

Synthesis of 3-Bromosubstituted Pyrroles *via* Palladium-Catalyzed Intermolecular Oxidative Cyclization of Bromoalkynes with *N*-Allylamines

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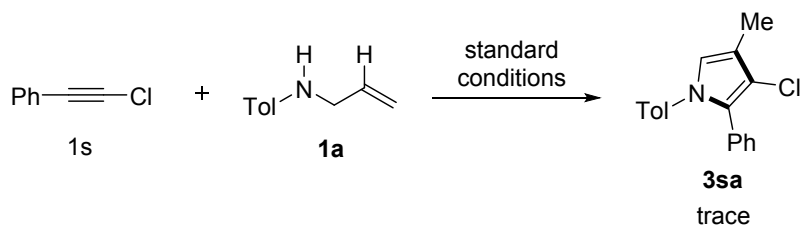
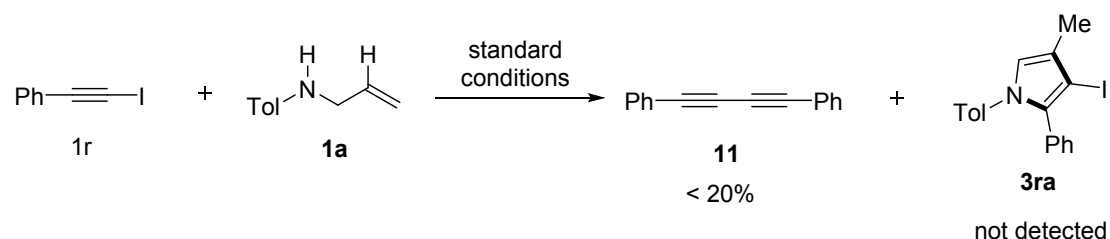
A. General methods

^1H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer using CDCl_3 as solvent and TMS as an internal standard. Mass spectra were obtained with gas chromatography mass spectrometer. IR spectra were obtained either as potassium bromide pellets or as liquid films between two potassium bromide pellets with a spectrometer. GC-MS was obtained using electron ionization. HRMS was obtained with a LCMS-IT-TOF mass spectrometer.

B. General procedure for the synthesis of pyrrole derivatives

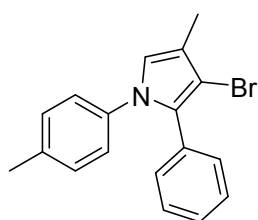
N-Allylamine (0.2 mmol), bromoalkynes (0.2 mmol), PdCl_2 (10 mol %) and BQ (2 equiv) were added to 2 mL toluene/DMSO (5/1). The mixture was stirred under air at 110 °C for the desired reaction time. After that, water was added and extracted with ethyl acetate twice. The combined organic phase was dried over Na_2SO_4 and concentrated. The residue was eventually purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate as the eluent to afford the corresponding pyrroles.

C. Reactions between other haloalkynes and *N*-allylamines



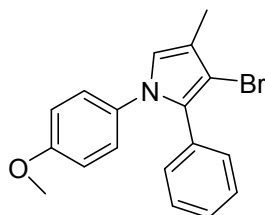
D. Analytical data for pyrrole derivatives

3-Bromo-4-methyl-2-phenyl-1-(*p*-tolyl)-1*H*-pyrrole (3aa)



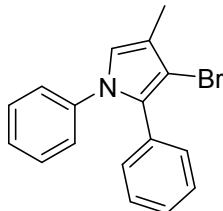
White solid. M.p.: 96-97 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.15 (dd, *J* = 12.6, 5.9 Hz, 5H), 6.96 (d, *J* = 7.9 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.66 (s, 1H), 2.22 (s, 3H), 2.08 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.8, 136.3, 131.3, 130.4, 130.3, 129.5, 127.9, 127.1, 125.1, 120.6, 119.5, 100.9, 20.9, 11.3 ppm. MS (EI, 70 eV) *m/z*: 91, 128, 231, 246, 325. HRMS (ESI) *m/z*: calcd for C₁₈H₁₇BrN [M+H]⁺, 326.0539; found, 326.0535. IR (KBr): 2922, 2854, 1670, 1608, 1514, 1445, 1356, 1042, 695 cm⁻¹.

3-Bromo-1-(4-methoxyphenyl)-4-methyl-2-phenyl-1*H*-pyrrole (3ab)



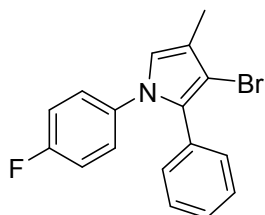
Red solid. M.p.: 90-92 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.14 (dd, *J* = 11.7, 5.9 Hz, 5H), 6.88 (d, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 8.5 Hz, 2H), 6.63 (s, 1H), 3.67 (s, 3H), 2.07 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.1, 133.5, 131.3, 130.6, 130.4, 127.9, 127.1, 126.6, 120.7, 119.3, 114.1, 100.6, 55.4, 11.3 ppm. MS (EI, 70 eV) *m/z*: 77, 128, 231, 262, 341. HRMS (ESI) *m/z*: calcd for C₁₈H₁₇BrNO [M+H]⁺, 342.0488; found, 342.0489. IR (KBr): 2924, 2850, 1605, 1512, 1463, 1248, 1039, 833 cm⁻¹.

3-Bromo-4-methyl-1,2-diphenyl-1*H*-pyrrole (3ac)



White solid. M.p.: 81-82 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.35 – 7.19 (m, 8H), 7.07 (d, *J* = 7.4 Hz, 2H), 6.81 (s, 1H), 2.20 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.3, 131.2, 130.4, 130.3, 128.9, 127.9, 127.2, 126.5, 125.3, 120.5, 119.7, 101.3, 11.3 ppm. MS (EI, 70 eV) *m/z*: 77, 128, 232, 311. HRMS (ESI) *m/z*: calcd for C₁₇H₁₅BrN [M+H]⁺, 312.0382; found, 312.0376. IR (KBr): 3063, 2922, 1851, 1598, 1498, 1355, 757, 697 cm⁻¹.

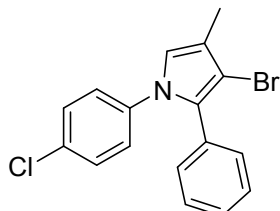
3-Bromo-1-(4-fluorophenyl)-4-methyl-2-phenyl-1*H*-pyrrole (3ad)



Yellow solid. M.p.: 116-117 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.14 (m, 5H), 6.95 – 6.88 (m, 2H), 6.84 (t, *J* = 8.3 Hz, 2H), 6.63 (s, 1H), 2.07 (s, 3H). ¹³C NMR (100 MHz,

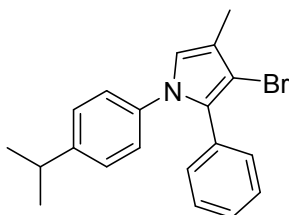
CDCl₃) δ 161.0 (d, $J = 245$ Hz), 136.4 (d, $J = 3$ Hz), 131.0, 130.7, 130.4, 130.1, 128.0, 127.3, 126.9 (d, $J = 8$ Hz), 120.6, 119.8, 115.8 (d, $J = 23$ Hz), 101.2, 11.3 ppm; MS (EI, 70 eV) m/z : 95, 125, 250, 329. HRMS (ESI) m/z : calcd for C₁₇H₁₄BrFN [M+H]⁺, 330.0288; found, 330.0285. IR (KBr): 2924, 2853, 1603, 1510, 1465, 1356, 1225, 839 cm⁻¹.

3-Bromo-1-(4-chlorophenyl)-4-methyl-2-phenyl-1H-pyrrole (3ae)



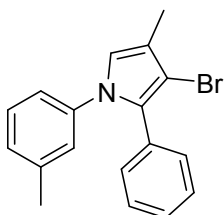
Yellow solid. M.p.: 101-103 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.21 – 7.09 (m, 7H), 6.87 (d, $J = 8.2$ Hz, 2H), 6.64 (s, 1H), 2.07 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 138.8, 132.2, 130.9, 130.5, 130.4, 129.1, 128.1, 127.4, 126.4, 120.3, 120.2, 101.8, 11.3 ppm. MS (EI, 70 eV) m/z : 115, 128, 231, 266, 347. HRMS (ESI) m/z : calcd for C₁₇H₁₄ClFN [M+H]⁺, 345.9993; found, 345.9990. IR (KBr): 3064, 2924, 2852, 1652, 1601, 1495, 1354, 1093, 1043, 832 cm⁻¹.

3-Bromo-1-(4-isopropylphenyl)-4-methyl-2-phenyl-1H-pyrrole (3af)



Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.23 (d, $J = 11.1$ Hz, 5H), 7.09 (d, $J = 7.6$ Hz, 2H), 6.94 (d, $J = 7.7$ Hz, 2H), 6.74 (s, 1H), 2.92 – 2.81 (m, 1H), 2.15 (s, 3H), 1.21 (d, $J = 6.7$ Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 138.0, 131.3, 130.4, 130.3, 127.8, 127.1, 126.9, 125.1, 120.6, 119.4, 100.9, 33.58, 23.89, 11.28. ppm; MS (EI, 70 eV) m/z : 128, 259, 231, 274, 353. HRMS (ESI) m/z : calcd for C₂₀H₂₁BrN [M+H]⁺, 354.0852; found, 354.0850. IR (KBr): 2961, 2927, 2868, 1688, 1514, 1452, 1370, 1023, 705 cm⁻¹.

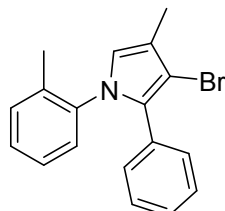
3-Bromo-4-methyl-2-phenyl-1-(*m*-tolyl)-1H-pyrrole (3ag)



White solid. M.p.: 90-91 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.29–7.23 (m, 5H), 7.13 (t, $J = 7.7$ Hz, 1H), 7.03 (d, $J = 7.5$ Hz, 1H), 6.93 (s, 1H), 6.80 (d, $J = 8.5$ Hz, 2H), 2.29

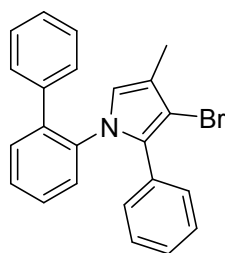
(s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 138.9, 131.3, 130.4, 130.3, 128.6, 127.8, 127.2, 127.1, 125.8, 122.5, 120.5, 119.5, 101.1, 21.3, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 129, 231, 246, 325. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$, 326.0539; found, 326.0537. IR (KBr): 3064, 2924, 2854, 1647, 1603, 1496, 1460, 1389, 1355, 1043, 766, 696 cm^{-1} .

3-Bromo-4-methyl-2-phenyl-1-(*o*-tolyl)-1*H*-pyrrole (3ah)



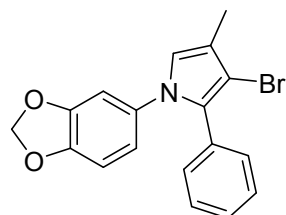
White solid. M.p.: 88-89 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.13 – 6.98 (m, 9H), 6.49 (s, 1H), 2.08 (s, 3H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.6, 135.4, 131.5, 131.2, 130.7, 129.8, 128.3, 128.0, 127.8, 126.9, 126.4, 120.8, 119.3, 99.6, 17.6, 11.4 ppm; MS (EI, 70 eV) m/z : 91, 129, 231, 246, 325. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$, 326.0539; found, 326.0534. IR (KBr): 3064, 2923, 2853, 1645, 1604, 1496, 1462, 1389, 1355, 1043, 766, 696 cm^{-1} .

1-([1,1'-Biphenyl]-2-yl)-3-bromo-4-methyl-2-phenyl-1*H*-pyrrole (3ai)



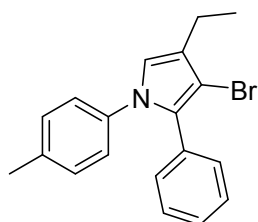
Yellow solid. M.p.: 134-135 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.25 (m, 3H), 7.14 (d, $J = 6.3$ Hz, 1H), 7.08 (d, $J = 7.2$ Hz, 1H), 7.01 (t, $J = 7.4$ Hz, 2H), 6.95 (d, $J = 7.0$ Hz, 1H), 6.89 (t, $J = 7.3$ Hz, 2H), 6.61 (s, 1H), 6.56 (d, $J = 7.5$ Hz, 2H), 6.49 (d, $J = 7.5$ Hz, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) 138.7, 138.2, 138.0, 131.4, 130.9, 130.8, 129.4, 128.1, 128.0, 127.9, 127.3, 127.0, 126.4, 120.7, 119.7, 99.9, 11.4 ppm; MS (EI, 70 eV) m/z : 145, 231, 307, 387. HRMS (ESI) m/z : calcd for $\text{C}_{23}\text{H}_{18}\text{BrNNa}$ $[\text{M}+\text{H}]^+$, 410.0515; found, 410.0513. IR (KBr): 3610, 2923, 2853, 1602, 1482, 1437, 1354, 1045, 766, 738, 696 cm^{-1} .

1-(Benzo[*d*][1,3]dioxol-5-yl)-3-bromo-4-methyl-2-phenyl-1*H*-pyrrole (3aj)



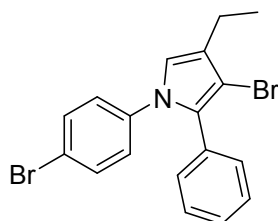
Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.03 (m, 6H), 6.62 (s, 1H), 6.59 (d, $J = 8.7$ Hz, 1H), 6.46 (s, 2H), 5.87 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 146.3, 134.6, 131.1, 130.6, 130.3, 127.9, 127.2, 120.8, 119.4, 118.9, 107.9, 107.1, 101.6, 100.7, 11.2. ppm; MS (EI, 70 eV) m/z : 108, 218, 246, 276, 355. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{14}\text{BrNNaO}_2$ $[\text{M}+\text{H}]^+$, 378.0100; found, 378.0095. IR (KBr): 2922, 2853, 1692, 1494, 1452, 1243, 1038 cm^{-1} .

3-Bromo-4-ethyl-2-phenyl-1-(*p*-tolyl)-1*H*-pyrrole (3ak)



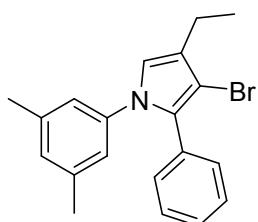
Red solid. M.p.: 65-66 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.26 – 7.20 (m, 5H), 7.03 (d, $J = 7.9$ Hz, 2H), 6.92 (d, $J = 7.9$ Hz, 2H), 6.71 (s, 1H), 2.56 (q, $J = 7.4$ Hz, 2H), 2.29 (s, 3H), 1.28 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 136.3, 131.30, 130.5, 130.4, 129.5, 127.9, 127.1, 126.0, 125.1, 119.7, 99.9, 20.9, 19.6, 14.01. ppm; MS (EI, 70 eV) m/z : 91, 115, 128, 202, 244, 341. HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{19}\text{BrN}$ $[\text{M}+\text{H}]^+$, 340.0695; found, 340.0695. IR (KBr): 2964, 2924, 2858, 1656, 1608, 1514, 1463, 1375, 1069, 821, 700 cm^{-1} .

3-Bromo-1-(4-bromophenyl)-4-ethyl-2-phenyl-1*H*-pyrrole (3al)



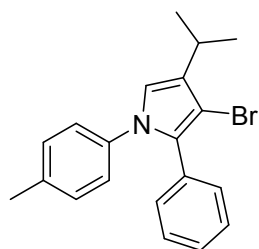
Yellow solid. M.p.: 132-134 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 7.9$ Hz, 2H), 7.20 – 7.18 (m, 3H), 7.12 (d, $J = 7.3$ Hz, 2H), 6.84 (d, $J = 7.9$ Hz, 2H), 6.63 (s, 1H), 2.48 (q, $J = 7.4$ Hz, 2H), 1.20 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 132.1, 130.9, 130.5, 130.4, 128.1, 127.4, 126.8, 126.7, 119.9, 119.4, 100.9, 19.6, 13.9. ppm; MS (EI, 70 eV) m/z : 115, 128, 155, 230, 405. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}$ $[\text{M}+\text{H}]^+$, 403.9644; found, 403.9646. IR (KBr): 2965, 2926, 2854, 1694, 1596, 1491, 1370, 1067, 828, 754, 699 cm^{-1} .

3-Bromo-1-(3,5-dimethylphenyl)-4-ethyl-2-phenyl-1*H*-pyrrole (3am)



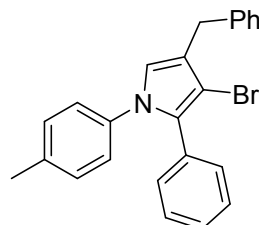
Red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.21(m, 5H), 6.82 (s, 1H), 6.72 (s, 1H), 6.65 (s, 2H), 2.56 (q, $J = 7.1$ Hz, 2H), 2.19 (s, 6H), 1.28 (d, $J = 7.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.2, 138.6, 131.3, 130.4, 130.3, 128.1, 127.8, 127.1, 125.9, 123.0, 119.6, 99.9, 21.1, 19.6, 14.0. ppm. MS (EI, 70 eV) m/z : 77, 128, 259, 353. HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{BrNNa}$ $[\text{M}+\text{H}]^+$, 376.0671; found, 376.0674. IR (KBr): 2965, 2925, 2855, 1686, 1602, 1458, 1369, 1267, 757 cm^{-1} .

3-Bromo-4-isopropyl-2-phenyl-1-(*p*-tolyl)-1*H*-pyrrole (3an)



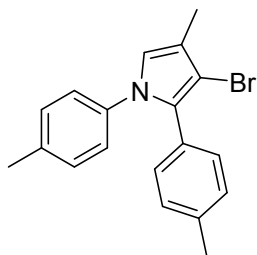
Yellow solid. M.p.: 73-74 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.17 – 7.13 (m, 5H), 6.96 (d, $J = 7.7$ Hz, 2H), 6.85 (d, $J = 7.7$ Hz, 2H), 6.62 (s, 1H), 2.95 – 2.83 (m, 1H), 2.22 (s, 3H), 1.22 (d, $J = 6.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.0, 136.2, 131.3, 130.9, 130.5, 129.5, 127.8, 127.1, 125.1, 118.5, 99.4, 26.3, 23.1, 20.9. ppm; MS (EI, 70 eV) m/z : 91, 202, 340, 355. HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{21}\text{BrN}$ $[\text{M}+\text{H}]^+$, 354.0852; found, 354.0847. IR (KBr): 2958, 2923, 2853, 1602, 1515, 1462, 1376, 821, 764, 697 cm^{-1} .

4-Benzyl-3-bromo-2-phenyl-1-(*p*-tolyl)-1*H*-pyrrole (3ao)



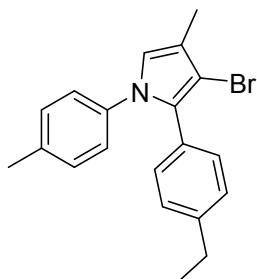
Yellow solid. M.p.: 141-142 $^{\circ}\text{C}$. ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.29 (m, 4H), 7.25 – 7.21 (m, 6H), 7.01 (d, $J = 7.8$ Hz, 2H), 6.89 (d, $J = 7.9$ Hz, 2H), 6.54 (s, 1H), 3.89 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 140.5, 137.8, 136.4, 131.1, 130.6, 130.4, 129.5, 128.9, 128.4, 127.9, 127.2, 126.02, 125.1, 123.7, 121.2, 100.1, 32.7, 20.9 ppm; MS (EI, 70 eV) m/z : 91, 202, 322, 403. HRMS (ESI) m/z : calcd for $\text{C}_{24}\text{H}_{20}\text{BrNNa}$ $[\text{M}+\text{H}]^+$, 424.0671; found, 424.0671. IR (KBr): 3029, 2919, 2850, 1605, 1514, 1463, 1368, 698 cm^{-1} .

3-Bromo-4-methyl-1,2-di-*p*-tolyl-1*H*-pyrrole (3ba)



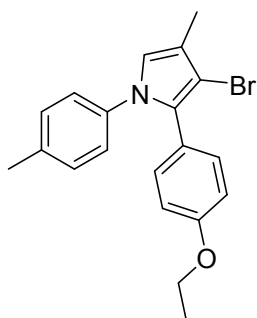
Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.15 – 7.03 (m, 6H), 6.94 (d, $J = 8.0$ Hz, 2H), 6.74 (s, 1H), 2.32 (s, 6H), 2.17 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.9, 136.9, 136.2, 130.5, 130.2, 129.5, 128.7, 128.4, 125.1, 120.3, 119.4, 100.7, 21.3, 20.9, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 128, 260, 339. HRMS (ESI) m/z : calcd for $\text{C}_{19}\text{H}_{18}\text{BrNNa}$ $[\text{M}+\text{H}]^+$, 362.0515; found, 362.0518. IR (KBr): 3030, 2922, 2857, 1695, 1611, 1514, 1356, 1042, 820 cm^{-1}

3-Bromo-2-(4-ethylphenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3ca)



Yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 7.18 – 7.05 (m, 6H), 6.95 (d, $J = 7.8$ Hz, 2H), 6.75 (s, 1H), 2.65 (q, $J = 7.6$ Hz, 2H), 2.34 (s, 3H), 2.18 (s, 3H), 1.25 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.0, 137.9, 136.2, 130.5, 130.2, 129.5, 128.5, 127.4, 125.1, 120.3, 119.4, 100.7, 28.6, 20.9, 15.1, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 128, 274, 353. HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{20}\text{BrNNa}$ $[\text{M}+\text{H}]^+$, 376.0671; found, 376.0674. IR (KBr): 3030, 2965, 2926, 1687, 1611, 1515, 1457, 1357, 1043, 828 cm^{-1} .

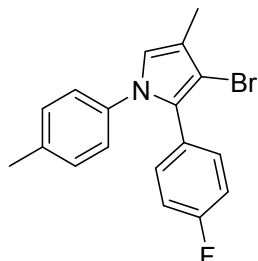
3-Bromo-2-(4-ethoxyphenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3da)



White solid. M.p.: 129-130 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.03 (d, $J = 7.8$ Hz, 2H), 6.96 (d, $J = 7.5$ Hz, 2H), 6.84 (d, $J = 7.4$ Hz, 2H), 6.70 (d, $J = 7.6$ Hz, 2H), 6.63 (s, 1H), 3.92 (q, $J = 6.5$ Hz, 2H), 2.22 (s, 3H), 2.06 (s, 3H), 1.31 (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 158.1, 137.9, 136.2, 131.6, 130.4, 129.5, 125.1, 123.6, 119.9, 119.2, 113.9, 100.5, 63.3, 20.9, 14.9, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 115,

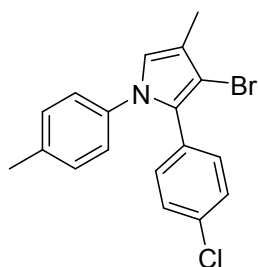
262, 290, 342, 269. HRMS (ESI) m/z : calcd for $C_{20}H_{21}BrNO$ $[M+H]^+$, 370.0801; found, 370.0801. IR (KBr): 3036, 2978, 2925, 1693, 1610, 1518, 1475, 1392, 1245, 1044, 827 cm^{-1} .

3-Bromo-2-(4-fluorophenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3ea)



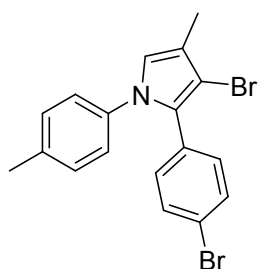
Yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.09 (dd, $J = 7.4, 5.9$ Hz, 2H), 6.97 (d, $J = 7.8$ Hz, 2H), 6.84 (dd, $J = 20.4, 8.2$ Hz, 4H), 6.64 (s, 1H), 2.23 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.9 (d, $J = 245$ Hz), 137.7, 136.5, 132.06 (d, $J = 8.1$ Hz), 129.6, 129.5, 127.4 (d, $J = 3$ Hz), 125.2, 120.6, 119.4, 115.0 (d, $J = 22$ Hz), 114.9, 100.9, 20.9, 11.2 ppm; MS (EI, 70 eV) m/z : 91, 146, 264, 343. HRMS (ESI) m/z : calcd for $C_{18}H_{16}BrFN$ $[M+H]^+$, 344.0445; found, 344.0449. IR (KBr): 2924, 2855, 1691, 1603, 1513, 1357, 1228, 835 cm^{-1} .

3-Bromo-2-(4-chlorophenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3fa)



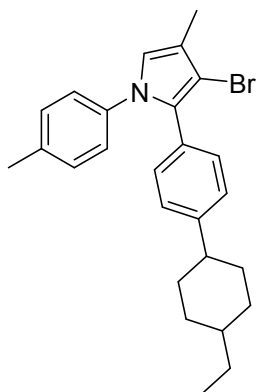
Orange solid. M.p.: 163-164 $^{\circ}C$. 1H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, $J = 8.0$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 6.92 (d, $J = 7.8$ Hz, 2H), 6.75 (s, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 136.6, 133.0, 131.5, 129.8, 129.7, 129.1, 128.2, 125.2, 120.9, 119.7, 101.2, 20.9, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 122, 163, 245, 280, 361. HRMS (ESI) m/z : calcd for $C_{18}H_{15}BrClNNa$ $[M+H]^+$, 381.9969; found, 381.9976. IR (KBr): 2923, 2856, 1653, 1514, 1464, 1407, 1356, 1092, 827 cm^{-1} .

3-Bromo-2-(4-bromophenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3ga)



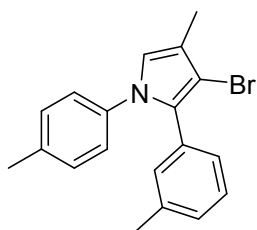
Yellow solid. M.p.: 185-187 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 4H), 6.91 (d, *J* = 7.6 Hz, 2H), 6.74 (s, 1H), 2.33 (s, 3H), 2.15 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 137.6, 136.7, 131.8, 131.2, 130.3, 129.7, 129.2, 125.2, 121.3, 121.0, 119.7, 101.24, 20.9, 11.2 ppm; MS (EI, 70 eV) *m/z*: 91, 122, 245, 324, 405. HRMS (ESI) *m/z*: calcd for C₁₈H₁₆Br₂N [M+H]⁺, 403.9644; found, 403.9646. IR (KBr): 2923, 2853, 1652, 1613, 1513, 1462, 1358, 824 cm⁻¹.

