Supporting Information

Chemoselective Synthesis of Substituted Pyrazoles through a AgOTf-Catalyzed Cascade Propargylic Substitution/Cyclization/Aromatization

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I. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification. Propargyl alcohols were prepared according to literature procedures. All reaction mixtures were stirred with a magnetic bar in flame-dried glassware.

Chromatography

Thin layer chromatography (TLC) was performed on Huanghai pre-coated glass-backed TLC plates and visualized by UV lamp (254 nm). Column chromatography on silica gel (300-400 mesh) was carried out using Technical Grade 60-90 ^{o}C v/v petroleum ether (distillated prior to use) and Analytical Grade EtOAc (without further purification). Concentration under reduced pressure was performed by rotary evaporation. Purified compounds were further addressed under high vacuum (3-5 mmHg). Yields referred to chromatographically purified compounds.

Nuclear Magnetic Resonance Spectra

^{1}H and ^{13}C spectra were recorded on a Bruker AV-400 spectrometer. Chemical shifts were reported in ppm. ^{1}H-NMR spectra were referenced to TMS in $CDCl_3$ (0 ppm) or d^6-DMSO (2.50 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) or d^6-DMSO (39.5 ppm). All ^{13}C-NMR spectra were measured with complete proton decoupling. Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and *J*, coupling constant in Hz.

Melting points

Melting points were measured on a Bűchi Melting Point B-540 Apparatus using open glass capillaries and are uncorrected.

IR Spectra

IR spectra were recorded on a Nicolet AVATER FTIR360 spectrometer as thin film. Absorptions were given in wavenumbers (cm^{-1}).

Mass Spectroscopy

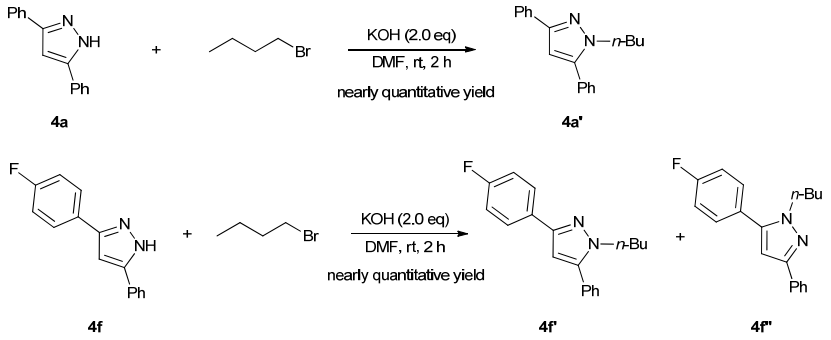
MS measurements were performed on Bruker Reflex III mass spectrometer.

High resolution mass spectroscopy

Data were obtained via Ultra-high Resolution Hybrid Qh-Fourier Transform Mass Spectrometer (En Apex ultra 7.0 FT-MS) operated by Department of Chemistry, Xiamen University.

II. Spectroscopic analysis

Because of the dynamic tautomeric forms of the NH-pyrazoles, their ^{13}C NMR spectra are unusual as normal organic compounds show. They often exhibit concentration and solvent-dependent NMR spectra (see the reference "M. T. Chenon, C. Coupry, D. M. Grant and R. J. Pugmire, *J. Org. Chem.*, 1977, **42**, 659." for more detailes). The biggest effect can be seen in the ^{13}C NMR spectra is that the C-3, C-5 and α-carbons appears as very broad signals that unresolved from the baseline. In other words, these carbons are missing from the spectra. To circumvent this issue, derivatization such as alkylation has been adopted to provide spectra where all carbons can be found.



The derivatization of **4a** and **4f**

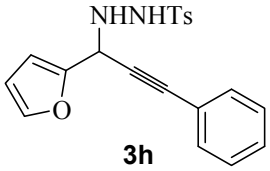
For example, compound **4a** and **4f** was treated with KOH and *n*-BuBr (1-bromobutane) in DMF at room temperature to readily generate the corresponding 1-butyl-3,5-diphenyl-1*H*-pyrazole (**4a'**), 1-butyl-3-(4-fluorophenyl)-5-phenyl-1*H*-pyrazole (**4f'**) and 1-butyl-5-(4-fluorophenyl)-3-phenyl-1*H*-pyrazole (**4f''**) in nearly quantitative yield (**4f'** and **4f''** were produced as a mixture which could not be seperated by column chromatography, and the isomers ratio is 3:5). These compounds are well dissolved in $CDCl_3$ (**4a** and **4f** are insoluble in $CDCl_3$), and analyzed by ^{13}C NMR to give ^{13}C spectra that provide sharp signals with all of the carbons being found (see the supporting information for more details). The two examples are provided as additional supports for characterization of the pyrazole products *via* ^{13}C NMR.

III. AgOTf-Catalyzed synthesis of pyrazoles from propargylic alcohols and *para*-tolylsulfonohydrazide

General procedure for the synthesis of pyrazoles: To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2

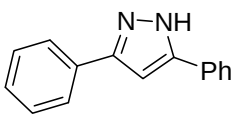
mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for an appropriate time, and monitored periodically by thin-layer chromatography. Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford the pyrazoles.

IV. ^{1}H, ^{13}C-NMR, IR, MS and HMRS Data of Substituted Pyrazoles



3h

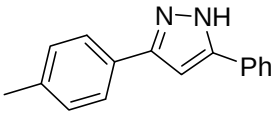
N'-(1-(Furan-2-yl)-3-phenylprop-2-ynyl)-4-methylbenzenesulfonohydrazide (3h): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1h** (1.0 mmol, 1.0 equiv), *p*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 2 hours, and monitored periodically by thin-layer chromatography (R_f = 0.22, v/v petroleum ether /ethyl acetate = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether /AcOEt = 15:1) to afford a white solid in 74% yield (m.p. 197-199 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 4.03 (d, 1H, J = 8.8 Hz), 4.88 (d, 1H, J = 8.8 Hz), 6.17 (d, 1H, J = 2.0 Hz), 6.32 (dd, 1H, J = 3.2, 2.0 Hz), 6.39 (d, 1H, J = 3.2 Hz), 7.28-7.36 (m, 4H), 7.42-7.44 (m, 3H), 7.85 (d, 2H, J = 8.4 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 21.6, 50.8, 83.4, 86.1, 109.3, 110.4, 121.2, 128.2, 128.3, 128.8, 129.5, 131.9, 135.3, 143.2, 144.0, 149.4; **IR** (film): 3256, 2232 (weak), 1597, 1493 cm^{-1}; **HRMS**(ESI): calc. for $C_{20}H_{18}N_2O_3S$ $[M+Na]^+$: *m/z* =389.0936; found: 389.0935.



4a

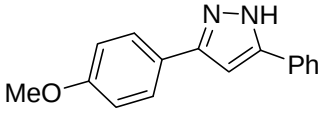
3,5-Diphenyl-1*H*-pyrazole (4a):[1-5] To a flame-dried 10-mL flask equipped with a magnetic bar,

propargylic alcohol **1a** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for one hour, and monitored periodically by thin-layer chromatography (R_f = 0.21, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether /AcOEt = 15:1) to afford a white solid in 90% yield (m.p. 190-192 ^{o}C). **^{1}H-NMR** (400 MHz, DMSO): δ 7.17 (s, 1H), 7.31-7.35 (m, 2H), 7.43-7.46 (m, 4H), 7.84 (m, 4H), 13.39 (brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 99.6, 125.2, 128.8; **IR** (film): 3417, 3101, 1610 1494 cm^{-1}; **ESI-MS**: calc. for $C_{15}H_{12}N_2$ $[M+H]^+$: m/z = 221.1; found: 221.3.



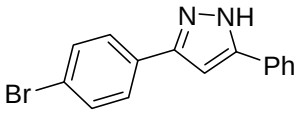
4b

3-(4-Methylphenyl)-5-phenyl-1*H*-Pyrazole (4b):[3,4,6] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1b** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for one hour, and monitored periodically by thin-layer chromatography (R_f = 0.17, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 91% yield (m.p. 162-164 ^{o}C). **^{1}H-NMR** (400 MHz, DMSO): δ 2.32 (s, 3H), 7.12 (s, 1H), 7.24-7.45 (m, 5H), 7.72 (d, 2H, J = 6.4 Hz), 7.84 (d, 2H, J = 6.0 Hz)，13.3 (brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 20.8, 99.3, 125.1, 125.2, 128.3, 128.8, 129.4; **IR** (film): 3421, 3021, 1608, 1508 cm^{-1}; **ESI-MS**: calc. for $C_{16}H_{14}N_2$ $[M+H]^+$: *m/z* = 235.1; found: 235.3.



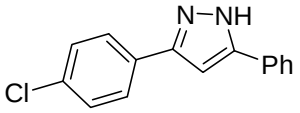
4c

3-(4-Methoxyphenyl)-5-phenyl-1*H*-pyrazole (4c):[1] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1c** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for one hour, and monitored periodically by thin-layer chromatography (R_f = 0.12, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 95% yield (m.p. 145-146 °C). **^{1}H-NMR** (400 MHz, DMSO): δ 3.78 (s, 3H), 7.02 (s, 2H), 7.06 (s, 1H), 7.32-7.43 (m, 3H), 7.71-7.82 (m, 4H), 13.23(brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 55.6, 99.2, 114.8, 125.5, 126.9, 129.2; **IR** (film): 3350, 3102, 1613, 1509, 1252 cm^{-1}; **ESI-MS**: calc. for $C_{16}H_{12}N_2O$ $[M+H]^+$: *m/z* = 251.1; found: 251.3.



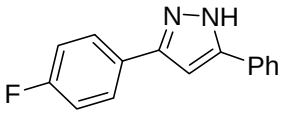
4d

3-(4-Bromophenyl)-5-phenyl-1*H*-Pyrazole (4d):[4] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1d** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 1.2 hours, and monitored periodically by thin-layer chromatography (R_f = 0.22, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 81% yield (m.p. 217-219 °C). **^{1}H-NMR** (400 MHz, DMSO): δ 7.19 (s, 1H), 7.34-7.45 (m, 3H), 7.56-7.63 (m, 2H), 7.73-7.81 (m, 4H), 13.46(brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 99.9, 125.2, 127.2, 128.4, 129.0, 129.4, 131.5, 131.7; **IR** (film): 3345, 3142, 1623, 1512 cm^{-1}; **ESI-MS**: calc. for $C_{15}H_{11}N_2Br$ $[M+H]^+$: *m/z* = 299.0, 301.0; found: 299.1, 301.2.



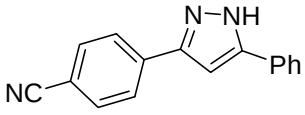
4e

3-(4-Chlorophenyl)-5-phenyl- 1*H*-Pyrazole (4e):[3,4] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1e** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 1.2 hours, and monitored periodically by thin-layer chromatography (R_f = 0.34, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 81% yield (m.p. 216-218 °C). **^{1}H-NMR** (400 MHz, DMSO): δ 7.20 (s, 1H), 7.32-7.49 (m, 5H), 7.82-7.86 (m, 4H), 13.44(brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 99.9, 125.1, 126.8, 128.9; **IR** (film): 3340, 3143, 1618, 1490 cm^{-1}; **ESI-MS**: calc. for $C_{15}H_{11}N_2Cl$ $[M+H]^+$: *m/z* = 255.1; found: 255.2.



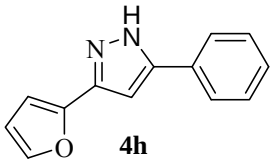
4f

3-(4-Fluorophenyl)-5-phenyl- 1*H*-Pyrazole (4f):[3,4] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1f** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for one hour, and monitored periodically by thin-layer chromatography (R_f = 0.22, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 80% yield (m.p. 167-169 °C). **^{1}H-NMR** (400 MHz, DMSO): δ 7.15 (s, 1H), 7.27-7.37 (m, 4H), 7.43-7.46 (m, 2H), 7.83-7.88 (m, 3H), 13.39(brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 100.0, 116.2, 125.6, 127.6, 128.0, 129.2, 131.5; **IR** (film): 3321, 3118, 1606, 1520 cm^{-1}; **ESI-MS**: calc. for $C_{15}H_{11}N_2F$ $[M+H]^+$: *m/z* = 239.1; found: 239.2.



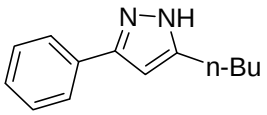
4g

4-(5-Phenyl-1*H*-pyrazol-3-yl)benzonitrile (4g):[5] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1g** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 10 hours, and monitored periodically by thin-layer chromatography (R_f = 0.15, v/v petroleum ether/AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a yellow oil in 62% yield. **^{1}H-NMR** (400 MHz, DMSO): δ 7.34 (s, 1H), 7.41-7.44 (m, 3H), 7.66-7.87 (m, 5H), 8.04 (s, 1H), 13.65 (brs, 1H); **^{13}C-NMR** (100 MHz, DMSO): δ 100.8, 110.5, 118.8, 125.3, 125.7, 127.0, 128.3, 128.5, 128.9, 129.9,132.6,146.9, 157.8; **IR** (film): 3335, 3120, 2223, 1608, 1497 cm^{-1}; **ESI-MS**: calc. for $C_{16}H_{11}N_3$ $[M+H]^+$: *m/z* (%) = 246.1; found: 246.3.



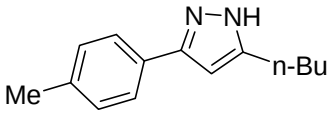
4h

3-(Furan-2-yl)-5-phenyl-1*H*-pyrazole (4h):[2] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1h** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 6 hours, and monitored periodically by thin-layer chromatography (R_f = 0.22, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a yellow solid in 45% yield (m.p. 172-173 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.49 (dd, 1H, *J* = 3.2, 1.6 Hz), 6.67 (d, 1H, *J* = 3.2 Hz), 6.78 (d, 1H, *J* = 1.6 Hz), 7.31-7.46 (m, 4H), 7.72 (d, 2H, *J* = 7.2 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$)：δ 99.4, 106.6, 111.4, 125.7, 128.4, 128.9, 129.5, 142.1, 146.7, 148.2; **IR** (film): 3371, 3054, 1609, 1596 cm^{-1}; **ESI-MS**: calc. for $C_{13}H_{10}N_2O$ $[M+H]^+$: *m/z* (%) = 211.1; found: 211.2.



4i

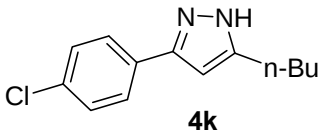
5-Butyl-3-phenyl-1*H*-pyrazole (4i):[7] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1i** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 0.8 hour, and monitored periodically by thin-layer chromatography (R_f = 0.30, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a yellow oil in 75% yield. **^{1}H-NMR** (400 MHz, DMSO): δ 0.91 (t, 3H, J = 7.6 Hz), 1.29-1.35 (m, 2H), 1.57-1.61 (m, 2H), 2.59 (t, 2H, J = 7.6 Hz), 6.44 (s, 1H), 7.25 (t, 1H, J = 7.6 Hz), 7.37 (dd, 2H, J = 7.6, 7.6 Hz), 7.75 (t, 2H, J = 7.6 Hz) ; **^{13}C-NMR** (100 MHz, DMSO): δ 13.7, 21.8, 31.1, 100.3, 125.0, 127.3, 128.7; **IR** (film): 3421, 3101, 1620, 1514 cm^{-1}; **HRMS**(ESI): calc. for $C_{13}H_{16}N_2$ $[M+H]^+$: *m/z* (%) = 201.1392; found: 201.1384.



4j

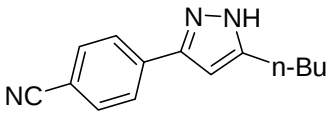
5-Butyl-3-p-tolyl-1*H*-pyrazole (4j): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1j** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for one hour, and monitored periodically by thin-layer chromatography (R_f = 0.16, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a yellow oil in 80% yield. **^{1}H-NMR** (400 MHz, $CDCl_3$) δ 0.90 (t, 3H, J = 7.6 Hz), 1.30-1.37 (m, 2H), 1.59-1.63 (m, 2H), 2.36 (s, 3H), 2.59 (t, 2H, J = 7.6 Hz), 6.32 (s, 1H), 7.16 (d, 2H, J = 8.0 Hz), 7.62 (d, 2H, J = 8.0 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 13.7, 21.2, 22.3, 26.1, 31.3, 100.6, 125.6, 129.2, 137.4; **IR** (film): 3420,

3092, 1598, 1517 cm^{-1}; **HRMS**(ESI): calc. for $C_{14}H_{18}N_2$ $[M+H]^+$: *m/z* (%) = 215.1548; found: 215.1541.



4k

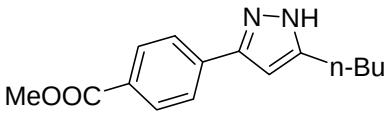
5-Butyl-3-(4-chlorophenyl)-1*H*-pyrazole (4k):[6] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1k** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 1.5 hours, and monitored periodically by thin-layer chromatography (R_f = 0.15, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a colorless crystal in 65% yield (m.p. 65-66 ^oC); **^{1}H-NMR** (400 MHz, DMSO): δ 0.90 (t, 3H, J = 7.2 Hz), 1.29-1.34 (m, 2H), 1.56-1.62 (m, 2H), 2.59 (t, 2H, J = 7.2 Hz), 6.46 (s, 1H), 7.41 (d, 2H, J = 8.4 Hz), 7.37 (d, 2H, J = 8.4 Hz), 12.66 (brs, 1H) ; **^{13}C-NMR** (100 MHz, DMSO): δ 13.7, 21.8, 31.1, 100.3, 126.7, 128.7; **IR** (film): 3417, 3116, 1643, 1510 cm^{-1}; **ESI-MS**: calc. for $C_{13}H_{15}N_2Cl$ $[M+H]^+$: *m/z* (%) = 235.1; found: 235.1.



4l

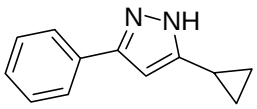
4-(5-Butyl-1*H*-pyrazol-3-yl)benzonitrile (4l):[8] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1l** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 7 hours, and monitored periodically by thin-layer chromatography (R_f = 0.27, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a yellow oil in 23% yield. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J = 7.6 Hz), 1.29-1,35 (m, 2H), 1.58-1.62 (m,

2H), 2.60 (t, 2H, J = 7.6 Hz), 6.40 (s, 1H), 7.62 (d, 2H, J = 8.4 Hz), 7.83 (d, 2H, J = 8.0 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 13.6, 22.2, 25.5, 31.1, 101.6, 110.8, 118.9, 125.9, 132.4, 137.6, 146.9, 149.4; **IR** (film): 3277, 2923, 2228, 1610, 1507 cm^{-1}; **ESI-MS**: calc. for $C_{14}H_{15}N_3$ $[M+H]^+$: *m/z* (%) = 226.1; found: 226.2.



