

Supplementary Material

LiO^tBu-promoted Intramolecular Cycloaddition of 2'-Alkynyl-biaryl-2-aldehyde N-tosylhydrazones approach to 3-Substituted 1H-Dibenzo[e,g]indazoles

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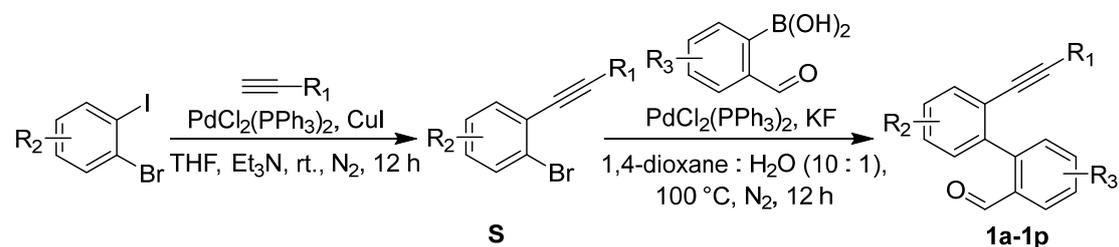
A. General methods	S2
B. Experimental procedures and characterization data	S3
B.1 Preparation of 2'-alkynyl-biaryl-2-aldehydes 1a-1p	S3
B.2 Preparation of 2'-alkynyl-biaryl-2-aldehyde N-tosylhydrazone 1a'	S15
B.3 Preparation of 3-substituted 1H-dibenzo[e,g]indazoles 2a-2p	S17
C. Single crystal structures	S27
D. Computational details	S35
E. NMR charts	S39
F. References	S78

A. General methods

All commercially available reagents, solvents and metal salts are analytically pure and were used without further purification. Column chromatography was performed with silica gel. Analytical thin-layer chromatography (TLC) was performed on 0.2 mm silica gel-coated glass sheets. All yields given referred to isolated yields. Nuclear magnetic resonance (NMR) spectra were recorded on JEOL 400 using CDCl₃ or DMSO-*d*₆ as solvents at 298 K. ¹H NMR (400 MHz) chemical shifts (δ) were referenced to internal standard TMS ($\delta = 0.00$ ppm) or internal solvent DMSO-*d*₆ ($\delta = 2.50$ ppm); ¹³C{¹H} NMR (101 MHz) chemical shifts were referenced to internal solvent CDCl₃ ($\delta = 77.16$ ppm) or DMSO-*d*₆ ($\delta = 39.52$ ppm). High Resolution Mass Spectroscopy (HRMS) spectra were obtained by high-resolution mass spectrometers with electrospray ionization (ESI) source. Single-crystal X-ray diffraction data were obtained from SuperNova diffractometer with Cu K α radiation at low temperature (173.15 K).

B. Experimental procedures and characterization data

B-1. Preparation of 2'-alkynyl-biaryl-2-aldehydes 1a-1p

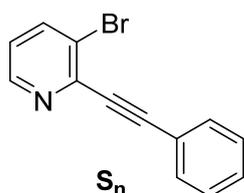


General procedures for the preparation of 2'-cyano-biaryl-2-aldehyde:

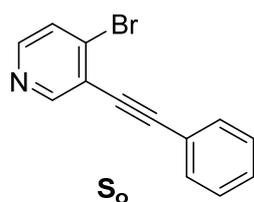
(1) To a mixture of 1-bromo-2-iodobenzenes (2.00 mmol), CuI (5.0 mol%, 0.10 mmol), PdCl₂(PPh₃)₂ (5.0 mol%, 0.10 mmol), THF (5.0 mL) and Et₃N (5.0 mL) in a 25 mL screw-capped thick-walled Pyrex tube with stirring under N₂ was dropwise added terminal alkynes (1.2 equiv., 2.40 mmol) at room temperature over 5 minutes, and the obtained mixture was then stirred at room temperature under nitrogen for 12 h. After the reaction was completed (checked by GC-MS), the reaction mixture was filtrated through a short pad of celite. The solution was then concentrated under reduced pressure to remove the volatiles, and the crude residue was purified by column chromatography on silica gel, eluting with pure petroleum ether to obtain the desired compounds **S_a-S_p** (checked by GC-MS) in 75% - 95% yields.

(2) The mixture of **S** (1.50 mmol), phenylboronic acids (1.1 equiv., 1.65 mmol), PdCl₂(PPh₃)₂ (5.0 mol%, 0.075 mmol), KF (3.0 equiv., 4.5 mmol), 1,4-dioxane (10.0 mL) and H₂O (1.0 mL) in a 25 mL screw-capped thick-walled Pyrex tube was stirred under nitrogen at 100 °C in an oil bath for 12 h. After the reaction was completed (checked by TLC), the reaction mixture was cooled to room temperature, and filtrated through a short pad of celite. The solution was then concentrated under reduced pressure

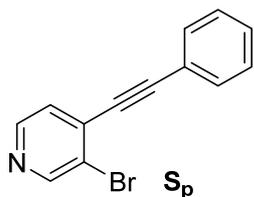
to remove the volatiles, and the crude residue was purified by column chromatography on silica gel, eluting with petroleum ether / ethyl acetate (gradient mixture ratio from 30 / 1 to 15 / 1) as eluent to afford product **1a-1p** in 24% - 94% yields.



3-Bromo-2-(phenylethynyl)pyridine (S_n). Pale yellow oil (478 mg, 1.85 mmol, 93%). $R_f = 0.70$ (pure PE). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.52 (dd, $J = 4.8, 1.5$ Hz, 1H), 7.89 (dd, $J = 8.2, 1.6$ Hz, 1H), 7.66 – 7.63 (m, 2H), 7.39 – 7.34 (m, 3H), 7.09 (dd, $J = 8.2, 4.6$ Hz, 1H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 148.28, 143.68, 139.82, 132.17, 129.40, 128.45, 123.85, 123.57, 121.92, 94.00, 87.51. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{BrN}$ 257.9913, found 257.9913.

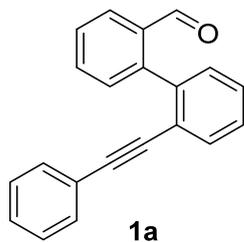


4-Bromo-3-(phenylethynyl)pyridine (S_o). Pale yellow oil (488 mg, 1.89 mmol, 95%). $R_f = 0.70$ (pure PE). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.70 (s, 1H), 8.29 (d, $J = 5.2$ Hz, 1H), 7.60 – 7.57 (m, 2H), 7.53 (d, $J = 5.4$ Hz, 1H), 7.38 – 7.35 (m, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 152.98, 148.62, 135.28, 131.83, 129.20, 128.50, 127.21, 123.14, 122.23, 97.08, 84.86. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{BrN}$ 257.9913, found 257.9913.

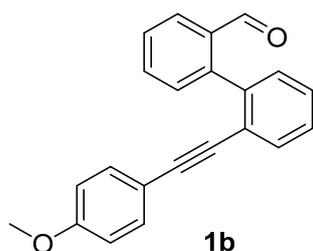


3-Bromo-4-(phenylethynyl)pyridine (S_p). Pale yellow oil (406 mg, 1.57 mmol, 79%). $R_f = 0.70$ (pure PE). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.77 (s, 1H), 8.47 (d, $J = 5.0$ Hz, 1H), 7.61 – 7.58 (m, 2H), 7.43 – 7.35 (m, 4H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 151.77, 147.79, 133.07, 132.07, 129.67, 128.58, 126.56, 123.11, 121.82, 98.75, 85.70. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{13}\text{H}_9\text{BrN}$ 257.9913, found 257.9913.

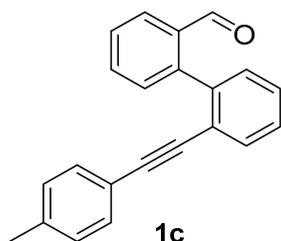
Compounds **1a**, **1c**, **1e**, **1f**, **1g** are known compounds, which were confirmed by their $^1\text{H NMR}$ and $^{13}\text{C NMR}$ data with the reported one³⁷.



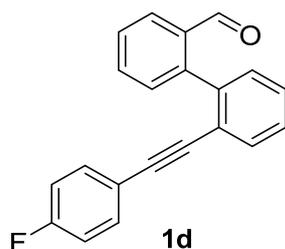
2'-(Phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (1a). Pale yellow oil (355 mg, 1.26 mmol, 84%). $R_f = 0.40$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.09 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.68 – 7.64 (m, 2H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.46 – 7.38 (m, 4H), 7.25 – 7.22 (m, 4H), 7.17 – 7.15 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 191.95, 144.42, 140.40, 134.34, 133.59, 132.10, 131.40, 130.37, 128.55, 128.37, 128.34, 126.98, 123.83, 122.79, 93.90, 88.30.



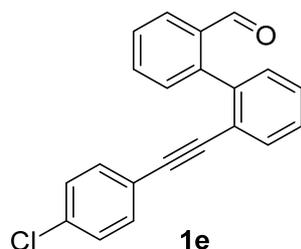
2'-((4-Methoxyphenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1b**). Yellow oil (332 mg, 1.07 mmol, 71%). $R_f = 0.55$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.08 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.66 – 7.59 (m, 2H), 7.52 (t, $J = 7.5$ Hz, 1H), 7.43 – 7.36 (m, 4H), 7.12 – 7.08 (m, 2H), 6.77 – 6.74 (m, 2H), 3.74 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 191.92, 159.83, 144.50, 140.08, 134.32, 133.54, 132.83, 131.80, 131.38, 130.27, 128.27, 128.23, 128.18, 126.82, 124.14, 114.85, 114.02, 94.04, 87.12, 55.32. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{17}\text{O}_2$ 313.1223, found 313.1223.



2'-(*p*-Tolyethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1c**). Pale yellow oil (417 mg, 1.41 mmol, 94%). $R_f = 0.50$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.08 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.66 – 7.61 (m, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.44 – 7.36 (m, 4H), 7.07 – 7.02 (m, 4H), 2.29 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 191.91, 144.44, 140.25, 138.71, 134.31, 133.53, 131.96, 131.38, 131.26, 130.31, 129.12, 128.34, 128.27, 126.89, 123.99, 119.68, 94.14, 87.70, 21.59.

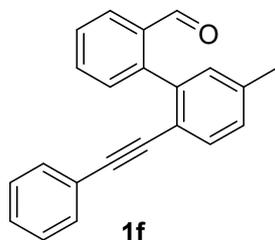


2'-((4-Fluorophenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (1d). Pale yellow oil (333 mg, 1.11 mmol, 74%). $R_f = 0.40$ (PE/EA = 10/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.08 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.67 – 7.61 (m, 2H), 7.53 (t, $J = 7.6$ Hz, 1H), 7.46 – 7.38 (m, 4H), 7.16 – 7.11 (m, 2H), 6.95 – 6.90 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.86, 162.65 (d, $J = 249.6$ Hz), 144.29, 140.33, 134.31, 133.60, 133.27 (d, $J = 8.3$ Hz), 131.95, 131.36, 130.29, 128.63, 128.34, 126.88, 123.64, 118.84 (d, $J = 3.6$ Hz), 115.67 (d, $J = 22.2$ Hz), 92.80, 88.01. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{14}\text{FO}$ 301.1023, found 301.1023.

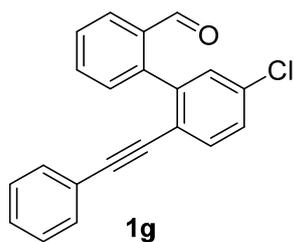


2'-((4-Chlorophenyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (1e). Pale yellow oil (436 mg, 1.38 mmol, 92%). $R_f = 0.40$ (PE/EA = 10/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 8.08 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.69 – 7.62 (m, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.49 – 7.40 (m, 4H), 7.22 – 7.19 (m, 2H), 7.09 – 7.07 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.90, 144.27, 140.47, 134.60, 134.33, 133.64,

132.58, 132.06, 131.39, 130.37, 128.82, 128.75, 128.42, 128.40, 126.97, 123.52, 121.26, 92.73, 89.25.

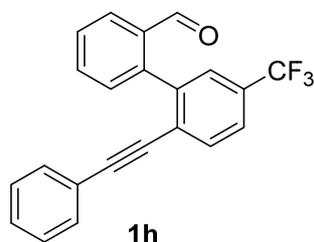


5'-Methyl-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1f**). Pale yellow oil (404 mg, 1.36 mmol, 91%). $R_f = 0.40$ (PE/EA = 10/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.94 (s, 1H), 8.08 (dd, $J = 7.9, 1.6$ Hz, 1H), 7.66 – 7.61 (m, 1H), 7.53 – 7.49 (m, 2H), 7.42 (d, $J = 7.5$ Hz, 1H), 7.23 – 7.20 (m, 5H), 7.16 – 7.14 (m, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.00, 144.53, 140.25, 138.78, 134.31, 133.50, 131.94, 131.33, 131.28, 131.11, 129.12, 128.30, 128.20, 126.84, 122.97, 120.82, 93.10, 88.45, 21.57.

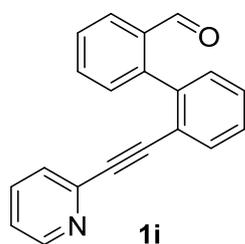


5'-Chloro-2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1g**). Pale yellow solid (374 mg, 1.18 mmol, 79%). $R_f = 0.40$ (PE/EA = 10/1). m.p. 83.7 – 84.2 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.09 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.67 (td, $J = 7.4, 1.5$ Hz, 1H), 7.58 – 7.54 (m, 2H), 7.42 – 7.39 (m, 3H), 7.26 – 7.21 (m, 4H), 7.16 – 7.13 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.35, 142.86, 142.06, 134.50,

134.25, 133.77, 133.12, 131.39, 131.17, 130.27, 128.83, 128.59, 128.42, 127.30, 122.45, 94.77, 87.27.

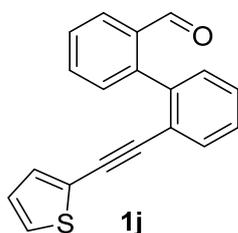


2'-(Phenylethynyl)-5'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbaldehyde (1h). Pale yellow solid (483 mg, 1.38 mmol, 92%). $R_f = 0.40$ (PE/EA = 10/1). m.p. 79.5 – 80.1 °C. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.92 (s, 1H), 8.11 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.75 – 7.67 (m, 4H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.8$ Hz, 1H), 7.28 – 7.26 (m, 3H), 7.18 – 7.15 (m, 2H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 191.09, 142.68, 141.21, 134.30, 133.87, 132.36, 131.56, 131.27, 130.33 (q, $J = 32.7$ Hz), 129.14, 128.99, 128.46, 127.60, 127.54, 126.88 (q, $J = 3.8$ Hz), 125.09 (q, $J = 3.5$ Hz), 123.85 (q, $J = 273.7$ Hz), 122.06, 96.35, 87.08. $^{19}\text{F NMR}$ (376 MHz, Chloroform-*d*) δ -62.53. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{14}\text{F}_3\text{O}$ 351.0991, found 351.0991.

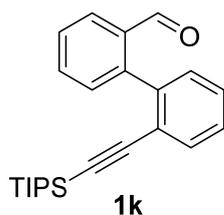


2'-(Pyridin-2-ylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (1i). Pale yellow solid (378 mg, 1.34 mmol, 89%). $R_f = 0.40$ (PE/EA = 10/1). m.p. 104.6 – 104.9 °C. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.50 (d, $J = 3.3$ Hz, 1H), 8.09 (d, $J = 7.7$ Hz, 1H),

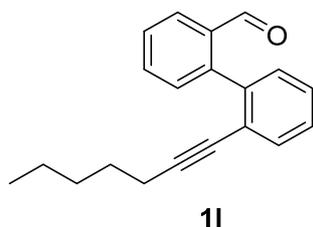
7.74 (dd, $J = 7.3, 1.7$ Hz, 1H), 7.66 (td, $J = 7.5, 1.4$ Hz, 1H), 7.55 – 7.39 (m, 6H), 7.15 – 7.11 (m, 1H), 7.00 (d, $J = 7.8$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 191.60, 149.85, 143.88, 142.79, 140.57, 136.03, 134.09, 133.50, 132.57, 131.31, 130.26, 129.12, 128.29, 128.26, 127.06, 126.81, 122.83, 122.60, 92.68, 87.76. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{NO}$ 284.1070, found 284.1069.



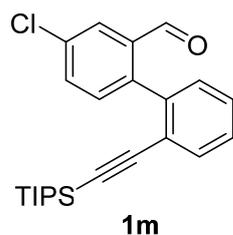
2'-(Thiophen-2-ylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1j**). Pale yellow oil (363 mg, 1.26 mmol, 84%). $R_f = 0.40$ (PE/EA = 10/1). ^1H NMR (400 MHz, Chloroform- d) δ 9.91 (s, 1H), 8.08 (dd, $J = 7.7, 1.5$ Hz, 1H), 7.67 – 7.59 (m, 2H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.45 – 7.36 (m, 4H), 7.18 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.98 (dd, $J = 3.7, 1.2$ Hz, 1H), 6.88 (dd, $J = 5.2, 3.6$ Hz, 1H). ^{13}C NMR (101 MHz, Chloroform- d) δ 191.72, 144.11, 140.17, 134.24, 133.56, 132.06, 131.68, 131.32, 130.38, 128.59, 128.33, 128.29, 127.71, 127.14, 127.08, 123.47, 122.63, 92.02, 87.32. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{13}\text{OS}$ 289.0682, found 289.0682.



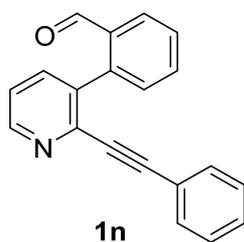
2'-((Triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1k**). White solid (391 mg, 1.08 mmol, 72%). $R_f = 0.50$ (PE/EA = 10/1). m.p. 68.0 – 68.3 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 8.01 (d, $J = 7.7$ Hz, 1H), 7.61 – 7.58 (m, 2H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.41 – 7.34 (m, 3H), 7.31 – 7.28 (m, 1H), 0.91 (s, 21H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.69, 144.63, 140.73, 134.10, 133.48, 132.78, 131.09, 130.19, 128.36, 128.10, 128.04, 127.07, 123.94, 105.21, 95.72, 18.52, 11.16. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{31}\text{OSi}$ 363.2139, found 363.2138.



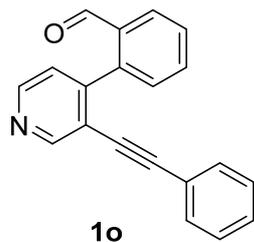
2'-(Hept-1-yn-1-yl)-[1,1'-biphenyl]-2-carbaldehyde (**1l**). Pale yellow oil (99 mg, 0.36 mmol, 24%). $R_f = 0.50$ (PE/EA = 10/1). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.85 (s, 1H), 8.03 (d, $J = 7.7$ Hz, 1H), 7.64 – 7.60 (m, 1H), 7.50 – 7.49 (m, 2H), 7.35 – 7.32 (m, 4H), 7.25 (s, 1H), 2.17 – 2.13 (s, 2H), 1.33 – 1.26 (m, 2H), 1.21 – 1.16 (m, 2H), 1.11 – 1.05 (m, 2H), 0.83 – 0.79 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.01, 144.75, 140.20, 134.19, 133.48, 132.08, 131.21, 130.18, 128.14, 128.04, 127.75, 126.76, 124.57, 95.57, 79.50, 30.83, 27.86, 22.23, 19.34, 14.02. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{O}$ 277.1587, found 277.1587.



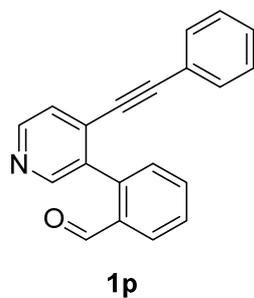
4-Chloro-2'-((triisopropylsilyl)ethynyl)-[1,1'-biphenyl]-2-carbaldehyde (1m). Pale yellow oil (422 mg, 1.07 mmol, 71%). $R_f = 0.50$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.77 (s, 1H), 7.98 (d, $J = 2.6$ Hz, 1H), 7.62 – 7.56 (m, 2H), 7.44 – 7.37 (m, 2H), 7.34 (d, $J = 8.2$ Hz, 1H), 7.30 – 7.28 (m, 1H), 0.92 (s, 21H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.42, 142.86, 139.53, 135.30, 134.74, 133.38, 132.91, 132.64, 130.08, 128.57, 128.46, 126.95, 124.06, 104.90, 96.42, 18.51, 11.19. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{24}\text{ClOSi}$ 355.1279, found 355.1278.



2-(2-(Phenylethynyl)pyridin-3-yl)benzaldehyde (1n). Pale yellow oil (365 mg, 1.29 mmol, 86%). $R_f = 0.40$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.96 (s, 1H), 8.69 (dd, $J = 4.7, 1.8$ Hz, 1H), 8.11 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.73 – 7.67 (m, 2H), 7.59 (t, $J = 7.5$ Hz, 1H), 7.43 – 7.36 (m, 2H), 7.30 – 7.19 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.85, 149.76, 142.85, 141.49, 137.52, 136.68, 134.22, 133.75, 131.74, 131.39, 129.18, 128.95, 128.31, 127.74, 122.65, 121.66, 93.72, 87.72. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{NO}$ 284.1070, found 284.1069.



2-(3-(Phenylethynyl)pyridin-4-yl)benzaldehyde (1o). Pale yellow oil (386 mg, 1.36 mmol, 91%). $R_f = 0.40$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.93 (s, 1H), 8.86 (s, 1H), 8.65 (d, $J = 5.1$ Hz, 1H), 8.11 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.71 (td, $J = 7.5, 1.5$ Hz, 1H), 7.61 (t, $J = 7.7$ Hz, 1H), 7.43 – 7.40 (m, 1H), 7.34 (d, $J = 5.1$ Hz, 1H), 7.31 – 7.20 (m, 6H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.69, 152.52, 148.75, 147.84, 141.12, 133.85, 131.47, 130.73, 129.36, 129.05, 128.43, 127.84, 124.25, 122.04, 120.65, 96.70, 84.94. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{NO}$ 284.1070, found 284.1069.

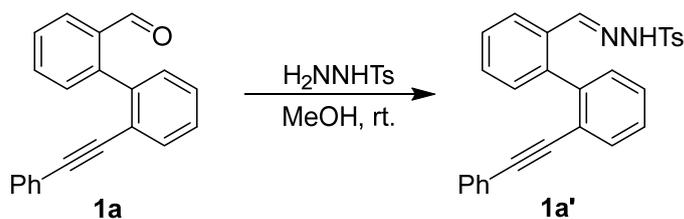


2-(4-(Phenylethynyl)pyridin-3-yl)benzaldehyde (1p). Pale yellow oil (378 mg, 1.33 mmol, 89%). $R_f = 0.40$ (PE/EA = 10/1). $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 9.95 (s, 1H), 8.67 – 8.66 (m, 2H), 8.12 (d, $J = 7.8$ Hz, 1H), 7.71 (td, $J = 7.4, 1.4$ Hz, 1H), 7.60 (t, $J = 7.6$ Hz, 1H), 7.49 (d, $J = 5.1$ Hz, 1H), 7.44 (d, $J = 7.6$ Hz, 1H), 7.32 – 7.19 (m, 5H). $^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.88, 150.23, 149.34, 140.16, 135.03, 134.48, 133.81, 131.67, 131.63, 131.42, 129.48, 129.07, 128.45, 127.78, 125.13,

121.52, 98.27, 85.70. HRMS (ESI IT-TOF) m/z $[M + H]^+$ Calcd for $C_{20}H_{14}NO$

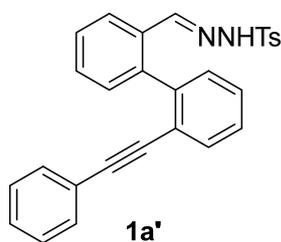
284.1070, found 284.1069.

B-2. Preparation of 2'-alkynyl-biaryl-2-aldehyde *N*-tosylhydrazone **1a'**



The Synthesis of 2'-alkynyl-biaryl-2-aldehyde *N*-tosylhydrazone **1a'**:

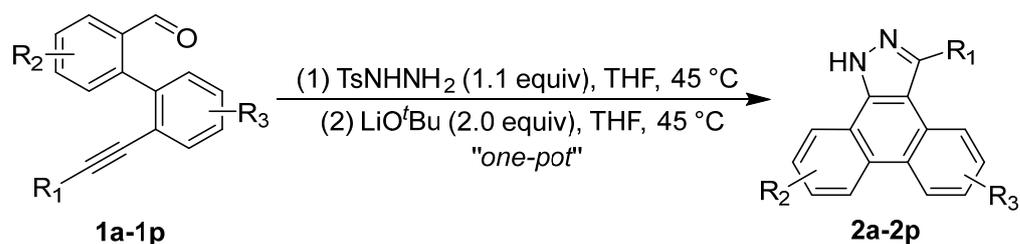
The mixture of H_2NNHTs (1.1 equiv., 1.10 mmol, 205 mg), 2'-(phenylethynyl)-[1,1'-biphenyl]-2-carbaldehyde (**1a**, 1.00 mmol, 282 mg) and methanol (5.0 mL) in a 25 mL screw-capped thick-walled Pyrex tube was stirred at room temperature for 2 h. After the reaction was completed (checked by TLC), the crude residue was purified by column chromatography on silica gel, eluting with petroleum ether / ethyl acetate (gradient mixture ratio from 5 / 1 to 3 / 1) as eluent to afford product **1a'** in 90% yields.



(E)-4-Methyl-*N'*-((2'-(phenylethynyl)-[1,1'-biphenyl]-2-yl)methylene)benzenesulfonylhydrazide (**1a'**). Yellow solid (405 mg, 0.90 mmol, 90%). $R_f = 0.45$ (PE/EA = 2/1). m.p. 77.3 – 77.8 °C. ^1H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 8.03 (m, 1H), 7.76 (d, $J = 8.5$ Hz, 3H), 7.59 (s, 1H), 7.56 (dd, $J = 5.7, 3.4$ Hz, 1H), 7.43 – 7.38 (m, 2H), 7.34 (dd, $J = 5.7, 3.3$ Hz, 2H), 7.31 – 7.29 (m, 1H), 7.22 – 7.16 (m, 6H), 7.08 (d, $J = 7.2$ Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.53, 144.04, 141.66, 141.14, 135.54, 132.08, 131.41, 130.71, 130.39, 129.81, 129.68, 128.37, 128.33, 128.29,

128.08, 127.96, 127.89, 125.61, 123.29, 122.86, 93.63, 88.29, 21.67. HRMS (ESI IT-TOF) m/z $[M + H]^+$ Calcd for $C_{21}H_{15}N_2$ 295.1230, found 295.1229.

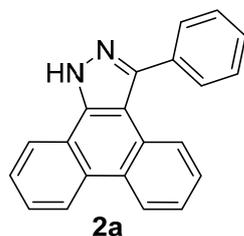
B-3. Preparation of 3-substituted 1*H*-dibenzo[*e,g*]indazoles **2a-2p**



General procedure for the preparation of 1*H*-dibenzo[*e,g*]indazoles **2a-2p**:

The mixture of H₂NNHTs (1.1 equiv.), 2'-alkynyl-biaryl-2-aldehydes (**1**, 1.0 equiv.) and THF (5.0 mL) in a 25 mL screw-capped thick-walled Pyrex tube was stirred at 45 °C for 1 h. After the reaction was completed (checked by TLC), LiO^tBu (1.5 equiv.) and additional 2.5 mL of THF was added and then the mixture was stirred at 45 °C for 1 h. After the reaction was completed (checked by TLC), the crude residue was purified by column chromatography on silica gel, eluting with petroleum ether / ethyl acetate (gradient mixture ratio from 5 / 1 to 2 / 1) as eluent to afford product **2a-2p** in 61% - 93% yields.

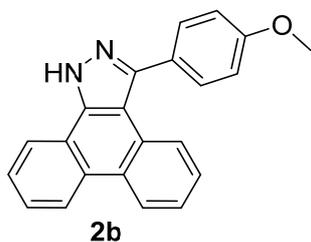
2a was known compounds³⁸.



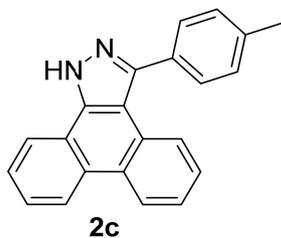
*3-Phenyl-1H-dibenzo[*e,g*]indazole (2a)*. White solid (259 mg, 0.88 mmol, 88%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 260.4 – 260.8 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 14.24 – 13.95 (s, 1H), 8.78 – 8.71 (m, 2H), 8.55 (d, $J = 7.8$ Hz, 1H), 8.02 (d, $J = 8.1$ Hz, 1H), 7.74 – 7.69 (m, 4H), 7.59 – 7.54 (m, 3H), 7.50 – 7.40 (m, 2H). ¹³C NMR (101 MHz,

DMSO-*d*₆) δ 147.37, 137.25, 135.45, 129.62, 128.61, 128.32, 127.51, 127.41, 127.13, 124.95, 124.18, 124.07, 122.63, 122.34, 121.00, 112.55.

To demonstrate the practical utility of the method as a synthetic tool, a gram-scale reaction of **1a** (5.0 mmol) in 38.0 mL of THF under standard conditions was conducted, and the desired **2a** was obtained in 85% yield (1.25 g).

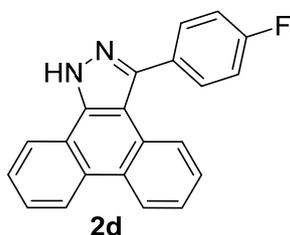


3-(4-Methoxyphenyl)-1H-dibenzo[e,g]indazole (2b). White solid (285 mg, 0.88 mmol, 88%). R_f = 0.40 (PE/EA = 1/1). m.p. 204.2 – 204.7 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 13.97 (s, 1H), 8.71 (dd, J = 16.9, 8.1 Hz, 2H), 8.56 (d, J = 7.7 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H), 7.74 – 7.63 (m, 4H), 7.49 – 7.40 (m, 2H), 7.14 (d, J = 8.4 Hz, 2H), 3.84 (s, 3H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 159.34, 147.25, 137.27, 130.91, 129.68, 127.45, 127.31, 127.12, 124.87, 124.09, 123.99, 122.67, 122.40, 121.14, 114.02, 112.64, 55.14. HRMS (ESI IT-TOF) m/z [M + H]⁺ Calcd for C₂₂H₁₇N₂O 325.1335, found 325.1334.

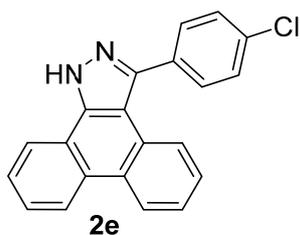


3-(p-Tolyl)-1H-dibenzo[e,g]indazole (2c). White solid (262 mg, 0.85 mmol, 85%). R_f = 0.40 (PE/EA = 1/1). m.p. 199.6 – 200.0 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.79 (s,

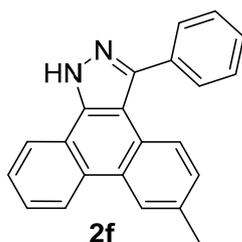
1H), 8.71 (dd, $J = 17.1, 8.1$ Hz, 2H), 8.57 (d, $J = 7.7$ Hz, 1H), 8.06 (d, $J = 7.7$ Hz, 1H), 7.73 (t, $J = 7.5$ Hz, 1H), 7.66 (t, $J = 7.5$ Hz, 1H), 7.61 (d, $J = 7.8$ Hz, 2H), 7.48 – 7.36 (m, 4H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 145.18, 139.07, 137.85, 131.46, 129.70, 129.49, 129.26, 127.59, 127.49, 127.36, 127.12, 125.64, 124.99, 124.15, 123.99, 122.67, 122.38, 112.36, 20.95. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2$ 309.1386, found 309.1385.



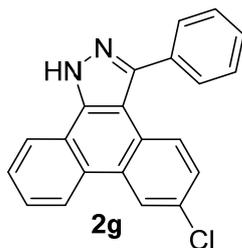
3-(4-Fluorophenyl)-1H-dibenzo[e,g]indazole (2d). White solid (262 mg, 0.84 mmol, 84%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 235.7 – 236.2 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 14.31 – 14.03 (s, 1H), 8.70 – 8.58 (m, 3H), 8.00 (s, 1H), 7.80 – 7.62 (m, 4H), 7.43 – 7.39 (m, 4H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 162.26 (d, $J = 245.1$ Hz), 146.41, 137.38, 131.89, 131.77, 131.69, 129.66, 127.48, 127.39, 127.17, 124.93, 124.13, 124.01, 122.60, 122.40, 121.04, 115.55 (d, $J = 21.5$ Hz), 112.66. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{14}\text{FN}_2$ 313.1136, found 313.1134.



