Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Consecutive 2-Azidoallylation/Click Cycloaddition of Active Methylene for Synthesis of Functionalized Hepta-1,6-dienes with Bis-1,2,3-triazole Scaffold

Zhenhua Liu,[a] Huimin Chen,[a] Xingxing Gan,[a] Lianxiao Wang,[b] Ping Lin,[a] Jiayi Li,[a] Xiuxiu Huang,[a] Rongbiao Tian,[a] Xuan Liu,[a] Wen Gao*[a] and Bo Tang*[a]

[a]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

[b]No.1 Middle School of Qihe Shandong, Dezhou, 253000,, P. R. China, P. R. China.

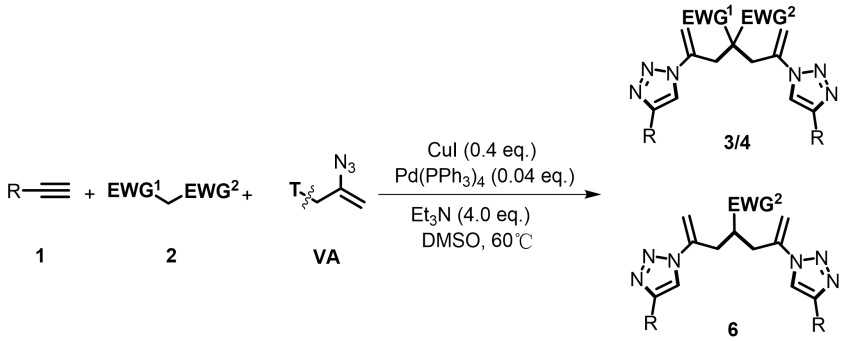
E-mail: gaowen@sdnu.edu.cn；tangb@sdnu.edu.cn

Contents

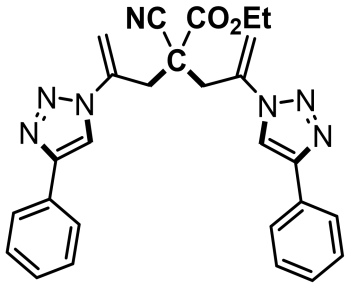
I. General information

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 ºC 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.

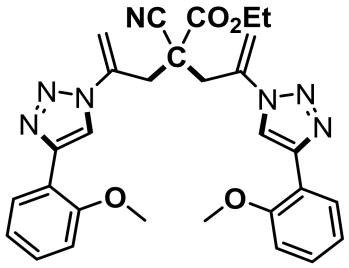
II. Synthesis and analytical data of product 3, 4 and 6



Genernal procedure: Under argon atmosphere, alkyne **1** (0.55 mmol, 2.2 eq.), 2-((2-azidoallyl)oxy)-1,3,5-tribromobenzene (**VA**) (0.55 mmol, 2.2 eq.), methylene compound **2** (0.25 mmol), triethylamine (Et_3N) (1.0 mmol, 4.0 eq.), CuI (0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (0.01 mmol, 0.04 eq.) were added in an oven-dried 10 mL Schlenk tube with 1 mL DMSO. The reaction mixture was then stirred for 2 h when TLC conformed that substrate **2** had been consumed. The reaction was cooled to room temperature 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/ethyl acetate) and the target product was afforded.

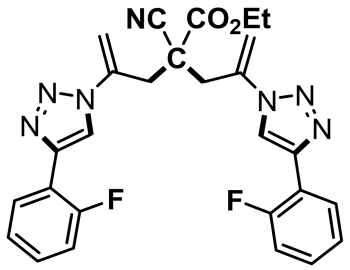


(3a) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (210.9 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.88–7.81 (m, 4H), 7.47–7.39 (m, 4H), 7.40–7.31 (m, 2H), 5.61 (d, *J* = 2.2 Hz, 2H), 5.34 (d, *J* = 2.1 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 14.9 Hz, 2H), 3.48 (d, *J* = 14.9 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.3, 137.7, 129.8, 128.9, 128.6, 125.9, 118.0, 116.6, 110.0, 63.8, 48.9, 39.1, 13.7; **HRMS** (ESI) m/z calculated for $C_{27}H_{25}N_2O_2Na$ $[M+Na]^+$: 502.1968, found: 502.1976.

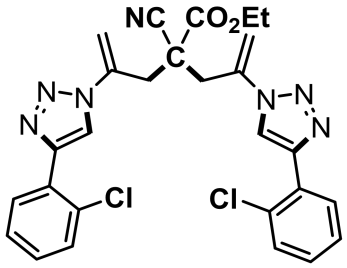


(3b) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-methoxyphenylacetylene (64.7 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (474.85 mg,

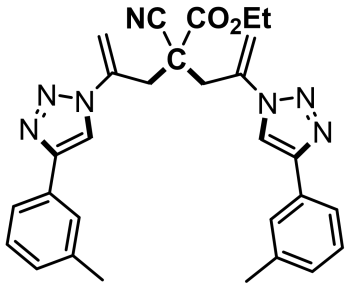
88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.41–8.30 (m, 2H), 8.29 (s, 2H), 7.40–7.29 (m, 2H), 7.11–7.03 (m, 2H), 6.99 (d, *J* = 8.3 Hz, 2H), 5.63 (d, *J* = 2.1 Hz, 2H), 5.33 (d, *J* = 2.0 Hz, 2H), 3.96 (s, 6H), 3.95–3.88 (m, 2H), 3.71 (d, *J* = 14.9 Hz, 2H), 3.49 (d, *J* = 14.9 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$), δ 166.6, 155.8, 143.7, 137.7, 129.3, 127.9, 121.1, 121.0, 118.7, 116.8, 110.8, 109.5, 63.7, 55.5, 49.0, 39.1, 13.6; **HRMS** (ESI) m/z calculated for $C_{29}H_{29}N_7O_4Na$ $[M+Na]^+$: 562.2179, found: 562.2149.



(3c) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-fluorophenylacetylene (60.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (226.83 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.34–8.26 (m, 2H), 8.19 (d, *J* = 3.4 Hz, 2H), 7.37–7.29 (m, 2H), 7.28–7.21 (m, 2H), 7.19–7.08 (m, 2H), 5.65 (d, *J* = 2.3 Hz, 2H), 5.37 (d, *J* = 2.2 Hz, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 3.70 (d, *J* = 14.9 Hz, 2H), 3.52 (d, *J* = 14.9 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 160.6 (d, *J* = 249.1Hz), 141.7, 137.6, 129.8 (d, *J* = 8.6 Hz), 128.0 (d, *J* = 3.4 Hz), 124.7 (d, *J* = 3.4 Hz), 121.0 (d, *J* = 13.2 Hz), 118.0 (d, *J* = 13.2 Hz), 116.5, 115.9 (d, *J* = 21.3 Hz), 110.2, 63.7, 48.7, 39.1, 13.7; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -114.12; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}F_2N_7O_2Na$ $[M+Na]^+$: 538.1779, found: 538.1787.

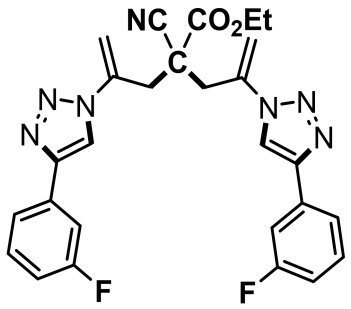


(3d) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-chlorophenylacetylene (68.3 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (244.05 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.44 (s, 2H), 8.26–8.20 (m, 2H), 7.47–7.42 (m, 2H), 7.40–7.36 (m, 2H), 7.32–7.26 (m, 2H), 5.66 (d, *J* = 2.3 Hz, 2H), 5.38 (d, *J* = 2.2 Hz, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 3.71 (d, *J* = 14.9 Hz, 2H), 3.51 (d, *J* = 14.9 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 144.5, 137.6, 131.4, 130.3, 129.9, 129.4, 128.5, 127.2, 121.5, 116.6, 110.4, 63.8, 48.8, 39.2, 13.7; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}Cl_2N_7O_2Na$ $[M+Na]^+$: 570.1188, found: 570.1149.

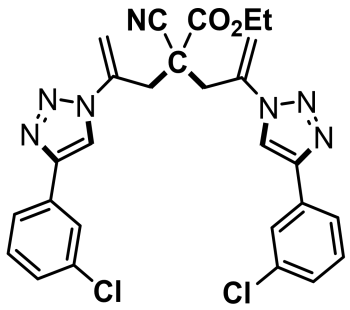


(3e) 0.25 mmol scale: Prepared following the genernal procedure showed above using 3-ethynyltoluene (63.4 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (220.81 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.69 (s, 2H), 7.62 (d, *J* = 7.7 Hz,

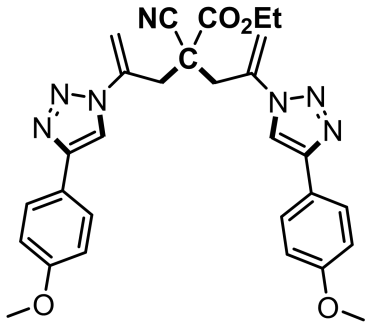
2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 5.60 (d, *J* = 2.2 Hz, 2H), 5.32 (d, *J* = 1.9 Hz, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.67 (d, *J* = 14.9 Hz, 2H), 3.47 (d, *J* = 14.9 Hz, 2H), 2.39 (s, 6H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.3, 138.6, 137.7, 129.7, 129.4, 128.8, 126.6, 123.0, 118.0, 116.6, 110.0, 63.8, 48.9, 39.0, 21.4, 13.7; **HRMS** (ESI) m/z calculated for $C_{29}H_{29}N_7O_2Na$ $[M+Na]^+$: 530.2281, found: 530.2251.



(3f) 0.25 mmol scale: Prepared following the generanal procedure showed above using 3-fluorophenylacetylene (60.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (213.95 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.65–7.52 (m, 4H), 7.42–7.35 (m, 2H), 7.07–7.01 (m, 2H), 5.62 (d, *J* = 2.3 Hz, 2H), 5.35 (d, *J* = 2.2 Hz, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 3.67 (d, *J* = 14.8 Hz, 2H), 3.49 (d, *J* = 14.9 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 164.4 (d, *J* = 245.4 Hz), 147.1 (d, *J* = 2.9 Hz), 137.6, 132.0 (d, *J* = 8.5 Hz), 130.6 (d, *J* = 8.5 Hz), 121.5 (*J* = 2.9 Hz), 118.5, 116.4, 115.5 (d, *J* = 22.0 Hz), 113.0 (d, *J* = 22.0 Hz), 110.4, 63.8, 48.8, 39.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.38; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}F_2N_7O_2Na$ $[M+Na]^+$: 538.1779, found: 538.1771.

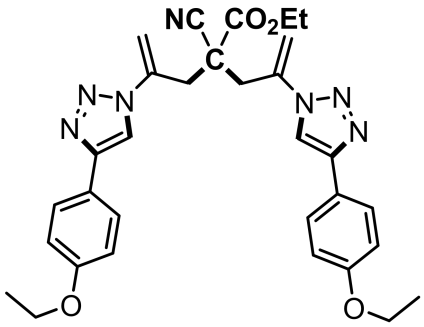


(3g) 0.25 mmol scale: Prepared following the genernal procedure showed above using 3-chlorophenylacetylene (68.3 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (233.08 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 2H), 7.85 (s, 2H), 7.77–7.70 (m, 2H), 7.41–7.30 (m, 4H), 5.62 (d, *J* = 2.3 Hz, 2H), 5.36 (d, *J* = 2.0 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.67 (d, *J* = 14.8 Hz, 2H), 3.49 (d, *J* = 14.8 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 147.0, 137.6, 134.9, 131.6, 130.2, 128.6, 126.0, 124.0, 118.4, 116.4, 110.4, 63.8, 48.8, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}Cl_2N_7O_2Na$ $[M+Na]^+$: 570.1188, found: 570.1149.

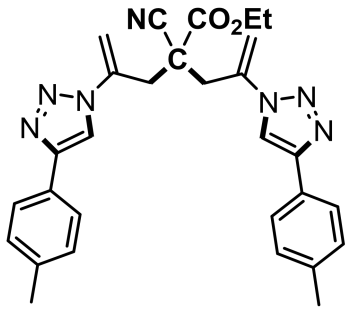


(3h) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethynylanisole (64.8 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (215.83 mg,

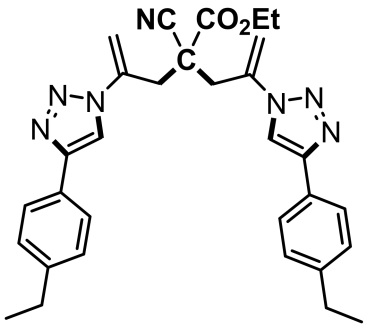
80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.80–7.73 (m, 4H), 6.98–6.93 (m, 4H), 5.59 (d, *J* = 2.2 Hz, 2H), 5.32 (d, *J* = 2.1 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.84 (s, 6H), 3.67 (d, *J* = 14.9 Hz, 2H), 3.47 (d, *J* = 14.9 Hz, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) 166.7, 159.9, 148.1, 137.7, 127.3, 122.5, 117.1, 116.6, 114.3, 109.7, 63.7, 55.4, 48.9, 39.0, 13.7; **HRMS** (ESI) m/z calculated for $C_{29}H_{29}N_7O_4Na$ $[M+Na]^+$: 526.2179, found: 526.2170.



(3i) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethoxyphenylacetylene (73.8 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (249.60 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (s, 2H), 7.80–7.70 (m, 4H), 7.01–6.84 (m, 4H), 5.59 (d, *J* = 2.2 Hz, 2H), 5.31 (d, *J* = 2.1 Hz, 2H), 4.06 (q, *J* = 7.0 Hz, 4H), 3.96 (q, *J* = 7.1 Hz, 2H), 3.66 (d, *J* = 14.9 Hz, 2H), 3.47 (d, *J* = 14.9 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 6H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 159.3, 148.2, 137.7, 127.2, 122.3, 117.0, 116.6, 114.8, 109.7, 63.7, 63.5, 48.9, 39.0, 14.8, 13.7; **HRMS** (ESI) m/z calculated for $C_{31}H_{33}N_7O_4Na$ $[M+Na]^+$: 590.2492, found: 590.2510.

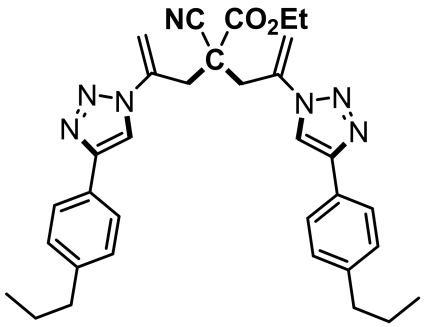


(3j) 0.25 mmol scale: Prepared following the generanal procedure showed above using 4-ethynyltoluene (63.4 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (223.33 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.73 (d, *J* = 8.1 Hz, 4H), 7.24 (d, *J* = 8.0 Hz, 4H), 5.60 (d, *J* = 2.2 Hz, 2H), 5.33 (d, *J* = 2.1 Hz, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 14.9 Hz, 2H), 3.47 (d, *J* = 14.9 Hz, 2H), 2.38 (s, 6H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.3, 138.5, 137.7, 129.6, 127.0, 125.8, 117.5, 116.6, 109.8, 63.8, 48.9, 39.0, 21.3, 13.7; **HRMS** (ESI) m/z calculated for $C_{29}H_{29}N_7O_2Na$ $[M+Na]^+$: 530.2281, found: 530.2280.

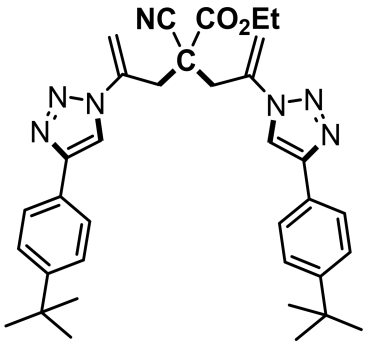


(3k) 0.25 mmol scale: Prepared following the generanal procedure showed above using 4-ethynyltoluene (63.4 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg,

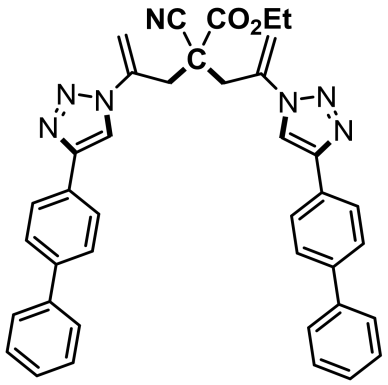
0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (222.30 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.81–7.70 (m, 4H), 7.26 (d, *J* = 8.3 Hz, 4H), 5.60 (d, *J* = 2.2 Hz, 2H), 5.33 (d, *J* = 2.1 Hz, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 14.9 Hz, 2H), 3.47 (d, *J* = 14.9 Hz, 2H), 2.68 (q, *J* = 7.6 Hz, 4H), 1.26 (t, *J* = 7.6 Hz, 6H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.3, 144.9, 137.7, 128.4, 127.3, 125.9, 117.6, 116.6, 109.8, 63.8, 48.9, 39.0, 28.7, 15.5, 13.7; **HRMS** (ESI) m/z calculated for $C_{31}H_{33}N_7O_2Na$ $[M+Na]^+$: 558.2594, found: 558.2592.



(3l) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-eth-1-ynyl-4-propylbenzene (79.2 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (247.86 mg, 88%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.77–7.73 (m, 4H), 7.25-7.21 (m, 4H), 5.59 (d, J = 2.2 Hz, 2H), 5.32 (s, 2H), 3.95 (q, J = 7.2 Hz, 2H), 3.65 (s, 2H), 3.46 (d, J = 14.9 Hz, 2H), 2.65–2.56 (m, 4H), 1.71–1.60 (m, 4H), 1.15 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.3 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.3, 143.3, 137.7, 129.0, 127.3, 125.8, 117.6, 116.6, 109.8, 63.7, 48.9, 39.0, 37.8, 24.5, 13.8, 13.7; **HRMS** (ESI) m/z calculated for $C_{33}H_{37}N_7O_2Na$ $[M+Na]^+$: 586.2907, found: 586.2910.

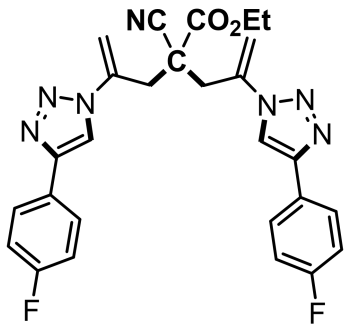


(3m) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-tert-butylphenylacetylene (90.2 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (239.67 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.80–7.75 (m, 4H), 7.49–7.43 (m, 4H), 5.61 (d, *J* = 2.2 Hz, 2H), 5.33 (d, *J* = 2.1 Hz, 2H), 3.95 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 14.9 Hz, 2H), 3.47 (d, *J* = 14.9 Hz, 2H), 1.34 (s, 18H), 1.16 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 151.8, 148.3, 137.7, 127.0, 125.8, 125.7, 117.6, 116.6, 109.8, 63.7, 48.9, 39.0, 34.7, 31.3, 13.7; **HRMS** (ESI) m/z calculated for $C_{35}H_{41}N_7O_2Na$ $[M+Na]^+$: 614.3220, found: 614.3297.



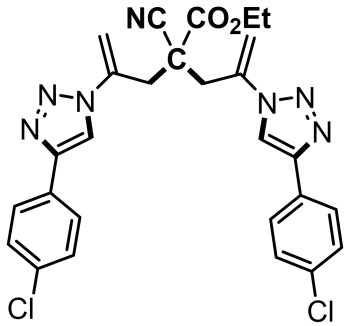
(3n) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethynyl-1,1'-biphenyl (89.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol,

2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:3) as yellow oily liquid (262.17 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.93 (d, *J* = 8.3 Hz, 4H), 7.67 (d, *J* = 8.3 Hz, 4H), 7.65–7.58 (m, 4H), 7.45 (t, *J* = 7.5 Hz, 4H), 7.36 (t, *J* = 7.3 Hz, 2H), 5.64 (d, *J* = 2.2 Hz, 2H), 5.37 (d, *J* = 2.1 Hz, 2H), 4.00 (q, *J* = 7.1 Hz, 2H), 3.71 (d, *J* = 14.9 Hz, 2H), 3.51 (d, *J* = 14.9 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 148.0, 141.4, 140.5, 137.7, 128.9, 128.8, 127.6, 127.6, 127.0, 126.3, 117.9, 116.6, 110.0, 63.8, 48.9, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{39}H_{33}N_7O_2Na$ $[M+Na]^+$: 654.2594, found: 654.2556.

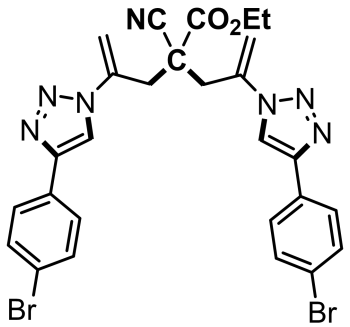


(3o) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-fluorophenylacetylene (57.3 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (219.09 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (s, 2H), 7.87–7.71 (m, 4H), 7.12 (t, *J* = 8.7 Hz, 4H), 5.61 (d, *J* = 2.2 Hz, 2H), 5.34 (d, *J* = 2.0 Hz, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.67 (d, *J* = 14.9 Hz, 2H), 3.49 (d, *J* = 14.8 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.8, 164.2 (d, *J* = 248.0 Hz), 147.5, 137.7, 127.7 (d, *J* = 8.3 Hz), 126.0 (d, *J* = 3.3 Hz), 117.8, 116.5, 116.1 (d, *J* = 21.8 Hz), 110.1, 63.8, 48.8,

39.0, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -112.74; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}F_2N_7O_2Na$ $[M+Na]^+$: 538.1179, found: 538.1787.

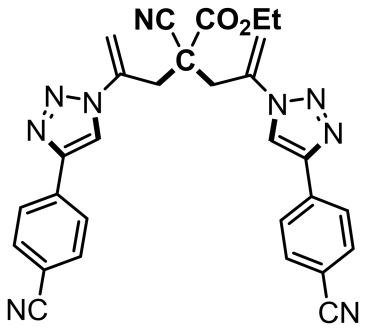


(3p) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-chlorophenylacetylene (68,3 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (238.00 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 2H), 7.81–7.75 (m, 4H), 7.43–7.36 (m, 4H), 5.61 (d, *J* = 2.3 Hz, 2H), 5.35 (d, *J* = 2.2 Hz, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 3.66 (d, *J* = 14.8 Hz, 2H), 3.49 (d, *J* = 14.9 Hz, 2H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 147.2, 137.6, 134.4, 129.1, 128.3, 127.2, 118.1, 116.4, 110.2, 63.8, 48.8, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}Cl_2N_7O_2Na$ $[M+Na]^+$: 570.1188, found: 570.1149.

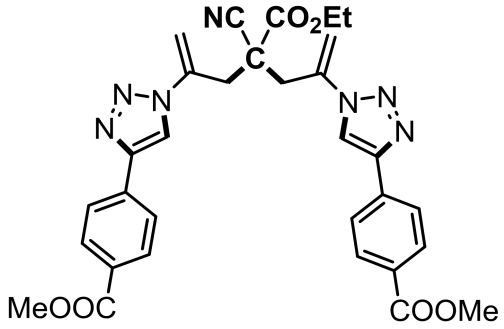


(3q) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-bromophenylacetylene (63.5 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N)

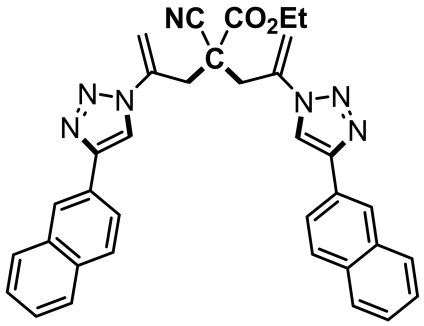
(139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (263.66 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 2H), 7.75–7.70 (m, 4H), 7.59–7.53 (m, 4H), 5.61 (d, *J* = 2.2 Hz, 2H), 5.36 (d, *J* = 2.8 Hz, 2H), 4.00 (q, *J* = 6.2 Hz, 2H), 3.69 (d, *J* = 12.9 Hz, 2H), 3.48 (d, *J* = 14.8 Hz, 2H), 1.18 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 147.3, 137.6 132.1, 128.8, 127.4, 122.6, 118.1, 116.4, 110.3, 63.8, 48.8, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{27}H_{23}Br_2N_7O_2Na$ $[M+Na]^+$: 660.0157, found: 660.0208.



(3r) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-cyanophenylacetylene (63.5 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (227.71 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (s, 2H), 7.99–7.89 (m, 4H), 7.80–7.65 (m, 4H), 5.65 (d, *J* = 2.3 Hz, 2H), 5.40 (d, *J* = 2.3 Hz, 2H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.68 (d, *J* = 14.8 Hz, 2H), 3.52 (d, *J* = 14.8 Hz, 2H), 1.21 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 146.4, 137.6, 134.1, 132.8, 126.3, 119.2, 118.6, 112.1, 110.9, 63.9, 53.5, 48.7, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{29}H_{23}N_9O_2Na$ $[M+Na]^+$: 552.1872, found: 552.1873.

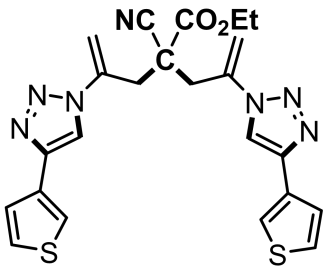


(3s) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethynyl-benzoic acid methyl ester (80.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:3) as yellow oily liquid (259.09 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 2H), 8.12–8.06 (m, 4H), 7.96–7.89 (m, 4H), 5.64 (d, *J* = 2.3 Hz, 2H), 5.37 (d, *J* = 2.2 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.94 (s, 6H), 3.68 (d, *J* = 14.9 Hz, 2H), 3.51 (d, *J* = 14.9 Hz, 2H), 1.19 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 166.6, 147.2, 137.6, 134.1, 130.3, 130.0, 125.7, 118.9, 116.4, 110.5, 63.9, 52.2, 48.8, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{31}H_{29}N_7O_6Na$ $[M+Na]^+$: 618.2077, found: 618.2092.

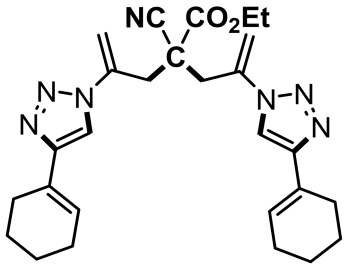


(3t) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-ethynyl naphthalene (76.10 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (243.46 mg,

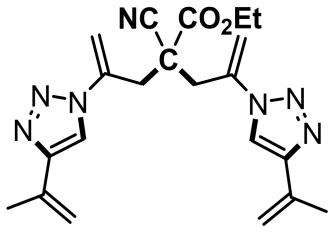
84%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (s, 2H), 8.14 (s, 2H), 7.96–7.80 (m, 8H), 7.54–7.46 (m, 4H), 5.65 (d, *J* = 2.2 Hz, 2H), 5.38 (d, *J* = 2.1 Hz, 2H), 4.00 (q, *J* = 7.2 Hz, 2H), 3.72 (d, *J* = 14.9 Hz, 2H), 3.52 (d, *J* = 14.9 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 148.4, 137.7, 133.5, 133.3, 128.7, 128.3, 127.8, 127.1, 126.6, 126.4, 124.9, 123.8, 118.2, 116.6, 110.1, 63.8, 48.9, 39.1, 13.8; **HRMS** (ESI) m/z calculated for $C_{35}H_{29}N_7O_2Na$ $[M+Na]^+$: 602.2281, found: 602.2300.



(3u) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-ethynylthiophene (50.1 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (194.18 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (s, 2H), 7.75–7.70 (m, 2H), 7.48–7.43 (m, 2H), 7.41–7.36 (m, 2H), 5.59 (d, *J* = 2.2 Hz, 2H), 5.33 (d, *J* = 2.2 Hz, 2H), 3.98 (q, *J* = 7.2 Hz, 2H), 3.66 (d, *J* = 14.8 Hz, 2H), 3.48 (d, *J* = 14.9 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 144.4, 137.6, 131.0, 126.6, 125.8, 121.9, 117.7, 116.5, 109.9, 63.8, 48.9, 39.0, 13.7; **HRMS** (ESI) m/z calculated for $C_{23}H_{21}N_7O_2S_2Na$ $[M+Na]^+$: 514.1096, found: 514.1088.

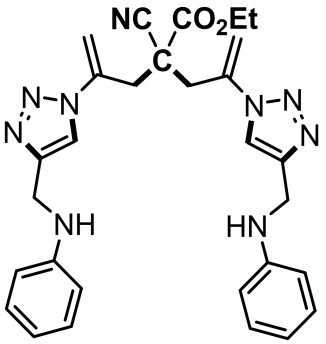


(3v) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-ethynylcyclohex-1-ene (58.8 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (216.99 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 6.62–6.57 (m, 2H), 5.51 (d, *J* = 2.1 Hz, 2H), 5.25 (d, *J* = 2.0 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.59 (d, *J* = 14.8 Hz, 2H), 3.42 (d, *J* = 14.8 Hz, 2H), 2.48–2.18 (m, 8H), 1.81–1.63 (m, 8H), 1.19 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 149.9, 137.7, 126.6, 126.3, 116.6, 116.5, 109.1, 63.7, 48.9, 38.9, 26.3, 25.3, 22.4, 22.1, 13.7; **HRMS** (ESI) m/z calculated for $C_{27}H_{33}N_7O_2Na$ $[M+Na]^+$: 510.2594, found: 510.2590.

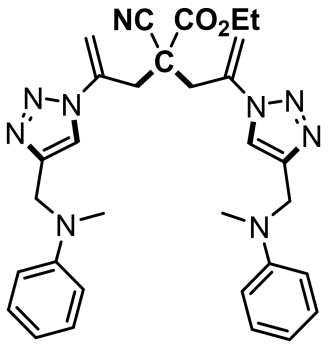


(3w) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethynyltoluene (63.4 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (187.21 mg, 89%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (s, 2H), 5.79 (s, 2H), 5.54 (d, *J* = 2.2 Hz,

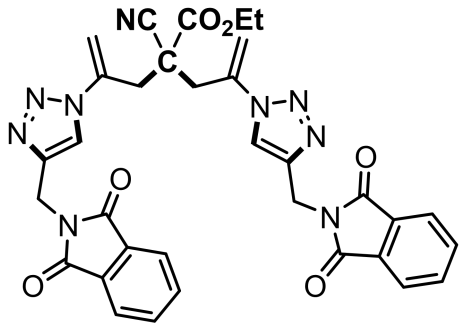
2H), 5.29 (d, *J* = 2.1 Hz, 2H), 5.23–5.08 (m, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.62 (d, *J* = 14.8 Hz, 2H), 3.44 (d, *J* = 14.8 Hz, 2H), 2.13 (s, 6H), 1.18 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 149.2, 137.7, 132.8, 117.9, 116.5, 113.7, 109.6, 63.7, 48.8, 39.0, 20.6, 13.7; **HRMS** (ESI) m/z calculated for $C_{21}H_{25}N_7O_2Na$ $[M+Na]^+$: 430.1968, found: 430.1992.



(3x) 0.25 mmol scale: Prepared following the genernal procedure showed above using N-(prop-2-yn-1-yl)aniline (65.6 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (228.50 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 2H), 7.22–7.12 (m, 4H), 6.77–6.71 (m, 2H), 6.70–6.62 (m, 4H), 5.48 (d, *J* = 2.2 Hz, 2H), 5.24 (d, *J* = 2.1 Hz, 2H), 4.47 (s, 4H), 3.94 (q, *J* = 7.1 Hz, 2H), 3.55 (d, *J* = 14.8 Hz, 2H), 3.39 (d, *J* = 14.8 Hz, 2H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 147.4, 147.1, 137.6, 129.3, 120.2, 118.2, 116.3, 113.2, 110.0, 63.6, 48.6, 39.8, 39.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{29}H_{31}N_9O_2Na$ $[M+Na]^+$: 560.2499, found: 560.2548.

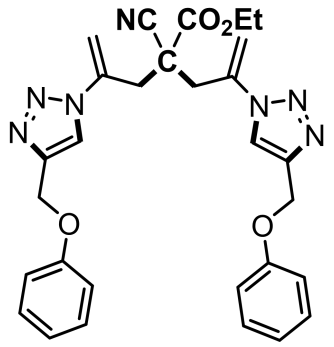


(3y) 0.25 mmol scale: Prepared following the genernal procedure showed above using N-methyl-N-(prop-2-yn-1-yl)aniline (72.5 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (226.27 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 2H), 7.26–7.20 (m, 4H), 6.79 (d, *J* = 8.6 Hz, 4H), 6.74 (t, *J* = 7.3 Hz, 2H), 5.42 (d, *J* = 2.2 Hz, 2H), 5.21 (d, *J* = 2.1 Hz, 2H), 4.64 (s, 4H), 3.87 (q, *J* = 7.2 Hz, 2H), 3.54 (d, *J* = 14.8 Hz, 2H), 3.36 (d, *J* = 14.9 Hz, 2H), 3.01 (s, 6H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 149.0, 146.2, 137.6, 129.3, 120.0, 117.4, 116.4, 113.0, 109.8, 63.6, 48.6, 39.0, 38.6, 13.8; **HRMS** (ESI) m/z calculated for $C_{31}H_{35}N_9O_2Na$ $[M+Na]^+$: 588.2812, found: 588.2860.

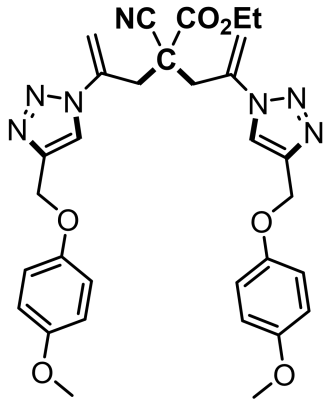


(3z) 0.5 mmol scale: Prepared following the genernal procedure showed above using 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (92.6 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and

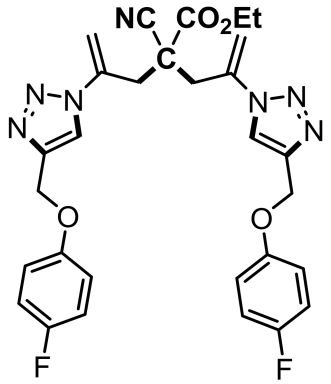
$Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (255.03 mg, 79%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.86–7.82(m, 4H), 7.75–7.70 (m, 4H), 5.53 (d, *J* = 2.3 Hz, 2H), 5.27 (d, *J* = 2.1 Hz, 2H), 5.00 (s, 4H), 3.91 (q, *J* = 7.1 Hz, 2H), 3.54 (s, 2H), 3.36 (d, *J* = 15.0 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.6, 166.4, 143.3, 137.4, 134.2, 132.0, 123.5, 121.4, 116.5, 110.2, 63.7, 48.5, 38.9, 32.9, 13.7; **HRMS** (ESI) m/z calculated for $C_{33}H_{27}N_9O_6Na$ $[M+Na]^+$: 668.1982, found: 668.2075.



(3za) 0.25 mmol scale: Prepared following the genernal procedure showed above using (prop-2-yn-1-yloxy)benzene (66.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (221.23 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 2H), 7.24–7.18 (m, 4H), 6.94–6.88 (m, 6H), 5.49 (d, *J* = 2.3 Hz, 2H), 5.24 (d, *J* = 2.2 Hz, 2H), 5.15 (s, 4H), 3.86 (q, *J* = 7.2 Hz, 2H), 3.55 (d, *J* = 14.9 Hz, 2H), 3.35 (d, *J* = 14.9 Hz, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.7, 157.0, 144.0, 136.6, 128.6, 120.4, 120.2, 115.4, 113.7, 109.3, 62.7, 60.7, 47.6, 38.1, 12.7; **HRMS** (ESI) m/z calculated for $C_{29}H_{29}N_7O_4Na$ $[M+Na]^+$: 562.2179, found: 562.2180.

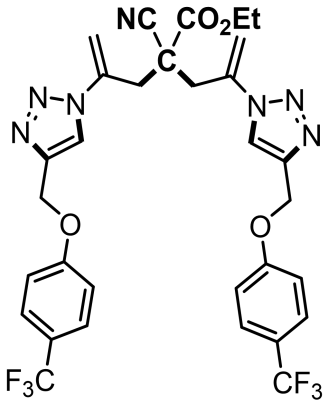


(3zb) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-methoxy-4-(prop-2-yn-1-yloxy)benzene (81.2 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (257.85 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (s, 2H), 6.95–6.89 (m, 4H), 6.87–6.80 (m, 4H), 5.55 (d, *J* = 2.3 Hz, 2H), 5.31 (d, *J* = 2.2 Hz, 2H), 5.17 (s, 4H), 3.94 (t, *J* = 7.2 Hz, 2H), 3.76 (s, 6H), 3.62 (d, *J* = 14.9 Hz, 2H), 3.42 (d, *J* = 14.9 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 154.3, 152.2, 145.2, 137.6, 121.2, 116.4, 115.8, 114.7, 110.3, 63.7, 62.5, 55.7, 48.7, 39.1, 13.8; **HRMS** (ESI) m/z calculated for $C_{31}H_{33}N_7O_6Na$ $[M+Na]^+$: 622.2390, found: 622.2351.



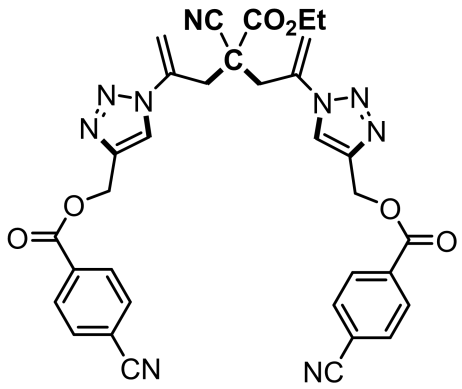
(3zc) 0.25 mmol scale: Prepared following the genernal procedure showed above

using 1-fluoro-4-(prop-2-yn-1-yloxy)benzene (75.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (233.11 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.01–6.88 (m, 8H), 5.56 (d, *J* = 2.3 Hz, 2H), 5.32 (d, *J* = 2.2 Hz, 2H), 5.18 (s, 4H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.62 (d, *J* = 14.9 Hz, 2H), 3.43 (d, *J* = 14.9 Hz, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 158.8 (d, *J* = 239.0 Hz), 154.2 (d, *J* = 2.1 Hz), 144.8, 137.6, 121.3, 116.3, 116.1 (d, *J* = 12.6 Hz), 115.9 (d, *J* = 2.1 Hz), 110.4, 63.7, 62.4, 48.7, 39.1, 13.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.05; **HRMS** (ESI) m/z calculated for $C_{29}H_{27}F_2N_7O_4Na$ $[M+Na]^+$: 598.1991, found: 598.1960.

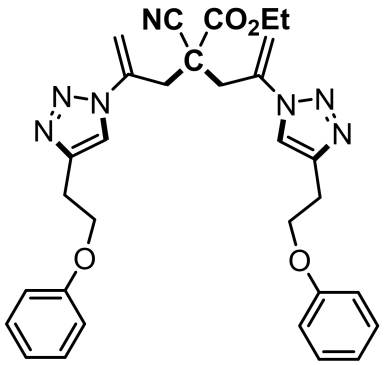


(3zd) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-(prop-2-yn-1-yloxy)-4-(trifluoromethyl)benzene (100.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as yellow oily liquid (280.37 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.55 (d, *J* = 8.7 Hz, 4H), 7.06 (d, *J* = 8.6 Hz, 4H), 5.57 (d, *J* = 2.3 Hz, 2H), 5.33 (d, *J* = 2.2 Hz, 2H), 5.27 (s, 4H), 3.94 (q, *J* = 7.2 Hz, 2H), 3.62 (d, *J* = 14.8 Hz, 2H), 3.44

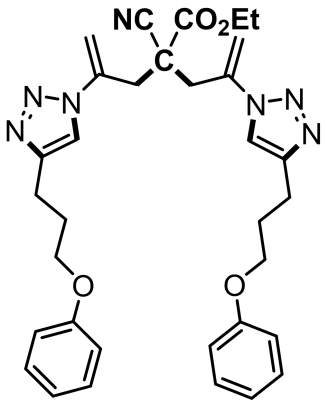
(d, J = 14.8 Hz, 2H), 1.18 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 160.4, 144.2, 137.6, 127.0 (q, J = 3.6 Hz), 125.6, 123.7, 123.4, 123.0, 121.5, 116.3, 114.8, 110.6, 63.7, 61.9, 48.6, 39.1, 13.7; **^{19}F NMR** (376 MHz, CDCl3) δ -61.57; **HRMS** (ESI) m/z calculated for $C_{31}H_{27}F_6N_7O_4Na$ $[M+Na]^+$: 698.1927, found: 698.1937.



(3ze) 0.25 mmol scale: Prepared following the genernal procedure showed above using prop-2-yn-1-yl 4-cyanobenzoate (92.6 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (277.63 mg, 86%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18–8.10 (m, 4H), 7.97 (s, 2H), 7.78–7.69 (m, 4H), 5.58 (d, J = 2.3 Hz, 2H), 5.55–5.48 (m, 4H), 5.33 (d, J = 2.2 Hz, 2H), 4.00 (q, J = 7.2 Hz, 2H), 3.60 (d, J = 14.9 Hz, 2H), 3.44 (d, J = 14.9 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 164.8, 142.9, 137.5, 133.4, 132.3, 130.3, 122.7, 117.8, 116.7, 116.2, 110.7, 63.7, 58.4, 48.5, 39.1, 13.8; **HRMS** (ESI) m/z calculated for $C_{33}H_{27}N_9O_6Na$ $[M+Na]^+$: 668.1982, found: 668.1983.

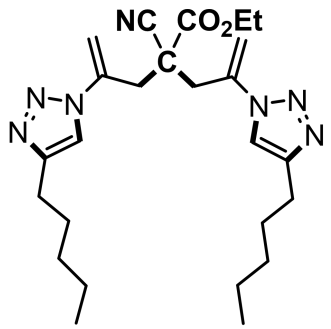


(3zf) 0.5 mmol scale: Prepared following the genernal procedure showed above using (but-3-yn-1-yloxy)benzene (73.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (227.06 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (s, 2H), 7.31–7.25 (m, 4H), 7.03–6.86 (m, 6H), 5.50 (d, *J* = 2.2 Hz, 2H), 5.26 (d, *J* = 2.0 Hz, 2H), 4.25 (t, *J* = 6.3 Hz, 4H), 3.92 (q, *J* = 7.2 Hz, 2H), 3.60 (d, *J* = 14.9 Hz, 2H), 3.40 (d, *J* = 14.9 Hz, 2H), 3.23 (t, *J* = 6.3 Hz, 4H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 158.5, 145.4, 137.7, 129.5, 121.0, 120.5, 116.5, 114.6, 109.6, 66.4, 63.6, 48.8, 39.0, 26.1, 13.7; **HRMS** (ESI) m/z calculated for $C_{31}H_{33}N_7O_4Na$ $[M+Na]^+$: 590.2492, found: 590.2576.



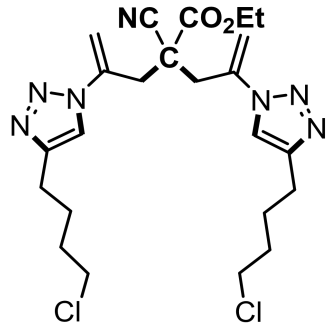
(3zg) 0.25 mmol scale: Prepared following the genernal procedure showed above

using (pent-4-yn-1-yloxy)benzene (80.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (259.13 mg, 87%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (s, 2H), 7.29–7.23 (m, 4H), 6.95–6.86 (m, 6H), 5.45 (d, *J* = 2.1 Hz, 2H), 5.22 (d, *J* = 2.0 Hz, 2H), 4.03–3.93 (m, 6H), 3.57 (d, *J* = 14.8 Hz, 2H), 3.40 (d, *J* = 14.8 Hz, 2H), 2.93 (t, *J* = 7.5 Hz, 4H), 2.96–2.13 (m, 4H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 158.9, 147.9, 137.7, 129.5, 120.7, 119.7, 116.4, 114.5, 109.4, 66.5, 63.5, 48.7, 39.0, 28.8, 22.1, 13.8; **HRMS** (ESI) m/z calculated for $C_{33}H_{37}N_7O_4Na$ $[M+Na]^+$: 618.2805, found: 618.2800.

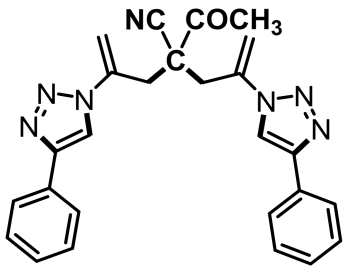


(3zh) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-heptyne (65.6 μL, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (191.72 mg, 82%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 2H), 5.49 (d, *J* = 2.1 Hz, 2H), 5.25 (d, *J* = 1.9 Hz, 2H), 3.97 (q, *J* = 7.2 Hz, 2H), 3.61 (d, *J* = 14.8 Hz, 2H), 3.41 (d, *J* = 14.8 Hz, 2H), 2.78– 2.66 (m, 4H), 1.76–1.59 (m, 4H), 1.35 (t, *J* = 5.4 Hz, 8H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.93–0.86 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 149.1, 137.8,

119.1, 116.6, 109.1, 63.5, 53.5, 48.8, 39.0, 31.4, 29.0, 25.5, 22.4, 14.0; **HRMS** (ESI) m/z calculated for $C_{25}H_{37}N_7O_2Na$ $[M+Na]^+$: 490.2907, found: 490.2998.

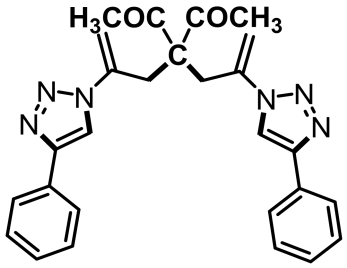


(3zi) 0.25 mmol scale: Prepared following the genernal procedure showed above using 6-chlorohex-1-yne (58.1 mg, 0.5 mmol, 2.0 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl cyanoacetate (26.6 μL , 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (205.51 mg, 81%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 2H), 5.49 (d, *J* = 2.1 Hz, 2H), 5.25 (d, *J* = 2.0 Hz, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.62–3.54 (m, 6H), 3.42 (d, *J* = 14.8 Hz, 2H), 2.77 (t, *J* = 6.9 Hz, 4H), 1.86 (d, *J* = 6.7 Hz, 8H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 148.2, 137.8, 119.4, 109.3, 63.6, 53.4, 48.7, 44.7, 39.0, 31.8, 26.5, 24.8, 13.8; **HRMS** (ESI) m/z calculated for $C_{23}H_{31}Cl_2N_7O_2Na$ $[M+Na]^+$: 530.1814, found: 530.1868.

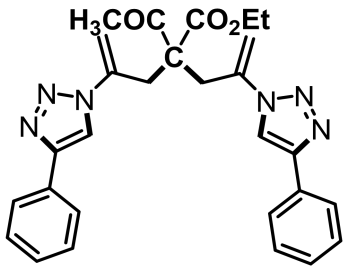


(4a) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2

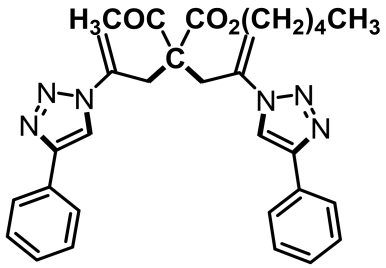
eq.), 3-Oxobutanenitrile (21.3 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (144.12 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 2H), 7.94–7.79 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 4H), 7.39–7.31 (m, 2H), 5.60 (d, *J* = 2.2 Hz, 2H), 5.26 (d, *J* = 2.1 Hz, 2H), 3.55 (d, *J* = 14.8 Hz, 2H), 3.45 (d, *J* = 14.9 Hz, 2H), 2.35 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.5, 148.3, 137.4, 129.9, 128.9, 128.6, 126.0, 117.8, 110.7, 106.8, 52.2, 40.3, 29.3; **HRMS** (ESI) m/z calculated for $C_{26}H_{23}N_7ONa$ $[M+Na]^+$: 472.1862, found: 472.1929.



(4b) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), acetylacetone (25.7 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (198.28 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.83–7.78 (m, 4H), 7.41 (t, *J* = 7.4 Hz, 4H), 7.37–7.29 (m, 2H), 5.47 (d, *J* = 2.1 Hz, 2H), 5.07 (d, *J* = 1.8 Hz, 2H), 3.60 (s, 4H), 2.15 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.4, 148.1, 139.3, 129.8, 128.9, 128.6, 125.9, 118.1, 109.4, 68.5, 33.7, 27.2; **HRMS** (ESI) m/z calculated for $C_{27}H_{26}N_6O_2Na$ $[M+Na]^+$: 489.2015, found: 489.2067.

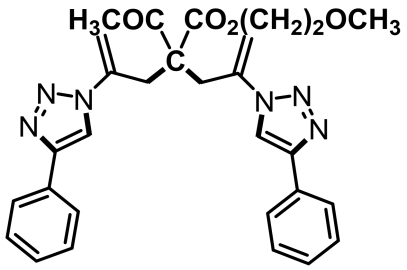


(4c) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 3-methoxypropanoate (33.7 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (198.63 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.87–7.75 (m, 4H), 7.50–7.39 (m, 4H), 7.38–7.30 (m, 2H), 5.50 (d, *J* = 1.8 Hz, 2H), 5.16 (d, *J* = 1.4 Hz, 2H), 3.99 (q, *J* = 7.2 Hz, 2H), 3.60 (d, *J* = 15.8 Hz, 2H), 3.47 (d, *J* = 15.8 Hz, 2H), 2.11 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.5, 170.4, 148.0, 139.2, 129.9, 128.9, 128.5, 125.9, 118.2, 110.1, 62.4, 61.7, 34.5, 27.0, 13.8; **HRMS** (ESI) m/z calculated for $C_{28}H_{28}N_6O_3Na$ $[M+Na]^+$: 519.2121, found: 519.2120.

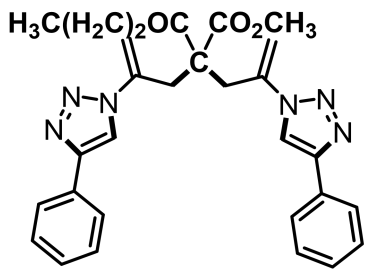


(4d) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), pentyl 3-oxobutanoate (44.8 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (223.55 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.86–7.77 (m, 4H), 7.42 (t, *J* = 7.4

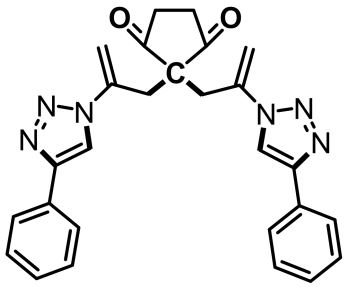
Hz, 4H), 7.37–7.30 (m, 2H), 5.50 (d, J = 1.7 Hz, 2H), 5.19–5.10 (m, 2H), 3.91 (t, J = 6.9 Hz, 2H), 3.61 (d, J = 15.8 Hz, 2H), 3.47 (d, J = 15.8 Hz, 2H), 2.12 (s, 3H), 1.59–1.51 (m, 2H), 1.37–1.12 (m, 6H), 0.85 (t, J = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 170.4, 147.9, 139.2, 129.9, 128.9, 128.5, 125.8, 118.2, 110.0, 66.6, 61.7, 34.4, 27.9, 27.8, 26.9, 22.2, 13.9; **HRMS** (ESI) m/z calculated for $C_{31}H_{34}N_6O_3Na$ $[M+Na]^+$: 561.2590, found: 561.2600.



(4e) 0.25 mmol scale: Prepared following the genernal procedure showed abov e using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 m mol, 2.2 eq.), 2-methoxyethyl acetoacetate (61.2 μL, 0.25 mmol, 1.0 eq.), trieth ylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was p urified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (210.63 mg, 80%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.86–7.80 (m, 4H), 7.45–7.39 (m, 4H), 7.37–7.30 (m, 2H), 5.50 (d, J = 1.7 Hz, 2H), 5.22–5.12 (m, 2H), 4.11–4.05 (m, 2H), 3.61 (d, J = 15.7 Hz, 2H), 3.53–3.49 (m, 2H), 3.45(d, J = 15.8 Hz, 2H), 3.30 (s, 3H), 2.12 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.5, 170.4, 147.9, 139.1, 129.9, 128.9, 128. 5, 125.8, 118.3, 110.4, 69.8, 64.9, 61.8, 58.8, 34.6, 27.0; **HRMS** (ESI) m/z cal culated for $C_{29}H_{30}N_6O_4Na$ $[M+Na]^+$: 549.2227, found:549.2200.

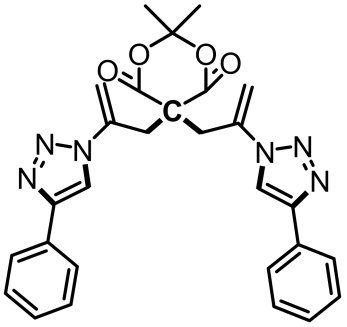


(4f) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), methyl 3-oxohexanoate (35.4 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (211.90 mg, 83%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91 (s, 2H), 7.83–7.78 (m, 4H), 7.42 (t, *J* = 7.4 Hz, 4H), 7.37–7.32 (m, 2H), 5.50 (d, *J* = 1.7 Hz, 2H), 5.15–5.10 (m, 2H), 3.62–3.49 (m, 7H), 2.44 (t, *J* = 7.3 Hz, 2H), 1.43 (q, *J* = 7.4 Hz, 2H), 0.84 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 204.8, 171.0, 147.9, 139.3, 129.9, 128.9, 128.5, 125.9, 118.2, 109.9, 61.4, 52.9, 41.1, 34.5, 16.9, 13.5; **HRMS** (ESI) m/z calculated for $C_{29}H_{30}N_6O_3Na$ $[M+Na]^+$: 533.2277, found: 533.2357.

