Supporting Information

Copper(I)-Mediated Carboamination of Vinyl Azides by Aryldiazonium Salts: Synthesis of N^2-substituted 1,2,3-Triazoles

Zhenhua Liu,† Huimin Ji,† Wen Gao,* Guangyu Zhu, Lili Tong, Fengcai Lei and Bo Tang*

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

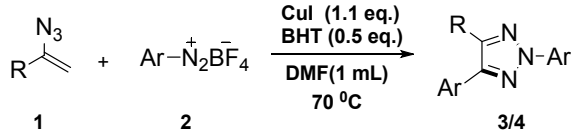
E-mail: gaowen@sdnu.edu.cn and E-mail: tangb@sdnu.edu.cn

Contents

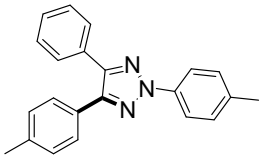
I. General information

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 compounds 3 and 4.

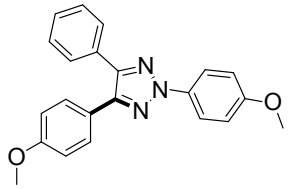


Typical synthetic procedure (with **3a** as an example): To a solution of α-azido styrene (**1a**) (72.5 mg, 0.5 mmol), 4-methylphenyldiazonium tetrafluoroborate (**2a**) (309 mg, 1.5 mmol), and 2,6-di-tert-butyl-4-methylphenol (BHT) (55 mg, 0.25 mmol) in DMF (1 mL) at room temperature, CuI (105 mg, 0.55 mmol) was added. The reaction mixture was then stirred for 6 h when TLC conformed that substrate **1a** had been consumed. The resulting reaction mixture was cooled to room temperature and taken up by dichloromethane (3 × 15 mL). The organic layer was washed with brine (3 × 40 mL), dried over $MgSO_4$ and concentrated. Purification of the crude product via flash column chromatography (silica gel; petroleum ether) and concentratinon *in vacuo* afforded **3a** in 83% yield as yellow solid.

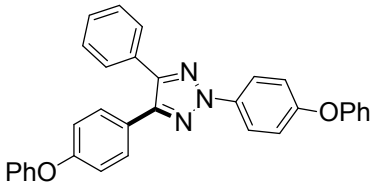


(**3a**) Yellow solid, m.p. 75-76 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.97−7.95 (d, *J* = 8.4 Hz, 2H), 7.58−7.52 (m, 2H), 7.45−7.43 (m, *J* = 8.0 Hz, 2H), 7.33−7.26 (m, 3H), 7.20−7.17 (d, *J* = 8.5 Hz, 2H), 7.11−7.09 (d, *J* = 7.9 Hz, 2H), 2.31 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$):

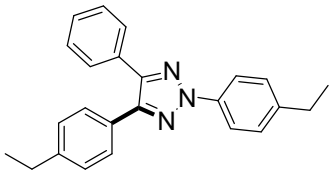
145.7, 145.5, 138.4, 137.6, 137.1, 131.0, 129.7, 129.3, 128.5, 128.4, 128.37, 128.3, 127.9, 118.6, 21.3, 21.1; **HRMS** (ESI) m/z calculated for $C_{22}H_{20}N_3$ $[M+H]^+$: 326.1657 found: 326.1669.



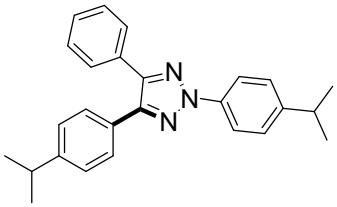
(**3b**) Yellow solid, m.p. 75-76 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.10−8.07 (d, *J* = 9.1 Hz, 2H), 7.67−7.62 (m, 2H), 7.58−7.56 (d, *J* = 8.9 Hz, 2H), 7.44−7.36 (m, 3H), 7.02−7.00 (d, *J* = 9.1 Hz, 2H), 6.94−6.92 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 3.85 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.8, 158.8, 145.3, 145.1, 133.6, 131.0, 129.7, 128.5, 128.4, 128.3, 123.2, 120.1, 114.3, 114.0, 55.5, 55.3; **HRMS** (ESI) m/z calculated for $C_{22}H_{20}N_3O_2$ $[M+H]^+$: 358.1556 found: 358.1551.



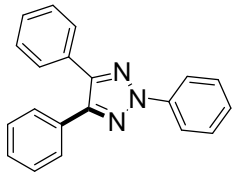
(**3c**) Yellow solid, m.p. 80-81 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14−8.12 (d, *J* = 9.0 Hz, 1H), 7.68−7.63 (m, 2H), 7.61−7.59 (d, *J* = 8.6 Hz, 2H), 7.44−7.34 (m, 7H), 7.16−7.12 (d, *J* = 9.4 Hz, 4H), 7.10−7.04 (m, 4H), 7.03−7.01 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 157.9, 156.9, 156.54, 156.51, 145.6, 145.3, 135.3, 130.7, 129.9, 129.83, 129.82, 128.6, 128.4, 125.4, 123.7, 123.6, 120.3, 119.4, 119.3, 119.0, 118.5; **HRMS** (ESI) m/z calculated for $C_{32}H_{24}N_3O_2$ $[M+H]^+$: 482.1869 found: 482.1860.



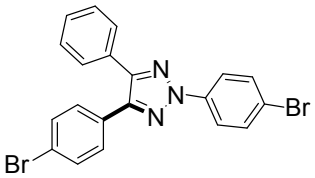
(**3d**) Yellow solid, m.p. 76-77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.09−8.07 (d, *J* = 8.4 Hz, 2H), 7.71−7.63 (m, 2H), 7.57−7.55 (d, *J* = 8.0 Hz, 2H), 7.41−7.40 (d, *J* = 5.0 Hz,3H), 7.33−7.31 (d, *J* = 8.2 Hz, 2H), 7.24−7.22 (d, *J* = 7.9 Hz, 2H), 2.78−2.64 (m, 4H), 1.31−1.24 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.7, 145.5, 144.7, 143.5, 137.7, 131.0, 128.6, 128.5, 128.45, 128.4, 128.3, 128.11, 118.7, 120.08, 28.7, 28.4, 15.5, 15.4; **HRMS** (ESI) m/z calculated for $C_{24}H_{24}N_3$ $[M+H]^+$: 354.1970 found: 354.1976.



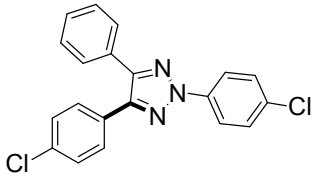
(**3e**) Yellow solid, m.p. 76-77 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.01−7.98 (d, *J* = 8.4 Hz, 2H), 7.61−7.55 (m, 2H), 7.50−7.48 (d, *J* = 8.0 Hz, 2H), 7.34−7.28 (m, 3H), 7.26−7.24 (d, *J* = 8.4 Hz, 2H), 7.18−7.16 (d, *J* = 7.9 Hz, 2H), 2.94−2.79 (m, 2H), 1.21−1.18 (t, *J* = 6.0 Hz, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$): 149.3, 148.1, 145.7, 145.4, 137.7, 131.0, 128.5, 128.43, 128.41, 128.3, 128.2, 127.1, 126.6, 118.7, 33.9, 33.7, 23.94, 23.89; **HRMS** (ESI) m/z calculated for $C_{26}H_{28}N_3$ $[M+H]^+$: 382.2283 found: 382.2281.



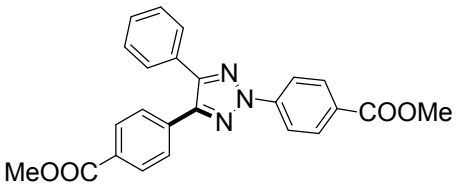
(**3f**) Yellow solid, m.p. 70-71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.15−8.07 (m, 2H), 7.60−7.54 (m, 4H), 7.45−7.40 (t, *J* = 7.9 Hz, 2H), 7.36−7.30 (m, 6H), 7.30−7.28 (d, *J* = 7.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.9, 143.4, 139.1, 137.8, 137.3, 135.6, 132.3, 129.9, 129.5, 128.6, 128.4, 127.2, 118.2, 21.4, 21.1; **HRMS** (ESI) m/z calculated for $C_{20}H_{16}N_3$ $[M+H]^+$: 298.1344 found: 298.1344.



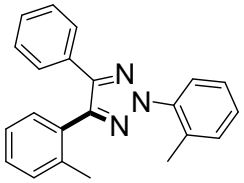
(3**g**) Yellow solid, m.p. 77-78 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.07−8.04 (d, *J* = 8.9 Hz, 2H), 7.65−7.57 (m, 4H), 7.56−7.48 (m, 4H), 7.46−7.38 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.3, 145.1, 138.5, 132.3, 131.8, 130.2, 129.9, 129.4, 129.0, 128.7, 128.4, 123.0, 121.0, 120.2; **HRMS** (ESI) m/z calculated for $C_{20}H_{14}Br_2N_3$ $[M+H]^+$: 453.9554 found: 454.9622.



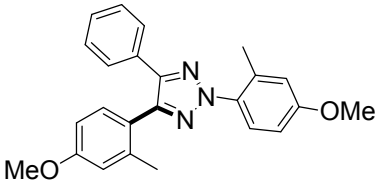
(**3h**) Yellow solid, m.p. 75-76 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.11−8.09 (d, *J* = 8.9 Hz, 2H), 7.62−7.58 (m, 2H), 7.57−7.55 (d, *J* = 8.6 Hz, 2H), 7.46−7.44 (d, *J* = 8.9 Hz, 2H), 7.42−7.39 (m, 3H), 7.37−7.35 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.3, 145.1, 138.1, 134.8, 133.1, 130.3, 129.6, 129.4, 128.97, 128.95, 128.9, 128.8, 119.9; **HRMS** (ESI) m/z calculated for $C_{20}H_{14}Cl_2N_3$ $[M+H]^+$: 366.0565 found: 366.0553.



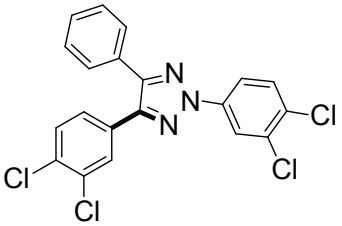
(**3i**) Yellow solid, m.p. 77-78 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.28−8.26 (d, *J* = 8.6 Hz, 2H), 8.21−8.19 (d, *J* = 8.6 Hz, 2H), 8.09−8.07 (d, *J* = 8.1 Hz, 2H), 7.75−7.73 (d, *J* = 8.1 Hz, 2H), 7.62−7.01 (d, *J* = 7.3 Hz, 2H), 7.44−7.43 (d, *J* = 4.8 Hz, 3H), 1.46−1.38 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 166.2, 165.9, 147.2, 145.7, 142.4, 134.7, 131.0, 130.7, 130.0, 129.9, 129.3, 129.2, 128.8, 128.5, 128.3, 118.3, 61.24, 61.16; **HRMS** (ESI) m/z calculated for $C_{24}H_{20}N_3O_4$ $[M+H]^+$: 414.1454 found: 414.1450.



(**3j**) Yellow solid, m.p. 74-75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.76−7.74 (t, *J* = 4.3 Hz, 1H), 7.59−7.57 (t, *J* = 3.6 Hz, 2H), 7.42−7.34 (m, 5H), 7.34−7.26 (m, 5H), 2.54 (s, 3H), 2.20 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.6, 145.2, 139.5, 137.4, 132.5, 132.8, 130.8, 130.7, 130.5, 129.0, 128.6, 128.3, 127.0, 126.6, 126.0, 125.0, 20.1, 19.3; **HRMS** (ESI) m/z calculated for $C_{22}H_{20}N_3$ $[M+H]^+$: 326.1657 found: 326.1657.

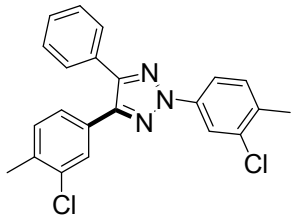


(**3k**) Yellow solid, m.p. 78-79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.63−7.53 (m, 3H), 7.32−7.27 (m, 4H), 6.87−6.78 (m, 4H), 3.86 (s, 6H), 2.45 (s, 3H), 2.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.9, 159.4, 145.3, 144.7, 139.0, 134.5, 133.2, 131.7, 131.0, 128.5, 128.1, 126.9, 126.5, 123.2, 116.5, 115.9, 111.6, 111.3, 55.5, 55.2, 20.4, 19.2; **HRMS** (ESI) m/z calculated for $C_{24}H_{24}N_3O_2$ $[M+H]^+$: 386.1869 found: 386.1880.

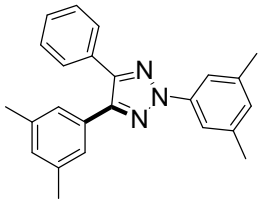


(**3l**) Yellow solid, m.p. 75-76 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.30−8.28 (d, *J* = 2.5 Hz, 1H),

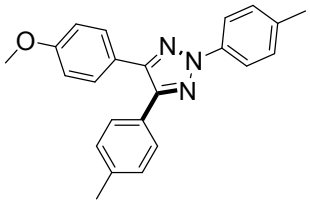
8.04−7.99 (m, 1H), 7.80−7.796 (d, *J* = 1.8 Hz, 1H), 7.62−7.55 (m, 3H), 7.47−7.43 (m, 4H), 7.43−7.40 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.8, 144.3, 138.4, 133.5, 133.1, 133.0, 131.5, 131.0, 130.6, 130.2, 130.0, 129.6, 129.3, 128.9, 128.4, 127.4, 120.5, 117.8; **HRMS** (ESI) m/z calculated for $C_{20}H_{12}Cl_4N_3$ $[M+H]^+$: 433.9785 found: 433.9779.



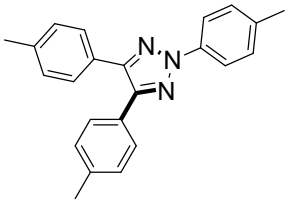
(**3m**) Yellow solid, m.p. 72-73 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.19 (s, 1H), 8.00−7.95 (d, *J* = 8.2 Hz, 1H), 7.69 (s, 1H), 7.65−7.59 (m, 2H), 7.45−7.40 (m, 3H), 7.38−7.33 (t, *J* = 9.2 Hz, 2H), 7.24−7.22 (d, *J* = 7.9 Hz, 1H), 2.43 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.1, 144.8, 138.4, 136.6, 135.3, 135.0, 134.7, 131.4, 131.0, 130.3, 129.7, 128.9, 128.72, 128.69, 128.4, 126.5, 119.3, 116.8, 20.0, 19.7; **HRMS** (ESI) m/z calculated for $C_{22}H_{18}Cl_2N_3$ $[M+H]^+$: 394.0878 found: 394.0880.



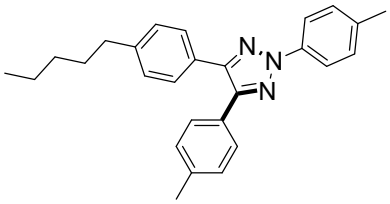
(**3n**) Yellow solid, m.p. 78-79 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.81 (s, 2H), 7.70−7.64 (m, 2H), 7.41−7.36 (m, 3H), 7.25 (s, 2H), 7.03 (s, 1H), 7.00 (s, 1H), 2.42 (s, 6H), 2.32 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.0, 145.6, 139.6, 139.1, 138.1, 130.9, 130.6, 130.3, 129.0, 128.5, 128.3, 126.2, 116.5, 21.4, 21.3; **HRMS** (ESI) m/z calculated for $C_{24}H_{24}N_3$ $[M+H]^+$: 354.1970 found: 354.1997.



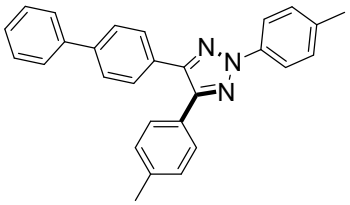
(**4a**) Yellow solid, m.p. 113-114 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.05−8.03 (d, *J* = 8.5 Hz, 2H), 7.59−7.57 (d, *J* = 8.8 Hz, 2H), 7.55−7.53 (d, *J* = 8.0 Hz, 2H), 7.30−7.27 (d, *J* = 8.5 Hz, 2H), 7.22−7.20 (d, *J* = 8.0 Hz, 2H), 6.94−6.92 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 159.8, 145.4, 145.3, 138.3, 137.6, 137.0, 129.71, 129.68, 129.3, 128.3, 128.1, 123.4, 118.6, 114.0, 55.3, 21.3, 21.0; **HRMS** (ESI) m/z calculated for $C_{23}H_{22}N_3O$ $[M+H]^+$: 356.1763 found: 356.1777.



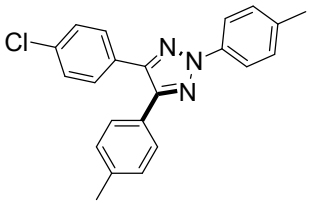
(**4b**) Yellow solid, m.p. 117-118°C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06−8.03 (d, *J* = 8.5 Hz, 2H), 7.55−7.53 (d, *J* = 8.5 Hz, 4H), 7.29−7.27 (d, *J* = 8.2 Hz, 2H), 7.21−7.19 (d, *J* = 7.9 Hz, 4H), 2.41 (s, 3H), 2.40 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.6, 138.3, 137.6, 137.0, 129.7, 129.2, 128.3, 128.1, 118.6, 21.3, 21.0; **HRMS** (ESI) m/z calculated for $C_{23}H_{22}N_3$ $[M+H]^+$: 340.1814 found: 340.1835.



(**4c**) Yellow solid, m.p. 118-119 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06−8.04 (d, *J* = 8.0 Hz, 2H), 7.60−7.51 (m, 4H), 7.30−7.28 (d, *J* = 7.8 Hz, 2H), 7.22−7.20 (d, *J* = 7.6 Hz, 4H), 2.70−2.60 (m, 2H), 2.41 (s, 3H), 2.40 (s, 3H), 1.65 (s, 2H), 1.34 (s, 4H), 0.91 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.6, 145.55, 143.4, 138.3, 137.6, 137.0, 132.1, 129.7, 129.2, 128.6, 128.3, 128.2, 128.1,118.6, 35.8, 31.5, 31.0, 22.5, 21.0, 14.0; **HRMS** (ESI) m/z calculated for ; **HRMS** (ESI) m/z calculated for $C_{27}H_{29}N_3$ $[M+H]^+$: 396.2440 found: 396.2440.

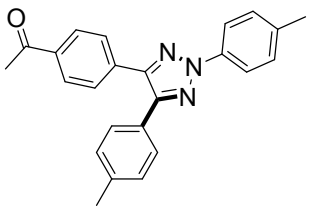


(**4d**) Yellow solid, m.p. 123-124 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08−8.06 (d, *J* = 8.5 Hz, 2H), 7.75−7.73 (d, *J* = 8.5 Hz, 2H), 7.68−7.61 (m, 4H), 7.59−7.57 (d, *J* = 8.1 Hz, 2H), 7.48−7.45 (t, *J* = 7.8 Hz, 2H), 7.39−7.38 (d, *J* = 7.2 Hz, 1H), 7.32−7.30 (d, *J* = 8.1 Hz, 2H), 7.25−7.23 (d, *J* = 7.9 Hz, 2H) 2.43 (s, 3H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.8, 145.1, 141.1, 140.5, 138.5, 137.6, 137.2, 129.9, 129.8, 129.3, 128.8, 128.7, 128.4, 128.0, 127.5, 127.2, 127.0, 118.6, 21.4, 21.1; **HRMS** (ESI) m/z calculated for $C_{28}H_{24}N_3$ $[M+H]^+$: 402.1970 found: 402.1979.

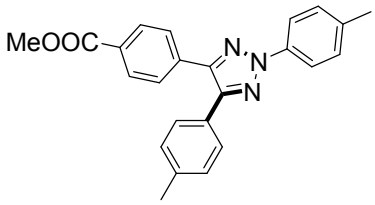


(**4e**) Yellow solid, m.p. 114-115 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04−8.02 (d, *J* = 8.5 Hz, 2H), 7.60−7.58 (d, *J* = 8.6 Hz, 2H), 7.51−7.49 (d, *J* = 8.1 Hz, 2H), 7.37−7.35 (d, *J* = 8.6 Hz, 2H), 7.30−7.28 (d, *J* = 8.2 Hz, 2H), 7.23−7.21 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H); **^{13}C NMR**

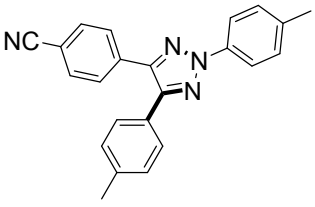
(100MHz, $CDCl_3$):145.8, 144.4, 138.7, 137.6, 137.4, 134.4, 129.8, 129.7, 129.5, 129.4, 128.8, 128.3, 127.7, 118.7, 21.4, 21.1; **HRMS** (ESI) m/z calculated for $C_{22}H_{19}ClN_3$ $[M+H]^+$: 360.1268 found: 360.1261.



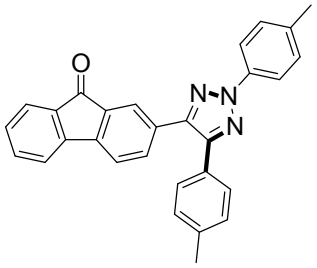
(**4f**) Yellow solid, m.p. 103-104 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06−8.04 (d, *J* = 8.5 Hz, 2H), 7.98−7.96 (d, *J* = 8.4 Hz, 2H), 7.78−7.75 (d, *J* = 8.4 Hz, 2H), 7.51−7.49 (d, *J* = 8.1 Hz, 2H), 7.30−7.28 (d, *J* = 8.4 Hz, 2H), 7.23−7.21 (d, *J* = 8.0 Hz, 2H), 2.62 (s, 3H), 2.41 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 197.6, 146.3, 144.2, 143.3, 138.8, 137.5, 137.4, 136.6, 135.6, 129.8, 129.4, 128.5, 128.4, 128.3, 118.7, 26.6, 21.3, 21.0; **HRMS** (ESI) m/z calculated for $C_{24}H_{22}N_3O$ $[M+H]^+$: 368.1763 found: 368.1760.



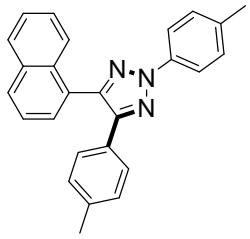
(**4g**) Yellow solid, m.p. 100-101 °C; **^{1}H NMR** NMR (400 MHz, $CDCl_3$): δ 8.04−8.01 (m, 4H), 7.72−7.70 (d, *J* = 8.3 Hz, 2H), 7.48−7.46 (d, *J* = 8.0 Hz, 2H), 7.25−7.23 (d, *J* = 8.2 Hz, 2H), 7.19−7.17 (d, *J* = 8.0 Hz, 2H), 3.89 (s, 3H), 2.37 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** (100MHz, $CDCl_3$): 166.6, 146.1, 144.1, 138.6, 137.33, 137.31, 135.4, 132.0, 129.71, 129.67, 129.3, 128.3, 128.0, 127.5, 118.5, 52.1, 21.2, 20.9; **HRMS** (ESI) m/z calculated for $C_{24}H_{22}N_3O_2$ $[M+H]^+$: 384.1712 found: 384.1740.



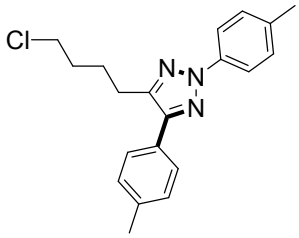
(**4h**) Yellow solid, m.p. 119-120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.04−8.02 (d, *J* = 8.2 Hz, 2H), 7.80−7.78 (d, *J* = 8.2 Hz, 2H), 7.67−7.65 (d, *J* = 8.1 Hz, 2H), 7.48−7.46 (d, *J* = 7.9 Hz, 2H), 7.31−7.29 (d, *J* = 8.2 Hz, 2H), 7.25−7.23 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.4, 143.4, 139.1, 137.8, 137.3, 135.6, 132.3, 129.9, 129.5, 128.6, 128.4, 127.2, 118.2, 21.4, 21.1; **HRMS** (ESI) m/z calculated for $C_{23}H_{19}N_4$ $[M+H]^+$: 351.1610 found: 351.1602.



