

Synthesis of Benzylidene-3-pyrrolines And Their Synthetic Transformation

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Spectral data of all products

(Z)-2-Benzylidene-3,5-di-*p*-tolyl-1-tosyl-3-pyrroline (4a)

168.9 mg, 86%, Light yellow powder; mp 92 - 94 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.43-7.39 (m, 4H), 7.25-7.14 (m, 9H), 6.40 (s, 1H), 6.00 (d, *J* = 1.7 Hz, 1H), 5.76 (d, *J* = 1.8 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 145.1, 143.7, 142.7, 139.2, 138.4, 137.7, 137.2, 134.7, 130.8, 130.4, 130.3, 130.2, 130.2, 130.1, 129.3, 128.9, 128.4, 127.9, 119.4, 71.1, 21.5, 21.3, 21.2; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₂H₃₀NO₂S: 492.1992, found 492.1991

(Z)-2-Benzylidene-3-(4-methoxyphenyl)-5-(*p*-tolyl)-1-tosyl-3-pyrroline (4b)

85.2 mg, 42%, yellow powder; mp 83 - 84 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 4H), 7.29-7.13 (m, 7H), 6.97 (d, *J* = 8.6 Hz, 2H), 6.40 (s, 1H), 5.98 (d, *J* = 2.6 Hz, 1H), 5.74 (d, *J* = 2.6 Hz, 1H), 3.83 (s, 3H), 2.38 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 160.9, 145.1, 143.4, 142.9, 138.4, 137.9, 137.3, 134.7, 130.7, 130.4, 130.3, 130.2, 129.7, 128.9, 128.4, 127.9, 127.8, 125.9, 119.4, 114.9, 71.0, 55.6, 21.4, 21.1; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₂H₃₀NO₃S: 508.1941, found 508.1934

(Z)-2-Benzylidene-3-(4-fluorophenyl)-5-(*p*-tolyl)-1-tosyl-3-pyrroline (4c)

160.4 mg, 81%, yellowish powder; mp 86 - 87 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.88 (d, *J* = 8.3 Hz, 2H), 7.76 (d, *J* = 7.32 Hz, 2H), 7.44 (d, *J* = 8.1 Hz, 2H), 7.41-7.35 (m, 4H), 7.25-7.14 (m, 7H), 6.40 (s, 1H), 6.05 (d, *J* = 2.7 Hz, 1H), 5.80 (d, *J* = 2.7 Hz, 1H), 2.36 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 163.6 (d, *J* = 246.2 Hz), 145.2, 142.7, 142.5, 138.5, 137.5, 137.1, 134.6, 131.5 (d, *J* = 8.1 Hz), 130.9, 130.4, 130.3, 130.2, 123.0, 129.9, 128.9, 128.4, 127.9, 119.5, 116.3 (d, *J* = 21.7 Hz), 71.1, 21.4, 21.1; ¹⁹F NMR (376 MHz, CD₃COCD₃): δ -115.1; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₁H₂₇FNO₂S: 496.1741, found 496.1742

(Z)-2-Benzylidene-3-(4-chlorophenyl)-5-(*p*-tolyl)-1-tosyl-3-pyrroline (4d)

143.1 mg, 70%, yellow powder; mp 88 - 89 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 7.45-7.39 (m, 6H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.25-7.13 (m, 5H), 6.39 (s, 1H), 6.09 (d, *J* = 2.6 Hz, 1H), 5.80 (d, *J* = 2.6 Hz, 1H), 2.37 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 145.2, 142.6, 142.3, 138.5, 137.4, 137.0, 134.8, 134.6, 132.5, 131.3, 131.1, 130.4, 130.3, 130.2, 129.6, 128.9, 128.4, 128.0, 127.9, 119.7, 71.2, 21.4, 21.1; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₁H₂₇ClNO₂S: 512.1446, 514.1428, found 512.1439, 514.1401

(Z)-2-Benzylidene-3-(4-bromophenyl)-5-(*p*-tolyl)-1-tosyl-3-pyrroline (4e)

123.2 mg, 55%, Brown solid; mp 90 - 91 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.74 (d, *J* = 7.3 Hz, 2H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.43-7.40 (m, 4H), 7.29-7.16 (m, 7H), 6.38 (s, 1H), 6.11 (d, *J* = 2.7 Hz, 1H), 5.79 (d, *J* = 2.7 Hz, 1H), 2.39 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 145.3, 142.7, 142.3, 138.5, 137.5, 137.1, 134.6, 132.9, 132.6, 131.4, 131.4, 130.4, 130.4, 130.2, 130.0, 128.4, 128.0, 127.9, 123.0, 119.7, 71.2, 21.4, 21.1; HRMS (ESI) *m/z*: [M+Na]⁺ calcd. for C₃₁H₂₆BrNNaO₂S: 578.0760, 580.0743, found 578.0740, 580.0732

(Z)-2-Benzylidene-5-(4-fluorophenyl)-3-(*p*-tolyl)-1-tosyl-3-pyrroline (4f)

140.6 mg, 71%, light yellow solid; mp 126 - 127 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.58 (dd, *J* = 8.7 Hz, *J* = 5.4 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.25-7.13 (m, 9H), 6.42 (s, 1H), 6.04 (d, *J* = 2.7 Hz, 1H), 5.82 (d, *J* = 2.7 Hz, 1H), 2.38 (s, 3H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 163.3 (d, *J* = 244.6 Hz), 145.2, 144.2, 142.4, 139.3, 137.1, 136.9 (d, *J* = 3.0 Hz), 134.6, 130.7, 130.3, 130.3, 130.1, 130.0 (d, *J* = 8.2 Hz), 129.7, 129.4, 129.0, 128.4, 127.9, 119.8, 116.3 (d, *J* = 21.7 Hz), 70.5, 21.4, 21.2; ¹⁹F NMR (376 MHz, CD₃COCD₃): δ -116.8; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₁H₂₇FNO₂S: 496.1741, found 496.1726

(Z)-2-Benzylidene-5-(4-chlorophenyl)-3-(*p*-tolyl)-1-tosyl-3-pyrroline (4g)

124.6 mg, 61%, light yellow powder; mp 134 - 136 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.86 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.26-7.14 (m, 7H), 6.41 (s, 1H), 6.05 (d, *J* = 2.7 Hz, 1H), 5.82 (d, *J* = 2.7 Hz, 1H), 2.39 (s, 3H), 2.36 (s, 3H); ¹³C

NMR (100 MHz, CD₃COCD₃): δ 145.3, 144.3, 142.4, 139.8, 139.4, 137.1, 134.5, 134.2, 130.7, 130.4, 130.1, 129.8, 129.7, 129.5, 129.4, 129.0, 128.5, 128.0, 119.8, 70.5, 21.4, 21.2; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₁H₂₇ClNO₂S: 512.1446, 514.1428, found 512.1466, 514.1461

(Z)-2-Benzylidene-3-(*o*-tolyl)-5-(*p*-tolyl)-1-tosyl-3-pyrroline (4h)

141.4 mg, 72%, light yellow powder; mp 78 - 79 °C; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.85 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.48-7.45 (m, 4H), 7.29-7.11 (m, 8H), 6.84 (d, *J* = 7.2 Hz, 1H), 5.96 (d, *J* = 2.5 Hz, 1H), 5.94 (d, *J* = 2.5 Hz, 1H), 5.85 (s, 1H), 2.45 (s, 3H), 2.35 (s, 3H), 2.01 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 145.3, 143.5, 142.9, 138.5, 138.0, 137.4, 137.4, 135.0, 133.6, 132.5, 131.1, 130.5, 130.4, 130.3, 130.2, 129.2, 128.4, 127.9, 127.7, 126.6, 118.1, 72.0, 21.5, 21.2, 19.9; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₂H₃₀NO₂S: 492.1992, found 492.1973

(Z)-2-Benzylidene-5-(naphthalen-1-yl)-3-(*p*-tolyl)-1-tosyl-3-pyrroline (4i)

134.5 mg, 64%, Brown oil; ¹H NMR (400 MHz, CD₃COCD₃): δ 8.42 (d, *J* = 8.4 Hz, 1H), 8.00-7.97 (m, 3H), 7.91-7.86 (m, 3H), 7.79 (d, *J* = 7.2 Hz, 1H), 7.65-7.44 (m, 5H), 7.29-7.25 (m, 2H), 7.21-7.15 (m, 5H), 6.62 (d, *J* = 2.4 Hz, 1H), 6.53 (s, 1H), 6.10 (d, *J* = 2.2 Hz, 1H), 2.39 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 145.3, 143.3, 143.1, 139.2, 137.0, 136.1, 135.0, 134.5, 131.3, 130.7, 130.5, 130.5, 130.3, 130.1, 129.8, 129.3, 129.1, 128.5, 128.0, 127.4, 126.7, 126.7, 125.2, 124.0, 120.0, 68.8, 21.5, 21.2; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₅H₃₀NO₂S: 528.1992, found 528.1960.

(Z)-2-Benzylidene-3,5-di-*p*-tolyl-1-mesyl-3-pyrroline (8a)

124.4 mg, 75%, light yellow oil; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.63 (d, *J* = 7.6 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.23-7.10 (m, 5H), 6.47 (d, *J* = 2.7 Hz, 1H), 6.43 (s, 1H), 5.94 (d, *J* = 2.6 Hz, 1H), 2.89 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 143.6, 142.2, 139.4, 138.4, 137.8, 137.1, 131.1, 130.9, 130.3, 130.3, 129.4, 128.3, 127.8, 127.7, 119.0, 71.2, 35.1, 21.2, 21.1; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₂₆H₂₆NO₂S: 416.1679, found 416.1667

(Z)-2-Benzylidene-3-(4-fluorophenyl)-5-(*p*-tolyl)-1-mesyl-3-pyrroline (8b)

102.5 mg, 61%, light yellow oil; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.68-7.63 (m, 4H), 7.41 (d, *J* = 8.0, 2H), 7.30-7.10 (m, 7H), 6.53 (d, *J* = 2.4 Hz, 1H), 6.40 (s, 1H), 5.96 (d, *J* = 2.4 Hz, 1H), 2.90 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 163.6 (d, *J* = 246.4 Hz), 124.5, 141.8, 138.4, 137.5, 136.9, 131.8, 131.6 (d, *J* = 8.4 Hz), 130.3, 130.2, 130.0 (d, *J* = 3.2 Hz), 128.3, 127.8, 127.6, 119.0, 116.4 (d, *J* = 21.7 Hz), 71.1, 34.8, 21.1 ¹⁹F NMR (376 MHz, CD₃COCD₃): δ -113.8; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₂₅H₂₃FNO₂S: 420.1428, found 420.1424

2-Methylene-3,5-di-*p*-tolyl-1-tosyl-3-pyrroline (9)

109.6 mg, 66%, light purple oil; ¹H NMR (400 MHz, CD₃COCD₃): δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.37-7.29 (m, 5H), 7.22-7.16 (m, 6H), 6.09 (s, 1H), 5.90 (s, 1H), 5.33 (s, 1H, =CHH), 4.65 (s, 1H, =CHH), 2.38 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H); ¹³C NMR (100 MHz, CD₃COCD₃): δ 148.9, 144.9, 140.1, 139.1, 138.3, 137.9, 136.4, 134.5, 132.6, 131.0, 130.3, 130.0, 129.0, 128.4, 128.0, 92.5, 71.3, 21.5, 21.2; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₂₆H₂₆NO₂S: 416.1679, found 416.1673

2-Benzyl-3,5-di-*p*-tolyl-1-tosylpyrrole (10).

To a solution of **4a** (98.3 mg, 0.2 mmol) in CH₂Cl₂ was added conc. HCl (5 mL, 0.06 mmol). The resulting mixture was stirred at ambient temperature for 1 h. The mixture was extracted with a saturated NaHCO₃ solution and the organic portion was dried over MgSO₄ and concentrated under reduced pressure to give **10** as yellowish powder (94.5 mg, 97%); mp 207 - 209 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.28-7.08 (m, 15H), 7.03 (d, *J* = 8.2 Hz, 2H), 6.27 (s, 1H), 4.46 (s, 2H), 2.38 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 144.1, 140.6, 138.1, 137.8, 136.7, 136.2, 131.9, 131.5, 130.6, 130.0, 129.7, 129.2, 129.1, 128.4, 128.2, 127.9, 126.7, 125.8, 117.3, 32.6, 21.5, 21.3, 21.1; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₂H₃₀NO₂S: 492.1992, found 492.1997.

2-Benzyl-3,5-di-*p*-tolyl-4-tosylpyrrole (11).

