Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

One Pot Highly Efficient Synthesis of Substituted Pyrroles and *N*-Bridgehead Pyrroles by Zinc-Catalyzed Multicomponent Reaction

Xiao-tao Liu, Lu Hao, Min Lin, Li Chen, and Zhuang-ping Zhan *

Department of Chemistry, College of Chemistry and Chemical Engineering,

and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University,

Xiamen 361005, Fujian, P. R. China

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*Correspondence : Prof. Zhuang-ping Zhan, Department of Chemistry, College of Chemistry and Chemical Engineering, and State Key Laboratory for Physical Chemistry of Solid Surfaces, Xiamen University, Xiamen 361005, Fujian, P. R. China;

Phone: (+86)-592-2180318;

Fax: (+86)-592-2180318;

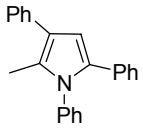
E-mail: zpzhan@xmu.edu.cn

Experimental

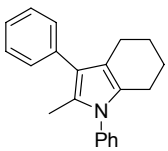
General methods: Propargylic acetates **1** and enoxysilanes **2** were prepared according to published procedures. All other compounds are commercially available and were used without further purification. Infrared spectra were recorded on a Nicolet AVATER FTIR360 spectrometer. NMR spectra were recorded on a Bruker AVANCE DPX-400 instrument at 400 MHz (^{1}H) or 100 MHz (^{13}C). The chemical shift values (δ) are given in parts per million (ppm) and are referred to the residual peak of the deuterated solvent ($CDCl_3$). MS measurements were performed on Bruker Reflex III mass spectrometer. Elemental analyses were performed with a Perkin–Elmer 2400 microanalyser. Flash chromatography was performed with QingDao silica gel (300–400 mesh).

General Procedure for the Synthesis of Substituted Pyrroles (5aa-5ja, 6aa)

To a 10-mL flask, propargylic acetates **1** (0.5 mmol), enoxysilanes **2** (1.0 mmol), chlorobenzene (2.0 mL) and $ZnCl_2$ (0.05 mmol) were successively added. The reaction was allowed to stir at 75 °C for 0.3 h, followed by the addition of primary amines **3** (1.0 mmol). The reaction mixture was heated to reflux temperature for an additional 1.5-12 h until completion by TLC. Upon cooling to room temperature, the reaction mixture was then quenched with 1M HCl (2 mL), the organic and aqueous layers were separated, and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/100) to afford corresponding substituted pyrroles.



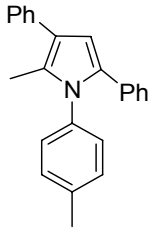
2-Methyl-1,3,5-triphenyl-1*H*-pyrrole(5aa): A white solid, m.p. 158-160 °C; Yield: 83 % (0.128 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.53 (m, 2H), 7.34-7.43 (m, 5H), 7.21-7.27 (m, 3H), 7.09-7.17 (m, 5H), 6.57 (s, 1H), 2.25 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 137.0, 134.0, 133.3, 129.2, 128.8, 128.5, 128.2, 128.1, 128.0, 127.7, 126.0, 125.6, 122.9, 109.4, 12.6 ppm; IR (film): 1489, 1595, 3023 cm^{-1}; MS (ESI): m/z (%): 310 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{23}H_{19}N$: C 89.28, H 6.19, N 4.53; found: C 89.39, H 6.04, N 4.56.



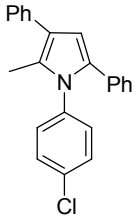
2-Methyl-1,3-diphenyl-4,5,6,7-tetrahydro-1*H*-indole(5ab or 5bb): A yellow oil; Yield: 78 % (0.112 g) or 73 % (0.104 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.48 (m, 2H), 7.36-7.39 (m, 5H), 7.27-7.30 (m, 2H), 7.20-7.24 (m, 1H), 2.60 (t, J = 5.6 Hz, 2H), 2.39 (t, J = 6.0 Hz, 2H), 2.12 (s, 3H), 1.75-1.81 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.7,

136.7, 129.5, 129.1, 128.2, 128.0, 127.5, 125.3, 124.9, 120.4, 116.0, 24.0, 23.6, 23.0, 22.9, 11.7 ppm; IR (film):1497, 1599, 3038 cm^{-1}; MS (ESI): m/z (%): 288 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{21}H_{21}N$: C 87.76, H 7.36, N 4.87; found: C 87.86, H 7.28, N 4.80.

