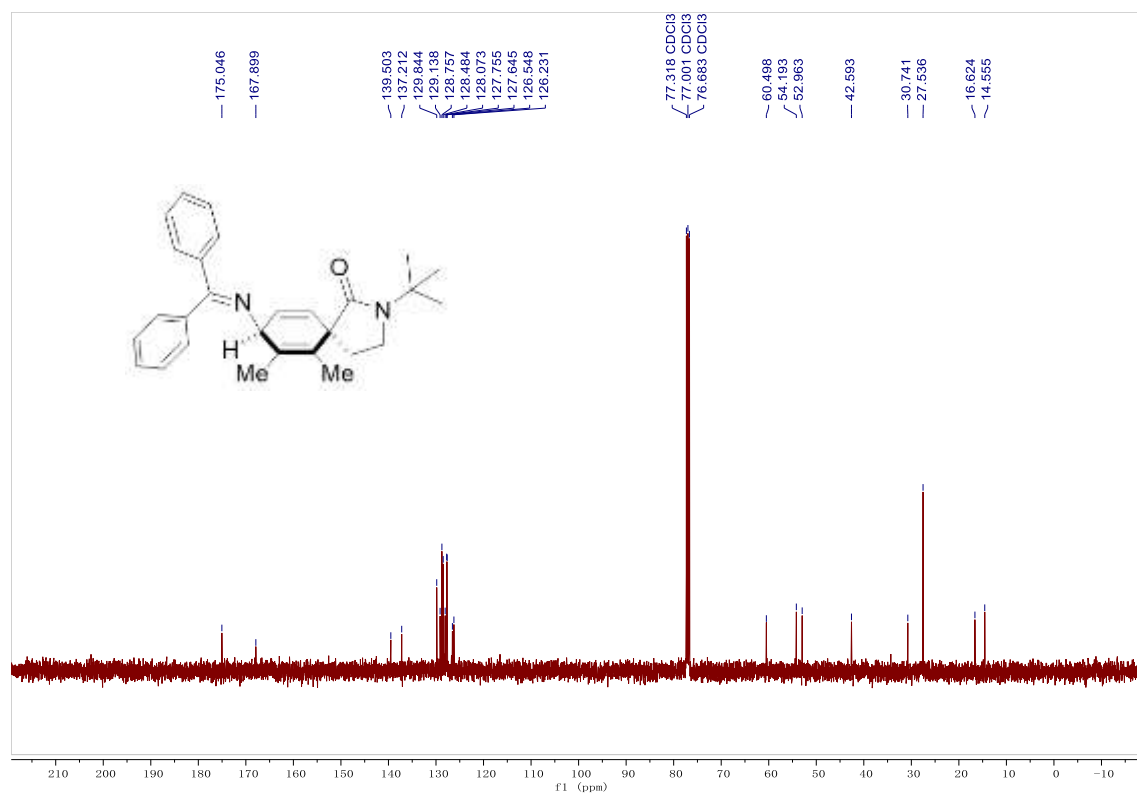
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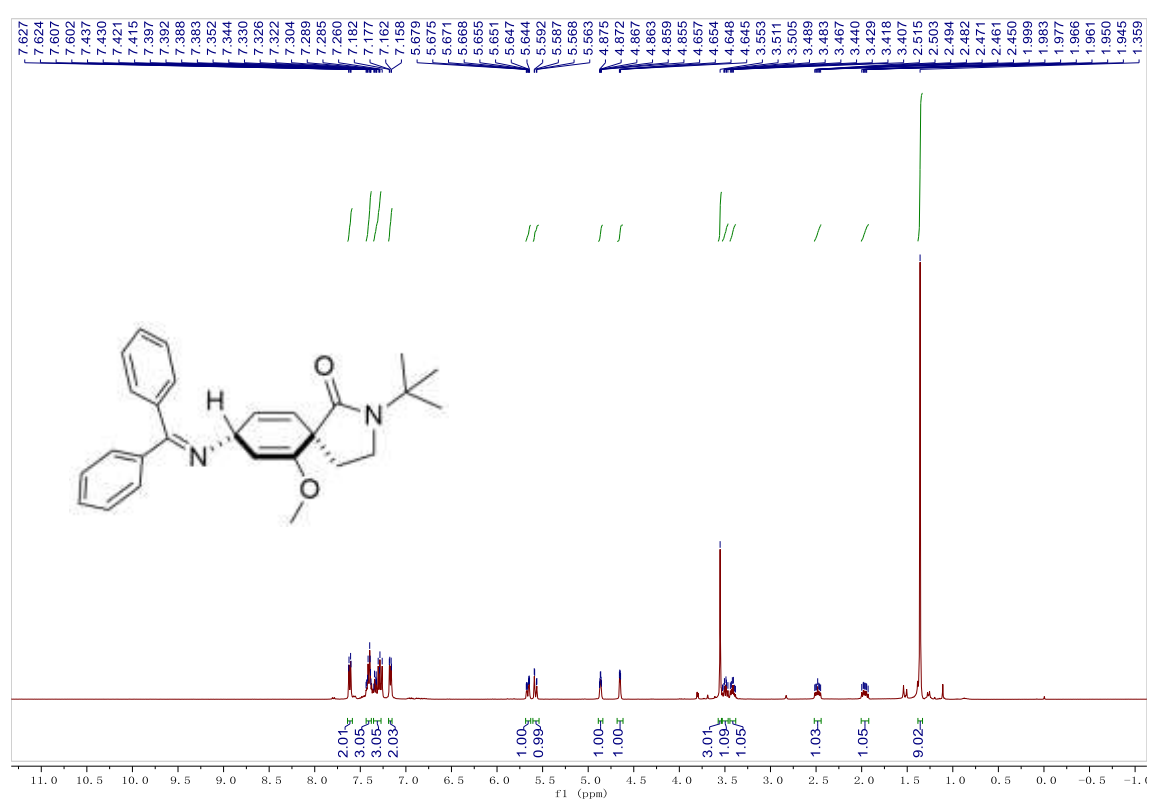
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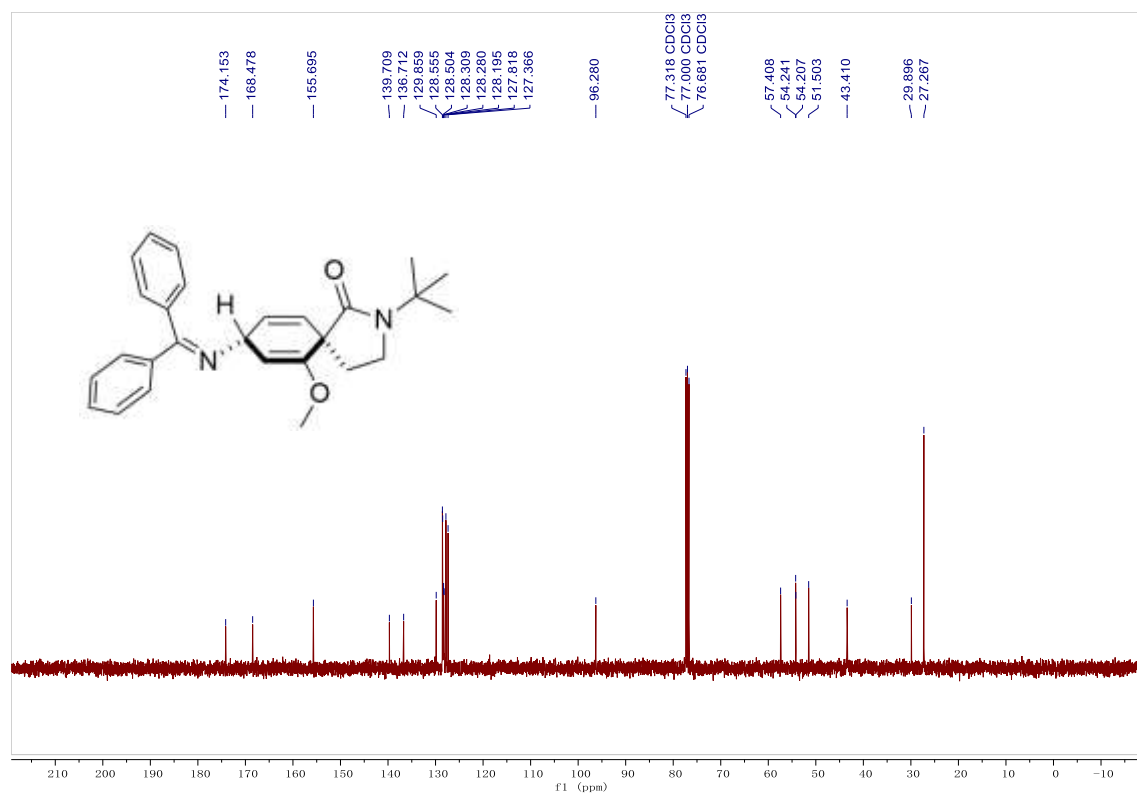
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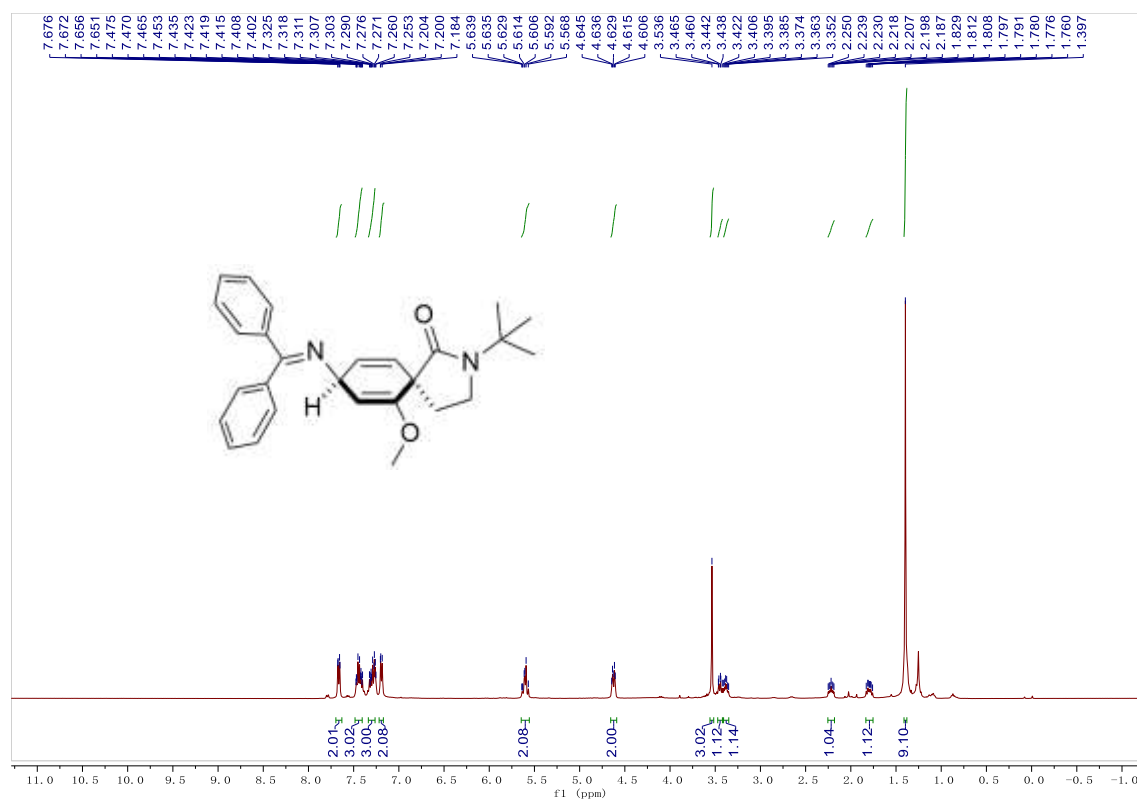
¹³C-NMR for *cis*-2-2



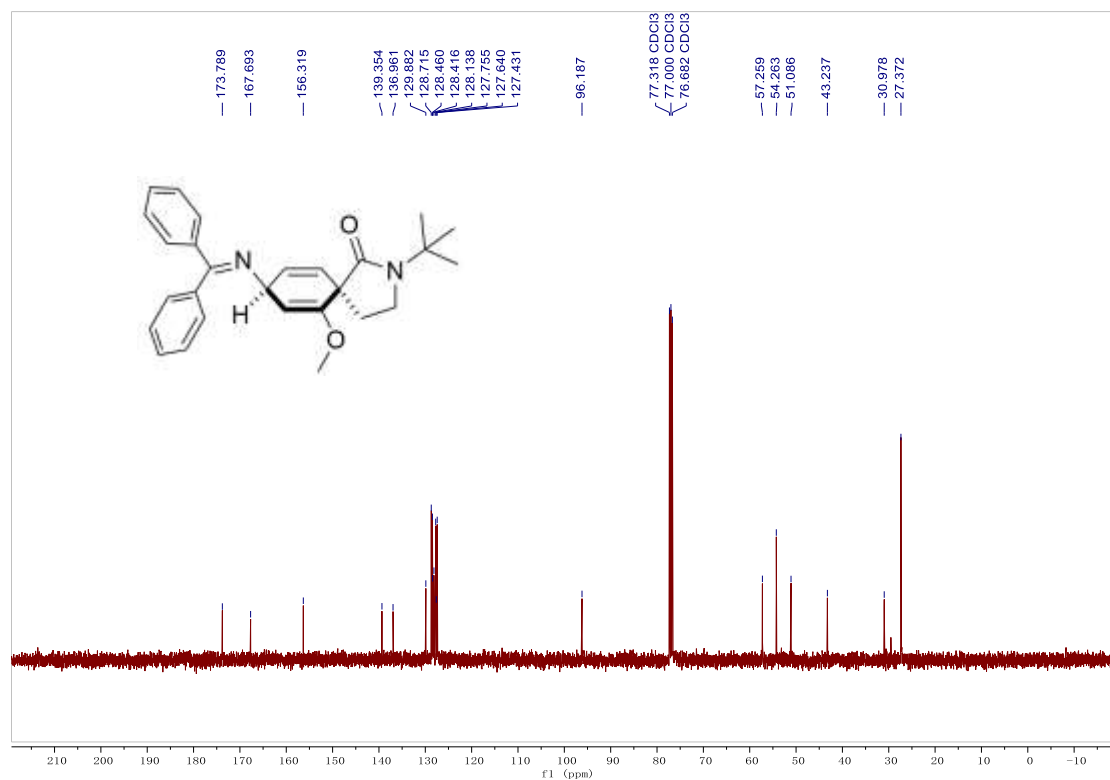
¹H-NMR for *trans*-2-3



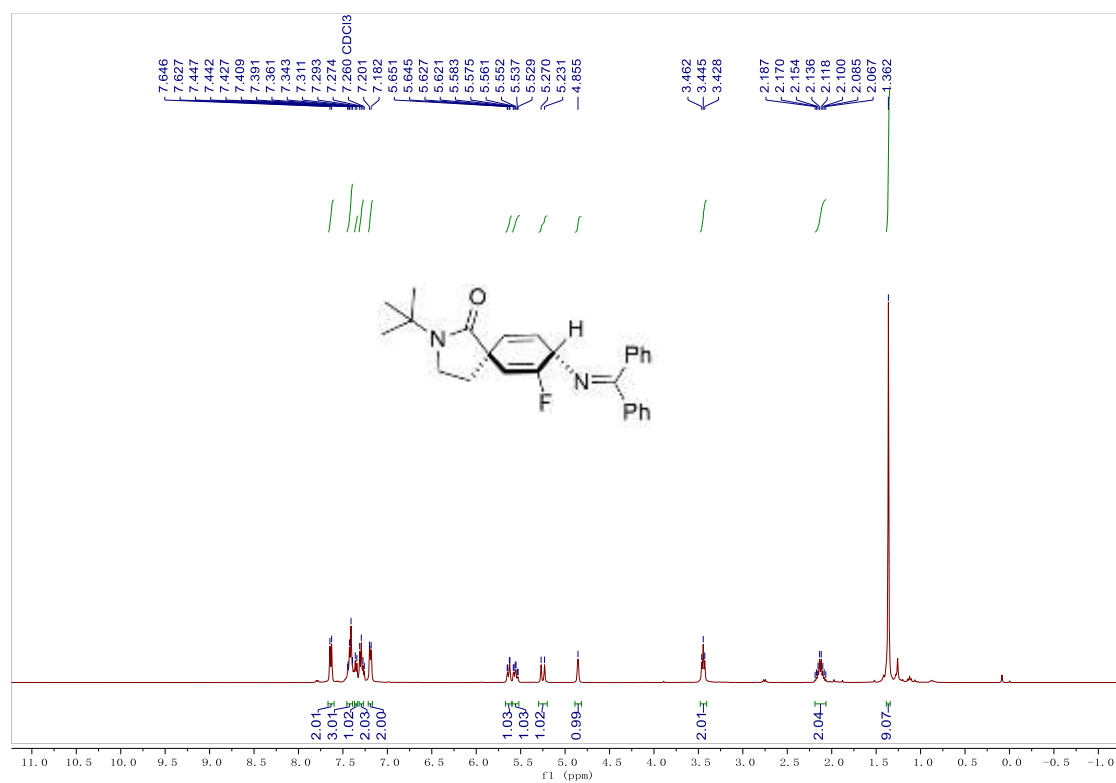
¹³C-NMR for trans-2-3



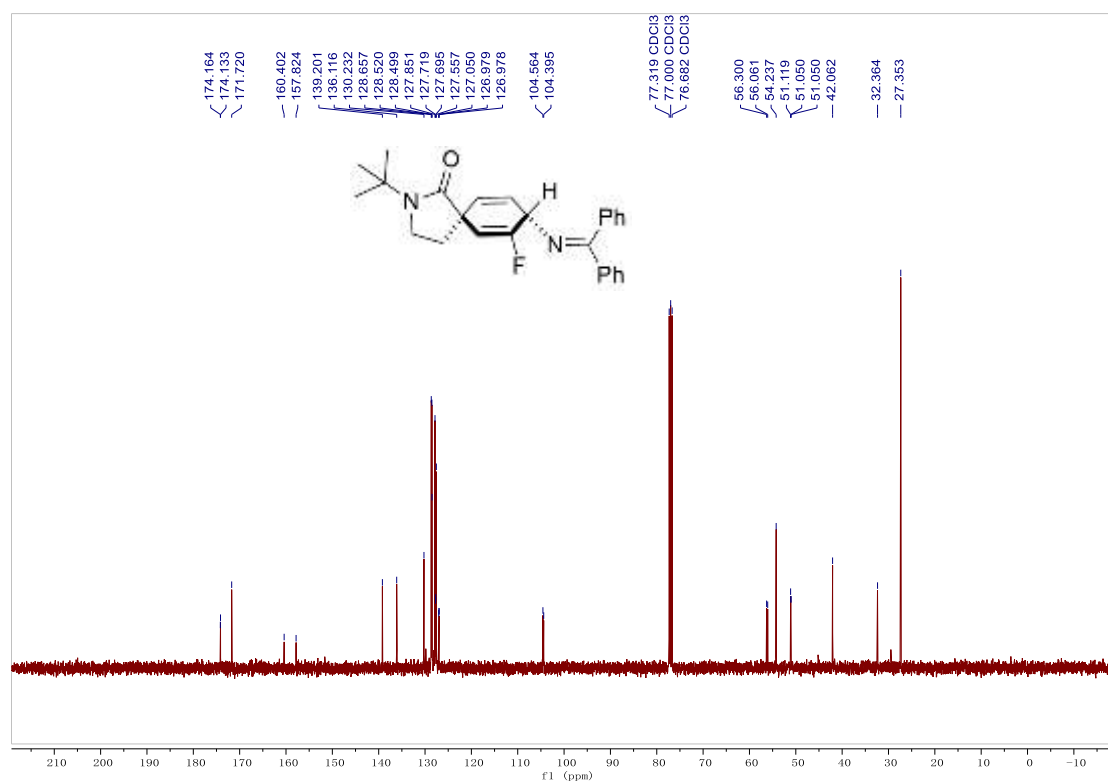
¹H-NMR for cis-2-3



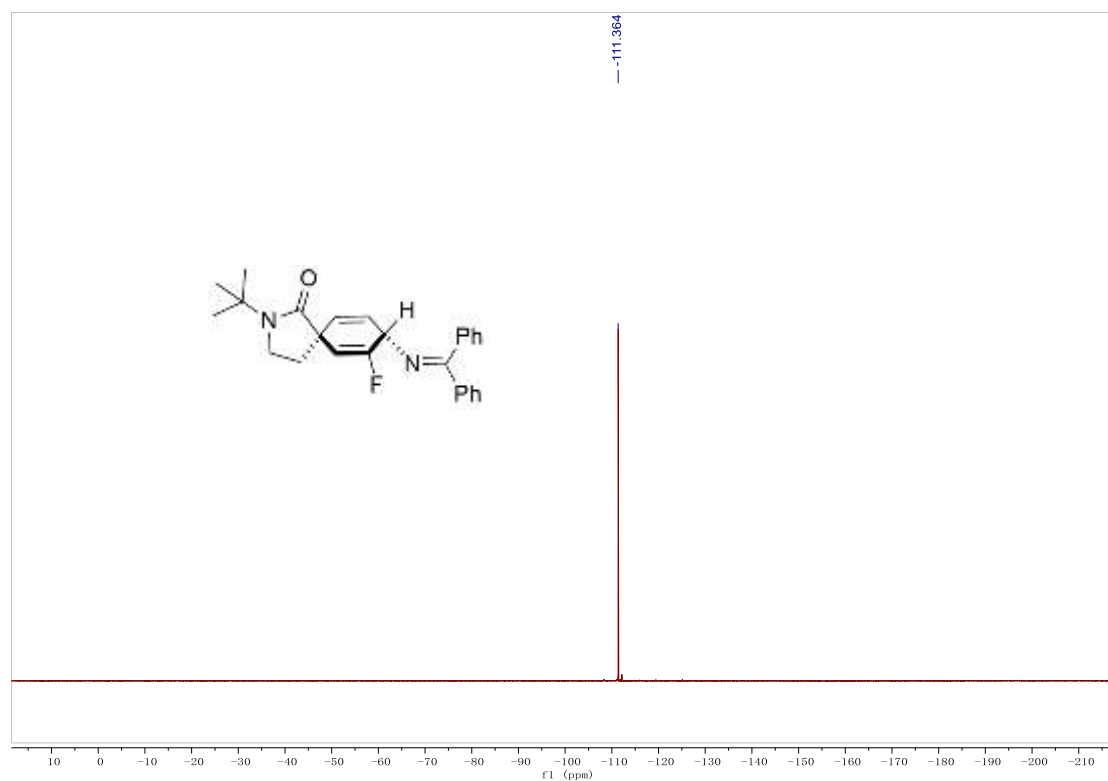
¹³C-NMR for *cis*-2-3



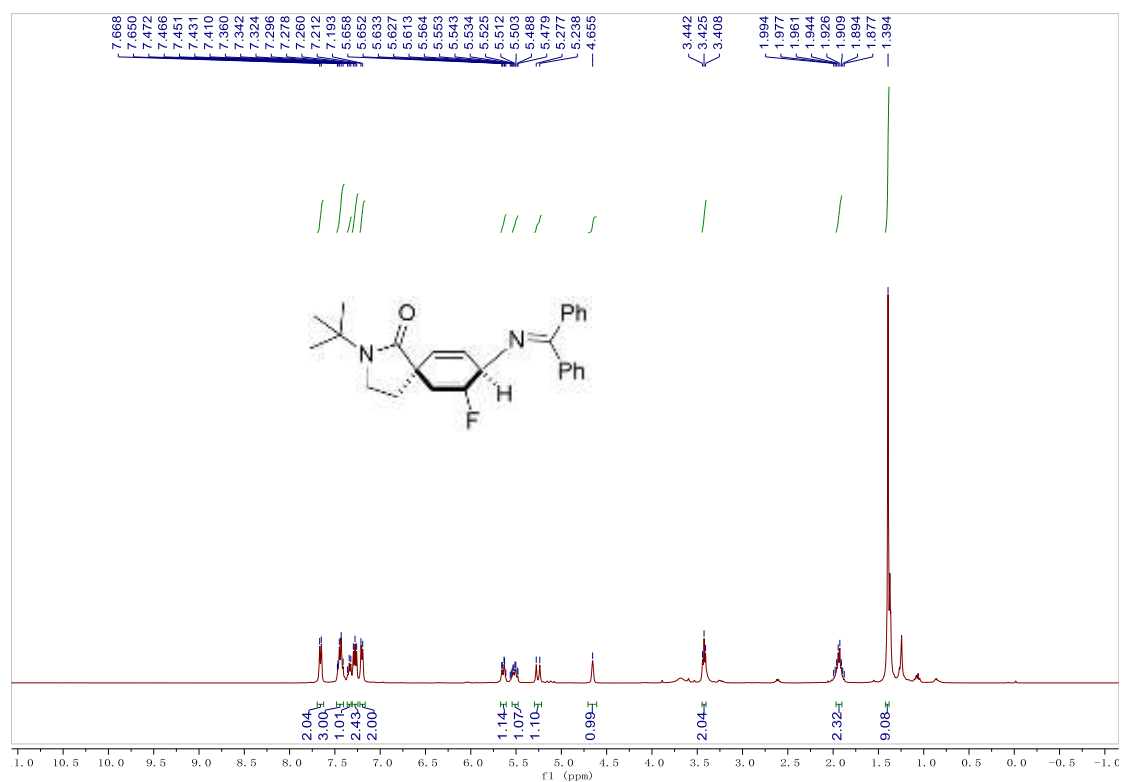
¹H-NMR for *trans*-2-4



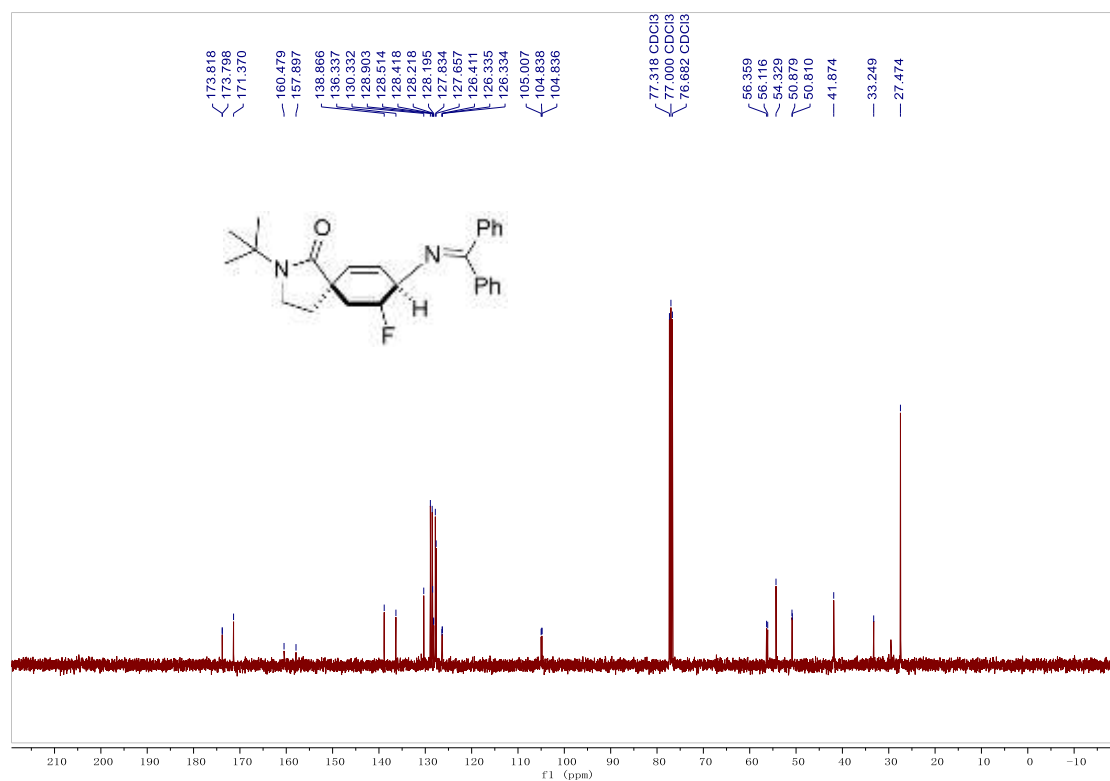
¹³C-NMR for trans-2-4



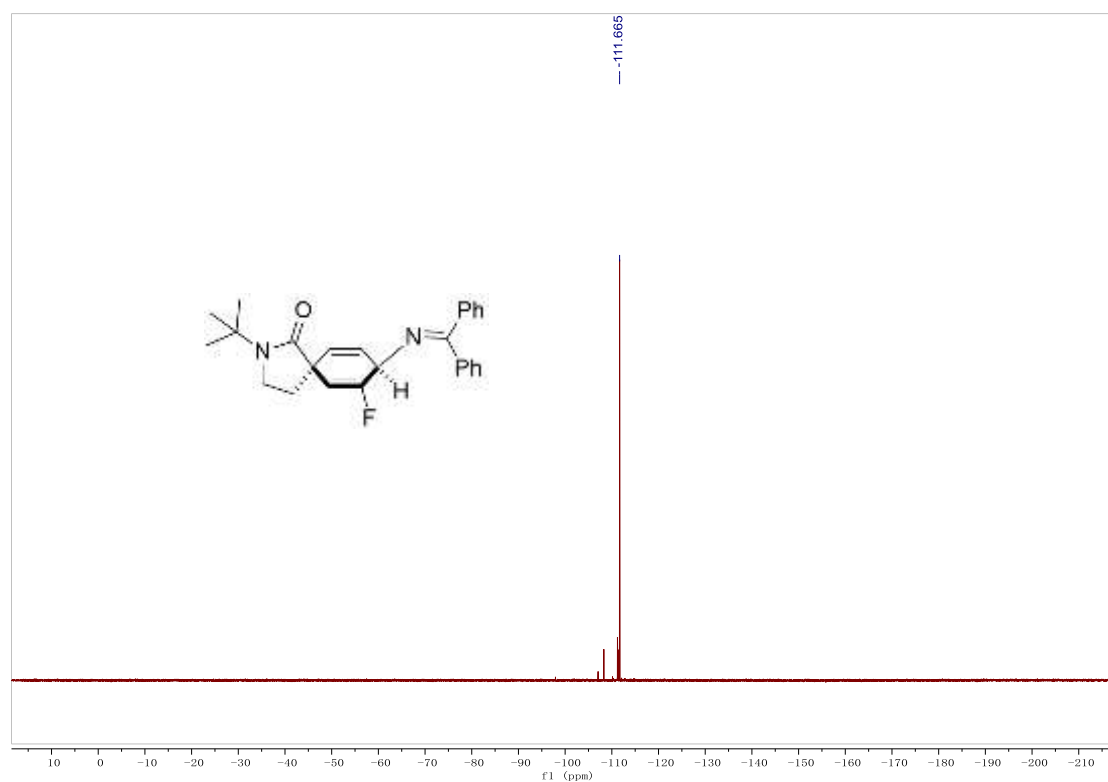
¹⁹F-NMR for trans-2-4



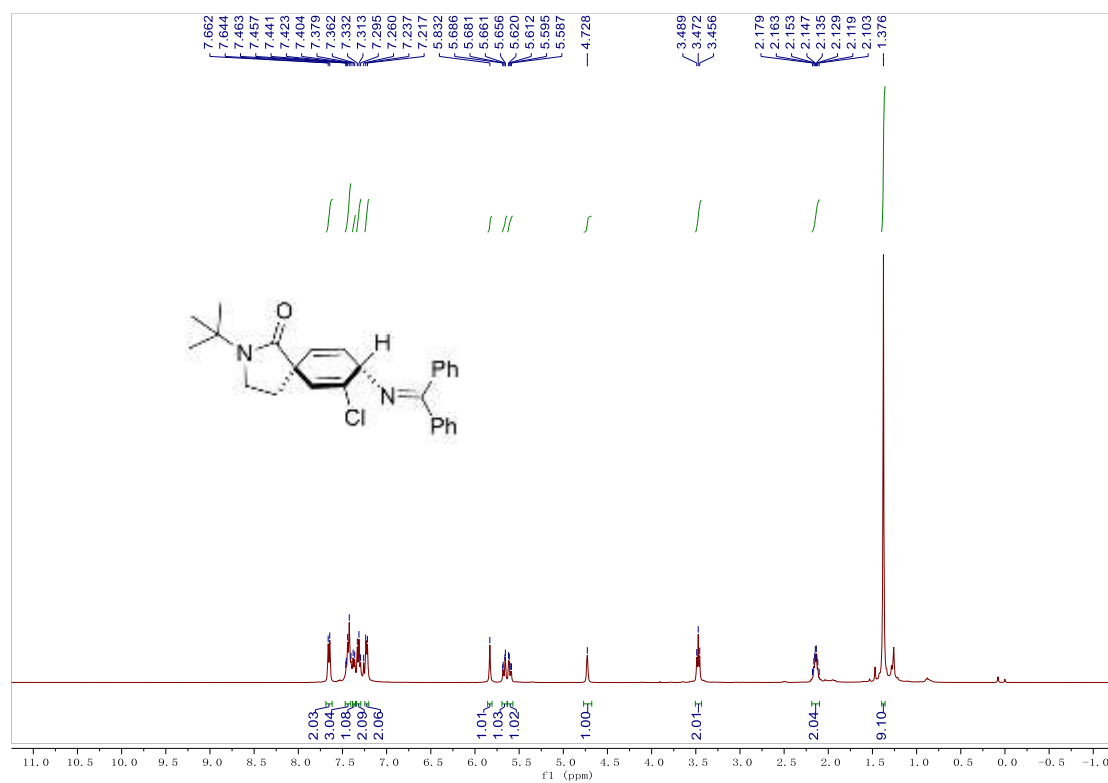
¹H-NMR for cis-2-4



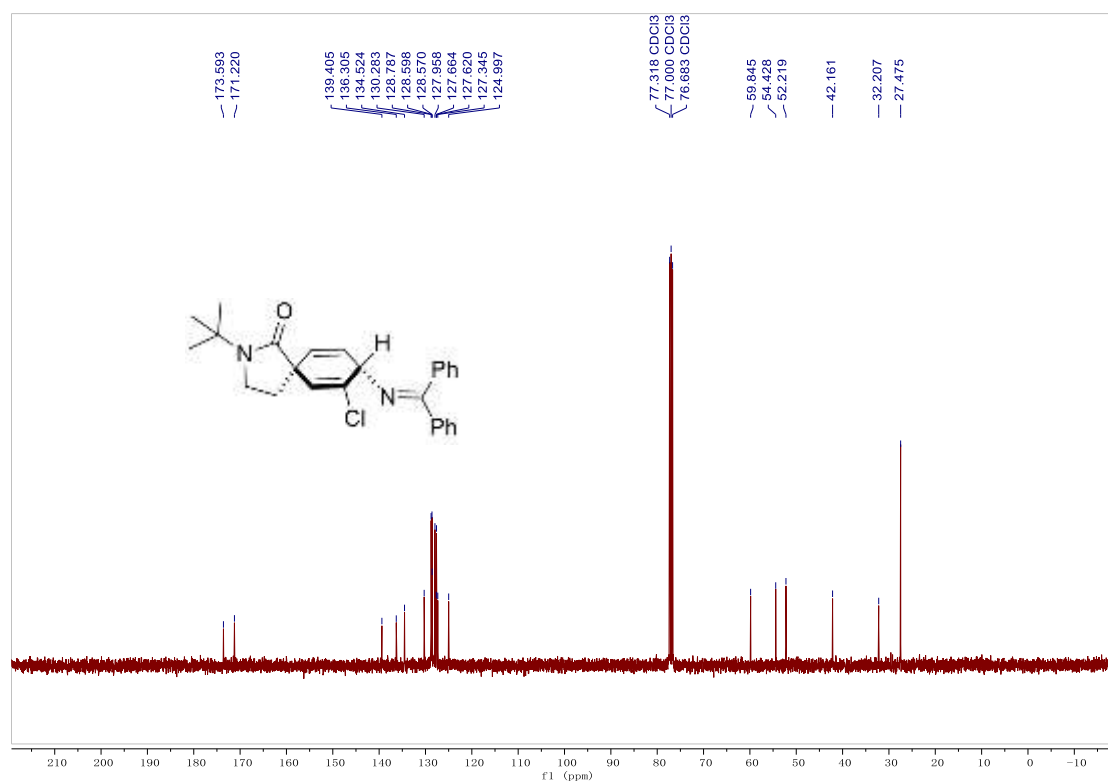
¹³C-NMR for cis-2-4



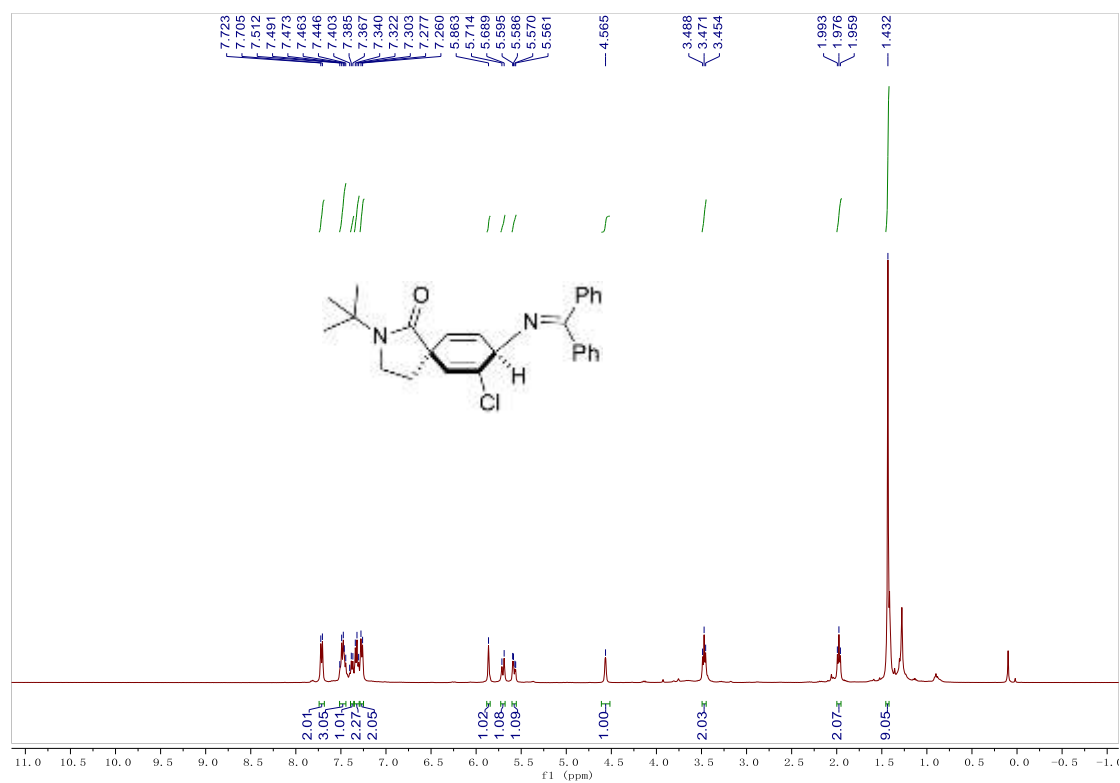
^{19}F -NMR for **cis-2-4**



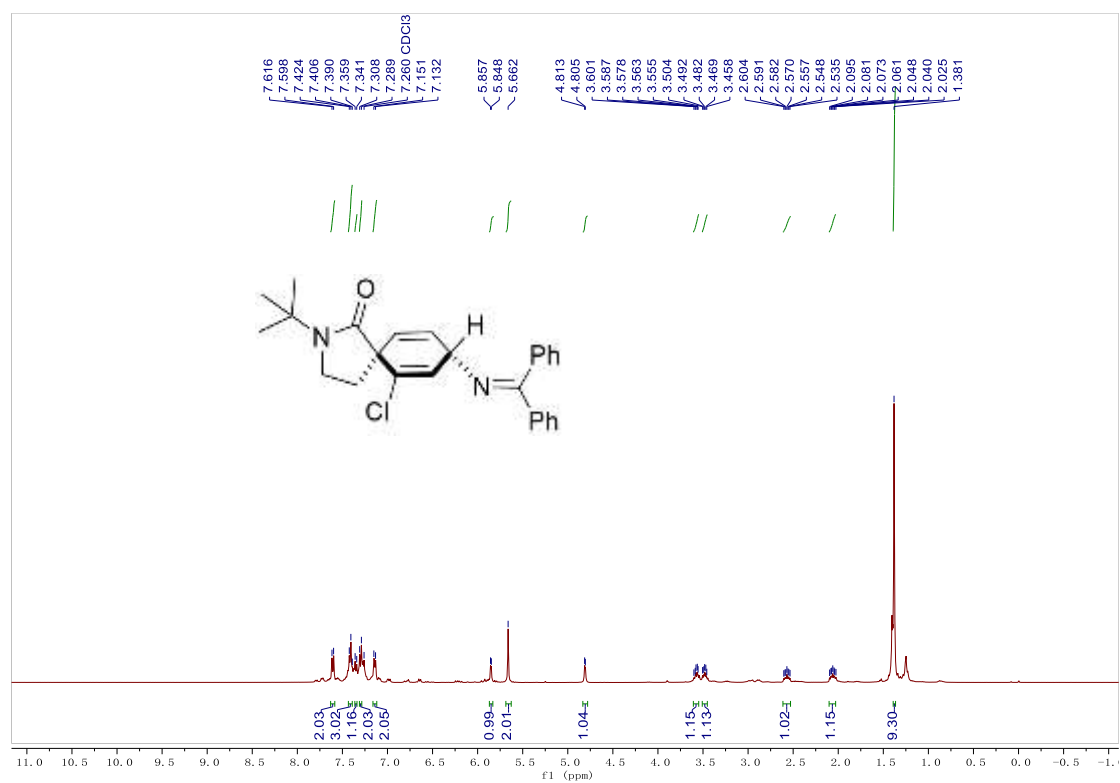
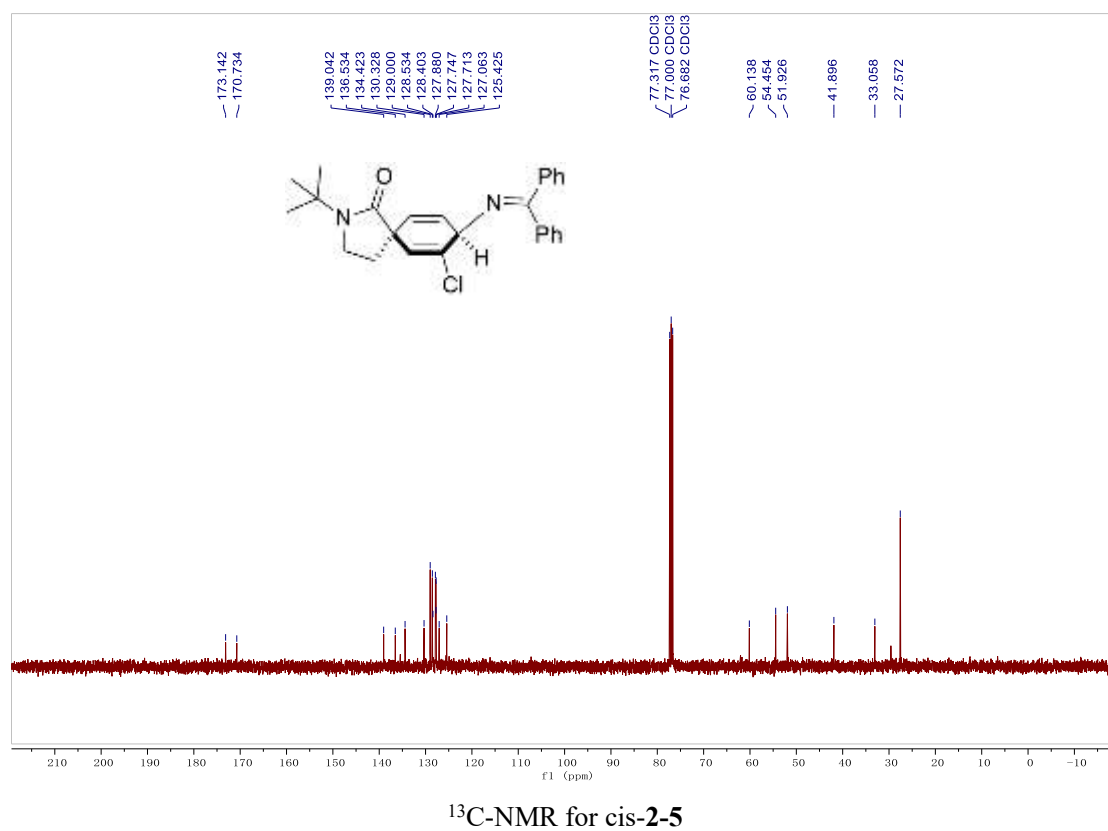
^1H -NMR for **trans-2-5**