To a solution of **4a** (98.3 mg, 0.2 mmol) in ClCH₂CH₂Cl was slowly added BF₃ etherate (40 mL, 0.3 mmol). The mixture was heated at 60 °C for several hours. Upon cooling, the mixture was washed with saturated NaHCO₃ and extracted with ether. The organic portion was dried and concentrated. The crude product

was filtrated through silica gel with elution CH₂Cl₂. Concentration of the eluent gave pyrrole **11** as white solid (80.7 mg, 82%); mp 197 - 198 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.96 (br, 1H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.26-7.22 (m, 2H), 7.19-7.14 (m, 5H), 7.11-7.04 (m, 6H), 6.95 (d, *J* = 8.0 Hz, 2H), 3.71 (s, 2H), 2.38 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 142.3, 140.8, 138.7, 138.2, 136.7, 135.3, 131.3, 130.1, 130.0, 128.8, 128.6, 128.5, 128.4, 128.3, 127.1, 126.7, 122.8, 119.5, 31.6, 21.4, 21.3, 21.3; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₂H₃₀NO₂S: 492.1992, found 492.1996.

Compound 11'. To a solution of **11** (98.3 mg, 0.2 mmol) and 4-dimethylaminopyridine (2.4 mg, 0.02 mmol) in THF (1 mL) was added Boc₂O (137.8 mL, 0.3 mmol). The mixture was stirred at room temperature overnight. After removal of solvent, the residue was chromatographed on silica gel with elution of dichloromethane/hexane (6:4) to give **11'** as white solid (94.2 mg, 80%); mp 213 - 215 °C; ¹H NMR (400 MHz, CDCl₃): δ 7.26 (d, *J* = 8.1 Hz, 2H), 7.18-7.03 (m, 11H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.90 (d, *J* = 7.4 Hz, 2H), 3.95 (s, 2H), 2.39 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H), 0.80 (s, 9H); ¹³C NMR (100 MHz, CDCl₃): δ 148.9, 142.7, 140.1, 138.7, 138.5, 137.1, 136.5, 131.3, 130.9, 130.7, 129.5, 128.7, 128.4, 128.3, 128.2, 128.1, 127.2, 126.0, 124.6, 123.1, 85.0, 30.8, 26.5, 21.4, 21.4, 21.3; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₃₇H₃₈NO₄S: 592.2516, found 592.2511

3,5-Di-*p*-tolyl-1-tosyl-1,5-dihydro-2H-pyrrol-2-one (**12**).

To a solution of **4a** (98.3 mg, 0.2 mmol) in CH₂Cl₂ was added mcpba (147.9 mg, 0.6 mmol) and the mixture was stirred at ambient temperature overnight. The reaction mixture was filtrated and the solution was dried and concentrated. The residue was chromatographed on silica gel with elution of CH₂Cl₂/hexane (v:v = 3:2) to give **12** as yellow oil (36.1 mg, 43%); ¹H NMR (400 MHz, CDCl₃): δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.17-7.15 (m, 3H), 7.12-7.09 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.77 (d, *J* = 2.2 Hz, 1H), 2.35 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 167.9, 144.6, 142.8, 139.4, 138.8, 135.7, 133.7, 131.2, 129.5, 129.3, 129.1, 128.1, 127.8, 127.0, 126.9, 64.3, 21.6, 21.3, 21.2; HRMS (ESI) *m/z*: [M+H]⁺ calcd. for C₂₅H₂₄NO₃S: 418.1471, found 418.1467.

Crystallography.

Crystals suitable for X-ray determination were obtained for **4a** by recrystallization. Cell parameters were determined either by a Xcalibur-Atlas-Gemini diffractometer. The structure was solved using the SHELXS-97 program [S1] and refined using the SHELXL-97 program [S2] by full-matrix least-squares on *F*² values. All crystal data and other parameters are collected in the supporting information. CCDC numbers for the compound are 2025408 (**4a**) and 2032689 (**11'**). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. All crystallographic data of complexes are deposited in the supporting information.

Crystal data for **4a**: C₃₂H₂₉NO₂·1/2(CH₃OH), *F*_w = 507.64, Triclinic, *P*-1, *a* = 10.5068(12) Å, *b* = 11.2477(11) Å, *c* = 12.6060(13) Å, α = 98.016(8)°, β = 113.343(11)°, γ = 92.447(9)°, *V* = 1346(3) Å³, *Z* = 2, *D*_{calcd} = 1.252 Mg/m³, *F*(000) = 5068, crystal size: 0.20 x 0.15 x 0.10 mm³, 3.6590 to 29.70000°, 11731 reflections collected, 6187 reflections [*R*(int) = 0.0414], Final *R* indices [*I*>2σ(*I*): *R*1 = 0.0618, *wR*2 = 0.1619, for all data *R*1 = 0.0821, *wR*2 = 0.1842, Goodness-of-fit on *F*² = 1.041.

Crystal data for **11'**: C₃₇H₃₇NO₄S, *F*_w = 591.73, Monoclinic, *P*2₁/*n*, *a* = 6.7526(8) Å, *b* = 23.4110(16) Å, *c* = 20.7626(16) Å, α = 90°, β = 90.847(8)°, γ = 90°, *V* = 3281.9(5) Å³, *Z* = 4, *D*_{calcd} = 1.198 Mg/m³, *F*(000) = 1256, crystal size: 0.25 x 0.15 x 0.10 mm³, 3.6700 to 27.1770°, 14818 reflections collected, 7496 reflections [*R*(int) = 0.0383], Final *R* indices [*I*>2σ(*I*): *R*1 = 0.0625, *wR*2 = 0.1452, for all data *R*1 = 0.1264, *wR*2 = 0.2036, Goodness-of-fit on *F*² = 1.054.

References:

S1 G.M. Sheldrick, SHELXS-97, Acta Crystallogr., Sect. A: Found. Crystallogr. **1990**, 46, 67.

S2 G.M. Sheldrick, SHELXL-97, University of Göttingen, Göttingen, Germany, **1997**.

Table S1. Bond lengths [\AA] and angles [$^\circ$] for **4a**.

S(1)-O(2)	1.4298(17)	C(13)-C(14)	1.390(3)
S(1)-O(1)	1.4380(17)	C(14)-C(15)	1.392(3)
S(1)-N(1)	1.6691(18)	C(15)-C(16)	1.393(3)
S(1)-C(26)	1.757(2)	C(15)-C(18)	1.508(3)
N(1)-C(4)	1.447(3)	C(16)-C(17)	1.389(3)
N(1)-C(1)	1.507(3)	C(19)-C(20)	1.389(3)
C(1)-C(2)	1.505(3)	C(19)-C(24)	1.401(3)
C(1)-C(12)	1.524(3)	C(20)-C(21)	1.394(4)
C(2)-C(3)	1.341(3)	C(21)-C(22)	1.393(4)
C(3)-C(19)	1.477(3)	C(22)-C(23)	1.392(4)
C(3)-C(4)	1.487(3)	C(22)-C(25)	1.511(4)
C(4)-C(5)	1.344(3)	C(23)-C(24)	1.382(3)
C(5)-C(6)	1.469(3)	C(26)-C(27)	1.391(3)
C(6)-C(11)	1.403(3)	C(26)-C(31)	1.393(3)
C(6)-C(7)	1.408(3)	C(27)-C(28)	1.380(3)
C(7)-C(8)	1.392(3)	C(28)-C(29)	1.397(4)
C(8)-C(9)	1.384(4)	C(29)-C(30)	1.391(4)
C(9)-C(10)	1.389(4)	C(29)-C(32)	1.499(3)
C(10)-C(11)	1.390(3)	C(30)-C(31)	1.382(3)
C(12)-C(13)	1.389(3)	O(3)-C(33)	1.380(6)
C(12)-C(17)	1.394(3)		
O(2)-S(1)-O(1)	119.60(11)	C(3)-C(2)-C(1)	111.5(2)
O(2)-S(1)-N(1)	107.31(9)	C(2)-C(3)-C(19)	128.0(2)
O(1)-S(1)-N(1)	105.03(10)	C(2)-C(3)-C(4)	108.7(2)
O(2)-S(1)-C(26)	108.49(10)	C(19)-C(3)-C(4)	123.3(2)
O(1)-S(1)-C(26)	107.76(10)	C(5)-C(4)-N(1)	126.9(2)
N(1)-S(1)-C(26)	108.16(10)	C(5)-C(4)-C(3)	125.3(2)
C(4)-N(1)-C(1)	106.74(17)	N(1)-C(4)-C(3)	106.48(18)
C(4)-N(1)-S(1)	116.62(14)	C(4)-C(5)-C(6)	133.3(2)
C(1)-N(1)-S(1)	114.45(13)	C(11)-C(6)-C(7)	117.8(2)
C(2)-C(1)-N(1)	102.91(17)	C(11)-C(6)-C(5)	125.1(2)
C(2)-C(1)-C(12)	115.13(18)	C(7)-C(6)-C(5)	116.9(2)
N(1)-C(1)-C(12)	110.89(17)	C(8)-C(7)-C(6)	121.3(2)

C(9)-C(8)-C(7)	120.0(2)	C(19)-C(20)-C(21)	120.7(2)
C(8)-C(9)-C(10)	119.5(2)	C(22)-C(21)-C(20)	121.0(2)
C(9)-C(10)-C(11)	121.0(3)	C(23)-C(22)-C(21)	117.9(2)
C(10)-C(11)-C(6)	120.4(2)	C(23)-C(22)-C(25)	120.6(3)
C(13)-C(12)-C(17)	118.9(2)	C(21)-C(22)-C(25)	121.5(3)
C(13)-C(12)-C(1)	122.0(2)	C(24)-C(23)-C(22)	121.4(2)
C(17)-C(12)-C(1)	119.09(19)	C(23)-C(24)-C(19)	120.6(2)
C(12)-C(13)-C(14)	120.2(2)	C(27)-C(26)-C(31)	121.1(2)
C(13)-C(14)-C(15)	121.3(2)	C(27)-C(26)-S(1)	120.17(18)
C(14)-C(15)-C(16)	118.1(2)	C(31)-C(26)-S(1)	118.74(18)
C(14)-C(15)-C(18)	120.5(2)	C(28)-C(27)-C(26)	119.1(2)
C(16)-C(15)-C(18)	121.4(2)	C(27)-C(28)-C(29)	121.3(2)
C(17)-C(16)-C(15)	121.0(2)	C(30)-C(29)-C(28)	118.2(2)
C(16)-C(17)-C(12)	120.5(2)	C(30)-C(29)-C(32)	121.5(2)
C(20)-C(19)-C(24)	118.3(2)	C(28)-C(29)-C(32)	120.3(2)
C(20)-C(19)-C(3)	121.9(2)	C(31)-C(30)-C(29)	121.8(2)
C(24)-C(19)-C(3)	119.8(2)	C(30)-C(31)-C(26)	118.6(2)

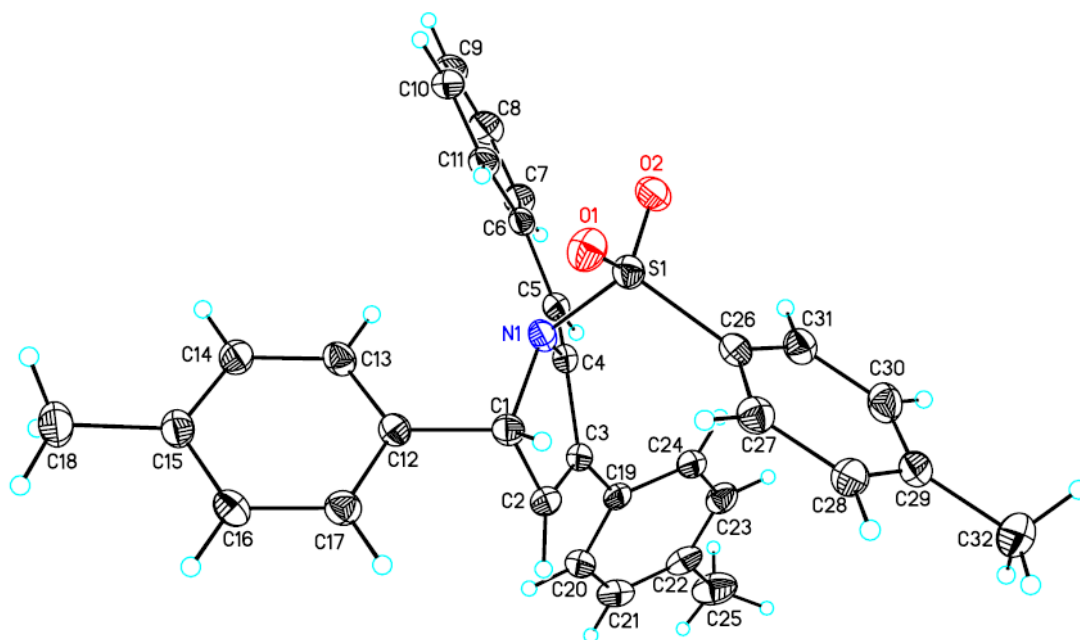


Figure S1. ORTEP plot of **4a** (30% probability ellipsoids).