4m

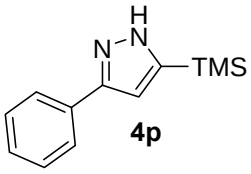
Methyl 4-(5-butyl-1*H*-pyrazol-3-yl)benzoate (4m): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1m** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 7.5 hours, and monitored periodically by thin-layer chromatography (R_f = 0.20, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 31% yield (m.p. 87-89 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.87 (t, 3H, J = 7.6 Hz), 1.28-1.33 (m, 2H), 1.55-1.63 (m, 2H), 2.59 (t, 2H, J = 7.6 Hz), 3.91 (s, 3H), 6.39 (s, 1H), 7.78 (d, 2H, J = 8.4 Hz), 8.00 (d, 2H, J = 8.4 Hz); **^{13}C-NMR** (100MHz, $CDCl_3$): δ 13.7, 22.2, 25.8, 31.2, 52.0, 101.5, 125.4, 129.0, 130.0, 137.3, 147.4, 149.5, 166.9; **IR** (film): 3322, 3002, 1772, 1604, 1095 cm^{-1}; **HRMS**(ESI): calc. for $C_{15}H_{18}N_2O_2$ $[M+H]^+$: *m/z* (%) = 259.1447; found: 259.1442.



4n

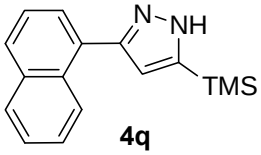
5-Cyclopropyl-3-phenyl-1*H*-pyrazole (4n):[9] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1n** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 4 hours, and monitored periodically by thin-layer chromatography (R_f = 0.24, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction,

the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 52% yield (m.p. 96-98 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.72-0.73 (m, 2H), 0.83-0.88 (m, 2H), 1.80-1.87 (m, 1H), 6.16 (s, 1H), 7.23-7.26 (m, 1H), 7.29-7.32 (m, 2H), 7.65-7.67 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 7.5, 7.8, 98.6, 125.7, 127.7, 128.6, 132.2, 149.1, 150.8; **IR** (film): 3404, 3130, 1600, 1503 cm^{-1}; **ESI-MS**: calc. for $C_{12}H_{12}N_2$ $[M+H]^+$: *m/z* (%) = 185.1; found: 185.2.



4p

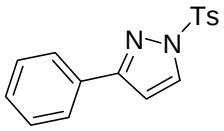
3-Phenyl-5-(trimethylsilyl)-1*H*-pyrazole (4p): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1p** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and nitromethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 3 hours, and monitored periodically by thin-layer chromatography (R_f = 0.32, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford **4p** (a yellow oil) and **5a** (a white solid, m.p. 139-140 ^{o}C) in 40% and 15% yields respectively. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.34 (s, 9H), 6.74 (s, 1H), 7.26-7.33 (m, 1H), 7.38-7.42 (m, 2H), 7.83-7.85 (m, 2H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ -1.2, 109.8, 125.9, 127.6, 128.6, 133.3, 152.0; **IR** (film): 3164, 3007, 1607, 1513 cm^{-1}; **HRMS**(ESI): calc. for $C_{12}H_{16}N_2Si$ $[M+H]^+$: *m/z* (%) = 217.1161; found: 217.1156.



4q

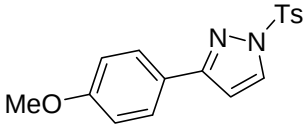
3-(Naphthalen-1-yl)-5-(trimethylsilyl)-1*H*-pyrazole (4q): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1q** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and nitromethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol

%, 0.1 mmol) was added. Then, the mixture was heated to reflux for 3 hours, and monitored periodically by thin-layer chromatography (R_f = 0.33, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford **4q** (a yellow oil) and **5d** (a white solid, m.p. 158-159 ^oC) in 35% and 12% yields respectively. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.33 (s, 9H), 6.72 (s, 1H), 7.48-7.52 (m, 3H), 7.68-7.70 (m, 1H), 7.85-7.90 (m, 2H), 8.46-8.49 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ -1.2, 113.5, 125.3, 125.7, 126.2, 127.1, 128.2, 129.3, 131.5, 131.6, 133.9; **IR** (film): 3485, 3202, 1599, 1490 cm^{-1}; **HRMS**(ESI): calc. for $C_{16}H_{18}N_2Si$ $[M+H]^+$: *m/z* (%) = 267.1318; found: 267.1316.



5a

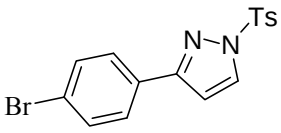
3-Phenyl-1-tosyl-1*H*-pyrazole (5a):[10] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1s** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 2.5 hours, and monitored periodically by thin-layer chromatography (R_f = 0.20, v/v petroleum ether /AcOEt = 5:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 60% yield (m.p. 139-140 ^oC). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 6.73-6.83 (m, 2H), 7.28-7.39 (m, 6H), 7.58 (d, 1H, J = 8.4 Hz), 7.86 (d, 2H, J = 8.4 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 21.6, 124.3, 127.0, 127.8, 128.9, 129.1, 129.7, 135.3, 135.5, 139.9, 144.3, 149.8; **IR** (film): 3180, 1607, 1353 cm^{-1}; **ESI-MS**: calc. for $C_{16}H_{14}N_2O_2S$ $[M+Na+H]^+$: *m/z* (%) = 322.1; found: 322.5.



5b

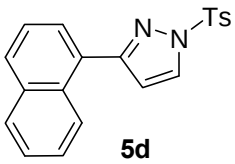
3-(4-Methoxyphenyl)-1-tosyl-1*H*-pyrazole (5b): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1t** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2

mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 2 hours, and monitored periodically by thin-layer chromatography (R_f = 0.22, v/v petroleum ether /AcOEt = 5:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 67% yield (m.p. 195-196 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 3.85 (s, 3H), 6.87 (d, 1H, J = 8.8 Hz), 6.95 (d, 1H, J = 8.8 Hz), 7.28-7.36 (m, 4H), 7.65(d, 1H, J = 8.0 Hz), 7.82(t, 3H, J = 8.0 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 21.5, 55.3, 114.2, 114.3, 122.2, 126.4, 127.0, 127.8, 128.5, 129.7, 139.2, 139.6, 143.5, 150.4; **IR** (film): 3168, 2919, 1611, 1510, 1307 cm^{-1}; **HRMS**(ESI): calc. for $C_{17}H_{16}N_2O_3S$ $[M+H]^+$: *m/z* (%) = 329.0960; found: 329.0961.



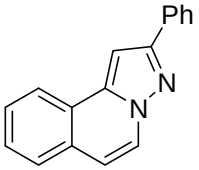
5c

3-(4-Bromophenyl)-1-tosyl-1*H*-pyrazole (5c): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1u** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 11 hours, and monitored periodically by thin-layer chromatography (R_f = 0.21, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 42% yield (m.p. 166-168 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 6.63-6.79 (m, 1H), 7.21 (d, 2H, J = 8.4 Hz), 7.30 (d, 2H, J =8.0 Hz), 7.42 (t, 1H, J = 8.8 Hz), 7.56 (d, 1H, J = 8.8 Hz), 7.83 (d, 2H, J = 8.4 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 21.6, 123.0, 125.0, 127.8, 128.4, 129.7, 131.9, 134.5, 135.2,138.4, 144.3, 149.2; **IR** (film): 3195, 1621, 1510, 1357 cm^{-1}; **HRMS**(ESI): calc. for $C_{16}H_{13}BrN_2O_2S$ $[M+H]^+$: *m/z* (%) = 376.9959; found: 376.9960.



5d

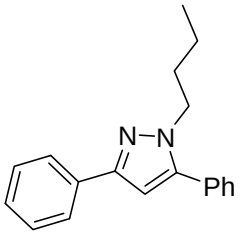
3-(Naphthalen-1-yl)-1-tosyl-1*H*-pyrazole (5d): To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1v** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 4 hours, and monitored periodically by thin-layer chromatography (R_f = 0.20, v/v petroleum ether /AcOEt = 5:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 45% yield (m.p. 158-159 ^{o}C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 2.39 (s, 3H), 6.87-6.93 (m, 1H), 7.31 (d, 2H, J = 8.4 Hz,), 7.43 (t, 1H, J = 8.0 Hz), 7.47-7.52 (m, 2H), 7.64 (d, 1H, J = 7.2 Hz), 7.71(d, 1H, J = 8.4 Hz), 7.79-7.85 (m, 2H), 7.89 (d, 2H, J = 8.4 Hz), 8.03 (d, 1H, J = 8.8 Hz) ;**^{13}C-NMR** (100 MHz, $CDCl_3$): δ 21.5, 123.0, 124.1, 125.5, 125.9, 126.5, 126.8, 127.9, 128.2, 128.7, 129.4, 129.7, 130.9, 132.7, 133.6, 135.3, 136.5, 144.3, 149.8; **IR** (film): 3188, 1613, 1507, 1335 cm^{-1}; **HRMS**(ESI): calc. for $C_{20}H_{16}N_2O_2S$ $[M+H]^+$: *m/z* (%) = 349.1011; found: 349.1014.



4r

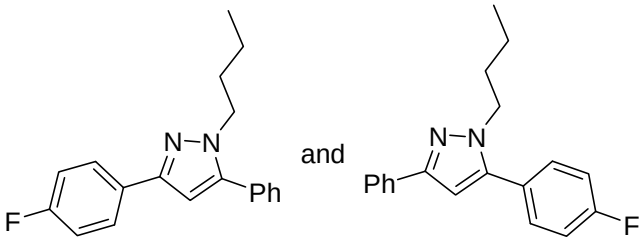
2-Phenylpyrazolo[5,1-*a*]isoquinoline (4r):[11] To a flame-dried 10-mL flask equipped with a magnetic bar, propargylic alcohol **1r** (1.0 mmol, 1.0 equiv), *para*-tolylsulfonohydrazide **2** (1.2 mmol, 1.2 equiv.), and 1,2-dicholroethane (5 mL) were successively added. The mixture was stirred until **2** was completely dissolved. Subsequently, AgOTf (10 mol %, 0.1 mmol) was added. Then, the mixture was heated to reflux for 2 hours, and monitored periodically by thin-layer chromatography (R_f = 0.25, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether/AcOEt = 15:1) to afford a white solid in 65%

yield (m.p. 115-116 °C). **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.99 (d, 1H, J = 7.6 Hz), 7.29 (d, 1H, J = 0.8 Hz), 7.36-7.30 (m, 1H), 7.46-7.50 (m, 2H), 7.52-7.60 (m, 2H), 7.72 (dd, 1H, J = 7.6, 1.2 Hz), 8.00-8.02 (m, 2H), 8.13 (dt, 1H, J = 7.6, 0.8 Hz), 8.27 (dd, 1H, J = 8.0, 0.8 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 94.8, 112.2, 123.8, 124.6, 126.5, 127.4, 127.8, 128.0, 128.5, 128.9, 129.0, 133.3, 140.0, 153.2; **IR** (film): 3188, 1602, 1501 cm^{-1}; **ESI-MS**: calc. for $C_{17}H_{12}N_2$ $[M+H]^+$: *m/z* (%) = 245.1; found: 245.4.



4a´

1-butyl-3,5-diphenyl-1*H*-pyrazole (4a´): To a flame-dried flask (10 mL) equipped with a magnetic stirring bar, the pyraozle **4a** (1.0 mmol, 1.0 equiv), KOH (2.0 mmol, 2.0 equiv.), and DMF (5 mL) were successively added. The mixture was stirred at room temperature for one hour. Subsequently, *n*-BuBr (1-bromobutane) (1.2 mmol, 1.0 equiv) was added dropwise. The mixture was stirred at room temperature for another hour, and monitored periodically by the thin-layer chromatography (R_f = 0.70, v/v petroleum ether /AcOEt = 7:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether /AcOEt = 20:1) to afford **4a'** as a yellow oil in nearly quantitative yield. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.88 (t, 3H, J=7.6 Hz), 1.24-1.32 (m, 2H), 1.83-1.90 (m, 2H), 4.16-4.20 (m, 2H), 6.60 (s, 1H), 7.31-7.34 (m, 1H), 7.41-7.51 (m,7H), 7.88 (d, 2H, J=7.6 Hz); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 13.6, 19.8, 32.6, 49.4, 103.2, 125.5, 127.4, 128.4, 128.5, 128.6, 128.9, 131.0, 133.6, 144.8, 150.4; **IR** (film): 3178, 1610, 1514 cm^{-1}; **HRMS**(ESI): calc. for $C_{19}H_{20}N_2$ $[M+H]^+$: *m/z* (%) = 277.1705; found: 277.1704.



4f´ **4f´´**

1-butyl-3-(4-fluorophenyl)-5-phenyl-1*H*-pyrazole(4f´) and 1-butyl-5-(4-fluorophenyl)-3-Phen

yl-1*H*-pyrazole(4f´´): To a flame-dried flask (10 mL) equipped with a magnetic stirring bar, the pyraozle **4f** (1.0 mmol, 1.0 equiv), KOH (2.0 mmol, 2.0 equiv.), and DMF (5 mL) were successively added. The mixture was stirred at room temperature for one hour. Subsequently, *n*-BuBr (1-bromobutane) (1.2 mmol, 1.0 equiv) was added dropwise. The mixture was stirred at room temperature for another hour, and monitored periodically by the thin-layer chromatography (R_f = 0.70, v/v petroleum ether /AcOEt = 5:1). Upon completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (v/v petroleum ether /AcOEt = 20:1) to afford **4f'** and **4f''** (a mixture of isomers, and the isomers ratio is 3:5) as a yellow oil in nearly quantitative yield. **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 0.86 (t, 4.96H, J =7.2 Hz), 1.25-1.31 (m, 3.26H), 1.83-1.84 (m, 3.61H), 4.10-4.16 (m, 3.42H), 6.52 (s, 1H), 6.55 (s, 0.65H), 7.08-7.12 (m, 2.31H), 7.15-7.19 (m, 1.5H), 7.31-7.48 (m, 8.32H), 7.80-7.86 (m, 3.24H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 13.6, 19.8, 32.7, 49.4, 49.5, 103.1, 103.3, 115.5 ($^2J_{CF}$ = 22 Hz), 115.8 ($^2J_{CF}$ = 22 Hz), 125.6, 127.2 ($^3J_{CF}$ = 8Hz), 127.6, 128.5, 128.6, 128.7, 128.9, 129.7, 129.9, 130.8 ($^3J_{CF}$ = 8Hz), 131.0, 133.6, 143.8, 145.0, 149.6, 150.5, 162.5($^1J_{CF}$ = 244 Hz), 162.8($^1J_{CF}$ = 244 Hz); **IR** (film): 3180, 1608, 1509, 1329 cm^{-1}; **HRMS**(ESI): calc. for $C_{19}H_{19}FN_2$ $[M+H]^+$: *m/z* (%) = 295.1611; found: 295.1604.