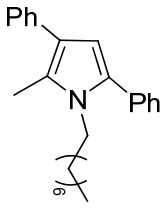
Data are in accordance with previously reported results.[1]



2-Methyl-3,5-diphenyl-1-*p*-tolyl-1*H*-pyrrole(5ac): A yellow oil; Yield: 84 % (0.136 g); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.53 (d, J = 7.2 Hz, 2H), 7.40-7.44 (m, 2H), 7.11-7.27 (m, 10H), 6.58 (s, 1H), 2.40 (s, 3H), 2.26 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.5, 137.1, 136.8, 134.0, 133.4, 129.8, 128.5(2), 128.2, 128.1, 128.0, 125.9, 125.5, 122.7, 109.2, 21.3, 12.5 ppm; IR (film):1516, 1602, 3027 cm^{-1}; MS (ESI): m/z (%): 324 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{24}H_{21}N$: C 89.12, H 6.54, N 4.33; found: C 89.26, H 6.48, N 4.37.

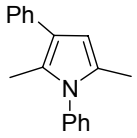


1-(4-Chlorophenyl)-2-methyl-3,5-diphenyl-1*H*-pyrrole(5ad): A yellow solid, m.p. 106-107 ^oC; Yield: 81 % (0.139 g); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.50 (m, 2H), 7.38-7.42 (m, 2H), 7.32-7.36 (m, 2H), 7.22-7.26 (m, 1H), 7.08-7.20 (m, 7H), 6.55 (s, 1H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.0, 136.8, 134.1, 133.5, 133.1, 130.0, 129.4, 128.6, 128.3, 128.2, 128.1, 127.9, 126.3, 125.8, 123.3, 109.8, 12.5 ppm; IR (film):1493, 1606, 3027 cm^{-1}; MS (ESI): m/z (%): 344 (100) and 346(29) [$M + H^+$]; elemental analysis calcd (%) for $C_{23}H_{18}ClN$: C 80.34, H 5.28, N 4.07; found: C 80.26, H 5.35, N 4.06.



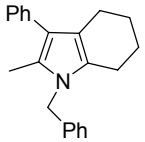
2-Methyl-1-octyl-3,5-diphenyl-1*H*-pyrrole(5ae): A yellow oil; Yield: 80 % (0.138 g); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.44 (m, 8H), 7.27-7.31 (m, 1H), 7.16-7.21 (m, 1H), 6.29 (s, 1H), 3.88 (t, J = 8.0 Hz, 2H), 2.42 (s, 3H), 1.59-1.62 (m, 2H), 1.18-1.29 (m, 10H), 0.86 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=137.5, 134.2, 133.7, 129.2, 128.5,

128.4, 128.2, 126.9, 126.0, 125.2, 122.2, 108.6, 44.6, 31.9, 31.2, 29.2, 29.1, 26.8, 22.8, 14.2, 11.6 ppm; IR (film):1489, 1602, 3023 cm^{-1}; MS (ESI): m/z (%): 346 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{25}H_{31}N$: C 86.90, H 9.04, N 4.05; found: C 86.81, H 9.07, N 4.06.



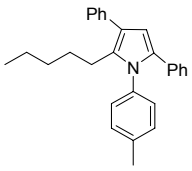
2,5-Dimethyl-1,3-diphenyl-1*H*-pyrrole(5af or 5ba): A yellow oil; Yield: 86 % (0.106 g) or 77 % (0.095 g); ^{1}HNMR (400 MHz, $CDCl_3$): δ = 7.34-7.50 (m, 7H), 7.25-7.28 (m, 2H), 7.17-7.22 (m, 1H), 6.15 (d, *J* = 0.8 Hz, 1H), 2.15 (s, 3H), 2.07 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 137.5, 129.3, 128.8, 128.5, 128.4, 128.0, 125.3, 125.1, 121.2, 106.7, 13.0, 12.4 ppm; IR (film):1502, 1597, 3027 cm^{-1}; MS (ESI): m/z (%): 248 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{18}H_{17}N$: C 87.41, H 6.93, N 5.66; found: C 87.36, H 7.02, N 5.55.