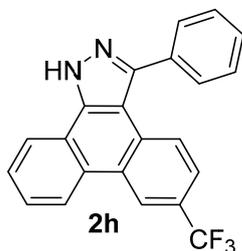
3-(4-Chlorophenyl)-1H-dibenzo[e,g]indazole (2e). White solid (262 mg, 0.80 mmol, 80%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 265.3 – 265.9 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 14.18 (s, 1H), 8.76 (dd, $J = 17.0, 8.0$ Hz, 2H), 8.53 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.96 (d, $J = 7.5$ Hz, 1H), 7.76 – 7.68 (m, 4H), 7.66 – 7.64 (m, 2H), 7.53 – 7.44 (m, 2H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 144.83, 138.58, 133.68, 133.32, 131.39, 129.69, 128.73, 127.61, 127.47, 127.40, 127.19, 127.12, 125.05, 124.13, 123.95, 122.64, 122.40, 121.72, 112.52. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{14}\text{ClN}_2$ 329.0840, found 329.0838.



6-Methyl-3-phenyl-1H-dibenzo[e,g]indazole (2f). White solid (265 mg, 0.86 mmol, 86%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 235.6 – 235.9 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 14.22 – 13.93 (s, 1H), 8.76 – 8.52 (m, 3H), 7.94 (d, $J = 8.3$ Hz, 1H), 7.76 – 7.52 (m, 7H), 7.19 (d, $J = 8.4$ Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 147.12, 137.04, 135.60, 134.02, 129.61, 129.51, 128.55, 128.40, 128.23, 127.53, 127.30, 127.19, 124.88, 123.99, 122.59, 122.34, 121.16, 112.64, 21.26. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{17}\text{N}_2$ 309.1386, found 309.1385.

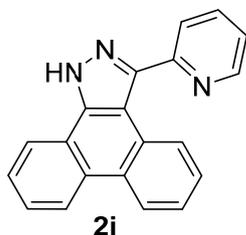


6-Chloro-3-phenyl-1H-dibenzo[e,g]indazole (2g). White solid (276 mg, 0.84 mmol, 84%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 286.9 – 287.3 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 13.77 (s, 1H), 8.73 – 8.69 (m, 2H), 8.51 (d, $J = 7.6$ Hz, 1H), 7.92 (d, $J = 8.6$ Hz, 1H), 7.75 – 7.64 (m, 4H), 7.60 – 7.52 (m, 3H), 7.40 (dd, $J = 8.6, 2.1$ Hz, 1H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 129.86, 129.55, 129.22, 128.74, 128.59, 128.12, 127.49, 127.08, 125.86, 124.32, 124.20, 123.65, 122.33, 111.74. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{21}\text{H}_{14}\text{ClN}_2$ 329.0840, found 329.0838.

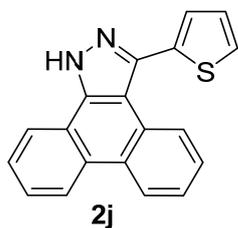


3-Phenyl-6-(trifluoromethyl)-1H-dibenzo[e,g]indazole (2h). White solid (300 mg, 0.83 mmol, 83%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 276.9 – 277.3 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 14.29 – 14.10 (s, 1H), 8.88 – 8.84 (m, 1H), 8.72 – 8.65 (m, 1H), 8.55 – 8.47 (m, 1H), 8.07 – 8.02 (m, 1H), 7.71 – 7.51 (m, 8H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 147.73, 138.05, 135.04, 129.87, 129.58, 128.80, 128.64, 128.45, 128.15, 127.61, 127.08, 126.02, 125.06 (q, $J = 31.7$ Hz), 124.14, 123.35 (d, $J = 6.7$ Hz), 122.84, 122.39,

121.13 (d, $J = 15.7$ Hz), 111.73. ^{19}F NMR (376 MHz, $\text{DMSO-}d_6$) δ -60.08. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{22}\text{H}_{14}\text{F}_3\text{N}_2$ 363.1104, found 363.1102.

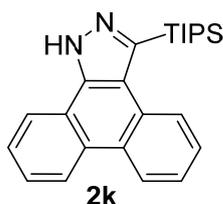


3-(Pyridin-2-yl)-1H-dibenzo[e,g]indazole (2i). White solid (230 mg, 0.78 mmol, 78%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 209.3 – 209.7 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.44 – 14.28 (s, 1H), 9.04 – 9.02 (m, 1H), 8.86 (d, $J = 4.9$ Hz, 1H), 8.79 – 8.58 (m, 3H), 8.06 – 7.97 (m, 2H), 7.78 – 7.67 (m, 2H), 7.52 – 7.49 (m, 3H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 154.35, 148.81, 147.16, 137.80, 137.04, 129.72, 127.58, 127.54, 127.48, 127.30, 127.05, 125.65, 125.24, 124.34, 124.04, 123.71, 123.15, 122.30, 120.92, 113.53. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3$ 296.1182, found 296.1181.

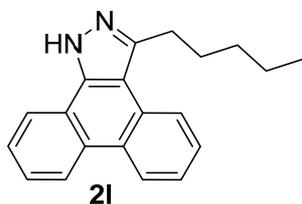


3-(Thiophen-2-yl)-1H-dibenzo[e,g]indazole (2j). White solid (273 mg, 0.91 mmol, 91%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 255.4 – 255.9 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 14.40 – 14.17 (s, 1H), 8.71 – 8.56 (m, 3H), 8.34 – 8.31 (m, 1H), 7.76 – 7.73 (m, 2H), 7.66 (t, $J = 7.7$ Hz, 1H), 7.56 (d, $J = 3.6$ Hz, 1H), 7.52 – 7.46 (m, 2H), 7.32 – 7.30 (m,

1H). ^{13}C NMR (101 MHz, $\text{DMSO-}d_6$) δ 140.47, 137.44, 136.12, 129.61, 128.07, 127.72, 127.55, 127.30, 127.10, 126.97, 125.19, 124.11, 124.03, 122.65, 122.36, 120.86, 113.25. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{13}\text{N}_2\text{S}$ 301.0794, found 301.0793.

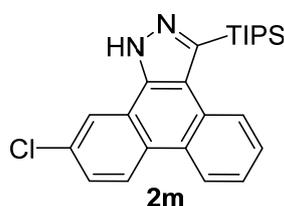


3-(Triisopropylsilyl)-1H-dibenzo[e,g]indazole (2k). White solid (348 mg, 0.93 mmol, 93%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 87.8 – 88.3 °C. ^1H NMR (400 MHz, Chloroform- d) δ 12.12 (s, 1H), 8.75 (d, $J = 7.6$ Hz, 1H), 8.58 – 8.53 (m, 2H), 8.27 (d, $J = 7.8$ Hz, 1H), 7.64 – 7.46 (m, 4H), 1.78 (hept, $J = 7.5$ Hz, 3H), 1.12 (d, $J = 7.7$ Hz, 18H). ^{13}C NMR (101 MHz, Chloroform- d) δ 130.58, 129.10, 128.79, 127.31, 127.26, 126.54, 126.04, 125.39, 124.01, 123.62, 123.40, 123.21, 18.89, 12.74. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{31}\text{N}_2\text{Si}$ 375.2251, found 375.2251.

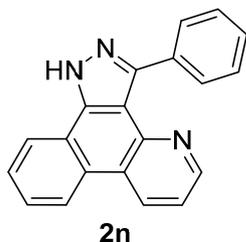


3-Pentyl-1H-dibenzo[e,g]indazole (2l). White solid (176 mg, 0.61 mmol, 61%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 188.5 – 188.9 °C. ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ 13.69 – 13.49 (s, 1H), 8.78 – 8.67 (m, 2H), 8.44 (d, $J = 7.5$ Hz, 1H), 8.24 – 8.15 (m, 1H), 7.69

– 7.52 (m, 4H), 3.19 (t, $J = 7.6$ Hz, 2H), 1.82 – 1.80 (m, 2H), 1.42 – 1.32 (m, 4H), 0.87 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 147.37, 137.15, 129.46, 127.67, 127.32, 127.11, 124.40, 124.08, 123.17, 122.21, 121.17, 112.43, 31.20, 28.96, 27.75, 21.97, 13.94. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{21}\text{N}_2$ 289.1699, found 289.1698.



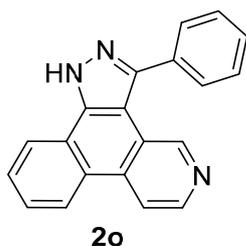
10-Chloro-3-(triisopropylsilyl)-1H-dibenzo[e,g]indazole (2m). White solid (335 mg, 0.82 mmol, 82%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 191.1 – 191.7 °C. ^1H NMR (400 MHz, Chloroform- d) δ 11.96 (s, 1H), 8.68 (s, 1H), 8.52 (d, $J = 7.9$ Hz, 1H), 8.47 (d, $J = 9.0$ Hz, 1H), 8.23 (d, $J = 7.7$ Hz, 1H), 7.58 – 7.50 (m, 3H), 1.76 (hept, $J = 7.5$ Hz, 3H), 1.15 (d, $J = 7.6$ Hz, 18H). ^{13}C NMR (101 MHz, Chloroform- d) δ 133.34, 129.03, 128.72, 128.55, 127.65, 126.94, 125.72, 125.52, 125.10, 124.01, 123.97, 122.83, 18.93, 12.78. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{24}\text{H}_{30}\text{ClN}_2\text{Si}$ 409.1861, found 409.1860.



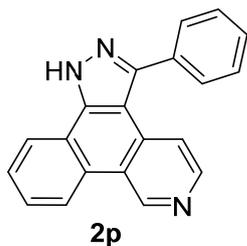
3-Phenyl-1H-benzo[f]pyrazolo[3,4-h]quinoline (2n). White solid (260 mg, 0.88 mmol, 88%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 265.7 – 266.2 °C. ^1H NMR (400 MHz, DMSO- d_6)

δ 14.39 – 14.16 (s, 1H), 9.02 – 8.92 (m, 1H), 8.78 – 8.56 (m, 3H), 8.29 – 8.14 (m, 2H), 7.79 – 7.62 (m, 2H), 7.55 – 7.42 (m, 4H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 148.60, 148.23, 147.43, 145.91, 144.68, 139.95, 139.70, 134.63, 131.70, 130.10, 129.96, 129.66, 128.92, 128.57, 128.08, 127.98, 127.63, 127.49, 126.03, 124.19, 123.89, 123.45, 122.44, 122.31, 120.87, 120.59, 120.16, 113.43, 112.53. ^1H NMR (400 MHz, Chloroform- d) δ 10.84 (s, 1H), 8.83 (d, $J = 8.3$ Hz, 1H), 8.78 (d, $J = 4.2$ Hz, 1H), 8.57 – 8.55 (m, 1H), 8.44 (s, 1H), 8.19 (d, $J = 7.9$ Hz, 2H), 7.70 (s, 2H), 7.56 – 7.43 (m, 4H)

^b. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3$ 296.1182, found 296.1181.



3-Phenyl-1H-benzo[ff]pyrazolo[3,4-h]isoquinoline (2o). White solid (266 mg, 0.90 mmol, 90%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 277.9 – 278.4 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 14.37 – 14.12 (s, 1H), 9.22 (s, 1H), 8.82 – 8.72 (m, 1H), 8.56 – 8.52 (m, 3H), 7.85 – 7.59 (m, 7H). ^{13}C NMR (101 MHz, DMSO- d_6) δ 146.96, 145.14, 144.19, 137.71, 135.14, 132.51, 129.63, 129.48, 128.76, 128.57, 127.74, 127.52, 124.76, 122.43, 117.54, 110.61. HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3$ 296.1182, found 296.1181.



3-Phenyl-1H-benzo[h]pyrazolo[4,3-f]isoquinoline (2p). White solid (221 mg, 0.75 mmol, 75%). $R_f = 0.40$ (PE/EA = 1/1). m.p. 324.3 – 324.8 °C. ^1H NMR (400 MHz, DMSO- d_6) δ 14.46 – 14.20 (s, 1H), 10.06 – 9.95 (m, 1H), 9.04 – 8.87 (m, 1H), 8.56 – 8.48 (m, 2H), 7.86 – 7.55 (m, 8H). HRMS (ESI IT-TOF) m/z $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{20}\text{H}_{14}\text{N}_3$ 296.1182, found 296.1181. The ^{13}C NMR spectroscopic data could not be recorded due to the poor solubility in deuterated solvents, such as DMSO- d_6 , CDCl_3 .

C. Single crystal structures

C-1. The X-ray crystal structural data of 2a.

Crystal Structure of C₂₁H₁₄N₂

The low temperature (173±2°K) single-crystal X-ray experiments were performed on a SuperNova diffractometer with Cu K_α radiation. Unit cell was obtained and refined by 5063 reflections with 4.7° < θ < 73.2°. No decay was observed in data collection. Raw intensities were corrected for Lorentz and polarization effects, and for absorption by empirical method. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C-H bonds of 0.95 Å according to criteria described in the SHELXTL manual (Bruker, 1997). They were included in the refinement with U_{iso}(H) = 1.2U_{eq} of their parent atoms. The final full-matrix least-square refinement on F² converged with R1 = 0.0457 and wR2 = 0.1101 for 2492 observed reflections [I ≥ 2σ(I)]. The final difference electron density map shows no features. Details of crystal parameters, data collection and structure refinement are given in Table 1.

Data collection was controlled by CrysAlisPro, Agilent Technologies, Version 1.171.36.32 (Oxford, 2013). Computations were performed using the SHELXTL NT ver. 5.10 program package (Bruker, 1997) on an IBM PC 586 computer. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion corrections were incorporated (*International Tables for X-ray Crystallography*, 1989). Crystal drawings were produced with XP (Bruker, 1997).

References

- Bruker. (1997) SHELXTL. Structure Determination Programs, Version 5.10, Bruker AXS Inc., 6300 Enterprise Lane, Madison, WI 53719-1173, USA.
- International Tables for X-ray Crystallography*: (1989) Vol. C (Kluwer Academic Publishers, Dordrecht) Tables 4.2.6.8 and 6.1.1.4.
- Oxford. (2013) CrysAlisPro, Agilent Technologies, Version 1.171.36.32, Oxford Diffraction Ltd., 68 Milton Park, Abingdon, Oxfordshire, OX14 4RX, UK.

Table 1. Details of Data Collection, Processing and Structure Refinement

Sample code	2a		
Molecular formula	C ₂₁ H ₁₄ N ₂		
Molecular weight	294.34		
Color and habit	orange prism		
Crystal size	0.2 × 0.3 × 0.5 mm		
Crystal system	monoclinic		
Space group	P2 ₁ /c (No. 14)		
Unit cell parameters	$a = 9.2011(2) \text{ \AA}$ $\alpha = 90.00^\circ$ $b = 12.9253(3) \text{ \AA}$ $\beta = 90.277(2)^\circ$ $c = 12.3868(2) \text{ \AA}$ $\gamma = 90.00^\circ$ $V = 1473.11(5) \text{ \AA}^3$ $Z = 4$ $F(000) = 616$		
Density (calcd)	1.327 g/cm ³		
Diffractometer	SuperNova, Dual, Cu at home/near, AtlasS2		
Radiation	Cu K α , $\lambda = 1.54178 \text{ \AA}$		
Temperature	173±2K		
Scan type	ω -scan		
Data collection range	-11 < h < 10, -15 < k < 16, -9 < l < 15; $\theta_{\max} = 73.8^\circ$		
Reflections measured	Total: 9738	Unique (n): 2937	Observed [$I \geq 2\sigma(I)$]: 2492
Absorption coefficient	0.609 mm ⁻¹		
Minimum and maximum transmission	0.927, 1.000		
No. of variables, p	212		
Weighting scheme	$w = \frac{1}{\sigma^2(F_o^2) + (0.0306P)^2 + 0.8796P}$ $P = (F_o^2 + 2F_c^2)/3$		
$R1 = \frac{\sum F_o - F_c }{\sum F_o }$ (for all reflections)	0.0550	0.0457 (for observed data)	
$wR2 = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum w(F_o^2)^2}}$ (for all reflections)	0.1139	0.1101 (for observed data)	
Goof = $S = \sqrt{\frac{\sum [w(F_o^2 - F_c^2)^2]}{n - p}}$	1.166		
Largest and mean Δ/σ	0.004, 0.000		
Residual extrema in final difference map	-0.243 to 0.219 e \AA^{-3}		

Table 2. Atomic coordinates and equivalent isotropic temperature factors* (\AA^2)

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq.}$
N(1)	0.91260(15)	0.53527(12)	0.60136(12)	0.0252(3)
N(2)	0.83731(16)	0.47314(12)	0.53256(12)	0.0244(3)
C(1)	0.82553(18)	0.55159(13)	0.68545(14)	0.0222(4)
C(2)	0.69066(17)	0.49933(13)	0.67016(13)	0.0214(3)
C(3)	0.70567(18)	0.44904(13)	0.57161(13)	0.0218(3)
C(4)	0.59796(18)	0.38125(13)	0.52552(14)	0.0233(4)
C(5)	0.6217(2)	0.32424(14)	0.43111(15)	0.0284(4)
C(6)	0.5170(2)	0.25703(15)	0.39322(16)	0.0352(5)
C(7)	0.3869(2)	0.24664(15)	0.44959(17)	0.0368(5)
C(8)	0.3613(2)	0.30325(15)	0.54149(16)	0.0322(4)
C(9)	0.46544(18)	0.37312(13)	0.58236(14)	0.0247(4)
C(10)	0.43881(18)	0.43705(13)	0.67843(14)	0.0244(4)
C(11)	0.55166(17)	0.49814(13)	0.72439(13)	0.0226(4)
C(12)	0.52156(19)	0.56063(15)	0.81447(15)	0.0288(4)
C(13)	0.3840(2)	0.56544(16)	0.85749(16)	0.0350(5)
C(14)	0.2724(2)	0.50747(16)	0.81138(16)	0.0352(5)
C(15)	0.29954(19)	0.44413(15)	0.72457(16)	0.0310(4)
C(16)	0.88687(17)	0.61370(13)	0.77483(13)	0.0218(4)
C(17)	0.87944(18)	0.58058(14)	0.88180(14)	0.0243(4)
C(18)	0.95271(19)	0.63455(15)	0.96241(14)	0.0283(4)
C(19)	1.0327(2)	0.72182(15)	0.93731(15)	0.0323(4)
C(20)	1.0389(2)	0.75641(15)	0.83176(16)	0.0332(4)
C(21)	0.96607(19)	0.70283(14)	0.75095(15)	0.0272(4)

* $U_{eq.}$ defined as one third of the trace of the orthogonalized **U** tensor.

Table 3. Bond lengths (Å) and bond angles (°)

N(1)-C(1)	1.334(2)	C(9)-C(10)	1.470(3)
N(1)-N(2)	1.358(2)	C(10)-C(15)	1.409(2)
N(2)-C(3)	1.343(2)	C(10)-C(11)	1.421(2)
C(1)-C(2)	1.425(2)	C(11)-C(12)	1.406(2)
C(1)-C(16)	1.477(2)	C(12)-C(13)	1.377(3)
C(2)-C(3)	1.390(2)	C(13)-C(14)	1.392(3)
C(2)-C(11)	1.448(2)	C(14)-C(15)	1.375(3)
C(3)-C(4)	1.439(2)	C(16)-C(17)	1.394(2)
C(4)-C(5)	1.400(2)	C(16)-C(21)	1.396(2)
C(4)-C(9)	1.415(3)	C(17)-C(18)	1.390(2)
C(5)-C(6)	1.378(3)	C(18)-C(19)	1.383(3)
C(6)-C(7)	1.395(3)	C(19)-C(20)	1.383(3)
C(7)-C(8)	1.375(3)	C(20)-C(21)	1.387(3)
C(8)-C(9)	1.409(2)		
C(1)-N(1)-N(2)	106.08(14)	C(4)-C(9)-C(10)	120.56(15)
C(3)-N(2)-N(1)	111.67(14)	C(15)-C(10)-C(11)	117.76(16)
N(1)-C(1)-C(2)	110.32(15)	C(15)-C(10)-C(9)	121.36(16)
N(1)-C(1)-C(16)	116.26(15)	C(11)-C(10)-C(9)	120.80(15)
C(2)-C(1)-C(16)	133.36(16)	C(12)-C(11)-C(10)	119.38(15)
C(3)-C(2)-C(1)	104.37(15)	C(12)-C(11)-C(2)	122.68(16)
C(3)-C(2)-C(11)	119.61(15)	C(10)-C(11)-C(2)	117.74(15)
C(1)-C(2)-C(11)	135.59(16)	C(13)-C(12)-C(11)	121.20(17)
N(2)-C(3)-C(2)	107.54(15)	C(12)-C(13)-C(14)	119.65(19)
N(2)-C(3)-C(4)	128.24(16)	C(15)-C(14)-C(13)	120.33(17)
C(2)-C(3)-C(4)	124.19(15)	C(14)-C(15)-C(10)	121.66(17)
C(5)-C(4)-C(9)	120.99(16)	C(17)-C(16)-C(21)	118.88(16)
C(5)-C(4)-C(3)	122.81(16)	C(17)-C(16)-C(1)	121.67(15)
C(9)-C(4)-C(3)	116.19(15)	C(21)-C(16)-C(1)	119.18(15)
C(6)-C(5)-C(4)	120.30(18)	C(18)-C(17)-C(16)	120.18(16)
C(5)-C(6)-C(7)	119.36(18)	C(19)-C(18)-C(17)	120.31(17)
C(8)-C(7)-C(6)	120.94(18)	C(20)-C(19)-C(18)	120.03(17)
C(7)-C(8)-C(9)	121.32(18)	C(19)-C(20)-C(21)	119.91(18)
C(8)-C(9)-C(4)	117.06(17)	C(20)-C(21)-C(16)	120.67(17)
C(8)-C(9)-C(10)	122.37(16)		
Hydrogen bonding			
H(2)···N(1) ^{#1}	2.11(2)	N(2)-H(2)···N(1) ^{#1}	139.7(19)

Symmetry transformations code: #1 (2-x, 1-y, 1-z).

Table 4. Anisotropic thermal parameters* (\AA^2)

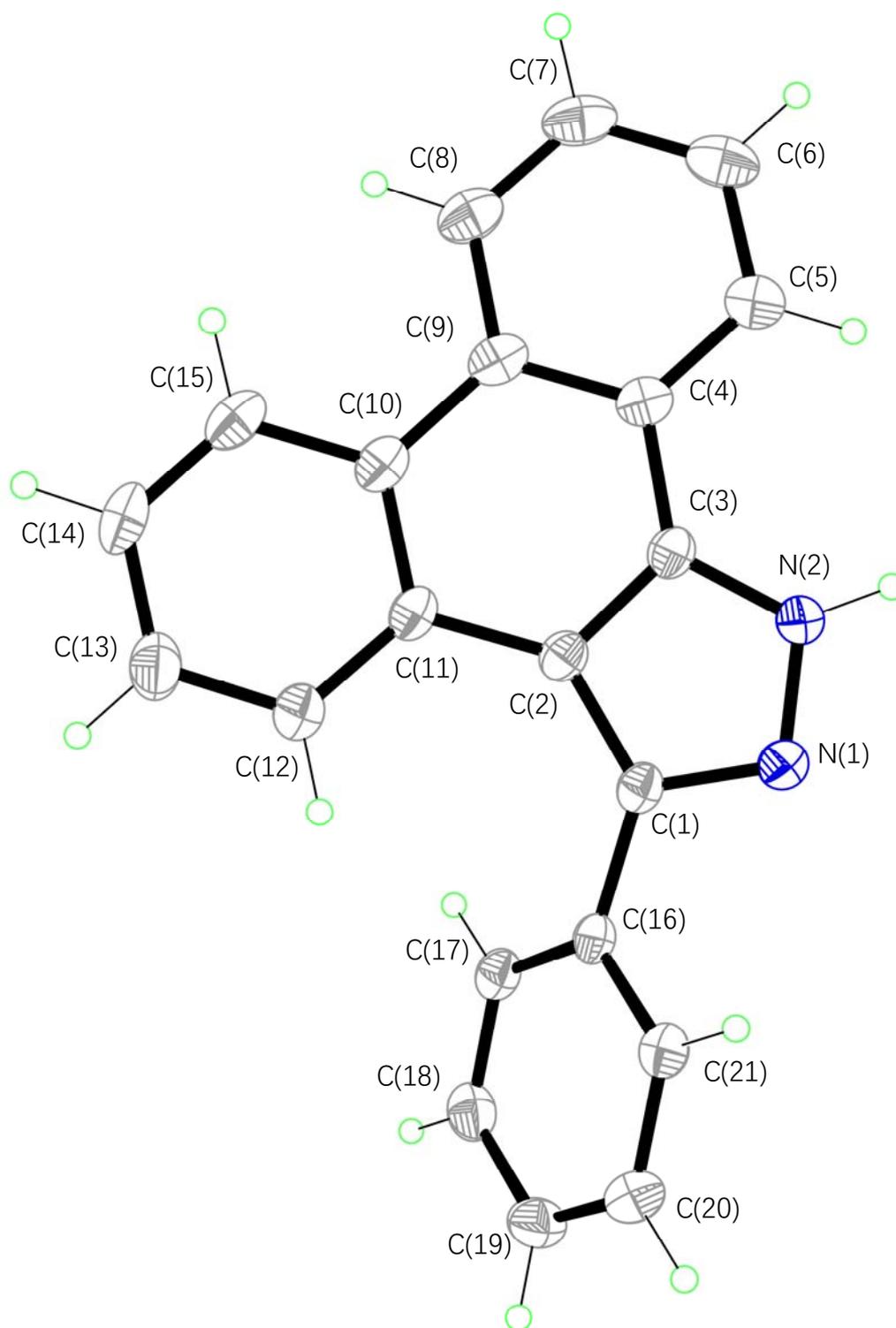
Atoms	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
N(1)	0.0212(7)	0.0282(8)	0.0262(7)	-0.0034(6)	0.0006(6)	-0.0016(6)
N(2)	0.0215(7)	0.0284(8)	0.0233(7)	-0.0042(6)	0.0017(6)	-0.0016(6)
C(1)	0.0181(8)	0.0238(8)	0.0248(8)	0.0004(7)	0.0020(7)	0.0010(6)
C(2)	0.0188(8)	0.0211(8)	0.0244(8)	0.0017(6)	0.0001(7)	0.0010(6)
C(3)	0.0188(8)	0.0222(8)	0.0244(8)	0.0024(6)	0.0011(7)	0.0018(6)
C(4)	0.0236(8)	0.0196(8)	0.0265(9)	0.0031(6)	-0.0041(7)	0.0002(6)
C(5)	0.0304(9)	0.0258(9)	0.0289(9)	-0.0001(7)	-0.0032(8)	0.0010(7)
C(6)	0.0449(12)	0.0264(9)	0.0343(10)	-0.0050(8)	-0.0103(9)	-0.0005(8)
C(7)	0.0377(11)	0.0290(10)	0.0437(11)	-0.0005(8)	-0.0101(9)	-0.0108(8)
C(8)	0.0278(9)	0.0289(9)	0.0399(11)	0.0045(8)	-0.0037(8)	-0.0071(7)
C(9)	0.0228(8)	0.0206(8)	0.0307(9)	0.0064(7)	-0.0046(7)	-0.0015(7)
C(10)	0.0207(8)	0.0233(8)	0.0290(9)	0.0070(7)	-0.0001(7)	-0.0002(6)
C(11)	0.0184(8)	0.0230(8)	0.0263(9)	0.0050(7)	0.0015(7)	0.0011(6)
C(12)	0.0227(8)	0.0331(10)	0.0305(10)	-0.0022(8)	0.0022(7)	0.0007(7)
C(13)	0.0287(10)	0.0416(11)	0.0346(10)	-0.0016(8)	0.0072(8)	0.0041(8)
C(14)	0.0213(9)	0.0433(11)	0.0409(11)	0.0061(9)	0.0101(8)	0.0010(8)
C(15)	0.0216(9)	0.0330(10)	0.0385(10)	0.0086(8)	-0.0002(8)	-0.0054(7)
C(16)	0.0155(7)	0.0251(8)	0.0249(8)	-0.0022(7)	0.0030(6)	0.0015(6)
C(17)	0.0190(8)	0.0261(9)	0.0280(9)	0.0007(7)	0.0029(7)	0.0012(7)
C(18)	0.0258(9)	0.0348(10)	0.0242(9)	-0.0002(7)	0.0010(7)	0.0051(7)
C(19)	0.0286(9)	0.0365(10)	0.0319(10)	-0.0095(8)	-0.0030(8)	-0.0025(8)
C(20)	0.0319(10)	0.0310(10)	0.0367(10)	-0.0035(8)	0.0030(8)	-0.0099(8)
C(21)	0.0265(9)	0.0296(9)	0.0255(9)	-0.0002(7)	0.0052(7)	-0.0038(7)

The exponent takes the form: $-2\pi^2 \sum \sum U_{ij} h_i h_j \mathbf{a}_i^ \mathbf{a}_j^*$

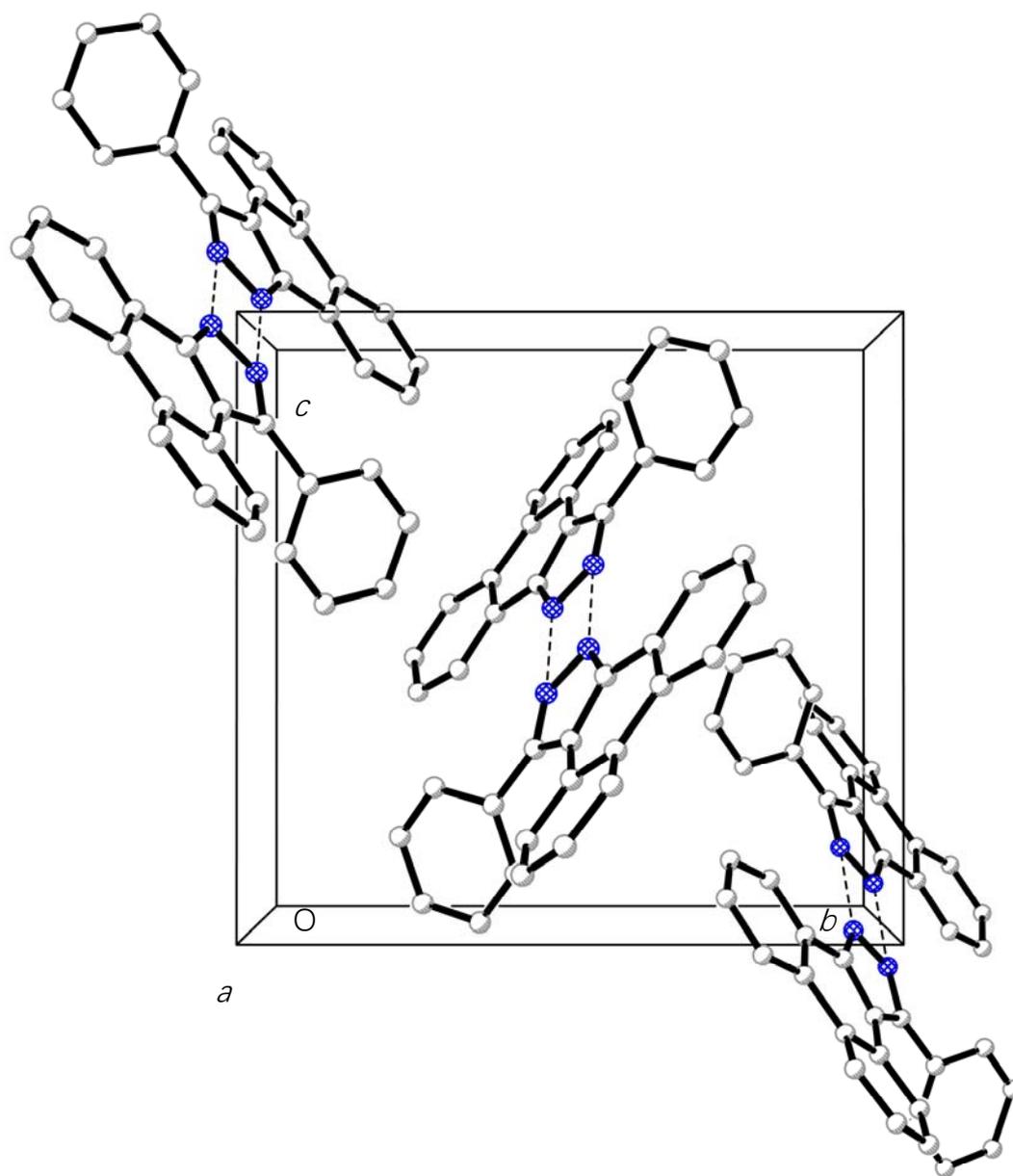
Table 5. Coordinates and isotropic temperature factors* (\AA^2) for H atoms

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq.}$
H(2)	0.882(2)	0.4547(17)	0.4717(18)	0.035(6)
H(5)	0.7104	0.3319	0.3930	0.034
H(6)	0.5333	0.2181	0.3293	0.042
H(7)	0.3150	0.1998	0.4241	0.044
H(8)	0.2716	0.2951	0.5782	0.039
H(12)	0.5975	0.6002	0.8462	0.035
H(13)	0.3654	0.6081	0.9183	0.042
H(14)	0.1770	0.5117	0.8400	0.042
H(15)	0.2224	0.4041	0.6950	0.037
H(17)	0.8241	0.5210	0.8996	0.029
H(18)	0.9478	0.6114	1.0351	0.034
H(19)	1.0834	0.7580	0.9926	0.039
H(20)	1.0930	0.8168	0.8146	0.040
H(21)	0.9701	0.7270	0.6786	0.033

*The exponent takes the form: $-8\pi^2 U \sin^2\theta/\lambda^2$



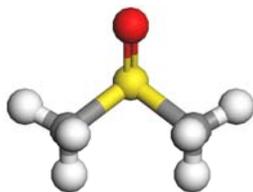
ORTEP drawing of C₂₁H₁₄N₂ with 50% probability ellipsoids, showing the atomic numbering scheme.