Table S1. Bond lengths [\AA] and angles [$^\circ$] for **11'**.

S(1)-O(2)	1.428(2)	C(12)-C(17)	1.389(4)
S(1)-O(1)	1.435(2)	C(13)-C(14)	1.383(4)
S(1)-C(9)	1.753(3)	C(14)-C(15)	1.381(5)
S(1)-C(1)	1.759(3)	C(15)-C(16)	1.393(5)
O(3)-C(33)	1.203(3)	C(15)-C(18)	1.516(4)
O(4)-C(33)	1.313(4)	C(16)-C(17)	1.378(4)
O(4)-C(34)	1.483(4)	C(19)-C(20)	1.386(4)
N(1)-C(8)	1.392(3)	C(19)-C(24)	1.394(4)
N(1)-C(11)	1.399(3)	C(20)-C(21)	1.386(4)
N(1)-C(33)	1.427(4)	C(21)-C(22)	1.383(5)
C(1)-C(6)	1.386(4)	C(22)-C(23)	1.389(5)
C(1)-C(2)	1.386(4)	C(22)-C(25)	1.512(4)
C(2)-C(3)	1.378(5)	C(23)-C(24)	1.383(4)
C(3)-C(4)	1.388(5)	C(26)-C(27)	1.513(4)
C(4)-C(5)	1.391(5)	C(27)-C(28)	1.379(4)
C(4)-C(7)	1.505(5)	C(27)-C(32)	1.390(4)
C(5)-C(6)	1.386(4)	C(28)-C(29)	1.395(5)
C(8)-C(9)	1.377(4)	C(29)-C(30)	1.368(5)
C(8)-C(12)	1.489(4)	C(30)-C(31)	1.376(6)
C(9)-C(10)	1.445(4)	C(31)-C(32)	1.377(5)
C(10)-C(11)	1.365(4)	C(34)-C(37)	1.506(5)
C(10)-C(19)	1.488(4)	C(34)-C(36)	1.519(5)
C(11)-C(26)	1.493(4)	C(34)-C(35)	1.521(5)
C(12)-C(13)	1.379(4)		
O(2)-S(1)-O(1)	118.60(13)	C(2)-C(1)-S(1)	118.8(2)
O(2)-S(1)-C(9)	108.61(13)	C(3)-C(2)-C(1)	118.8(3)
O(1)-S(1)-C(9)	107.95(13)	C(2)-C(3)-C(4)	122.2(3)
O(2)-S(1)-C(1)	108.57(14)	C(3)-C(4)-C(5)	117.8(3)
O(1)-S(1)-C(1)	108.07(13)	C(3)-C(4)-C(7)	121.1(4)
C(9)-S(1)-C(1)	104.10(13)	C(5)-C(4)-C(7)	121.1(4)
C(33)-O(4)-C(34)	120.5(2)	C(6)-C(5)-C(4)	121.3(3)
C(8)-N(1)-C(11)	110.2(2)	C(1)-C(6)-C(5)	119.2(3)
C(8)-N(1)-C(33)	126.7(2)	C(9)-C(8)-N(1)	106.1(2)
C(11)-N(1)-C(33)	123.1(2)	C(9)-C(8)-C(12)	130.6(3)
C(6)-C(1)-C(2)	120.7(3)	N(1)-C(8)-C(12)	123.3(2)
C(6)-C(1)-S(1)	120.5(2)	C(8)-C(9)-C(10)	109.0(2)

C(8)-C(9)-S(1)	125.3(2)	C(21)-C(22)-C(23)	117.4(3)
C(10)-C(9)-S(1)	125.7(2)	C(21)-C(22)-C(25)	121.4(3)
C(11)-C(10)-C(9)	106.9(2)	C(23)-C(22)-C(25)	121.2(3)
C(11)-C(10)-C(19)	124.8(2)	C(24)-C(23)-C(22)	121.2(3)
C(9)-C(10)-C(19)	128.1(2)	C(23)-C(24)-C(19)	121.0(3)
C(10)-C(11)-N(1)	107.8(2)	C(11)-C(26)-C(27)	116.0(3)
C(10)-C(11)-C(26)	129.0(3)	C(28)-C(27)-C(32)	117.5(3)
N(1)-C(11)-C(26)	123.1(3)	C(28)-C(27)-C(26)	123.0(3)
C(13)-C(12)-C(17)	118.7(3)	C(32)-C(27)-C(26)	119.4(3)
C(13)-C(12)-C(8)	121.4(3)	C(27)-C(28)-C(29)	121.1(3)
C(17)-C(12)-C(8)	119.9(3)	C(30)-C(29)-C(28)	120.4(3)
C(12)-C(13)-C(14)	120.4(3)	C(29)-C(30)-C(31)	119.2(4)
C(15)-C(14)-C(13)	121.5(3)	C(30)-C(31)-C(32)	120.5(3)
C(14)-C(15)-C(16)	117.7(3)	C(31)-C(32)-C(27)	121.4(4)
C(14)-C(15)-C(18)	121.8(3)	O(3)-C(33)-O(4)	127.9(3)
C(16)-C(15)-C(18)	120.5(4)	O(3)-C(33)-N(1)	122.2(3)
C(17)-C(16)-C(15)	121.1(3)	O(4)-C(33)-N(1)	109.9(2)
C(16)-C(17)-C(12)	120.5(3)	O(4)-C(34)-C(37)	109.2(3)
C(20)-C(19)-C(24)	117.8(3)	O(4)-C(34)-C(36)	109.6(3)
C(20)-C(19)-C(10)	122.1(3)	C(37)-C(34)-C(36)	112.8(3)
C(24)-C(19)-C(10)	120.0(3)	O(4)-C(34)-C(35)	101.3(3)
C(19)-C(20)-C(21)	120.7(3)	C(37)-C(34)-C(35)	111.8(3)
C(22)-C(21)-C(20)	121.8(3)	C(36)-C(34)-C(35)	111.5(3)

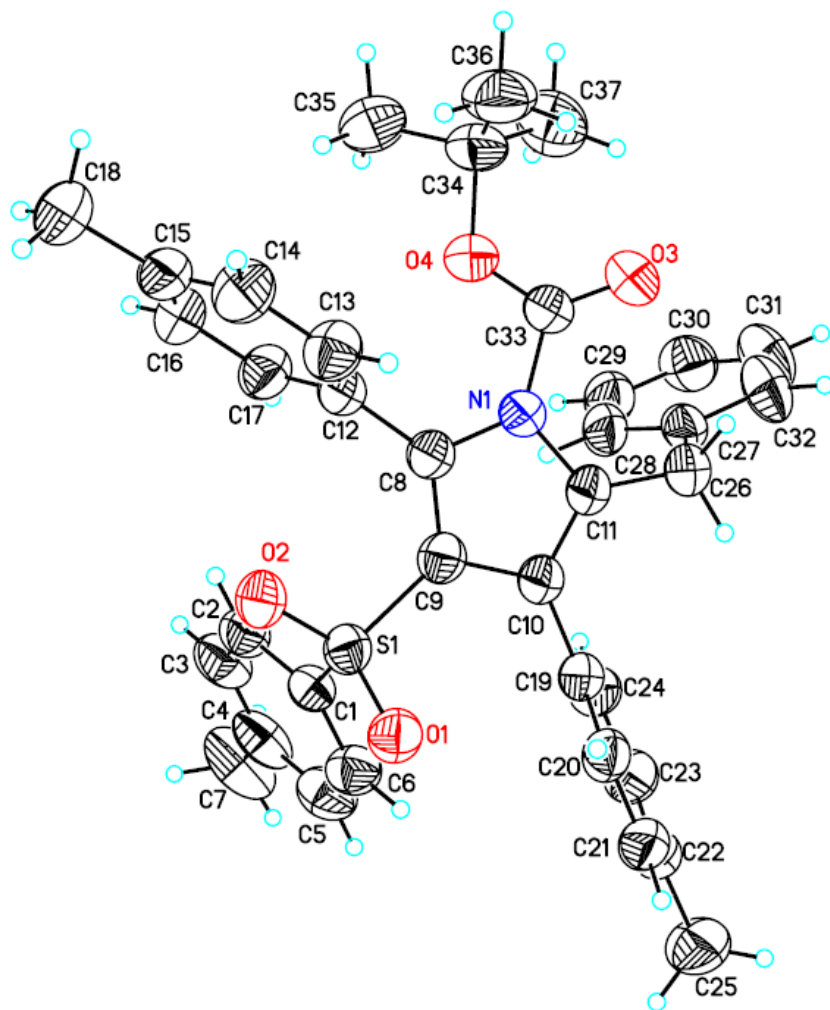
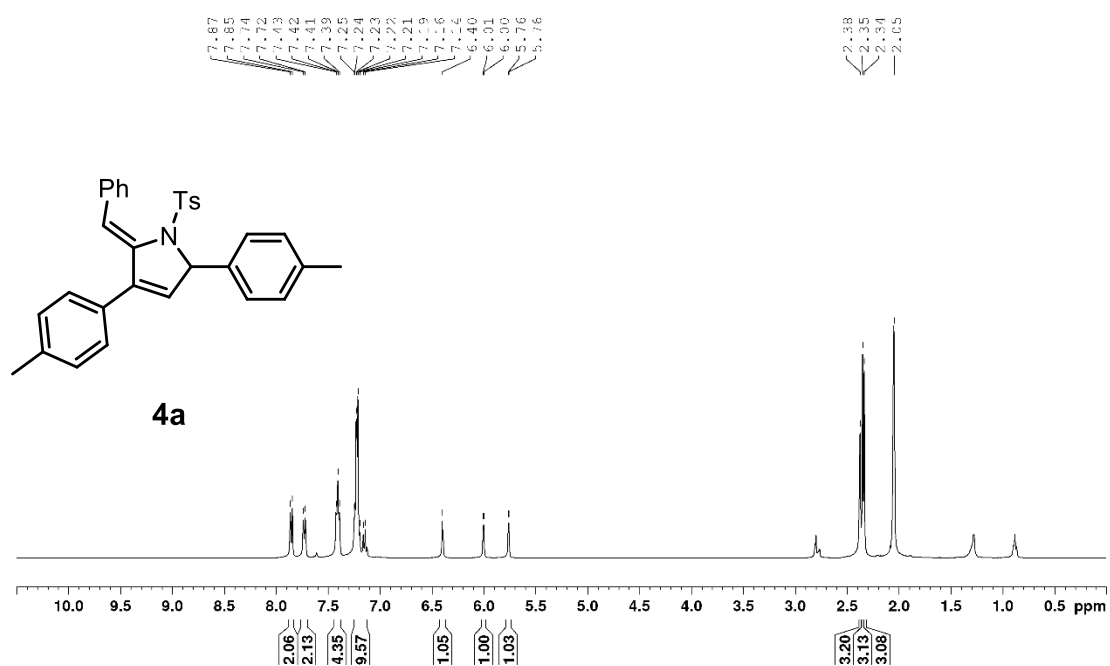
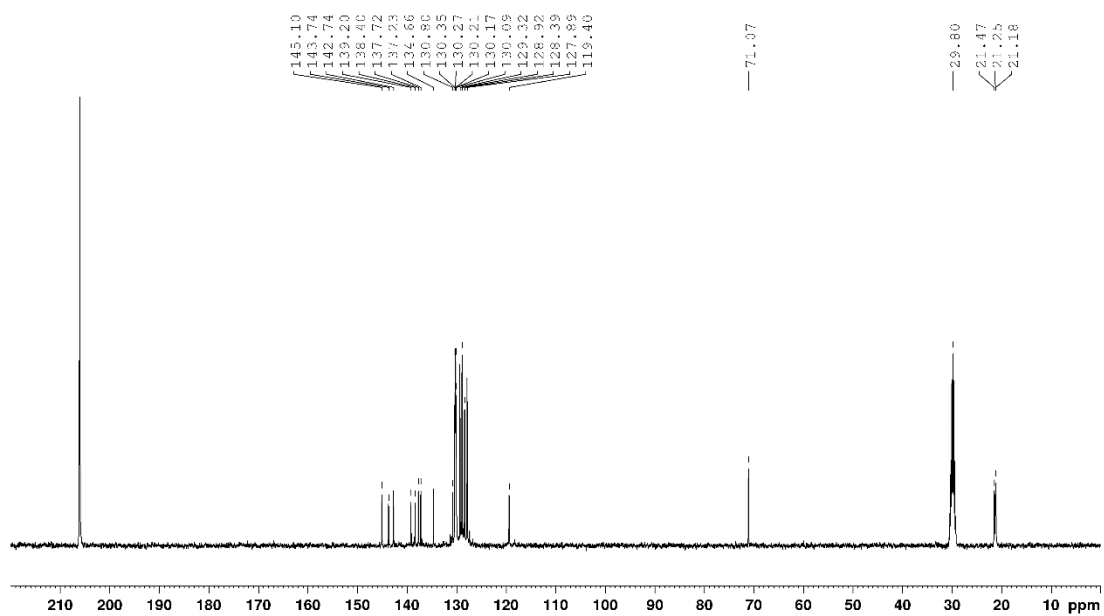


Figure S2. ORTEP plot of **11** (30% probability ellipsoids).

