Supporting information

Bisphosphonium salt catalyzed [3+2] annulation of N-tosylimino(iso)quinolinium ylides with aryl olefins under Blue LED Irradiation

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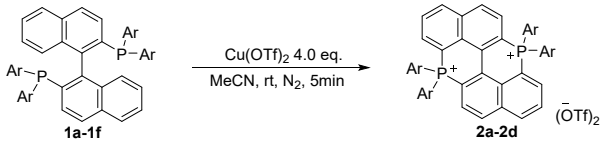
1. General methods and materials

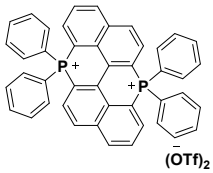
NMR spectra were obtained using Bruker AV300 spectrometer and Bruker AV400 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS (^{1}H). All coupling constants (J values) are reported in Hertz (Hz). HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-T of HR-MS spectrometer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Melting points were obtained on an X-4 micromelting point apparatus. The UV−vis absorption spectra were measured on a VARIAN Cary 5000 instrument. The fluorescence emission spectra were performed on Hitachi F-4600 Fluorescence spectrometers. All reactions except noted especially were routinely performed under an inert atmosphere of nitrogen by using standard Schlenk techniques and dry deoxygenated solvents. THF were obtained by distillation from Na/benzophenone. All commercially available reagents were used without further purification. Silica gel (200−300 mesh) purchased from Qingdao Hai Yang Chemical Industry Co. Ltd. was used for chromatographic separations.

2. Experimental procedures and characterization data

2.1 Synthesis and characterization of bisphosphonium salts

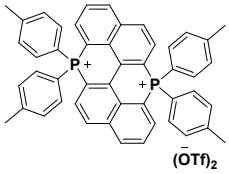


A 25 mL Schlenk flask equipped with a suitable magnetic stirrer, addition bisphosphine compound (**1a-1c**, commercial, 0.2 mmol; the procedure and analytical data of **1e** and **1f** are identical to previous report (*Chem. Eur. J.* 2011, **17**, 10828 – 10831)) and copper trifluoromesulfonate $Cu(OTf)_2$, commercial, 0.8 mmol, then the ultra-dry acetonitrile (6.0 mL) was added via syringe under nitrogen atmosphere. The reaction mixture turned black immediately with the addition of acetonitrile. After 5 minutes, the reaction mixture turned a bright yellow-green. With TLC analysis (CH_2Cl_2: MeOH = 40:1) showed the complete consumption of bisphosphine compound, and ^{31}P-NMR was used to determine the end of the reaction. The 10.0 mL of water and 1.0 mL of aqueous solution of hydrochloric acid (4.0 M) to the mixture, and extracted with CH_2Cl_2 after the solvent was removed under reduced pressure. TLC determines the end of extraction. The organic layer was combined, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and a mixture of acetone: methanol: chloroform: dichloromethane (1:1:1:1) 2.0 mL was added to the residue. After the solution was fully dissolved by ultrasound, 10.0 – 20.0 mL anhydrous ether was added until no solid was precipitated, then the mixture was filtered, washed twice with ether, collected filter residue, and removed solvent under vacuum to afford the title compound as a yellow solid. Analytical data are identical to the previous report.[1]

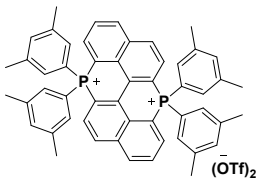


(2a): yellow solid, yield 84%. (DCM/MeOH = 10:1, Rf = 0.1). ^{1}H NMR (300 MHz, DMSO) δ 8.87 (d, J = 8.0 Hz, 2H), 8.74 (t, J = 10.4 Hz, 4H), 8.36 - 8.23 (m, 4H), 7.93 - 7.89 (m, 12H), 7.81 - 7.78 (m, 8H). ^{13}C{^{1}H} NMR (75 MHz, DMSO) δ 140.24 (d, J = 6.2 Hz), 139.23, 136.65 (q, J =

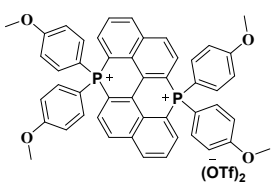
4.1 Hz), 136.16 (d, *J* = 2.2 Hz), 135.10 (d, *J* = 11.6 Hz), 134.87 (d, *J* = 1.1 Hz), 132.81 (q, *J* = 5.4 Hz), 131.02 (d, *J* = 13.6 Hz), 130.67 (d, *J* = 2.6 Hz), 130.52 (d, *J* = 1.2 Hz), 129.08 (q, *J* = 5.9 Hz), 121.12 (d, *J* = 322.4 Hz), 120.24 (d, *J* = 92.5 Hz), 116.34 (q, *J* = 29.2 Hz), 112.22 (q, *J* = 30.3 Hz). $^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO) δ 0.32. $^{19}F\{^{1}H\}$ NMR (282 MHz, DMSO) *δ* -78.54.



(2b): yellow solid, yield 87%. (DCM/MeOH = 10:1, Rf = 0.1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.85 (d, *J* = 7.7 Hz, 2H), 8.69 -8.63 (m, 4H), 8.29 -8.23 (m, 4H), 7.77 (m, 8H), 7.60 (s, 8H), 2.46 (s, 12H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6) δ 147.25 (d, *J* = 3.5 Hz), 139.92 (q, *J* = 4.3 Hz), 139.00 (d, *J* = 2.3 Hz), 136.57 (q, *J* = 4.2 Hz), 134.97 (d, *J* = 12.1 Hz), 134.90 (d, *J* = 12.6 Hz), 132.50 (q, *J* = 6.1 Hz), 131.62 (d, *J* = 14.0 Hz), 130.58 (d, *J* = 5.5 Hz), 130.41, 128.93 (q, *J* = 3.8 Hz), 120.27 (d, *J* = 334.6 Hz), 116.87 (d, *J* = 2.4, 85.5 Hz), 116.71 (d, *J* = 95.5 Hz), 112.82 (q, *J* = 30.5 Hz), 21.79. $^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO-d_6) δ -0.24. $^{19}F\{^{1}H\}$ NMR (282 MHz, DMSO-d_6) δ -78.09.



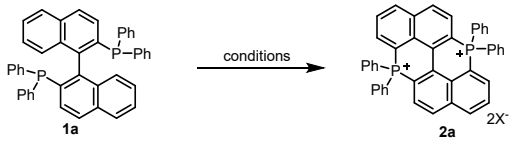
(2c): yellow solid, yield 92%. (DCM/MeOH = 10:1, Rf = 0.1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.85 (d, *J* = 6.8 Hz, 2H), 8.72 (s, 4H), 8.33 - 8.23 (m, 4H), 7.51 (t, *J* = 14.6 Hz, 12H), 2.31 (s, 24H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6) δ 140.78 (d, *J* = 14.4 Hz), 140.08 (d, *J* = 8.4 Hz), 139.08 (d, *J* = 1.5 Hz), 137.65, 136.66 (q, *J* = 3.7 Hz), 135.03 (d, *J* = 13.2 Hz), 132.41 (d, *J* = 4.3 Hz), 132.14 (d, *J* = 11.6 Hz), 130.68, 130.53 (d, *J* = 8.6 Hz), 128.99 (q, *J* = 5.7 Hz), 121.14 (d, *J* = 324.8 Hz), 120.04 (d, *J* = 91.2 Hz), 116.60 (q, *J* = 28.9 Hz), 112.49 (d, *J* = 89.2 Hz), 21.25. $^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO-d_6) δ 0.62. $^{19}F\{^{1}H\}$ NMR (282 MHz, DMSO-d_6) δ -78.02.



(2d): yellow solid, yield > 95%. (DCM/MeOH = 10:1, Rf = 0.1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 8.84 (d, *J* = 8.0 Hz, 2H), 8.73 - 8.60 (m, 4H), 8.24 (q, *J* = 7.5 Hz, 4H), 7.76 (q, *J* = 7.2 Hz, 8H), 7.29 (d, *J* = 6.7 Hz, 8H), 3.88 (s, 12H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6) δ 165.22 (d, *J* = 2.8 Hz), 139.64 (d, *J* = 10.4 Hz), 138.75, 137.17 (d, *J* = 13.4 Hz), 136.50 (q, *J* = 3.8 Hz), 134.82 (q, *J* = 4.3 Hz), 132.29 (q, *J* = 5.5 Hz),

130.44 (q, J = 3.2 Hz), 130.29, 128.89 (q, J = 6.0 Hz), 121.13 (d, J = 323.1 Hz), 117.66 (q, J = 29.5 Hz), 116.83 (d, J = 14.7 Hz), 113.67 (q, J = 30.6 Hz), 110.00 (d, J = 101.0 Hz), 56.57. $^{31}P\{^{1}H\}$ NMR (121 MHz, DMSO-d_6) δ -0.19. $^{19}F\{^{1}H\}$ NMR (282 MHz, DMSO-d_6) δ -78.28. HRMS (ESI): m/z calcd for $C_{48}H_{38}O_4P_2$ $(M)^{2+}$ 370.1117, found 370.1149. m/z calcd for $C_2F_6O_6S_2(M)^{2-}$ 148.9525, found 148.9532

2.2 The conditions that have been tried for synthesis bisphosphonium salts.



1a 2a

Entry	Conditions	Yield of **2a**
1	Ph_2IOTf (4 eq.), N_2, MeCN	N.D.
2	$PhICl_2$ (4 eq.), N_2, MeCN	N.D.
3	ICl (4 eq.), N_2, MeCN	N.D.
4	$Cu(OTf)_2$ (2 eq.), TCQ (2 eq.), N_2, MeCN	35%
5	$Cu(OTf)_2$ (2 eq.), $PhI(OAc)_2$ (4 eq.), N_2, MeCN	20%
6	$Cu(OAc)_2 \cdot H_2O$ (4 eq.), N_2, MeCN	N.D.
7	$Cu(BF_4)_2 \cdot 6H_2O$ (4 eq.), N_2, MeCN	N.D.
8	$Fe(OTf)_3$ (4 eq.), N_2, MeCN	30%

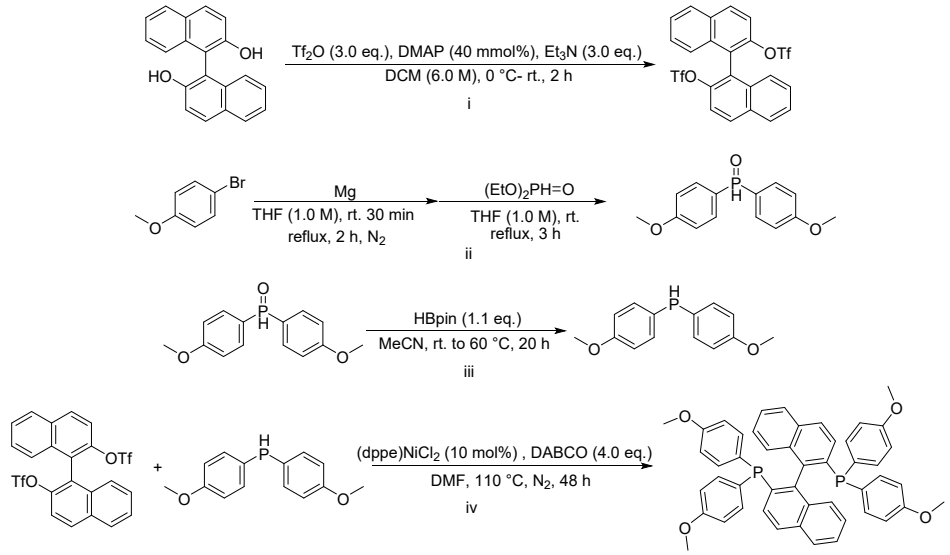
Reaction conditions: **1a** (0.1 mmol), room temperature. The reaction detected by TLC (MeOH/DCM = 1/20). Yields were determined by silica gel column chromatography (MeOH/DCM = 1/10). N. D. = Not detected.

2.3 Gram scale (2 mmol, 1.3 g) preparation for 2a

A 250 mL Schlenk flask equipped with a suitable magnetic stirrer, addition Binap (**1a**, commercial, 2.0 mmol, 1.3 g) and copper trifluoromesulfonate ($Cu(OTf)_2$), 8.0 mmol, 2.9 g), the ultra-dry acetonitrile (60.0 mL) was added via syringe under nitrogen atmosphere. The reaction mixture turned black immediately with the addition of acetonitrile. After 5 min, the reaction mixture turned a bright yellow-green. TLC analysis (CH_2Cl_2/MeOH = 40/1) showed the complete consumption of the bisphosphine compound, and ^{31}P-NMR was used to determine the end of the reaction. Here we use two treatment methods for purification: 1. The 50.0 mL water and 3.0 mL aqueous solution of hydrochloric acid (4.0 M) to the mixture after the solvent was removed under reduced pressure. The mixture was extracted by CH_2Cl_2. TLC determines the end of extraction. The organic layer was combined, and then dried over anhydrous Na_2SO_4.

The solvent was removed under reduced pressure and the mixture of acetone: methanol: chloroform: dichloromethane (1:1:1:1) 10.0 mL was added to the residue. After the solution was fully dissolved by ultrasound, 10.0 – 20.0 mL anhydrous ether was added until no solid was precipitated, then the mixture was filtered, washed twice with ether, collected filter residue, and removed solvent under vacuum to afford the title compound as a yellow solid (1.52 g, isolated yield 82%). 2. The reaction mixture was chromatographed on silica gel (EA→DCM/MeOH (50:1→20:1→10:1) →MeOH) to give the concentrated solution of crude product, then the anhydrous ether was added until no solid was precipitated, and the mixture was filtered, washed with ether and hexane to afford the title compound as a yellow solid (1.6 g, isolated yield 87%).

2.4. Synthesis and characterization of 2,2'-bis(bis(4-methoxyphenyl)phosphaneyl)-1,1'-binaphthalene (1d)



i: The procedure and analytical data are identical to previous report.[2-3] A 200 mL round bottom was equipped with a suitable magnetic stirrer, the [1,1'-binaphthalene]-2,2'-diol (12.0 mmol, 3.4 g), Et_3N (35.0 mmol, 5.0 mL), DMAP (4.7 mmol, 0.58 g), DCM (73.0 mL) was added, then the Trifluoromethanesulfonic anhydride (35.0 mmol, 5.0 mL) was added dropwise slowly via syringe. The reaction mixture was stirred at room temperature for 1 h with TLC detected (PE/EA = 8/1). It's quenched by $NaHCO_{3\,(aq.)}$ (100.0 mL) after the complete consumption of the [1,1'-binaphthalene]-2,2'-diol

compound. The reaction mixture was extracted by DCM three times. The organic layer was combined, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the mixture was chromatographed on silica gel (PE→PE/EA = 8/1(v/v)) to give the product as a white solid (5.5 g, 83%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 9.1 Hz, 2H), 8.00 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 9.1 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H).

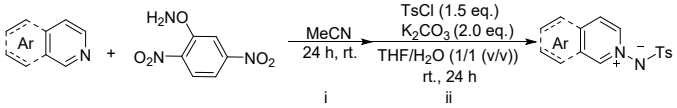
ii: In a 200 mL Schlenk flask equipped with a suitable magnetic stirrer, the magnesium turnings (100.0 mmol, 2.4 g) were added, exchanged N_2 three times by Schlenk line, then the anhydrous, degassed THF (50.0 mL) was added under nitrogen atmosphere. A drop of 1,2-dibromoethane was added and the mixture was stirred at room temperature. To this was added dropwise a solution of 5mL 1-bromo-4-methoxybenzene (100.0 mmol ,12.5 mL) in THF (30.0 mL) via a constant-pressure drip funnel. It's allowed to heat up 75 °C with a blower gun, then removed the blower gun and continue to drip the solution of 1-bromo-4-methoxybenzene (100.0 mmol, 12.5 mL) in THF (30.0 mL) in a slightly boiling state. The reaction mixture was stirred at 75 °C for 2 h after the drop was completed and was then cooled down to room temperature. To this was added dropwise a solution of diarylbromophosphine (30.0 mmol) in THF (20.0 mL) via constant pressure drip funnel during 30 min. After the addition was completed, the mixture was further stirred at 60 °C for 3 h and then cooled down to room temperature. To the solution was added 50.0 mL of 10% aqueous NH_4Cl solution and the mixture was stirred for 10 minutes at room temperature. The organic layer was separated, washed successively with 20.0 mL of saturated $NaHCO_3$ solution and two 20.0 mL portions of water and then dried over anhydrous Na_2SO_4. Solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (DCM/MeOH = 100/1 to 25/1 (v/v)) to afford the title compound as a white solid (5.03 g, 64%). ^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) δ 21.05. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 478.8 Hz, 1H), 7.61 (q, *J* = 7.2 Hz, 4H), 6.99 (q, *J* = 3.3 Hz, 4H), 3.85 (s, 6H).

iii: A 50 mL Schlenk flask equipped with a suitable magnetic stirrer, the bis(4-

methoxyphenyl)phosphine oxide (7.0 mmol, 1.8 g) was added and exchanged N_2 three times by Schlenk line. Then the degassed MeCN (20.0 mL) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10.5 mmol, 1.5 mL) was added. The reaction mixture was stirred for 20 h at 60 °C detected by ^{31}P-NMR. The reaction mixture for 1 h under vacuum after it's completed at room temperature. The product was obtained as colorless liquid. $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) δ -44.44. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (q, *J* = 5.2 Hz, 4H), 6.86 (d, *J* = 8.3 Hz, 4H), 5.19 (d, *J* = 218.9 Hz, 1H), 3.79 (s, 6H).

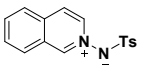
iv: A 25 mL Schlenk flask equipped with a suitable magnetic stirrer, the [1,1'-binaphthalene]-2,2'-diylbis(trifluoromethanesulfonate) (2.0 mmol, 1.1 g) was added to the solution of bis(4-methoxyphenyl)phosphane (>5.0 mmol) in ultra-dry DMF (10.0 mL) under nitrogen atmosphere, then the (dppe)$NiCl_2$ (0.2 mmol，0.105 g) and DABCO (8.0 mmol，0.9 g) was added. The reaction mixture was stirred at 110 ℃ for 48 h with TLC analysis (PE/EA = 8/1) showed the complete consumption of [1,1'-binaphthalene]-2,2'-diylbis(trifluoromethanesulfonate) compound and then kept at room temperature for another 30 min. The 20.0 mL NaCl aq was added, and extract with EA. At the end of extraction determined by TLC, the organic layer was combined, washed twice with NaCl aq. The organic layer was combined, and then dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the mixture was chromatographed on silica gel (PE to (DCM/MeOH= 100/1 to 50/1 to 25/1) to give the product as a white solid **1d** (0.5 g, isolated yield 30%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ -18.08. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (q, *J* = 9.4 Hz, 4H), 7.44 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.1 Hz, 2H), 7.04 - 6.92 (m, 10H), 6.80 (d, *J* = 8.3 Hz, 2H), 6.66 (q, *J* = 10.1 Hz, 8H), 3.73 (s, 12H).

2.5 Synthesis of dipoles

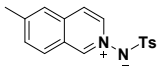


i: To a solution of corresponding (iso)quinoline (1.0 eq., 5.0 mmol) in acetonitrile

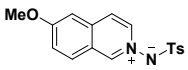
(15.0 mL) was added *O*-(2,4-dinitrophenyl) hydroxylamine (1.1 eq., 5.5 mmol). The reaction flask was sealed with a balloon, and the reaction mixture was stirred for 24 h at room temperature. ii: Upon filtering off the solvent, the orange precipitate was dissolved in THF/H_2O (30.0 mL, 1/1 (v/v)). The reaction mixture was added to K_2CO_3 (2.0 eq., 10.0 mmol) at room temperature, and 4-toluenesulfonyl chloride (1.5 eq., 7.5 mmol) was added slowly. After 24 h, the reaction mixture was filtered, and the residue washed with H_2O and Et_2O. The tittle product was obtained as a solid. Analytical data are identical to the previous report [4-6].



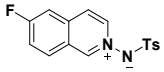
isoquinolin-2-ium-2-yl(tosyl)amide (3a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.11 (q, *J* = 2.8 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.95 (q, *J* = 5.8 Hz, 2H), 7.87 - 7.80 (m, 2H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 2.35 (s, 3H).



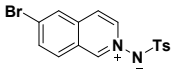
(6-methylisoquinolin-2-ium-2-yl)(tosyl)amide (3b): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.16 (s, 1H), 8.04 (q, *J* = 2.8 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 1H), 7.73 (t, *J* = 3.2 Hz, 2H), 7.64 (t, *J* = 8.7 Hz, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 2.63 (s, 3H), 2.35 (s, 3H).



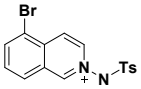
(6-methoxyisoquinolin-2-ium-2-yl)(tosyl)amide (3c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.02 (s, 1H), 7.99 (d, *J* = 7.0 Hz, 1H), 7.92 (d, *J* = 9.1 Hz, 1H), 7.68 (d, *J* = 7.0 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.41 (q, *J* = 3.8 Hz, 1H), 7.16 (q, *J* = 5.2 Hz, 3H), 4.02 (s, 3H), 2.36 (s,3H).



(6-fluoroisoquinolin-2-ium-2-yl)(tosyl)amide (3d): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.17 - 8.11 (m, 2H), 7.81 (d, *J* = 7.0 Hz, 1H), 7.62 (q, *J* = 7.7 Hz, 4H), 7.17 (d, *J* = 7.7 Hz, 2H), 2.36 (s, 3H).

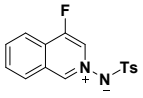


(6-bromoisoquinolin-2-ium-2-yl)(tosyl)amide (3e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.29 (d, *J* = 6.2 Hz, 1H), 8.14 (d, *J* = 6.7 Hz, 2H), 7.92 (t, *J* = 4.1 Hz, 2H), 7.76 (q, *J* = 3.1 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 3H).

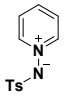


(5-bromoisoquinolin-2-ium-2-yl)(tosyl)amide (3f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.20 (d, *J* = 0.7 Hz, 2H), 8.17 (q, *J* = 2.8 Hz, 1H),

8.03 (d, *J* = 8.3 Hz, 1H), 7.70 - 7.65 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H).

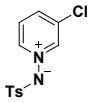


(4-fluoroisoquinolin-2-ium-2-yl)(tosyl)amide (3g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.18 (q, *J* = 2.9 z, 2H), 8.10 (d, *J* = 8.2 Hz, 1H), 8.01 (t, *J* = 7.3 Hz, 1H), 7.90 (t, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.1 Hz, 2H), 2.37 (s, 3H).



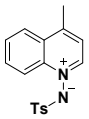
pyridin-1-ium-1-yl(tosyl)amide (3h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.8 Hz, 2H), 8.00 (t, *J* = 7.7 Hz, 1H), 7.64 - 7.58 (m, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 2.35 (s, 3H).

(2-methylpyridin-1-ium-1-yl)(tosyl)amide (3i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 5.9 Hz, 1H), 7.87 - 7.82 (m, 1H), 7.57 (d, *J* = 8.2 Hz, 2H), 7.46 (q, *J* = 7.9 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.37 (s, 3H).

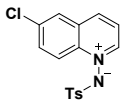


(3-chloropyridin-1-ium-1-yl)(tosyl)amide (3g): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.5 Hz, 1H), 8.42 (d, *J* = 6.4 Hz, 1H), 7.91 - 7.88 (m, 1H), 7.65 (d, *J* = 8.2 Hz, 2H), 7.54 (q, *J* = 4.9 Hz, 1H), 7.21 (d, *J* = 8.1 Hz, 2H), 2.3 (s, 3H).

quinolin-1-ium-1-yl(tosyl)amide (3k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (d, *J* = 5.4 Hz, 1H), 8.54 - 8.46 (m, 2H), 7.97 (d, *J* = 5.9 Hz, 1H), 7.64 (q, *J* = 6.9 Hz, 3H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 2.26 (s, 3H).

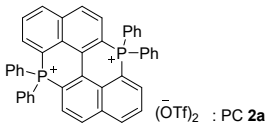


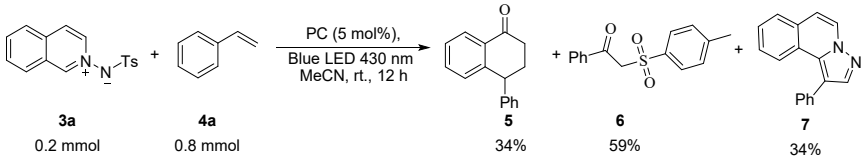
(4-methylquinolin-1-ium-1-yl)(tosyl)amide (3m): ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.89 (d, *J* = 6.2 Hz, 1H), 8.62 - 8.57 (m, 1H), 8.08 - 8.04 (m, 1H), 7.74 - 7.65 (m, 2H), 7.52 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 6.2 Hz, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 2.87 (s, 3H), 2.29 (s, 3H).



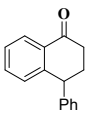
(6-chloroquinolin-1-ium-1-yl)(tosyl)amide (3n): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.08 (d, *J* = 6.0 Hz, 1H), 8.58 (d, *J* = 9.5 Hz, 1H), 8.36 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 2.1 Hz, 1H), 7.70 - 7.61 (m, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 2.31 (s, 3H).

2.6 The cyclization of dipoles (3a) with styrene (4a) catalyzed by bisphosphonium salt (2a) under blue LED

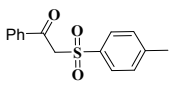




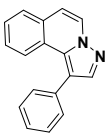
A 5 mL Quartz glass bottle equipped with a suitable magnetic stirrer, addition isoquinolin-2-ium-2-yl(tosyl)amide **3a** (0.2 mmol, 60.0 mg) and PC **2a** (0.01 mmol, 9.0 mg), the MeCN (3.0 mL) and styrene (**4a**, 0.8 mmol, 0.12 mL) was added via Pipette gun. The reaction mixture stirred under blue LED 430 nm 9 w for 12 h. Then the reaction mixture was purified by preparative TLC using PE/EA (v/v = 10/1) to give the yield of target product.



Side product (5): light yellow oil, 30.2 mg, 0.136 mmol, petroleum ether/ethyl acetate = 10:1, Rf = 0.50, yield = 34%. Analytical data are identical to previous report (*Adv. Synth. Catal.* 2016, **358**, 3887 – 3896).

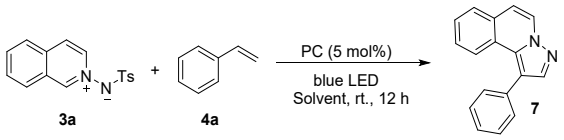


Side product (6): light yellow oil, 32.5 mg, 0.118 mmol, petroleum ether/ethyl acetate = 10:1, Rf = 0.10, yield = 59%. Analytical data are identical to previous report (*Org. Lett*. 2023, **25**, 5454 – 5458).



Target product (7): yellow oil, 24.9 mg, yield = 34%. (PE/EA = 10:1, Rf = 0.40). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.4 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.94 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.61 - 7.45 (m, 6H), 7.37 - 7.32 (m, 1H), 7.01 (d, *J* = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.95, 134.13, 133.70, 129.99, 129.41, 128.74, 127.79, 127.44, 127.28, 127.22, 126.63, 125.18, 123.41, 116.84, 112.41. HRMS (ESI): m/z calcd for $C_{17}H_{13}N_2$ $(M+H)^+$ 245.1074, found 245.1085.

2.7 Optimization of the reaction conditions



A 5 mL Quartz glass bottle equipped with a suitable magnetic stirrer, addition isoquinolin-2-ium-2-yl(tosyl)amide (0.2 mmol, 60.0 mg) and PC **2a** (0.01 mmol, 9.0 mg), the solvent (3.0 mL) and **4a** (0.8 or 0.5 mmol,) was added via Pipette gun. The reaction mixture stirred under blue LED for 12 h. Then the reaction mixture was purified by PTLC using PE/EA (v/v = 10/1) to give the yield of target product.

Solvent effect:

Entry	**4a**	Solvent	Yield of **7**
1	4.0 eq.	MeCN	35%
2	4.0 eq.	PhMe	Trace
3	4.0 eq.	MeOH	10%
4	4.0 eq.	THF	16%
5	4.0 eq.	Acetone	40%
6	4.0 eq.	DCM	35%
7	4.0 eq.	$CHCl_3$	54%
8	4.0 eq.	EtOH	Trace
9	4.0 eq.	TFE	Trace
10	4.0 eq.	HFIP	Trace
11	4.0 eq.	H_2O	N.D.
12	2.5 eq.	$CHCl_3$	51%

Reaction conditions: **3a** (0.2 mmol), **4a** (4.0 eq.), catalyst **2a** (5 mol%), solvent (3.0 mL), rt = room temperature, 430 nm Blue LED 9 w, 12 h under air atmosphere. Yields were determined by preparative TLC. N. D. = Not detected.

Catalyst effect:

Entry	Catalyst	Yield of **7**
1	**2b**	30%
2	**2c**	42%
3	**2d**	35%

Reaction conditions: **3a** (0.2 mmol), **4a** (2.5 eq.), catalyst (5 mol%), $CHCl_3$ (3.0 mL), rt = room temperature, 430 nm Blue LED 9 w, 12 h under air atmosphere. Yields were determined by preparative TLC.

Base effect:

Entry	**4a**	Additives	Solvent	Yield of **7**
1	2.5 eq.	$NaCO_3$ (3.0 eq.)	$CHCl_3$	N.D.
2	2.5 eq.	$CsCO_3$ (3.0 eq.)	$CHCl_2$	N.D.
3	2.5 eq.	Et_3N (3.0 eq.)	$CHCl_3$	N.D.
4	2.5 eq.	DMAP (3.0 eq.)	$CHCl_3$	Trace
5	2.5 eq.	DDQ (0.5 eq.)	$CHCl_3$	43%
6	2.5 eq.	Tetrachloro-p-benzoquinone (0.5 eq.)	$CHCl_3$	64%
7	2.5 eq.	Selectfluor (0.5 eq.)	$CHCl_3$	50%
8	2.5 eq.	Tetrachloro-p-benzoquinone (1.0 eq.)	$CHCl_3$	80%

Reaction conditions: **3a** (0.2 mmol), **4a** (2.5 eq.), photocatalyst **2a** (5 mol%), solvent (3 mL), 430 nm blue LED 9 w, rt for12 h under air atmosphere. Yields were determined by PTLC. N. D. = Not detected.

Lamp power effect:

Entry	**4a**	Additives	Solvent	P (w)	Yield of **7**
1	2.5 eq	Tetrachloro-p-benzoquinone (1.0 eq.)	$CHCl_3$	6 w	84%
2	2.5 eq	Tetrachloro-p-benzoquinone (1.0 eq.)	$CHCl_3$	40 w	86%

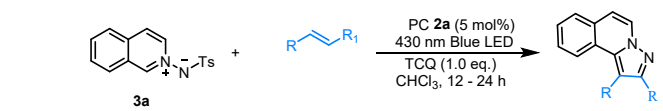
Reaction conditions: **4a** (0.2 mmol), **4a** (2.5 eq.), photocatalyst **2a** (5 mol%), Tetrachloro-p-benzoquinone (1.0 eq.), solvent (3.0. mL), 430 nm Blue LED, rt for 12 h under air atmosphere. Yields were determined by PTLC.

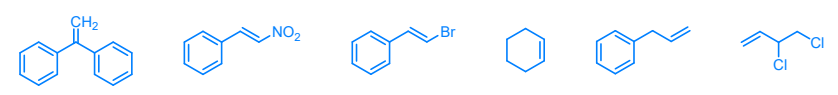
Control experiment:

Entry	**4a**	Other conditions	Solvent	λ(nm) / P(w)	Yield of **7**
1	2.5 eq.	TEMPO	$CHCl_3$	430 / 9 w	N.R.
2	2.5 eq.	rt to 60 ℃	$CHCl_3$	Without Blue LED	N.R.
3	2.5 eq.	No PC	$CHCl_3$	430 / 9 w	N.R.

Reaction conditions: **3a** (0.2 mmol), **4a** (2.5 eq.), photocatalyst **2a** (5 mol%), Tetrachloro-p-benzoquinone (1.0 eq.), $CHCl_3$ (3.0 mL), TEMPO (1.2 mmol, 187 mg), 430 nm blue LED, rt for 12 h under air atmosphere. Yields were determined by preparative TLC. N. R. = No reaction.

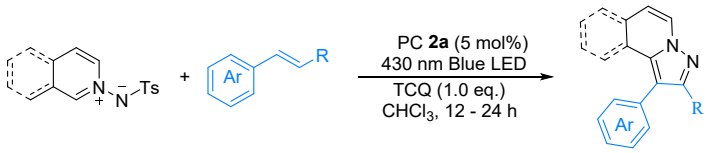
Olefins that have been tried:



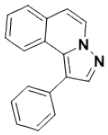


A 5 mL Quartz glass bottle equipped with a suitable magnetic stirrer, addition **3a** (0.2 mmol) and PC **2a** (0.01 mmol), Tetrachloro-p-benzoquinone (0.2 mmol), the $CHCl_3$ (3.0 mL) and olefins as above (commercial, 0.5 mmol) was added. The reaction mixture stirred under blue LED 430 nm 6 w for 12 - 24 h with TLC analysis (PE/EA (v/v = 10/1) to EA). No target products were detected using the above olefins as substrates for formation.

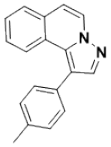
2.8 Synthesis and characterization of compounds 7-48



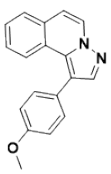
A 5 mL Quartz glass bottle equipped with a suitable magnetic stirrer, addition **3a-3n** (0.2 mmol) and PC **2a** (0.01 mmol), Tetrachloro-p-benzoquinone (0.2 mmol), the $CHCl_3$ (3.0 mL) and aryl olefins (**4a-4t**, commercial, 0.5 mmol) was added. The reaction mixture stirred under blue LED 430 nm 6 w for 12 - 24 h with TLC analysis (PE/EA (v/v = 10/1) to EA) showed the completely consumption of isoquinolin-2-ium-2-yl(tosyl)amide. Then the reaction mixture was purified by PTLC using PE/EA (v/v = 10/1) to give the target product.



1-phenylpyrazolo[5,1-a]isoquinoline (7): yellow oil, yield = 84%.

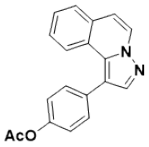


1-(p-tolyl)pyrazolo[5,1-*a*]isoquinoline (8): yellow oil, yield = 68%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 7.4 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.91 (s, 1H), 7.70 (d, J = 7.8 Hz, 1H),7.52 - 7.46 (m, 3H), 7.38 - 7.31 (m, 3H), 7.00 (d, J = 7.4 Hz, 1H), 2.48 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.99, 137.16, 133.67, 131.03, 129.84, 129.45, 129.37, 127.72, 127.23, 127.17, 126.64, 125.27, 123.44, 116.78, 112.31, 21.33. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2$ $(M+H)^+$ 259.1230, found 259.1234.

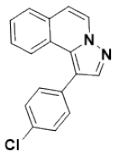


1-(4-methoxyphenyl)pyrazolo[5,1-*a*]isoquinoline (9): yellow oil, yield =

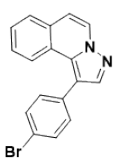
81%. (PE/EA = 10/1, Rf ≈ 0.4) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 7.4 Hz, 1H), 8.05 (d, J = 8.2 Hz, 1H), 7.90 (s, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.37 – 7.31 (m, 1H), 7.07 – 7.07 (m, 2H), 6.98 (d, J = 7.4 Hz, 1H), 3.91 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.06, 141.98, 133.71, 131.12, 129.34, 127.68, 127.24, 127.20, 126.63, 126.22, 125.29, 123.34, 116.43, 114.17, 112.28, 55.36. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2O$ $(M+H)^+$ 275.1179, found 275.1180.



4-(pyrazolo[5,1-*a*]isoquinolin-1-yl)phenyl acetate (10): white solid, m.p. = 89.3 - 91.4 °C, yield = 80%. (PE/EA = 5/1, Rf ≈ 0.5) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 7.4 Hz, 1H), 8.05 (d, J = 8.1 Hz, 1H), 7.90 (s, 1H), 7.69 (d, J = 7.8 Hz, 1H), 7.57 (d, J = 8.5 Hz, 2H), 7.51 - 7.46 (m, 1H), 7.38 - 7.33 (m, 1H), 7.24 (d, J = 8.5 Hz, 2H), 7.00 (d, J = 7.4 Hz, 1H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 169.55, 150.08, 141.85, 133.75, 131.64, 130.96, 129.41, 127.95, 127.37, 127.35, 126.48, 124.98, 123.37, 121.91, 115.85, 112.61, 21.21. HRMS (ESI): m/z calcd for $C_{19}H_{15}N_2O_2$ $(M+H)^+$ 303.1129, found 303.1126.

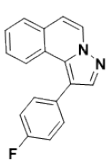


1-(4-chlorophenyl)pyrazolo[5,1-*a*]isoquinoline (11): yellow solid, m.p. = 58.9 – 60.3 °C, yield = 86%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, J = 7.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.90 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.52 (m, 1H), 7.49 (s, 2H), 7.47 - 7.44 (m, 1H), 7.41 - 7.33 (m, 2H), 7.03 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.67, 133.78, 133.45, 132.52, 131.27, 129.45, 128.98, 128.04, 127.43, 127.38, 126.46, 124.90, 123.27, 115.53, 112.71. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2$ $(M+H)^+$ 279.0684, found 279.0684.