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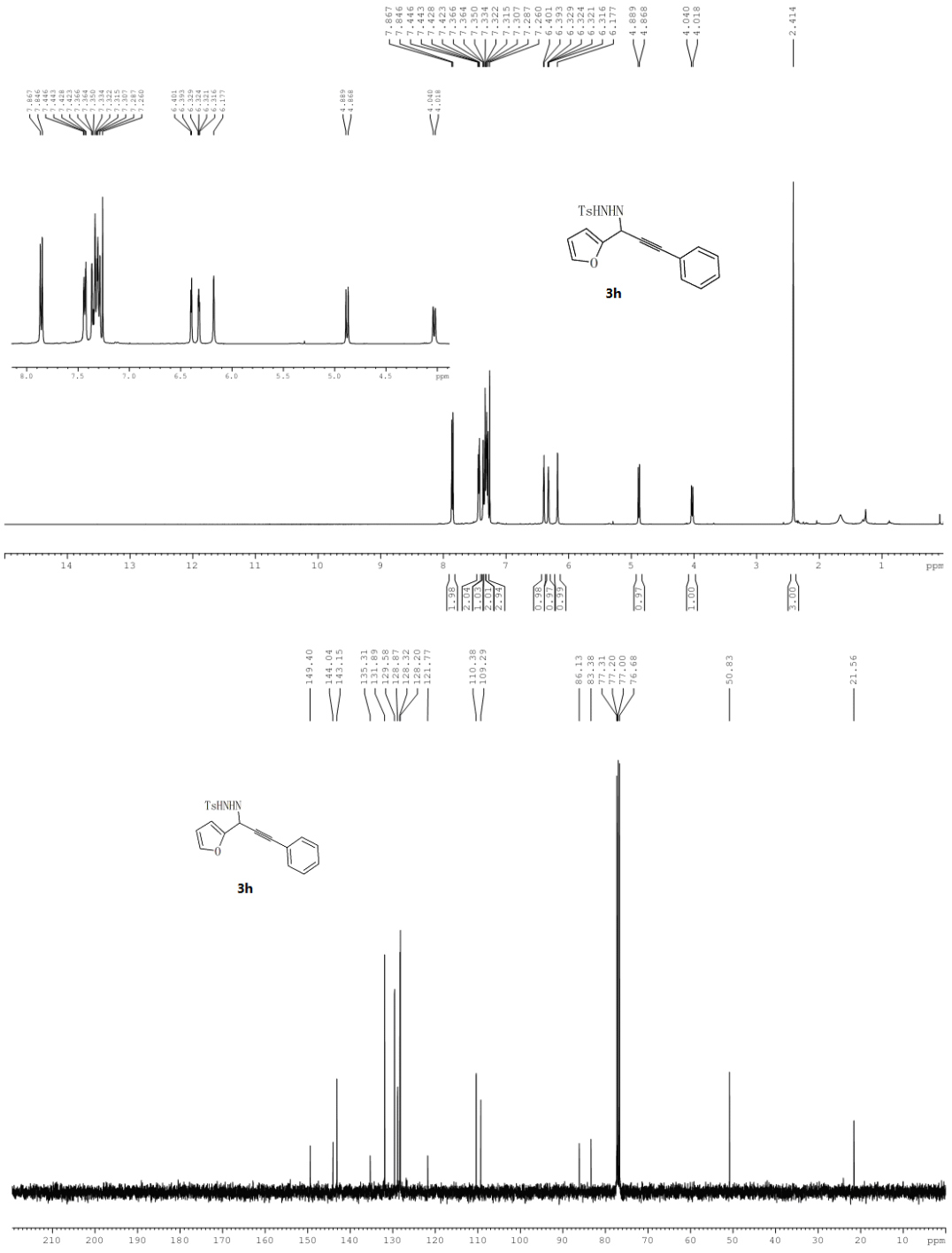
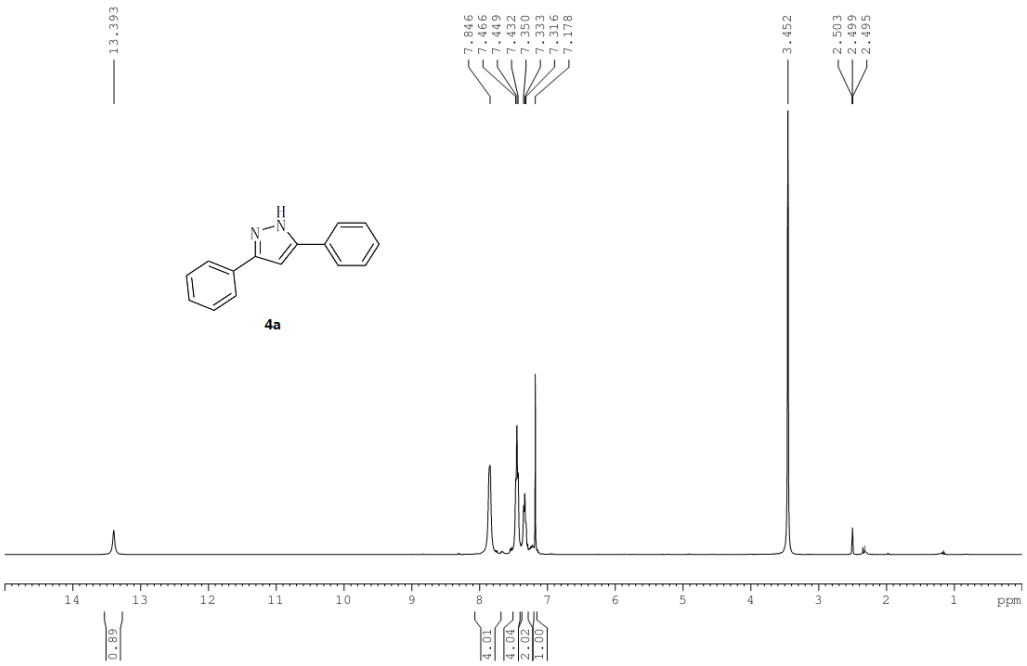
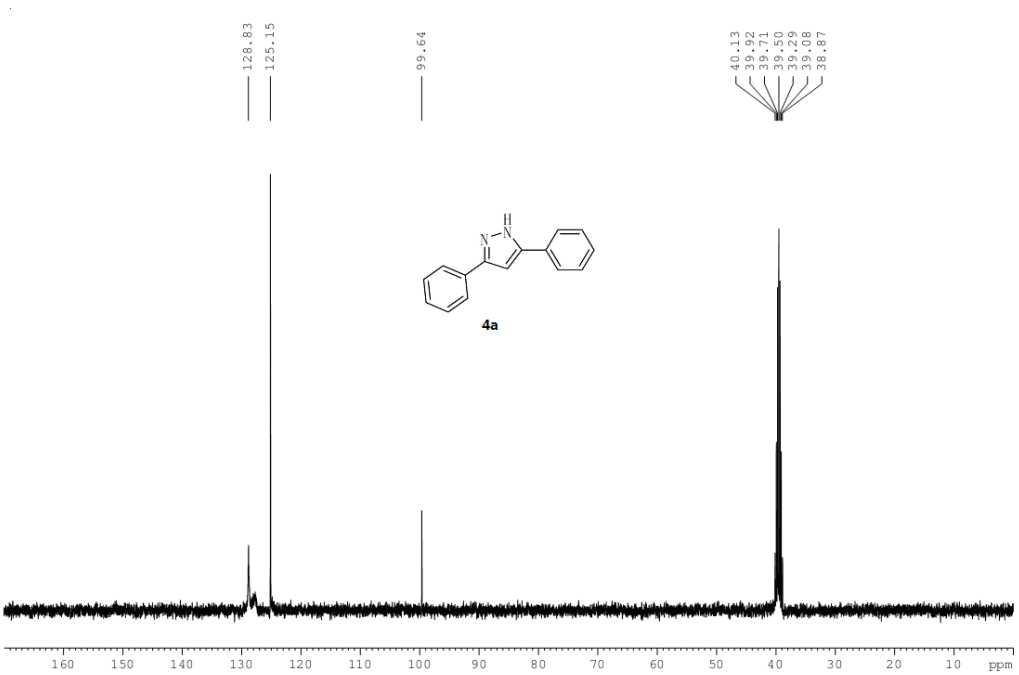
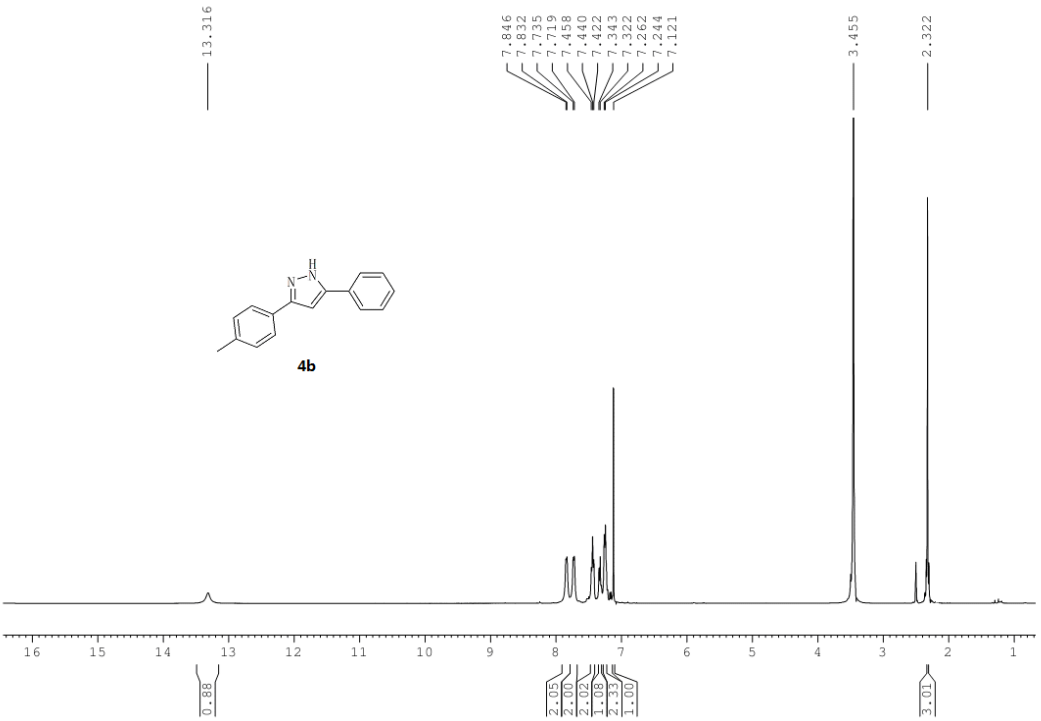
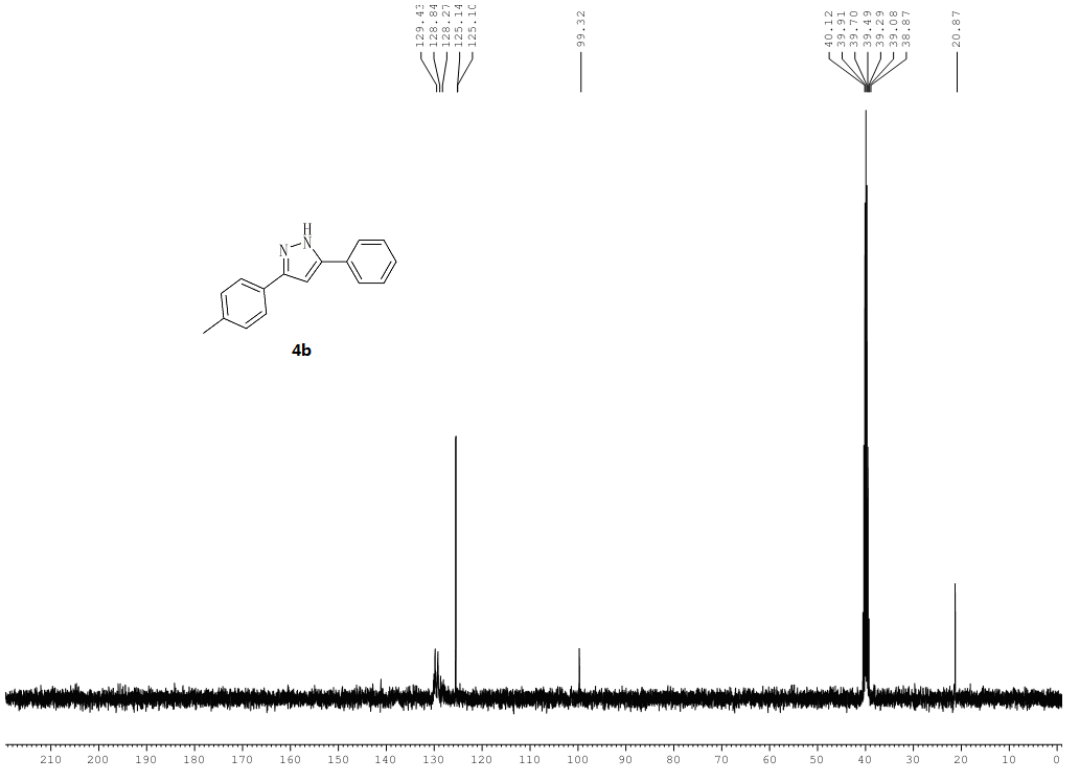
V. ^{1}H, ^{13}C-NMR Spectra