3-Bromo-2-(4-(4-ethylcyclohexyl)phenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3ha)



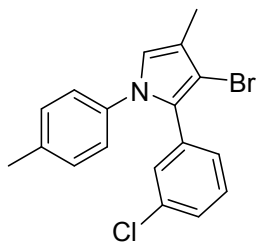
Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.02 (q, *J* = 7.9 Hz, 4H), 6.95 (d, *J* = 7.8 Hz, 2H), 6.83 (d, *J* = 7.8 Hz, 2H), 6.63 (s, 1H), 2.34 (t, *J* = 12.1 Hz, 1H), 2.22 (s, 3H), 2.06 (s, 3H), 1.78 (d, *J* = 11.6 Hz, 4H), 1.33 (dd, *J* = 22.8, 12.4 Hz, 2H), 1.19 – 1.14 (m, 3H), 0.96 (dd, *J* = 18.9, 8.4 Hz, 2H), 0.83 (d, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.7, 137.9, 136.1, 130.6, 130.1, 129.5, 128.6, 126.3, 125.1, 120.3, 119.4, 100.7, 44.3, 39.1, 34.2, 33.2, 30.0, 20.9, 11.5, 11.3 ppm; MS (EI, 70 eV) *m/z*: 128, 203, 293, 372. HRMS (ESI) *m/z*: calcd for C₂₆H₃₀BrNNa [M+H]⁺, 458.1454; found, 458.1455. IR (KBr): 2922, 2851, 1694, 1614, 1515, 1454, 1357, 825 cm⁻¹.

3-Bromo-4-methyl-2-(*m*-tolyl)-1-(*p*-tolyl)-1*H*-pyrrole (3ia)



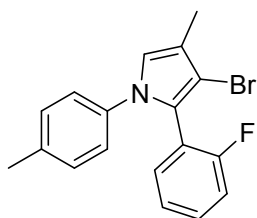
Yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.05 – 6.98 (m, 2H), 6.94 (d, *J* = 6.9 Hz, 3H), 6.84 (t, *J* = 10.9 Hz, 3H), 6.63 (s, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 2.06 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 137.9, 137.4, 136.2, 131.3, 131.1, 130.6, 129.5, 127.9, 127.8, 127.5, 125.1, 120.4, 119.4, 100.9, 21.4, 20.9, 11.3 ppm; MS (EI, 70 eV) *m/z*: 91, 115, 245, 260, 341. HRMS (ESI) *m/z*: calcd for C₁₉H₁₈BrNNa [M+H]⁺, 362.0515; found, 362.0518. IR (KBr): 3034, 2922, 2857, 1690, 1609, 1514, 1454, 1357, 1043 cm⁻¹.

3-Bromo-2-(3-chlorophenyl)-4-methyl-1-(*p*-tolyl)-1*H*-pyrrole (3ja)



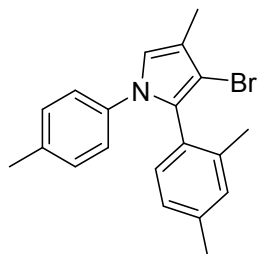
Red oil. ^1H NMR (400 MHz, CDCl_3) δ 7.27 (s, 3H), 7.16 (dd, $J = 18.7, 7.9$ Hz, 2H), 7.07 (d, $J = 7.7$ Hz, 2H), 7.01 (d, $J = 7.4$ Hz, 1H), 6.91 (d, $J = 7.6$ Hz, 2H), 6.74 (s, 1H), 2.32 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 136.7, 133.7, 133.1, 130.2, 129.7, 129.1, 128.9, 128.5, 127.2, 125.2, 121.2, 119.7, 101.5, 20.9, 11.2 ppm; MS (EI, 70 eV) m/z : 91, 115, 163, 245, 280, 361. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{BrClN}$ $[\text{M}+\text{H}]^+$, 360.0149; found, 360.0144. IR (KBr): 2924, 2854, 1693, 1600, 1514, 1461, 1356, 1044 cm^{-1} .

3-Bromo-2-(2-fluorophenyl)-4-methyl-1-(p-tolyl)-1H-pyrrole (3ka)



Yellow solid. M.p.: 148-150 °C ^1H NMR (400 MHz, CDCl_3) δ 7.35 – 7.28 (m, 2H), 7.13 (t, $J = 7.5$ Hz, 1H), 7.06 (d, $J = 7.7$ Hz, 2H), 6.99 (dd, $J = 17.9, 8.4$ Hz, 3H), 6.82 (s, 1H), 2.32 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.0 (d, $J = 247$ Hz), 158.8, 137.8, 136.4, 132.9 (d, $J = 2.6$ Hz), 129.9 (d, $J = 8.1$ Hz,), 129.5, 124.9, 124.4, 124.3, 123.7 (d, $J = 3.6$ Hz,), 120.6, 119.8, 119.7, (d, $J = 16$ Hz), 115.70 (d, $J = 22.0$ Hz,), 102.28 (s, 5H), 20.94 (s, 4H), 11.22 (s, 3H). ppm; MS (EI, 70 eV) m/z : 91, 146, 249, 264, 343. HRMS (ESI) m/z : calcd for $\text{C}_{18}\text{H}_{16}\text{BrFN}$ $[\text{M}+\text{H}]^+$, 344.0445; found, 344.0449. IR (KBr): 2924, 2854, 1692, 1611, 1515, 1455, 1358, 1043, 756 cm^{-1} .

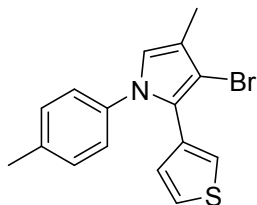
3-Bromo-2-(2,4-dimethylphenyl)-4-methyl-1-(p-tolyl)-1H-pyrrole (3la)



Yellow solid. M.p.: 148-150 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.07 (d, $J = 8.0$ Hz, 1H), 7.00 (d, $J = 7.7$ Hz, 2H), 6.96 (s, 2H), 6.89 (d, $J = 7.7$ Hz, 2H), 6.77 (s, 1H), 2.31 (s, 3H), 2.28 (s, 3H), 2.16 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 138.2, 138.1, 138.0, 135.8, 131.8, 130.7, 130.5, 129.4, 128.5, 126.2, 124.1, 119.0, 118.9, 101.5, 21.3, 20.9, 19.8, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 274, 355. HRMS

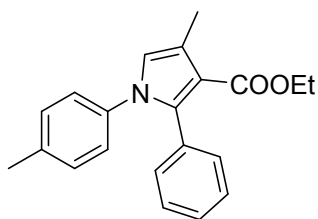
(ESI) m/z : calcd for $C_{20}H_{21}BrN$ $[M+H]^+$, 354.0852; found, 354.0856. IR (KBr): 2922, 2856, 1612, 1515, 1448, 1393, 1354, 1043, 821 cm^{-1} .

3-bromo-4-methyl-2-(thiophen-3-yl)-1-(*p*-tolyl)-1*H*-pyrrole (3ma)



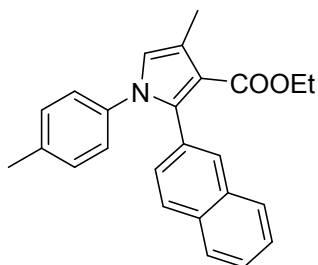
Orange solid. M.p.: 137-138°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 2H), 7.08 (d, $J = 7.8$ Hz, 2H), 6.96 (d, $J = 7.8$ Hz, 2H), 6.85 (d, $J = 4.4$ Hz, 1H), 6.69 (s, 1H), 2.33 (s, 3H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.7, 131.3, 129.6, 128.7, 126.3, 125.3, 124.3, 120.4, 119.5, 100.8, 21.0, 11.3 ppm; MS (EI, 70 eV) m/z : 91, 118, 237, 252, 333. HRMS (ESI) m/z : calcd for $C_{16}H_{14}BrNNaS$ $[M+H]^+$, 353.9923; found, 353.9935. IR (KBr): 2922, 2853, 1658, 1514, 1414, 1355, 1044, 784 cm^{-1} .

Ethyl 4-methyl-2-phenyl-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (5a)



Yellow solid. M.p.: 97-98°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.15 – 7.09 (m, 5H), 6.91 (d, $J = 7.9$ Hz, 2H), 6.80 (d, $J = 7.9$ Hz, 2H), 6.57 (s, 1H), 4.03 (q, $J = 7.1$ Hz, 2H), 2.27 (s, 3H), 2.18 (s, 3H), 1.00 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 138.2, 137.0, 136.8, 132.3, 131.2, 129.4, 127.5, 127.4, 125.8, 121.8, 121.6, 113.8, 59.3, 20.9, 14.1, 12.3 ppm; MS (EI, 70 eV) m/z : 91, 128, 274, 319. HRMS (ESI) m/z : calcd for $C_{21}H_{21}NNaO_2$ $[M+H]^+$, 342.1464; found, 342.1449. IR (KBr): 2977, 2923, 2854, 1699, 1604, 1516, 1477, 1410, 1256, 1086 cm^{-1} .

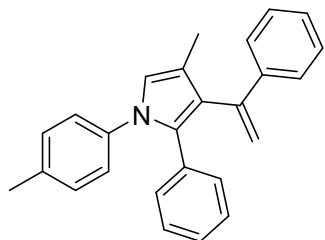
Ethyl 4-methyl-2-(naphthalen-2-yl)-1-(*p*-tolyl)-1*H*-pyrrole-3-carboxylate (5b)



Yellow solid. M.p.: 128-130°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 7.6$ Hz, 1H), 7.73 (d, $J = 7.1$ Hz, 3H), 7.47 (dd, $J = 11.7, 6.0$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 1H), 6.99 (q, $J = 8.2$ Hz, 4H), 6.76 (s, 1H), 4.14 (q, $J = 7.0$ Hz, 2H), 2.45 (s, 3H), 2.27 (s, 3H), 1.06 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 137.9, 137.0,

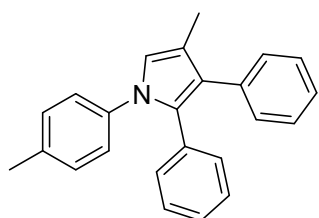
136.8, 132.7, 132.6, 130.6, 129.8, 129.5, 128.9, 128.2, 127.6, 126.7, 126.1, 125.8, 125.7, 122.1, 121.8, 114.2, 59.3, 20.9, 14.1, 12.4 ppm; MS (EI, 70 eV) m/z : 91, 178, 296, 324, 369. HRMS (ESI) m/z : calcd for $C_{25}H_{24}NO_2$ $[M+H]^+$, 370.1802; found, 370.1803. IR (KBr): 2980, 2923, 2851, 1699, 1515, 1464, 1411, 1256, 1085 cm^{-1}

4-Methyl-2-phenyl-3-(1-phenylvinyl)-1-(*p*-tolyl)-1*H*-pyrrole (9)



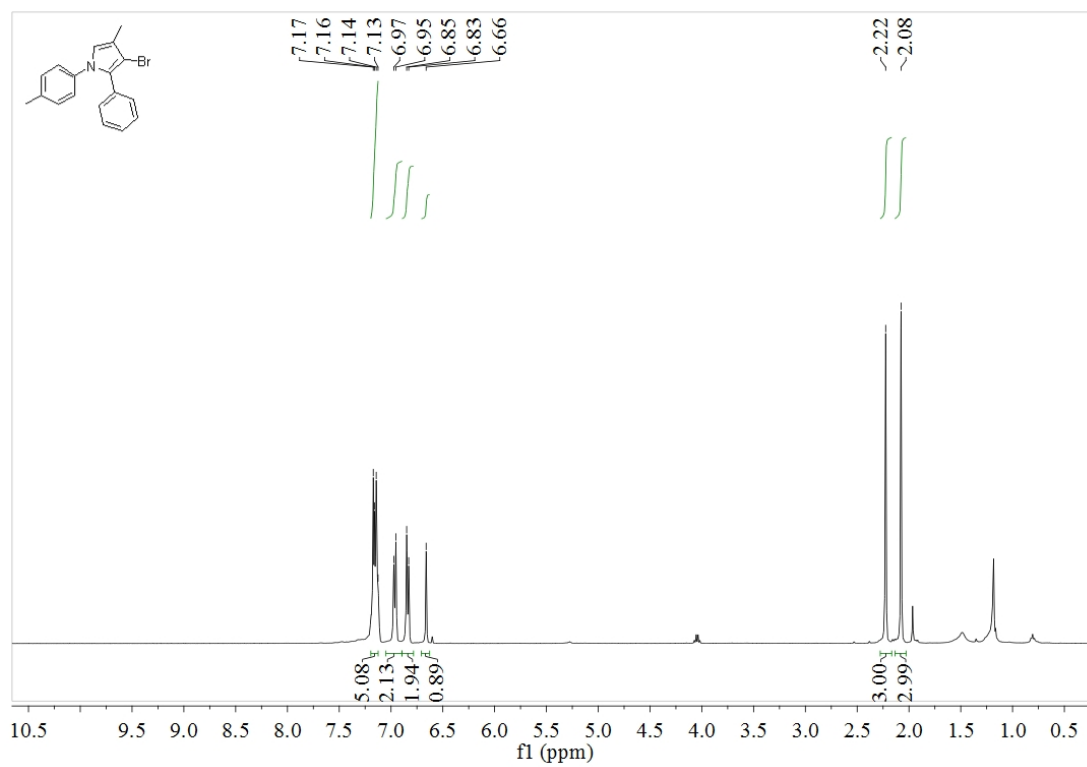
White solid. M.p.: 107-108°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, $J = 7.4$ Hz, 2H), 7.32 – 7.23 (m, 4H), 7.09 – 7.08(m, 7H), 7.02 (d, $J = 7.9$ Hz, 2H), 6.78 (s, 1H), 5.66 (s, 1H), 5.07 (s, 1H), 2.35 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.9, 141.8, 138.1, 135.7, 132.6, 131.4, 130.3, 129.4, 128.1, 127.6, 127.2, 126.8, 126.2, 125.4, 124.6, 121.0, 119.3, 116.6, 20.9, 10.8 ppm; MS (EI, 70 eV) m/z : 91, 215, 272, 334, 348. HRMS (ESI) m/z : calcd for $C_{26}H_{24}N$ $[M+H]^+$, 350.1903; found, 350.1899. IR (KBr): 3057, 2923, 2853, 1695, 1572, 1515, 1400, 698 cm^{-1} .

4-Methyl-2,3-diphenyl-1-(*p*-tolyl)-1*H*-pyrrole (10)

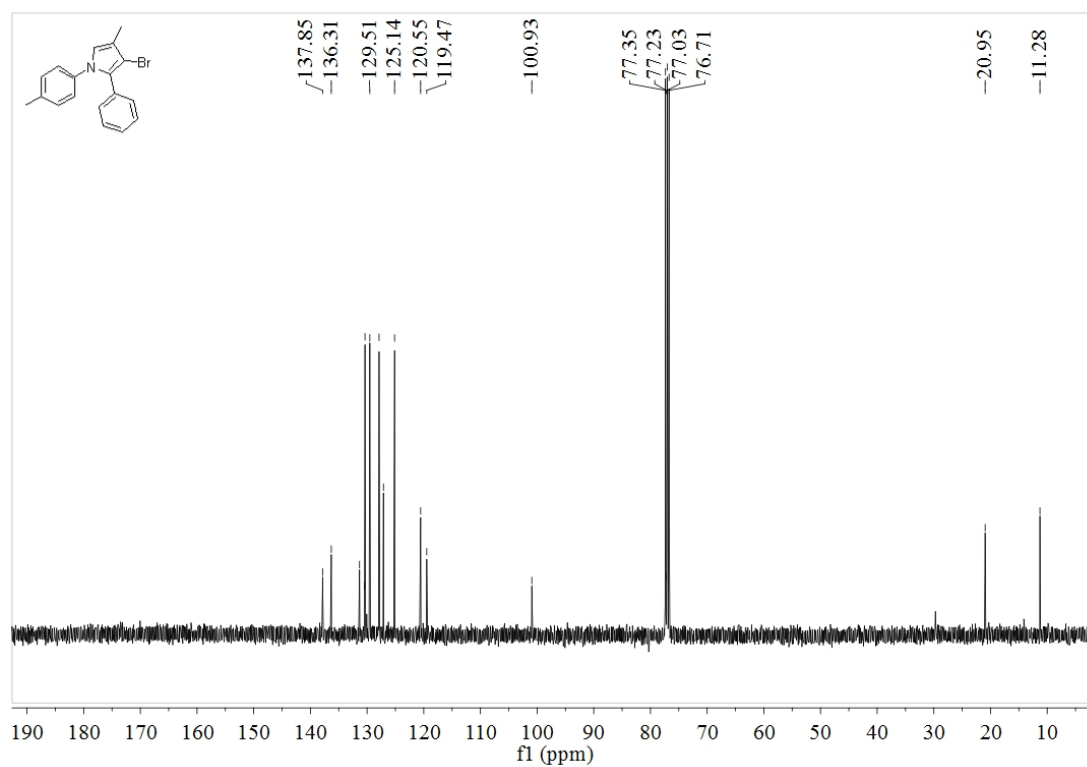


White solid. M.p.: 145-146°C. 1H NMR (400 MHz, $CDCl_3$) δ 7.25– 7.22 (m, 2H), 7.16– 7.14 (m, 3H), 7.08– 7.03(m, , 5H), 6.97– 76.93 (m, 4H), 6.80 (s, 1H), 2.31 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.9, 136.1, 135.8, 132.4, 130.8, 130.45, 130.4, 129.4, 127.8, 127.7, 126.3, 125.6, 125.5, 124.6, 121.5, 118.5, 20.9, 11.0 ppm; MS (EI, 70 eV) m/z : 91, 145, 191, 205, 323. HRMS (ESI) m/z : calcd for $C_{24}H_{22}N$ $[M+H]^+$, 324.1747; found, 324.1743. IR (KBr): 3058, 2922, 2853, 1601, 1516, 1369, 698 cm^{-1} .

