Supporting Information

Rh(II)-Catalyzed Cycloadditions of 1-Tosyl 1,2,3-Triazoles with *2H*-Azirines: Switchable Reactivity of Rh-Azavinylcarbene as [2C]- or Aza-[3C]-Synthon

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1. General Information

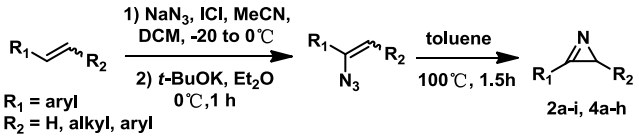
NMR spectra were recorded on Bruker AV400 instrument. TMS was used as internal standard for ^{1}H NMR (0 ppm), and solvent signal was used as reference for ^{13}C NMR ($CDCl_3$, 77.16 ppm; Acetone-d_6, 29.84 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, td = triple doublet, qd = quarter doublet, m = multiplet. Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Waters Xevo G2 QTOF MS. Gas chromatography-mass spectra (GC-MS) were recorded on SHIMADZU GC-MS-QP2010SE.

Reactions were monitored by Thin Layer Chromatography on plates (GF_{254}) supplied by Yantai Chemicals (China) using UV light as visualizing agent and an ethanolic solution of Potassium permanganate, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).

Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

2. General Procedures for Preparation of 2*H*-Azirines

1) Procedure A (for 2a-i and 4a-h)[1]



To a suspension of NaN_3 (452 mg, 7.0 mmol, 2.5 equiv) in acetonitrile (2.2 mL) was added dropwise a solution of iodine monochloride (680 mg, 4.2 mmol, 1.5 equiv) in CH_2Cl_2 (3.6 mL) at -20℃, and the mixture was stirred at the same temperature. After 30 min, a solution of corresponding alkene (2.8 mmol, 1.0 equiv) in CH_2Cl_2 (3.6 mL) was added slowly, and the mixture was stirred for 1 h. The reaction was quenched with saturated aqueous $Na_2S_2O_3$, and the

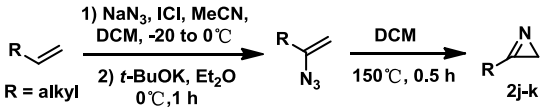
[1] Y. -F. Wang, K. K. Toh, J. -Y. Lee and S. Chiba, *Angew. Chem. Int. Ed.* 2011, **50**, 5927-5931.

organic materials were extracted with Et_2O. The combined extracts were washed with brine and dried over Na_2SO_4. After evaporation of solvents, the resulting crude materials were used immediately for the next step without any further purification.

To a solution of the above obtained compound in Et_2O (8 mL) was added *t*-BuOK (374 mg, 3.3 mmol, 1.2 equiv) at 0℃, and the mixture was stirred for 1 h at the same temperature. The reaction was quenched by adding ammonium buffer (pH = 9), and the organic materials were extracted with Et_2O. The Et_2O solution was washed with brine and dried over Na_2SO_4. The solvent was removed in vacuo, and the resulting crude materials were purified by flash column chromatography (silica gel; pure hexane) to give the corresponding vinyl azide.

A solution of the obtaind vinyl azide in toluene (15 mL) was heated for 1.5 h at 100℃. Evaporation of solvent gave a crude mixture which was purified by flash column chromatography (silica gel, hexanes/EtOAc) to give the 2*H*-azirines **2a-i/4a-h**.

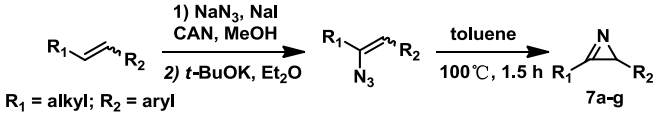
2) Procedure B (for 2j-k)[2]



The synthesis of the corresponding vinyl azide was completed by following the procedure described in **Procedure A.**

A solution of the obtained vinyl azide (4.0 mmol, 1.0 equiv) in dichloromethane (40 mL) was placed in a pressure tube and heated at 150℃ for 0.5 h. Evaporation of the solvent gave a crude mixture which was purified by flash column chromatography (silica gel, hexanes/EtOAc) to give the 2*H*-azirines **2j-k**.

3) Procedure C (for 7a-g)[3]



To a mixture of alkene (3.0 mmol, 1.0 equiv), sodium azide (200 mg, 3.0 mmol, 1.0 equiv), and sodium iodide (450 mg, 3.0 mmol, 1.0 equiv) in methanol (4.5 mL) at 0℃ was added a solution

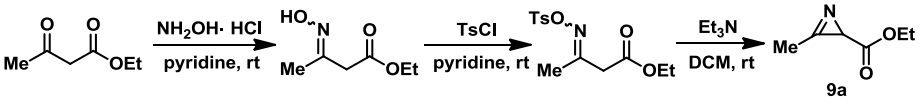
[2] A. S. Timén, E. Risberg and P. Somfai, *Tetrahedron. Lett.* 2003, **44**, 5339-5341.
[3] X. M. Zhang, S. K. Sarkar, G. K. Weragoda, S. Rajam, B. S. Ault and A. D. Gudmundsdottir. *J. Org. Chem.* 2014, **79**, 653-663.

of ceric ammonium nitrate (3.45 g, 6.3 mmol, 2.1 equiv) in methanol (18 mL) dropwise. Upon completion of the reaction as indicated by TLC, saturated aqueous $NaHSO_3$ (10 mL) was added, and the resulting mixture was extracted with dichloromethane (3×30 mL). The combined organic extracts were washed with distilled water (12 mL) and saturated brine (12 mL) and dried over anhydrous Na_2SO_4, and the solvent was removed under vacuum. The resulting crude materials were used immediately for the next step without any further purification.

To a solution of the above obtained compound in dry Et_2O (10 mL) in an ice bath was added *t*-BuOK (670 mg, 6.0 mmol, 2.0 equiv). The reaction mixture was stirred for 4h at 0℃ and then washed twice with water (25 mL). The organic extract was dried over Na_2SO_4, and the solvent was removed under vacuum. The residue was subjected to chromatography (silica gel, hexanes/EtOAc) to yield the corresponding vinyl azide.

The conversion of above vinyl azides into **8a-g** was completed by following the procedure described in **Procedure A.**

4) Procedure D (for 9a)[4]



To a solution of $NH_2OH·HCl$ (1.08 g, 15.5 mmol, 2.0 equiv) in pyridine (7.5 mL, 93.0 mmol, 12 equiv) was added *β*-ketoester (1.0 g, 7.75 mmol, 1.0 equiv) dropwise. The solution was stirred for 1 h, and solvent was removed under reduced pressure. The residue was extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to give ketoxime, which was used for the next step without purification.

To the ketoxime was added TsCl (1.77g, 9.3 mmol, 1.2 equiv) and pyridine (7.5 mL, 93.0 mmol, 12 equiv). The solution was stirred for 20 h and quenched with saturated aqueous NH_4Cl. The mixture was extracted three times with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by column chromatography (hexane/ ethyl acetate: 4/1) to yield the ketoximetosylate.

To a solution of ketoximetosylate in DCM (10 mL) was added Et_3N (1.0 mL, 7.75 mmol, 1.0 equiv) dropwise, and the mixture was stirred at room temperature for 3 h. Upon completion of the

[4] N. S. Y. Loy, A. Singh, X. X. Xu and C. M. Park, *Angew. Chem. Int. Ed.* 2013, **52**, 2212-2216.

reaction as indicated by TLC, the reaction mixture was quenched with water. The aqueous layer was extracted with DCM, and the combined organic layers were washed with water, brine and dried over anhydrous Na_2SO_4. The crude material was purified by column chromatography (hexane/ethyl acetate : 6/1) to yield 2*H*-azirine **10a**.

5) Procedure E (for 9b-d)[5]

To a mixture of *β*-ketoester (2.2 mmol, 1.0 equiv), NH_2OH ·HCl (160 mg, 2.2 mmol, 1.0 equiv) and sodium acetate (210 mg, 2.2 mmol, 1.0 equiv) was added methanol (15 mL) and water (0.7 mL). After stirring at room temperature for 4 h, the solvent was removed in vacuo. The reaction mixture was partitioned between Et_2O and water. After saperation, the organic extract was washed with saturated aqueous $NaHCO_3$, brine and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo, and the resulting crude was used directly in the next reaction.

To an ice cold solution of crude oxime and Et_3N (0.9 mL, 6.6 mmol, 3.0 equiv) in DCM (20 mL) was slowly added TsCl (500 mg, 2.6 mmol, 1.2 equiv), and the mixture was stirred at the same temperature for 2.5 h. The reaction was quenched with water, and the organic material was extracted three times with ethyl acetate. The combined extracts were washed with water, brine, and dried over anhydrous Na_2SO_4. The solvents were removed in vacuo, and the resulting crude materials were used immediately for the next step without further purification.

To an ice cold solution of crude ketoximetosylate in DCM (8 mL) was slowly added DBU (0.4 mL, 2.6 mmol, 1.2 equiv), and the mixture was stirred at the same temperature for 1h. The reaction quenched with water, and the organic materials were extracted with DCM. The combined extracts were washed with brine, and dried over anhydrous Na_2SO_4. After the solvents were removed in vacuo, the residue was purified by column chromatography to give the corresponding 2*H*-azirines **10b-d.**

[5] a) D. F. Taber and W. Tian, *J. Am. Chem. Soc*. 2006, **128**, 1058-1059; b) S. Chiba, G. Hattori and K. Narasaka, *Chem. Lett*. 2007, **36**, 52-53.

3. General Procedures for Rh(II)-catalyzed Formal [3+2] and [3+3] Cycloadditions of 1,2,3-Triazoles with 2*H*-Azirines

1) Procedure A (for 3a-p, 8a-g and 10a-d)

A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.30 mmol, 1.0 equiv), $Rh_2(esp)_2$ (3.5 mg, 0.005 mmol, 0.015 equiv) and 2*H*-azirine (0.60 mmol, 2.0 equiv). The reaction vessel was added freshly distilled 1,2-dichloroethane (0.8 mL), sealed with a teflon screwcap and then placed in an oil bath preheated to 160 ℃. The resulting solution was heated at this temperature for 1.0 hour before being cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) to give the corresponding [3+2] or [3+3] product**.**

2) Procedure B (for 6a-h)

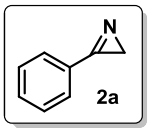
A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.30 mmol, 1.0 equiv), $Rh_2(esp)_2$ (3.5 mg, 0.005 mmol, 0.015 equiv) and 2*H*-azirine (0.60 mmol, 2.0 equiv). The reaction vessel was added freshly distilled toluene (0.8 mL), sealed with a teflon screwcap and then placed in an oil bath preheated to 160 ℃. The resulting solution was heated at this temperature for 1.0 hour before being cooled to room temperature and concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) to give the corresponding [3+3] product**.**

3) Procedure C (for 5a-h):

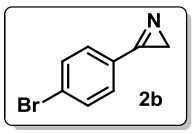
A 10 mL pressure tube, fitted with a rubber septum, was charged with triazole (0.30 mmol, 1.0 equiv), $Rh_2(esp)_2$ (3.5 mg, 0.005 mmol, 0.015 equiv) and 2H-azirine (0.60 mmol, 2.0 equiv). The reaction vessel was added freshly distilled 1,2-dichloroethane (0.8 mL) and $ClCH_2COOH$ (14.1 mg, 0.15 mmol, 0.5 equiv), sealed with a teflon screwcap and then was placed in an oil bath preheated to 160 ℃. The resulting solution was heated at this temperature for 0.5 hour before being cooled to room temperature add concentrated in vacuo. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) to give the corresponding [3+2] products**.**

4. Analysis Data of 2*H*-Azirines

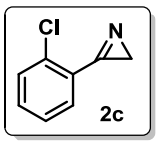
Note: For 2*H*-azirines **2a-b, 2d-h, 2j, 4a, 4e, 7a** and **9a-c** which are known compounds[6], the corresponding ^{1}H-NMR, ^{13}C-NMR and GC-MS data are provided. For 2*H*-azirines **2c, 2i, 2k, 4b-d, 4f-h, 7b-g** and **9d** which are new compounds, the corresponding ^{1}H-NMR, ^{13}C-NMR, and HRMS data are provided.



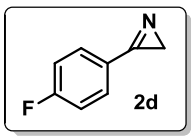
3-phenyl-2*H*-azirine (2a): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 2H), 7.54-7.62 (m, 3H), 7.90 (dd, *J* = 7.2 Hz, 0.4 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 19.8, 125.6, 129.2, 129.7, 133.0, 165.9; GC/MS (EI): m/z 51, 77, 91, 104, 117.



3-(4-bromophenyl)-2*H*-azirine (2a): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.81 (s, 2H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 20.1, 124.6, 127.9, 131.0, 132.7, 165.4; GC/MS (EI): m/z 89, 116, 155, 157, 195, 197.



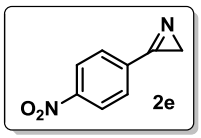
3-(2-chlorophenyl)-2*H*-azirine (2c): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 2H), 7.46 (dt, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.52 (dt, *J* = 7.2 Hz, 1.6 Hz, 1H), 7.55 (dd, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.86 (dd, *J* = 7.2 Hz, 1.6 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 20.3, 124.1, 127.3, 130.8, 132.4, 133.6, 136.3, 165.0; HRMS m/z calcd for C_8H_6ClN $[M+H]^+$: 152.0267; found: 152.0262.



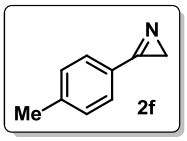
3-(4-fluorophenyl)-2*H*-azirine (2d): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 2H), 7.26 (t, *J* = 8.8 Hz, 2H), 7.92 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 19.9, 116.6 (d, *J* = 22.3

[6] (a) A. G. Hortmann, D. A. Robertson and B. K. Gillard, *J. Org. Chem*. 1972, **37**, 322-324; (b) Å. S. Timén, E. Risberg and P. Somfai, *Tetrahedron. Lett.* 2003, **44**, 5339-5341; (c) P. N. D. Singh, C. L. Carter and A. D. Gudmundsdóttir, *Tetrahedron. Lett*. 2003, **44**, 5339-5341; (d) X. M. Zhang, S. K. Sarkar, G. K. Weragoda, S. Rajam, B. S. Ault and A. D. Gudmundsdottir, *J. Org. Chem*. 2014, **79**, 653-663; (e) A. Padwa, M. Dharan, J. Smolanoff and S. I. Wetmore, *J. Am. Chem. Soc*. 1973, **95**, 1945-1954; (f) G. R. Harvey and K. W. Ratts, *J. Org. Chem*. 1966, **31**, 3907-3910; (g) D. Brown, G. A. Brown, M. Andrews, J. M. Large, D. Urban, C. P. Butts, N. J. Hales and T. Gallagher, *J. Chem. Soc. Perkin Transactions 1*. 2002, 2014-2021; (h) S. Guenter, M. Karl and M. Wolfgang, *Chem. Ber*. 1977, **110**, 2922-2938.

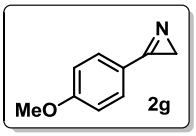
Hz), 122.0 (d, *J* = 3.1 Hz), 132.0 (d, *J* = 9.2 Hz), 164.8, 165.5 (d, *J* = 253.3 Hz); GC/MS (EI): m/z 94, 100, 120, 135.



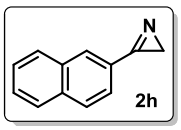
3-(4-nitrophenyl)-2*H*-azirine (2e): The product was obtained as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 8.43 (d, *J* = 8.8 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 20.9, 124.4, 130.4, 131.0, 150.3, 165.7; GC/MS (EI): m/z 50, 63, 89, 116, 162.



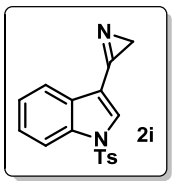
3-(*p*-tolyl)-2*H*-azirine (2f): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.75 (s, 2H), 2.45 (s, 3H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 19.5, 21.9, 122.9, 129.7, 129.9, 143.8, 165.3; GC/MS (EI): m/z 77, 91, 115, 117, 131.



3-(4-methoxyphenyl)-2*H*-azirine (2g): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.74 (s, 2H), 3.89 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.84 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 19.4, 55.6, 114.7, 118.2, 131.6, 163.4, 164.5; GC/MS (EI): m/z 77, 132, 147.

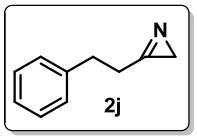


3-(naphthalen-2-yl)-2*H*-azirine (2h): The product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89 (s, 2H), 7.61 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.98-8.03 (m, 3H), 8.36 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 20.1, 123.1, 124.5, 127.2, 128.2, 128.6, 129.2, 132.0, 133.0, 135.6, 166.0; GC/MS (EI): m/z 127, 139, 167.

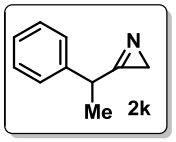


3-(2*H*-azirin-3-yl)-1-tosyl-1*H*-indole (2i): The product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (s, 2H), 2.32 (s, 3H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.36 (dt, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.42 (dt, *J* = 7.6 Hz, 0.8 Hz, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 8.01 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 16.9, 21.6, 109.5, 113.6, 121.4, 124.7, 126.2, 127.2, 127.6, 130.3, 131.2, 134.5, 135.2, 146.0, 158.2; HRMS m/z calcd for $C_{17}H_{14}N_2O_2S$ $[M+H]^+$: 311.0854; found:

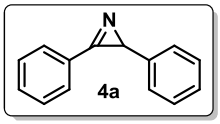
311.0849.



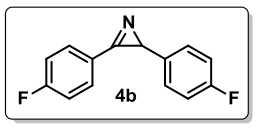
3-phenethyl-2*H*-azirine (2j): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (s, 2H), 3.04-3.13 (m, 4H), 7.22 (d, *J* = 7.6 Hz, 3H), 7.30 (t, *J* = 7.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 19.4, 30.4, 30.4, 126.6, 128.4, 128.7, 140.1, 169.5; GC/MS (EI): m/z 54, 91, 117, 144, 145.



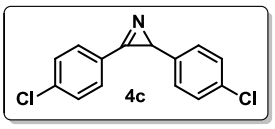
3-(1-phenylethyl)-2*H*-azirine (2k): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, *J* = 1.2 Hz, 2H), 1.64 (d, *J* = 7.2 Hz, 3H), 4.16 (q, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 17.8, 20.3, 39.6, 127.5, 127.7, 129.0, 139.2, 172.0; HRMS m/z calcd for $C_{10}H_{11}N$ $[M+H]^+$: 146.0970; found: 146.0965.



2,3-diphenyl-2*H*-azirine (4a): The product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.33 (s, 1H), 7.15 (dd, *J* = 8.0 Hz, 1.6 Hz, 2H), 7.22-7.31 (m, 3H), 7.53-7.63 (m, 3H), 7.91 (dd, *J* = 8.0 Hz, 1.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 34.6, 124.2, 126.2, 127.2, 128.4, 129.4, 130.0, 133.3, 141.0, 163.6; GC/MS (EI): m/z 89, 165, 193.

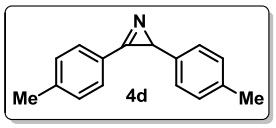


2,3-bis(4-fluorophenyl)-2*H*-azirine (4b): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.31 (s, 1H), 6.97 (t, *J* = 8.8 Hz, 2H), 7.09 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H), 7.25 (t, *J* = 8.8 Hz, 2H), 7.91 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 34.0, 115.4 (d, *J* = 21.6 Hz), 117.0 (d, *J* = 22.2 Hz), 120.4 (d, *J* = 3.2 Hz), 127.6 (d, *J* = 8.0 Hz), 132.3 (d, *J* = 9.3 Hz), 136.4 (d, *J* = 2.9 Hz), 162.4 (d, *J* = 243.9 Hz), 162.8, 165.8 (d, *J* = 254.3 Hz); HRMS m/z calcd for $C_{14}H_9F_2N$ $[M+H]^+$: 230.0781; found: 230.0784.

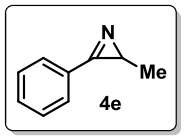


2,3-bis(4-chlorophenyl)-2*H*-azirine (4c): The product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.30 (s, 1H), 7.05 (d, *J* =

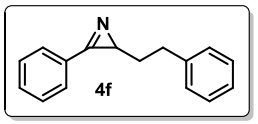
8.8 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 34.2, 122.4, 127.4, 128.7, 130.0, 131.2, 133.2, 139.2, 140.0, 162.8; HRMS m/z calcd for $C_{14}H_9Cl_2N$ $[M+H]^+$: 262.0190; found: 262.0187.



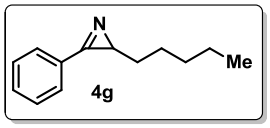
2,3-di-*p*-tolyl-2*H*-azirine (4d): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (s, 3H), 2.44 (s, 3H), 3.26 (s, 1H), 7.03 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.2, 22.0, 34.2, 121.5, 126.1, 129.1, 130.0, 130.1, 136.8, 138.1, 144.1, 163.3; HRMS m/z calcd for $C_{16}H_{15}N$ $[M+H]^+$: 222.1283; found: 222.1280.



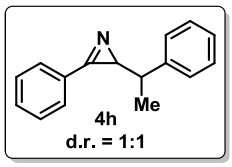
2-methyl-3-phenyl-2*H*-azirine (4e): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36 (d, *J* = 4.8 Hz, 3H), 2.30 (q, *J* = 4.8 Hz, 1H), 7.52-7.60 (m, 3H), 7.86 (dd, *J* = 8.0 Hz, 2.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 19.0, 27.6, 125.8, 129.2, 129.4, 132.8, 172.6; GC/MS (EI): m/z 51, 77, 105, 131.



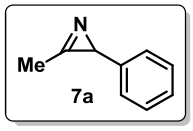
2-phenethyl-3-phenyl-2*H*-azirine (4f): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.89-2.03 (m, 2H), 2.30 (t, *J* = 4.8 Hz, 1H), 2.72-2.83 (m, 2H), 7.19-7.29 (m, 5H), 7.48-7.57 (m, 3H), 7.71 (d, *J* = 6.8 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 32.1, 33.8, 35.0, 125.8, 126.0, 128.5, 128.6, 129.1, 129.4, 132.9, 141.8, 171.9; HRMS m/z calcd for $C_{16}H_{15}N$ $[M+H]^+$: 222.1283; found: 222.1275.



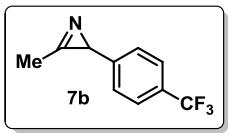
2-pentyl-3-phenyl-2*H*-azirine (4g): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3H), 1.26-1.48 (m, 6H), 1.59-1.64 (m, 2H), 2.27 (t, *J* = 4.8 Hz, 1H), 7.52-7.59 (m, 3H), 7.86 (dd, *J* = 8.0 Hz, 2.4 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.2, 22.7, 27.4, 31.8, 32.7, 33.2, 126.2, 129.2, 129.3, 132.8, 172.2; HRMS m/z calcd for $C_{13}H_{17}N$ $[M+H]^+$: 188.1439; found: 188.1434.



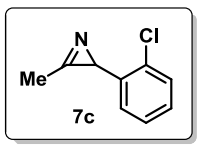
3-phenyl-2-(1-phenylethyl)-2*H*-azirine (4h): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.18 (d, *J* = 7.2 Hz, 3H), 1.34 (d, *J* = 7.2 Hz, 3H), 2.45 (d, *J* = 5.6 Hz, 1H), 2.51 (d, *J* = 4.4 Hz, 1H), 2.74 (m, 1H), 3.07 (m, 1H), 7.21-7.26 (m, 2H), 7.33-7.35 (m, 8H), 7.45-7.59 (m, 6H), 7.69 (dd, *J* = 6.8 Hz, 1.6 Hz, 2H), 7.83 (dd, *J* = 8.0 Hz, 1.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 18.7, 19.4, 38.6, 38.8, 42.1, 43.3, 125.8, 126.2, 126.5, 126.5, 127.5, 127.6, 128.6, 128.7, 129.1, 129.2, 129.4, 129.5, 132.9, 132.9, 144.9, 145.6, 171.3, 171.8; HRMS m/z calcd for $C_{16}H_{15}N$ $[M+H]^+$: 222.1283; found: 222.1285.



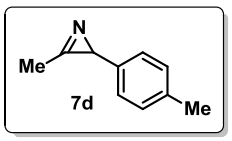
3-methyl-2-phenyl-2*H*-azirine (7a): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 2.89 (s, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.23-7.31 (m, 3H); ^{13}C (100 MHz, $CDCl_3$) δ 13.0, 33.5, 125.7, 126.9, 128.4, 141.3, 164.6; GC/MS (EI): m/z 63, 89, 131.



3-methyl-2-(4-(trifluoromethyl)phenyl)-2*H*-azirine (7b): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.51(s, 3H), 2.91 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 2.51(s, 3H), 2.91 (s, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 12.6, 32.9, 124.3 (q, *J* = 270.1 Hz), 125.2 (q, *J* = 3.8 Hz), 125.8, 128.9 (q, *J* = 32.2 Hz), 145.6, 163.8; HRMS m/z calcd for $C_{10}H_8F_3N$ $[M+H]^+$: 200.0687; found: 200.0686.

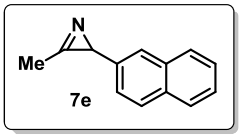


2-(2-chlorophenyl)-3-methyl-2*H*-azirine (7c): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.52 (s, 3H), 3.27 (s, 1H), 6.73 (dd, *J* = 6.8 Hz, 2.4 Hz, 1H), 7.12-7.19 (m, 2H), 7.32 (dd, *J* = 6.8 Hz, 2.4 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 13.2, 30.3, 125.7, 126.7, 127.7, 129.5, 133.7, 138.4, 165.0; HRMS m/z calcd for C_9H_8ClN $[M+H]^+$: 166.0424; found: 166.0419.

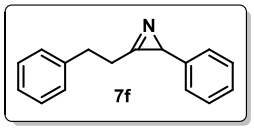


3-methyl-2-(*p*-tolyl)-2*H*-azirine (7d): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.32 (s, 3H), 2.51 (s, 3H), 2.86

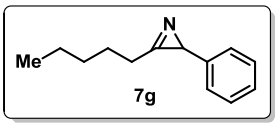
(s, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 13.0, 21.2, 33.4, 125.6, 129.1, 136.6, 138.3, 164.9; HRMS m/z calcd for $C_{10}H_{11}N$ $[M+H]^+$: 146.0970; found: 146.0965.



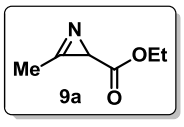
3-methyl-2-(naphthalen-2-yl)-2*H*-azirine (7e): The product was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.57 (s, 3H), 3.05 (s, 1H), 7.16 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.44 (m, 2H), 7.52 (s, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 13.1, 33.8, 123.9, 124.4, 125.6, 126.4, 127.6, 127.8, 128.1, 132.8, 133.4, 138.9, 164.8; HRMS m/z calcd for $C_{13}H_{11}N$ $[M+H]^+$: 182.0970; found: 182.0970.



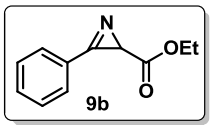
3-phenethyl-2-phenyl-2*H*-azirine (7f): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.89 (s, 1H), 3.09-3.16 (m, 4H), 6.98 (d, *J* = 6.4 Hz, 2H), 7.00-7.32 (m, 8H); ^{13}C (100 MHz, $CDCl_3$) δ 29.1, 30.6, 34.0, 125.7, 126.7, 126.9, 128.3, 128.5, 128.8, 140.0, 141.4, 167.3; HRMS m/z calcd for $C_{16}H_{15}N$ $[M+H]^+$: 222.1283; found: 222.1279.



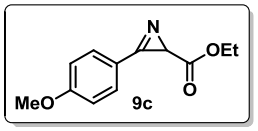
3-pentyl-2-phenyl-2*H*-azirine (7g): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, *J* = 7.2 Hz, 3H), 1.32-1.44 (m, 4H), 1.73-1.79 (m, 2H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.88 (s, 1H), 7.05 (d, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.28 (t, *J* = 7.2 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.0, 22.4, 24.2, 27.1, 31.5, 33.5, 125.6, 126.8, 128.3, 141.7, 167.6; HRMS m/z calcd for $C_{13}H_{17}N$ $[M+H]^+$: 188.1439; found: 188.1432.



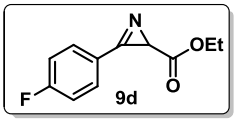
Ethyl 3-methyl-2*H*-azirine-2-carboxylate (9a): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.2 Hz, 3H), 2.44 (s, 1H), 2.54 (s, 3H), 4.19 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 12.7, 14.3, 28.9, 61.2, 159.3, 172.1; GC/MS (EI): m/z 54, 67, 81, 106, 108.



Ethyl 3-phenyl-2*H*-azirine-2-carboxylate (9b): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (dt, J = 7.2 Hz, 0.8 Hz, 3H), 2.84 (d, J = 0.8 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 7.56-7.65 (m, 3H), 7.89 (d, J = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) 14.4, 29.8, 61.4, 122.5, 129.5, 130.6, 134.0, 158.7, 171.8; GC/MS (EI): m/z 77, 105, 133, 161.

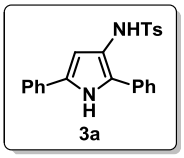


Ethyl 3-(4-methoxyphenyl)-2*H*-azirine-2-carboxylate (9c): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.2 Hz, 3H), 2.79 (s, 1H), 3.90 (s, 3H), 4.20 (q, J = 7.2 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 7.83 (d, J = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.4, 29.6, 55.8, 61.3, 114.7, 115.0, 132.7, 157.3, 164.2, 172.2; GC/MS (EI): m/z 107, 146, 219.

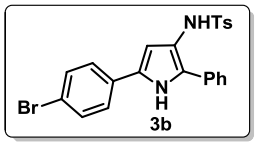


Ethyl 3-(4-fluorophenyl)-2*H*-azirine-2-carboxylate (9d): The product was obtained as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, J = 7.2 Hz, 3H), 2.85 (s, 1H), 4.22 (qd, J = 7.2 Hz, 2.0 Hz, 2H), 7.26-7.30 (m, 2H), 7.91 (dd, J = 7.6 Hz, 5.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.4, 29.9, 61.5, 117.1 (d, *J* = 22.4 Hz), 118.9 (d, *J* = 3.2 Hz), 133.0 (d, *J* = 9.5 Hz,), 157.8, 166.2 (d, *J* = 255.4 Hz), 171.7; HRMS m/z calcd for $C_{11}H_{10}FNO_2$ $[M+H]^+$: 208.0774; found: 208.0777.

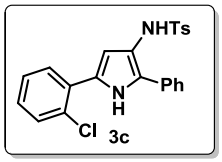
5. Analysis Data of [3+2]/[3+3] Cycloaddition Products



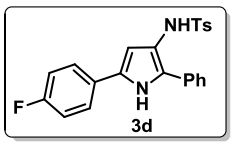
***N*-(2,5-diphenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3a):** The product was obtained as a yellow solid. Yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3H), 6.15 (s, 1H), 6.45 (d, *J* = 2.8 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 7.2 Hz, 2H), 7.22-7.29 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 8.29 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 106.2, 118.1, 123.9, 126.5, 127.0, 127.4, 127.6, 129.0, 129.1, 129.4, 130.8, 130.9, 131.9, 136.3, 143.6; IR ν_{max} (film): 2336.01, 1717.38, 1699.23, 1157.64, 761.66, 758.50, 711.76, 700.54, 691.14 cm^{-1}; HRMS m/z calcd for $C_{23}H_{20}N_2O_2S$ $[M+H]^+$: 389.1324; found: 389.1317.



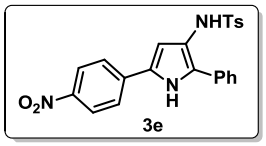
***N*-(5-(4-bromophenyl)-2-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3b):** The product was obtained as a yellow solid. Yield: 65%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.36 (s, 3H), 6.32 (d, *J* = 2.4 Hz, 1H), 7.20-7.24 (m, 3H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.50-7.62 (m, 8H), 8.11 (s, 1H), 10.49 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 108.2, 119.2, 120.0, 126.5, 127.5, 127.7, 128.1, 129.0, 130.0, 130.1, 130.3, 132.1, 132.5, 132.5, 138.8, 143.8; IR ν_{max} (film): 1490.40, 1303.64, 1156.99, 1092.95, 697.79, 689.94, 685.75, 681.14, 679.92 cm^{-1}; HRMS m/z calcd for $C_{23}H_{19}BrN_2O_2S$ $[M+H]^+$: 467.0429; found: 467.0432.



***N*-(5-(2-chlorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3c):** The product was obtained as a yellow solid. Yield: 57%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.38 (s, 3H), 6.27 (d, *J* = 3.2 Hz, 1H), 7.22-7.36 (m, 7H), 7.46 (dd, *J* = 8.0Hz, *J* = 1.2 Hz, 1H), 7.63 (dd, *J* = 7.6 Hz, *J* = 1.6 Hz, 1H), 7.66-7.71 (m, 4H), 7.99 (s, 1H), 10.40 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 112.0, 118.4, 127.5, 127.6, 127.7, 128.0, 128.3, 128.7, 129.0, 130.0, 130.1, 130.3, 131.3, 131.6, 132.0, 132.2, 139.0, 143.8; IR ν_{max} (film): 1699.86, 1303.67, 1158.57, 1092.54, 764.78, 756.38, 758.43, 688.20, 681.53 cm^{-1}; HRMS m/z calcd for $C_{23}H_{19}ClN_2O_2S$ $[M+H]^+$: 423.0934; found: 423.0921.

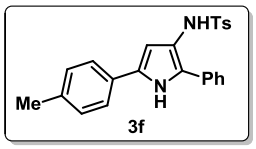


***N*-(5-(4-fluorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3d):** The product was obtained as a yellow solid. Yield: 79%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.37 (s, 3H), 6.23 (d, *J* = 2.4 Hz, 1H), 7.12 (t, *J* = 8.8 Hz, 2H), 7.19-7.30 (m, 5H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.66 (dd, *J* = 6.0 Hz, *J* = 8.8 Hz, 2H), 8.09 (s, 1H), 10.41 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 107.6, 116.3 (d, *J* = 21.7 Hz), 119.1, 126.7 (d, *J* = 7.9 Hz), 127.4, 127.7, 128.2, 129.0, 129.8, 130.0 (d, *J* = 3.2 Hz), 130.0, 130.5, 132.3, 138.9, 143.8, 162.3 (d, *J* = 242.2 Hz); IR ν_{max} (film): 2988.93, 2970.72, 1498.68, 1158.03, 1090.63, 705.45, 694.03, 690.66, 679.43, 677.81 cm^{-1}; HRMS m/z calcd for $C_{23}H_{19}FN_2O_2S$ $[M+H]^+$: 407.1230; found: 407.1227.

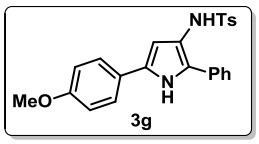


4-methyl-*N*-(5-(4-nitrophenyl)-2-phenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (3e): The product was obtained as a orange solid. Yield: 64%;

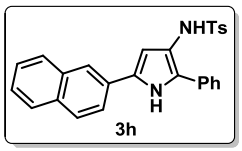
^{1}H NMR (400 MHz, Acetone-d_6) δ 2.37 (s, 3H), 6.60 (d, *J* = 2.8 Hz, 1H), 7.22-7.33 (m, 5H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 9.2 Hz, 2H), 10.80 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 111.0, 120.1, 124.7, 125.1, 128.0, 128.1, 128.1, 129.1, 130.1, 131.6, 132.4, 138.6, 139.3, 144.0, 146.3; IR ν_{max} (film): 1506.57, 1336.98, 1156.38, 738.74, 763.78, 684.74, 681.45, 678.32, 675.86 cm^{-1}; HRMS m/z calcd for $C_{23}H_{19}N_3O_4S$ $[M+H]^+$: 434.1175; found: 434.1161.



4-methyl-*N*-(2-phenyl-5-(*p*-tolyl)-1*H*-pyrrol-3-yl)benzenesulfonamide (3f): The product was obtained as a yellow solid. Yield: 74%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.30 (s, 3H), 2.37 (s, 3H), 6.19 (s, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.19-7.30 (m, 5H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 8.05 (s, 1H), 10.34 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.1, 21.4, 107.0, 118.9, 124.7, 127.2, 127.6, 128.2, 128.9, 129.3, 130.0, 130.1, 130.6, 131.5, 132.4, 136.6, 138.9, 143.7; IR ν_{max} (film): 1576.10, 1559.66, 1157.06, 948.69, 943.92, 692.71, 688.11, 679.16, 675.48 cm^{-1}; HRMS m/z calcd for $C_{24}H_{22}N_2O_2S$ $[M+H]^+$: 403.1480; found: 403.1474.

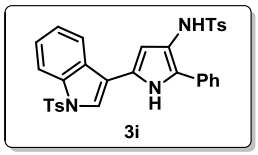


***N*-(5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3g):** The product was obtained as a yellow solid. Yield: 70%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.37 (s, 3H), 3.79 (s, 3H), 6.11 (d, *J* = 2.8 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.23-7.29 (m, 4H), 7.56 (t, *J* = 8.8Hz, 4H), 7.62 (d, *J* = 8.0 Hz, 2H), 8.05 (s, 1H), 10.28 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 55.6, 106.4, 115.0, 118.9, 126.2, 127.1, 127.5, 128.2, 128.8, 128.9, 130.0, 131.4, 131.5, 132.5, 139.0, 143.7, 159.4; IR ν_{max} (film): 2918.62, 2854.24, 1499.22, 1457.41, 1447.90, 1250.58, 1180.40, 1159.45, 838.60, 833.10, 691.81, 687.54, 676.37 cm^{-1}; HRMS m/z calcd for $C_{24}H_{22}N_2O_3S$ $[M+H]^+$: 419.1429; found: 419.1421.

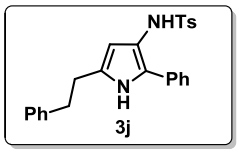


4-methyl-*N*-(5-(naphthalen-2-yl)-2-phenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (3h): The product was obtained as a yellow solid. Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 6.15 (s, 1H), 6.61 (d, *J* = 2.8 Hz, 1H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.2 Hz, 2H), 7.30 (m, 3H), 7.46 (m, 2H), 7.60 (m,

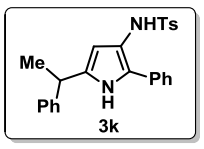
3H), 7.83 (m, 4H), 8.38 (s, 1H); ^{13}C (100 MHz,$CDCl_3$) δ 21.7, 106.8, 118.4, 121.4, 122.9, 125.9, 126.5, 126.8, 127.5, 127.6, 127.9, 127.9, 128.9, 129.1, 129.3, 129.5, 130.7, 130.9, 132.5, 133.8, 136.3, 143.6; IR ν_{max} (film): 2989.30, 1652.72, 1158.13, 1065.94, 681.90, 680.27, 678.10, 676.44 cm^{-1}; HRMS m/z calcd for $C_{27}H_{22}N_2O_2S$ $[M+H]^+$: 439.1480; found: 439.1476.



4-methyl-*N*-(2-phenyl-5-(1-tosyl-1*H*-indol-2-yl)-1H-pyrrol-3-yl)benzenesulfonamide (3i): The product was obtained as a yellow solid. Yield: 72%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.30 (s, 3H), 2.41 (s, 3H), 6.14 (d, *J* = 2.4 Hz, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.30-7.36 (m, 7H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.69-7.73 (m, 4H), 7.86 (d, *J* = 8.0 Hz, 2H), 8.05 (d, *J* = 8.4 Hz, 1H), 8.12 (d, *J* = 6.4 Hz, 2H), 10.55 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 21.5, 109.2, 114.7, 116.5, 118.6, 121.4, 122.3, 123.6, 124.6, 125.9, 127.5, 127.6, 127.7, 128.5, 129.1, 129.4, 129.5, 130.1, 130.9, 132.2, 135.7, 136.2, 139.0, 144.0, 146.4; IR ν_{max} (film): 1700.58, 1560.11, 1158.53, 724.72, 713.02, 688.62 cm^{-1}; HRMS m/z calcd for $C_{32}H_{27}N_3O_4S_2$ $[M+H]^+$: 582.1521; found: 582.1509.

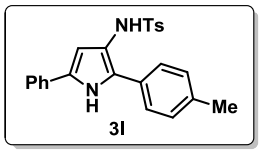


4-methyl-*N*-(5-phenethyl-2-phenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (3j): The product was obtained as a yellow solid. Yield: 65%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.38 (s, 3H), 2.86 (m, 4H), 5.56 (d, *J* = 2.8 Hz, 1H), 7.14 (t, *J* = 7.2 Hz, 1H), 7.17-7.30 (m, 9H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J*= 8.4 Hz, 2H), 7.86 (s, 1H), 10.00 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 30.3, 36.7, 107.3, 117.2, 126.6, 126.7, 126.7, 126.8, 128.2, 128.9, 129.1, 129.2, 129.9, 131.8, 133.0, 139.1, 142.6, 143.5; IR ν_{max} (film): 1700.55, 1559.86, 1160.26, 718.06, 681.30, 677.37 cm^{-1}; HRMS m/z calcd for $C_{25}H_{24}N_2O_2S$ $[M+H]^+$: 417.1637; found: 417.1629.

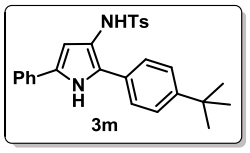


4-methyl-N-(2-phenyl-5-(1-phenylethyl)-1H-pyrrol-3-yl)benzenesulfonamide (3k): The product was obtained as a yellow solid. Yield: 72%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 1.47 (d, *J* = 7.2 Hz, 3H), 2.38 (s, 3H), 4.07 (q, *J* = 6.8 Hz, 1H), 5.49 (dd, *J* = 3.2 Hz, *J*= 0.8 Hz, 1H), 7.10-7.36 (m, 10H), 7.55-7.61 (m, 4H), 7.86 (s, 1H), 9.97 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 22.0, 39.3, 107.0, 117.1, 126.7, 126.9, 126.9, 127.5, 128.1, 128.3, 128.9, 129.1, 129.9, 132.9, 136.0, 138.9, 143.7, 146.7; IR ν_{max} (film): 1700.39,

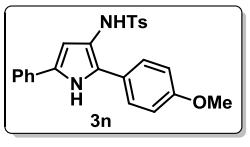
1559.78, 1318.76, 1159.80, 1091.90, 719.72, 699.19, 692.50, 680.89 cm^{-1}; HRMS m/z calcd for $C_{25}H_{24}N_2O_2S$ $[M+H]^+$: 417.1637; found: 417.1620.



4-methyl-*N*-(5-phenyl-2-(*p*-tolyl)-1*H*-pyrrol-3-yl)benzenesulfonamide (3l): The product was obtained as a yellow solid. Yield: 71%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.32 (s, 3H), 2.37 (s, 3H), 6.25 (d, *J* = 2.8 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 4H), 7.99 (s, 1H), 10.36 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.2, 21.4, 107.5, 118.7, 124.7, 126.9, 127.6, 128.2, 129.5, 129.6, 129.9, 130.0, 131.0, 133.4, 137.0, 139.0, 143.7; IR ν_{max} (film): 3360.51, 1501.98, 1317.32, 1158.46, 1090.58, 679.31, 676.83 cm^{-1}; HRMS m/z calcd for $C_{24}H_{22}N_2O_2S$ $[M+H]^+$: 403.1480; found: 403.1478.

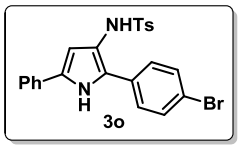


***N*-(2-(4-(*tert*-butyl)phenyl)-5-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3m):** The product was obtained as a yellow solid. Yield: 70%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 1.33 (s, 9H), 2.37 (s, 3H), 6.28 (d, *J* = 2.8 Hz, 1H), 7.17-7.23 (m, 3H), 7.32-7.36 (m, 4H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 8.03 (s, 1H), 10.33 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.5, 31.6, 35.0, 107.5, 118.7, 124.6, 125.7, 126.9, 127.5, 128.2, 129.4, 129.5, 129.9, 129.9, 131.0, 133.4, 138.8, 143.6, 150.2; IR ν_{max} (film): 2958.45, 1501.52, 1320.22, 1303.27, 1157.78, 1092.67, 760.19, 694.28, 686.61, 676.82 cm^{-1}; HRMS m/z calcd for $C_{27}H_{28}N_2O_2S$ $[M+H]^+$: 445.1950; found: 445.1938.

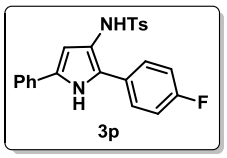


***N*-(2-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3n):** The product was obtained as a yellow solid. Yield: 72%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.36 (s, 3H), 3.80 (s, 3H), 6.22 (d, *J* = 2.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 8.8 Hz, 2H), 7.59-7.62 (m, 4H), 7.99 (s, 1H), 10.31 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 55.5, 107.4, 114.4, 118.1, 124.5, 124.9, 126.8, 128.2, 129.1, 129.5, 130.0, 130.0, 130.6, 133.4, 139.0, 143.7, 159.6; IR ν_{max} (film): 3362.88, 1700.19, 1606.34, 1501.78, 1303.13, 1249.40, 1156.59, 1091.52, 762.86, 760.19, 756.37, 707.89 cm^{-1}; HRMS m/z

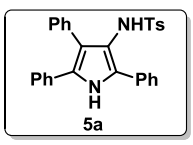
calcd for $C_{24}H_{22}N_2O_3S$ $[M+H]^+$: 419.1429; found: 419.1421.



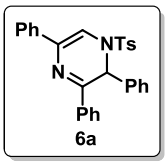
***N*-(2-(4-bromophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3o):** The product was obtained as a yellow solid. Yield: 67%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.39 (s, 3H), 6.27 (t, *J* = 2.8 Hz, 1H), 7.20-7.25 (m, 3H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.53 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 8.18 (s, 1H), 10.54 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.5, 108.1, 119.5, 120.6, 124.8, 127.3, 128.2, 128.6, 129.4, 129.6, 130.0, 131.5, 131.9, 131.9, 133.1, 138.8, 143.9; IR ν_{max} (film): 3359.79, 1699.99, 1489.63, 1303.83, 1156.74, 1091.64, 761.86, 759.73, 677.42, 675.98 cm^{-1}; HRMS m/z calcd for $C_{23}H_{19}BrN_2O_2S$ $[M+H]^+$: 467.0429; found: 467.0420.



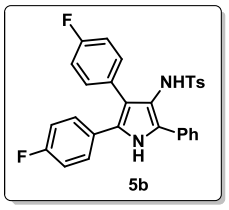
***N*-(2-(4-fluorophenyl)-5-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (3p):** The product was obtained as a yellow solid. Yield: 70%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.36 (s, 3H), 6.24 (d, *J* = 2.8 Hz, 1H), 7.05 (t, *J* = 8.8 Hz, 2H), 7.18 (t, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.58-7.61 (m, 6H), 8.08 (s, 1H), 10.45 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 107.6, 115.6 (d, *J* = 21.4 Hz), 118.8, 124.7, 127.1, 128.1, 128.7 (d, *J* = 3.2 Hz) 129.1, 129.5, 129.7 (d, *J* = 7.9 Hz), 130.0, 131.3, 133.2, 138.8, 143.8, 162.5 (d, *J* = 243.0 Hz); IR ν_{max} (film): 3369.50, 1700.09, 1500.76, 1304.10, 1227.48, 1159.50, 1092.02, 693.66, 687.11, 680.68, 677.92 cm^{-1}; HRMS m/z calcd for $C_{23}H_{19}FN_2O_2S$ $[M+H]^+$: 407.1230; found: 407.1217.



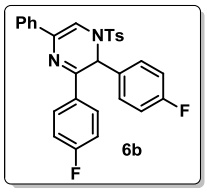
4-methyl-*N*-(2,4,5-triphenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (5a): The product was obtained as a yellow solid. Yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.27 (s, 1H), 6.81 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 6.8 Hz, 2H), 7.11-7.22 (m, 9H), 7.26 (t, *J* = 6.8 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 8.29 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 21.4, 115.5, 121.9, 126.3, 126.4, 126.7, 126.8, 127.0, 127.1, 127.7, 128.3, 128.6, 128.7, 129.0, 129.4, 129.9, 131.4, 132.2, 133.2, 136.6, 142.6; IR ν_{max} (film): 1700.53, 1322.43, 1159.46, 1091.59, 700.01, 695.34, 682.59, 678.92, 675.82 cm^{-1}; HRMS m/z calcd for $C_{29}H_{24}N_2O_2S$ $[M+H]^+$: 465.1637; found: 465.1626.



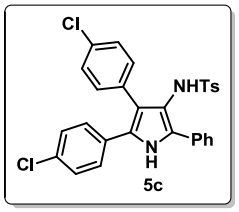
2,3,5-triphenyl-1-tosyl-1,2-dihydropyrazine (6a): The product was obtained as a yellow solid. Yield: 82%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H), 6.39 (s, 1H), 6.84 (s, 1H), 6.97 (d, *J* = 8.4 Hz, 2H), 7.23-7.44 (m, 11H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.74 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 53.8, 108.7, 125.2, 126.3, 127.4, 127.7, 128.1, 128.6, 128.7, 128.8, 128.8, 129.7, 130.9, 135.1, 136.0, 136.0, 136.4, 137.0, 144.4, 152.5; IR ν_{max} (film): 2986.03, 2972.19, 2365.34, 1700.08, 1066.74, 718.95, 688.45, 686.25, 683.68 cm^{-1}; HRMS m/z calcd for $C_{29}H_{24}N_2O_2S$ $[M+H]^+$: 465.1637; found: 465.1624.



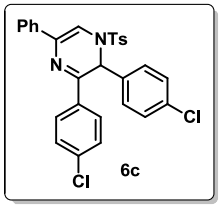
***N*-(4,5-bis(4-fluorophenyl)-2-phenyl-1*H*-pyrrol-3-yl)-4-methylbenzenes ulfonamide (5b):** The product was obtained as a yellow solid. Yield: 74%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.27 (s, 3H), 6.85-6.90 (m, 4H), 6.99-7.04 (m, 2H), 7.07-7.11 (m, 2H), 7.19-7.23 (m, 3H), 7.28 (d, *J* = 5.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H), 8.12 (s, 1H), 10.51 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.3, 115.4 (d, *J* = 21.2 Hz), 115.9 (d, *J* = 21.6 Hz), 116.4, 122.5, 127.3, 127.5, 127.7, 127.9, 128.9, 129.6, 129.9 (d, *J* = 3.3 Hz), 130.3 (d, *J* = 8.0 Hz), 131.3 (d, *J* = 3.2 Hz), 131.4, 132.7, 132.9 (d, *J* = 8.0 Hz), 139.6, 142.9, 162.4 (d, *J* = 241.4 Hz), 162.4 (d, *J* = 243.0 Hz); IR ν_{max} (film): 2984.44, 1495.49, 1221.43, 1159.91, 1065.64, 693.40, 683.98, 680.67, 679.37 cm^{-1}; HRMS m/z calcd for $C_{29}H_{22}F_2N_2O_2S$ $[M+H]^+$: 501.1448; found: 501.1439.



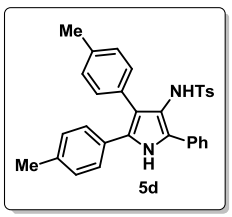
2,3-bis(4-fluorophenyl)-5-phenyl-1-tosyl-1,2-dihydropyrazine (6b): The product was obtained as a yellow solid. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 6.30 (s, 1H), 6.83 (d, *J* = 1.2 Hz, 1H), 6.95 (t, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.06 (t, *J* = 8.4 Hz, 2H), 7.29-7.40 (m, 5H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.71-7.77 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 53.0, 108.4, 115.7 (d, *J* = 4.2 Hz), 116.0 (d, *J* = 4.0 Hz), 125.1, 126.2, 128.2, 128.7, 129.4 (d, *J* = 8.6 Hz), 129.5 (d, *J* = 8.4 Hz), 129.7, 130.5 (d, *J* = 3.1 Hz), 132.4 (d, *J* = 3.2 Hz), 135.7, 135.8, 136.9, 144.6, 151.0, 163.1 (d, *J* = 246.6 Hz), 164.5 (d, *J* = 251.3 Hz); IR ν_{max} (film): 2968.33, 2962.30, 2926.02, 1601.16, 1508.48, 1357.22, 1230.01, 1168.96, 1158.00, 1089.22, 1010.04, 757.04, 681.80, 675.48 cm^{-1}; HRMS m/z calcd for $C_{29}H_{22}F_2N_2O_2S$ $[M+H]^+$: 501.1448; found: 501.1443.



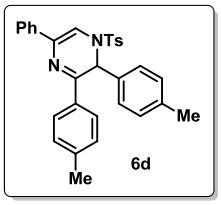
N-(4,5-bis(4-chlorophenyl)-2-phenyl-1H-pyrrol-3-yl)-4-methylbenzene sulfonamide (5c): The product was obtained as a yellow solid. Yield: 69%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.30 (s, 3H), 6.89 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.23-7.33 (m, 7H), 7.81 (d, *J* = 7.6 Hz, 2H), 8.18 (s, 1H), 10.60 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.4, 116.5, 122.7, 127.4, 127.5, 127.6, 127.8, 128.9, 129.0, 129.2, 129.6, 129.9, 132.1, 132.2, 132.5, 132.5, 132.6, 132.7, 133.8, 139.5, 143.1; IR ν_{max} (film): 3332.27, 1502.20, 1489.77, 1319.09, 1158.93, 1091.06, 690.33, 677.49 cm^{-1}; HRMS m/z calcd for $C_{29}H_{22}Cl_2N_2O_2S$ $[M+H]^+$: 533.0857; found: 533.0853.



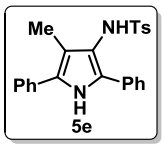
2,3-bis(4-chlorophenyl)-5-phenyl-1-tosyl-1,2-dihydropyrazine (6c): The product was obtained as a yellow solid. Yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 6.28 (s, 1H), 6.84 (d, *J* = 1.2 Hz, 1H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.20-7.38 (m, 9H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.66-7.71 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 52.9, 108.8, 125.1, 126.2, 128.3, 128.5, 128.7, 129.0, 129.1, 129.8, 133.3, 134.5, 135.1, 135.5, 135.8, 136.9, 137.3, 144.7, 150.7; IR ν_{max} (film): 1363.25, 1359.63, 1167.75, 1090.12, 1010.00, 755.02, 681.29, 676.36 cm^{-1}; HRMS m/z calcd for $C_{29}H_{22}Cl_2N_2O_2S$ $[M+H]^+$: 533.0857; found: 533.0848.



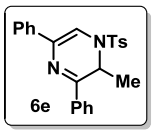
4-methyl-*N*-(2-phenyl-4,5-di-*p*-tolyl-1*H*-pyrrol-3-yl)benzenesulfonamide (5d): The product was obtained as a yellow solid. Yield: 70%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.25 (s, 3H), 2.27 (s, 3H), 2.31 (s, 3H), 6.85 (d, *J* = 8.0 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.16-7.21 (m, 5H), 7.28 (t, *J* = 7.6 Hz, 2H), 7.82 (d, *J* = 8.0 Hz, 2H), 8.00 (s, 1H), 10.33 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.1, 21.3, 21.4, 116.5, 123.1, 127.0, 127.4, 127.7, 128.2, 128.7, 128.9, 129.3, 129.5, 129.6, 130.9, 131.0, 131.0, 132.3, 133.0, 135.9, 136.7, 139.7, 142.7; IR ν_{max} (film): 3335.93, 1523.12, 1496.48, 1325.61, 1303.69, 1157.93, 1091.95, 701.50, 687.35, 683.67, 676.91 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1945.



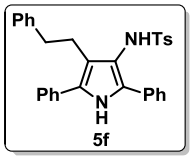
5-phenyl-2,3-di-*p*-tolyl-1-tosyl-1,2-dihydropyrazine (6d): The product was obtained as a yellow solid. Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.27 (s, 3H), 2.38 (s, 3H), 6.34 (s, 1H), 6.80 (d, *J* = 0.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 1H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.73 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.3, 21.6, 21.6, 53.6, 108.4, 125.1, 126.3, 127.4, 127.7, 127.9, 128.6, 129.4, 129.5, 129.7, 132.1, 133.8, 136.0, 136.2, 136.9, 138.7, 141.4, 144.2, 152.8; IR ν_{max} (film): 2989.27, 2969.49, 2920.34, 1559.78, 1167.62, 1052.31, 1045.83, 683.16, 678.96 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1950.



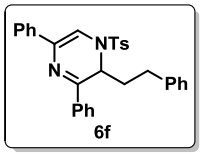
4-methyl-*N*-(4-methyl-2,5-diphenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (5e): The product was obtained as a yellow solid. Yield: 60%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.01 (s, 3H), 2.29 (s, 3H), 7.05 (d, *J* = 8.0 Hz, 2H), 7.11-7.20 (m, 3H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.38-7.45 (m, 4H), 7.53-7.56 (m, 4H), 8.04 (s, 1H), 10.15 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 10.3, 21.4, 117.7, 118.0, 126.8, 127.4, 127.9, 128.2, 128.7, 129.3, 129.7, 129.9, 132.7, 134.4, 139.2, 143.3; IR ν_{max} (film): 3353.80, 2922.72, 1704.30, 1302.67, 1156.13, 1092.41, 695.31, 681.84, 678.23 cm^{-1}; HRMS m/z calcd for $C_{24}H_{22}N_2O_2S$ $[M+H]^+$: 403.1480; found: 403.1477.



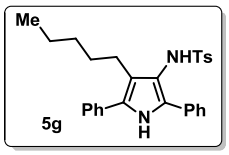
2-methyl-3,5-diphenyl-1-tosyl-1,2-dihydropyrazine (6e): The product was obtained as a light yellow oil. Yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (d, *J* = 7.2 Hz, 3H), 2.24 (s, 3H), 5.38 (q, *J* = 7.2 Hz, 1H), 6.93 (s, 1H), 7.00 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.38-7.43 (m, 5H), 7.51 (d, J = 8.4 Hz, 2H), 7.81 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 16.4, 21.6, 46.8, 108.4, 125.1, 126.3, 127.0, 127.9, 128.7, 128.7, 129.7, 130.9, 135.2, 135.4, 136.1, 136.2, 144.3, 154.9; IR ν_{max} (film): 2956.56, 1700.03, 1652.68, 1358.15, 1169.00, 706.35, 686.53, 678.98 cm^{-1}; HRMS m/z calcd for $C_{24}H_{22}N_2O_2S$ $[M+H]^+$: 403.1480; found: 403.1475.



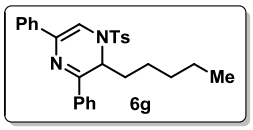
4-methyl-*N*-(4-phenethyl-2,5-diphenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (5f): The product was obtained as a yellow solid. Yield: 50%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 2.26 (s, 3H), 2.87 (s, 4H), 6.99 (d, *J* = 8.0 Hz, 2H), 7.11-7.21 (m, 6H), 7.25-7.29 (m, 3H), 7.41-7.48 (m, 4H), 7.49 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 7.59 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 8.00 (s, 1H), 10.17 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 21.3, 27.3, 37.1, 117.3, 122.2, 126.5, 126.8, 127.2, 127.5, 127.8, 127.8, 128.6, 128.7, 129.1, 129.2, 129.4, 129.8, 130.3, 132.7, 134.5, 139.4, 143.3, 143.6; IR ν_{max} (film): 3346.57, 1160.02, 700.50, 697.41, 693.77, 687.61, 678.46 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1953.



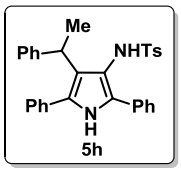
2-phenethyl-3,5-diphenyl-1-tosyl-1,2-dihydropyrazine (6f): The product was obtained as a light yellow oil. Yield: 79%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.72 (m, 1H), 1.96 (m, 1H), 2.20 (s, 3H), 2.85 (m, 2H), 5.28 (dd, *J* = 10.0 Hz, 3.6 Hz, 1H), 6.89 (s, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 7.18-7.34 (m, 8H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 7.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.5, 30.5, 31.3, 50.8, 108.1, 125.1, 126.2, 126.2, 127.1, 128.1, 128.6, 128.6, 128.7, 128.8, 129.6, 130.9, 135.5, 135.9, 136.1, 136.8, 141.1, 144.3, 154.6; IR ν_{max} (film): 2953.18, 2924.79, 1652.76, 1448.25, 1358.75, 1168.44, 1091.45, 1028.37, 699.09, 690.36, 687.49 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1947.



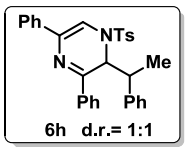
4-methyl-*N*-(4-pentyl-2,5-diphenyl-1*H*-pyrrol-3-yl)benzenesulfonamide (5g): The product was obtained as a yellow solid. Yield: 65%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 0.86 (t, *J* = 6.8 Hz, 3H), 1.23-1.29 (m, 4H), 1.52 (m, 2H), 2.29 (s, 3H), 2.56 (m, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 7.09-7.18 (m, 3H), 7.25 (t, *J* = 7.2 Hz, 1H), 7.41 (t, *J* = 8.4 Hz, 4H), 7.50 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.56 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 8.03 (s, 1H), 10.09 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 14.4, 21.3, 23.1, 24.6, 30.8, 32.9, 117.3, 123.3, 126.7, 127.0, 127.5, 127.7, 127.8, 128.2, 128.7, 129.3, 129.7, 130.2, 132.8, 134.7, 139.6, 143.2; IR ν_{max} (film): 3358.34, 2928.88, 1601.79, 1493.29, 1316.86, 1304.51, 1158.70, 1094.34, 696.10, 688.93, 678.42, 676.78 cm^{-1}; HRMS m/z calcd for $C_{28}H_{30}N_2O_2S$ $[M+H]^+$: 459.2106; found: 459.2091.