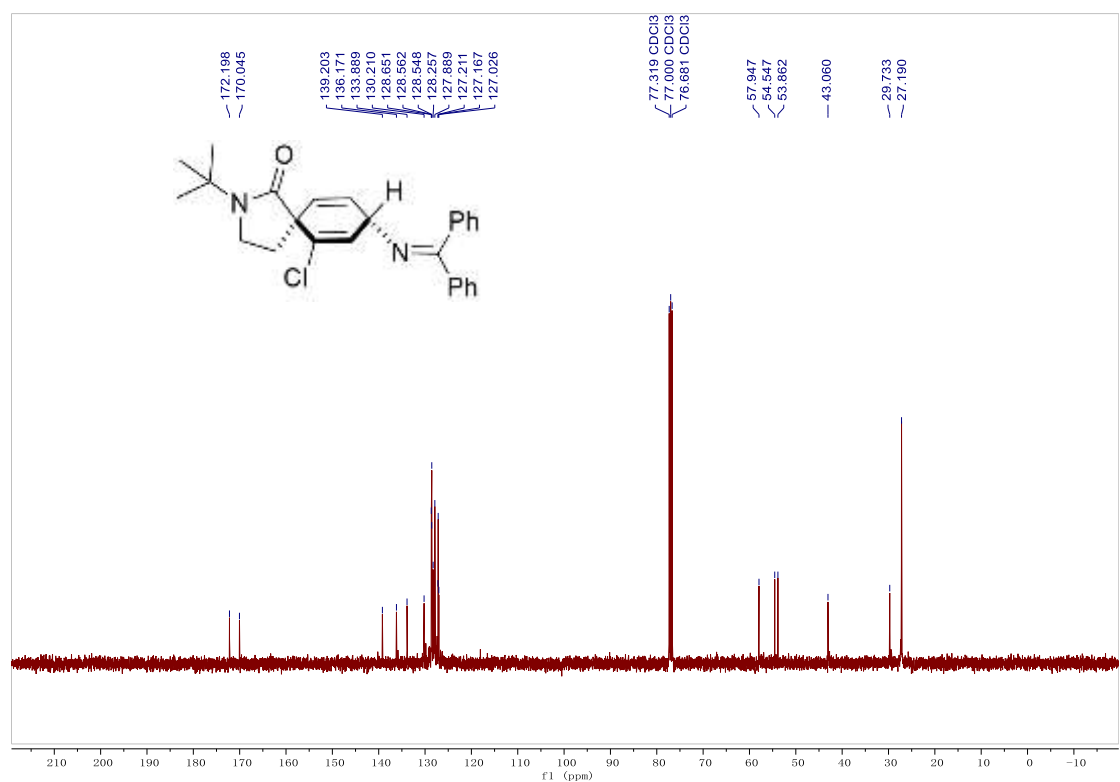


¹³C-NMR for trans-2-5

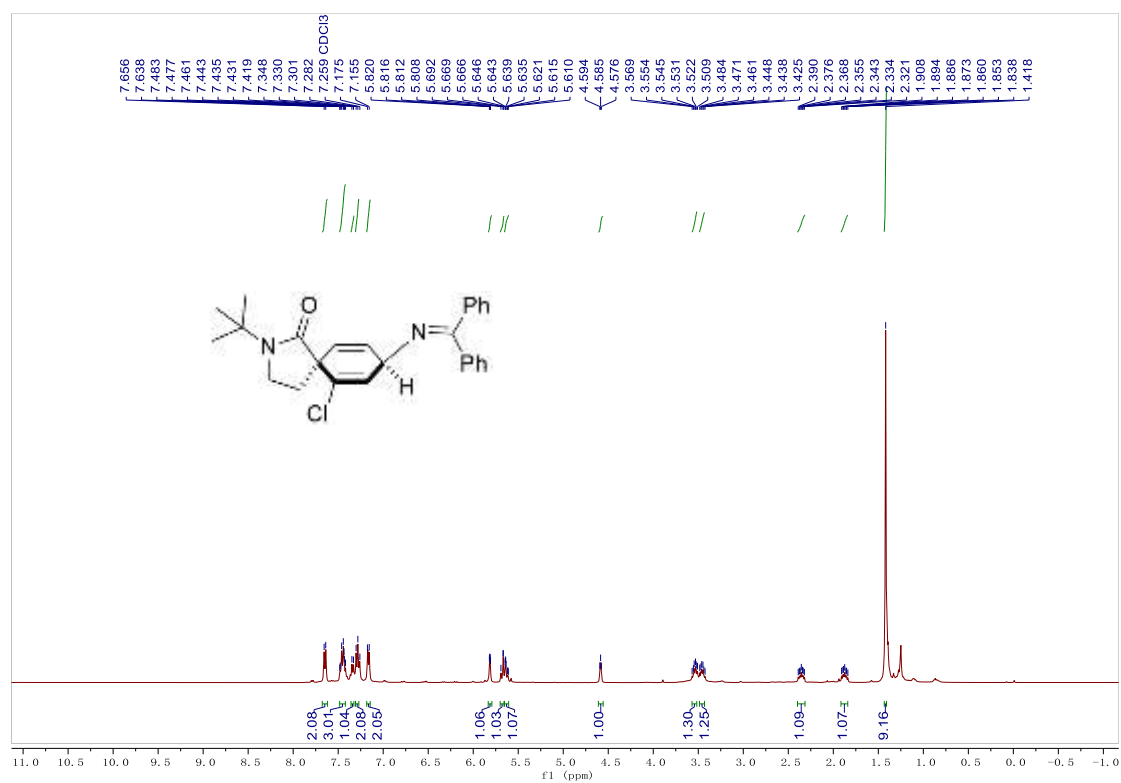


¹H-NMR for cis-2-5

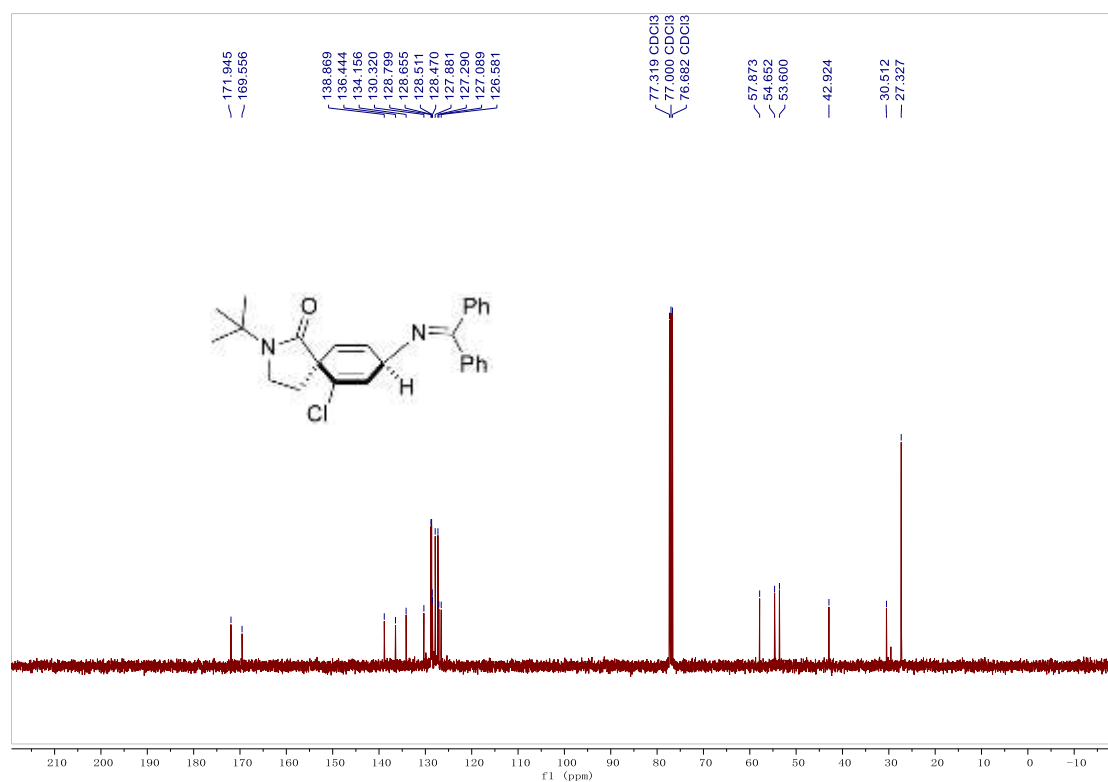




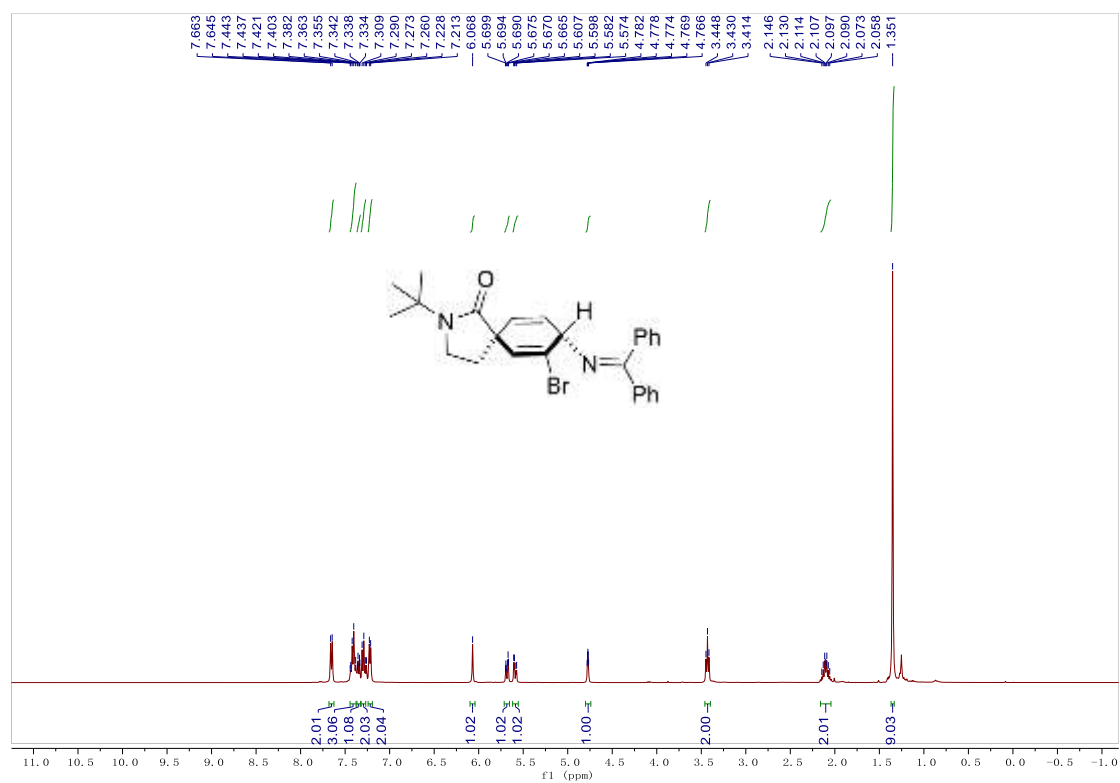
¹³C-NMR for **trans-2-6**



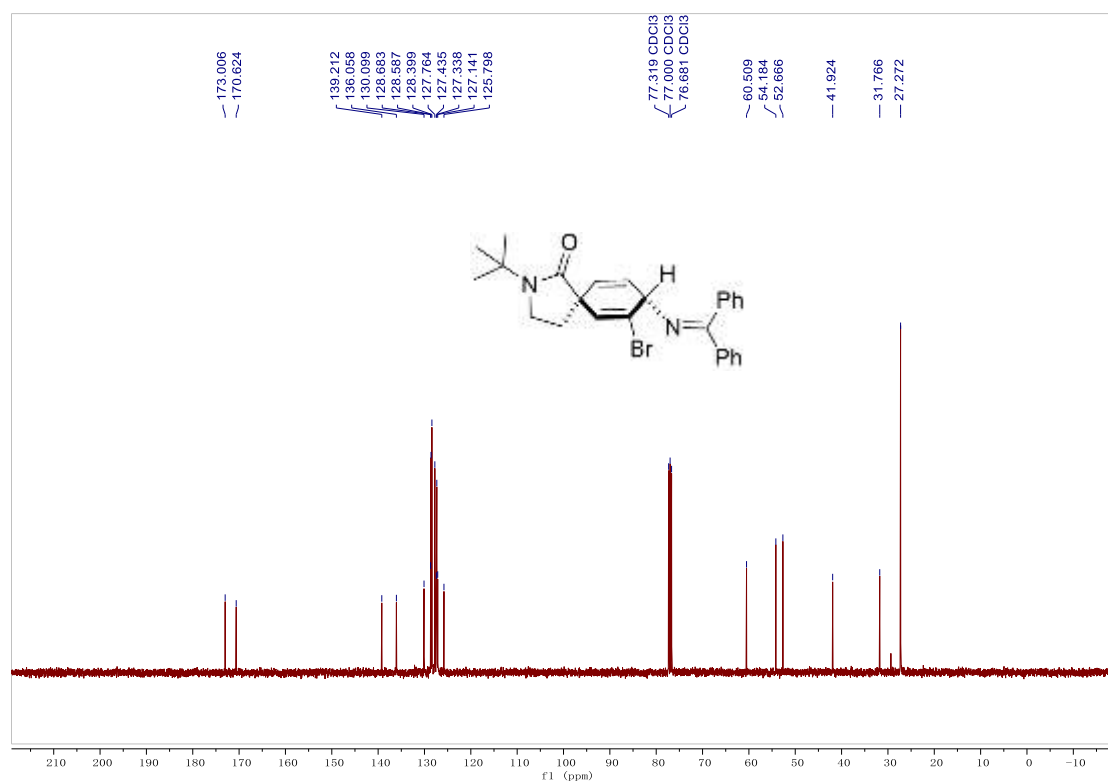
¹H-NMR for **cis-2-6**



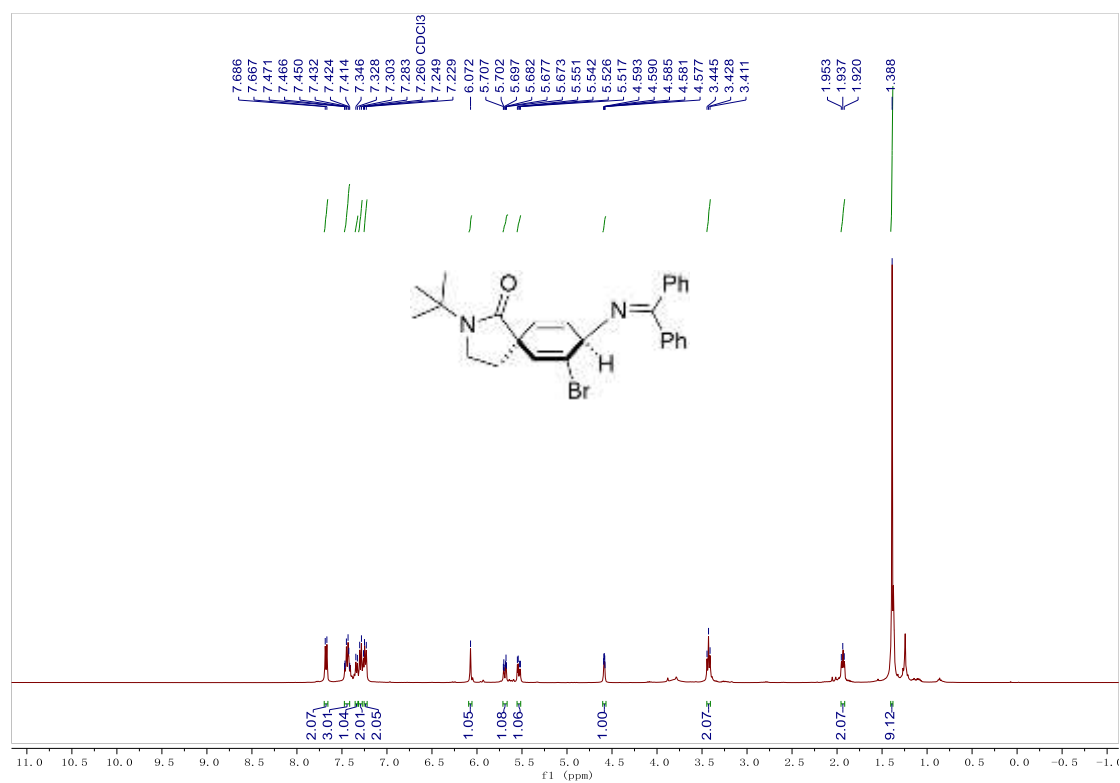
¹³C-NMR for *cis*-2-6



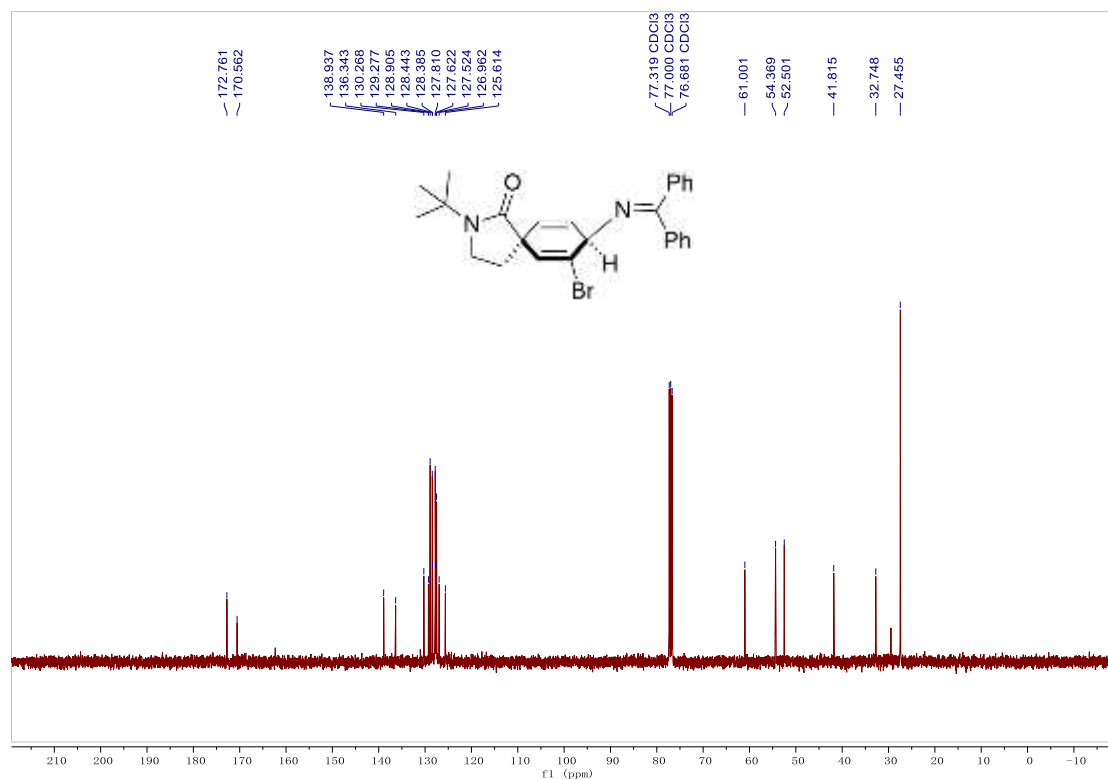
¹H-NMR for *trans*-2-7



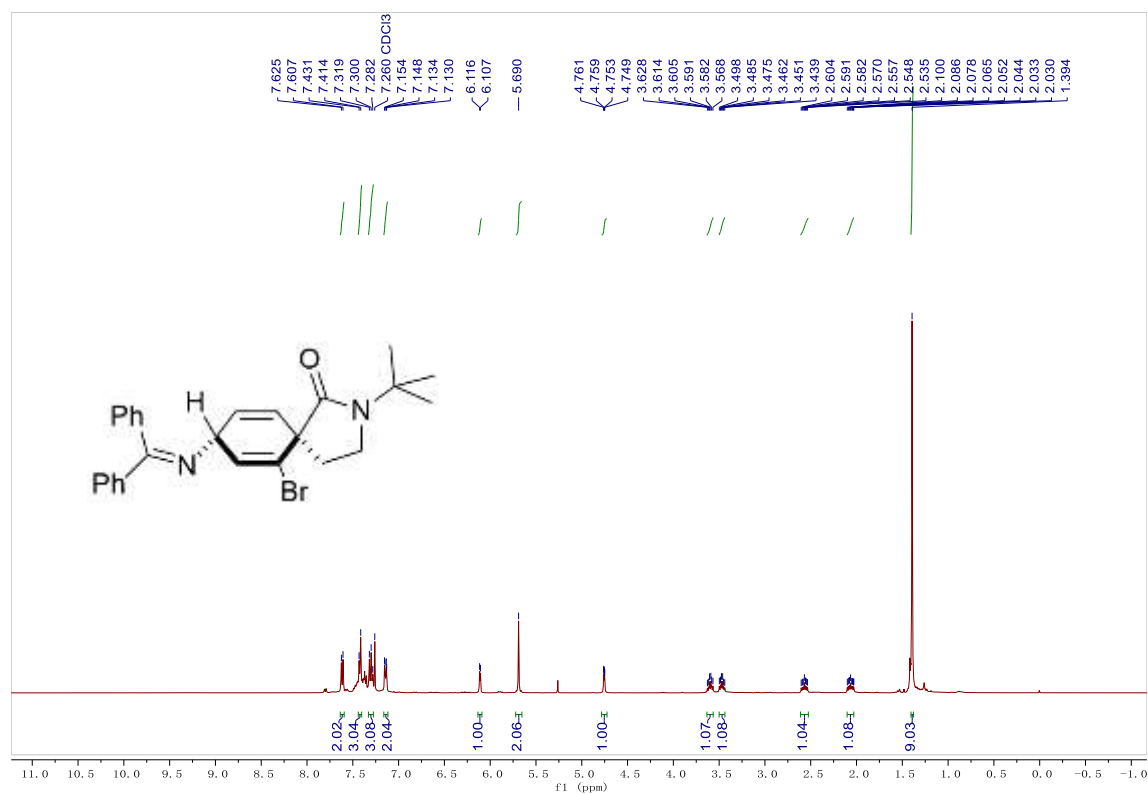
¹³C-NMR for **trans-2-7**



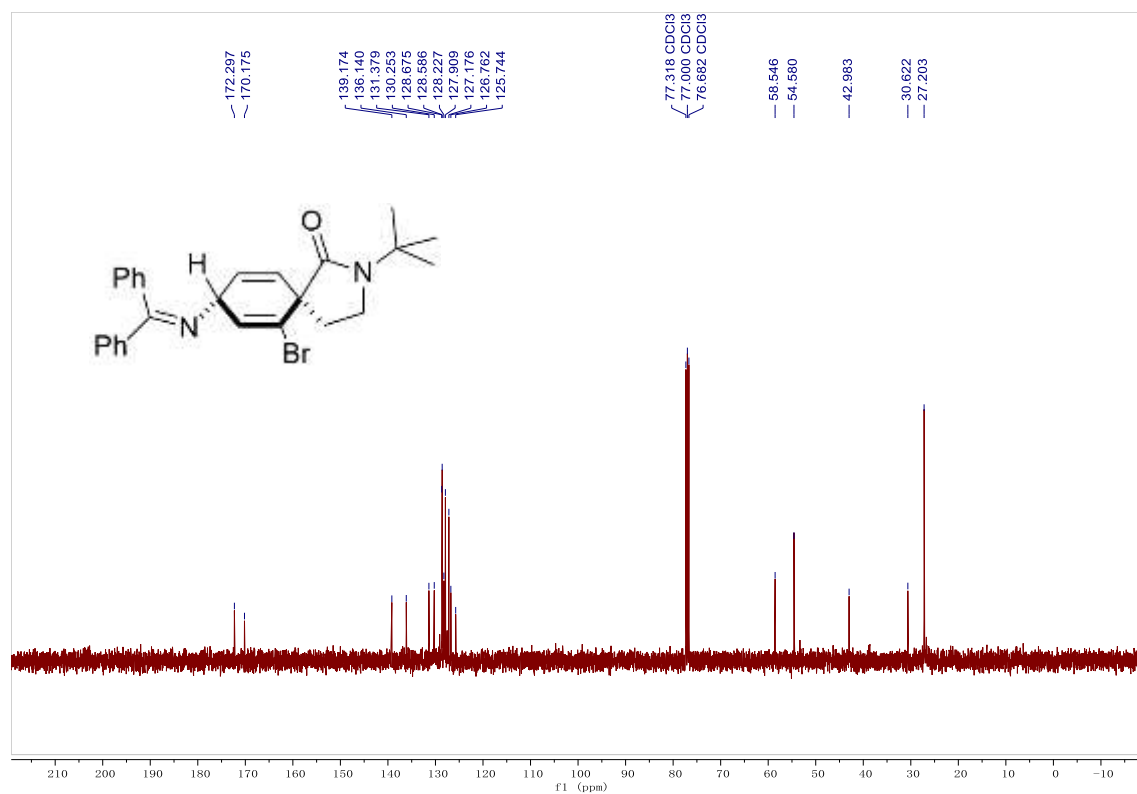
¹H-NMR for **cis-2-7**



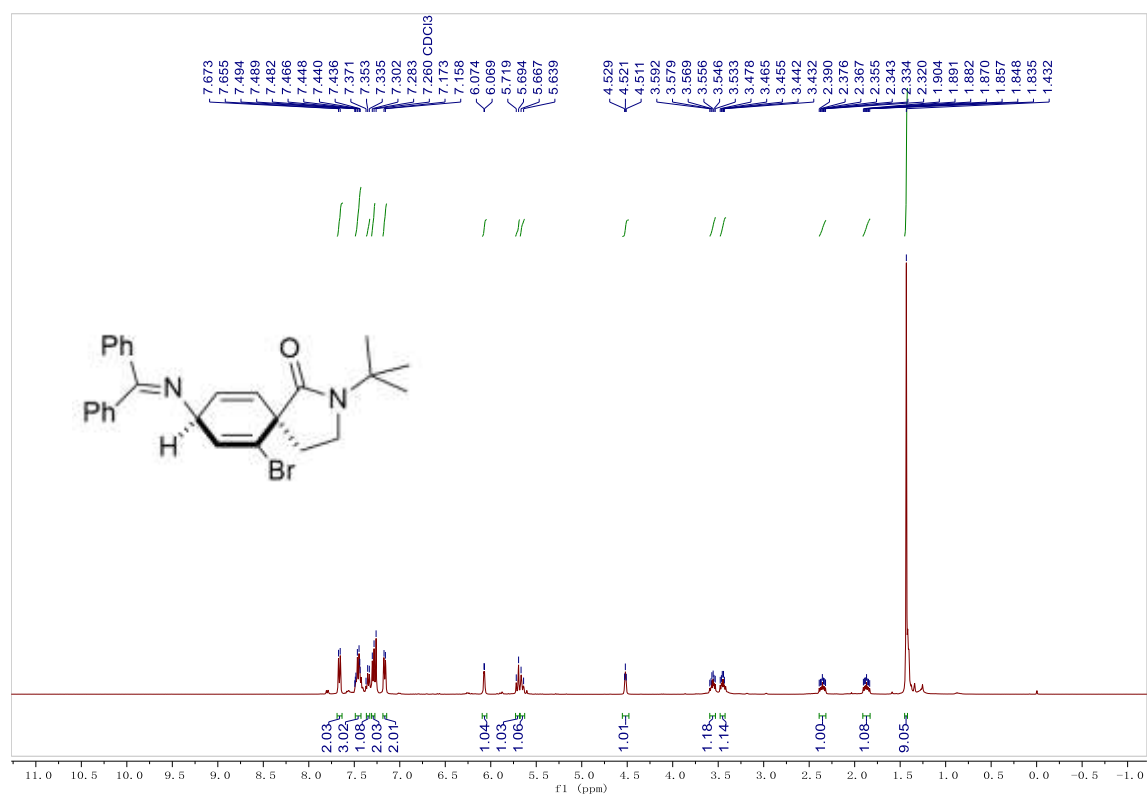
¹³C-NMR for *cis*-2-7



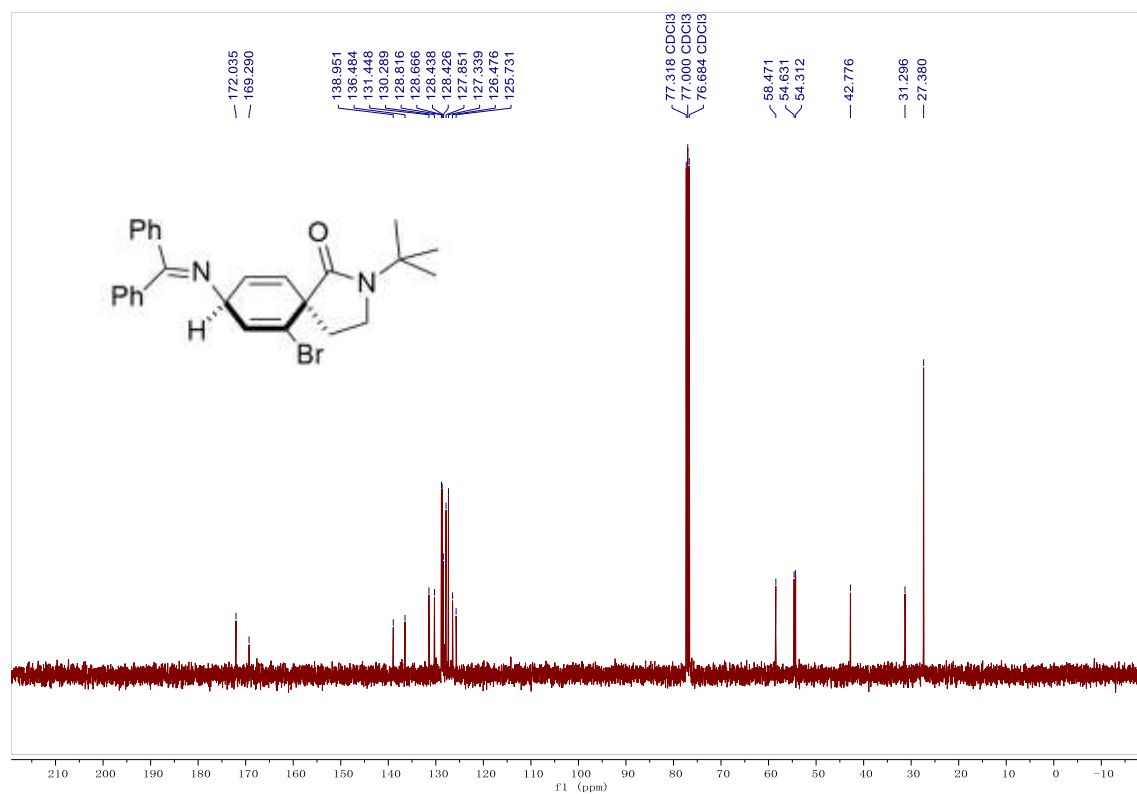
¹H-NMR for *trans*-2-8



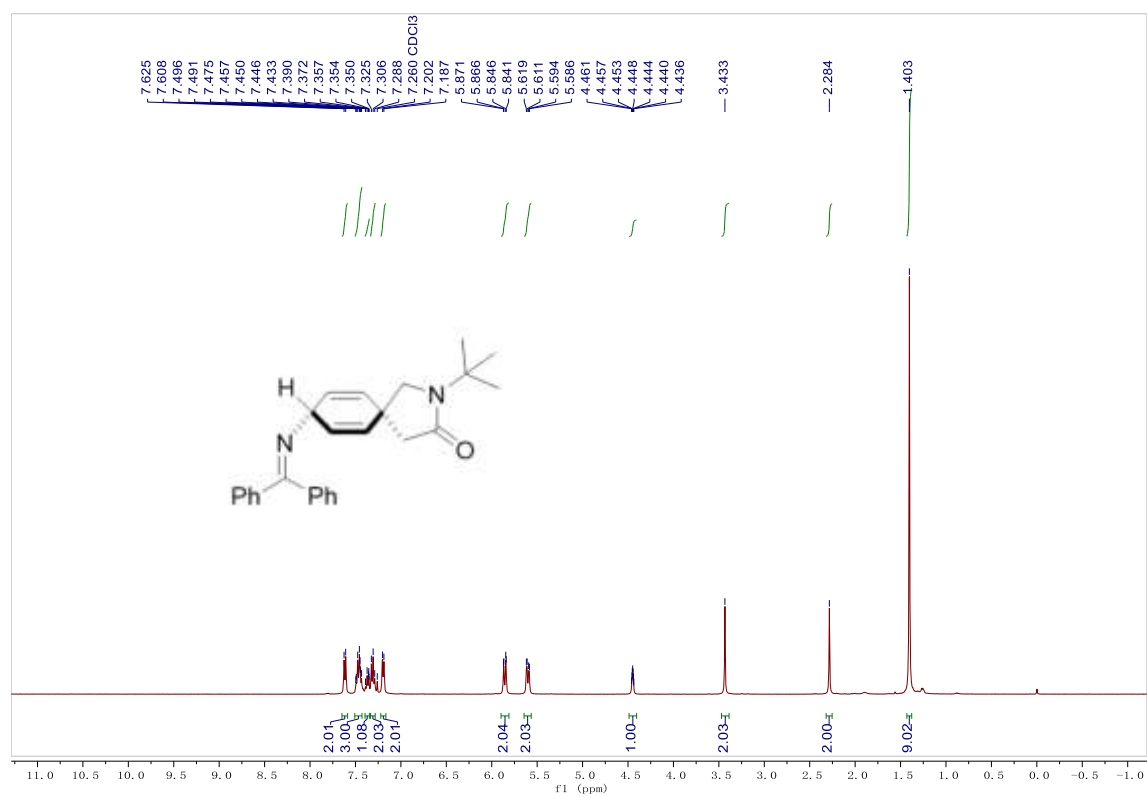
¹³C-NMR for trans-2-8



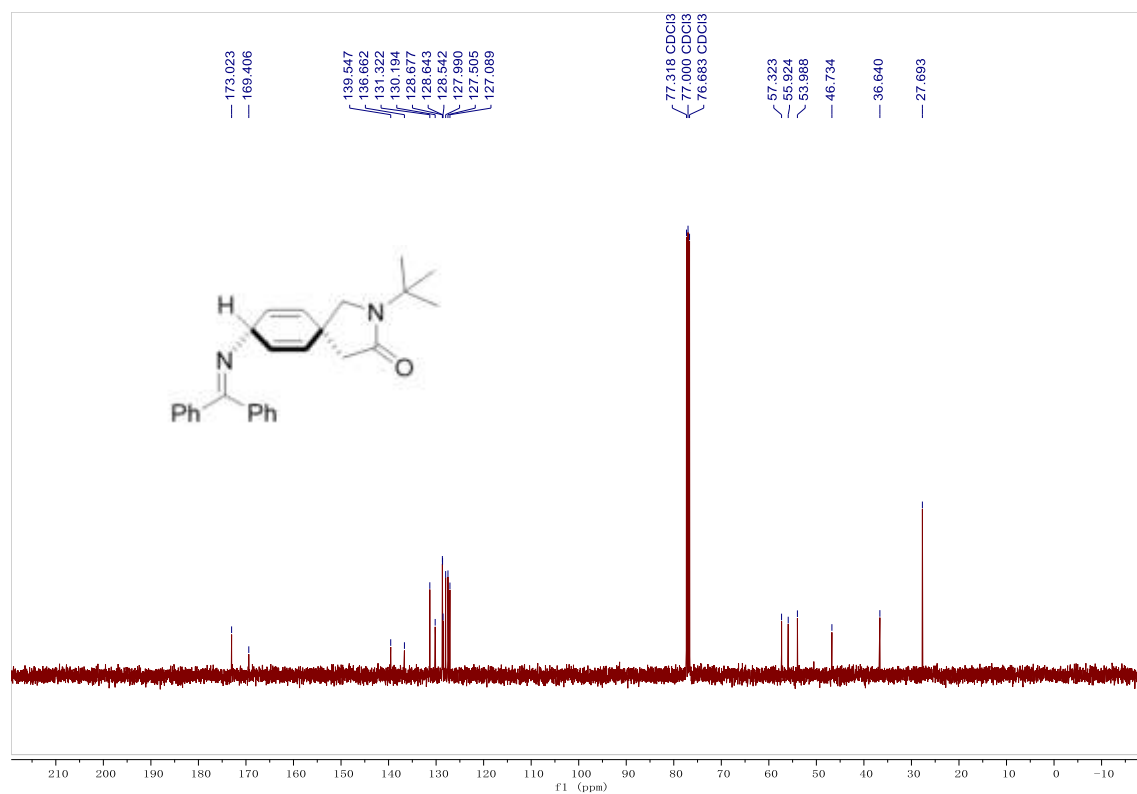
¹H-NMR for cis-2-8



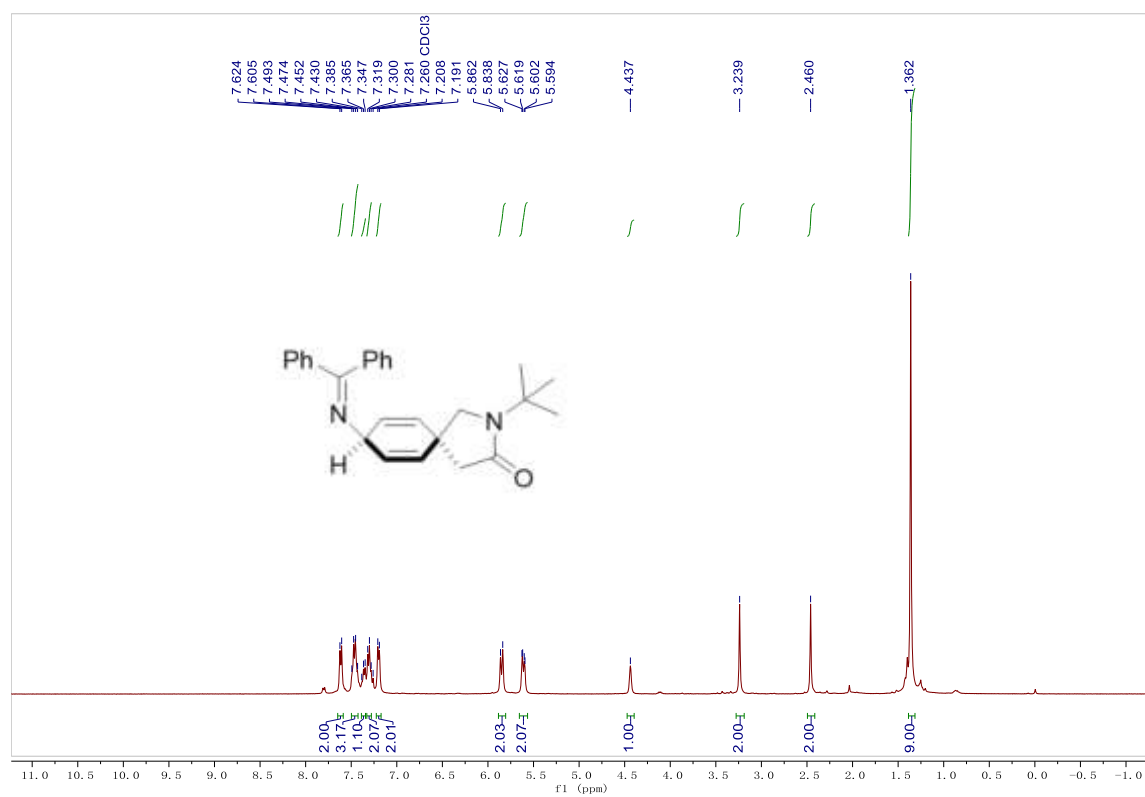
¹³C-NMR for cis-2-8



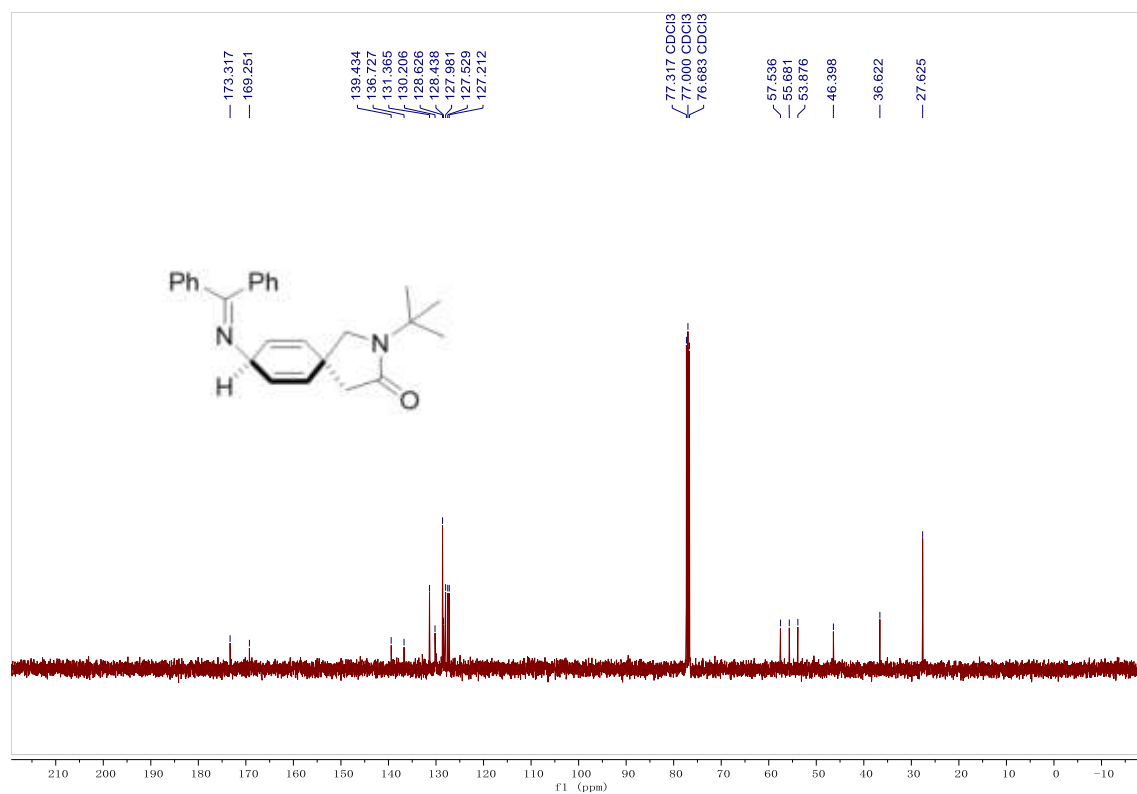
¹H-NMR for trans-2-9



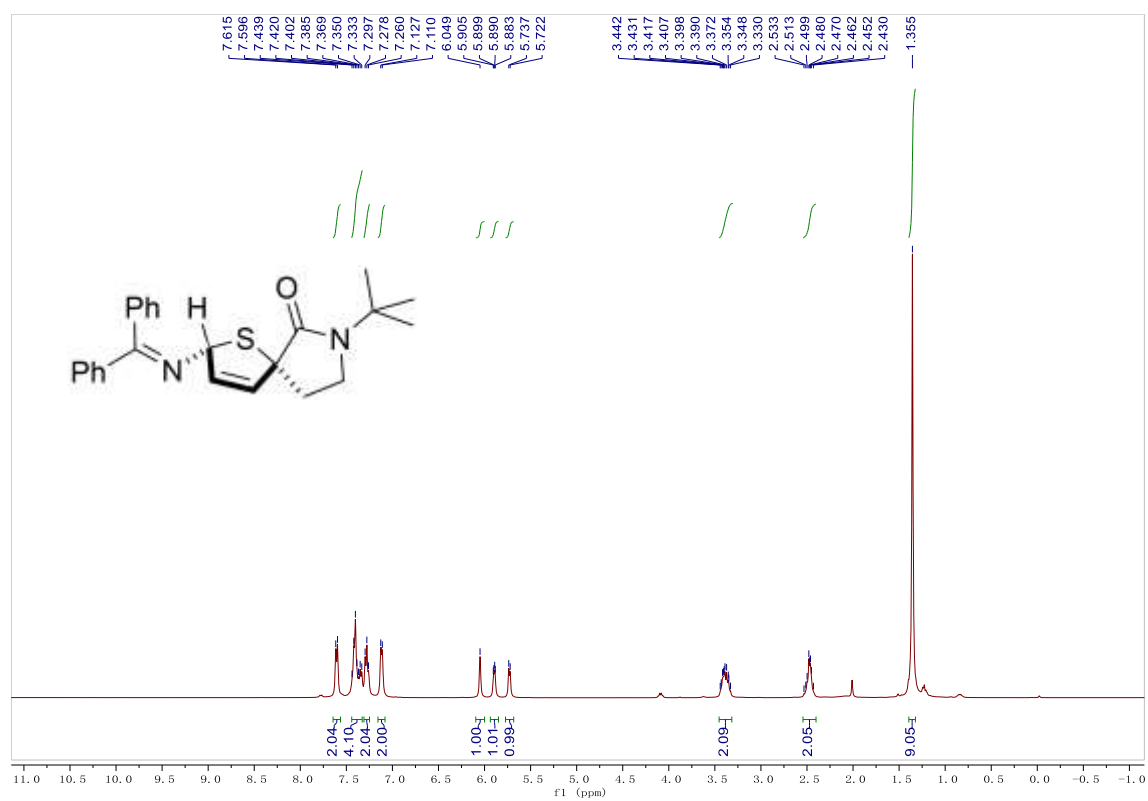
¹³C-NMR for trans-2-9



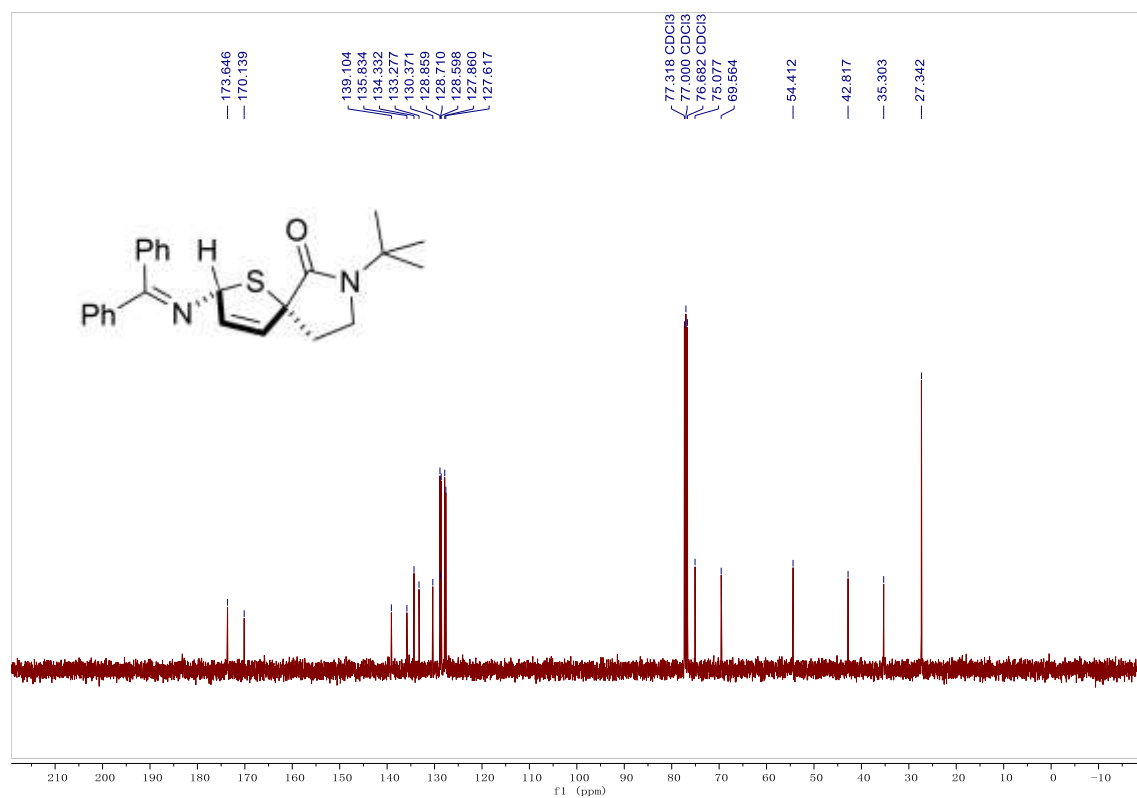
¹H-NMR for cis-2-9



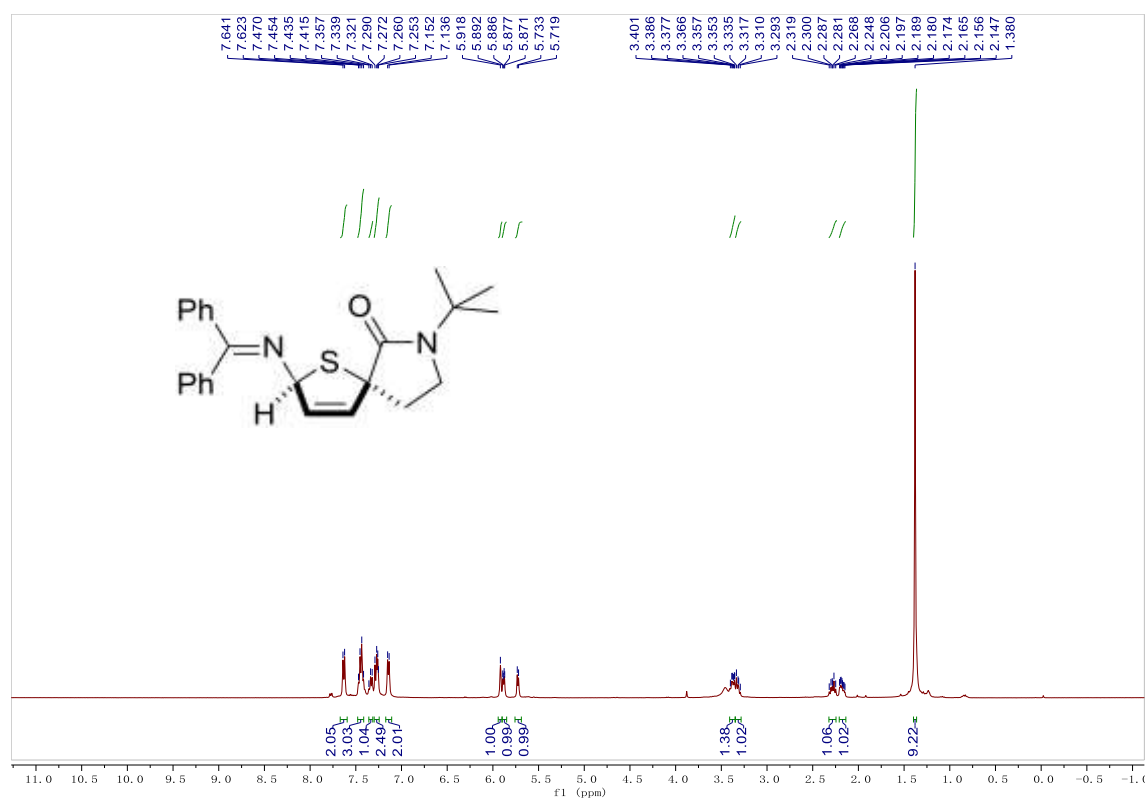
¹³C-NMR for *cis*-2-9



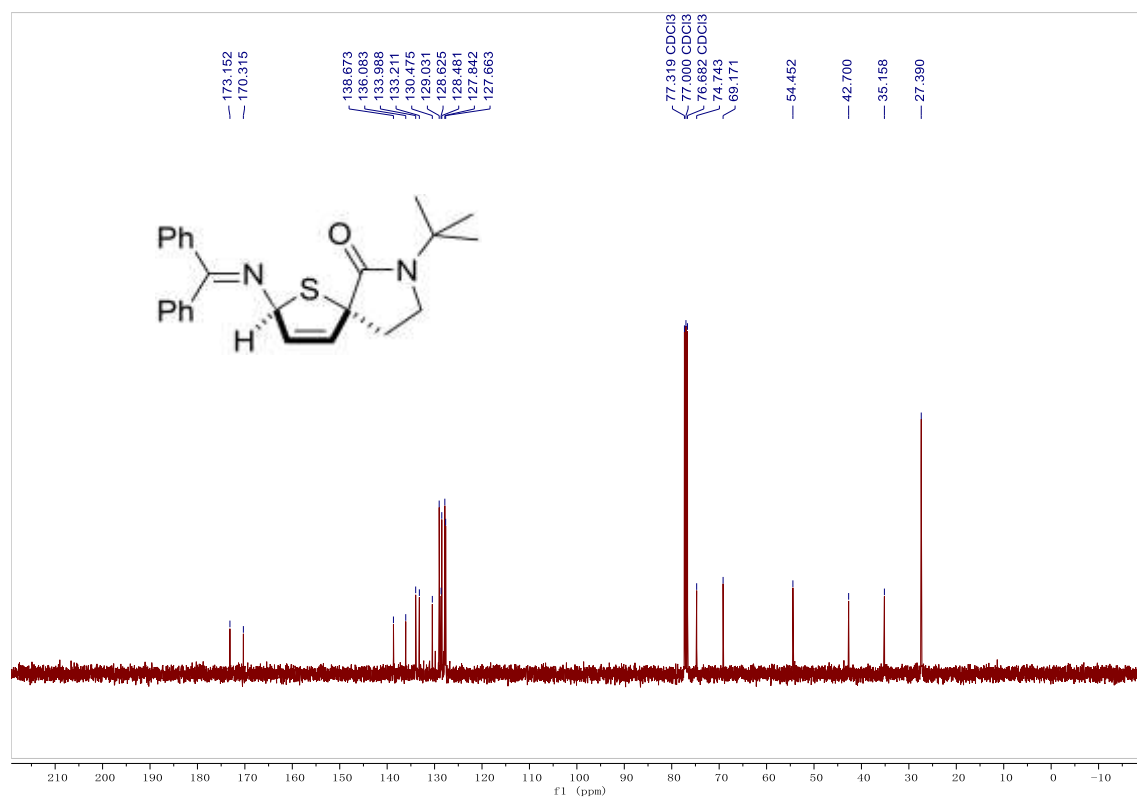
¹H-NMR for *trans*-2-10



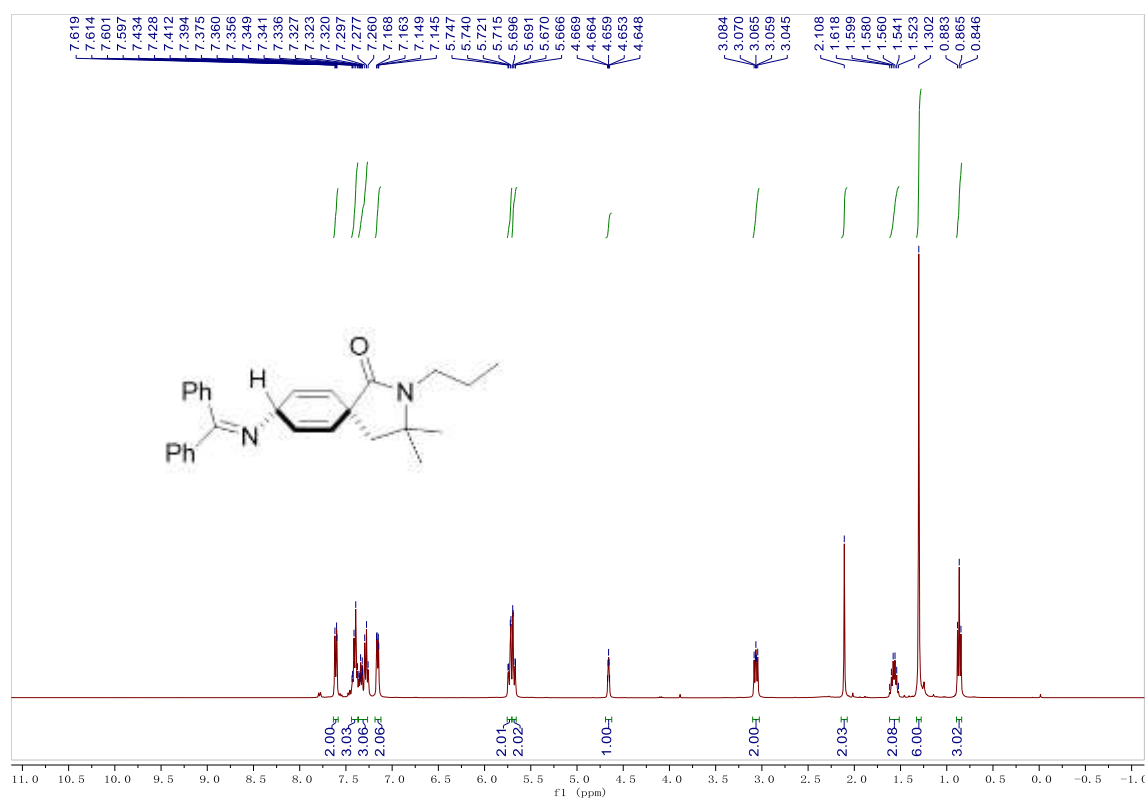
^{13}C -NMR for trans-2-10



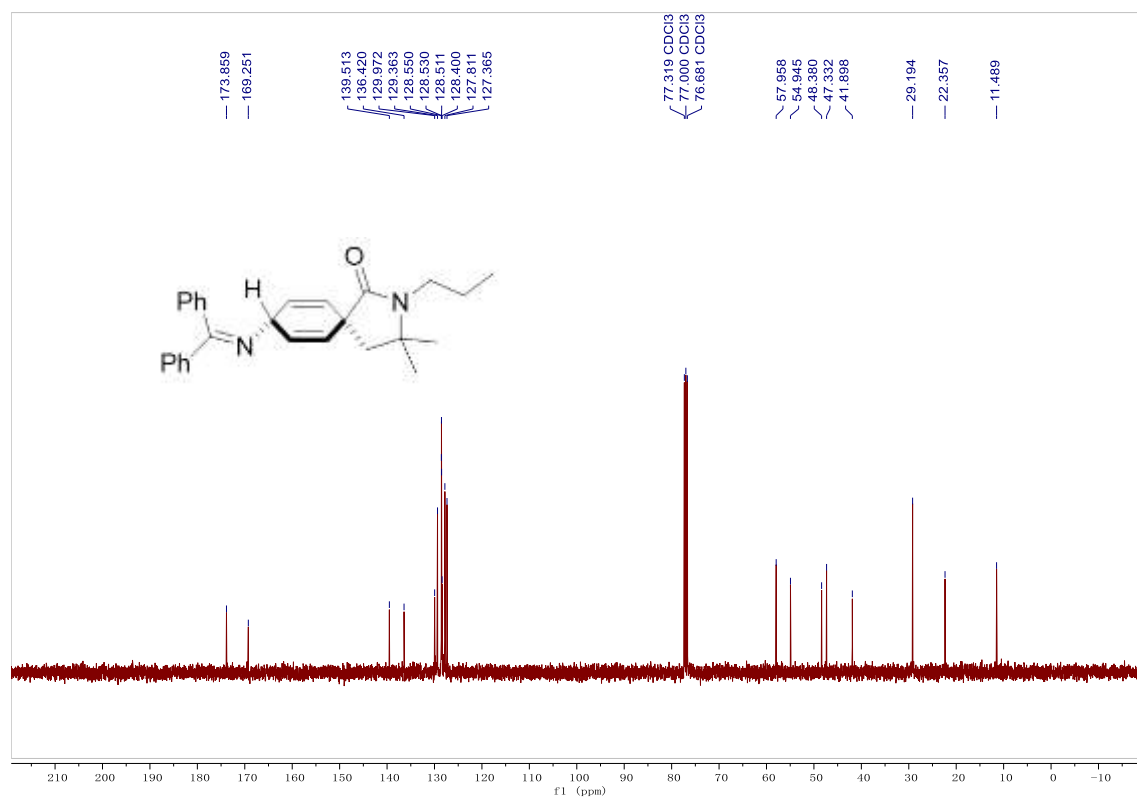
^1H -NMR for cis-2-10



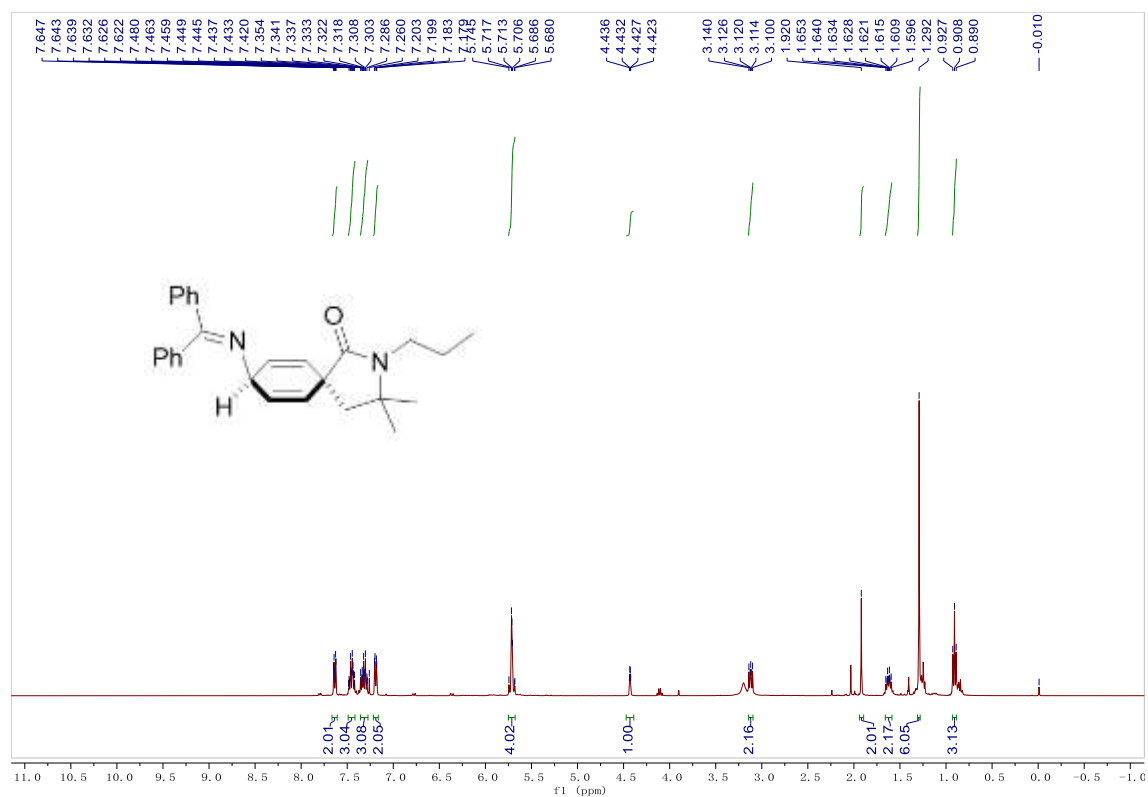
¹³C-NMR for **cis-2-10**



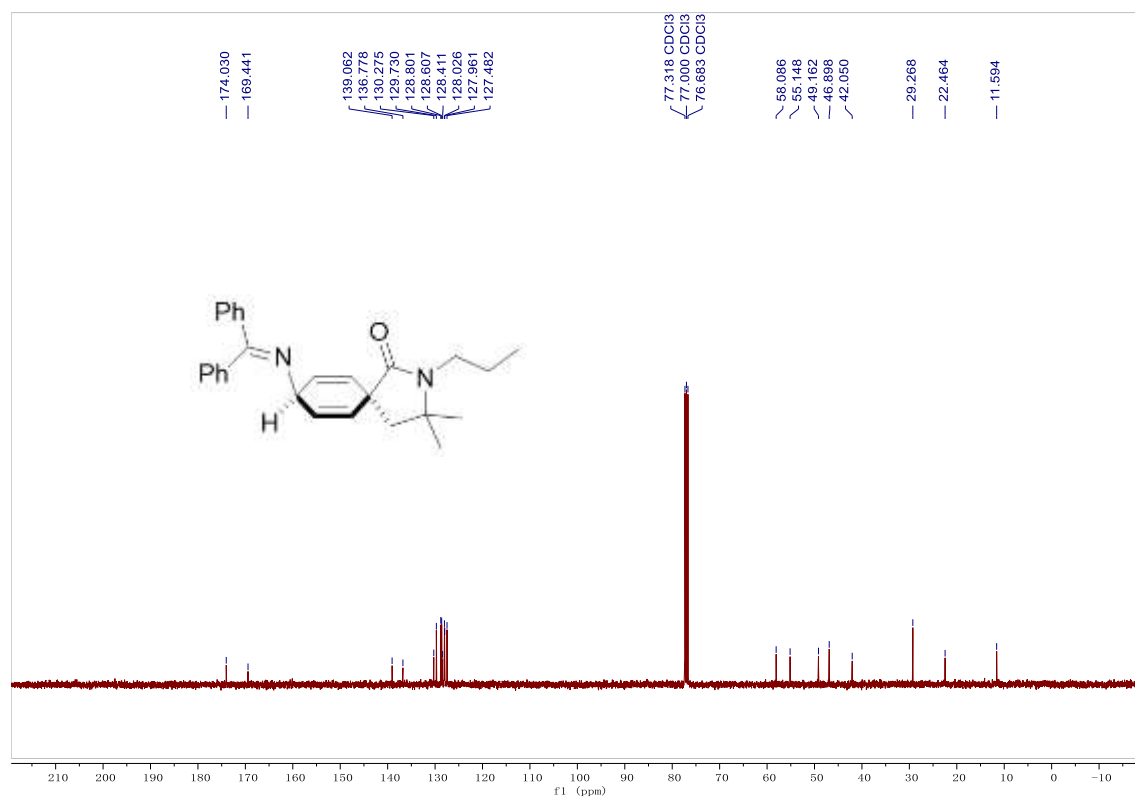
¹H-NMR for **trans-2-11**



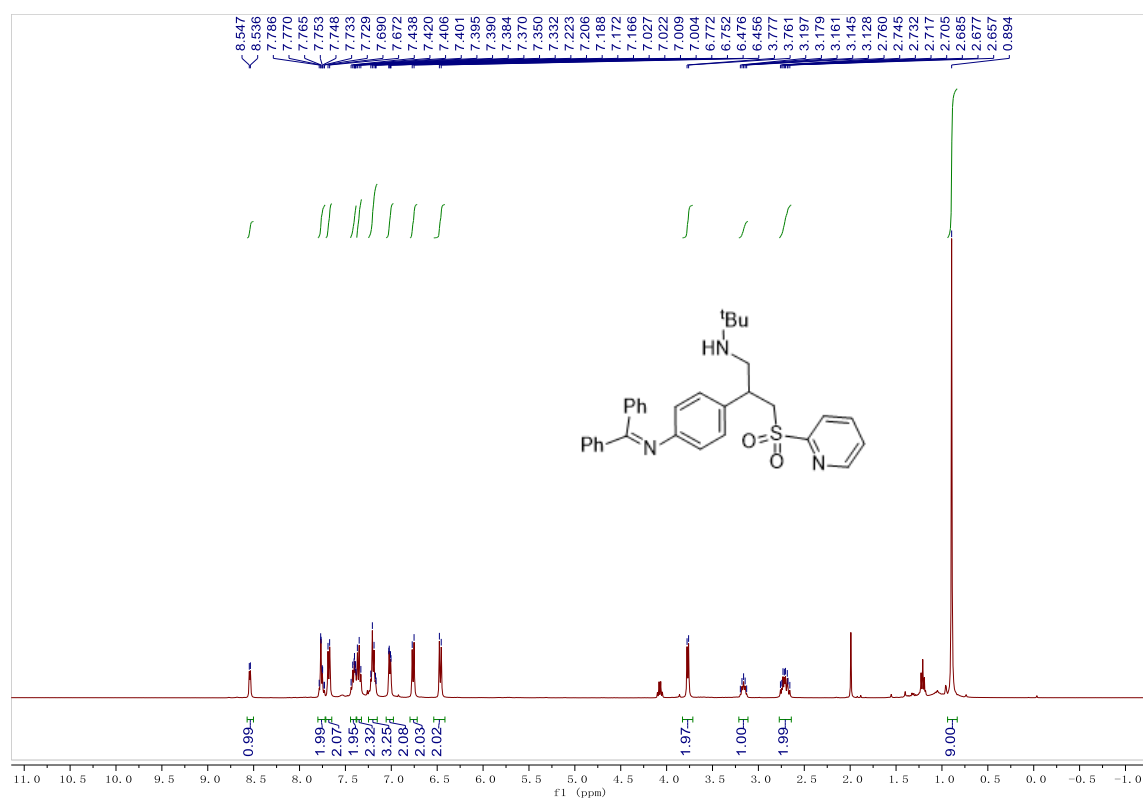
¹³C-NMR for trans-2-11



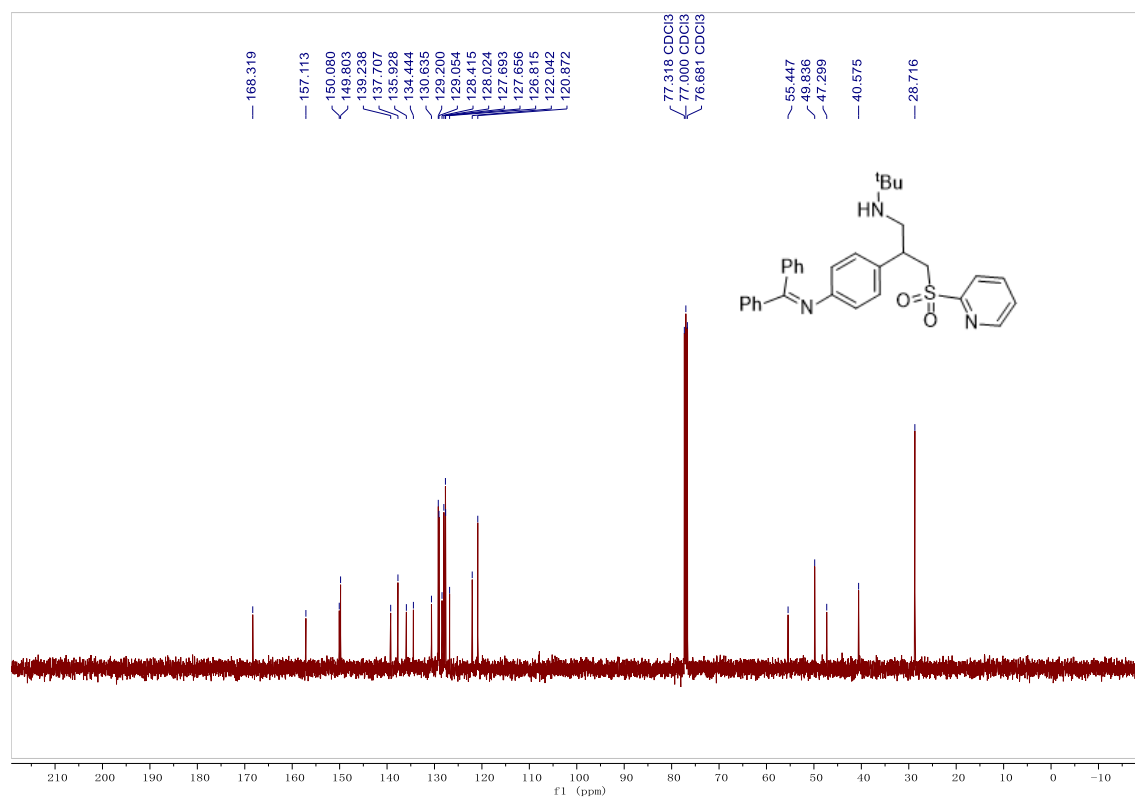
¹H-NMR for cis-2-11



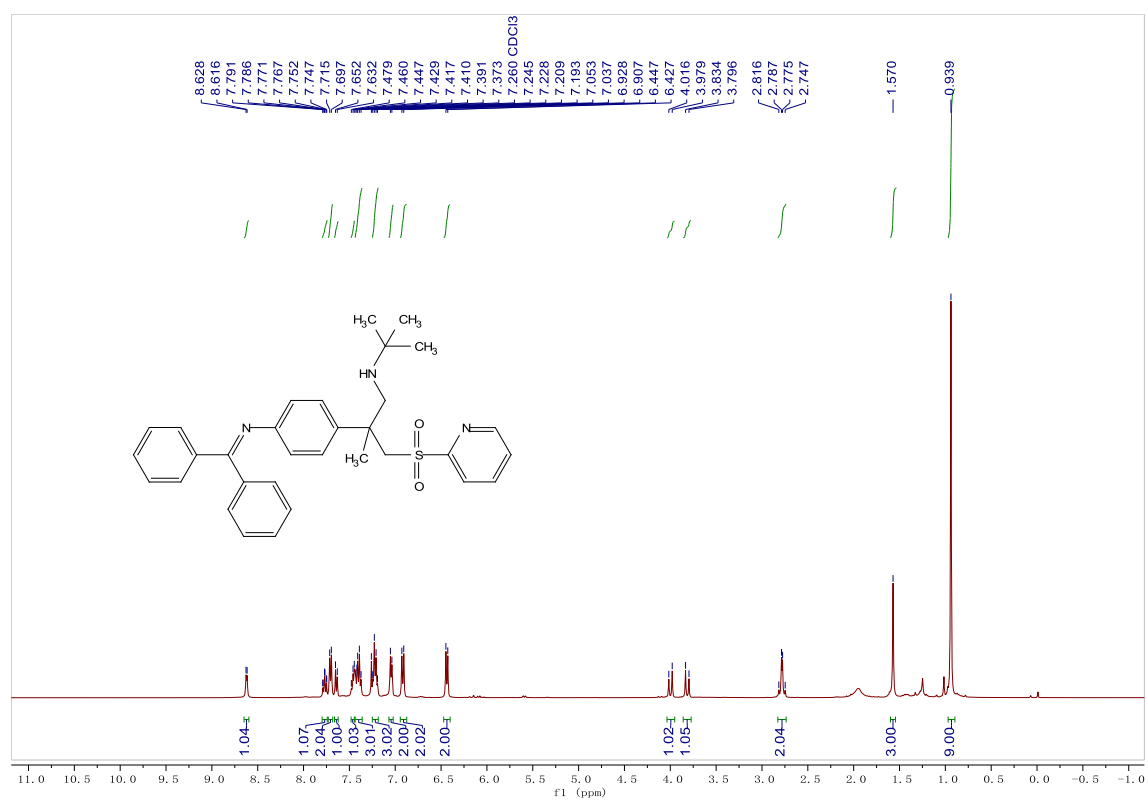
¹³C-NMR for cis-2-11



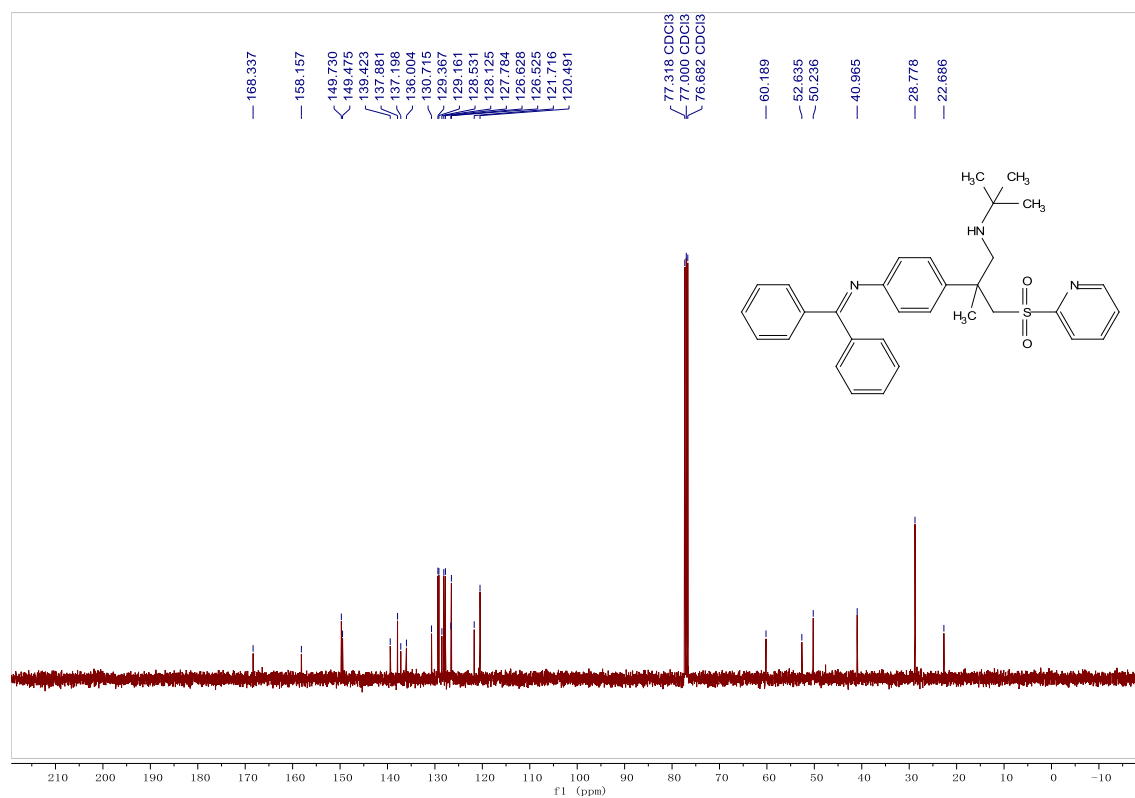
¹H-NMR for 6-1



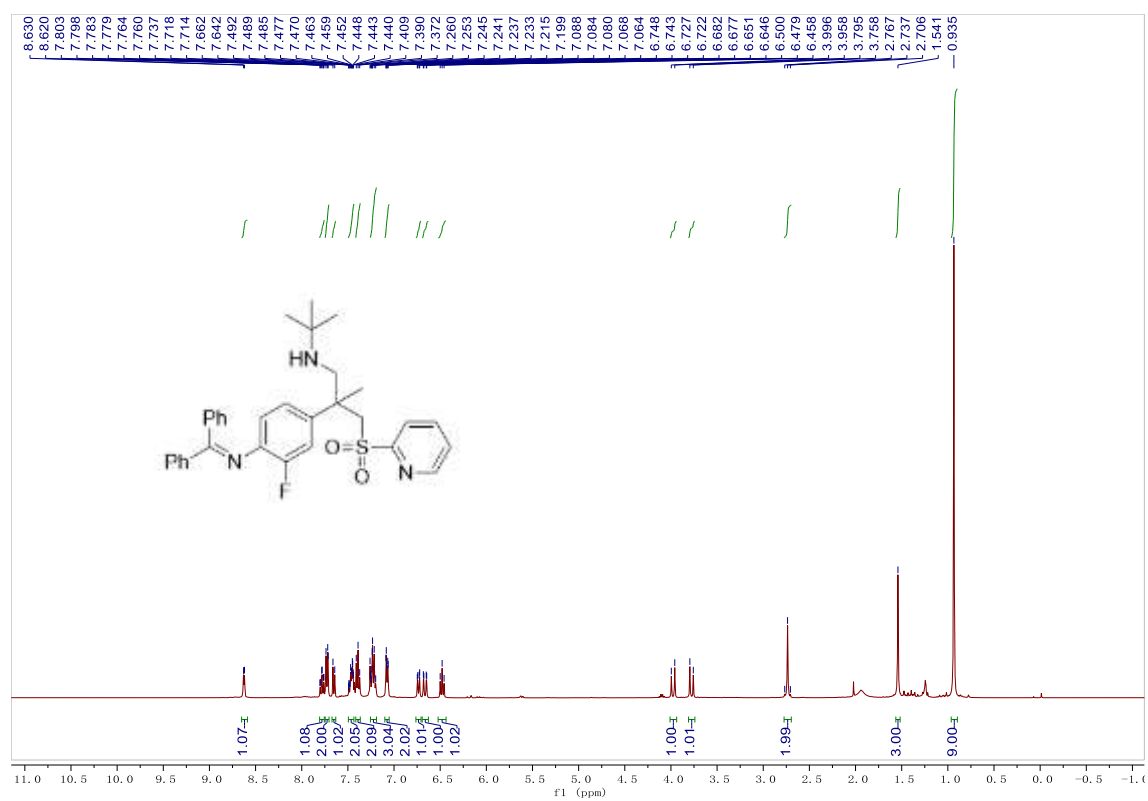
¹³C-NMR for 6-1



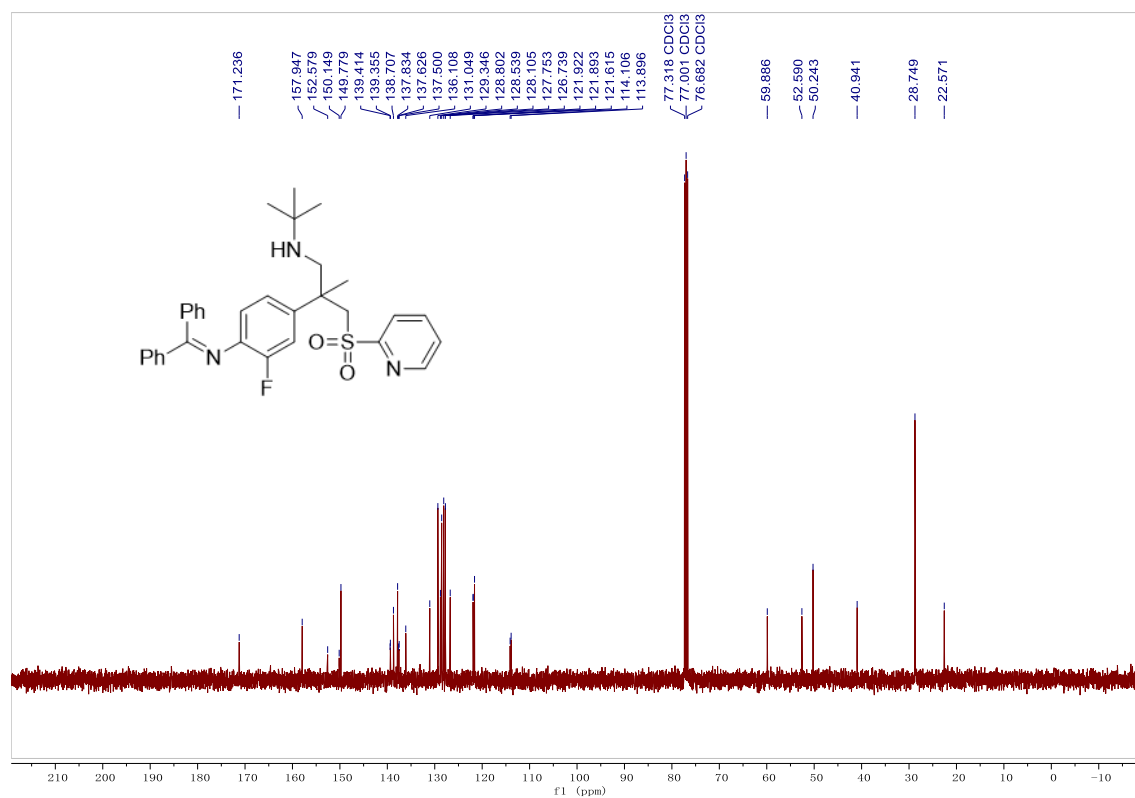
¹H-NMR for 6-2



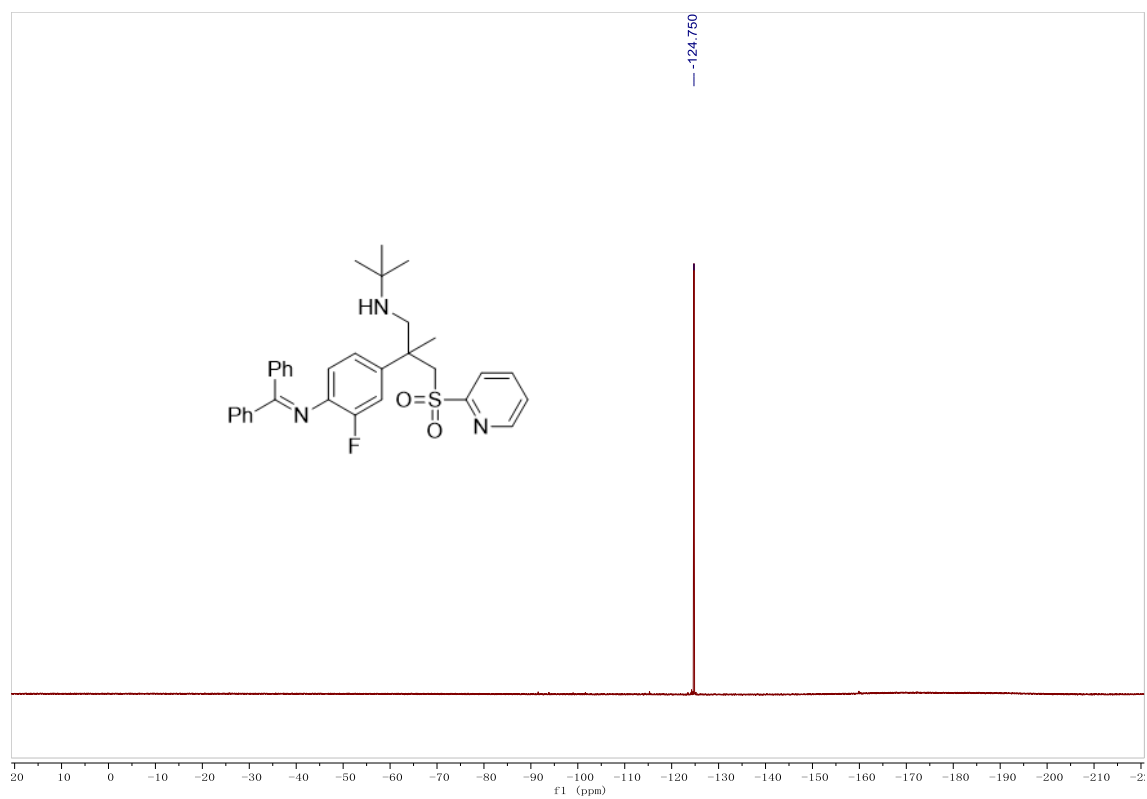
¹³C-NMR for 6-2



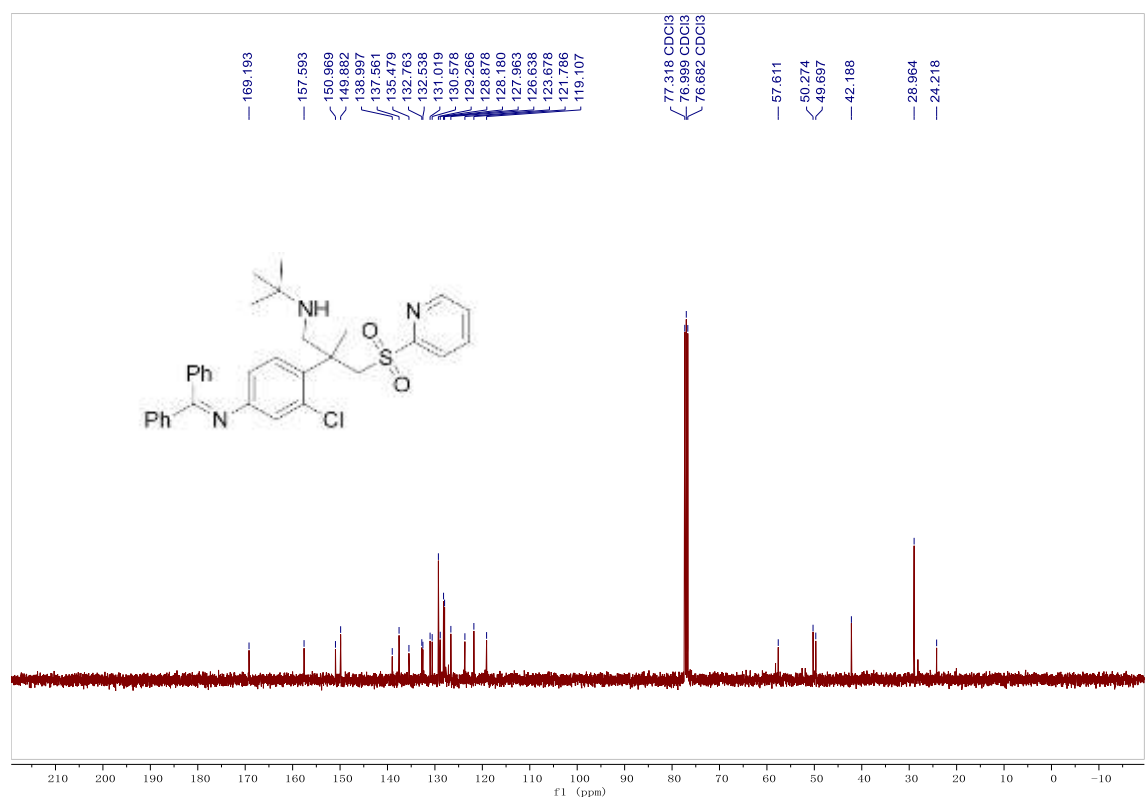
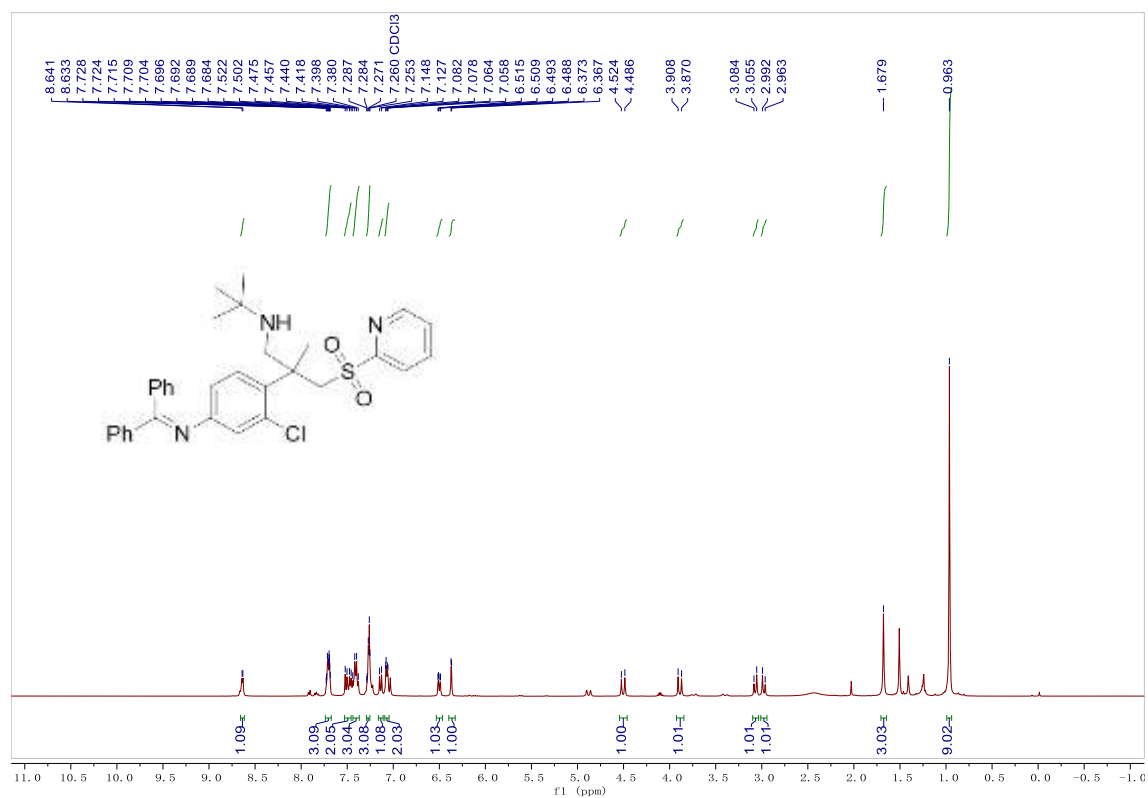
¹H-NMR for 6-3