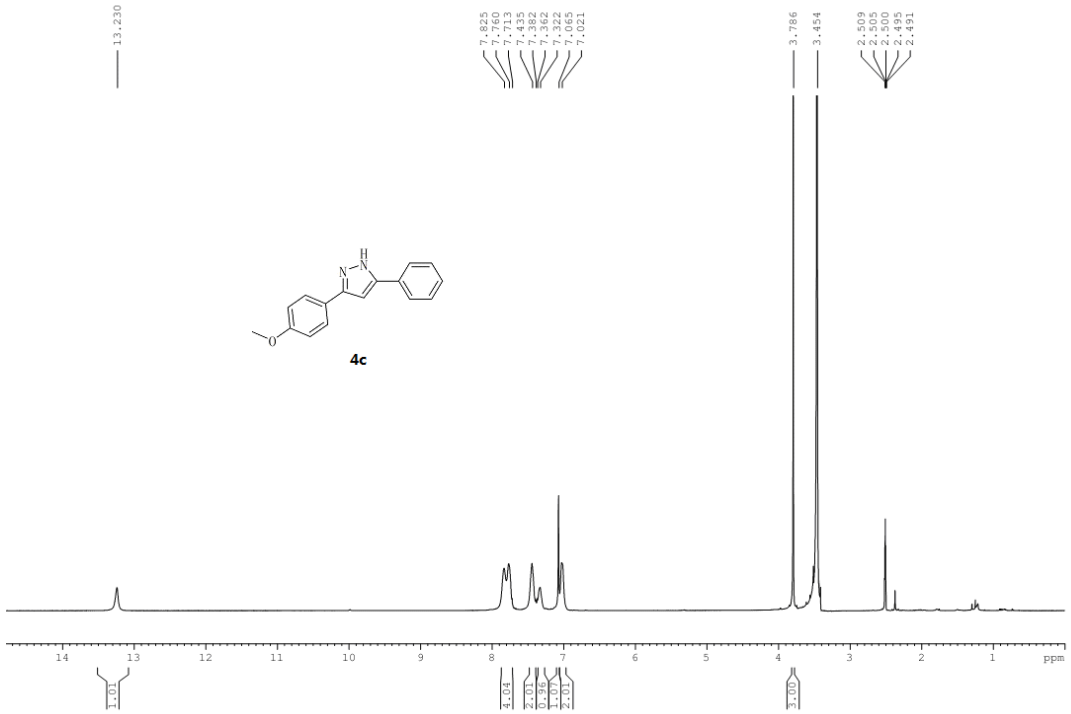


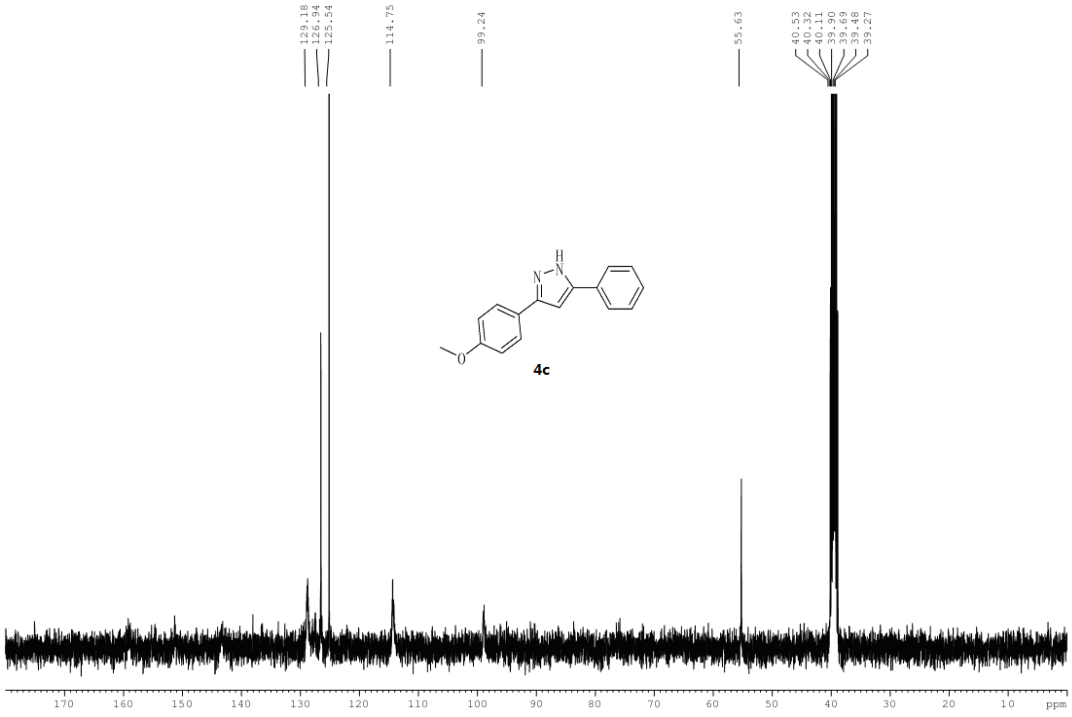


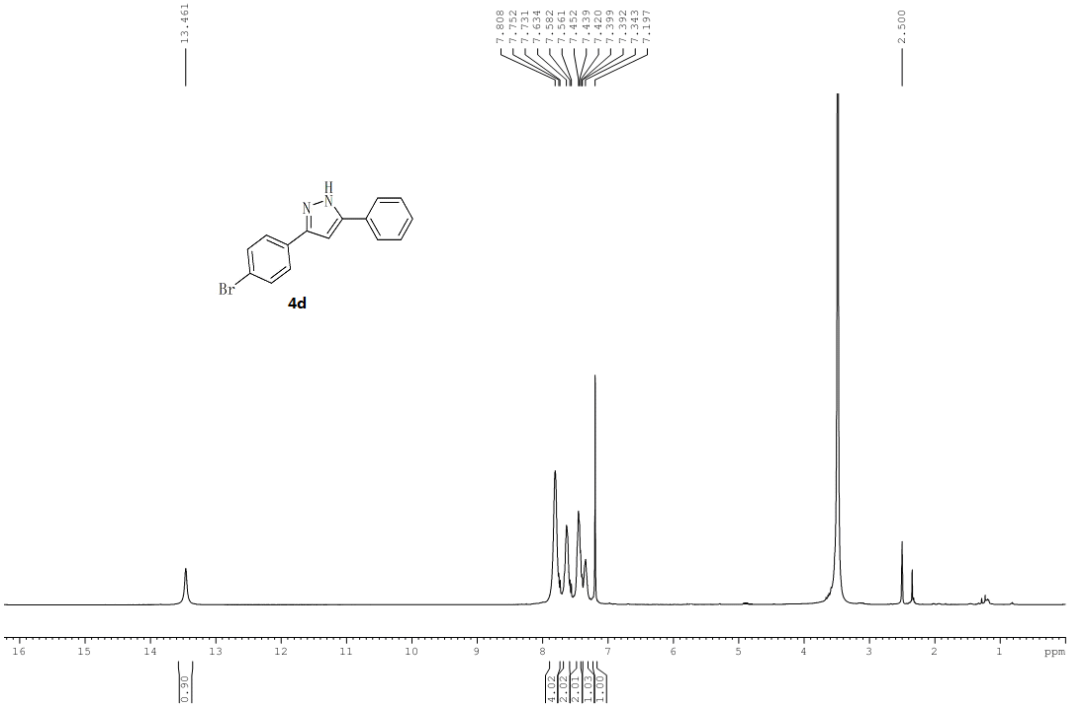


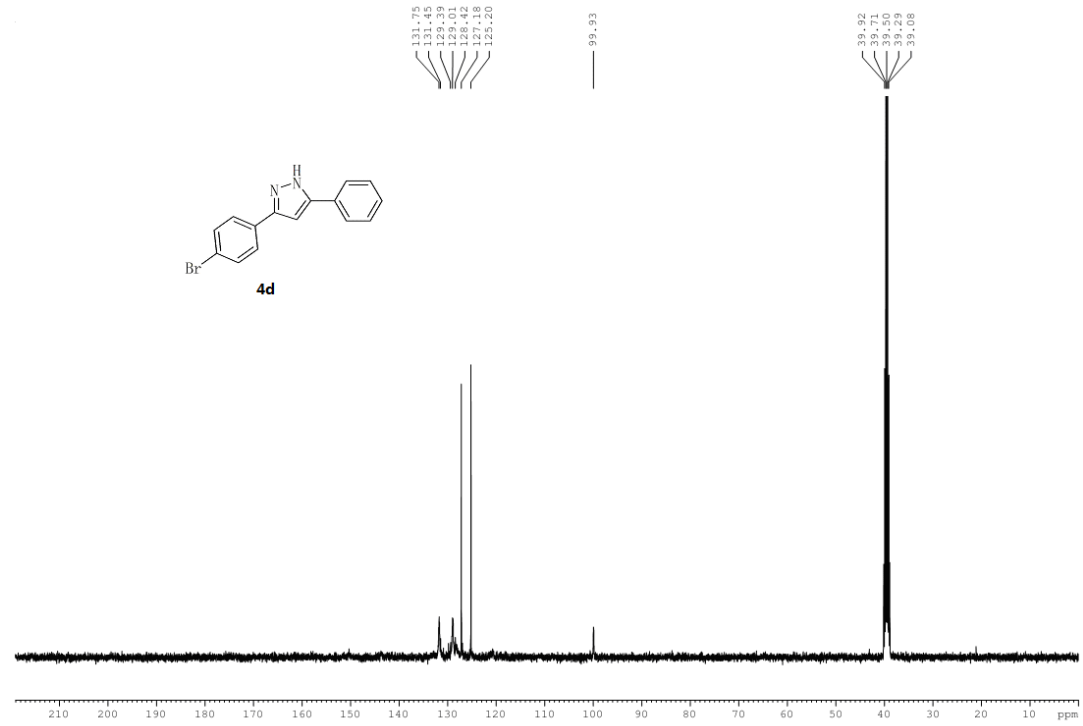


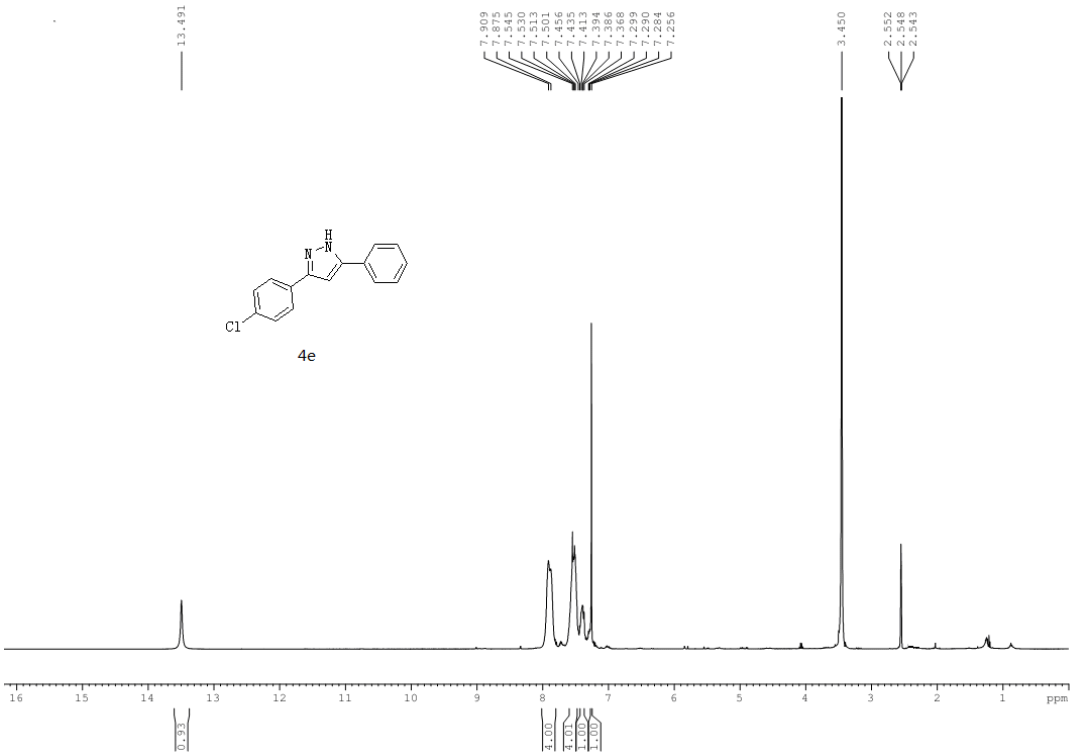


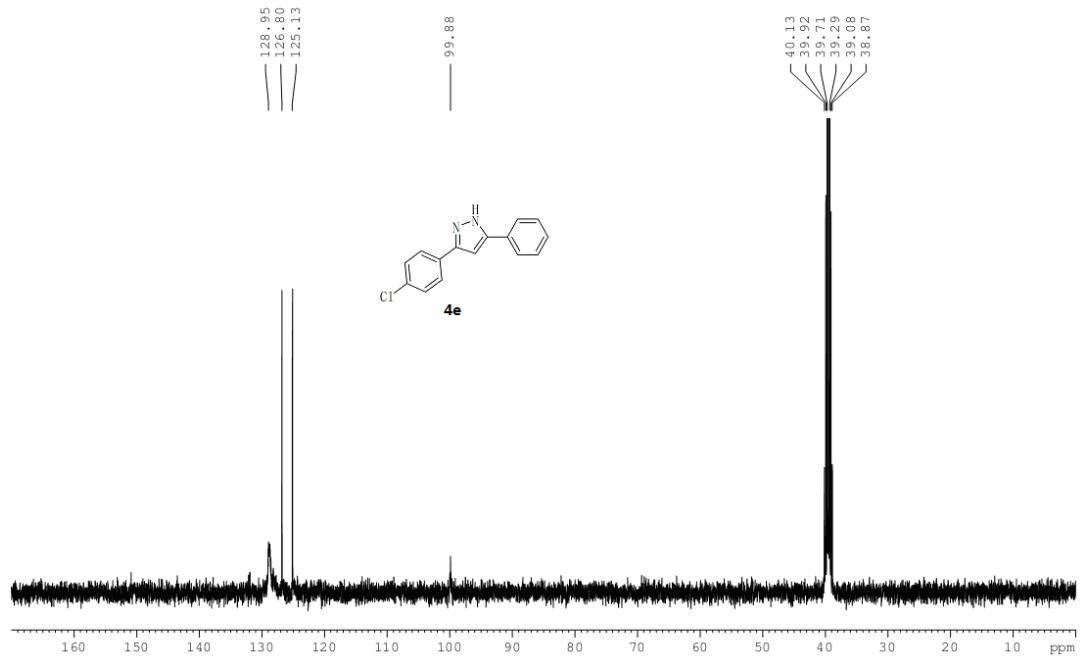


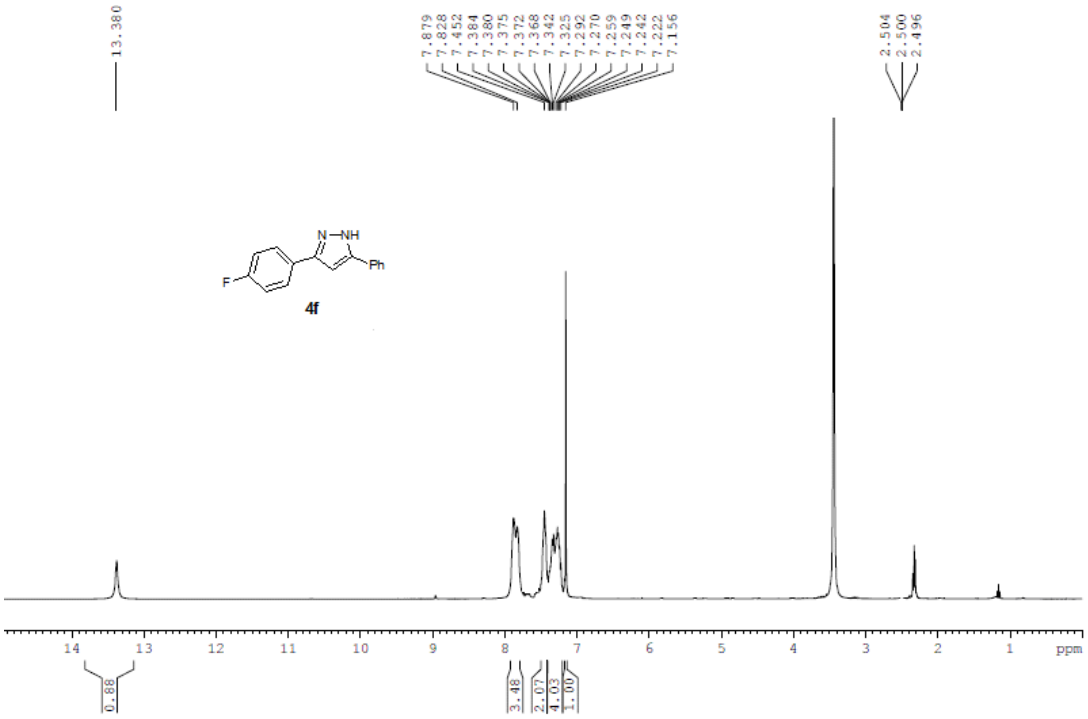


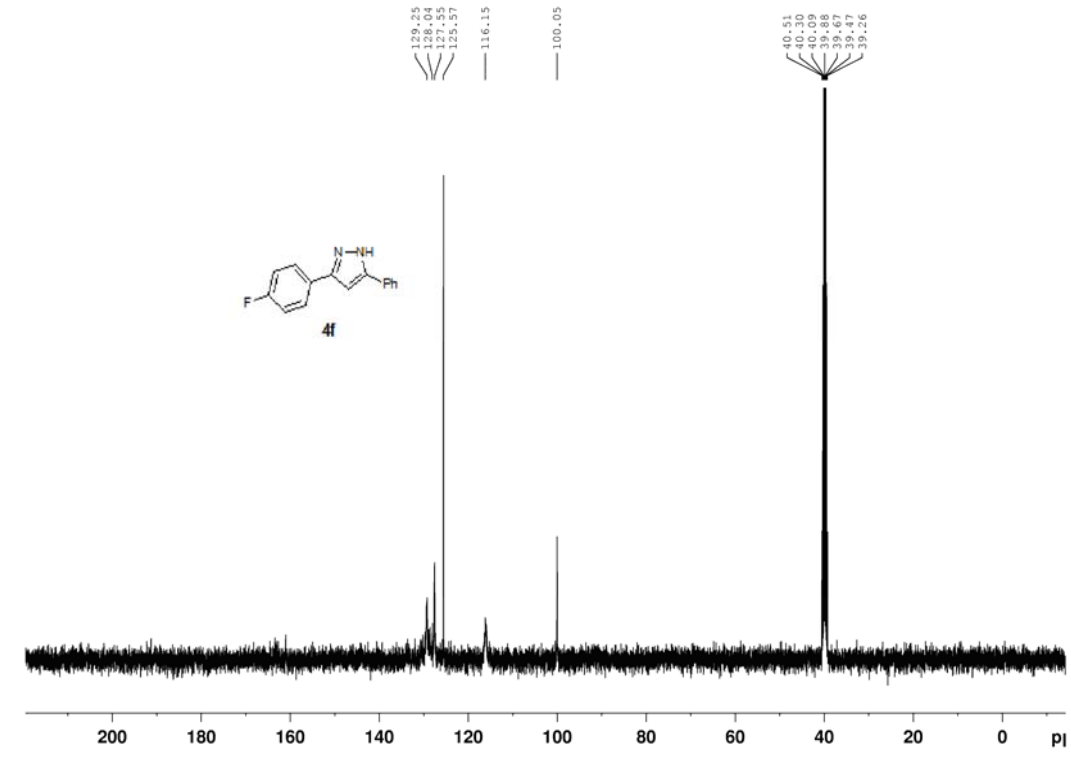


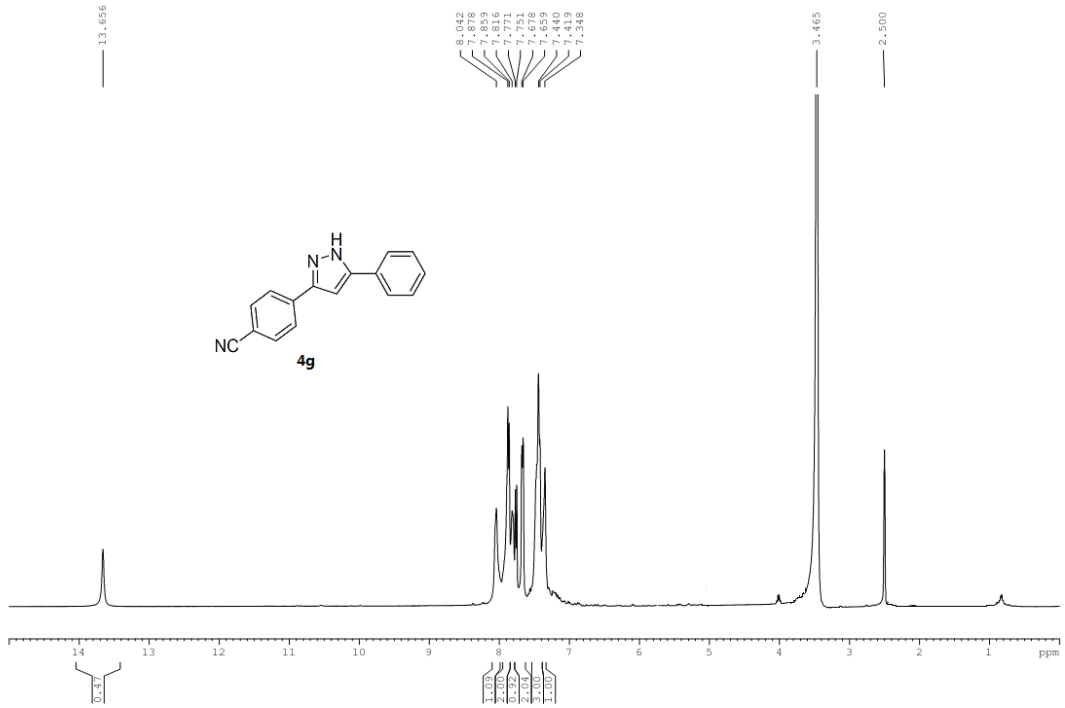


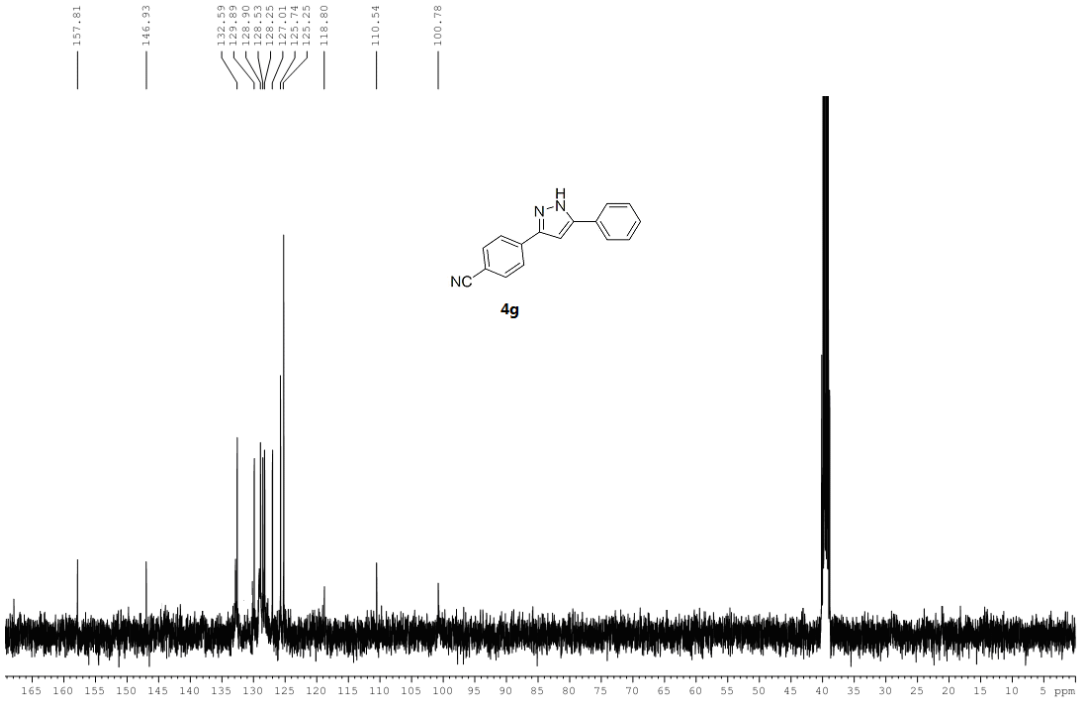


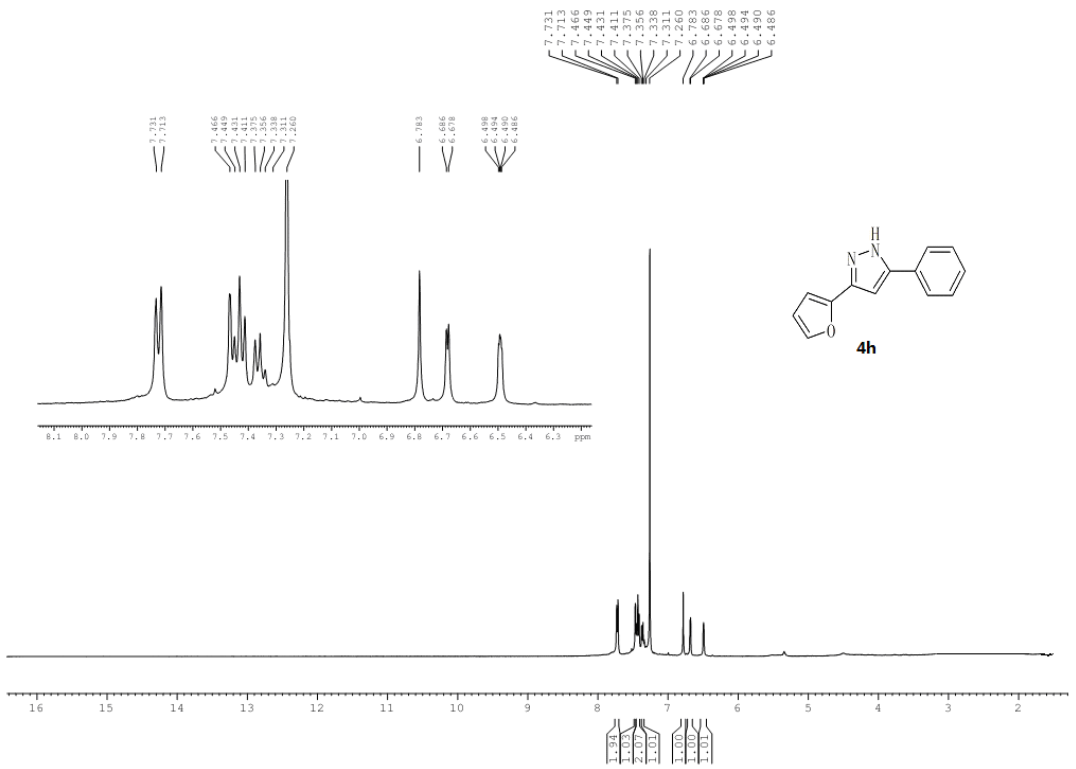


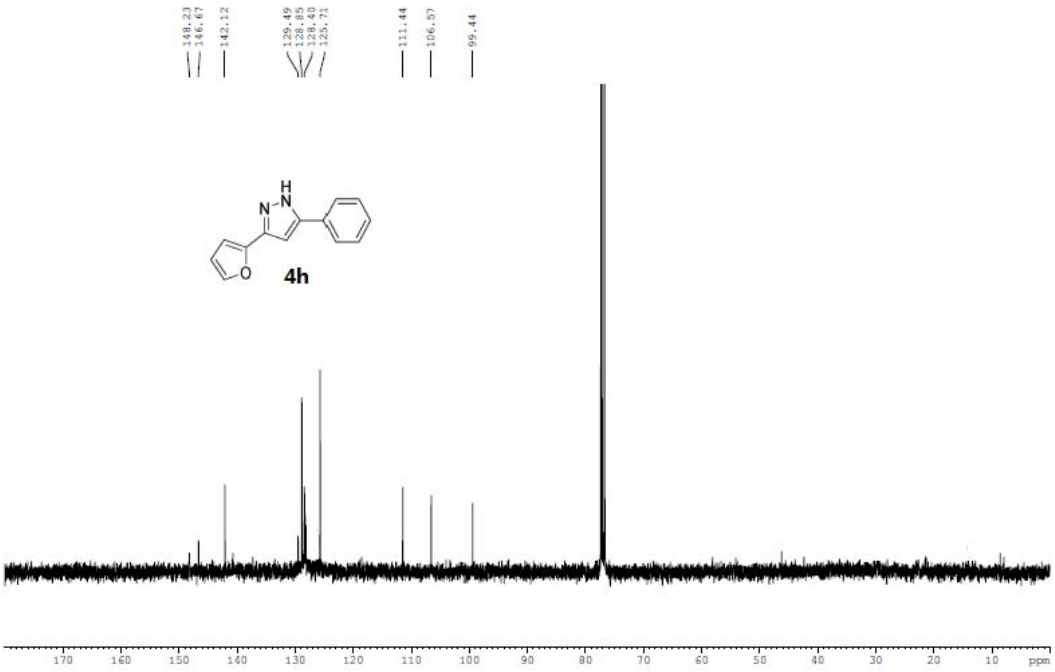


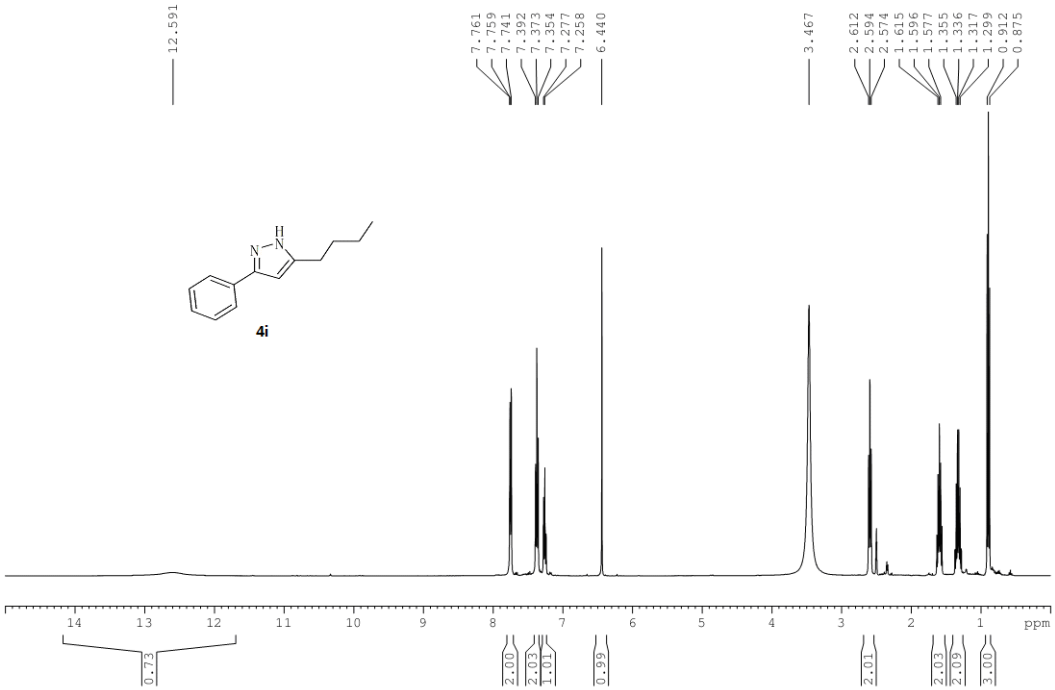