2-pentyl-3,5-diphenyl-1-tosyl-1,2-dihydropyrazine (6g): The product was obtained as a light yellow oil. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H), 1.26-1.61 (m, 8H), 2.20 (s, 3H), 5.25 (dd, *J* = 8.8 Hz, 3.2 Hz, 1H), 6.88 (d, *J* = 1.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.37-7.43 (m, 5H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.76 (dd, *J* = 8.0 Hz, 1.2 Hz, 2H), 7.80 (d, *J* = 6.8 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.2, 21.6, 22.6, 24.9, 28.9, 31.4, 51.3, 108.1, 125.0, 126.1, 127.1, 128.0, 128.6, 129.6, 130.8, 135.8, 136.0, 136.0, 136.5, 144.2, 154.9; IR ν_{max} (film): 2921.18, 2848.80, 1357.77, 1168.14, 1089.18, 758.40, 677.23 cm^{-1}; HRMS m/z calcd for $C_{28}H_{30}N_2O_2S$ $[M+H]^+$: 459.2106; found: 459.2101.

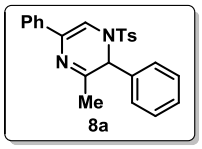


***N*-(2,5-diphenyl-4-(1-phenylethyl)-1*H*-pyrrol-3-yl)-4-methylbenzenesulfonamide (5h):** The product was obtained as a yellow solid. Yield: 58%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 1.48 (d, *J* = 7.2 Hz, 3H), 2.26 (s, 3H), 4.57 (q, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 7.09-7.13 (m, 4H), 7.19-7.24 (m, 7H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.48 (dd, *J* = 7.2 Hz, 2.4 Hz, 2H), 8.07 (s, 1H), 10.11 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 19.5, 21.3, 34.2, 117.0, 126.0, 126.6, 126.9, 127.5, 127.5, 127.8, 128.3, 128.6, 128.6, 128.7, 128.8, 129.6, 129.7, 129.7, 132.8, 135.0, 139.6, 143.1, 147.9; IR ν_{max} (film): 1699.99, 1158.61, 1559.69, 680.25, 678.21, 676.43 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1949.



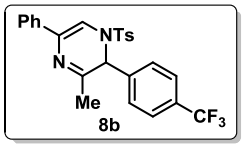
3,5-diphenyl-2-(1-phenylethyl)-1-tosyl-1,2-dihydropyrazine (6h): The product was obtained as a light yellow oil. Yield: 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.26 (d, *J* = 7.2 Hz, 3H), 1.50 (d, *J* = 7.2 Hz, 3H), 2.13 (s, 3H), 2.16 (s, 3H), 2.89 (m, 1H), 2.97 (m, 1H), 5.16 (dd, *J* = 10.0 Hz, 1.2 Hz, 1H), 5.45 (dd, *J* = 8.8 Hz, 1.2 Hz, 1H), 6.67 (d, *J* = 1.2 Hz, 1H), 6.84 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 1.2 Hz, 1H), 6.97-7.25 (m, 15H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.32-7.35 (m, 4H), 7.37-7.45 (m, 10H), 7.73 (d, *J* = 7.2 Hz, 2H), 7.86 (d, *J* = 7.2 Hz, 2H), 7.90 (dd, *J* = 7.6 Hz, 2.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 17.7, 18.3, 21.5, 21.5, 38.5, 39.6, 55.9, 56.8, 107.1, 108.6, 125.1, 125.2, 126.0, 126.1, 127.2, 127.2, 127.2, 127.4, 127.6, 128.1, 128.1, 128.2, 128.3, 128.4, 128.6, 128.6, 128.7, 128.7, 129.5, 129.5, 129.8, 130.7, 135.7, 135.9, 136.0, 136.5, 137.1, 137.3, 137.4, 141.0, 141.8,

144.1, 144.1, 153.2, 153.7; IR ν_{max} (film): 2925.63, 1360.37, 1167.96, 1025.96, 755.39, 695.70, 683.69 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1948.



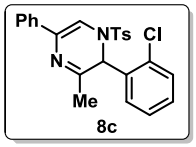
8a

3-methyl-2,5-diphenyl-1-tosyl-1,2-dihydropyrazine (8a): The product was obtained as a light yellow oil. Yield: 75%; ^1H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 3H), 2.39 (s, 3H), 5.51 (d, *J* = 1.2 Hz, 1H), 6.79 (d, *J* = 0.8 Hz, 1H), 7.23-7.30 (m, 8H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.64-7.66 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 21.7, 25.3, 57.0, 109.0, 124.9, 126.5, 127.7, 127.9, 128.6, 128.9, 129.0, 130.0, 134.6, 135.1, 135.9, 136.1, 144.5, 157.4; IR ν_{max} (film): 2970.54, 2919.80, 1699.92, 1456.39, 1163.87, 1066.21, 683.60, 676.42 cm^{-1}; HRMS m/z calcd for $C_{24}H_{22}N_2O_2S$ $[M+H]^+$: 403.1480; found: 403.1469.



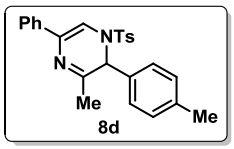
8b

3-methyl-5-phenyl-1-tosyl-2-(4-(trifluoromethyl)phenyl)-1,2-dihydrop yrazine (8b): The product was obtained as a light yellow oil. Yield: 70%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.40 (s, 3H), 5.55 (s, 1H), 6.81 (s, 1H), 7.24-7.31 (m, 3H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.63-7.65 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 21.6, 25.3, 56.3, 108.7, 123.8 (q, *J* = 270.7 Hz), 124.8, 125.8 (q, *J* = 3.8 Hz), 126.4, 127.9, 128.0, 128.6, 130.0, 131.1 (q, *J* = 32.3 Hz), 135.0, 135.5, 135.8, 138.6, 144.7, 156.2; IR ν_{max} (film): 2927.05, 1652.40, 1325.82, 1164.82, 1123.03, 1067.08, 686.59, 683.65, 675.48 cm^{-1}; HRMS m/z calcd for $C_{25}H_{21}F_3N_2O_2S$ $[M+H]^+$: 471.1354; found: 471.1354.

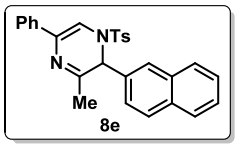


8c

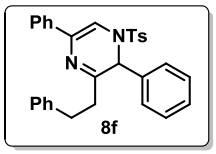
2-(2-chlorophenyl)-3-methyl-5-phenyl-1-tosyl-1,2-dihydropyrazine (8c): The product was obtained as a light yellow oil. Yield: 76%; ^1H NMR (400 MHz, $CDCl_3$) δ 2.00 (s, 3H), 2.37 (s, 3H), 6.03 (d, *J* = 0.8 Hz, 1H), 7.01 (dt, *J* = 7.6 Hz, *J* = 1.2 Hz, 1H), 7.07 (s, 1H), 7.15-7.20 (m, 3H), 7.25-7.41 (m, 5H), 7.63 (dd, *J* = 6.8 Hz, *J* = 2.0 Hz, 2H), 7.70-7.73 (m, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.7, 24.7, 54.1, 110.9, 124.6, 126.9, 127.7, 127.9, 128.7, 128.9, 129.9, 129.9, 130.2, 131.8, 132.4, 134.9, 135.4, 136.2, 144.5, 158.1; IR ν_{max} (film): 2926.64, 1161.43, 1126.04, 1035.99, 1010.64, 683.62, 681.65, 678.18 cm^{-1}; HRMS m/z calcd for $C_{24}H_{21}ClN_2O_2S$ $[M+H]^+$: 437.1091; found: 437.1087.



3-methyl-5-phenyl-2-(*p*-tolyl)-1-tosyl-1,2-dihydropyrazine (8d): The product was obtained as a light yellow oil. Yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 3H), 2.29 (s, 3H), 2.39 (s, 3H), 5.47 (s, 1H), 6.77 (s, 1H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.22-7.29 (m, 3H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.63-7.66 (m, 4H); ^{13}C (100 MHz, $CDCl_3$) δ 21.3, 21.7, 25.3, 56.8, 109.0, 124.9, 126.5, 127.7, 127.8, 128.6, 129.6, 130.0, 131.6, 135.1, 136.0, 136.2, 138.9, 144.4, 157.6; IR ν_{max} (film): 1700.60, 1160.07, 1124.84, 1034.23, 1009.22, 688.53, 680.42 cm^{-1}; HRMS m/z calcd for $C_{25}H_{24}N_2O_2S$ $[M+H]^+$: 417.1637; found: 417.1625.

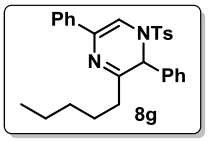


3-methyl-2-(naphthalen-2-yl)-5-phenyl-1-tosyl-1,2-dihydropyrazine (8e): The product was obtained as a light yellow oil. Yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.03 (s, 3H), 2.35 (s, 3H), 5.67 (s, 1H), 6.80 (s, 1H), 7.19-7.29 (m, 3H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.40-7.47 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.57 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 4H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.7, 25.4, 57.2, 109.1, 125.0, 125.5, 126.5, 126.5, 126.7, 126.7, 127.7, 127.9, 128.3, 128.6, 129.0, 130.0. 131.8, 133.1, 133.5, 135.3, 136.0, 136.1, 144.5, 157.5; IR ν_{max} (film): 1652.11, 1166.33, 1036.20, 812.43, 754.23, 746.71, 683.72 cm^{-1}; HRMS m/z calcd for $C_{28}H_{24}N_2O_2S$ $[M+H]^+$: 453.1637; found: 453.1631.

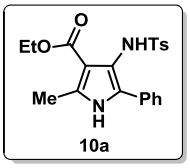


3-phenethyl-2,5-diphenyl-1-tosyl-1,2-dihydropyrazine (8f): The product was obtained as a light yellow oil. Yield: 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (m, 1H), 2.39 (s, 3H), 2.62-2.81 (m, 3H), 5.47 (d, *J* = 1.2 Hz, 1H), 6.81 (d, *J* = 1.2 Hz, 1H), 7.06 (d, *J* = 7.2 Hz, 2H), 7.14-7.31 (m, 11H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 21.7, 31.2, 39.8, 56.7, 109.2, 125.0, 126.2, 126.6, 127.8, 127.9, 128.4, 128.5, 128.6, 128.9, 129.0, 130.0, 134.8, 134.9, 136.1, 136.3, 141.2, 144.5, 159.0; IR ν_{max} (film): 1559.72, 1653.81, 684.48, 679.78, 676.84 cm^{-1}; HRMS m/z calcd for $C_{31}H_{28}N_2O_2S$ $[M+H]^+$: 493.1950; found: 493.1926.

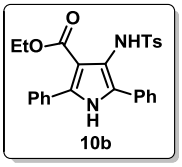
3-pentyl-2,5-diphenyl-1-tosyl-1,2-dihydropyrazine (8g): The product was obtained as a light yellow oil. Yield: 75%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, *J* = 7.2 Hz, 3H), 1.13-1.36 (m, 6H),



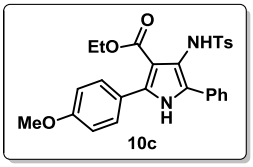
2.02 (m, 1H), 2.32 (m, 1H), 2.39 (s, 3H), 5.46 (s, 1H), 6.81 (s, 1H), 7.23-7.31 (m, 8H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 7.6 Hz, 2H); ^{13}C (100 MHz, $CDCl_3$) δ 14.0, 21.6, 22.4, 24.9, 31.4, 38.2, 56.2, 108.8, 124.8, 126.5, 127.7, 127.8, 128.5, 128.8, 129.9, 134.8, 134.9, 136.1, 136.3, 144.3, 160.1; IR ν_{max} (film): 2926.43, 1160.57, 1125.32, 1035.51, 1008.98, 685.14, 681.99, 679.48 cm^{-1}; HRMS m/z calcd for $C_{28}H_{30}N_2O_2S$ $[M+H]^+$: 459.2106; found: 459.2096.



Ethyl-2-methyl-4-(4-methylphenylsulfonamido)-5-phenyl-1*H*-pyrrole-3-carboxylate (10a): The product was obtained as a colorless oil. Yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, *J* = 7.2 Hz, 3H), 2.33 (s, 3H), 2.36 (s, 3H), 3.95 (q, *J* = 7.2 Hz, 2H), 7.06 (s, 1H), 7.08 (d, *J* = 4.4 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.25-7.29 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 8.47 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 13.8, 14.4, 21.6, 59.7, 108.6, 117.1, 126.3, 126.4, 127.1, 127.9, 128.6, 129.0, 131.1, 134.0, 136.0, 143.3, 164.8; IR ν_{max} (film): 1700.42, 1162.51, 687.10, 684.98, 679.28 cm^{-1}; HRMS m/z calcd for $C_{21}H_{22}N_2O_4S$ $[M+H]^+$: 399.1379; found: 399.1375.

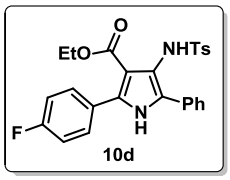


Ethyl-4-(4-methylphenylsulfonamido)-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (10b): The product was obtained as a colorless oil. Yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (t, *J* = 7.2 Hz, 3H), 2.32 (s, 3H), 3.81 (q, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.19 (s, 1H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.31-7.42 (m, 7H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 7.6 Hz, 2H), 8.49 (s, 1H); ^{13}C (100 MHz, $CDCl_3$) δ 14.0, 21.6, 59.9, 109.2, 118.3, 126.5, 127.6, 127.9, 128.2, 128.6, 128.7, 129.0, 129.1, 130.8, 131.6, 135.4, 135.9, 143.3, 164.3; IR ν_{max} (film): 3316.35, 1683.30, 1459.85, 1163.73, 690.00, 686.96, 685.09, 677.08 cm^{-1}; HRMS m/z calcd for $C_{26}H_{24}N_2O_4S$ $[M+H]^+$: 461.1535; found: 461.1529.



Ethyl-2-(4-methoxyphenyl)-4-(4-methylphenylsulfonamido)-5-phenyl-1H-pyrrole-3-carboxylate (10c): The product was obtained as a colorless oil. Yield: 90%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 1.08 (t, *J* = 7.2 Hz, 3H), 2.35 (s, 3H), 3.83 (s, 3H), 3.85 (q, *J* = 7.2 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.47 (d,

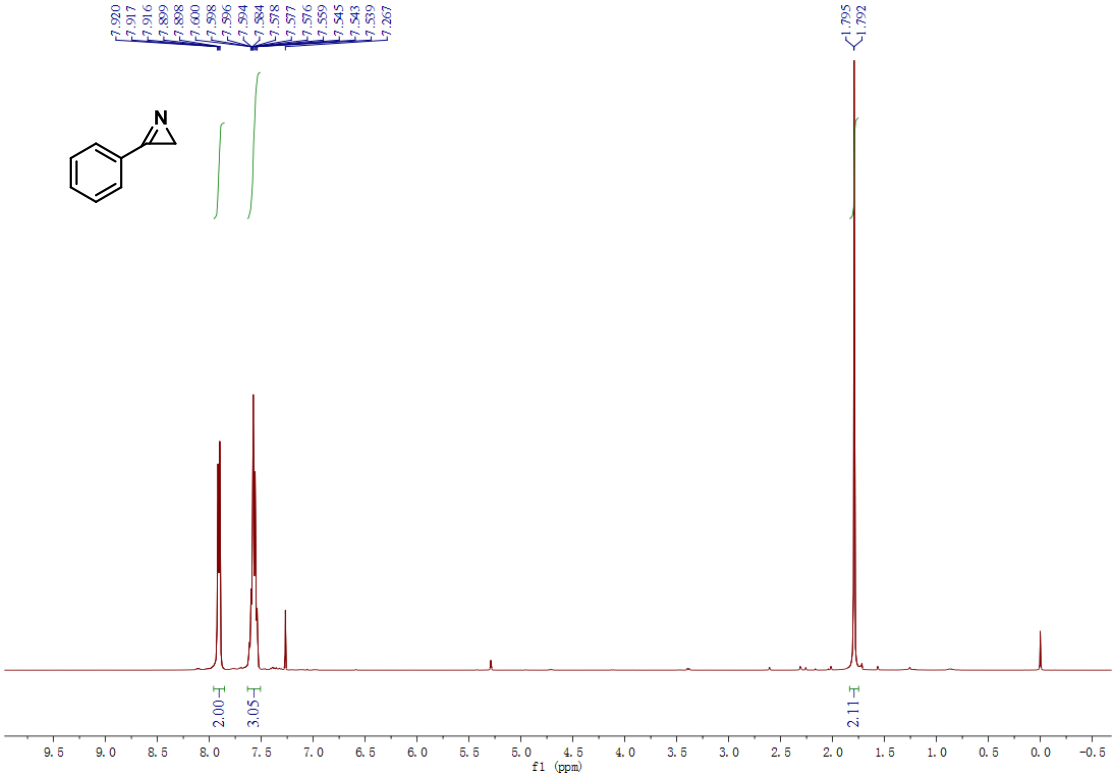
J = 8.8 Hz, 2H), 7.74 (s, 1H), 7.85 (d, *J* = 8.0 Hz, 2H), 10.67 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 14.3, 21.4, 55.6, 60.1, 113.9, 118.8, 125.0, 127.6, 127.8, 128.5, 128.9, 129.4, 129.7, 131.6, 132.2, 132.2, 136.3, 137.6, 143.8, 160.7, 165.0; IR ν_{max} (film): 1699.90, 1159.19, 691.39, 682.70, 675.84 cm^{-1}; HRMS m/z calcd for $C_{27}H_{26}N_2O_5S$ $[M+H]^+$: 491.1641; found: 491.1638.



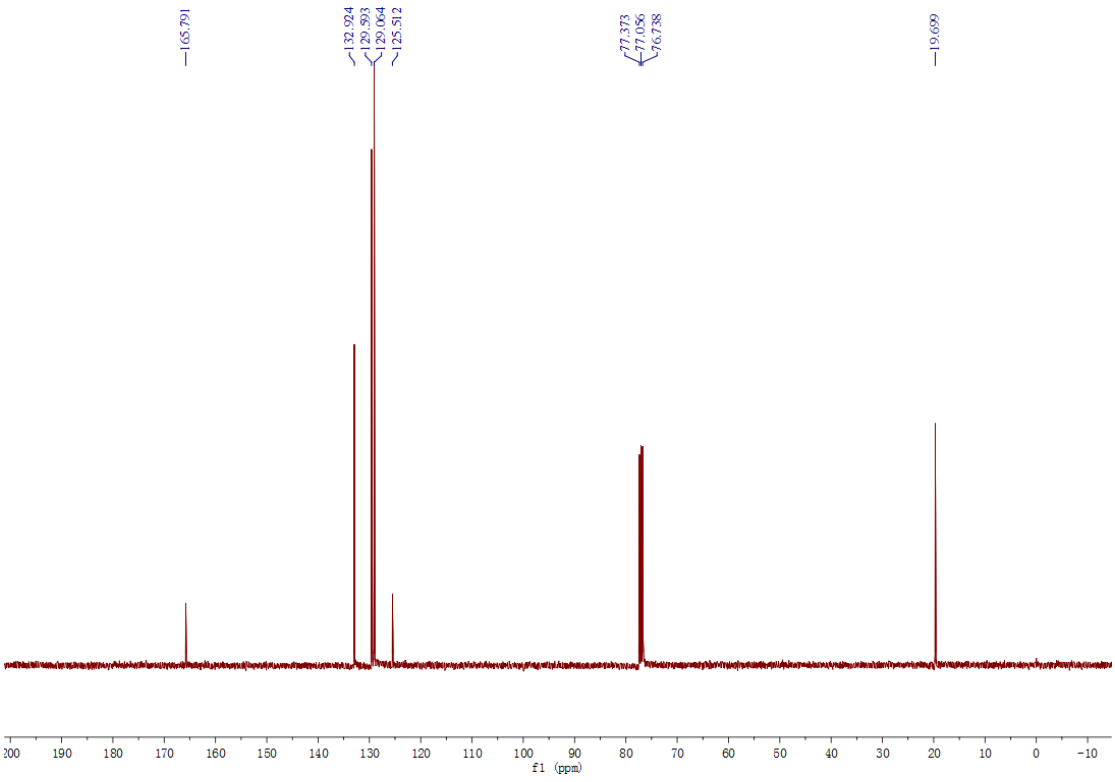
10d

Ethyl-2-(4-fluorophenyl)-4-(4-methylphenylsulfonamido)-5-phenyl-1H-pyrrole-3-carboxylate (10d): The product was obtained as a colorless oil. Yield: 88%; ^{1}H NMR (400 MHz, Acetone-d_6) δ 1.07 (t, *J* = 7.2 Hz, 3H), 2.34 (s, 3H), 3.85 (q, *J* = 7.2 Hz, 2H), 7.14-7.26 (m, 4H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.59 (dd, *J* = 8.8 Hz, 5.6 Hz, 2H), 7.75 (s, 1H), 7.84 (d, *J* = 7.6 Hz, 2H), 10.82 (s, 1H); ^{13}C (100 MHz, Acetone-d_6) δ 14.2, 21.4, 60.2, 110.9, 115.3 (d, *J* = 21.6 Hz), 118.9, 127.8, 127.8, 128.5, 128.9, 129.1 (d, *J* = 3.3 Hz), 129.7, 130.0, 132.1, 132.5 (d, *J* = 8.2 Hz), 135.1, 137.6, 143.9, 163.5 (d, *J* = 244.3 Hz), 164.8; IR ν_{max} (film): 2955.88, 2920.33, 2849.88, 1457.08, 1377.91, 1253.84, 1161.08, 1066.17, 683.41, 676.10 cm^{-1}; HRMS m/z calcd for $C_{26}H_{23}FN_2O_4S$ $[M+H]^+$: 479.1441; found: 479.1440.

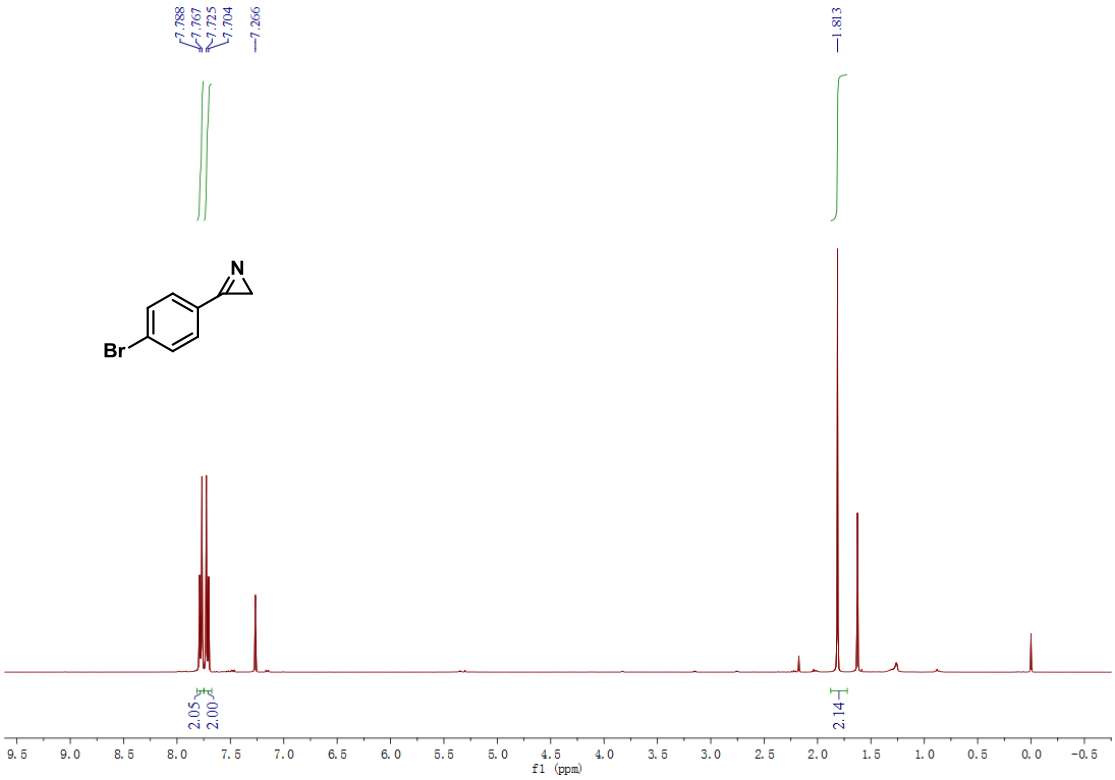
6. NMR Spectra of 2*H*-Azirines



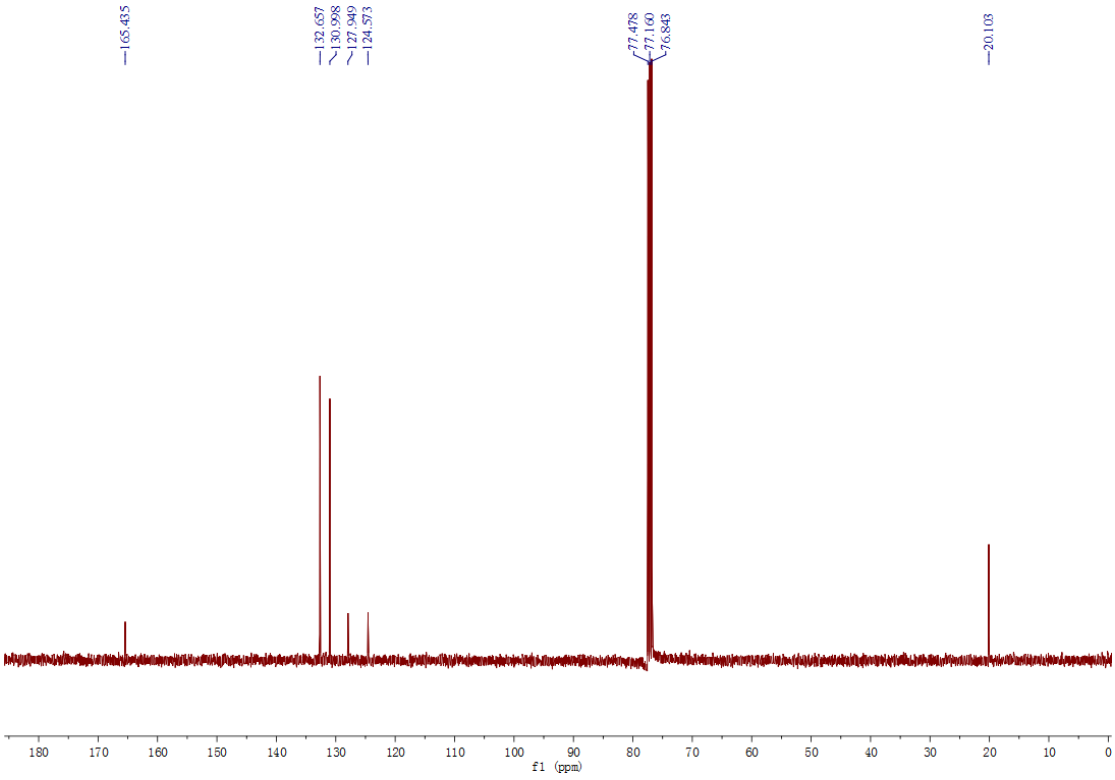
^{1}H NMR Spectrum for **2a** ($CDCl_3$, 400 MHz)



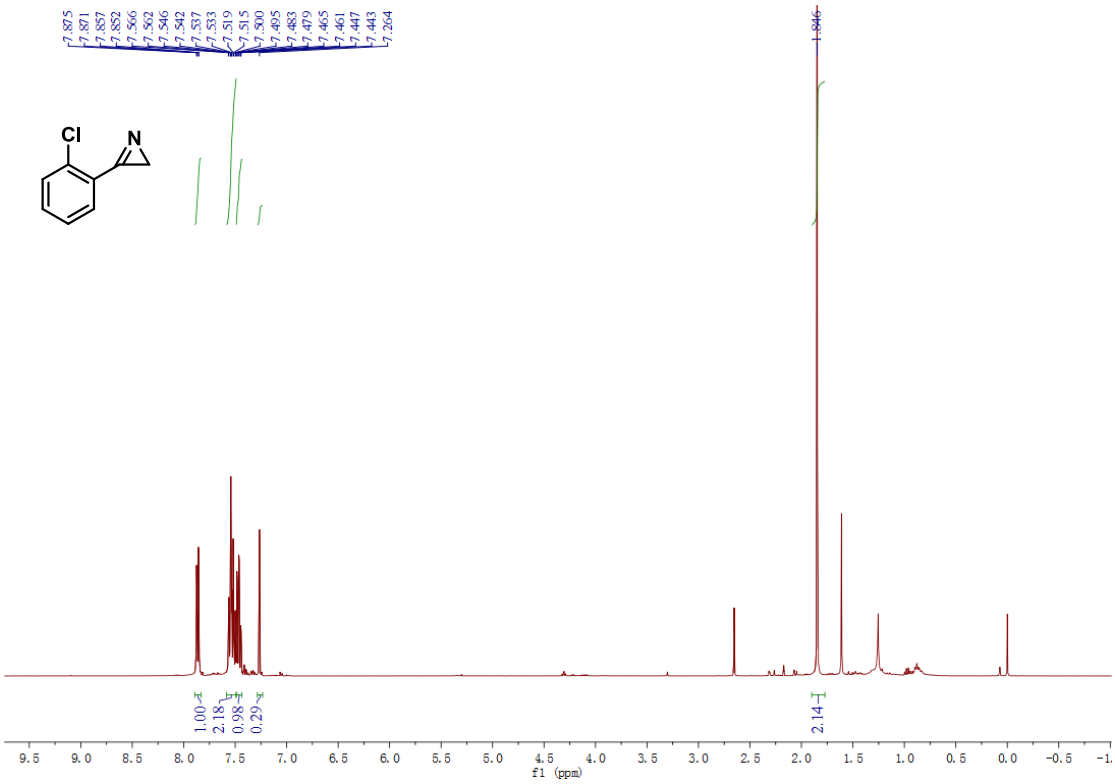
^{13}C NMR Spectrum for **2a** ($CDCl_3$, 100 MHz)



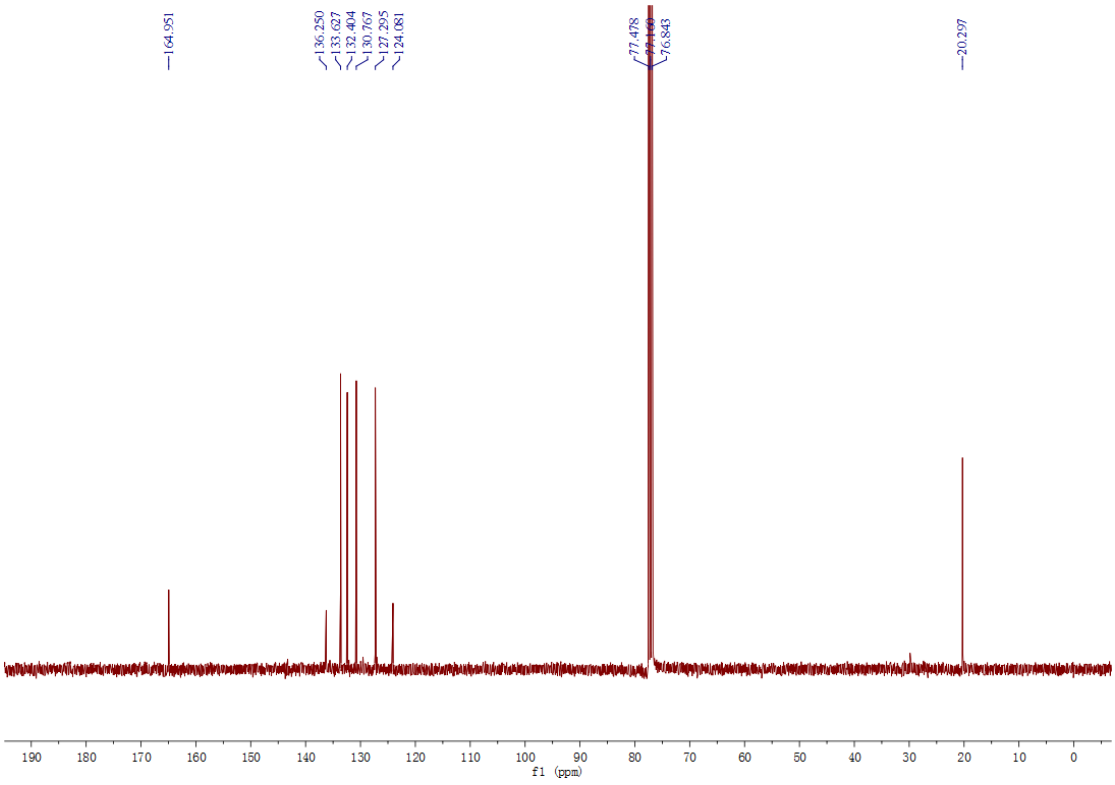
^{1}H NMR Spectrum for **2b** ($CDCl_3$, 400 MHz)



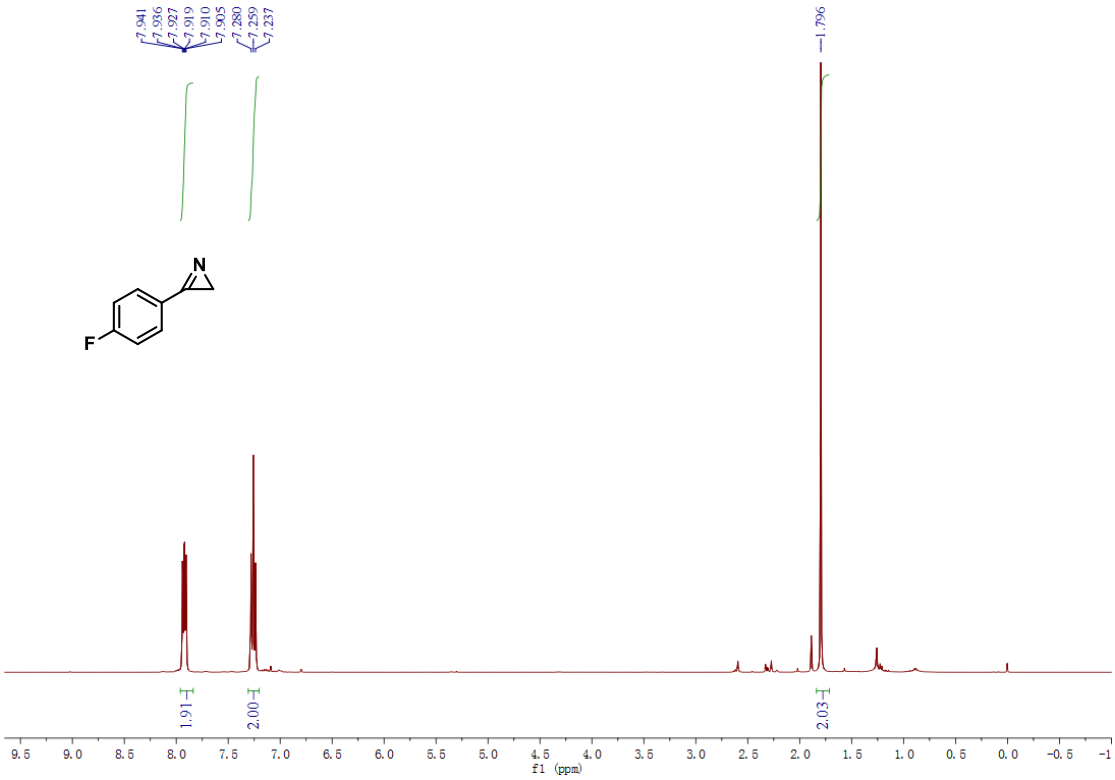
^{13}C NMR Spectrum for **2b** ($CDCl_3$, 100 MHz)



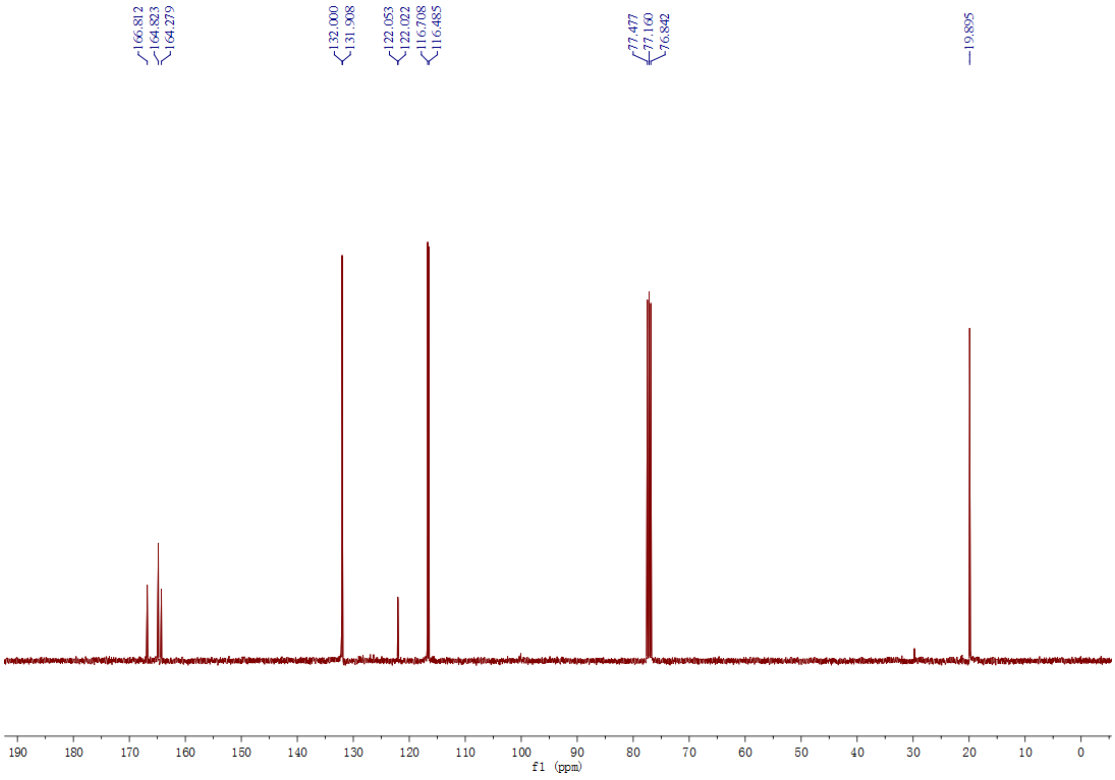
^{1}H NMR Spectrum for **2c** ($CDCl_3$, 400 MHz)



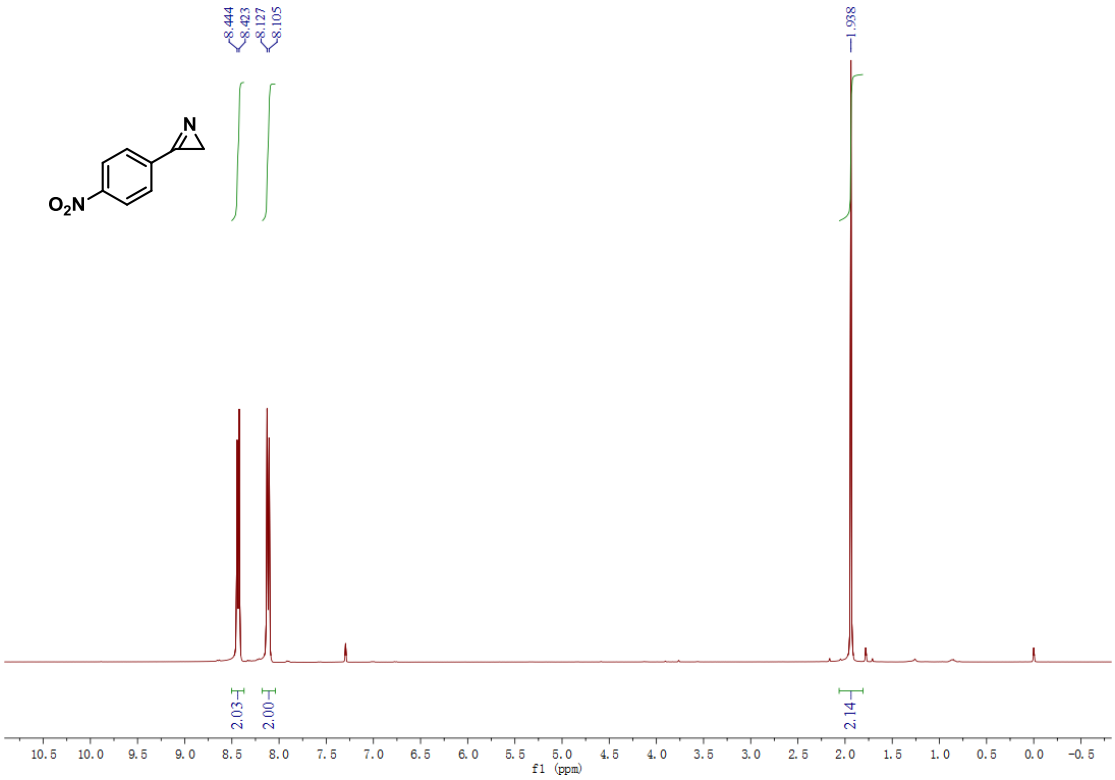
^{13}C NMR Spectrum for **2c** ($CDCl_3$, 100 MHz)



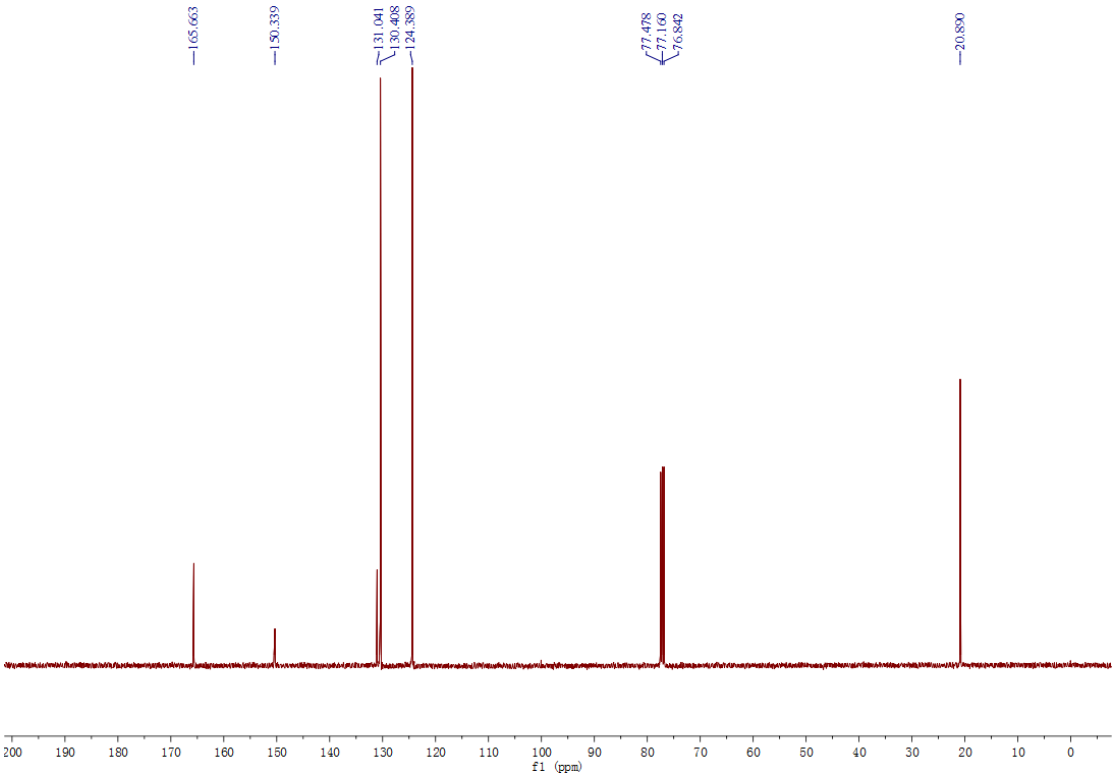
^{1}H NMR Spectrum for **2d** ($CDCl_3$, 400 MHz)



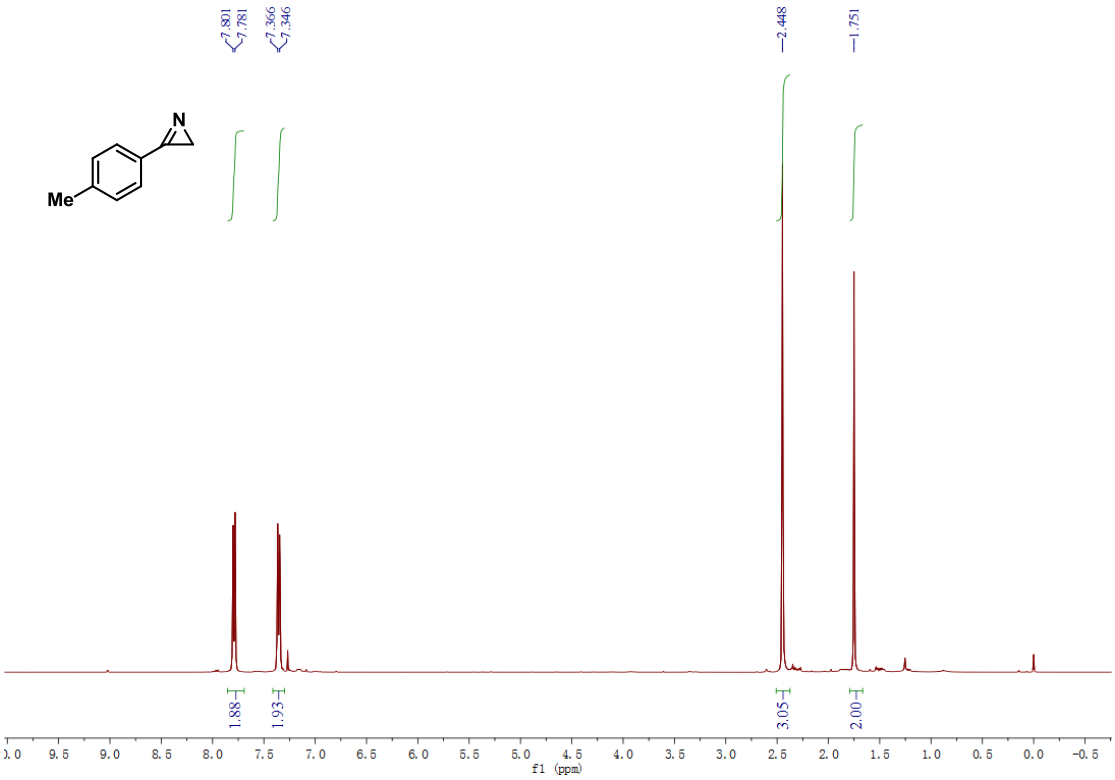
^{13}C NMR Spectrum for **2d** ($CDCl_3$, 100 MHz)



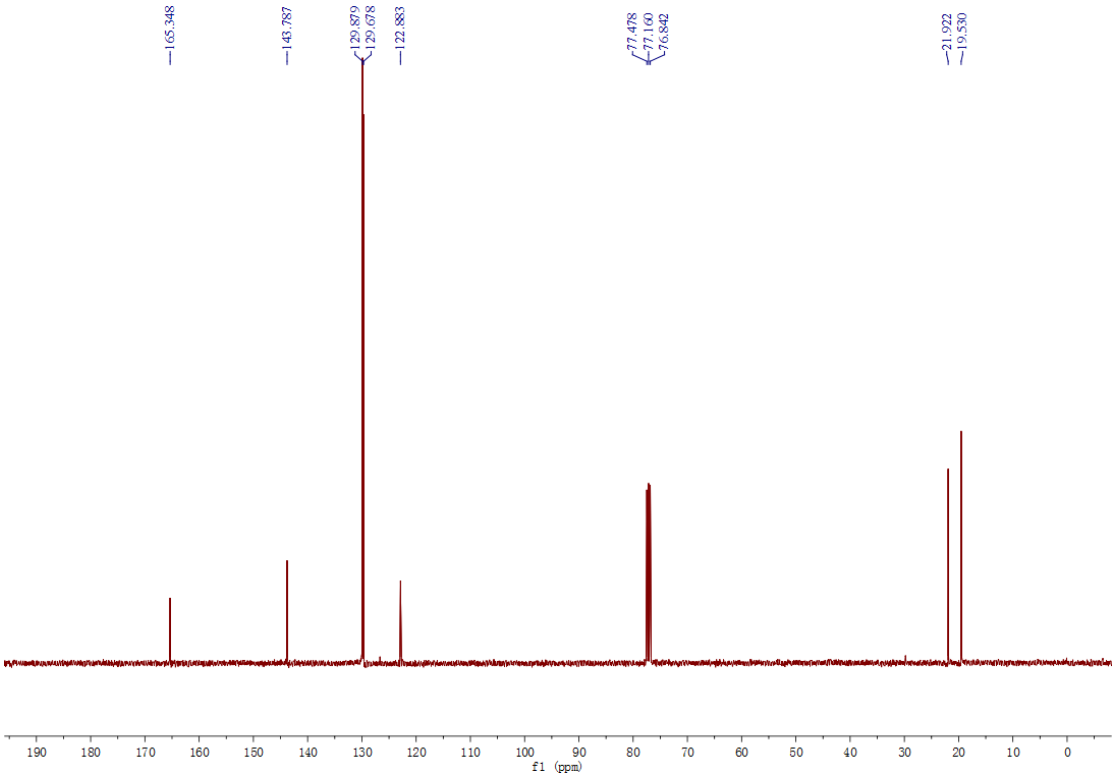
^{1}H NMR Spectrum for **2e** ($CDCl_3$, 400 MHz)



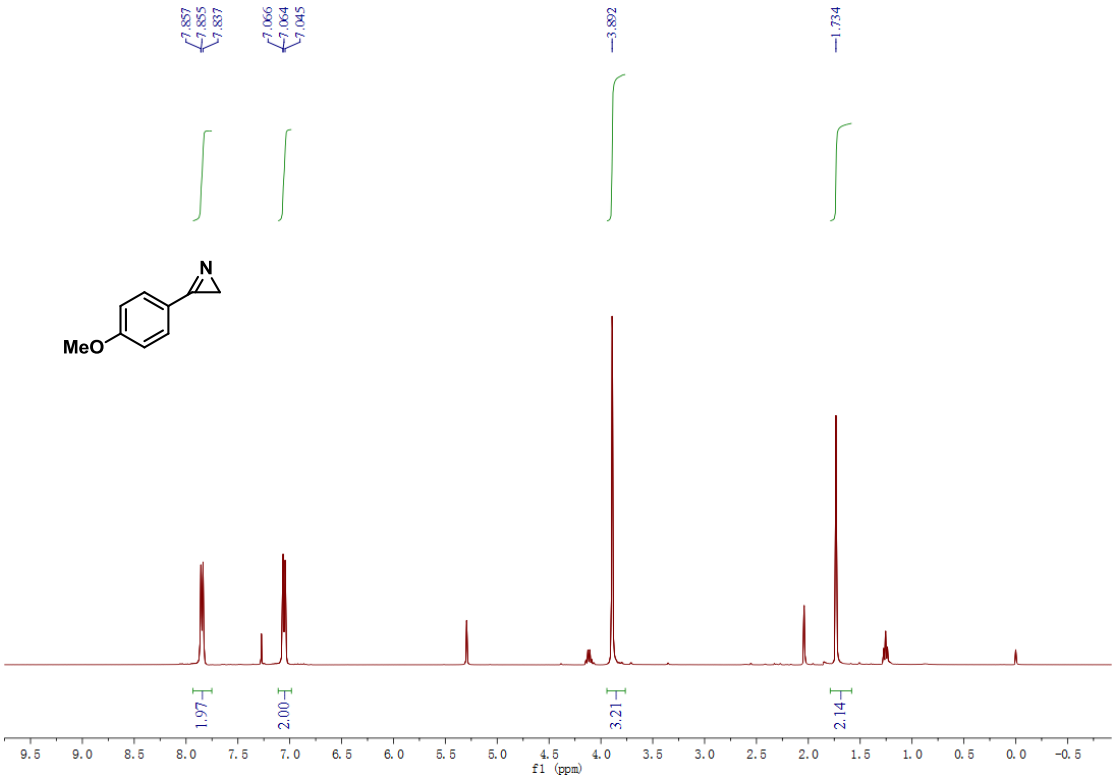
^{13}C NMR Spectrum for **2e** ($CDCl_3$, 100 MHz)



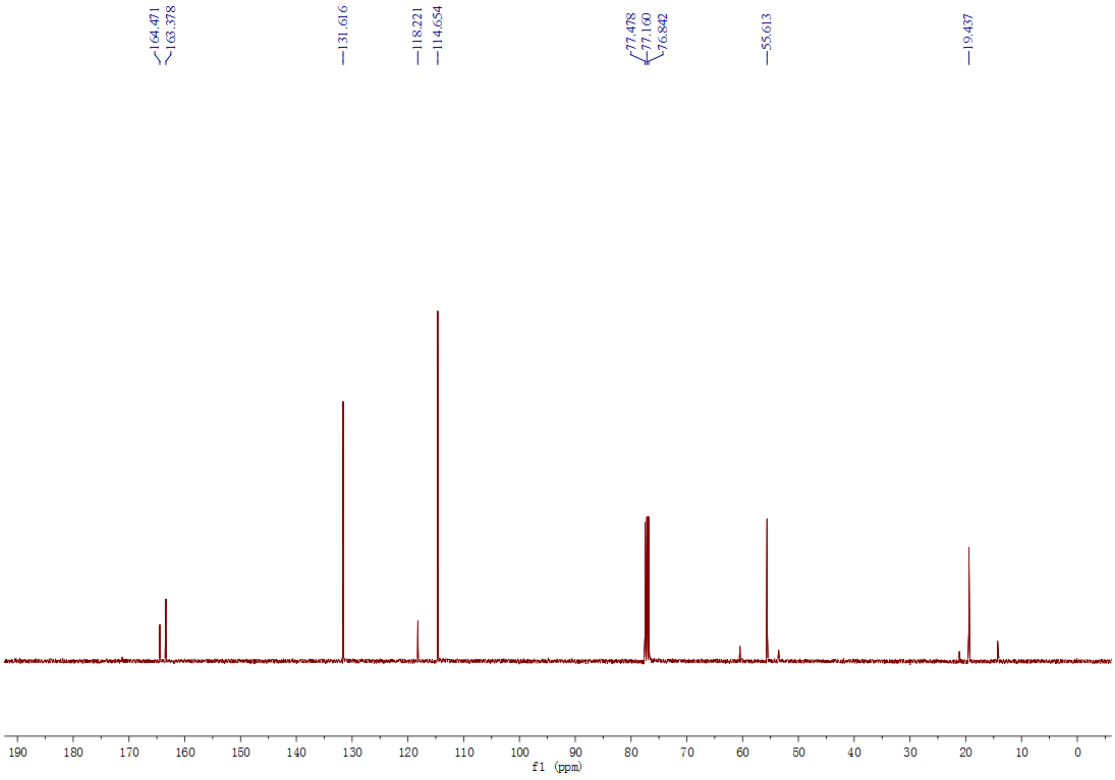
^{1}H NMR Spectrum for **2f** ($CDCl_3$, 400 MHz)



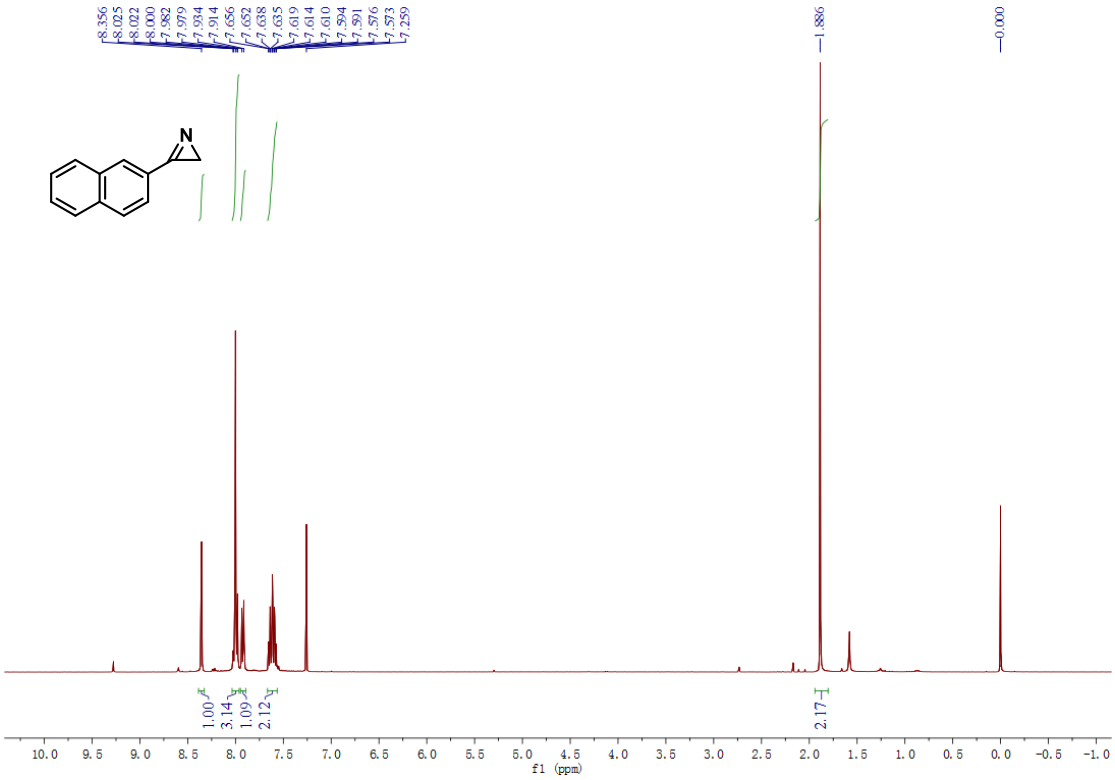
^{13}C NMR Spectrum for **2f** ($CDCl_3$, 100 MHz)



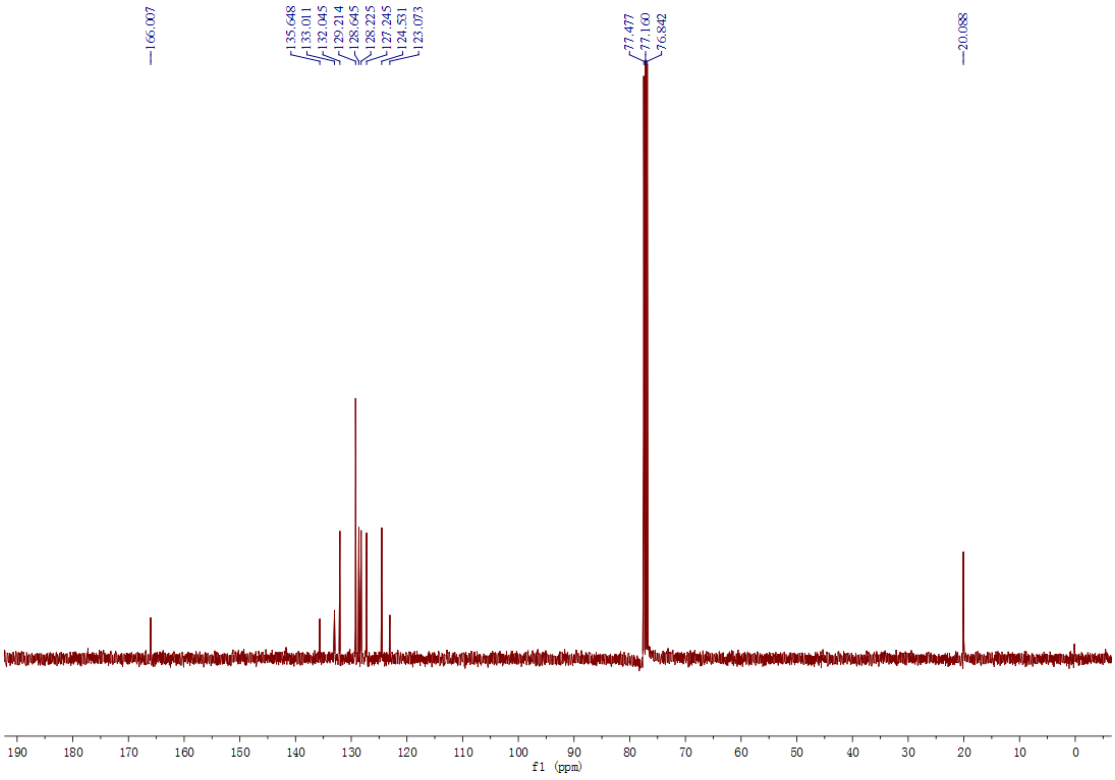
^{1}H NMR Spectrum for **2g** ($CDCl_3$, 400 MHz)