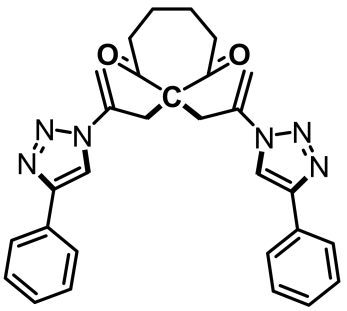


(4g) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), 1,3-cyclopentanedione (22.2 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (197.42 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 2H), 7.85–7.79 (m, 4H), 7.42 (t, *J* = 7.4

Hz, 4H), 7.38–7.31 (m, 2H), 5.50 (d, *J* = 1.6 Hz, 2H), 5.12 (d, *J* = 1.6 Hz, 2H), 3.23 (s, 4H), 2.70 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 213.1, 148.3, 138.2, 129.8, 128.9, 128.6, 125.9, 117.9, 110.0, 57.8, 37.5, 35.5; **HRMS** (ESI) m/z calculated for $C_{27}H_{24}N_6O_2Na$ $[M+Na]^+$: 487.1859, found: 487.1882.

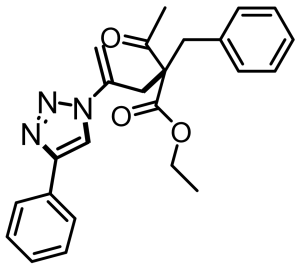


(4h) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.), 2,2-dimethyl-1,3-dioxane-4,6-dione (31.9 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (216.99 mg, 85%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.86–7.79 (m, 4H), 7.42 (t, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 5.67 (d, *J* = 1.8 Hz, 2H), 5.23 (d, *J* = 1.6 Hz, 2H), 3.66 (s, 4H), 1.74 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.9, 148.5, 137.7, 129.8, 128.9, 128.7, 126.0, 118.0, 117.9, 110.0, 53.1, 38.0, 28.2; **HRMS** (ESI) m/z calculated for $C_{28}H_{26}N_6O_4Na$ $[M+Na]^+$: 533.1914, found: 533.1930.

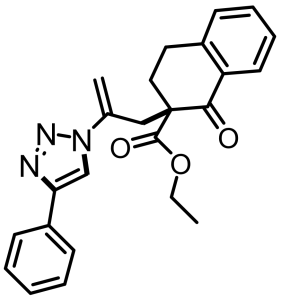


(4i) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), **VA** (224.8 mg, 0.55 mmol, 2.2 eq.),

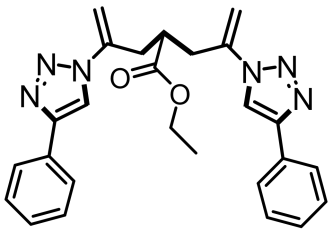
1,3-cycloheptanedione (28.7 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=5:1) as white solid (184.72 mg, 75%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (s, 2H), 7.88–7.81 (m, 4H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.39-7.33 (m, 2H), 5.48 (d, *J* = 1.5 Hz, 2H), 5.27–5.21 (m, 2H), 3.47 (s, 4H), 2.28 (s, 4H), 1.74 (s, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 210.2, 148.2, 139.5, 129.8, 128.9, 128.6, 125.9, 118.5, 110.9, 66.6, 42.4, 33.7, 28.6; **HRMS** (ESI) m/z calculated for $C_{29}H_{28}N_6O_2Na$ $[M+Na]^+$: 515.2172, found: 515.2155.



(4j) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (30.2 μL, 0.28 mmol, 1.1 eq.), **VA** (112.4 mg, 0.28 mmol, 1.1 eq.), 1,3-cycloheptanedione (28.7 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=8:1) as white solid (85.68 mg, 85%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 24.5 Hz, 3H), 7.41 (d, *J* = 33.6 Hz, 3H), 7.25 (s, 3H), 7.10 (s, 2H), 5.61 (s, 1H), 5.19 (s, 1H), 3.58 (s, 3H), 3.46 (t, *J* = 13.3 Hz, 2H), 3.27 (d, *J* = 5.2 Hz, 2H), 2.03 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 204.1, 171.5, 147.8, 139.6, 135.5, 130.0, 129.9, 128.9, 128.6, 128.5, 127.3, 125.9, 118.4, 110.4, 63.8, 52.6, 39.0, 35.6, 29.7, 28.1; **HRMS** (ESI) m/z calculated for $C_{24}H_{25}N_3O_3Na$ $[M+Na]^+$: 426.1794, found: 426.1765.

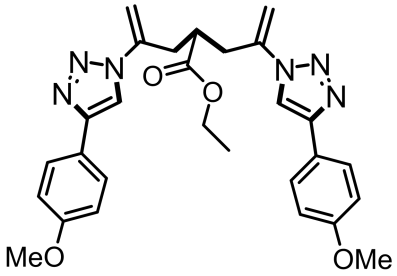


(4k) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (30.2 μL, 0.28 mmol, 1.1 eq.), **VA** (112.4 mg, 0.28 mmol, 1.1 eq.), 1,3-cycloheptanedione (28.7 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=8:1) as white solid (73.21 mg, 73%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 7.2 Hz, 2H), 7.90- 7.80 (m, 2H), 7.44 (m, 3H), 7.38-7.32 (m, 1H), 7.30-7.26 (m, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 5.55 (s, 1H), 5.24 (s, 1H), 4.03 (q, *J* = 7.1 Hz, 2H), 3.81 (d, *J* = 14.8 Hz, 1H), 3.48 (d, *J* = 14.8 Hz, 1H), 3.12-2.98 (m, 1H), 2.83 (m, 1H), 2.53-2.43 (m, 1H), 2.04-1.97 (m, 1H), 1.11 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 193.9, 171.1, 147.8, 142.9, 139.3, 134.1, 131.9, 130.2, 128.9, 128.7, 128.4, 128.1, 126.8, 125.8, 118.0, 110.1, 61.8, 57.6, 36.4, 31.0, 25.9, 13.4; **HRMS** (ESI) m/z calculated for $C_{24}H_{23}N_3O_3Na$ $[M+Na]^+$:424.1637, found: 424.1664.

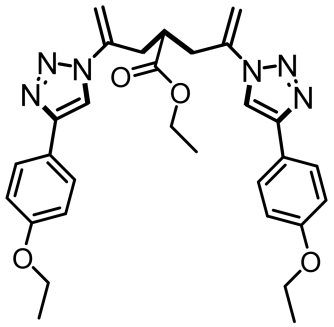


(6a) 0.25 mmol scale: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a

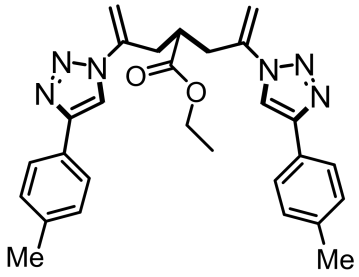
silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (99.93 mg, 88%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.02 (s, 2H), 7.85 (d, *J* = 7.5 Hz, 4H), 7.42 (t, *J* = 7.5 Hz, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 5.48 (s, 2H), 5.11 (s, 2H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.18 (d, *J* = 7.1 Hz, 4H), 3.07 (q, *J* = 7.3, 6.9 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 147.9, 140.7, 130.1, 128.9, 128.4, 125.9, 117.5, 106.3, 61.0, 41.8, 35.3, 14.2. **HRMS** (ESI) m/z calculated for $C_{28}H_{30}N_5O_4Na$ $[M+Na]^+$: 477.2015, found: 477.2065.



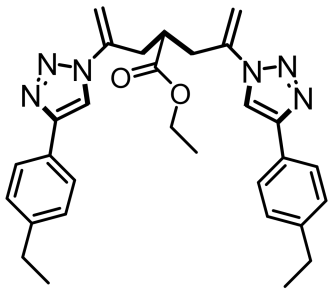
(6b) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-methoxyphenylacetylene (74.1 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (110.56 mg, 86%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.86 (s, 2H), 7.73 – 7.67 (m, 4H), 6.91 – 6.84 (m, 4H), 5.39 (s, 2H), 5.02 (s, 2H), 4.02 (q, *J* = 7.1 Hz, 2H), 3.78 (s, 6H), 3.10 (d, *J* = 7.0 Hz, 4H), 3.02 – 2.95 (m, 1H), 1.12 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.3, 146.0, 140.5, 134.4, 132.7, 126.2, 118.9, 118.6, 111.9, 107.2, 61.1, 41.6, 35.2, 14.3. **HRMS** (ESI) m/z calculated for $C_{28}H_{30}N_5O_4Na$ $[M+Na]^+$: 537.2226, found: 537.2256.



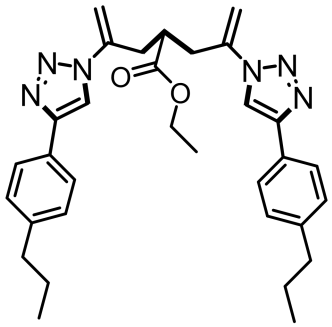
(6c) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethoxyphenylacetylene (81.2 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (111.16 mg, 82%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 2H), 7.75 (d, *J* = 7.8 Hz, 4H), 6.93 (d, *J* = 8.1 Hz, 4H), 5.46 (s, 2H), 5.08 (s, 2H), 4.07 (q, *J* = 7.0 Hz, 6H), 3.16 (d, *J* = 6.8 Hz, 4H), 3.06 (q, *J* = 6.9 Hz, 1H), 1.44 (t, *J* = 6.9 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 159.2, 147.8, 140.6, 127.2, 122.6, 116.6, 114.8, 106.0, 63.5, 61.0, 41.7, 35.2, 14.8, 14.2. **HRMS** (ESI) m/z calculated for $C_{30}H_{34}N_6O_4Na$ $[M+Na]^+$: 565.2539, found: 565.2547.



(6d) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-methylphenylacetylene (47.7 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (96.50 mg, 80%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 7.73 (d, *J* = 7.6 Hz, 4H), 7.22 (d, *J* = 7.6 Hz, 4H), 5.46 (s, 2H), 5.09 (s, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.17 (d, *J* = 6.7 Hz, 4H), 3.08 (q, *J* = 7.5, 6.8 Hz, 1H), 2.38 (s, 6H), 1.19 (t, *J* = 7.2 Hz, 3H);**^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 147.9, 140.6, 138.3, 129.5, 127.3, 125.8, 117.2, 106.1, 61.0, 41.8, 35.2, 21.3, 14.2. **HRMS** (ESI) m/z calculated for $C_{28}H_{30}N_6O_2Na$ $[M+Na]^+$: 505.2328, found: 505.2378.

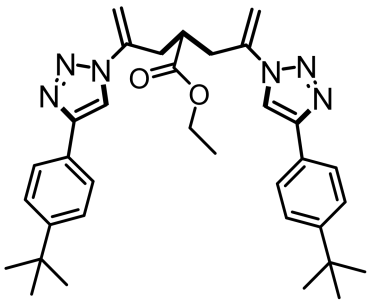


(6e) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-ethylphenylacetylene (77.8 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (103.33 mg, 81%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 7.77 (d, *J* = 8.1 Hz, 4H), 7.25 (d, *J* = 7.4 Hz, 4H), 5.47 (s, 2H), 5.10 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 7.0 Hz, 4H), 3.11 – 3.03 (m, 1H), 2.68 (q, *J* = 7.6 Hz, 4H), 1.26 (t, *J* = 7.6 Hz, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 148.0, 144.7, 140.7, 128.4, 127.5, 125.9, 117.2, 106.1, 61.0, 41.8, 35.3, 28.7, 15.5, 14.2. **HRMS** (ESI) m/z calculated for $C_{30}H_{34}N_6O_2Na$ $[M+Na]^+$: 533.2641, found: 533.2657.

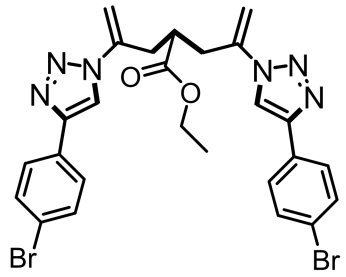


(6f) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-n-propyl phenylacetylene (87.2 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily

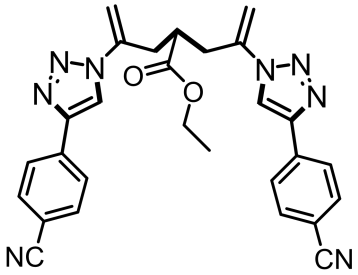
liquid (104.97 mg, 78%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.97 (s, 2H), 7.76 (d, *J* = 7.9 Hz, 4H), 7.22 (d, *J* = 7.9 Hz, 4H), 5.47 (s, 2H), 5.09 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 7.0 Hz, 4H), 3.10 – 3.02 (m, 1H), 2.61 (t, *J* = 7.6 Hz, 4H), 1.70 – 1.64 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 148.0, 143.1, 140.6, 127.5, 125.8, 117.2, 106.1, 61.0, 41.8, 37.9, 35.3, 24.5, 14.2, 13.8. **HRMS** (ESI) m/z calculated for $C_{32}H_{38}N_6O_2Na$ $[M+Na]^+$: 561.2954, found: 561.2974.



(6g) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-tert-butyl phenylacetylene (99.2 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (107.60 mg, 76%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 (s, 2H), 7.79 (d, *J* = 7.8 Hz, 4H), 7.44 (d, *J* = 7.9 Hz, 4H), 5.48 (s, 2H), 5.09 (s, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 3.17 (d, *J* = 6.8 Hz, 4H), 3.06 (q, *J* = 10.1, 5.8 Hz, 1H), 1.35 (s, 18H), 1.19 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 151.5, 147.9, 140.6, 127.3, 125.8, 125.7, 117.2, 106.1, 61.0, 41.8, 35.3, 34.7, 31.3, 14.2. **HRMS** (ESI) m/z calculated for $C_{34}H_{42}N_6O_2Na$ $[M+Na]^+$: 589.3267, found: 589.3245.

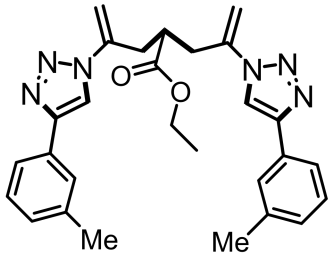


(6h) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-bromophenylacetylene (99.6 mg, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (115.90 mg, 78%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (s, 2H), 7.70 (d, *J* = 8.6 Hz, 4H), 7.54 (d, *J* = 8.5 Hz, 4H), 5.47 (s, 2H), 5.12 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.22 – 3.11 (m, 4H), 3.04 – 2.95 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 146.8, 140.6, 132.0, 129.0, 127.4, 122.4, 117.8, 106.7, 61.1, 41.6, 35.2, 14.3. **HRMS** (ESI) m/z calculated for $C_{26}H_{24}Br_2N_6O_2Na$ $[M+Na]^+$: 635.0205, found: 635.0227.

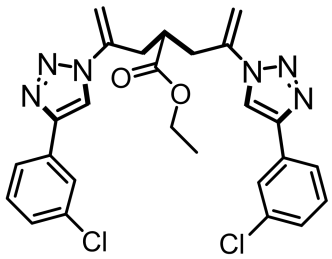


(6i) 0.25 mmol scale: Prepared following the genernal procedure showed above using 4-cyanophenylacetylene (69.9 mg, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (95.80 mg, 76%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.14 (s, 2H), 7.99 – 7.94 (m, 4H), 7.72 (d, *J* = 8.4 Hz, 4H), 5.51 (s, 2H), 5.17 (s, 2H), 4.11 (q, *J* = 7.1 Hz,

2H), 3.19 (d, *J* = 7.1 Hz, 4H), 3.05 – 2.98 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.3, 146.0, 140.5, 134.4, 132.7, 126.2, 118.9, 118.6, 111.9, 107.2, 61.1, 41.6, 35.3, 14.3. **HRMS** (ESI) m/z calculated for $C_{28}H_{24}N_6O_2Na$ $[M+Na]^+$: 527.1920, found: 527.1928.

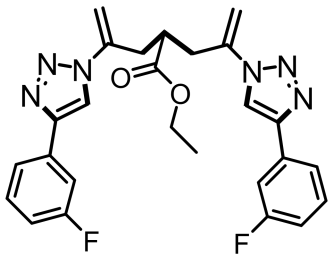


(6j) 0.25 mmol scale: Prepared following the genernal procedure showed above using 3-methylphenylacetylene (71.0 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (98.90 mg, 82%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (s, 2H), 7.70 (s, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.15 (d, *J* = 7.6 Hz, 2H), 5.47 (s, 2H), 5.10 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 6.9 Hz, 4H), 3.08 (q, *J* = 7.0, 6.6 Hz, 1H), 2.39 (s, 6H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 148.0, 140.7, 138.5, 123.0, 129.2, 128.8, 126.6, 123.0, 117.5, 106, 61.00, 41.8, 35.2, 21.4, 14.2.**HRMS** (ESI) m/z calculated for $C_{28}H_{30}N_6O_2Na$ $[M+Na]^+$: 505.2328, found: 505.2386.

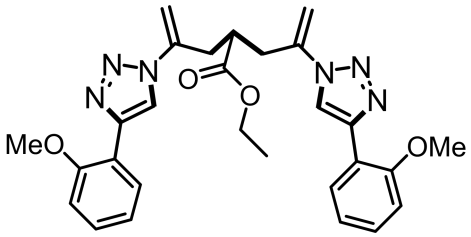


(6k) 0.25 mmol scale: Prepared following the genernal procedure showed above using 3-chlorophenylacetylene (67.7 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.),

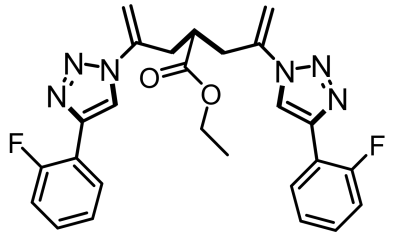
triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (97.90 mg, 75%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (s, 2H), 7.86 (s, 2H), 7.74 (d, *J* = 7.4 Hz, 2H), 7.38 – 7.28 (m, 4H), 5.48 (s, 2H), 5.13 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 5.7 Hz, 4H), 3.04 – 2.96 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 146.6, 140.6, 134.9, 131.8, 130.2, 128.4, 125.9, 124.0, 118.1, 106.8, 61.1, 41.6, 35.3, 14.3. **HRMS** (ESI) m/z calculated for $C_{26}H_{24}Cl_2N_6O_2Na$ $[M+Na]^+$: 545.1236, found: 545.1356.



(6l) 0.25 mmol scale: Prepared following the genernal procedure showed above using 3-fluorophenylacetylene (63.6 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (88.30 mg, 72%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.05 (s, 2H), 7.65 – 7.55 (m, 4H), 7.42 – 7.33 (m, 2H), 7.03 (t, *J* = 8.5 Hz, 2H), 5.49 (s, 2H), 5.13 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.17 (d, *J* = 6.1 Hz, 4H), 3.02 (q, *J* = 6.6 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 164.4 (d, *J* = 247.4 Hz), 146.8 (d, *J* = 2.5 Hz), 140.6, 132.2 (d, *J* = 8.6 Hz), 130.5 (d, *J* = 8.6 Hz), 121.5 (d, *J* = 2.8 Hz), 118.1, 115.4 (d, *J* = 21.0 Hz), 113.0 (d, *J* = 23.0 Hz), 106.8, 61.1, 41.6, 35.3, 14.2. **HRMS** (ESI) m/z calculated for $C_{26}H_{24}F_2N_6O_2Na$ $[M+Na]^+$: 513.1827, found: 513.1878.

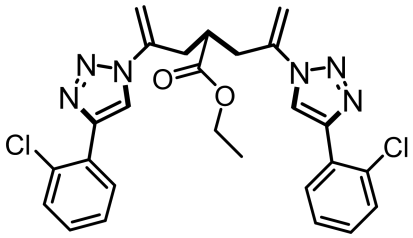


(6m) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-methoxyphenylacetylene (71.1 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid 102.85 mg, 80%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.33 (d, *J* = 7.7 Hz, 2H), 8.25 (s, 2H), 7.35 – 7.29 (m, 2H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 5.47 (s, 2H), 5.07 (s, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.94 (s, 6H), 3.19 (s, 5H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 155.8, 143.2, 140.8, 129.2, 127.8, 121.0, 120.7, 119.0, 110.8, 105.7, 60.9, 55.5, 41.9, 35.2, 14.2. **HRMS** (ESI) m/z calculated for $C_{28}H_{30}N_6O_4Na$ $[M+Na]^+$: 537.2227, found: 537.2256.

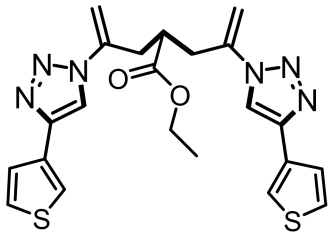


(6n) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-fluorophenylacetylene (62.3 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (91.90 mg, 75%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.19 (t, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 3.4 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.18 – 7.13 (m, 2H), 7.09 – 7.02

(m, 2H), 5.41 (s, 2H), 5.04 (s, 2H), 4.01 (q, *J* = 7.2 Hz, 2H), 3.12 (d, *J* = 6.8 Hz, 4H), 3.04 (d, *J* = 6.8 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 160.6 (d, *J* = 249.6 Hz), 141.3 (d, *J* = 2.2 Hz), 140.6, 129.6 (d, *J* = 8.5 Hz), , 128.0 (d *J* = 3.4 Hz), 124.6 (d, *J* = 3.4 Hz), 120.6 (d, *J* = 12.9 Hz), 118.2 (d, *J* = 12.9 Hz), 115.6 (d, *J* = 21.6 Hz), 106.3, 61.0, 41.67, 35.2, 14.2. **HRMS** (ESI) m/z calculated for $C_{26}H_{24}F_2N_6O_2Na$ $[M+Na]^+$: 513.1827, found: 513.1867.

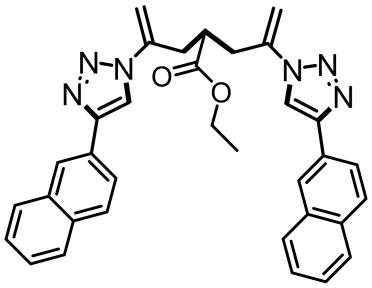


(6o) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-chlorophenylacetylene (66.8 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (93.98 mg, 72%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.41 (s, 2H), 8.23 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 6.5 Hz, 2H), 7.36 (t, *J* = 6.9 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 5.51 (s, 2H), 5.14 (s, 2H), 4.10 (q, *J* = 7.2 Hz, 2H), 3.21 (d, *J* = 6.4 Hz, 4H), 3.17 – 3.10 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 144.1, 140.6, 131.4, 130.2, 123.0, 129.2, 128.8, 127.2, 121.0, 106.5, 61.0, 41.7, 35.2, 14.3, 14.2. **HRMS** (ESI) m/z calculated for $C_{26}H_{24}Cl_2N_6O_2Na$ $[M+Na]^+$: 545.1236, found: 545.1287.

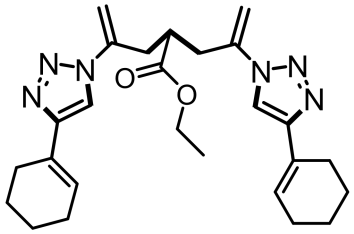


(6p) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-ethynylthiophene (55.1 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol,

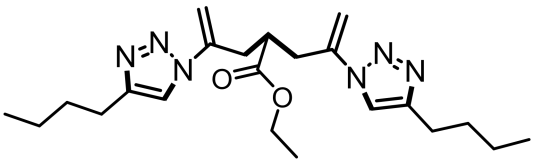
2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (88.56 mg, 76%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.91 (s, 2H), 7.73 (s, 2H), 7.47 (d, *J* = 5.0 Hz, 2H), 7.42 – 7.34 (m, 2H), 5.47 (s, 2H), 5.10 (s, 2H), 4.09 (q, *J* = 6.9 Hz, 2H), 3.16 (d, *J* = 6.9 Hz, 4H), 3.03 (q, *J* = 7.2 Hz, 1H), 1.19 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 144.1, 140.5, 131.3, 126.4, 125.9, 121.7, 117.3, 106.3, 61.0, 41.7, 35.3, 14.2. **HRMS** (ESI) m/z calculated for $C_{22}H_{34}N_6O_2S_2Na$ $[M+Na]^+$: 437.2641, found: 437.2641.



(6q) 0.25 mmol scale: Prepared following the genernal procedure showed above using 2-ethynyl naphthalene (83.7 mg, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (98.38 mg, 71%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.35 (s, 2H), 8.15 (s, 2H), 7.92 (d, *J* = 10.2 Hz, 2H), 7.85 – 7.79 (m, 6H), 7.47 (q, *J* = 5.2, 4.4 Hz, 4H), 5.52 (s, 2H), 5.14 (s, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.21 (d, *J* = 6.9 Hz, 4H), 3.11 (q, *J* = 6.7 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 147.9, 140.7, 133.5, 133.3, 128.6, 128.3, 127.8, 127.4, 126.5, 126.3, 123.9, 117.9, 106.5, 61.1, 41.7, 35.3, 14.3. **HRMS** (ESI) m/z calculated for $C_{34}H_{30}N_6O_2Na$ $[M+Na]^+$: 577.2328, found: 577.2356.

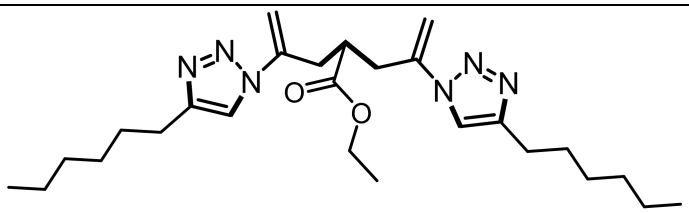


(6r) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-ethynylcyclohex-1-ene (64.7 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (80.90 mg, 70%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (s, 2H), 6.59 (s, 2H), 5.36 (s, 2H), 5.01 (s, 2H), 4.07 (d, *J* = 7.1 Hz, 2H), 3.10 (d, *J* = 7.1 Hz, 4H), 2.98 – 2.94 (m, 1H), 2.39 (s, 4H), 2.22 (s, 4H), 1.81 – 1.75 (m, 4H), 1.68 (q, *J* = 5.8, 4.8 Hz, 4H), 1.18 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 149.4, 126.8, 125.8, 116.1, 105.6, 60.9, 41.7, 35.2, 26.3, 25.3, 22.4, 22.2, 14.2. **HRMS** (ESI) m/z calculated for $C_{26}H_{34}N_6O_2Na$ $[M+Na]^+$: 485.2641, found: 485.2661.

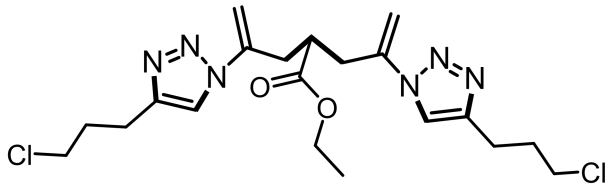


(6s) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-hexyne (63.2 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (82.85 mg, 80%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 5.35 (s, 2H), 5.00 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.10 (d, *J* = 6.8 Hz, 4H), 3.02 (q, *J* = 7.1, 6.6 Hz, 1H), 2.72 (t, *J* = 7.8 Hz, 4H), 1.71-1.63 (m,4H), 1.45-1.36 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 148.6, 140.7, 118.6, 105.3, 60.8, 41.7, 35.1, 31.4, 25.3, 22.3, 14.2, 13.8. **HRMS** (ESI) m/z calculated for

$C_{22}H_{34}N_6O_2Na$ $[M+Na]^+$: 437.2641, found: 437.2669.

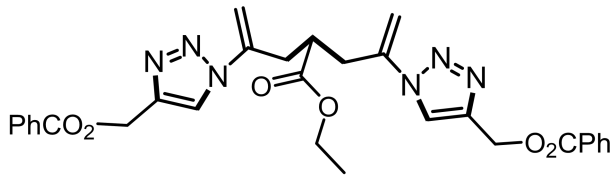


(6t) 0.25 mmol scale: Prepared following the genernal procedure showed above using 1-octyne (81.1 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (92.90 mg, 79%);**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.50 (s, 2H), 5.34 (s, 2H), 5.00 (s, 2H), 4.07 (q, *J* = 7.1 Hz, 2H), 3.10 (d, *J* = 6.8 Hz, 4H), 3.02 (q, *J* = 7.0, 6.6 Hz, 1H), 2.71 (t, *J* = 7.8 Hz, 4H), 1.67 (q, *J* = 7.6 Hz, 4H), 1.40 – 1.28 (m, 12H), 1.19 (t, *J* = 7.1 Hz, 3H), 0.92 – 0.85 (m, 6H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.6, 148.6, 140.7, 118.5, 105.3, 60.8, 41.8, 35.1, 31.6, 29.3, 29.0, 25.6, 22.6, 14.2, 14.1., 13.8.**HRMS** (ESI) m/z calculated for $C_{26}H_{42}N_6O_2Na$ $[M+Na]^+$: 493.3267, found: 493.3247.

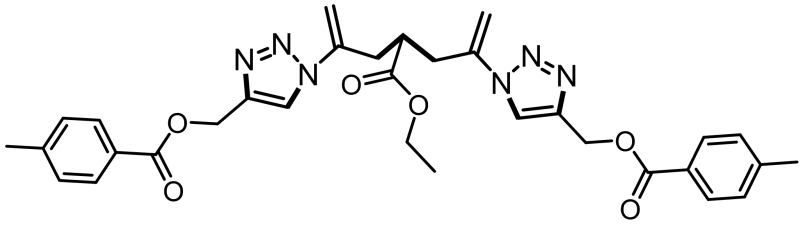


(6u) 0.25 mmol scale: Prepared following the genernal procedure showed above using 5-chloropentyne (58.3 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (86.50 mg, 76%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 (s, 2H), 5.36 (s, 2H), 5.03 (s, 2H), 4.08 (q, *J* = 7.2 Hz, 2H), 3.60 (t, *J* = 6.4 Hz, 4H), 3.10 (d, *J* = 7.0 Hz, 4H), 3.00 (q, *J* = 6.7 Hz, 1H), 2.90 (t, *J* = 7.3 Hz, 4H), 2.23-2.16 (m, 4H), 1.20 (t,

J = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.5, 146.6, 140.6, 119.2, 105.7, 60.9, 44.2, 41.6, 35.1, 31.7, 22.6, 14.2. **HRMS** (ESI) m/z calculated for $C_{20}H_{28}N_6O_2Na$ $[M+Na]^+$: 477.1549, found: 477.1549.

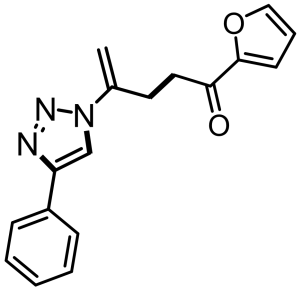


(6v) 0.25 mmol scale: Prepared following the genernal procedure showed above using prop-2-yn-1-yl benzoate (88.0 mg, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (111.19 mg, 78%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 8.2 Hz, 4H), 7.93 (s, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 4H), 5.47 (s, 4H), 5.41 (d, *J* = 1.8 Hz, 2H), 5.07 (s, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 3.12 (d, *J* = 6.5 Hz, 4H), 3.08 – 3.02 (m, 1H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.4, 166.4, 143.1, 140.5, 133.3, 130.0, 128.4, 122.0, 106.5, 61.0, 57.9, 41.6, 35.01, 14.2. **HRMS** (ESI) m/z calculated for $C_{30}H_{30}N_6O_6Na$ $[M+Na]^+$: 593.2125, found: 593.2165.

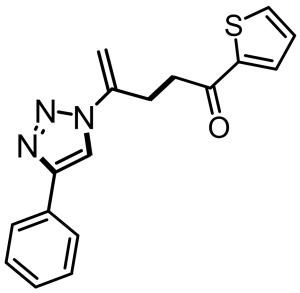


(6w) 0.25 mmol scale: Prepared following the genernal procedure showed above using prop-2-yn-1-yl 4-methylbenzoate (95.7 mg, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), ethyl 4,4,4-trifluoro-3-oxobutanoate (36.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as

yellow oily liquid (107.70 mg, 72%); **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 7.9 Hz, 6H), 7.22 (d, *J* = 8.0 Hz, 4H), 5.45 (s, 4H), 5.41 (d, *J* = 1.8 Hz, 2H), 5.06 (s, 2H), 4.04 (q, *J* = 7.2 Hz, 2H), 3.11 (d, *J* = 6.3 Hz, 4H), 3.09 – 3.02 (m, 1H), 2.39 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 173.4, 166.5, 144.0, 143.3, 140.5, 129.8, 129.1, 126.9, 121.9, 106.5, 61.0, 57.8, 41.6, 21.7, 14.2. **HRMS** (ESI) m/z calculated for $C_{32}H_{24}N_6O_6Na$ $[M+Na]^+$:621.2438, found: 621.2445.

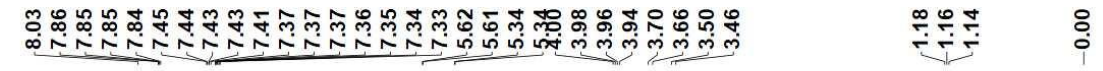


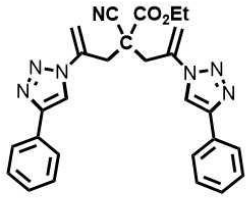
(6x) **0.25 mmol scale**: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), 4,4,4-trifluoro-1-(2-furanyl)-1,3-butanedione (37.1 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (57.16 mg, 78%); **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.02 (s, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.56 (s, 1H), 7.45 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 3.6 Hz, 1H), 6.53 (d, J = 3.6 Hz, 1H), 5.48 (s, 1H), 5.11 (s, 1H), 3.26 – 3.18 (m, 4H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 191.3, 143.8, 142.4, 134.0, 132.3, 130.1, 128.9, 128.5, 128.3, 117.4, 105.0, 37.1, 27.9. **HRMS** (ESI) m/z calculated for$C_{17}H_{15}N_3O_2Na$ [M+Na]+: 316.1062, found: 316.1036.



(6y) **0.25 mmol scale**: Prepared following the genernal procedure showed above using phenylacetylene (60.4 μL, 0.55 mmol, 2.2 eq.), VA (224.8 mg, 0.55 mmol, 2.2 eq.), 4,4,4-trifluoro-1-(thiophen-2-yl)butane-1,3-dione (38.6 μL, 0.25 mmol, 1.0 eq.), triethylamine (Et_3N) (139.0 μL, 1.0 mmol, 4.0 eq.), CuI (190.4 mg, 0.1 mmol, 0.4 eq.) and $Pd(PPh_3)_4$ (11.5 mg, 0.01 mmol, 0.04 eq.). The desired product was purified by a silica gel column chromatography (petroleumether/ethyl acetate=2:1) as yellow oily liquid (58.72 mg, 76%); **^{1}H NMR** (400 MHz, Chloroform-d) δ 8.05 (s, 1H), 7.87 (d, J = 7.4 Hz, 2H), 7.70 (s, 1H), 7.62 (d, J = 4.8 Hz, 1H), 7.42 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.1 Hz, 1H), 7.11 (s, 1H), 5.47 (s, 1H), 5.11 (s, 1H), 3.26 (s, 4H); **^{13}C NMR** (100 MHz, Chloroform-d) δ 187.4, 152.4, 147.8, 146.6, 142.4, 130.2, 128.9, 128.5, 125.9, 117.5, 117.3, 112.3, 105.0, 36.1, 27.4. **HRMS** (ESI) m/z calculated for $C_{17}H_{15}N_3OSNa$ [M+Na]+: 332.0834, found: 332.0838.