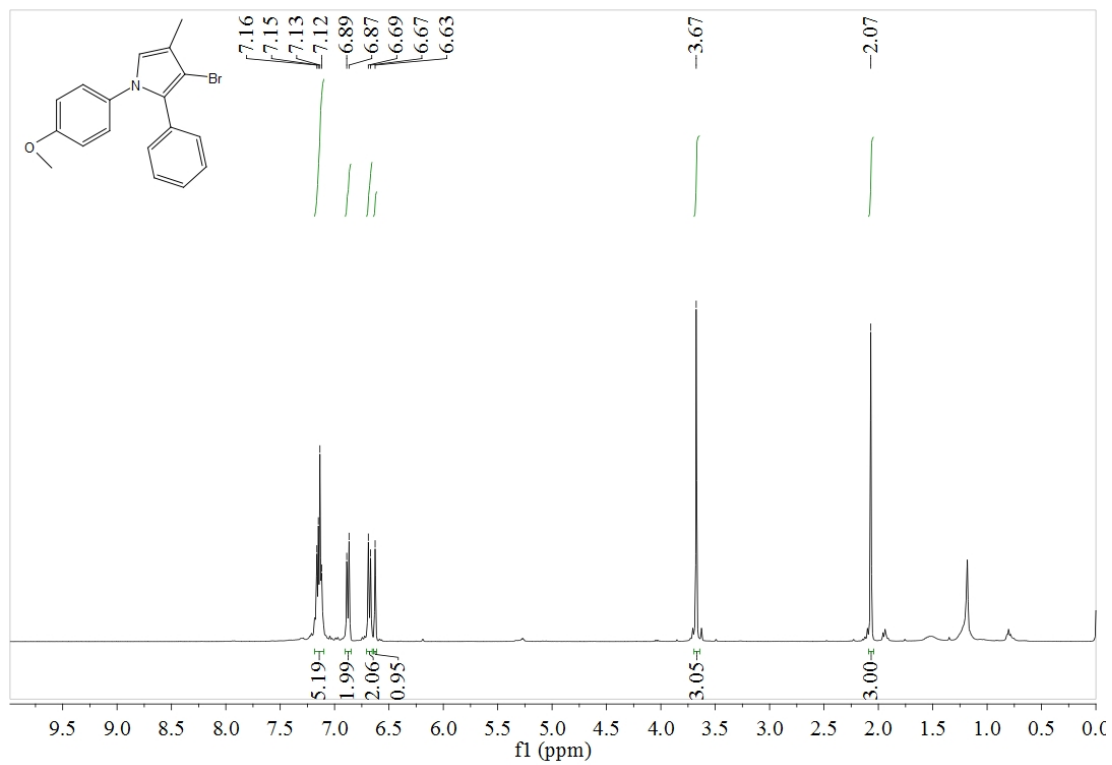
E. NMR Spectra



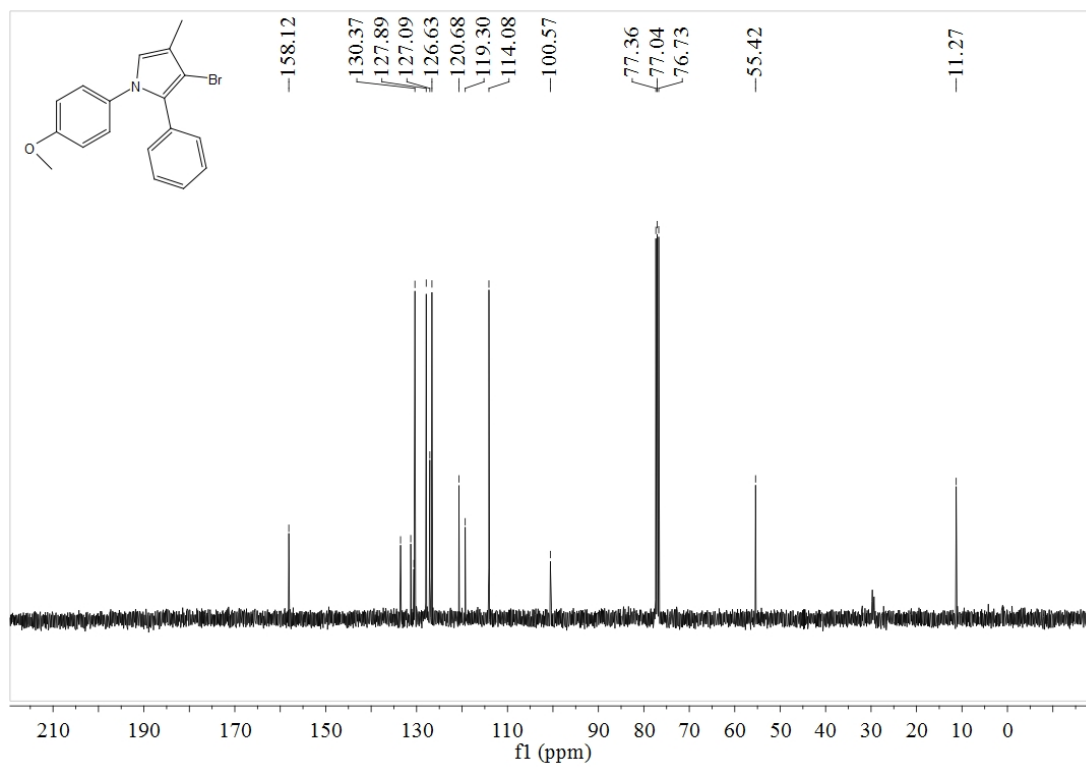
3aa-¹H



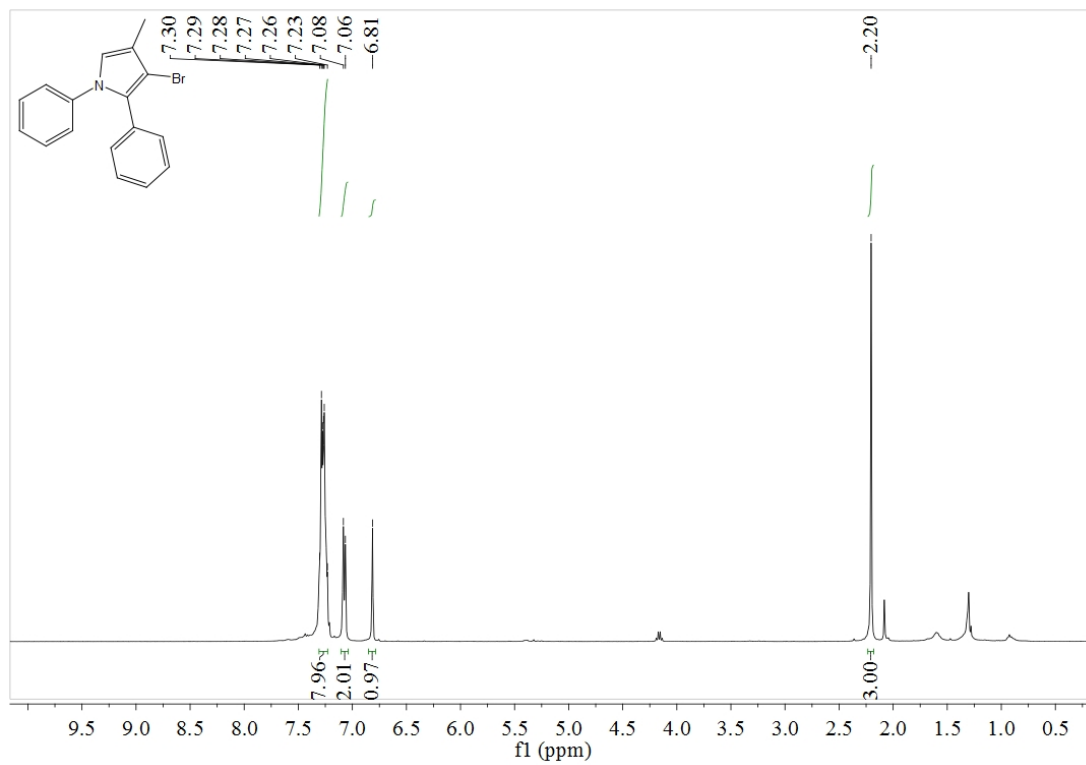
3aa-¹³C



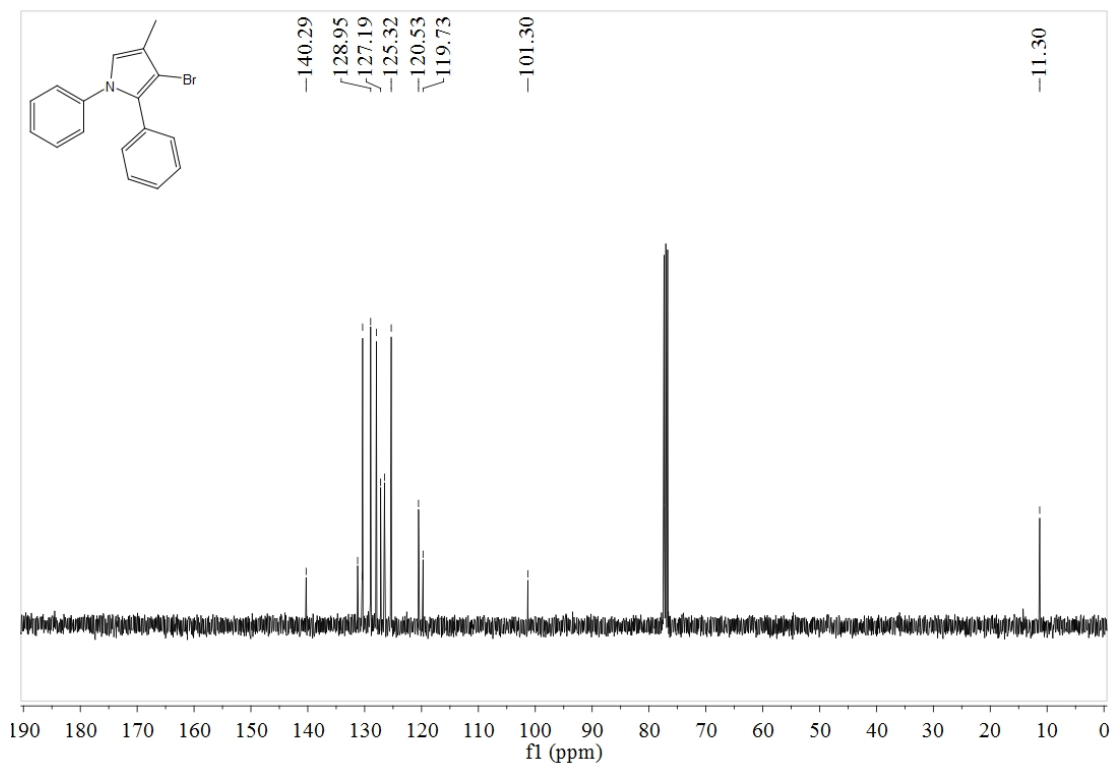
3ab-¹H



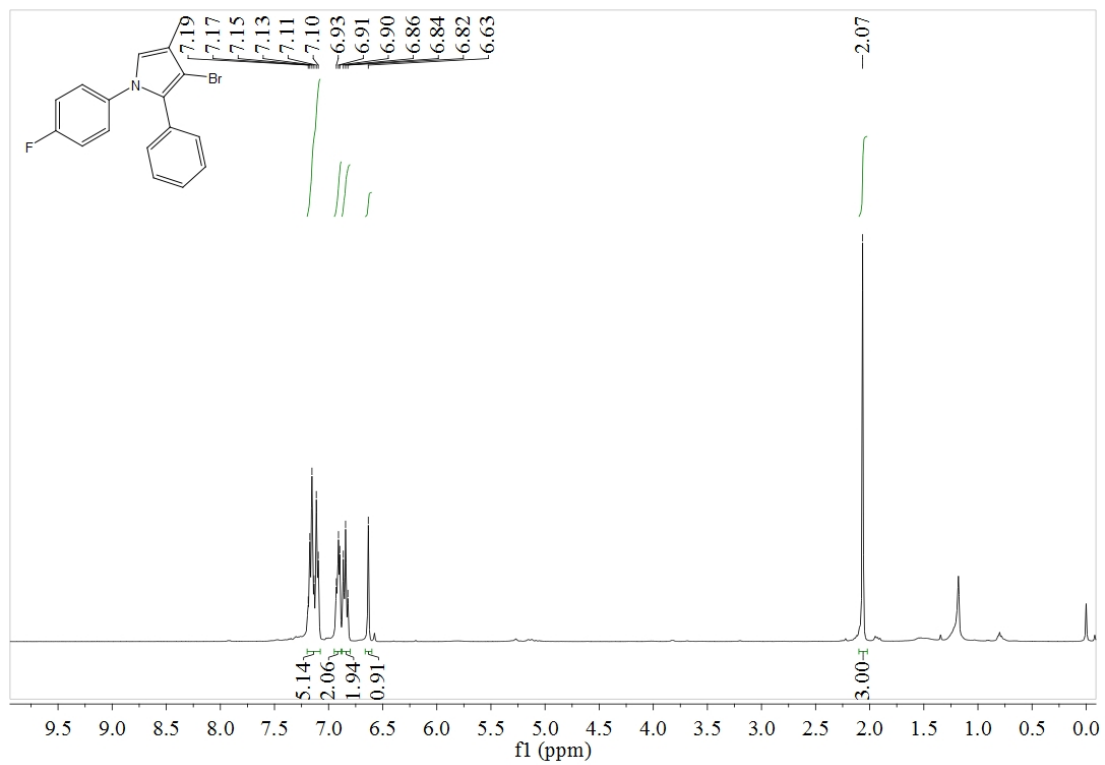
3ab-¹³C



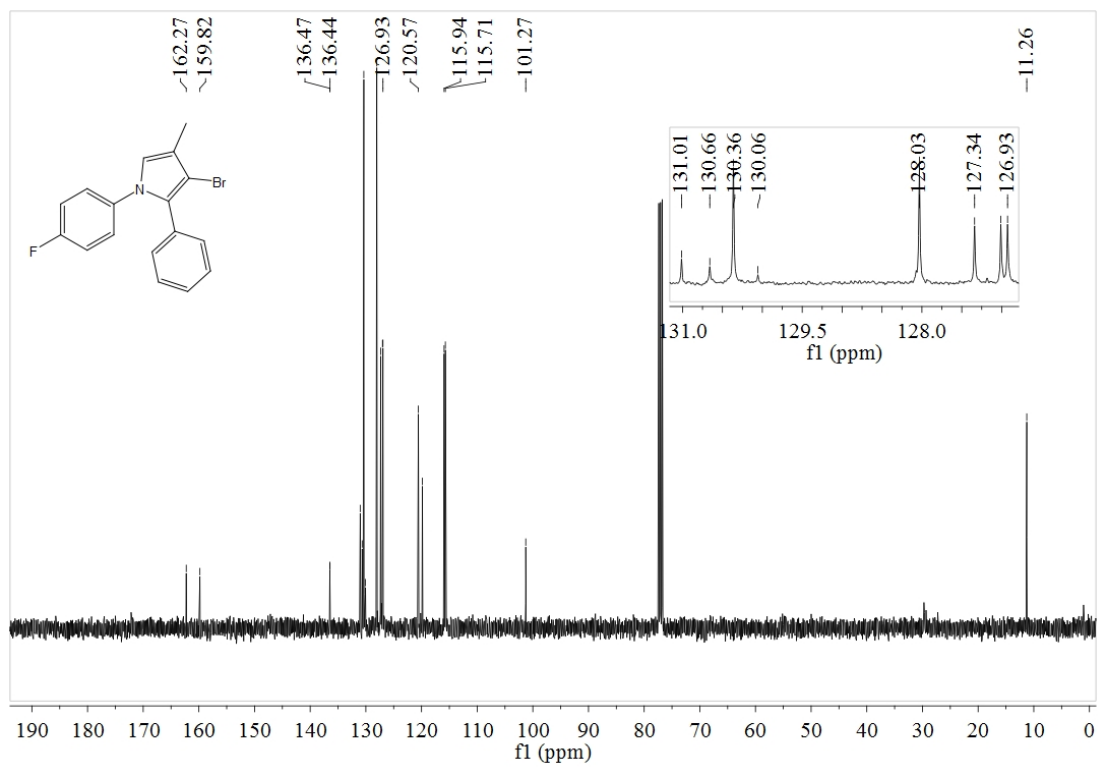
3ac-¹H



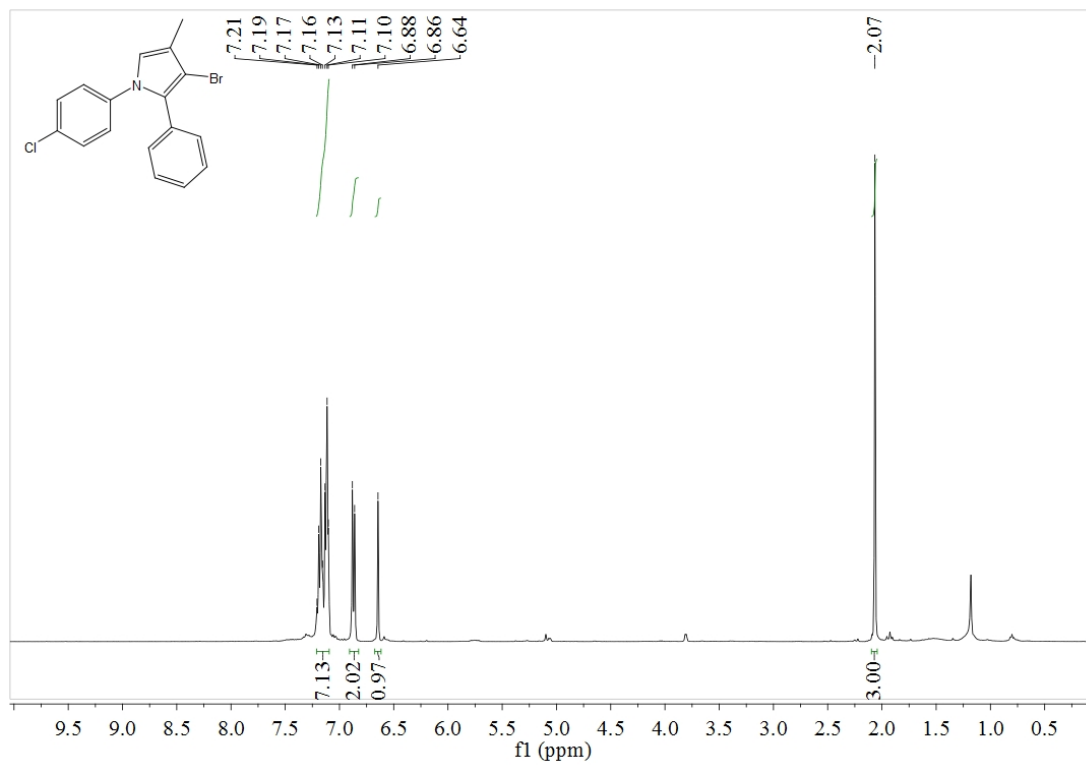
3ac-¹³C



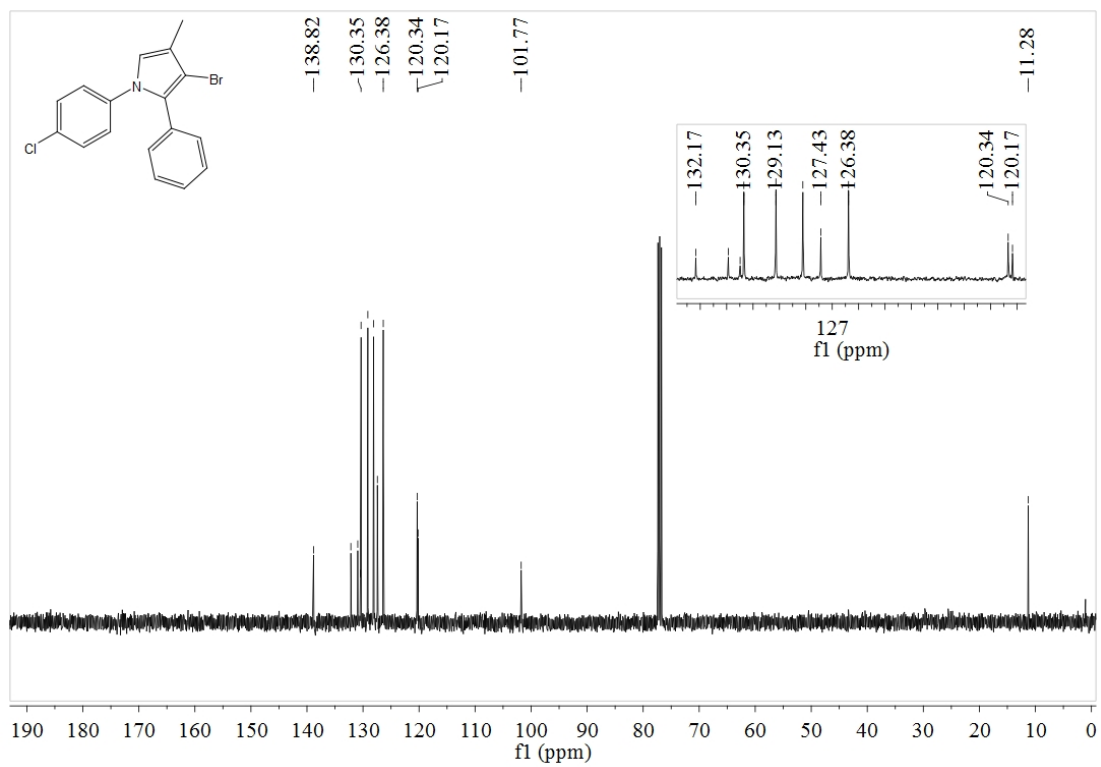
3ad-¹H



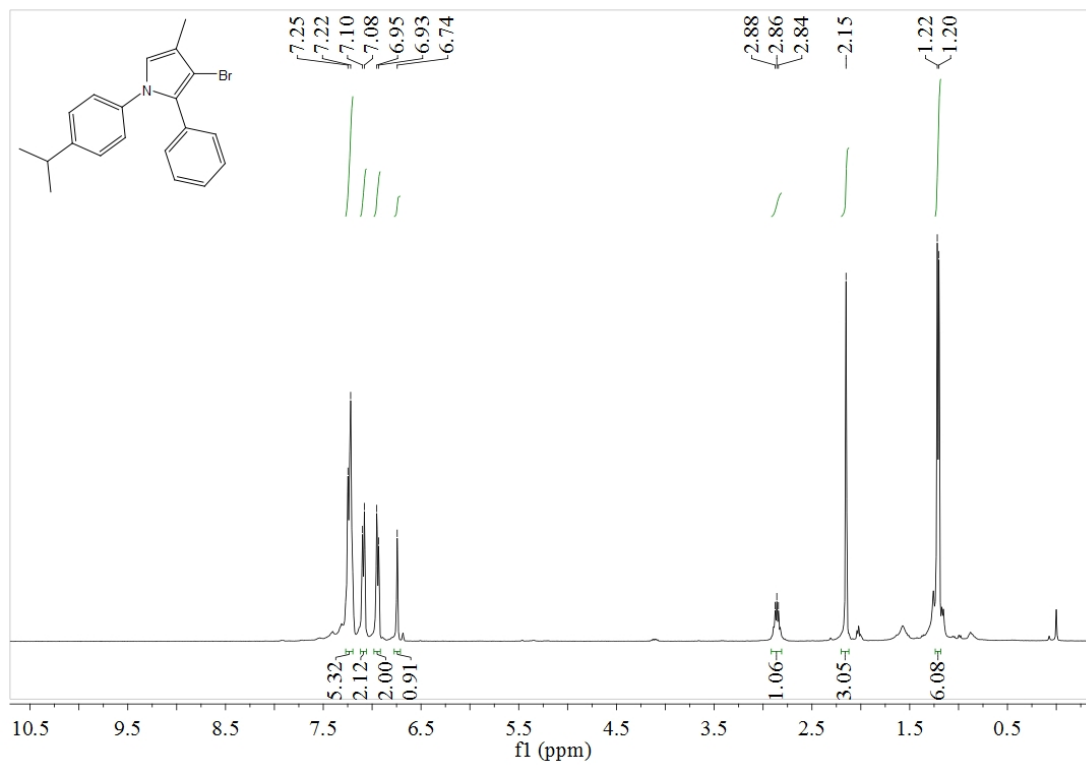
3ad-¹³C



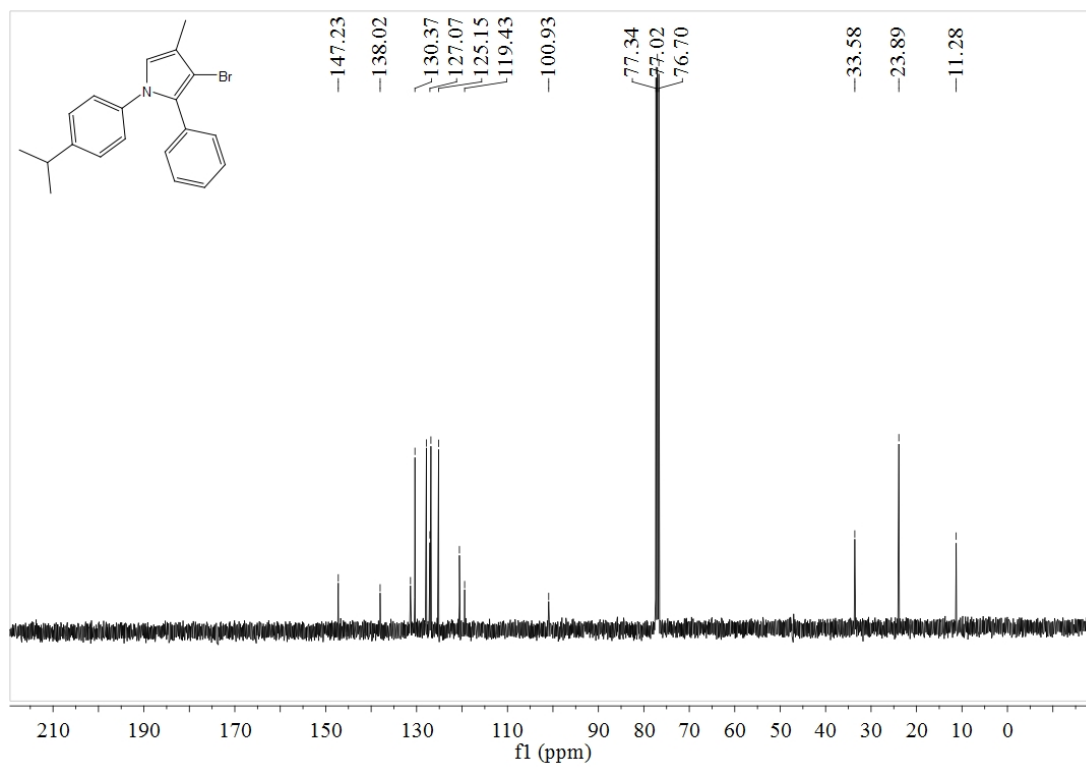
3ae- ^1H



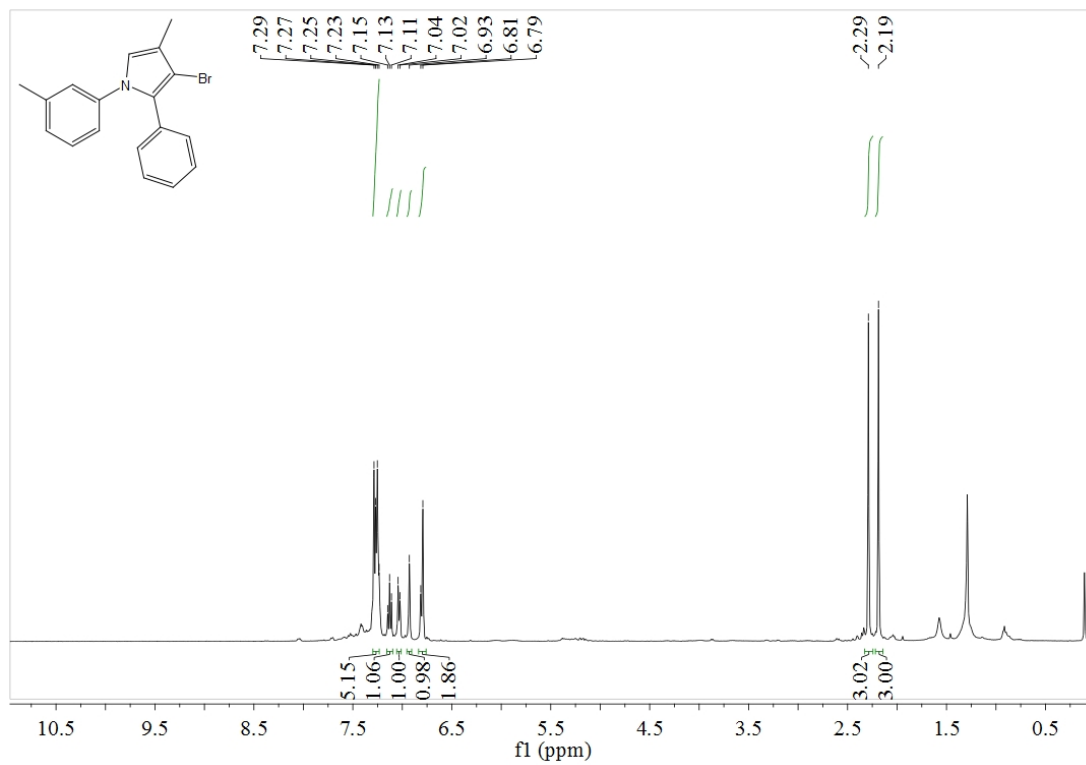
3ae- ^{13}C