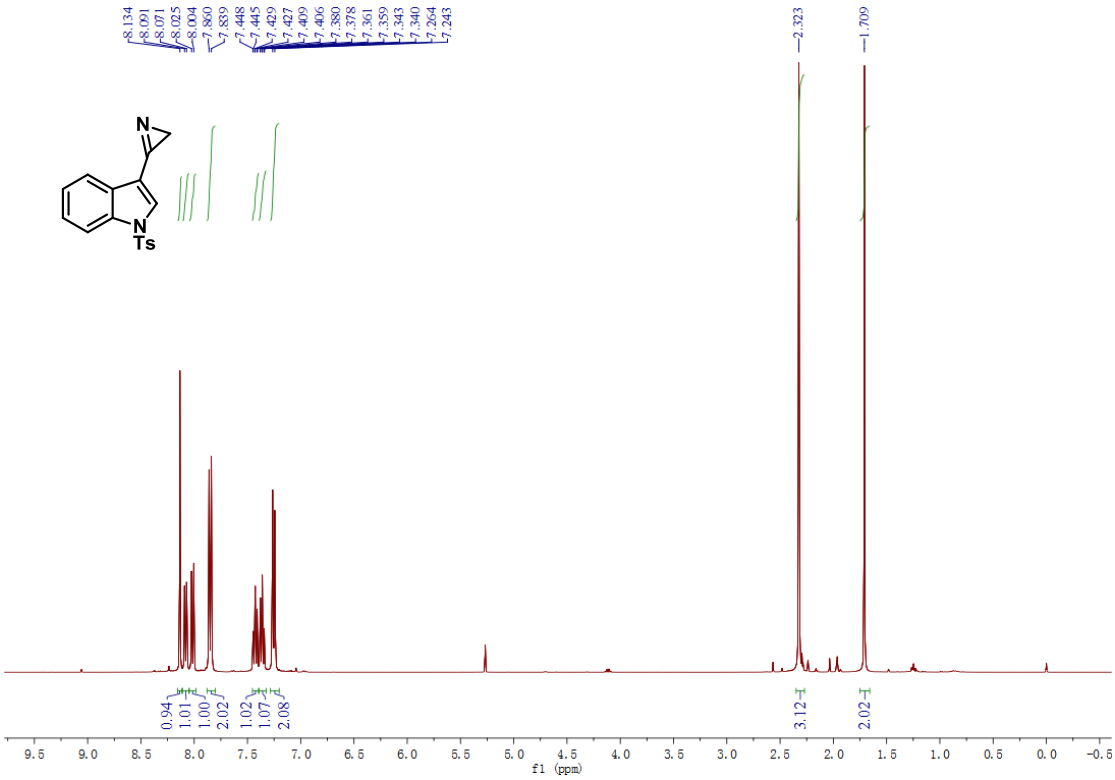
^{13}C NMR Spectrum for **2g** ($CDCl_3$, 100 MHz)



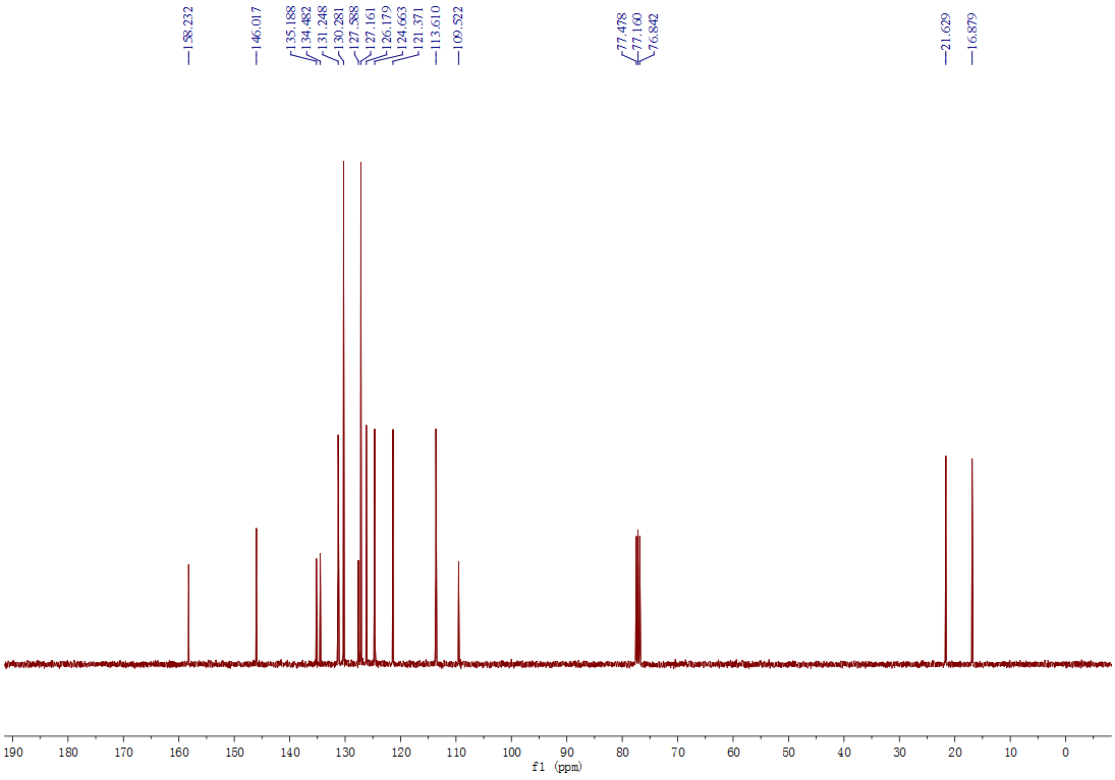
^{1}H NMR Spectrum for **2h** ($CDCl_3$, 400 MHz)



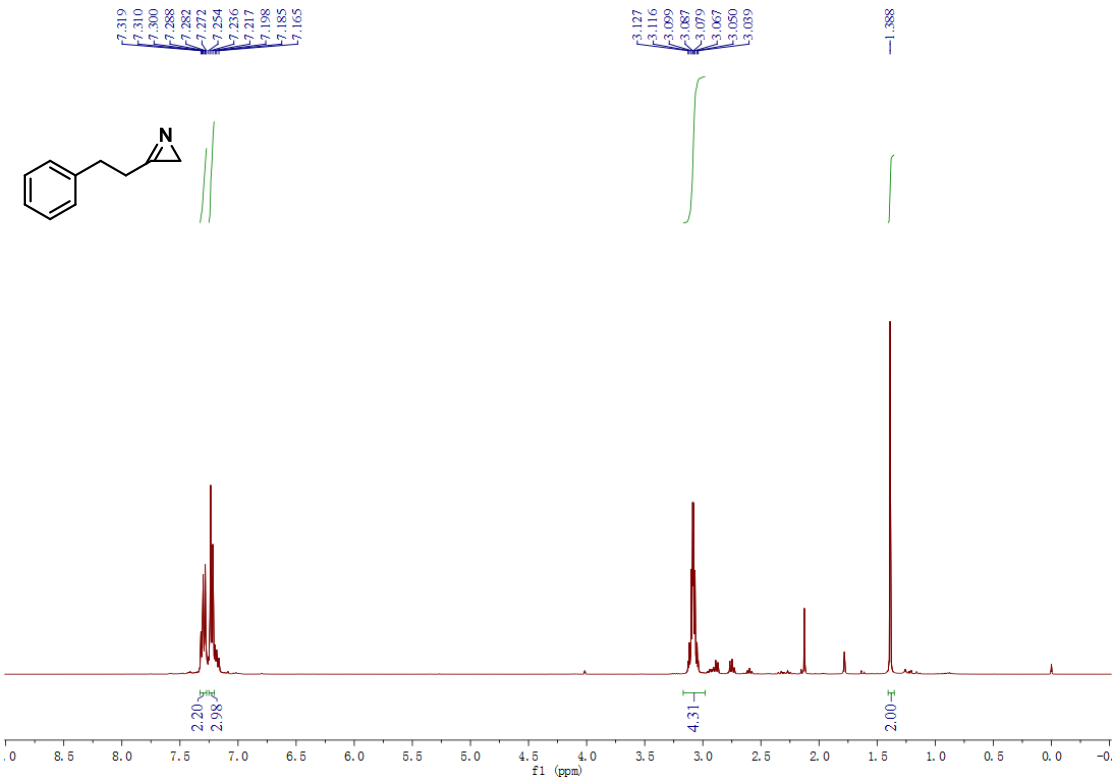
^{13}C NMR Spectrum for **2h** ($CDCl_3$, 100 MHz)



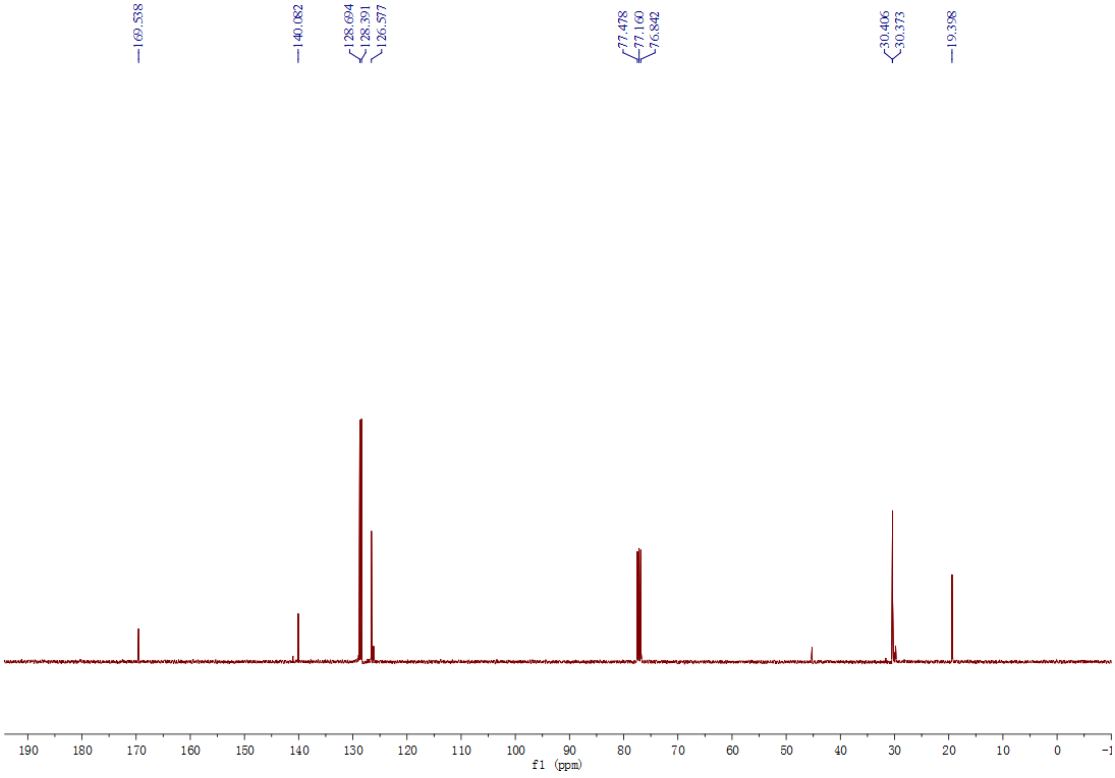
^{1}H NMR Spectrum for **2i** ($CDCl_3$, 400 MHz)



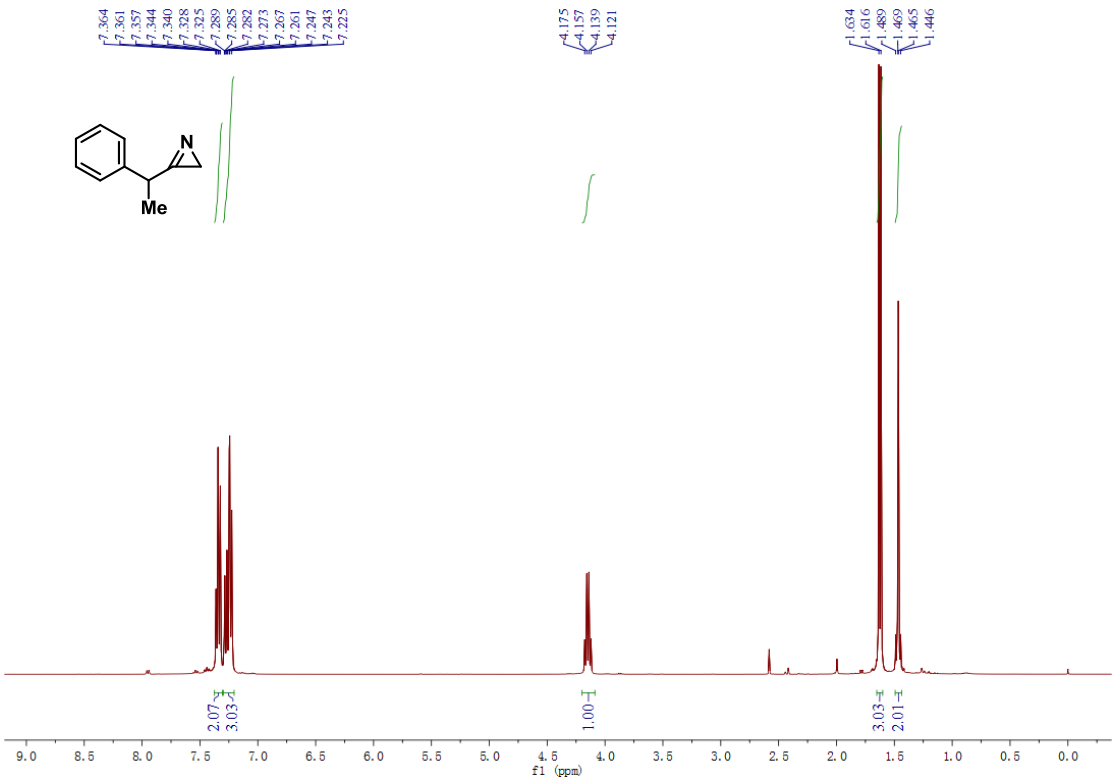
^{13}C NMR Spectrum for **2i** ($CDCl_3$, 100 MHz)



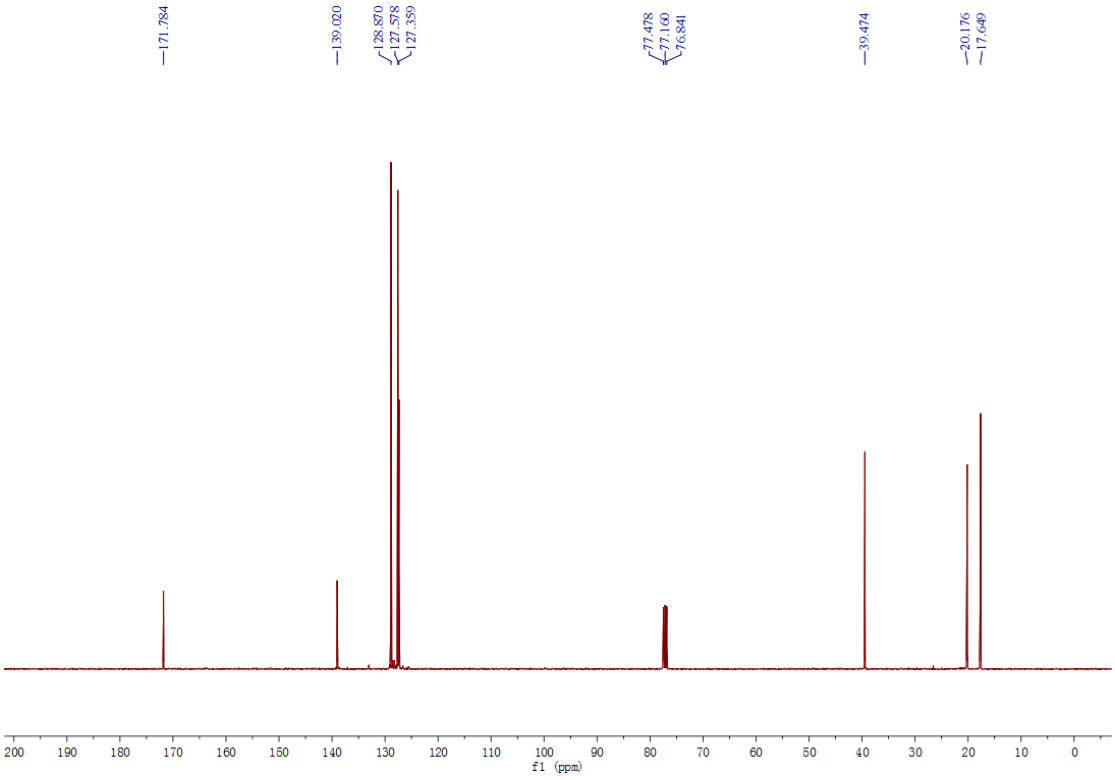
^{1}H NMR Spectrum for **2j** ($CDCl_3$, 400 MHz)



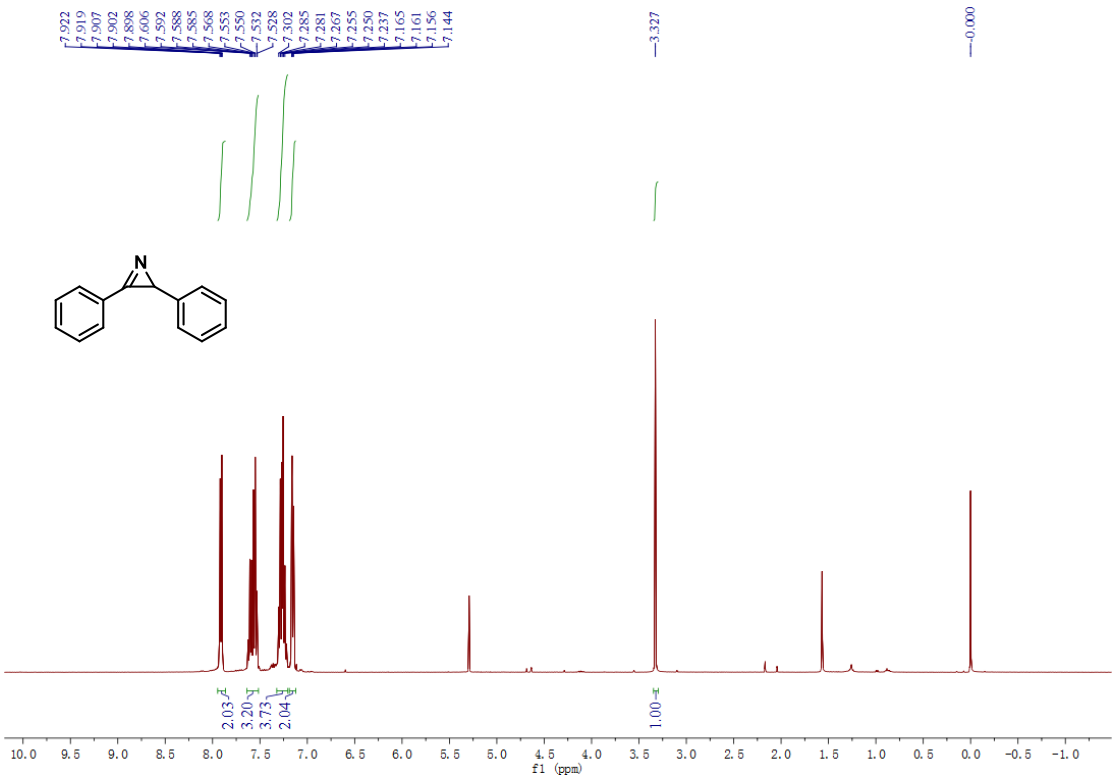
^{13}C NMR Spectrum for **2j** ($CDCl_3$, 100 MHz)



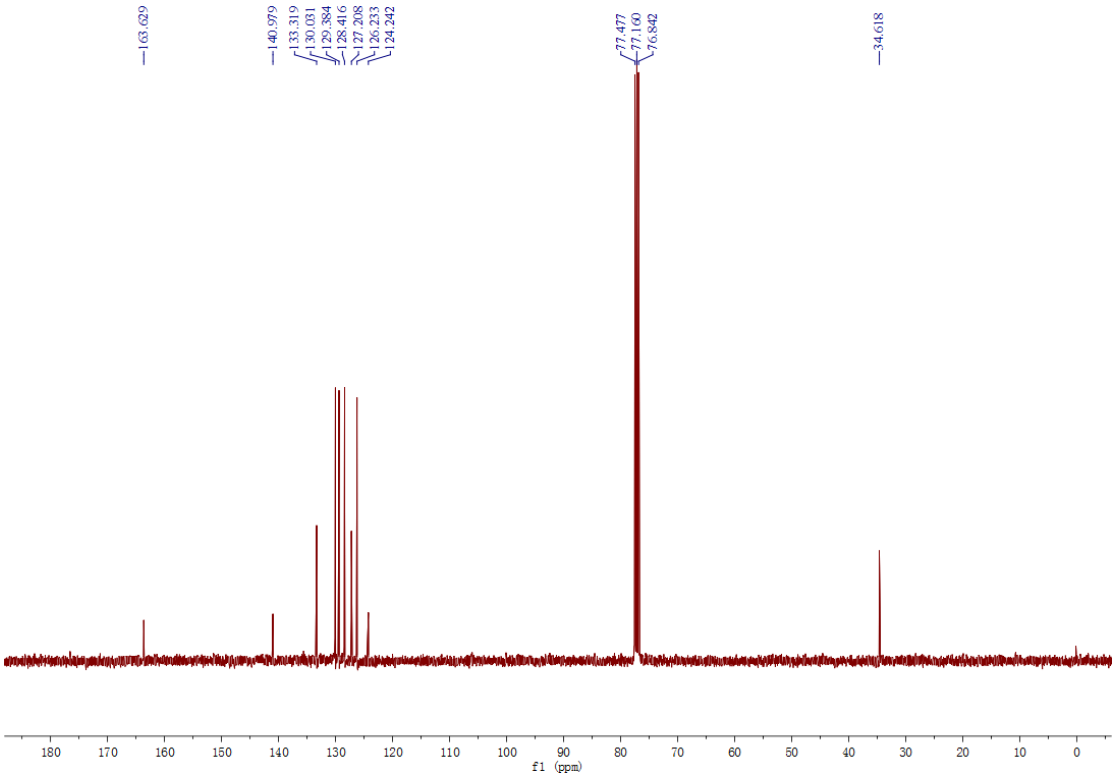
^{1}H NMR Spectrum for **2k** ($CDCl_3$, 400 MHz)



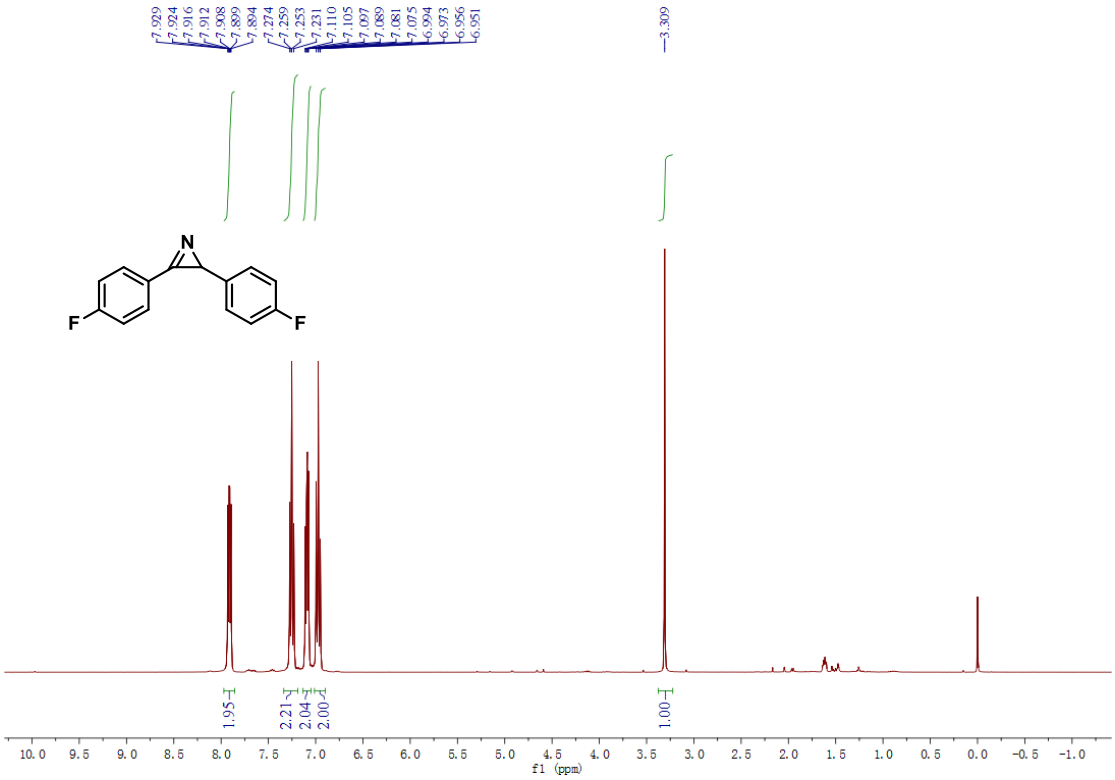
^{13}C NMR Spectrum for **2k** ($CDCl_3$, 100 MHz)



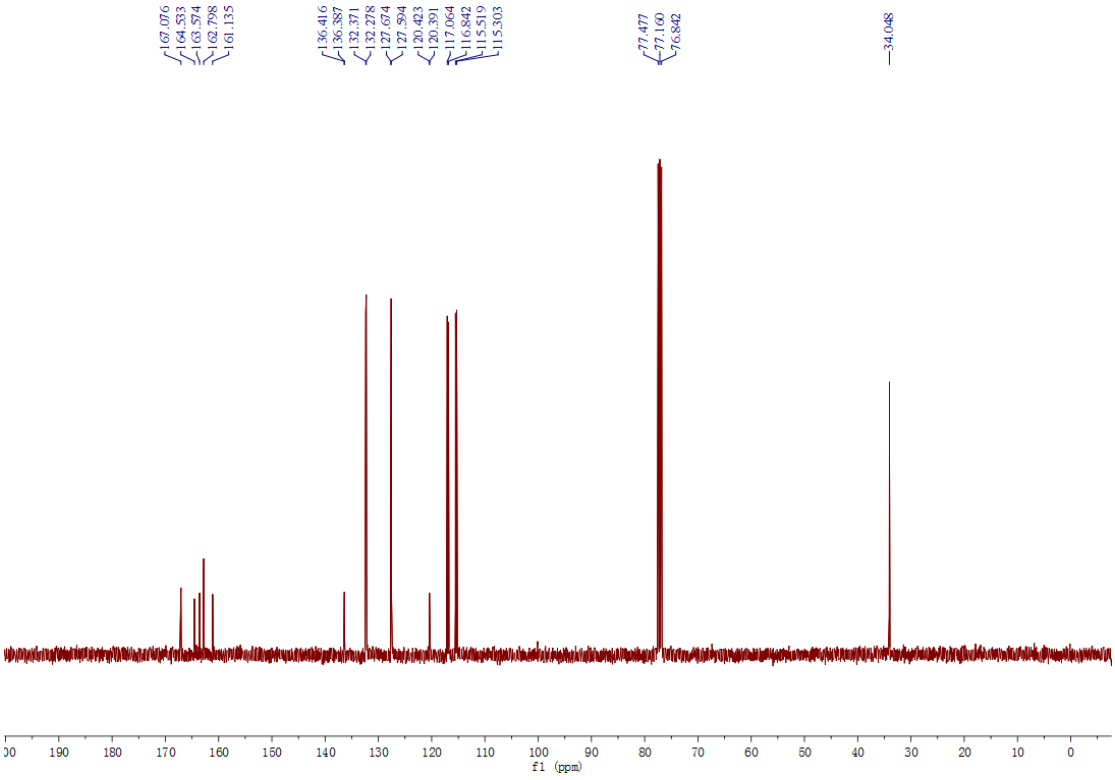
^{1}H NMR Spectrum for **4a** ($CDCl_3$, 400 MHz)



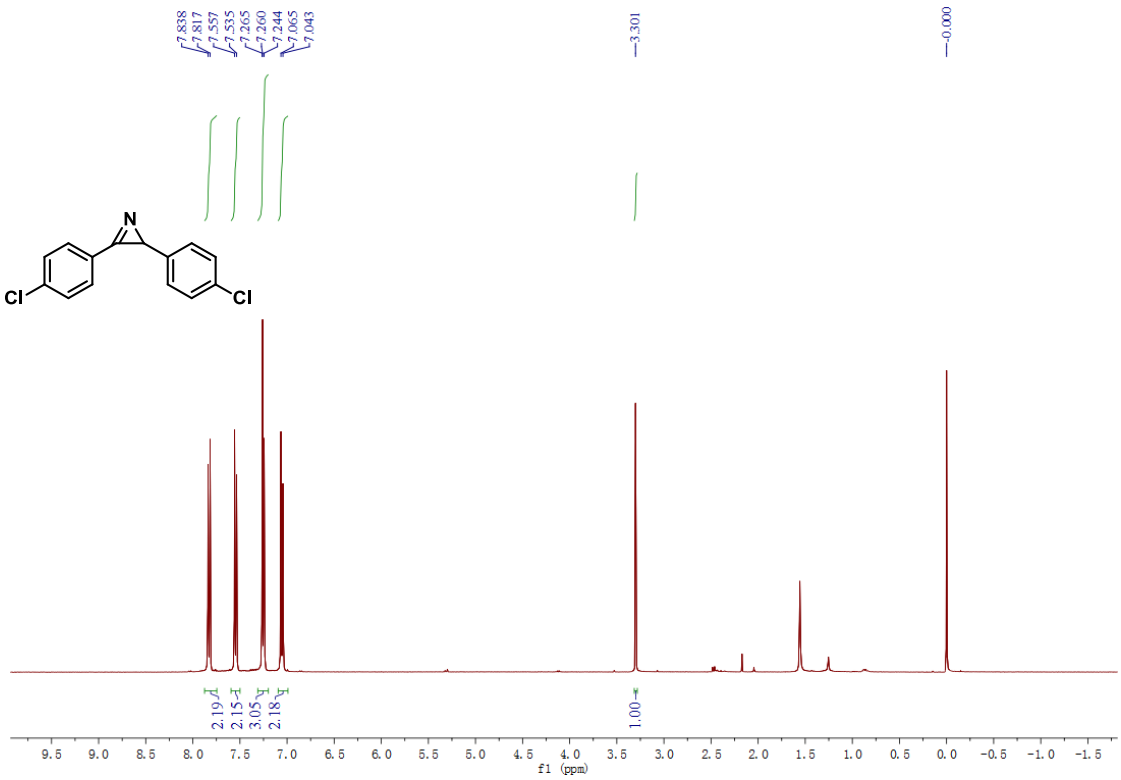
^{13}C NMR Spectrum for **4a** ($CDCl_3$, 100 MHz)



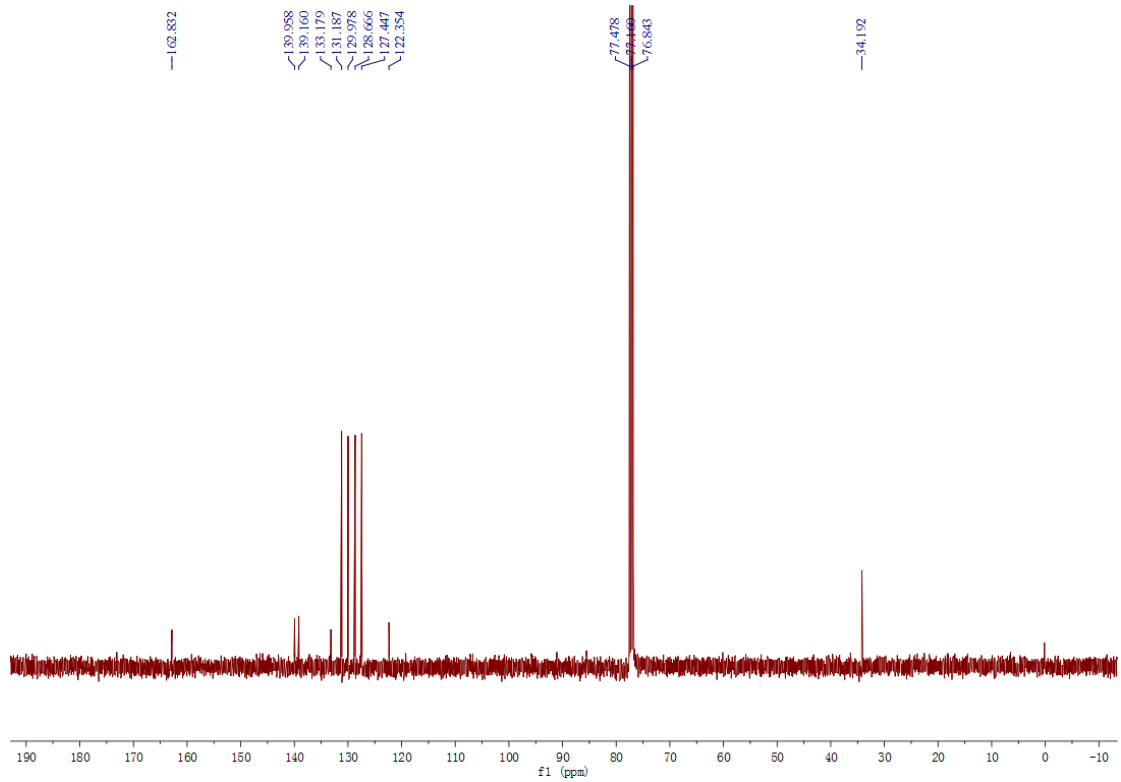
^{1}H NMR Spectrum for **4b** ($CDCl_3$, 400 MHz)



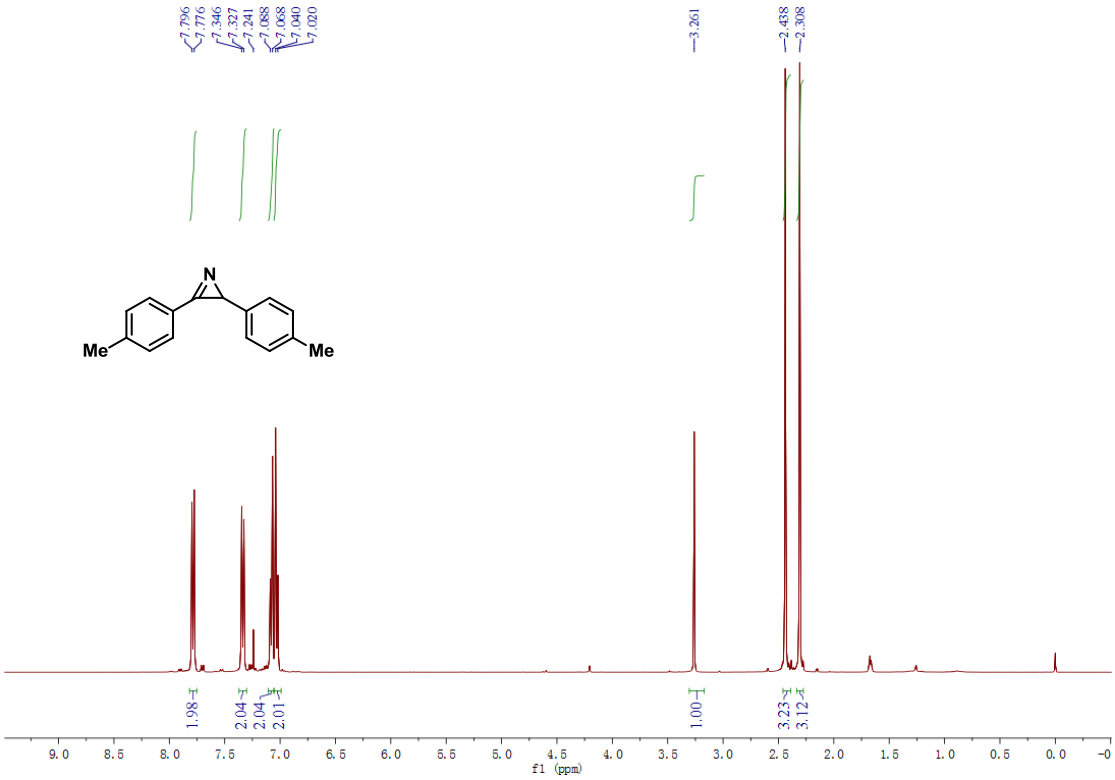
^{13}C NMR Spectrum for **4b** ($CDCl_3$, 100 MHz)



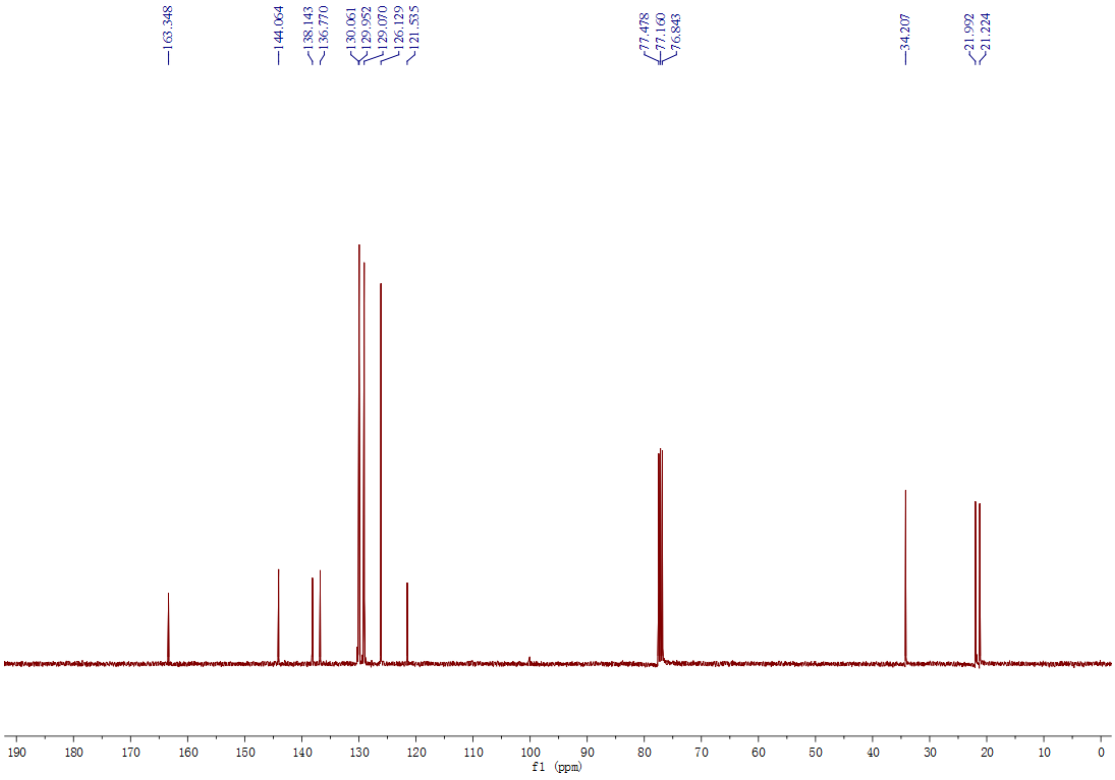
^{1}H NMR Spectrum for **4c** ($CDCl_3$, 400 MHz)



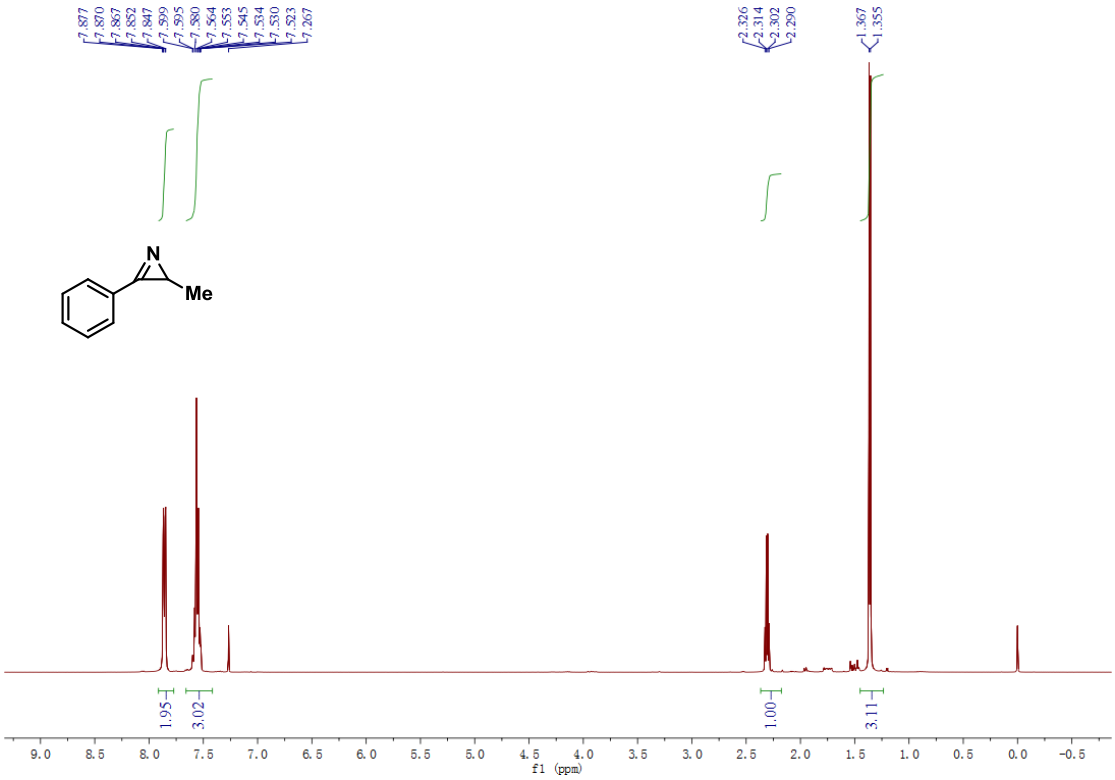
^{13}C NMR Spectrum for **4c** ($CDCl_3$, 100 MHz)



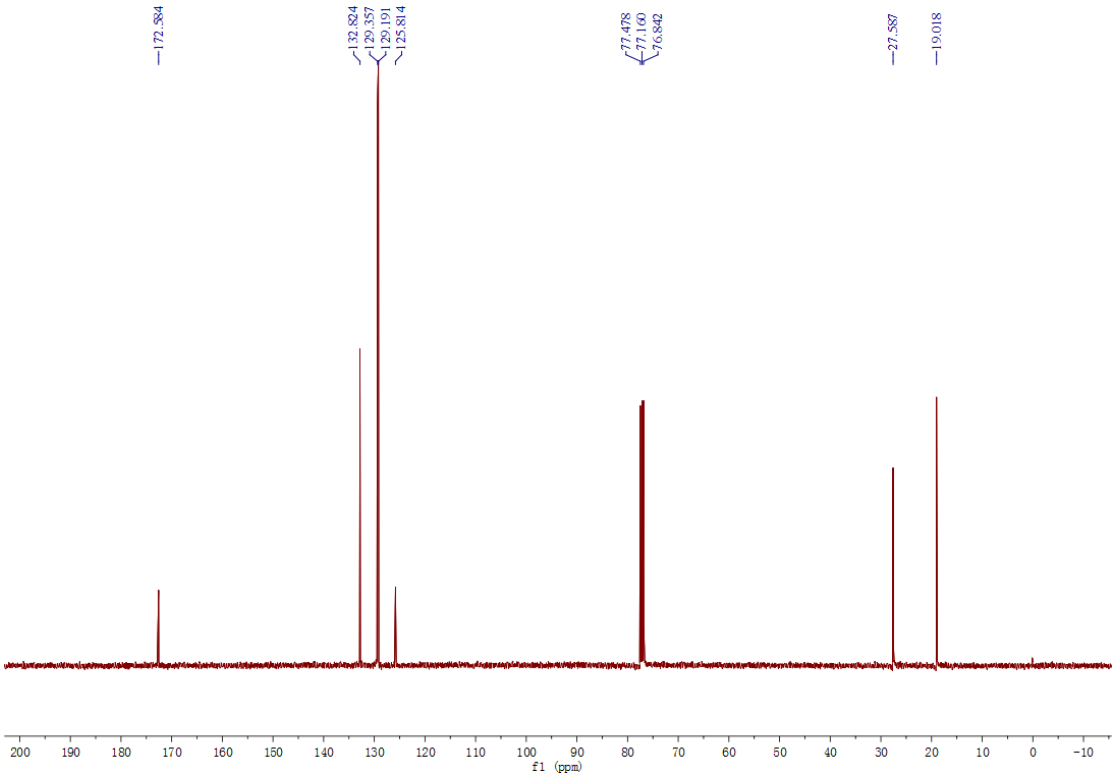
^{1}H NMR Spectrum for **4d** ($CDCl_3$, 400 MHz)



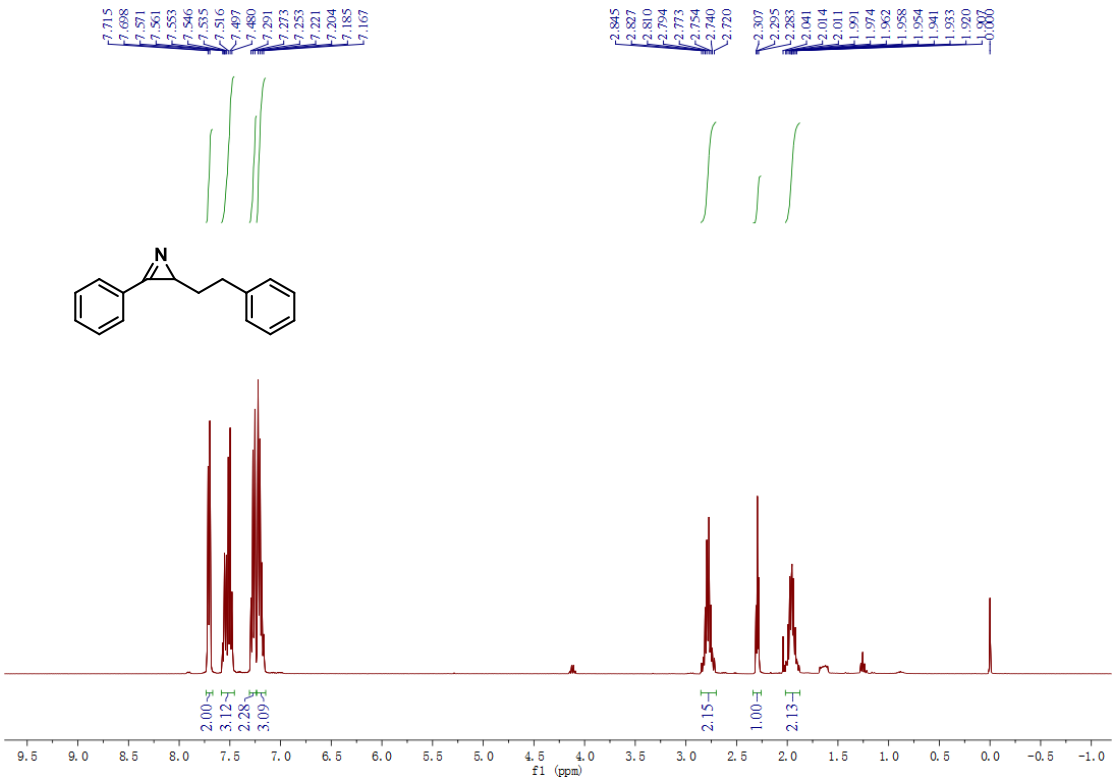
^{13}C NMR Spectrum for **4d** ($CDCl_3$, 100 MHz)



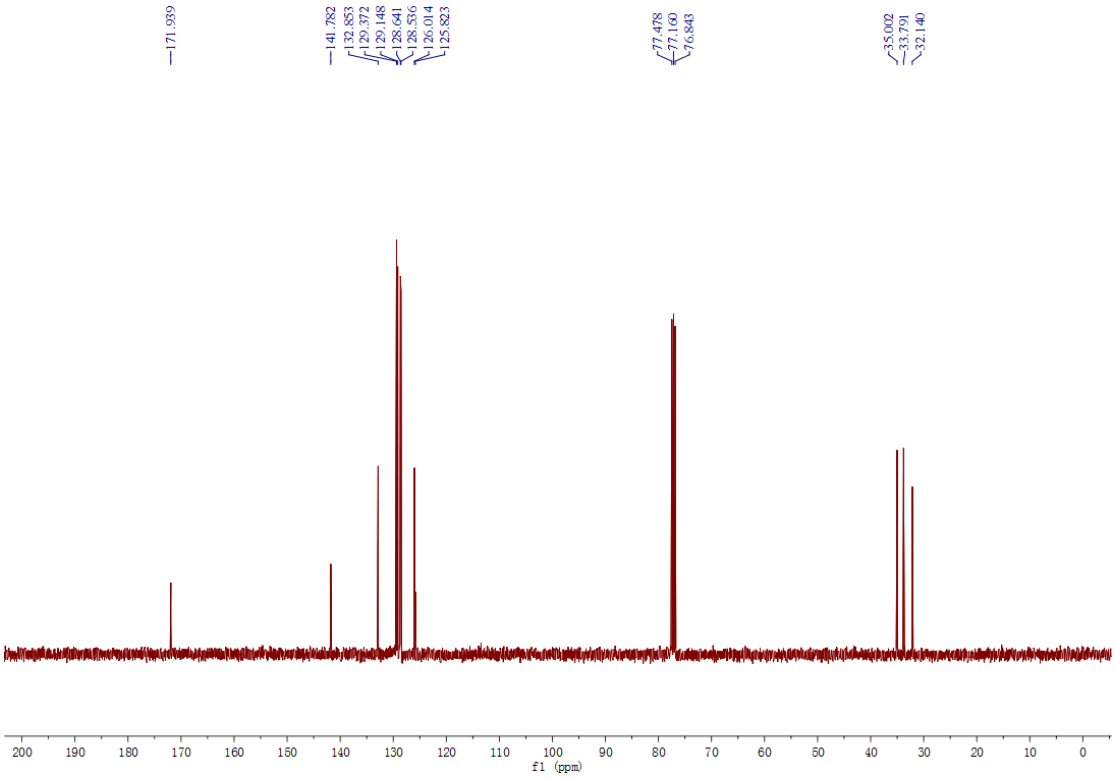
^{1}H NMR Spectrum for **4e** ($CDCl_3$, 400 MHz)



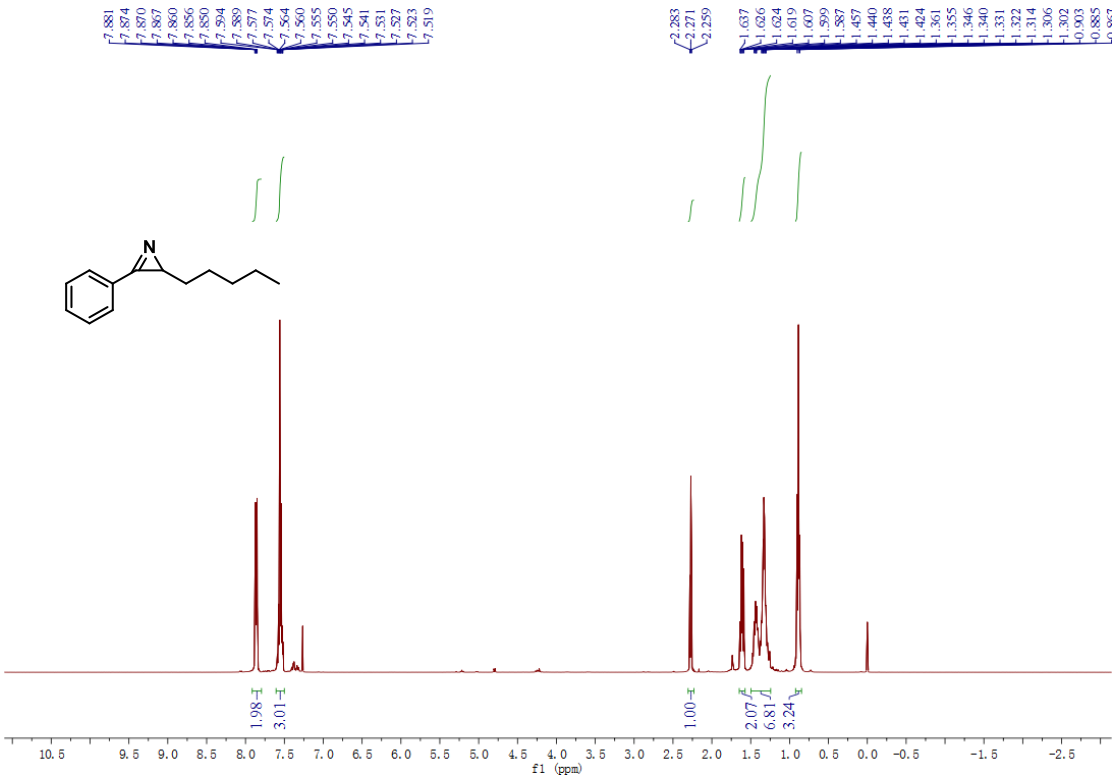
^{13}C NMR Spectrum for **4e** ($CDCl_3$, 100 MHz)



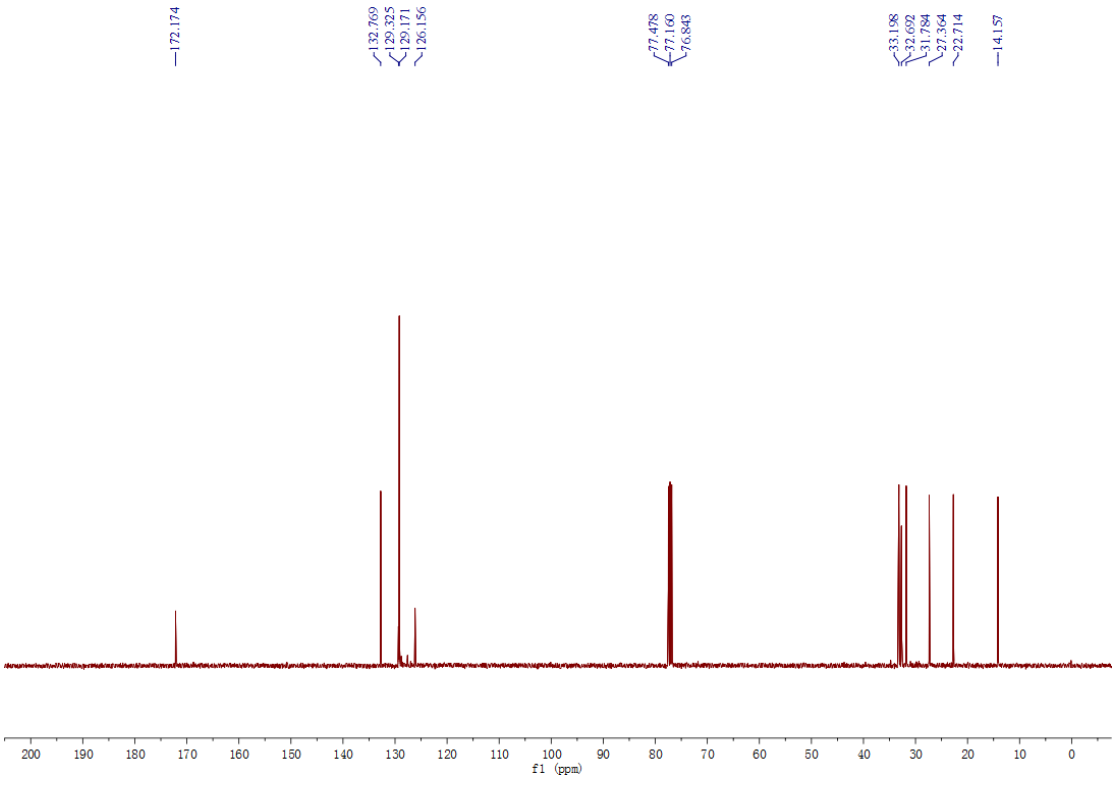
^{1}H NMR Spectrum for **4f** ($CDCl_3$, 400 MHz)



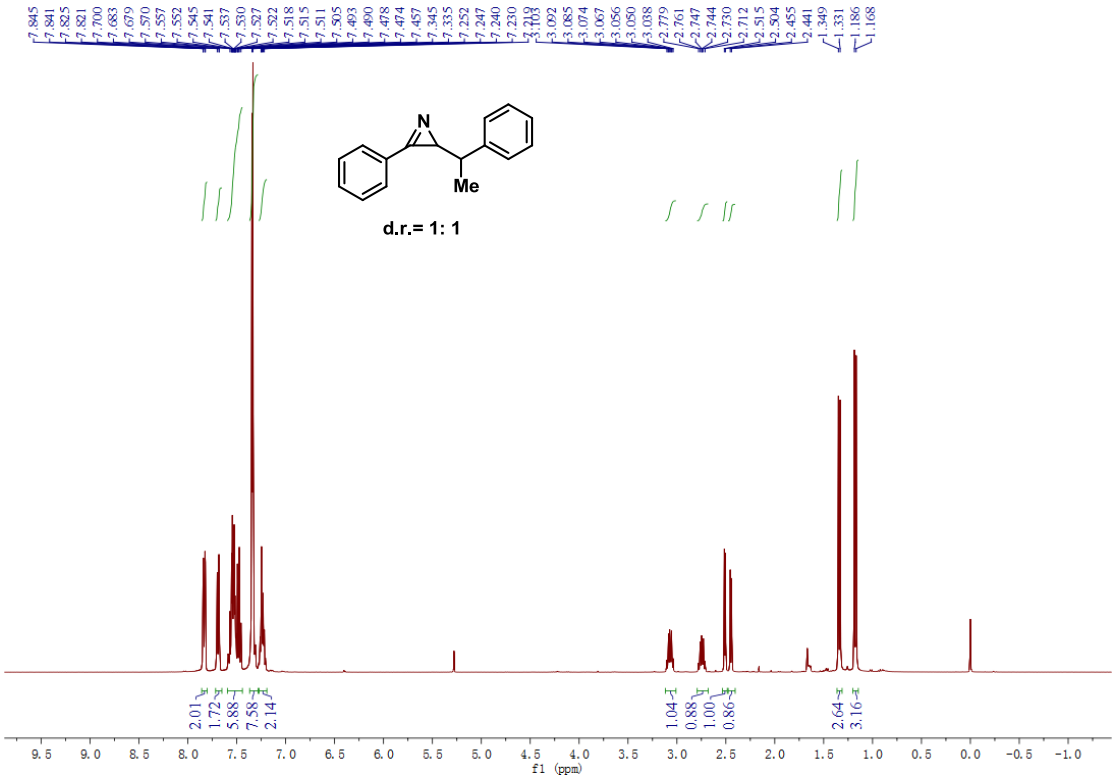
^{13}C NMR Spectrum for **4f** ($CDCl_3$, 100 MHz)



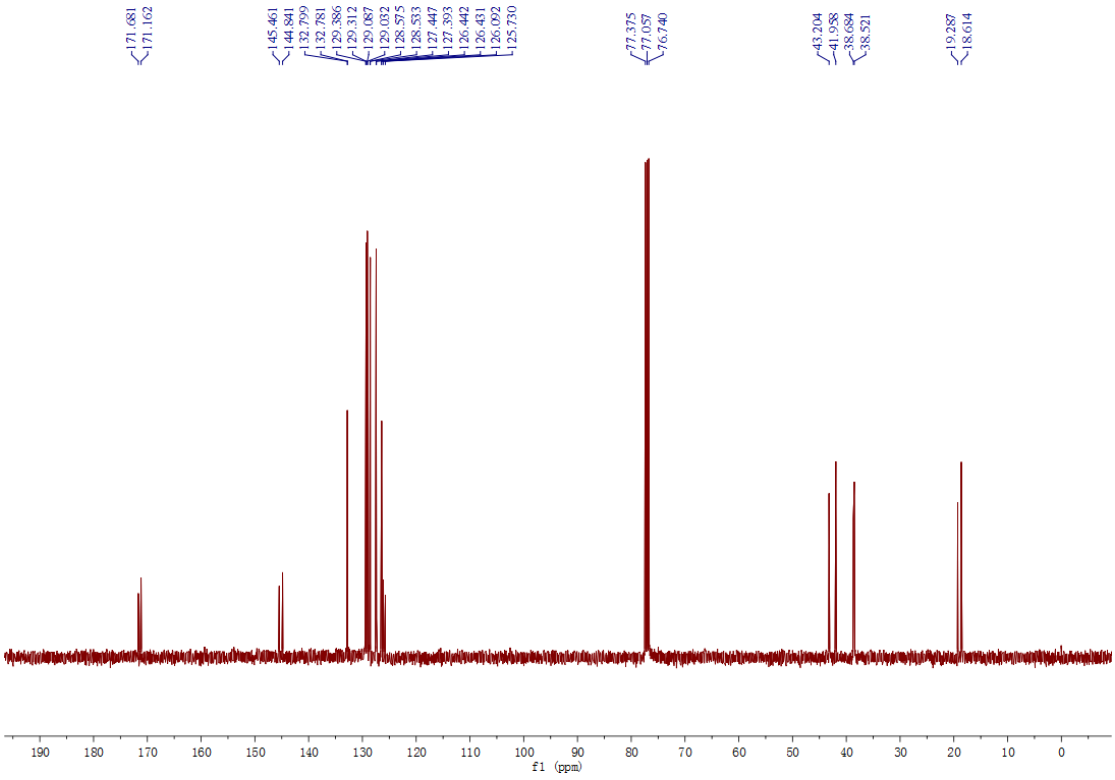
^{1}H NMR Spectrum for **4g** ($CDCl_3$, 400 MHz)