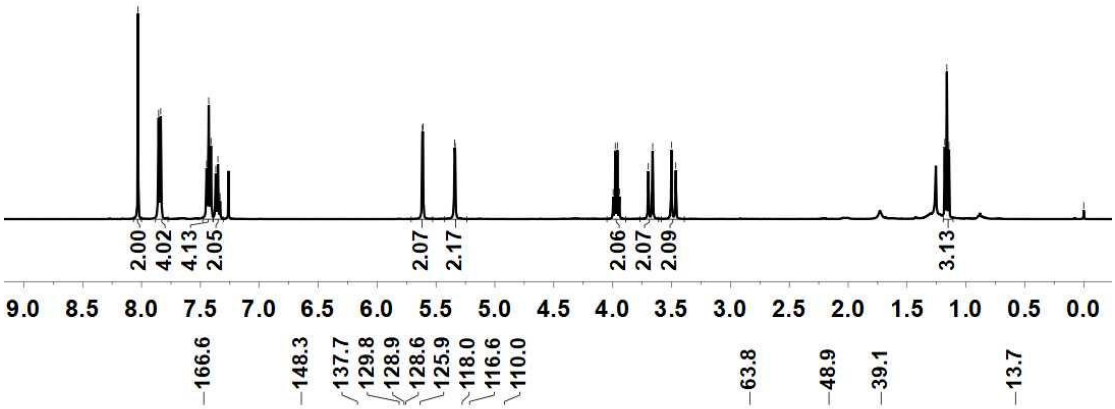
III. NMR spectra copies

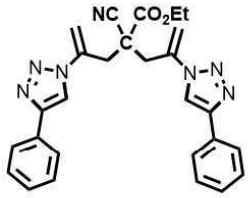




3a

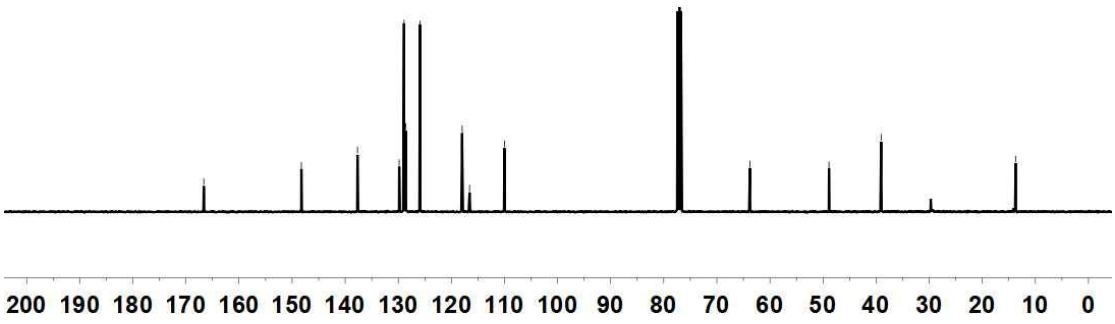
$CDCl_3$ 400MHz

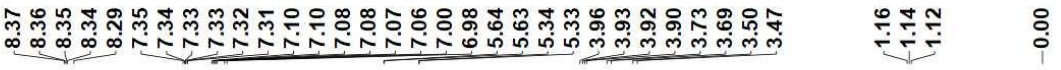


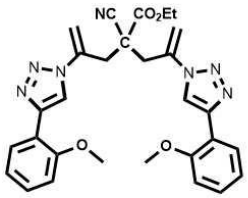


3a

$CDCl_3$ 100MHz

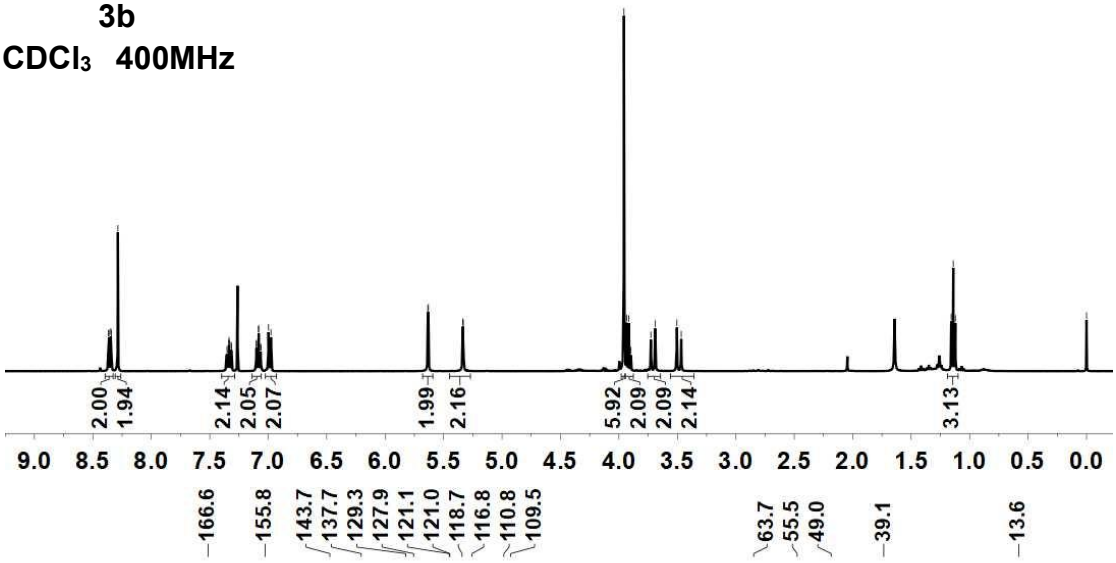


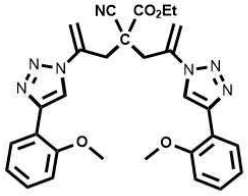




3b

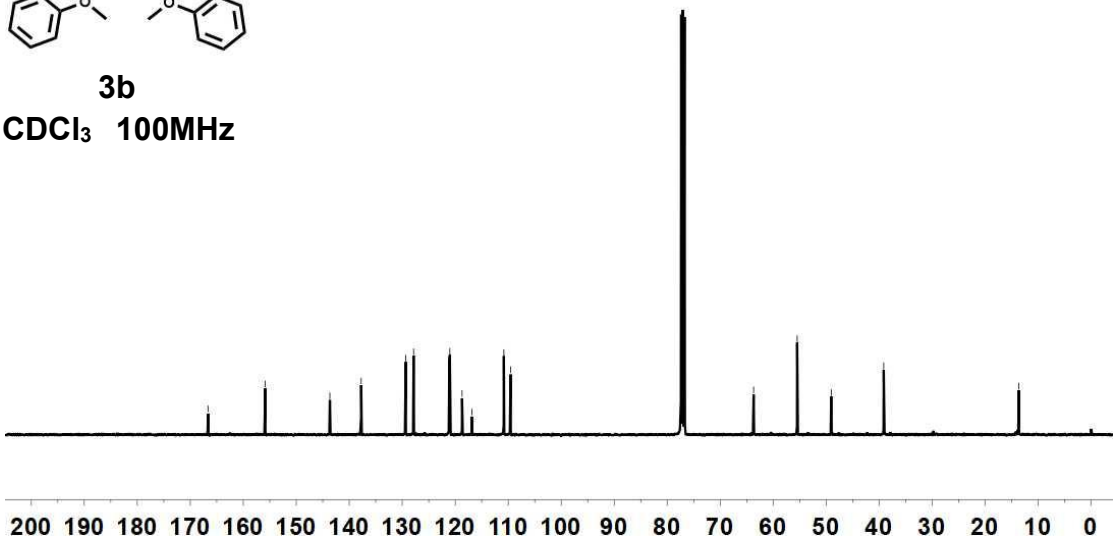
$CDCl_3$ 400MHz

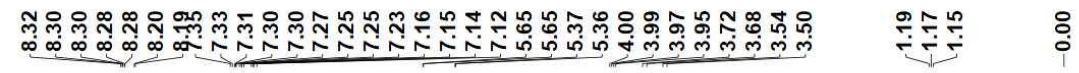


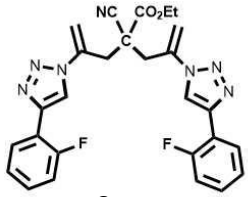


3b

$CDCl_3$ 100MHz

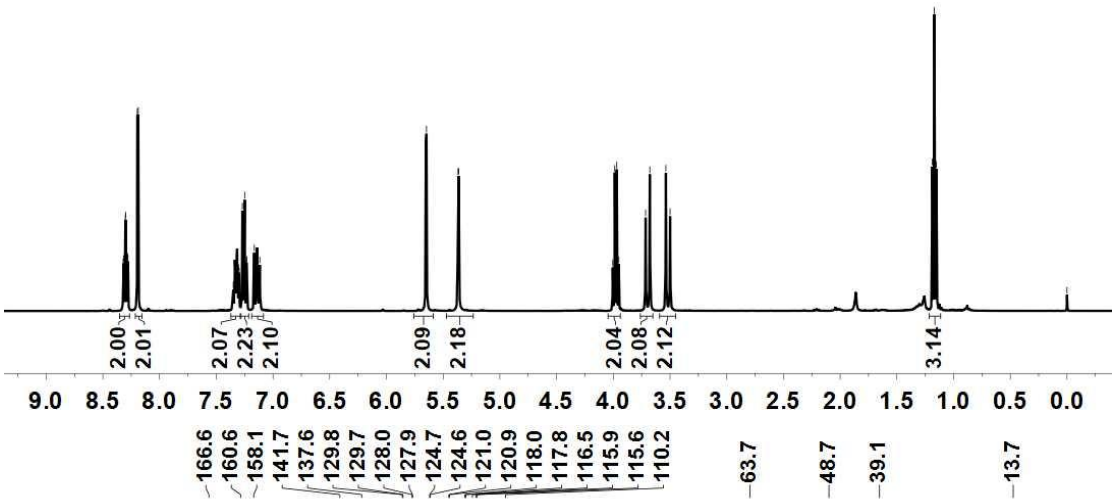


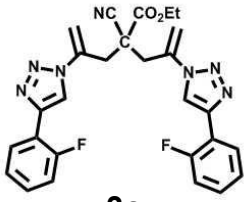




3c

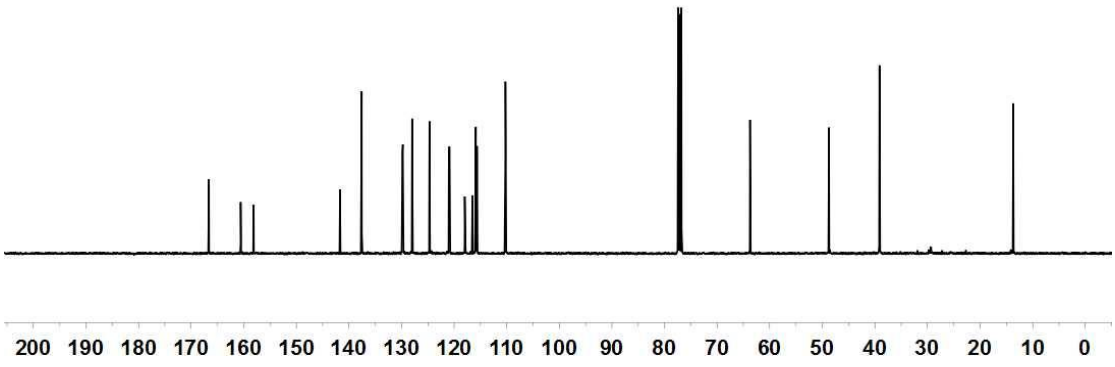
$CDCl_3$ 400MHz

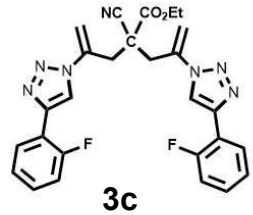




3c

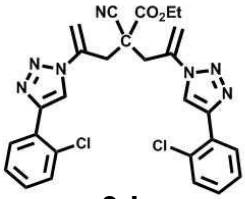
$CDCl_3$ 100MHz





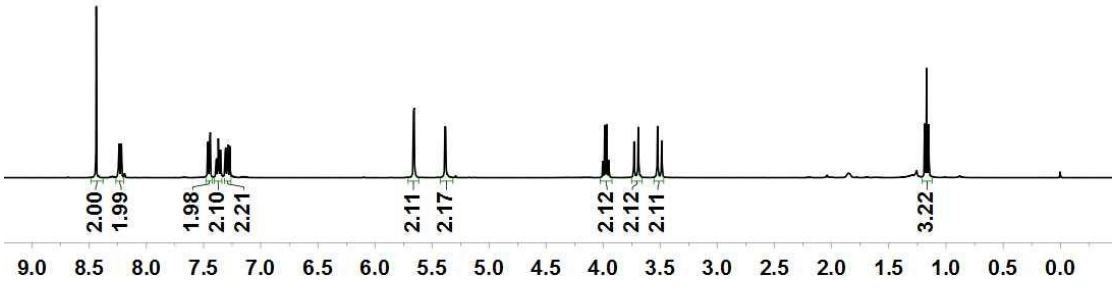
3c

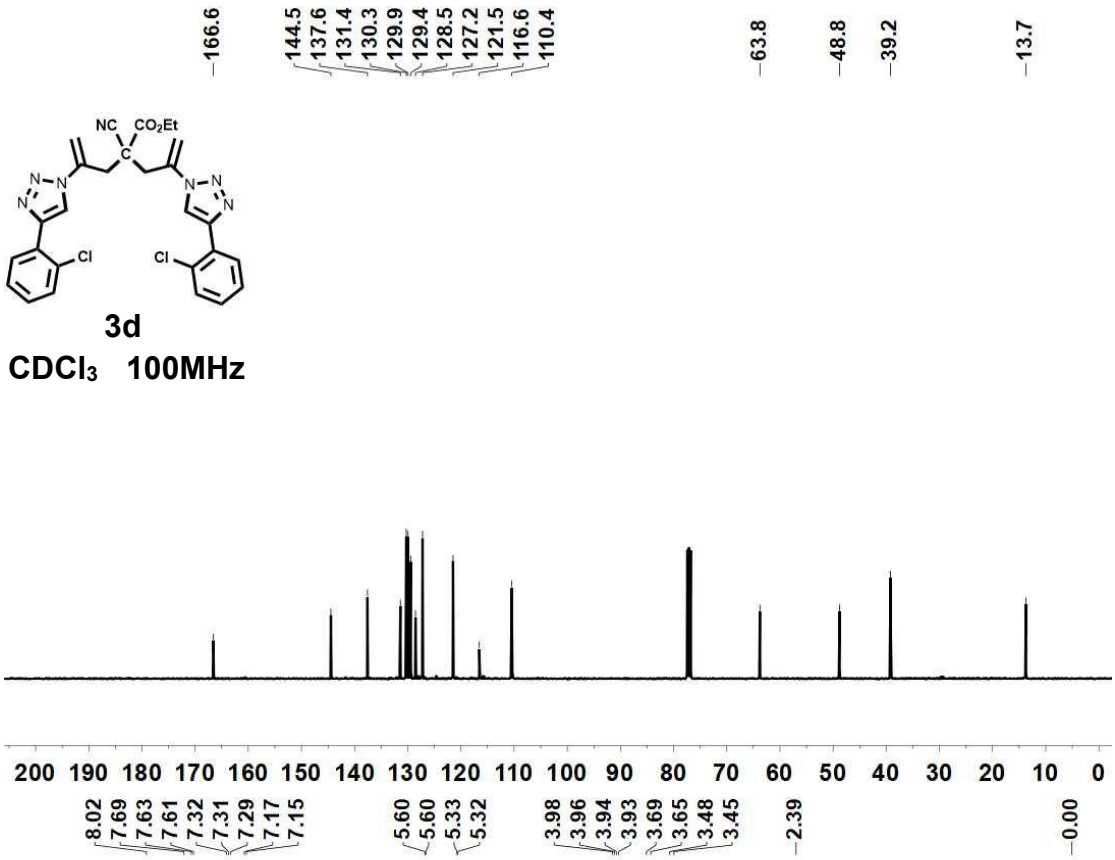
$CDCl_3$ 376MHz



3d

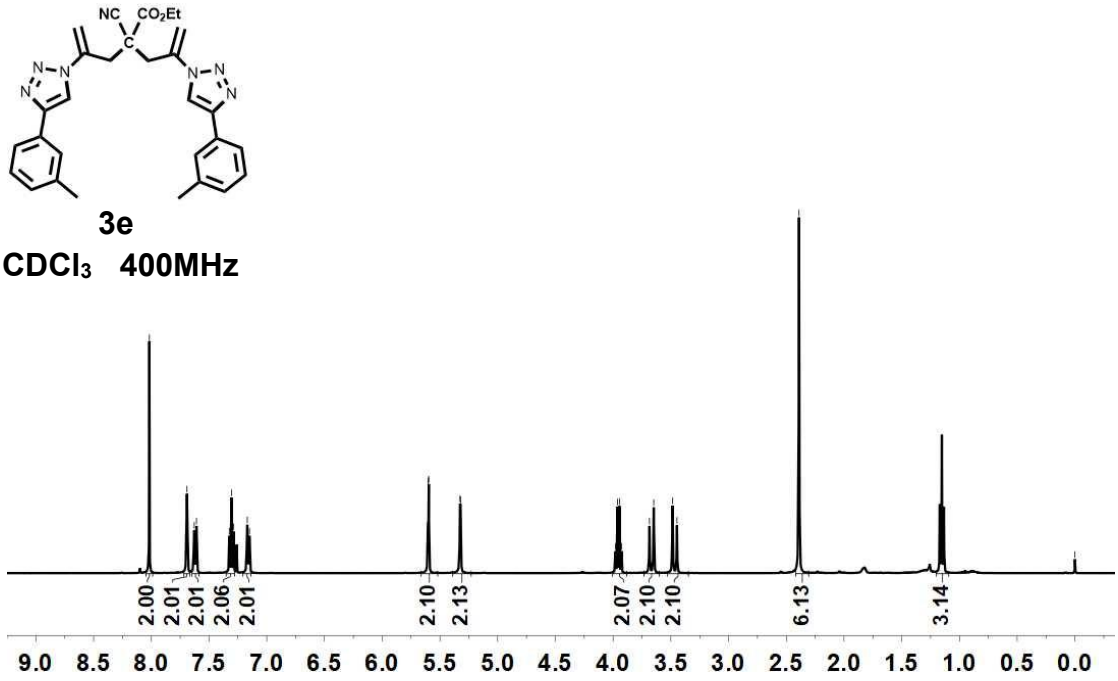
$CDCl_3$ 400MHz





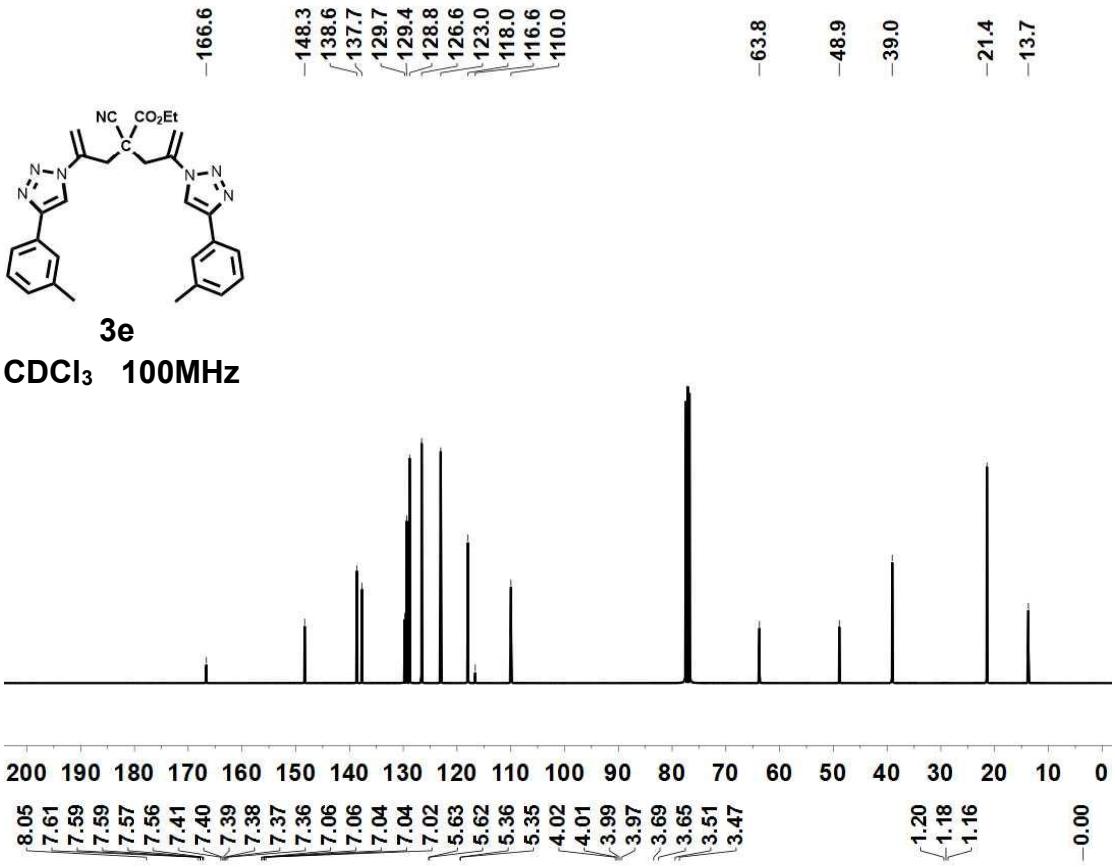
3d

$CDCl_3$ 100MHz



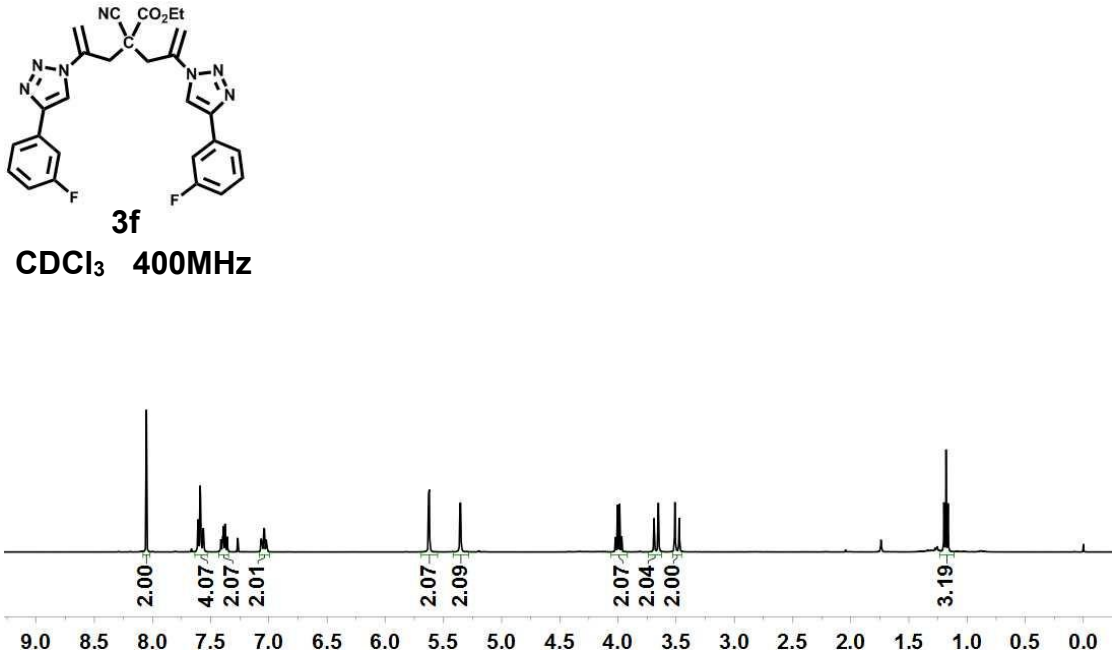
3e

$CDCl_3$ 400MHz



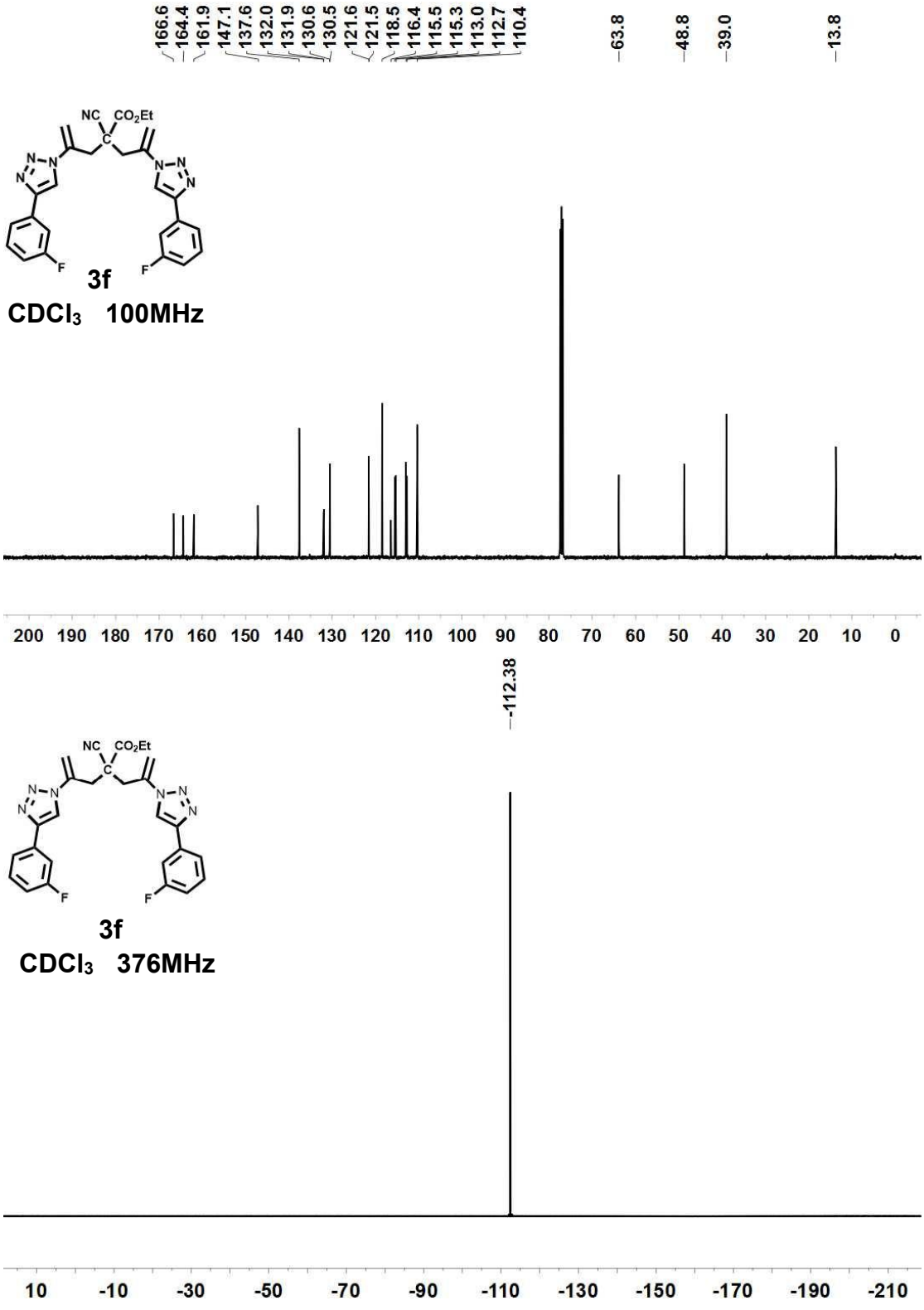
3e

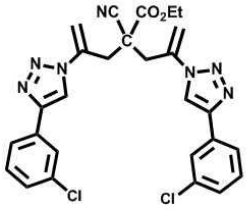
$CDCl_3$ 100MHz



3f

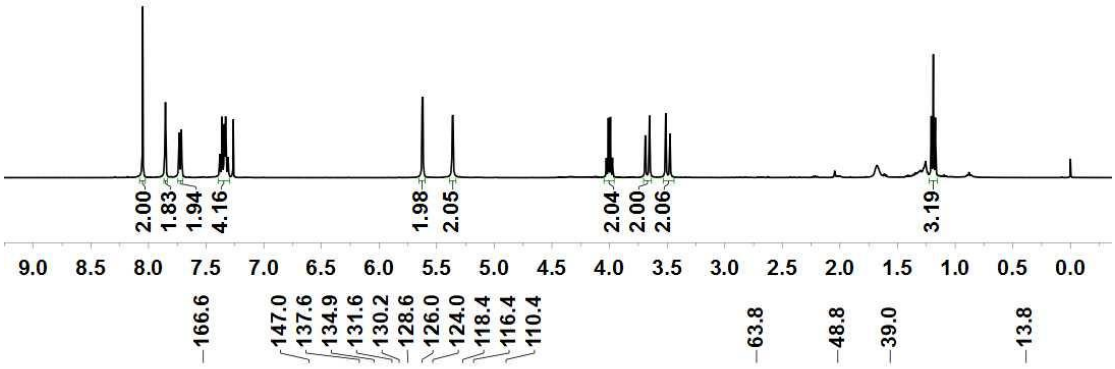
$CDCl_3$ 400MHz

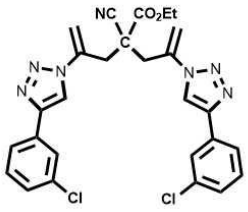

166.6
164.4
161.9
147.1
137.6
132.0
131.9
130.6
130.5
121.6
121.5
118.5
116.4
115.5
115.3
113.0
112.7
110.4
63.8
48.8
39.0
13.8
NC
CO2Et
3f
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
-112.38
NC
CO2Et
3f
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210



3g

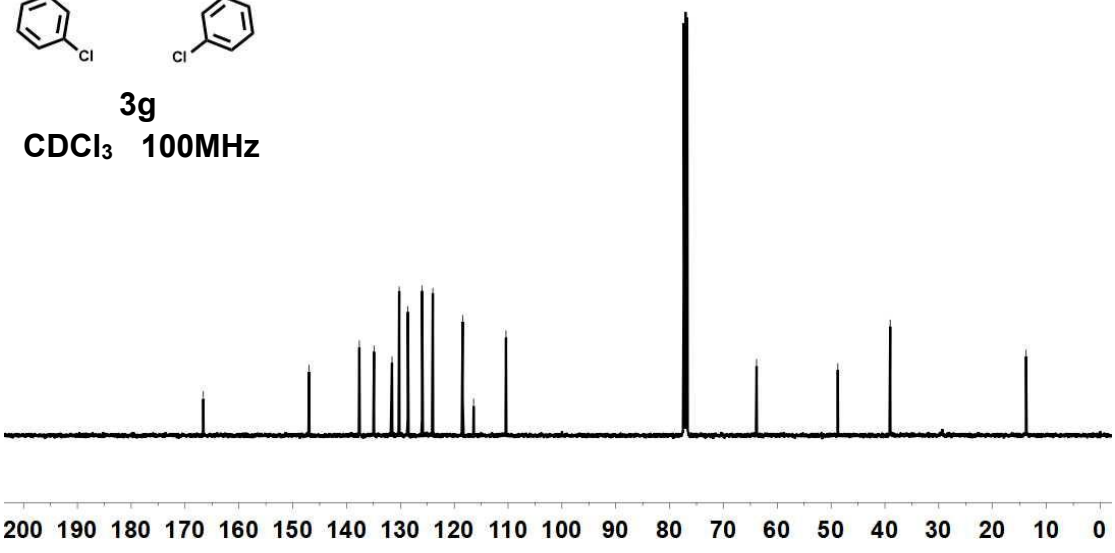
$CDCl_3$ 400MHz

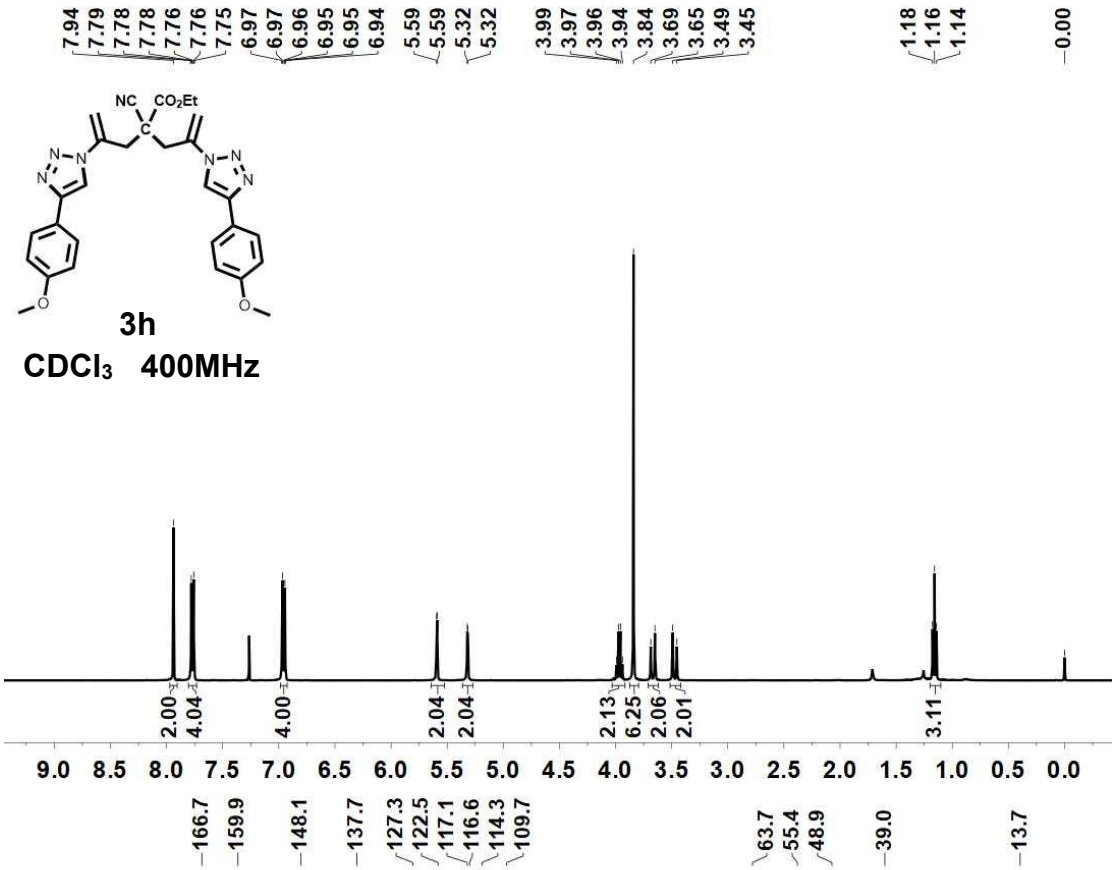


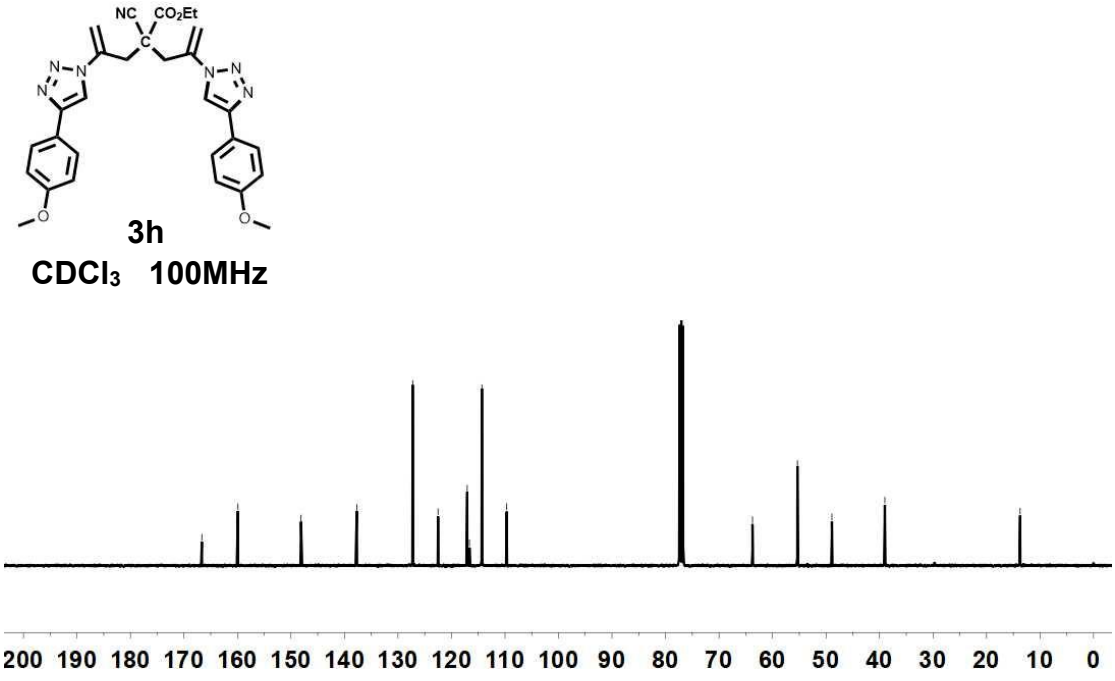


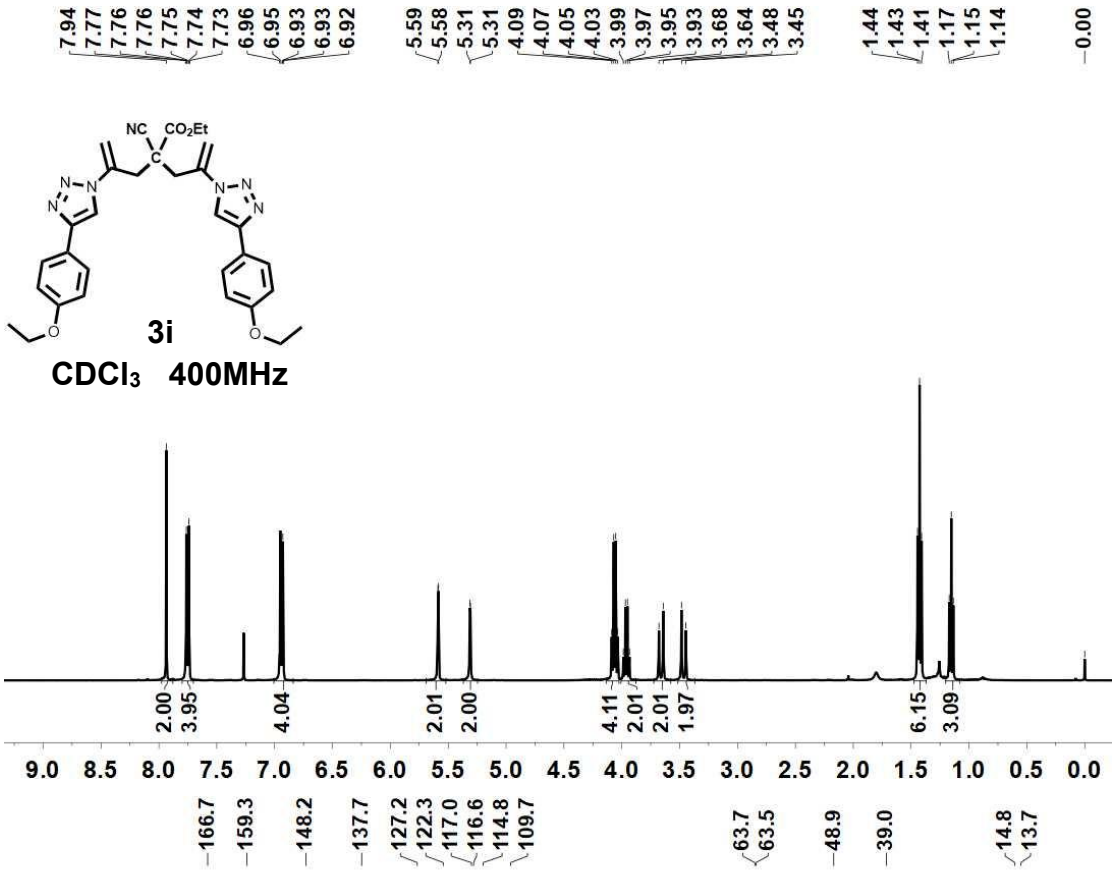
3g

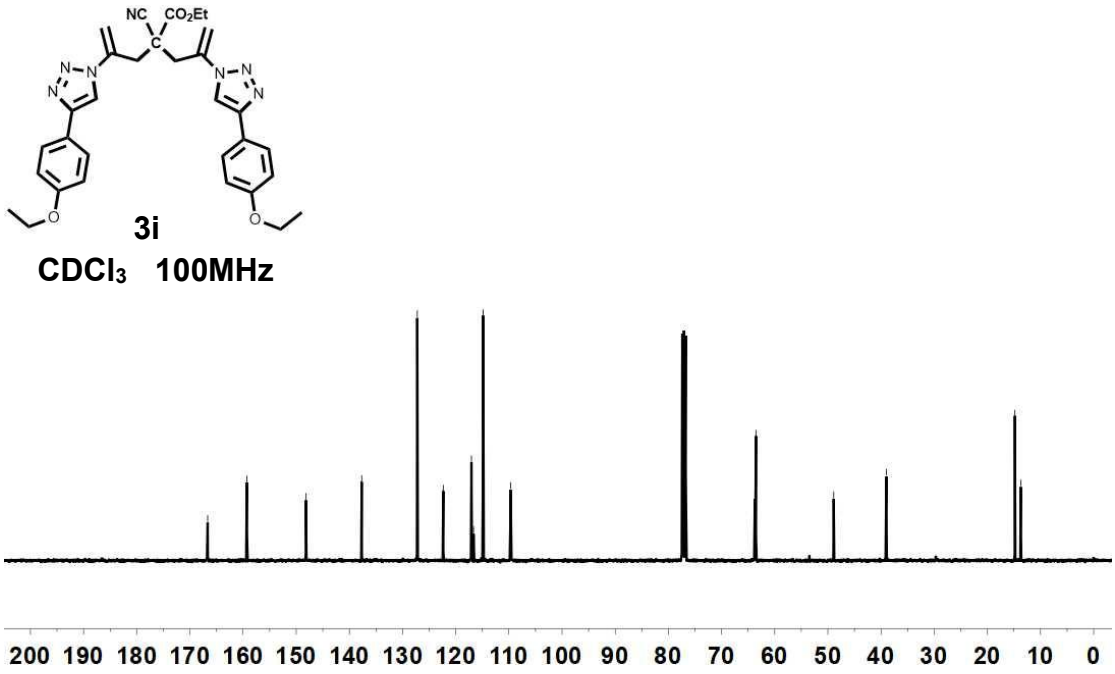
$CDCl_3$ 100MHz

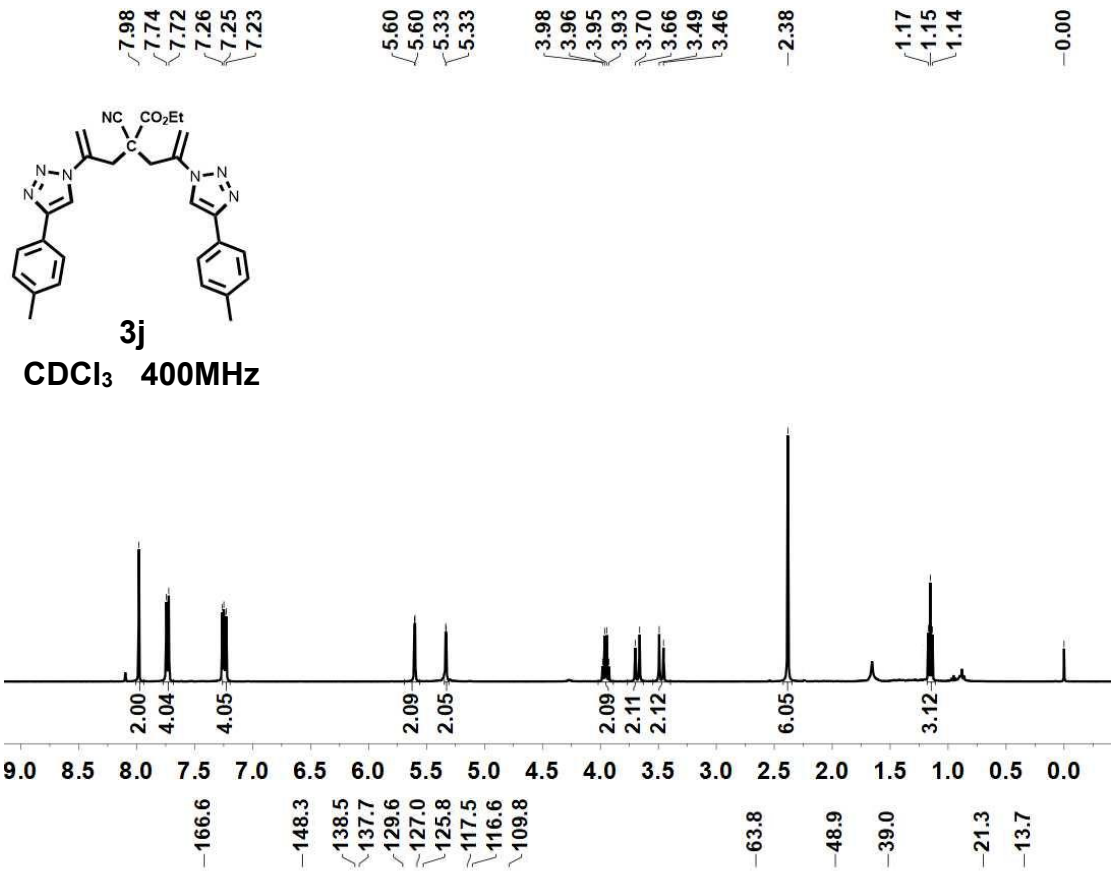



7.94
7.79
7.78
7.78
7.76
7.76
7.75
6.97
6.97
6.96
6.95
6.95
6.94
5.59
5.59
5.32
5.32
3.99
3.97
3.96
3.94
3.84
3.69
3.65
3.49
3.45
1.18
1.16
1.14
0.00
NC
CO2Et
3h
CDCl3 400MHz
2.00
4.04
4.00
2.04
2.04
2.13
6.25
2.06
2.01
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


166.7
159.9
148.1
137.7
127.3
122.5
117.1
116.6
114.3
109.7
63.7
55.4
48.9
39.0
13.7
NC
CO2Et
3h
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.94 7.77 7.76 7.76 7.75 7.74 7.73 6.96 6.95 6.93 6.93 6.92
5.59 5.58 5.31 5.31 4.09 4.07 4.05 4.03 3.99 3.97 3.95 3.93 3.68 3.64 3.48 3.45
1.44 1.43 1.41 1.17 1.15 1.14
0.00
NC CO2Et
3i
CDCl3 400MHz
2.00 3.95 4.04 2.01 2.00 4.11 2.01 2.01 1.97 6.15 3.09
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
166.7 159.3 148.2 137.7 127.2 122.3 117.0 116.6 114.8 109.7
63.7 63.5 48.9 39.0 14.8 13.7


NC CO2Et
3i
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

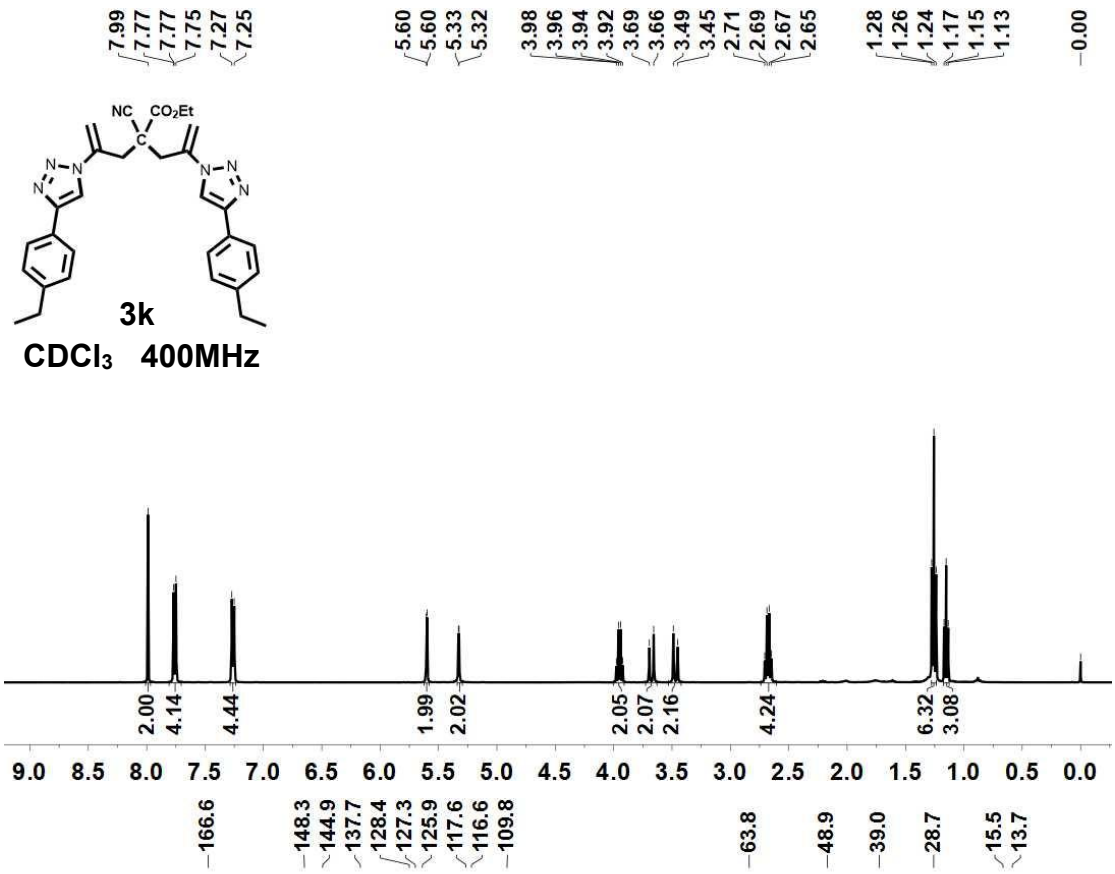


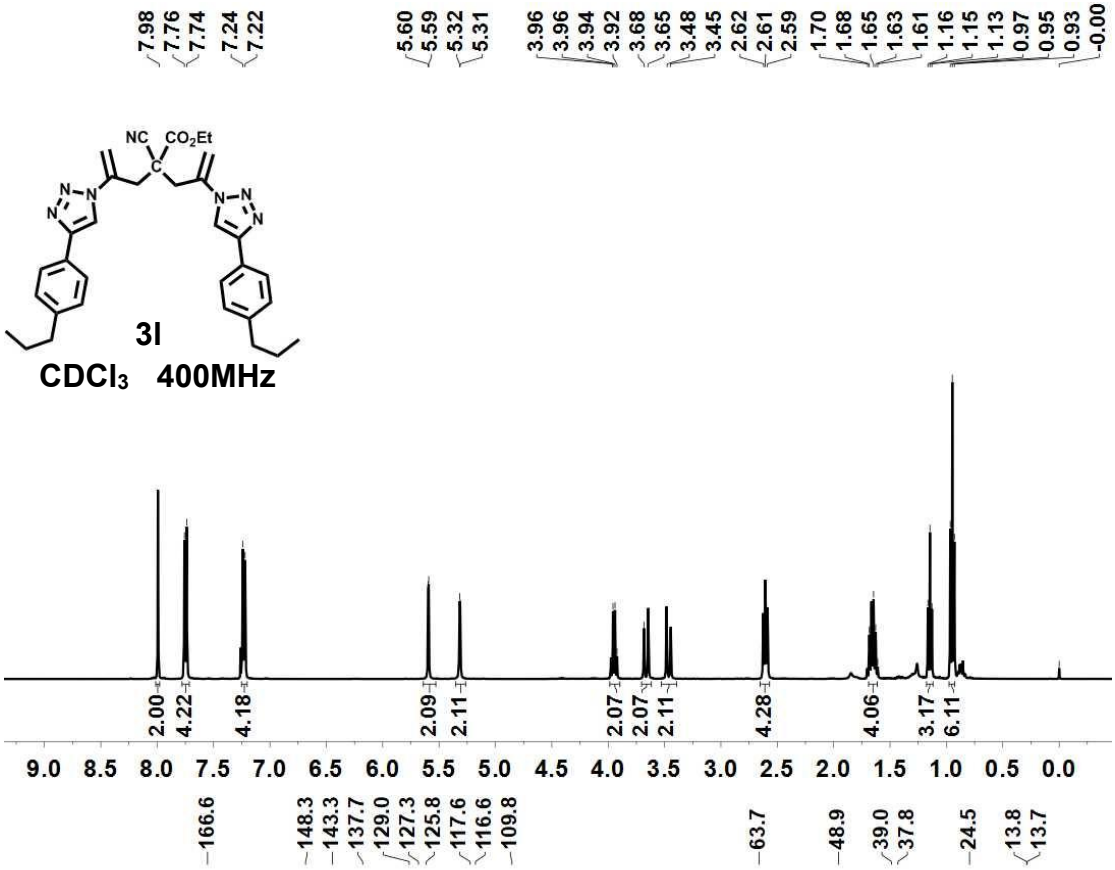
3j

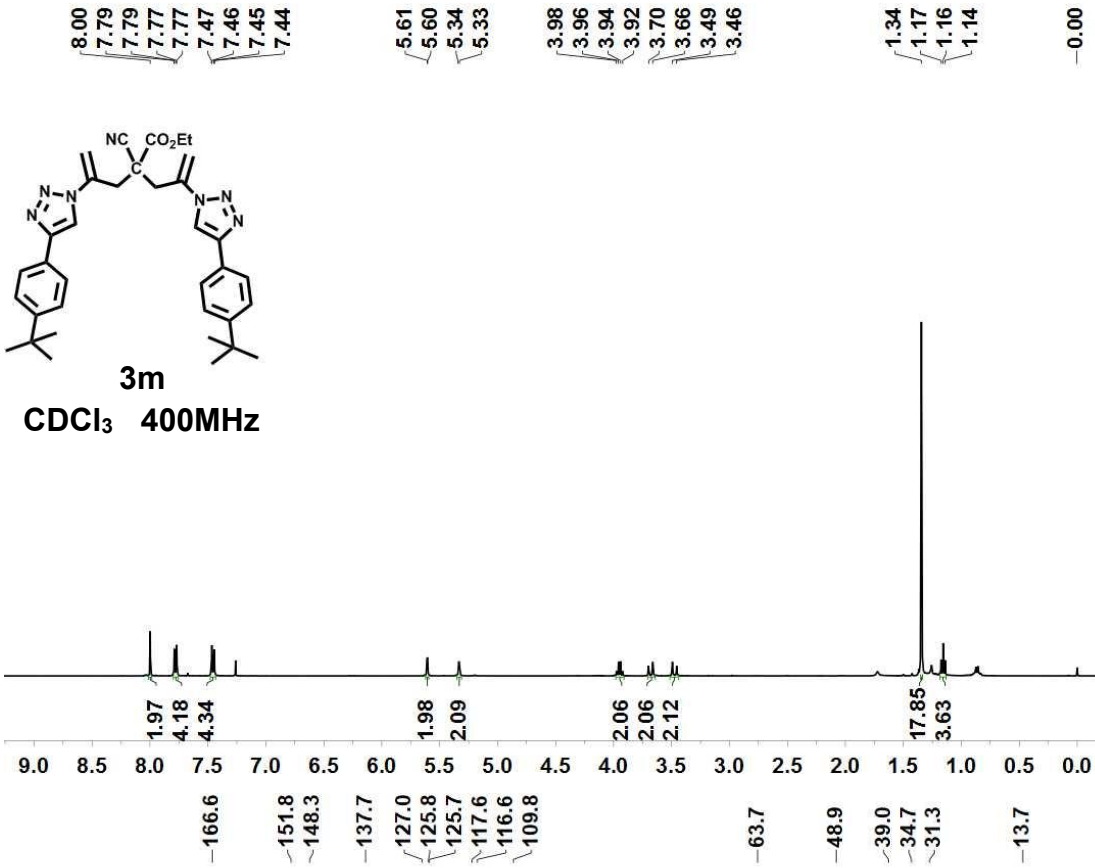
$CDCl_3$ 400MHz

3j

$CDCl_3$ 100MHz

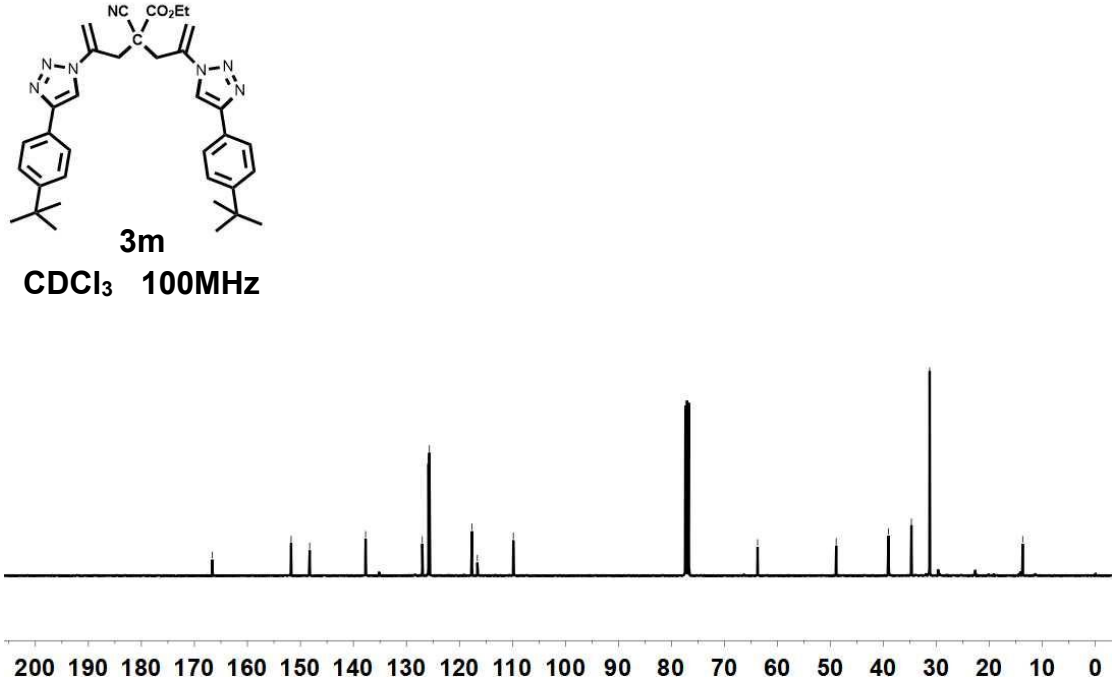

7.99
7.77
7.77
7.75
7.27
7.25
5.60
5.60
5.33
5.32
3.98
3.96
3.94
3.92
3.69
3.66
3.49
3.45
2.71
2.69
2.67
2.65
1.28
1.26
1.24
1.17
1.15
1.13
0.00
NC
CO2Et
3k
CDCl3 400MHz
2.00
4.14
4.44
1.99
2.02
2.05
2.07
2.16
4.24
6.32
3.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
166.6
148.3
144.9
137.7
128.4
127.3
125.9
117.6
116.6
109.8
63.8
48.9
39.0
28.7
15.5
13.7
NC
CO2Et
3k
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


7.98
7.76
7.74
7.24
7.22
5.60
5.59
5.32
5.31
3.96
3.96
3.94
3.92
3.68
3.65
3.48
3.45
2.62
2.61
2.59
1.70
1.68
1.65
1.63
1.61
1.16
1.15
1.13
0.97
0.95
0.93
-0.00
NC
CO2Et
3l
CDCl3 400MHz
2.00
4.22
4.18
2.09
2.11
2.07
2.07
2.11
4.28
4.06
3.17
6.11
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
166.6
148.3
143.3
137.7
129.0
127.3
125.8
117.6
116.6
109.8
63.7
48.9
39.0
37.8
24.5
13.8
13.7
NC
CO2Et
3l
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0