A packing view along the a direction

D. Computational details

(1) DMSO- d_6

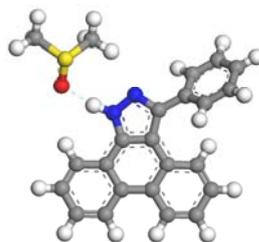


Name: DMSO- d_6

Charge: 0

Multiplicity: 1

E(RB3LYP) = -553.323419802 Ha



Name: complex-1

Charge: 0

Multiplicity: 1

E(RB3LYP) = -1471.95978420 Ha

Corrected Total Energy = -1471.959395 Ha

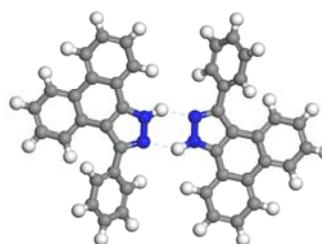
C	-1.353758	-0.804446	0.180931
S	-0.000001	0.236198	-0.438766
O	-0.000109	1.477491	0.384666
C	1.353851	-0.804292	0.180945
H	-2.281374	-0.290209	-0.063253
H	-1.257037	-0.907291	1.261736
H	-1.325405	-1.776106	-0.312671
H	1.325855	-1.775803	-0.312973
H	1.256893	-0.907502	1.261692
H	2.281406	-0.289758	-0.062862

C	1.217444	-4.962371	0.061466
C	2.159880	-3.954951	0.063035
C	1.791801	-2.598530	0.002983
C	0.405535	-2.307791	-0.052526
C	-0.545804	-3.340675	-0.055213
C	-0.146005	-4.657494	-0.000008
C	2.776836	-1.512864	-0.020968
C	2.362487	-0.150176	-0.061060
C	0.948158	0.129129	-0.047552
C	0.038346	-0.927581	-0.088067
C	4.157125	-1.781369	-0.031735
C	5.096199	-0.774042	-0.095764

(2) complex-1

C	4.681857	0.557564	-0.165454	H	1.308994	6.514842	0.229693
C	3.337193	0.858512	-0.150040	H	-0.164188	5.669382	-1.573196
C	0.129381	1.301328	-0.069636	H	-0.689561	3.255472	-1.710582
N	-1.156584	0.959970	-0.142964	C	-4.526202	1.218387	-0.466326
N	-1.195769	-0.385758	-0.156557	S	-4.725712	-0.268697	0.539539
C	0.480378	2.729210	0.002544	C	-6.407233	-0.690323	0.026312
C	1.303128	3.218126	1.020081	O	-3.845176	-1.322642	-0.079742
C	1.599984	4.571703	1.100793	H	-5.205549	1.987473	-0.098034
C	1.075325	5.459803	0.167838	H	-4.732686	0.974902	-1.508567
C	0.247831	4.984514	-0.842899	H	-3.488657	1.533167	-0.346002
C	-0.048406	3.630084	-0.924021	H	-6.669034	-1.621653	0.524588
H	1.538815	-5.994832	0.109028	H	-6.423915	-0.823507	-1.054997
H	3.202659	-4.229819	0.114053	H	-7.086910	0.102966	0.337176
H	-1.599983	-3.096529	-0.095017				
H	-0.882625	-5.450111	-0.000827				
H	4.504947	-2.803065	0.000035				
H	6.150234	-1.019407	-0.103675				
H	5.412089	1.353424	-0.236759				
H	3.022117	1.887777	-0.220032				
H	-2.106909	-0.847564	-0.160939				
H	1.702260	2.531743	1.755198				
H	2.235752	4.934992	1.898117				

(3) complex-2



Name: complex-2

Charge: 0

Multiplicity: 1

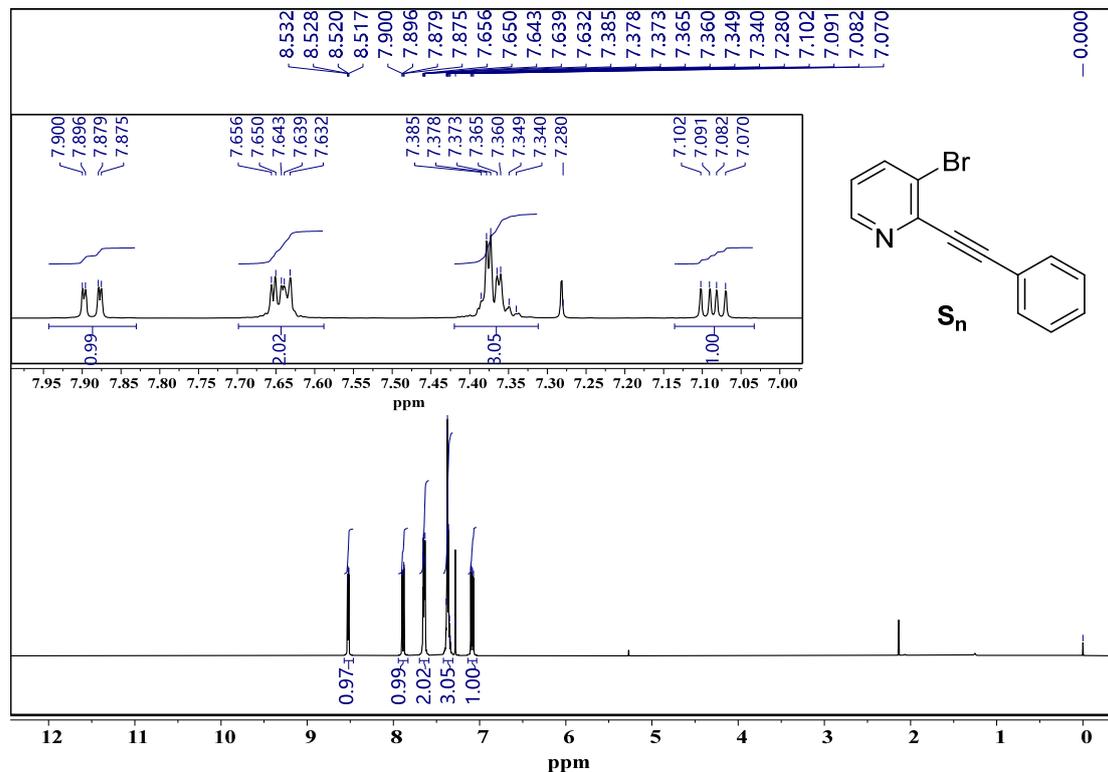
E(RB3LYP) = -1837.25679266 Ha

Corrected Total Energy = -1837.256412 Ha				C	2.911959	5.628551	0.040928
				C	2.165085	5.024165	-0.963768
C	4.448389	-4.685540	0.274432	C	2.069919	3.640015	-1.026287
C	5.252652	-3.564878	0.252335	H	4.898784	-5.664286	0.376821
C	4.714930	-2.271359	0.123487	H	6.320194	-3.699638	0.339354
C	3.305026	-2.166682	0.024832	H	1.420552	-3.213160	-0.029133
C	2.496227	-3.313881	0.044240	H	2.430830	-5.444873	0.185931
C	3.059439	-4.564528	0.167111	H	7.431947	-2.121322	0.179126
C	5.552537	-1.068908	0.071872	H	8.833910	-0.144177	0.022785
C	4.967404	0.225496	-0.033741	H	7.798912	2.104127	-0.229049
C	3.529029	0.318880	-0.054351	H	5.359876	2.323953	-0.273692
C	2.763473	-0.847995	-0.071449	H	0.611154	-1.021588	-0.186109
C	6.955633	-1.155947	0.096341	H	3.954609	2.846571	1.671350
C	7.757148	-0.038104	0.003019	H	4.132315	5.303625	1.778900
C	7.176006	1.224216	-0.133041	H	2.988426	6.707091	0.088344
C	5.803842	1.348275	-0.152182	H	1.659892	5.631122	-1.704181
C	2.571012	1.376909	-0.127034	H	1.493878	3.166104	-1.809863
N	1.343111	0.868911	-0.207497	C	-4.447128	4.685722	0.275251
N	1.471980	-0.473336	-0.176589	C	-5.251699	3.565291	0.252898
C	2.722598	2.840179	-0.085637	C	-4.714279	2.271594	0.124497
C	3.463343	3.456861	0.925197	C	-3.304361	2.166511	0.026564
C	3.558850	4.840123	0.986472	C	-2.495236	3.313482	0.046222

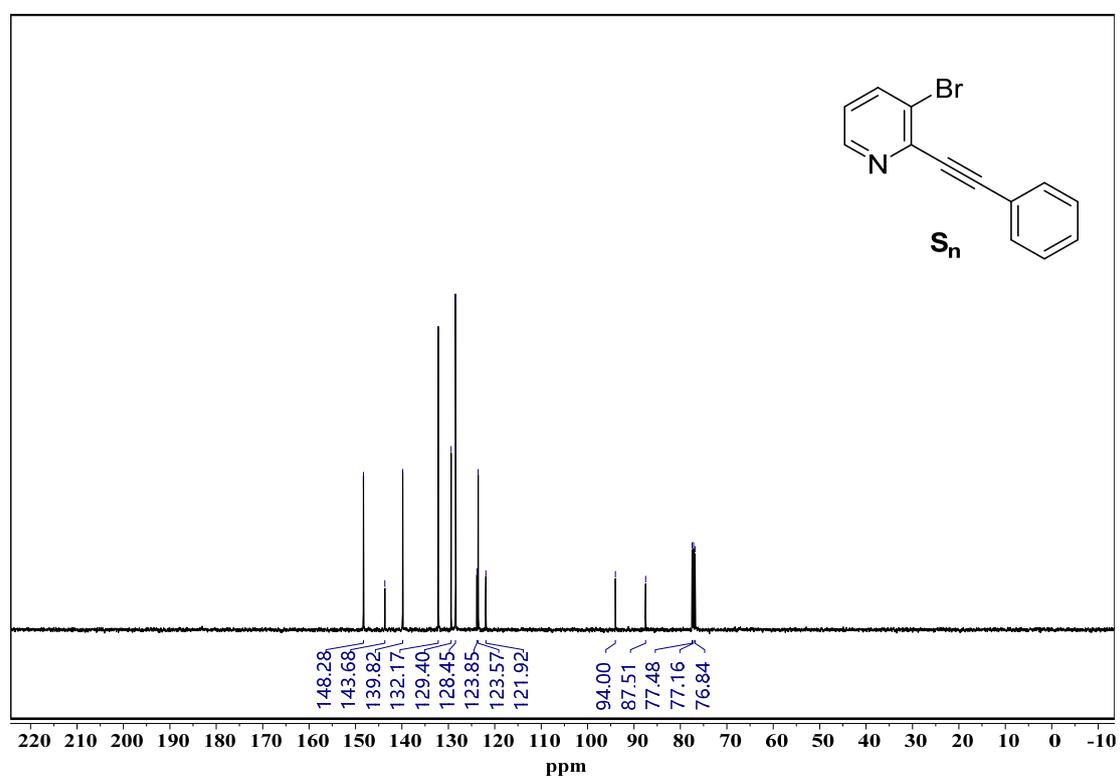
C	-3.058154	4.564303	0.168646	C	-2.070555	-3.640503	-1.024408
C	-5.552191	1.069362	0.072594	H	-4.897292	5.664614	0.377263
C	-4.967364	-0.225206	-0.032748	H	-6.319246	3.700375	0.339324
C	-3.529010	-0.319010	-0.052673	H	-1.419554	3.212442	-0.026636
C	-2.763126	0.847666	-0.069383	H	-2.429309	5.444474	0.187654
C	-6.955278	1.156774	0.096494	H	-7.431361	2.122270	0.179159
C	-7.757063	0.039156	0.002798	H	-8.833805	0.145515	0.022143
C	-7.176203	-1.223312	-0.133091	H	-7.799299	-2.103053	-0.229421
C	-5.804066	-1.347743	-0.151617	H	-5.360323	-2.323545	-0.272966
C	-2.571252	-1.377287	-0.125197	H	-0.610686	1.020649	-0.184245
N	-1.343174	-0.869605	-0.205052	H	-3.955730	-2.846621	1.672750
N	-1.471691	0.472665	-0.173801	H	-4.134188	-5.303626	1.780150
C	-2.723253	-2.840508	-0.083906	H	-2.990231	-6.707360	0.089847
C	-3.464457	-3.457025	0.926698	H	-1.660921	-5.631702	-1.702272
C	-3.560371	-4.840262	0.987898	H	-1.494213	-3.166733	-1.807848
C	-2.913443	-5.628841	0.042504				
C	-2.166129	-5.024626	-0.961969				

E. NMR charts

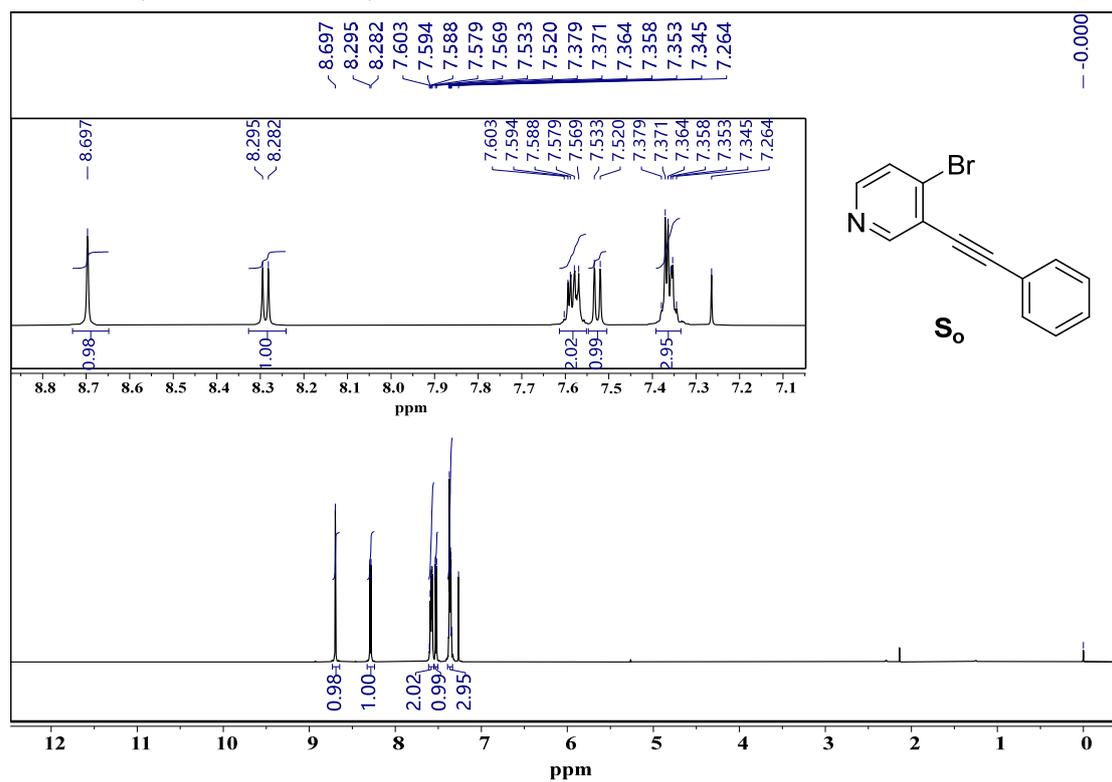
^1H NMR (400 MHz, CDCl_3) chart of S_n



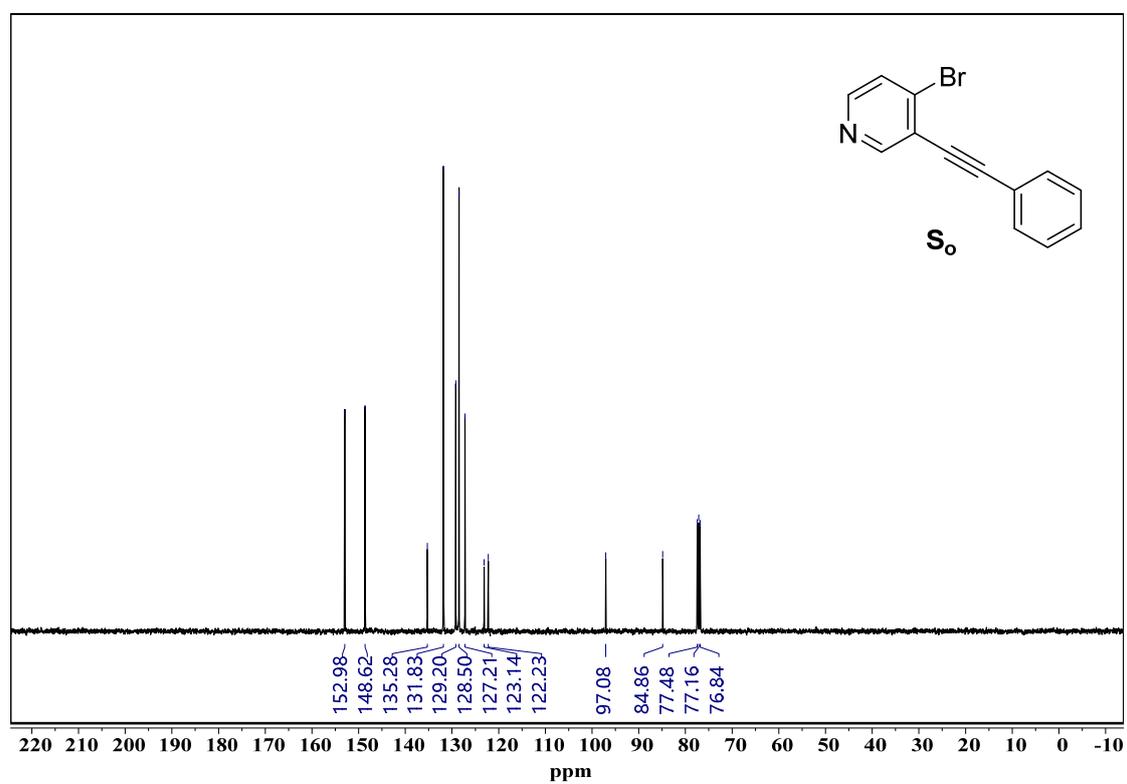
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of S_n



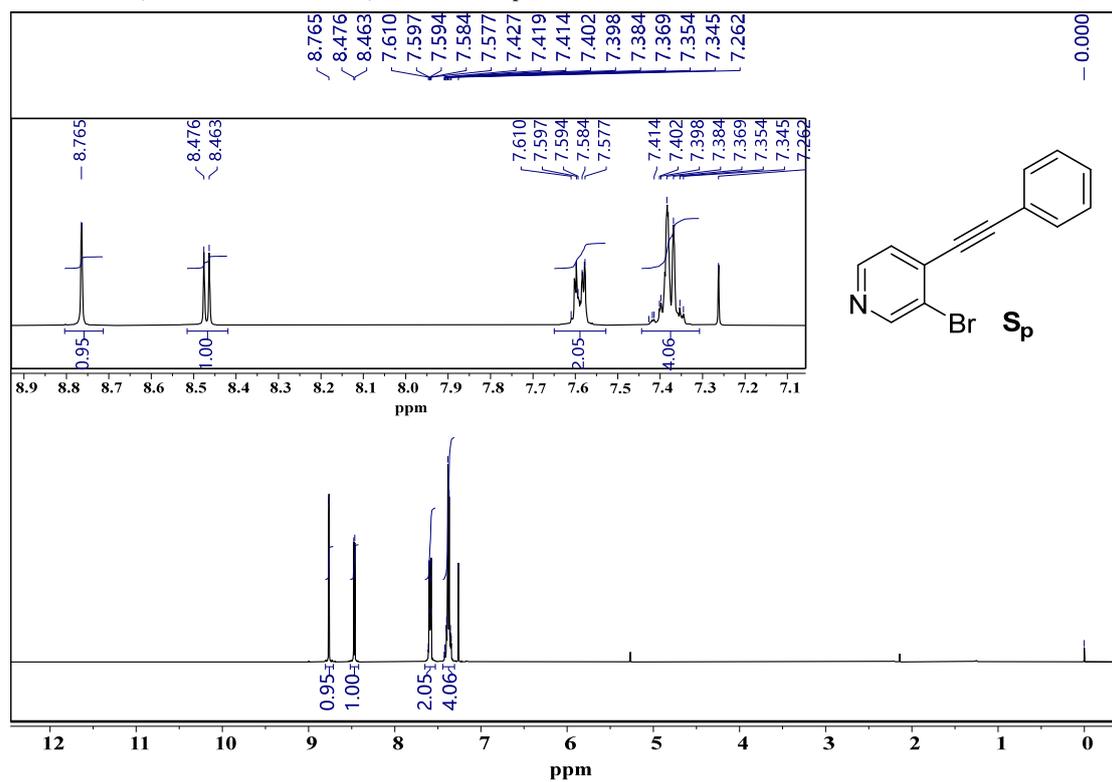
^1H NMR (400 MHz, CDCl_3) chart of S_0



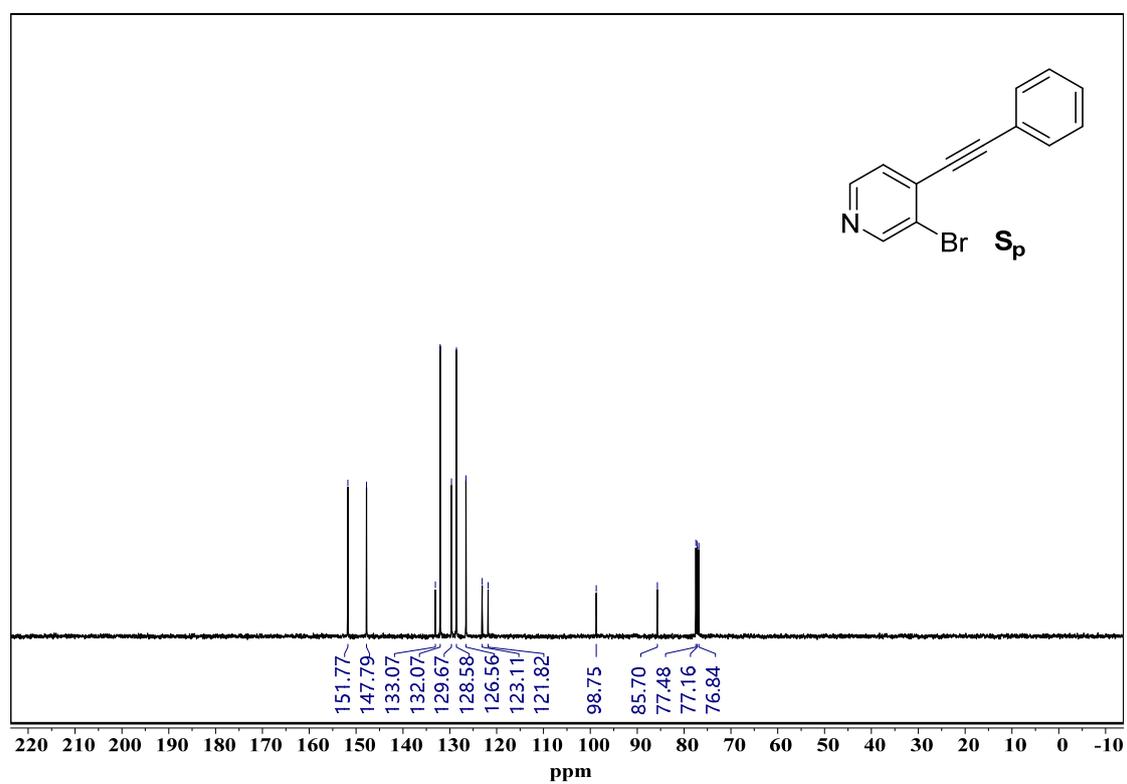
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of S_0



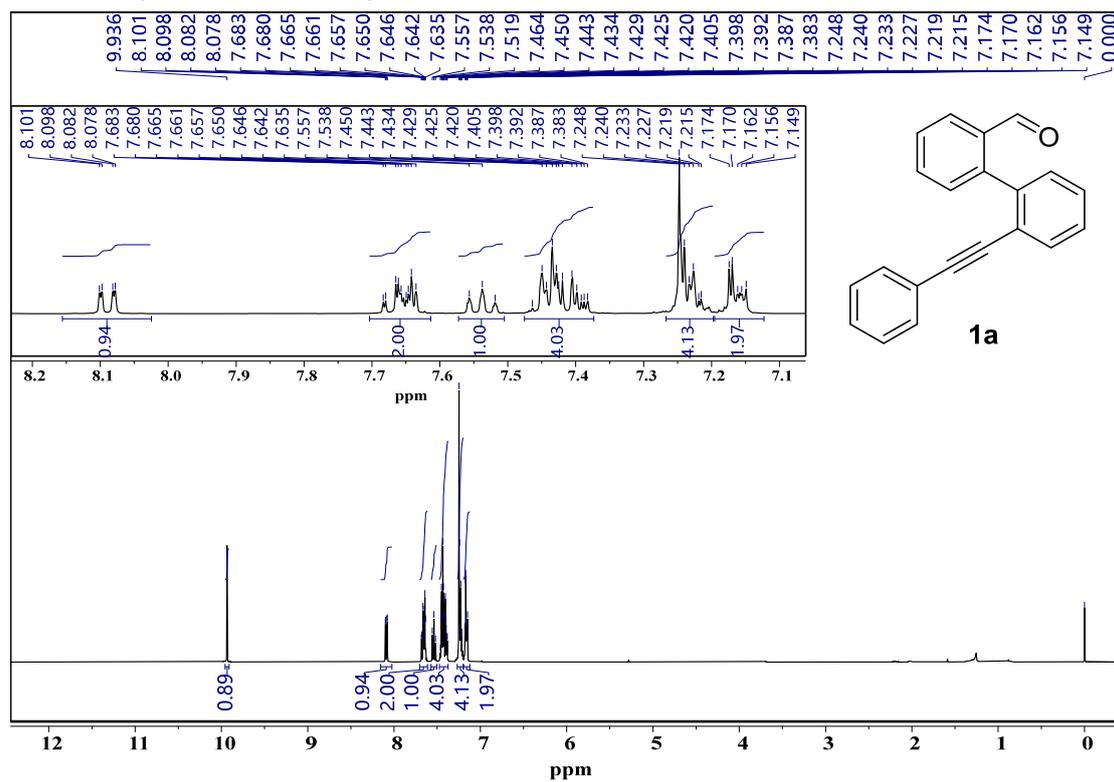
^1H NMR (400 MHz, CDCl_3) chart of S_p



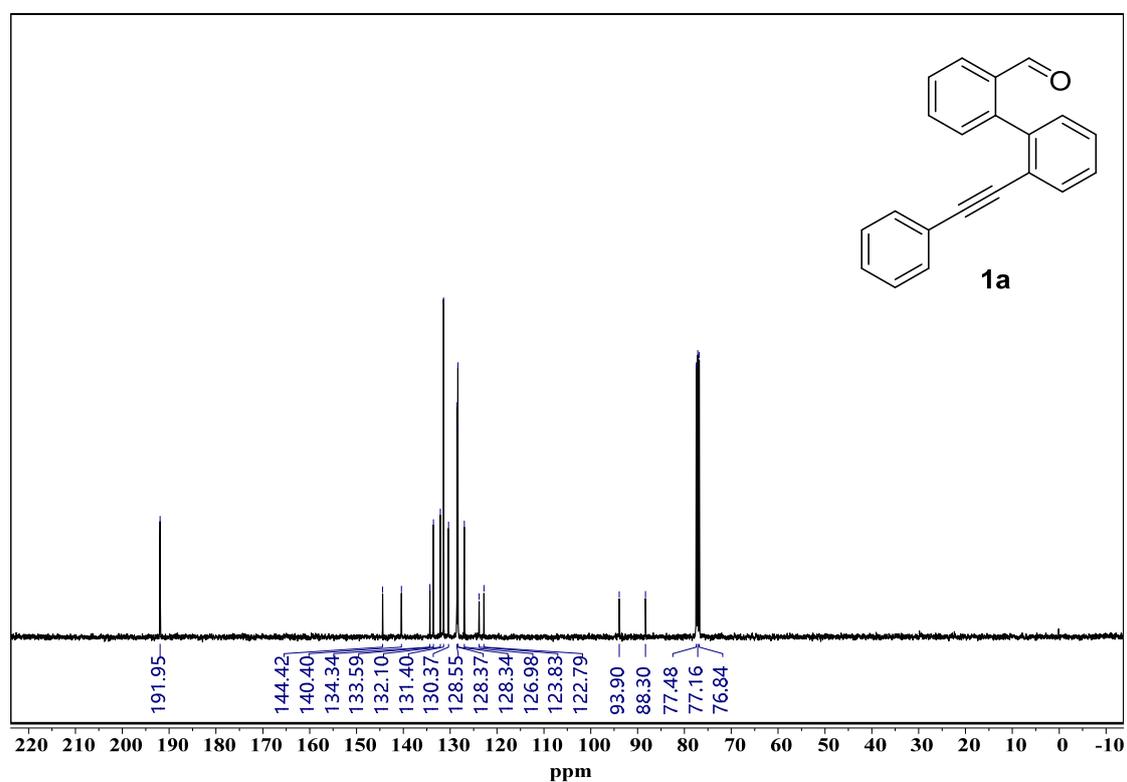
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of S_p



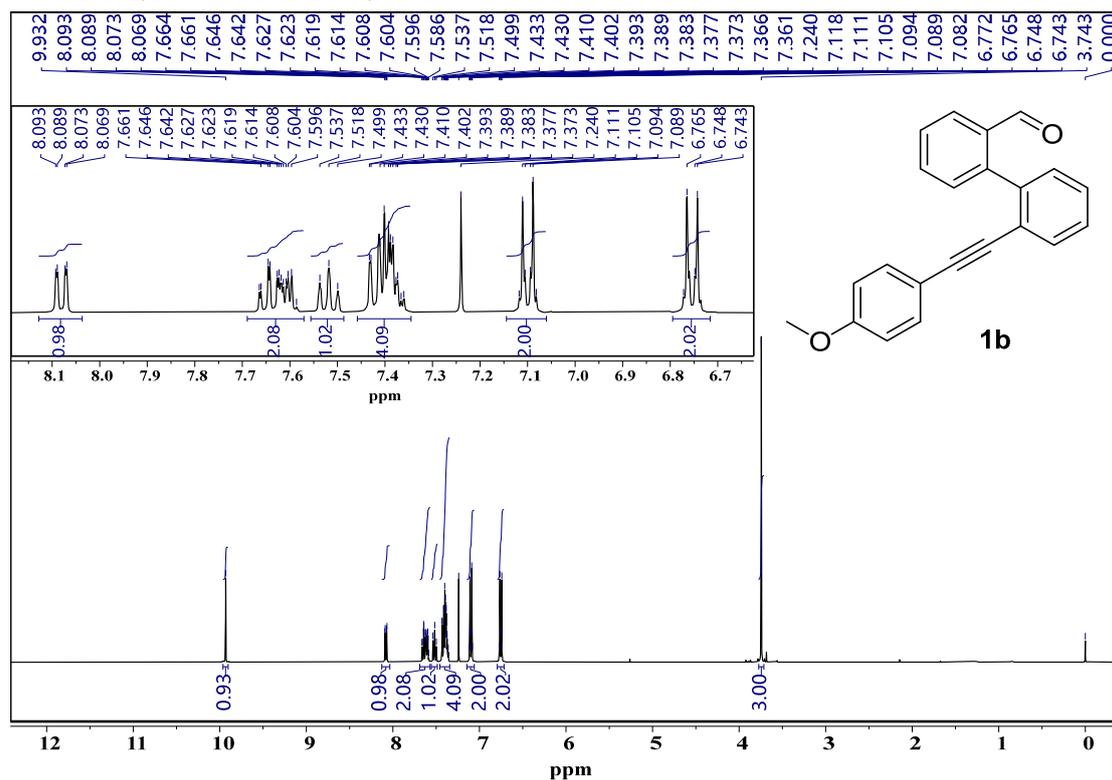
^1H NMR (400 MHz, CDCl_3) chart of **1a**