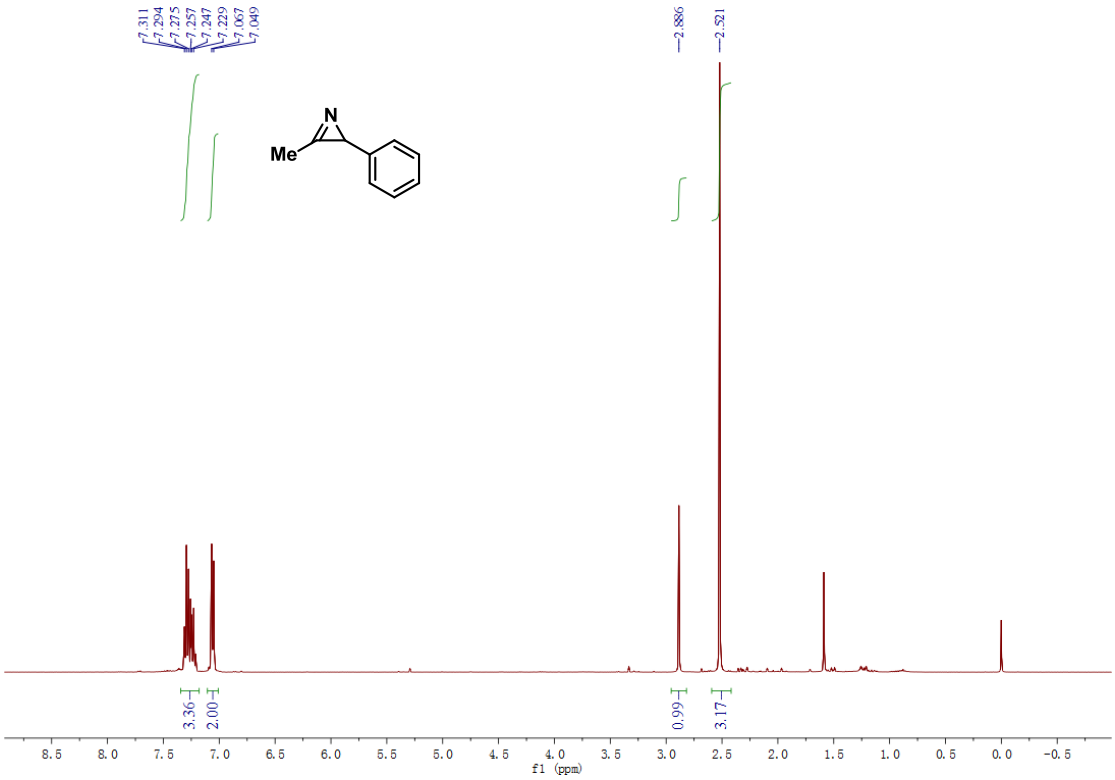
^{13}C NMR Spectrum for **4g** ($CDCl_3$, 100 MHz)



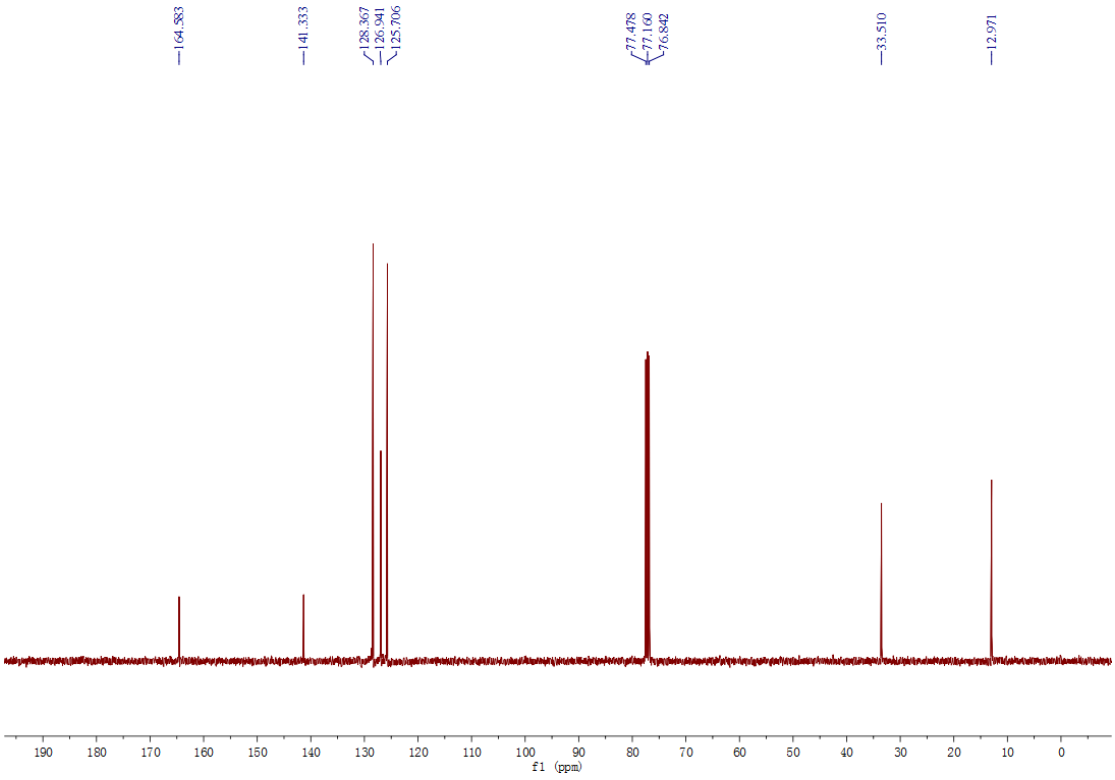
^{1}H NMR Spectrum for **4h** ($CDCl_3$, 400 MHz)



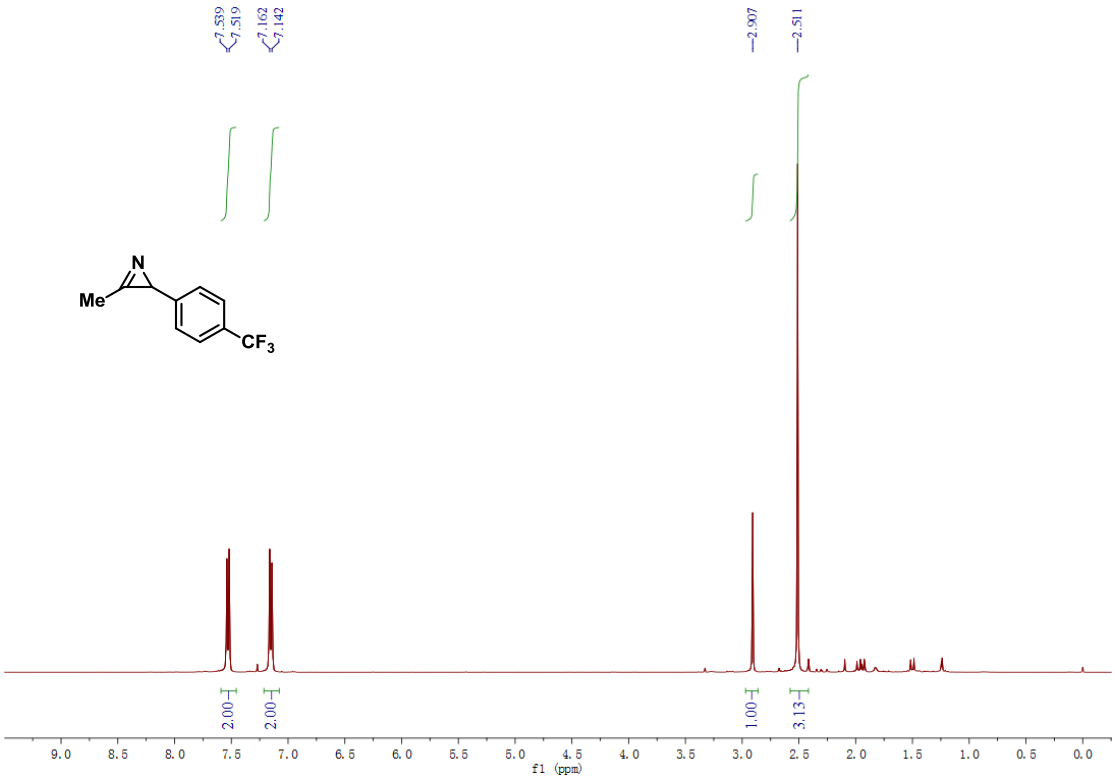
^{13}C NMR Spectrum for **4h** ($CDCl_3$, 100 MHz)



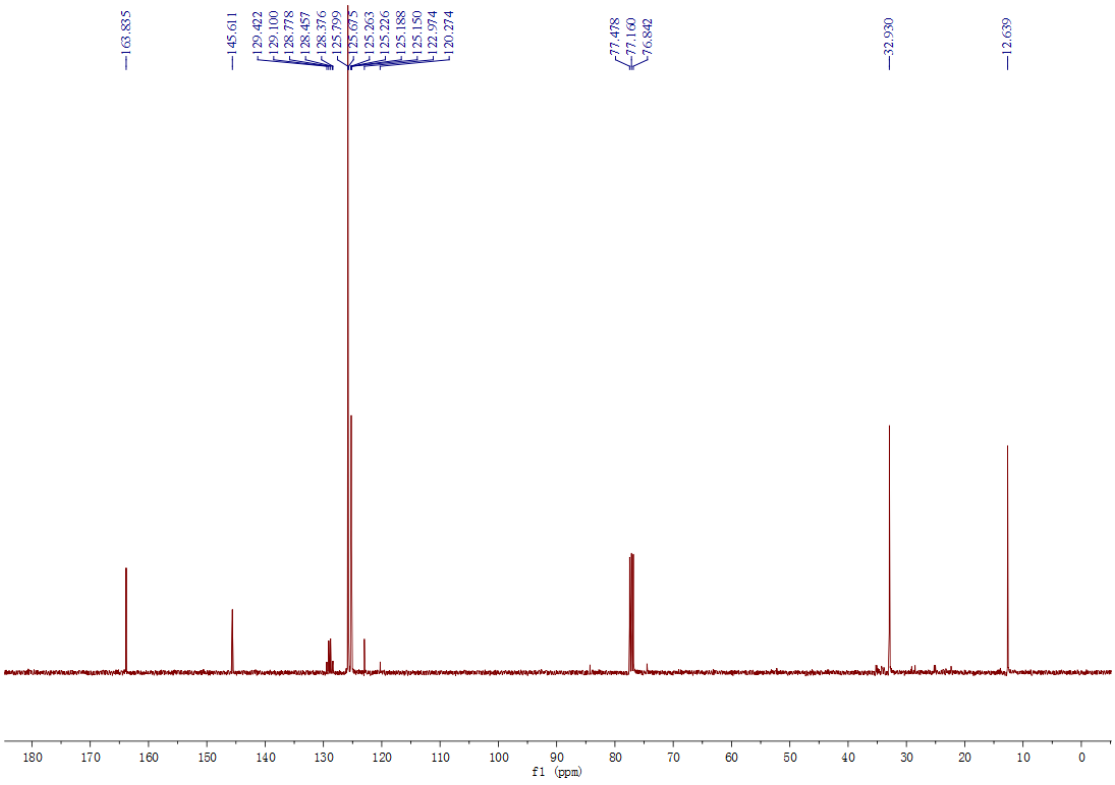
^{1}H NMR Spectrum for **7a** ($CDCl_3$, 400 MHz)



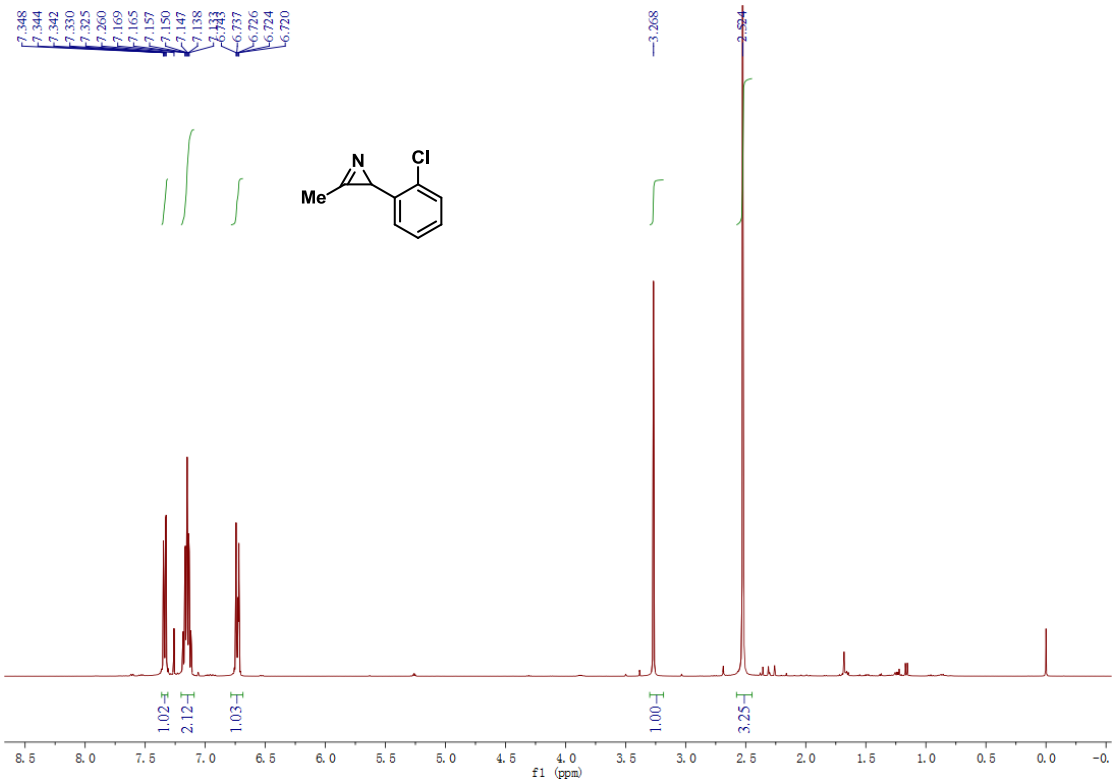
^{13}C NMR Spectrum for **7a** ($CDCl_3$, 100 MHz)



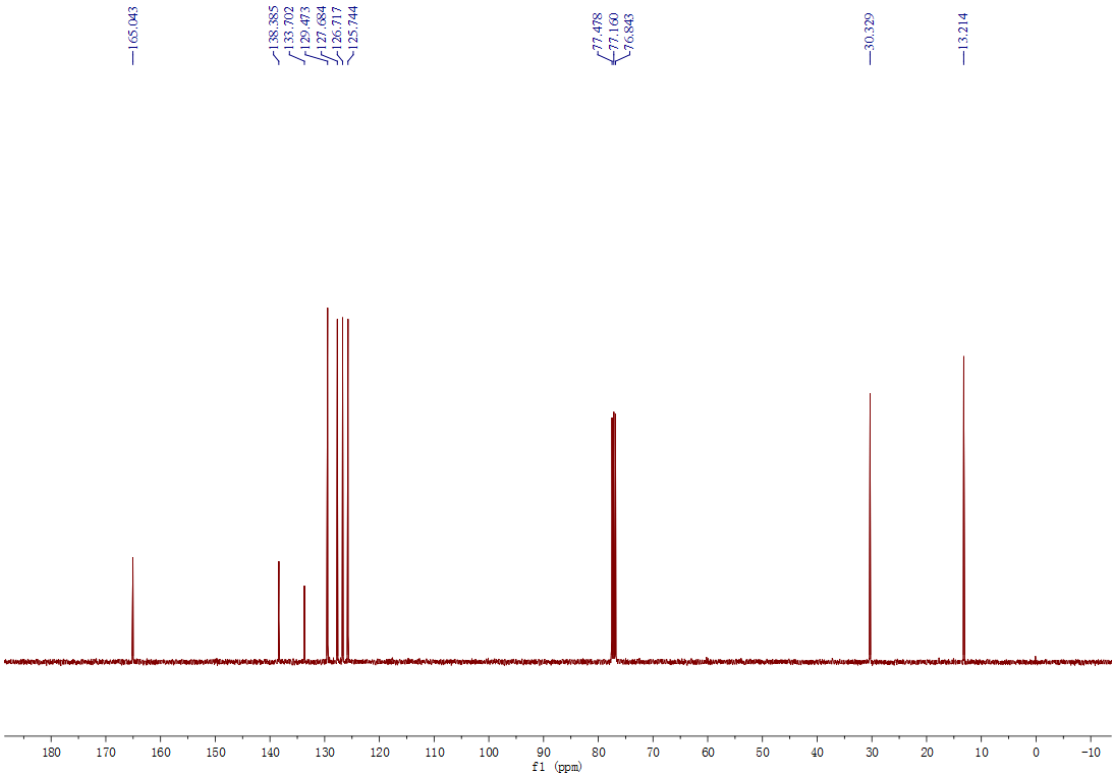
^{1}H NMR Spectrum for **7b** ($CDCl_3$, 400 MHz)



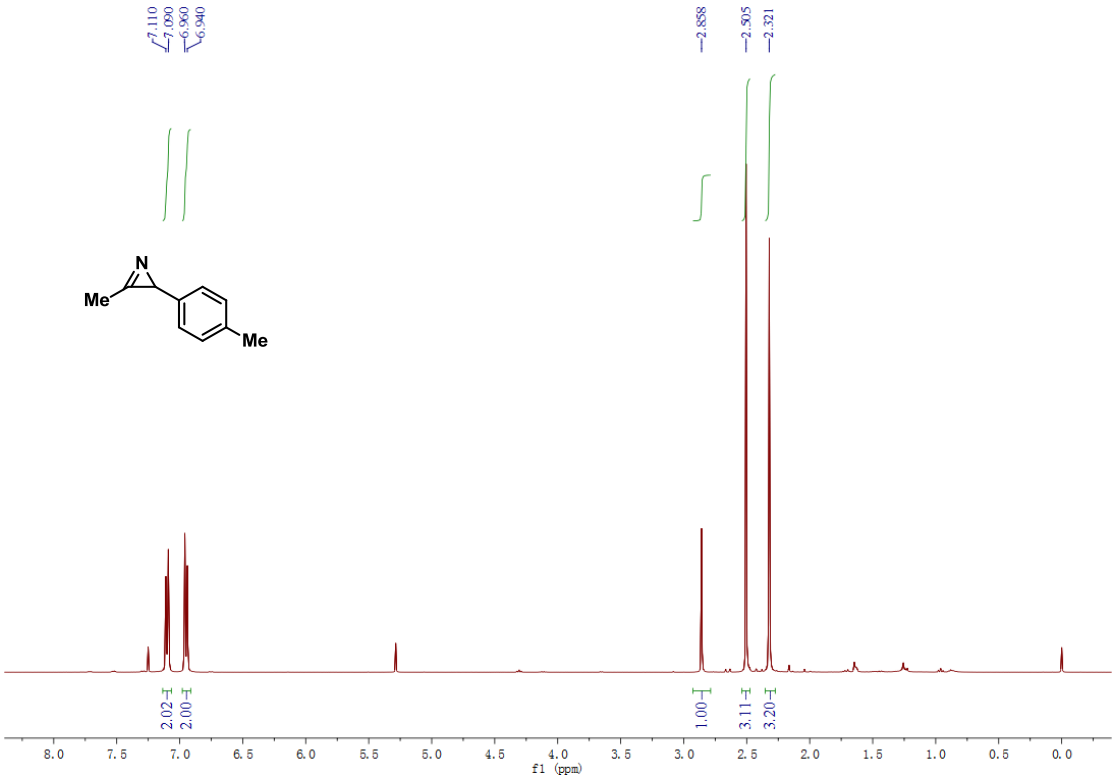
^{13}C NMR Spectrum for **7b** ($CDCl_3$, 100 MHz)



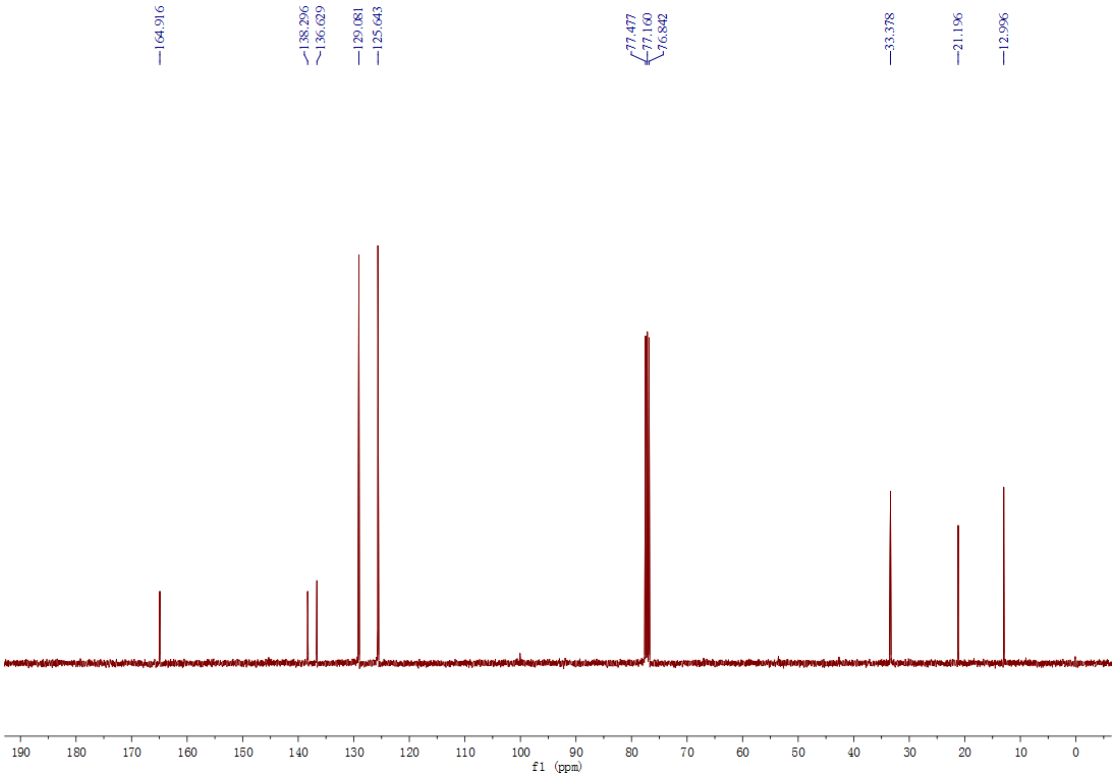
^{1}H NMR Spectrum for **7c** ($CDCl_3$, 400 MHz)



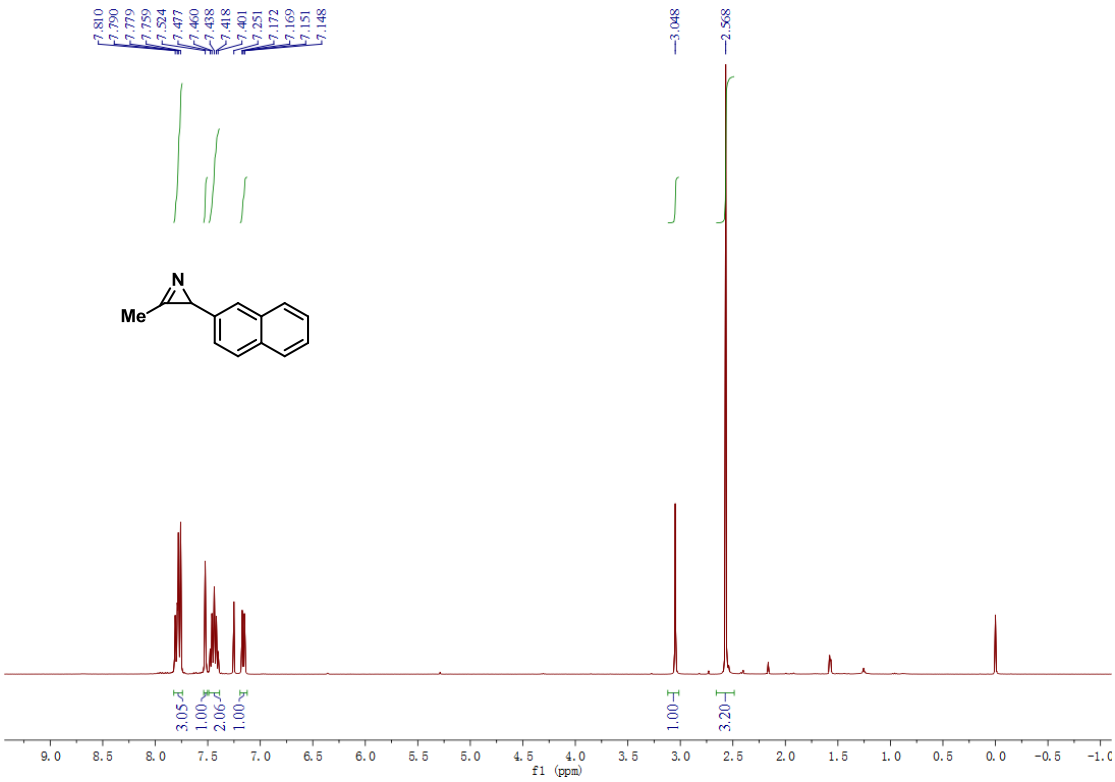
^{13}C NMR Spectrum for **7c** ($CDCl_3$, 100 MHz)



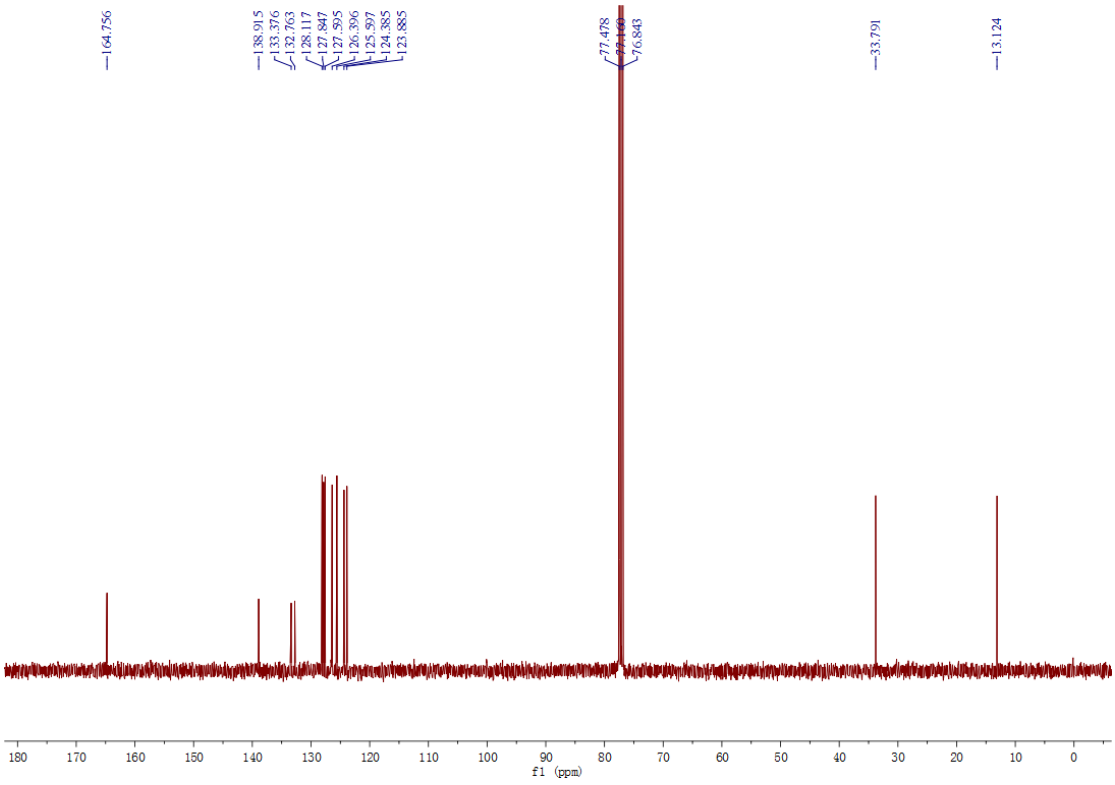
^{1}H NMR Spectrum for **7d** ($CDCl_3$, 400 MHz)



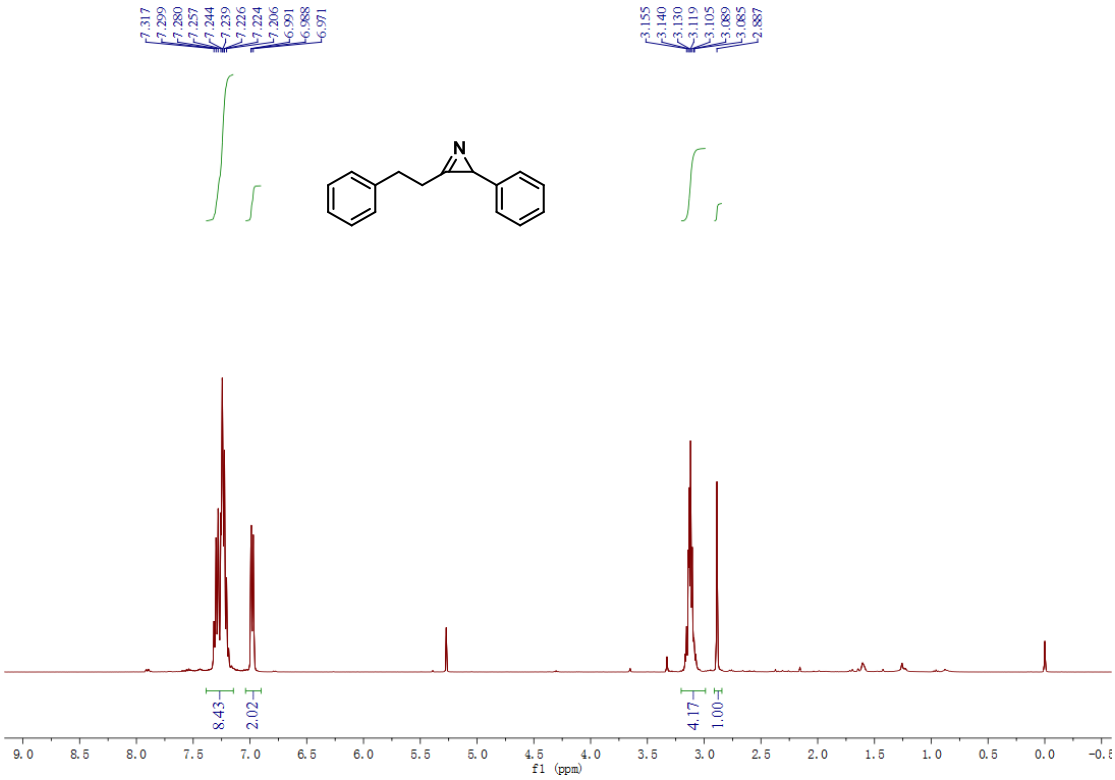
^{13}C NMR Spectrum for **7d** ($CDCl_3$, 100 MHz)



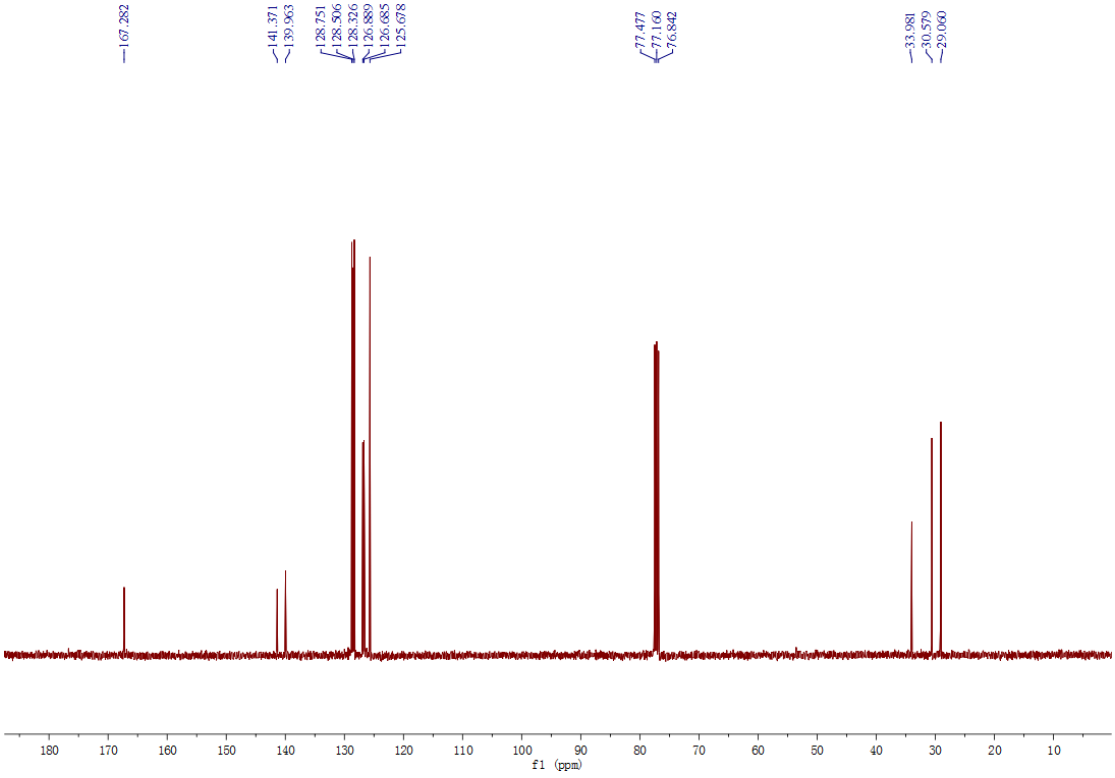
^{1}H NMR Spectrum for **7e** ($CDCl_3$, 400 MHz)



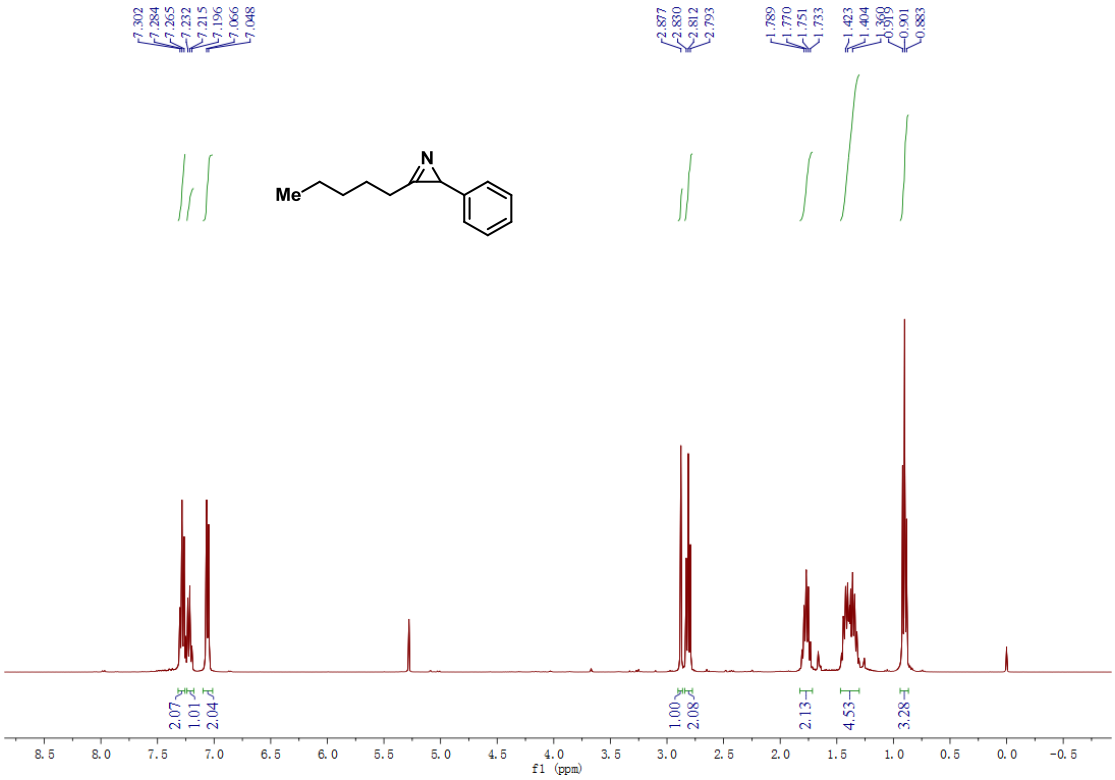
^{13}C NMR Spectrum for **7e** ($CDCl_3$, 100 MHz)



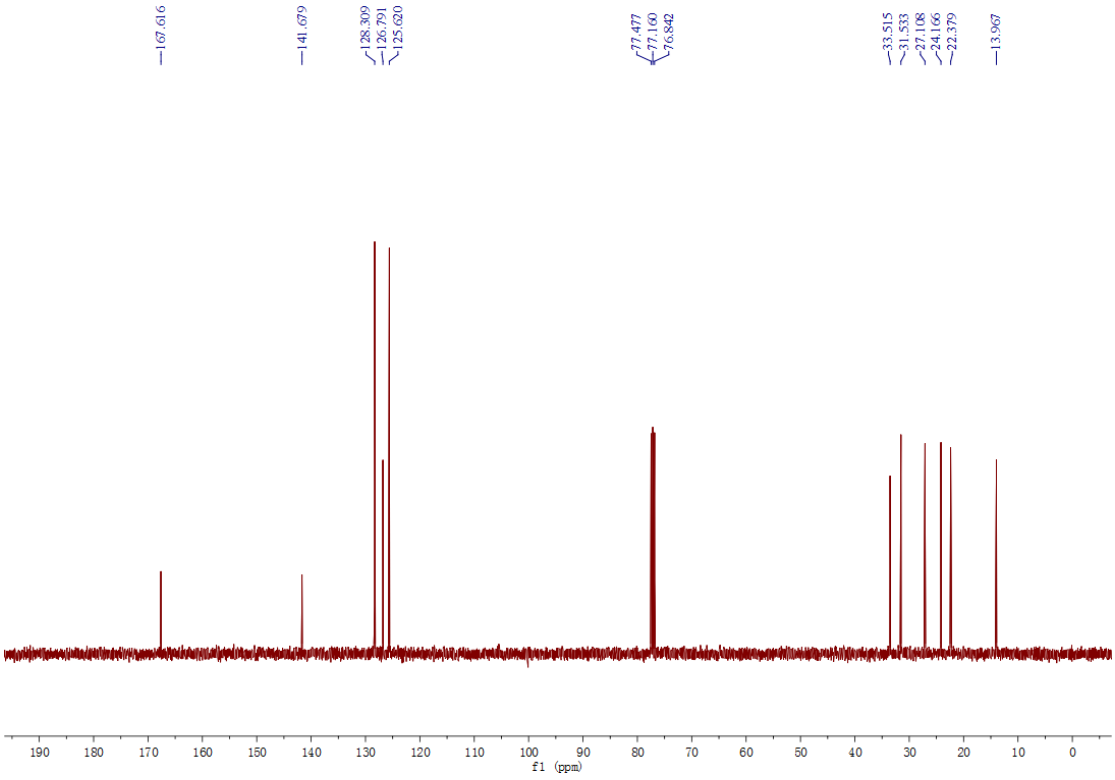
^{1}H NMR Spectrum for **7f** ($CDCl_3$, 400 MHz)



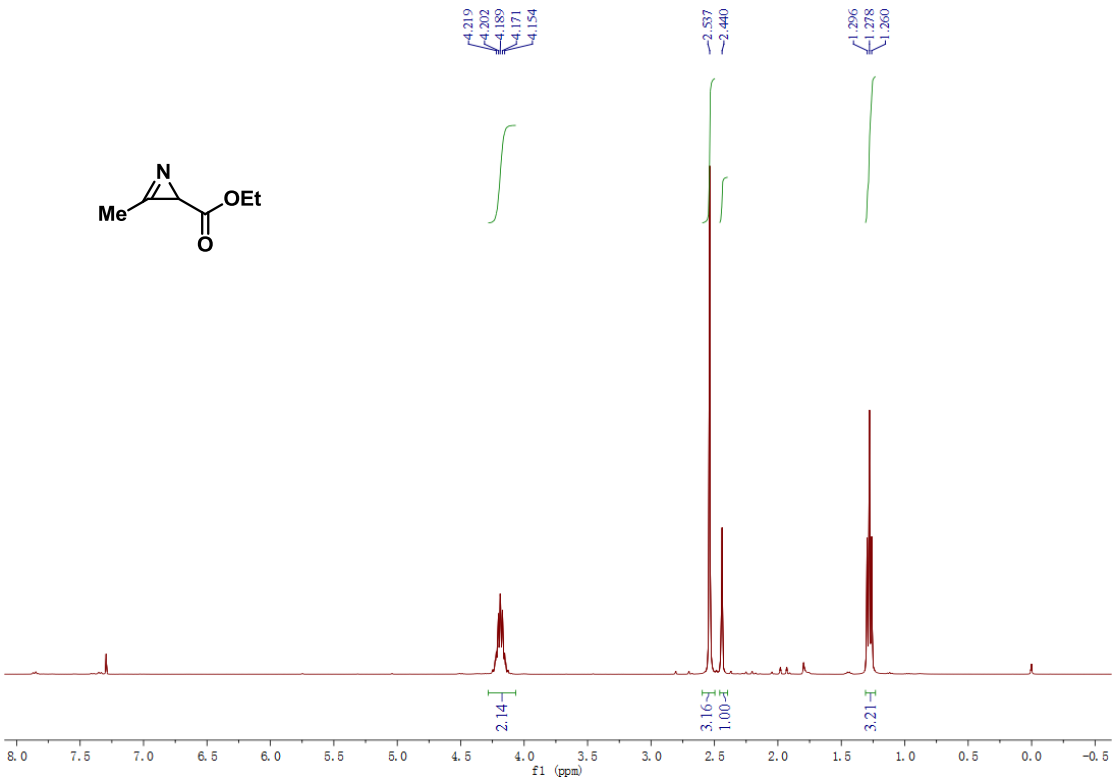
^{13}C NMR Spectrum for **7f** ($CDCl_3$, 100 MHz)



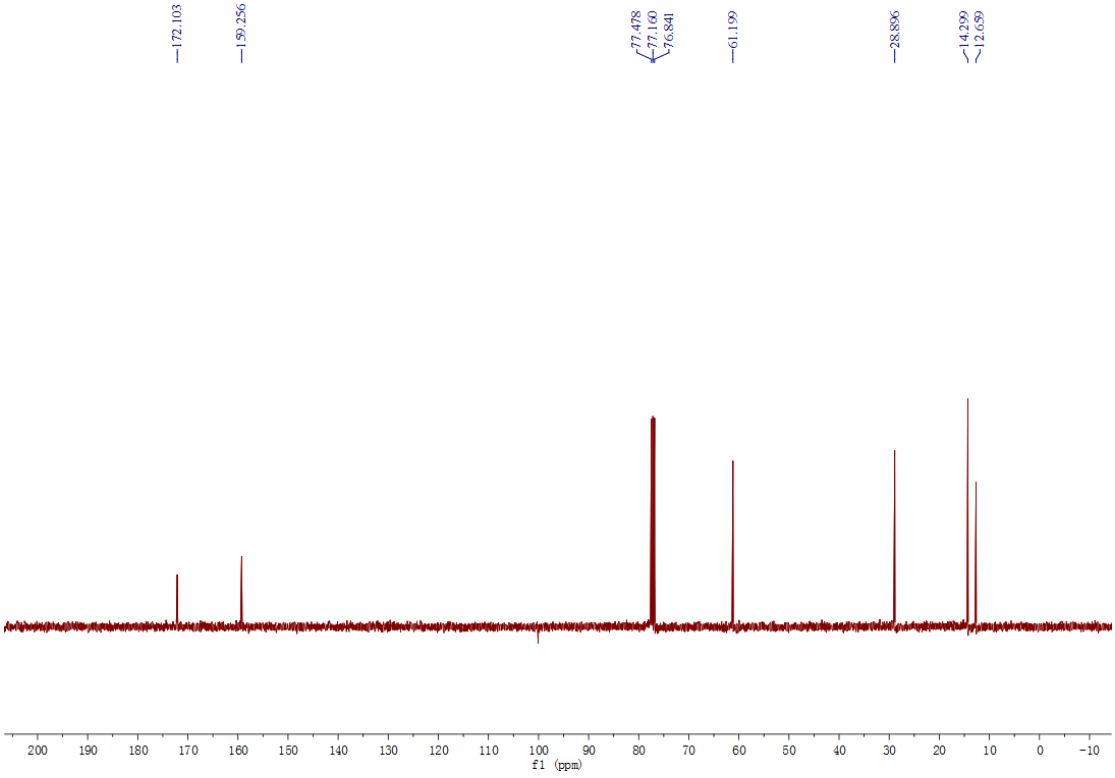
^{1}H NMR Spectrum for **7g** ($CDCl_3$, 400 MHz)



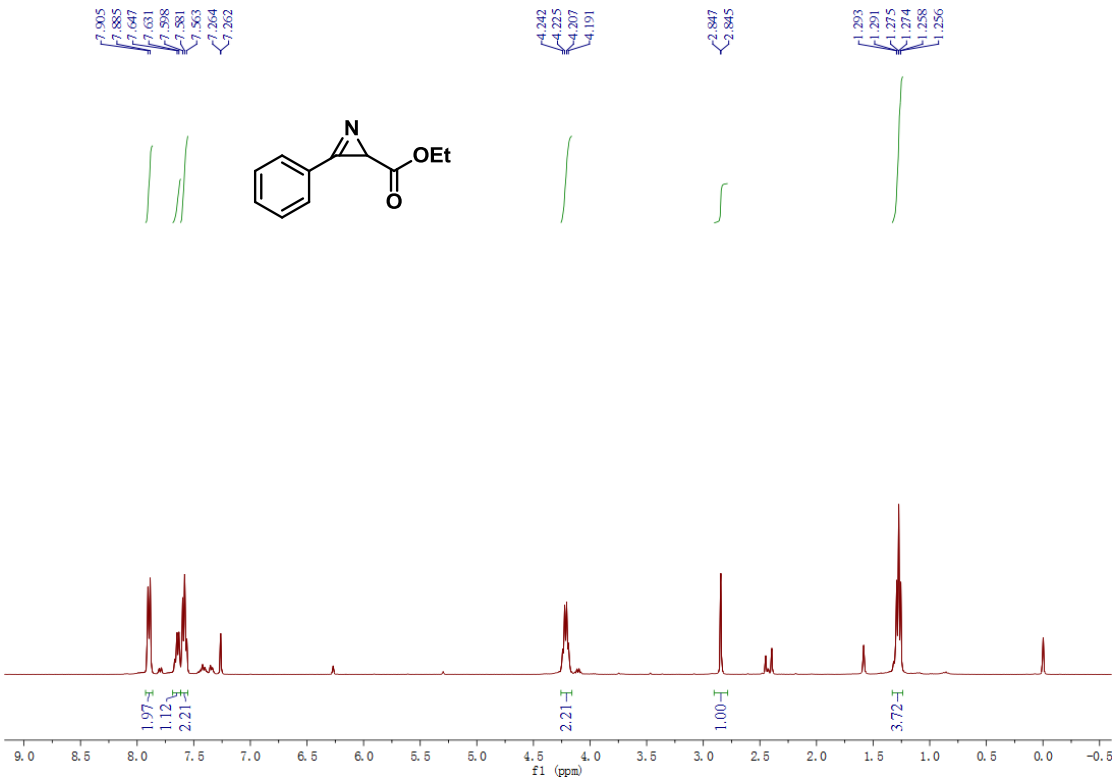
^{13}C NMR Spectrum for **7g** ($CDCl_3$, 100 MHz)



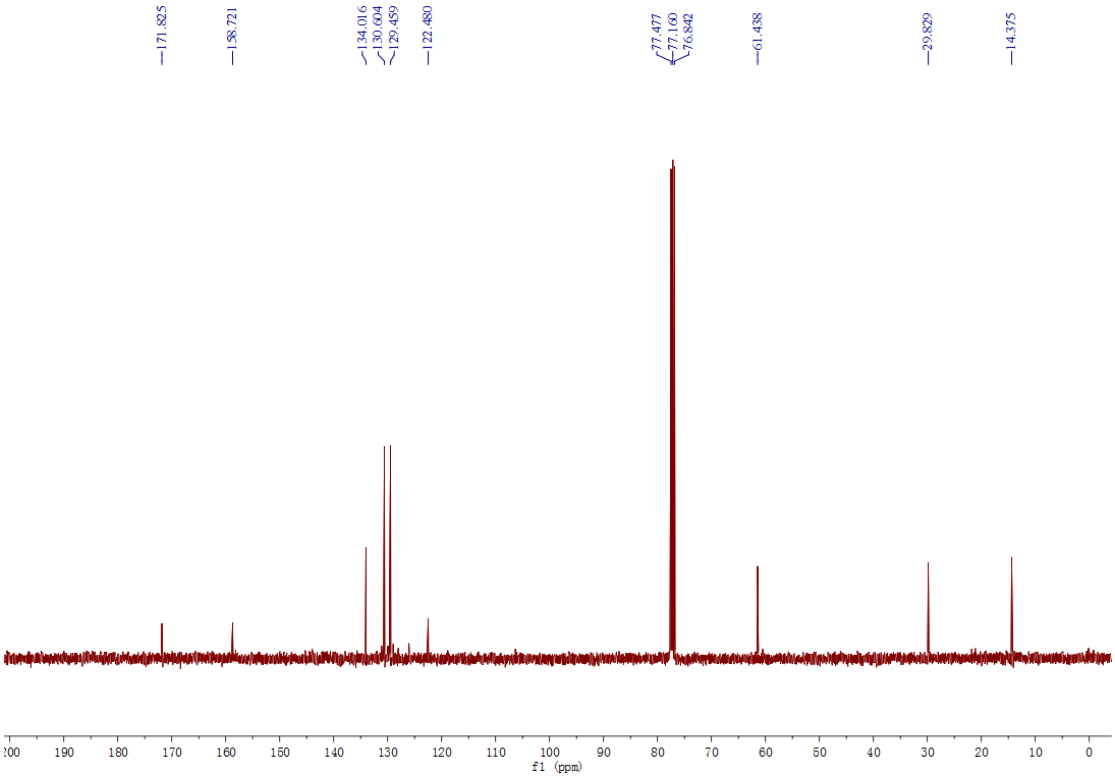
^{1}H NMR Spectrum for **9a** ($CDCl_3$, 400 MHz)



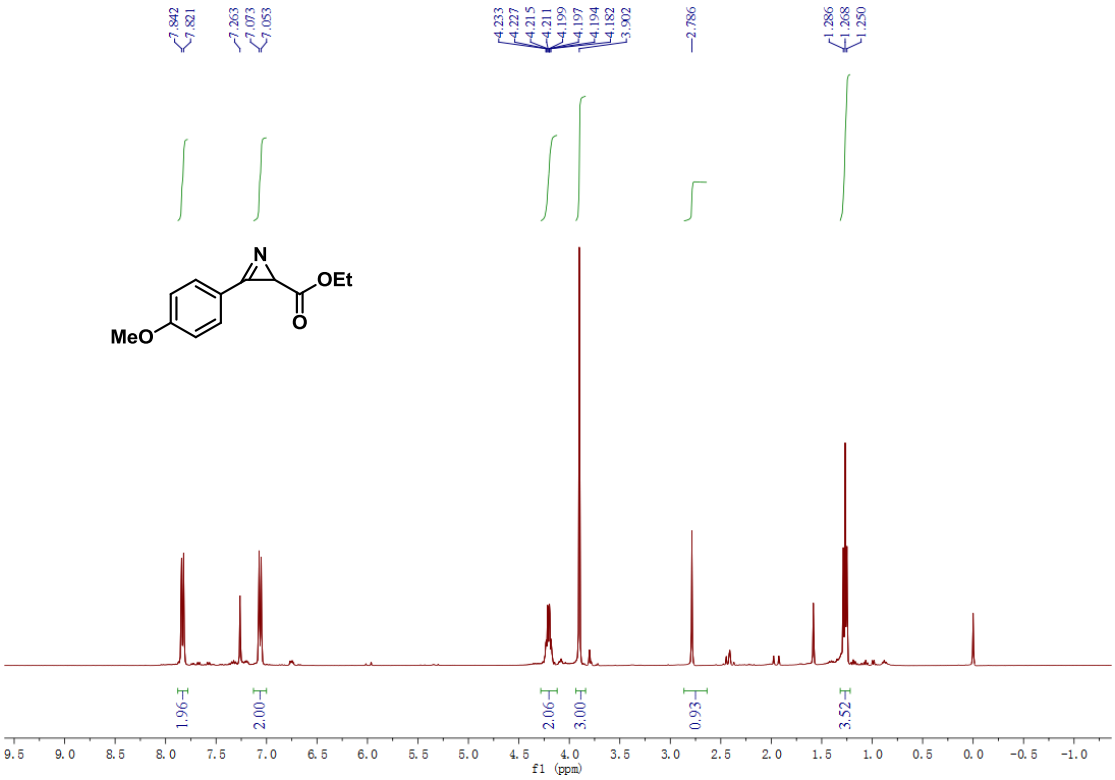
^{13}C NMR Spectrum for **9a** ($CDCl_3$, 100 MHz)



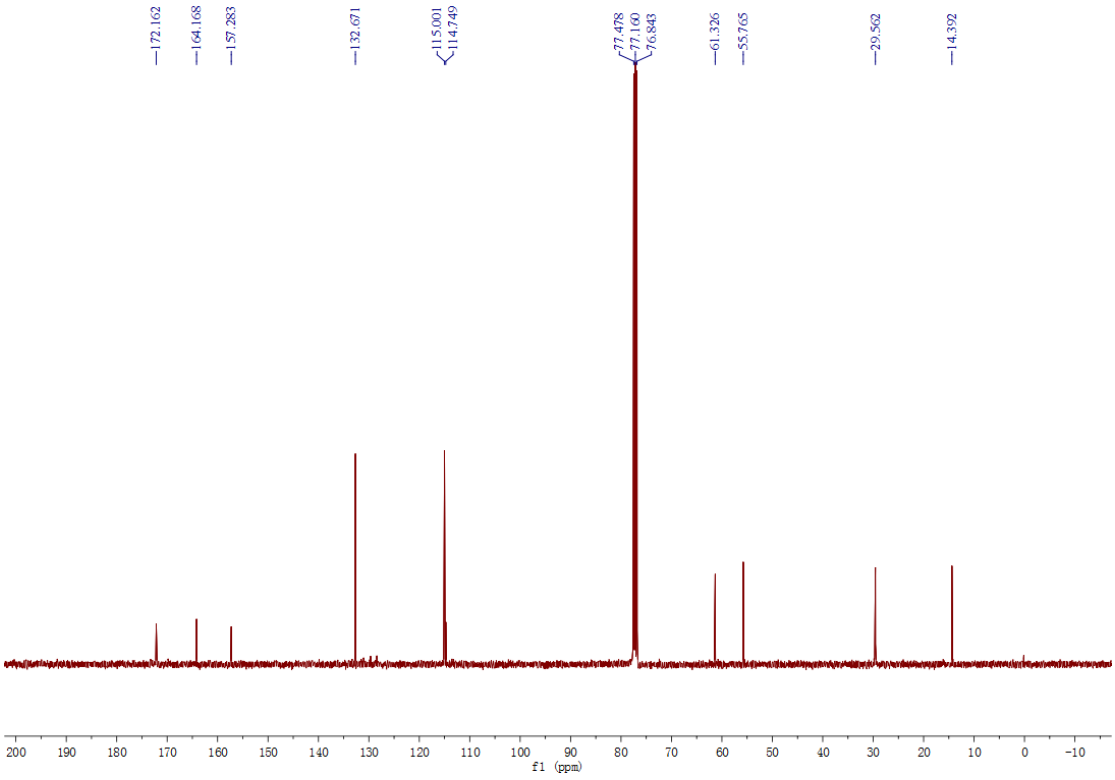
^{1}H NMR Spectrum for **9b** ($CDCl_3$, 400 MHz)



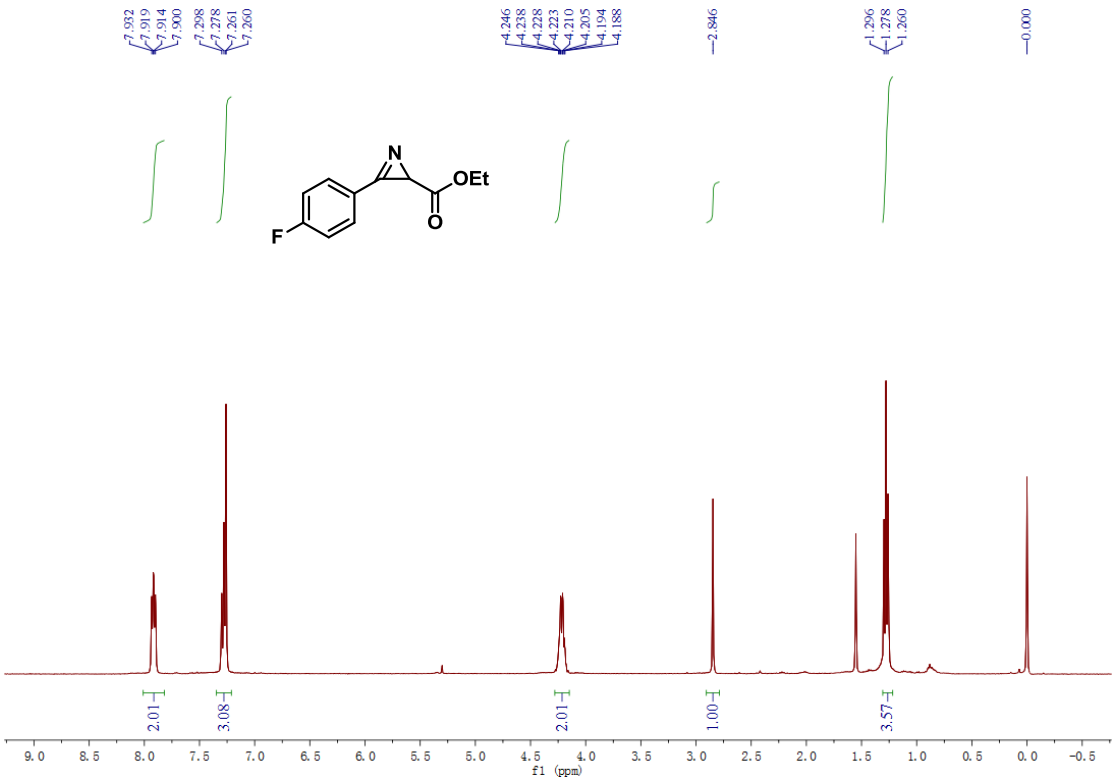
^{13}C NMR Spectrum for **9b** ($CDCl_3$, 100 MHz)



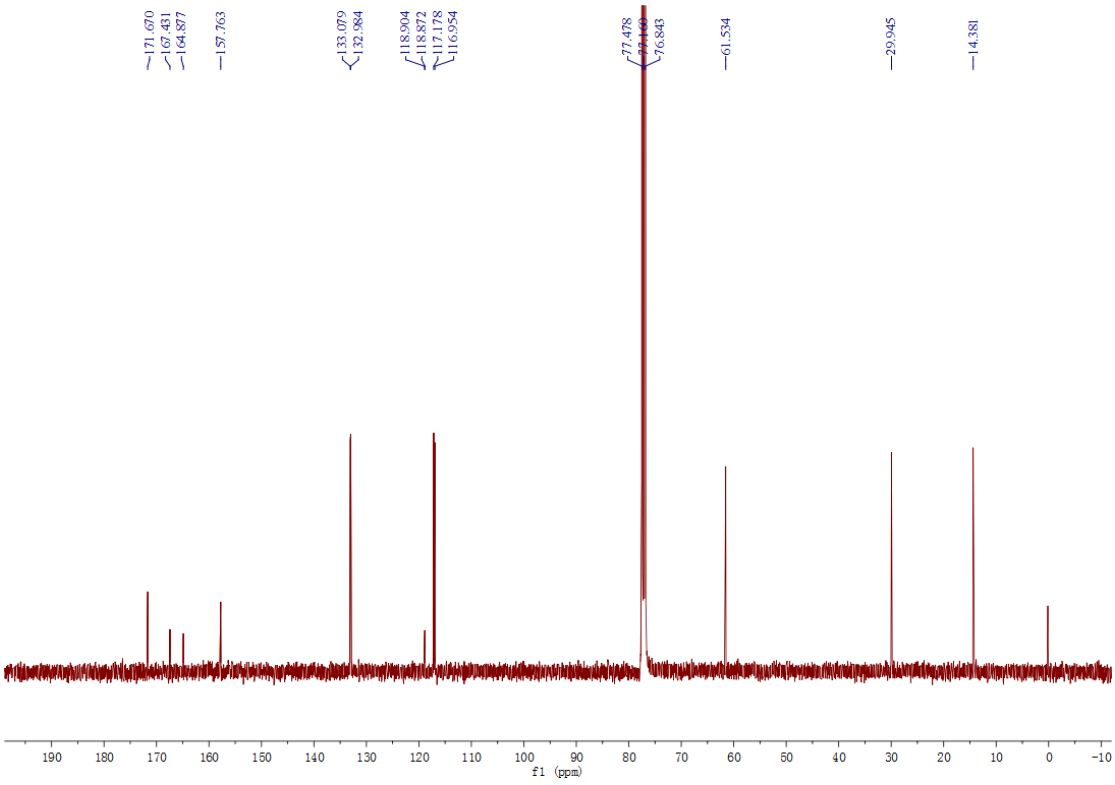
^{1}H NMR Spectrum for **9c** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum for **9c** ($CDCl_3$, 100 MHz)