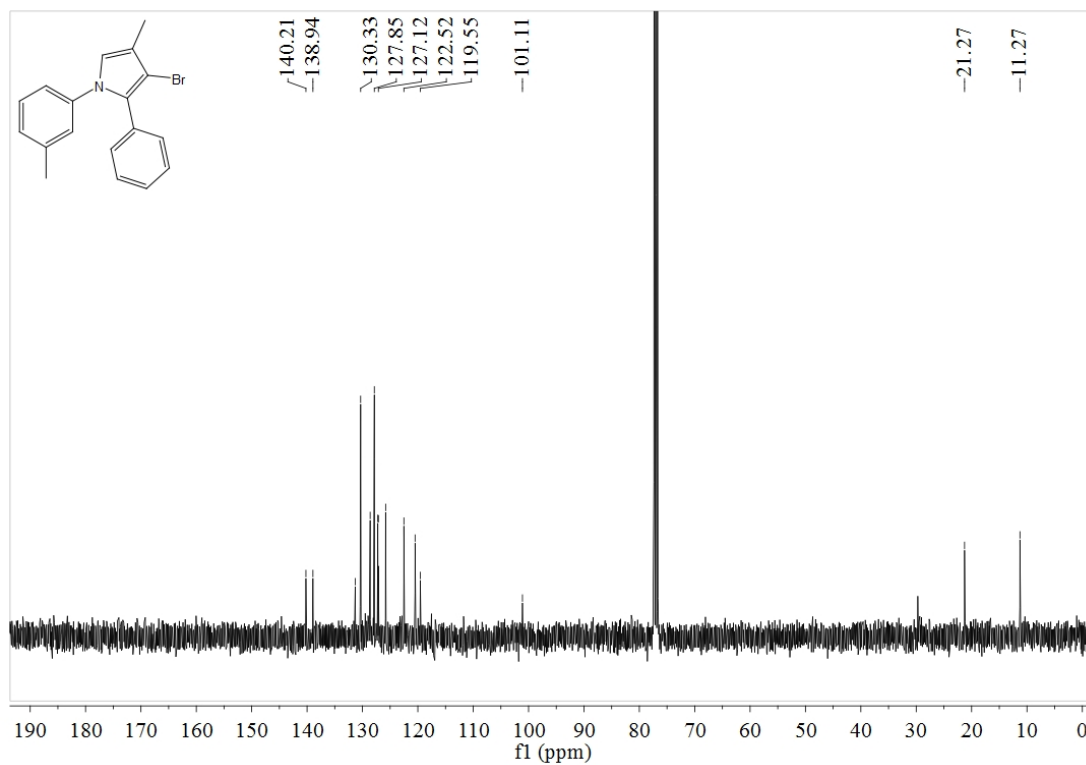
3af-¹H



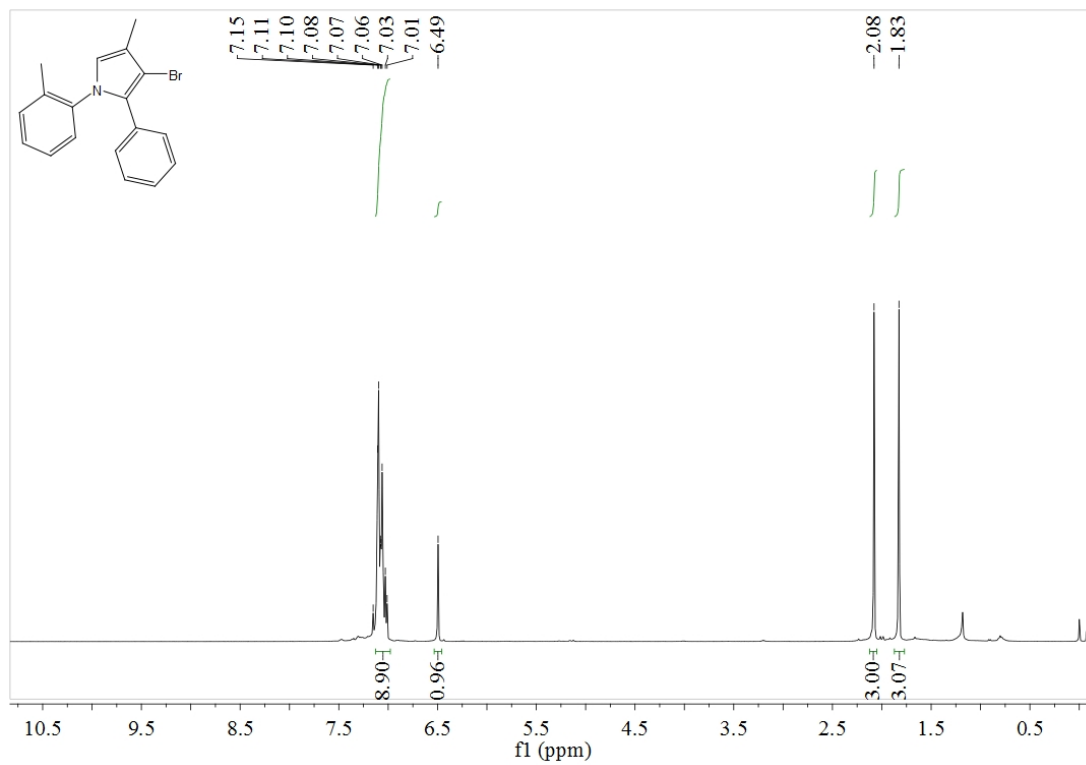
3af-¹³C



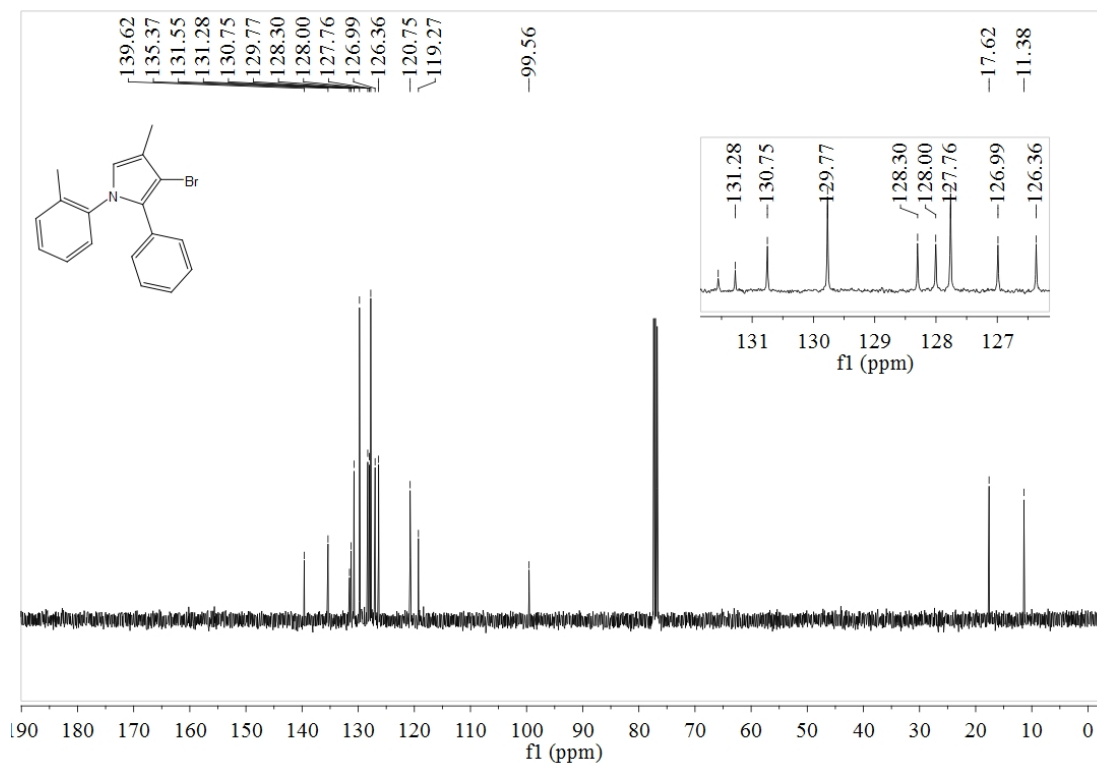
3ag-¹H



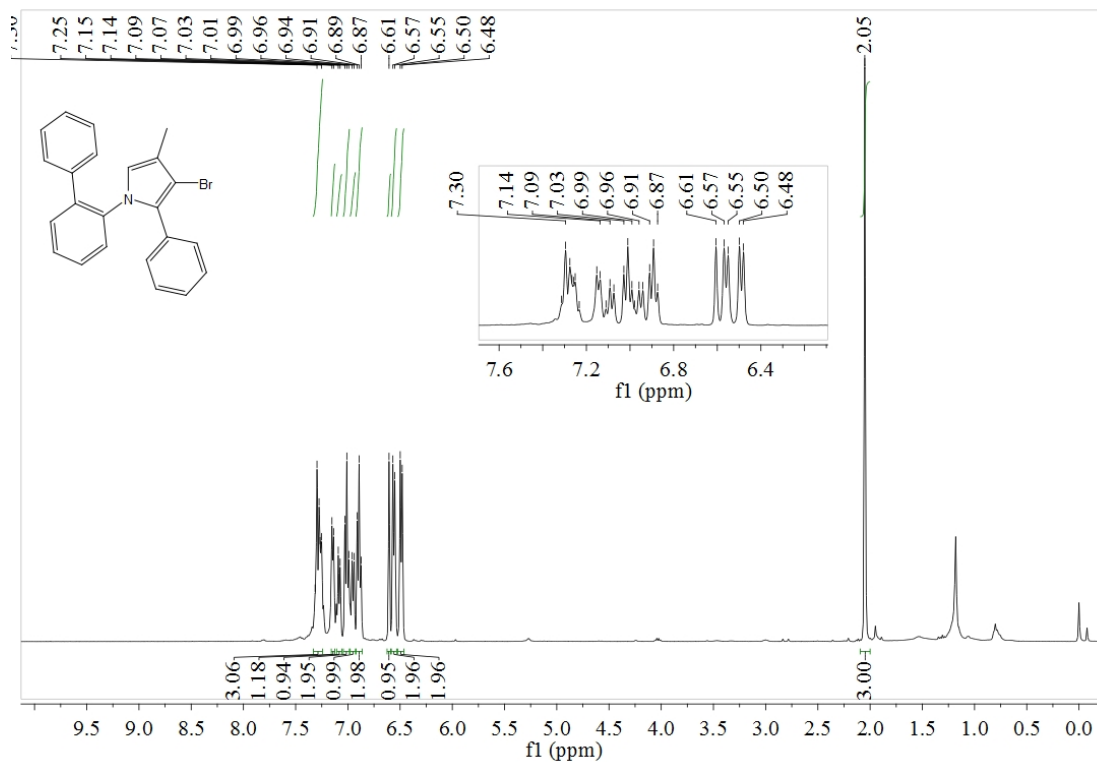
3ag-¹³C



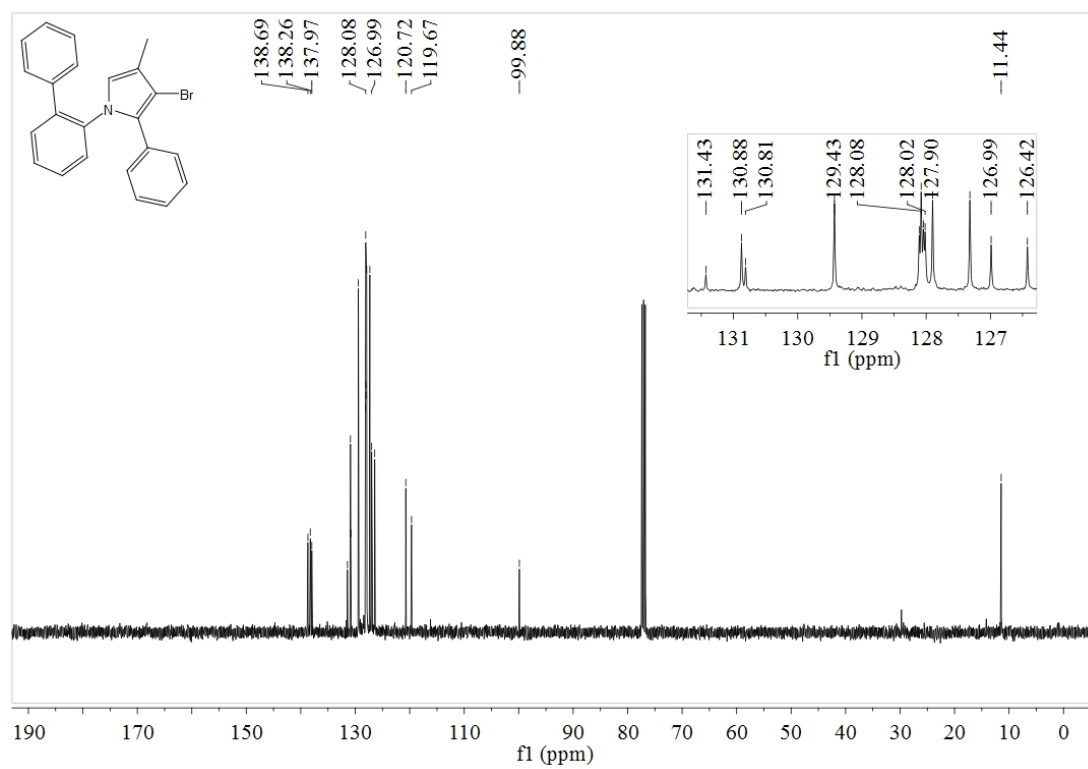
3ah-¹H



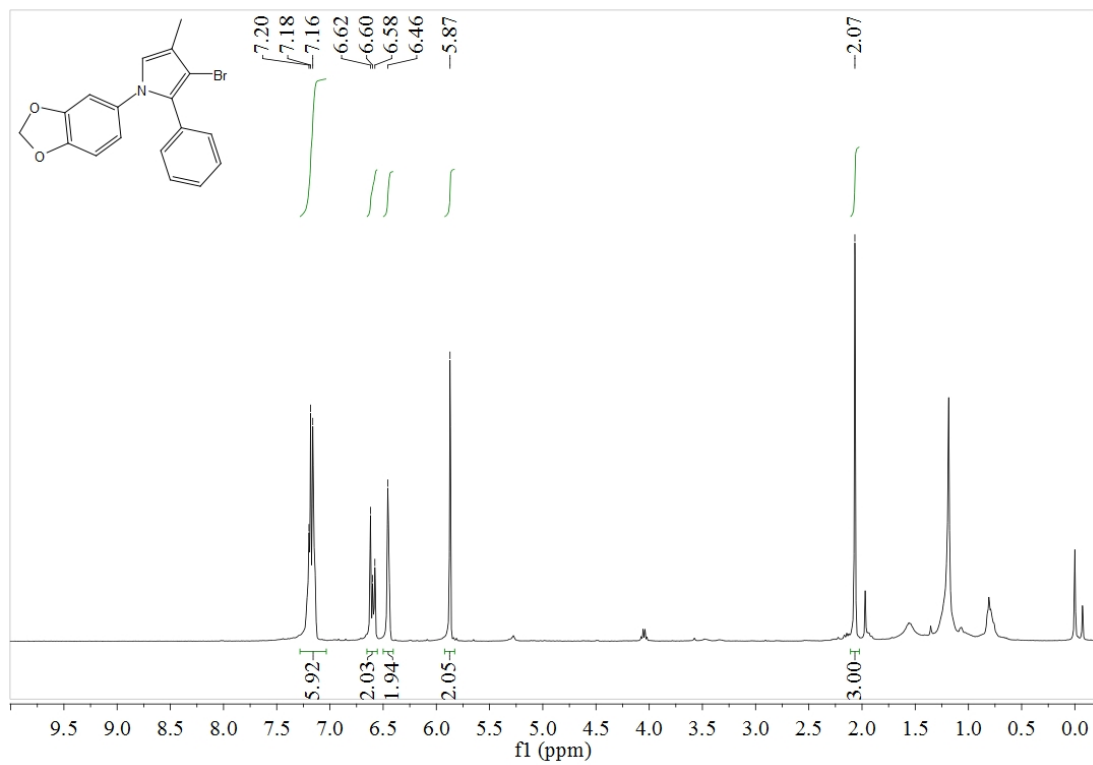
3ah-¹³C



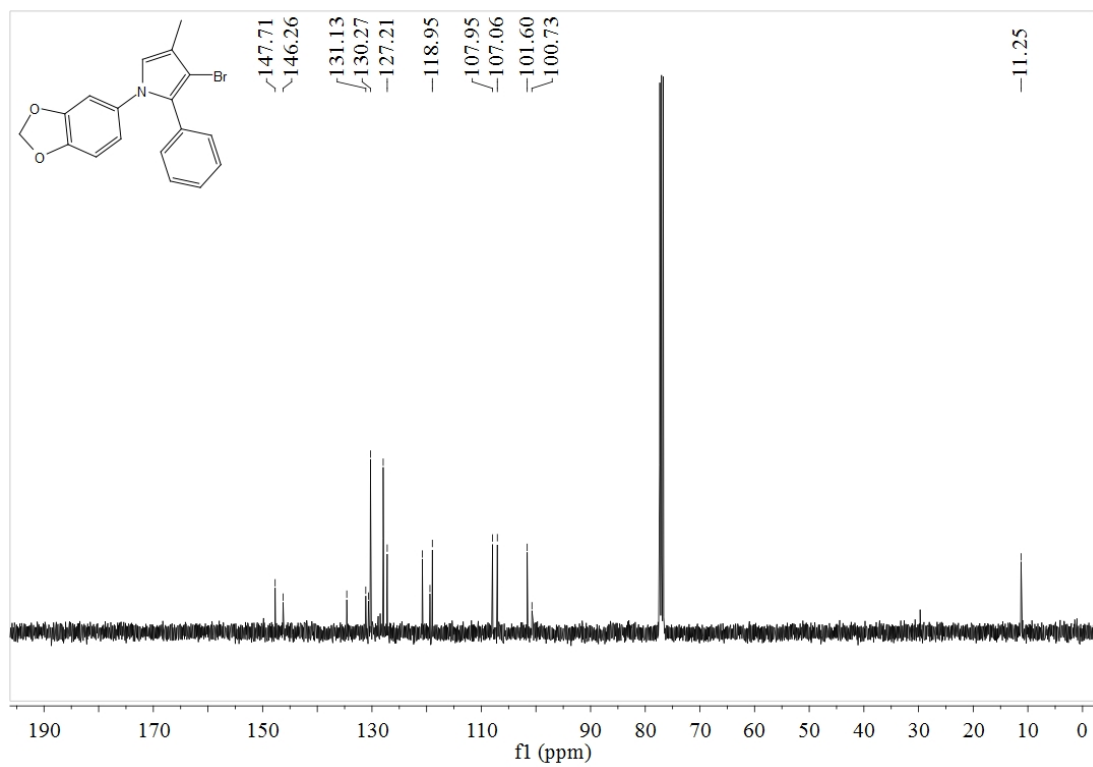
3ai-¹H



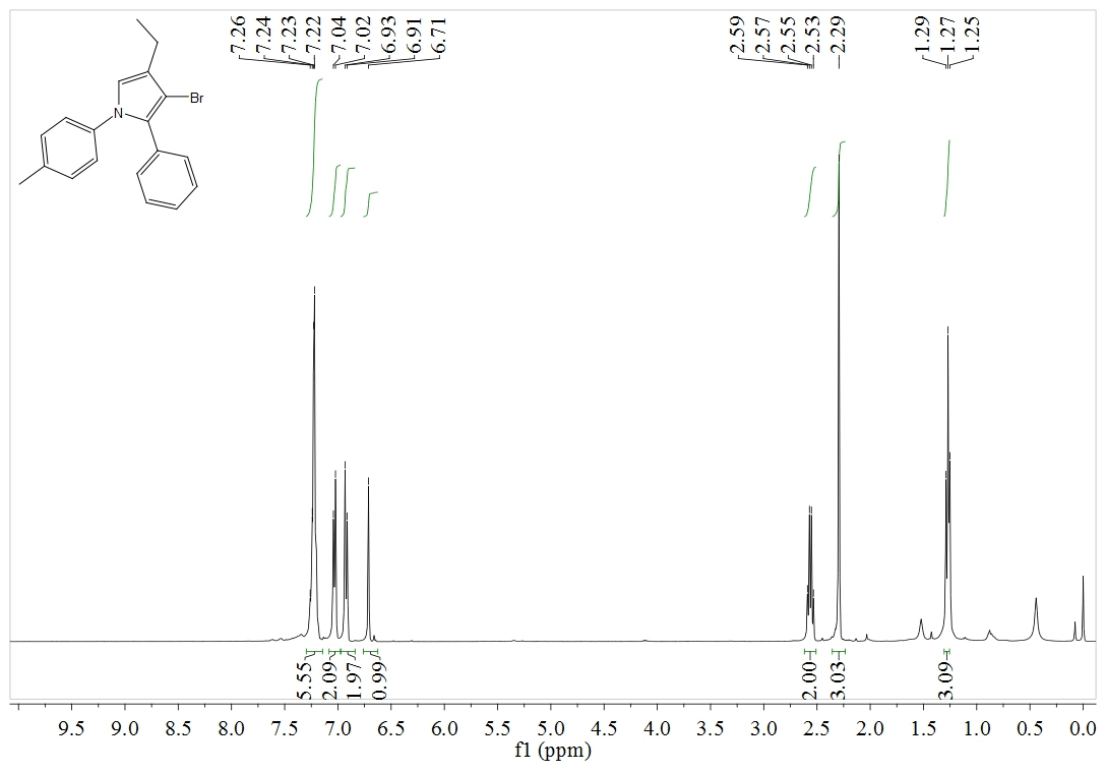
3ai-¹³C



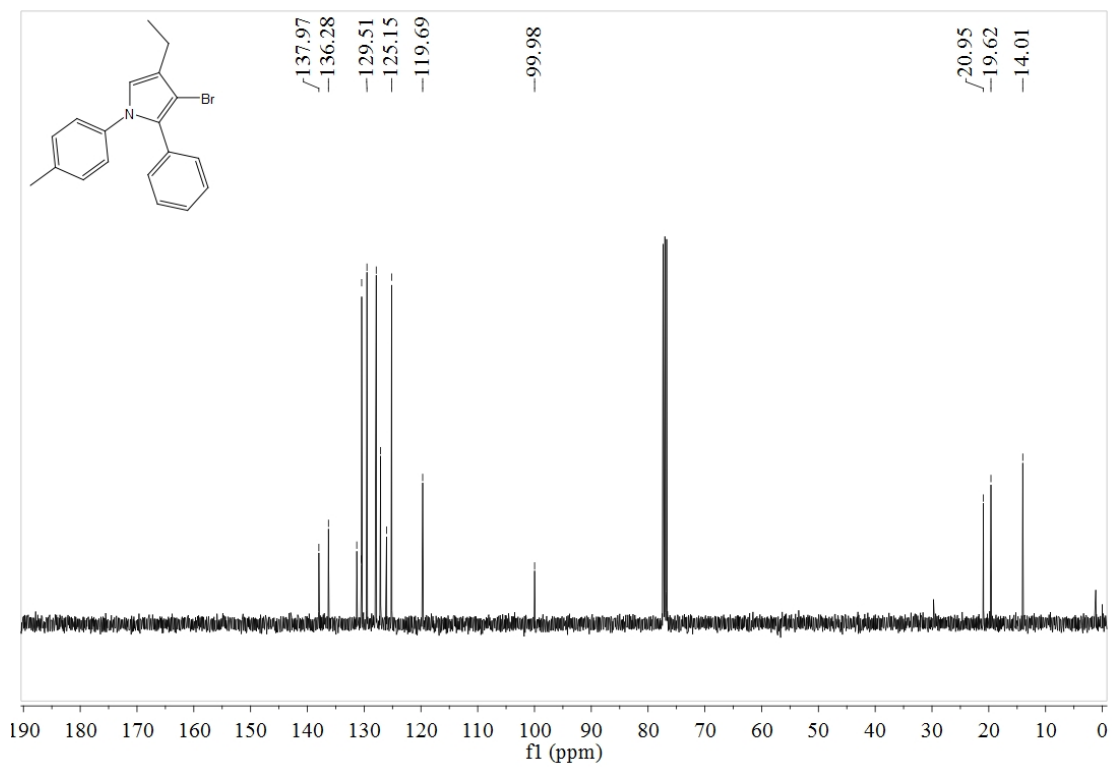
3aj-¹H



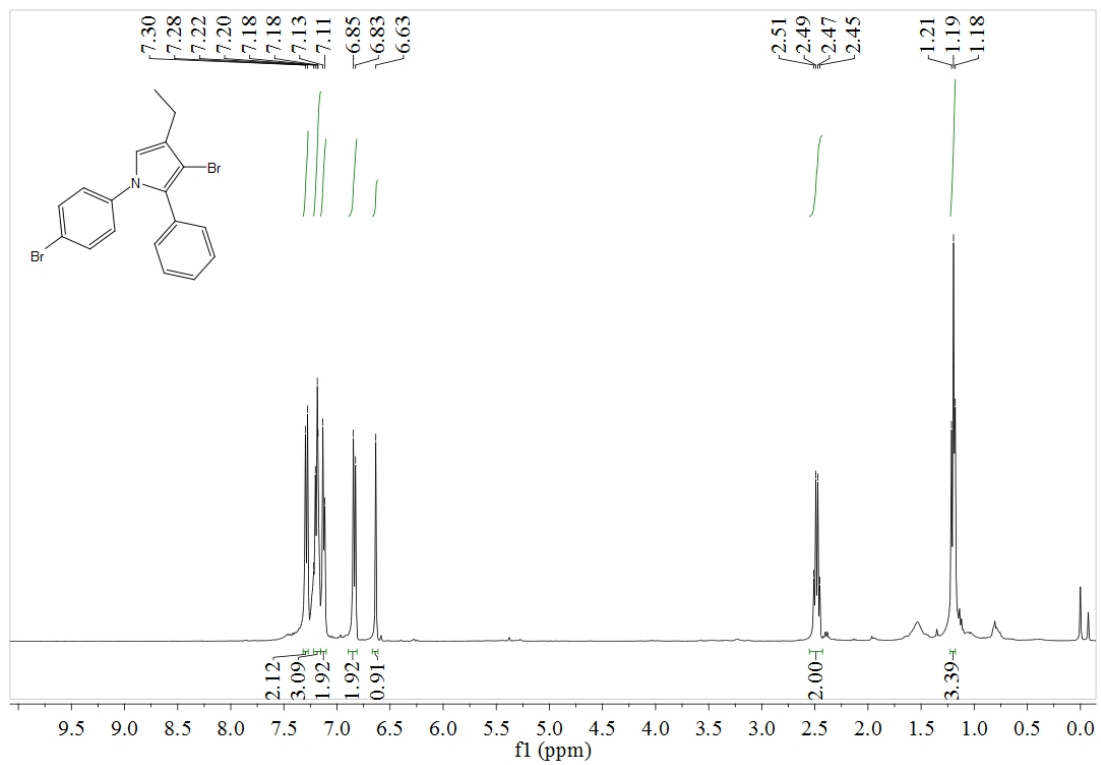
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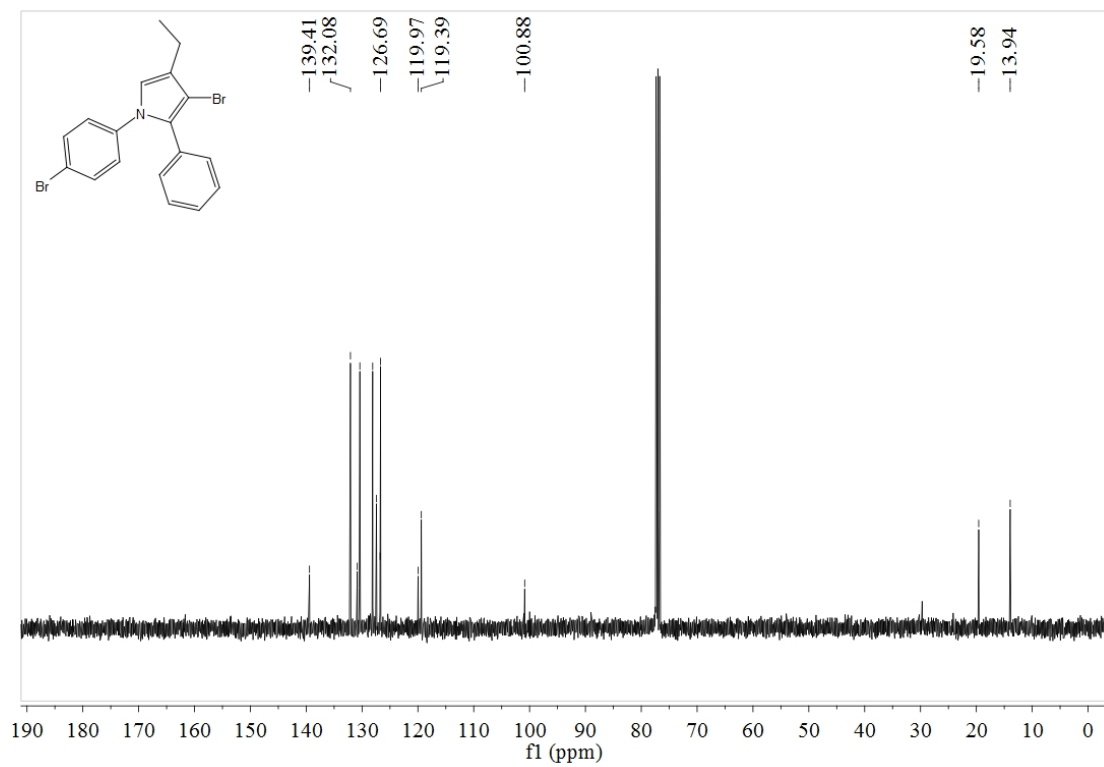
3ak-¹H