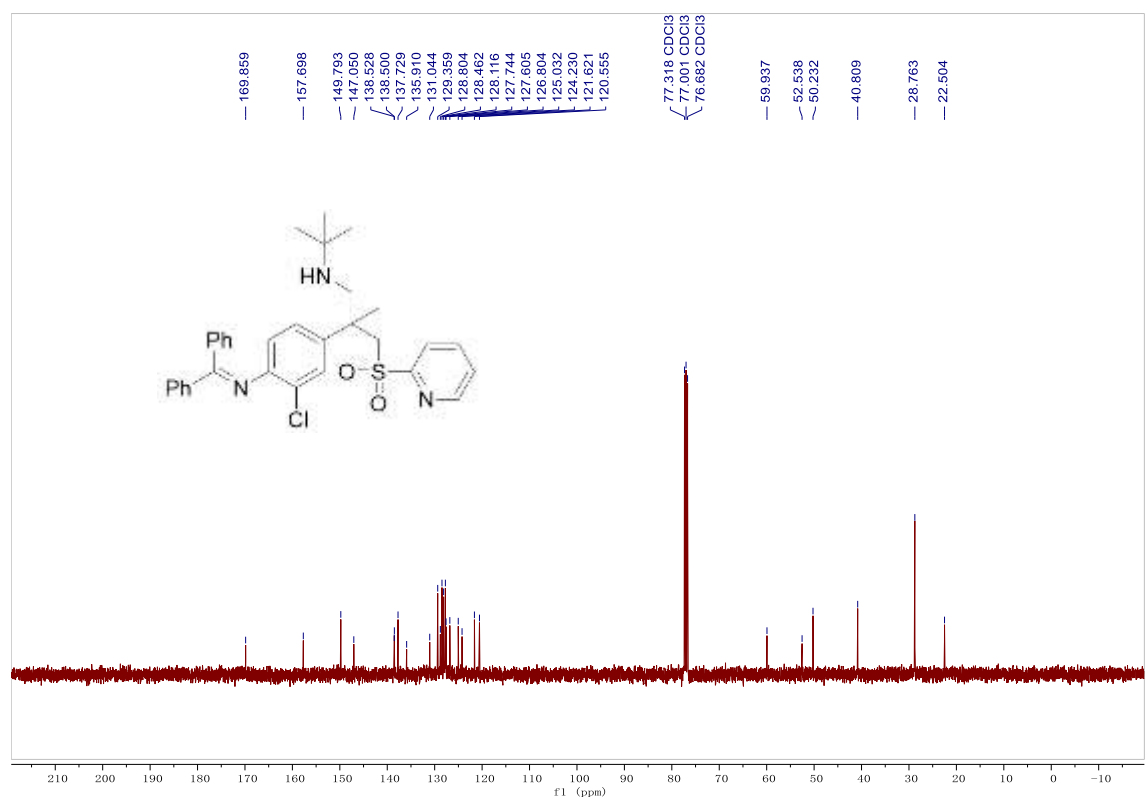
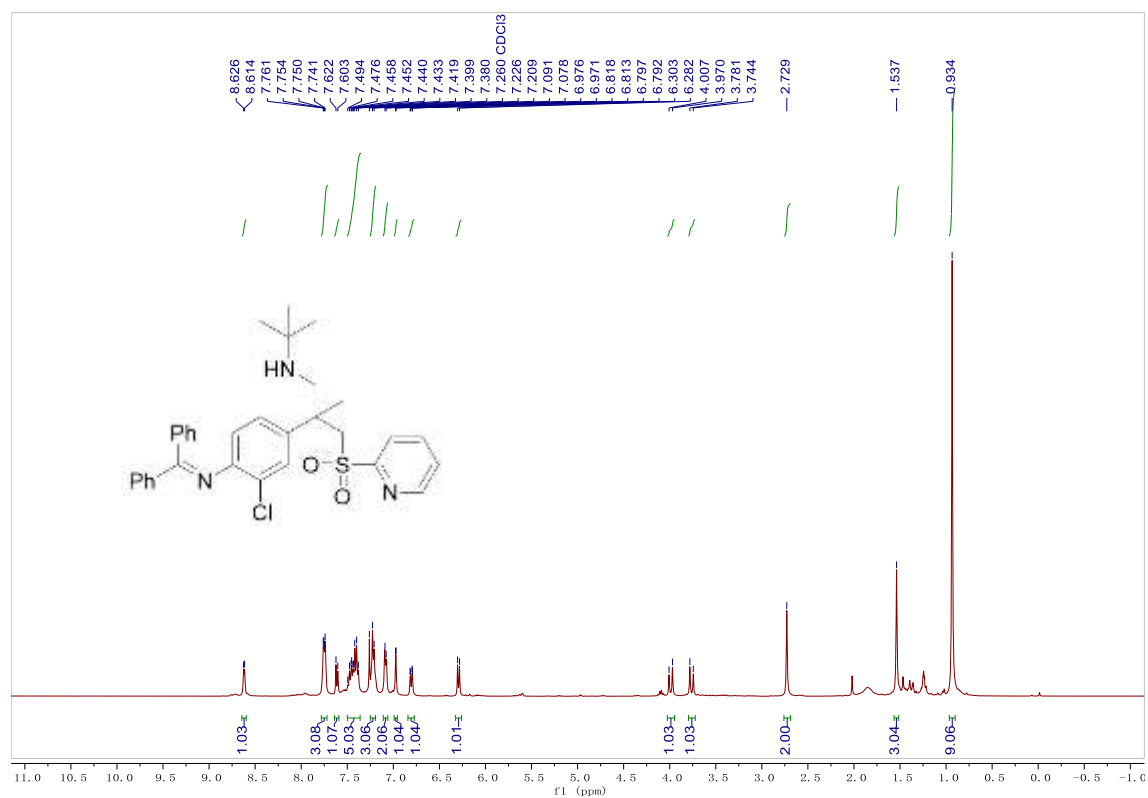


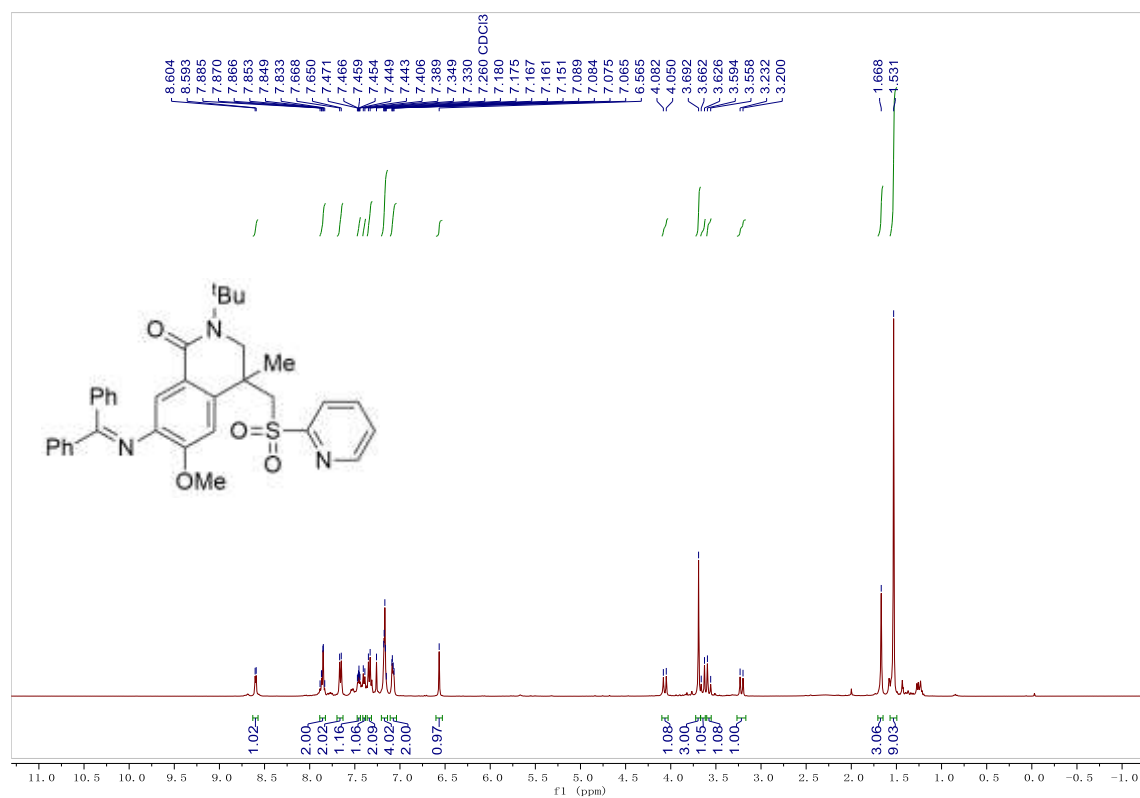
¹³C-NMR for 6-3



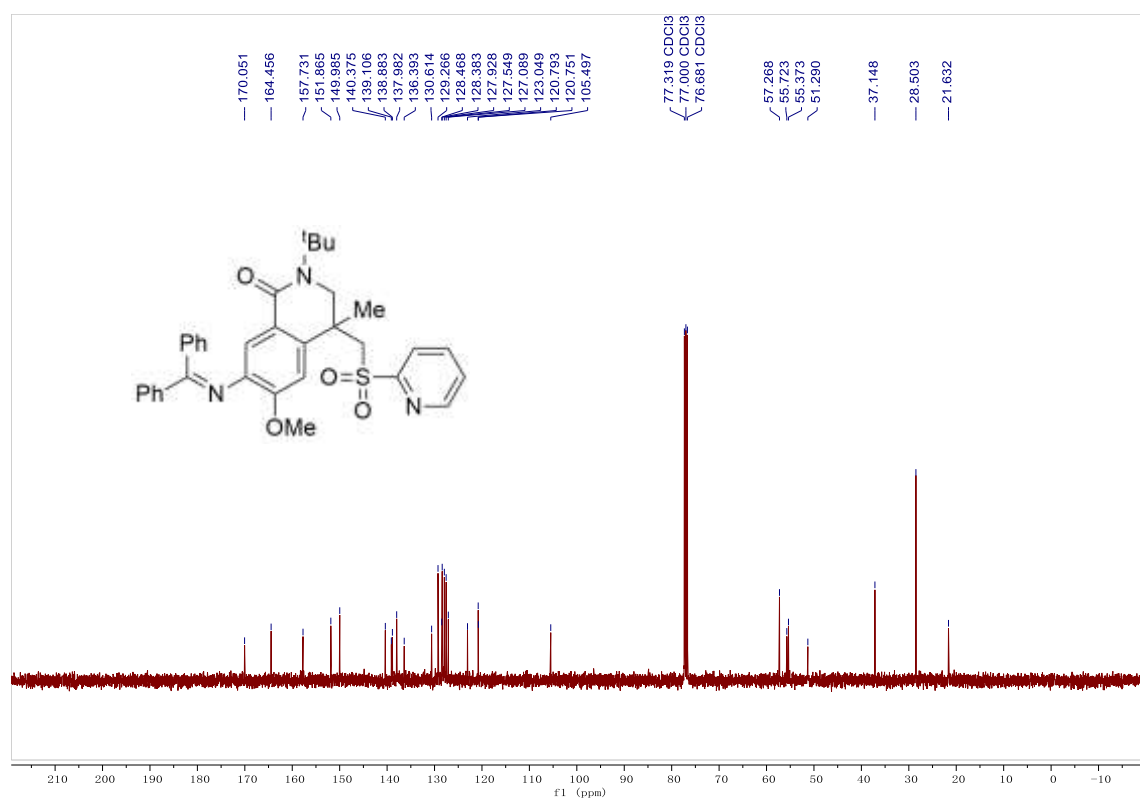
¹⁹F-NMR for 6-3



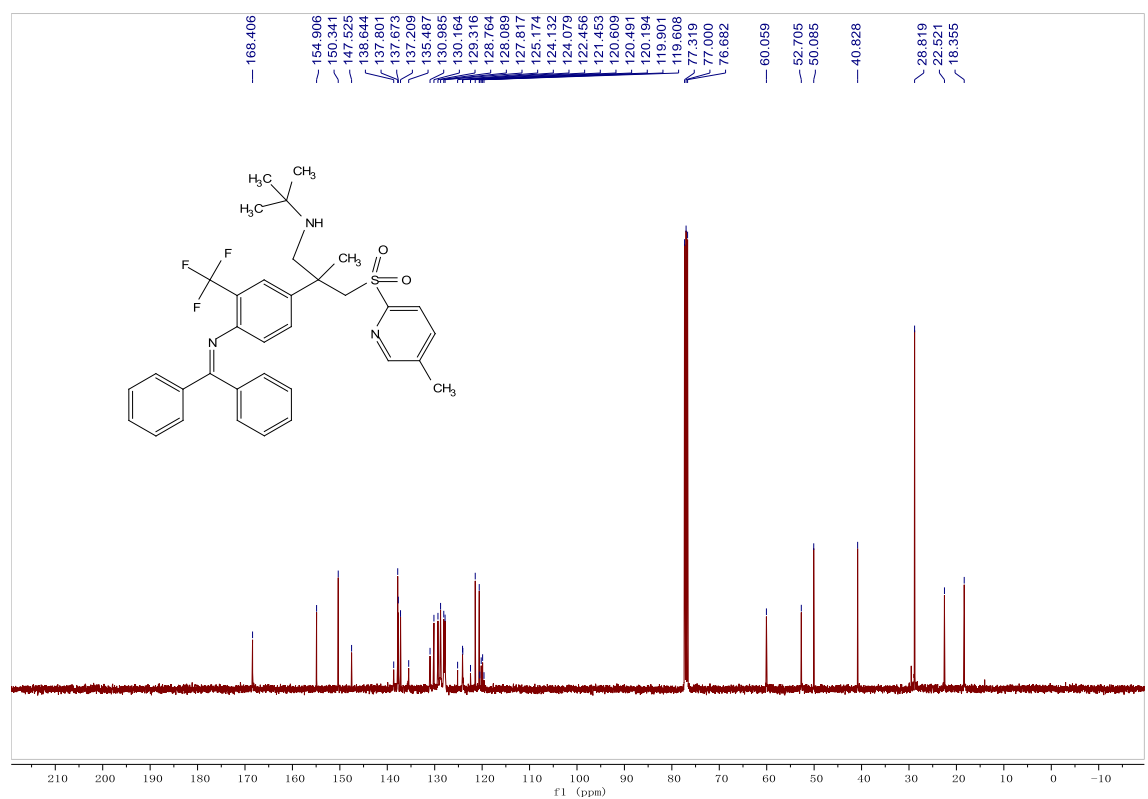
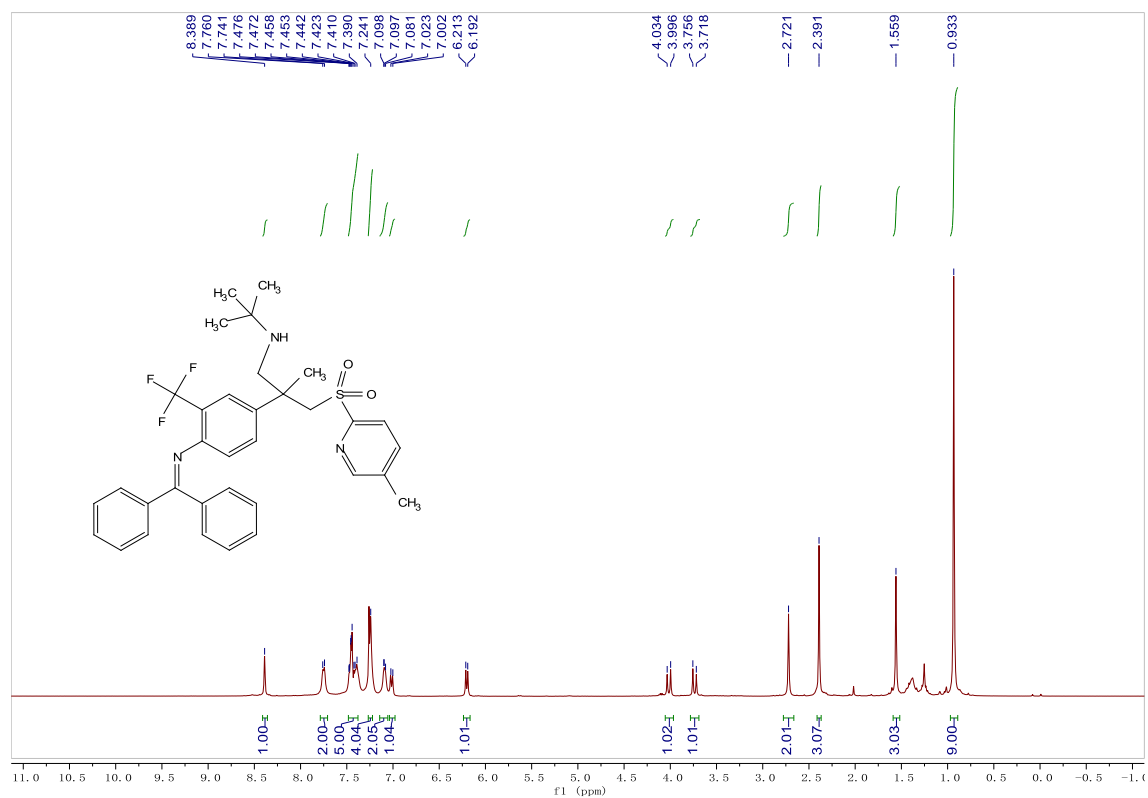




¹H-NMR for 6-6

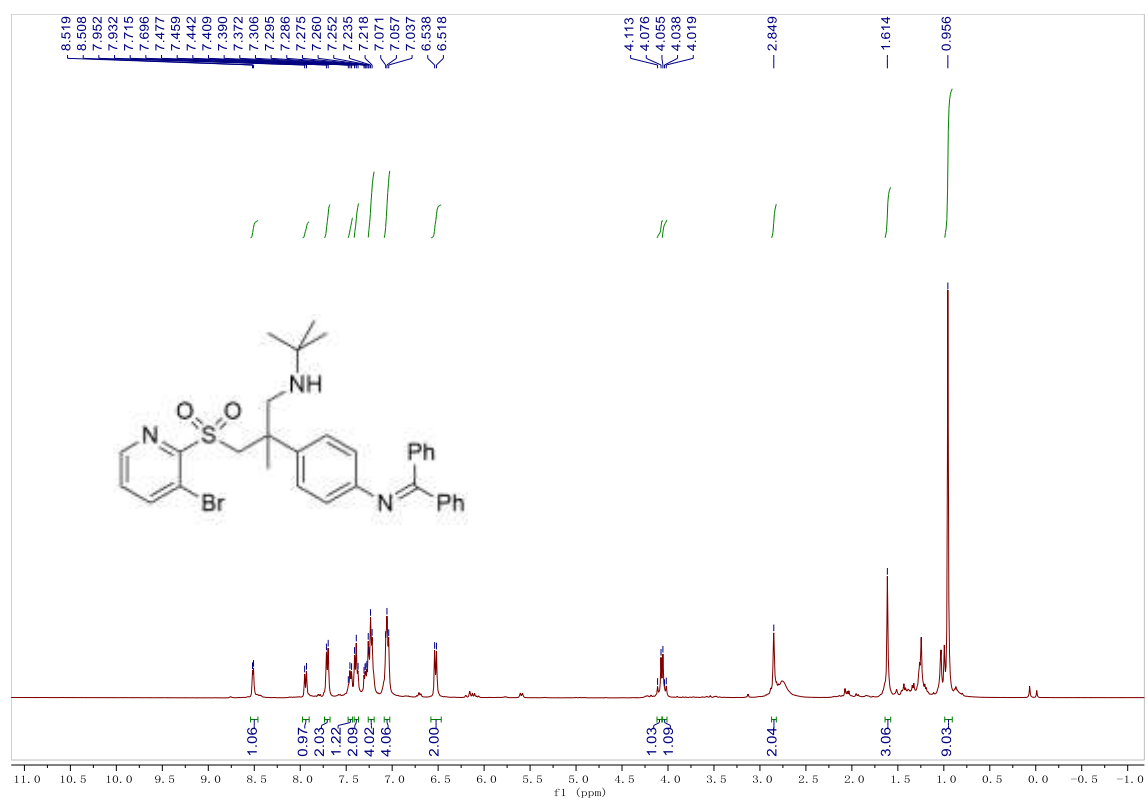


¹³C-NMR for 6-6

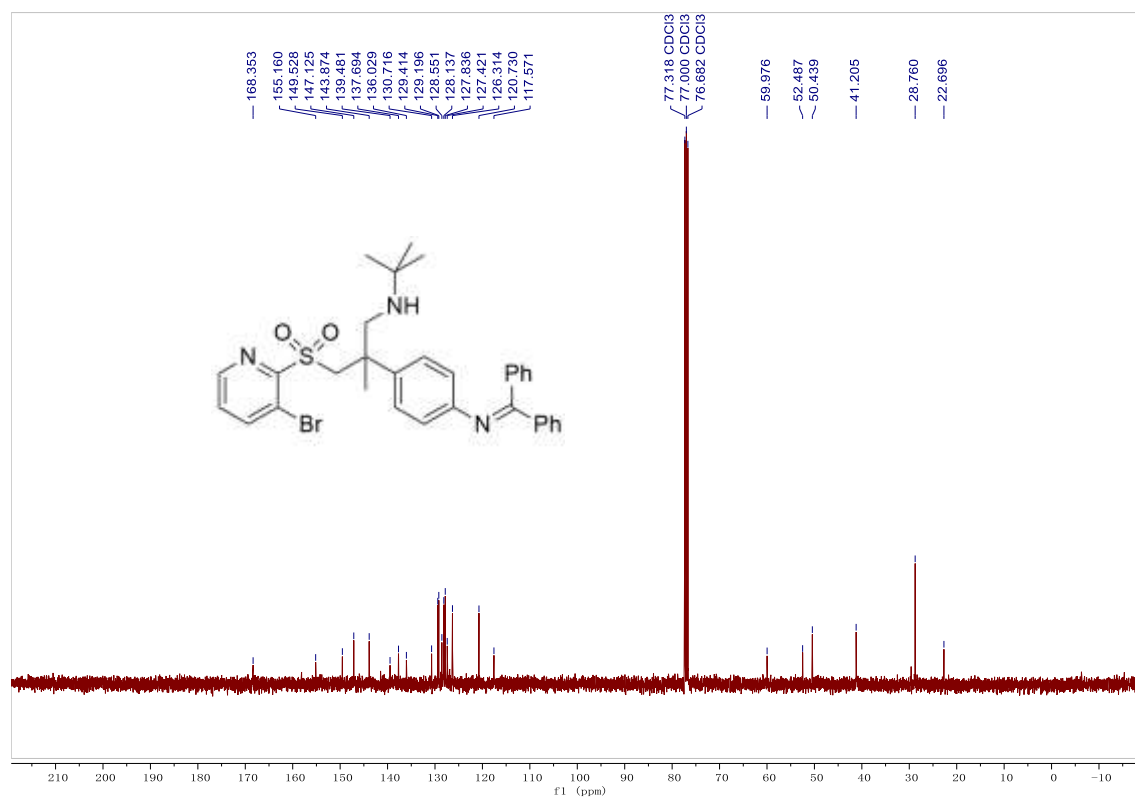




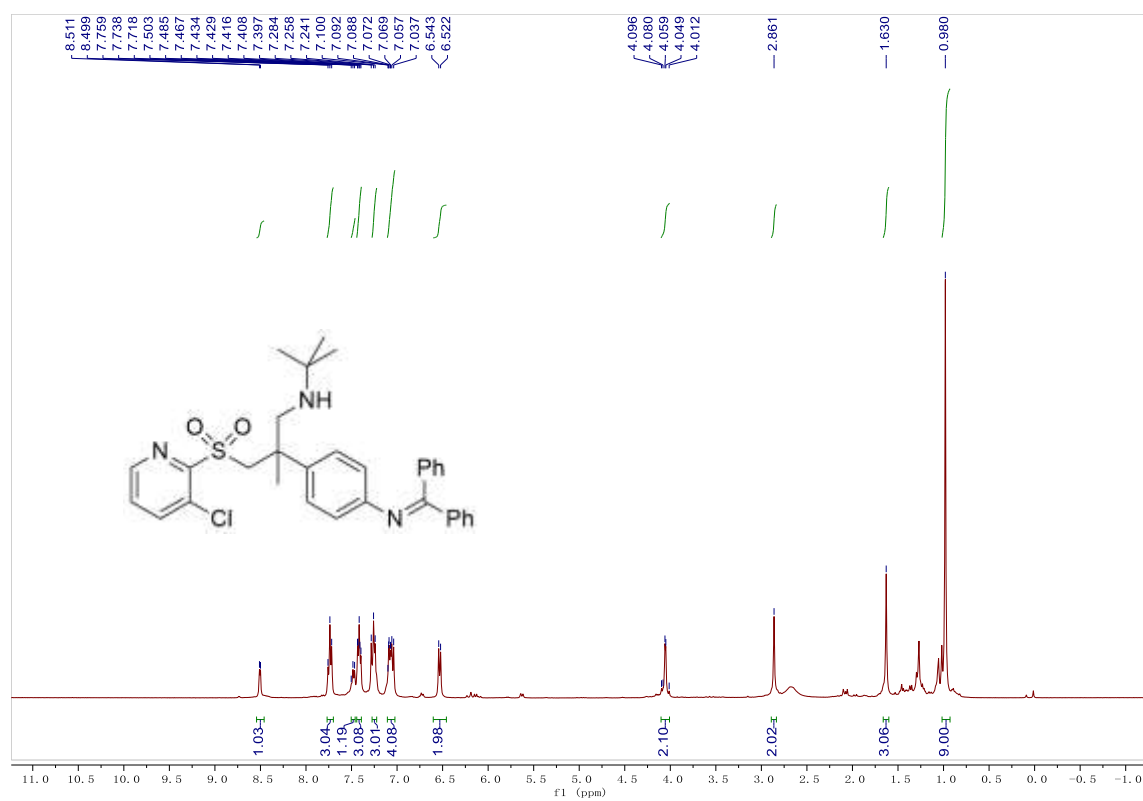
¹⁹F-NMR for 6-7



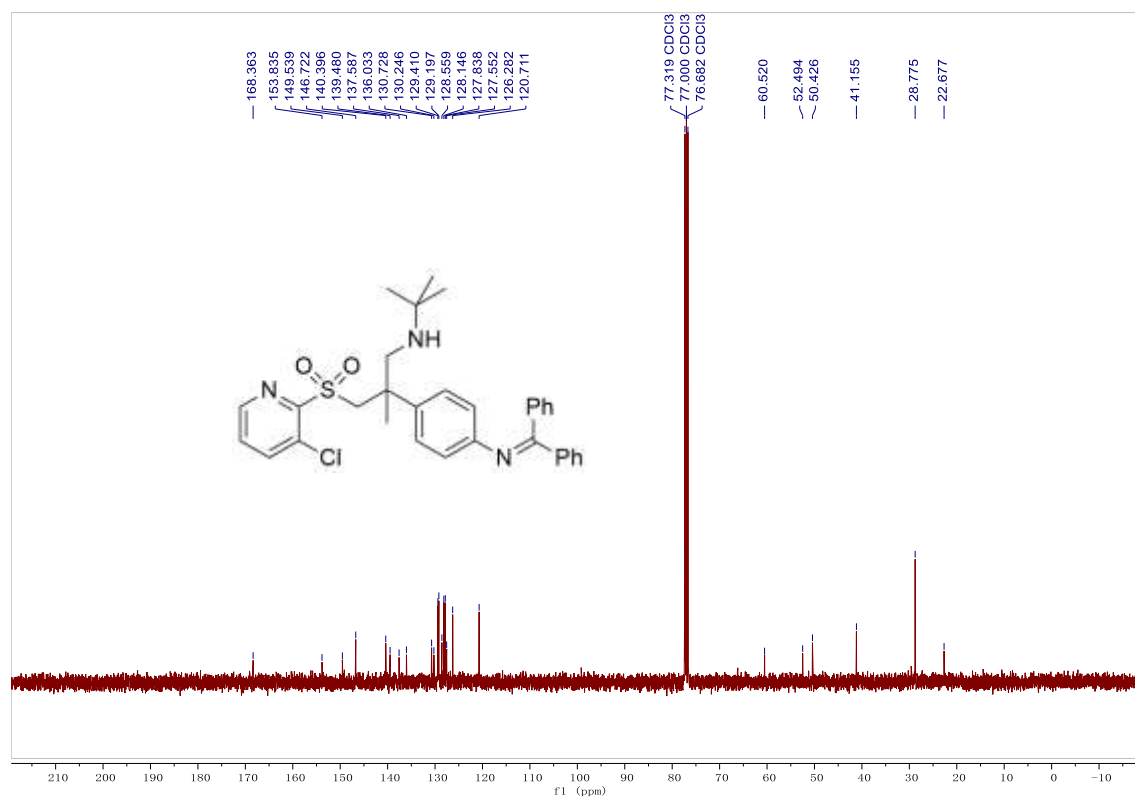
¹H-NMR for 6-8



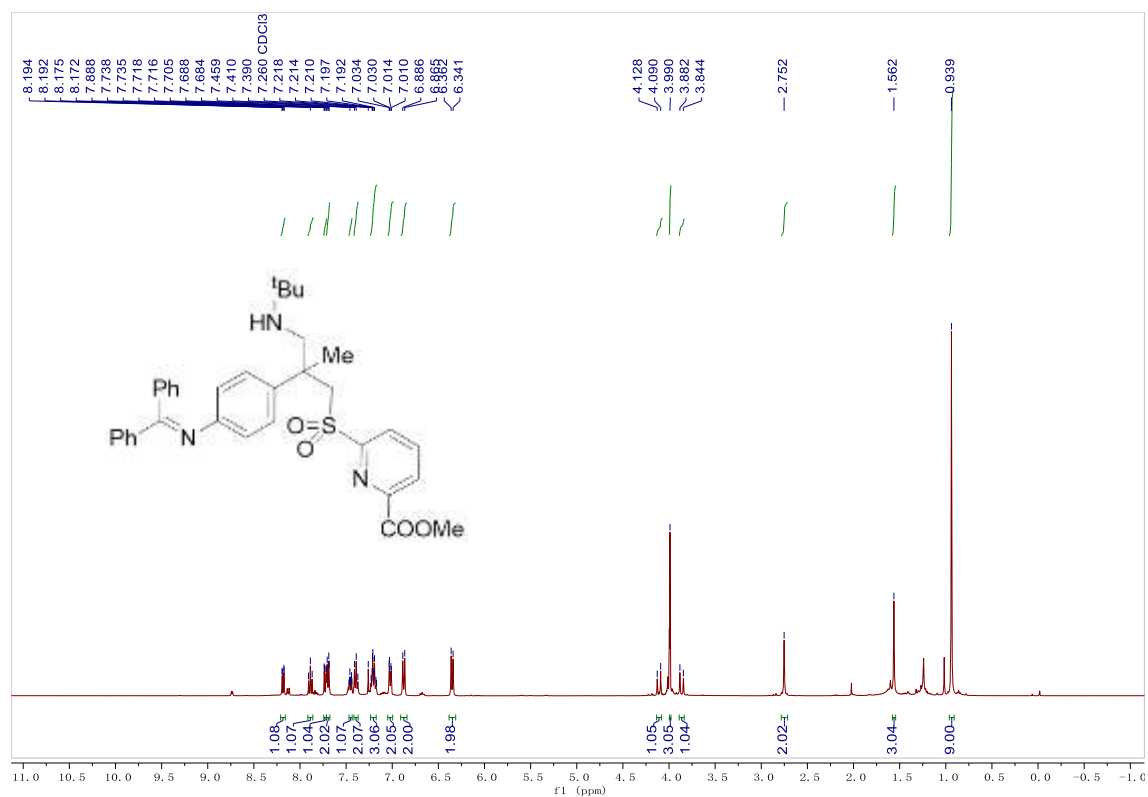
¹³C-NMR for 6-8



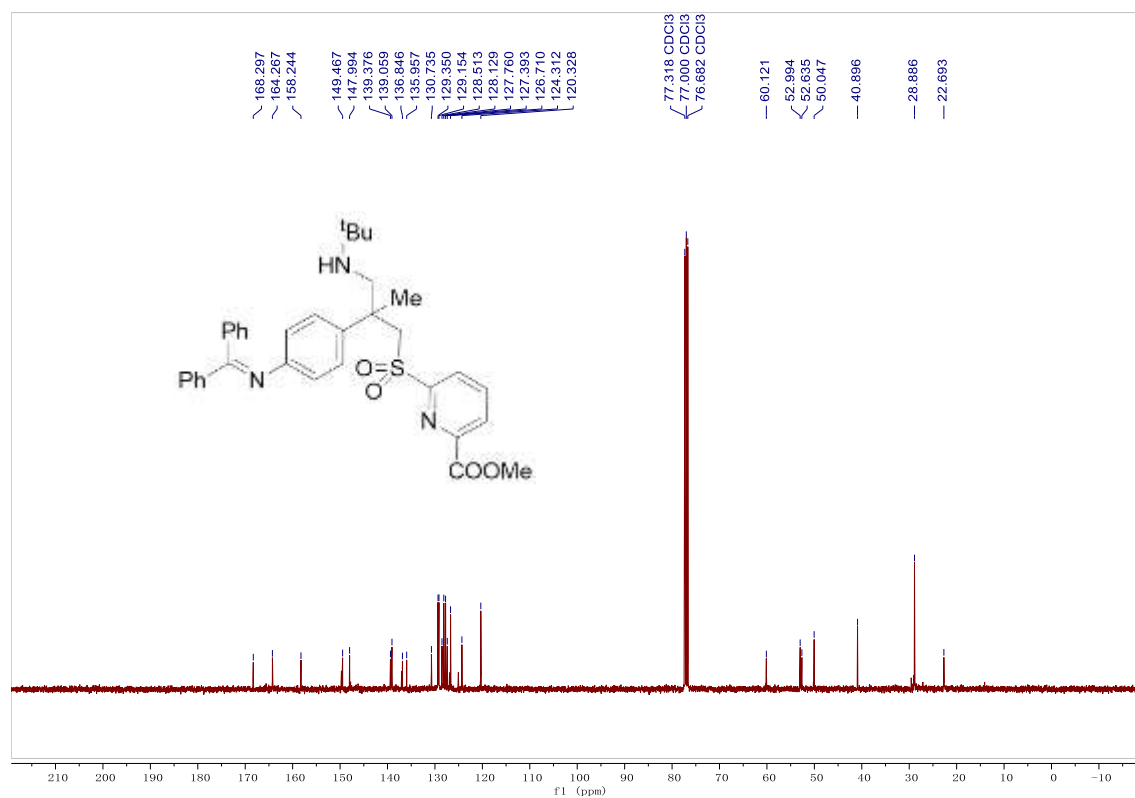
¹H-NMR for 6-9



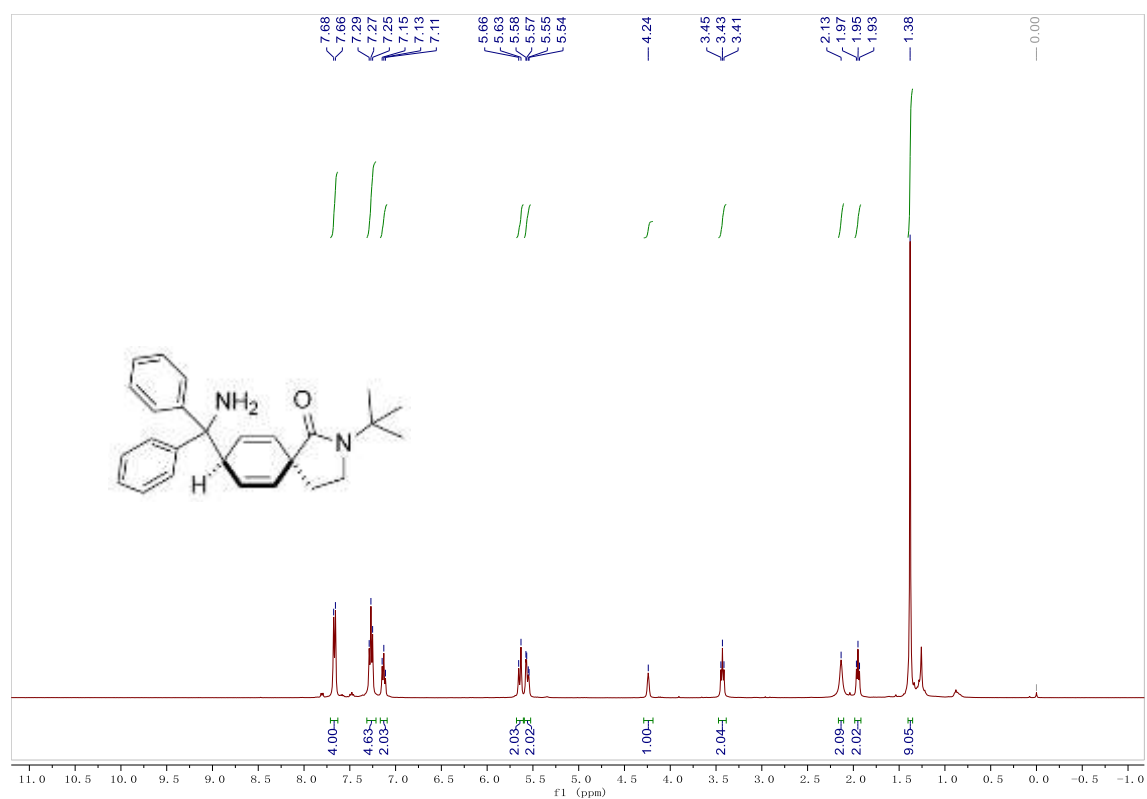
¹³C-NMR for 6-9



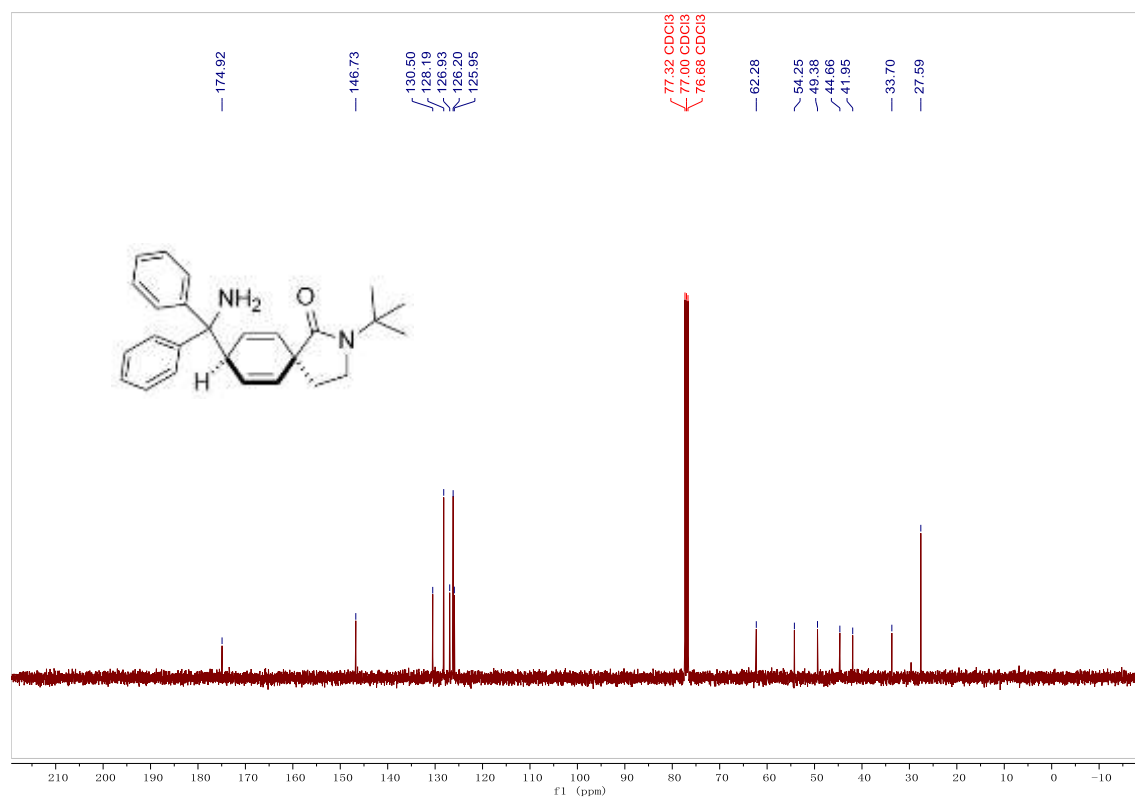
¹H-NMR for 6-10



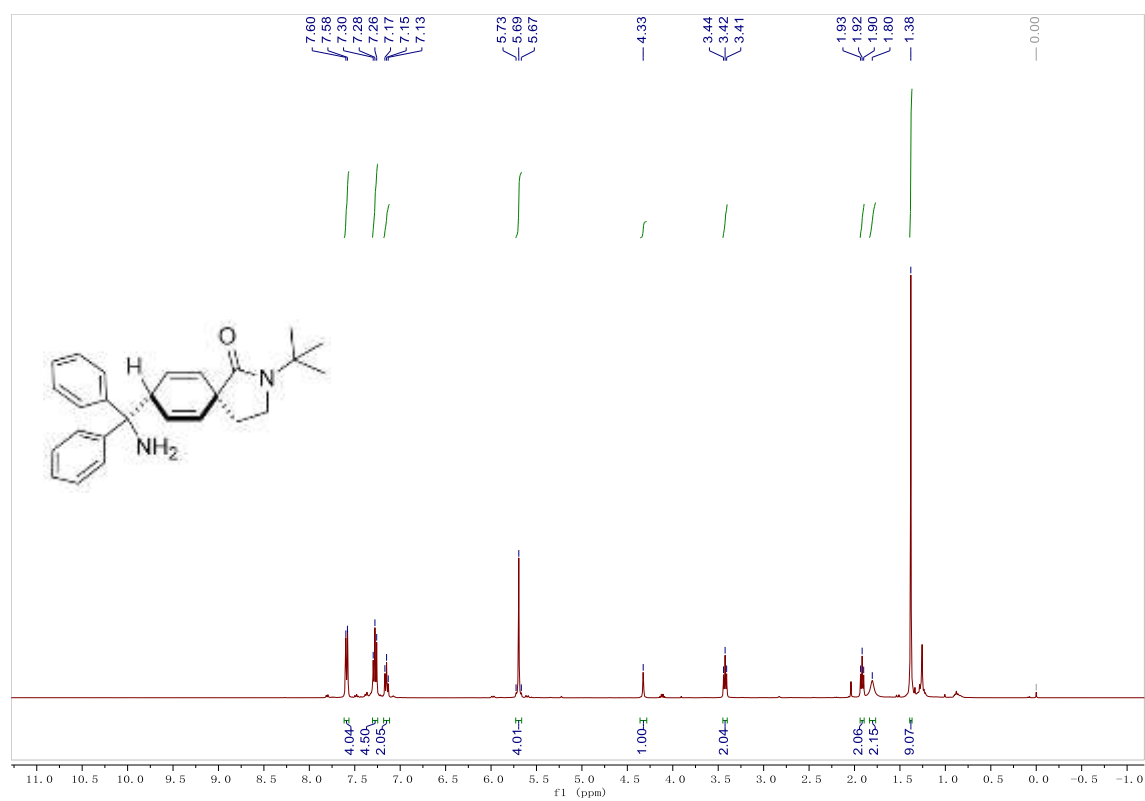
^{13}C -NMR for 6-10



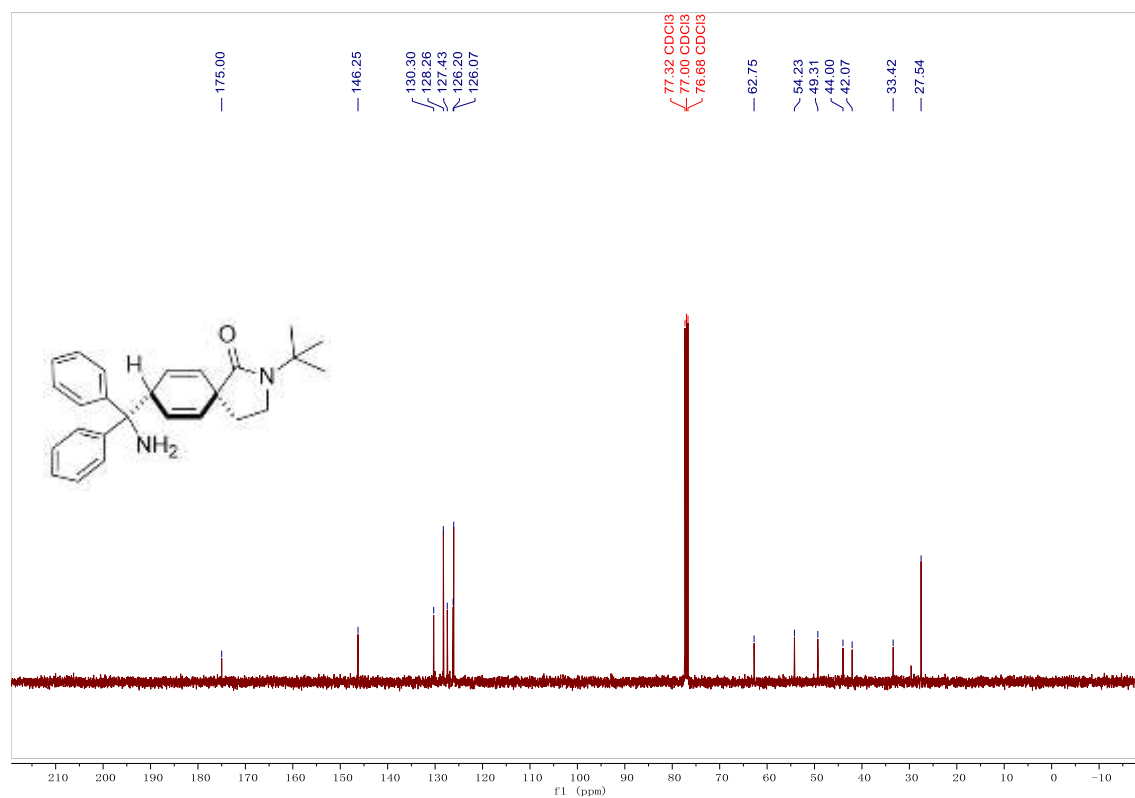
^1H -NMR for cis-3-1



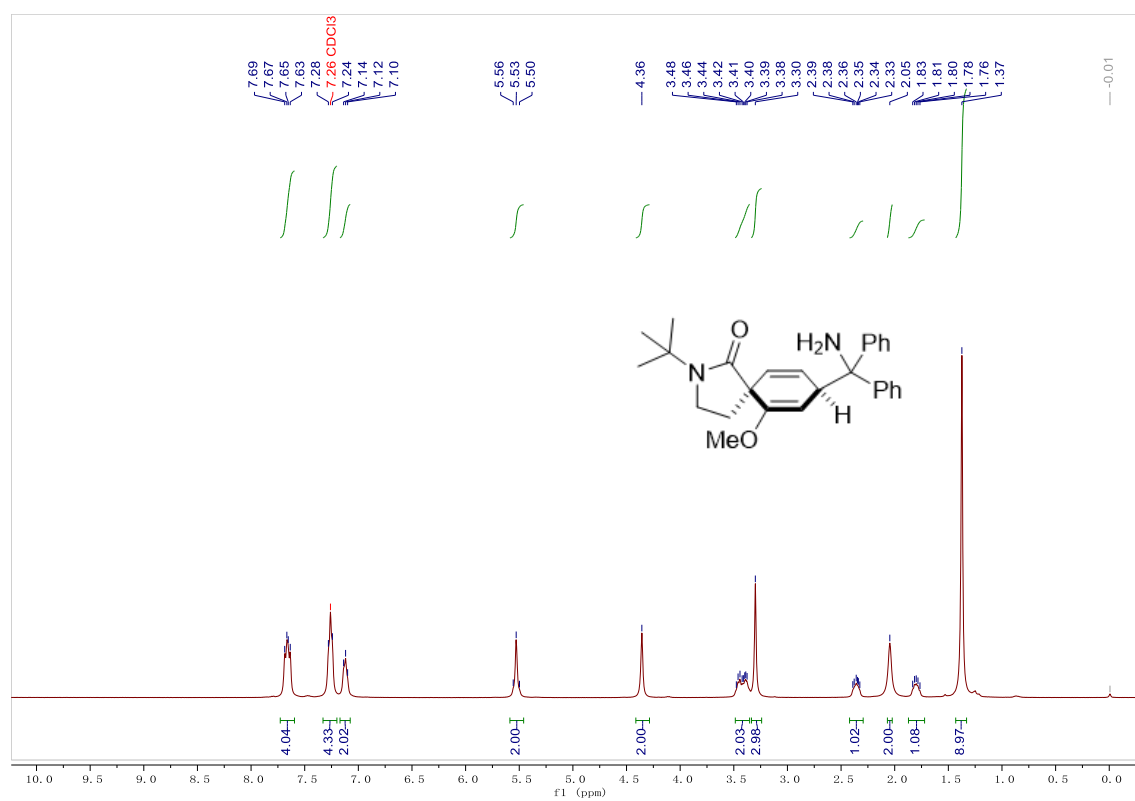
^{13}C -NMR for **cis-3-1**



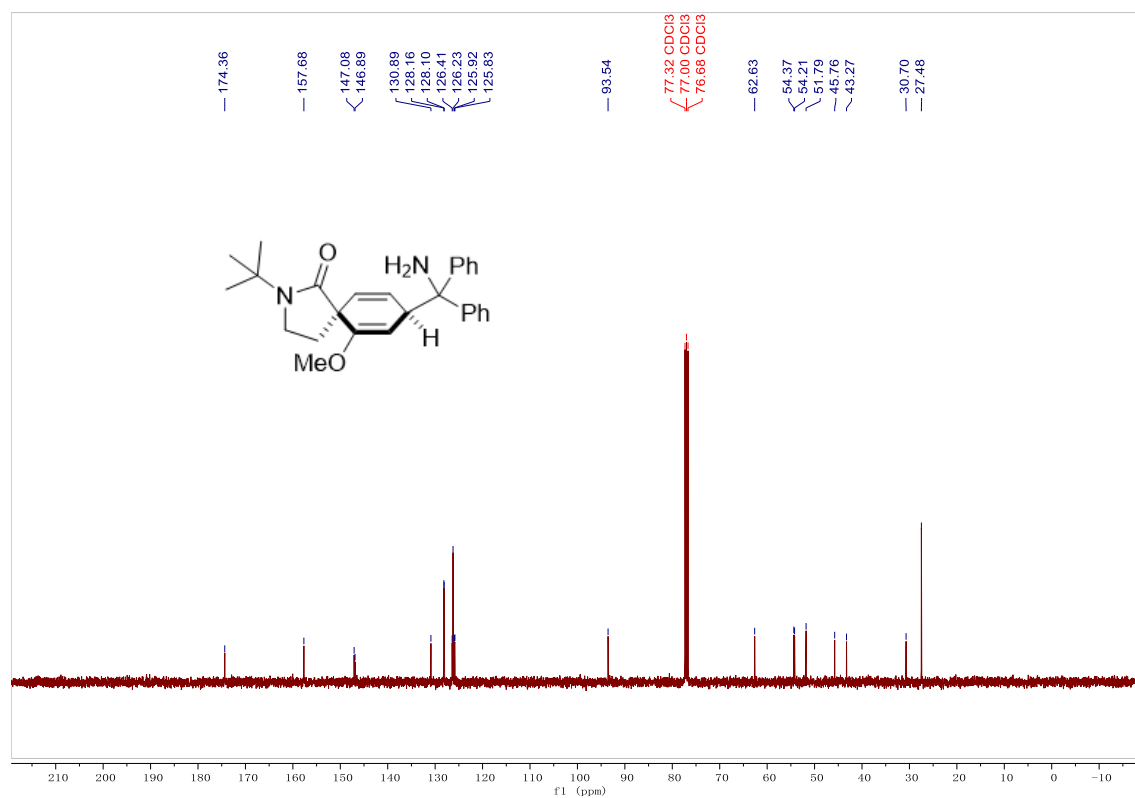
^1H -NMR for **trans-3-1**



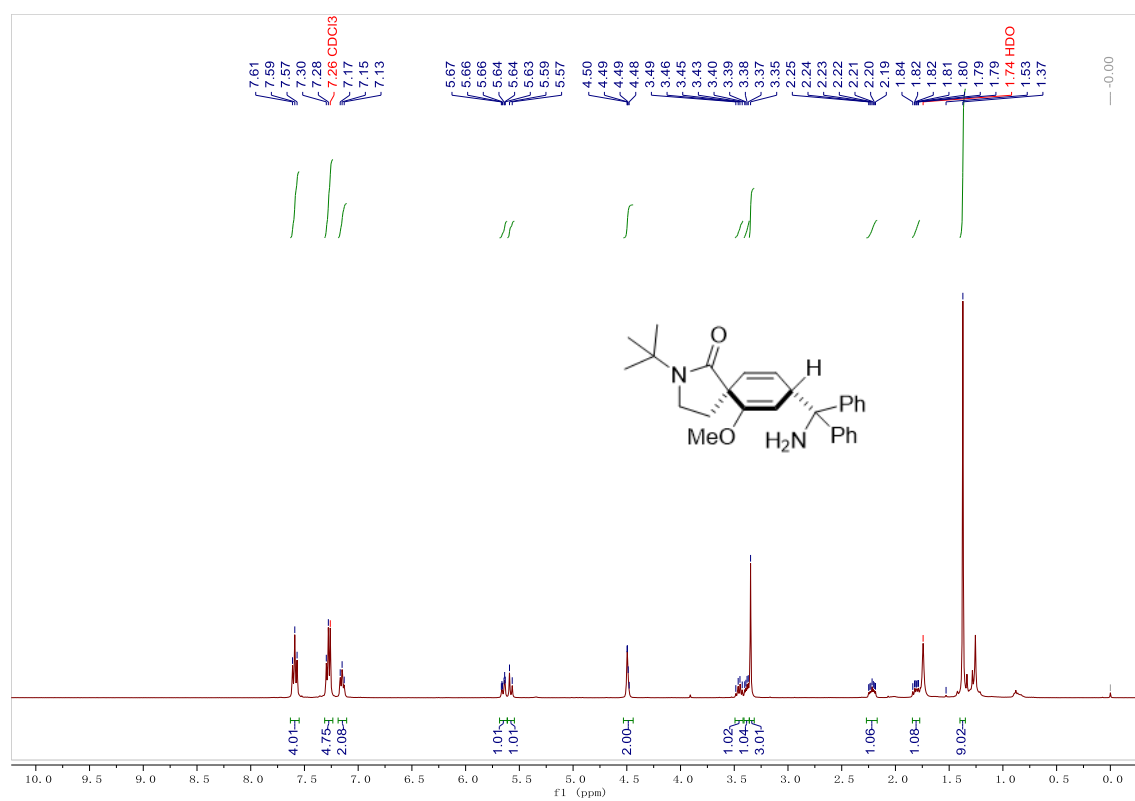
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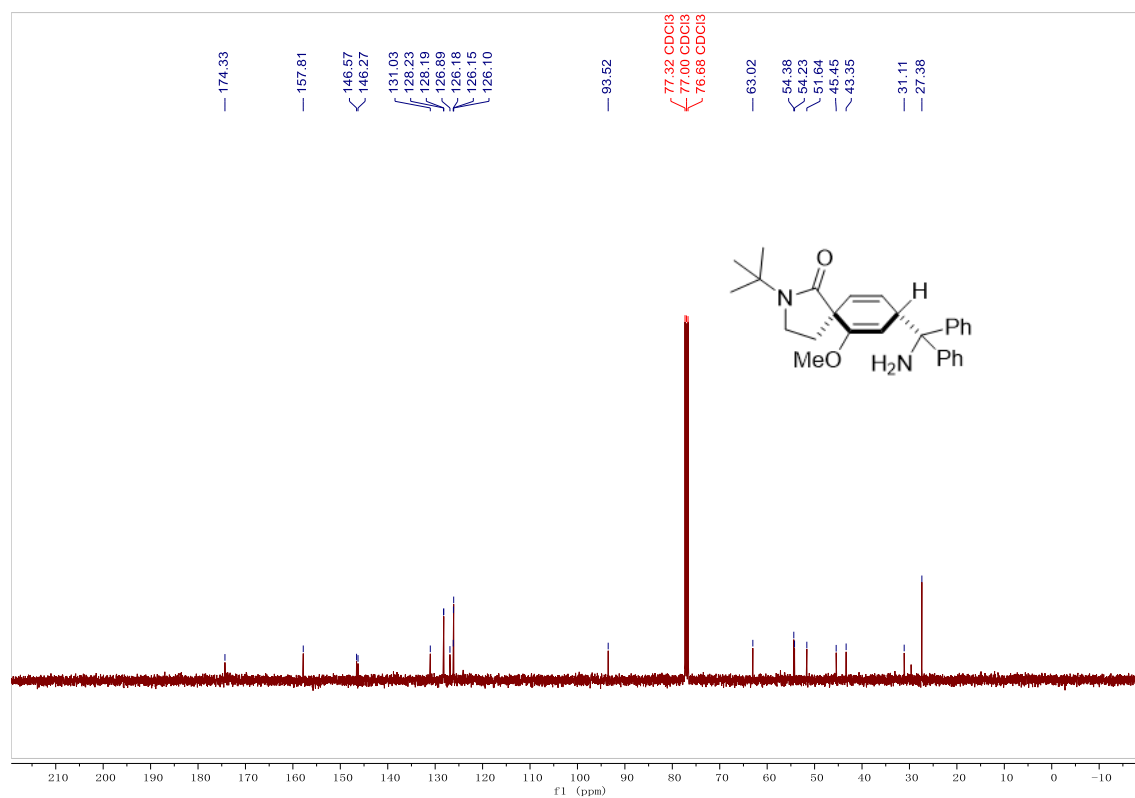
¹H-NMR for cis-3-2