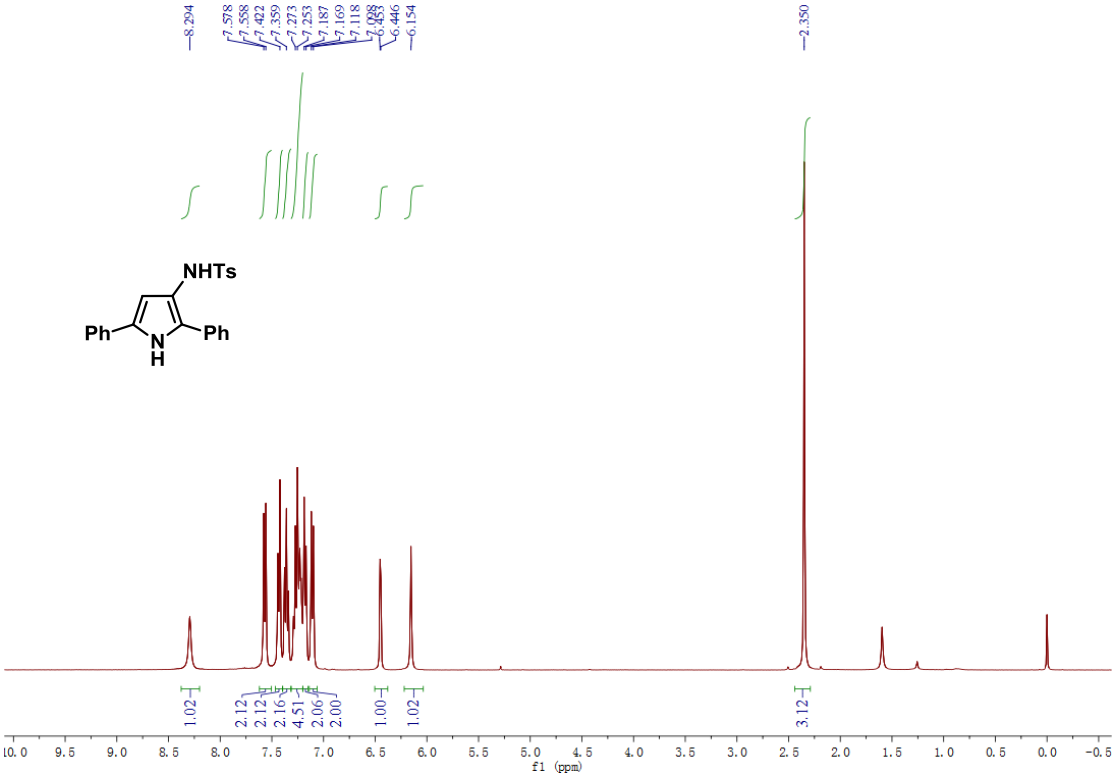


^{1}H NMR Spectrum for **9d** ($CDCl_3$, 400 MHz)

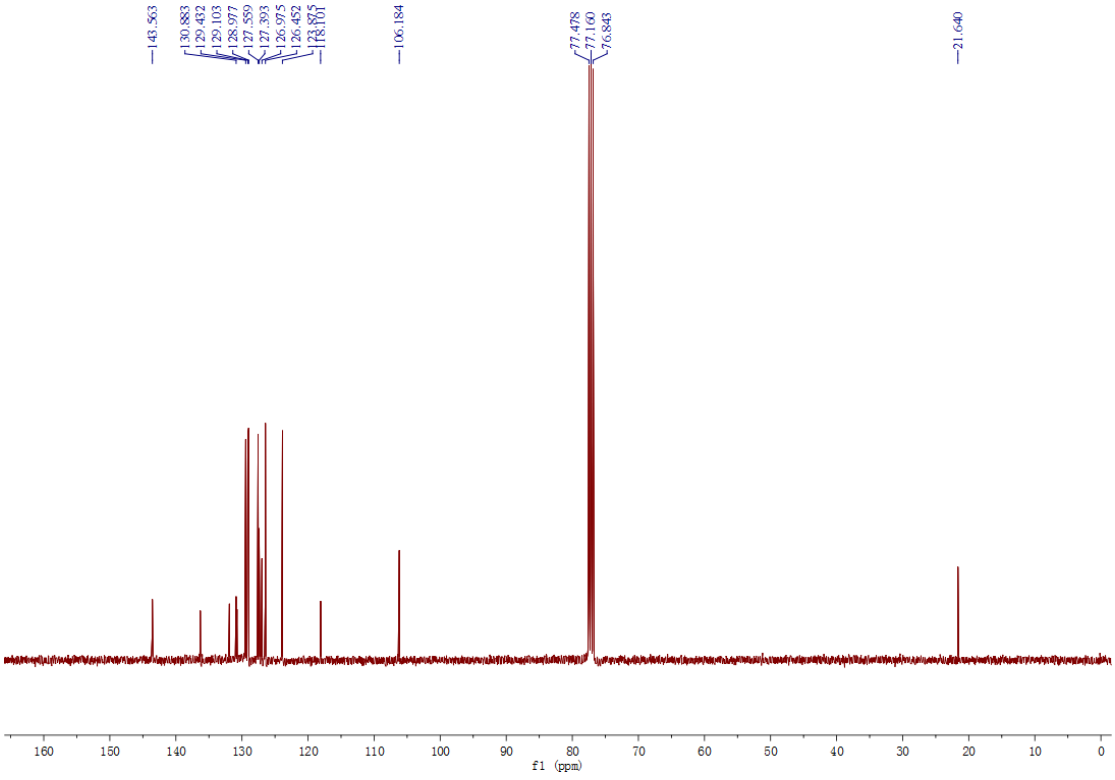


^{13}C NMR Spectrum for **9d** ($CDCl_3$, 100 MHz)

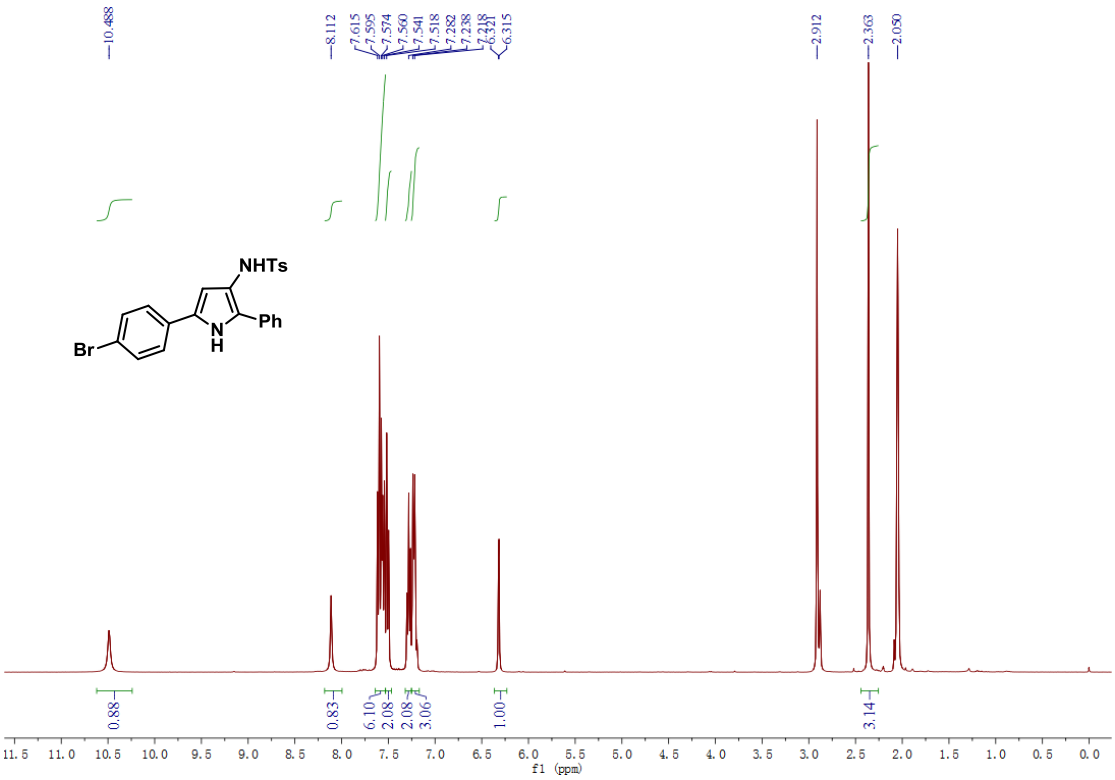
7. NMR Spectra of [3+2] and [3+3] Products



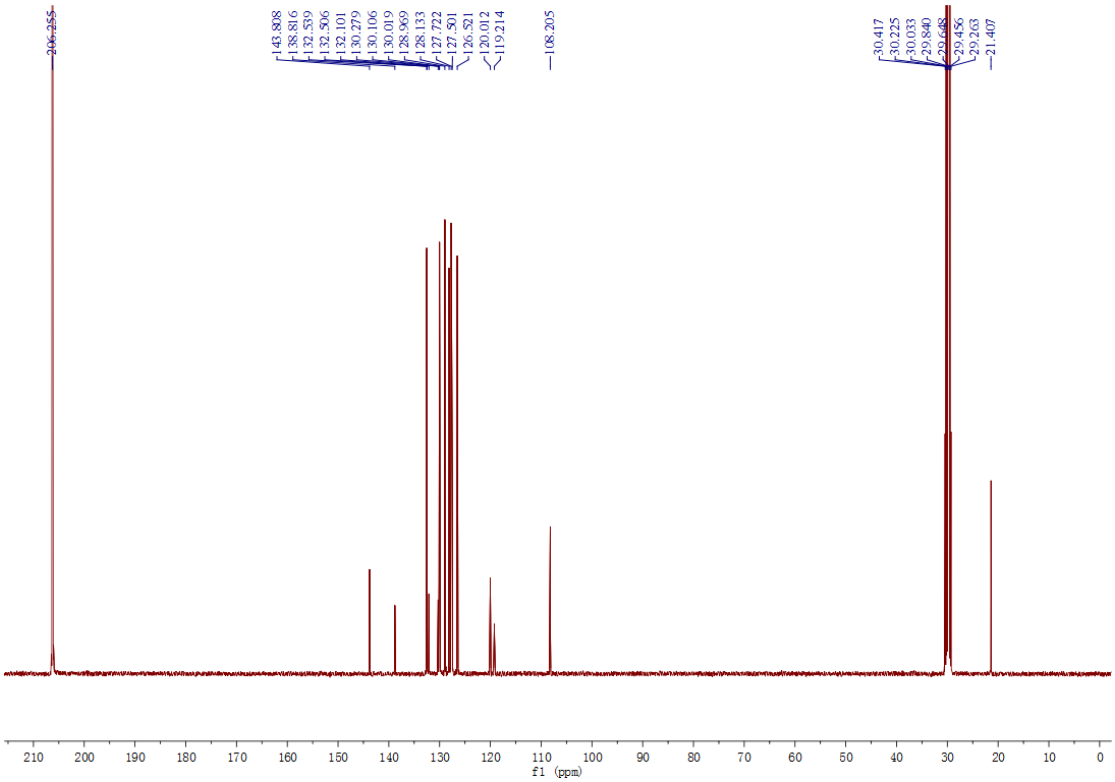
^{1}H NMR Spectrum for **3a** ($CDCl_3$, 400 MHz)



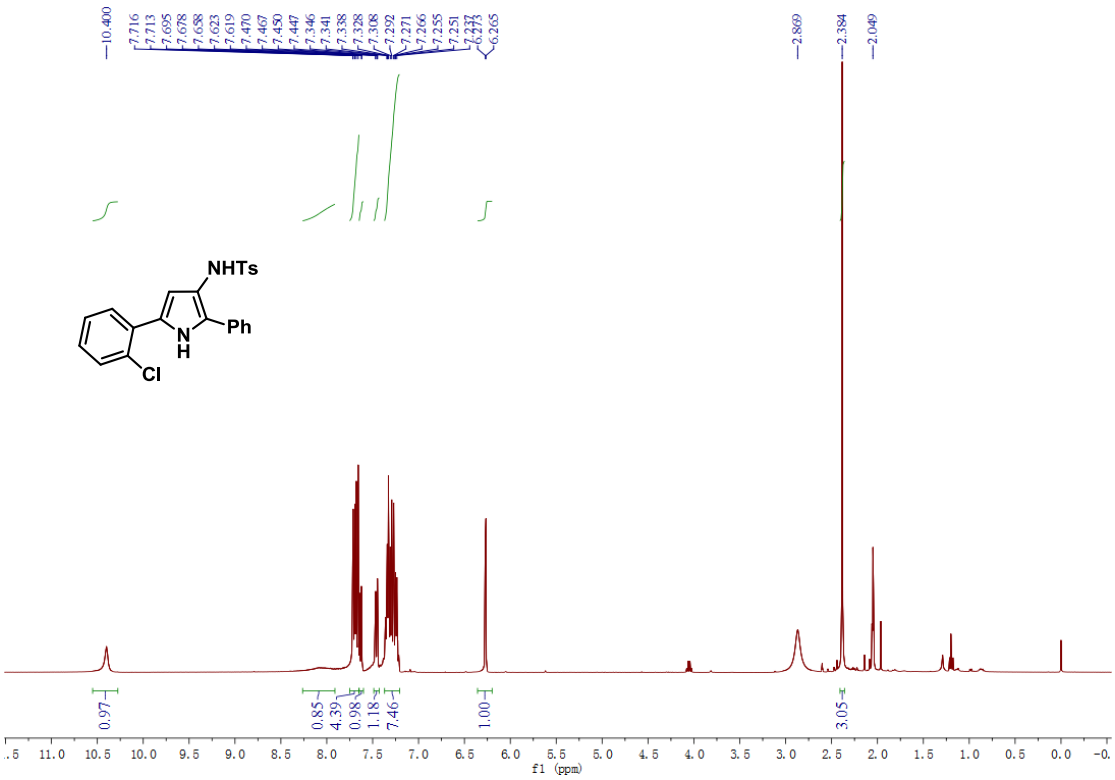
^{13}C NMR Spectrum for **3a** ($CDCl_3$, 100 MHz)



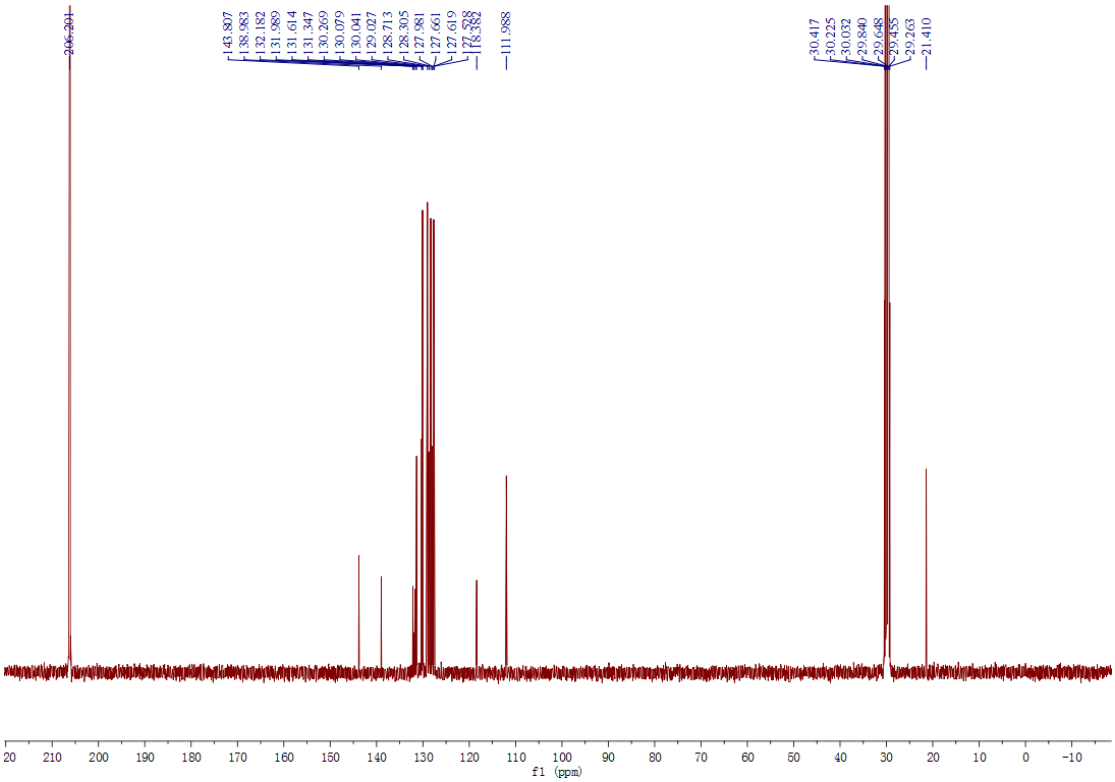
^{1}H NMR Spectrum for **3b** (Acetone-d_6, 400 MHz)



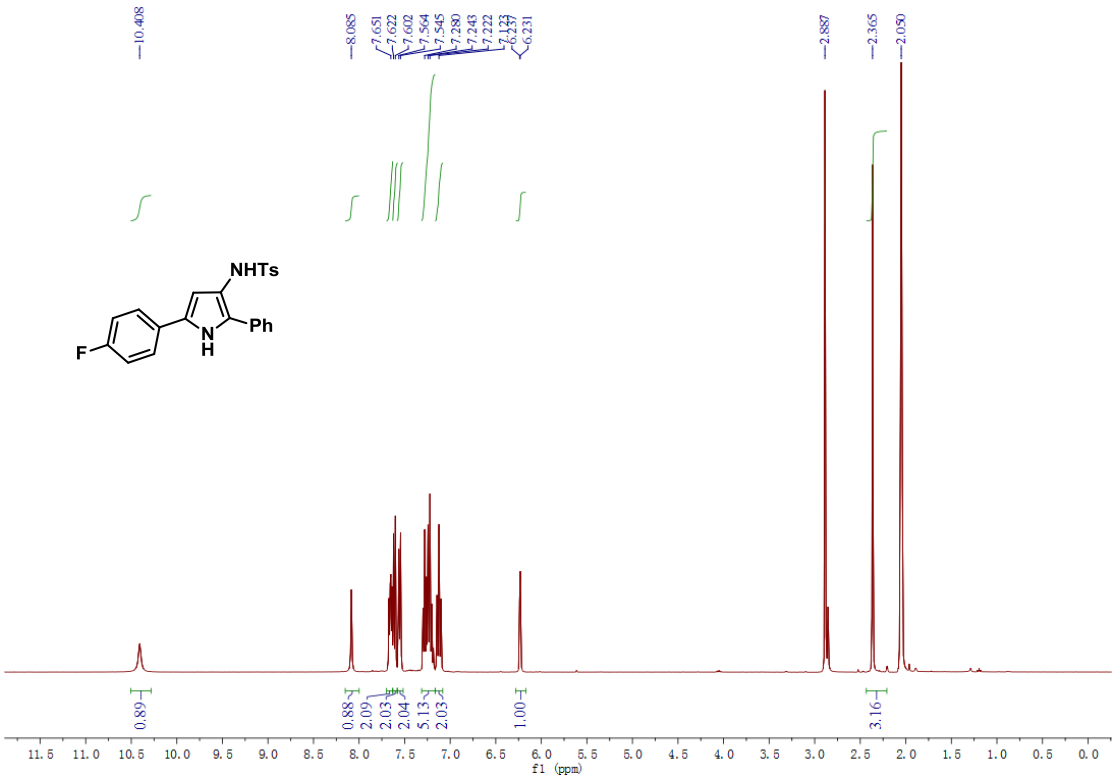
^{13}C NMR Spectrum for **3b** (Acetone-d_6, 100 MHz)



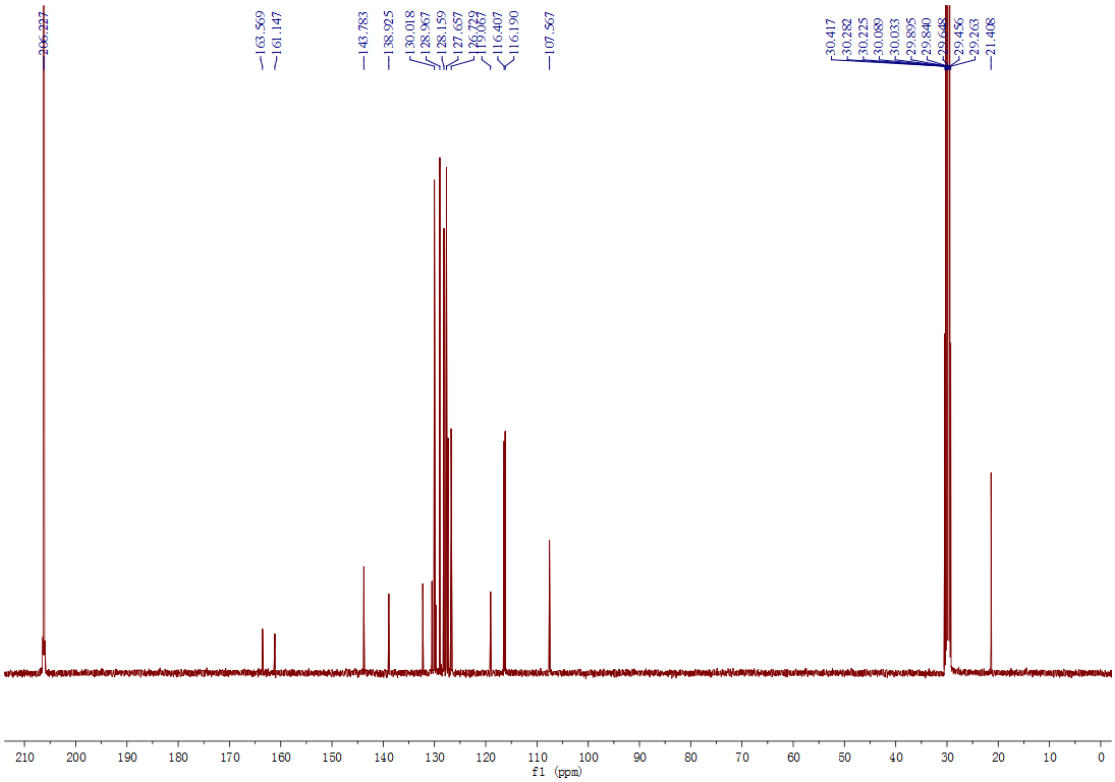
^{1}H NMR Spectrum for **3c** (Acetone-d_6, 400 MHz)



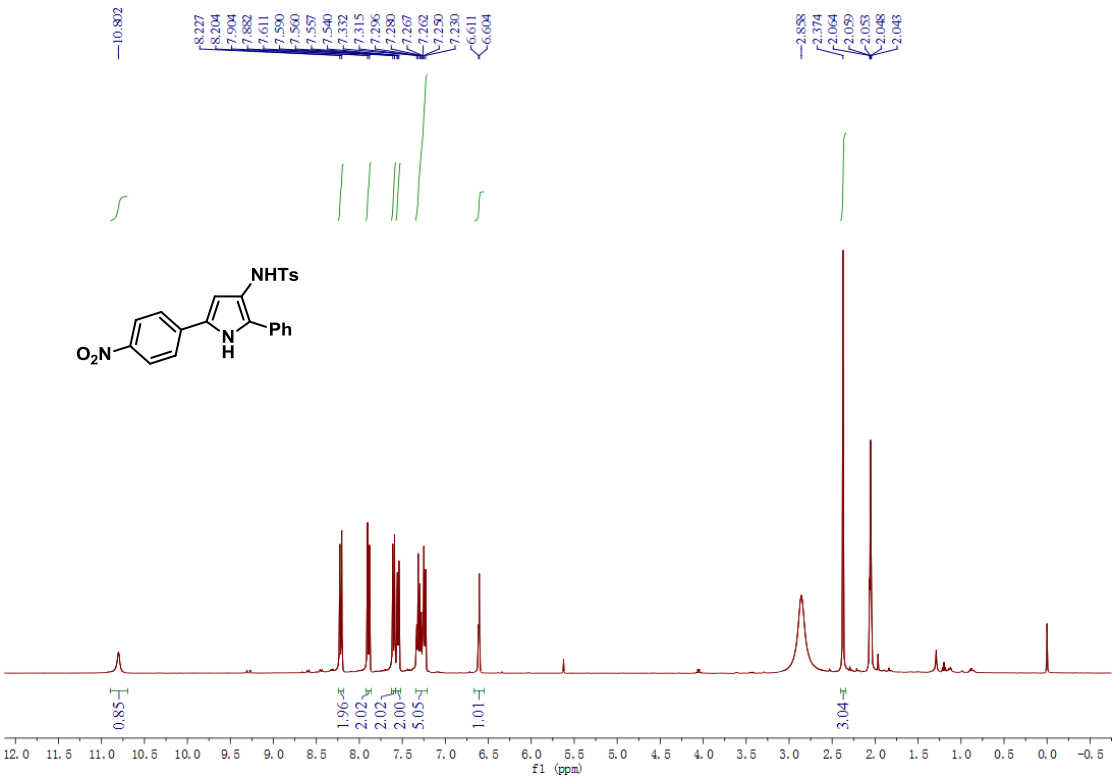
^{13}C NMR Spectrum for **3c** (Acetone-d_6, 100 MHz)



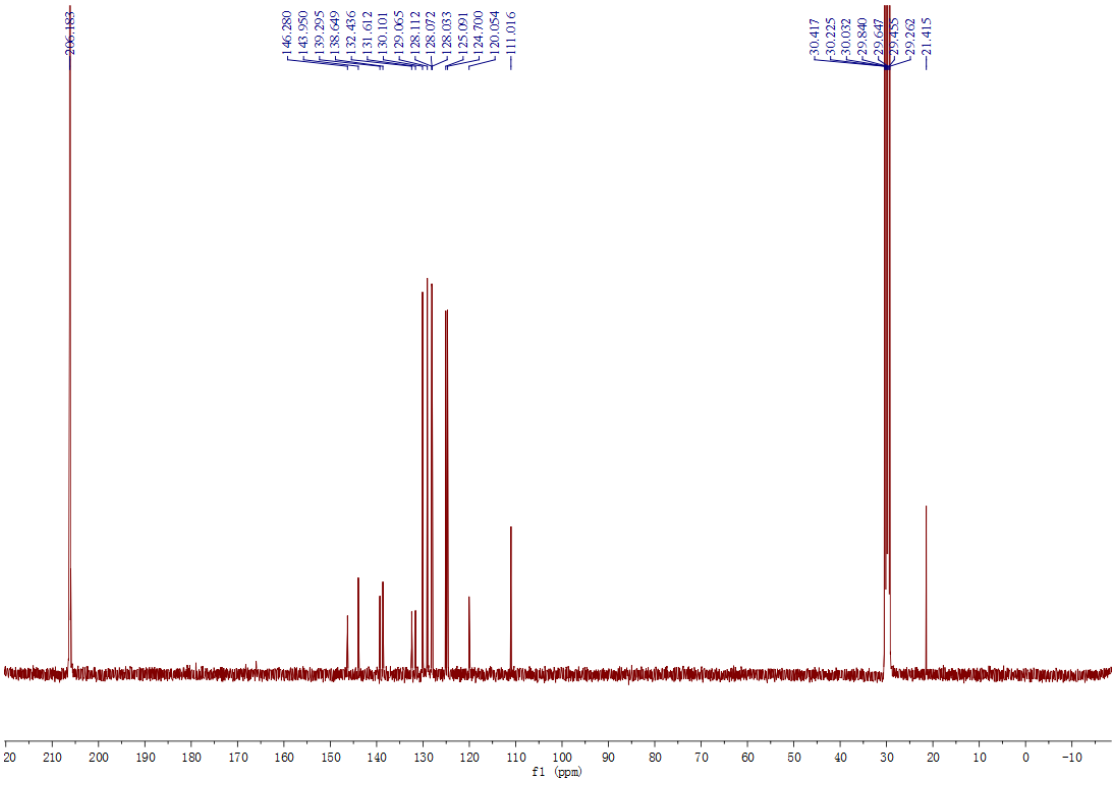
^{1}H NMR Spectrum for **3d** (Acetone-d_6, 400 MHz)



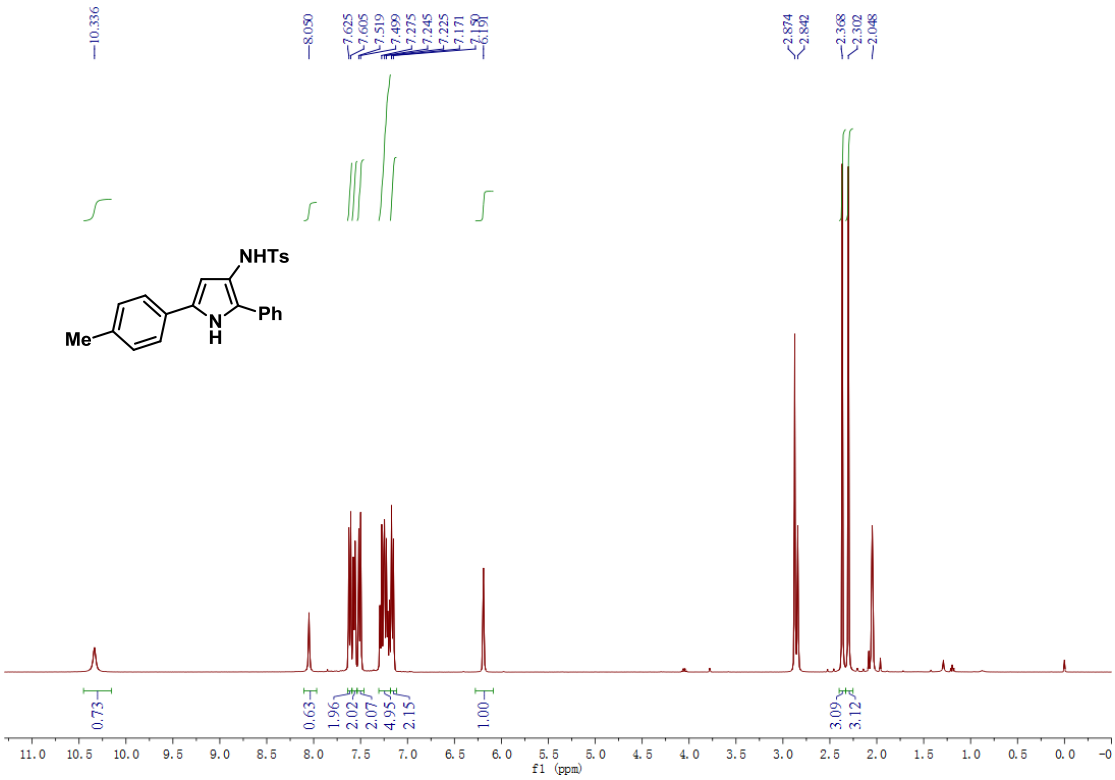
^{13}C NMR Spectrum for **3d** (Acetone-d_6, 100 MHz)



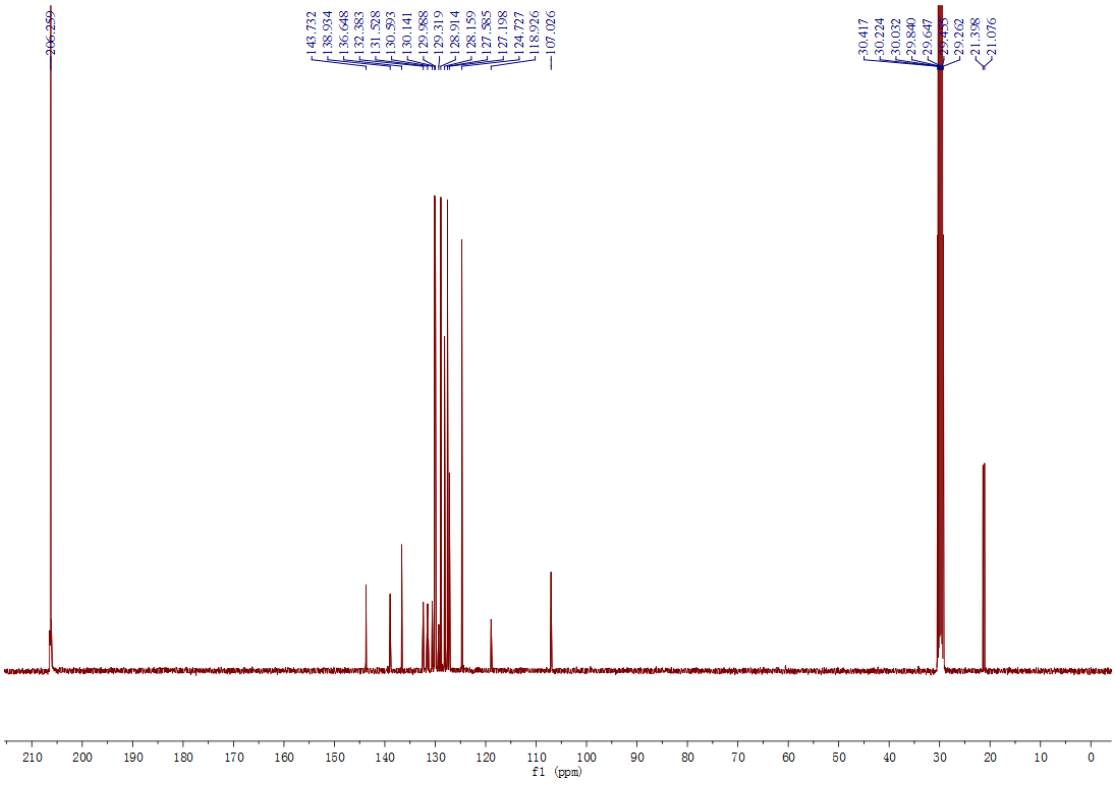
^{1}H NMR Spectrum for **3e** (Acetone-d_6, 400 MHz)



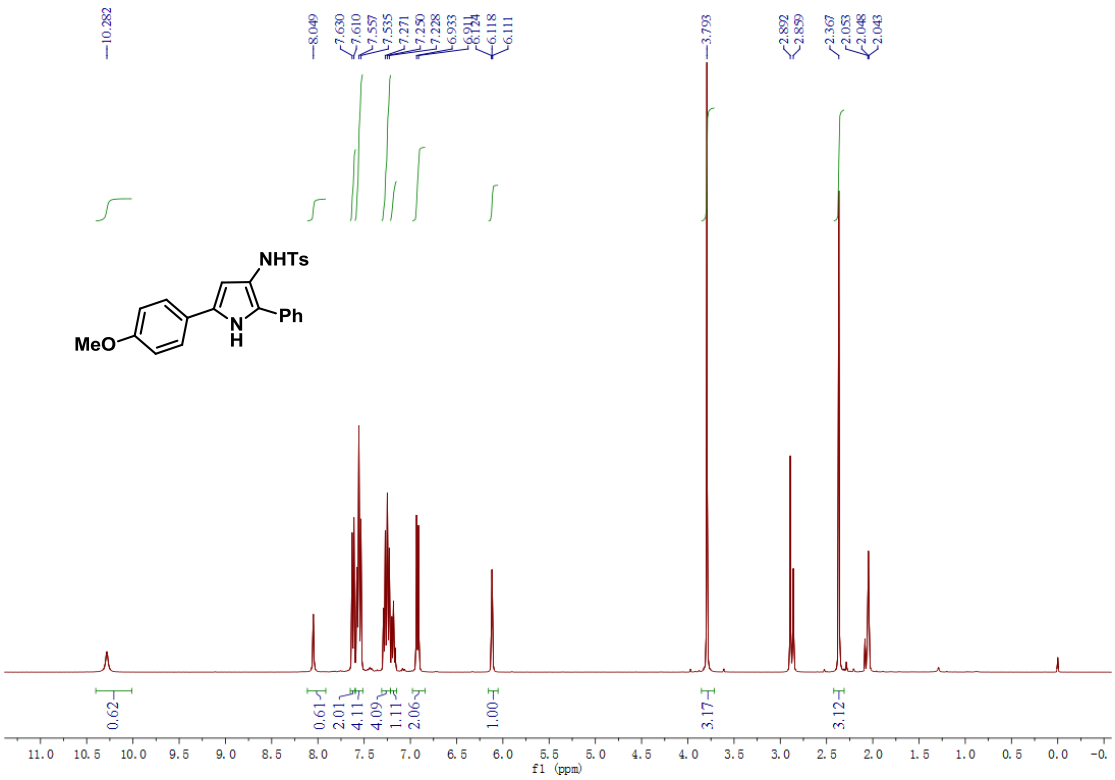
^{13}C NMR Spectrum for **3e** (Acetone-d_6, 100 MHz)



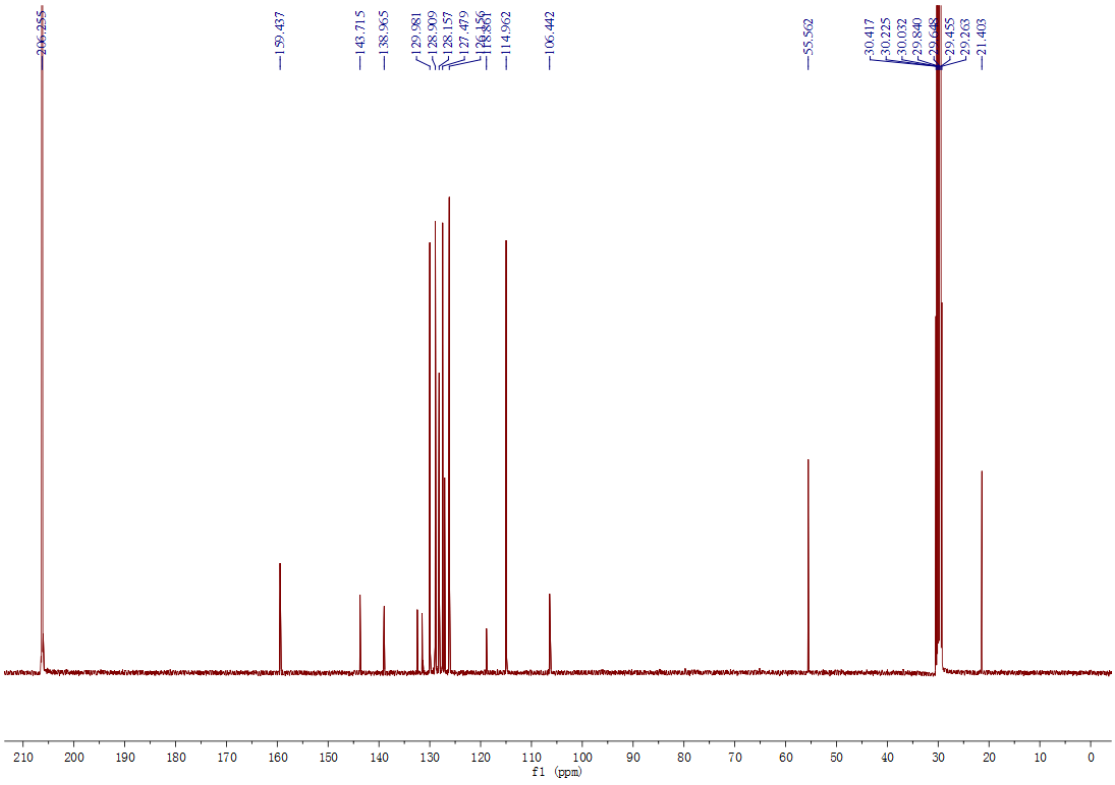
^{1}H NMR Spectrum for **3f** (Acetone-d_6, 400 MHz)



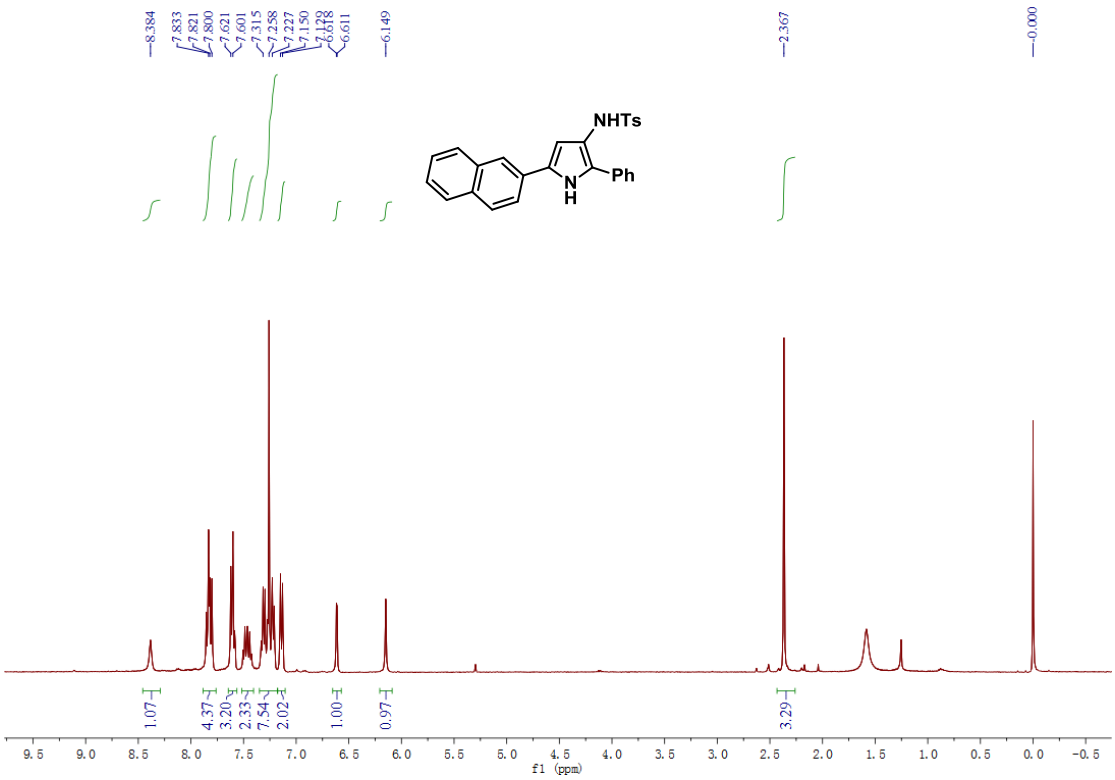
^{13}C NMR Spectrum for **3f** (Acetone-d_6, 100 MHz)



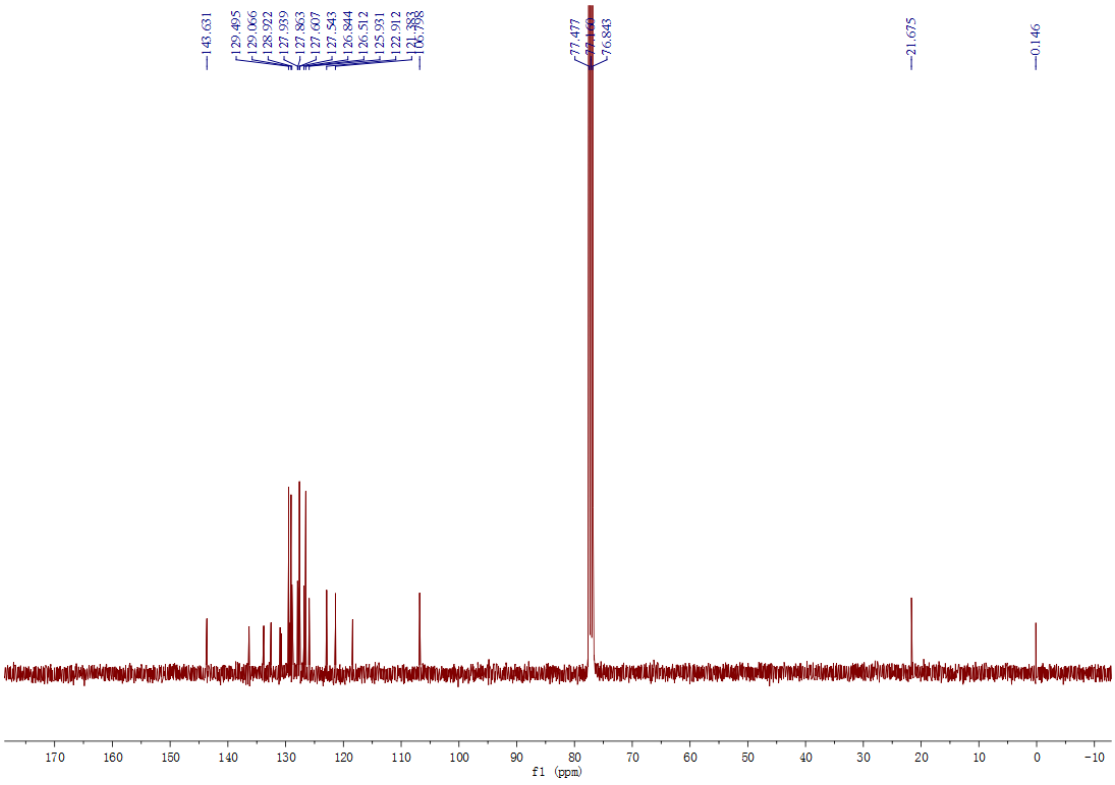
^{1}H NMR Spectrum for **3g** (Acetone-d_6, 400 MHz)



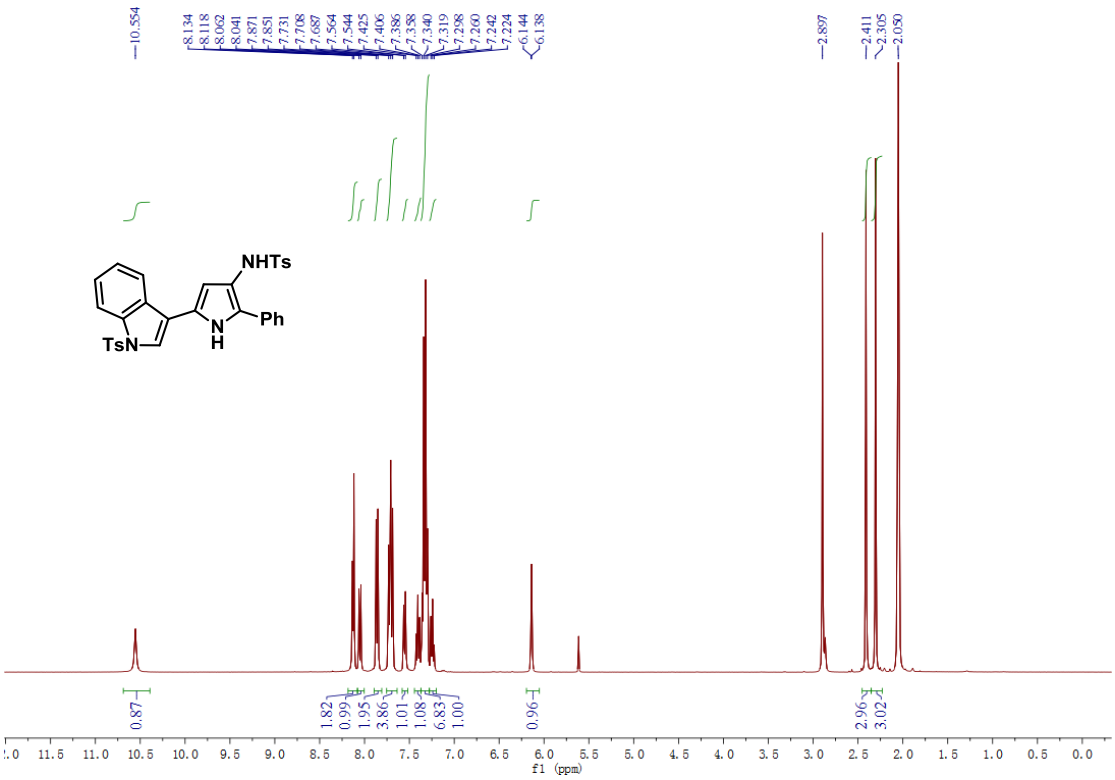
^{13}C NMR Spectrum for **3g** (Acetone-d_6, 100 MHz)



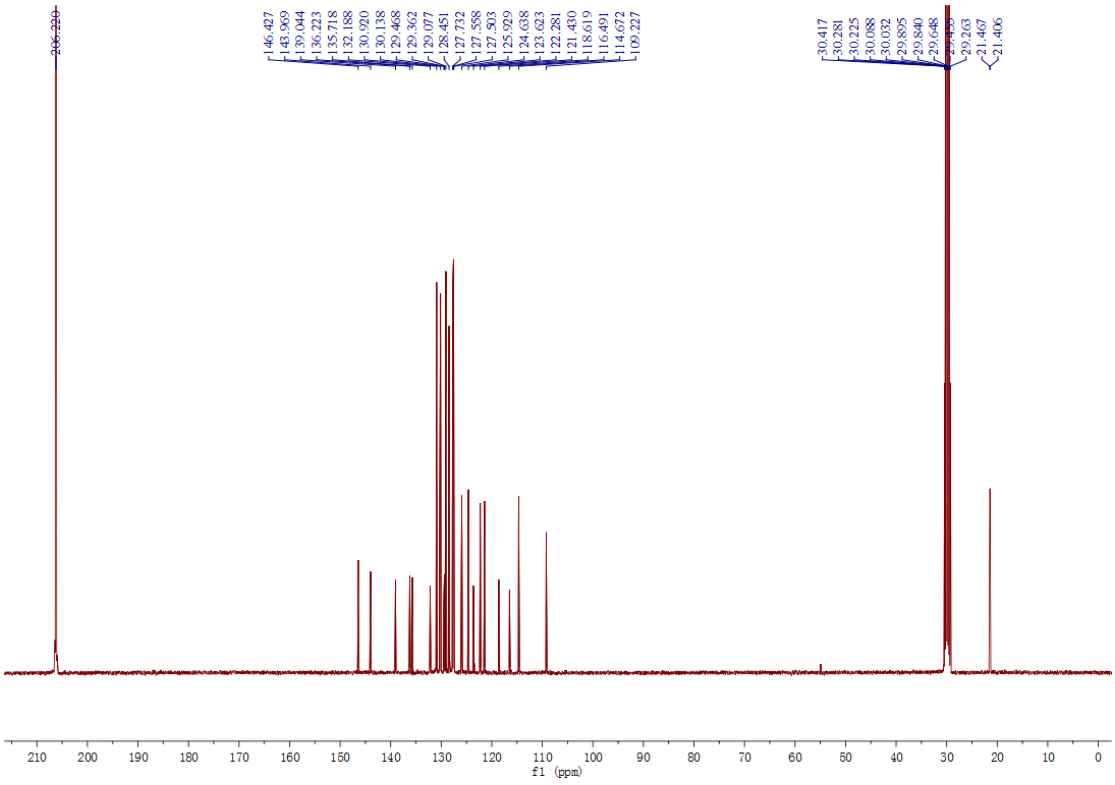
^{1}H NMR Spectrum for **3h** ($CDCl_3$, 400 MHz)



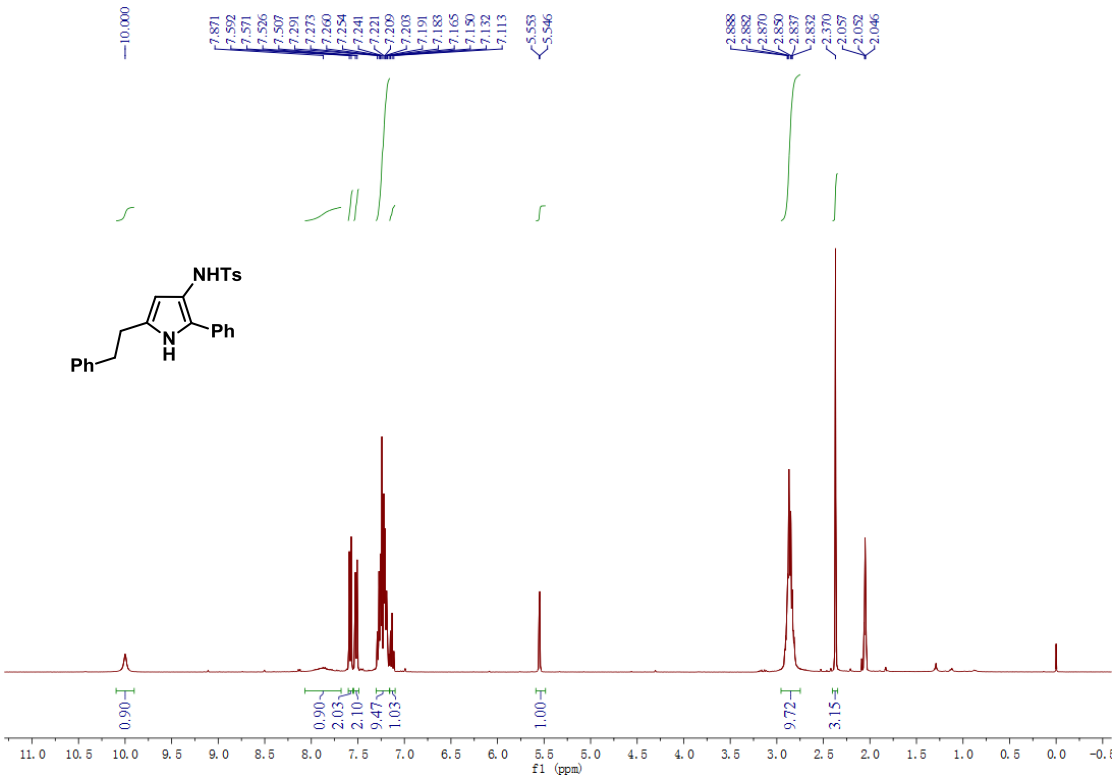
^{13}C NMR Spectrum for **3h** ($CDCl_3$, 100 MHz)



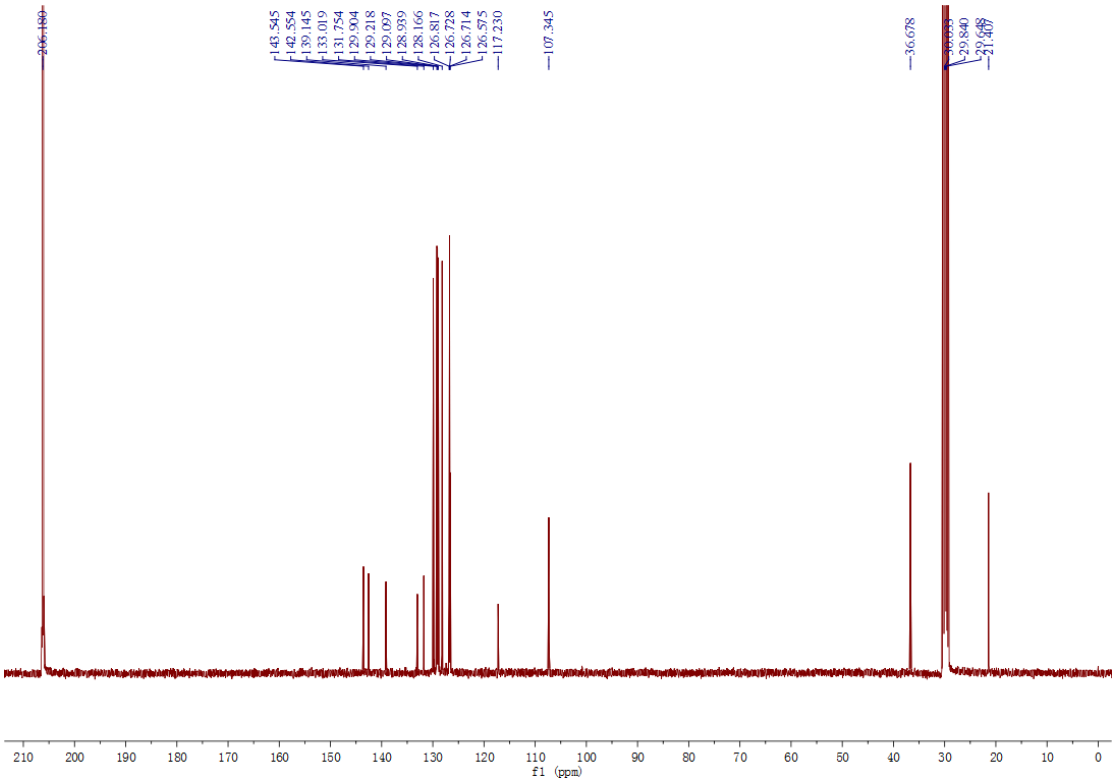
^{1}H NMR Spectrum for **3i** (Acetone-d_6, 400 MHz)



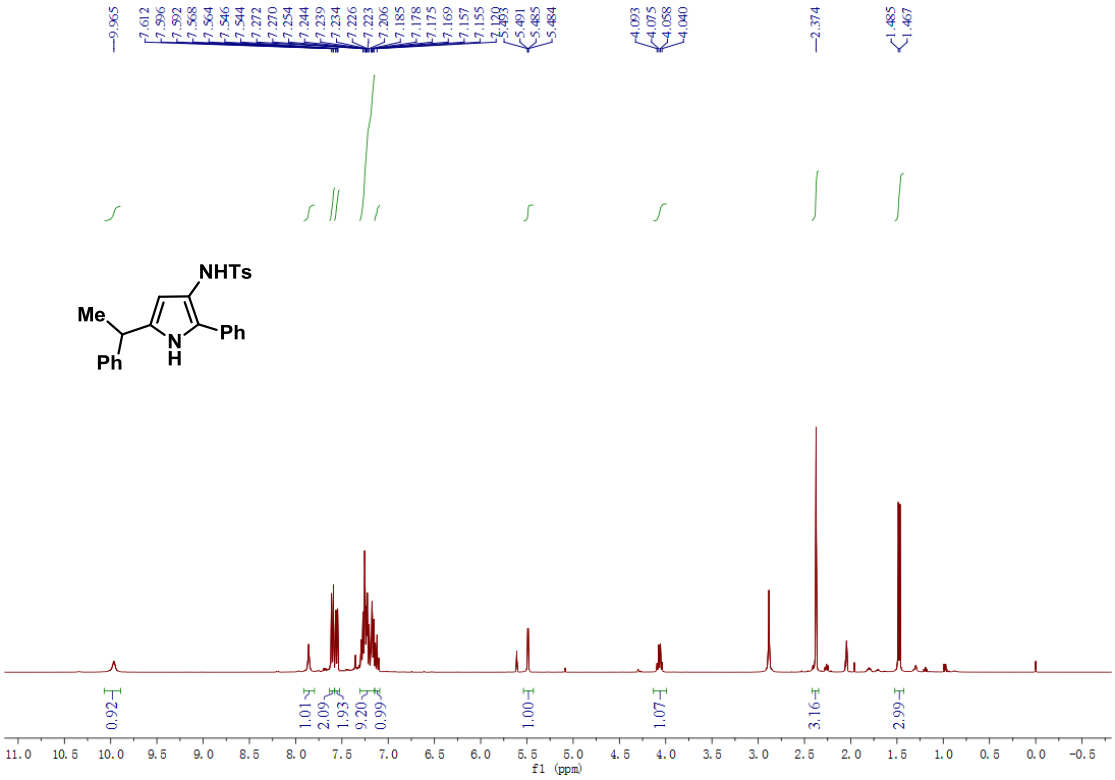
^{13}C NMR Spectrum for **3i** (Acetone-d_6, 100 MHz)



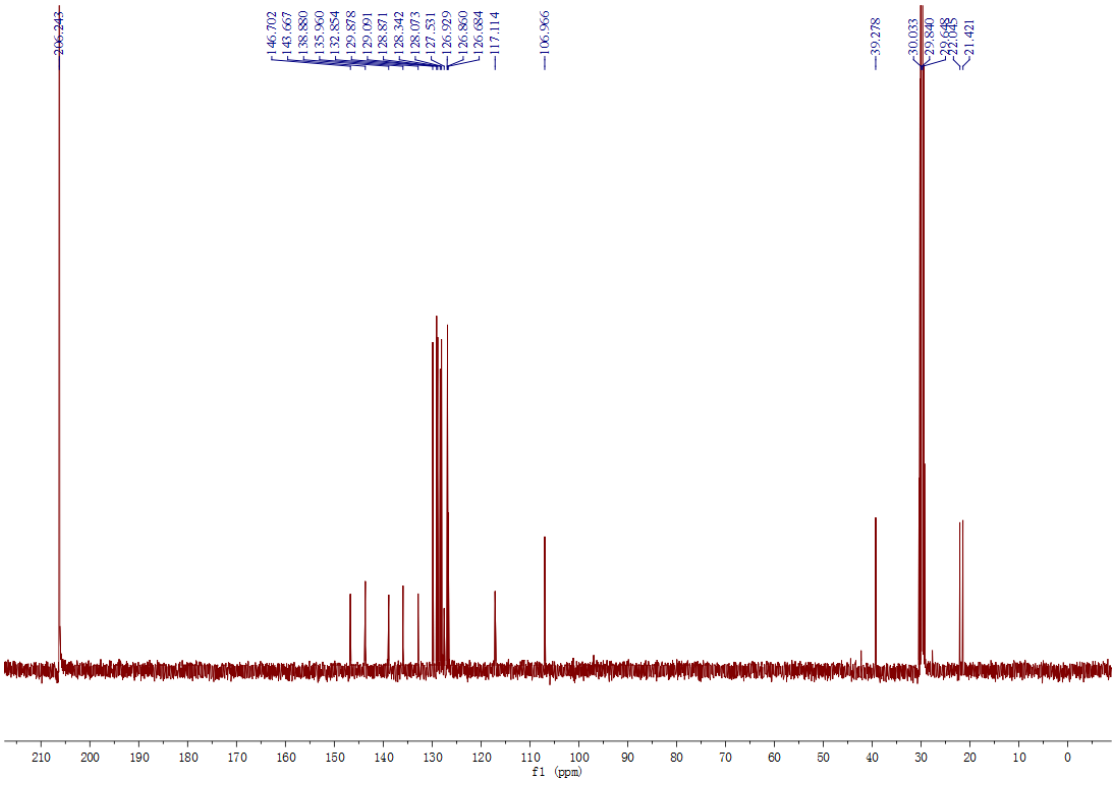
^{1}H NMR Spectrum for **3j** (Acetone-d_6, 400 MHz)