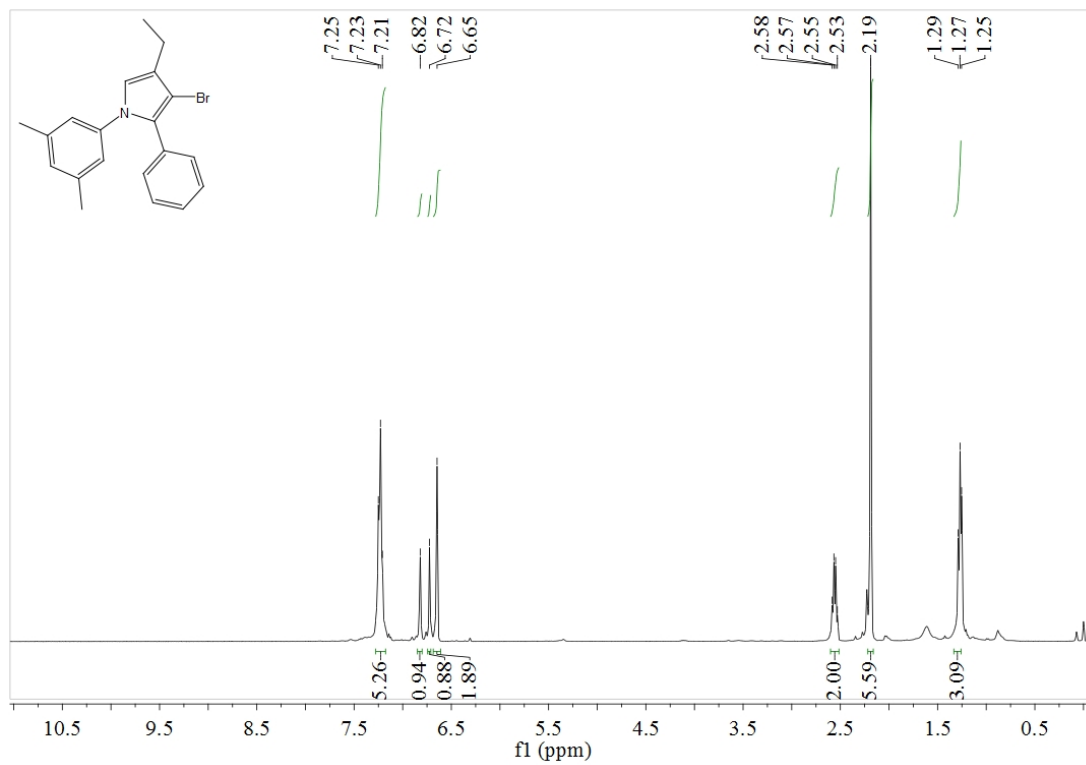
3ak-¹³C



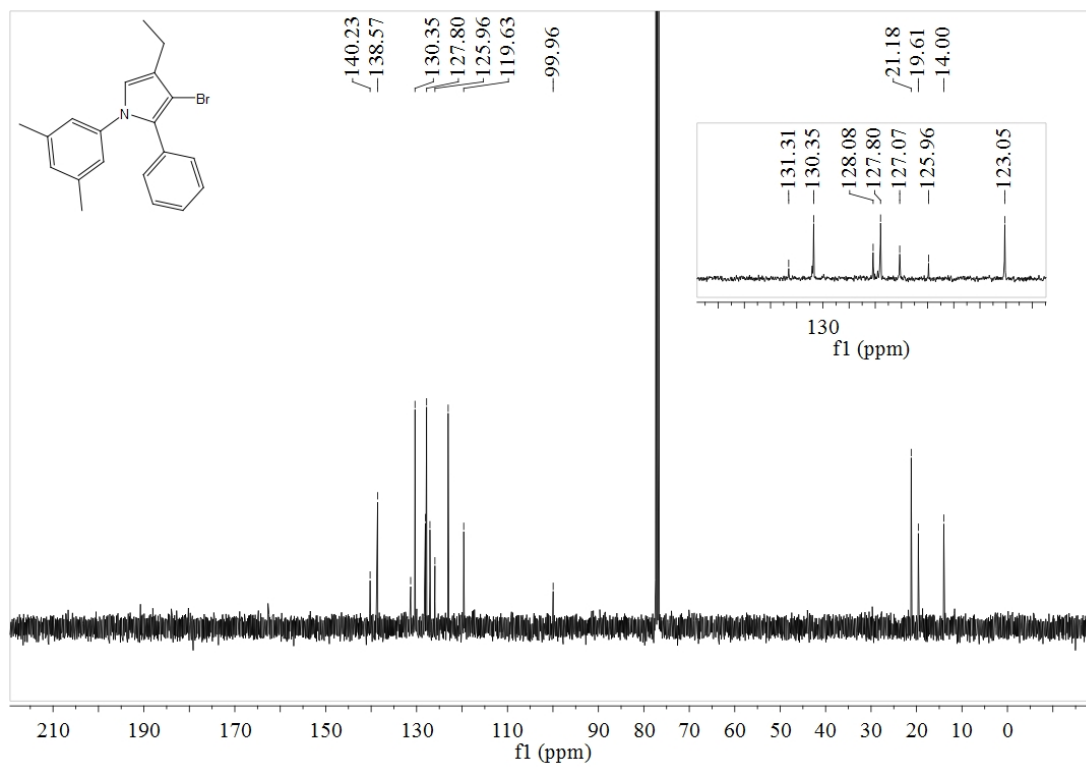
3a-¹H



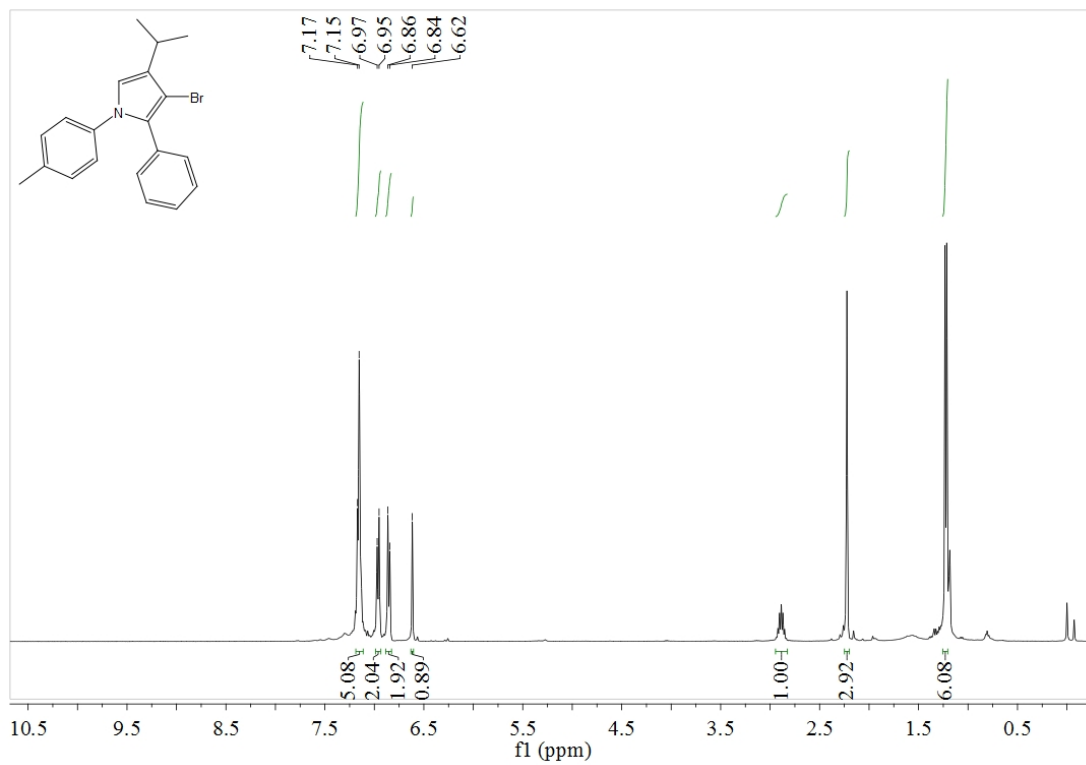
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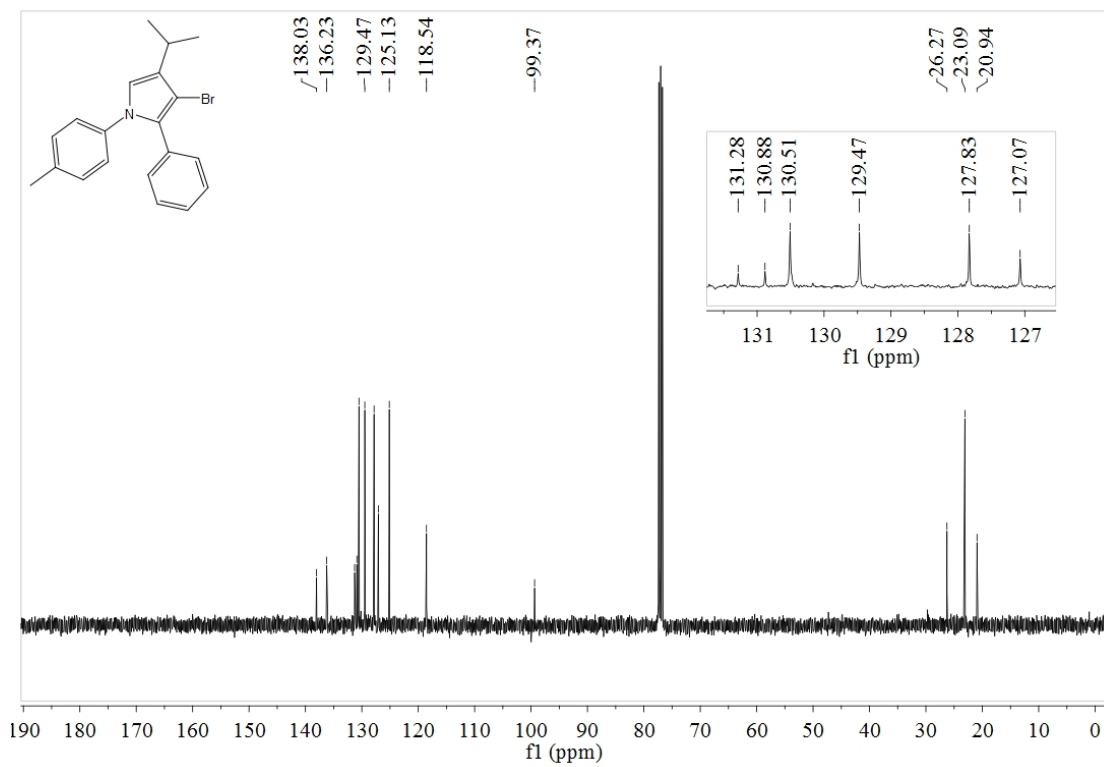
3am-¹H



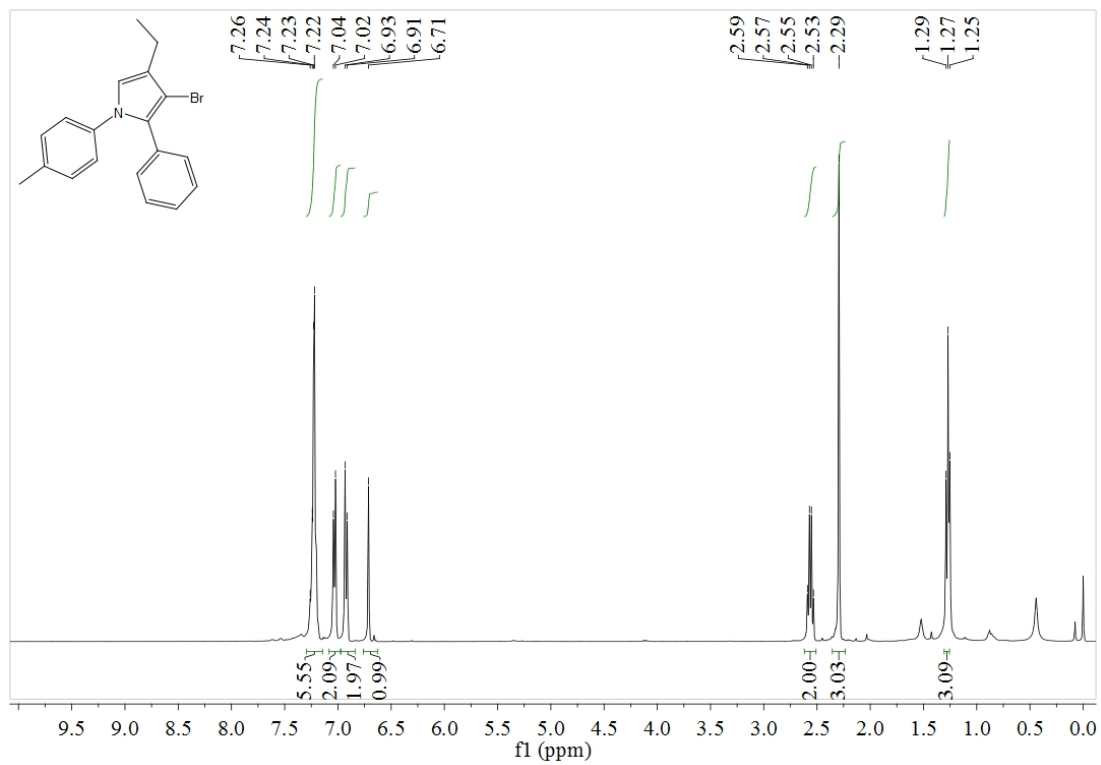
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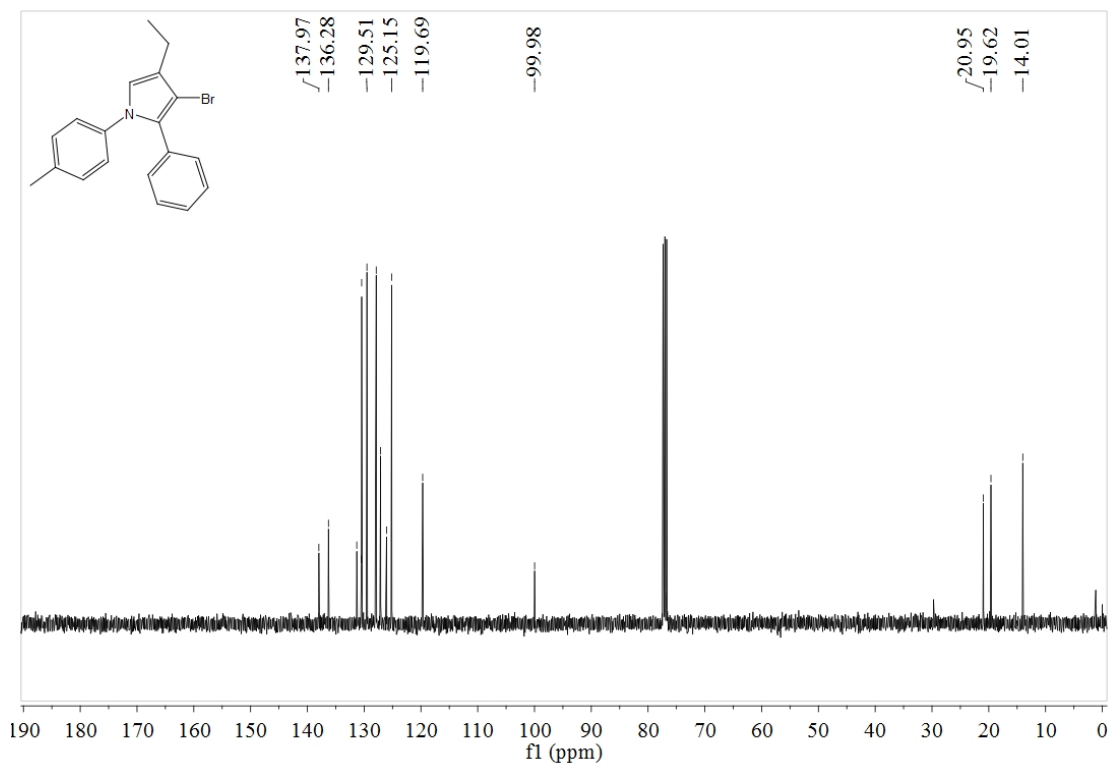
3an-¹H



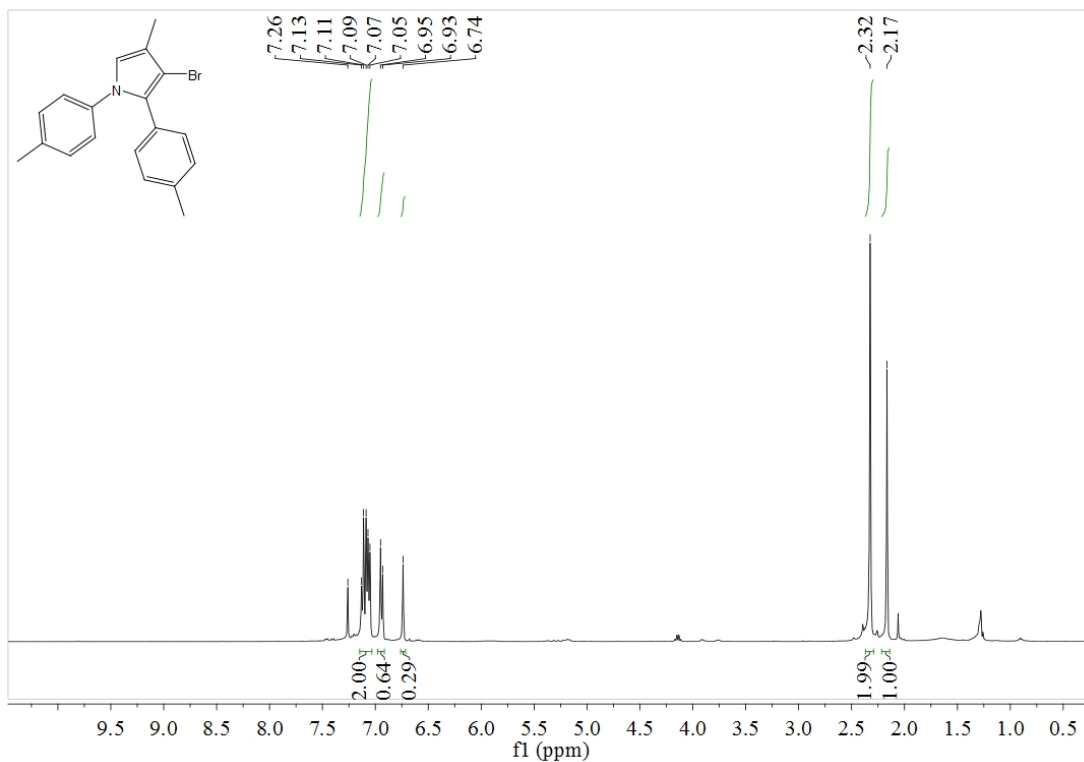
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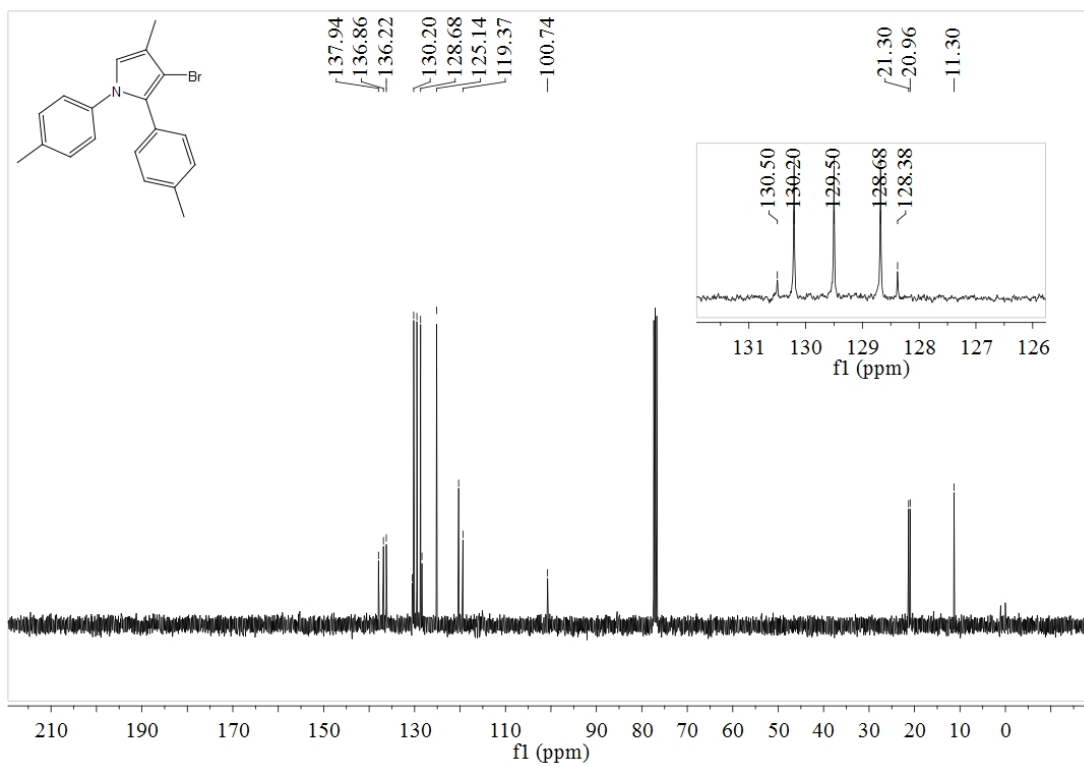
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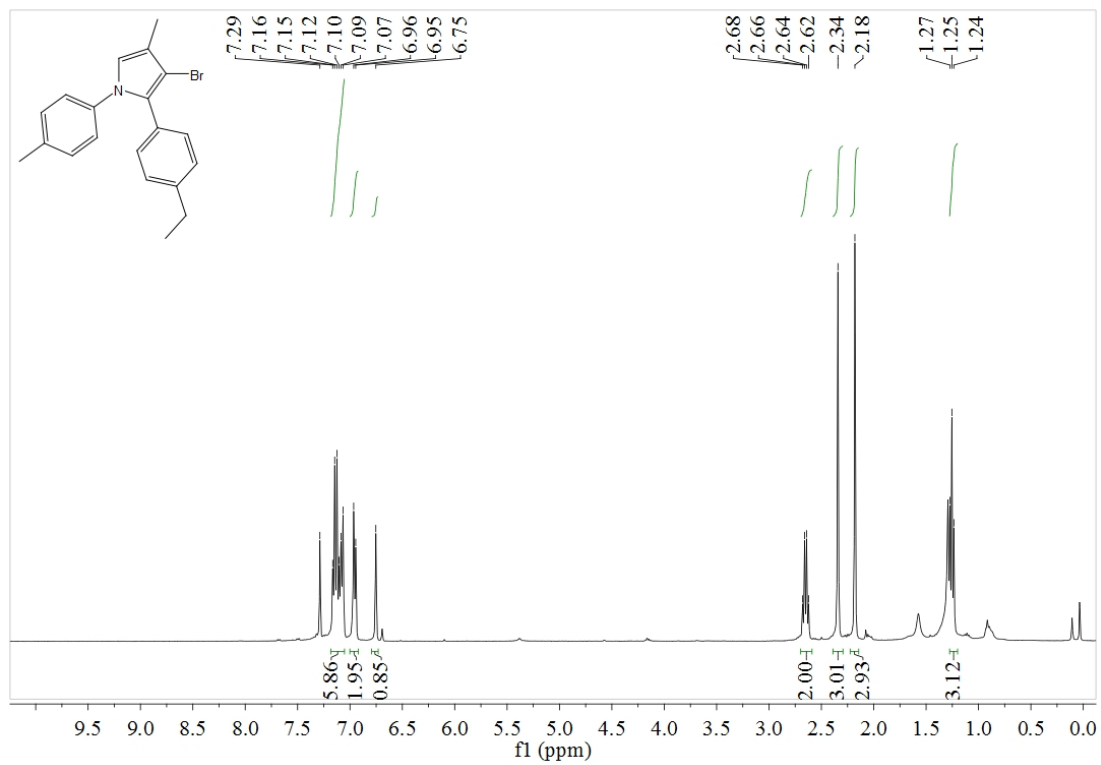
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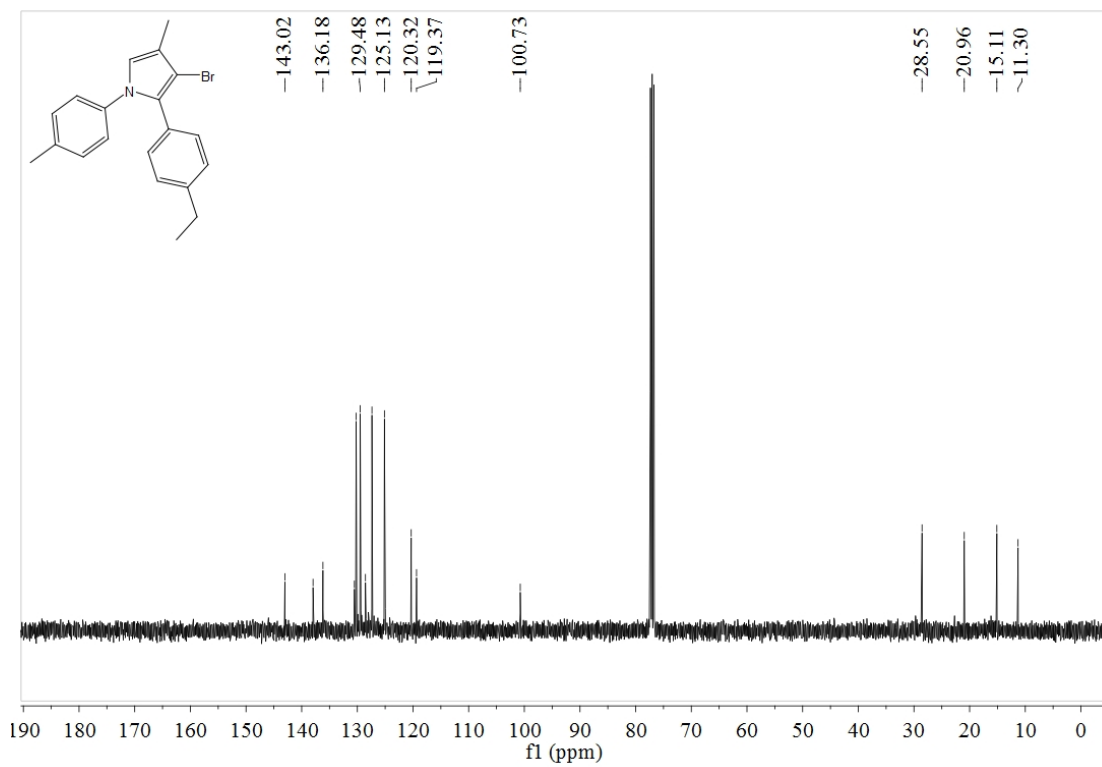
3ba-¹H