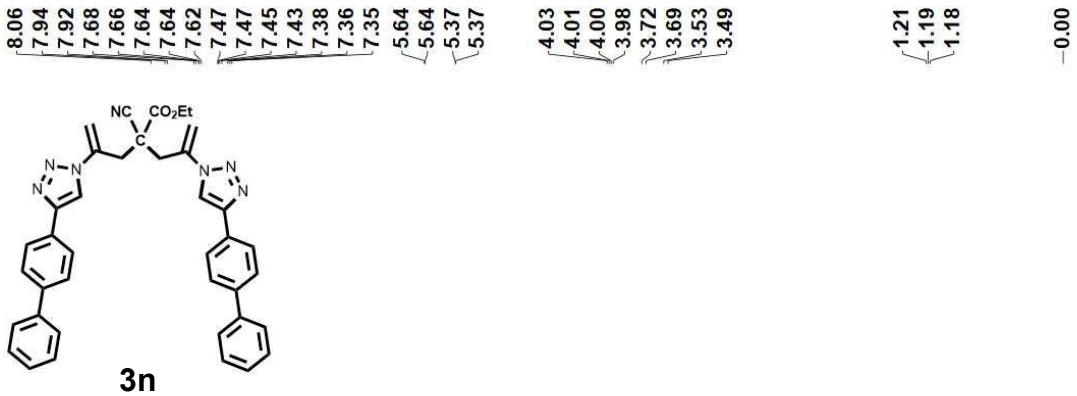
3m

$CDCl_3$ 400MHz



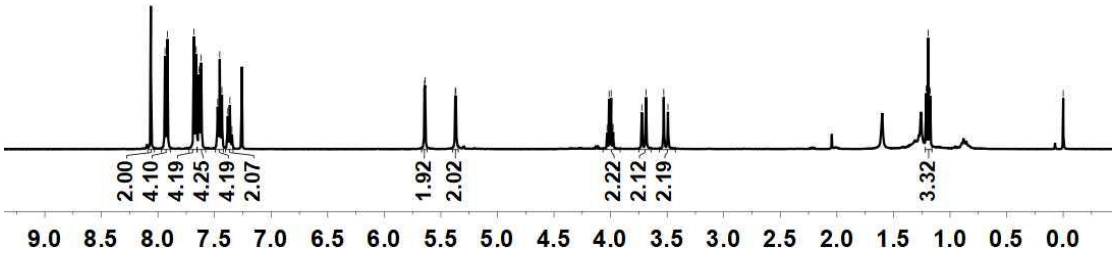
3m

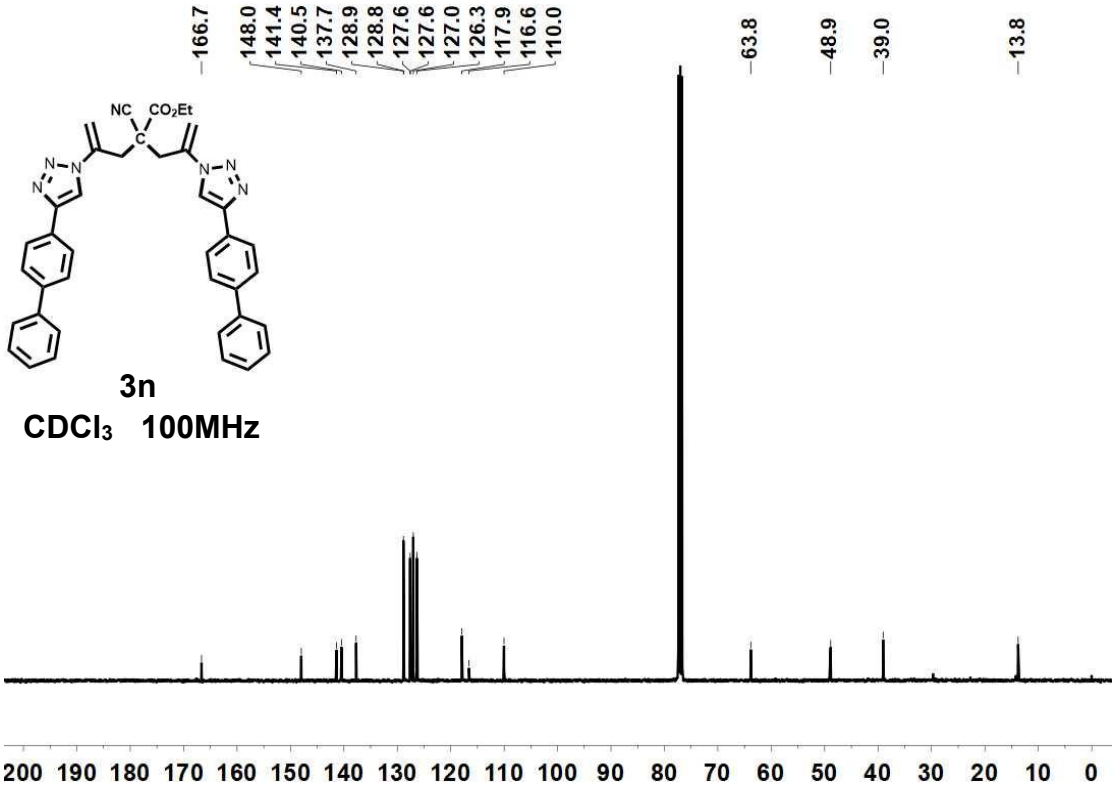
$CDCl_3$ 100MHz



3n

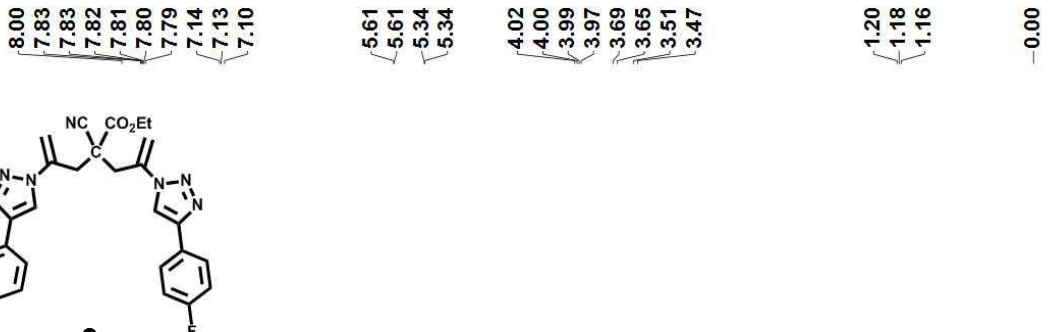
$CDCl_3$ 400MHz





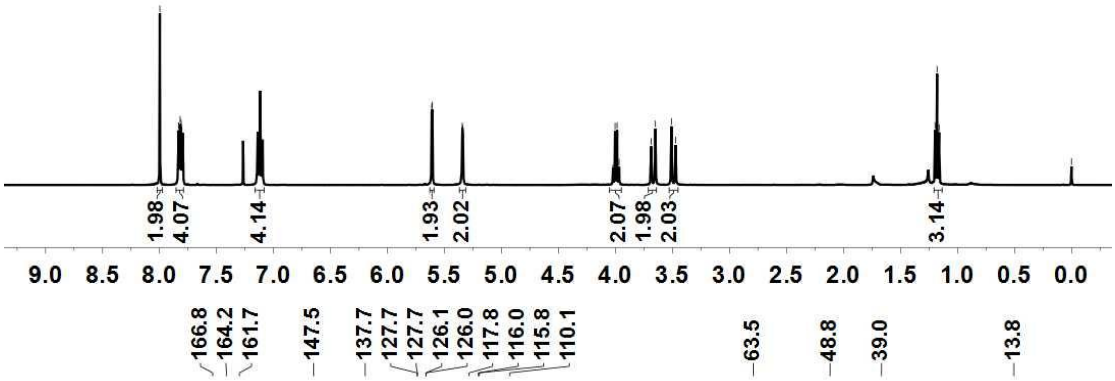
3n

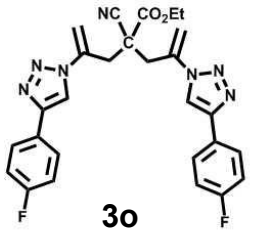
$CDCl_3$ 100MHz



3o

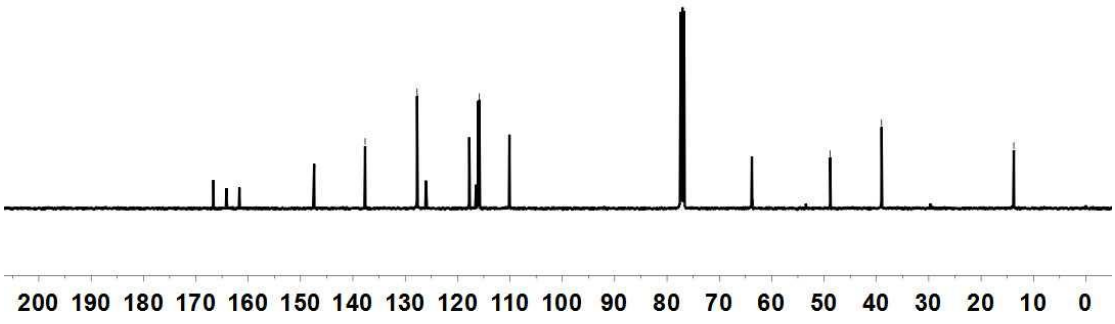
$CDCl_3$ 400MHz

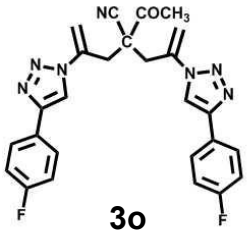




3o

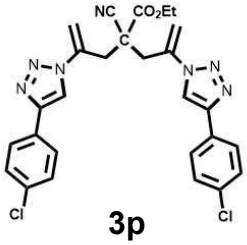
$CDCl_3$ 100MHz





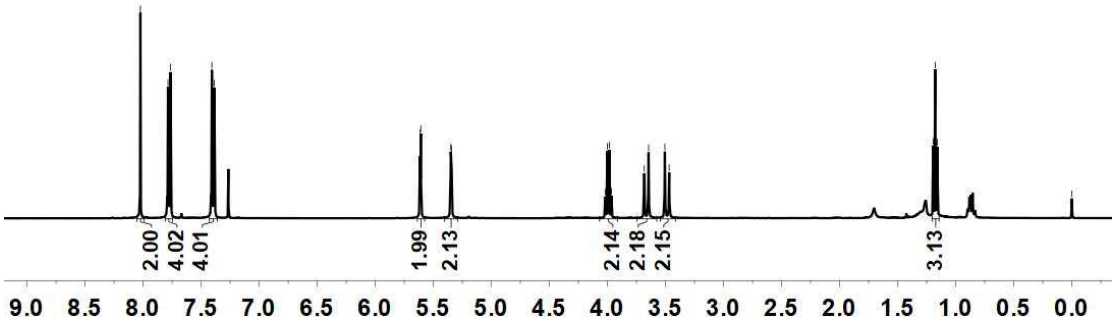
3o

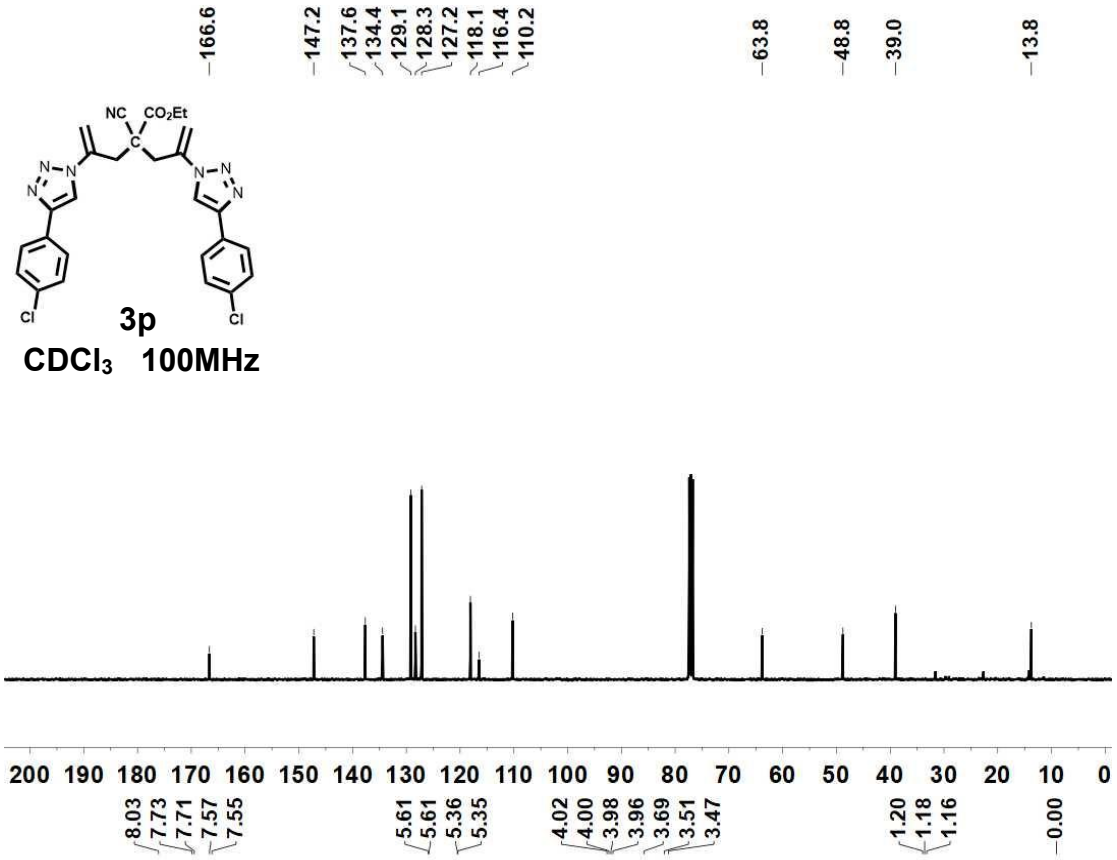
$CDCl_3$ 376MHz



3p

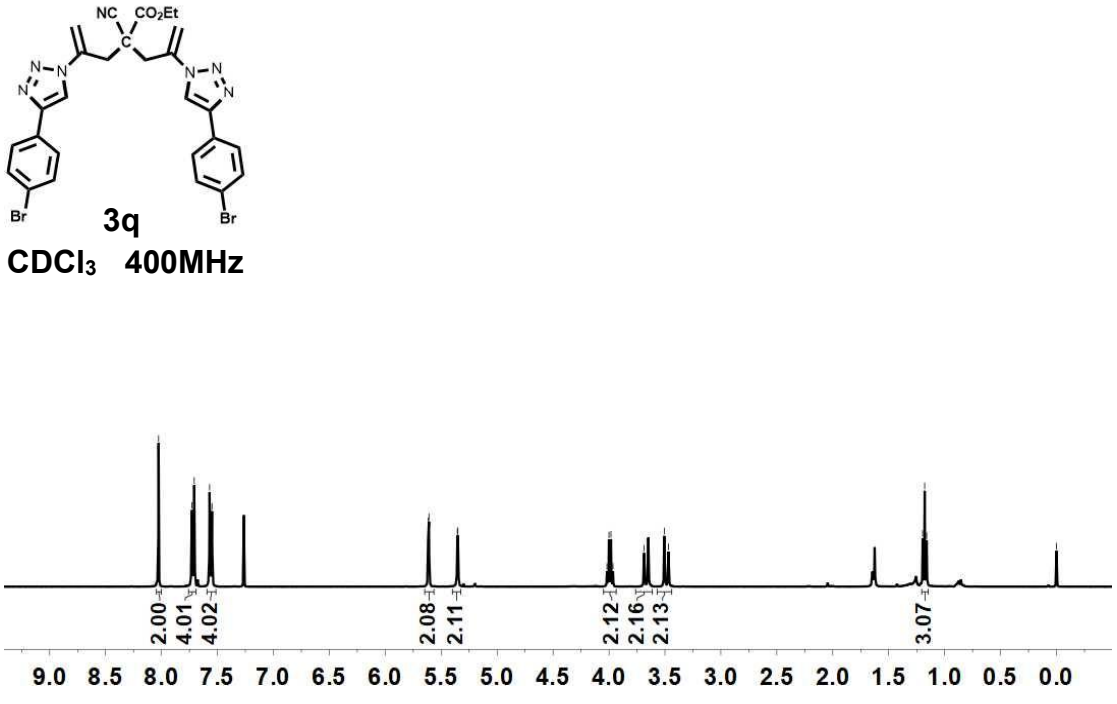
$CDCl_3$ 400MHz





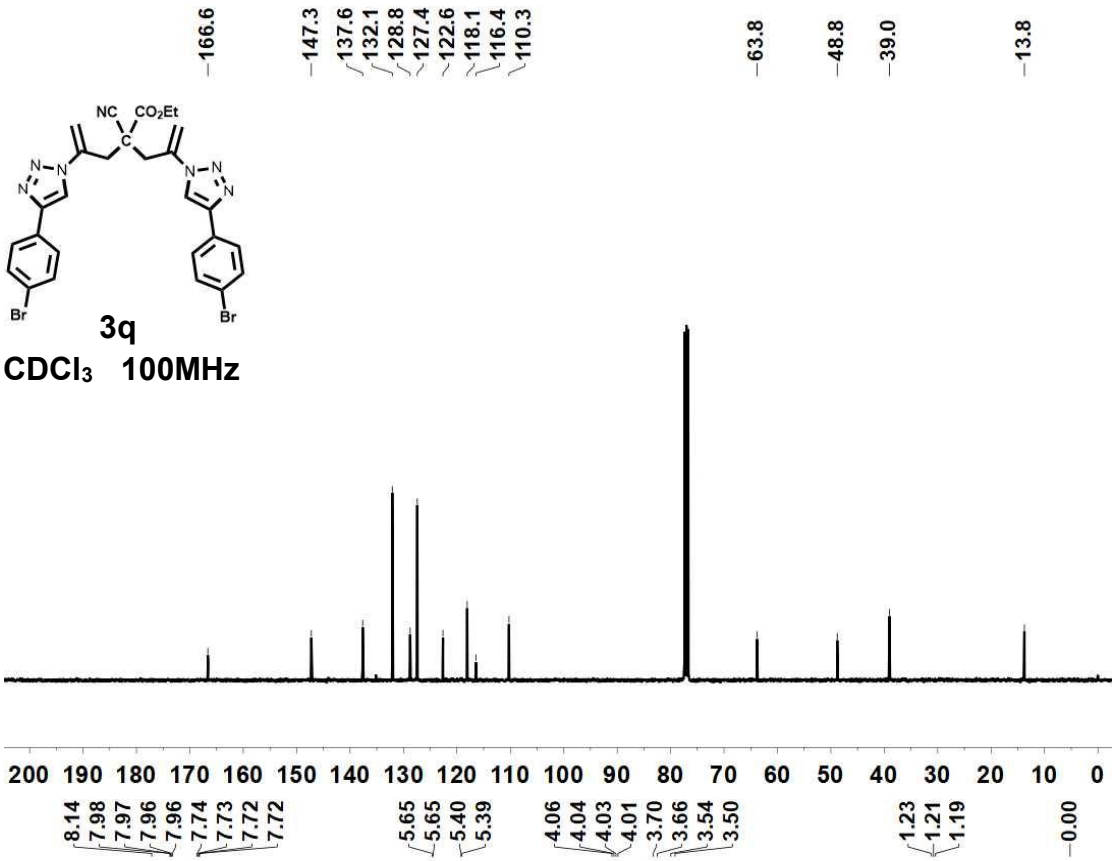
3p

$CDCl_3$ 100MHz



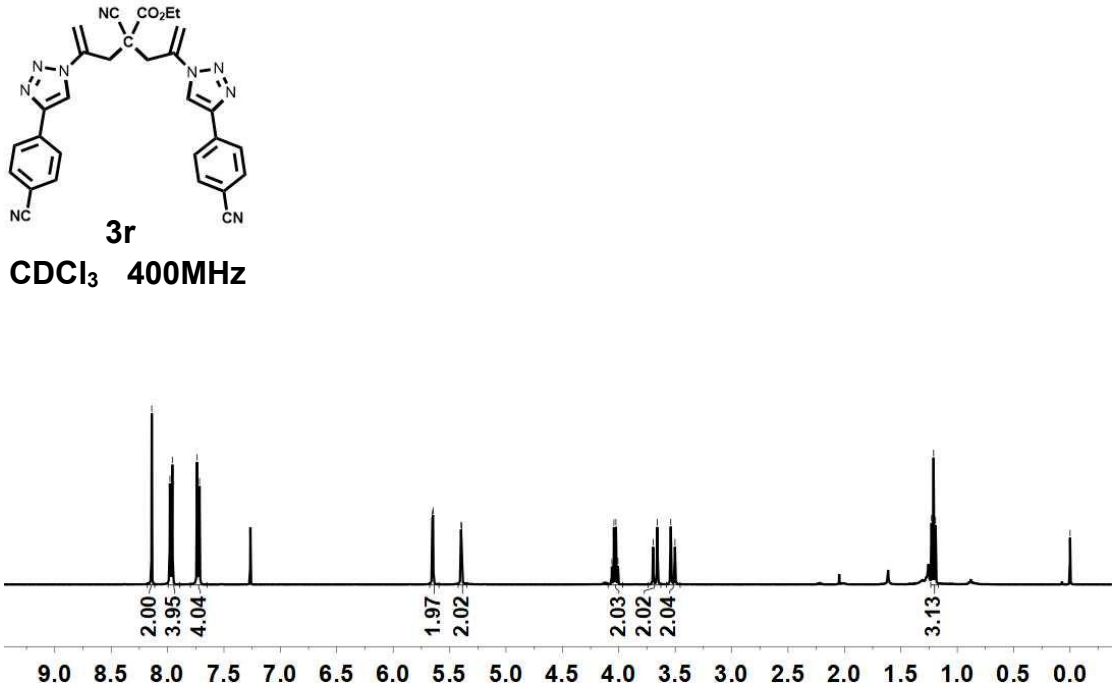
3q

$CDCl_3$ 400MHz



3q

$CDCl_3$ 100MHz

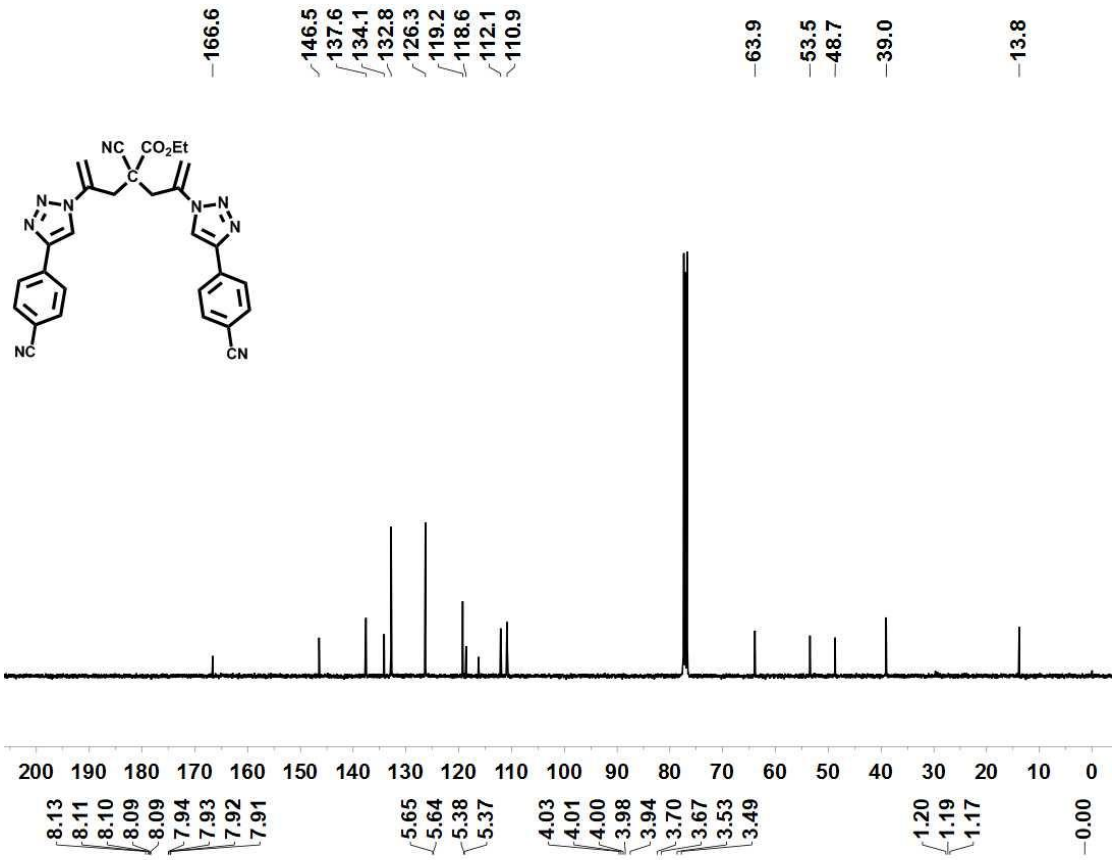


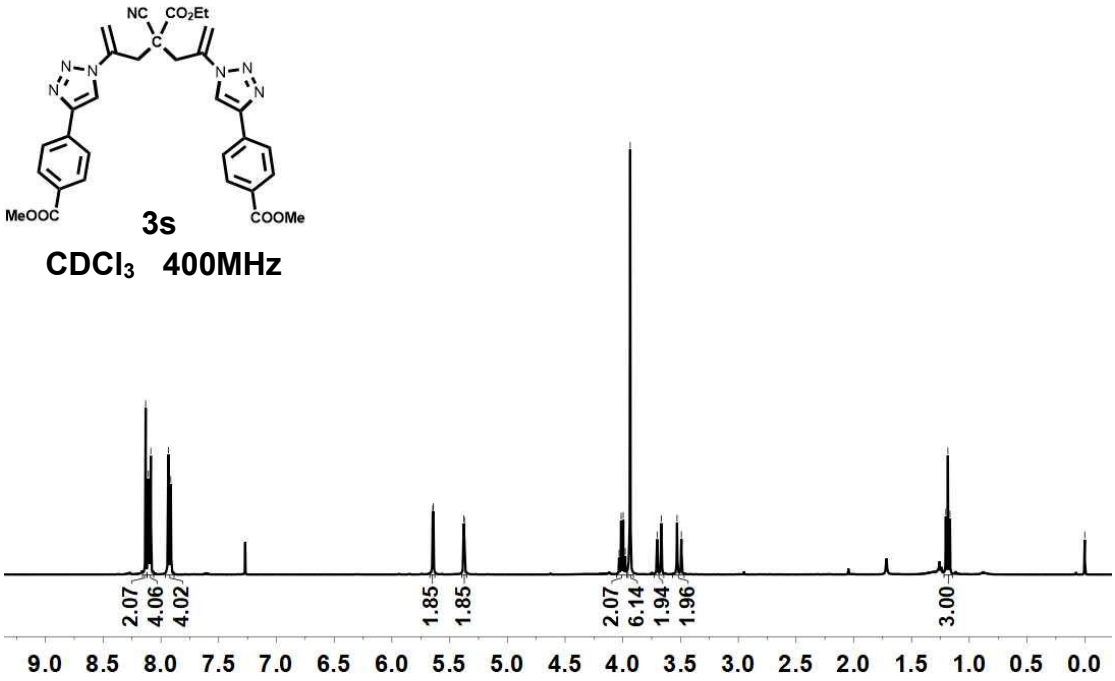
3r

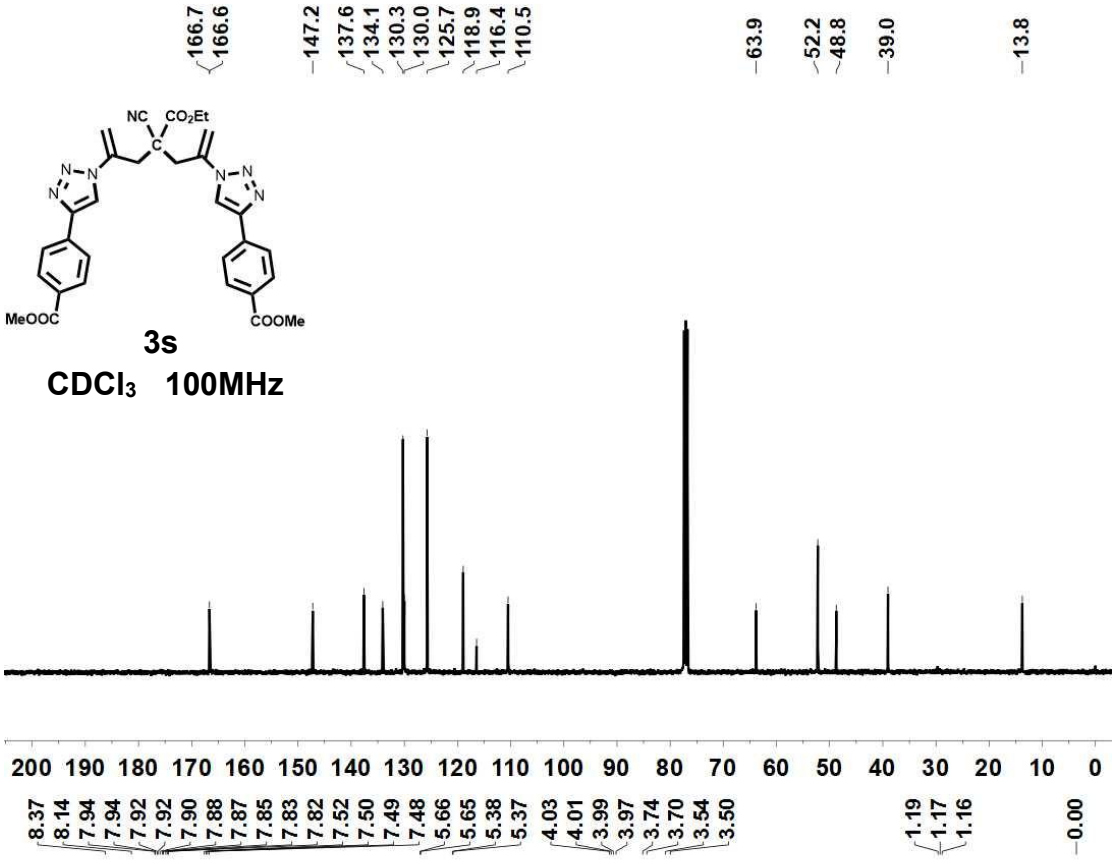
$CDCl_3$ 400MHz

3r

$CDCl_3$ 100MHz

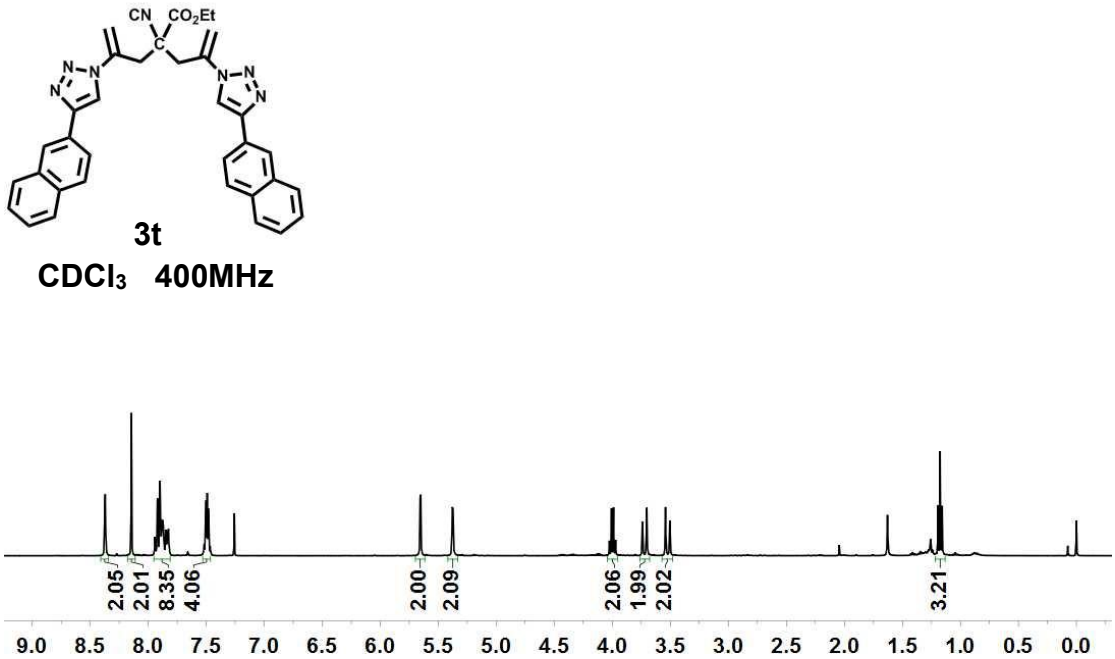

166.6
146.5
137.6
134.1
132.8
126.3
119.2
118.6
112.1
110.9
63.9
53.5
48.7
39.0
13.8
NC
CO2Et
NC
CN
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.13
8.11
8.10
8.09
8.09
7.94
7.93
7.92
7.91
5.65
5.64
5.38
5.37
4.03
4.01
4.00
3.98
3.94
3.70
3.67
3.53
3.49
1.20
1.19
1.17
0.00


NC
CO2Et
MeOOC
COOMe
3s
CDCl3 400MHz
2.07
4.06
4.02
1.85
1.85
2.07
6.14
1.94
1.96
3.00
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



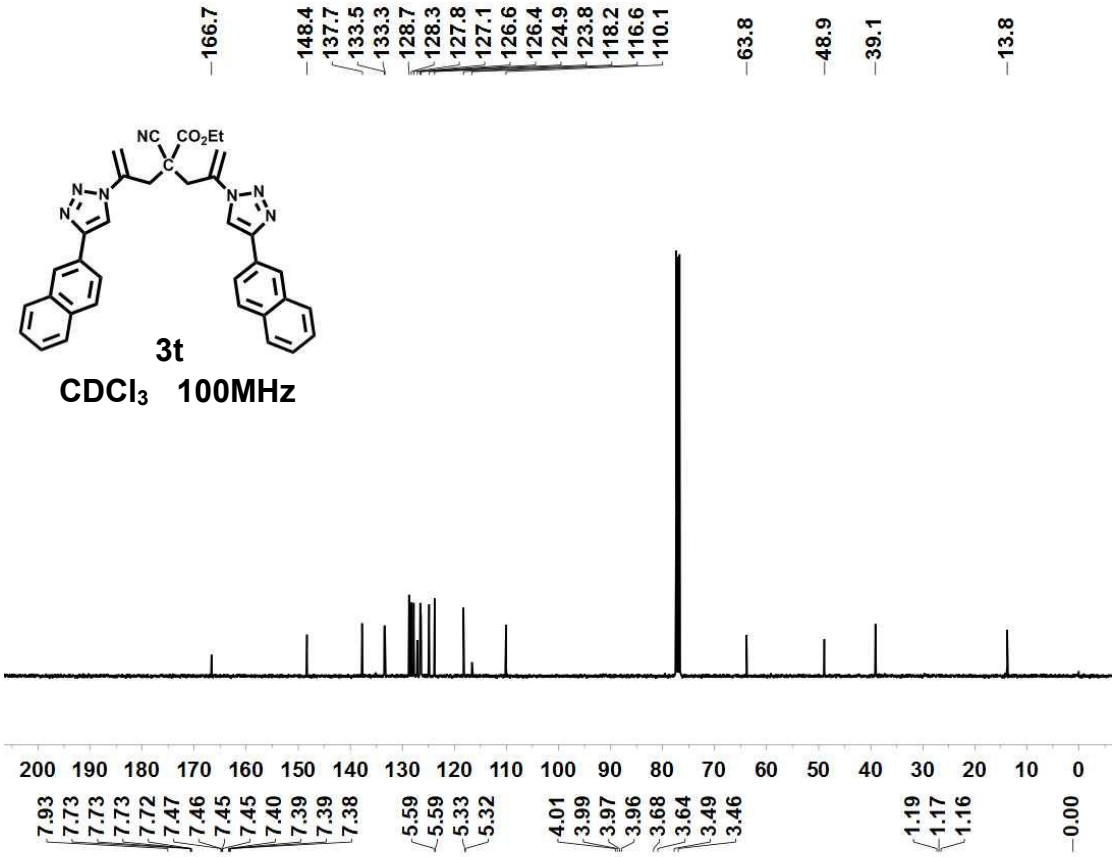
3s

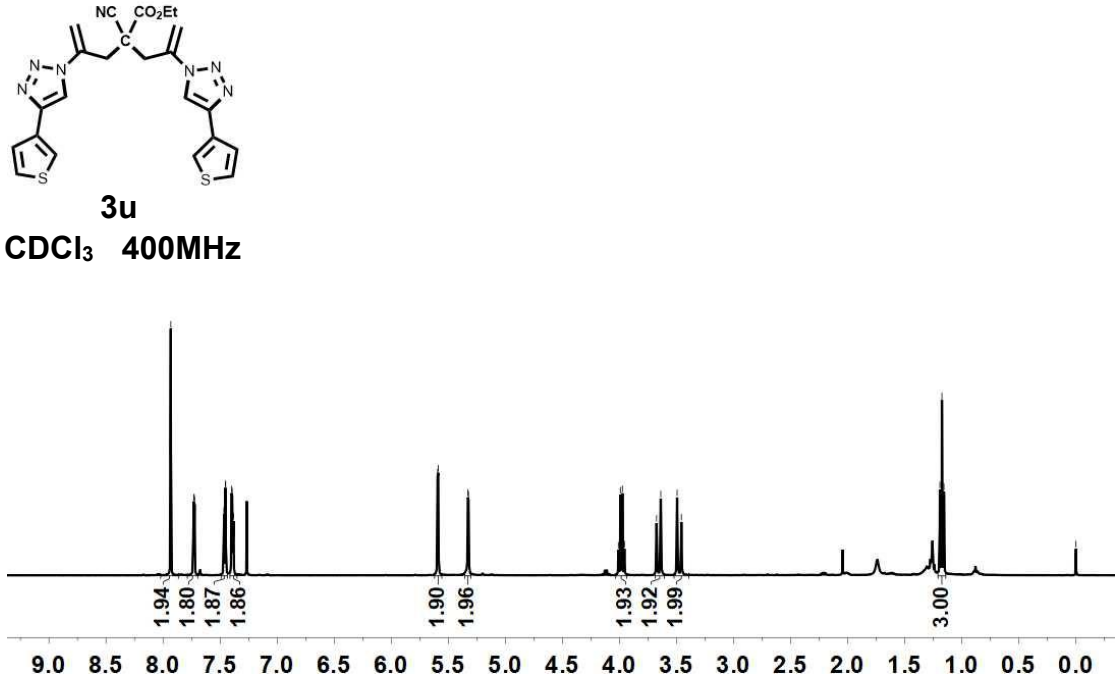
$CDCl_3$ 100MHz

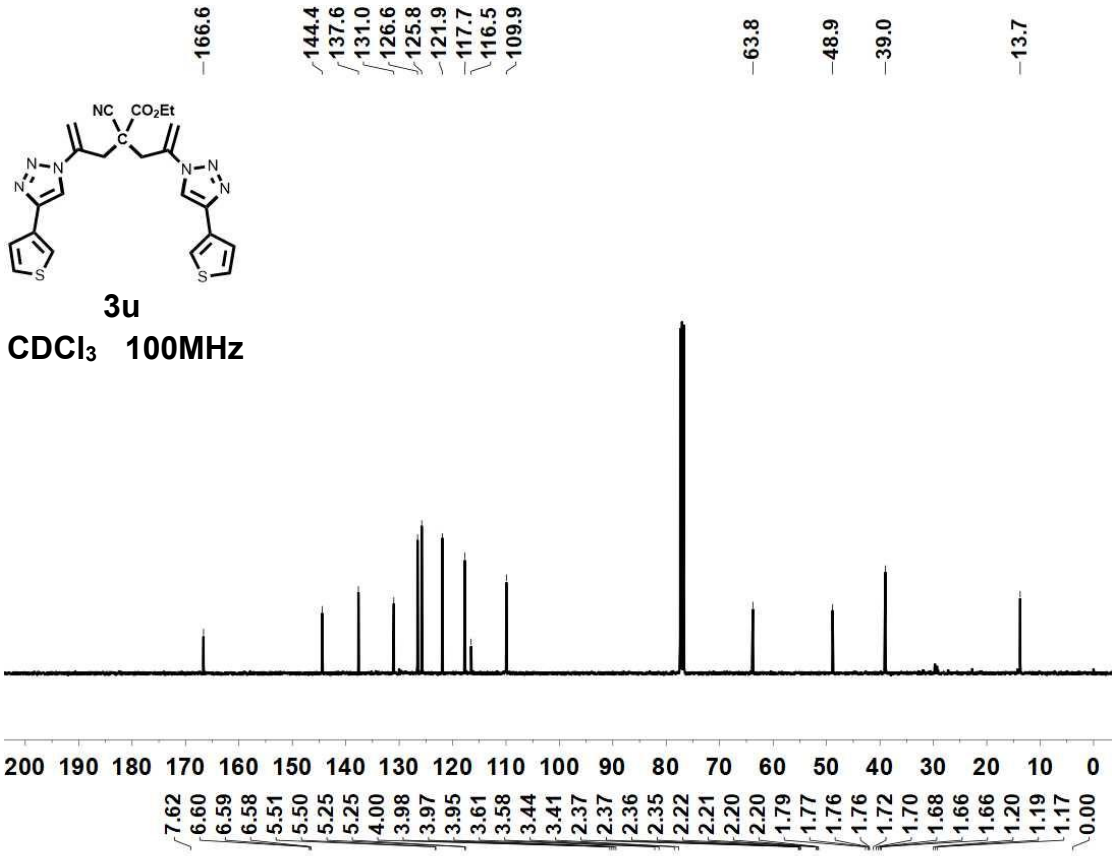


3t

$CDCl_3$ 400MHz

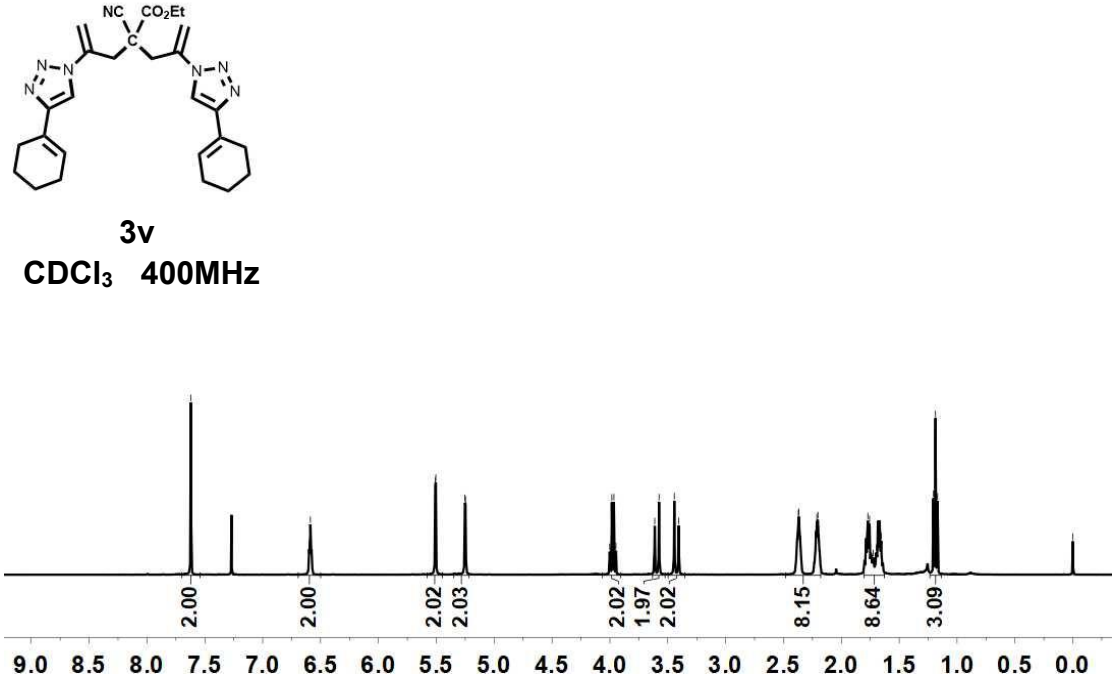

166.7
148.4
137.7
133.5
133.3
128.7
128.3
127.8
127.1
126.6
126.4
124.9
123.8
118.2
116.6
110.1
63.8
48.9
39.1
13.8
NC
CO2Et
3t
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.93
7.73
7.73
7.73
7.72
7.47
7.46
7.45
7.45
7.40
7.39
7.39
7.38
5.59
5.59
5.33
5.32
4.01
3.99
3.97
3.96
3.68
3.64
3.49
3.46
1.19
1.17
1.16
0.00


NC
CO2Et
S
S
3u
CDCl3 400MHz
1.94
1.80
1.87
1.86
1.90
1.96
1.93
1.92
1.99
3.00
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