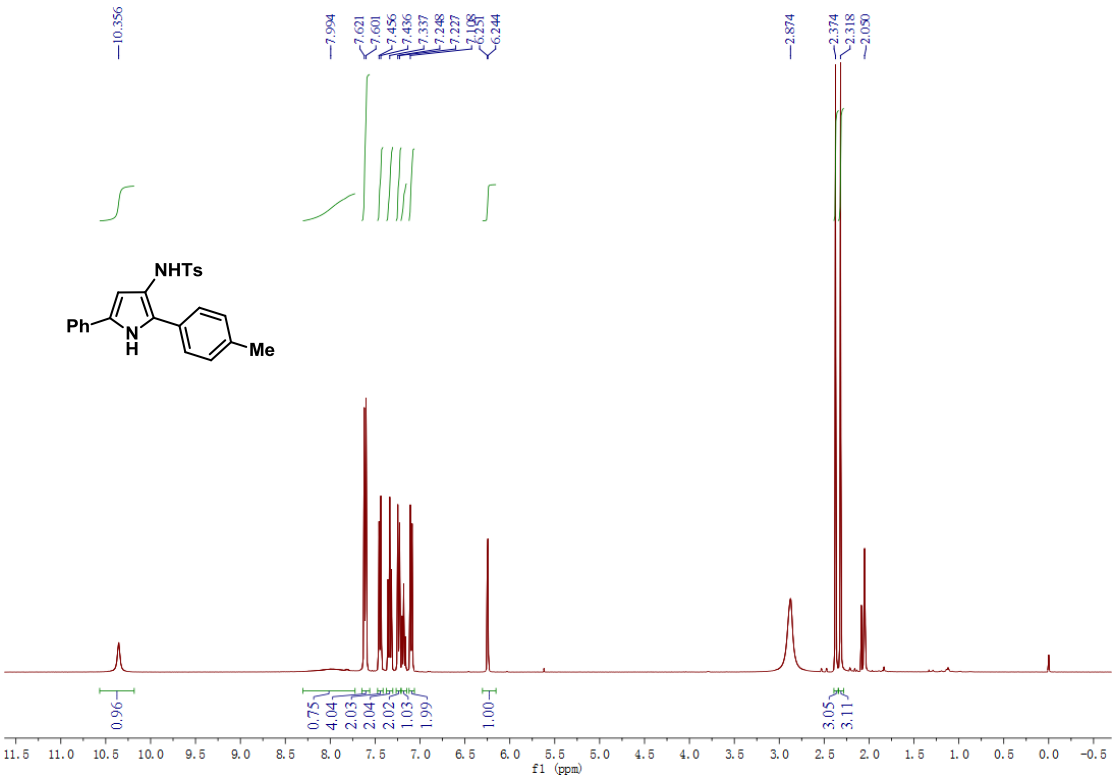
^{13}C NMR Spectrum for **3j** (Acetone-d_6, 100 MHz)



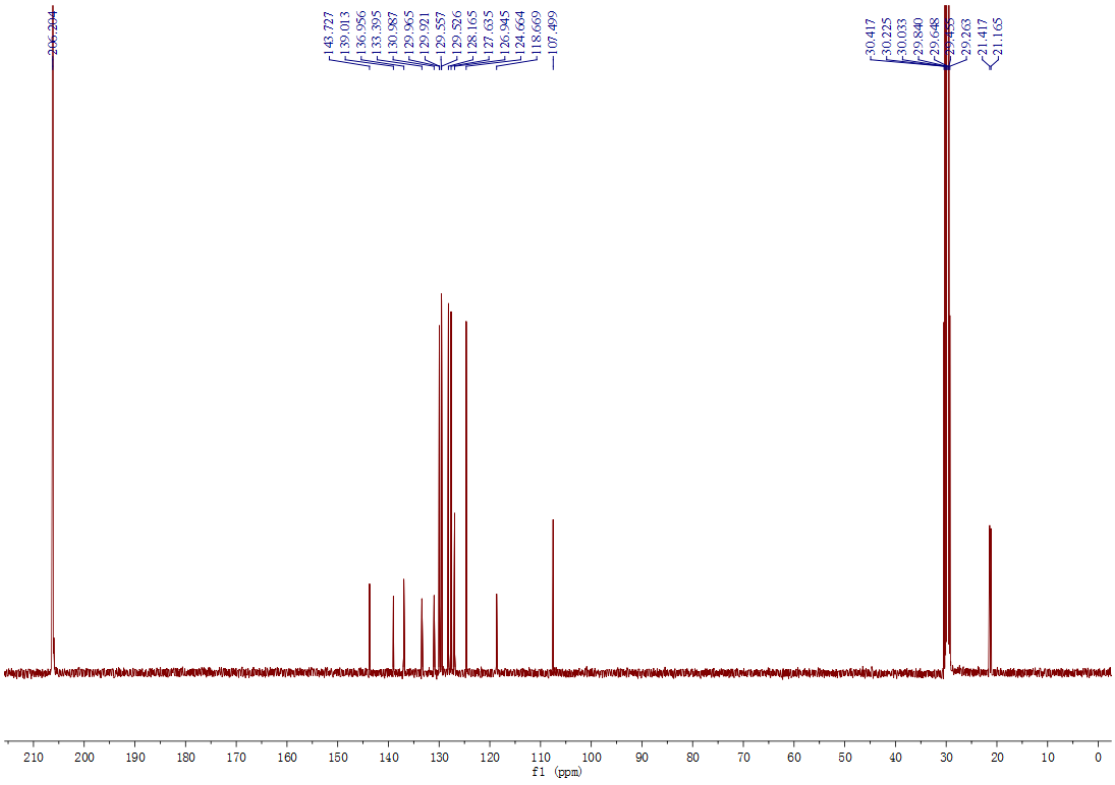
^{1}H NMR Spectrum for **3k** (Acetone-d_6, 400 MHz)



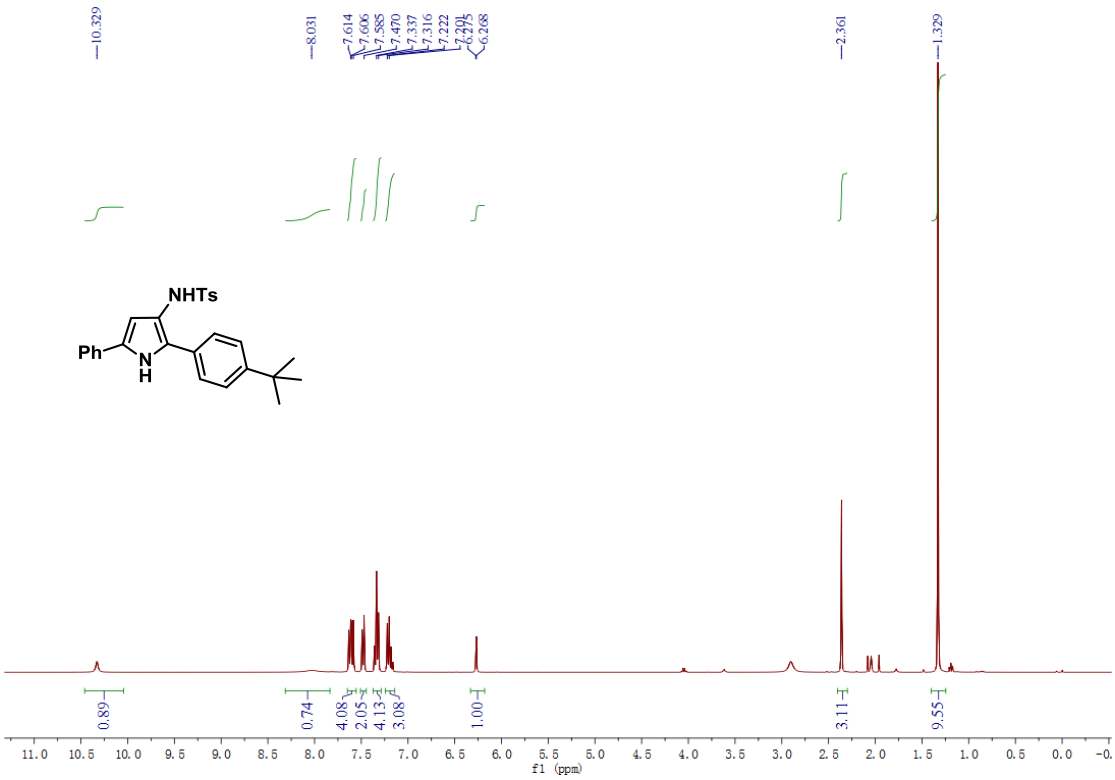
^{13}C NMR Spectrum for **3k** (Acetone-d_6, 100 MHz)



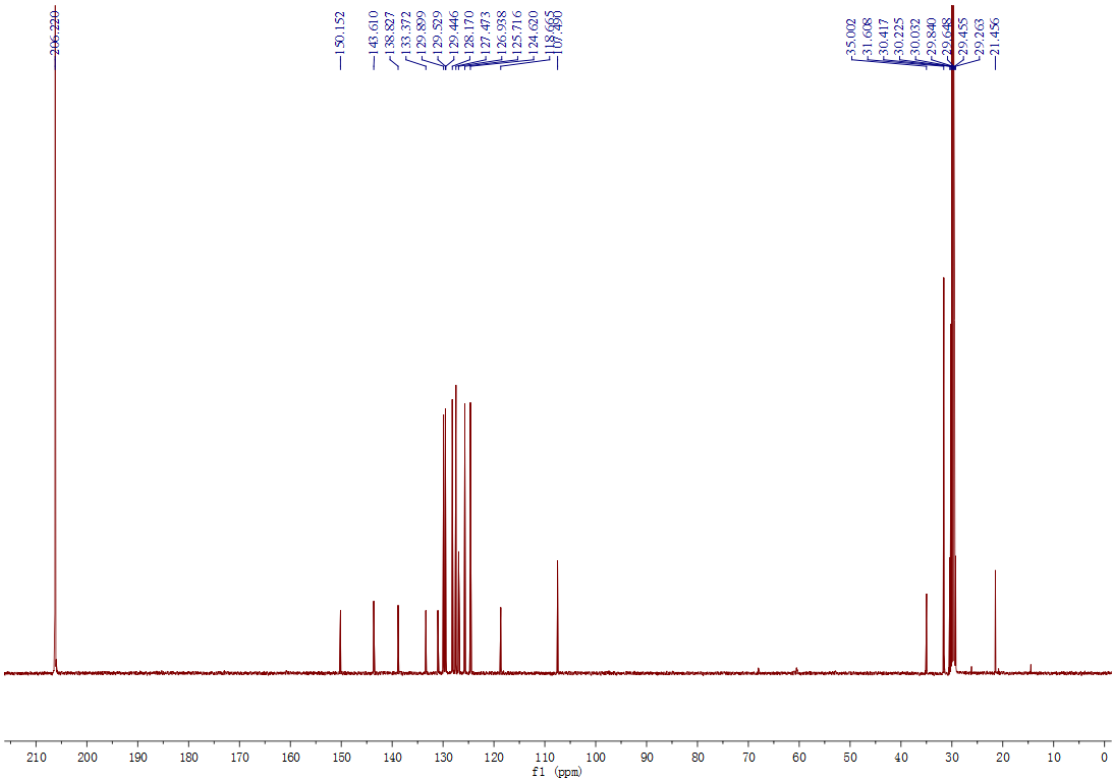
^{1}H NMR Spectrum for **3l** (Acetone-d_6, 400 MHz)



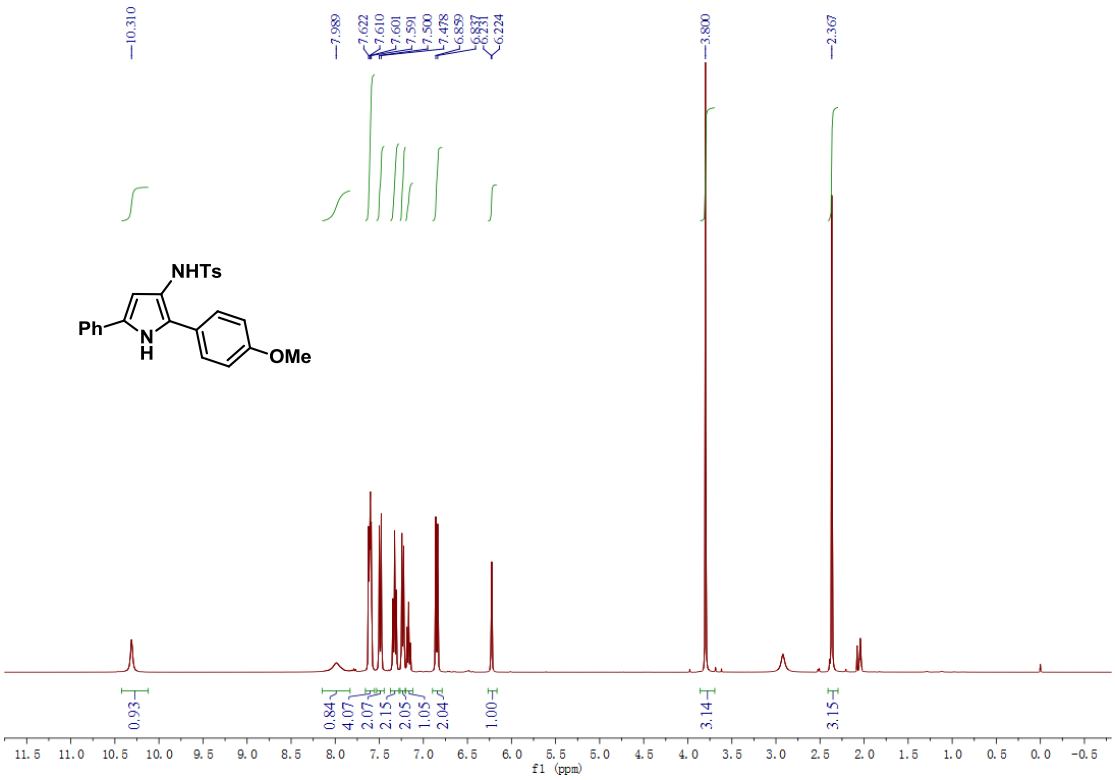
^{13}C NMR Spectrum for **3l** (Acetone-d_6, 100 MHz)



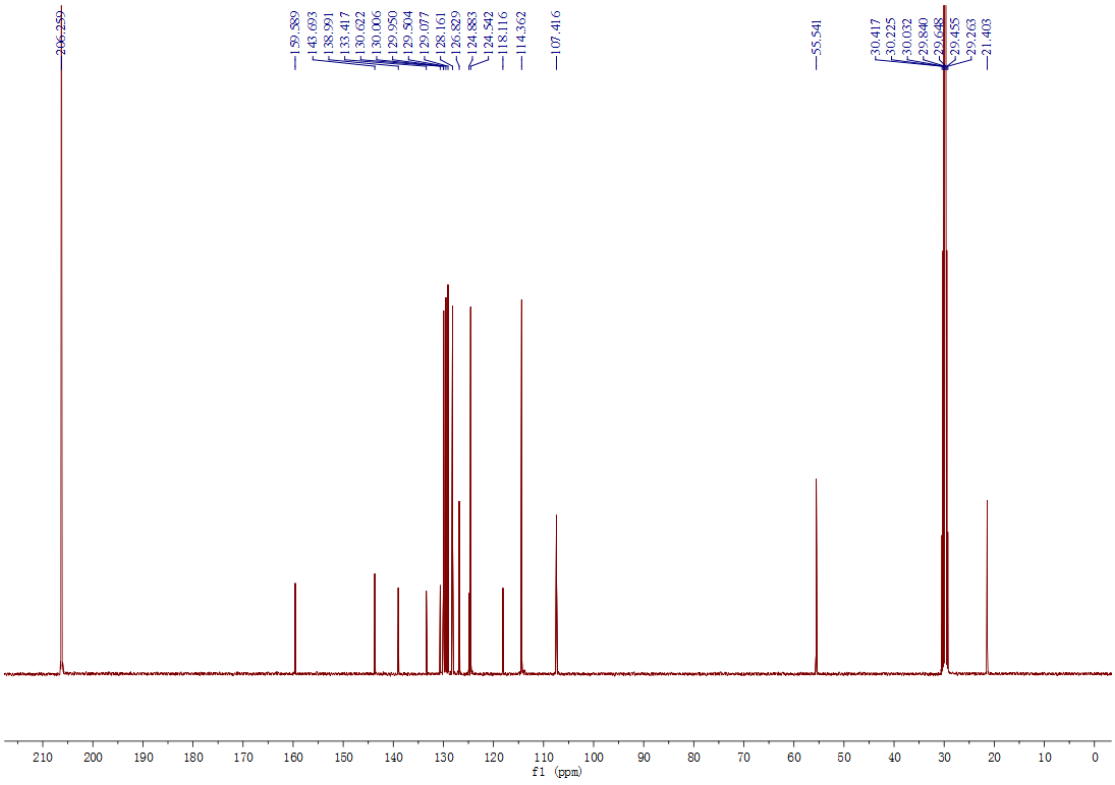
^{1}H NMR Spectrum for **3m** (Acetone-d_6, 400 MHz)



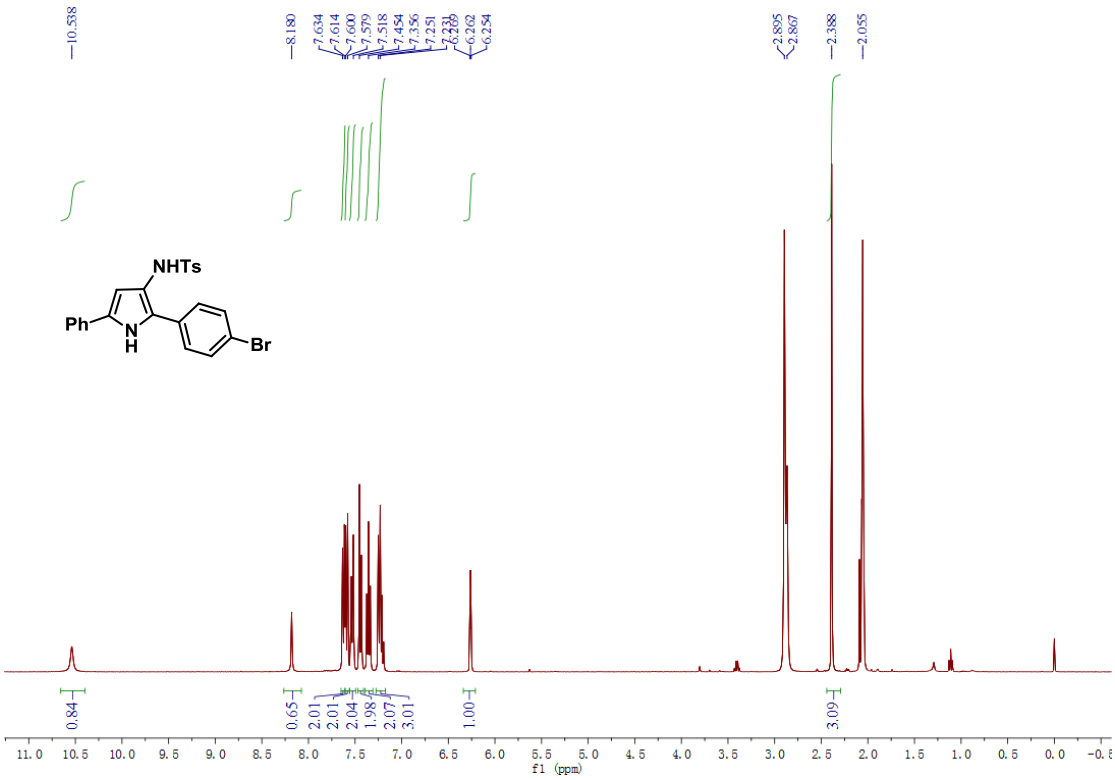
^{13}C NMR Spectrum for **3m** (Acetone-d_6, 100 MHz)



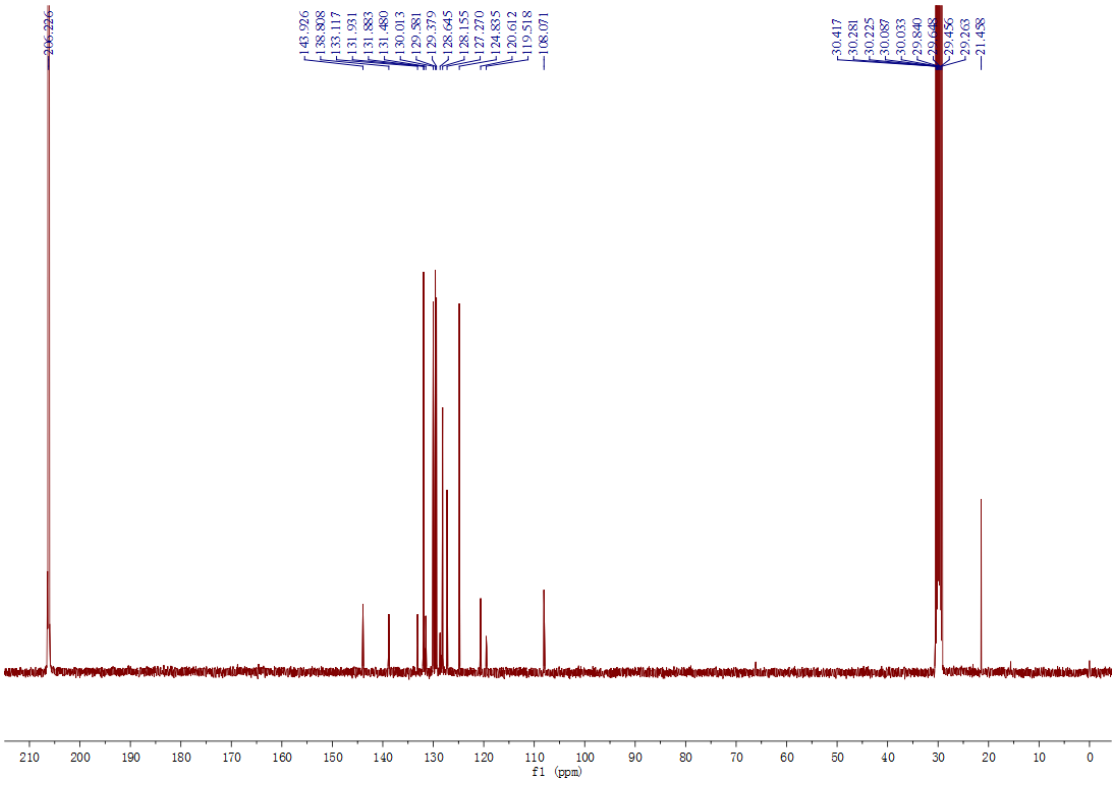
^{1}H NMR Spectrum for **3n** (Acetone-d_6, 400 MHz)



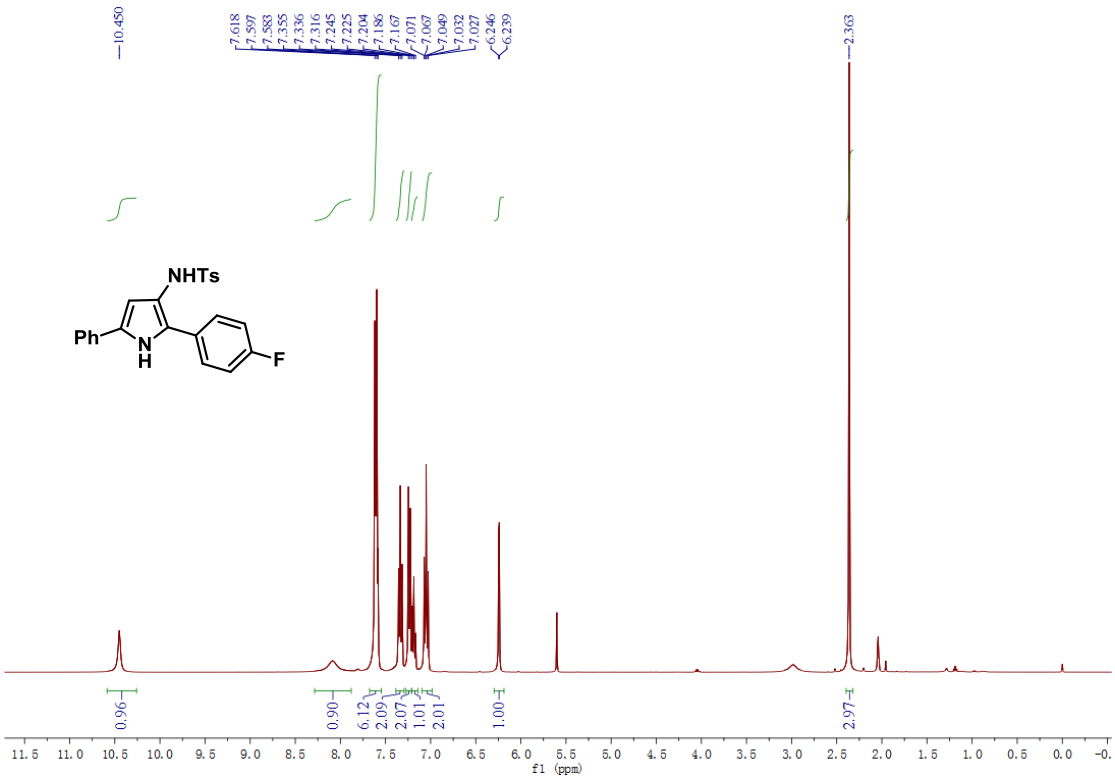
^{13}C NMR Spectrum for **3n** (Acetone-d_6, 100 MHz)



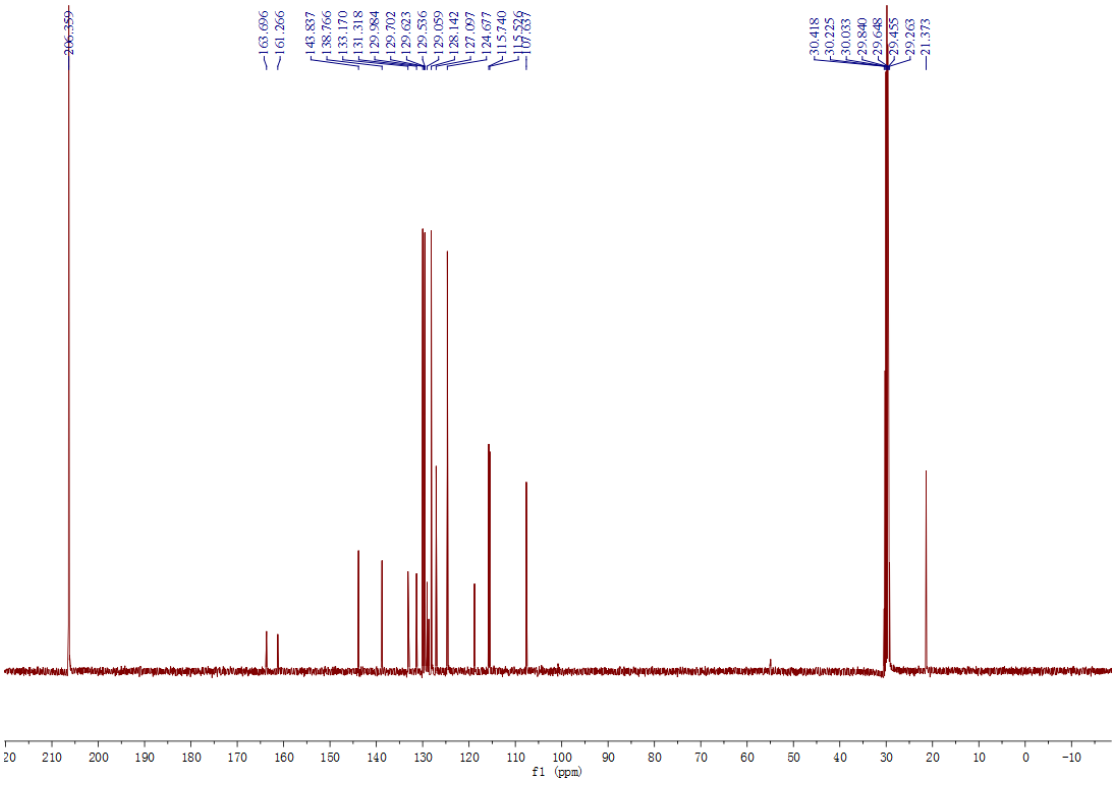
^{1}H NMR Spectrum for **3o** (Acetone-d_6, 400 MHz)



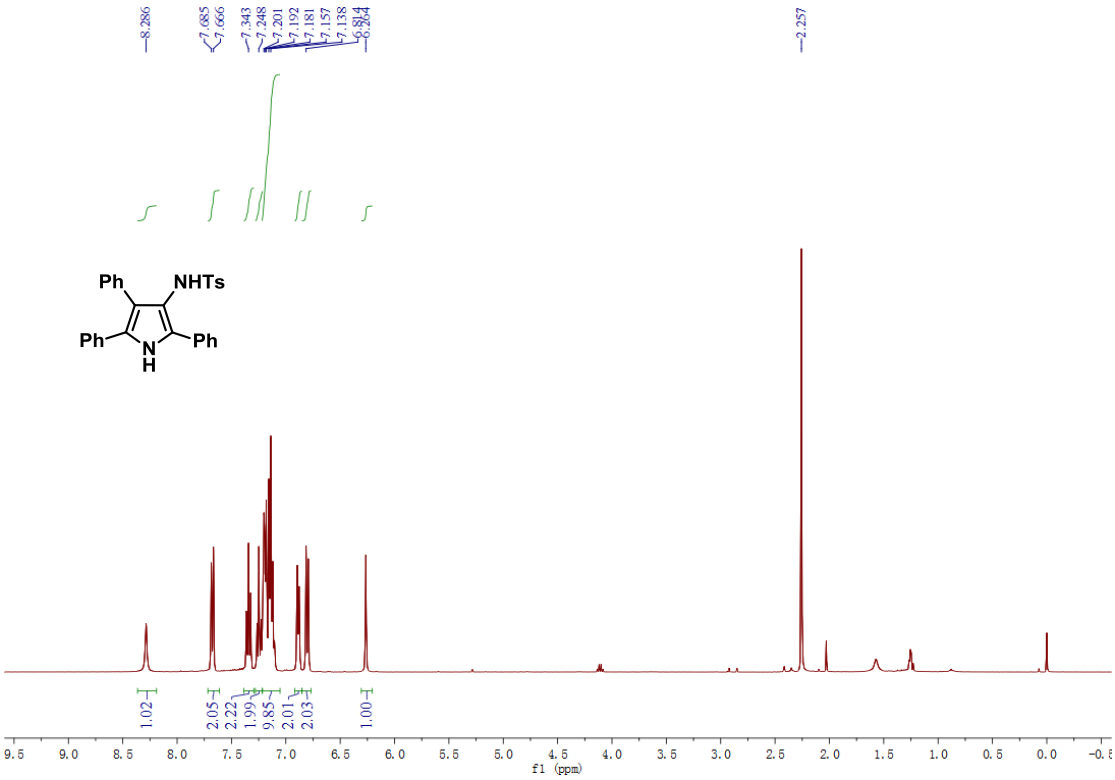
^{13}C NMR Spectrum for **3o** (Acetone-d_6, 100 MHz)



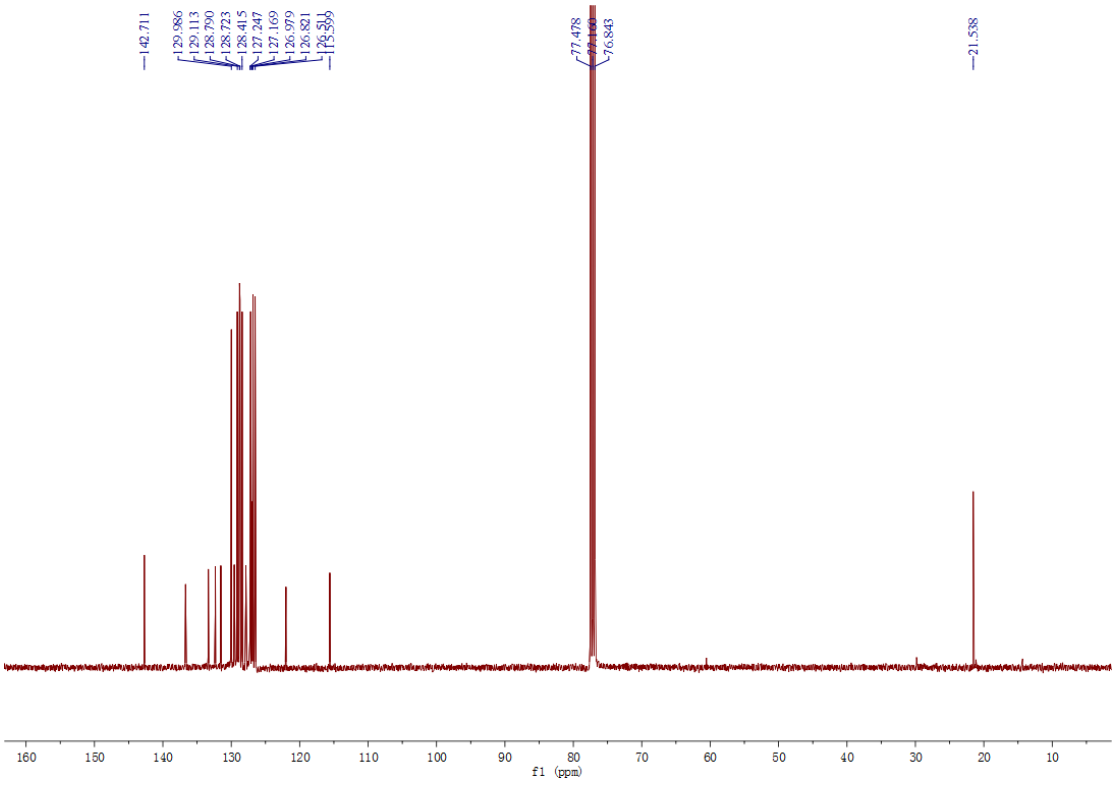
^{1}H NMR Spectrum for **3p** (Acetone-d_6, 400 MHz)



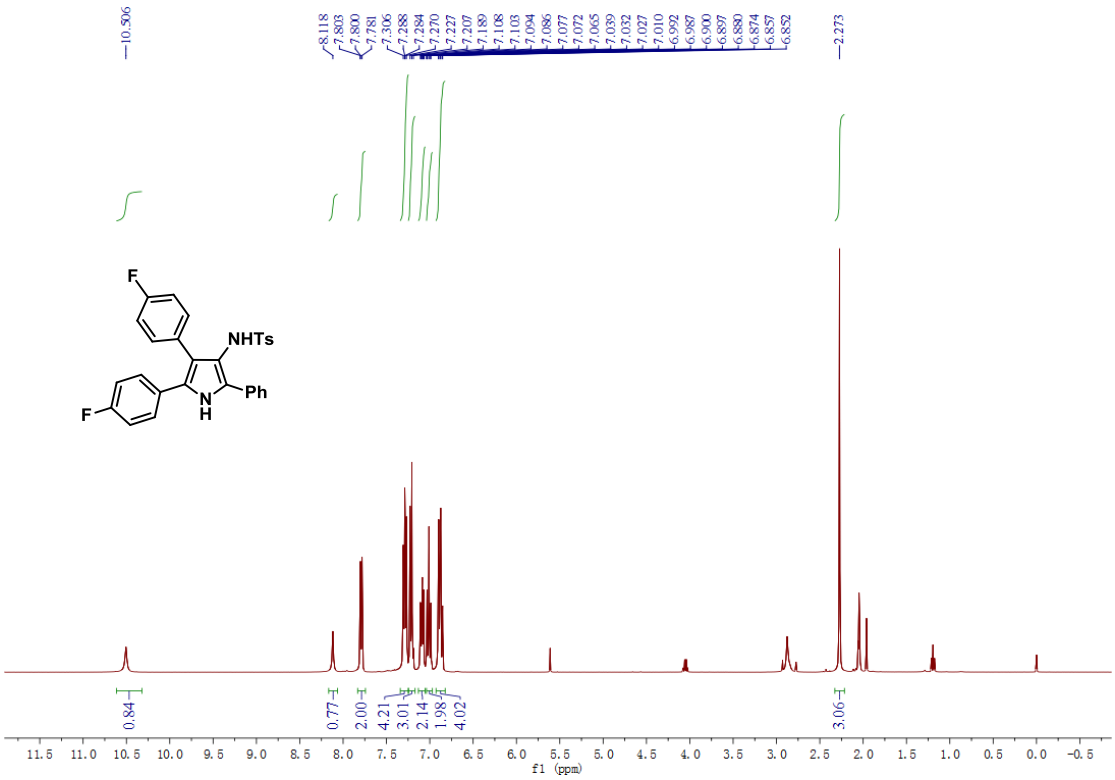
^{13}C NMR Spectrum for **3p** (Acetone-d_6, 100 MHz)



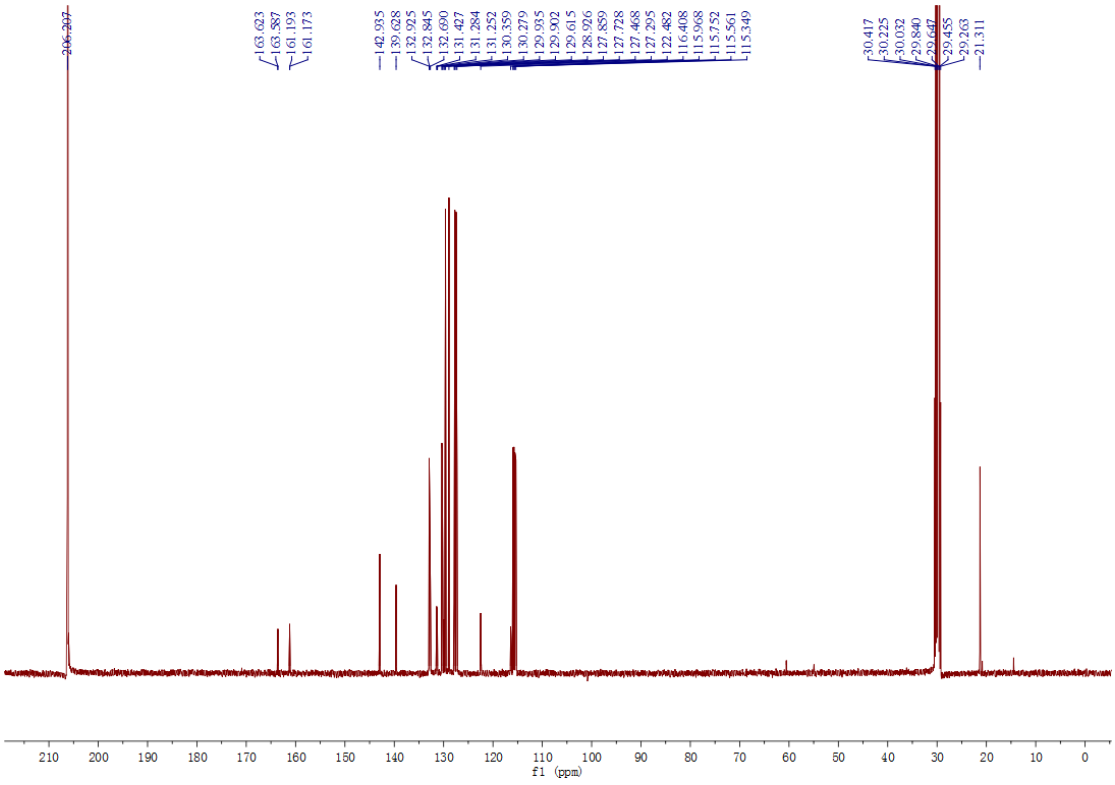
^{1}H NMR Spectrum for **5a** ($CDCl_3$, 400 MHz)



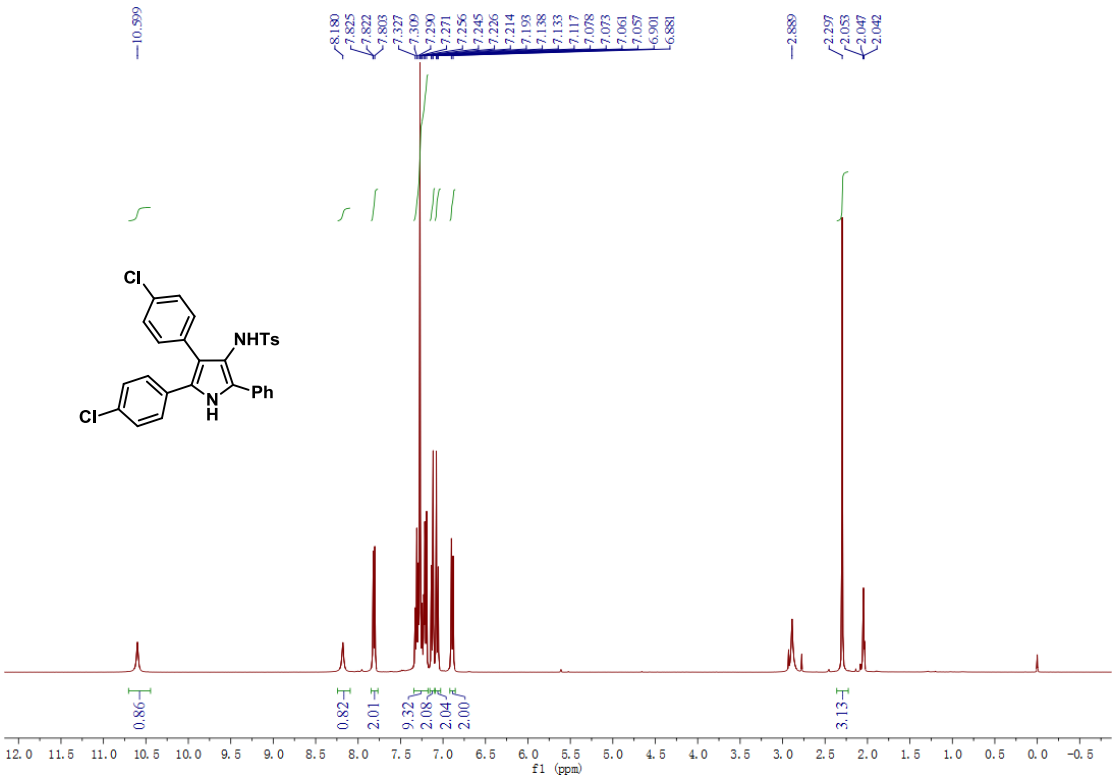
^{13}C NMR Spectrum for **5a** ($CDCl_3$, 100 MHz)



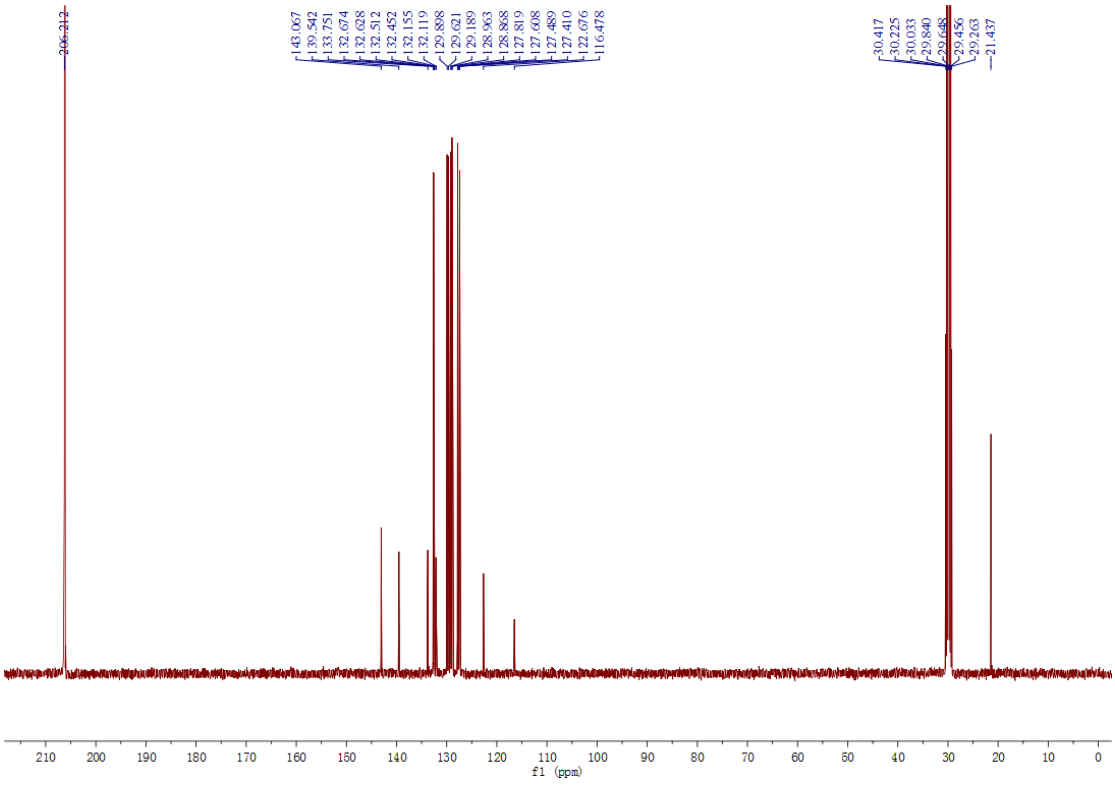
^{1}H NMR Spectrum for **5b** (Acetone-d_6, 400 MHz)



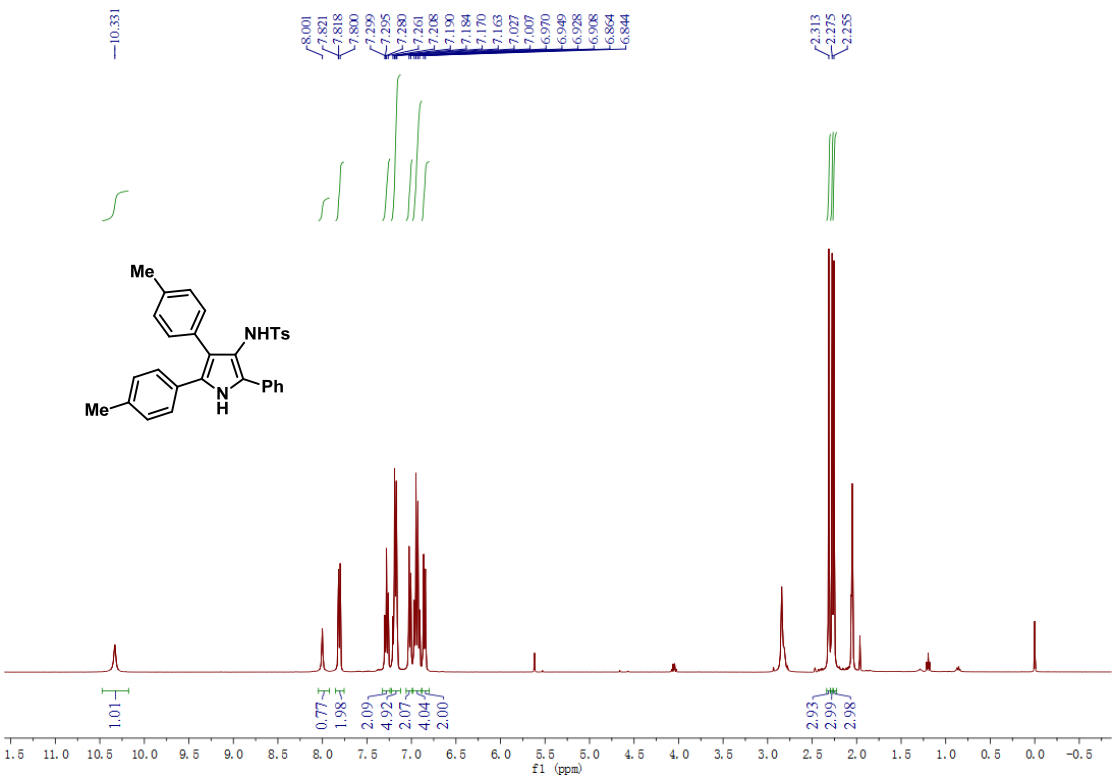
^{13}C NMR Spectrum for **5b** (Acetone-d_6, 100 MHz)



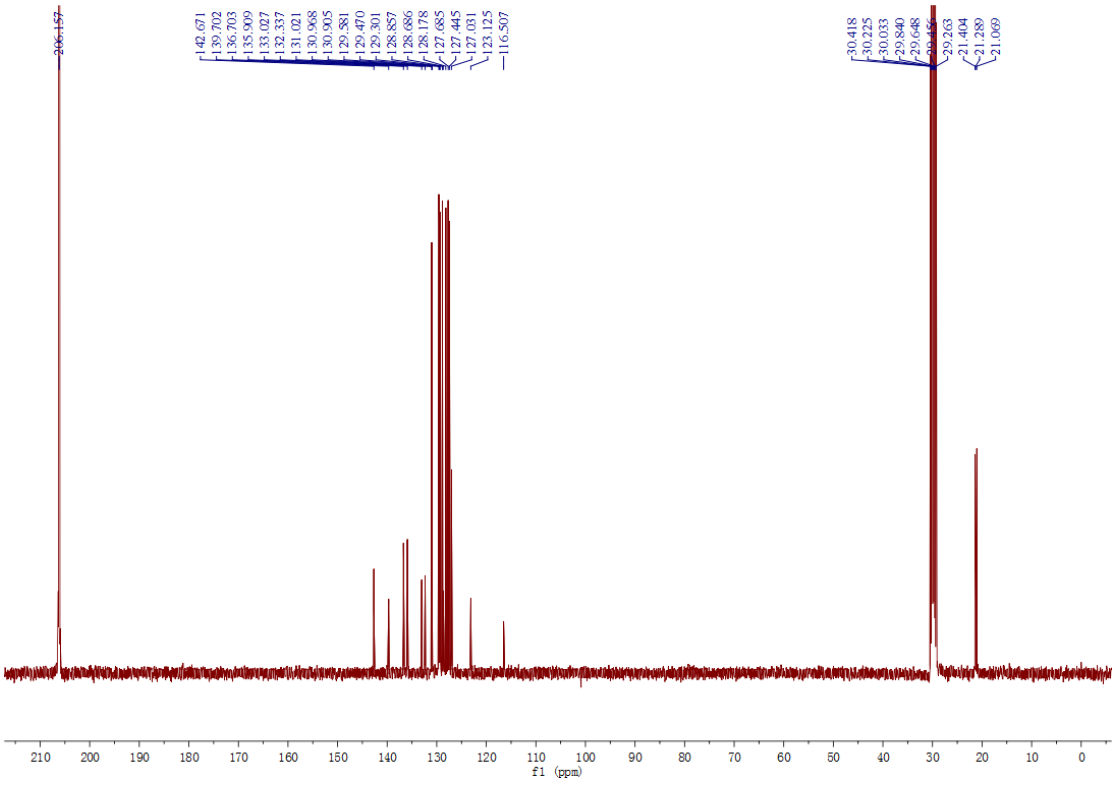
^{1}H NMR Spectrum for **5c** (Acetone-d_6, 400 MHz)



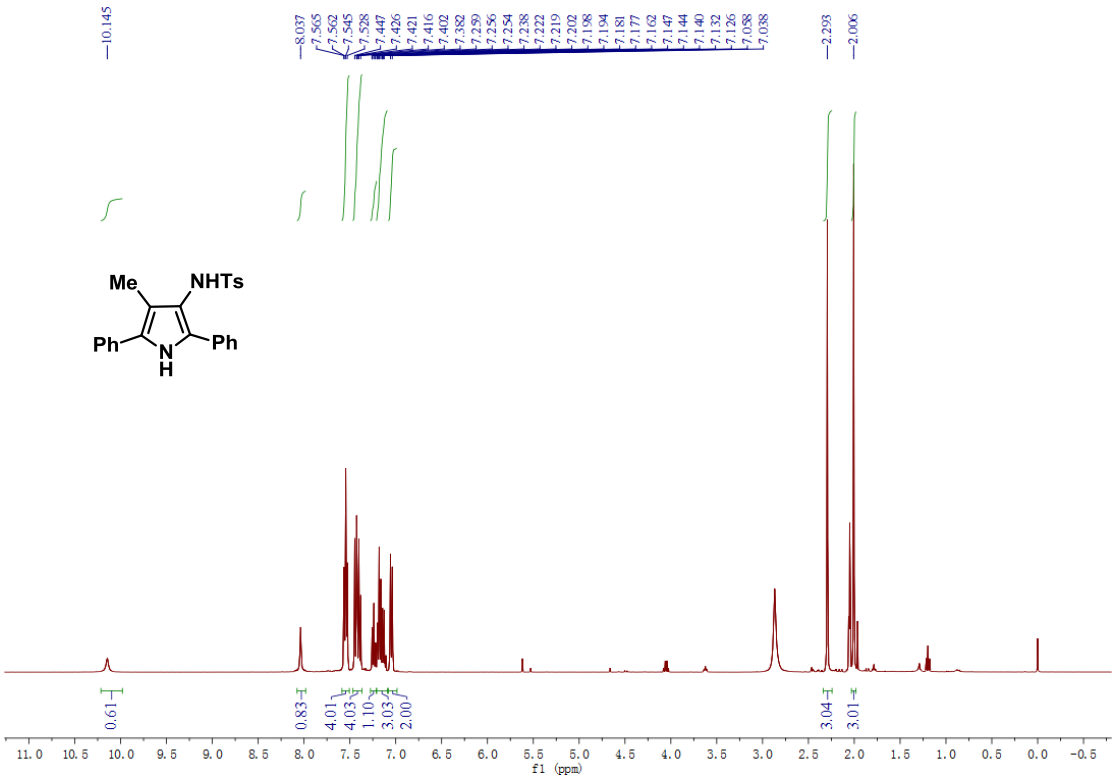
^{13}C NMR Spectrum for **5c** (Acetone-d_6, 100 MHz)



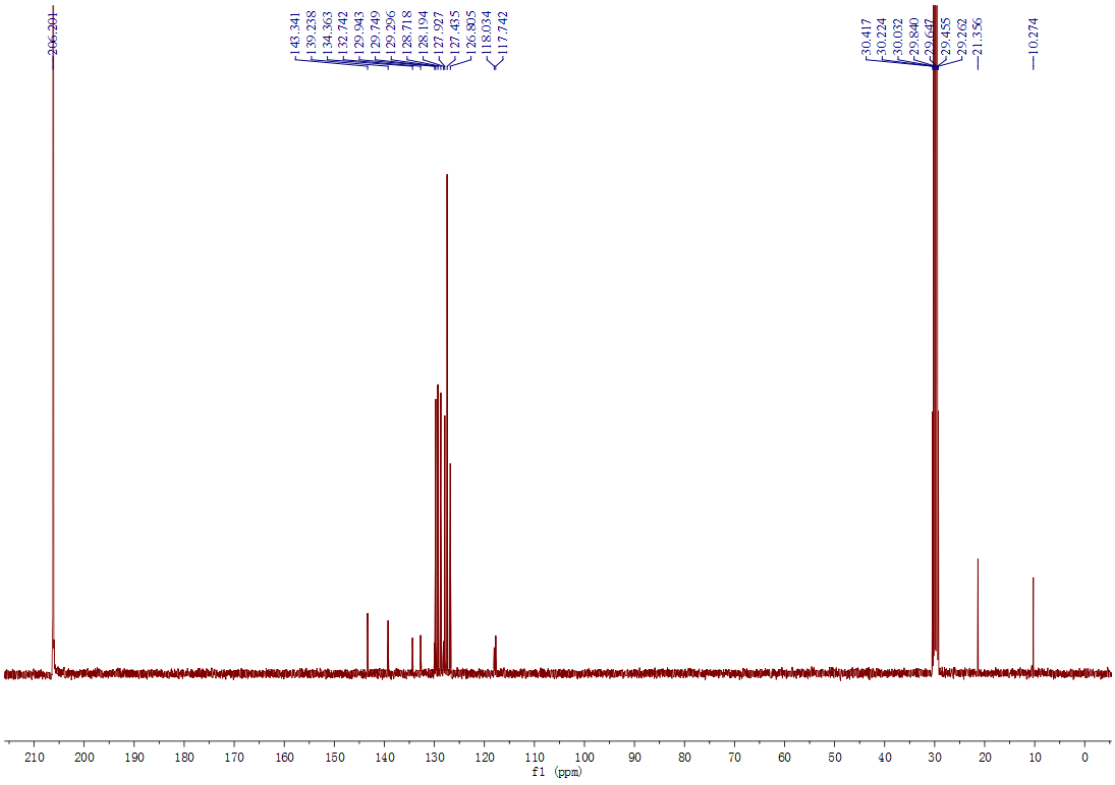
^{1}H NMR Spectrum for **5d** (Acetone-d_6, 400 MHz)



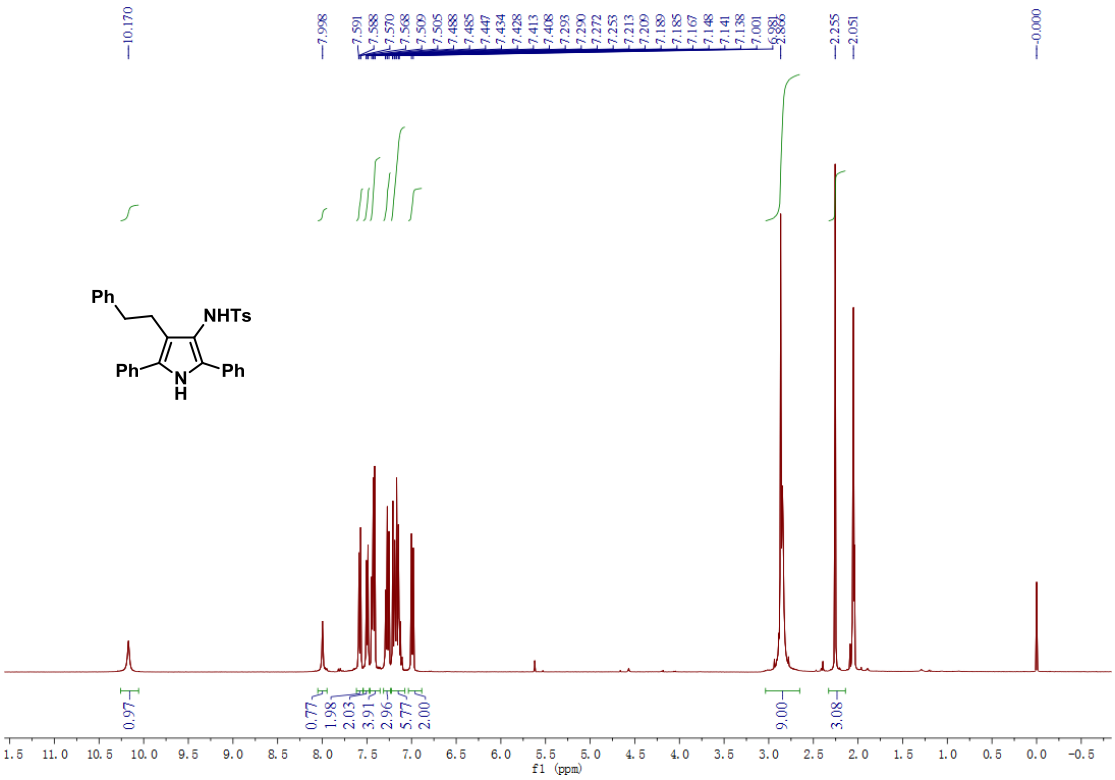
^{13}C NMR Spectrum for **5d** (Acetone-d_6, 100 MHz)