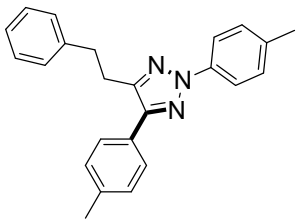
(**4i**) Yellow solid, m.p. 126-127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06−8.04 (d, *J* = 8.5 Hz, 2H), 8.01 (s, 1H), 7.76−7.72 (m,1H), 7.68−7.66 (d, *J* = 7.3 Hz, 1H), 7.56−7.46 (m, 5H), 7.31−7.29 (d, *J* = 8.4 Hz, 2H), 7.24−7.22 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.41 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 193.3, 145.8, 144.2, 144.1, 144.0, 138.8, 137.41, 137.38, 134.8, 134.5, 134.3, 132.0, 129.8, 129.4, 129.2, 128.3, 127.5, 124.4, 124.2, 120.5, 120.4, 118.6, 21.4, 21.0; **HRMS** (ESI) m/z calculated for $C_{29}H_{22}N_3O$ $[M+H]^+$: 428.1763 found: 428.1750.



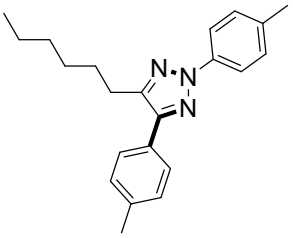
(**4j**) Yellow solid, m.p. 121-122 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.11 (s, 1H), 8.00−7.91 (m, 2H), 7.88−7.86 (s, 1H), 7.62−7.48 (m, 3H), 7.44−7.40 (d, *J* = 8.1 Hz, 3H), 7.33−7.31 (d, *J* = 8.3 Hz, 2H), 7.04−7.02 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.7, 144.3, 138.1, 137.6, 137.2, 133.8, 132.6, 132.0, 129.8, 129.4, 129.2, 128.8, 128.3, 127.4, 127.2, 126.6, 126.1, 125.8, 125.3, 118.7, 21.2, 21.0; **HRMS** (ESI) m/z calculated for $C_{26}H_{22}N_3$ $[M+H]^+$: 376.1814 found: 376.1837.



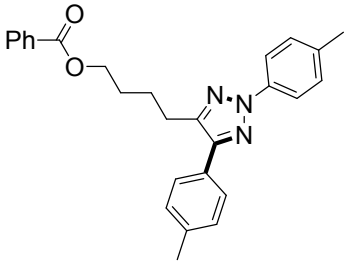
(**4k**) Yellow solid, m.p. 53-54 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96−7.94 (d, *J* = 8.5 Hz, 2H), 7.63−7.61 (d, *J* = 8.1 Hz, 2H), 7.28−7.24 (d, *J* = 8.1 Hz, 2H), 3.58−3.54 (t, *J* = 6.3 Hz, 2H), 2.95−2.92 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 2.38 (s, 3H), 1.97−1.84 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.0, 145.8, 138.1, 137.7, 136.8, 129.7, 129.4, 128.1, 127.4, 118.4, 44.6, 32.1, 25.9, 25.1, 21.3, 21.0; **HRMS** (ESI) m/z calculated for $C_{20}H_{23}ClN_3$ $[M+H]^+$: 340.1581 found: 340.1599.



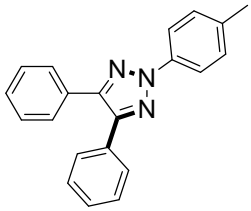
(**4l**) Yellow solid, m.p. 64-65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.98−7.96 (d, *J* = 8.5 Hz, 2H), 7.60−7.58 (d, *J* = 8.1 Hz, 2H), 7.33−7.17 (m, 9H), 3.24−3.17 (m, 2H), 3.14−3.07 (m, 2H), 2.39 (s, 6H); **^{13}C NMR** (100MHz, $CDCl_3$):146.1, 145.7, 141.4, 138.1, 137.7, 136.8, 129.7, 129.4, 128.4, 128.1, 127.4, 126.1, 120.3, 118.5, 34.9, 28.2, 21.3, 21.0; **HRMS** (ESI) m/z calculated for $C_{24}H_{24}N_3$ $[M+H]^+$: 354.1970 found: 354.1988.



(**4m**) Yellow solid, m.p. 50-51 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.96−7.94 (d, *J* = 8.0 Hz, 2H), 7.64−7.62 (d, *J* = 7.6 Hz, 2H), 7.30-7.22 (m, 4H), 2.91−2.87 (t, *J* = 7.8 Hz, 2H), 2.40 (s, 3H), 2.39 (s, 3H), 1.80−1.70 (s, 2H), 1.44−1.36 (s, 2H), 1.33−1.26 (s, 4H), 0.92−0.84 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 146.7, 145.9, 138.0, 137.7, 136.6, 129.7, 129.4, 128.3, 127.4, 118.4, 31.5, 29.1, 28.9, 26.0, 22.6, 21.3, 21.0, 14.1; **HRMS** (ESI) m/z calculated for $C_{22}H_{28}N_3$ $[M+H]^+$: 334.2283 found: 334.2296.



(**4n**) Yellow solid, m.p. 52-53 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.03−8.01 (d, *J* = 7.8 Hz, 2H), 7.97−7.95 (d, *J* = 8.2 Hz, 2H), 7.64−7.62 (d, *J* = 7.9 Hz, 2H), 7.56−7.52 (t, *J* = 7.4 Hz, 1H), 7.43−7.40 (t, *J* = 8.2 Hz, 2H), 7.43−7.40 (d, *J* = 7.6 Hz, 2H), 4.37−4.34 (t, *J* = 6.0 Hz, 4H), 3.02−2.98 (t, *J* = 7.2 Hz, 2H), 2.38 (s, 6H), 2.01−1.86 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$): 166.6, 145.9, 138.1, 137.6, 136.7, 132.8, 130.3, 129.7, 129.6, 129.5, 129.4, 128.3, 128.1, 127.3, 118.3, 64.6, 28.4, 25.6, 25.2, 21.3, 20.1; **HRMS** (ESI) m/z calculated for $C_{27}H_{28}N_3O_2$ $[M+H]^+$: 426.5301 found: 426.5312.



(**6**) Yellow solid, m.p. 72-73 ºC; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.06−8.05 (d, *J* = 7.6 Hz, 2H), 7.65−7.64 (m, 4H), 7.39 (s, 6H), 7.30−7.28 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$): 145.6, 137.6, 137.3, 130.9, 129.8, 128.6, 128.5, 128.4, 118.7, 21.1; **HRMS** (ESI) m/z calculated for $C_{21}H_{17}N_3$ $[M+H]^+$: 312.1482 found: 312.1512.

III. Crystallography of compound 3f

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

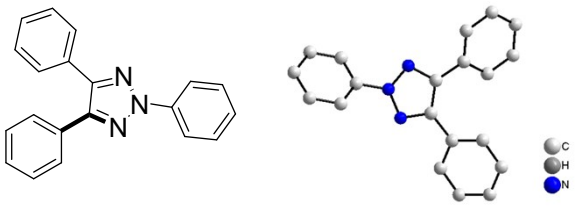
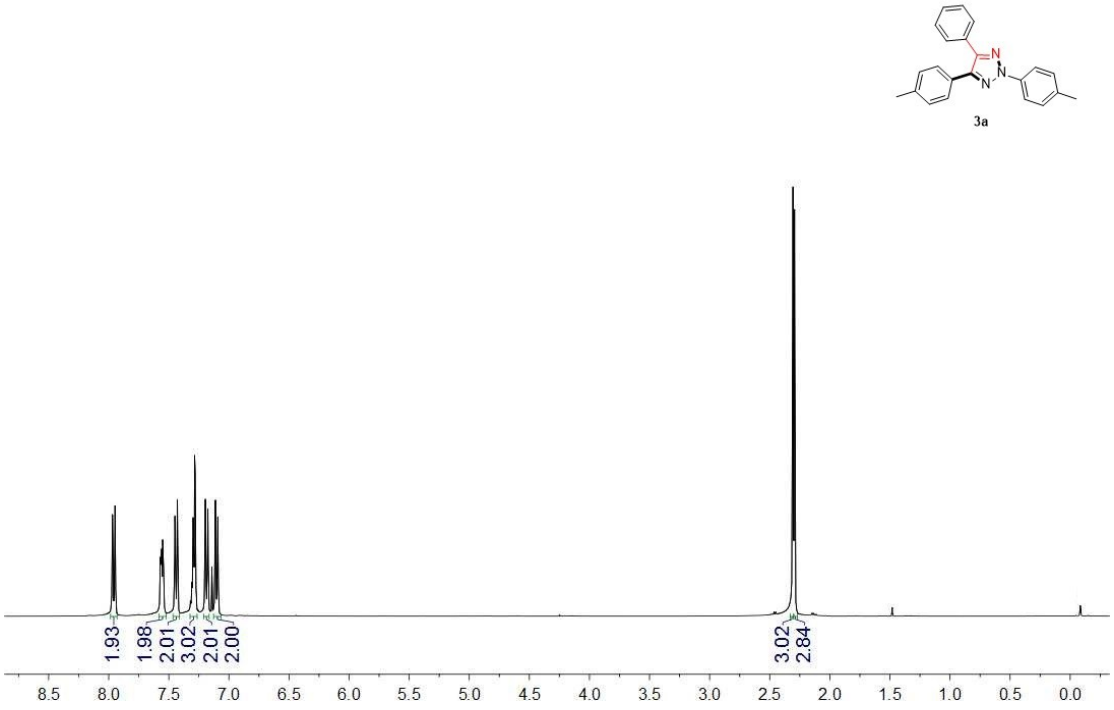


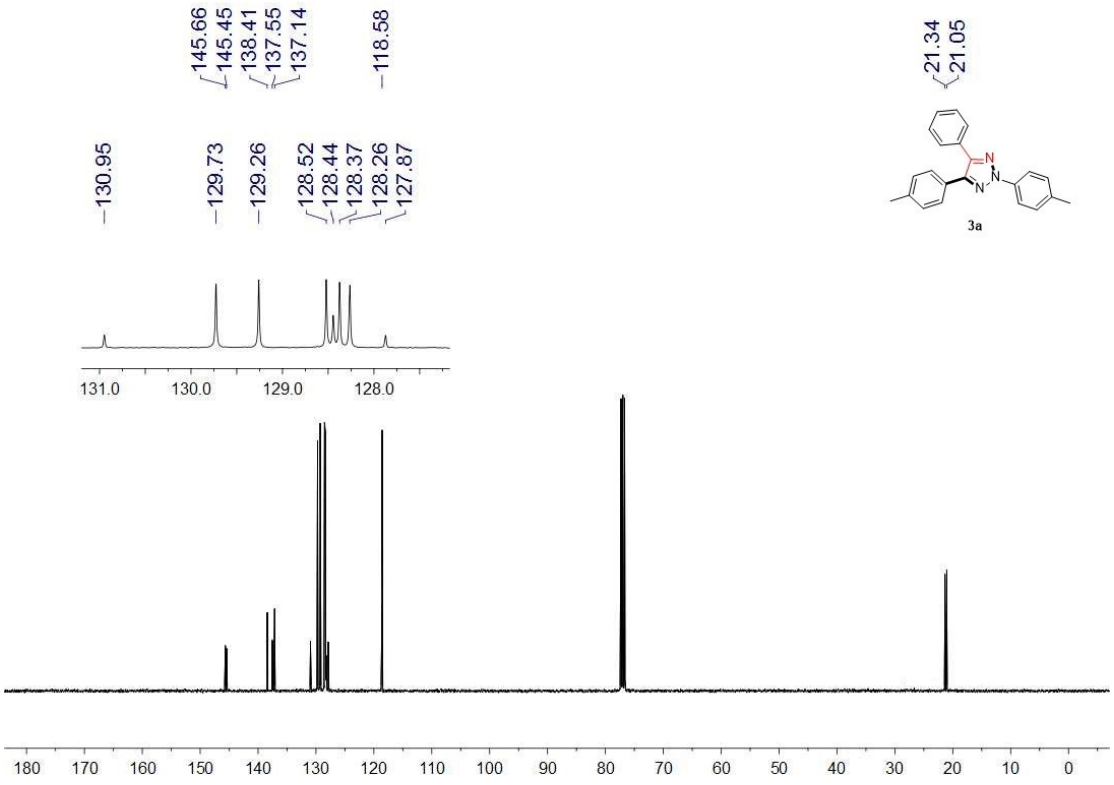
Table 1. Crystal data and structure refinement.

Empirical formula	C_{20} H_{15} N_3
Temperature	298(2)K
Wavelength	1.54184 Å
Unit cell dimensions	a = 19.5551(4) Å alpha = 90 deg. b = 7.59507(14) Å beta = 90 deg. c = 20.2815(4) Å gamma = 90 deg.
Volume	3012.27(10) Å ^{3}
Z	8
Calculated density	1.311 Mg/m^3
Absorption coefficient	0.618 mm^{-1}
F(000)	1248
Crystal size	0.42 x 0.25 x 0.02 mm
Theta range for data collection	4.52 to 67.07 deg.

Reflections collected / unique	6117 / 2683 [R(int) = 0.0225]
Data / restraints / parameters	2683 / 0 / 209
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0389, wR2 = 0.1025
R indices (all data)	R1 = 0.0447, wR2 = 0.1078

