Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Bench-Stable Low-Molecular-Weight Vinyl Azide Surrogate for Cascade Reaction: Facile Access to Novel N-Vinyl-1,2,3-Triazoles

Zhenhua Liu, Lianxiao Wang, Tian Yu, Yanan Sun, Huimin Chen, Wen Gao*, and Bo Tang*.

College of Chemistry, Chemical Engineering and Materials Science, Collaborative Innovation Center of Functionalized Probes for Chemical Imaging in Universities of Shandong, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Provincial Key Laboratory of Clean Production of Fine Chemicals, Shandong Normal University, Jinan, 250014, P. R. China

E-mail: gaowen@sdnu.edu.cn；tangb@sdnu.edu.cn

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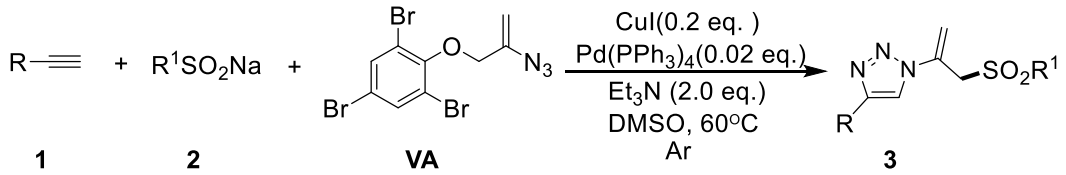
I. General information

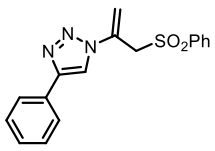
All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H NMR and ^{13}C NMR spectra were recorded at 25 ℃ on a Varian 400 MHz and 100 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

II. Synthesis and analytical data of compounds 3 and 4



1 **2** **VA** **3**

Genernal procedure: Under argon atmosphere, alkyne (0.5 mmol, 1.0 eq.), 2-((2-azidoallyl)oxy)-1,3,5-tribromobenzene (**VA**) (0.6 mmol, 1.2 eq.), sodium sulfinate (0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.) were added in an oven-dried 15 mL Schlenk tube with 1 mL DMSO. The reaction mixture was then stirred for 2 h when TLC conformed that substrate **1** had been consumed. The reaction was cooled to room temperature followed by adding 30 mL H_2O and taken up with dichloromethane (3 × 15 mL). The combined organic layer was washed with brine (3 × 40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (petroleum ether/ethyl acetate) and the target product was afforded.



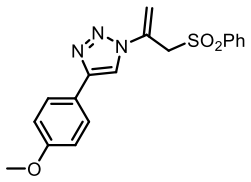
(3a) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.),

sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.) The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (146.3 mg, 90%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.85–7.80 (m, 2H), 7.79–7.72 (m, 2H), 7.59–7.49 (m, 1H), 7.50–7.40 (m, 4H), 7.40–7.37 (m, 1H), 5.72 (d, *J* = 2.2 Hz, 1H), 5.40 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 138.0, 134.1, 132.6, 129.7, 129.2, 128.9, 128.7, 128.4, 125.9, 117.6, 112.3, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{15}N_3O_2SNa$ $[M+Na]^+$: 348.0777, found: 348.0791.

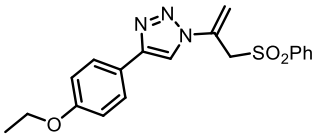
1.0 mmol scale: Under argon atmosphere, phenylacetylene (109.8 μL, 1 mmol, 1.0 eq.), **VA** (494 mg, 1.2 mmol, 1.2 eq.), sodium sulfinate (197 mg, 1.2 mmol, 1.2 eq.), triethylamine (Et_3N) (280.0 μL, 2.0 mmol, 2.0 eq.), CuI (380.8 mg, 0.2 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (23.1 mg, 0.02 mmol, 0.02 eq.) were added in an oven-dried 15 mL Schlenk tube with 2 mL DMSO. The reaction mixture was then stirred for 2 h when TLC conformed that substrate **1a** had been consumed. The reaction was cooled to room temperature followed by adding 30 mL H_2O and taken up by dichloromethane (3 × 15 mL). The combined organic layer was washed with brine (3 × 40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (petroleum ether/ethylacetate=5:1) and the target product **3a** was afforded (273.1 mg, 84%) as white solid.

5.0 mmol scale: Under argon atmosphere, phenylacetylene (549.0 μL, 5 mmol, 1.0 eq.), **VA** (2.47 g, 6.0 mmol, 1.2 eq.), sodium sulfinate (985.0 mg, 6.0 mmol, 1.2 eq.), triethylamine (Et_3N) (1.40 mL, 10.0 mmol, 2.0 eq.), CuI (190.4 mg, 1.0 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (115.5 mg, 0.1 mmol, 0.02 eq.) were added in an oven-dried 25 mL Schlenk tube with 10 mL DMSO. The reaction mixture was then stirred for 4 h when TLC conformed that substrate **1a** had been consumed. The reaction was cooled to room temperature followed by adding 100 mL H_2O and taken up by dichloromethane (3 × 15 mL). The combined organic layer was washed with brine (3 × 40 mL), dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by a

silica gel column chromatography (petroleum ether/ethylacetate=5:1) and the target product **3a** was afforded (1.17 g, 72%) as white solid.

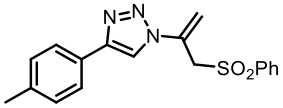


(3b) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-ethynylanisole (64.8 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (150.9 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) 7.85–7.80 (m, 2H), δ 7.88 (s, 1H),7.72–7.63 (m, 2H), 7.60–7.49 (m, 1H), 7.50–7.39 (m, 2H), 7.08–6.89 (m, 2H), 5.70 (d, *J* = 2.2 Hz, 1H), 5.38 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H), 3.85 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 159.9, 148.1, 138.0, 134.1, 132.6, 129.2, 128.4, 127.2, 122.3, 116.7, 114.3, 112.0, 56.0, 55.4; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{17}N_3O_3SNa$ $[M+Na]^+$: 378.0883, found: 378.0877.

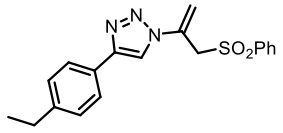


(3c) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-ethoxyphenylacetylene (73.8 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (151.3 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.79 (m, 2H) 7.77 (s, 1H), 7.70–7.65 (m, 2H),

7.58–7.51(m, 1H), 7.49–7.39 (m, 2H), 6.98-6.92 (m, 2H), 5.69 (d, *J* = 2.2Hz, 1H), 5.39 (d, *J* = 2.2Hz, 1H), 4.70 (s, 2H), 4.08 (q, *J* = 7.0Hz, 2H), 1.44 (t, *J* = 7.0Hz, 3H); **^{13}C NMR** (100MHz, $CDCl_3$) δ 159.3, 148.1, 138.0, 134.1, 132.6, 129.2, 128.4, 127.2, 122.1, 116.6, 114.8, 111.9, 63.5, 59.0, 14.8; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{19}N_3O_3SNa$ $[M+Na]^+$: 392.1039, found: 392.1025.

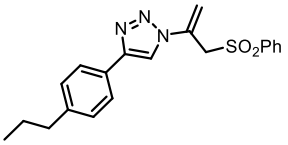


(3d) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-ethynyltoluene (63.4 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (149.2 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.82–7.79 (m, 2H), 7.68–7.60 (m, 2H), 7.58–7.48 (m, 1H), 7.48–7.38 (m, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.70 (d, *J* = 2.2 Hz, 1H), 5.38 (d, *J* = 2.2 Hz, 1H), 4.69 (s, 2H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 138.0, 134.1, 132.6, 129.7, 129.2, 128.9, 128.7, 128.4, 125.9, 117.6, 112.2, 59.0, 21.3; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{17}N_3O_2SNa$ $[M+Na]^+$: 362.0934, found: 362.0935.

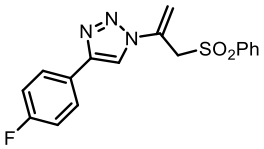


(3e) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-ethylphenylacetylene (72.3 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (148.3 mg, 84%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.83–7.75 (m, 2H), 7.60–7.64 (m, 2H), 7.58–7.50 (m, 1H), 7.48–7.38 (m, 2H), 7.21–7.29 (m, 2H), 5.71 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H), 2.69 (q, *J* = 7.6 Hz, 2H), 1.29-1.25 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 144.9, 137.9, 134.1, 132.6, 129.2, 128.4, 128.3, 127.0, 125.8, 117.1, 112.0. 59.0, 28.7, 15.5; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{19}N_3O_2SNa$ $[M+Na]^+$: 376.1090, found: 376.1078.

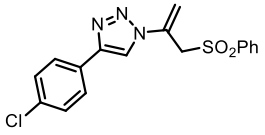


(3f) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-eth-1-ynyl-4-propylbenzene (79.2 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (154.2 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.83–7.79 (m, 2H), 7.71–7.60 (m, 2H), 7.59–7.49 (m, 1H), 7.49–7.34 (m, 2H), 7.26-7.22 (m, 2H), 5.71 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H), 2.62 (t, *J* = 7.6Hz, 2H), 1.69-1.62 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 143.4, 137.9, 134.1, 132.6, 129.2, 129.0, 128.3, 127.1, 125.8, 117.2, 112.0, 59.0, 37.8, 24.4, 13.8; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{21}N_3O_2SNa$ $[M+Na]^+$: 390.1247, found: 390.1273.

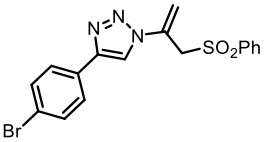


(3g) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-fluorophenylacetylene (57.3 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (151.0 mg, 88%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.85–7.77 (m, 2H), 7.81–7.69 (m, 2H), 7.62–7.52 (m, 1H), 7.51–7.39 (m, 2H), 7.19–7.08 (m, 2H), 5.73 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 4.69 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.2 (d, *J* = 248.5 Hz), 147.3, 138.0, 134.2, 132.5, 129.2, 128.4, 127.7 (d, *J* = 8.3 Hz), 125.9 (d, *J* = 3.2 Hz), 117.4, 116.1, 115.9, 112.4, 59.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.65; **HRMS** (ESI-TOF) m calculated for $C_{17}H_{14}FN_3O_2SNa$ $[M+Na]^+$: 366.0683, found: 366.0685.

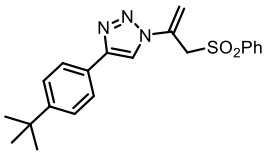


(3h) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-chlorophenylacetylene (68,3 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (154.4 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.85–7.79 (m, 2H), 7.73–7.66 (m, 2H), 7.60–7.52 (m, 1H), 7.50–7.37 (m, 4H), 5.73 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.3 Hz, 1H), 4.68 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 137.9, 134.4, 134.2, 132.4, 129.2, 129.2, 128.4, 128.2, 127.1, 117.8, 112.6, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}ClN_3O_2SNa$ $[M+Na]^+$: 382.0387, found: 382.0412.

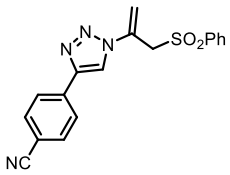


(3i) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-bromophenylacetylene (63.5 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (175.3 mg, 87%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.86–7.79 (m, 2H), 7.69–7.60 (m, 2H), 7.59–7.52 (m, 3H), 7.49-7.42 (m, 2H), 5.73 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 4.68 (s, 2H); **^{13}CNMR** (100 MHz, $CDCl_3$) δ 147.2, 137.9, 134.2, 132.4, 132.1, 129.2, 128.6, 128.3, 127.3, 122.6, 117.8, 112.2, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}BrN_3O_2SNa$ $[M+Na]^+$: 425.9882, found: 425.9874.

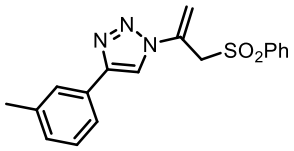


(3j) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-tert-butylphenylacetylene (90.2 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (158.2 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 7.84–7.77 (m, 2H), 7.71–7.63 (m, 2H), 7.57–7.50 (m, 1H), 7.48–7.35 (m, 4H), 5.71 (d, *J* = 2.2 Hz, 1H), 5.38 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H), 1.35 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 151.8, 148.2, 138.0, 134.1, 132.6, 129.2, 128.4, 126.8, 125.8, 125.6, 117.2, 112.0, 59.0, 34.7, 31.3; **HRMS** (ESI-TOF) m/z calculated for $C_{21}H_{23}N_3O_2SNa$ $[M+Na]^+$: 404.1403, found: 404.1423.

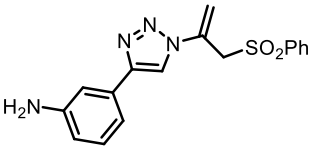


(3k) 0.5 mmol scale: Prepared following the genernal procedure showed above using 4-cyanophenylacetylene (63.6 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (147.0 mg, 84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.94–7.88 (m, 2H), 7.87–7.78 (m, 2H),

7.79–7.69 (m, 2H), 7.60–7.55 (m, 1H), 7.49 (m, 2H), 5.79 (d, *J* = 2.3 Hz, 1H), 5.40 (d, *J* = 2.3 Hz, 1H), 4.67 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 137.9, 134.3, 134.1, 132.8, 132.3, 129.3, 128.4, 126.2, 119.0, 118.6, 113.4, 112.1, 59.1; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{14}N_4O_2SNa$ $[M+Na]^+$: 373.0730, found: 373.0734.

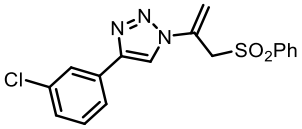


(3l) 0.5 mmol scale: Prepared following the genernal procedure showed above using 3-ethynyltoluene (63.4 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (149.2 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.85–7.76 (m, 2H), 7.65–7.58 (m, 1H), 7.59–7.48 (m, 2H), 7.49–7.38 (m, 2H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 1H), 5.72 (d, *J* = 2.2 Hz, 1H), 5.40 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 138.6, 137.9, 134.1, 132.6, 129.5, 129.4, 129.2, 128.8, 128.3, 126.5, 122.9, 117.5, 112.1, 59.0, 21.4; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{17}N_3O_2SNa$ $[M+Na]^+$: 362.0934, found: 362.0933.

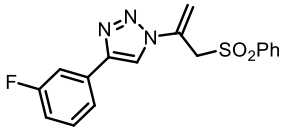


(3m) 0.5 mmol scale: Prepared following the genernal procedure showed above using 3-ethynylaniline (56.8 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), Sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (132.3 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.81–7.78 (m, 2H), 7.59–7.50 (m, 1H), 7.49–7.40 (m, 2H), 7.31 (t, *J* = 4.6, 1H), 7.19–7.09 (m, 1H), 7.10-1.04 (m, 1H),

6.74–6.63 (m, 1H), 5.70 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 4.70 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 146.9, 137.9, 134.1, 132.6, 130.6, 129.8, 129.2, 128.3, 117.5, 116.1, 115.3, 112.3, 112.1, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{16}N_4O_2SNa$ $[M+Na]^+$: 363.0886, found: 363.0899.

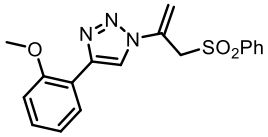


(3n) 0.5 mmol scale: Prepared following the genernal procedure showed above using 3-chlorophenylacetylene (68.3 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (154.4 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.89–7.79 (m, 2H), 7.79–7.73 (m, 1H), 7.69-7.60 (m, 1H), 7.61–7.52 (m, 1H), 7.53–7.41 (m, 2H), 7.41–7.30 (m, 2H), 5.74 (d, *J* = 2.3 Hz, 1H), 5.40 (d, *J* = 2.3 Hz, 1H), 4.68 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.8, 137.8, 134.9, 134.2, 132.4, 131.4, 130.2, 129.2, 128.6, 128.3, 125.9, 123.9, 118.0, 112.7, 58.9; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}ClN_3O_2SNa$ $[M+Na]^+$: 382.0387, found: 382.0393.

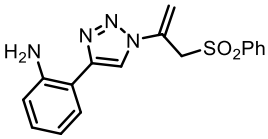


(3o) 0.5 mmol scale: Prepared following the genernal procedure showed above using 3-fluorophenylacetylene (60.1 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (149.2 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.90–7.75 (m, 2H), 7.64–7.32 (m, 6H), 7.09–7.01 (m, 1H), 5.74 (d, *J* = 2.2 Hz, 1H), 5.40 (d, *J* = 2.2 Hz, 1H), 4.69 (s, 2H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3 (d, *J* = 245.6 Hz), 147.1 (d, *J* = 2.9 Hz), 137.9, 134.2, 132.4, 131.8 (d, *J* = 8.4 Hz), 130.6 (d, *J* = 8.6 Hz), 129.2, 128.3, 121.5 (d, *J* = 3.1 Hz), 118.1, 115.6 (d, *J* = 23.0 Hz), 112.9, 112.7, 59.0; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.32; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}FN_3O_2SNa$ $[M+Na]^+$: 366.0683, found: 366.0694.

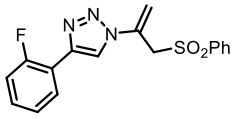


(3p) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-methoxyphenylacetylene (64.7 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (147.3 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28-8.21 (m, 1H), 8.15 (s, 1H), 7.85–7.72 (m, 2H), 7.56–7.47 (m, 1H), 7.46–7.38 (m, 2H), 7.38–7.29 (m, 1H), 7.07 (t, *J* = 7.6, 1.2 Hz, 1H), 6.99 (d, *J* = 8.2, 1H), 5.72 (d, *J* = 2.2 Hz, 1H), 5.39 (d, *J* = 2.2 Hz, 1H), 4.72 (s, 2H), 3.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.7, 143.6, 137.9, 134.0, 132.6, 129.4, 129.1, 128.3, 127.7, 121.0, 120.7, 118.4, 111.6, 110.7, 58.9, 55.4; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{17}N_3O_3SNa$ $[M+Na]^+$: 378.0883, found: 378.0891.

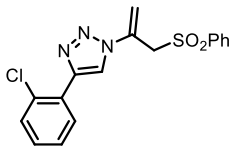


(3q) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-ethynylaniline (56.8 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (132.6 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 1H),7.86–7.77 (m, 2H), 7.62–7.50 (m, 1H),

7.49–7.40 (m, 2H), 7.31–7.24 (m, 1H), 7.14 (m, 1H), 6.74 (m, 2H), 5.73 (d, *J* = 2.2 Hz, 1H), 5.41 (d, *J* = 2.2 Hz, 1H), 4.69 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 145.2, 137.9, 134.2, 132.5, 129.6, 129.2, 128.3, 127.9, 117.8, 117.5, 116.8, 112.7, 112.6, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{16}N_4O_2SNa$ $[M+Na]^+$: 363.0886, found: 363.0896.

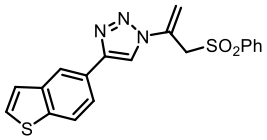


(3r) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-fluorophenylacetylene (60.1 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (137.2 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.24-8.15 (m, 1H), 8.01 (d, *J* = 3.4 Hz, 1H), 7.90–7.77 (m, 2H), 7.56–7.46 (m, 1H), 7.48–7.38 (m, 2H), 7.38–7.29 (m, 1H), 7.24–7.20 (m, 1H), 7.19–7.11 (m, 1H), 5.74 (d, *J* = 2.2 Hz, 1H), 5.42 (d, *J* = 2.2Hz, 1H), 4.72 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.5 (d, *J* = 248.3 Hz), 141.7, 137.9, 134.1, 132.5, 129.9 (d, *J* = 8.6 Hz), 129.2, 128.4, 127.9 (d, *J* = 3.4 Hz), 124.7 (d, *J* = 3.4 Hz), 120.7 (d, *J* = 13.1 Hz), 117.7 (d, *J* = 13.2 Hz), 115.9 (d, *J* = 21.5 Hz), 112.4, 58.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.36; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}FN_3O_2SNa$ $[M+Na]^+$: 366.0683, found: 366.0667.

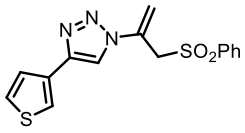


(3s) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-chlorophenylacetylene (68.3 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mm ol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (143.6 mg, 80%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.15-8.09 (m, 1H), 7.88–7.67 (m, 2H), 7.58–7.49 (m, 1H), 7.48–7.42 (m, 3H), 7.38–7.34 (m, 1H), 7.33–7.28 (m, 1H), 5.75 (d, *J* = 2.2 Hz, 1H), 5.44 (d, *J* = 2.2 Hz, 1H), 4.72 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 137.9, 134.1, 132.6, 131.3, 130.3, 129.9, 129.5, 129.2, 128.3, 127.2, 121.1, 112.6, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}ClN_3O_2SNa$ $[M+Na]^+$: 382.0387, found: 382.0369.

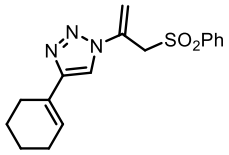


(3t) 0.5 mmol scale: Prepared following the genernal procedure showed above using 5-ethynyl benzothiophene (79.1 mg,, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (146.7 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23–8.17 (m, 1H), 7.99 (s, 1H), 7.94–7.88 (m, 1H), 7.86–7.80 (m, 2H), 7.77 (s, 1H), 7.57–7.37 (m, 5H), 5.77 (d, *J* = 2.2 Hz, 1H), 5.62 (d, *J* = 2.2 Hz, 1H), 4.73 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.6, 140.5, 138.0, 136.6, 134.2, 132.5, 129.2, 128.4, 125.6, 125.01, 124.8, 124.8, 123.2, 122.9, 118.3, 112.5, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{15}N_3O_2S_2Na$ $[M+Na]^+$: 404.0498, found: 404.0512.

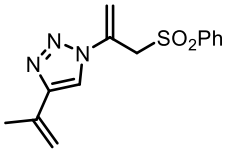


(3u) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-ethynylthiophene (50.1 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (124.1 mg, 75%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.77 (m, 3H), 7.66 (t, *J* = 2.1 Hz, 1H), 7.60–7.51 (m, 1H), 7.49–7.42 (m, 2H), 7.39 (d, *J* = 2.1 Hz, 2H), 5.71 (d, *J* = 2.2 Hz, 1H), 5.37 (d, *J* = 2.2 Hz, 1H), 4.68 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 144.4, 138.0, 134.2, 132.5, 130.9, 129.2, 128.4, 126.6, 125.7, 121.9, 117.4, 112.2, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{13}N_3O_2S_2Na$ $[M+Na]^+$: 354.0341, found: 354.0333.

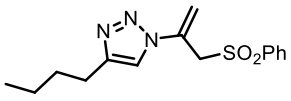


(3v) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-ethynylcyclohex-1-ene (58.8 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (134.9 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88–7.75 (m, 2H), 7.64–7.53 (m, 1H), 7.50 (s, 1H), 7.49–7.42 (m, 2H), 6.50 (s, 1H), 5.62 (d, *J* = 2.2 Hz, 1H), 5.30 (d, *J* = 2.2 Hz, 1H), 4.66 (s, 2H), 2.42–2.00 (m, 4H), 1.84–1.58 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.8, 138.0, 134.1, 132.5, 129.2, 128.3, 126.5, 126.3, 116.2, 111.5, 58.9, 26.3, 25.3, 22.4, 22.1; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{19}N_3O_2SNa$ $[M+Na]^+$: 352.1090, found : 352.1080.

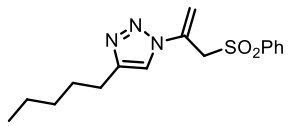


(3w) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-methyl-1-buten-3-yne (33.1 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=4:1) as white solid (107.1 mg, 81%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.73 (m, 2H), 7.65–7.53 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 5.71 (d, *J* = 2.2 Hz, 1H), 5.57 (d, *J* = 2.2 Hz, 1H), 5.36 (s, 1H), 5.13 (s, 1H), 4.67 (s, 2H), 2.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 137.9, 134.0, 132.7, 132.4, 129.2, 128.3, 117.5, 113.7, 112.0, 58.9, 20.5; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{15}N_3O_2SNa$ $[M+Na]^+$: 312.0777, found: 312.0778.

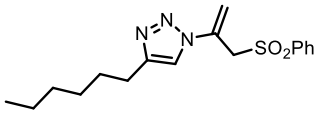


(3x) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-hexyne (57.4 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (112.9 mg, 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.63–7.54 (m, 1H), 7.50–7.43 (m, 2H), 7.41 (s, 1H), 5.61 (d, *J* = 2.2 Hz, 1H), 5.32 (d, *J* = 2.2 Hz, 1H), 4.66 (s, 2H), 2.62 (t, *J* = 7.2Hz, 2H), 1.70–1.48 (m, 2H), 1.29-1.41 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 138.0, 134.0, 132.6, 129.1, 128.4, 118.6, 111.3, 58.8, 31.3, 25.1, 22.3, 13.8; **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{19}N_3O_2SNa$ $[M+Na]^+$: 328.1090, found: 328.1093.

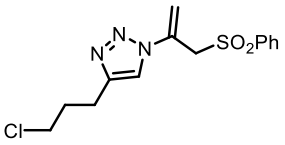


(3y) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-heptyne (65.6 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (111.7 mg, 72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.76 (m, 2H), 7.61–7.52 (m, 1H), 7.50–7.40 (m, 3H), 5.62 (d, *J*

= 2.2 Hz, 1H), 5.29 (d, *J* = 2.2 Hz, 1H), 4.68 (s, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 1.66-1.55 (m, 2H), 1.40-1.23 (m, 4H), 0.90 (t, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.0, 137.9, 134.0, 132.4, 129.1, 128.3, 118.7, 111.4, 58.8, 31.3, 28.9, 25.4, 22.4, 14.0; **HRMS** (ESI-TOF) m/z calculated for $C_{16}H_{21}N_3O_2SNa$ $[M+Na]^+$: 342.1247, found: 342.1229.

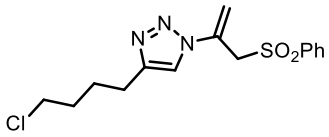


(3z) 0.5 mmol scale: Prepared following the genernal procedure showed above using 1-octyne (73.8 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (121.6 mg, 73%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90–7.70 (m, 2H), 7.65–7.51 (m, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.41 (s, 1H), 5.61 (d, *J* = 2.2 Hz, 1H), 5.31 (d, *J* = 2.2 Hz, 1H), 4.66 (s, 2H), 2.81–2.39 (m, 2H), 1.66–1.53 (m, 2H), 1.40–1.23 (m, 6H), 1.07–0.70 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 149.1, 138.0, 134.0, 132.6, 129.1, 128.4, 118.6, 111.3, 58.8, 31.6, 29.2, 28.9, 25.5, 22.6, 14.1; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{23}N_3O_2SNa$ $[M+Na]^+$: 356.1403, found: 356.1420.

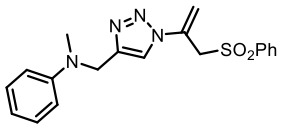


(3za) 0.5 mmol scale: Prepared following the genernal procedure showed above using 5-chloropent-1-yne (51.0 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=4:1) as white solid (121.9 mg, 75%);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.79 (m, 2H), 7.64–7.57 (m, 1H), 7.52–7.42 (m, 3H), 5.63 (d, *J* = 2.2 Hz, 1H), 5.34 (d, *J* = 2.2 Hz, 1H), 4.66 (s, 2H), 3.54 (t, *J* = 6.4 Hz, 2H), 2.82 (t, *J* = 7.3 Hz, 2H), 2.20–2.01 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 138.0, 134.1, 132.5, 129.2, 128.4, 119.20, 111.7, 58.8, 44.0, 31.6, 22.5; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{16}ClN_3O_2SNa$ $[M+Na]^+$: 348.0544, found: 348.0550.

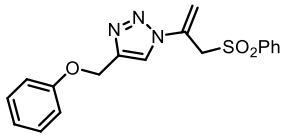


(3zb) 0.5 mmol scale: Prepared following the genernal procedure showed above using 6-chlorohex-1-yne (58.1 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), Sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=4:1) as white solid (125.5 mg, 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84–7.77 (m, 2H), 7.63–7.55 (m, 1H), 7.53–7.42 (m, 3H), 5.63 (d, *J* = 2.2 Hz, 1H), 5.32 (d, *J* = 2.2 Hz, 1H), 4.66 (s, 2H), 3.57 (t, *J* = 5.6 Hz, 2H), 2.67 (t, *J* = 5.6 Hz, 2H), 1.88-1.72 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 138.0,134.1, 132.5, 129.2, 128.4, 118.8, 111.6, 58.8, 44.7, 31.9, 26.4, 24.6; **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{18}ClN_3O_2SNa$ $[M+Na]^+$: 362.0700, found: 362.0688.

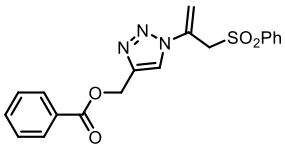


(3zc) 0.5 mmol scale: Prepared following the genernal procedure showed above using N-methyl-N-(prop-2-yn-1-yl)aniline (72.5 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column

chromatography (petroleumether/ethyl acetate=3:1) as white solid (139.9 mg, 76%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83–7.66 (m, 2H), 7.55–7.46 (m, 1H), 7.43 (s, 1H), 7.42-7.35 (m, 2H), 7.28–7.22 (m, 2H), 6.83–6.70 (m, 3H), 5.55 (d, *J* = 2.2 Hz, 1H), 5.29 (d, *J* = 2.2 Hz, 1H), 4.62 (s, 2H), 4.54 (s, 2H), 2.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 146.1, 137.8, 134.1, 132.3, 129.3, 129.1, 128.3, 119.4, 117.3, 112.8, 111.9, 58.6, 48.3, 38.6; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{20}N_4O_2SNa$ $[M+Na]^+$: 391.1199, found: 391.1215.

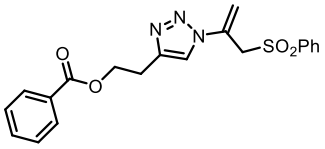


(3zd) 0.5 mmol scale: Prepared following the genernal procedure showed above using (prop-2-yn-1-yloxy)benzene (66.0 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (136.7 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83–7.74 (m, 3H), 7.59–7.49 (m, 1H), 7.48–7.49 (m, 7.1 Hz, 2H), 7.38–7.28 (m, 2H), 7.04–6.91 (m, 3H), 5.68 (d, *J* = 2.2 Hz, 1H), 5.37 (d, *J* = 2.2 Hz, 1H), 5.13 (s, 2H), 4.65 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.1, 144.9, 137.9, 134.2, 132.5, 129.6, 129.2, 128.3, 121.5, 120.9, 114.7, 112.7, 61.6, 58.9; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{17}N_3O_3SNa$ $[M+Na]^+$: 378.0883, found: 378.0858.

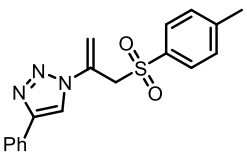


(3ze) 0.5 mmol scale: Prepared following the genernal procedure showed above using prop-2-yn-1-yl benzoate (63.5 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01

mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (151.3 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12–8.01 (m, 2H), 7.81 (s, 1H), 7.80–7.72 (m, 2H), 7.63–7.55 (m, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.43–7.34 (m, 3H), 5.68 (d, *J* = 2.2 Hz, 1H), 5.40 (d, *J* = 2.2 Hz, 1H), 5.39 (s, 2H), 4.66 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.3, 143.4, 137.7, 134.1, 133.4, 132.4, 129.7, 19.5, 129.1, 128.5, 128.3, 122.2, 112.8, 58.7, 57.6; **HRMS** (ESI-TOF) m/z calculated for $C_{19}H_{17}N_3O_4SNa$ $[M+Na]^+$: 406.0832, found: 406.0804.

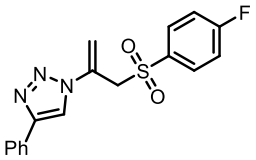


(3zf) 0.5 mmol scale: Prepared following the genernal procedure showed above using but-3-yn-1-yl benzoate (87.1 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium sulfinate (98.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (152.9 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23–7.98 (m, 2H), 7.89–7.74 (m, 2H), 7.63–7.52 (m, 3H), 7.49–7.36 (m, 4H), 5.62 (d, *J* = 2.2 Hz, 1H), 5.31 (d, *J* = 2.2 Hz, 1H), 4.65 (s, 2H), 4.54 (t, *J* = 6.6 Hz, 2H), 3.15 (t, *J* = 6.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.4, 144.8, 137.9, 134.1, 133.2, 132.4, 129.9, 129.6, 129.2, 128.5, 128.4, 119.6, 112.1, 63.4, 58.9, 25.4; **HRMS** (ESI-TOF) m/z calculated for $C_{20}H_{20}N_3O_4S$ $[M+H]^+$: 398.1169, found: 398.1182.

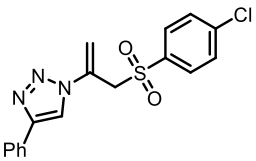


(4a) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium p-toluenesulfinate (106.9 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg,

0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (150.9 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.80–7.72 (m, 2H), 7.70–7.63 (m, 2H), 7.49–7.41 (m, 2H), 7.40–7.31 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 5.72 (d, *J* = 2.1 Hz, 1H), 5.40 (d, *J* = 2.1 Hz, 1H), 4.66 (s, 2H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 145.4, 134.9, 132.7, 129.8, 128.9, 128.6, 128.4, 125.8, 117.8, 112.5, 100.0, 59.2, 21.5; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{17}N_3O_2SNa$ $[M+Na]^+$: 362.0934, found: 362.0916.

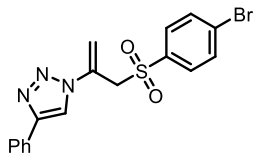


(4b) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), 4-fluorobenzenesulfinic acid sodium (109.2 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (149.2 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.89–7.80 (m, 2H), 7.80–7.74 (m, 2H), 7.52–7.42 (m, 2H), 7.41–7.33 (m, 1H), 7.16–7.07 (m, 2H), 5.74 (d, *J* = 2.3 Hz, 1H), 5.42 (d, *J* = 2.3 Hz, 1H), 4.71 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.3 (d, *J* = 258.7 Hz), 148.4, 134.1 (d, *J* = 3.3 Hz), 132.5, 131.3 (d, *J* = 9.7 Hz), 129.5, 129.0, 128.8, 125.9, 117.4, 116.7, 116.4, 112.0, 59.1; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -102.13; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}FN_3O_2SNa$ $[M+Na]^+$: 366.0683, found: 366.0676.

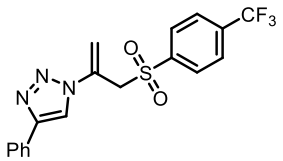


(4c) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.),

4-chlorobenzene sulfinate sodium (99.3 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (158.0 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.85–7.65 (m, 4H), 7.52–7.30 (m, 5H), 5.73 (d, *J* = 2.4 Hz, 1H), 5.42 (d, *J* = 2.4 Hz, 1H), 4.71 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.4, 141.1, 136.4, 132.4, 129.8, 129.5, 129.5, 129.0, 128.8, 125.9, 117.4, 112.1, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}ClN_3O_2SNa$ $[M+Na]^+$: 382.0387, found: 382.0391.

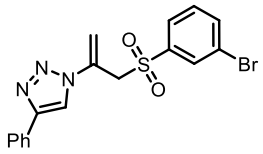


(4d) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), 4-bromobenzenesulfinate sodium (121.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (177.3 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.82–7.74 (m, 2H), 7.70–7.63 (m, 2H), 7.62–7.54 (m, 2H), 7.50–7.42 (m, 2H), 7.42–7.32 (m, 1H), 5.73 (d, *J* = 2.3 Hz, 1H), 5.43 (d, *J* = 2.3 Hz, 1H), 4.71 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 136.9, 132.5, 132.4, 129.8, 129.7, 129.5, 129.0 , 128.8, 126.0, 117.4, 112.1, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}BrN_3O_2SNa$ $[M+Na]^+$: 425.9882, found: 425.9869.

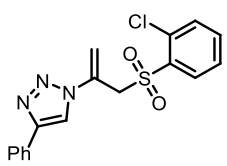


(4e) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.),

4-(trifluoromethyl)benzenesulfinate sodium (116.0 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (153.3 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.90 (s, 1H), 7.80–7.66 (m, 4H), 7.50–7 .32 (m, 3H), 5.74 (d, *J* = 2.4 Hz, 1H), 5.46 (d, *J* = 2.4 Hz, 1H), 4.78 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 141.5, 135.9 (q, *J* = 33.4 Hz), 132.2, 129.2, 129.0, 128.9, 128.8, 126.3 (q, *J* = 3.7 Hz), 125.8, 124.2, 121.5, 117.2, 112.0, 58.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.30; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{14}F_3N_3O_2SNa$ $[M+Na]^+$: 416.0651, found: 416.0635.