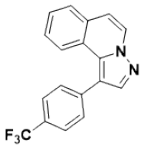


1-(4-bromophenyl)pyrazolo[5,1-*a*]isoquinoline (12): yellow oil, yield = 81%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 7.4 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.89 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.64 (d, J = 8.4 Hz, 2H), 7.53 (t, J = 4.1 Hz, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.38 (m, 1H), 7.03 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.67, 133.71, 133.04, 131.92, 131.59, 129.45, 128.03, 127.43, 127.38, 126.53, 124.90,

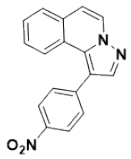
123.27, 121.53, 115.51, 112.68. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2$ $(M+H)^+$ 323.0179, found 323.0178.



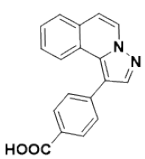
1-(4-fluorophenyl)pyrazolo[5,1-*a*]isoquinoline (13): yellow oil, yield = 74%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, J = 7.4 Hz, 1H), 7.97 (d, J = 8.2 Hz, 1H), 7.90 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.56 - 7.47 (m, 3H), 7.39 - 7.33 (m, 1H), 7.24 - 7.17 (m, 2H), 7.02 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.39 (d, J = 245.0 Hz), 141.87, 133.79, 131.68, 131.58, 130.02 (d, J = 3.6 Hz), 129.41, 127.87, 127.33 (d, J = 6.2 Hz), 126.61, 125.04, 123.20, 115.72 (d, J = 21.3 Hz), 115.67, 112.49. HRMS (ESI): m/z calcd for $C_{17}H_{12}FN_2$ $(M+H)^+$ 263.0980, found 263.0980.



(4-(trifluoromethyl)phenyl)pyrazolo[5,1-*a*]isoquinoline (14): white solid, m.p. = 148.0 – 148.7 °C, yield = 46%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, J = 7.4 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.93 (s, 1H), 7.79 – 7.70 (m, 5H), 7.56 - 7.51 (m, 1H), 7.42 - 7.37 (m, 1H), 7.06 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.82, 138.05, 133.85, 130.14, 129.55, 129.28, 128.18, 127.48 (d, J = 5.0 Hz), 126.56, 125.70 (d, J = 3.8 Hz), 125.70 (d, J = 11.3 Hz), 124.78, 124.28 (d, J = 271.9 Hz), 123.22, 115.38, 112.83. HRMS (ESI): m/z calcd for $C_{18}H_{12}F_3N_2$ $(M+H)^+$ 313.0948, found 313.0947.

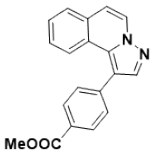


1-(4-nitrophenyl)pyrazolo[5,1-*a*]isoquinoline (15): yellow solid, m.p. = 135.8 – 136.5 °C, yield = 34%.Analytical data are identical to previous report (*Journal of Heterocyclic Chemistry* 1982, **19**, 573-576). (PE/EA = 10/1, Rf ≈ 0.3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.36 (d, J = 8.8 Hz, 2H), 8.29 (d, J = 7.4 Hz, 1H), 8.00 (d, J = 9.2 Hz, 1H), 7.95 (s, 1H), 7.76 (d, J = 8.8 Hz, 3H), 7.58 - 7.53 (m, 1H), 7.43 - 7.38 (m, 1H), 7.10 (q, J = 3.5 Hz, 1H). HRMS (ESI): m/z calcd for $C_{17}H_{12}O_2N_3$ $(M+H)^+$ 290.0925, found 290.0924.

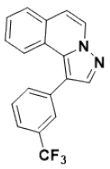


4-(pyrazolo[5,1-a]isoquinolin-1-yl)benzoic acid (16): light yellow solid, m.p. = 253.2 – 254.1 °C, yield = 46%.(PE/EA = 1/1, Rf ≈ 0.1). ^{1}H NMR (300 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.53 (d, J = 7.4 Hz, 1H), 8.09 (d,

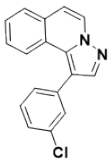
J = 9.1 Hz, 3H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.60 (t, *J* = 7.2 Hz, 1H), 7.48 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, DMSO-d_6) δ 167.58, 142.28, 138.69, 133.25, 130.30, 130.18, 130.08, 129.72, 128.80, 128.26, 128.09, 127.42, 124.49, 122.93, 115.79, 113.20. HRMS (ESI): m/z calcd for $C_{18}H_{11}O_2N_2$ $(M-H)^-$ 287.0826, found 287.0826.



methyl 4-(pyrazolo[5,1-*a*]isoquinolin-1-yl)benzoate (17): yellow oil, yield = 55%. (PE/EA = 5/1, Rf ≈ 0.3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.4 Hz, 1H), 8.19 - 8.16 (m, 2H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.94 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.68 - 7.65 (m, 2H), 7.54 - 7.49 (m, 1H),7.38 - 7.33 (m, 1H), 7.04 (d, *J* = 7.4 Hz, 1H), 3.99 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 166.98, 141.73, 139.05, 133.83, 130.03, 129.80, 129.54, 129.03, 128.14, 127.46, 127.39, 126.53, 124.81, 123.34, 115.86, 112.83, 52.23. HRMS (ESI): m/z calcd for $C_{19}H_{15}N_2O_2$ $(M+H)^+$ 303.1129, found 303.1128.

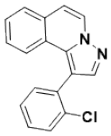


(3-(trifluoromethyl)phenyl)pyrazolo[5,1-*a*]isoquinoline (18): white solid, m.p. = 99.0 – 100.1 °C, yield = 64%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.4 Hz, 1H), 7.95 (d, *J* = 6.2 Hz, 2H), 7.85 (s, 1H), 7.79 - 7.61 (m, 4H), 7.56 - 7.50 (m, 1H), 7.40 - 7.35 (m, 1H), 7.06 (d, *J* = 7.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 141.82, 135.05, 133.87, 133.25, 131.19 (d, *J* = 32.2 Hz), 129.52, 128.67 (d, *J* = 82.1 Hz), 127.51, 127.41, 126.68 (d, *J* = 3.8 Hz), 126.60, 124.80, 124.17 (d, *J* = 12.5 Hz), 124.17 (d, *J* = 3.8 Hz), 124.08 (d, *J* = 272.5 Hz), 123.09, 115.26, 112.77. HRMS (ESI): m/z calcd for $C_{18}H_{12}F_3N_2$ $(M+H)^+$ 313.0948, found 313.0948.

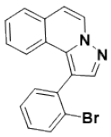


(3-chlorophenyl)pyrazolo[5,1-*a*]isoquinoline (19): yellow oil, yield = 69%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (d, *J* = 7.4 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 1.3 Hz, 1H), 7.54 - 7.49 (m, 1H), 7.47 - 7.41 (m, 3H), 7.38 - 7.35 (m, 1H), 7.03 (d, *J* = 7.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 141.74, 135.99, 134.55, 133.80, 129.95, 129.94, 129.48, 128.15, 128.04, 127.58, 127.43, 127.42, 126.52,

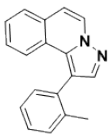
124.85, 123.30, 115.39, 112.71. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2$ $(M+H)^+$ 279.0684, found 279.0684.



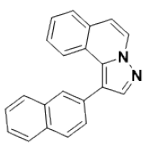
1-(2-chlorophenyl)pyrazolo[5,1-*a*]isoquinoline (20): yellow oil, yield = 53%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 7.4 Hz, 1H), 7.94 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.6 Hz, 1H), 7.61 – 7.61 (m, 1H), 7.53 - 7.47 (m, 2H), 7.43 - 7.39 (m, 2H), 7.38 - 7.33 (m, 1H), 7.05 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.85, 135.13, 134.51, 132.97, 132.70, 129.91, 129.39, 129.30, 127.90, 127.45, 127.11, 126.99, 126.55, 125.03, 123.58, 113.11, 112.59. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2$ $(M+H)^+$ 279.0684, found 279.0684.



1-(2-bromophenyl)pyrazolo[5,1-*a*]isoquinoline (21): yellow oil, yield = 72%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 7.4 Hz, 1H), 7.93 (s, 1H), 7.81 – 7.78 (m, 1H), 7.71 (d, J = 7.9 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H), 7.52 - 7.42 (m, 3H), 7.37 - 7.31 (m, 2H), 7.05 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.71, 135.00, 134.33, 133.10, 132.71, 129.52, 129.37, 127.91, 127.61, 127.49, 127.14, 126.52, 125.78, 124.97, 123.63, 115.06, 112.61. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2$ $(M+H)^+$ 323.0179, found 323.0177.

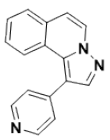


1-(o-tolyl)pyrazolo[5,1-*a*]isoquinoline (22): yellow oil, yield = 95%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 7.4 Hz, 1H), 7.88 (s, 1H), 7.71 (d, J = 7.8 Hz, 1H), 7.56 (d, J = 8.1 Hz, 1H), 7.50 - 7.45 (m, 1H), 7.39 (t, J = 3.8 Hz, 3H), 7.35 - 7.28 (m, 2H), 7.03 (d, J = 7.4 Hz, 1H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.61, 137.99, 134.08, 133.38, 131.18, 130.25, 129.25, 128.09, 127.67, 127.53, 127.07, 126.63, 126.10, 125.34, 123.18, 115.26, 112.28, 20.25. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2$ $(M+H)^+$ 259.1230, found 259.1237.

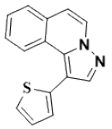


3-phenylpyrazolo[1,5-*a*]quinoline (23): yellow oil, yield = 94%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 7.4 Hz, 1H), 8.07 (t, J = 5.7 Hz, 2H), 8.03 (s, 1H), 7.99 (d, J = 8.6 Hz, 1H), 7.97 - 7.89

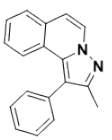
(m, 2H), 7.74 - 7.69 (m, 2H), 7.60 - 7.55 (m, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.30 (t, J = 8.2 Hz, 1H), 7.04 (d, J = 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.13, 133.92, 133.64, 132.66, 131.54, 129.46, 128.53, 128.32, 128.25, 127.99, 127.87, 127.83, 127.31, 126.67, 126. 45, 126.13, 125.19, 123.53, 116.77, 112.51. HRMS (ESI): m/z calcd for $C_{21}H_{15}N_2$ $(M+H)^+$ 295.1230, found 295.1233.



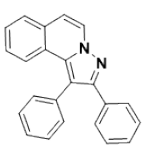
1-(pyridin-4-yl)pyrazolo[5,1-*a*]isoquinoline (24): light yellow solid, m.p. = 83.9 – 85.3 °C yield = 33%.(PE/EA = 3/1, Rf ≈ 0.5). ^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (d, J = 5.9 Hz, 2H), 8.28 (d, J = 7.4 Hz, 1H), 8.09 (d, J = 8.2 Hz, 1H), 7.94 (s, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.55 – 7.52 (m, 2H), 7.44 - 7.39 (m, 1H), 7.08 (d, J = 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 150.16, 142.61, 141.75, 133.97, 129.65, 128.40, 127.61, 127.54, 126.58, 124.57, 124.53, 123.28, 114.07, 113.09. HRMS (ESI): m/z calcd for $C_{16}H_{12}N_3$ $(M+H)^+$ 246.1026, found 246.1032.



1-(thiophen-2-yl)pyrazolo[5,1-*a*]isoquinoline (25): yellow oil, yield = 37%. (PE/EA = 10/1, Rf ≈ 0.4). ^1H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 7.4 Hz, 1H), 8.17 (d, J = 8.1 Hz, 1H), 7.97 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.55 - 7.49 (m 1H), 7.47 -7.47 (m, 1H), 7.43 - 7.38 (m, 1H), 7.24 - 7.19 (m, 2H), 7.04 (d, J = 7.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 142.88, 136.49, 134.74, 129.50, 128.07, 127.82, 127.57, 127.47, 127.26, 126.52, 126.16, 124.92, 123.52, 112.74, 108.46. HRMS (ESI): m/z calcd for $C_{15}H_{11}N_2S$ $(M+H)^+$ 251.0638, found 251.0637.

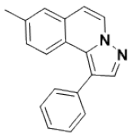


2-methyl-1-phenylpyrazolo[5,1-*a*]isoquinoline (26): yellow oil, yield = 87%. (PE/EA = 10/1, Rf ≈ 0.4). ^1H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 7.4 Hz, 1H), 7.75 (d, J = 8.2 Hz, 1H), 7.67 (d, J = 7.9 Hz, 1H), 7.56 - 7.42 (m, 6H), 7.30 - 7.24 (m, 1H), 6.93 (d, J = 7.4 Hz, 1H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 149.72, 134.69, 134.27, 130.75, 129.51, 128.82, 127.50, 127.46, 127.11, 127.01, 126.14, 124.81, 123.30, 114.86, 111.28, 12.30. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2$ $(M+H)^+$ 259.1230, found 259.1232

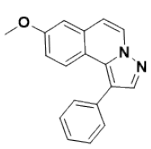


1,2-diphenylpyrazolo[5,1-a]isoquinoline (27): yellow solid, m.p. =

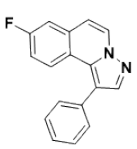
135.3 – 134.7 °C, yield = 45%. (PE/EA = 10/1, Rf ≈ 0.3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (d, J = 7.4 Hz, 1H), 7.71 – 7.63 (m, 2H), 7.58 – 7.55 (m, 2H), 7.51- 7.44 (m, 6H), 7.29 – 7.25 (m, 4H), 7.02 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 150.93, 135.61, 134.54, 133.08, 131.28, 129.44, 129.15, 128.37, 128.24, 127.79, 127.60, 127.27, 127.23, 126.31, 125.22, 123.39, 114.10, 112.40. HRMS (ESI): m/z calcd for $C_{23}H_{17}N_2$ $(M+H)^+$ 321.1387, found 321.1390.



8-methyl-1-phenylpyrazolo[5,1-*a*]isoquinoline (28): light yellow solid, m.p. = 75.8 – 76.2 °C, yield = 72%. (PE/EA = 10/1, Rf ≈ 0.4) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.25 (d, J = 7.4 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.91 (s, 1H), 7.60 -7.57 (m, 2H), 7.54 - 7.44 (m, 4H), 7.19 – 7.16 (m , 1H), 6.95 (d, J = 7.4 Hz, 1H), 2.47 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 141.88, 137.83, 134.25, 133.82, 129.96, 129.58, 128.74, 128.69, 127.32, 127.07, 126.59, 123.29, 122.86, 116.29, 112.24, 21.49. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2$ $(M+H)^+$ 259.1230, found 259.1234.

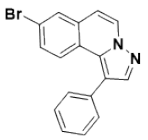


8-methoxy-1-phenylpyrazolo[5,1-*a*]isoquinoline (29): yellow oil, yield = 62%. (PE/EA = 10/1, Rf ≈ 0.3). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (d, J = 7.4 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.90 (s, 1H), 7.59 – 7.56 (m, 2H), 7.53 - 7.48 (m, 2H), 7.46 - 7.43 (m, 1H), 7.11 (d, J = 2.6 Hz, 1H), 6.99 - 6.93 (m, 2H), 3.90 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 159.10, 141.95, 134.22, 133.92, 131.21, 129.96, 128.74, 127.32, 126.94, 124.99, 119.15, 116.63, 115.57, 112.11, 108.58, 55.41. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2O$ $(M+H)^+$ 275.1179, found 275.1179.

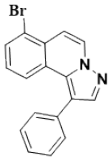


8-fluoro-1-phenylpyrazolo[5,1-*a*]isoquinoline (30): yellow solid, m.p. = 130.3 – 130.9 °C, yield = 77%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, J = 7.4 Hz, 1H), 8.06 – 8.02 (m, 1H), 7.94 (s, 1H), 7.57 - 7.45 (m, 5H), 7.40 – 7.34 (m, 1H), 7.11 - 7.04 (m, 1H), 6.95 (d, J = 7.4 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.81 (d, J = 248.3 Hz), 142.09, 133.78, 133.46, 131.33 (d, J = 9.0 Hz), 129.92, 128.88, 127.64, 127.54, 125.66 (d, J = 8.7 Hz), 121.74

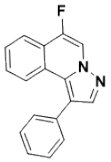
(d, J = 1.9 Hz), 116.49, 115.78 (d, J = 23.3 Hz), 112.23 (d, J = 21.8 Hz), 111.71 (d, J = 3.3 Hz). HRMS (ESI): m/z calcd for $C_{17}H_{12}FN_2$ $(M+H)^+$ 263.0980, found 263.0980.



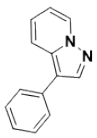
8-bromo-1-phenylpyrazolo[5,1-*a*]isoquinoline (31): yellow solid, m.p. = 80.8 – 82.1 °C, yield = 61%. (PE/EA = 10/1, Rf ≈ 0.4).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29 (d, J = 7.4 Hz, 1H), 7.94 (s, 1H), 7.90 (d, J = 8.8 Hz, 1H), 7.84 (d, J = 1.9 Hz, 1H), 7.56 - 7.51 (m, 3H), 7.49 - 7.46 (m, 1H), 7.45 – 7.43 (m, 1H), 7.39 – 7.38 (m, 1H), 6.91 (d, J = 7.4 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.18, 133.64, 133.27, 130.97, 130.36, 129.84, 129.57, 128.88, 127.69, 127.61, 124.86, 123.78, 121.76, 117.12, 111.26. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2$ $(M+H)^+$ 323.0179, found 323.0177.



7-bromo-1-phenylpyrazolo[5,1-*a*]isoquinoline (32): yellow oil, yield = 55%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (d, J = 7.7 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 7.96 (s, 1H), 7.75 – 7.73 (m, 1H), 7.57 - 7.45 (m, 6H), 7.16 (t, J = 8.0 Hz, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 142.56, 133.72, 133.00, 131.77, 129.95, 128.85, 128.55, 127.83, 127.78, 127.69, 126.68, 122.84, 122.16, 117.36, 111.02. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2$ $(M+H)^+$ 323.0179, found 323.0179.

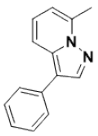


6-fluoro-1-phenylpyrazolo[5,1-*a*]isoquinoline (33): yellow solid, m.p. = 105.3 – 106.1 °C, yield = 38%. (PE/EA = 10/1, Rf ≈ 0.4). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (d, J = 5.2 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.91 (s, 1H), 7.61 - 7.40 (m, 7H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 149.88 (d, J = 241.2 Hz), 141.96 (d, J = 2.6 Hz), 133.67, 131.85, 129.92, 128.82, 128.54, 127.93 (d, J = 0.9 Hz), 127.62, 124.55 (d, J = 6.0 Hz), 123.37 (d, J = 2.8 Hz), 122.93 (d, J = 18.7 Hz), 120.72 (d, J = 5.0 Hz), 117.18, 112.90 (d, J = 40.0 Hz). HRMS (ESI): m/z calcd for $C_{17}H_{12}FN_2$ $(M+H)^+$ 263.0980, found 263.0978.

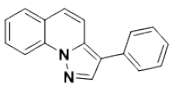


3-phenylpyrazolo[1,5-*a*]pyridine (34) is identical to previous report (*Adv. Synth. Catal.* **2016***,* 358, 2661–2670): yellow oil, yield = 43%.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.51 (d, J = 7.0 Hz, 1H), 8.16 (s, 1H), 7.83 (d, J = 9.0 Hz,

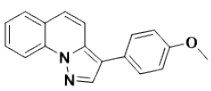
1H), 7.62 (t, *J* = 4.2 Hz, 2H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.21 - 7.16 (m, 1H), 6.83 -6.78 (m, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 140.39, 136.98, 133.19, 129.05, 129.01, 127.08, 126.25, 123.98, 117.50, 112.90, 112.05.



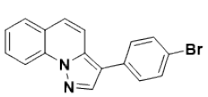
7-methyl-3-phenylpyrazolo[1,5-*a*]pyridine (35) is identical to previous report (*Adv. Synth. Catal.* **2016***,* 358, 2661 – 2670): light yellow oil, yield = 35%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.77 (d, *J* = 8.9 Hz, 1H), 7.65 - 7.62 (m, 2H), 7.47 (t, *J* = 5.1 Hz, 2H), 7.34 – 7.28 (m, 1H), 7.18 – 7.13 (m, 1H), 6.69 (d, *J* = 6.8 Hz, 1H), 2.80 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.90, 138.48, 137.36, 133.51, 128.98, 127.17, 126.14, 124.07, 115.08, 113.08, 111.45, 17.98.



3-phenylpyrazolo[1,5-*a*]quinoline (37): white solid, m.p. = 96.9 – 97.3 °C, yield = 56%. (PE/EA = 10/1, Rf ≈ 0.6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.22 (s, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 9.4 Hz, 2H), 7.68 - 7.63 (m, 2H), 7.53 - 7.45 (m, 4H), 7.35 (t, *J* = 7.4 Hz, 1H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 139.93, 135.05, 134.70, 133.04, 129.57, 129.04, 128.29, 127.46, 126.58, 125.14, 124.87, 123.42, 115.92, 115.86, 115.51. HRMS (ESI): m/z calcd for $C_{17}H_{12}N_2$ $(M+H)^+$ 245.1074, found 245.1079.

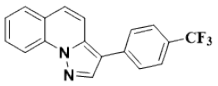


3-(4-methoxyphenyl)pyrazolo[1,5-*a*]quinoline (38): light yellow solid, m.p. = 137.0 – 138.6 °C yield = 51%. (PE/EA = 10/1, Rf ≈ 0.5). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.4 Hz, 1H), 8.16 (s, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.72 – 7.64 (m, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.45 (t, *J* = 8.9 Hz, 2H), 7.04 (d, *J* = 8.6 Hz, 2H), 3.88 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 158.52, 139.72, 135.07, 134.48, 129.49, 128.64, 128.27, 125.47, 124.79, 124.78, 123.41, 115.96, 115.60, 115.44, 114.51, 55.39. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2O$ $(M+H)^+$ 275.1179, found 275.1179.

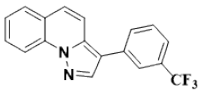


3-(4-bromophenyl)pyrazolo[1,5-*a*]quinoline (39): light yellow solid, m.p. = 159.2 – 160.1 °C, yield = 78%. (PE/EA = 10:1, Rf ≈ 0.6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.18 (s, 1H), 7.80 (d, *J* =

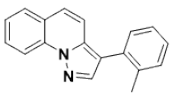
8.0 Hz, 1H), 7.72 (t, J = 7.8 Hz, 1H), 7.66 (d, J = 9.4 Hz, 1H), 7.61 (d, J = 8.4 Hz, 2H), 7.53 – 7.47 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.77, 134.98, 134.66, 132.13, 131.99, 129.74, 128.92, 128.35, 125.56, 125.04, 123.37, 120.34, 115.55, 114.67. HRMS (ESI): m/z calcd for $C_{17}H_{12}BrN_2$ $(M+H)^+$ 323.0179, found 323.0169.



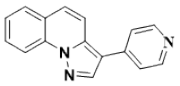
3-(4-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]quinoline (40): light yellow-white solid, yield = 37%. (PE/EA = 10/1, Rf ≈ 0.6). ^1H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.76 - 7.69 (m, 6H), 7.57 – 7.48 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 140.01, 136.79, 134.94, 129.88, 128.41 (d, J = 32.5 Hz), 128.38, 127.34, 126.01, 125.95, 125.91, 125.18, 124.29 (d, J = 271.6 Hz), 123.39, 115.64, 115.38, 114.42. HRMS (ESI): m/z calcd for $C_{18}H_{12}F_3N_2$ $(M+H)^+$ 313.0948, found 313.0946.



3-(3-(trifluoromethyl)phenyl)pyrazolo[1,5-*a*]quinoline (41): pale yellow-white solid, yield = 61%. (PE/EA = 10/1, Rf ≈ 0.6). ^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, J = 8.3 Hz, 1H), 8.23 (s, 1H), 7.87 (s, 1H), 7.82 (d, J = 7.89 Hz, 2H), 7.76 – 7.68 (m, 2H), 7.61 - 7.48 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.91, 134.93 (d, J = 6.2 Hz), 133.93, 130.56, 129.85, 129.51, 128.40, 125.93, 125.15, 124.21 (d, J = 275.4 Hz), 123.93 (d, J = 3.6 Hz), 123.61 (d, J = 58.5 Hz), 123.47 (d, J = 58.1 Hz), 123.40, 123.15 (d, J = 4.1 Hz), 115.63, 115.32, 114.45. HRMS (ESI): m/z calcd for $C_{18}H_{12}F_3N_2$ $(M+H)^+$ 313.0948, found 313.0947.

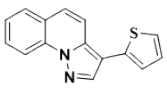


3-(o-tolyl)pyrazolo[1,5-*a*]quinoline (42): white solid, m.p. = 76.1 – 77.2 °C, yield = 79%. (PE/EA = 10/1, Rf ≈ 0.6). ^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, J = 8.4 Hz, 1H), 8.09 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.74 - 7.69 (m, 1H), 7.50 - 7.28 (m, 7H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 141.09, 136.87, 135.56, 134.98, 131.84, 130.60, 129.50, 128.35, 127.41, 125.94, 124.80, 124.73, 123.43, 116.08, 115.37, 114.97, 20.60. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2$ $(M+H)^+$ 259.1230, found 259.1223.

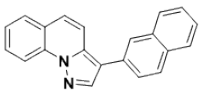


3-(pyridin-4-yl)pyrazolo[1,5-*a*]quinoline (43): yellow solid, m.p. = 132.4 – 133.2 °C, yield = 31%. (PE/EA = 10/1, Rf ≈ 0.3). ^1H NMR

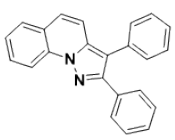
(300 MHz, $CDCl_3$) δ 8.66 (d, J = 5.6 Hz, 2H), 8.61 (d, J = 8.5 Hz, 1H), 8.28 (s, 1H), 7.80 (d, J = 8.0 Hz, 1H), 7.75 - 7.70 (m, 2H), 7.58 - 7.47 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 150.26, 140.92, 140.07, 135.20, 134.87, 130.04, 128.40, 126.55, 125.35, 123.33, 121.40, 115.72, 115.26, 112.80. HRMS (ESI): m/z calcd for $C_{16}H_{12}N_3$ $(M+H)^+$ 246.1026, found 246.1032.



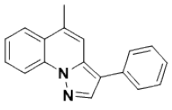
3-(thiophen-2-yl)pyrazolo[1,5-a]quinoline (44): brine solid, m.p. = 88.6 – 89.4 °C, yield = 38%. (PE/EA = 10/1, Rf ≈ 0.6). ^1H NMR (300 MHz, $CDCl_3$) δ 8.59 (d, J = 8.4 Hz, 1H), 8.21 (s, 1H), 7.79 – 7.76 (m, 2H), 7.73 - 7.67 (m, 1H), 7.51 - 7.44 (m, 2H), 7.32 – 7.30 (m, 1H), 7.28 - 7.26 (m, 1H), 7.17 -7.14 (m, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 139.70, 134.89, 134.69, 134.43, 129.70, 128.33, 127.71, 125.37 124.99, 123.56, 123.41, 123.35, 115.90, 115.52, 109.60. HRMS (ESI): m/z calcd for $C_{15}H_{11}N_2S$ $(M+H)^+$ 251.0638, found 251.0637.



3-(naphthalen-2-yl)pyrazolo[1,5-*a*]quinoline (45): white solid, m.p. = 150.6 – 151.3 °C yield = 74%. (PE/EA = 10:1, Rf ≈ 0.6).^1H NMR (300 MHz, $CDCl_3$) δ 8.65 (d, J = 8.4 Hz, 1H), 8.33 (s, 1H), 8.07 (s, 1H), 7.96 (d, J = 8.5 Hz, 1H), 7.91 (t, J = 6.5 Hz, 2H), 7.82 - 7.76 (m, 3H), 7.72 (t, J = 7.8 Hz, 1H), 7.57 - 7.46 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 140.18, 135.08, 134.89, 133.89, 132.84, 132.19, 130.48, 129.63, 128.68, 128.32, 127.78, 126.44, 126.12, 125.70, 125.48, 125.33, 124.92, 123.48, 115.98, 115.84, 115.56. HRMS (ESI): m/z calcd for $C_{21}H_{15}N_2$ $(M+H)^+$ 295.1230, found 295.1229.

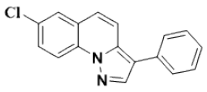


2,3-diphenylpyrazolo[1,5-*a*]quinoline (46): light yellow solid, m.p. = 120.3 – 121.0 °C, yield = 61%. (PE/EA = 10/1, Rf ≈ 0.5). ^1H NMR (300 MHz, $CDCl_3$) δ 8.72 (d, J = 8.4 Hz, 1H), 7.77 - 7.67 (m, 4H), 7.48 - 7.36 (m, 11H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 150.56, 137.19, 134.76, 133.32, 133.00, 130.06, 129.43, 128.91, 128.73, 128.36, 128.30, 127.99, 126.87, 124.92, 124.74, 123.62, 115.82, 115.63, 113.32. HRMS (ESI): m/z calcd for $C_{23}H_{17}N_2$ $(M+H)^+$ 321.1387, found 321.1389.



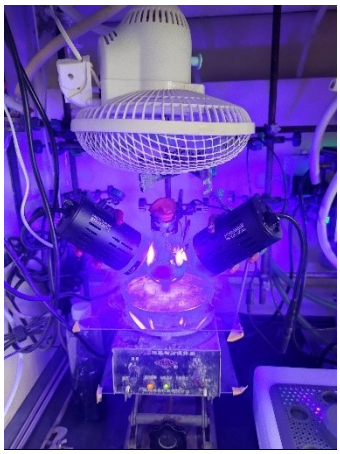
5-methyl-3-phenylpyrazolo[1,5-*a*]quinoline (47): light yellow solid,

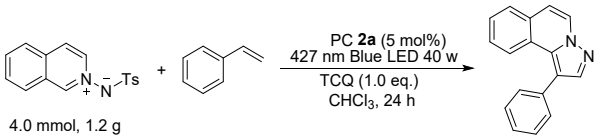
m.p. = 94.9 – 95.7 °C, yield = 92%. (PE/EA = 10/1, Rf ≈ 0.6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (d, J = 4.2 Hz, 1H), 8.17 (s, 1H), 7.87 (d, J = 8.1 Hz, 1H), 7.73 - 7.67 (m, 1H), 7.66 – 7.63 (m, 2H), 7.54 – 7.52 (m, 2H), 7.50 – 7.47 (m, 2H), 7.37 – 7.32 (m, 1H), 2.62 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 139.88, 134.73, 134.50, 133.27, 132.14, 129.31, 129.00, 127.38, 126.39, 125.08, 124.69, 123.78, 115.72, 115.09, 114.85, 19.39. HRMS (ESI): m/z calcd for $C_{18}H_{15}N_2$ $(M+H)^+$ 259.1230, found 259.1231



7-chloro-3-phenylpyrazolo[1,5-*a*]quinoline (48): light yellow solid, m.p. = 147.0 – 147.9 °C yield = 89%. (PE/EA = 10/1, Rf ≈ 0.6). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.53 (d, J = 8.9 Hz, 1H), 8.20 (s, 1H), 7.71 (d, J = 9.8 Hz, 2H), 7.63 (s, 3H), 7.50 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 140.17, 134.47, 133.46, 132.69, 130.38, 129.73, 129.09, 127.47, 127.33, 126.79, 124.45, 123.92, 117.25, 117.08, 116.37. HRMS (ESI): m/z calcd for $C_{17}H_{12}ClN_2$ $(M+H)^+$ 279.0684, found 279.0684.

2.9 Experiment of gram scale (4 mmol, 1.2 g)

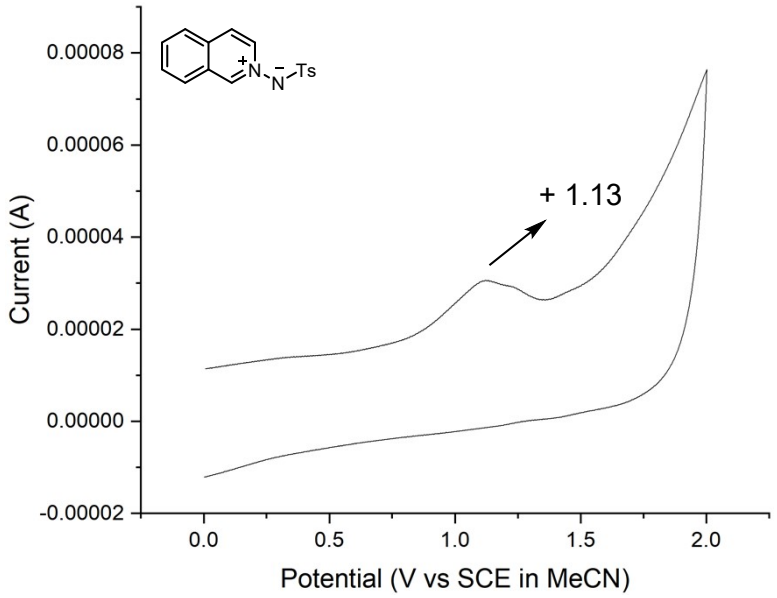




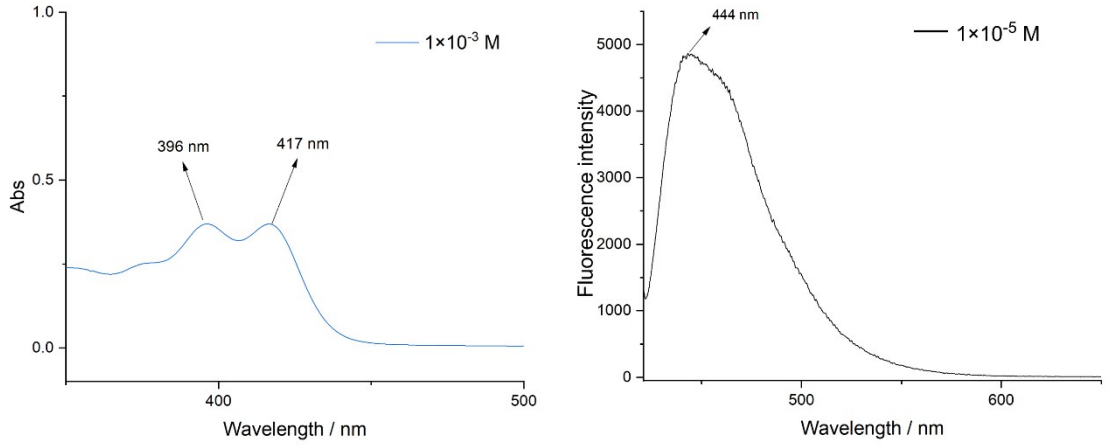
A 100 mL eggplant shaped flask equipped with a suitable magnetic stirrer, addition

3a (4.0 mmol, 1.2 g) and PC **2a** (0.2 mmol, 0.18 g), Tetrachloro-p-benzoquinone (4.0 mmol, 0.98 g), the $CHCl_3$ (50.0 mL) and styrene **4a** (10.0 mmol, 1.2 mL) was added. The reaction mixture stirred under blue LED 427 nm 40 w for 24 h with TLC analysis (PE/EA (v/v = 10/1) showed the completely consumption of isoquinolin-2-ium-2-yl(tosyl)amide. Then the reaction mixture was purified by gel silica column chromatography using PE/EA (v/v = 10/1) to EA after the solvent was removed under reduced pressure to give the target product as yellow oil (0.68 g, 70%).

2.10 Cyclic voltammogram of 3a.



2.11 Basic photophysical data of bisphosphonium salt 2d.



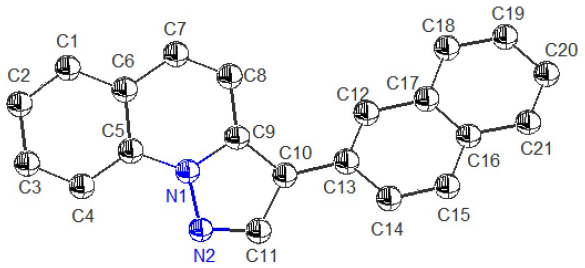
2d: in degassed CH_2Cl_2

Here are the UV-Vis absorption and fluorescence emission spectra of the compound **2d** (The basic photophysical properties of the compound **2a-2c** are detailed in *J. Am. Chem. Soc.*, 2021, **143**, 6357-6362).

3. X-ray crystallographic data of compound 45

Method for single crystal cultivation: A pure solid sample (10-30 mg) was dissolved in THF (1.0 mL) in a vial at room temperature, and hexane (2-4 mL) was slowly added into the above solution while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

A suitable crystal was selected and the data were collected on a Bruker APEX-II CCD diffractometer and an Oxford diffraction Gemini E diffractometer. The crystal was kept at 293 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimization, with anisotropic displacement parameters for all the nonhydrogen atoms. The crystallographic data have already been deposited at the Cambridge Crystallographic Data Center.