Data are in accordance with previously reported results.[1]



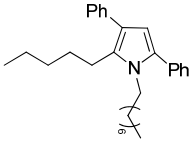
1-benzyl-2-methyl-3-phenyl-4,5,6,7-tetrahydro-1*H*-indole(5bc): A yellow oil; Yield: 72 % (0.108 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.36 (m, 6H), 7.17-7.25 (m, 2H), 6.97-6.99 (m, 2H), 5.02 (s, 2H), 2.55 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 6.0 Hz, 2H), 2.20 (s, 3H), 1.80-1.86 (m, 2H), 1.70-1.75 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.8, 137.1, 129.6, 128.8, 128.2, 127.2, 127.1, 126.1, 125.1, 124.1, 120.1, 115.6, 46.8, 24.1, 23.6, 22.9, 22.2, 10.7 ppm; IR (film):1491, 1600, 3028 cm^{-1}; MS (ESI): m/z (%): 302 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{22}H_{23}N$: C 87.66, H 7.69, N 4.65; found: C 87.59, H 7.74, N 4.59.

Data are in accordance with previously reported results.[2]

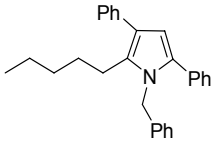


2-Pentyl-3,5-diphenyl-1-*p*-tolyl-1*H*-pyrrole(5ca): A yellow solid, m.p. 85-86 ^oC; Yield: 86 % (0.163 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (dd, *J* = 7.6 and 1.2 Hz, 2H), 7.39-7.43 (m, 2H), 7.23-7.27 (m, 1H), 7.08-7.20 (m, 9H), 6.55 (s, 1H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 1.26-1.33 (m, 2H), 1.06-1.12 (m, 4H), 0.72 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 137.4, 136.8, 134.0, 133.4, 133.2, 129.7, 128.8, 128.5, 128.2, 128.1, 128.0, 125.9, 125.6, 122.6, 109.5, 31.6, 29.7, 25.3, 22.1, 21.3, 13.9 ppm; IR (film):1510, 1605, 3027 cm^{-1}; MS (ESI): m/z (%): 380 (100) [*M* +

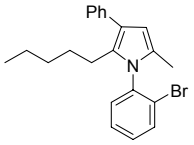
H^+]; elemental analysis calcd (%) for $C_{28}H_{29}N$: C 88.61, H 7.70, N 3.69; found: C 88.55, H 7.73, N 3.66.



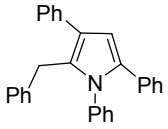
1-Octyl-2-pentyl-3,5-diphenyl-1*H*-pyrrole(5cb): A yellow oil; Yield: 80 % (0.160 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29-7.46 (m, 9H), 7.19-7.24 (m, 1H), 6.29 (s, 1H), 3.93 (t, *J* = 8.0 Hz, 2H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.63-1.71 (m, 2H), 1.51-1.55 (m, 2H), 1.34-1.41 (m, 4H), 1.17-1.28 (m, 10H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 134.4, 133.5, 131.2, 129.1, 128.5, 128.4, 128.1, 126.9, 125.3, 122.0, 109.2, 44.5, 32.1, 31.8, 31.5, 30.7, 29.2, 29.1, 26.8, 25.4, 22.7, 22.5, 14.2(2) ppm; IR (film): 1466, 1600, 3028 cm^{-1}; MS (ESI): m/z (%): 402 (100) [*M* + H^+]; elemental analysis calcd (%) for $C_{29}H_{39}N$: C 86.72, H 9.79, N 3.49; found: C 86.65, H 9.83, N 3.50.