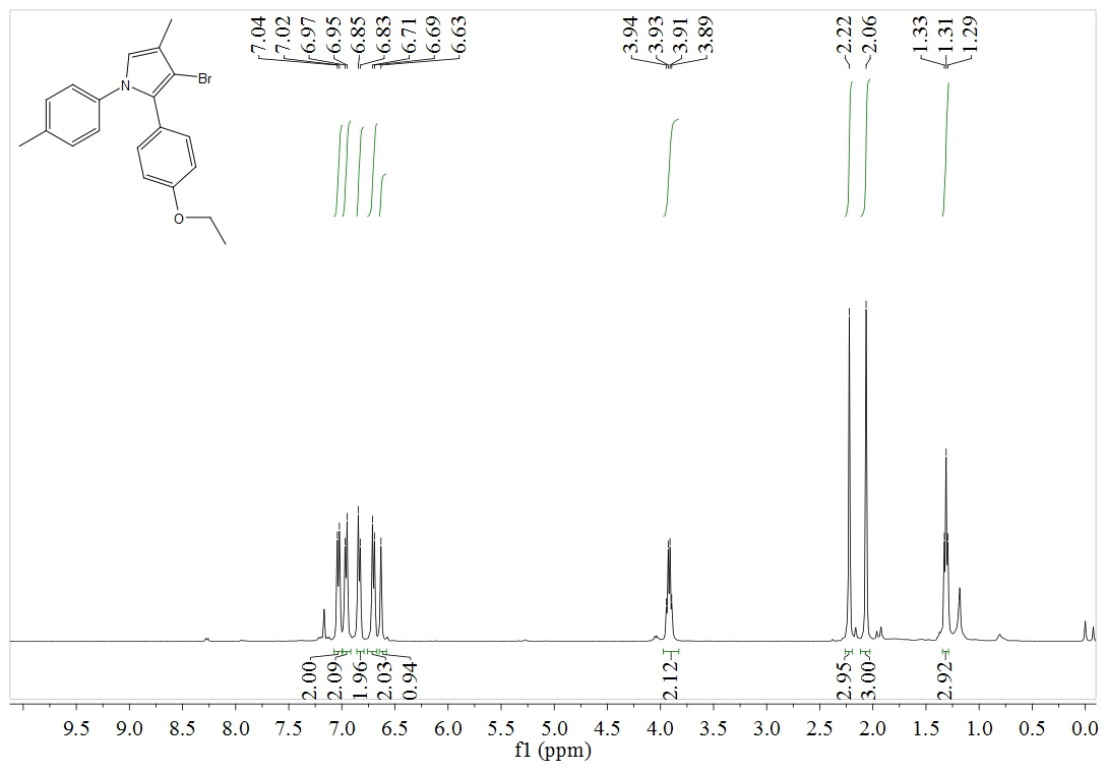
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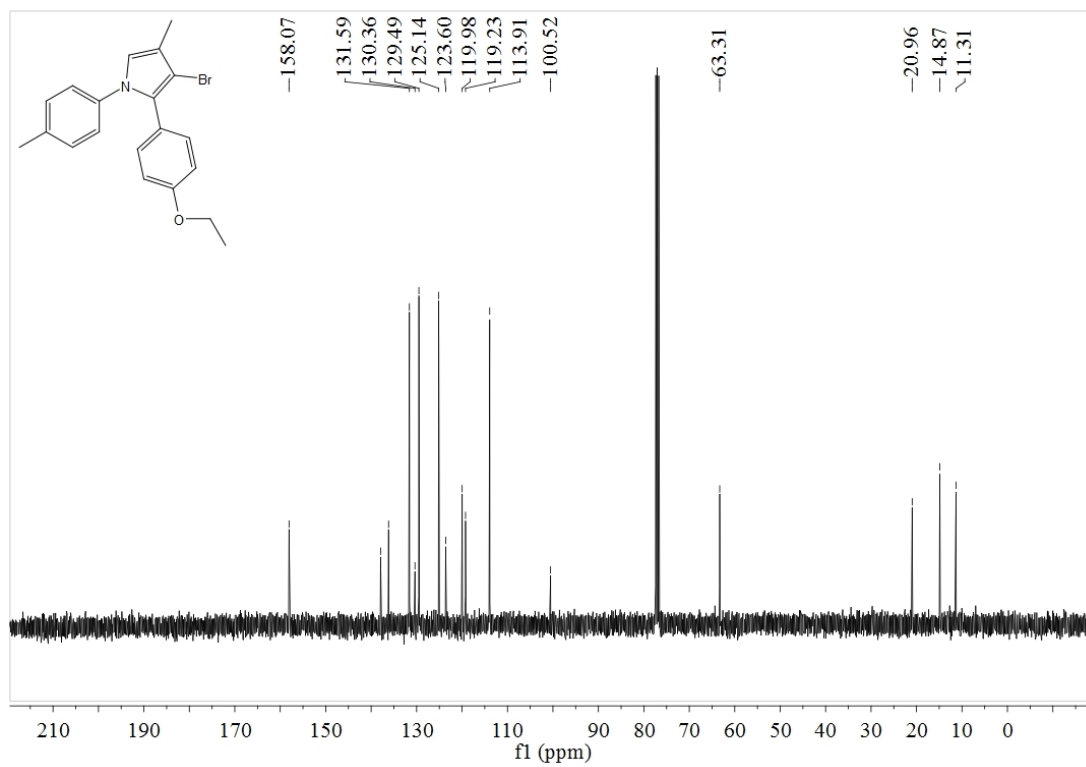
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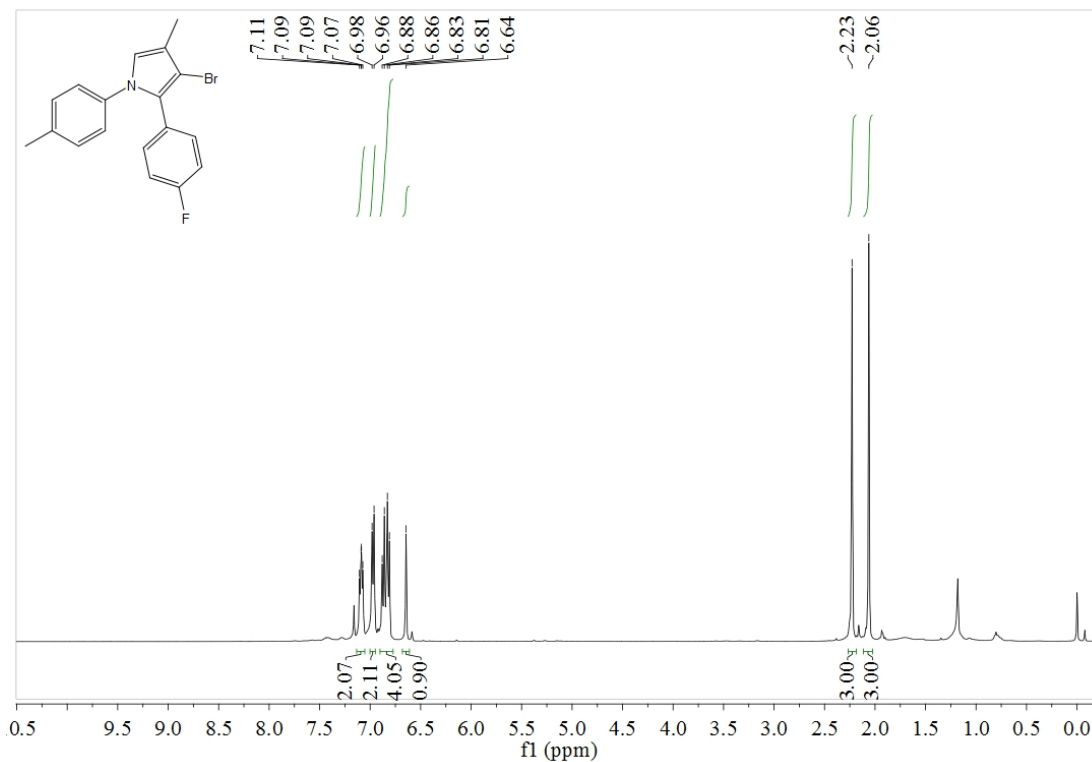
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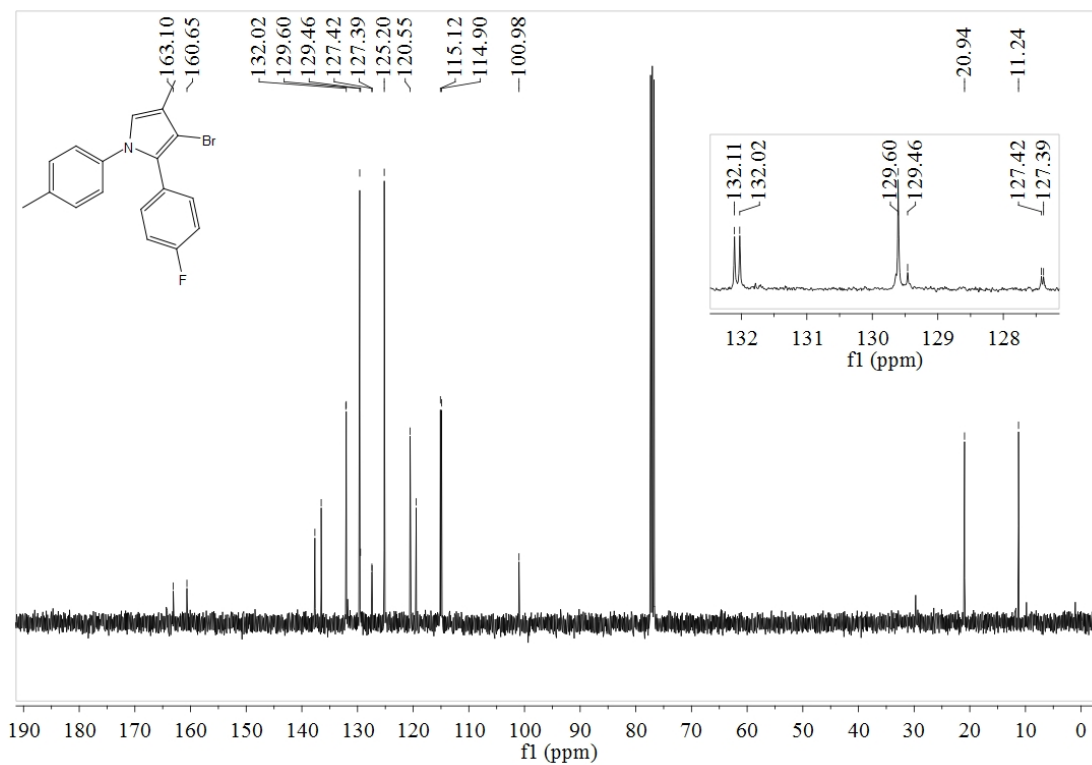
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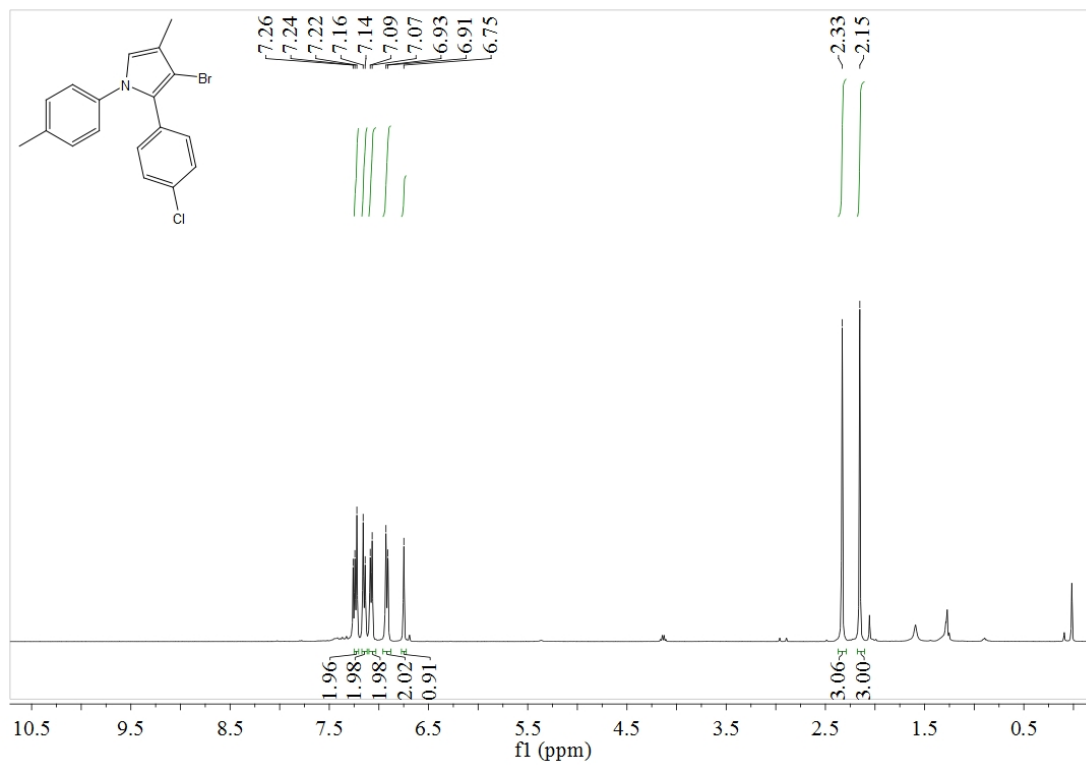
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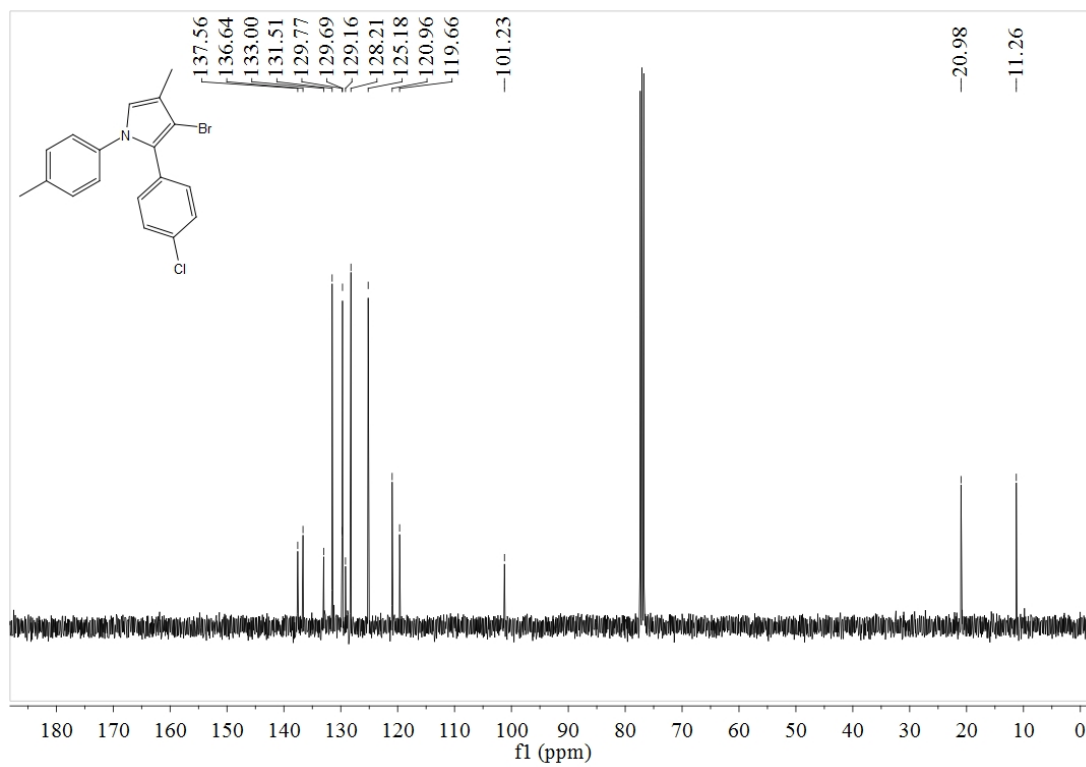
3ea-¹H



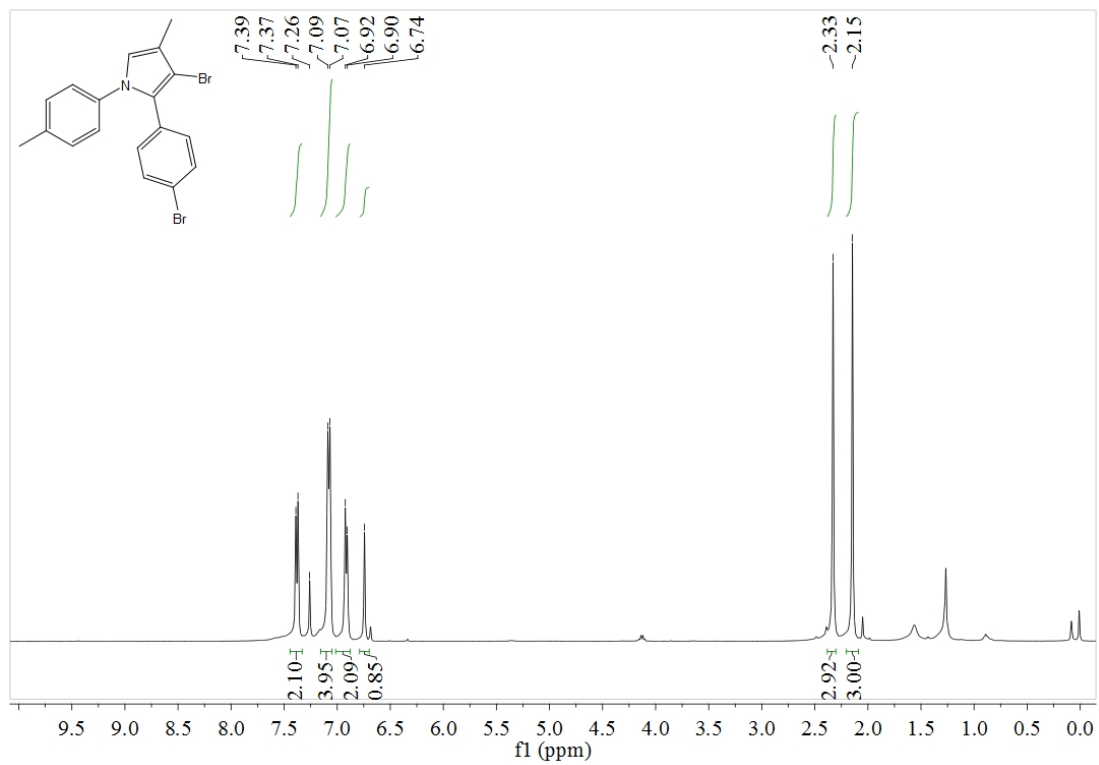
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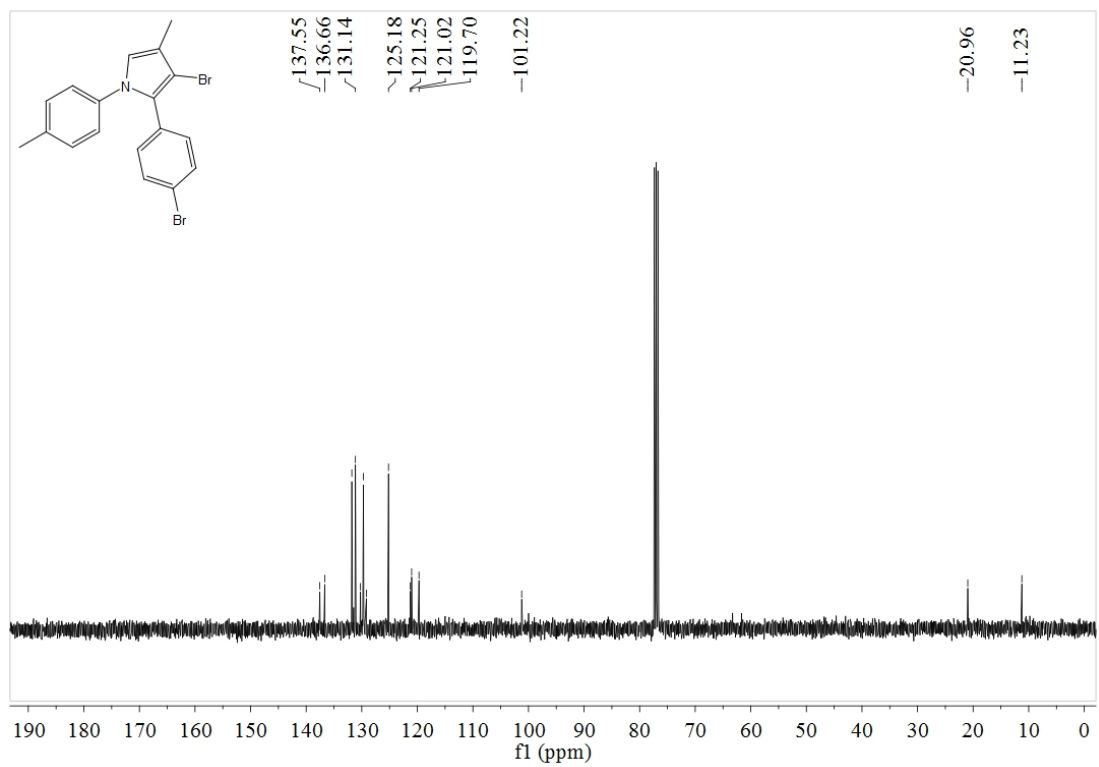
3fa-¹H



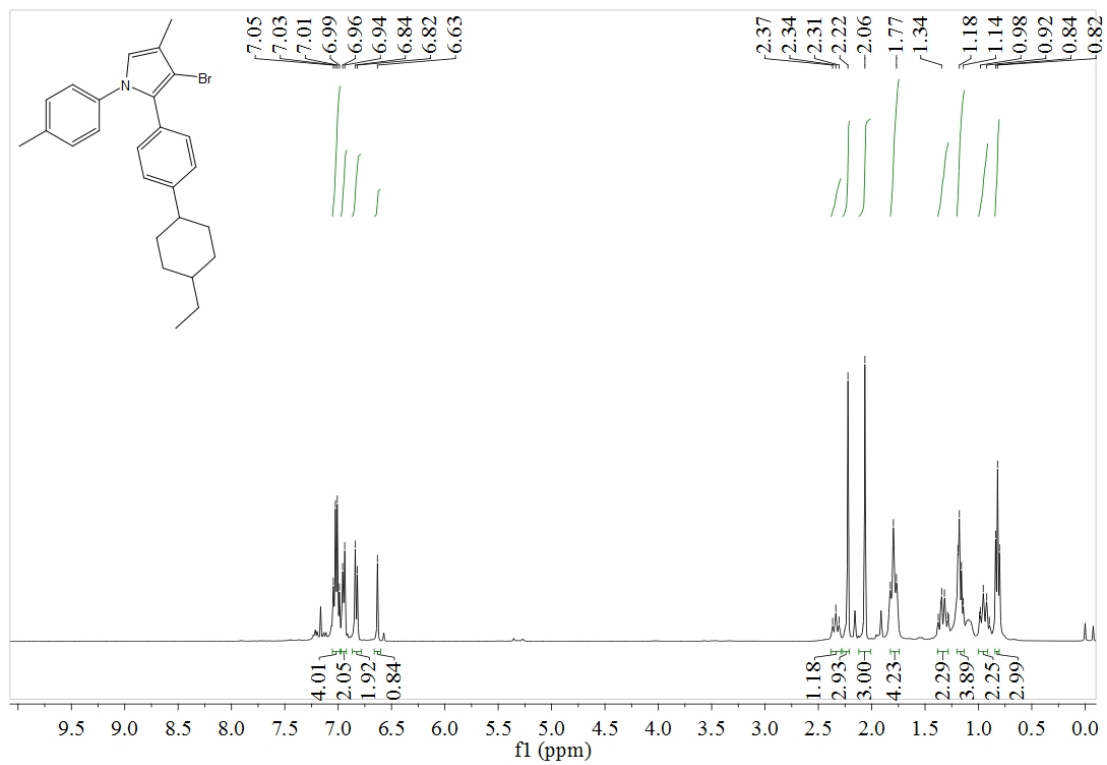
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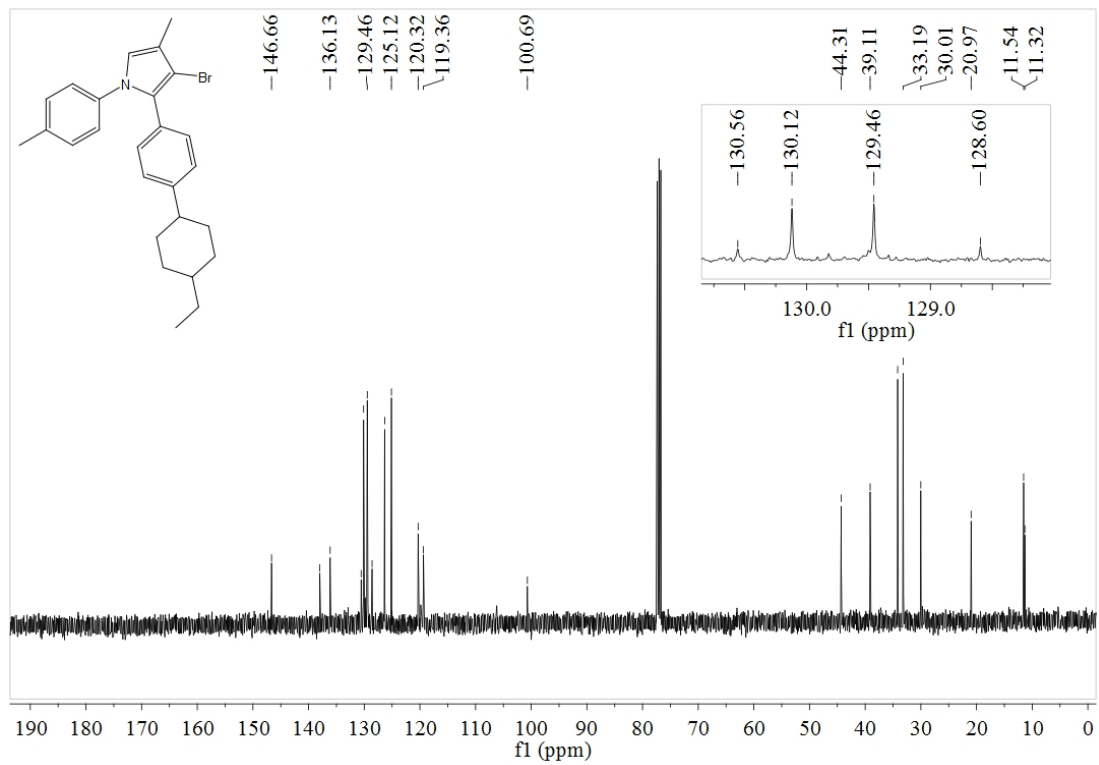
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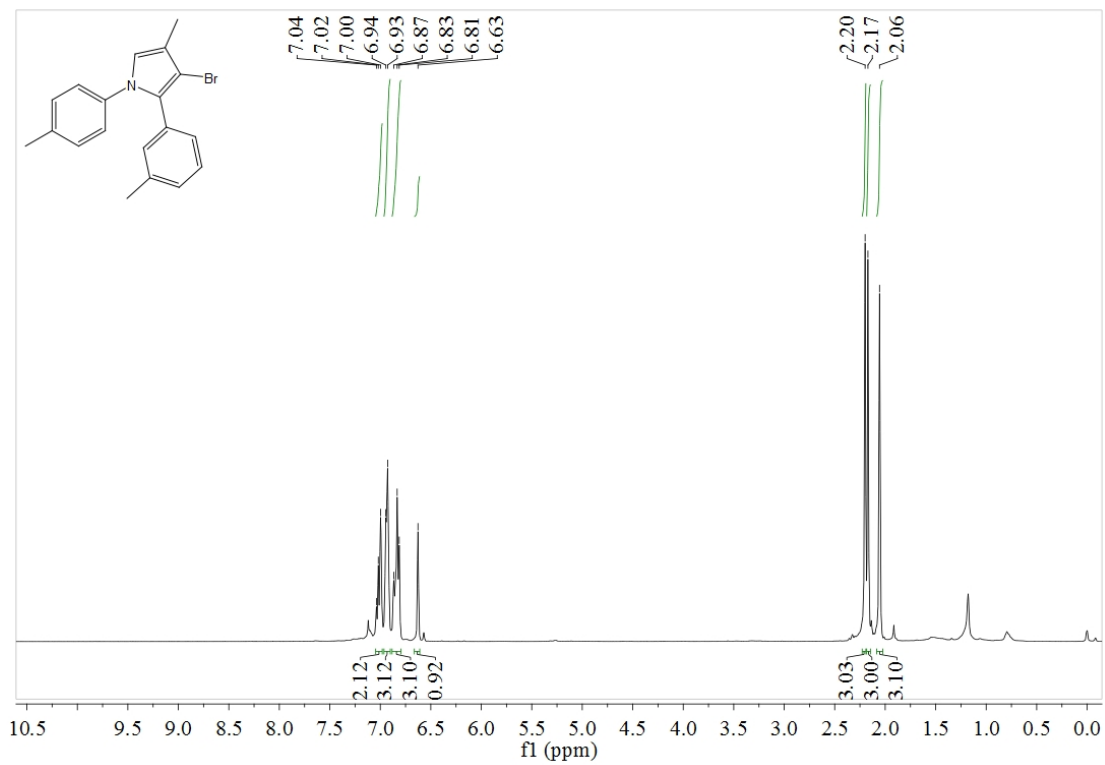
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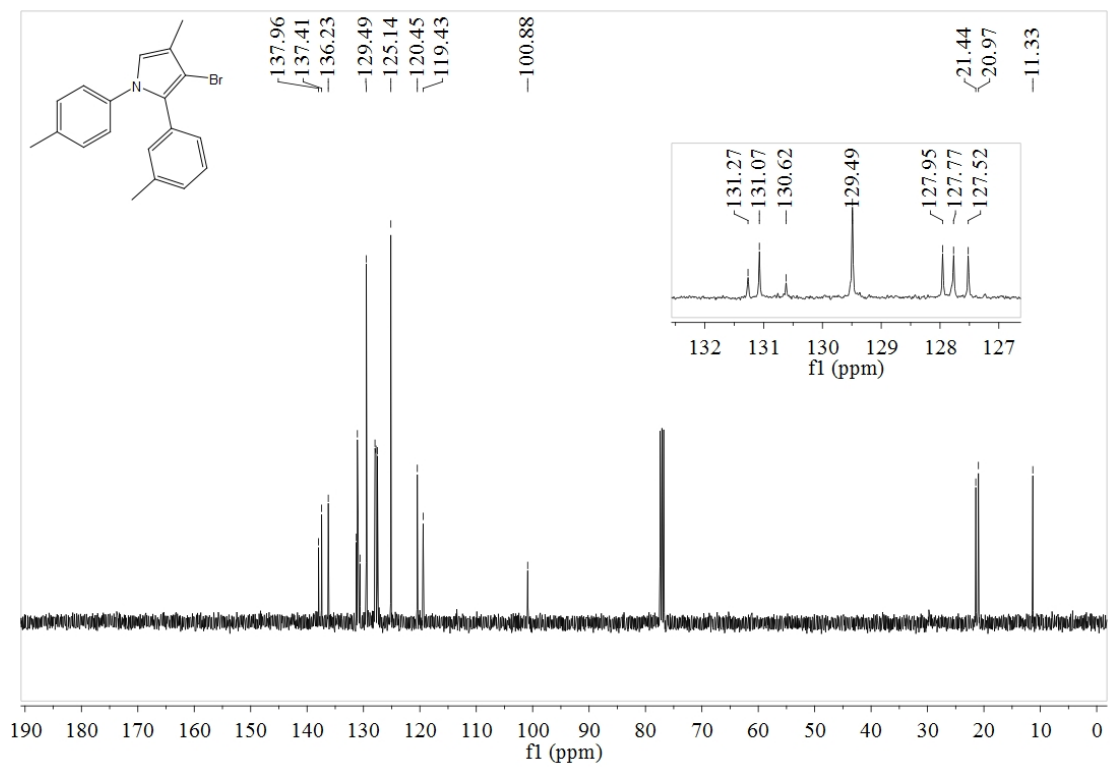
3ha-¹H