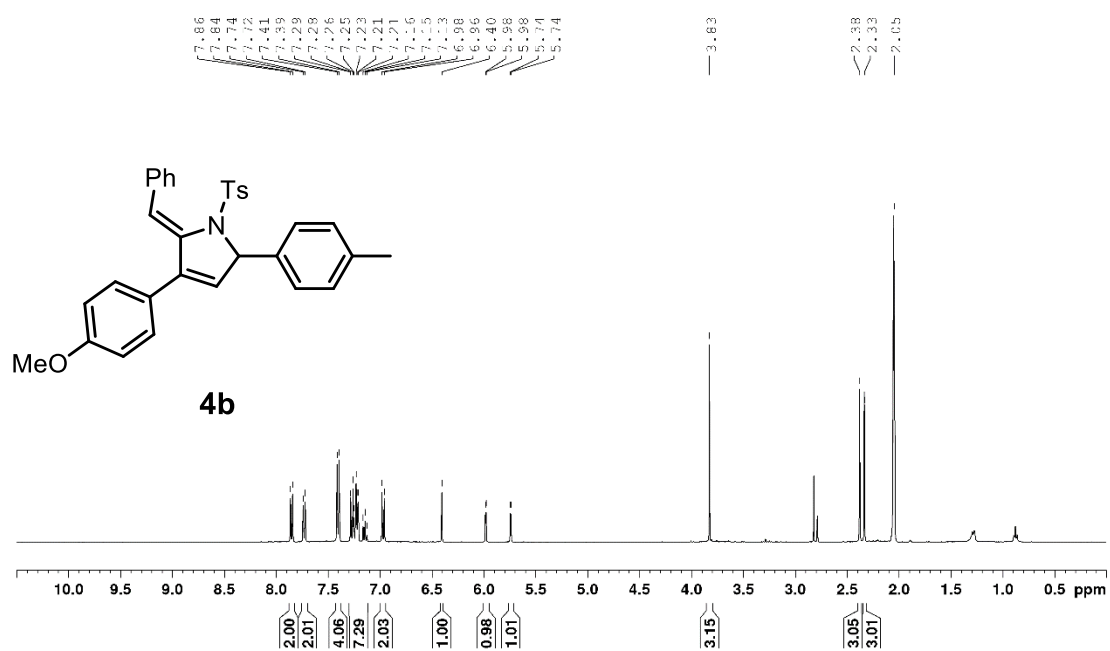
¹H NMR spectrum of compound **4a** (400 MHz, CD₃COCD₃)



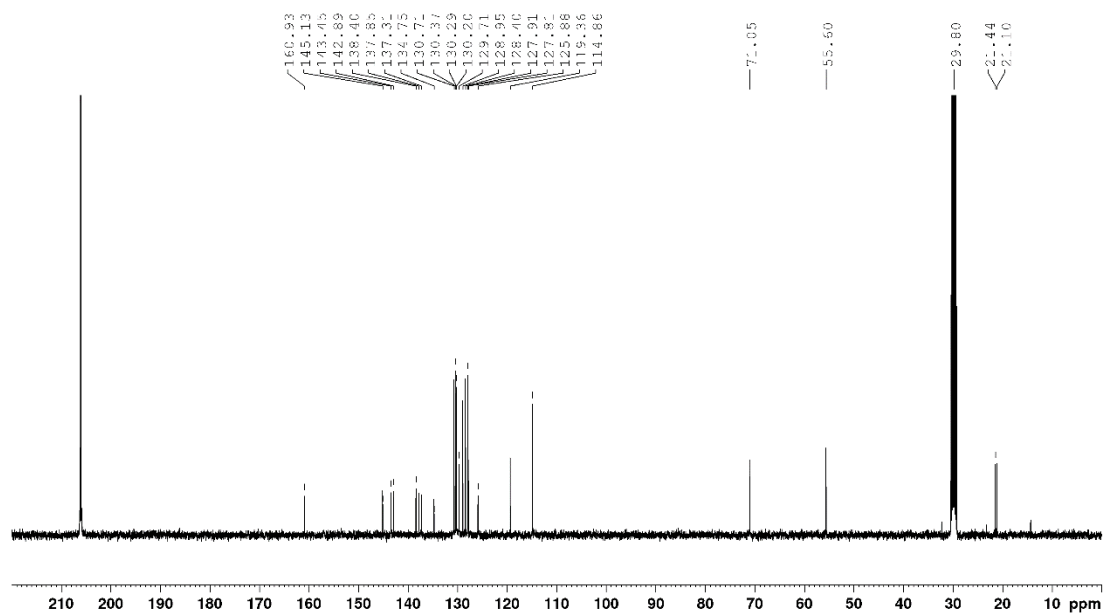
¹³C NMR spectrum of compound **4a** (100 MHz, CD₃COCD₃)



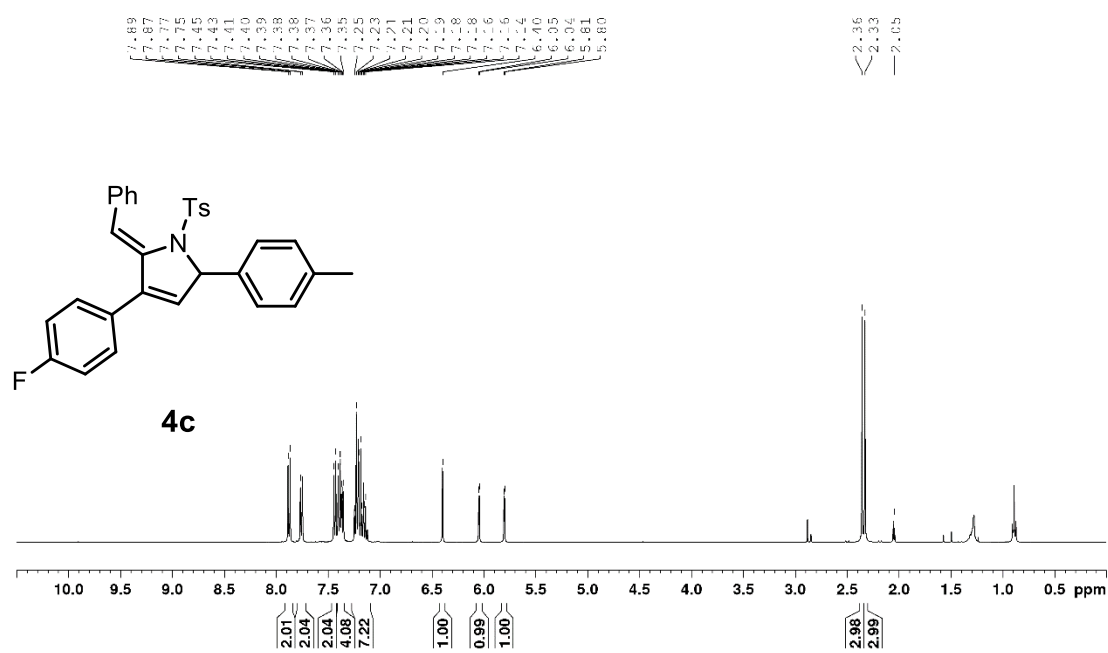
¹H NMR spectrum of compound **4b** (400 MHz, CD₃COCD₃)



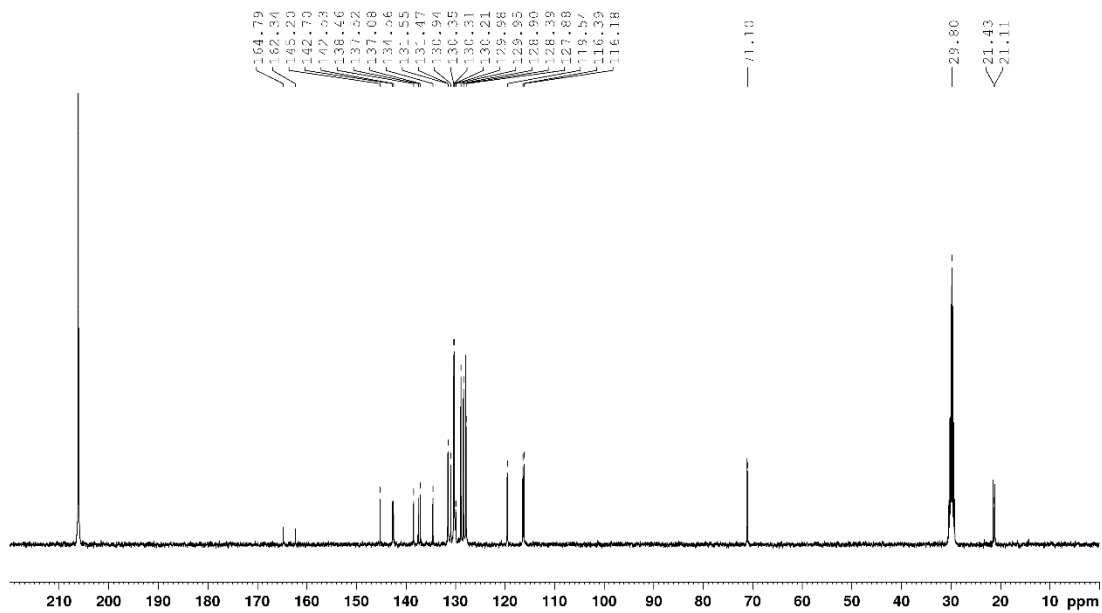
¹³C NMR spectrum of compound **4b** (100 MHz, CD₃COCD₃)



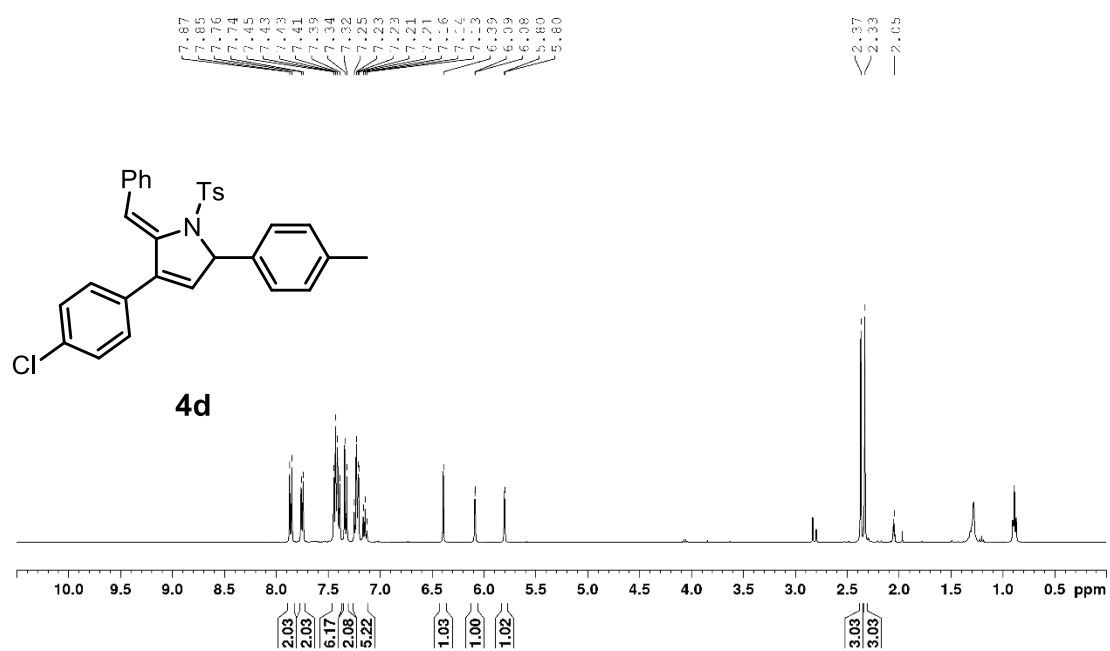
¹H NMR spectrum of compound **4c** (400 MHz, CD₃COCD₃)