1-Benzyl-2-pentyl-3,5-diphenyl-1*H*-pyrrole(5cc): A yellow oil; Yield: 83 % (0.157 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.50 (m, 2H), 7.23-7.39 (m, 11H), 6.93-6.95 (m, 2H), 6.44 (s, 1H), 5.22 (s, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 1.50-1.56 (m, 2H), 1.23-1.27 (m, 4H), 0.82 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=139.4, 137.5, 134.3, 133.7, 131.7, 129.0, 128.8, 128.5, 128.0, 127.2, 127.0, 125.8, 125.4, 122.6, 109.3, 47.9, 32.0, 30.5, 25.5, 22.4, 14.1 ppm; IR (film): 1497, 1600, 3028 cm^{-1}; MS (ESI): m/z (%): 380 (100) [*M* + H^+]; elemental analysis calcd (%) for $C_{28}H_{29}N$: C 88.61, H 7.70, N 3.69; found: C 88.57, H 7.68, N 3.71.

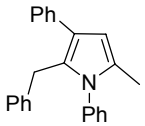


1-(2-Bromophenyl)-5-methyl-2-pentyl-3-phenyl-1*H*-pyrrole(5cd): A yellow oil; Yield: 82 % (0.156 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (dd, *J* = 8.0 and 1.2 Hz, 1H), 7.42-7.46 (m, 3H), 7.30-7.38 (m, 4H), 7.17-7.21 (m, 1H), 6.16 (d, *J* = 0.8 Hz, 1H), 2.50-2.58 (m, 1H), 2.32-2.40 (m, 1H), 1.98 (d, *J* = 0.4 Hz, 3H), 1.29-1.37 (m, 2H), 1.04-1.10 (m, 4H), 0.71 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 138.6, 137.6, 133.5, 131.2, 130.0, 128.5, 128.4, 128.2, 127.9, 125.2, 124.9, 121.4, 106.9, 31.6, 29.8, 25.5, 22.1, 13.9, 12.6 ppm; IR (film): 1482, 1602, 3028 cm^{-1}; MS (ESI): m/z (%): 382 (100) and 384 (100) [*M* + H^+]; elemental analysis calcd (%) for $C_{22}H_{24}BrN$: C 69.11, H 6.33, N 3.66; found: C 69.23, H 6.30, N 3.62.

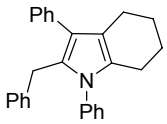


2-Benzyl-1,3,5-triphenyl-1*H*-pyrrole(5da): A yellow solid, m.p. 146-147 °C; Yield: 87 % (0.167 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.52 (m, 2H), 7.33-7.37 (m, 2H), 7.07-7.24 (m, 12H), 6.95-6.97 (m, 2H), 6.88-6.90 (m, 2H), 6.66 (s, 1H), 4.04 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.5, 139.1, 136.9, 134.8, 133.2, 130.2, 129.0, 128.8, 128.7, 128.3, 128.2, 128.1, 128.0, 127.7, 126.1, 125.9(3), 124.4, 109.6, 31.5 ppm; IR (film): 1493, 1599, 3024 cm^{-1}; MS (ESI): m/z (%): 386 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{29}H_{23}N$: C 90.35, H 6.01, N, 3.63; found: C 90.38, H 6.00, N 3.63.

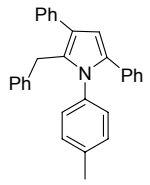
Data are in accordance with previously reported results.[3]



2-Benzyl-5-methyl-1,3-diphenyl-1*H*-pyrrole(5db): A yellow solid, m.p. 120-121 °C; Yield: 91 % (0.146 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44-7.47 (m, 2H), 7.23-7.33 (m, 5H), 7.15-7.19 (m, 1H), 7.06-7.12 (m, 3H), 6.96-6.99 (m, 2H), 6.81-6.83 (m, 2H), 6.23 (d, J = 0.8 Hz, 1H), 3.95 (s, 2H), 2.03 (d, J = 0.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 138.6, 137.3, 129.6, 128.8(2), 128.5, 128.2(2), 127.9, 127.8, 127.4, 125.7, 125.5, 122.9, 106.8, 31.4, 12.9 ppm; IR (film): 1493, 1599, 3027 cm^{-1}; MS (ESI): m/z (%): 324 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{24}H_{21}N$: C 89.12, H 6.54, N 4.33; found: C 89.23, H 6.46, N 4.30.