X-ray crystal structure of **45** (**CCDC: 2341296**)
Ellipsoids are at the 50% probability level

Table 3.1 Crystal data and structure refinement for **45**

Identification code	**45**
Empirical formula	$C_{21}H_{14}N_2$
Formula weight	294.34
Temperature/K	293(2)
Crystal system	monoclinic
Space group	Cc
a/Å	10.0458(2)
b/Å	10.0442(3)
c/Å	29.4099(9)
α/°	90
β/°	98.558(3)
γ/°	90
Volume/Å3	2934.49(14)

Z	8
ρcalcg/cm3	1.332
μ/mm-1	0.612
F(000)	1232.0
Crystal size/mm3	0.14 × 0.1 × 0.07
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	12.174 to 141.08
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 9, -35 ≤ l ≤ 35
Reflections collected	20404
Independent reflections	5491 [R_{int} = 0.0505, R_{sigma} = 0.0354]
Data/restraints/parameters	5491/2/415
Goodness-of-fit on F2	1.026
Final R indexes [I>=2σ (I)]	R1 = 0.0716, wR2 = 0.2079
Final R indexes [all data]	R1 = 0.0759, wR2 = 0.2126
Largest diff. peak/hole / e Å-3	0.29/-0.22
Flack parameter	-0.1(4)

Table 3.2 Bond Lengths for **45**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.370(10)	C1'	C2'	1.359(10)
C1	C6	1.393(9)	C1'	C6'	1.412(9)
C2	C3	1.397(12)	C2'	C3'	1.403(12)
C3	C4	1.363(10)	C3'	C4'	1.358(10)
C4	C5	1.373(9)	C4'	C5'	1.372(9)
C5	C6	1.432(9)	C5'	C6'	1.421(9)
C5	N1	1.381(8)	C5'	N1'	1.384(8)
C6	C7	1.420(8)	C6'	C7'	1.432(9)
C7	C8	1.325(9)	C7'	C8'	1.342(9)
C8	C9	1.421(9)	C8'	C9'	1.409(9)
C9	C10	1.411(8)	C9'	C10'	1.400(9)
C9	N1	1.374(7)	C9'	N1'	1.368(8)
C10	C11	1.404(9)	C10'	C11'	1.413(9)
C10	C13	1.452(8)	C10'	C13'	1.450(9)
C11	N2	1.321(8)	C11'	N2'	1.317(8)
C12	C13	1.393(8)	C12'	C13'	1.379(8)
C12	C17	1.410(9)	C12'	C17'	1.404(8)
C13	C14	1.411(9)	C13'	C14'	1.430(8)
C14	C15	1.355(9)	C14'	C15'	1.350(9)
C15	C16	1.426(10)	C15'	C16'	1.427(10)
C16	C17	1.411(8)	C16'	C17'	1.410(8)
C16	C21	1.395(9)	C16'	C21'	1.408(9)
C17	C18	1.427(9)	C17'	C18'	1.420(9)
C18	C19	1.353(9)	C18'	C19'	1.352(9)
C19	C20	1.400(11)	C19'	C20'	1.374(12)
C20	C21	1.363(11)	C20'	C21'	1.383(11)
N1	N2	1.364(7)	N1'	N2'	1.357(7)

Table 3.3 Bond Angles for **45**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	122.0(7)	C2'	C1'	C6'	121.3(7)
C1	C2	C3	119.7(7)	C1'	C2'	C3'	119.9(7)
C4	C3	C2	120.0(7)	C4'	C3'	C2'	120.0(7)
C3	C4	C5	121.1(7)	C3'	C4'	C5'	121.1(7)
C4	C5	C6	120.3(6)	C4'	C5'	C6'	120.4(6)
C4	C5	N1	123.8(6)	C4'	C5'	N1'	123.6(6)
N1	C5	C6	115.9(5)	N1'	C5'	C6'	116.0(5)
C1	C6	C5	116.9(6)	C1'	C6'	C5'	117.2(6)
C1	C6	C7	124.4(6)	C1'	C6'	C7'	123.3(6)
C7	C6	C5	118.7(6)	C5'	C6'	C7'	119.5(6)
C8	C7	C6	122.9(6)	C8'	C7'	C6'	120.8(6)
C7	C8	C9	119.7(6)	C7'	C8'	C9'	120.8(6)
C10	C9	C8	135.7(6)	C10'	C9'	C8'	135.1(6)
N1	C9	C8	117.7(5)	N1'	C9'	C8'	117.8(5)
N1	C9	C10	106.5(5)	N1'	C9'	C10'	107.1(5)
C9	C10	C13	129.0(5)	C9'	C10'	C11'	102.4(5)
C11	C10	C9	102.8(5)	C9'	C10'	C13'	129.5(6)
C11	C10	C13	128.1(6)	C11'	C10'	C13'	128.1(6)
N2	C11	C10	114.5(5)	N2'	C11'	C10'	114.3(5)
C13	C12	C17	121.9(5)	C13'	C12'	C17'	121.8(5)
C12	C13	C10	121.8(5)	C12'	C13'	C10'	122.6(5)
C12	C13	C14	117.5(6)	C12'	C13'	C14'	117.6(6)
C14	C13	C10	120.7(5)	C14'	C13'	C10'	119.8(5)
C15	C14	C13	121.9(6)	C15'	C14'	C13'	121.6(6)
C14	C15	C16	121.5(6)	C14'	C15'	C16'	121.2(6)
C17	C16	C15	117.6(5)	C17'	C16'	C15'	117.6(6)
C21	C16	C15	123.0(6)	C21'	C16'	C15'	122.4(6)
C21	C16	C17	119.4(6)	C21'	C16'	C17'	120.0(6)
C12	C17	C16	119.7(6)	C12'	C17'	C16'	120.2(5)
C12	C17	C18	121.6(5)	C12'	C17'	C18'	121.7(5)
C16	C17	C18	118.7(6)	C16'	C17'	C18'	118.1(6)
C19	C18	C17	119.7(6)	C19'	C18'	C17'	119.9(6)
C18	C19	C20	121.4(7)	C18'	C19'	C20'	122.7(7)
C21	C20	C19	119.7(7)	C19'	C20'	C21'	119.4(7)
C20	C21	C16	121.0(7)	C20'	C21'	C16'	119.9(7)
C9	N1	C5	125.1(5)	C9'	N1'	C5'	125.0(5)
N2	N1	C5	122.7(5)	N2'	N1'	C5'	122.7(5)
N2	N1	C9	112.2(5)	N2'	N1'	C9'	112.3(5)
C11	N2	N1	103.9(5)	C11'	N2'	N1'	103.9(5)

4. Reference

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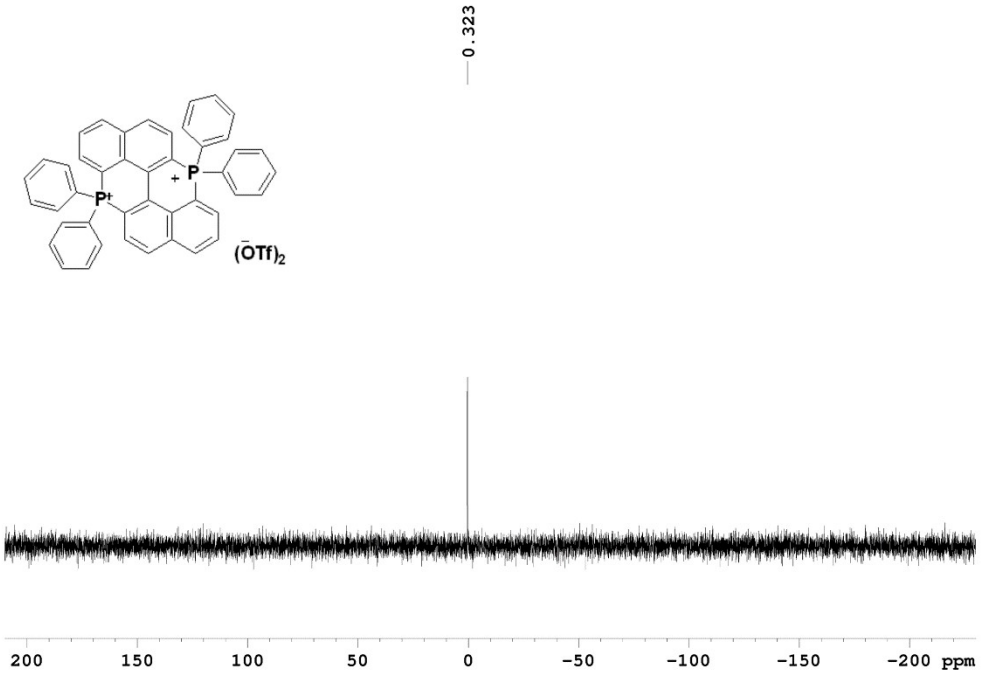
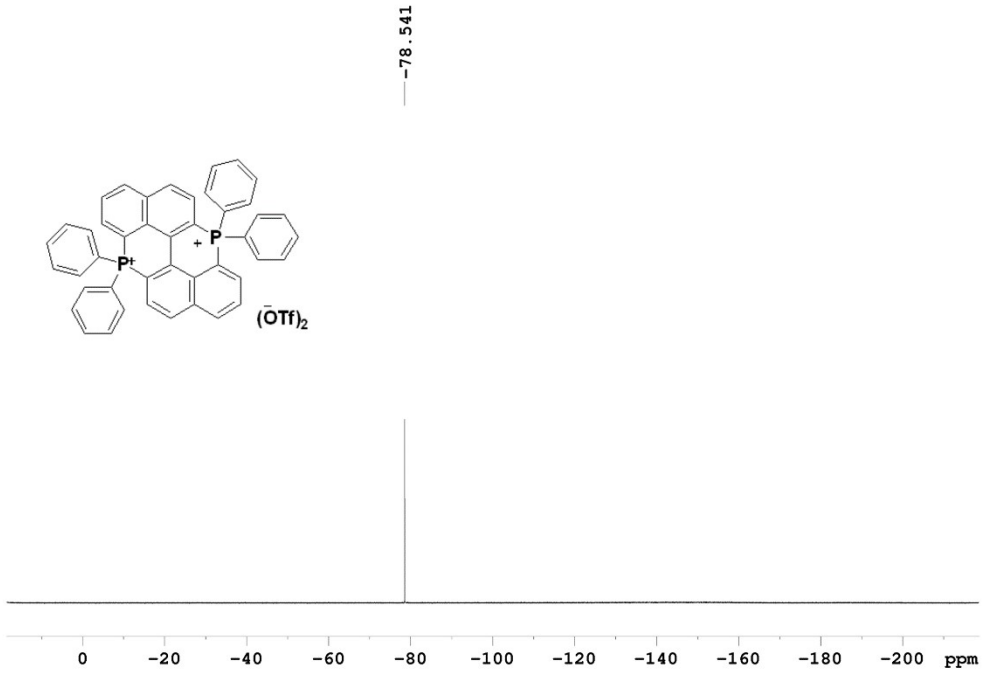
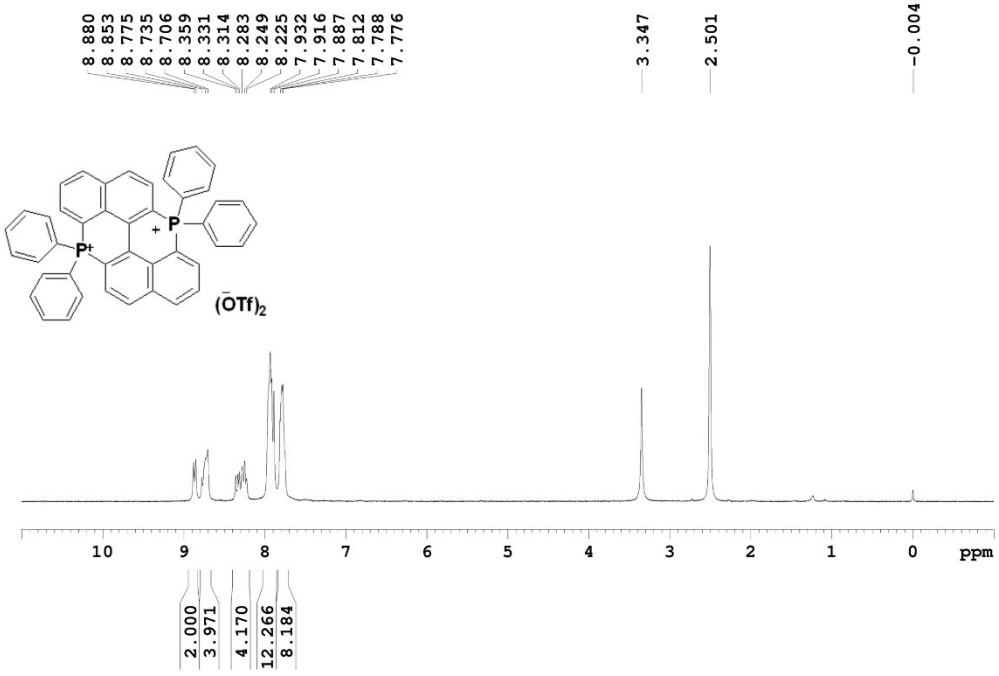


5. NMR spectra

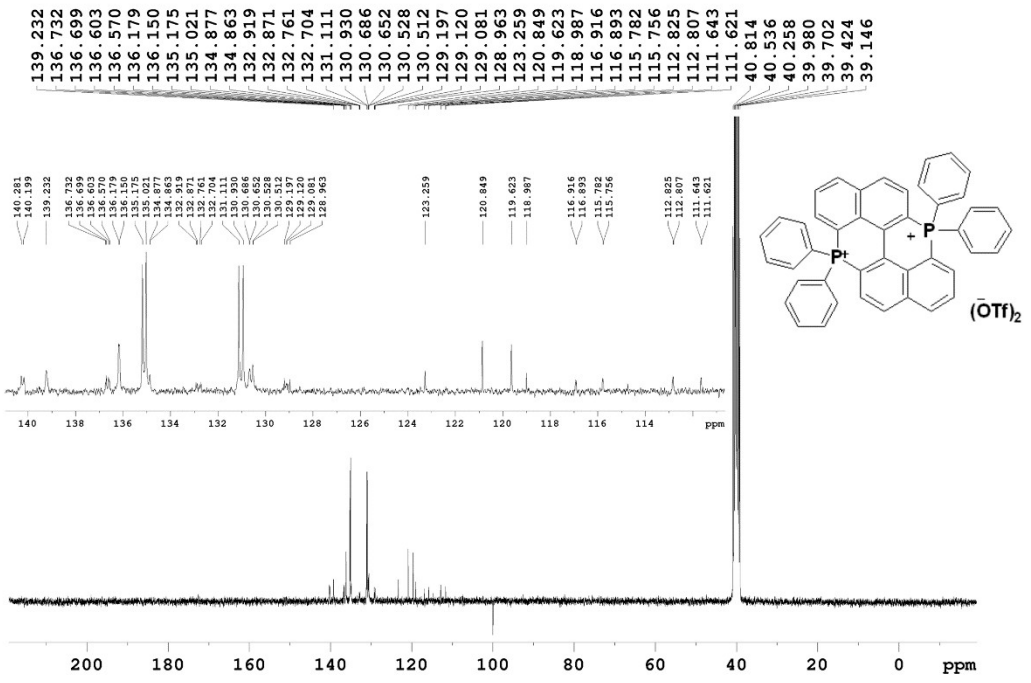
^{31}P NMR (121 MHz, DMSO-d_6) of **2a**



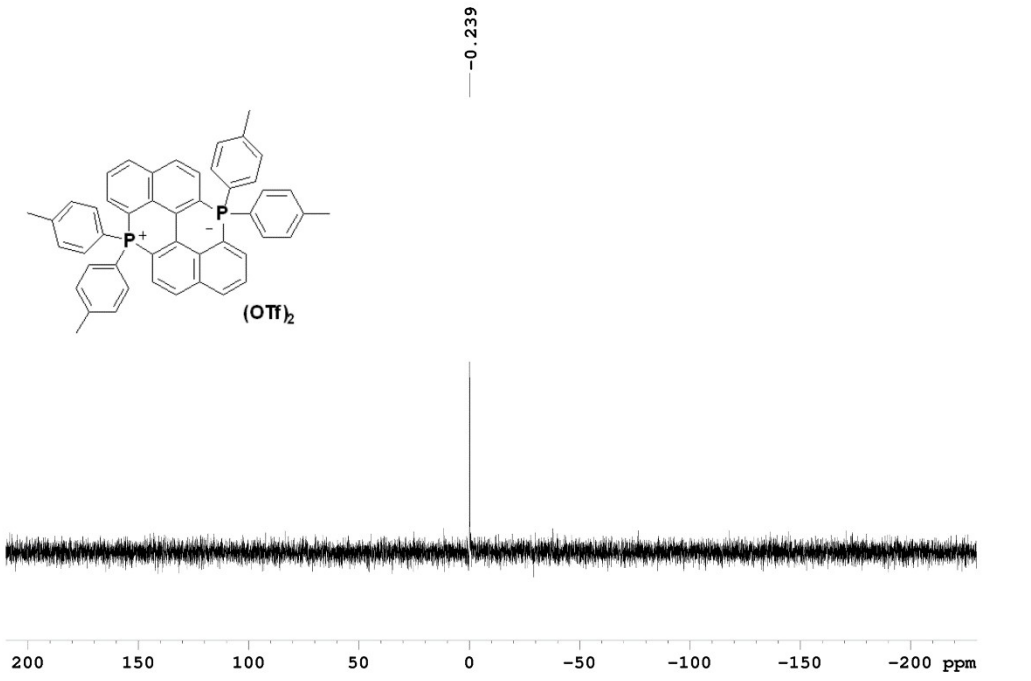
^{19}F NMR (282 MHz, DMSO-d_6) of **2a**



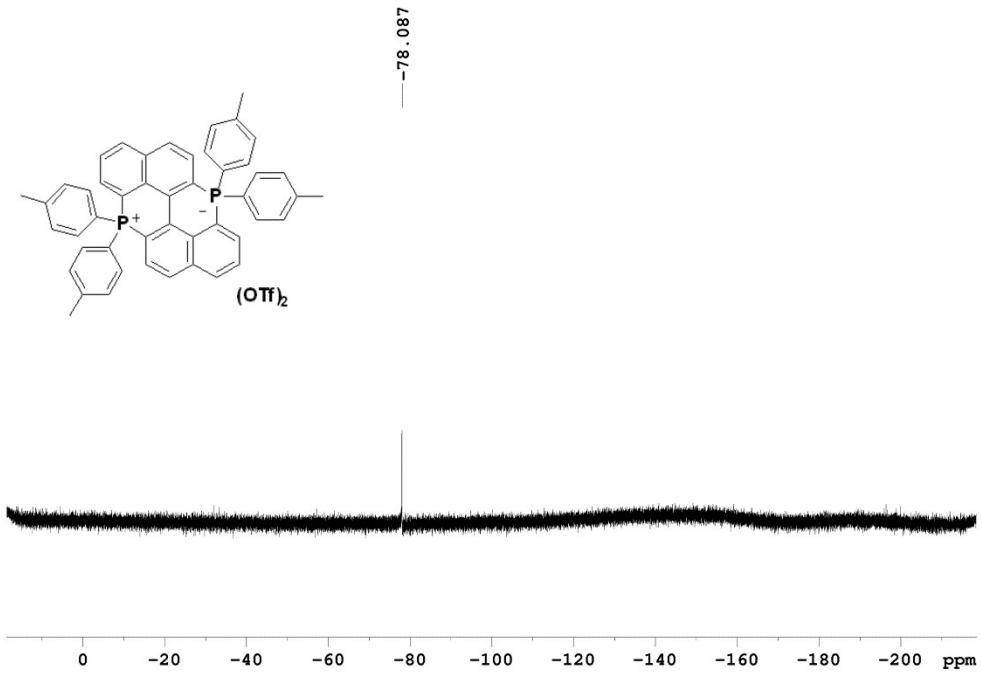
^{1}H NMR (300 MHz, DMSO-d_6) of **2a**



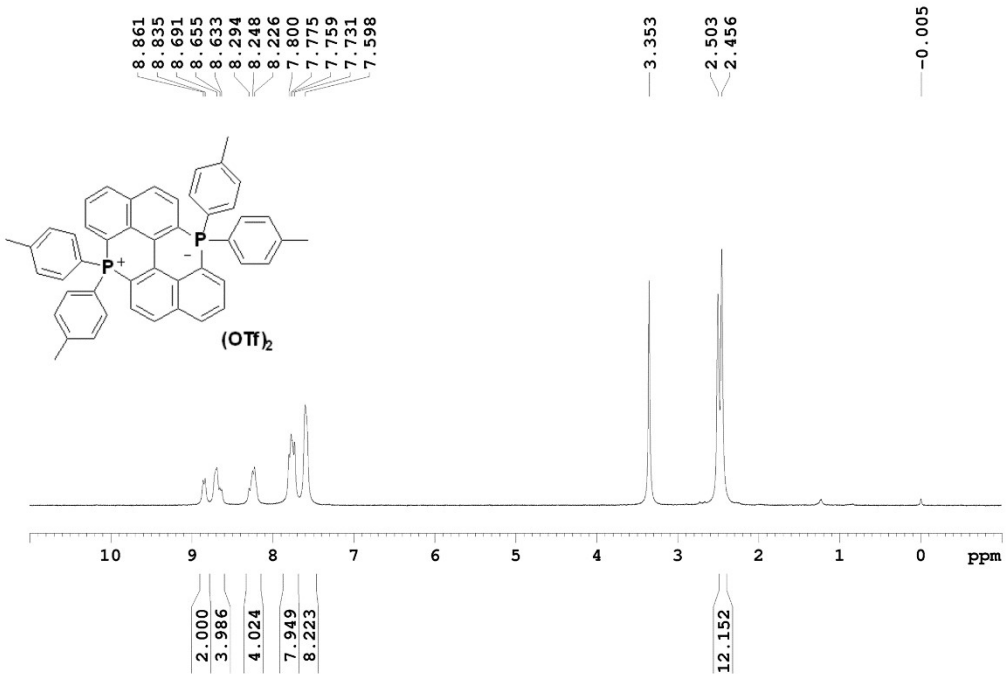
^{13}C NMR (75 MHz, DMSO-d$_6$) of **2a**



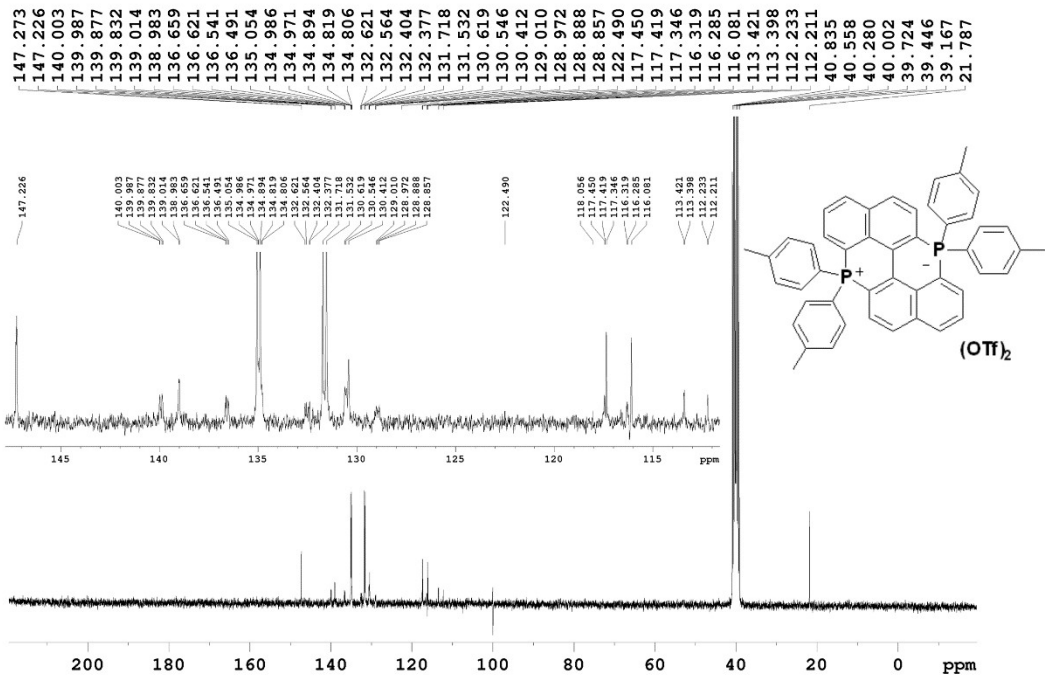
^{31}P NMR (121 MHz, DMSO-d$_6$) of **2b**



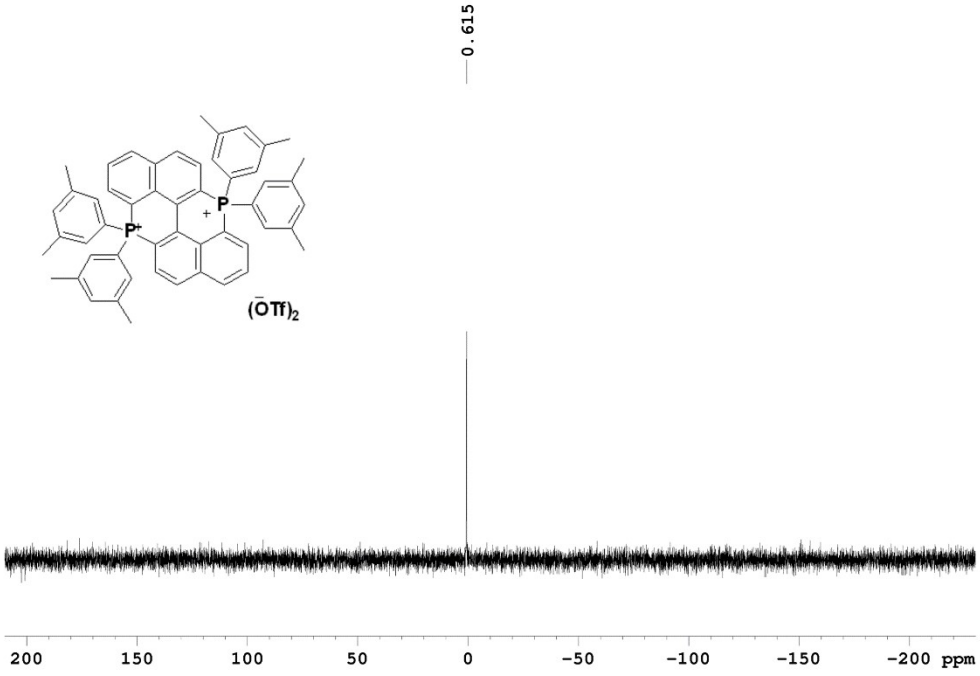
^{19}F NMR (282 MHz, DMSO-d_6) of **2b**



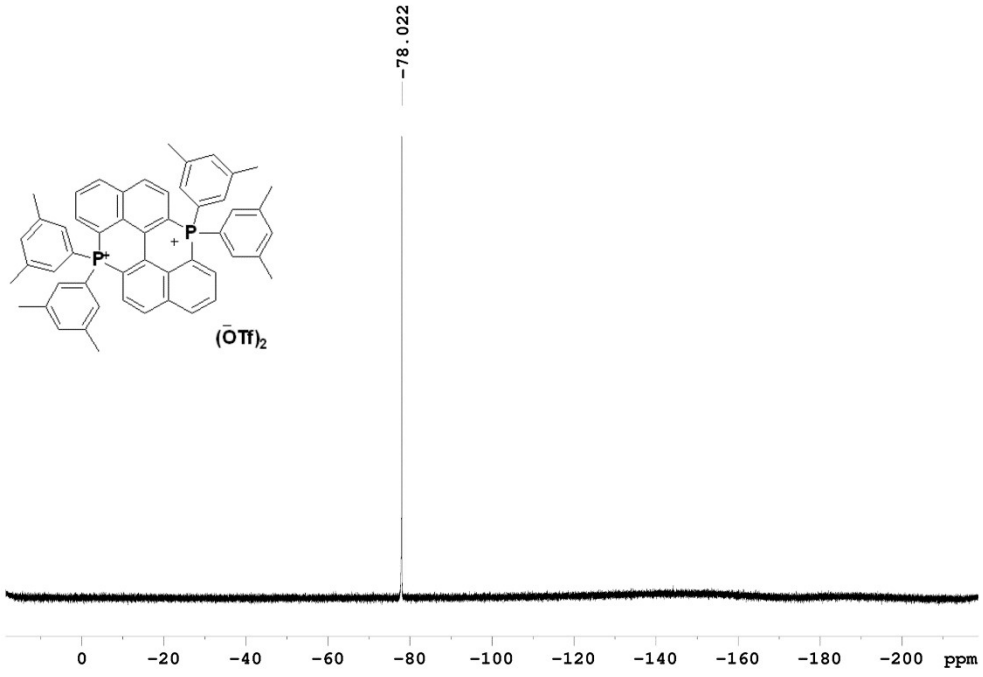
^{1}H NMR (300 MHz, DMSO-d_6) of **2b**



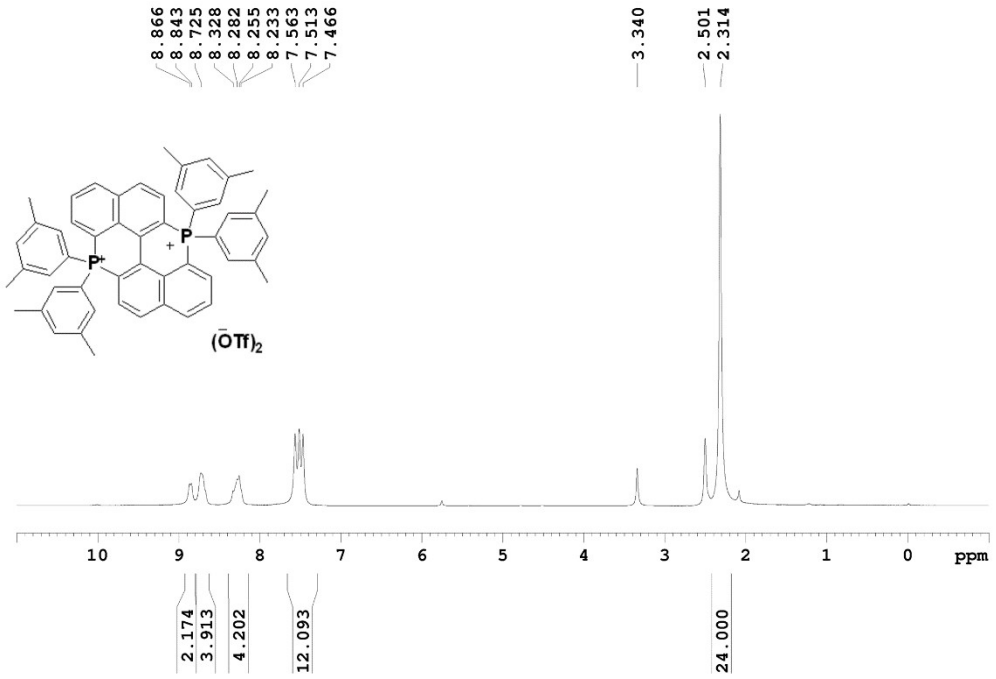
^{13}C NMR (75 MHz, DMSO-d_6) of **2b**



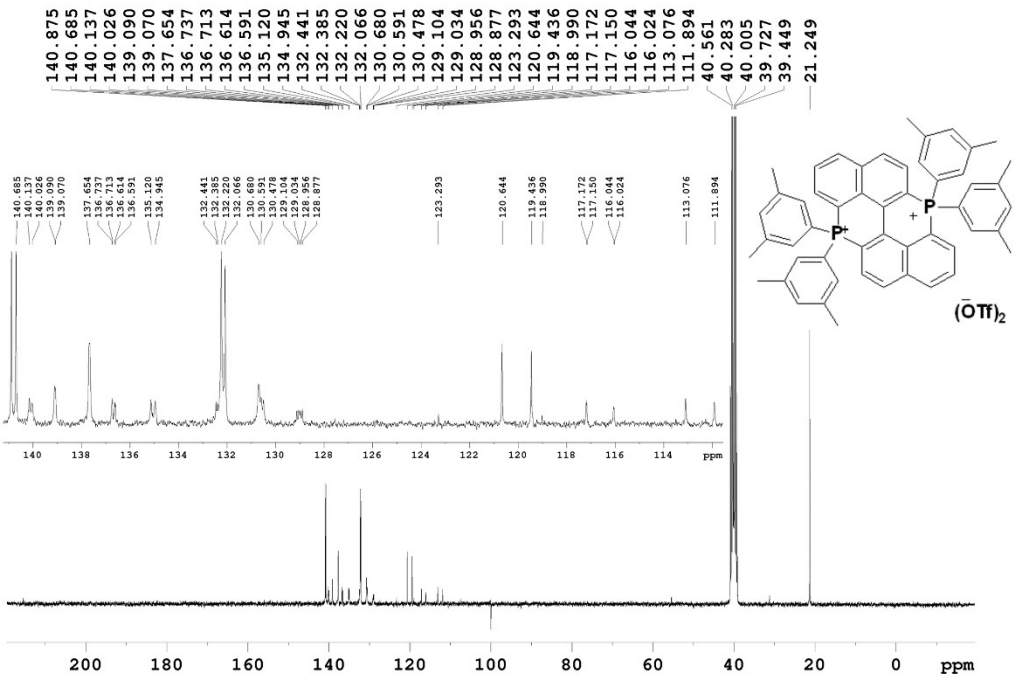
^{31}P NMR (121 MHz, DMSO-d_6) of **2c**



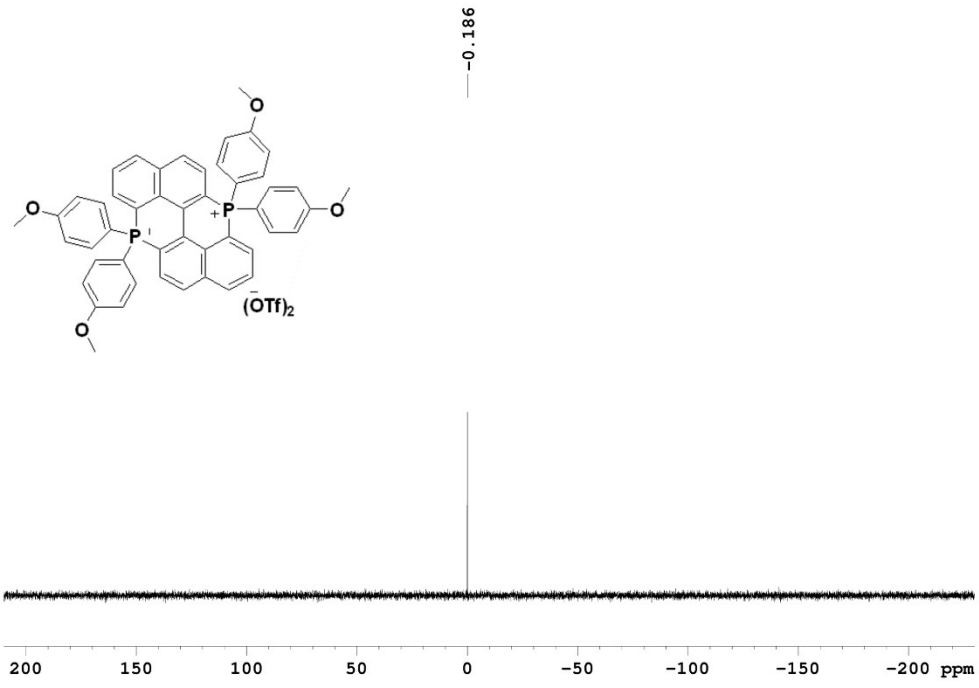
^{19}F NMR (282 MHz, DMSO-d_6) of **2c**



