

Supplementary Information

Synthesis of Highly Substituted 5,6-Dihydrobenzo[*j*]phenanthridine Derivatives via Domino Reaction

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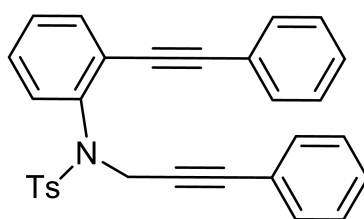
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1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. The chemicals were purchased from Alfa Aesar and Acros Chemicals. All solvents and materials were pre-dried, redistilled or recrystallized before use. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on a Bruker Avance 300 spectrometer with CDCl_3 as the solvent. Chemical shifts are reported in ppm by assigning TMS resonance in the ^1H NMR spectra as 0.00 ppm and CDCl_3 resonance in the ^{13}C spectra as 77.0 ppm. All coupling constants (J values) were reported in Hertz (Hz). Column chromatography was performed on silica gel 300–400 mesh. Melting points were determined using a Gallenkamp melting point apparatus and are uncorrected. The FT-IR spectra were recorded from KBr pellets or thin film from CHCl_3 on the NaCl window in the 4000–400 cm^{-1} ranges on a Nicolet 5DX spectrometer. All HRMS spectra were recorded using EI or APCI at 70 eV. X-ray Crystallography diffraction data of **3b** and **3j** were collected at r.t. with a Bruker SMART Apex CCD diffractometer with Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator using the ω -scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically.

General procedures:

General Procedure for the Preparation of Starting Materials(1a-1i):¹

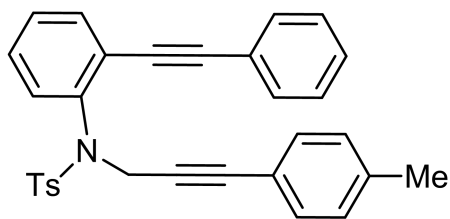


4-Methyl-N-(2-(phenylethynyl)phenyl)-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1a)

White solid; m.p. 126–127 °C.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.79$ (d, 2H, $J = 8.1$ Hz), 7.59 (s, 1H), 7.37–7.45 (m, 7H), 7.25–7.32 (m, 5H), 7.19 (d, 3H, $J = 8.1$ Hz), 4.86 (s, 2H), 2.31 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 143.5, 139.9, 137.4, 133.3, 131.7, 131.7, 131.6, 129.5, 128.9, 128.6, 128.6, 128.4, 128.3, 128.2, 127.8, 124.3, 122.9, 122.5, 94.4, 86.0, 85.4, 83.7, 41.2, 21.5$.

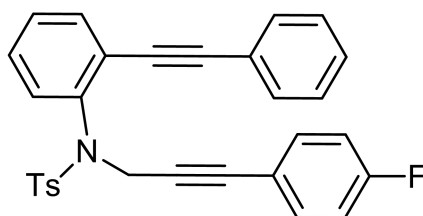


4-Methyl-N-(2-(phenylethynyl)phenyl)-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1b)

White solid; m.p. 104-105 °C.

^1H NMR (300 MHz, CDCl_3): δ = 7.75 (d, 2H, J = 8.1 Hz), 7.54–7.56 (m, 1H), 7.33–7.41 (m, 8H), 7.03–7.16 (m, 6H), 4.80 (s, 2H), 2.31 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): δ = 143.5, 140.0, 138.5, 137.5, 133.3, 131.7, 131.5, 129.6, 129.0, 128.9, 128.7, 128.6, 128.3, 128.2, 127.9, 124.4, 122.9, 119.5, 94.5, 86.1, 85.6, 83.1, 41.3, 21.5, 21.4.



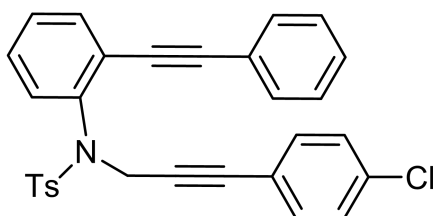
N-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-4-methyl-N-(2-(phenylethynyl)phenyl)benzenesulfonamide (1c)

White solid; m.p. 98-99 °C.

^1H NMR (300 MHz, CDCl_3): δ = 7.74 (d, 2H, J = 8.1 Hz), 7.56 (d, 1H, J = 4.8 Hz), 7.41 (d, 1H, J = 3.3 Hz), 7.33 (s, 7H), 7.12–7.21 (m, 4H), 6.93 (t, 2H, J = 8.4 Hz), 4.80 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): δ = 164.1 (d, $J_{\text{C-F}}$ = 246.1 Hz), 143.5, 139.8, 137.3, 133.4, 133.3, 131.7, 131.6, 129.5, 128.9, 128.7, 128.6, 128.3, 127.8, 124.2, 122.2, 115.6, 1

15.3, 94.4, 86.0, 84.3, 83.5, 41.1, 21.5.

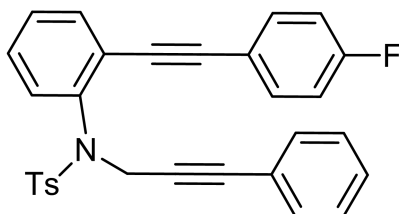


N-(3-(4-Chlorophenyl)prop-2-yn-1-yl)-4-methyl-N-(2-(phenylethynyl)phenyl)benzenesulfonamide (1d)

White solid; m.p. 119-120 °C.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.73$ (d, 2H, $J = 8.1$ Hz), 7.54–7.57 (m, 1H), 7.33–7.43 (m, 8H), 7.22 (d, 3H, $J = 8.4$ Hz), 7.17–7.19 (m, 3H), 4.80 (s, 2H), 2.26 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 143.5, 139.8, 137.3, 134.5, 133.4, 132.8, 131.7, 131.6, 129.5, 128.9, 128.7, 128.6, 128.5, 128.3, 127.8, 124.3, 122.8, 121.1, 94.6, 86.0, 84.8, 84.3, 41.1, 21.5$.

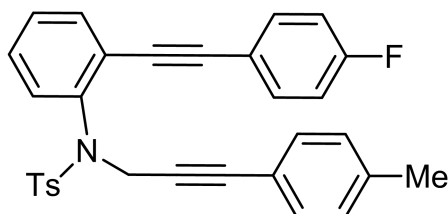


***N*-(2-((4-Fluorophenyl)ethynyl)phenyl)-4-methyl-*N*-(3-phenylprop-2-yn-1-yl)benzenesulfonamide (1e)**

White solid; m.p. 120-121 °C.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.76$ (d, 2H, $J = 8.1$ Hz), 7.55 (d, 1H, $J = 2.1$ Hz), 7.37–7.40 (m, 4H), 7.16–7.35 (m, 8H), 7.01 (t, 2H, $J = 9.0$ Hz), 4.78 (s, 2H), 2.30 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 164.5$ (d, $J_{\text{C-F}} = 255.7$ Hz), 143.5, 140.1, 137.5, 133.7, 133.2, 131.6, 131.4, 129.5, 128.9, 128.7, 128.4, 128.2, 127.9, 124.5, 122.5, 115.7, 115.4, 93.4, 85.9, 85.5, 83.7, 41.3, 21.5.

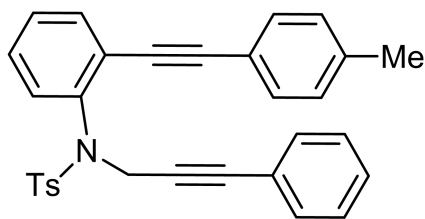


***N*-(2-((4-fluorophenyl)ethynyl)phenyl)-4-methyl-*N*-(3-(*p*-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1f)**

White solid; m.p. 129-130 °C.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.75$ (d, 2H, $J = 7.8$ Hz), 7.57 (d, 1H, $J = 8.4$ Hz), 7.32–7.40 (m, 5H), 7.18 (d, 2H, $J = 8.1$ Hz), 7.01–7.07 (m, 6H), 4.77 (s, 2H), 2.31 (s, 6H).

^{13}C NMR (75.5 MHz, CDCl_3): $\delta = 164.4$ (d, $J_{\text{C-F}} = 255.8$ Hz), 143.5, 140.1, 138.6, 137.6, 133.7, 133.2, 131.5, 131.4, 129.6, 129.0, 128.9, 128.7, 127.9, 124.5, 119.4, 115.7, 115.5, 93.4, 86.0, 85.7, 83.0, 41.4, 21.5, 21.4.

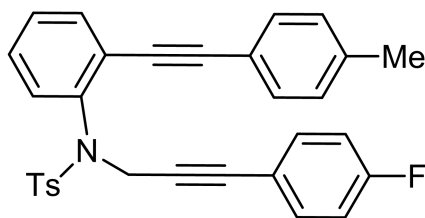


4-Methyl-N-(3-phenylprop-2-yn-1-yl)-N-(2-(p-tolylolethynyl)phenyl)benzenesulfonamide (1g)

White solid; m.p. 123-124 °C.

^1H NMR (300 MHz, CDCl_3): δ = 7.75 (d, 2H, J = 7.5 Hz), 7.54 (d, 1H, J = 6.0 Hz), 7.41 (d, 1H, J = 3.0 Hz), 7.32 (t, 2H, J = 3.9 Hz), 7.22–7.25 (m, 7H), 7.13 (t, 4H, J = 7.5 Hz), 4.81 (s, 2H), 2.37 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): δ = 143.5, 139.8, 138.8, 137.5, 133.3, 131.7, 131.6, 131.6, 129.5, 129.0, 128.7, 128.6, 128.4, 128.2, 127.8, 124.5, 122.6, 119.8, 94.8, 85.4, 85.4, 83.8, 41.1, 21.6, 21.5.

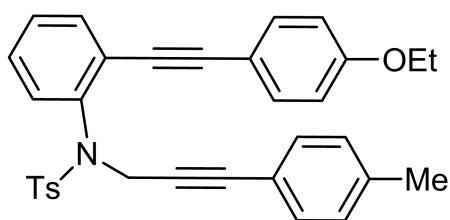


N-(3-(4-Fluorophenyl)prop-2-yn-1-yl)-4-methyl-N-(2-(p-tolylolethynyl)phenyl)benzenesulfonamide (1h)

White solid; m.p. 87-88 °C.

^1H NMR (300 MHz, CDCl_3): δ = 7.73 (d, 2H, J = 8.1 Hz), 7.53 (d, 1H, J = 4.8 Hz), 7.41 (d, 1H, J = 3.6 Hz), 7.32 (t, 2H, J = 3.9 Hz), 7.10–7.24 (m, 8H), 6.92 (t, 2H, J = 8.4 Hz), 4.79 (s, 2H), 2.37 (s, 3H), 2.27 (s, 3H).

^{13}C NMR (75.5 MHz, CDCl_3): δ = 164.1 (d, $J_{\text{C-F}}$ = 249.9 Hz), 143.5, 139.7, 138.8, 137.4, 133.5, 133.3, 131.8, 131.5, 129.5, 129.0, 128.7, 128.6, 127.8, 124.4, 119.7, 115.6, 115.3, 94.8, 85.4, 84.3, 83.6, 41.4, 21.6, 21.4.



N-(2-((4-Ethoxyphenyl)ethynyl)phenyl)-4-methyl-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide (1i)

White solid; m.p. 90-91 °C.

¹H NMR (300 MHz, CDCl₃): δ = 7.75 (d, 2H, *J* = 8.1 Hz), 7.53 (d, 1H, *J* = 7.2 Hz), 7.39 (d, 1H, *J* = 7.5 Hz), 7.28–7.32 (m, 4H), 7.02–7.16 (m, 6H), 6.84 (d, 2H, *J* = 8.4 Hz), 4.80 (s, 2H), 4.06 (q, 2H, *J* = 6.9 Hz), 2.31 (s, 3H), 2.29 (s, 3H), 1.43 (t, 3H, *J* = 6.9 Hz).

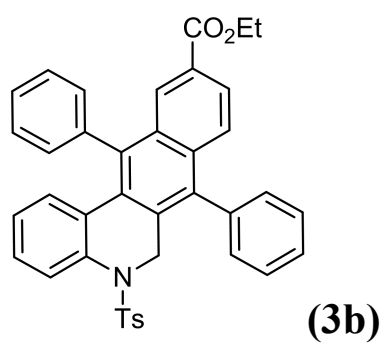
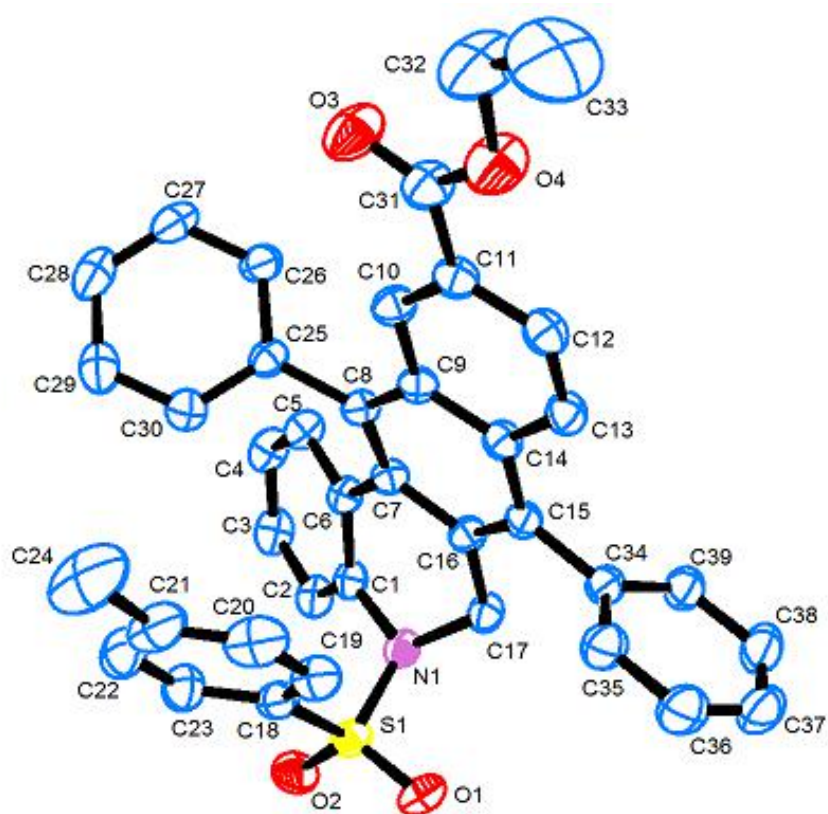
¹³C NMR (75.5 MHz, CDCl₃): δ = 159.3, 143.4, 139.7, 138.5, 137.6, 133.1, 133.1, 131.7, 131.5, 129.5, 128.9, 128.5, 128.4, 127.8, 124.7, 119.5, 114.8, 114.4, 94.7, 85.5, 84.8, 83.6, 63.6, 41.2, 21.5, 21.4, 14.8.

Preparation of 5,6-Dihydrobenzo[*j*]phenanthridines: Typical procedure: Diyne **1a-1i** (1.0 mmol), aryl halide (1.1 mmol), [Pd(OAc)₂] (2 mmol %), Ph₃P (4 mmol %), and (*n*-Bu)₃N (2 mmol) were added to a degassed DMF (7 mL). The mixture was stirred at r. t. for 30 min then heated to 130 °C for 24 h. The mixture was then cooled and the reaction was quenched with H₂O (5 mL). The mixture was extracted with EtOAc (30 mL) and the organic layers were combined and washed successively with 10% aq HCl (6 mL), 10% aq NaHCO₃ (6 mL), and sat. aq NaCl (6 mL) then dried (MgSO₄) and concentrated. The residue was purified by flash column chromatography (silica gel, PE–EtOAc, 30:1) to give **3a-3v**.

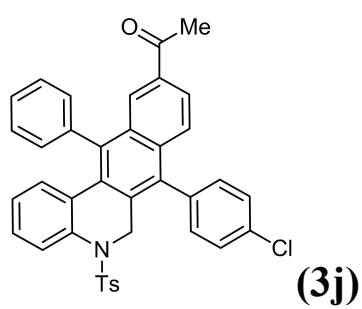
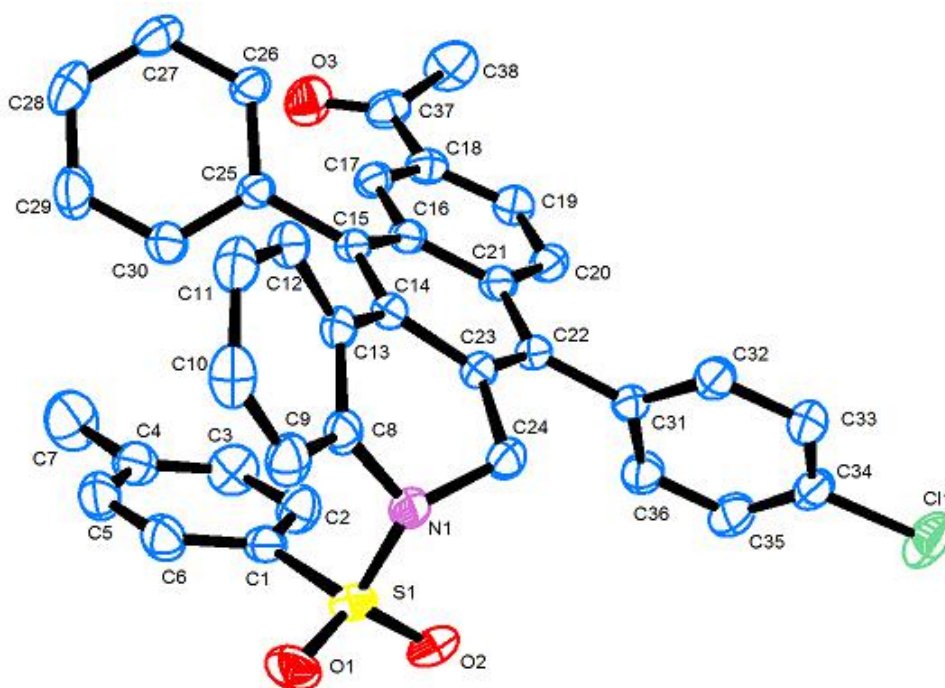
References

- (1) (a) J. Liu, X. Xie, Y. Liu. *Chem. Commun.* 2013, **49**, 11794; (b) Z. Hu, X. Tong, G. Liu. *Org. Lett.* 2016, **18**, 2058; (c) T. Meng, Y. Hu, S. Wang. *J. Org. Chem.* 2010, **75**, 582.

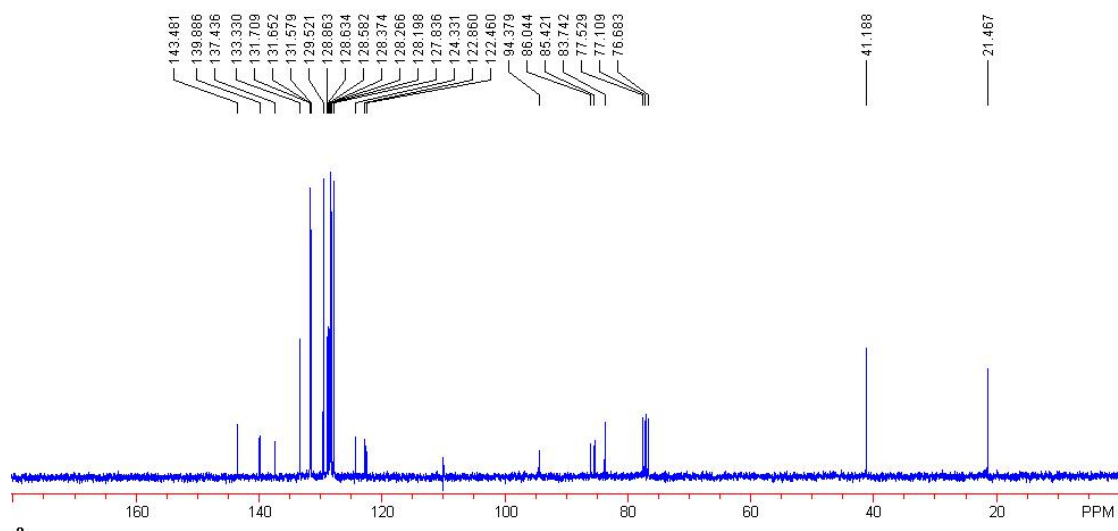
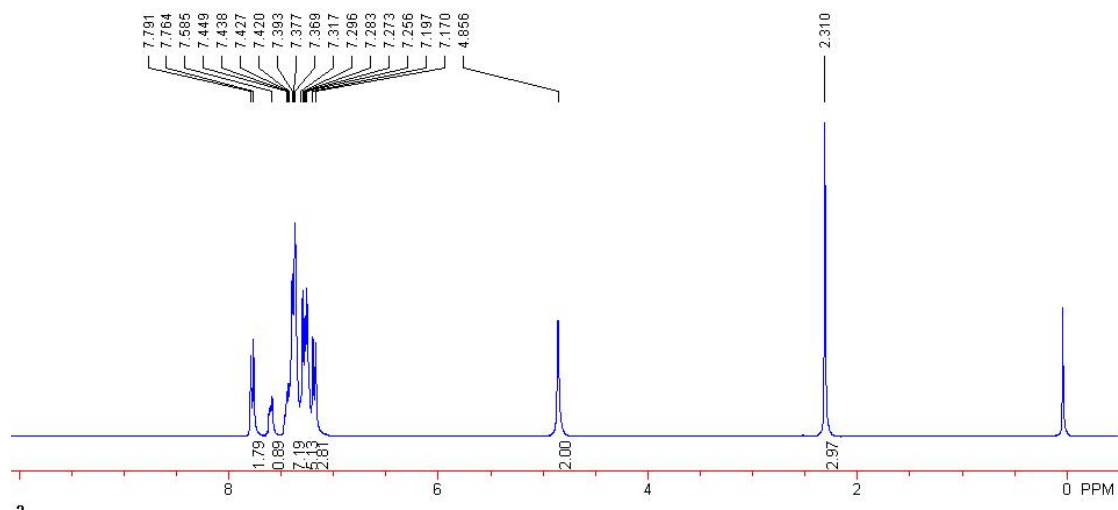
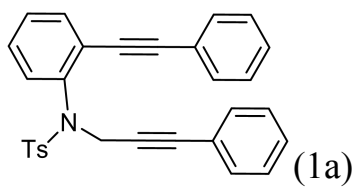
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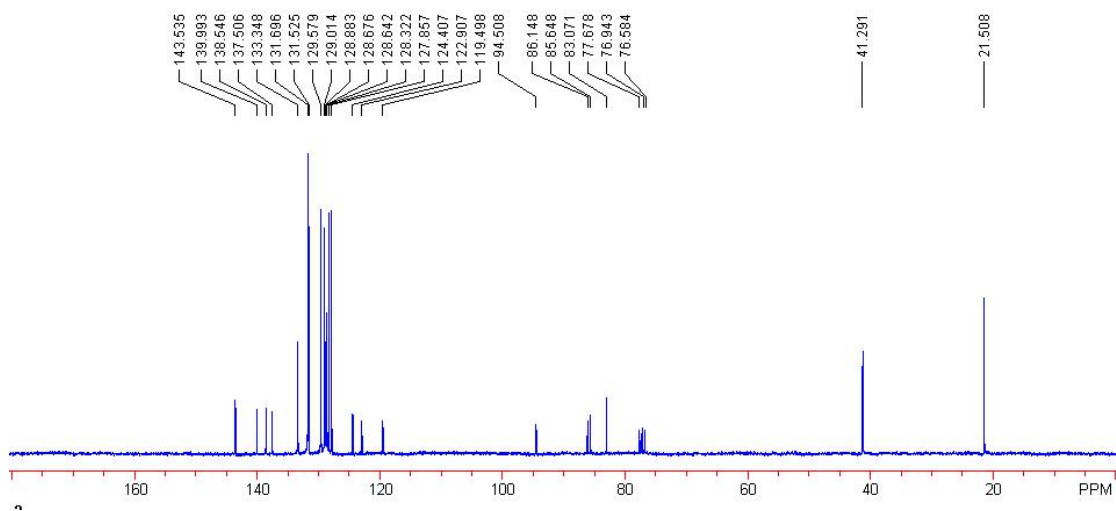
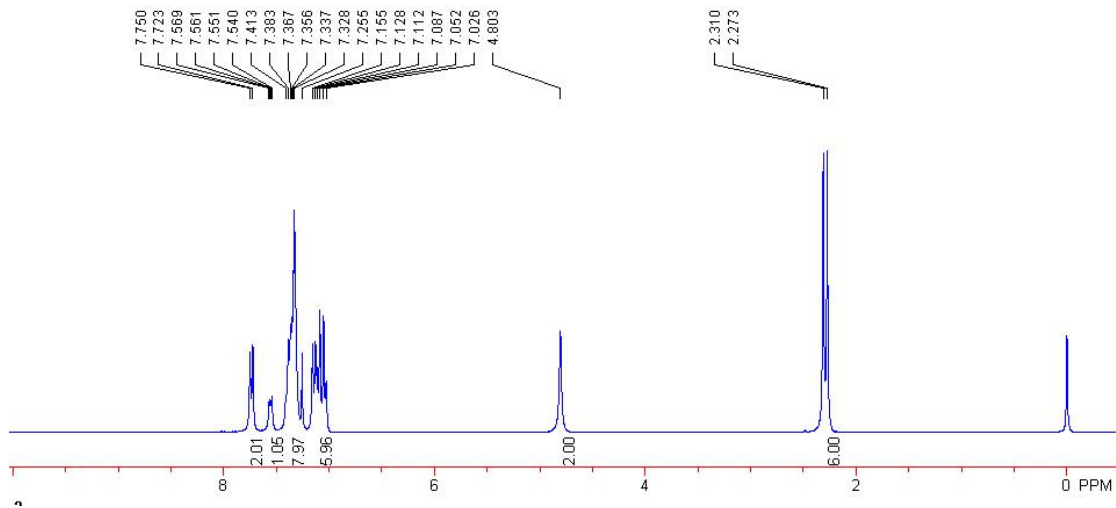
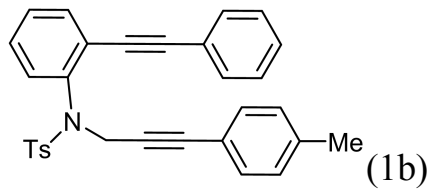


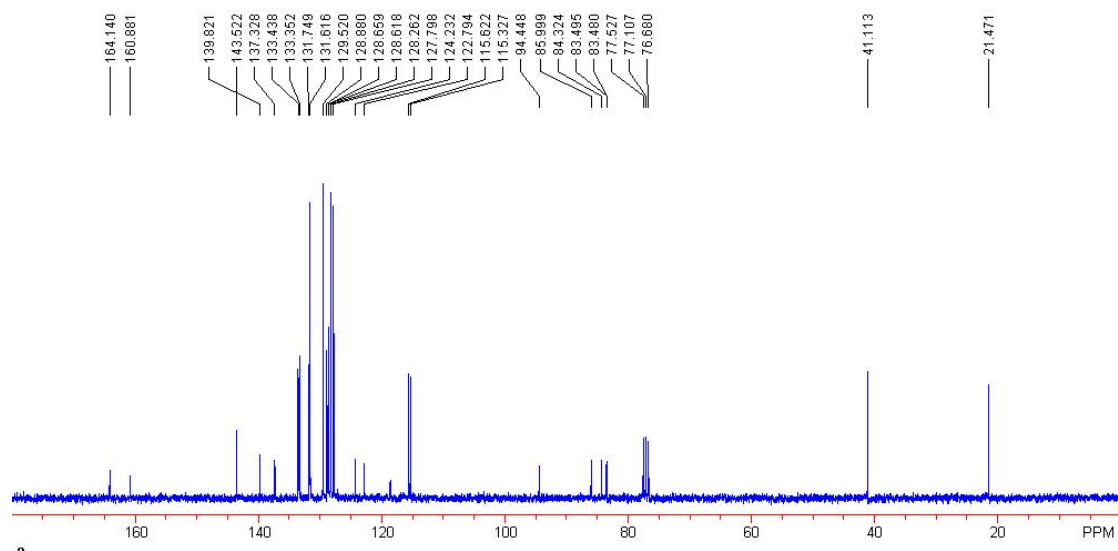
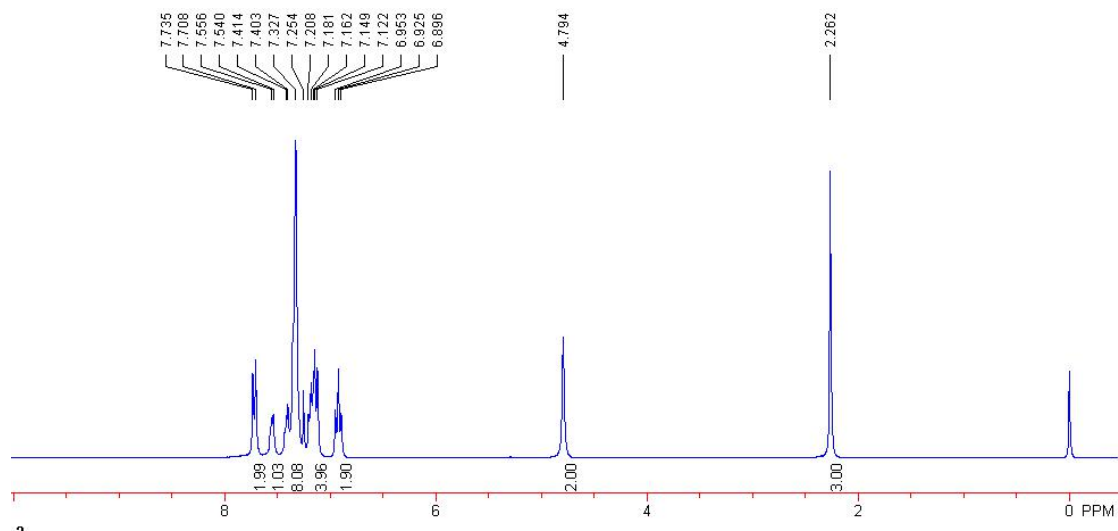
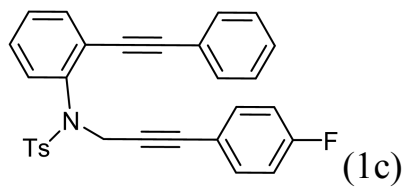
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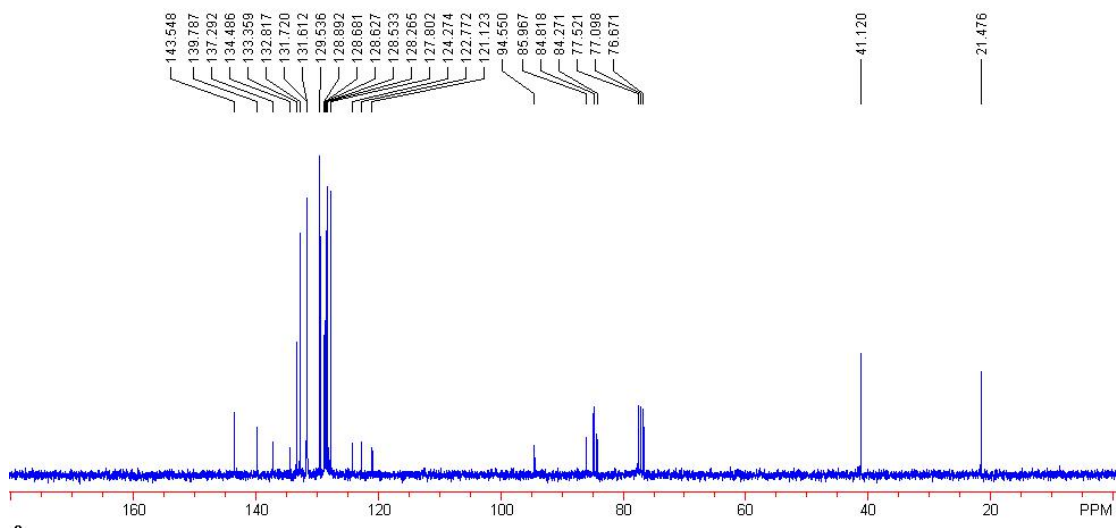
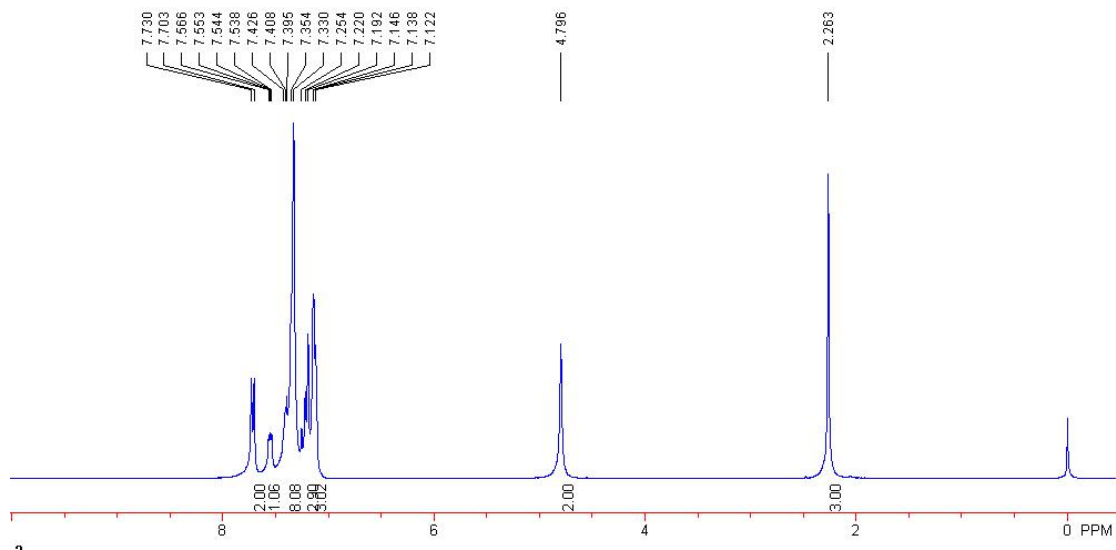
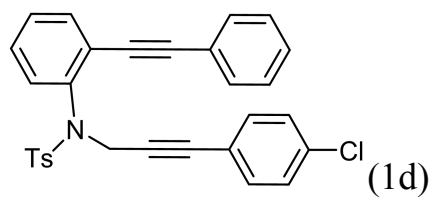


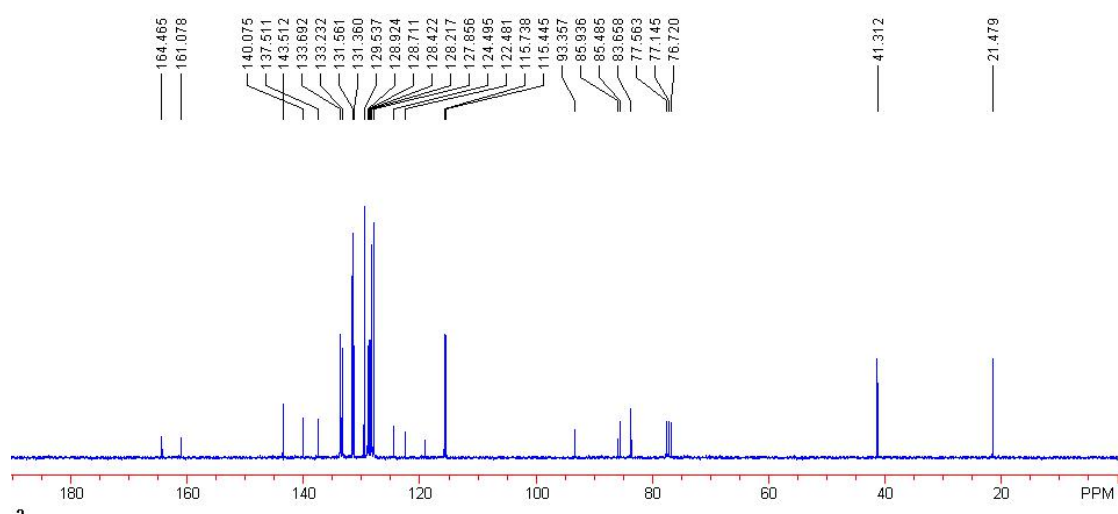
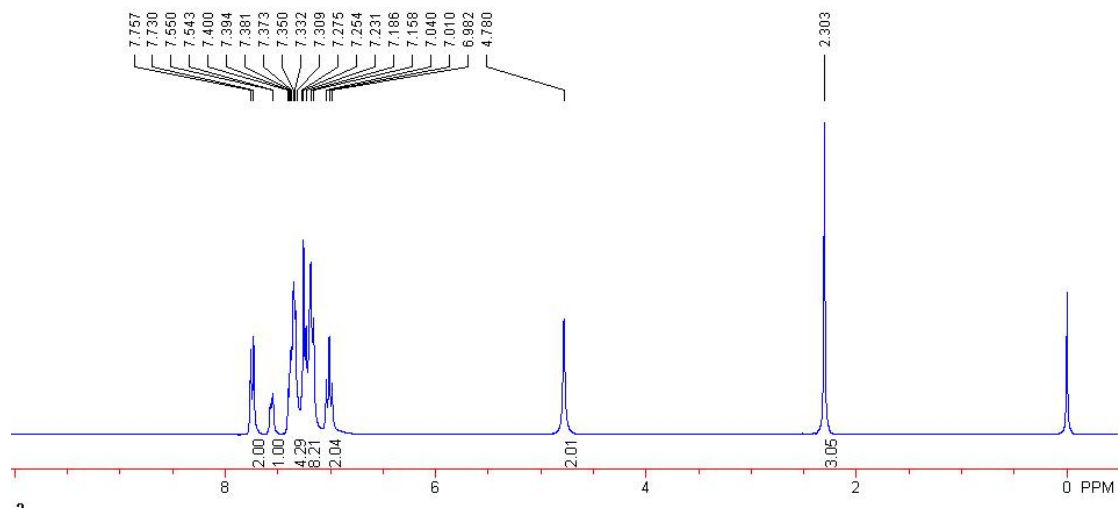
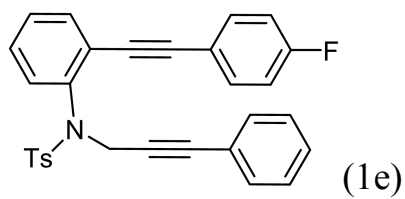
4. ^1H NMR & ^{13}C NMR Spectra for New Compounds

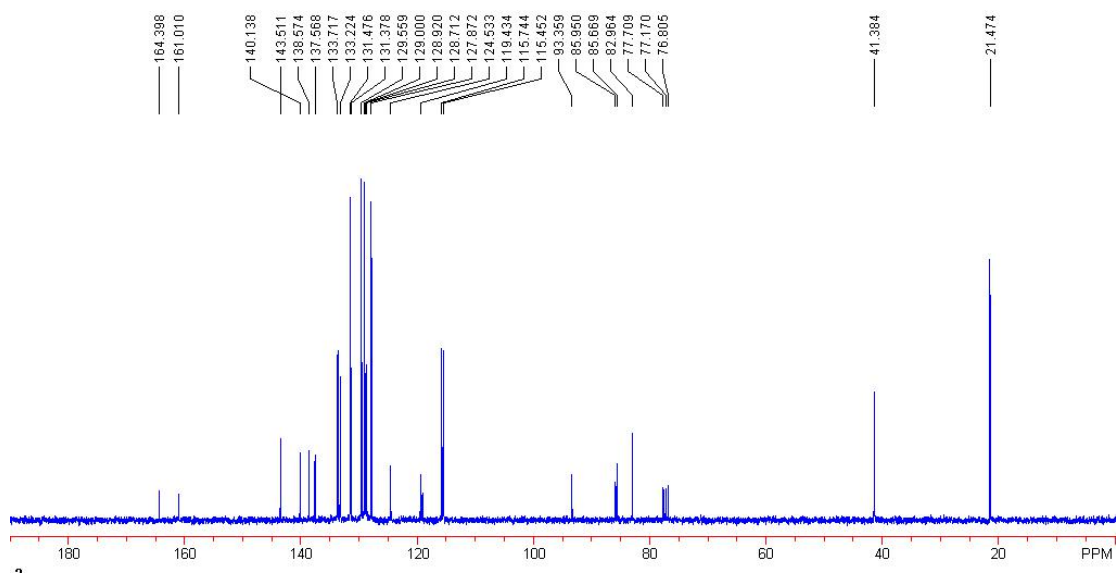
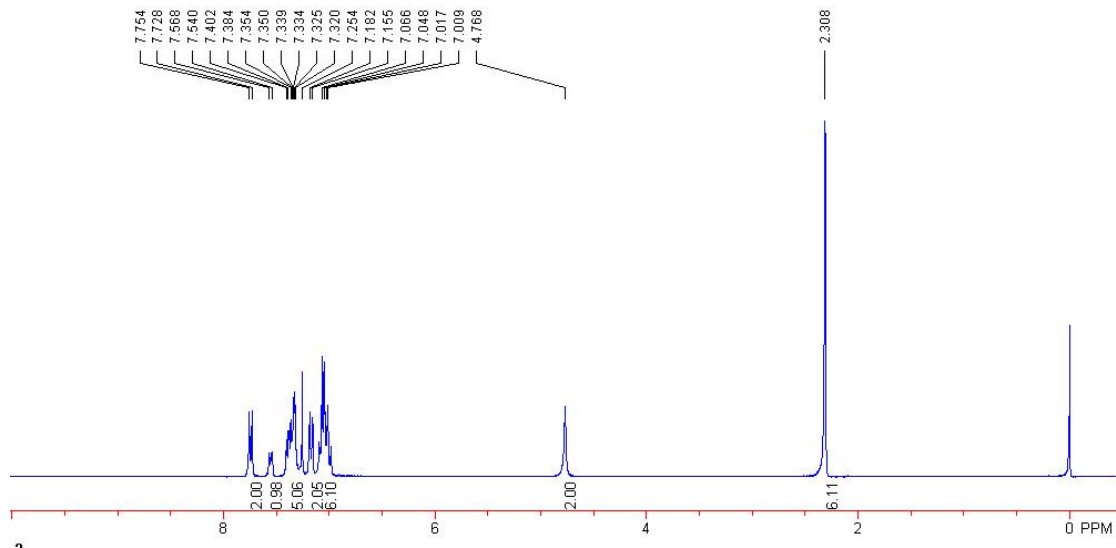
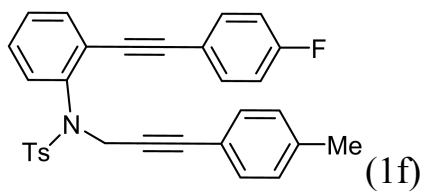


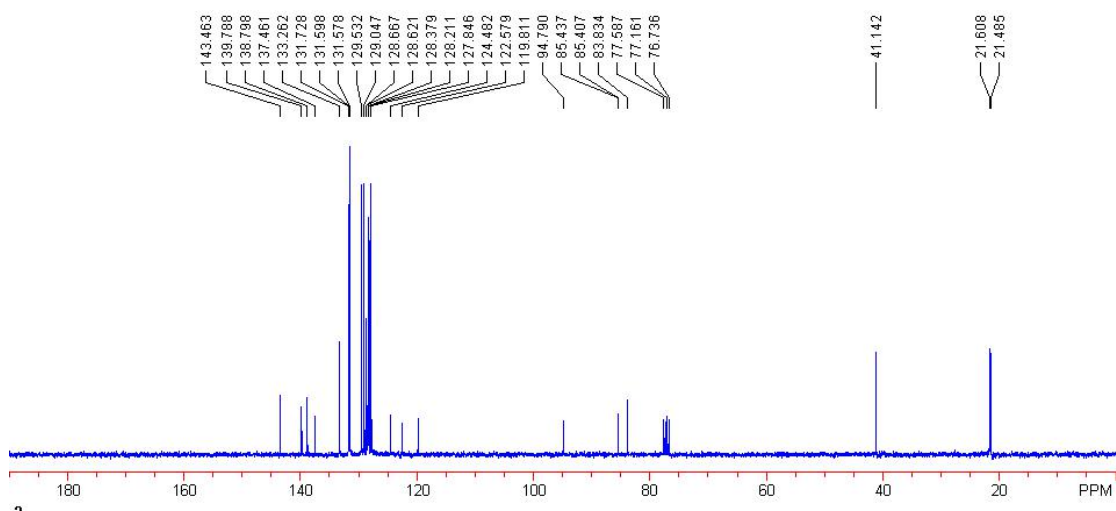
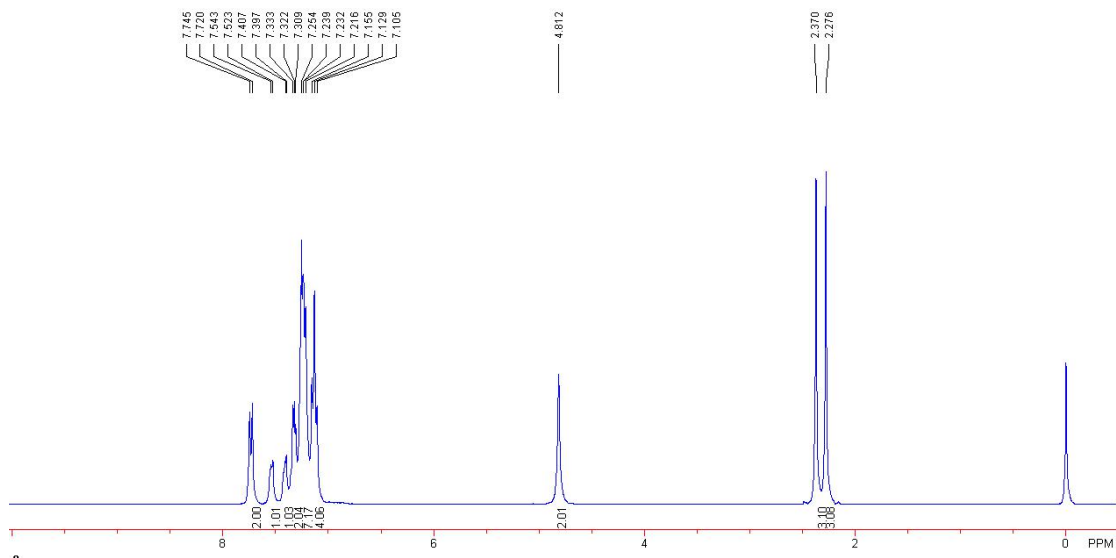
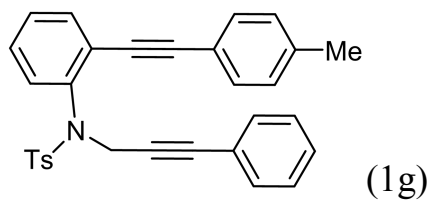


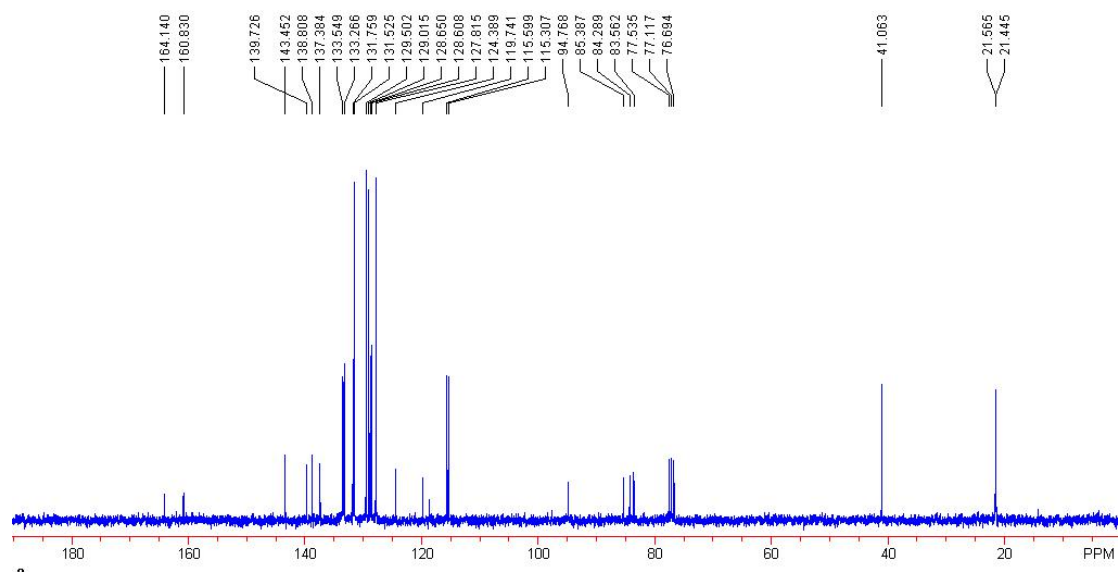
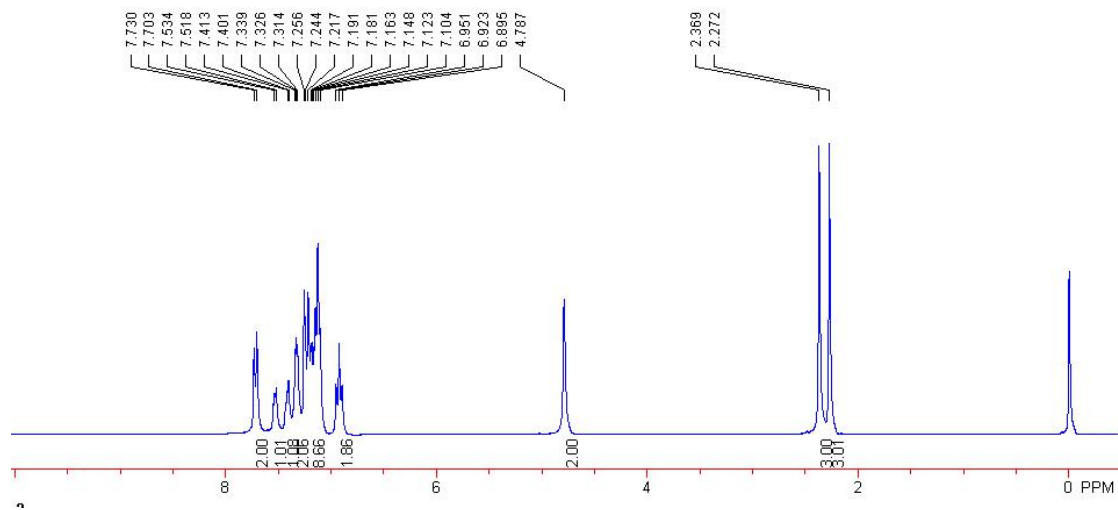
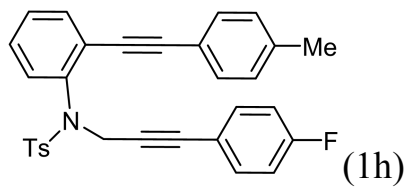


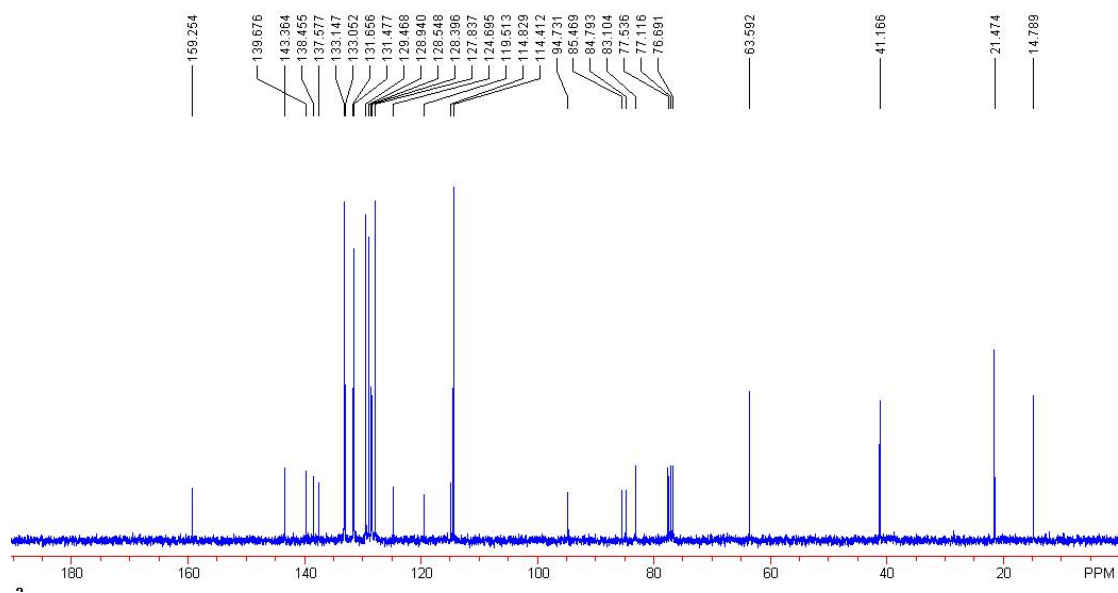
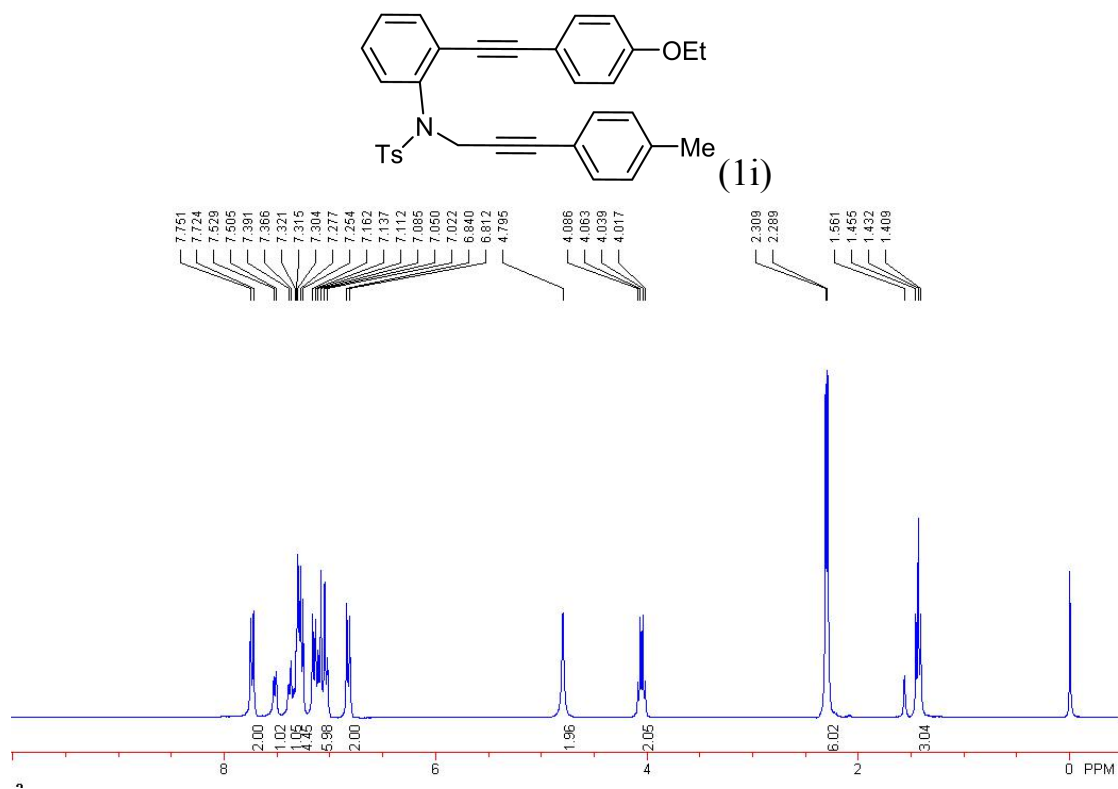


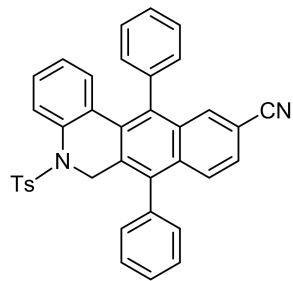




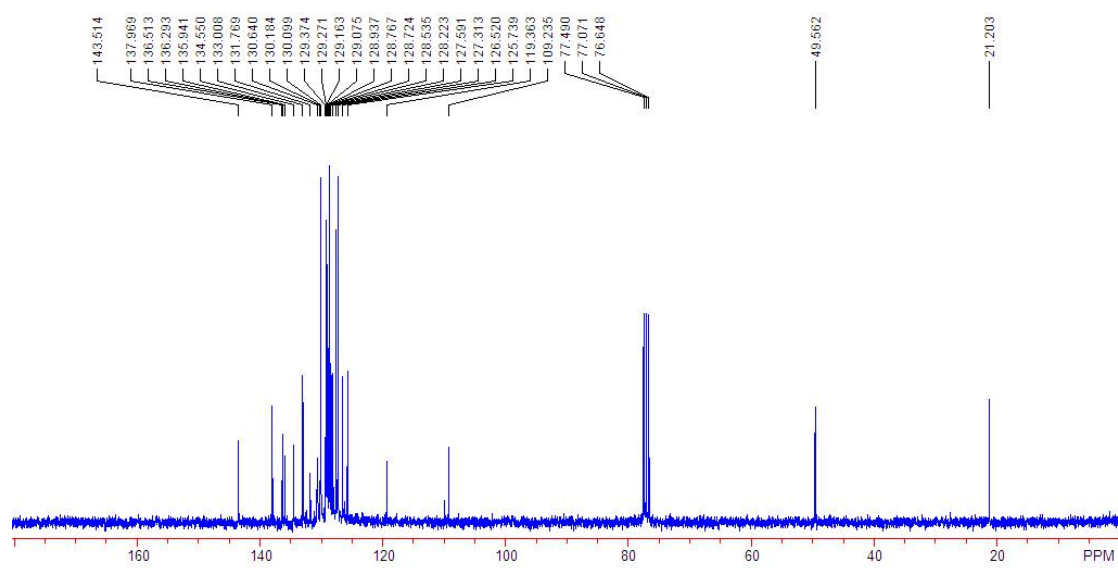
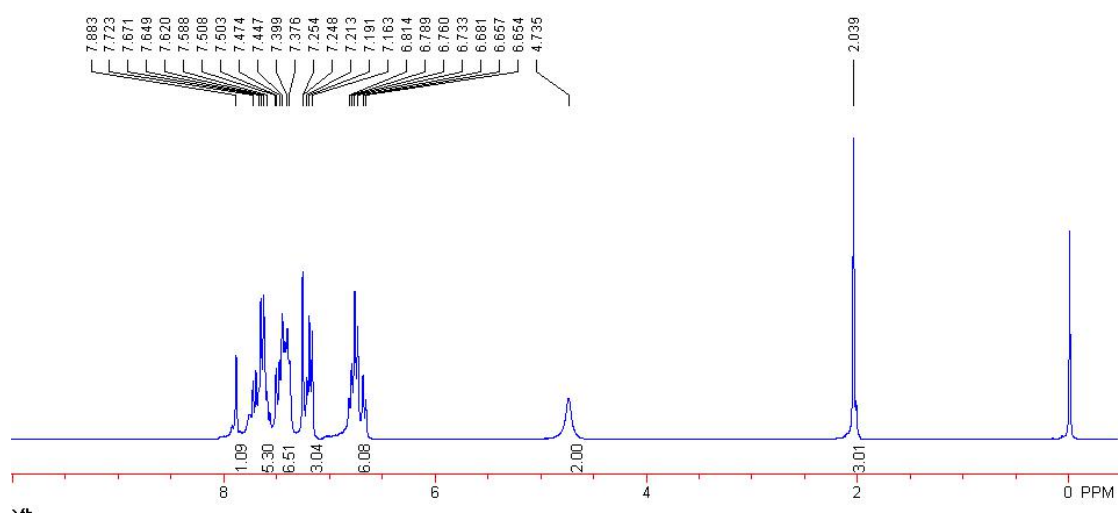


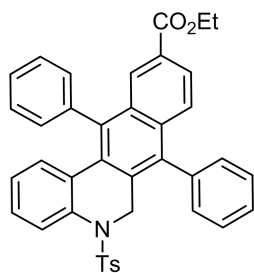




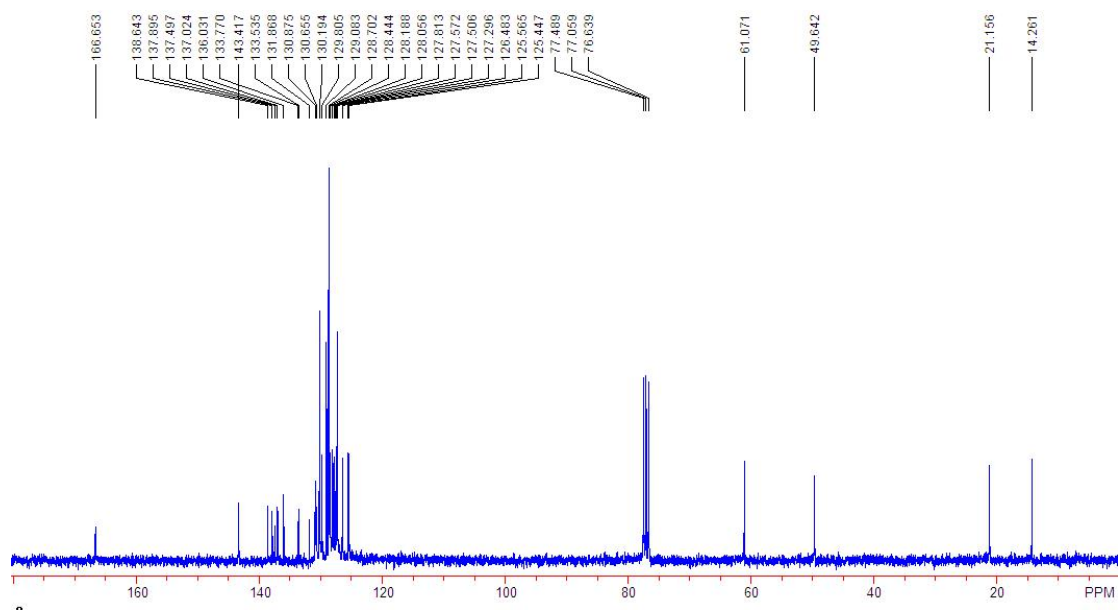
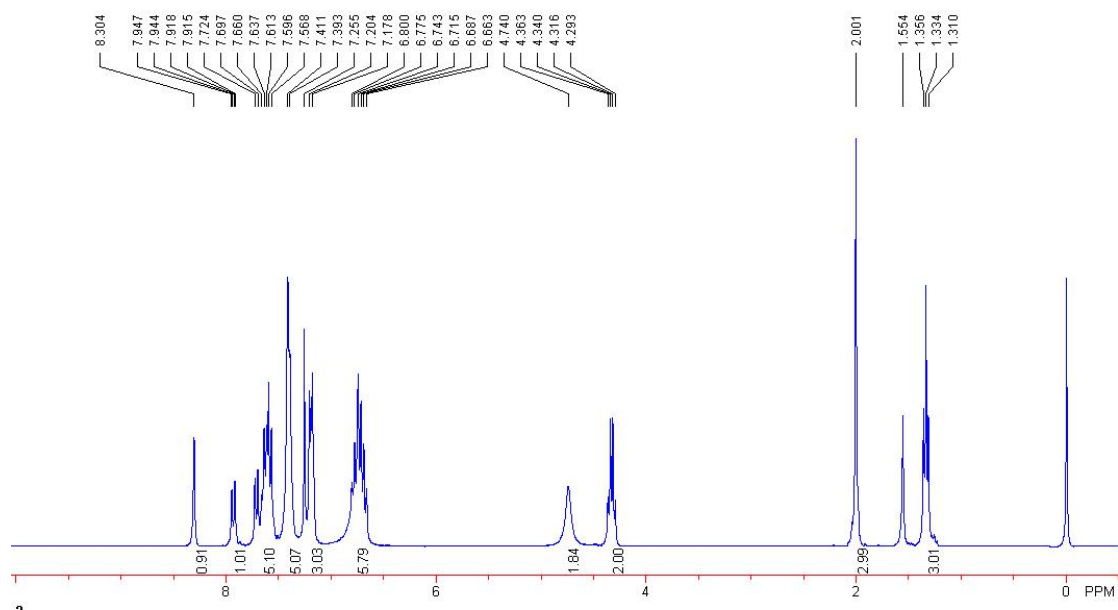


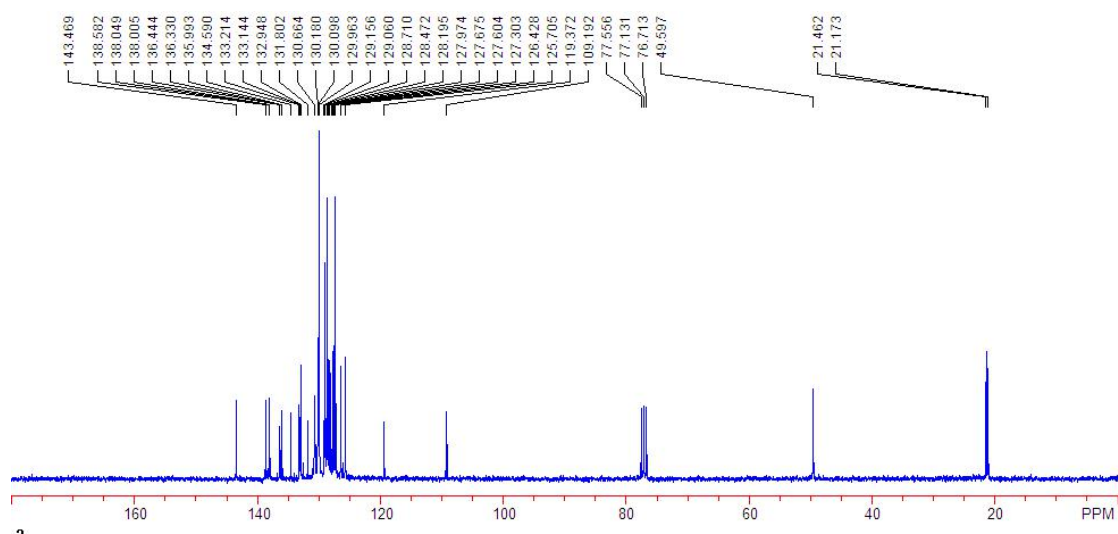
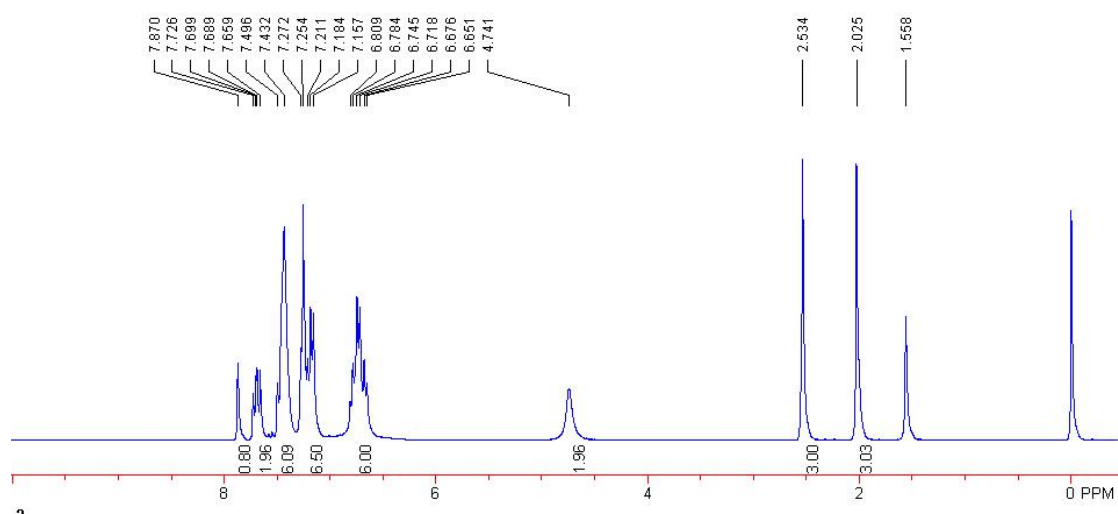
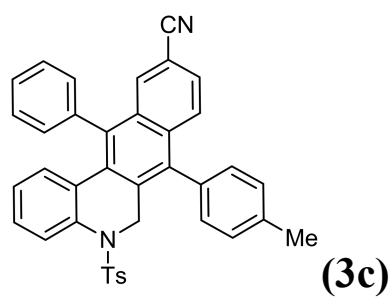
(3a)

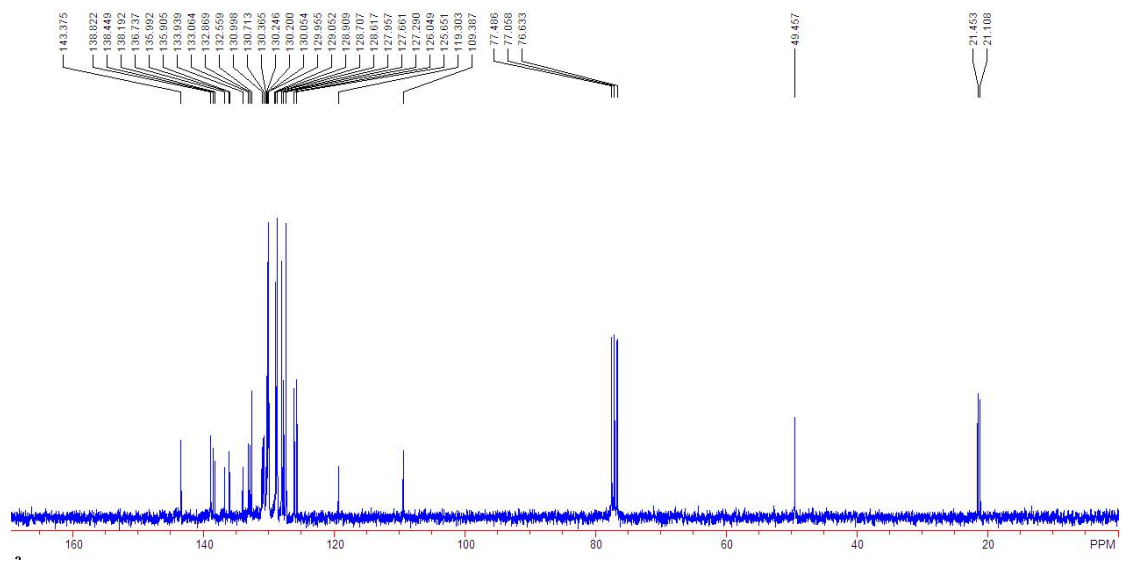
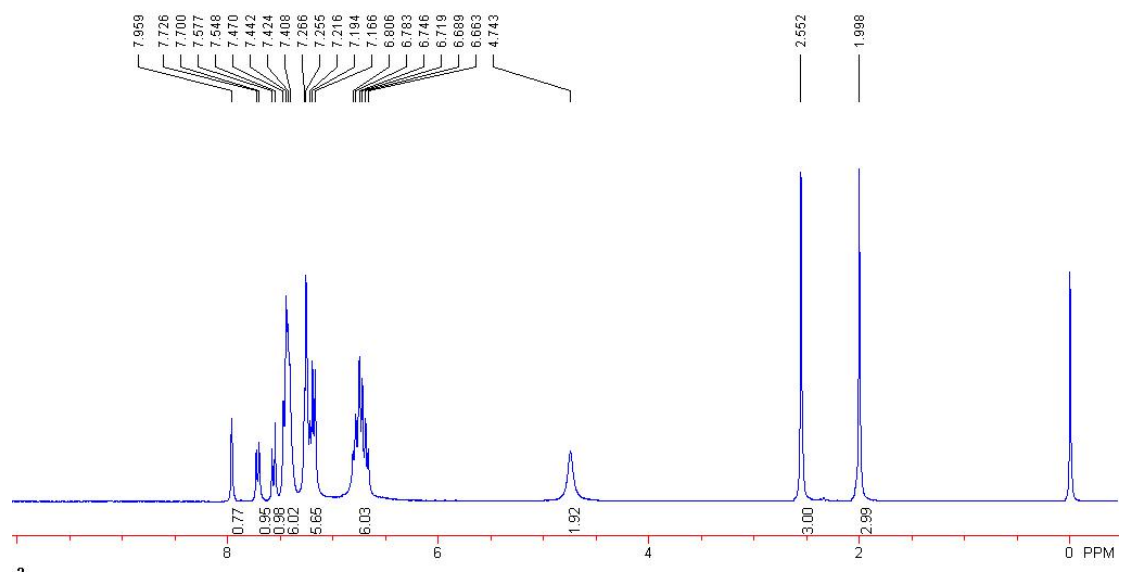
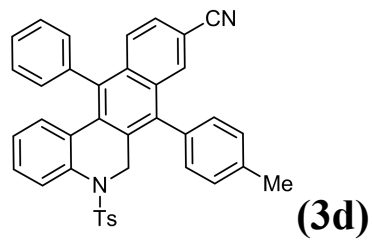


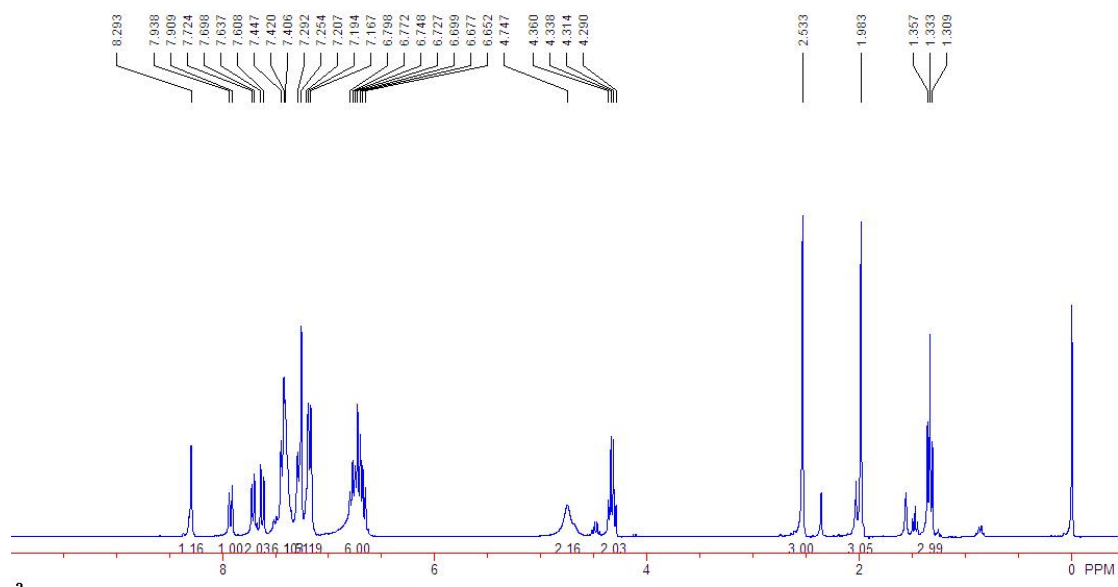
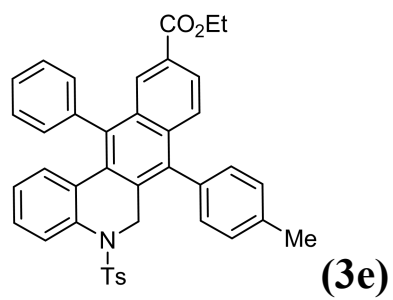


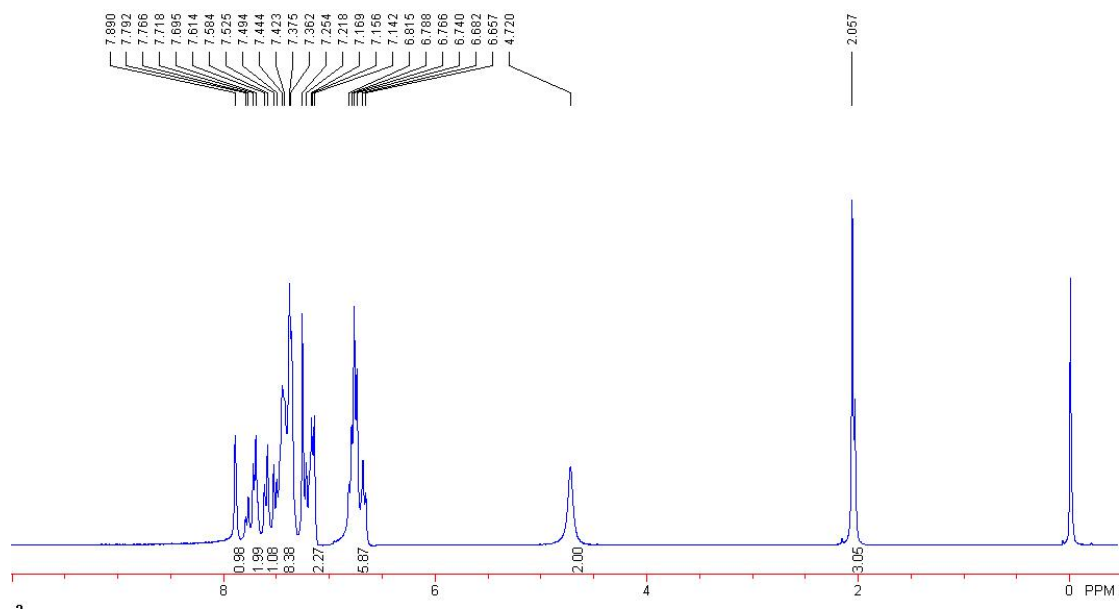
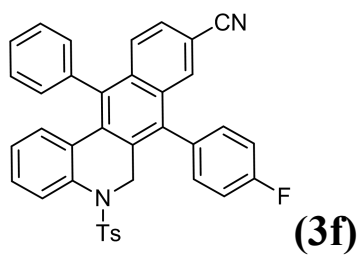
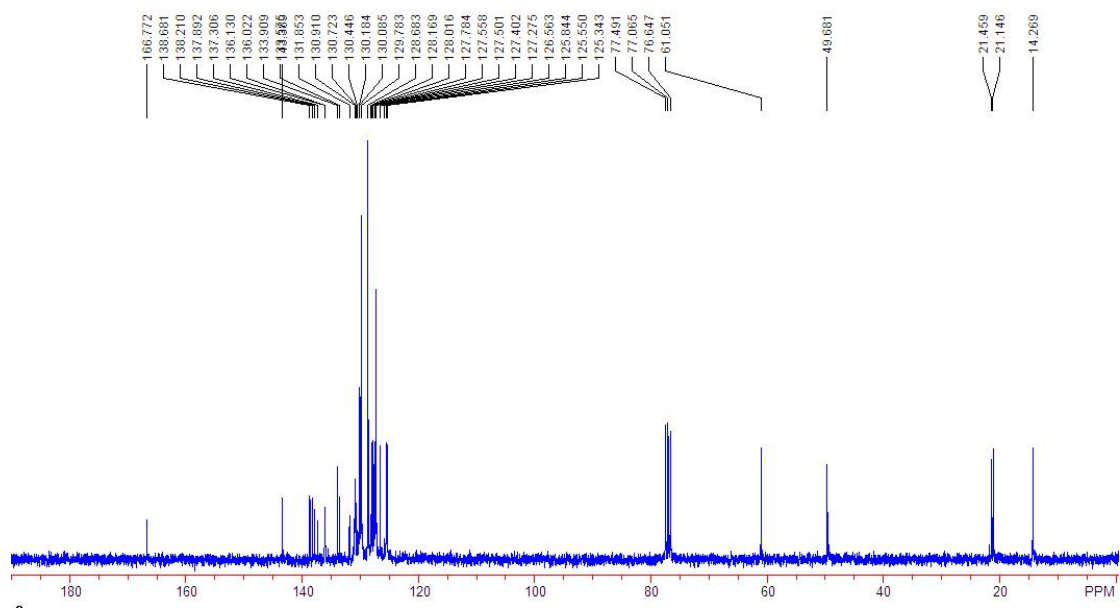
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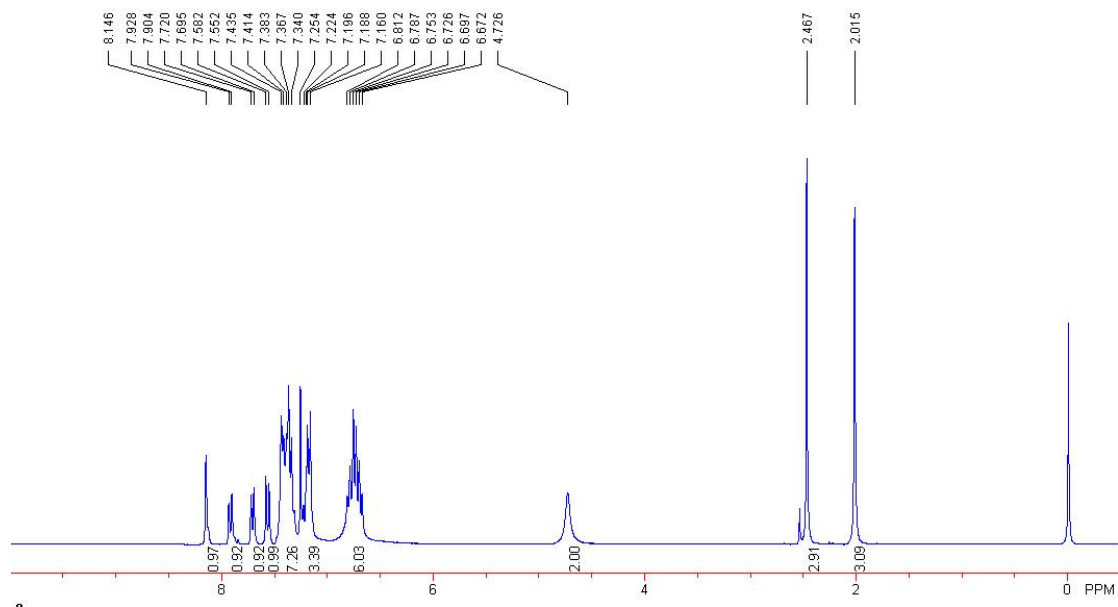
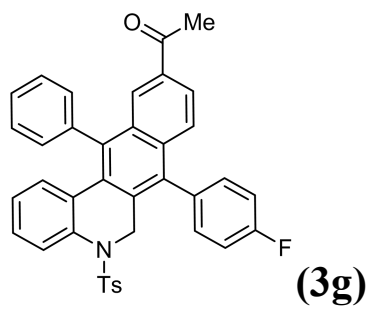
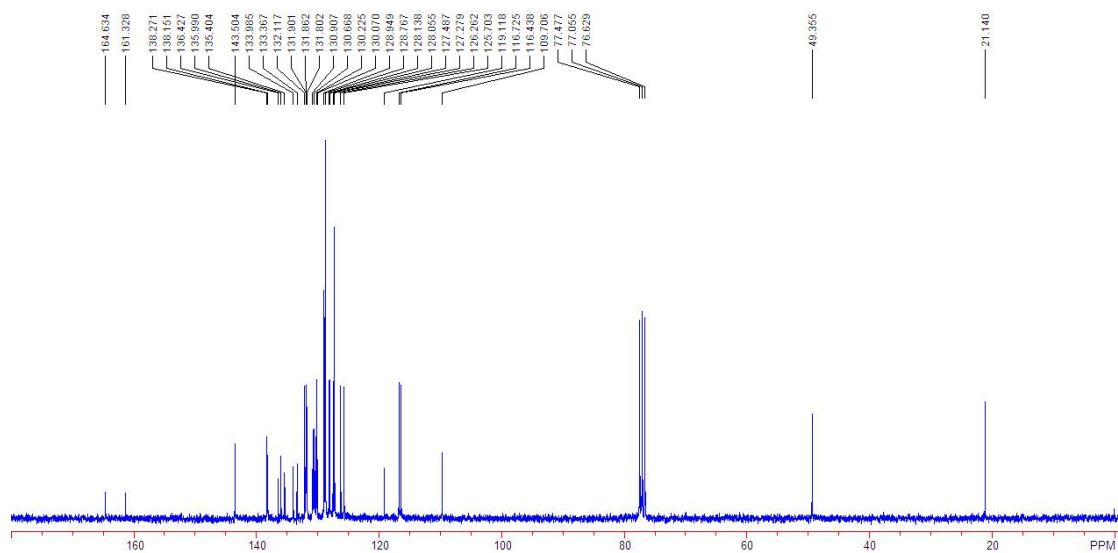


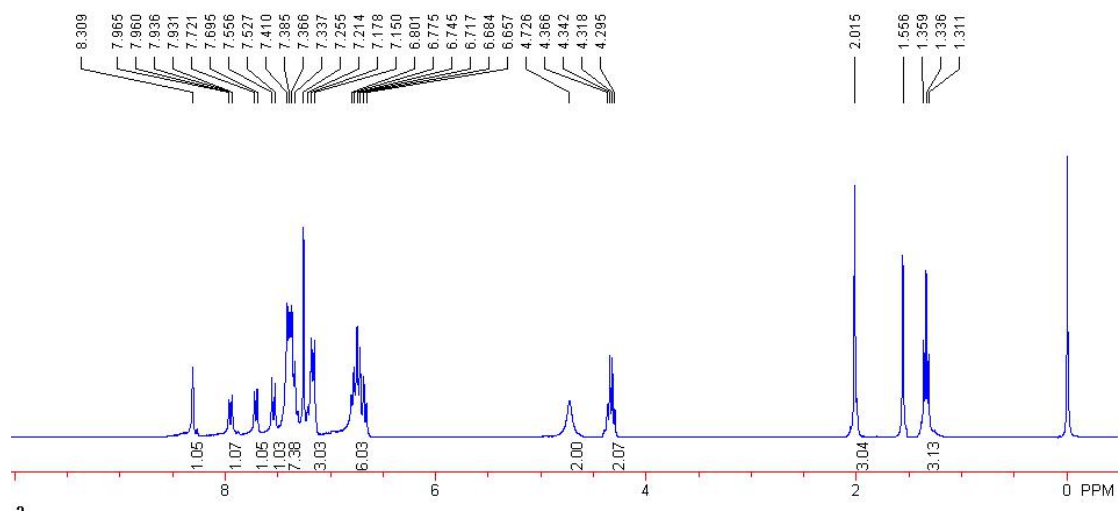
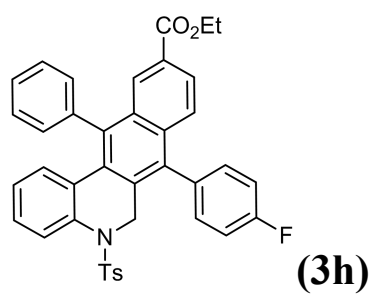
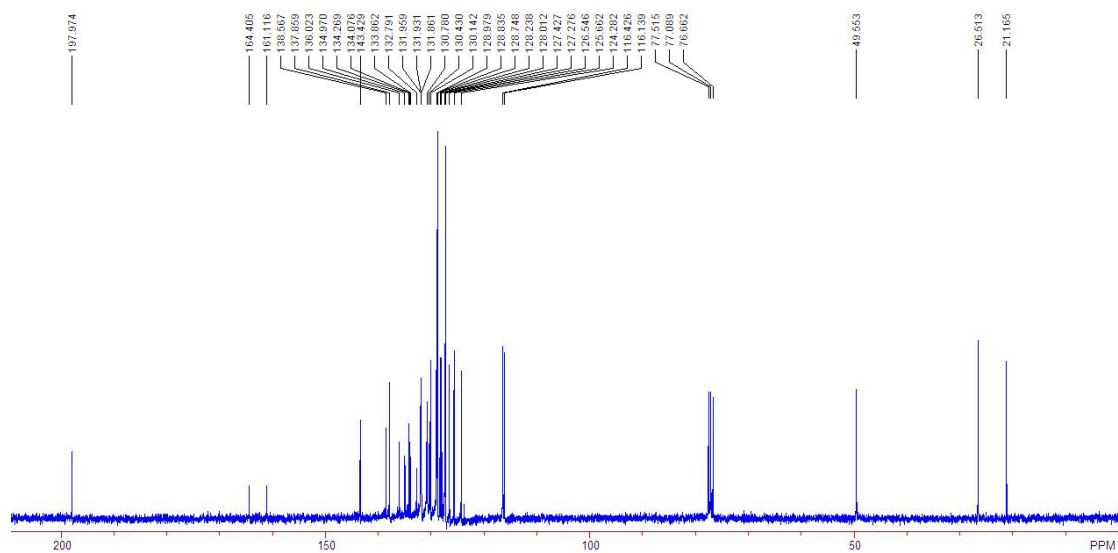


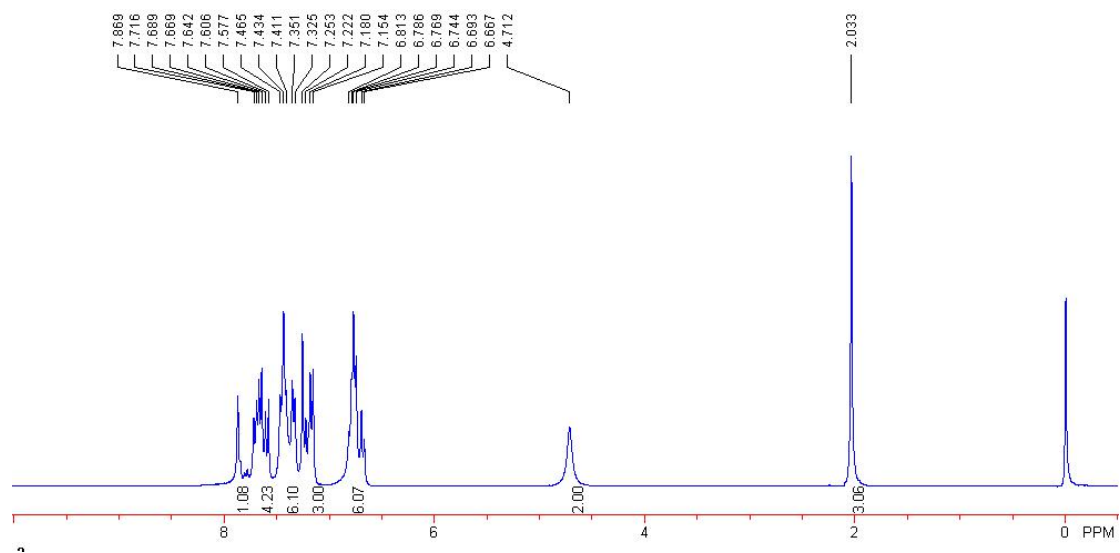
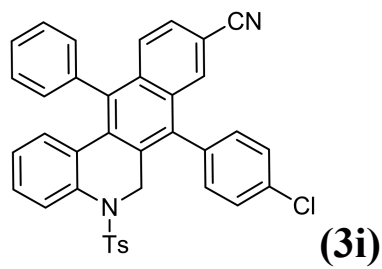
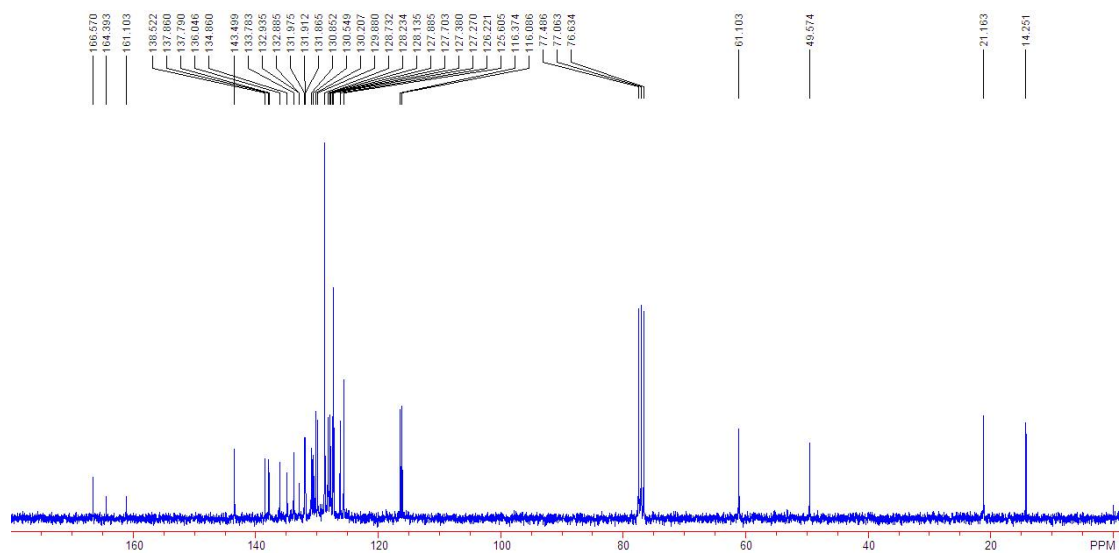


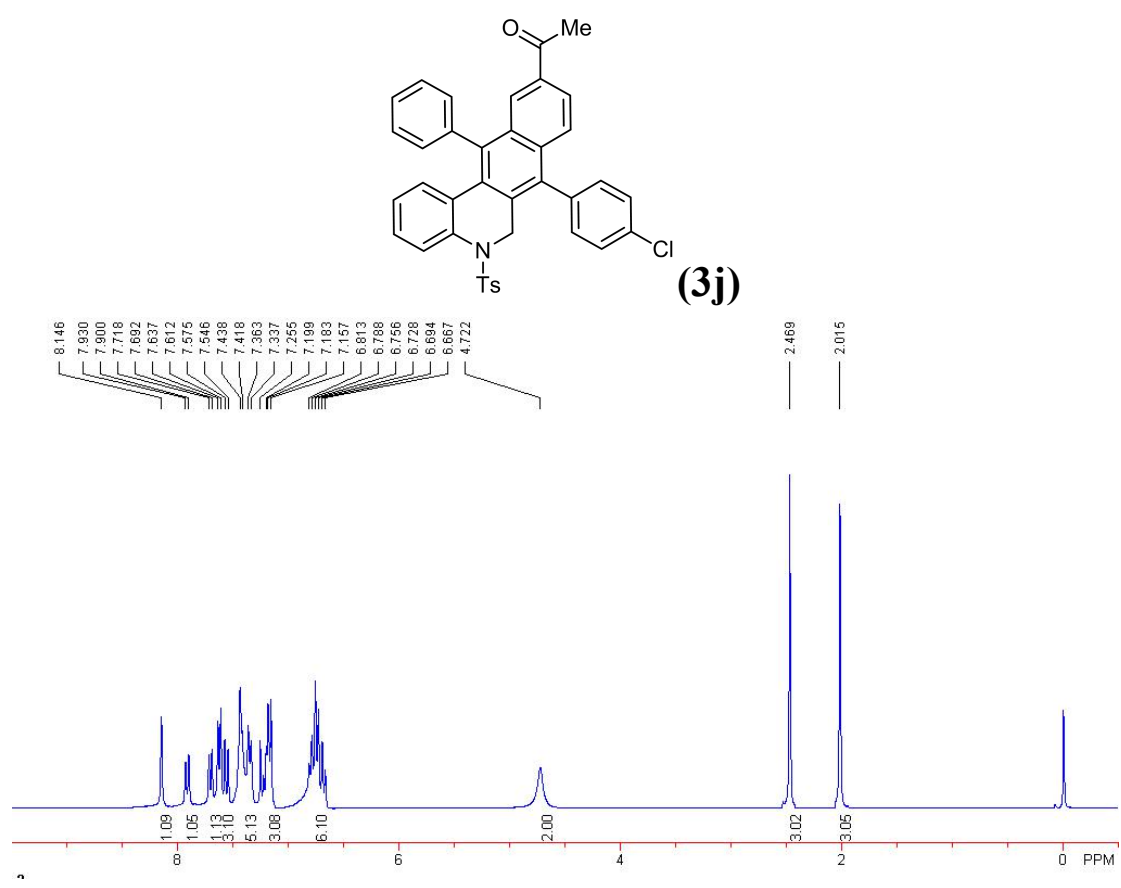
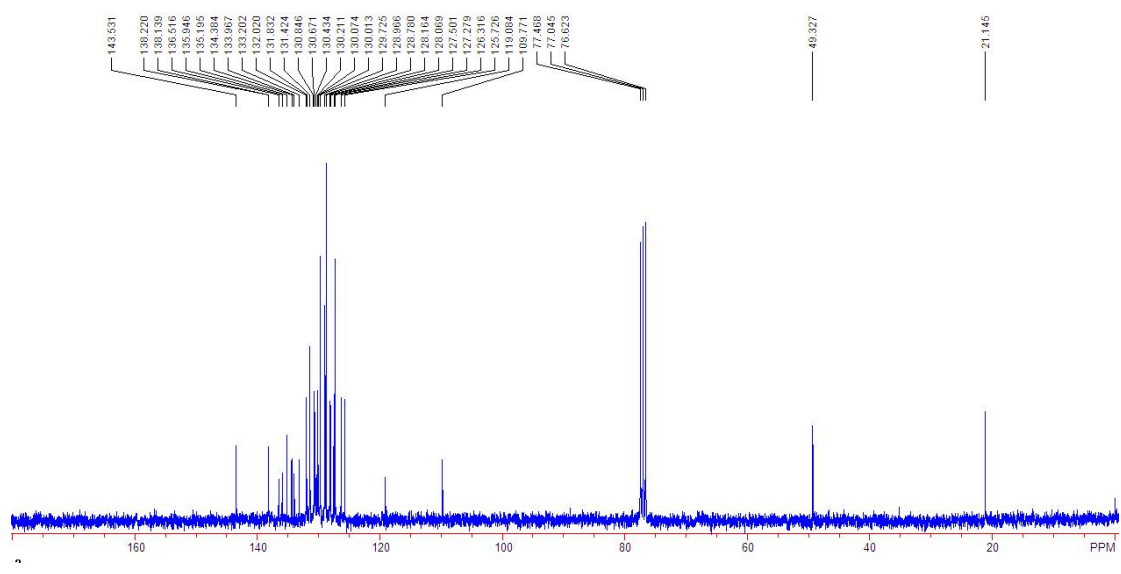


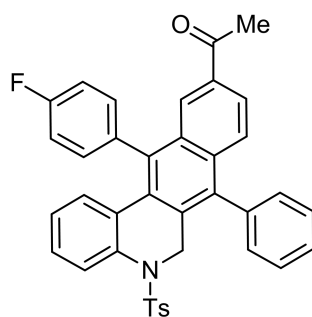
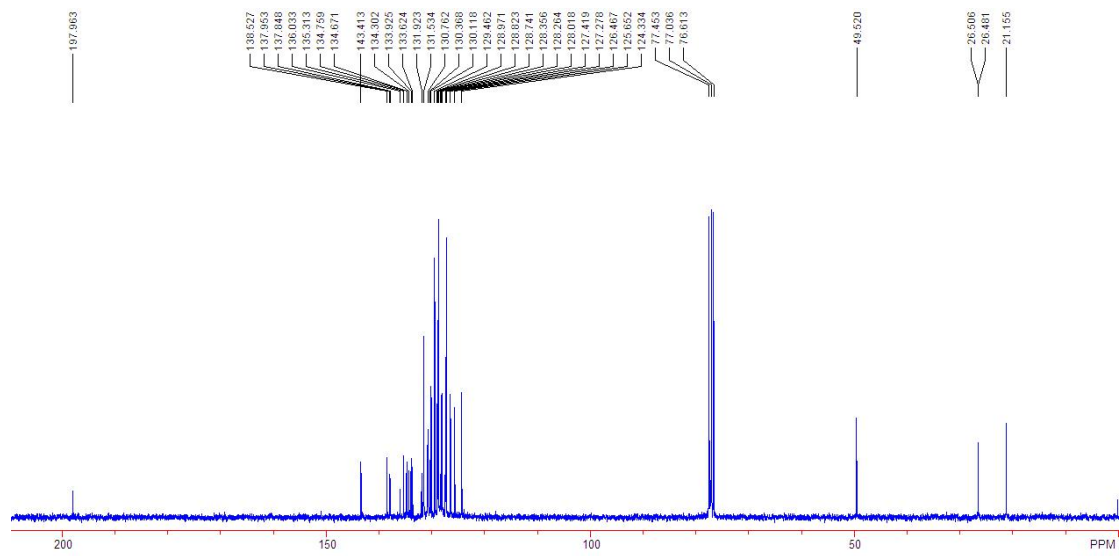




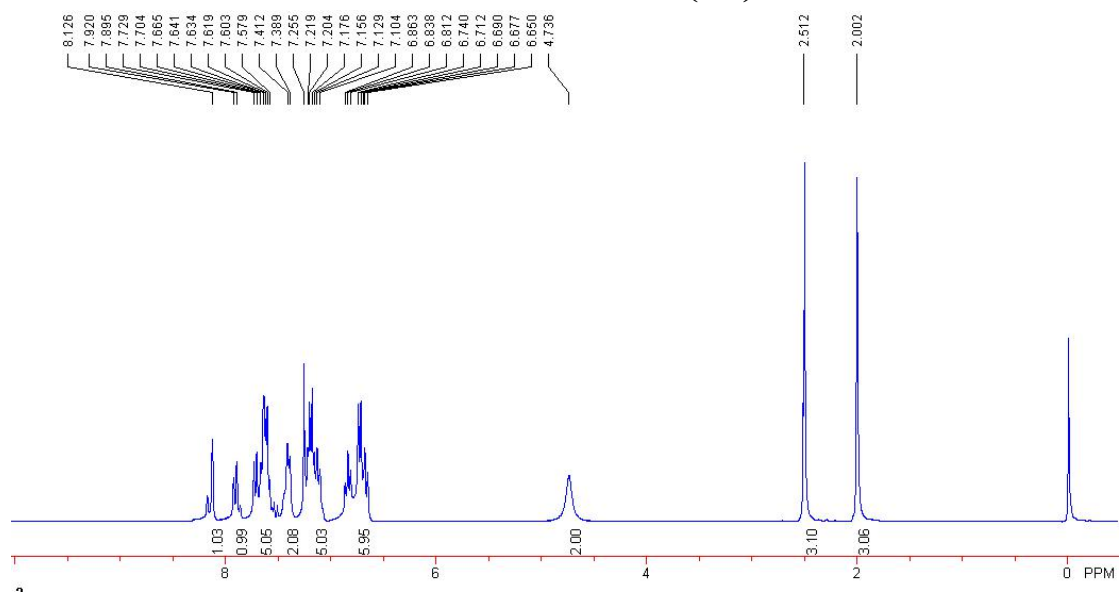


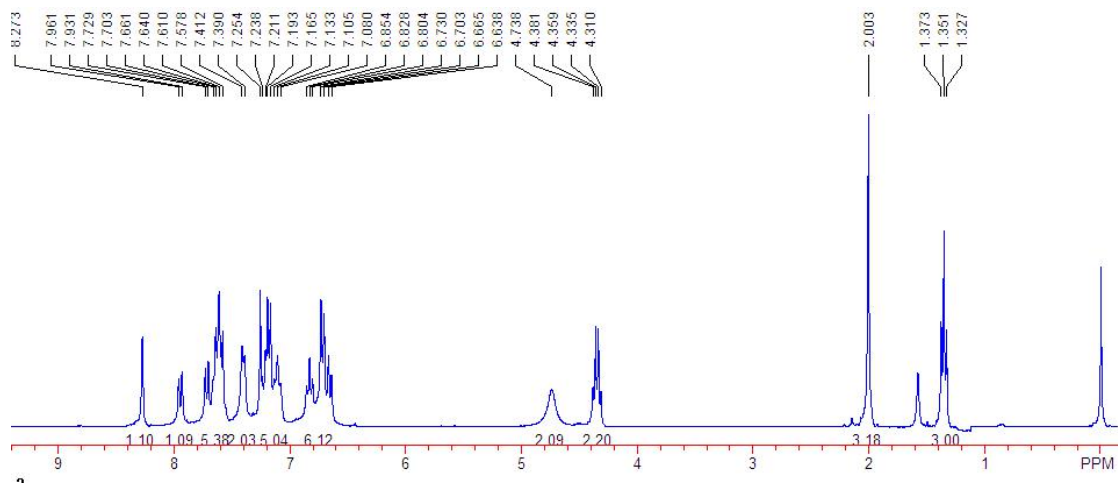
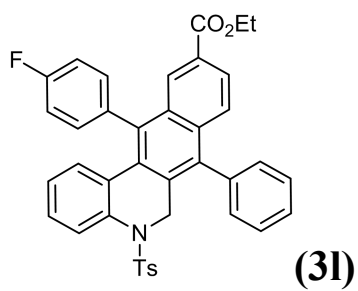
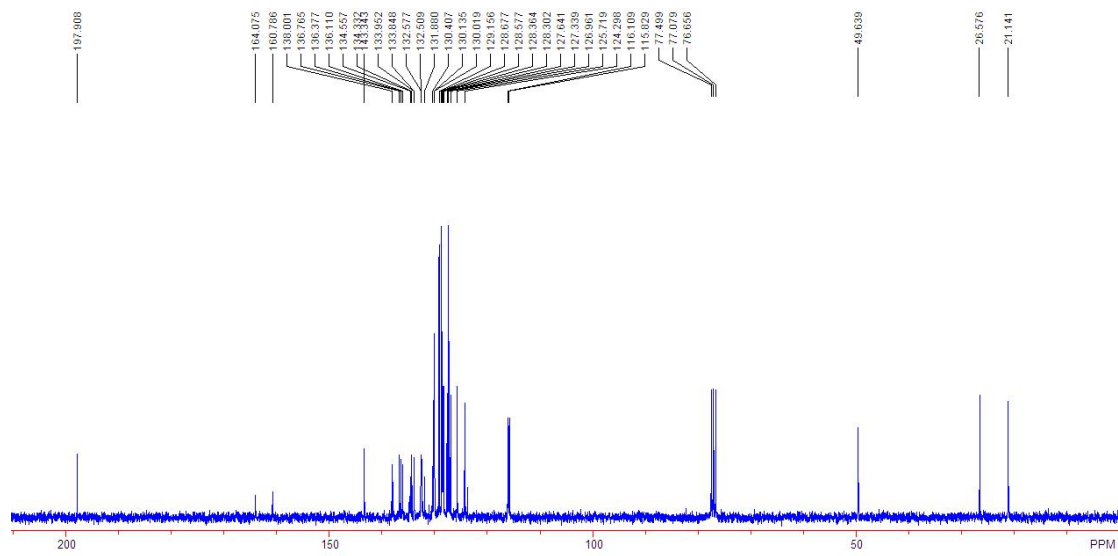


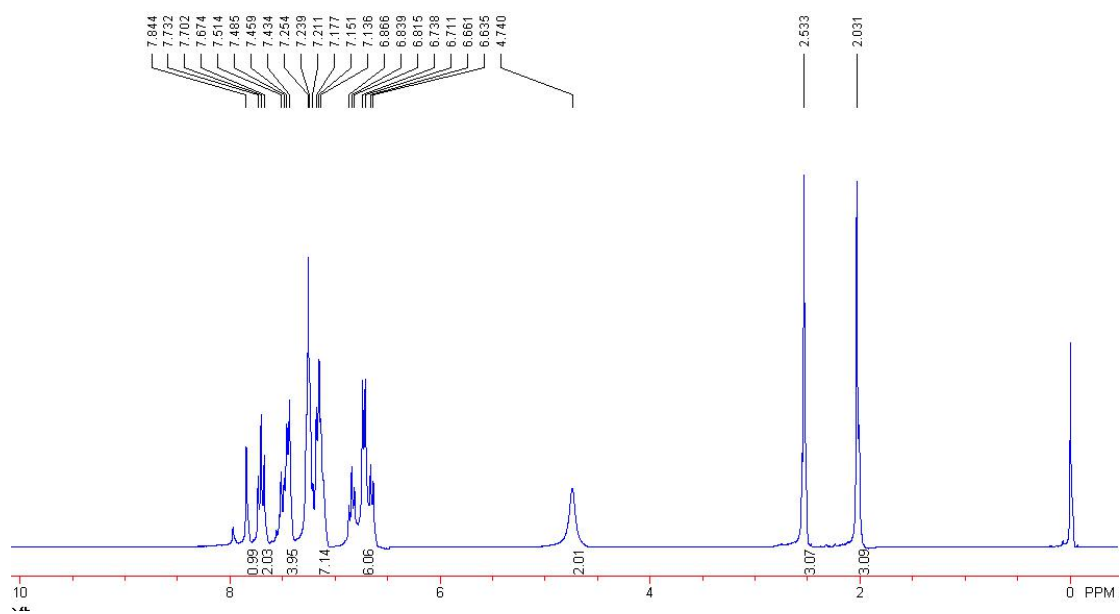
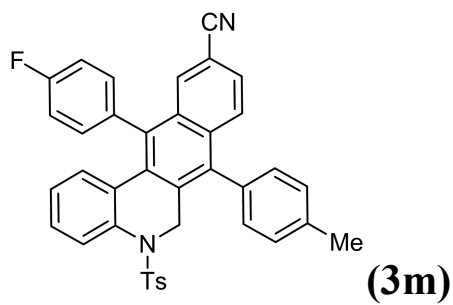
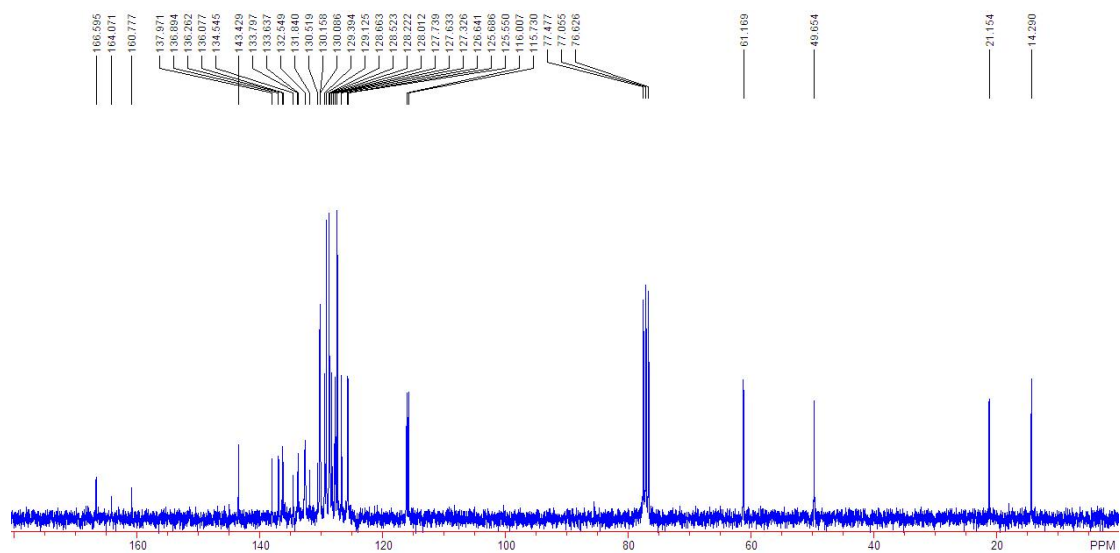