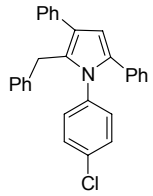


2-Benzyl-1,3-diphenyl-4,5,6,7-tetrahydro-1*H*-indole(5dc): A yellow oil; Yield: 86 % (0.156 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38-7.41 (m, 2H), 7.31-7.35 (m, 2H), 7.17-7.26 (m, 4H), 7.00-7.05 (m, 5H), 6.71-6.74 (m, 2H), 3.93 (s, 2H), 2.60 (d, J = 5.2 Hz, 2H), 2.30 (d, J = 5.6 Hz, 2H), 1.75-1.79 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.8, 138.6, 136.8, 129.5, 128.8, 128.7, 128.6, 128.3, 128.2, 128.0, 127.5, 127.2, 125.6, 125.5, 122.0, 116.0, 30.9, 24.0, 23.5, 22.9, 22.8 ppm; IR (film):1493, 1597, 3024 cm^{-1}; MS (ESI): m/z (%): 364 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{27}H_{25}N$: C 89.21, H 6.93, N 3.85; found: C 89.10, H 7.03, N 3.86.

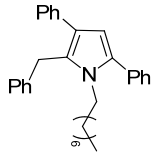


2-Benzyl-3,5-diphenyl-1-*p*-tolyl-1*H*-pyrrole(5dd): A yellow solid, m.p. 167-169 ^{o}C; Yield: 90 % (0.180 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.55 (m, 2H), 7.34-7.39 (m, 2H), 7.10-7.27 (m, 9H), 6.94-7.01 (m, 4H), 6.86-6.89 (m, 2H), 6.69 (s, 1H), 4.06 (s, 2H), 2.32 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.7, 137.5, 136.9, 136.5, 134.8, 133.3, 130.3, 129.4, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0(2), 126.0, 125.9, 125.8, 124.3, 109.5, 31.5, 21.2 ppm; IR (film):1512, 1600, 3023 cm^{-1}; MS (ESI): m/z (%): 400 (100) [M + H^{+}]; elemental analysis calcd (%) for $C_{30}H_{25}N$: C 90.19, H 6.31, N 3.51; found: C 90.27, H 6.26, N 3.48.

Data are in accordance with previously reported results.[3]

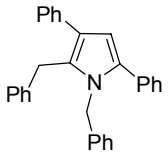


2-Benzyl-1-(4-chlorophenyl)-3,5-diphenyl-1*H*-pyrrole(5de): A yellow solid, m.p. 164-165 ^{o}C; Yield: 85 % (0.178 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49-7.51 (m, 2H), 7.32-7.36 (m, 2H), 7.09-7.24 (m, 11H), 6.85-6.91 (m, 4H), 6.65 (s, 1H), 4.02 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.3, 137.8, 136.6, 134.9, 133.6, 132.9, 130.2, 130.1, 129.0, 128.7, 128.5, 128.3, 128.2, 128.1, 128.0, 126.4, 126.1, 124.9, 110.0, 31.5 ppm; IR (film):1491, 1602, 3023 cm^{-1}; MS (ESI): m/z (%): 420 (100) and 422 (31) [M + H^{+}]; elemental analysis calcd (%) for $C_{29}H_{22}ClN$: C 82.94, H 5.28, N 3.34; found: C 82.82, H 5.31, N 3.29.

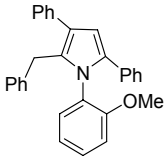


2-Benzyl-1-octyl-3,5-diphenyl-1*H*-pyrrole (5df): A yellow oil; Yield: 80 % (0.168 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.36-7.44 (m, 6H), 7.28-7.32 (m, 5H), 7.16-7.23 (m, 4H), 6.38 (s, 1H), 4.21 (s, 2H), 3.72 (t, J=8.0 Hz, 2H), 1.30-1.37 (m, 2H), 1.19-1.24 (m, 2H), 0.97-1.13 (m, 8H), 0.84 ppm (t, J=7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=140.4, 137.3, 134.3(2), 129.2, 128.8, 128.5(2), 128.1, 128.0, 127.6, 127.0, 126.4, 125.6, 124.0, 109.1, 44.7, 31.8, 31.3, 31.2, 29.1, 29.0, 26.7, 22.7, 14.2 ppm; IR (film):1491, 1608, 3031 cm^{-1}; MS (ESI): m/z (%): 422 (100) [M^{+}+H]; elemental analysis calcd (%) for $C_{31}H_{35}N$: C 88.31, H 8.37, N 3.32; found: C 88.45, H 8.26, N 3.28.