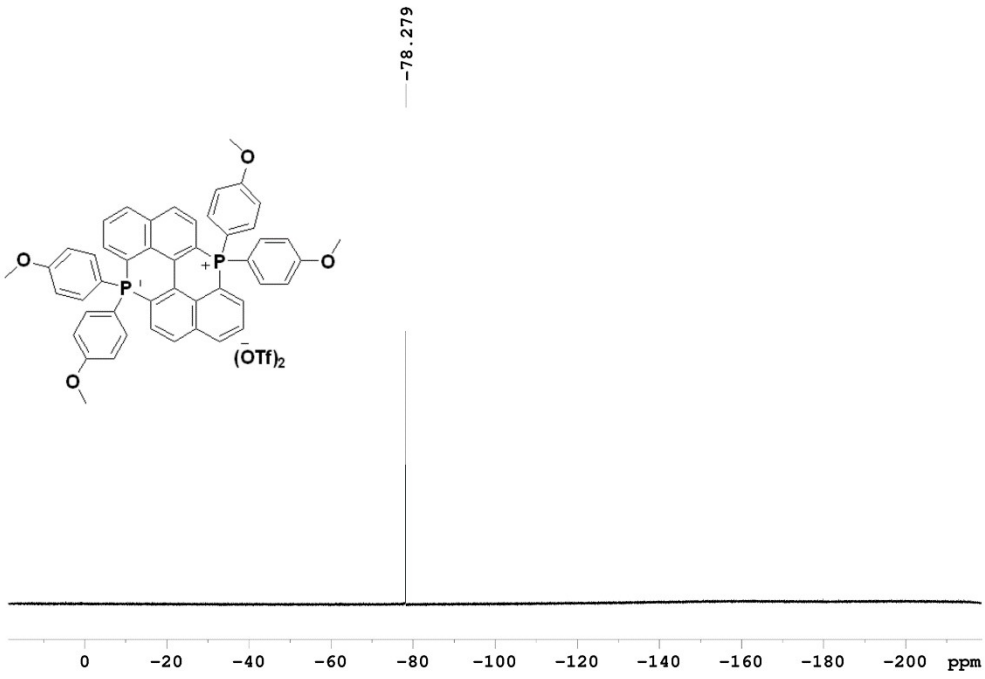
^{1}H NMR (300 MHz, DMSO-d_6) of **2c**



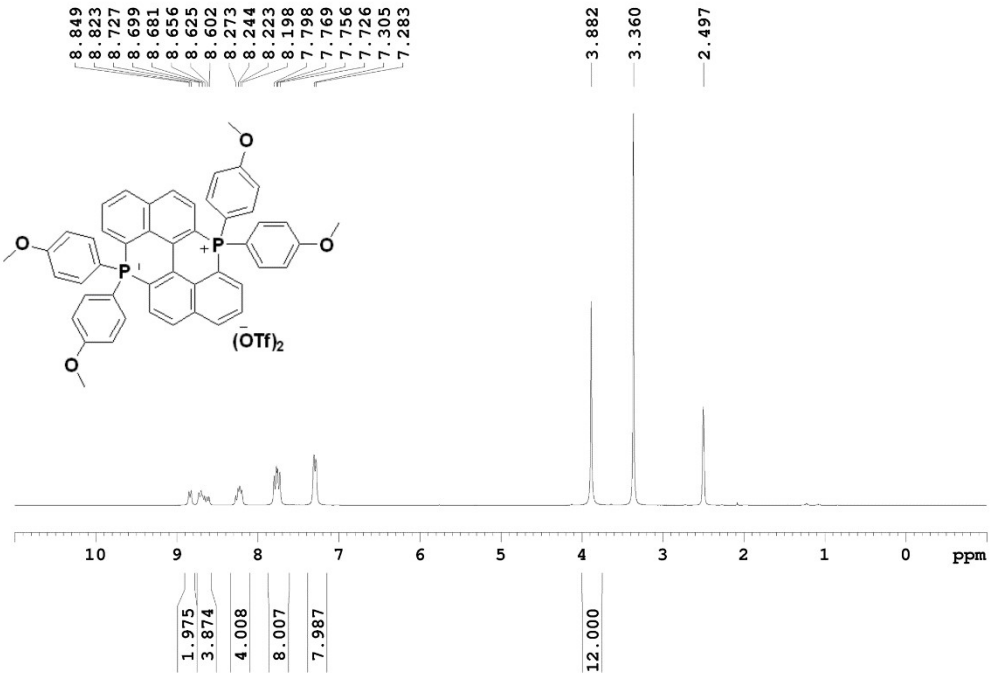
^{13}C NMR (75 MHz, DMSO-d_6) of **2c**



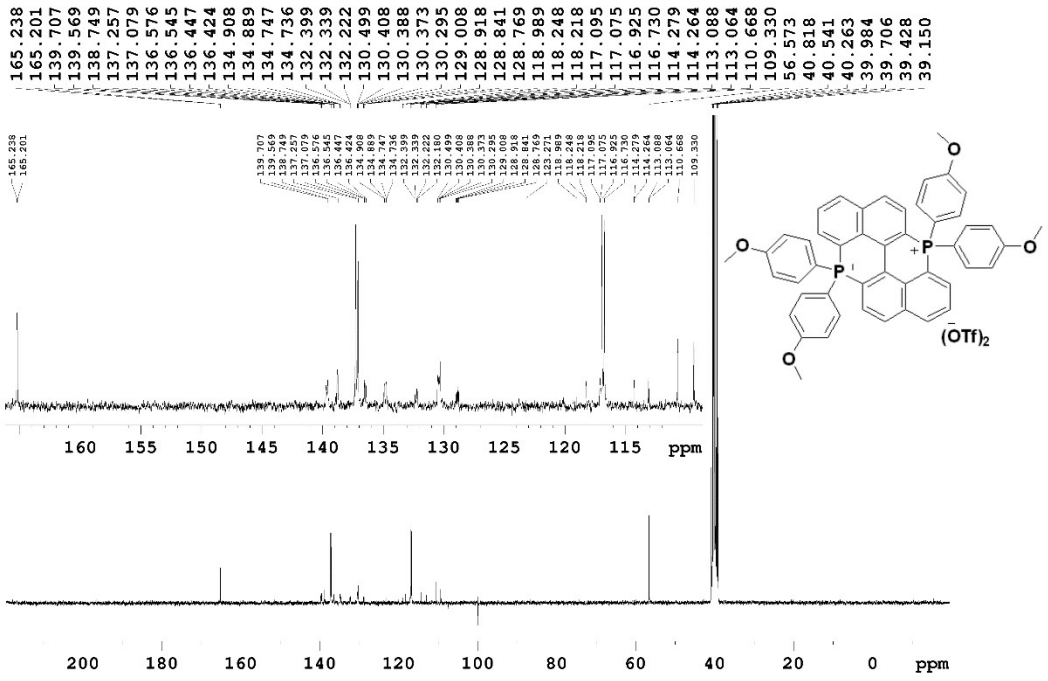
^{31}P NMR (121 MHz, DMSO-d_6) of **2d**



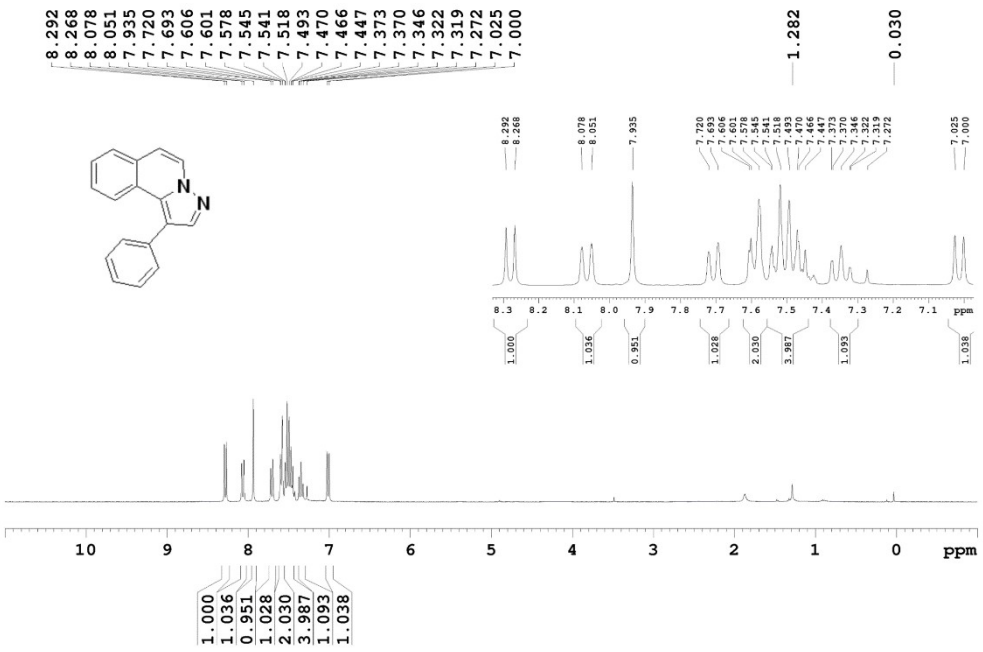
^{19}F NMR (282 MHz, DMSO-d_6) of **2d**