IV. NMR spectra copies

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127.87
21.34
21.05
3a
131.0
130.0
129.0
128.0
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120
110
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70
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10
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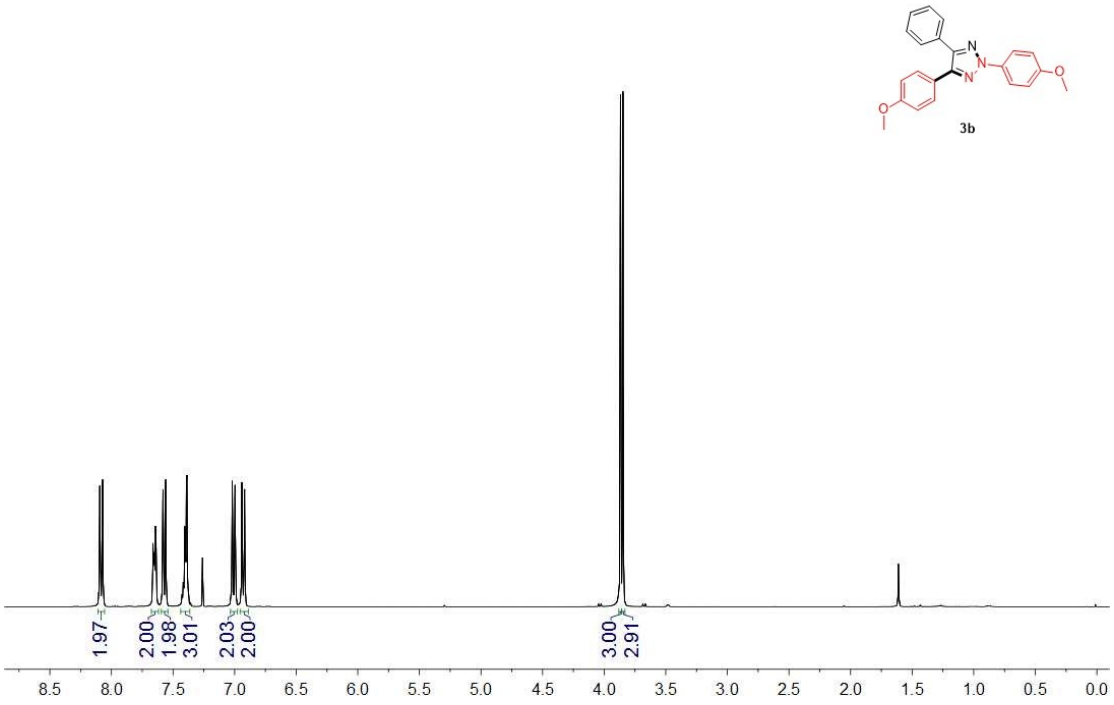
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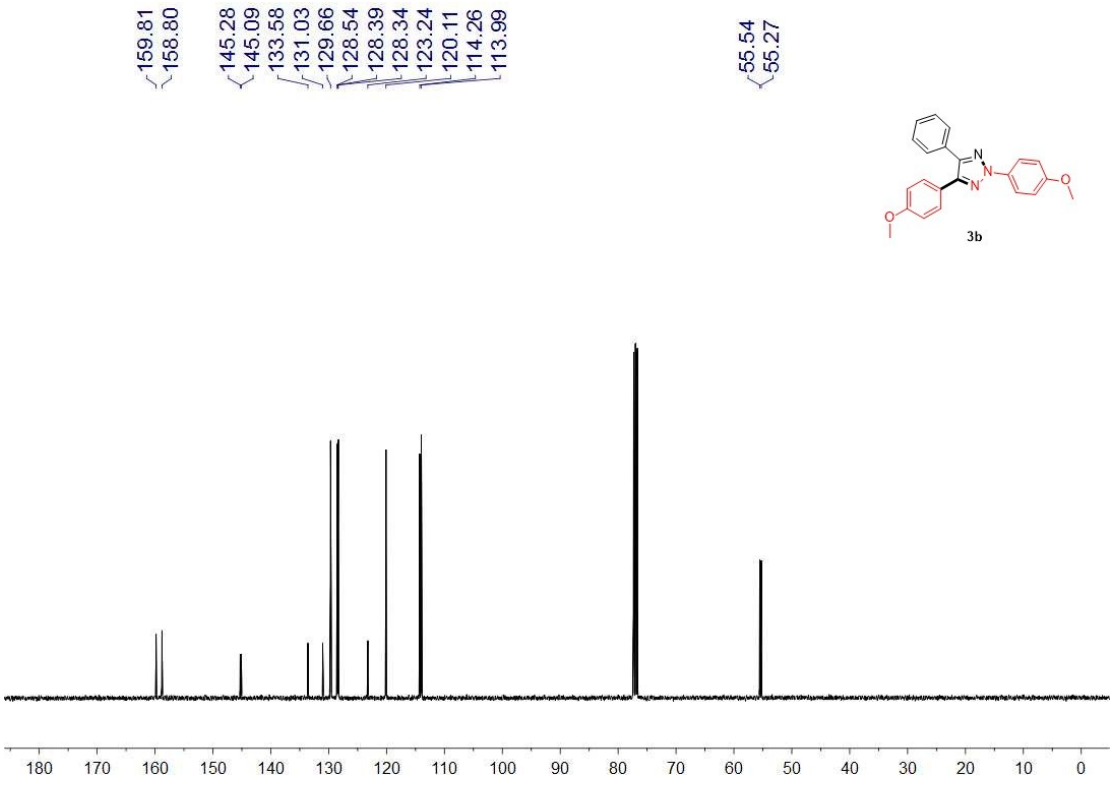
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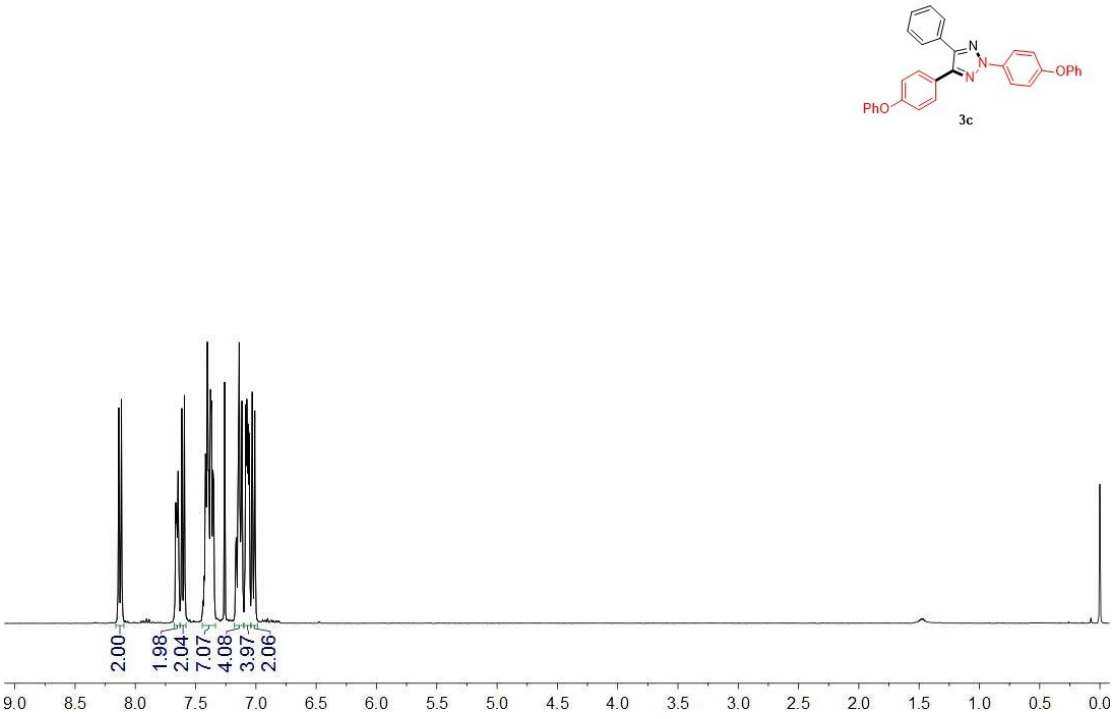
55.27
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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3.97
2.06
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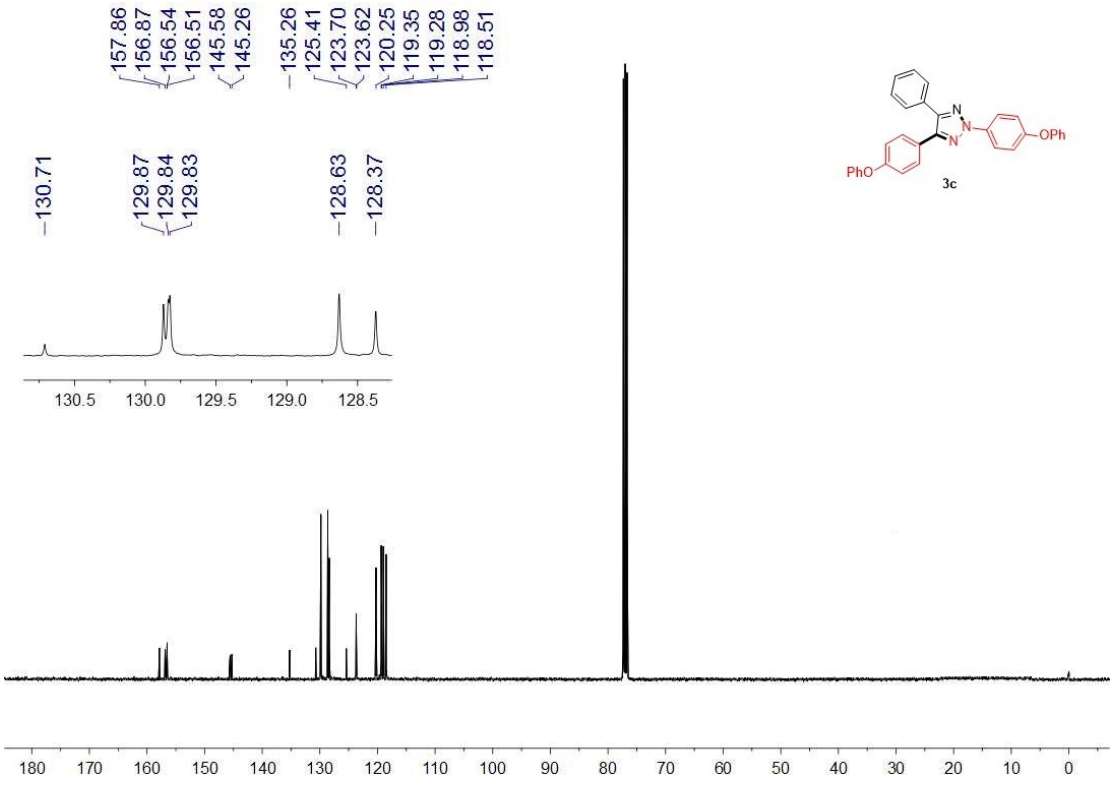
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129.84
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128.63
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128.5
OPh
PhO
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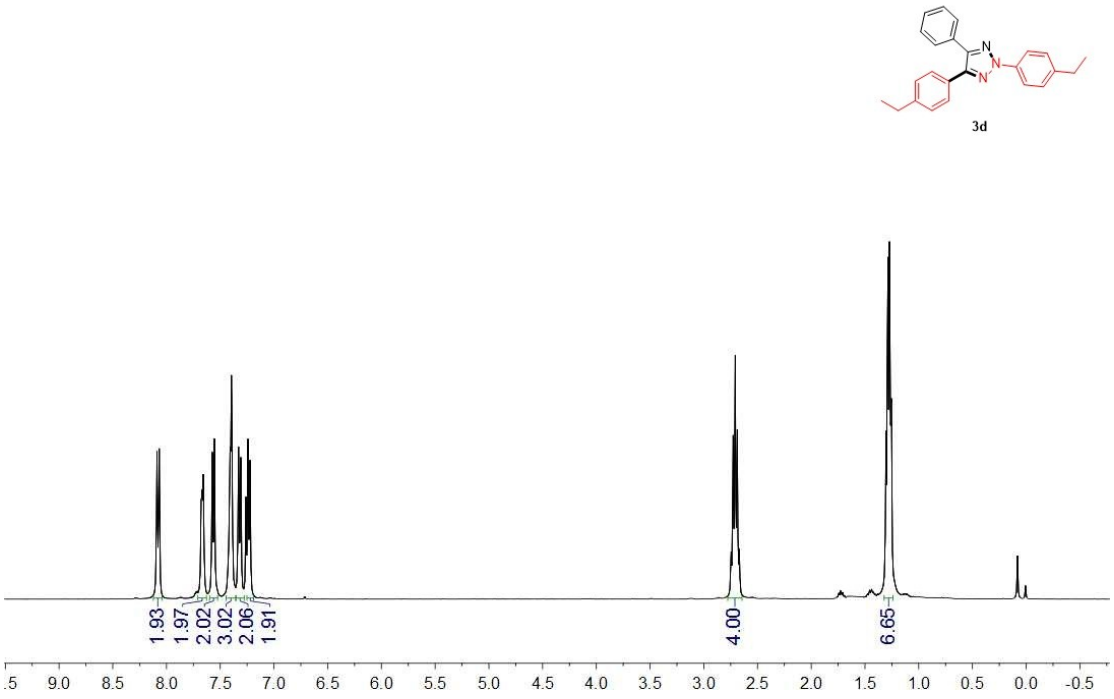
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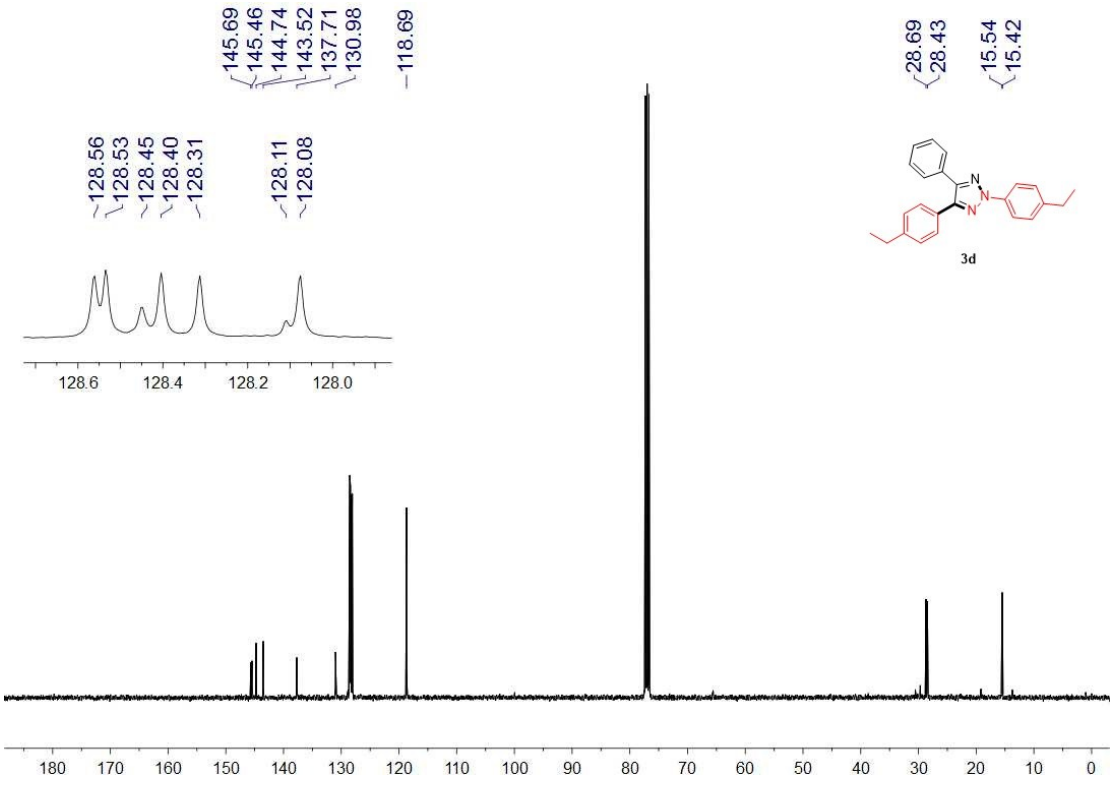
145.69
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28.69
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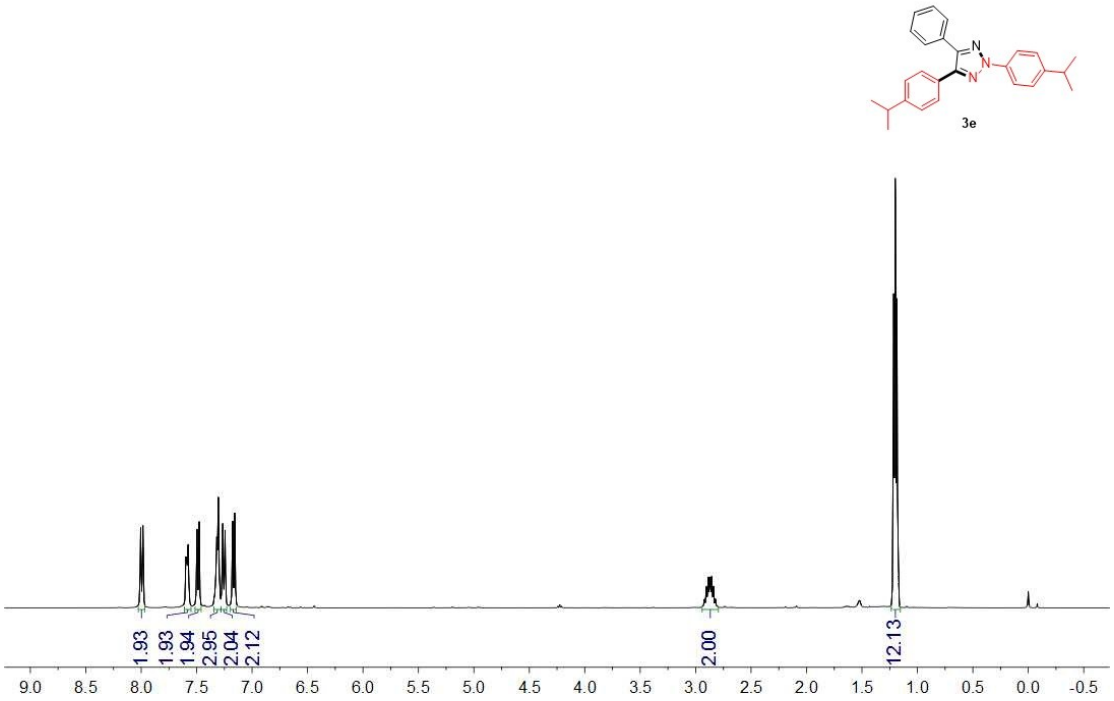
15.42
3d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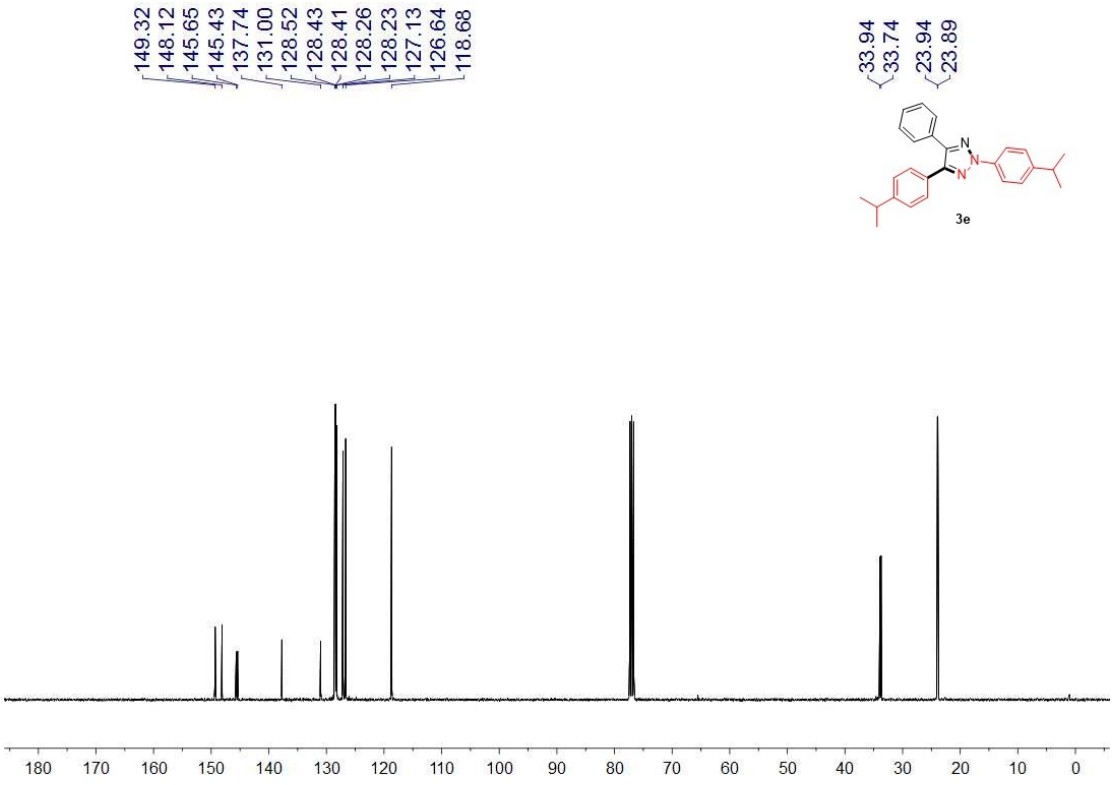
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23.94
23.89
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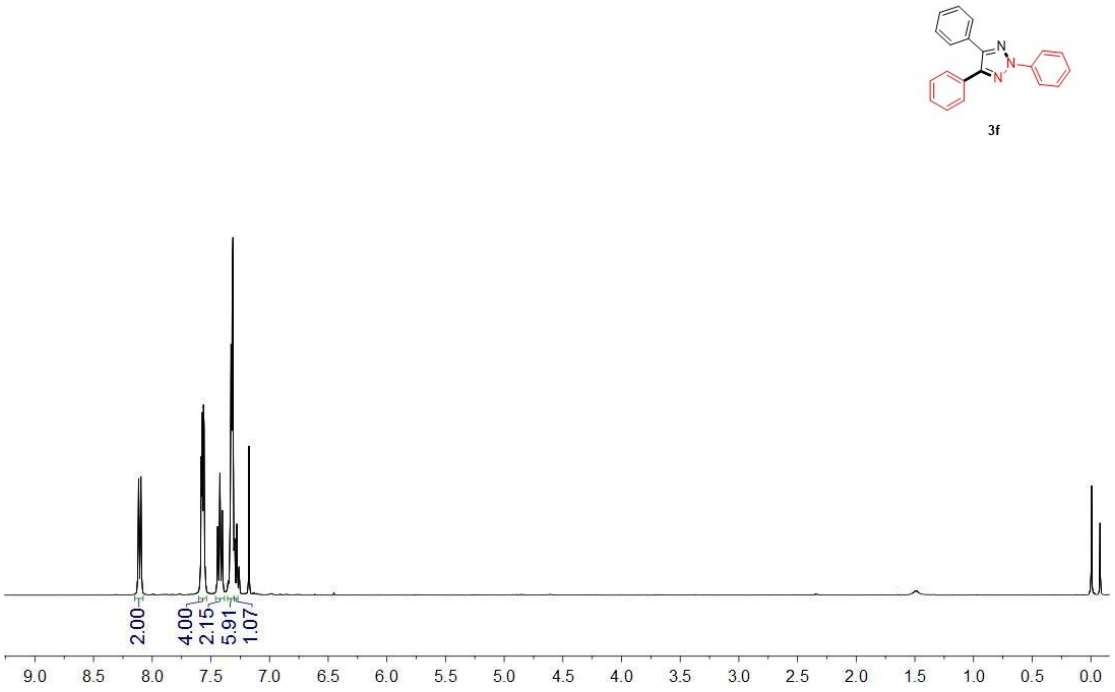
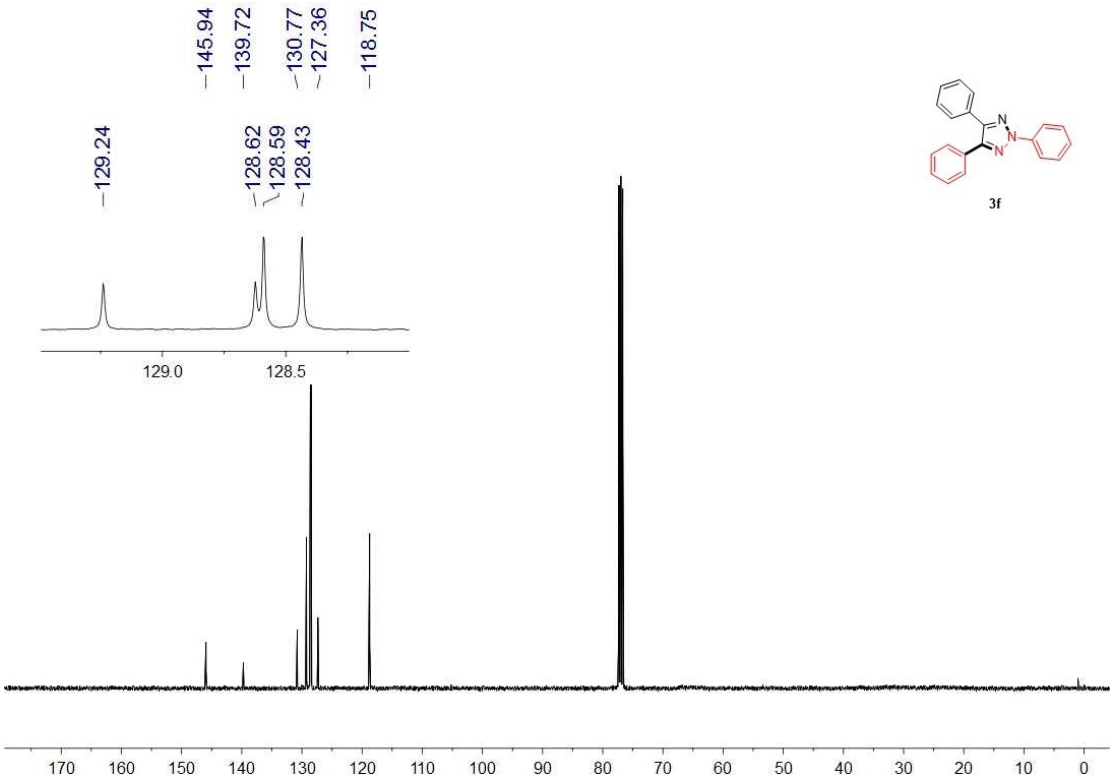

3f
2.00
4.00
2.15
5.91
1.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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3f
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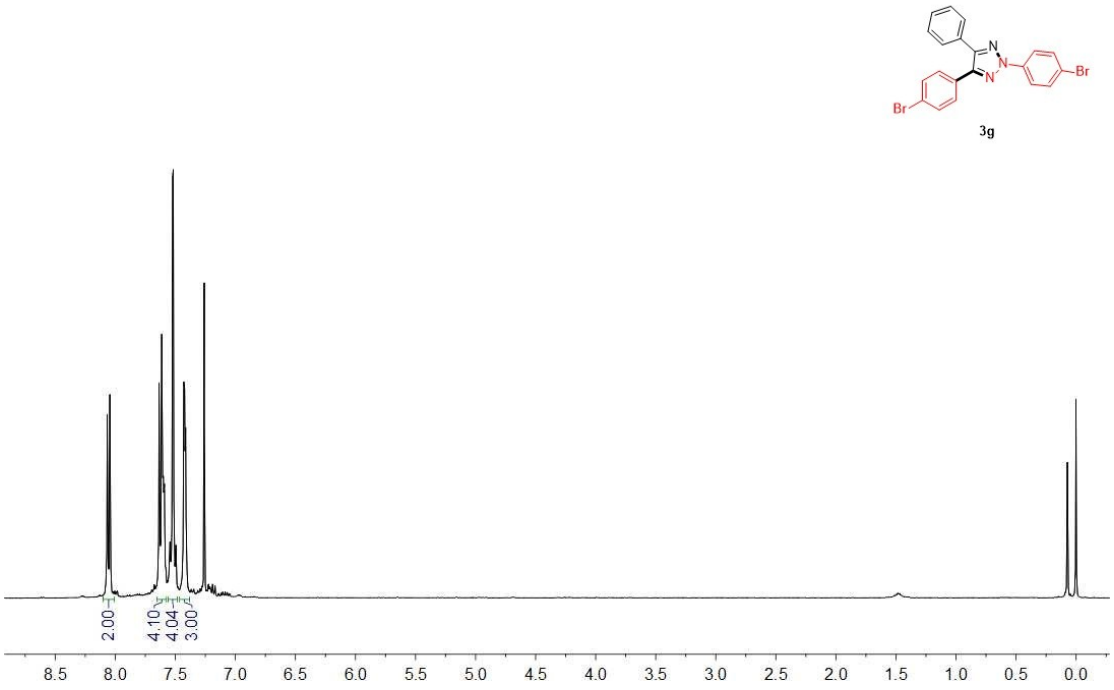
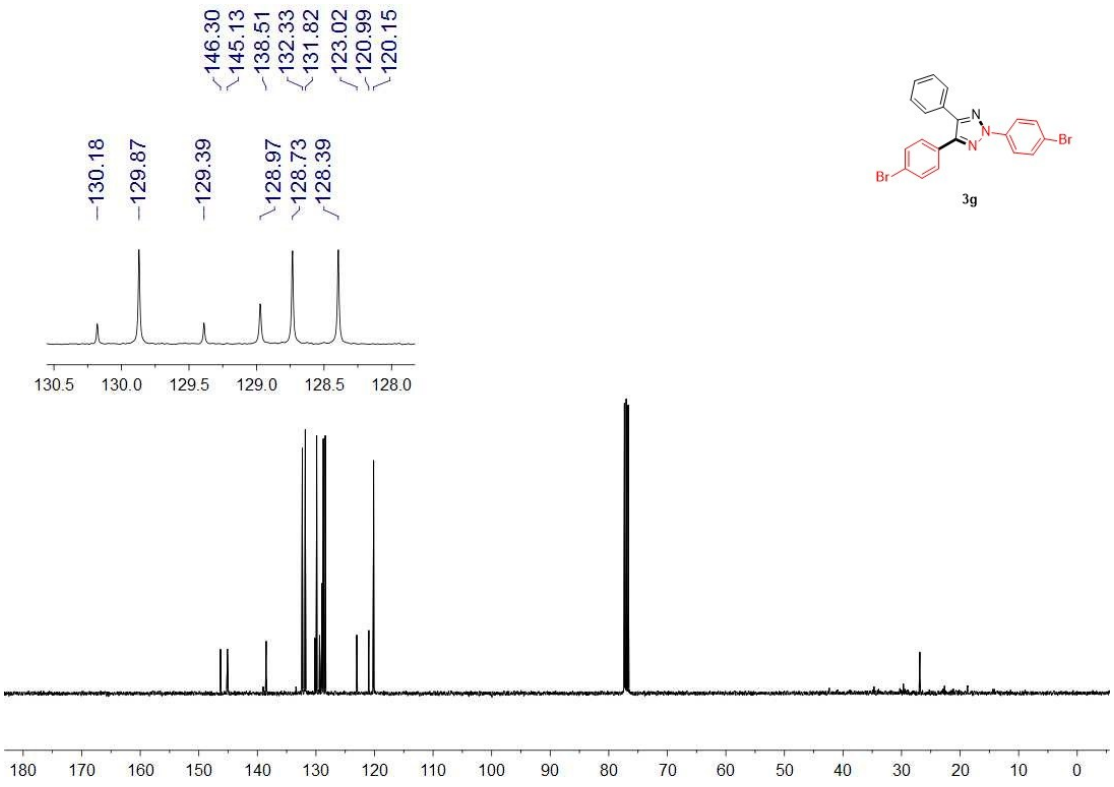

Br
Br
3g
2.00
4.10
4.04
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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128.73
128.39
130.5
130.0
129.5
129.0
128.5
128.0
180
170
160
150
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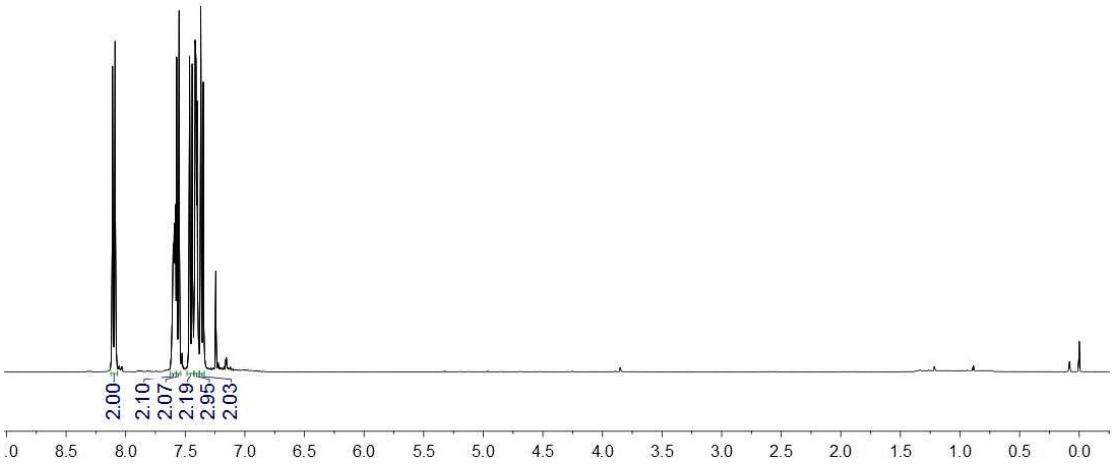
N
N
Br
Br