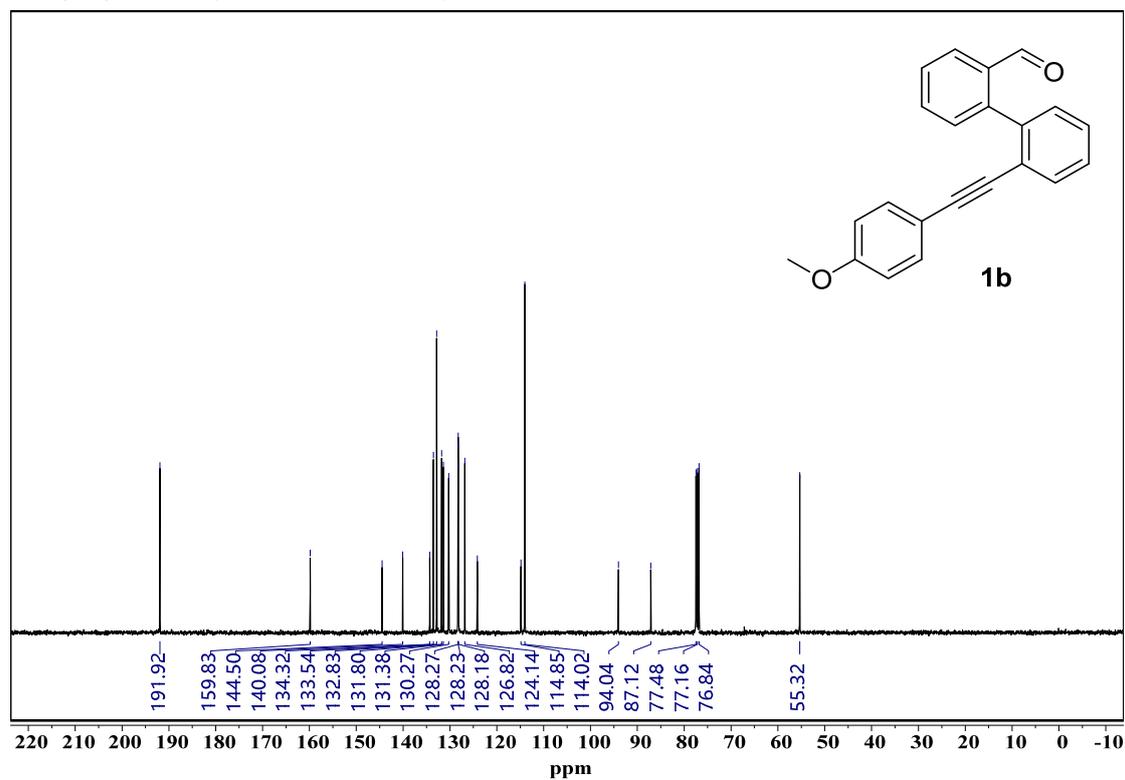
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1a**



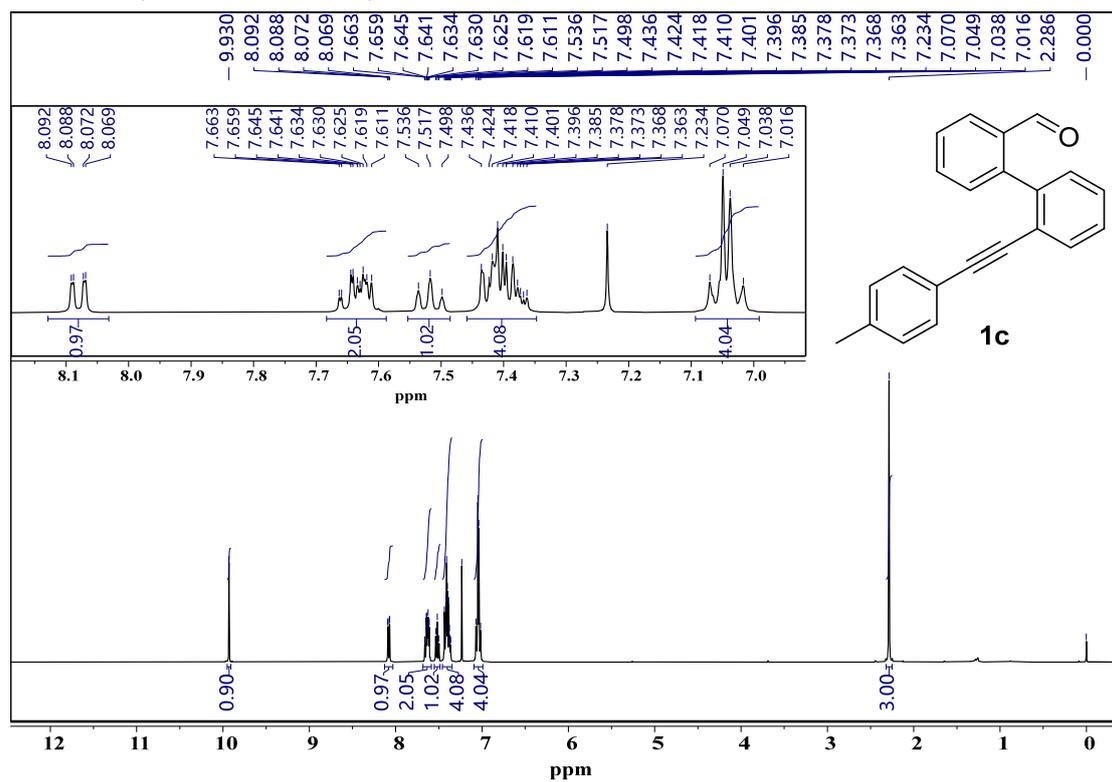
^1H NMR (400 MHz, CDCl_3) chart of **1b**



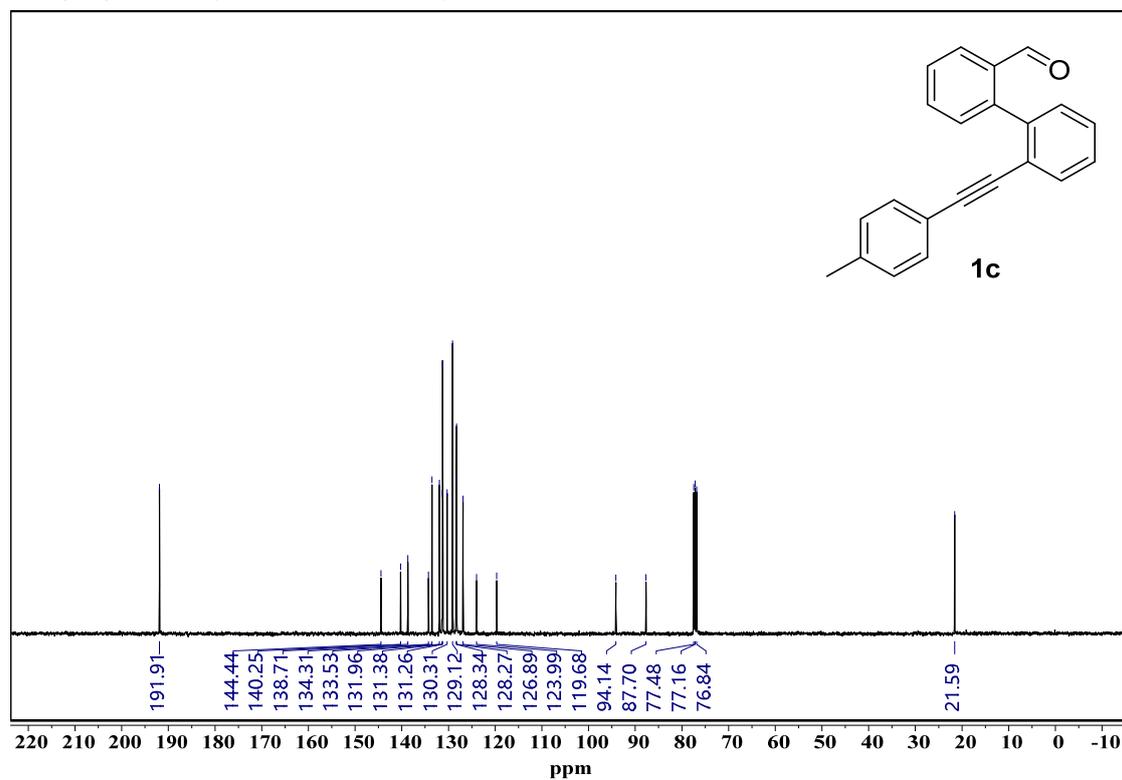
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1b**



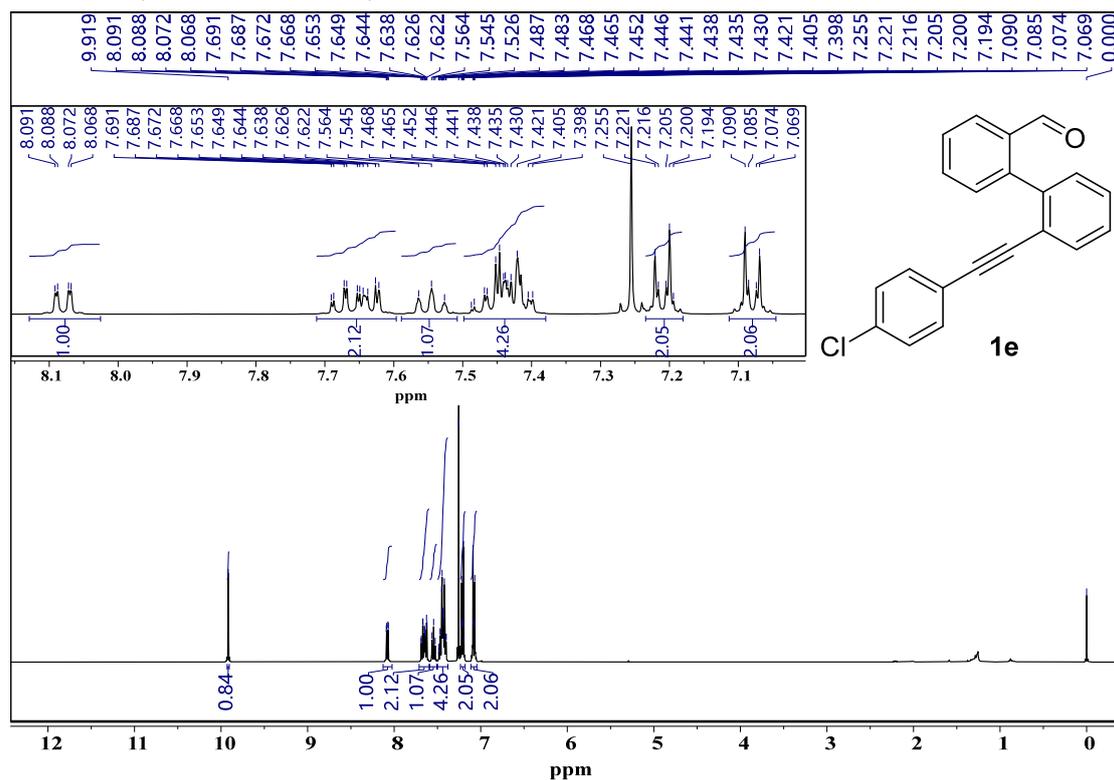
^1H NMR (400 MHz, CDCl_3) chart of **1c**



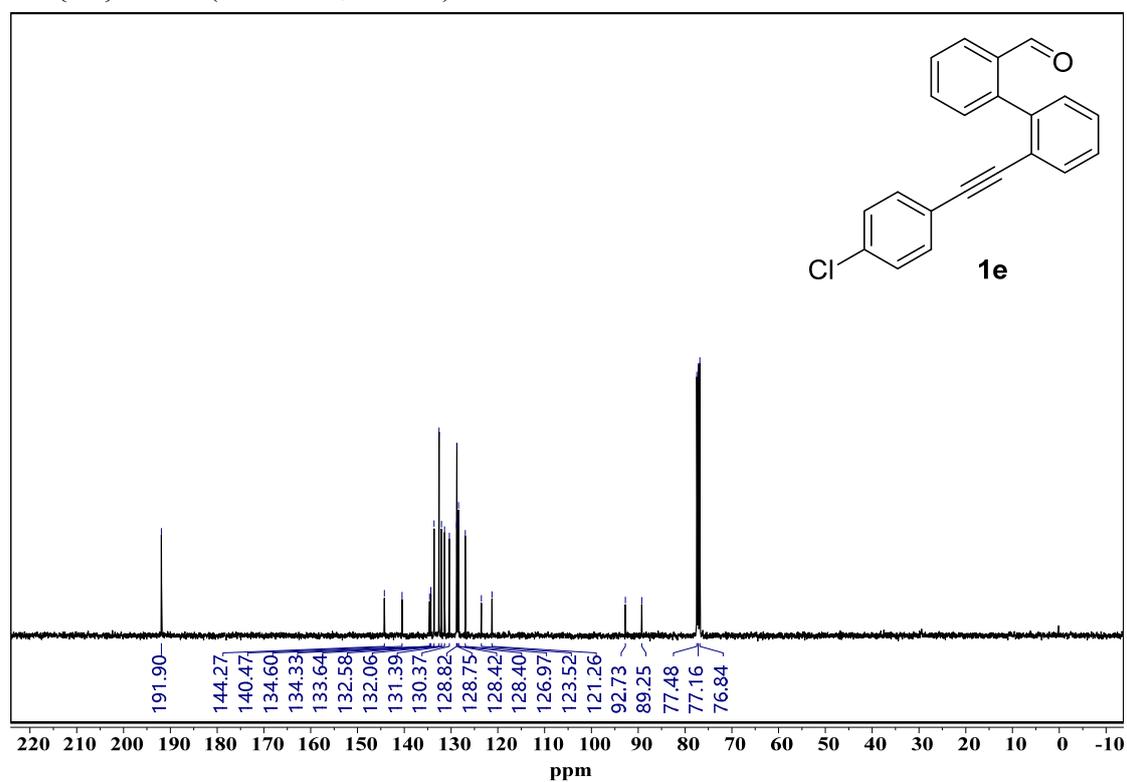
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1c**



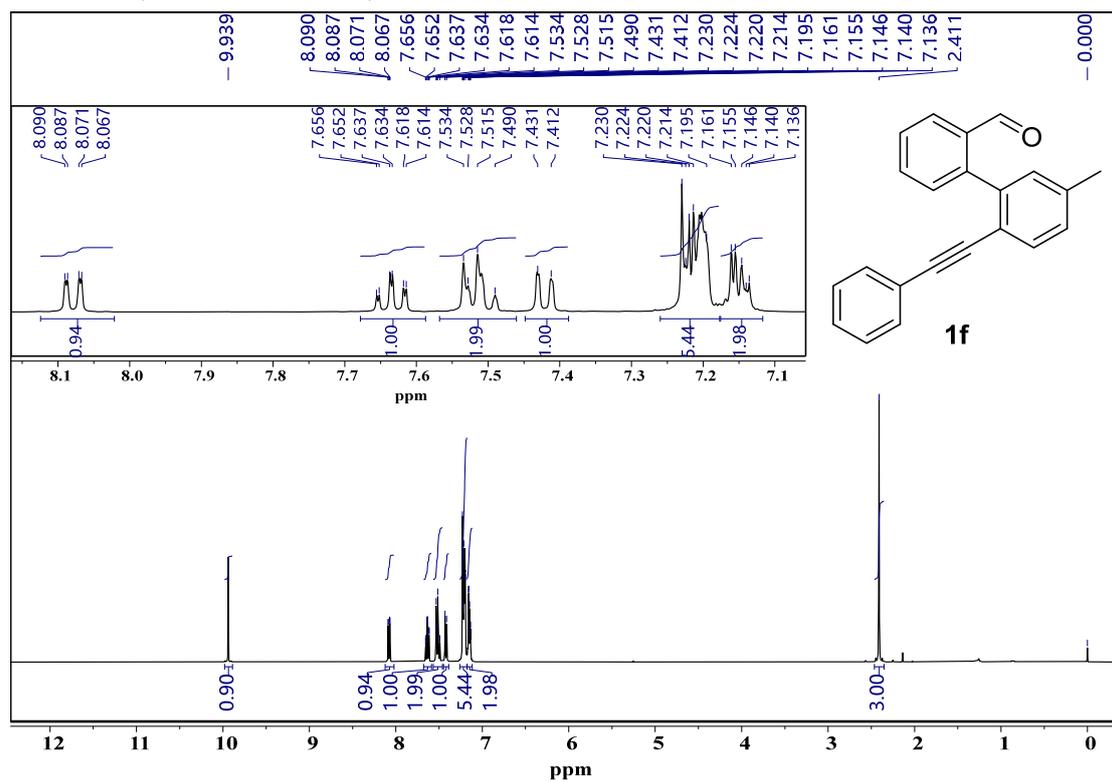
^1H NMR (400 MHz, CDCl_3) chart of **1e**



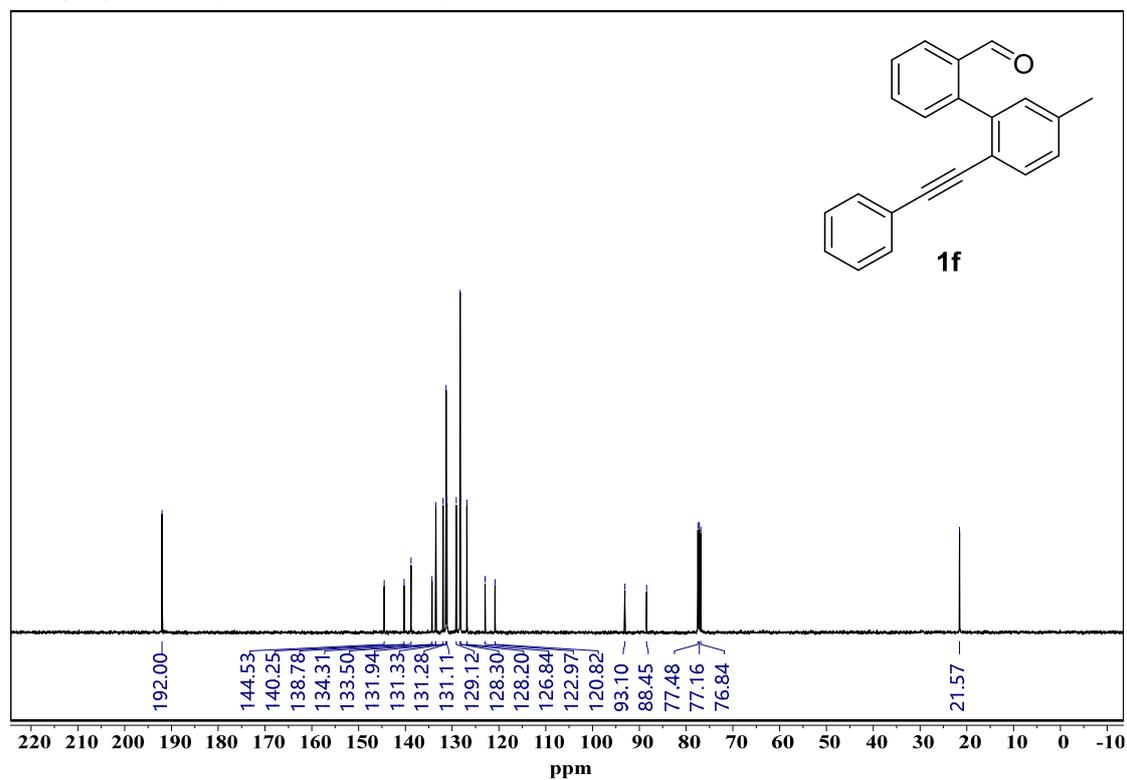
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1e**



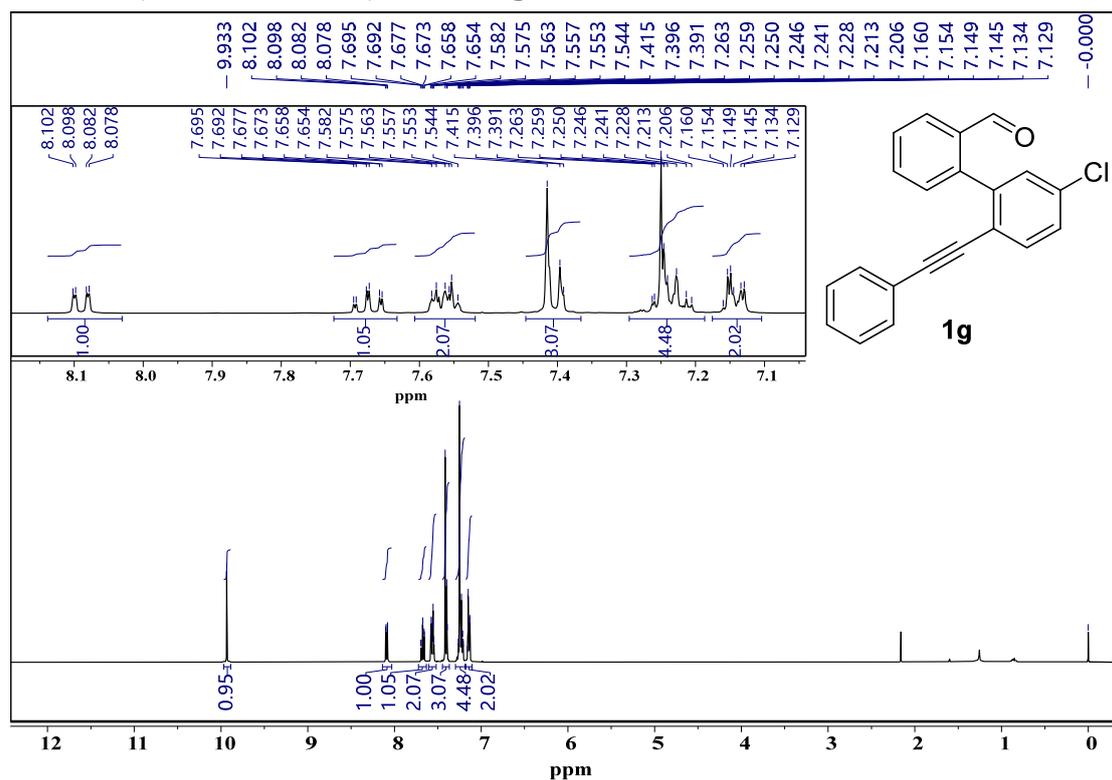
^1H NMR (400 MHz, CDCl_3) chart of **1f**



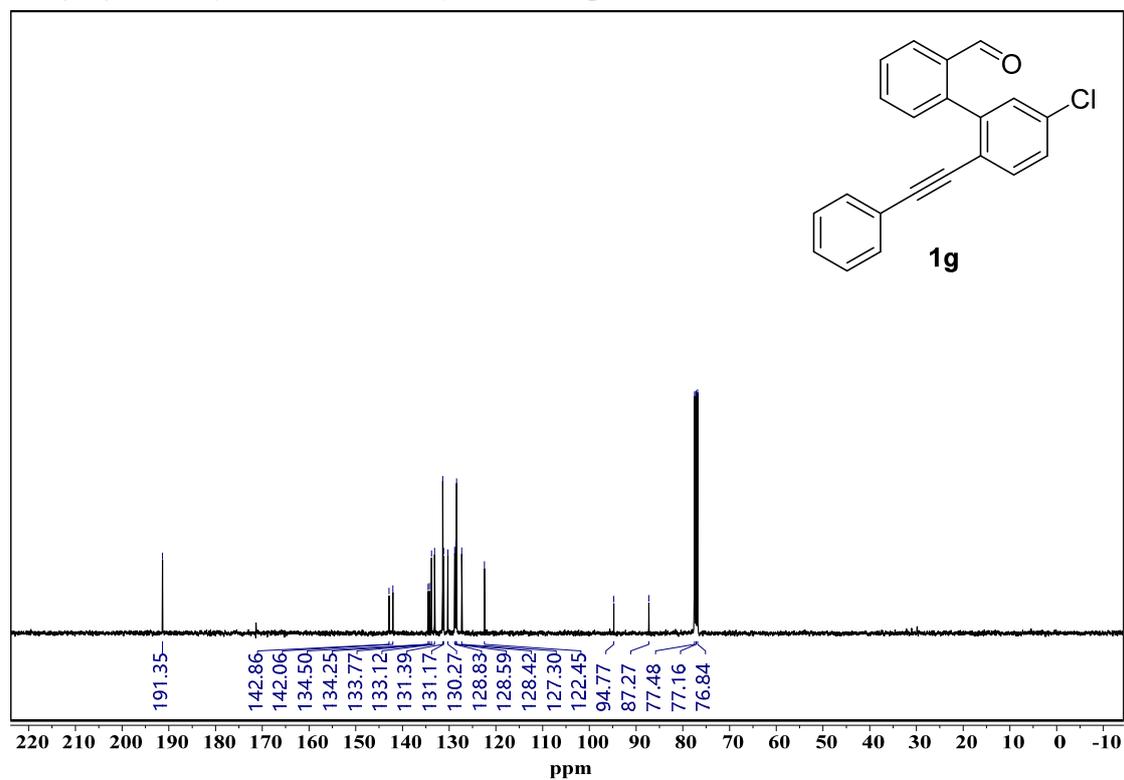
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1f**



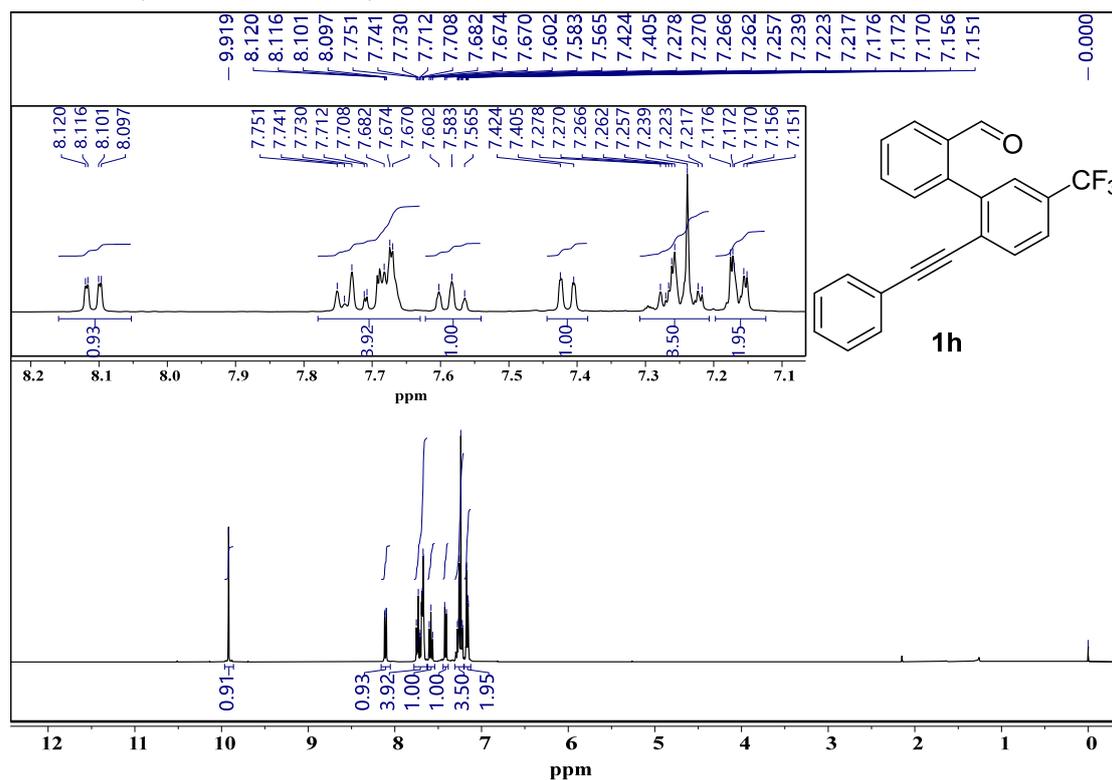
^1H NMR (400 MHz, CDCl_3) chart of **1g**



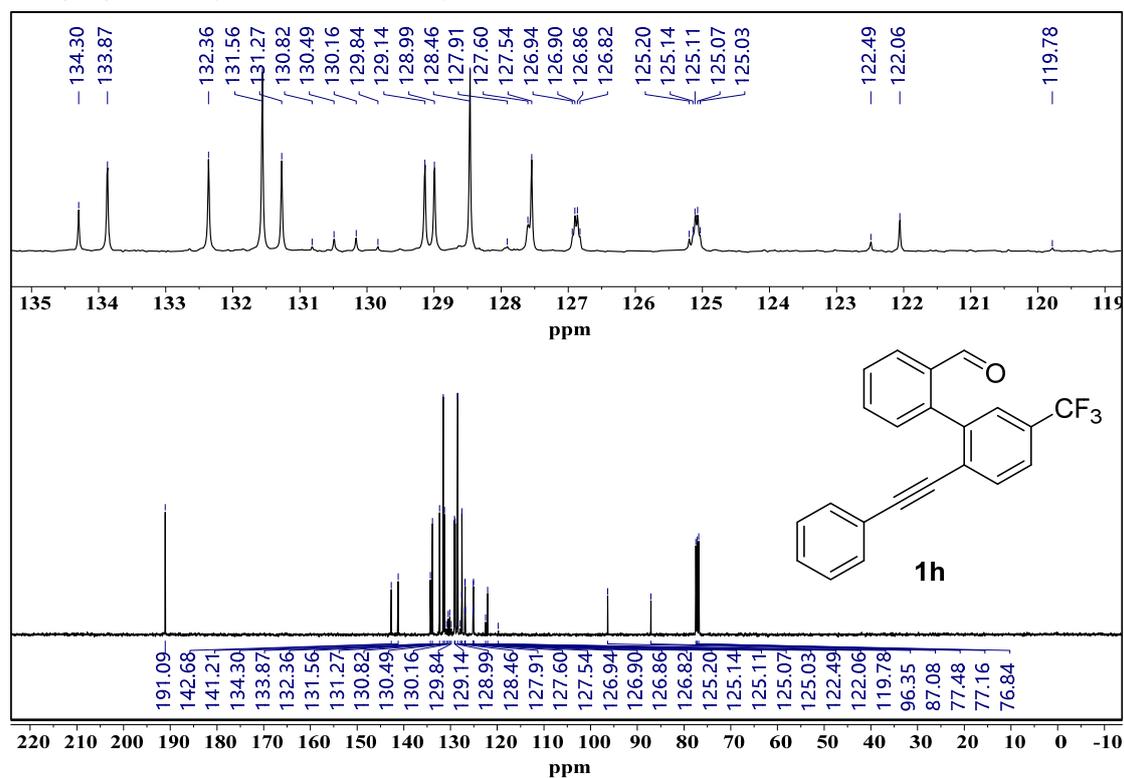
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1g**



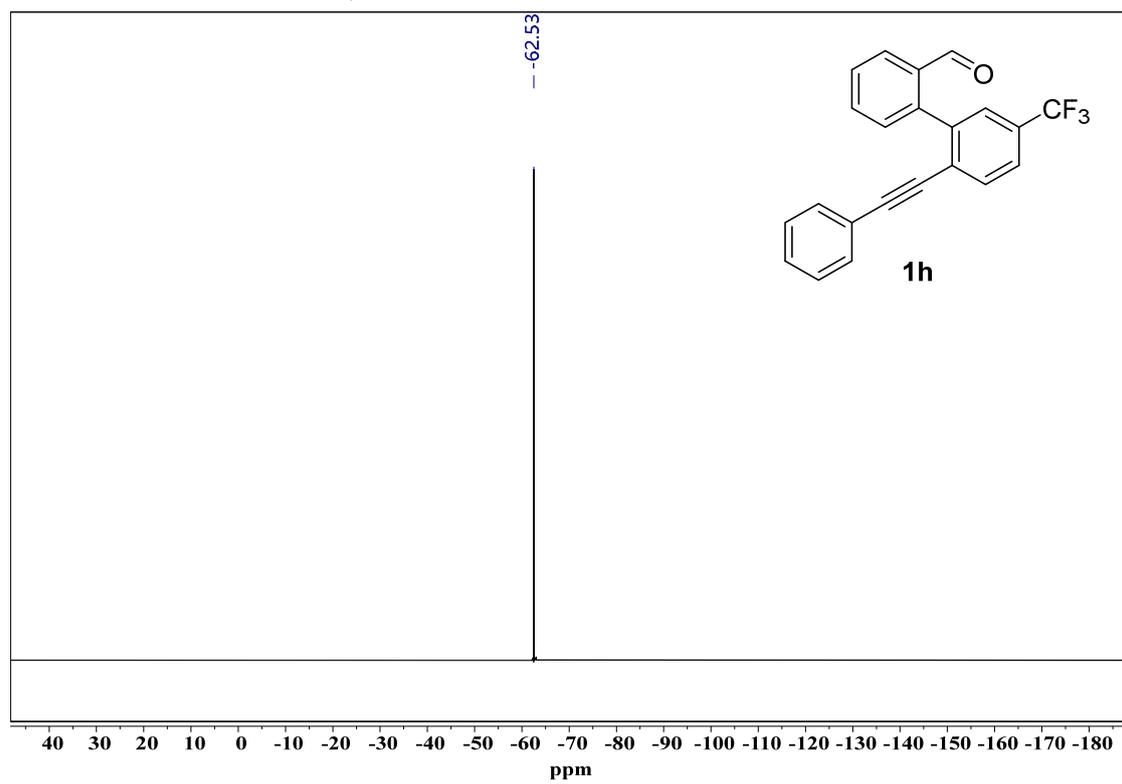
¹H NMR (400 MHz, CDCl₃) chart of **1h**



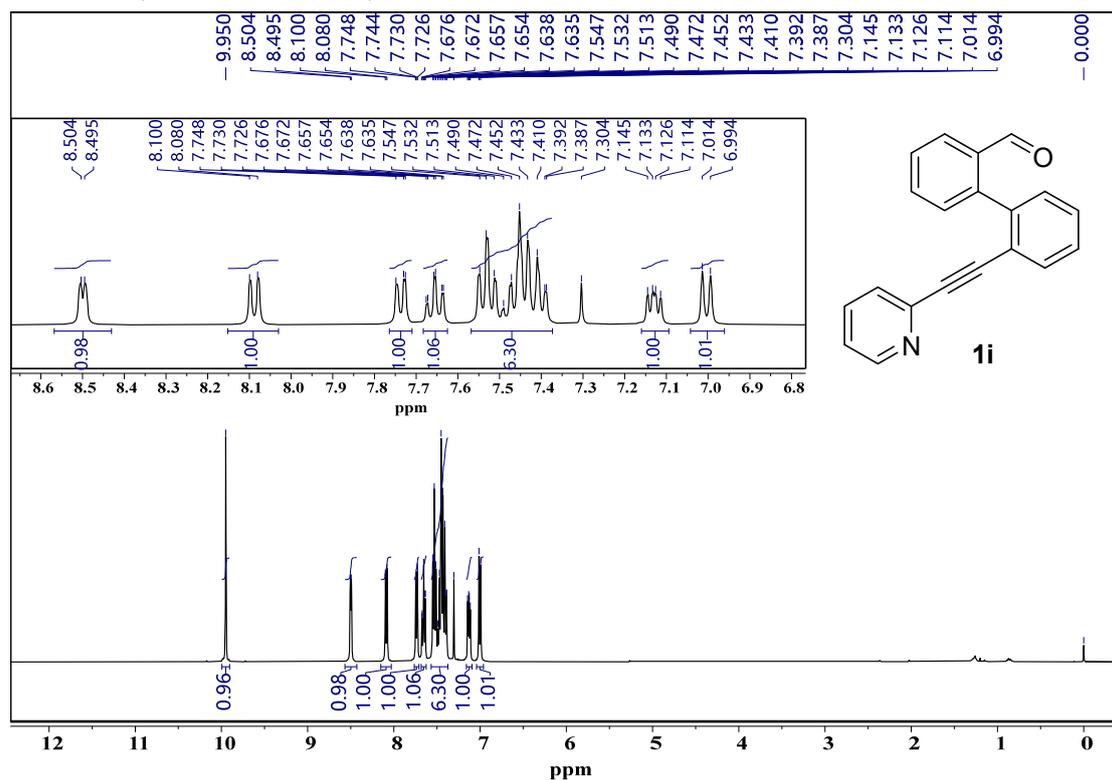
¹³C{¹H} NMR (101 MHz, CDCl₃) chart of **1h**