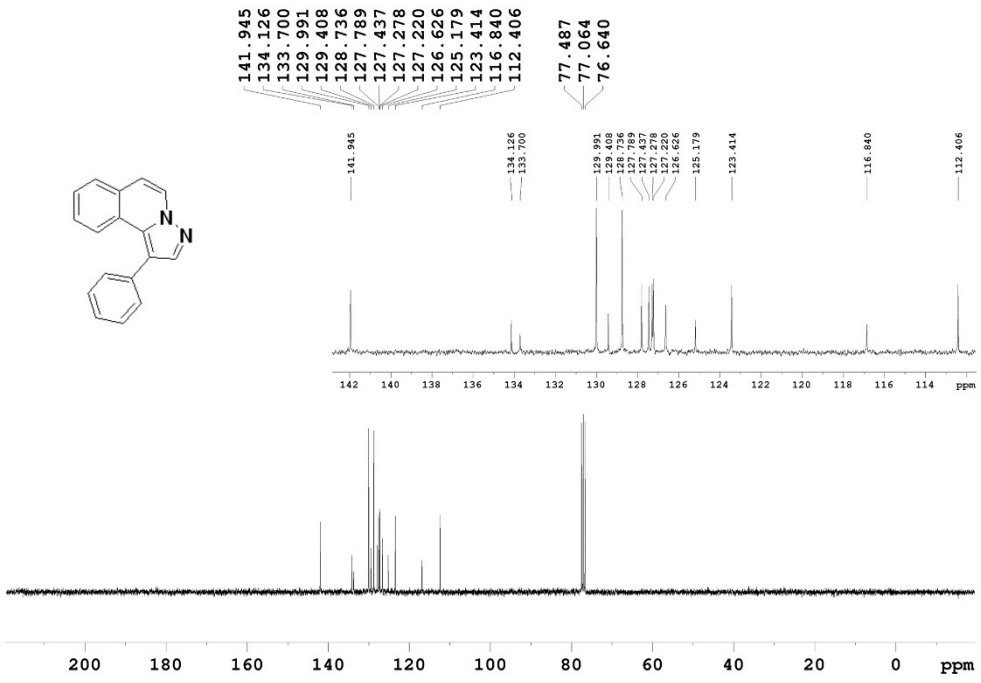
^{1}H NMR (300 MHz, DMSO-d_6) of **2d**



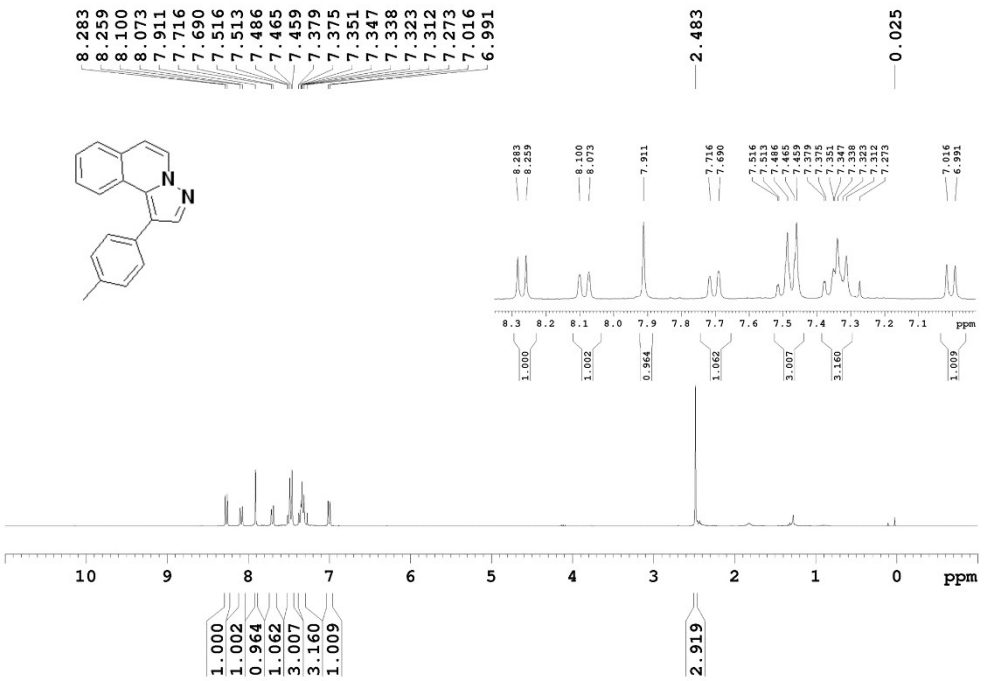
^{13}C NMR (75 MHz, DMSO-d_6) of **2d**



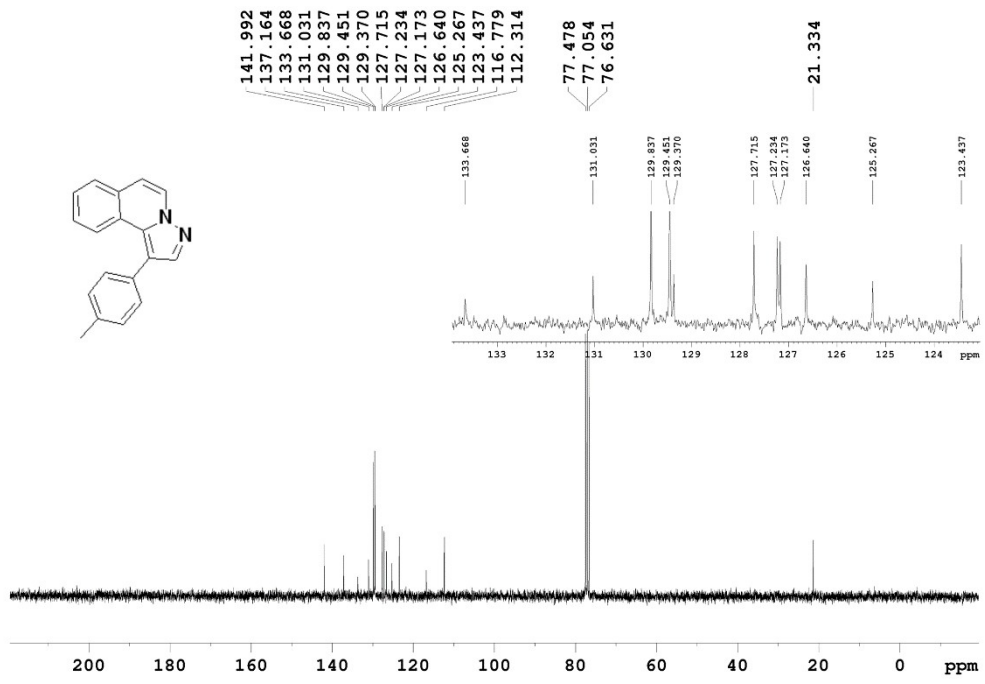
^{1}H NMR (300 MHz, $CDCl_3$) of **7**



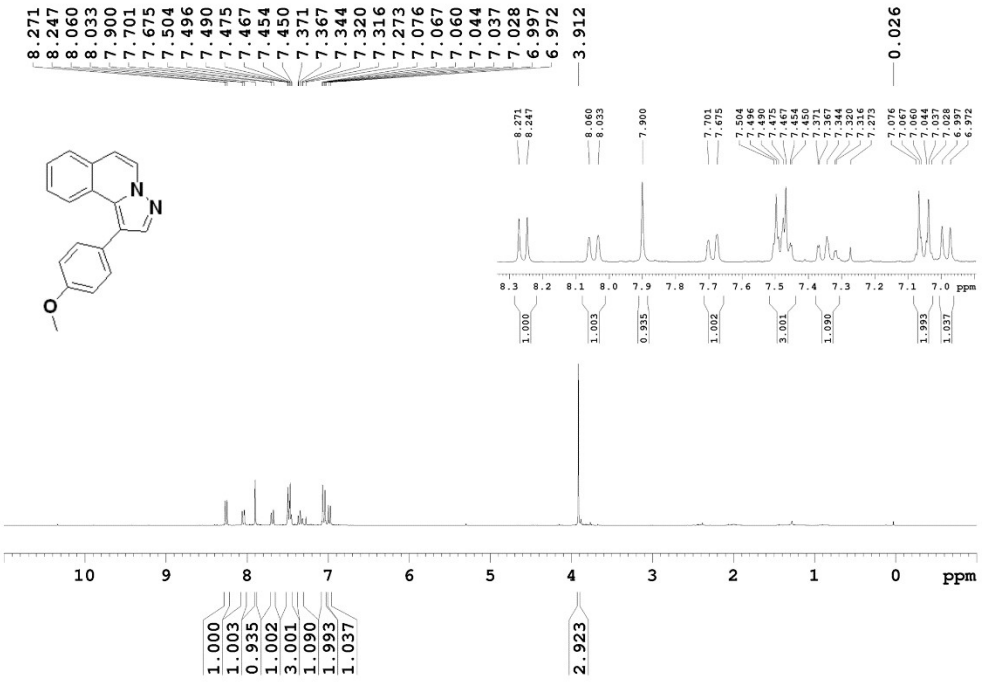
^{13}C NMR (75 MHz, $CDCl_3$) of **7**



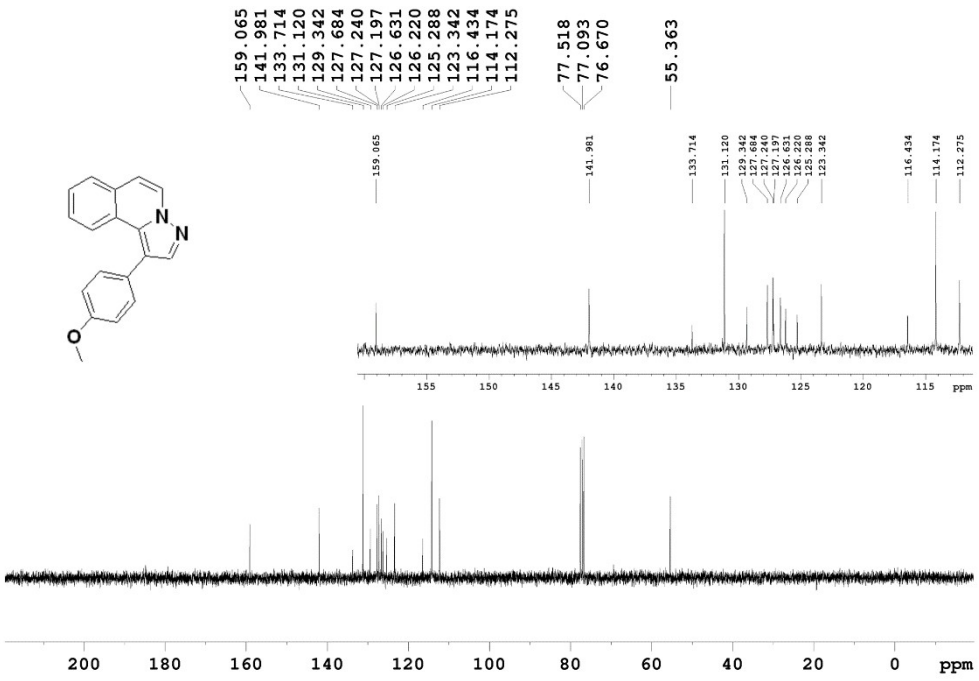
^{1}H NMR (300 MHz, $CDCl_3$) of **8**



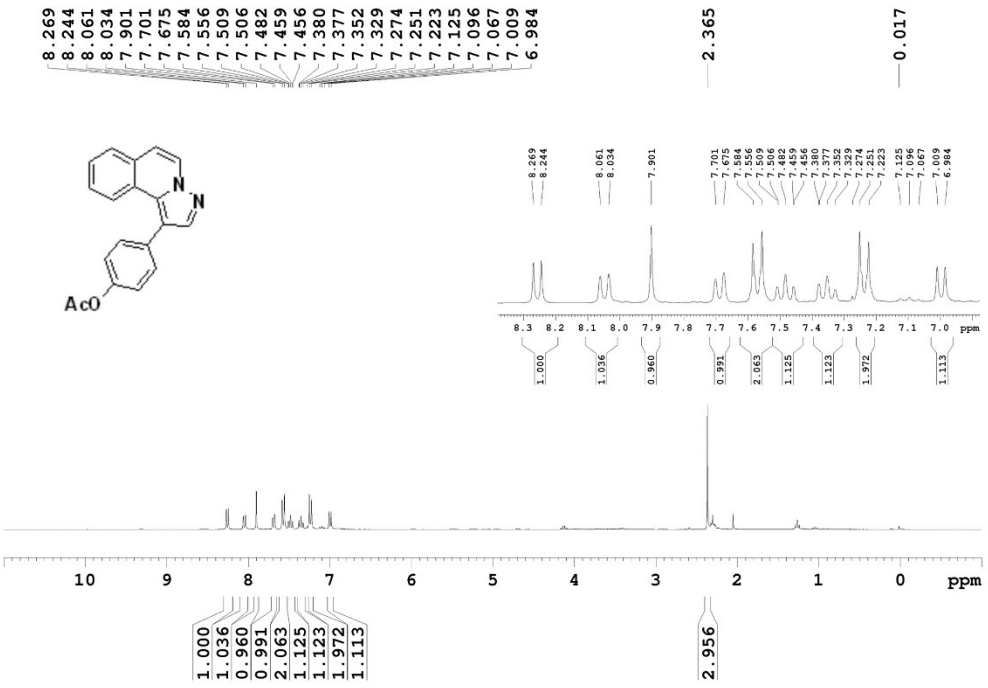
^{13}C NMR (75 MHz, $CDCl_3$) of **8**



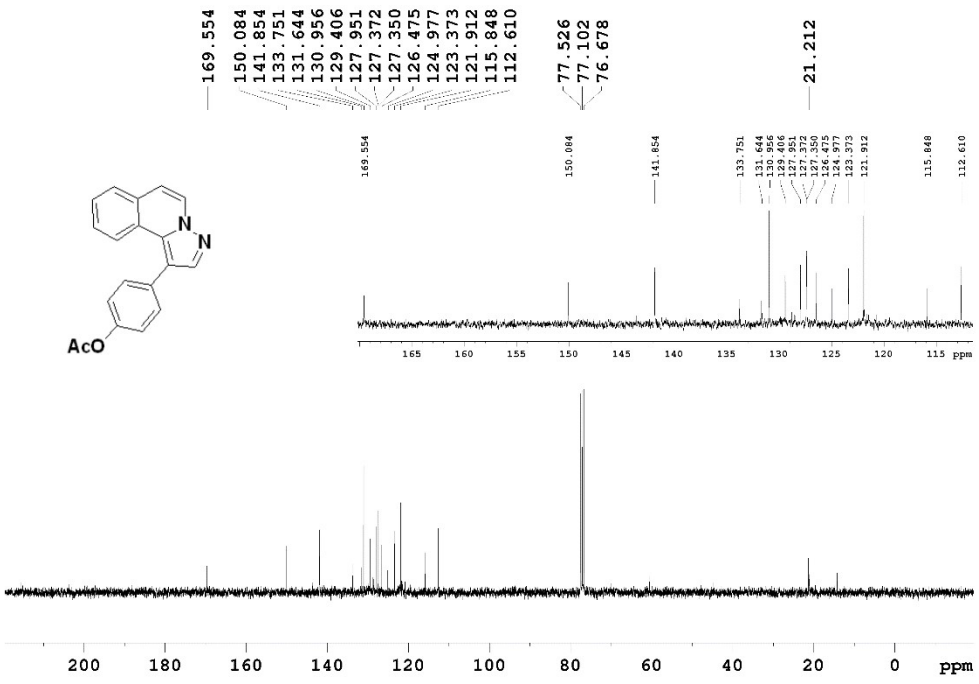
^{1}H NMR (300 MHz, $CDCl_3$) of **9**



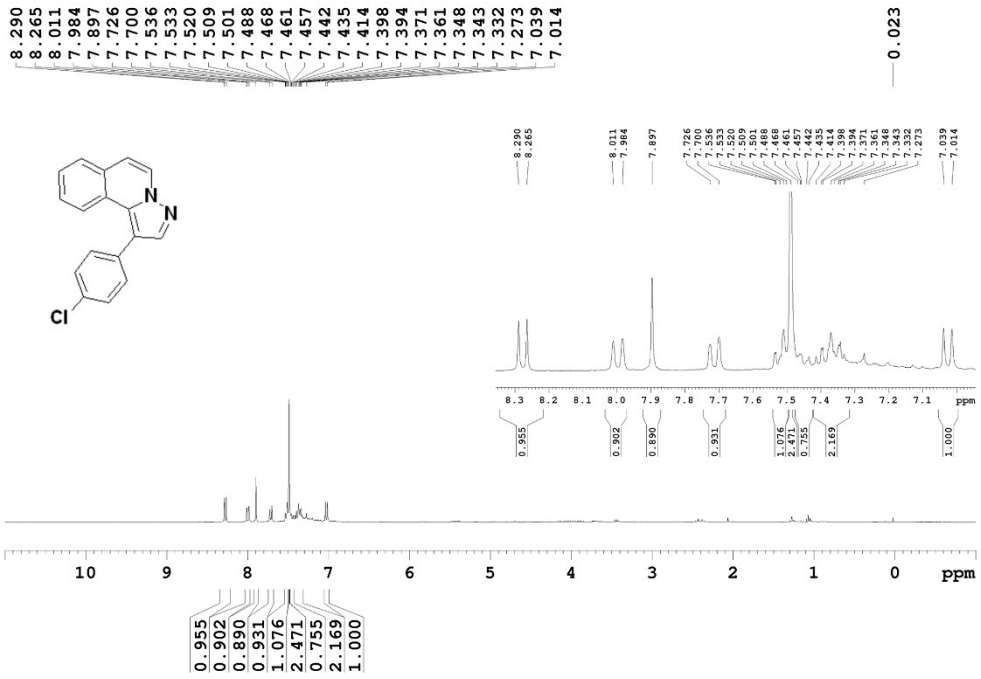
^{13}C NMR (75 MHz, $CDCl_3$) of **9**



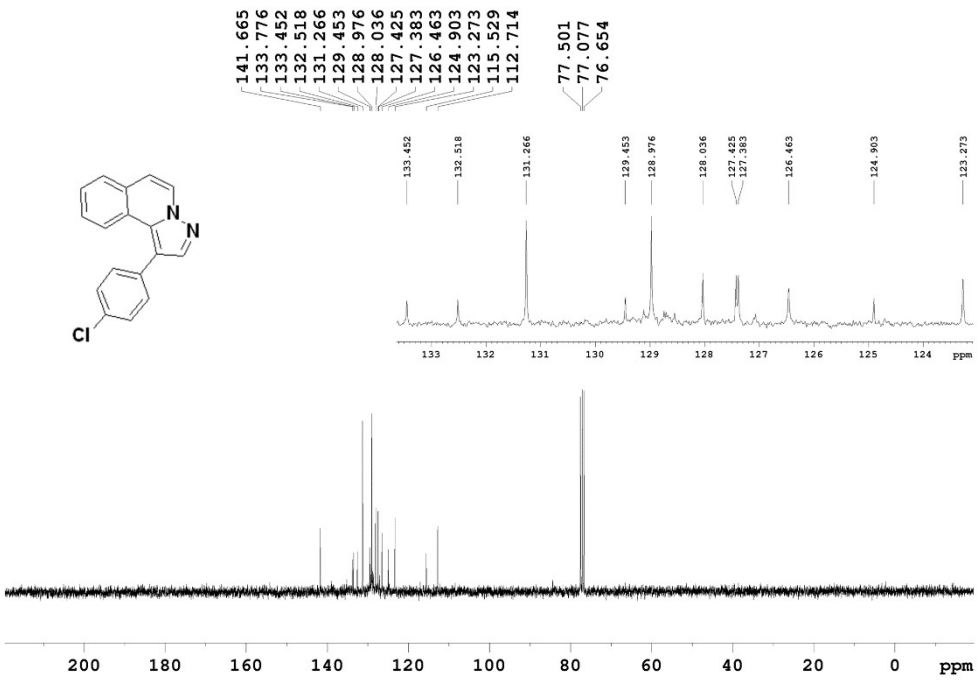
^{1}H NMR (300 MHz, $CDCl_3$) of **10**



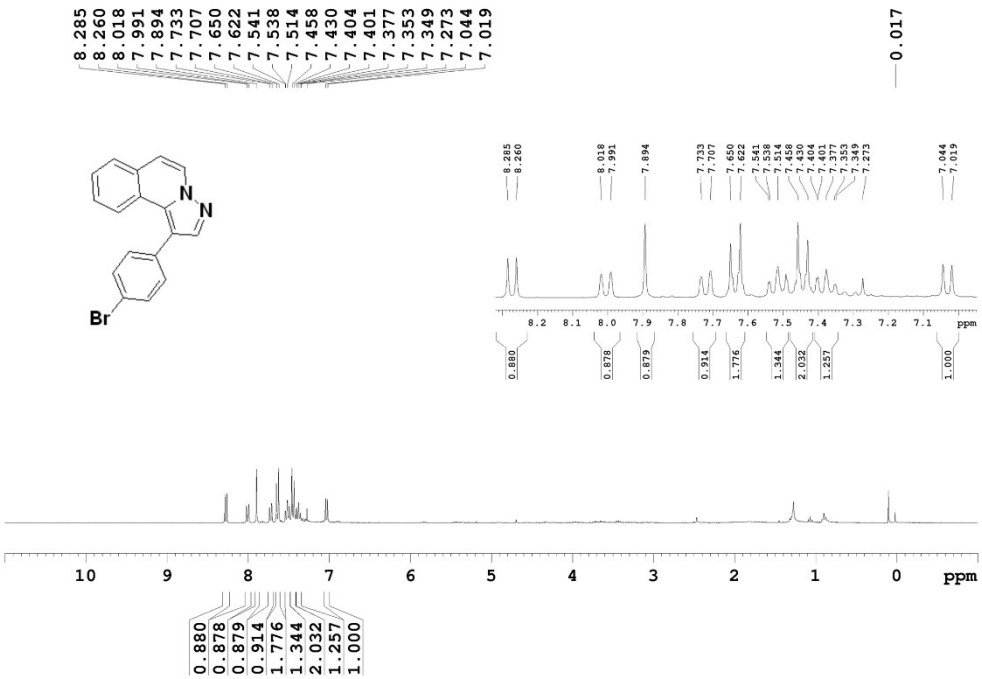
^{13}C NMR (75 MHz, $CDCl_3$) of **10**



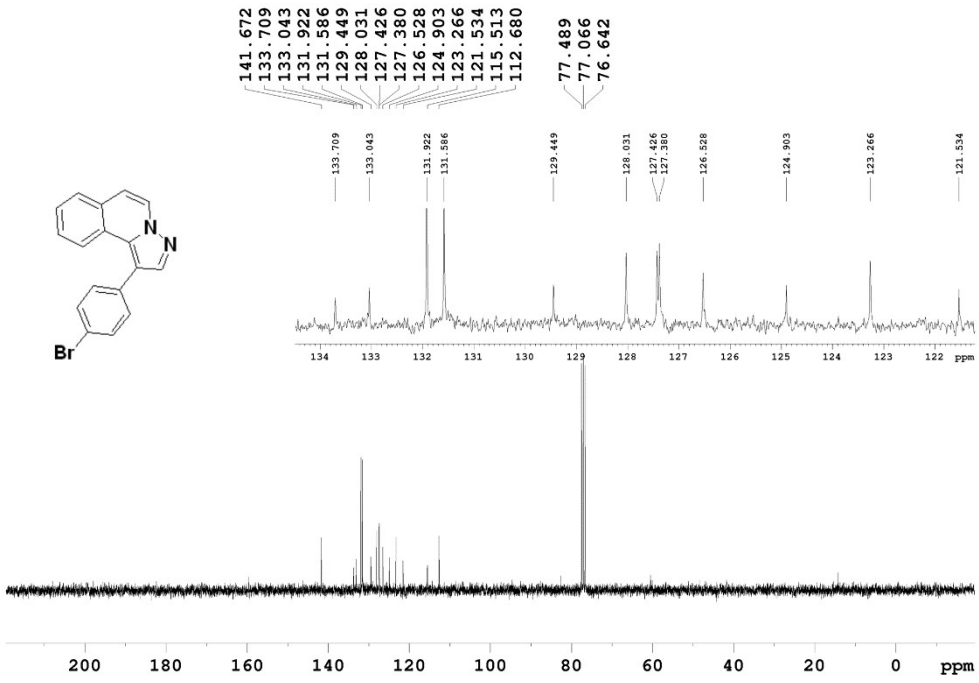
^{1}H NMR (300 MHz, $CDCl_3$) of **11**



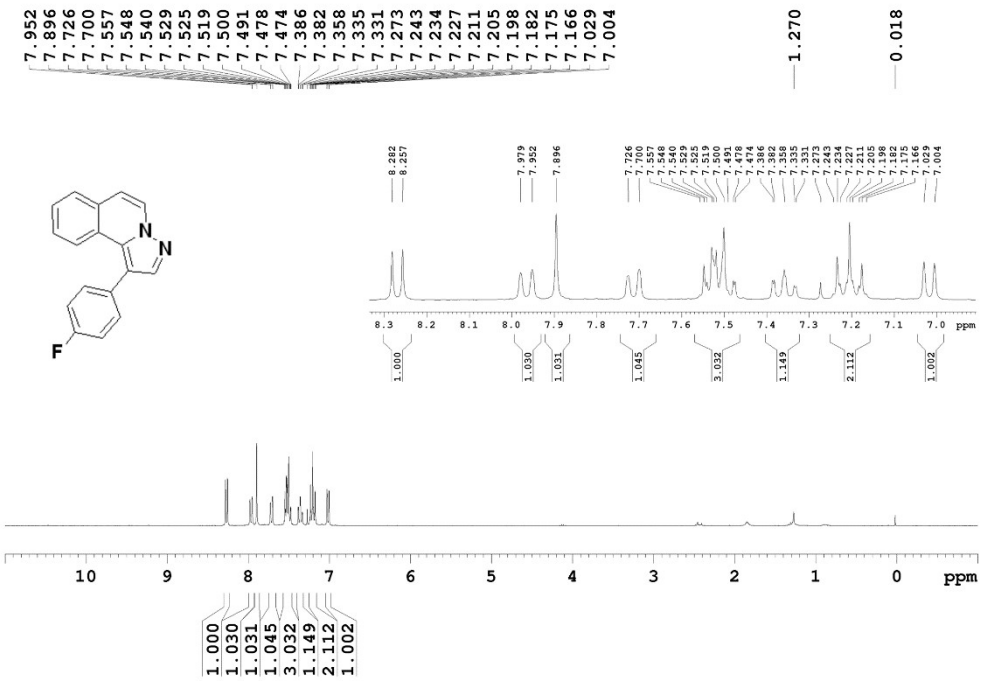
^{13}C NMR (75 MHz, $CDCl_3$) of **11**



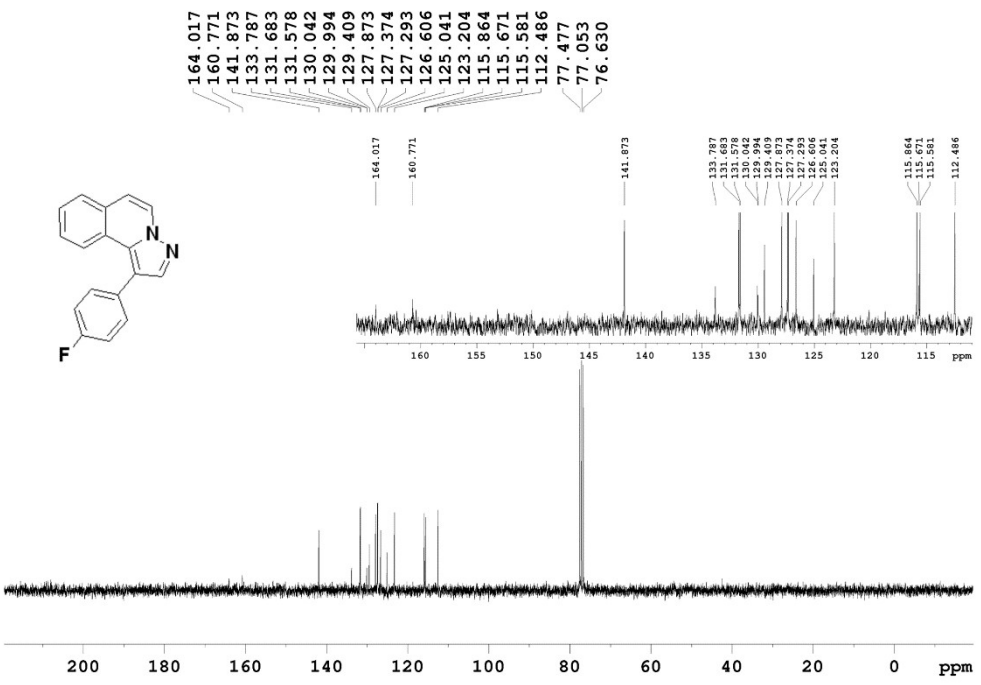
^{1}H NMR (300 MHz, $CDCl_3$) of **12**



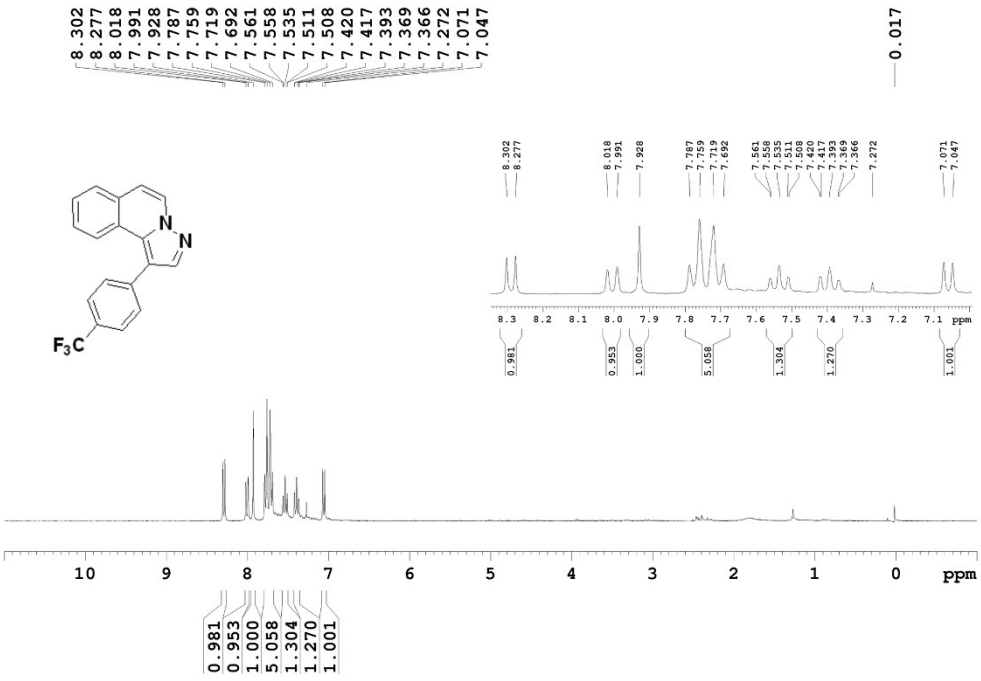
^{13}C NMR (75 MHz, $CDCl_3$) of **12**



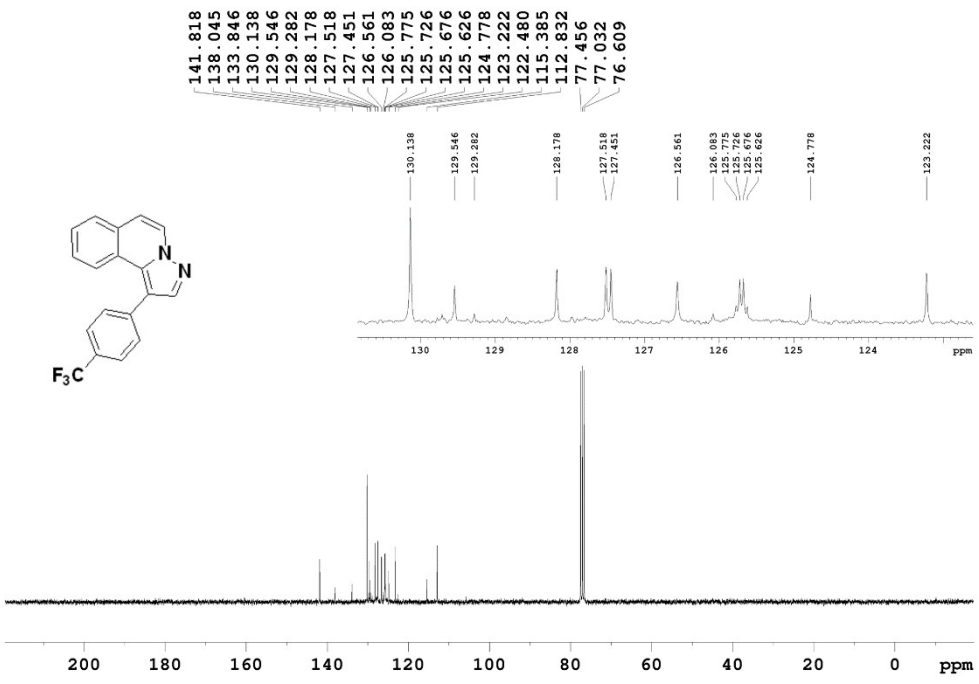
^{1}H NMR (300 MHz, $CDCl_3$) of **13**



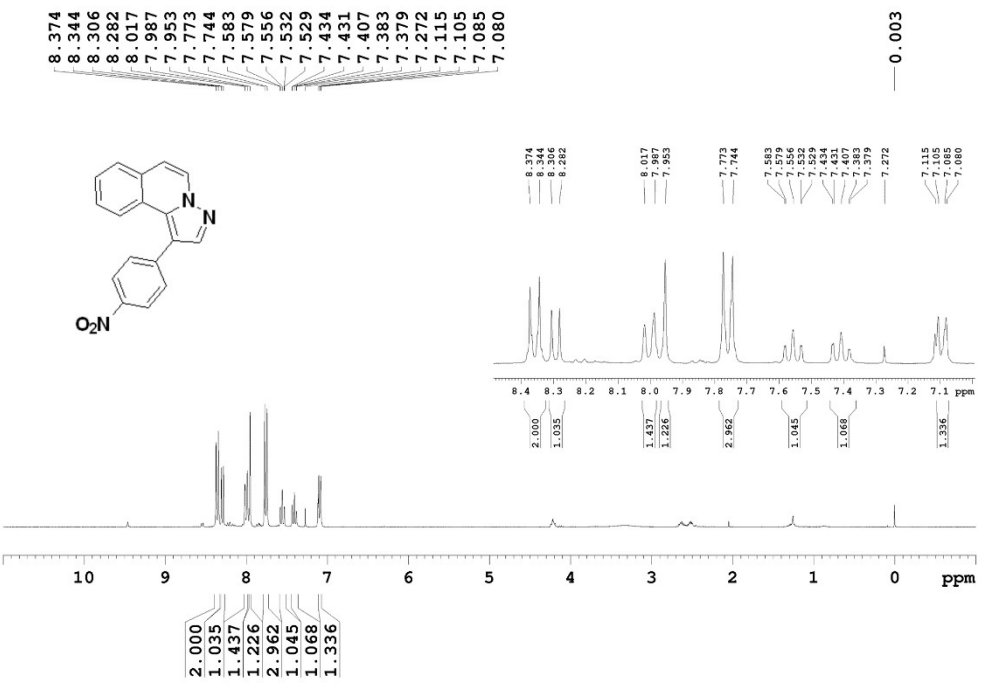
^{13}C NMR (75 MHz, $CDCl_3$) of **13**



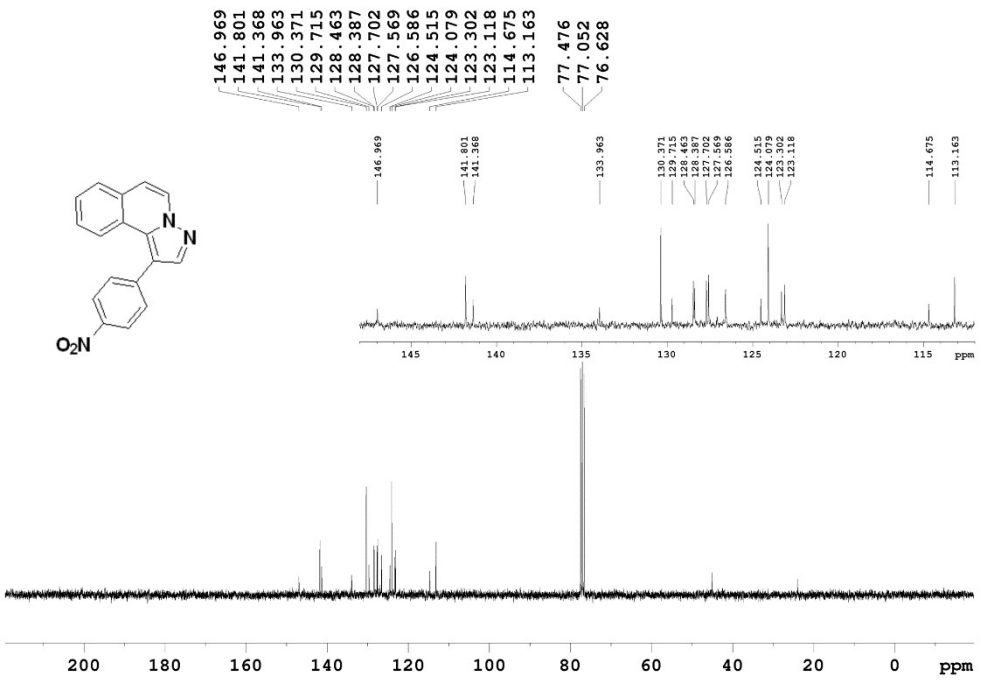
^{1}H NMR (300 MHz, $CDCl_3$) of **14**



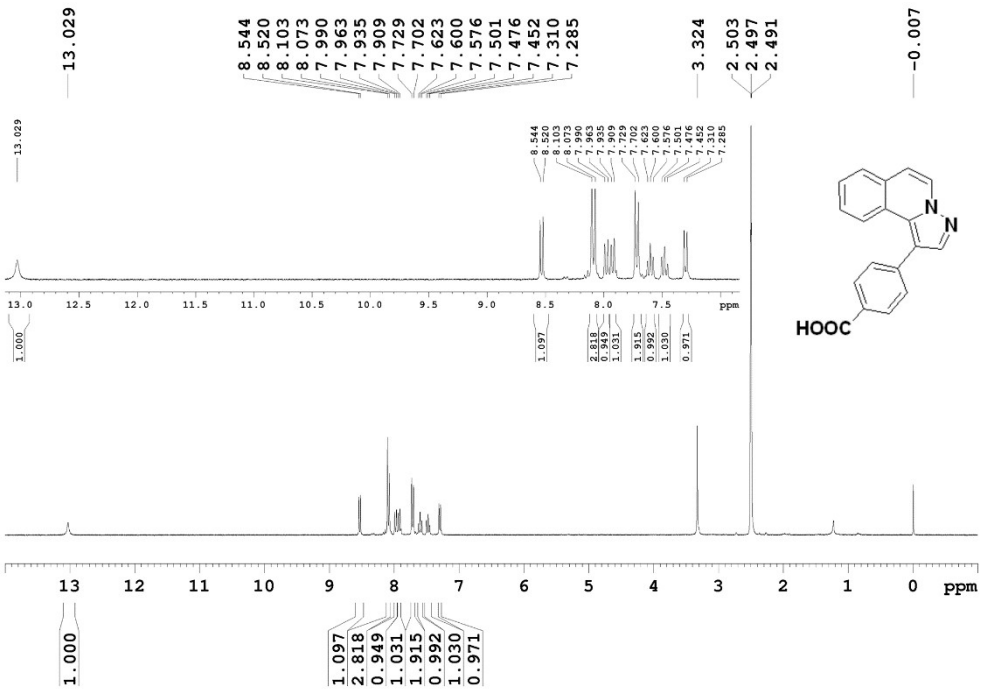
^{13}C NMR (75 MHz, $CDCl_3$) of **14**



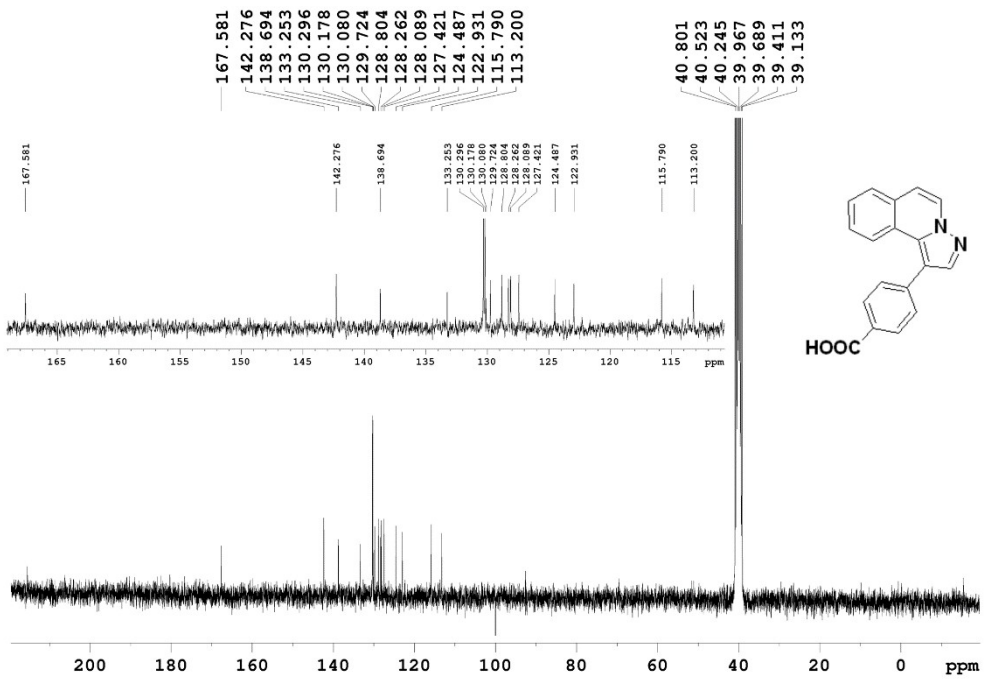
^{1}H NMR (300 MHz, $CDCl_3$) of **15**



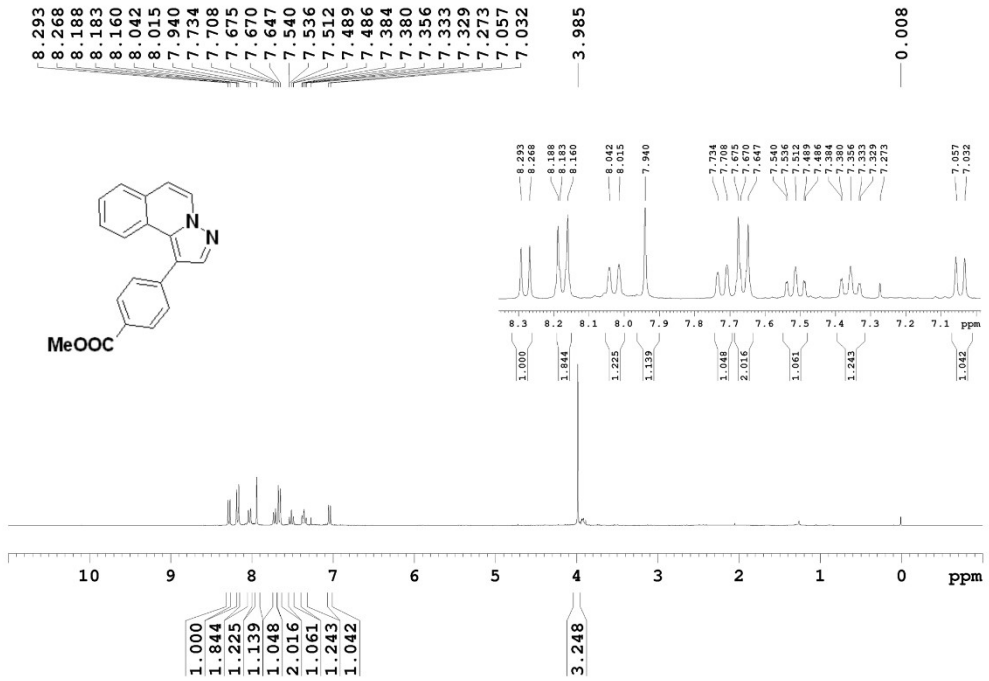
^{13}C NMR (75 MHz, $CDCl_3$) of **15**



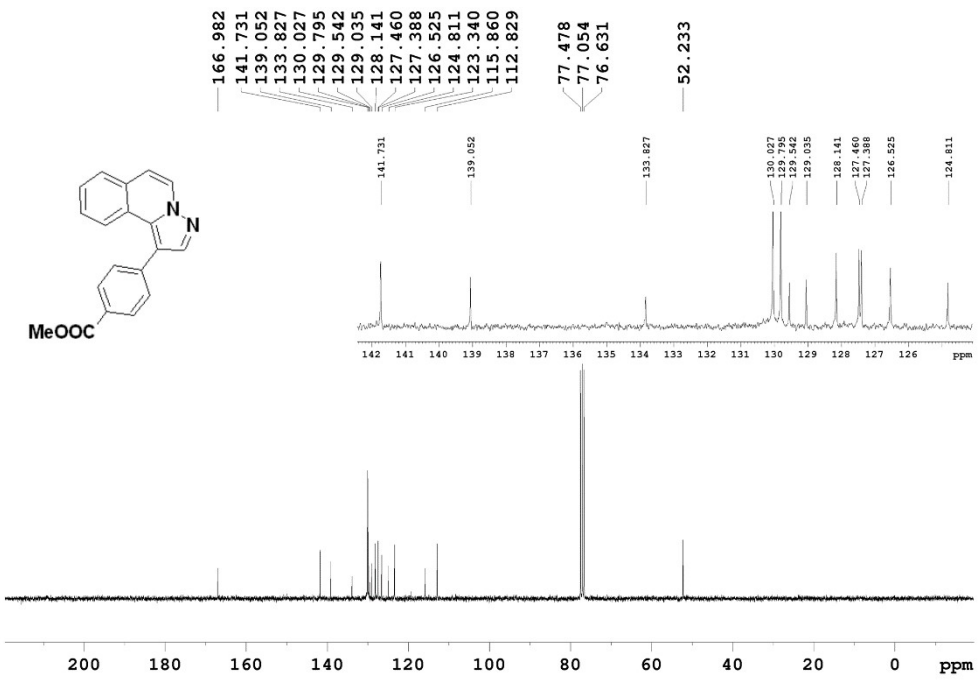
^{1}H NMR (300 MHz, DMSO-d_6) of **16**



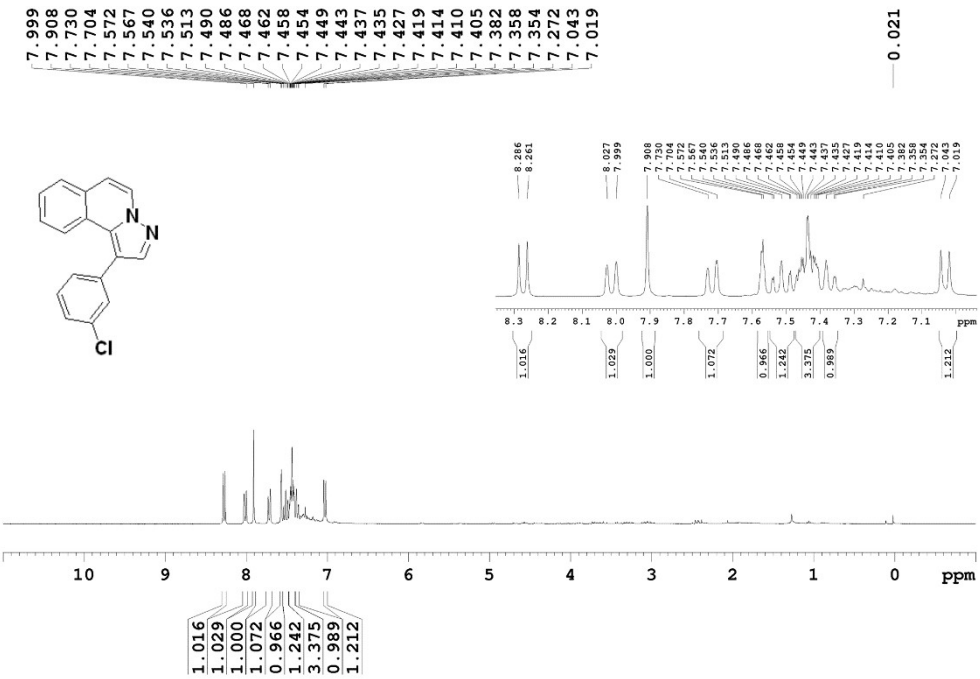
^{13}C NMR (75 MHz, DMSO-d_6) of **16**



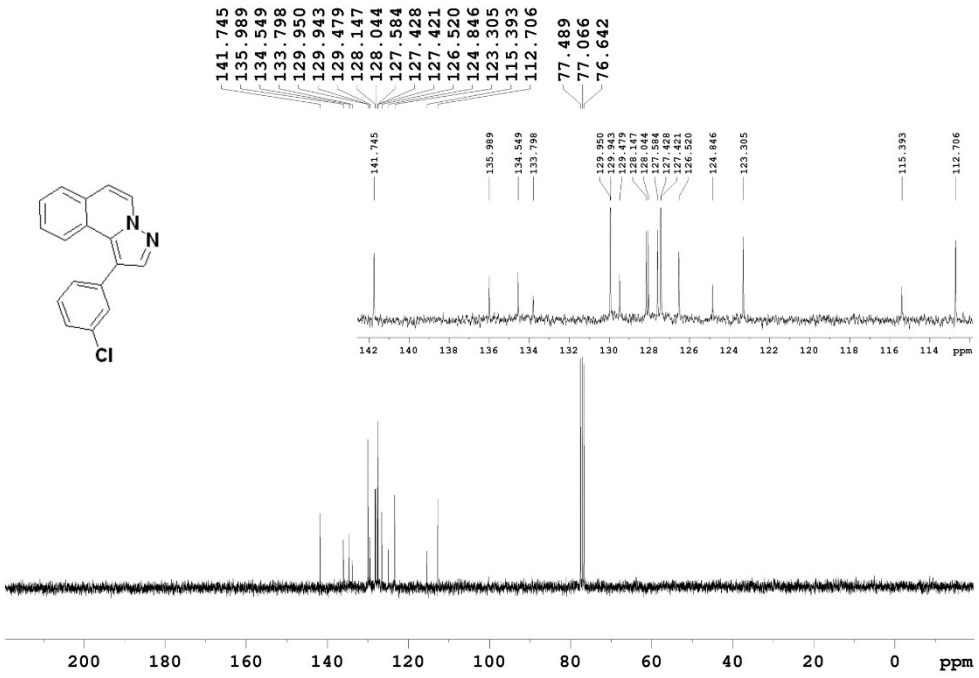