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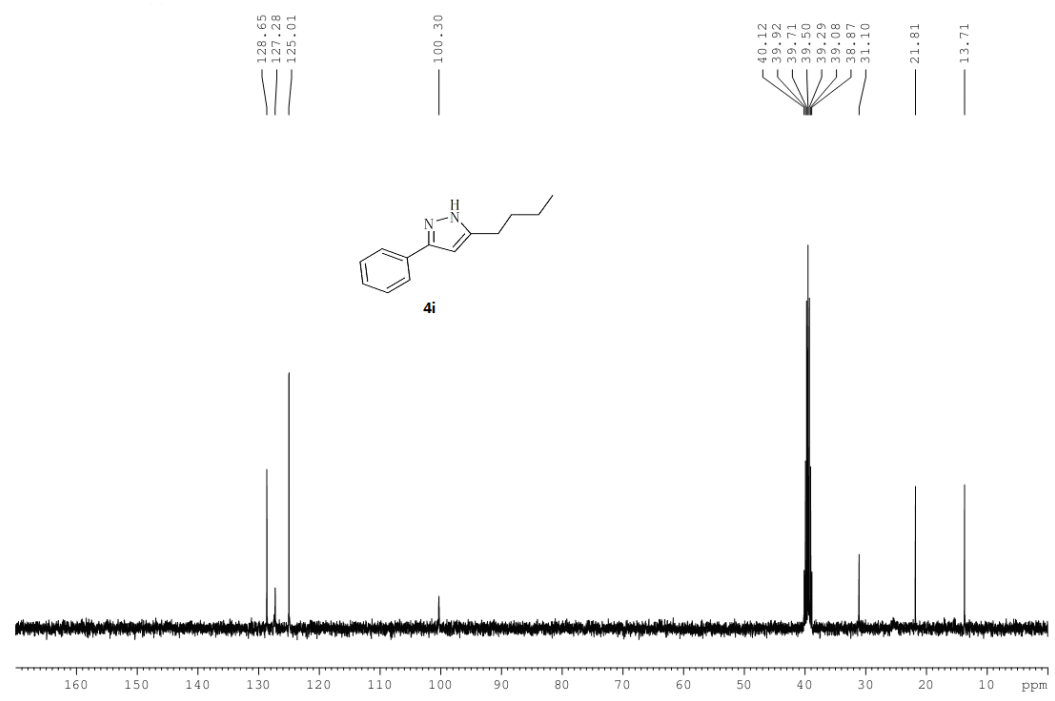
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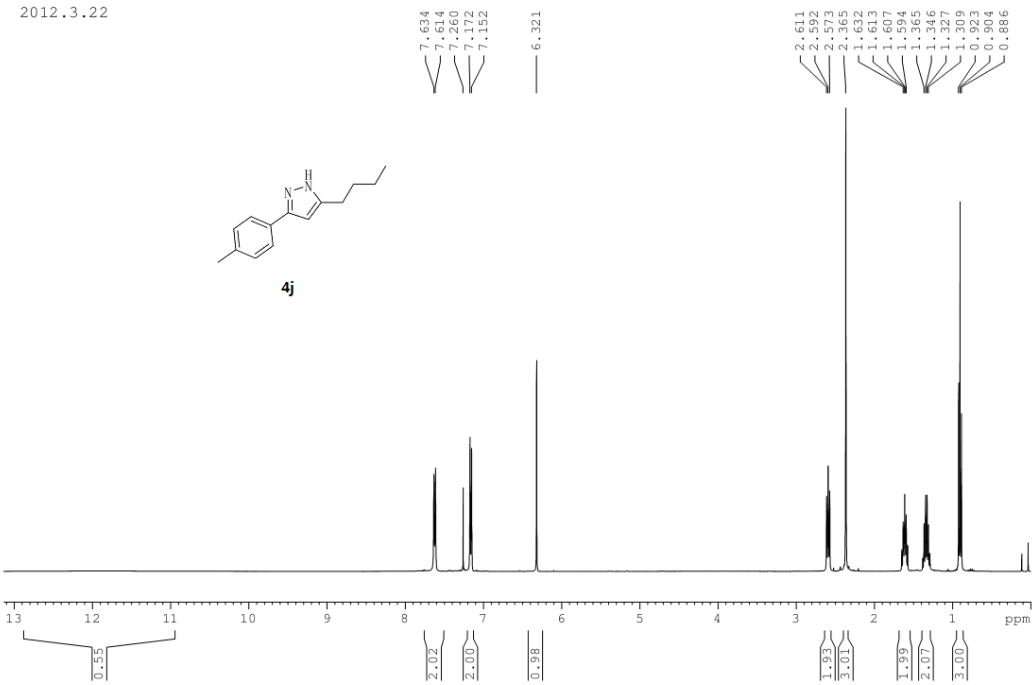
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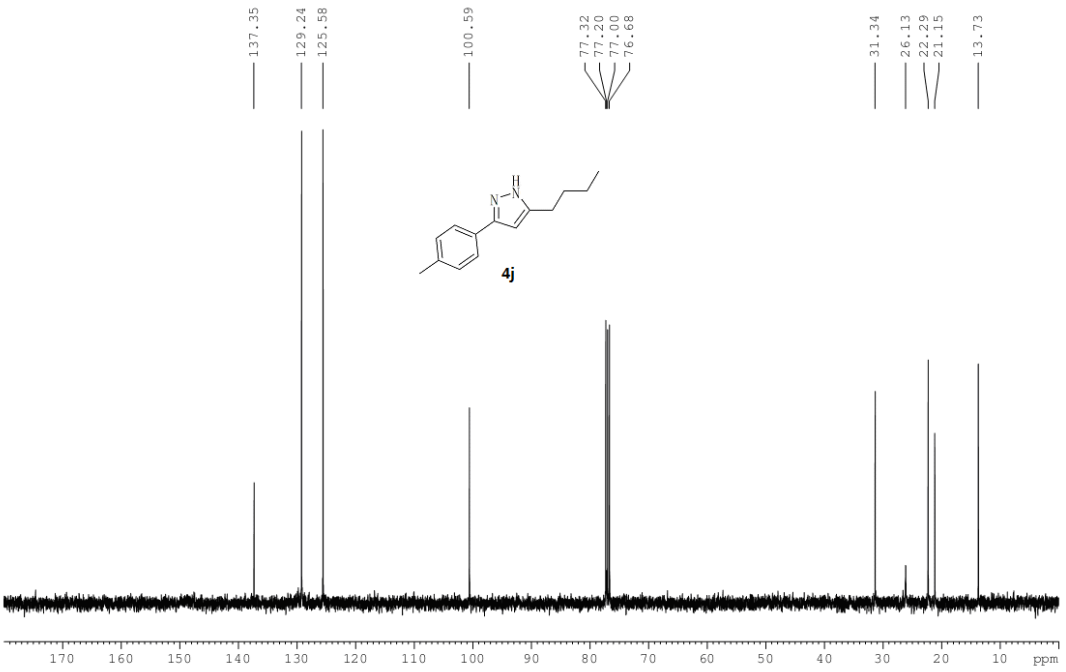
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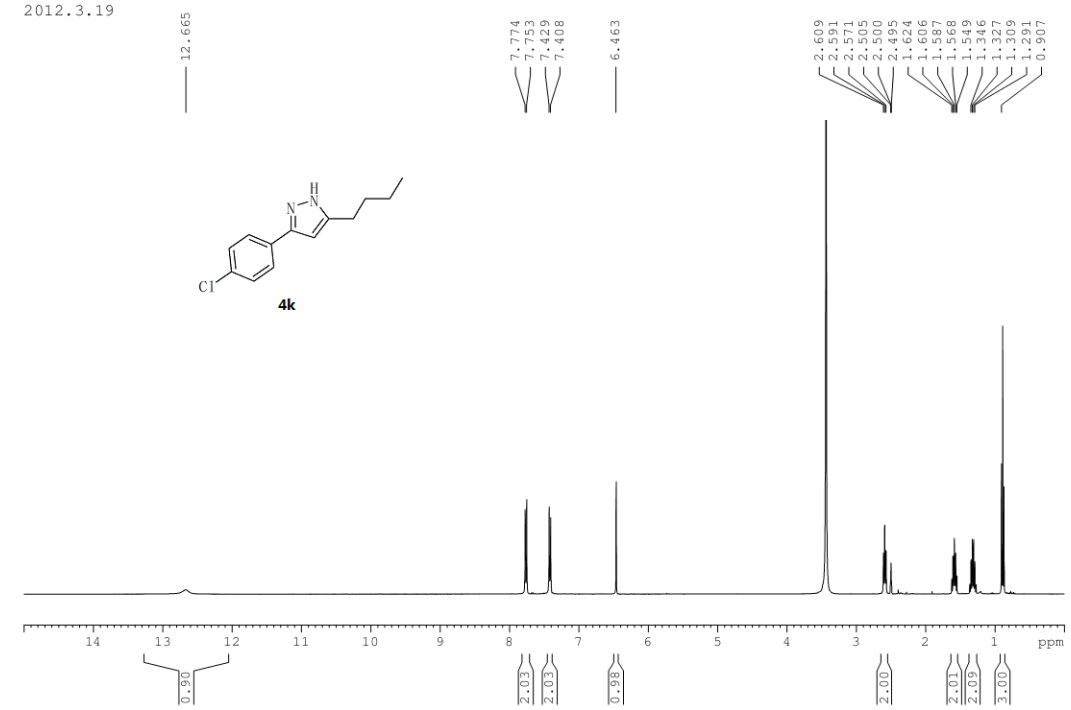
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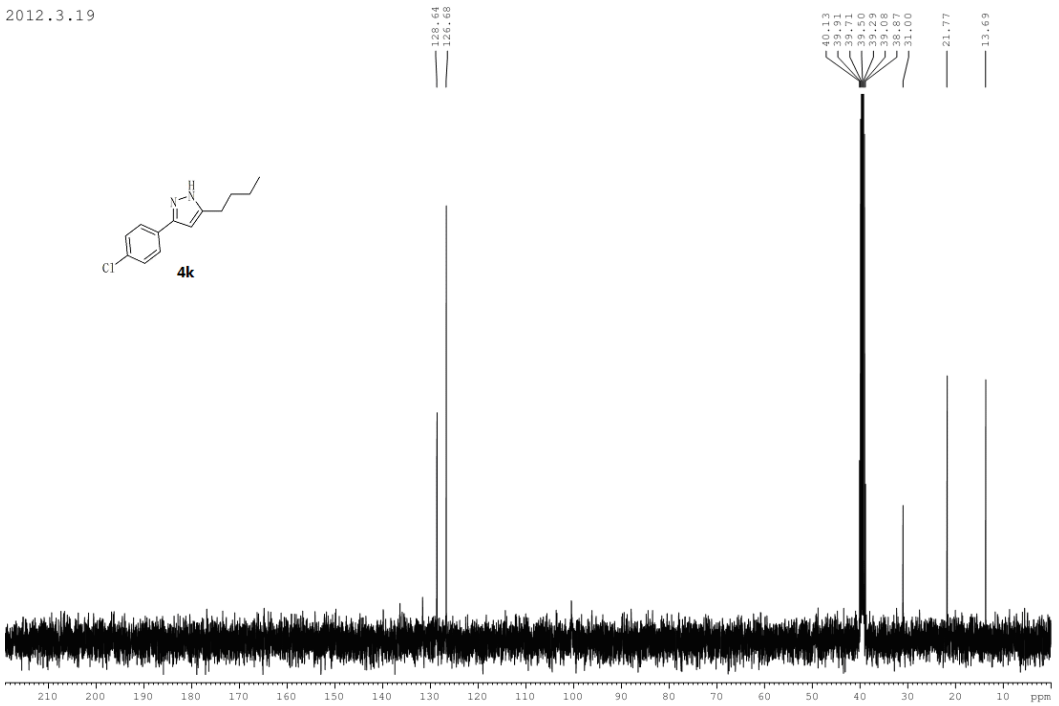
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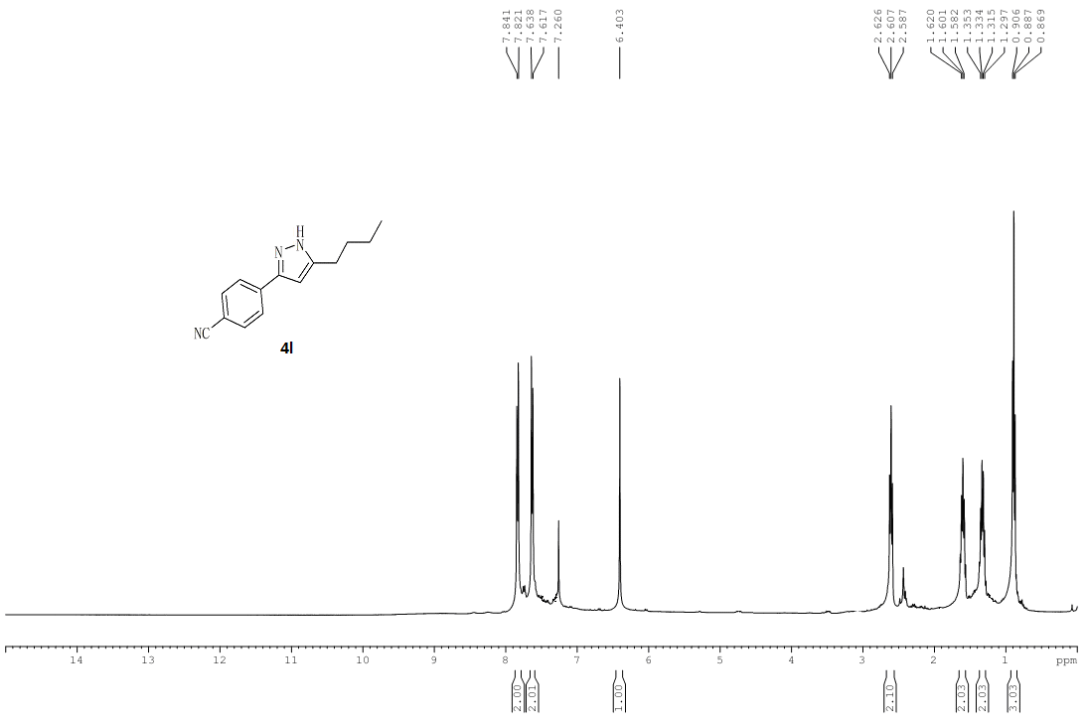