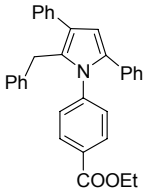
Data are in accordance with previously reported results.[3]



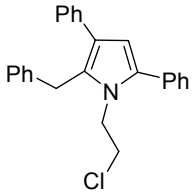
1,2-Dibenzyl-3,5-diphenyl-1*H*-pyrrole(5dg): A yellow solid, m.p. 134-135 °C; Yield: 83 % (0.165 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43-7.46 (m, 2H), 7.15-7.36 (m, 14H), 7.08-7.10 (m, 2H), 6.85-6.87 (m, 2H), 6.54 (s, 1H), 4.93 (s, 2H), 3.98 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.1, 139.1, 137.1, 135.1, 133.5, 128.9(2), 128.8, 128.6, 128.5, 128.1, 128.0, 127.9, 127.2, 127.1, 126.4, 125.7, 124.6, 109.1, 47.9, 31.1 ppm; IR (film):1493, 1602, 3026 cm^{-1}; MS (ESI): m/z (%): 400 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{30}H_{25}N$: C 90.19, H 6.31, N 3.51; found: C 90.11, H 6.40, N 3.48.



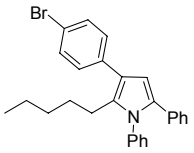
2-Benzyl-1-(2-methoxyphenyl)-3,5-diphenyl-1*H*-pyrrole(5dh): A yellow oil; Yield: 86 % (0.178 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.55 (m, 2H), 7.31-7.35 (m, 2H), 7.02-7.21 (m, 10H), 6.92-6.94 (m, 1H), 6.84-6.86 (m, 2H), 6.68-6.76(m, 2H), 6.65(d, J = 1.2 Hz,1H), 4.00 (q, J = 17.2 Hz, 2H), 3.38 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9, 140.1, 137.1, 135.1, 133.6, 130.7, 130.2, 129.6, 128.6, 128.3, 128.0(3), 127.9, 127.6, 126.1, 125.7, 125.6, 124.0, 120.3, 111.7, 108.8, 55.2, 31.5 ppm; IR (film):1502, 1603, 3027 cm^{-1}; MS (ESI): m/z (%): 416 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{30}H_{25}NO$: C 86.71, H 6.06, N 3.37; found: C 86.77, H 6.01, N 3.49.



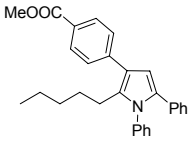
Ethyl 4-(2-benzyl-3,5-diphenyl-1*H*-pyrrol-1-yl)benzoate(5di): A yellow solid; m.p. 141-142 °C; Yield: 76 % (0.174 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83-7.87 (m, 2H), 7.49-7.52 (m, 2H), 7.33-7.37 (m, 2H), 7.21-7.25 (m, 1H), 7.07-7.17 (m, 8H), 7.00-7.03 (m, 2H), 6.88-7.00 (m, 2H), 6.67 (s, 1H), 4.34 (q, J = 7.2 Hz, 2H), 4.04 (s, 2H), 1.37 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.0, 143.3, 140.2, 136.6, 134.9, 132.9, 130.2, 130.0, 129.6, 128.8, 128.7, 128.5, 128.3, 128.1(2), 126.4, 126.1, 125.2, 110.4, 61.3, 31.4, 14.4 ppm; IR (film):1516, 1602, 1722, 3028 cm^{-1}; MS (ESI): m/z (%): 458 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{32}H_{27}NO_2$: C 84.00, H 5.95, N 3.06; found: C 84.13, H 5.90, N 3.11.