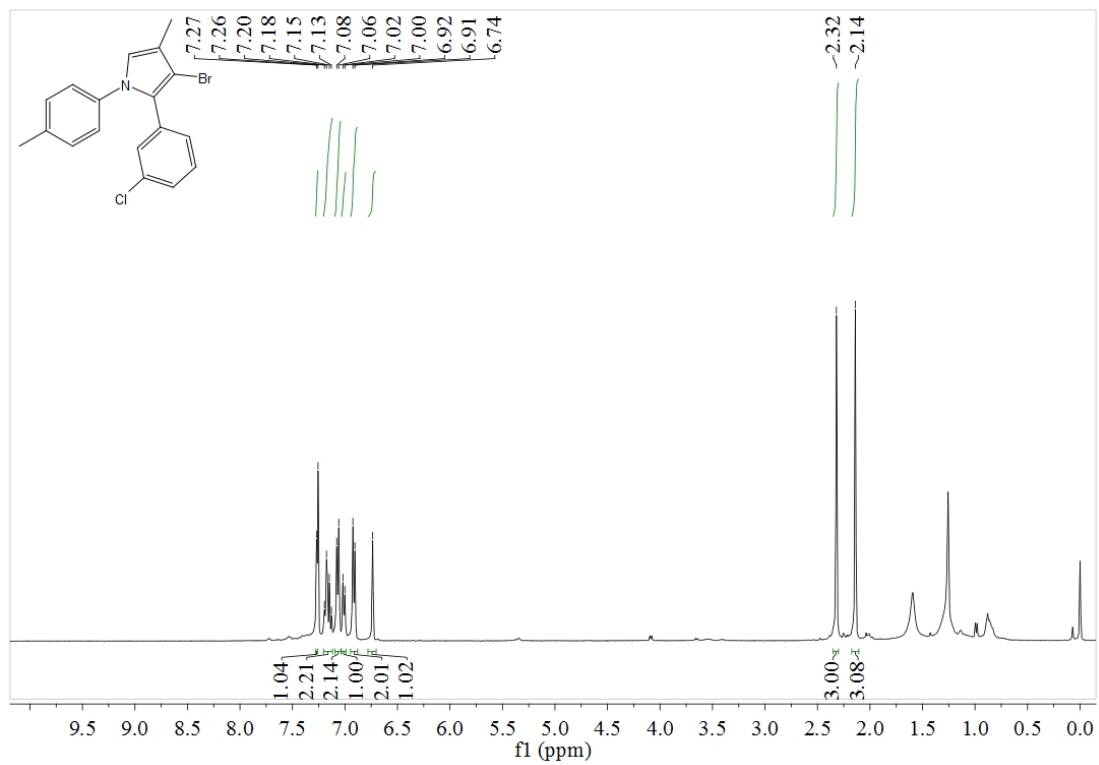
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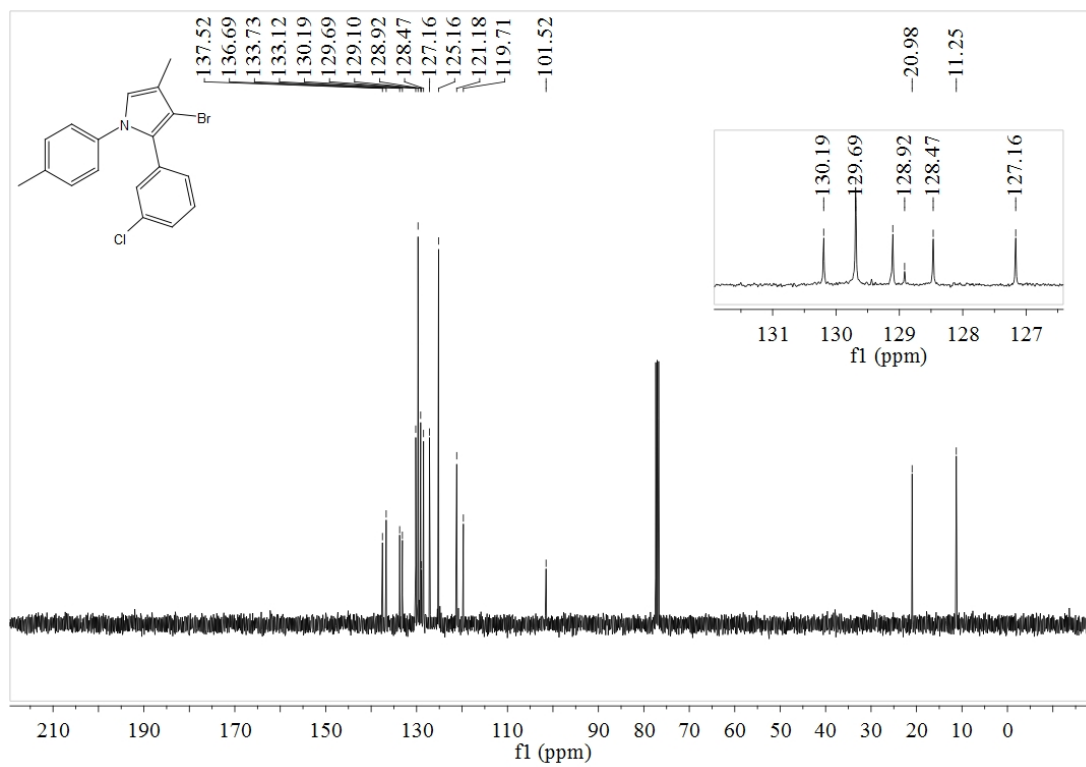
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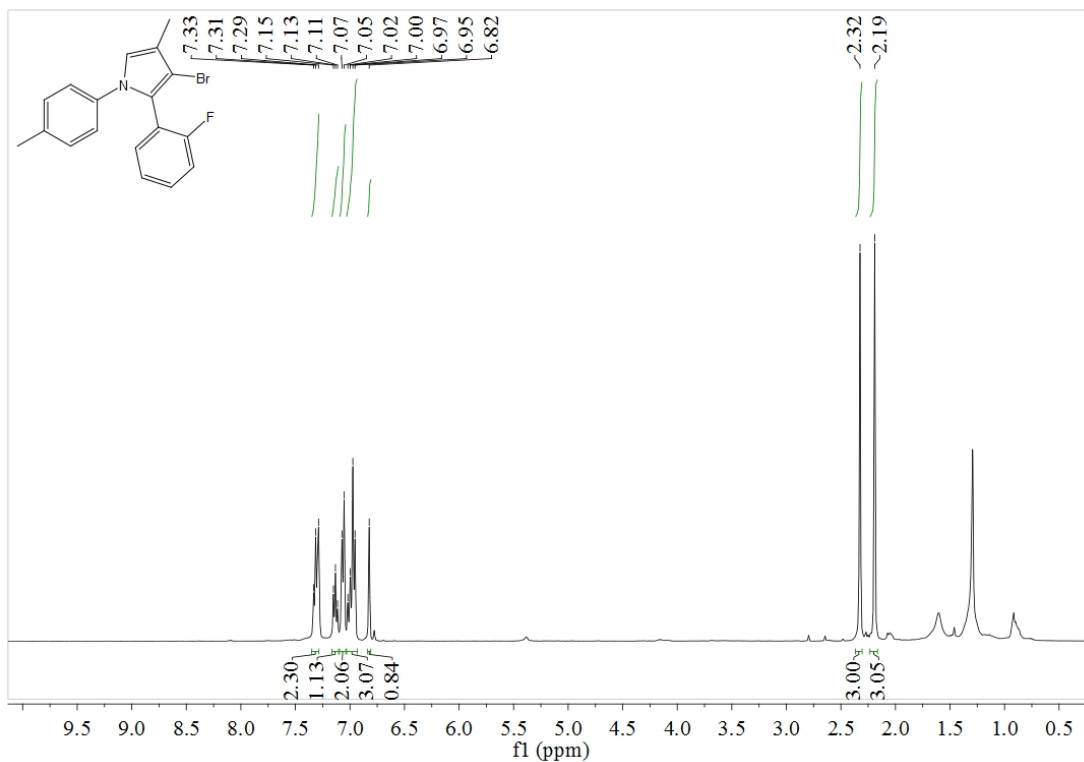
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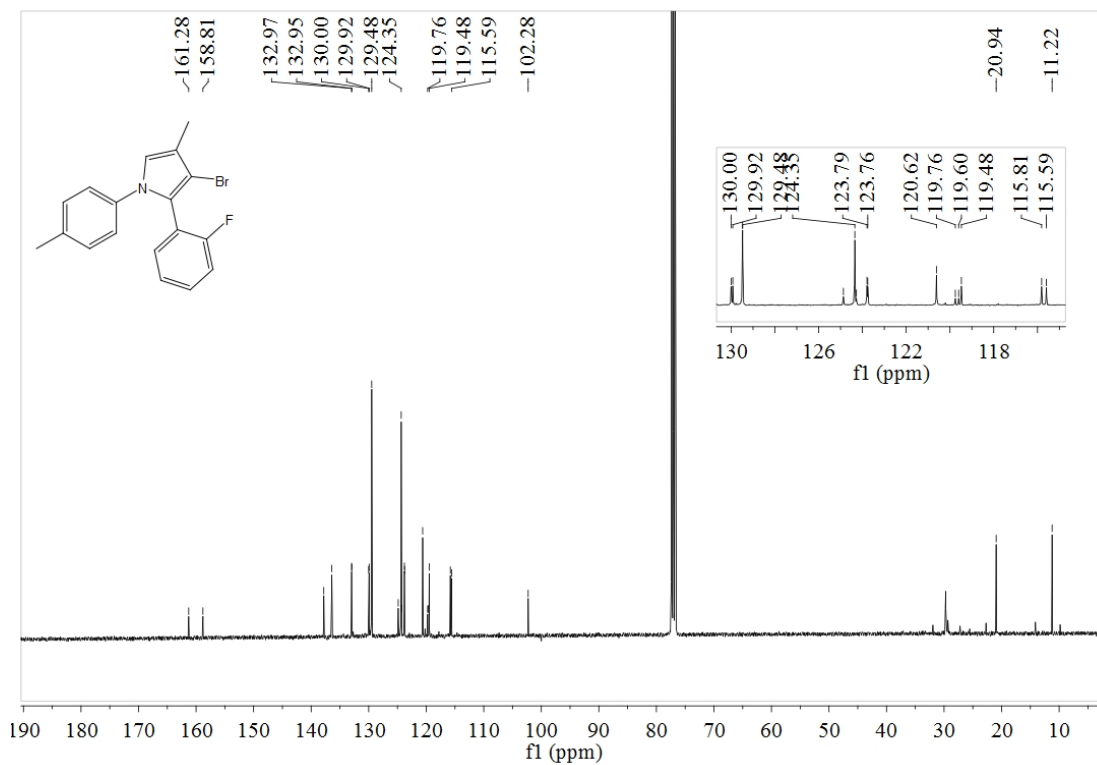
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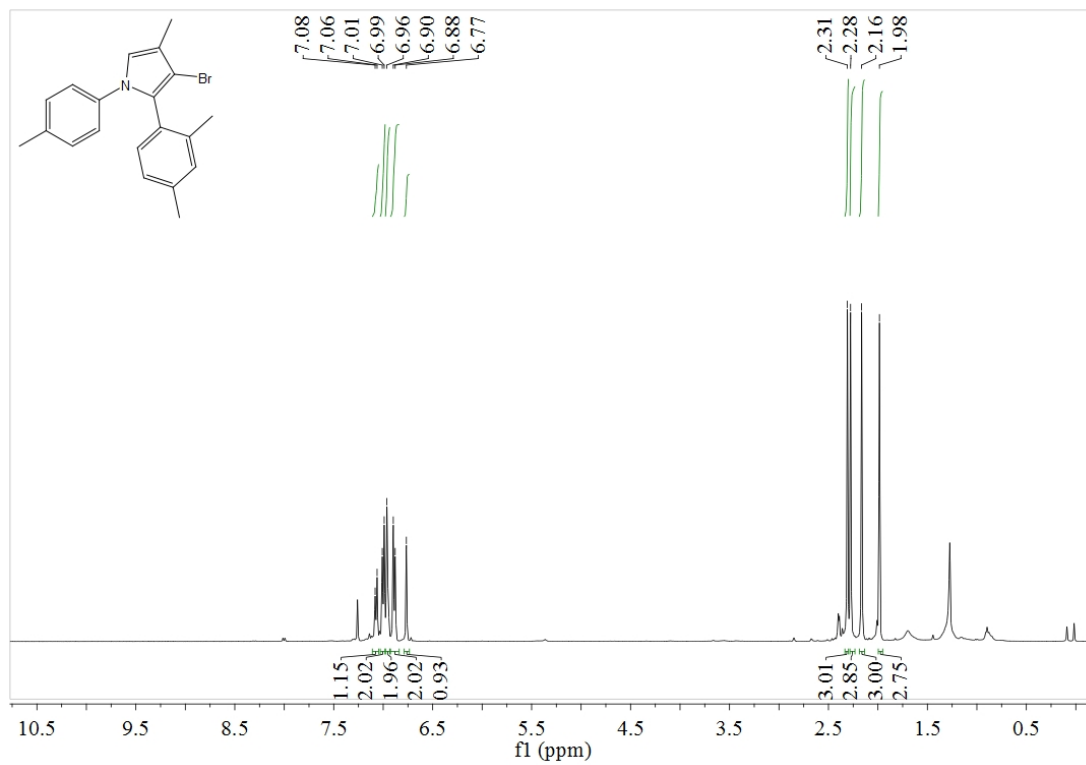
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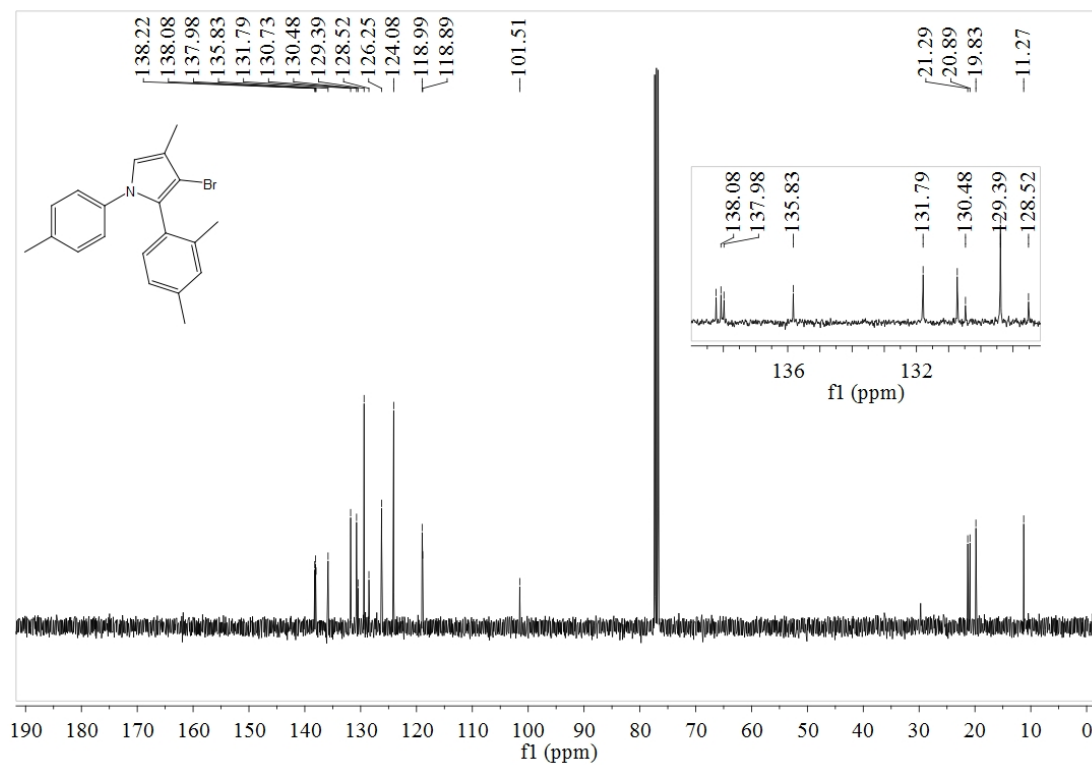
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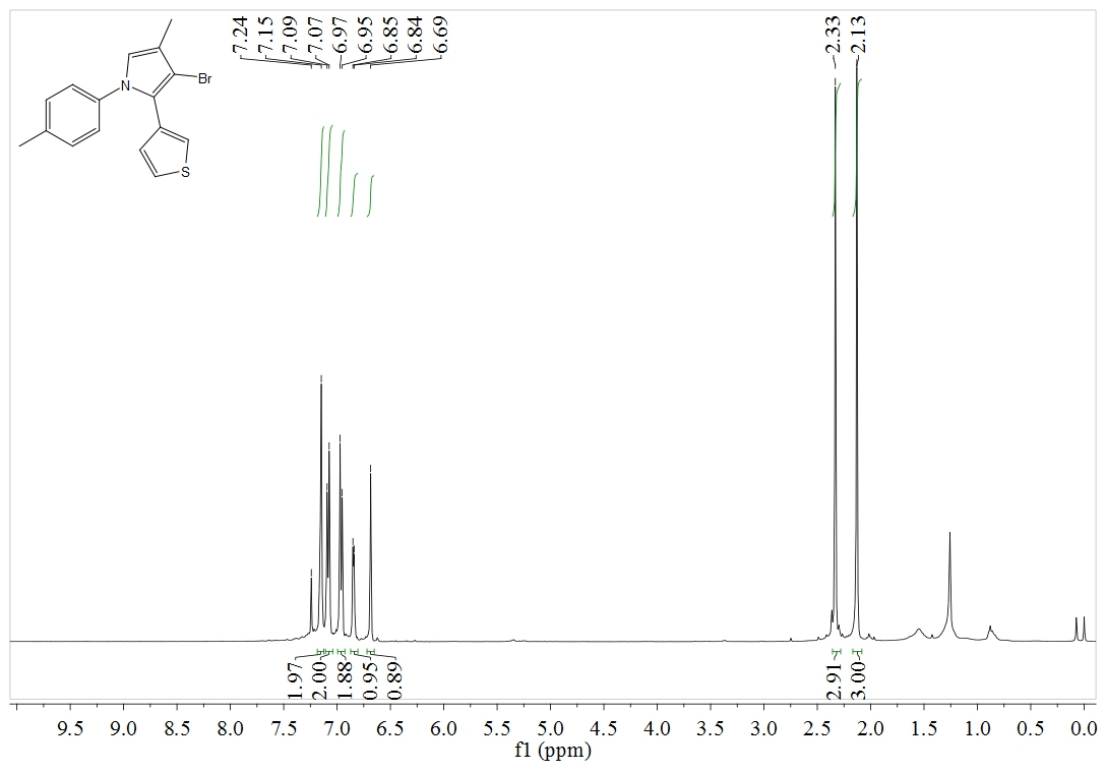
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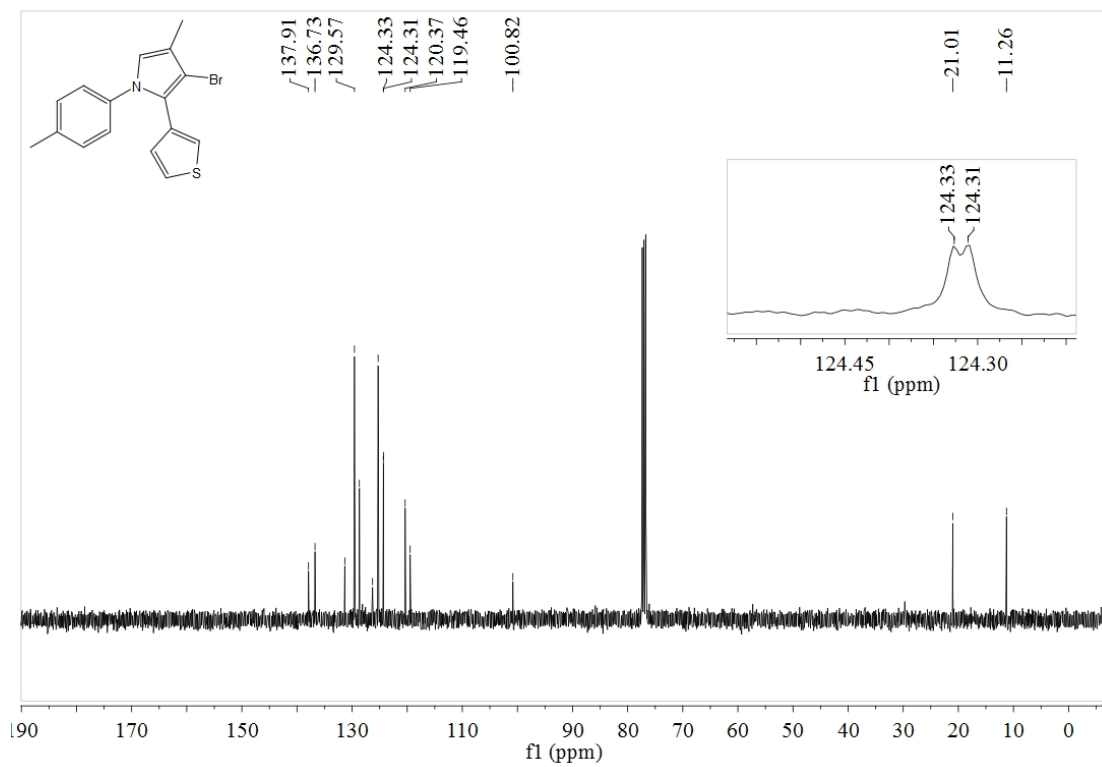
3la-¹H



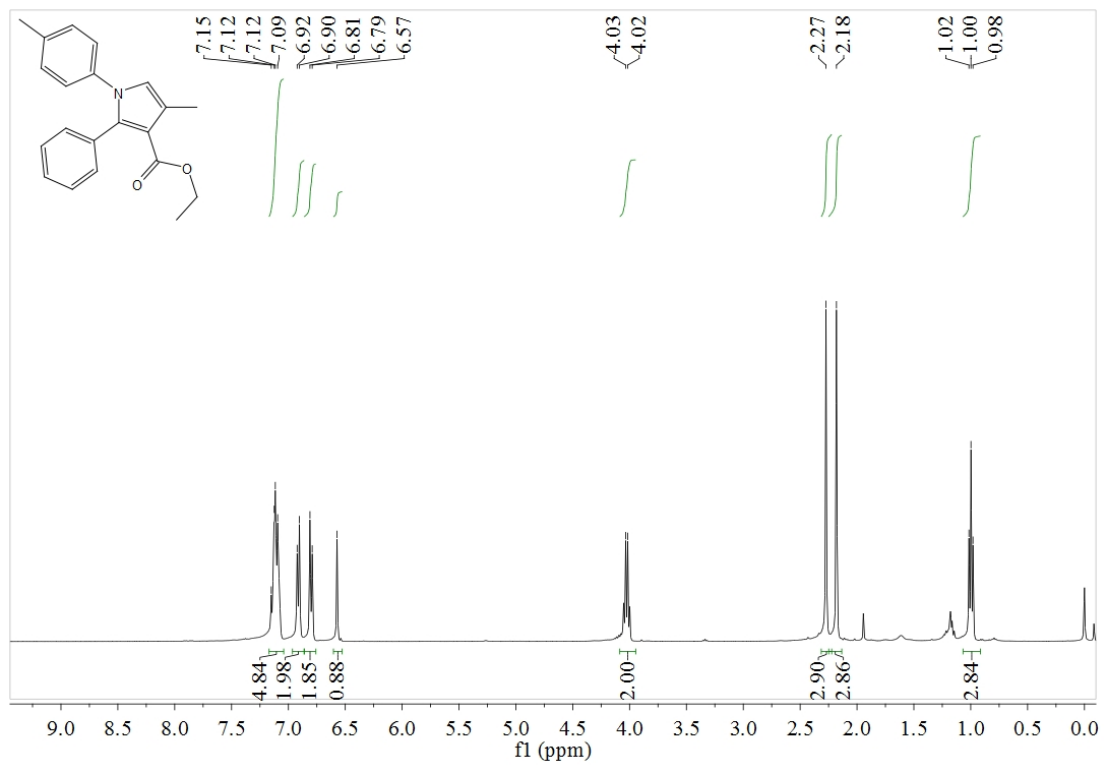
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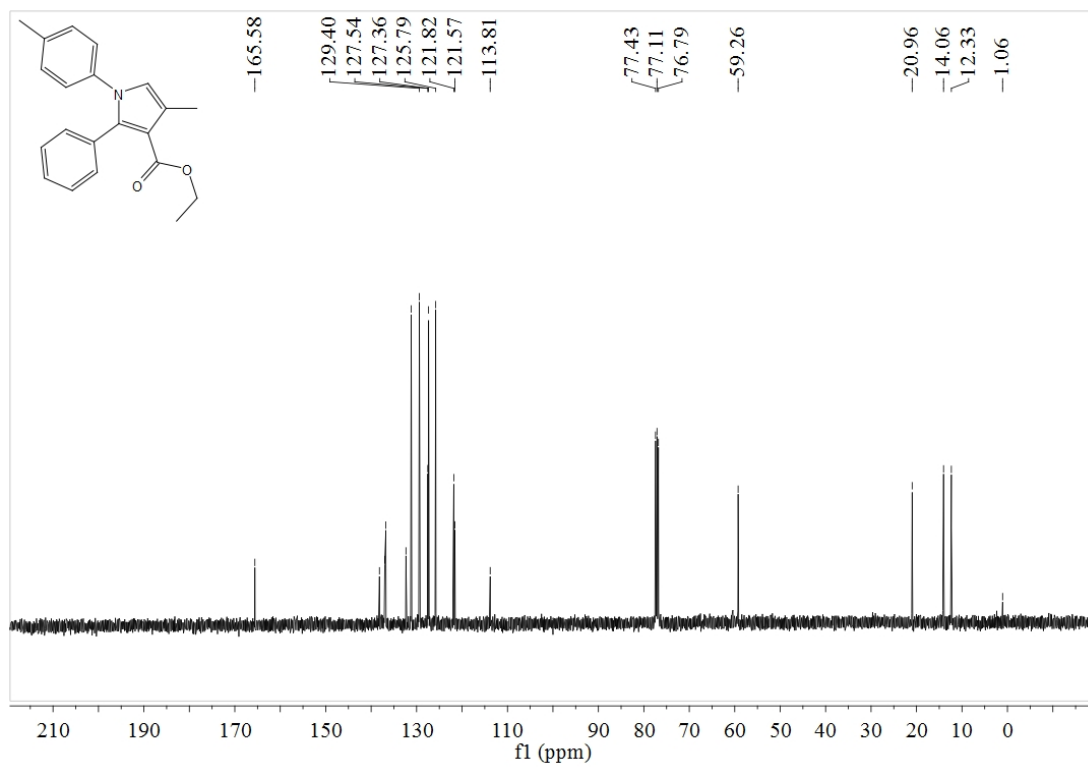
3ma-¹H