3g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2.07
2.19
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2.03
.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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2.0
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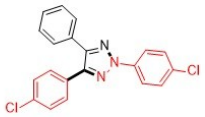
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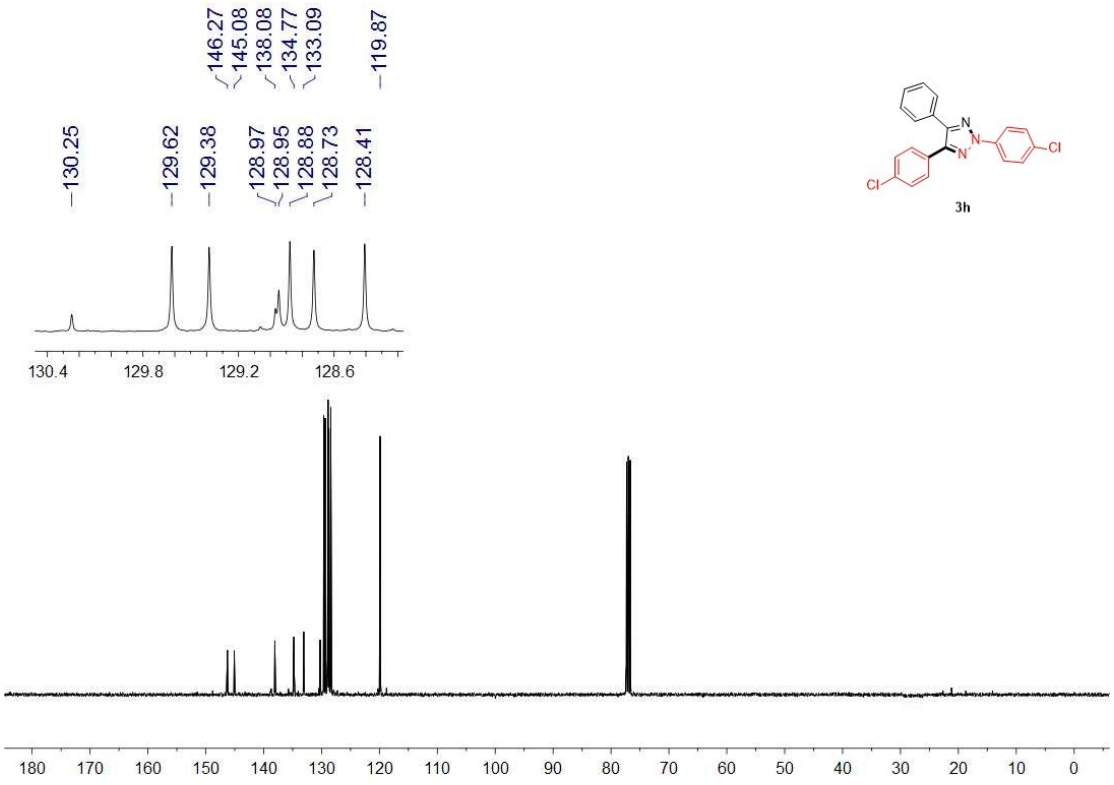
Cl
Cl

3h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138.08
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133.09
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130.25
129.62
129.38
128.97
128.95
128.88
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128.41
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129.8
129.2
128.6
Cl
Cl
3h
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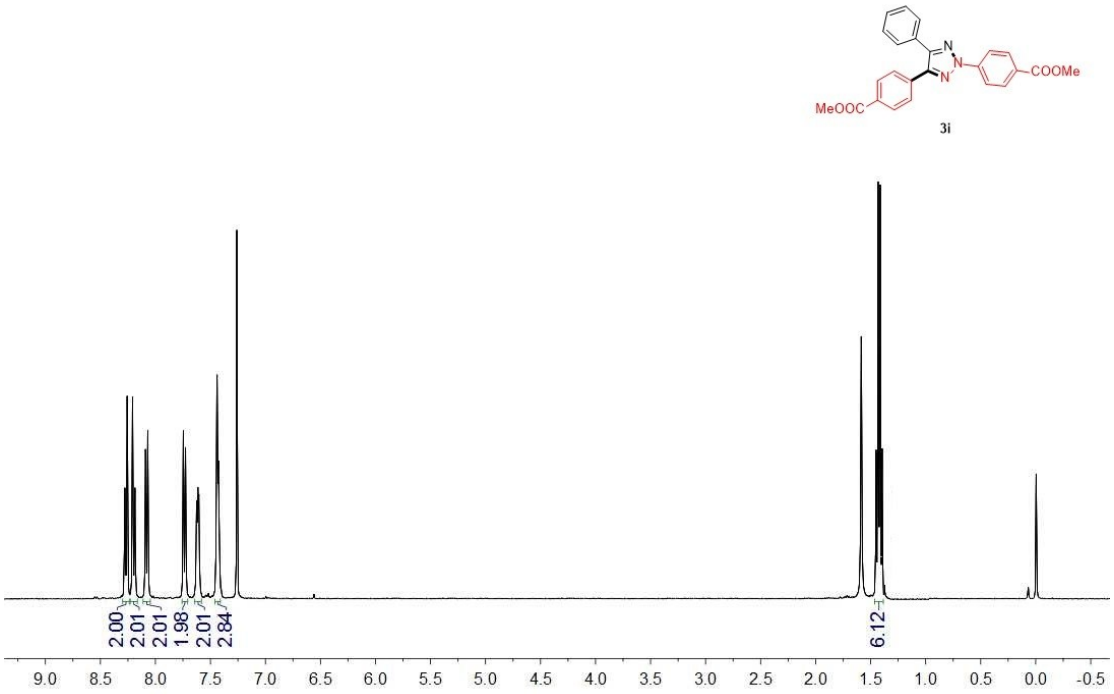
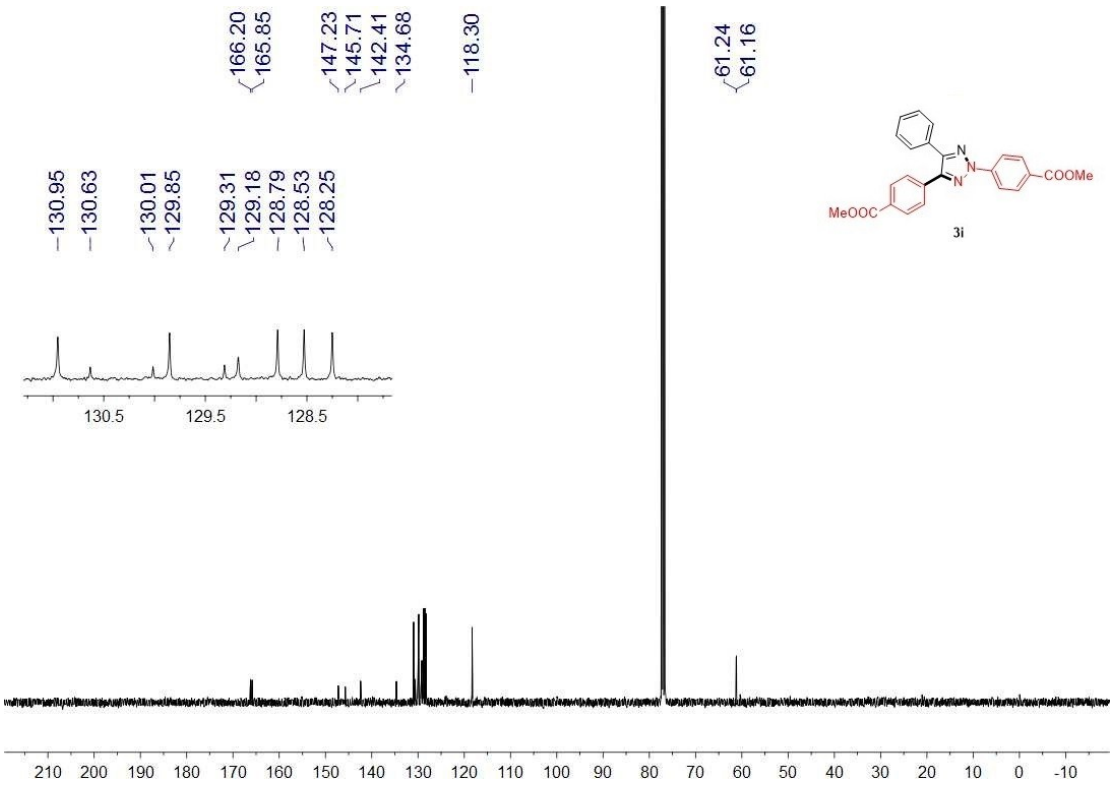

COOMe
MeOOC
3i
2.00
2.01
2.01
1.98
2.01
2.84
6.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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165.85
147.23
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142.41
134.68
118.30
61.24
61.16
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130.63
130.01
129.85
129.31
129.18
128.79
128.53
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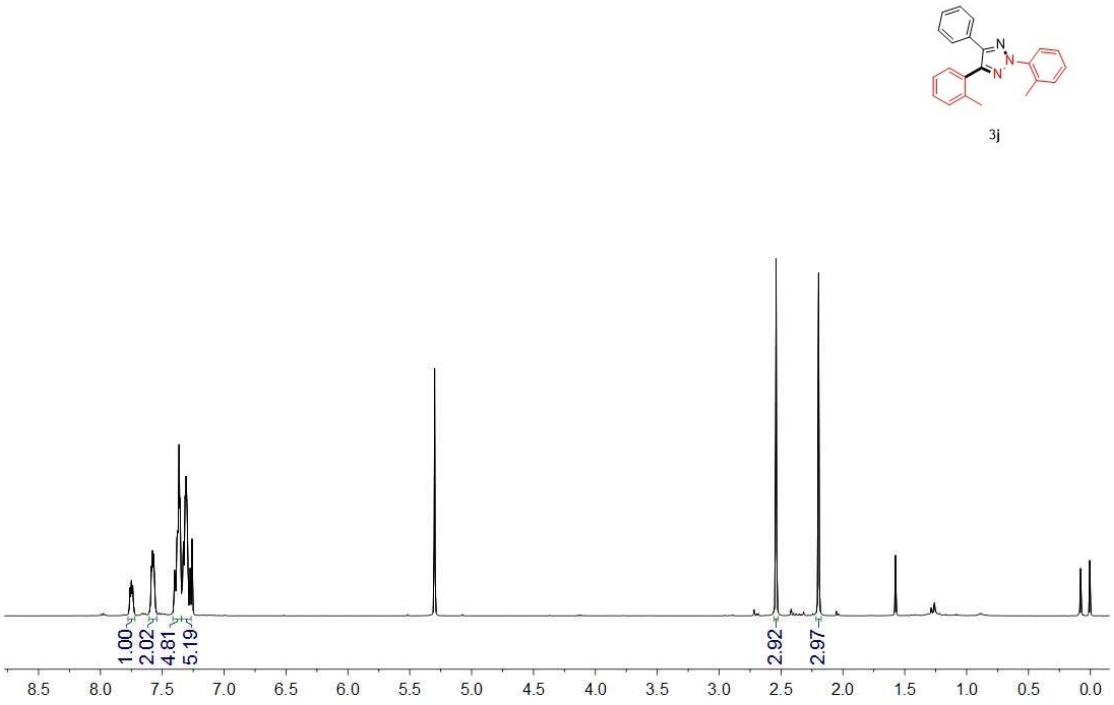
129.5
128.5
COOMe
MeOOC
3i
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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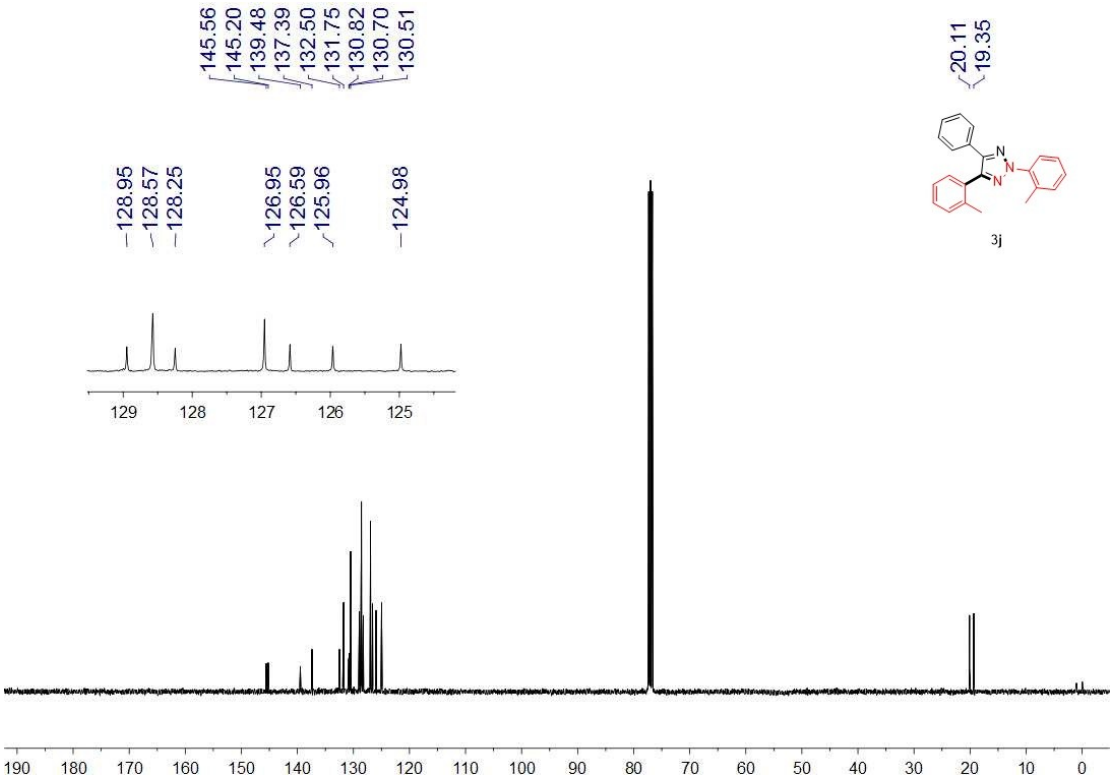
2.02
4.81
5.19
2.92
2.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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128.25
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125.96
124.98
20.11
19.35
3j
129
128
127
126
125
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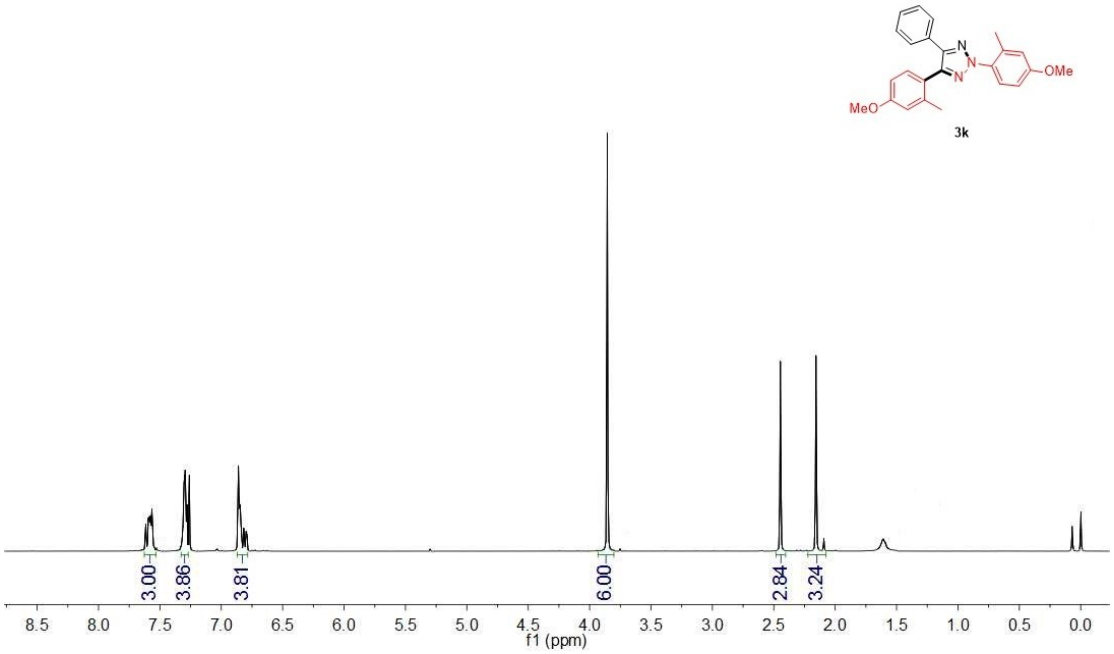
10
0