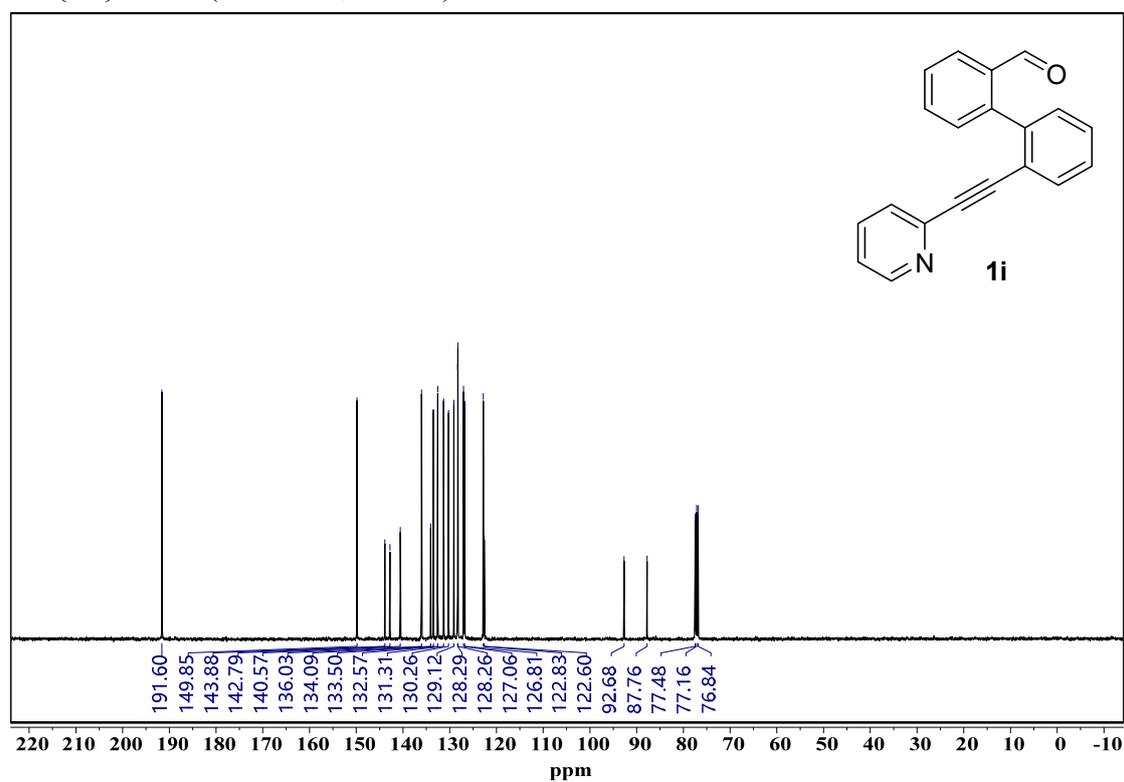
^{19}F NMR (376 MHz, CDCl_3) chart of **1h**



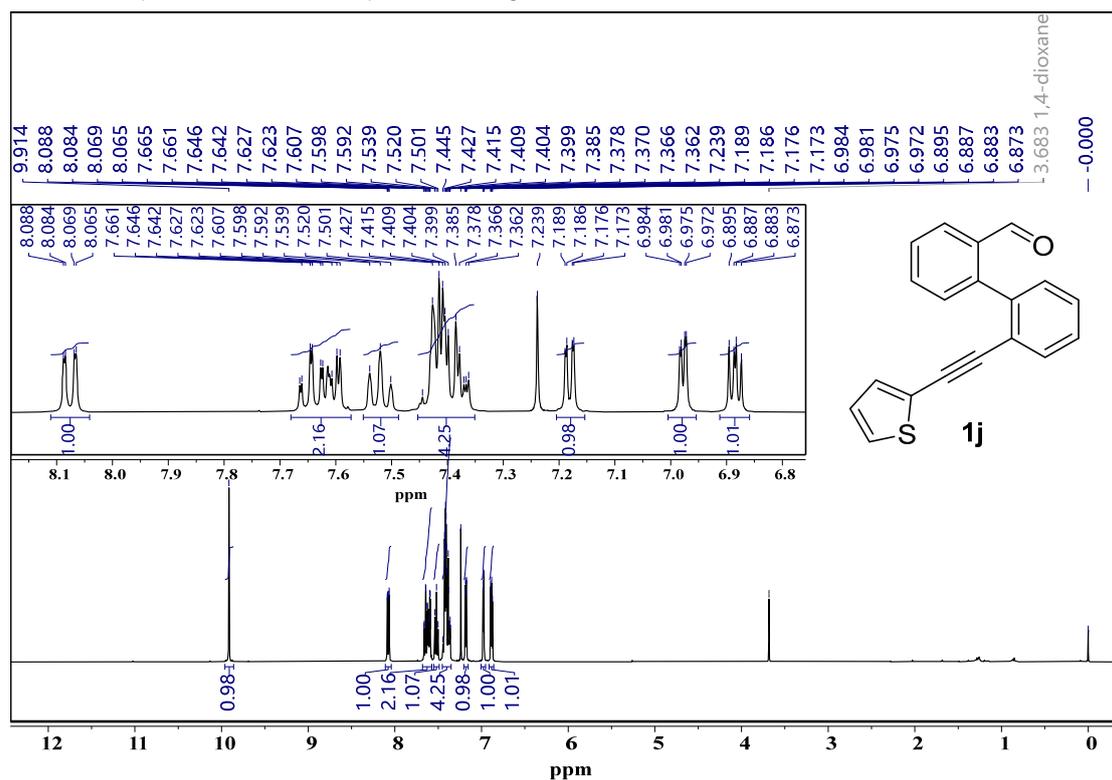
^1H NMR (400 MHz, CDCl_3) chart of **1i**



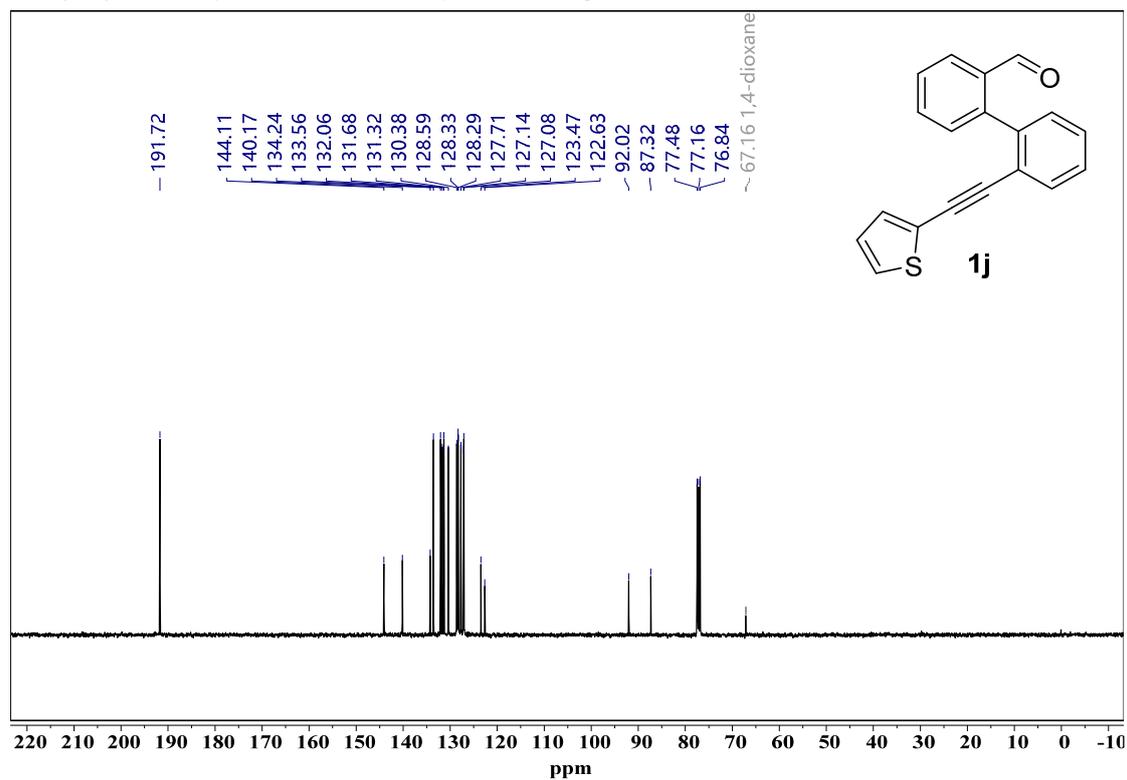
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1i**



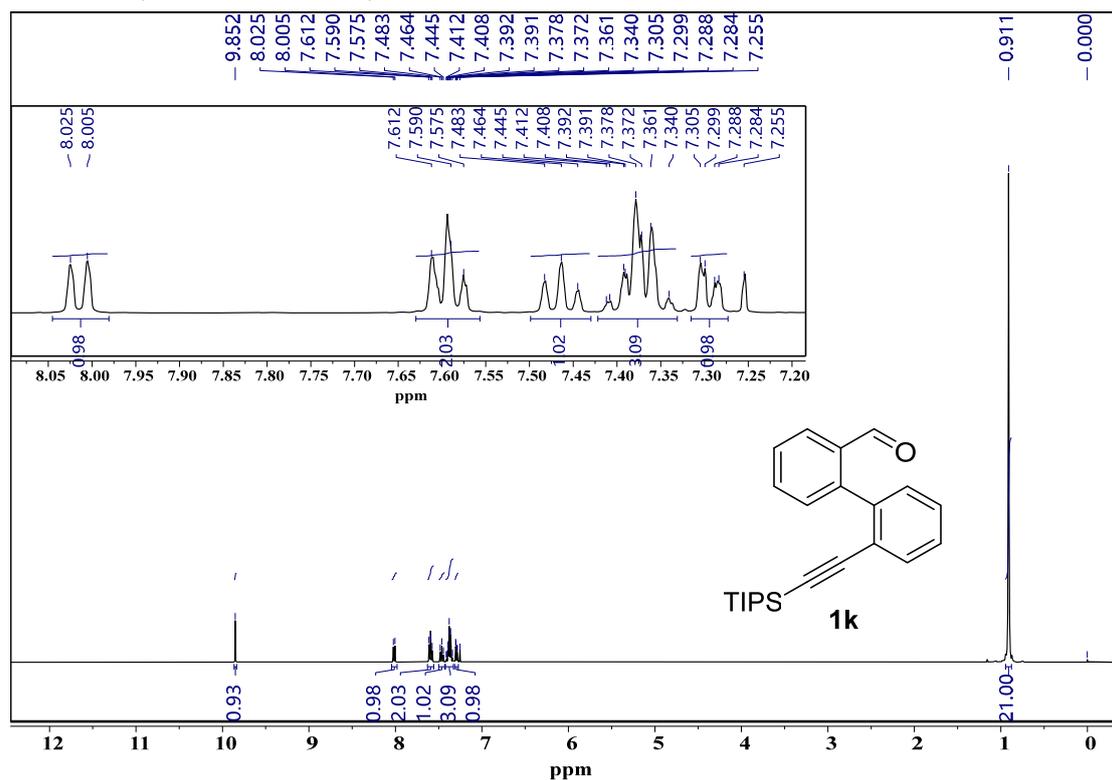
^1H NMR (400 MHz, CDCl_3) chart of **1j**



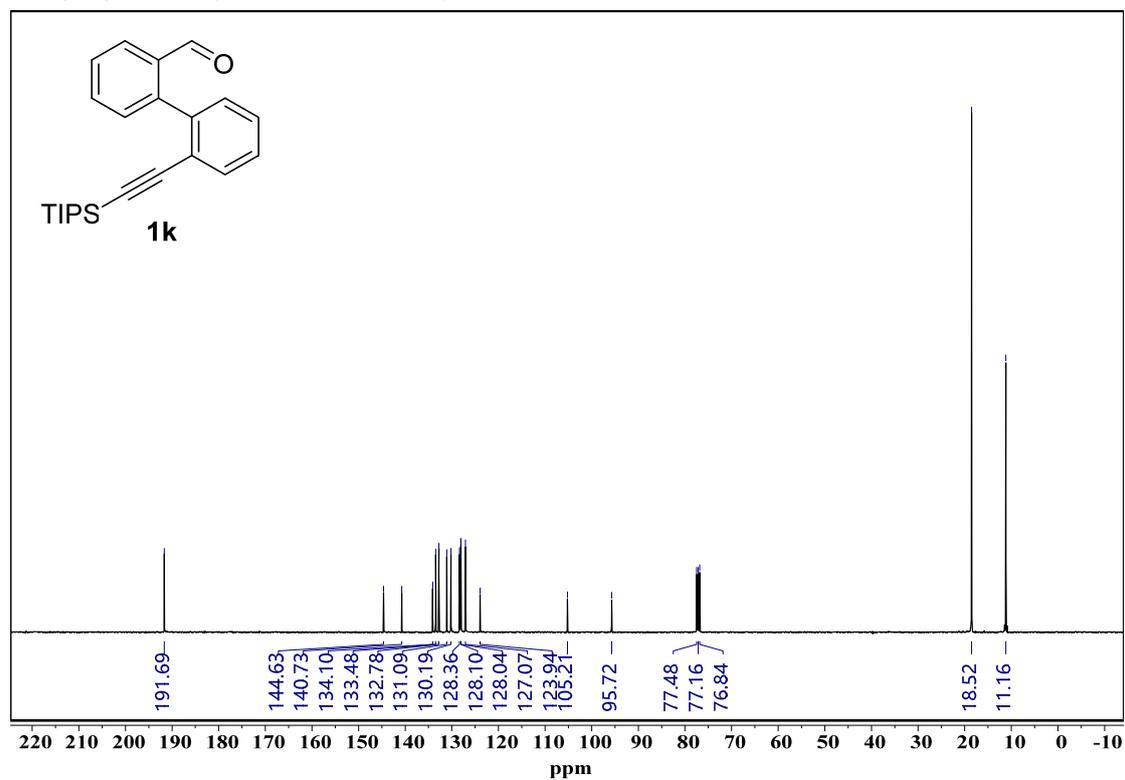
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1j**



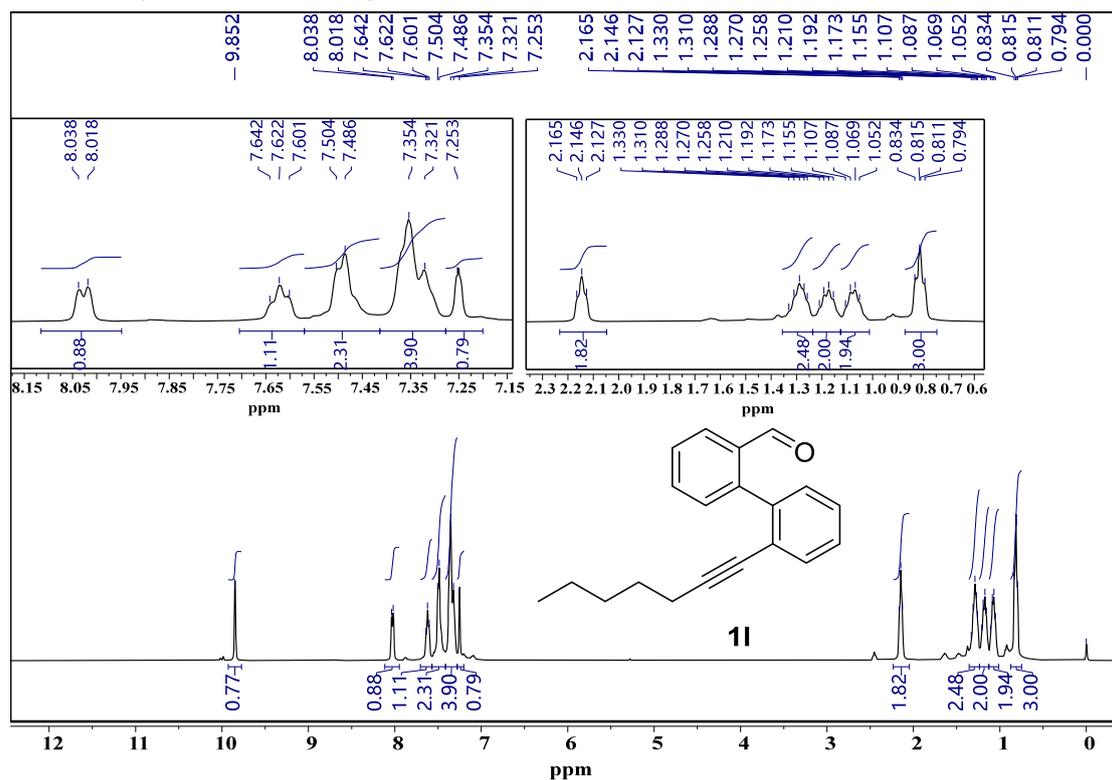
^1H NMR (400 MHz, CDCl_3) chart of **1k**



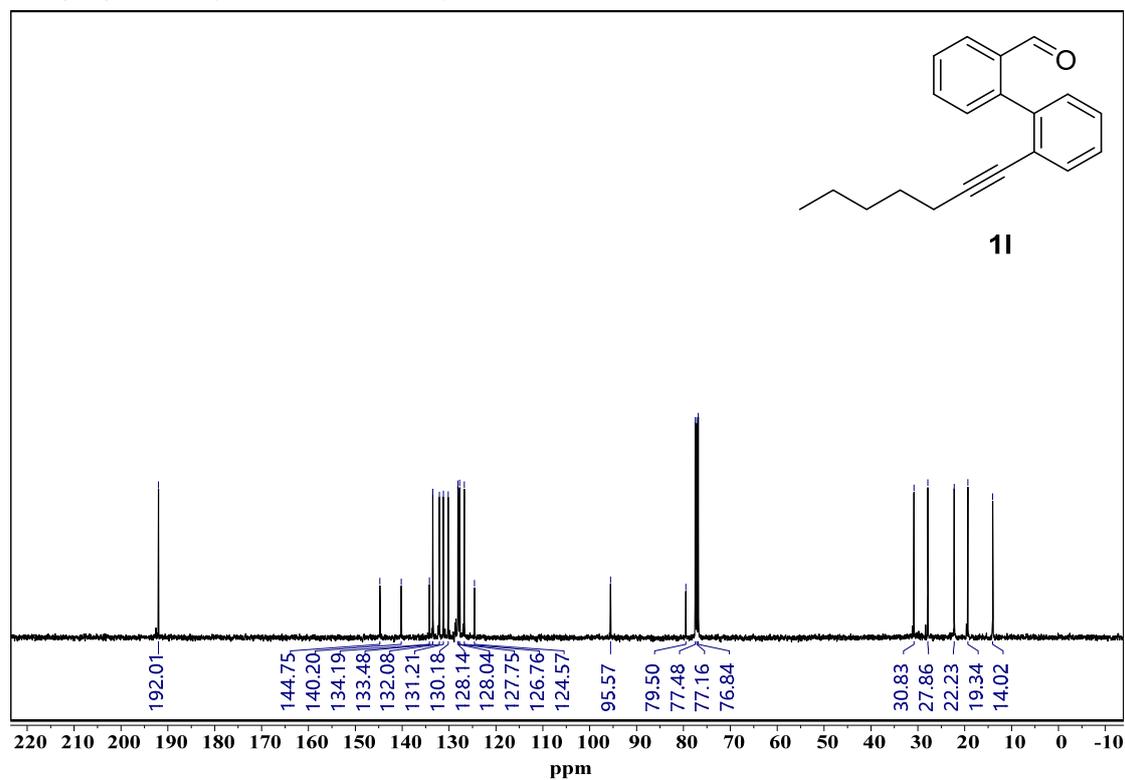
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1k**



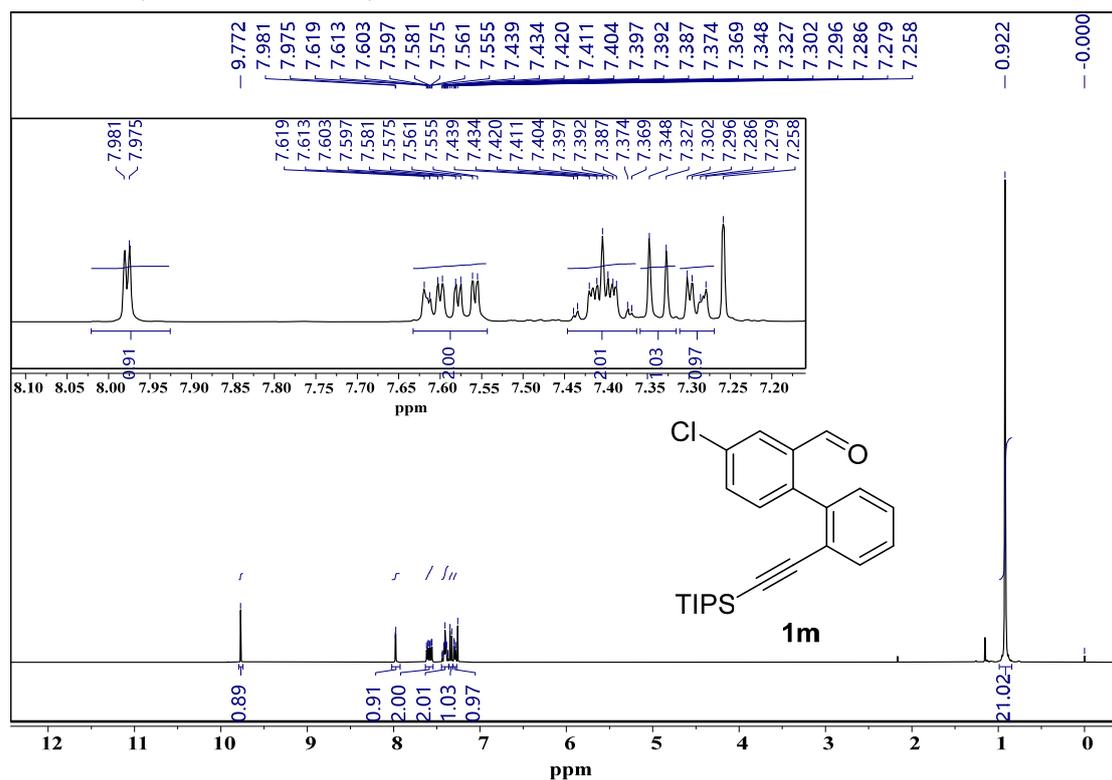
^1H NMR (400 MHz, CDCl_3) chart of **11**



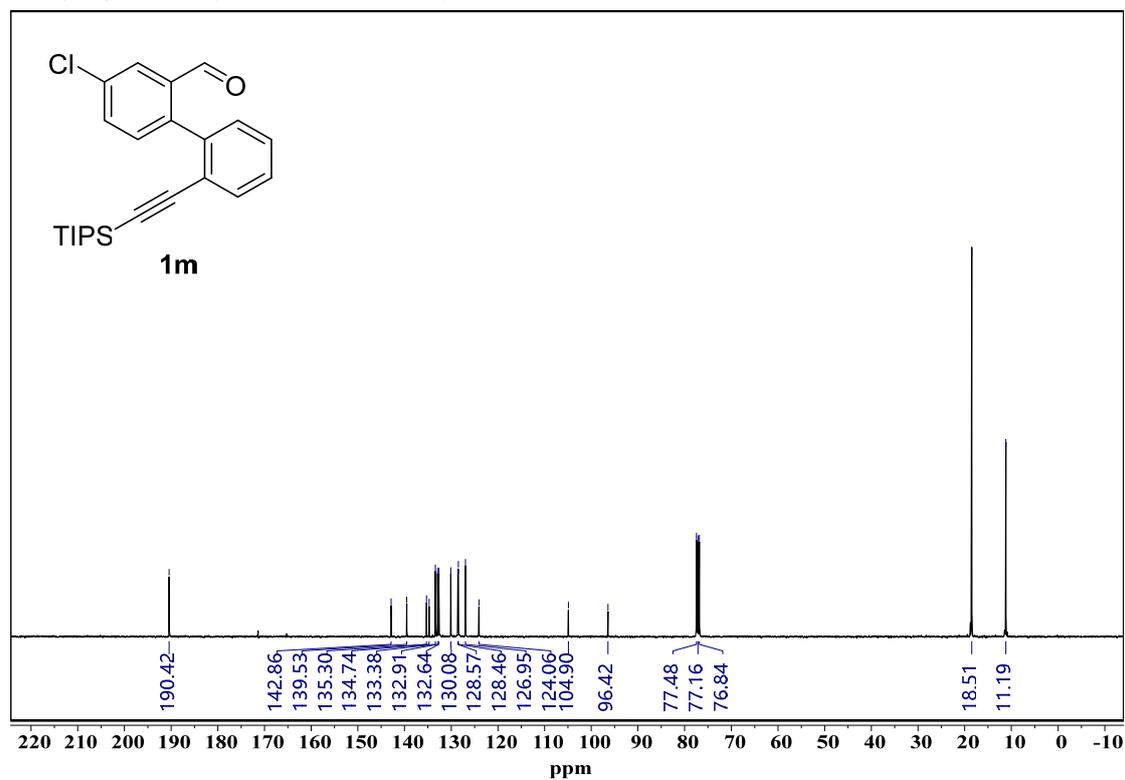
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **11**



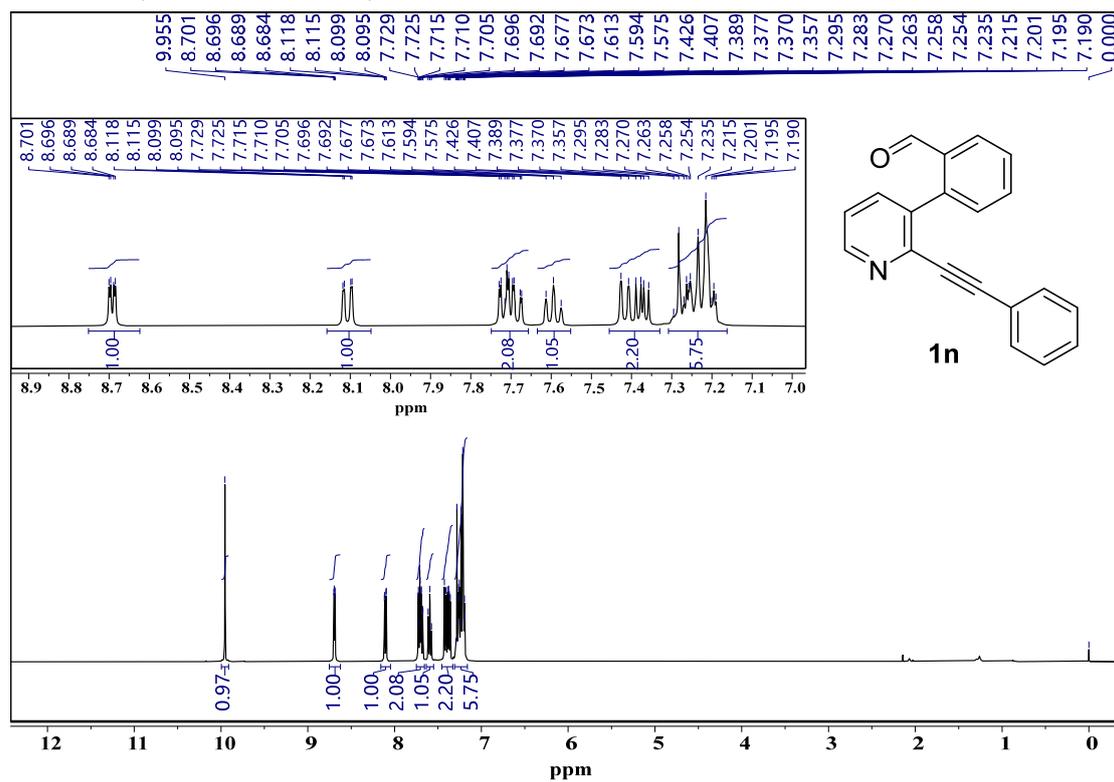
^1H NMR (400 MHz, CDCl_3) chart of **1m**



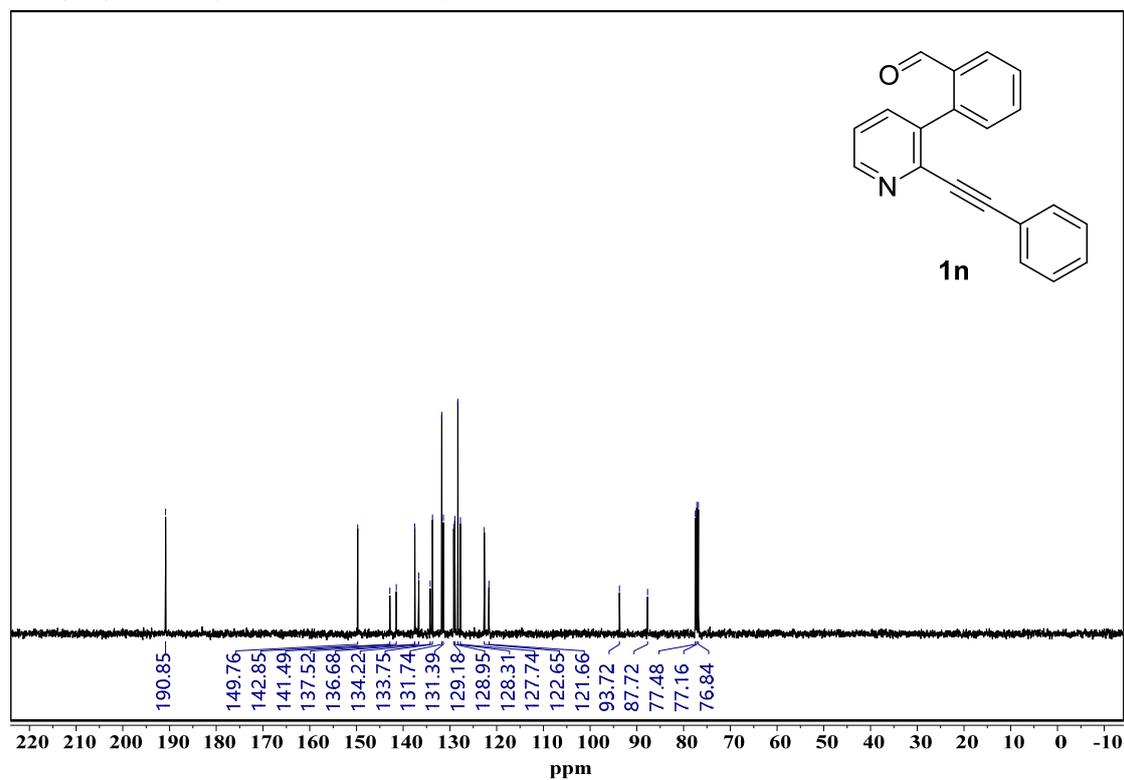
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1m**