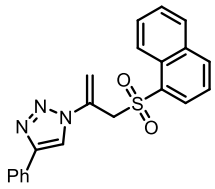


(4f) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), 3-bromobenzenesulfinate sodium (121.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (165.2 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 1.9 Hz, 1H), 7.90 (s, 1H), 7.83–7.73 (m, 3H), 7.66–7.65 (m, 1H), 7.50–7.41 (m, 2H), 7.40–7.35 (m, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 5.74 (d, *J* = 2.3 Hz, 1H), 5.46 (d, *J* = 2.3 Hz, 1H), 4.73 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) 148.4, 139.7, 137.1, 132.3, 131.1, 130.8, 129.5, 128.9, 128.7, 126.9, 125.9, 123.1, 117.4, 112.3, 59.0; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}BrN_3O_2SNa$ $[M+Na]^+$: 425.9882, found: 425.9871.

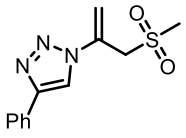


(4g) 0.5 mmol scale: Prepared following the genernal procedure showed above using

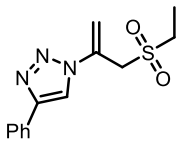
2-chlorobenzene sulfinate sodium (99.3 mg, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (149.0 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.91 (s, 1H), 7.83–7.74 (m, 2H), 7.55–7.48 (m, 2H), 7.48–7.40 (m, 2H), 7.40–7.30 (m, 2H), 5.75 (d, *J* = 2.0 Hz, 1H), 5.44 (d, *J* = 1.9 Hz, 1H), 4.96 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 135.5, 135.2, 133.1, 132.3, 132.0, 131.8, 129.6, 128.9, 128.6, 127.2, 125.8, 117.8, 113.4, 57.2; **HRMS** (ESI-TOF) m/z calculated for $C_{17}H_{14}ClN_3O_2SNa$ $[M+Na]^+$: 382.0387, found: 382.0396.



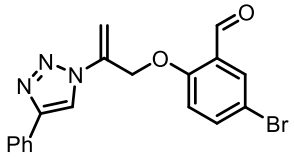
(4h) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), 2-naphthalenebenzenesulfonate (128.5 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (159.4 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.91–7.86 (m, 2H), 7.82–7.75 (m, 2H), 7.73 (s, 1H), 7.63–7.48 (m, 4H), 7.41–7.30 (m, 3H), 5.71 (d, *J* = 2.2 Hz, 1H), 5.43 (d, *J* = 2.2 Hz, 1H), 4.76 (s, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 135.3, 134.6, 132.6, 131.8, 130.4, 129.6, 129.4, 129.3, 128.7, 128.5, 127.9, 127.8, 125.7, 122.5, 117.7, 112.6, 59.2 ; **HRMS** (ESI-TOF) m/z calculated for $C_{21}H_{17}N_3O_2SNa$ $[M+Na]^+$: 398.0934, found: 398.0925.



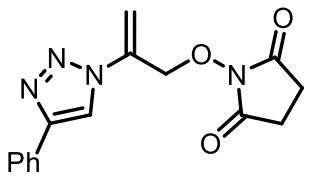
(4i) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium methylsulfinate (61.2 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (97.3 mg, 74%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.94–7.79 (m, 2H), 7.49–7.42 (m, 2H), 7.42–7.35 (m, 1H), 5.81 (d, *J* = 2.5 Hz, 1H), 5.53 (d, *J* = 2.5 Hz, 1H), 4.62 (s, 2H), 2.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.8, 132.5, 129.4, 129.0, 128.9, 125.9, 117.4, 111.7, 57.6, 41.4; **HRMS** (ESI-TOF) m/z calculated for $C_{12}H_{14}N_3O_2S$ $[M+H]^+$: 264.0801, found: 264.0800.



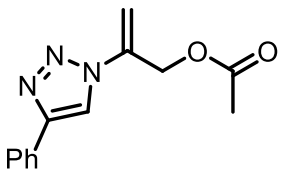
(4j) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), **VA** (246.5 mg, 0.6 mmol, 1.2 eq.), sodium ethylsulfinate (58.1 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 2.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (106.7 mg, 77%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.93–7.79 (m, 2H), 7.52–7.42 (m, 2H), 7.41–7.32 (m, 1H), 5.79 (d, *J* = 2.4 Hz, 1H), 5.53 (d, *J* = 2.4 Hz, 1H), 4.57 (s, 2H), 3.01 (q, *J* = 7.4 Hz, 2H), 1.39 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 132.4, 129.5, 129.0, 128.9, 125.9, 117.5, 111.8, 55.2, 48.2, 6.4; **HRMS** (ESI-TOF) m/z calculated for $C_{13}H_{15}N_3O_2SNa$ $[M+Na]^+$: 300.0777, found: 300.0787.



(4k) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), VA (246.5 mg, 0.6 mmol, 1.2 eq.), 5-bromosalicylaldehyde (120.6 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (138.6 μL, 1.0 mmol, 2.0 eq.), CuI (19.0 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=3:1) as white solid (138.24 mg; 72%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 10.36 (s, 1H), 8.14 (s, 1H), 7.96 (d, *J* = 2.6 Hz, 1H), 7.89 – 7.85 (m, 2H), 7.70 – 7.65 (m, 1H), 7.49 – 7.43 (m, 2H), 7.41 – 7.35 (m, 1H), 7.05 (d, *J* = 8.8 Hz, 1H), 5.74 (d, *J* = 2.1 Hz, 1H), 5.50 (d, *J* = 2.0 Hz, 1H), 5.33 (s, 2H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 187.7, 158.8, 148.2, 138.4, 138.0, 131.8, 129.7, 129.0, 128.7, 126.5, 125.9, 117.3, 115.1, 114.8, 106.2, 66.9.; **HRMS** (ESI-TOF) m/z calculated for $C_{18}H_{15}BrN_3O_2$ $[M+H]^+$: 384.0342, found: 384.0345.



(4l) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), VA (246.5 mg, 0.6 mmol, 1.2 eq.), N-hydroxysuccinimide (69.1 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (138.6 μL, 1.0 mmol, 2.0 eq.), CuI (19.0 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as white solid (102.9 mg; 69%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 7.86 – 7.82 (m, 2H), 7.40 – 7.35 (m, 2H), 7.32 – 7.23 (m, 1H), 6.02 (d, *J* = 1.6 Hz, 1H), 5.42 (d, *J* = 1.2 Hz, 1H), 5.03 (s, 2H), 2.66 (s, 4H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.8, 147.1, 135.1, 129.1, 127.9, 127.4, 124.8, 117.8, 111.2, 74.1, 24.4 ; **HRMS** (ESI-TOF) m/z calculated for $C_{15}H_{15}N_4O_3$ $[M+H]^+$: 299.1139, found: 299.1148.



(4m) 0.5 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (54.9 μL, 0.5 mmol, 1.0 eq.), VA (246.5 mg, 0.6 mmol, 1.2 eq.), sodium acetate (49.2 mg, 0.6 mmol, 1.2 eq.), triethylamine (Et_3N) (138.6 μL, 1.0 mmol, 2.0 eq.), CuI (19.0 mg, 0.1 mmol, 0.2 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.02 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=4:1) as white solid (101.3mg; 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.89 – 7.84 (m, 2H), 7.51 – 7.41 (m, 2H), 7.40 – 7.33 (m, 1H), 5.77 (d, *J* = 1.8 Hz, 1H), 5.37 (d, *J* = 1.6 Hz, 1H), 5.22 (s, 2H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 147.9, 138.1, 130.0, 128.9, 128.6, 125.9, 117.3, 107.7, 62.3, 20.8; **HRMS** (ESI-TOF) m/z calculated for $C_{13}H_{14}N_3O_2$ $[M+H]^+$: 244.1081, found: 244.1108.

IV. Crystallography of compound 3d

Single-crystal X-ray diffraction data for the reported complex was recorded at a temperature of 293(2) K on a Oxford Diffraction Gemini R Ultra diffractometer, using a ω scan technique with Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.1 Non-hydrogen atoms were refined with anisotropic temperature parameters, and hydrogen atoms of the ligands were refined as rigid groups. Basic information pertaining to crystal parameters and structure refinement is summarized in Table 1. 1 (a) G. M. Sheldrick, SHELXS-97, Program for Solution of Crystal Structures, University of Gottingen, Germany, 1997; (b) G. M. Sheldrick, SHELXL-97, Program for Refinement of Crystal Structures, University of Gottingen, Germany, 1997.

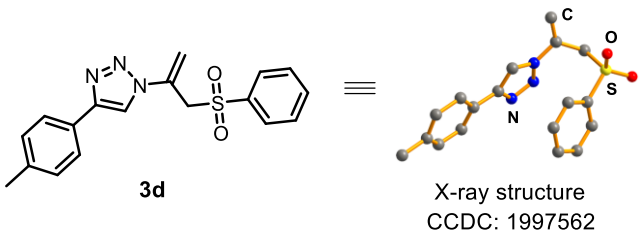
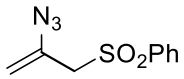


Table 1. Crystal data and structure refinement.

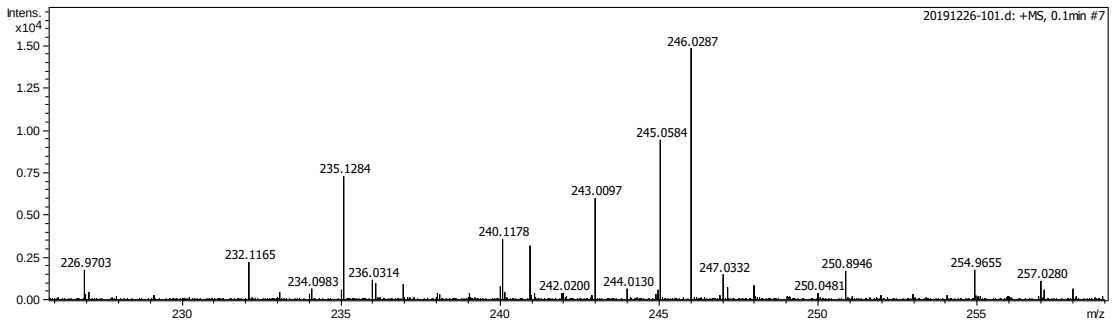
Empirical formula	$C_{18}H_{17}N_3O_2S$
Temperature	293(2) K
Wavelength	1.54178 Å
Unit cell dimensions	a = 16.2468(10) Å alpha = 90.00 ° b = 5.4421(2) Å beta = 112.695(7) ° c = 20.7446(12) Å gamma = 90.00 °
Volume	1692.15(16) $Å^3$
Z	22
Calculated density	1.332 mg/mm^3
Absorption coefficient	1.826 mm^{-1}
F(000)	712
Crystal size	0.27 × 0.06 × 0.02 mm^3
Theta range for data collection	8.84 to 141.56°.
Reflections collected / unique	3187[R(int) = 0.0233]
Data / restraints / parameters	3187 / 0 / 256
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R_1 = 0.0456, wR_2 = 0.1173
R indices (all data)	R_1 = 0.0612, wR_2 = 0.1321

IV. HRMS data of intermediate 5

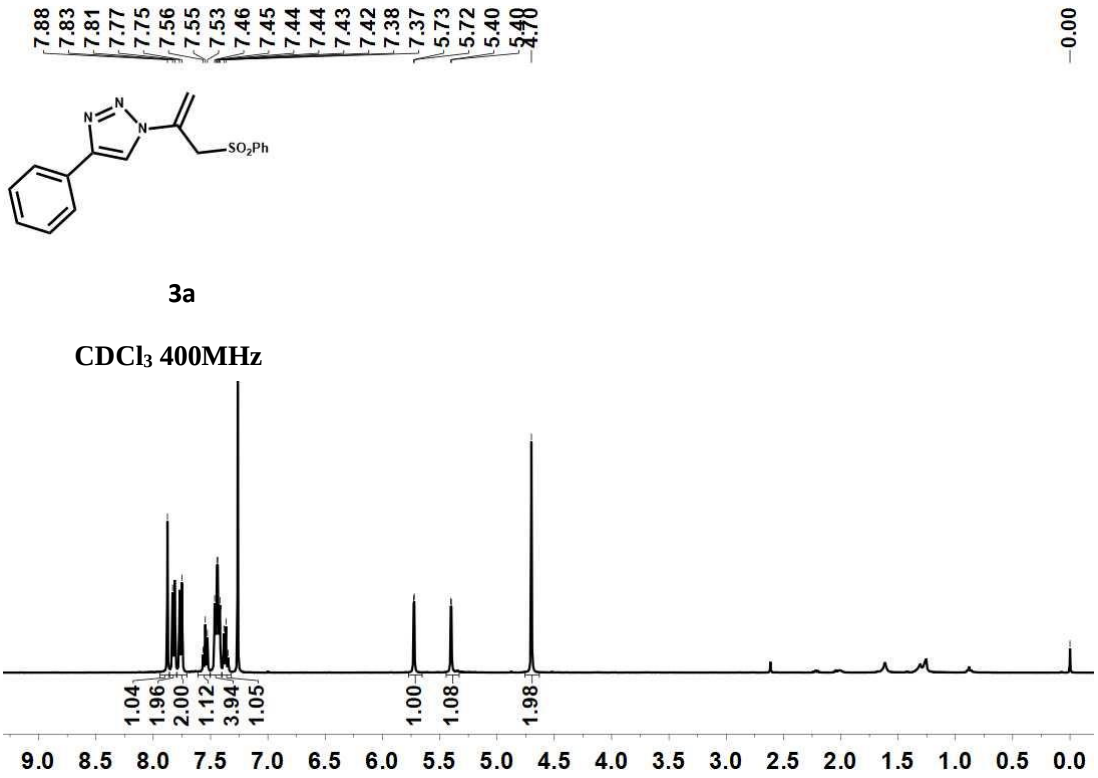


5

HRMS (ESI-TOF) m/z calculated for $C_9H_9N_3O_2SNa$ $[M+Na]^+$: 246.0308, found: 246.0287.