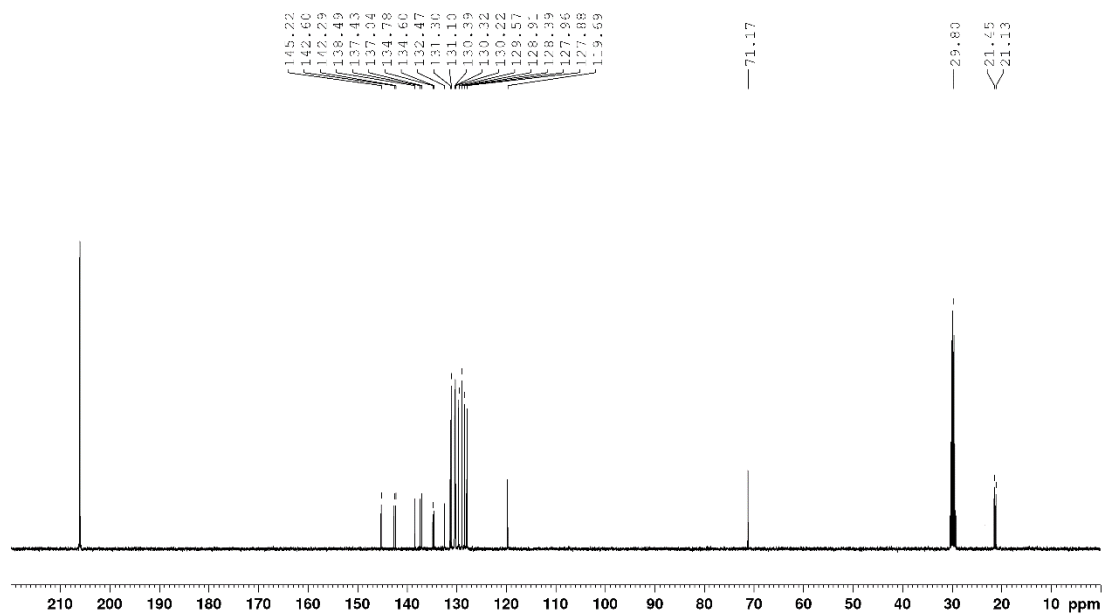
¹³C NMR spectrum of compound **4c** (100 MHz, CD₃COCD₃)



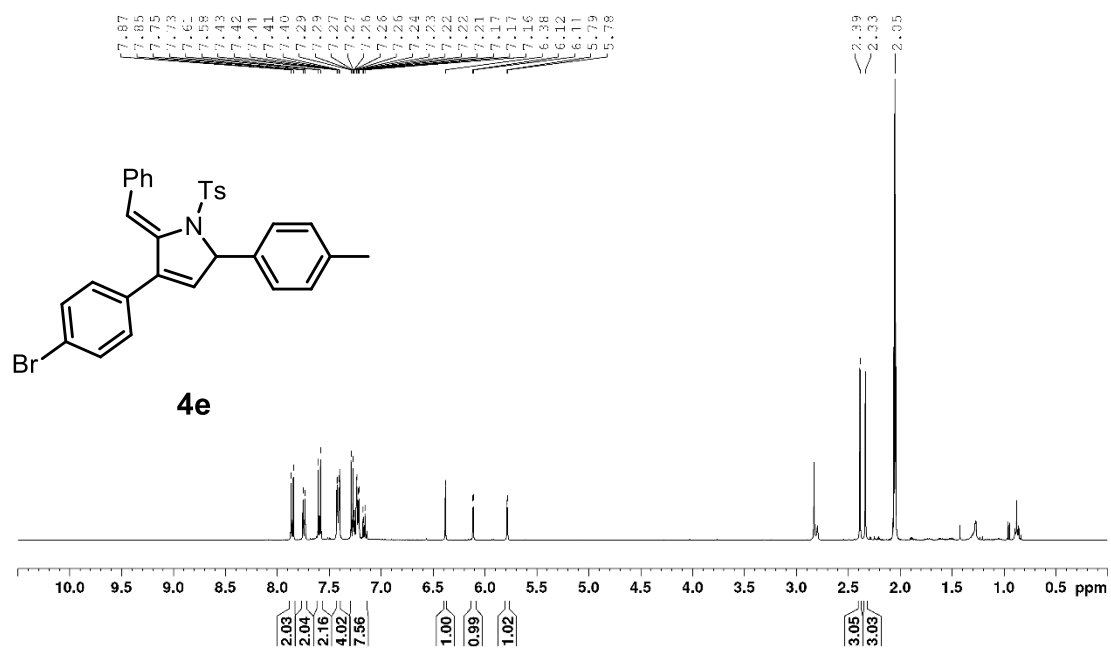
^1H NMR spectrum of compound **4d** (400 MHz, CD_3COCD_3)



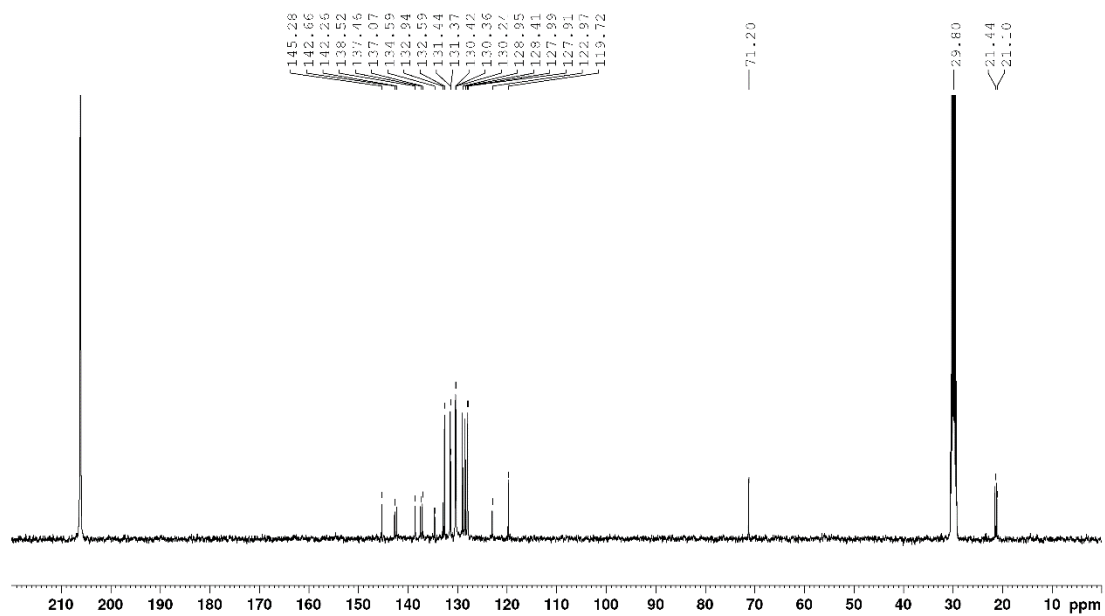
^{13}C NMR spectrum of compound **4d** (100 MHz, CD_3COCD_3)



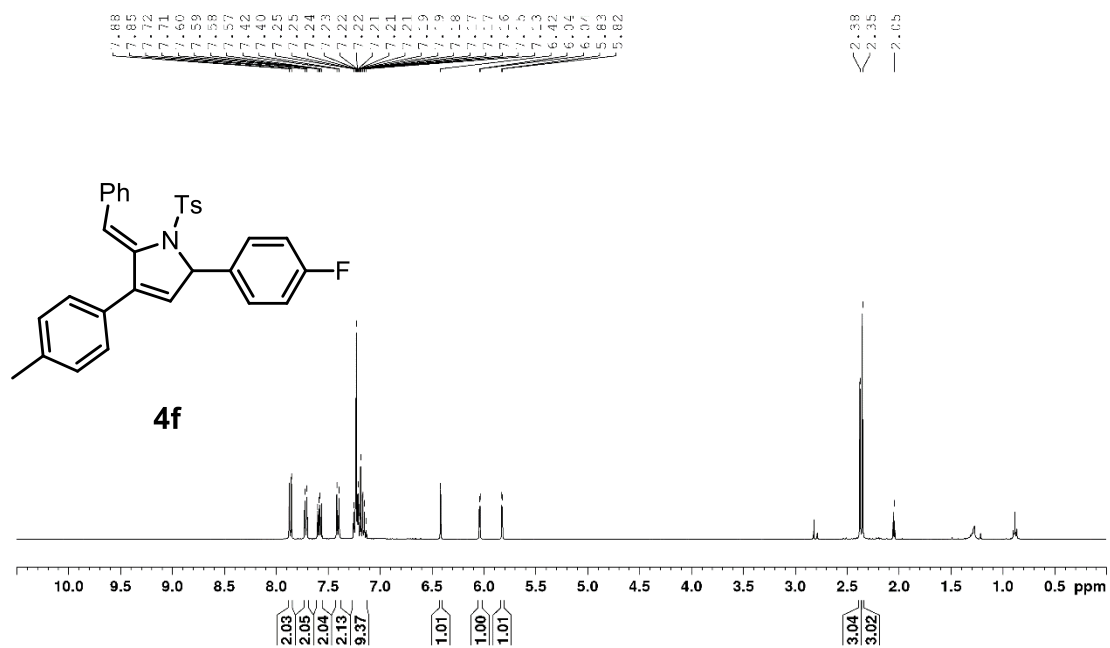
¹H NMR spectrum of compound **4e** (400 MHz, CD₃COCD₃)



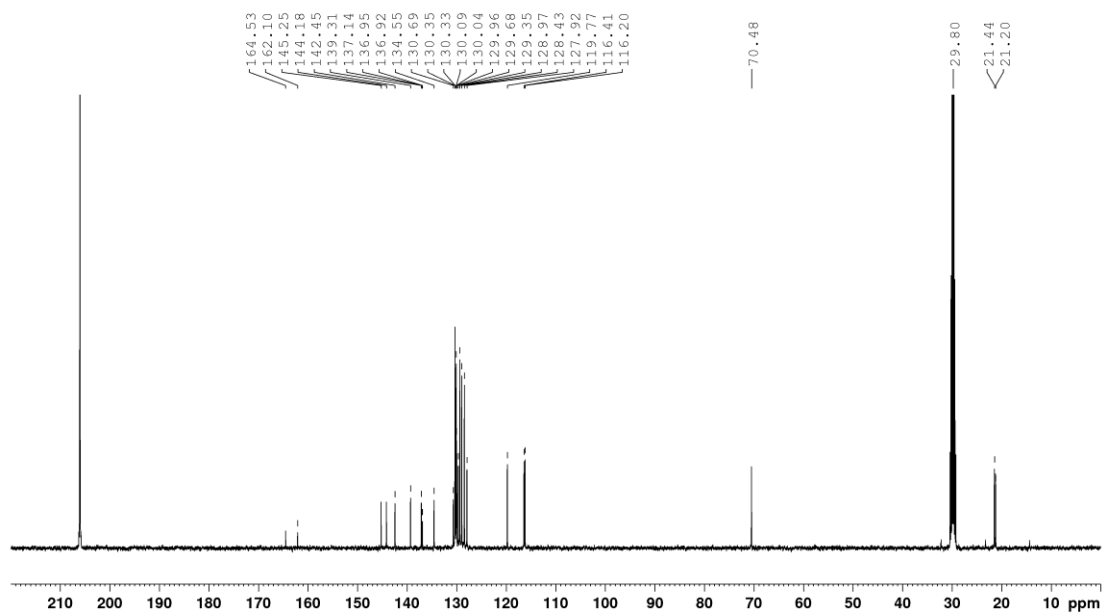
¹³C NMR spectrum of compound **4e** (100 MHz, CD₃COCD₃)



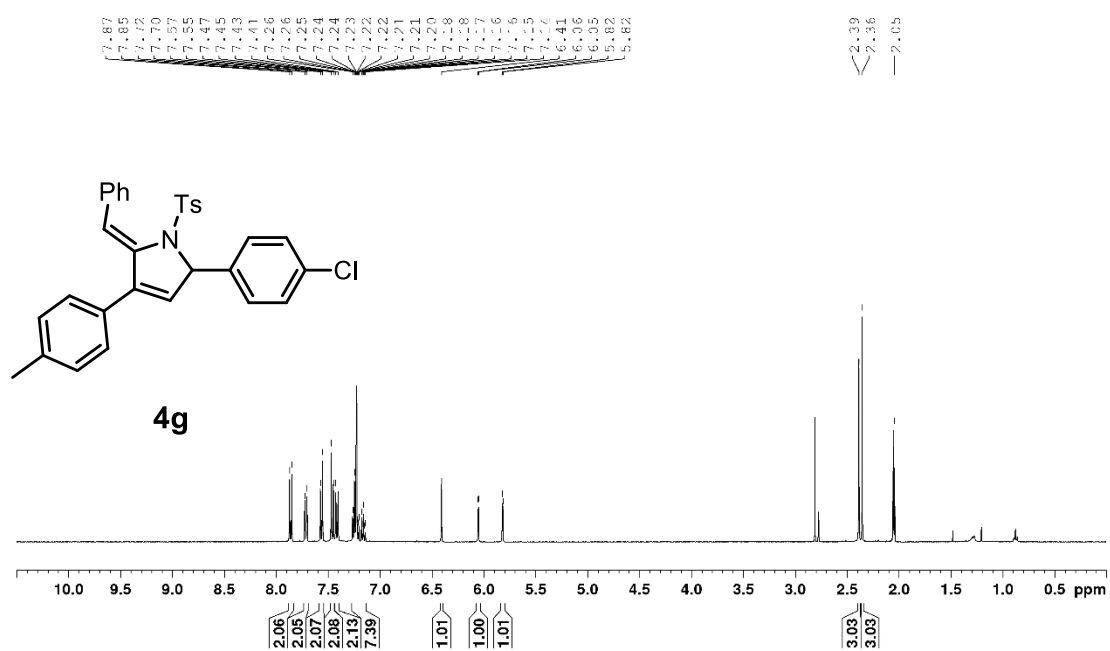
¹H NMR spectrum of compound **4f** (400 MHz, CD₃COCD₃)



