Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Multicomponent cascade reaction: Dual role of copper in the synthesis of 1,2,3-triazole tethered benzimidazo[1,2-*a*]quinoline and their photophysical studies

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Contents

1. General procedure for the synthesis of starting materials

Synthesis of substituted 2-(azidomethyl)-1*H*-benzo[*d*]imidazole:

Step 1: Substituted 2-(chloromethyl)-1*H*-benzo[*d*]imidazole was prepared according to the literature procedure.[1] Substituted *o*-phenylenediamine (0.05 mol), chloroacetic acid (0.075 mol) and 4N hydrochloric acid (50 mL) was heated under reflux for 45 minutes. The mixture was allowed to stand overnight, diluted with 100 mL of water, cooled and neutralized with sodium bicarbonate. The resultant solid was filtered, washed with cold water and dried over vacuum. The crude product was taken as such for the step 2 without further purification.

Step 2: Substituted 2-(azidomethyl)-1*H*-benzo[*d*]imidazole was prepared according to the literature procedure.[1] Substituted 2-(chloromethyl)-1*H*-benzo[*d*]imidazole (0.05 mol) and NaN_3 (0.055 mol) in DMSO (40 mL) was stirred at room temperature. The reaction was monitored by TLC. After completion, diluted with 100 mL of water and extracted with diethyl ether (10 mL x 3). The combined organic extracts were washed with brine, and dried over anhydrous Na_2SO_4. After the organic solvent was removed under reduced pressure, the residue was purified by column chromatography to provide the title compound.

2-(azidomethyl)-1*H*-benzo[*d*]imidazole (1a):

Off-white solid, 6.5 g 75%, m.p. 120-121 °C; IR ν_{max} (KBr) 2103, 1433, 1309, 1271, 1031, 997, 747cm^{-1}; Characterization details (^1H and ^{13}C NMR) correlate with the literature reports.[1]

2-(azidomethyl)-5-methyl-1*H*-benzo[*d*]imidazole (1b):

Beige solid, 7.6 g 82%, m.p. 102-103 °C; IR ν_{max} (KBr) 2173, 2103, 1450, 1326, 1280, 1254, 1188, 1140, 1027, 801 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 1H), 7.38 (s, 1H), 7.11 (dd, *J* = 8.4, 1.3 Hz, 1H), 4.73 (s, 2H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.64, 138.19, 137.02, 133.14, 124.67, 115.33, 114.66, 48.45, 21.81.

2-(azidomethyl)-5-chloro-1*H*-benzo[*d*]imidazole (1c):

Light brown solid, 7.4 g 72%, m.p. 112-113 °C; IR ν_{max} (KBr) 2178, 2105, 1424, 1318, 1276, 1061, 1023, 800 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.30

– 7.26 (m, 1H), 4.79 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.57, 132.46, 132.28, 130.44, 127.04, 115.43, 114.39, 45.65.

2-(azidomethyl)-5-fluoro-1*H*-benzo[*d*]imidazole (1d):

Light brown solid, 6.3 g 68%, m.p. 81-82 °C; IR ν_{max} (KBr) 2186, 2101, 1445, 1328, 1256, 1139, 1027, 860, 809 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (m, 1H), 7.21 (m, 1H), 6.98 (m, 1H), 4.69 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.62 (d, $^1J_{CF}$ = 240.38 Hz), 150.00, 138.31, 134.99, 116.04 (d, $^3J_{CF}$ = 10.1 Hz), 111.59 (d, $^2J_{CF}$ = 25.25 Hz), 101.21 (d, $^2J_{CF}$ = 27.27 Hz), 48.39.

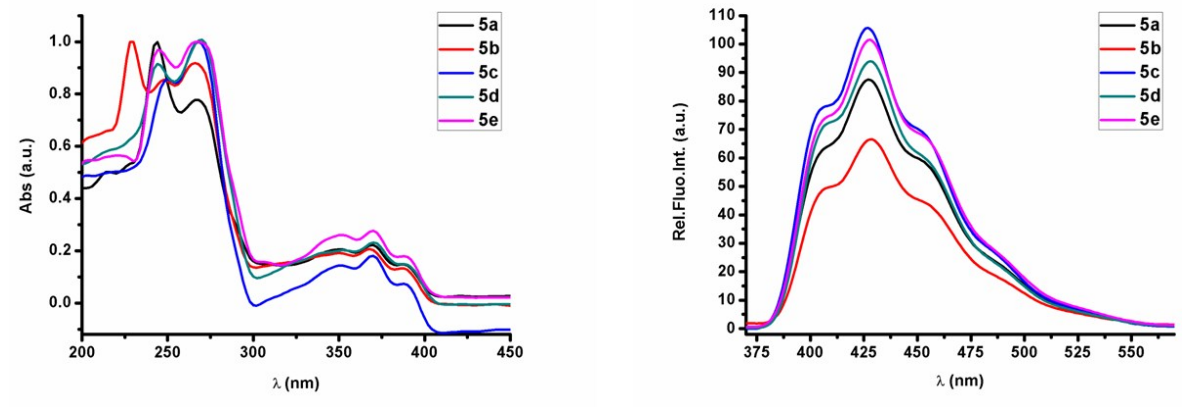
Synthesis of 6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)benzimidazo[1,2-*a*]quinoline (4a):

2-(azidomethyl)-1*H*-benzo[*d*]imidazole **1a** (3 mmol), phenylacetylene **3a** (3 mmol), $CuSO_4.5H_2O$ (0.1 mmol), sodium ascorbate (0.2 mmol) and *t*-BuOH:H_2O (1:1, 5mL) were added into a 10 mL round bottom flask. The reaction mixture was stirred at room temperature for 30 min. Reaction progress was monitored by TLC. After completion, the reaction mass was diluted with water (10 mL). Resultant precipitate was filtered and dried to obtain analytical pure product **4a**. colorless solid, 775 mg 94%, m.p. 209-210 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.20 (s, 1H), 8.05 (s, 1H), 7.79-7.77 (d, *J* = 7.8 Hz, 3H), 7.42-7.38 (t, *J* = 7.5 Hz, 2H), 7.36-7.29 (m, 2H), 7.27-7.25 (dd, *J* = 5.8, 2.8 Hz, 2H), 5.89 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.96, 130.24, 128.70, 128.10, 125.52, 120.44, 48.03; HRMS (ESI, m/z): Calcd for $C_{16}H_{14}N_5$ $[M+H]^+$ 276.1249, found 276.1251.

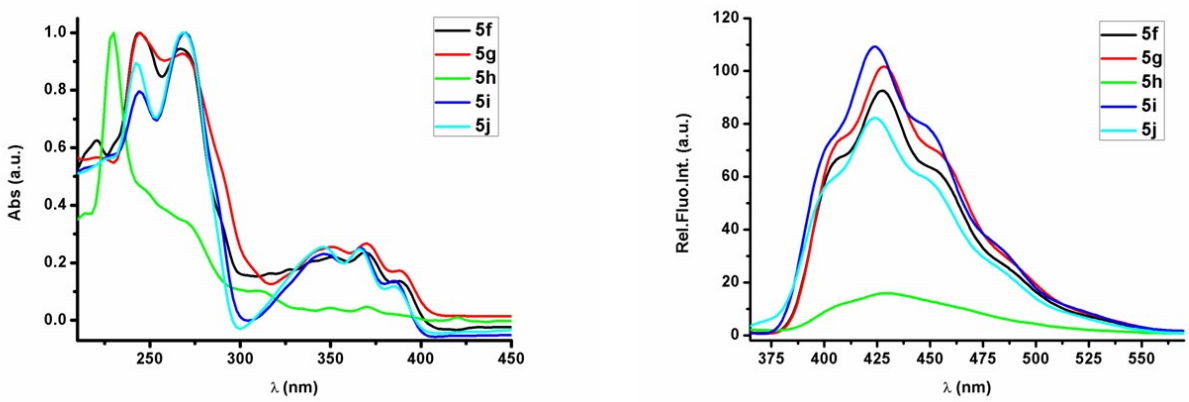
References:

1. J. Hou, Z. Li, Q. Fang, C. Feng, H. Zhang, W. Guo, H. Wang, G. Gu, Y. Tian, P. Liu, R. Liu, J. Lin, Y.–K. Shi, Z. Yin, J. Shen, P. G. Wang, *J. Med. Chem.,* 2012, **55**, 3066-3075.

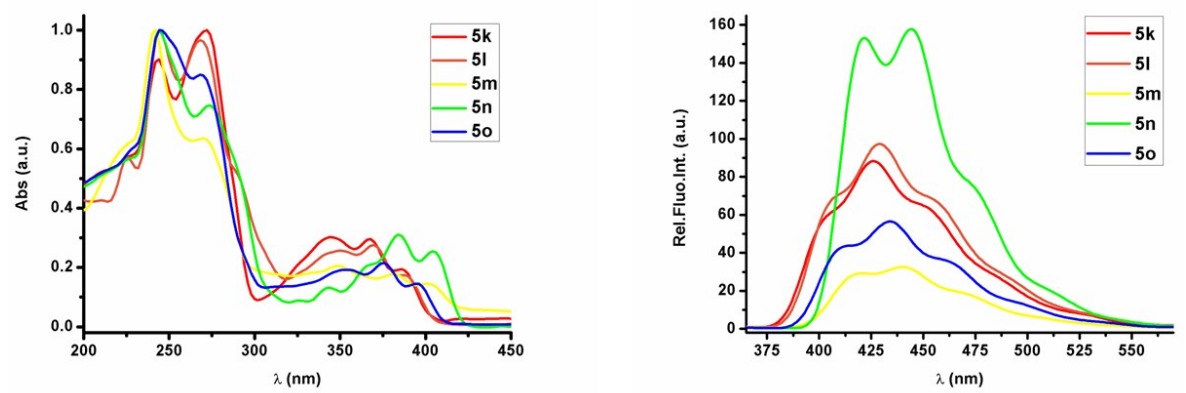
2. UV-Visible and Fluorescence spectra of 1,2,3-triazole anchored benzimidazo[1,2-*a*]quinoline (5a-u)



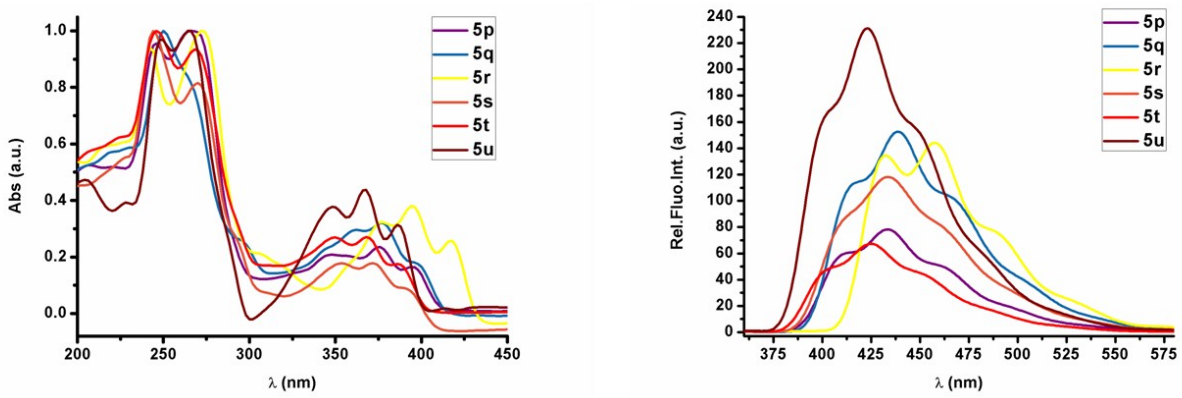
Normalized UV-Visible (left) and Fluorescence (right) spectra for compound **5a-e**



Normalized UV-Visible (left) and Fluorescence (right) spectra for compound **5f-j**



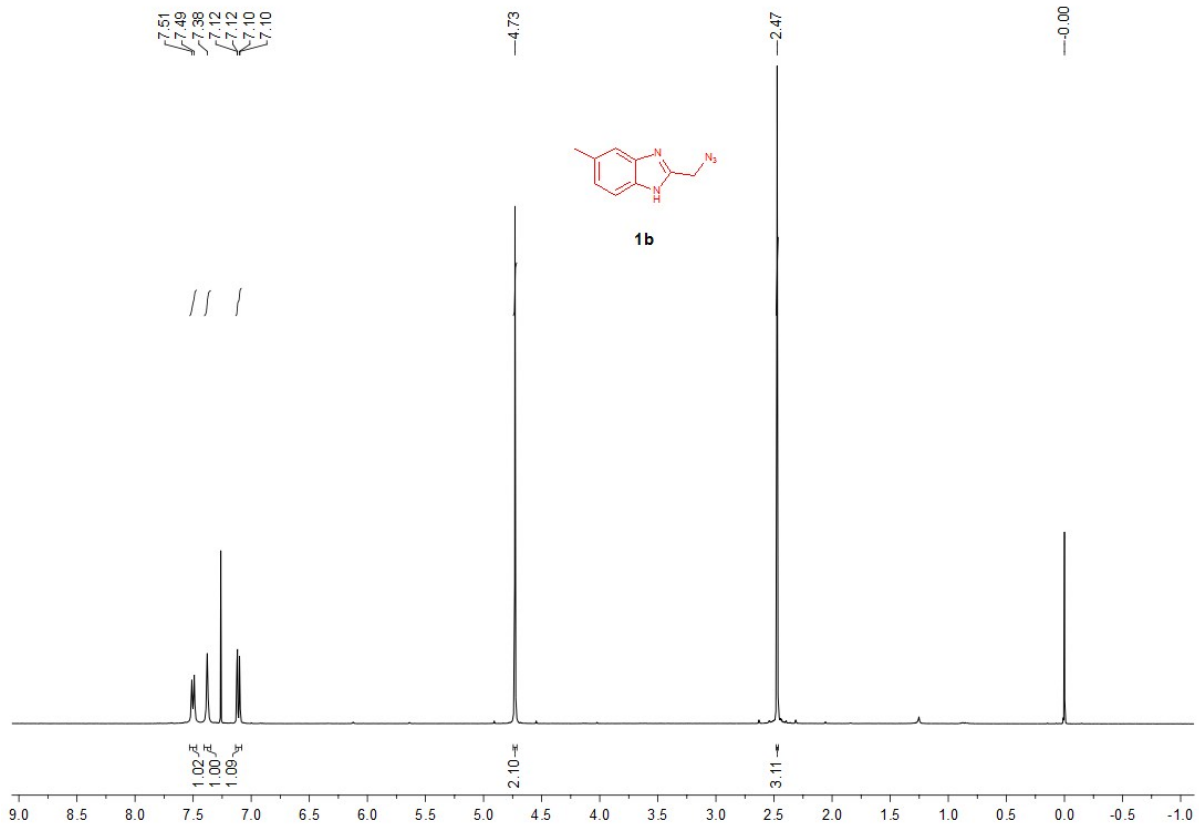
Normalized UV-Visible (left) and Fluorescence (right) spectra for compound **5k-o**



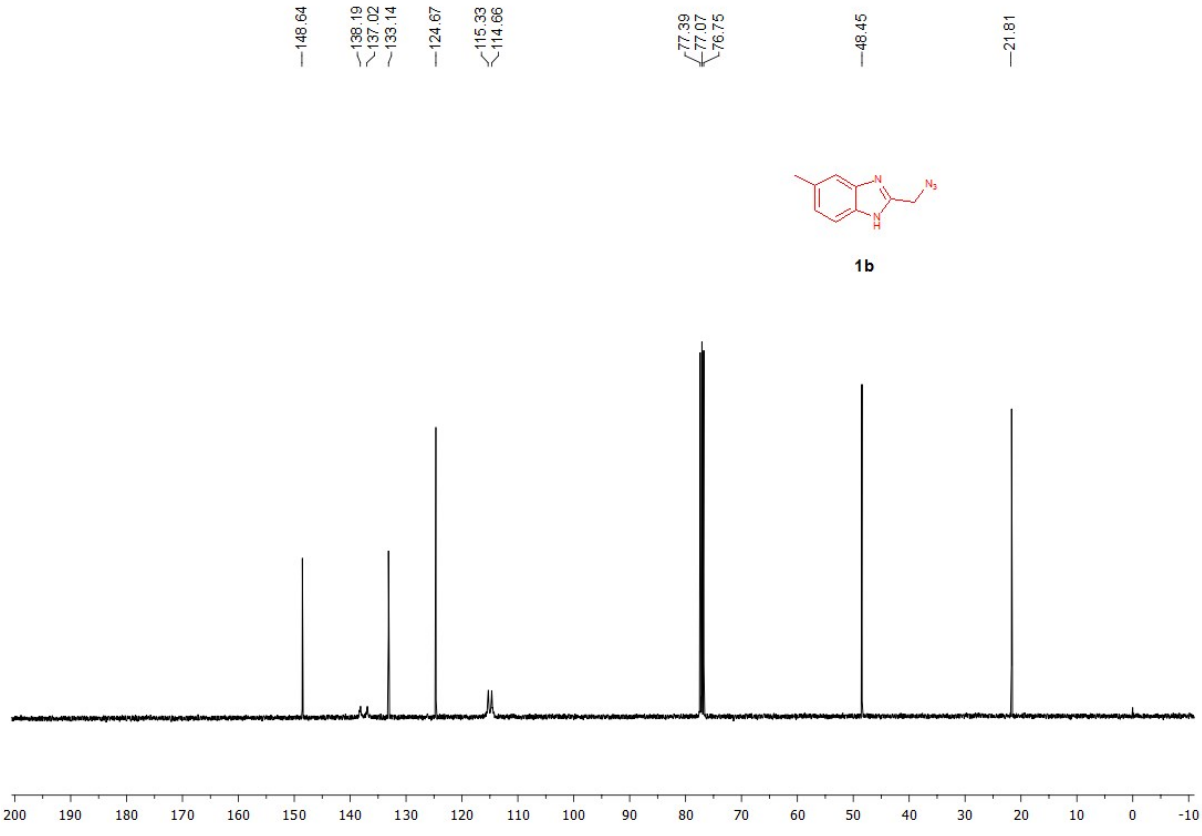
Normalized UV-Visible (left) and Fluorescence (right) spectra for compound **5p-u**

3. Copies of ^{1}H and ^{13}C NMR spectra:

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



1b (^{13}C NMR, $CDCl_3$, 100 MHz)



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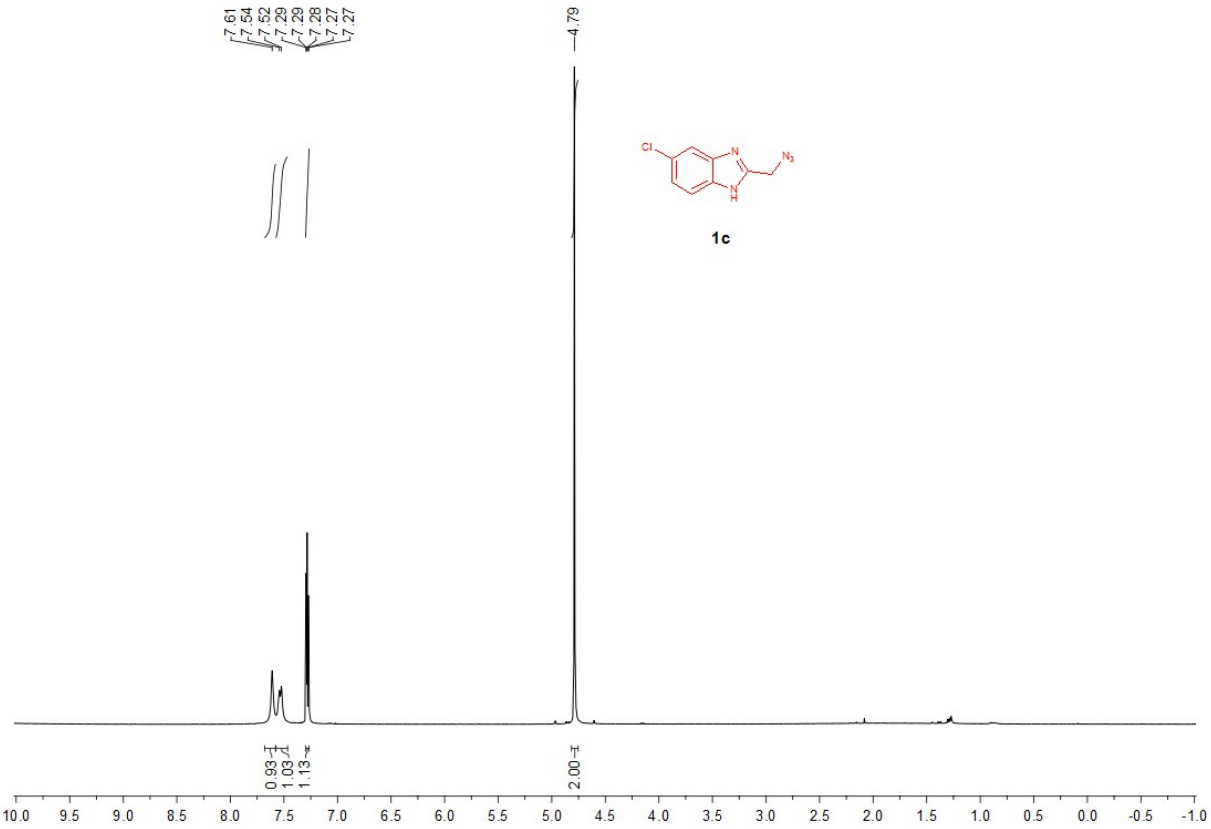