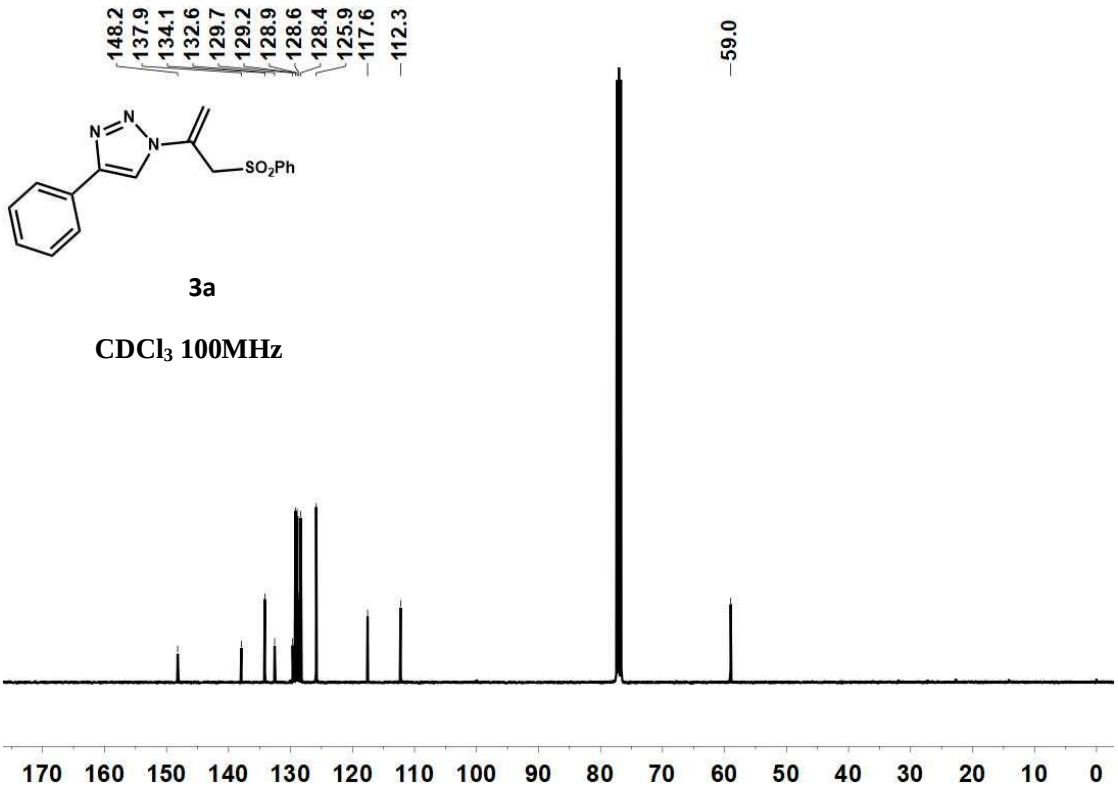


V. NMR spectra copies



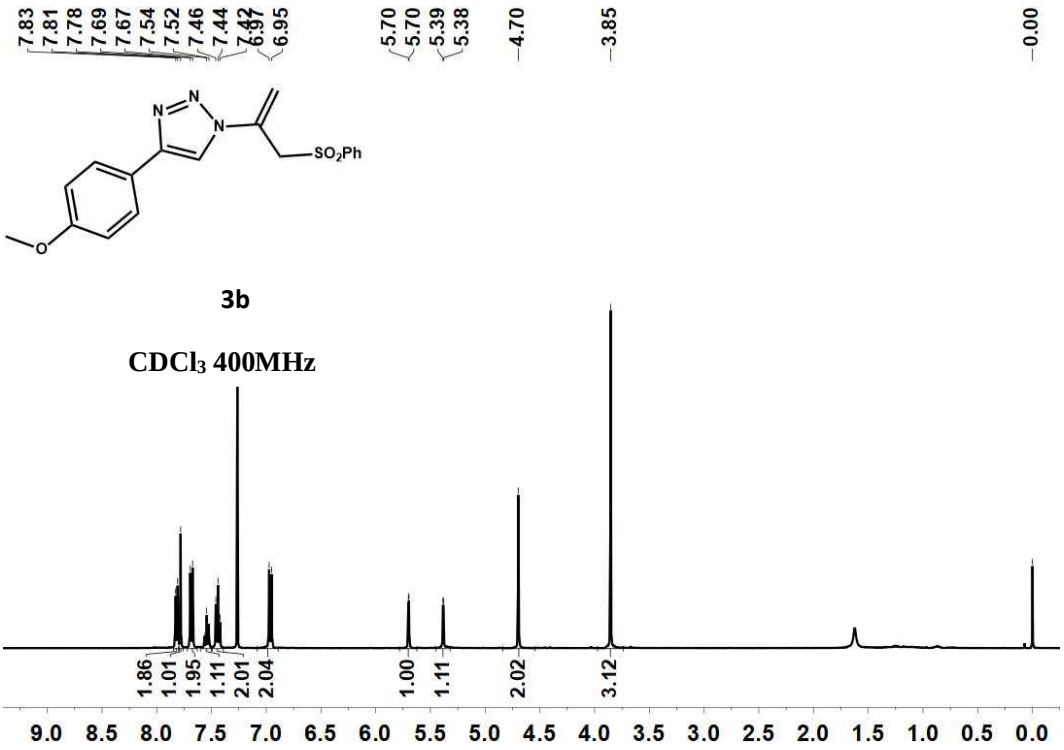
3a

$CDCl_3$ 400MHz



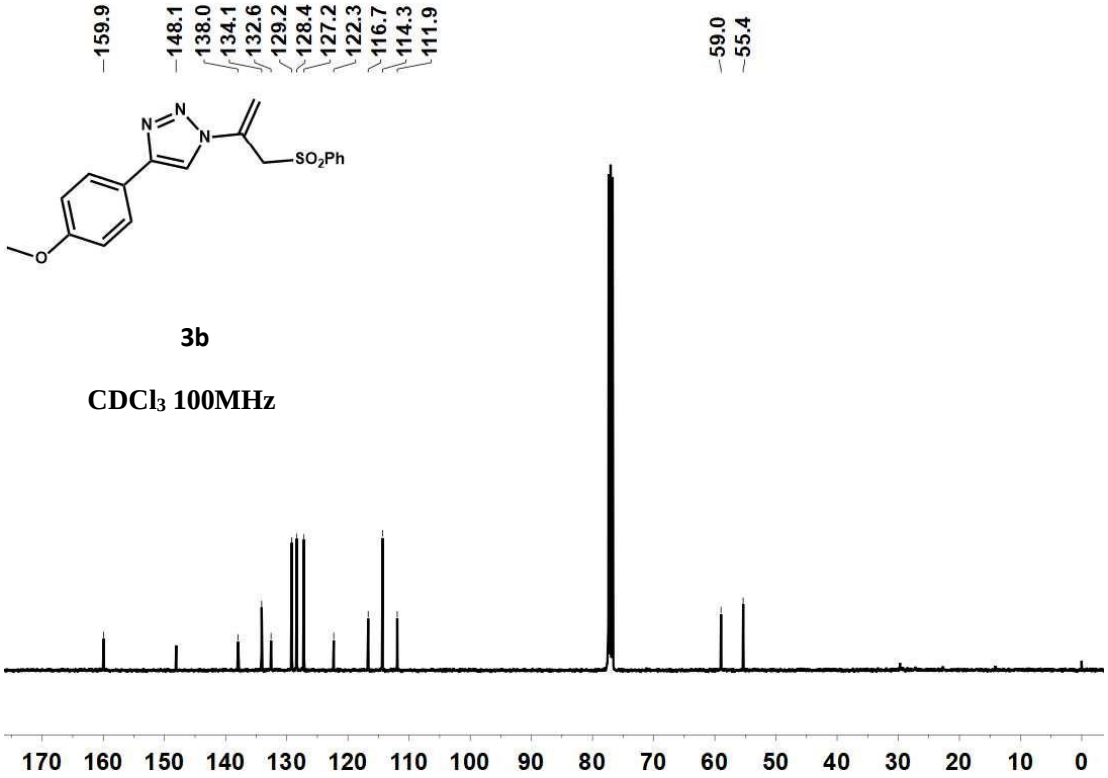
3a

$CDCl_3$ 100MHz



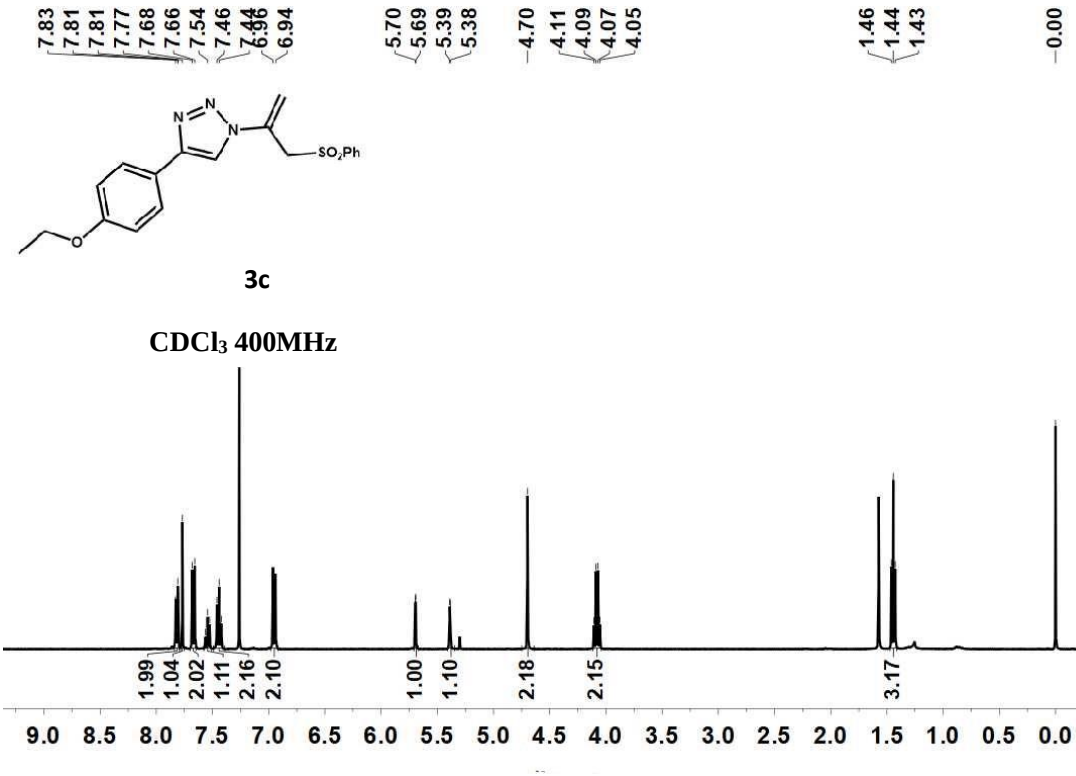
3b

$CDCl_3$ 400MHz



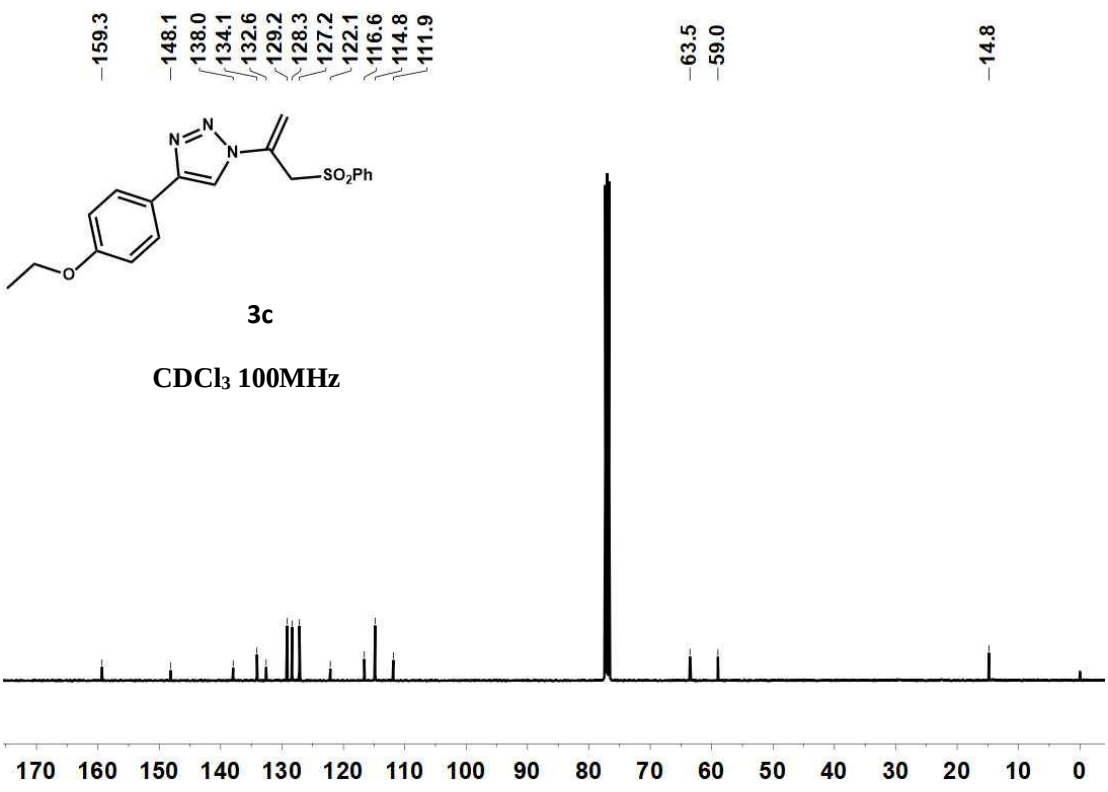
3b

$CDCl_3$ 100MHz



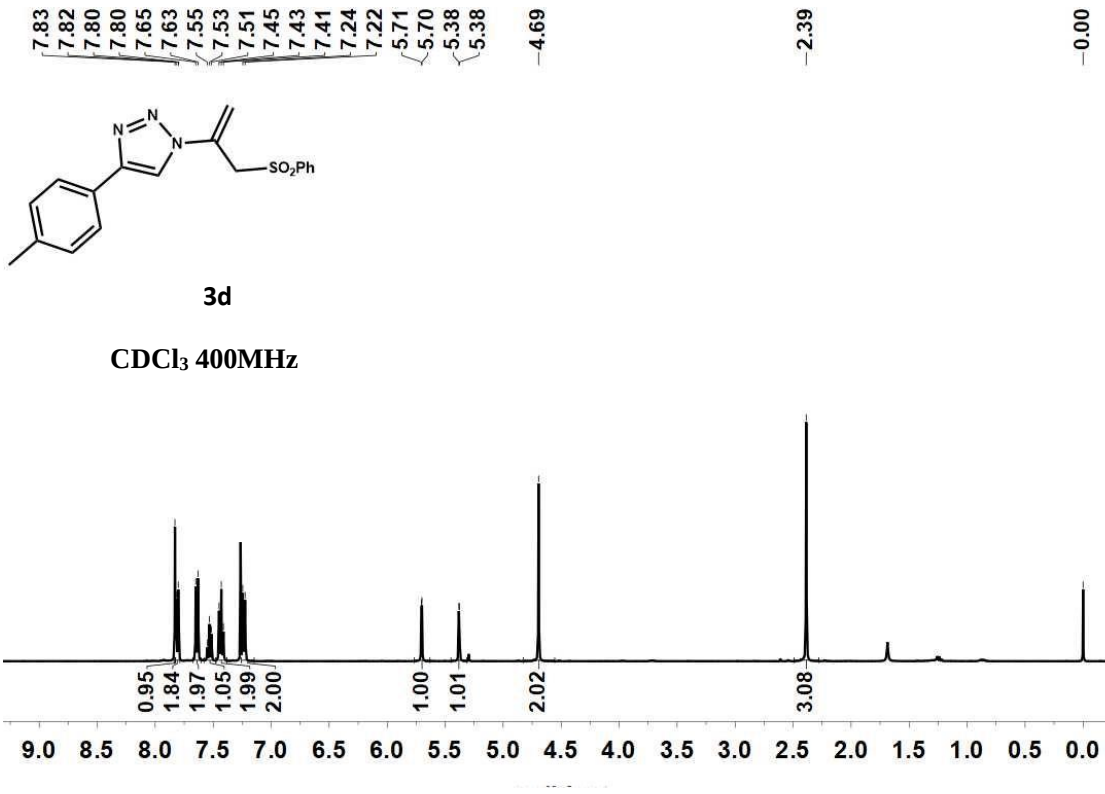
3c

$CDCl_3$ 400MHz



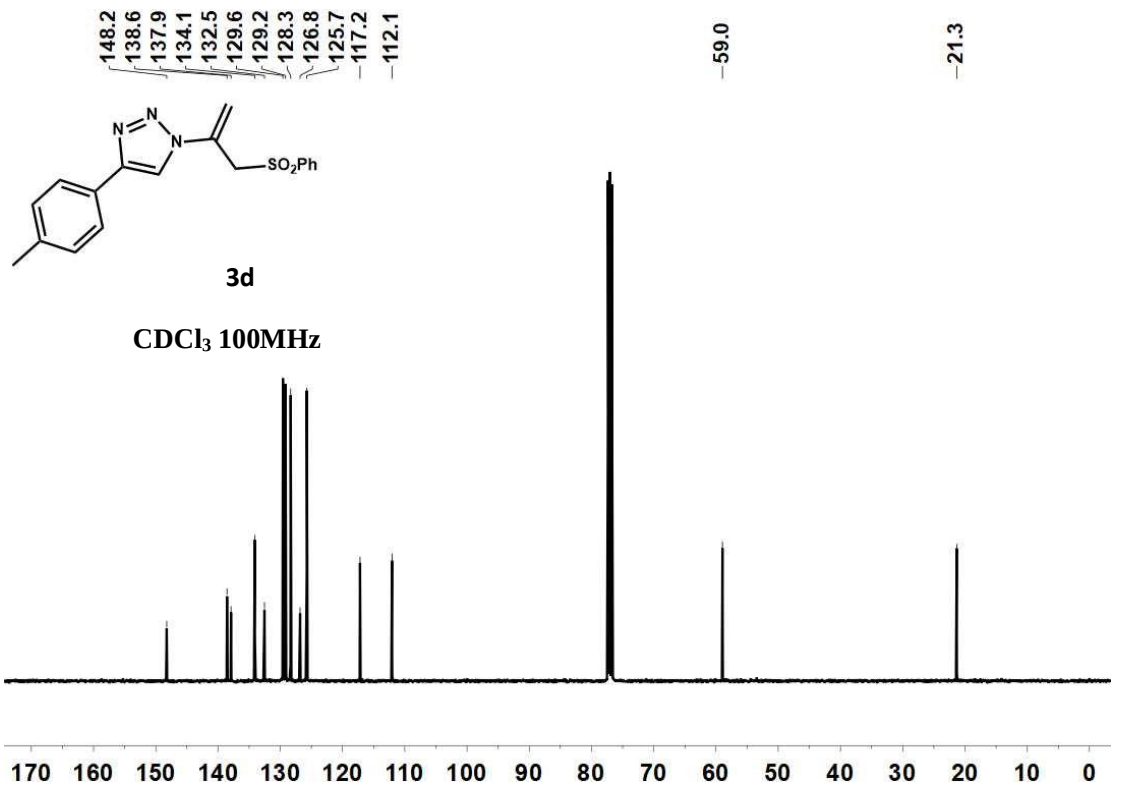
3c

$CDCl_3$ 100MHz



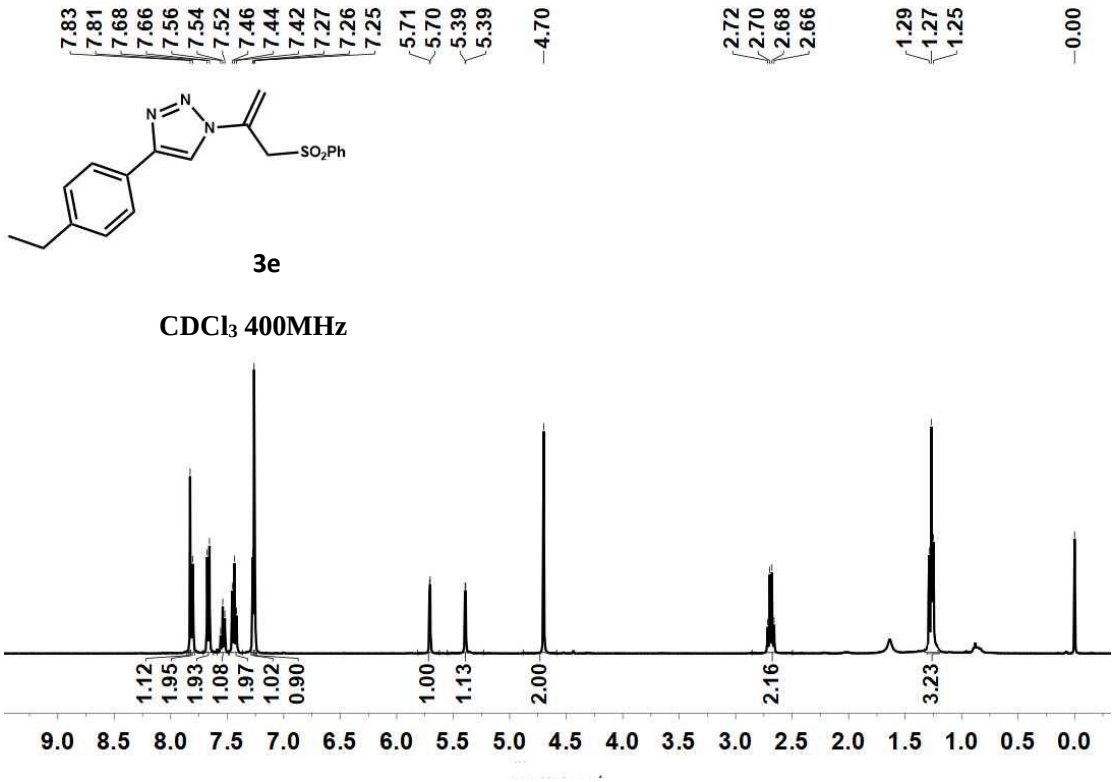
3d

$CDCl_3$ 400MHz



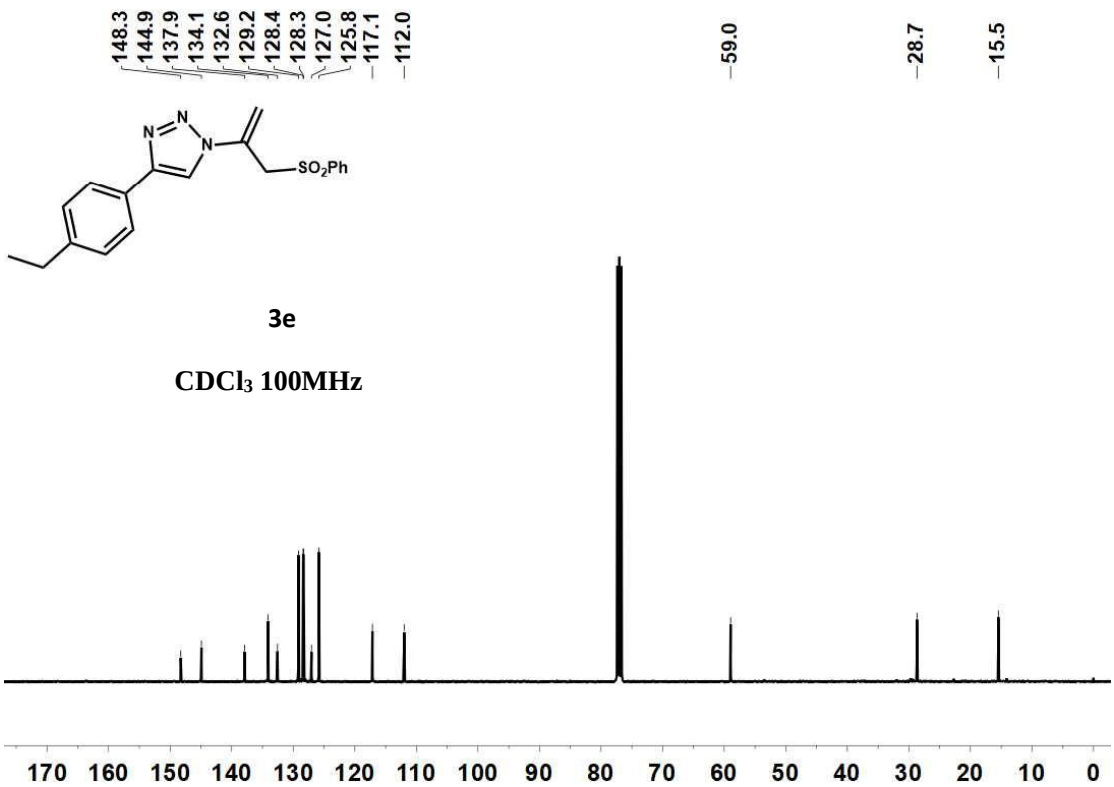
3d

$CDCl_3$ 100MHz



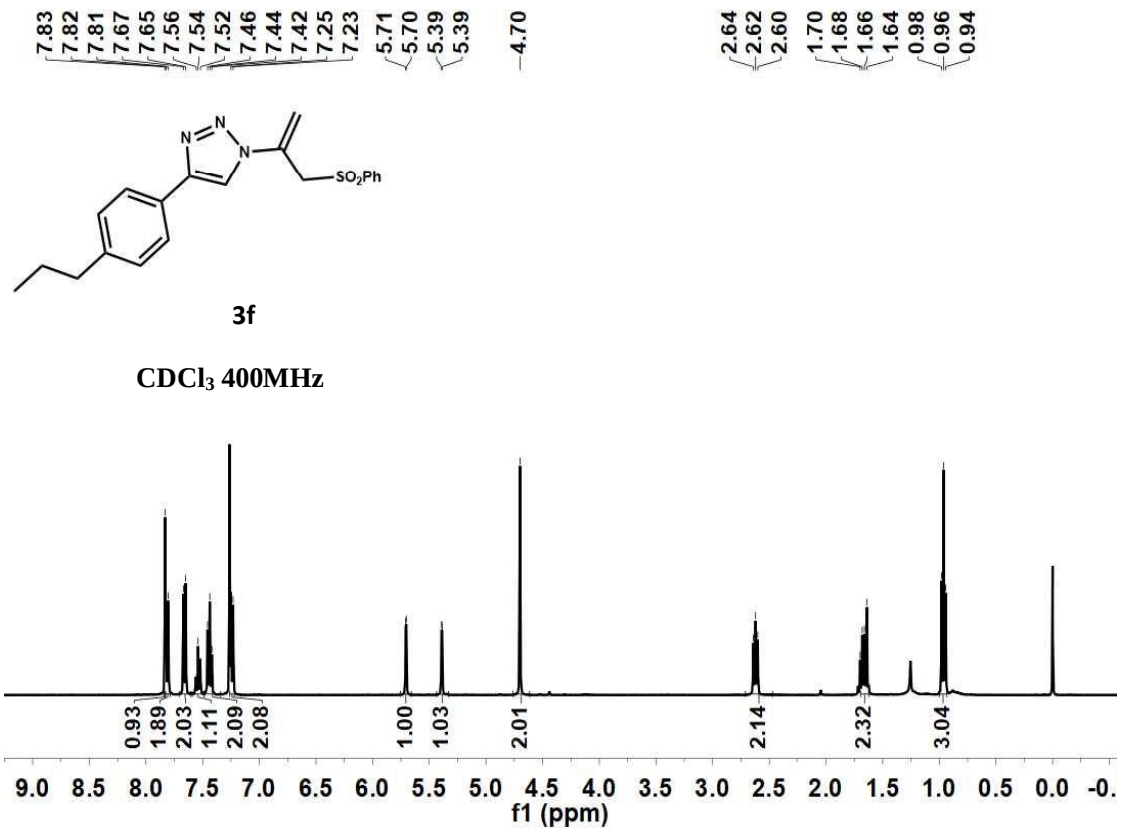
3e

$CDCl_3$ 400MHz



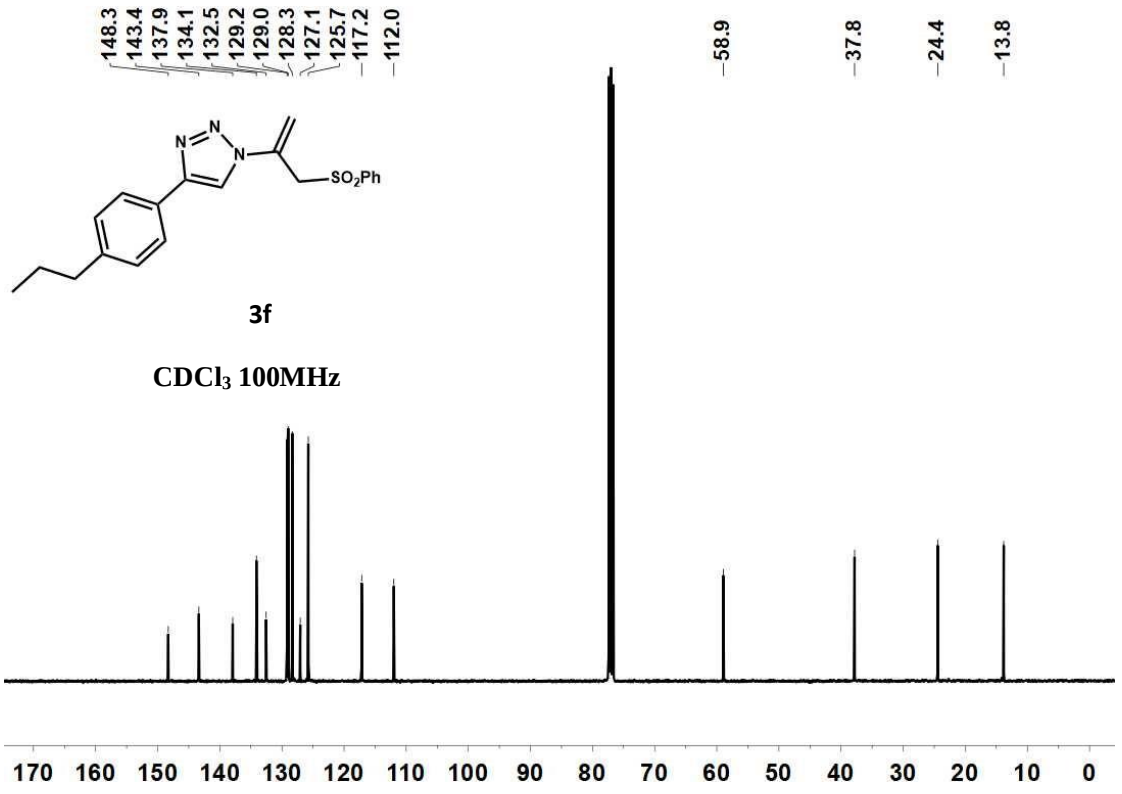
3e

$CDCl_3$ 100MHz



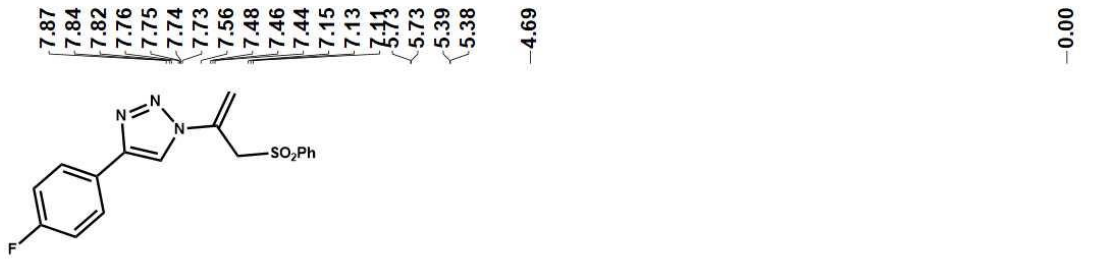
3f

$CDCl_3$ 400MHz



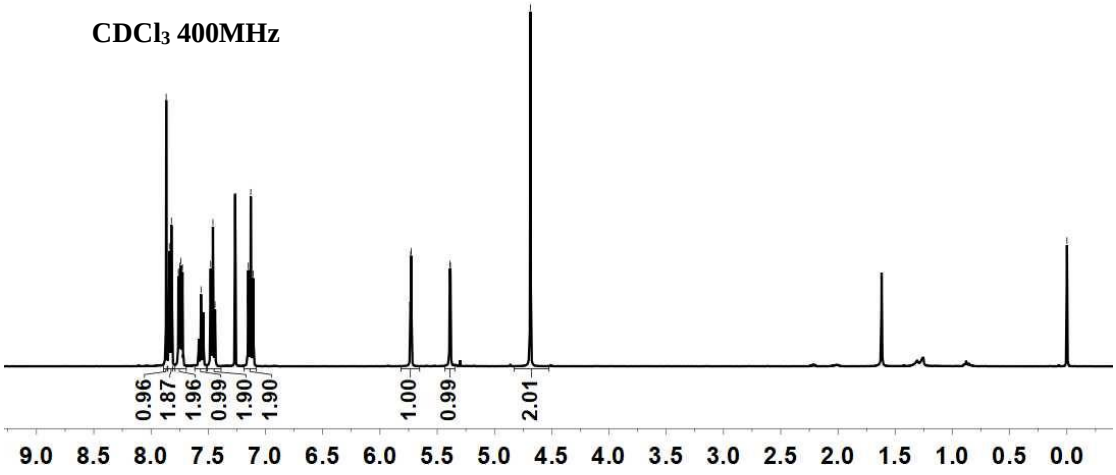
3f

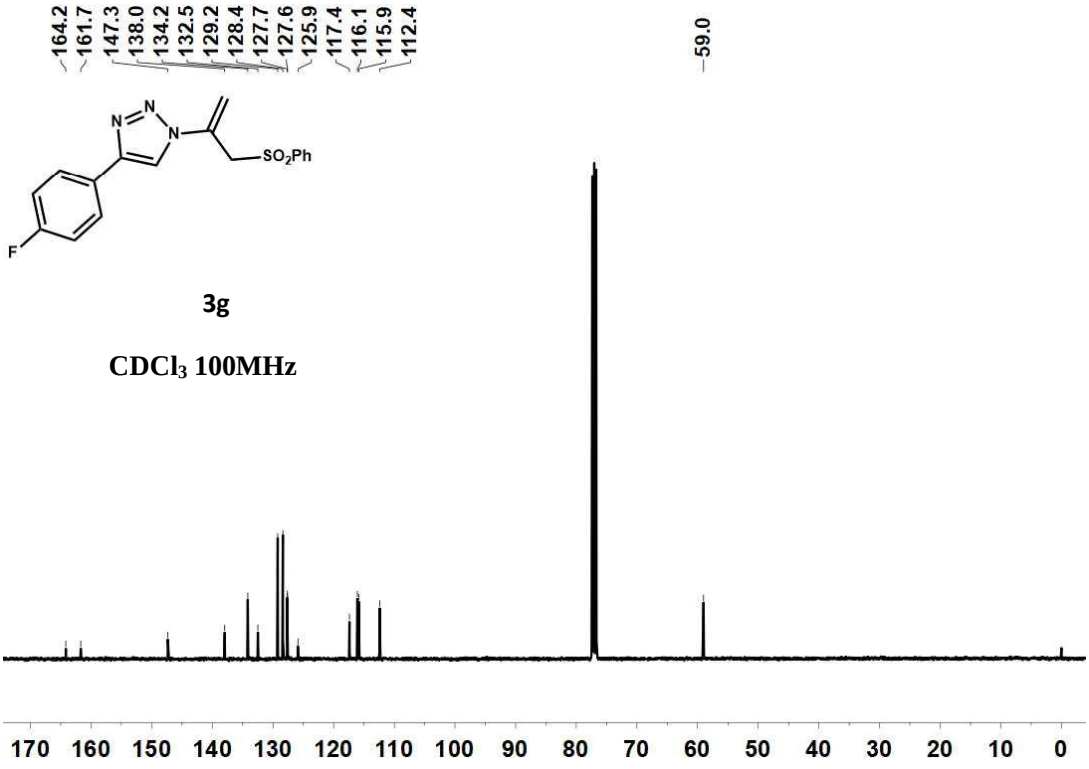
$CDCl_3$ 100MHz



3g

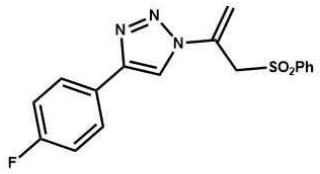
$CDCl_3$ 400MHz





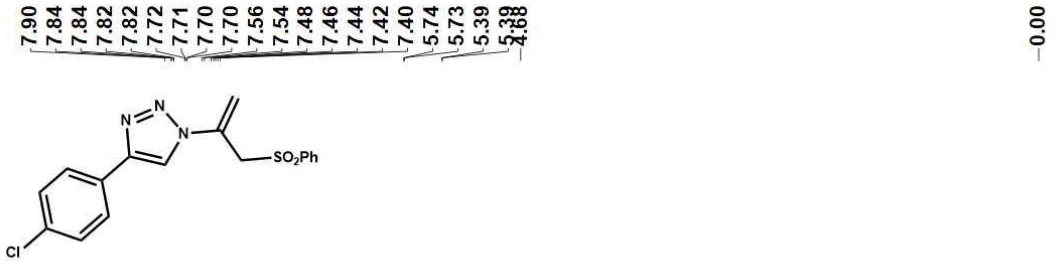
3g

$CDCl_3$ 100MHz



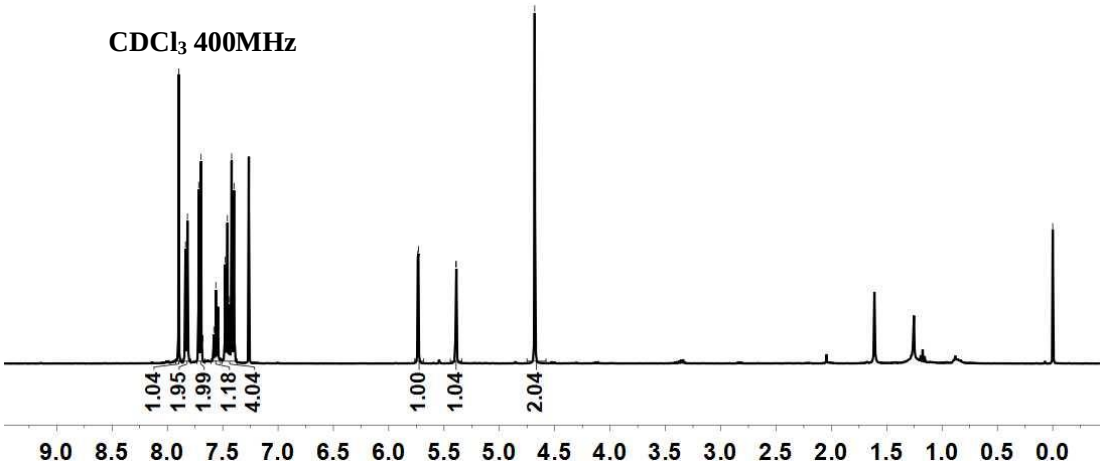
3g

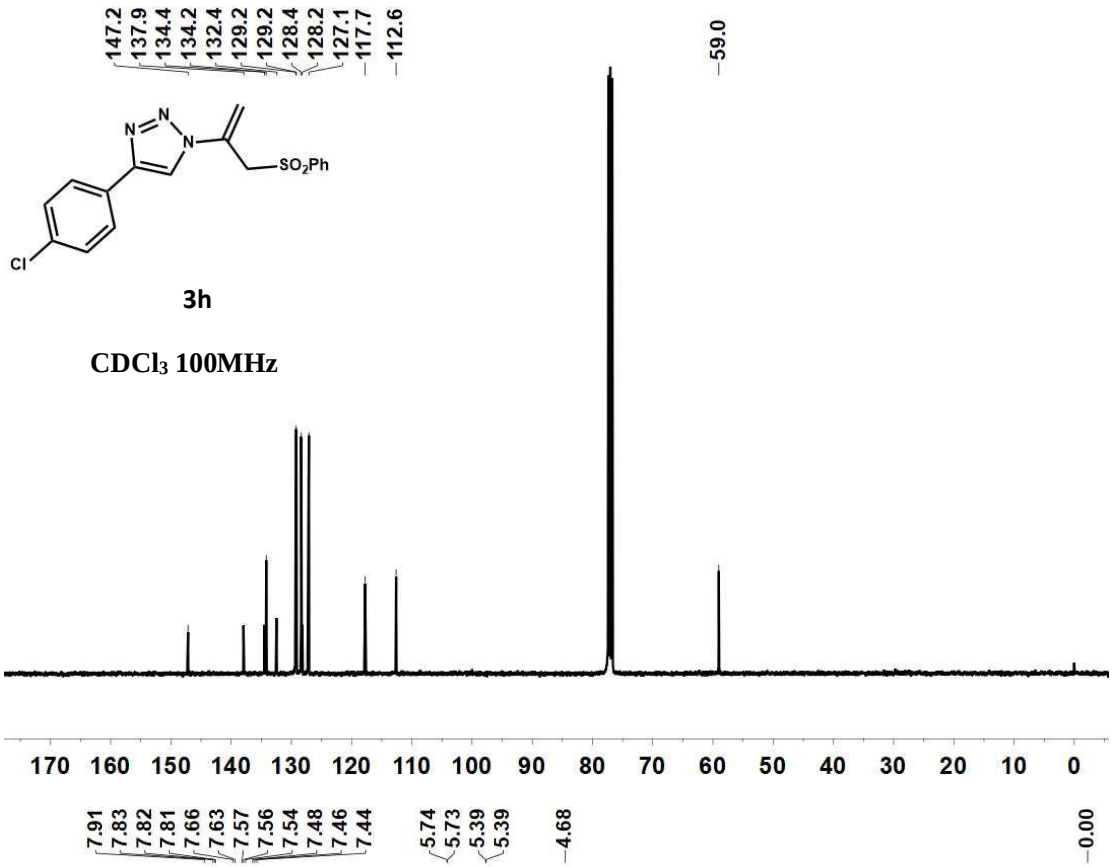
$CDCl_3$ 376MHz



3h

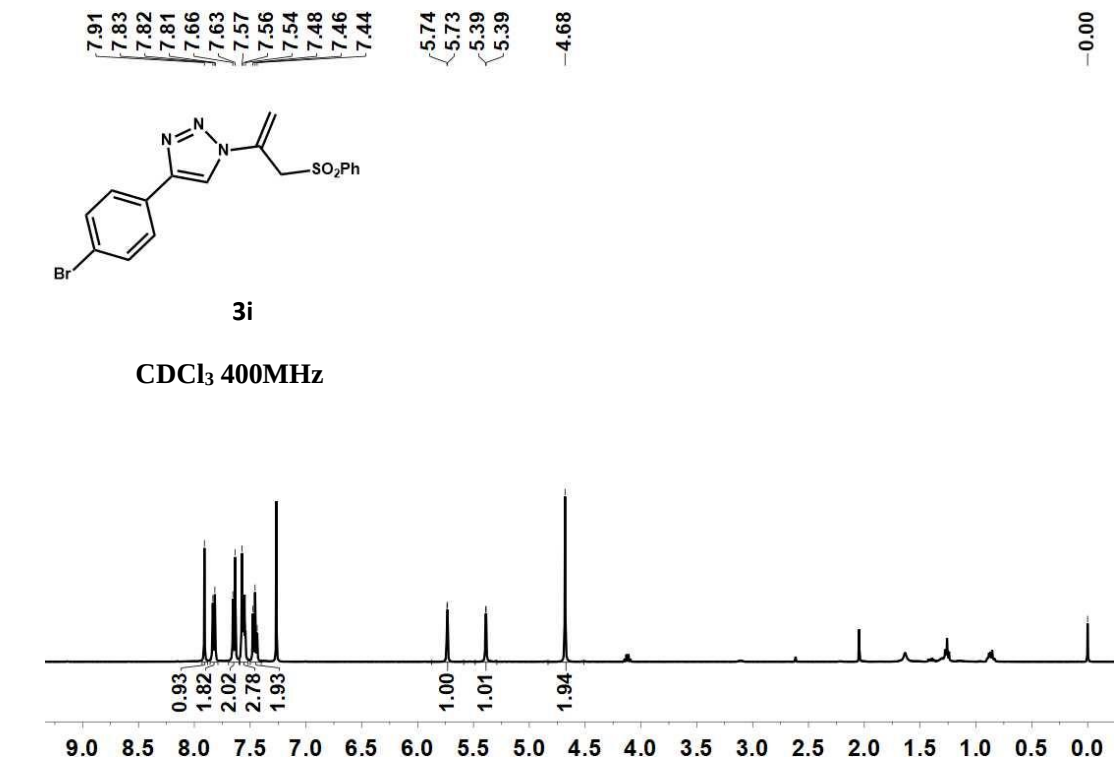
$CDCl_3$ 400MHz





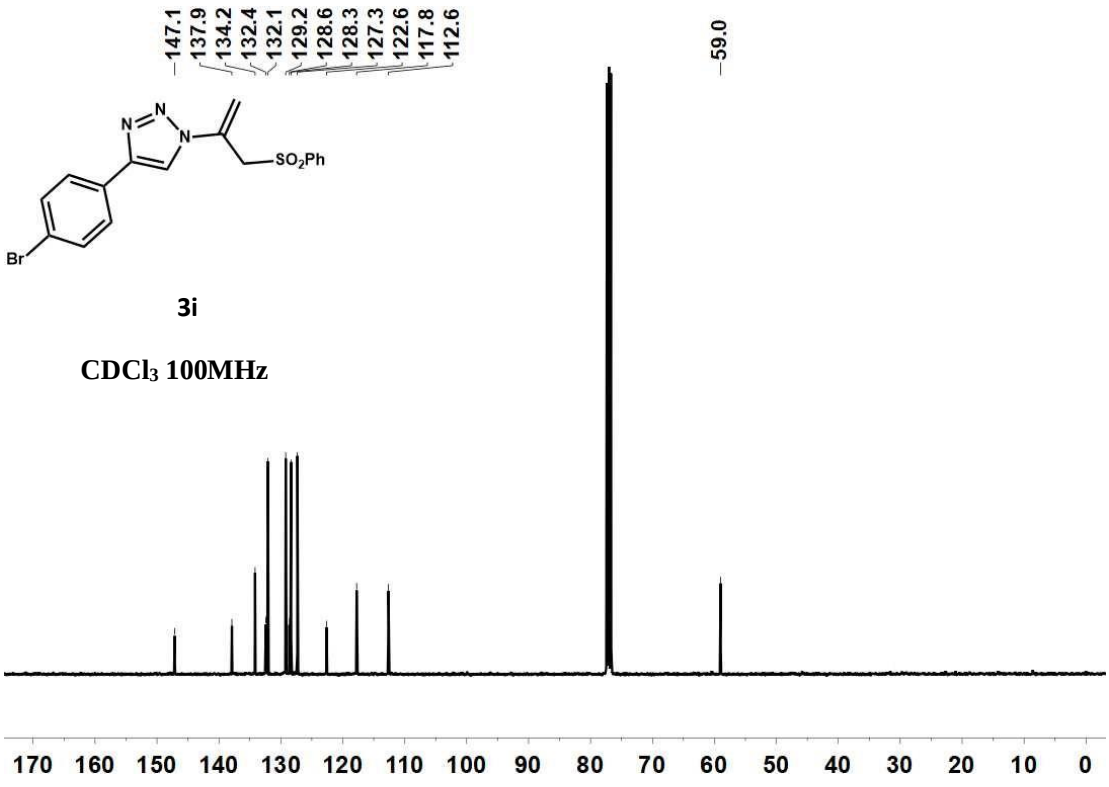
3h

$CDCl_3$ 100MHz