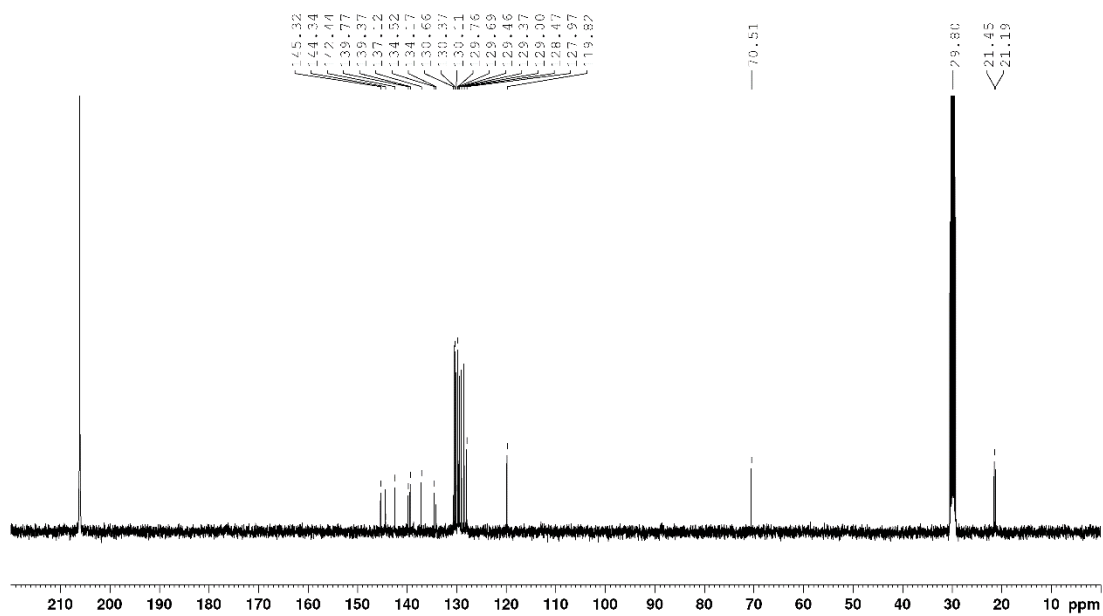
¹³C NMR spectrum of compound **4f** (100 MHz, CD₃COCD₃)



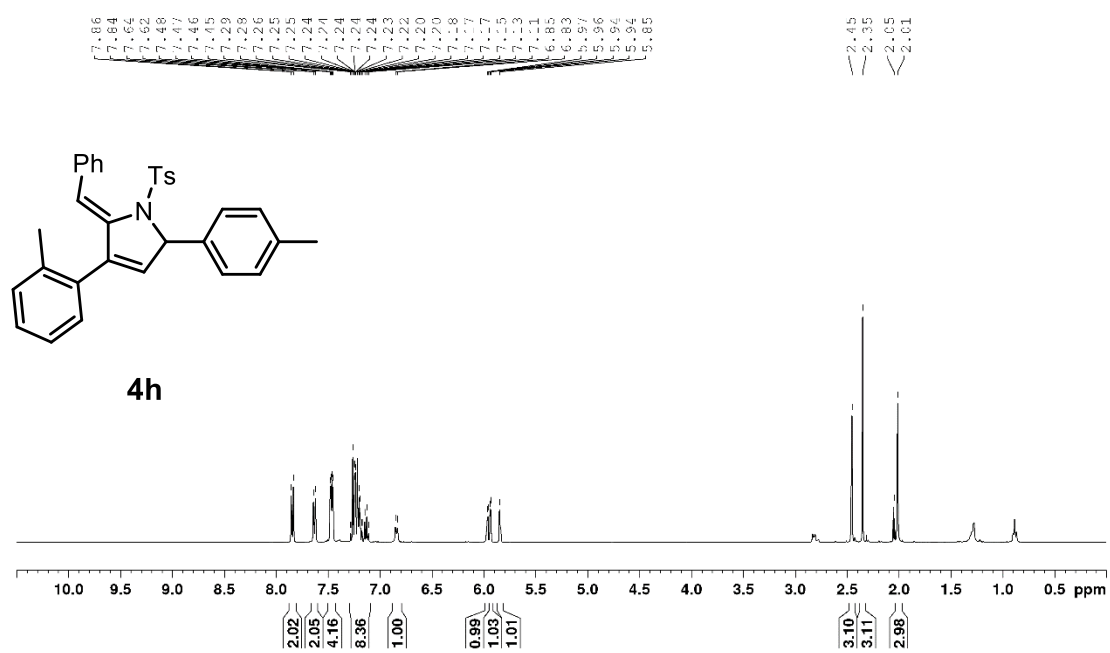
¹H NMR spectrum of compound **4g** (400 MHz, CD₃COCD₃)



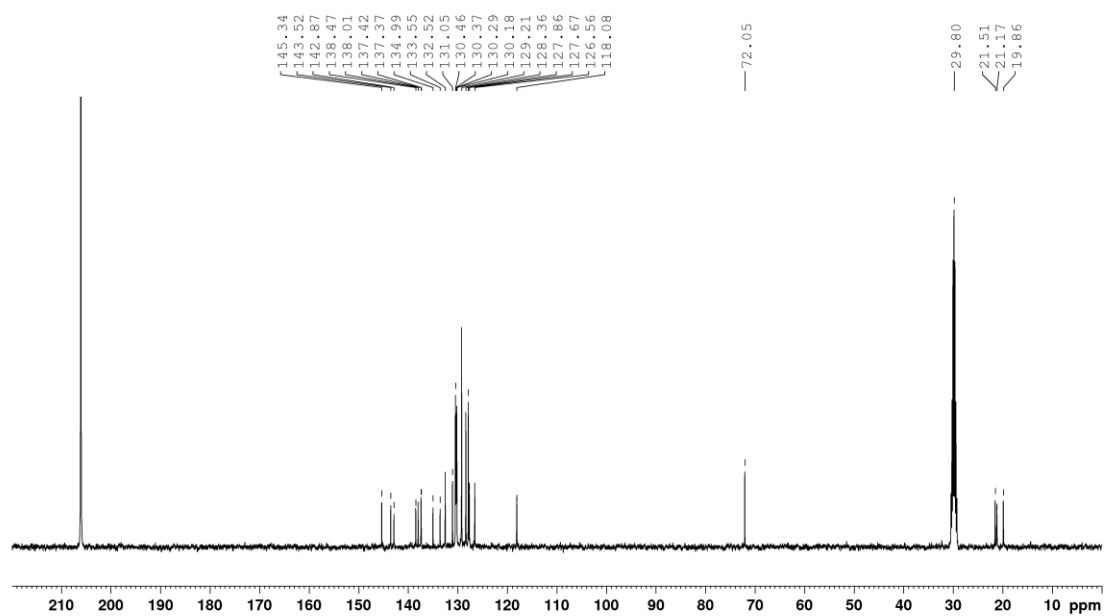
¹³C NMR spectrum of compound **4g** (100 MHz, CD₃COCD₃)



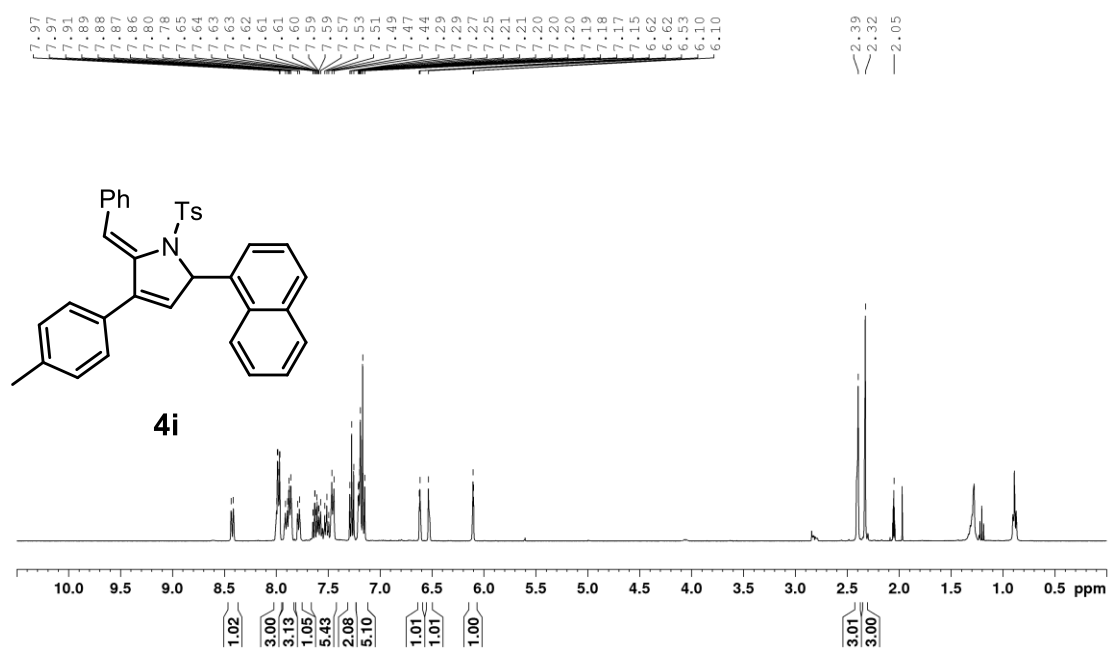
¹H NMR spectrum of compound **4h** (400 MHz, CD₃COCD₃)



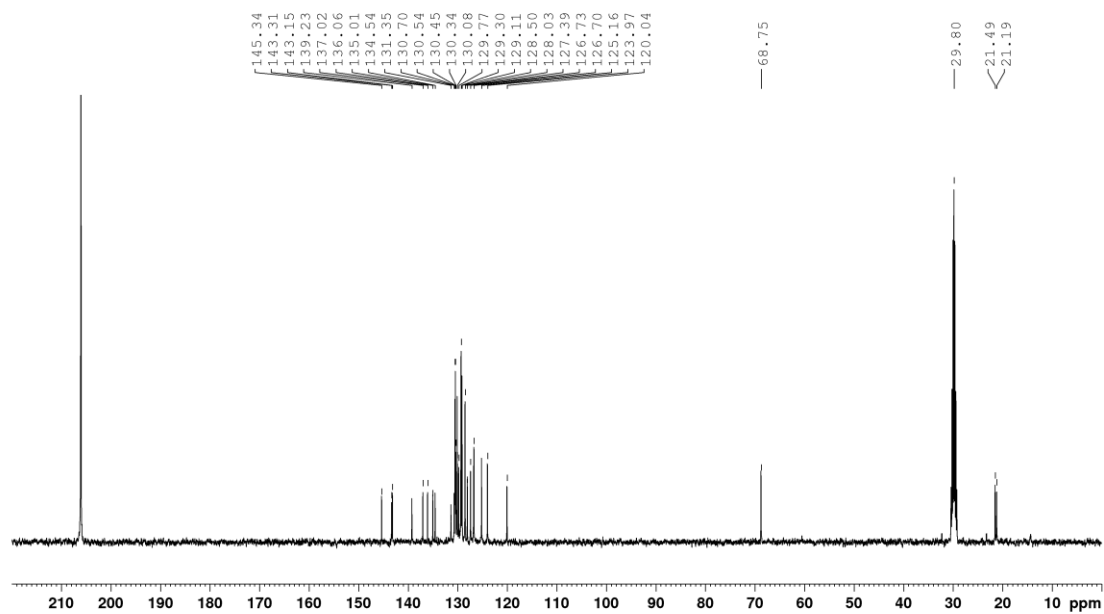
¹³C NMR spectrum of compound **4h** (100 MHz, CD₃COCD₃)