^{1}H NMR (300 MHz, $CDCl_3$) of **17**



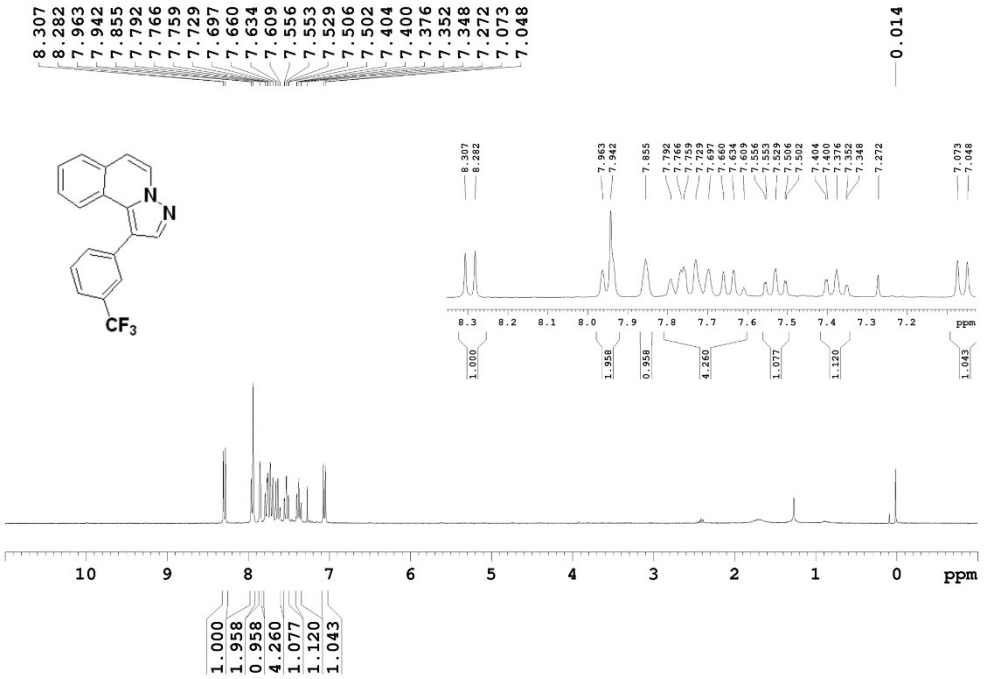
^{13}C NMR (75 MHz, $CDCl_3$) of **17**



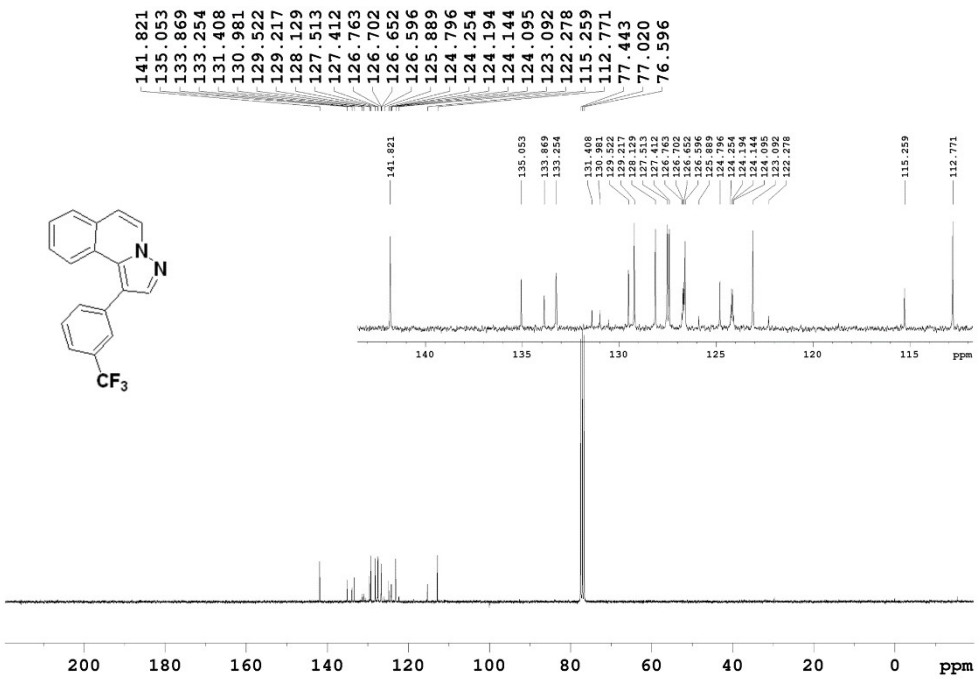
^{1}H NMR (300 MHz, $CDCl_3$) of **19**



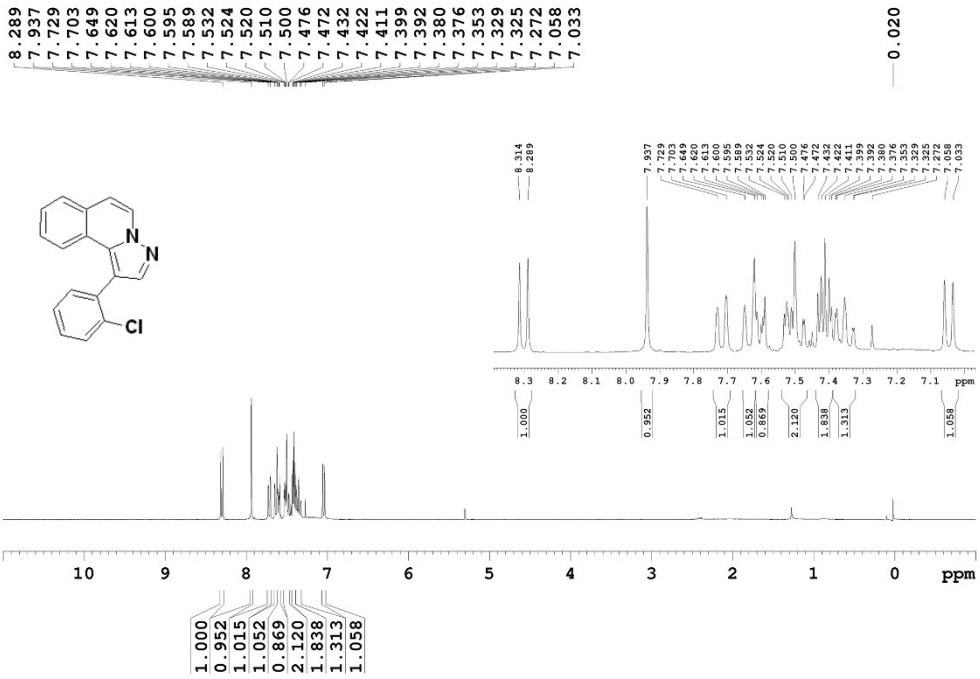
^{13}C NMR (75 MHz, $CDCl_3$) of **19**



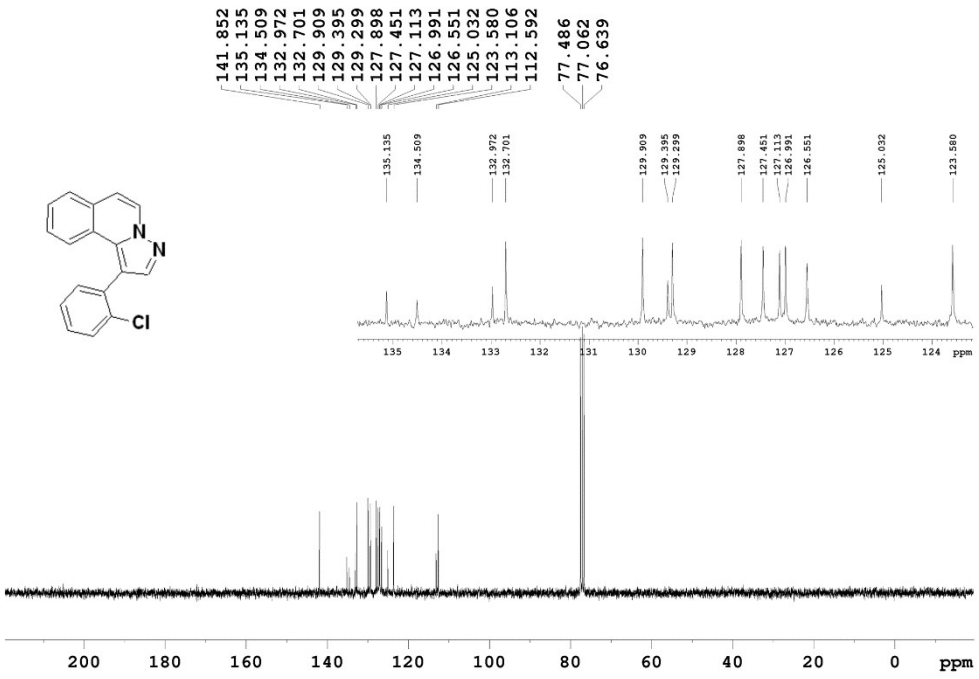
^{1}H NMR (300 MHz, $CDCl_3$) of **18**



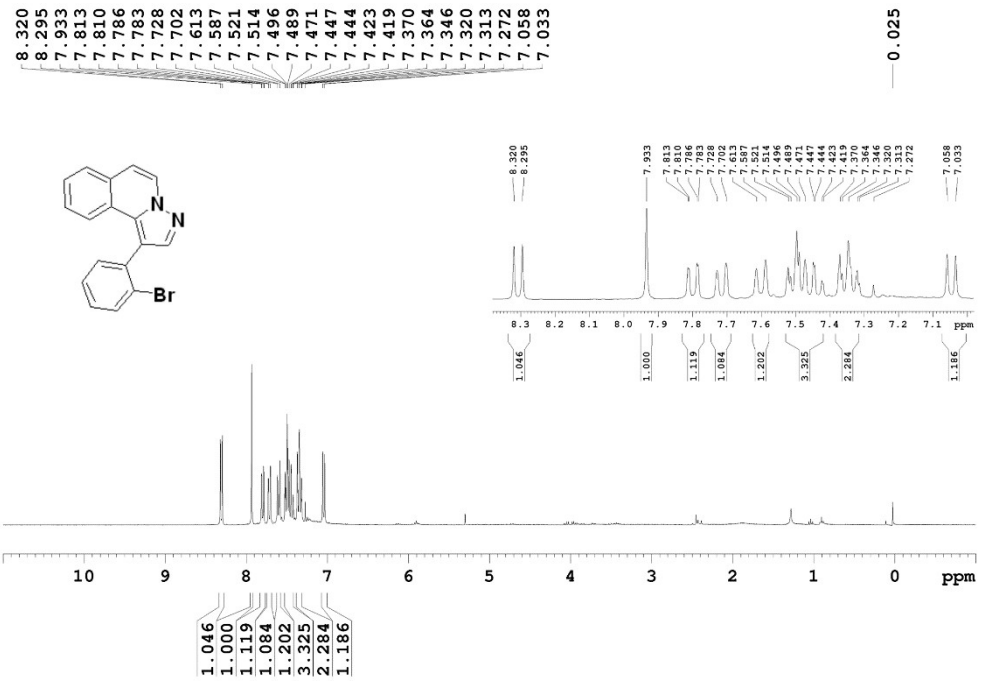
^{13}C NMR (75 MHz, $CDCl_3$) of **18**



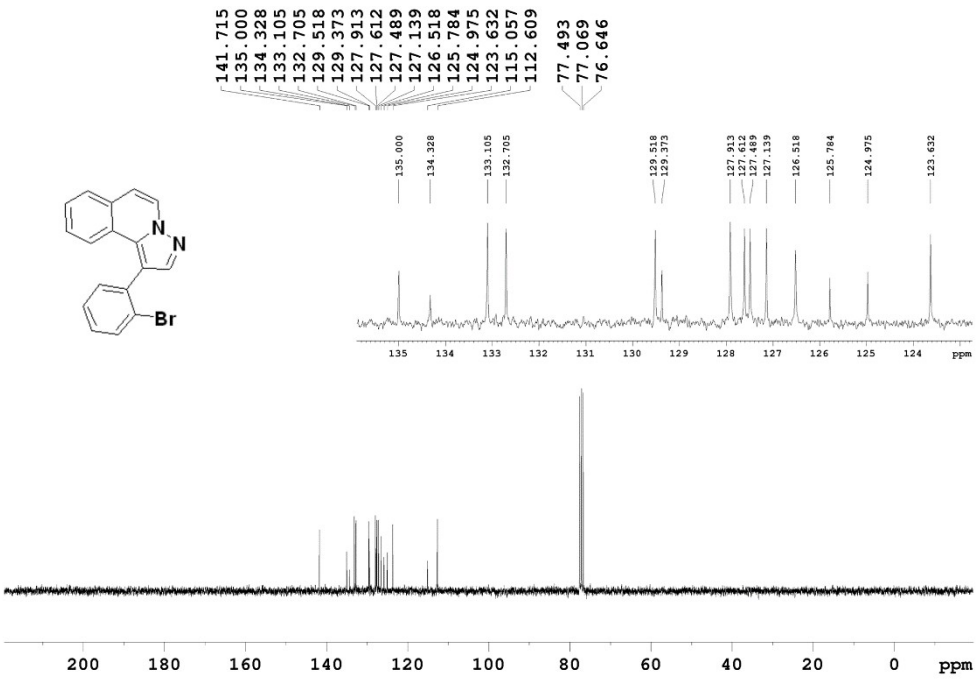
^{1}H NMR (300 MHz, $CDCl_3$) of **20**



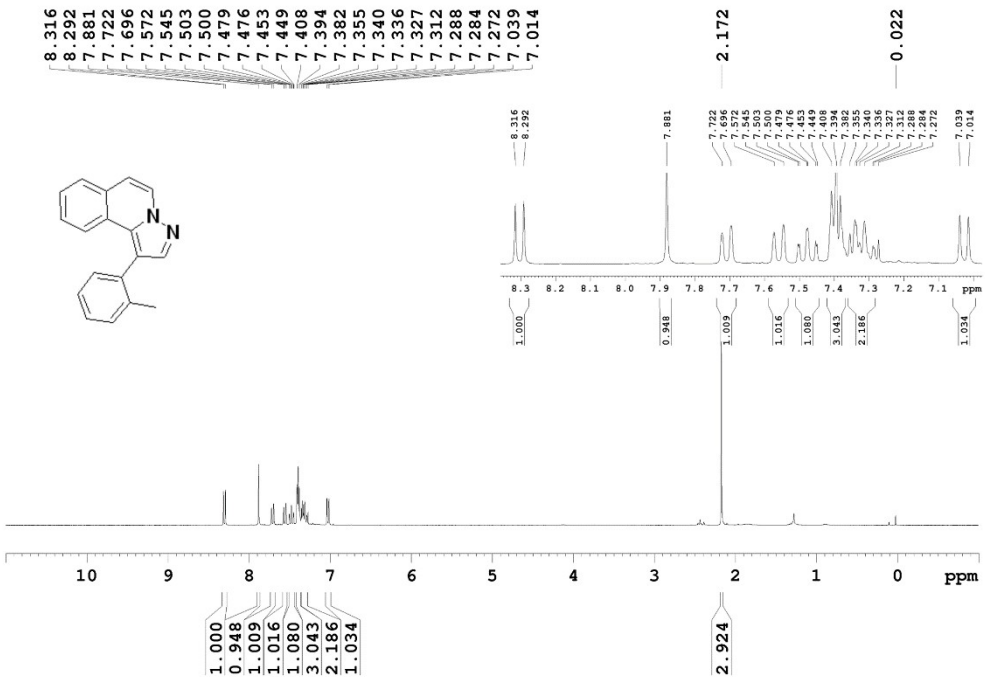
^{13}C NMR (75 MHz, $CDCl_3$) of **20**



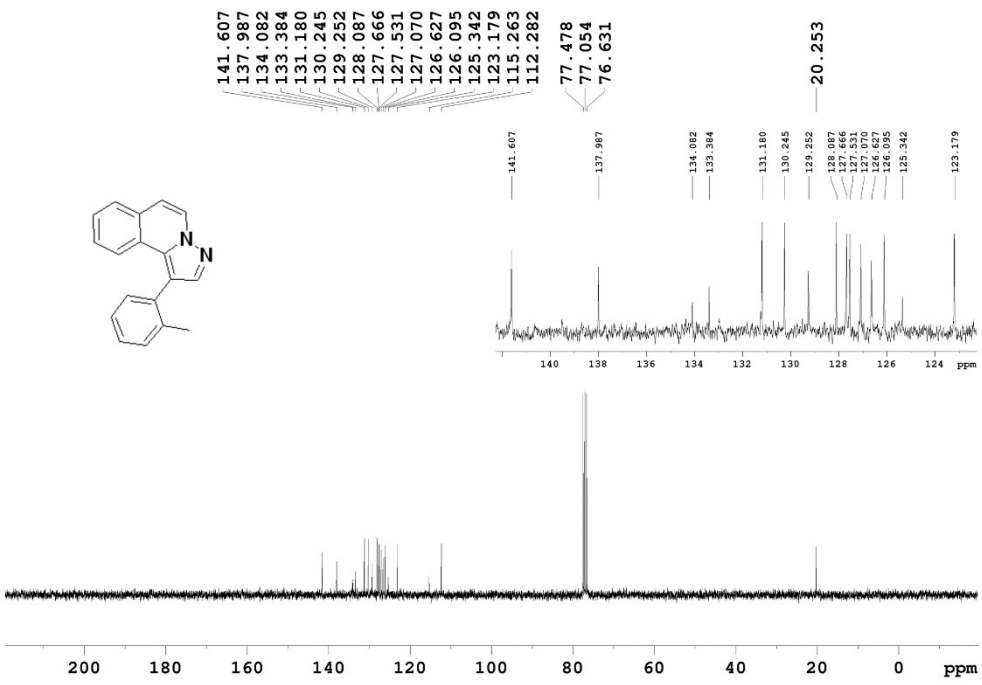
^{1}H NMR (300 MHz, $CDCl_3$) of **21**



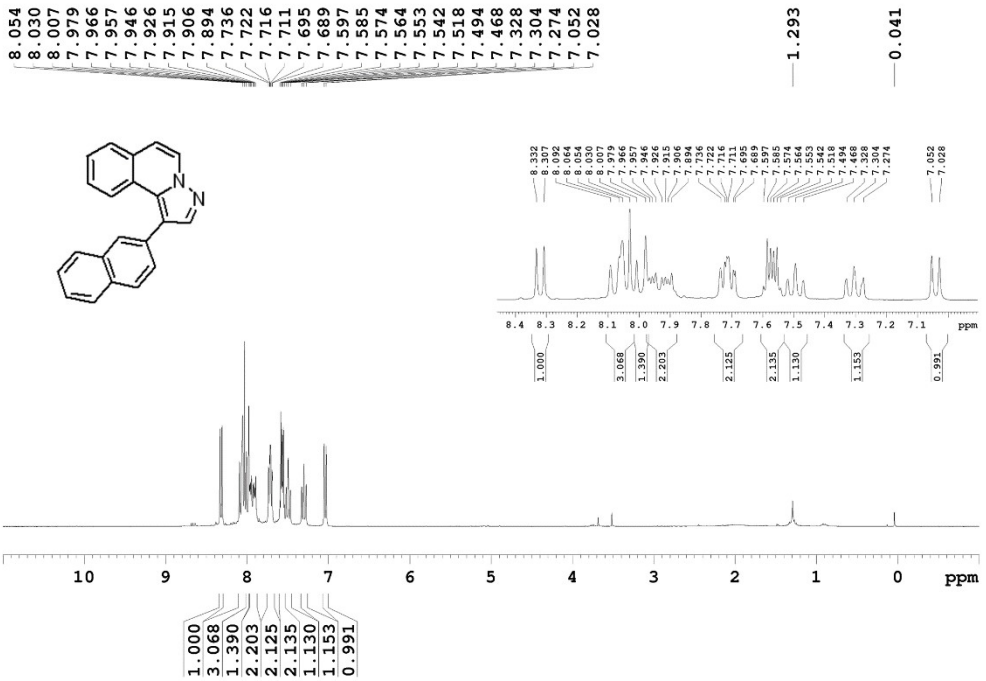
^{13}C NMR (75 MHz, $CDCl_3$) of **21**



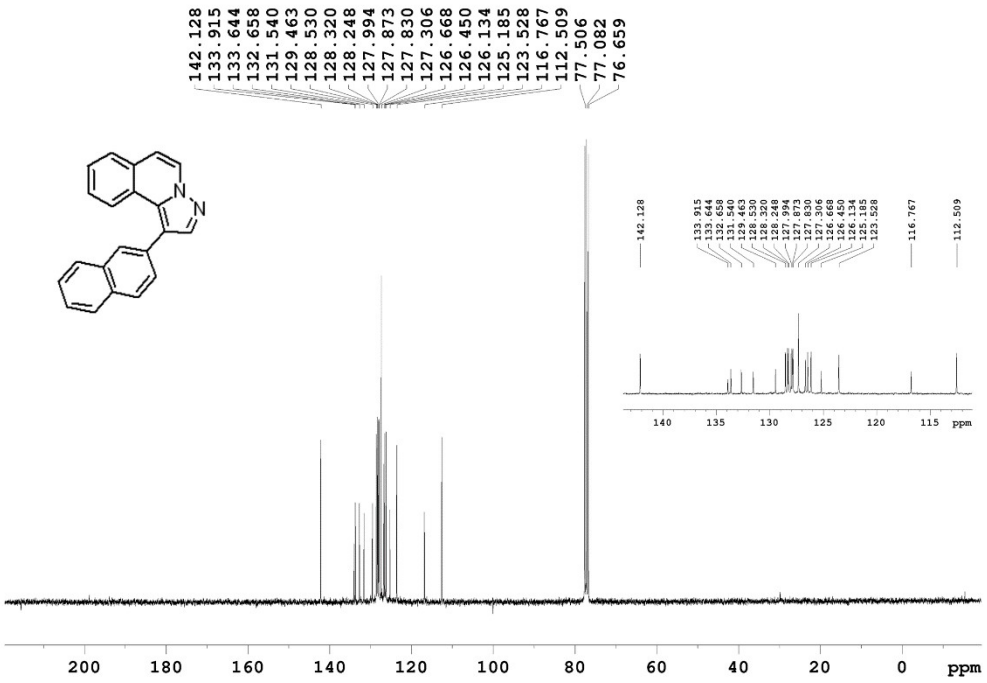
^{1}H NMR (300 MHz, $CDCl_3$) of **22**



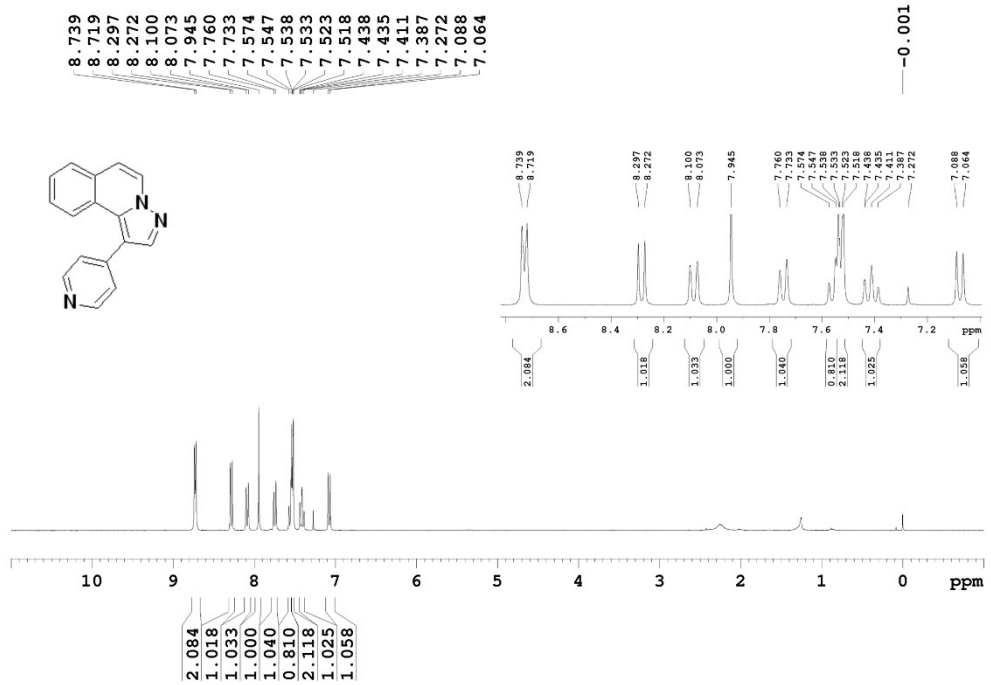
^{13}C NMR (75 MHz, $CDCl_3$) of **22**



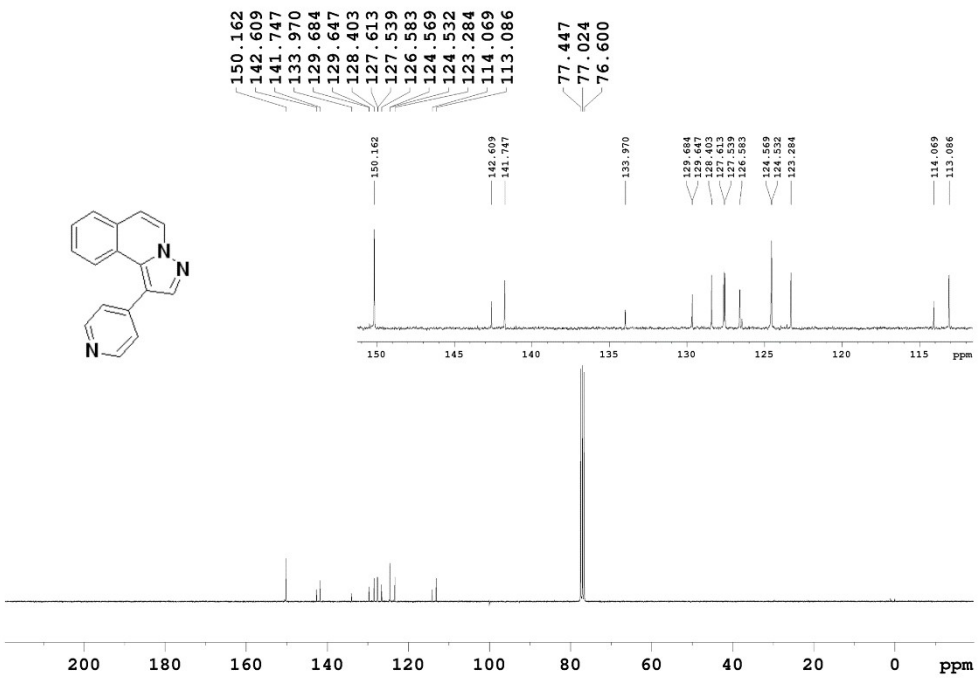
^{1}H NMR (300 MHz, $CDCl_3$) of **23**



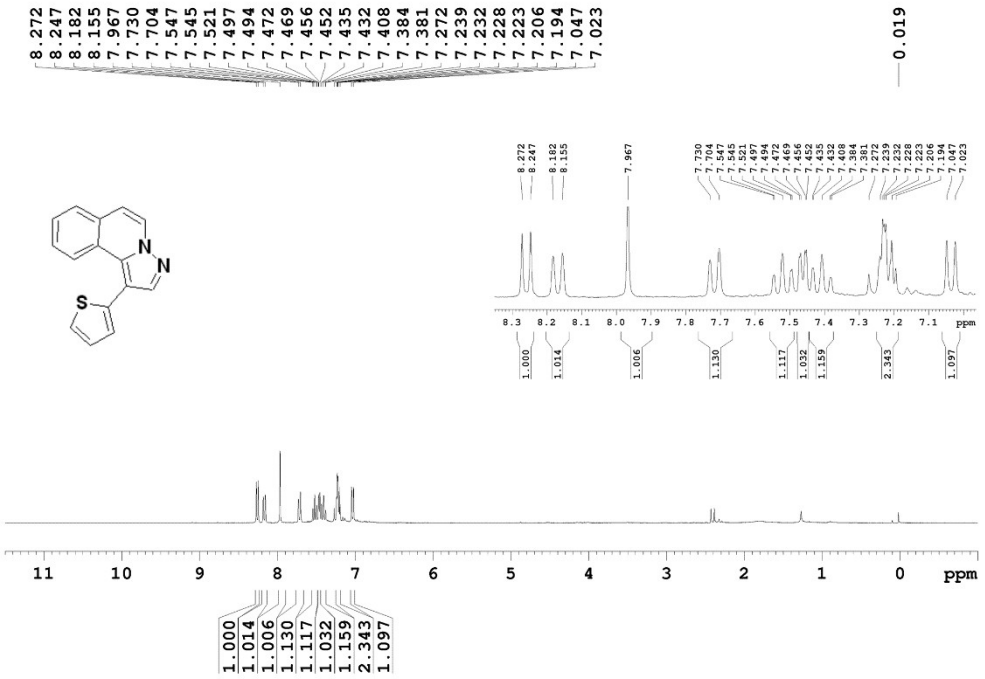
^{13}C NMR (75 MHz, $CDCl_3$) of **23**



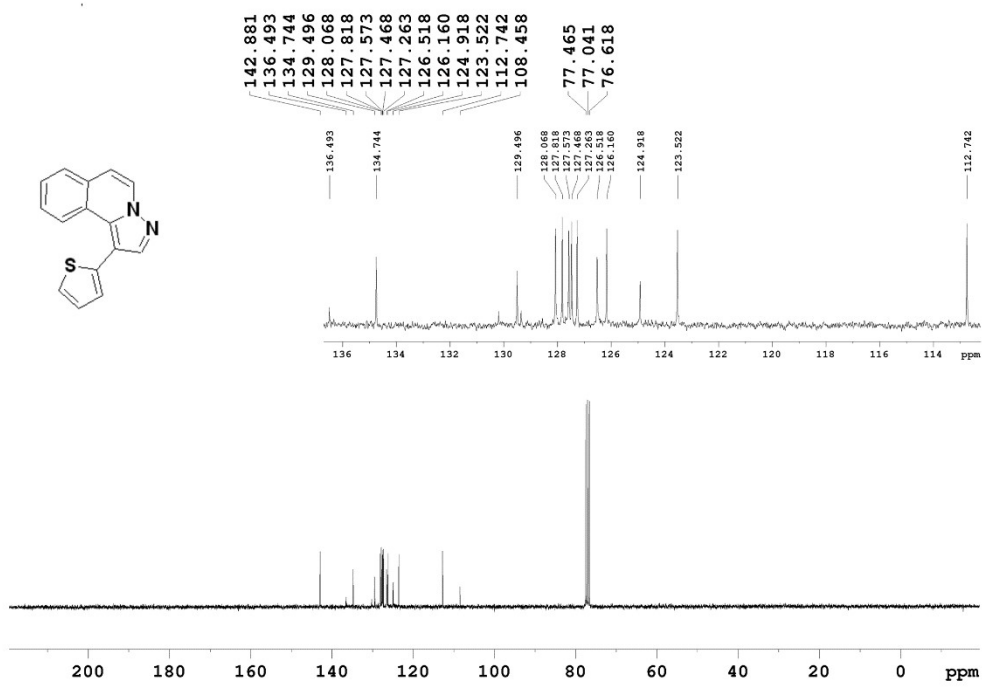
^{1}H NMR (300 MHz, $CDCl_3$) of **24**



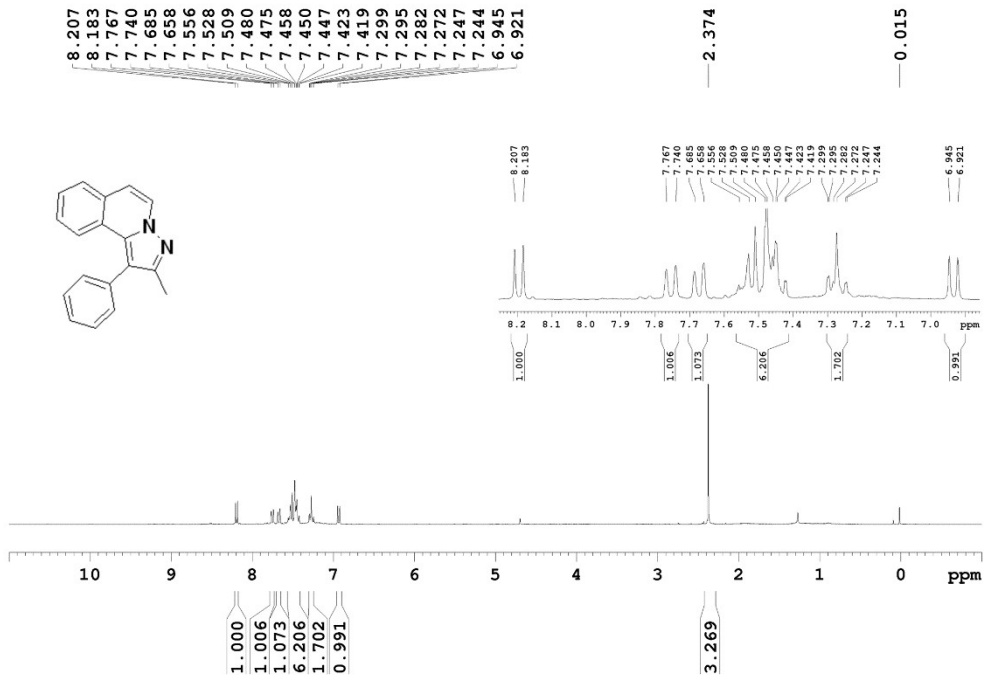
^{13}C NMR (75 MHz, $CDCl_3$) of **24**



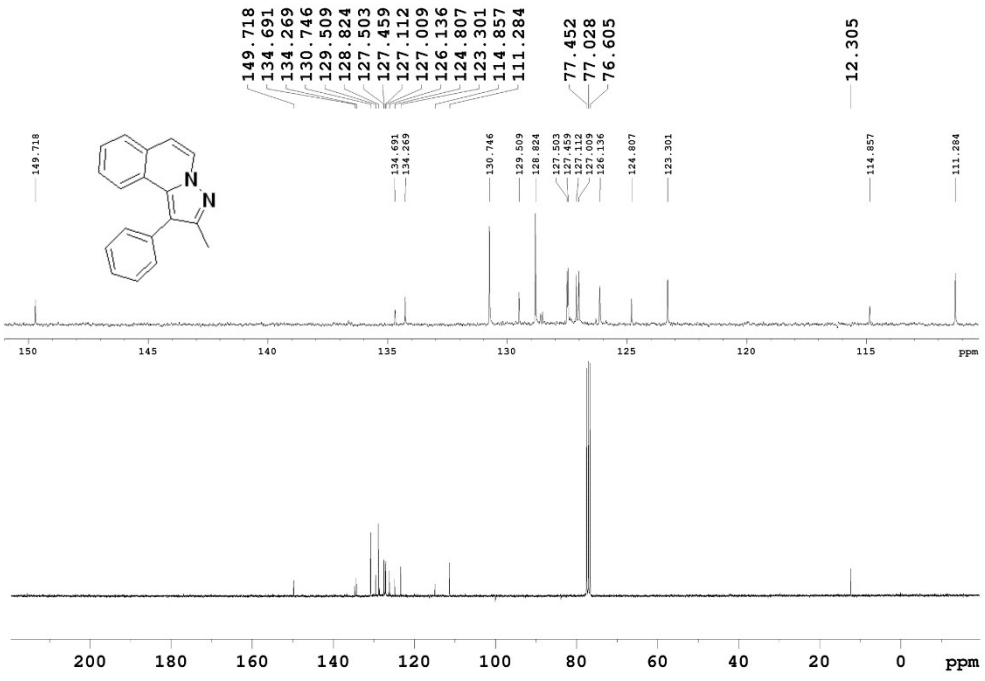
^{1}H NMR (300 MHz, $CDCl_3$) of **25**



^{13}C NMR (75 MHz, $CDCl_3$) of **25**



^{1}H NMR (300 MHz, $CDCl_3$) of **26**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134.269
130.746
129.509
128.824
127.503
127.459
127.112
127.009
126.136
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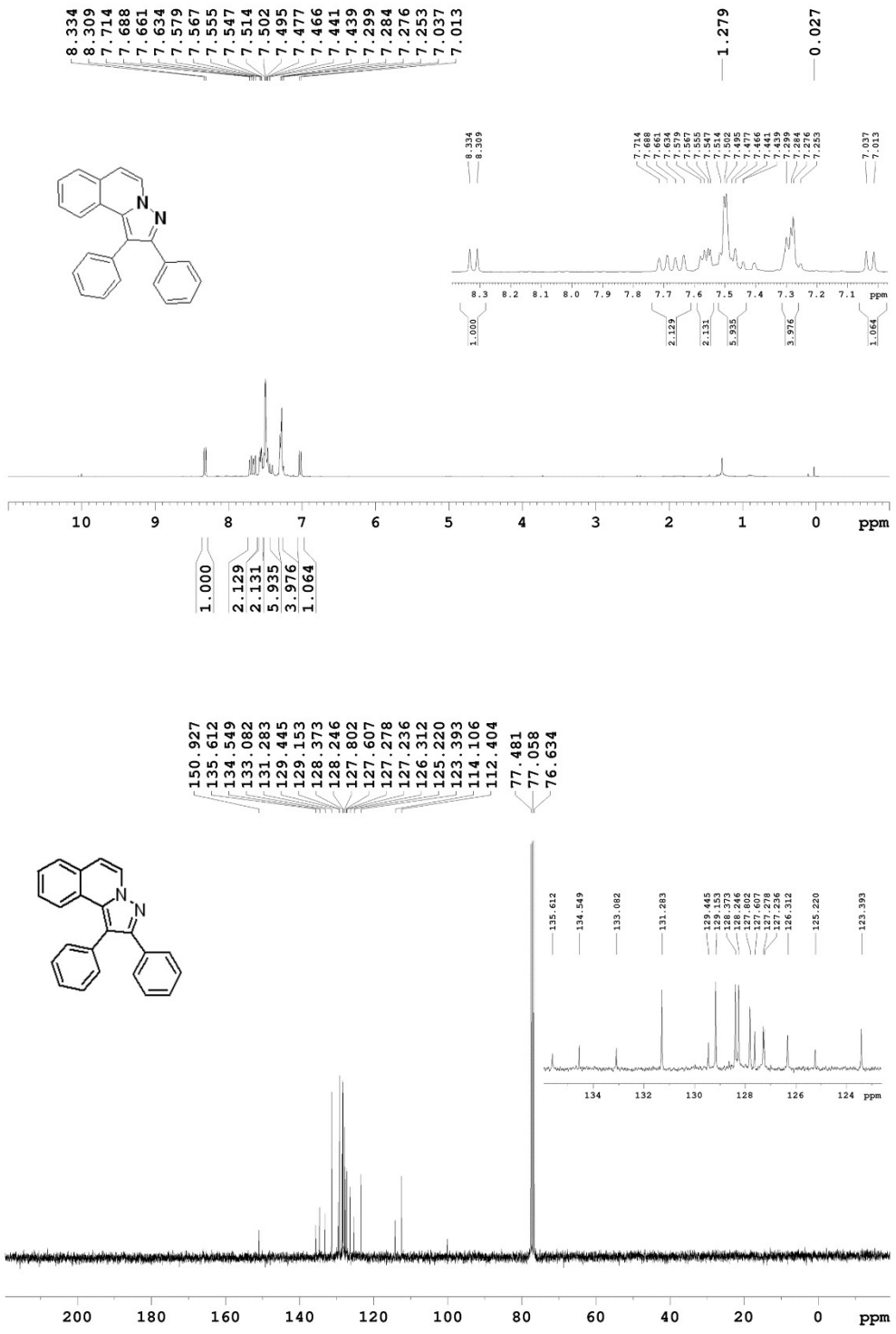
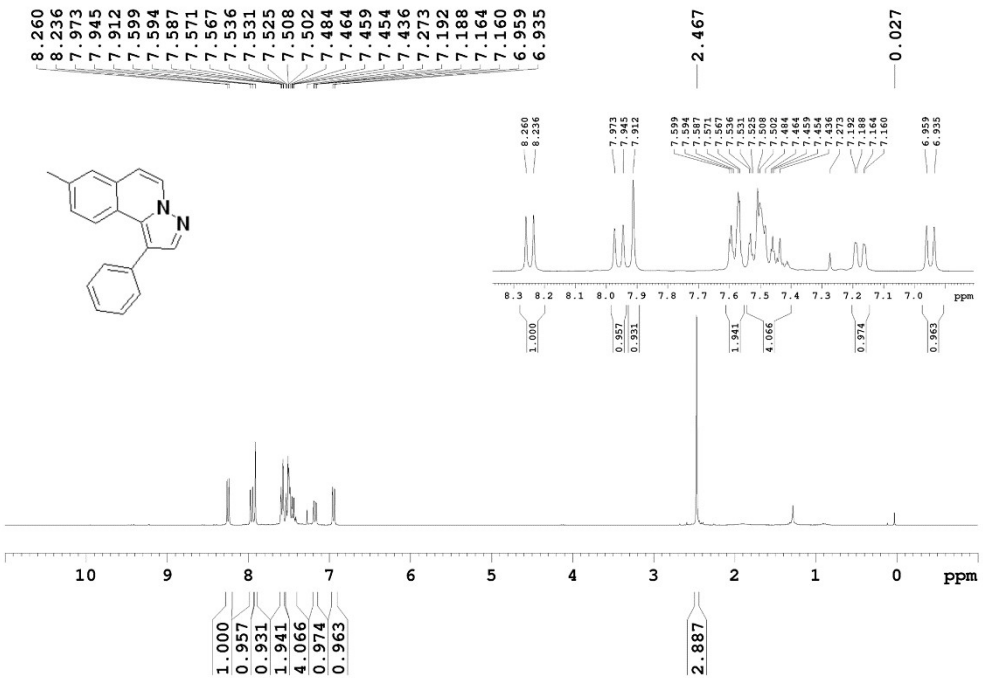
123.301
114.857
111.284
77.452
77.028
76.605
12.305
N
N
150
145
140
135
130
125
120
115
ppm
200
180
160
140
120
100
80
60
40
20
0
ppm