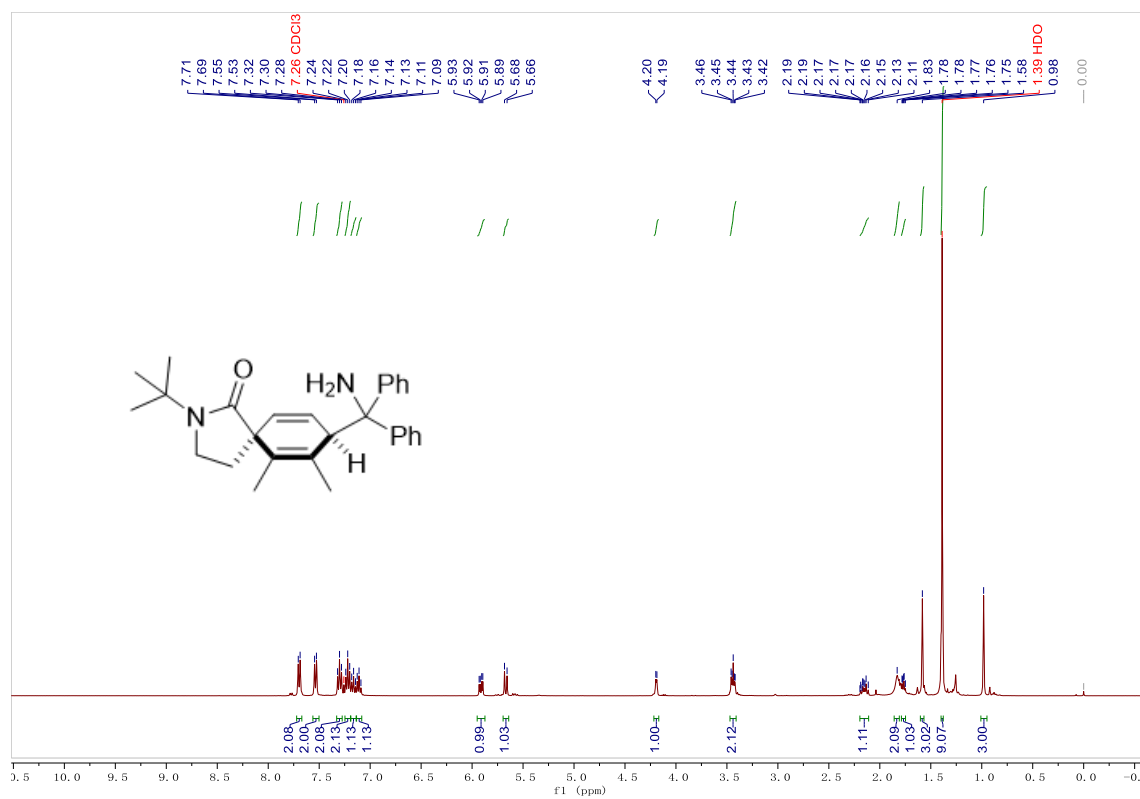
¹³C-NMR for cis-3-2



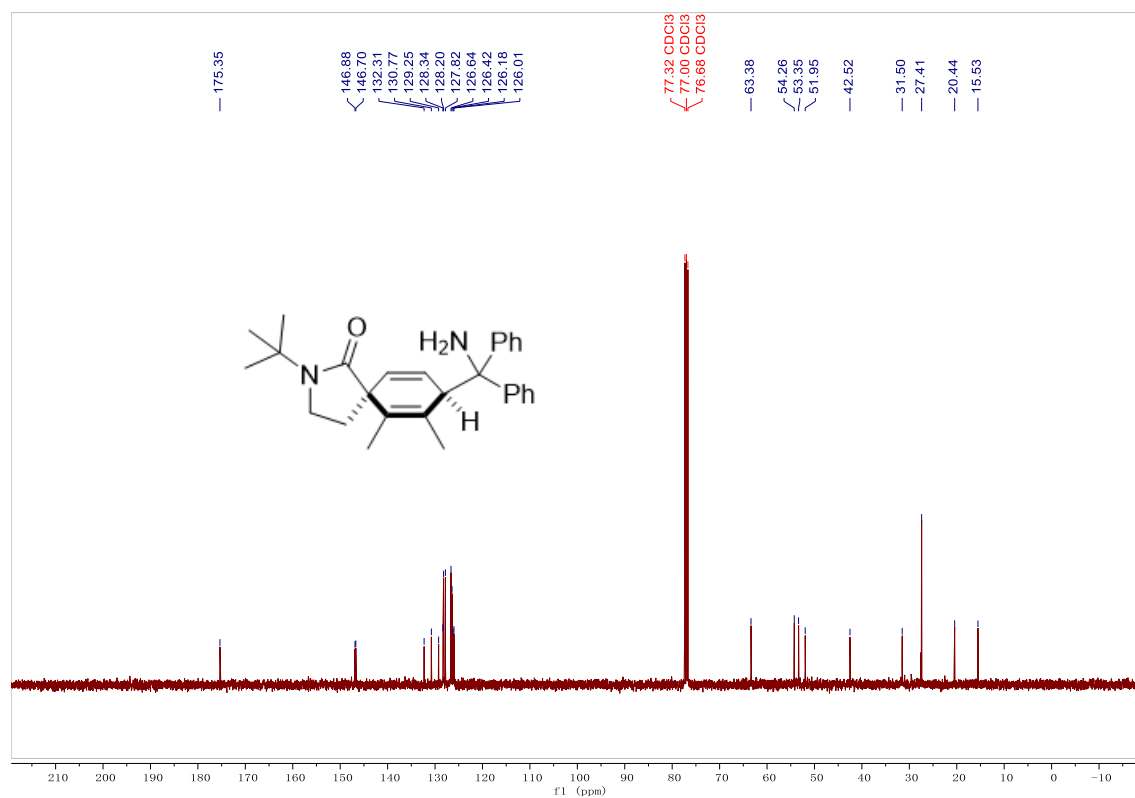
¹H-NMR for trans-3-2



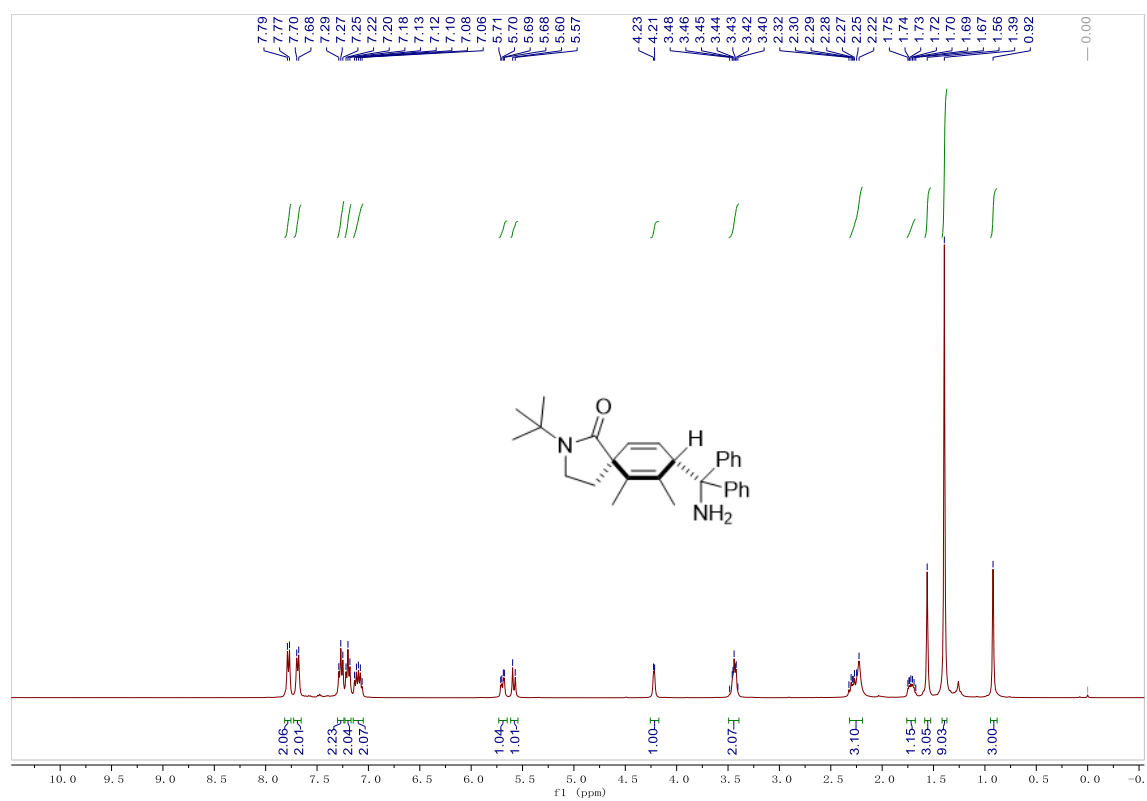
¹³C-NMR for **trans-3-2**



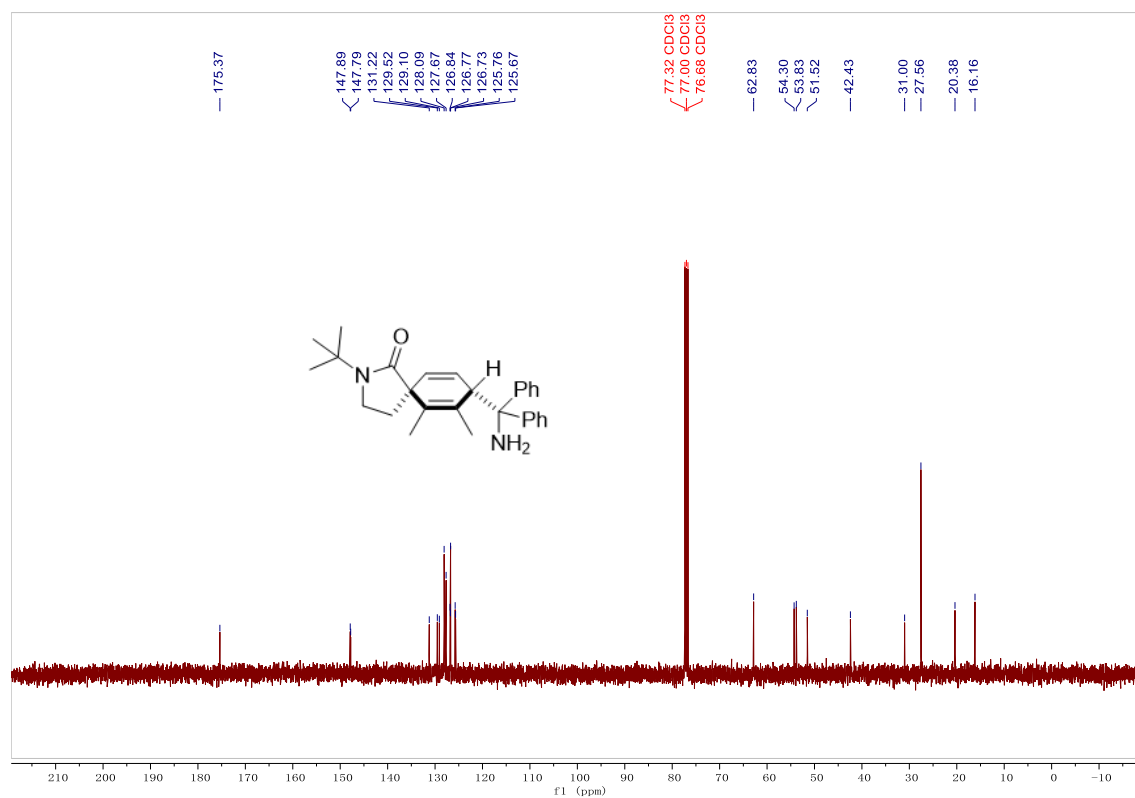
¹H-NMR for **cis-3-3**



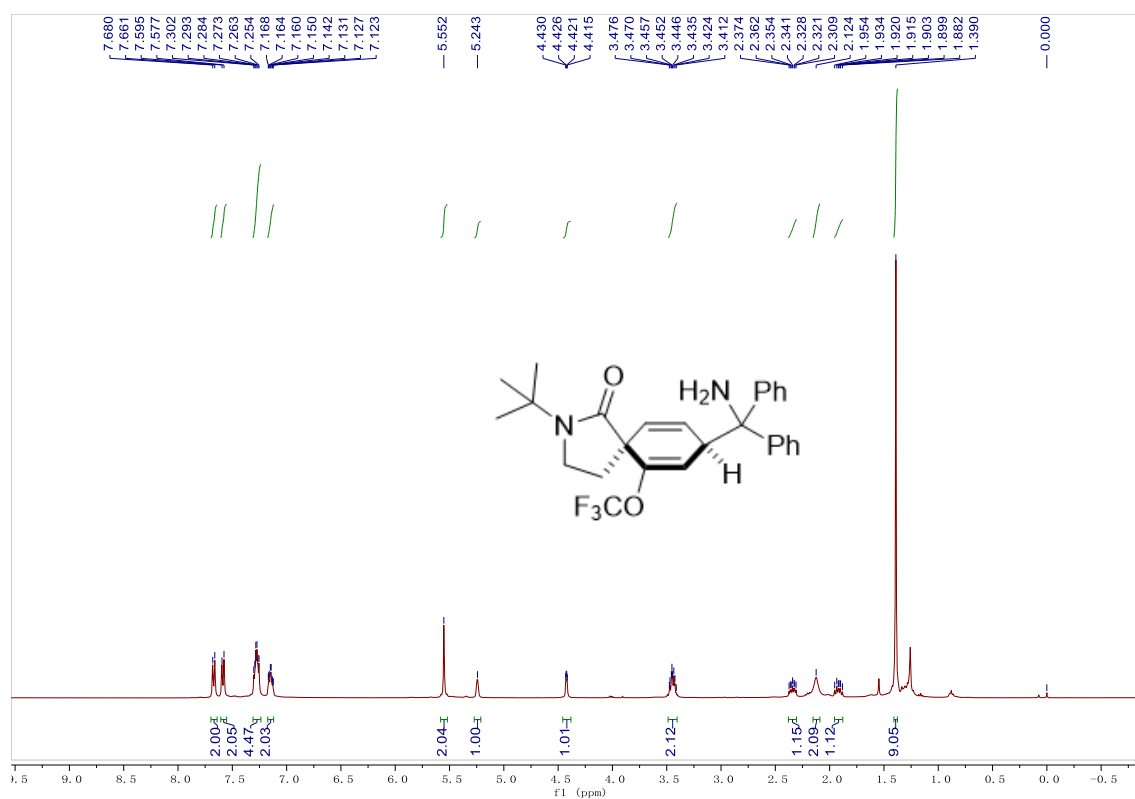
¹³C-NMR for cis-3-3



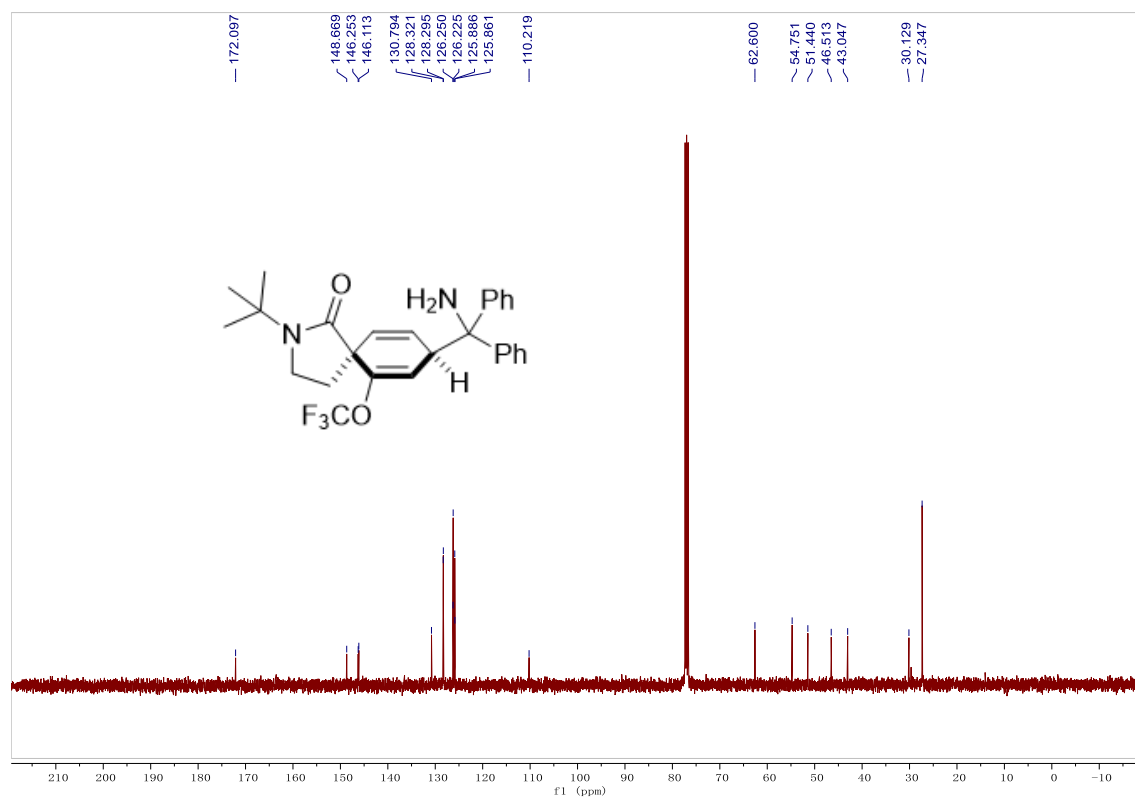
¹H-NMR for trans-3-3



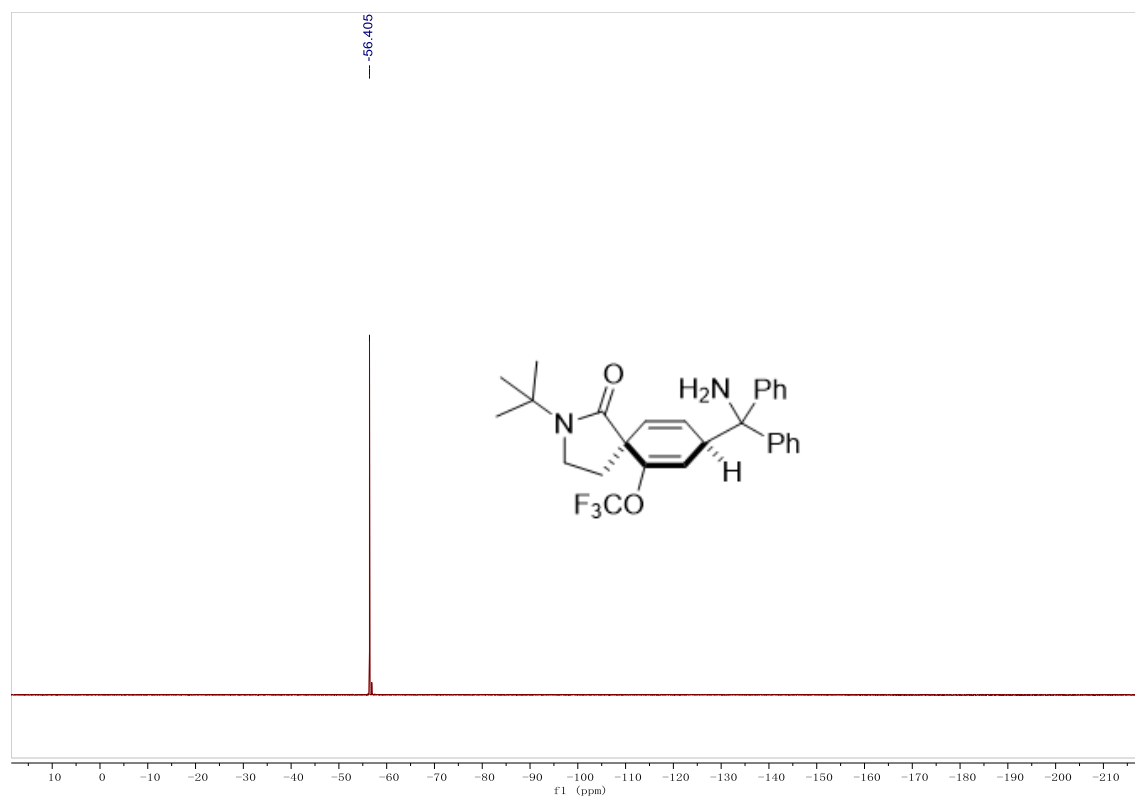
¹³C-NMR for trans-3-3



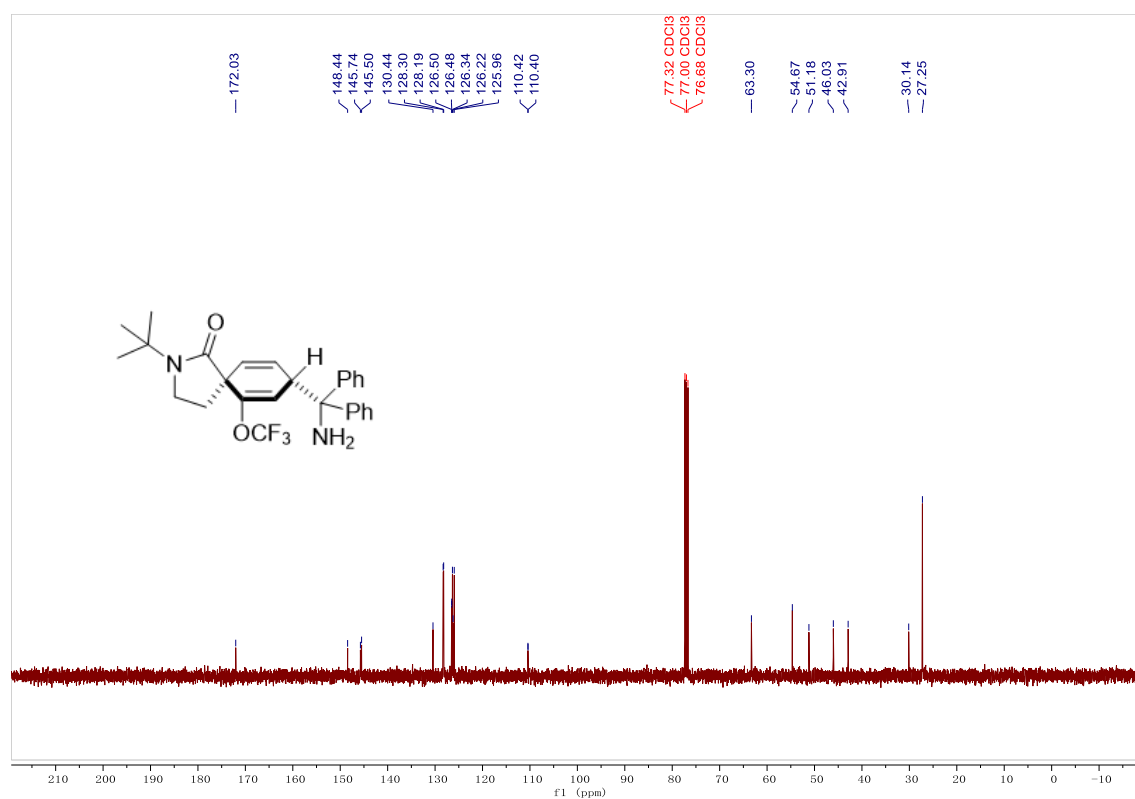
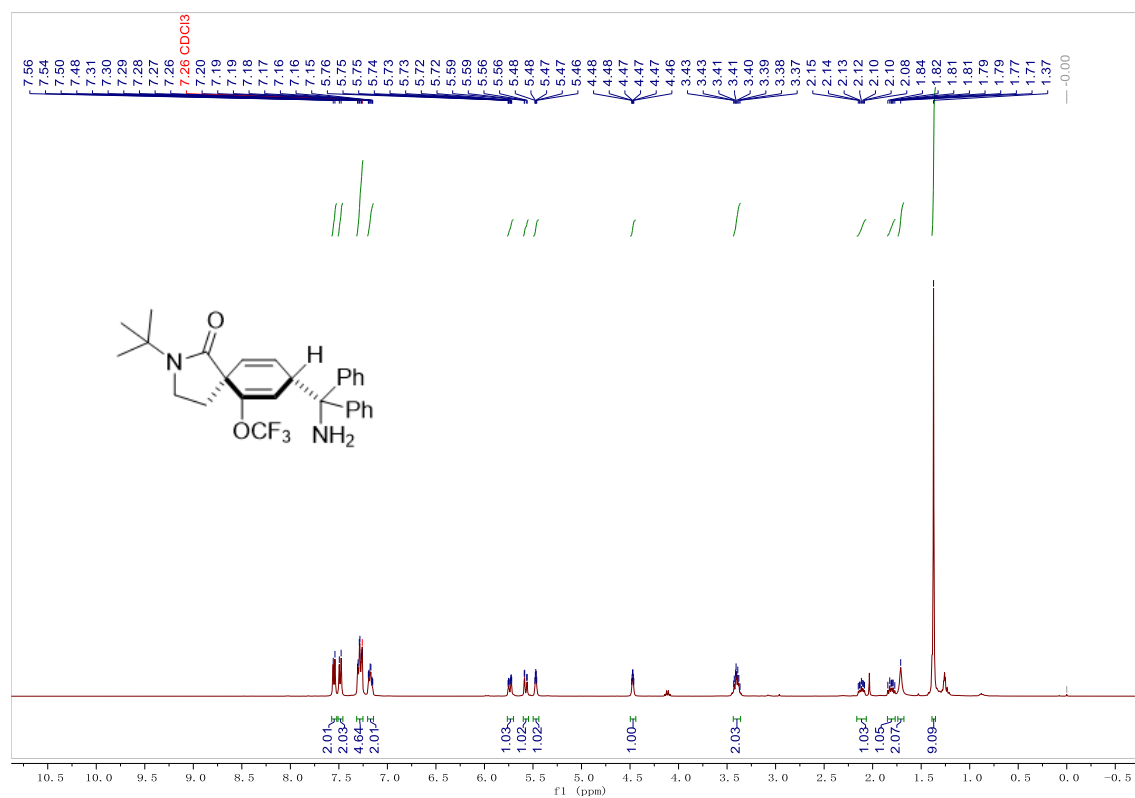
¹H-NMR for cis-3-4

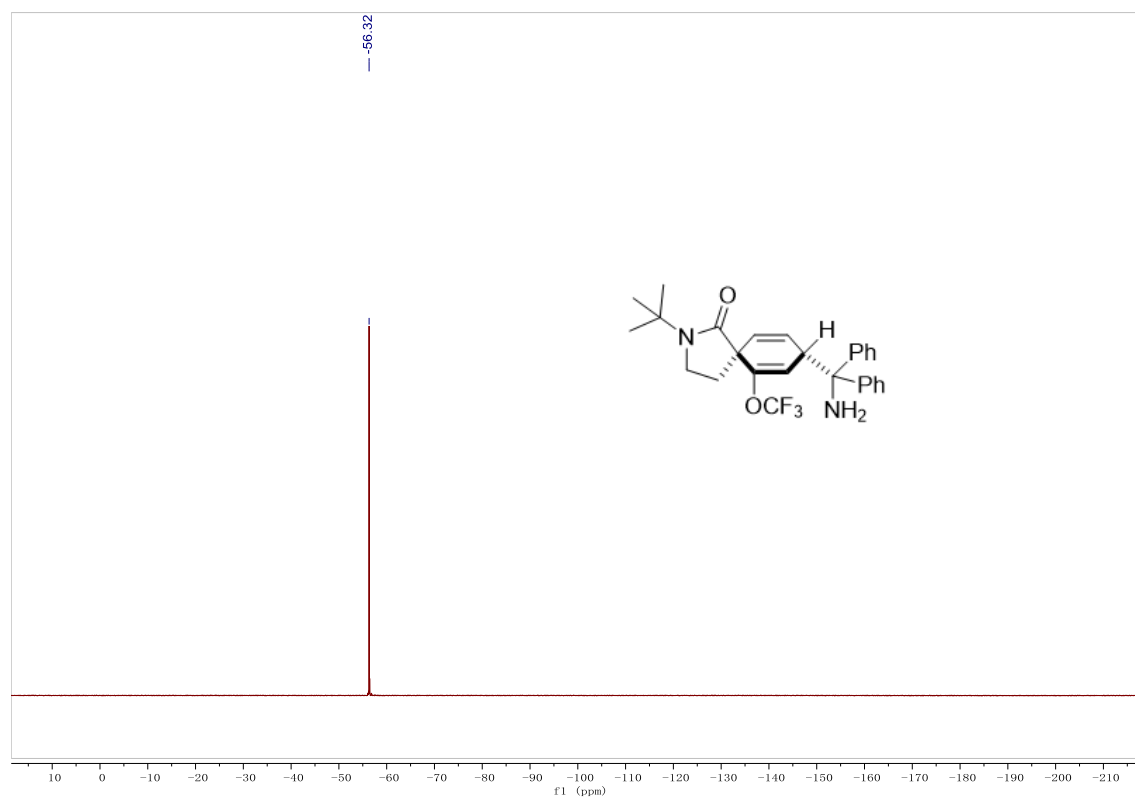


¹³C-NMR for **cis-3-4**

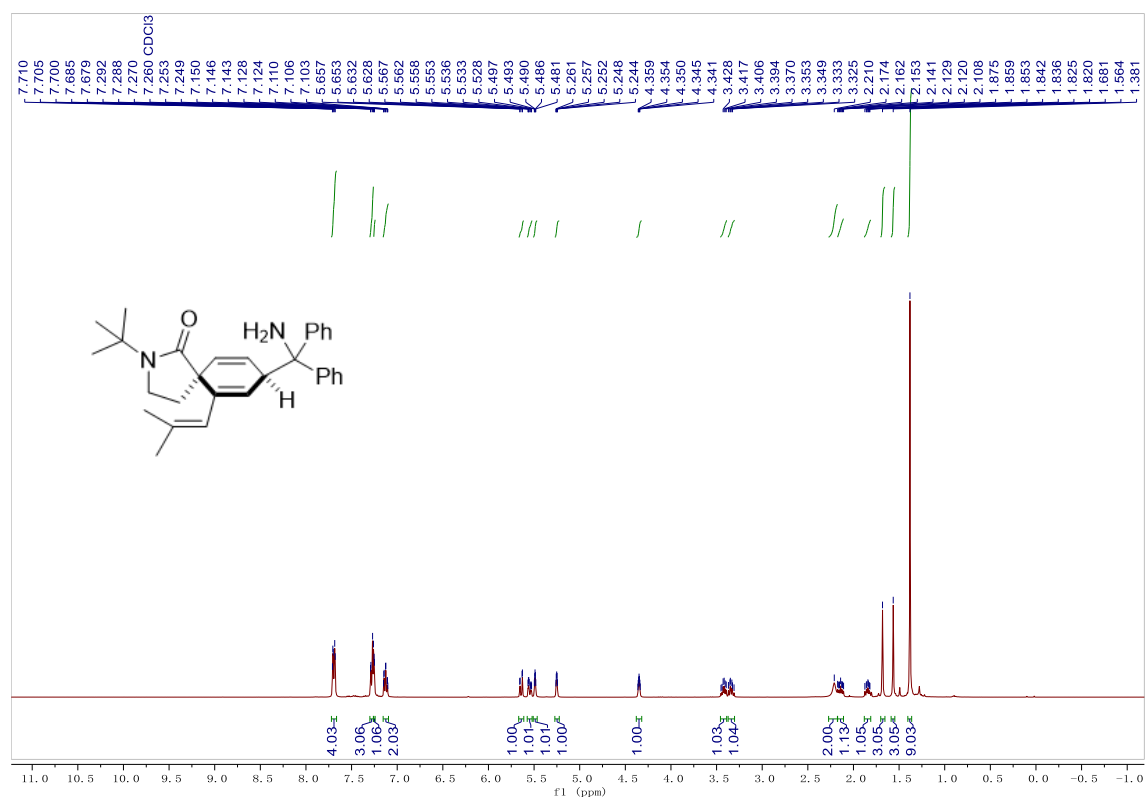


¹⁹F-NMR for **cis-3-4**

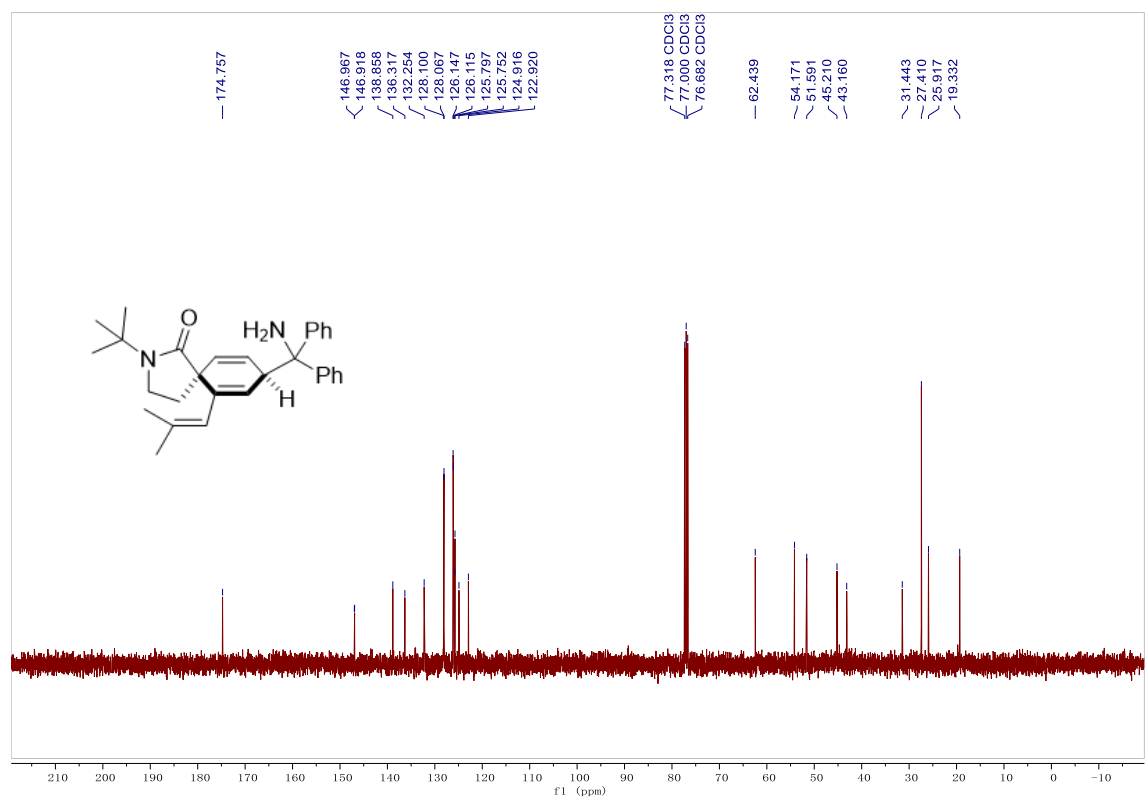




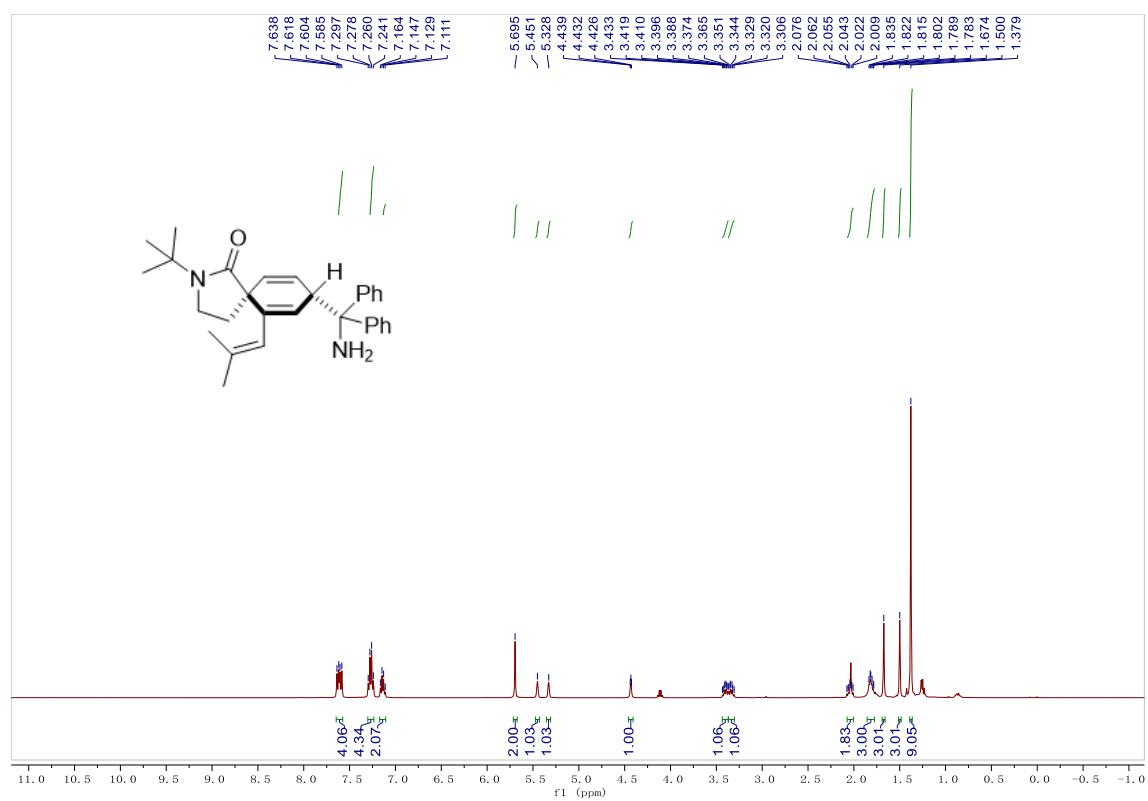
¹⁹F-NMR for **trans-3-4**



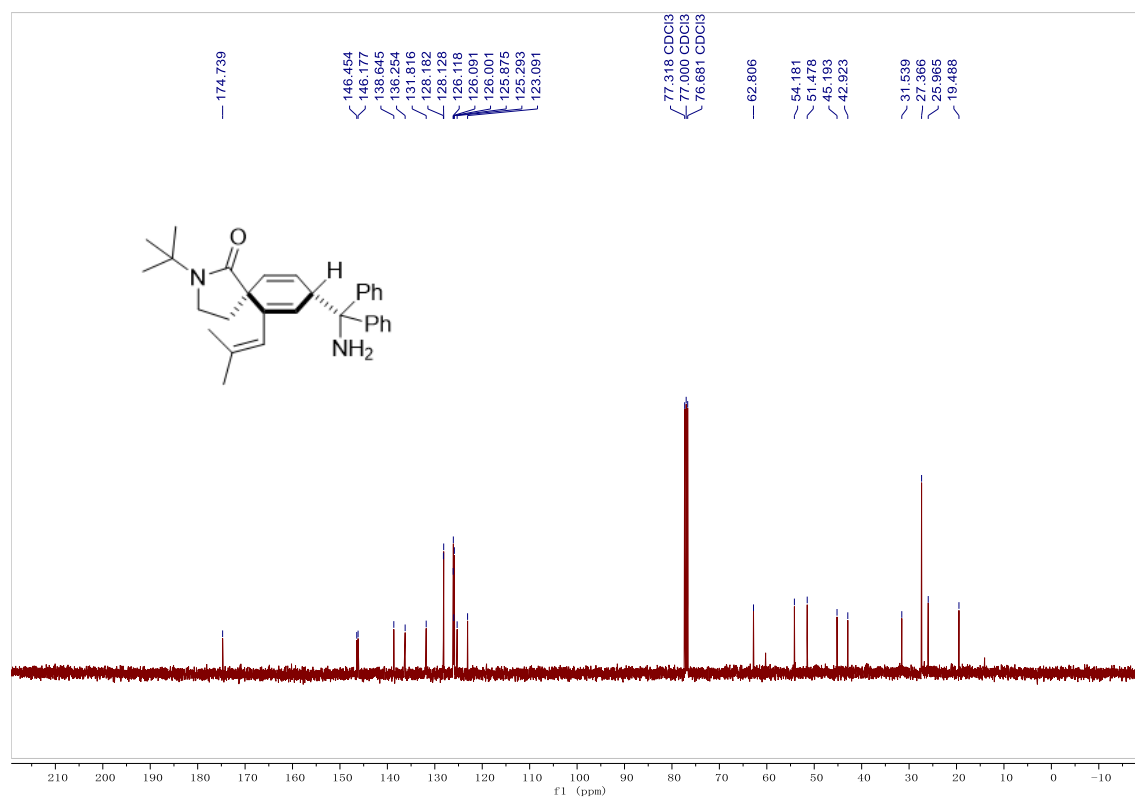
¹H-NMR for **cis-3-5**



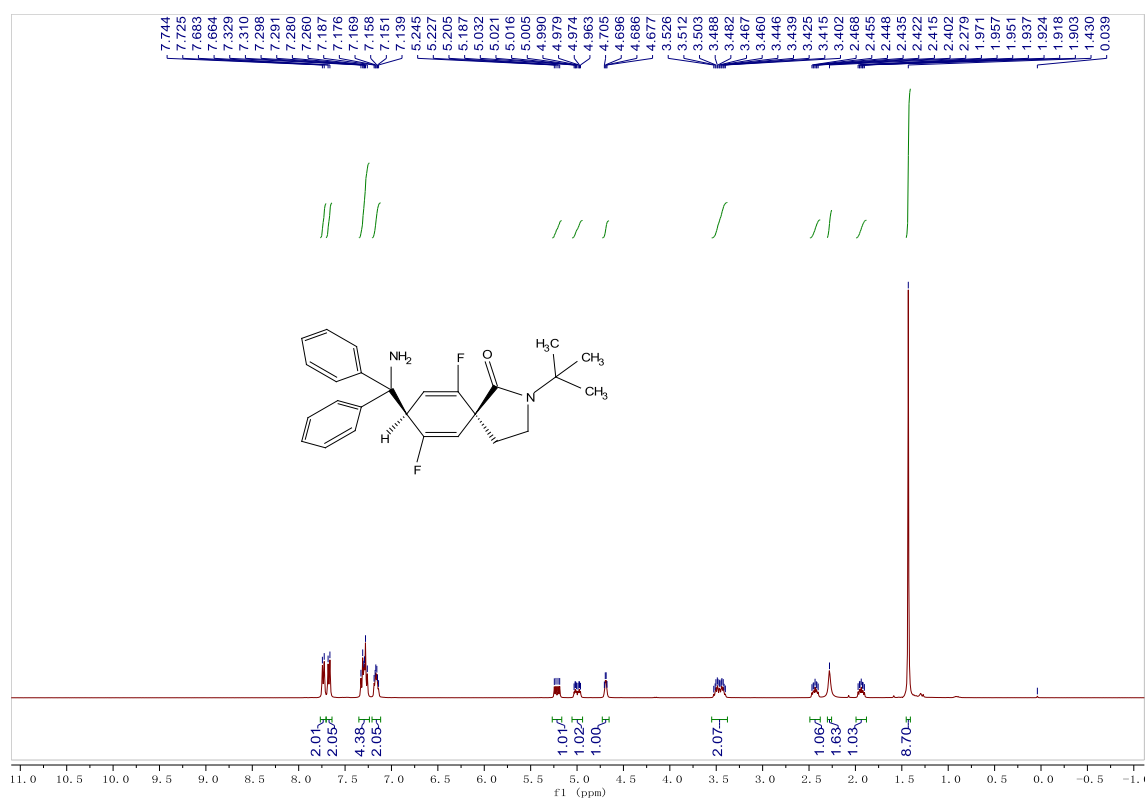
¹³C-NMR for cis-3-5



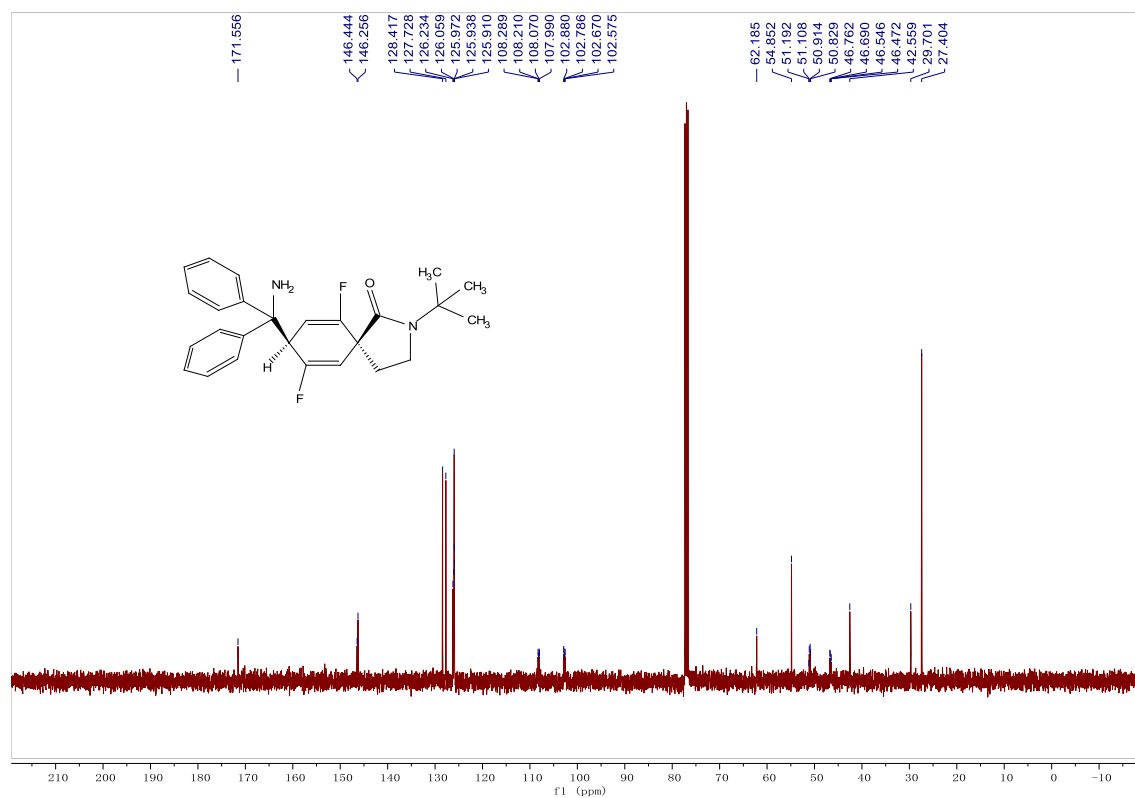
¹H-NMR for trans-3-5



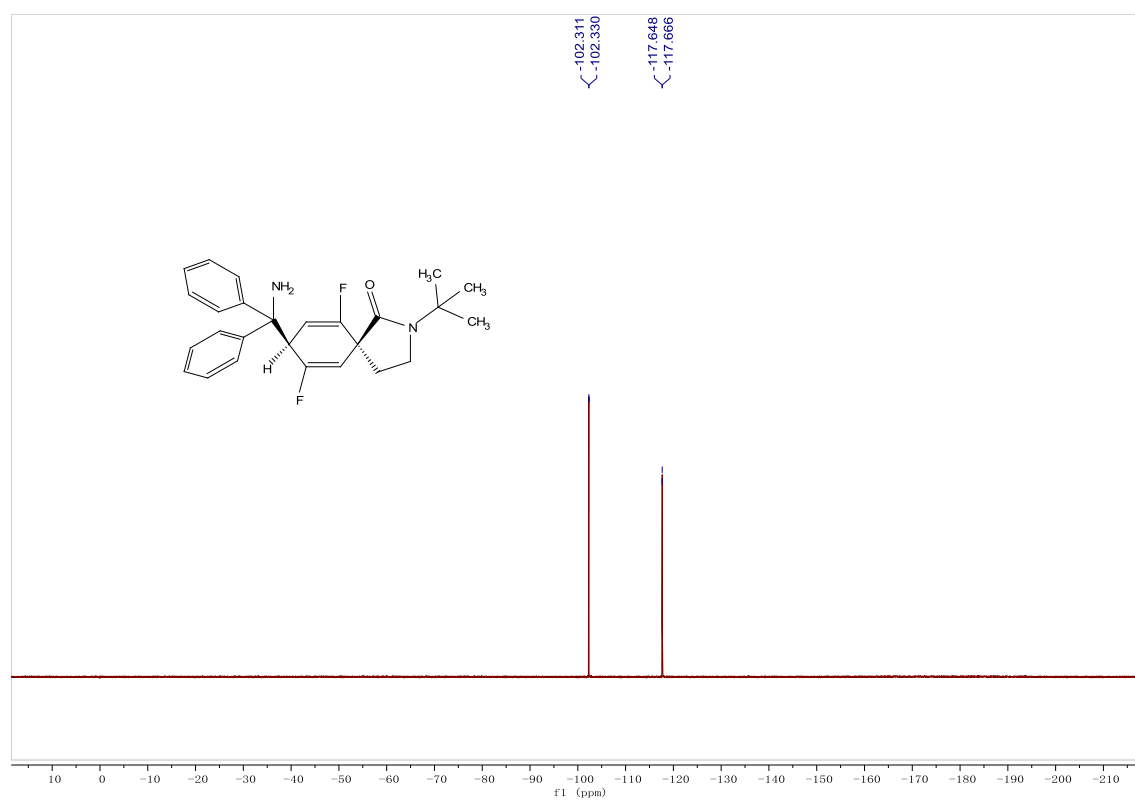
^{13}C -NMR for trans-3-5



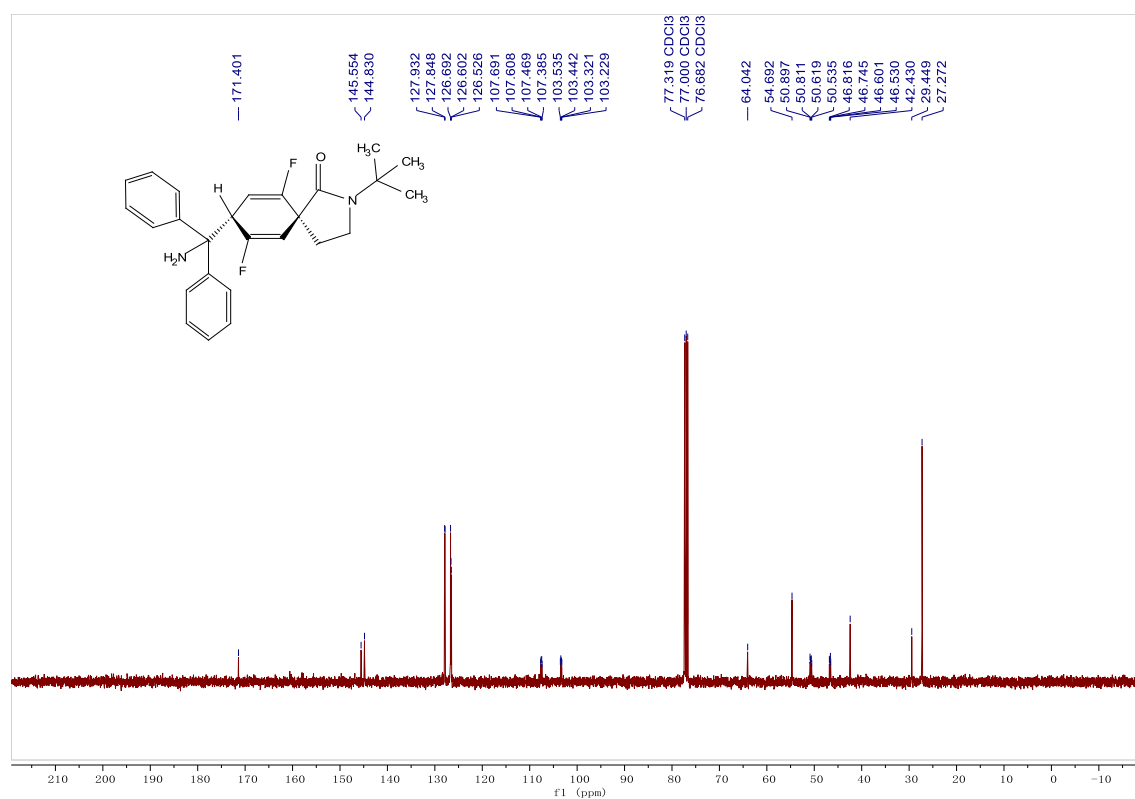
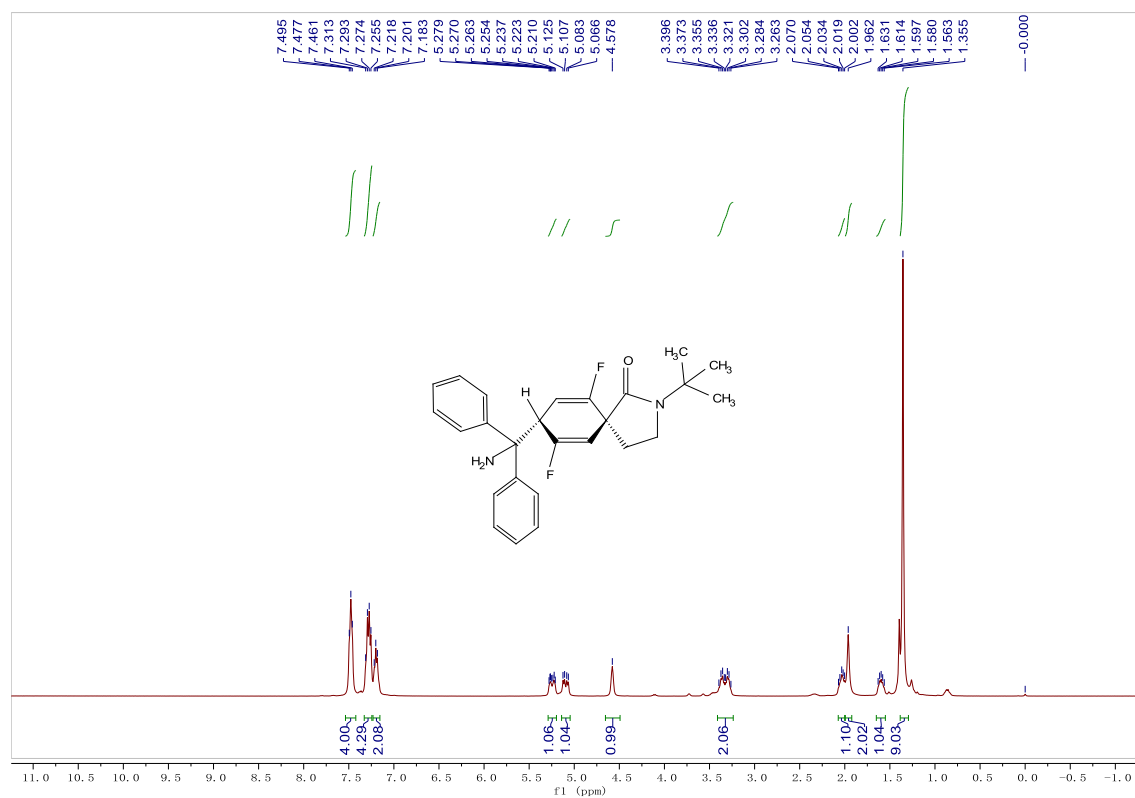
^1H -NMR for cis-3-6