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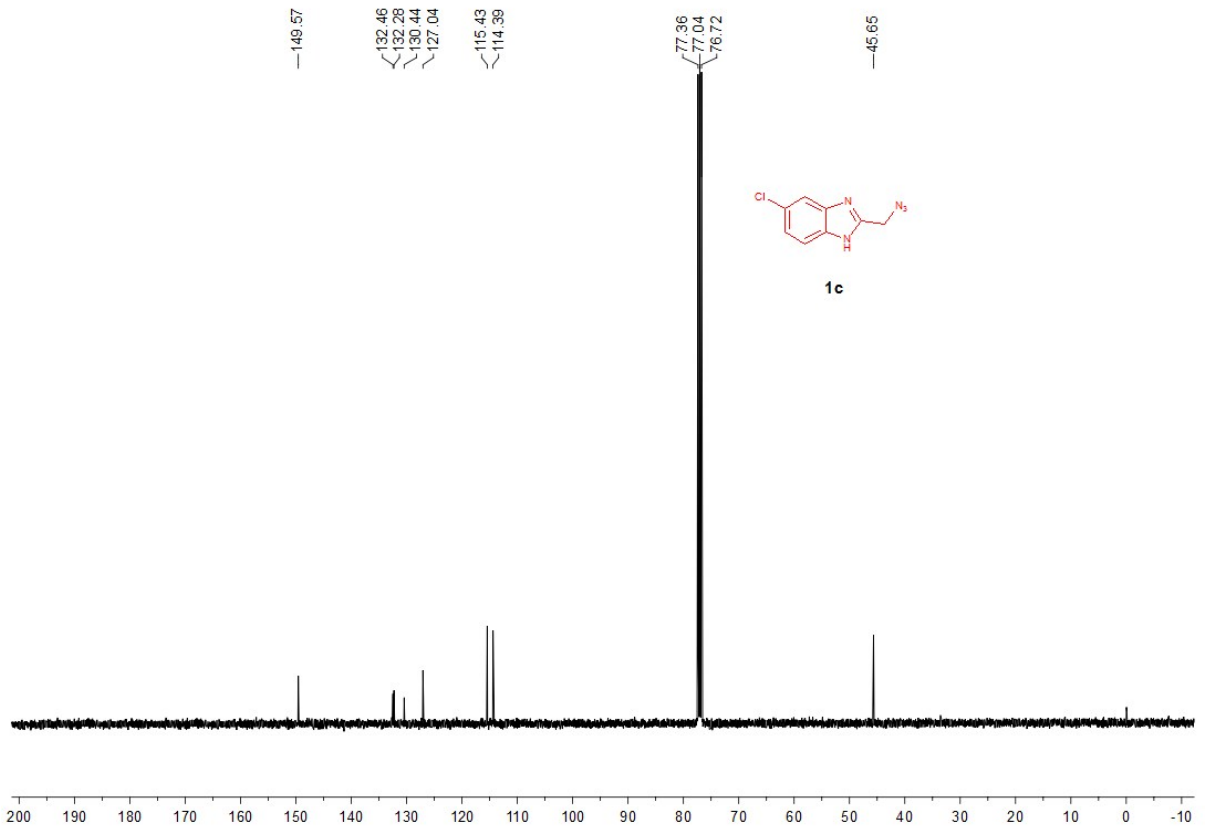

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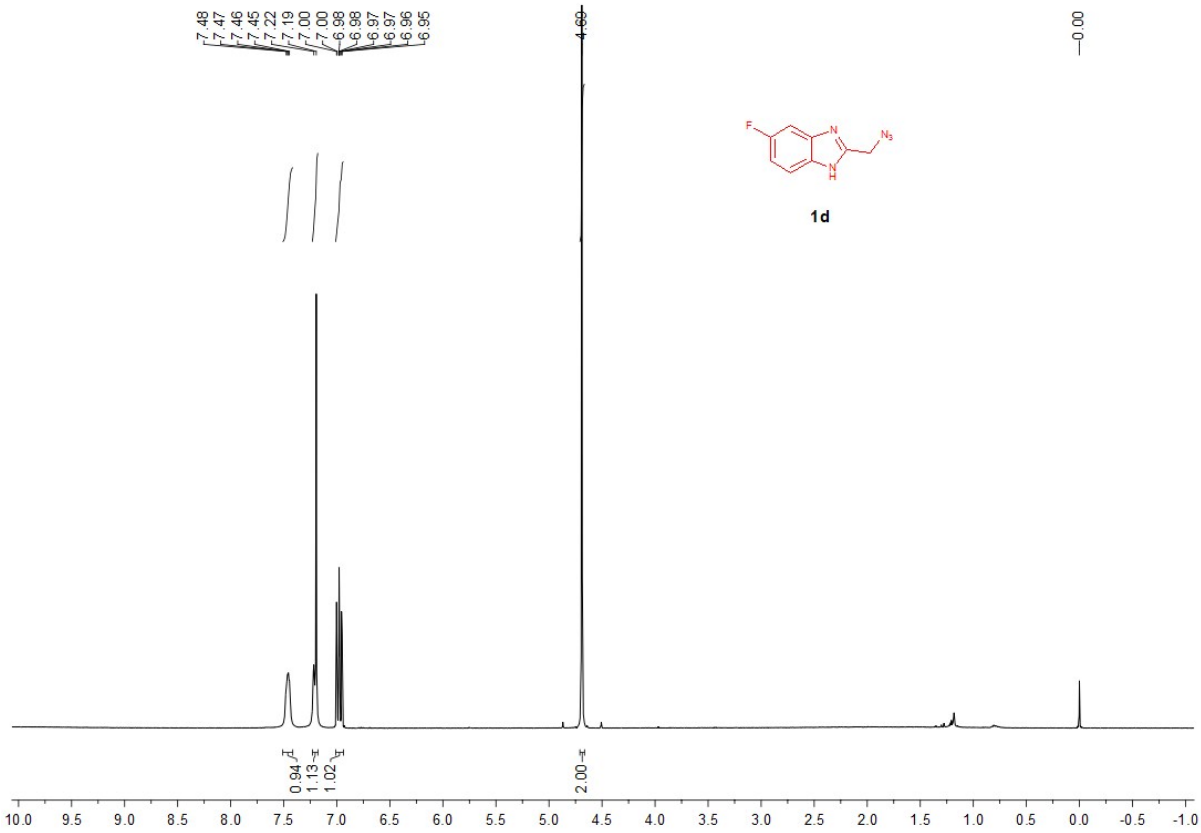

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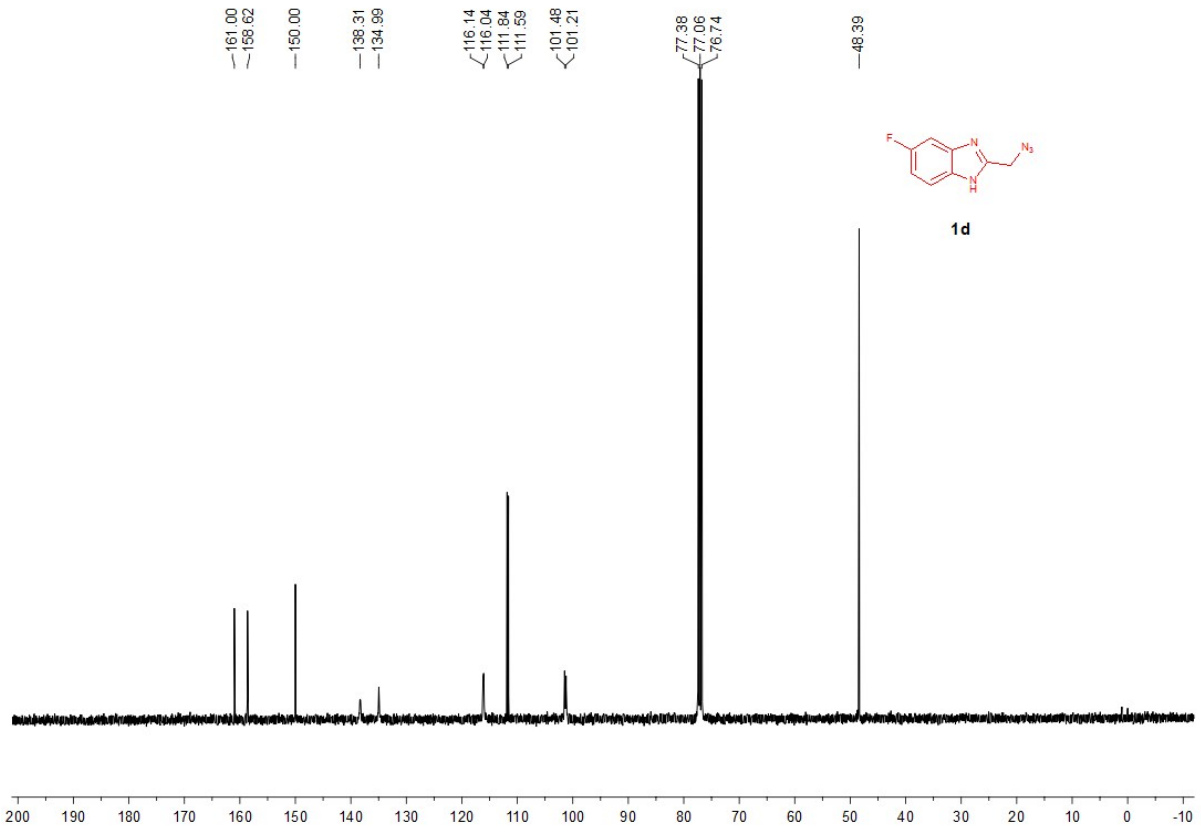
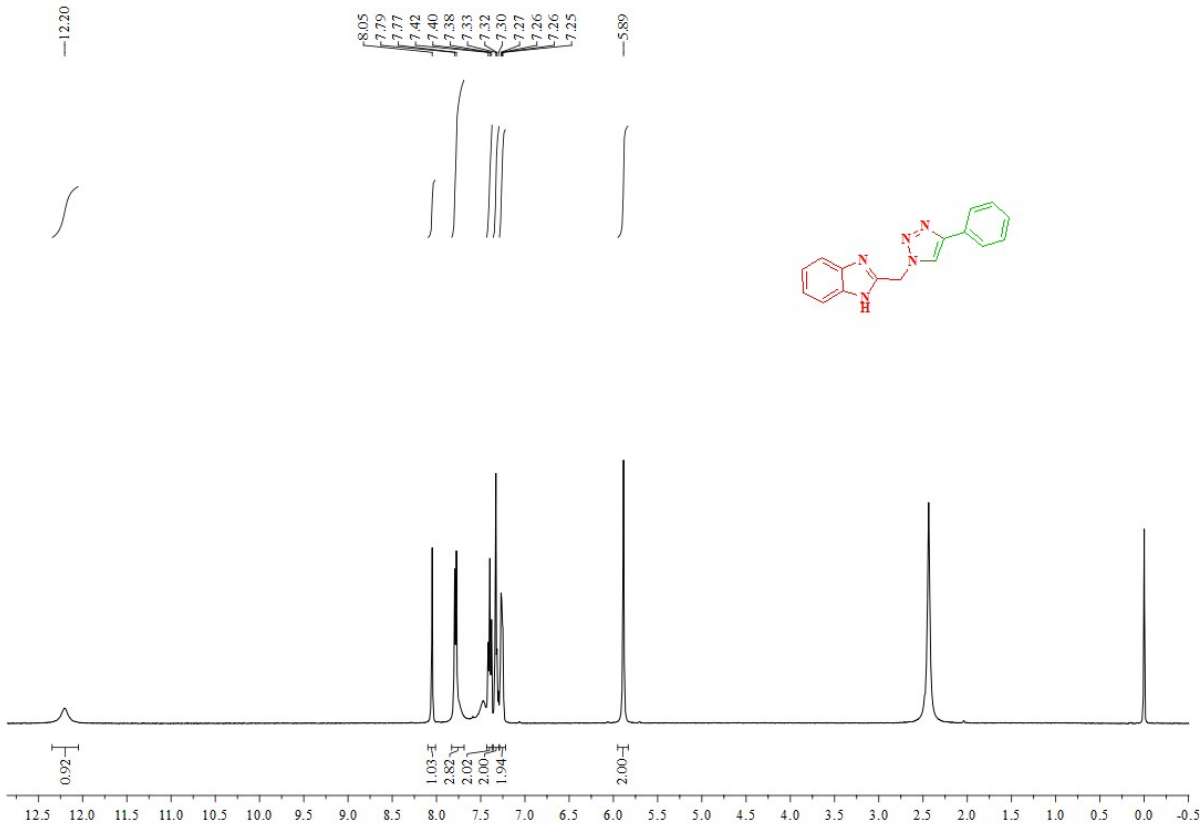


4a (^{1}H NMR, DMSO-d_6, 400 MHz)



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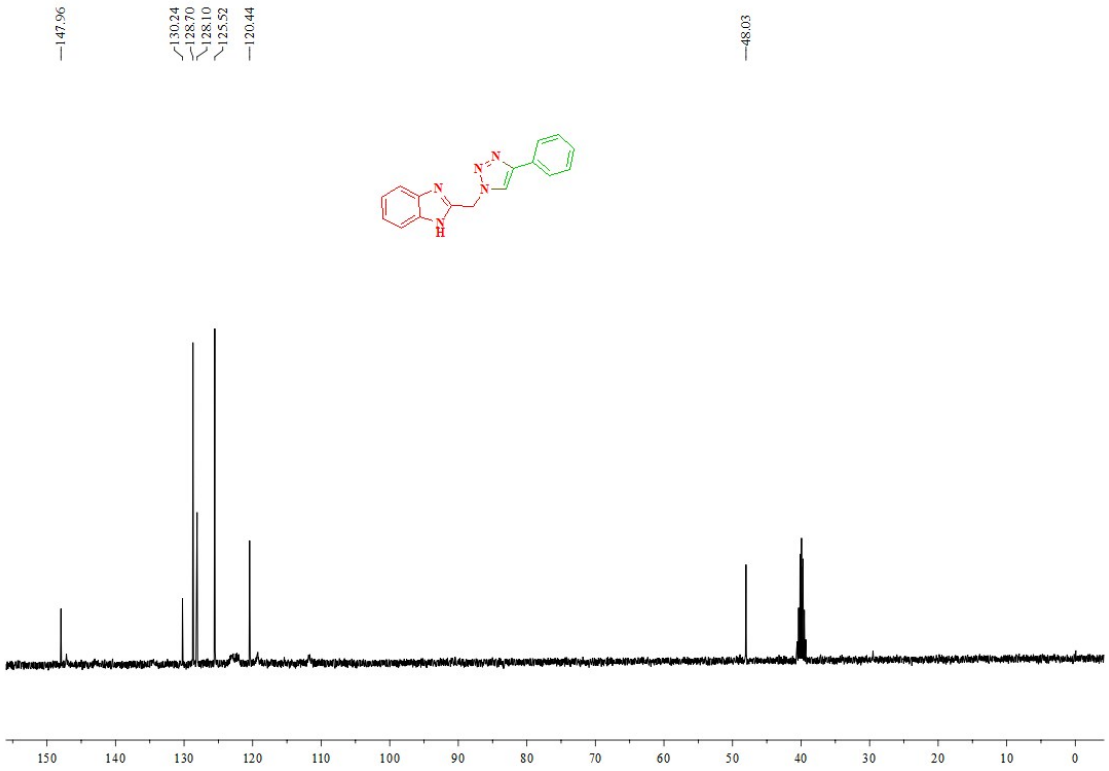
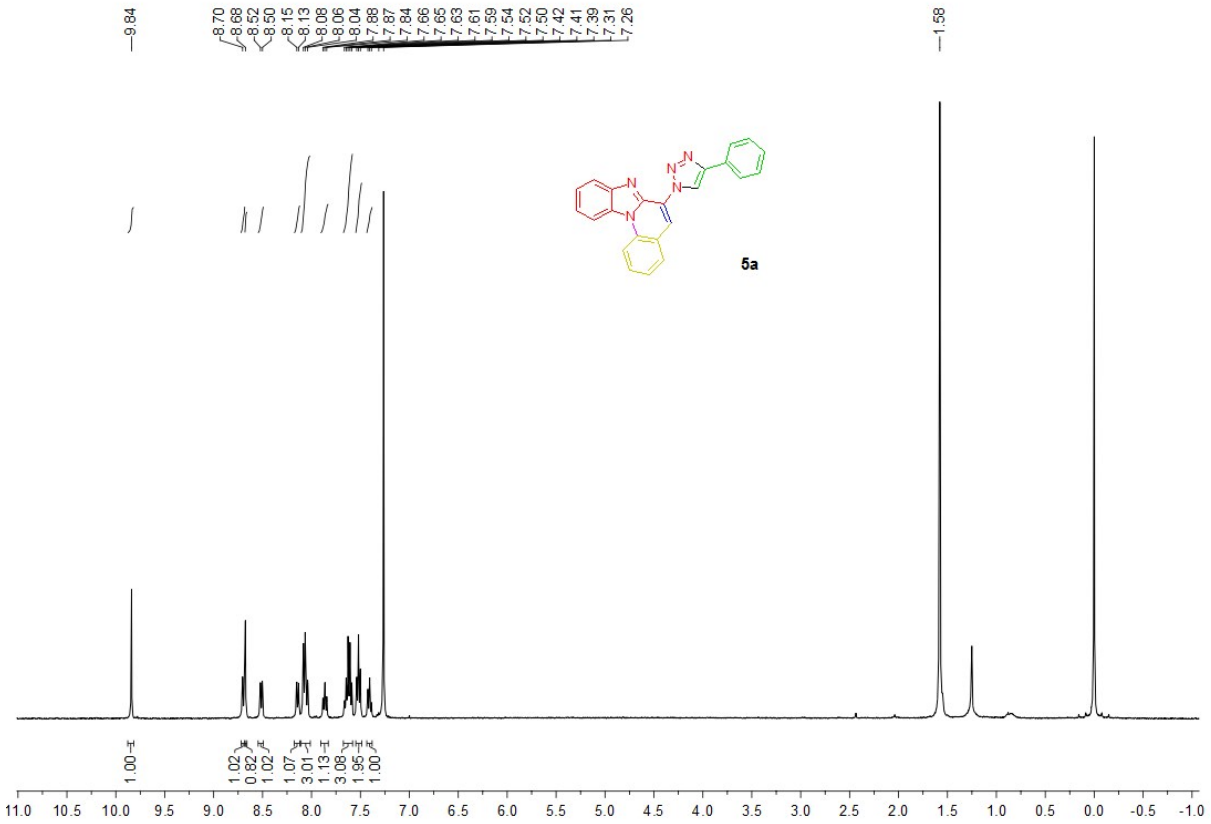
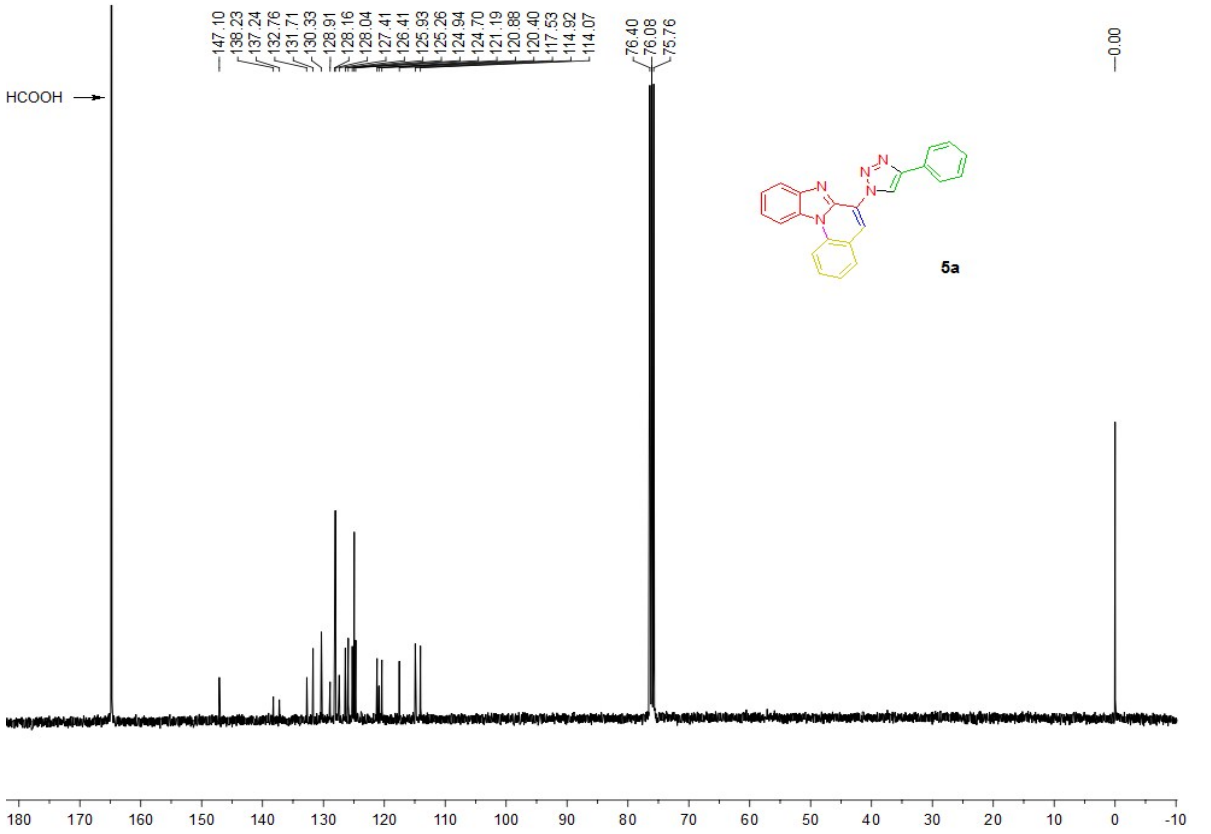


5a (^{1}H NMR, $CDCl_3$, 400 MHz)



5a (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



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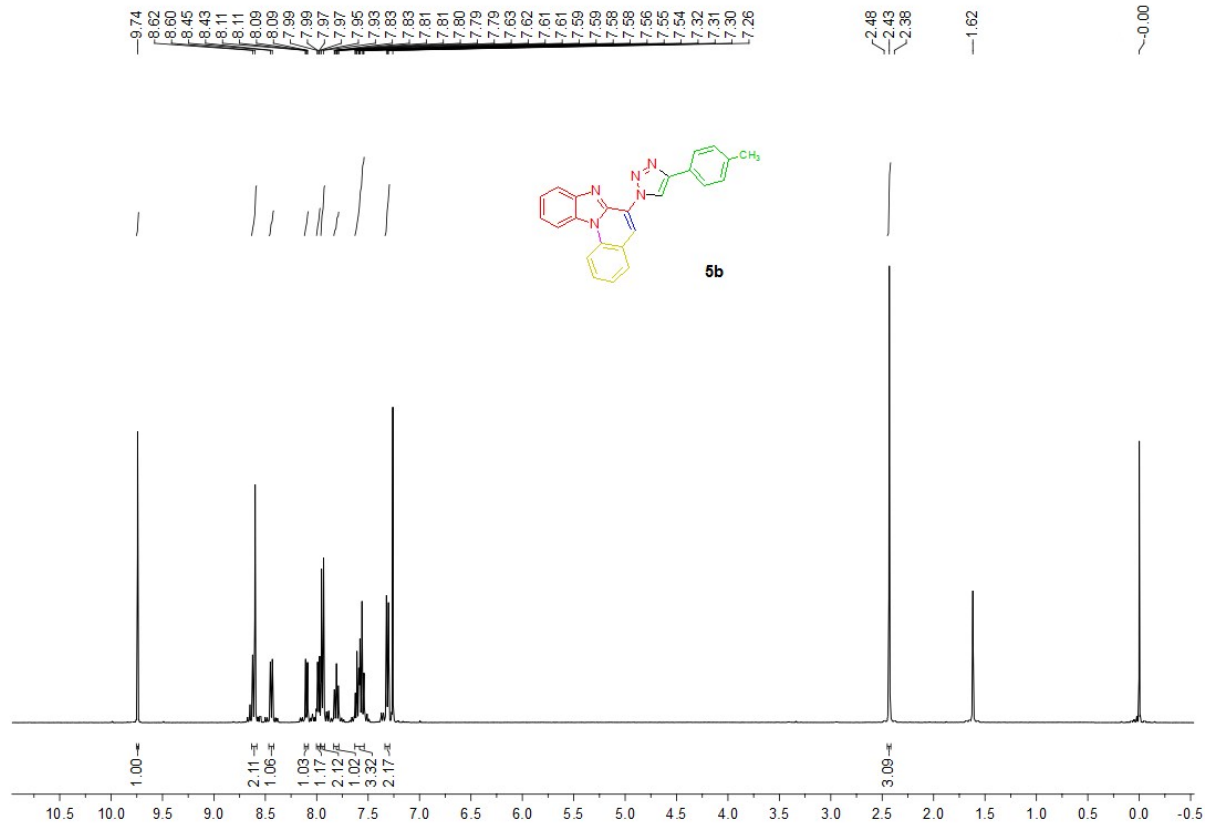

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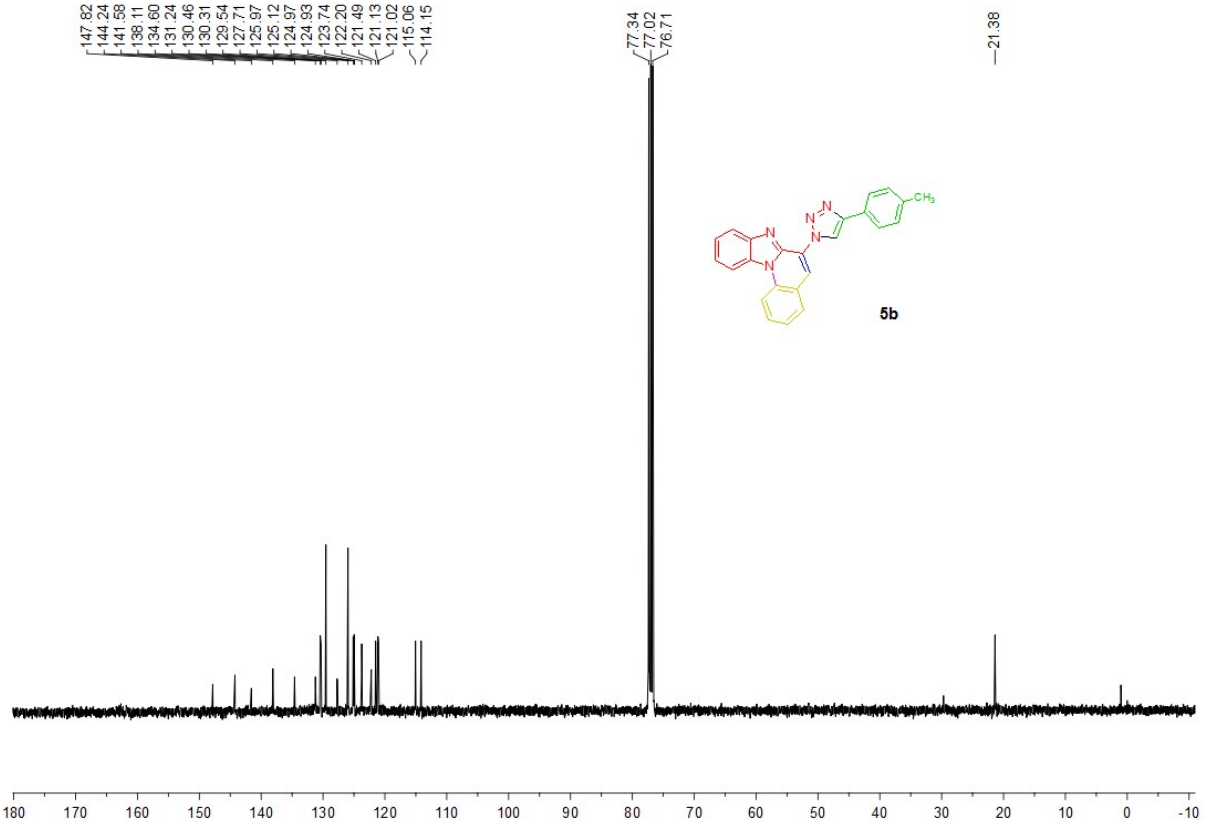

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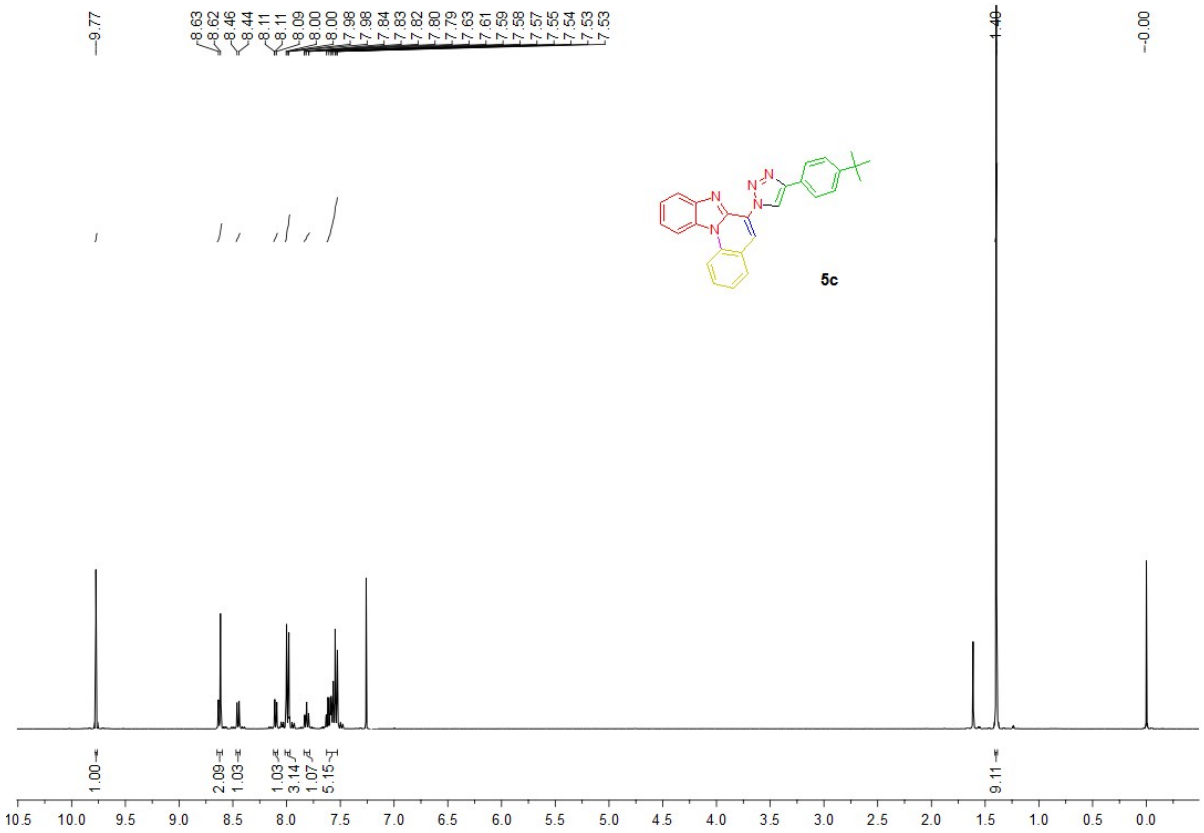

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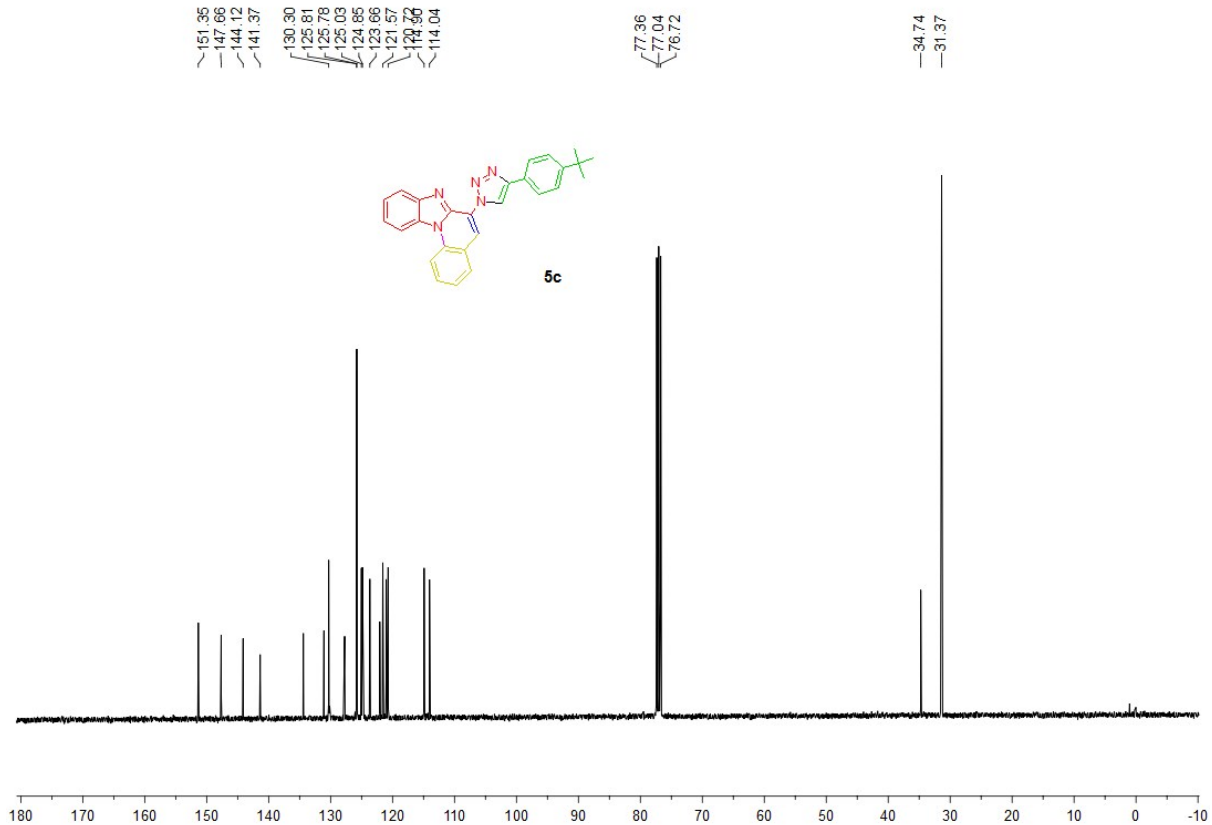

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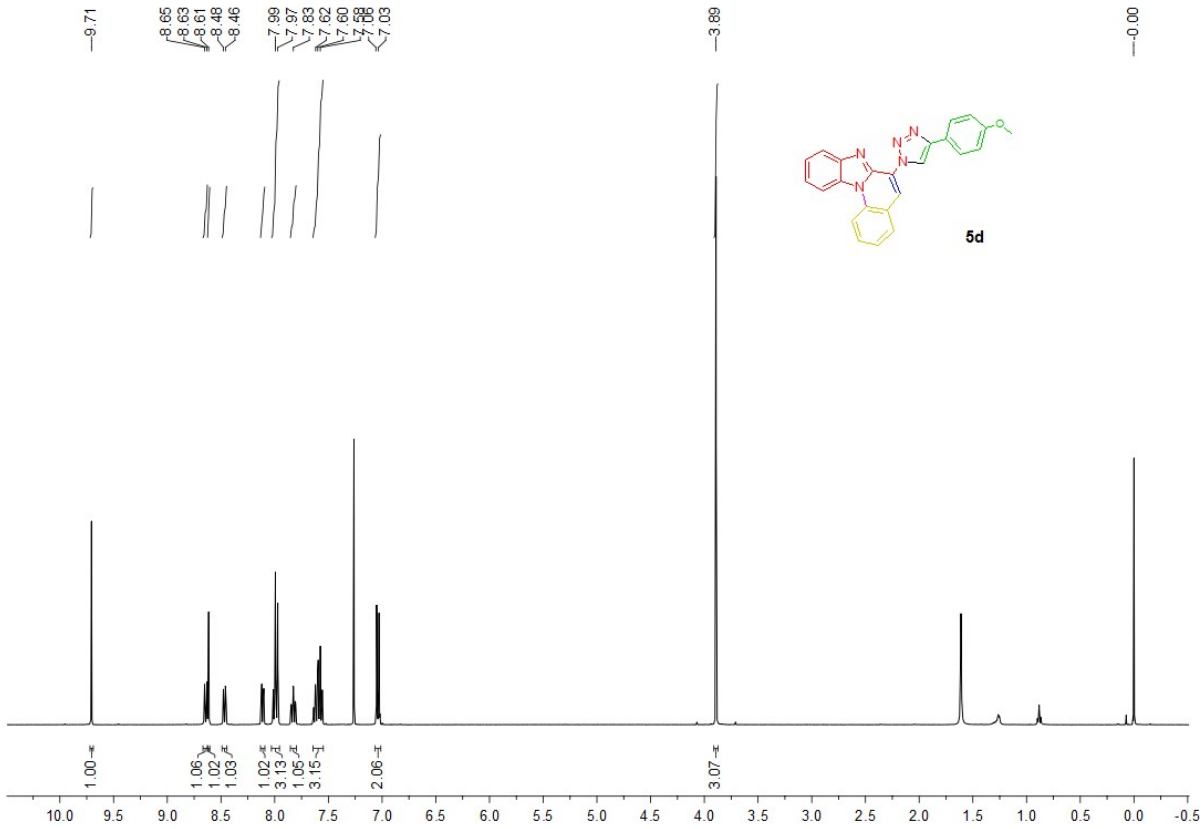

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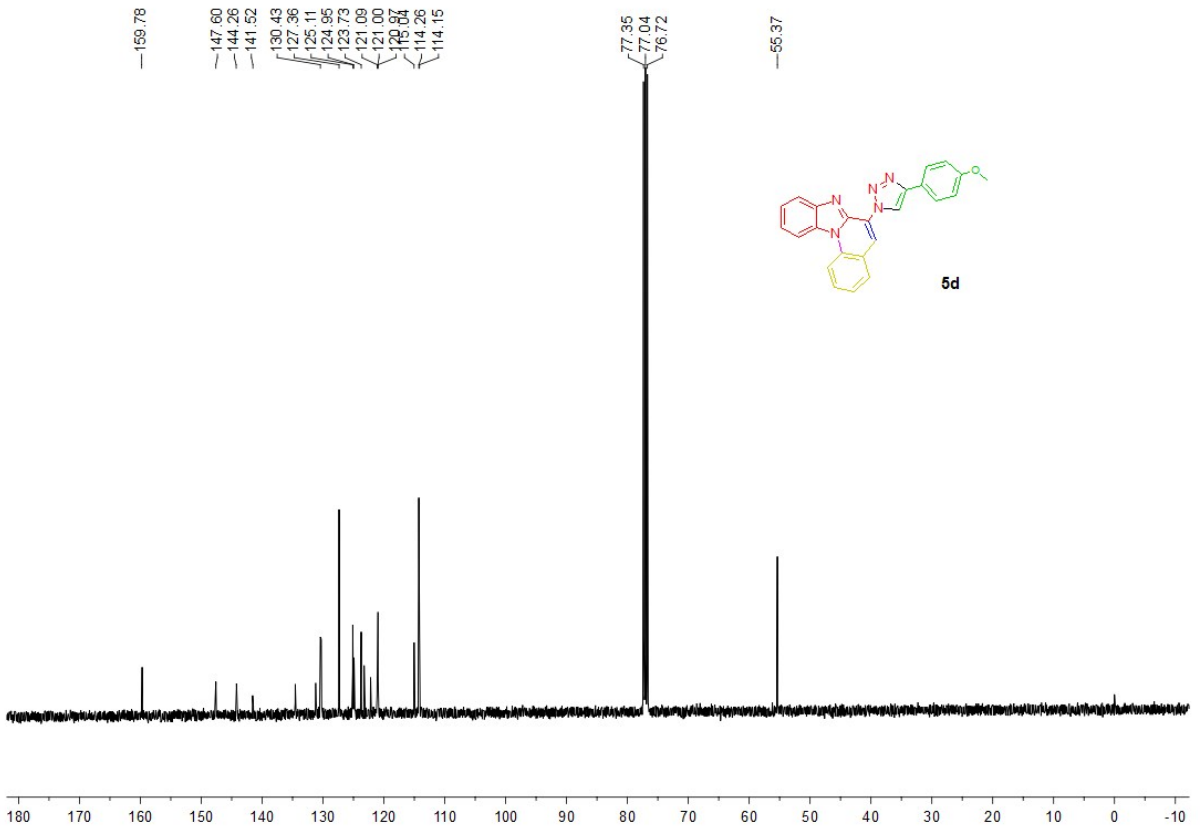
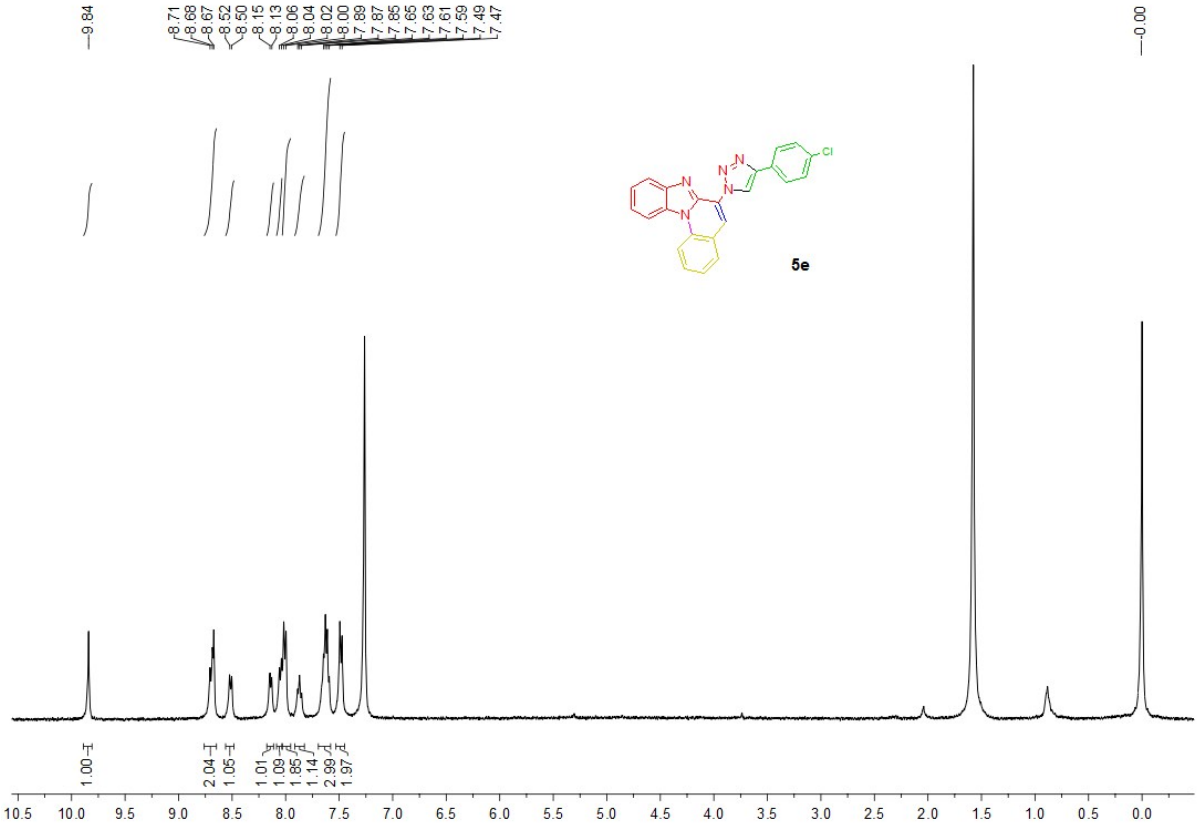
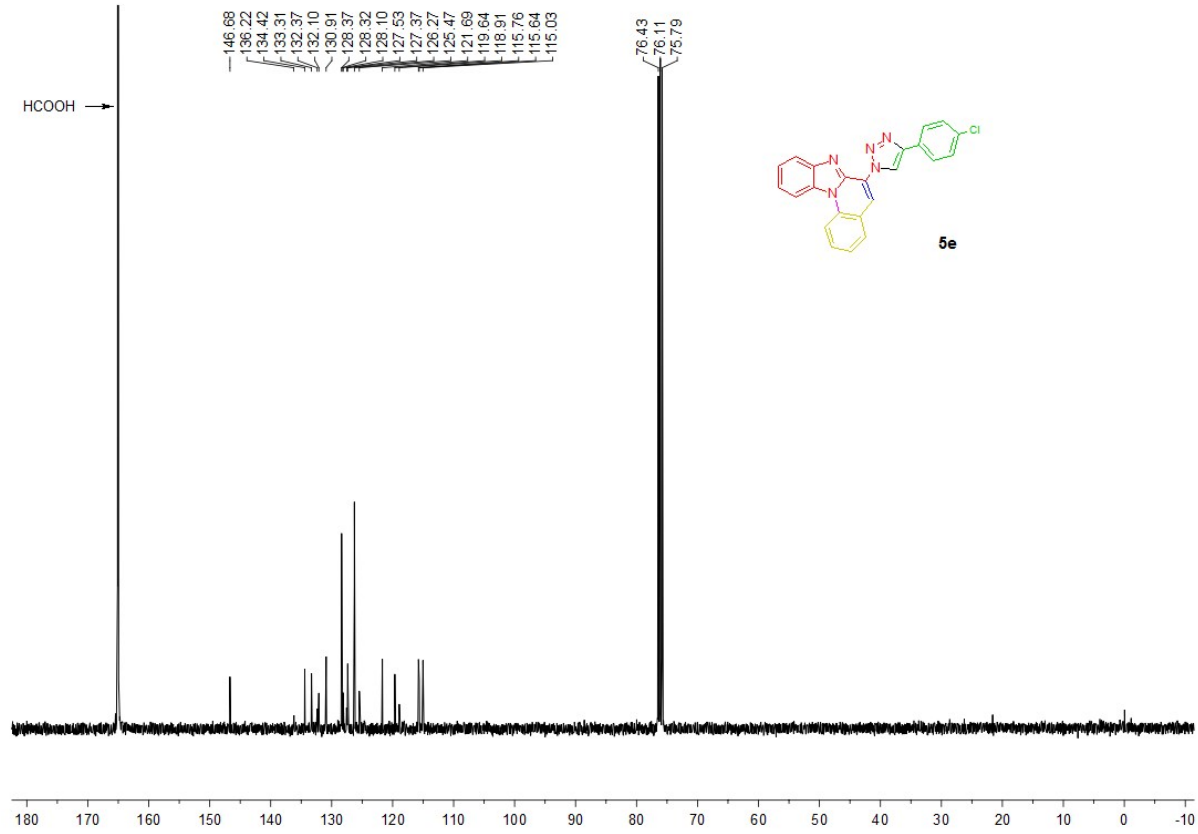


5e (^{1}H NMR, $CDCl_3$, 400 MHz)



5e (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



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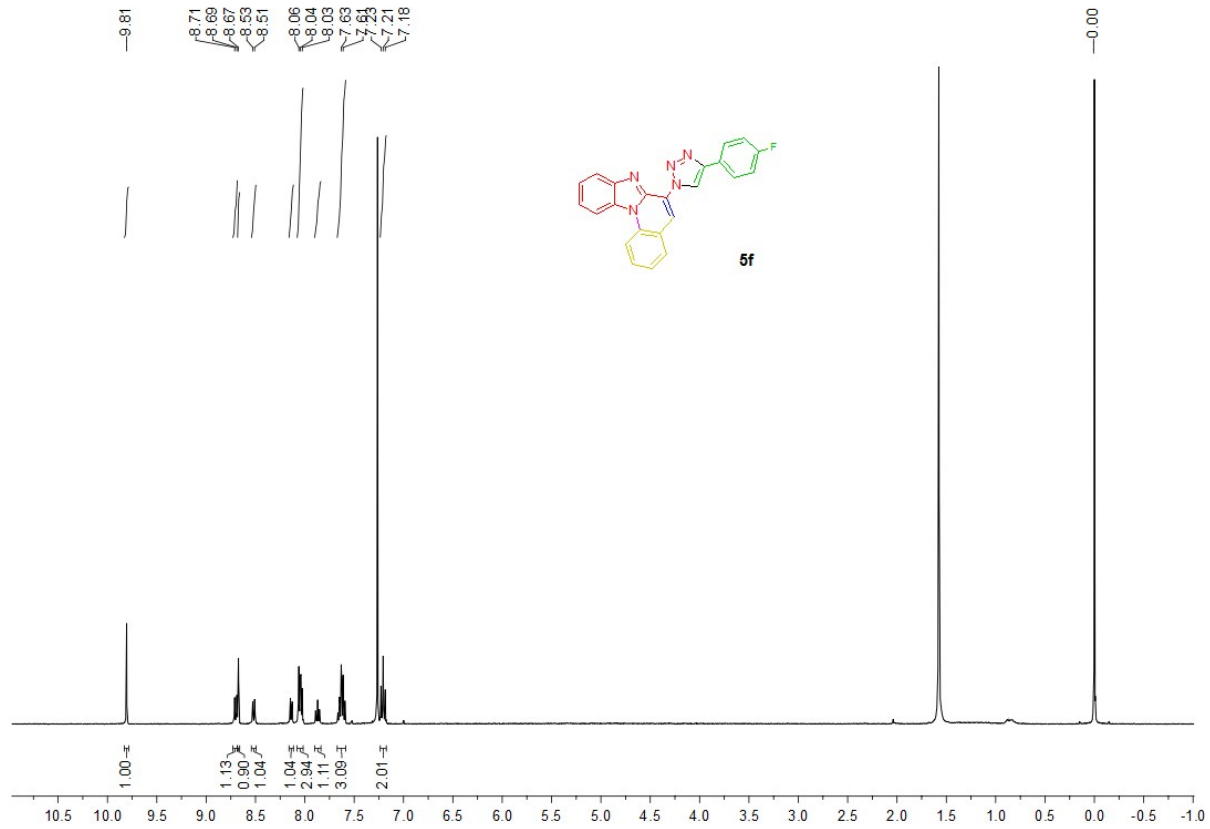

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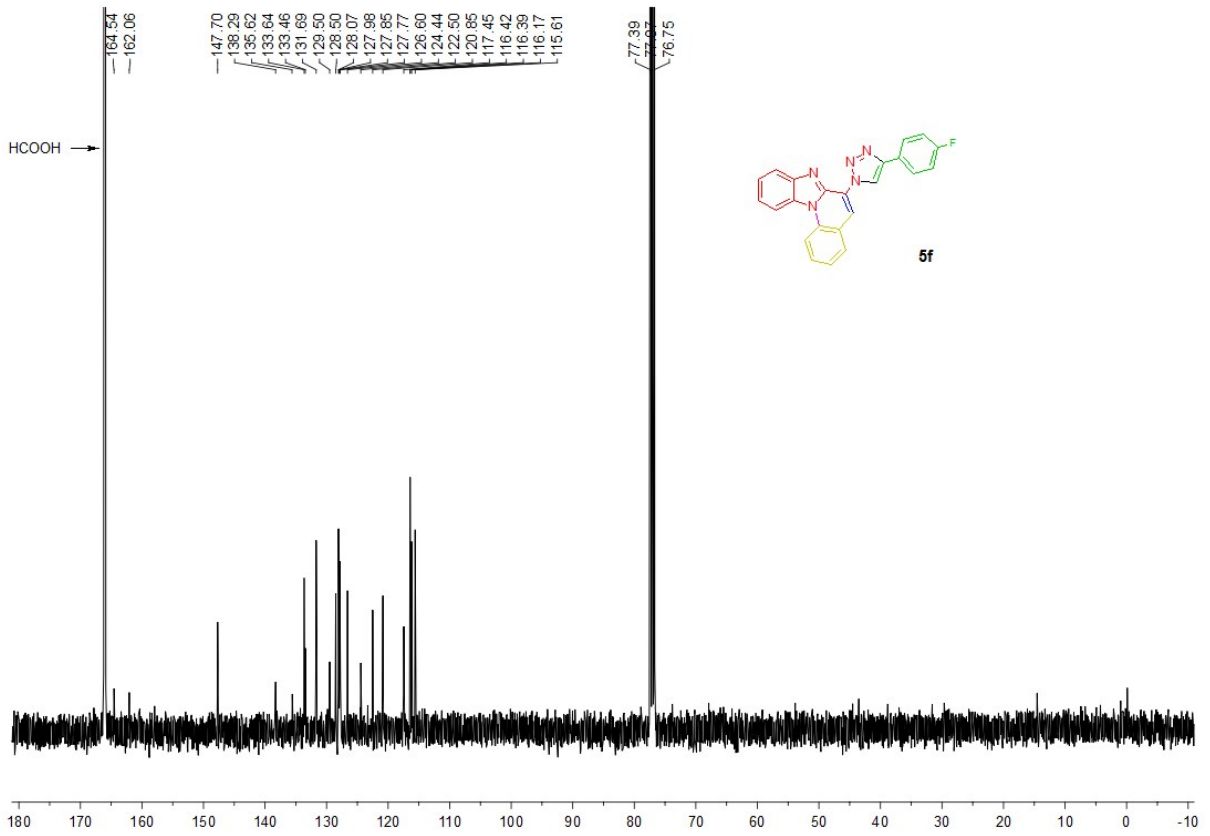

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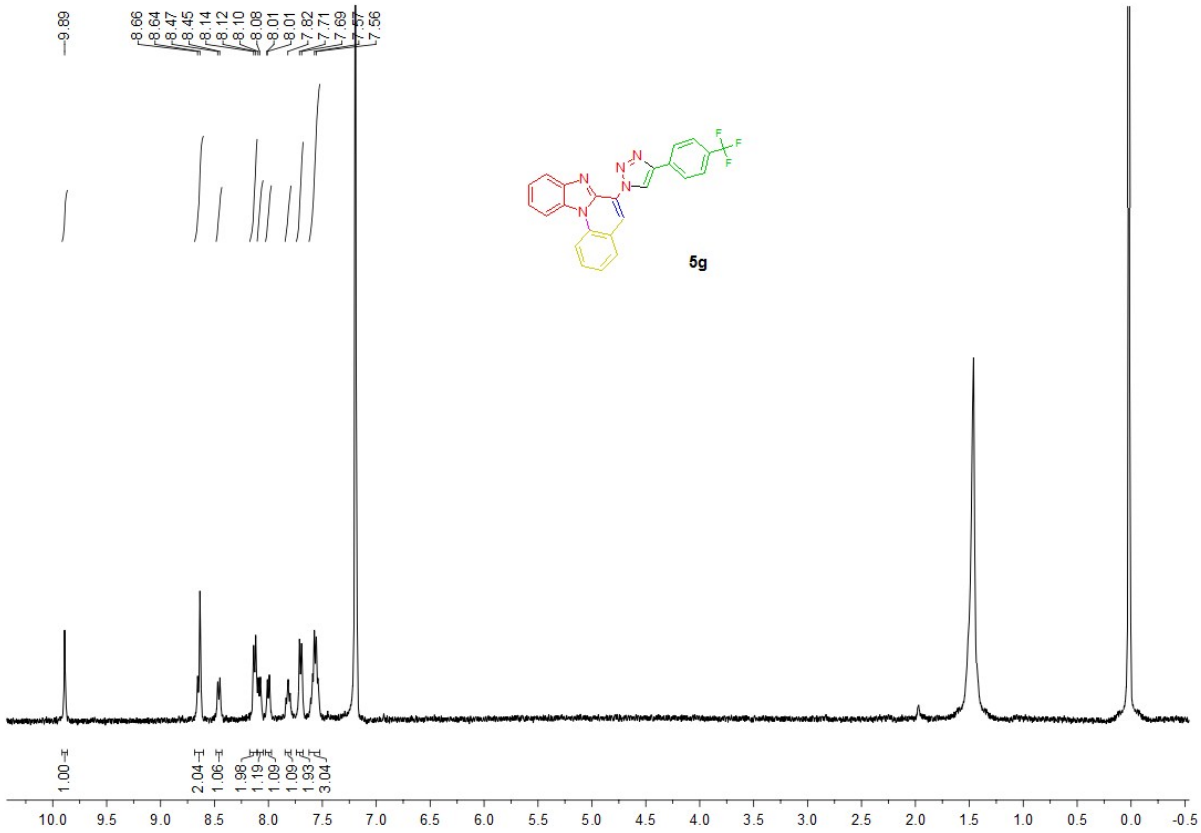

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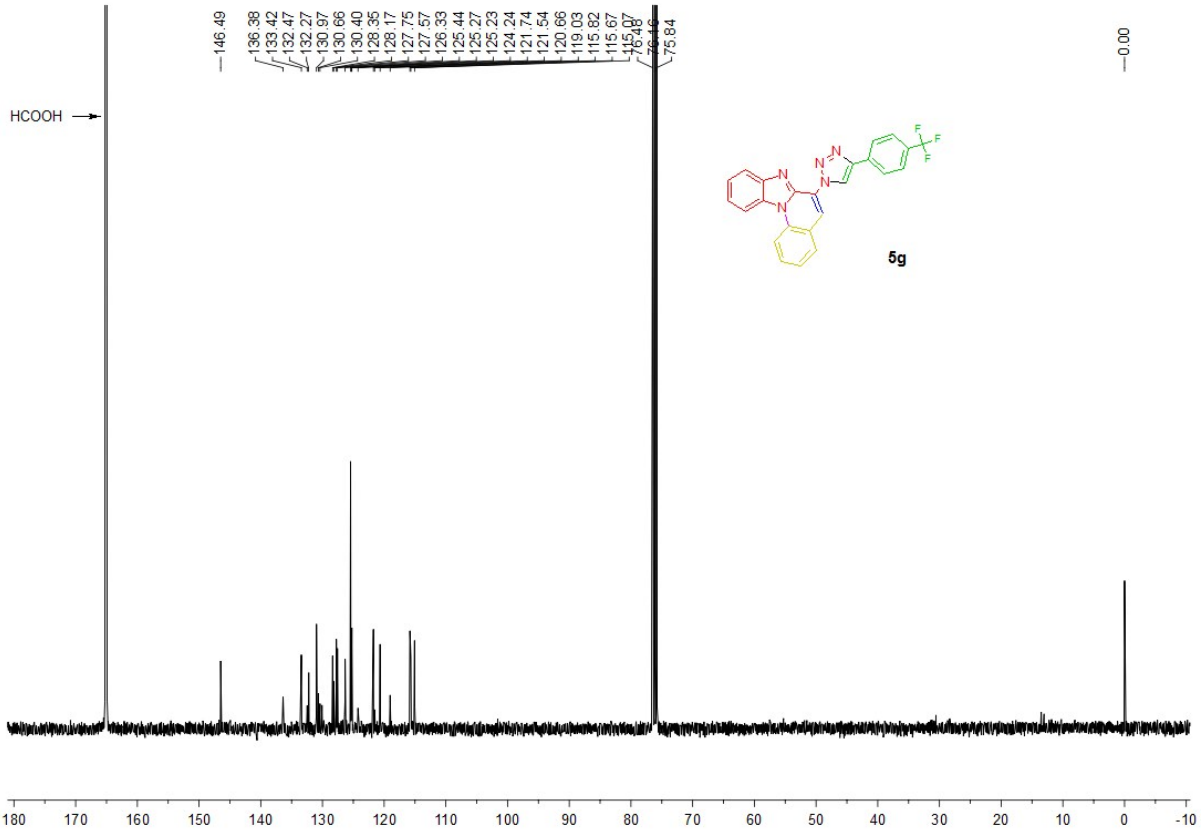

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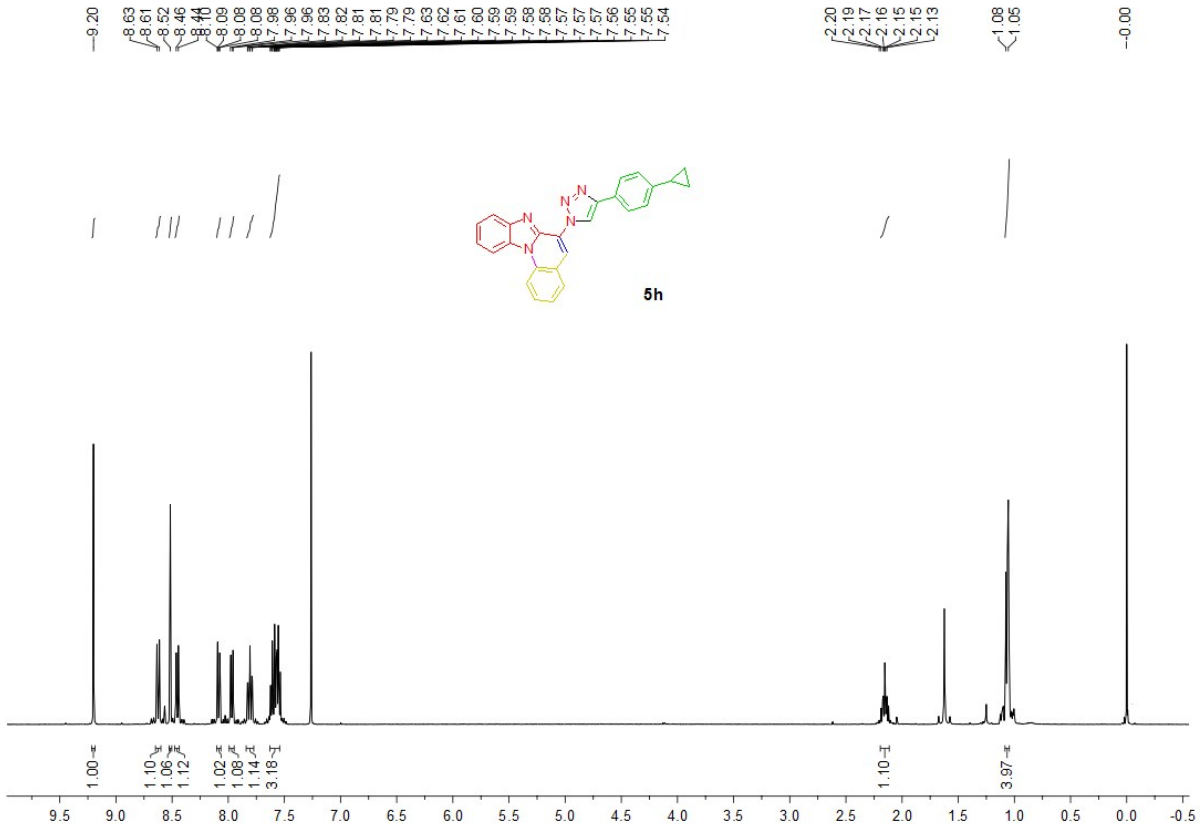

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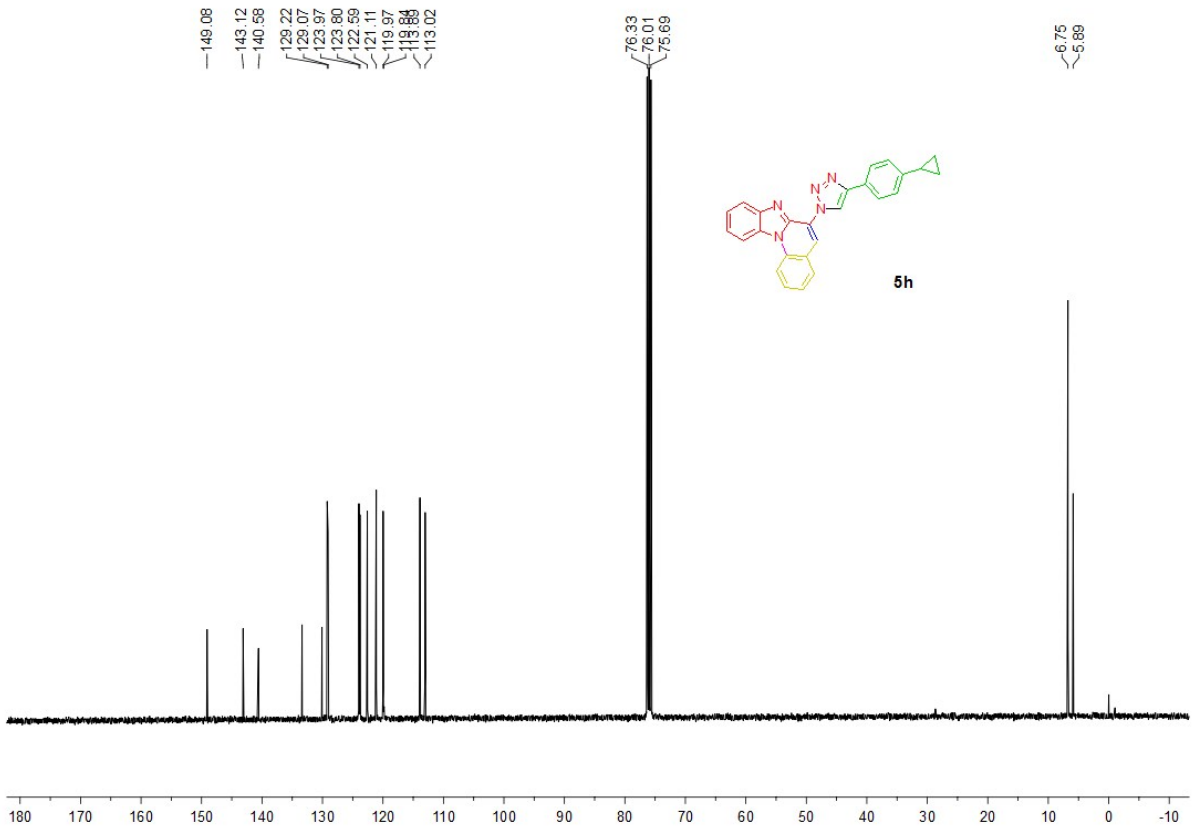

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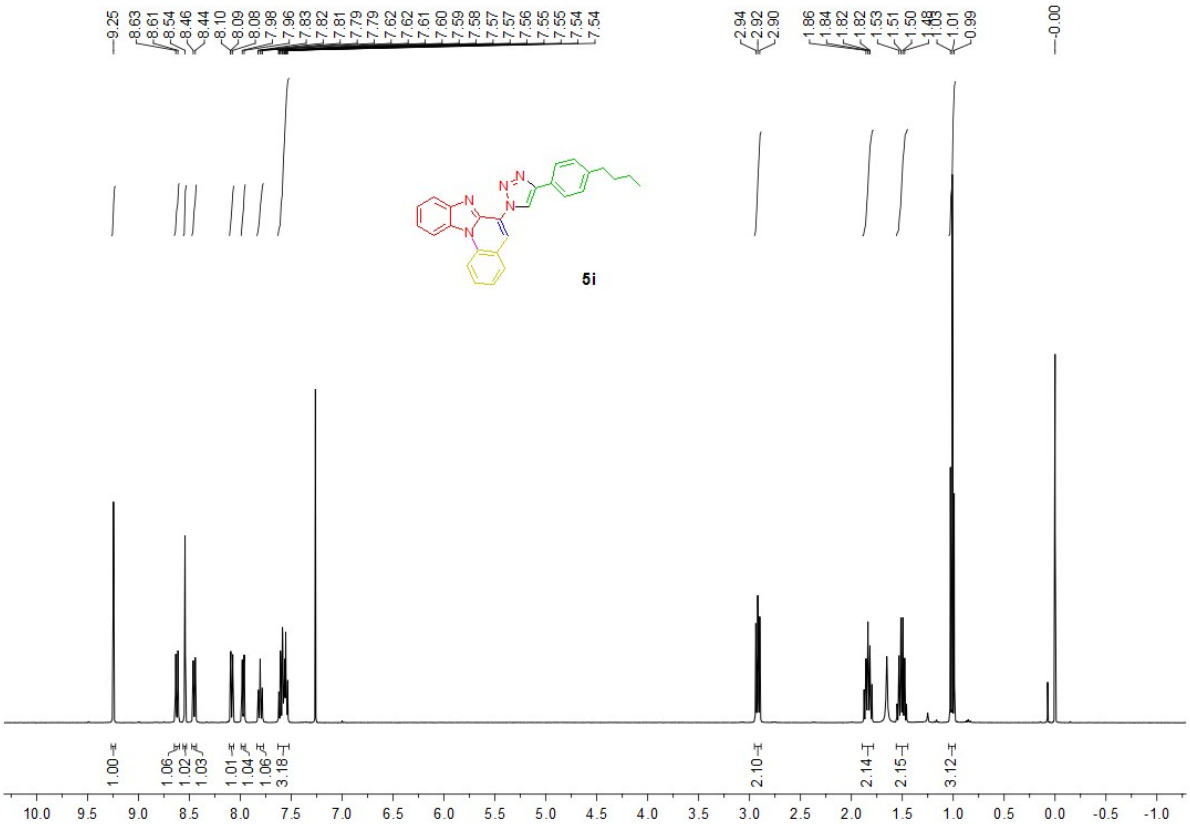

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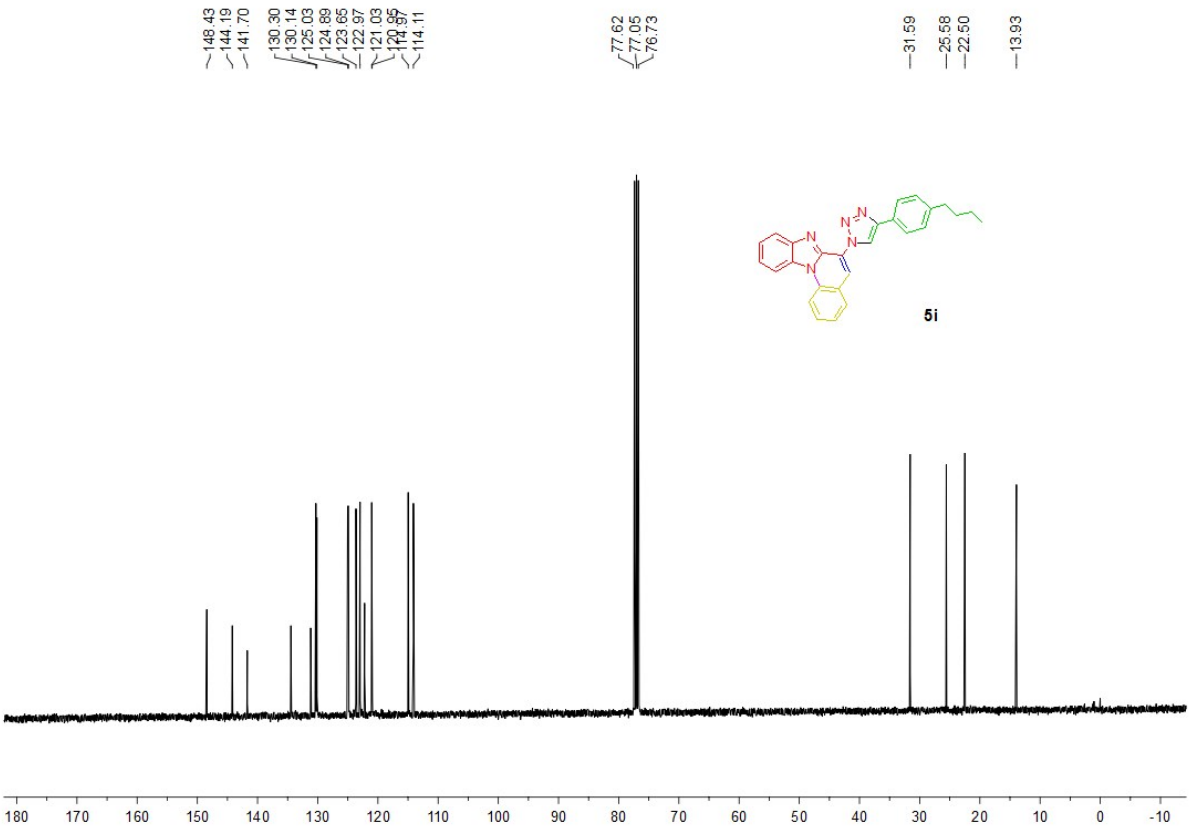

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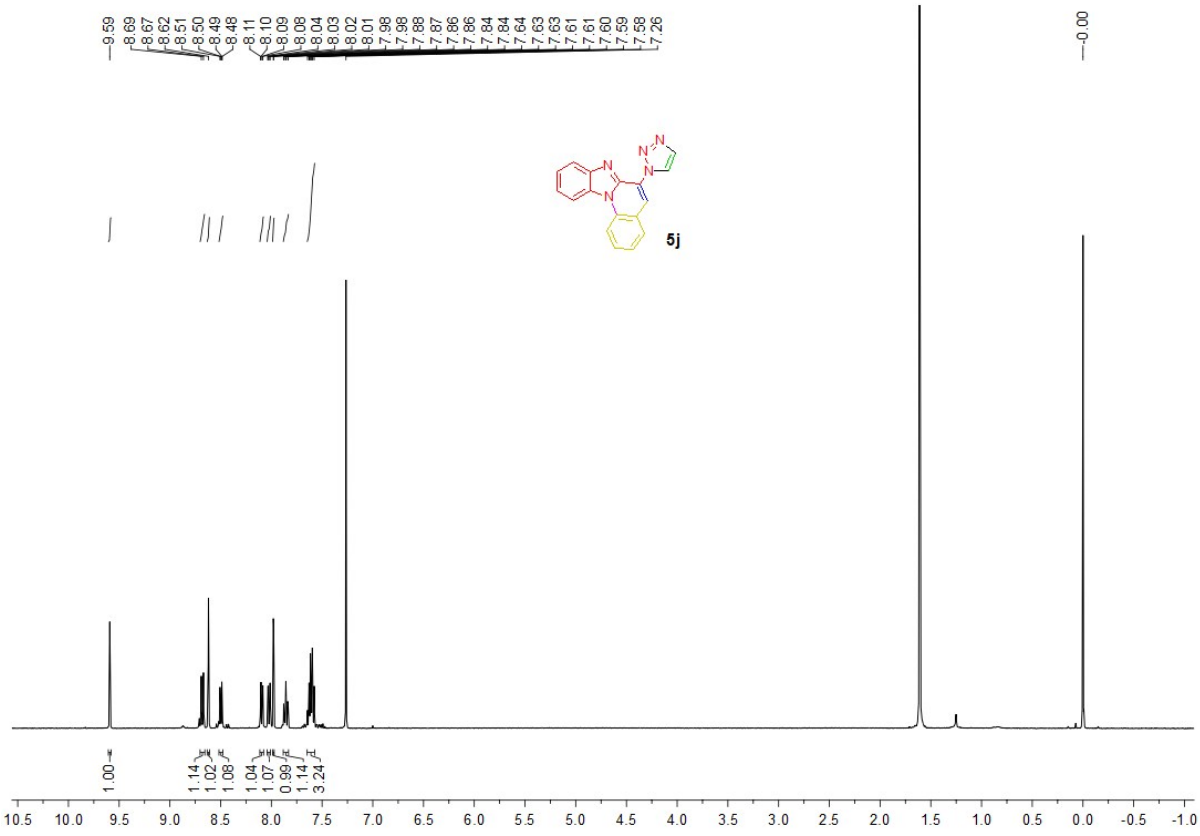

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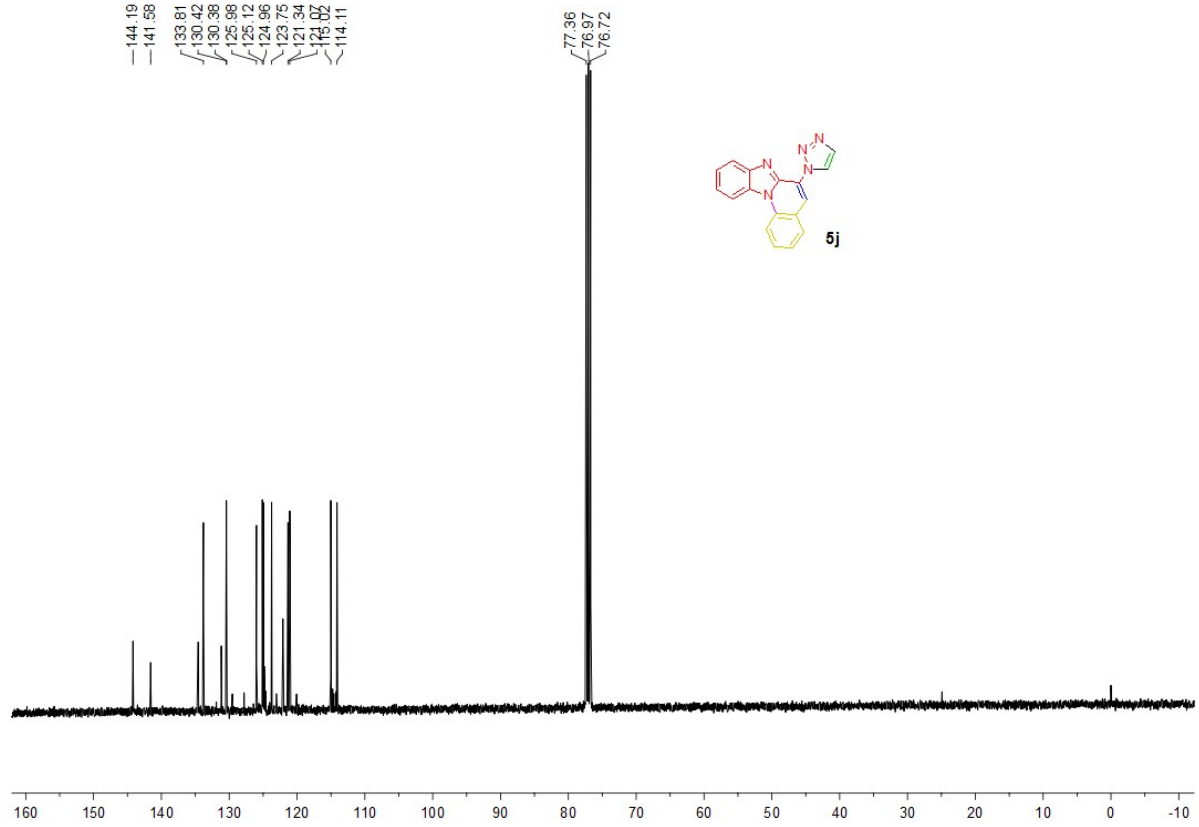
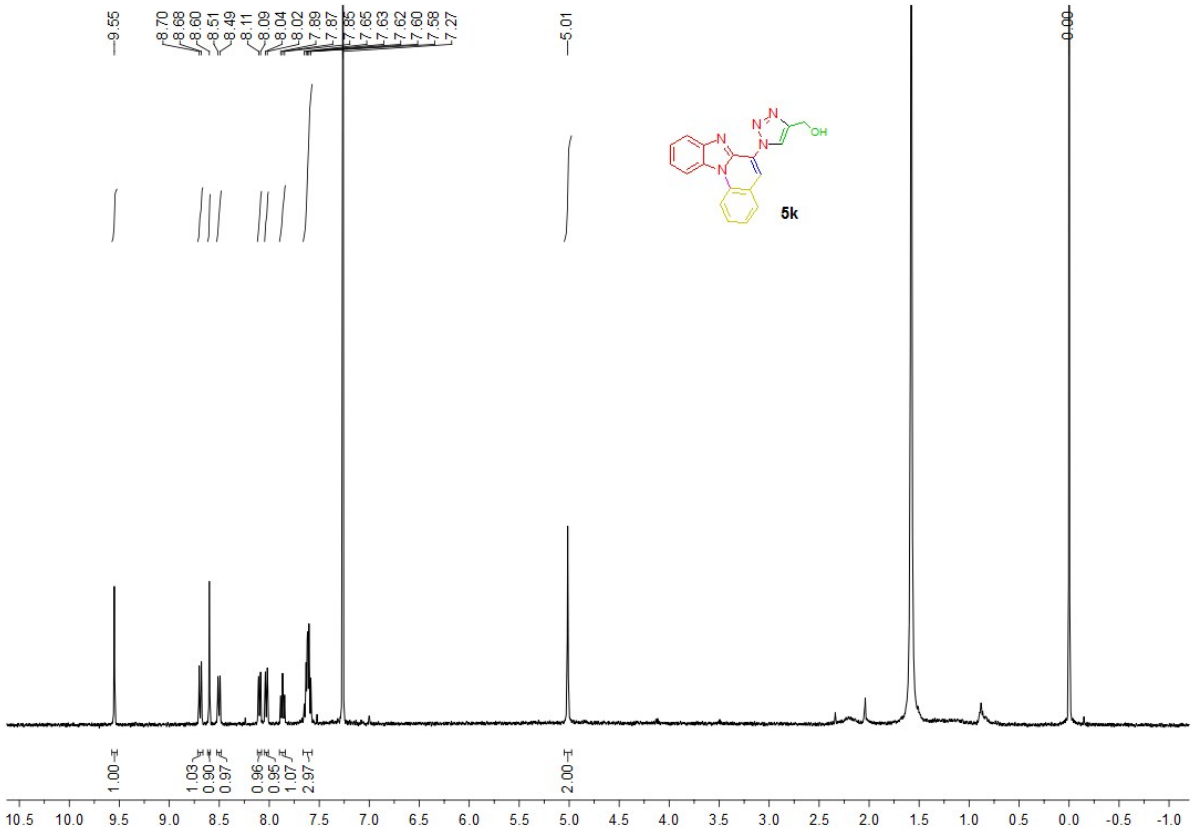
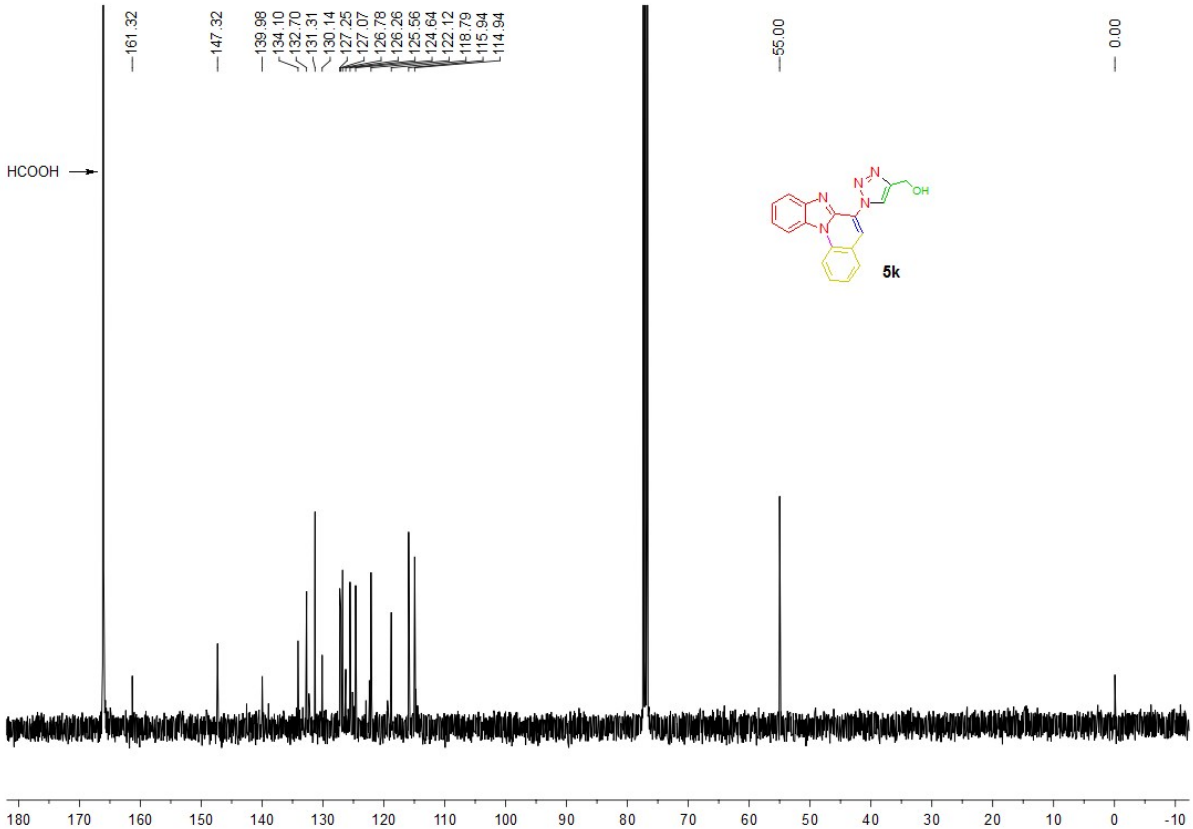