^{13}C NMR (75 MHz, $CDCl_3$) of **26**

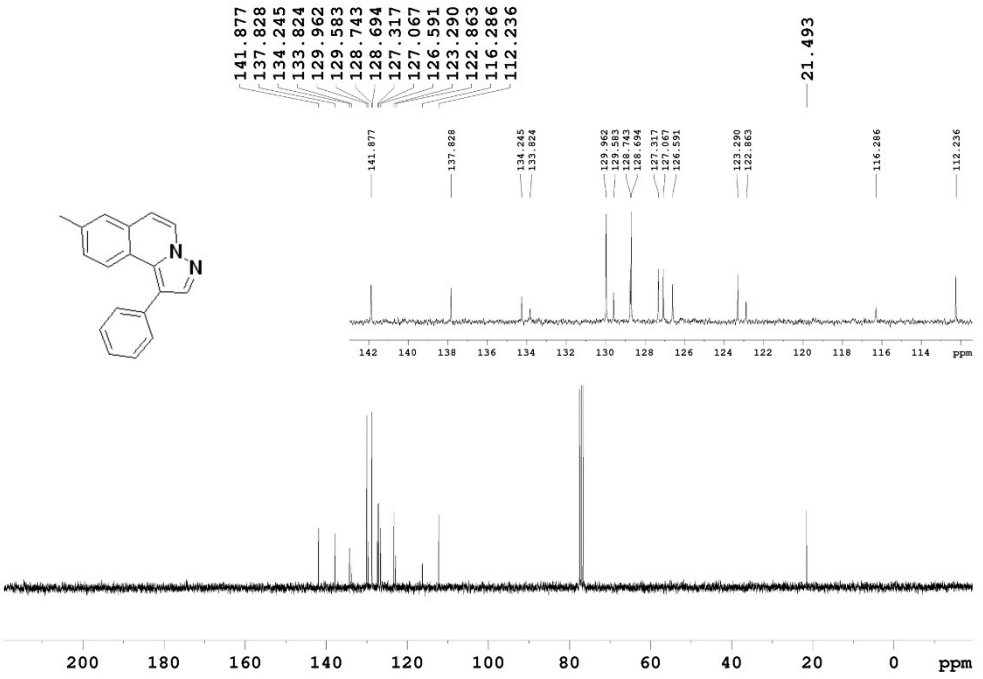


^{1}H NMR (300 MHz, $CDCl_3$) of **27**

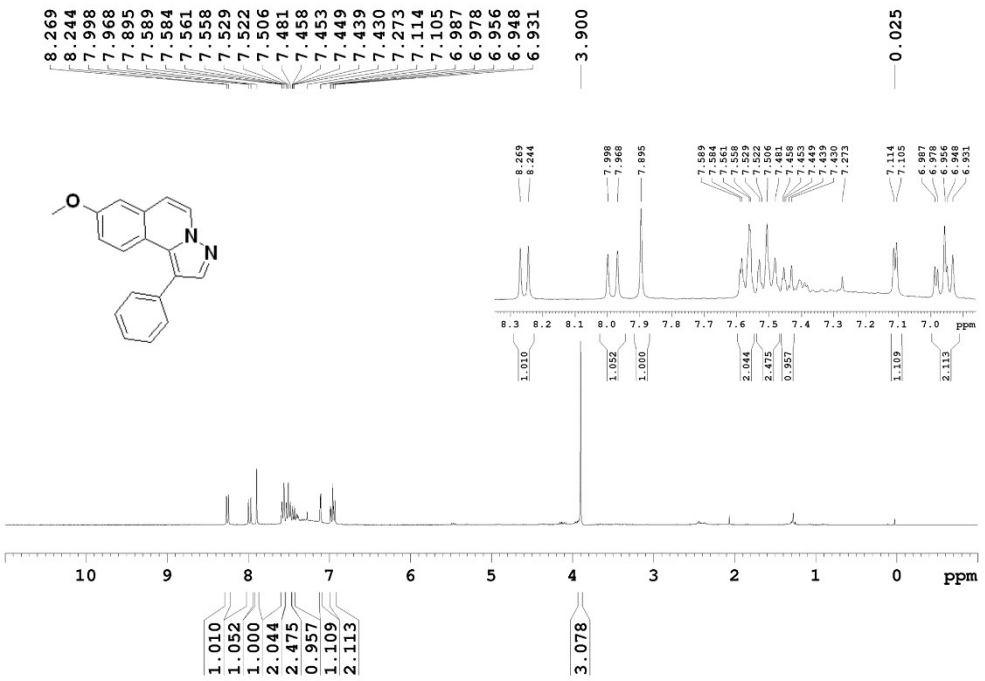
^{13}C NMR (75 MHz, $CDCl_3$) of **27**



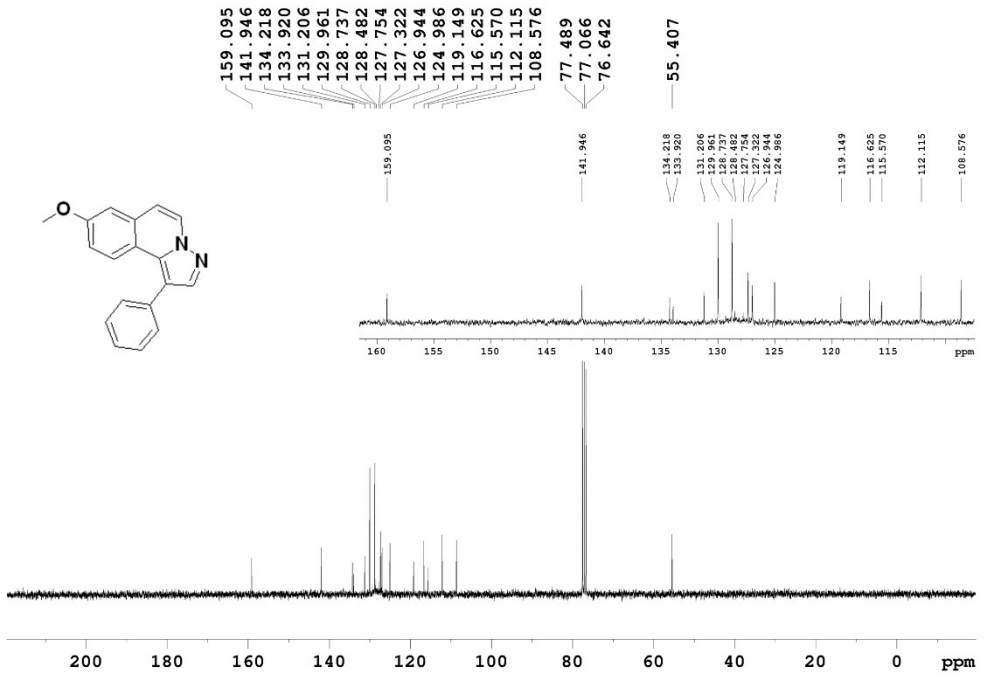
^{1}H NMR (300 MHz, $CDCl_3$) of **28**



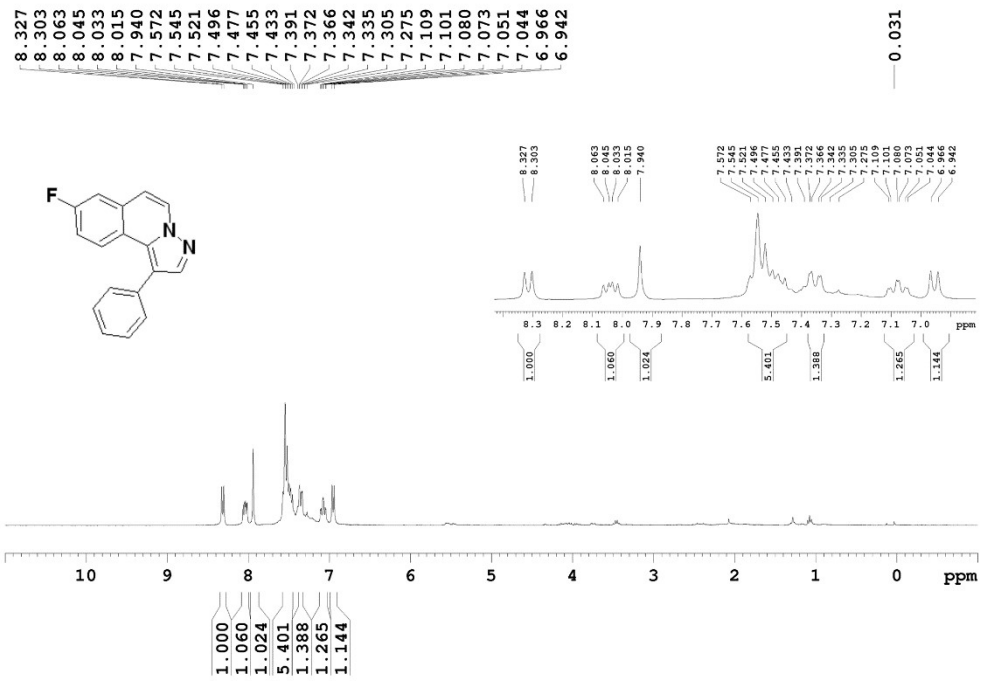
^{13}C NMR (75 MHz, $CDCl_3$) of **28**



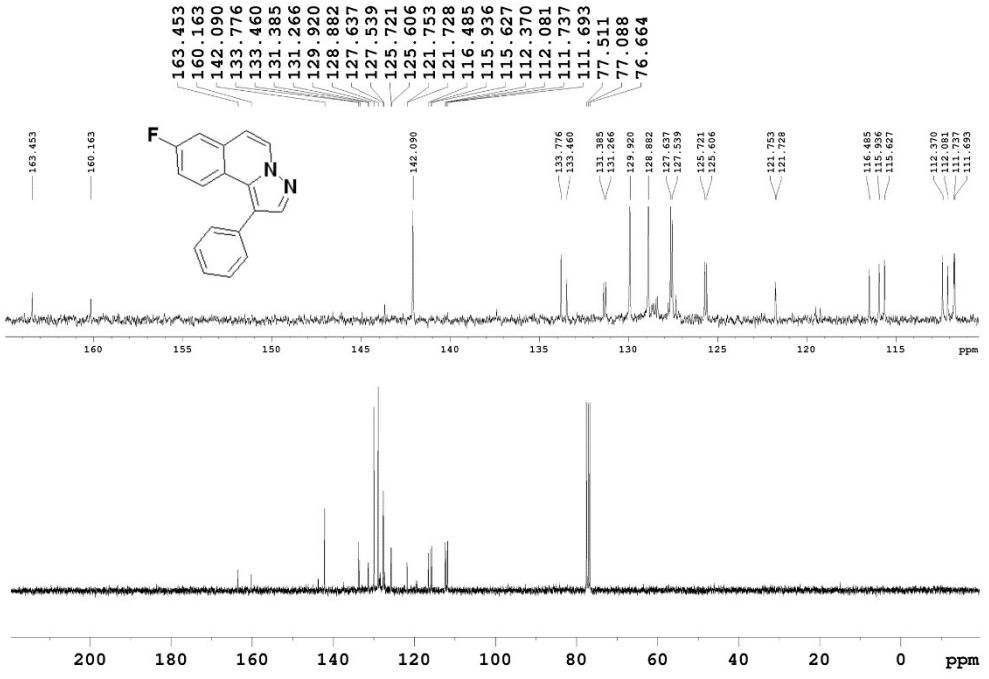
^{1}H NMR (300 MHz, $CDCl_3$) of **29**



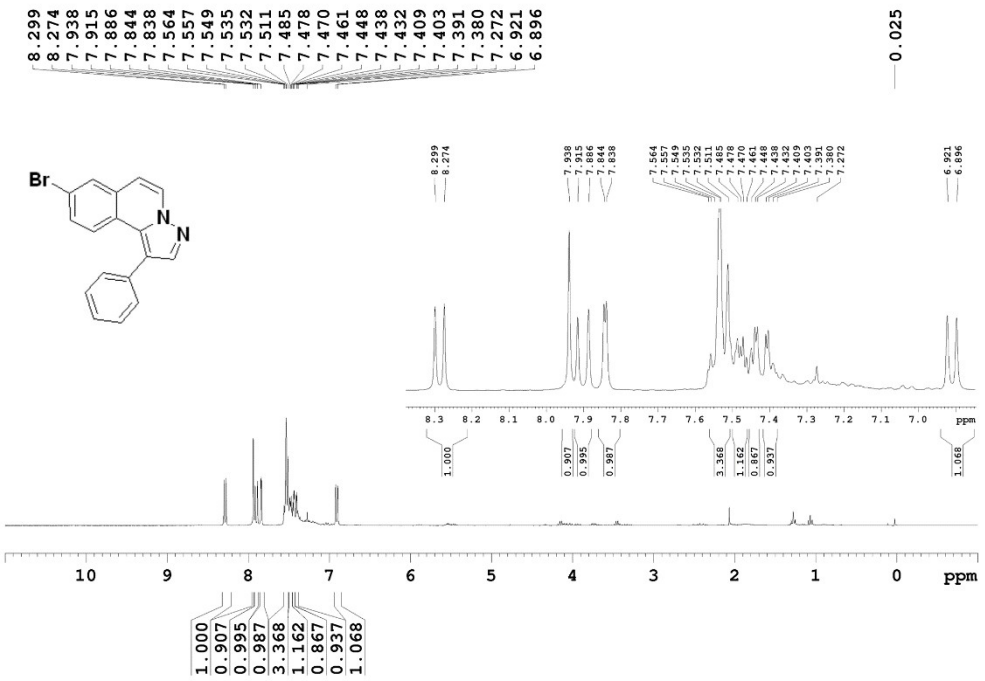
^{13}C NMR (75 MHz, $CDCl_3$) of **29**



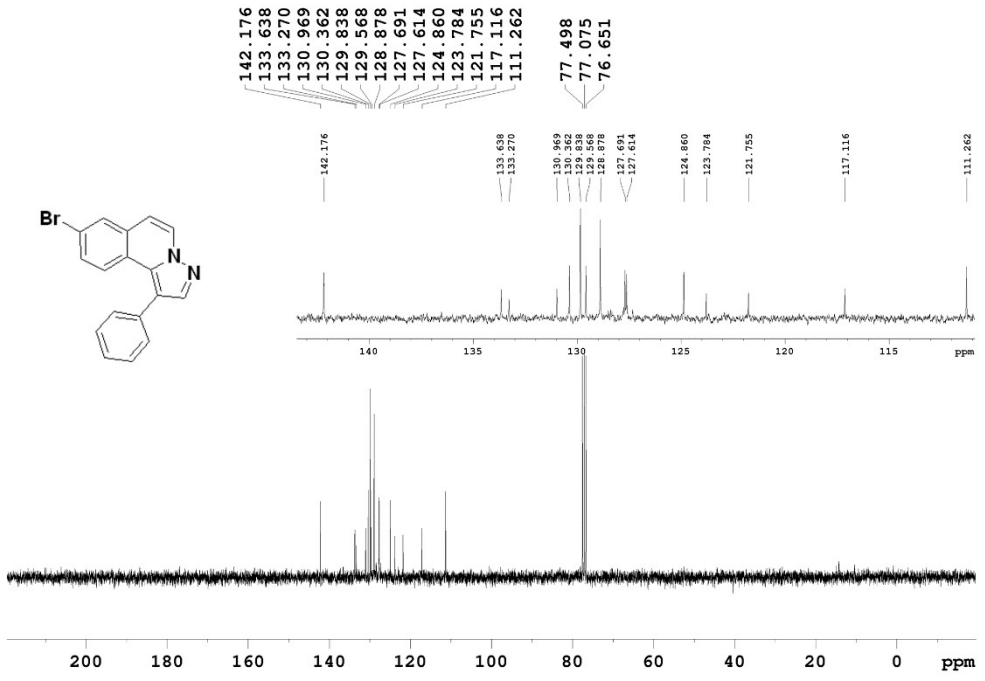
^{1}H NMR (300 MHz, $CDCl_3$) of **30**



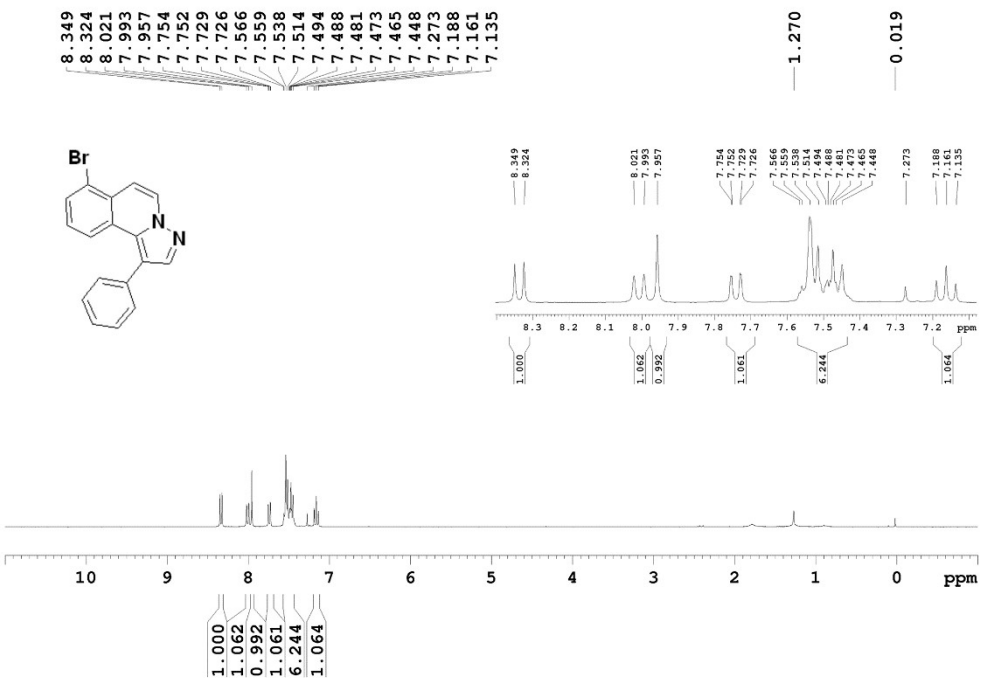
^{13}C NMR (75 MHz, $CDCl_3$) of **30**



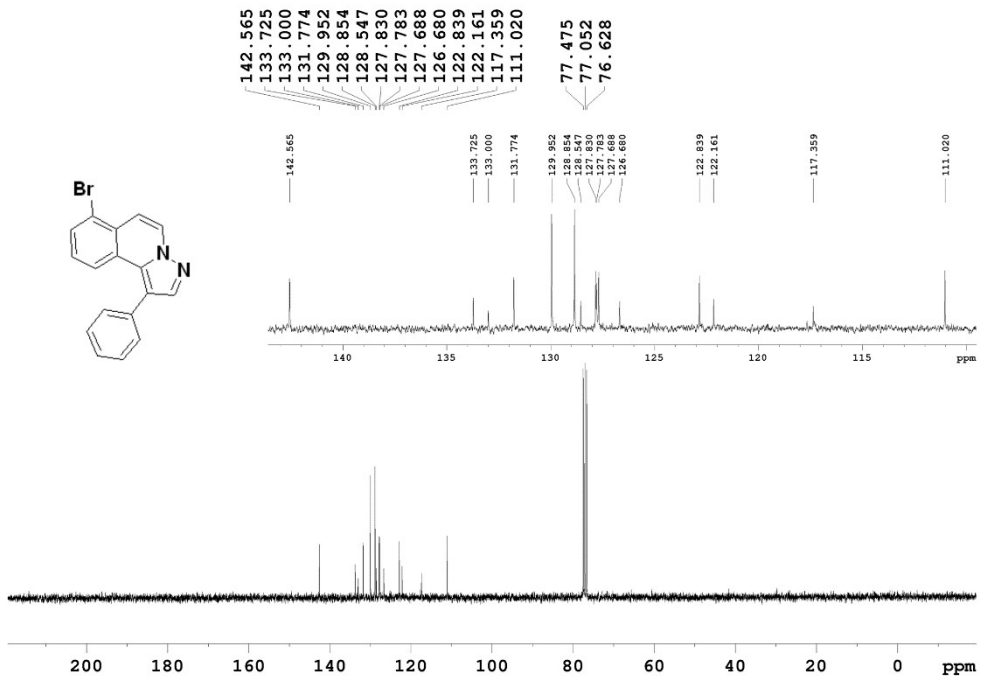
^{1}H NMR (300 MHz, $CDCl_3$) of **31**



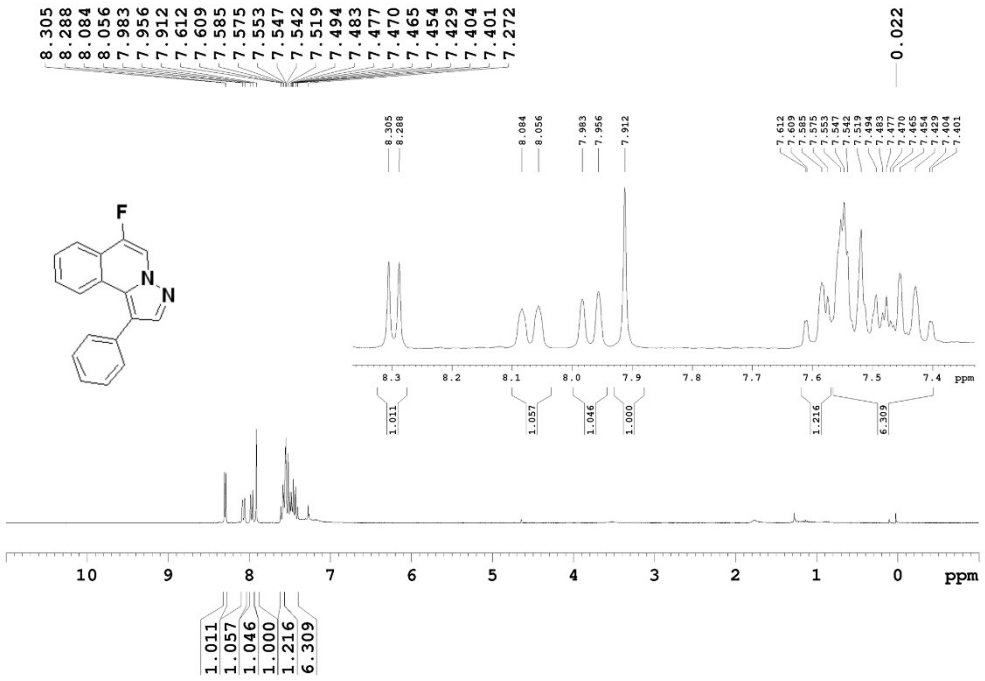
^{13}C NMR (75 MHz, $CDCl_3$) of **31**



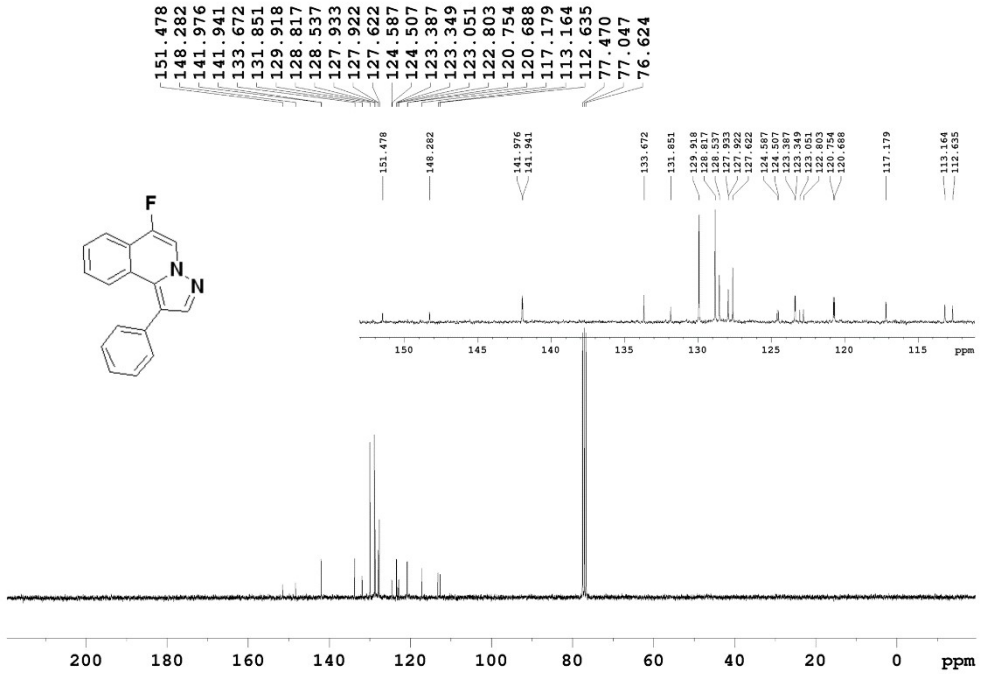
^{1}H NMR (300 MHz, $CDCl_3$) of **32**



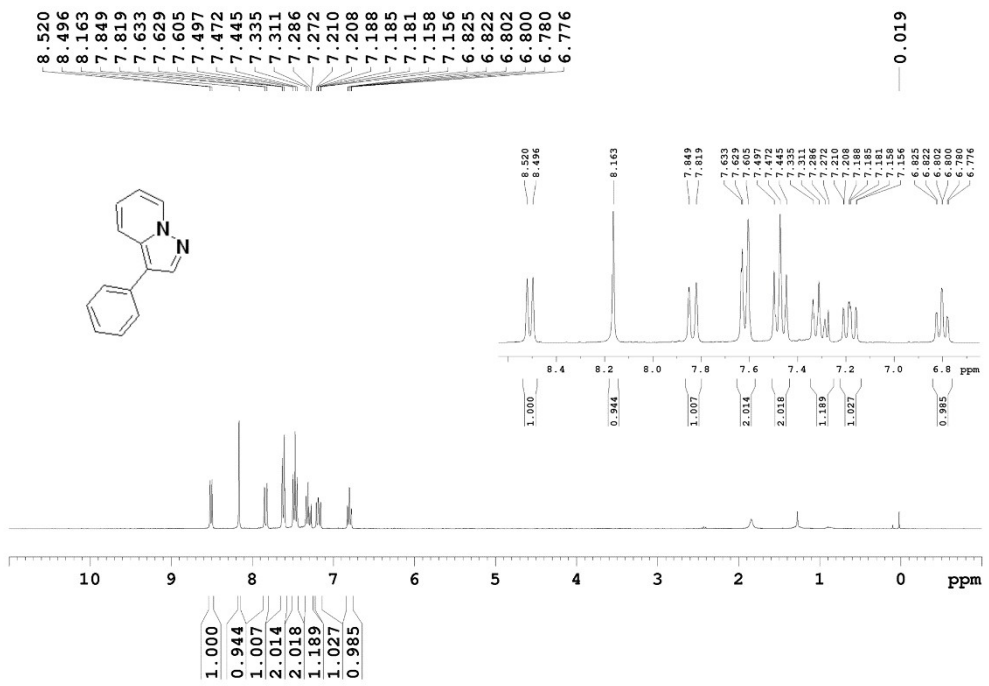
^{13}C NMR (75 MHz, $CDCl_3$) of **32**



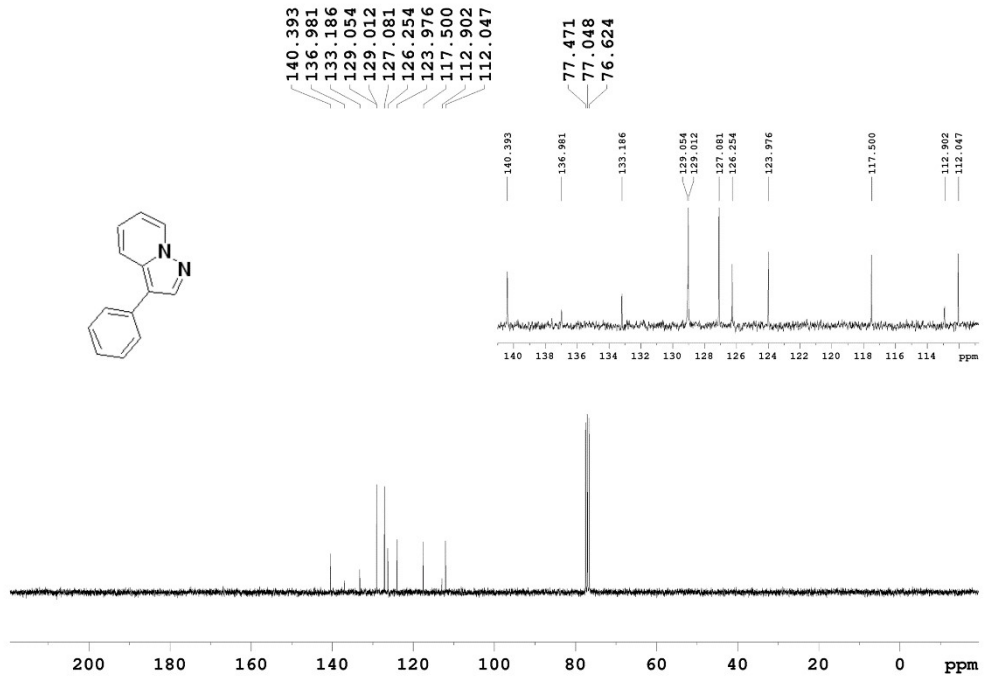
^{1}H NMR (300 MHz, $CDCl_3$) of **33**



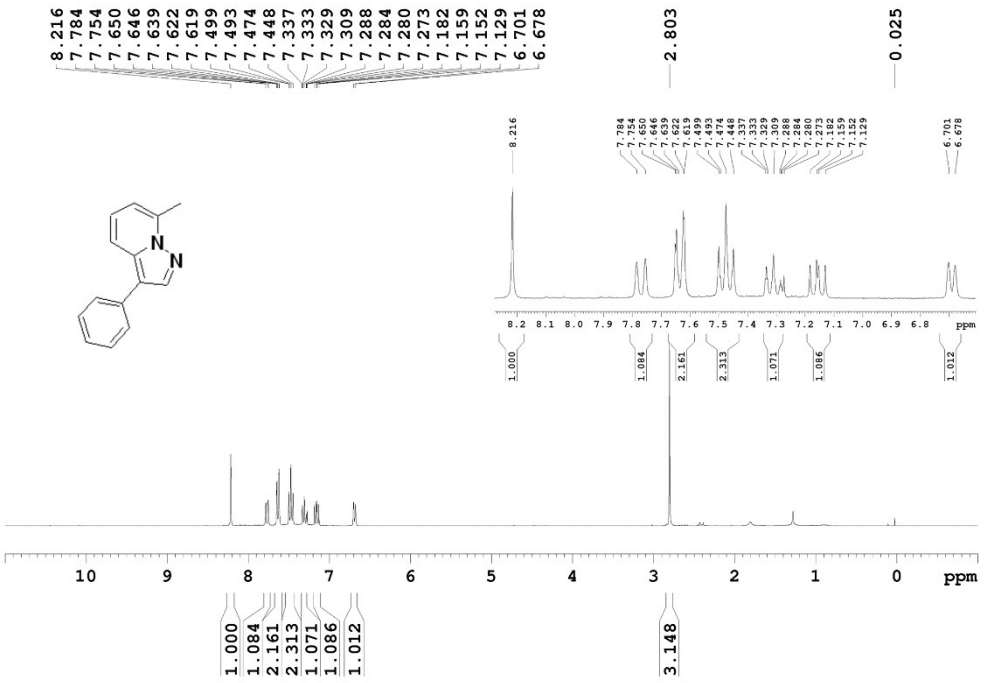
^{13}C NMR (75 MHz, $CDCl_3$) of **33**



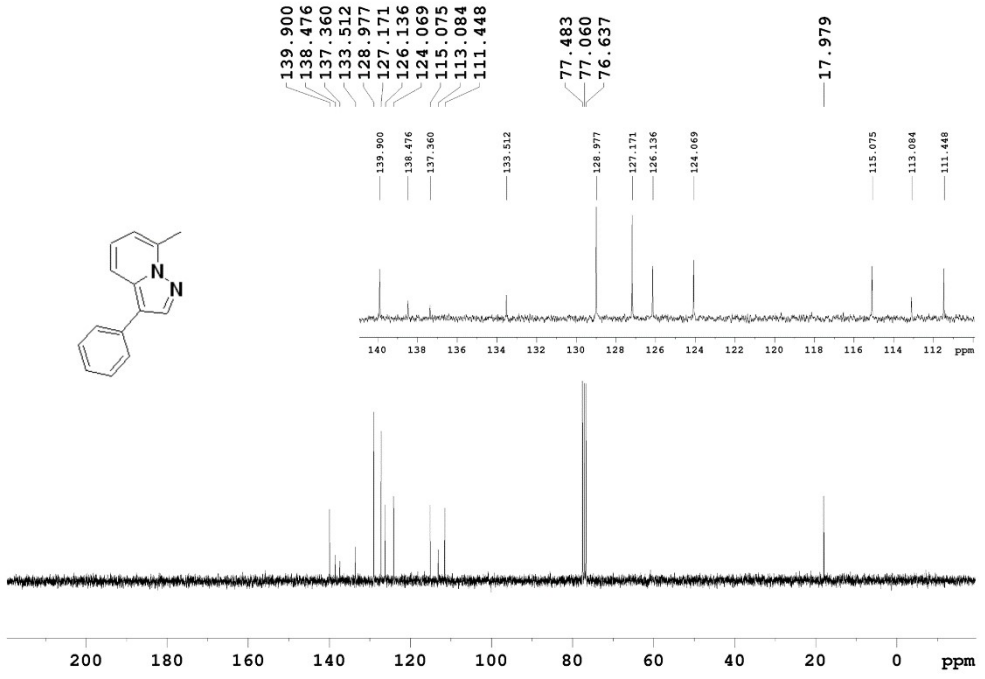
^{1}H NMR (300 MHz, $CDCl_3$) of **34**



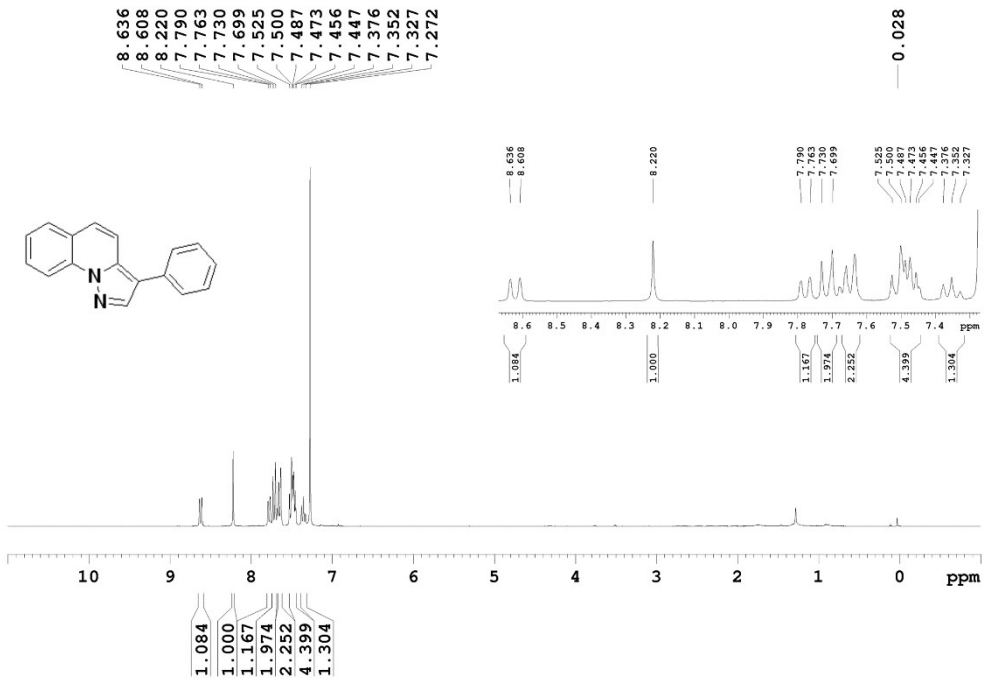
^{13}C NMR (75 MHz, $CDCl_3$) of **34**



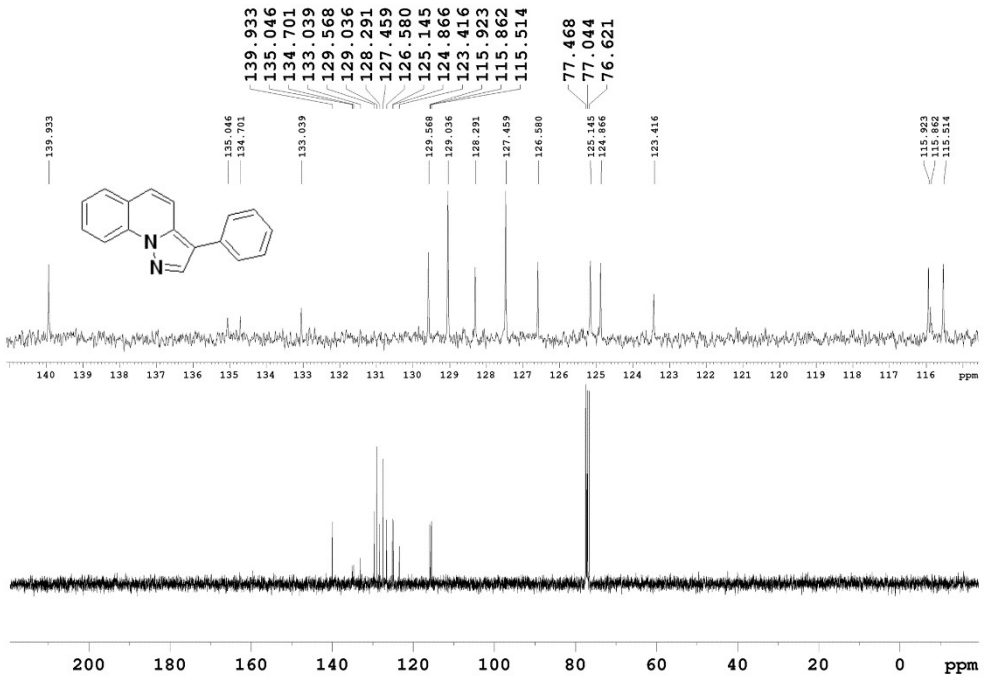
^{1}H NMR (300 MHz, $CDCl_3$) of **35**



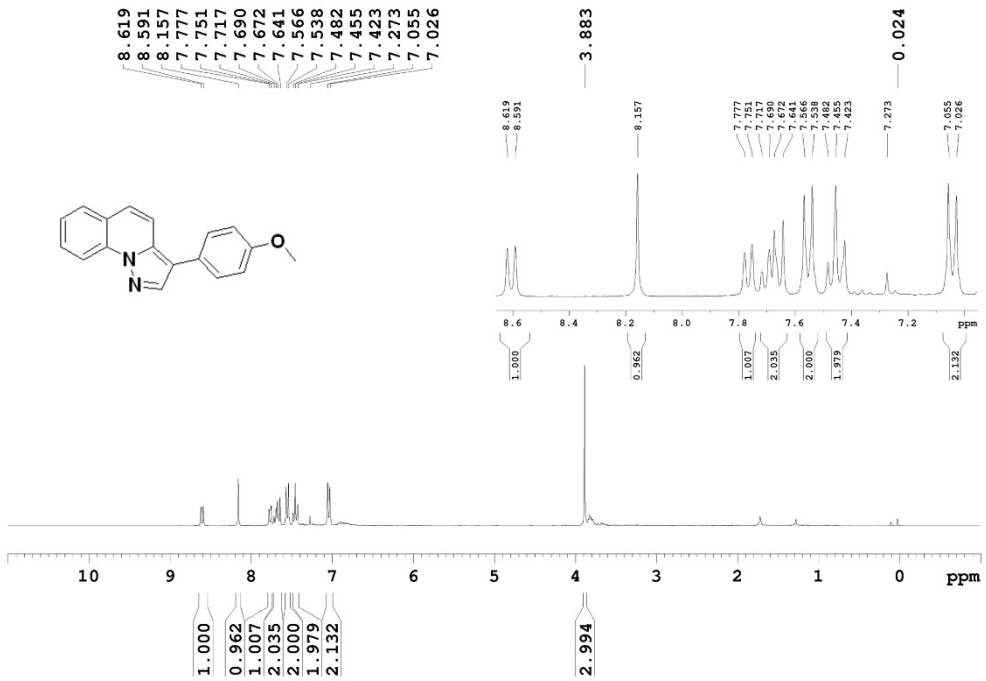
^{13}C NMR (75 MHz, $CDCl_3$) of **35**



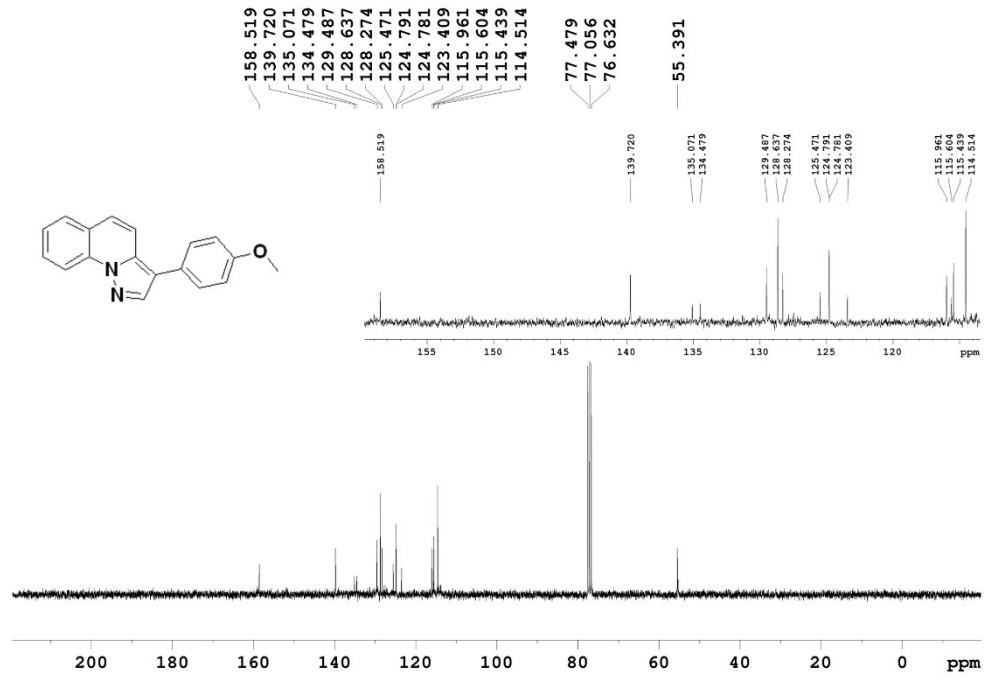
^{1}H NMR (300 MHz, $CDCl_3$) of **37**



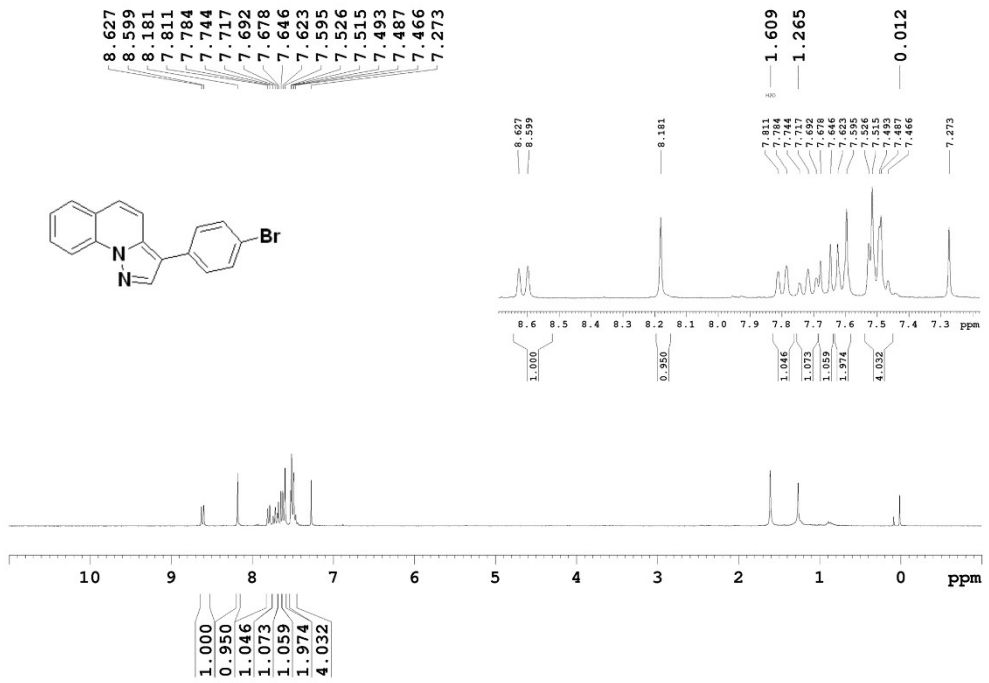
^{13}C NMR (75 MHz, $CDCl_3$) of **37**