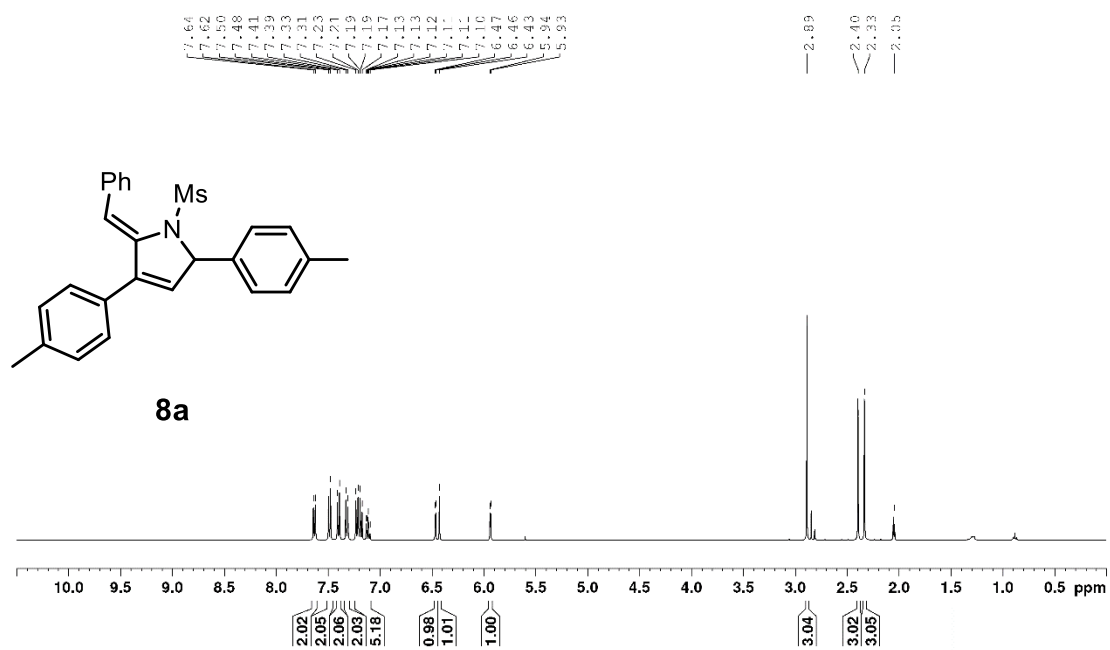
^1H NMR spectrum of compound **4i** (400 MHz, CD_3COCD_3)



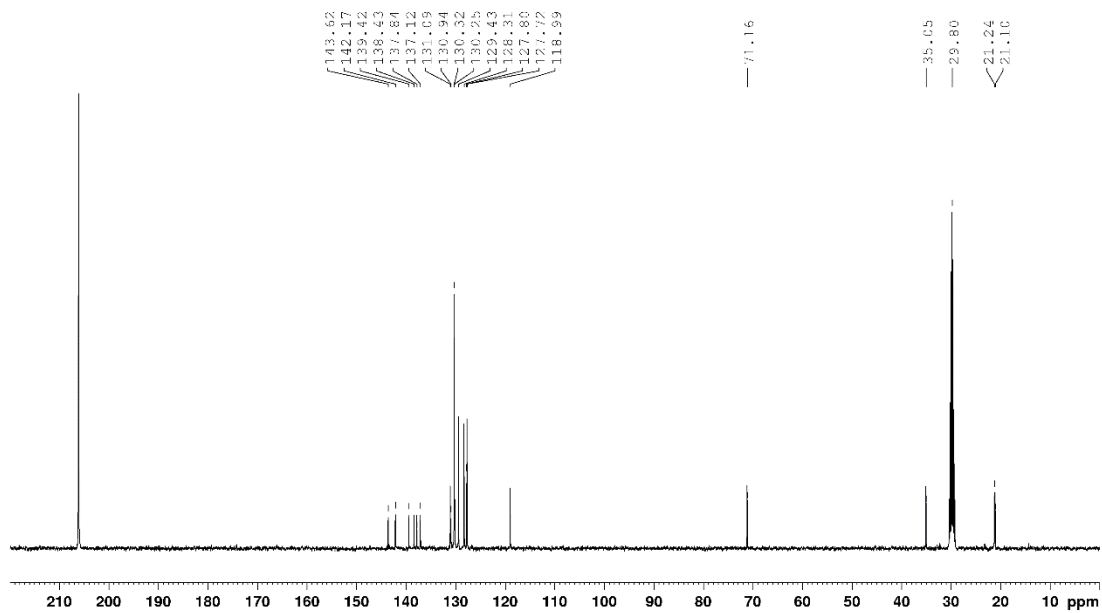
^{13}C NMR spectrum of compound **4i** (100 MHz, CD_3COCD_3)



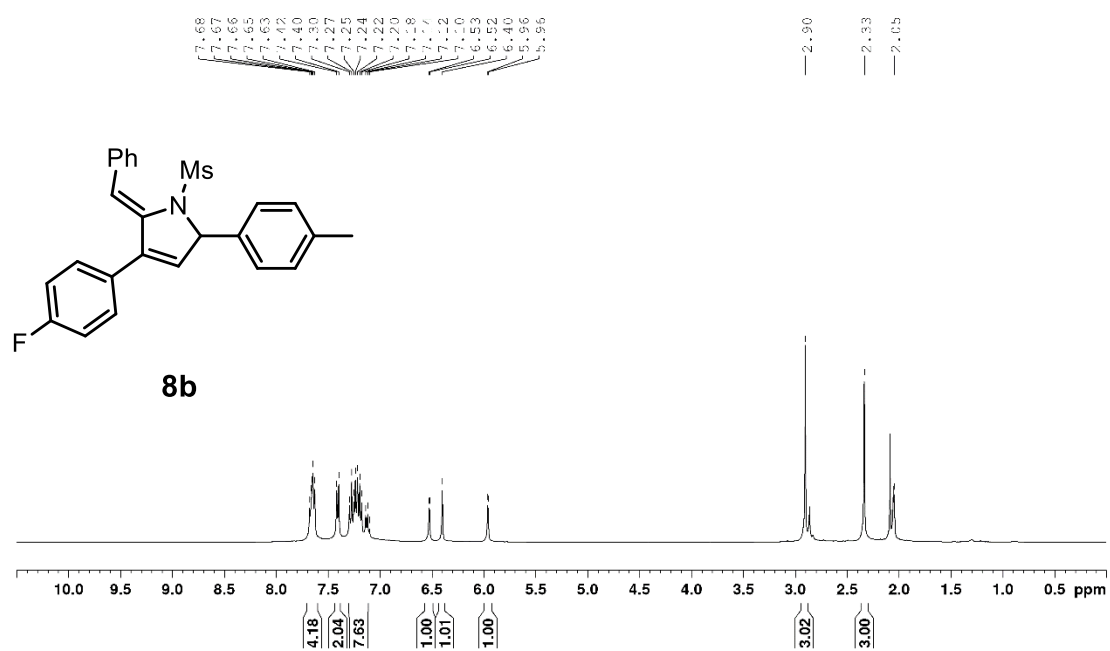
^1H NMR spectrum of compound **8a** (400 MHz, CD_3COCD_3)



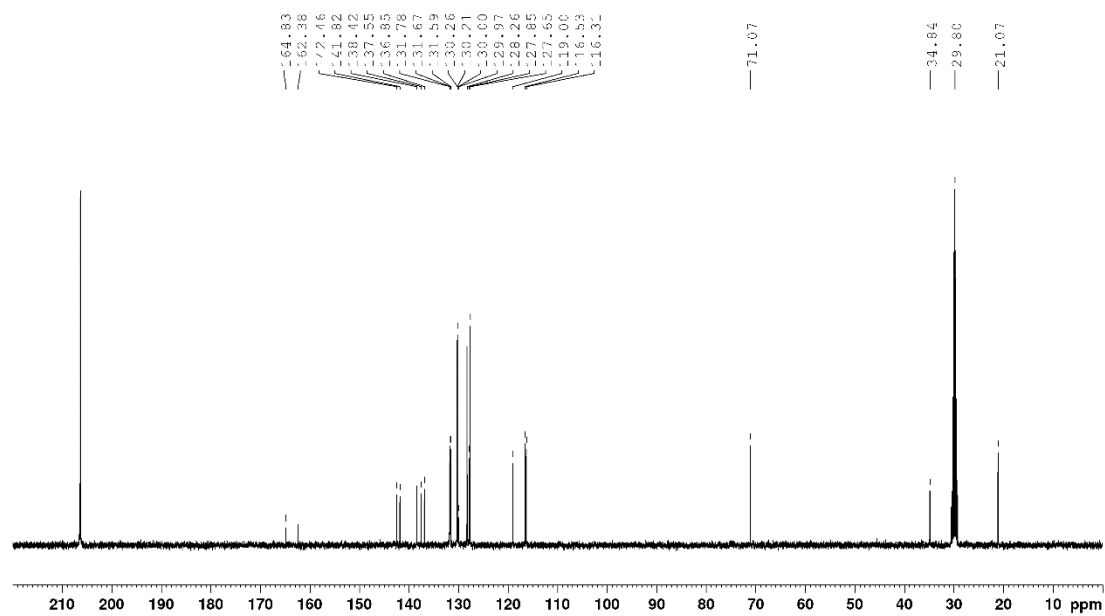
^{13}C NMR spectrum of compound **8a** (100 MHz, CD_3COCD_3)



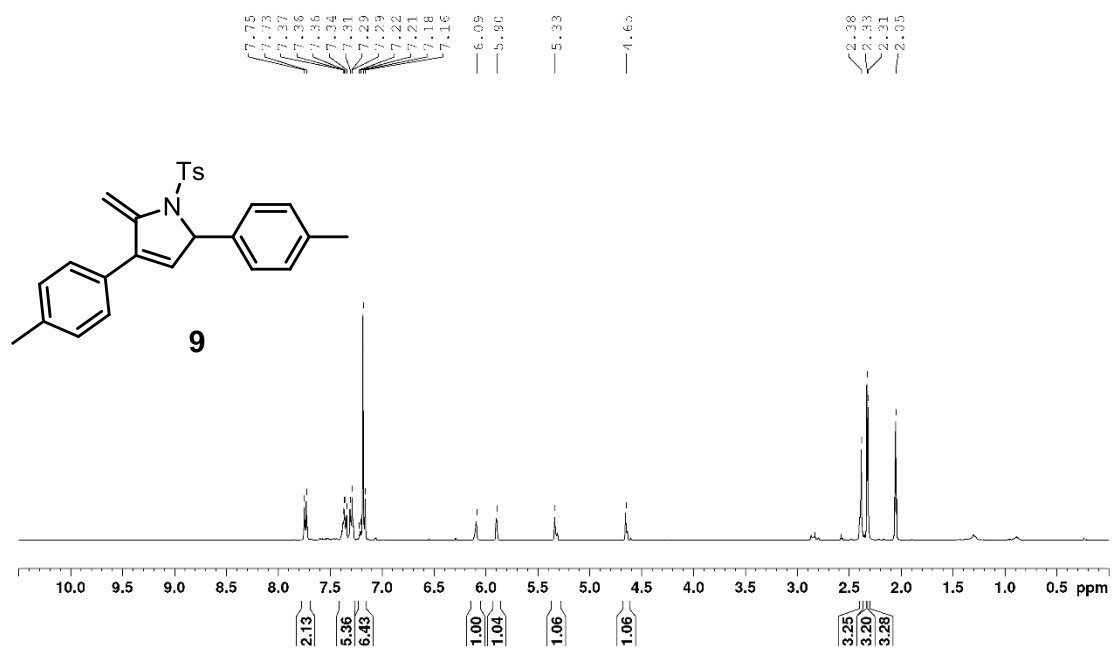
¹H NMR spectrum of compound **8b** (400 MHz, CD₃COCD₃)



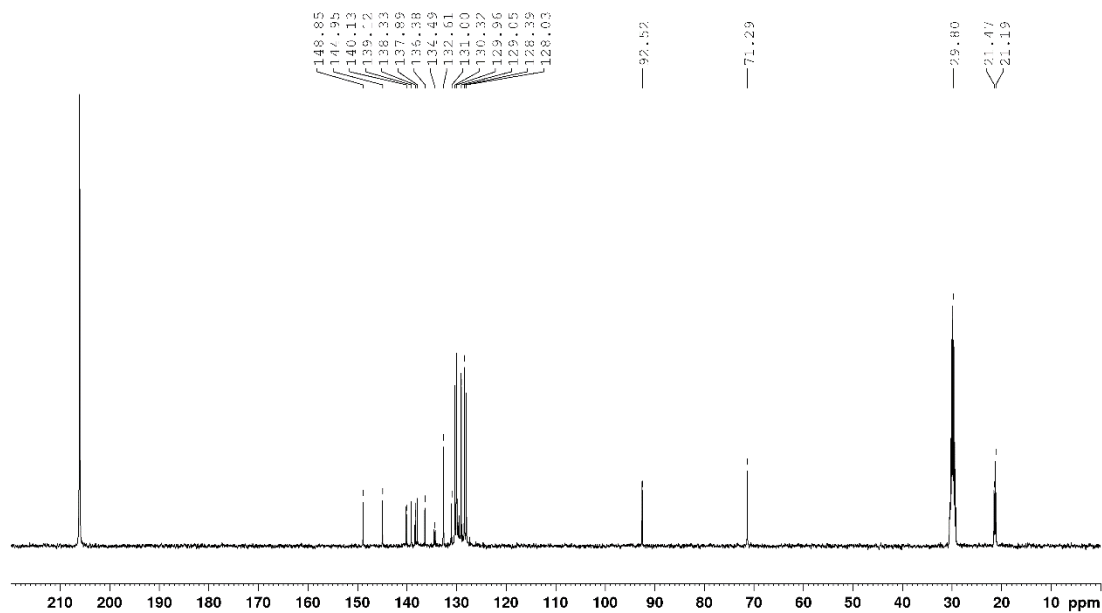
¹³C NMR spectrum of compound **8b** (100 MHz, CD₃COCD₃)