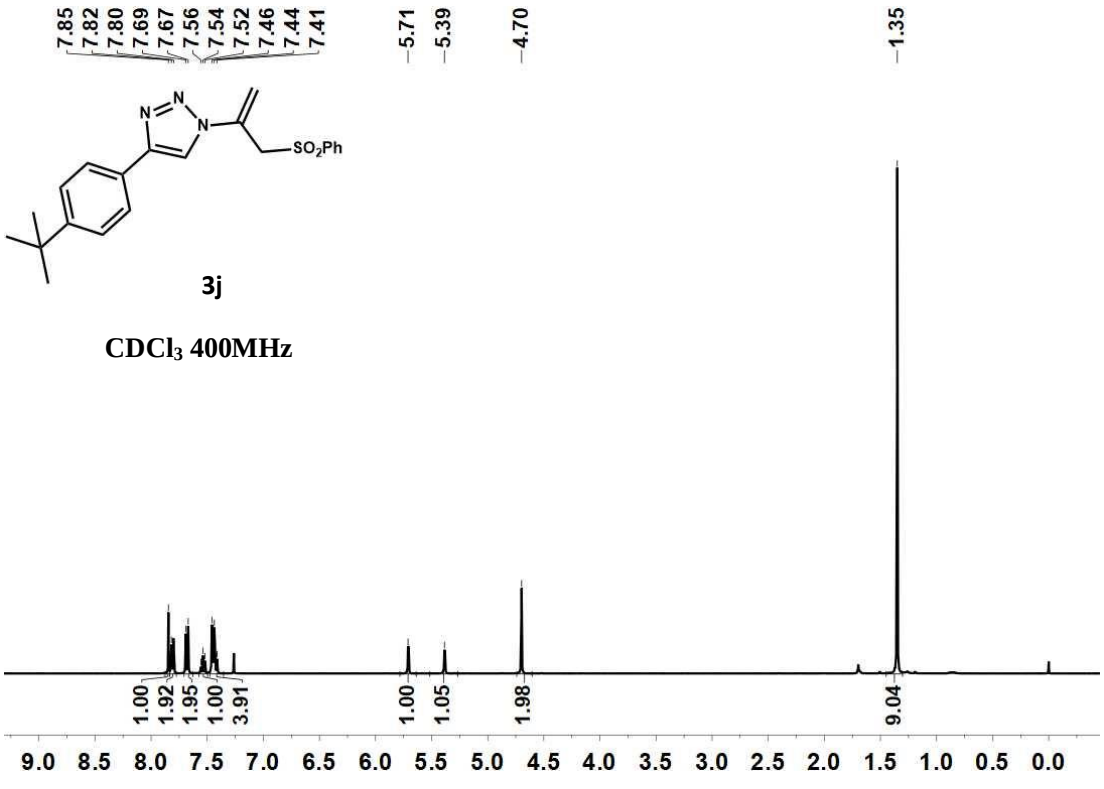
3i

$CDCl_3$ 400MHz



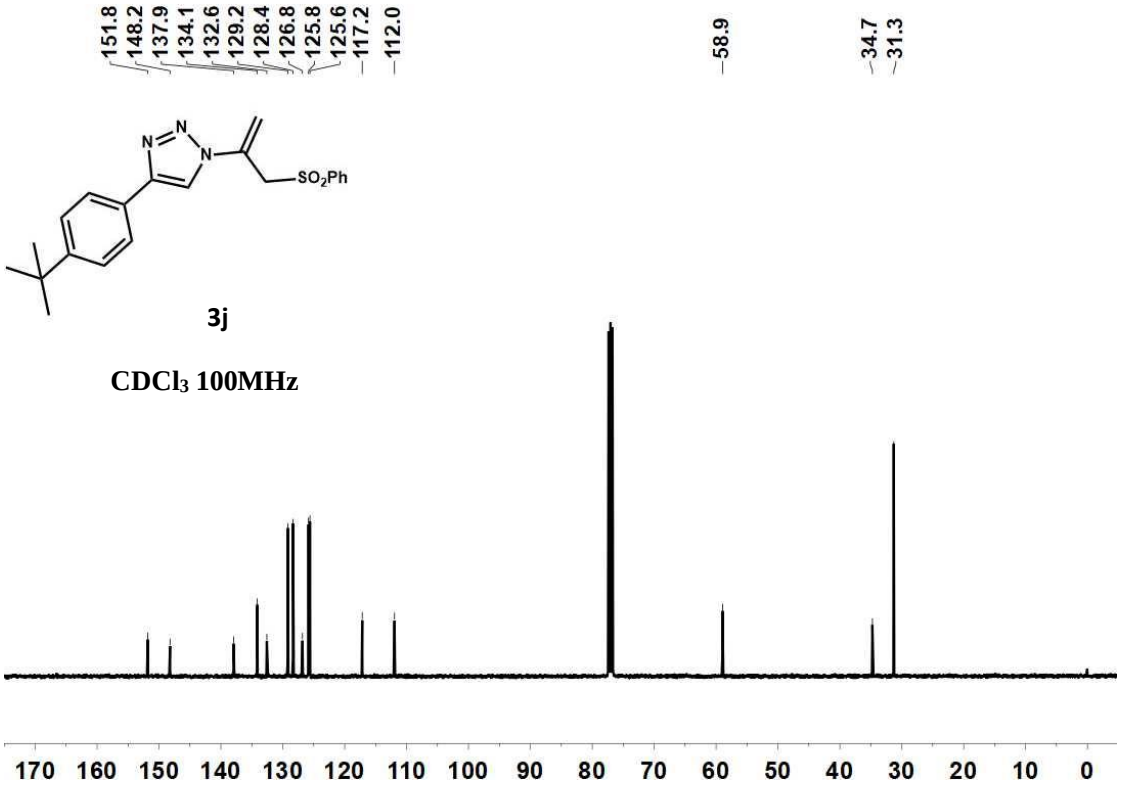
3i

$CDCl_3$ 100MHz



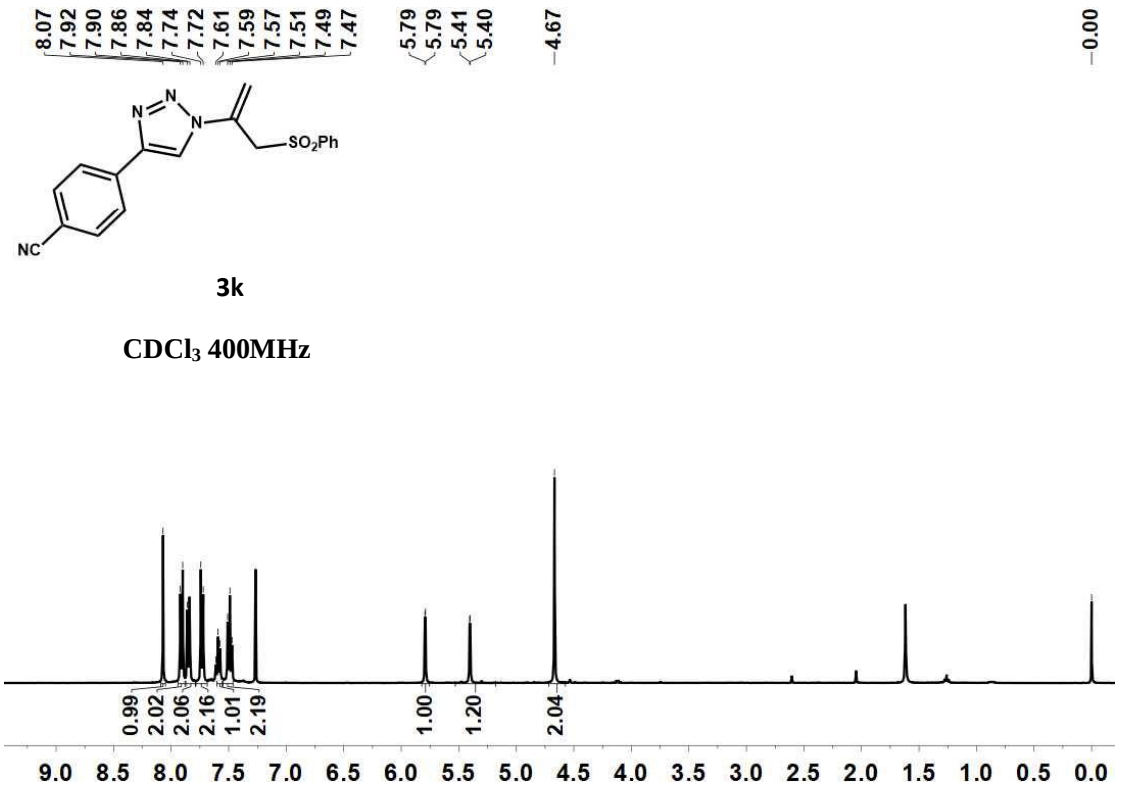
3j

$CDCl_3$ 400MHz



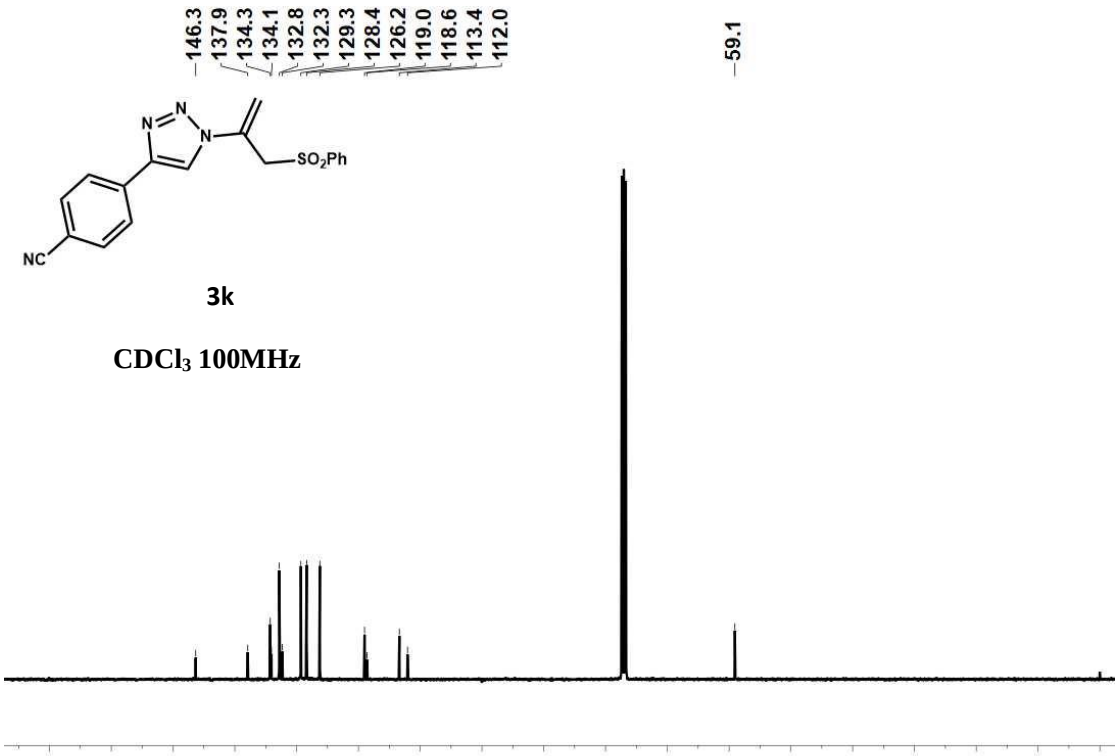
3j

$CDCl_3$ 100MHz



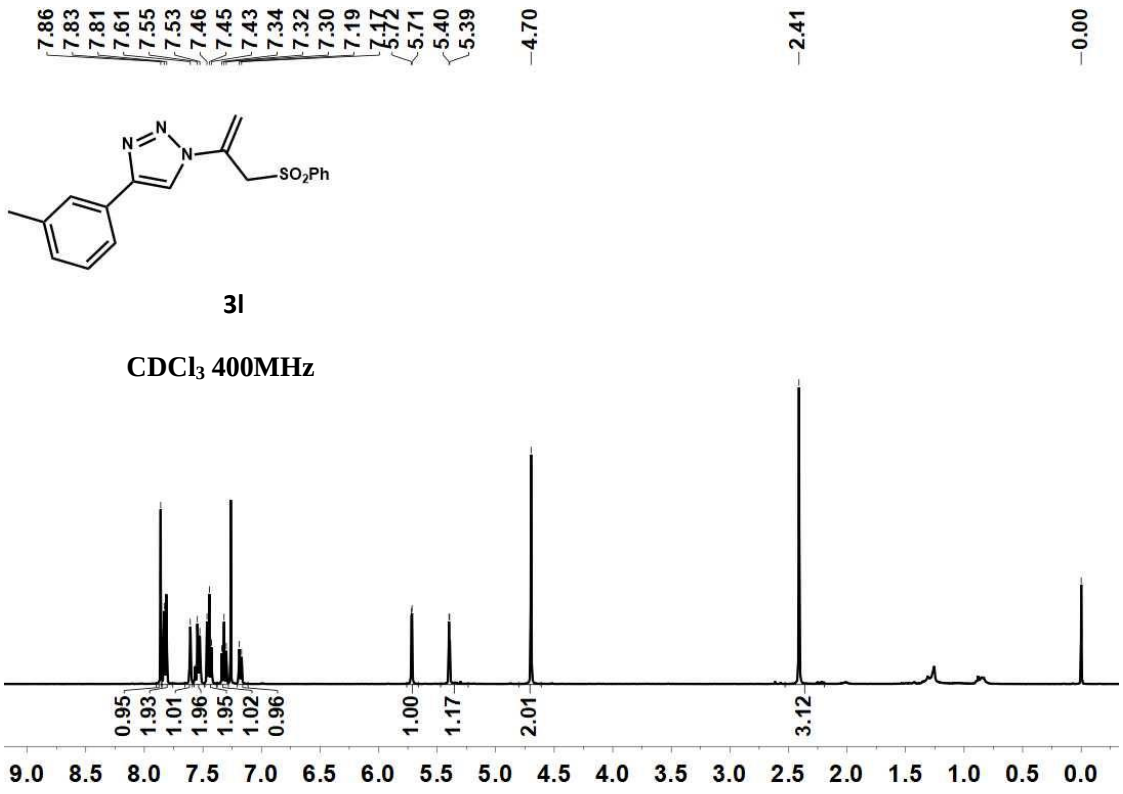
3k

$CDCl_3$ 400MHz



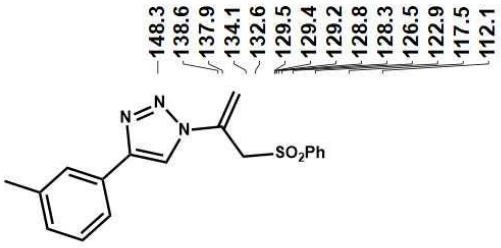
3k

$CDCl_3$ 100MHz



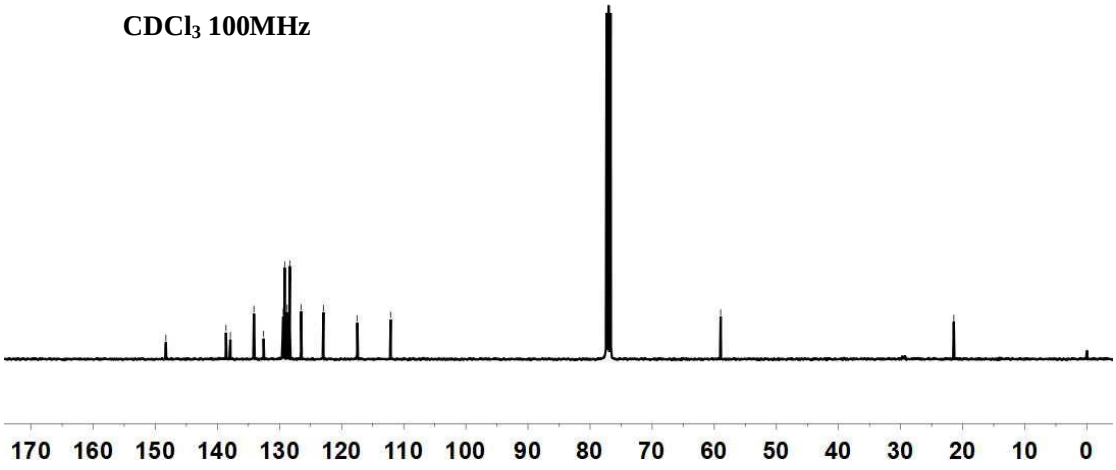
3l

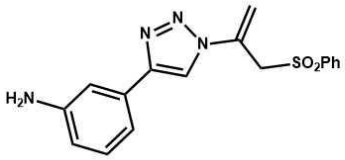
$CDCl_3$ 400MHz



3l

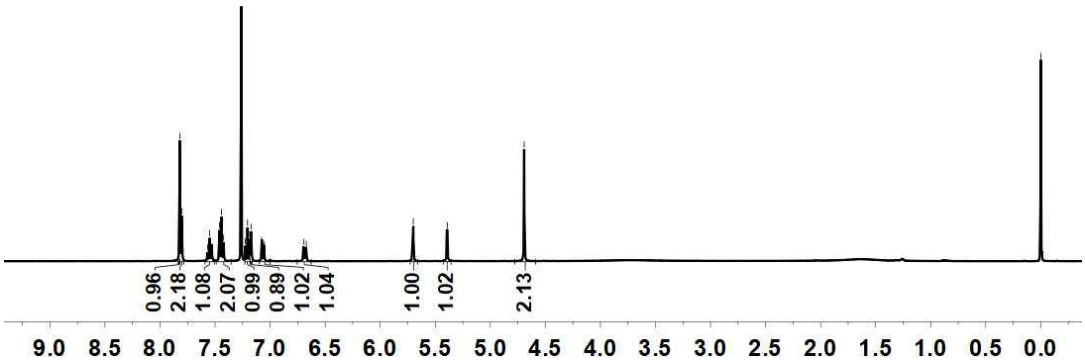
$CDCl_3$ 100MHz

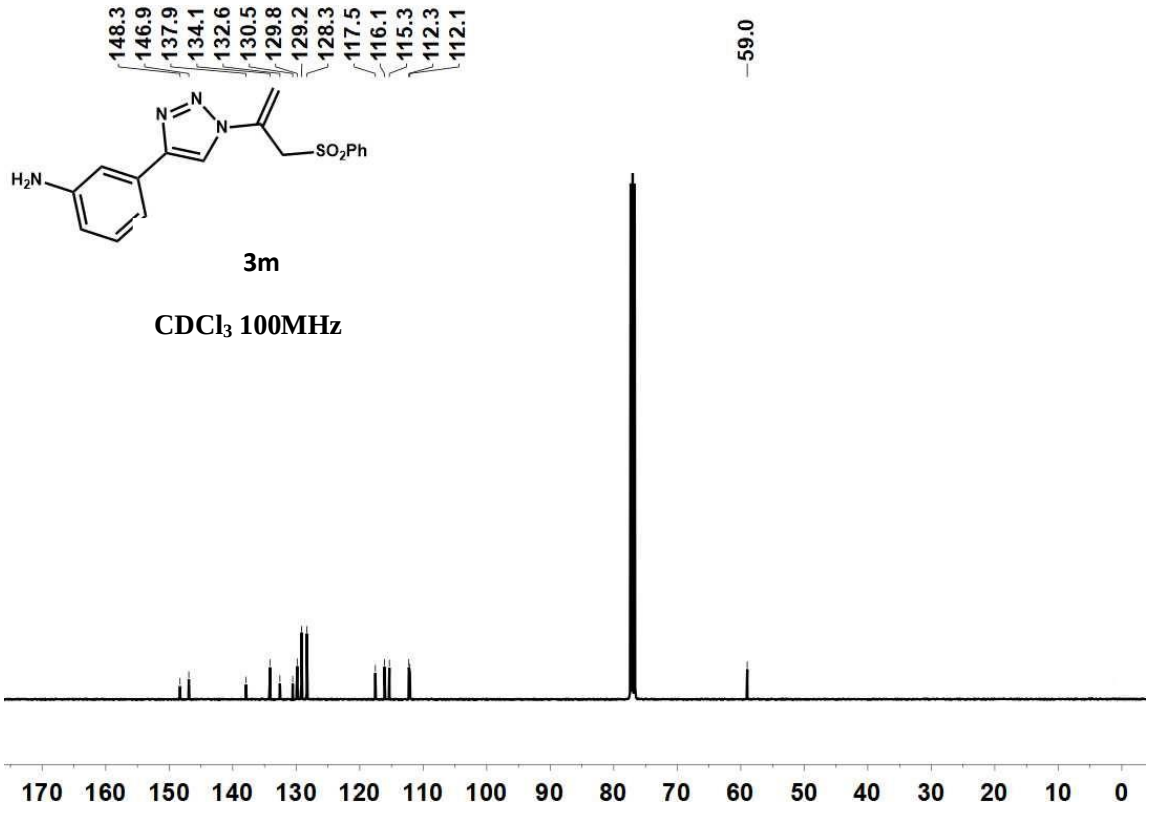




3m

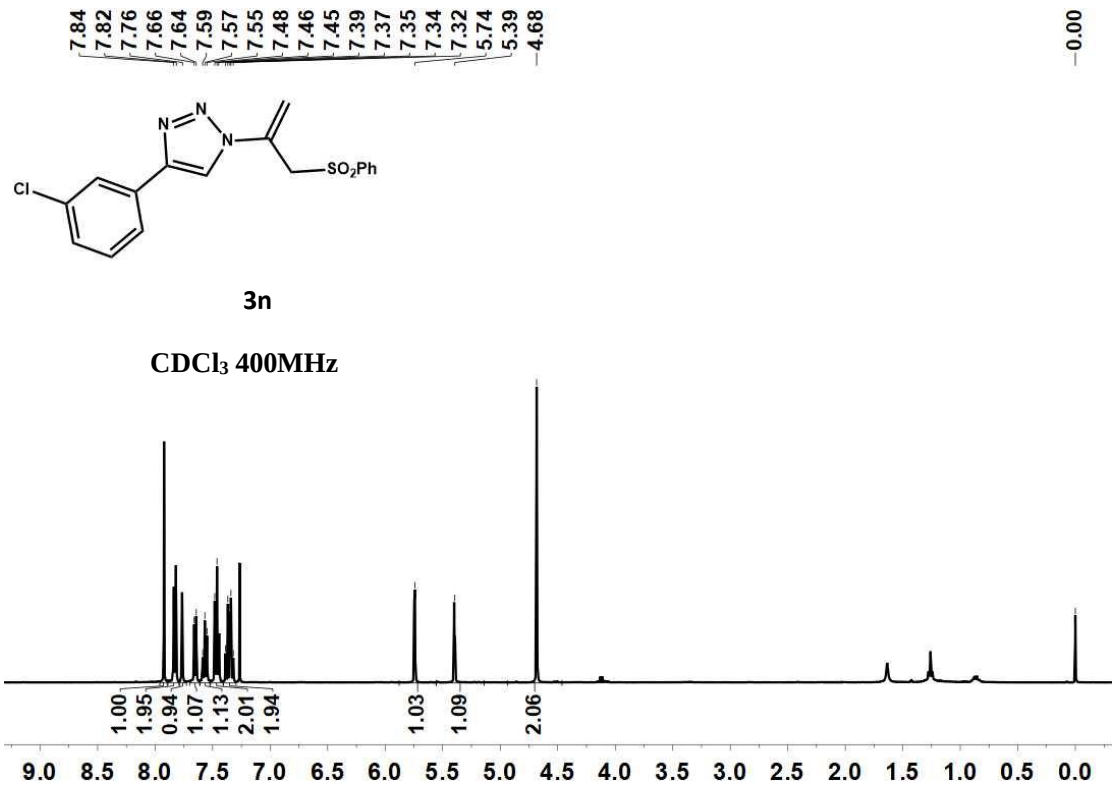
$CDCl_3$ 400MHz





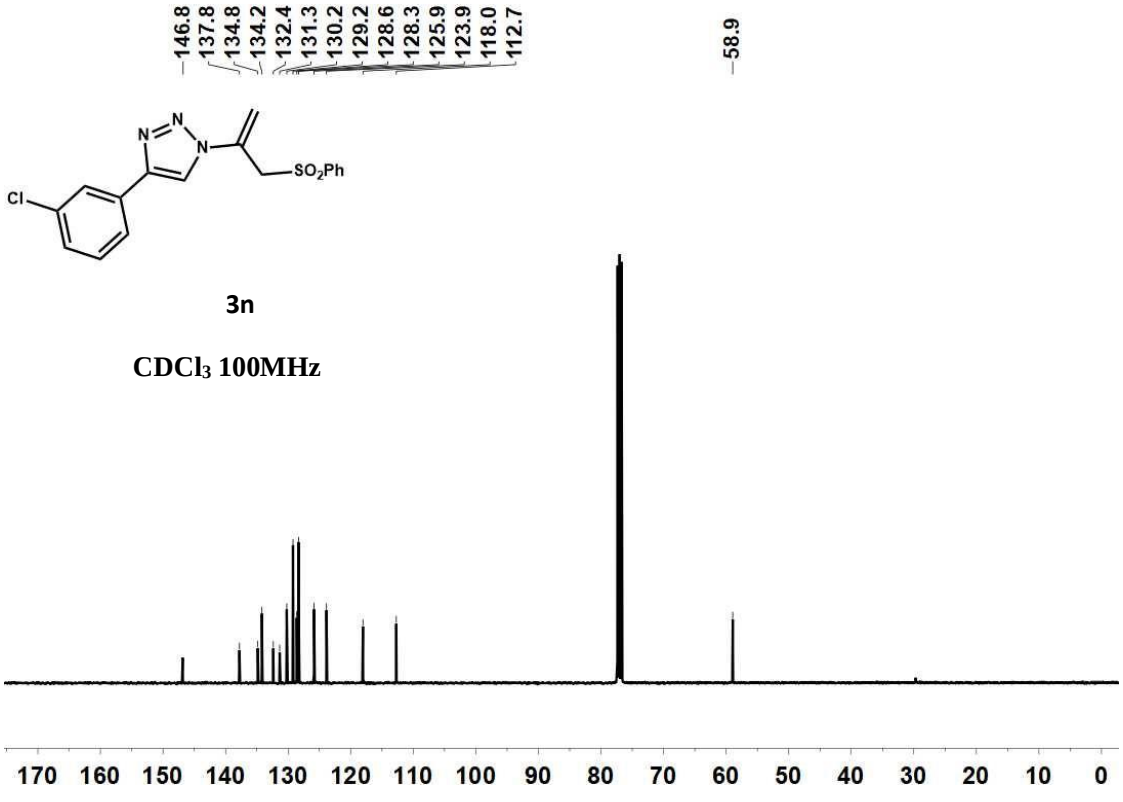
3m

$CDCl_3$ 100MHz



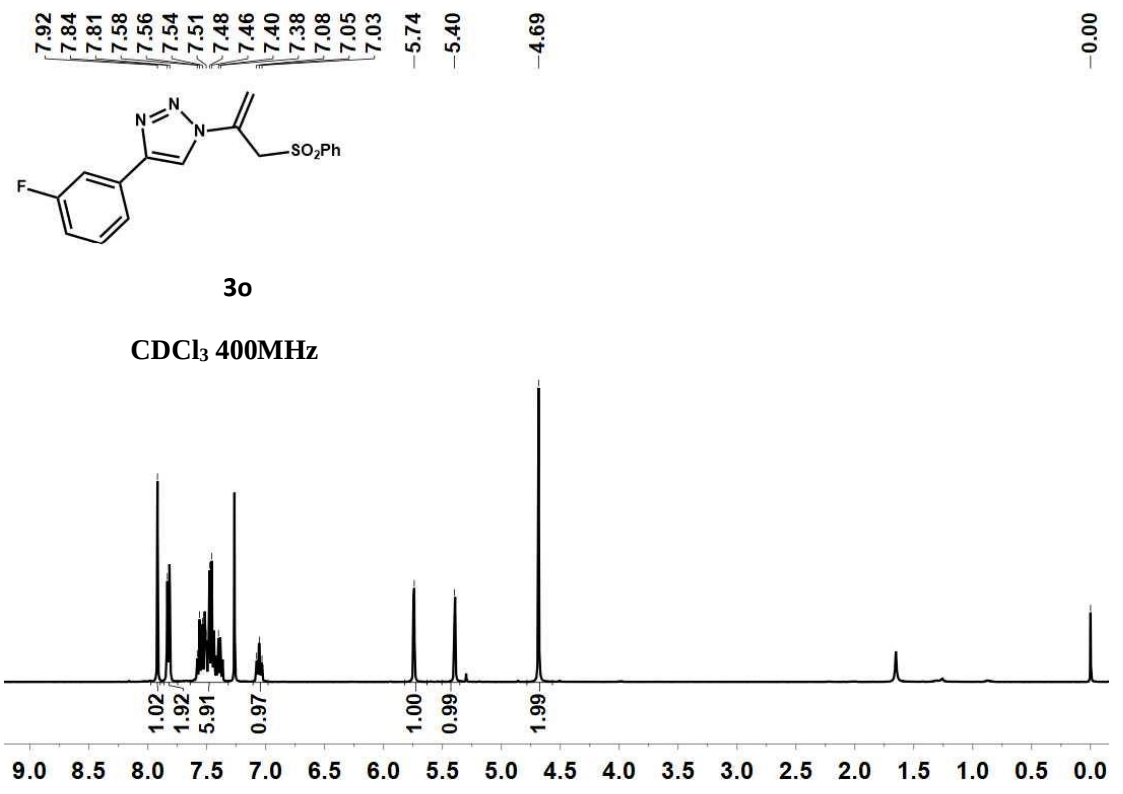
3n

$CDCl_3$ 400MHz



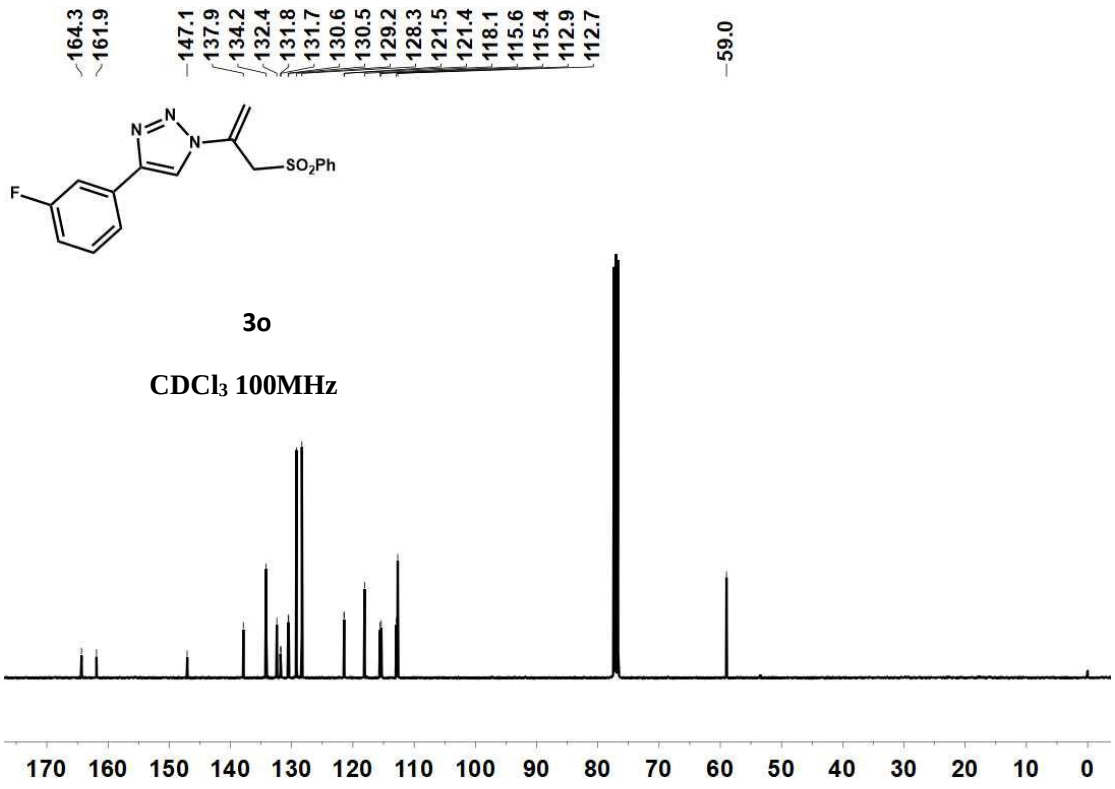
3n

$CDCl_3$ 100MHz



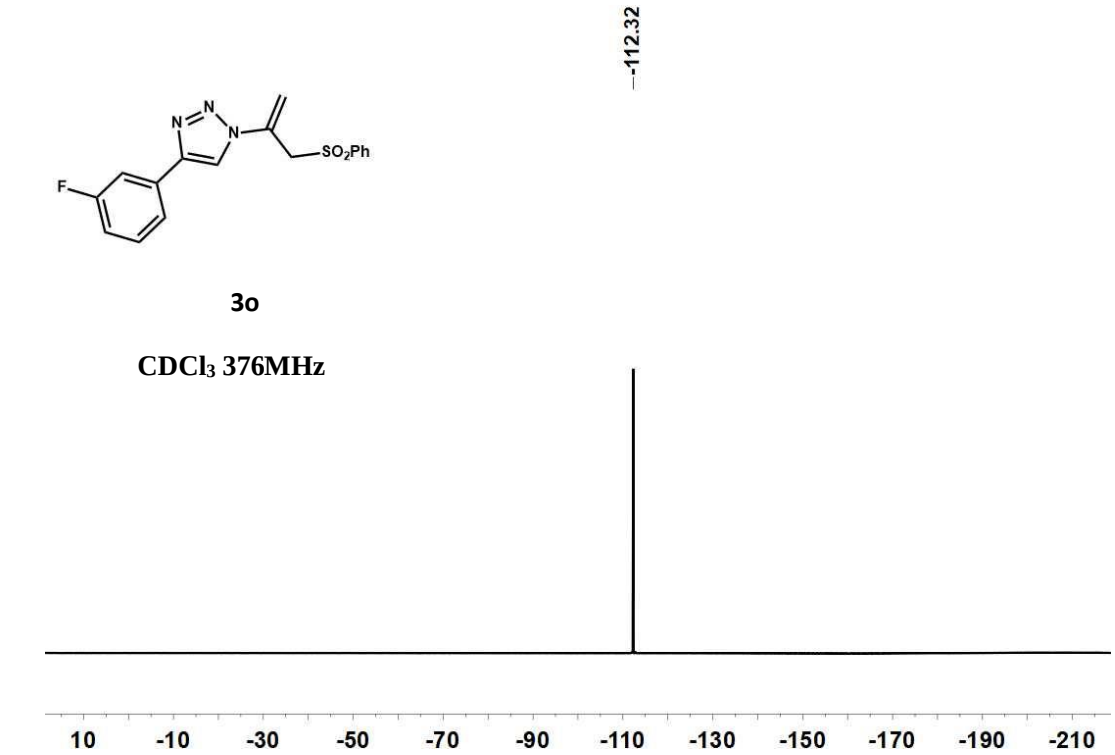
3o

$CDCl_3$ 400MHz



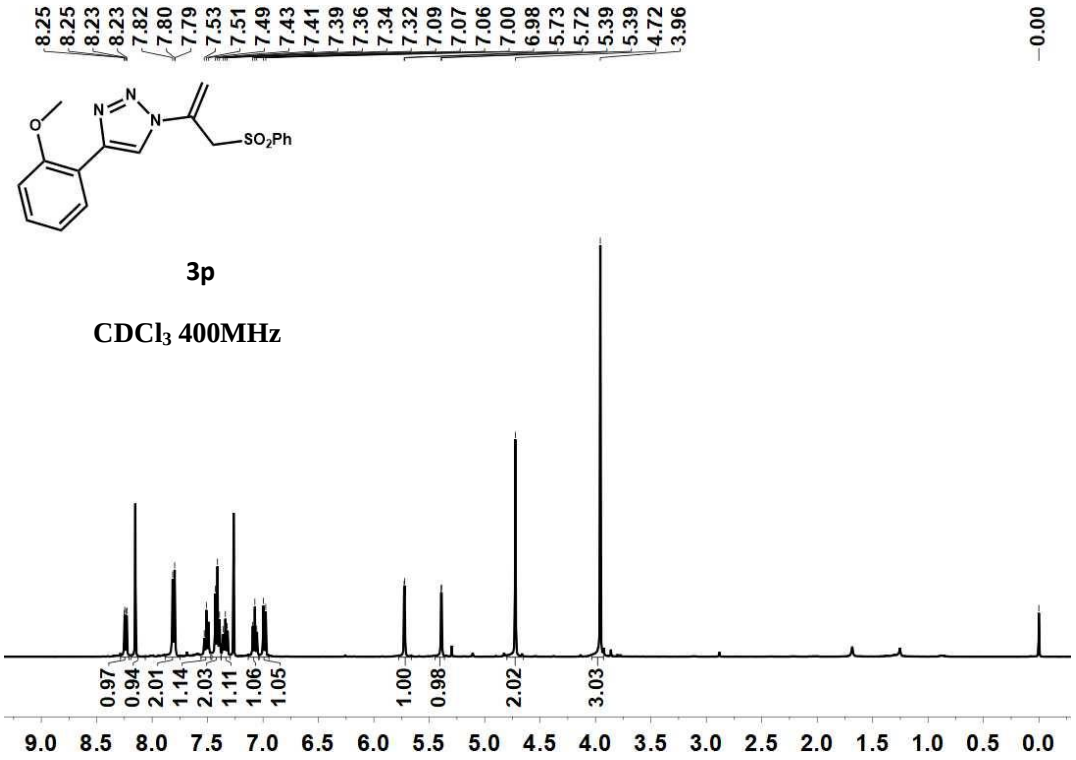
3o

$CDCl_3$ 100MHz



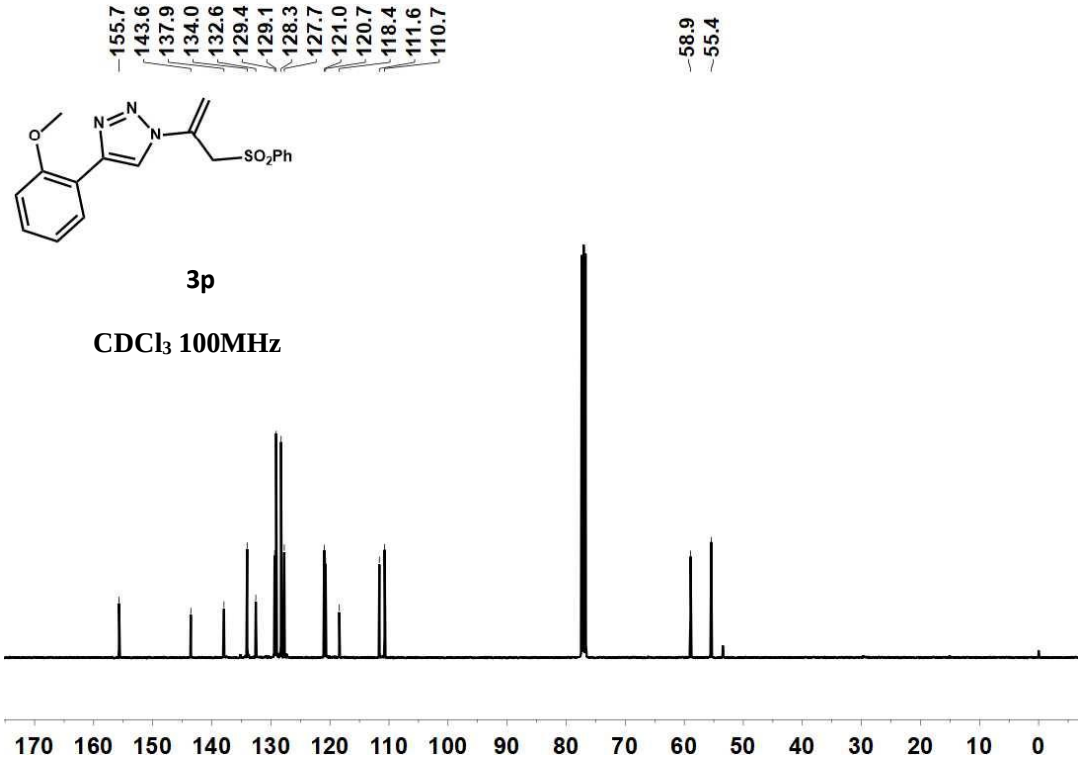
3o

$CDCl_3$ 376MHz



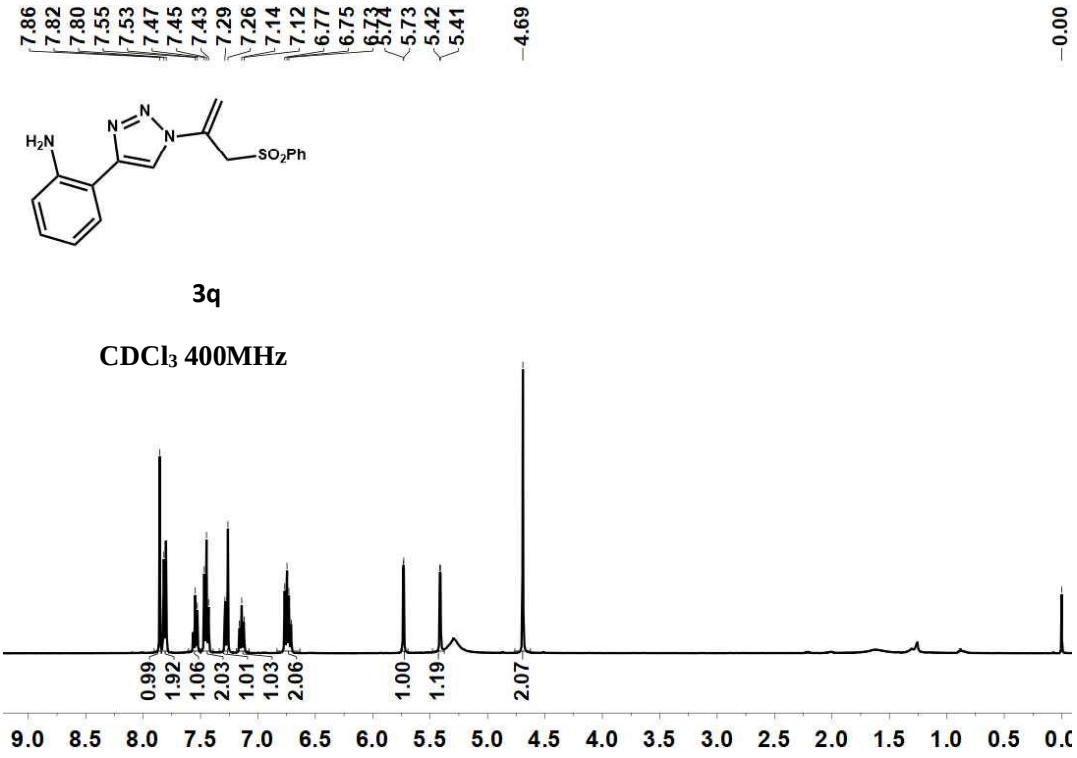
3p

$CDCl_3$ 400MHz



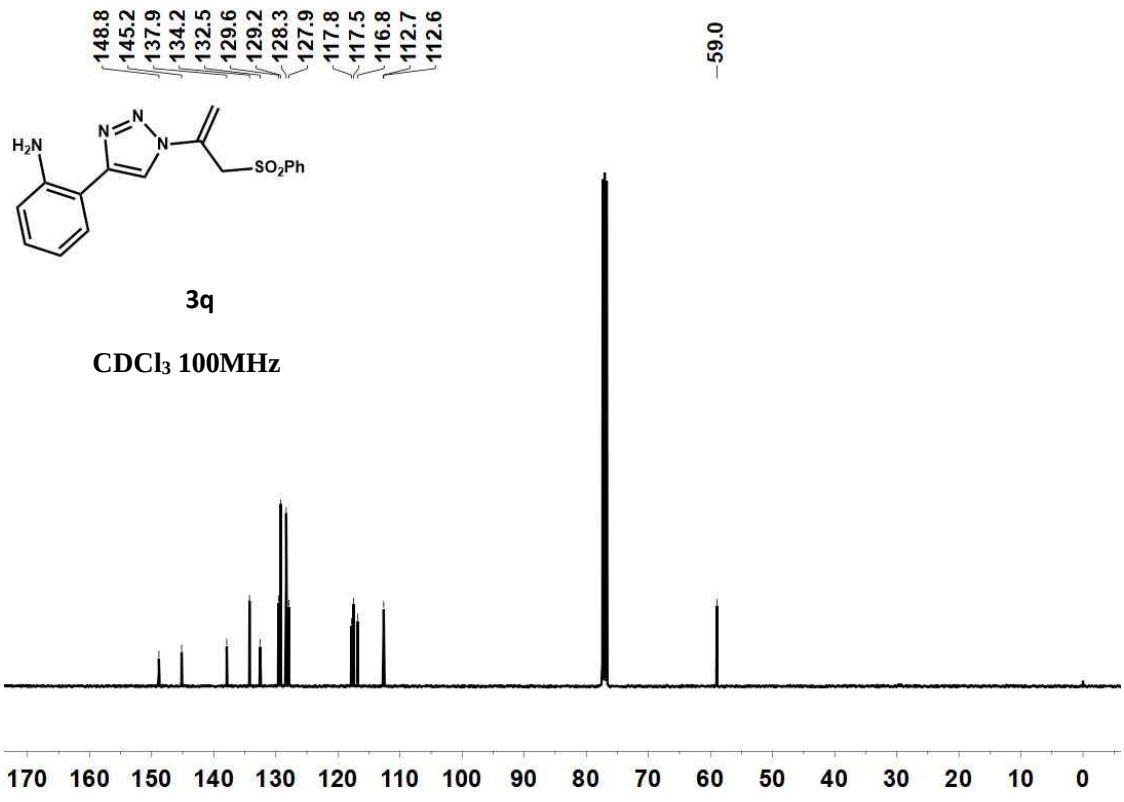
3p

$CDCl_3$ 100MHz



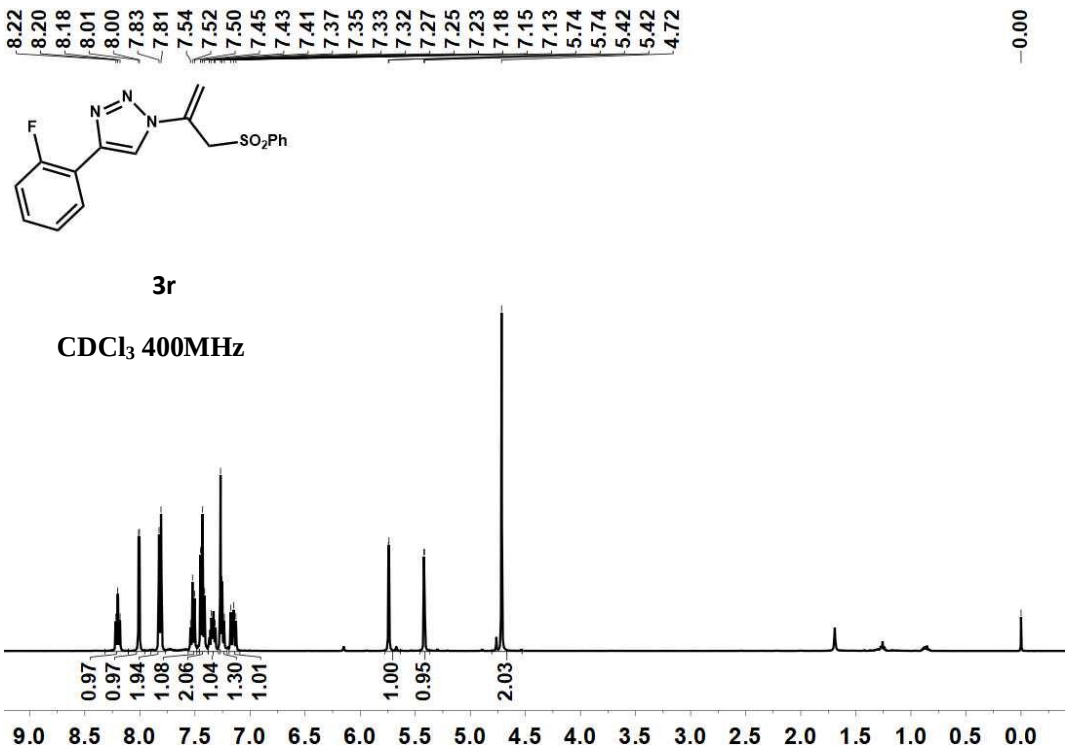
3q

$CDCl_3$ 400MHz