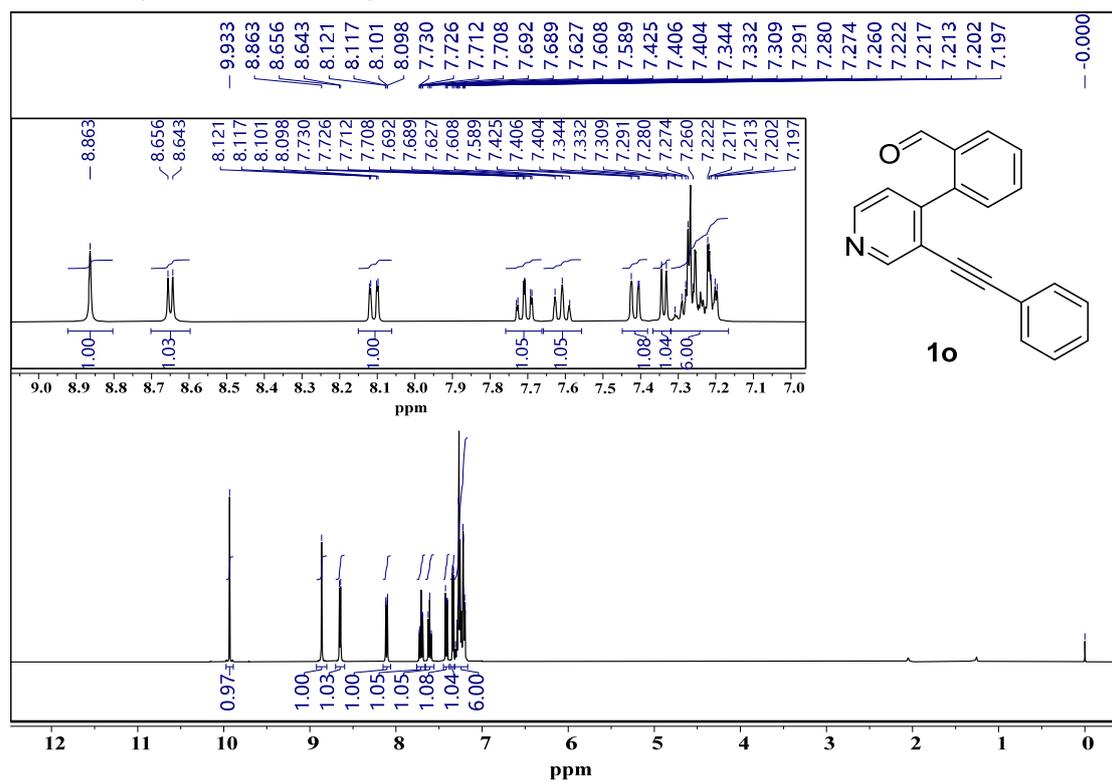
^1H NMR (400 MHz, CDCl_3) chart of **1n**



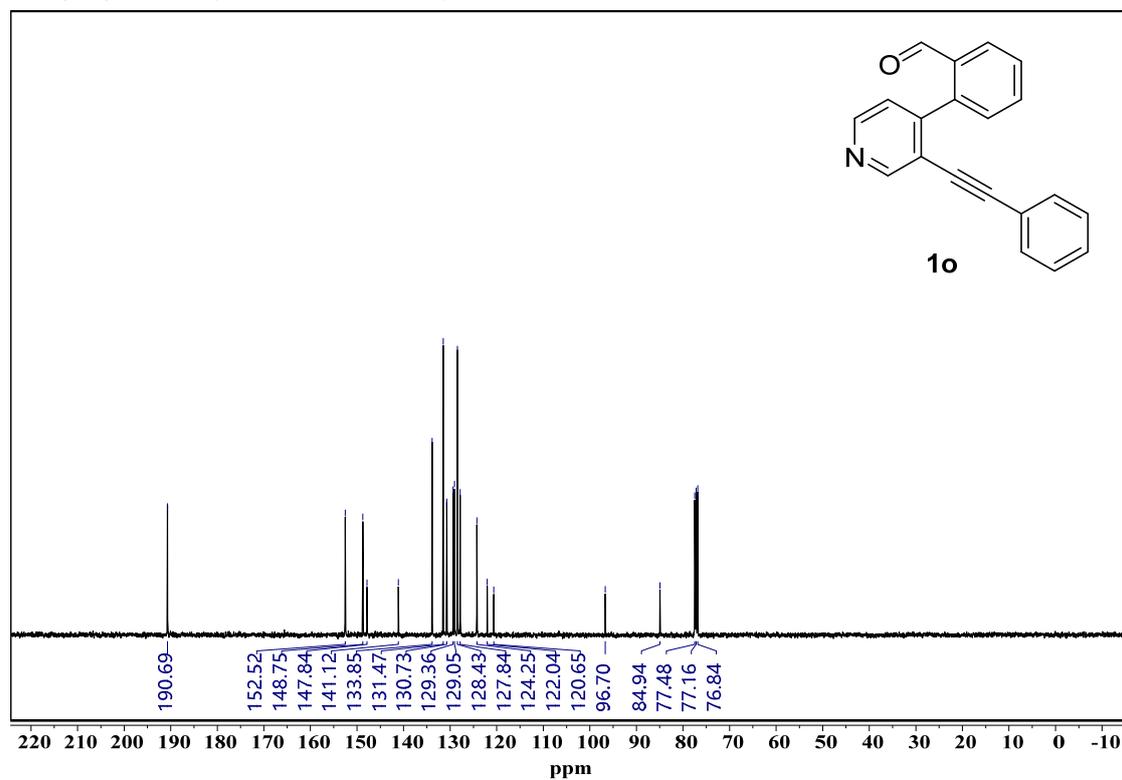
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1n**



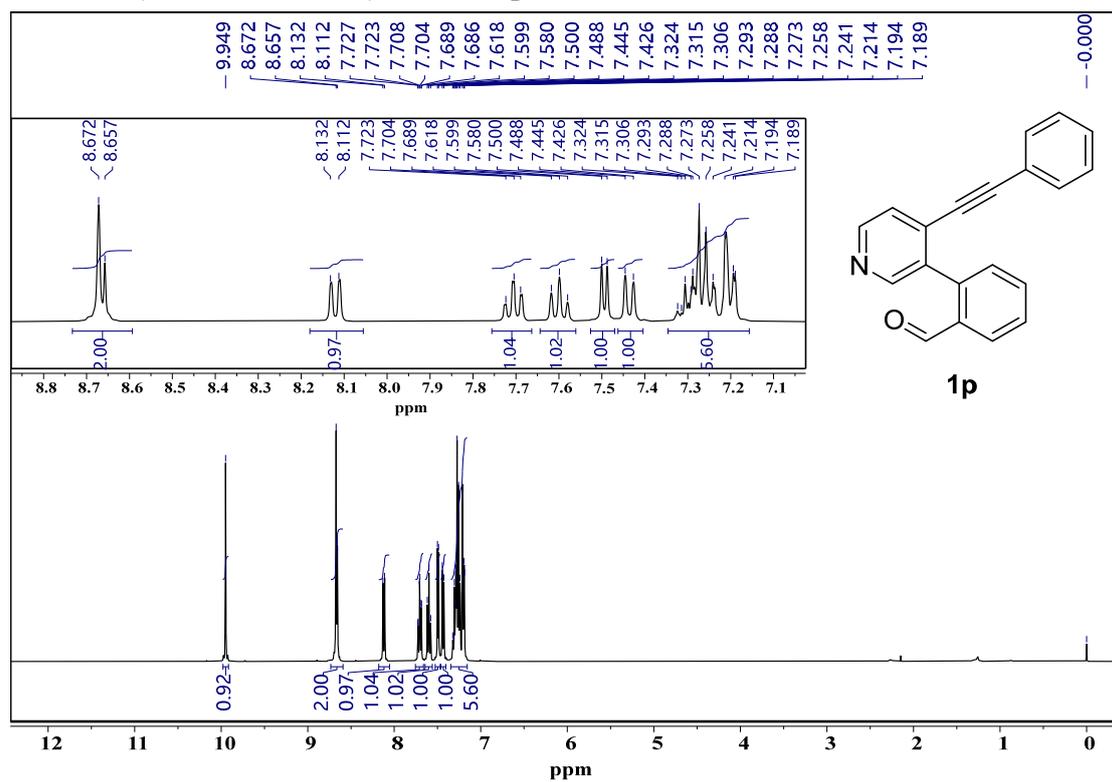
¹H NMR (400 MHz, CDCl₃) chart of **1o**



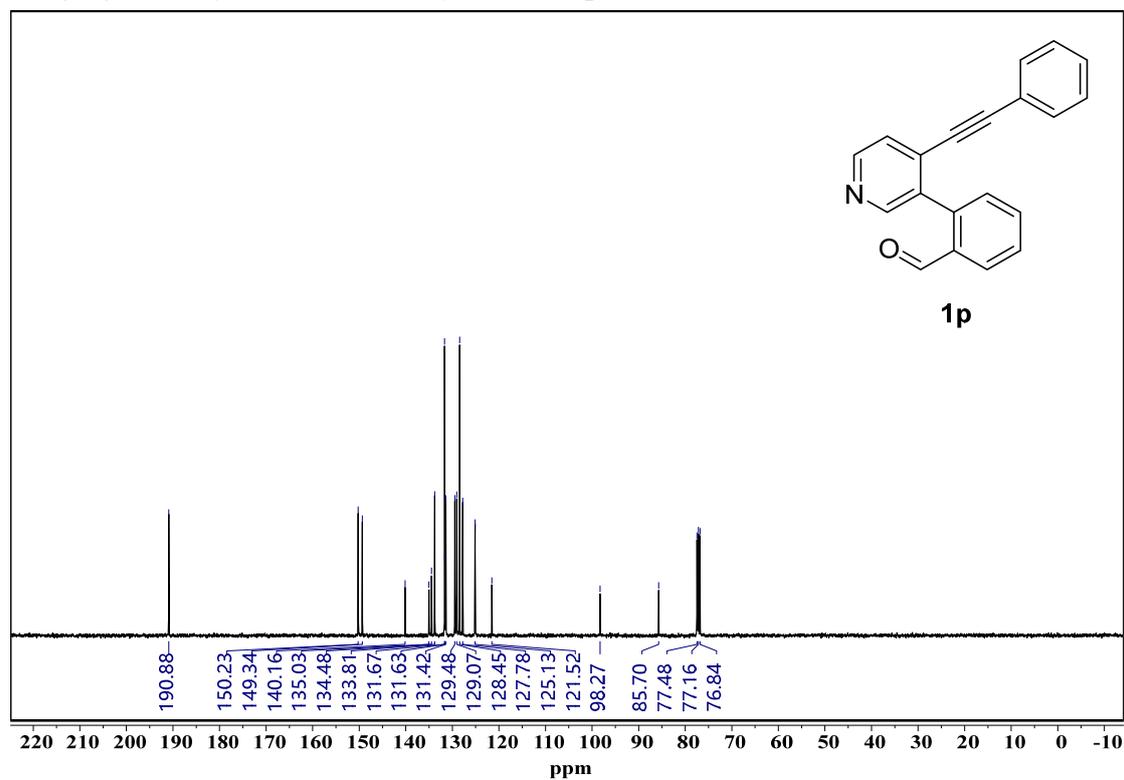
¹³C{¹H} NMR (101 MHz, CDCl₃) chart of **1o**



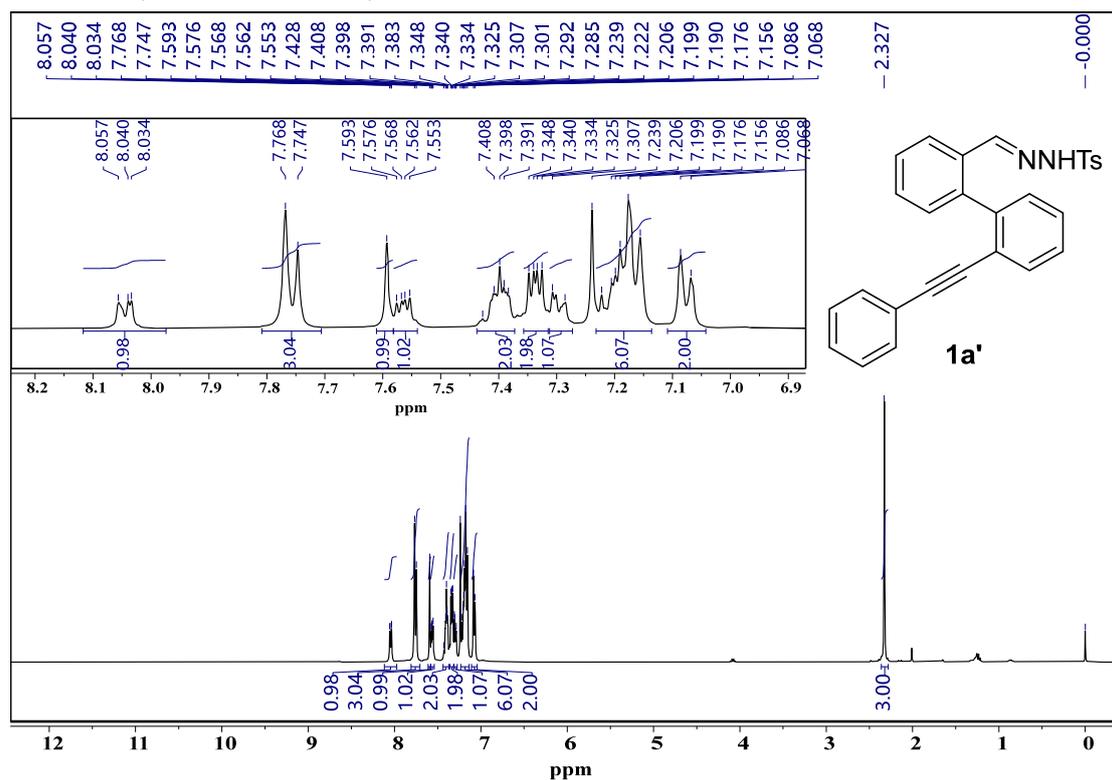
^1H NMR (400 MHz, CDCl_3) chart of **1p**



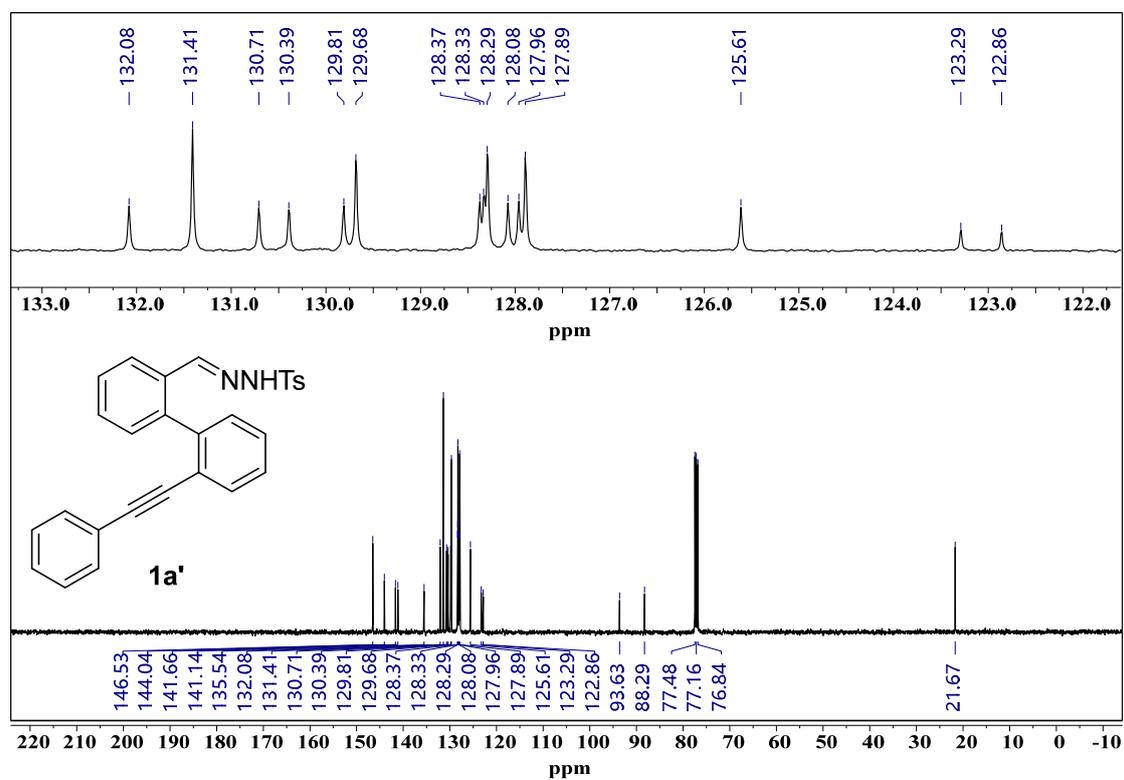
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1p**



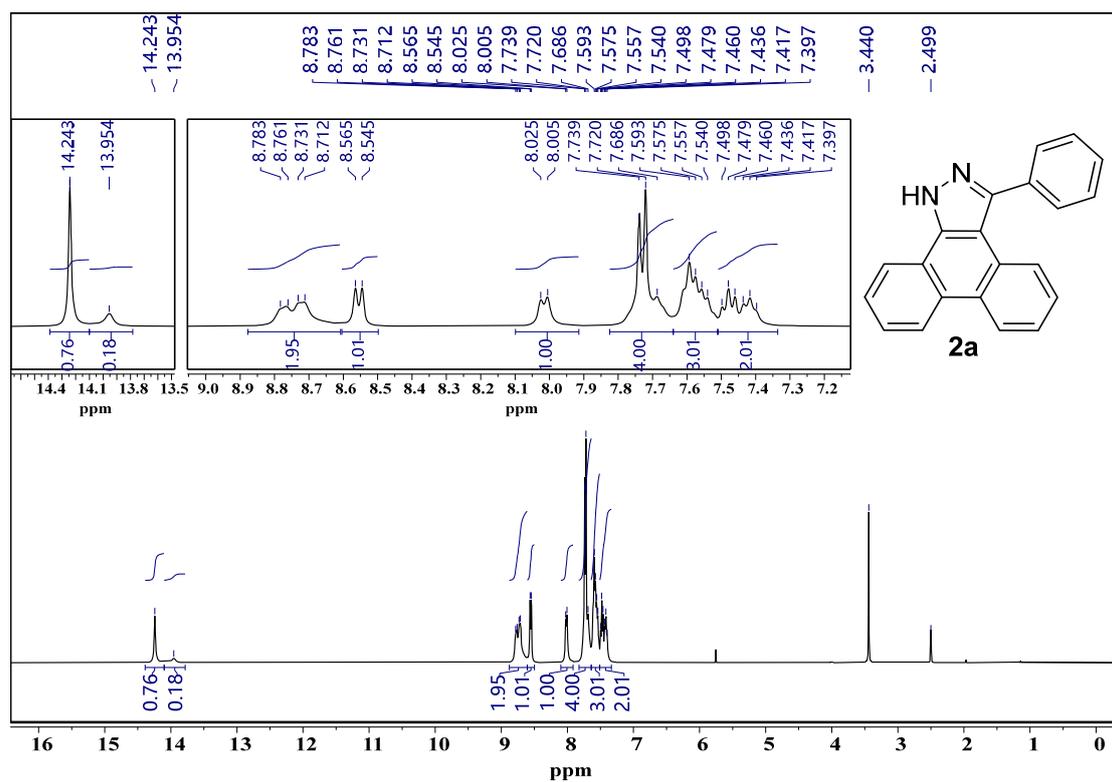
^1H NMR (400 MHz, CDCl_3) chart of **1a'**



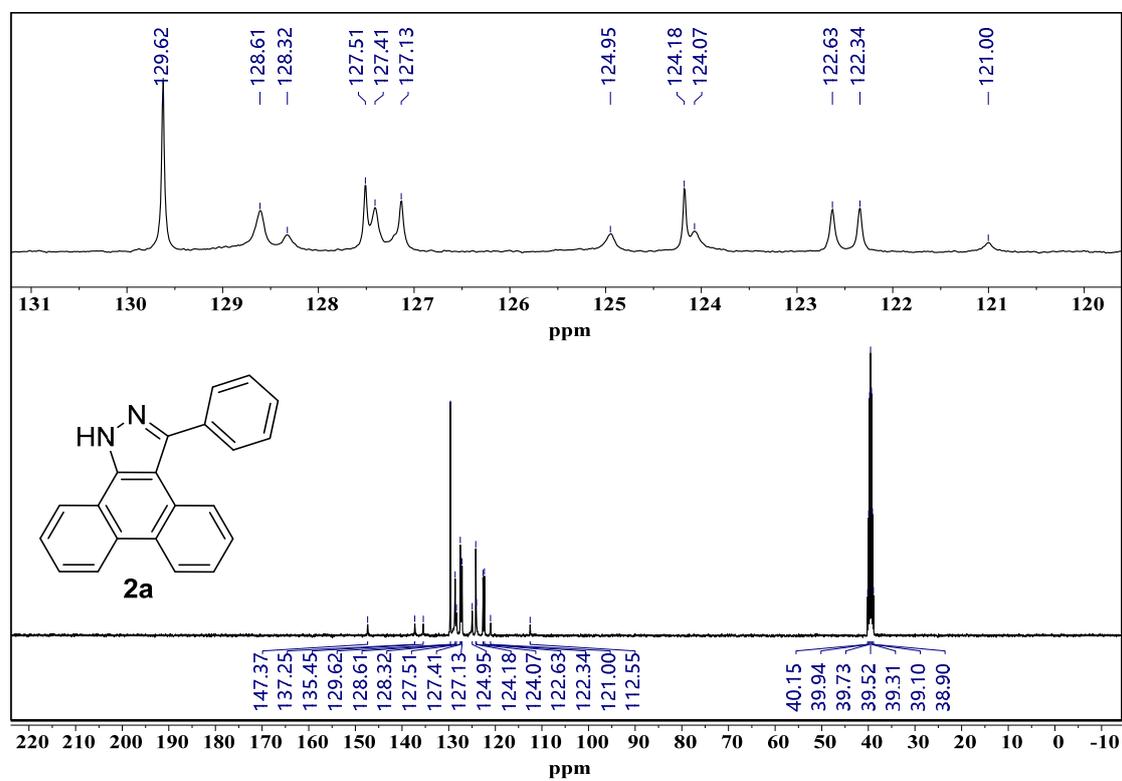
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **1a'**



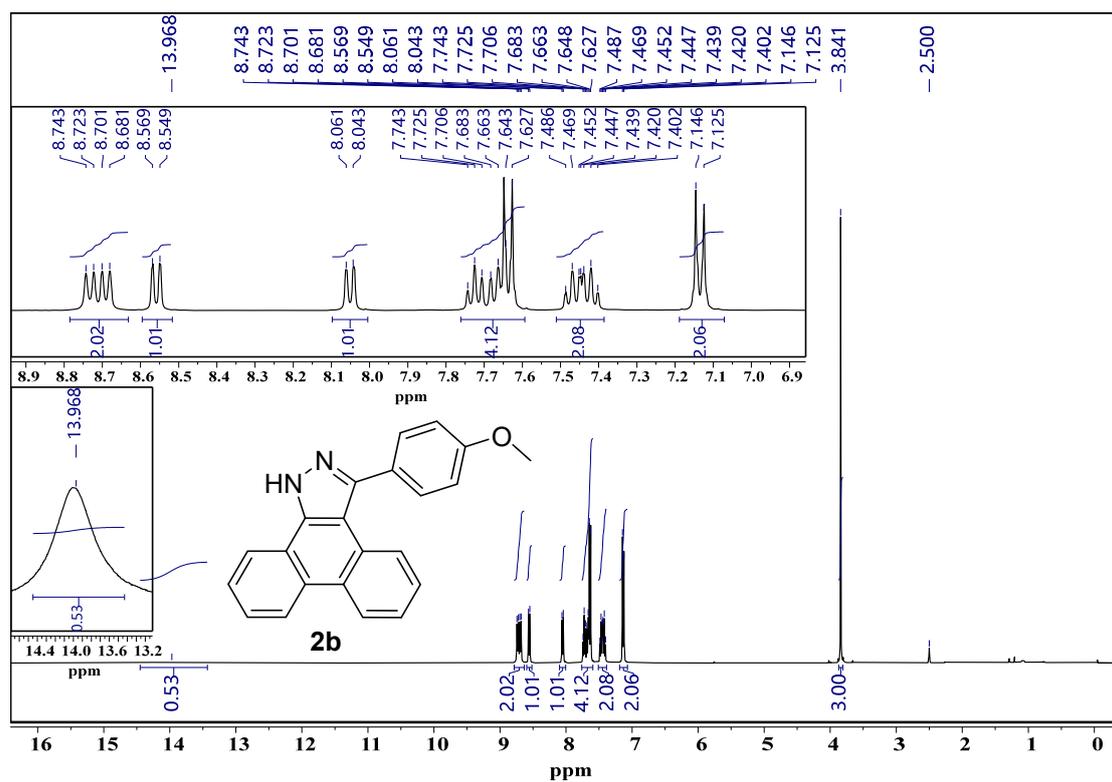
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2a**



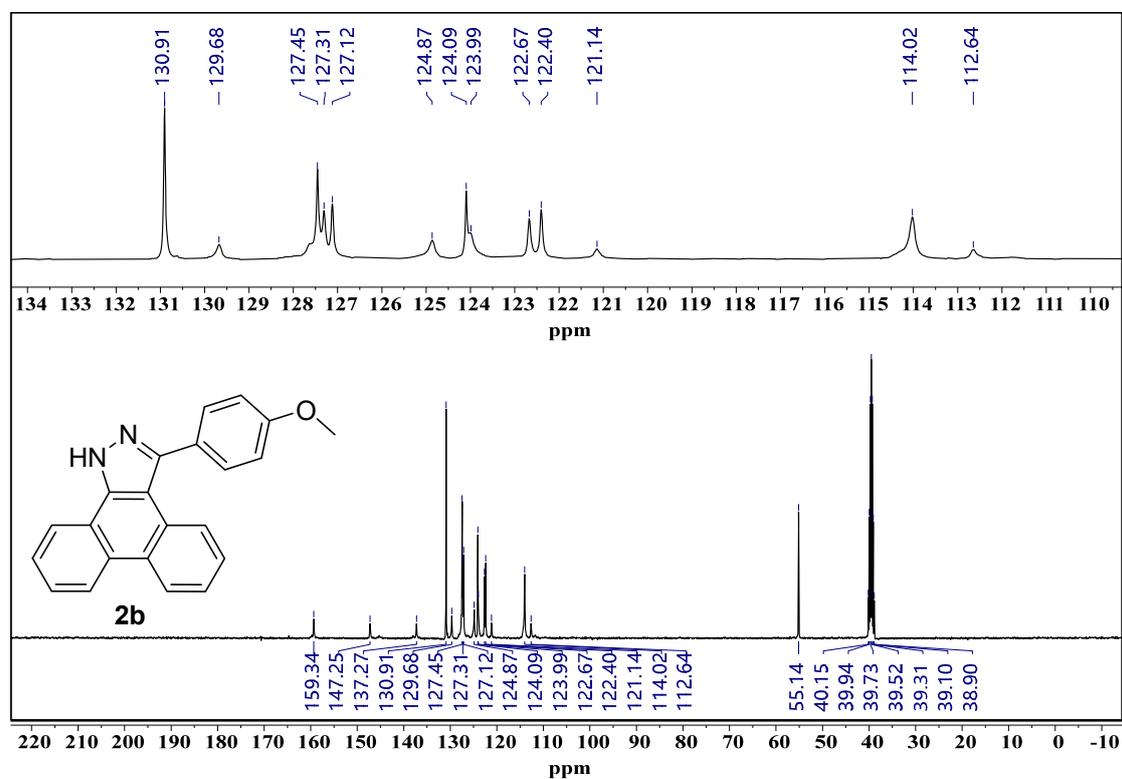
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2a**



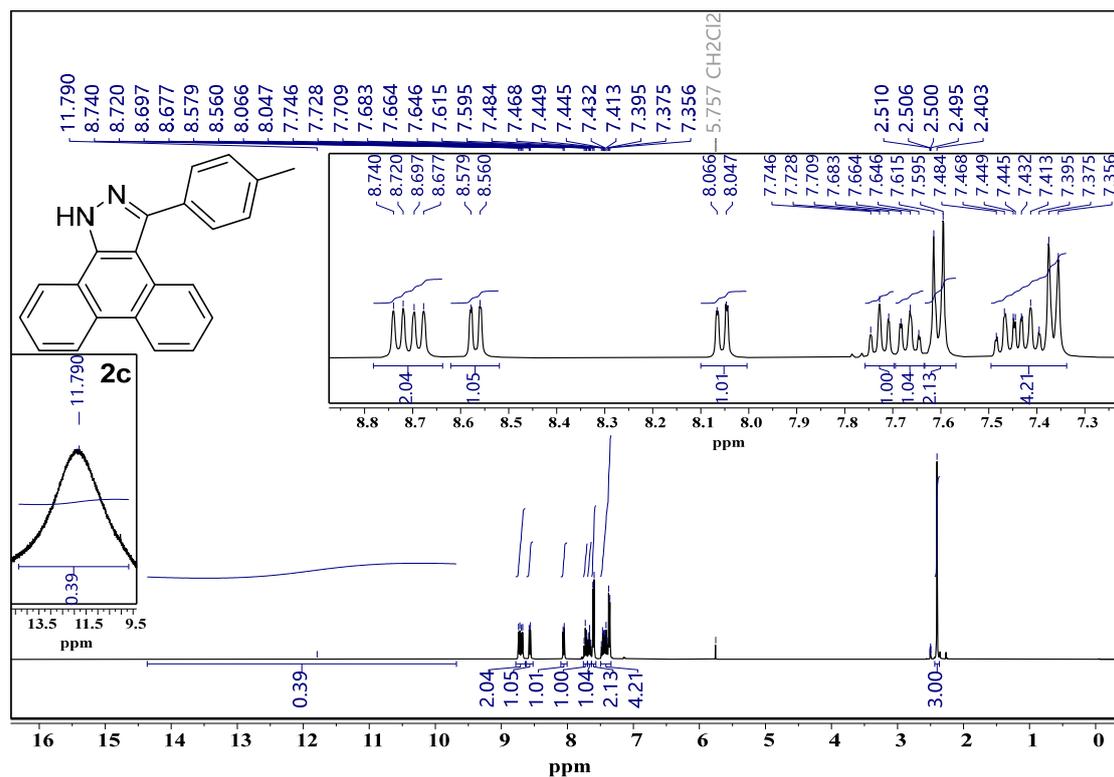
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2b**



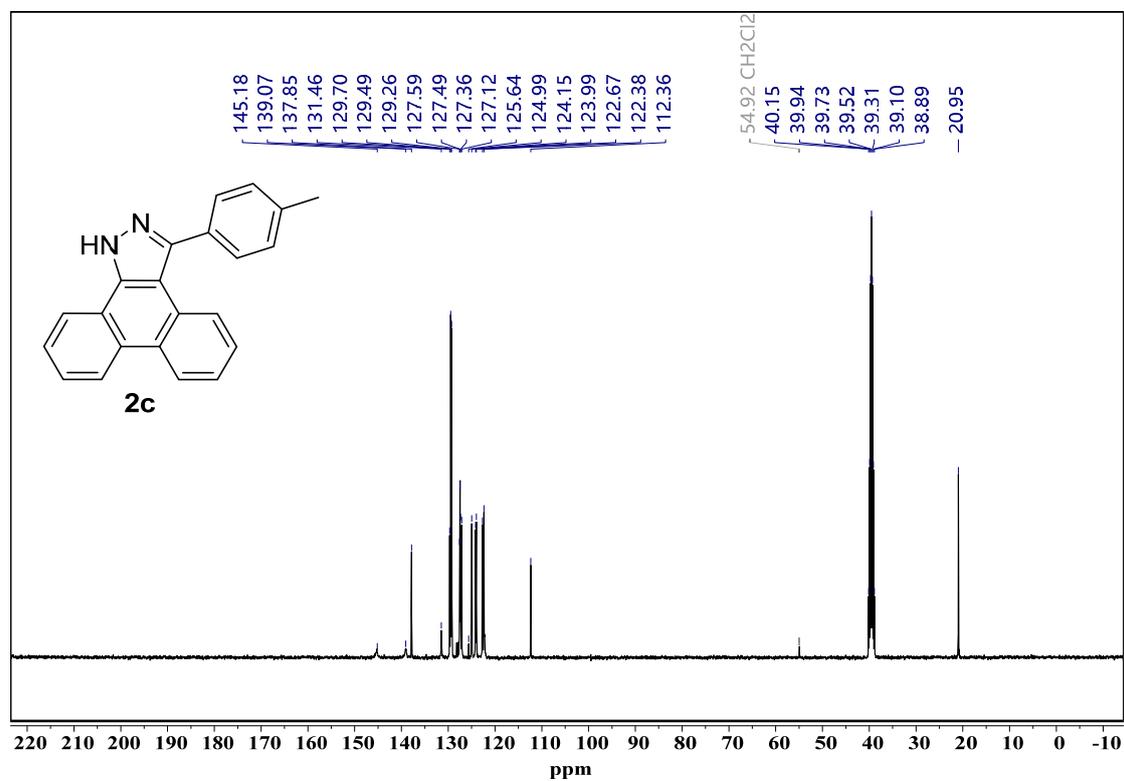
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2b**