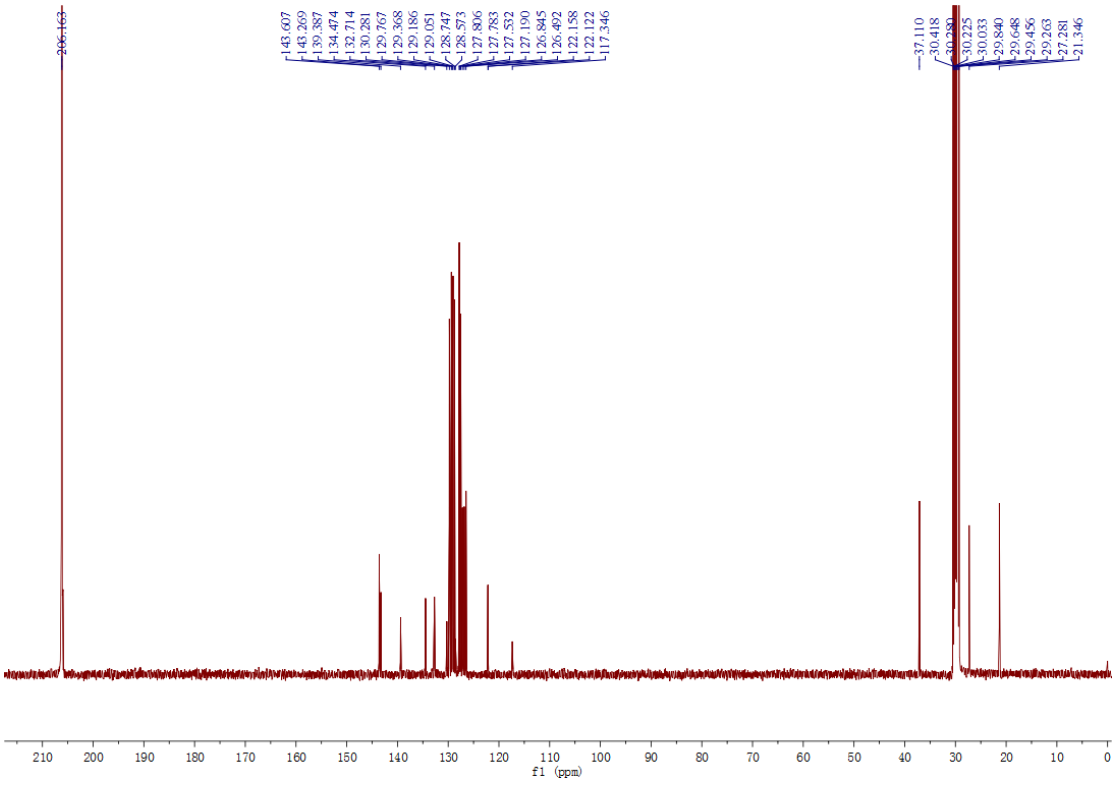
^{1}H NMR Spectrum for **5e** (Acetone-d_6, 400 MHz)



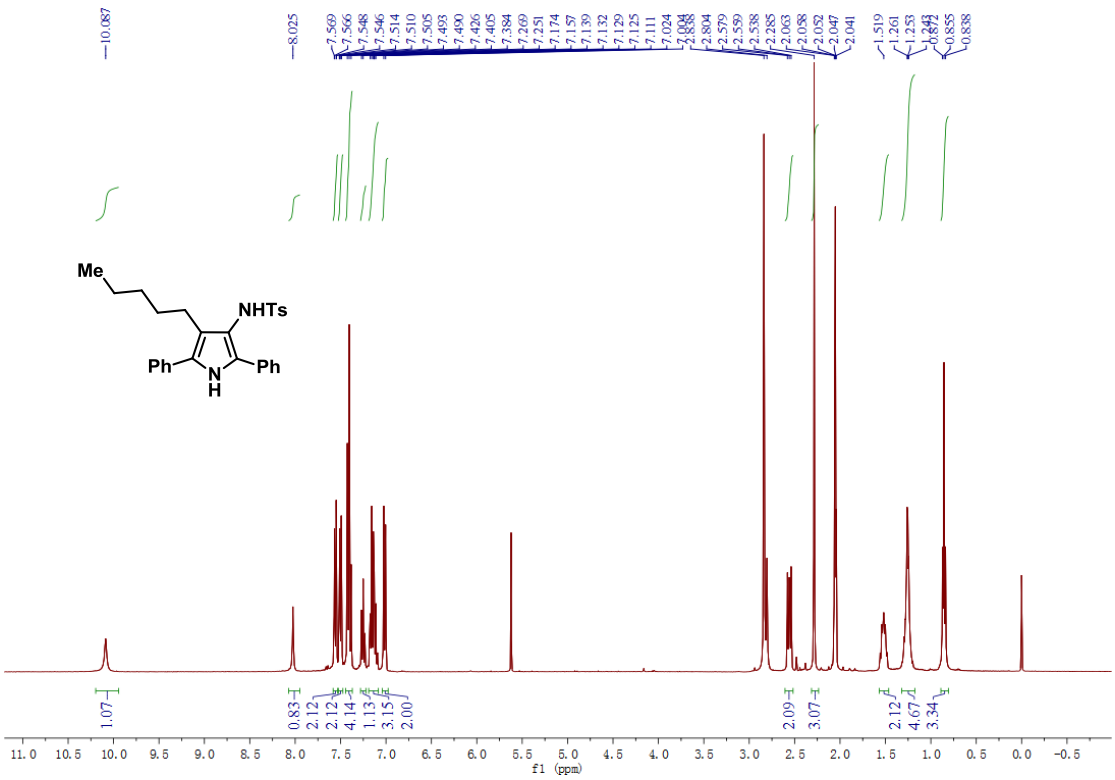
^{13}C NMR Spectrum for **5e** (Acetone-d_6, 100 MHz)



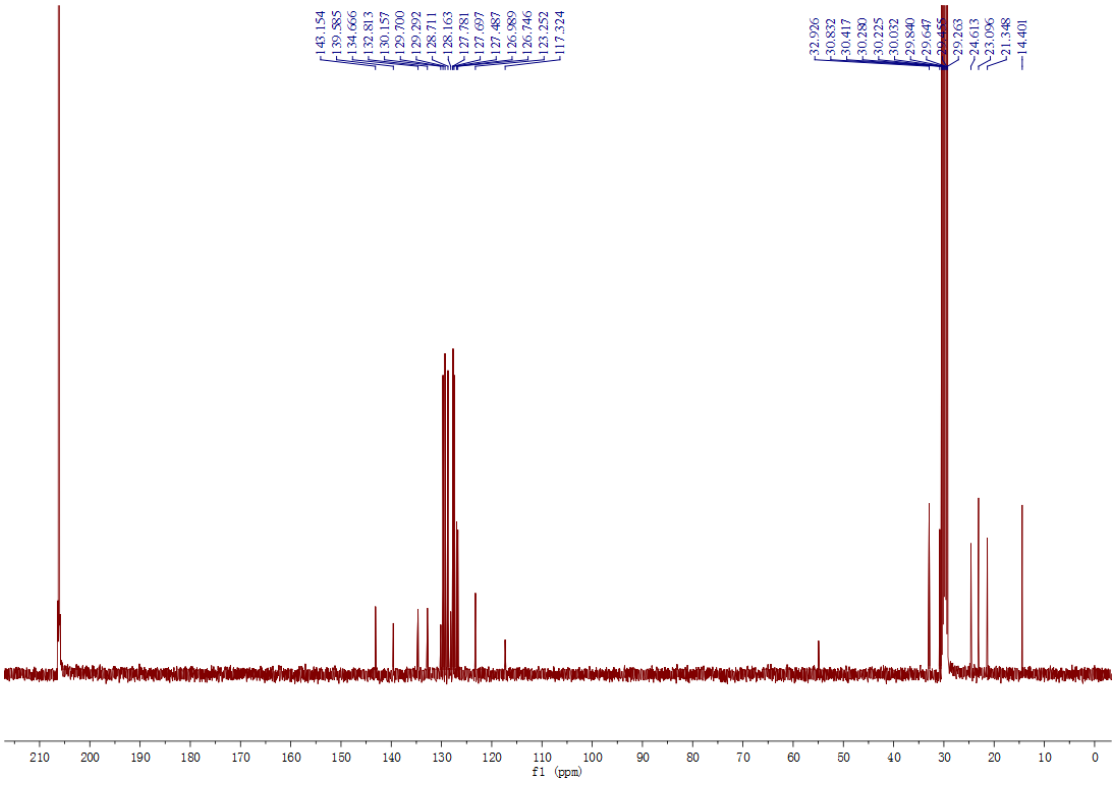
^{1}H NMR Spectrum for **5f** (Acetone-d_6, 400 MHz)



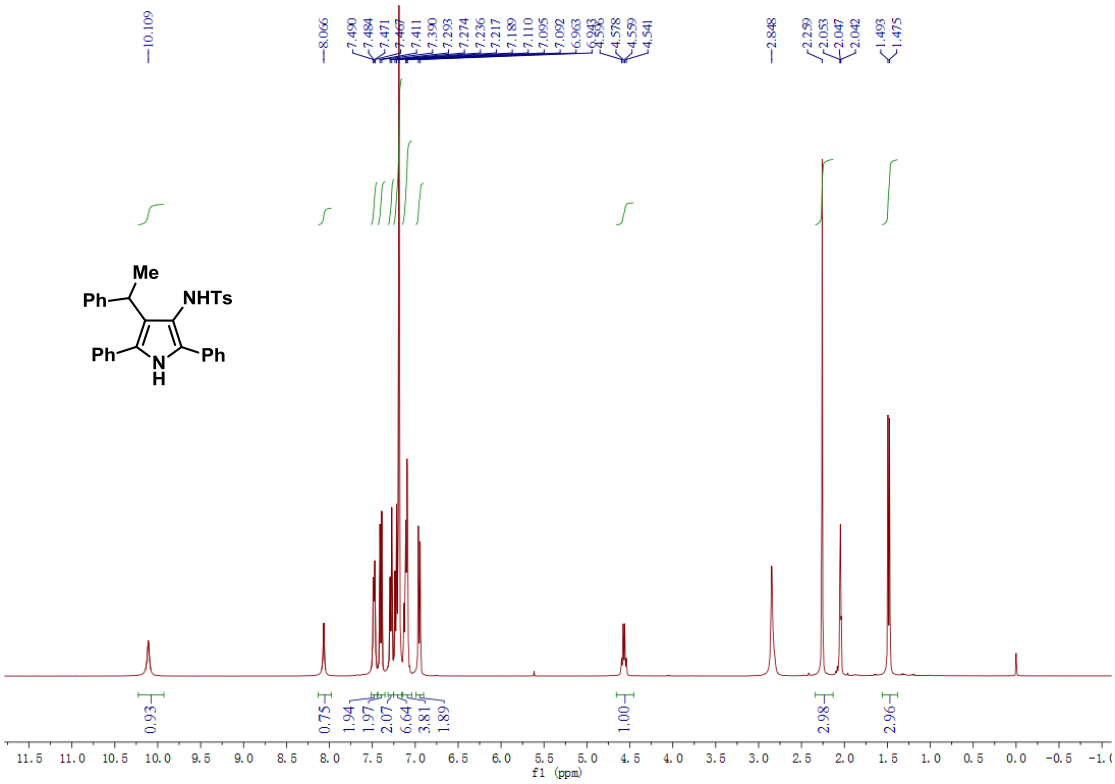
^{13}C NMR Spectrum for **5f** (Acetone-d_6, 100 MHz)



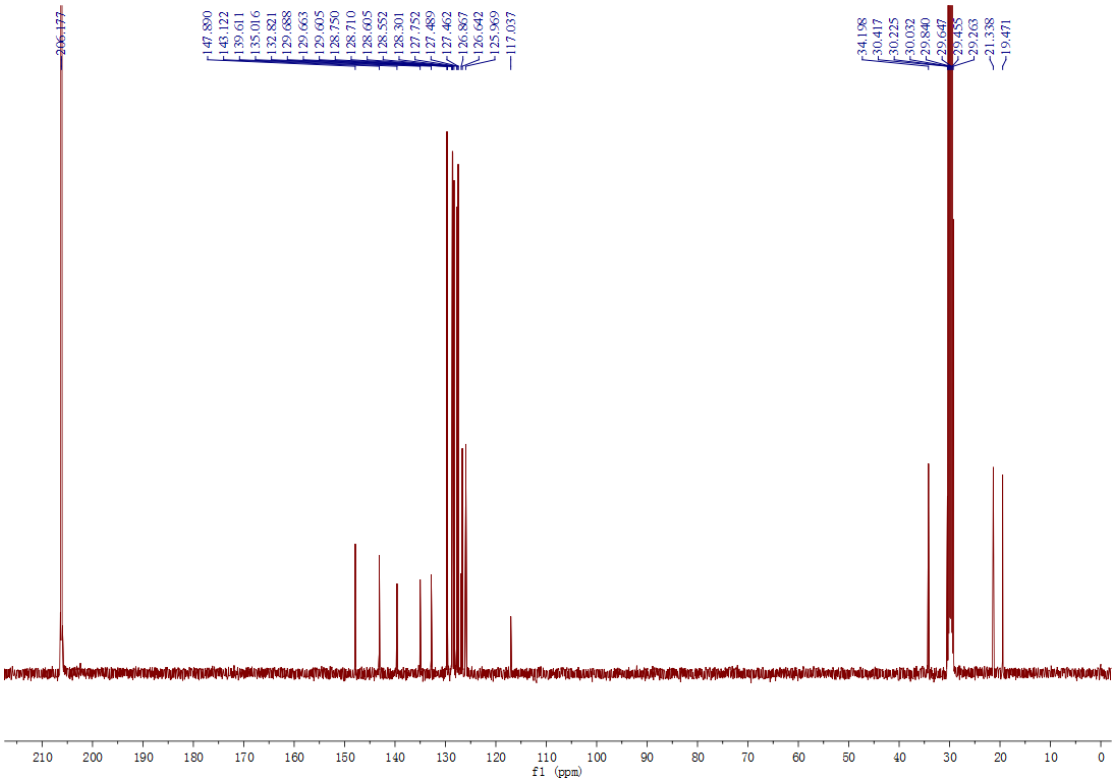
^{1}H NMR Spectrum for **5g** (Acetone-d_6, 400 MHz)



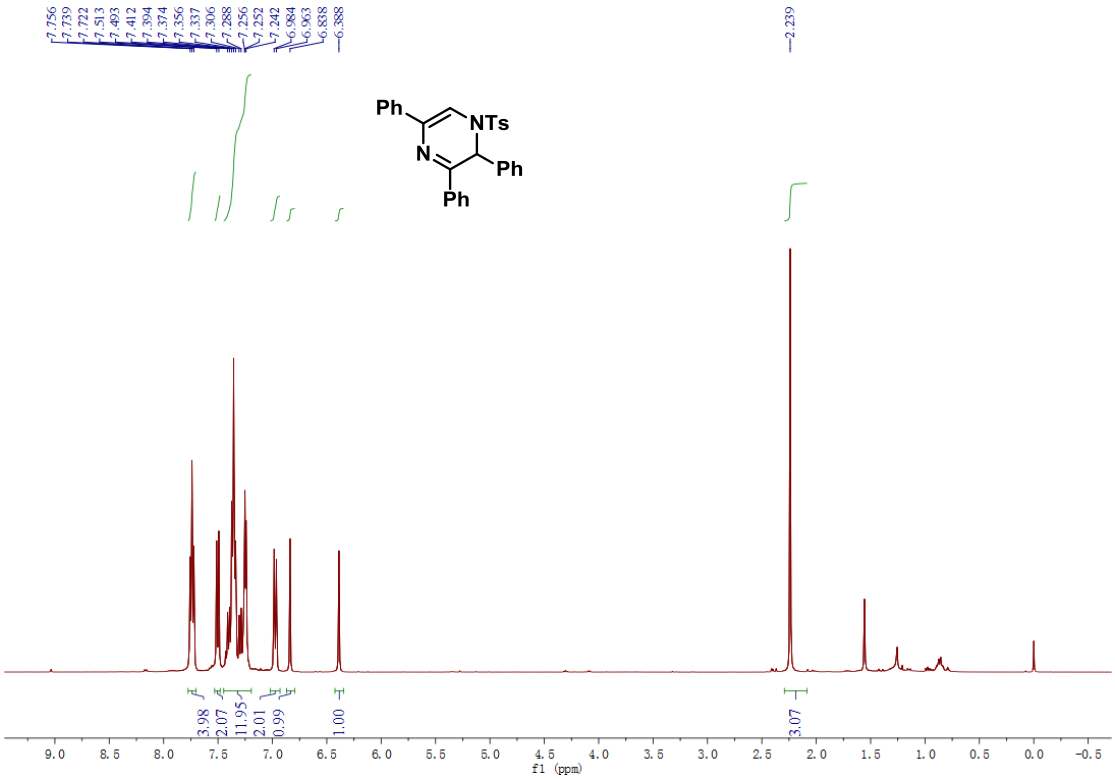
^{13}C NMR Spectrum for **5g** (Acetone-d_6, 100 MHz)



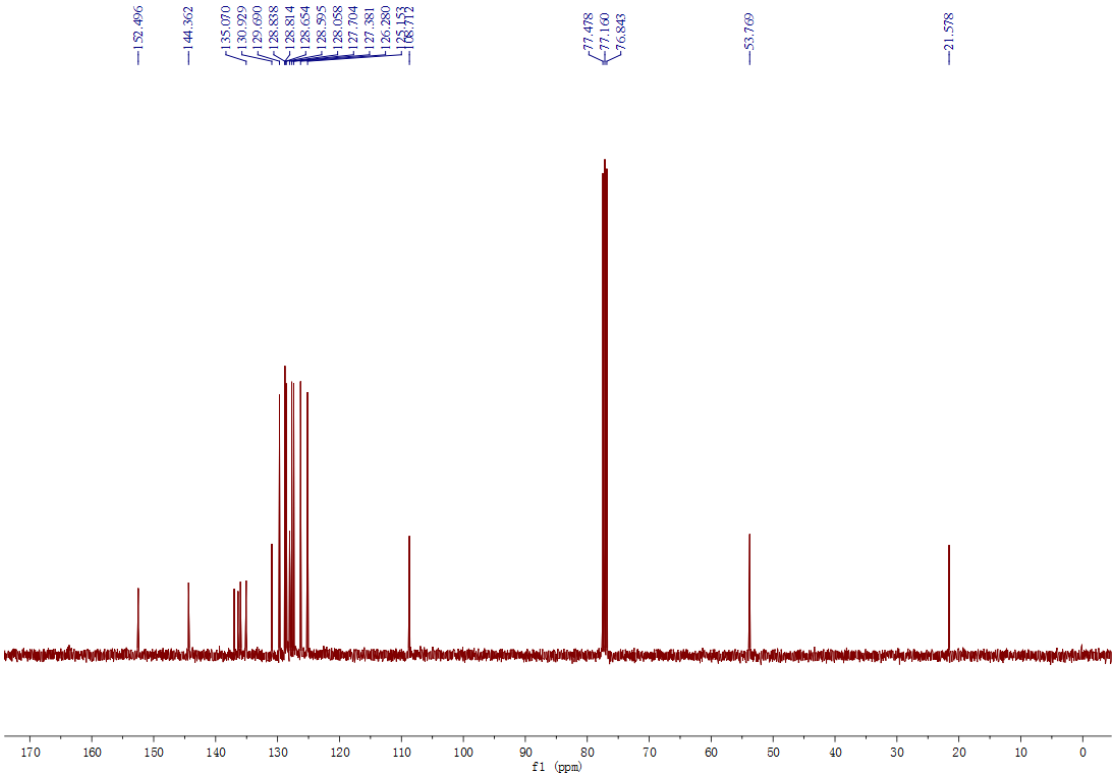
^{1}H NMR Spectrum for **5h** (Acetone-d_6, 400 MHz)



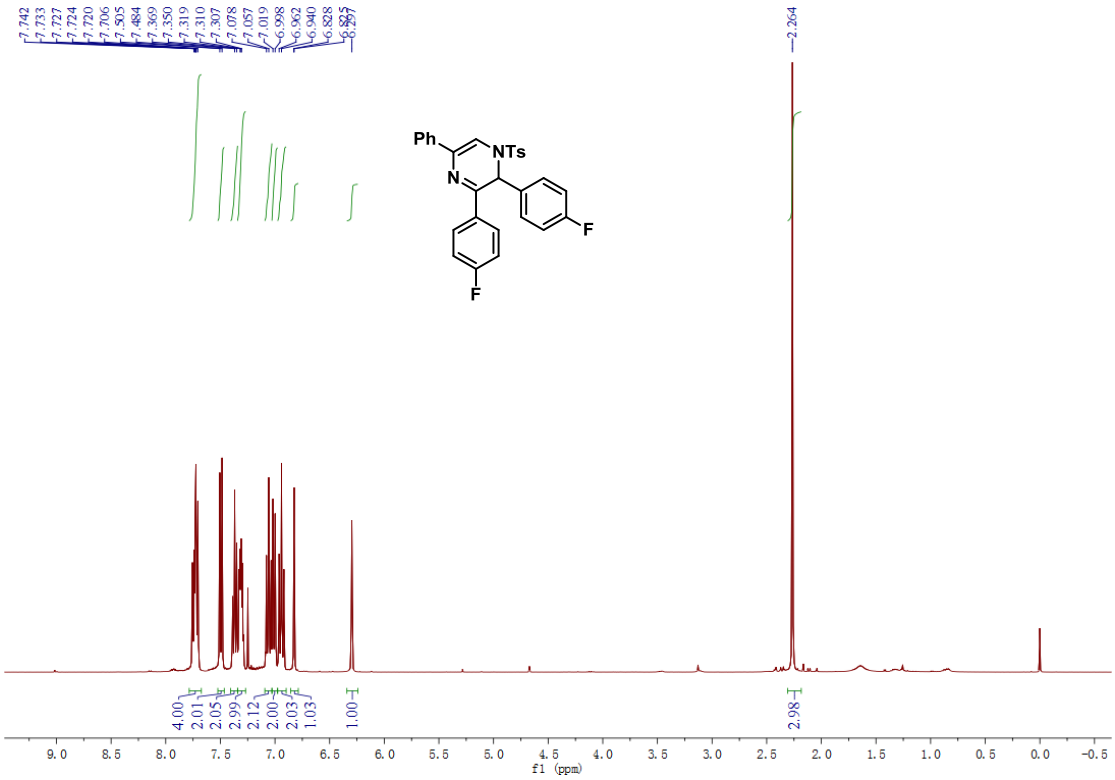
^{13}C NMR Spectrum for **5h** (Acetone-d_6, 100 MHz)



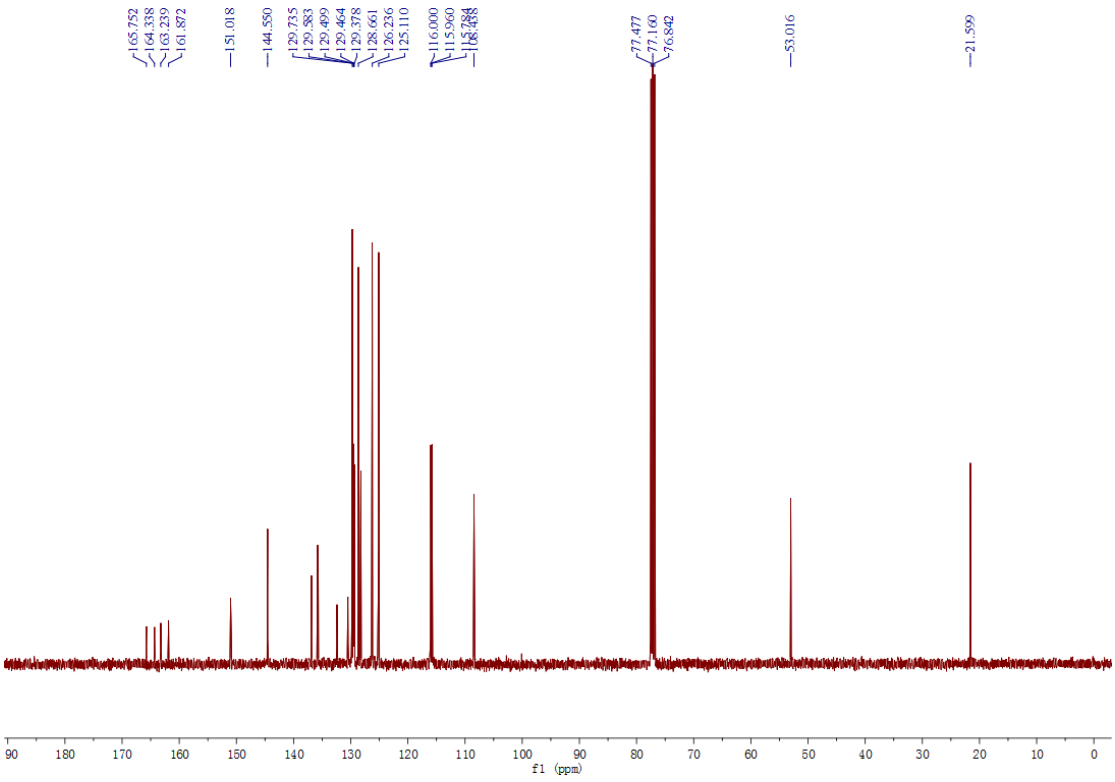
^{1}H NMR Spectrum for **6a** ($CDCl_3$, 400 MHz)



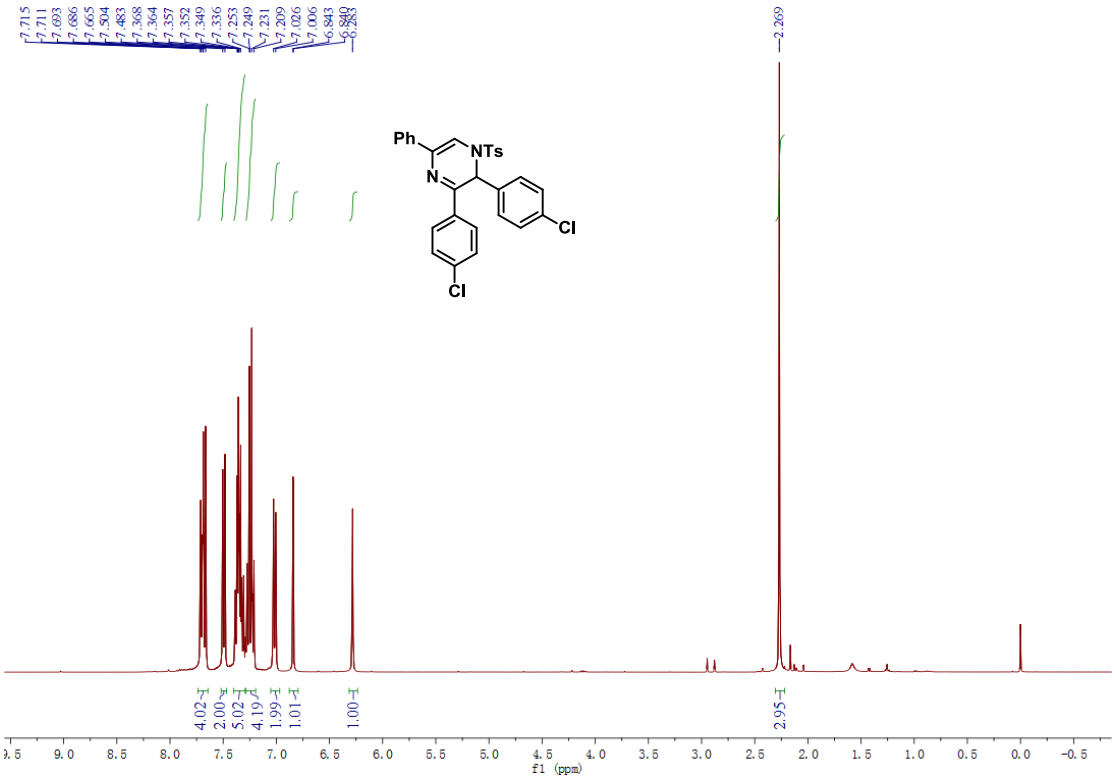
^{13}C NMR Spectrum for **6a** ($CDCl_3$, 100 MHz)



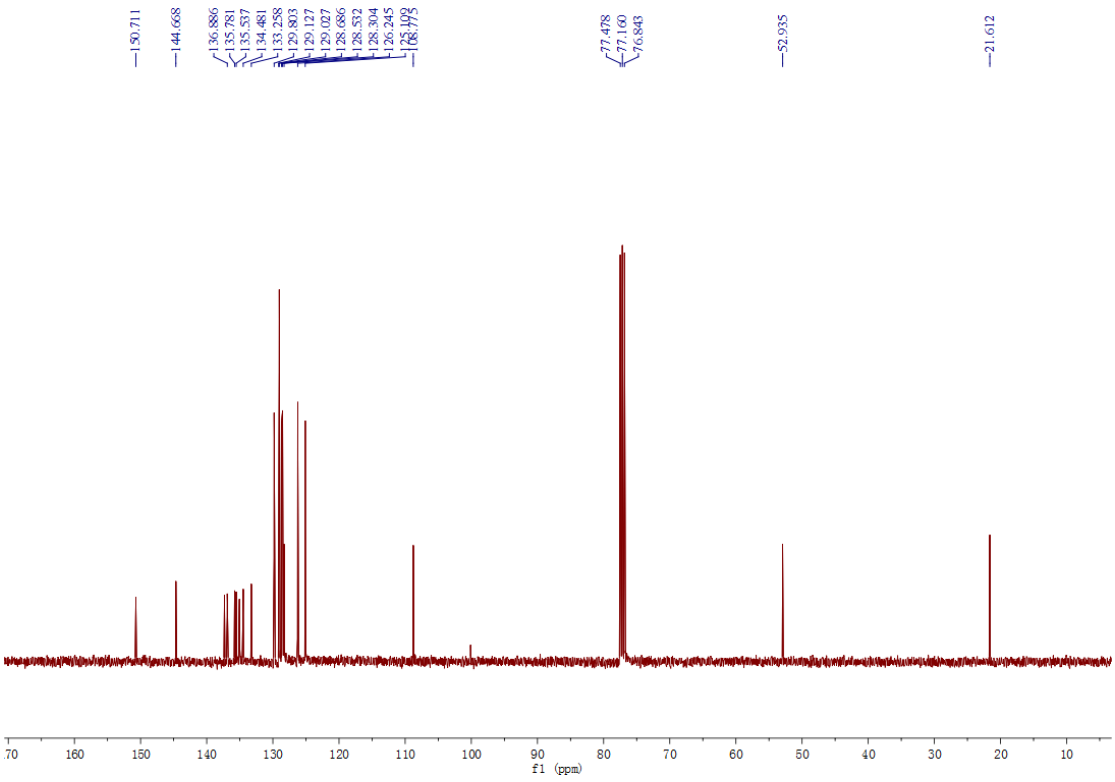
^{1}H NMR Spectrum for **6b** ($CDCl_3$, 400 MHz)



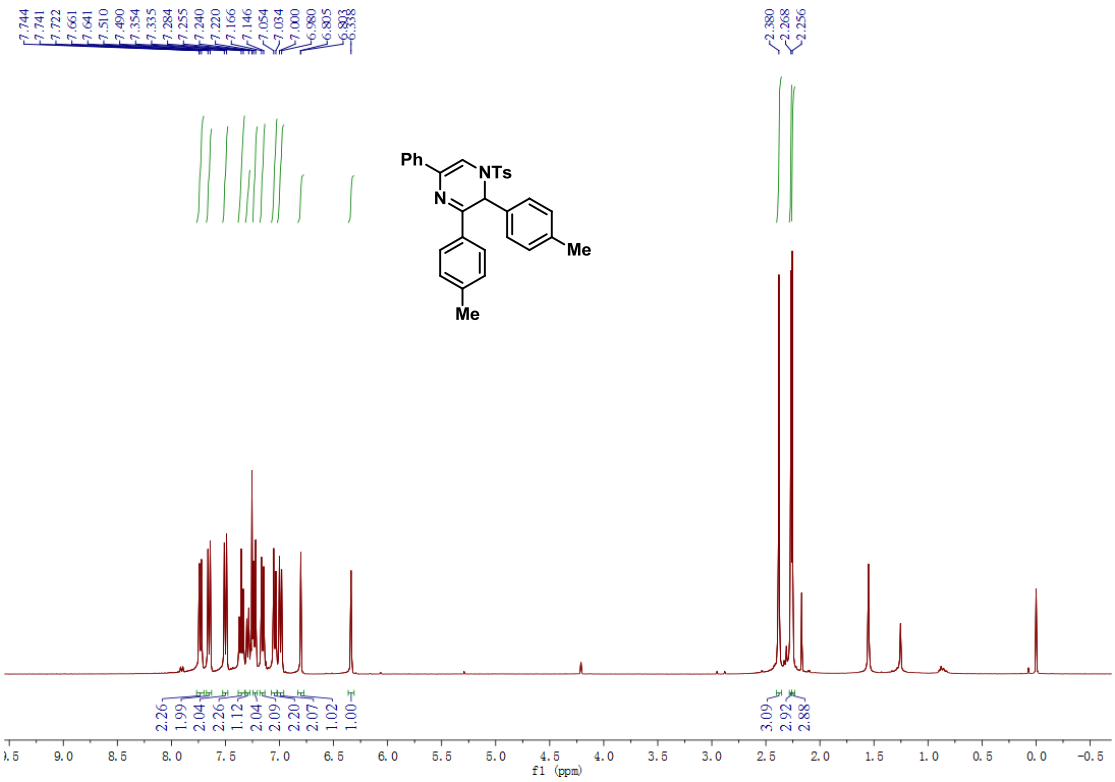
^{13}C NMR Spectrum for **6b** ($CDCl_3$, 100 MHz)



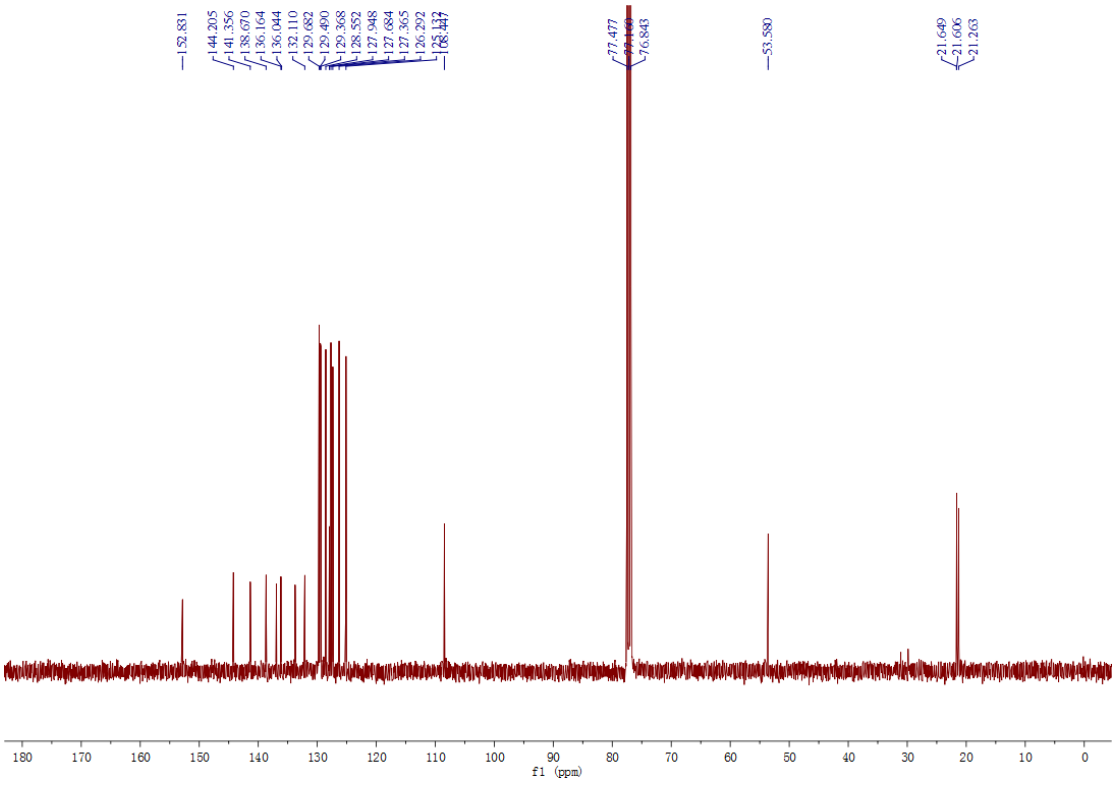
^{1}H NMR Spectrum for **6c** ($CDCl_3$, 400 MHz)



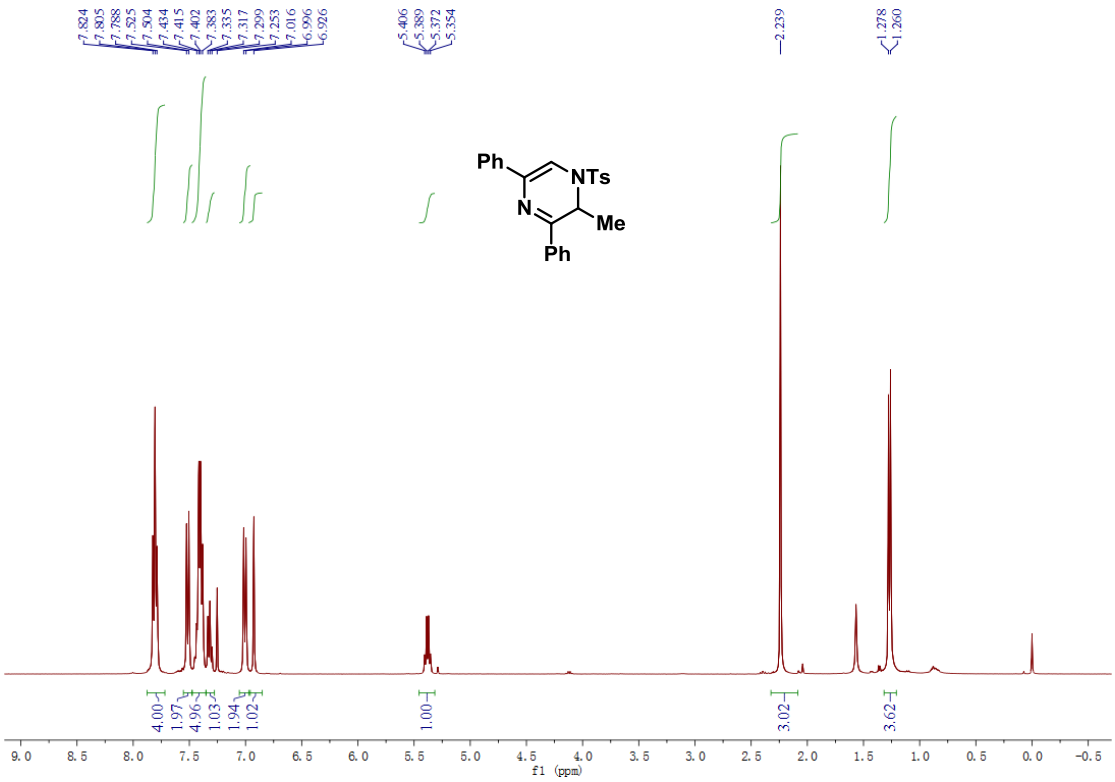
^{13}C NMR Spectrum for **6c** ($CDCl_3$, 100 MHz)



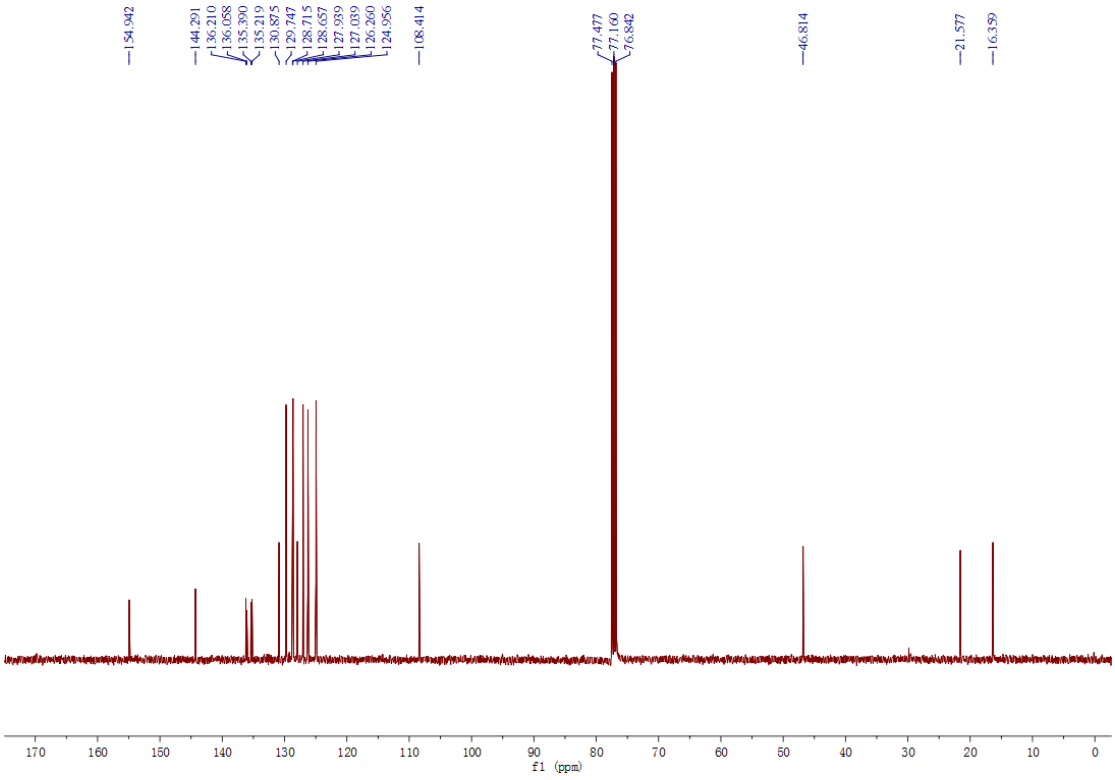
^{1}H NMR Spectrum for **6d** ($CDCl_3$, 400 MHz)



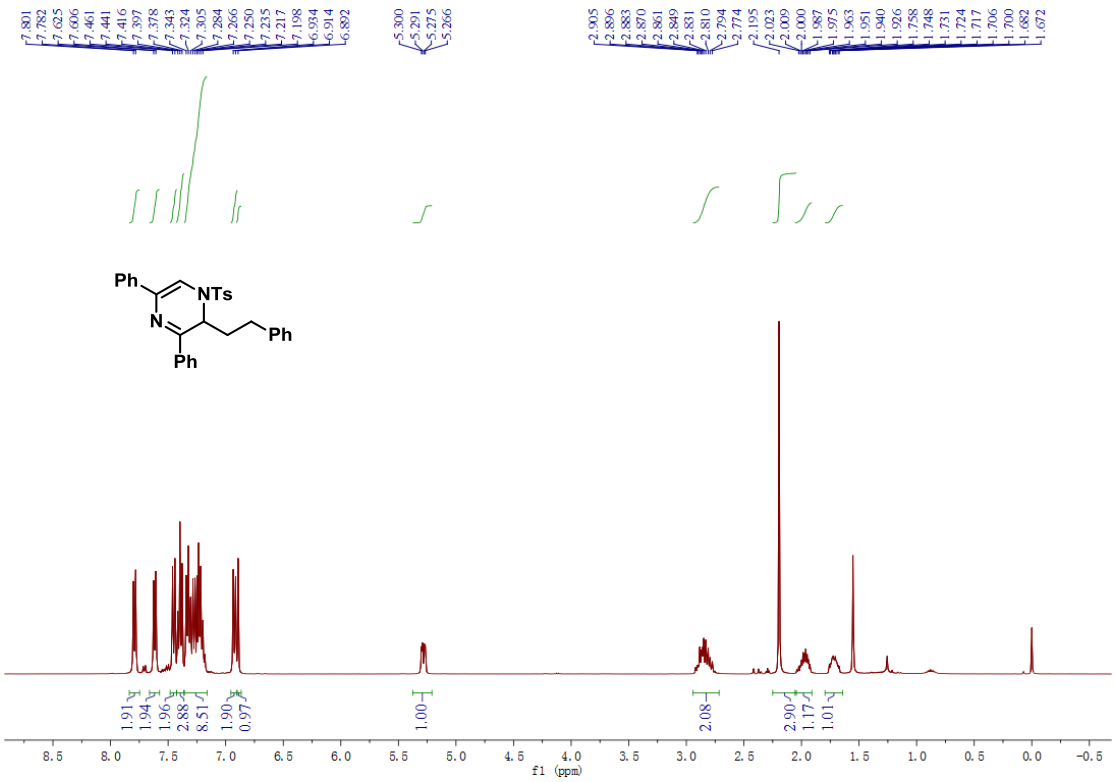
^{13}C NMR Spectrum for **6d** ($CDCl_3$, 100 MHz)



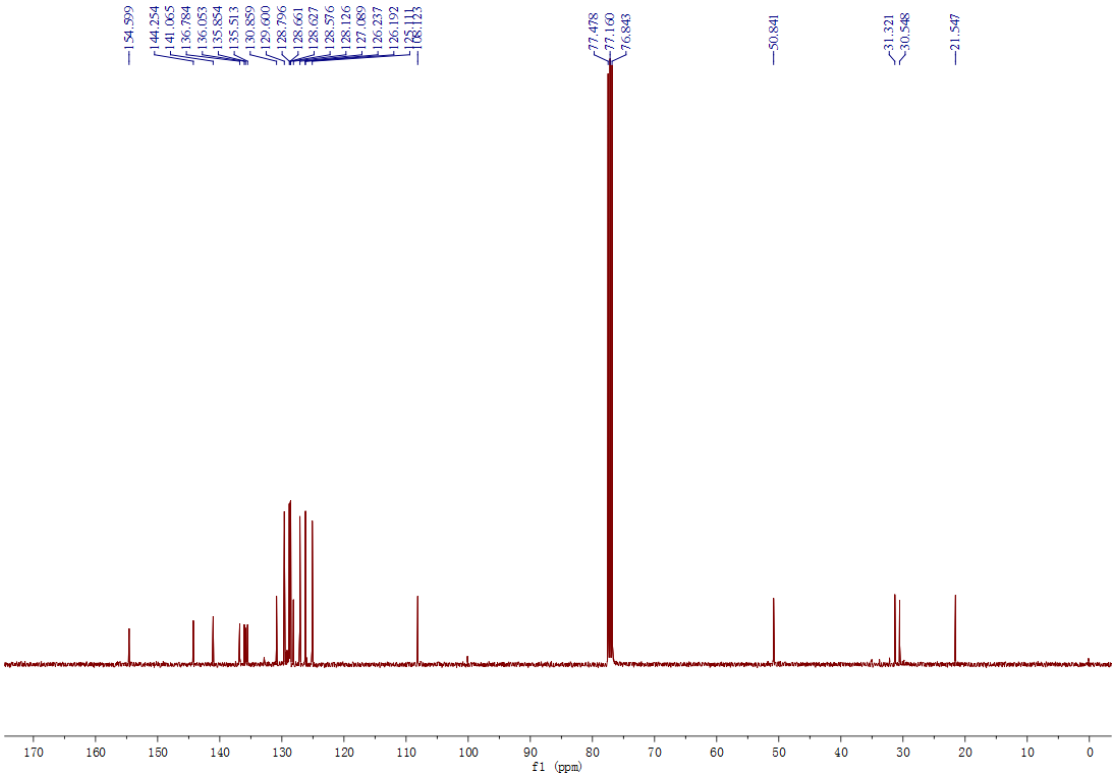
^{1}H NMR Spectrum for **6e** ($CDCl_3$, 400 MHz)



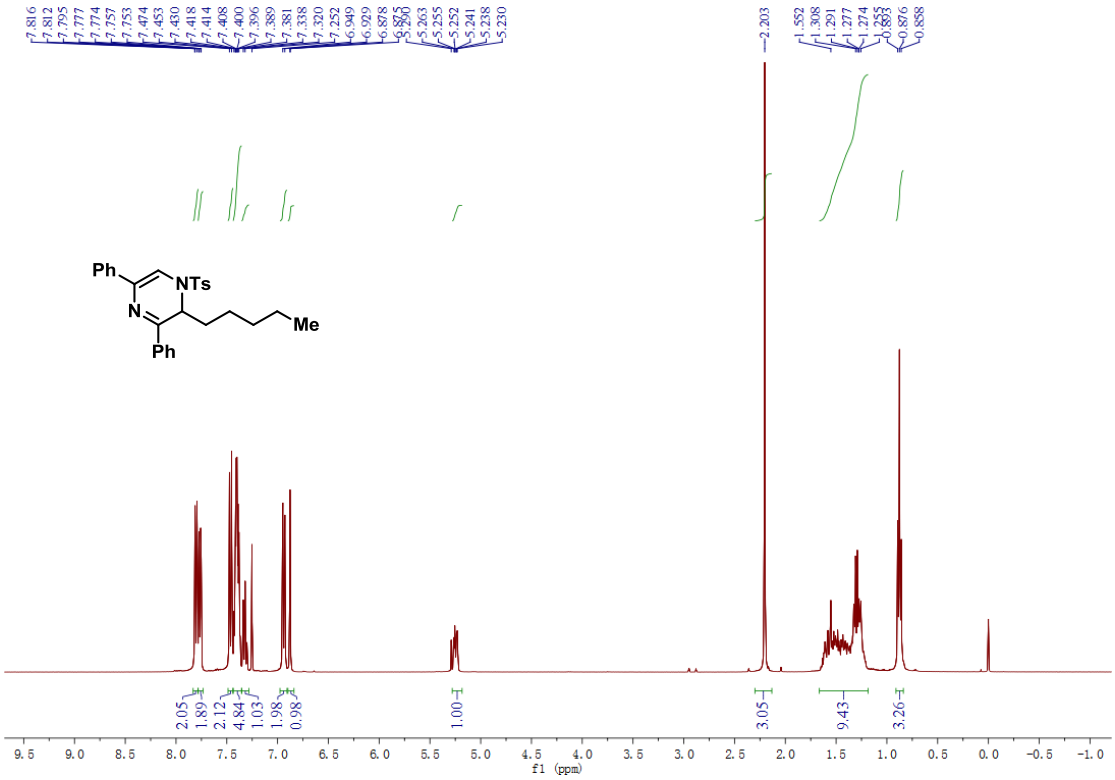
^{13}C NMR Spectrum for **6e** ($CDCl_3$, 100 MHz)



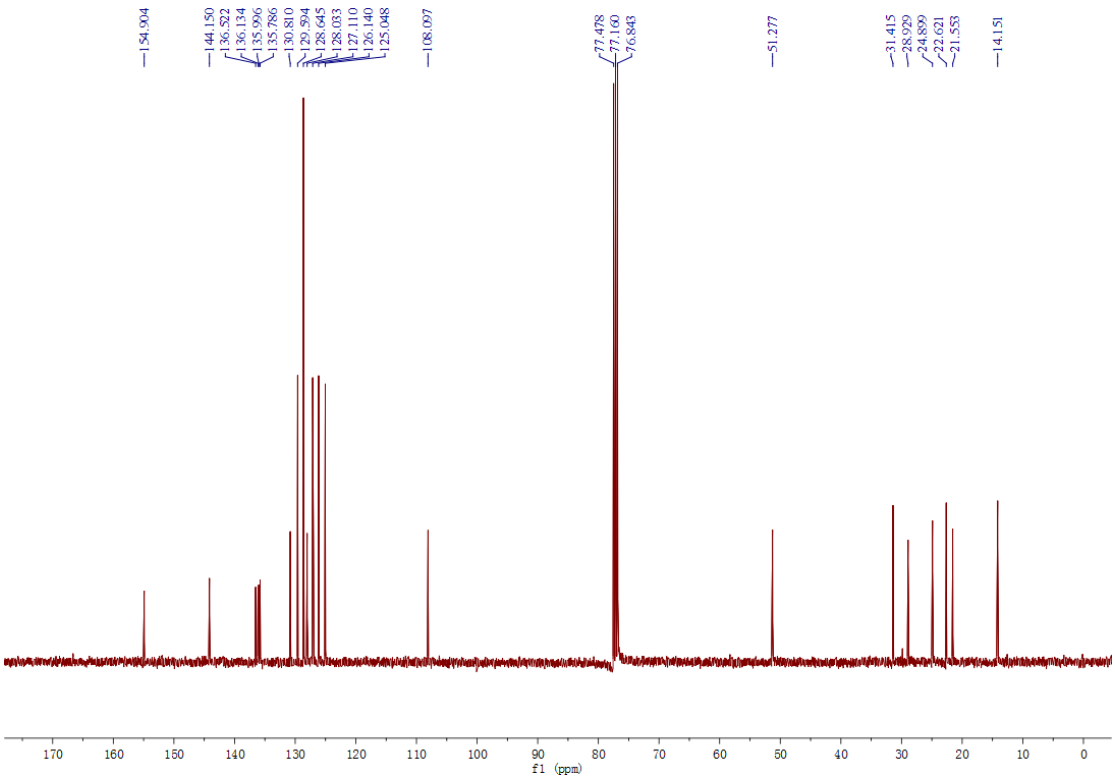
^{1}H NMR Spectrum for **6f** ($CDCl_3$, 400 MHz)



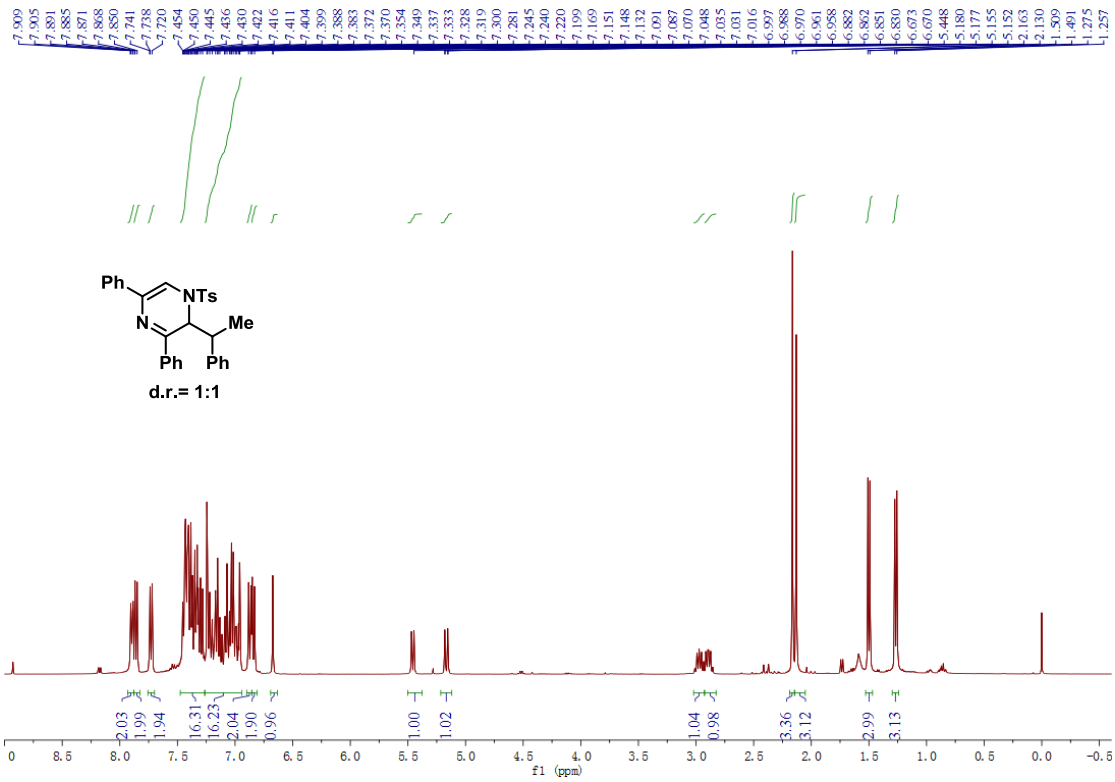
^{13}C NMR Spectrum for **6f** ($CDCl_3$, 100 MHz)



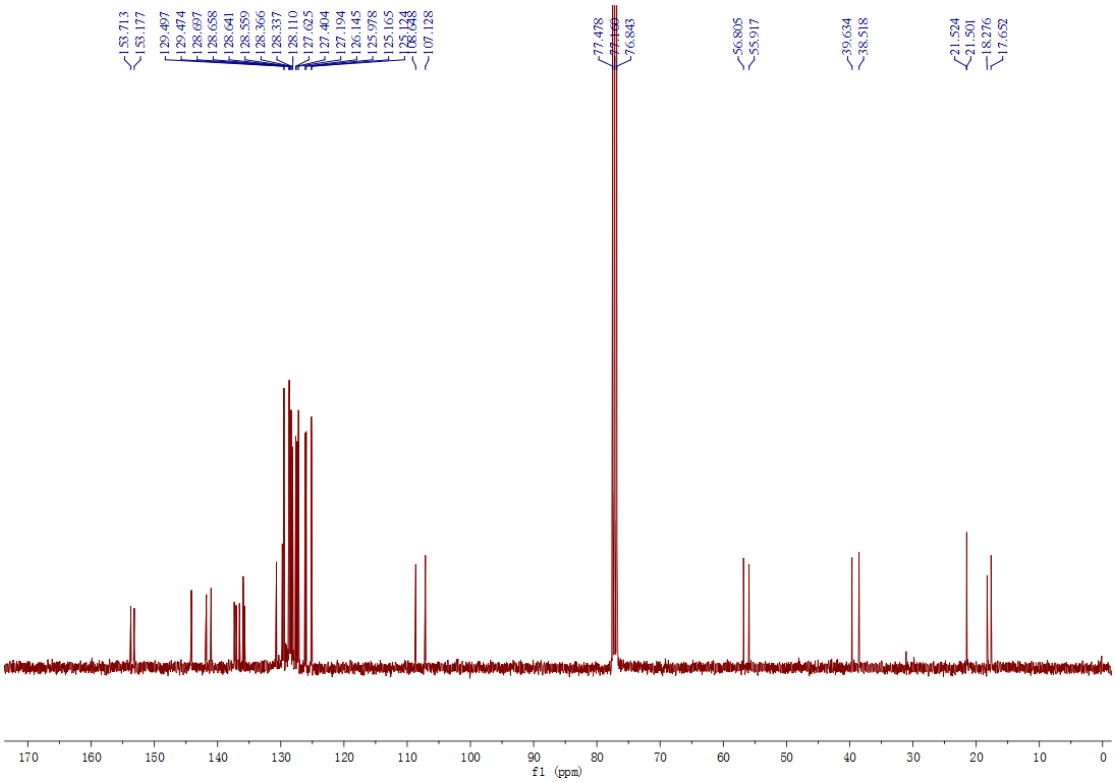
^{1}H NMR Spectrum for **6g** ($CDCl_3$, 400 MHz)



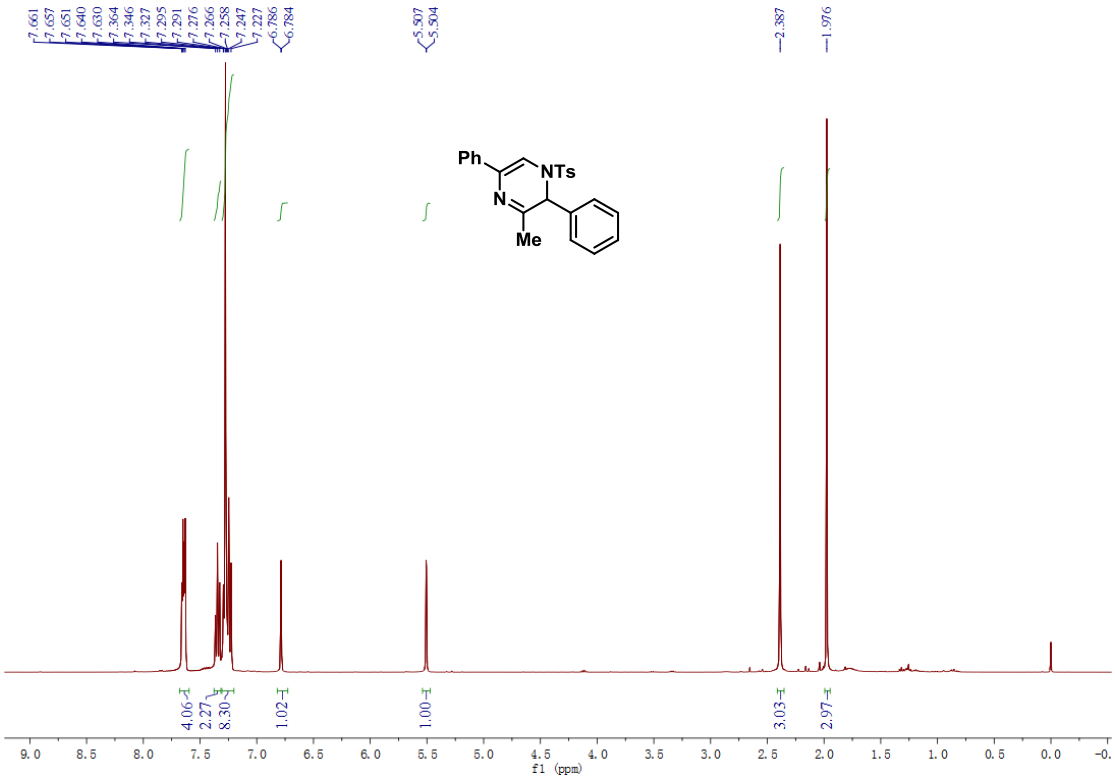
^{13}C NMR Spectrum for **6g** ($CDCl_3$, 100 MHz)