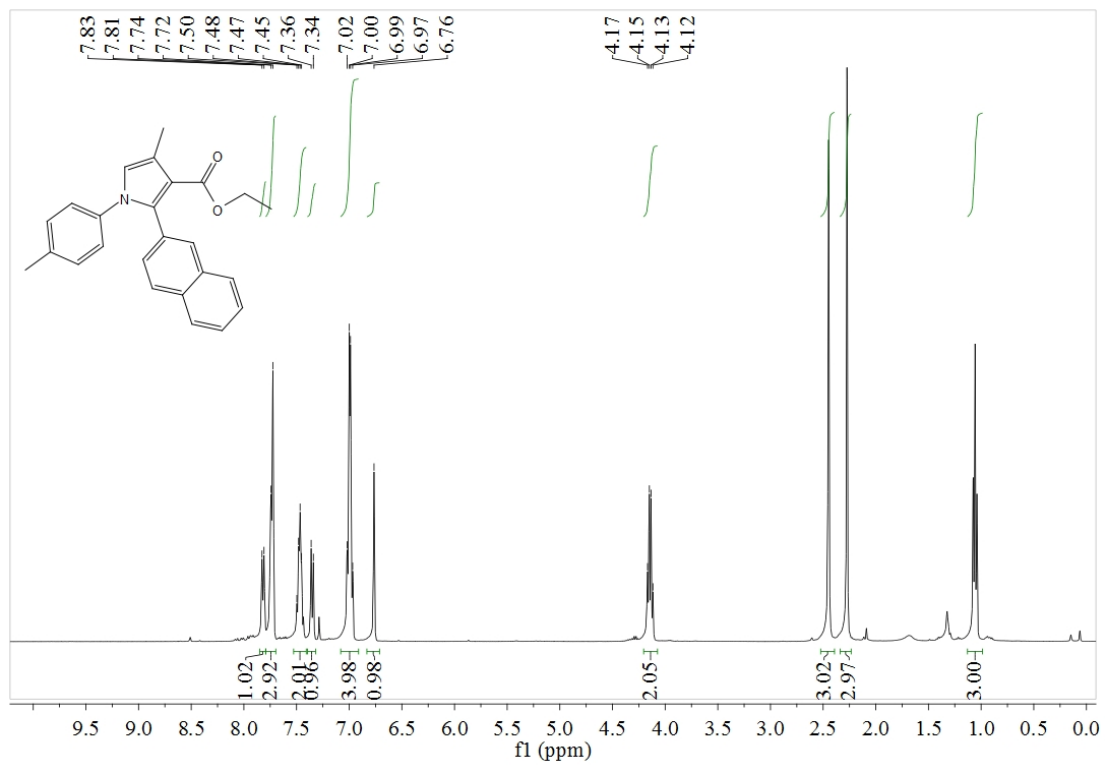
3ma-¹³C



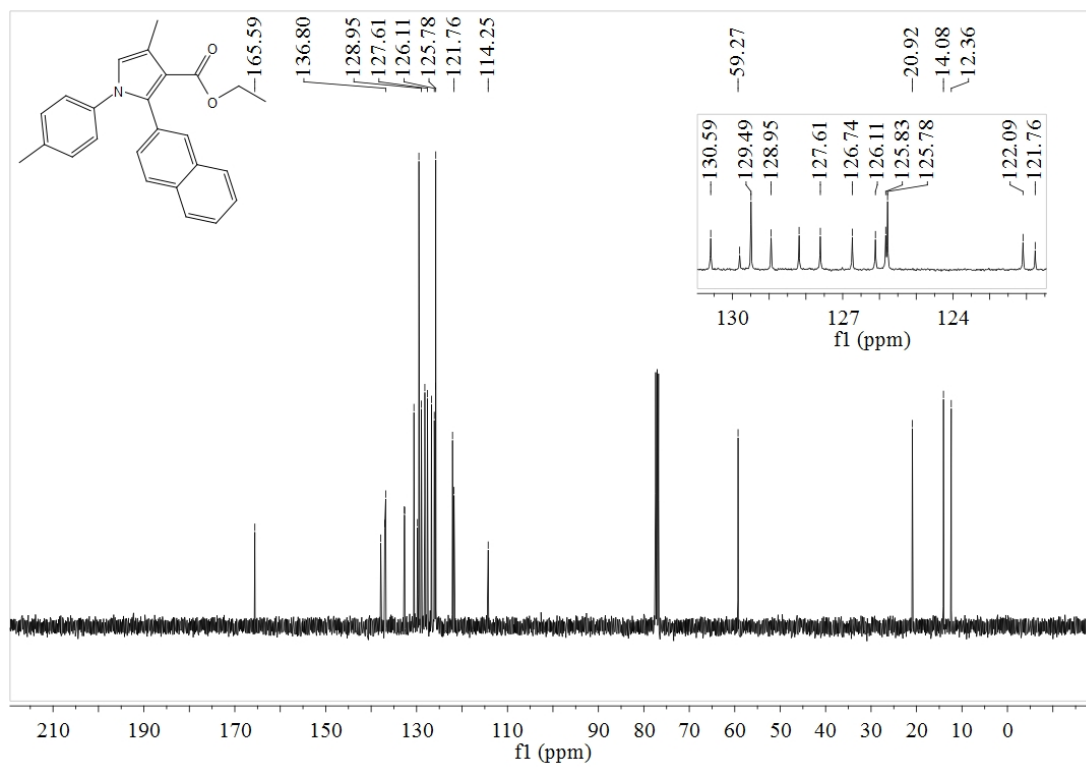
5a-¹H



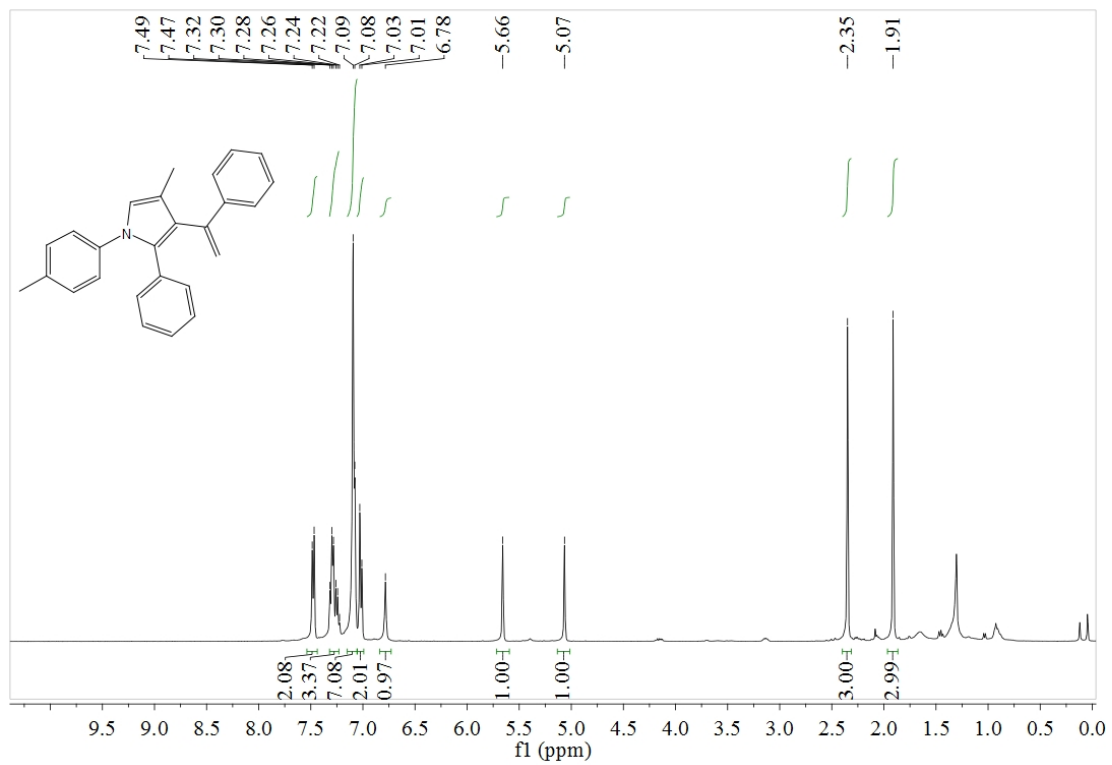
5a-¹³C



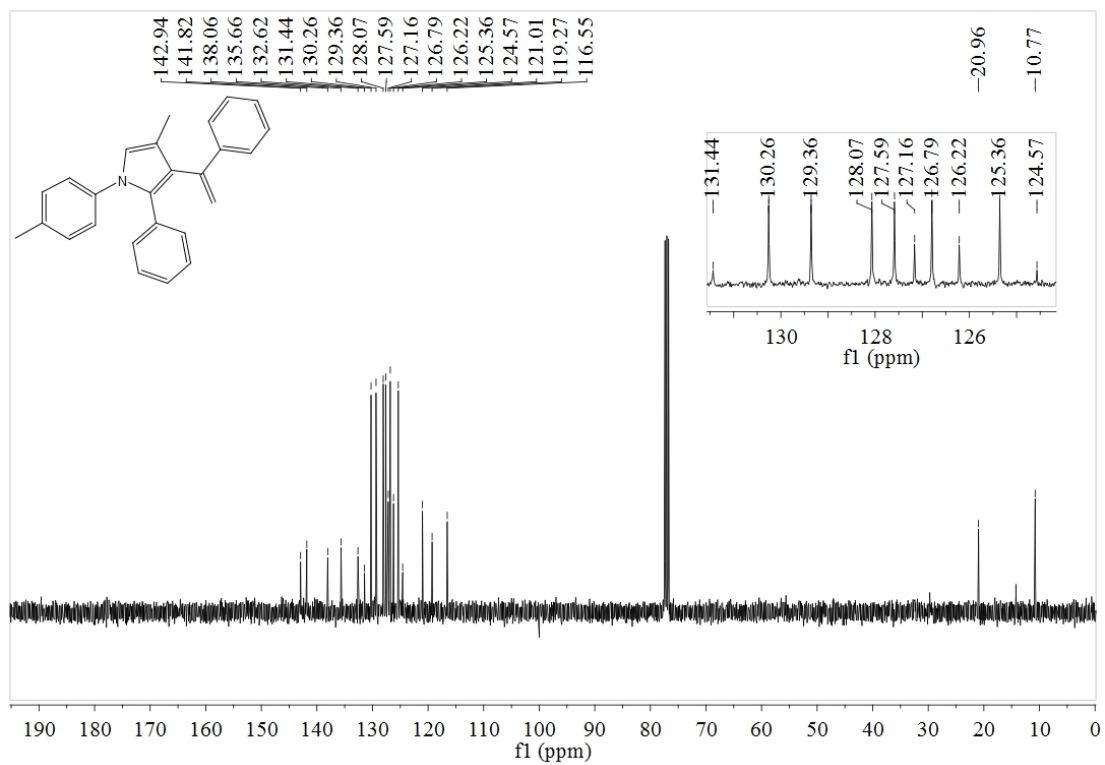
5b-¹H



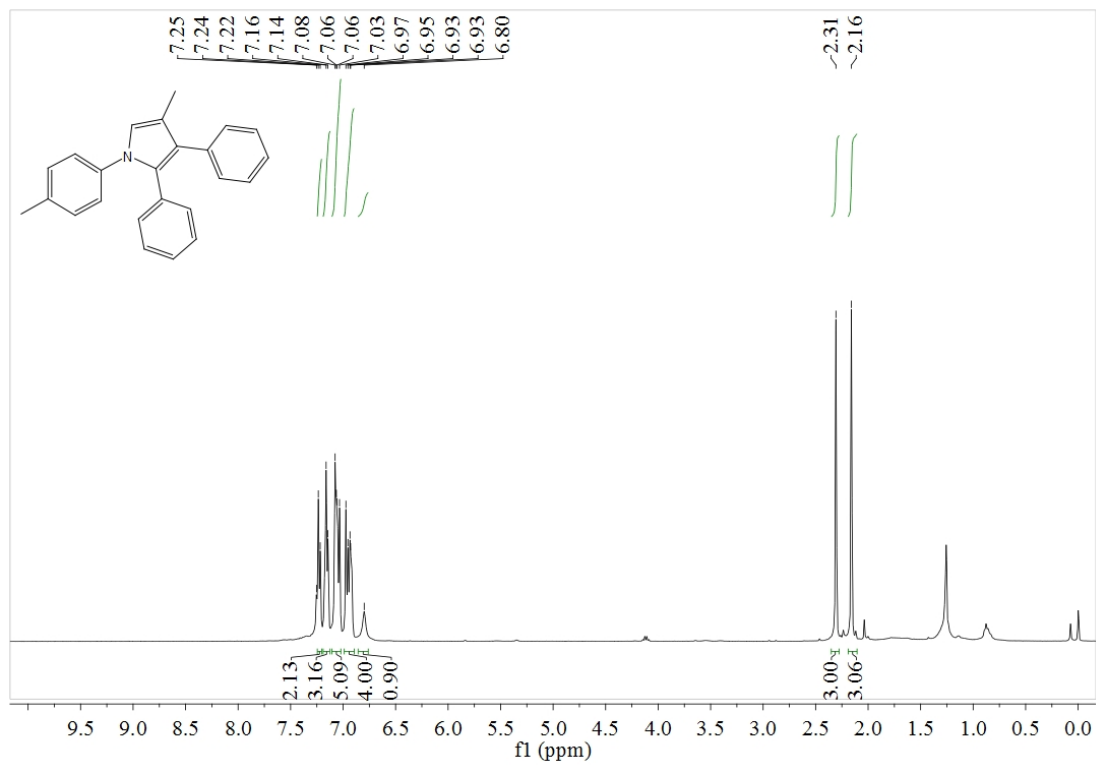
5b-¹³C



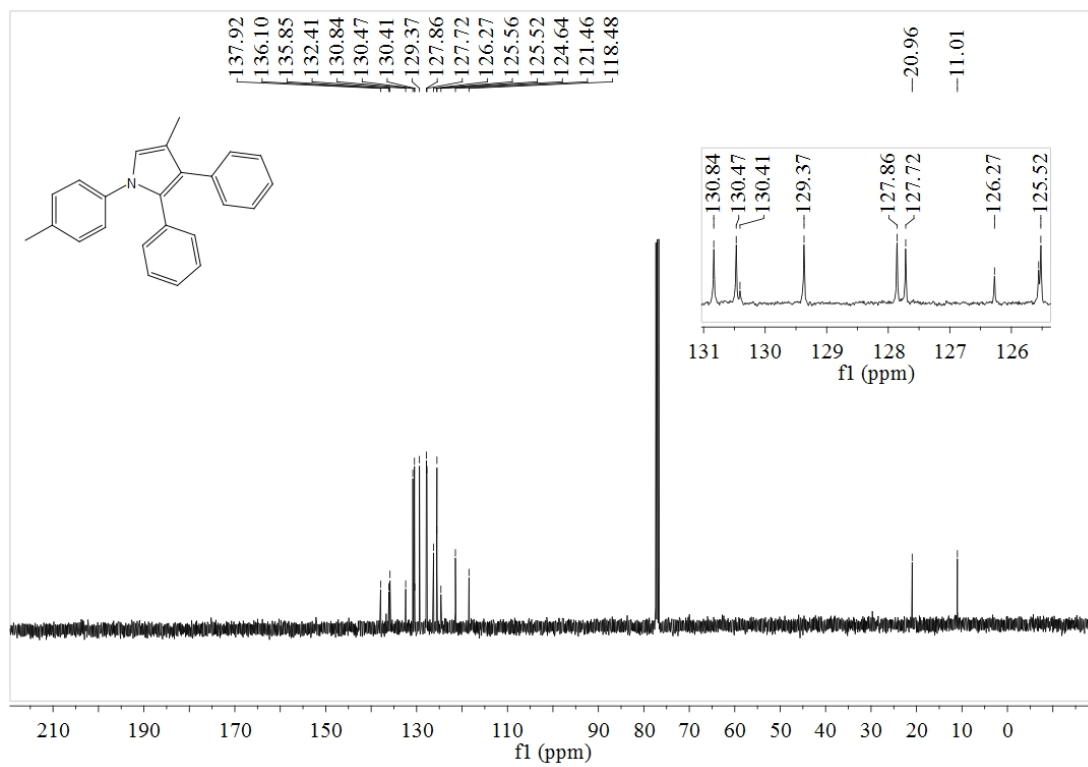
9-¹H



9-¹³C

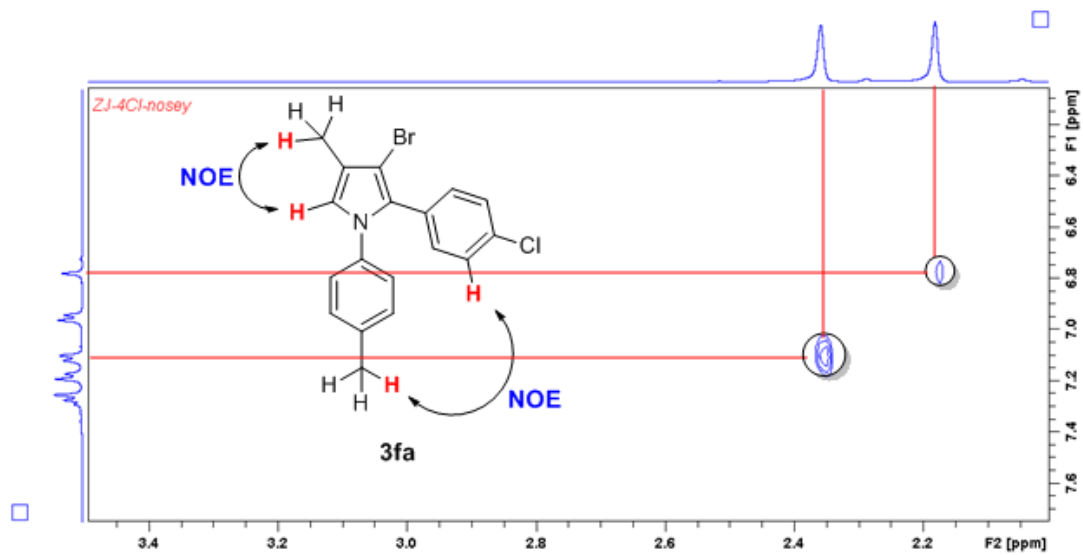
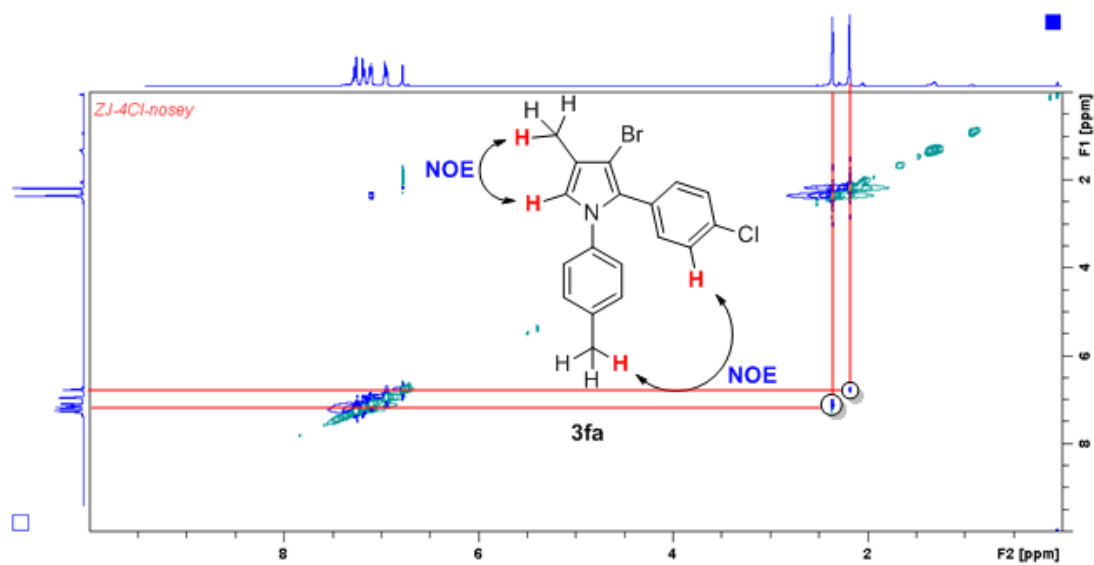


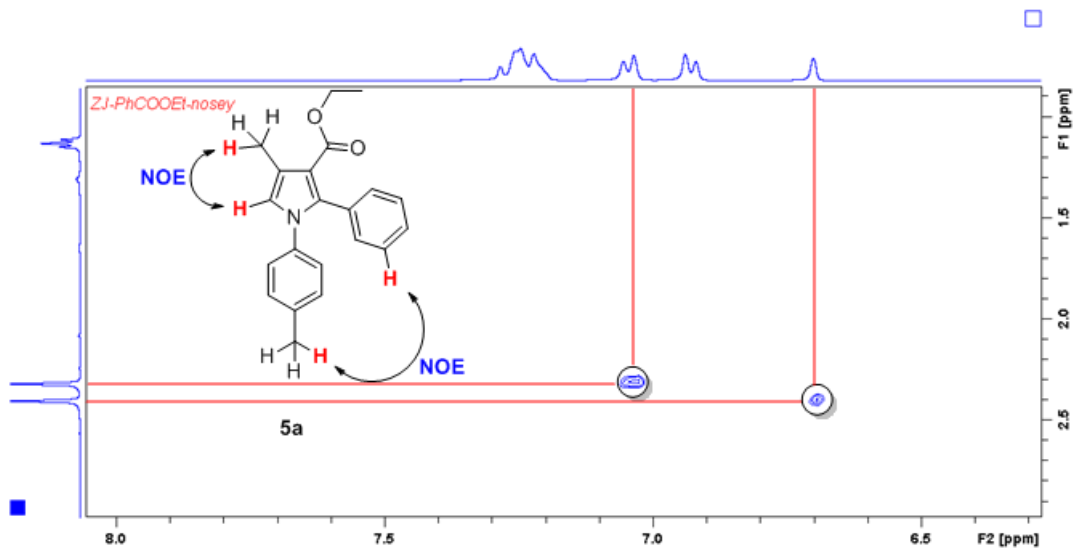
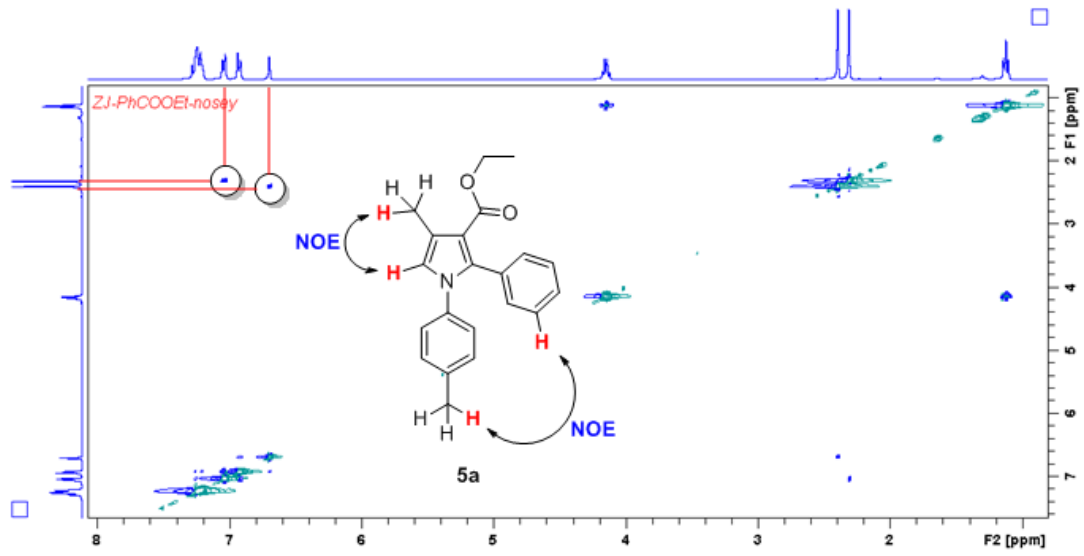
$^{10}\text{-}^1\text{H}$



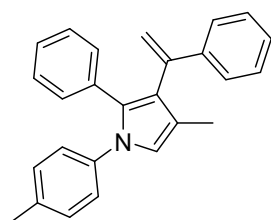
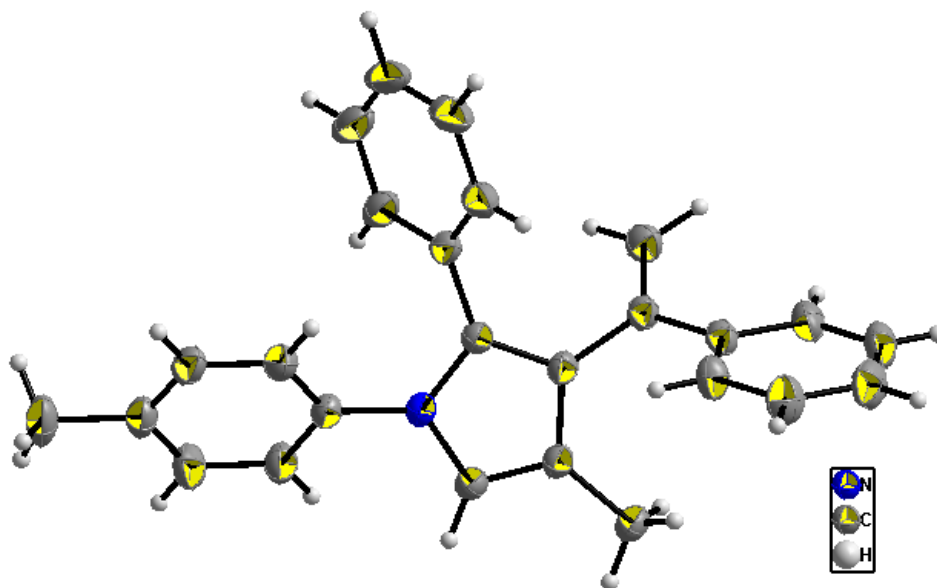
$^{10}\text{-}^{13}\text{C}$

F. Studies on the stereochemistry of 3fa and 5a





G. X-ray Crystallographic Analysis of 9



9

Summary of Data CCDC 1047287

Formula: C₂₆ H₂₃ N₁

Unit Cell Parameters: a 15.205(3) b 7.3621(15) c 18.007(4) P2₁/n