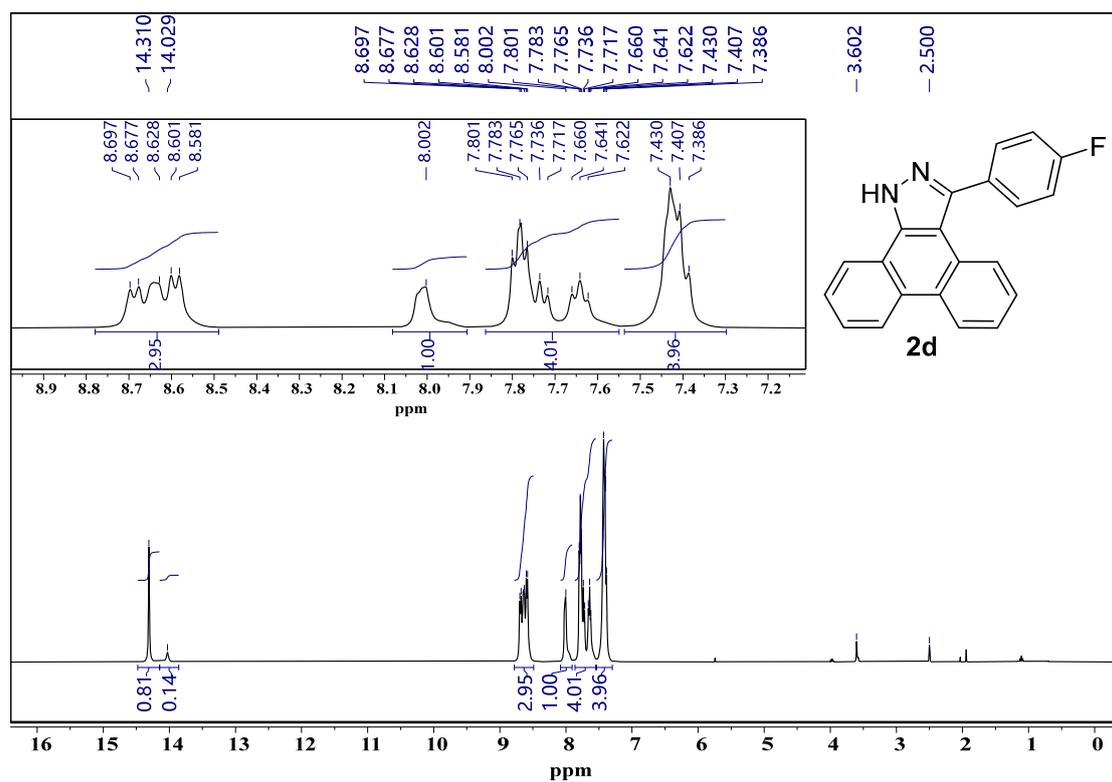
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2c**



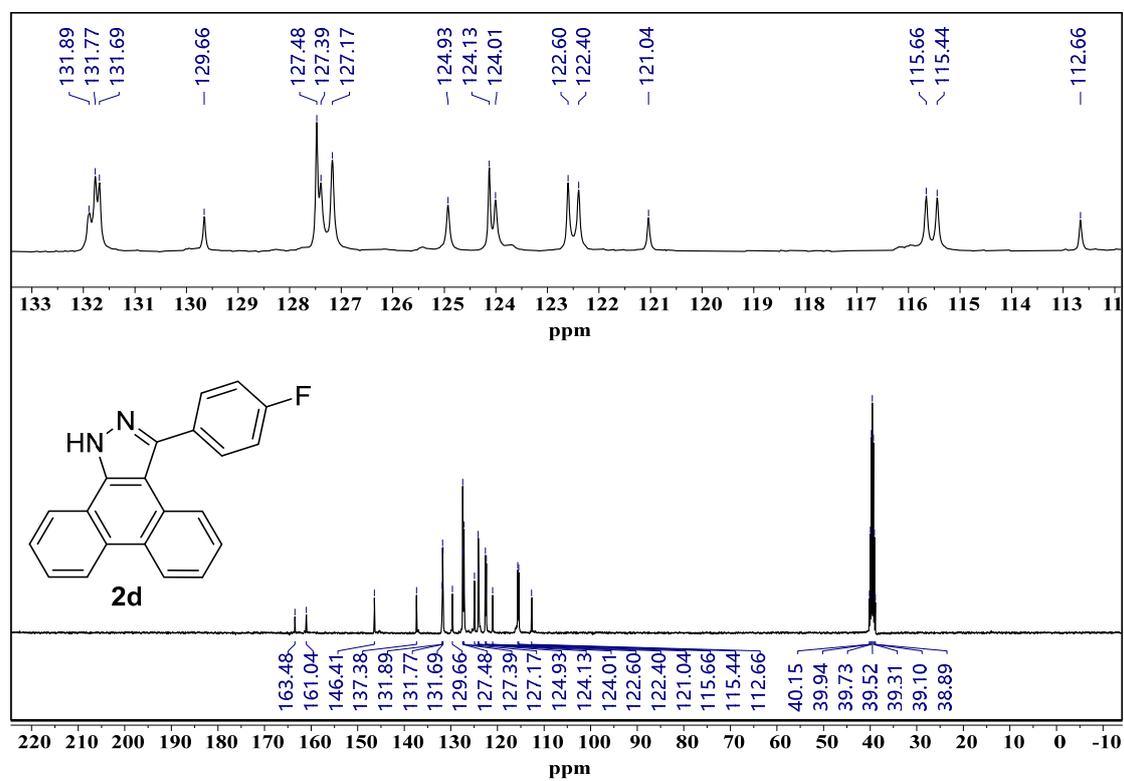
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2c**



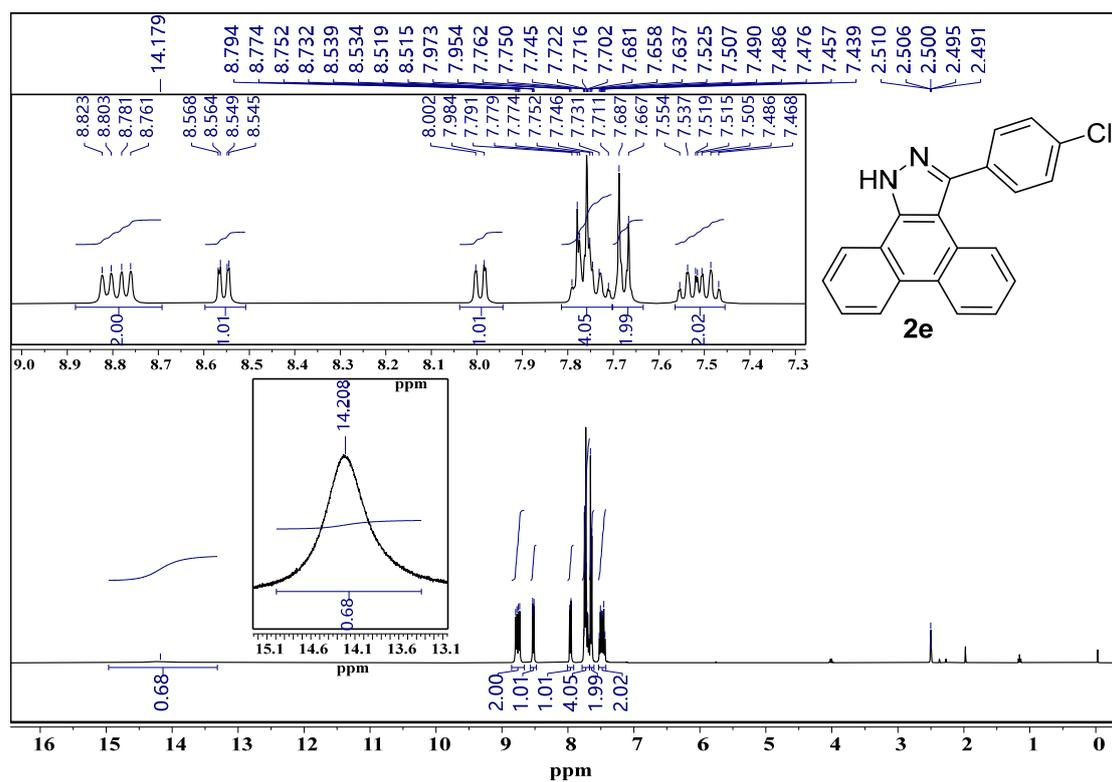
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2d**



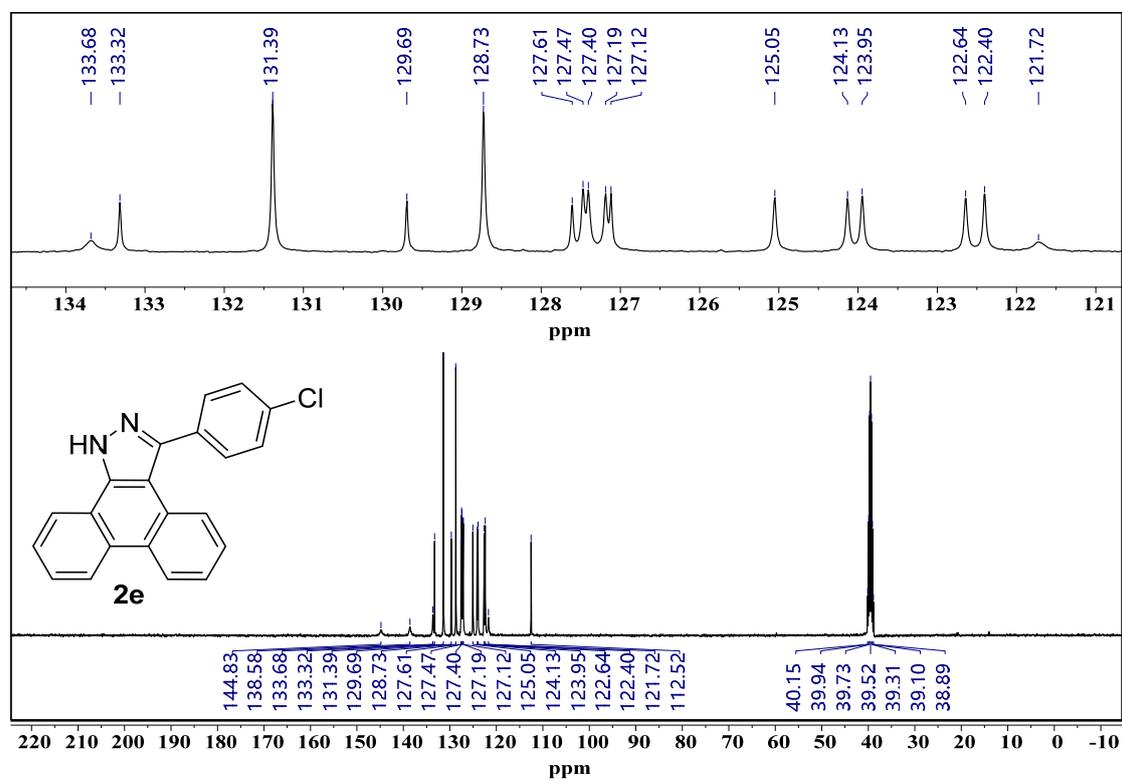
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2d**



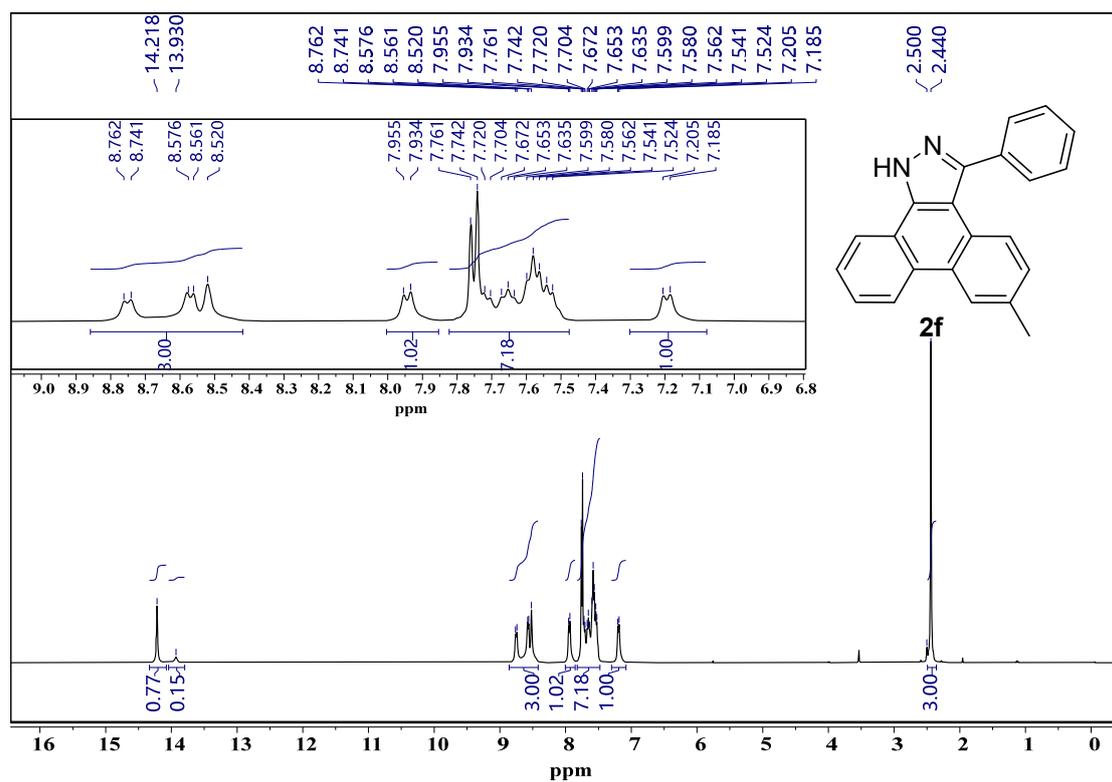
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2e**



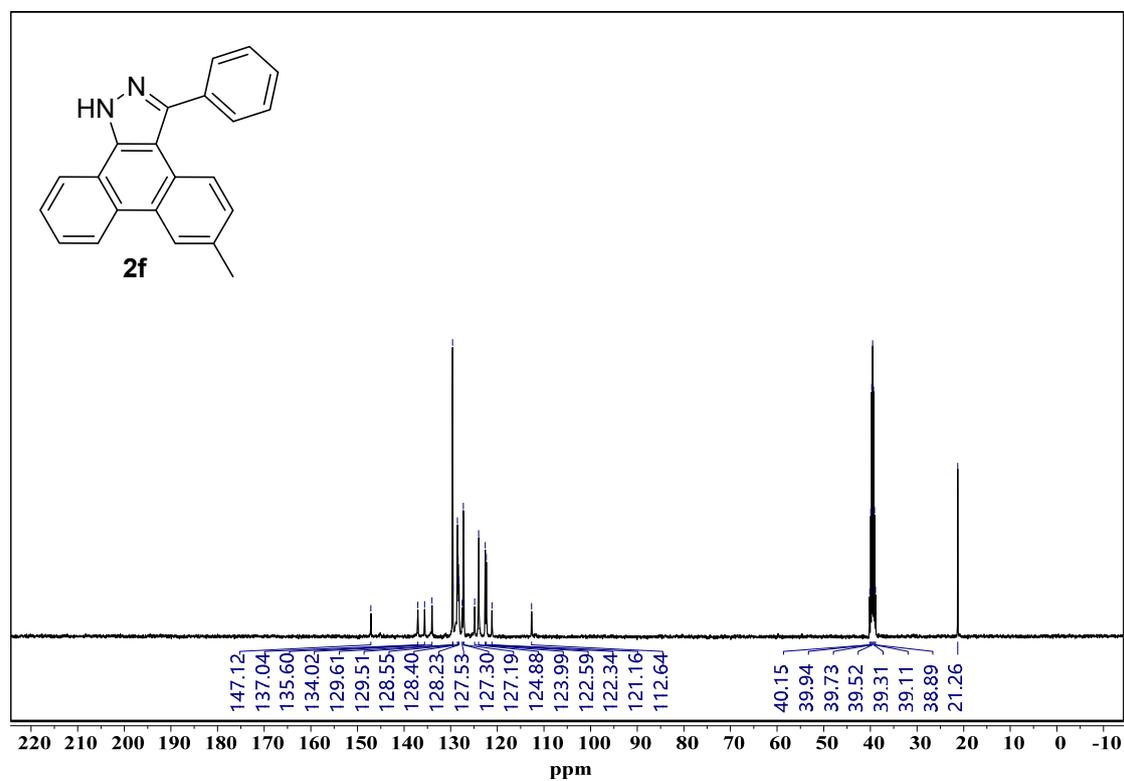
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2e**



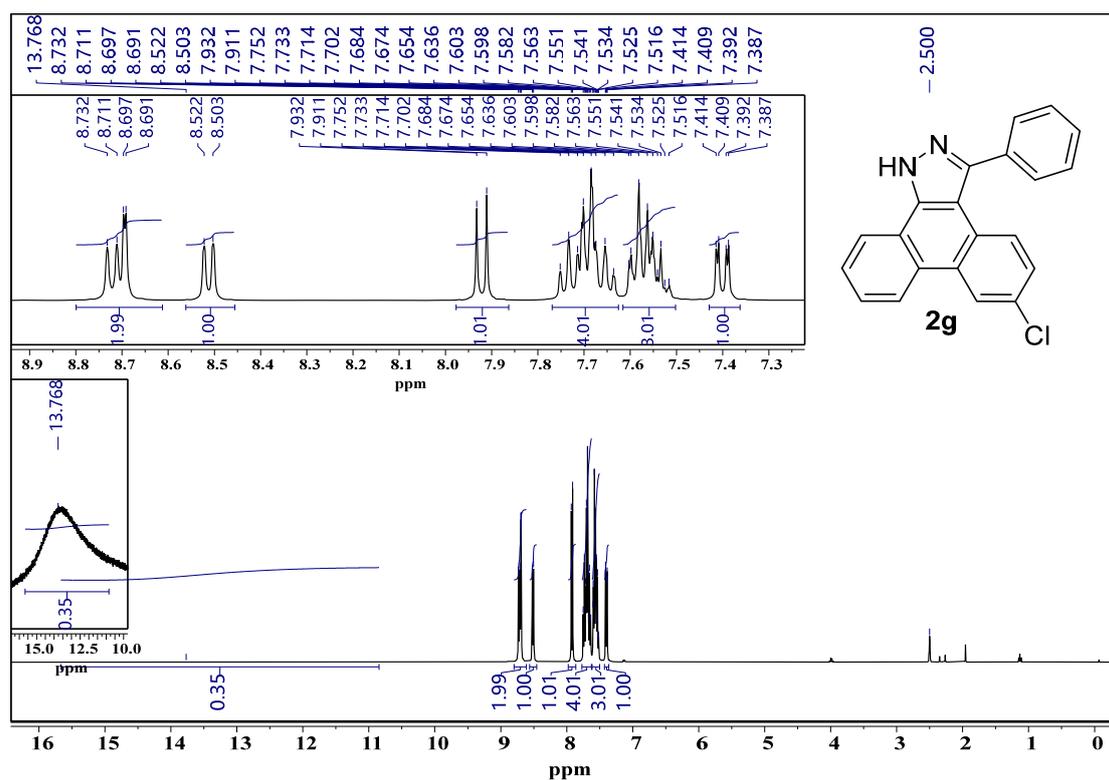
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2f**



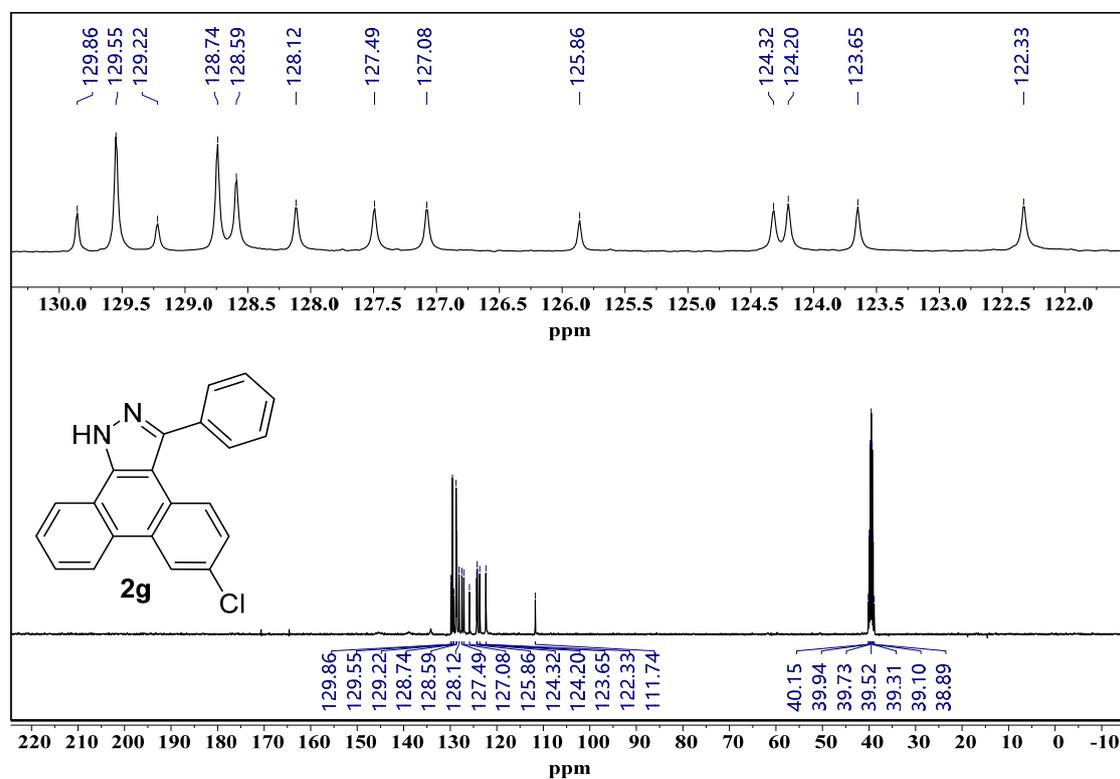
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2f**



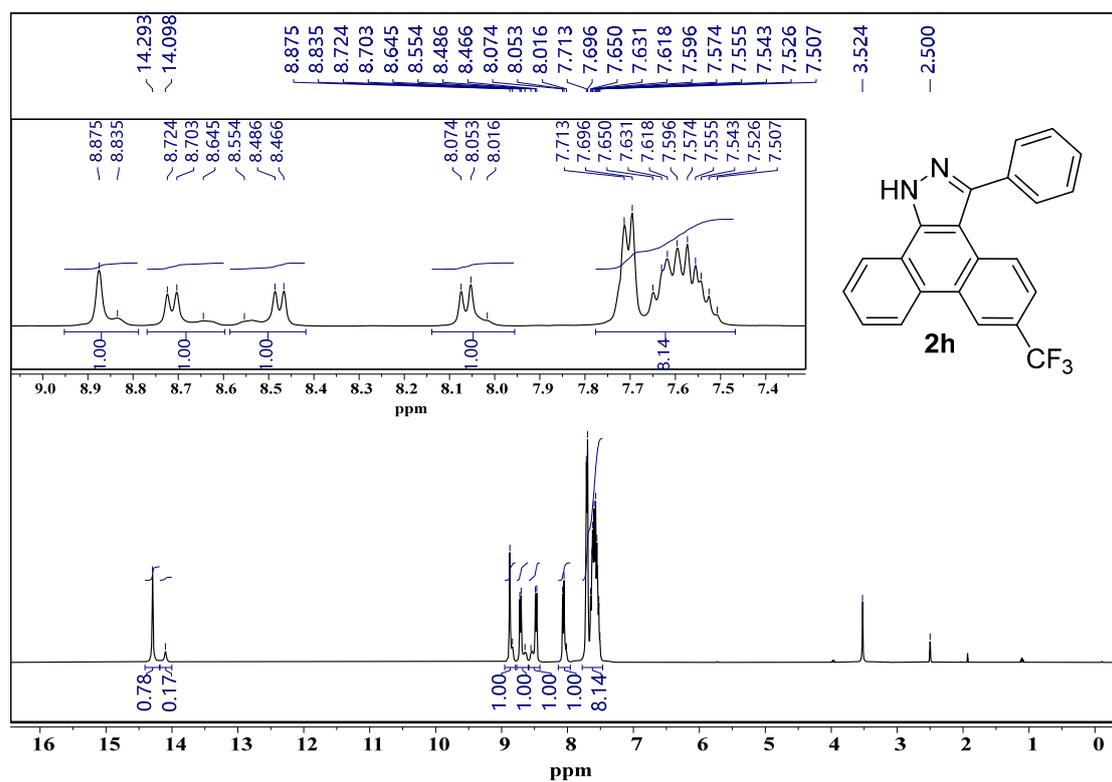
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2g**



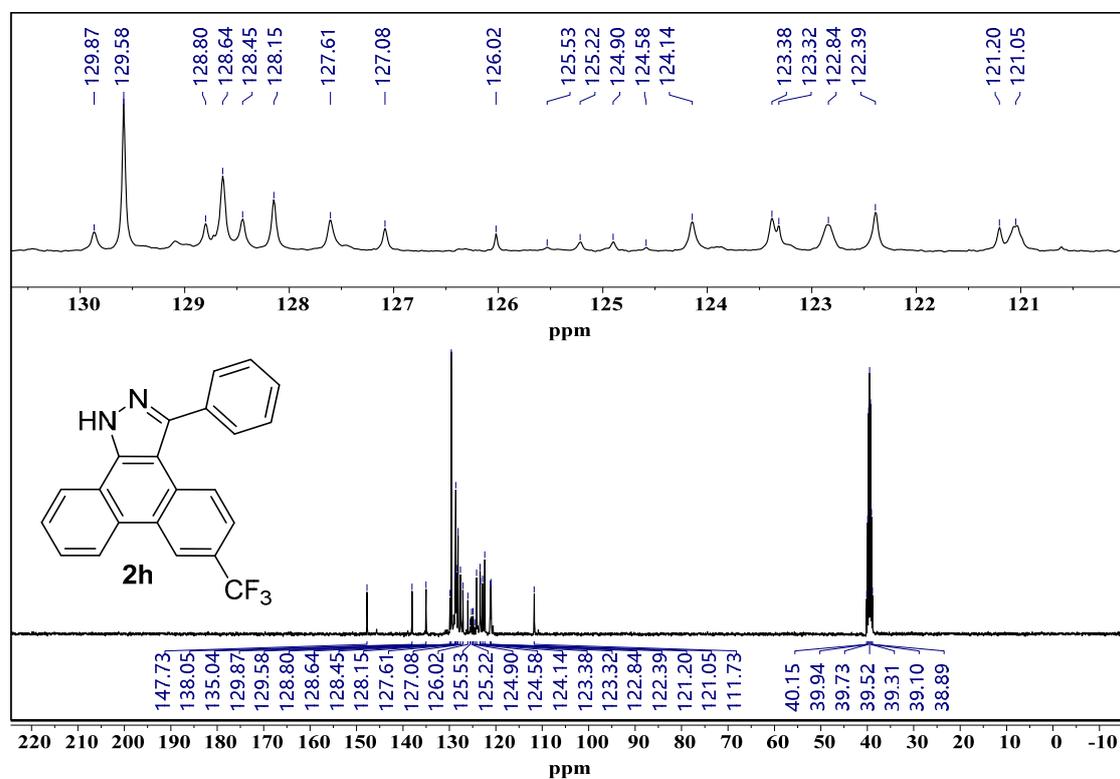
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2g**



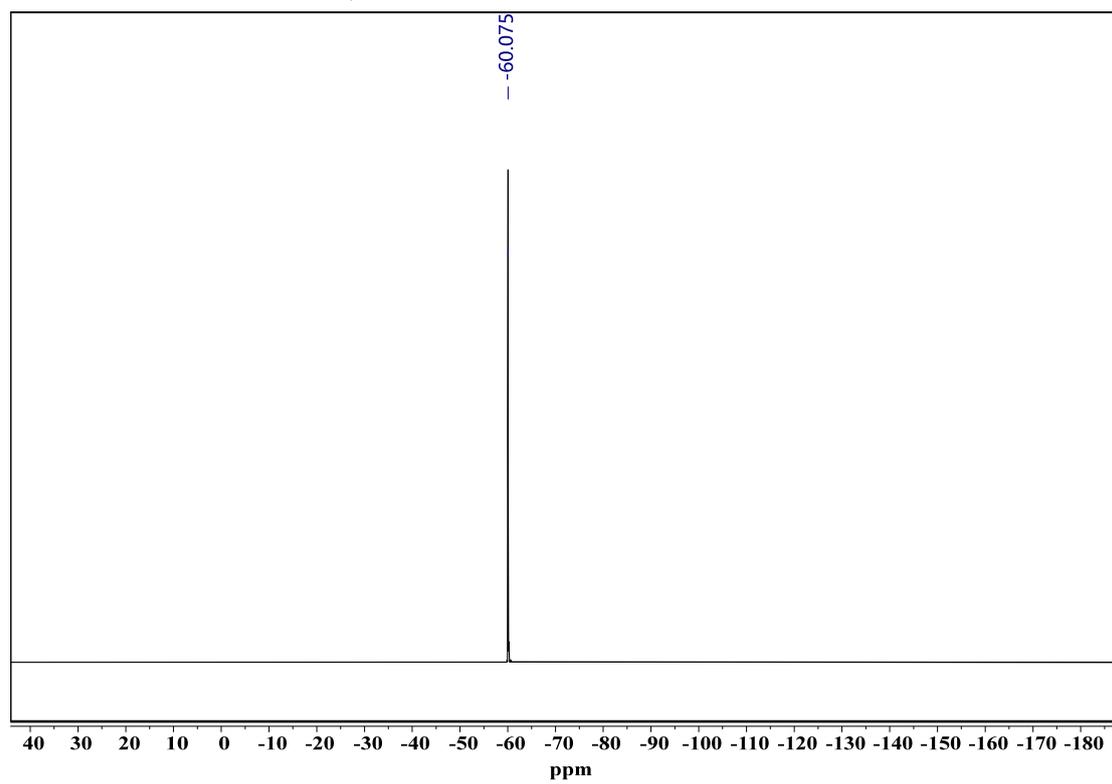
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2h**



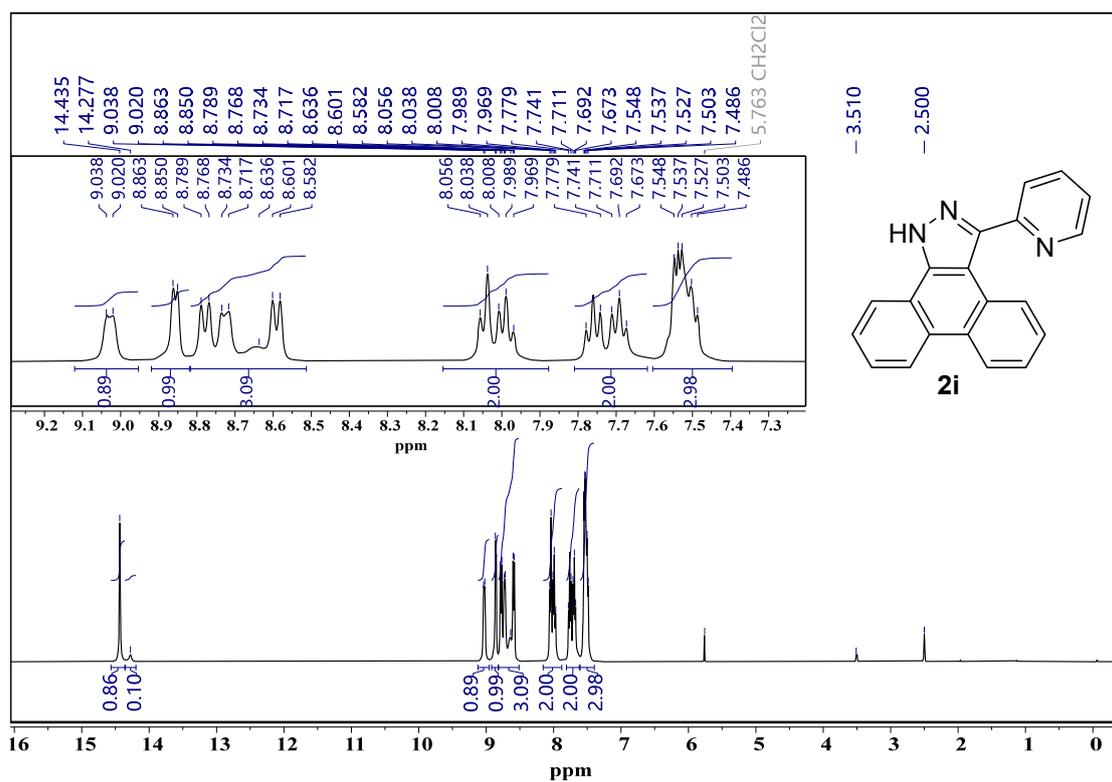
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2h**