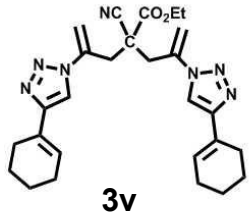
3u

$CDCl_3$ 100MHz



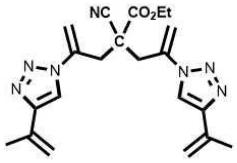
3v

$CDCl_3$ 400MHz



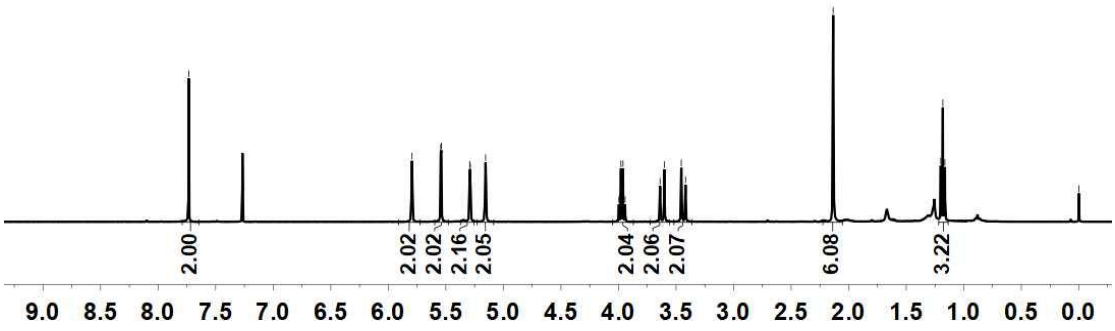
3v

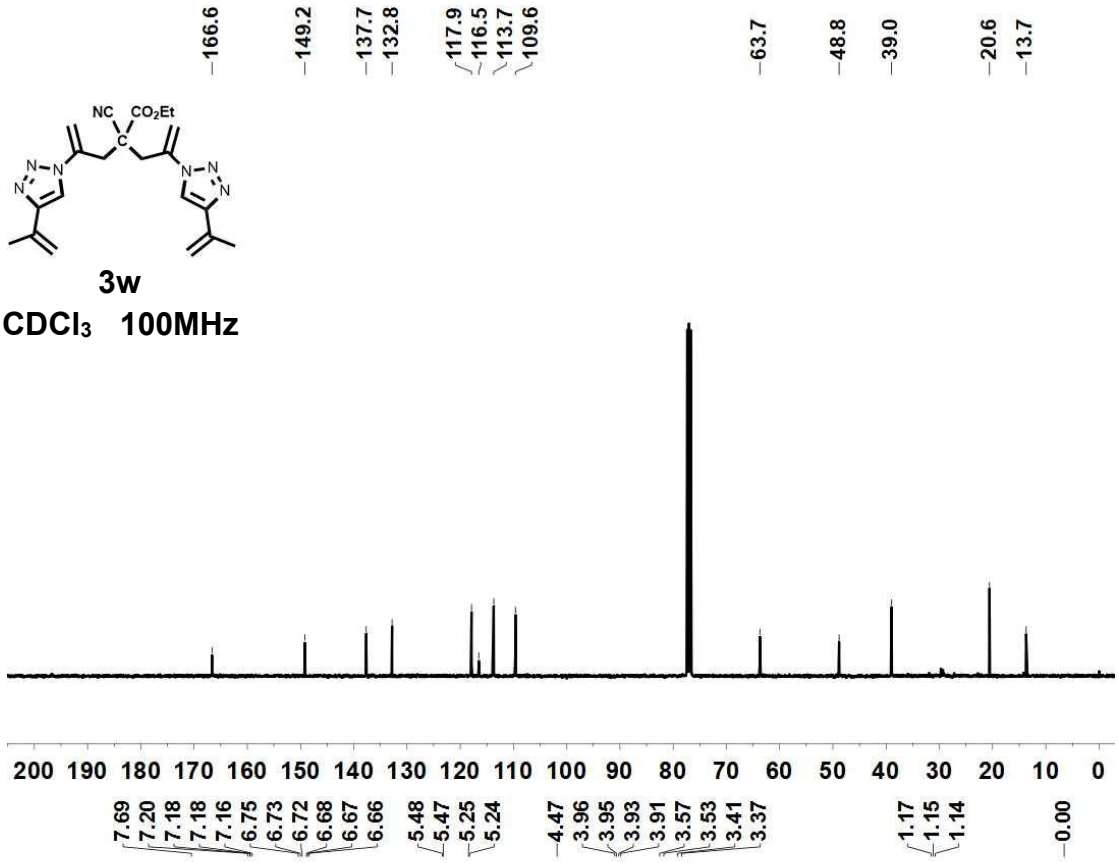
$CDCl_3$ 100MHz



3w

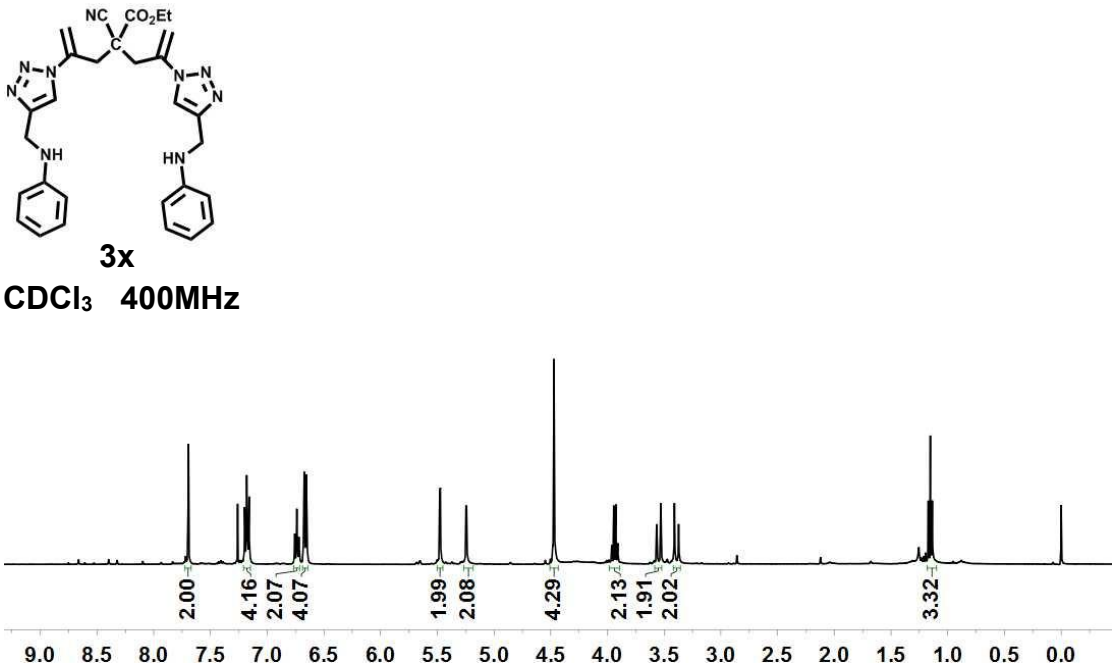
$CDCl_3$ 400MHz





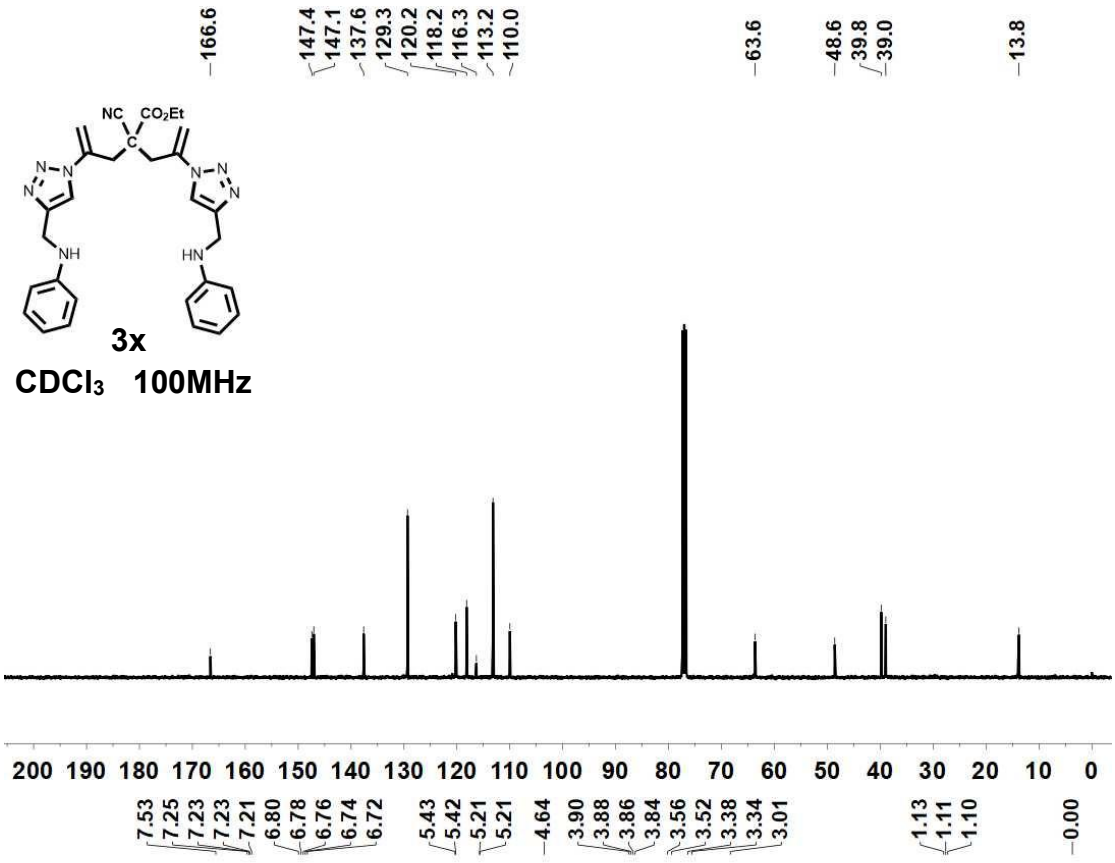
3w

$CDCl_3$ 100MHz



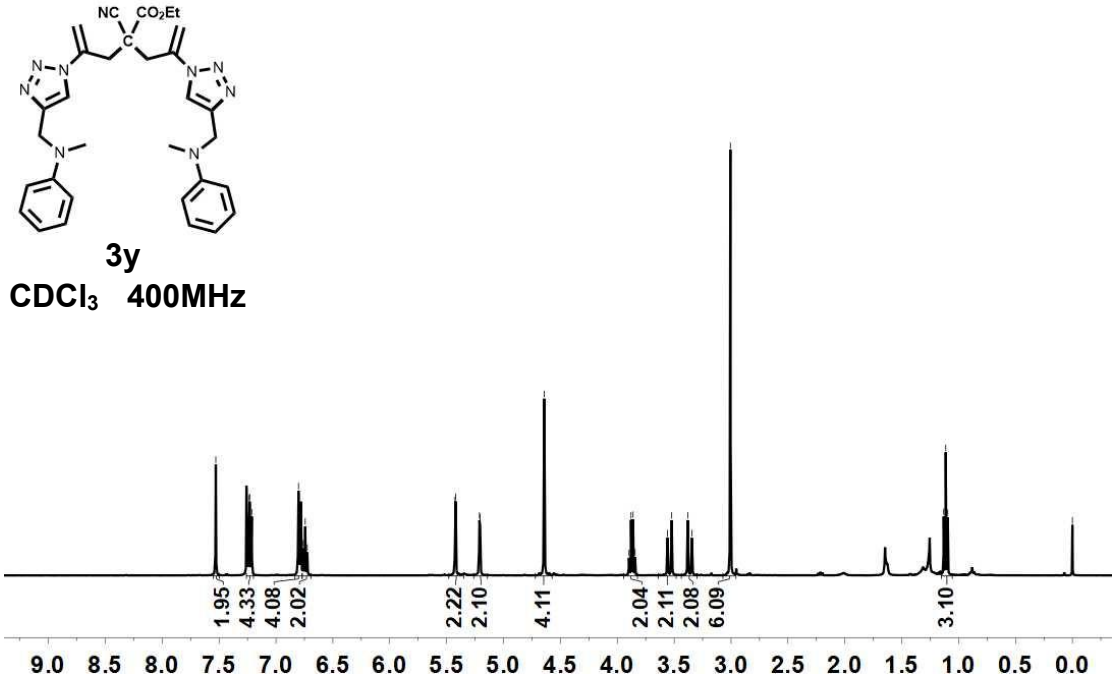
3x

$CDCl_3$ 400MHz



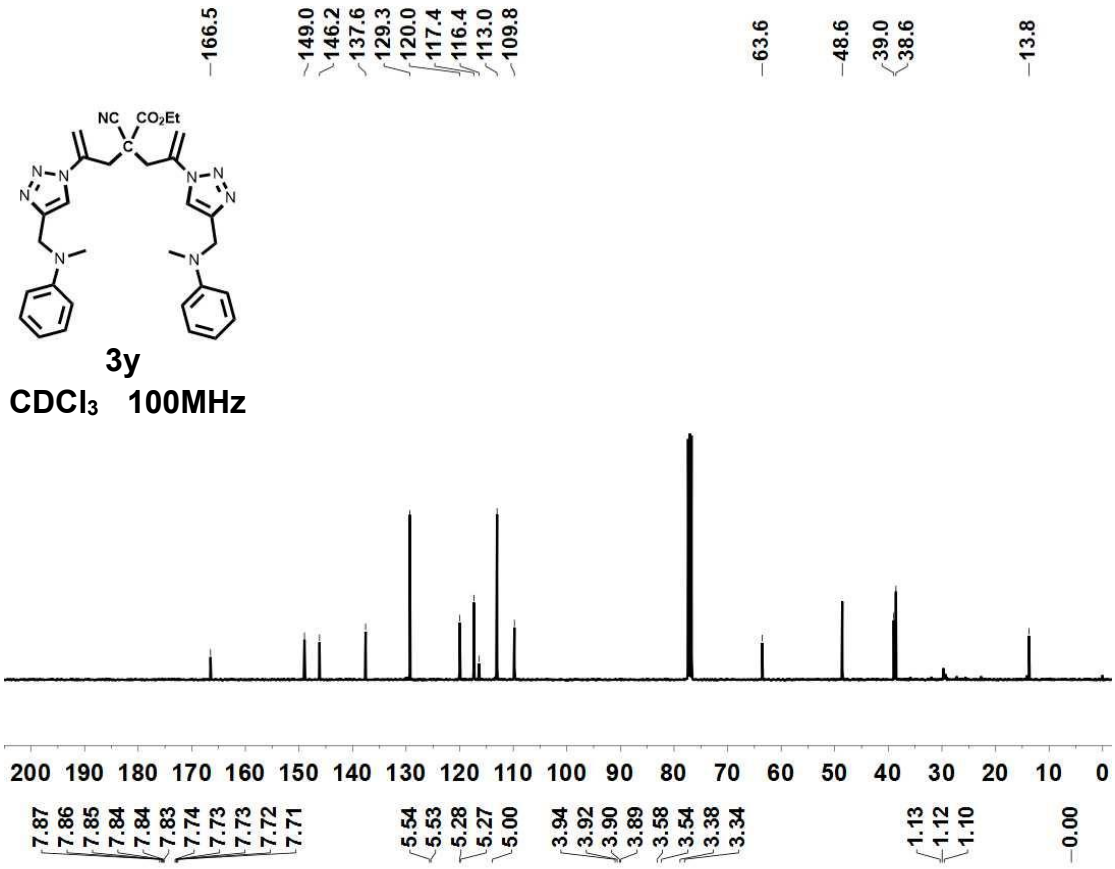
3x

$CDCl_3$ 100MHz



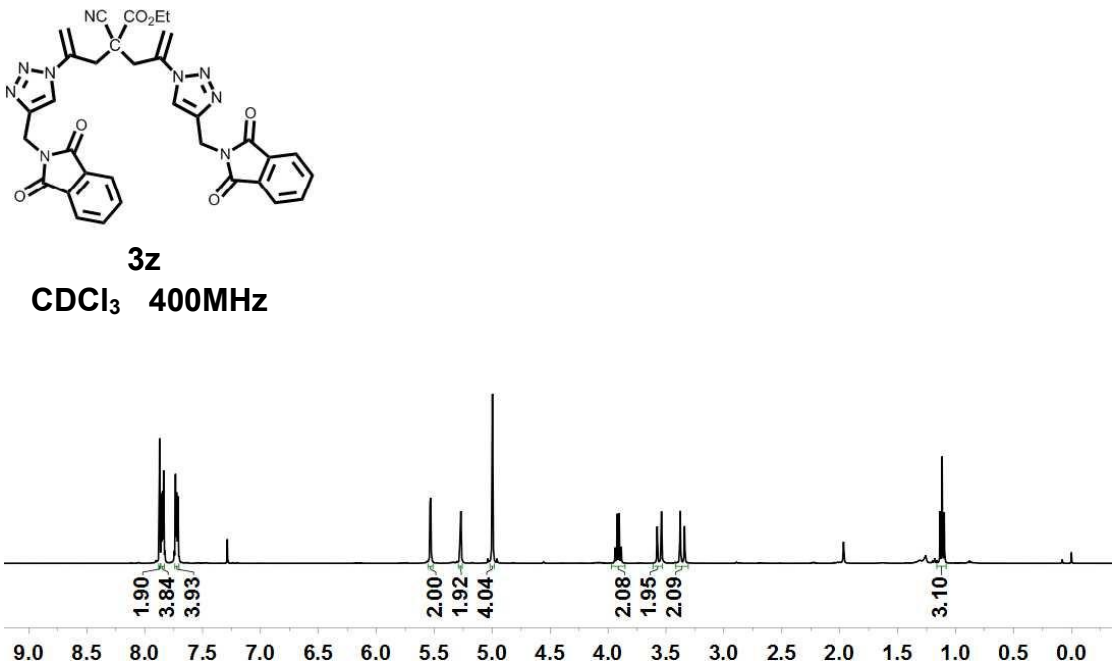
3y

$CDCl_3$ 400MHz



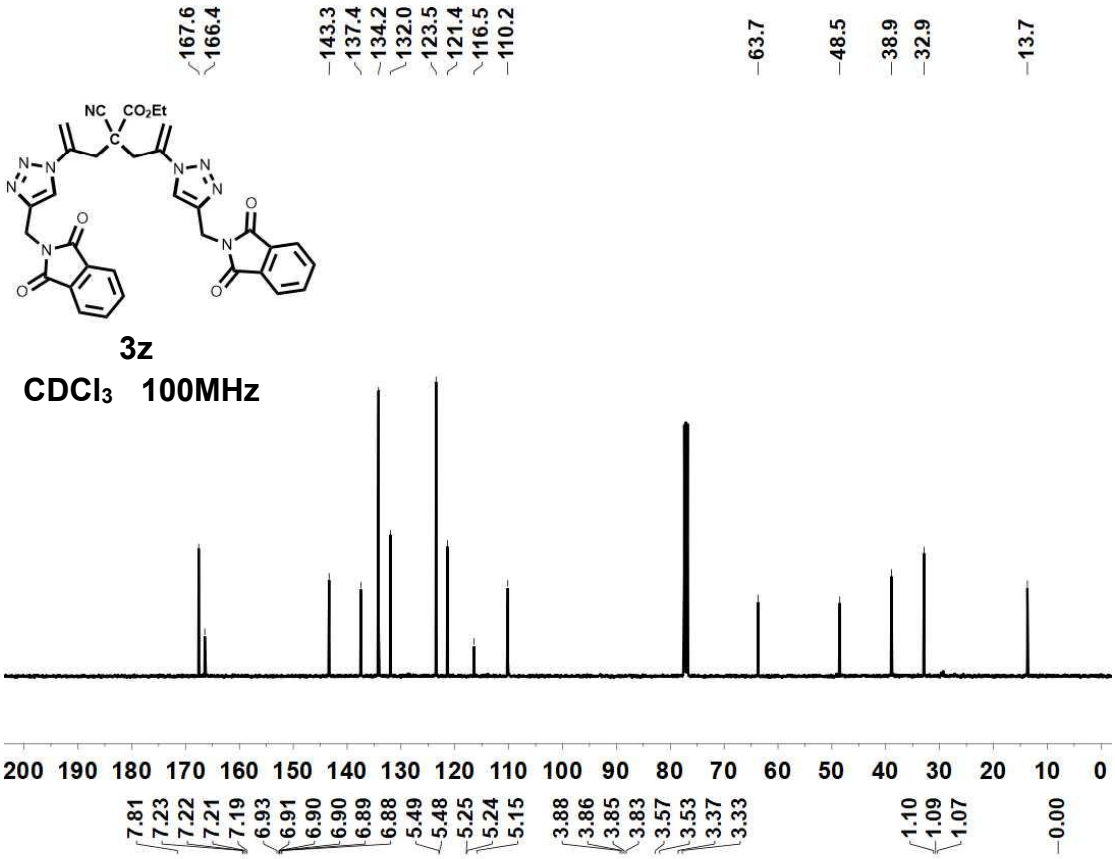
3y

$CDCl_3$ 100MHz



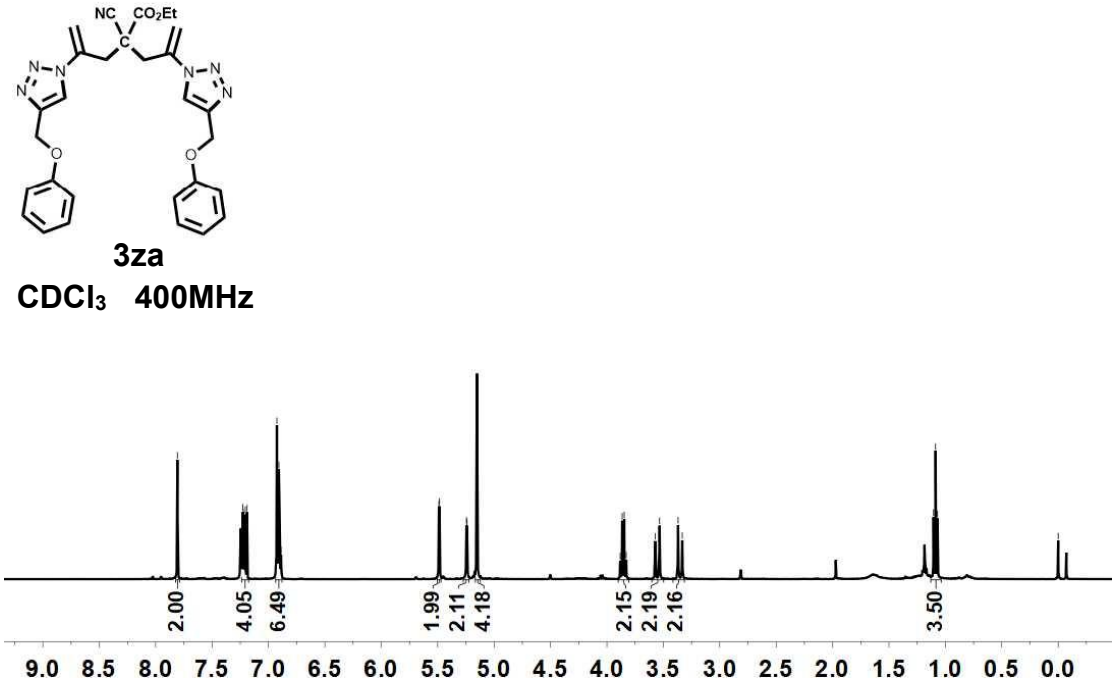
3z

$CDCl_3$ 400MHz



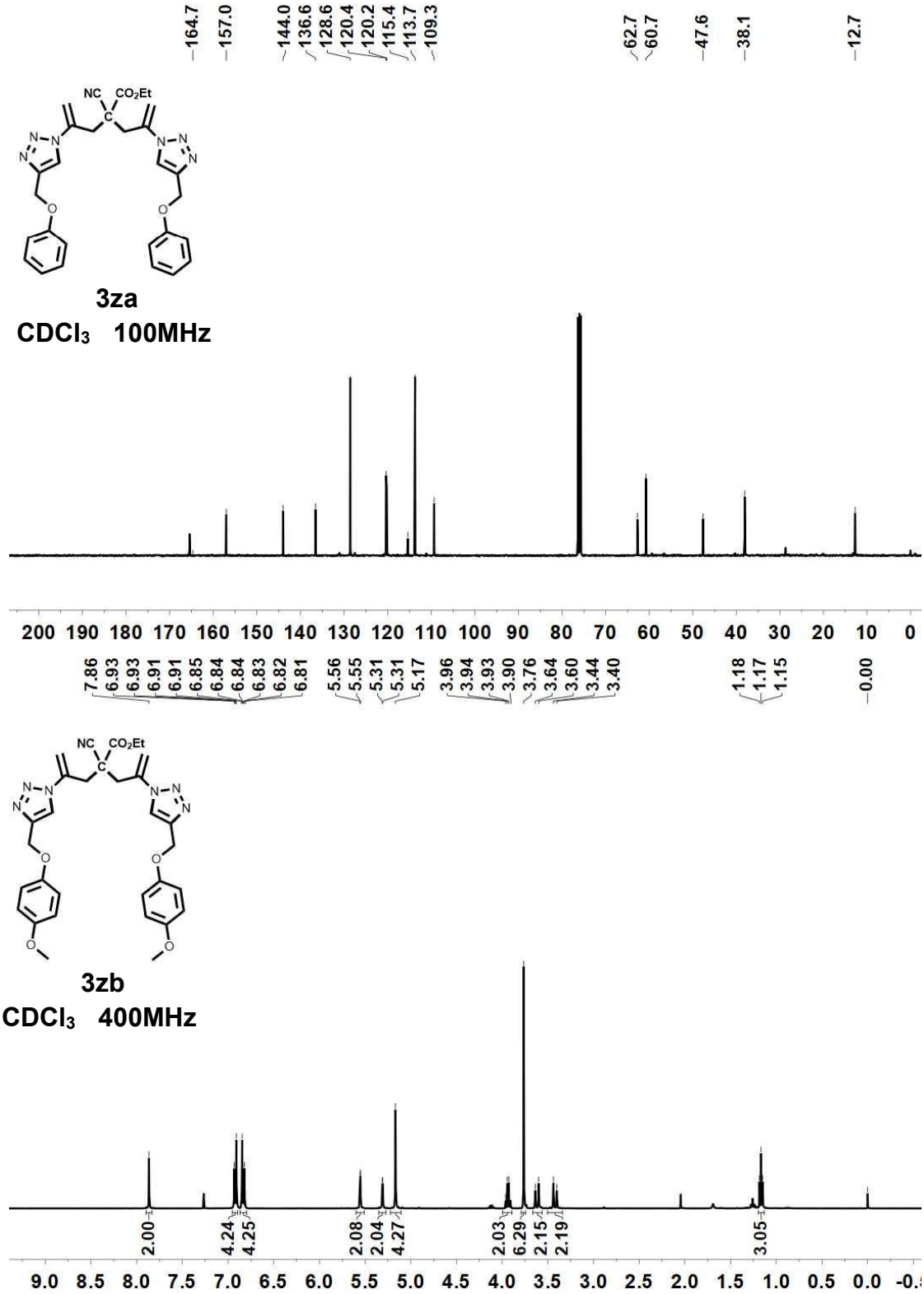
3z

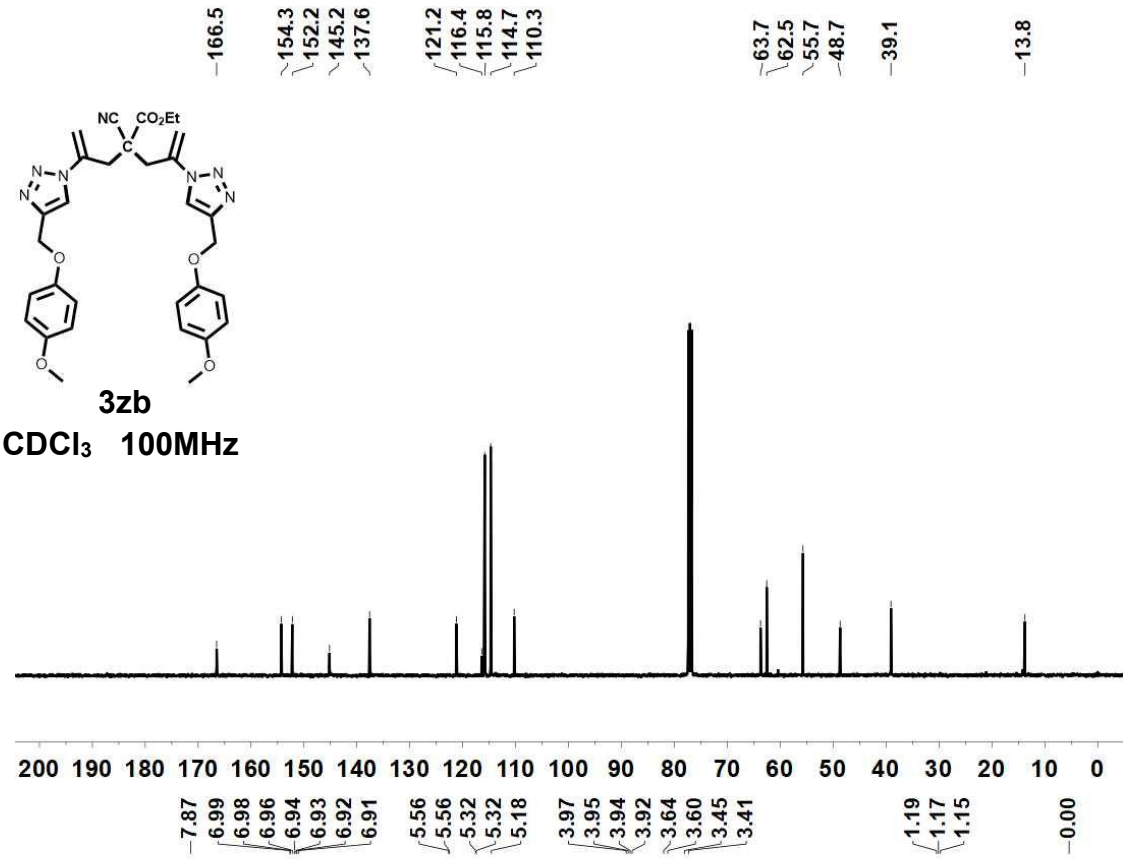
$CDCl_3$ 100MHz



3za

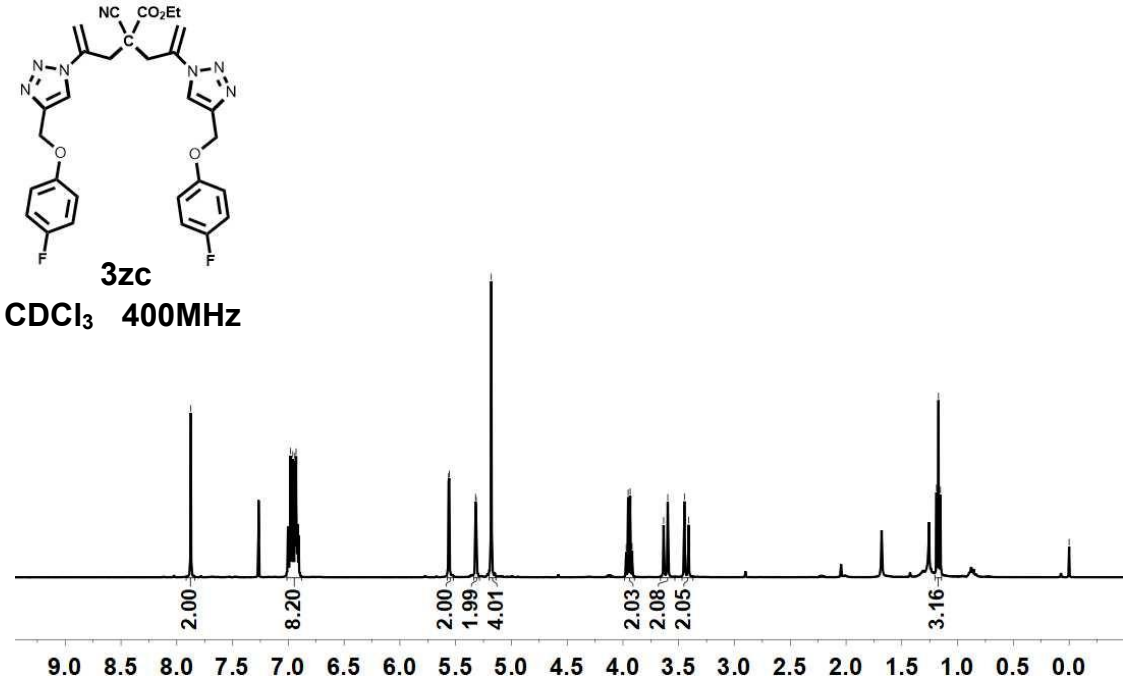
$CDCl_3$ 400MHz


164.7
157.0
144.0
136.6
128.6
120.4
120.2
115.4
113.7
109.3
62.7
60.7
47.6
38.1
12.7
NC
CO2Et
3za
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.86
6.93
6.93
6.91
6.91
6.85
6.84
6.84
6.83
6.82
6.81
5.56
5.55
5.31
5.31
5.17
3.96
3.94
3.93
3.90
3.76
3.64
3.60
3.44
3.40
1.18
1.17
1.15
0.00
NC
CO2Et
3zb
CDCl3 400MHz
2.00
4.24
4.25
2.08
2.04
4.27
2.03
6.29
2.15
2.19
3.05
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



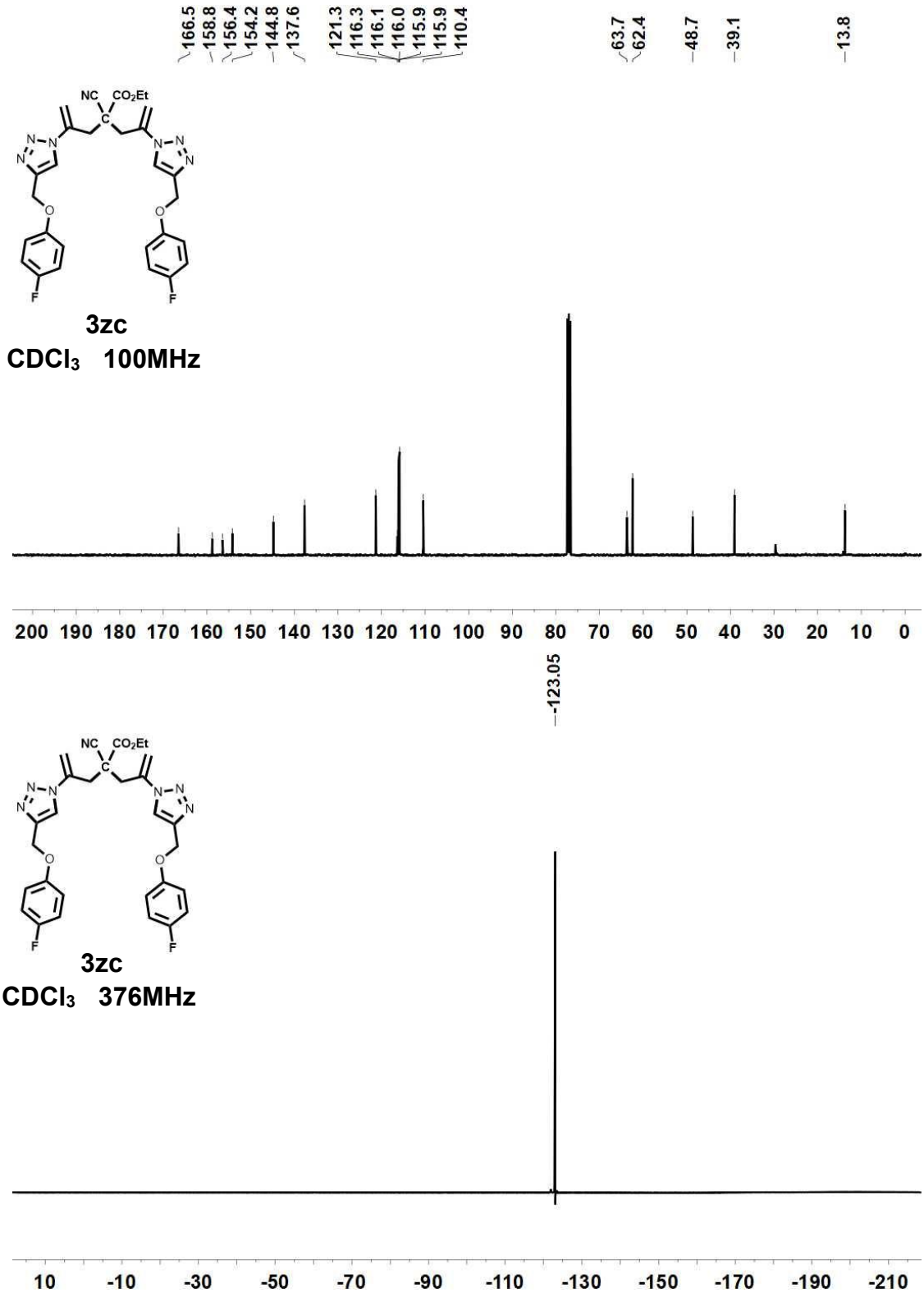
3zb

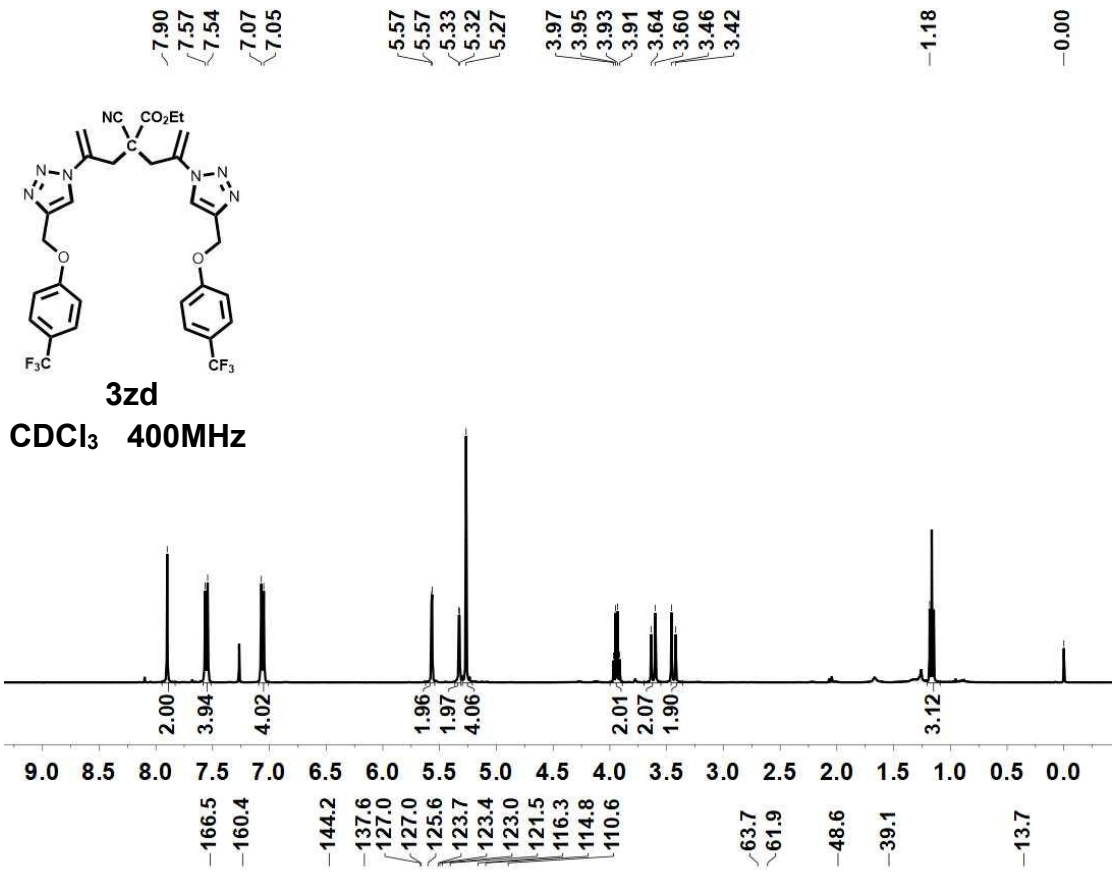
$CDCl_3$ 100MHz



3zc

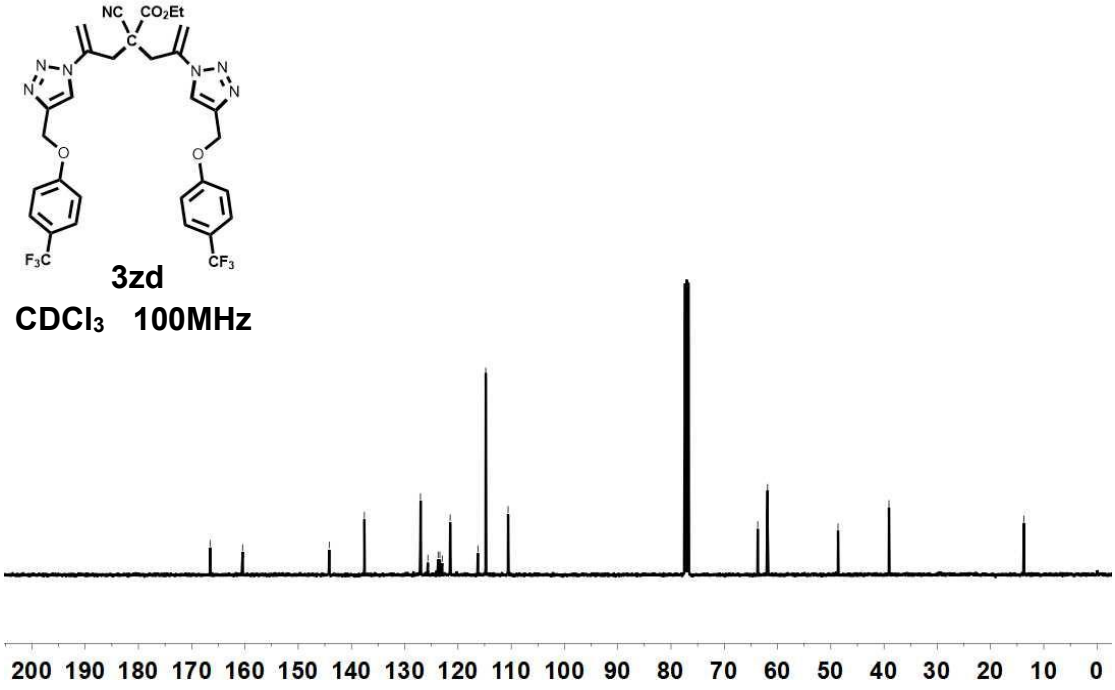
$CDCl_3$ 400MHz


166.5
158.8
156.4
154.2
144.8
137.6
121.3
116.3
116.1
116.0
115.9
115.9
110.4
63.7
62.4
48.7
39.1
13.8
NC
CO2Et
C
N
O
F
3zc
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
-123.05
NC
CO2Et
C
N
O
F
3zc
CDCl3 376MHz
10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210



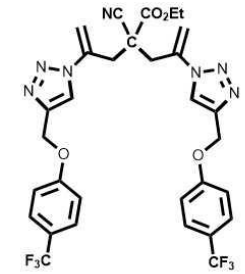
3zd

$CDCl_3$ 400MHz



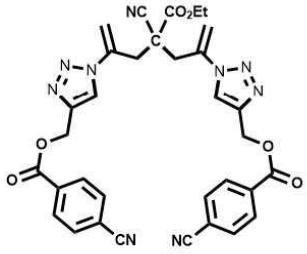
3zd

$CDCl_3$ 100MHz



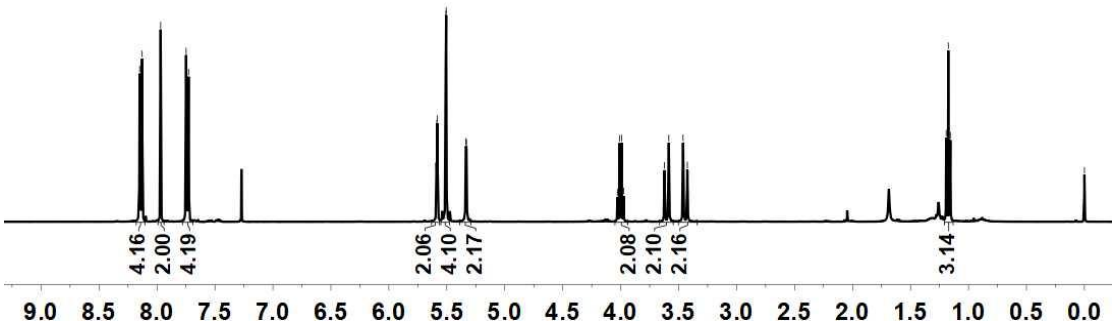
3zd

$CDCl_3$ 376MHz



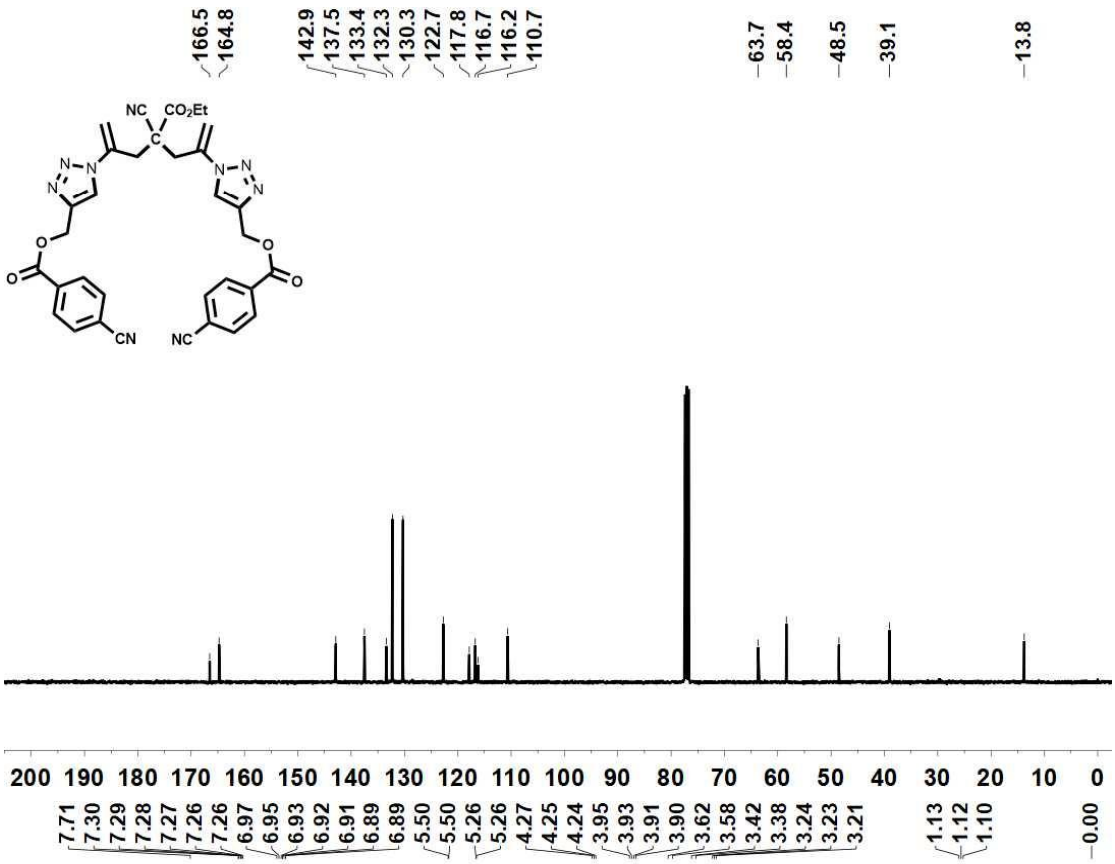
3ze

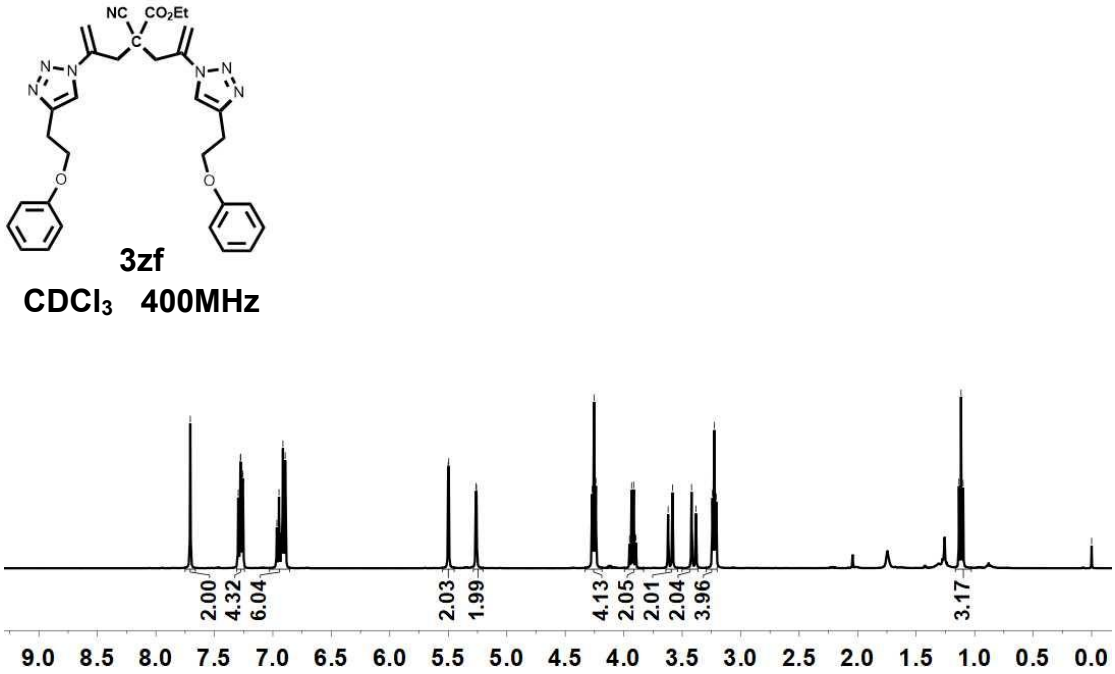
$CDCl_3$ 400MHz

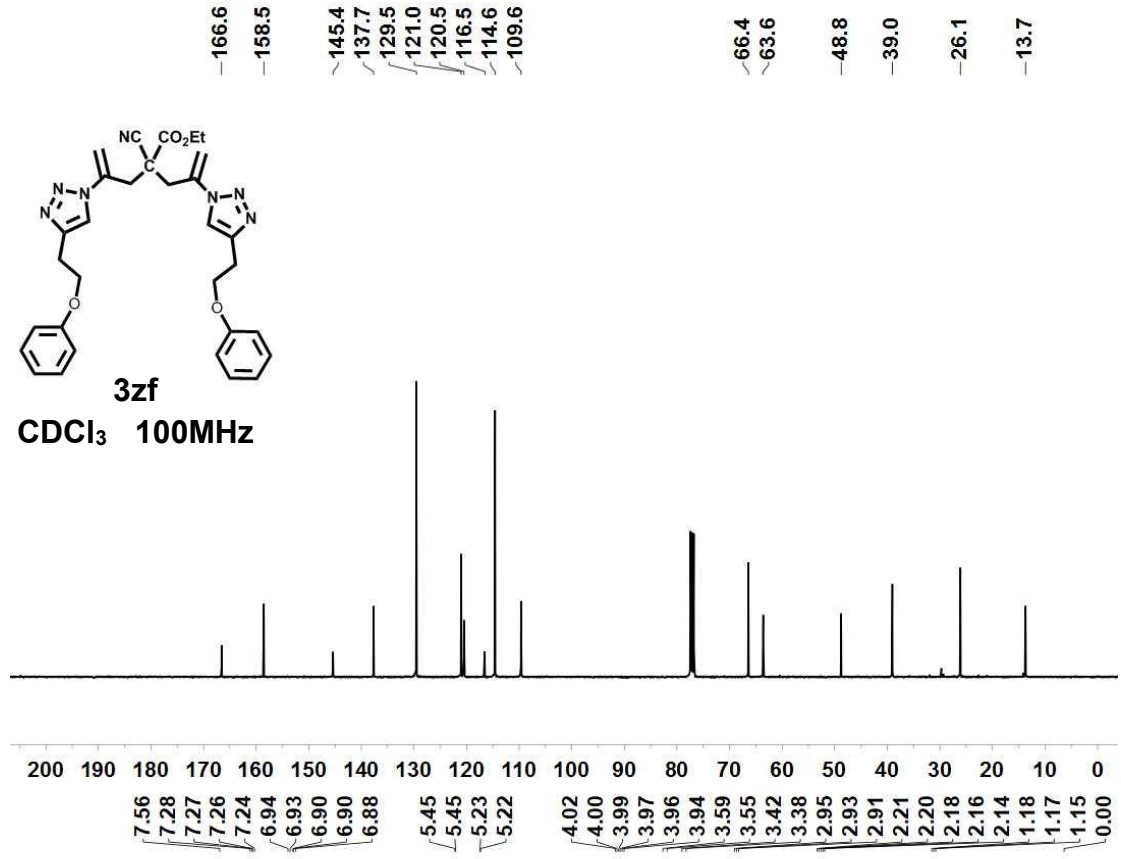


3ze

$CDCl_3$ 100MHz

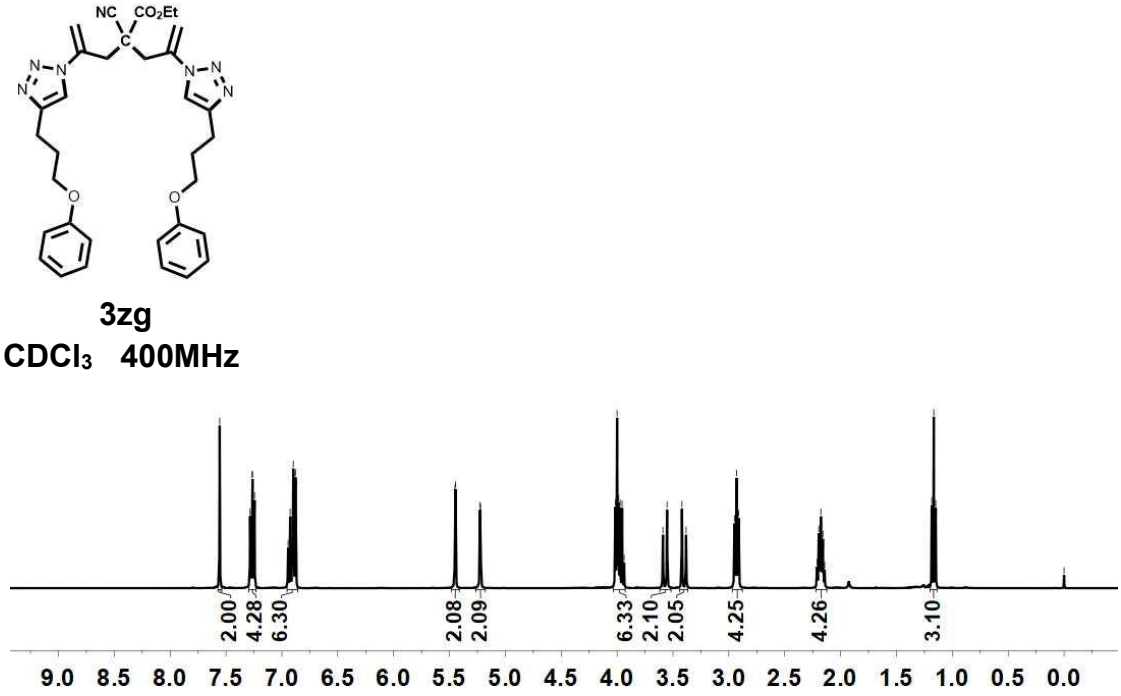

166.5
164.8
142.9
137.5
133.4
132.3
130.3
122.7
117.8
116.7
116.2
110.7
63.7
58.4
48.5
39.1
13.8
NC
CO2Et
CN
NC
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.71
7.30
7.29
7.28
7.27
7.26
7.26
6.97
6.95
6.93
6.92
6.91
6.89
6.89
5.50
5.50
5.26
5.26
4.27
4.25
4.24
3.95
3.93
3.91
3.90
3.62
3.58
3.42
3.38
3.24
3.23
3.21
1.13
1.12
1.10
0.00


NC
CO2Et
3zf
CDCl3 400MHz
2.00
4.32
6.04
2.03
1.99
4.13
2.05
2.01
2.04
3.96
3.17
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