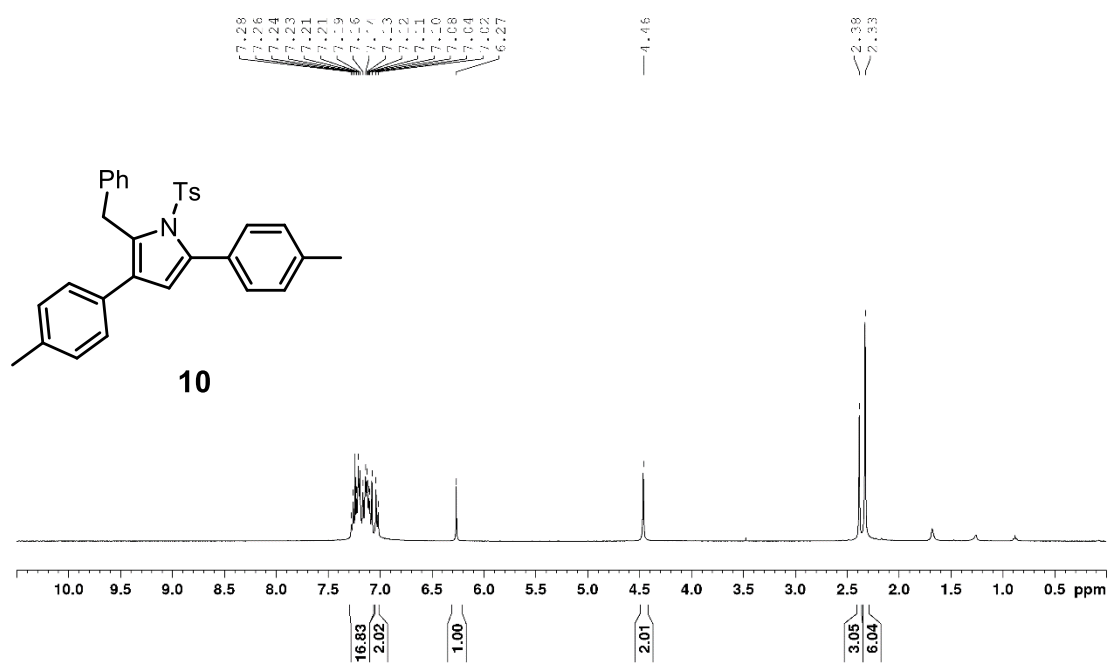
^1H NMR spectrum of compound **9** (400 MHz, CD_3COCD_3)



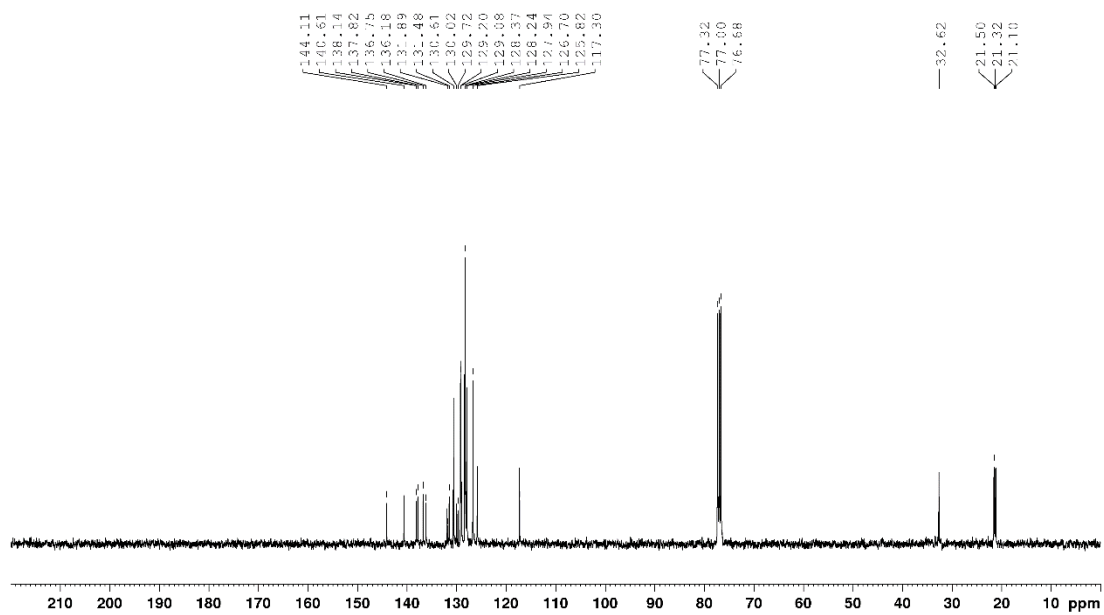
^{13}C NMR spectrum of compound **9** (100 MHz, CD_3COCD_3)



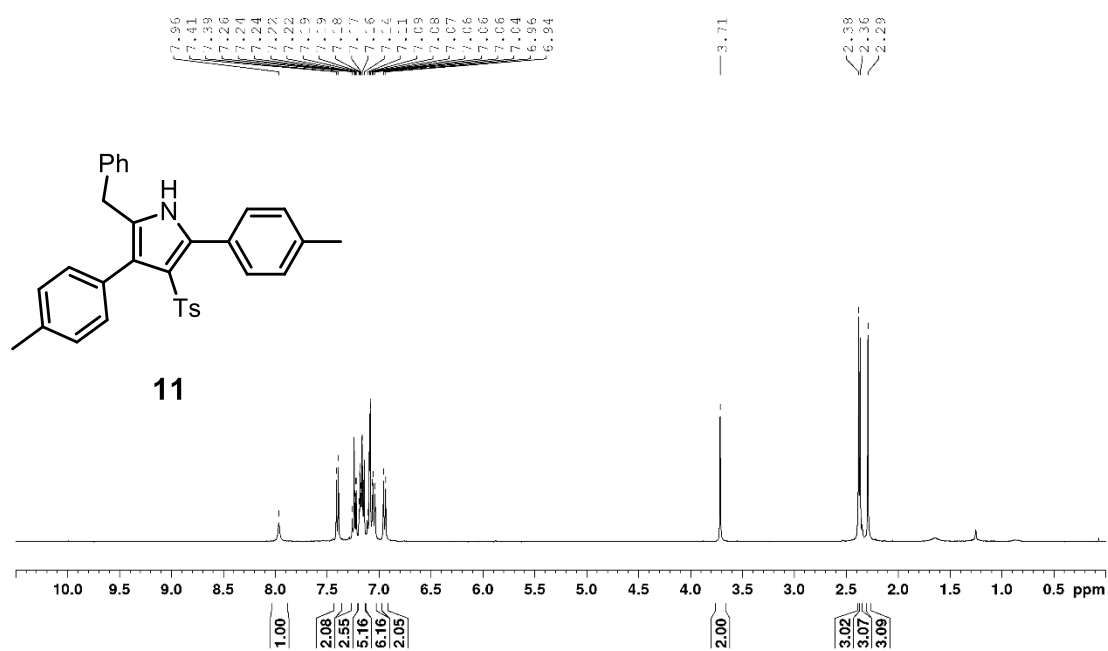
¹H NMR spectrum of compound **10** (400 MHz, CDCl₃)



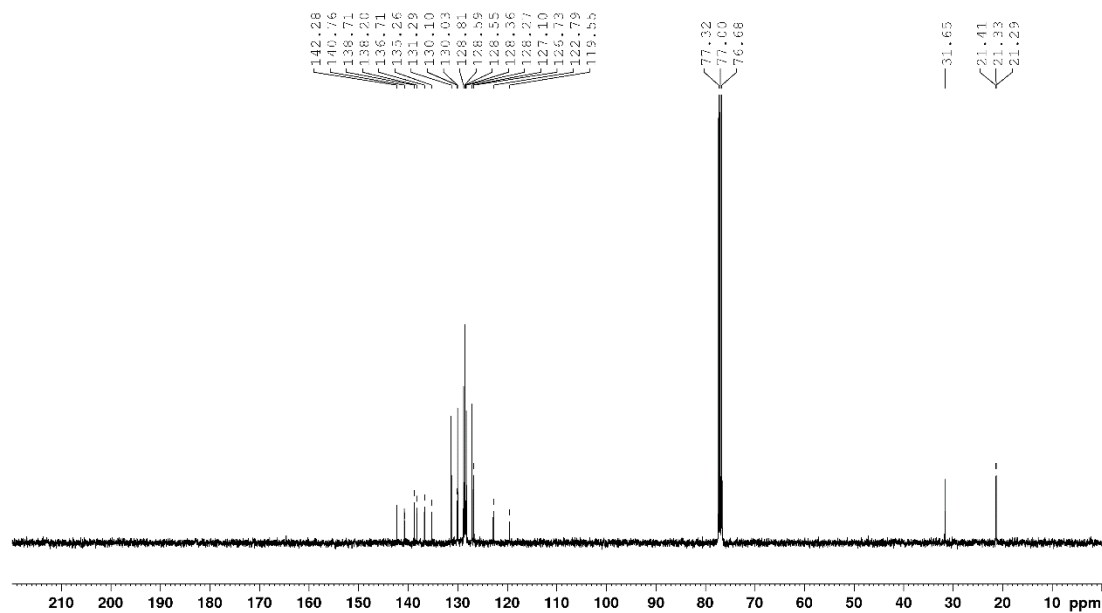
¹³C NMR spectrum of compound **10** (100 MHz, CDCl₃)



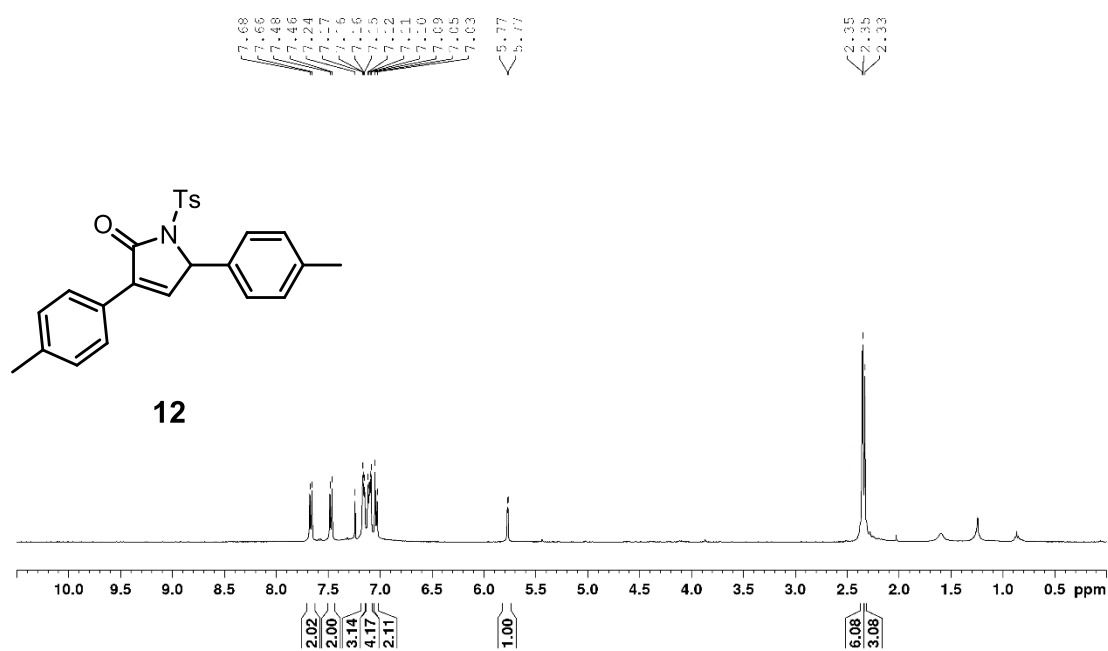
¹H NMR spectrum of compound **11** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **11** (100 MHz, CDCl₃)



¹H NMR spectrum of compound **12** (400 MHz, CDCl₃)



¹³C NMR spectrum of compound **12** (100 MHz, CDCl₃)