OMe
MeO
3k
3.00
3.86
3.81
6.00
2.84
3.24
8.5
8.0
7.5
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6.5
6.0
5.5
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2.0
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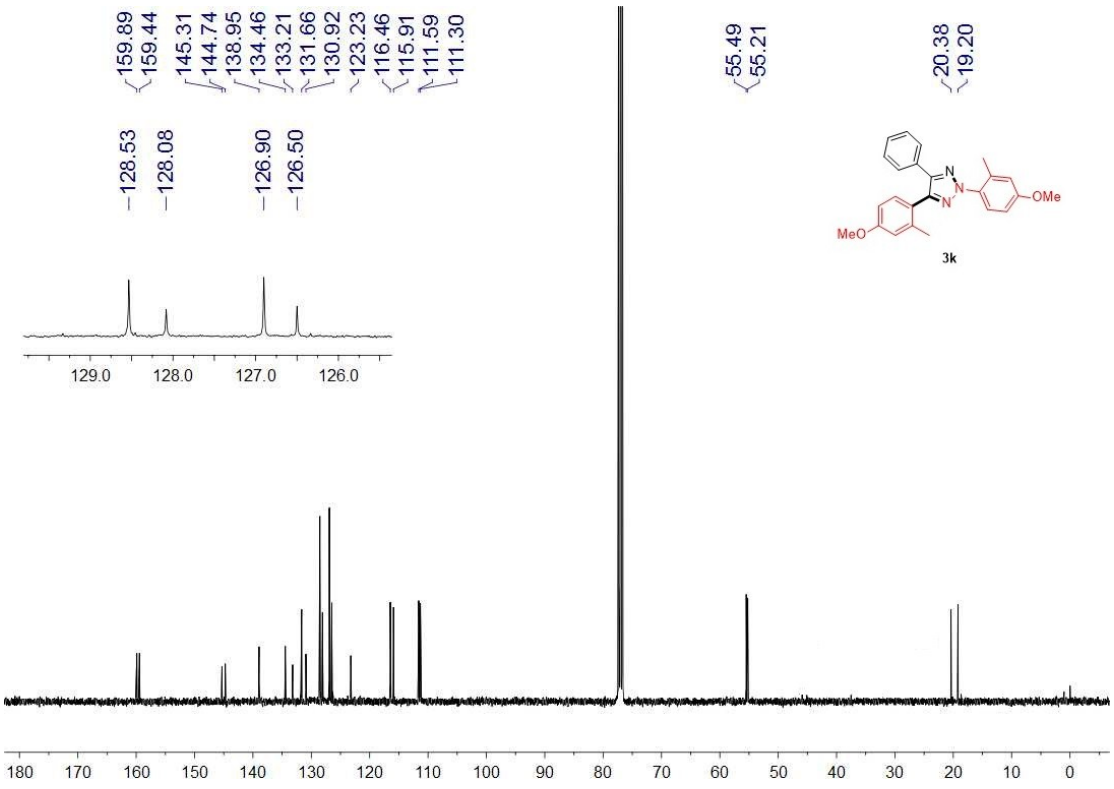
0.0
f1 (ppm)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128.53
128.08
126.90
126.50
55.49
55.21
20.38
19.20
OMe
MeO
3k
129.0
128.0
127.0
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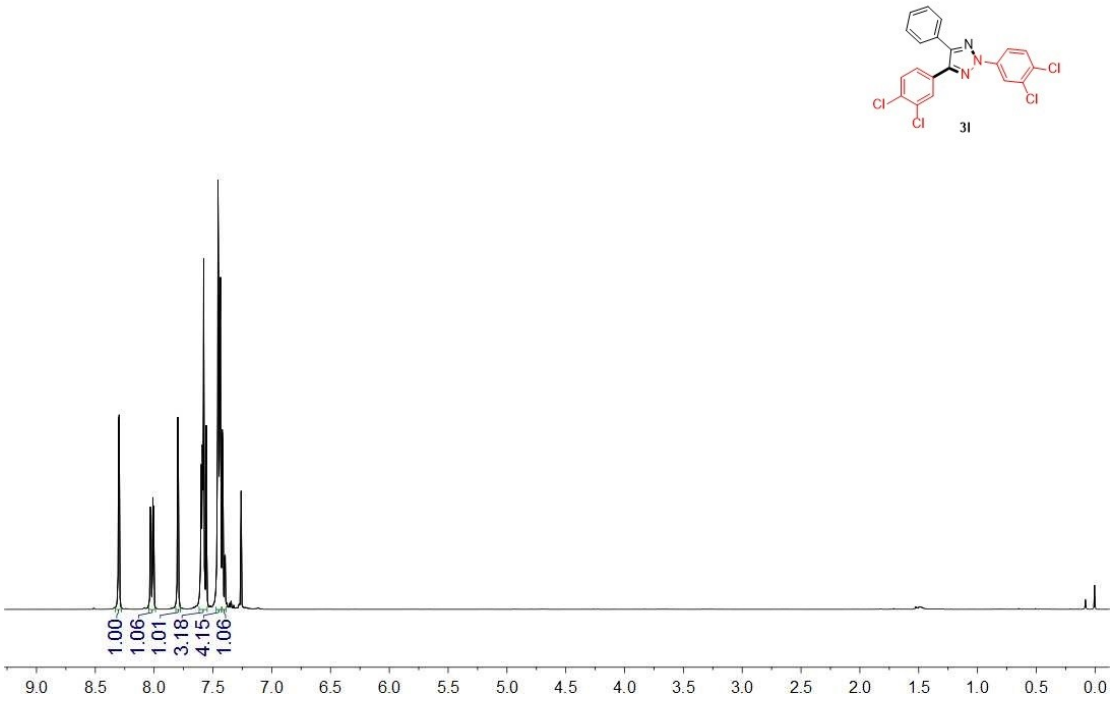
Cl
Cl
Cl
Cl
3l
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1.06
1.01
3.18
4.15
1.06
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
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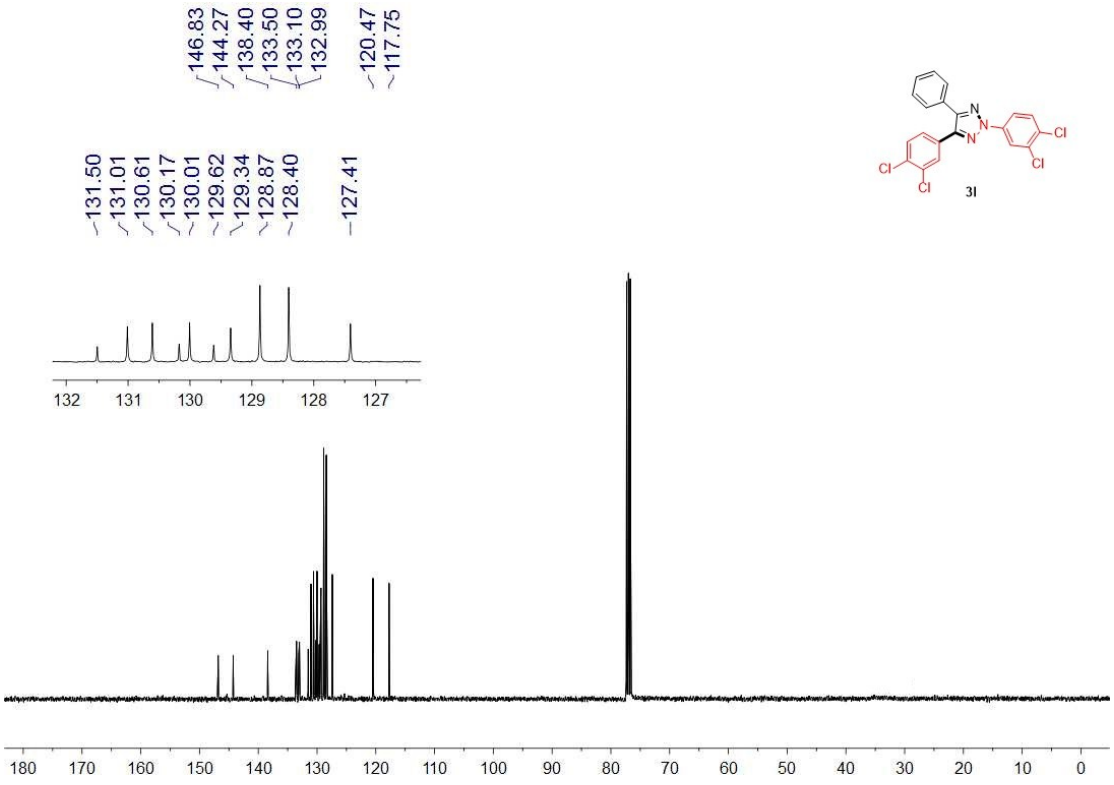
2.0
1.5
1.0
0.5
0.0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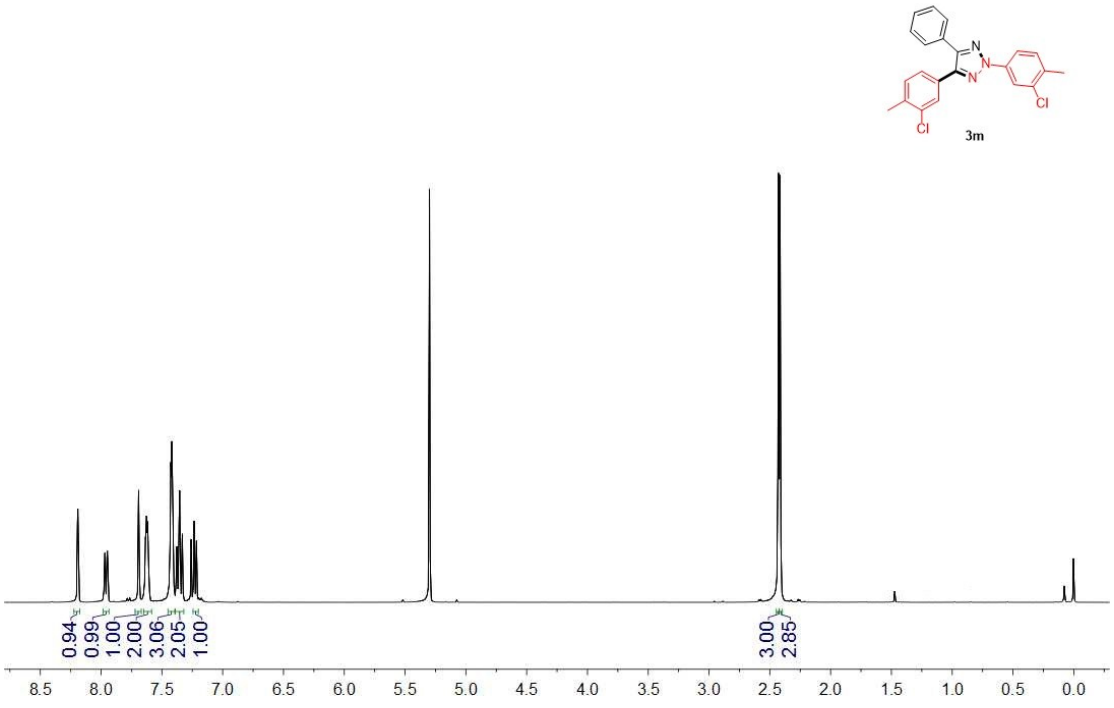
3l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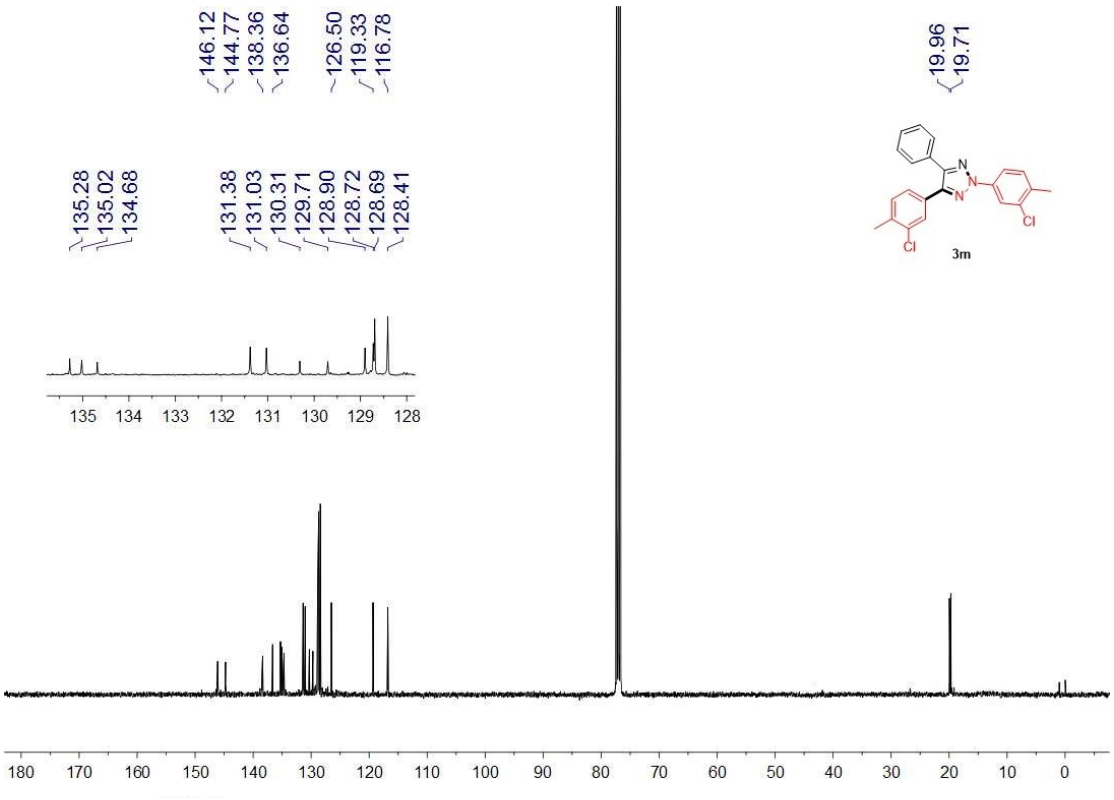
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126.50
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135.28
135.02
134.68
131.38
131.03
130.31
129.71
128.90
128.72
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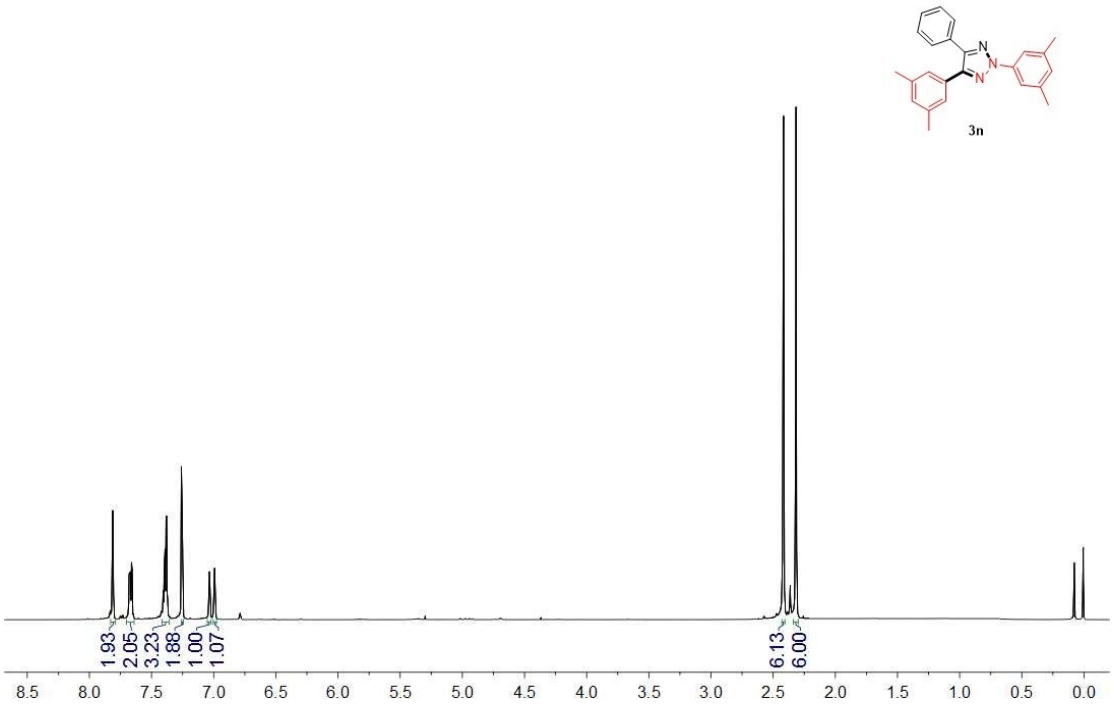
128.41
19.96
19.71
Cl
Cl
3m
135 134 133 132 131 130 129 128
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0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N
N
3n
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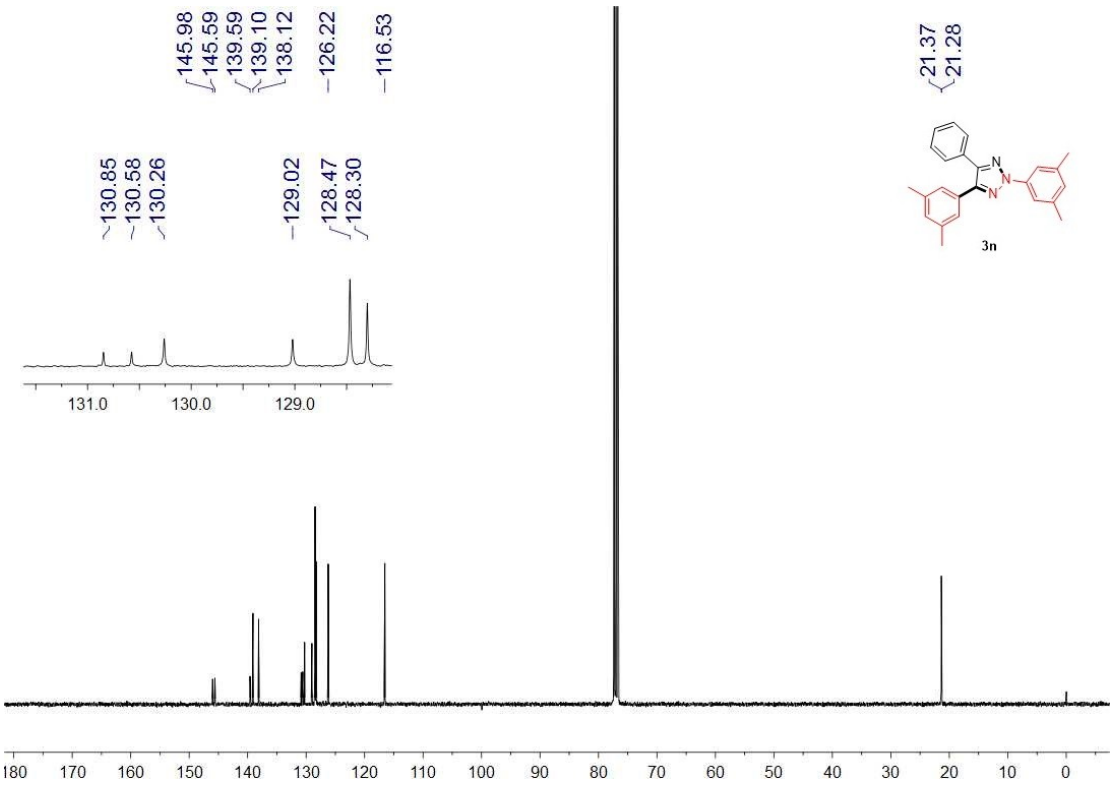
2.05
3.23
1.88
1.00
1.07
6.13
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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131.0
130.0
129.0
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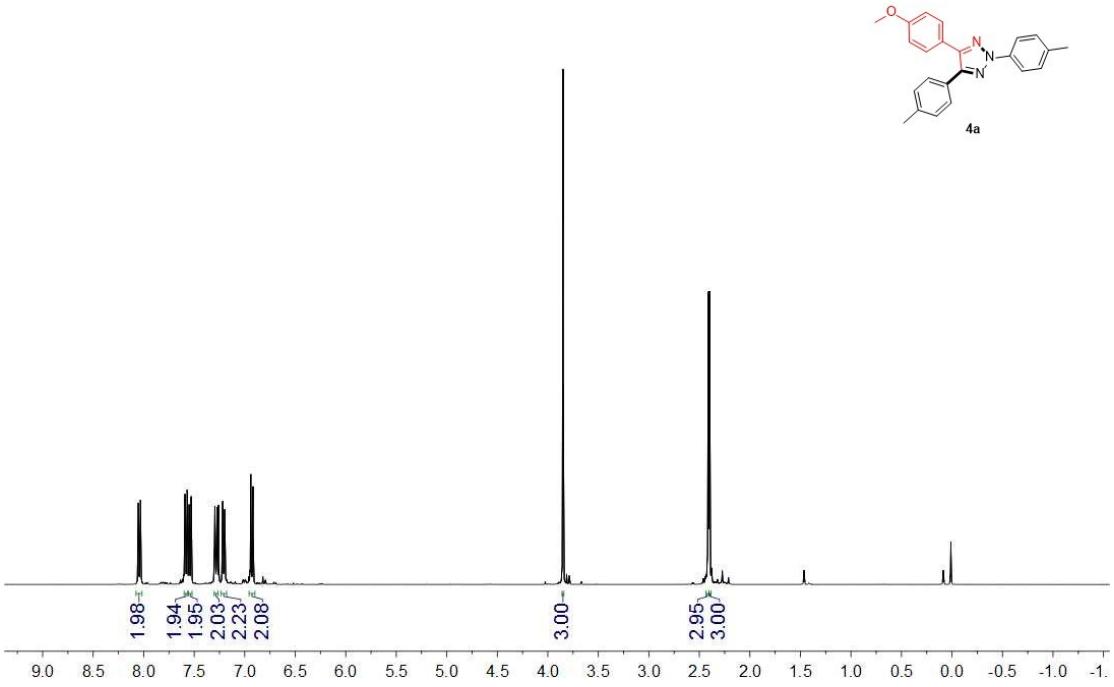
4a
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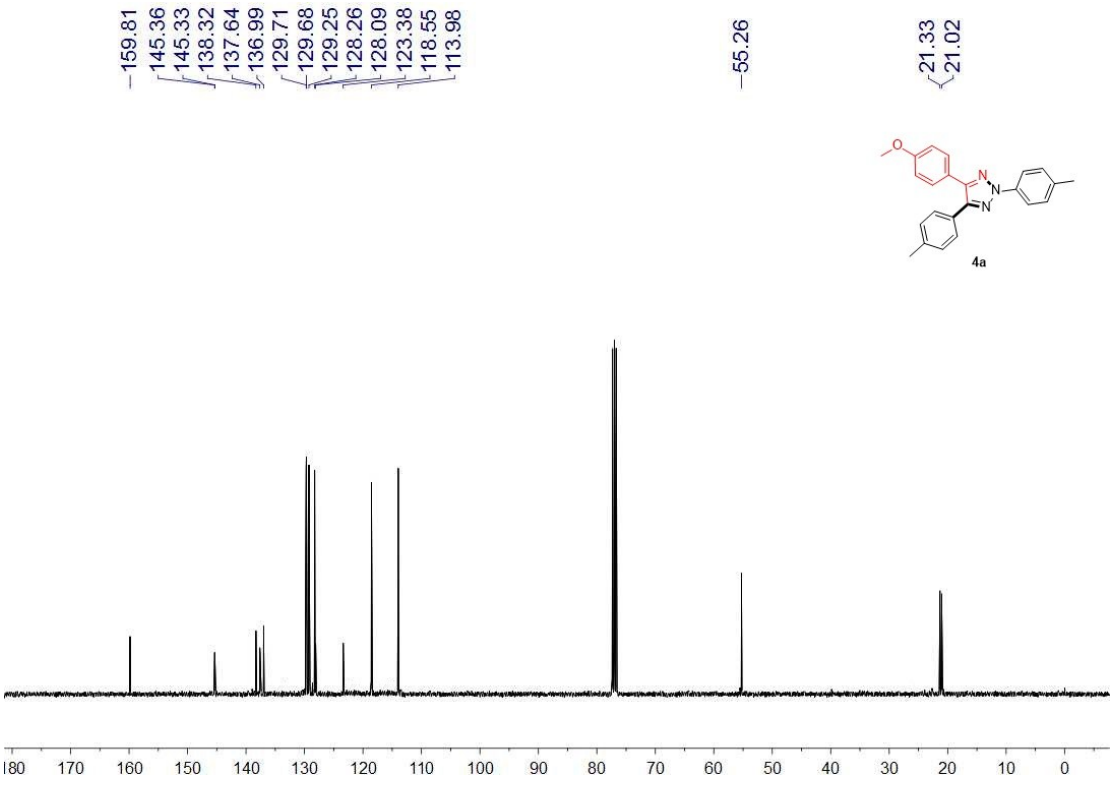
1.94
1.95
2.03
2.23
2.08
3.00
2.95
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0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113.98
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21.33
21.02
4a
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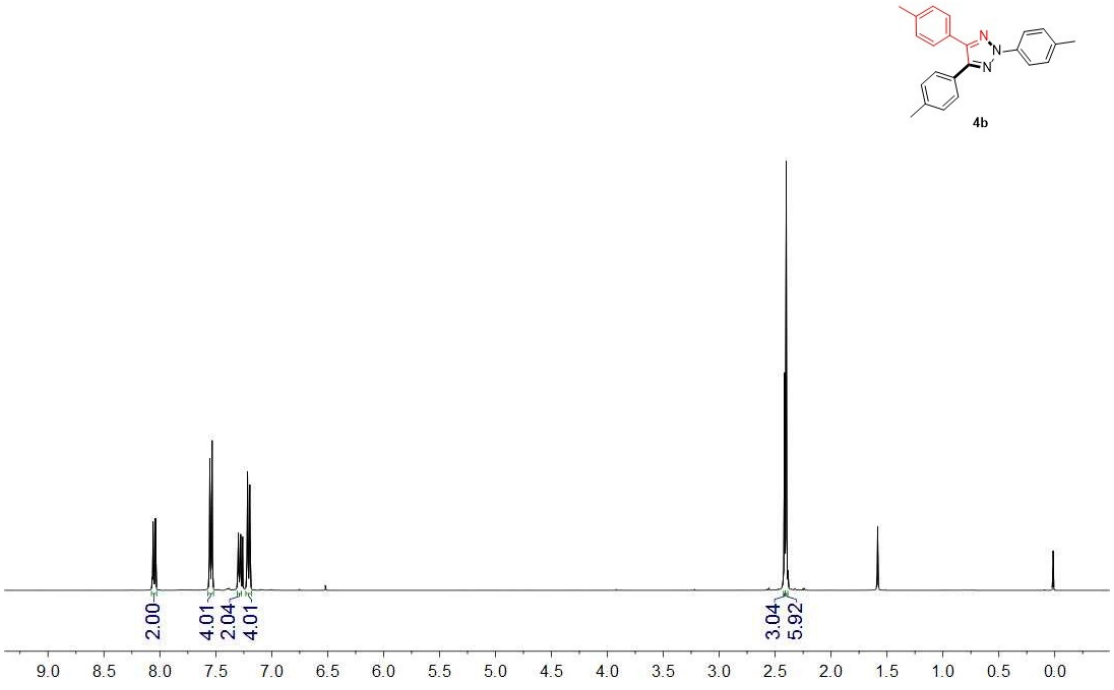
4b
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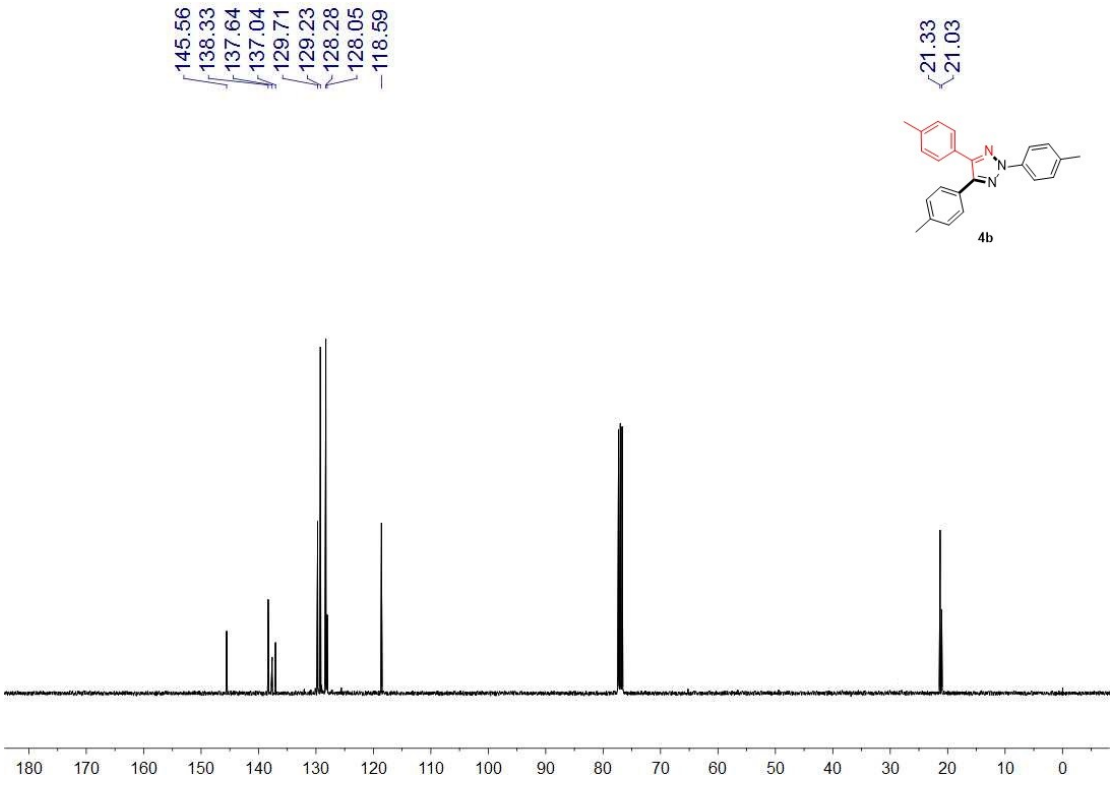
2.04
4.01
3.04
5.92
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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21.33
21.03
4b
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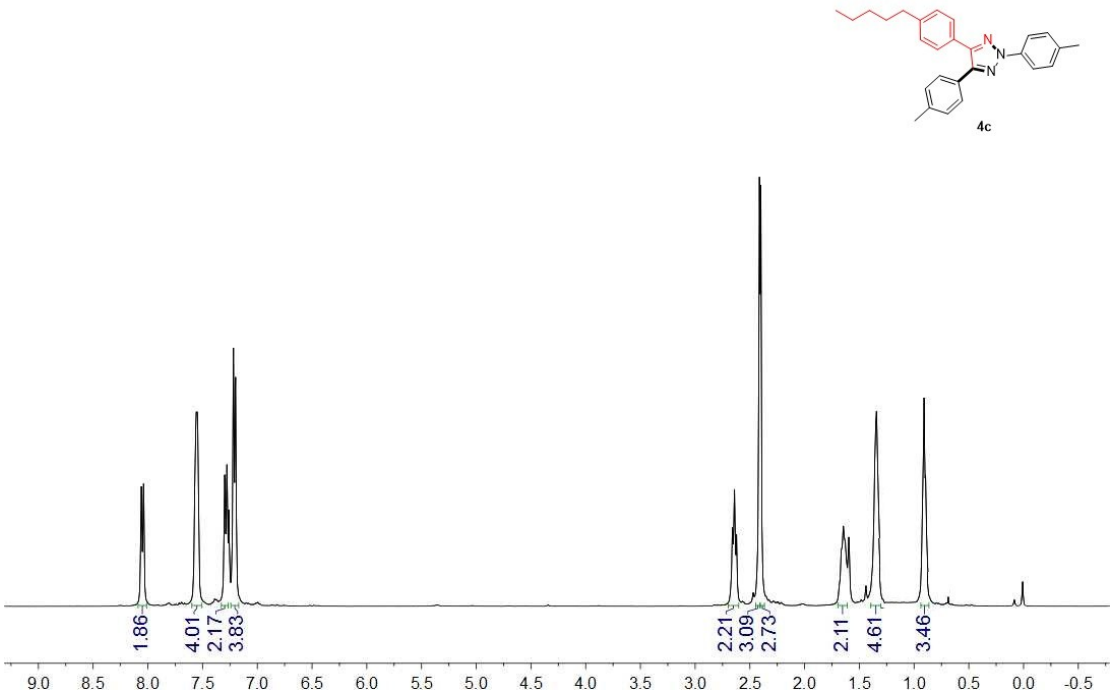
4c
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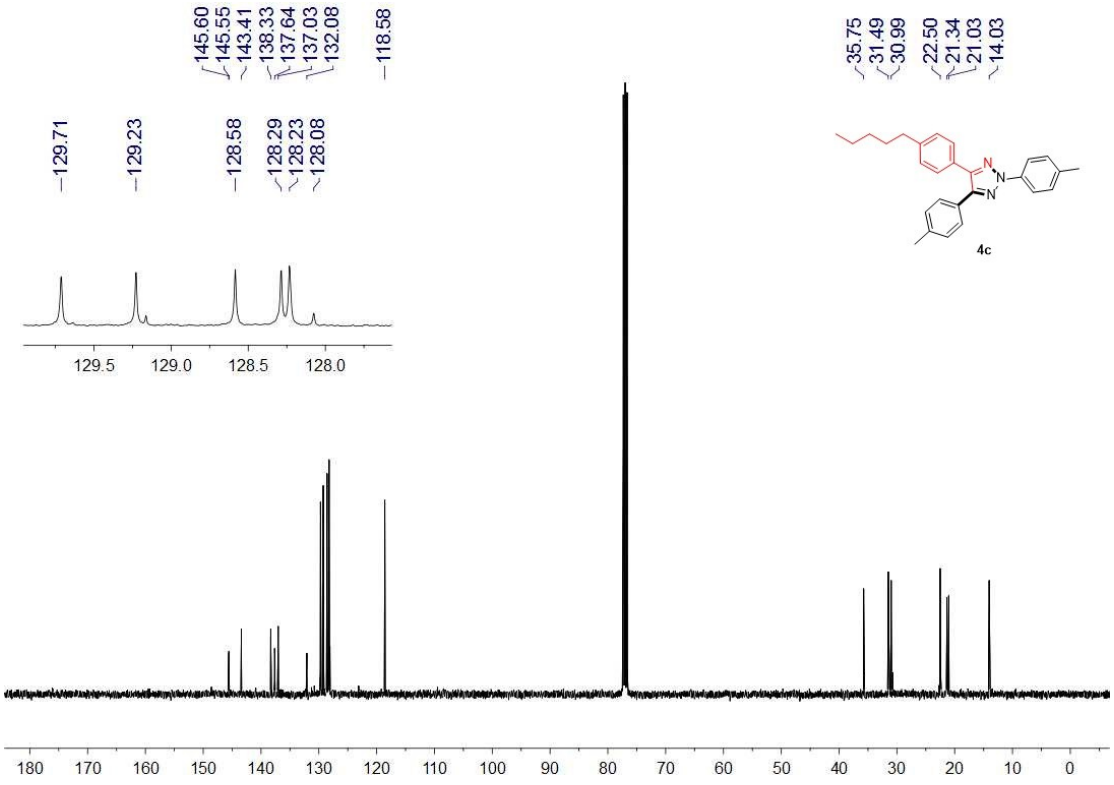
3.09
2.73
2.11
4.61
3.46
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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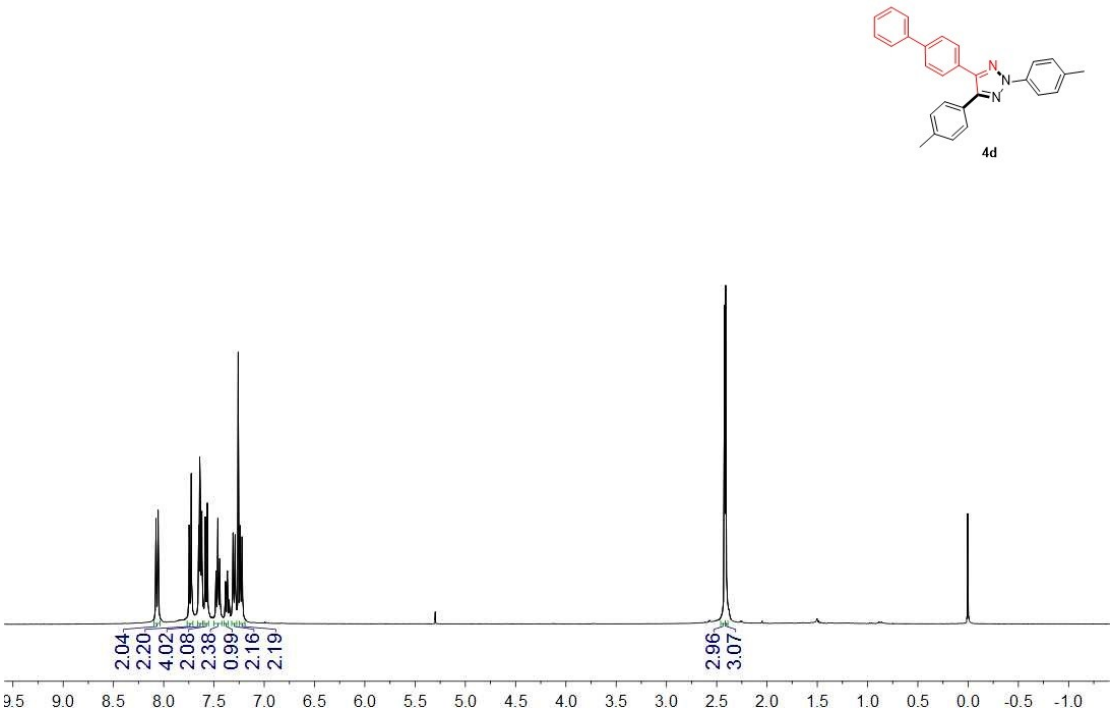
14.03
4c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2.19
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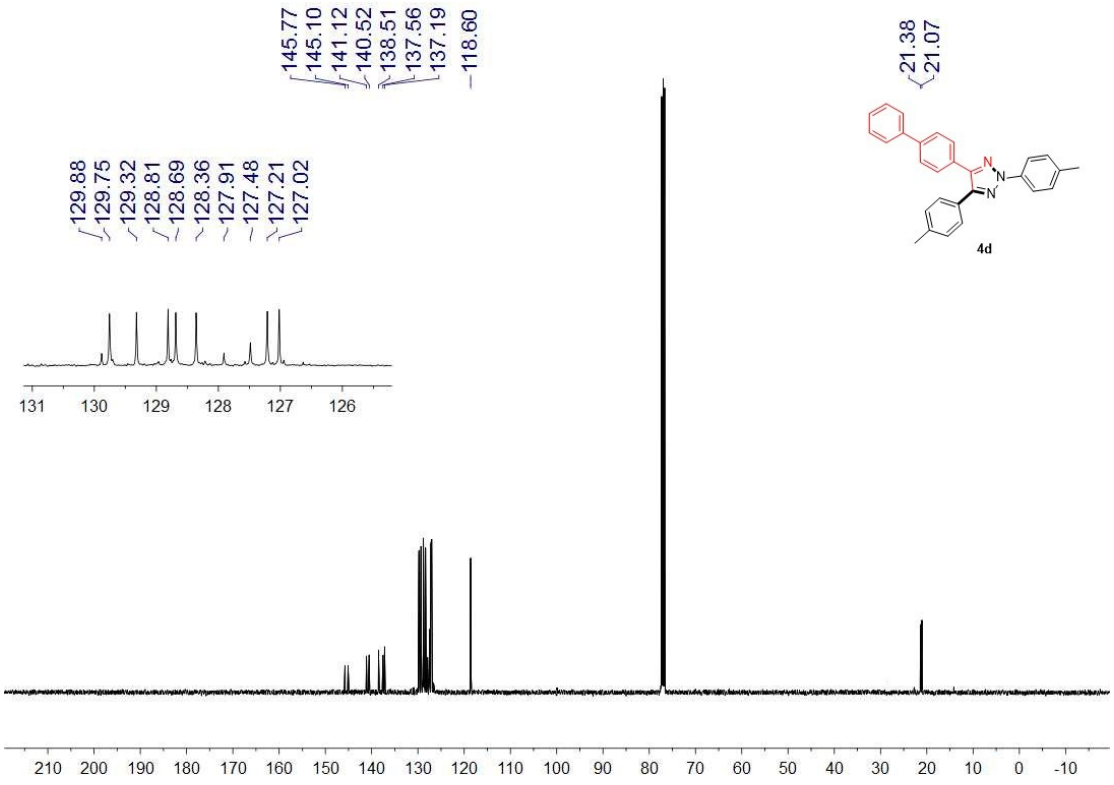
3.07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128.81
128.69
128.36
127.91
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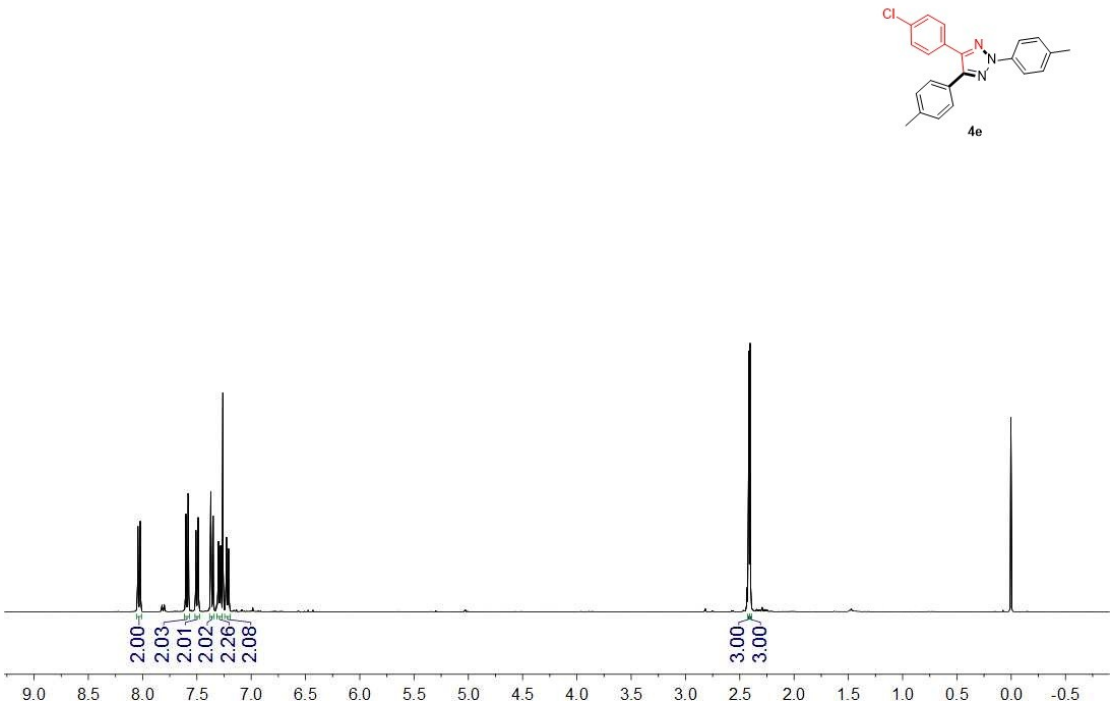
21.38
21.07
4d
131 130 129 128 127 126
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