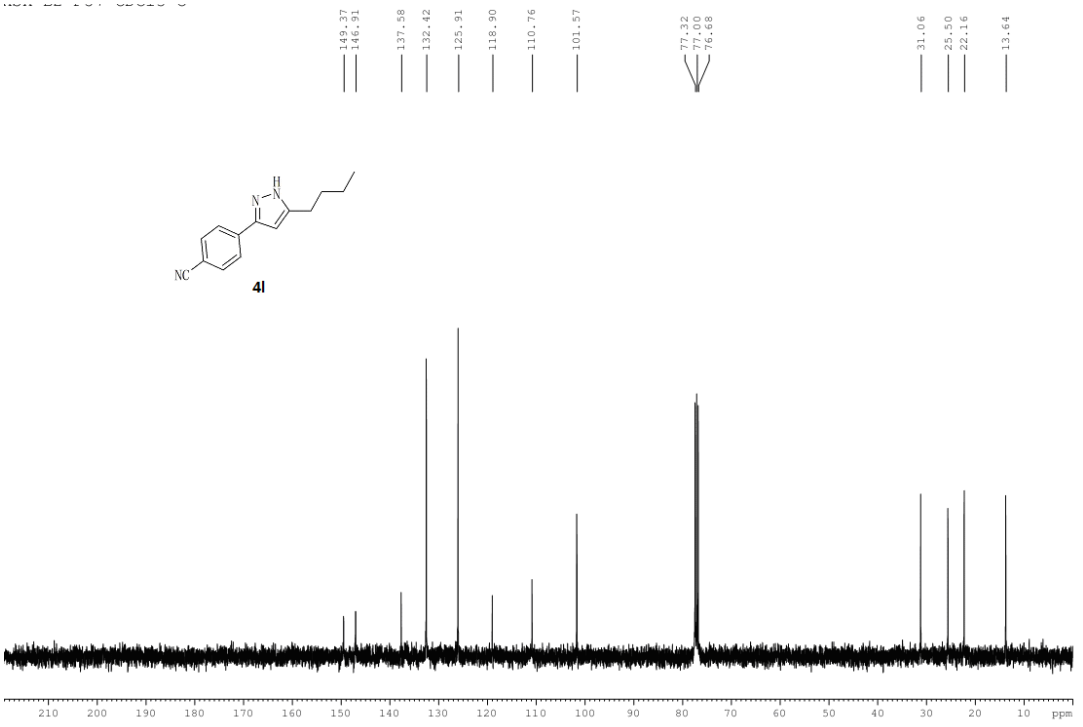

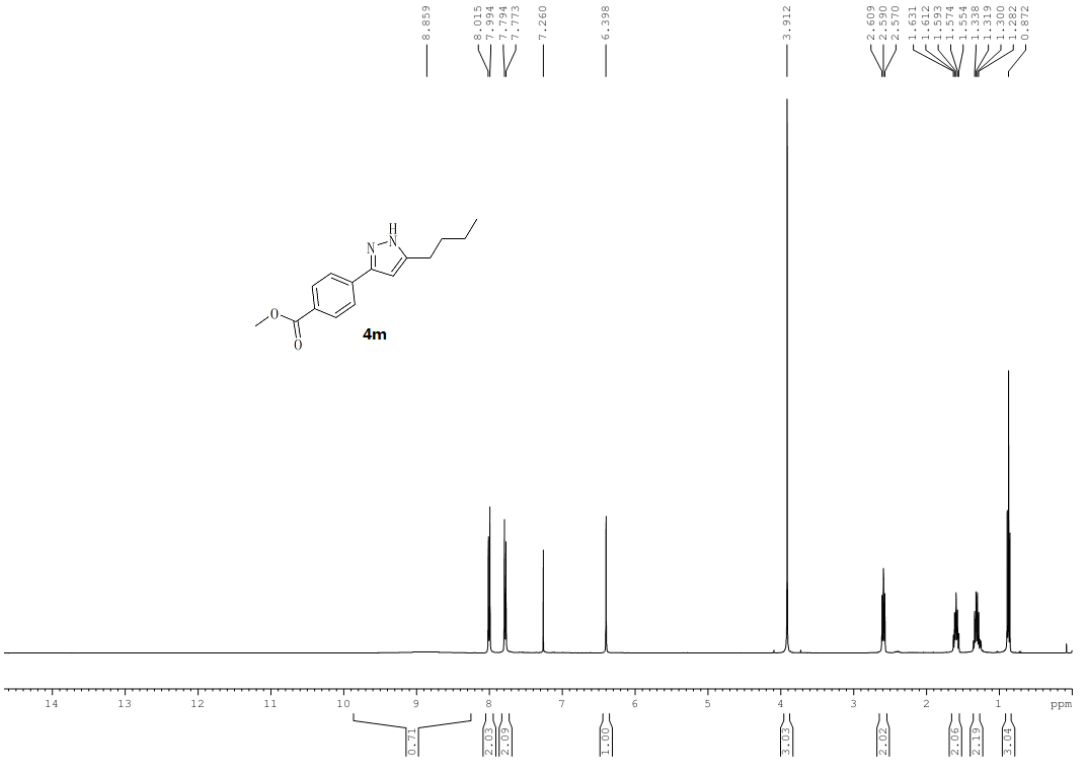

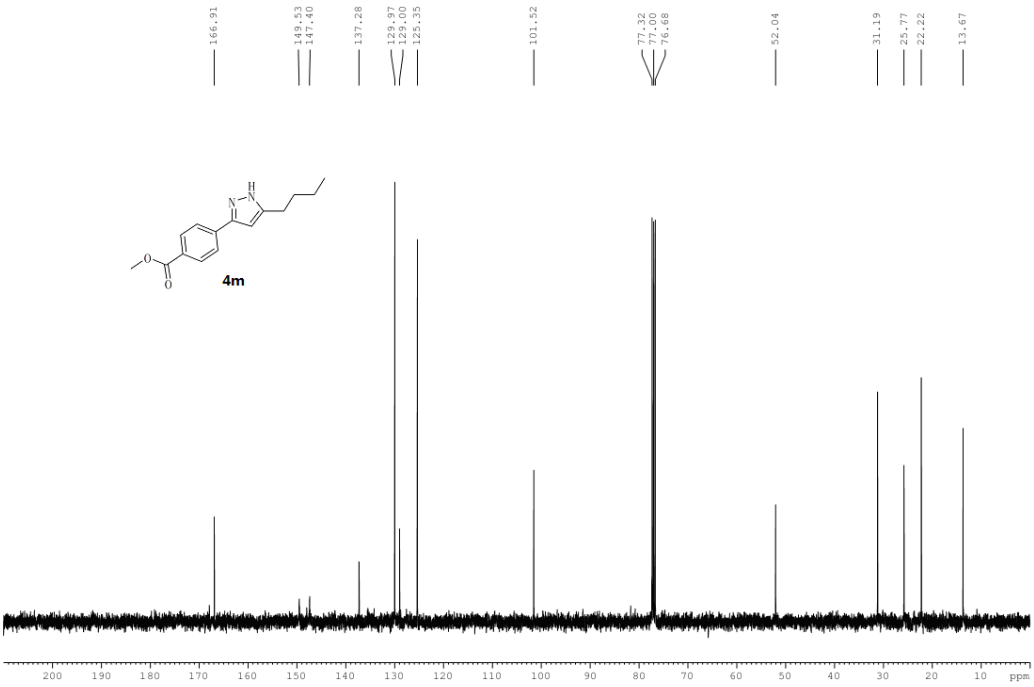

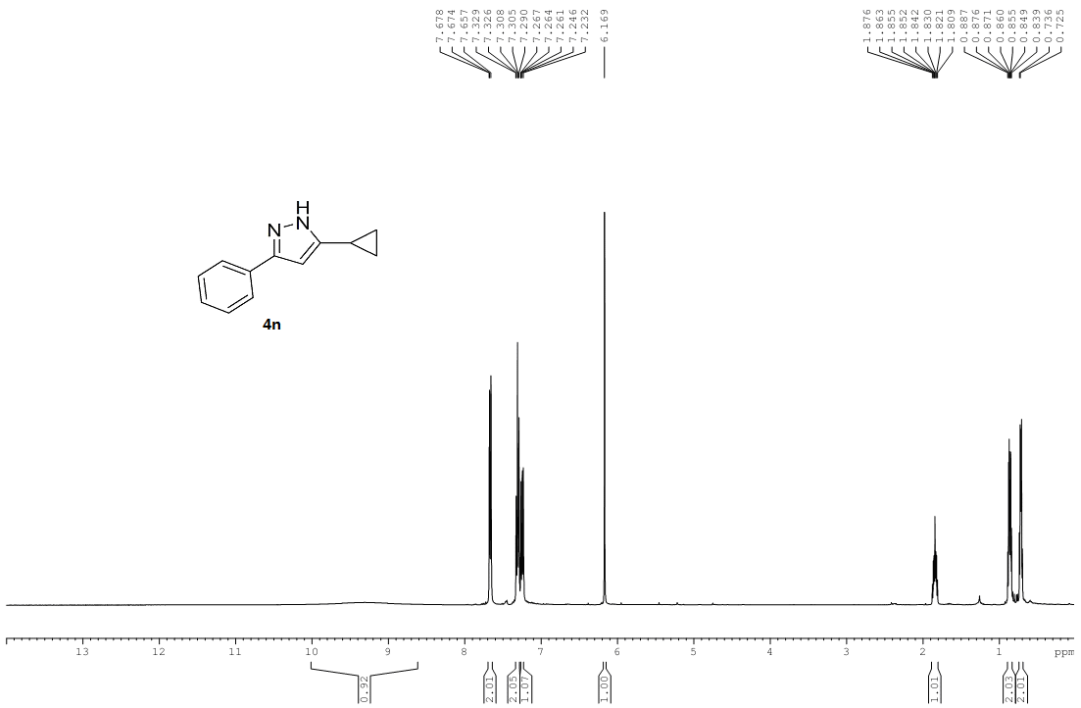

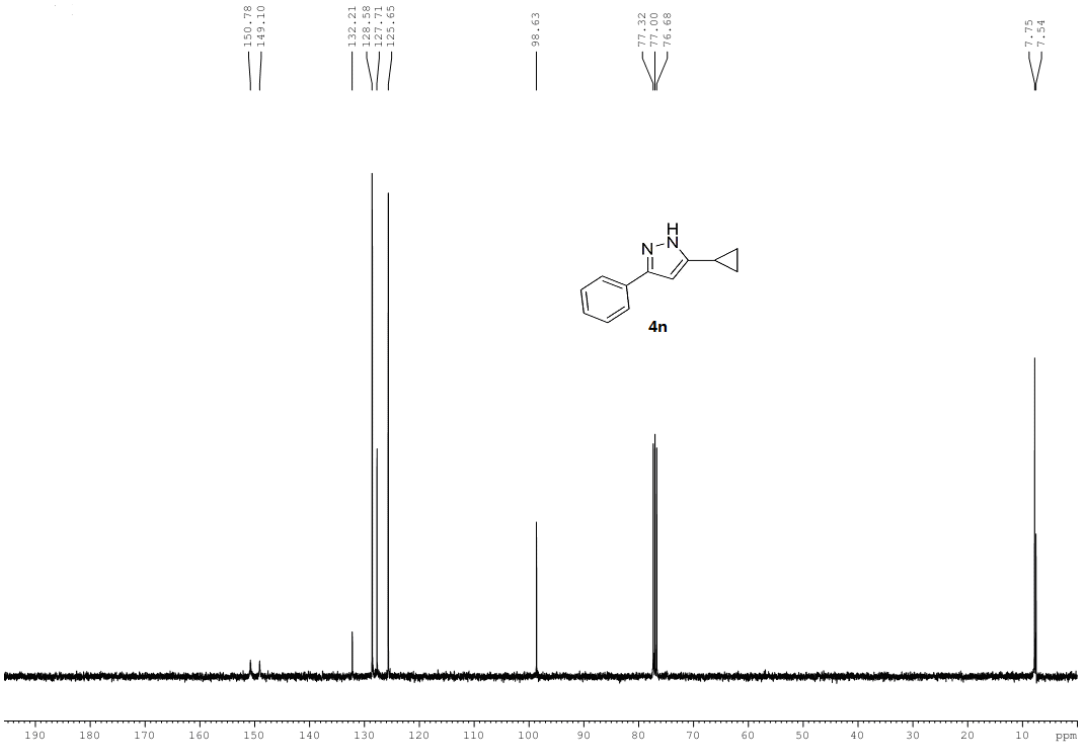

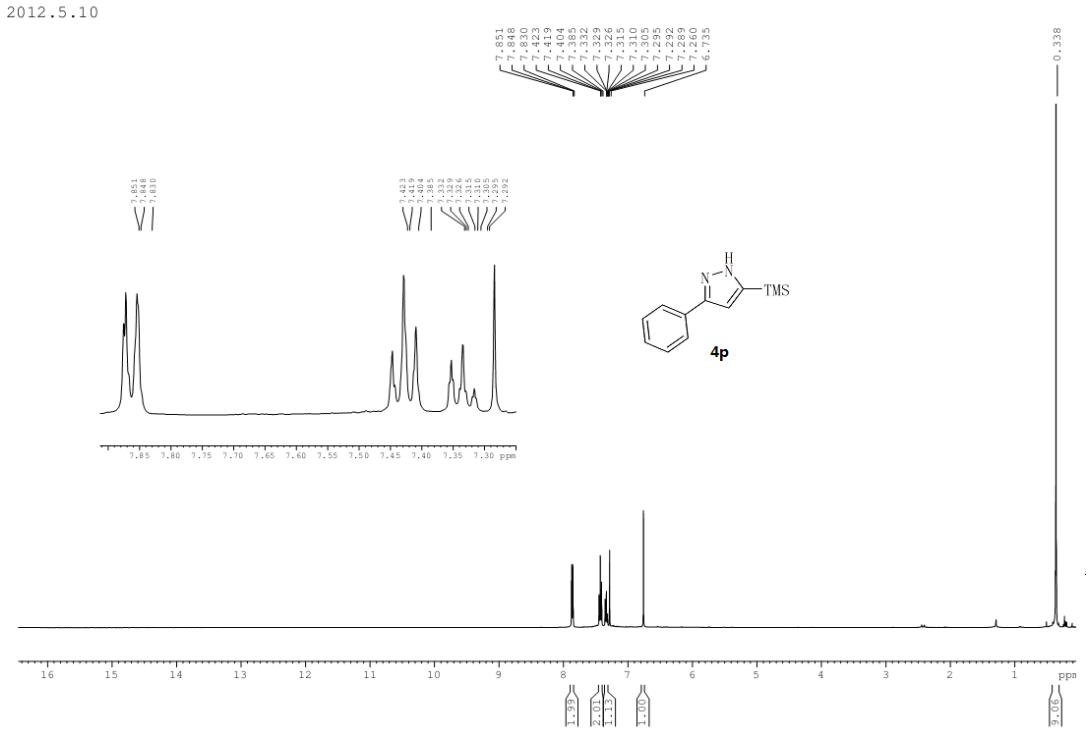
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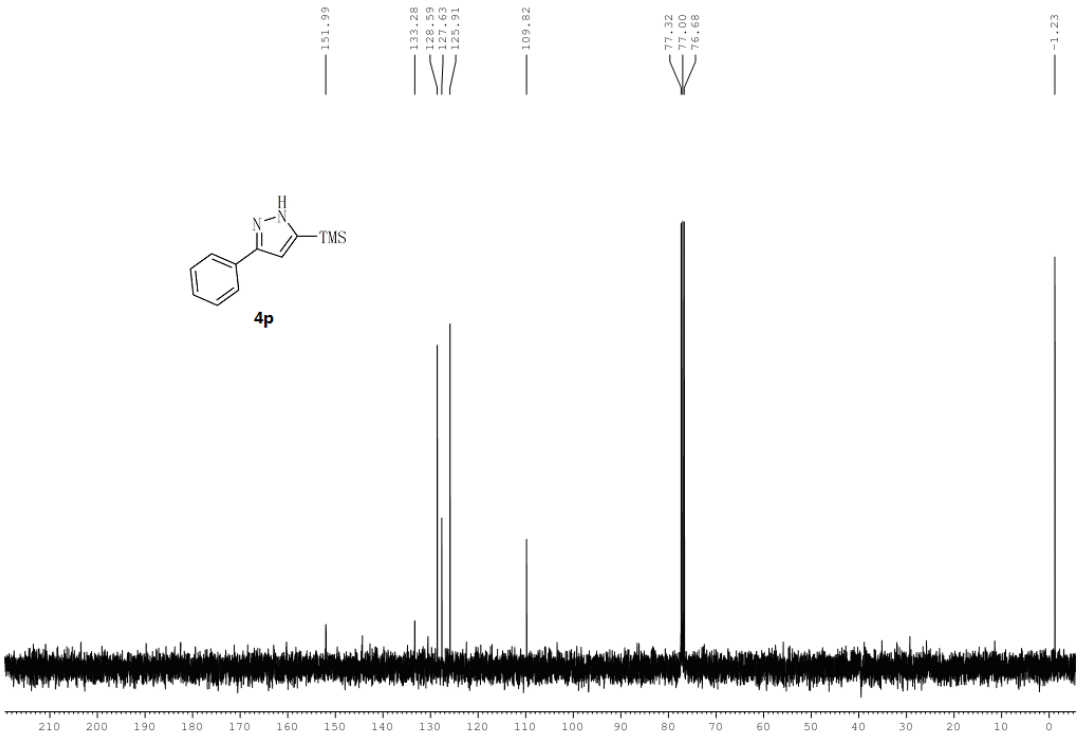
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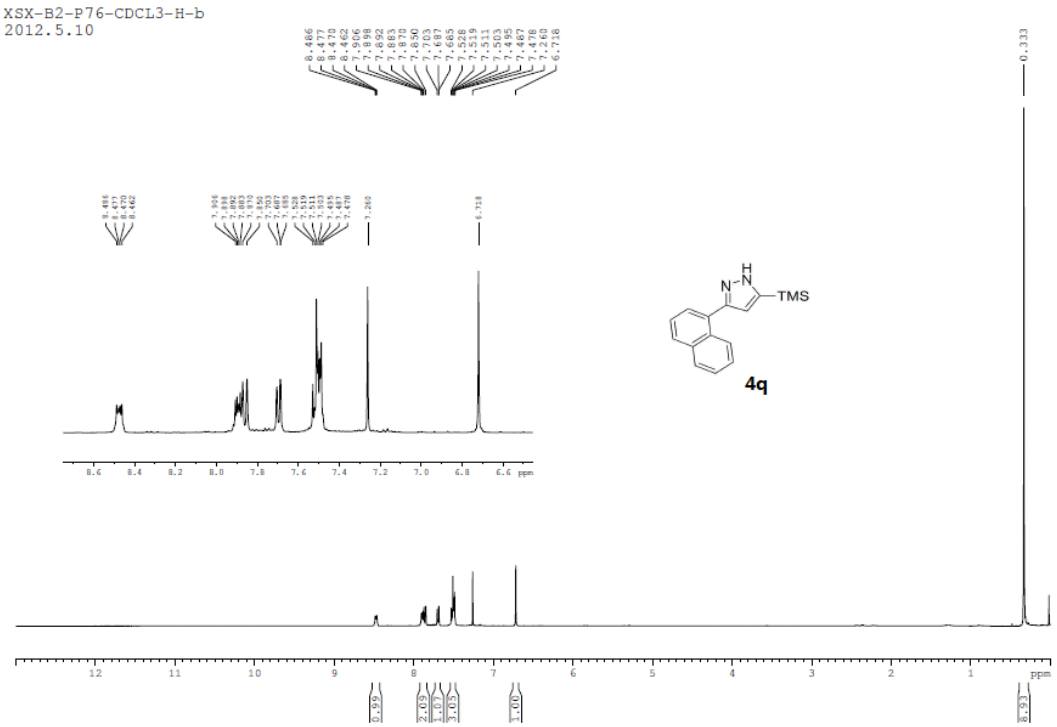
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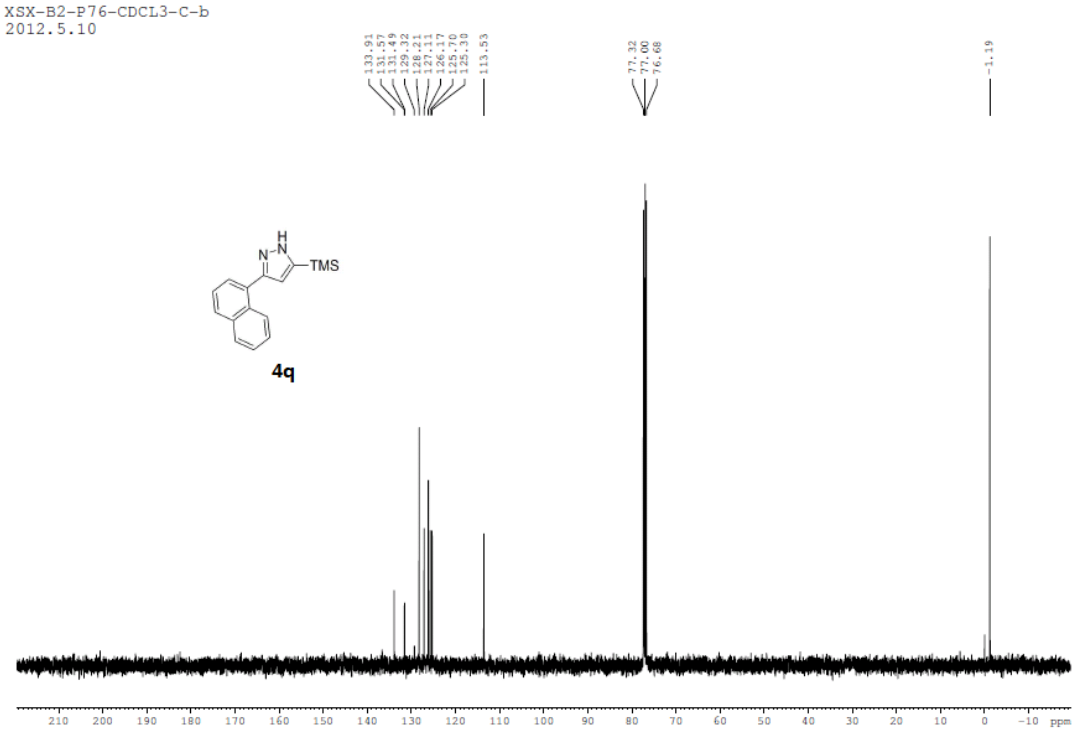
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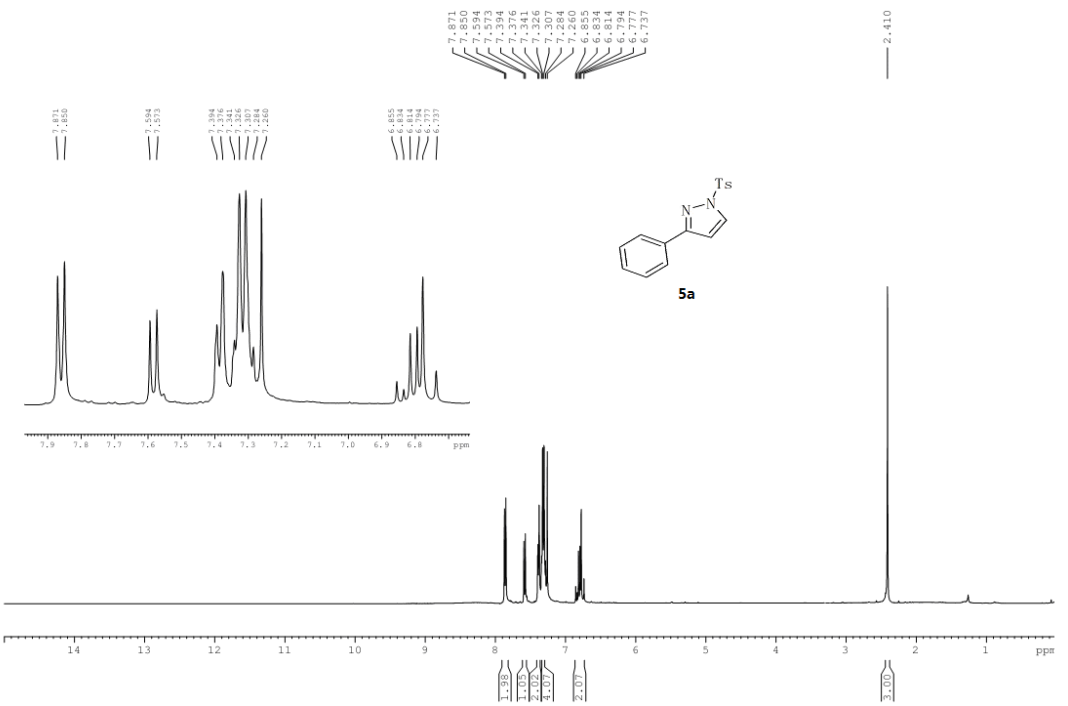