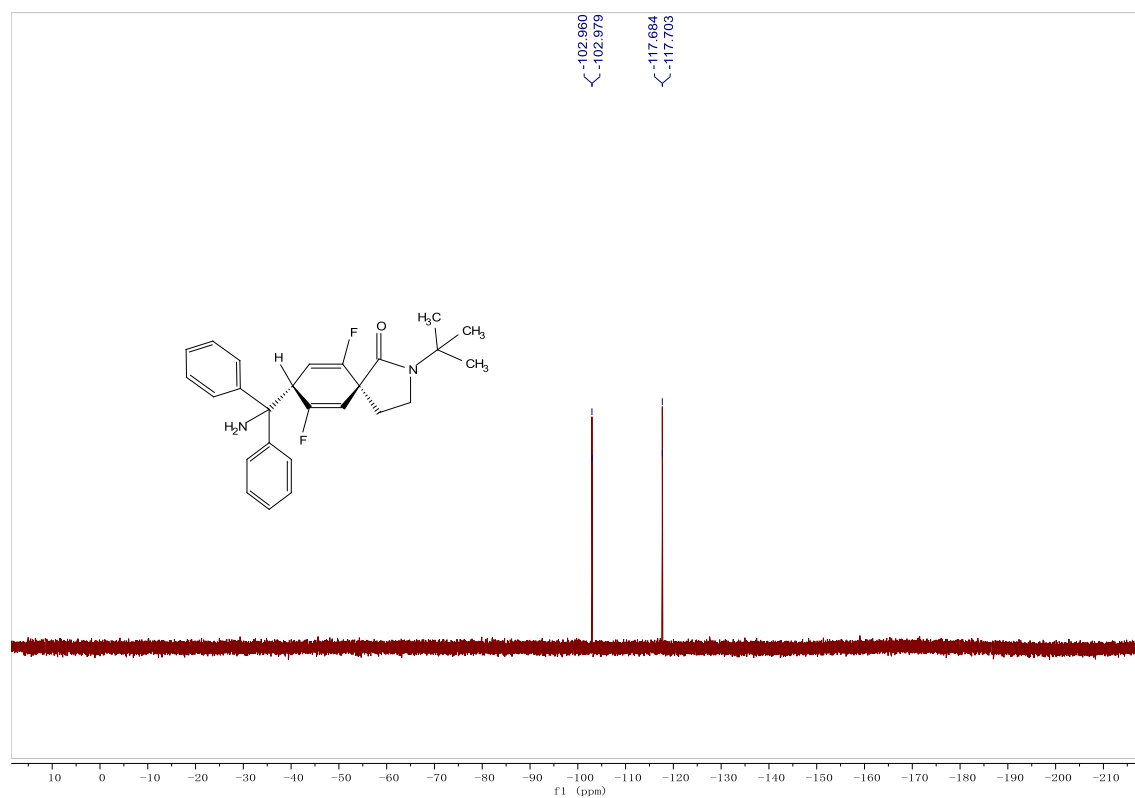


¹³C-NMR for **cis-3-6**

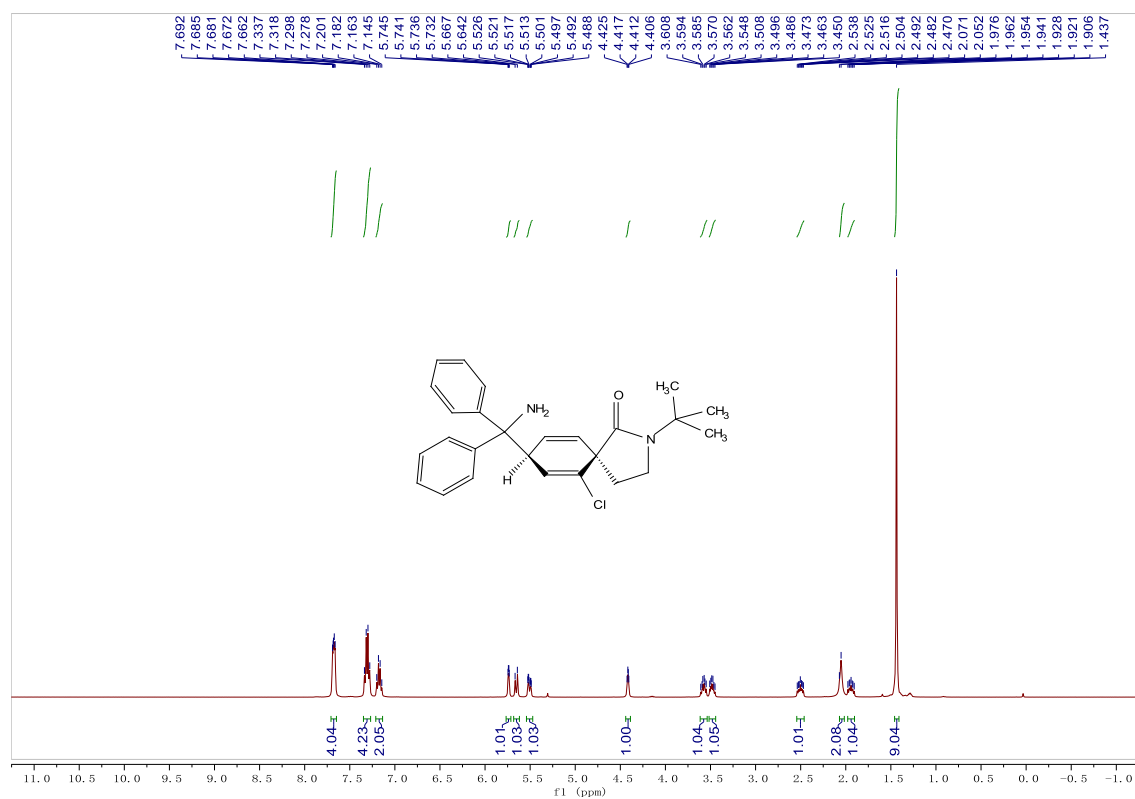


¹⁹F-NMR for **cis-3-6**

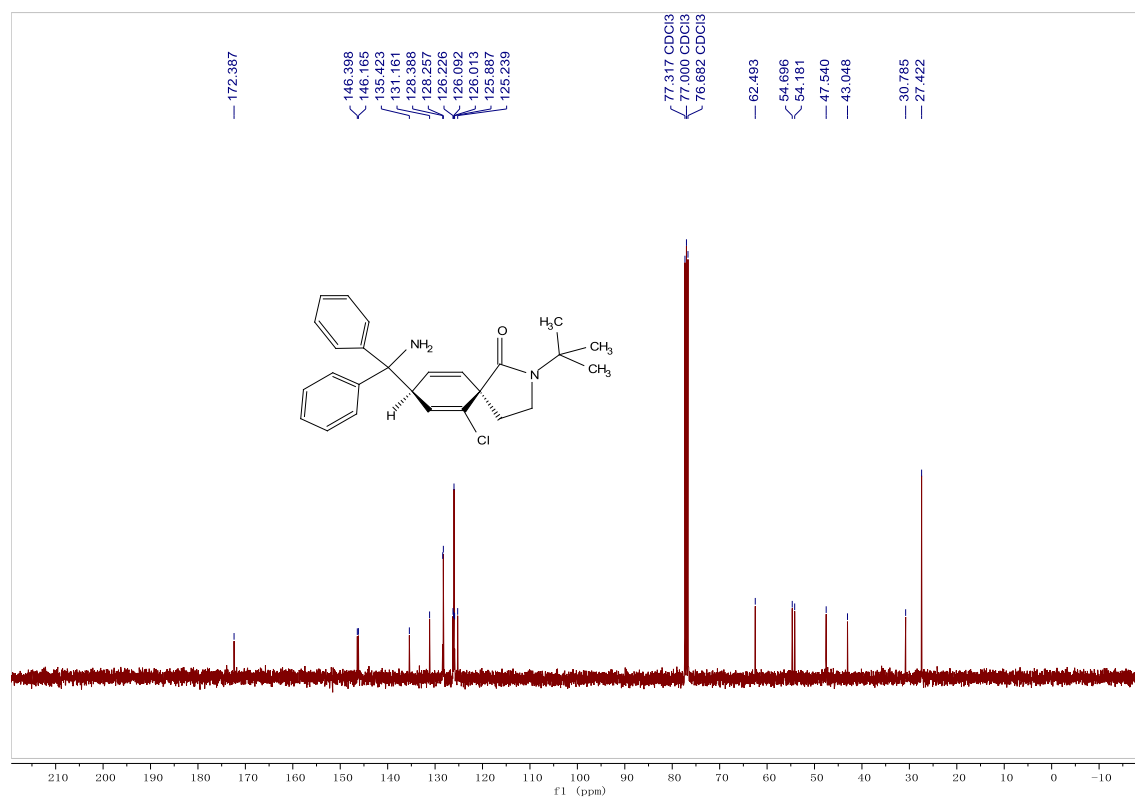




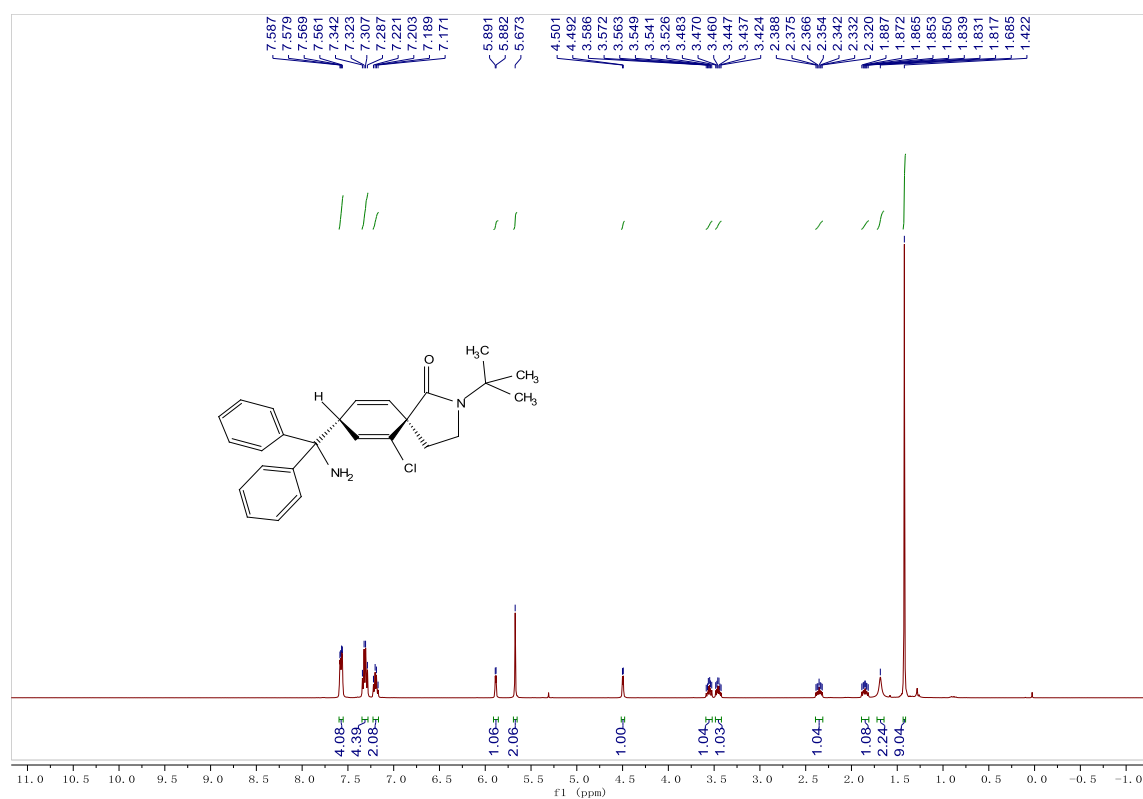
¹⁹F-NMR for trans-3-6



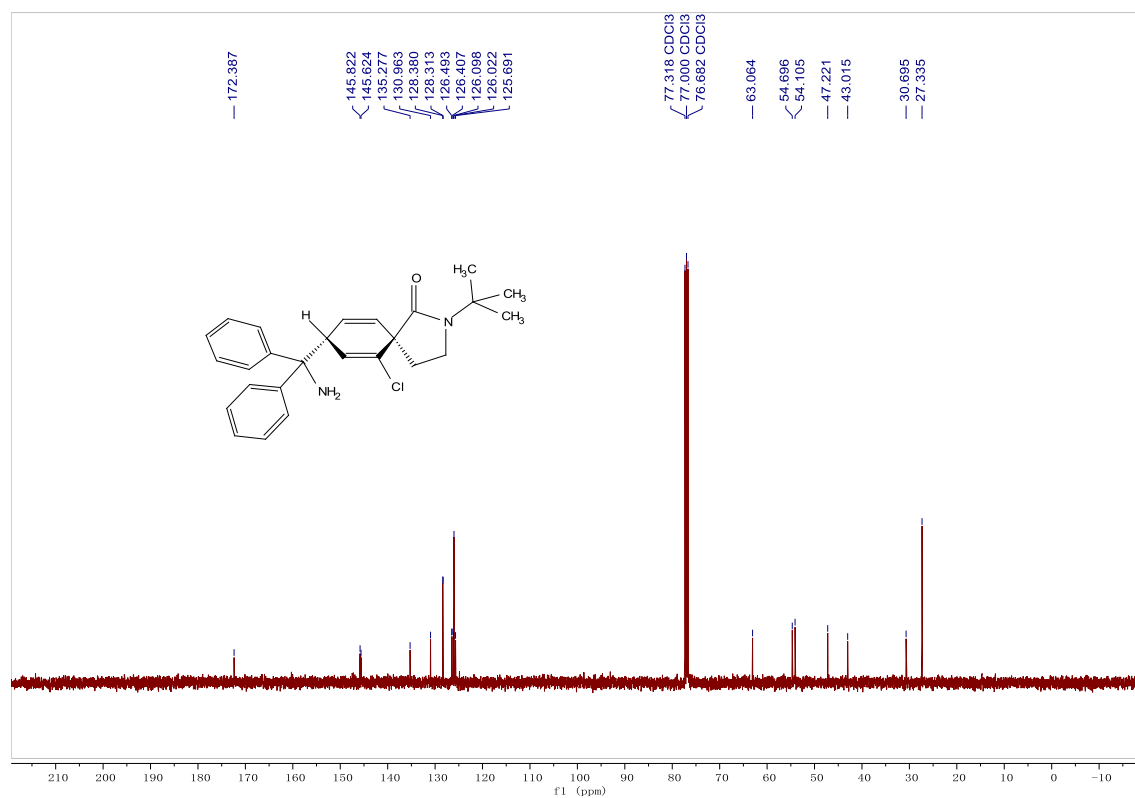
¹H-NMR for cis-3-7



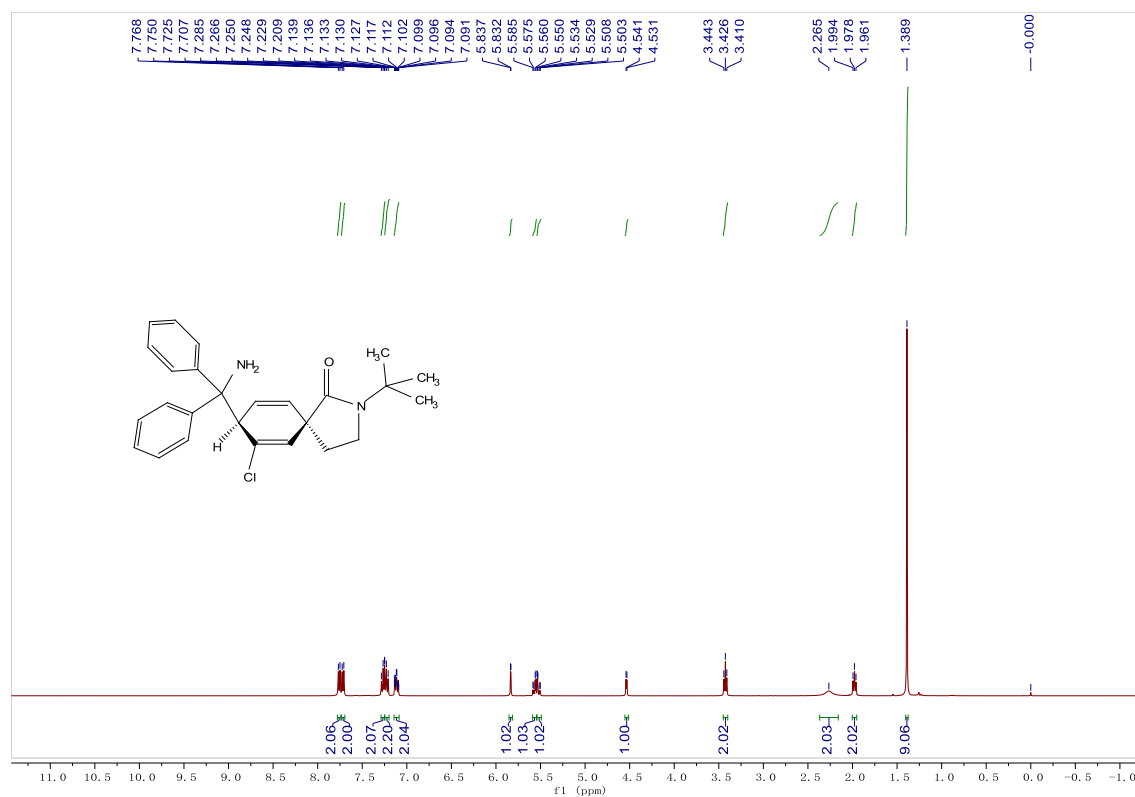
¹³C-NMR for *cis*-3-7



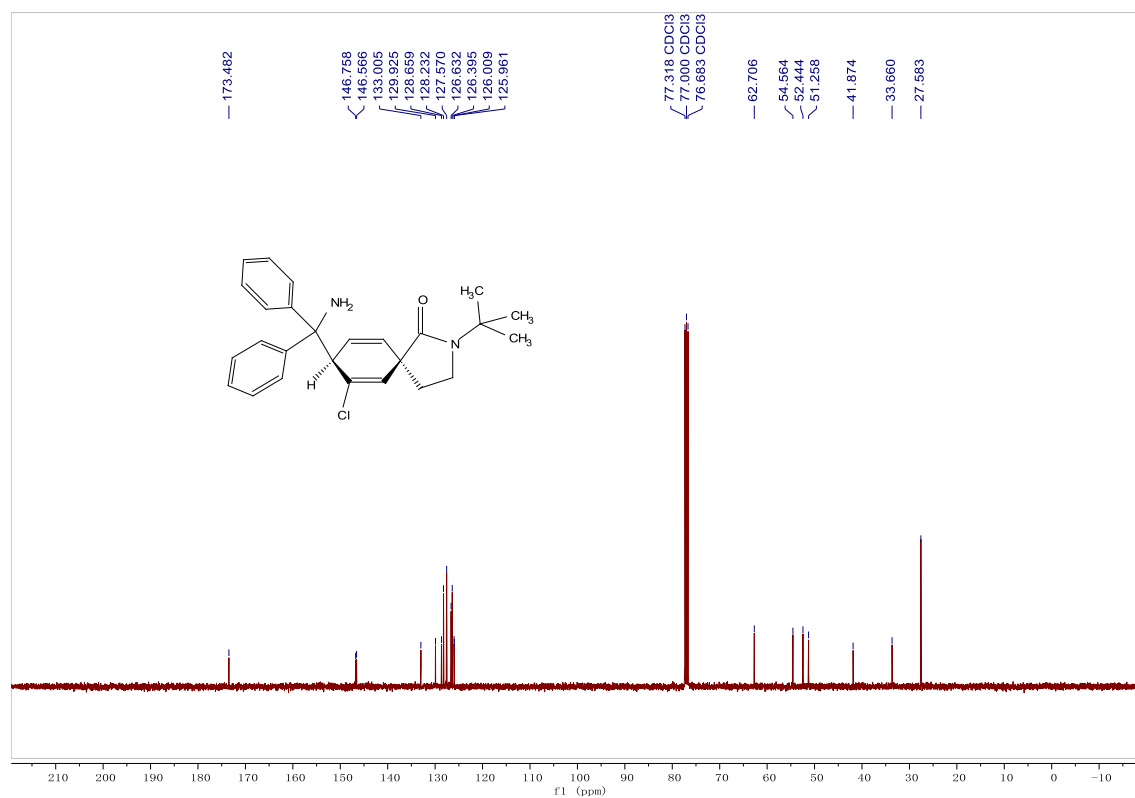
¹H-NMR for *trans*-3-7



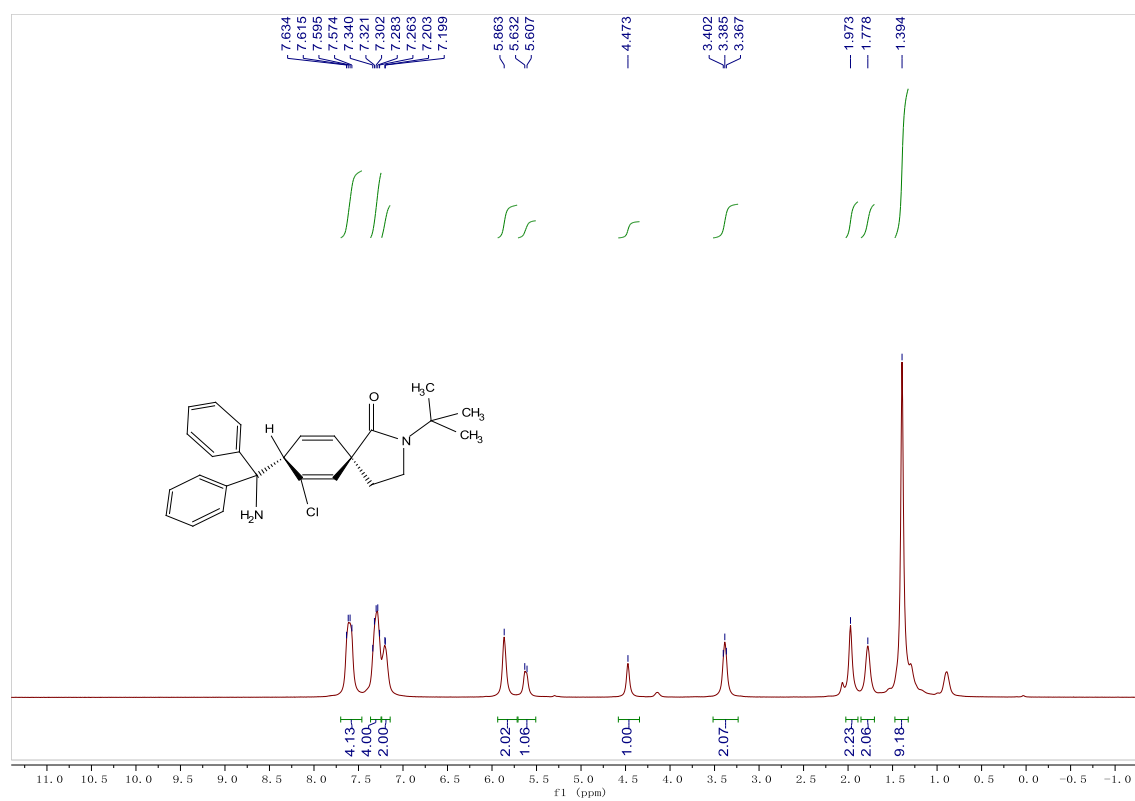
¹³C-NMR for trans-3-7



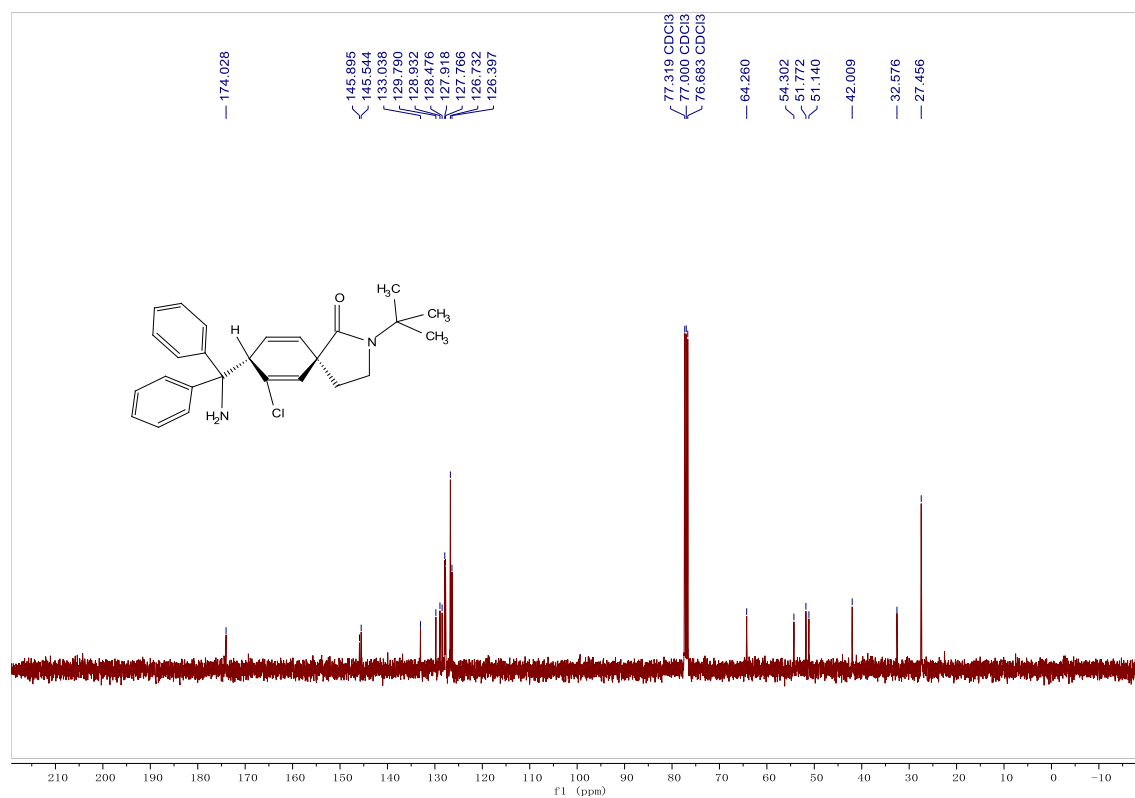
¹H-NMR for cis-3-8



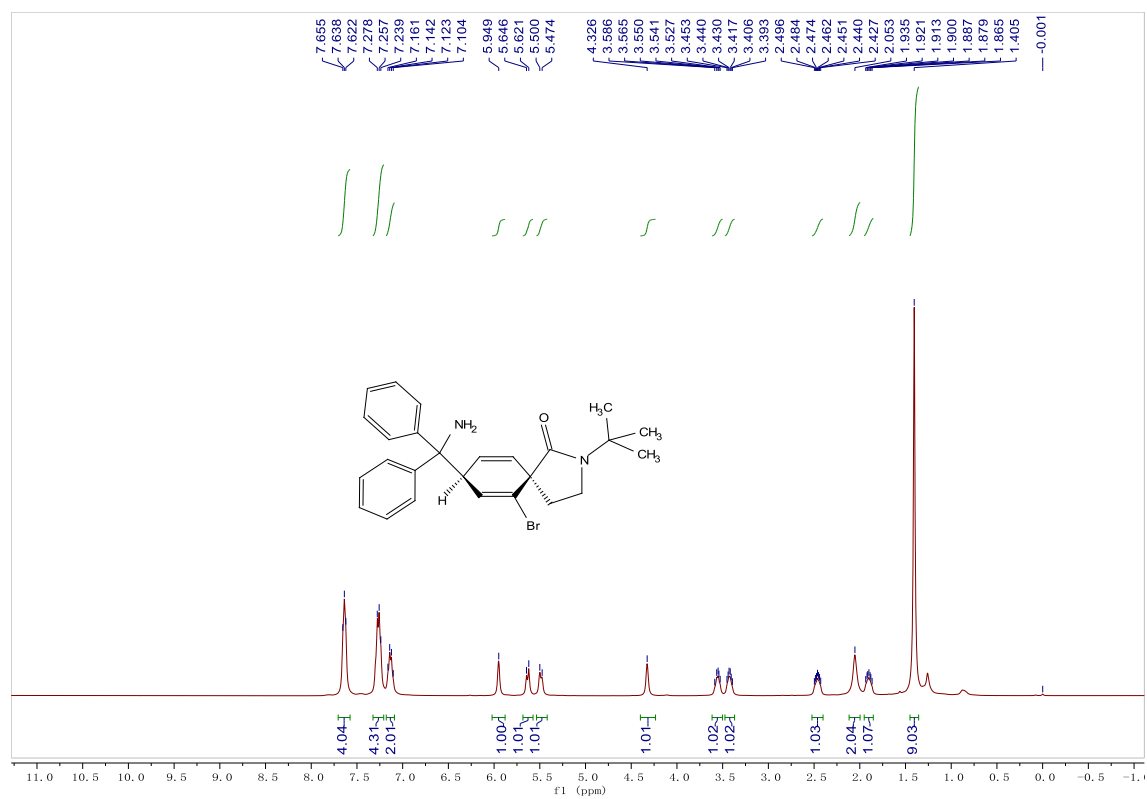
¹³C-NMR for *cis*-3-8



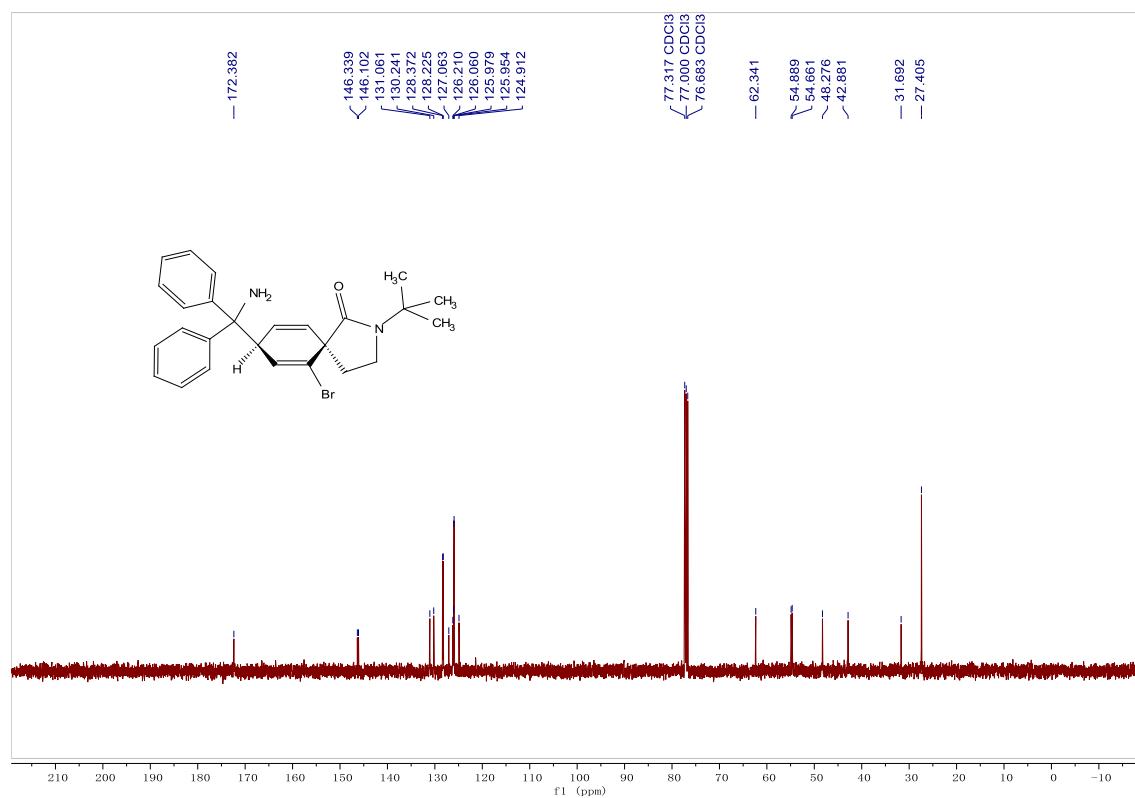
¹H-NMR for *trans*-3-8



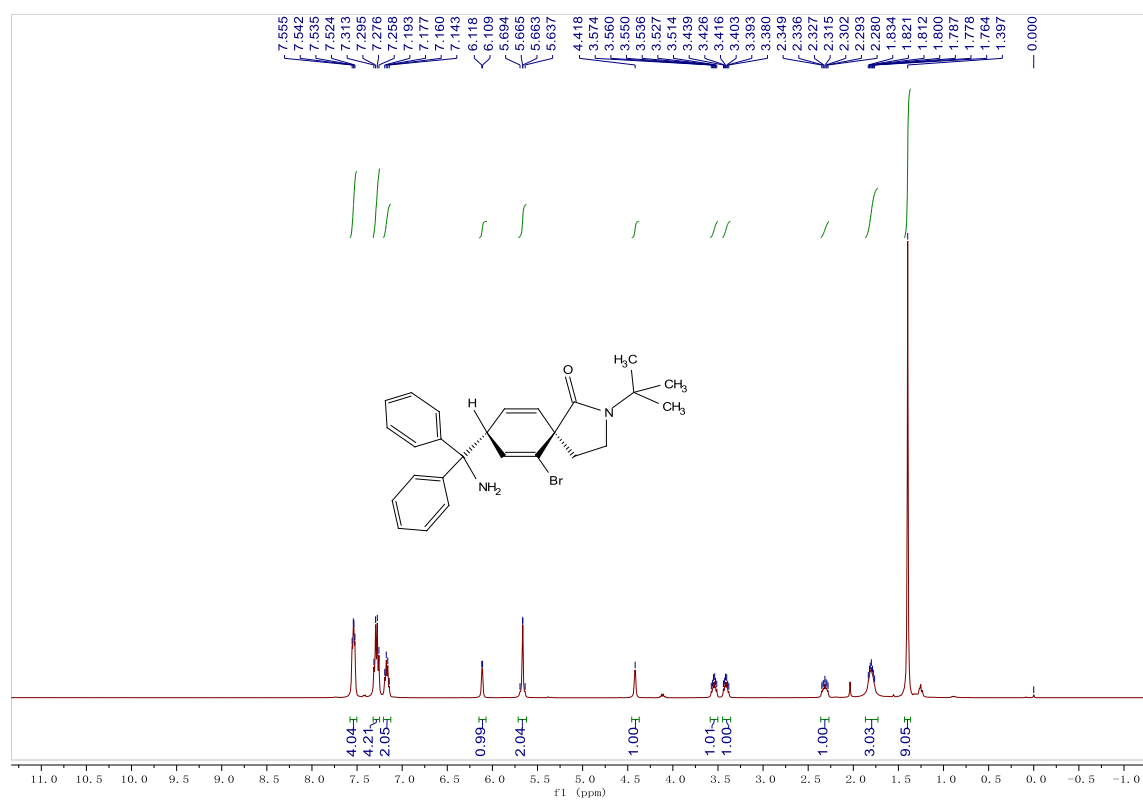
¹³C-NMR for trans-3-8



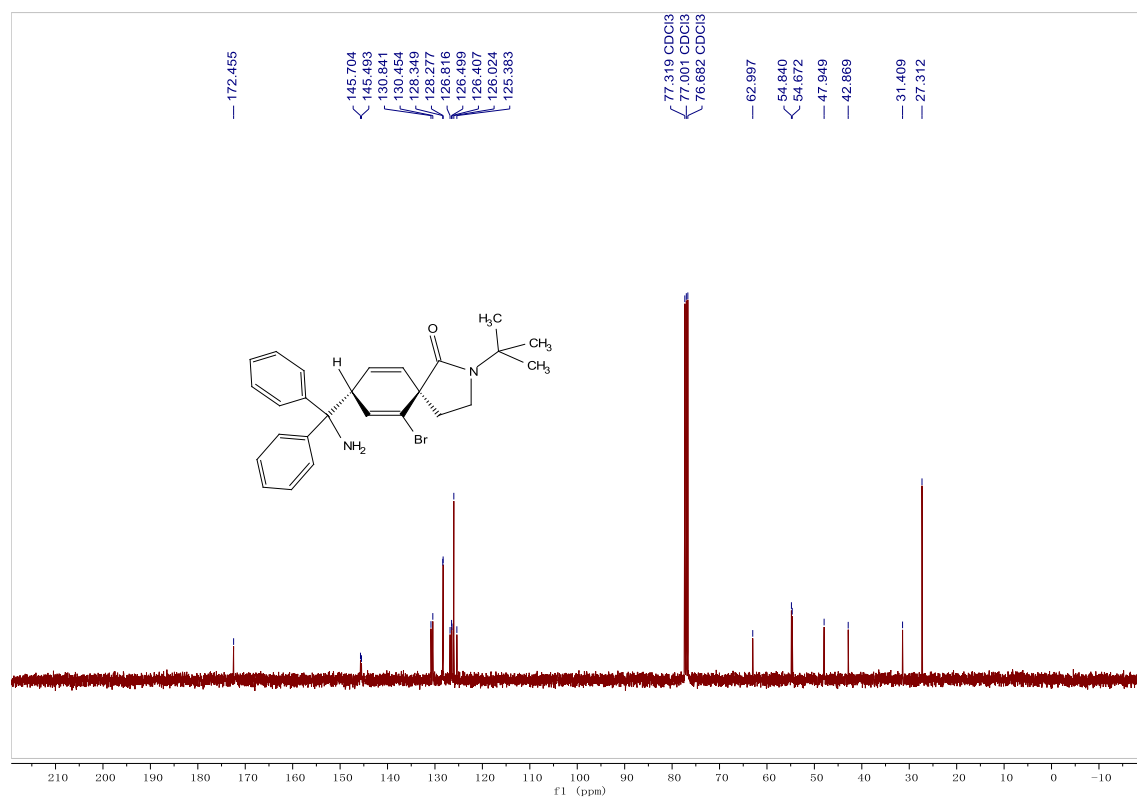
¹H-NMR for cis-3-9



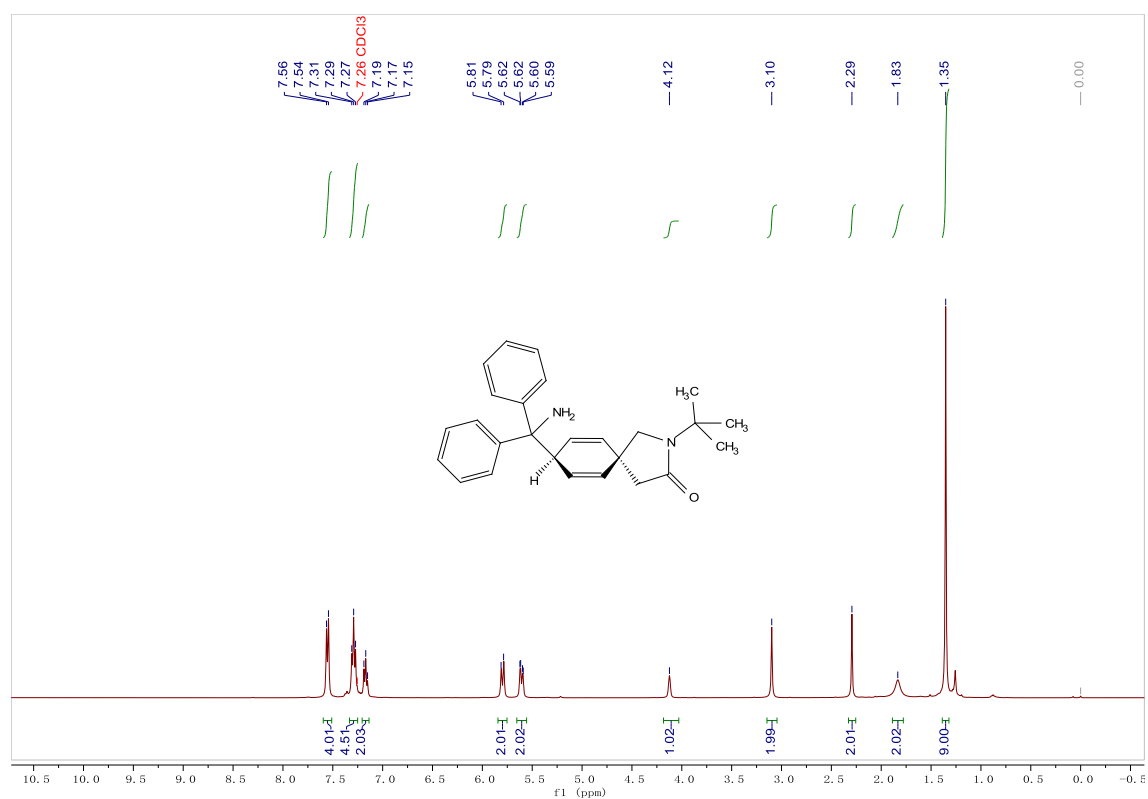
¹³C-NMR for cis-3-9



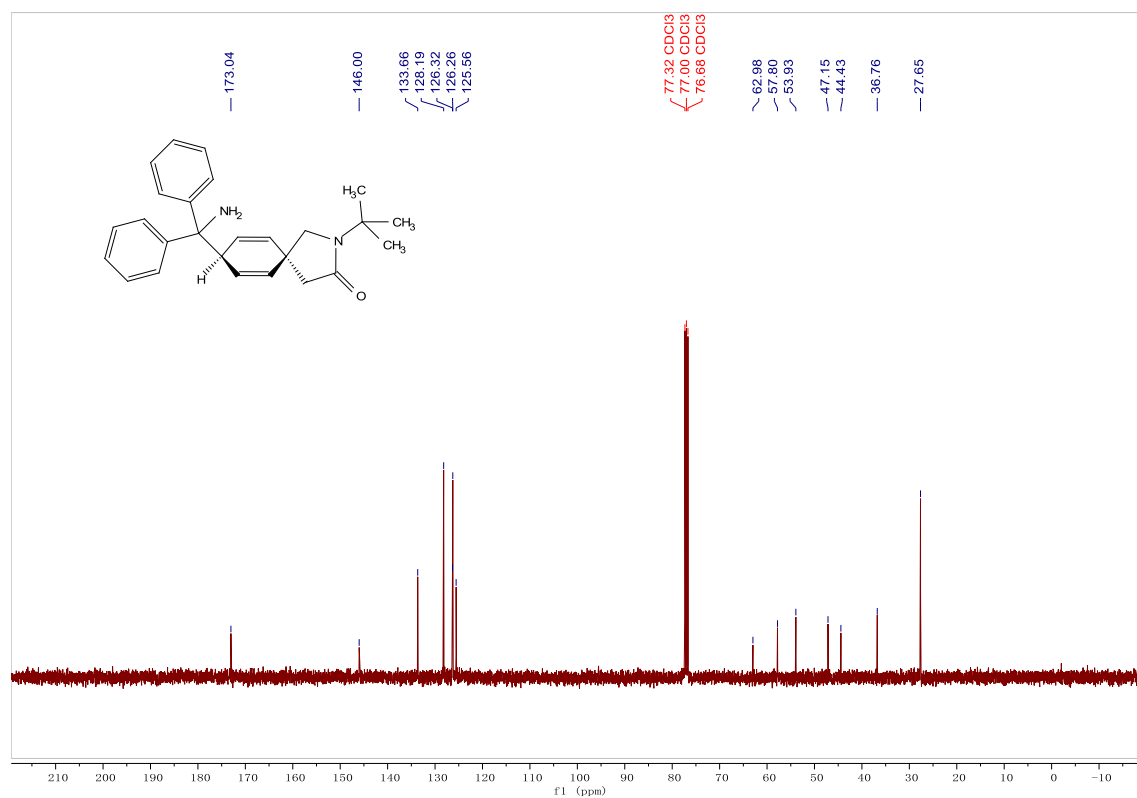
¹H-NMR for trans-3-9



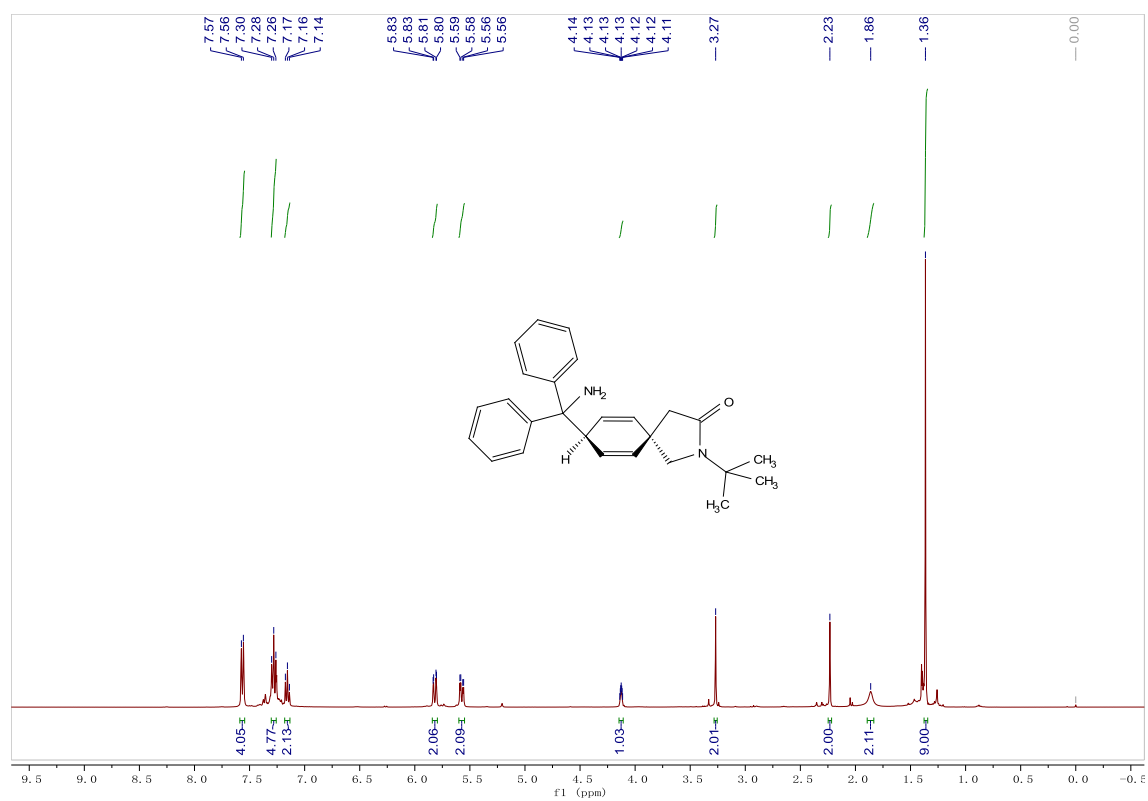
¹³C-NMR for trans-3-9



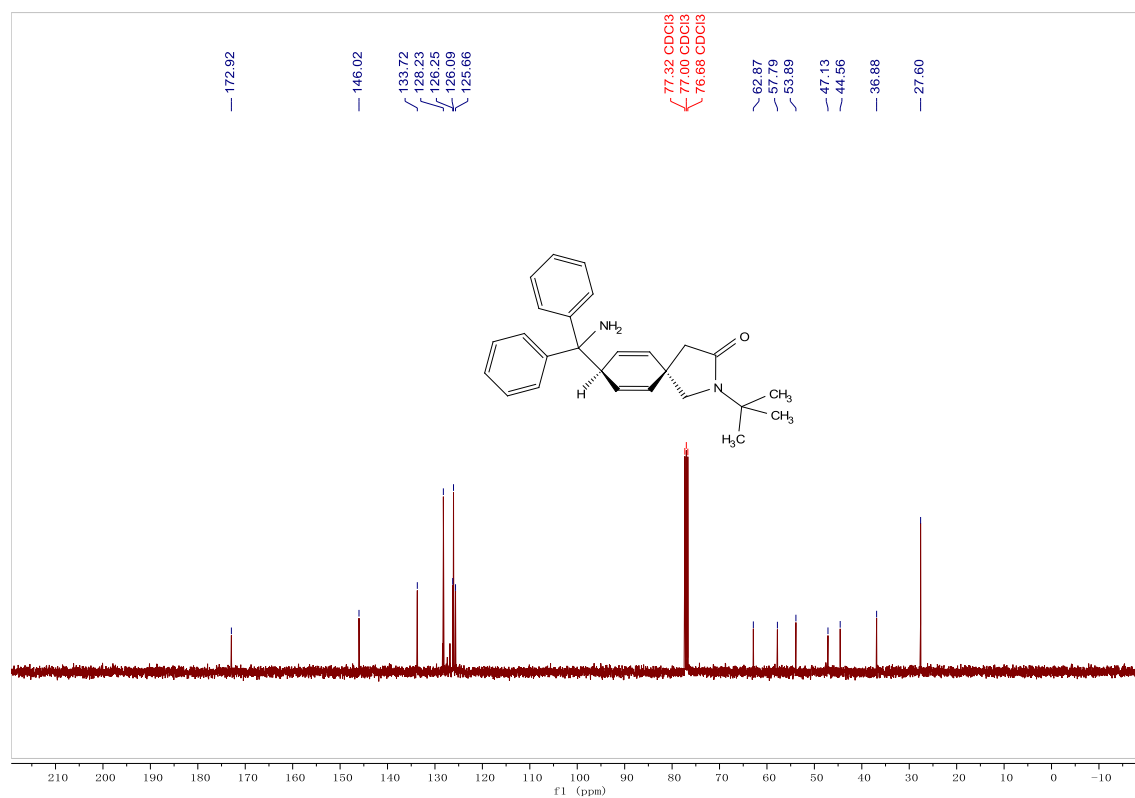
¹H-NMR for cis-3-10



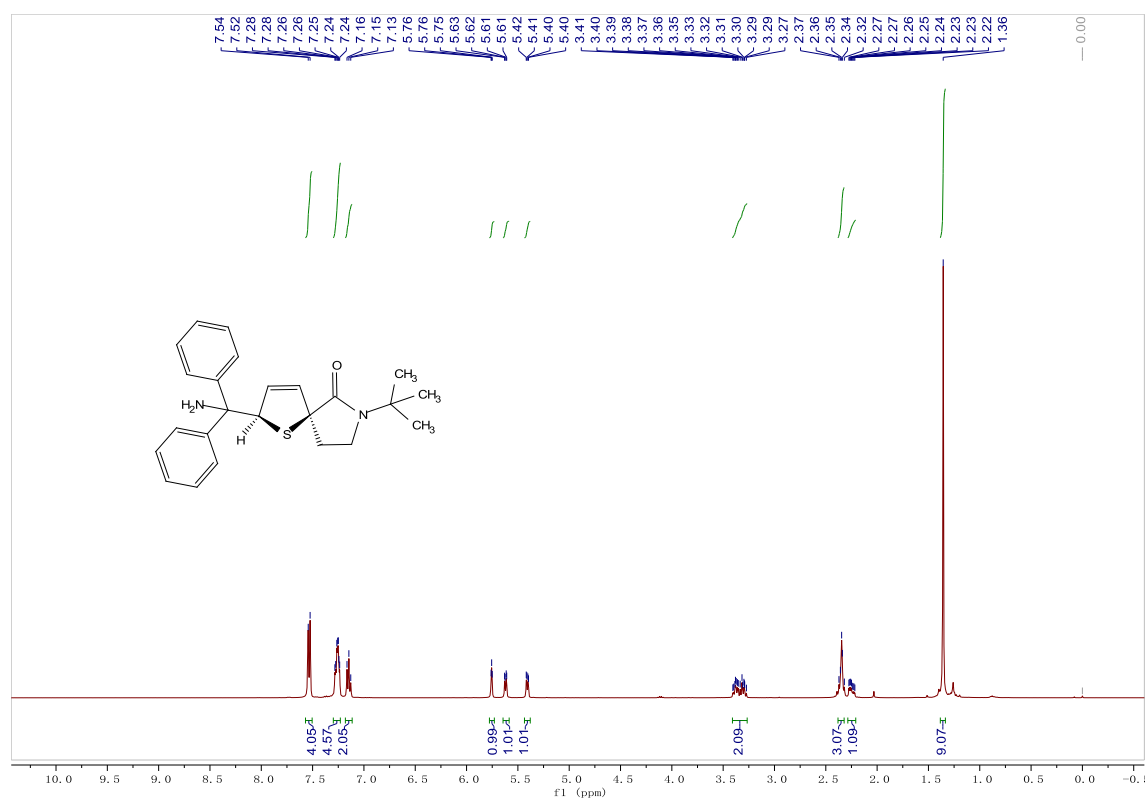
¹³C-NMR for cis-3-10



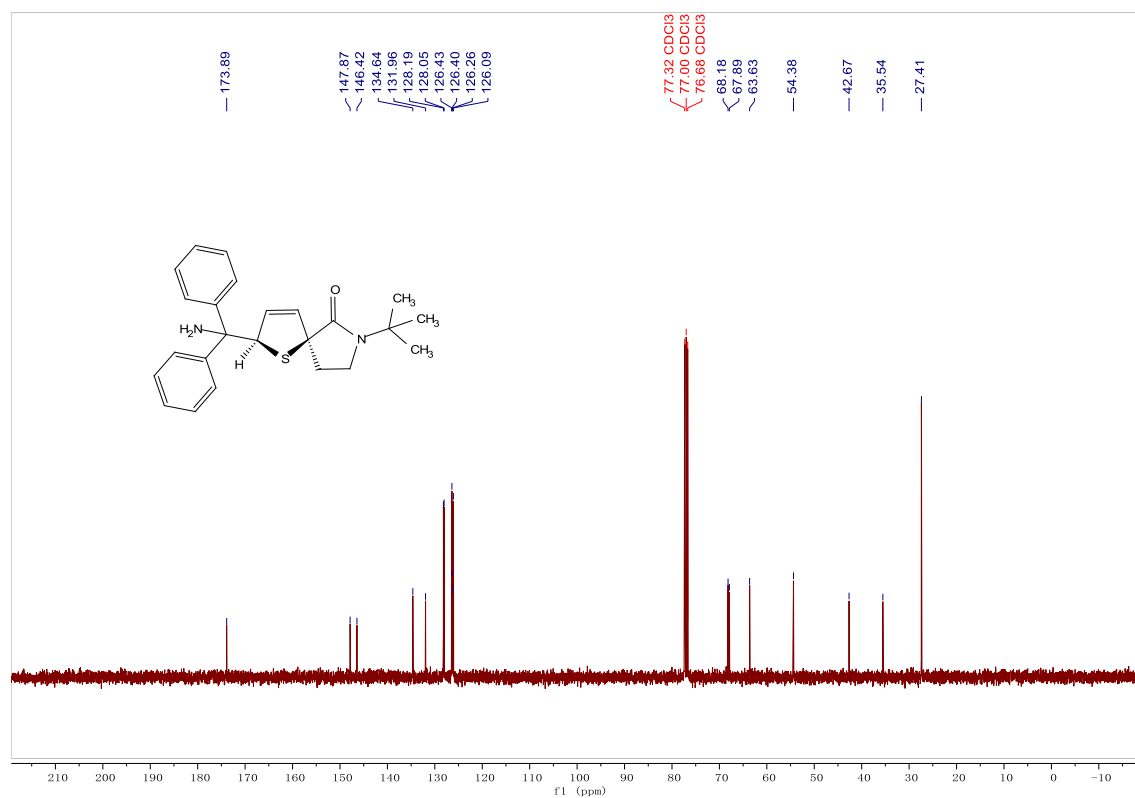
¹H-NMR for trans-3-10