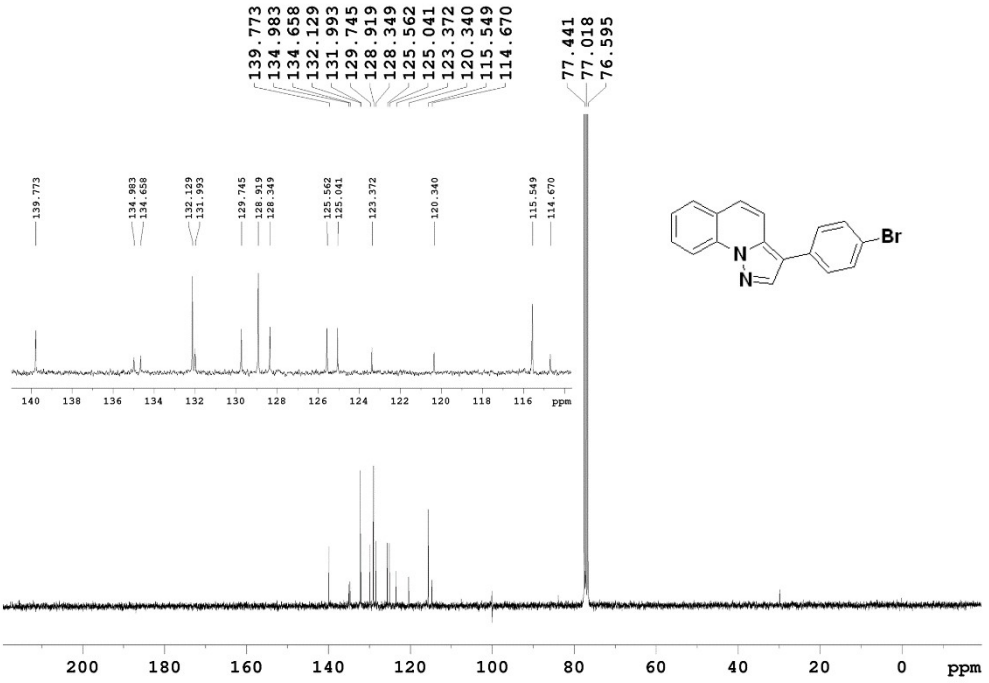
^{1}H NMR (300 MHz, $CDCl_3$) of **38**



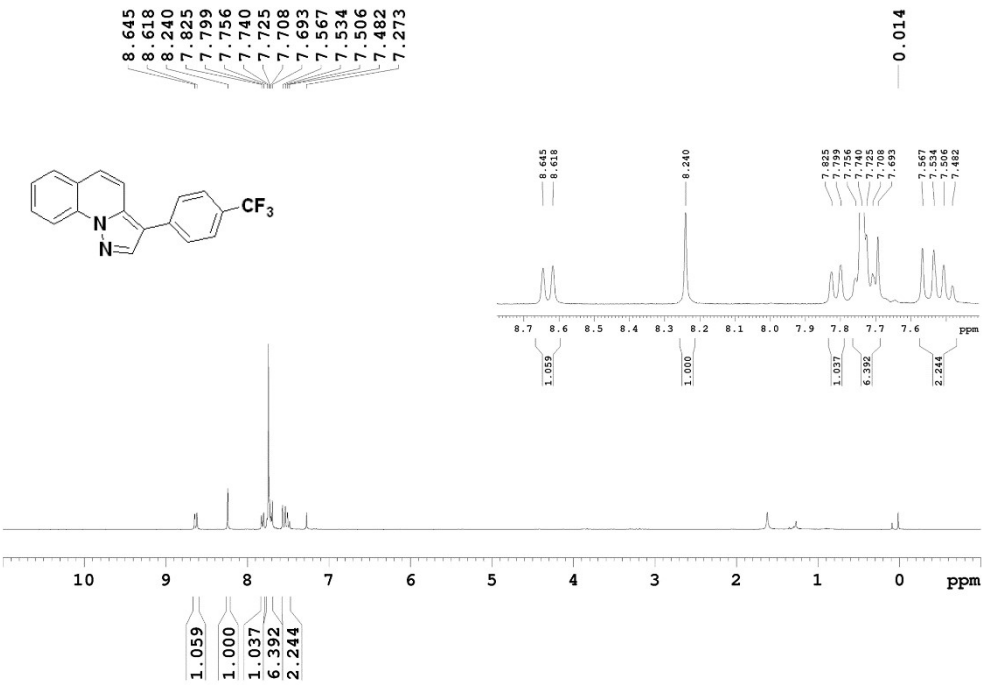
^{13}C NMR (75 MHz, $CDCl_3$) of **38**



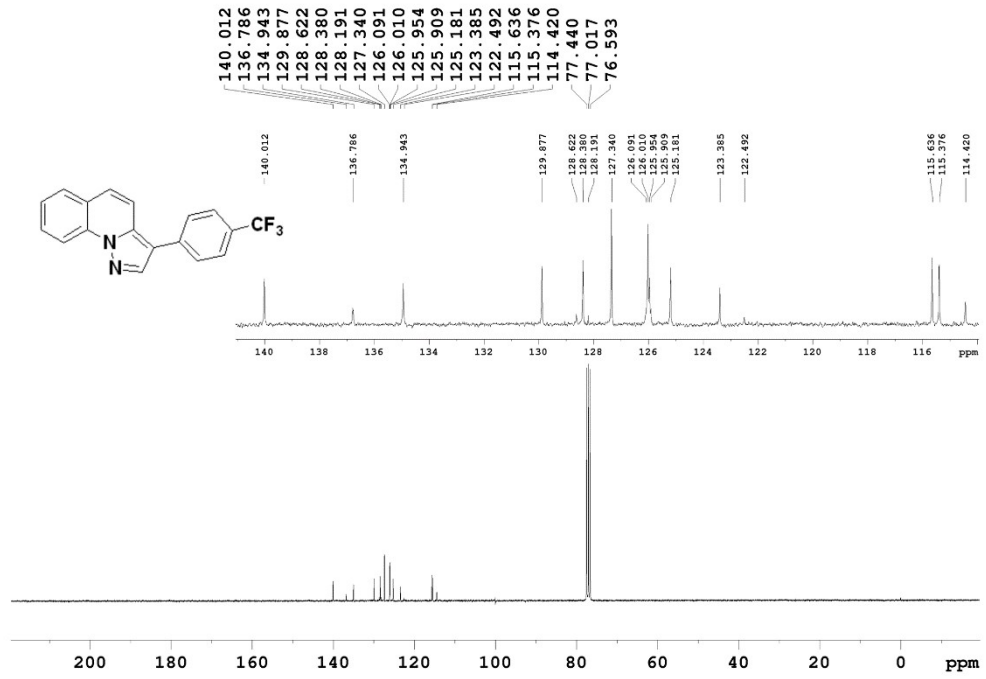
^{1}H NMR (300 MHz, $CDCl_3$) of **39**



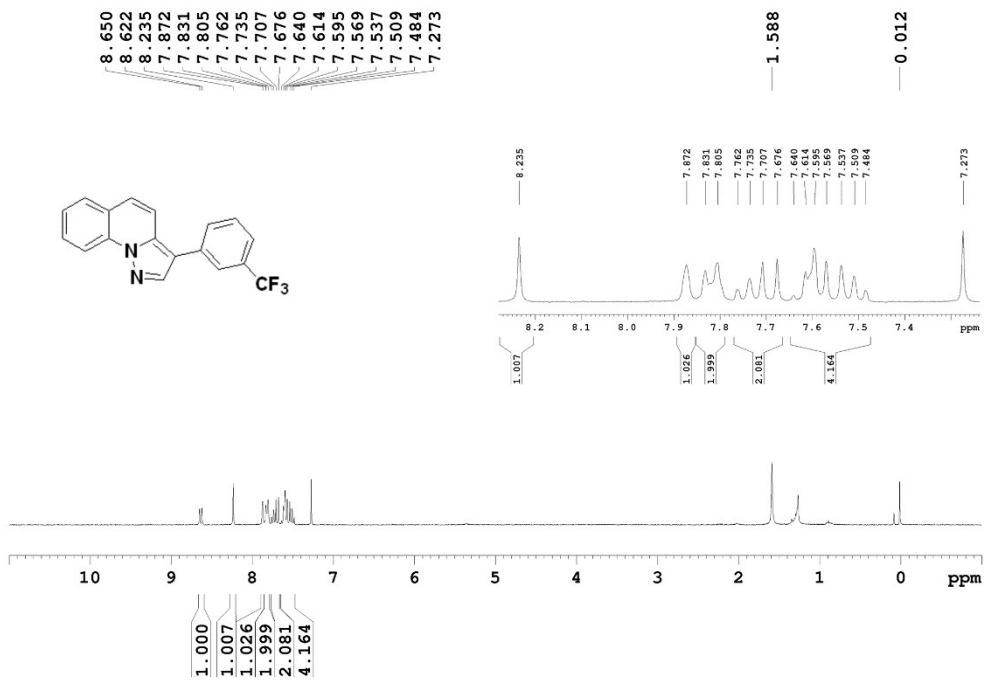
^{13}C NMR (75 MHz, $CDCl_3$) of **39**



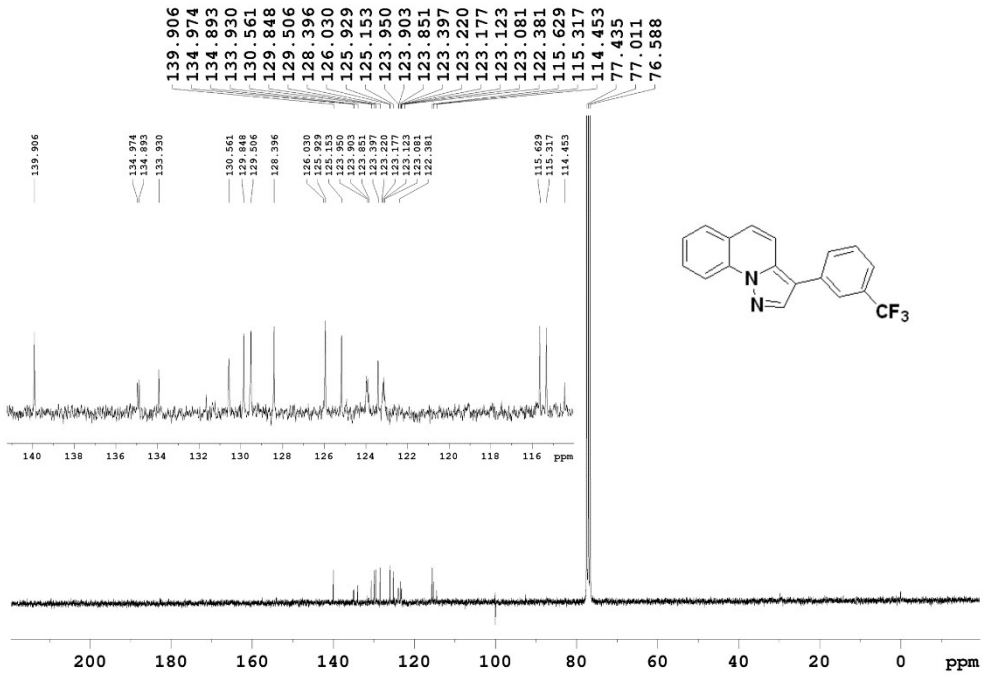
^{1}H NMR (300 MHz, $CDCl_3$) of **40**



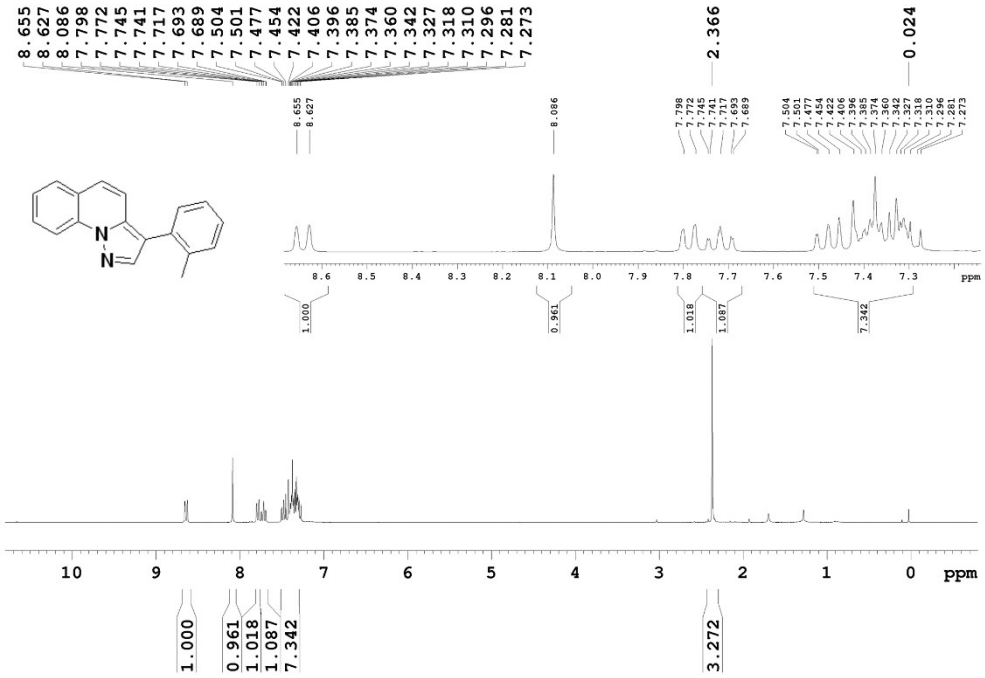
^{13}C NMR (75 MHz, $CDCl_3$) of **40**



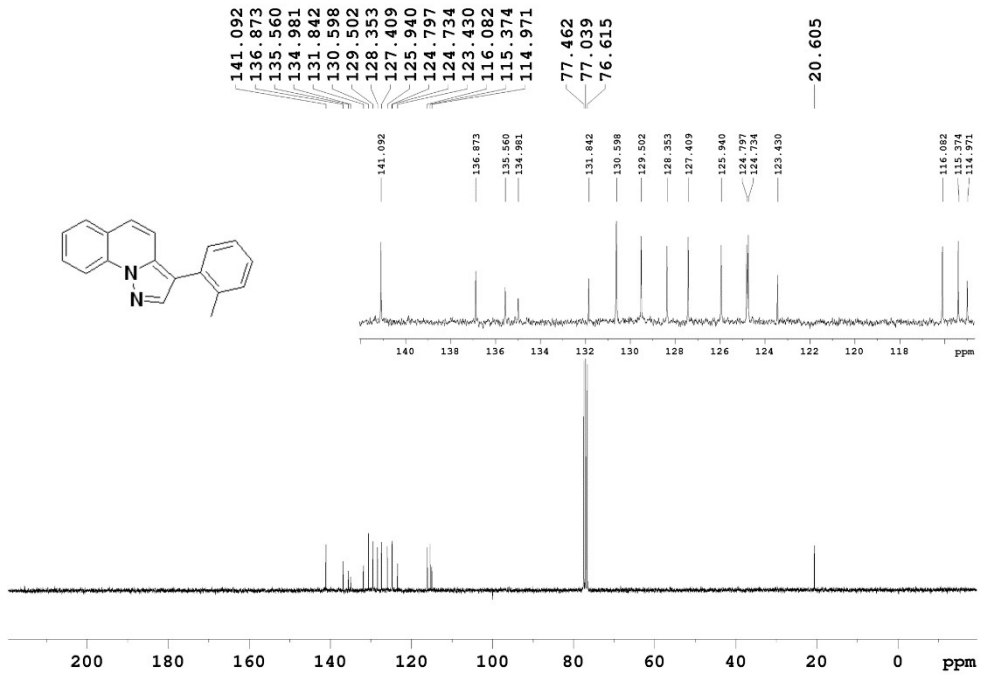
^{1}H NMR (300 MHz, $CDCl_3$) of **41**



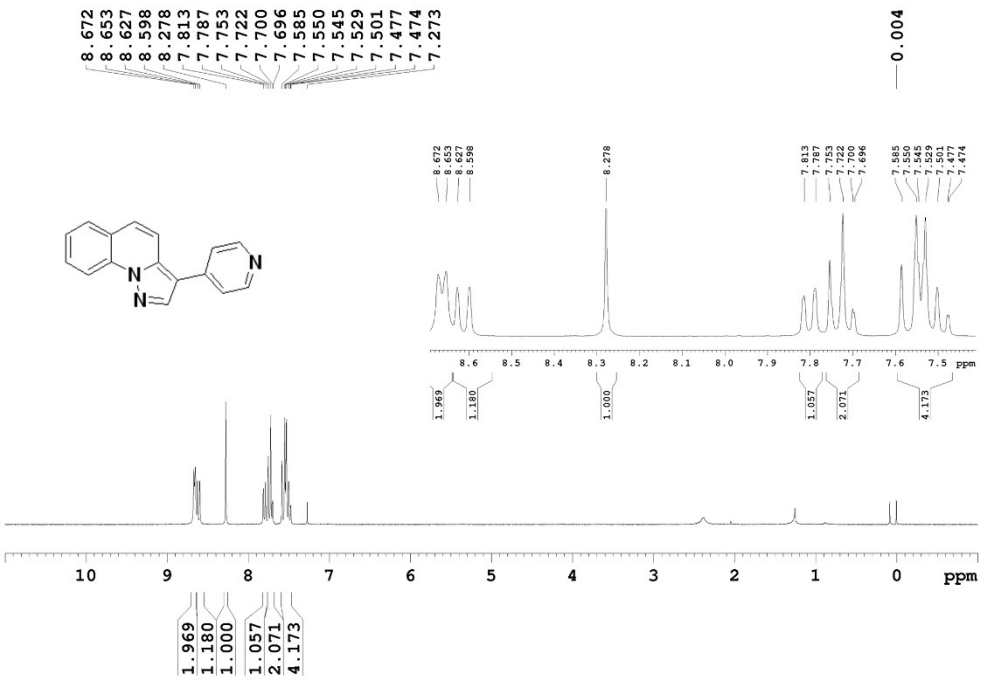
^{13}C NMR (75 MHz, $CDCl_3$) of **41**



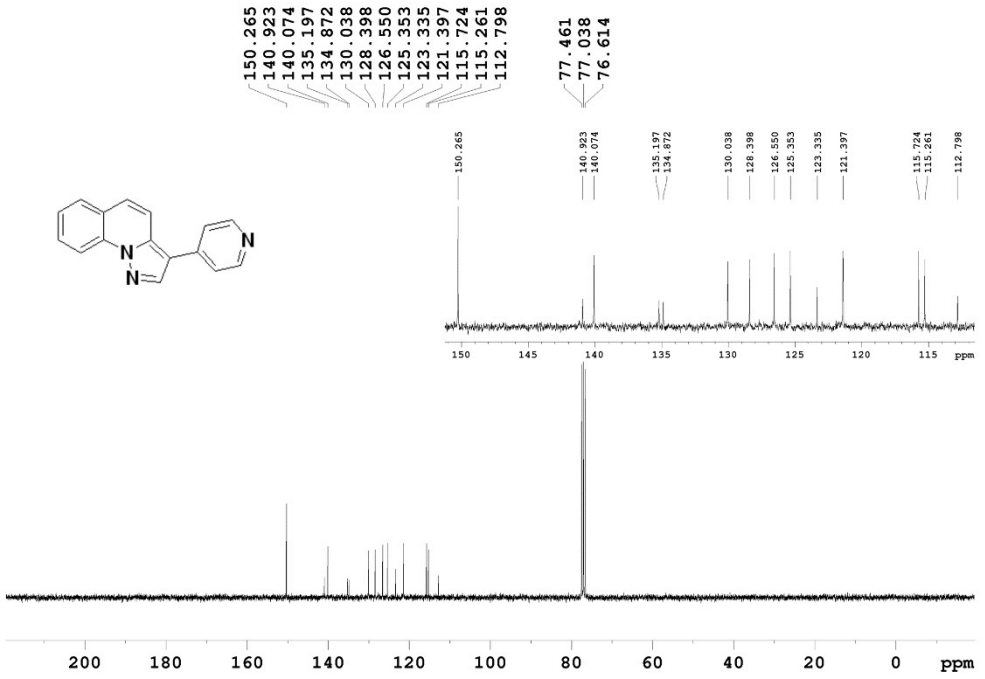
^{1}H NMR (300 MHz, $CDCl_3$) of **42**



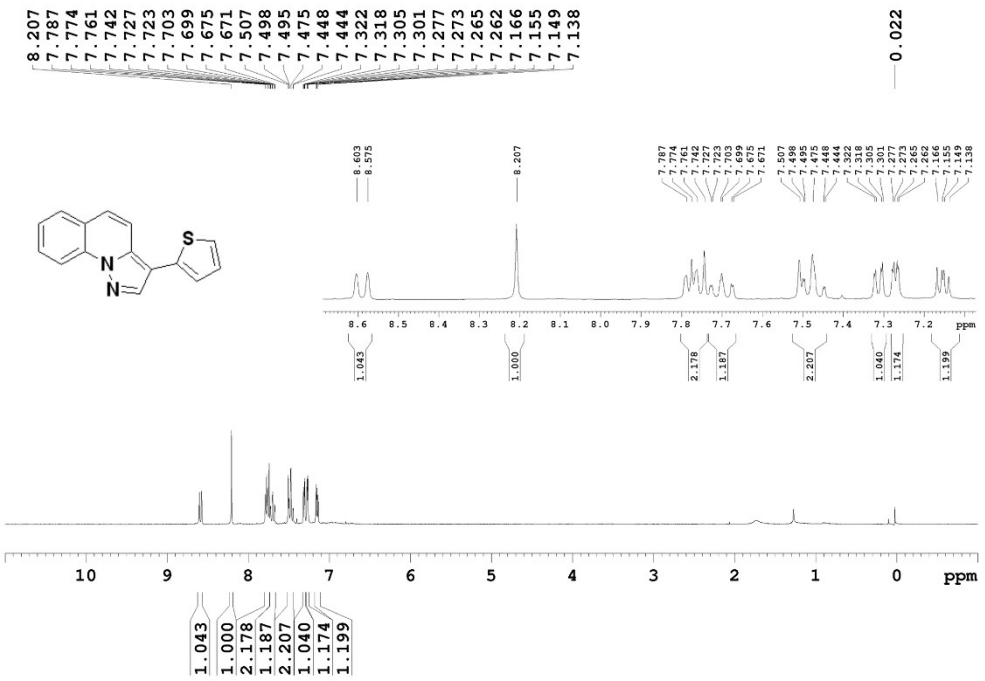
^{13}C NMR (75 MHz, $CDCl_3$) of **42**



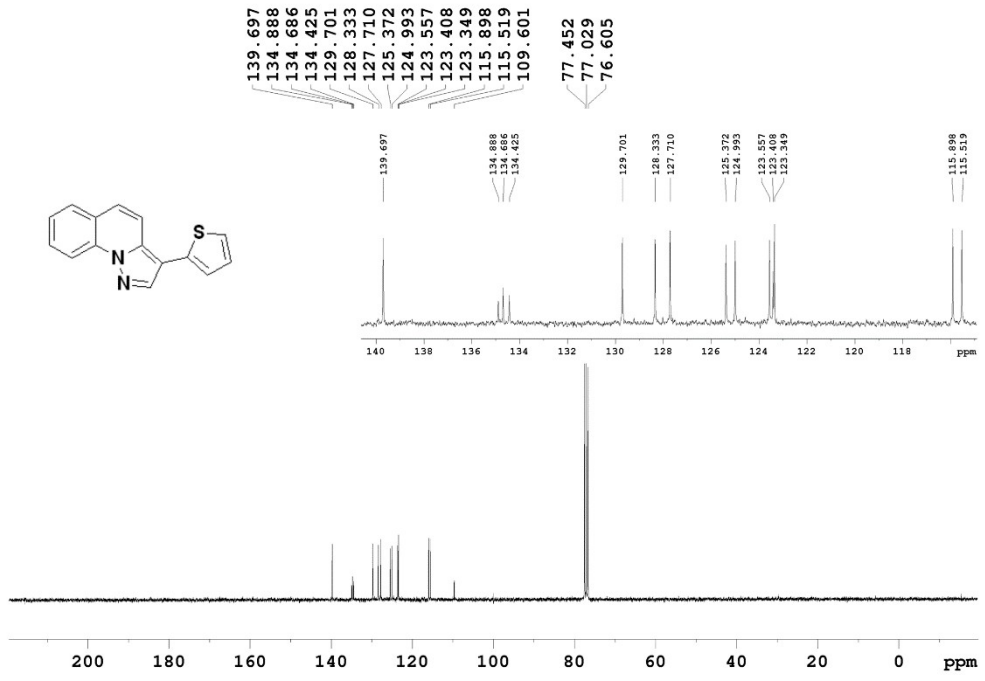
^{1}H NMR (300 MHz, $CDCl_3$) of **43**



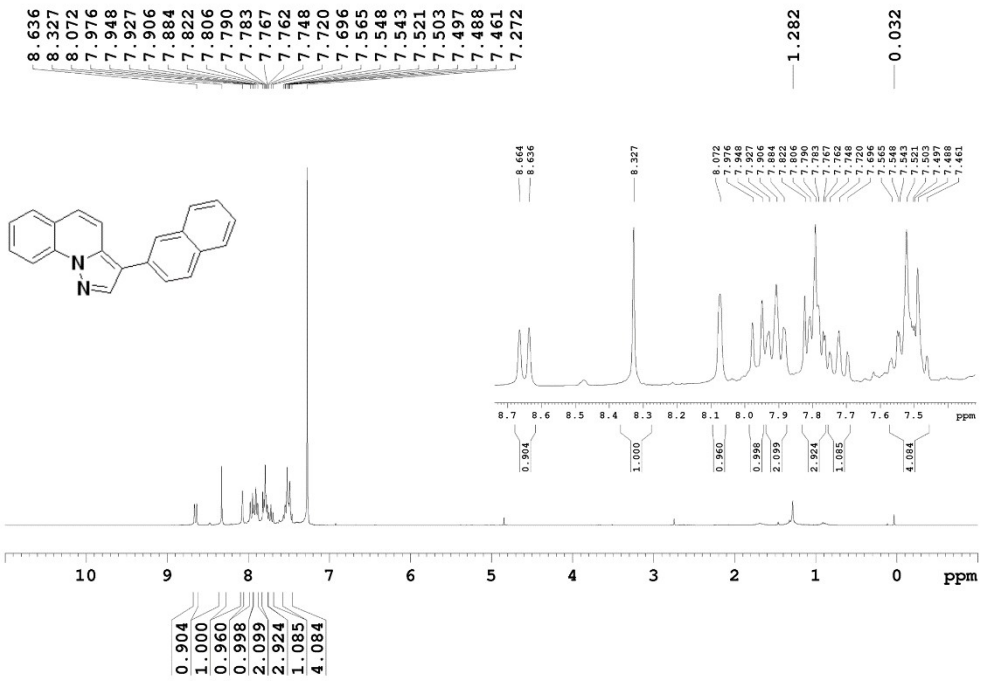
^{13}C NMR (75 MHz, $CDCl_3$) of **43**



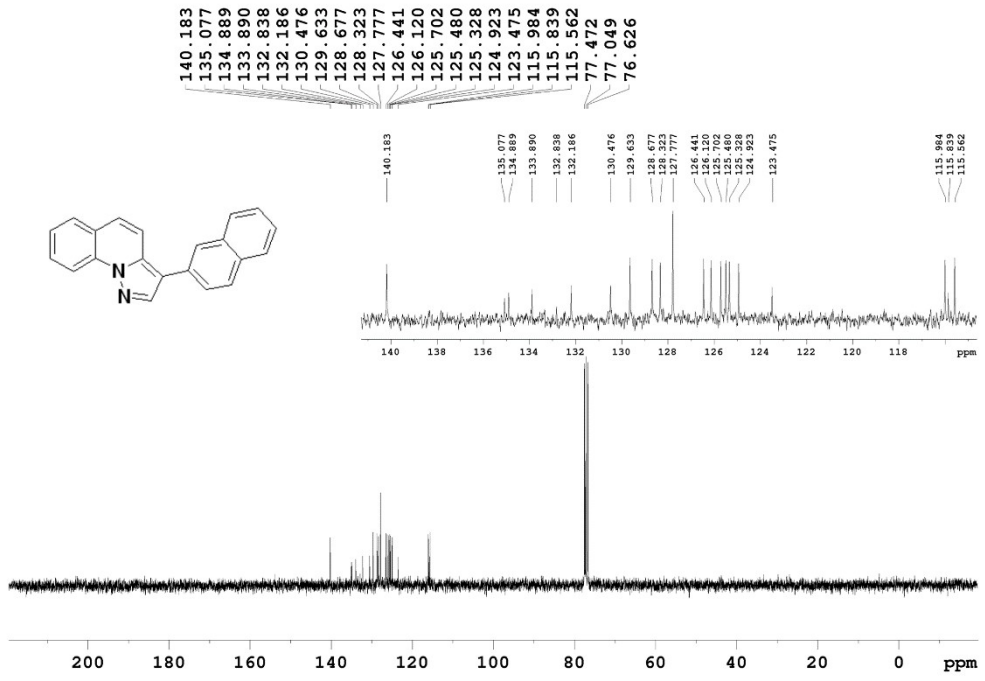
^{1}H NMR (300 MHz, $CDCl_3$) of **44**



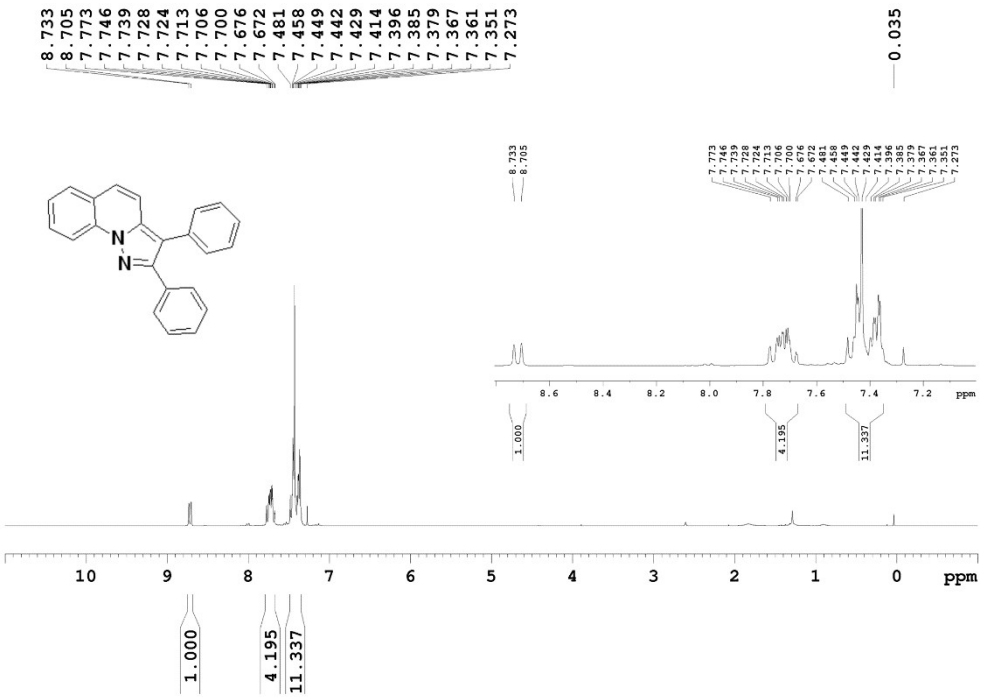
^{13}C NMR (75 MHz, $CDCl_3$) of **44**



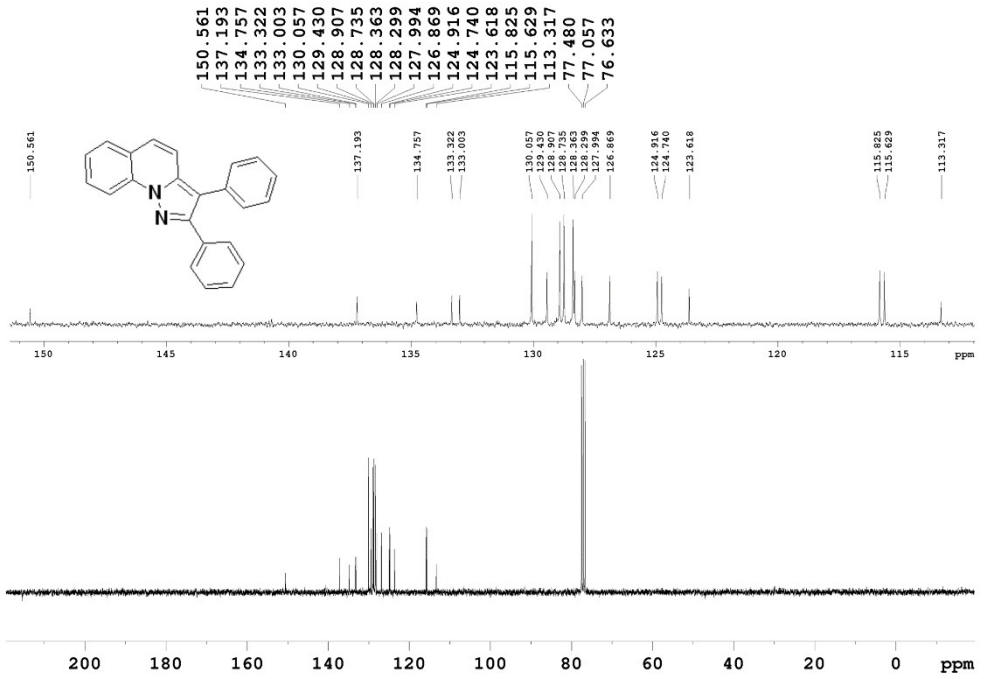
^{1}H NMR (300 MHz, $CDCl_3$) of **45**



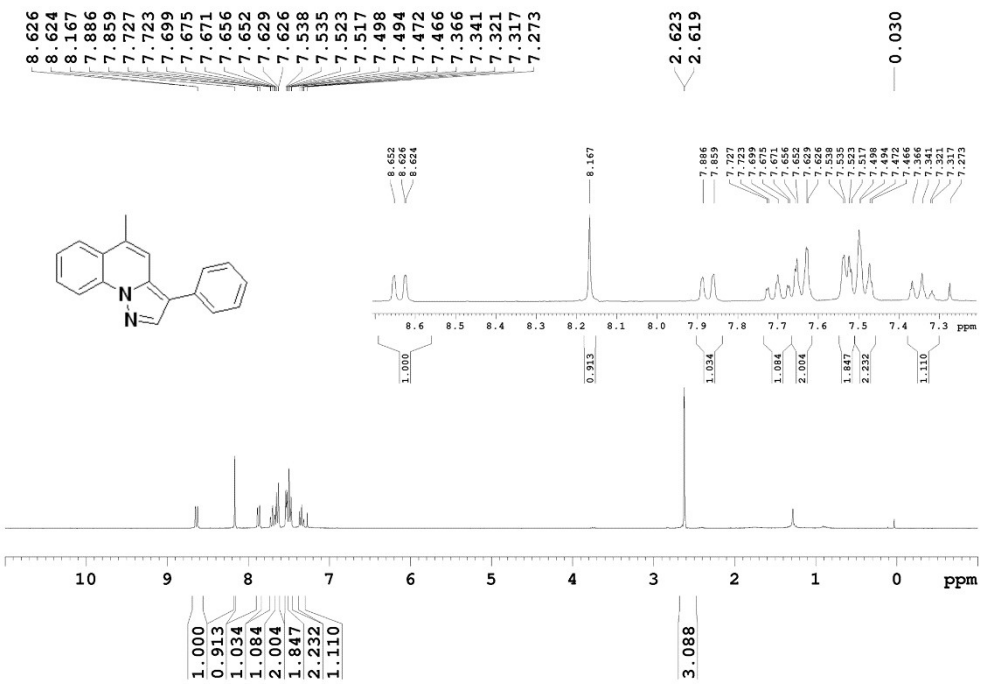
^{13}C NMR (75 MHz, $CDCl_3$) of **45**



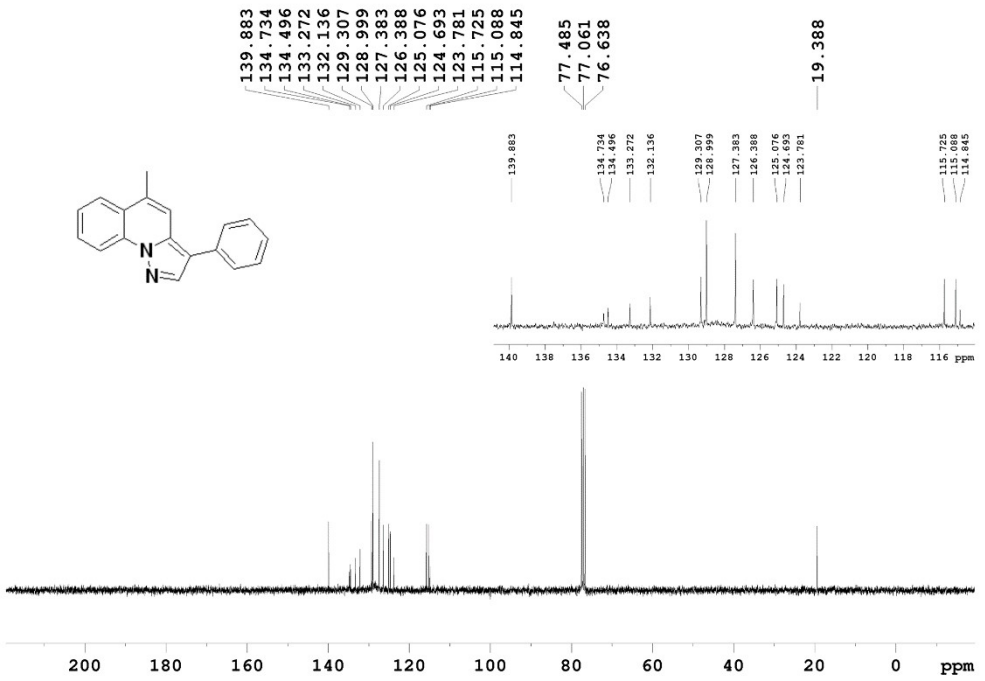
^{1}H NMR (300 MHz, $CDCl_3$) of **46**



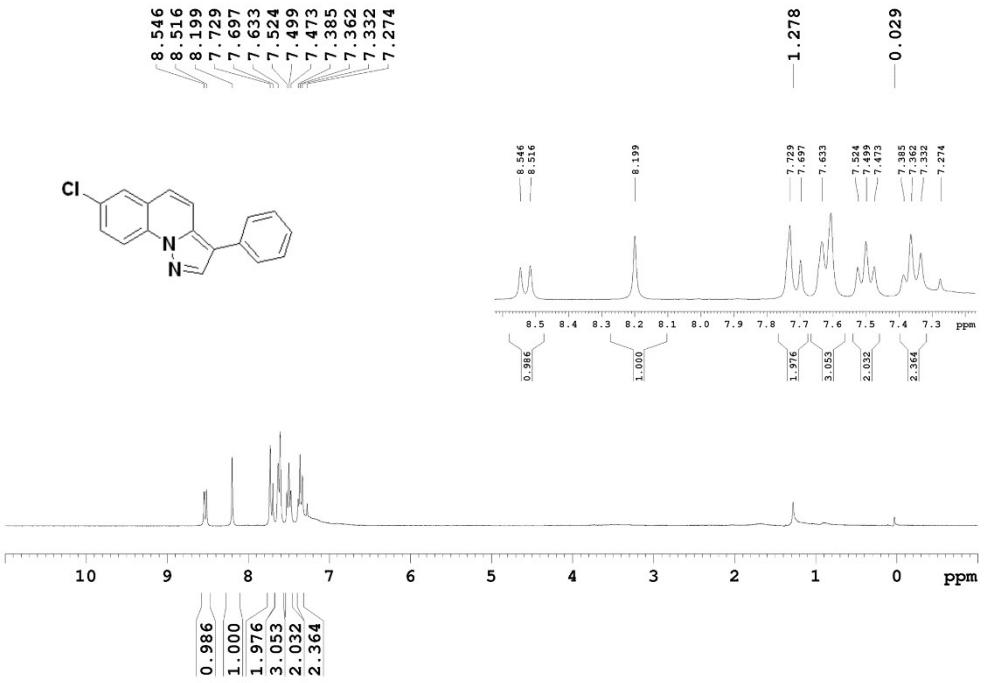
^{13}C NMR (75 MHz, $CDCl_3$) of **46**



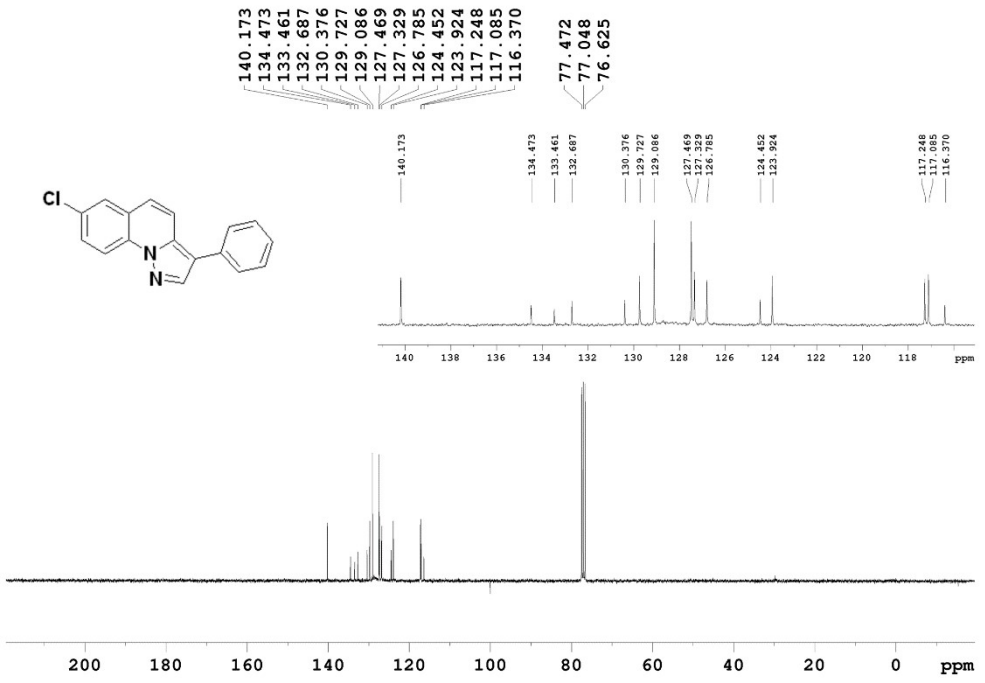
^{1}H NMR (300 MHz, $CDCl_3$) of **47**



^{13}C NMR (75 MHz, $CDCl_3$) of **47**



^{1}H NMR (300 MHz, $CDCl_3$) of **48**



^{13}C NMR (75 MHz, $CDCl_3$) of **48**