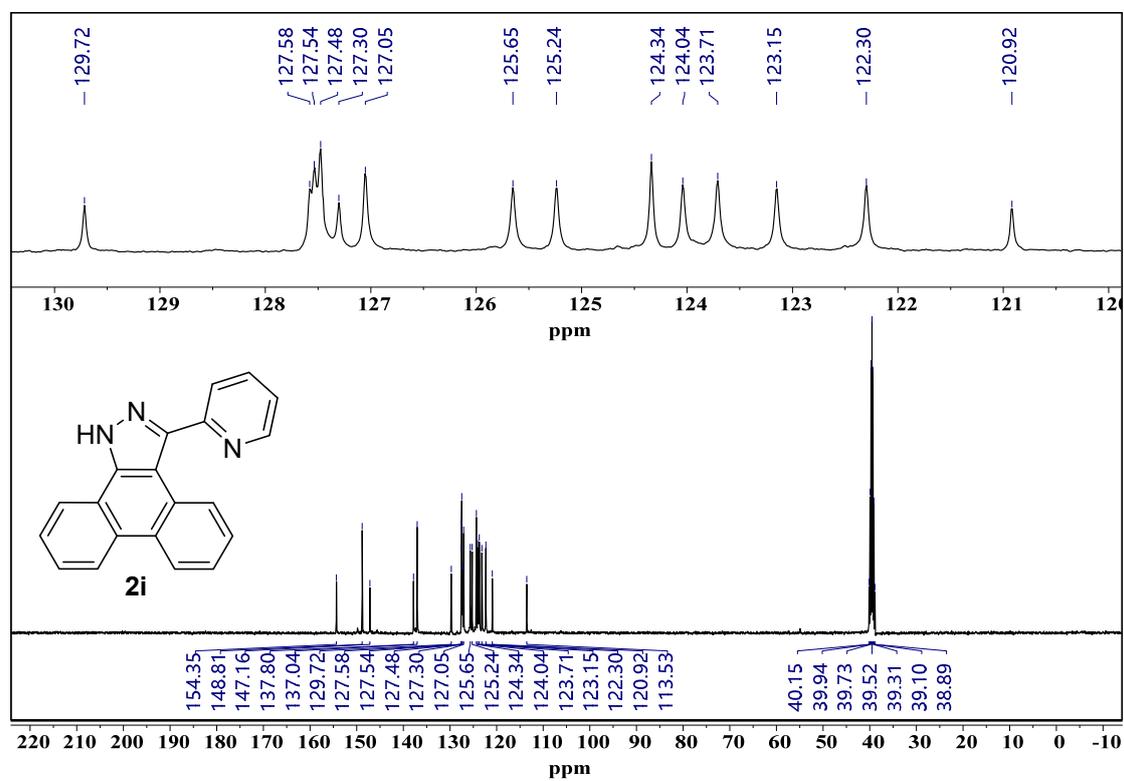
^{19}F NMR (376 MHz, CDCl_3) chart of **2h**



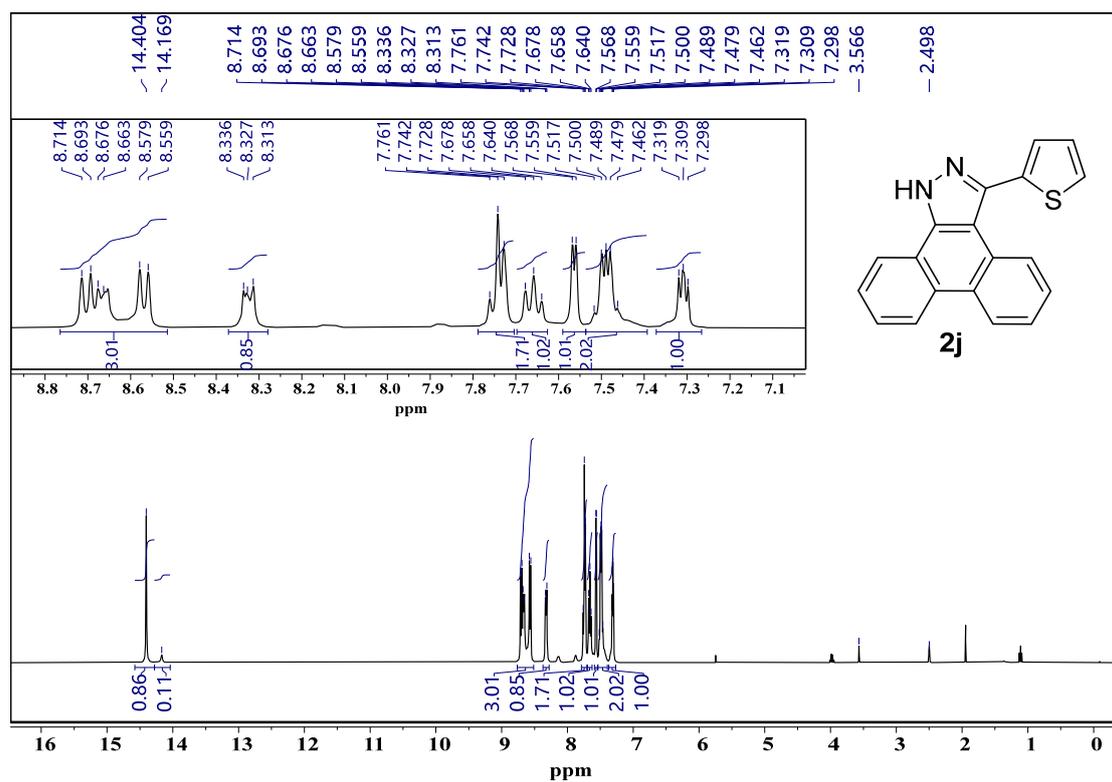
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2i**



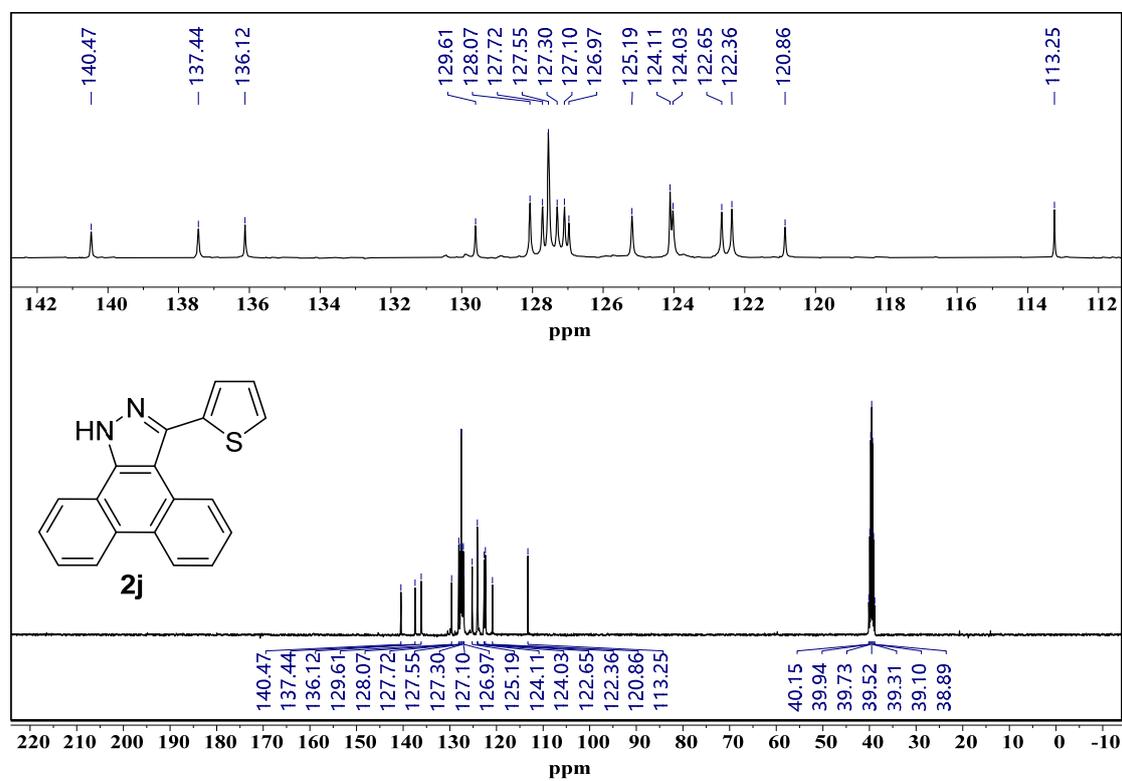
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2i**



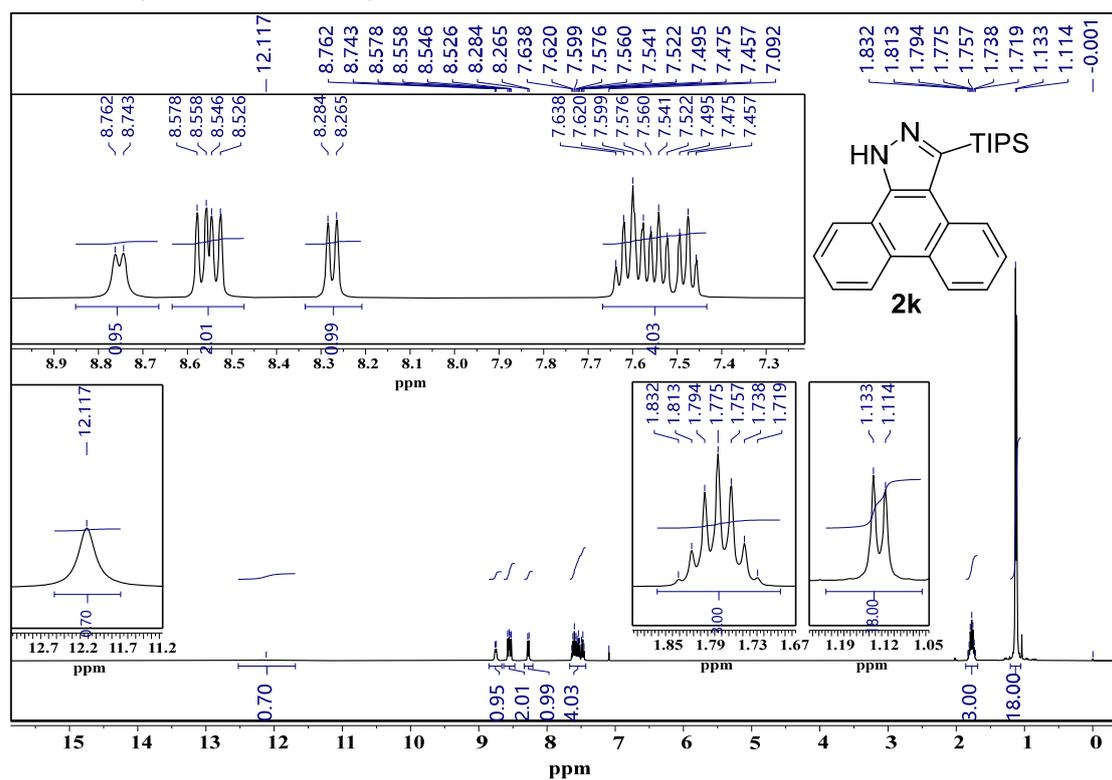
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2j**



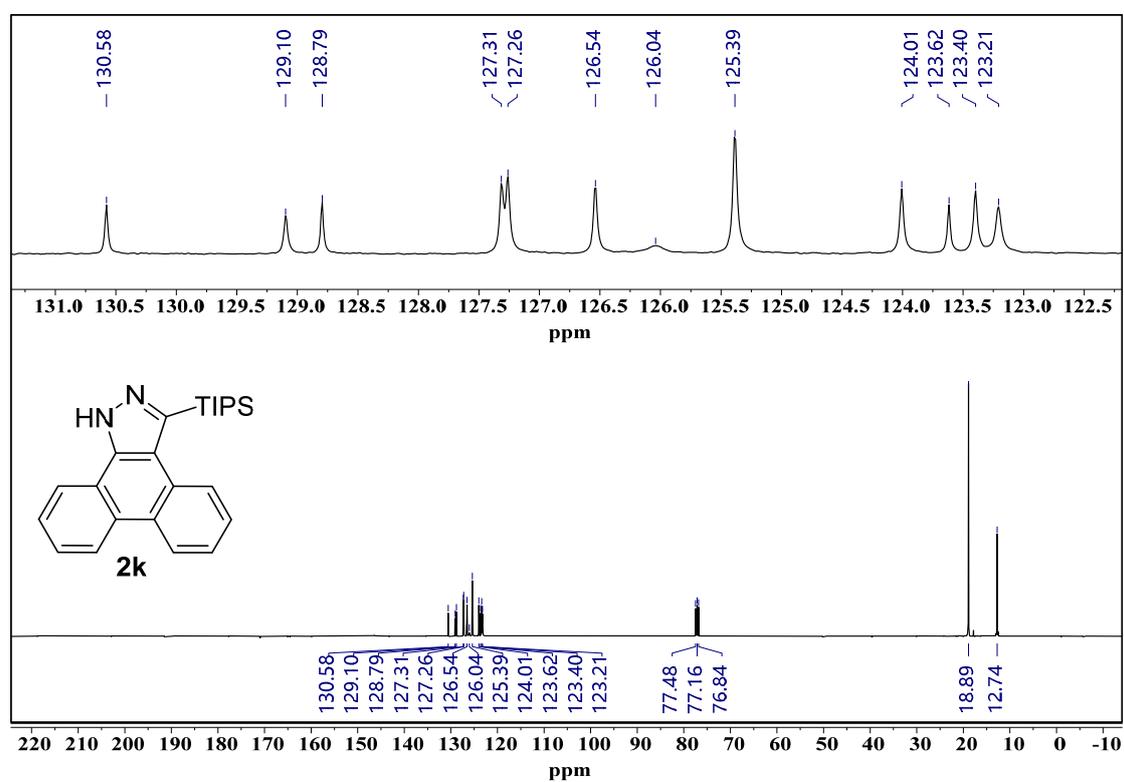
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2j**



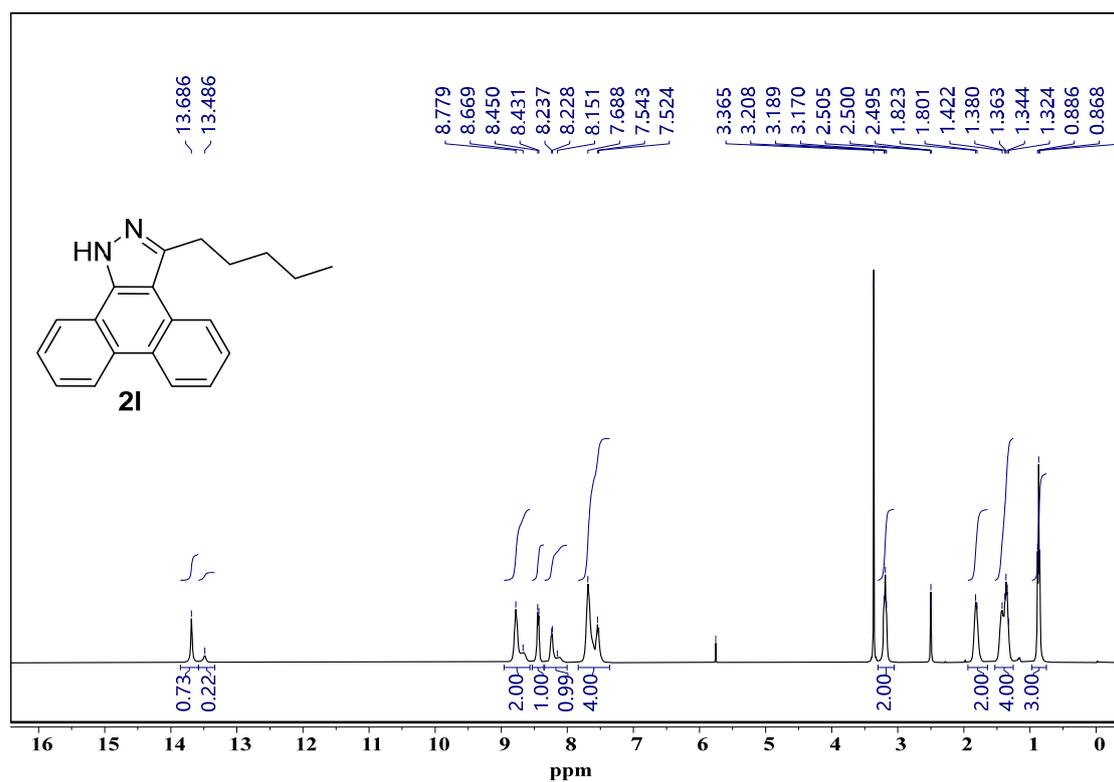
^1H NMR (400 MHz, CDCl_3) chart of **2k**



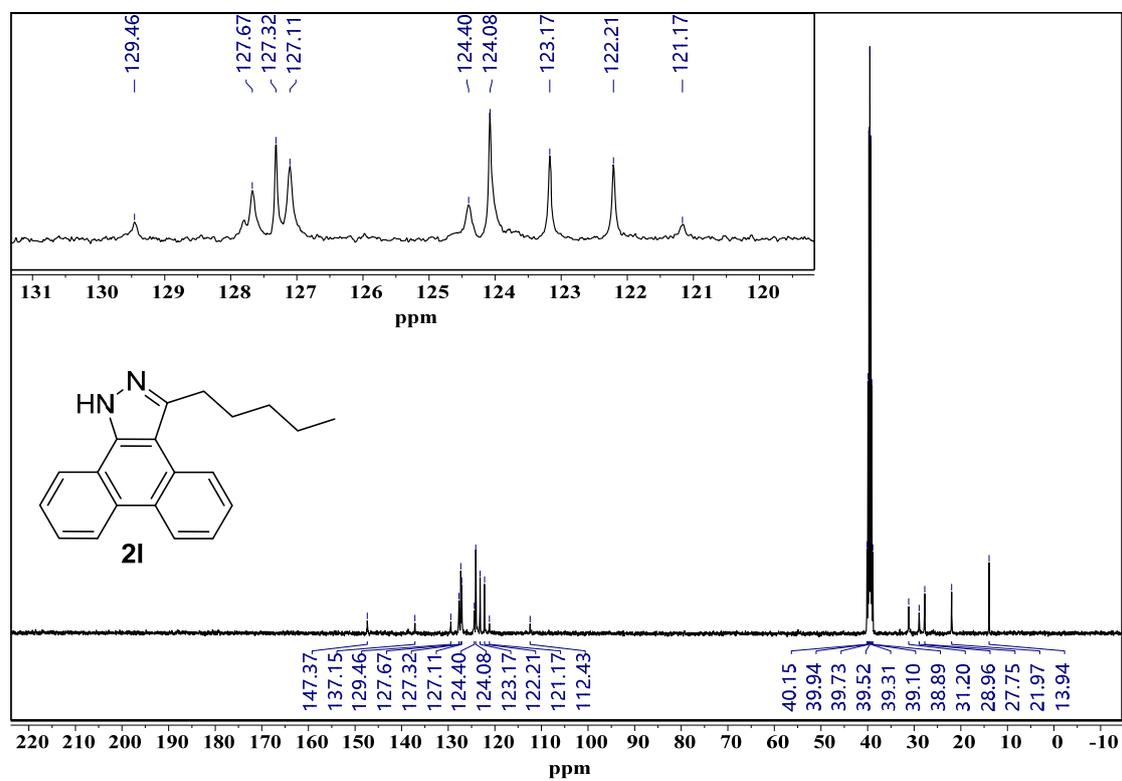
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **2k**



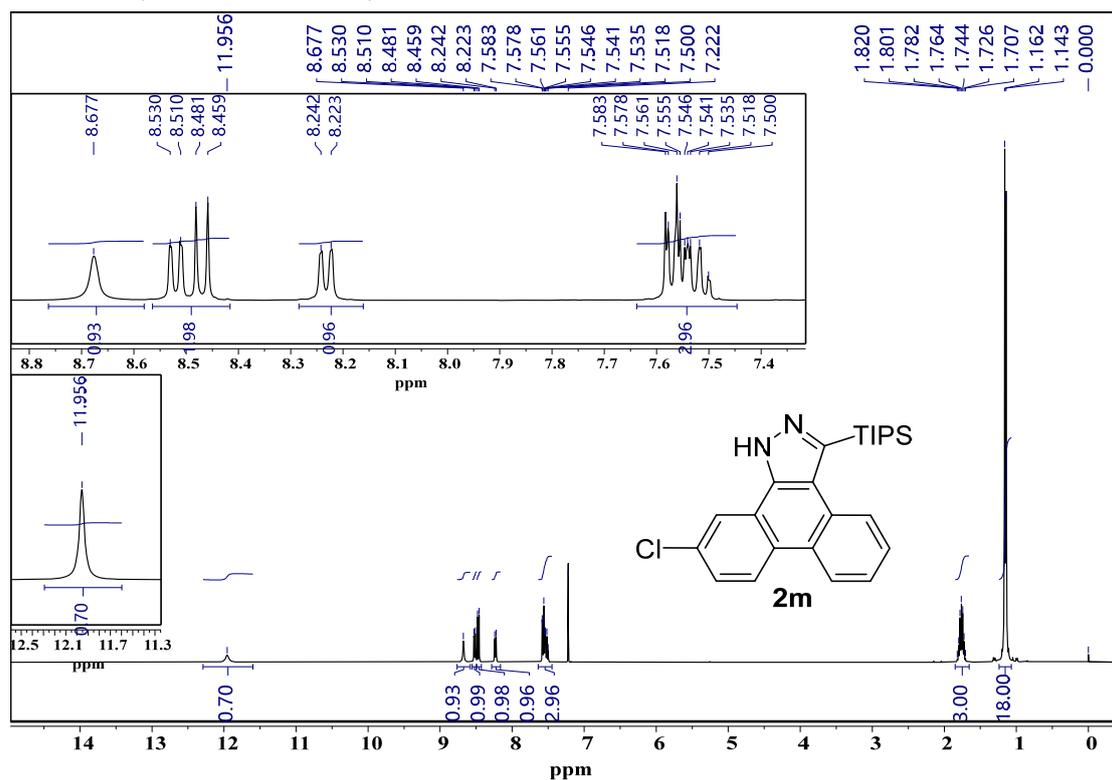
^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **21**



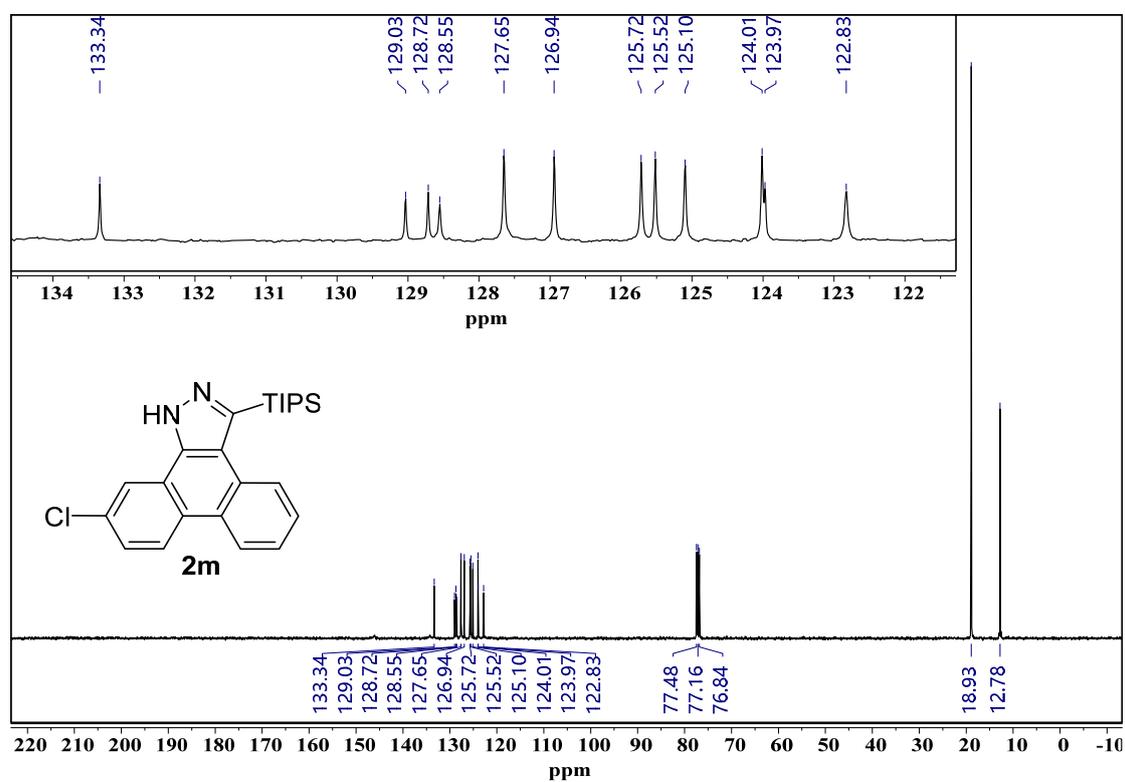
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **21**



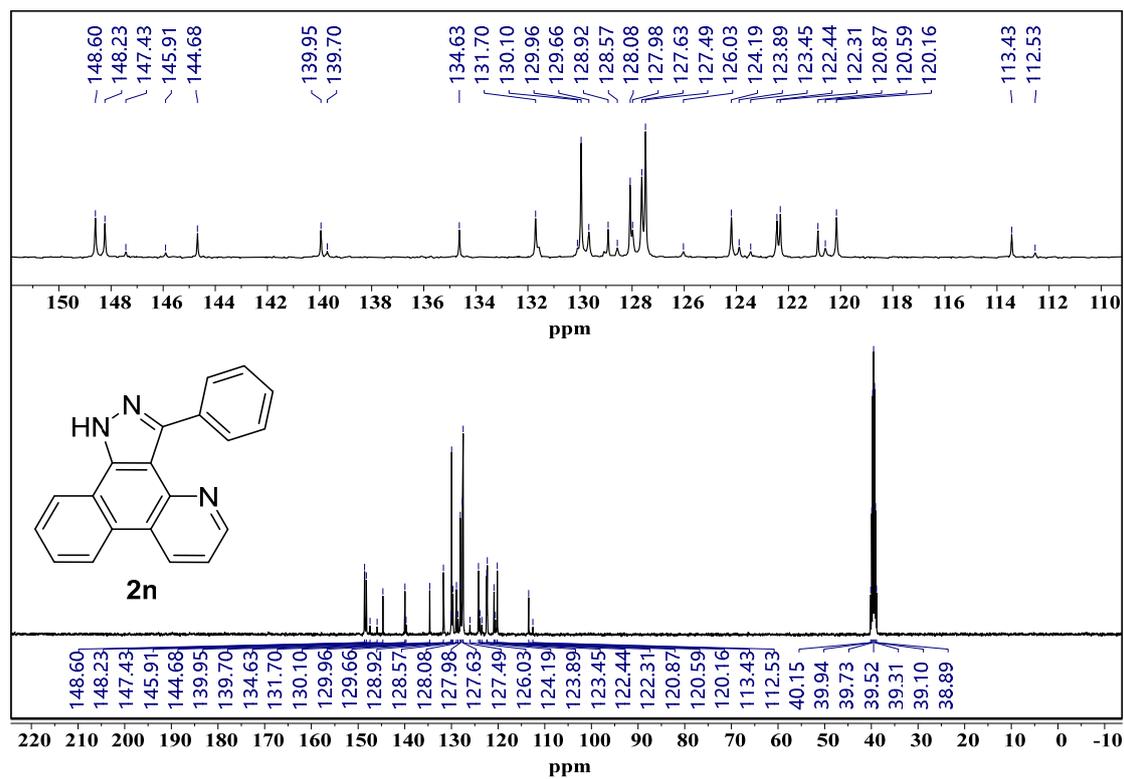
^1H NMR (400 MHz, CDCl_3) chart of **2m**



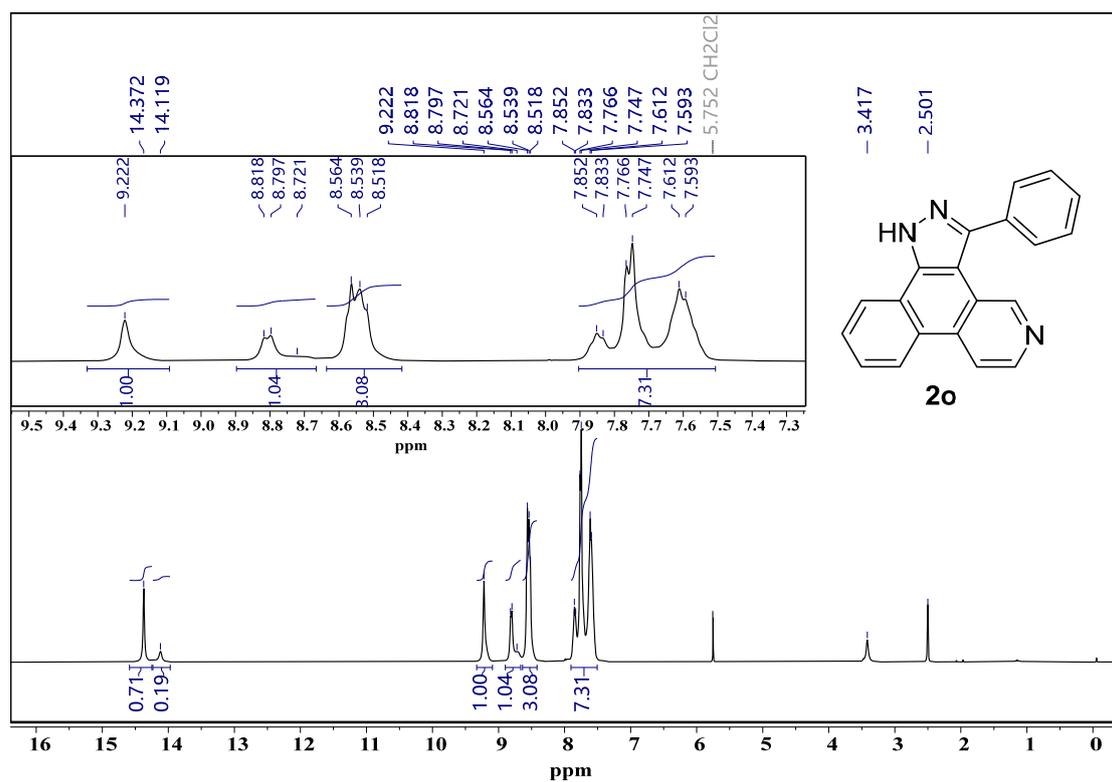
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3) chart of **2m**



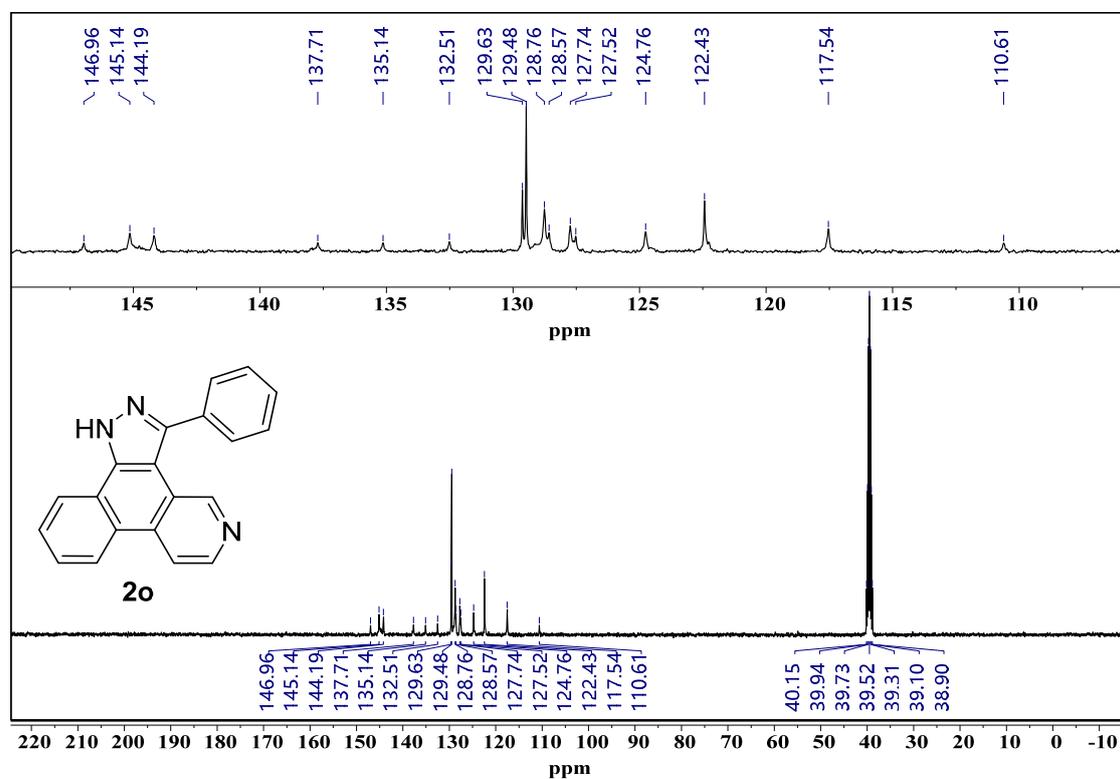
$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, DMSO- d_6) chart of **2n**



^1H NMR (400 MHz, $\text{DMSO-}d_6$) chart of **2o**



$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $\text{DMSO-}d_6$) chart of **2o**



F. References

[37] K. Bera, S. Sarkar, S. Jalal and U. Jana, *J. Org. Chem.*, 2012, **77**, 8780-8786.

[38] L. Hao, J.-J. Hong, J. Zhu and Z.-P. Zhan, *Chem. Eur. J.*, 2013, **19**, 5715-5720.