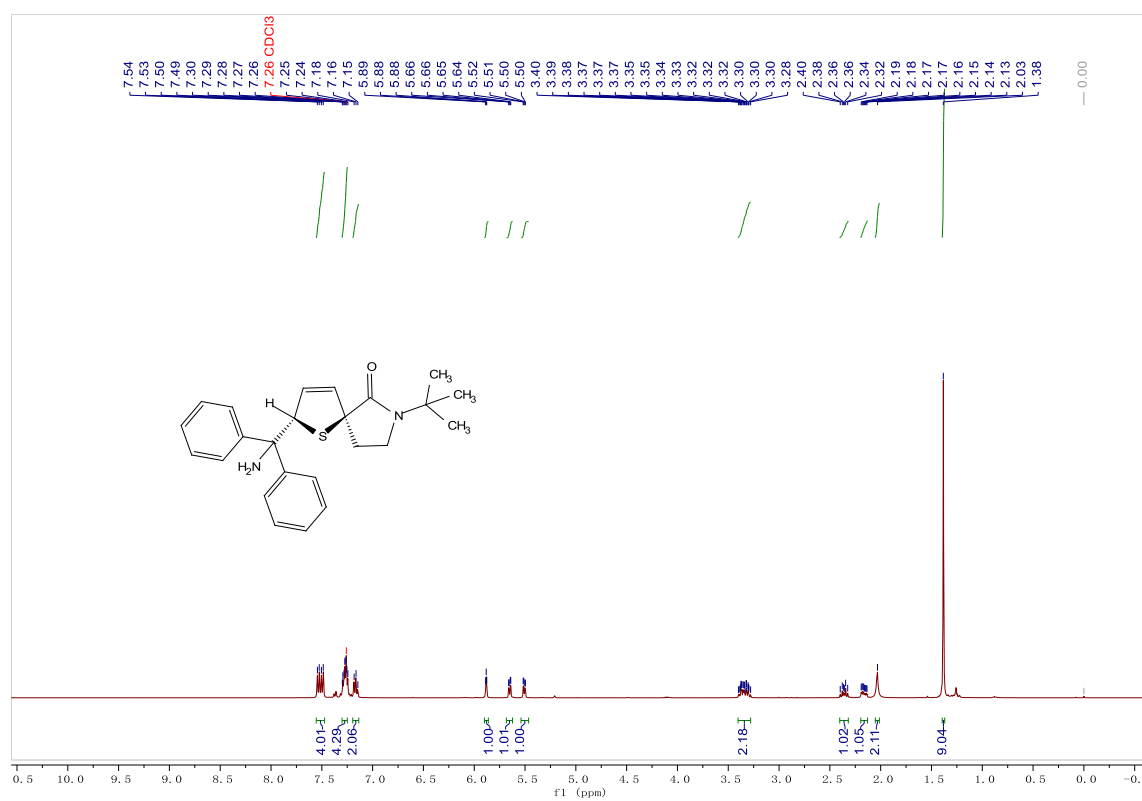
¹³C-NMR for trans-3-10



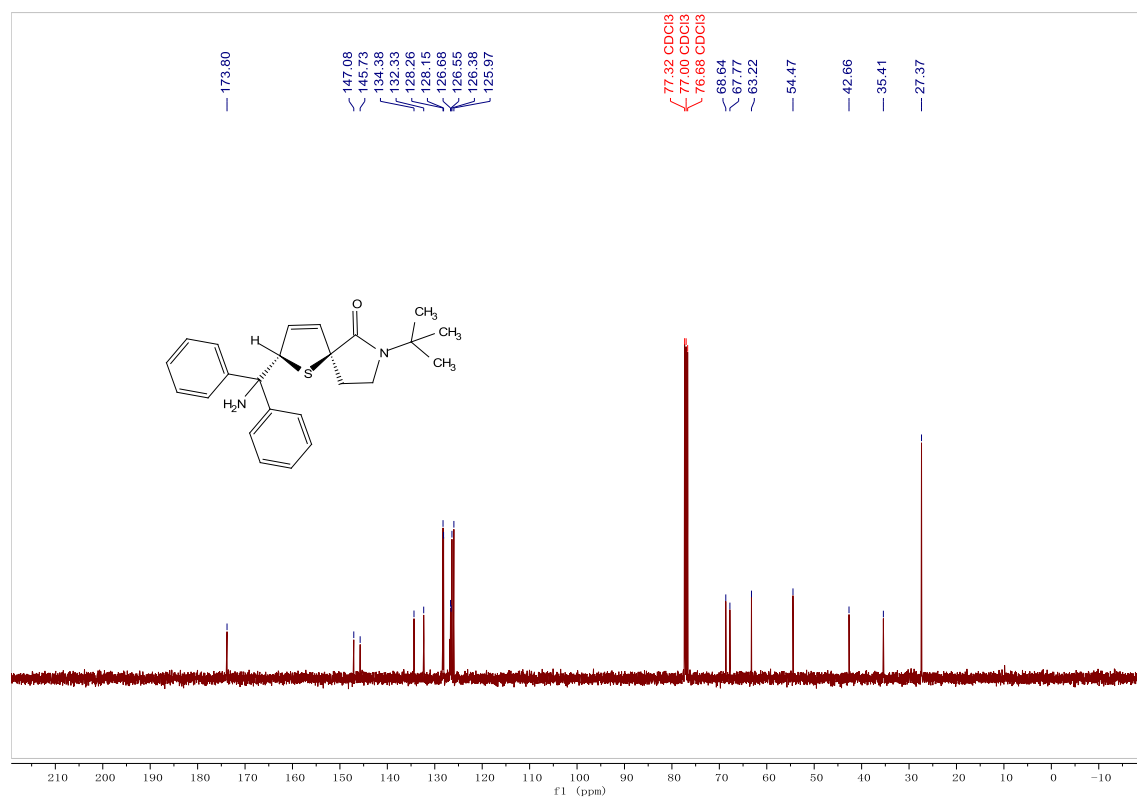
¹H-NMR for cis-3-11



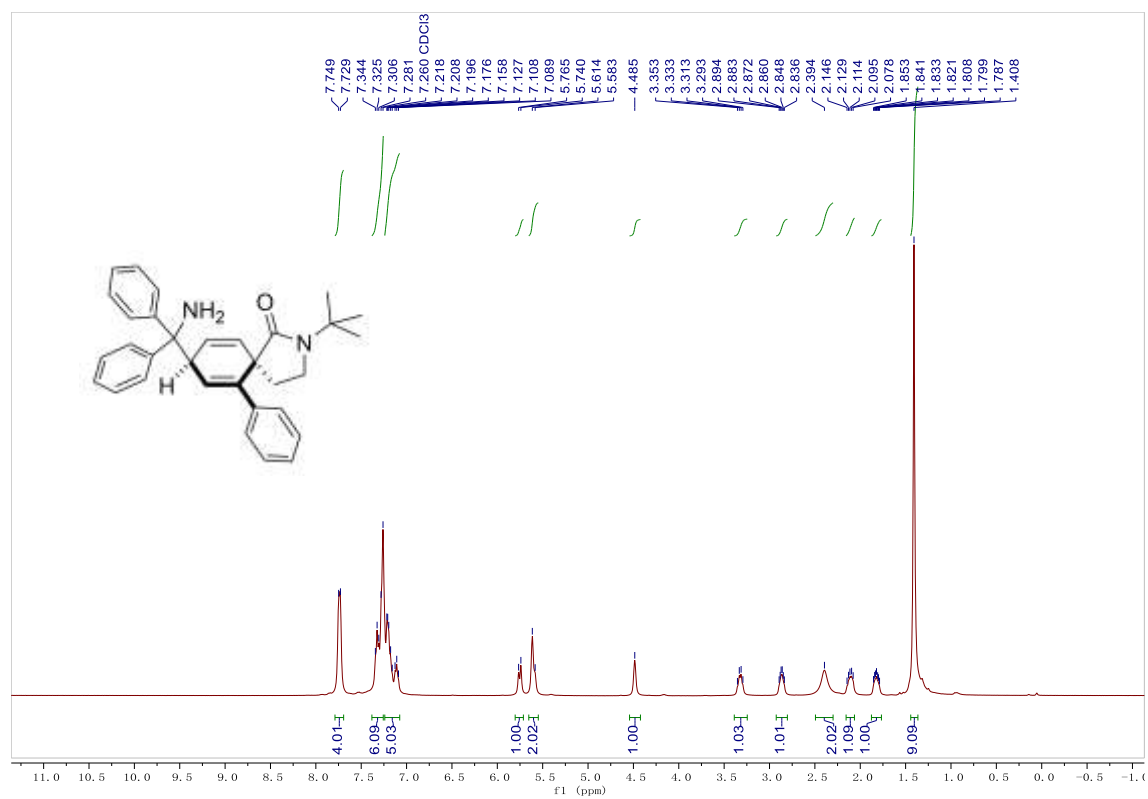
¹³C-NMR for cis-3-11



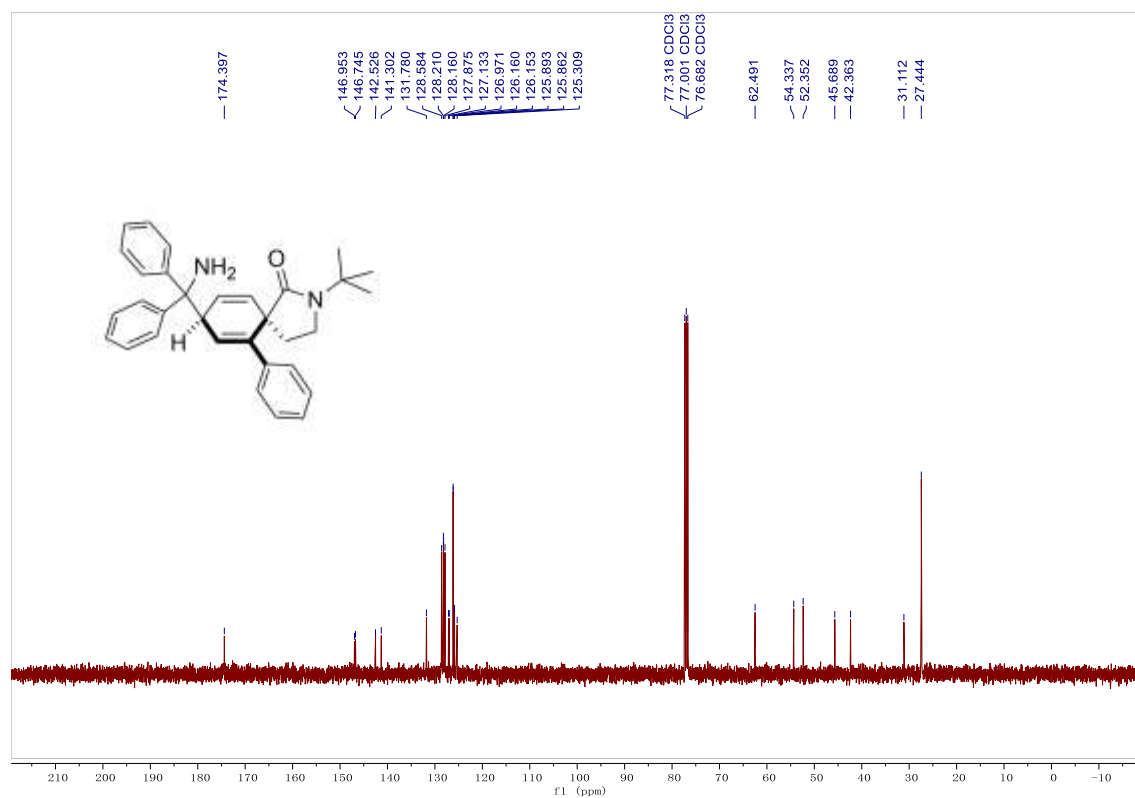
¹H-NMR for trans-3-11



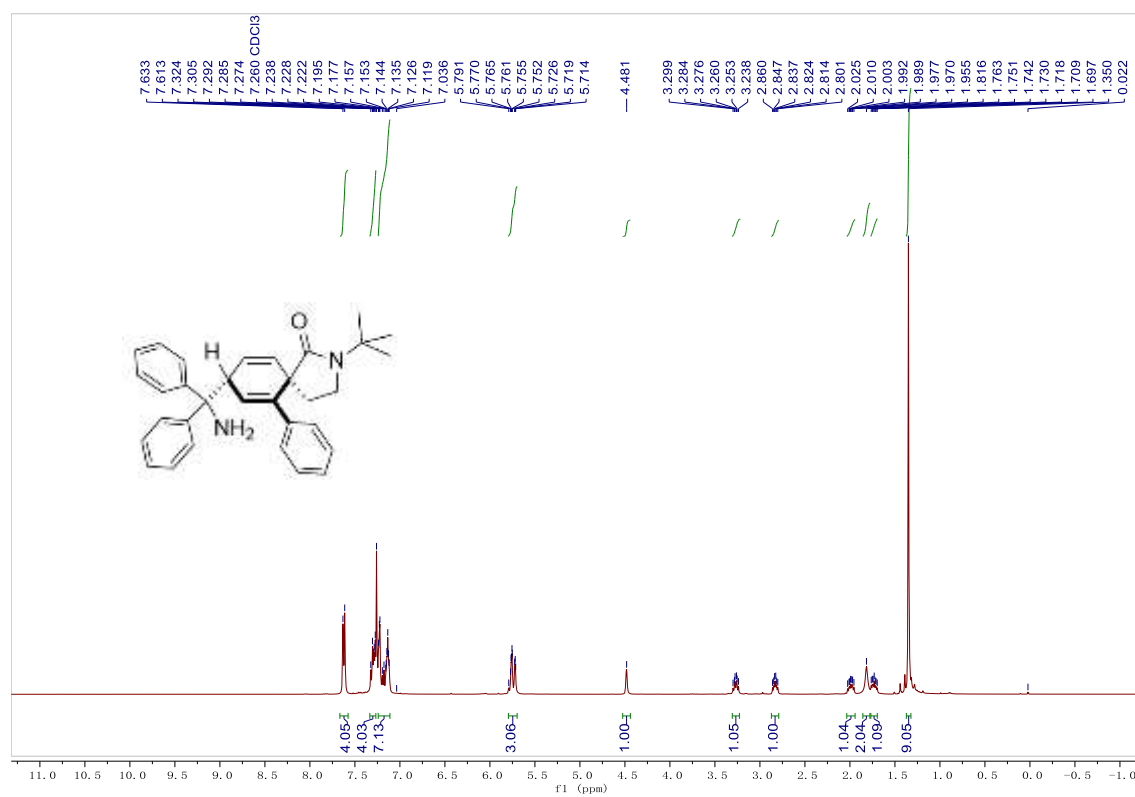
¹³C-NMR for trans-3-11



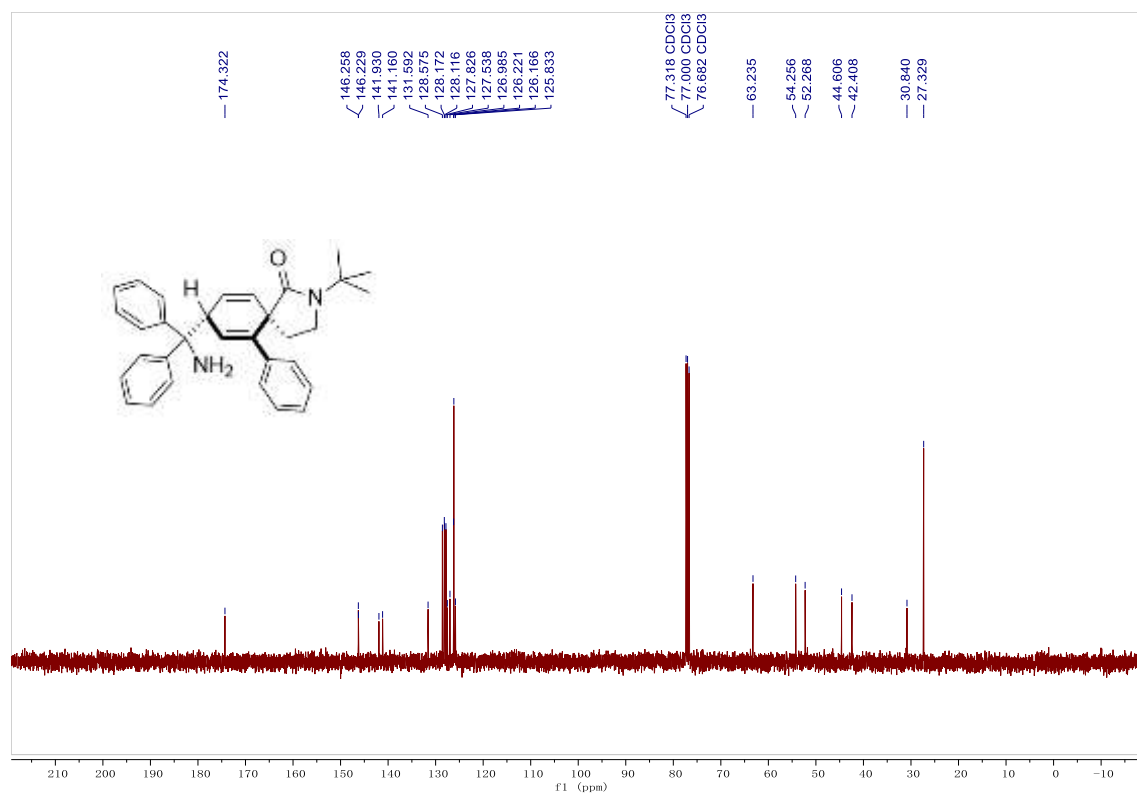
¹H-NMR for cis-3-12



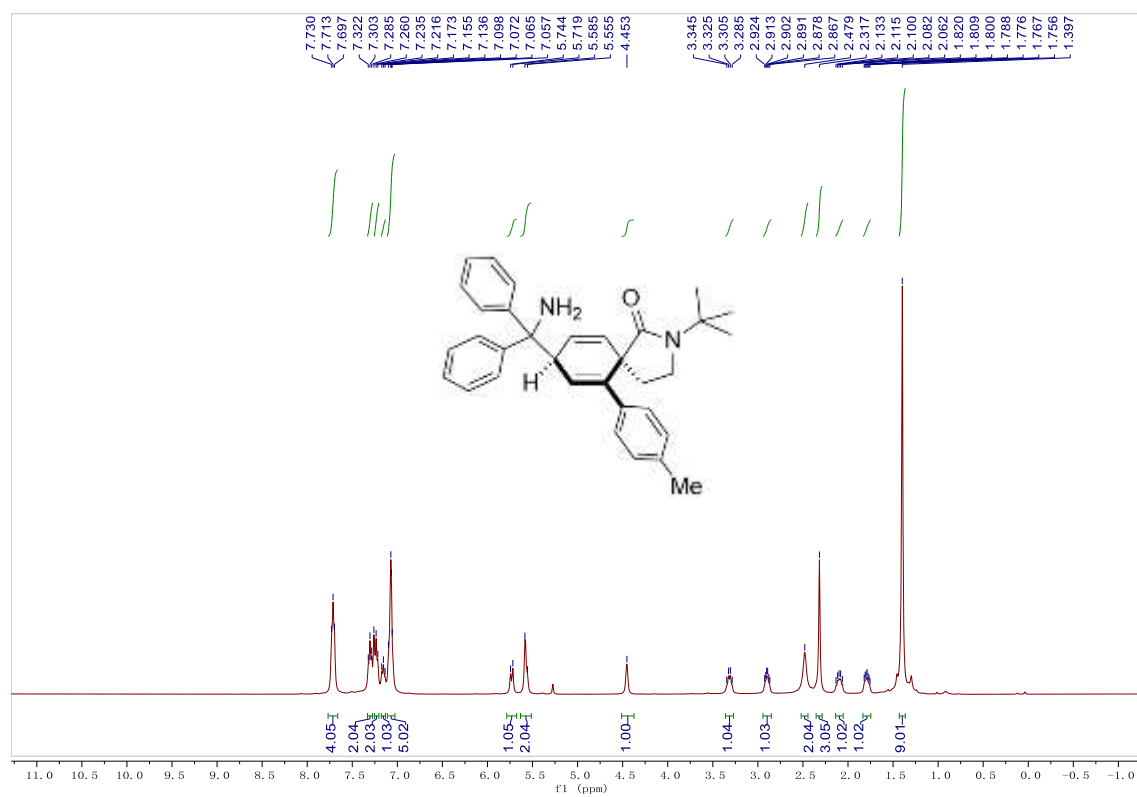
^{13}C -NMR for **cis-3-12**



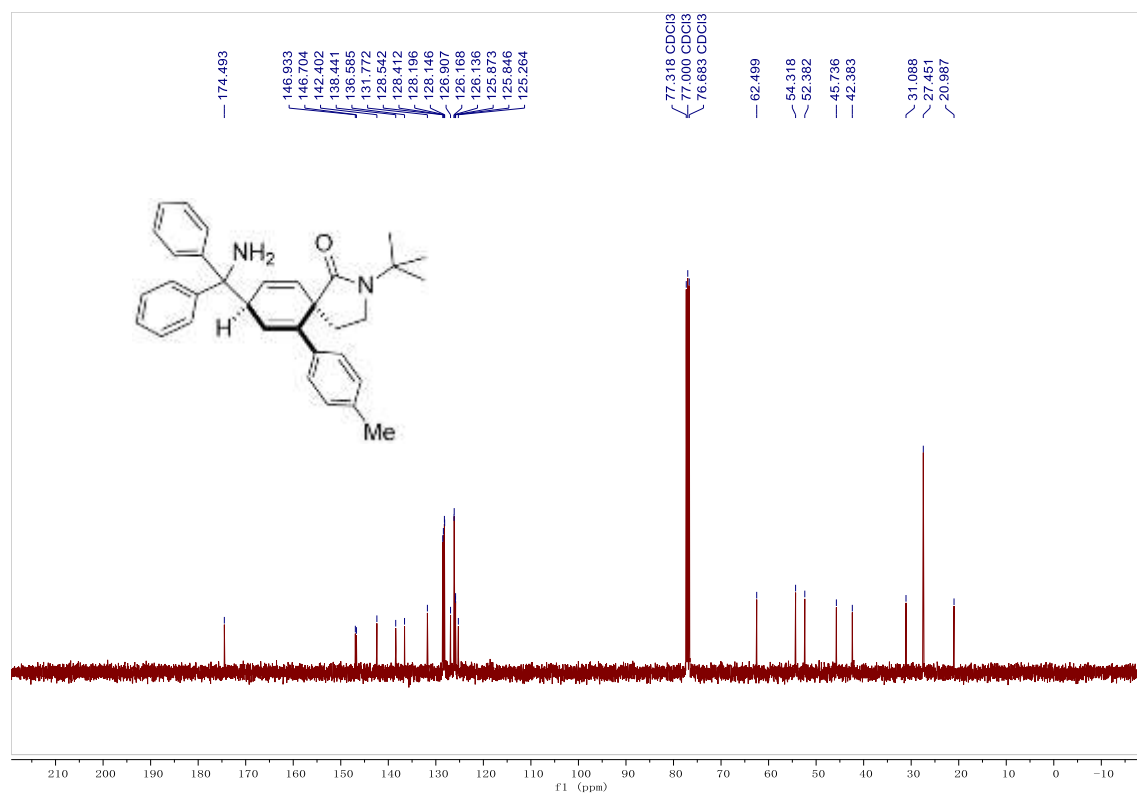
^1H -NMR for **trans-3-12**



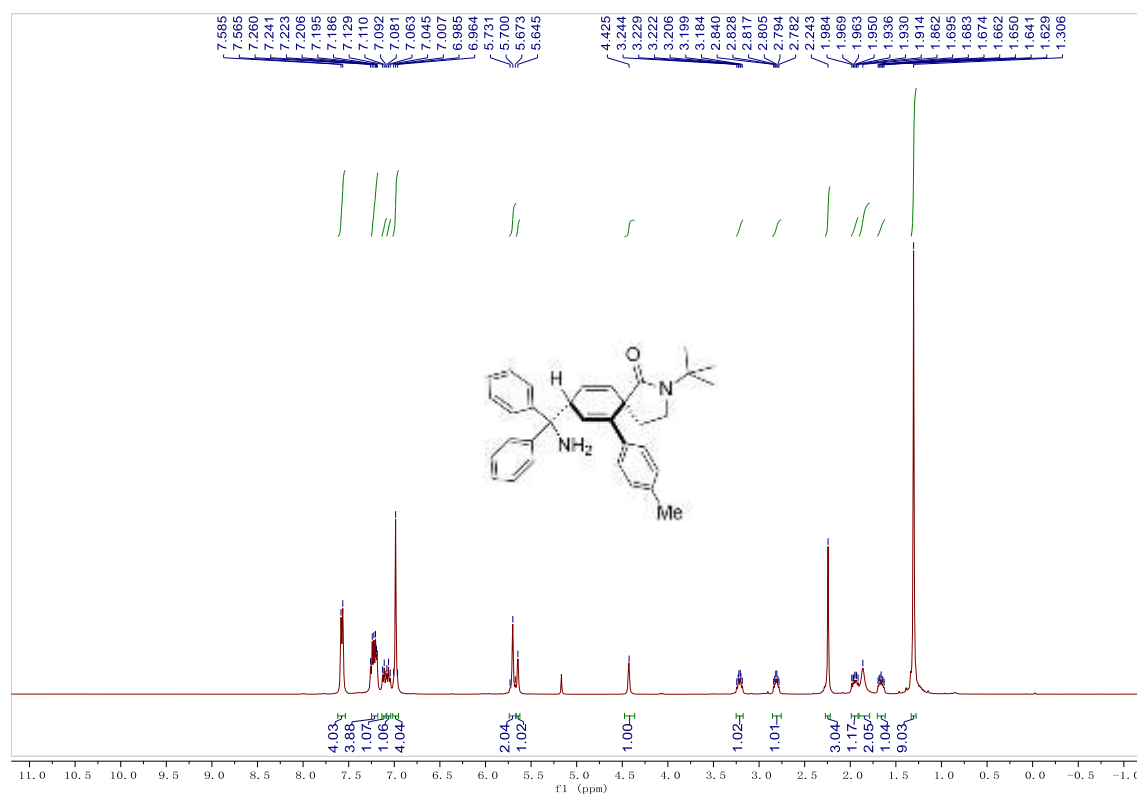
¹³C-NMR for trans-3-12



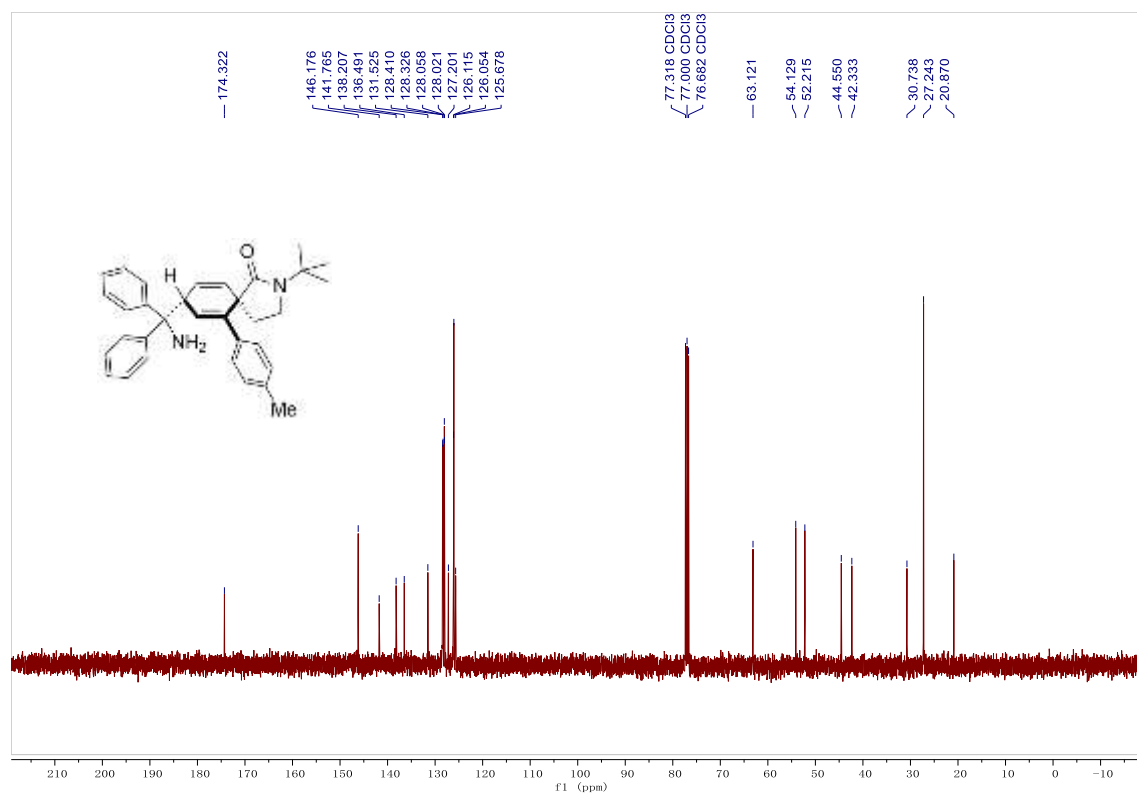
¹H-NMR for cis-3-13



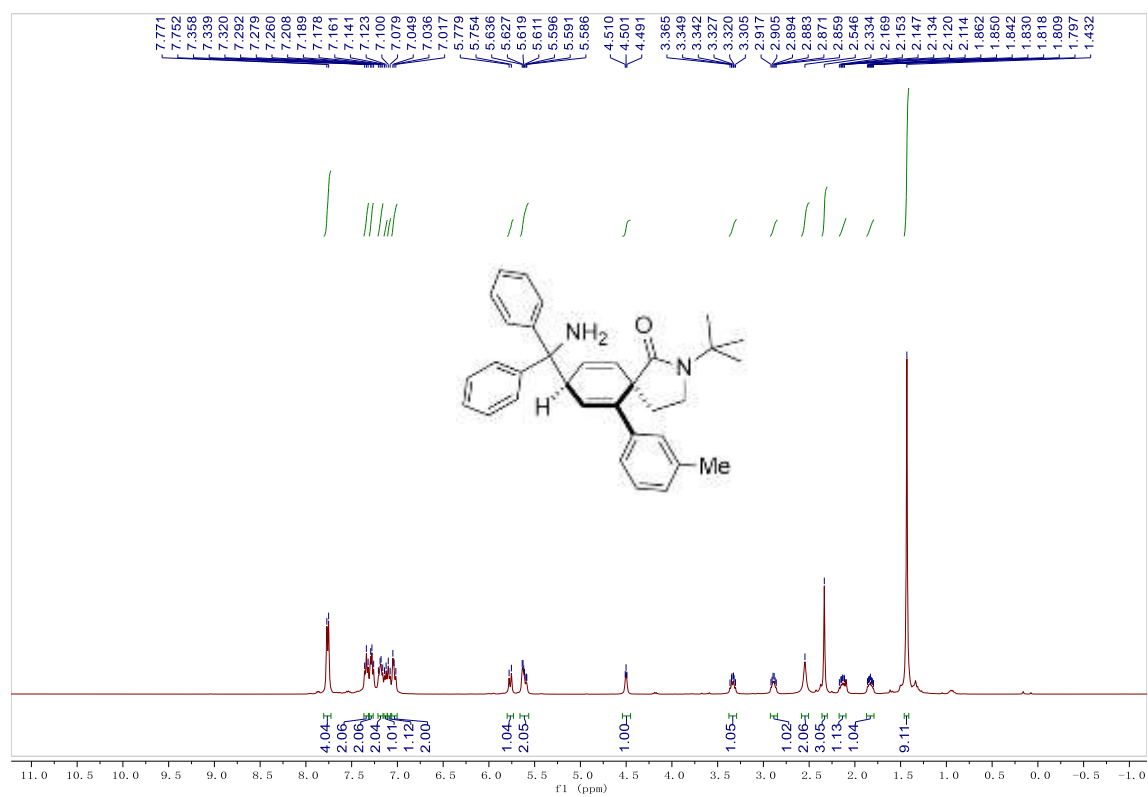
¹³C-NMR for cis-3-13



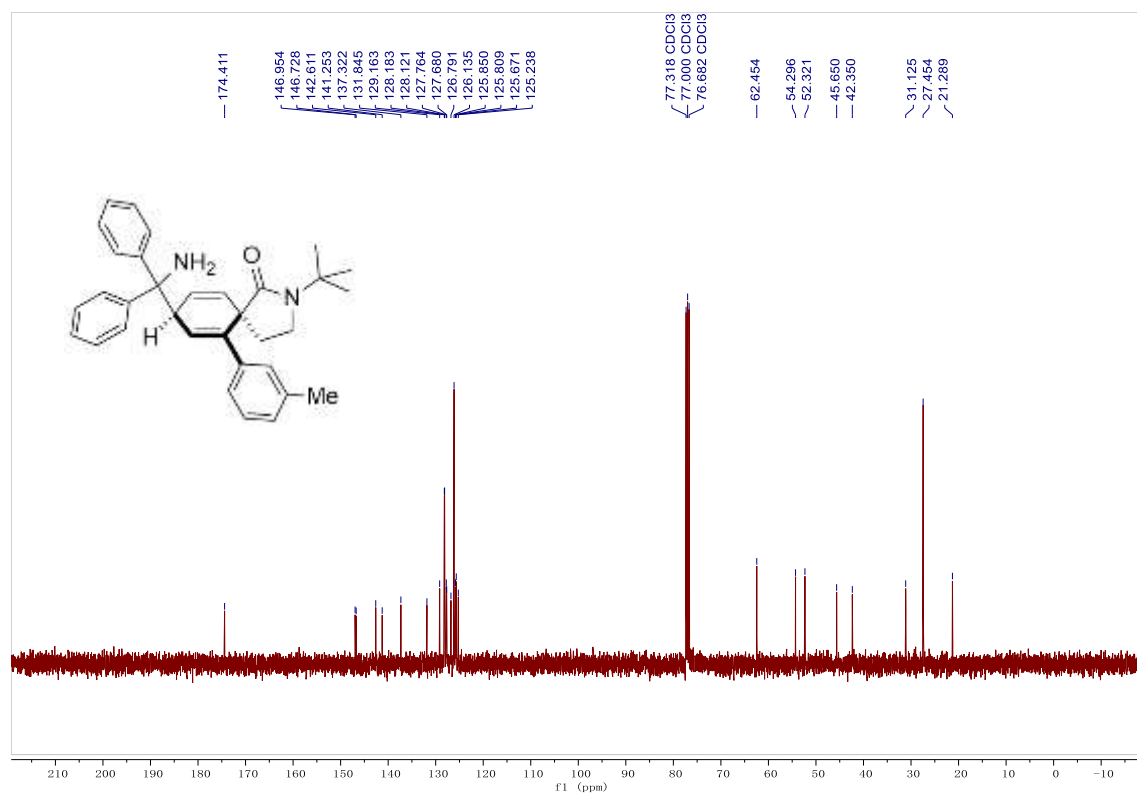
¹H-NMR for trans-3-13



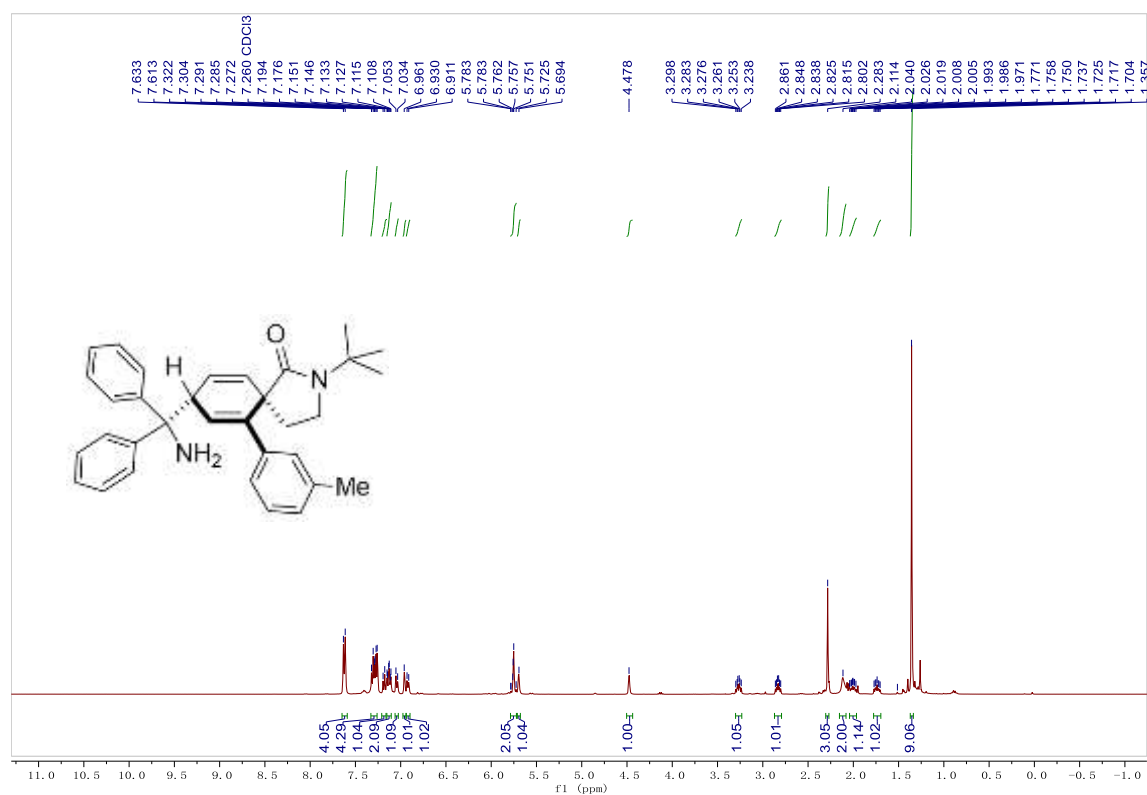
¹³C-NMR for trans-3-13



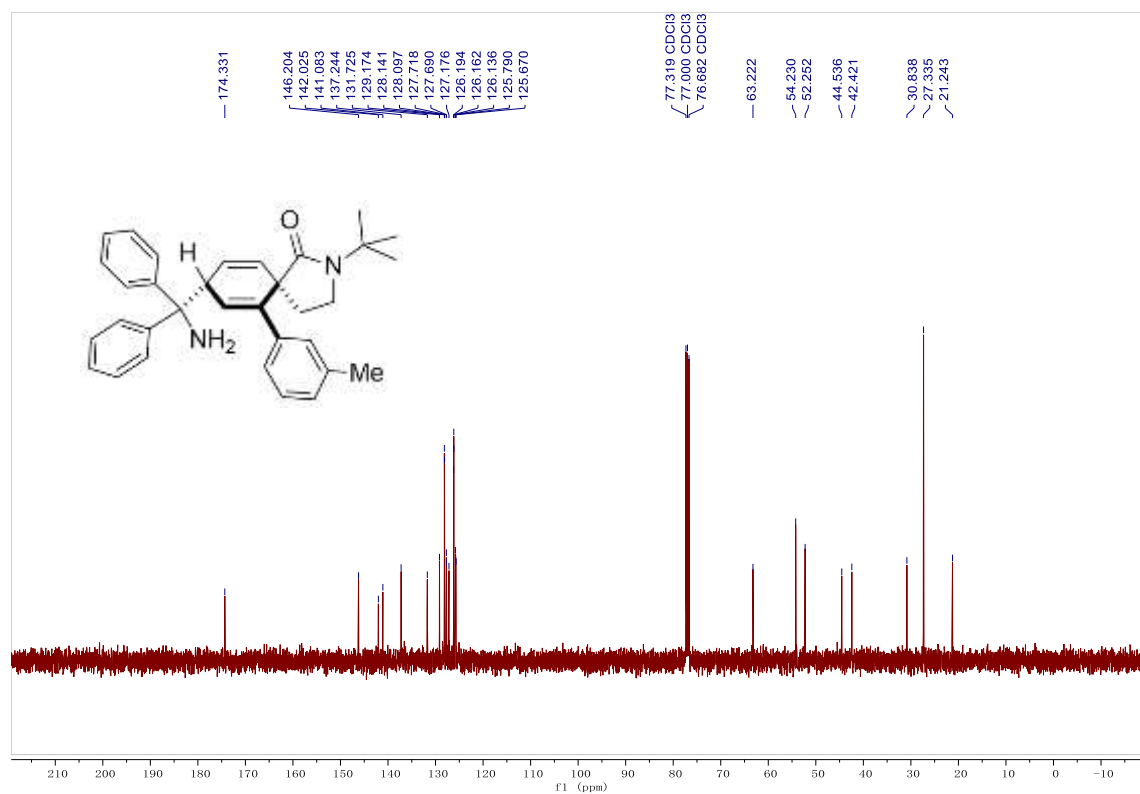
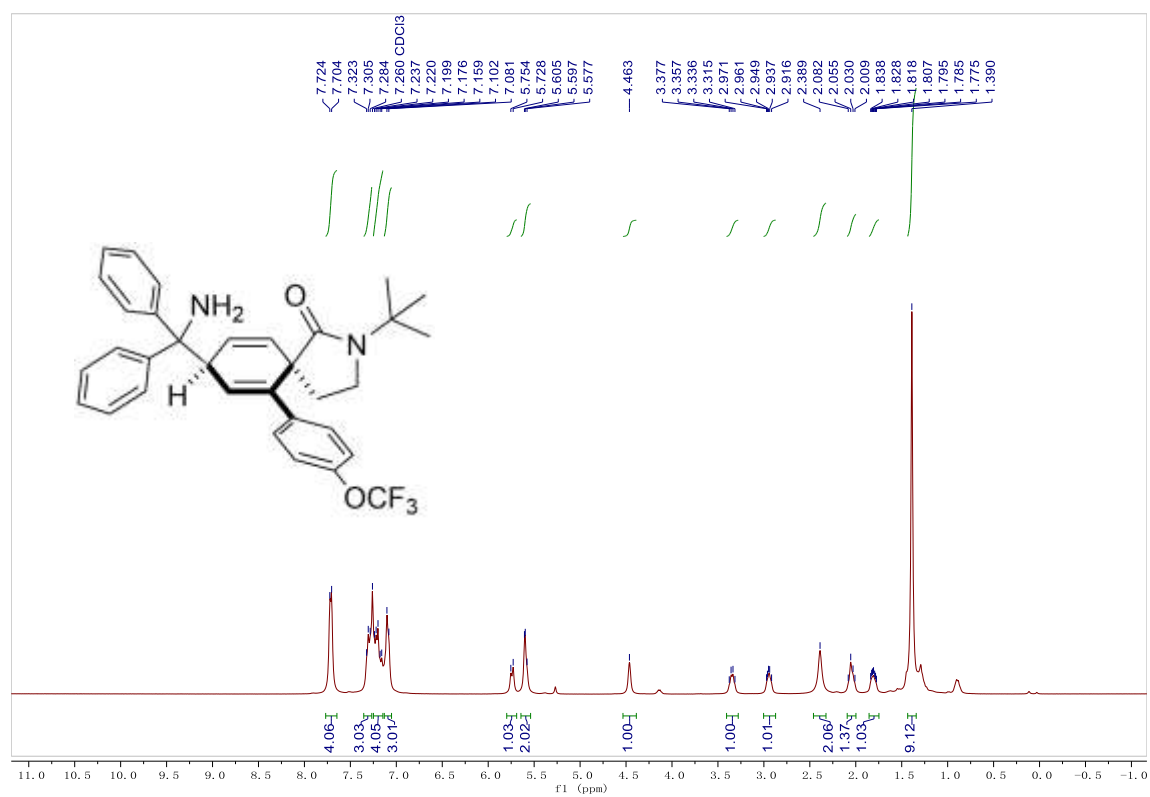
¹H-NMR for cis-3-14

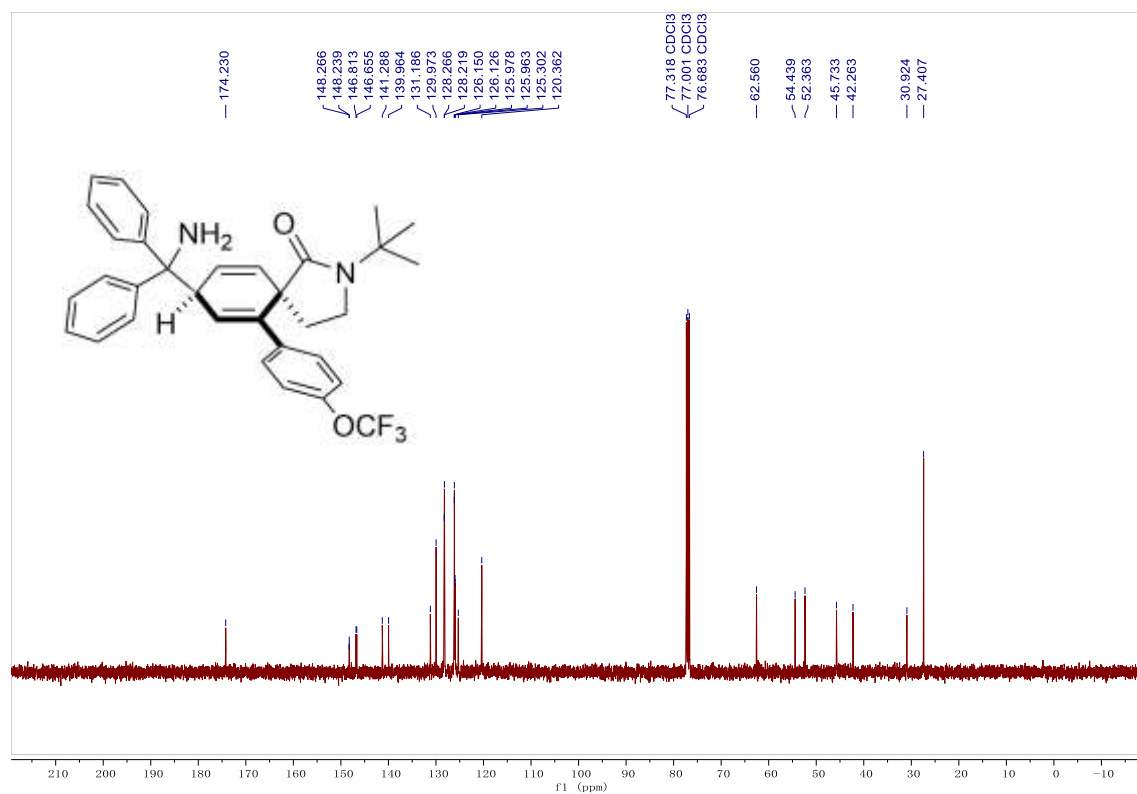


¹³C-NMR for cis-3-14

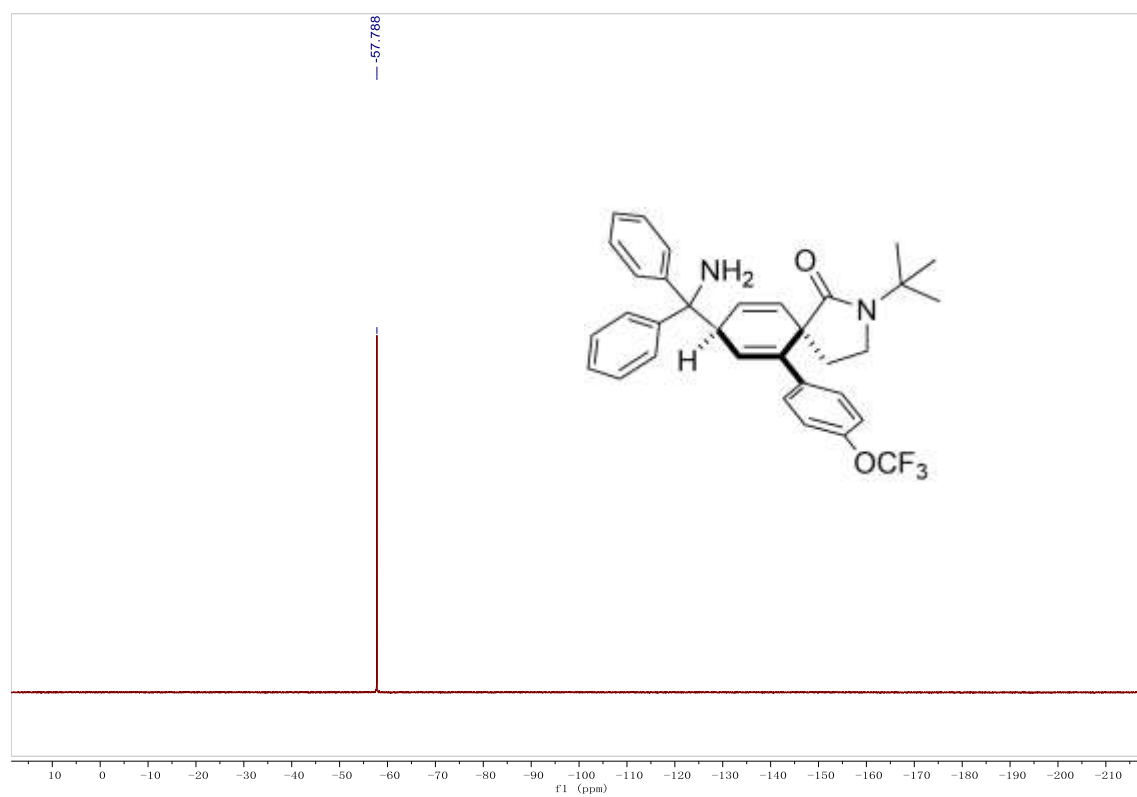


¹H-NMR for trans-3-14

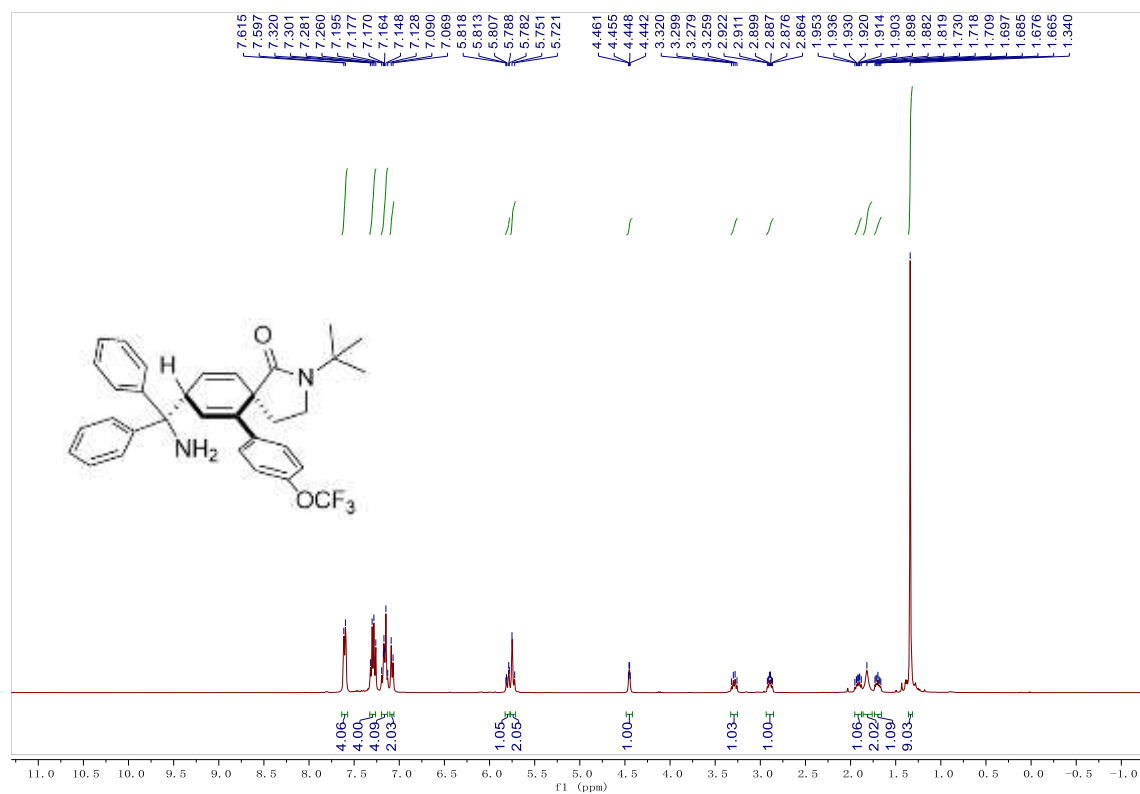
 ^{13}C -NMR for trans-**3-14**¹H-NMR for cis-**3-15**