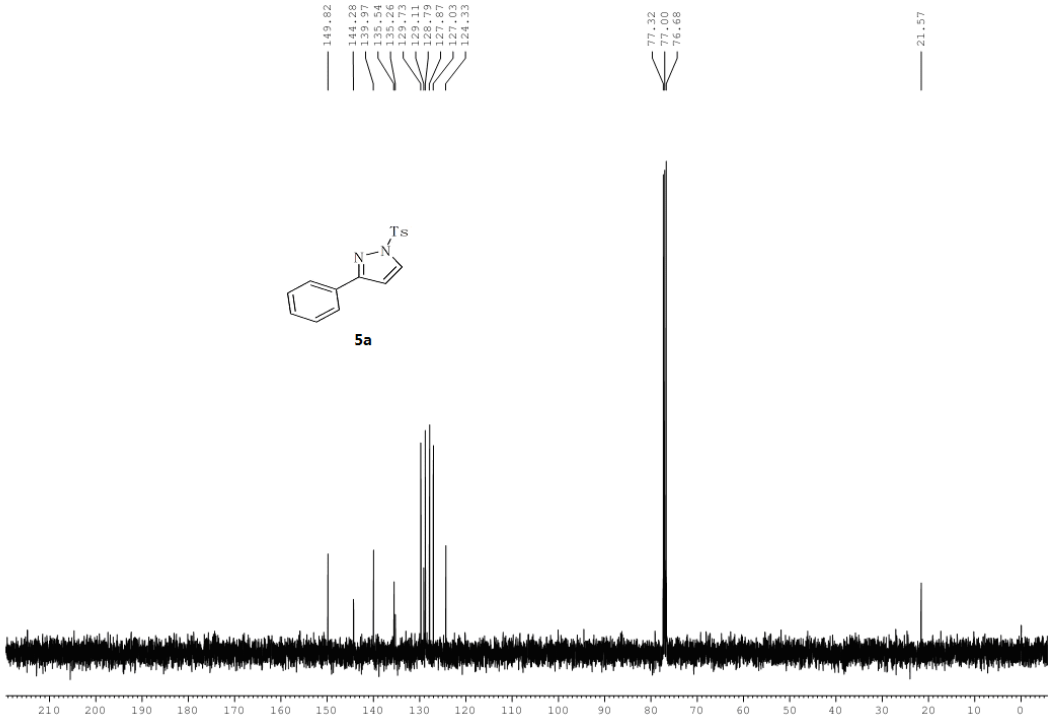

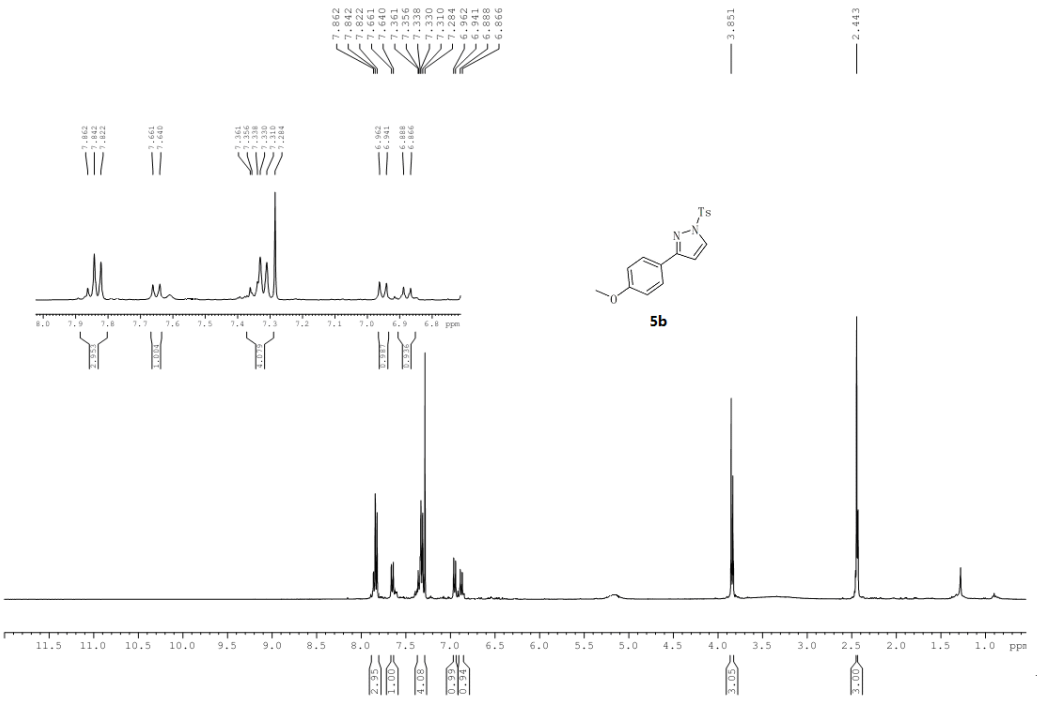
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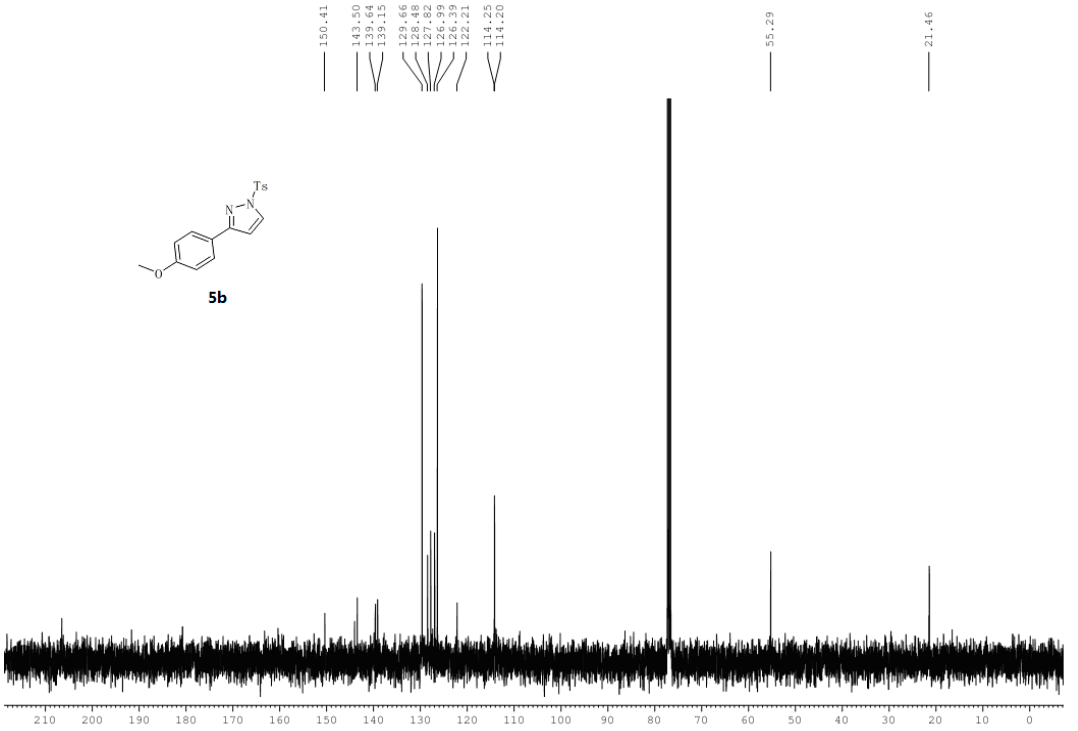
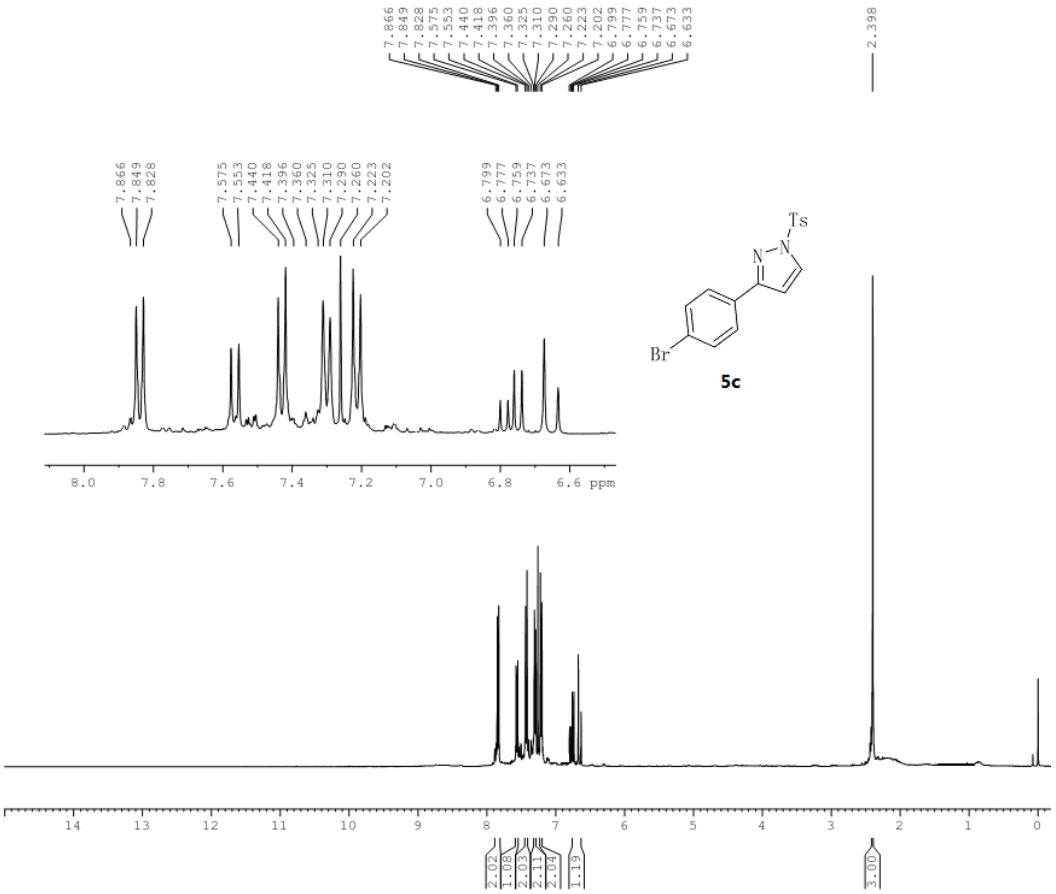
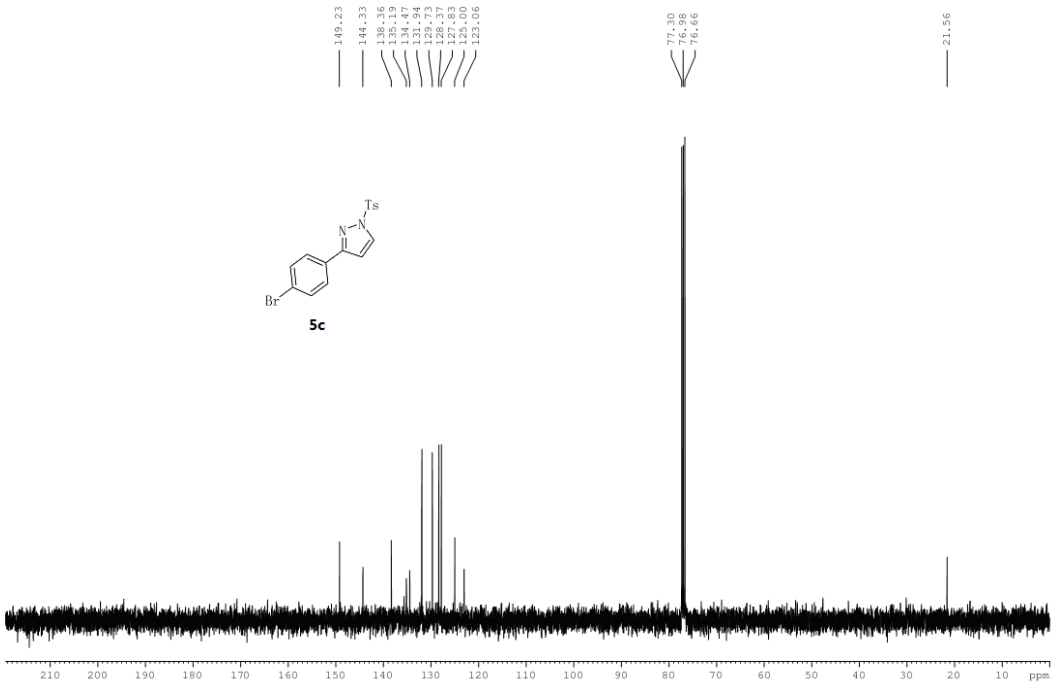
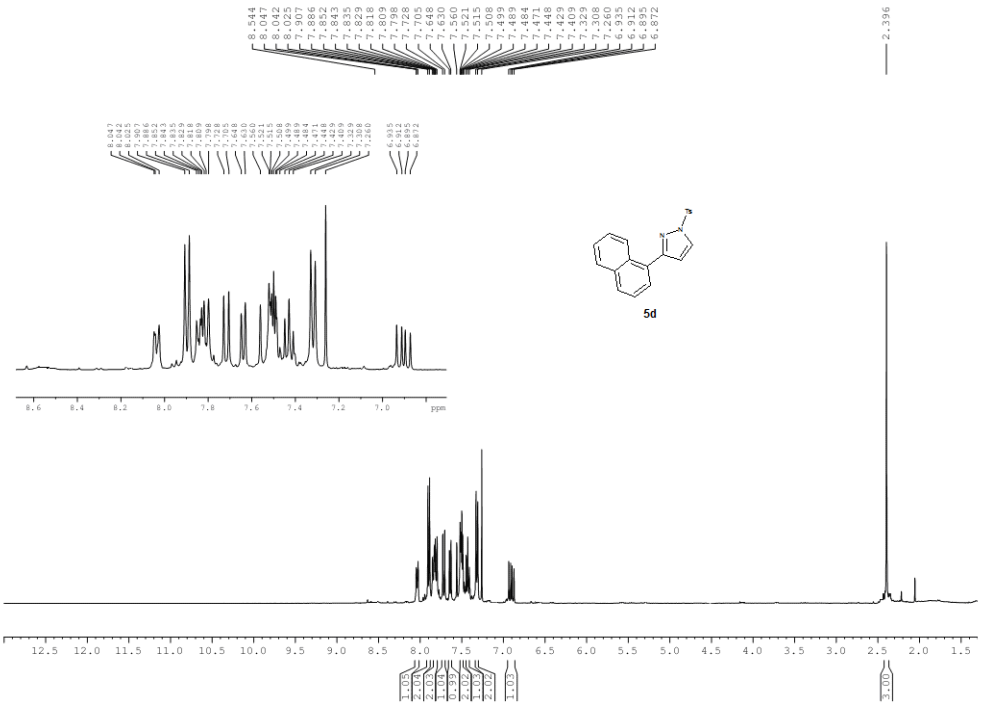
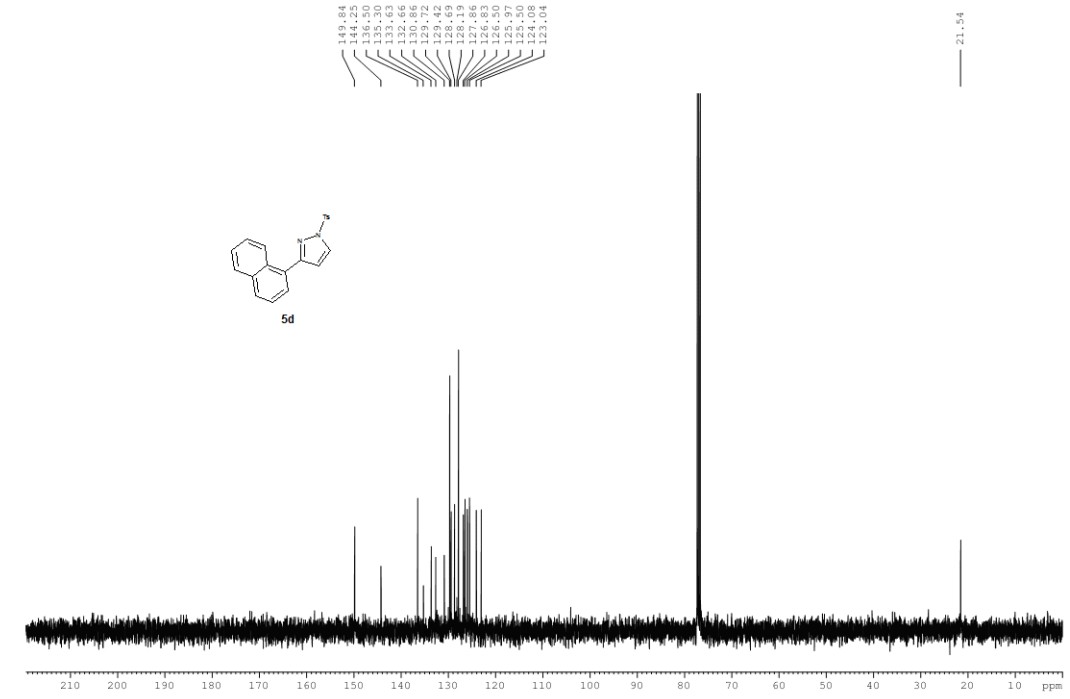
O
5b
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
2.95
1.00
4.08
0.99
0.94
3.05
3.00