Cl
4e
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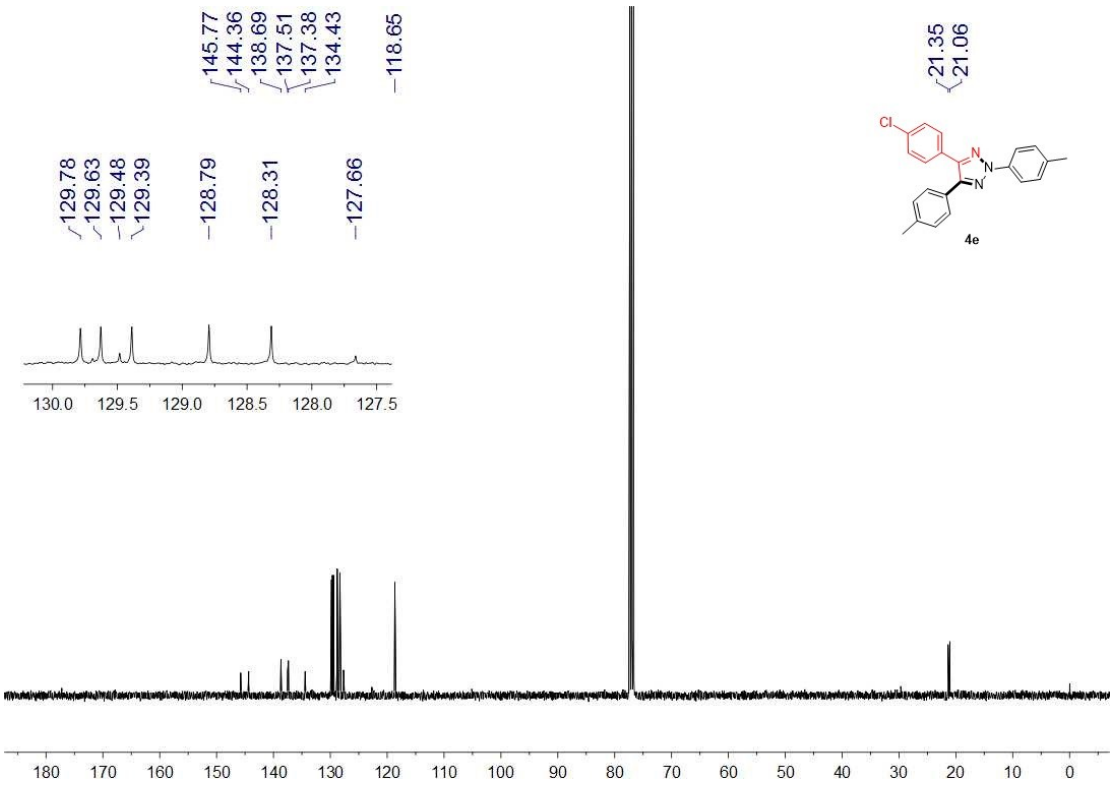
2.03
2.01
2.02
2.26
2.08
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5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128.31
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21.35
21.06
Cl
N
N
N
4e
130.0
129.5
129.0
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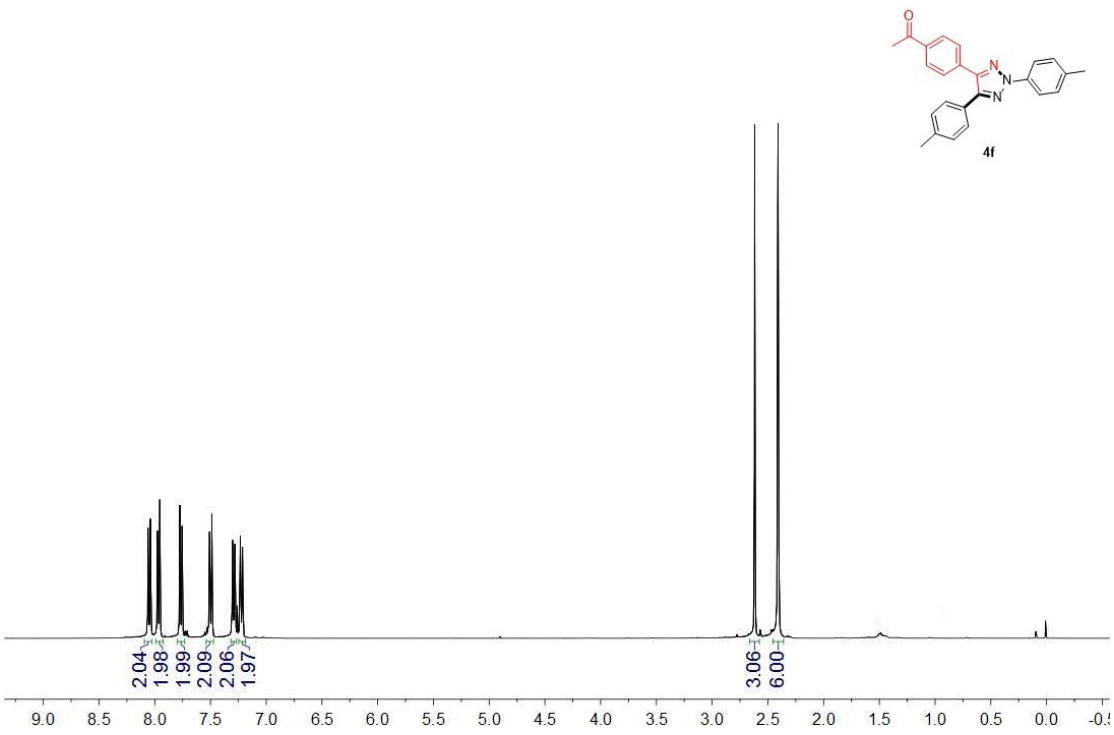
0


O
N
N
N
4f
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1.99
2.09
2.06
1.97
3.06
6.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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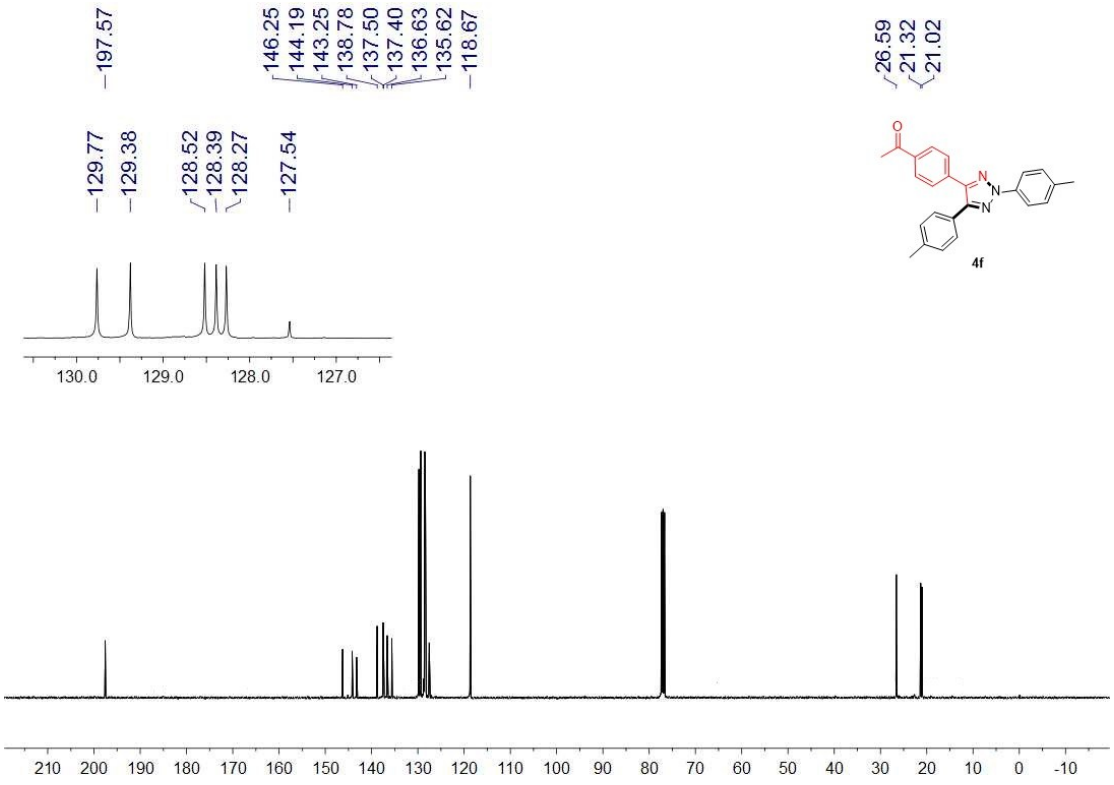
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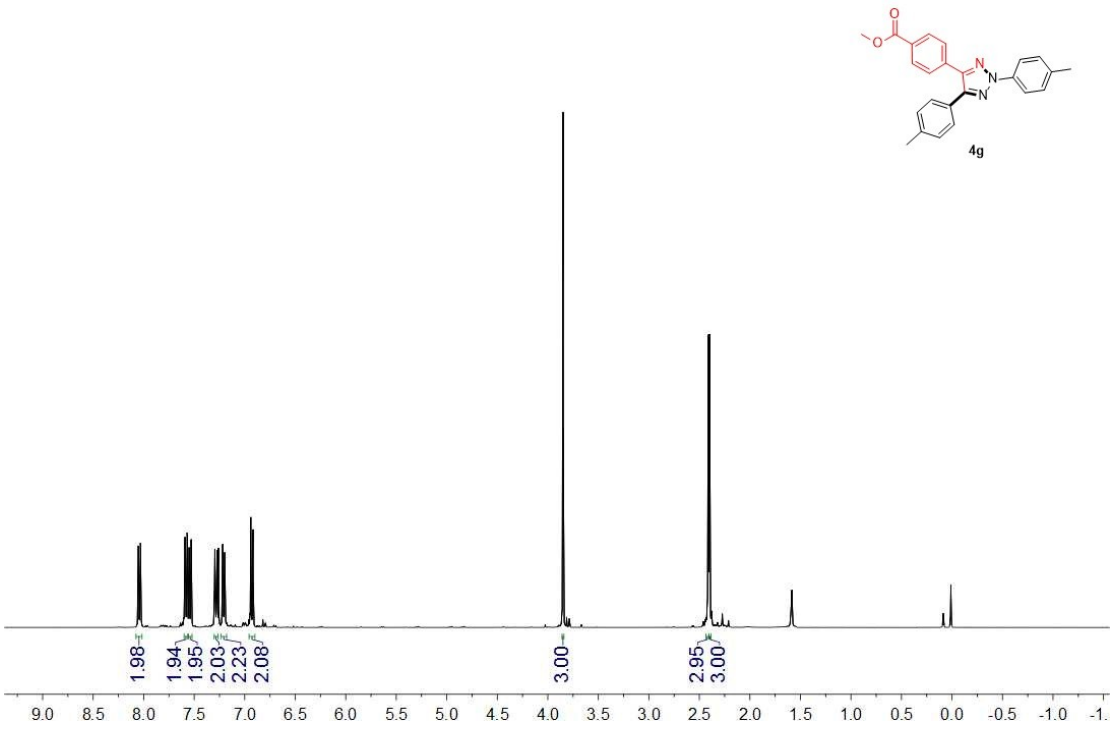
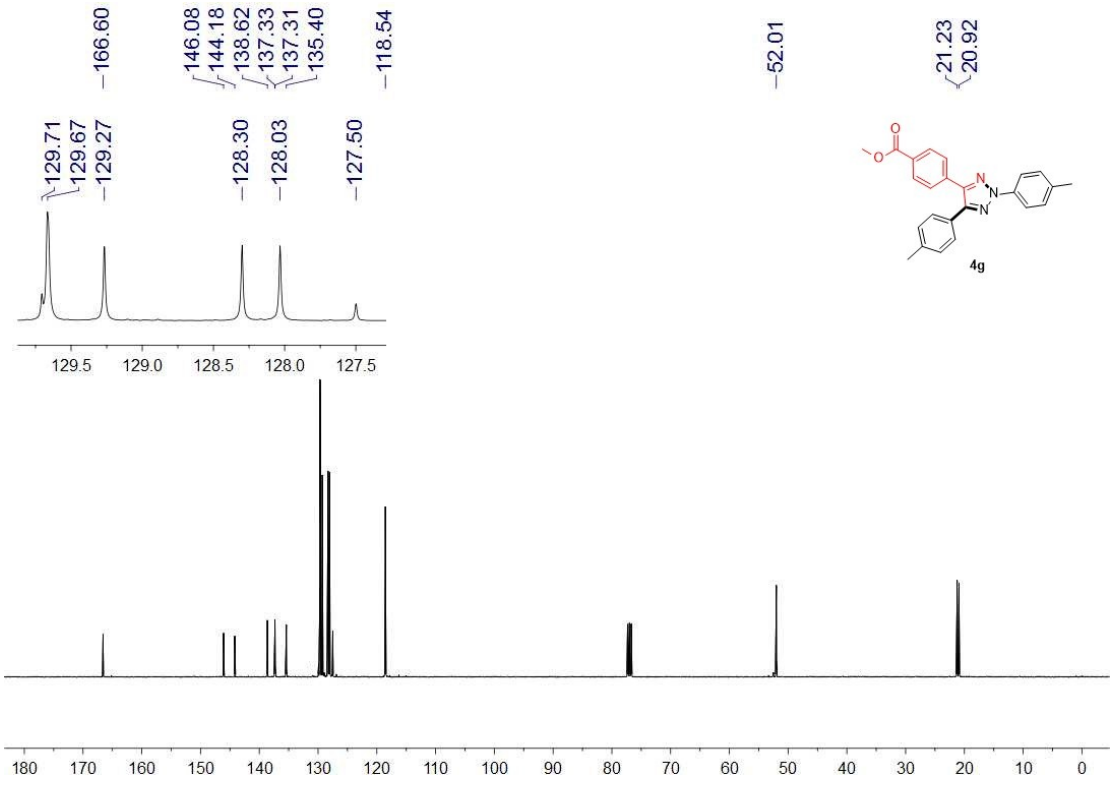
128.39
128.27
127.54
130.0
129.0
128.0
127.0
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10