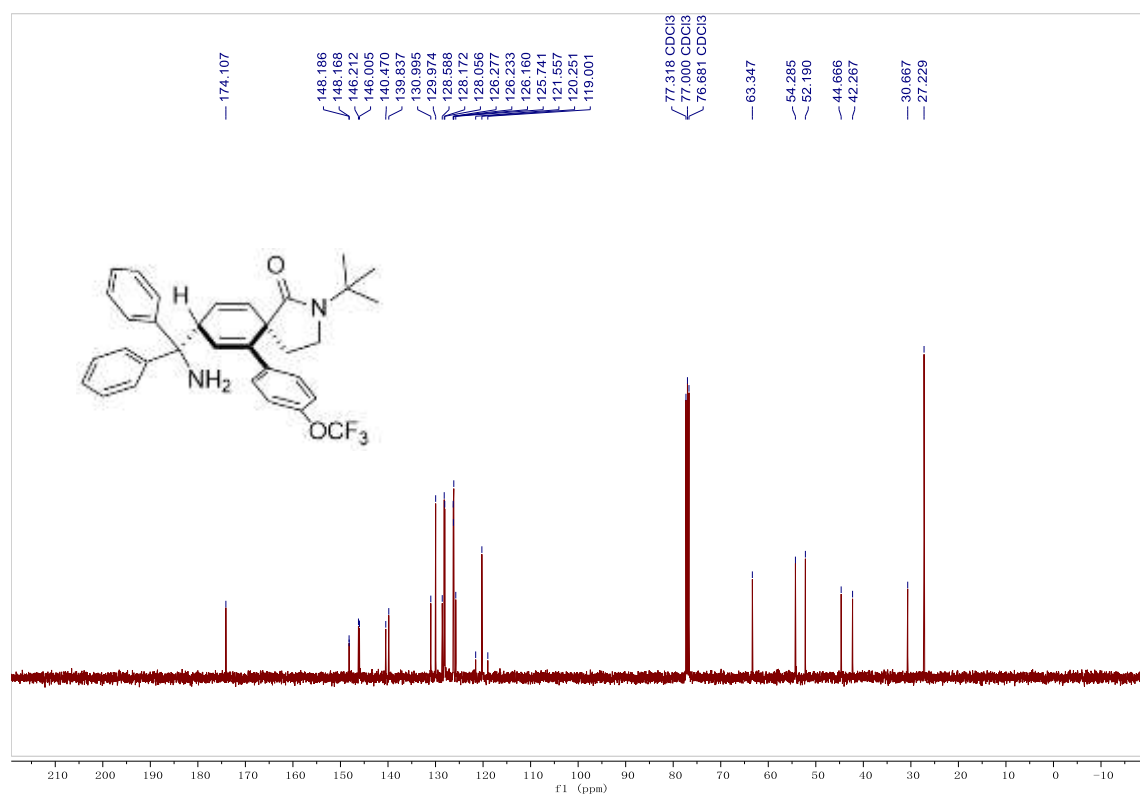
¹³C-NMR for cis-3-15



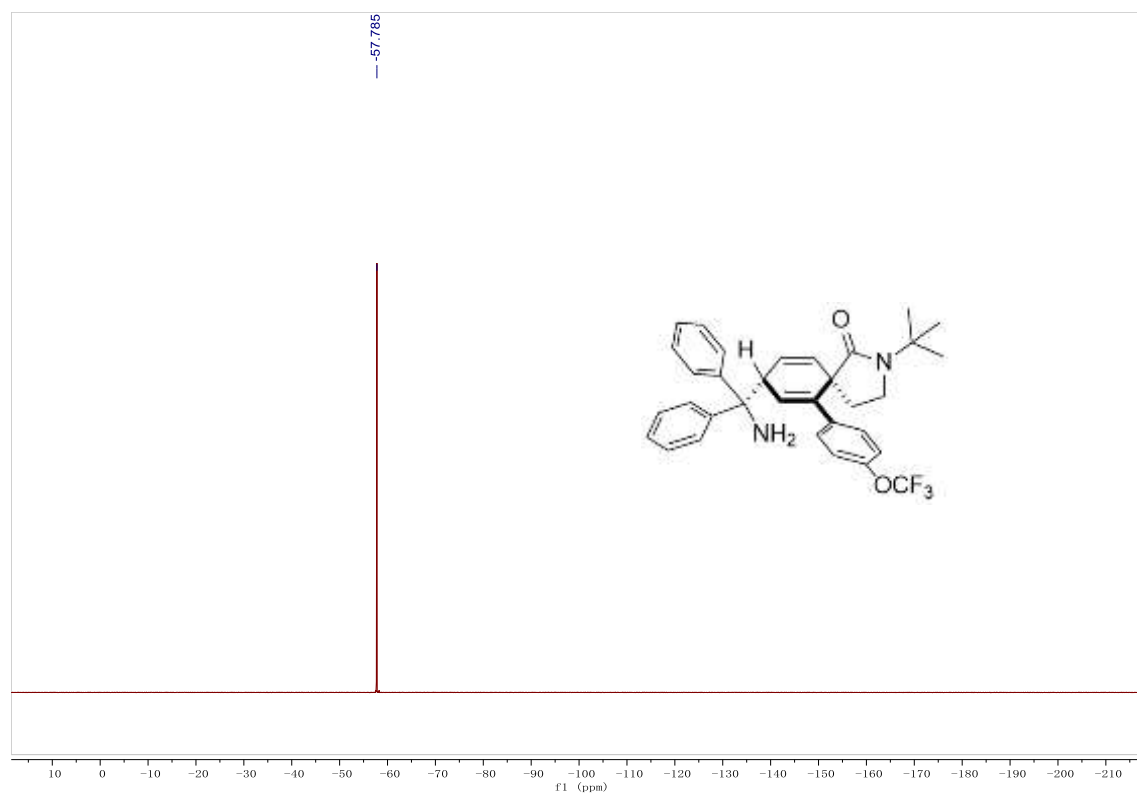
¹⁹F-NMR for cis-3-15



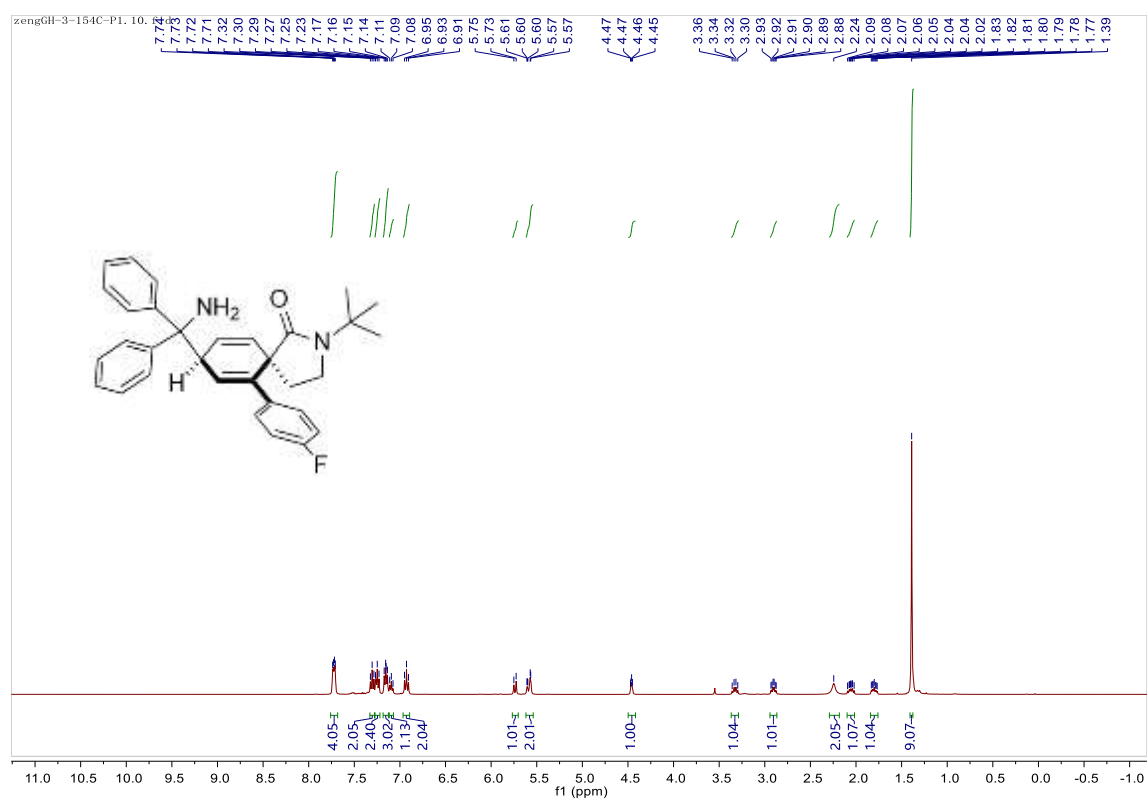
¹H-NMR for trans-3-15



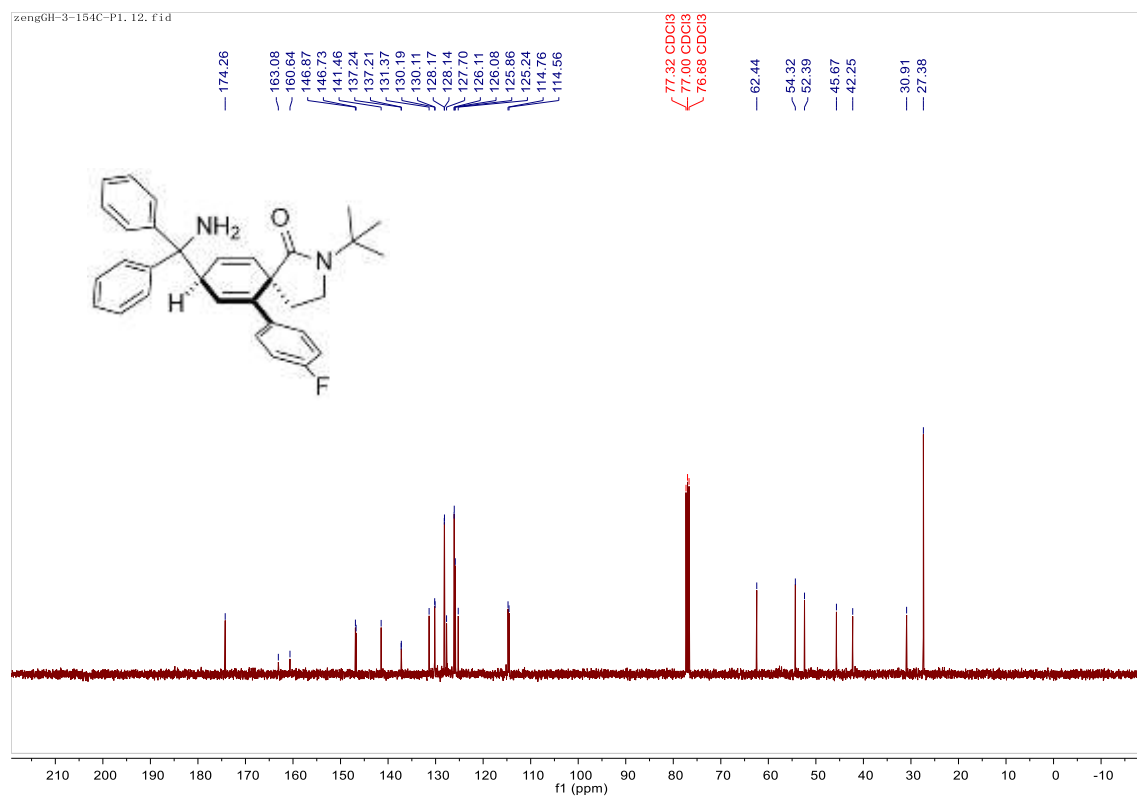
¹³C-NMR for trans-3-15



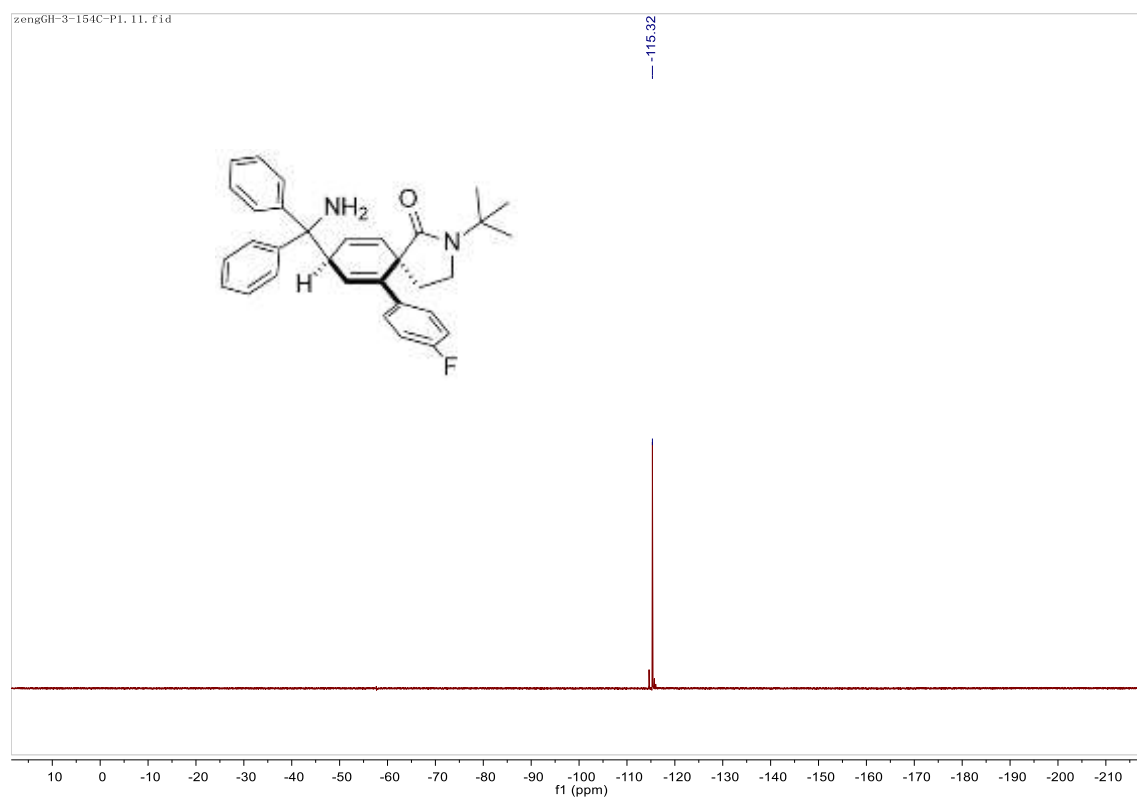
¹⁹F-NMR for trans-3-15



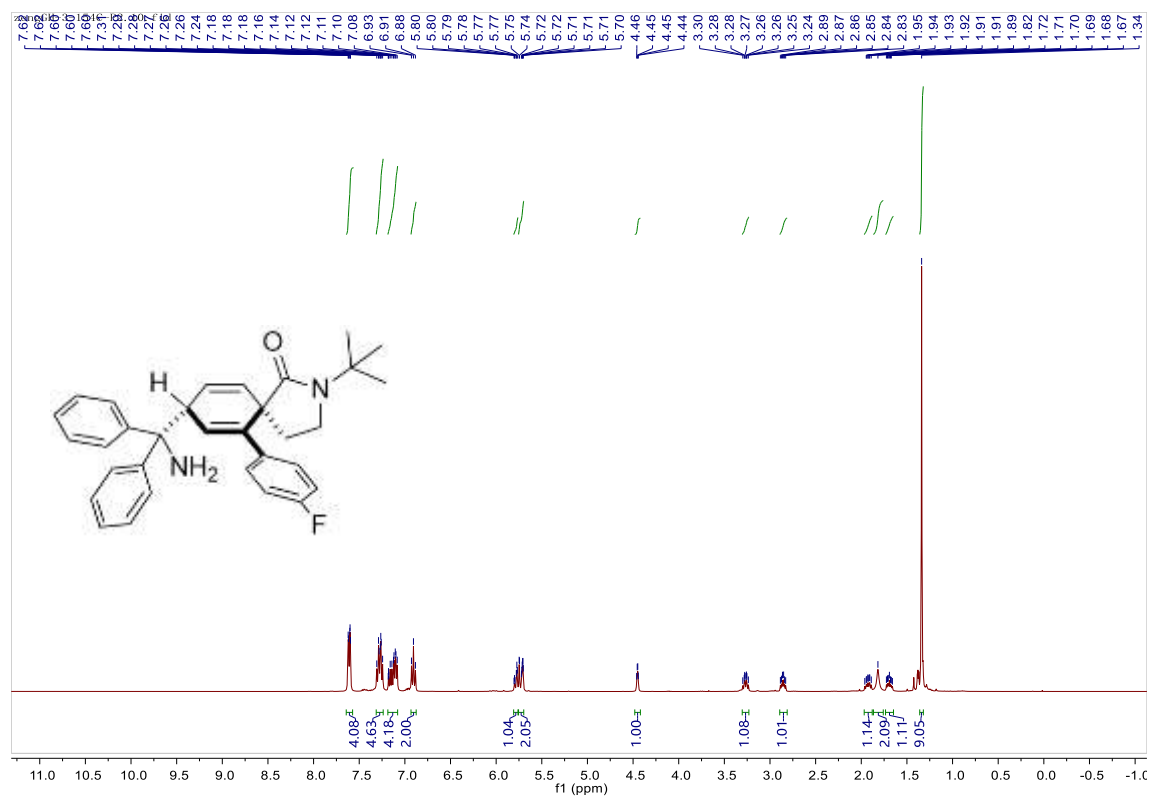
¹H-NMR for cis-3-16



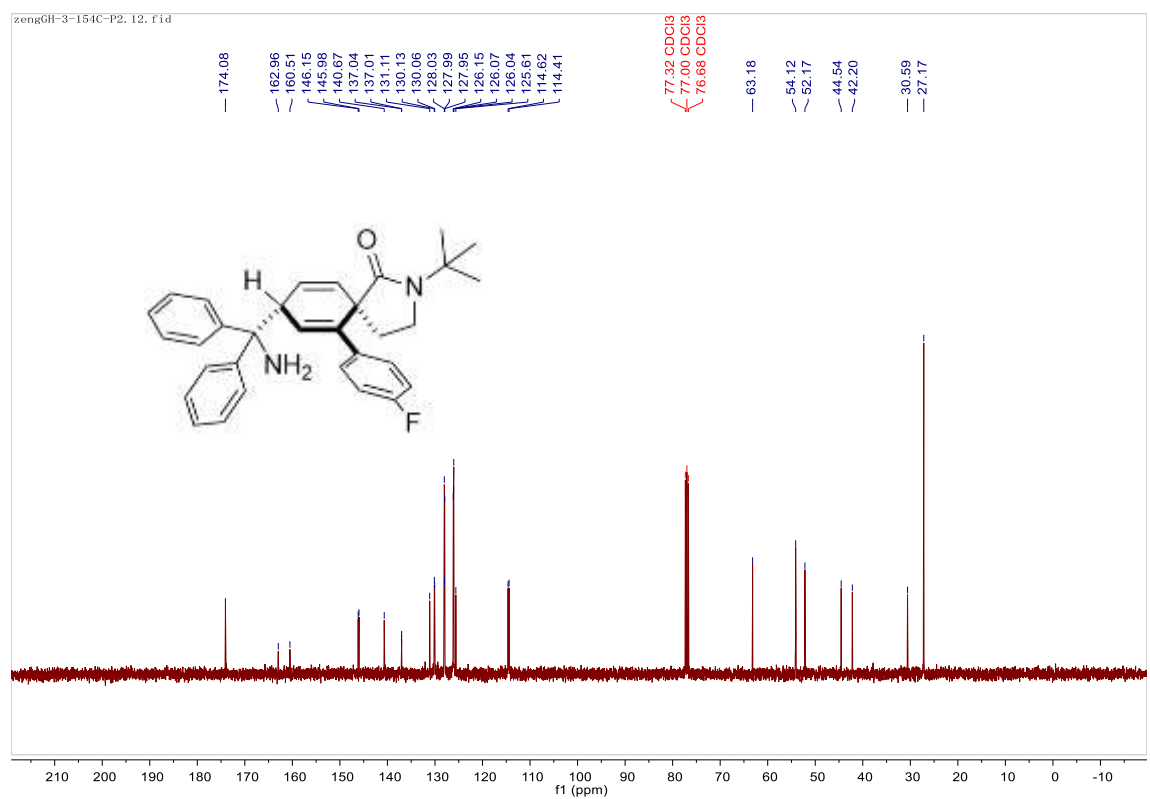
¹³C-NMR for **cis-3-16**



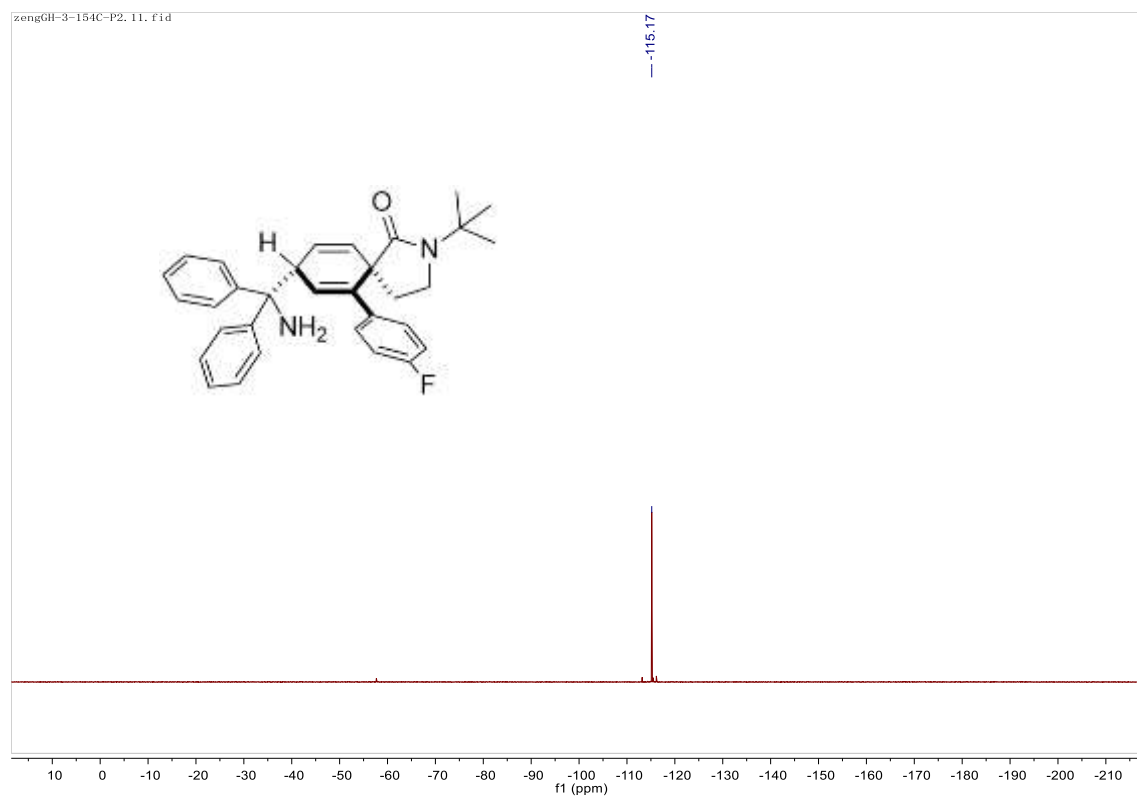
¹⁹F-NMR for **cis-3-16**



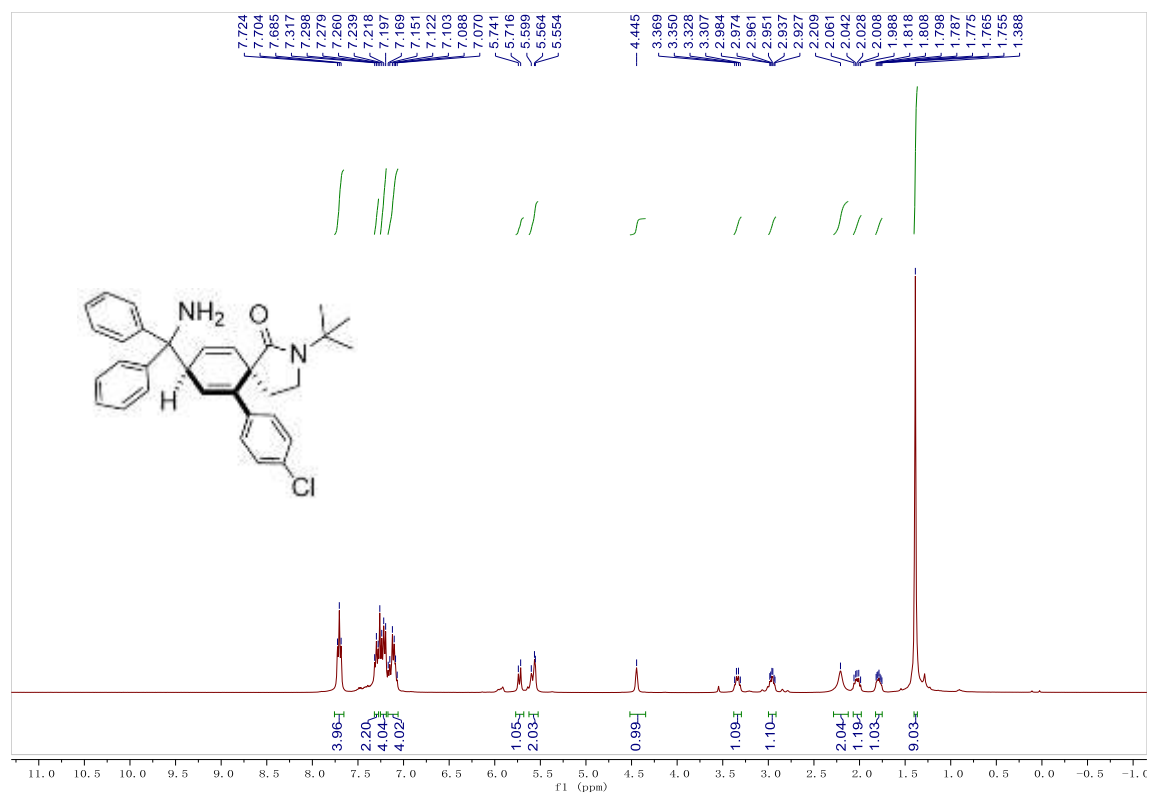
¹H-NMR for trans-3-16



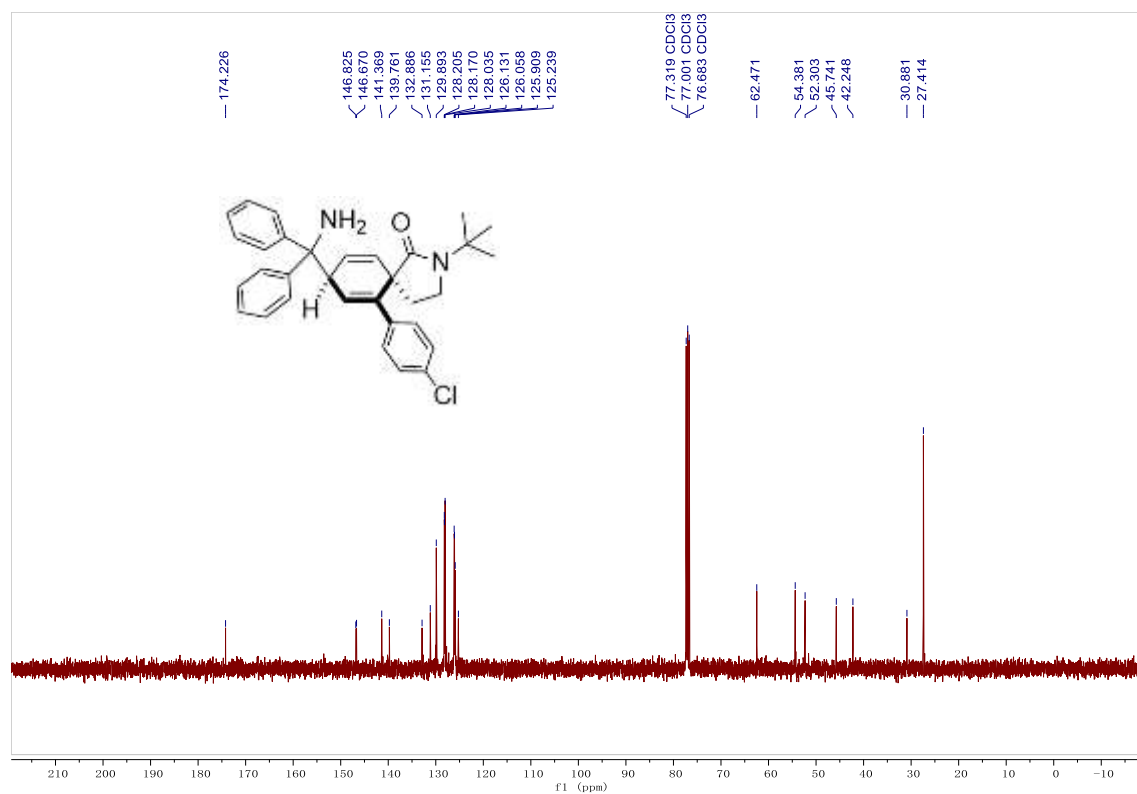
¹³C-NMR for trans-3-16



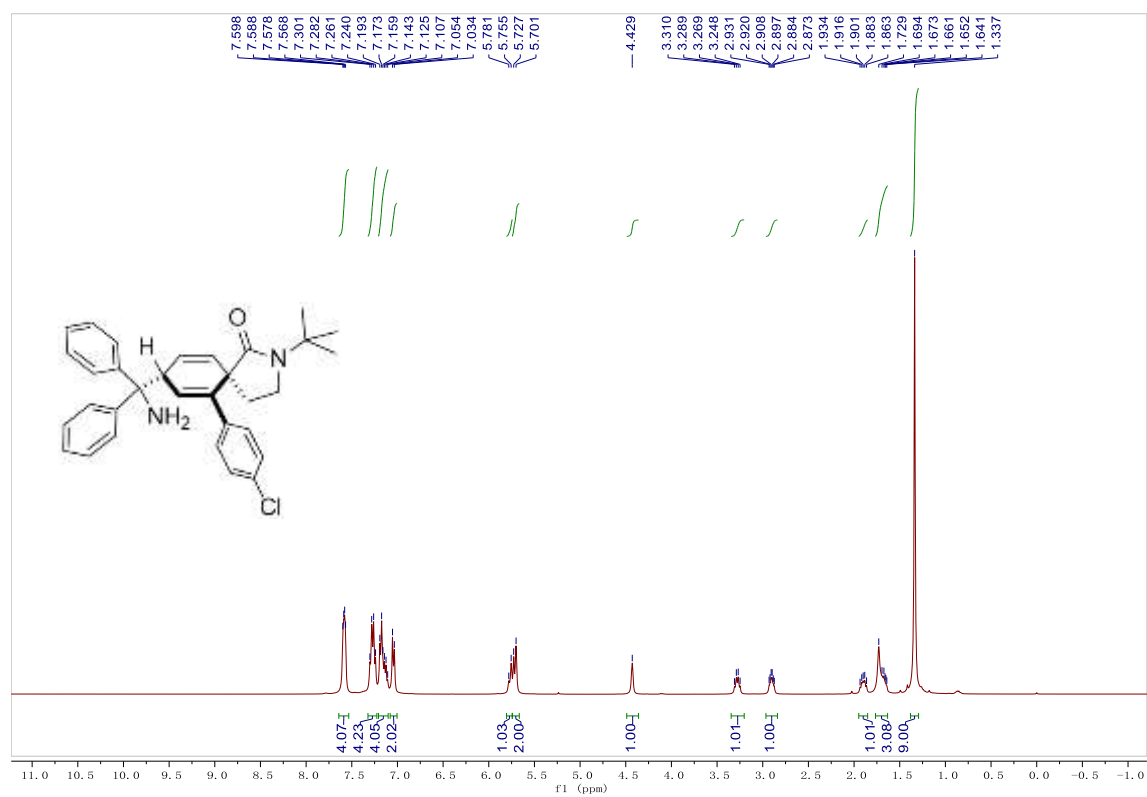
^{19}F -NMR for **trans-3-16**



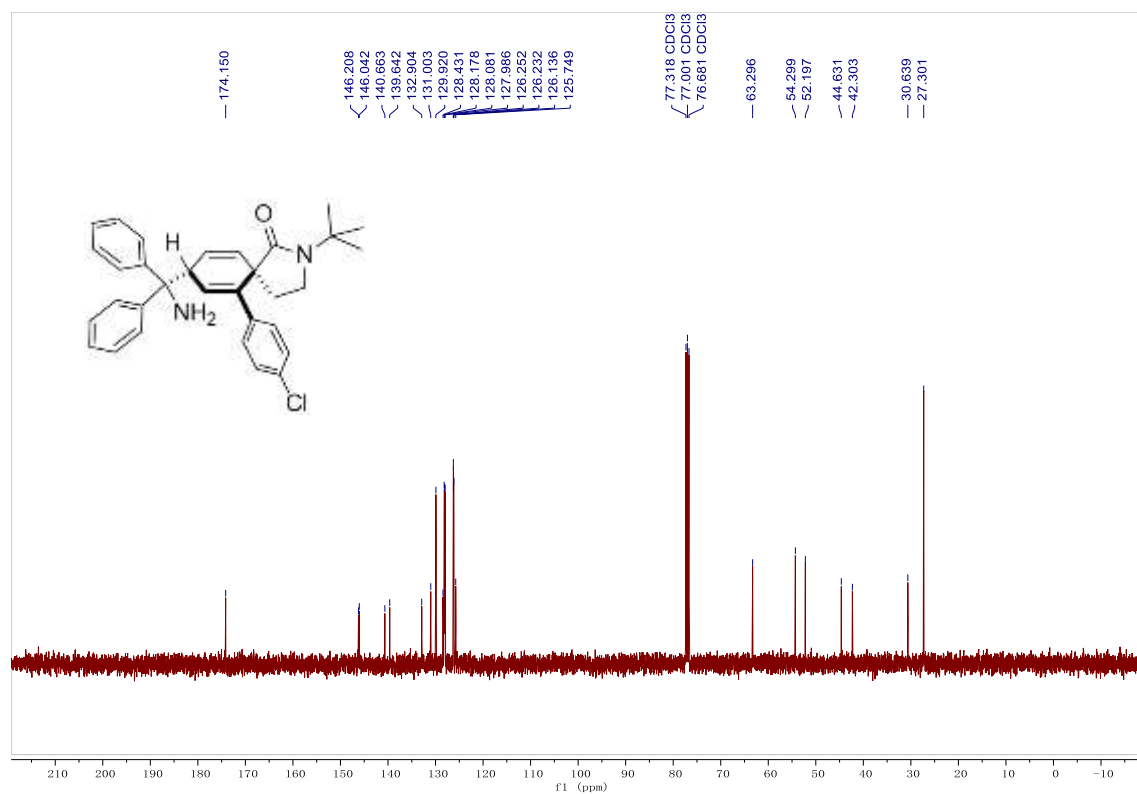
^1H -NMR for **cis-3-17**



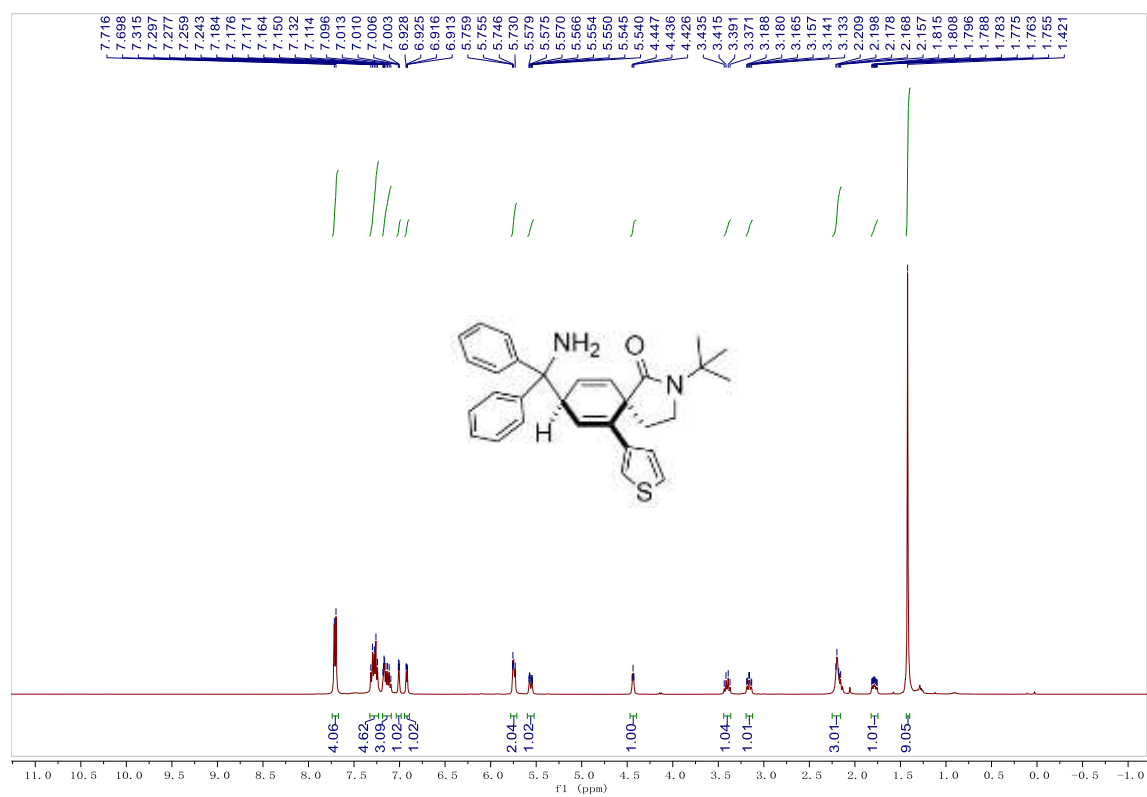
¹³C-NMR for cis-3-17



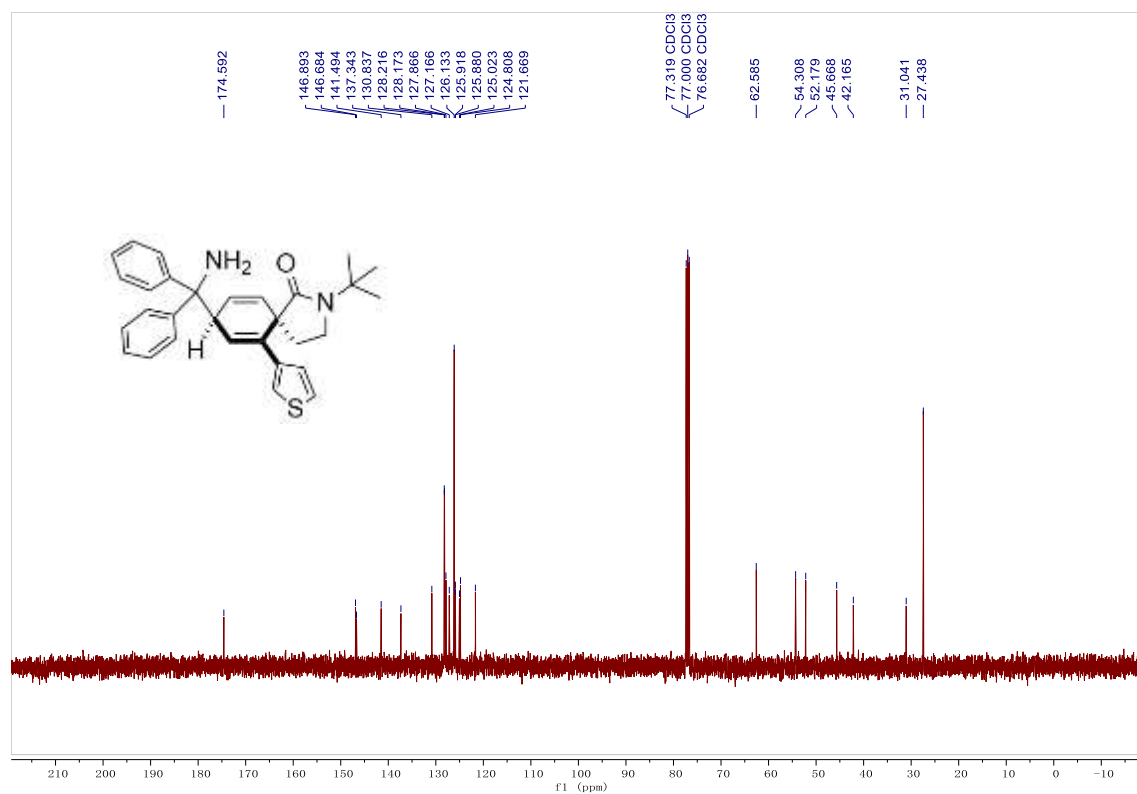
¹H-NMR for trans-3-17



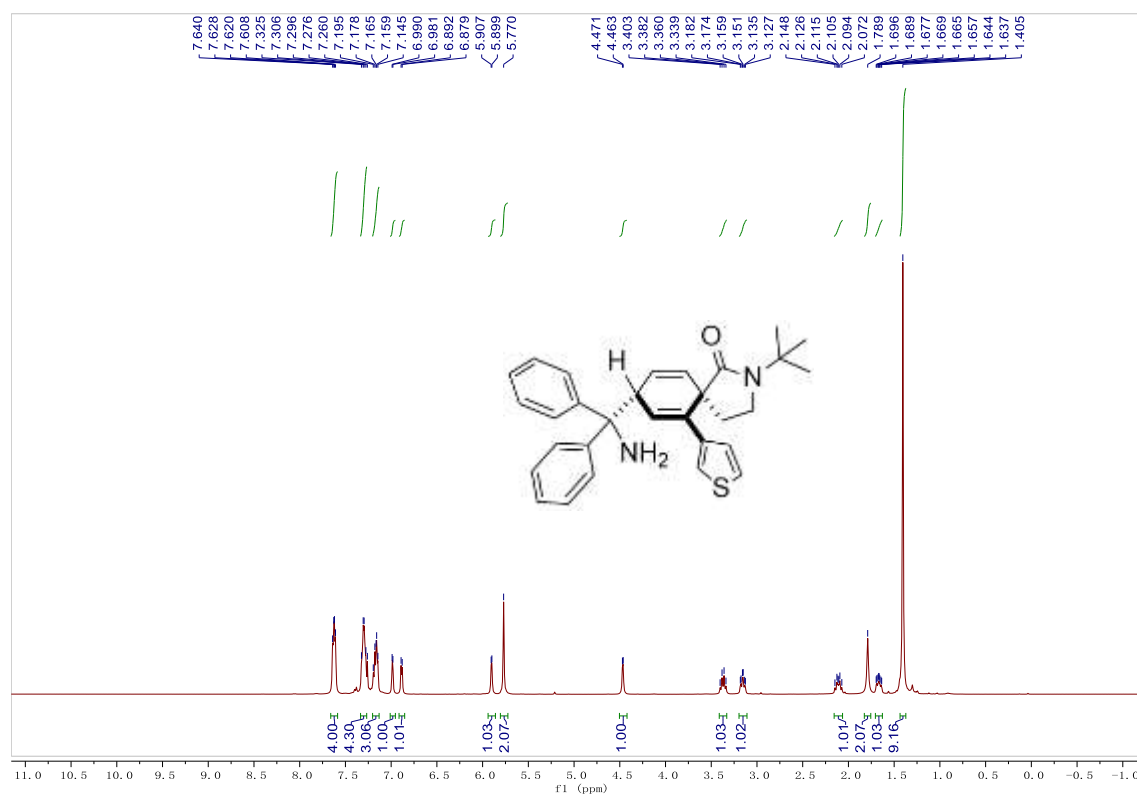
¹³C-NMR for trans-3-17



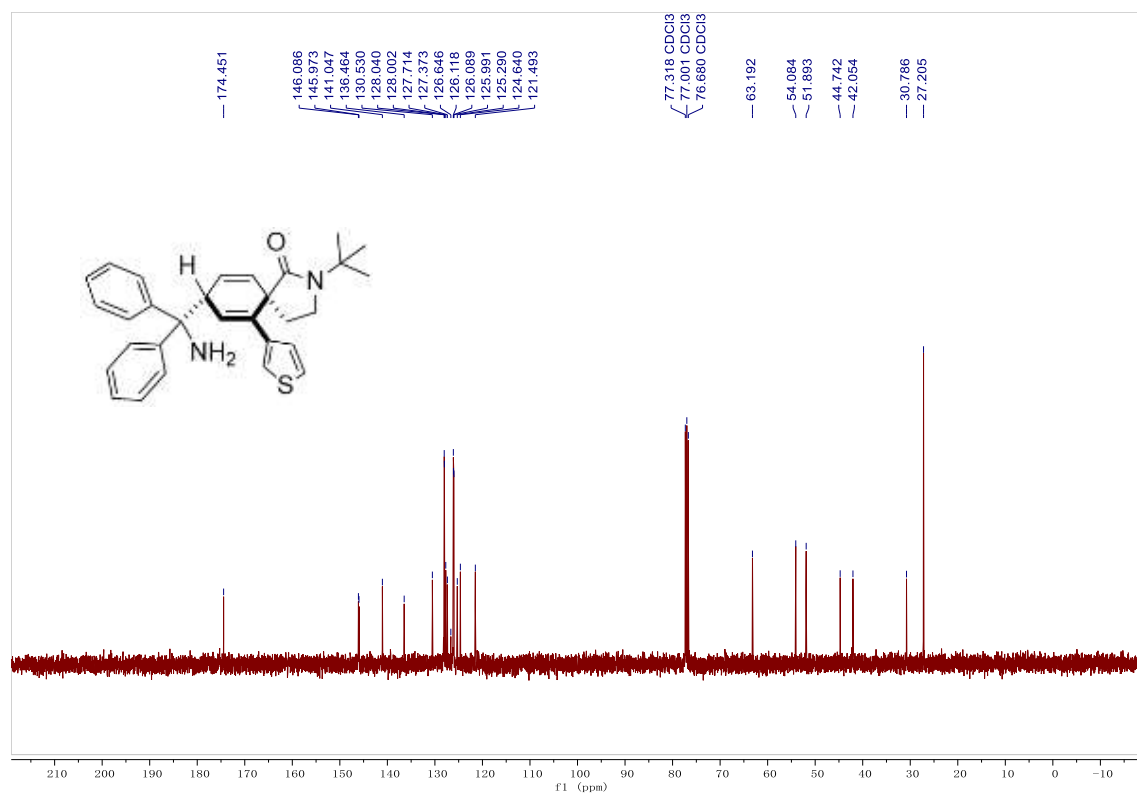
¹H-NMR for cis-3-18



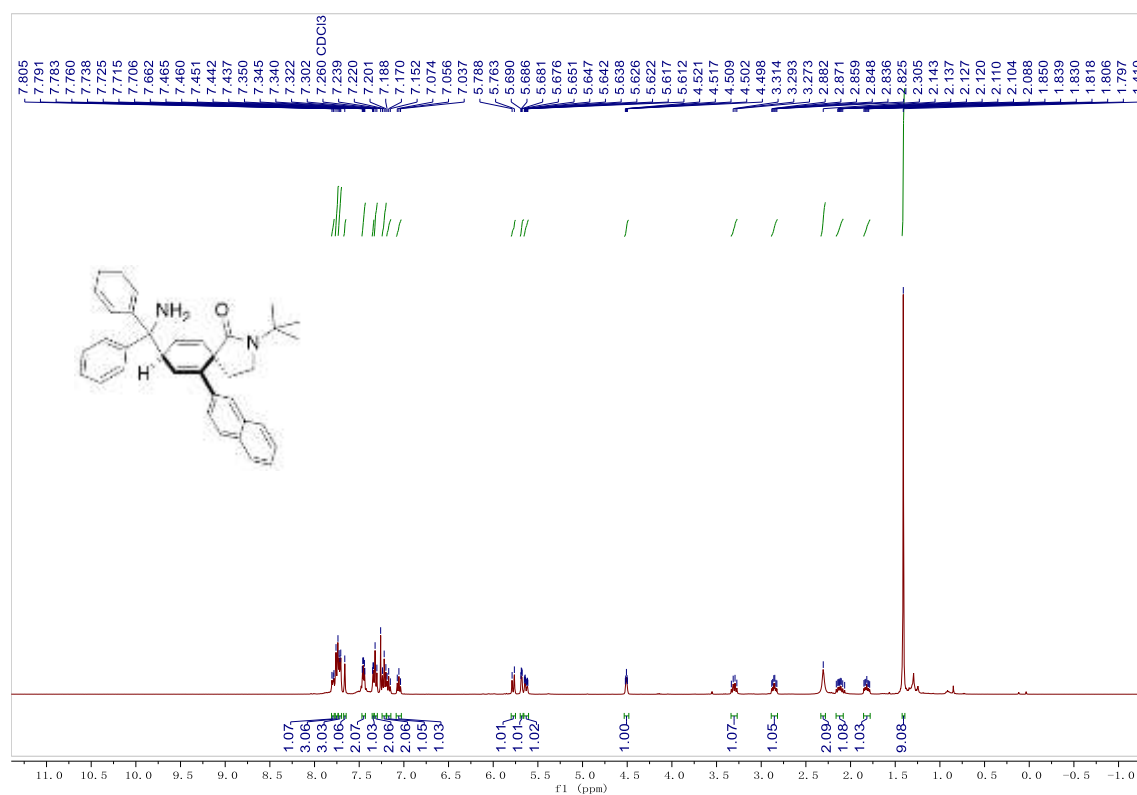
¹³C-NMR for cis-3-18



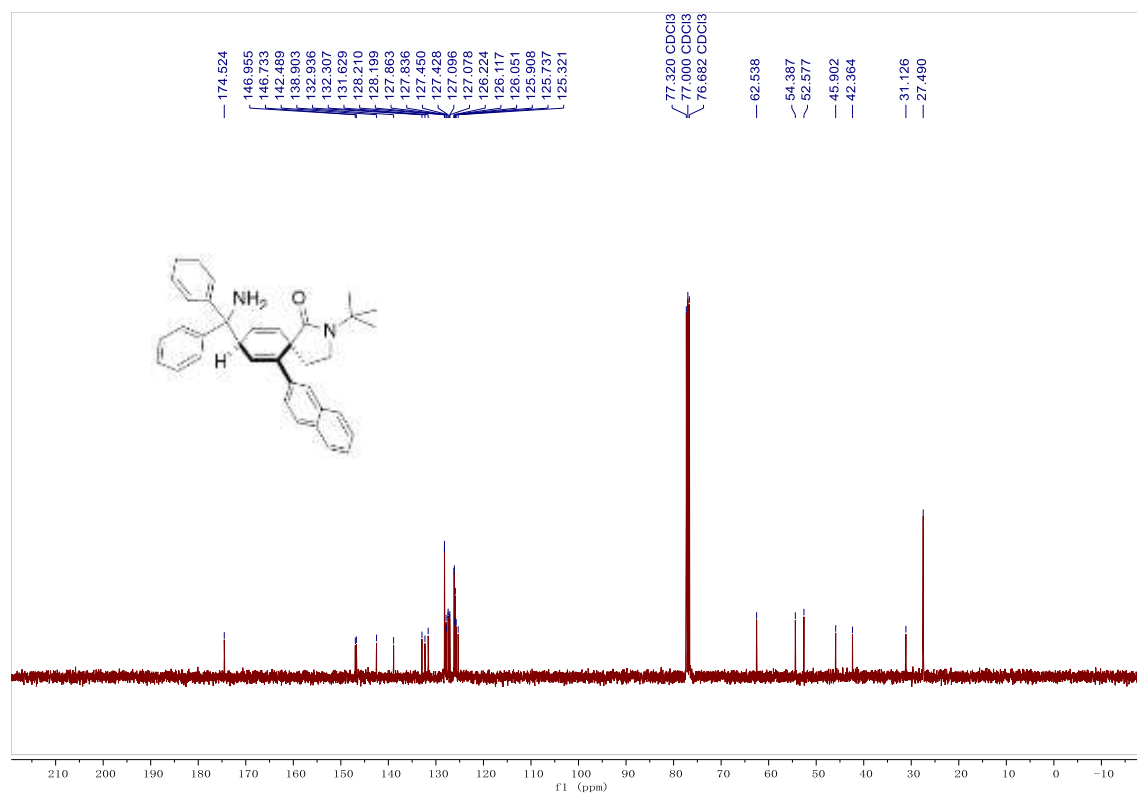
¹H-NMR for trans-3-18



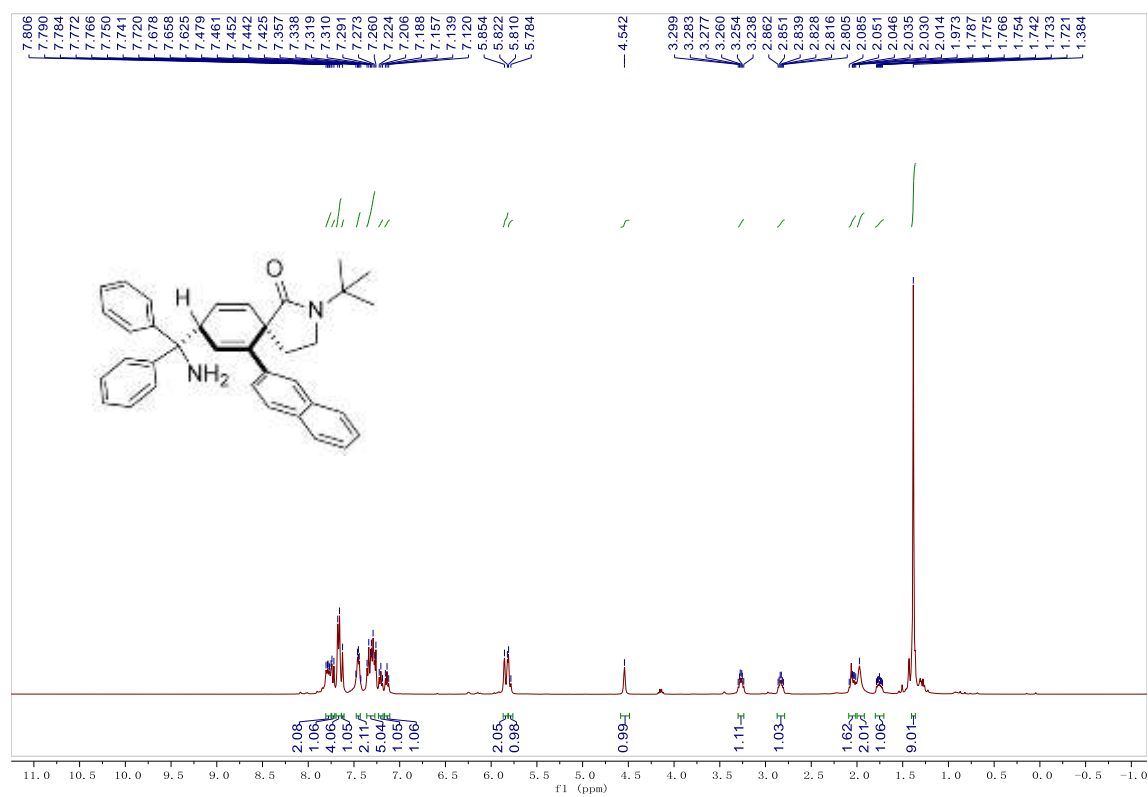
¹³C-NMR for trans-3-18



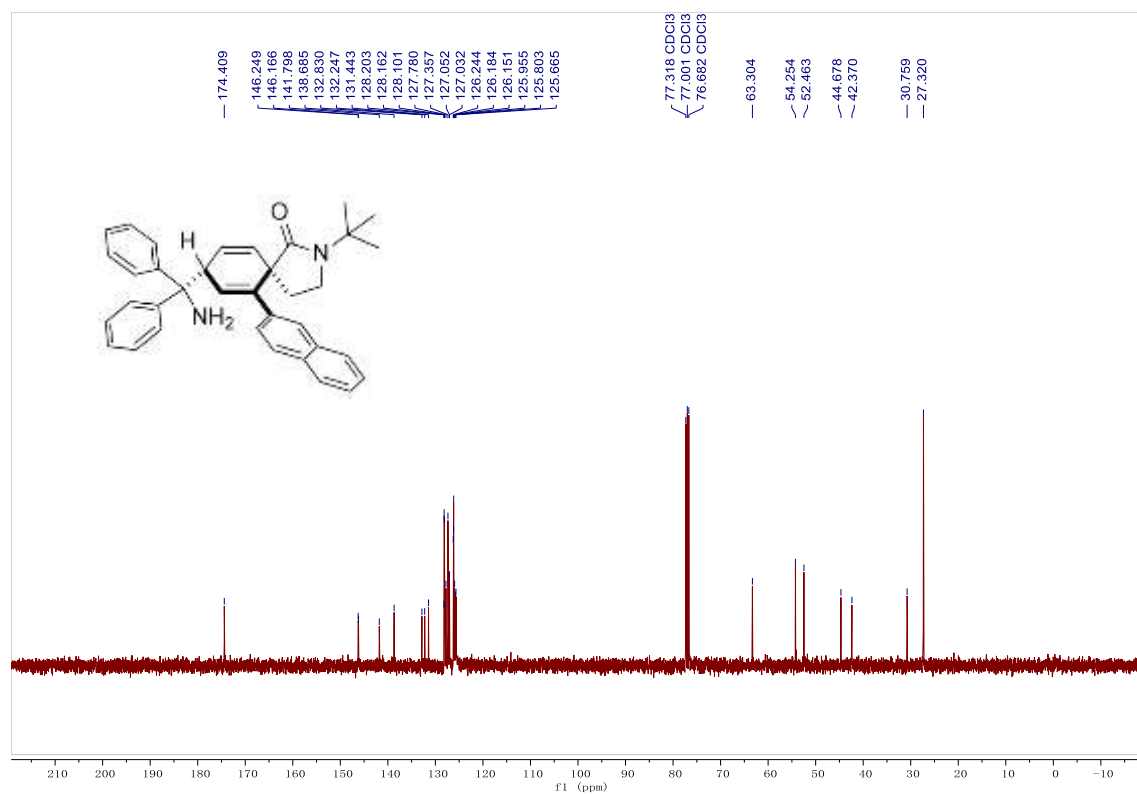
¹H-NMR for cis-3-19



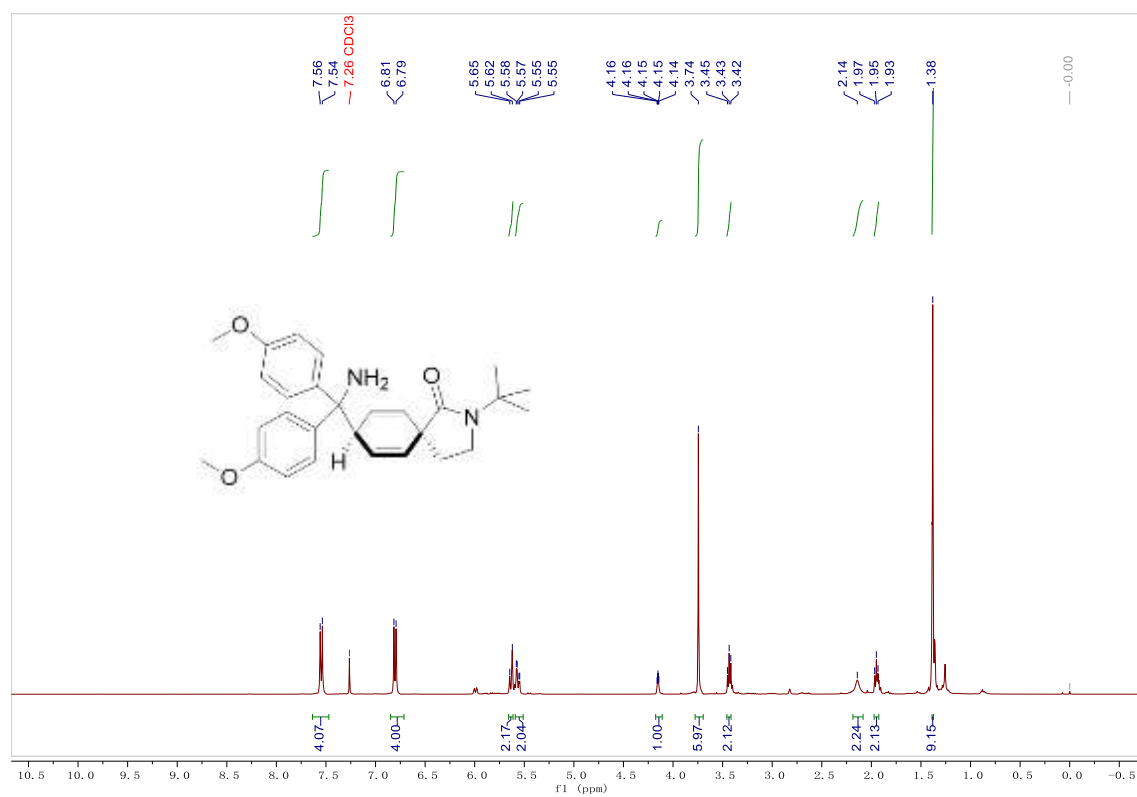
¹³C-NMR for cis-3-19



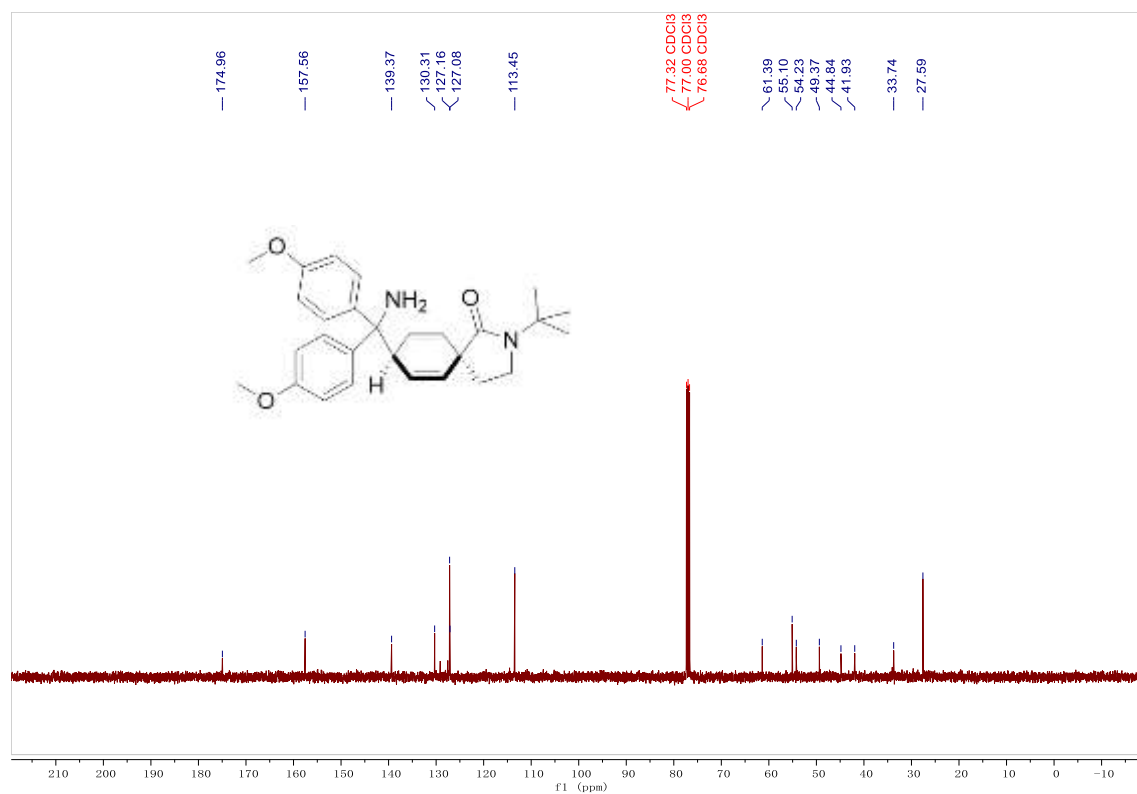
¹H-NMR for trans-3-19



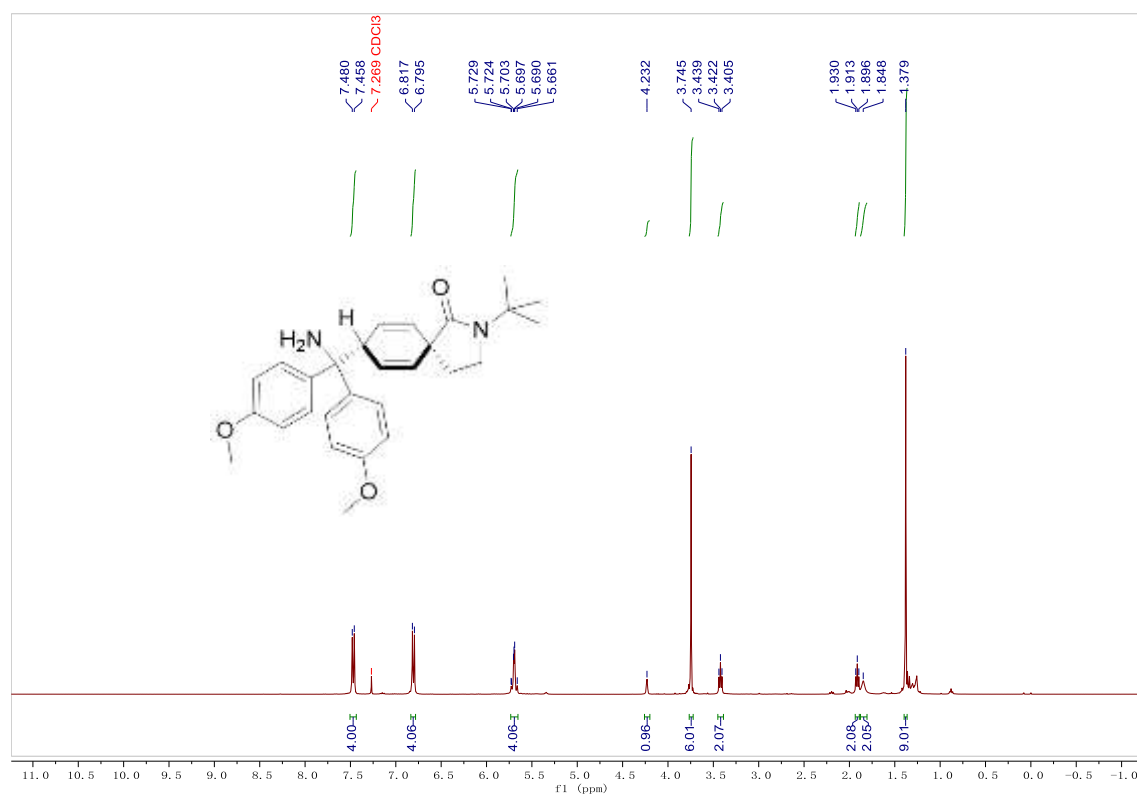
¹³C-NMR for trans-3-19



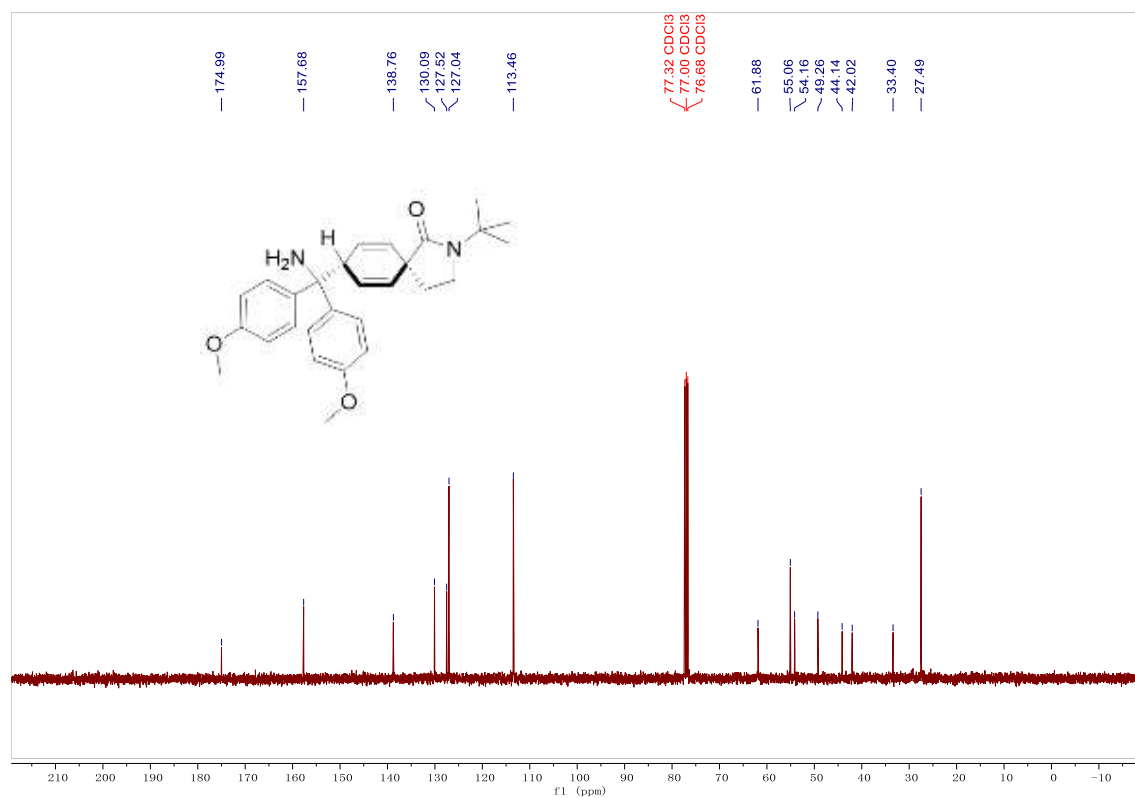
¹H-NMR for cis-3-20



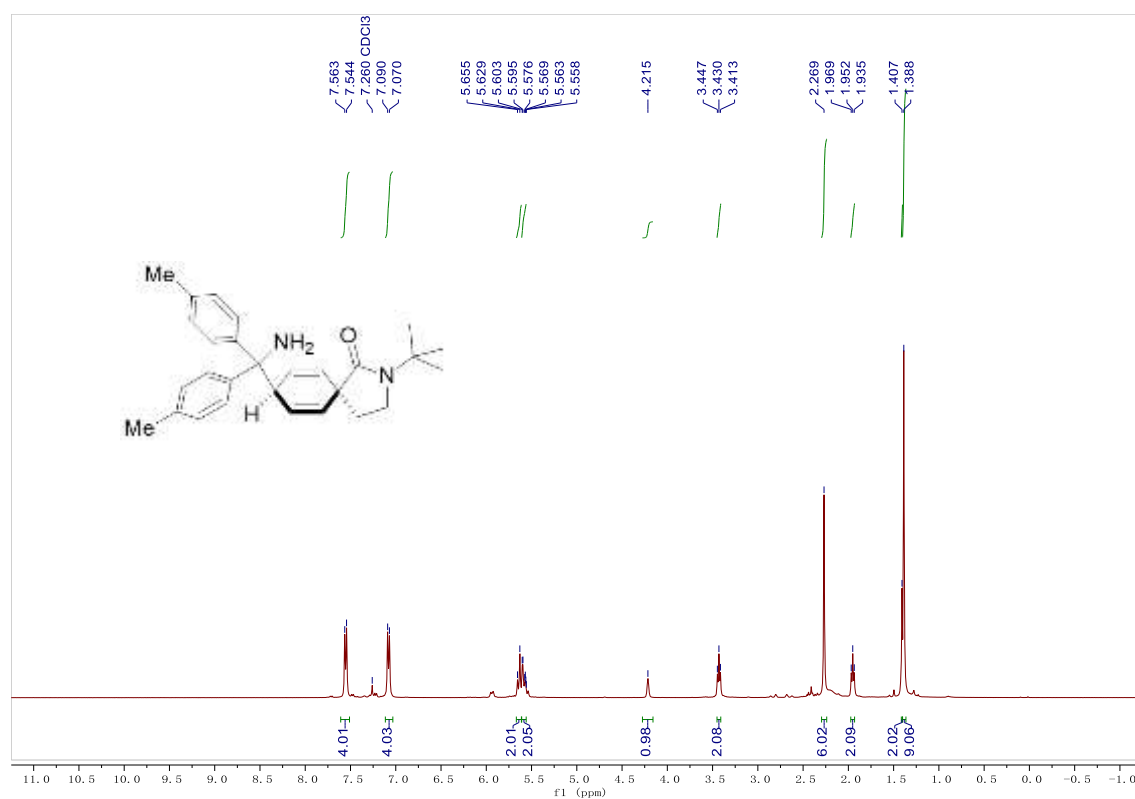
¹³C-NMR for **cis-3-20**



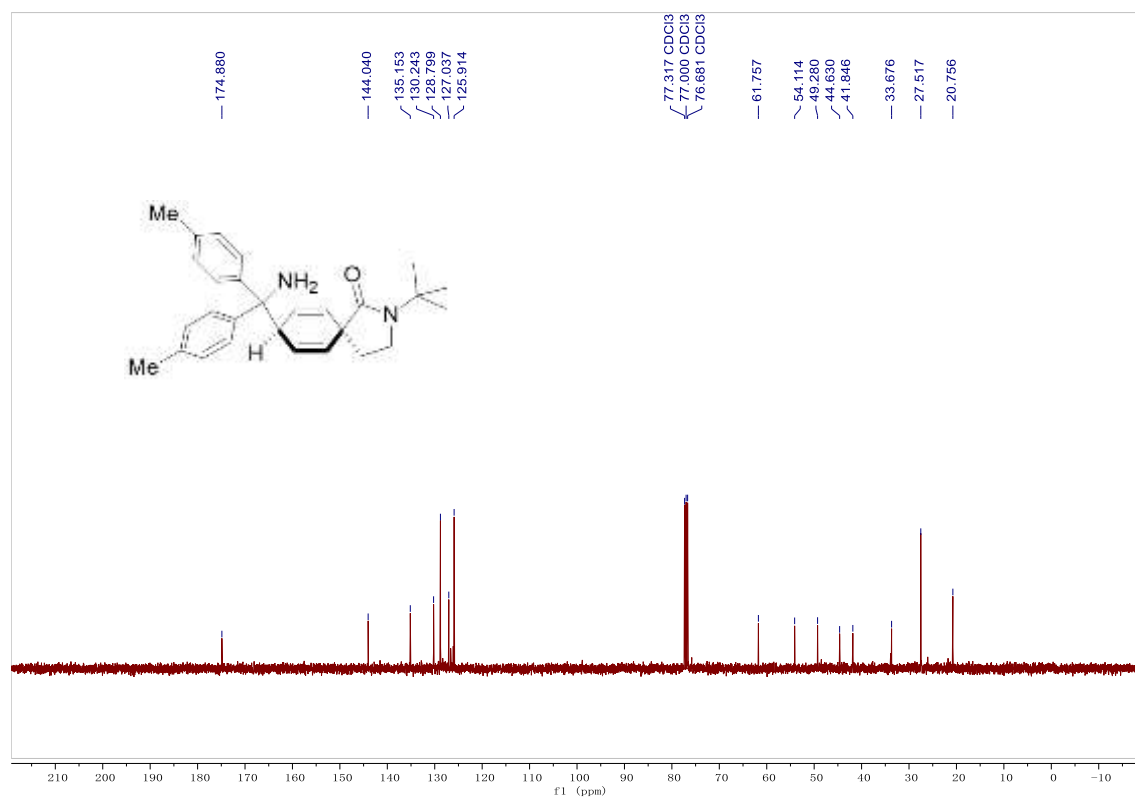
¹H-NMR for **trans-3-20**



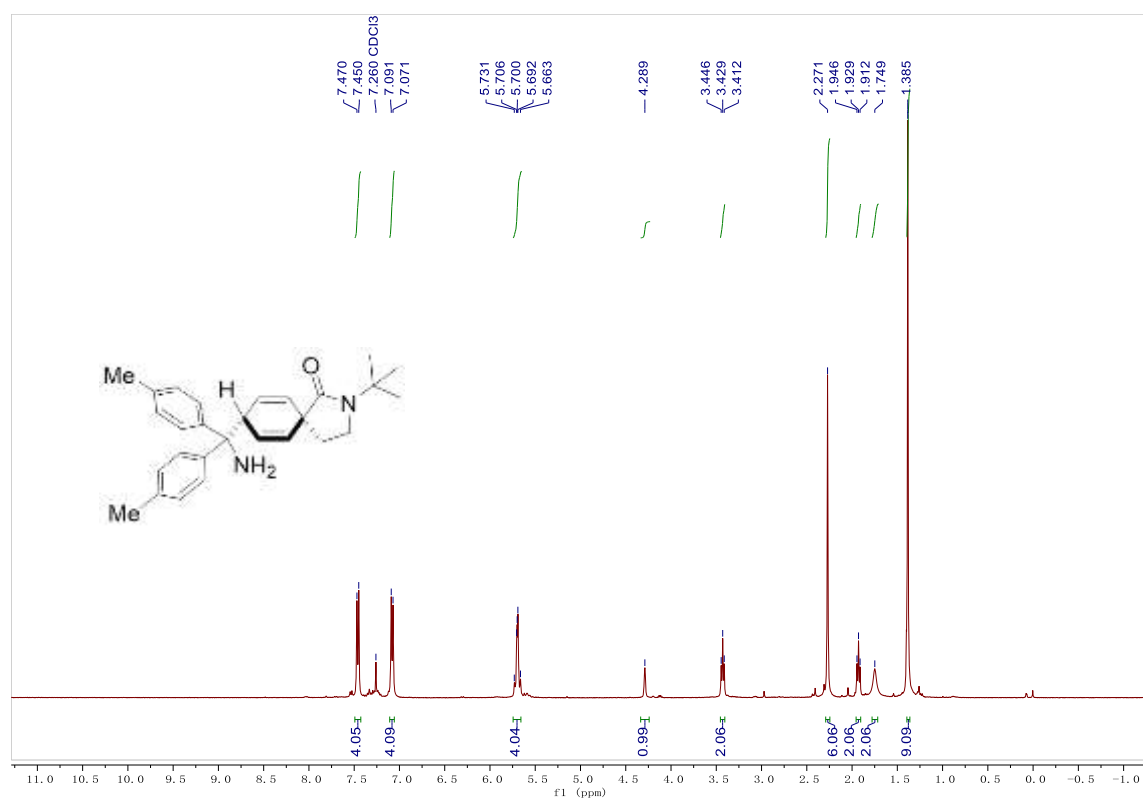
^{13}C -NMR for trans-3-20



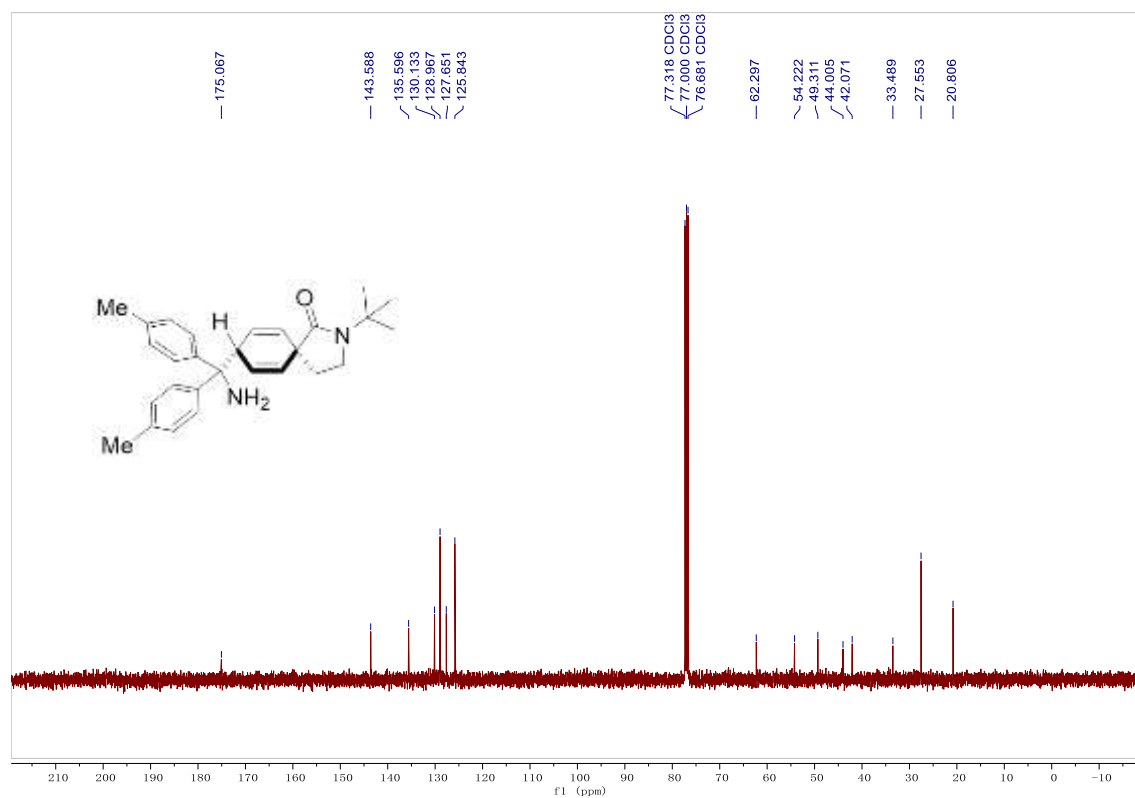
^1H -NMR for cis-3-21



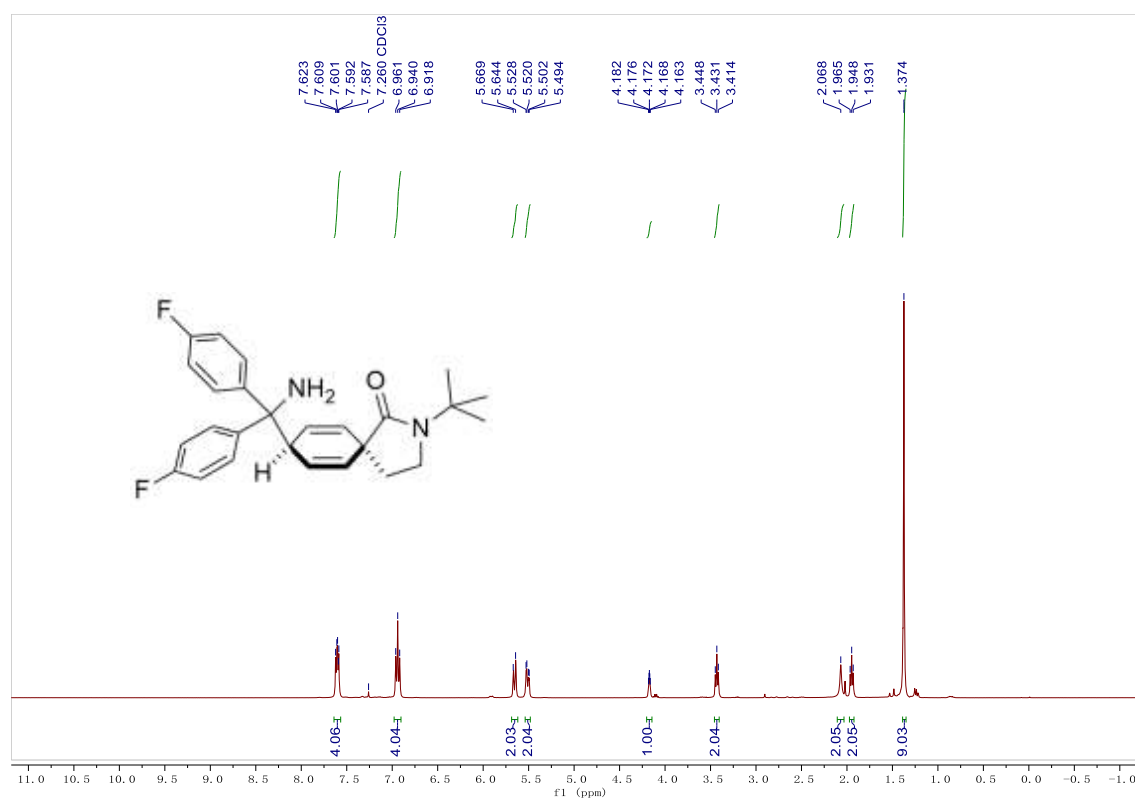
¹³C-NMR for **cis-3-21**



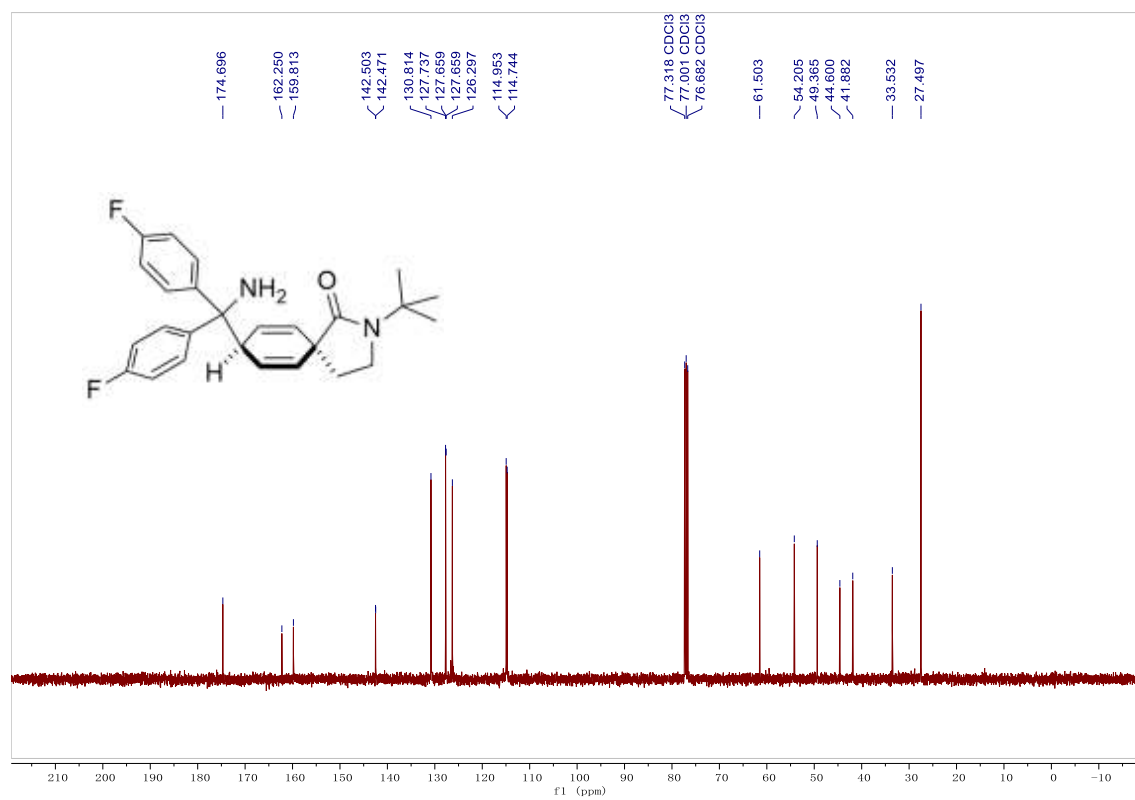
¹H-NMR for **trans-3-21**



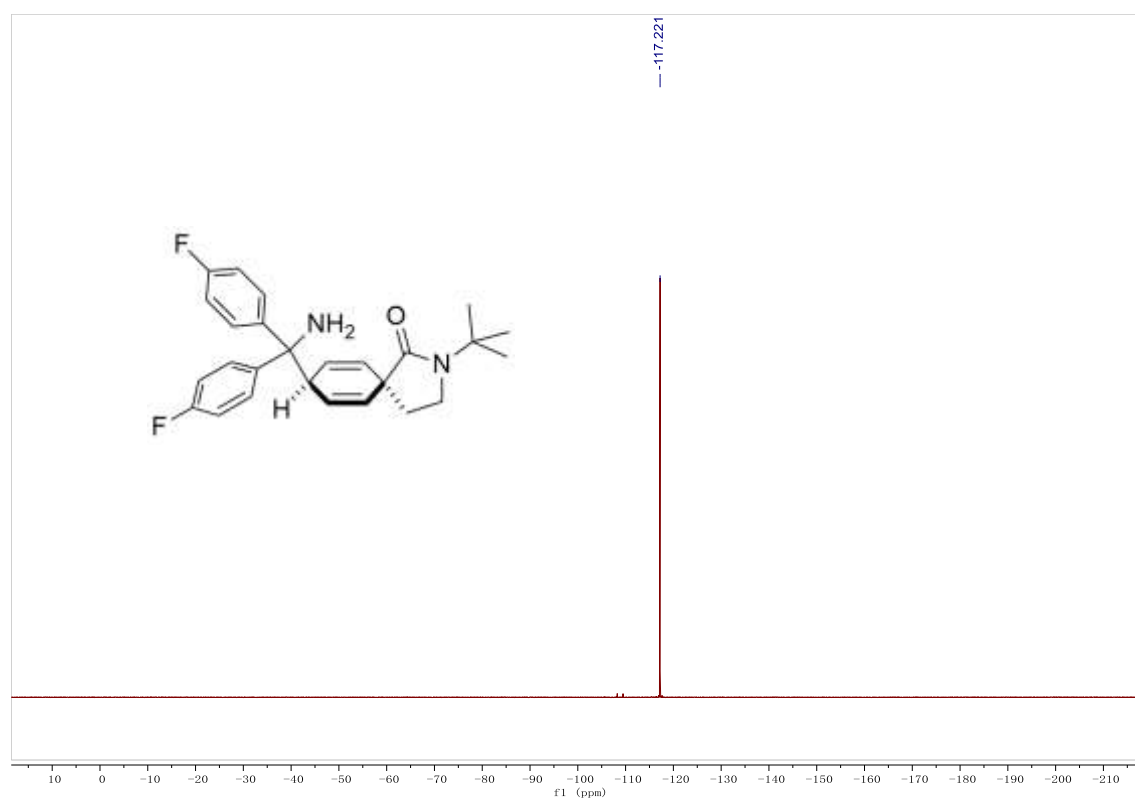
¹³C-NMR for trans-3-21



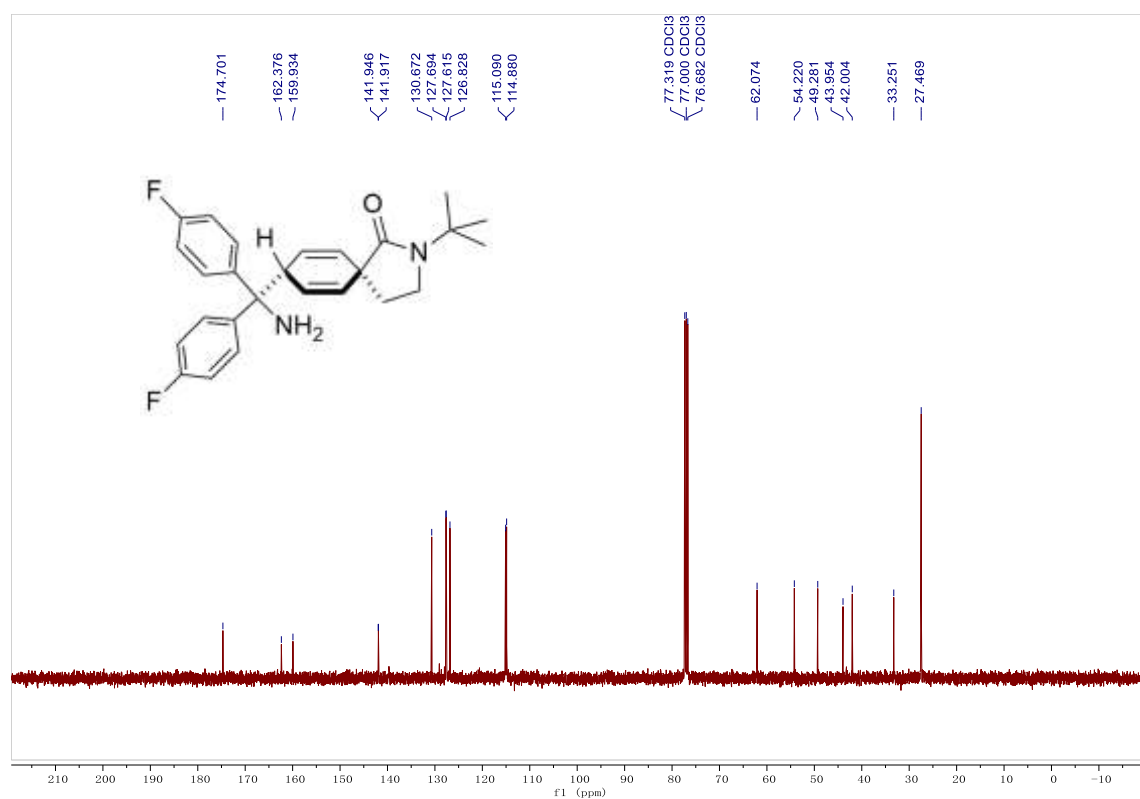
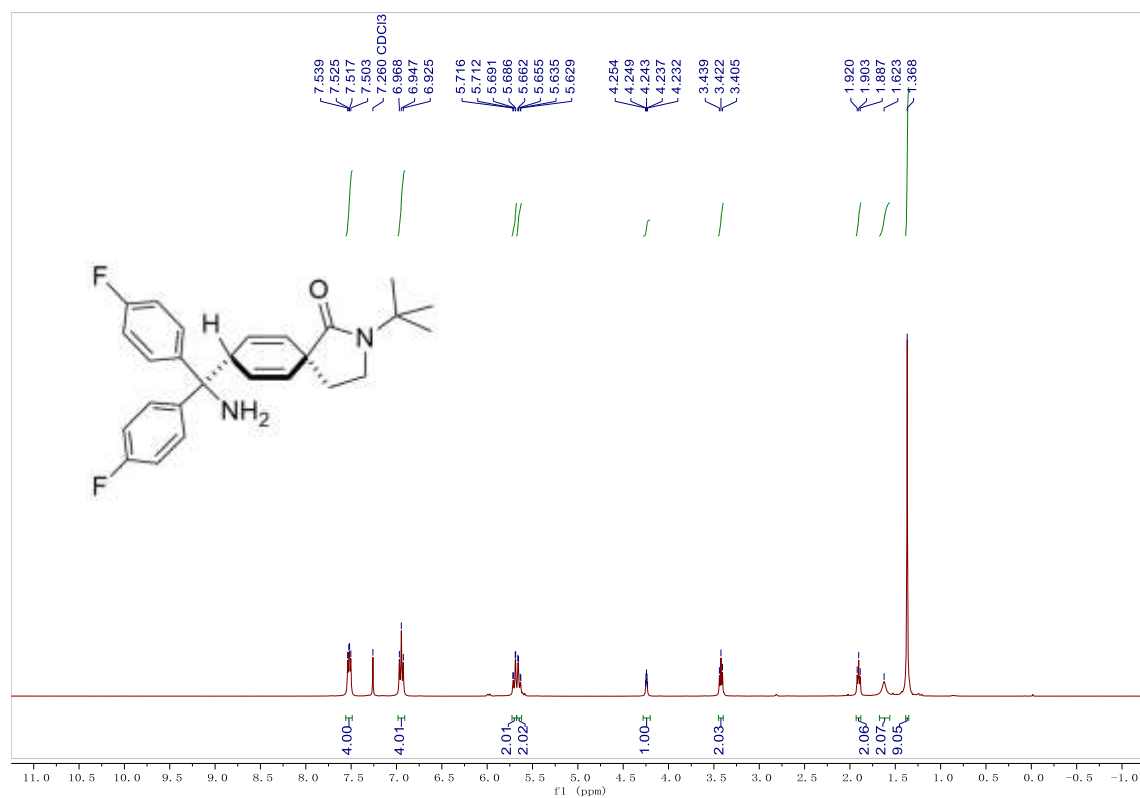
¹H-NMR for cis-3-22