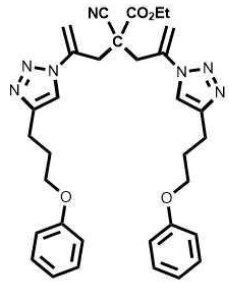
3zf

$CDCl_3$ 100MHz



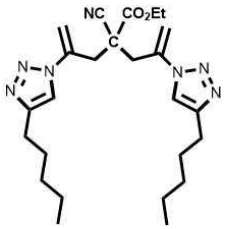
3zg

$CDCl_3$ 400MHz



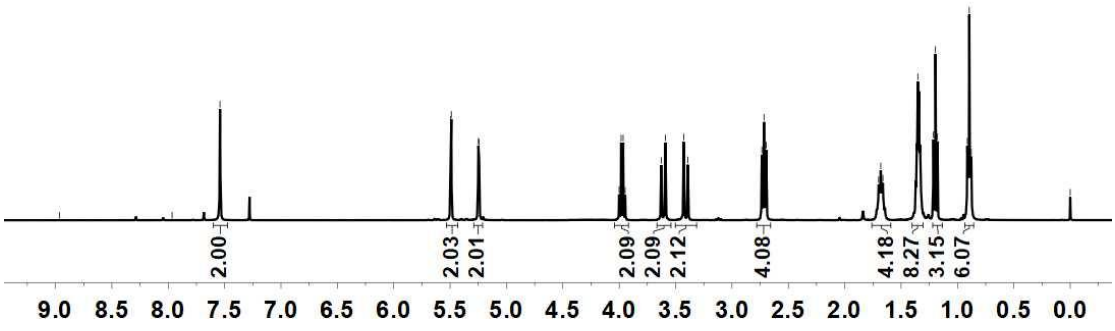
3zg

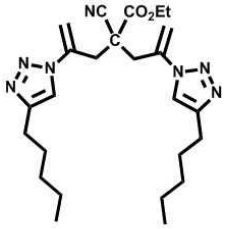
$CDCl_3$ 100MHz



3zh

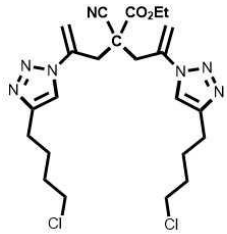
$CDCl_3$ 400MHz





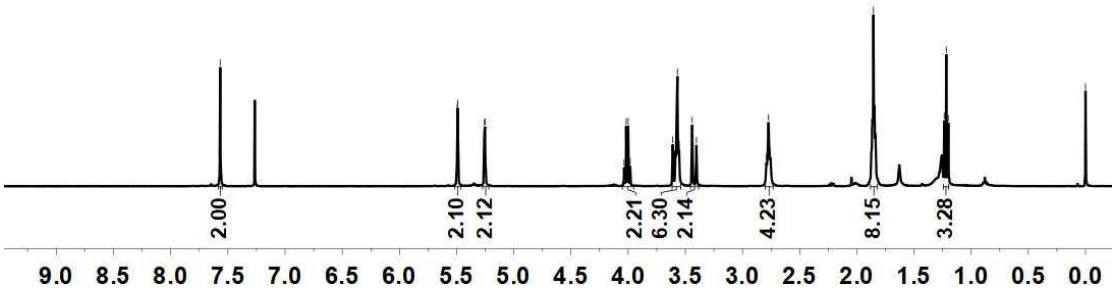
3zh

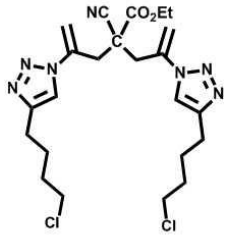
$CDCl_3$ 100MHz



3zi

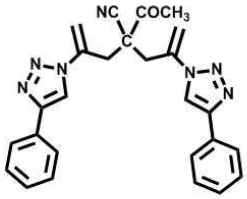
$CDCl_3$ 400MHz





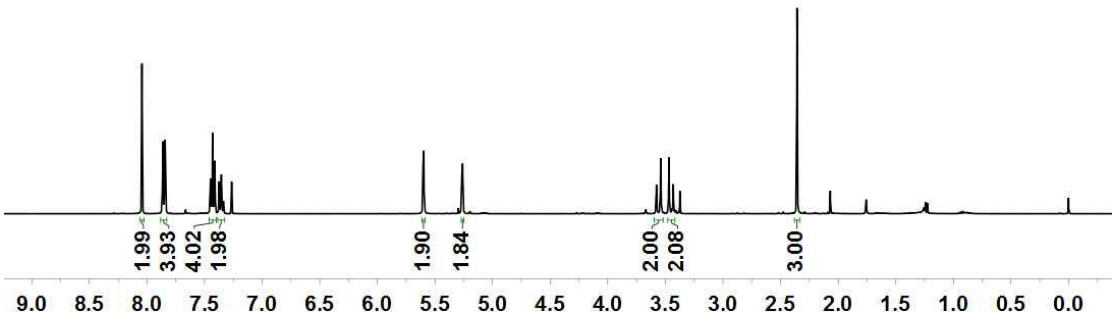
3zi

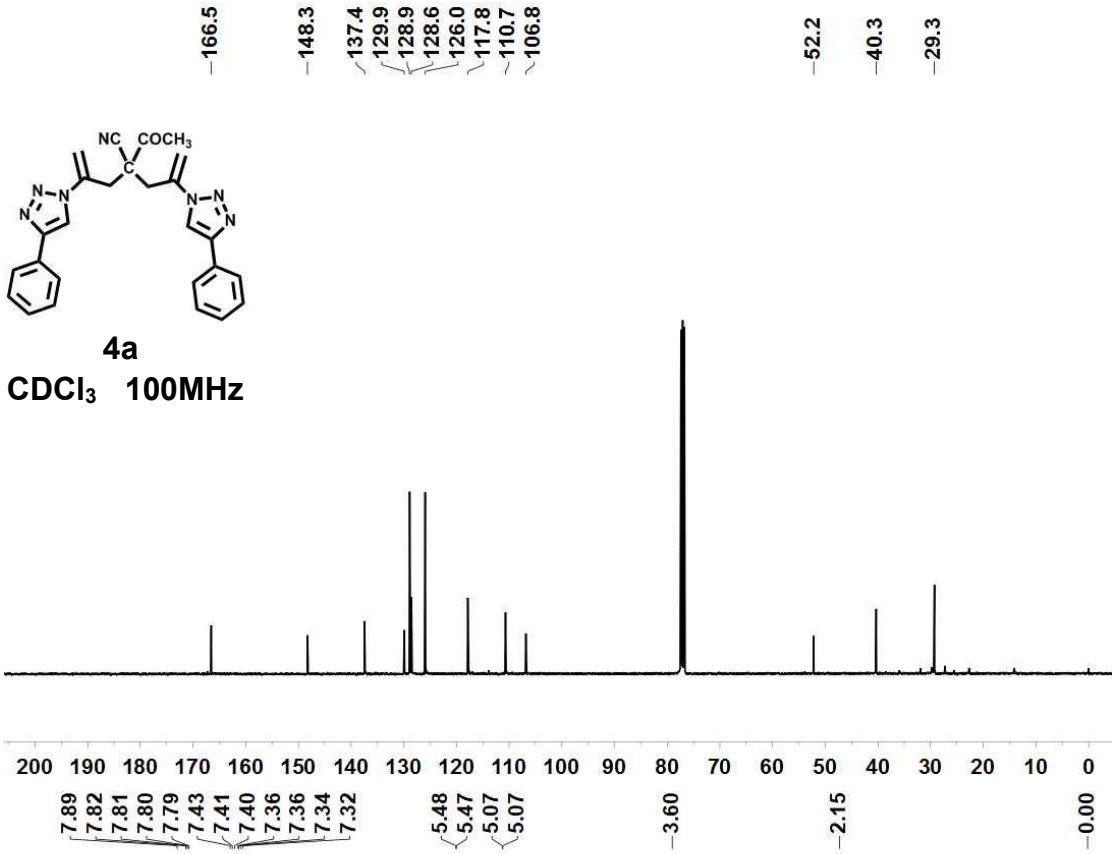
$CDCl_3$ 100MHz



4a

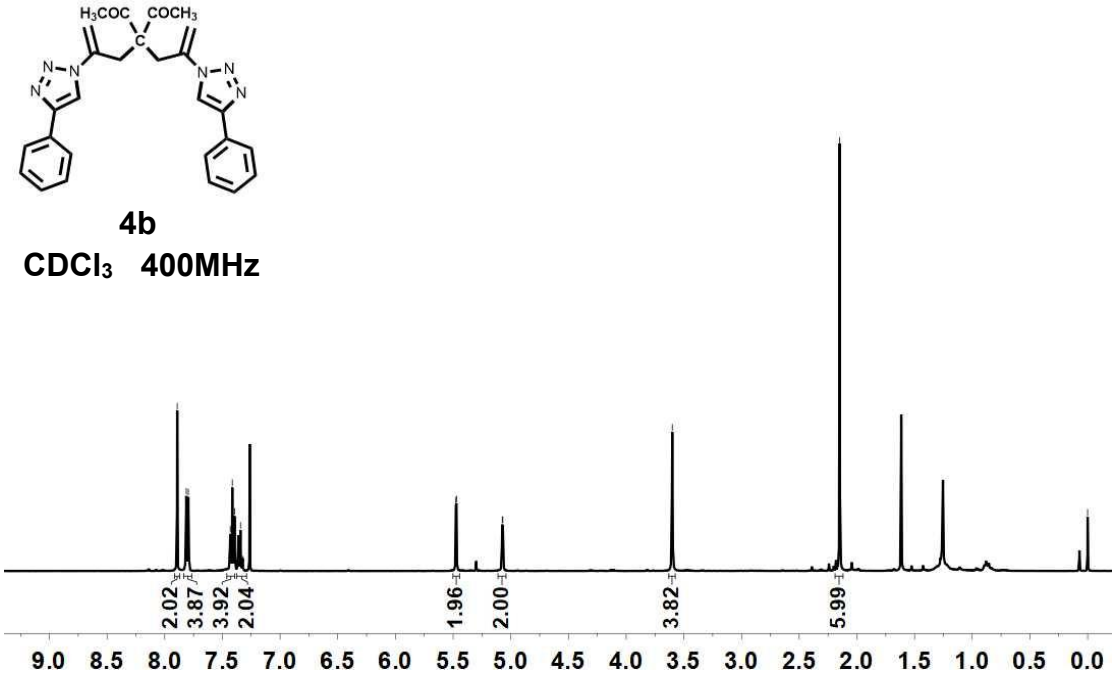
$CDCl_3$ 400MHz





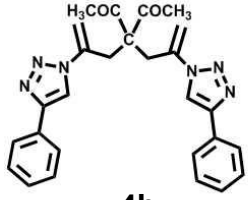
4a

$CDCl_3$ 100MHz



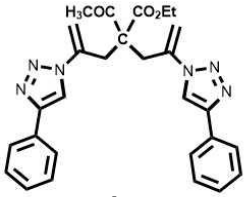
4b

$CDCl_3$ 400MHz



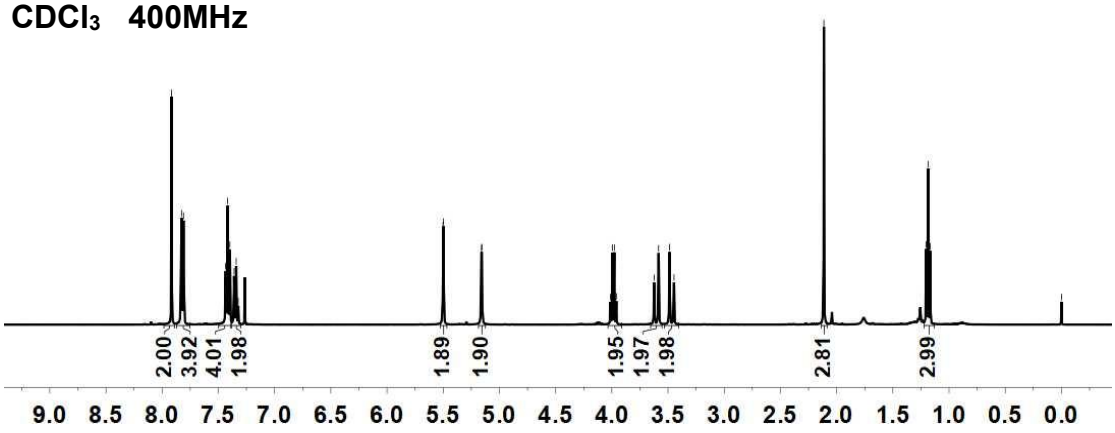
4b

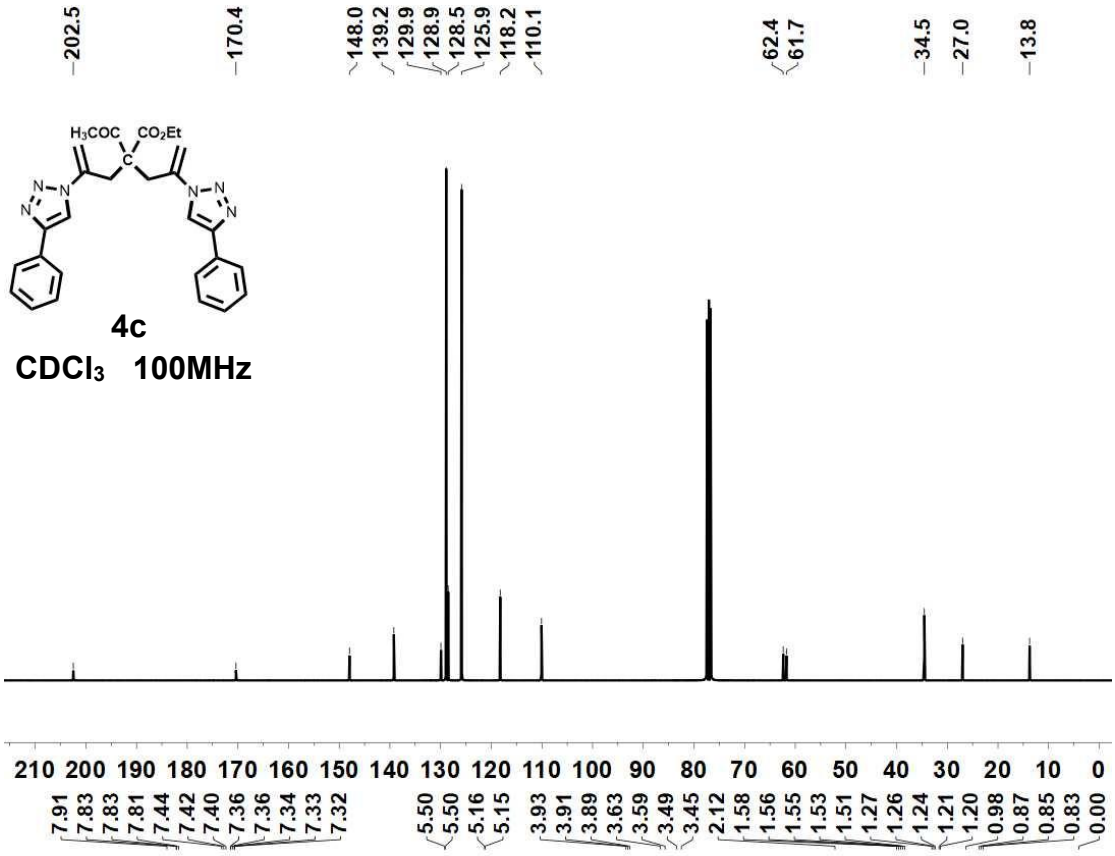
$CDCl_3$ 100MHz



4c

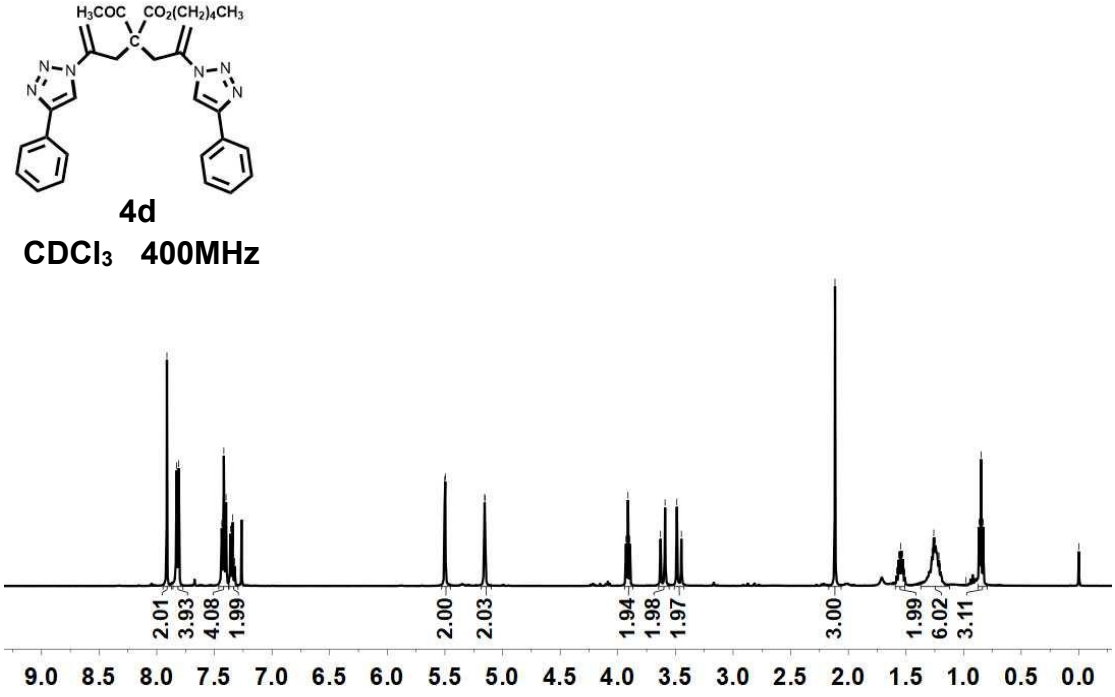
$CDCl_3$ 400MHz





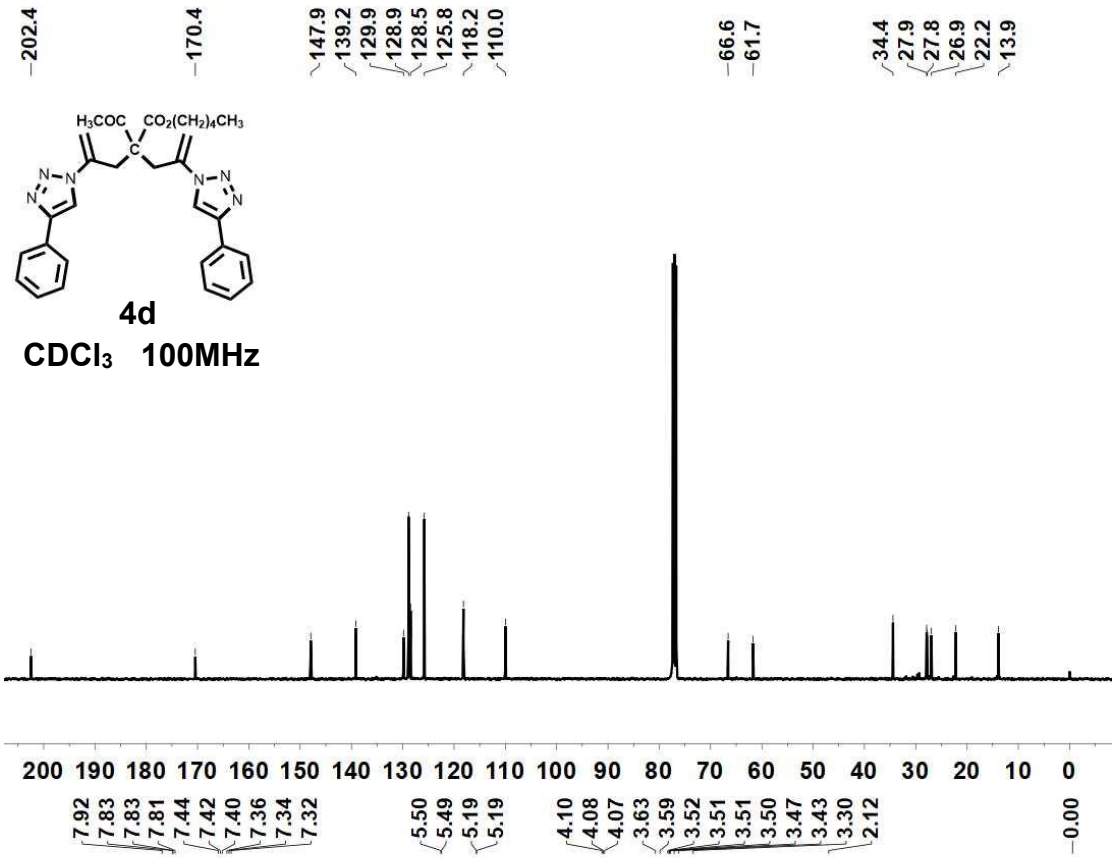
4c

$CDCl_3$ 100MHz



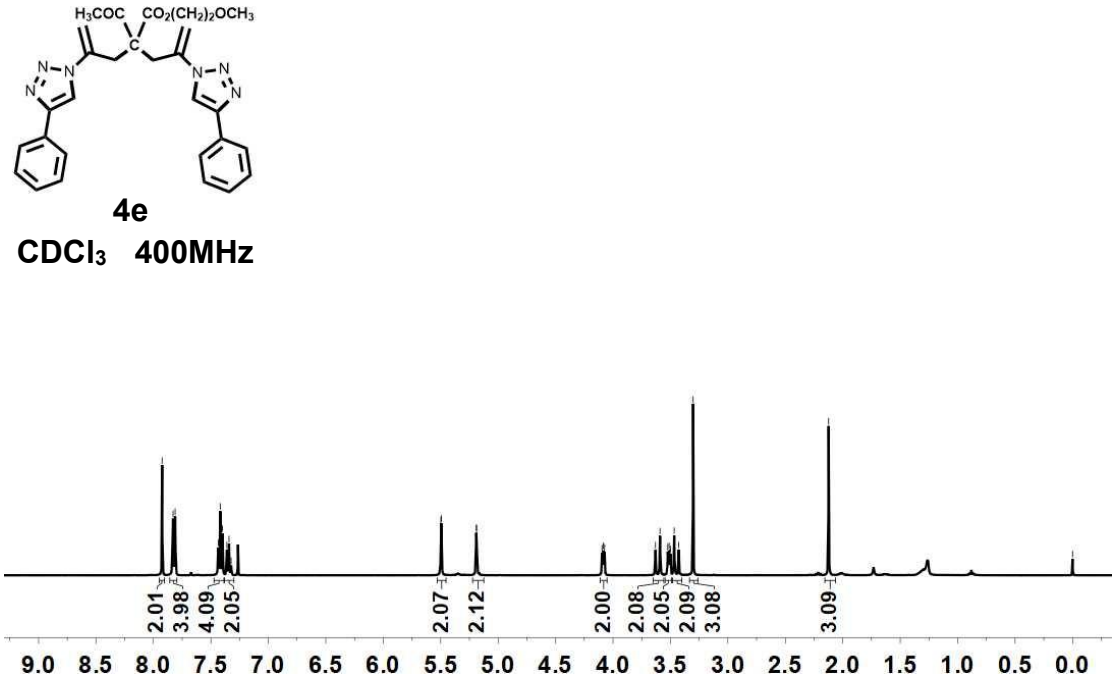
4d

$CDCl_3$ 400MHz



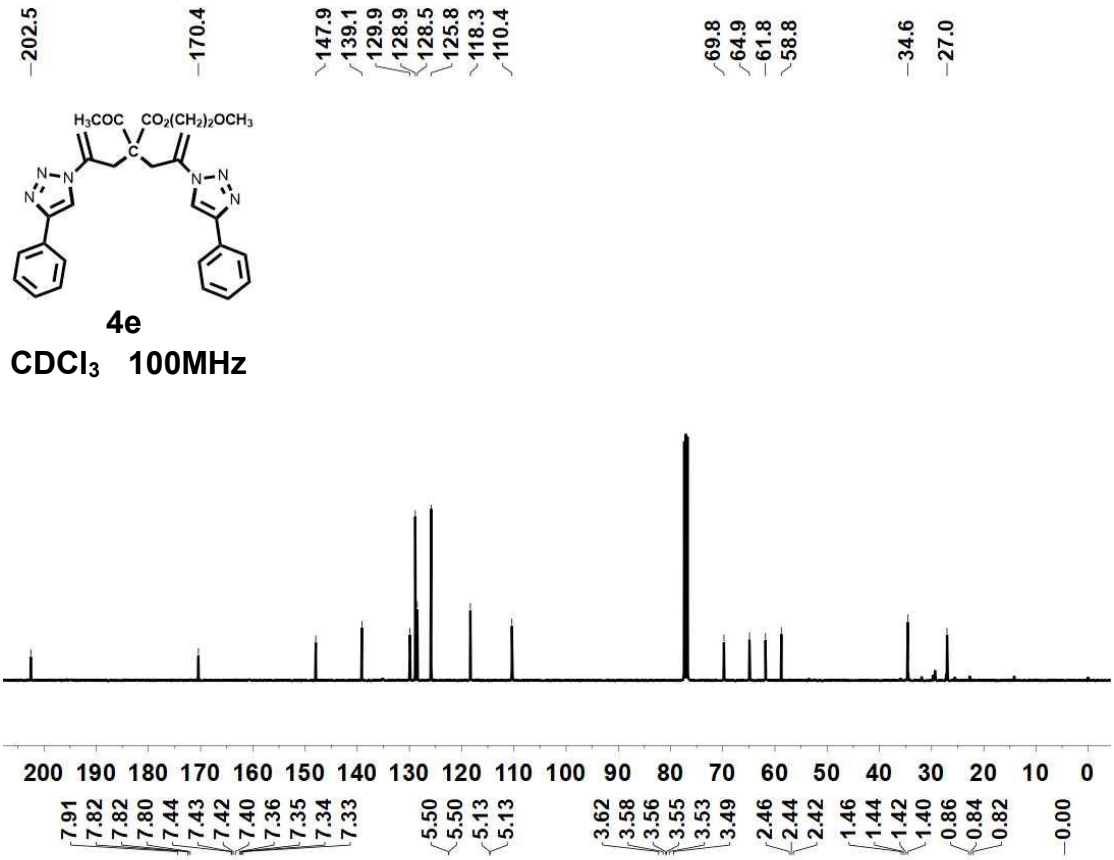
4d

$CDCl_3$ 100MHz



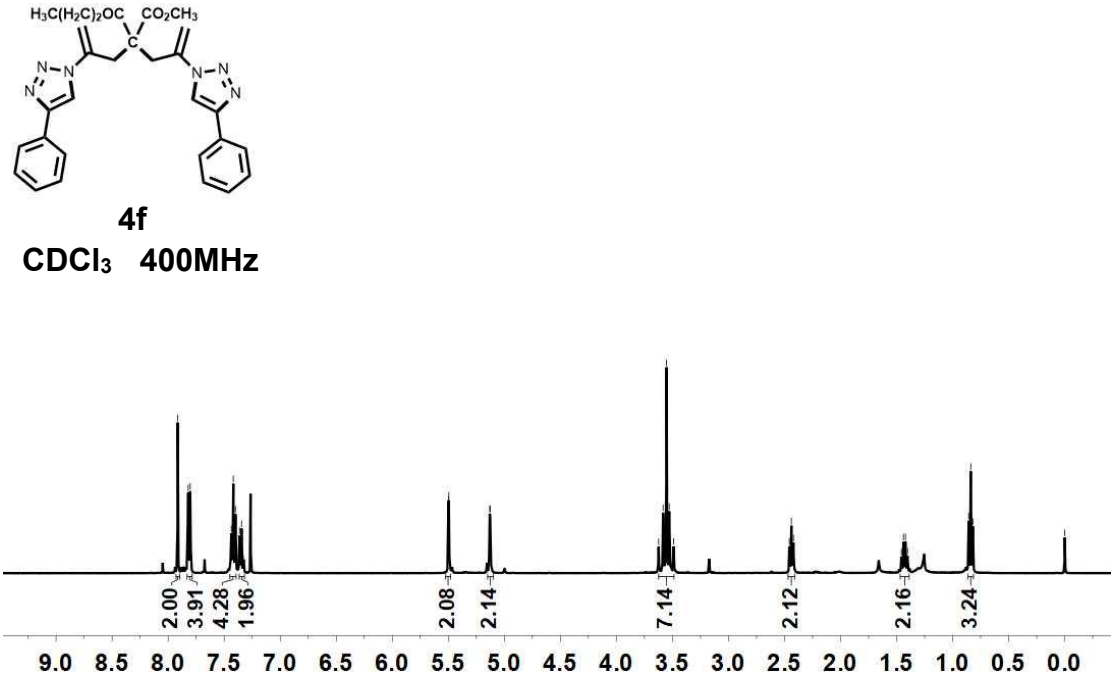
4e

$CDCl_3$ 400MHz



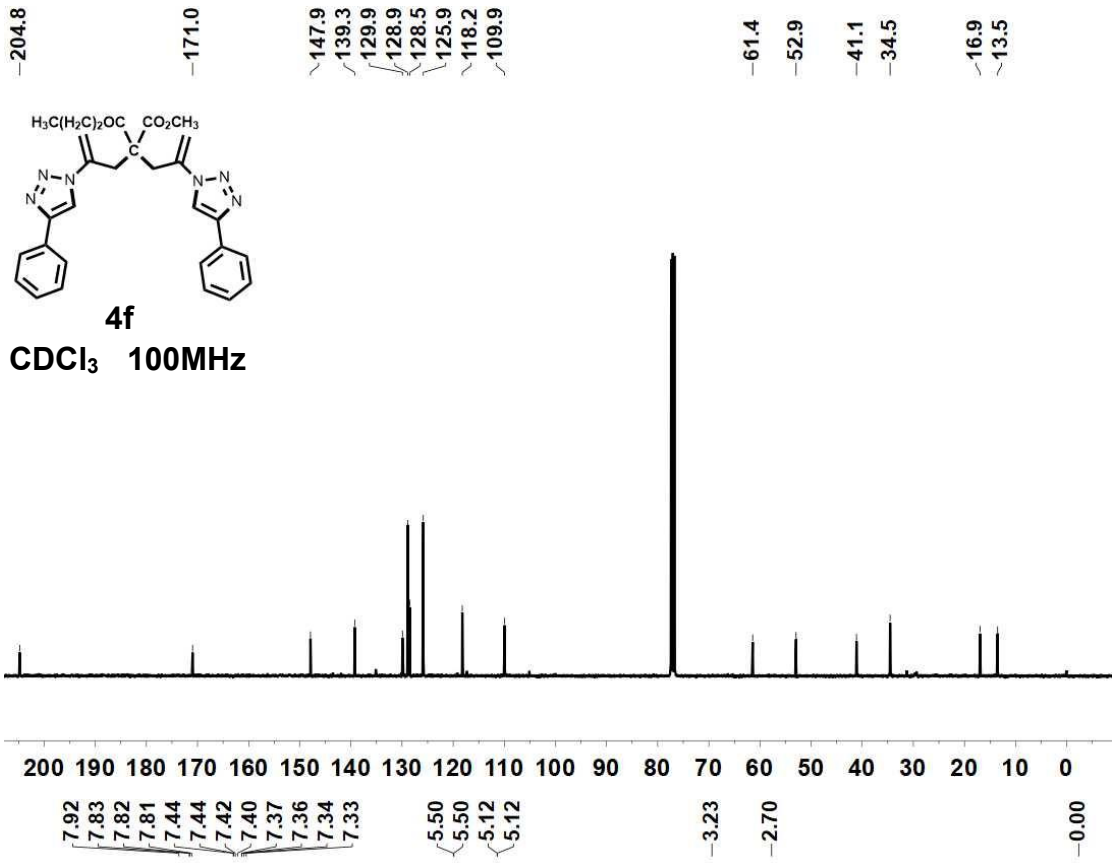
4e

$CDCl_3$ 100MHz



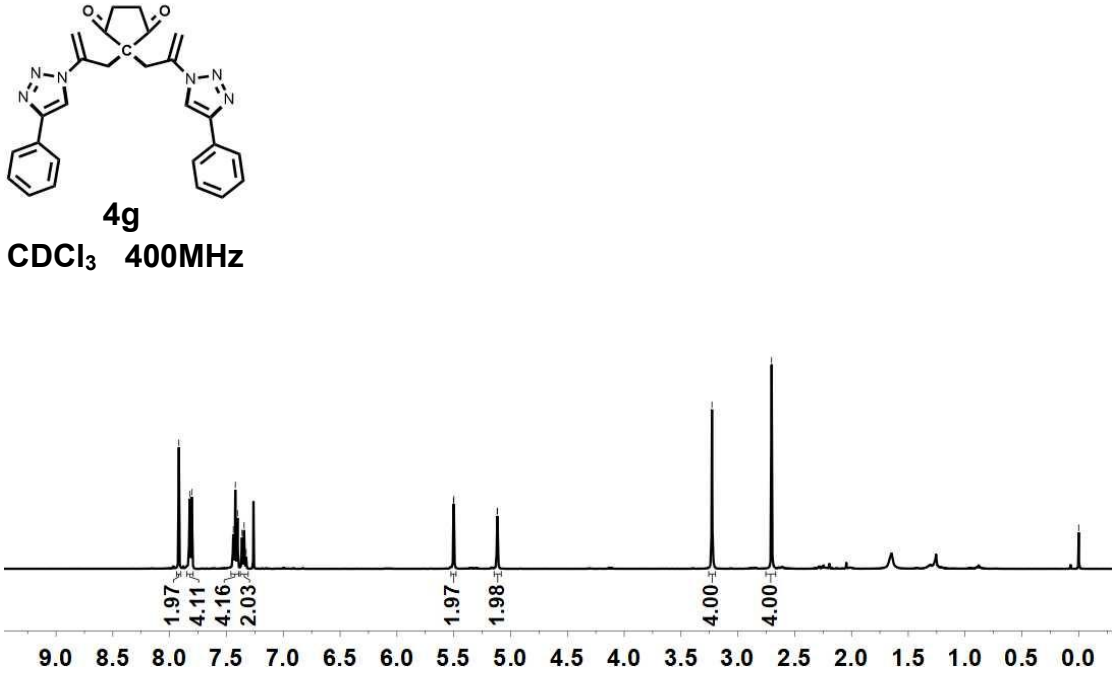
4f

$CDCl_3$ 400MHz



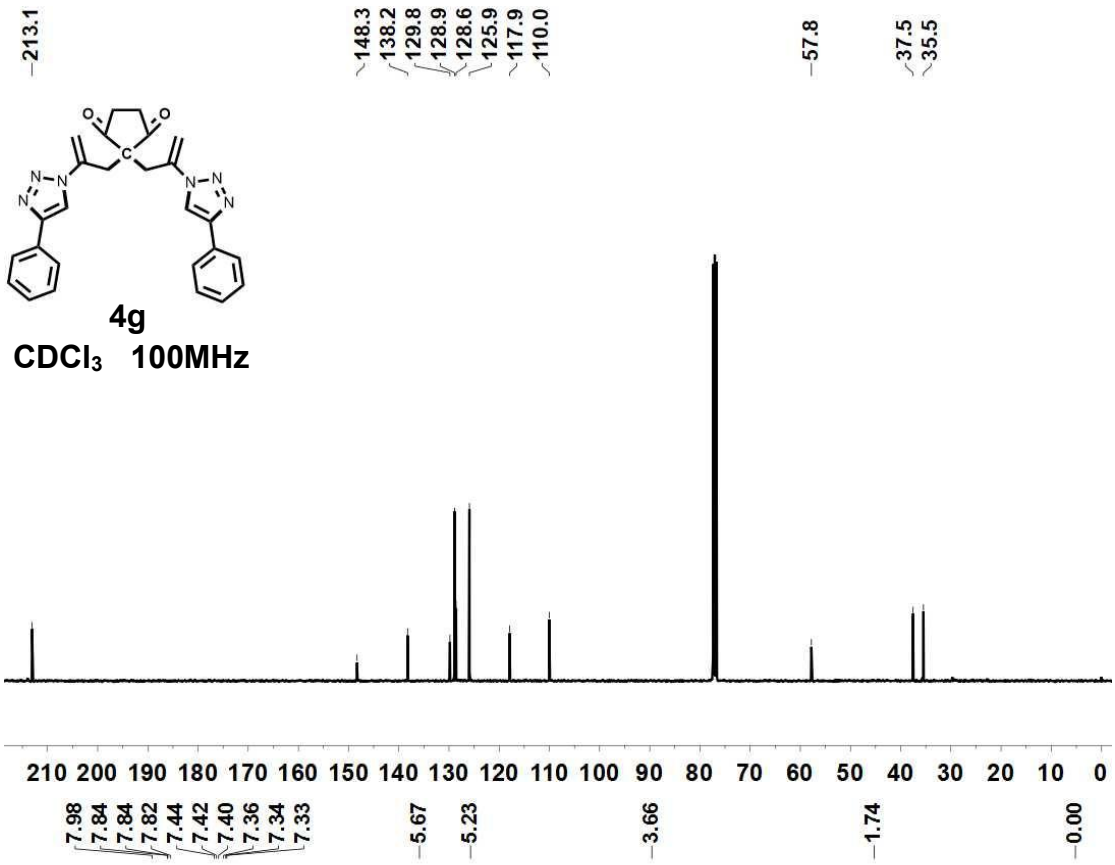
4f

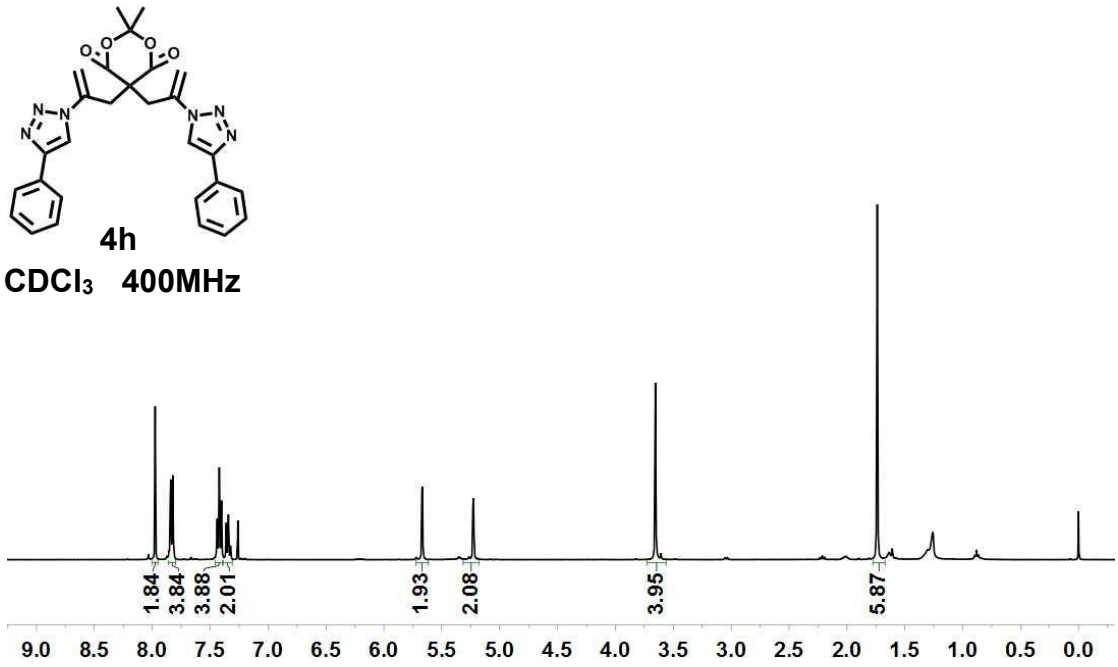
$CDCl_3$ 100MHz

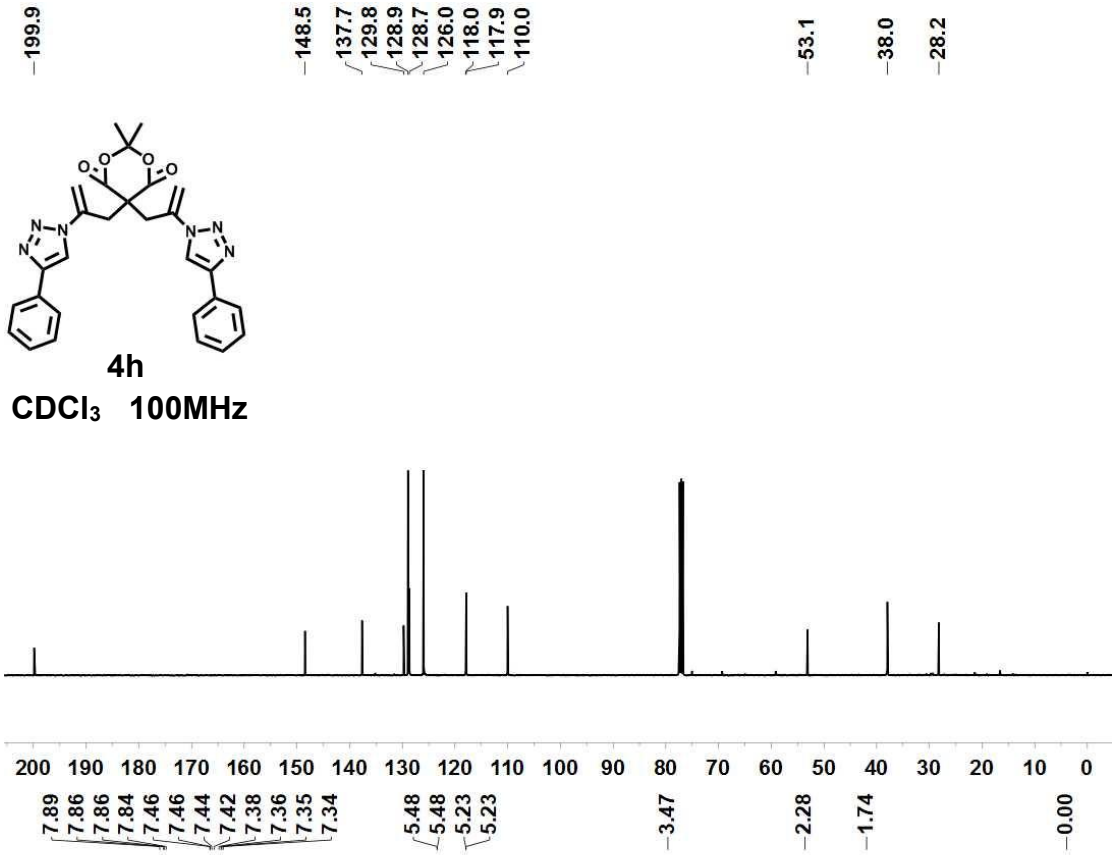


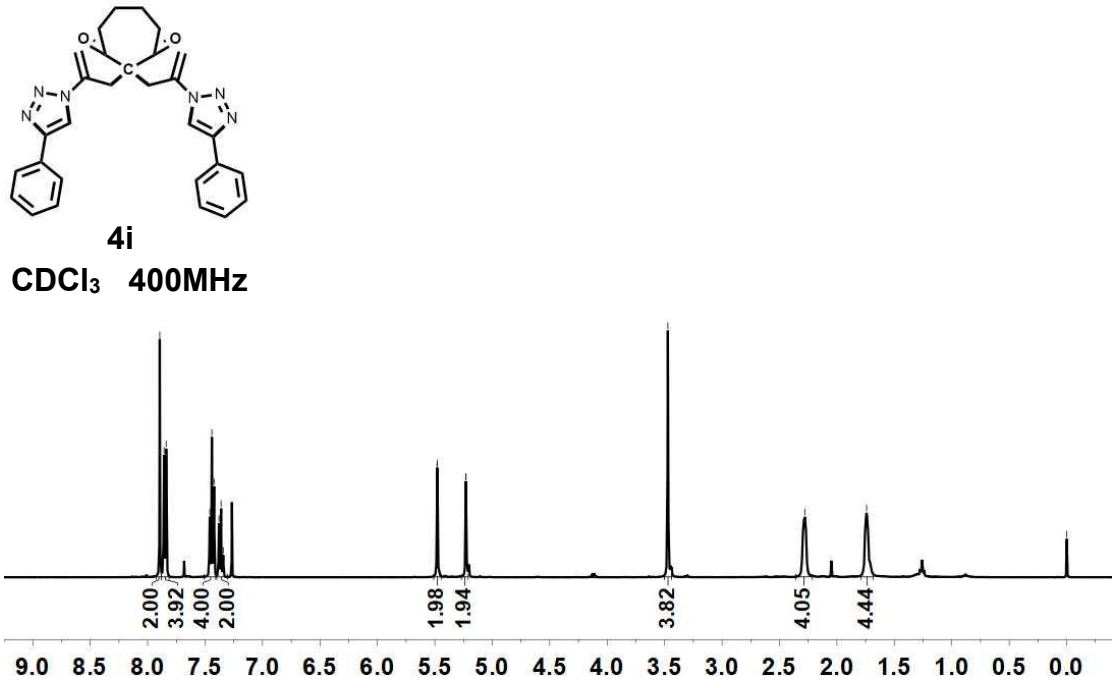
4g

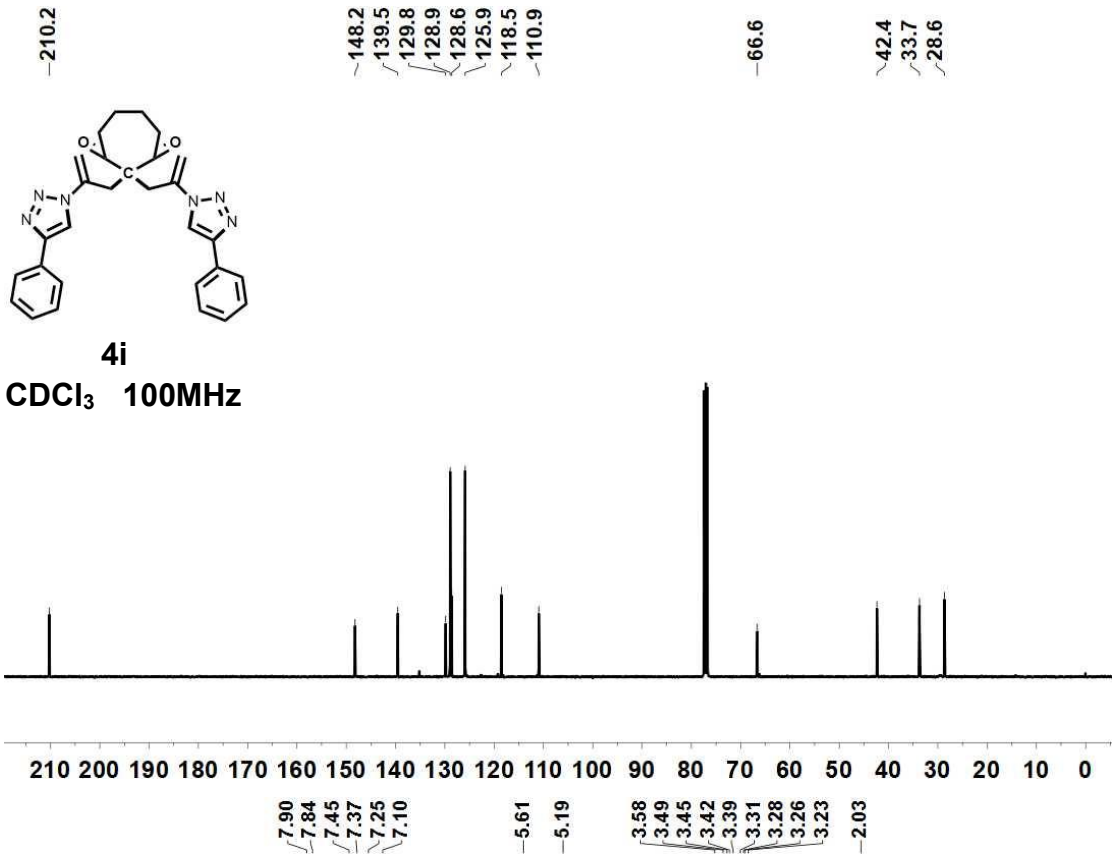
$CDCl_3$ 400MHz


213.1
148.3
138.2
129.8
128.9
128.6
125.9
117.9
110.0
57.8
37.5
35.5
4g
CDCl3 100MHz
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.98
7.84
7.84
7.82
7.44
7.42
7.40
7.36
7.34
7.33
5.67
5.23
3.66
1.74
0.00


4h
CDCl3 400MHz
1.84
3.84
3.88
2.01
1.93
2.08
3.95
5.87
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

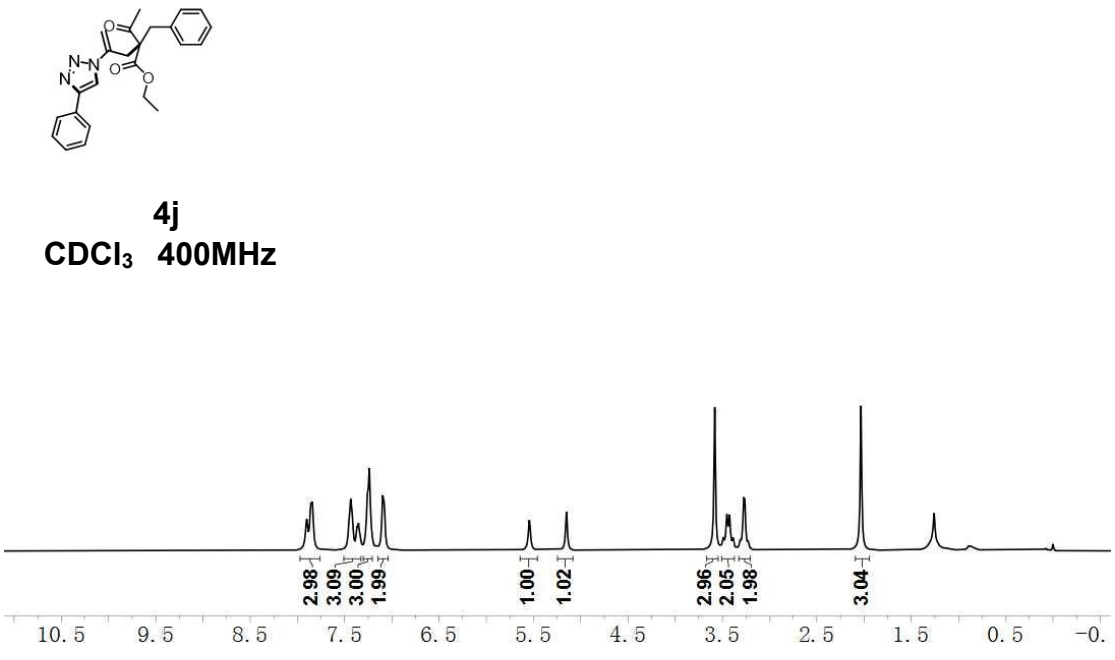

199.9
148.5
137.7
129.8
128.9
128.7
126.0
118.0
117.9
110.0
53.1
38.0
28.2
4h
CDCl3 100MHz
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
7.89
7.86
7.86
7.84
7.46
7.46
7.44
7.42
7.38
7.36
7.35
7.34
5.48
5.48
5.23
5.23
3.47
2.28
1.74
0.00


4i
CDCl3 400MHz
2.00
3.92
4.00
2.00
1.98
1.94
3.82
4.05
4.44
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