4g
1.98
1.94
1.95
2.03
2.23
2.08
3.00
2.95
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 -0.5 -1.0


166.60
146.08
144.18
138.62
137.33
137.31
135.40
118.54
52.01
21.23
20.92
129.71
129.67
129.27
128.30
128.03
127.50
129.5
129.0
128.5
128.0
127.5
180
170
160
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140
130
120
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100
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80
70
60
50
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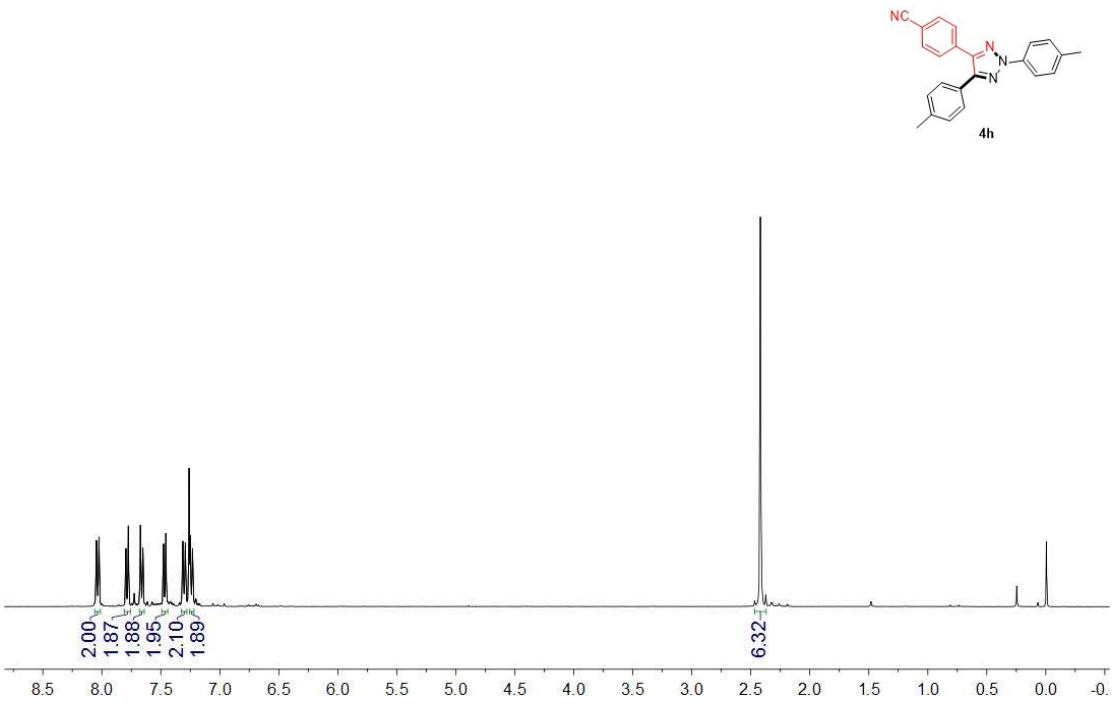
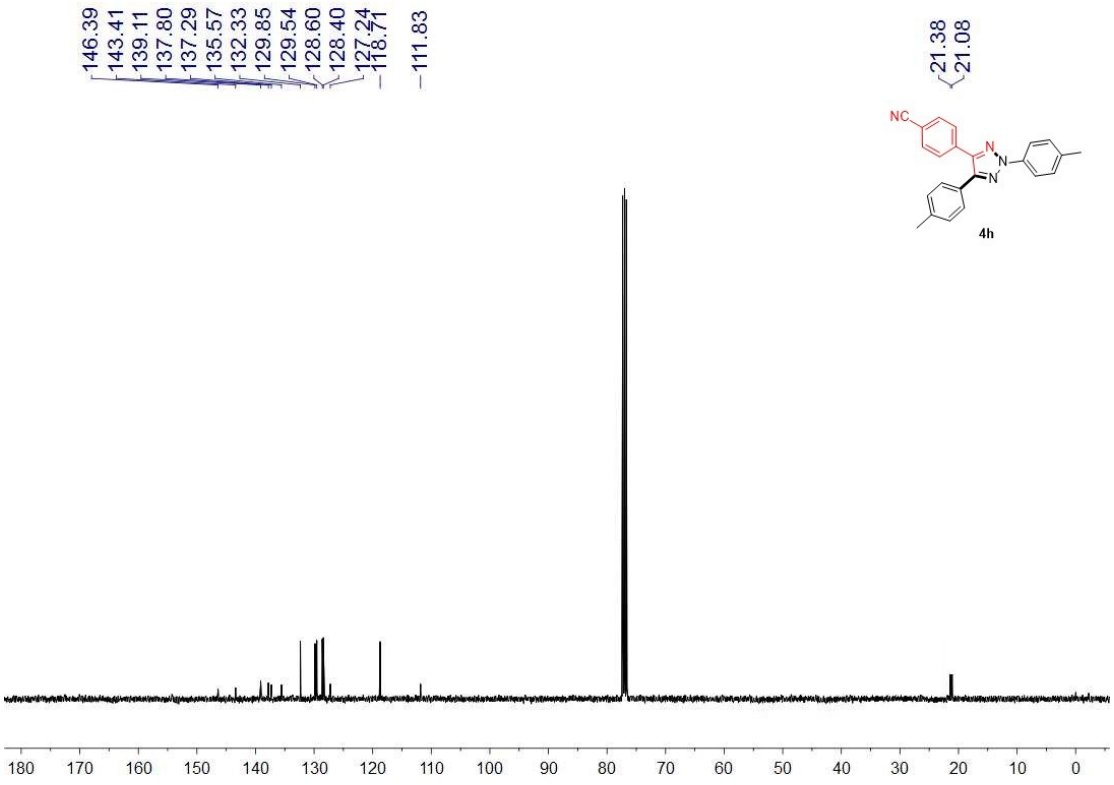
20
10
0

4g


2.00
1.87
1.88
1.95
2.10
1.89
6.32
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

4h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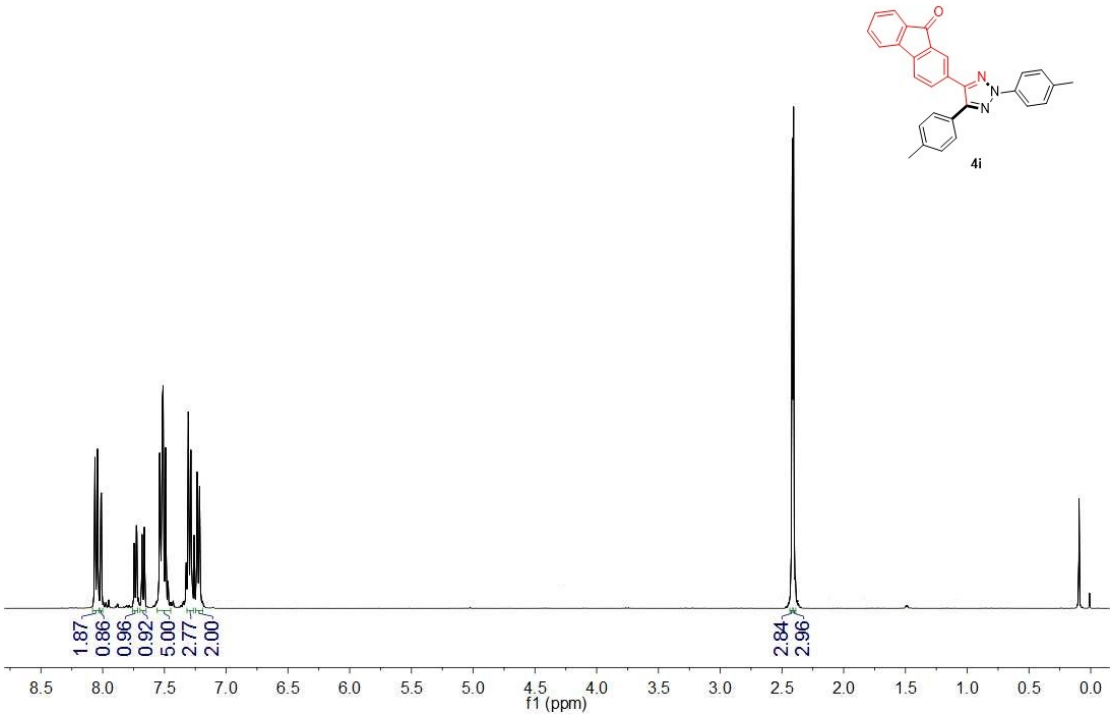
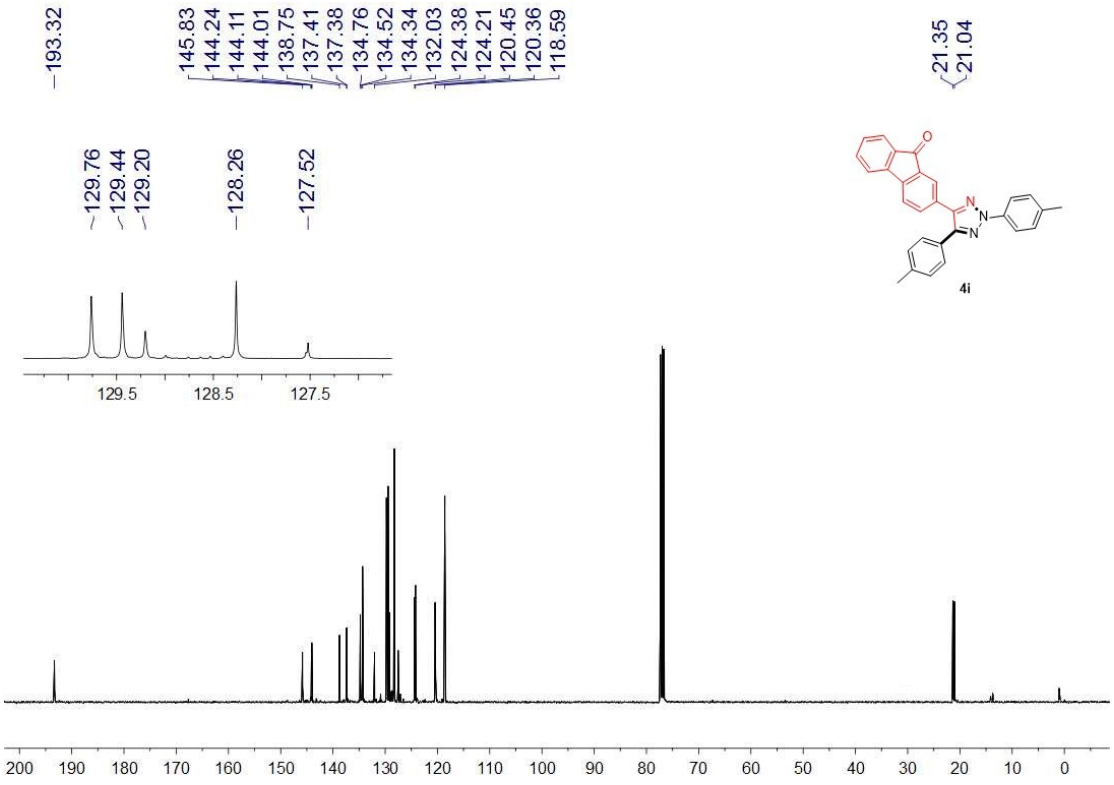
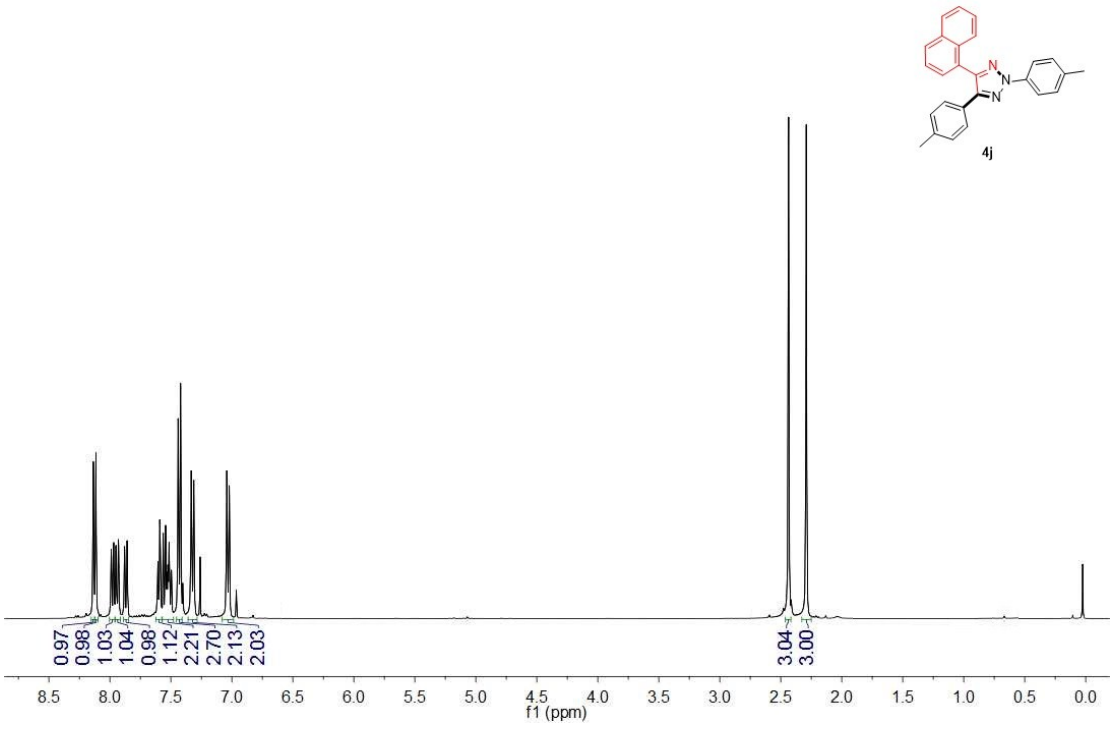
143.41
139.11
137.80
137.29
135.57
132.33
129.85
129.54
128.60
128.40
127.24
118.71
111.83
21.38
21.08
NC
N
N
4h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


O
N
N
4i
1.87
0.86
0.96
0.92
5.00
2.77
2.00
2.84
2.96
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
f1 (ppm)


193.32
145.83
144.24
144.11
144.01
138.75
137.41
137.38
134.76
134.52
134.34
132.03
124.38
124.21
120.45
120.36
118.59
21.35
21.04
129.76
129.44
129.20
128.26
127.52
129.5
128.5
127.5
4i
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


4j
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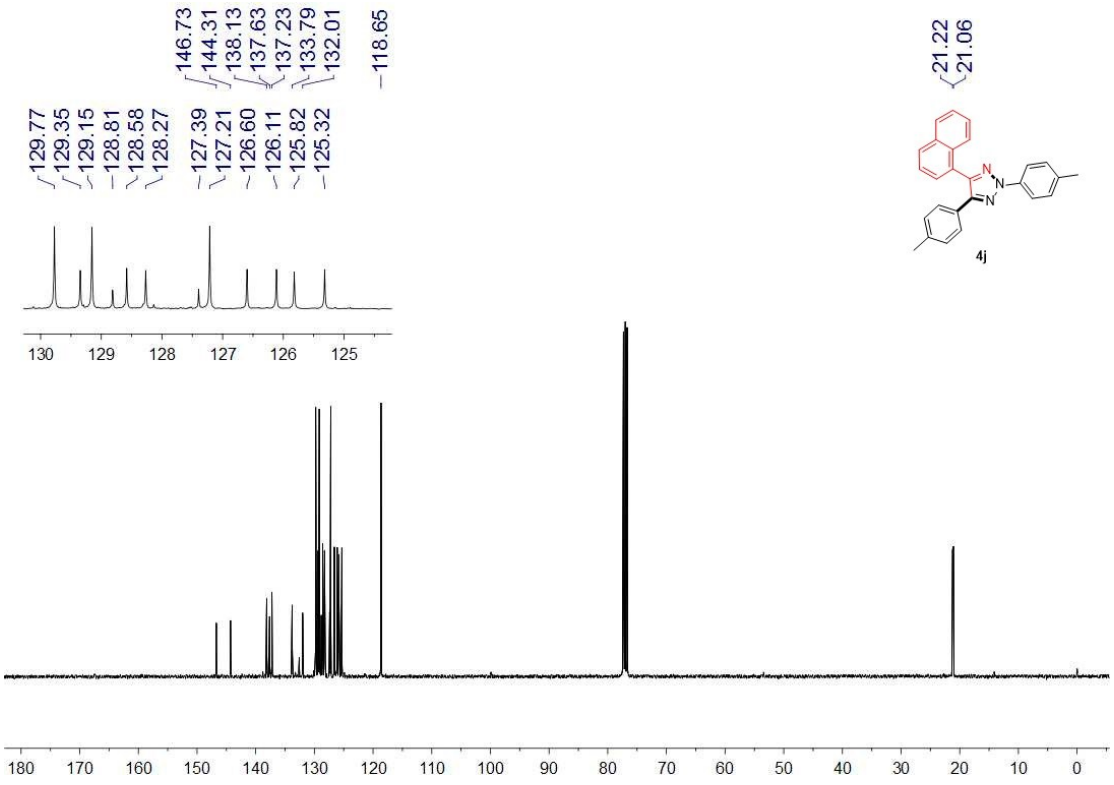
0.98
1.03
1.04
0.98
1.12
2.21
2.70
2.13
2.03
3.04
3.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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138.13
137.63
137.23
133.79
132.01
118.65
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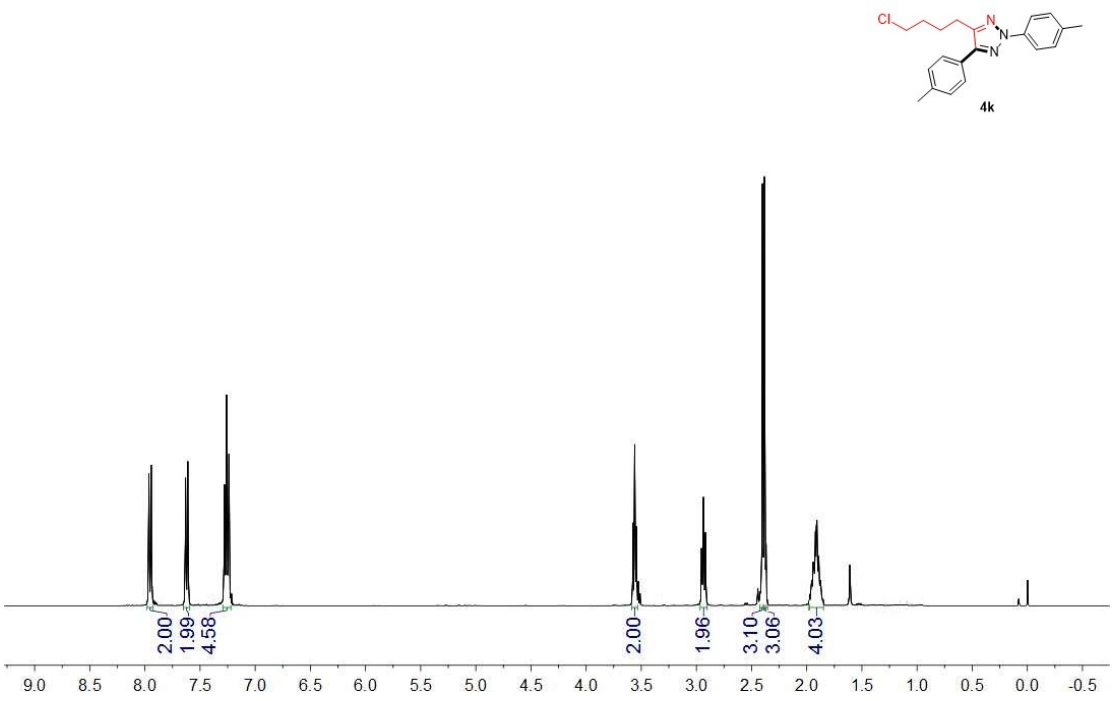
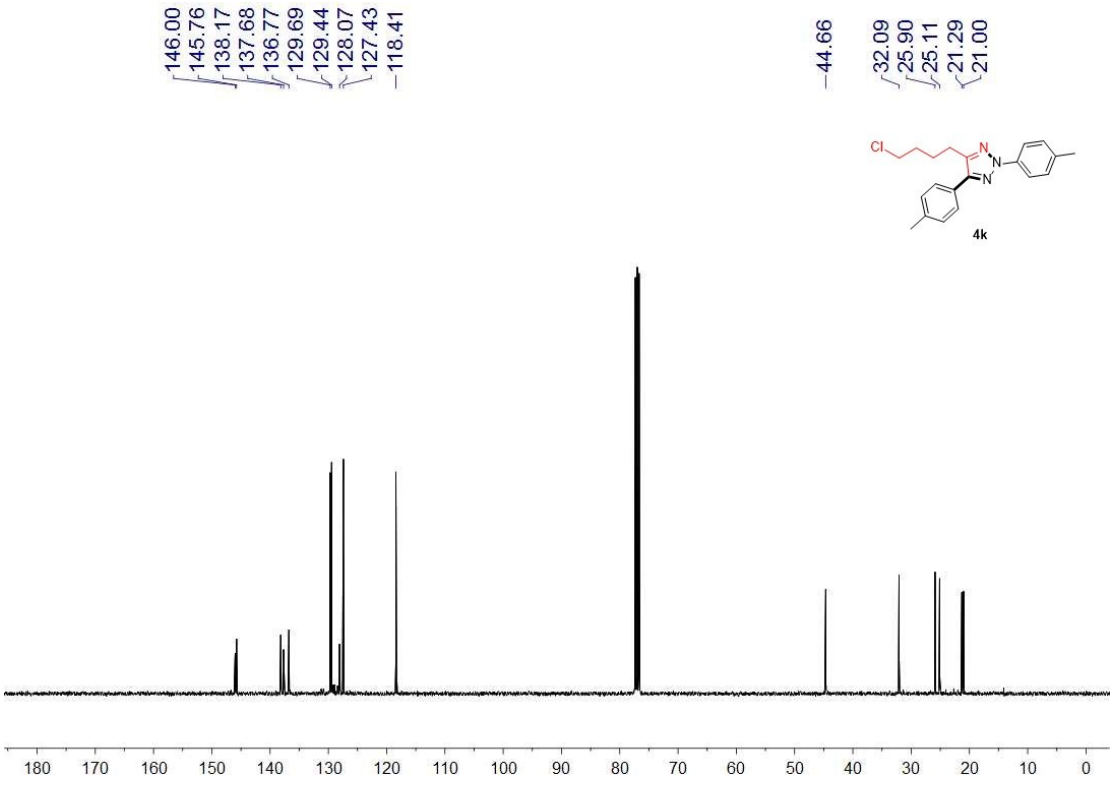
129.35
129.15
128.81
128.58
128.27
127.39
127.21
126.60
126.11
125.82
125.32
21.22
21.06
4j
130 129 128 127 126 125
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