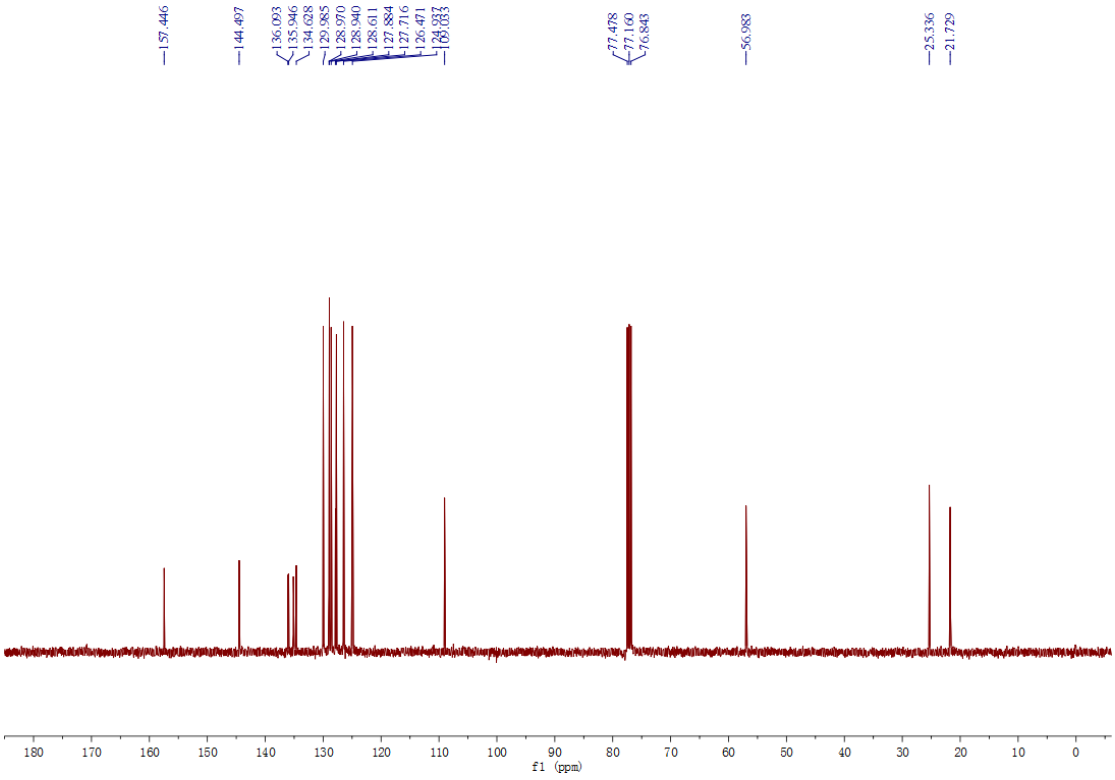
^{1}H NMR Spectrum for **6h** ($CDCl_3$, 400 MHz)



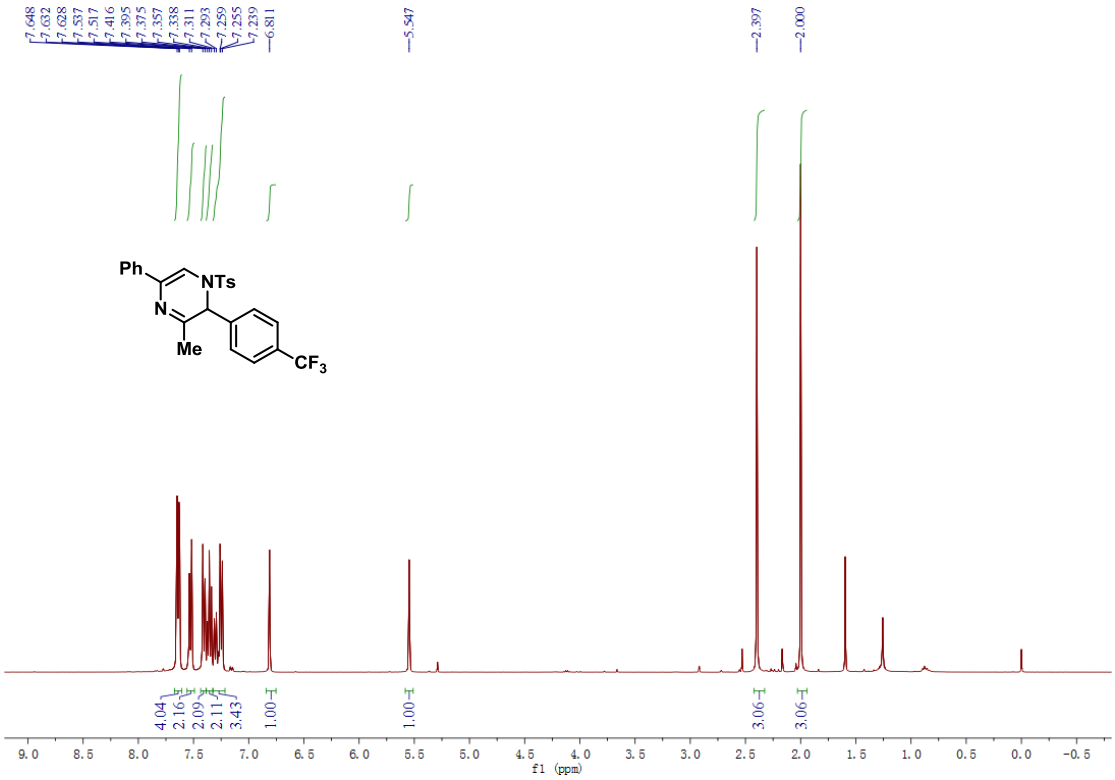
^{13}C NMR Spectrum for **6h** ($CDCl_3$, 100 MHz)



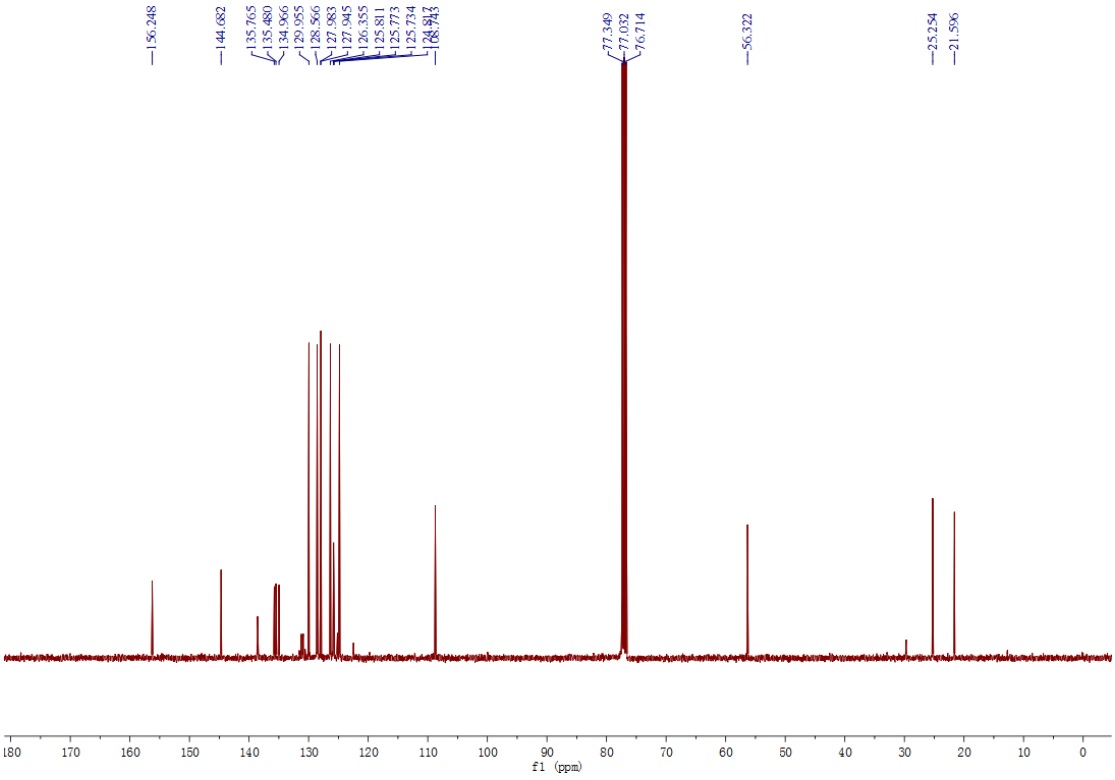
^{1}H NMR Spectrum for **8a** ($CDCl_3$, 400 MHz)



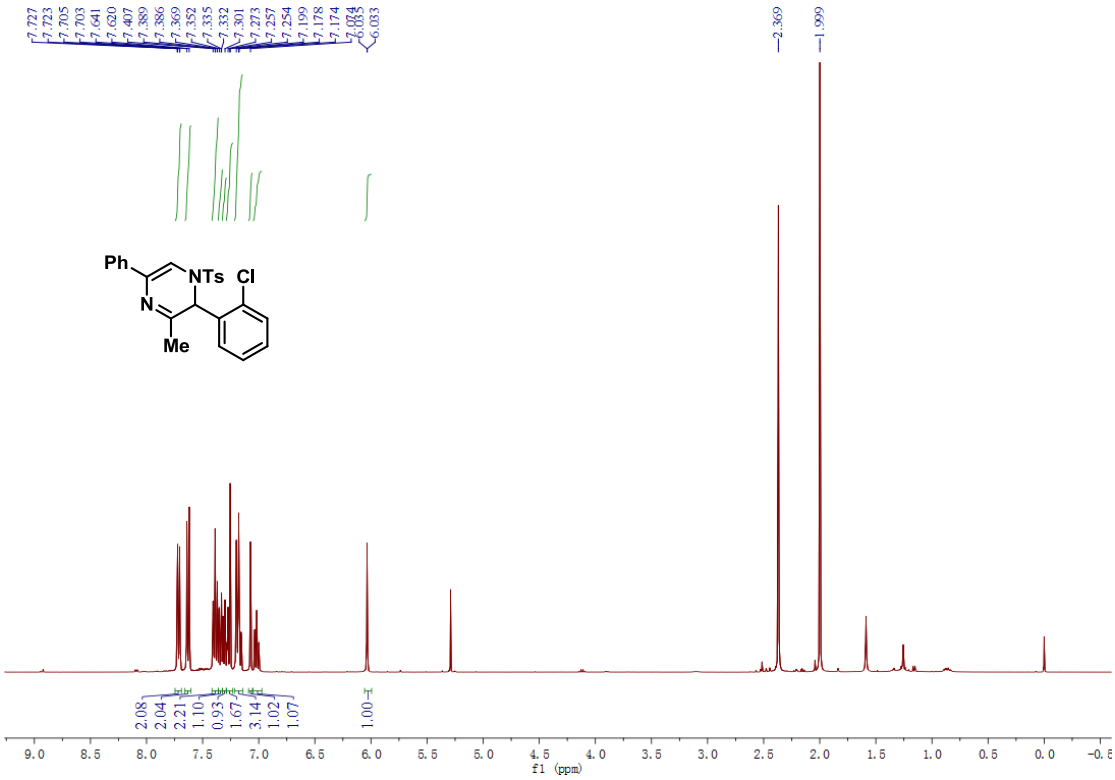
^{13}C NMR Spectrum for **8a** ($CDCl_3$, 100 MHz)



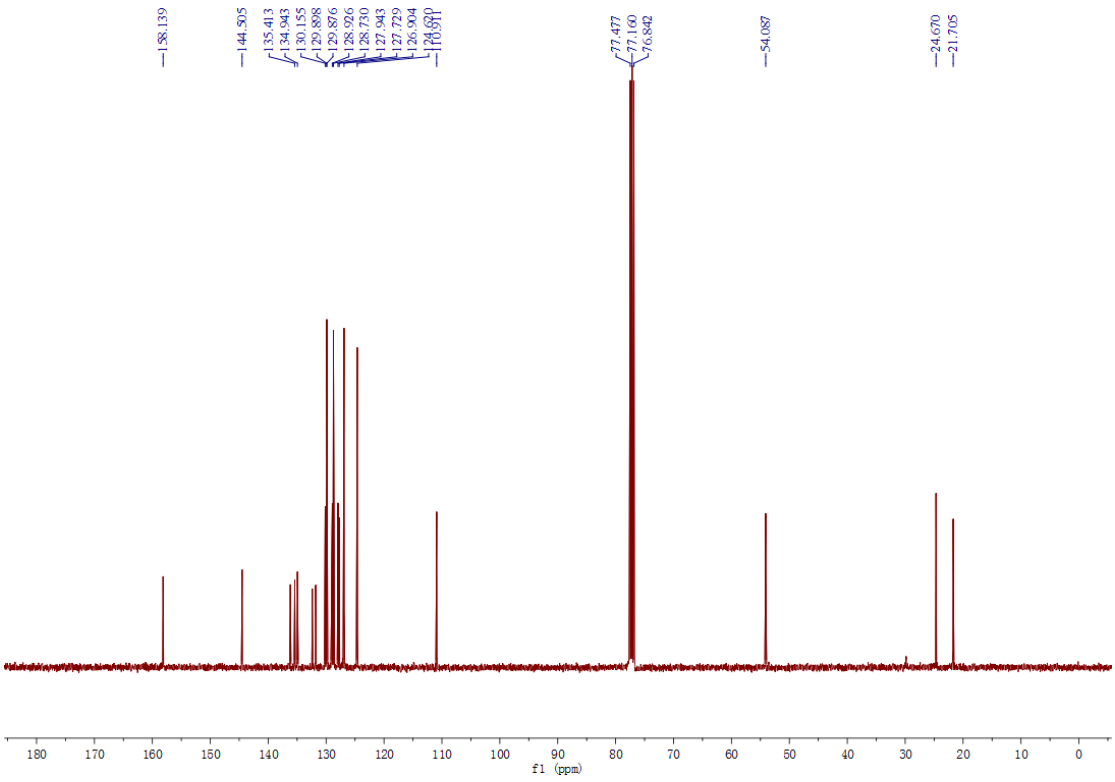
^{1}H NMR Spectrum for **8b** ($CDCl_3$, 400 MHz)



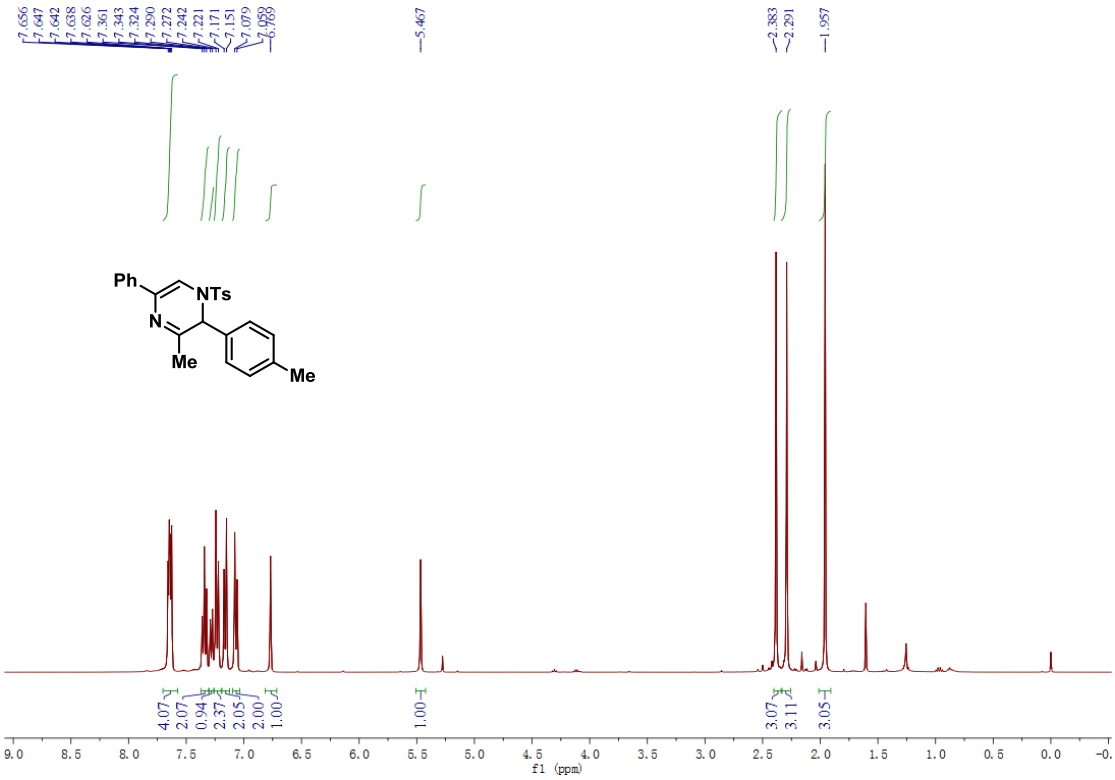
^{13}C NMR Spectrum for **8b** ($CDCl_3$, 100 MHz)



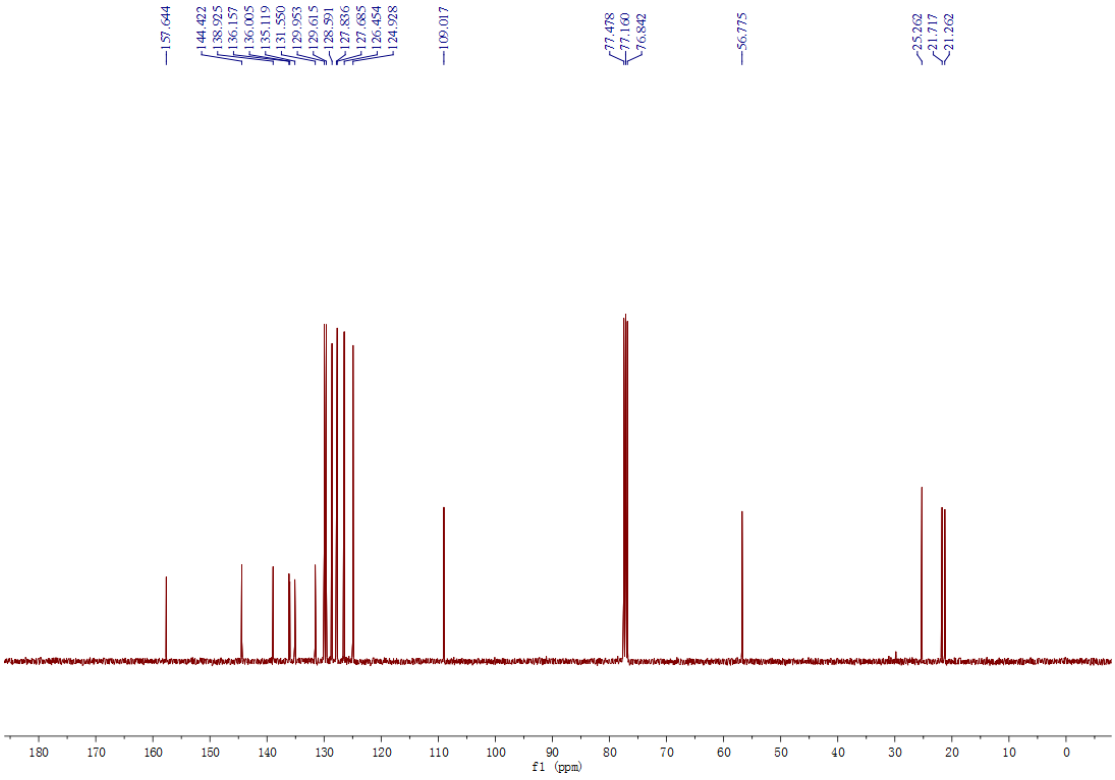
^{1}H NMR Spectrum for **8c** ($CDCl_3$, 400 MHz)



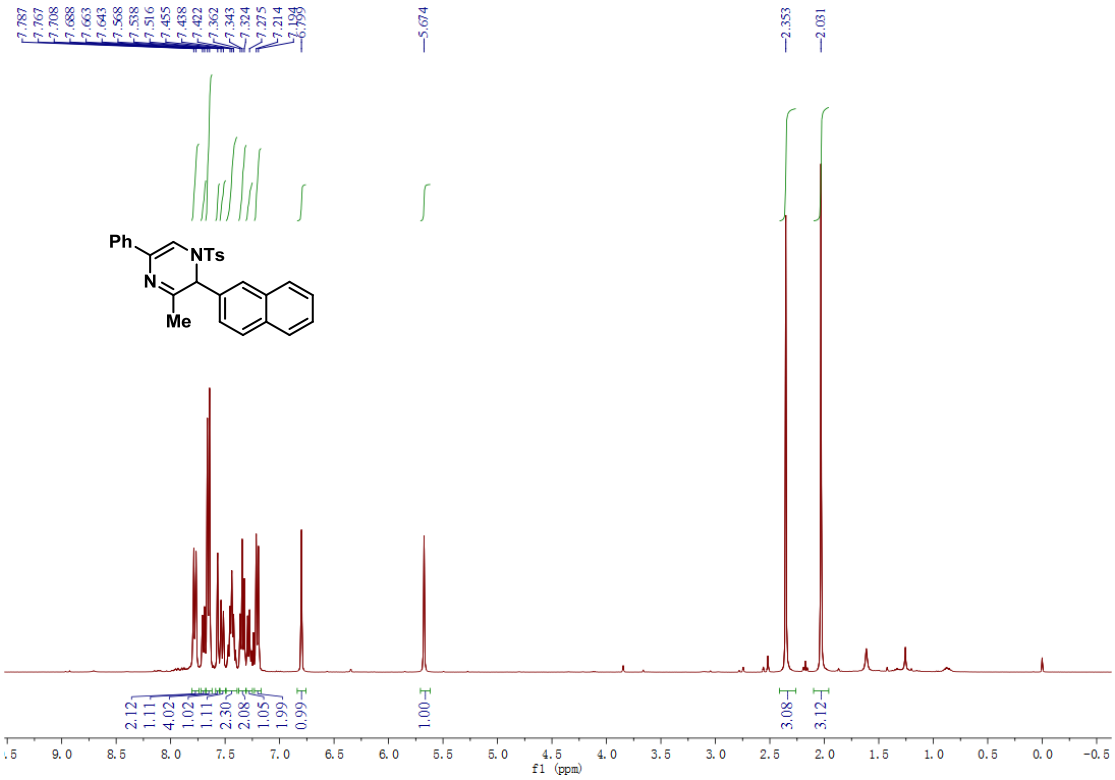
^{13}C NMR Spectrum for **8c** ($CDCl_3$, 100 MHz)



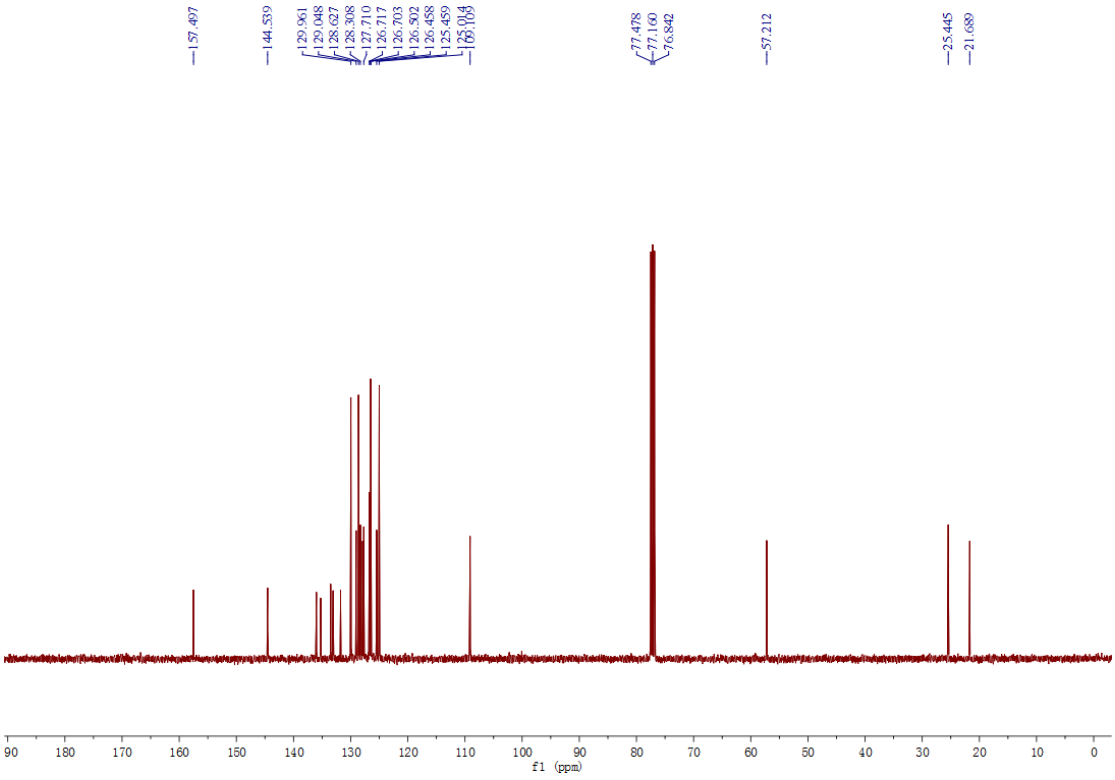
^{1}H NMR Spectrum for **8d** ($CDCl_3$, 400 MHz)



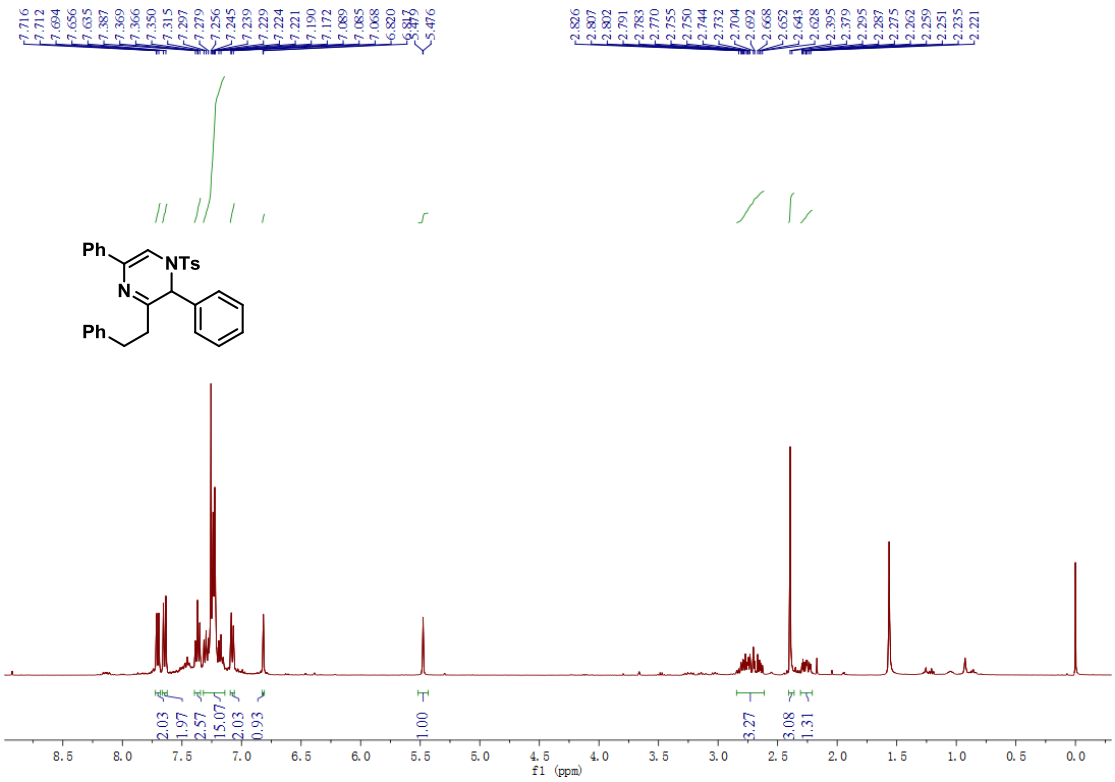
^{13}C NMR Spectrum for **8d** ($CDCl_3$, 100 MHz)



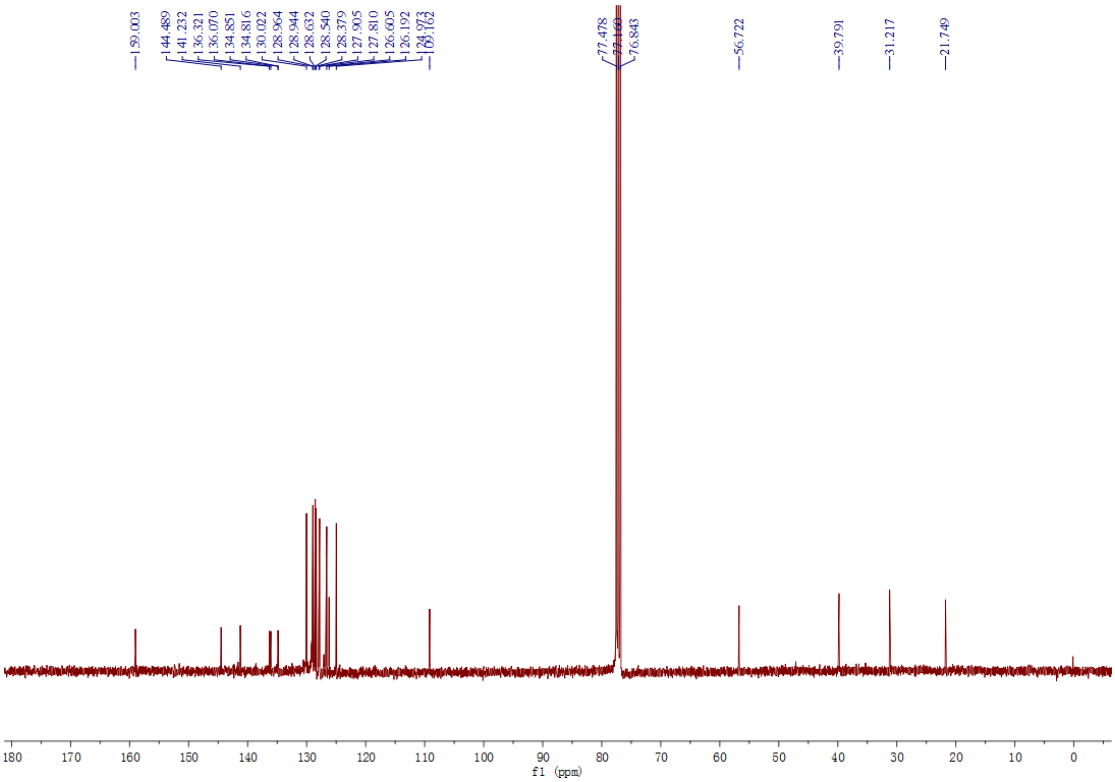
^{1}H NMR Spectrum for **8e** ($CDCl_3$, 400 MHz)



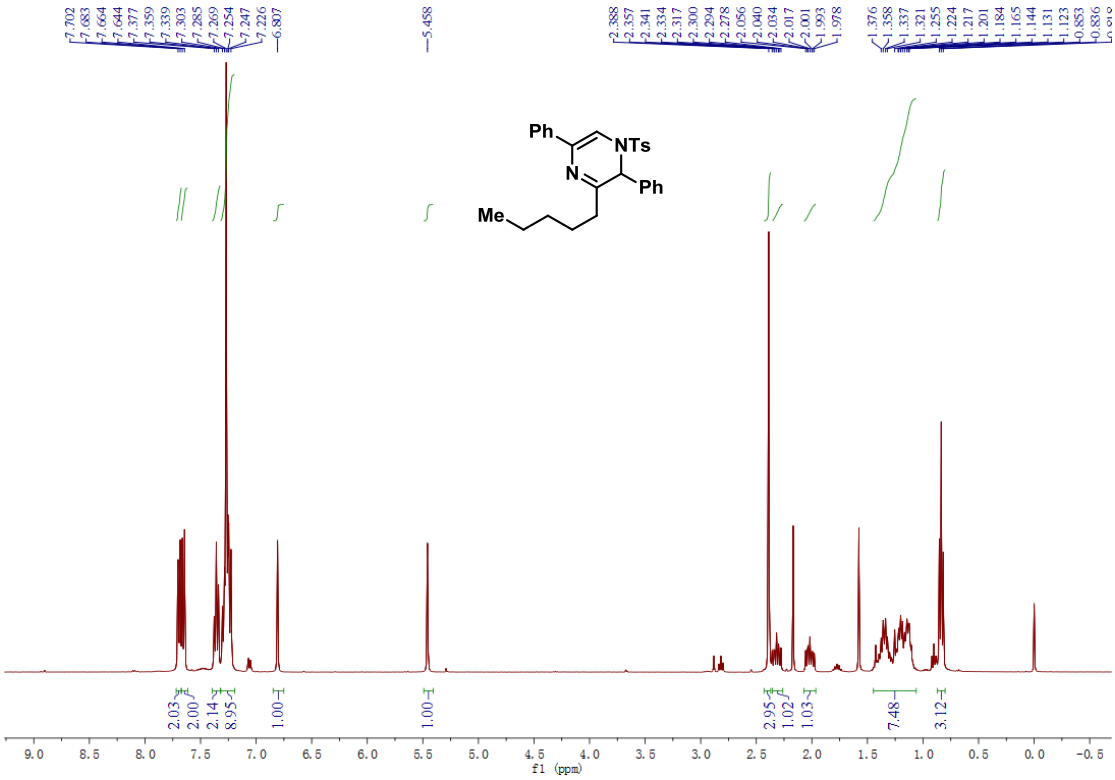
^{13}C NMR Spectrum for **8e** ($CDCl_3$, 100 MHz)



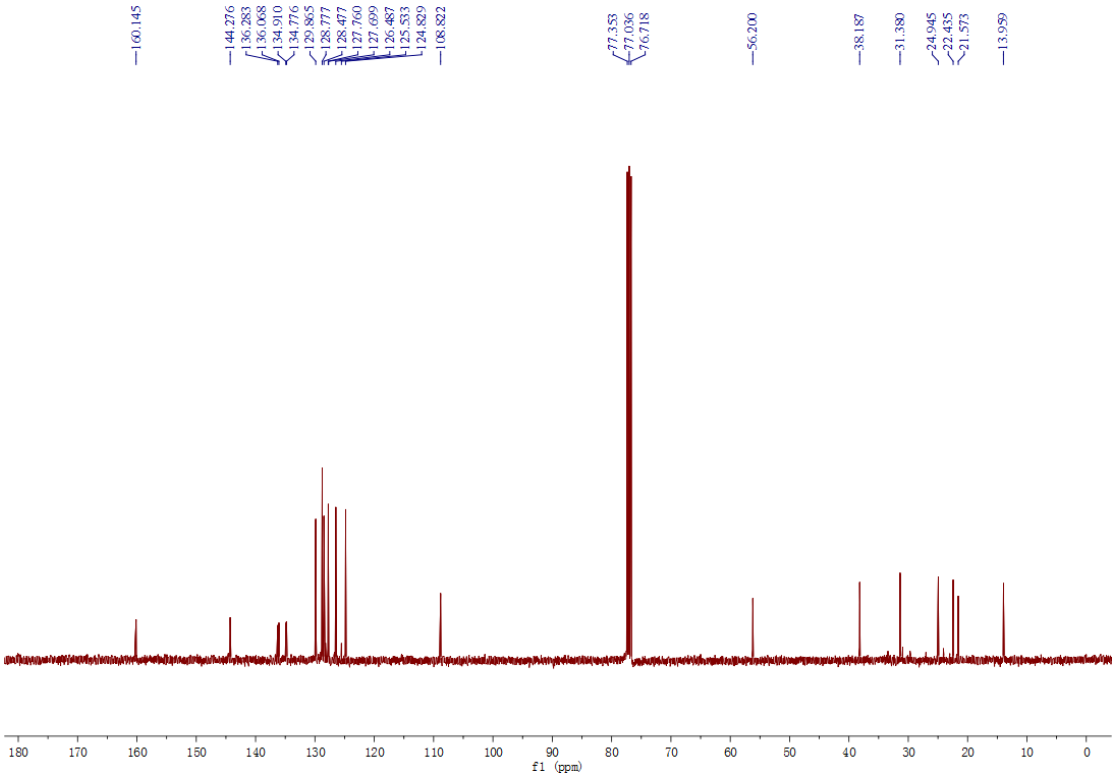
^{1}H NMR Spectrum for **8f** ($CDCl_3$, 400 MHz)



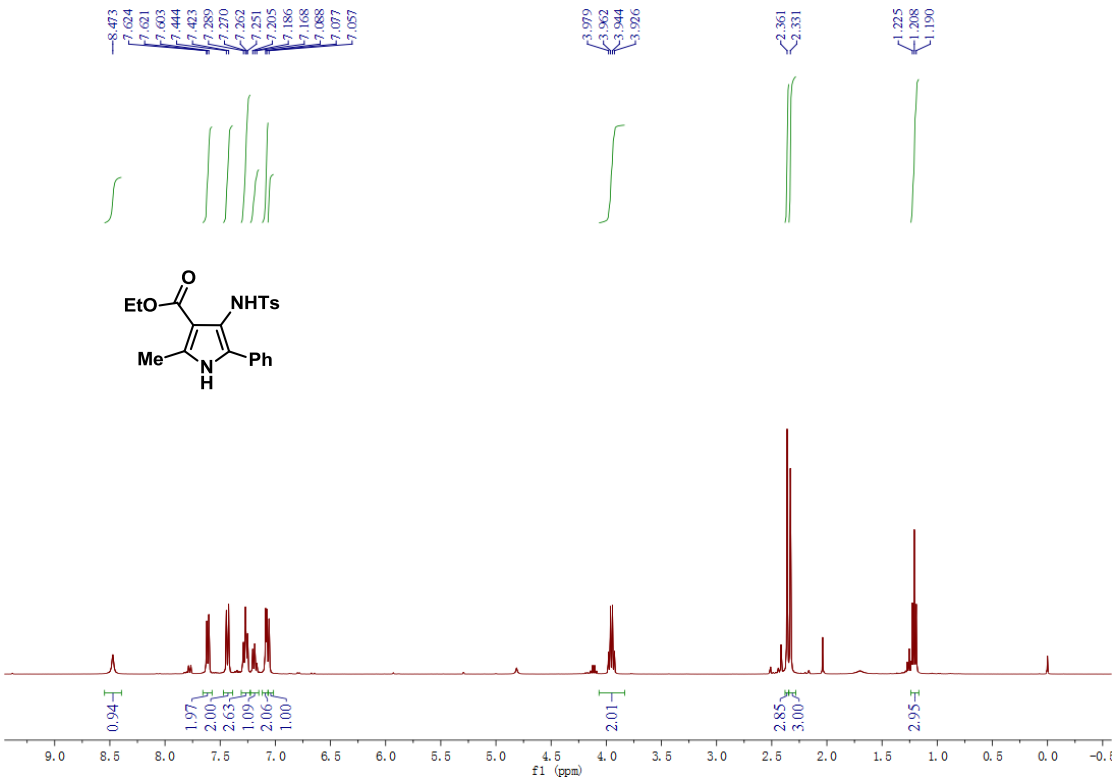
^{13}C NMR Spectrum for **8f** ($CDCl_3$, 100 MHz)



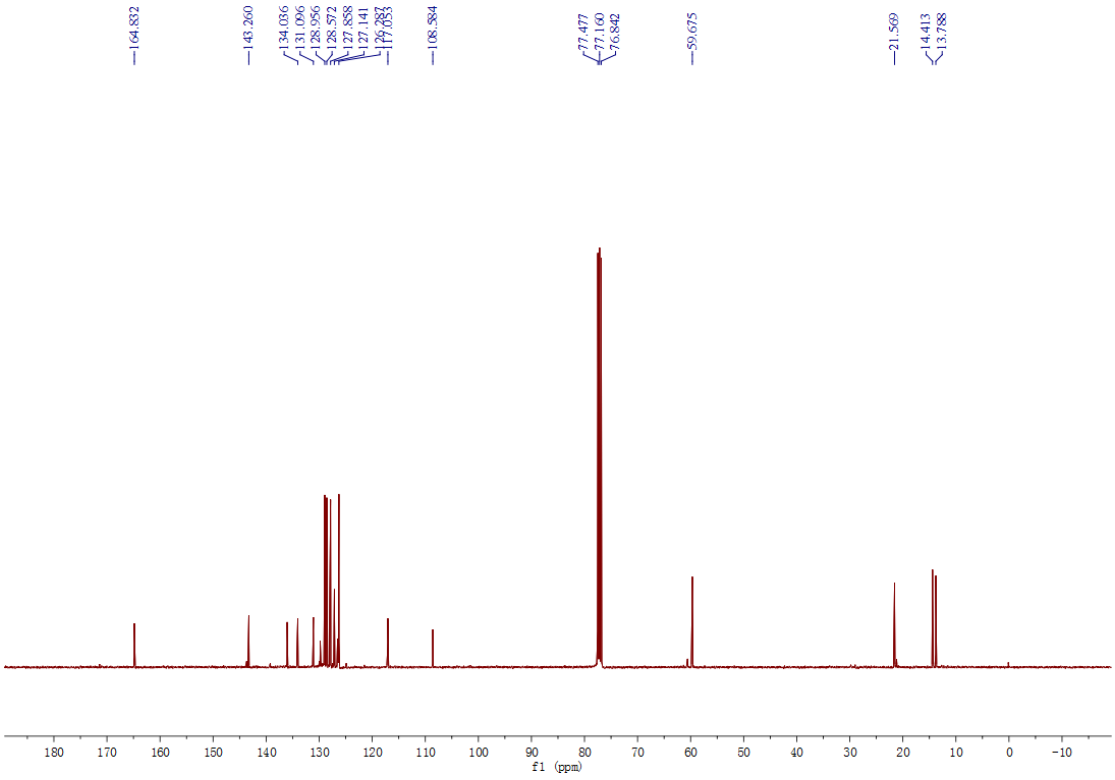
^{1}H NMR Spectrum for **8g** ($CDCl_3$, 400 MHz)



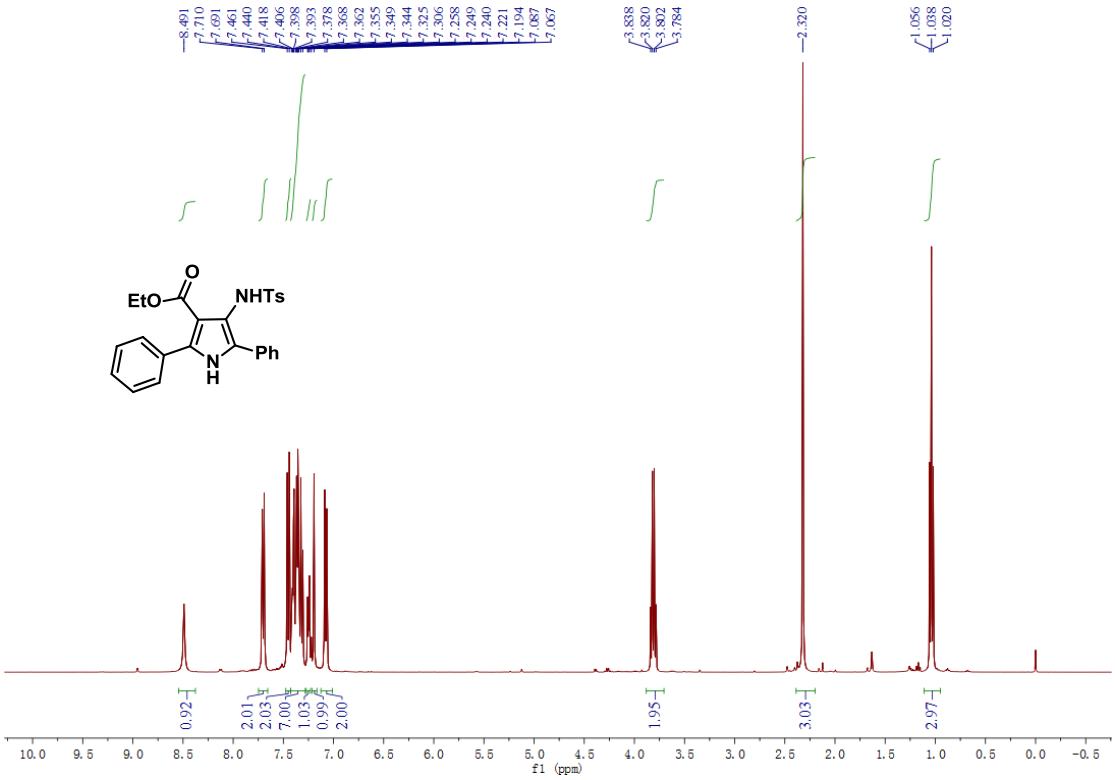
^{13}C NMR Spectrum for **8g** ($CDCl_3$, 100 MHz)



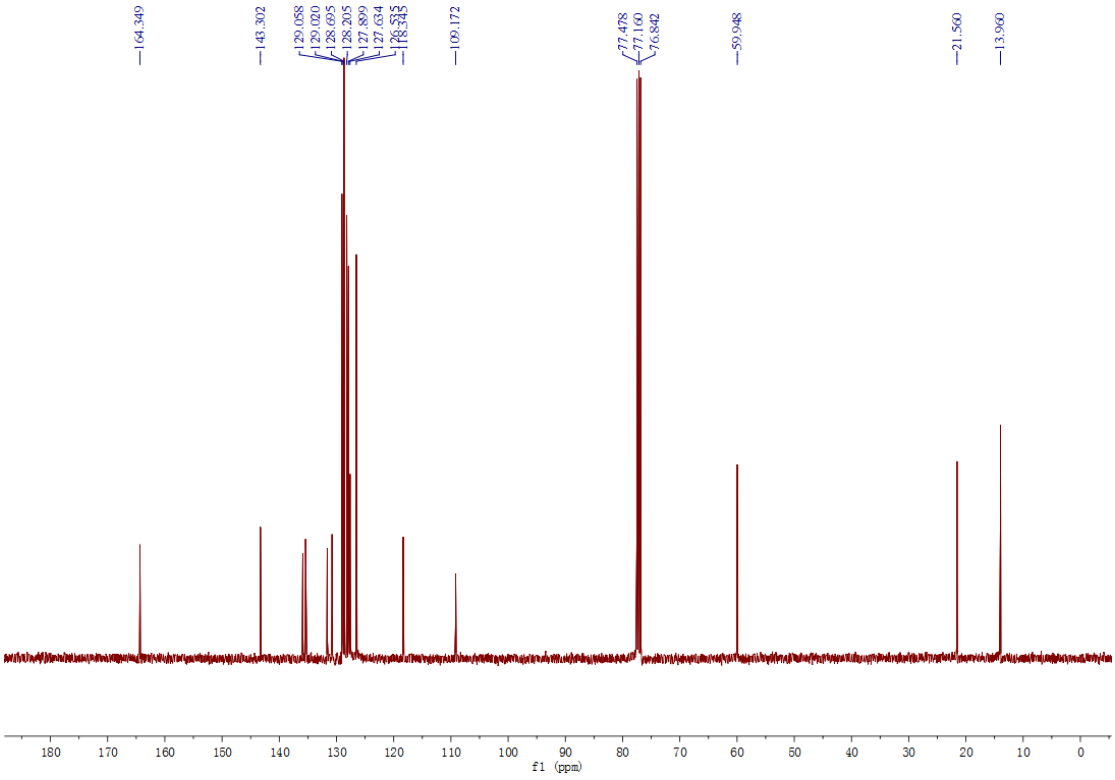
^{1}H NMR Spectrum for **10a** ($CDCl_3$, 400 MHz)



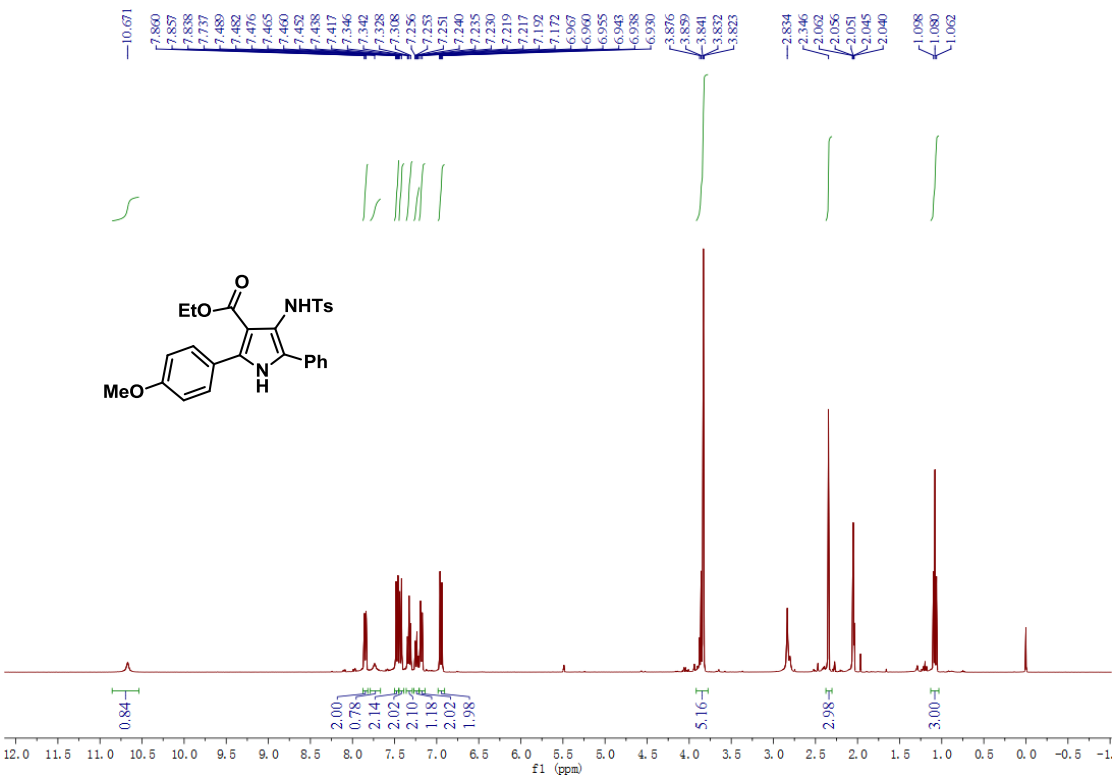
^{13}C NMR Spectrum for **10a** ($CDCl_3$, 100 MHz)



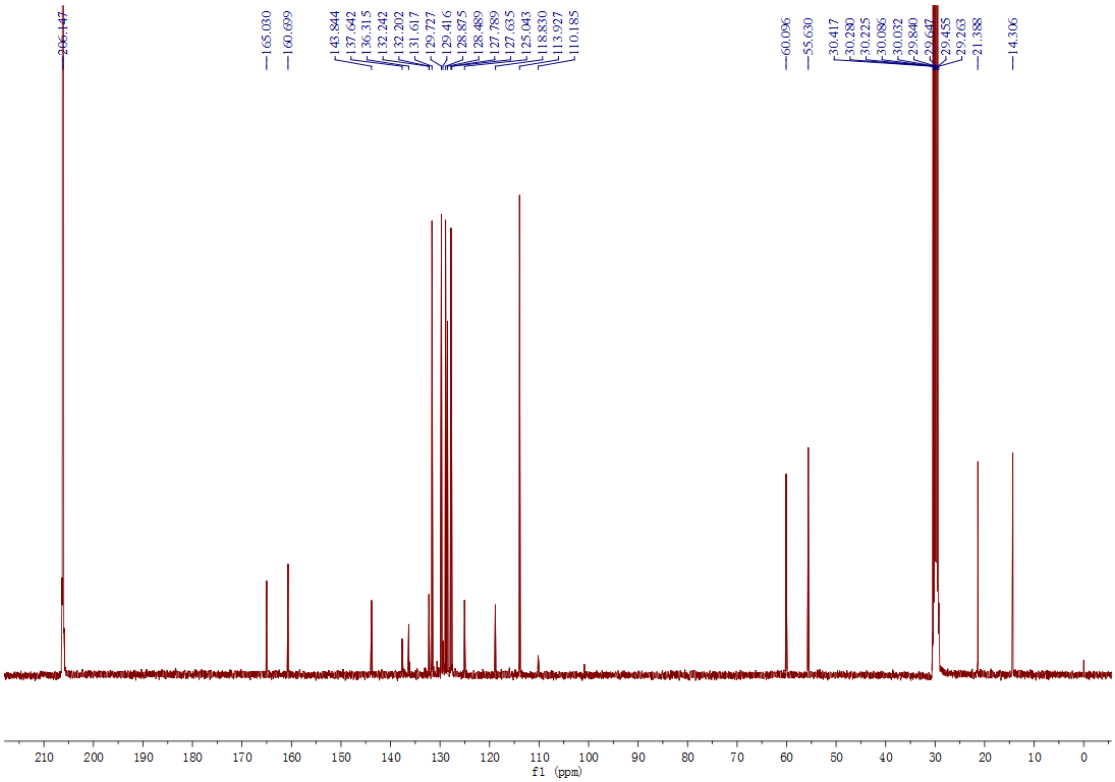
^{1}H NMR Spectrum for **10b** ($CDCl_3$, 400 MHz)



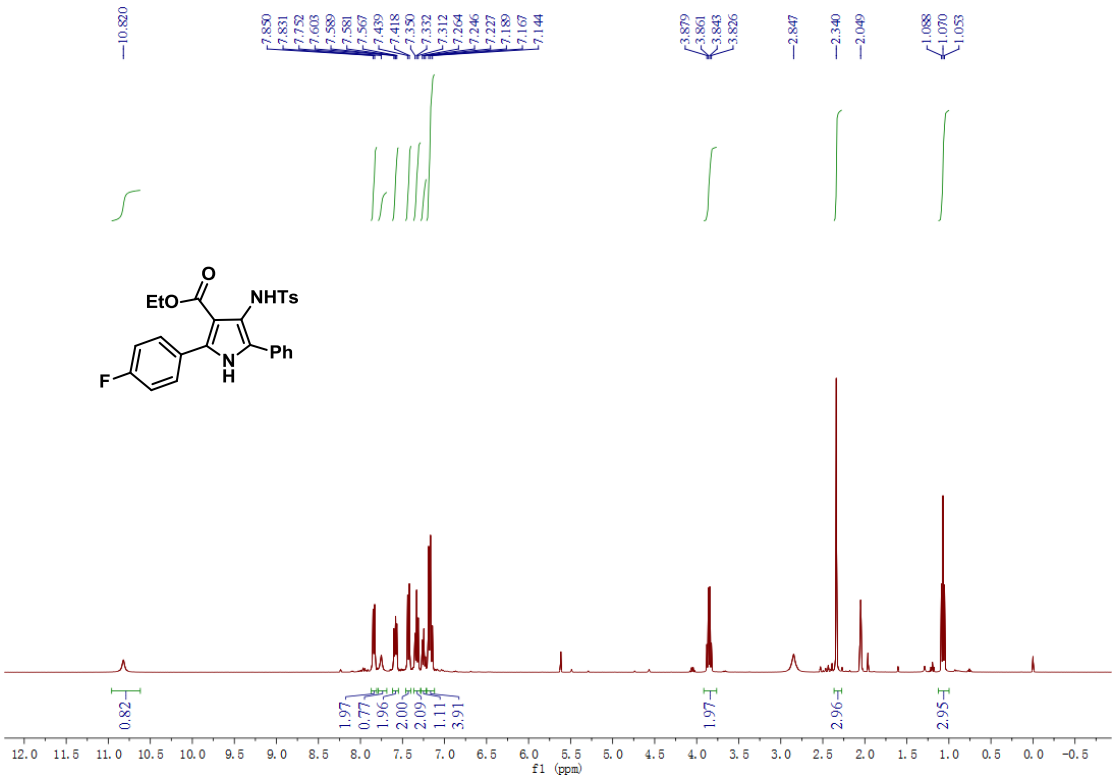
^{13}C NMR Spectrum for **10b** ($CDCl_3$, 100 MHz)



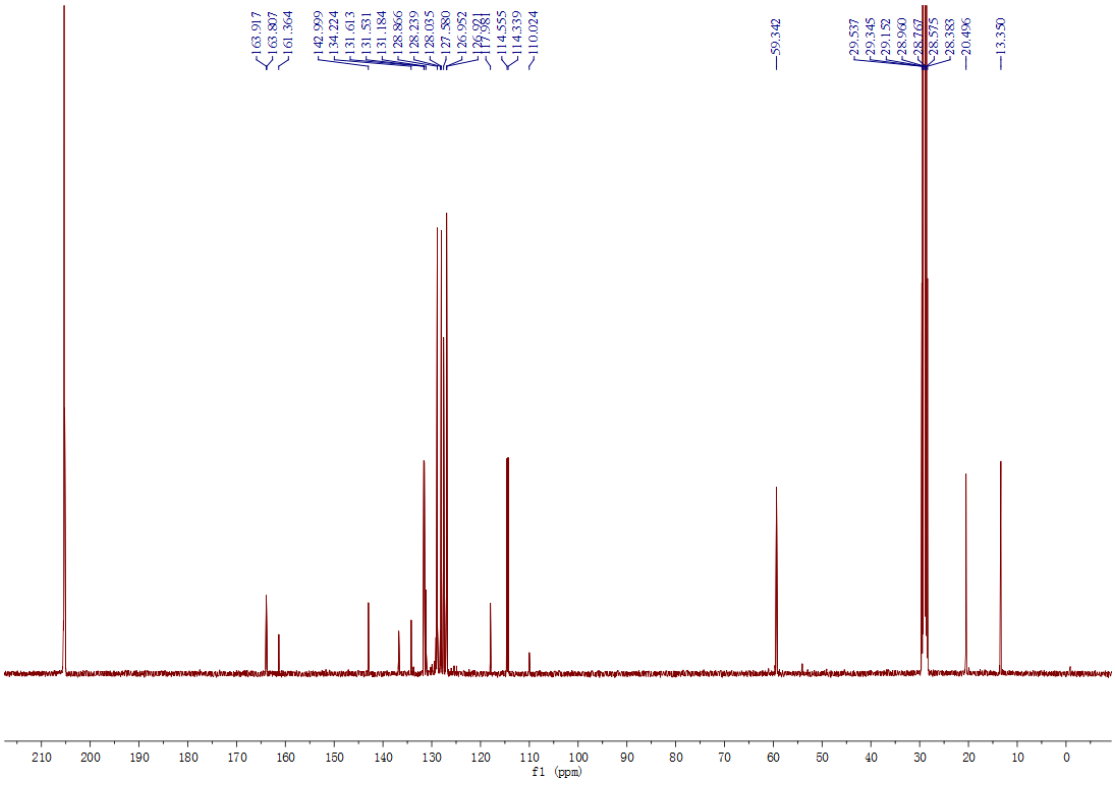
^{1}H NMR Spectrum for **10c** (Acetone-d_6, 400 MHz)



^{13}C NMR Spectrum for **10c** (Acetone-d_6, 100 MHz)

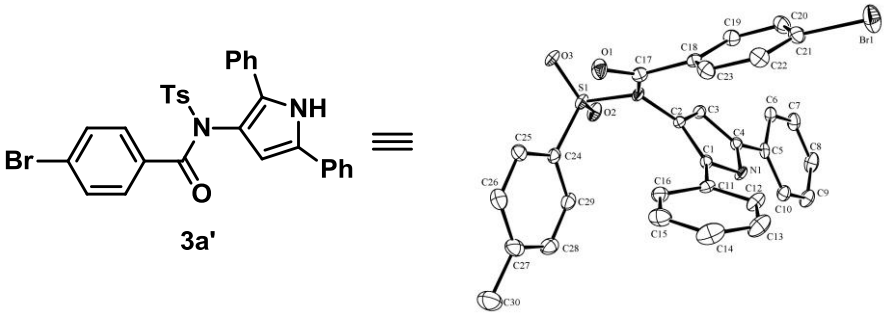


^{1}H NMR Spectrum for **10d** (Acetone-d_6, 400 MHz)



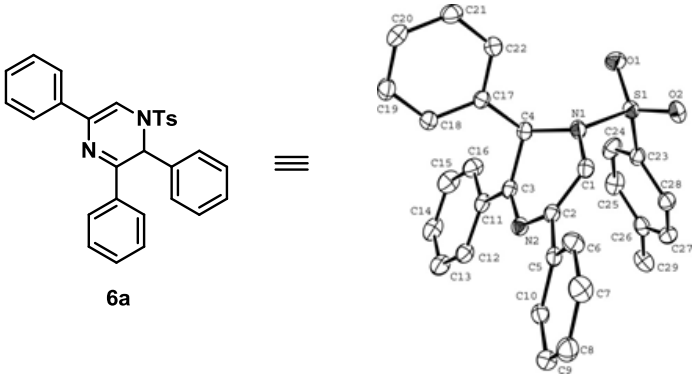
^{13}C NMR Spectrum for **10d** (Acetone-d_6, 100 MHz)

8. *X*-ray Crystallographic Structure of 3a' and 6a



X-ray Crystallographic structure and data of **3a'**

Compound	**3a**'
formula	$C_{30}H_{23}BrN_2O_3S$
FW	571.47
crystal system	monoclinic
space group	*P 1 21/c 1*
a/Å	15.2526(8)
b/Å	8.7689(4)
c/Å	19.1451(11)
α/deg	90
β/deg	90.857(5)
γ/deg	90
V/Å^3	2560.3(2)
Z	4
D_c/g cm^{-3}	1.483
μ/mm^{-1}	1.723
R_1[a] ($I > 2\sigma$)	0.0502(3632)
wR_2[b] (all data)	0.1125(5004)
GOF	1.046



X-ray Crystallographic structure and data of **6a**

Compound	**6a**
formula	$C_{29}\ H_{24}\ N_2\ O_2\ S$
FW	464.56
crystal system	monoclinic
space group	*P 1 21/c 1*
a/Å	13.7344(7)
b/Å	11.3573(6)
c/Å	15.3726(9)
α/deg	90
β/deg	95.591(5)
γ/deg	90
V/Å^3	2386.5(2)
Z	4
D_c/g cm^{-3}	1.293
μ/mm^{-1}	0.165
R_1[a] ($I > 2\sigma$)	0.0433(3611)
wR_2[b] (all data)	0.1150(4665)
GOF	1.053