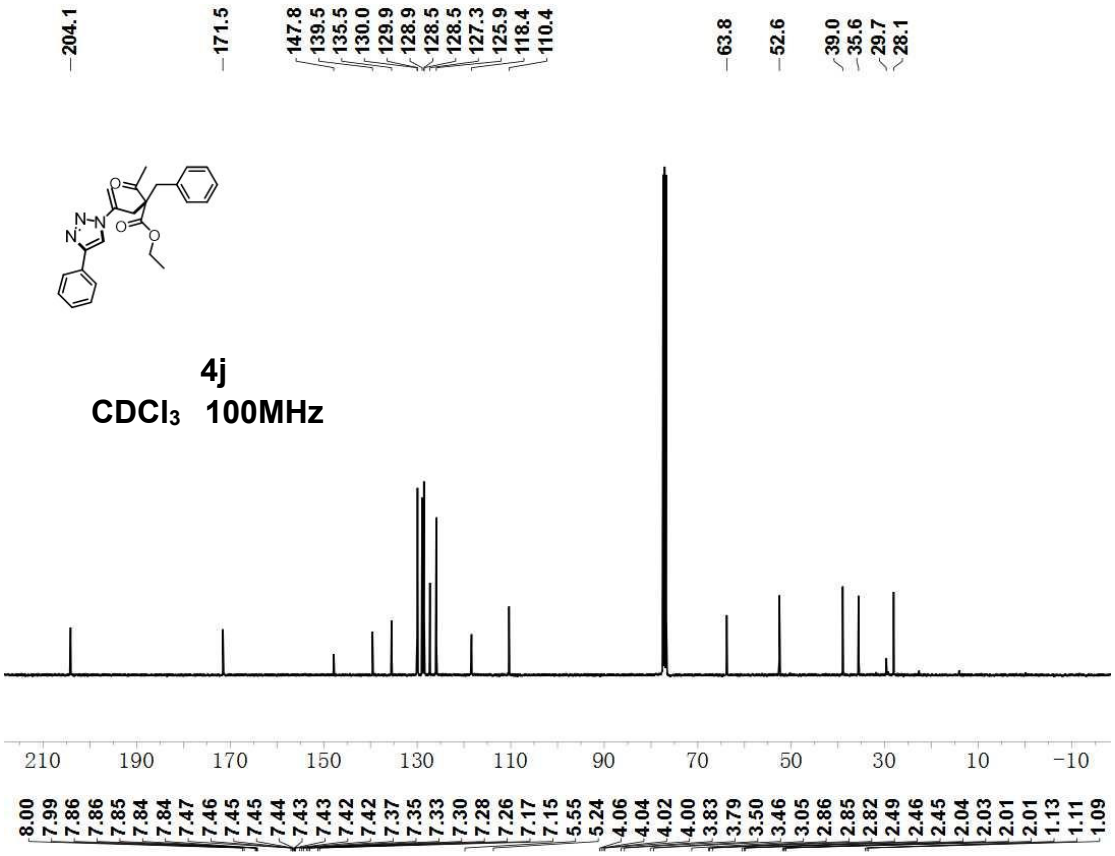
4i

$CDCl_3$ 100MHz



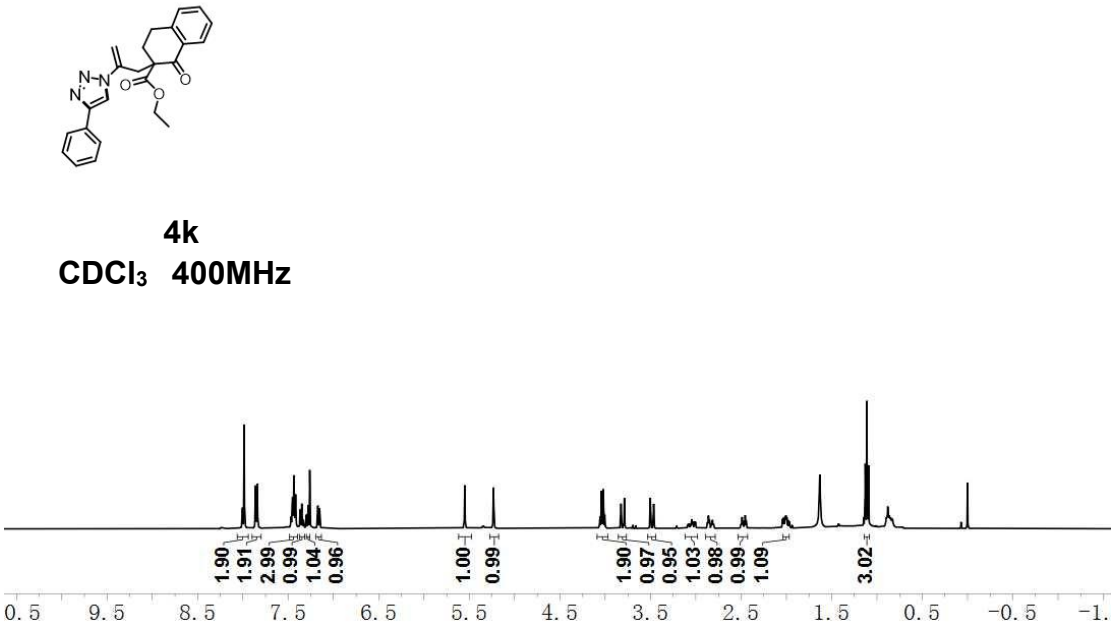
4j

$CDCl_3$ 400MHz



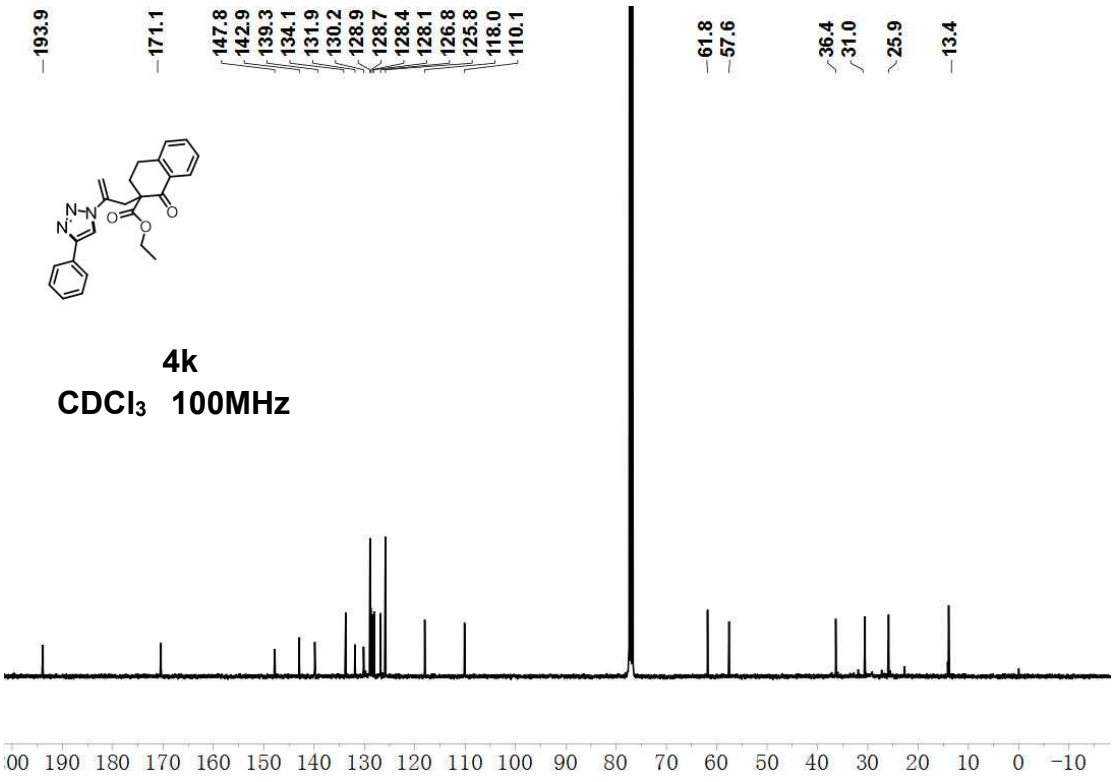
4j

$CDCl_3$ 100MHz



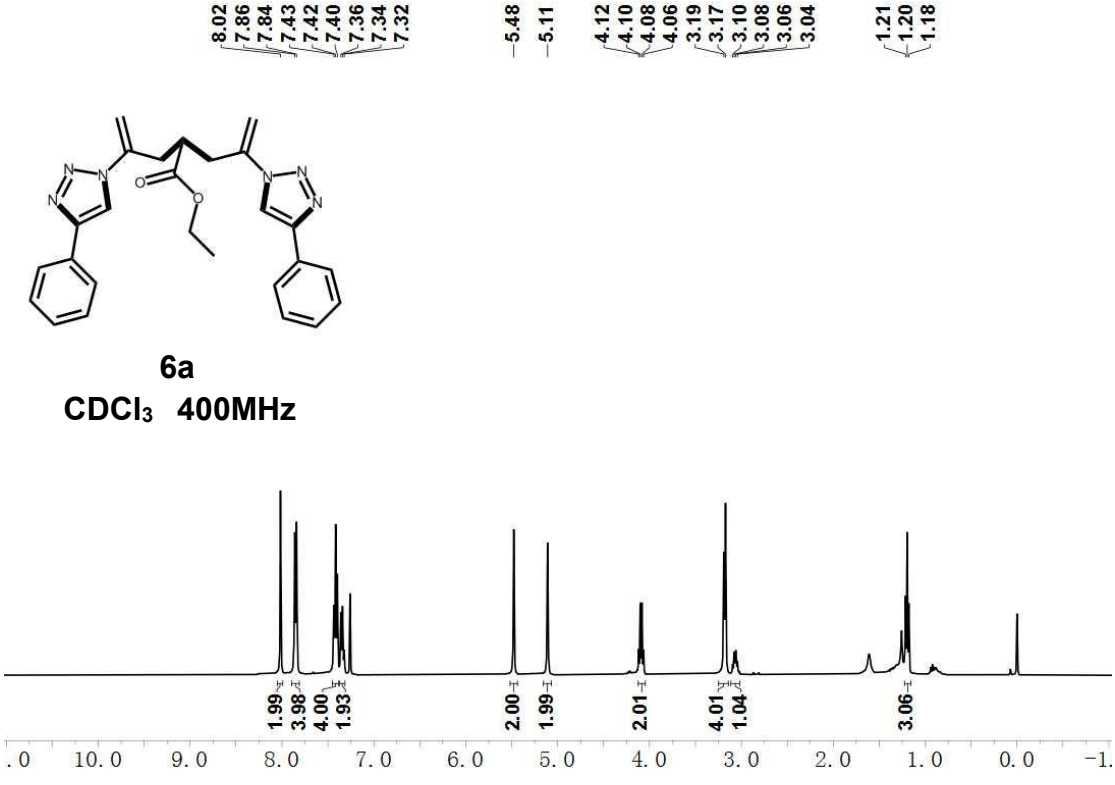
4k

$CDCl_3$ 400MHz



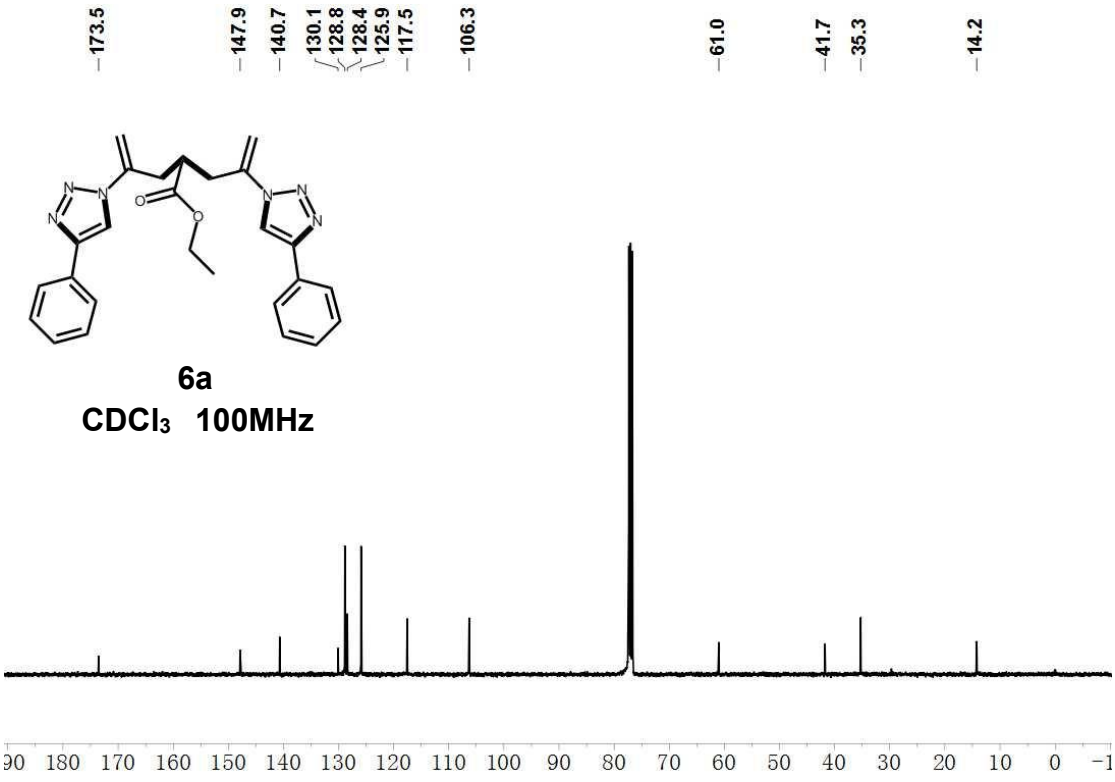
4k

$CDCl_3$ 100MHz



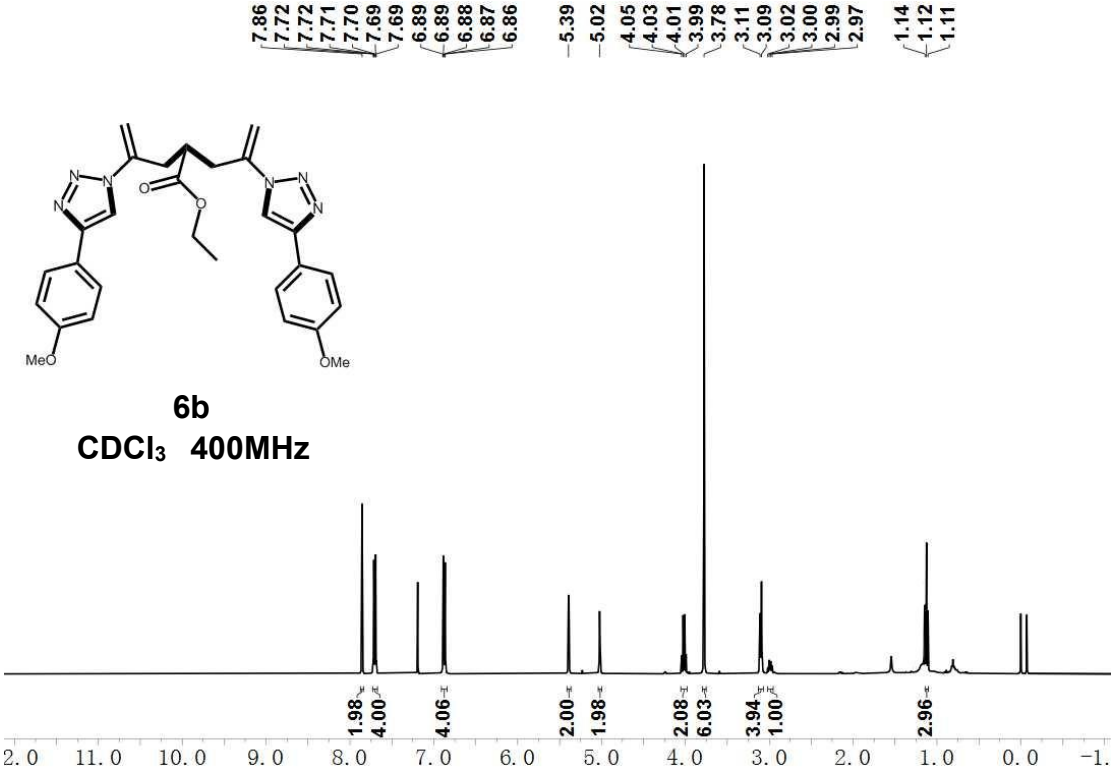
6a

$CDCl_3$ 400MHz



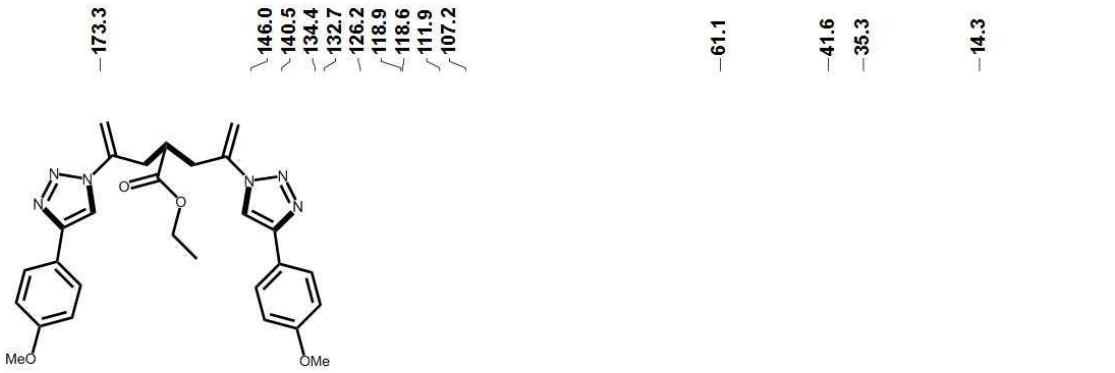
6a

$CDCl_3$ 100MHz



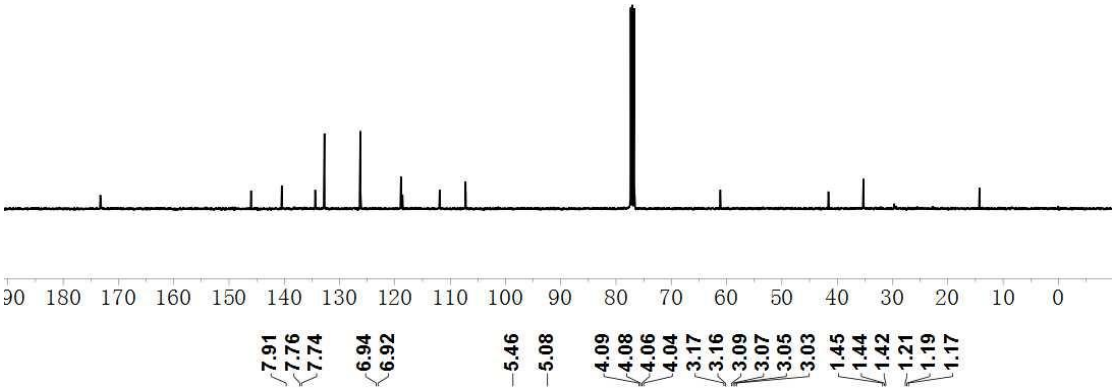
6b

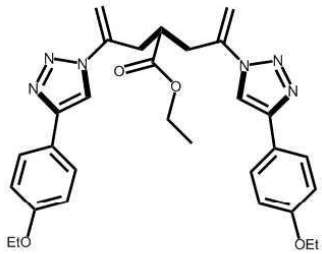
$CDCl_3$ 400MHz



6b

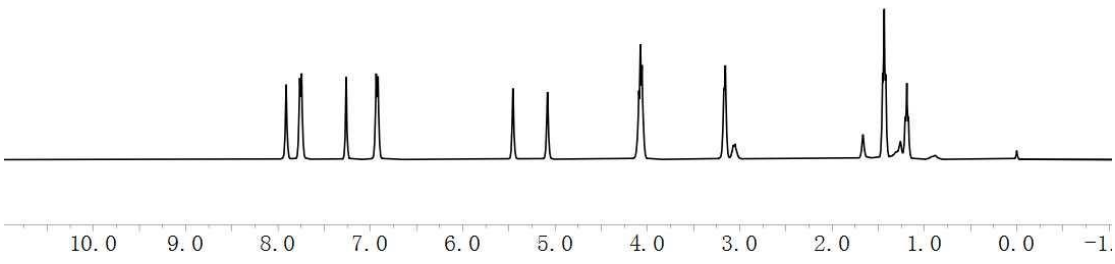
$CDCl_3$ 100MHz

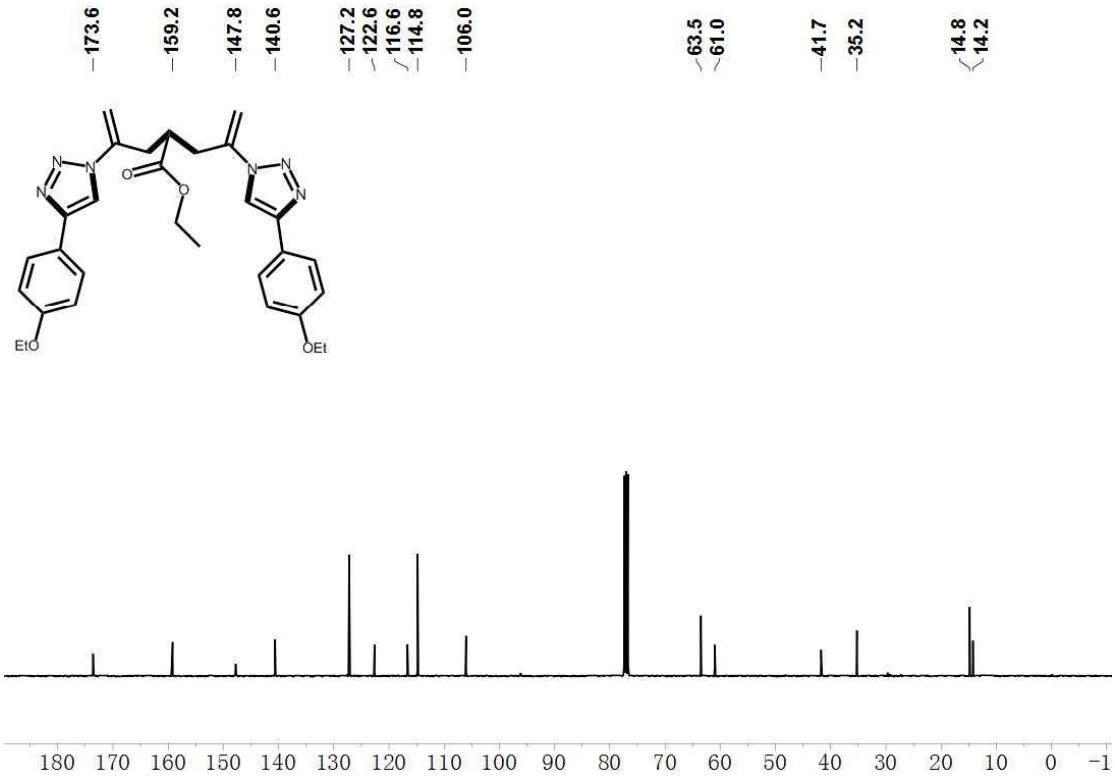


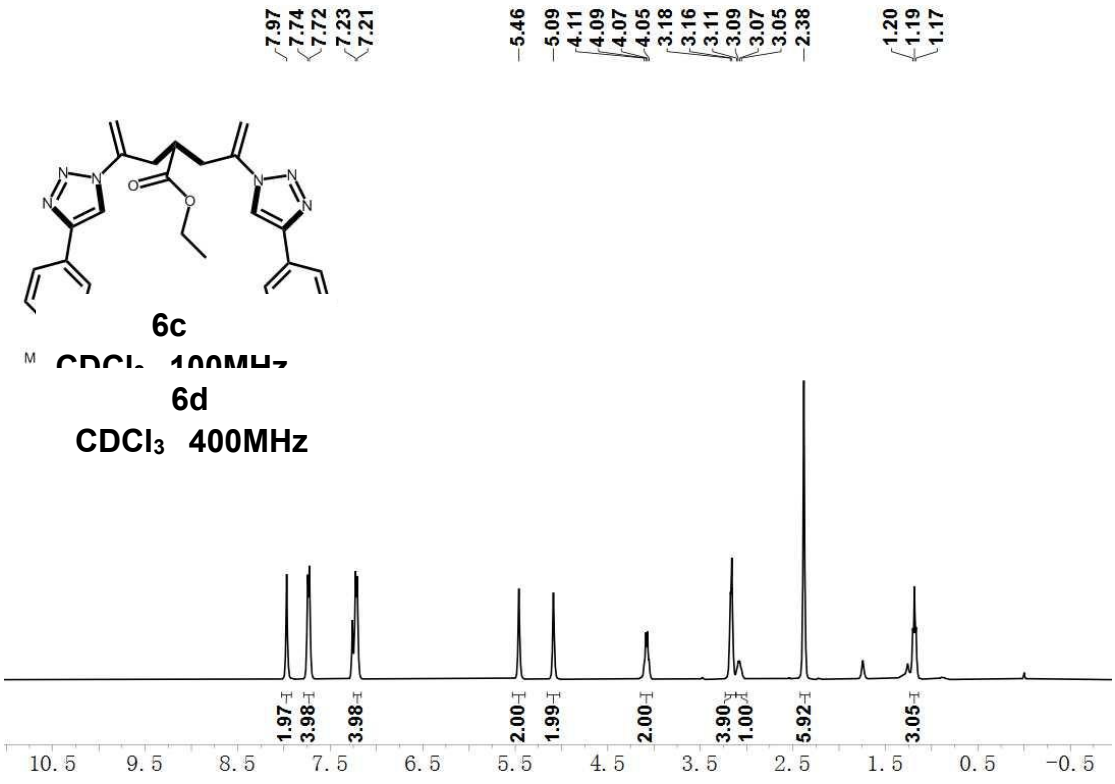


6c

$CDCl_3$ 400MHz



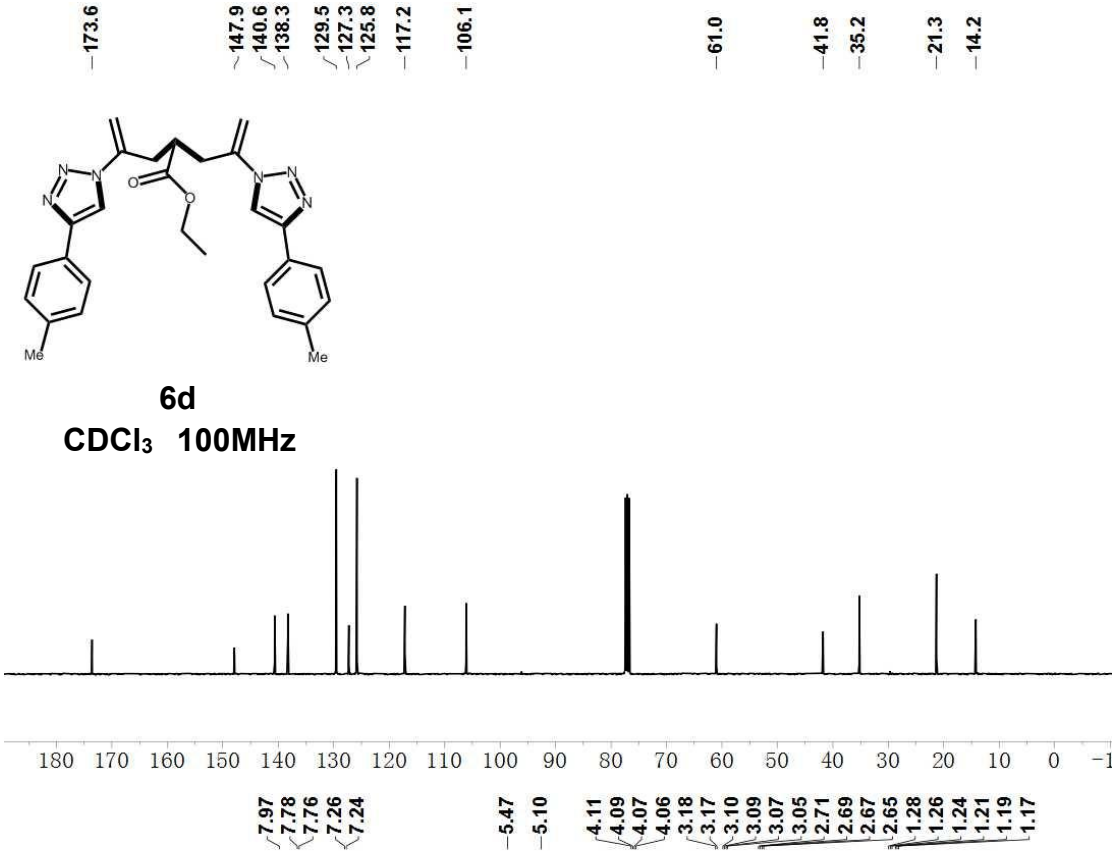




6c

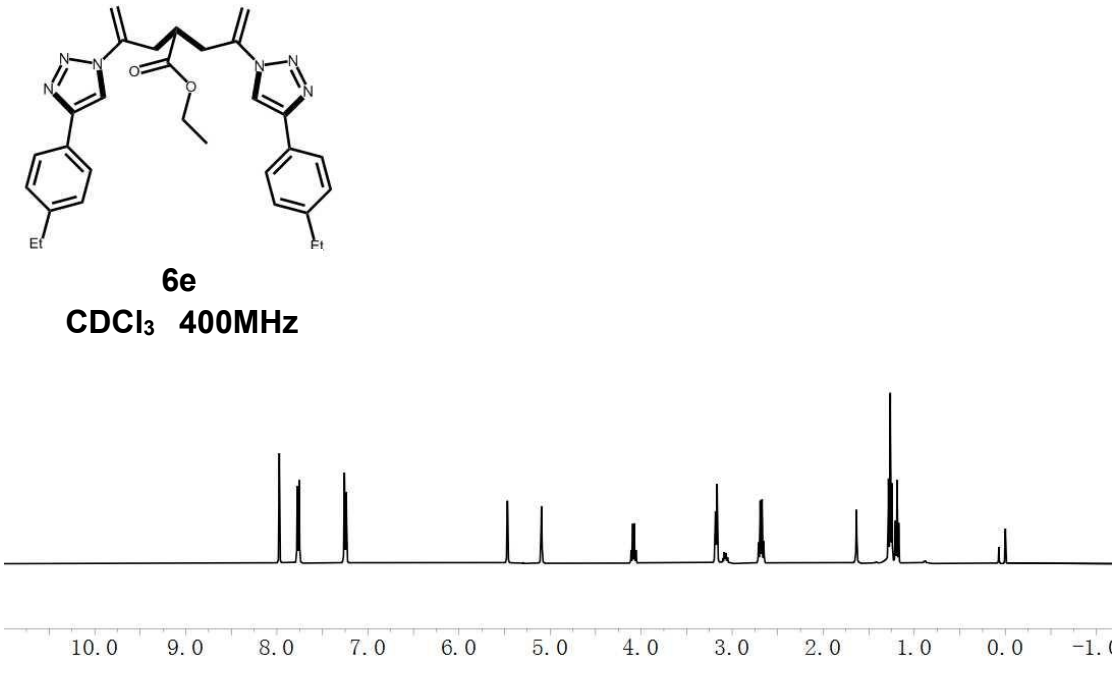
6d

$CDCl_3$ 400MHz



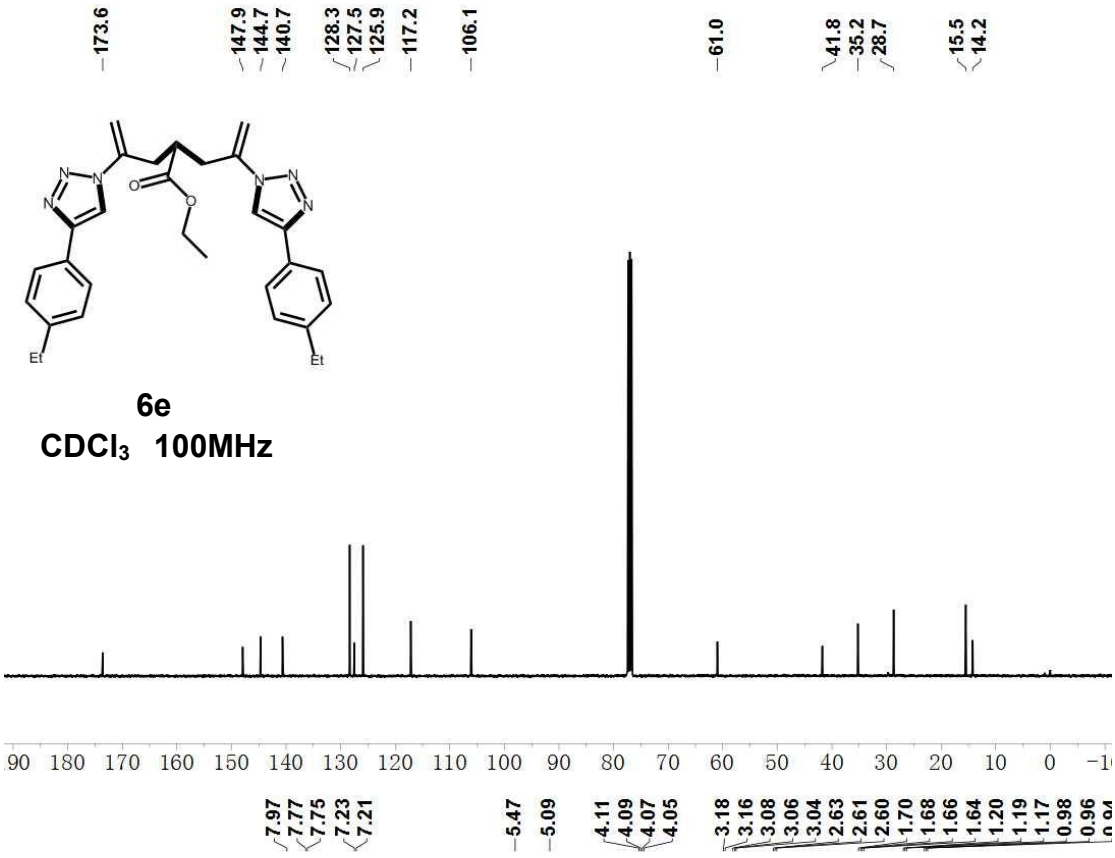
6d

$CDCl_3$ 100MHz



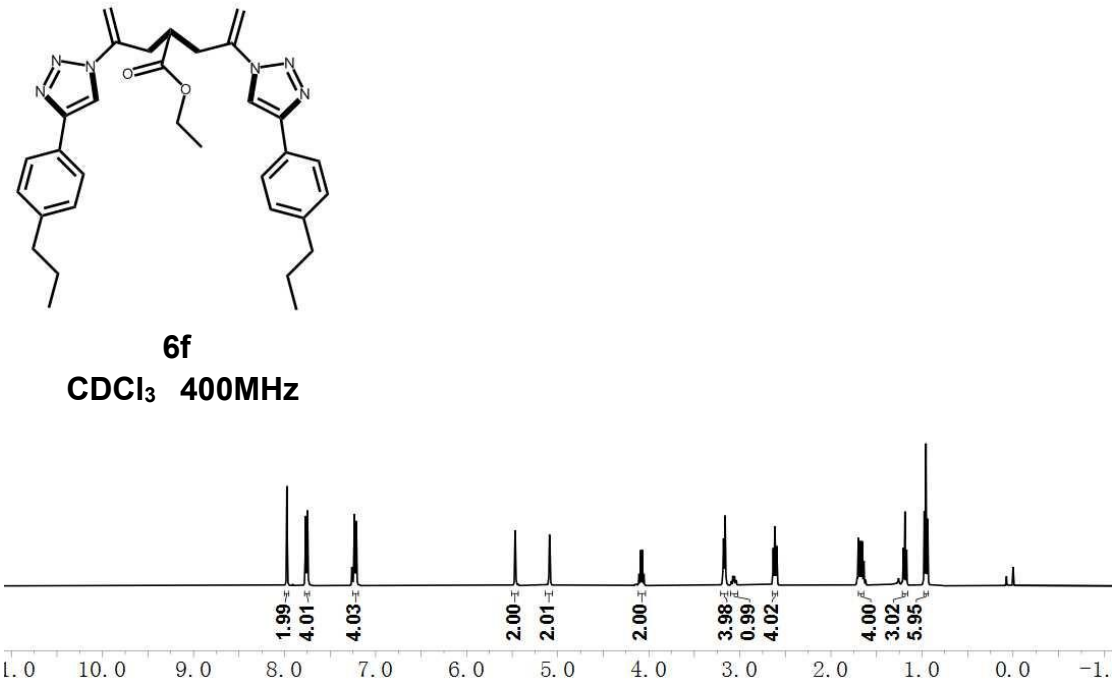
6e

$CDCl_3$ 400MHz



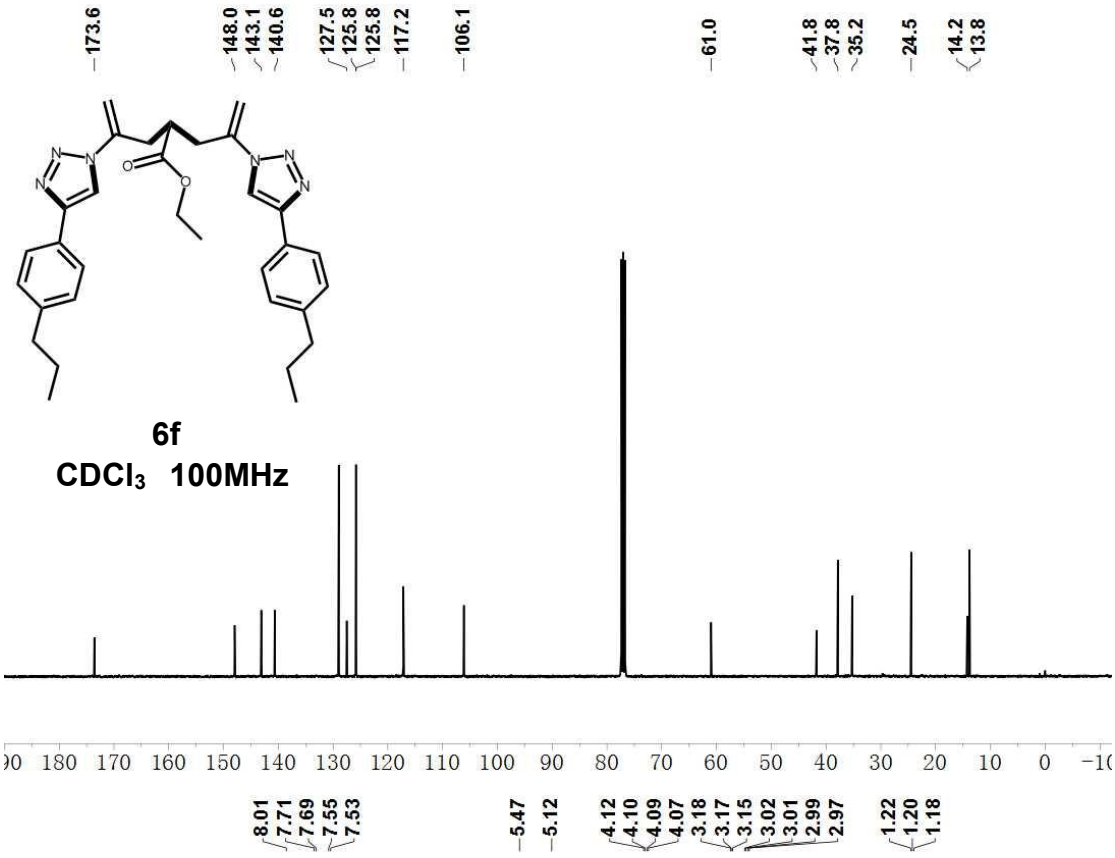
6e

$CDCl_3$ 100MHz



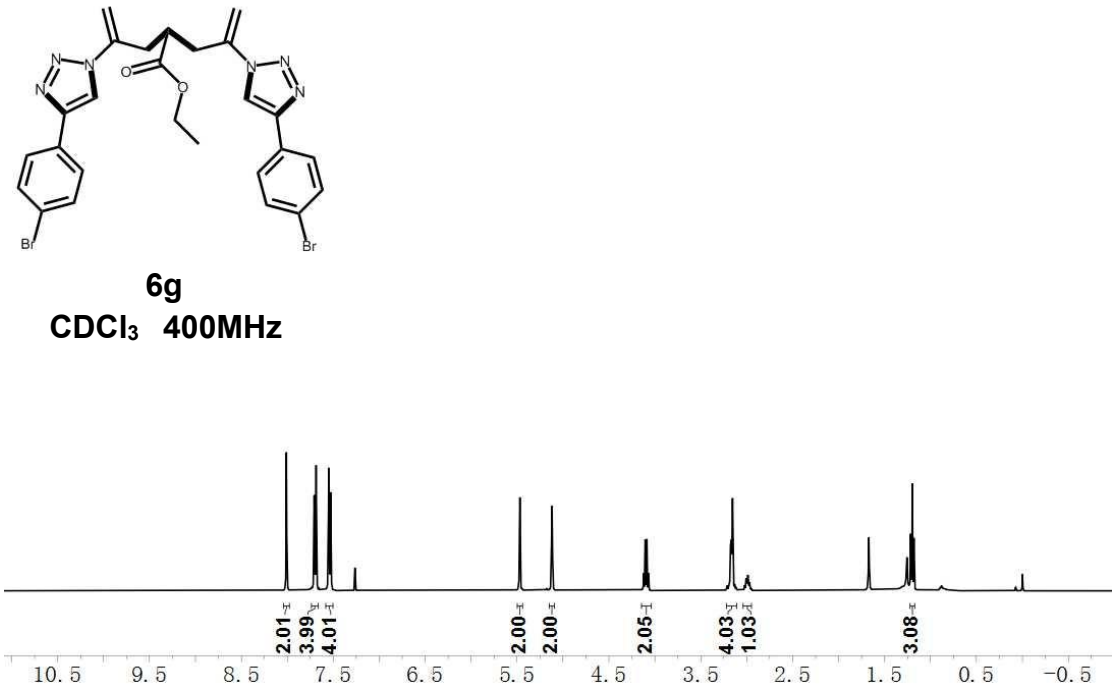
6f

$CDCl_3$ 400MHz



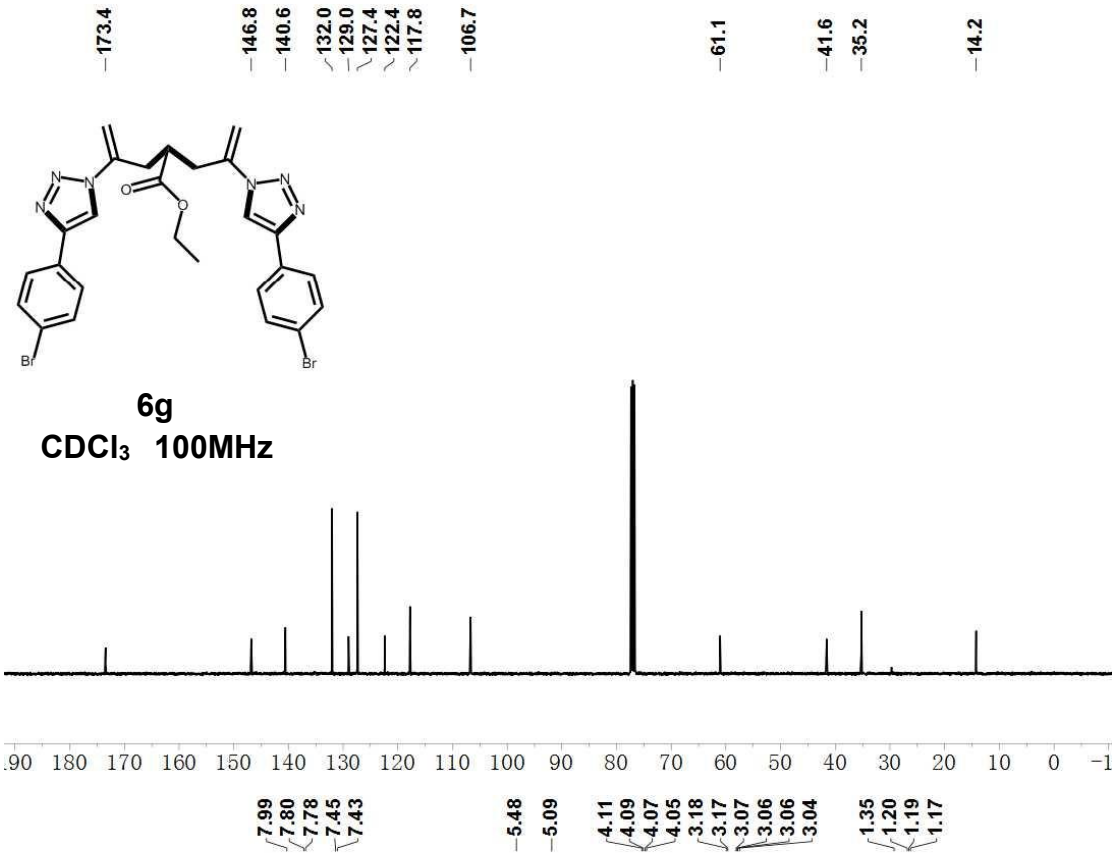
6f

$CDCl_3$ 100MHz



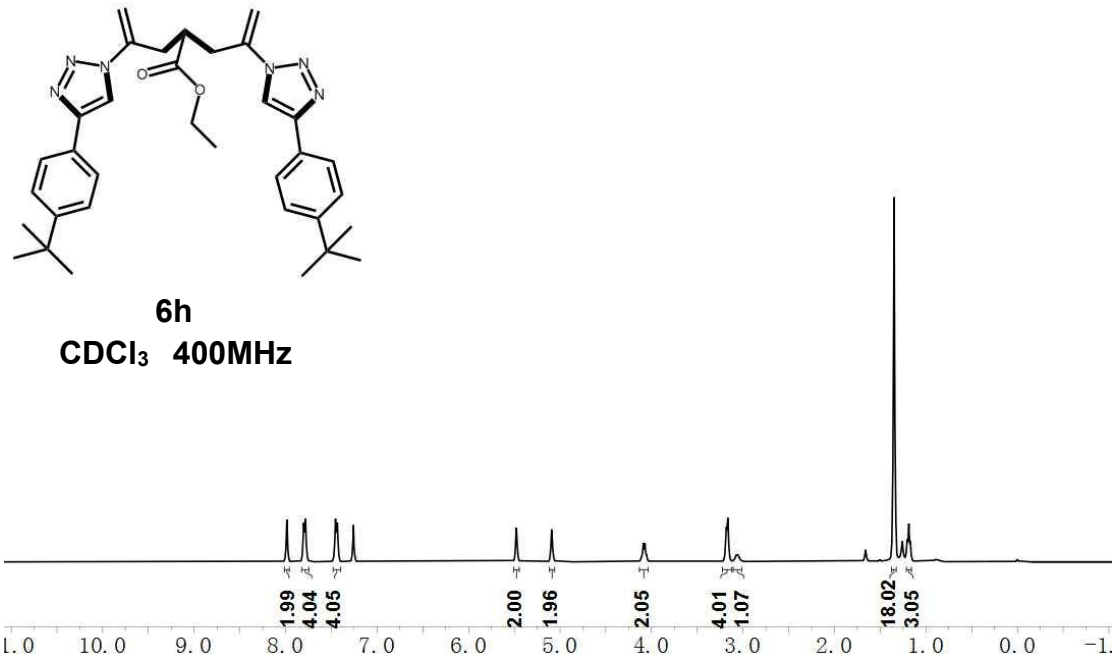
6g

$CDCl_3$ 400MHz



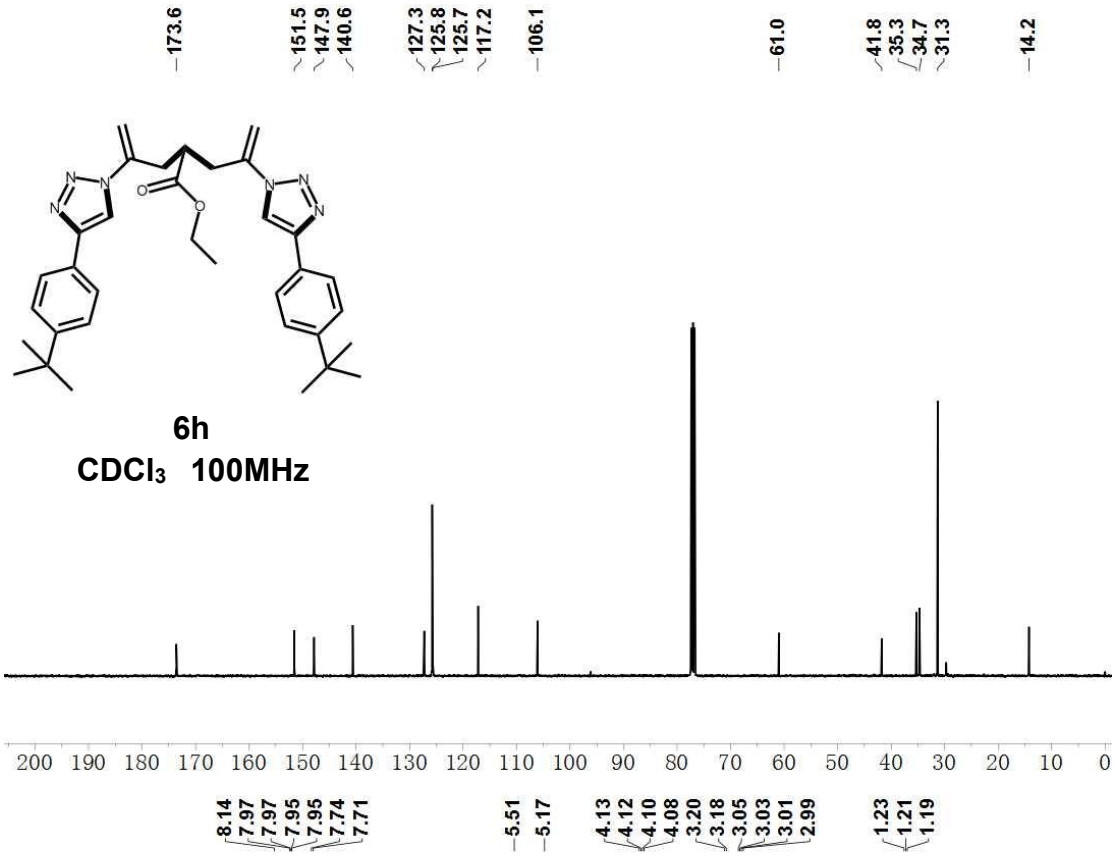
6g

$CDCl_3$ 100MHz



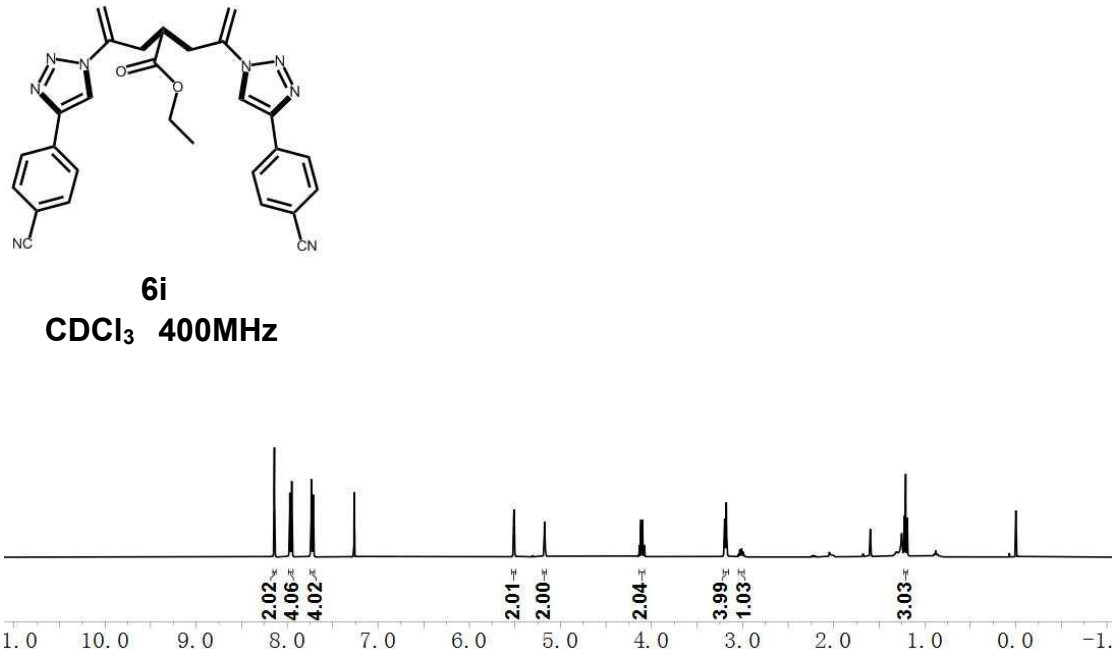
6h

$CDCl_3$ 400MHz



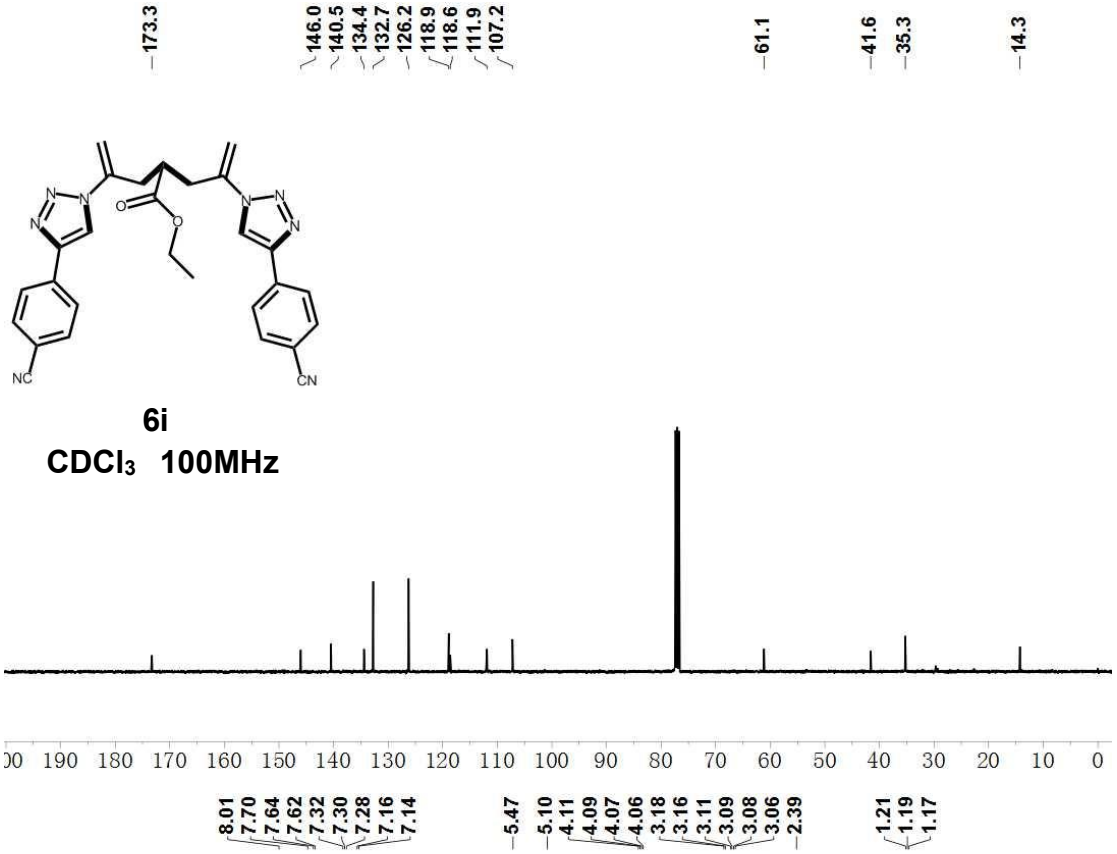
6h

$CDCl_3$ 100MHz



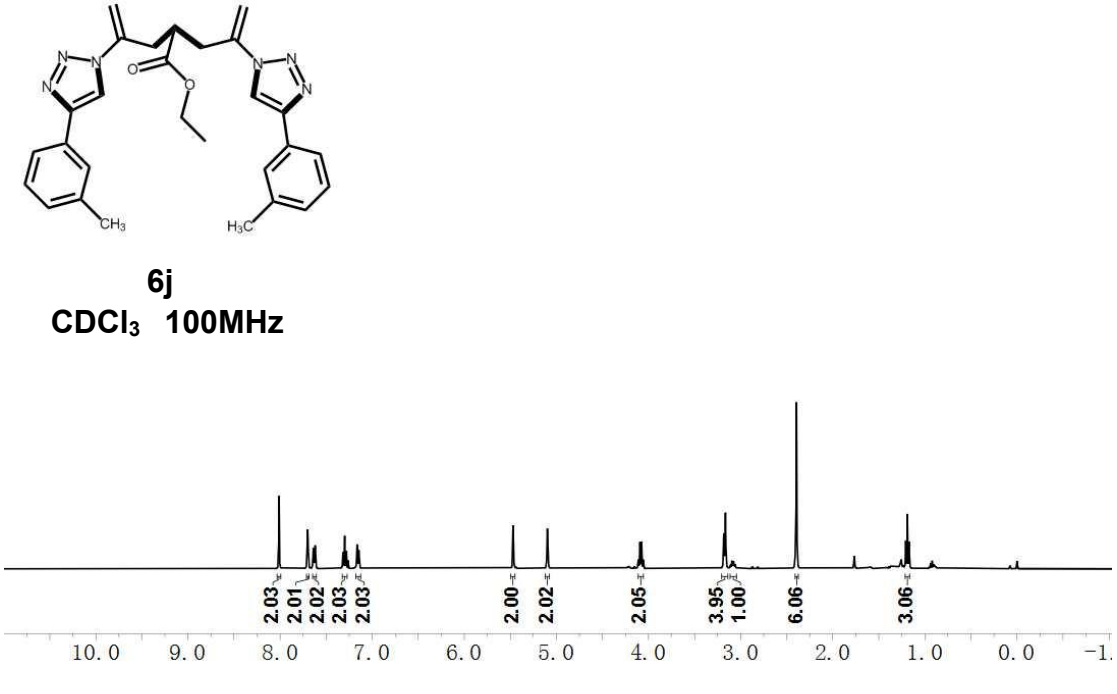
6i

$CDCl_3$ 400MHz



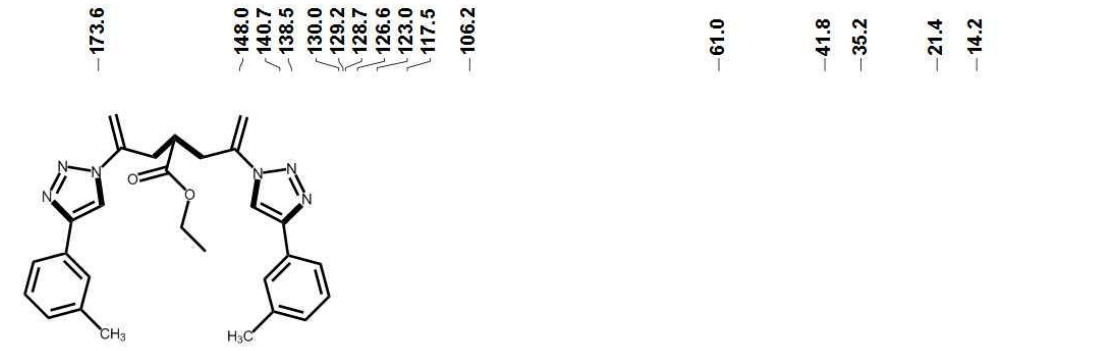
6i

$CDCl_3$ 100MHz



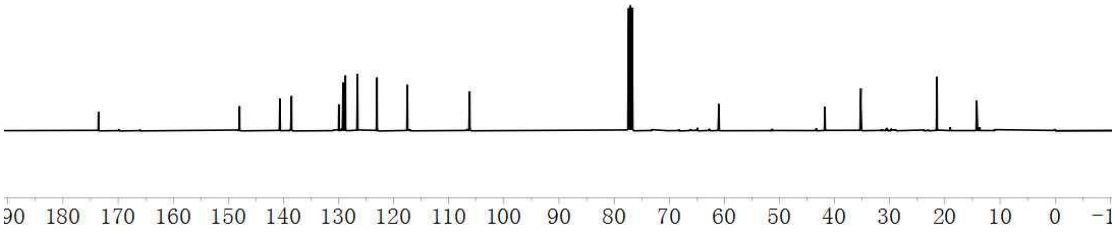
6j

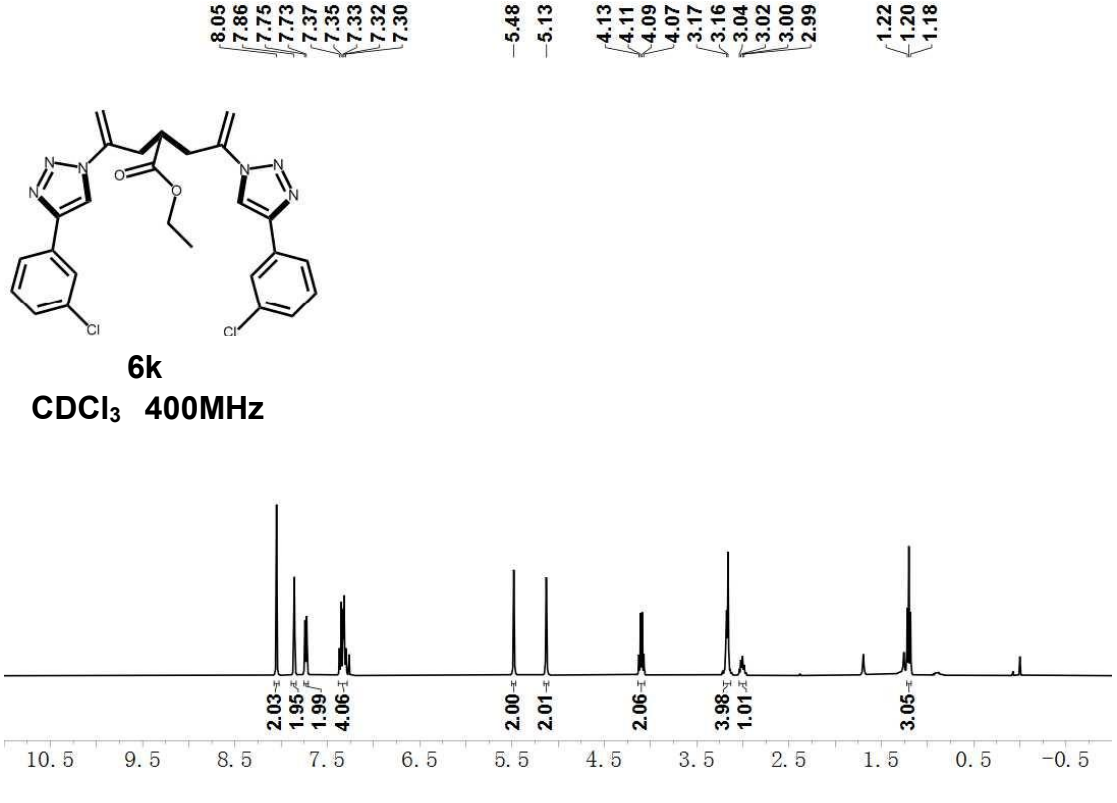
$CDCl_3$ 100MHz



6j

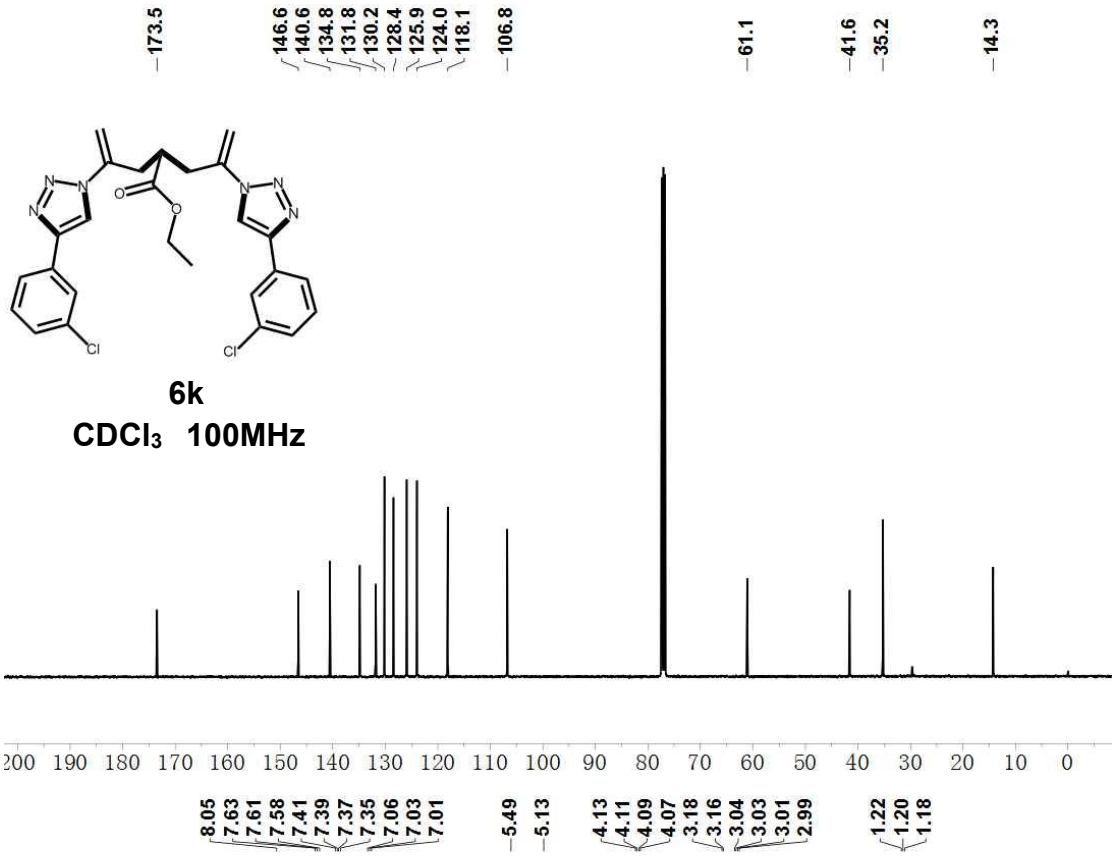
$CDCl_3$ 100MHz





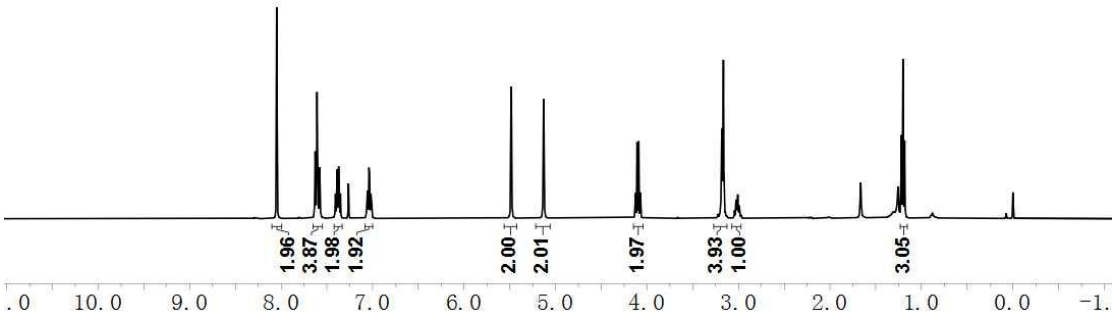
6k

$CDCl_3$ 400MHz



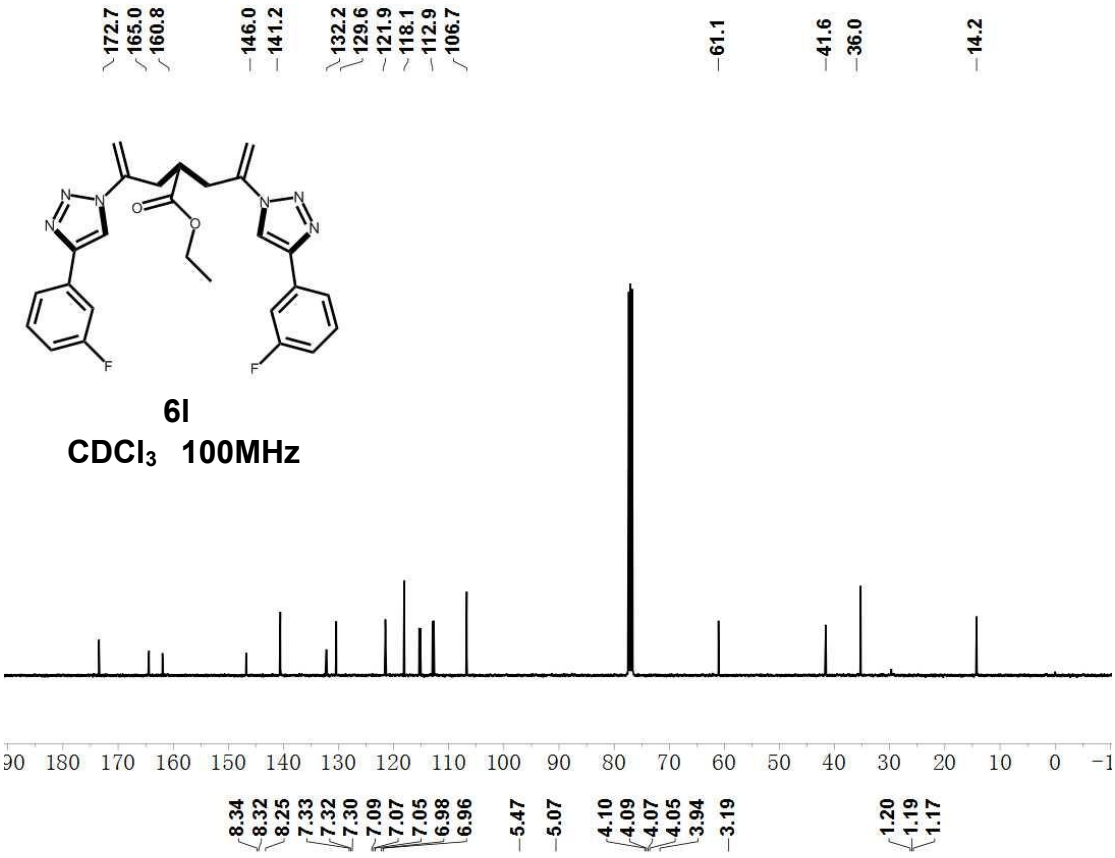
6k

$CDCl_3$ 100MHz



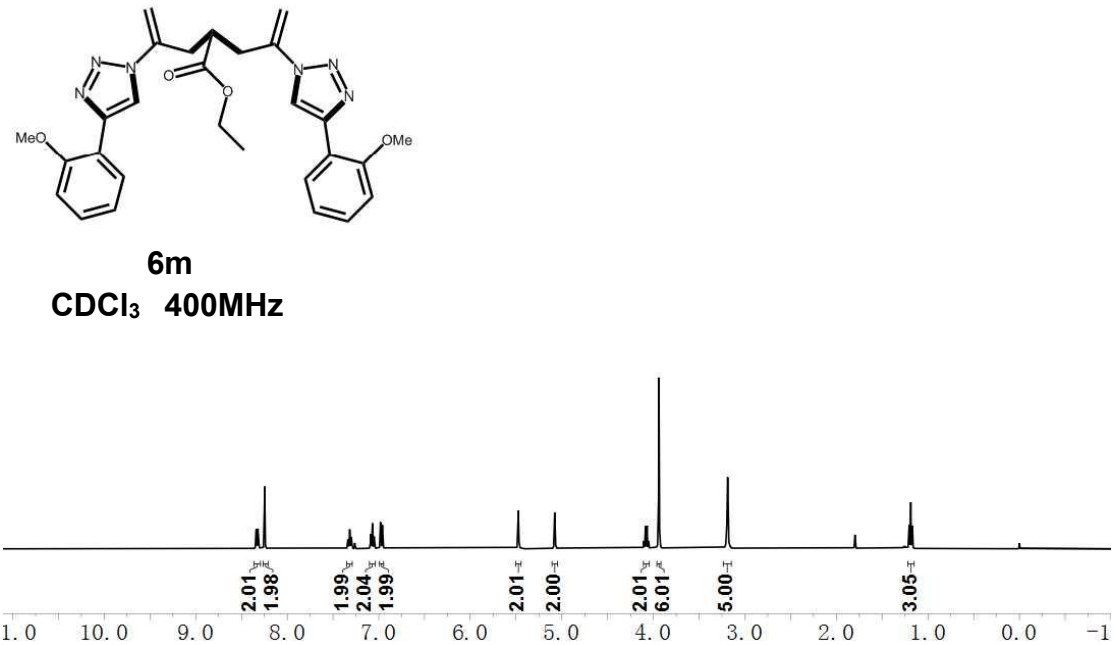
6l

$CDCl_3$ 400MHz



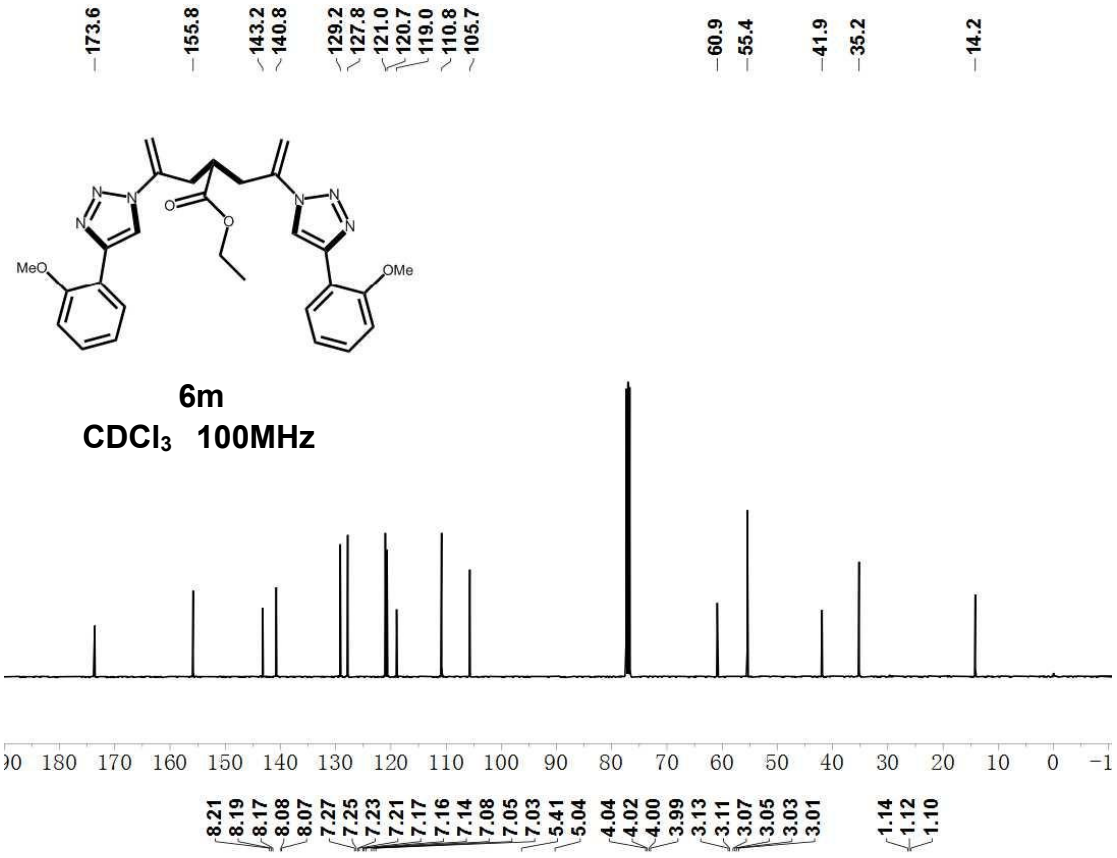
6l

$CDCl_3$ 100MHz



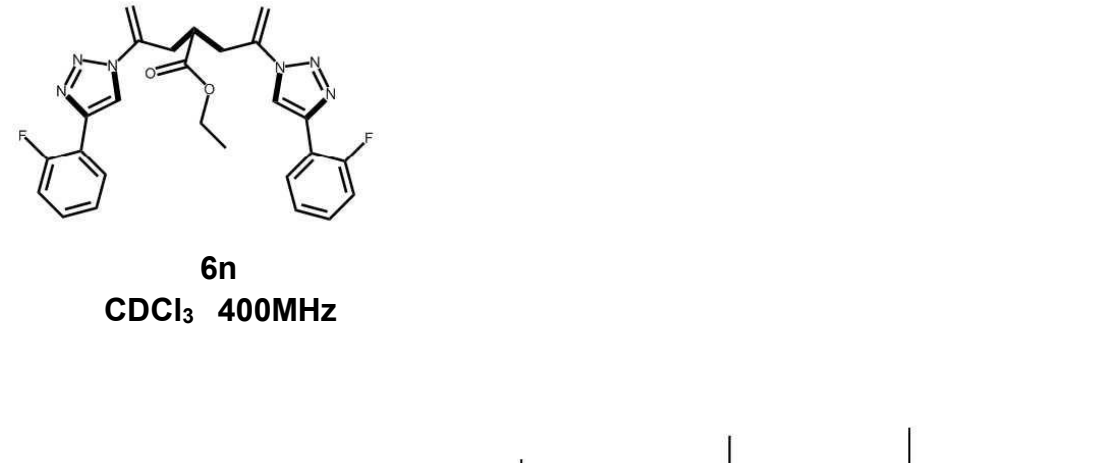
6m

$CDCl_3$ 400MHz



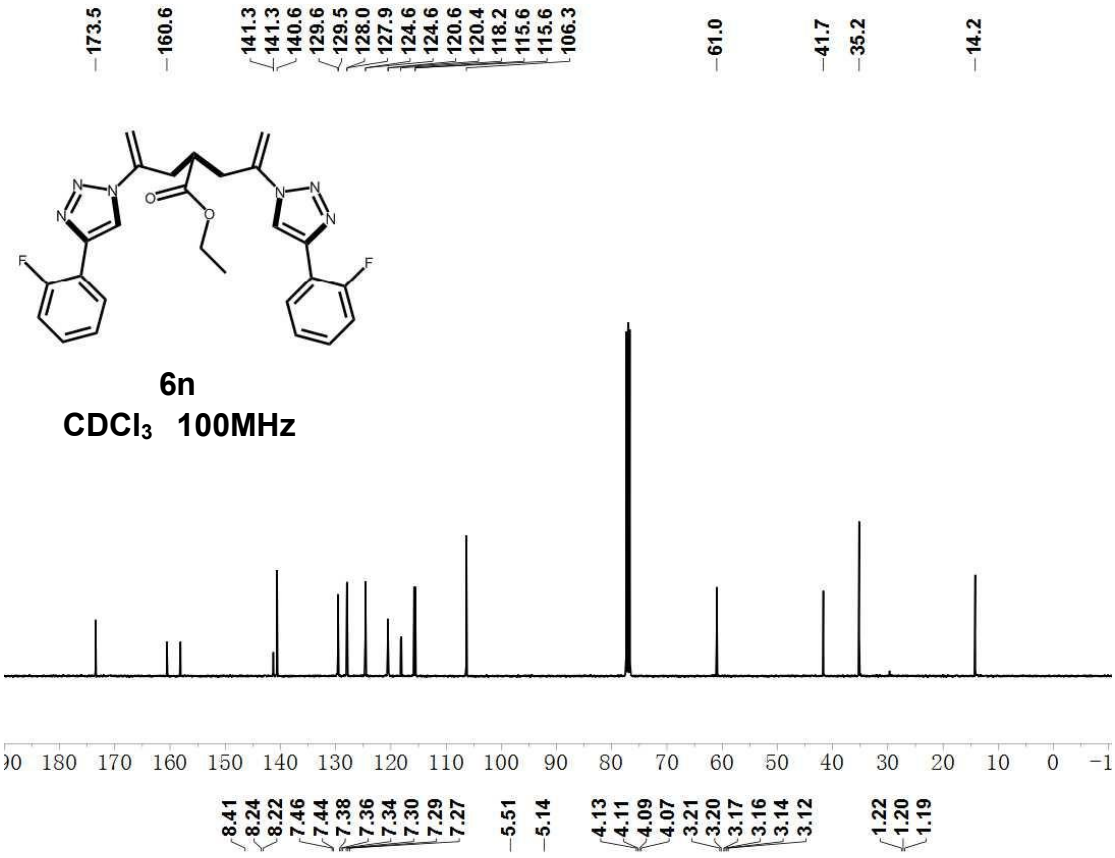
6m

$CDCl_3$ 100MHz



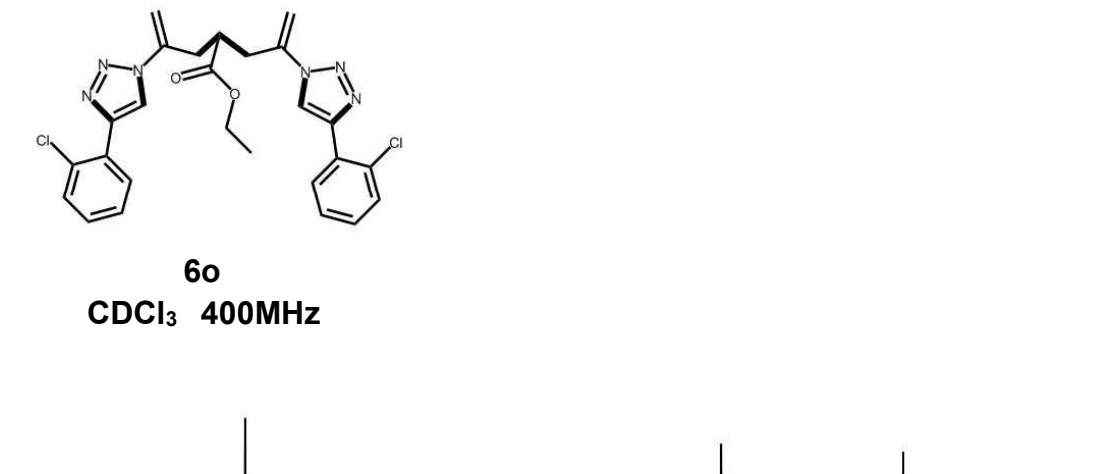
6n

$CDCl_3$ 400MHz



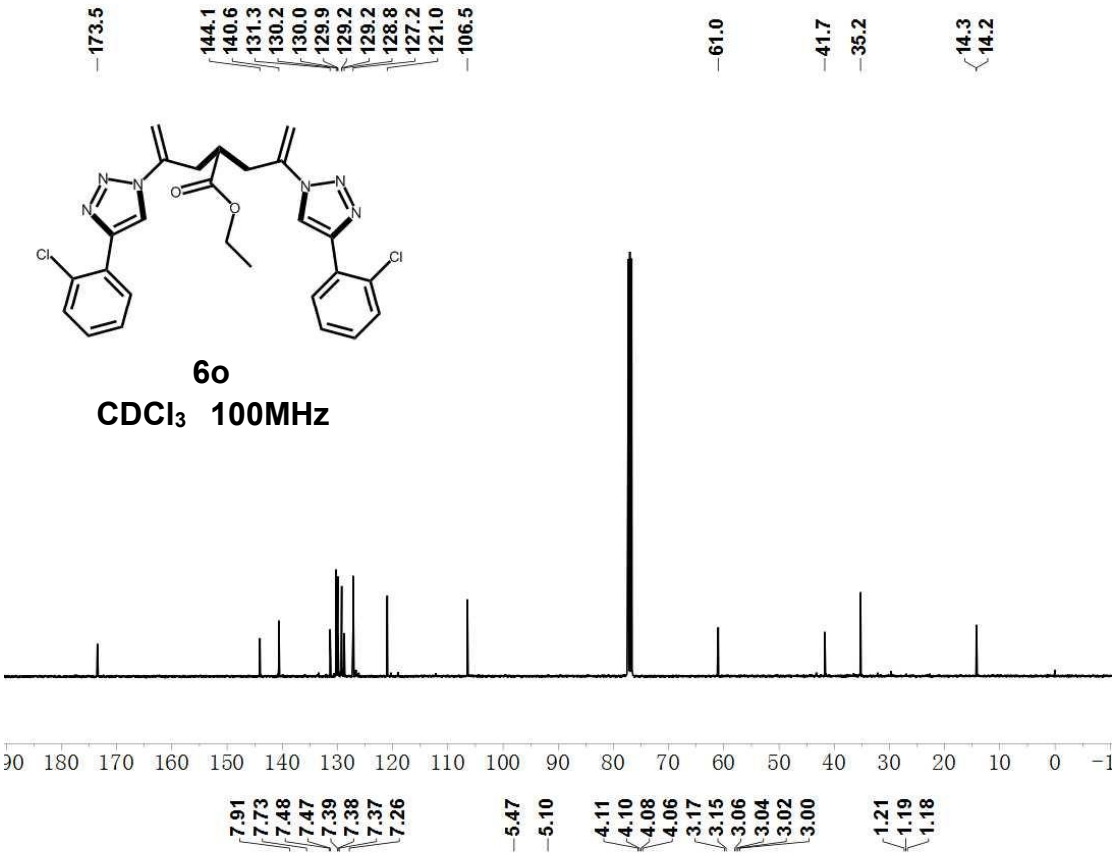
6n

$CDCl_3$ 100MHz



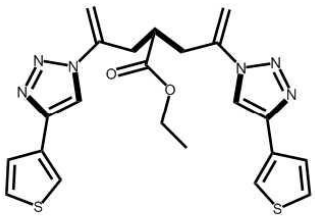
6o

$CDCl_3$ 400MHz