Cl
4k
2.00
1.99
4.58
2.00
1.96
3.10
3.06
4.03
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 -0.5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138.17
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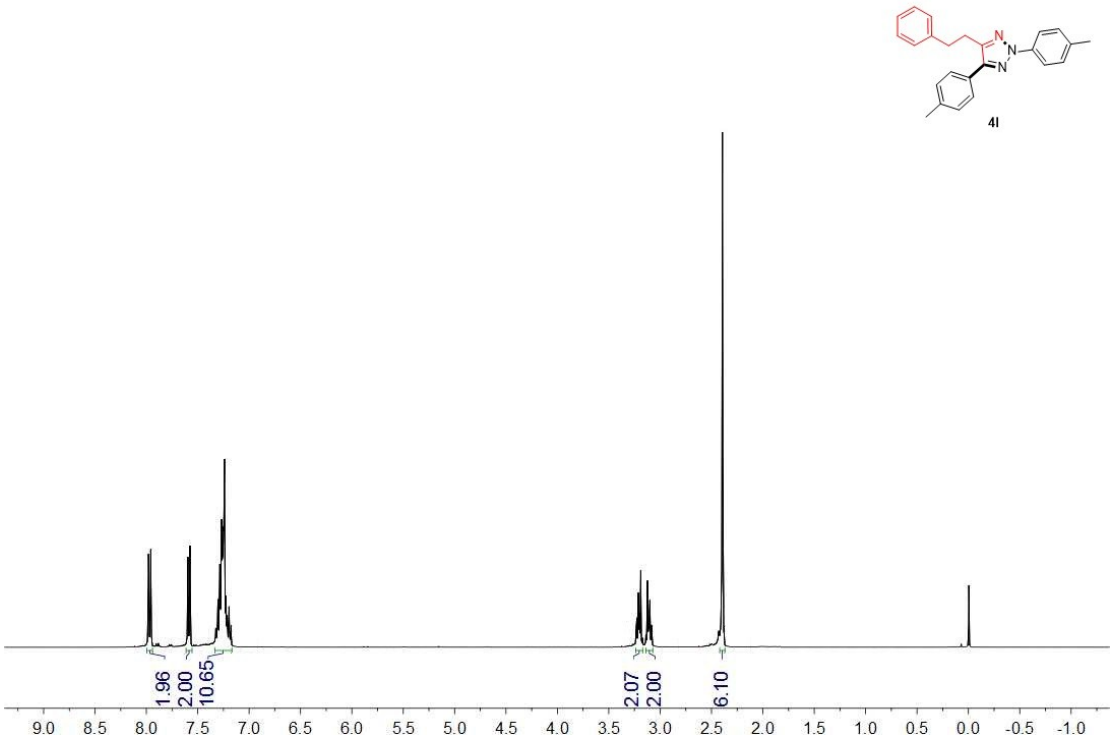
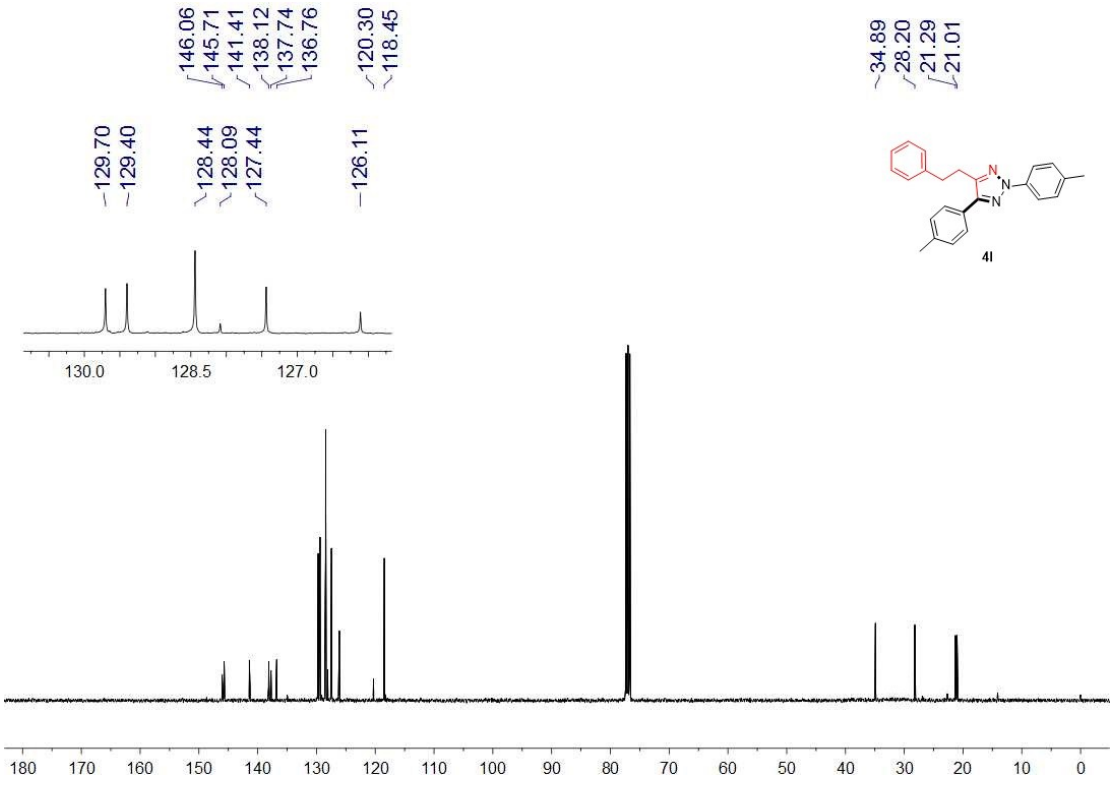
136.77
129.69
129.44
128.07
127.43
118.41
44.66
32.09
25.90
25.11
21.29
21.00
Cl
N
N
N
4k
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


N
N
N
4l
1.96
2.00
10.65
2.07
2.00
6.10
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 -0.5 -1.0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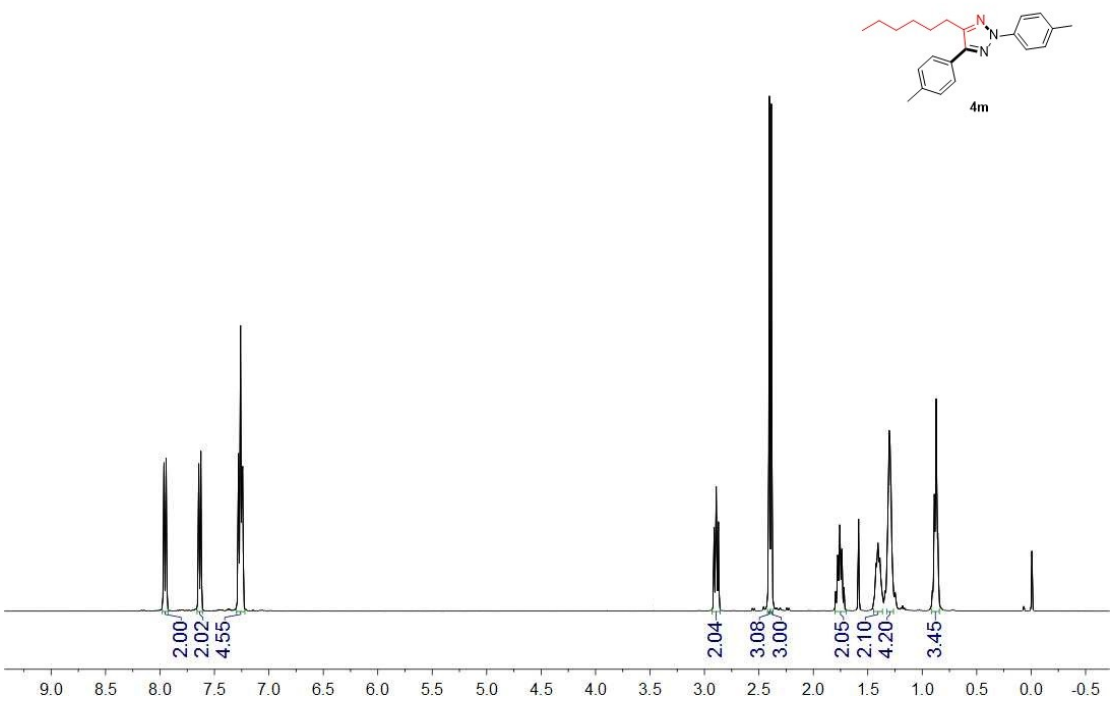
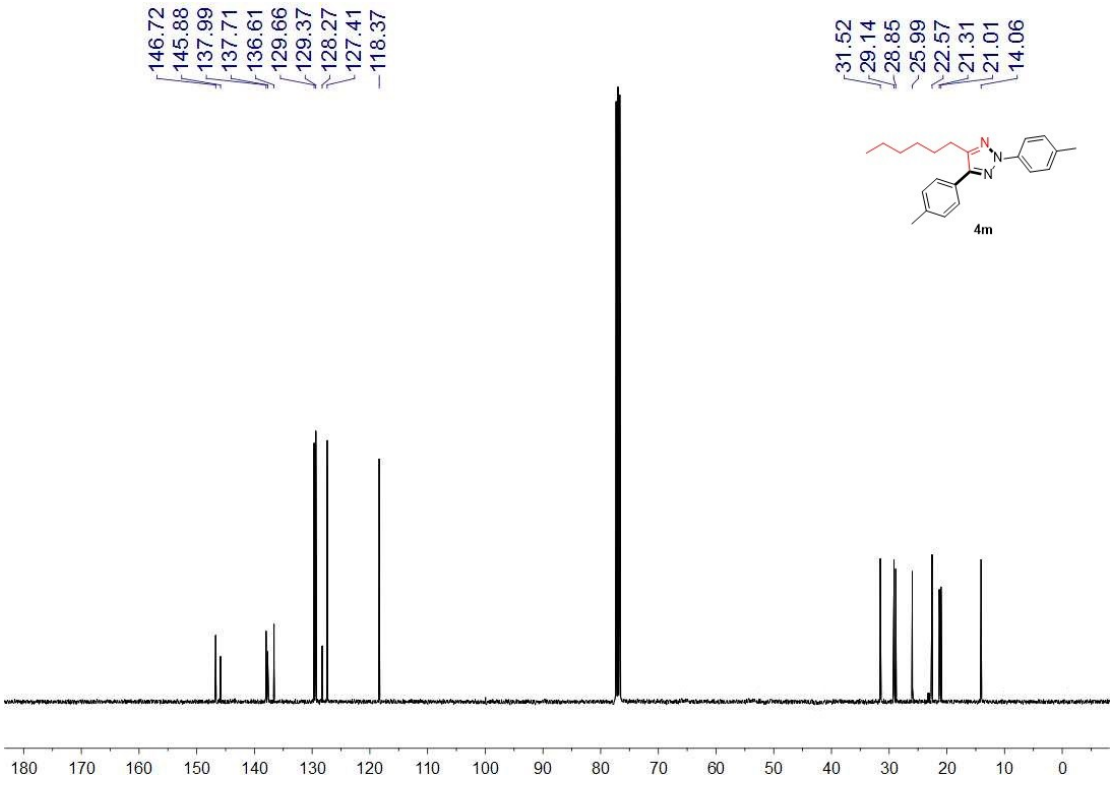
141.41
138.12
137.74
136.76
120.30
118.45
129.70
129.40
128.44
128.09
127.44
126.11
34.89
28.20
21.29
21.01
4l
130.0
128.5
127.0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


4m
2.00
2.02
4.55
2.04
3.08
3.00
2.05
2.10
4.20
3.45
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 -0.5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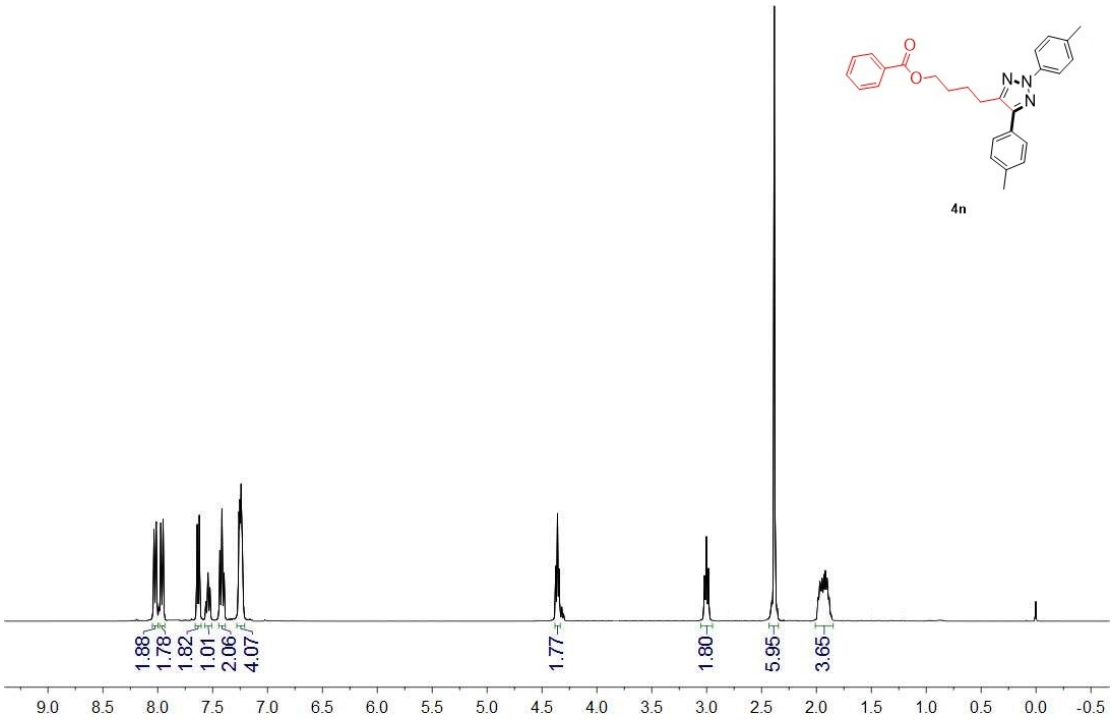
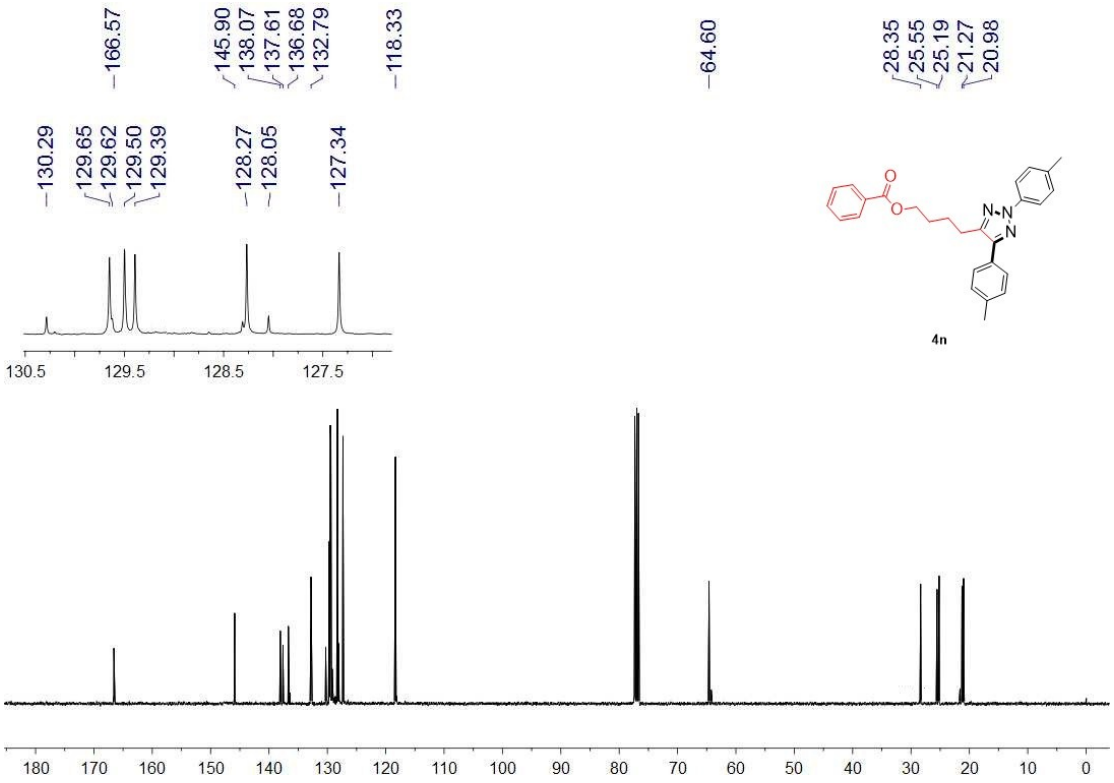
145.88
137.99
137.71
136.61
129.66
129.37
128.27
127.41
118.37
31.52
29.14
28.85
25.99
22.57
21.31
21.01
14.06
4m
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


4n
1.88
1.78
1.82
1.01
2.06
4.07
1.77
1.80
5.95
3.65
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 -0.5


166.57
145.90
138.07
137.61
136.68
132.79
118.33
64.60
28.35
25.55
25.19
21.27
20.98
130.29
129.65
129.62
129.50
129.39
128.27
128.05
127.34
130.5
129.5
128.5
127.5
4n
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90
80
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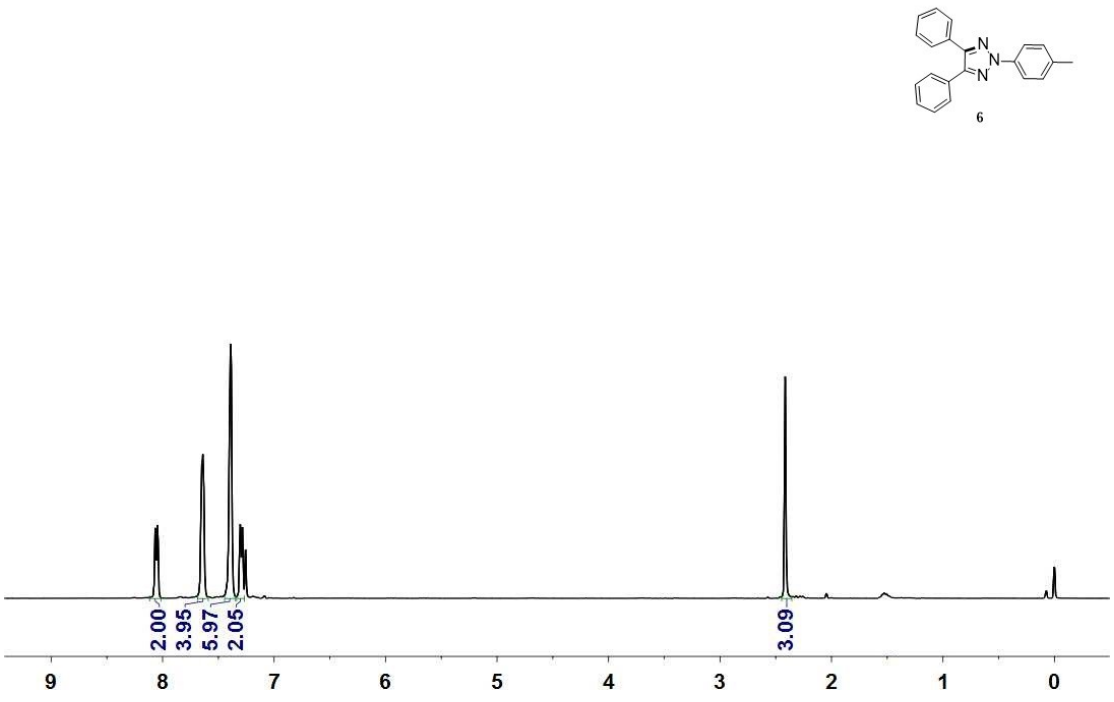
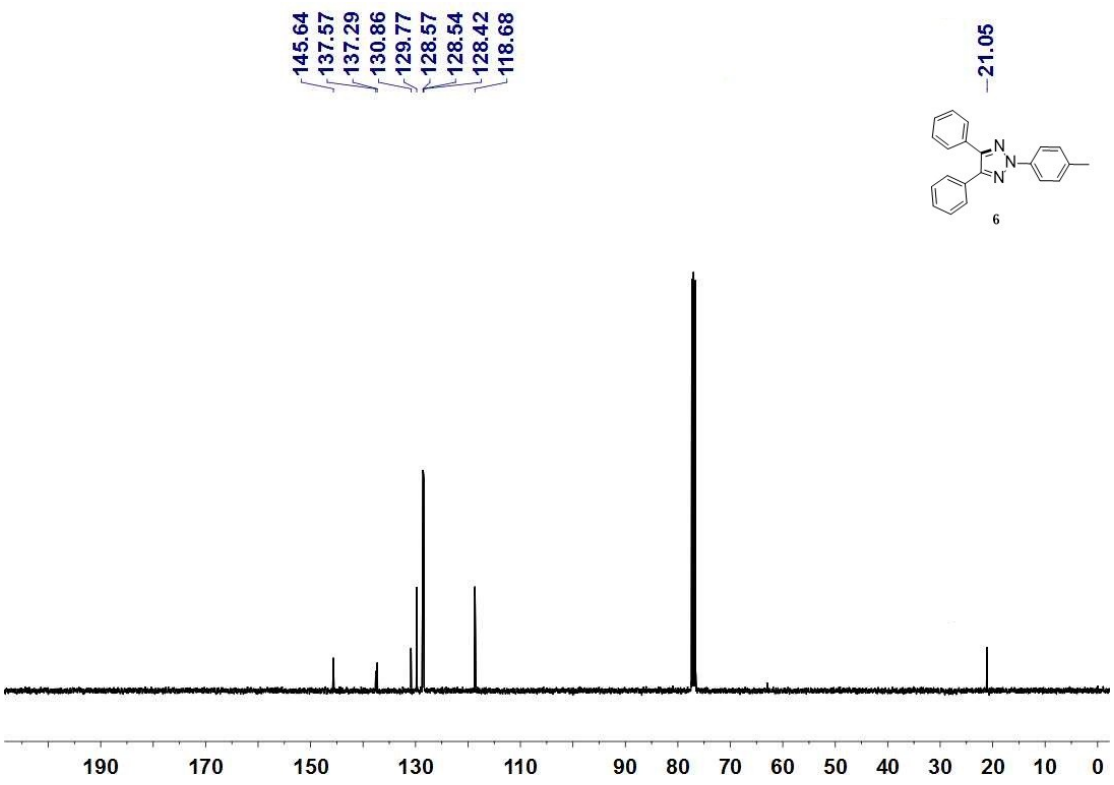
60
50
40
30
20
10
0


6
2.00
3.95
5.97
2.05
3.09
9
8
7
6
5
4
3
2
1
0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137.57
137.29
130.86
129.77
128.57
128.54
128.42
118.68
21.05
N
N
N
6
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0