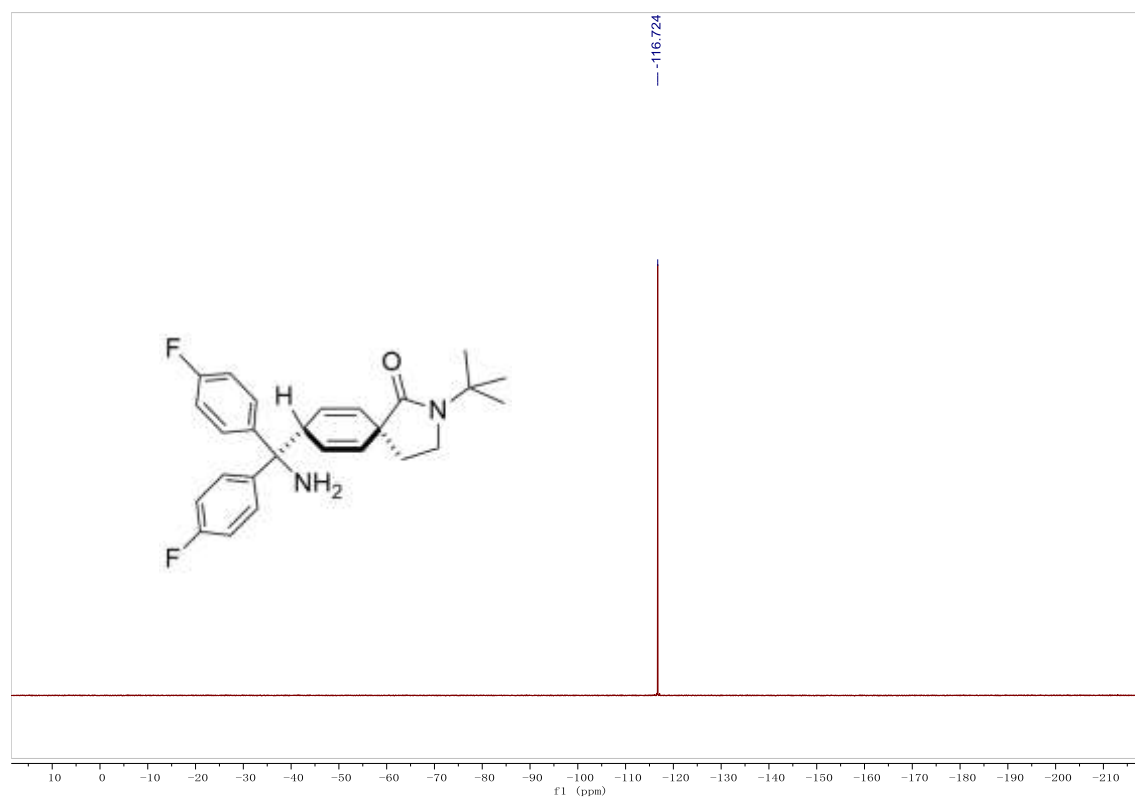


¹³C-NMR for **cis-3-22**

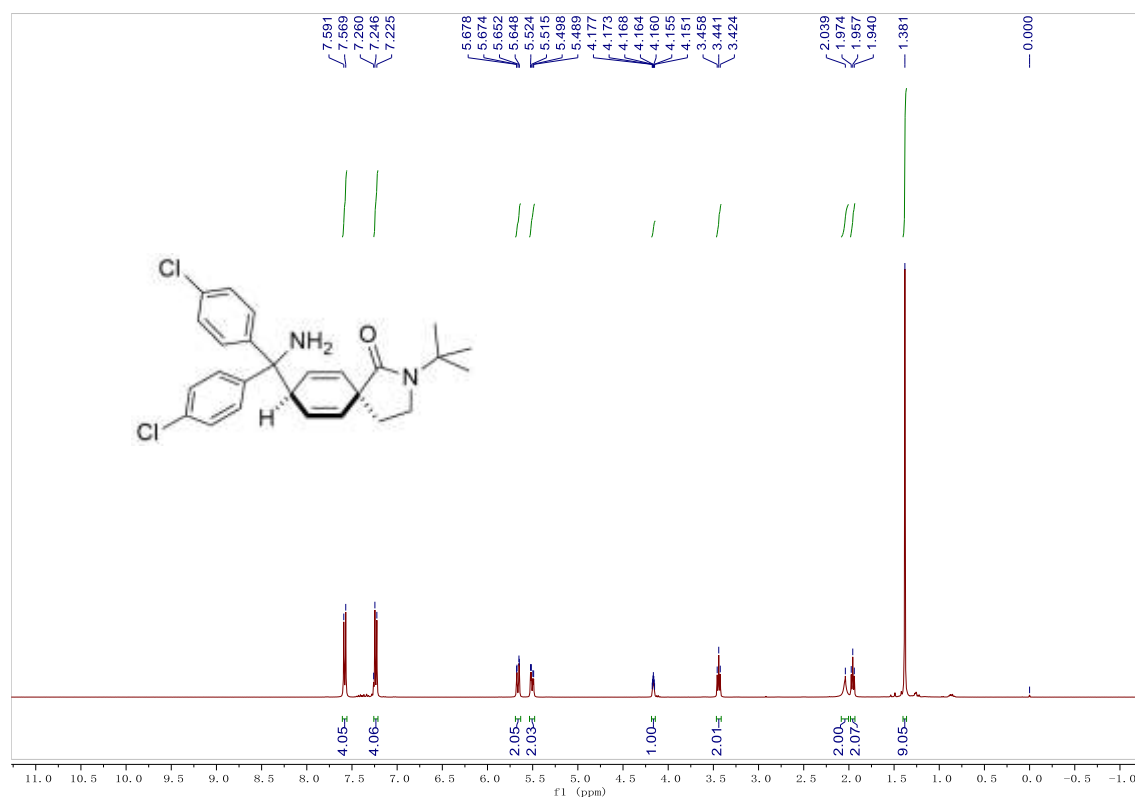


¹⁹F-NMR for **cis-3-22**

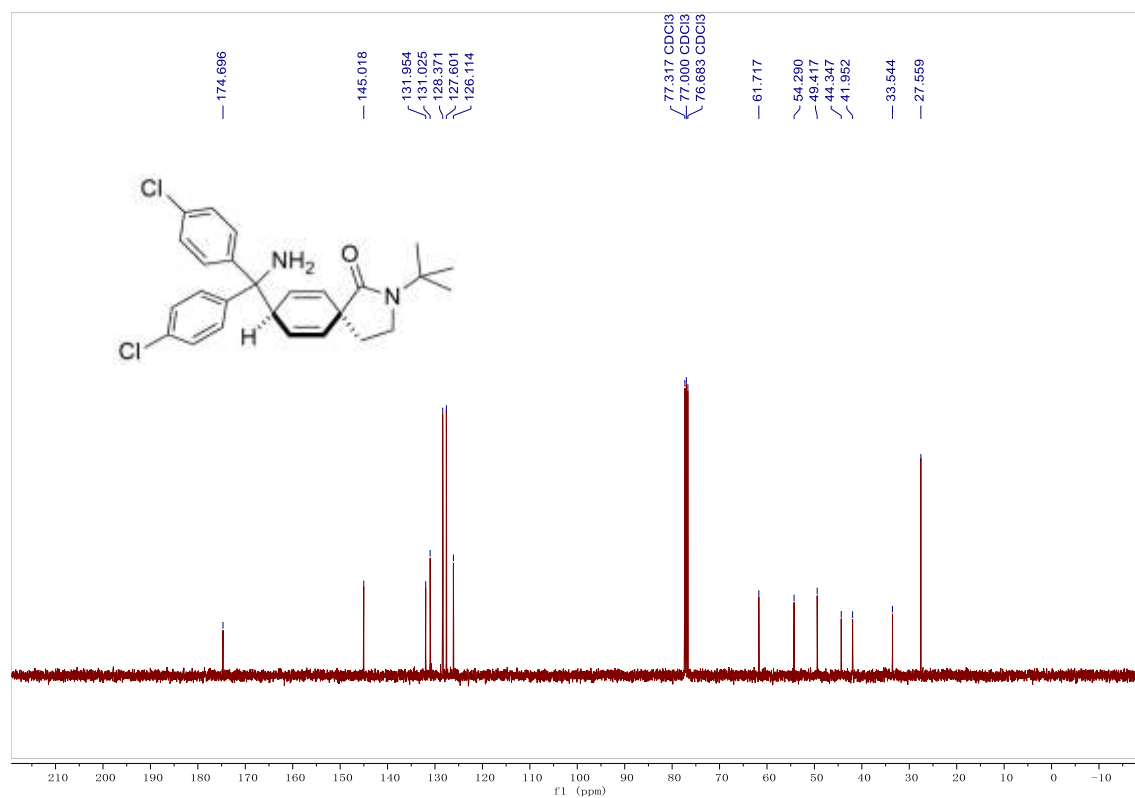




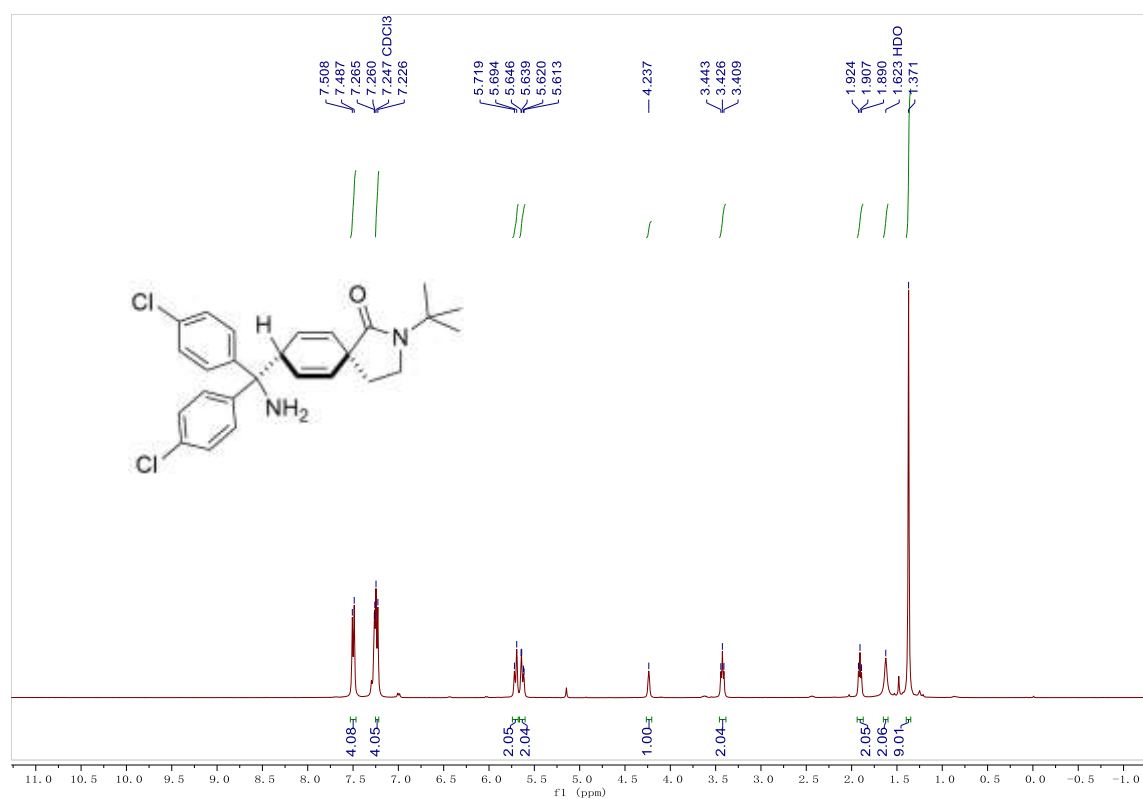
^{19}F -NMR for trans-3-22



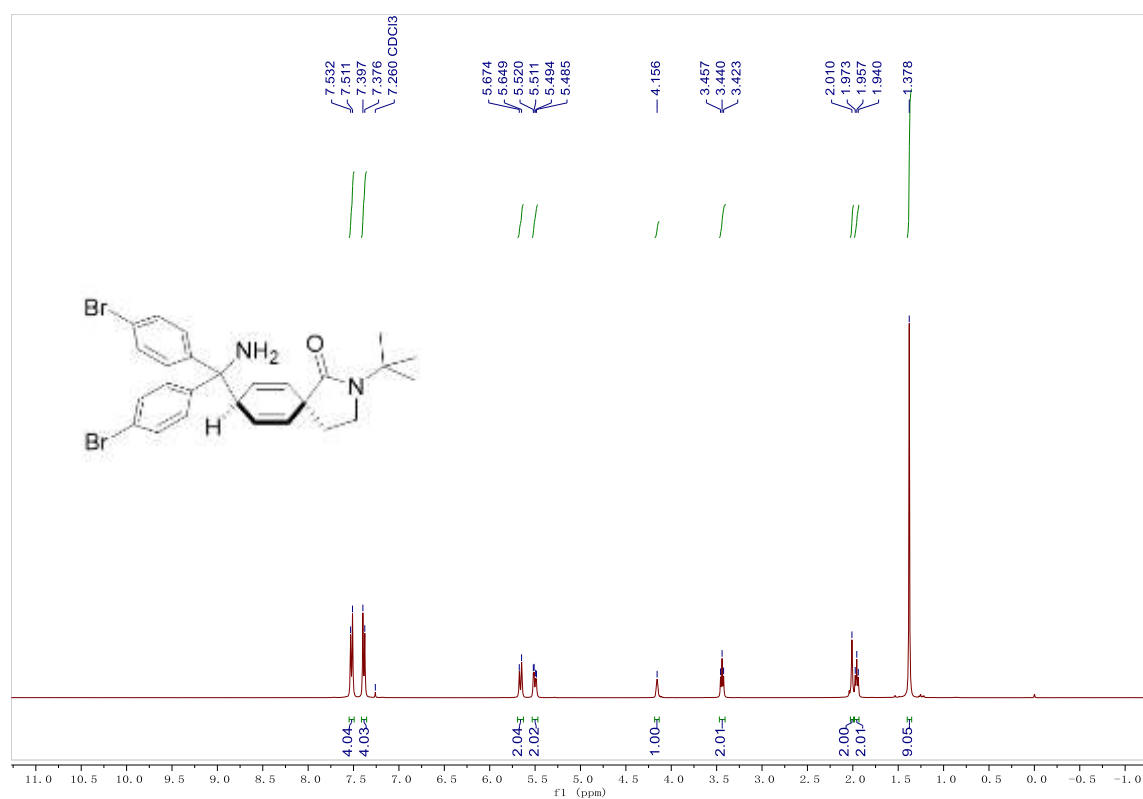
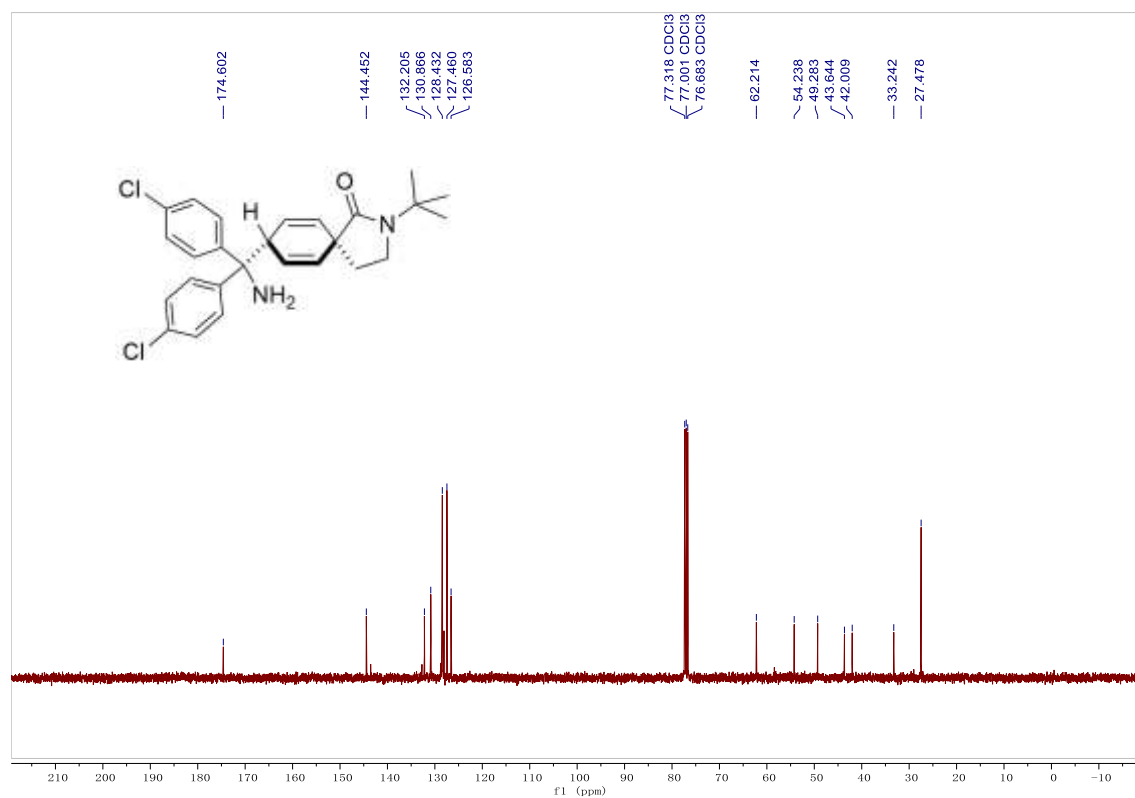
^1H -NMR for cis-3-23

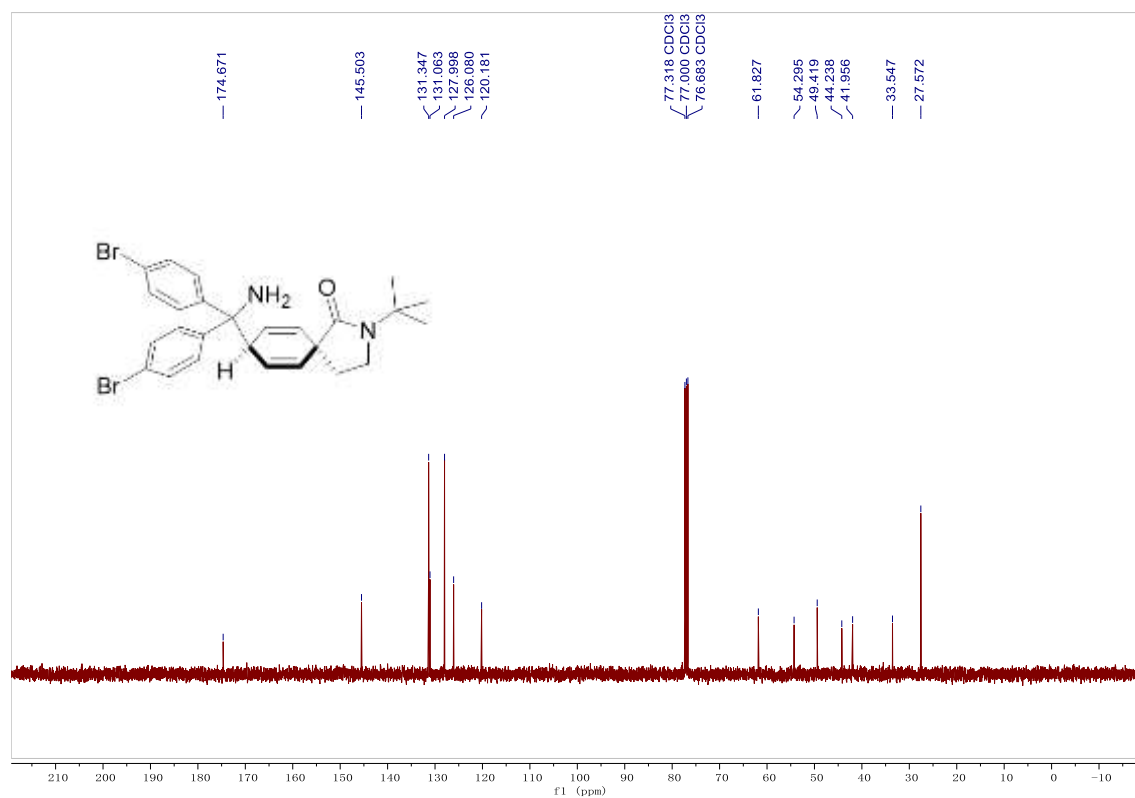


¹³C-NMR for cis-3-23

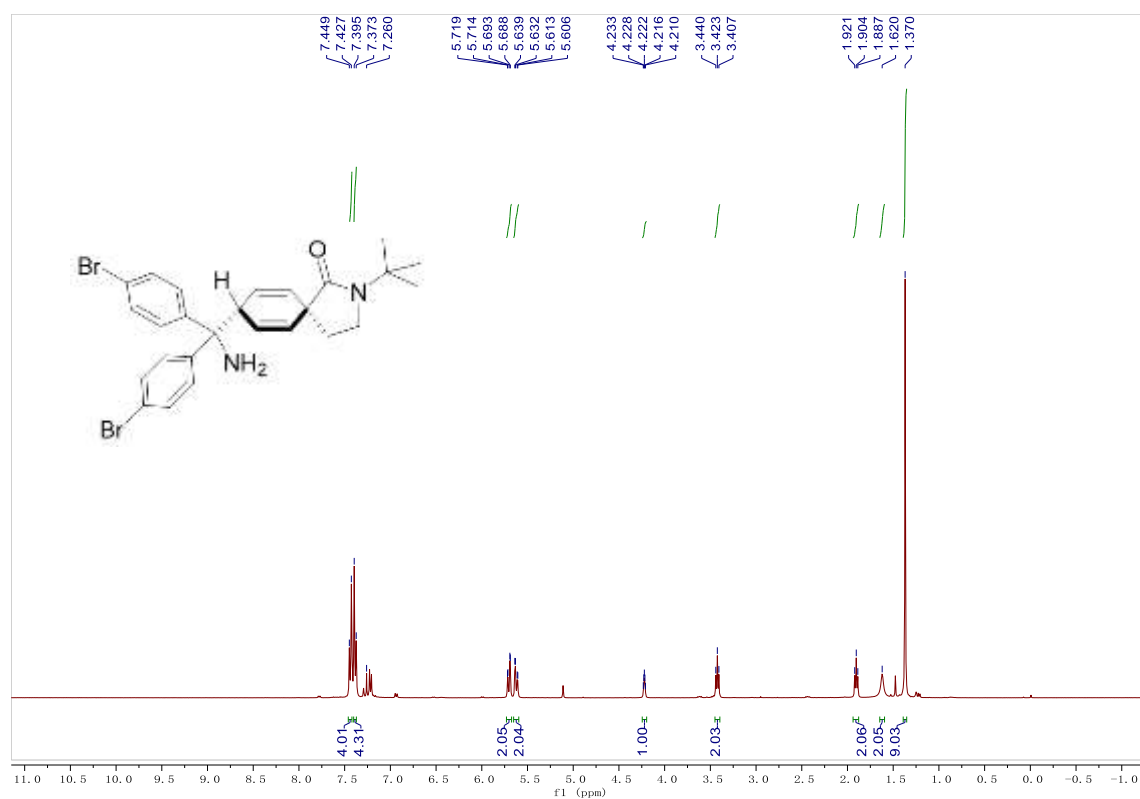


¹H-NMR for trans-3-23

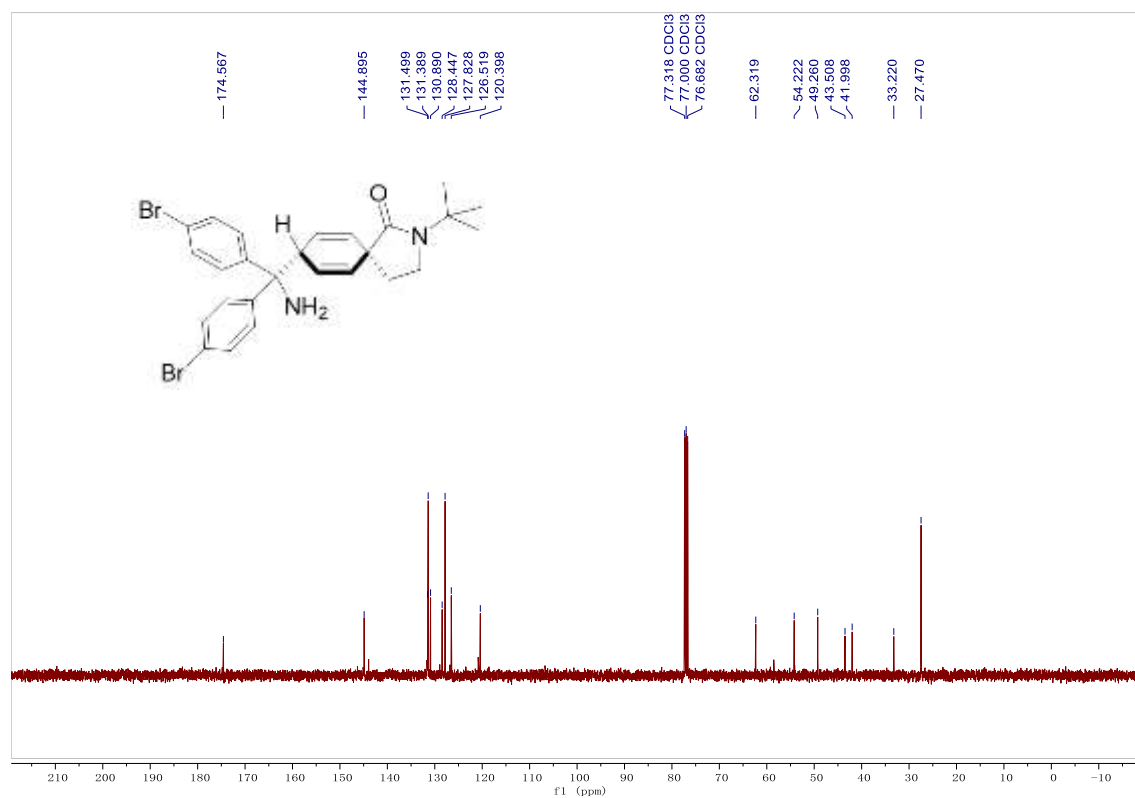




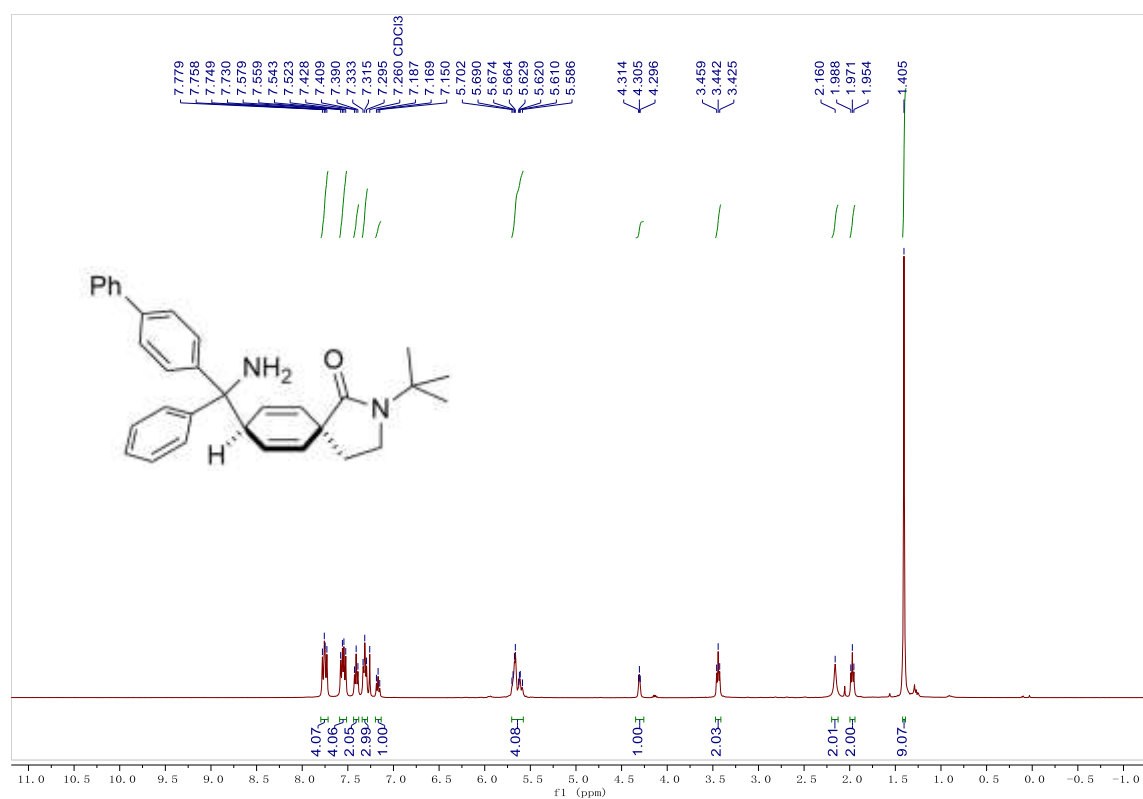
¹³C-NMR for cis-3-24



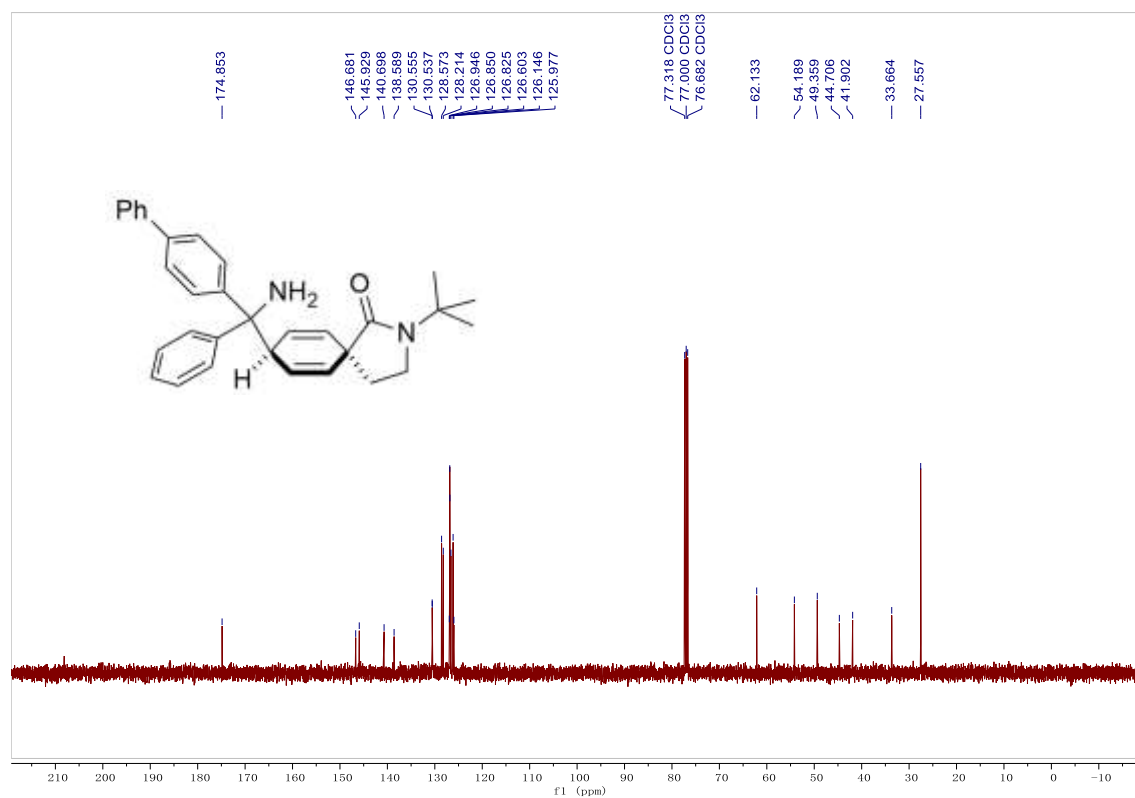
¹H-NMR for trans-3-24



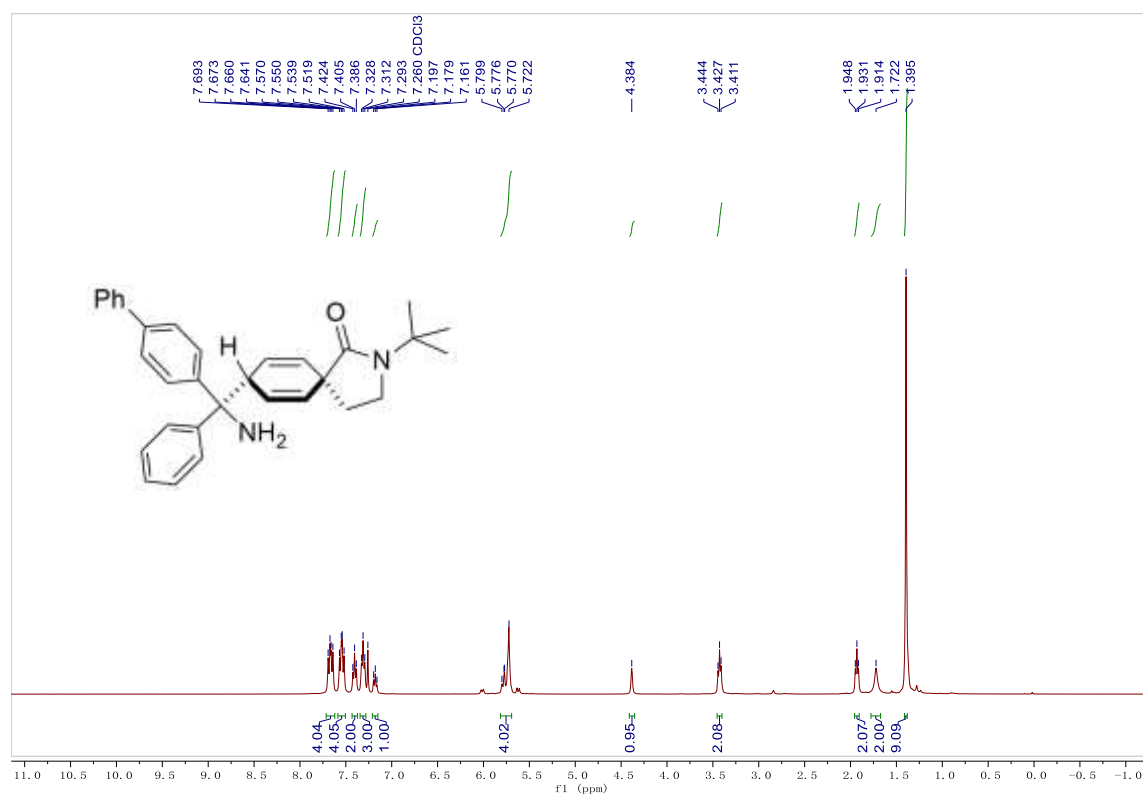
^{13}C -NMR for trans-3-24



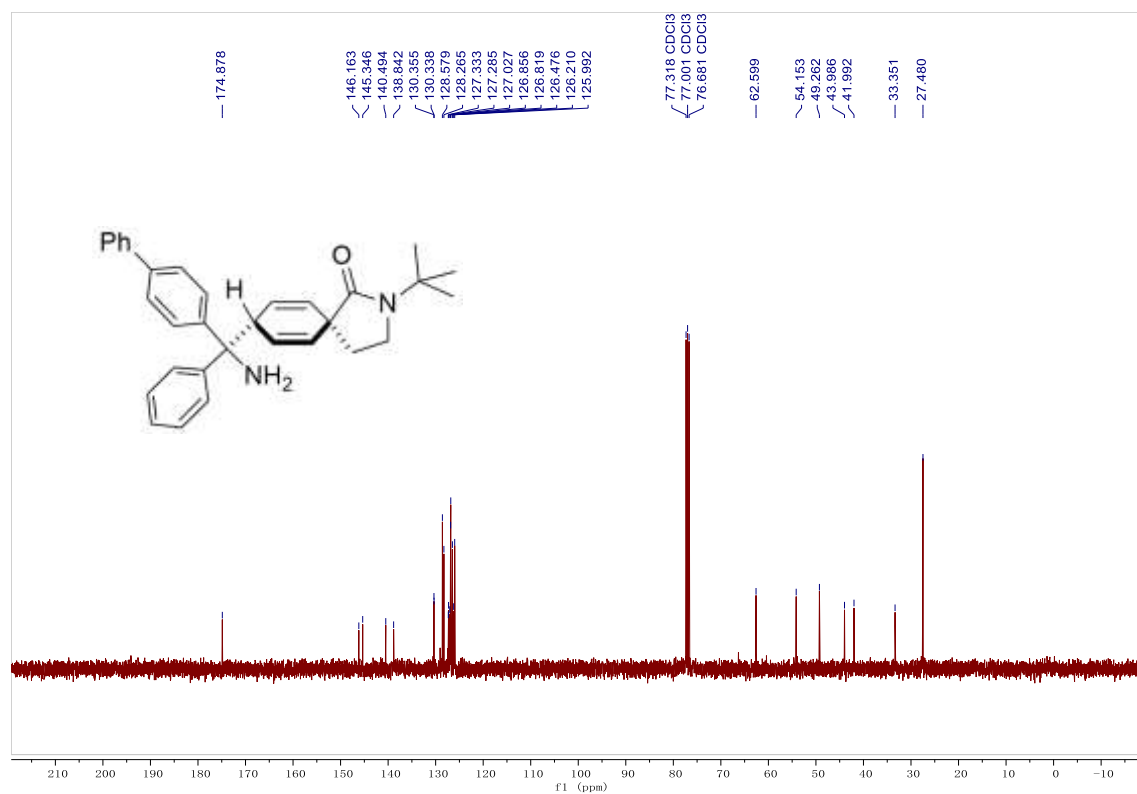
^1H -NMR for cis-3-25



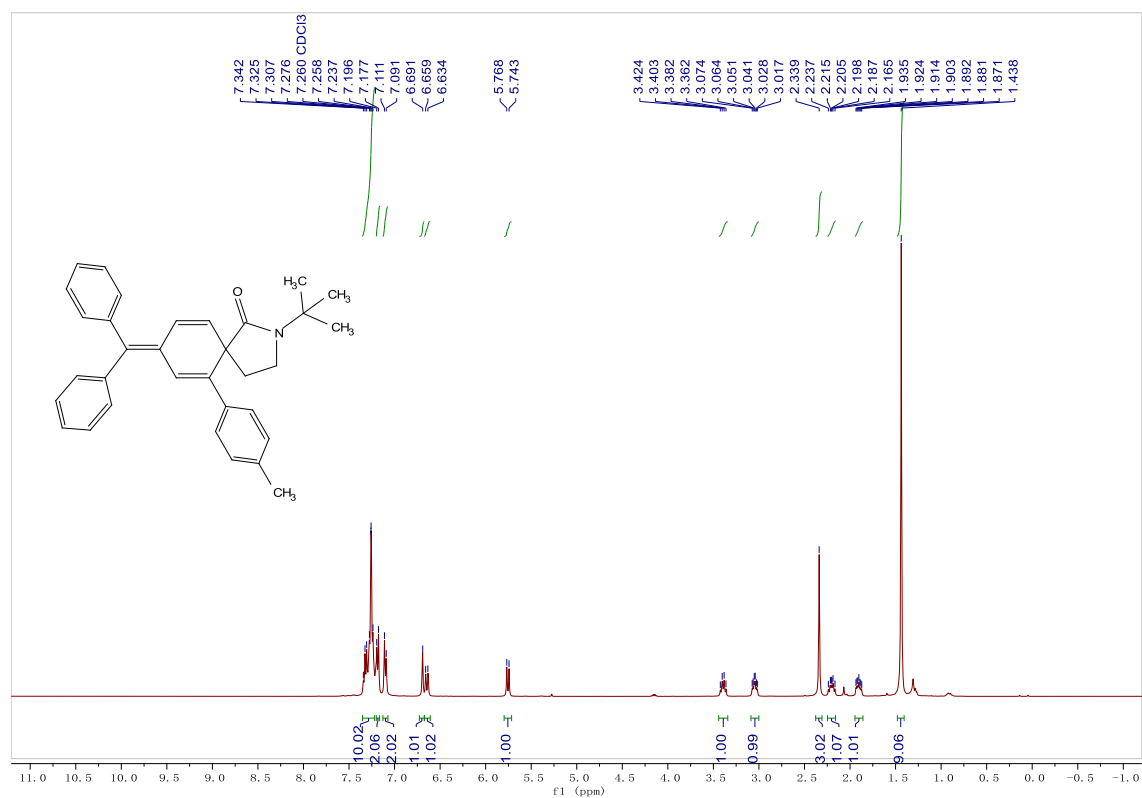
¹³C-NMR for cis-3-25



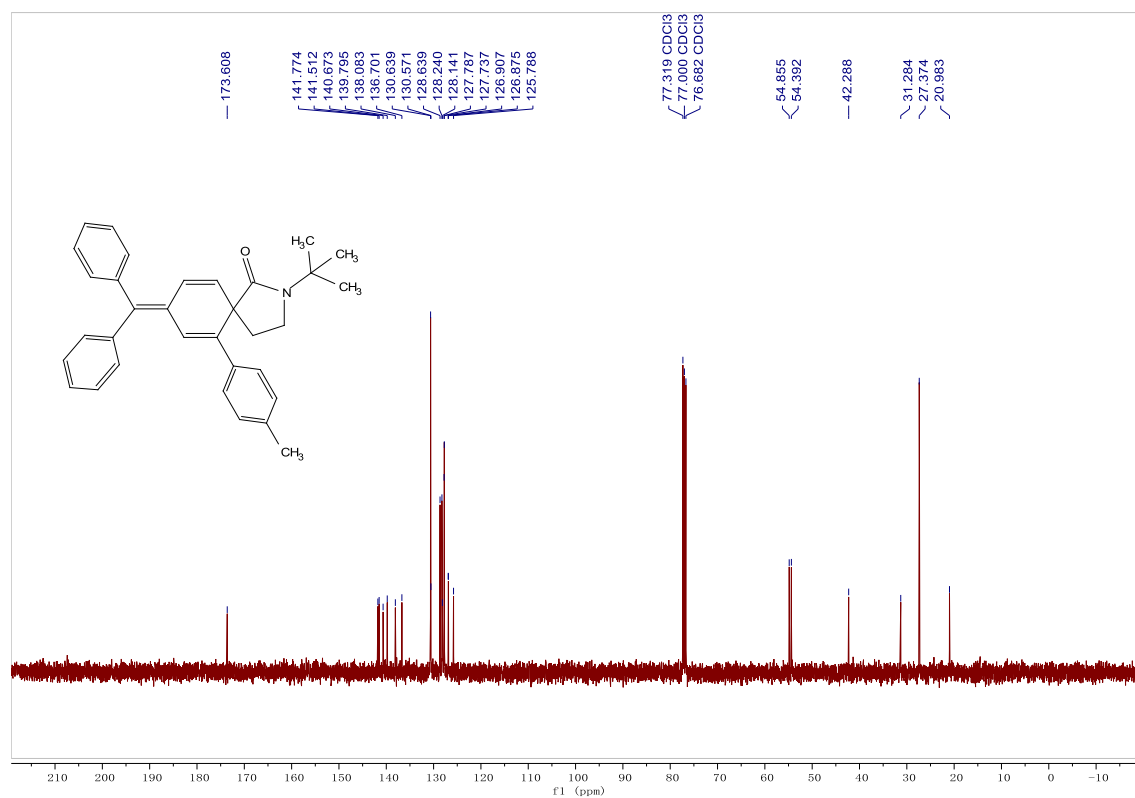
¹H-NMR for trans-3-25



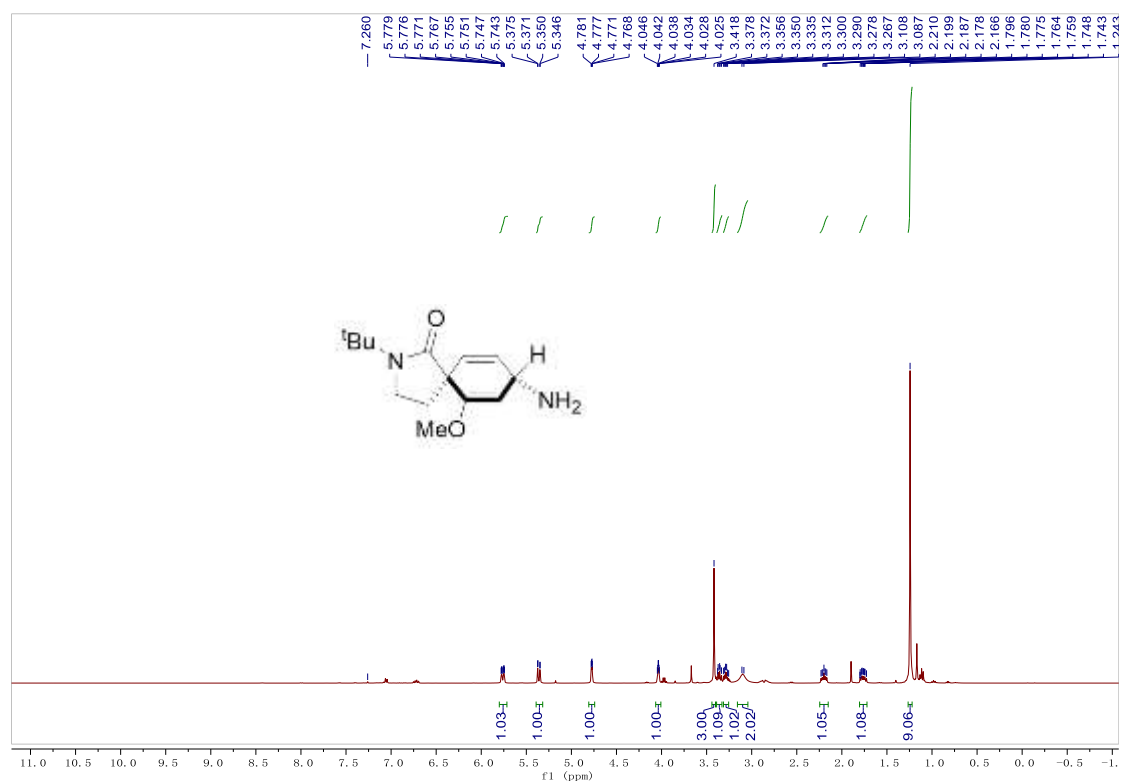
¹³C-NMR for trans-3-25



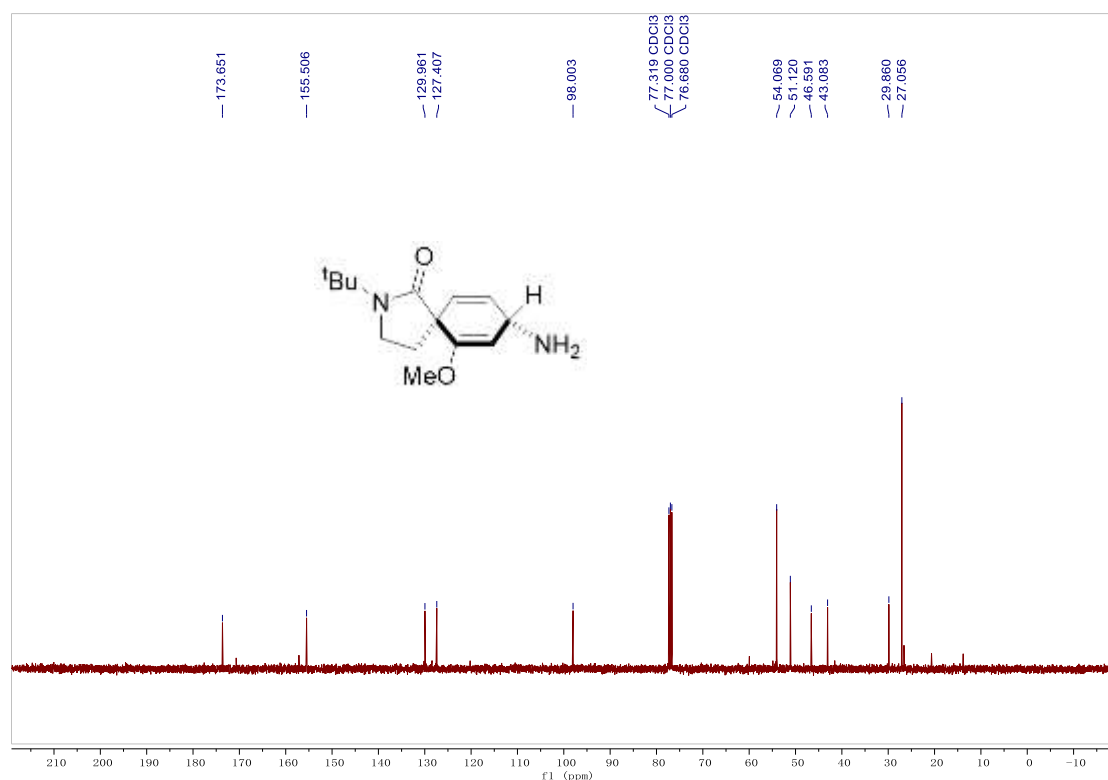
¹H-NMR for 7-1



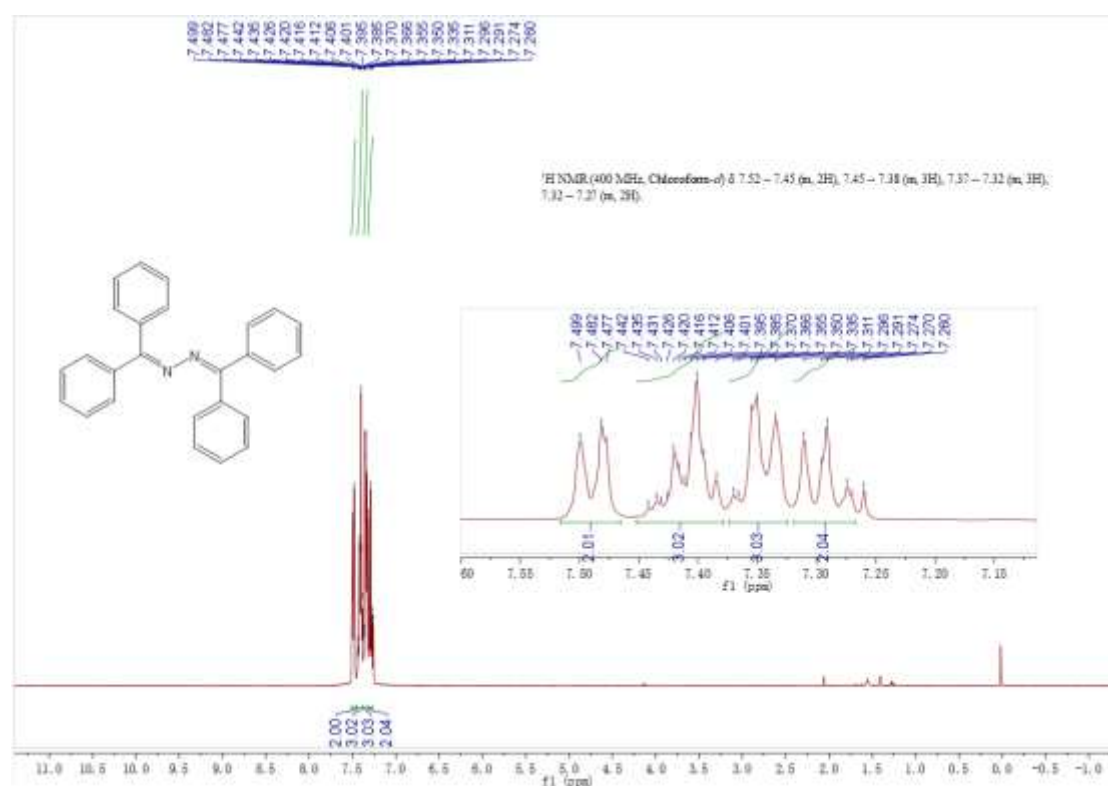
¹³C-NMR for 7-1



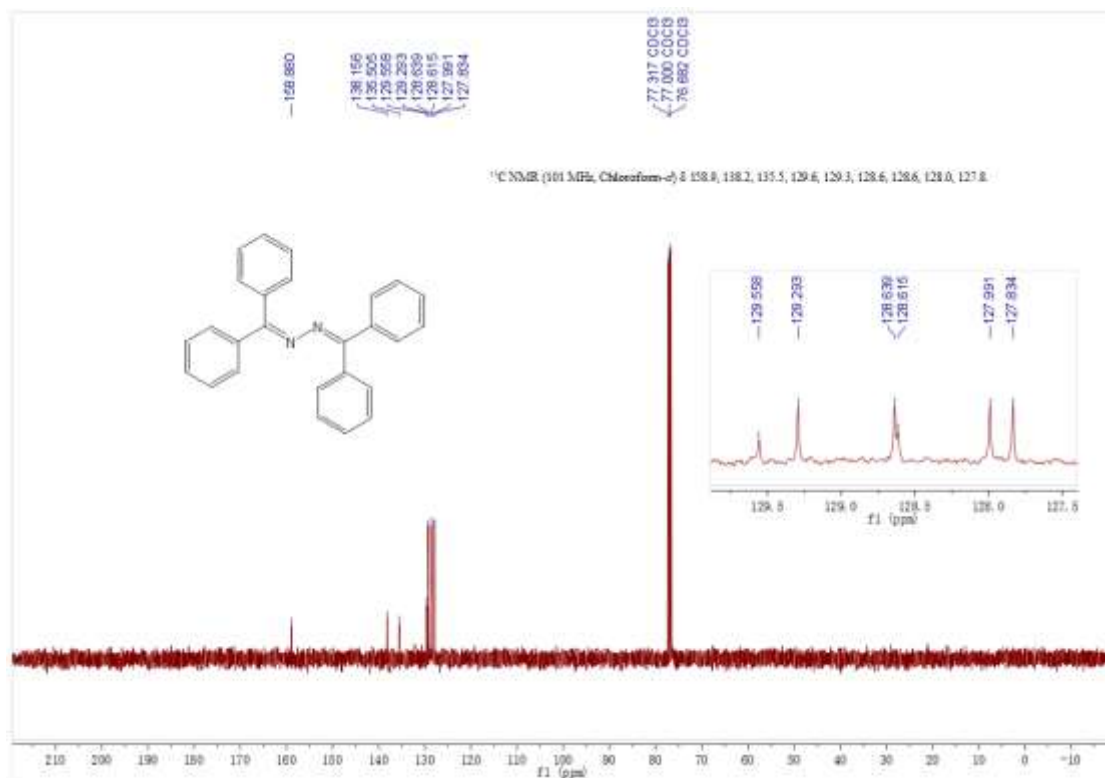
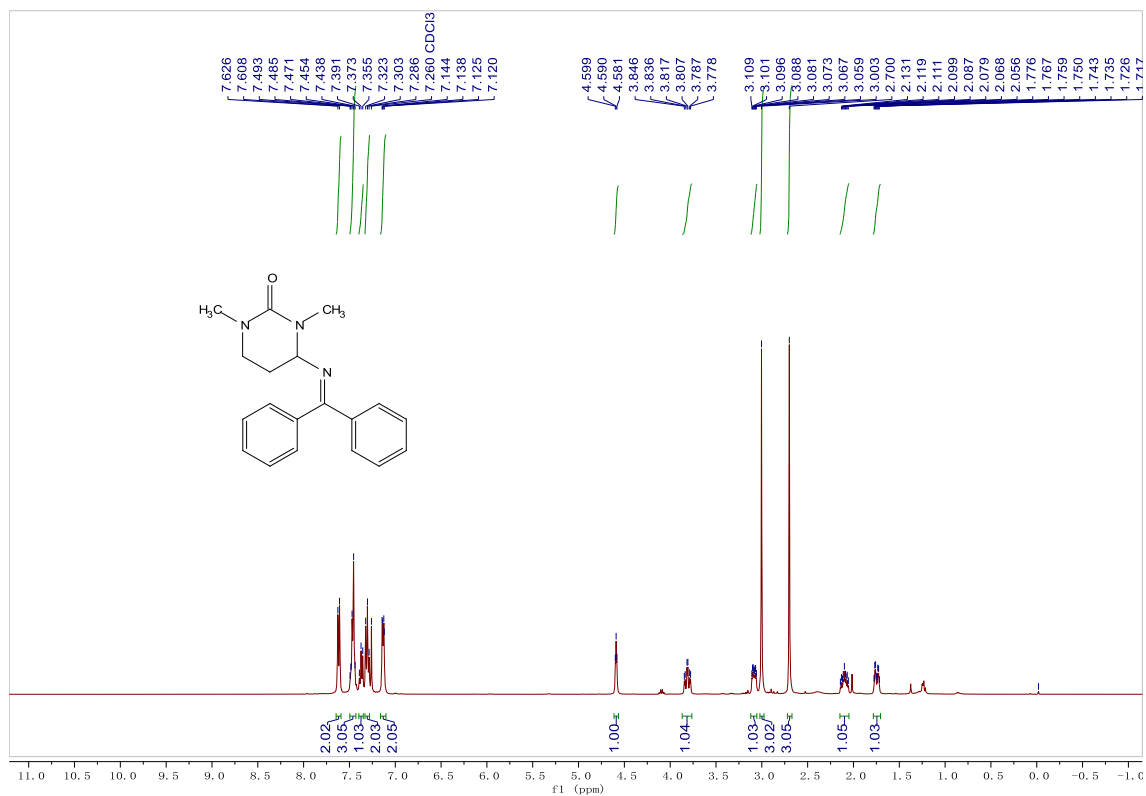
¹H-NMR for trans-2-3-NH₂

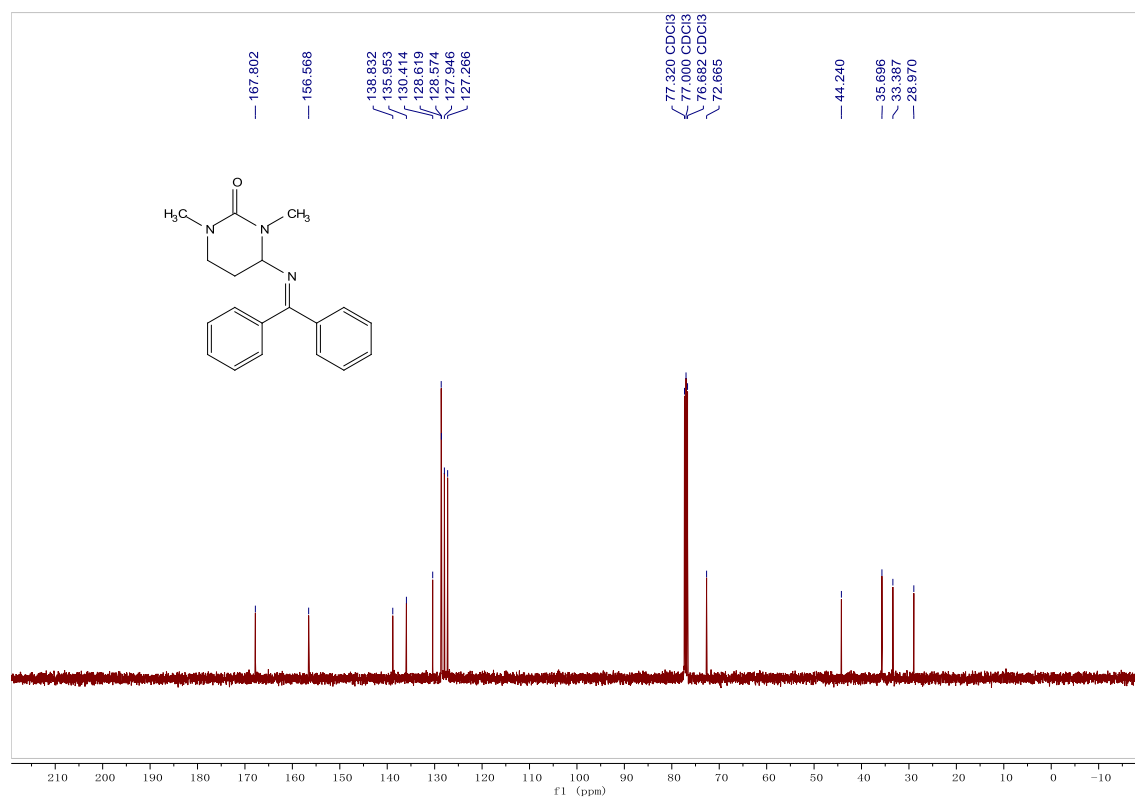


¹³C-NMR for trans-2-3-NH₂



¹H-NMR for Dimer-2

¹³C-NMR for **Dimer-2**¹H-NMR for **DMPU-1**



¹³C-NMR for **DMPU-1**