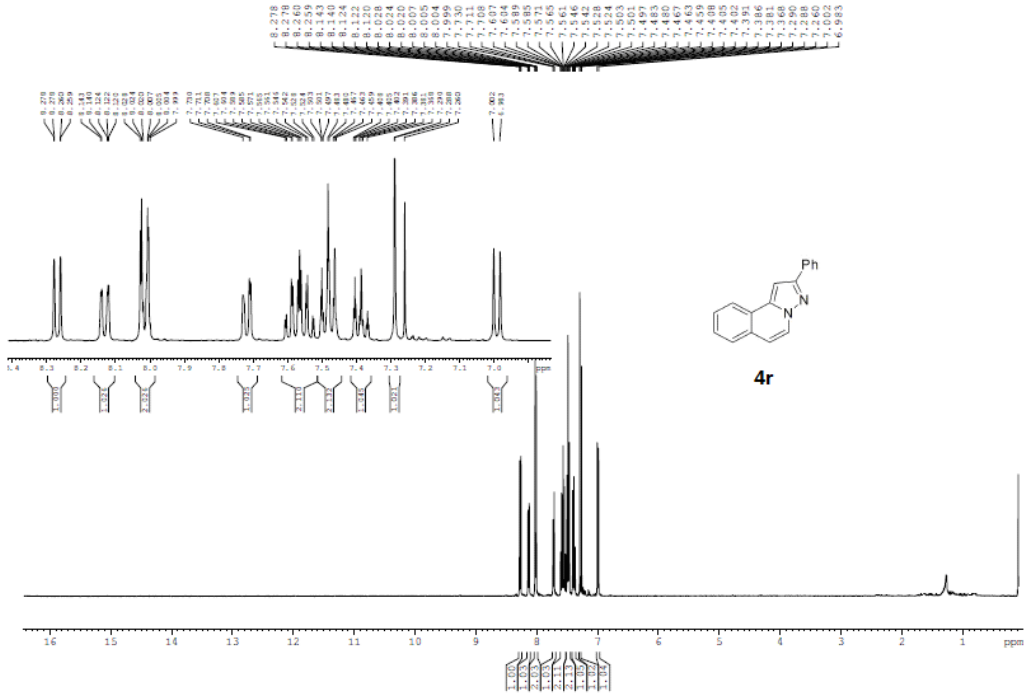

150.41
143.50
139.64
139.15
129.66
128.48
127.82
126.99
126.39
122.21
114.25
114.20
55.29
21.46
Ts
N
O
5b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

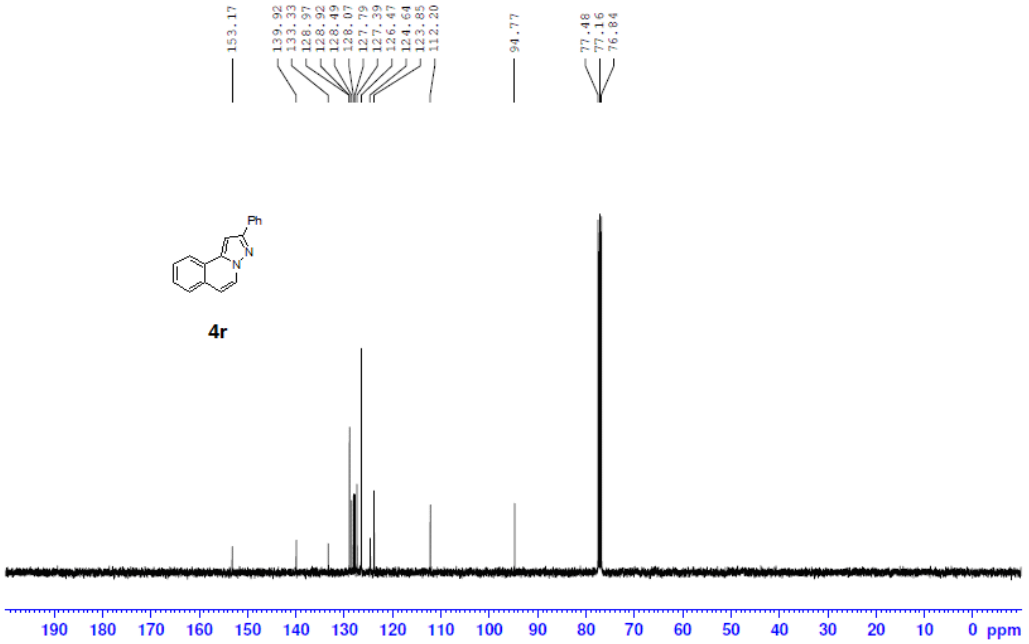


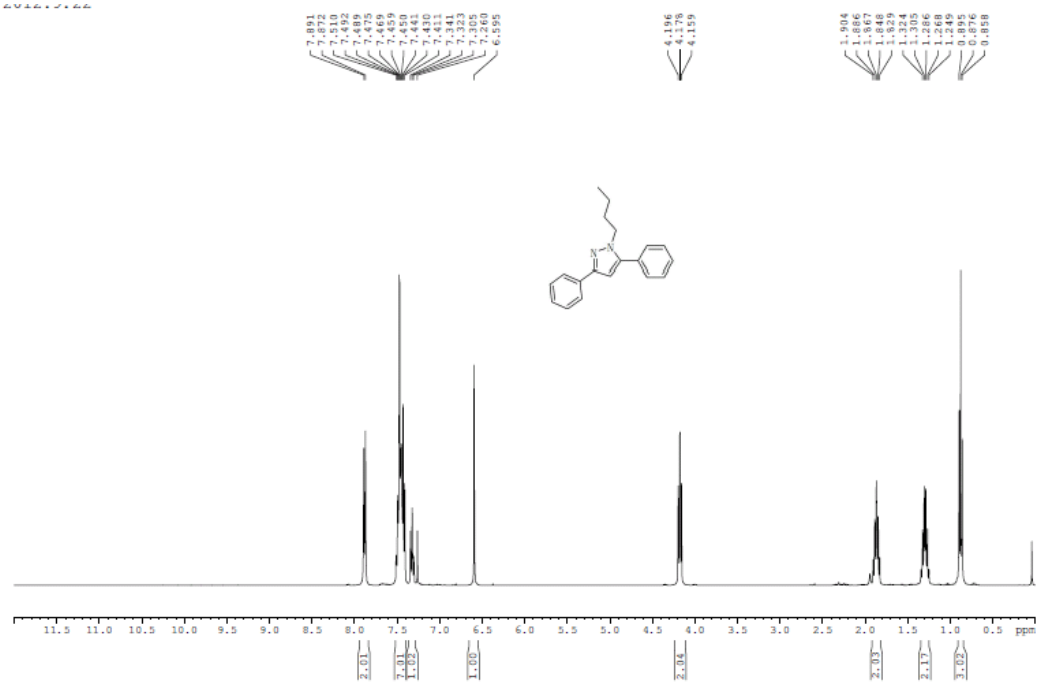


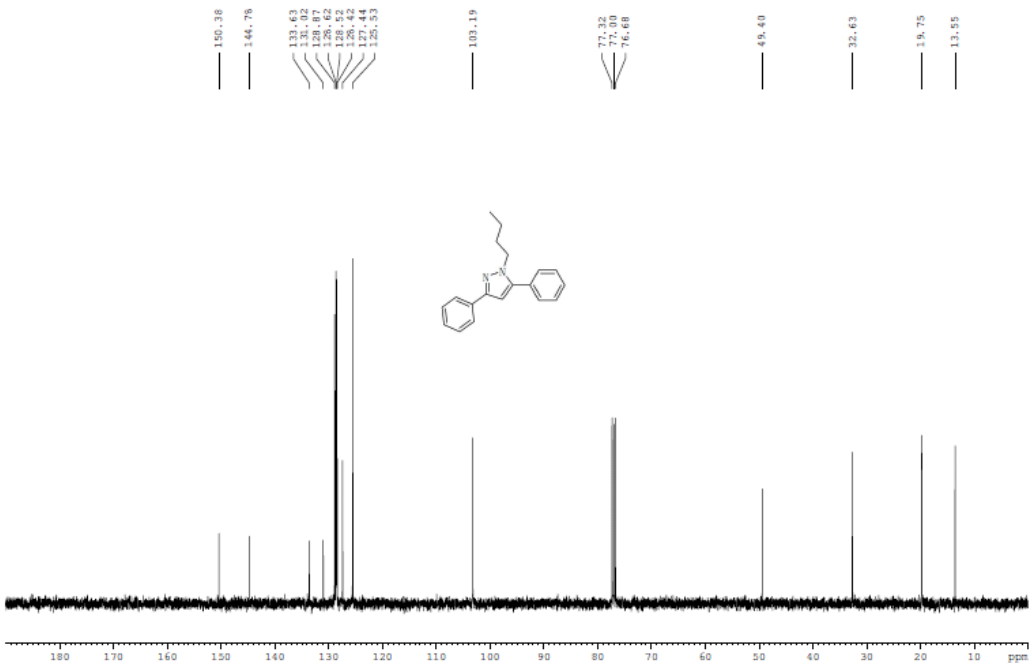


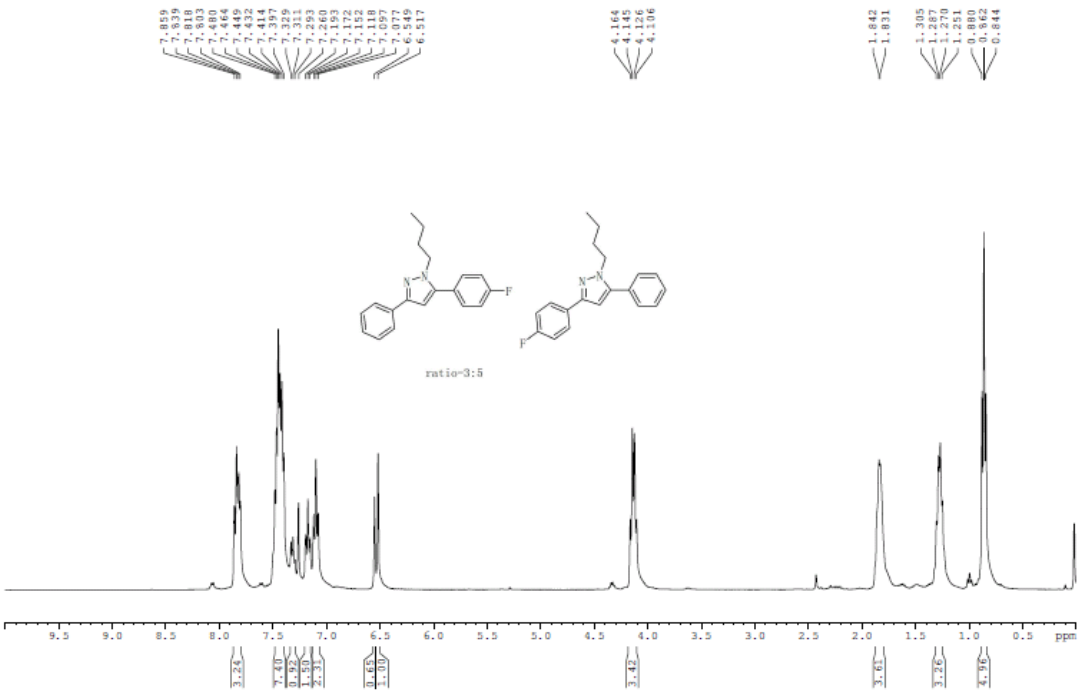


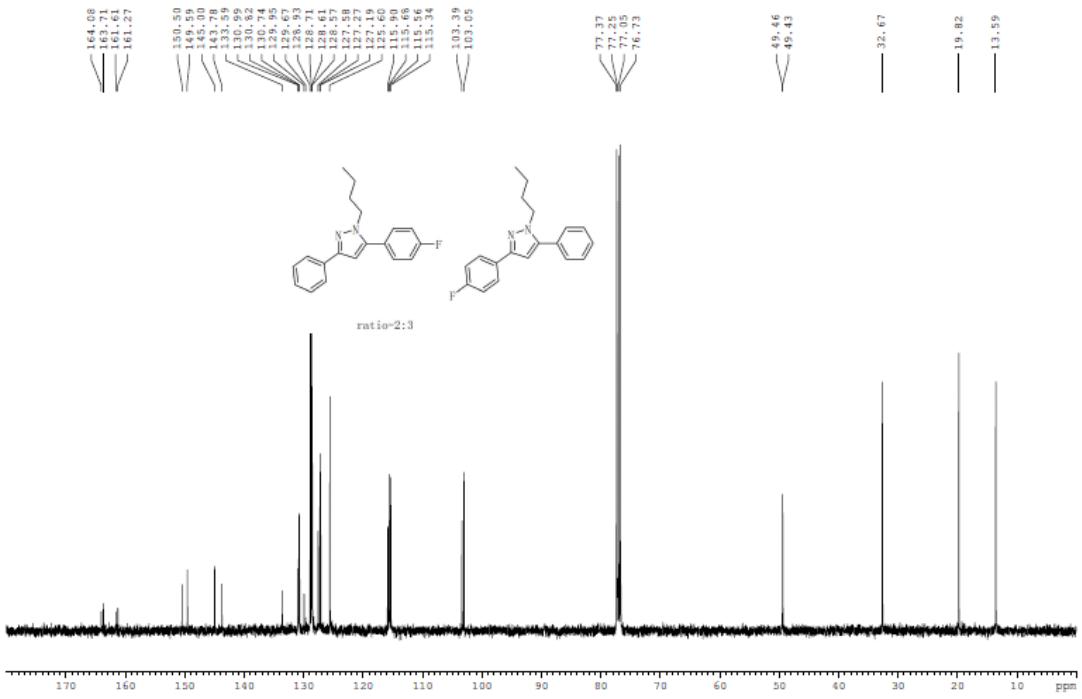

Ph
N
N
4r
ppm


153.17
139.92
133.33
128.97
128.92
128.49
128.07
127.79
127.39
126.47
124.64
123.85
112.20
94.77
77.48
77.16
76.84
Ph
N
N
4r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm






7.859
7.839
7.818
7.803
7.680
7.664
7.449
7.432
7.414
7.397
7.329
7.311
7.293
7.260
7.193
7.172
7.152
7.118
7.097
7.077
6.549
6.517
4.164
4.145
4.126
4.106
1.842
1.831
1.305
1.287
1.270
1.251
0.880
0.862
0.844
ratio=3:5
9.5 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 ppm
3.24
7.40
0.92
1.50
2.31
0.65
1.00
3.42
3.61
3.26
4.96


164.08
163.71
161.61
161.27
150.50
149.59
145.00
143.78
130.59
130.52
130.82
130.74
129.95
129.67
128.93
128.71
128.61
128.57
127.58
127.27
127.19
125.60
115.98
115.78
115.56
115.34
103.39
103.05
77.37
77.25
77.05
76.73
49.46
49.43
32.67
19.82
13.59
ratio=2:3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm