

Supporting Information

Efficient Construction of Five-Membered Aromatic and Nonaromatic Heterocycles from 1,6-Enynes by a Palladium-Catalyzed Domino Coupling / Cycloisomerization Process

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1. General experimental procedures

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. All solvents and materials were pre-dried, redistilled or recrystallized before use. The ^1H and ^{13}C NMR spectra were recored at 300 and 75 MHz, respectively. Melting points were uncorrected. Infrared spectra were recorded on FT-IR spectrometer as KBr pellets or thin film from CHCl_3 on the NaCl window. All HRMS spectra were record using EI at 70 eV. X-ray Crystallography diffraction data of **1h** were collected at room temperature with Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) with a graphite monochromator using the ω -scan mode. Enynes, *N*-allyl-4-methyl-*N*-(3-phenylprop-2-ynyl)benzenesulfonamide (**1**)¹, (3-(allyloxy)prop-1-ynyl)benzene (**2**)¹, *N*-allyl-4-methyl-*N*-(but-2-ynyl)benzenesulfonamide (**3**)¹ and *N*-allyl-*N*-benzylbut-2-ynamide (**4**)² were prepared by published procedures.

General procedures: A typical procedure for the palladium-catalyzed cyclization reaction of the linear 1,6-dienynes with aryl halides: Enyne (1.0 equiv), aryl bromide (1.2 equiv), $\text{Pd}(\text{OAc})_2$ (3 mol%), and PPh_3 (6 mol%) were added to a degassed solution of $(n\text{Bu})_3\text{N}$ (2 equiv) in DMF (5 mL), and the mixture was stirred at room temperature for half an hour and then heated at 140 °C for 20 h. The reaction mixture was then cooled, quenched with water, and extracted with ethyl acetate (20 mL). The combined organic layers were washed with hydrochloric acid (5%, 20 mL), sodium carbonate (5%, 20 mL), and saturated sodium chloride solution, dried over MgSO_4 , and concentrated. A flash chromatography on a silica gel eluting with petroleum ether and ethyl acetate gave the product.

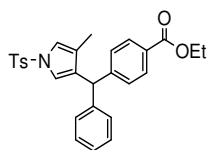
2. Synthesis of *N*-allyl-4-methyl-*N*-(but-2,3-dien)benzenesulfonamide

To a mixture of *N*-allyl-4-methyl-benzenesulfonamide (4.22 g, 20 mmol), buta-2,3-dien-1-ol³ (2.09 g, 20 mmol), and triphenylphosphane (5.24 g, 20 mmol) in THF (50 mL) was added diisopropylazodicarboxylate (4.2 mL, 20 mmol) at 0°C, and the reaction mixture was gradually warmed to room temperature and then stirred overnight. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel to give *N*-allyl-4-methyl-*N*-(but-2,3-dien)benzenesulfonamide 2.74 g in 52% yield. ¹H NMR (300 MHz, CDCl₃): δ 7.71 (d, *J* = 7.2 Hz, 2 H), 7.30 (d, *J* = 7.5 Hz, 2 H), 5.69-5.59 (m, 1 H), 5.20-5.15 (m, 2 H), 4.92-4.86 (m, 1 H), 4.70-4.68 (m, 2 H), 3.86-3.84 (m, 4 H), 2.43 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 209.6, 143.2, 137.5, 132.5, 129.6, 127.1, 118.9, 85.5, 76.1, 49.2, 45.5, 21.4.

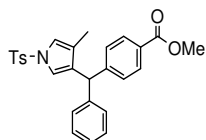
References:

1. Tang, Y.; Zhang, L.; Dong, G.; Chen, J.; Yang, Z. *Org. Lett.* **2005**, 7, 1657.
2. Jiang, H.; Ma, S.; Zhu, G.; Lu, X. *Tetrahedron.* **1996**, 52, 10945.
3. Molander, G. A.; Cormier, E. P.; *J. Org. Chem.* **2005**, 70, 2622.

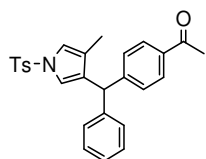
3. Characterization Data for the New Compounds



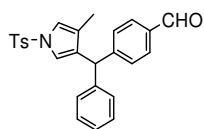
Ethyl 4-((4-methyl-1-tosyl-pyrrol-3-yl)(phenyl)methyl)benzoate (1a). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.48. ^1H NMR (300 MHz, CDCl_3): δ 7.94 (d, J = 7.5 Hz, 2 H), 7.65 (d, J = 7.5 Hz, 2 H), 7.30–7.25 (m, 5 H), 7.13 (d, J = 7.5 Hz, 2 H), 7.04 (d, J = 7.5 Hz, 2 H), 6.90 (s, 1 H), 6.44 (s, 1 H), 5.19 (s, 1 H), 4.37 (q, J = 6.9 Hz, 2 H), 2.44 (s, 3H), 1.68(s, 3H), 1.39 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.5, 147.9, 144.7, 141.9, 136.2, 131.9, 129.8, 129.7, 128.8, 128.7, 128.5, 126.8, 126.7, 124.3, 120.4, 119.0, 60.9, 48.6, 21.6, 14.4, 10.5; FT-IR (neat): ν_{max} 1718, 1597, 1363, 1276, 1168, 813, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{28}\text{H}_{27}\text{NO}_4\text{S}$: 473.1661; found: 473.1659.



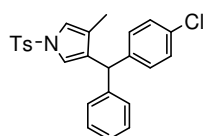
Methyl 4-((4-methyl-1-tosyl-pyrrol-3-yl)(phenyl)methyl)benzoate (1b). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.48. ^1H NMR (300 MHz, CDCl_3): δ 7.95 (d, J = 7.8 Hz, 2 H), 7.66 (d, J = 7.8 Hz, 2 H), 7.30–7.26 (m, 5 H), 7.15 (d, J = 7.8 Hz, 2 H), 7.06 (d, J = 7.5 Hz, 2 H), 6.92 (s, 1 H), 6.46 (s, 1 H), 5.21 (s, 1 H), 3.91 (s, 3 H), 2.43 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.9, 147.9, 144.7, 141.7, 135.0, 131.9, 129.8, 129.7, 128.8, 128.7, 128.5, 128.4, 126.7, 126.6, 124.3, 120.3, 118.9, 52.0, 48.5, 21.6, 10.4; FT-IR (neat): ν_{max} 1720, 1597, 1369, 1278, 1168, 813, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_4\text{S}$: 459.1504; found: 459.1499.



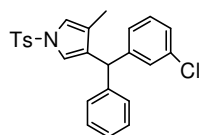
1-(4-((4-methyl-1-tosyl-pyrrol-3-yl)(phenyl)methyl)phenyl)ethanone (1c). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.50. ^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, J = 7.5 Hz, 2 H), 7.66 (d, J = 7.8 Hz, 2 H), 7.30–7.26 (m, 5H), 7.17 (d, J = 7.8 Hz, 2 H), 7.05 (d, J = 6.6 Hz, 2 H), 6.91 (s, 1 H), 6.46 (s, 1 H), 5.20 (s, 1 H), 2.59 (s, 3 H), 2.44 (s, 3 H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.6, 148.2, 144.7, 141.7, 136.0, 135.5, 131.7, 129.8, 128.9, 128.6, 128.5, 126.7, 126.6, 124.2, 120.3, 119.0, 48.5, 26.6, 21.6, 10.4; FT-IR (neat): ν_{max} 1681, 1599, 1365, 1168, 1066, 812, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{27}\text{H}_{25}\text{NO}_3\text{S}$: 443.1555; found: 443.1558.



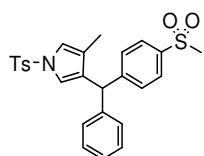
4-((4-Methyl-1-tosyl-pyrrol-3-yl)(phenyl)methyl)benzaldehyde (1d). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.50. ^1H NMR (300 MHz, CDCl_3): δ 9.98 (s, 1 H), 7.78 (d, J = 7.2 Hz, 2 H), 7.65 (d, J = 6.9 Hz, 2 H), 7.30–7.17 (m, 7 H), 7.05 (d, J = 6.0 Hz, 2 H), 6.92 (s, 1 H), 6.46 (s, 1 H), 5.22 (s, 1 H), 2.43 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 191.9, 149.9, 144.8, 141.5, 136.1, 134.9, 131.6, 129.9, 129.5, 129.3, 128.7, 128.6, 125.9, 125.7, 124.2, 120.4, 119.1, 48.8, 21.7, 10.5; FT-IR (neat): ν_{max} 1697, 1604, 1367, 1168, 1068, 812, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{23}\text{NO}_3\text{S}$: 429.1399; found: 429.1396.



3-((4-Chlorophenyl)(phenyl)methyl)-4-methyl-1-tosyl-pyrrole (1e). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.52. ^1H NMR (300 MHz, CDCl_3): δ = 7.66 (d, J = 7.5 Hz, 2 H), 7.30–7.22 (m, 7 H), 7.05–6.89 (m, 5 H), 6.45 (s, 1 H), 5.12 (s, 1 H), 2.44 (s, 3H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.6, 142.1, 141.2, 132.3, 130.1, 129.8, 128.8, 128.7, 128.6, 128.5, 128.4, 126.7, 126.4, 124.3, 120.3, 119.0, 48.0, 21.6, 10.5; FT-IR (neat): ν_{max} 1597, 1357, 1172, 1062, 806, 675 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{25}\text{H}_{22}\text{ClNO}_2\text{S}$: 435.1060; found: 435.1063.

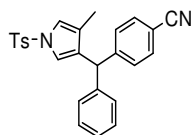


3-((3-Chlorophenyl)(phenyl)methyl)-4-methyl-1-tosyl-pyrrole (1f). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.52. ^1H NMR (300 MHz, CDCl_3): δ 7.66 (d, J = 8.4 Hz, 2 H), 7.30–7.19 (m, 7 H), 7.05–6.90 (m, 5 H), 6.47 (s, 1 H), 5.12 (s, 1 H), 2.43 (s, 3H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.8, 144.7, 141.9, 136.2, 134.3, 132.1, 129.9, 129.7, 128.8, 128.7, 128.6, 128.4, 127.0, 126.8, 126.7, 124.4, 120.5, 119.1, 48.3, 21.7, 10.5; FT-IR (neat): ν_{max} 1591, 1359, 1172, 1060, 806, 671 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{25}\text{H}_{22}\text{ClNO}_2\text{S}$: 435.1060; found: 435.1066.

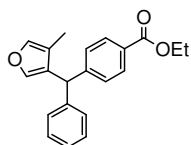


3-Methyl-4-((4-(methanesulfonyl)phenyl)(phenyl)methyl)-1-tosyl-pyrrole (1g). Yellow oil. TLC (petroleum ether–EtOAc = 4:1): R_f = 0.40. ^1H NMR (300 MHz, CDCl_3): δ 7.84 (d, J = 8.1 Hz, 2 H), 7.67 (d, J = 7.8 Hz, 2 H), 7.31–7.26 (m, 7 H), 7.03 (d, J = 7.8 Hz, 2 H), 6.92 (s, 1 H), 6.47 (s, 1 H), 5.23 (s, 1 H), 3.07 (s, 3 H), 2.44 (s, 3 H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 149.2, 144.8, 141.2, 138.6, 135.9, 131.2, 129.9, 129.7, 128.6, 127.5, 127.0, 126.6, 124.0, 120.2, 119.1, 48.4, 44.5,

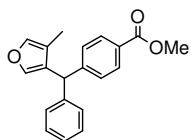
21.6, 10.4; FT-IR (neat): $\nu_{\max}$ 1595, 1365, 1305, 1168, 1147, 813, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4\text{S}_2$: 479.1225; found: 479.1221.



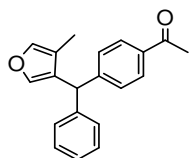
4-((4-Methyl-1-tosyl-pyrrol-3-yl)(phenyl)methyl)benzonitrile (1h). White solide. mp 166-167 $^{\circ}\text{C}$. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.49. ^1H NMR (300 MHz, CDCl_3): δ 7.66 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 7.8 Hz, 2 H), 7.31-7.24 (m, 5H), 7.18 (d, J = 8.1 Hz, 2 H), 7.02 (d, J = 7.8 Hz, 2 H), 6.91 (s, 1 H), 6.43 (s, 1 H), 5.19 (s, 1 H), 2.43 (s, 3 H), 1.68 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.3, 144.8, 141.2, 136.1, 132.3, 131.2, 129.9, 129.6, 128.7, 127.1, 126.8, 124.1, 120.3, 119.2, 118.9, 110.5, 48.6, 21.7, 10.5; FT-IR (KBr): $\nu_{\max}$ 2224, 1597, 1371, 1170, 1072, 812, 667 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{26}\text{H}_{22}\text{N}_2\text{O}_2\text{S}$: 426.1402; found: 426.1397.



Ethyl 4-((4-methylfuran-3-yl)(phenyl)methyl)benzoate (2a). Yellow oil. TLC (petroleum ether–EtOAc = 8:1): R_f = 0.53. ^1H NMR (300 MHz, CDCl_3): δ 7.97 (d, J = 8.1 Hz, 2 H), 7.30-7.15 (m, 8 H), 6.70 (s, 1 H), 5.22 (s, 1 H), 4.37 (q, J = 7.2 Hz, 2 H), 1.70 (s, 3H), 1.38 (t, J = 6.9 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.6, 148.1, 142.1, 142.0, 140.3, 129.7, 128.8, 128.7, 128.6, 128.5, 128.2, 126.7, 120.0, 60.9, 47.5, 14.4, 8.3; FT-IR (neat): $\nu_{\max}$ 3130, 1714, 1612, 1278, 1174, 702 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{20}\text{O}_3$: 320.1412; found: 320.1405.

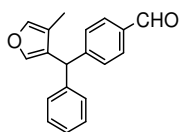


Methyl 4-((4-methylfuran-3-yl)(phenyl)methyl)benzoate (2b). Yellow oil.. TLC (petroleum ether–EtOAc = 8:1): R_f = 0.51. ^1H NMR (300 MHz, CDCl_3): δ 7.97 (d, J = 8.1 Hz, 2 H), 7.30-7.15 (m, 8 H), 6.70 (s, 1 H), 5.22 (s, 1 H), 3.90 (s, 3 H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 167.0, 148.2, 142.0, 141.9, 140.3, 129.8, 129.5, 128.8, 128.7, 128.5, 128.2, 126.8, 119.9, 52.1, 47.5, 8.3; FT-IR (neat): $\nu_{\max}$ 3134, 1720, 1610, 1280, 1178, 702 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{18}\text{O}_3$: 306.1256; found: 306.1250.

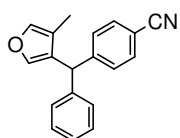


1-(4-((4-Methylfuran-3-yl)(phenyl)methyl)phenyl)ethanone (2c). Yellow oil. TLC (petroleum ether–EtOAc = 8:1): R_f = 0.54. ^1H NMR (300 MHz, CDCl_3): δ 7.90 (d, J = 8.1 Hz, 2 H), 7.30-7.15

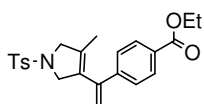
(m, 8 H), 6.72 (s, 1 H), 5.23 (s, 1 H), 2.59 (s, 3 H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.9, 148.5, 141.9, 140.4, 135.7, 128.9, 128.7, 128.6, 128.1, 126.8, 119.9, 47.5, 26.6, 8.3; FT-IR (neat): ν_{max} 3132, 1681, 1606, 702 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2$: 290.1307; found: 290.1305.



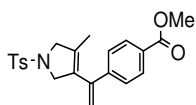
4-((4-Methylfuran-3-yl)(phenyl)methyl)benzaldehyde (2d). Yellow oil. TLC (petroleum ether–EtOAc = 8:1): R_f = 0.53. ^1H NMR (300 MHz, CDCl_3): δ 9.99 (s, 1 H), 7.82 (d, J = 8.4 Hz, 2 H), 7.46–7.16 (m, 8 H), 6.72 (s, 1 H), 5.25 (s, 1 H), 1.71 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 191.9, 150.1, 141.9, 140.4, 135.0, 130.3, 130.0, 129.4, 128.7, 128.6, 128.0, 126.9, 119.9, 47.6, 8.3; FT-IR (neat): ν_{max} 3134, 1695, 1608, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{19}\text{H}_{16}\text{O}_2$: 276.1150; found: 276.1154.



4-((4-Methylfuran-3-yl)(phenyl)methyl)benzonitrile (2e). Yellow oil. TLC (petroleum ether–EtOAc = 8:1): R_f = 0.50. ^1H NMR (300 MHz, CDCl_3): δ 7.59 (d, J = 8.1 Hz, 2 H), 7.31–7.23 (m, 6 H), 7.14 (d, J = 7.2 Hz, 2 H), 6.70 (s, 1 H), 5.22 (s, 1 H), 1.70 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.5, 142.0, 141.4, 140.6, 132.3, 129.5, 128.7, 128.6, 127.7, 127.0, 119.8, 118.9, 110.5, 47.5, 8.3; FT-IR (neat): ν_{max} 3132, 2227, 1604, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{19}\text{H}_{15}\text{NO}$: 273.1154; found: 273.1155.

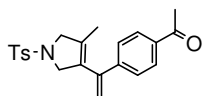


Ethyl 4-(1-(2,5-dihydro-4-methyl-1-tosyl-pyrrol-3-yl)vinyl)benzoate (3a). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.48. ^1H NMR (300 MHz, CDCl_3): δ 7.94 (d, J = 8.4 Hz, 2 H), 7.73 (d, J = 8.1 Hz, 2 H), 7.34 (d, J = 8.1 Hz, 2 H), 7.17 (d, J = 8.4 Hz, 2 H), 5.48 (s, 1 H), 5.15 (s, 1 H), 4.37 (q, J = 7.2 Hz, 2 H), 4.16 (s, 4H), 2.47 (s, 3 H), 1.42–1.37(m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.3, 144.0, 143.6, 141.5, 134.0, 132.4, 130.0, 129.8, 129.7, 127.6, 127.2, 126.8, 117.9, 61.0, 59.7, 57.6, 21.6, 14.2, 12.8; FT-IR (neat): ν_{max} 1716, 1595, 1344, 1274, 1163, 815, 667 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{23}\text{H}_{25}\text{NO}_4\text{S}$: 411.1504; found: 411.1501.

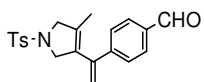


Methyl 4-(1-(2,5-dihydro-4-methyl-1-tosyl-pyrrol-3-yl)vinyl)benzoate (3b). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.48. ^1H NMR (300 MHz, CDCl_3): δ 7.93 (d, J = 7.8 Hz, 2 H),

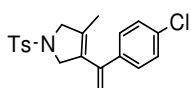
7.73 (d, $J = 7.5$ Hz, 2 H), 7.35 (d, $J = 8.1$ Hz, 2 H), 7.17 (d, $J = 7.5$ Hz, 2 H), 5.49 (s, 1 H), 5.16 (s, 1 H), 4.16 (s, 4H), 3.91 (s, 3 H), 2.46 (s, 3 H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 166.9, 144.1, 143.6, 141.4, 133.9, 132.4, 129.9, 129.8, 129.7, 129.5, 127.6, 126.9, 117.9, 59.7, 57.5, 52.2, 21.6, 12.8; FT-IR (neat): ν_{max} 1720, 1595, 1346, 1274, 1163, 813, 665 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_4\text{S}$: 397.1348; found: 397.1343.



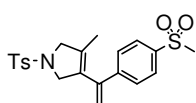
1-(4-(1-(2,5-Dihydro-4-methyl-1-tosyl-pyrrol-3-yl)vinyl)phenyl)ethanone (3c). Yellow oil. TLC (petroleum ether–EtOAc = 4:1): $R_f = 0.47$. ^1H NMR (300 MHz, CDCl_3): δ 7.86 (d, $J = 8.4$ Hz, 2 H), 7.72 (d, $J = 8.1$ Hz, 2 H), 7.34 (d, $J = 8.1$ Hz, 2 H), 7.21 (d, $J = 8.4$ Hz, 2 H), 5.49 (s, 1 H), 5.16 (s, 1 H), 4.15 (s, 4H), 2.59 (s, 3 H), 2.46 (s, 3 H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.6, 144.1, 143.5, 141.3, 136.3, 133.9, 132.4, 129.8, 128.5, 127.5, 127.3, 127.0, 118.0, 59.6, 57.4, 26.6, 21.5, 12.8; FT-IR (neat): ν_{max} 1681, 1602, 1344, 1269, 1163, 813, 663 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_3\text{S}$: 381.1399; found: 381.1393.



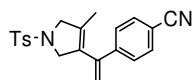
4-(1-(2,5-Dihydro-4-methyl-1-tosyl-pyrrol-3-yl)vinyl)benzaldehyde (3d). Yellow oil. TLC (petroleum ether–EtOAc = 4:1): $R_f = 0.48$. ^1H NMR (300 MHz, CDCl_3): δ 9.98 (s, 1 H), 7.77 (d, $J = 8.1$ Hz, 2 H), 7.71 (d, $J = 8.1$ Hz, 2 H), 7.34 (d, $J = 7.8$ Hz, 2 H), 7.27 (d, $J = 8.1$ Hz, 2 H), 5.51 (s, 1 H), 5.19 (s, 1 H), 4.15 (s, 4H), 2.44 (s, 3 H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 191.7, 145.6, 143.7, 141.3, 135.7, 133.9, 132.6, 129.9, 129.8, 129.7, 127.5, 127.3, 118.6, 59.6, 57.5, 21.6, 12.9; FT-IR (neat): ν_{max} 1697, 1604, 1342, 1211, 1163, 815, 665 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{21}\text{NO}_3\text{S}$: 367.1242; found: 367.1249.



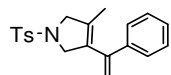
3-(1-(4-Chlorophenyl)vinyl)-2,5-dihydro-4-methyl-1-tosylpyrrole (3e). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): $R_f = 0.50$. ^1H NMR (300 MHz, CDCl_3): δ 7.73 (d, $J = 8.1$ Hz, 2 H), 7.35 (d, $J = 8.1$ Hz, 2 H), 7.24 (d, $J = 8.4$ Hz, 2 H), 7.06 (d, $J = 7.8$ Hz, 2 H), 5.40 (s, 1 H), 5.08 (s, 1 H), 4.15 (s, 4H), 2.46 (s, 3 H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.5, 141.0, 137.9, 134.0, 133.7, 132.1, 130.1, 129.7, 128.5, 128.1, 127.5, 116.7, 59.6, 57.5, 21.5, 12.7; FT-IR (neat): ν_{max} 1597, 1344, 1163, 1068, 813, 667 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{ClNO}_2\text{S}$: 373.0903; found: 373.0899.



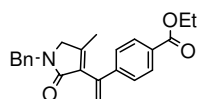
2,5-Dihydro-3-methyl-4-(1-(4-(methylsulfonyl)phenyl)vinyl)-1-tosyl-pyrrole (3f). Yellow oil. TLC (petroleum ether–EtOAc = 4:1): R_f = 0.40. ^1H NMR (300 MHz, CDCl_3): δ 7.84 (d, J = 7.8 Hz, 2 H), 7.72 (d, J = 8.1 Hz, 2 H), 7.36–7.31 (m, 4 H), 5.51 (s, 1 H), 5.22 (s, 1 H), 4.15 (s, 4H), 3.06 (s, 3 H), 2.46 (s, 3 H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 145.1, 143.7, 140.7, 139.8, 133.9, 133.0, 129.9, 129.5, 127.8, 127.6, 127.5, 119.2, 59.6, 57.4, 44.5, 21.6, 12.9; FT-IR (neat): ν_{max} 1595, 1342, 1311, 1159, 815, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{S}_2$: 417.1068; found: 417.1062.



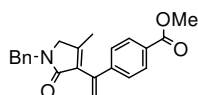
4-(1-(2,5-Dihydro-4-methyl-1-tosyl-pyrrol-3-yl)vinyl)benzonitrile (3g). Yellow oil. TLC (petroleum ether–EtOAc = 4:1): R_f = 0.46. ^1H NMR (300 MHz, CDCl_3): δ 7.73 (d, J = 8.4 Hz, 2 H), 7.57 (d, J = 7.8 Hz, 2 H), 7.35 (d, J = 8.1 Hz, 2 H), 7.24 (d, J = 8.1 Hz, 2 H), 5.50 (s, 1 H), 5.21 (s, 1 H), 4.15 (s, 4H), 2.46 (s, 3 H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 144.1, 143.7, 140.8, 133.0, 132.5, 132.3, 129.9, 129.5, 127.6, 118.9, 118.6, 111.6, 59.6, 57.4, 21.6, 12.9; FT-IR (neat): ν_{max} 2227, 1604, 1342, 1163, 815, 669 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{20}\text{N}_2\text{O}_2\text{S}$: 364.1245; found: 364.1250.



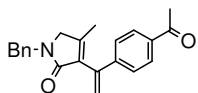
2,5-Dihydro-3-methyl-4-(1-phenylvinyl)-1-tosyl-pyrrole (3h). Yellow oil. TLC (petroleum ether–EtOAc = 6:1): R_f = 0.50. ^1H NMR (300 MHz, CDCl_3): δ 7.74 (d, J = 7.8 Hz, 2 H), 7.35–7.14 (m, 7 H), 5.42 (s, 1 H), 5.07 (s, 1 H), 4.17 (s, 4H), 2.46(s, 3 H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.5, 142.2, 139.5, 134.1, 131.7, 130.6, 129.8, 128.4, 127.9, 127.6, 126.9, 116.3, 59.7, 57.7, 21.6, 12.7; FT-IR (neat): ν_{max} 1598, 1344, 1161, 1070, 813, 665 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{S}$: 339.1293; found: 339.1284.



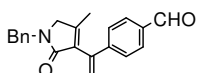
Ethyl 4-(1-(1-benzyl-2,5-dihydro-4-methyl-2-oxo-pyrrol-3-yl)vinyl)benzoate (4a). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.44. ^1H NMR (300 MHz, CDCl_3): δ 8.00 (d, J = 7.2 Hz, 2 H), 7.41–7.27 (m, 7 H), 5.86 (s, 1 H), 5.63 (s, 1 H), 4.65 (s, 2H), 4.37 (q, J = 7.2 Hz, 2 H), 3.78 (s, 2 H), 1.76 (s, 3H), 1.39 (t, J = 7.2 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.5, 166.6, 150.1, 144.6, 138.9, 137.4, 132.4, 129.7, 129.6, 128.8, 128.2, 127.6, 126.6, 120.3, 60.9, 53.8, 46.3, 14.5, 14.4; FT-IR (neat): ν_{max} 1714, 1645, 1604, 1276, 916, 702 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_3$: 361.1678; found: 361.1684.



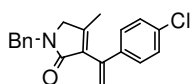
Methyl 4-(1-(1-benzyl-2,5-dihydro-4-methyl-2-oxo-pyrrol-3-yl)vinyl)benzoate (4b). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.44. ^1H NMR (300 MHz, CDCl_3): δ 7.99 (d, J = 8.4 Hz, 2 H), 7.40 (d, J = 8.4 Hz, 2 H), 7.34–7.26 (m, 5 H), 5.85 (s, 1 H), 5.62 (s, 1 H), 4.64 (s, 2H), 3.90 (s, 3 H), 3.77 (s, 2H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.5, 166.9, 150.2, 144.6, 138.9, 137.4, 129.8, 129.2, 128.8, 128.2, 128.1, 127.6, 126.6, 120.4, 53.8, 52.1, 46.3, 14.4; FT-IR (neat): ν_{max} 1718, 1639, 1608, 1280, 914, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_3$: 347.1521; found: 347.1527.



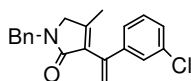
3-(1-(4-Acetylphenyl)vinyl)-1-benzyl-4-methyl-pyrrol-2(5H)-one (4c). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.43. ^1H NMR (300 MHz, CDCl_3): δ 7.91 (d, J = 8.4 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 7.34–7.25 (m, 5 H), 5.87 (s, 1 H), 5.60 (s, 1 H), 4.64 (s, 2H), 3.79 (s, 2 H), 2.58 (s, 3H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 197.7, 170.5, 150.3, 144.7, 138.9, 137.4, 136.2, 128.8, 128.6, 128.2, 127.7, 126.8, 120.5, 53.8, 46.3, 26.6, 14.4; FT-IR (neat): ν_{max} 1681, 1639, 1606, 916, 702 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_2$: 331.1572; found: 331.1579.



4-(1-(1-Benzyl-2,5-dihydro-4-methyl-2-oxo-pyrrol-3-yl)vinyl)benzaldehyde (4d). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.43. ^1H NMR (300 MHz, CDCl_3): δ 9.99 (s, 1H), 7.84 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 8.1 Hz, 2 H), 7.35–7.27 (m, 5 H), 5.91 (s, 1 H), 5.64 (s, 1 H), 4.64 (s, 2H), 3.80 (s, 2 H), 1.81 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 191.9, 170.5, 150.4, 146.1, 138.9, 137.3, 135.6, 132.4, 129.9, 128.8, 128.2, 127.6, 127.2, 121.0, 53.9, 46.3, 14.4; FT-IR (neat): ν_{max} 1695, 1639, 1608, 916, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_2$: 317.1416; found: 317.1423.

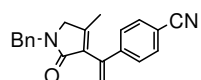


1-Benzyl-3-(1-(4-chlorophenyl)vinyl)-4-methyl-pyrrol-2(5H)-one (4e). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.45. ^1H NMR (300 MHz, CDCl_3): δ 7.34–7.28 (m, 9 H), 5.77 (s, 1 H), 5.51 (s, 1 H), 4.64 (s, 2H), 3.77 (s, 2 H), 1.79 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.7, 150.0, 138.6, 138.5, 137.4, 133.5, 132.6, 128.8, 128.5, 128.2, 127.9, 127.6, 118.9, 53.8, 46.2, 14.4; FT-IR (neat): ν_{max} 1639, 1610, 1089, 912, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}$: 323.1077; found: 323.1086.

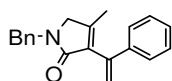


1-Benzyl-3-(1-(3-chlorophenyl)vinyl)-4-methyl-pyrrol-2(5H)-one (4f). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.45. ^1H NMR (300 MHz, CDCl_3): δ 7.35–7.22 (m, 9 H), 5.79 (s, 1 H), 5.55 (s, 1 H), 4.65 (s, 2H), 3.78 (s, 2 H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.5,

150.1, 142.0, 138.6, 137.4, 134.3, 132.5, 129.6, 128.8, 128.2, 127.7, 127.6, 126.7, 124.9, 119.6, 53.8, 46.3, 14.4; FT-IR (neat): $\nu_{\max}$ 1639, 1610, 1076, 908, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{18}\text{ClNO}$: 323.1077; found: 323.1086.



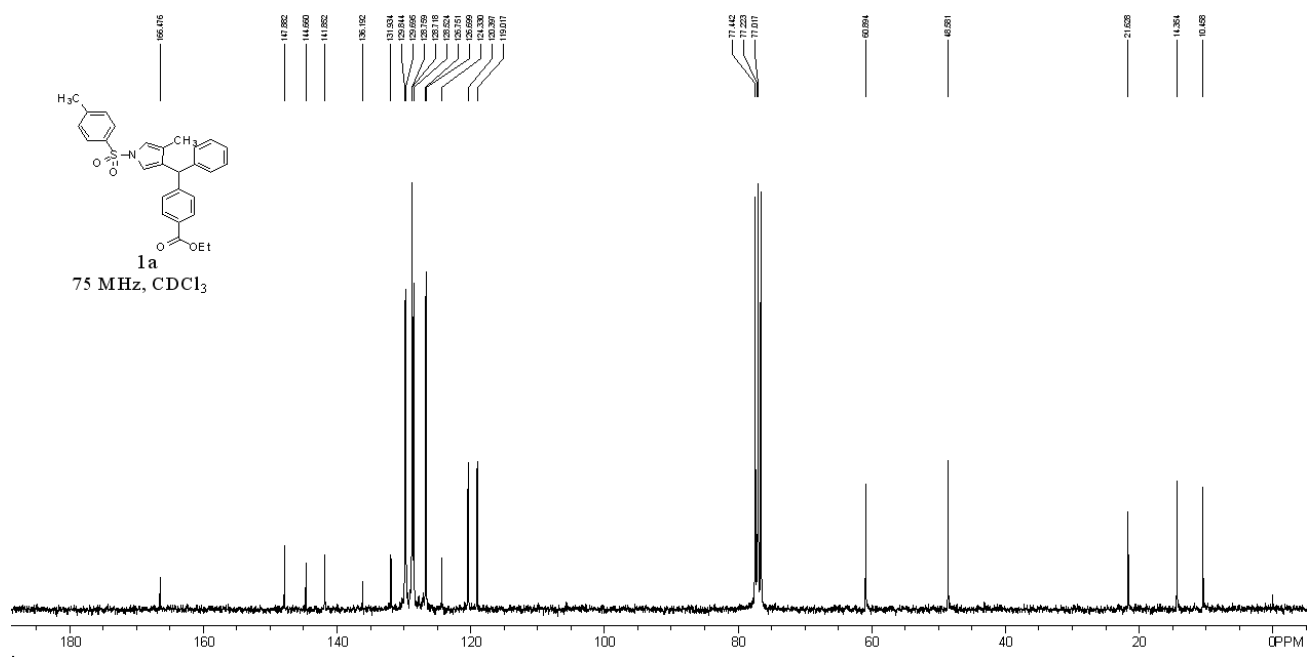
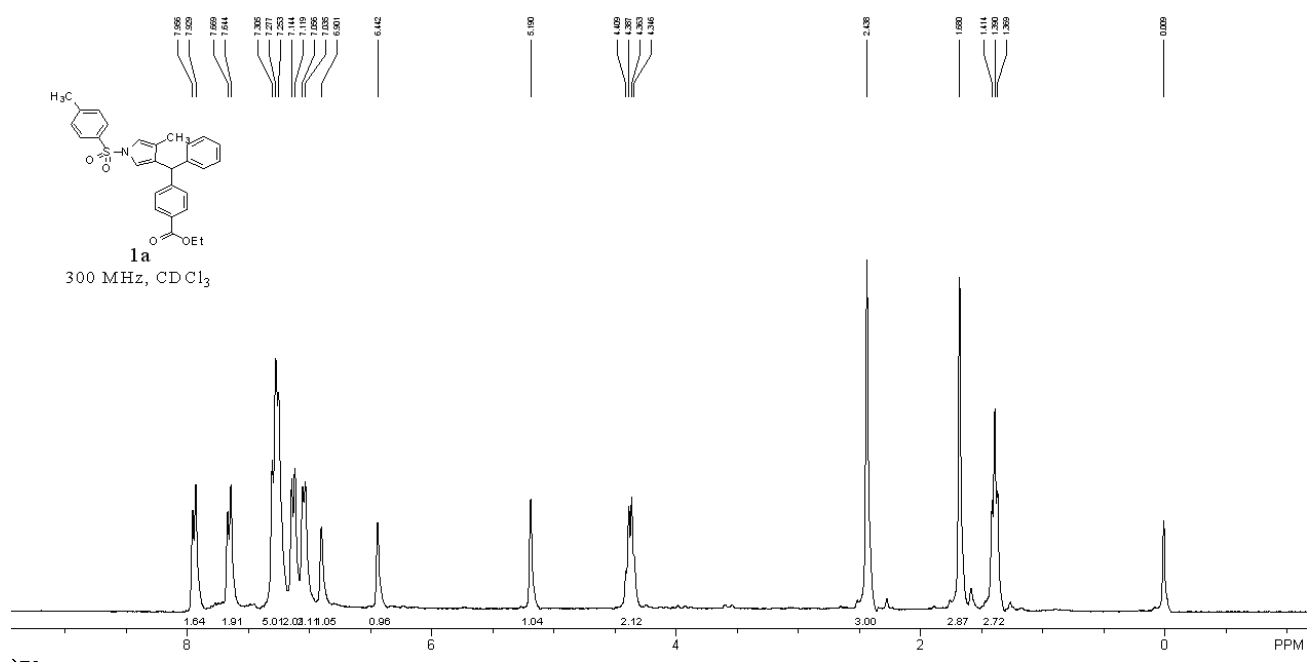
4-(1-(1-Benzyl-2,5-dihydro-4-methyl-2-oxo-pyrrol-3-yl)vinyl)benzonitrile (4g). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.42. ^1H NMR (300 MHz, CDCl_3): δ 7.61 (d, J = 8.4 Hz, 2 H), 7.44 (d, J = 8.1 Hz, 2 H), 7.35–7.26 (m, 5 H), 5.86 (s, 1 H), 5.61 (s, 1 H), 4.63 (s, 2H), 3.80 (s, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.3, 150.7, 144.5, 138.5, 137.2, 132.3, 128.8, 128.2, 128.1, 127.7, 127.3, 121.3, 118.9, 111.2, 53.9, 46.3, 14.4; FT-IR (neat): $\nu_{\max}$ 2225, 1639, 1612, 912, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}$: 314.1419; found: 314.1427.

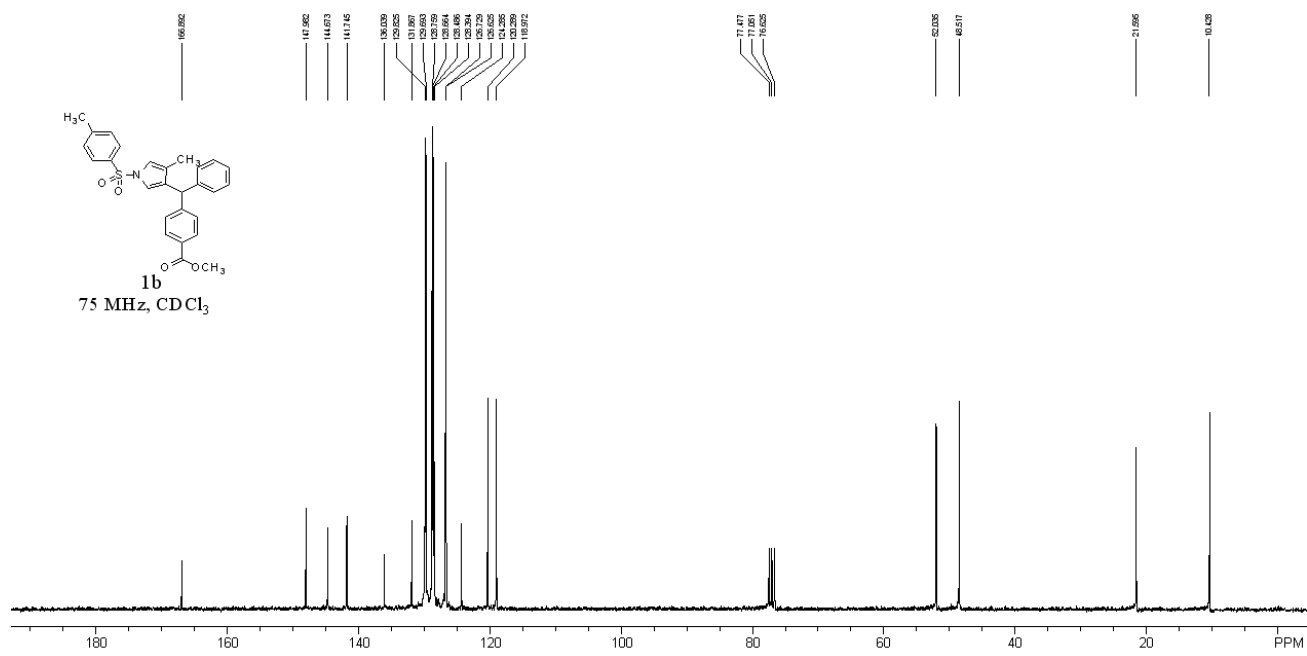
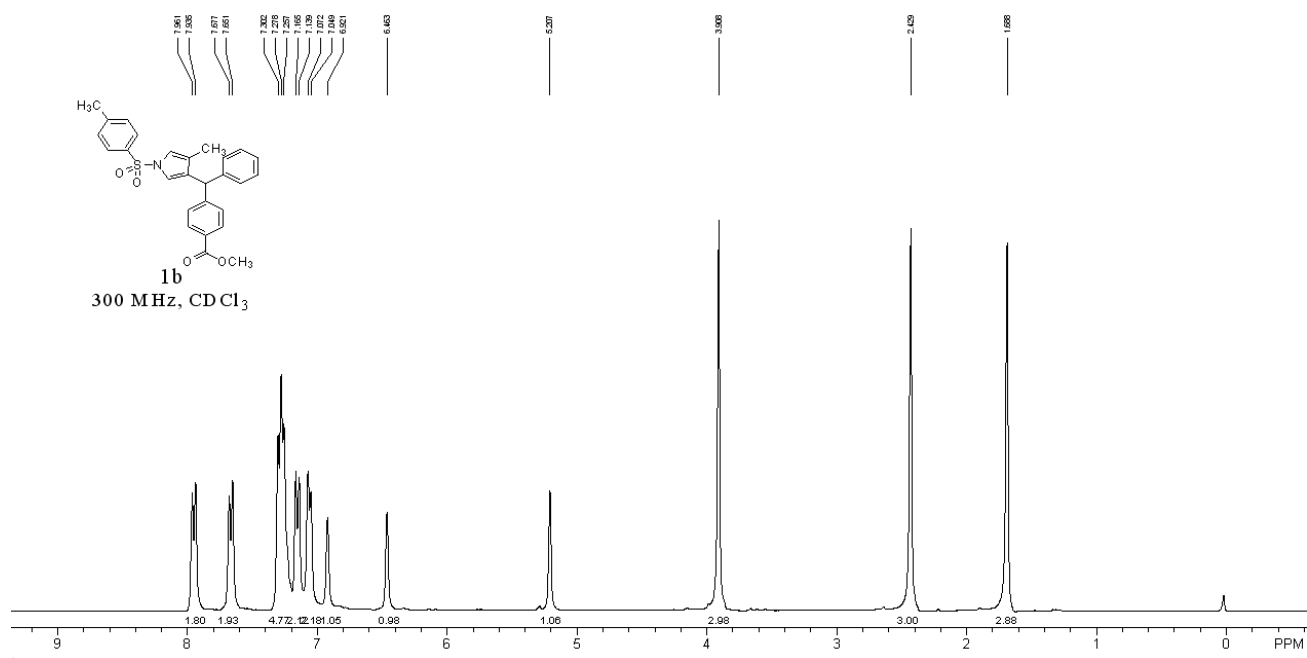


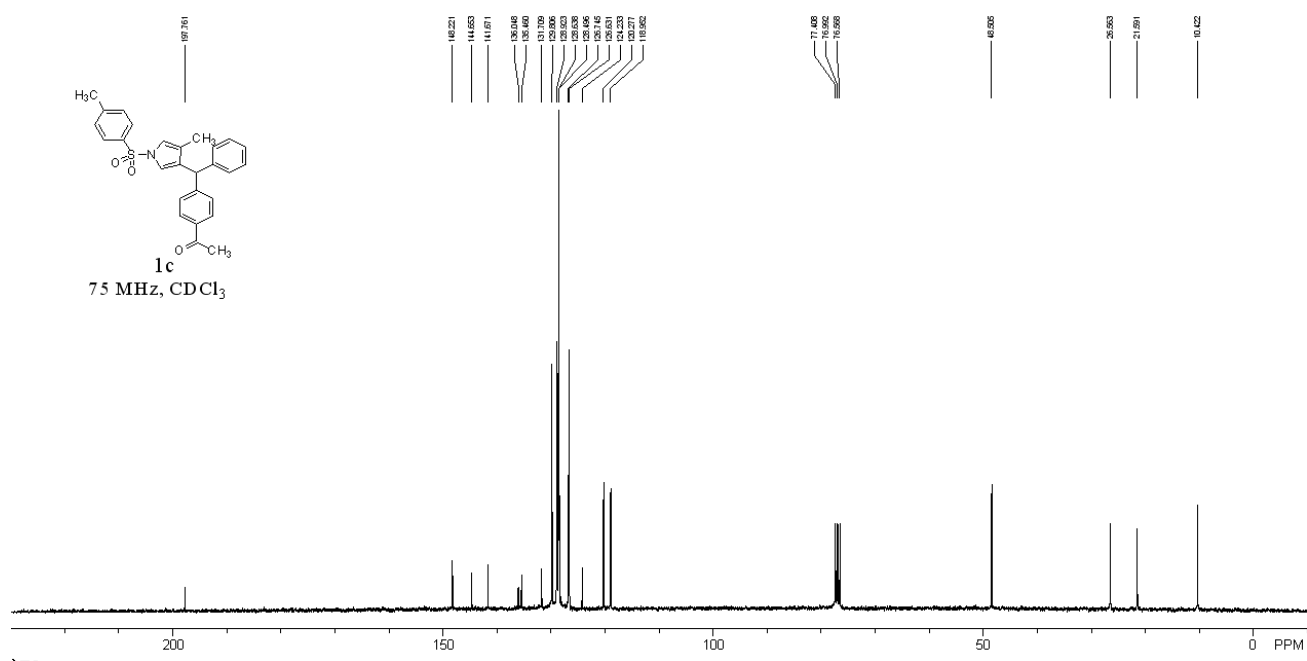
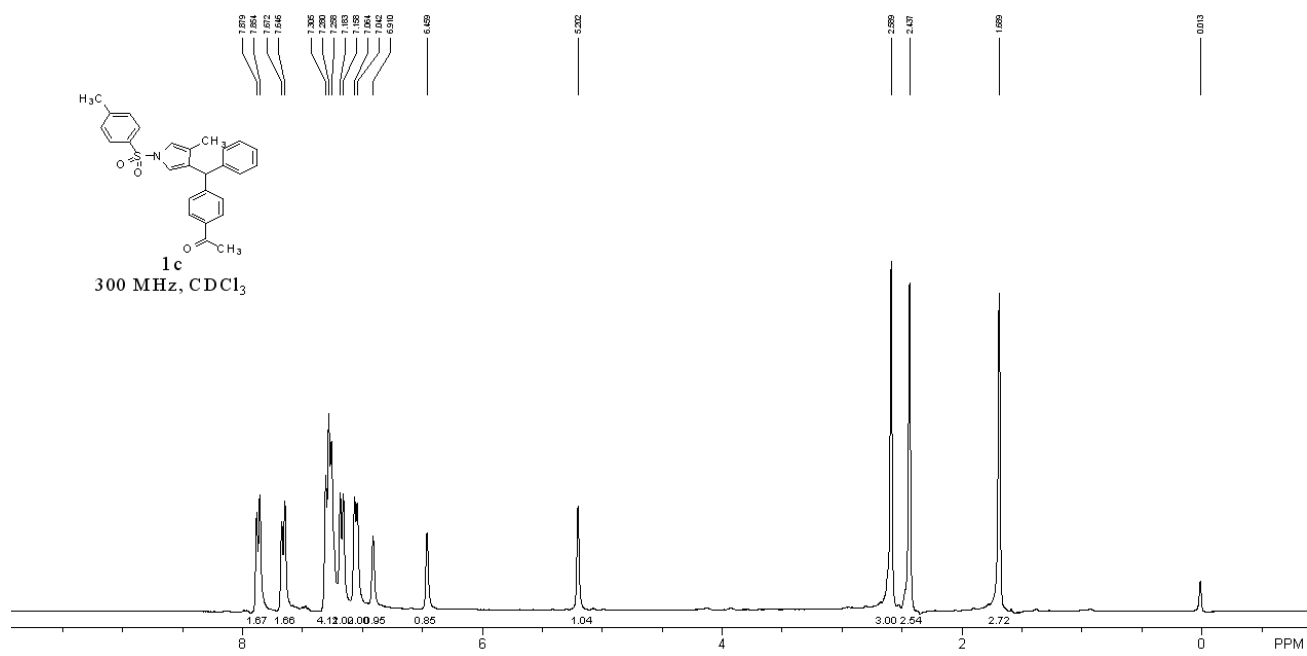
1-Benzyl-4-methyl-3-(1-phenylvinyl)-pyrrol-2(5H)-one (4h). Yellow oil. TLC (petroleum ether–EtOAc = 5:1): R_f = 0.47. ^1H NMR (300 MHz, CDCl_3): δ 7.33–7.30 (m, 10 H), 5.79 (s, 1 H), 5.53 (s, 1 H), 4.66 (s, 2H), 3.76 (s, 2H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 170.8, 149.6, 140.0, 139.7, 137.5, 133.0, 128.7, 128.4, 128.2, 127.6, 127.5, 126.6, 118.5, 53.7, 46.3, 14.4; FT-IR (neat): $\nu_{\max}$ 1639, 1610, 912, 700 cm^{-1} . HRMS (EI) m/z : calcd for $\text{C}_{20}\text{H}_{19}\text{NO}$: 289.1467; found: 289.1475.

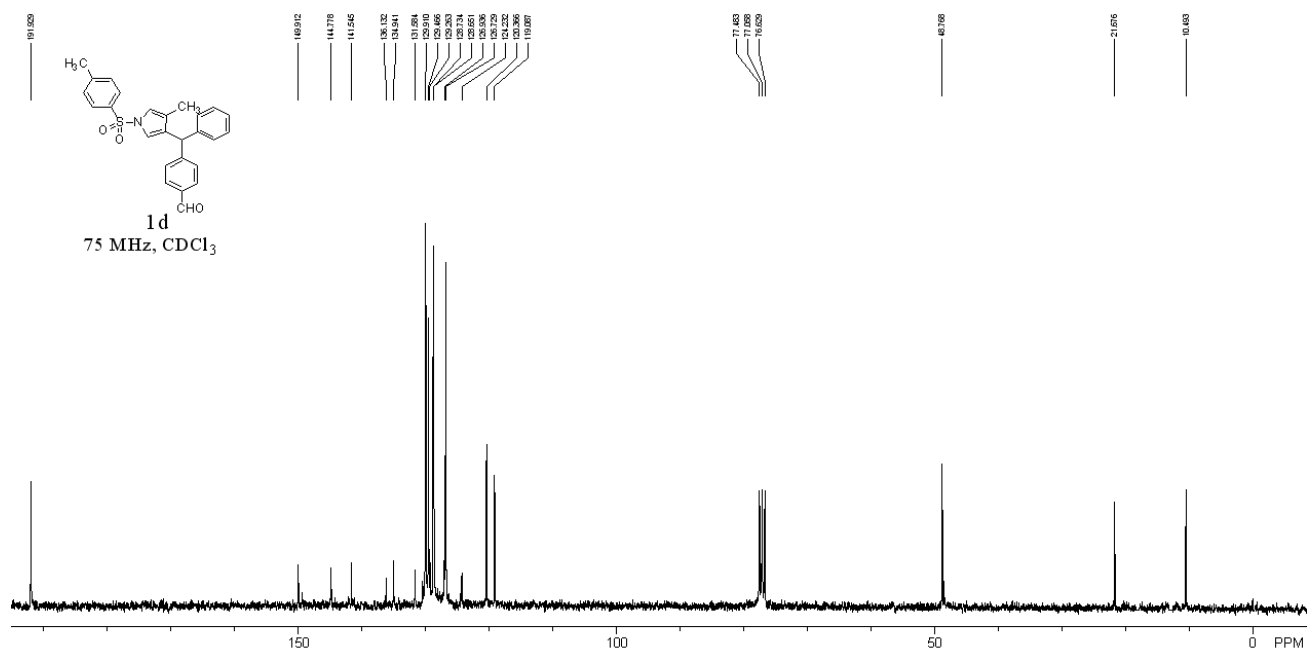
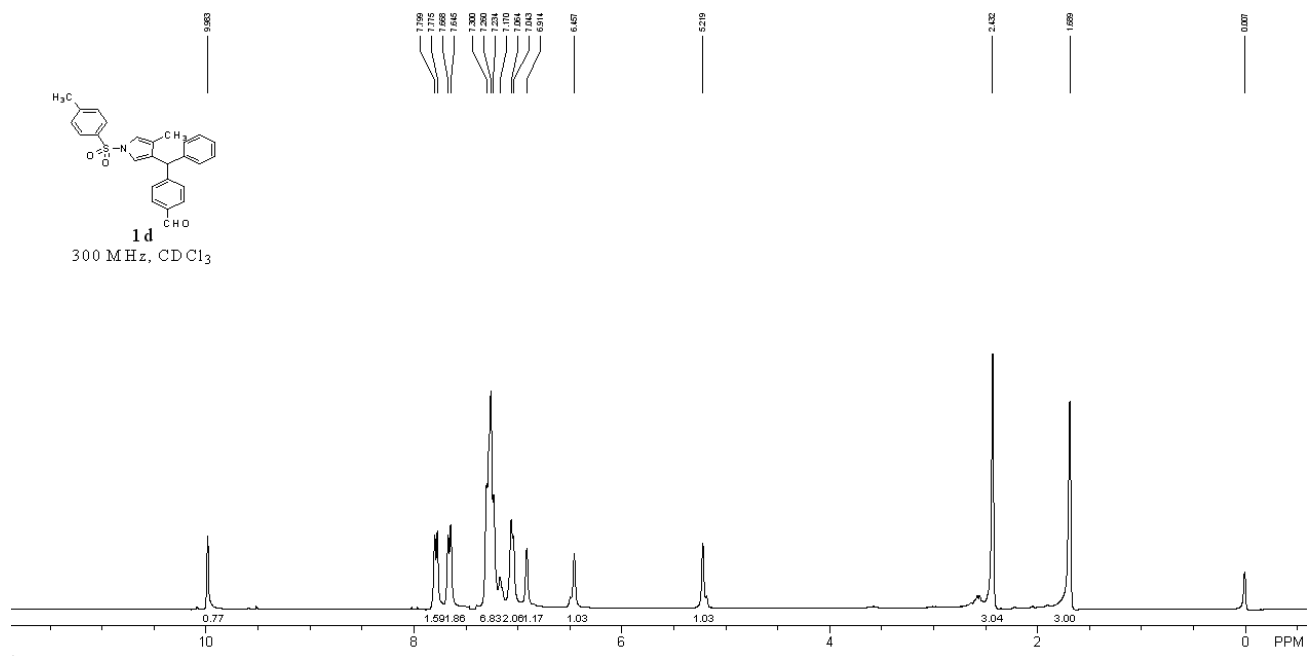


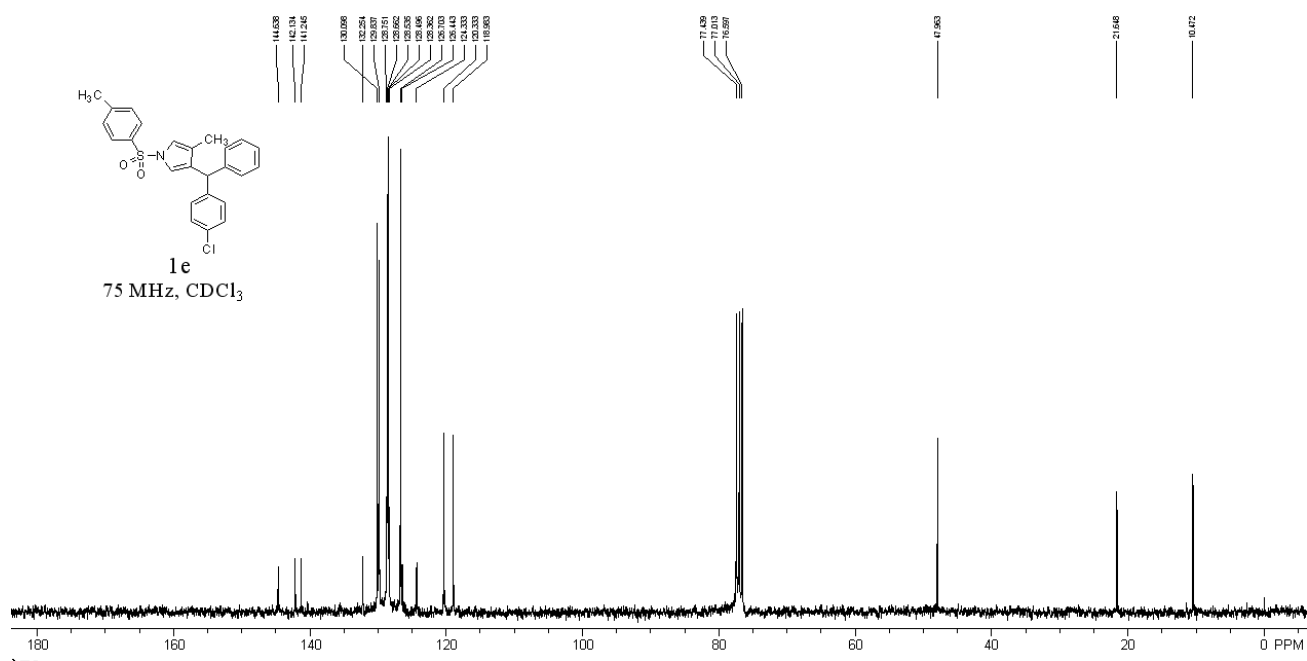
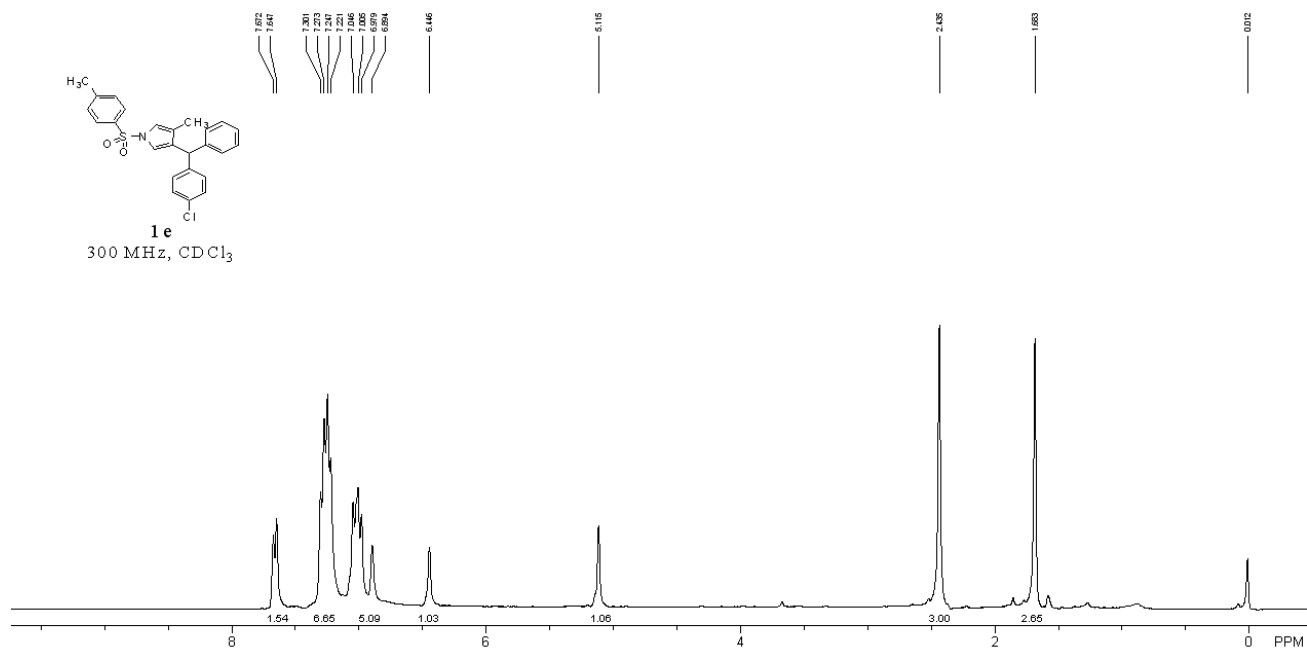
3. ^1H NMR and ^{13}C NMR Spectra for the New Compounds

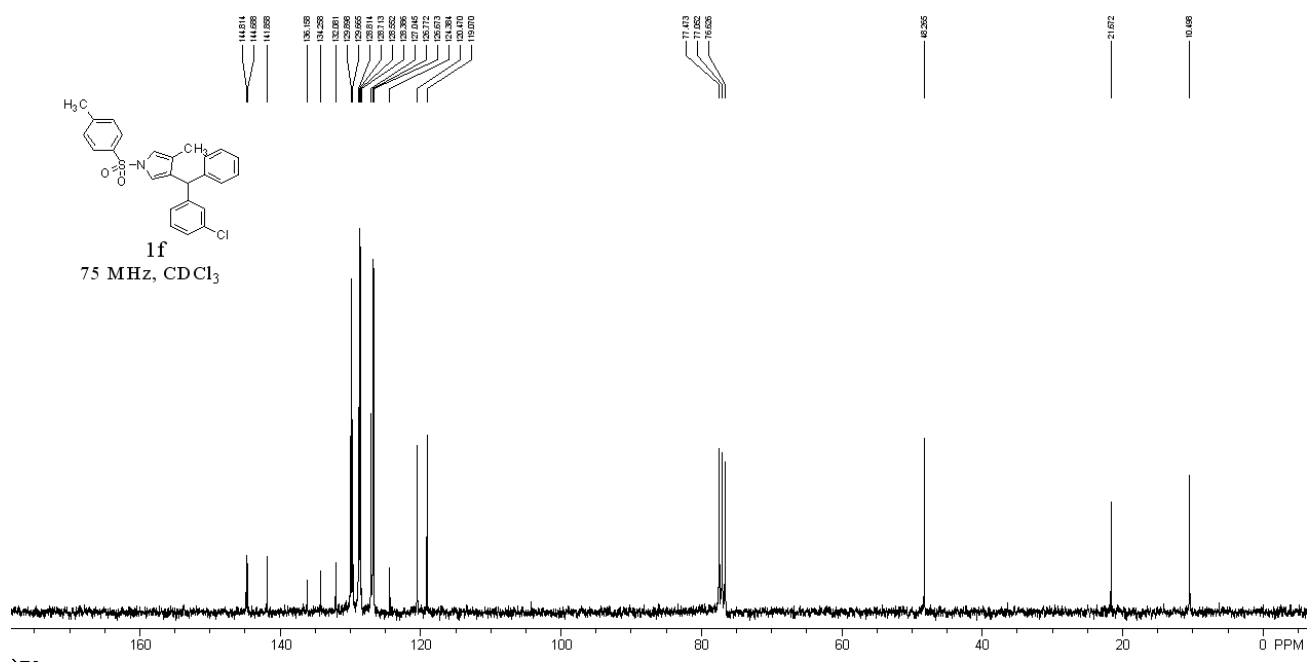
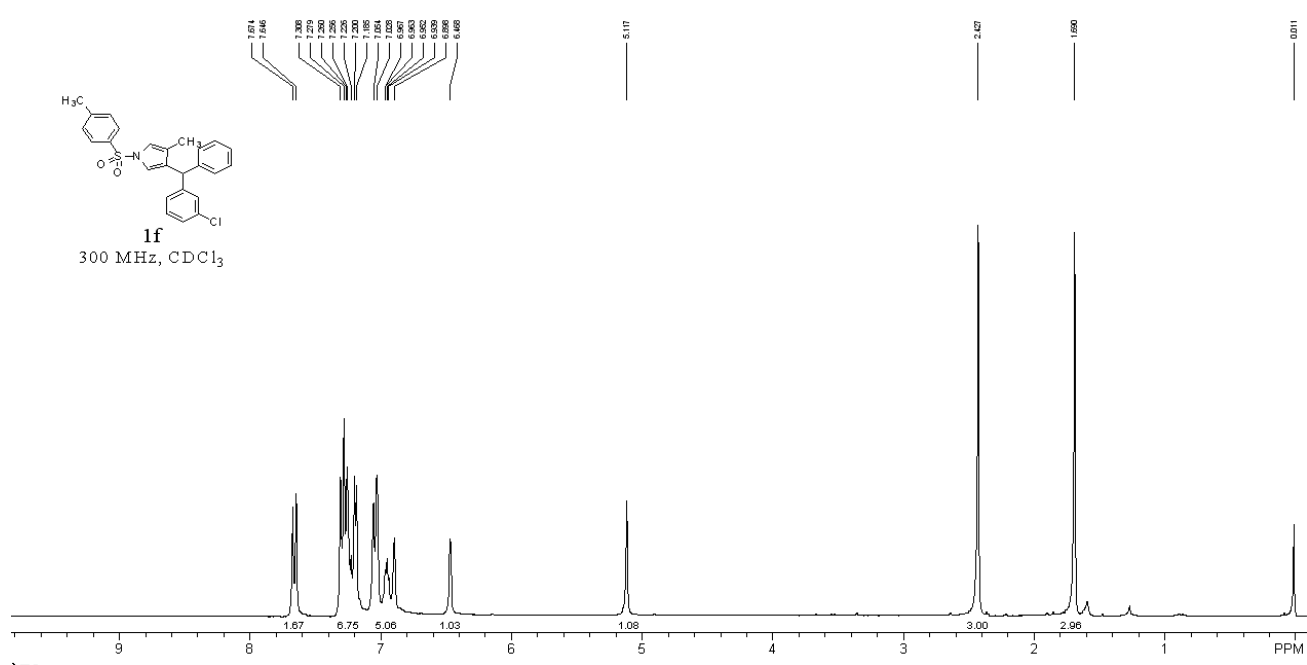


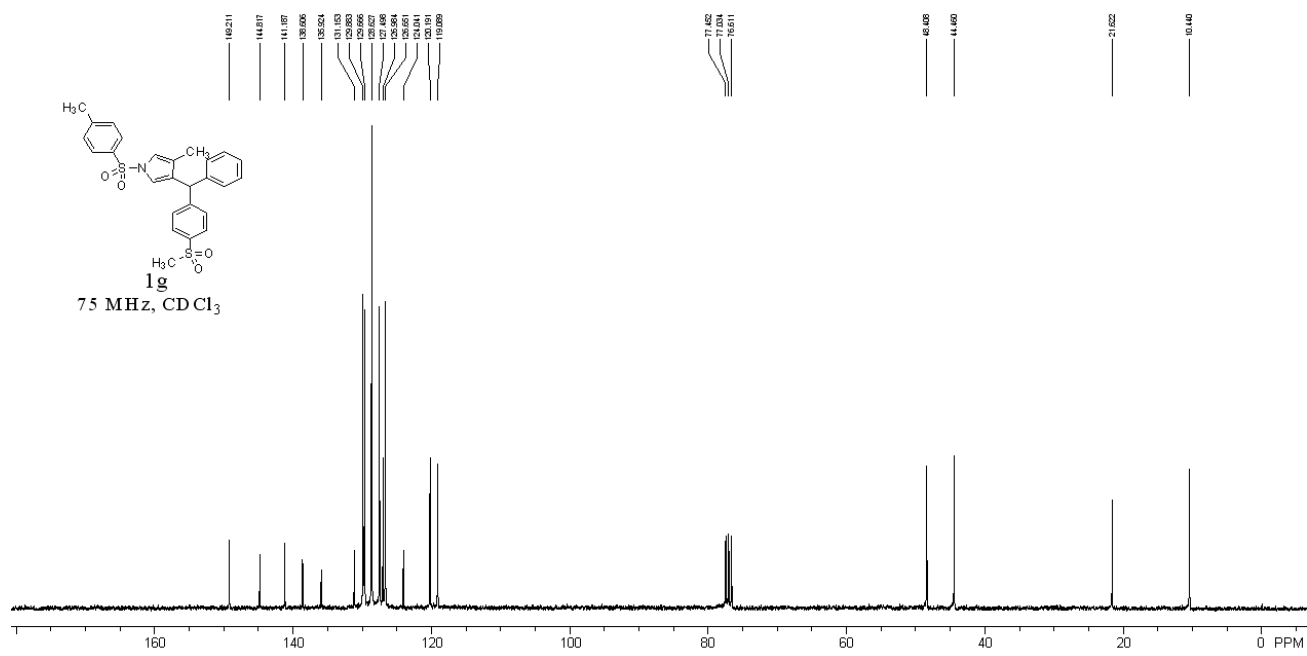
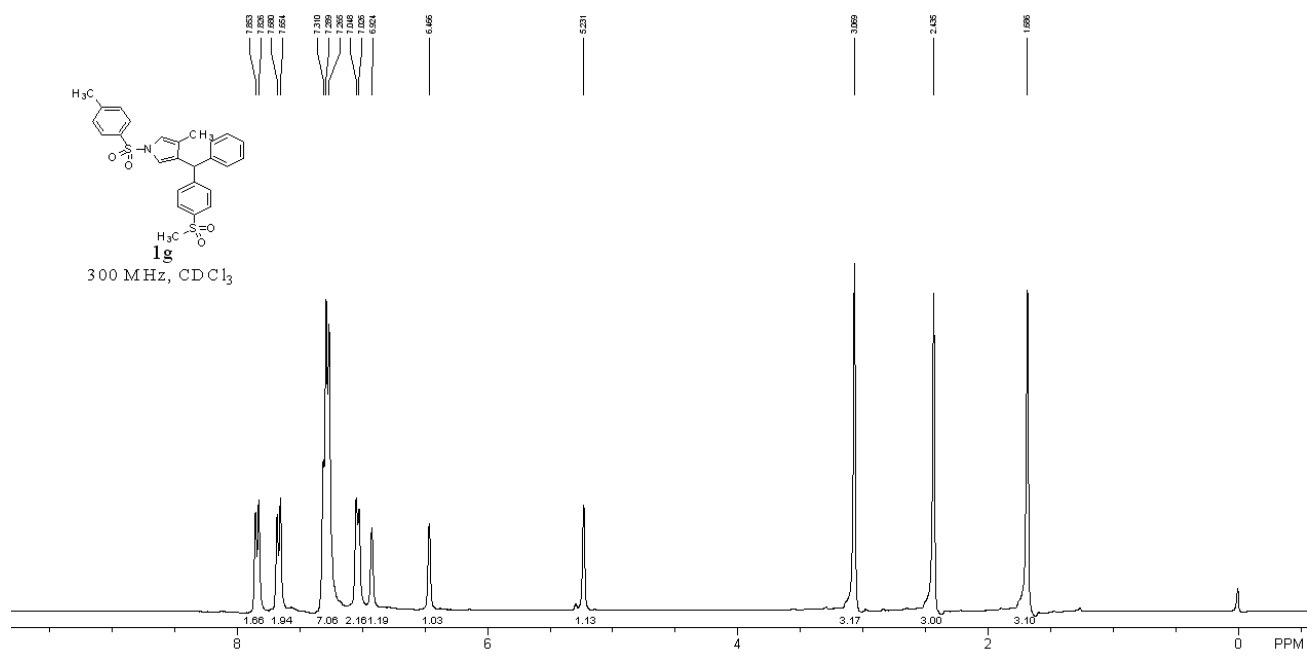


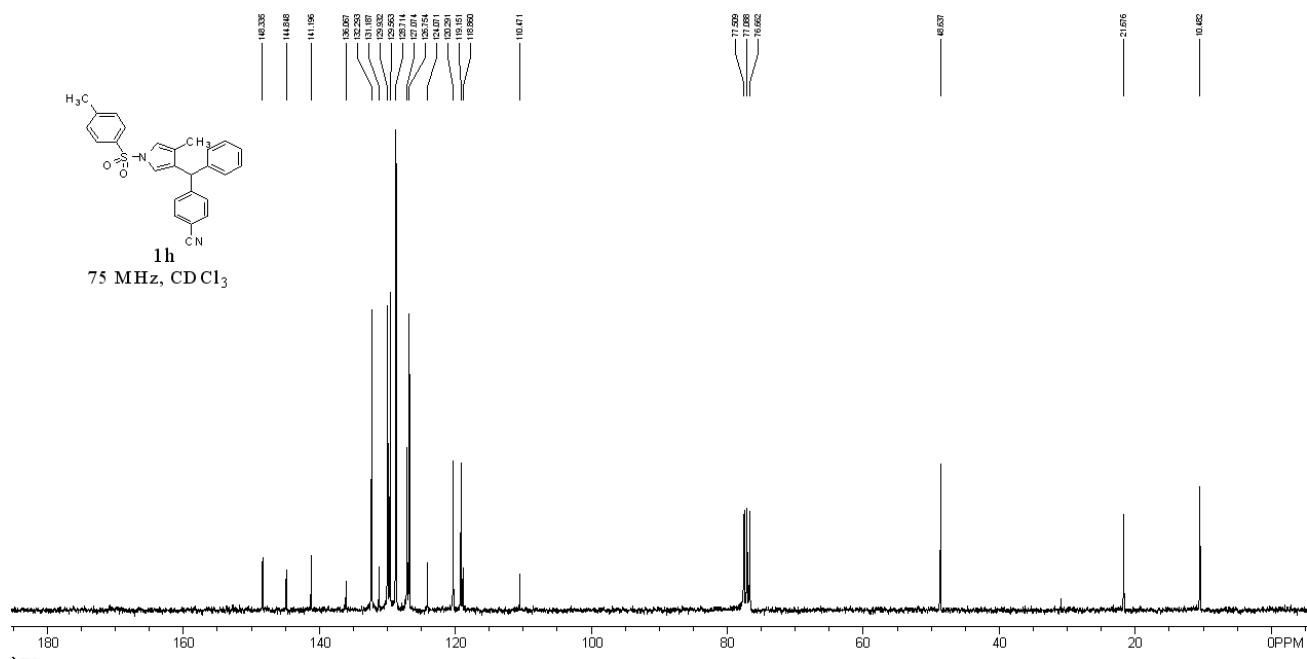
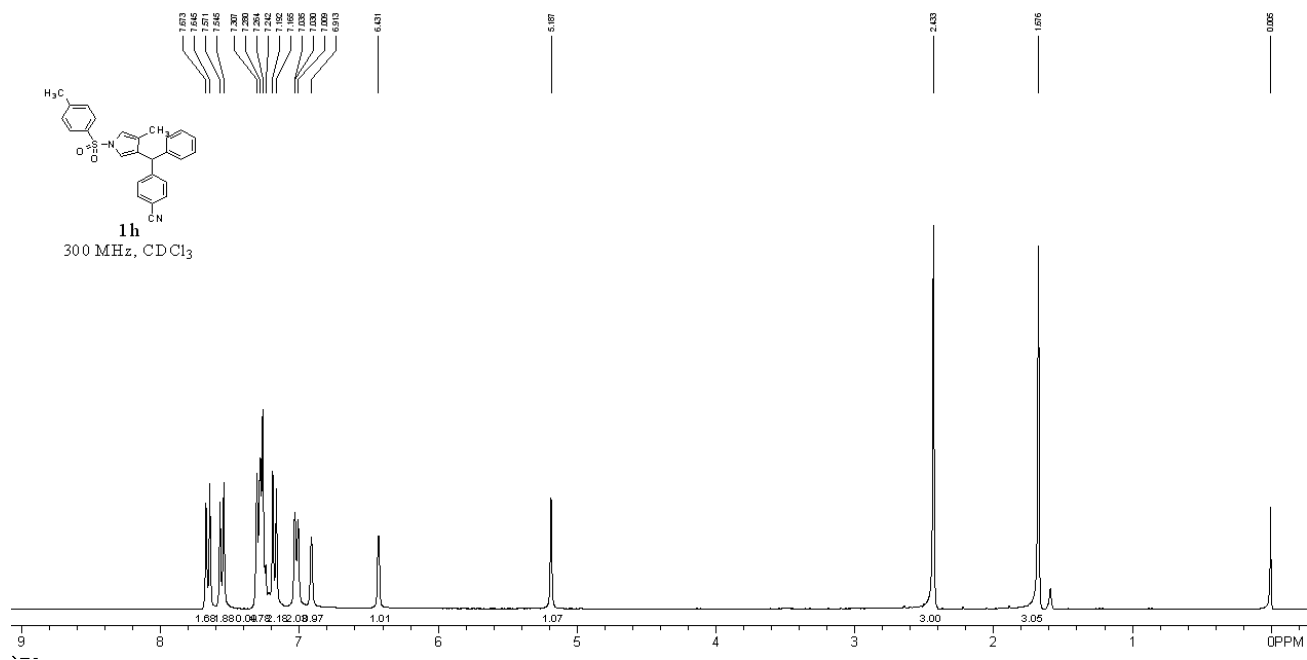


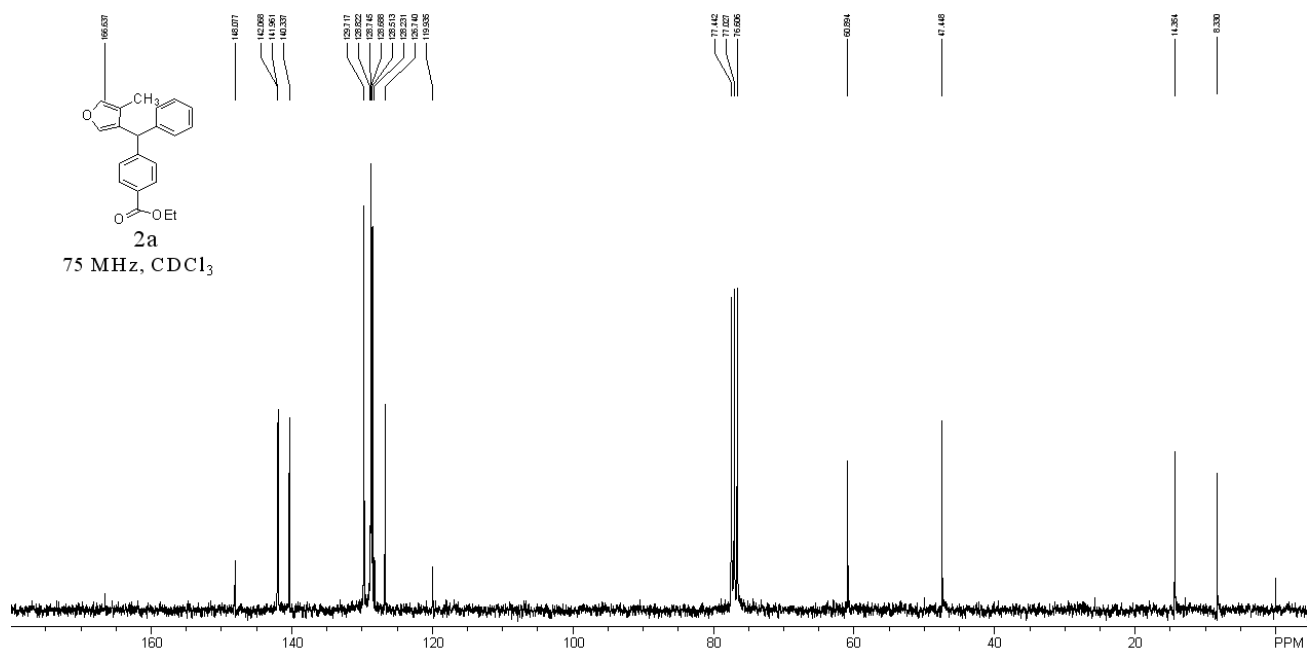
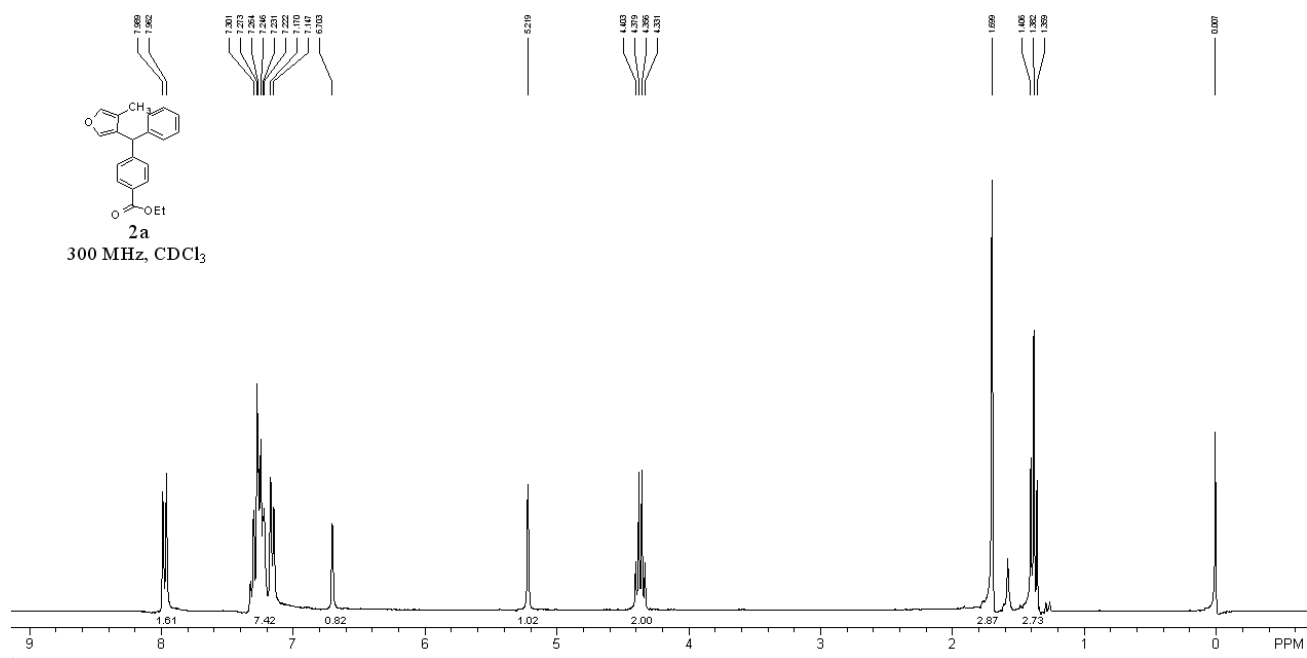


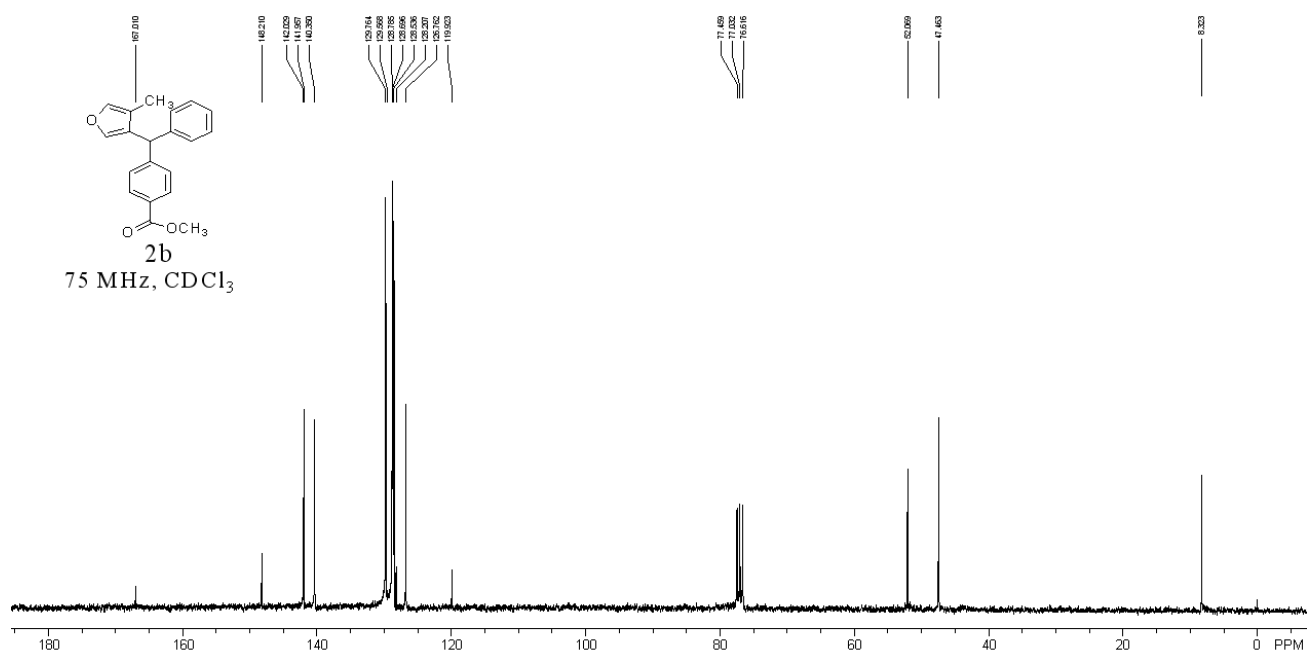
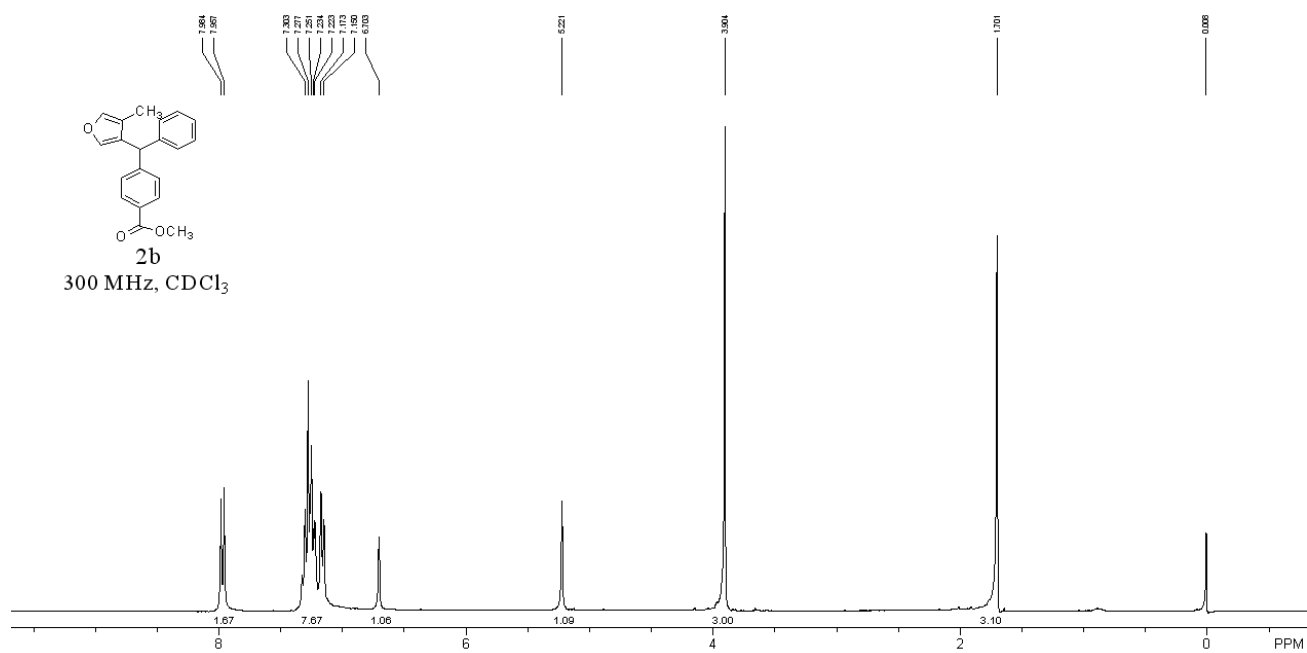


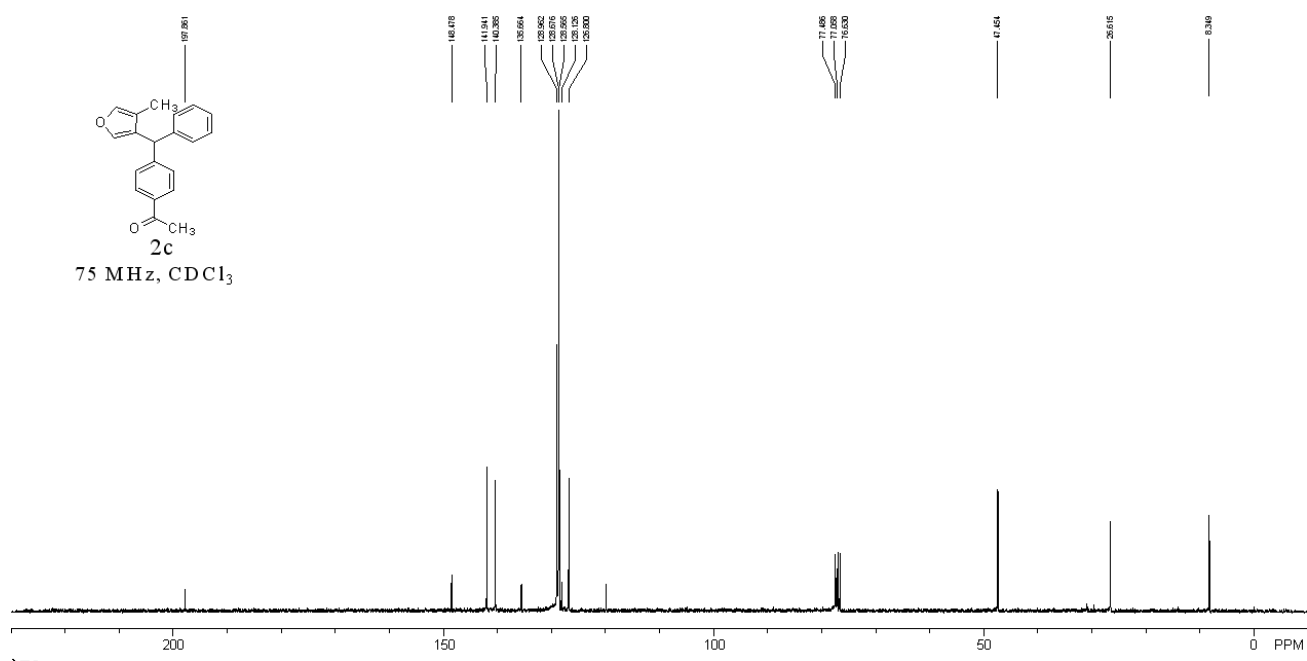
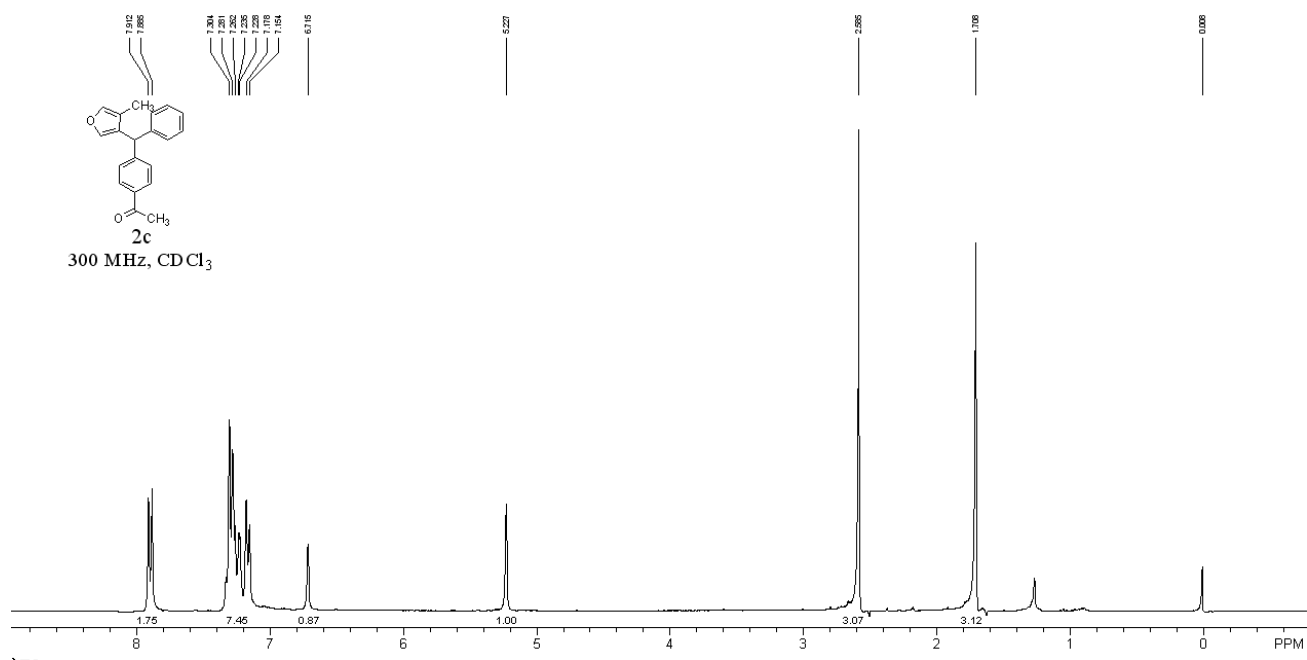


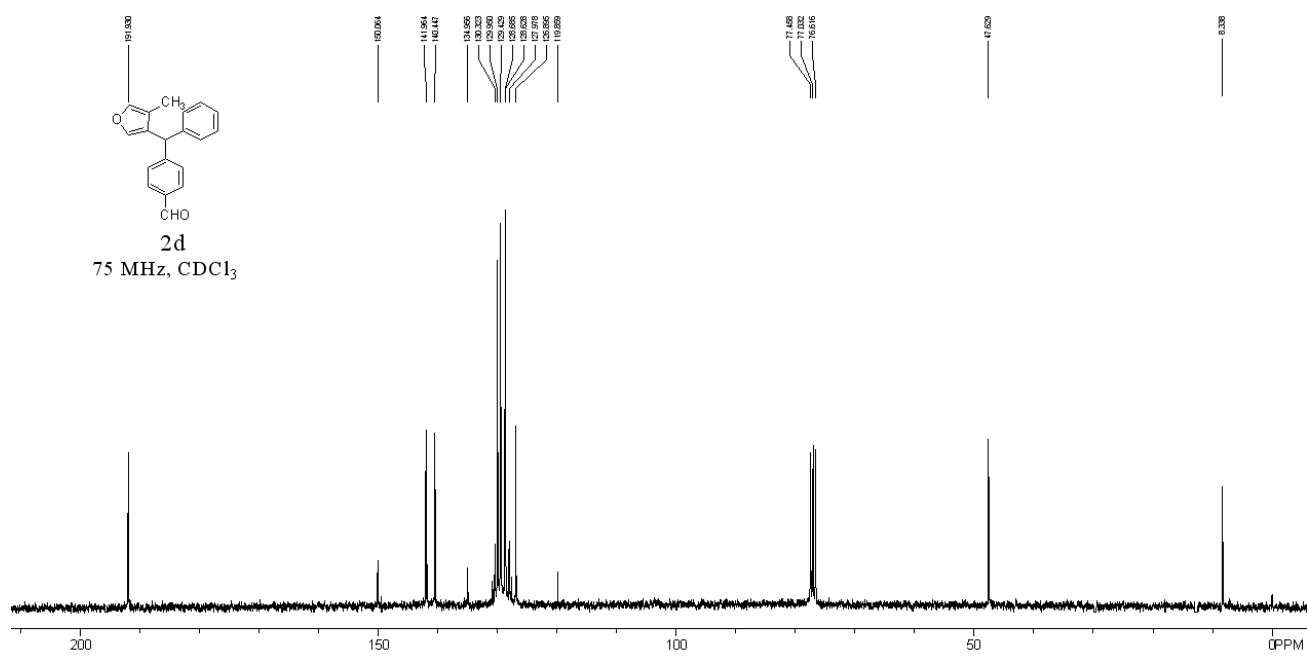
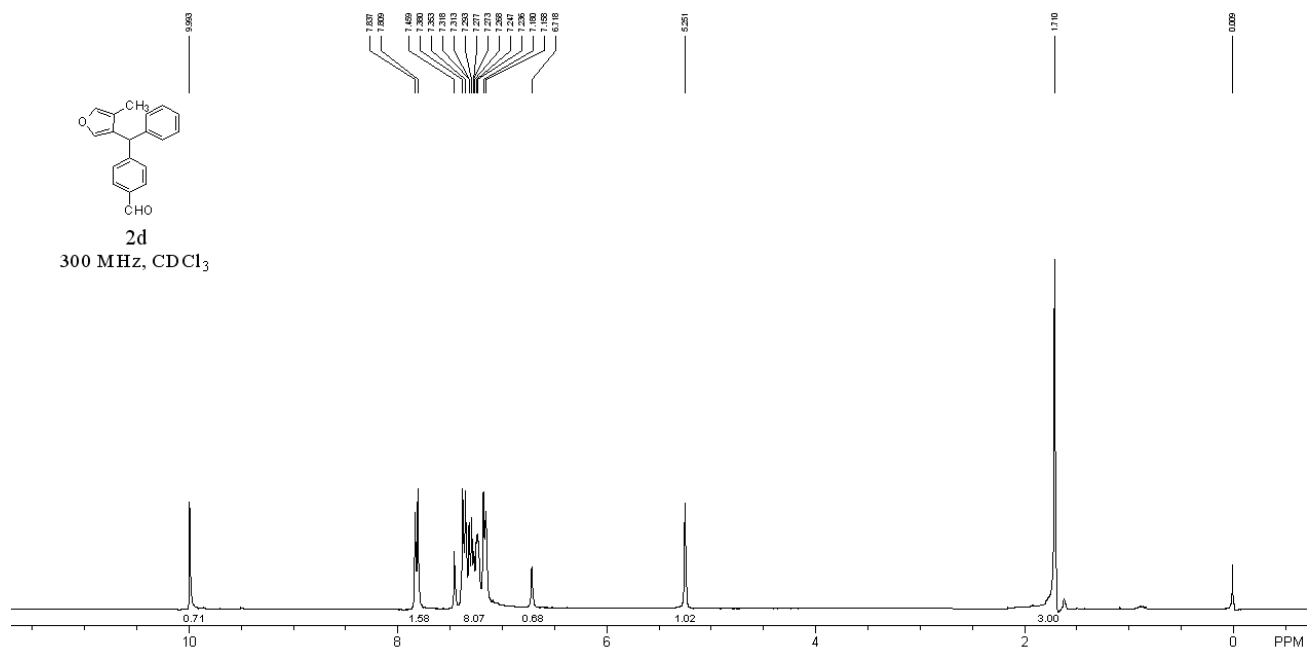


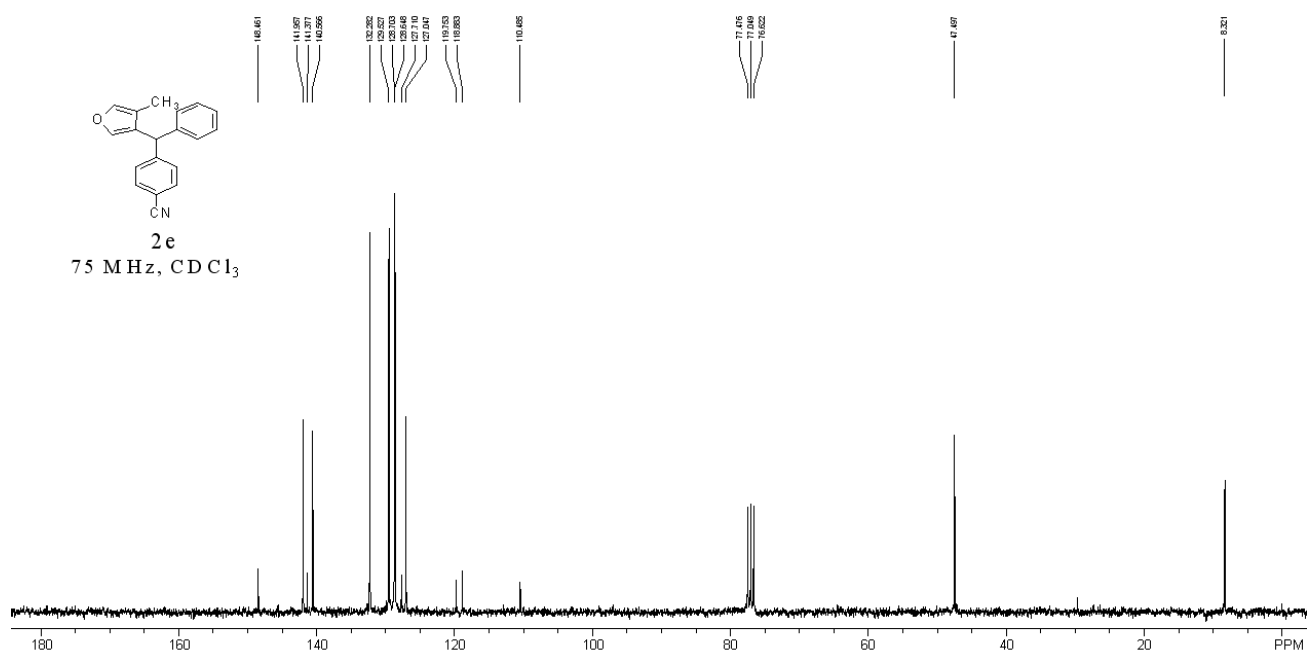
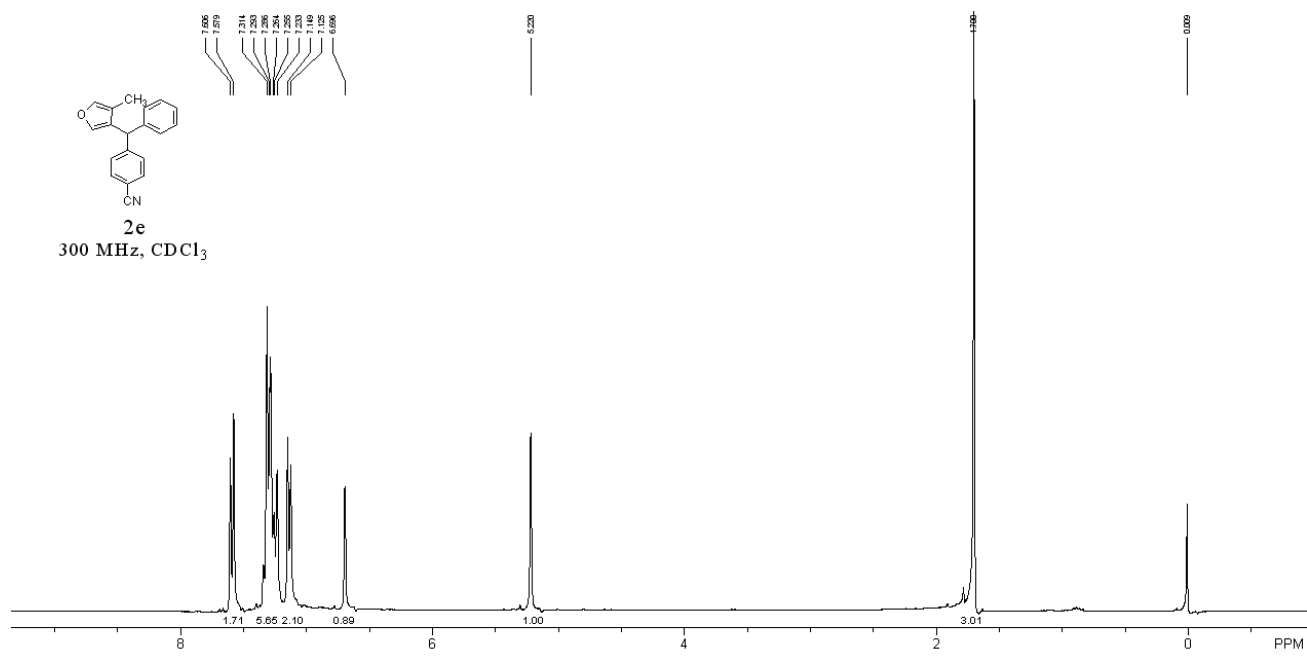


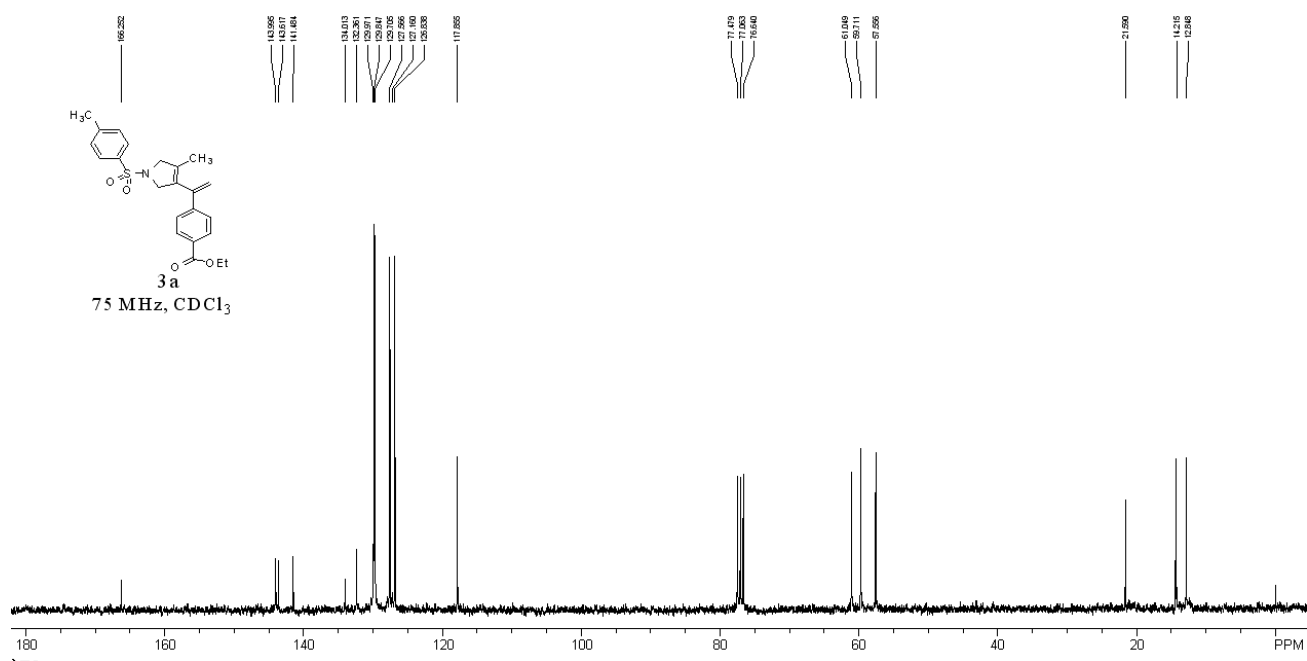
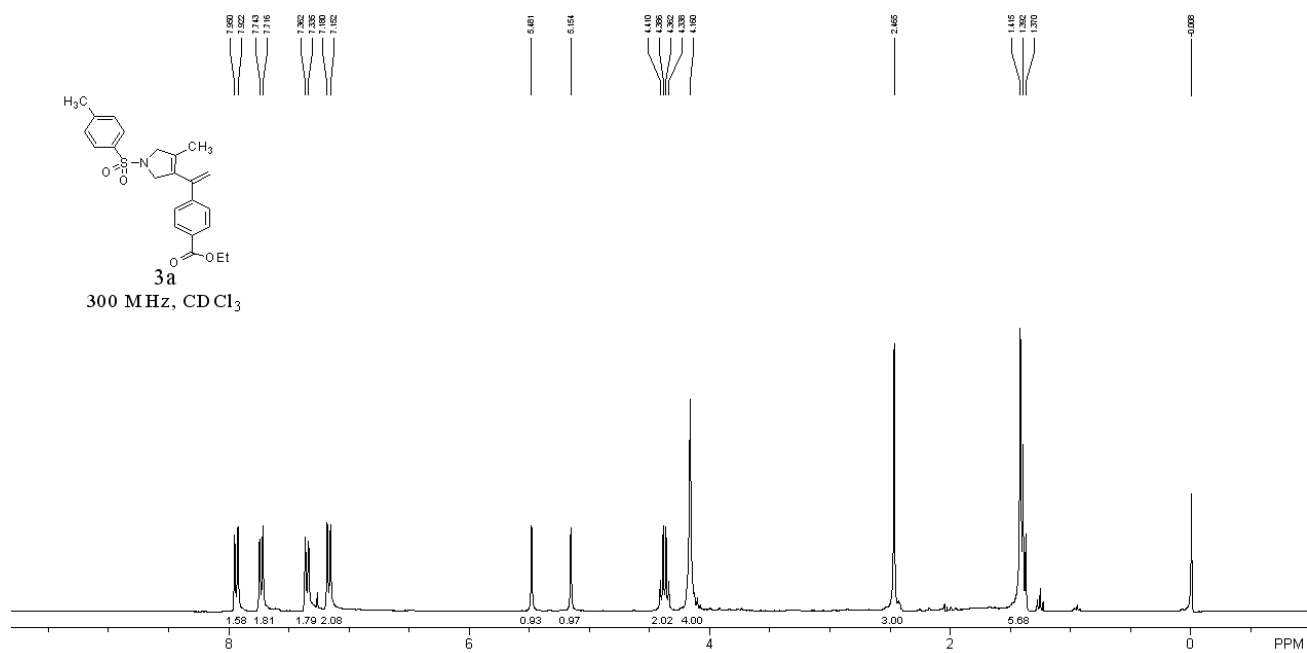


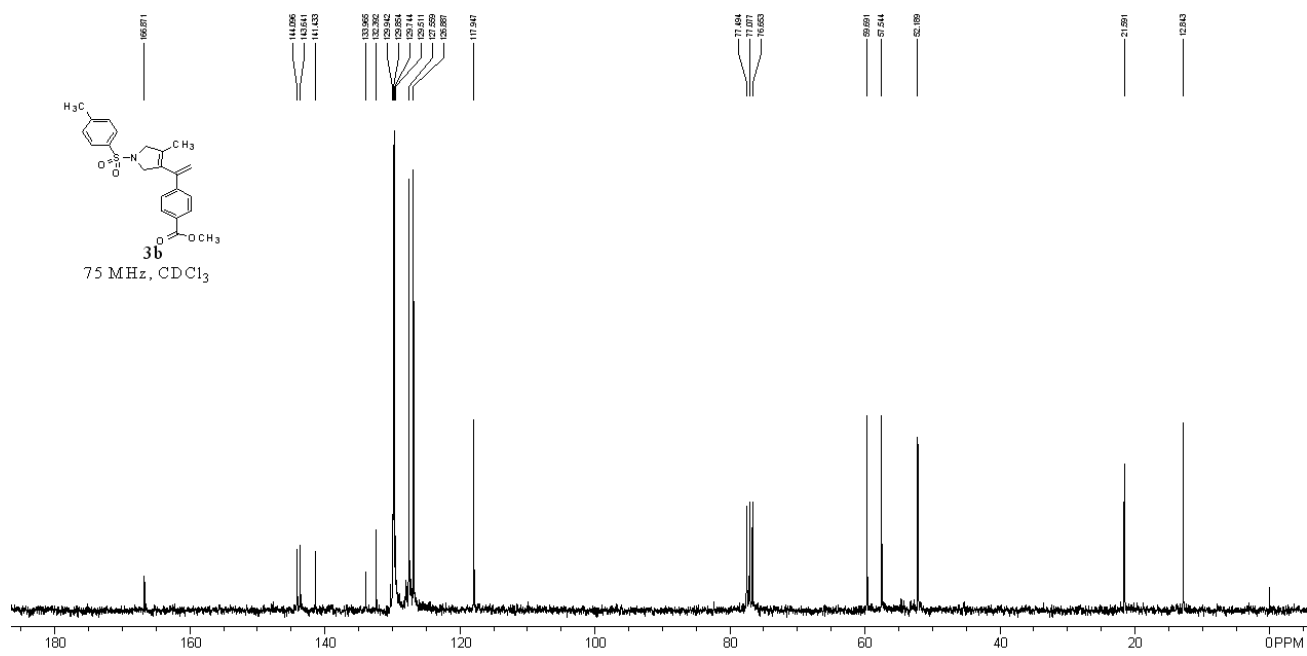
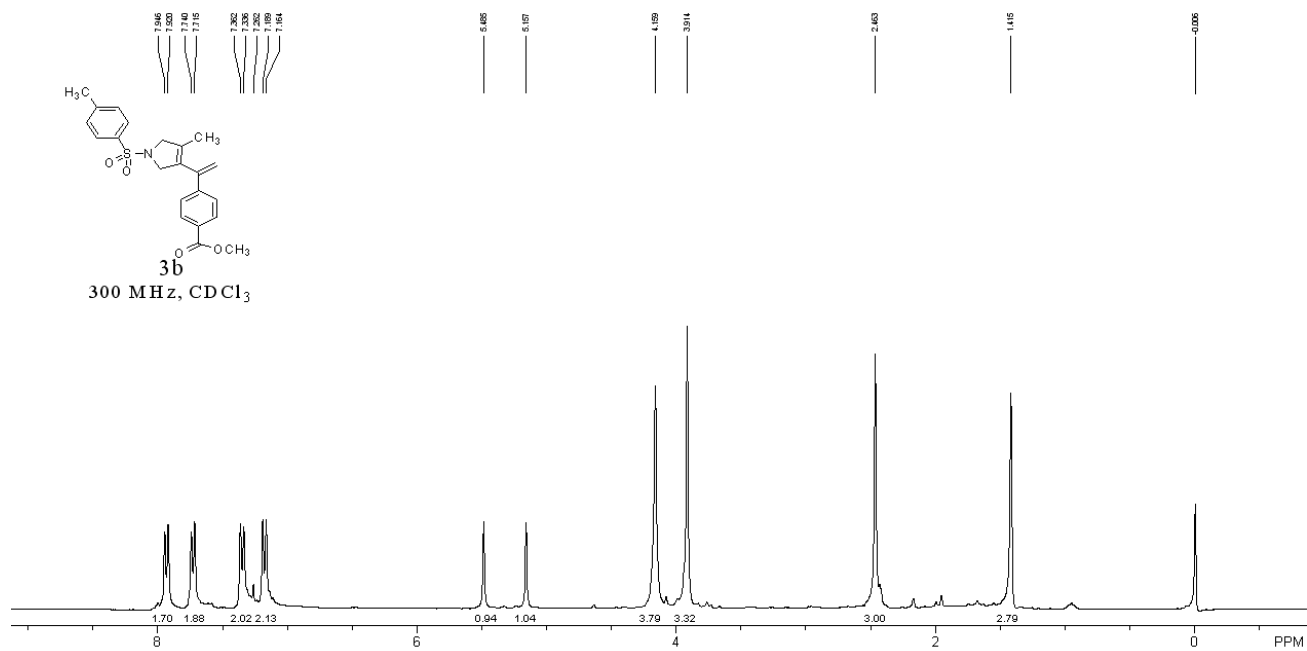


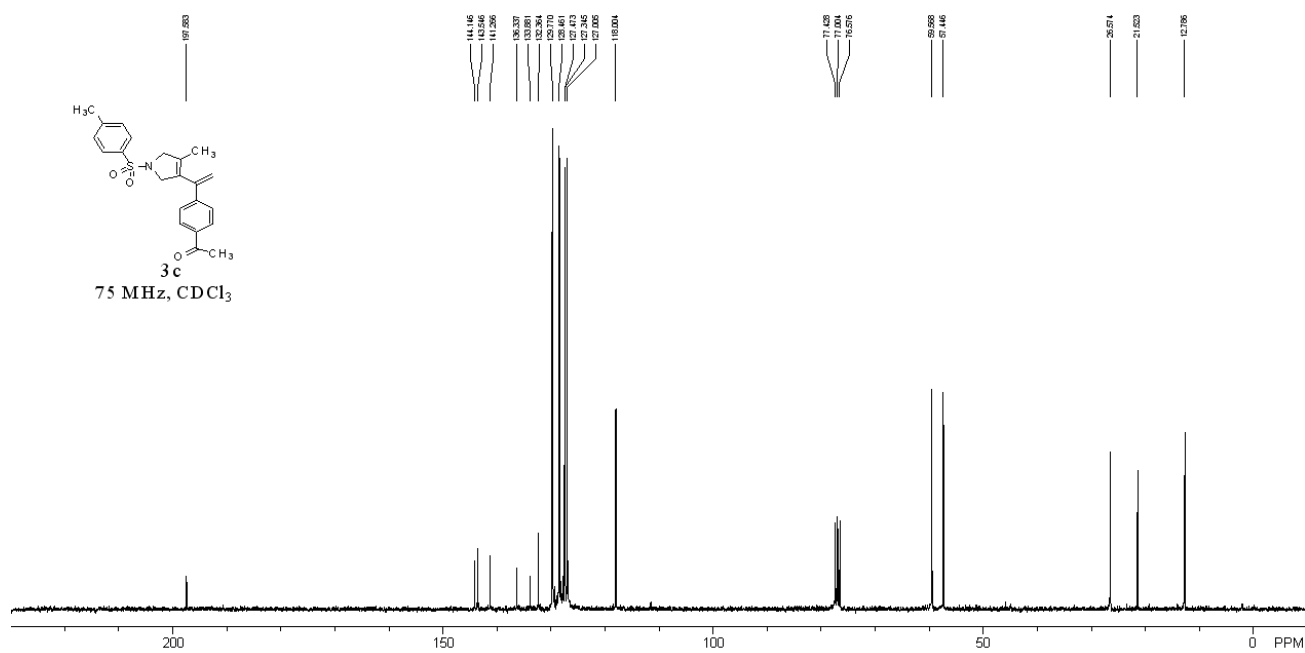
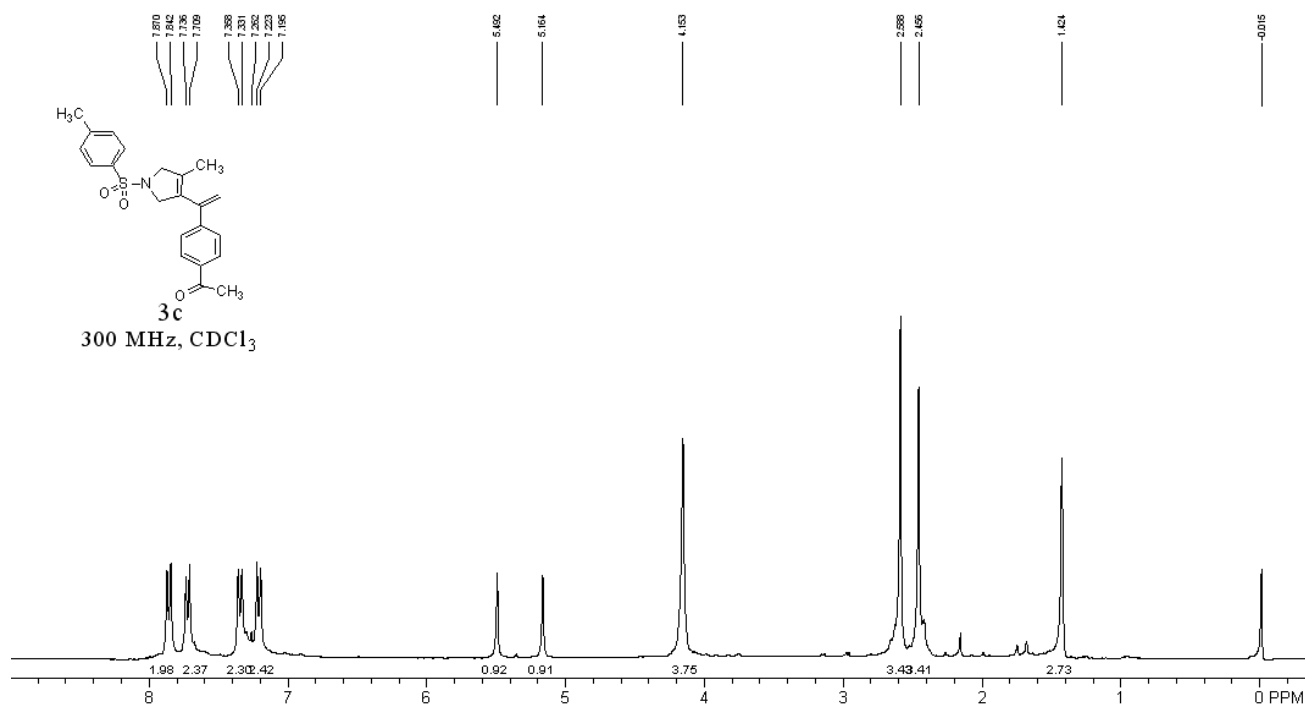


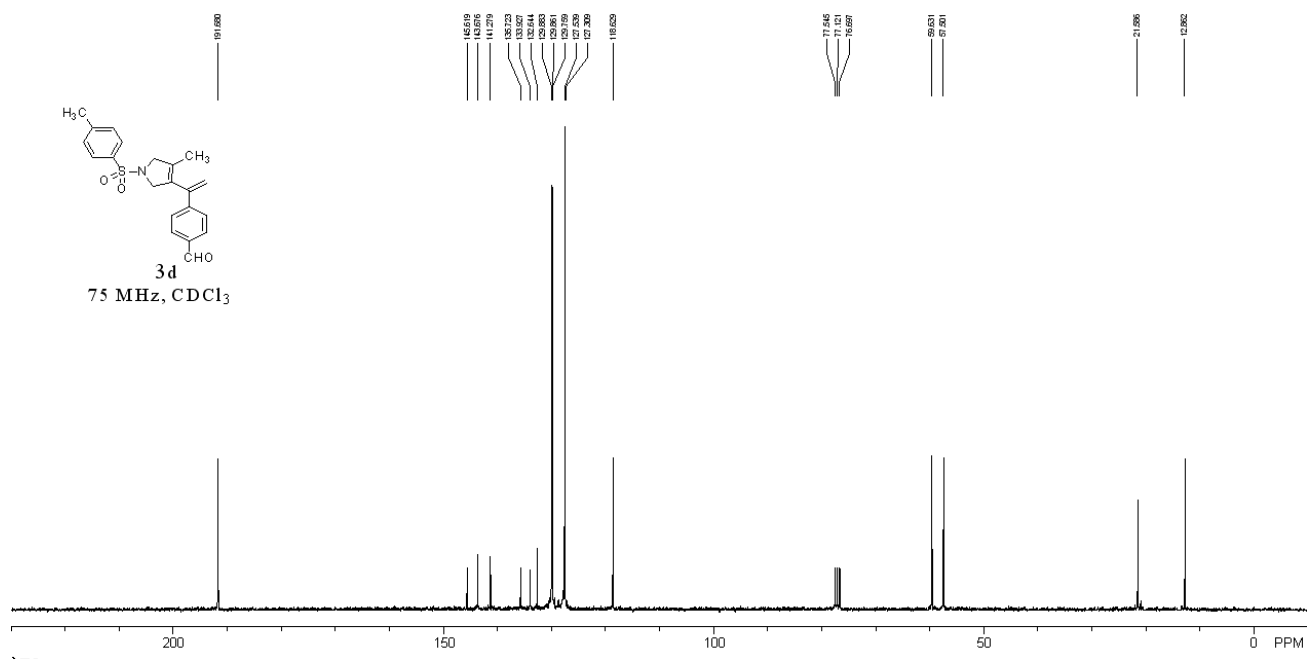
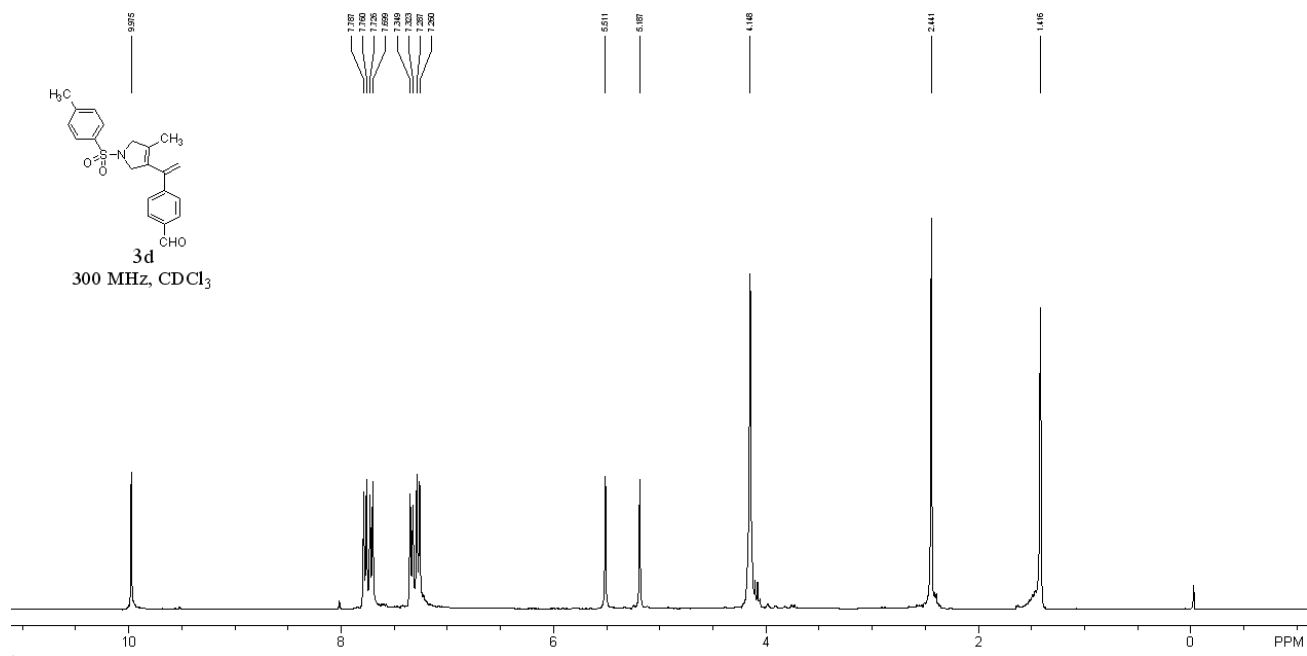


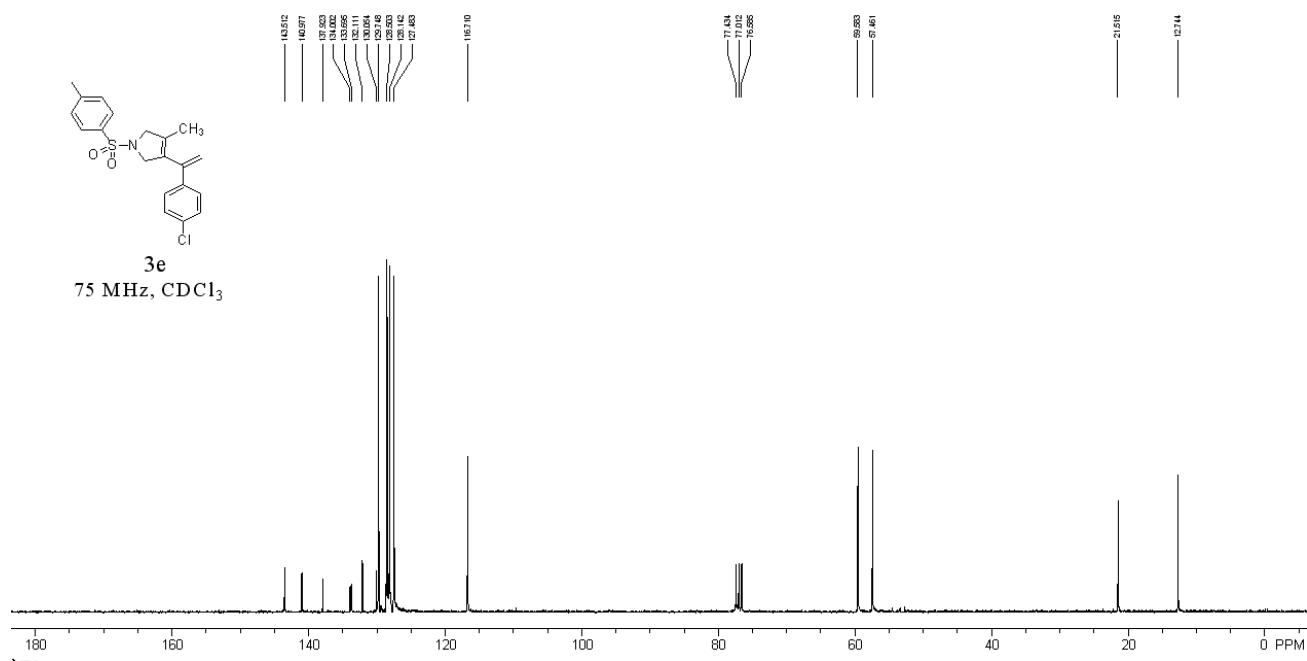
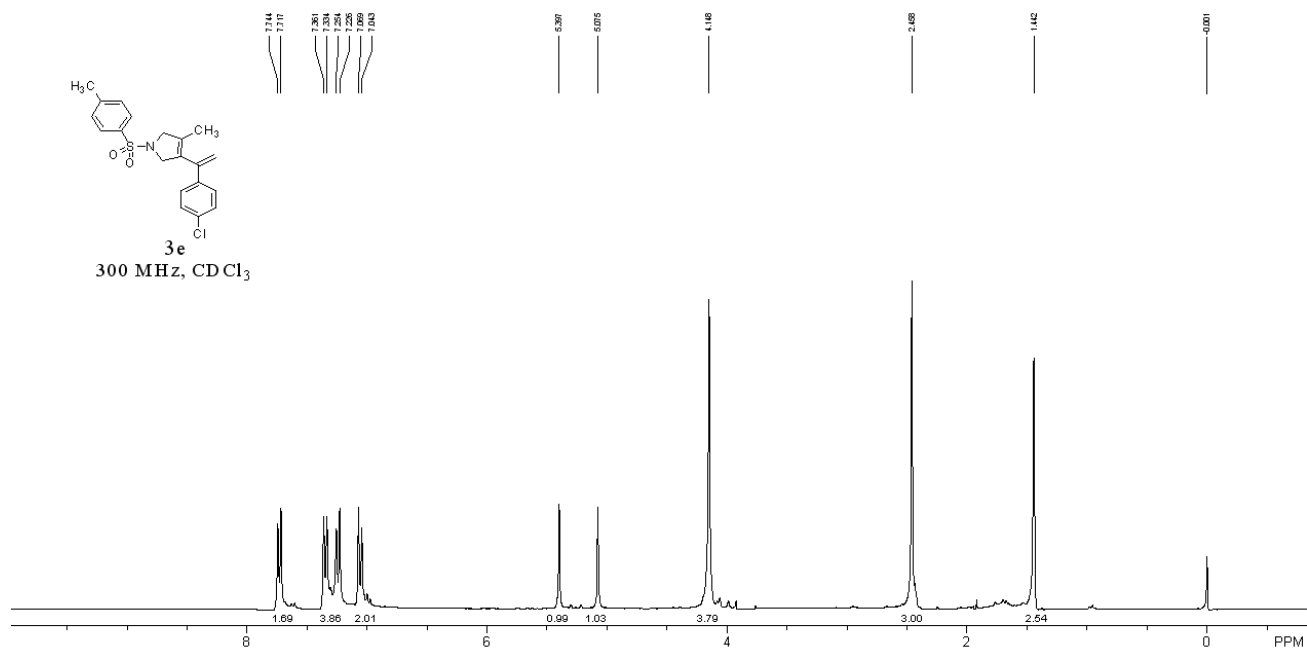


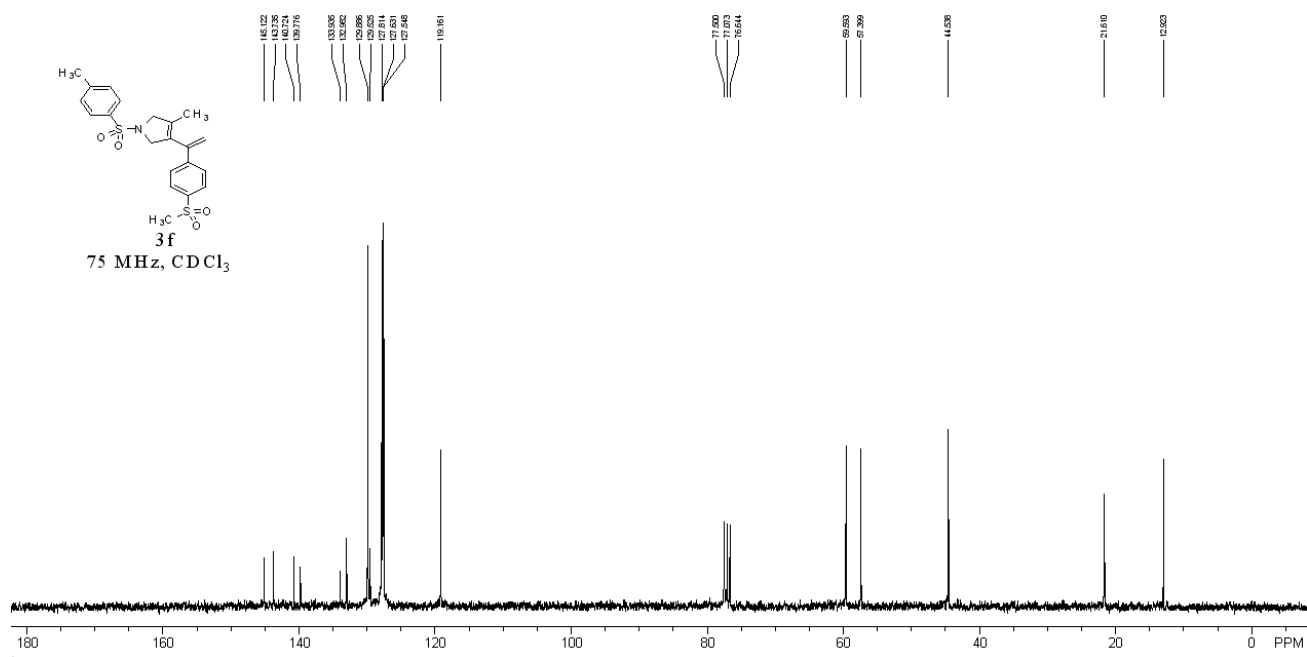
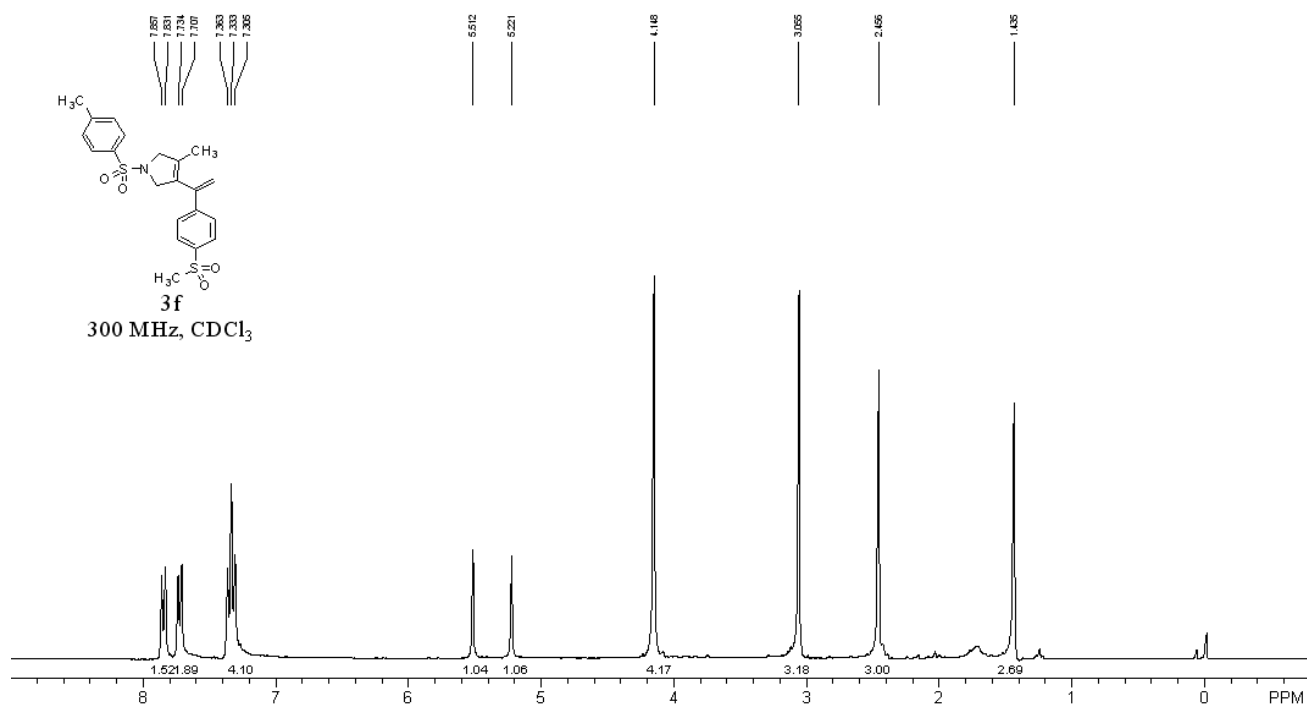


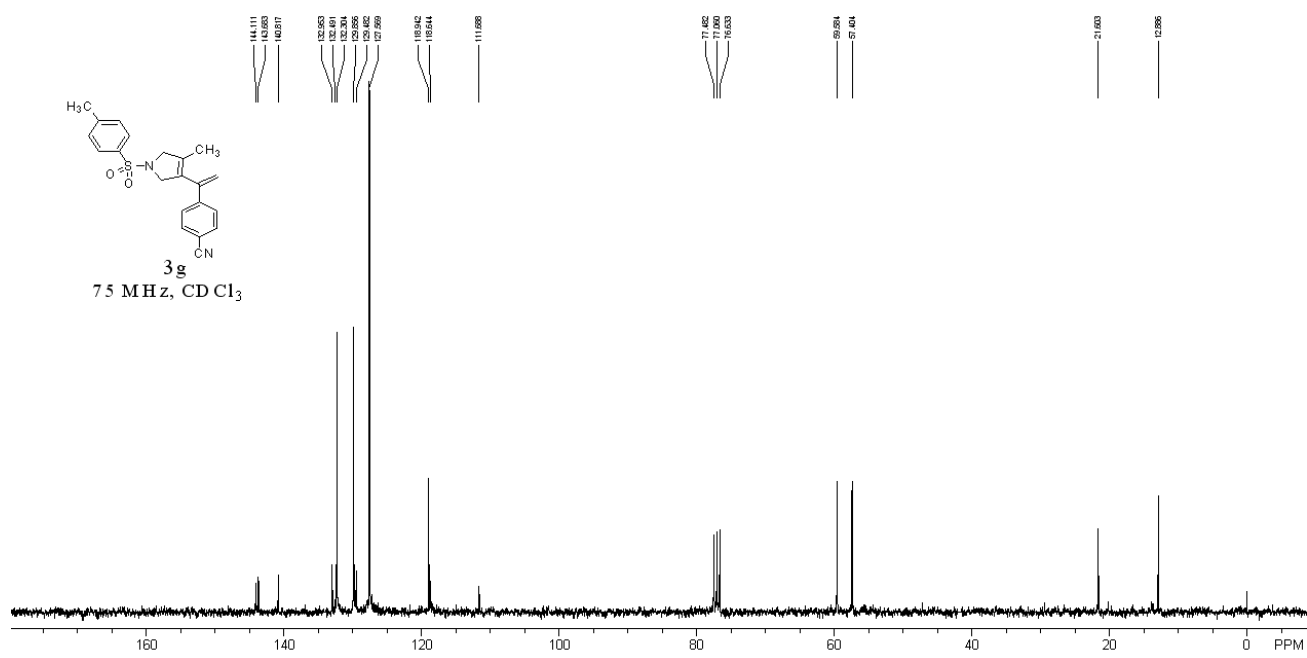
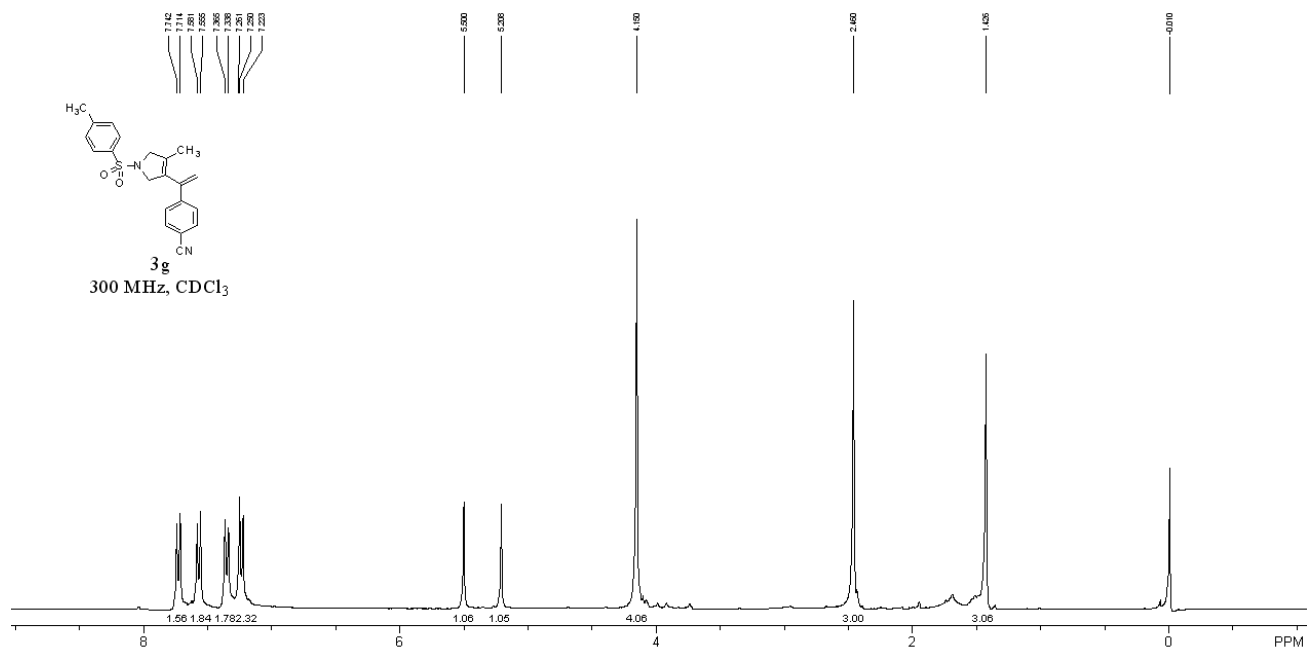


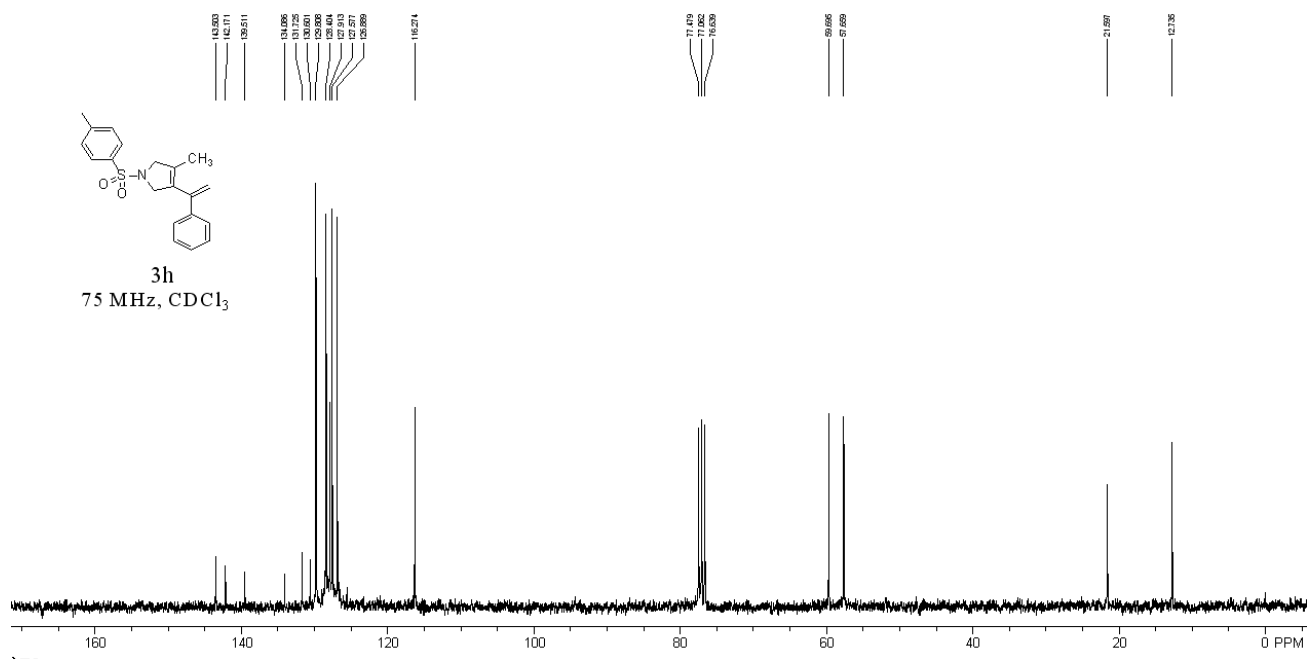
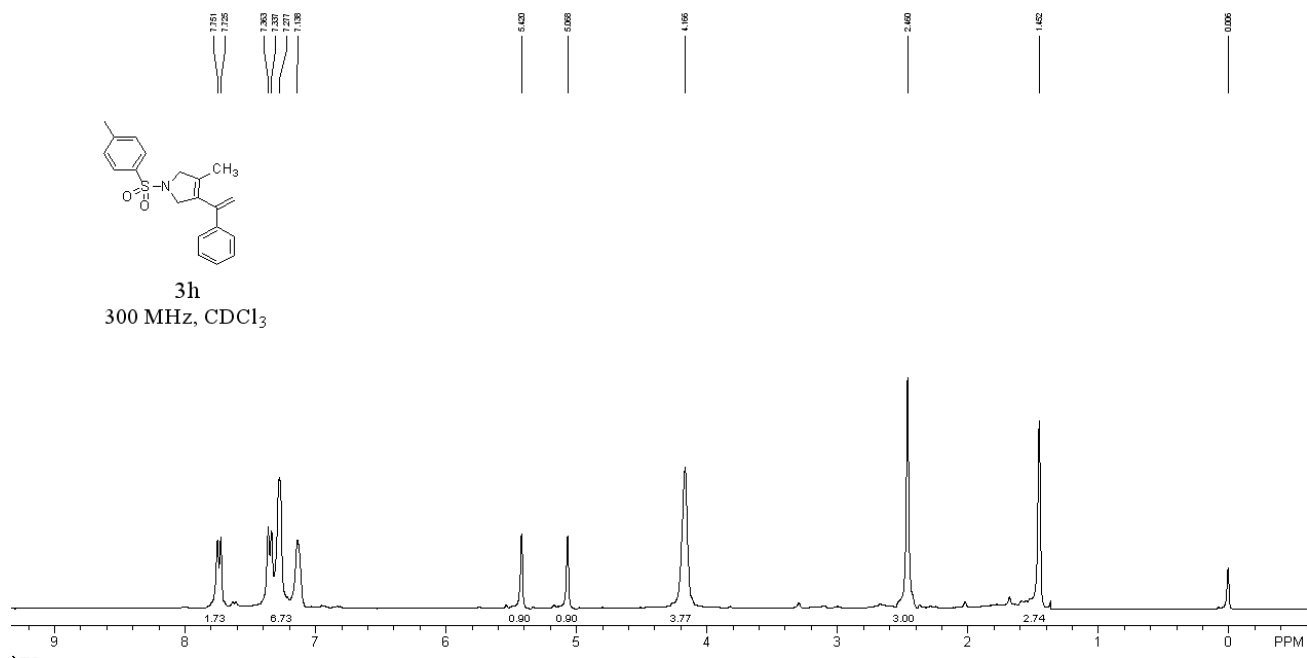


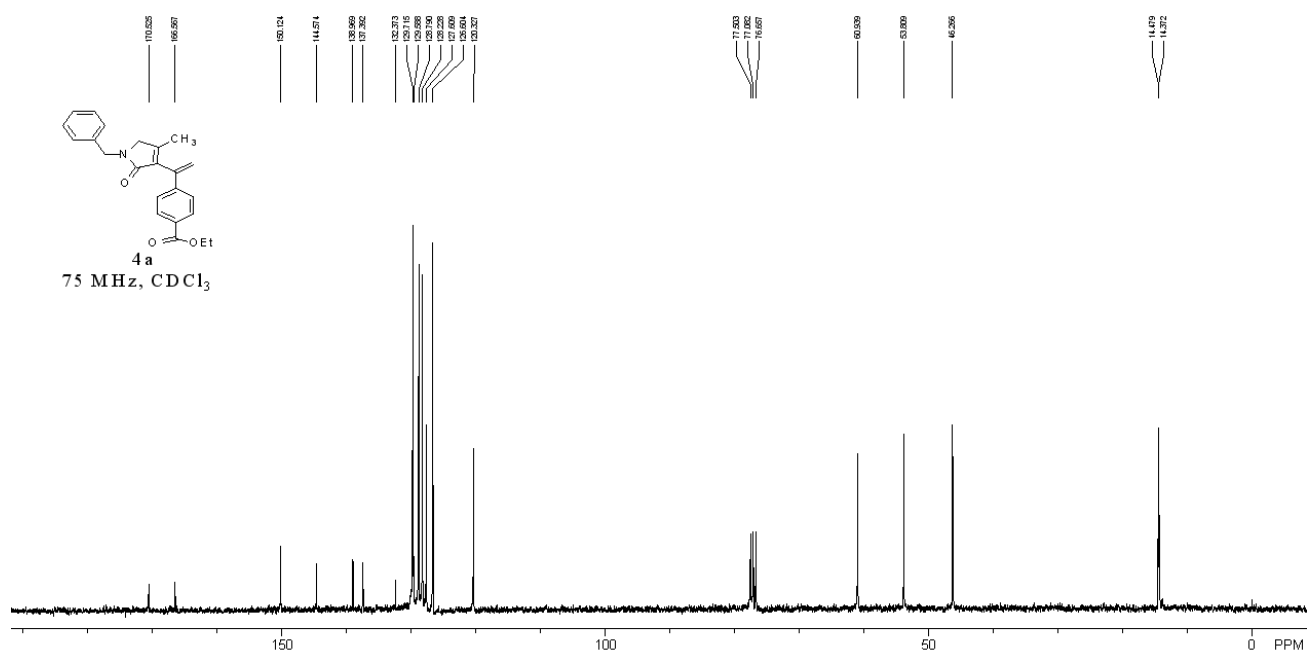
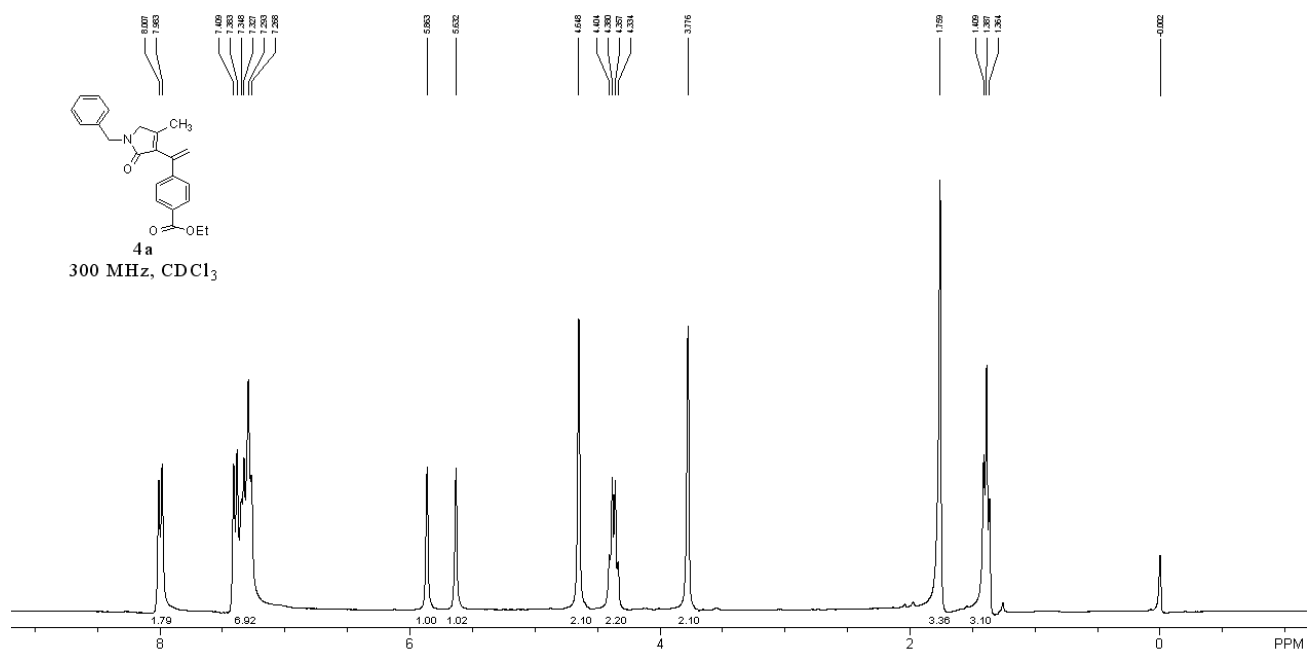


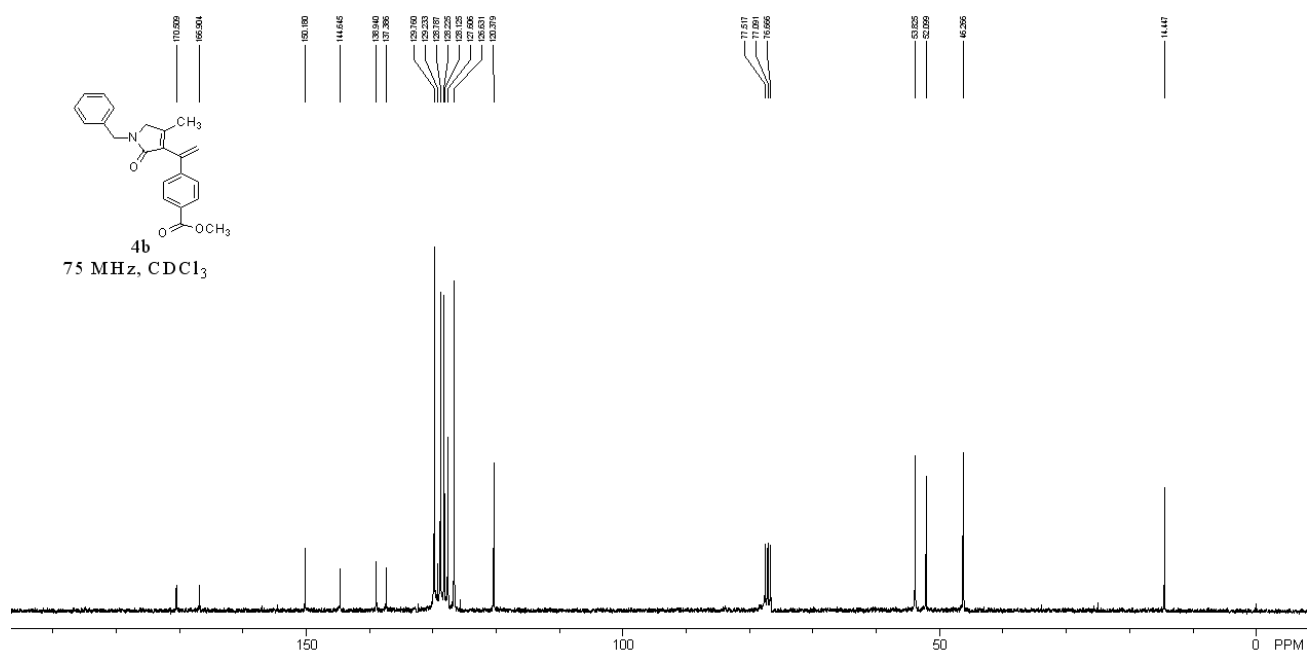
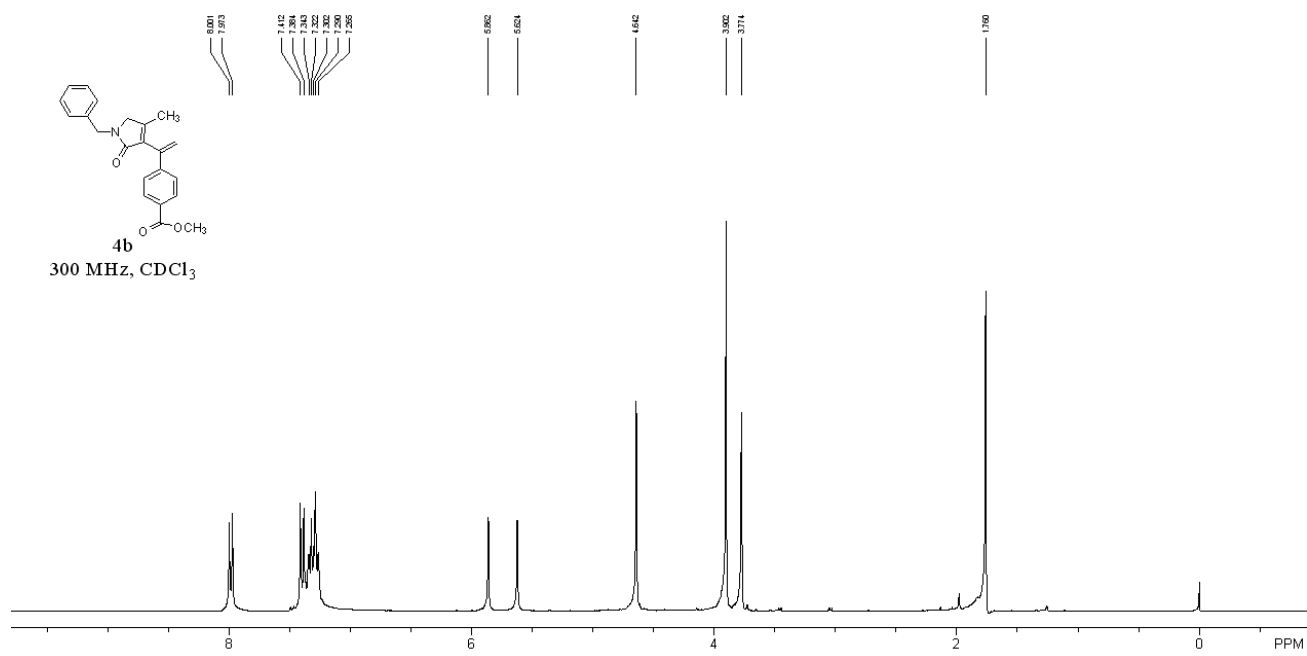


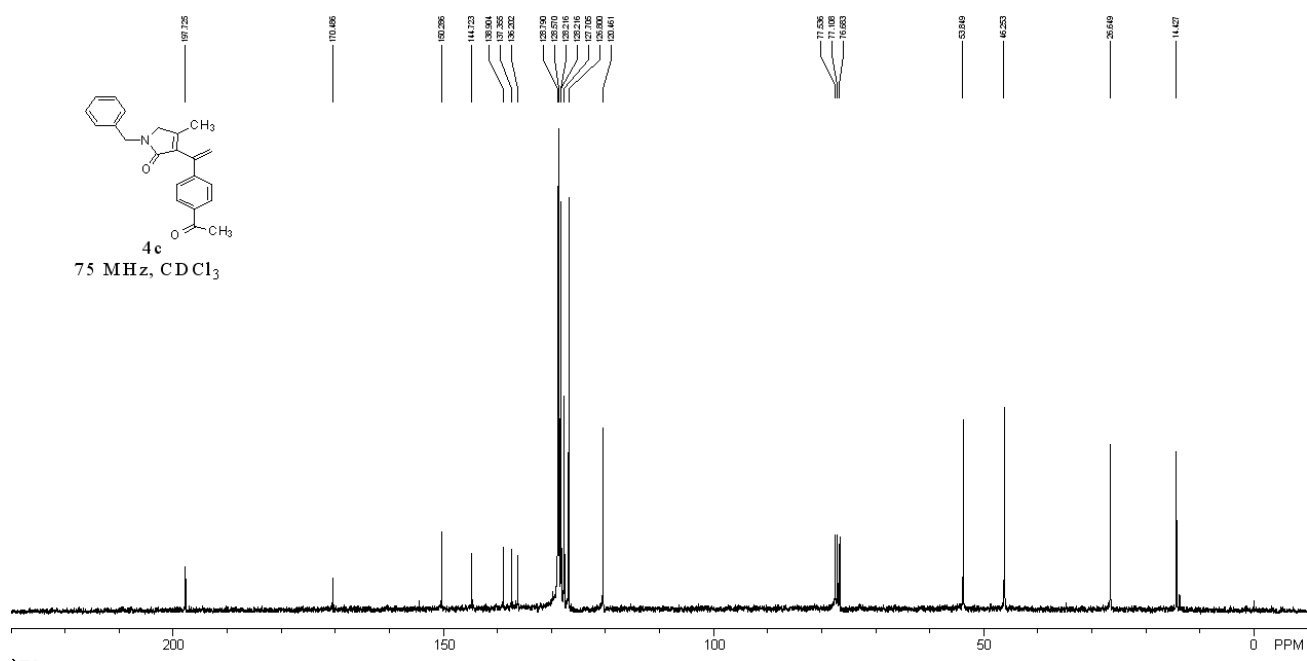
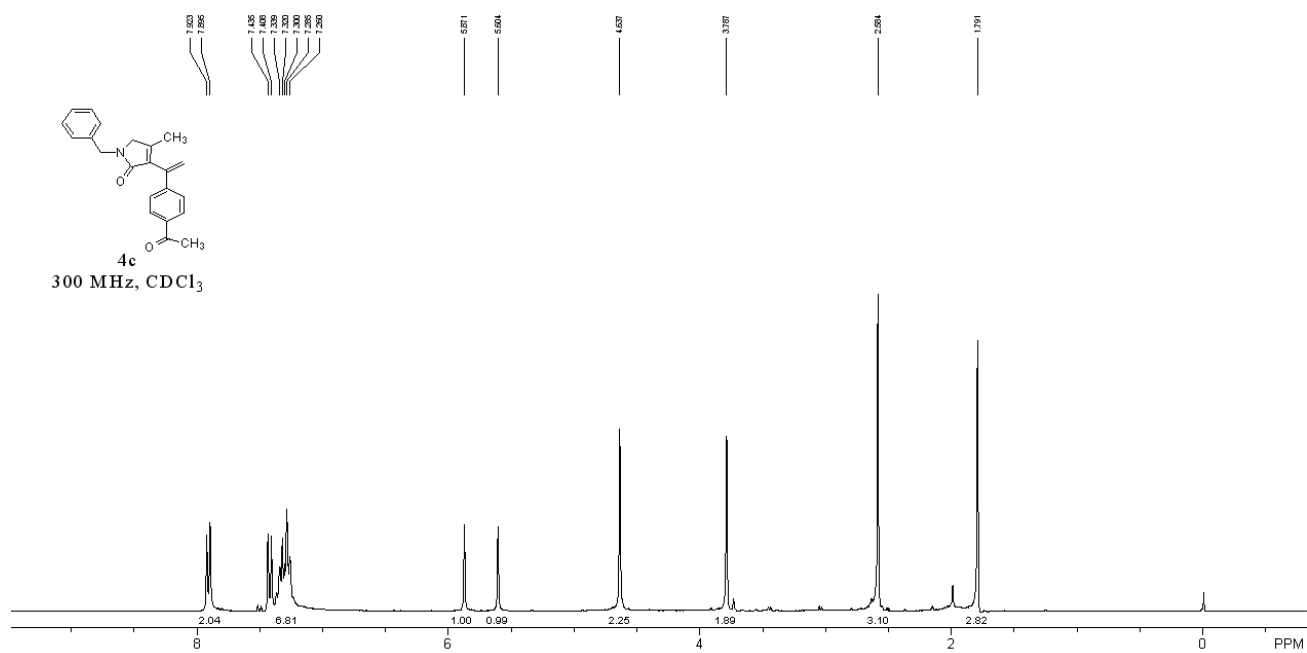


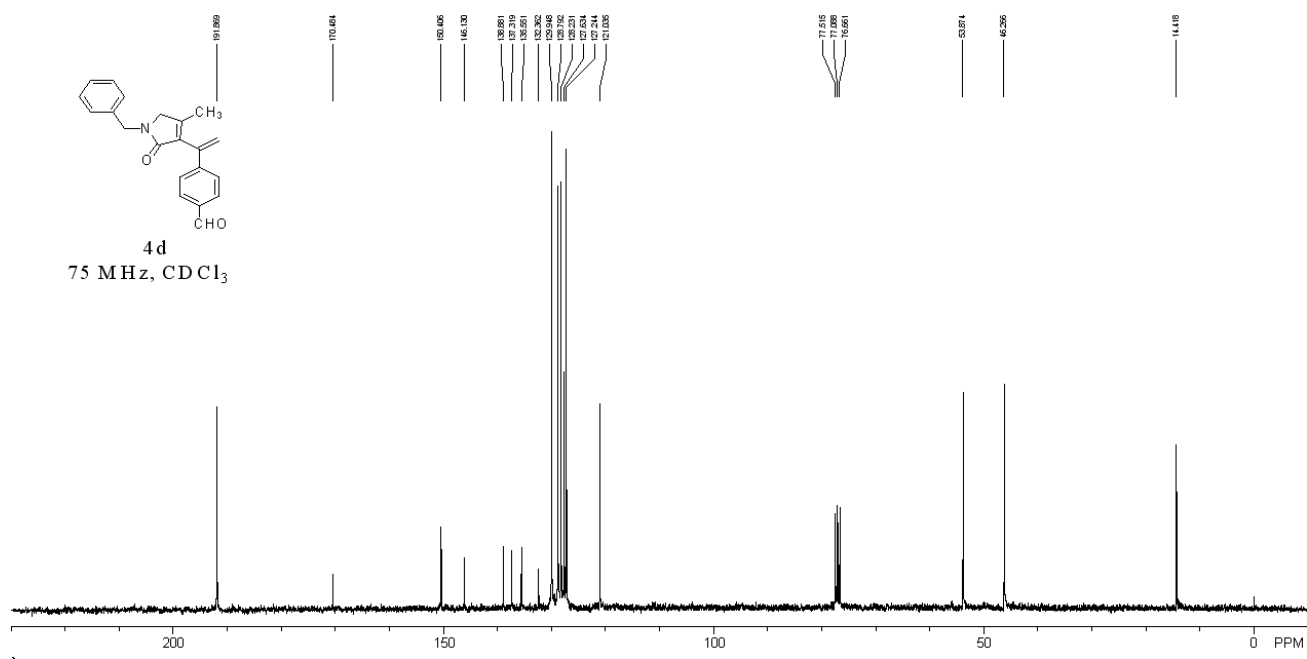
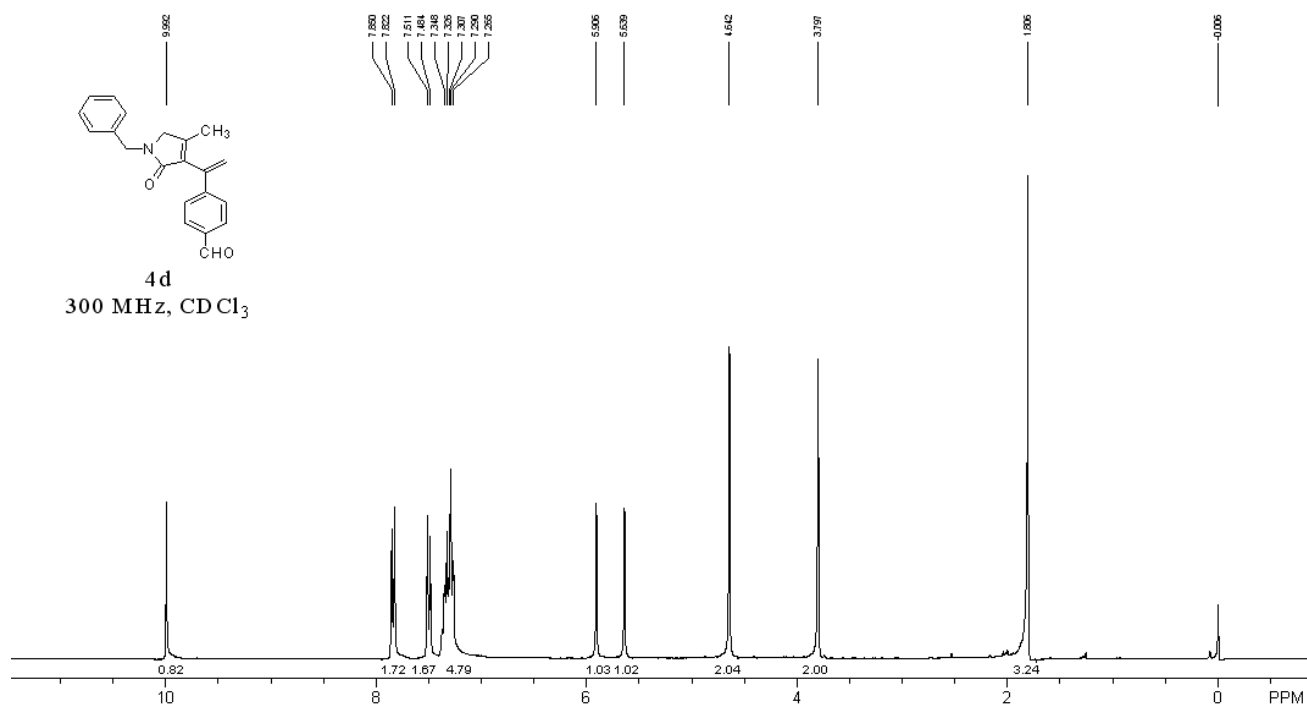


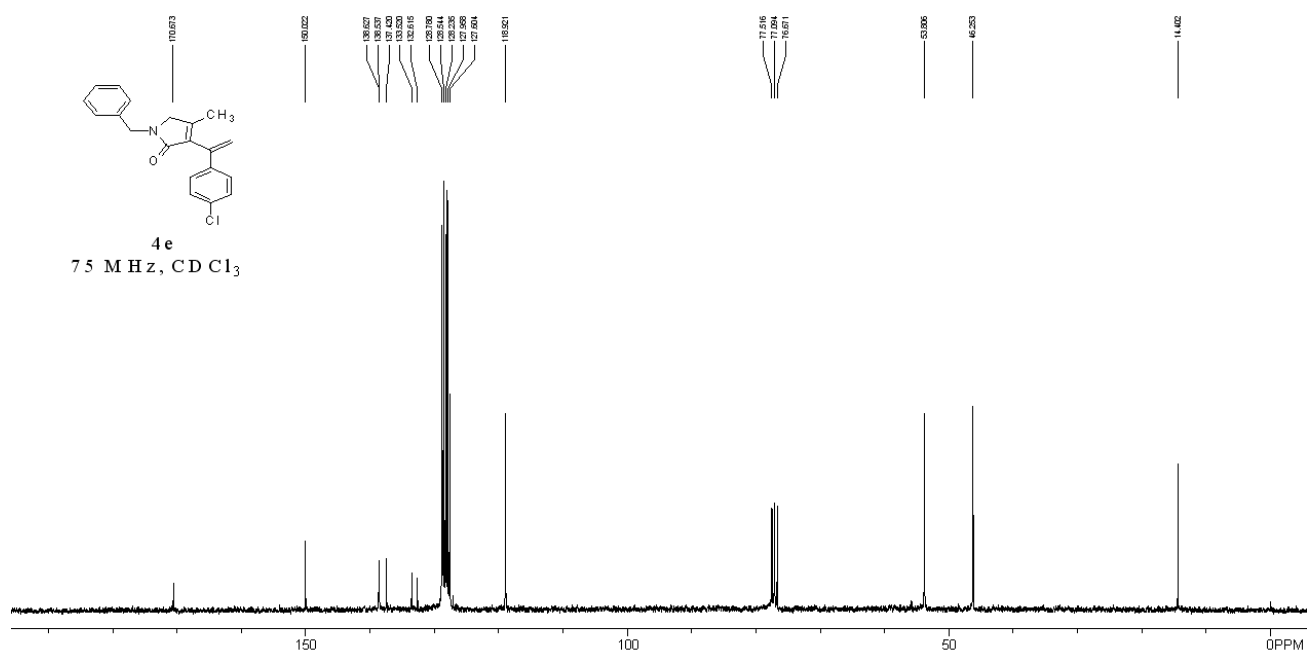
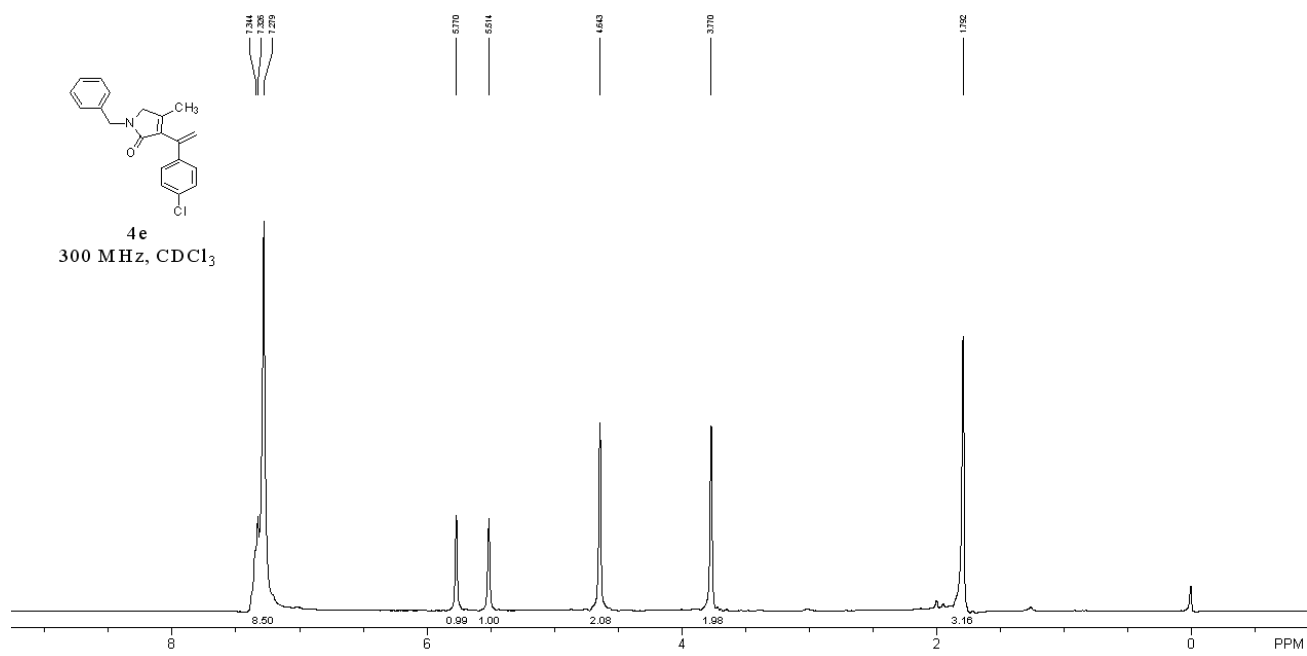


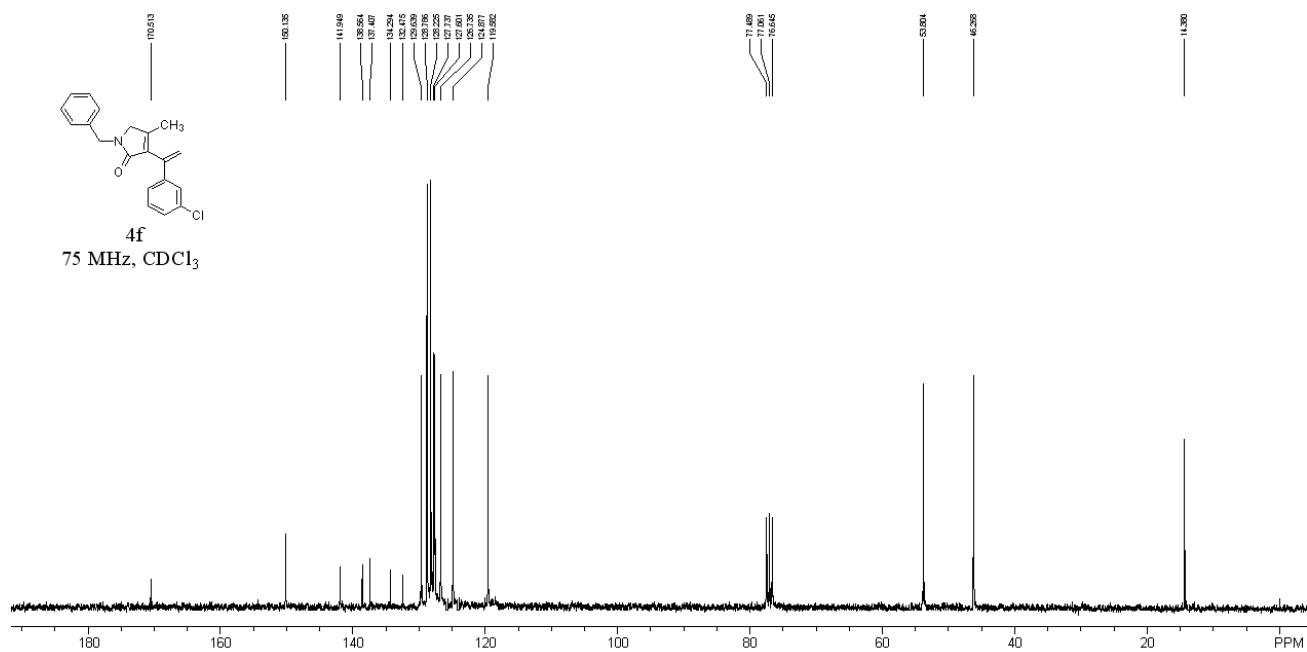
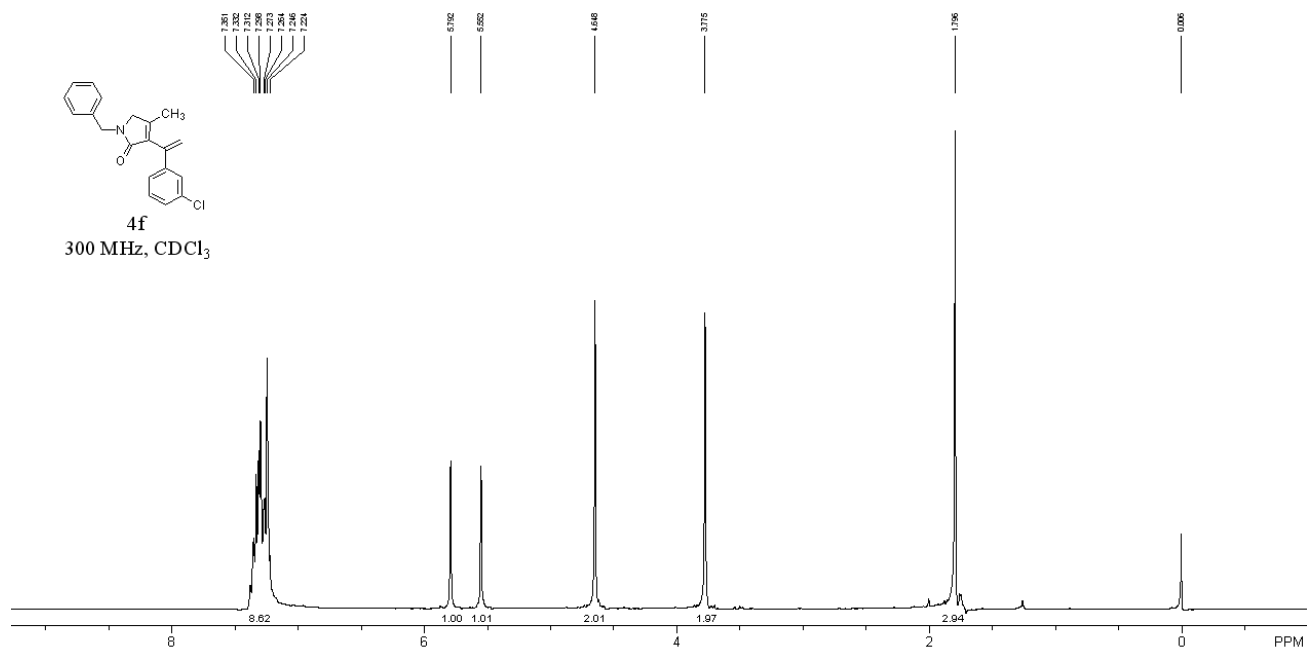


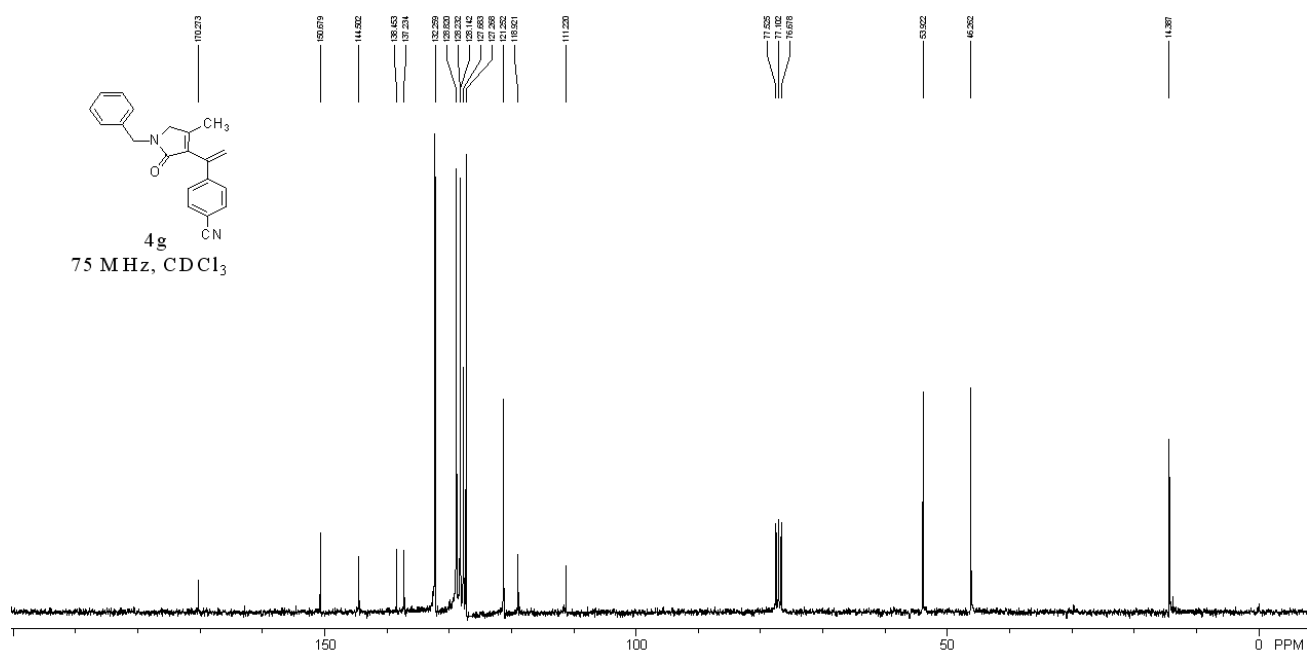
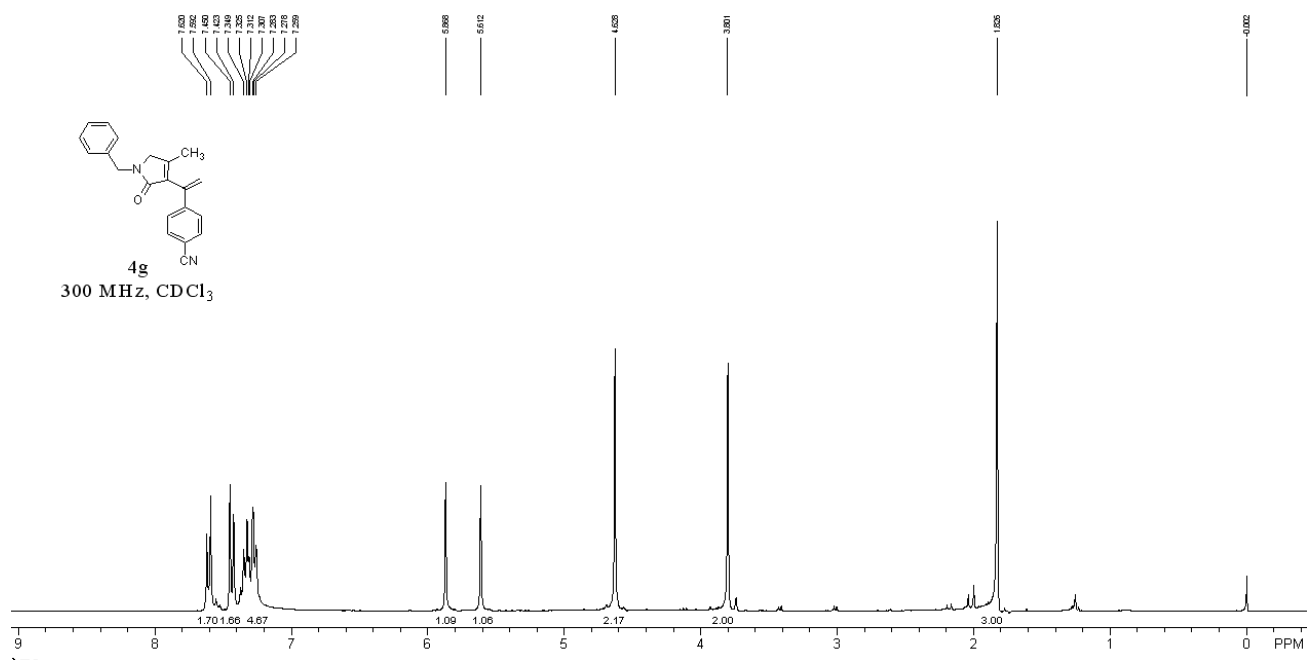


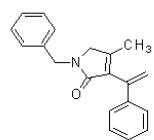




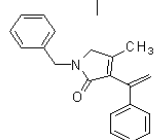
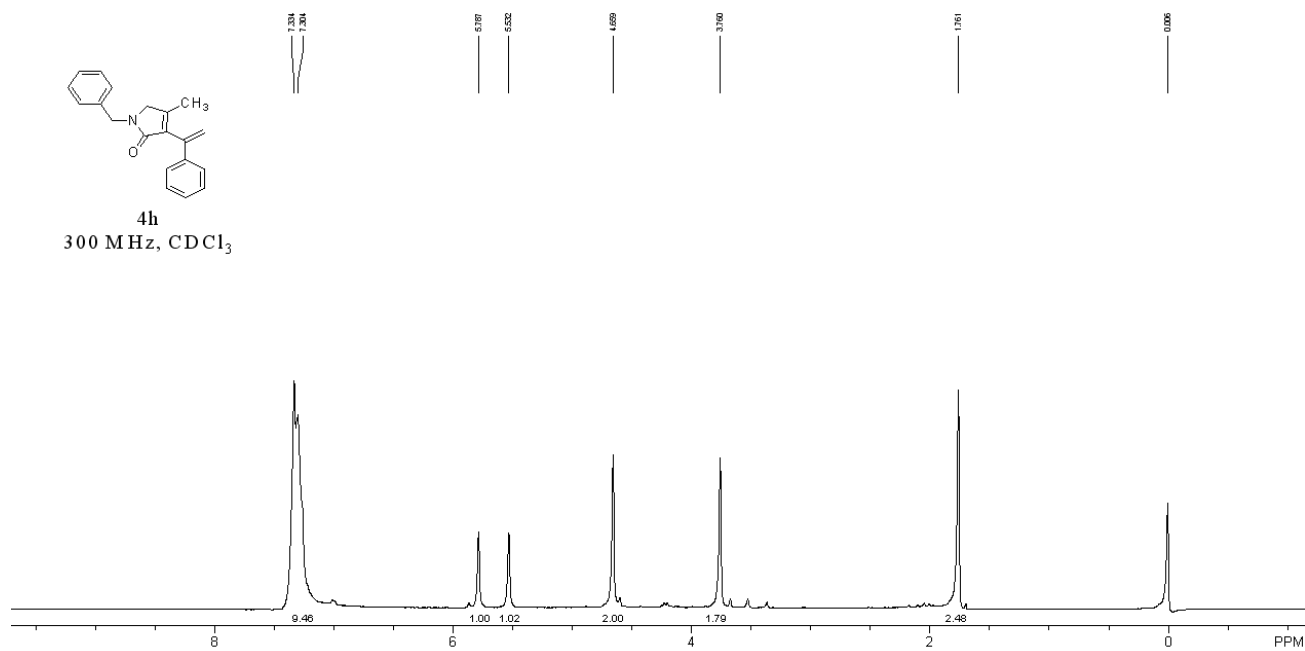








4h
300 MHz, CDCl₃



4h
75 MHz, CDCl₃