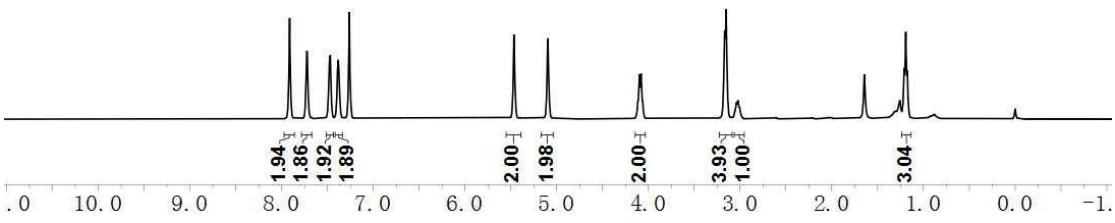
6o

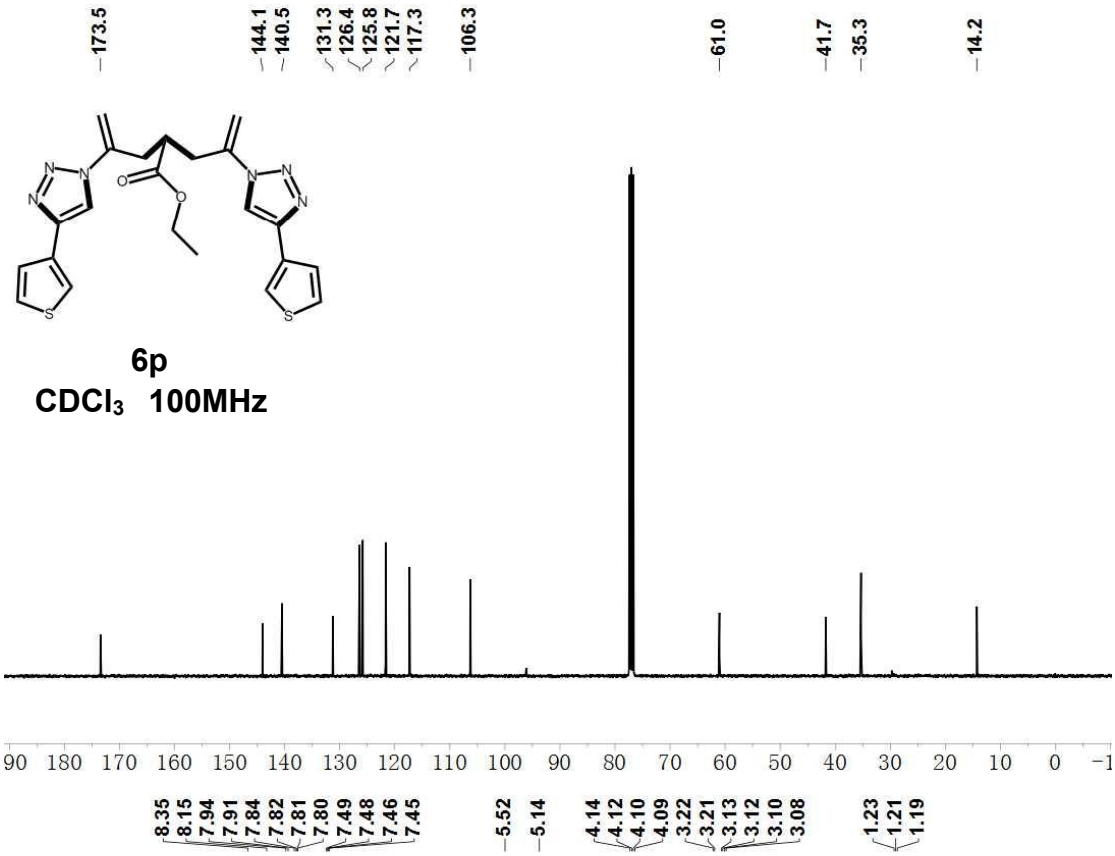
$CDCl_3$ 100MHz



6p

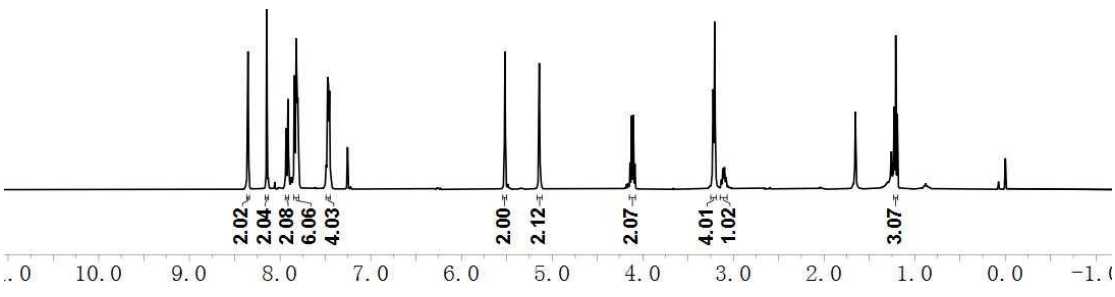
$CDCl_3$ 400MHz





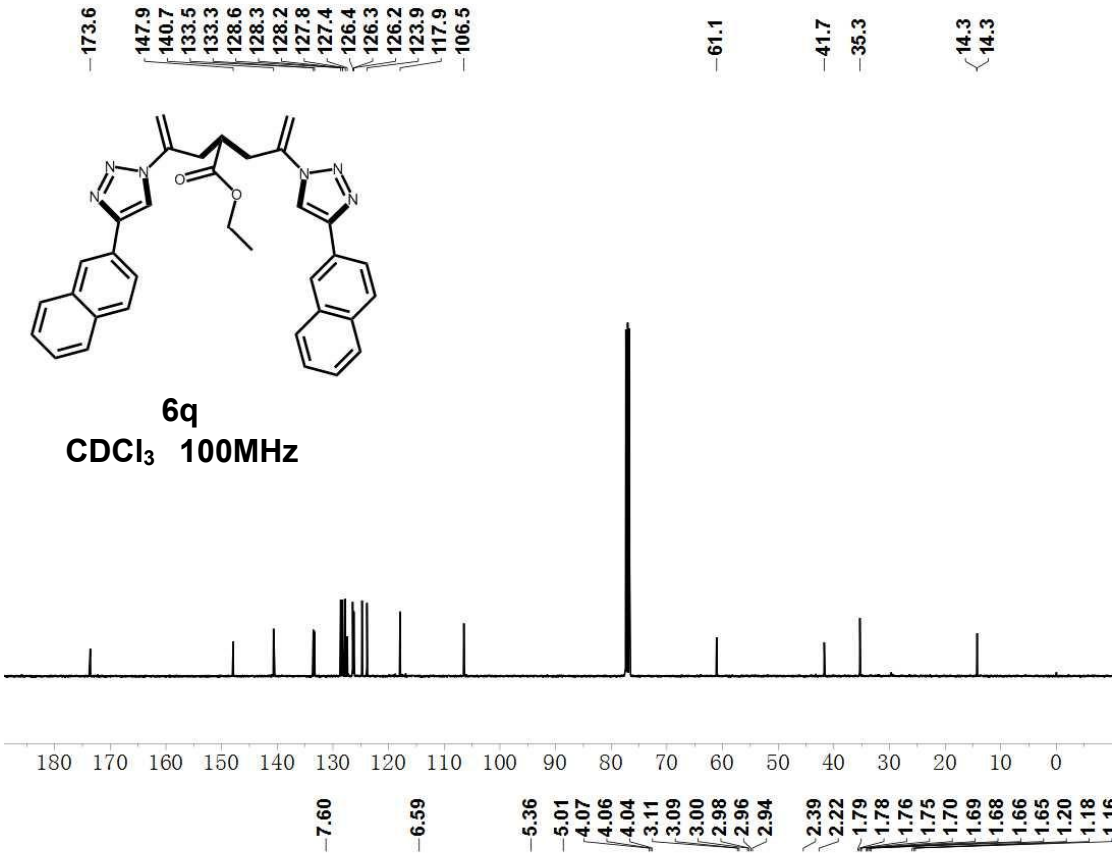
6p

$CDCl_3$ 100MHz



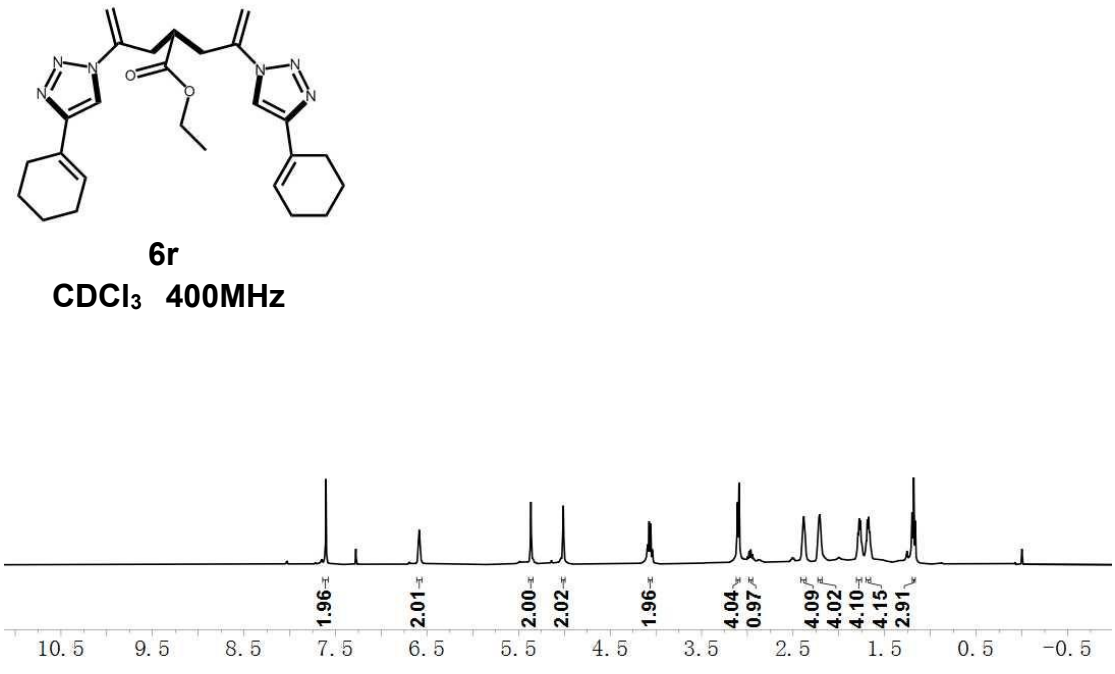
6q

$CDCl_3$ 400MHz



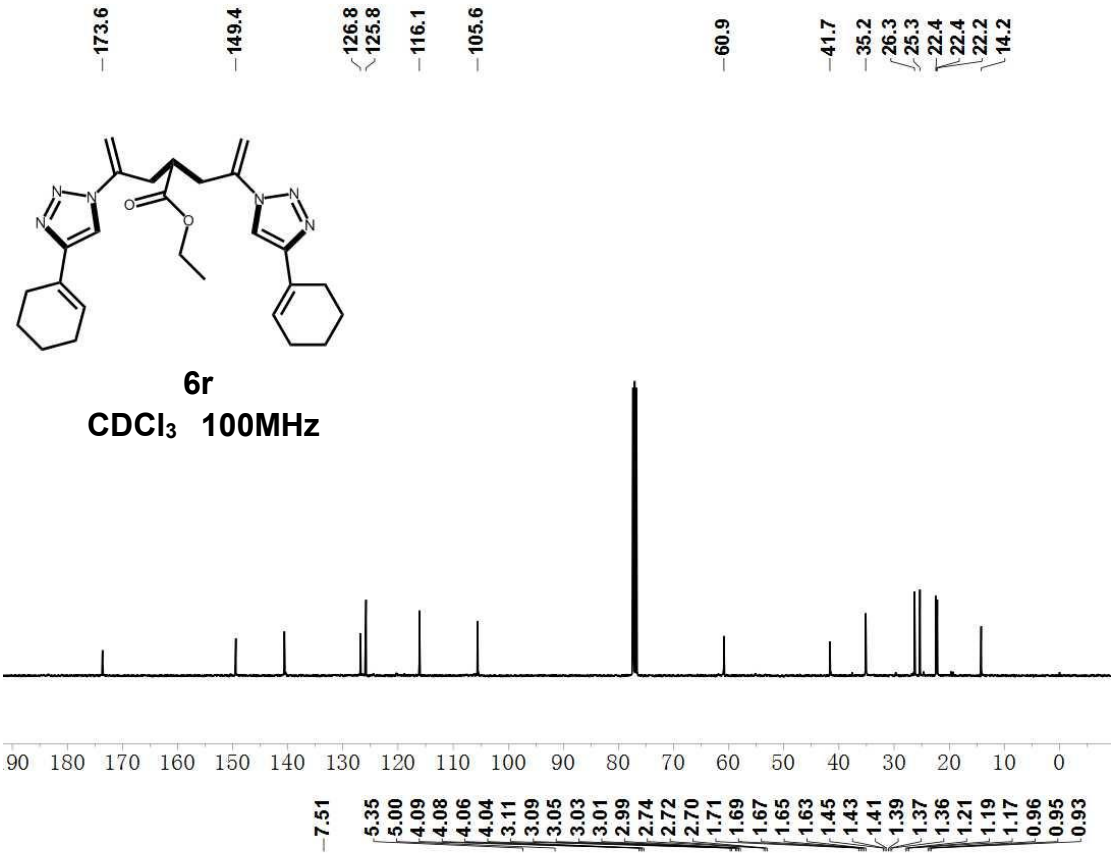
6q

$CDCl_3$ 100MHz



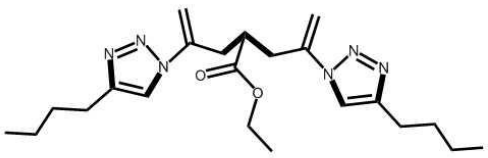
6r

$CDCl_3$ 400MHz



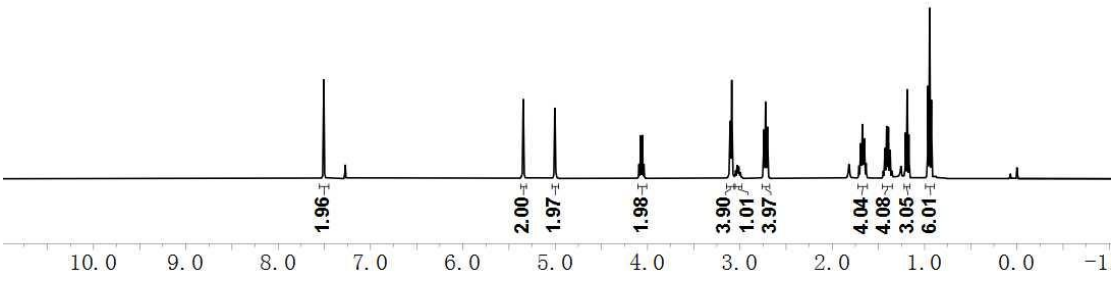
6r

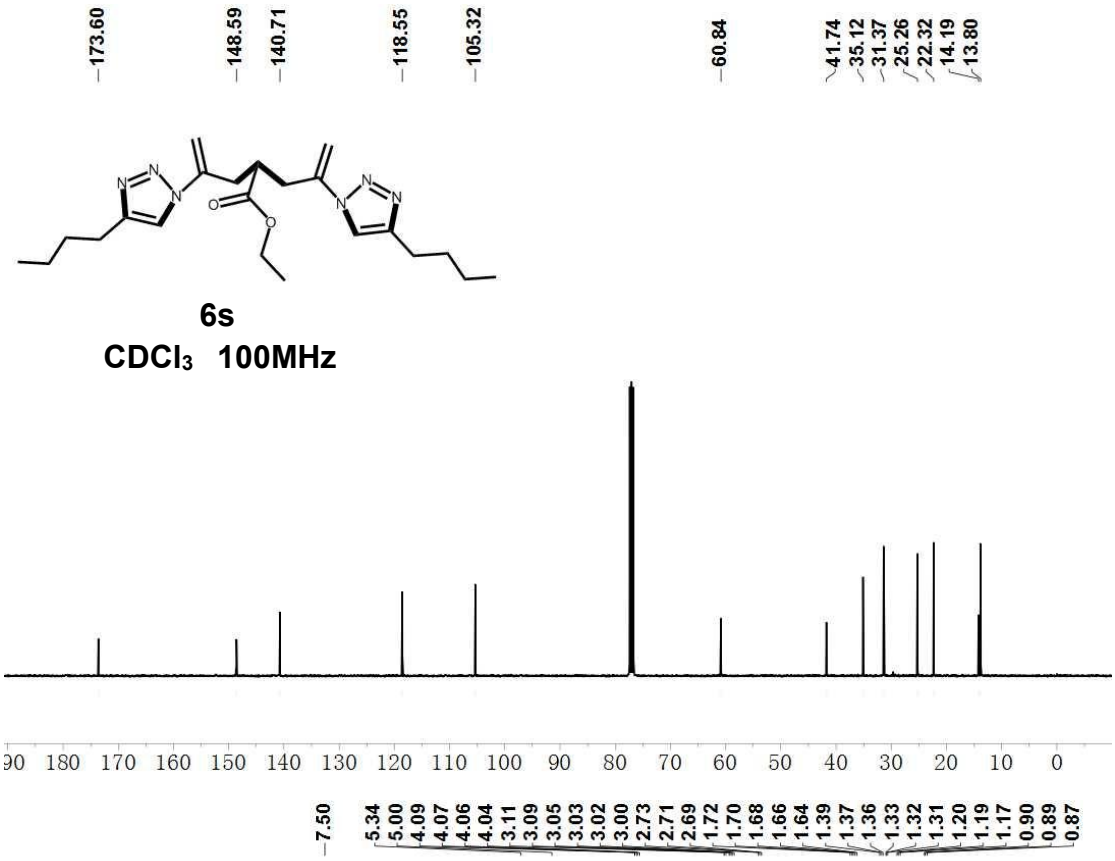
$CDCl_3$ 100MHz



6s

$CDCl_3$ 400MHz





6s

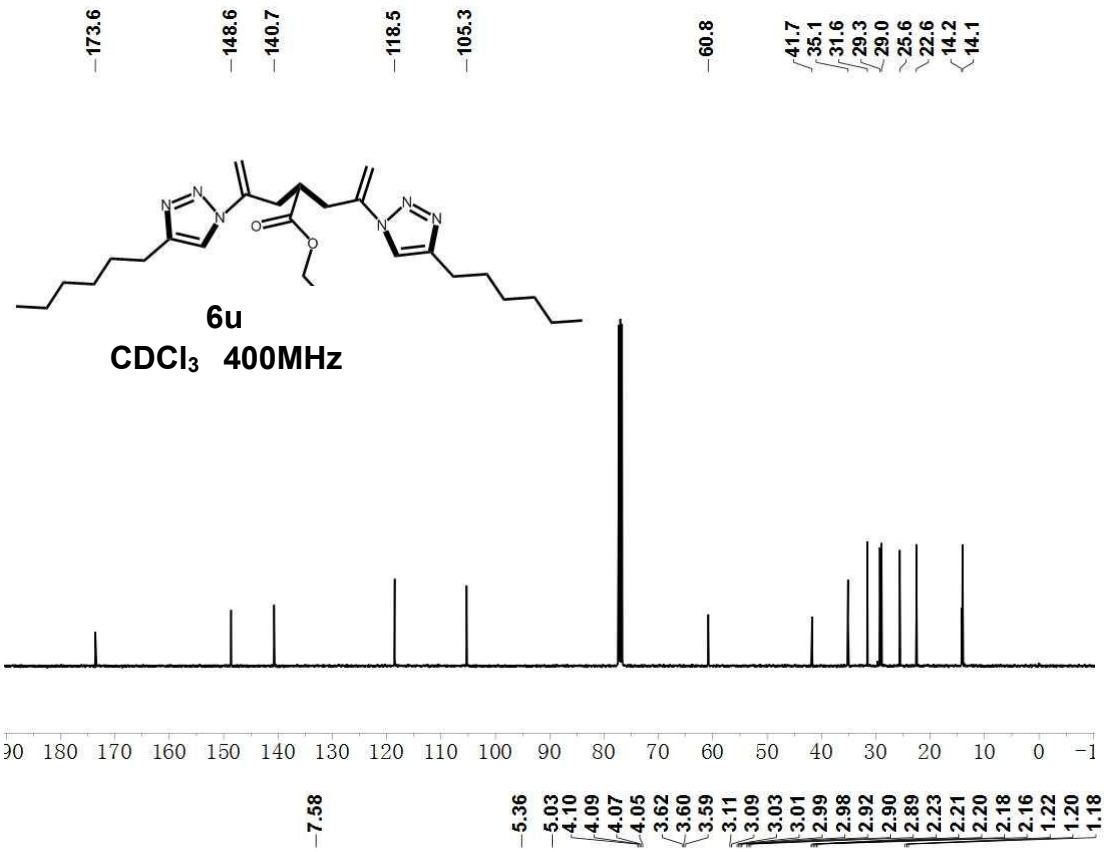
$CDCl_3$ 100MHz

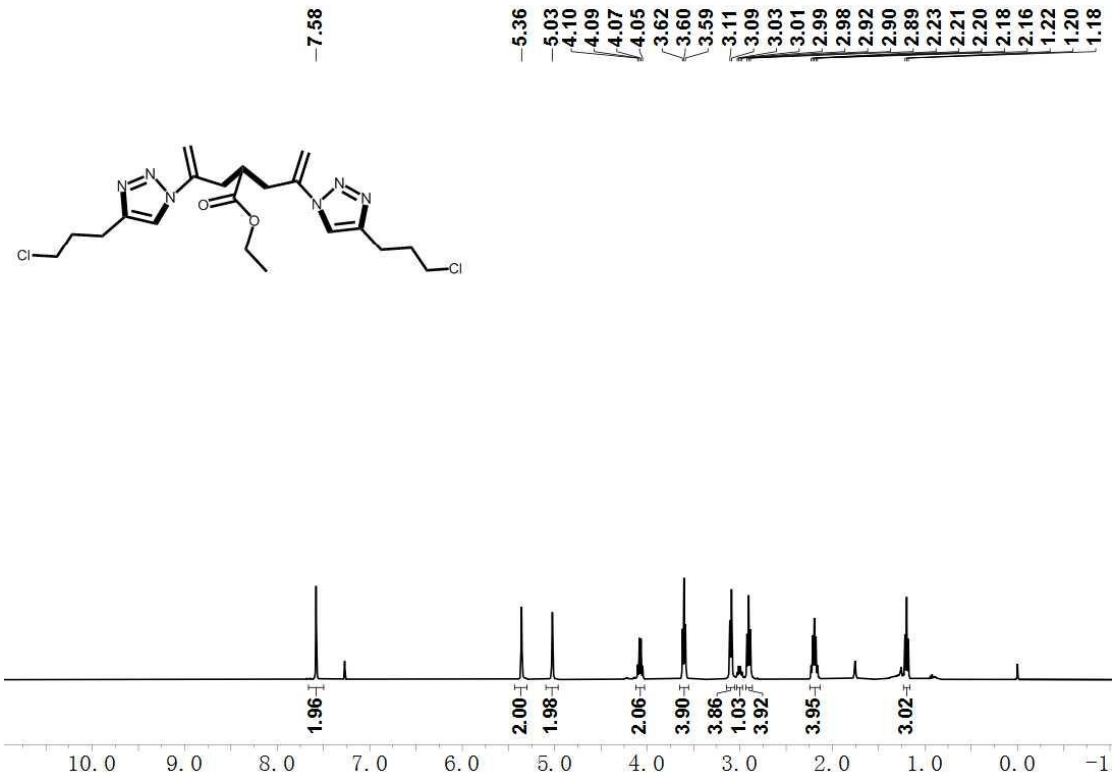
6t

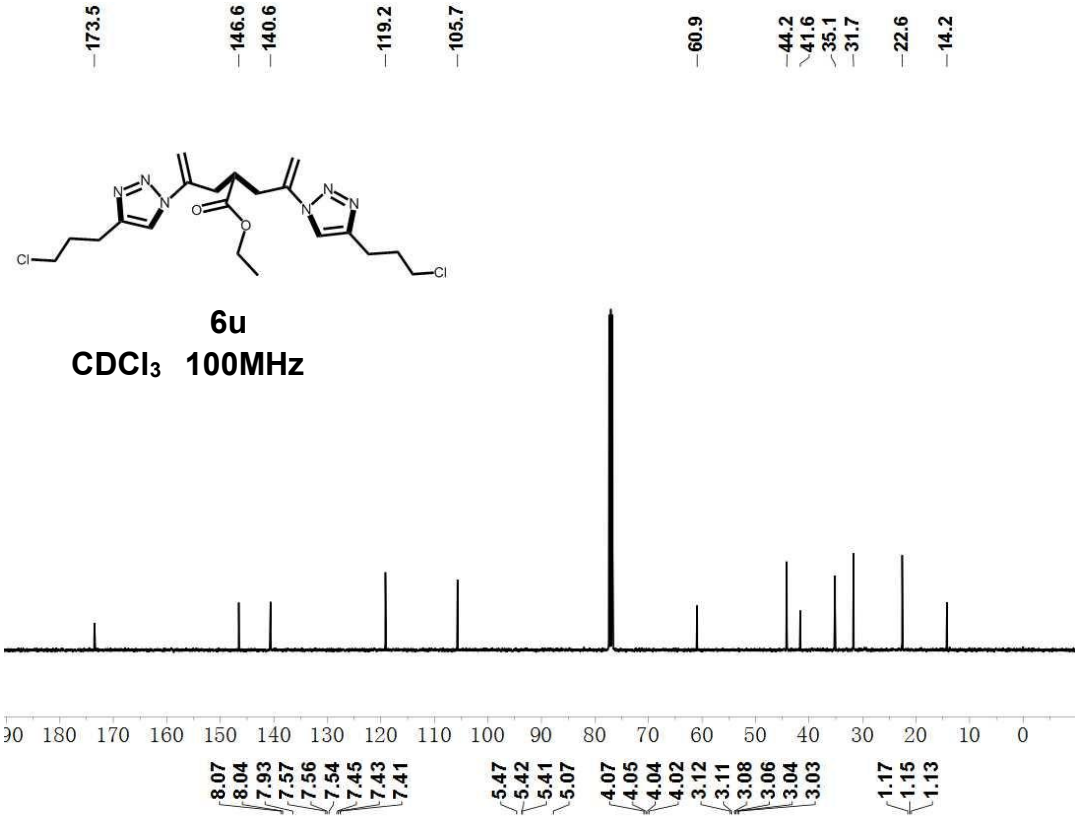
$CDCl_3$ 400MHz

6t

$CDCl_3$ 100MHz

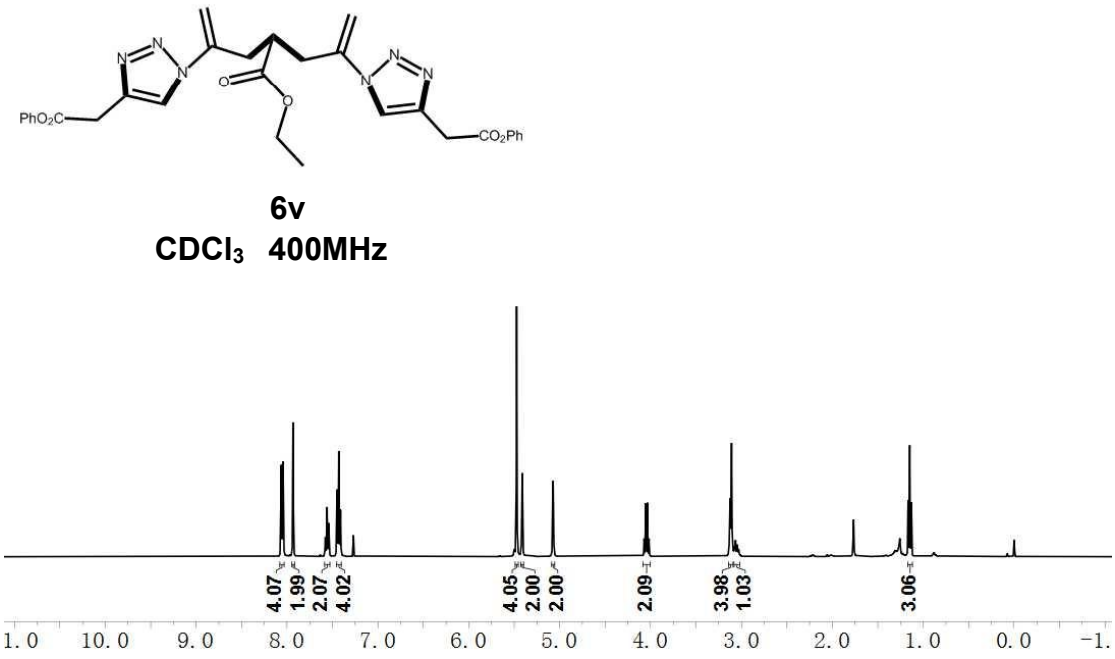

173.6
148.6
140.7
118.5
105.3
60.8
41.7
35.1
31.6
29.3
29.0
25.6
22.6
14.2
14.1
6u
CDCl3 400MHz
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1


7.58
5.36
5.03
4.10
4.09
4.07
4.05
3.62
3.60
3.59
3.11
3.09
3.03
3.01
2.99
2.98
2.92
2.90
2.89
2.23
2.21
2.20
2.18
2.16
1.22
1.20
1.18
Cl
Cl
1.96
2.00
1.98
2.06
3.90
3.86
1.03
3.92
3.95
3.02
10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 −1



6u

$CDCl_3$ 100MHz

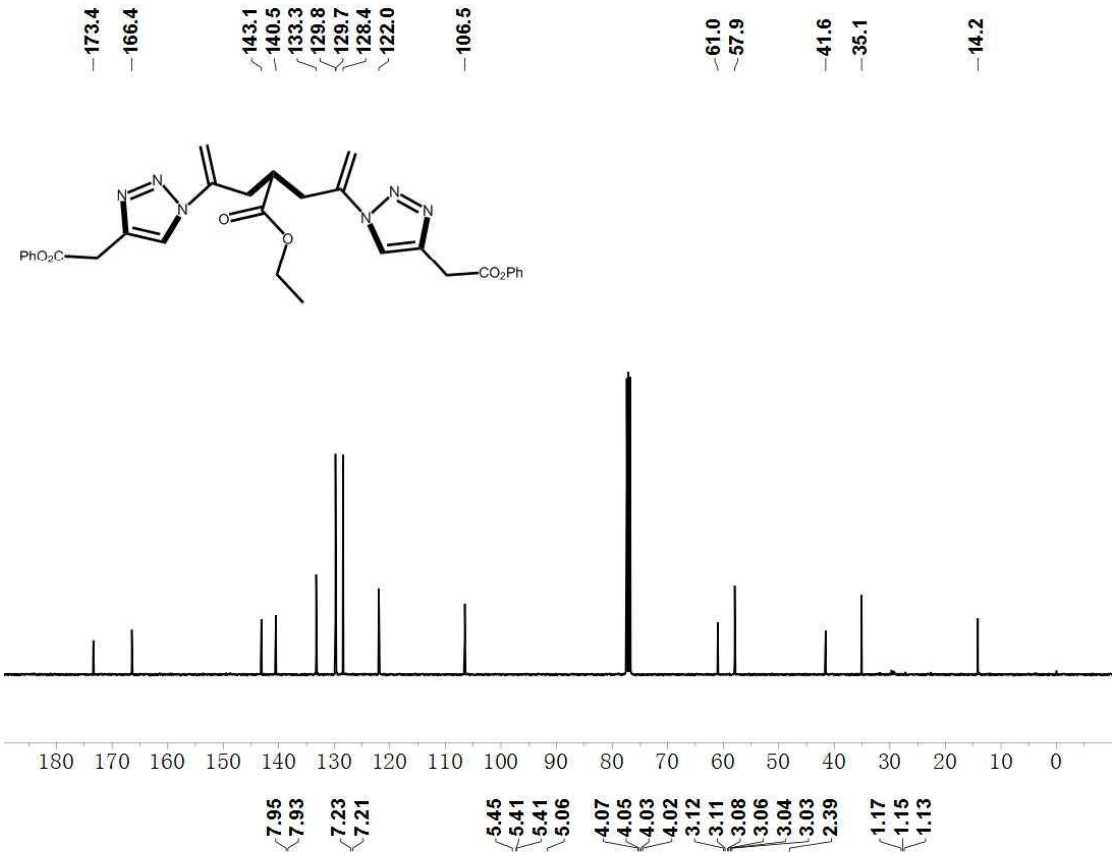


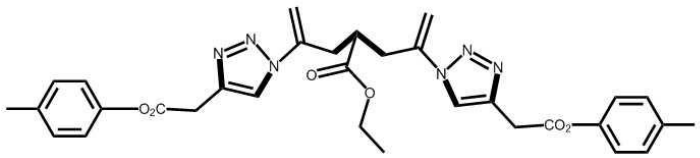
6v

$CDCl_3$ 400MHz

6v

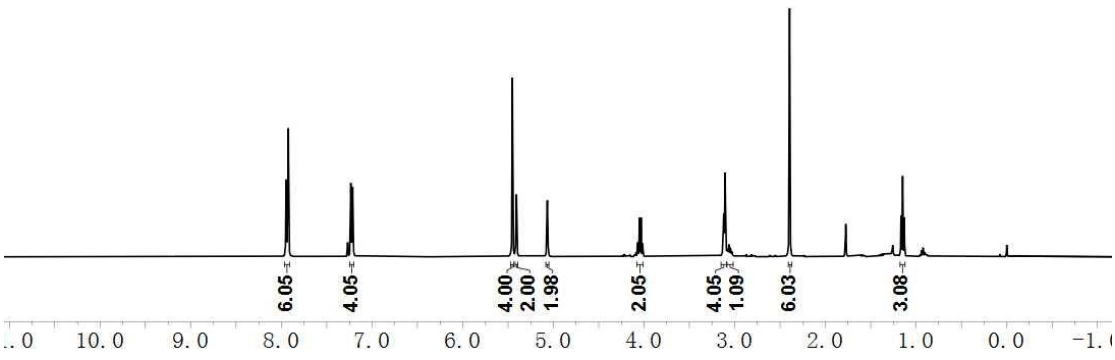
$CDCl_3$ 100MHz

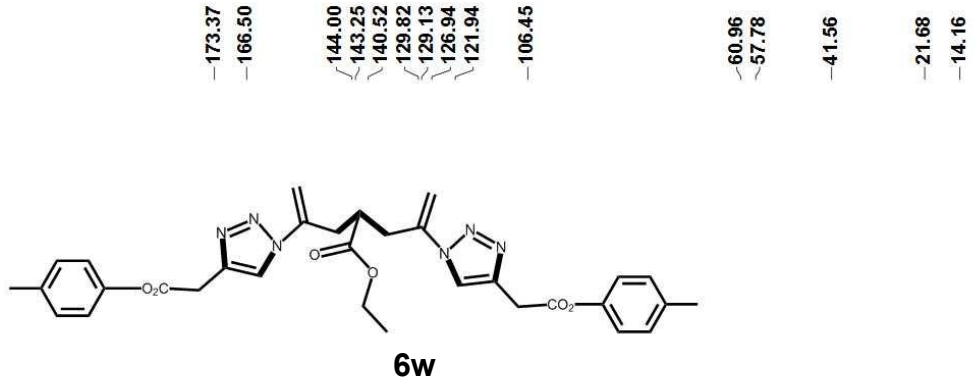




6w

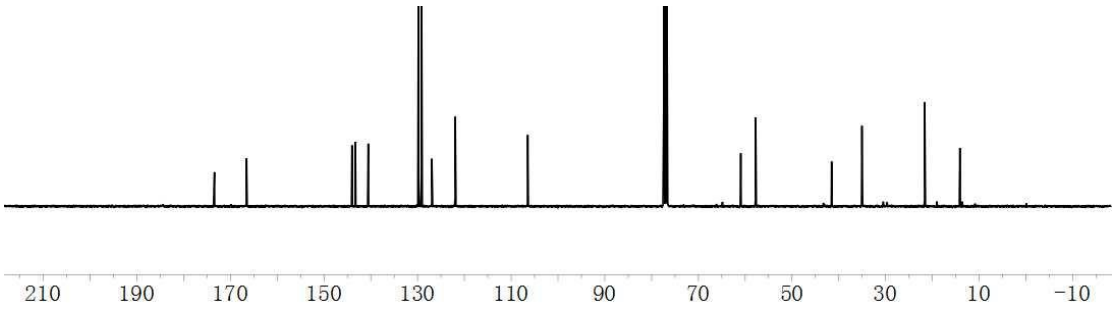
$CDCl_3$ 400MHz

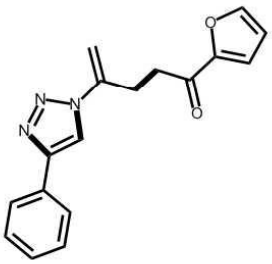




6w

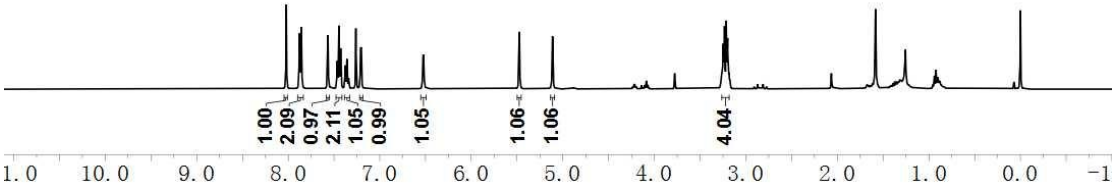
$CDCl_3$ 100MHz

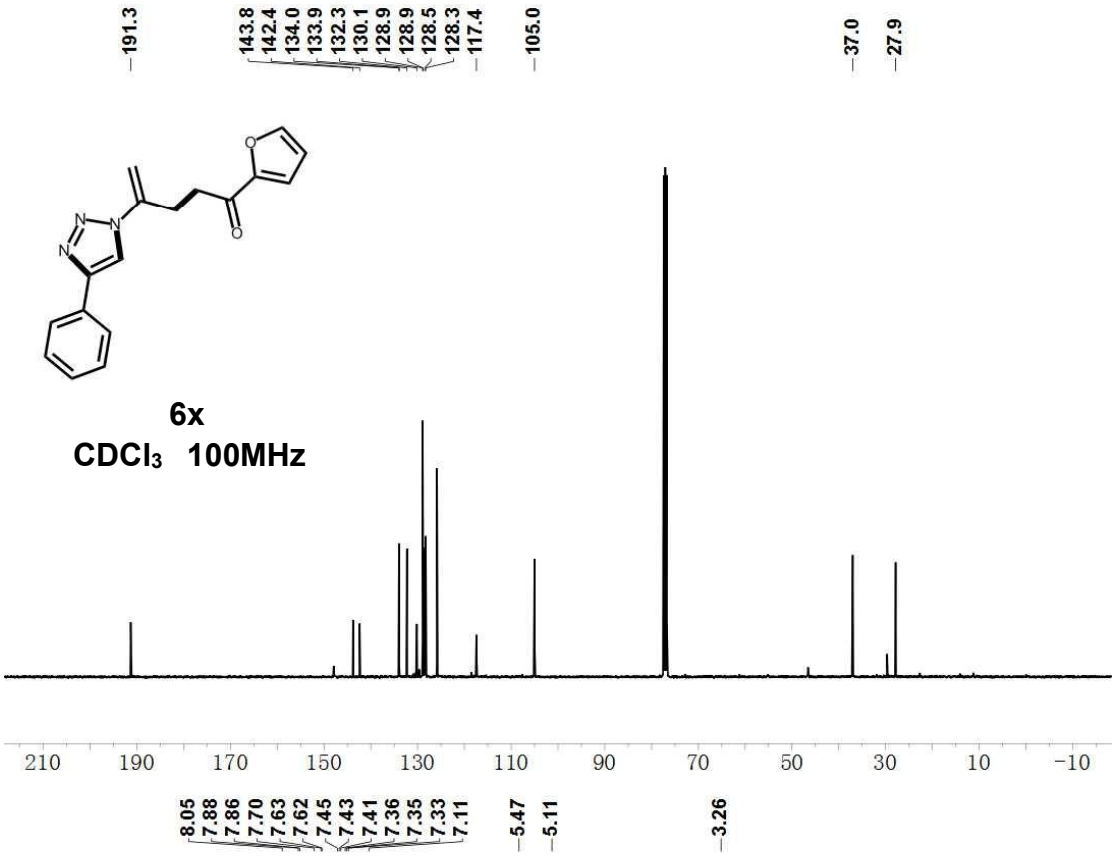


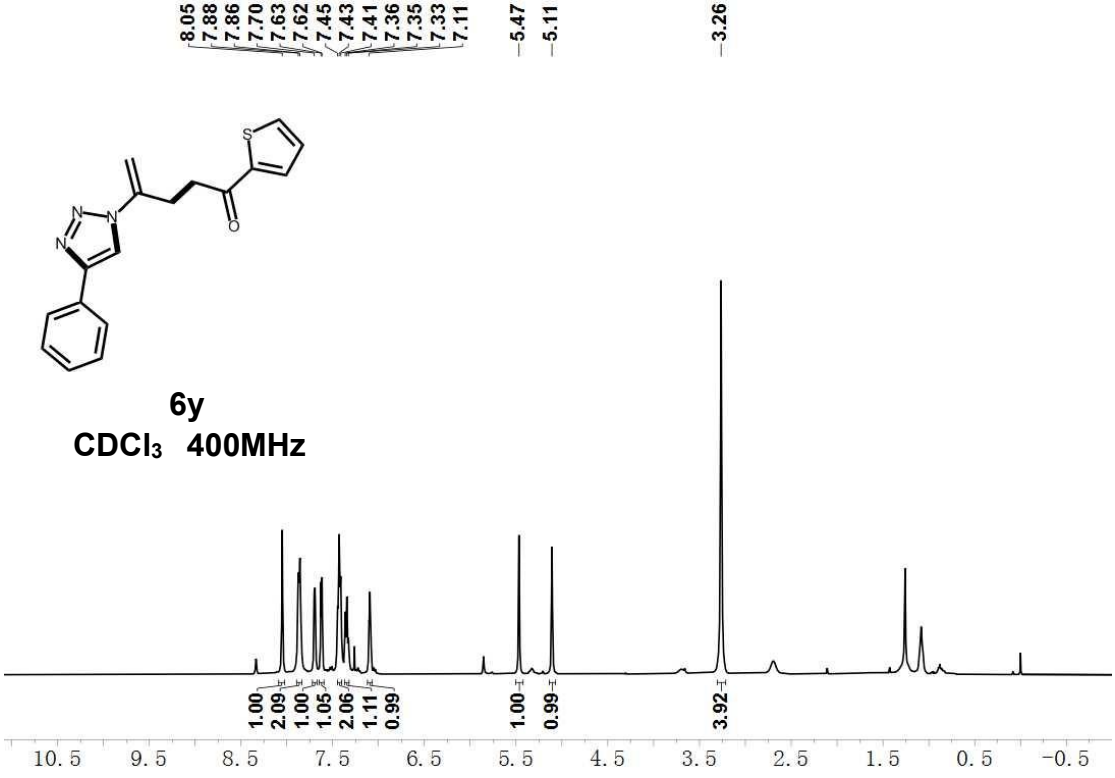


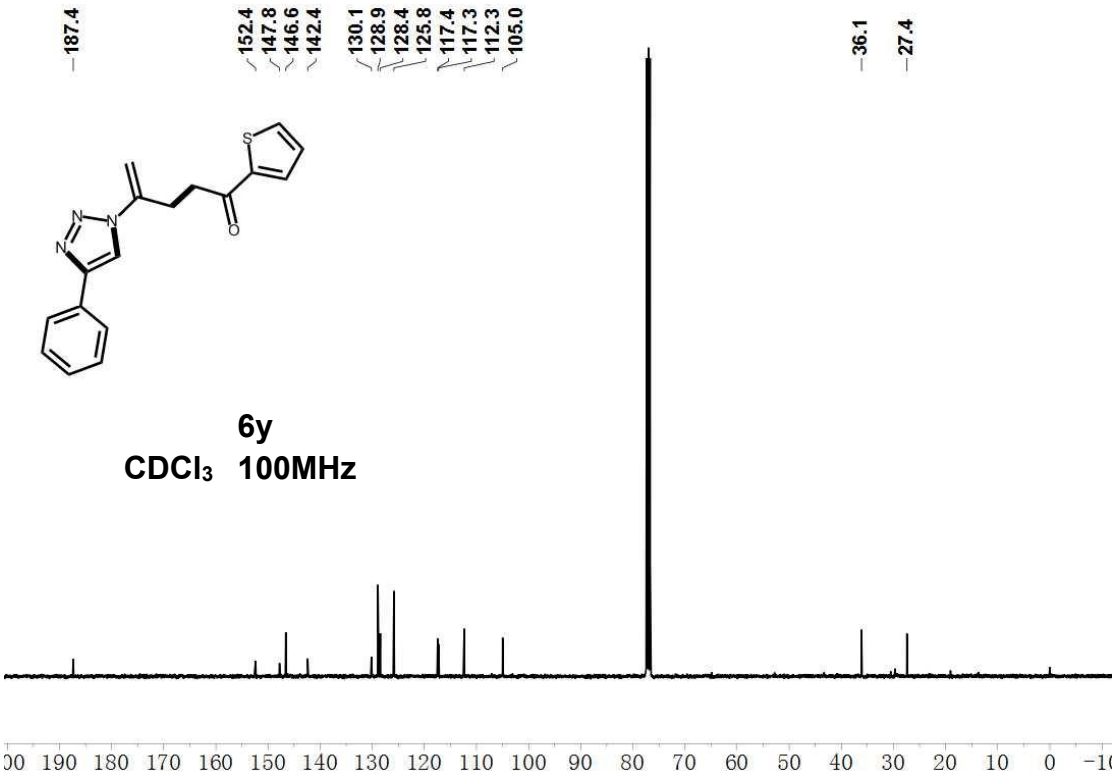
6x

$CDCl_3$ 400MHz




191.3
143.8
142.4
134.0
133.9
132.3
130.1
128.9
128.9
128.5
128.3
117.4
105.0
37.0
27.9
O
N
N
N
O
6x
CDCl3 100MHz
210
190
170
150
130
110
90
70
50
30
10
−10


8.05
7.88
7.86
7.70
7.63
7.62
7.45
7.43
7.41
7.36
7.35
7.33
7.11
5.47
5.11
3.26
S
N
N
N
O
6y
CDCl3 400MHz
1.00
2.09
1.00
1.05
2.06
1.11
0.99
1.00
0.99
3.92
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
−0.5


187.4
152.4
147.8
146.6
142.4
130.1
128.9
128.4
125.8
117.4
117.3
112.3
105.0
36.1
27.4
S
O
N
N
N
6y
CDCl3 100MHz
00 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1