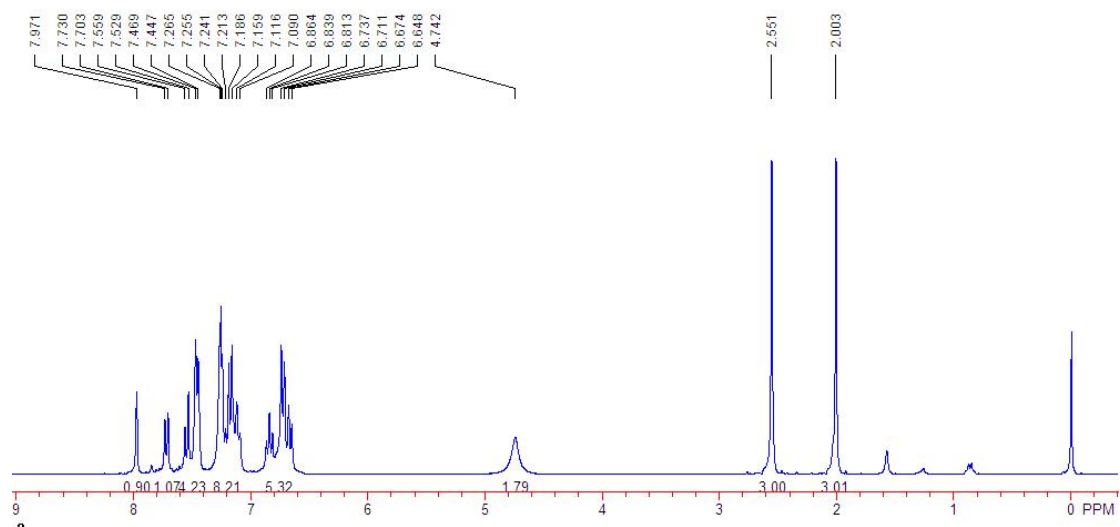
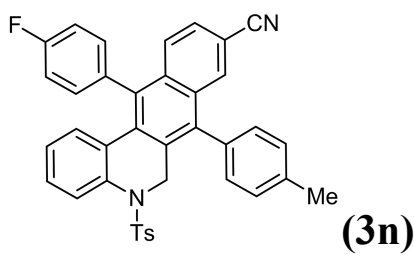
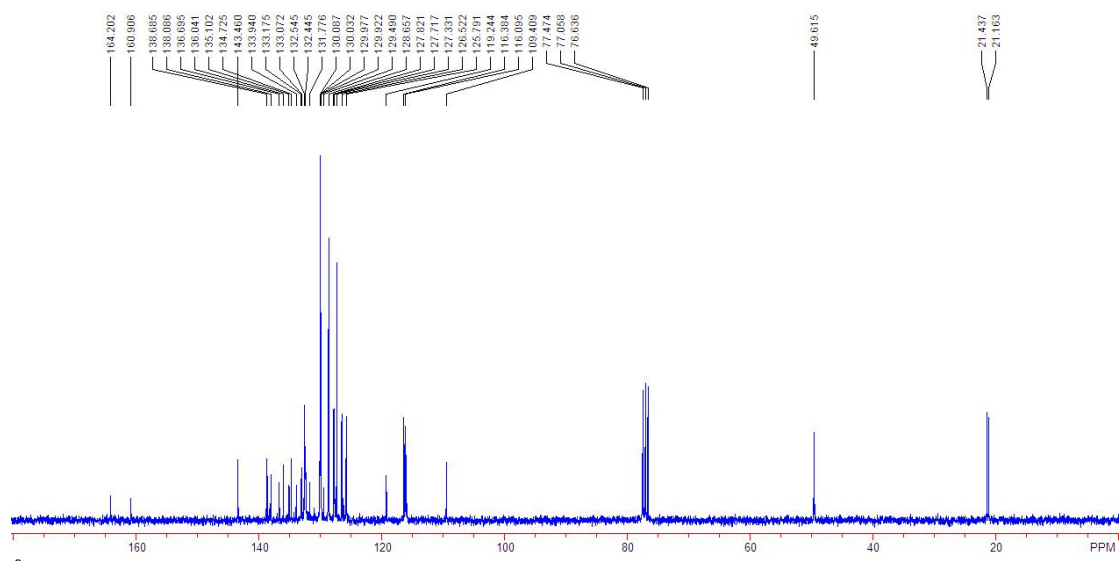


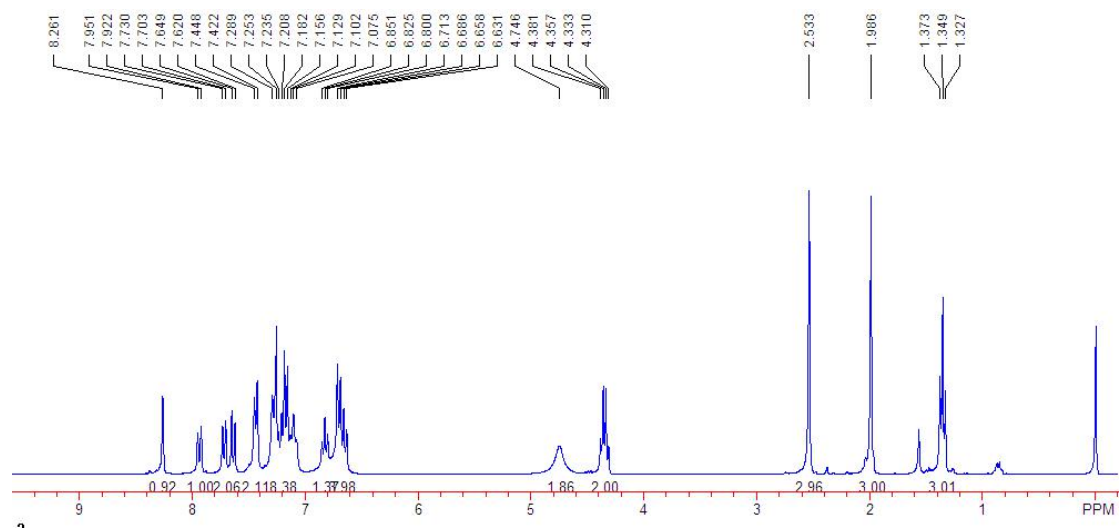
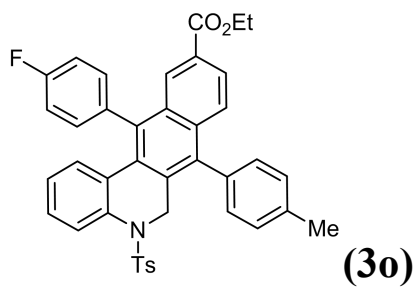
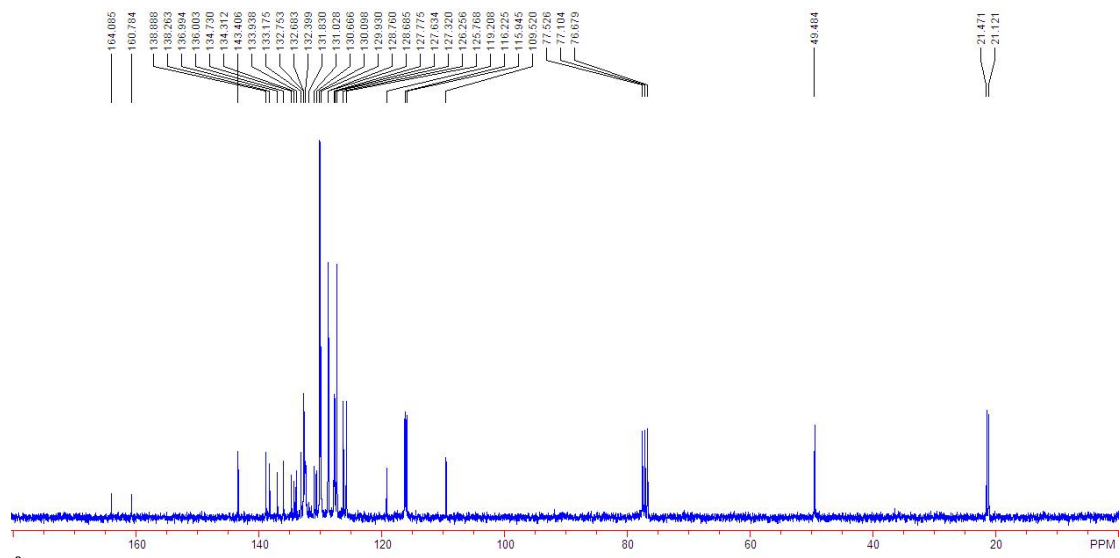
(3k)

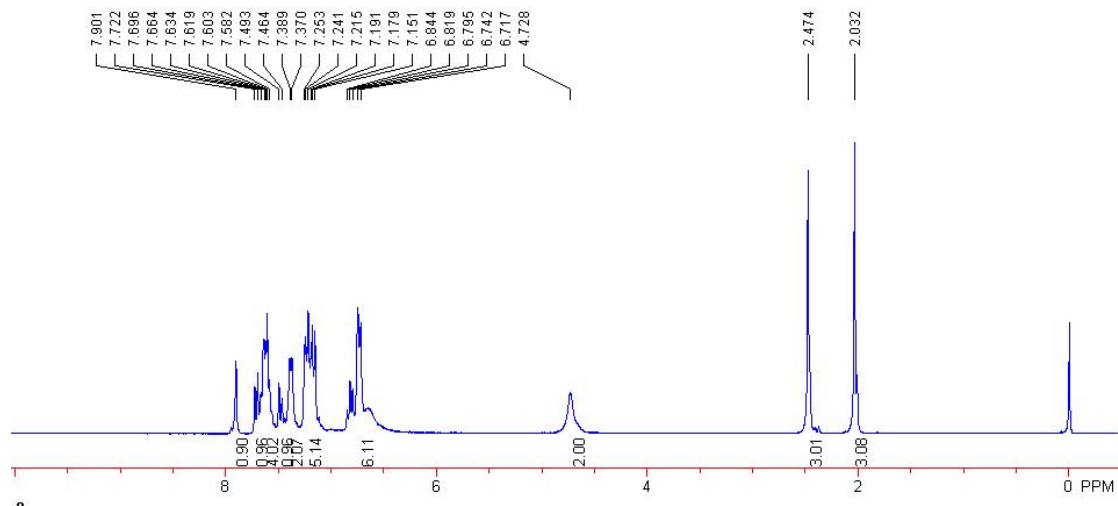
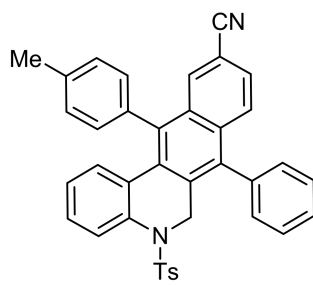
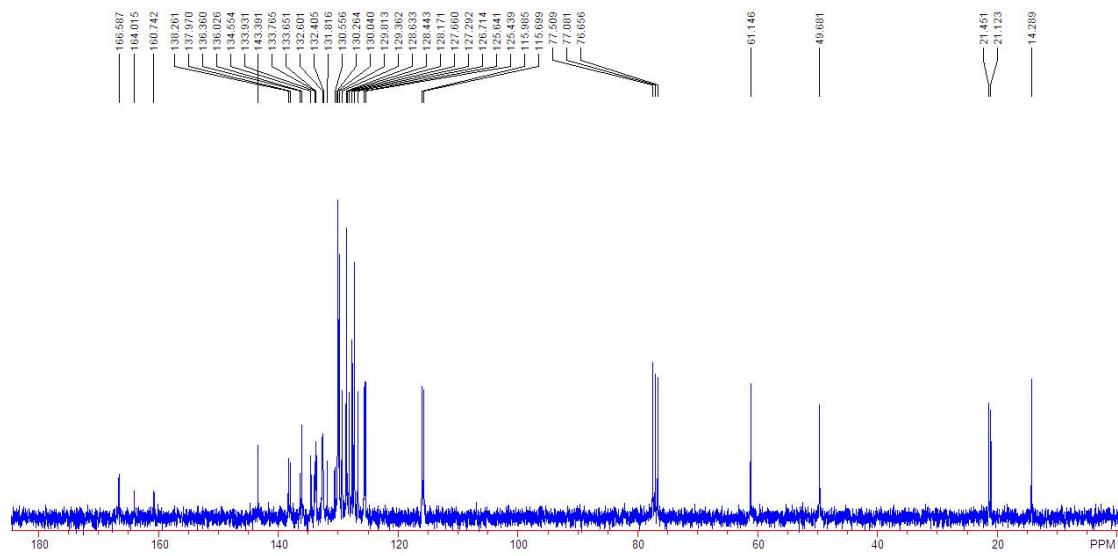


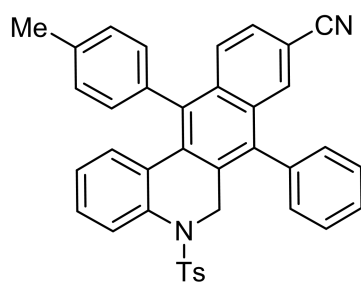
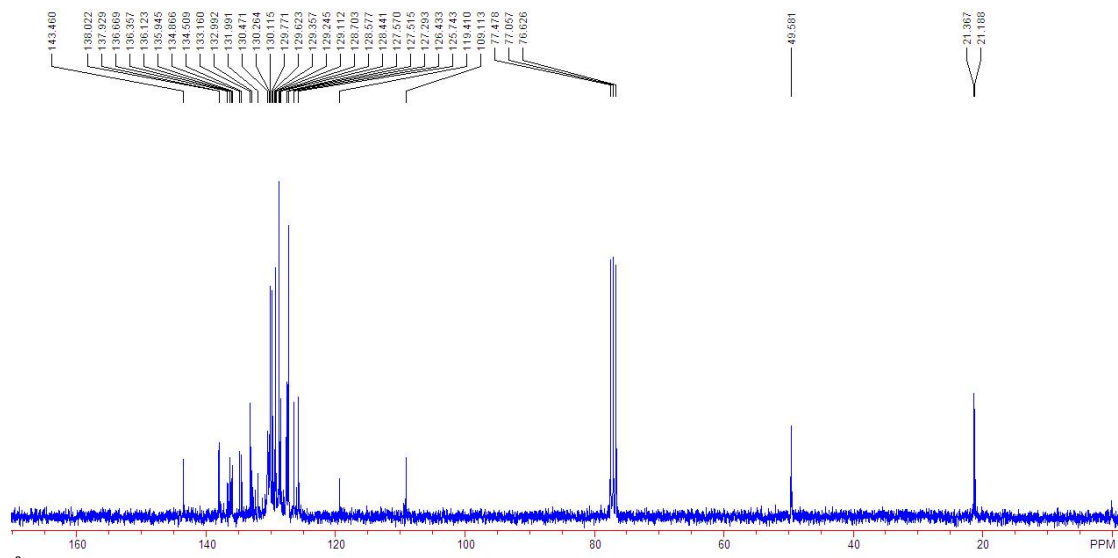












(3q)