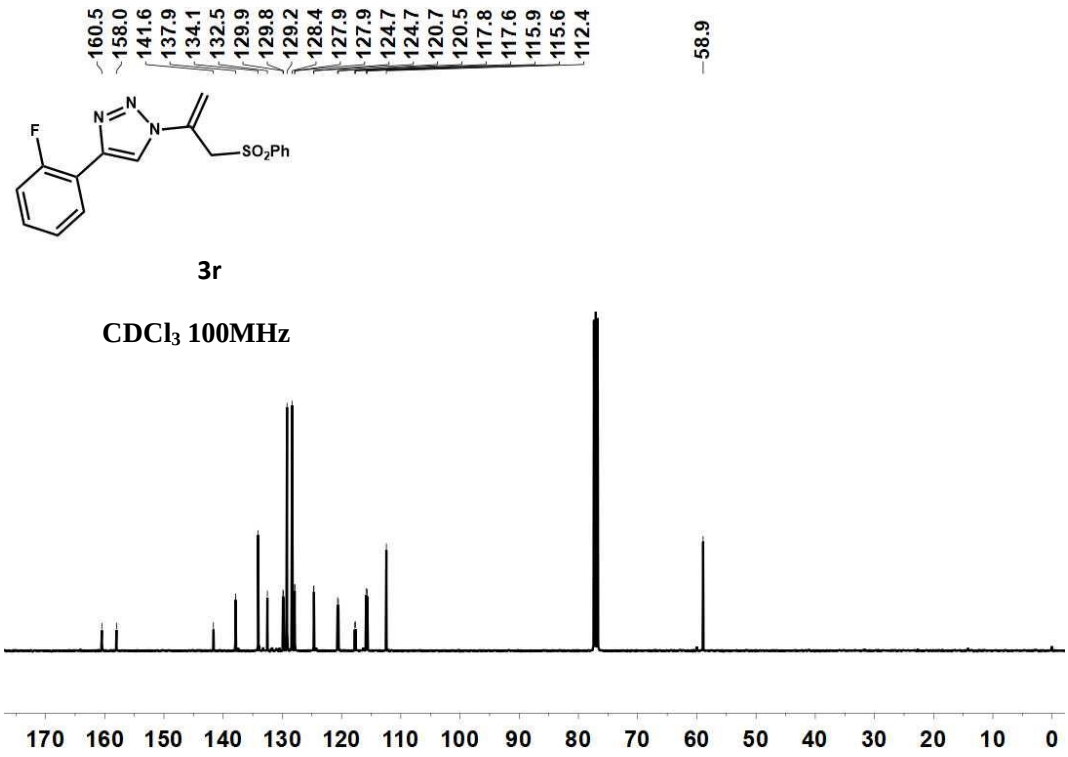
3q

$CDCl_3$ 100MHz



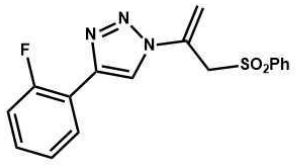
3r

$CDCl_3$ 400MHz



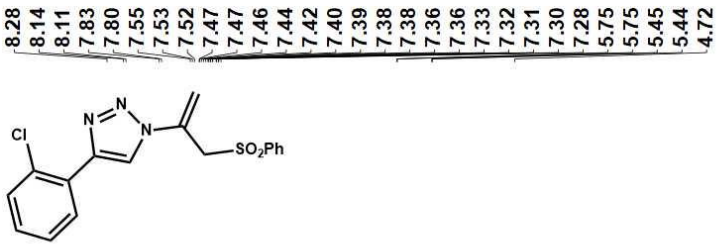
3r

$CDCl_3$ 100MHz



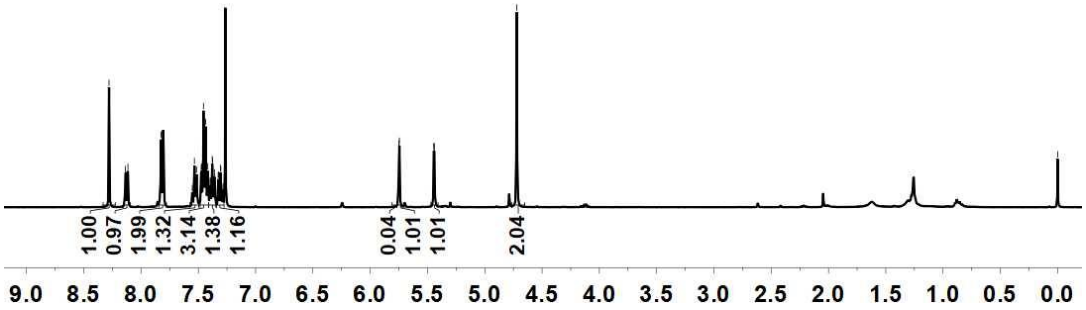
3r

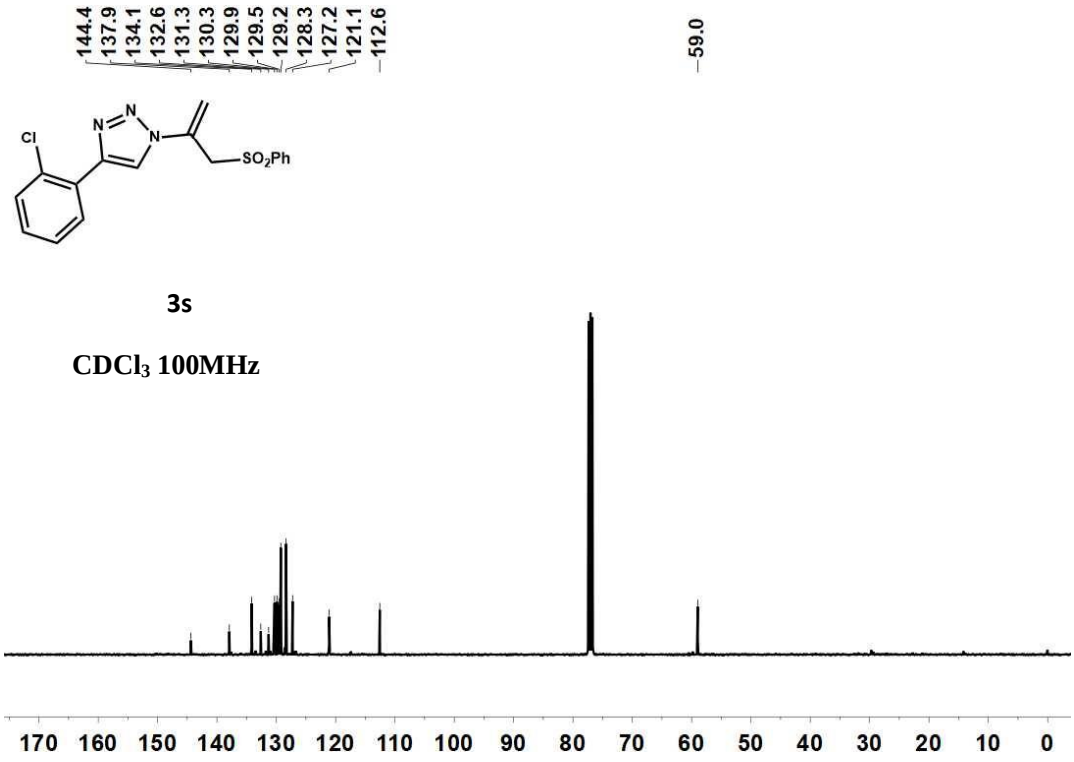
$CDCl_3$ 376MHz



3s

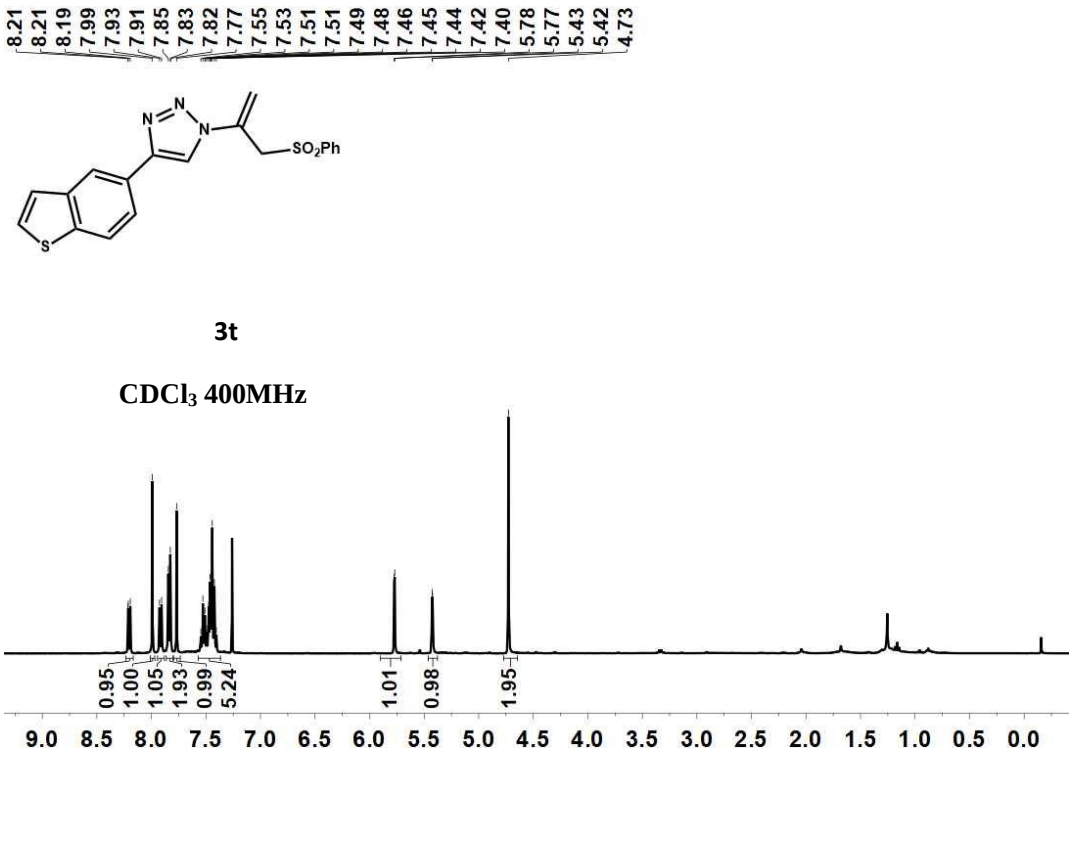
$CDCl_3$ 400MHz





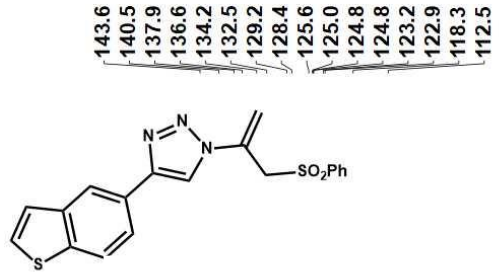
3s

$CDCl_3$ 100MHz



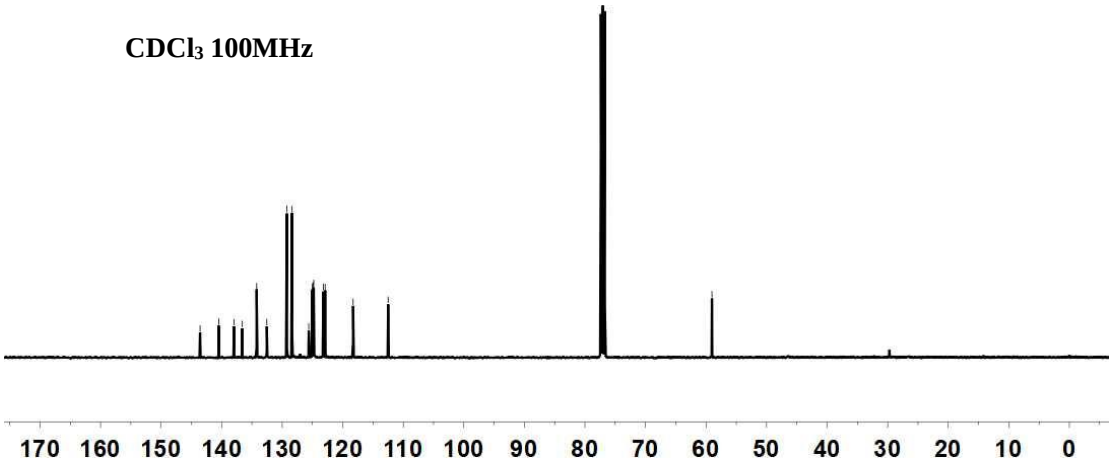
3t

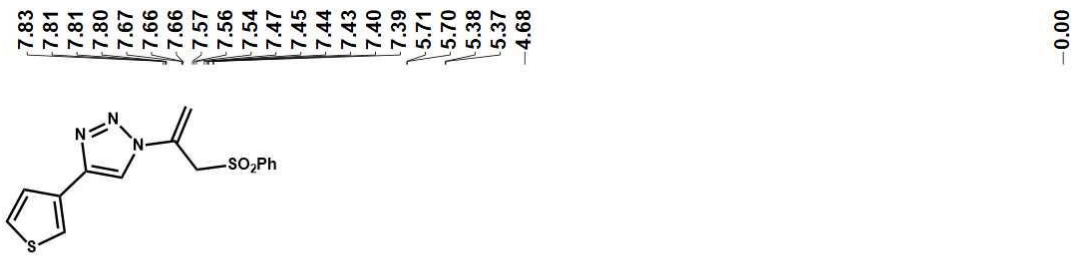
$CDCl_3$ 400MHz



3t

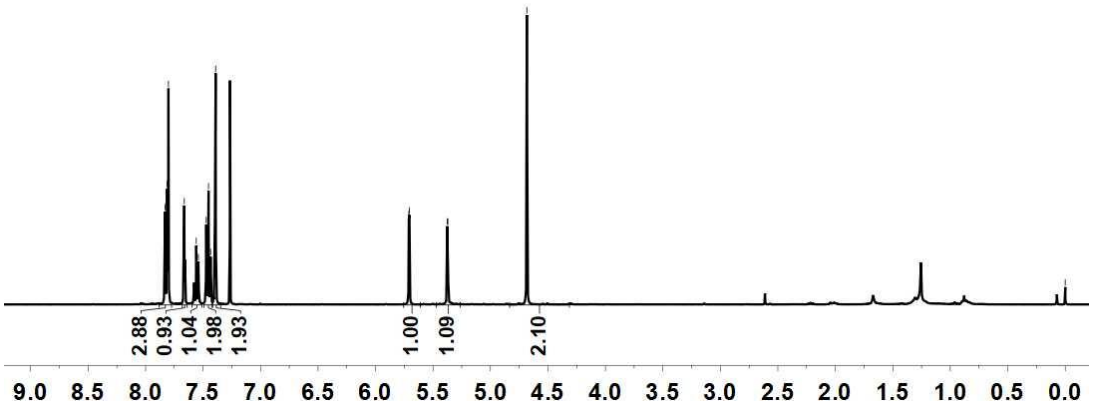
$CDCl_3$ 100MHz

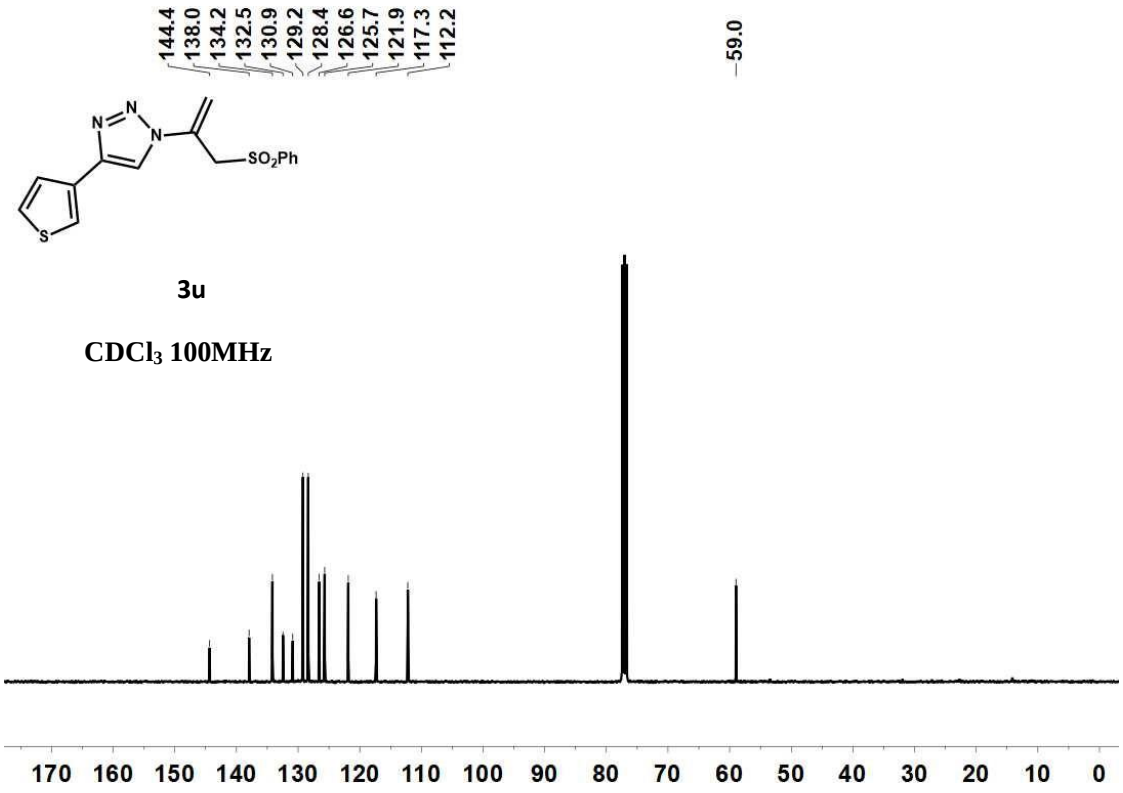




3u

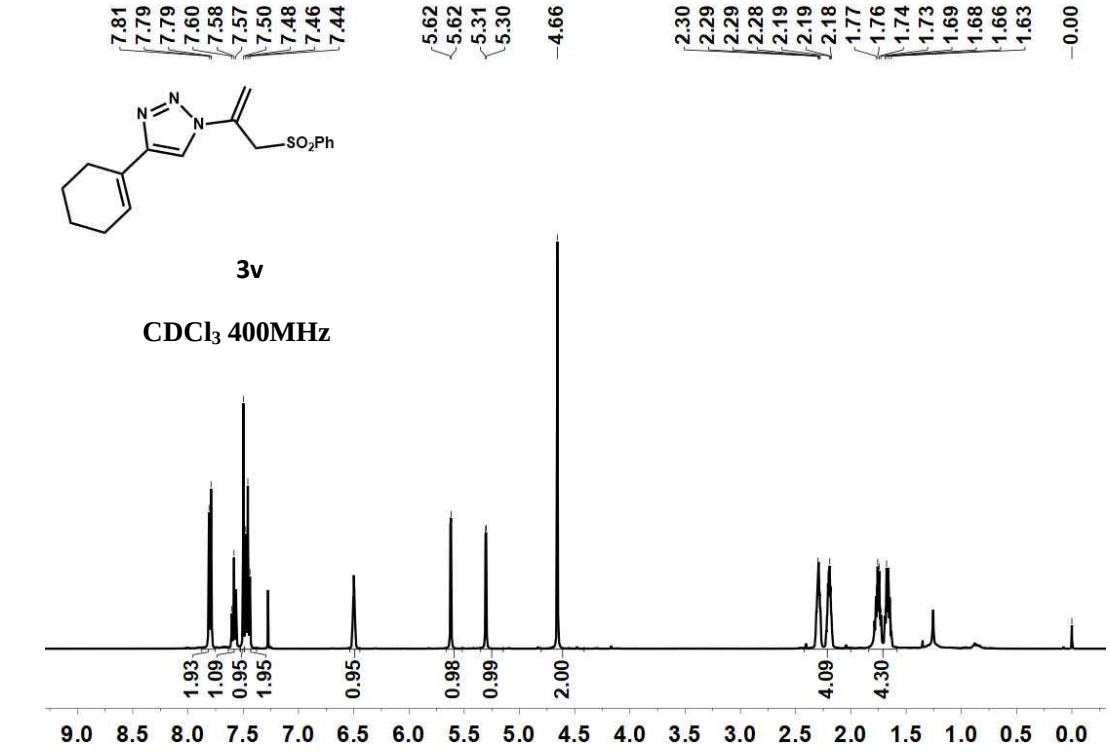
$CDCl_3$ 400MHz





3u

$CDCl_3$ 100MHz

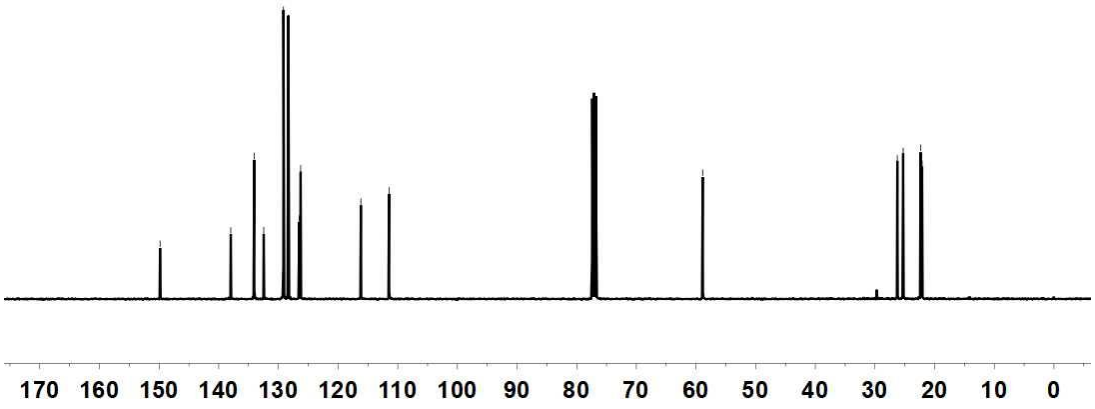


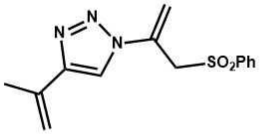
3v

$CDCl_3$ 400MHz

3v

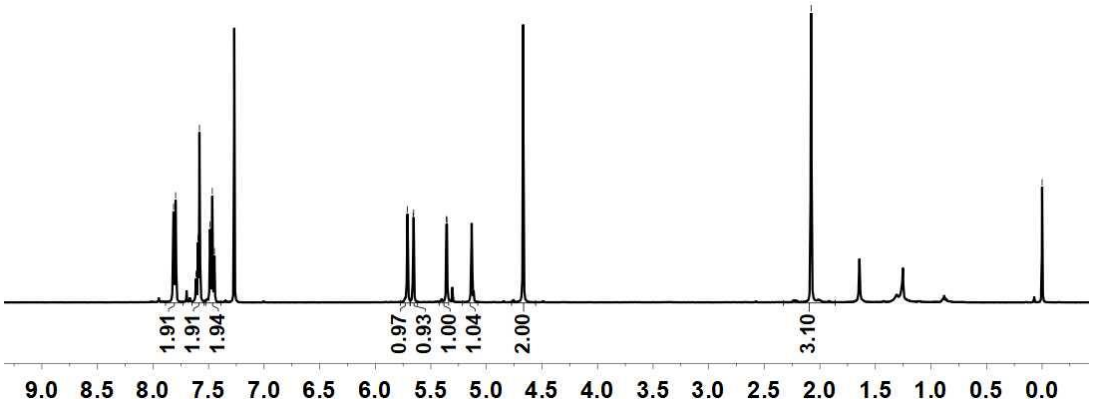
$CDCl_3$ 100MHz

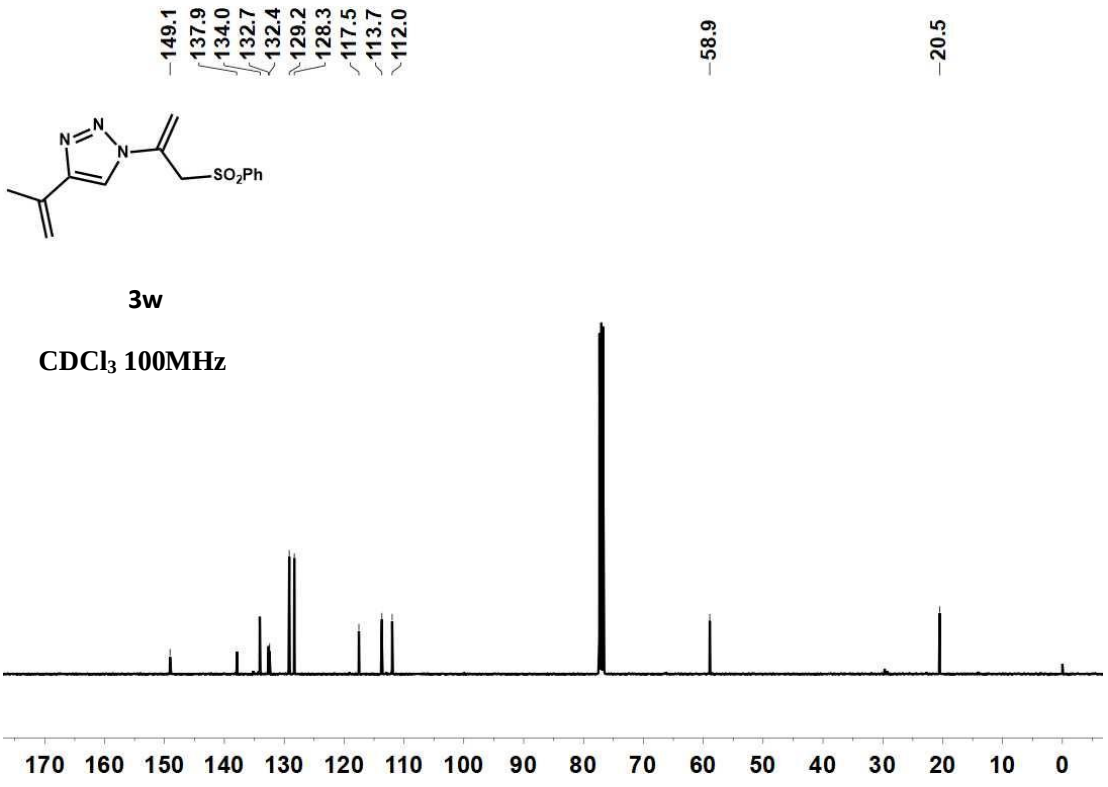




3w

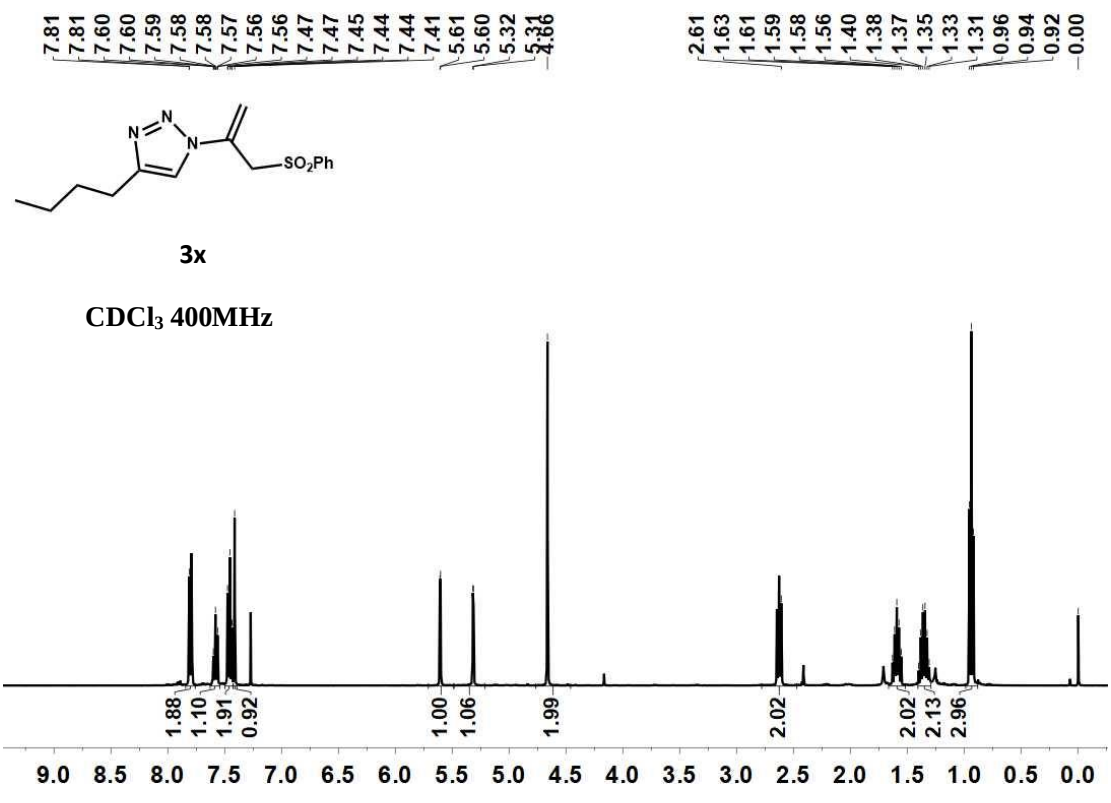
$CDCl_3$ 400MHz





3w

$CDCl_3$ 100MHz

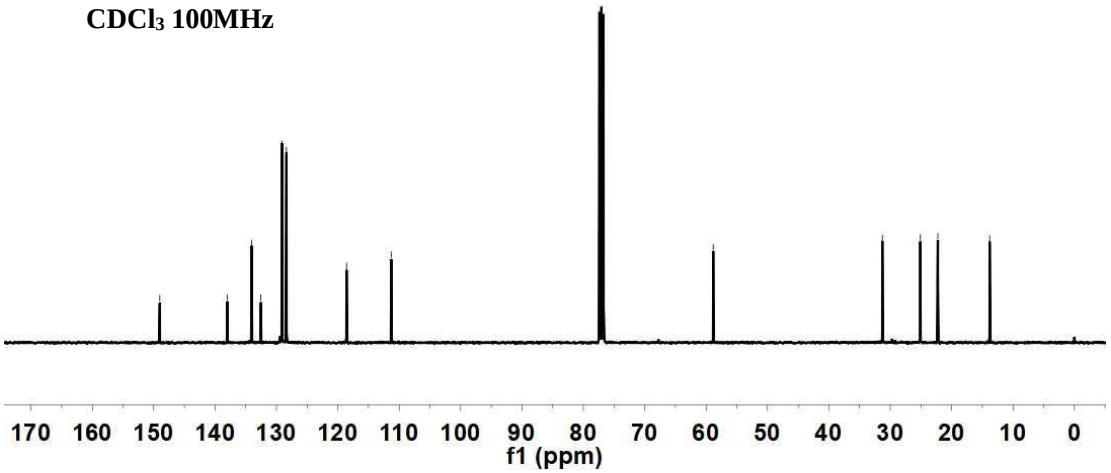


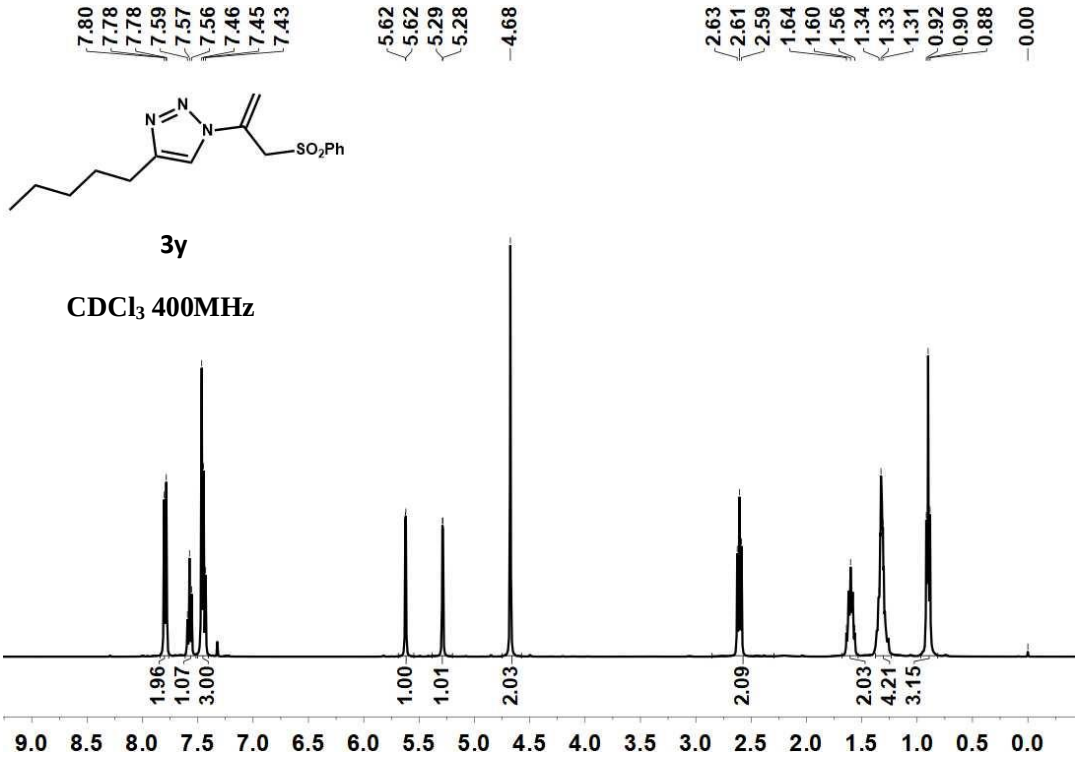
3x

$CDCl_3$ 400MHz

3x

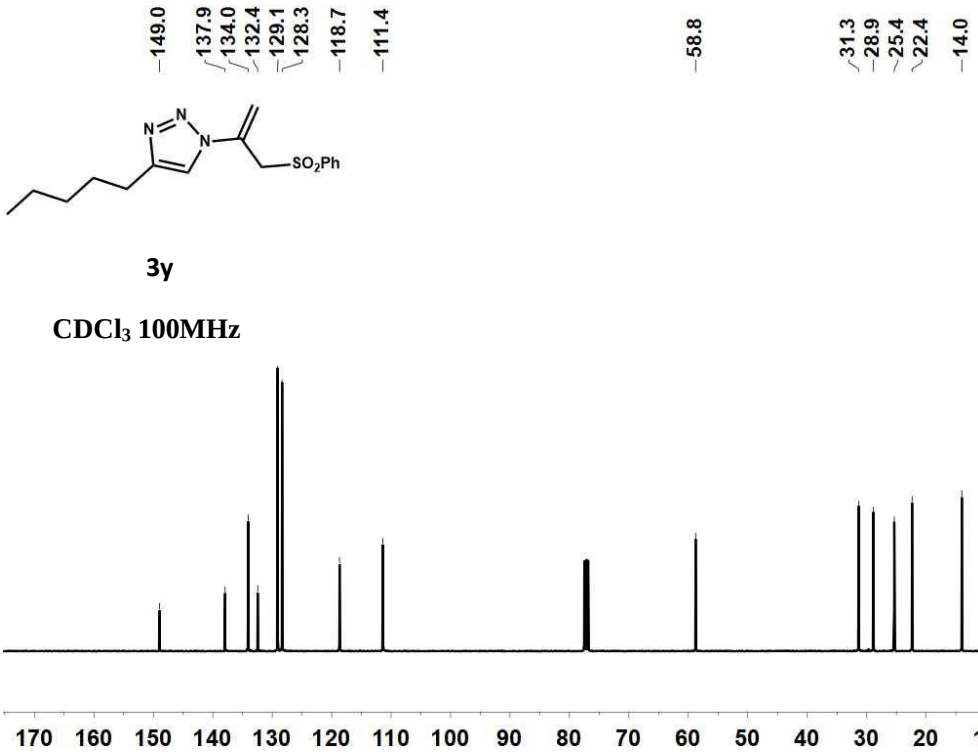
$CDCl_3$ 100MHz





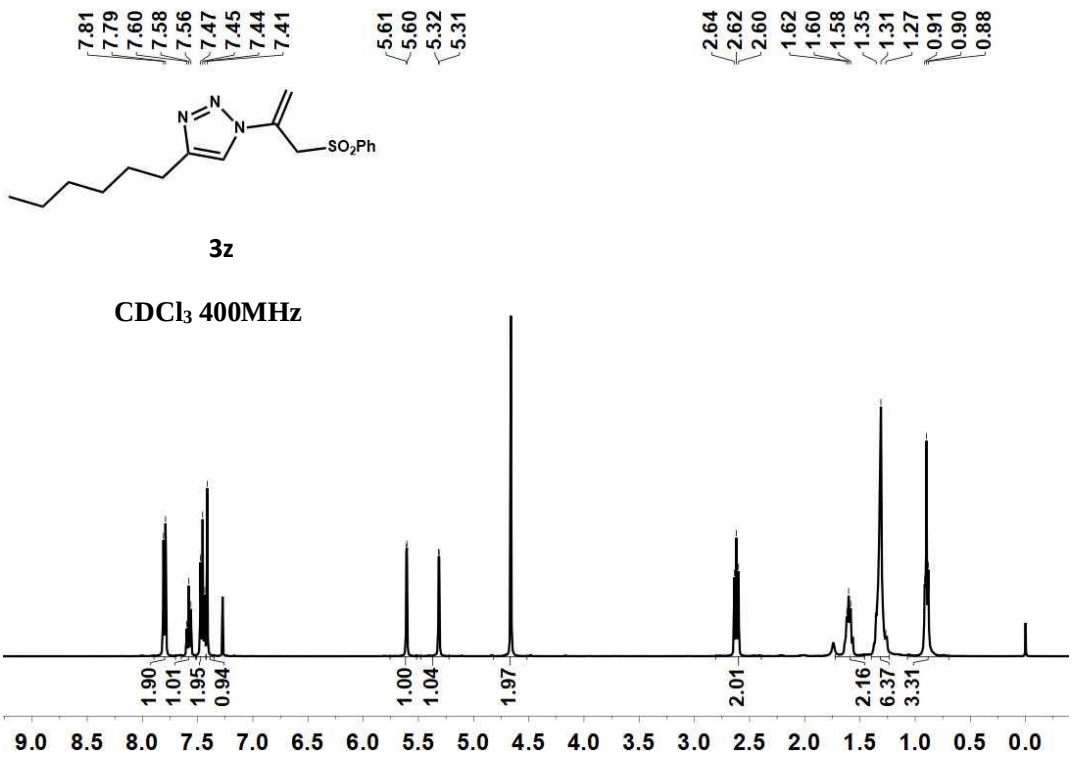
3y

$CDCl_3$ 400MHz



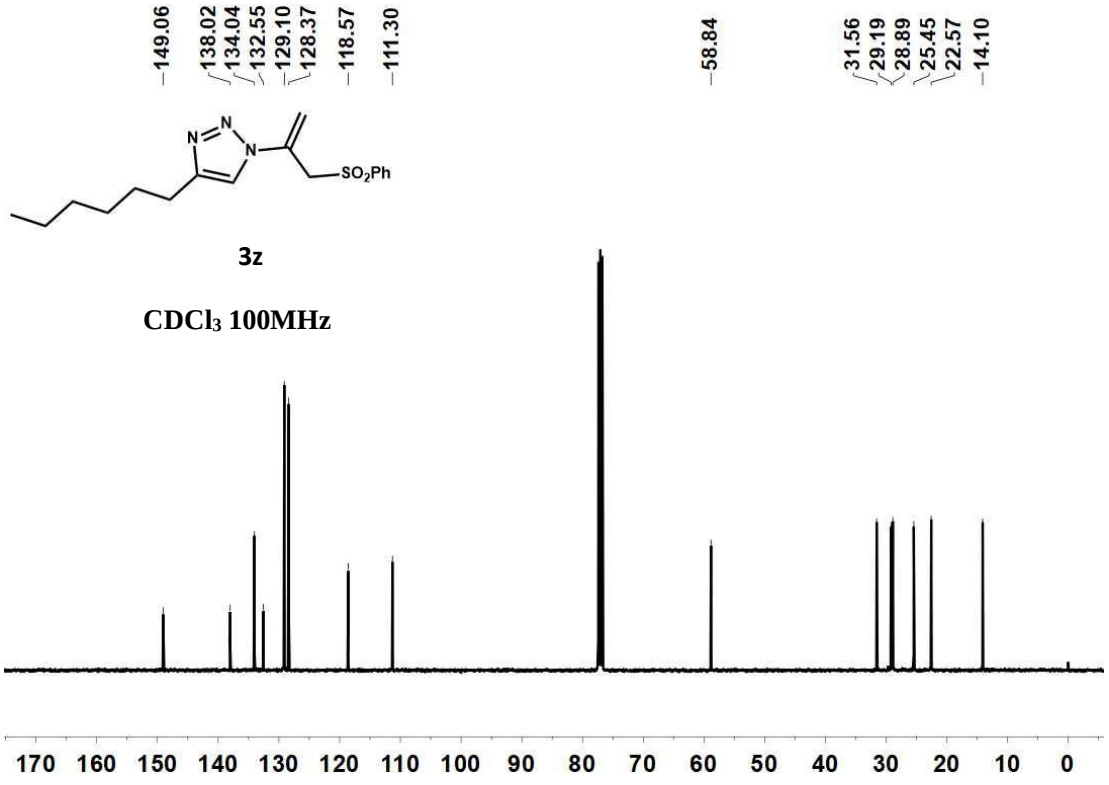
3y

$CDCl_3$ 100MHz



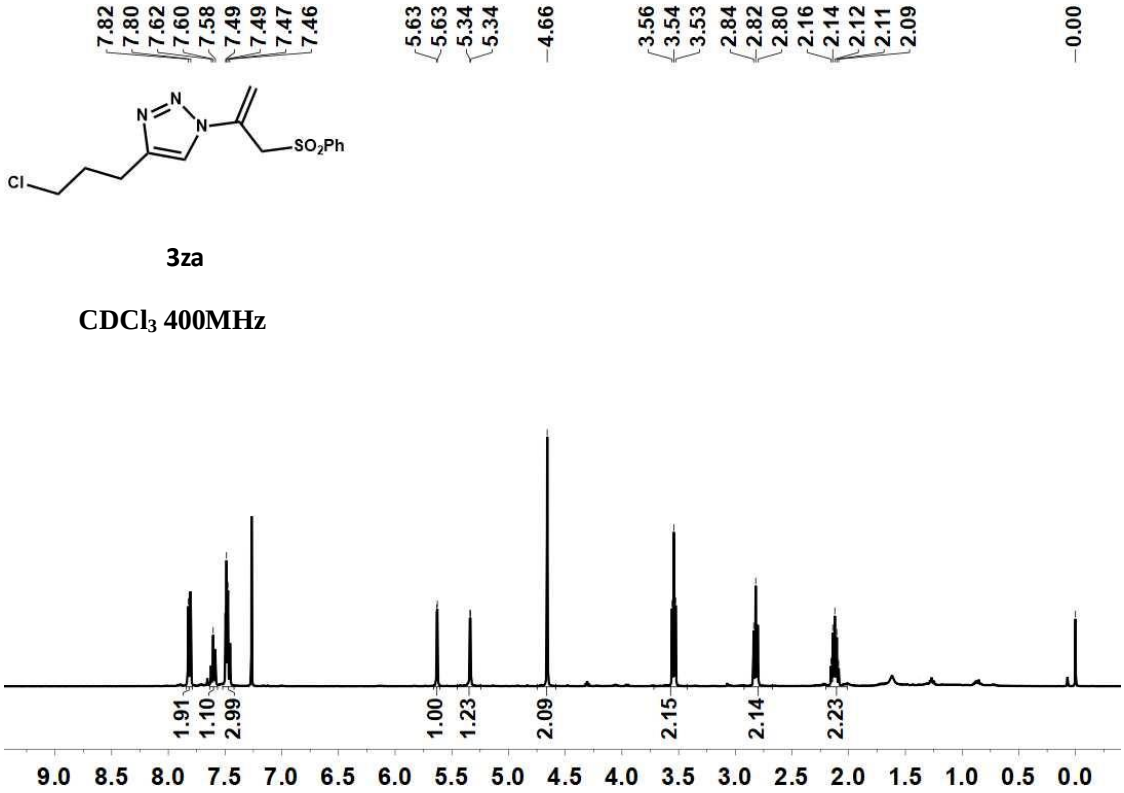
3z

$CDCl_3$ 400MHz



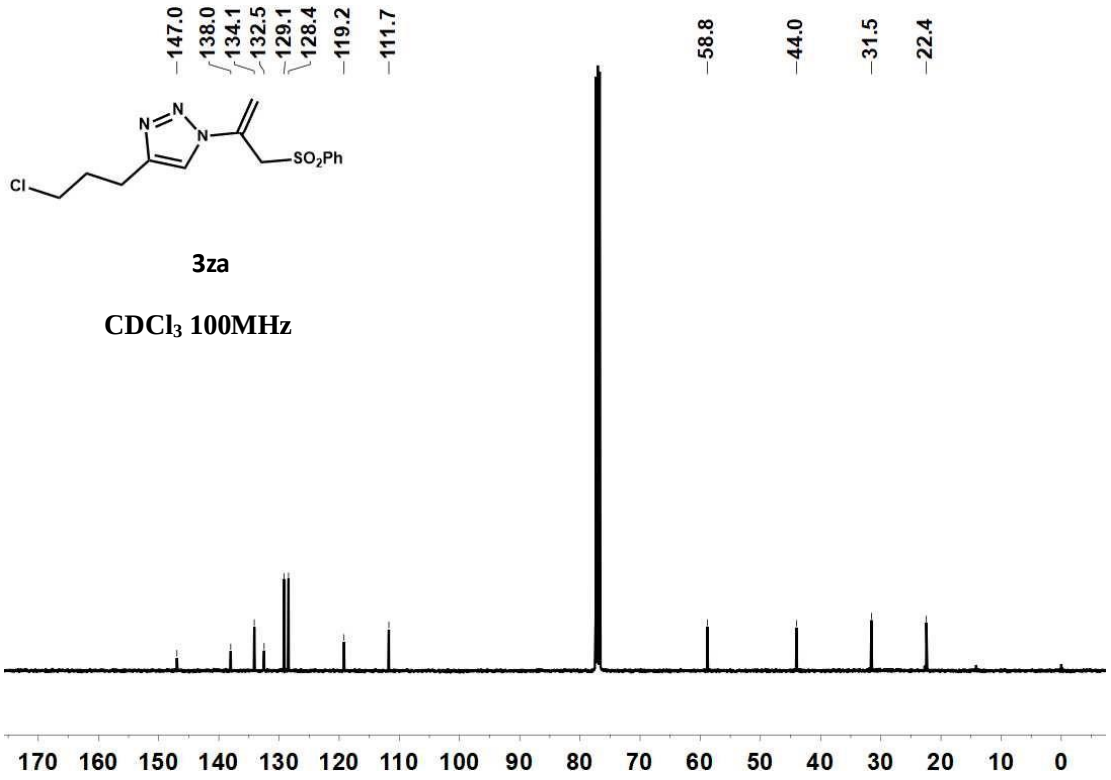
3z

$CDCl_3$ 100MHz



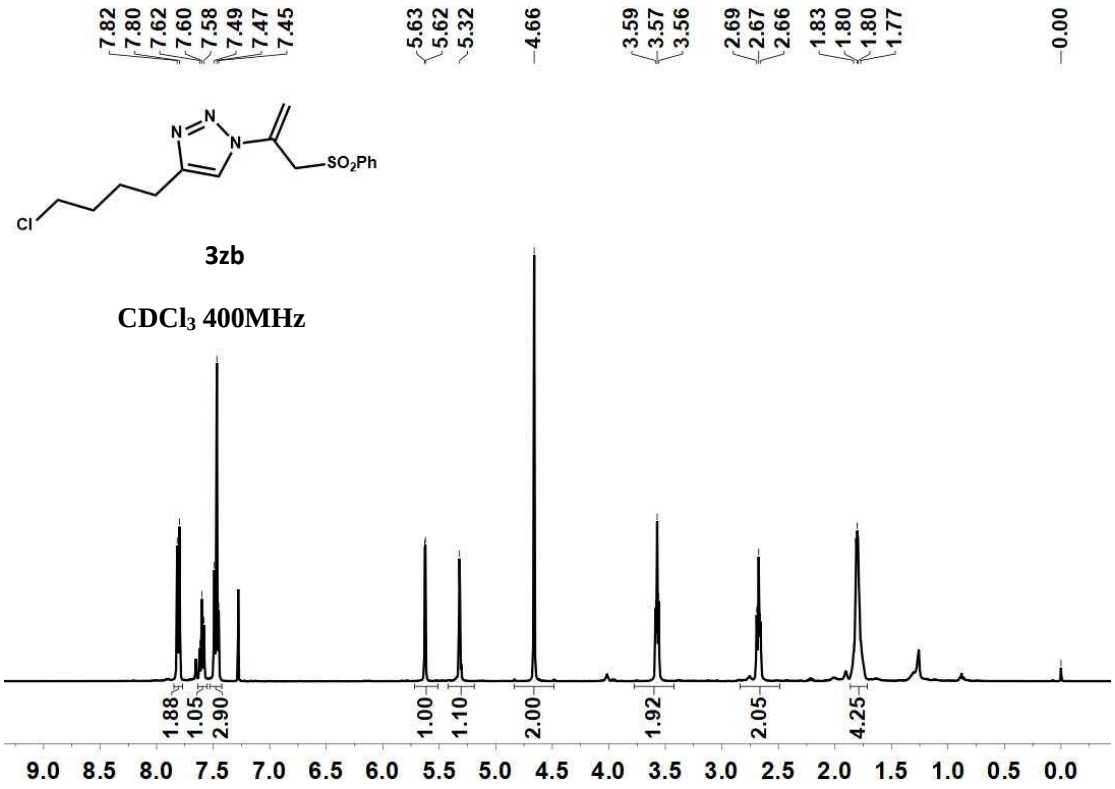
3za

$CDCl_3$ 400MHz



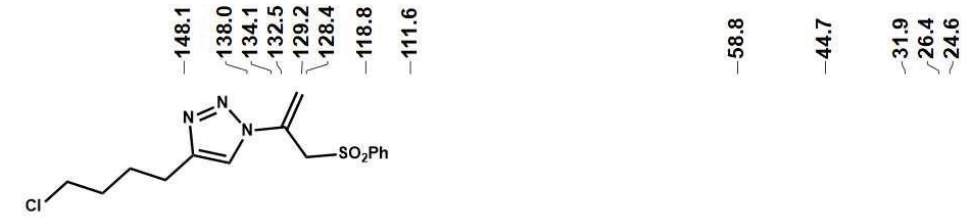
3za

$CDCl_3$ 100MHz



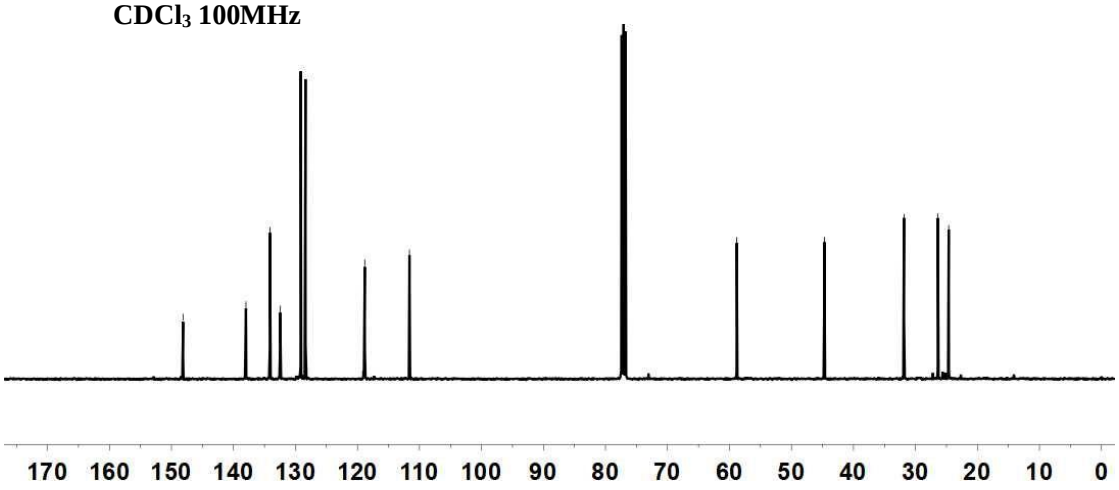
3zb

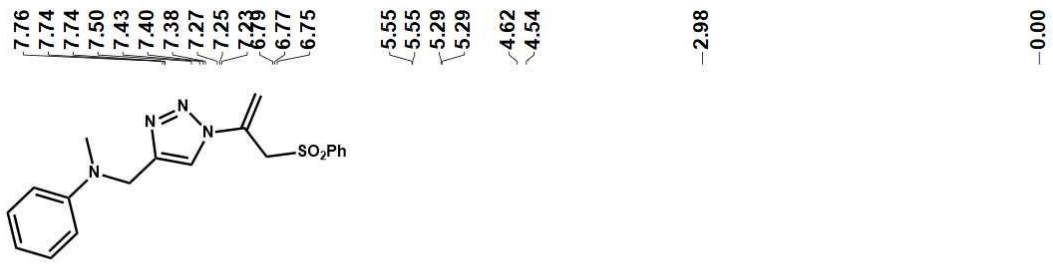
$CDCl_3$ 400MHz



3zb

$CDCl_3$ 100MHz





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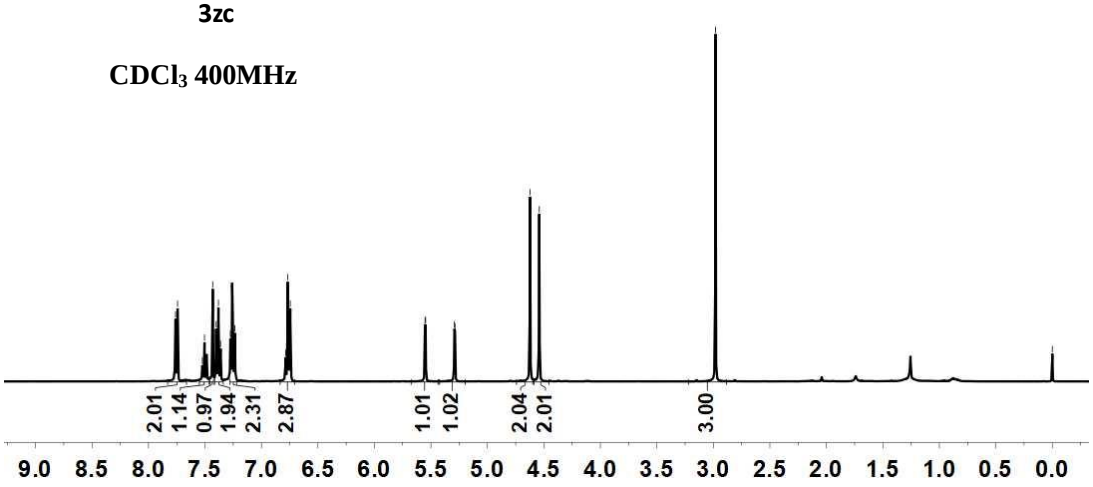

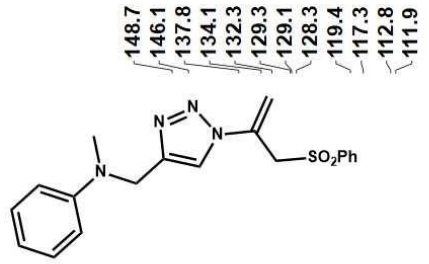

3zc

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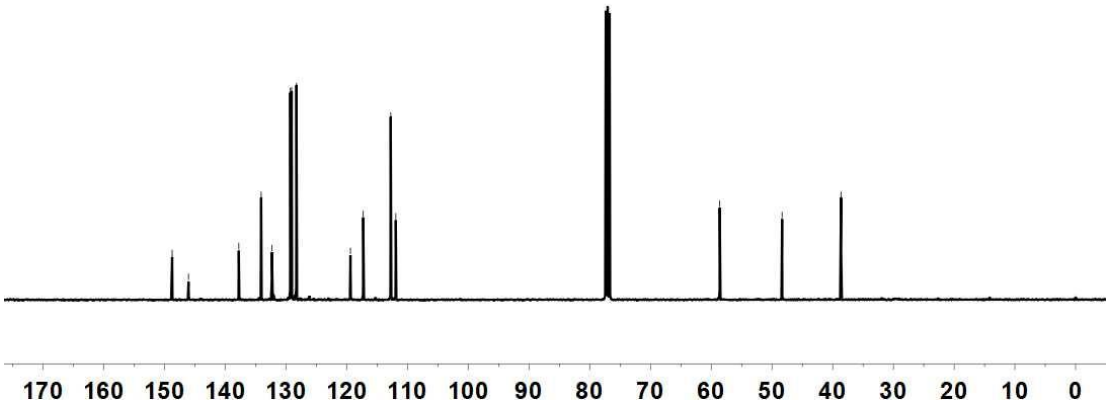

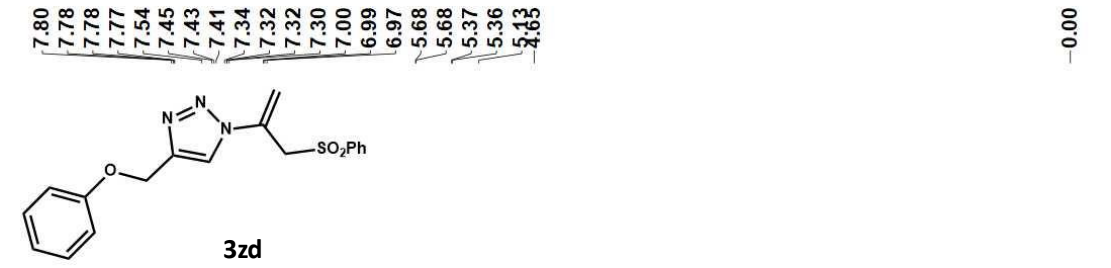

3zd

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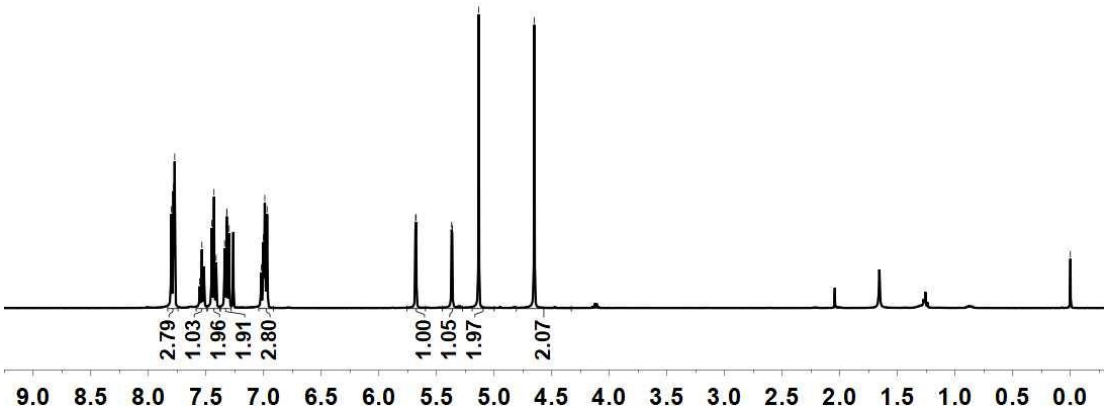

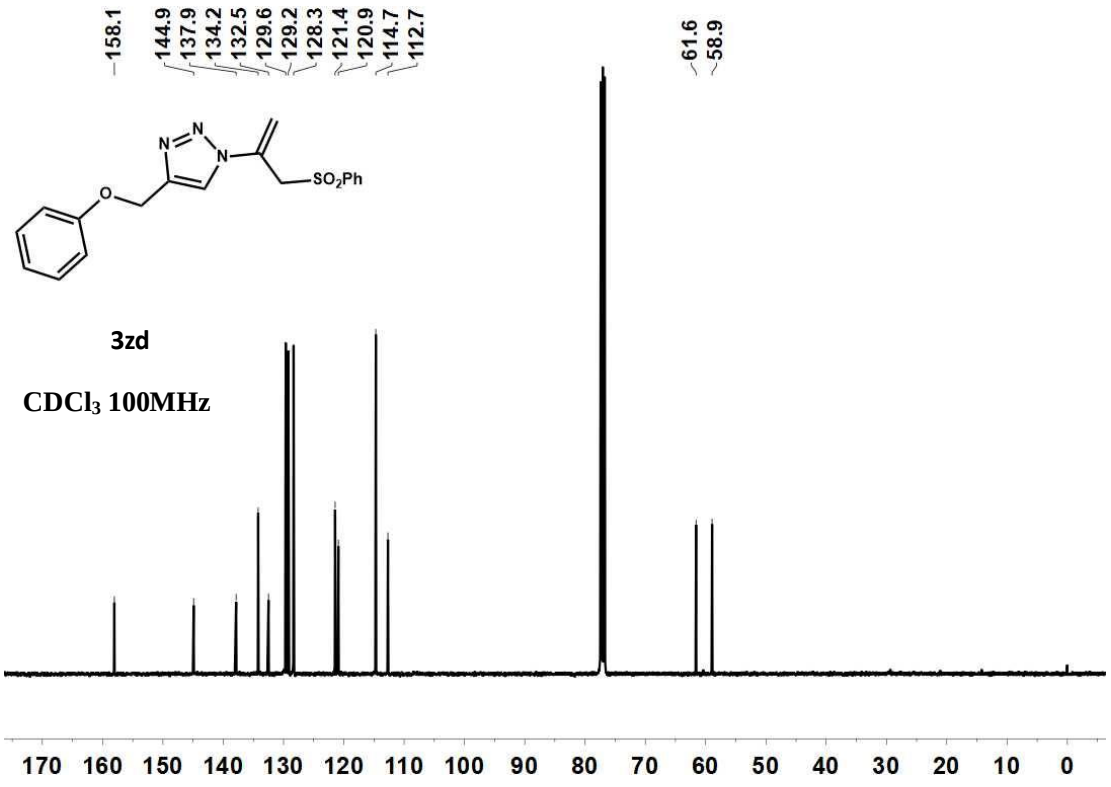

3zd

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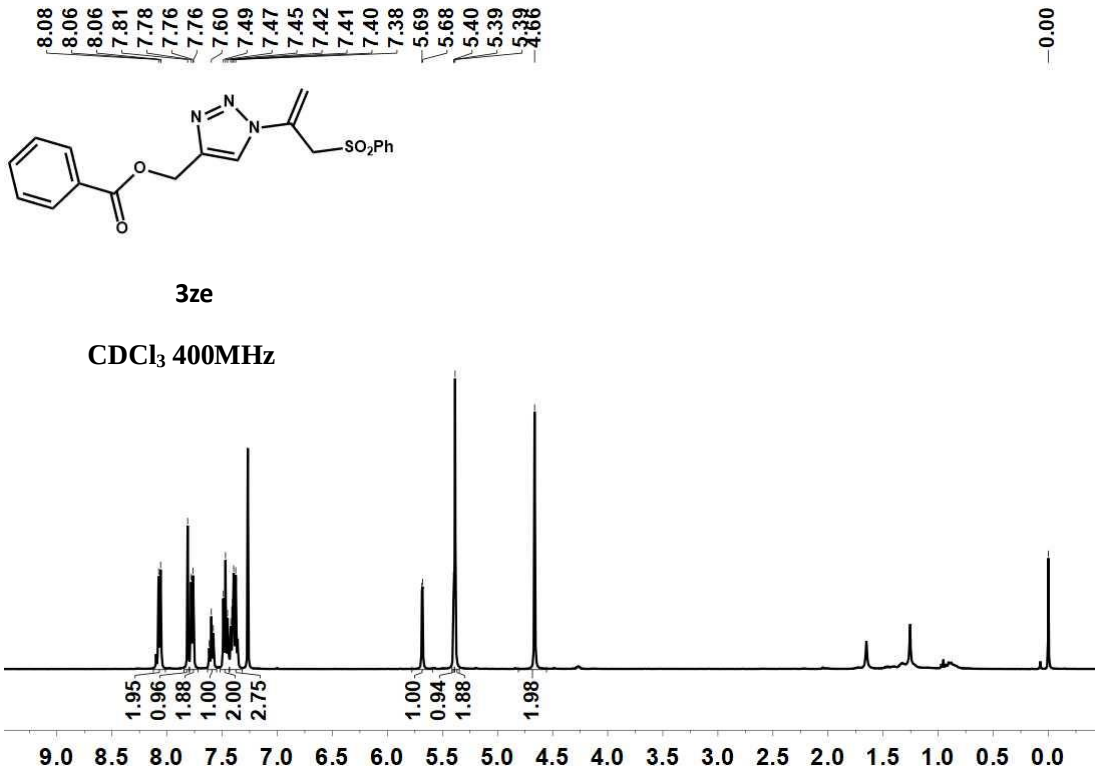

3ze

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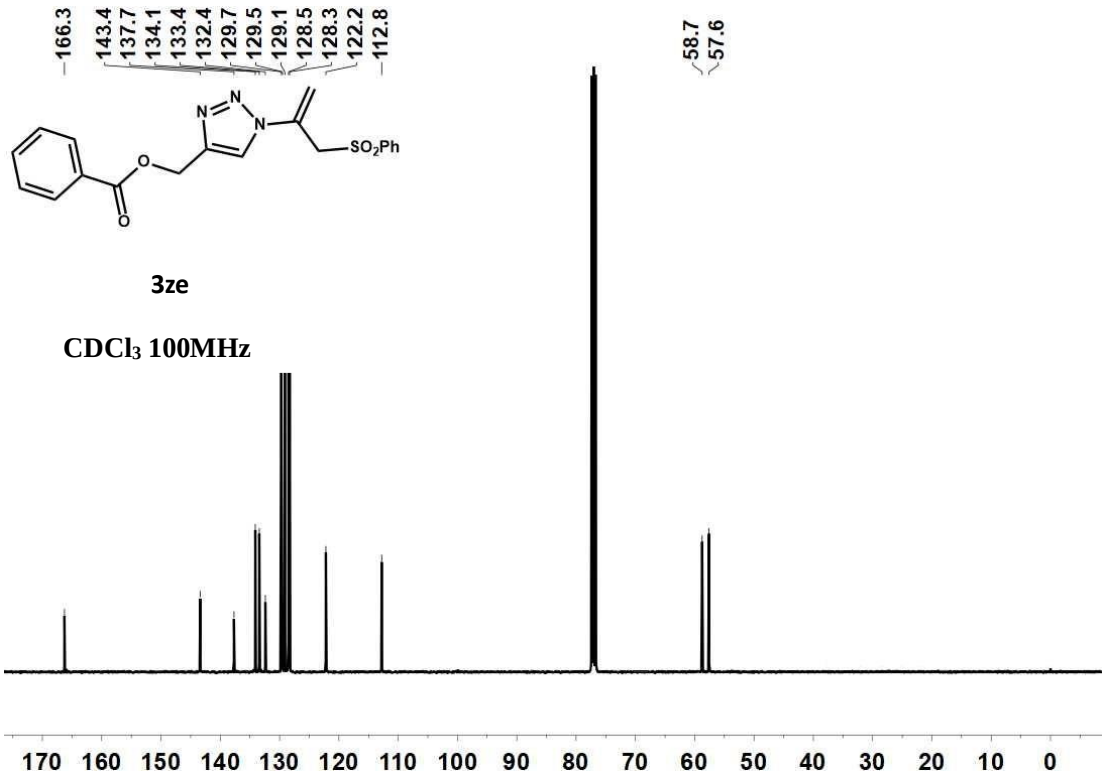

3ze

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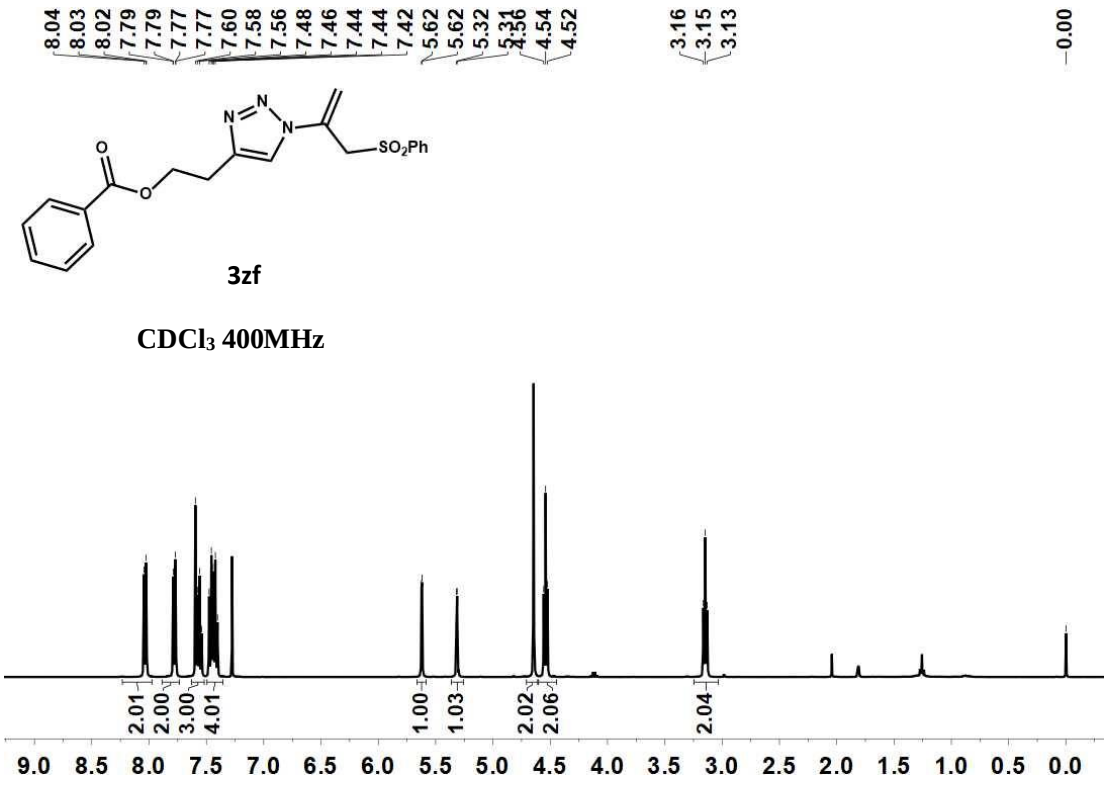
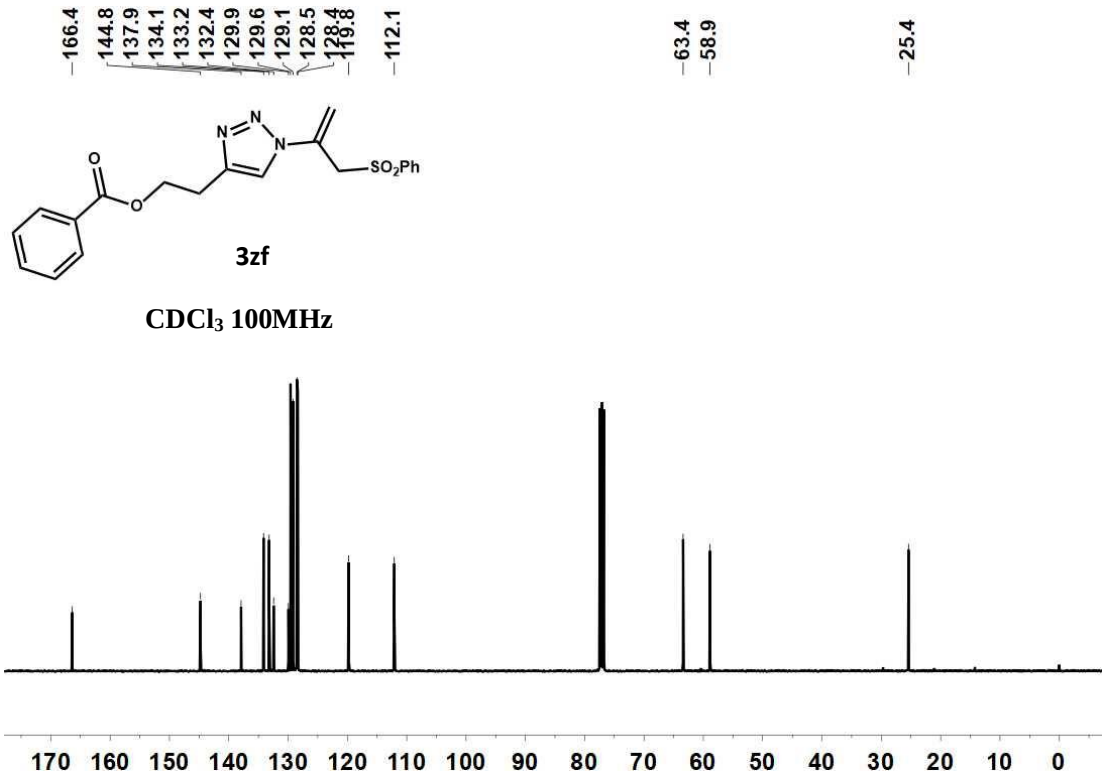


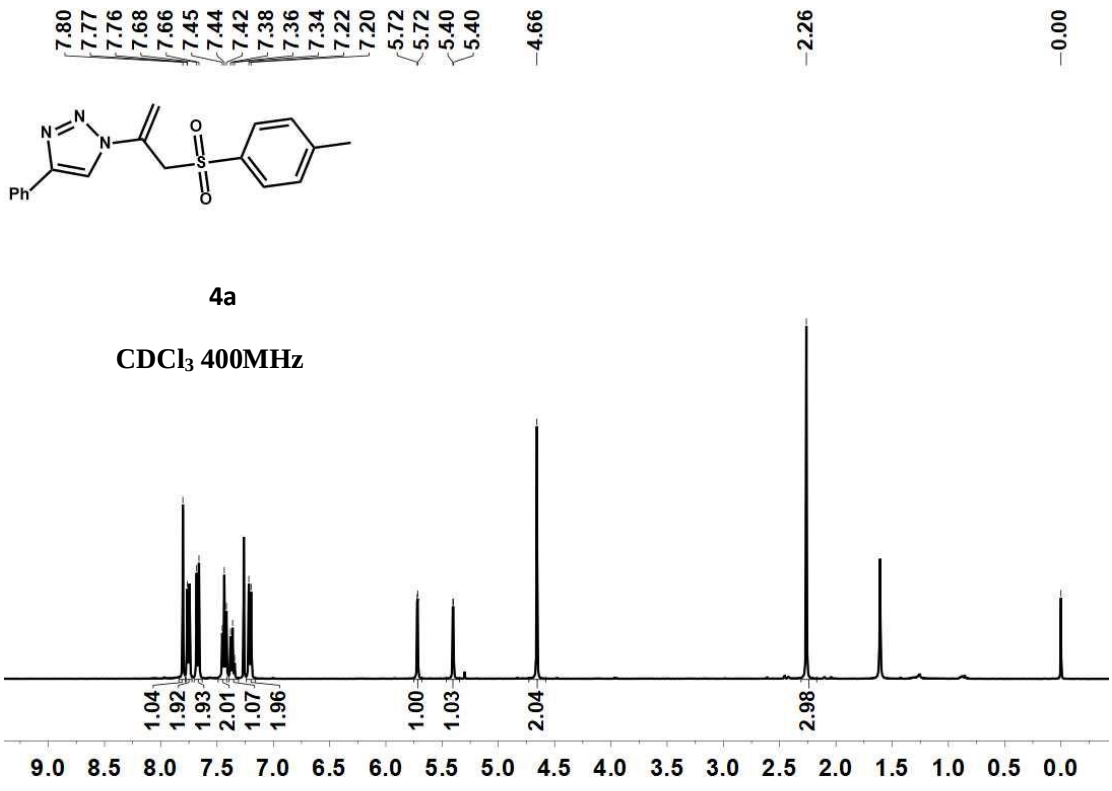
3zf

$CDCl_3$ 400MHz



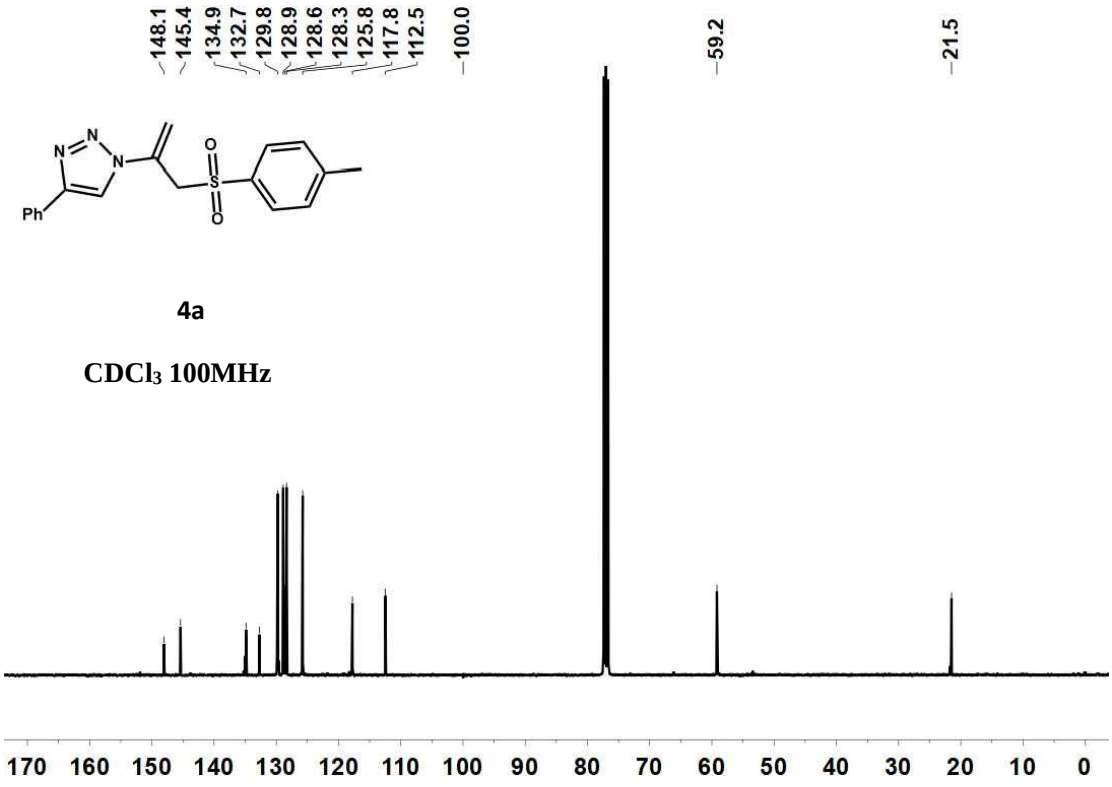
3zf

$CDCl_3$ 100MHz



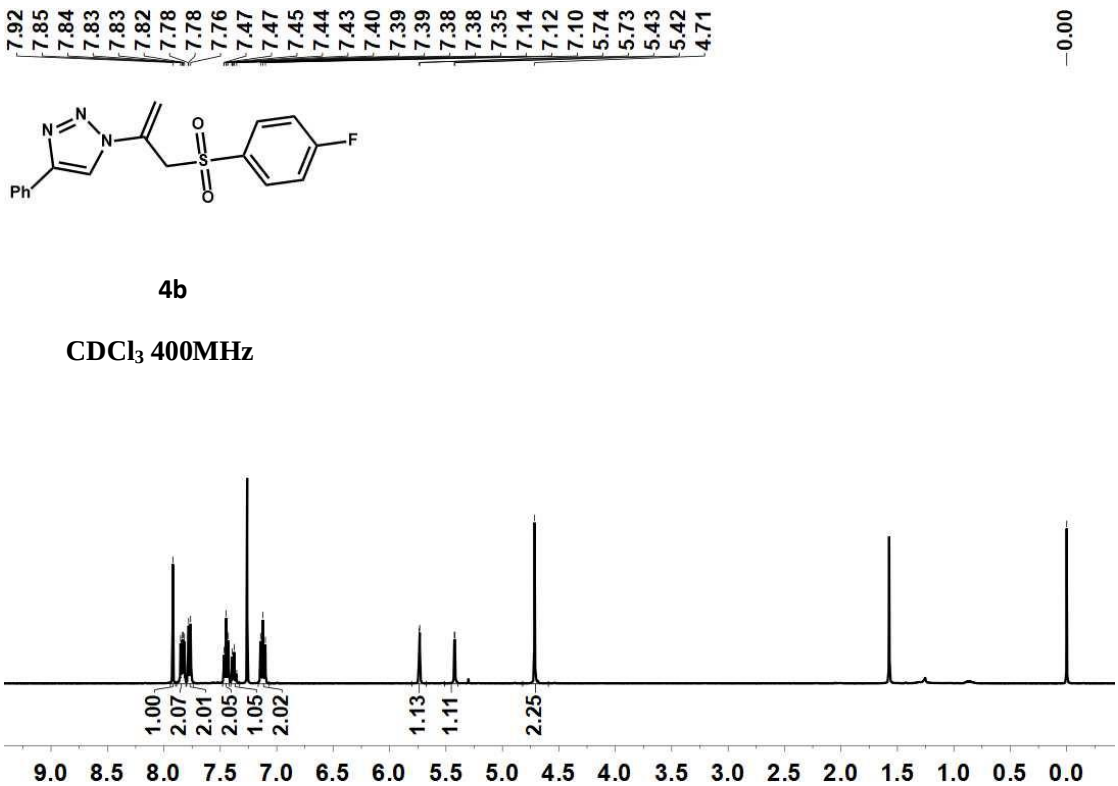
4a

$CDCl_3$ 400MHz



4a

$CDCl_3$ 100MHz



4b

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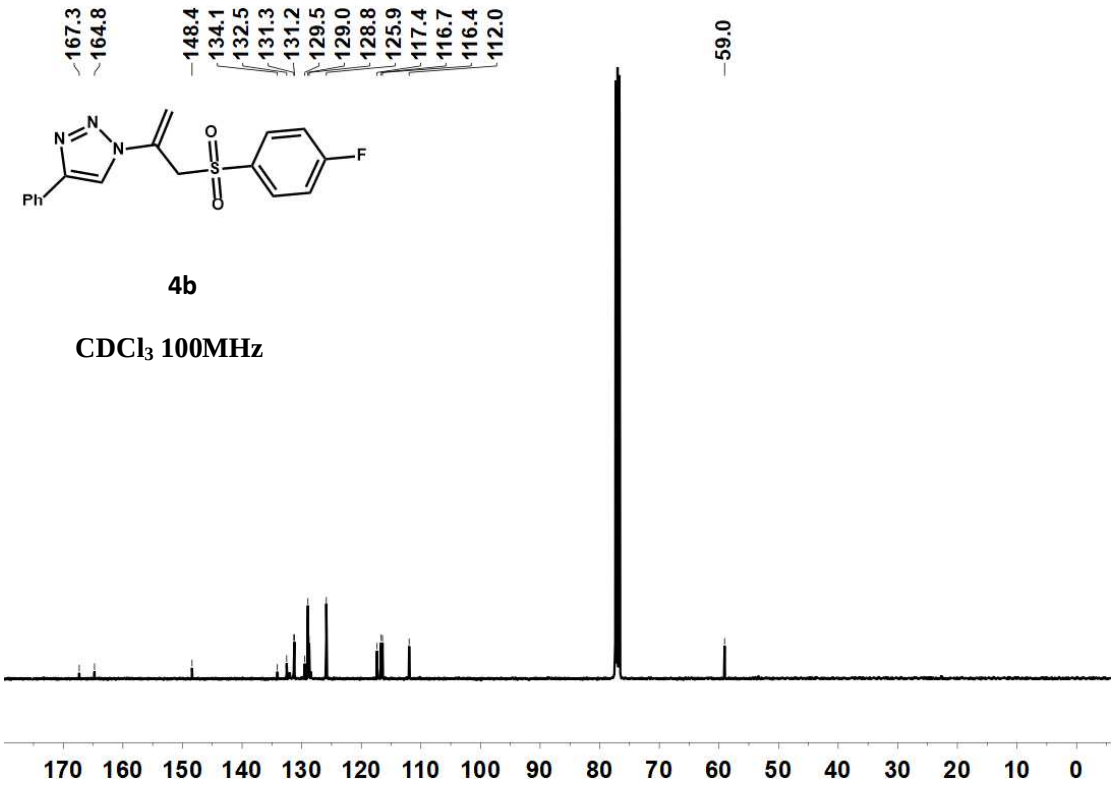
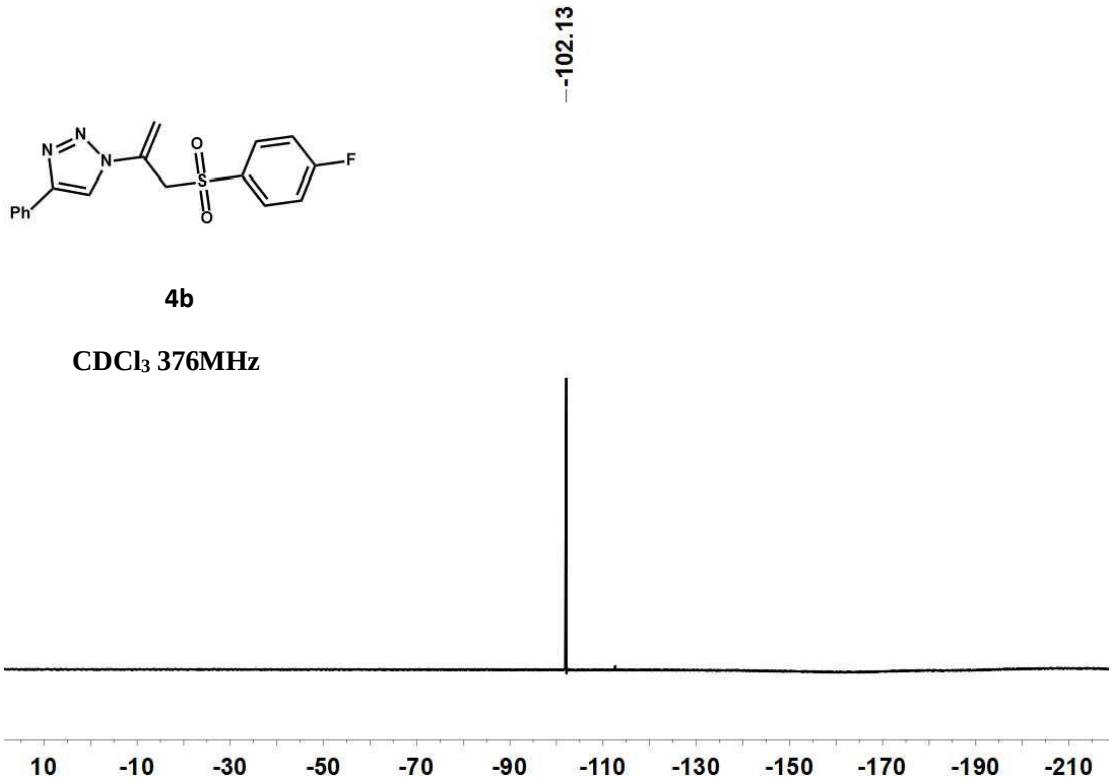


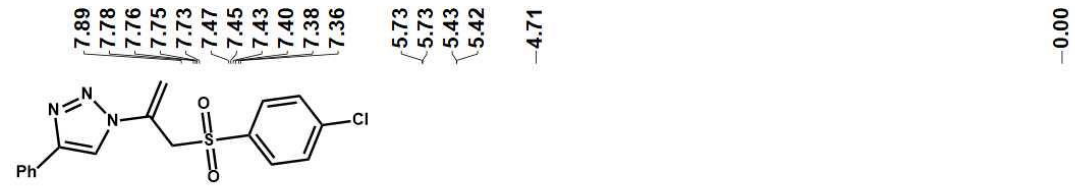
4b

$CDCl_3$ 100MHz



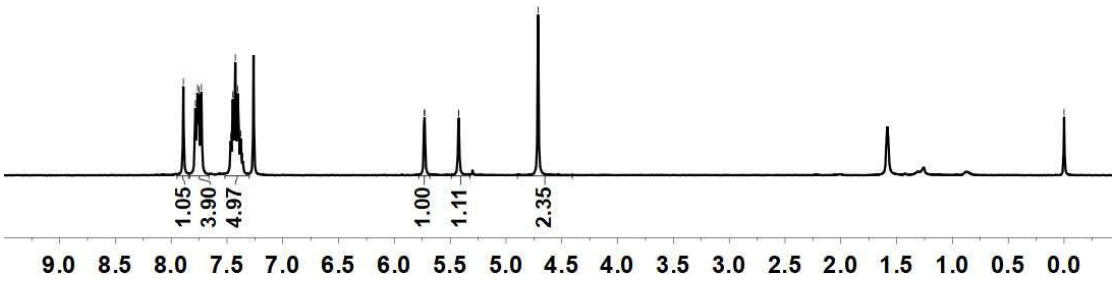
4b

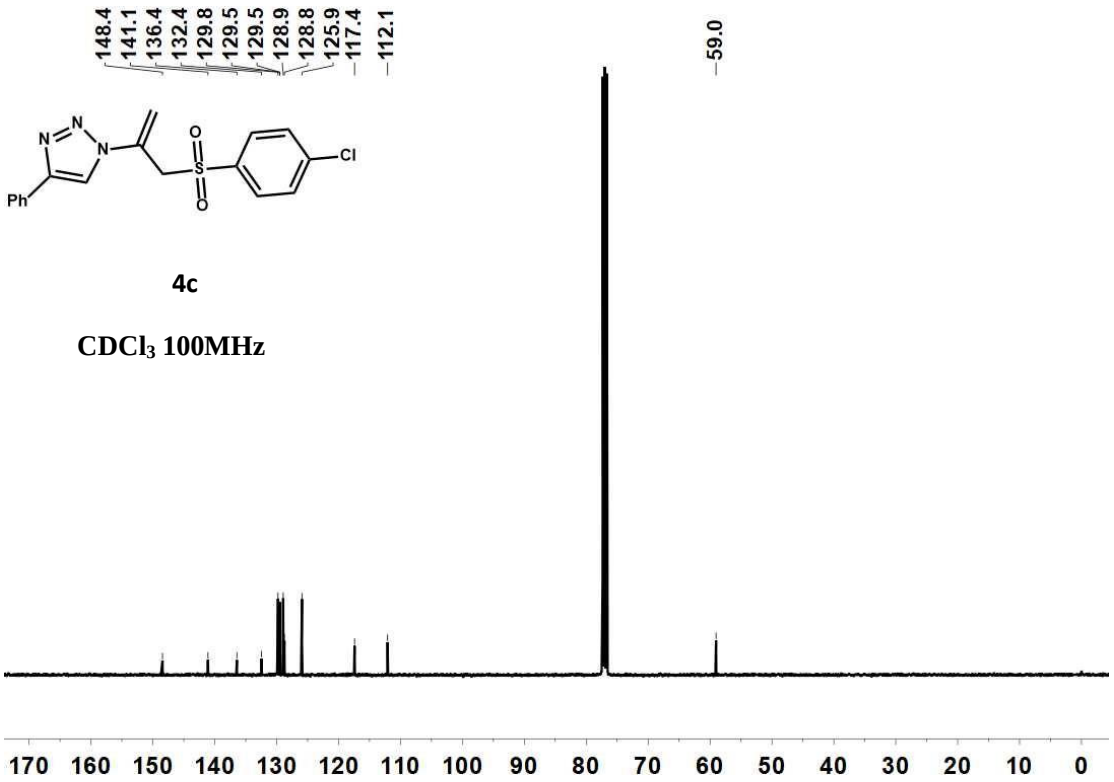
$CDCl_3$ 376MHz



4c

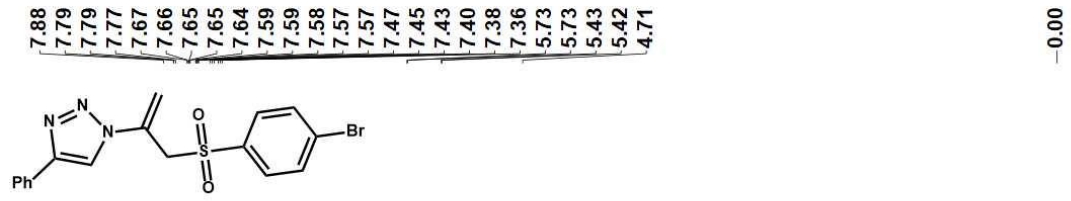
$CDCl_3$ 400MHz





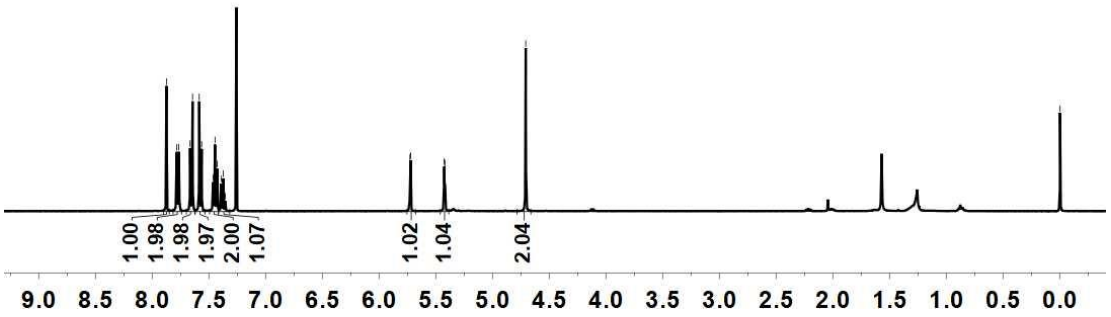
4c

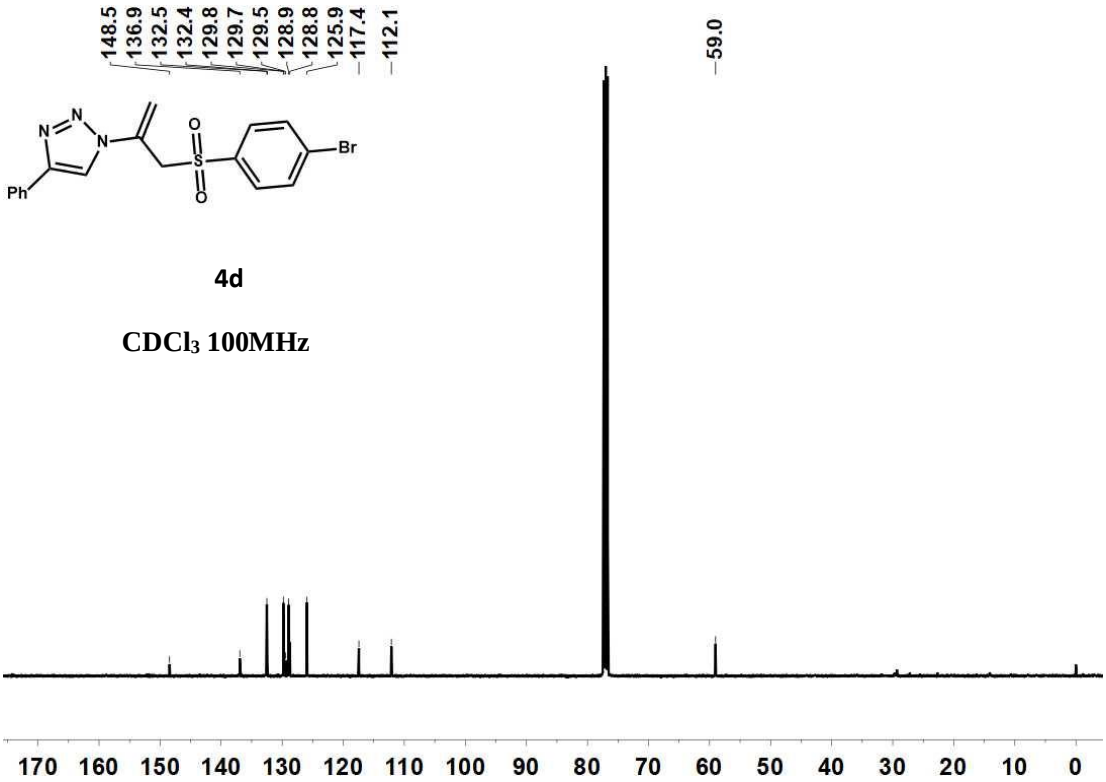
$CDCl_3$ 100MHz



4d

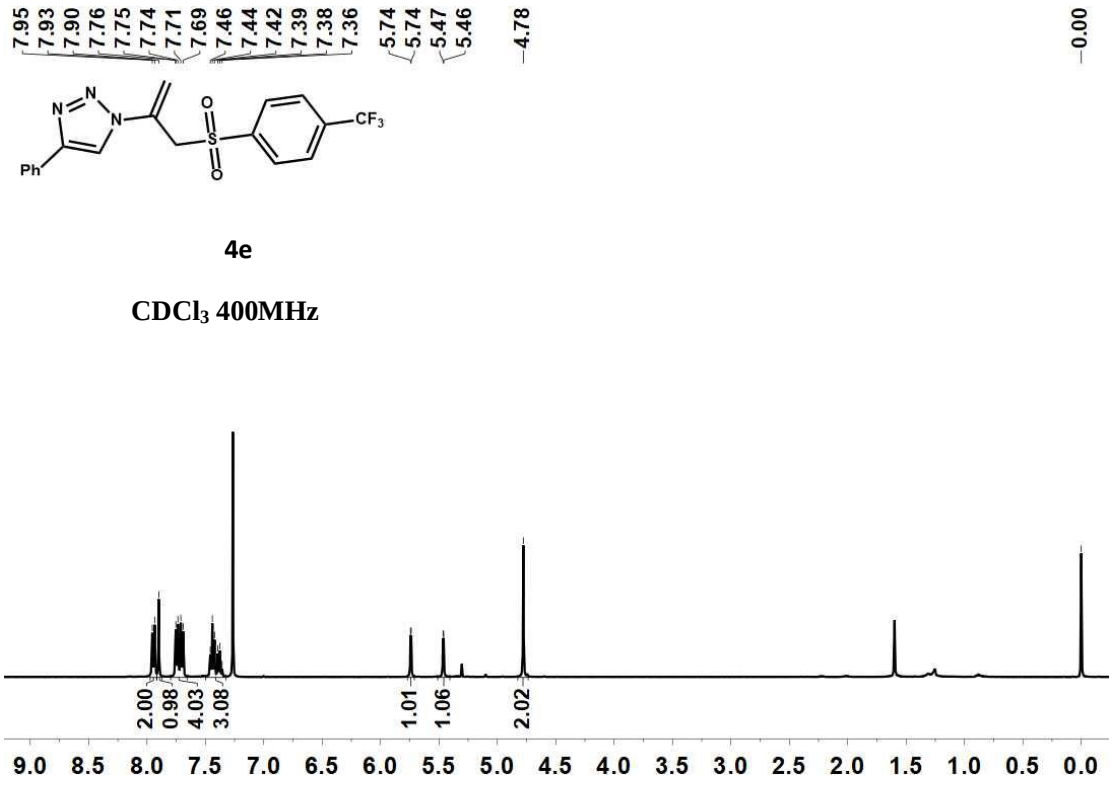
$CDCl_3$ 400MHz





4d

$CDCl_3$ 100MHz



4e

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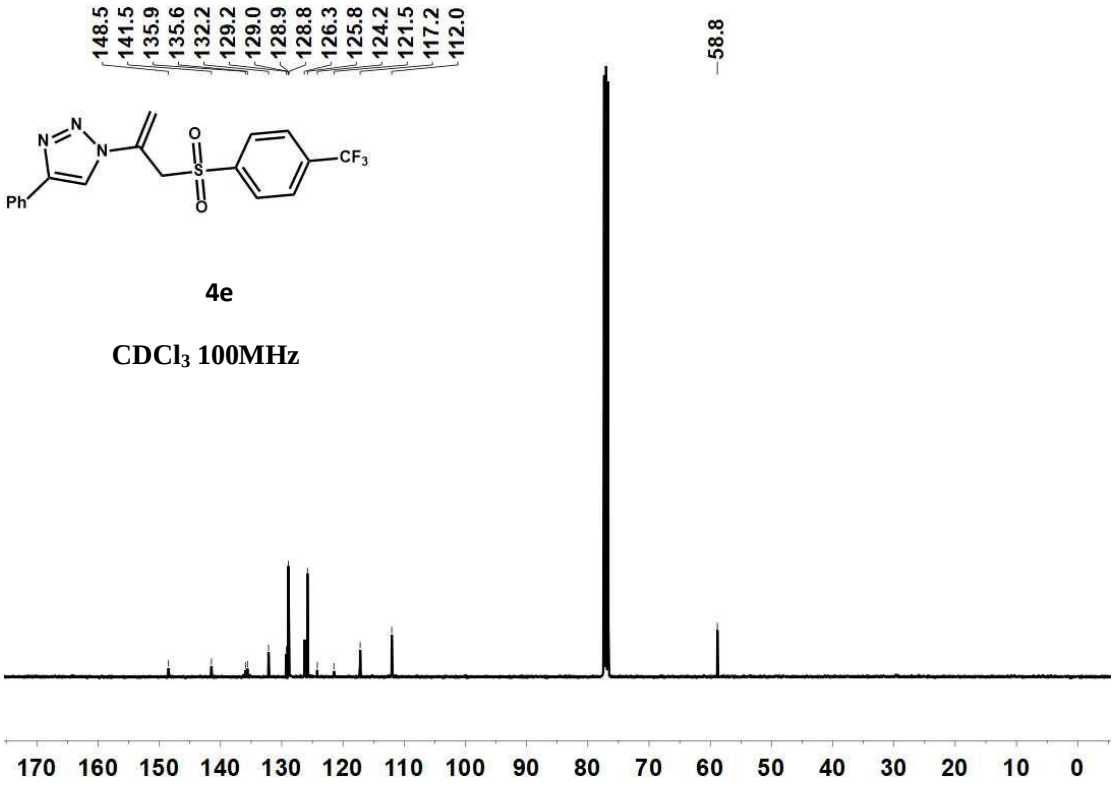

4e

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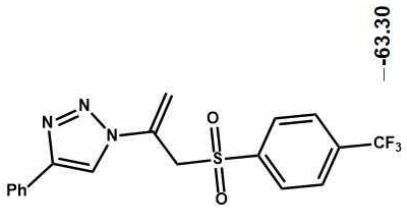
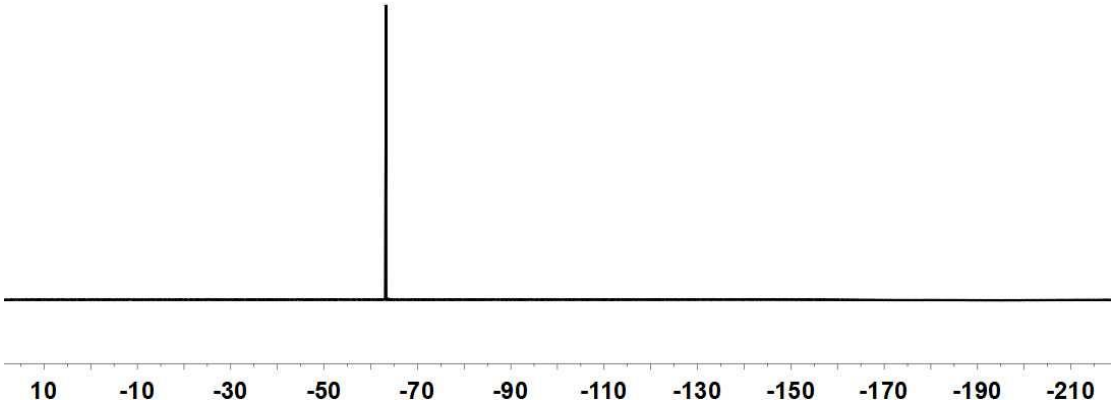
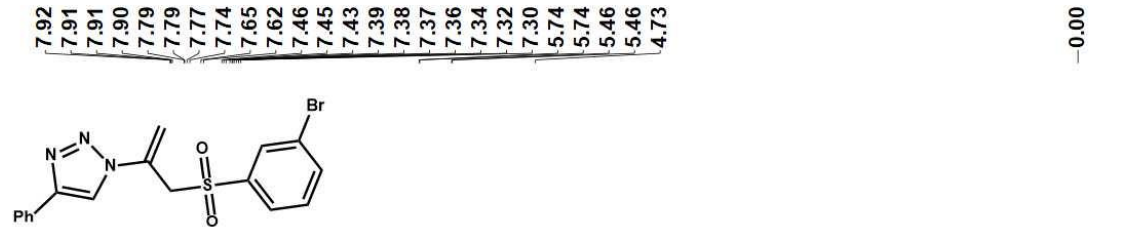


4e

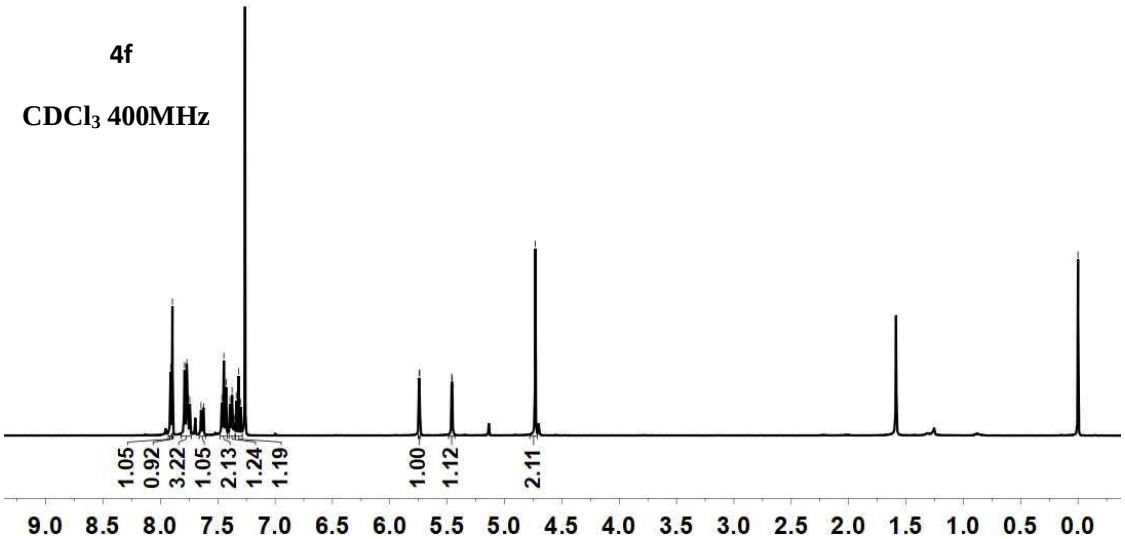
$CDCl_3$ 376MHz

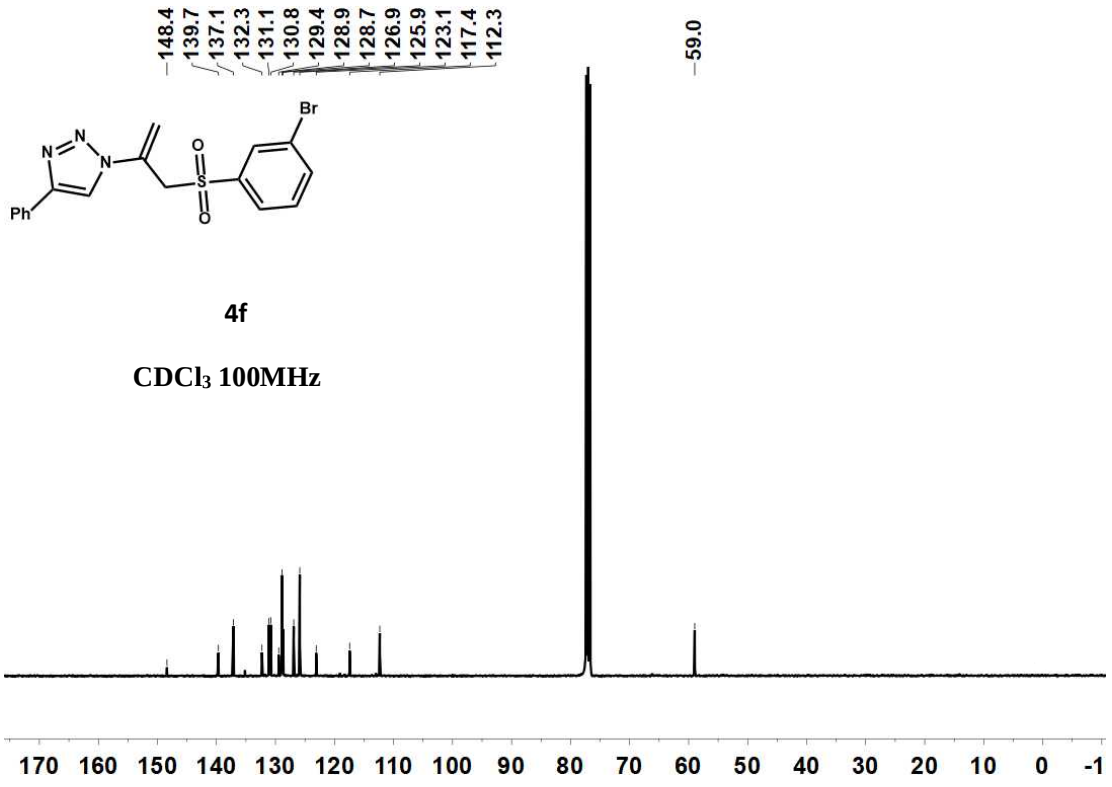




4f

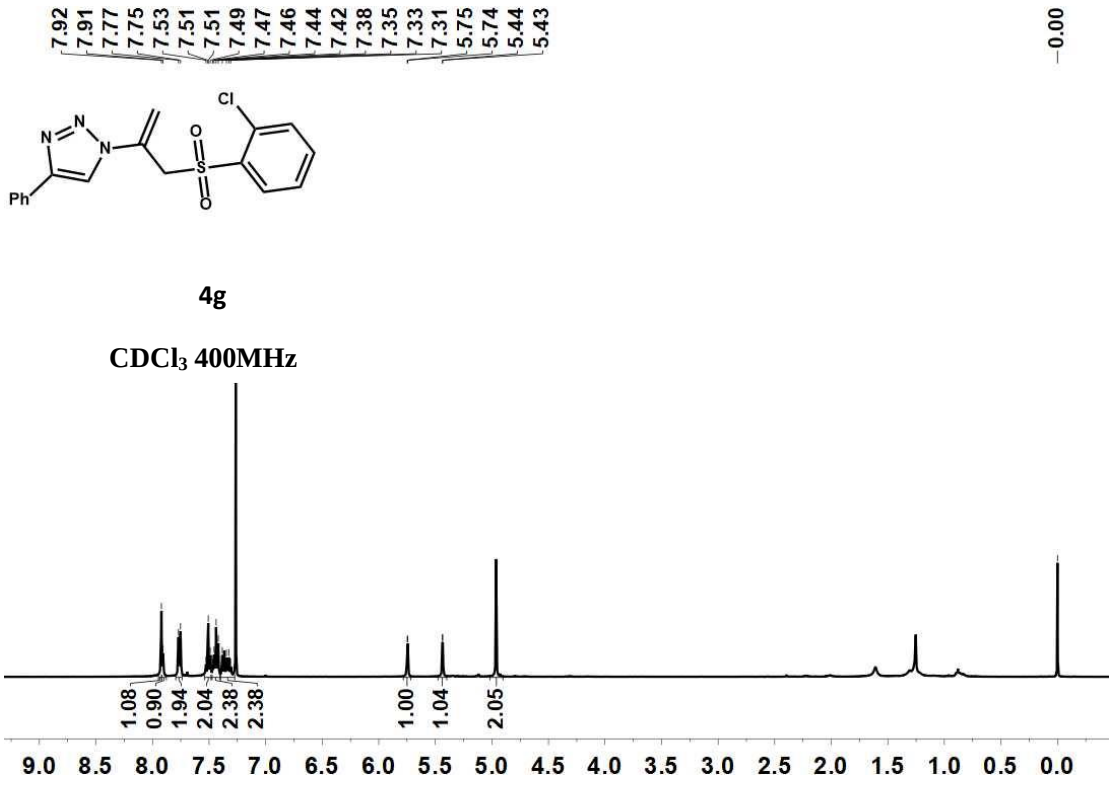
$CDCl_3$ 400MHz





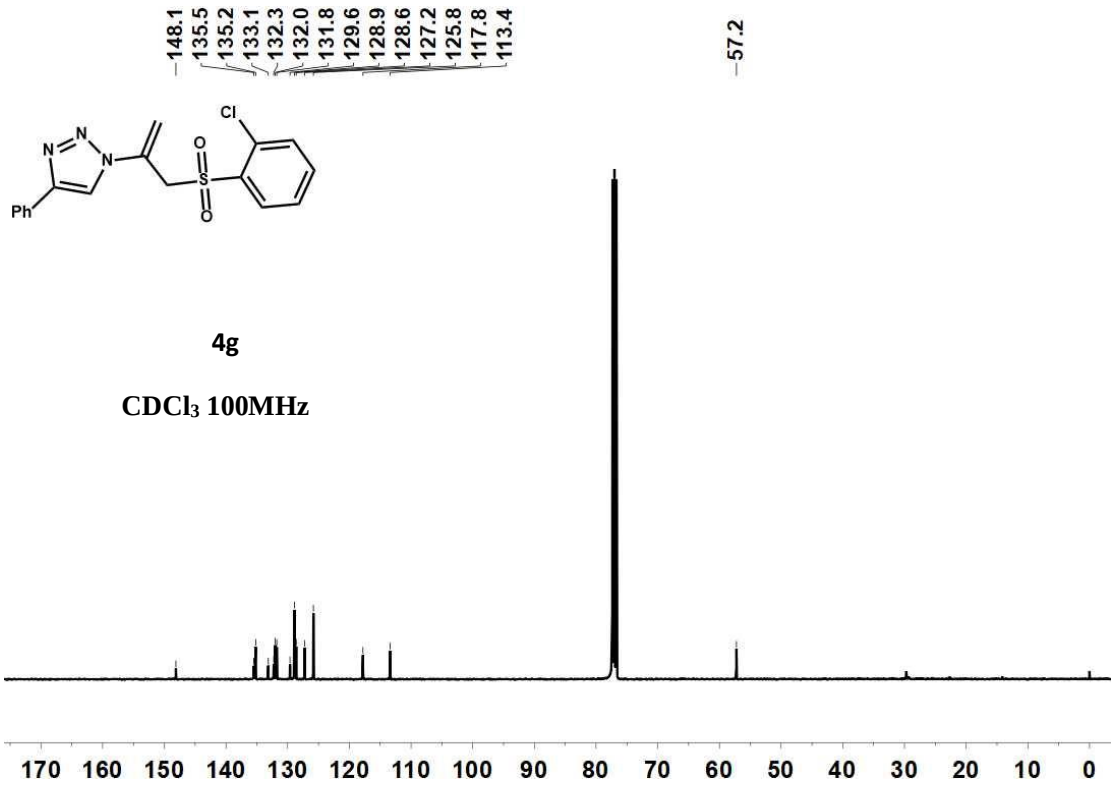
4f

$CDCl_3$ 100MHz



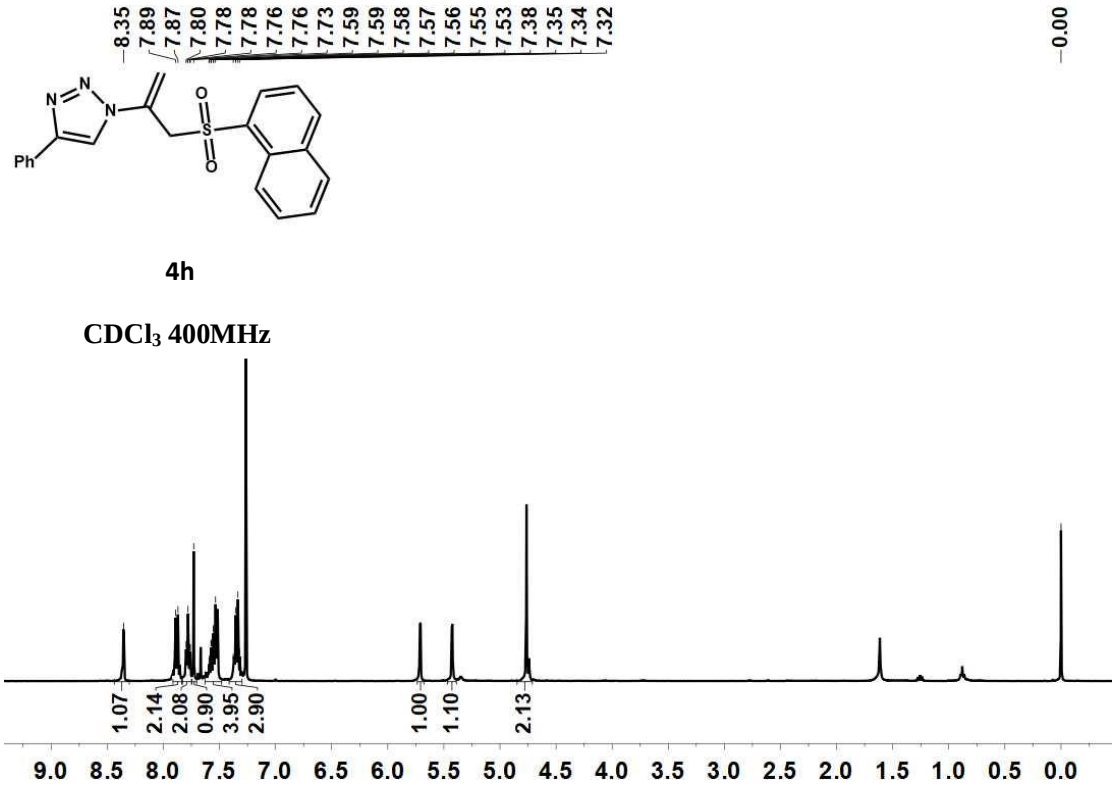
4g

$CDCl_3$ 400MHz



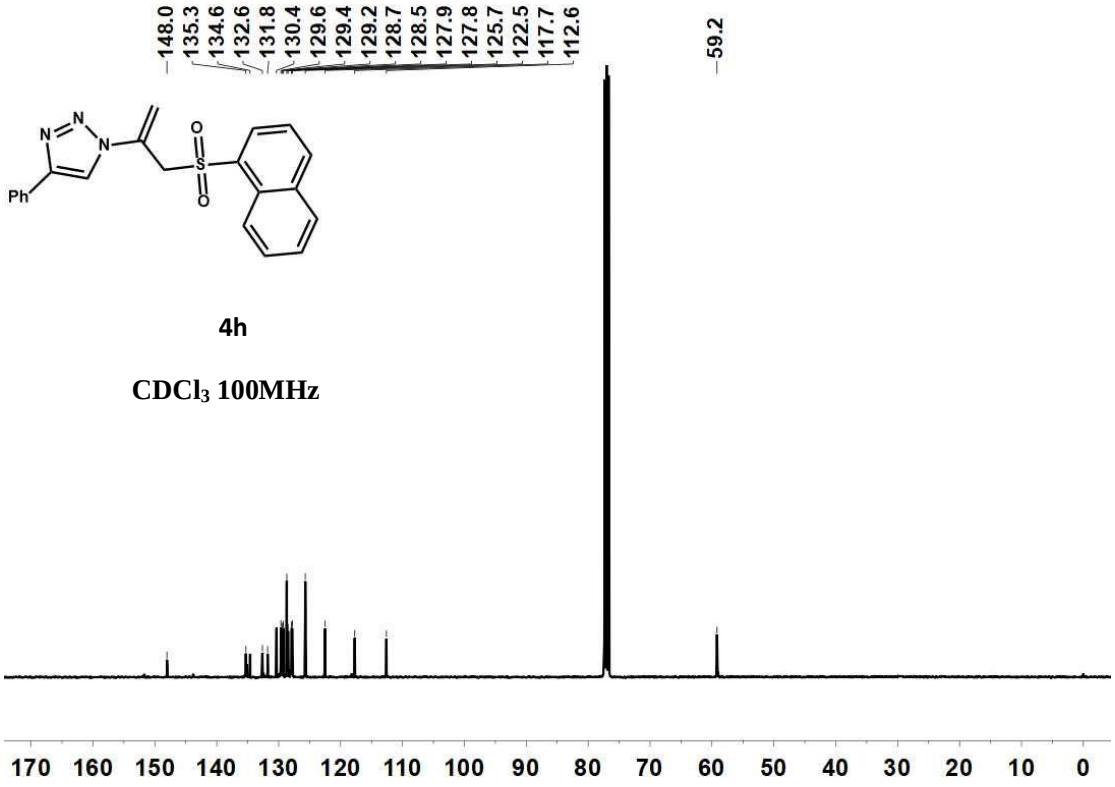
4g

$CDCl_3$ 100MHz



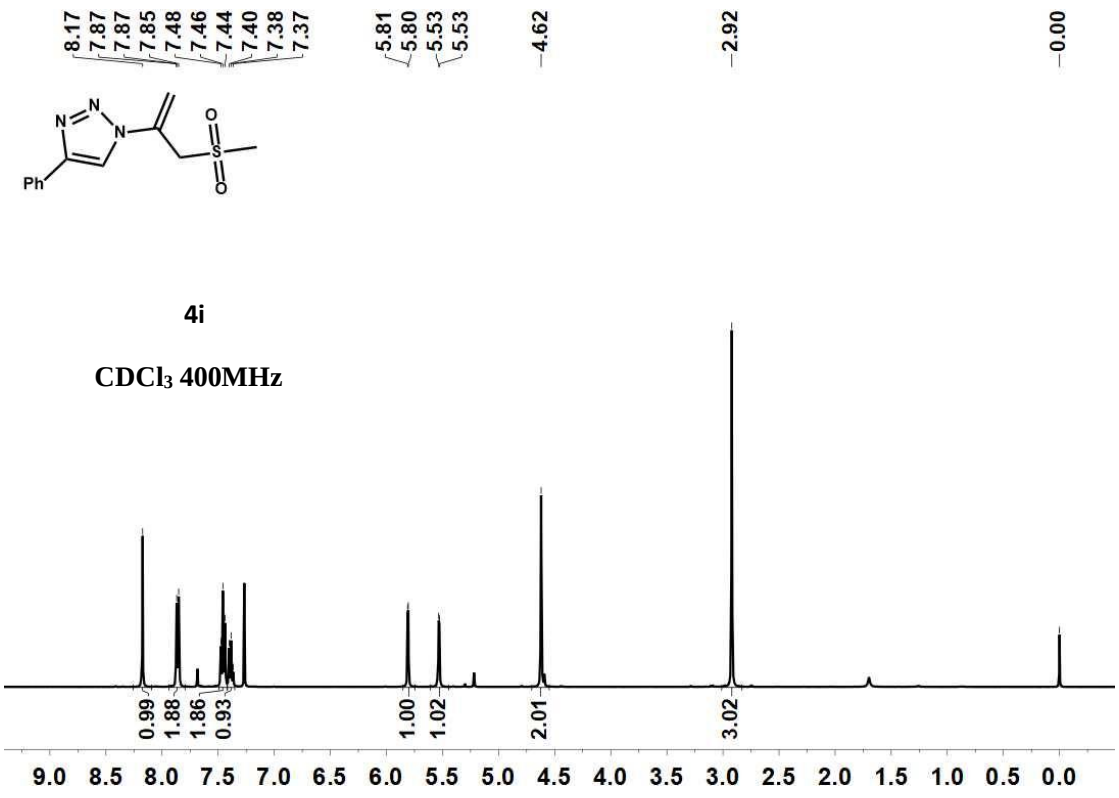
4h

$CDCl_3$ 400MHz



4h

$CDCl_3$ 100MHz

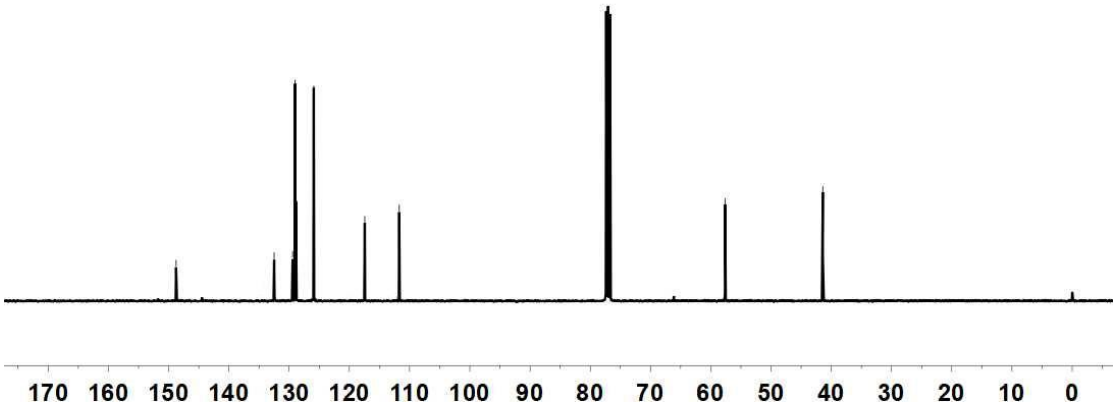


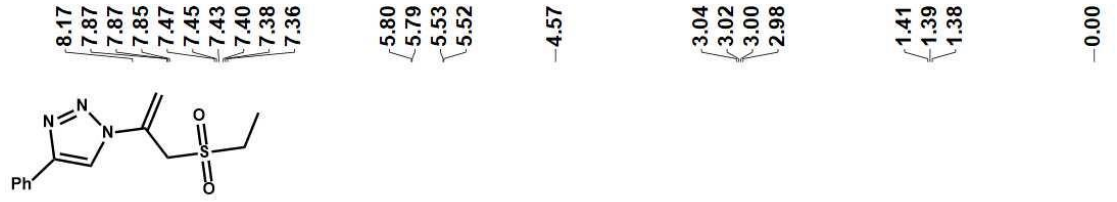
4i

$CDCl_3$ 400MHz

4i

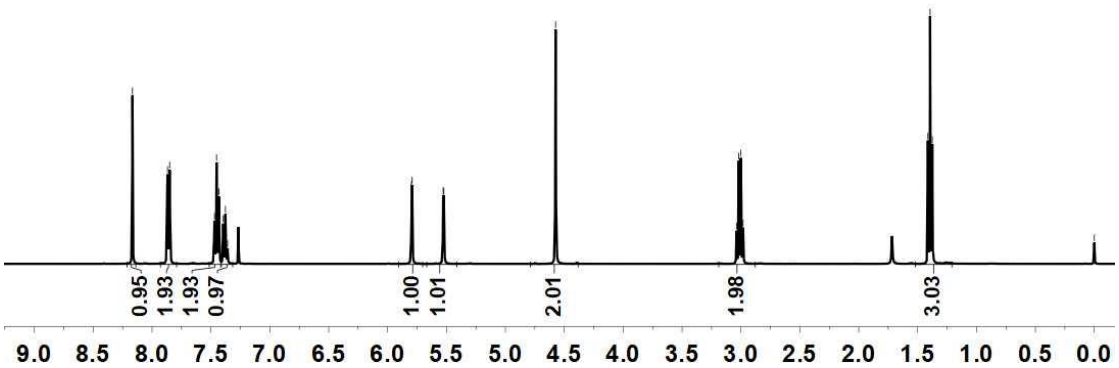
$CDCl_3$ 100MHz





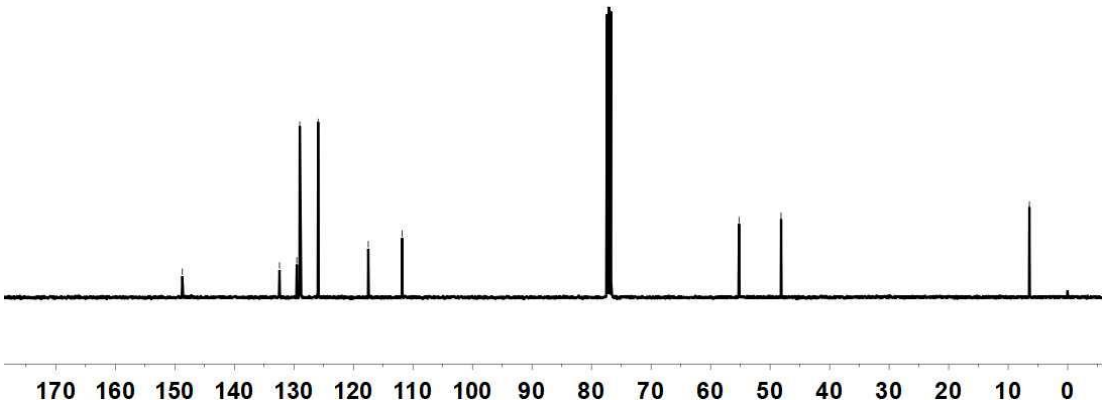
4j

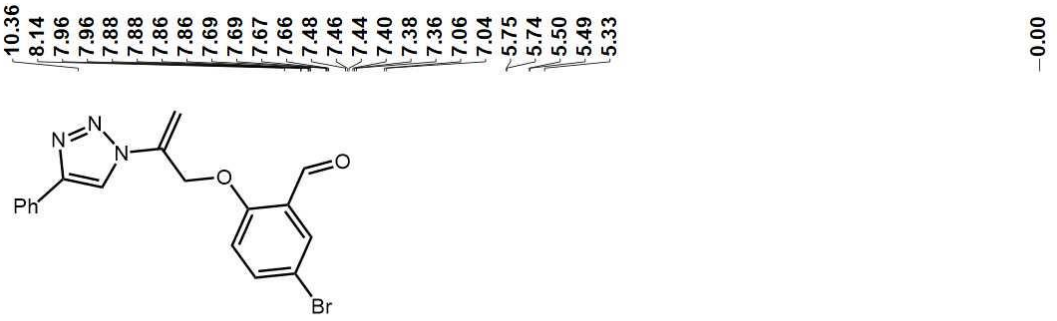
$CDCl_3$ 400MHz



4j

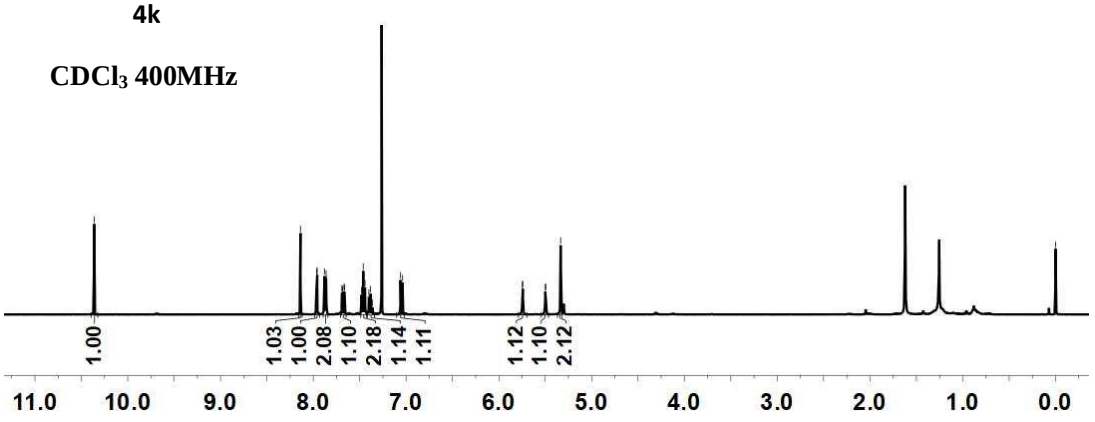
$CDCl_3$ 100MHz

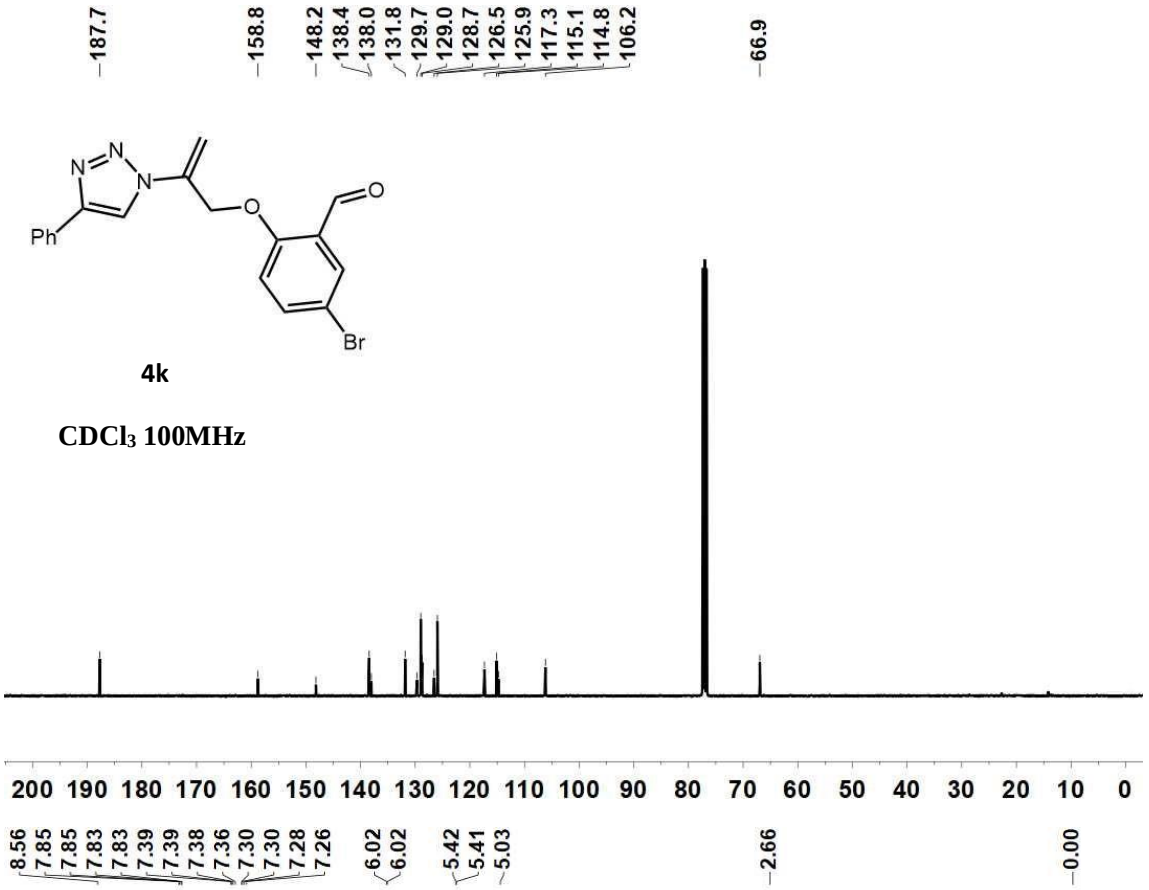




4k

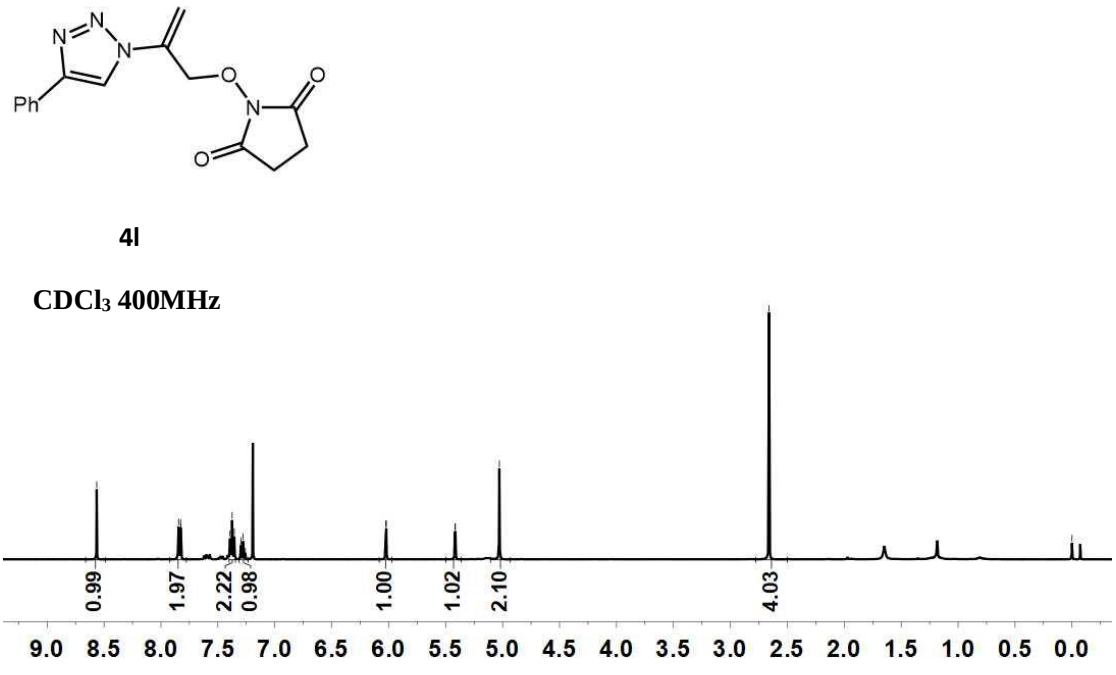
$CDCl_3$ 400MHz





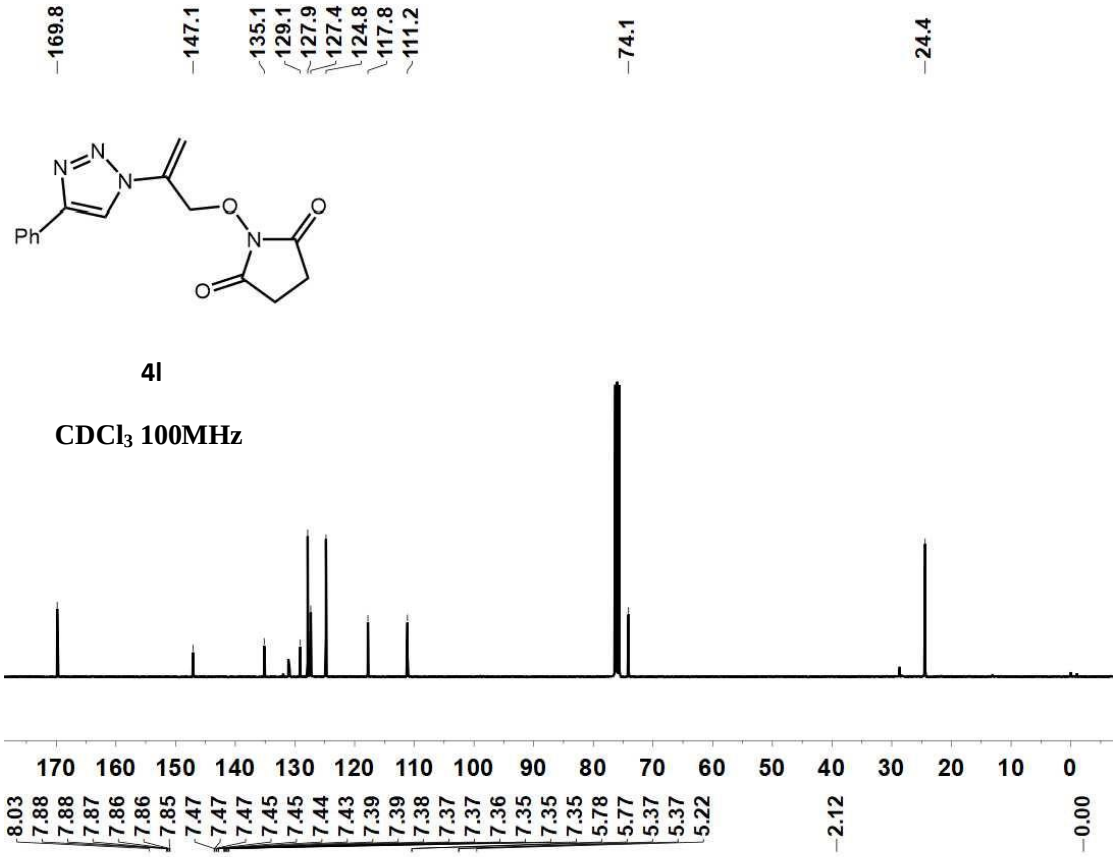
4k

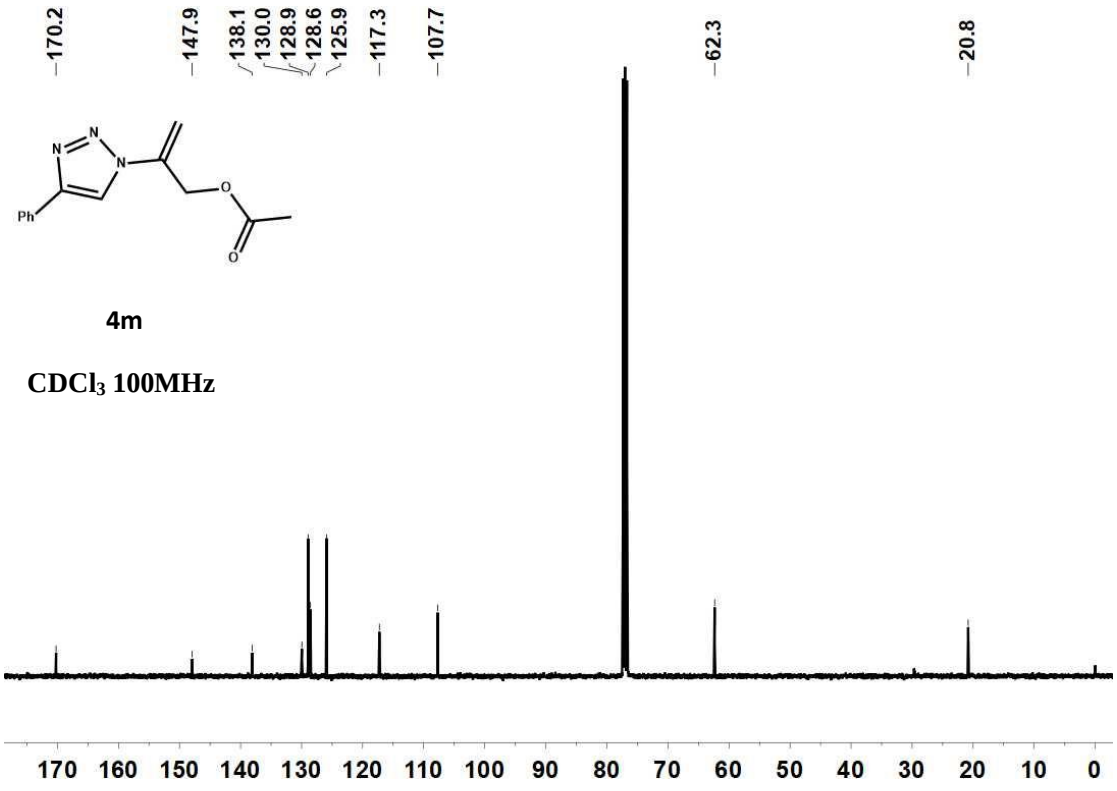
$CDCl_3$ 100MHz



4l

$CDCl_3$ 400MHz


169.8
147.1
135.1
129.1
127.9
127.4
124.8
117.8
111.2
74.1
24.4
Ph
O
N
4l
CDCl3 100MHz
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.03 7.88 7.88 7.87 7.86 7.86 7.85 7.47 7.47 7.47 7.45 7.45 7.44 7.43 7.39 7.39 7.38 7.37 7.37 7.36 7.35 7.35 7.35 5.78 5.77 5.37 5.37 5.22
2.12
0.00
Ph
4m
CDCl3 400MHz
1.11 2.03 2.09 1.08 1.00 1.09 2.13 3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0



4m

$CDCl_3$ 100MHz