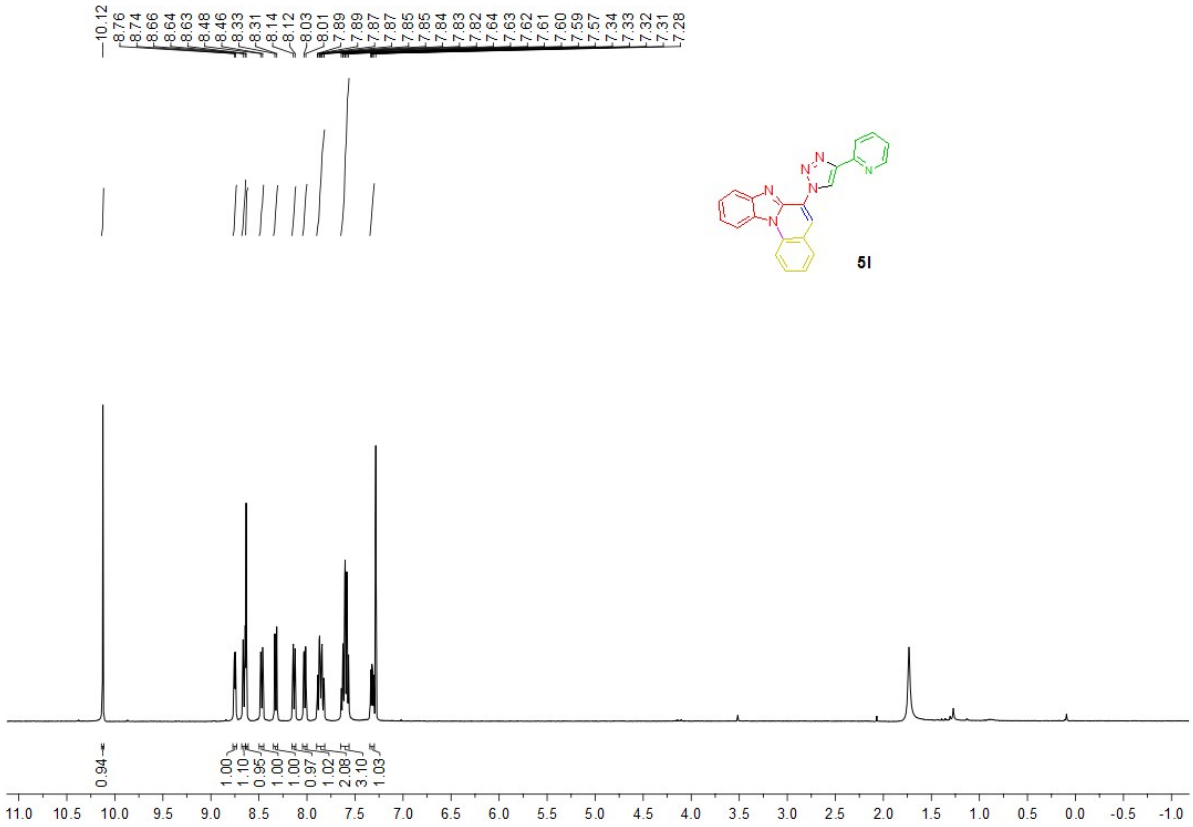
5k (^{1}H NMR, $CDCl_3$, 400 MHz)



5k (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



5l (^{1}H NMR, $CDCl_3$, 400 MHz)



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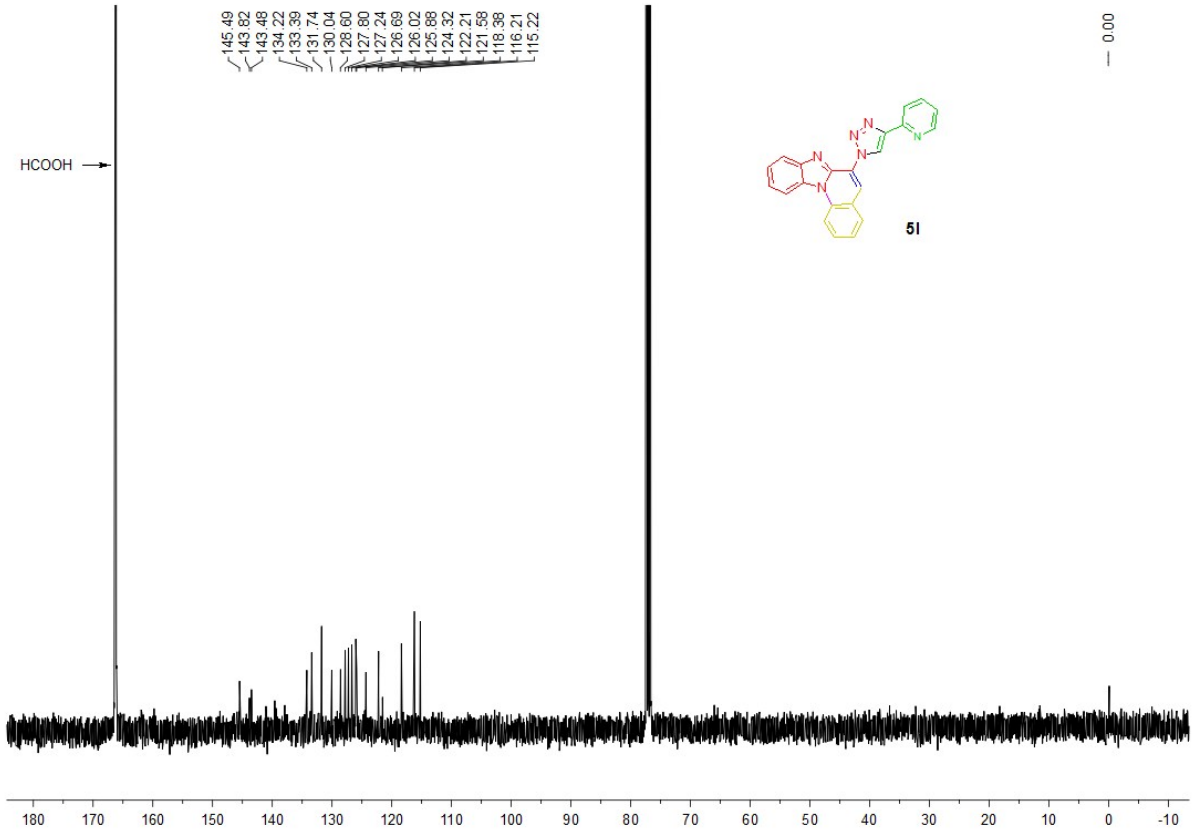

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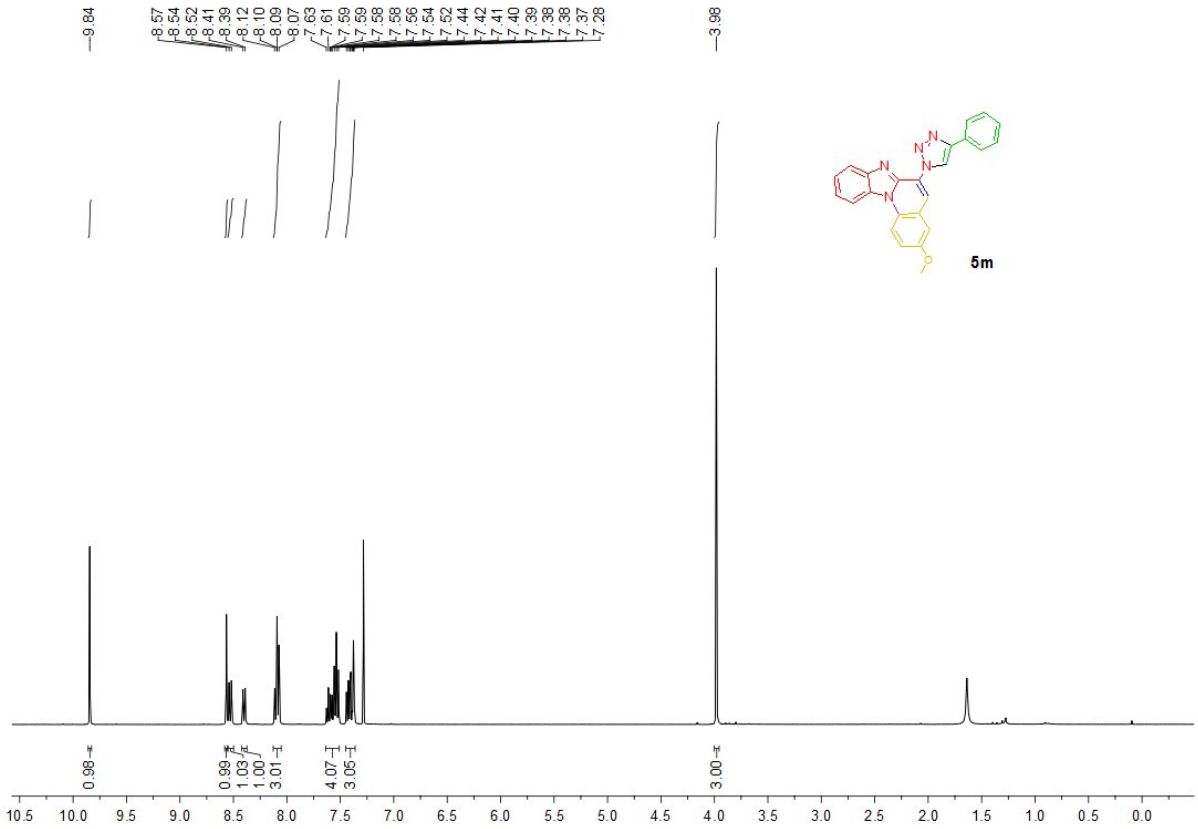
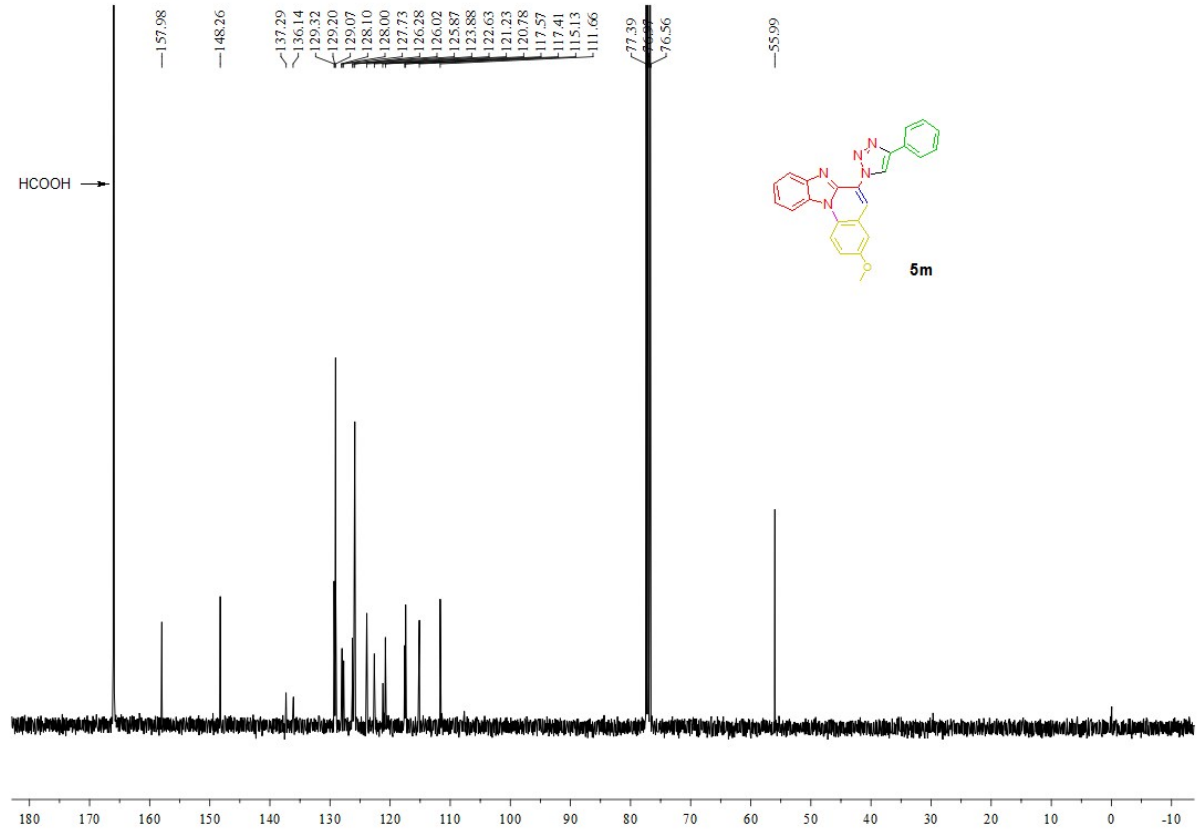
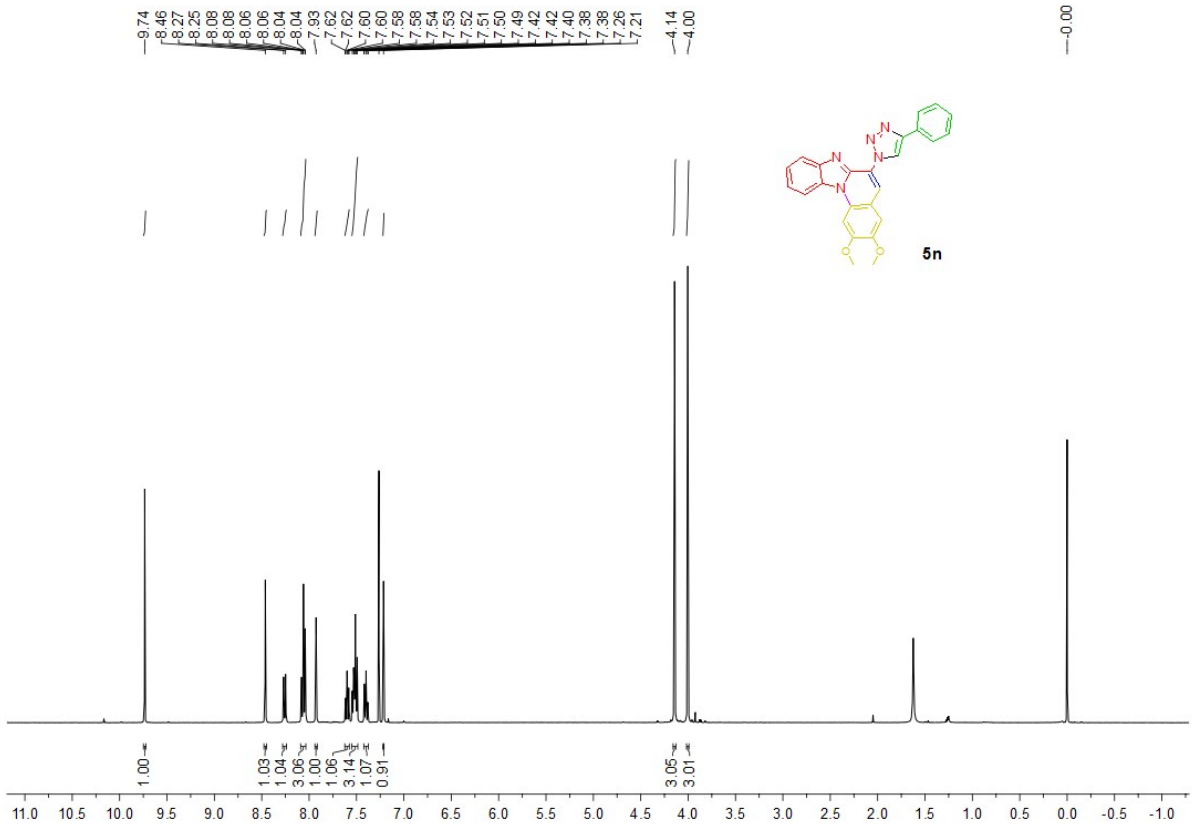


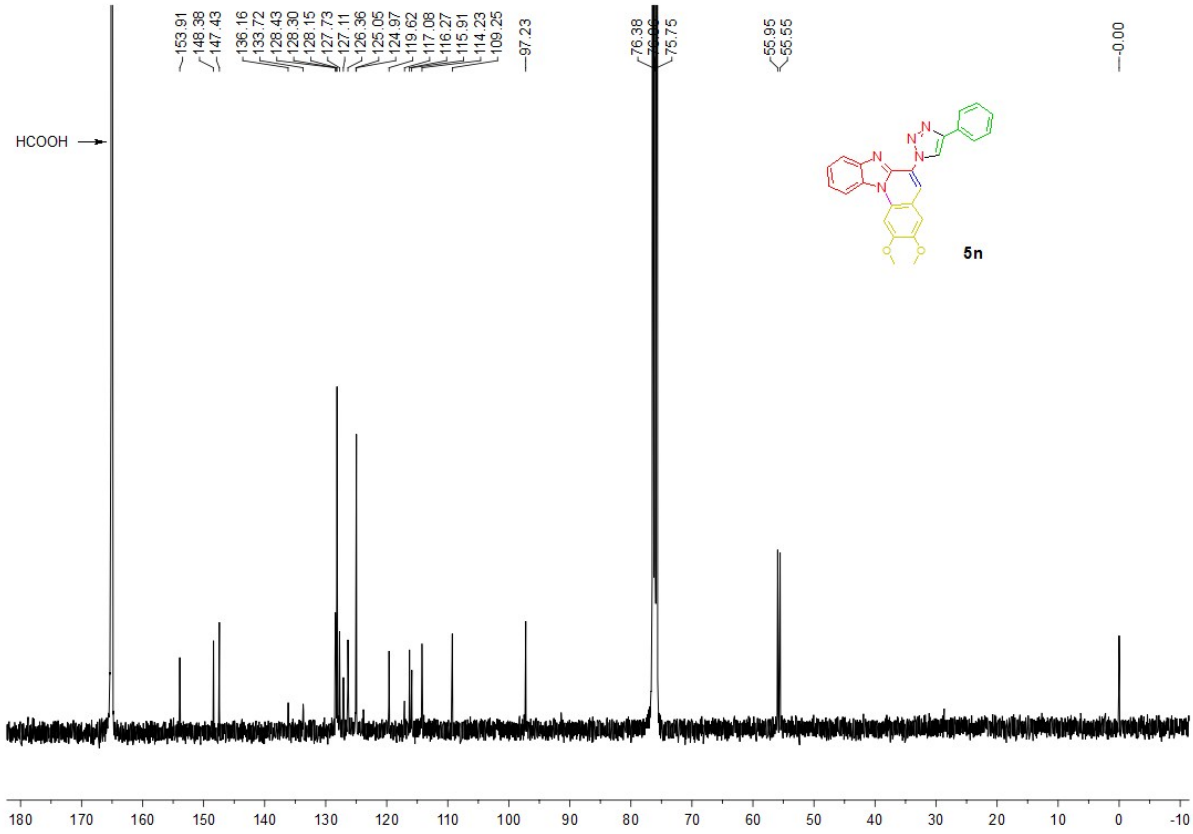
5m (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



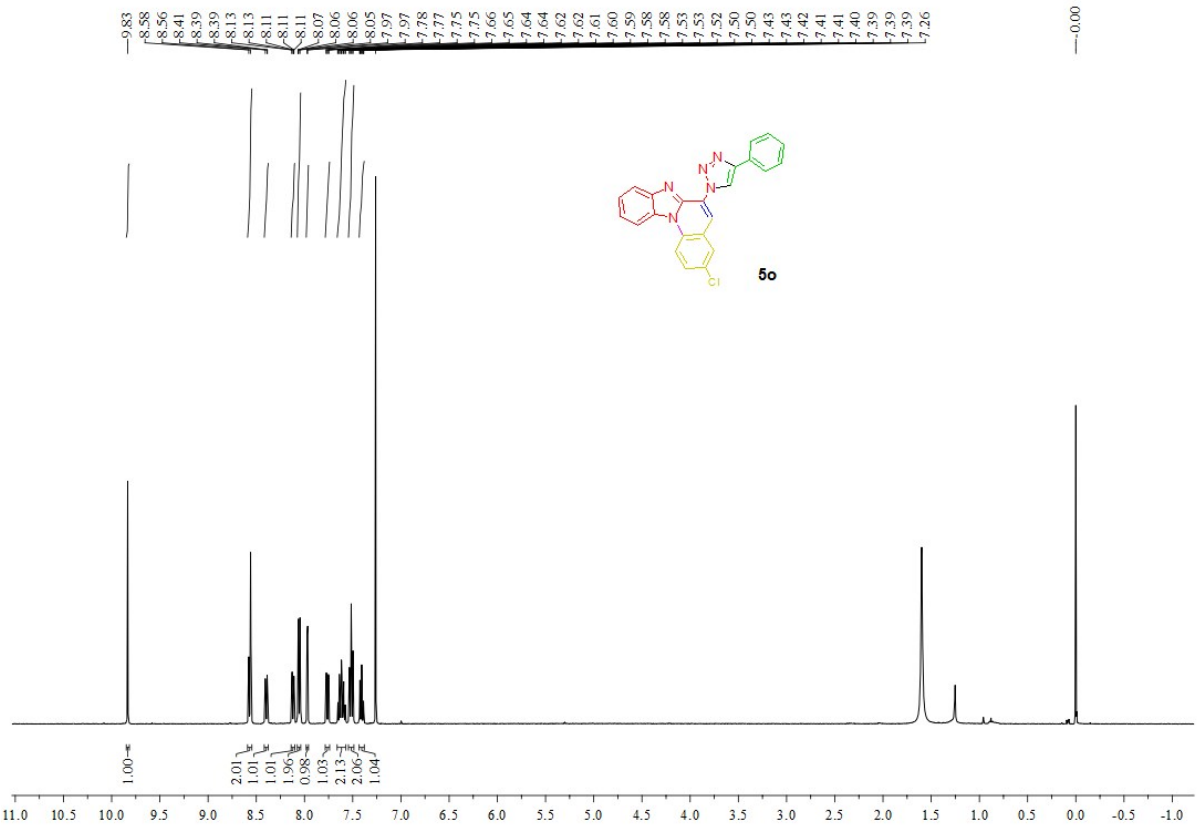
5n (^{1}H NMR, $CDCl_3$, 400 MHz)



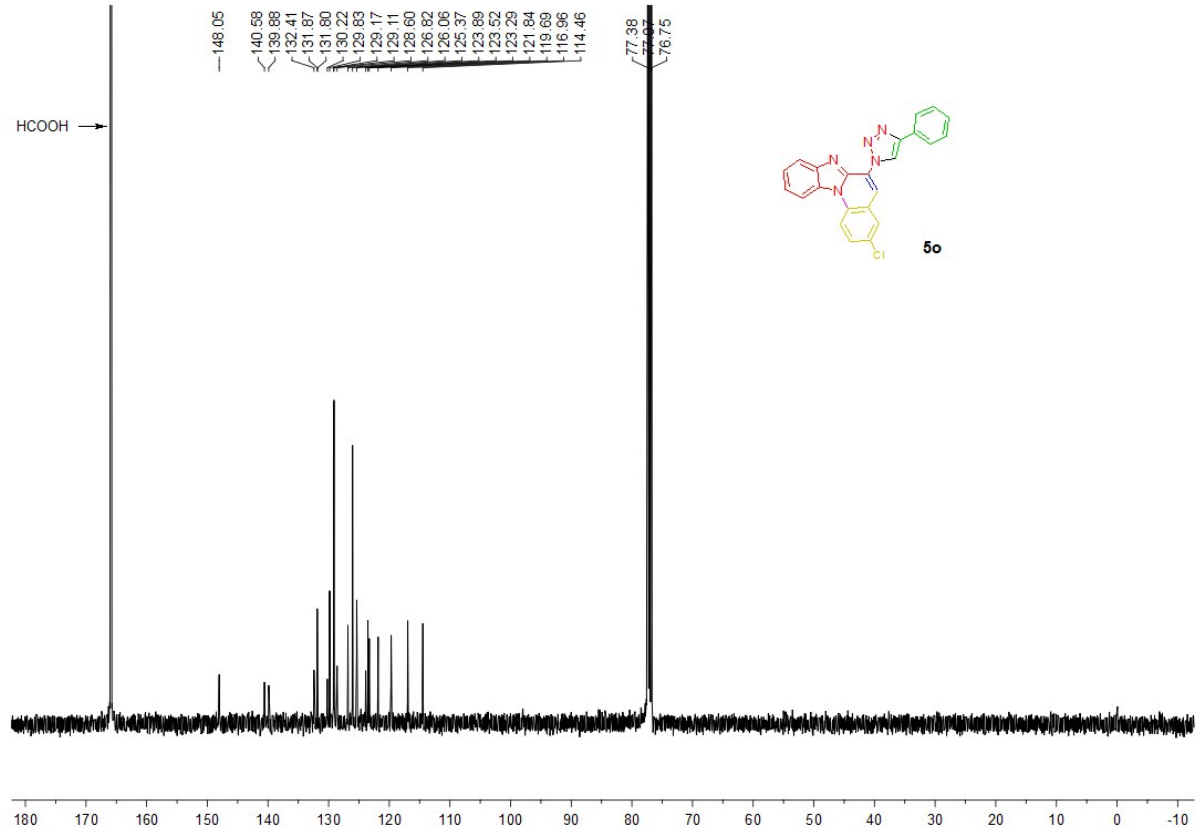
5n (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



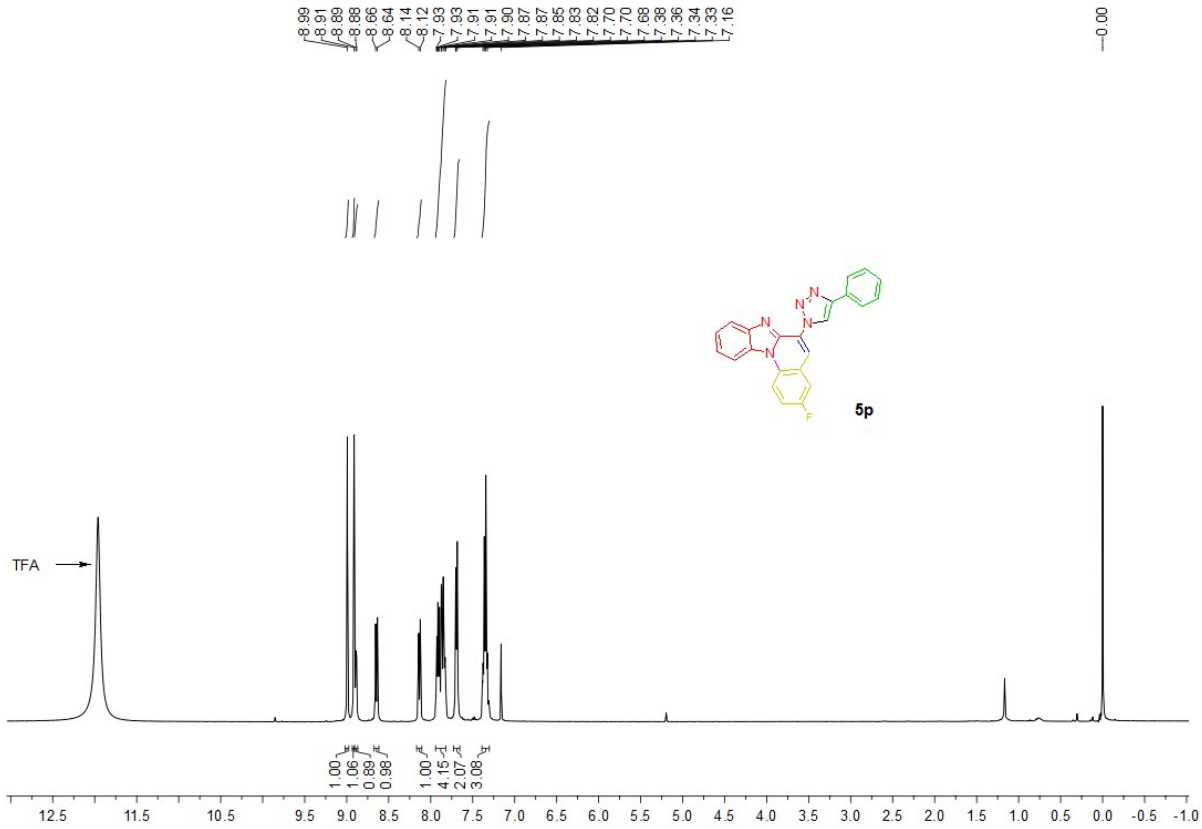
5o (^{1}H NMR, $CDCl_3$, 400 MHz)



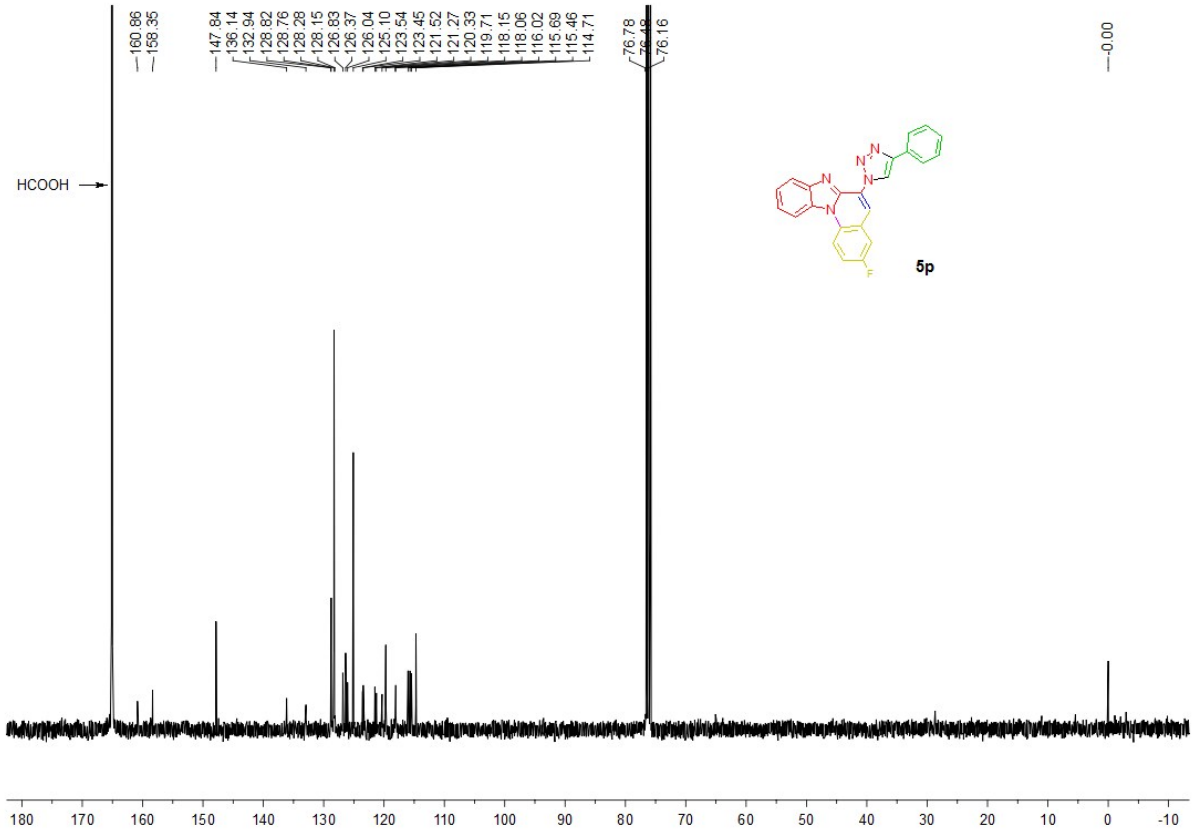
5o (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



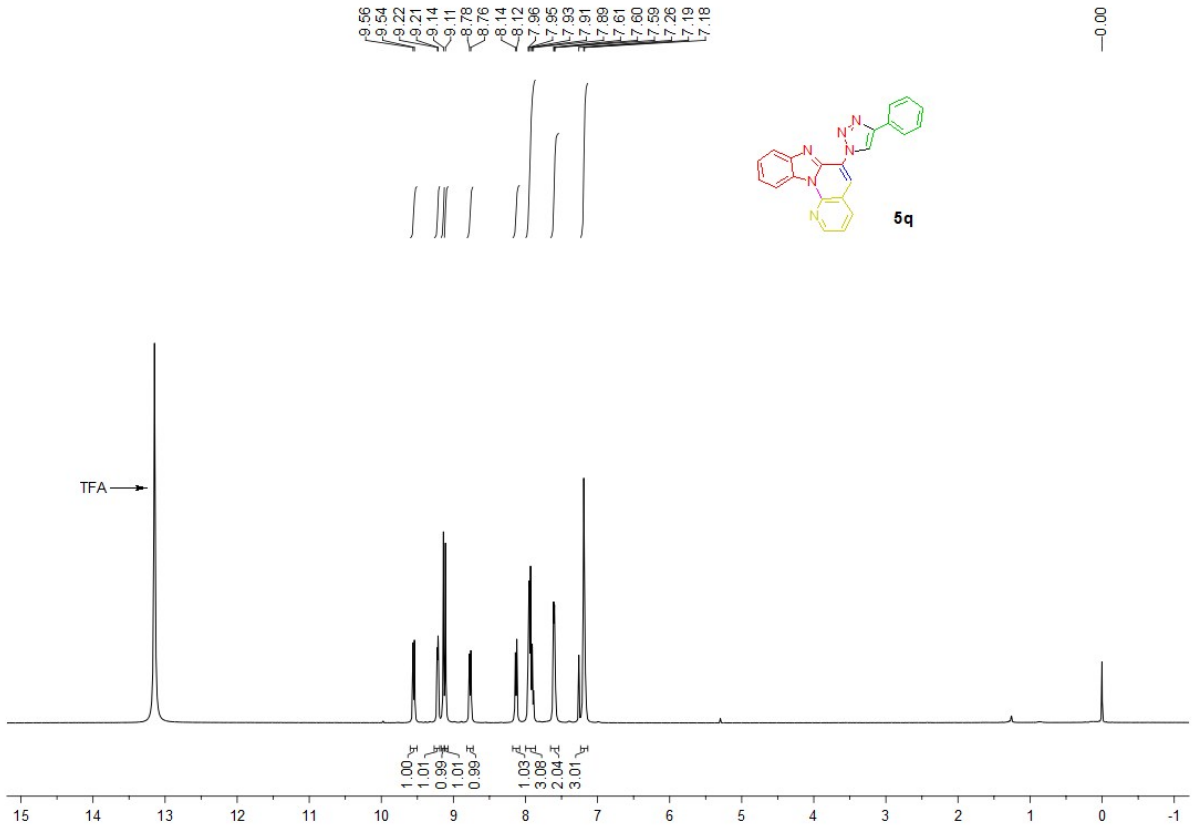
5p (^{1}H NMR, $CDCl_3$ + 10µL trifluoroacetic acid, 400 MHz)



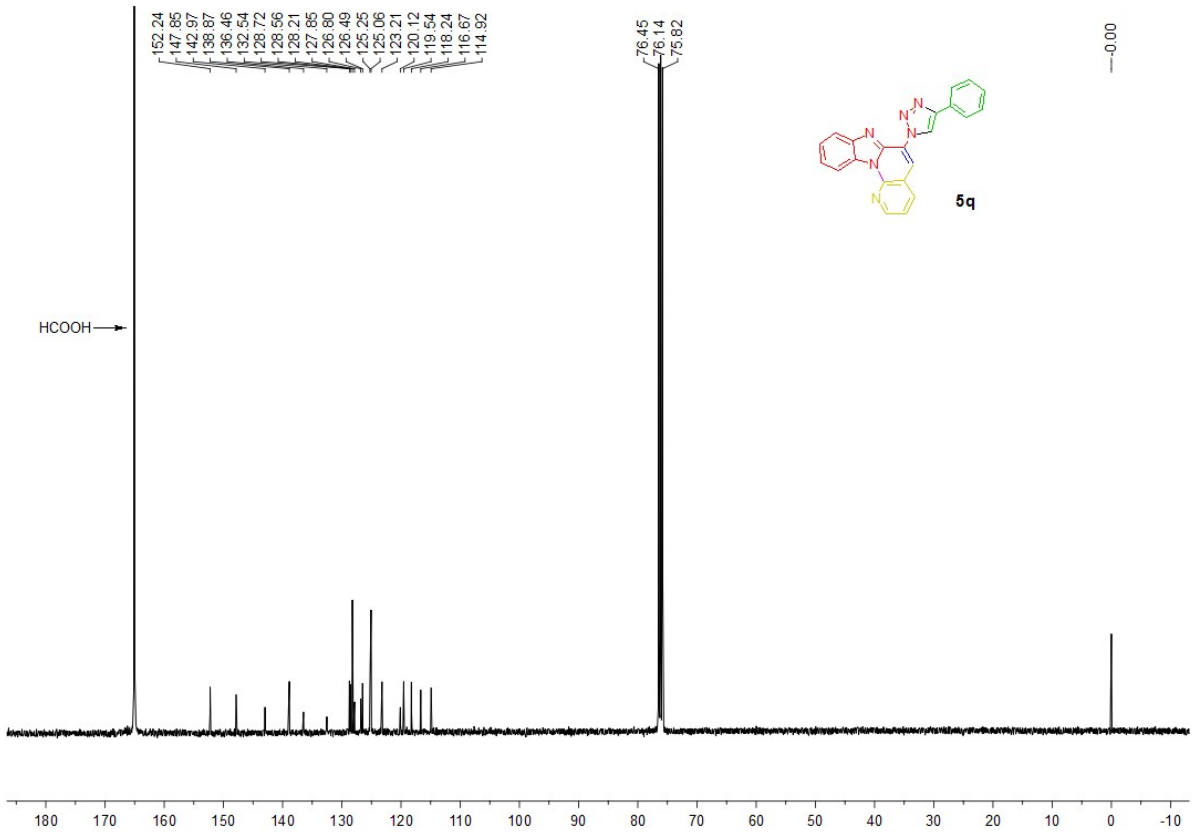
5p (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



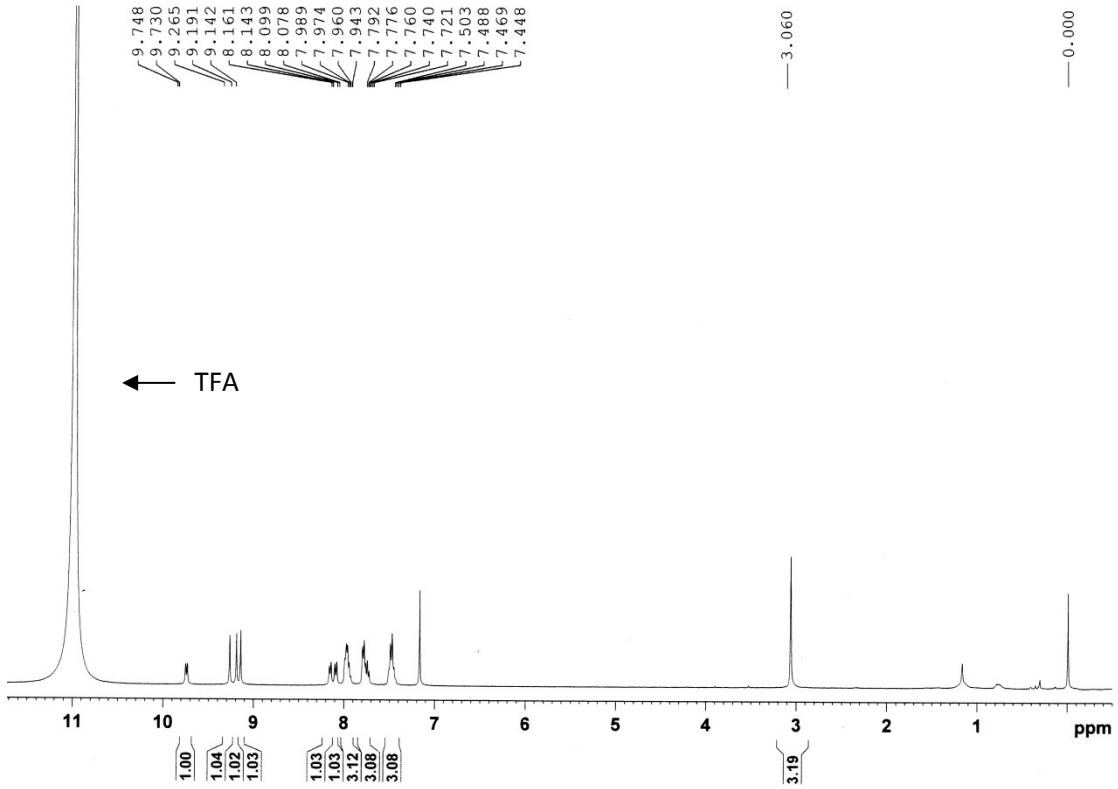
5q (^{1}H NMR, $CDCl_3$ + 10µL trifluoroacetic acid, 400 MHz)



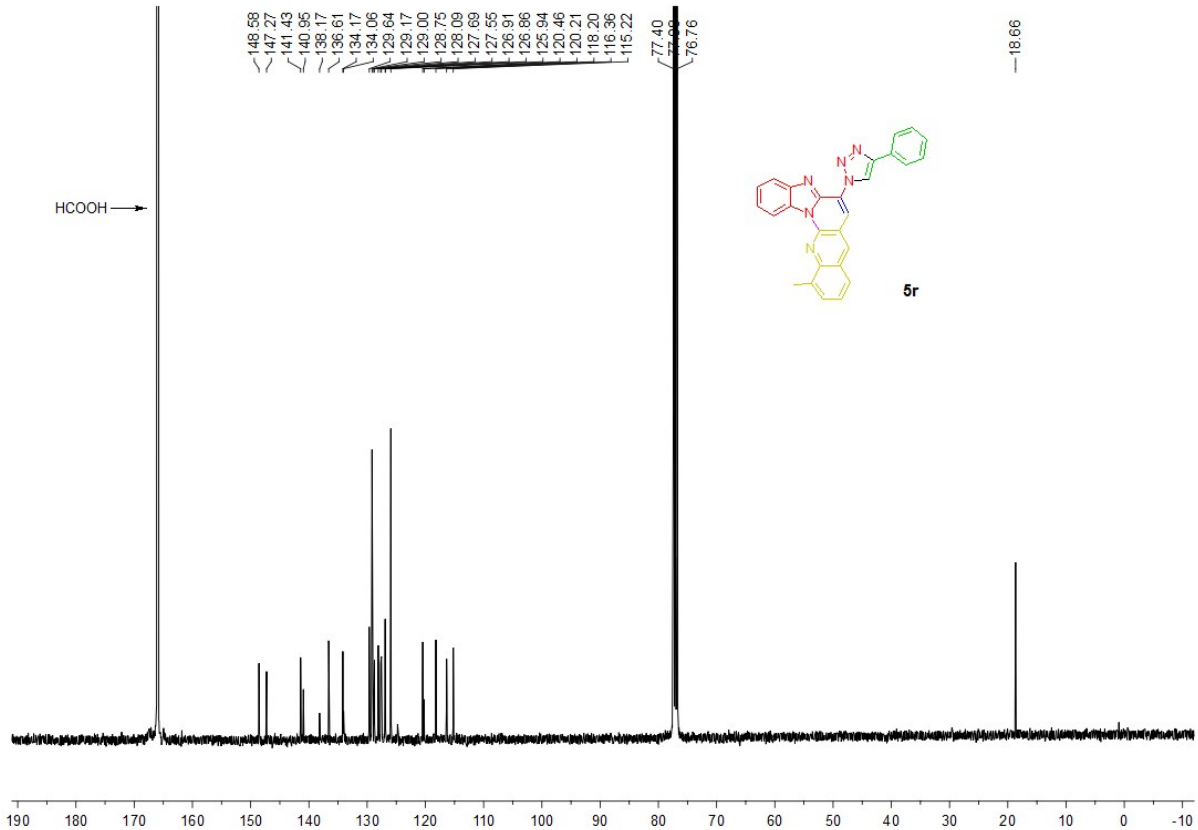
5q (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



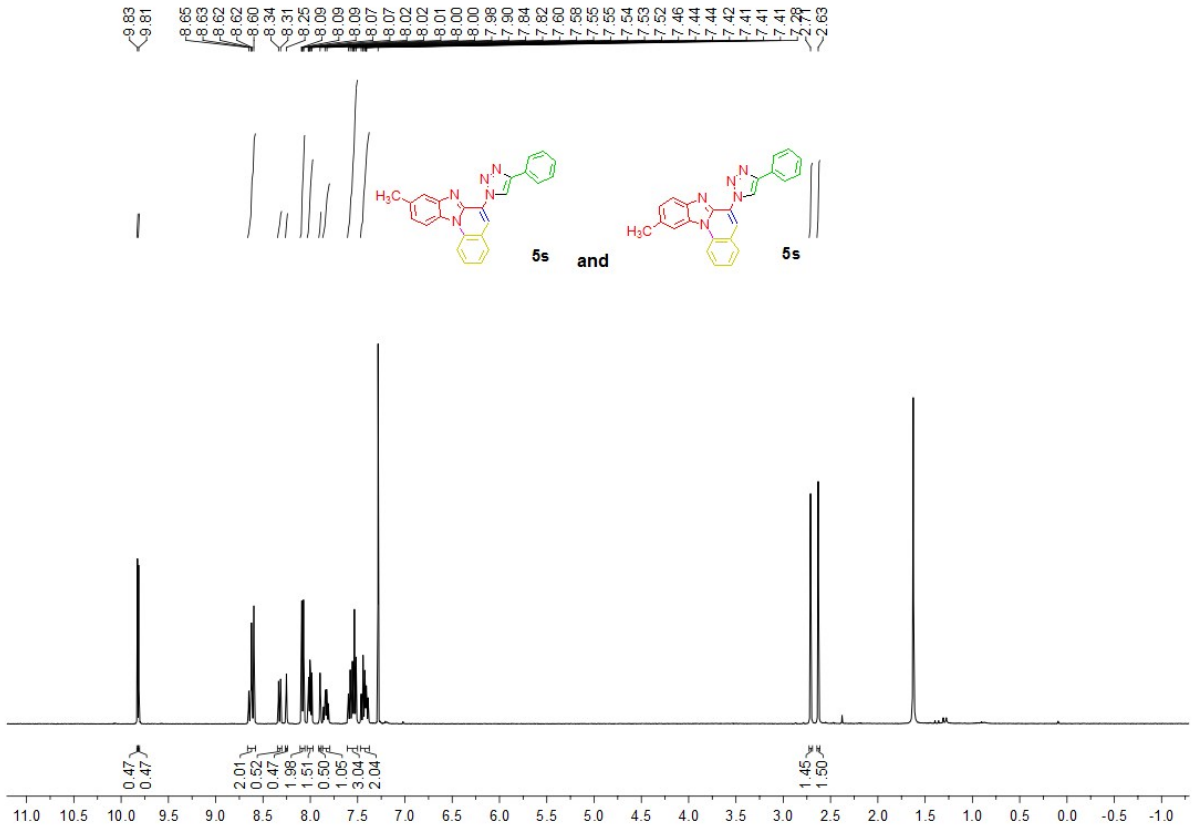
5r (^{1}H NMR, $CDCl_3$ + 10µL trifluoroacetic acid, 400 MHz)



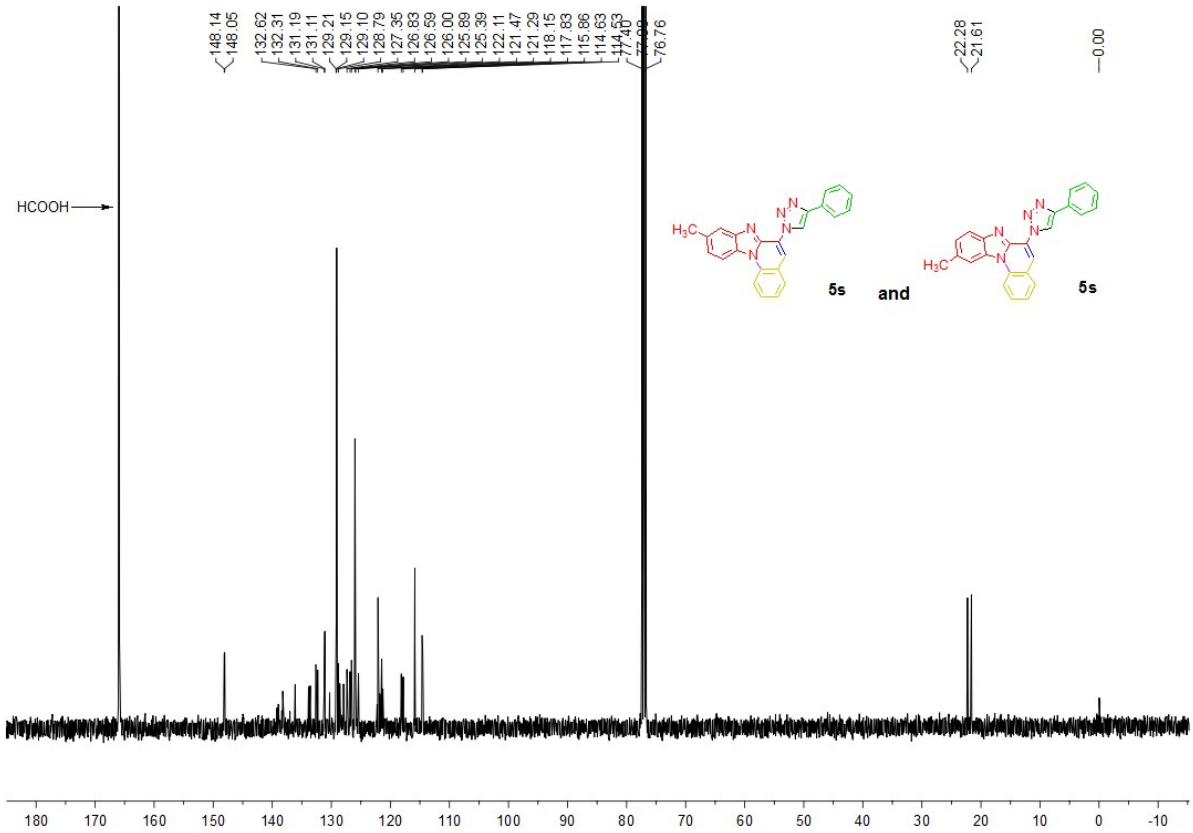
5r (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



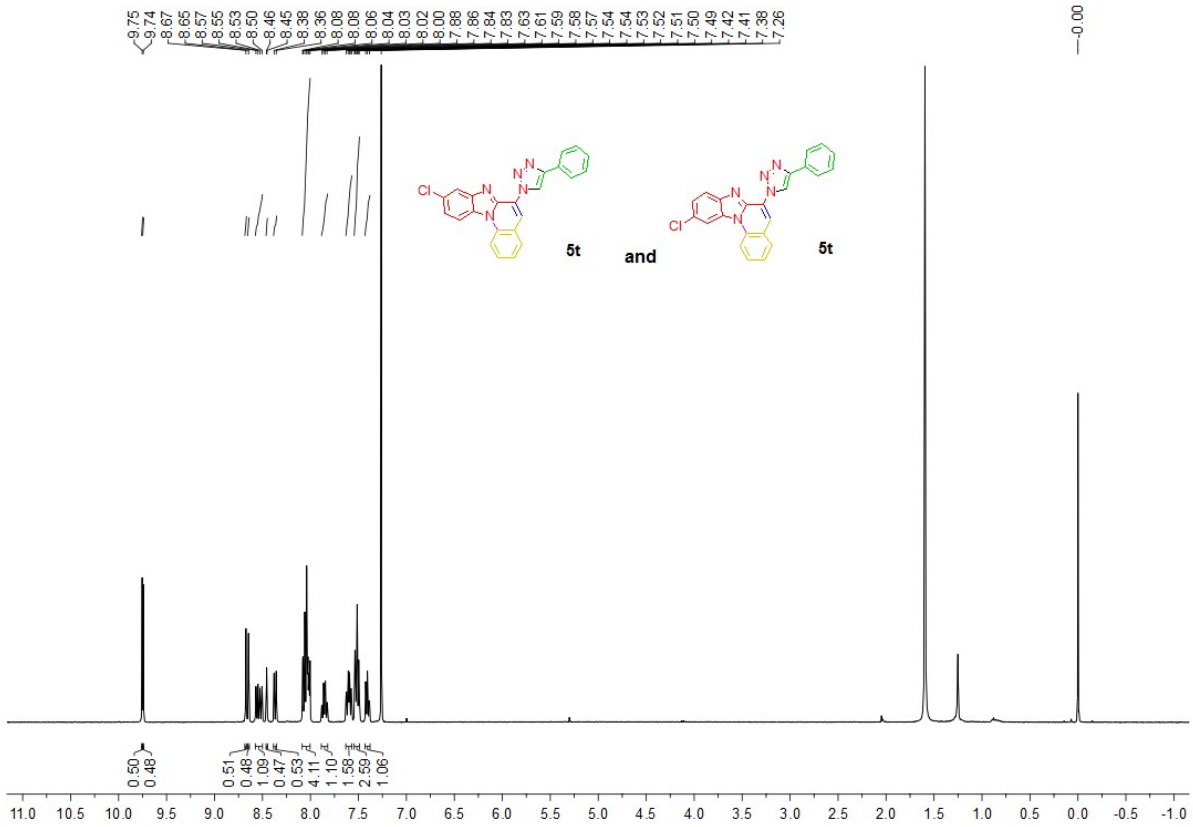
5s (^{1}H NMR, $CDCl_3$, 400 MHz)



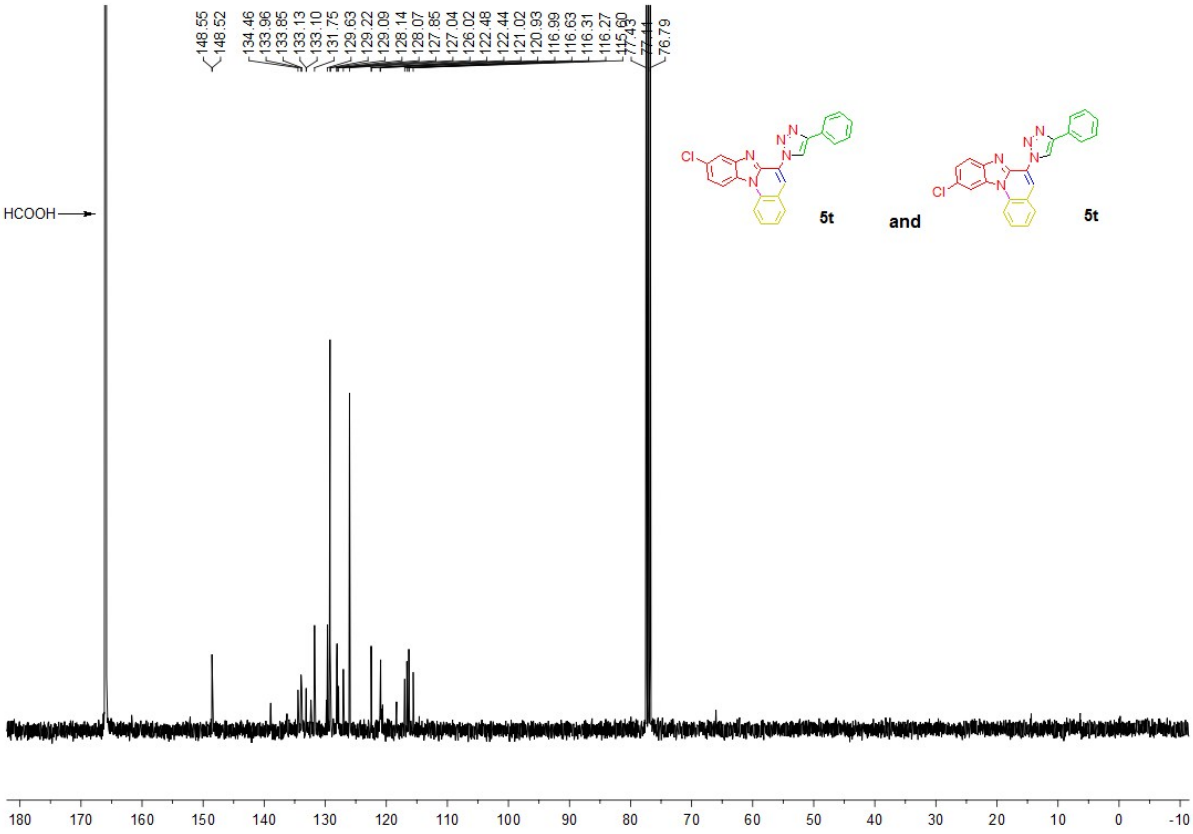
5s (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



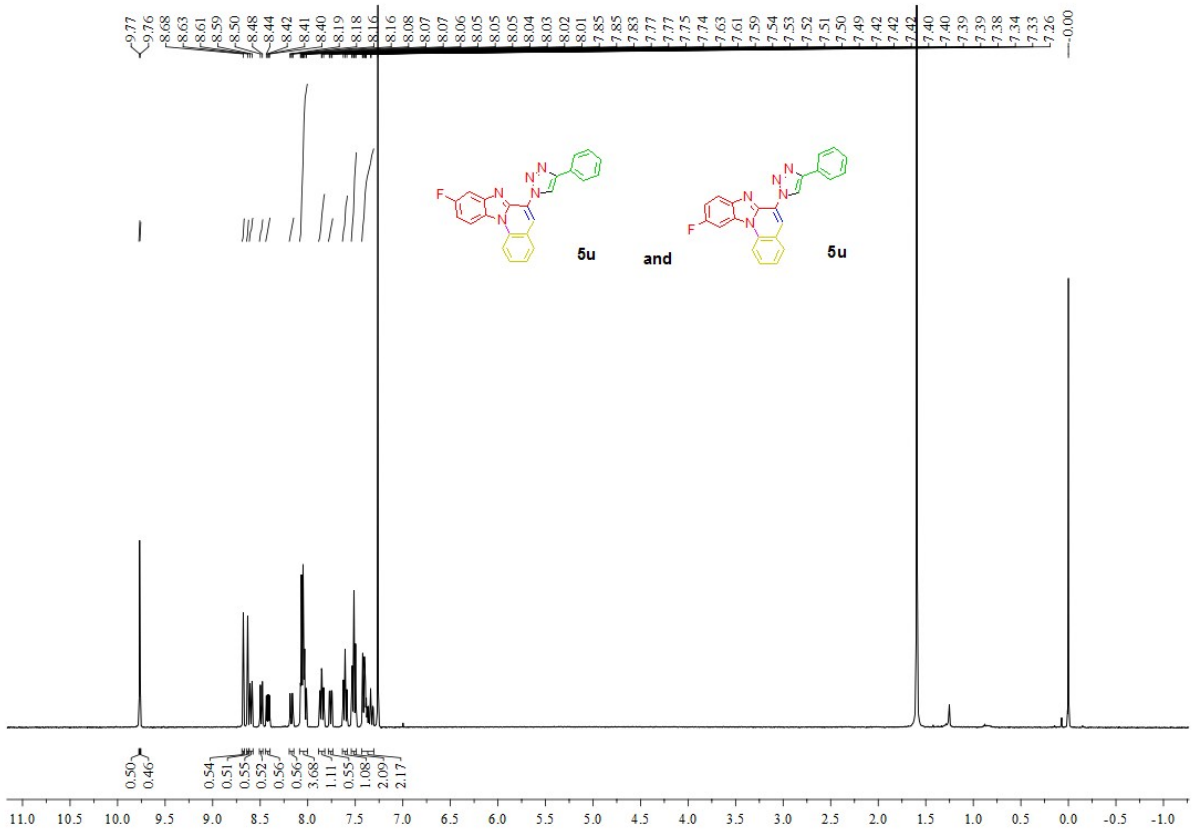
5t (^{1}H NMR, $CDCl_3$, 400 MHz)



5t (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)



5u (^{1}H NMR, $CDCl_3$, 400 MHz)



5u (^{13}C NMR, $CDCl_3$ + 10µL formic acid, 100 MHz)