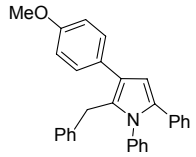
2-Benzyl-1-(2-chloroethyl)-3,5-diphenyl-1*H*-pyrrole(5dk): A yellow oil; Yield: 67% (0.124 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40-7.43 (m, 6H), 7.31-7.36 (m, 5H), 7.20-7.26 (m, 4H), 6.39 (d, *J* = 2.8 Hz, 1H), 4.24(s, 2H), 4.08 (td, *J* = 6.4 and 2.8 Hz, 2H), 3.14 (td, *J* = 6.4 and 2.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, CDCl3): δ = 139.8, 136.8, 134.2, 133.3, 129.1, 129.0, 128.8, 128.6, 128.1(2), 127.9, 127.6, 126.7, 126.0, 124.6, 110.1, 45.8, 41.8, 31.2 ppm; IR (film):1498, 1597, 3029 cm^{-1}; MS (ESI): m/z (%): 372 (100) and 374 (30) [*M* + H^{+}]; elemental analysis calcd (%) for $C_{25}H_{22}ClN$: C 80.74, H 5.96, N 3.77; found: C 80.66, H 6.03, N 3.68.



3-(4-Bromophenyl)-2-pentyl-1,5-diphenyl-1*H*-pyrrole(5ea): A yellow solid, m.p. 107-109 °C; Yield: 81 % (0.179 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.50-7.53 (m, 2H), 7.36-7.39 (m, 5H), 7.22-7.25 (m, 2H), 7.07-7.17 (m, 5H), 6.50 (s, 1H), 2.63 (t, *J* = 8.0 Hz, 2H), 1.21-1.29 (m, 2H), 1.02-1.10 (m, 4H), 0.71 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 136.3, 134.3, 133.2, 133.1, 131.6, 129.8, 129.1(2), 128.1(2), 128.0, 126.1, 121.6, 119.4, 109.4, 31.6, 29.6, 25.3, 22.1, 13.9 ppm; IR (film):1493, 1595, 3027 cm^{-1}; MS (ESI): m/z (%): 444 (100) and 446 (100) [*M* + H^{+}]; elemental analysis calcd (%) for $C_{27}H_{26}BrN$: C 72.97, H 5.90, N 3.15; found: C 72.88, H 5.92, N 3.18.

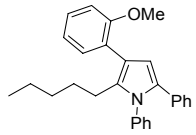


Methyl 4-(2-pentyl-1,5-diphenyl-1*H*-pyrrol-3-yl)benzoate(5fa): A white solid, m.p. 157-158 °C; Yield: 77 % (0.163 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.36-7.42 (m, 3H), 7.23-7.26 (m, 2H), 7.07-7.17 (m, 5H), 6.58 (s, 1H), 3.93 (m, 3H), 2.68 (t, *J* = 8.0 Hz, 2H), 1.25-1.32 (m, 2H), 1.04-1.09 (m, 4H), 0.70 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.5, 142.2, 139.1, 134.6, 134.0, 133.0(2), 129.2, 129.1, 128.2, 128.1, 127.7, 127.0, 126.2, 121.7, 109.4, 52.1, 31.6, 29.6, 25.5, 22.0, 13.9 ppm; IR (film):1499, 1599, 1712, 3027 cm^{-1}; MS (ESI): m/z (%): 424 (100) [*M* + H^{+}]; elemental analysis calcd (%) for $C_{29}H_{29}NO_2$: C 82.24, H 6.90, N 3.31; found: C 82.31, H 6.87, N 3.32.

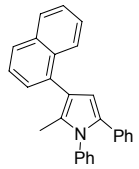


2-Benzyl-3-(4-methoxyphenyl)-1,5-diphenyl-1*H*-pyrrole(5ga): A white solid, m.p. 112-114 ^{o}C; Yield: 91 % (0.189 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41-7.44 (m, 2H), 7.06-7.22 (m, 11H), 6.94-6.96 (m, 2H), 6.88-6.91 (m, 4H), 6.62 (s, 1H), 4.01 (s, 2H), 3.79 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.0, 140.6, 139.2, 134.6, 133.2, 129.8, 129.4, 129.1, 129.0, 128.8, 128.3, 128.2, 128.1, 128.0, 127.7, 126.0, 125.9, 124.0, 114.1, 109.6, 55.4, 31.4 ppm; IR (film):1493, 1602, 3024 cm^{-1}; MS (ESI): m/z (%): 416 (100) [M + H^{+}]; elemental analysis calcd (%) for $C_{30}H_{25}NO$: C 86.71, H 6.06, N 3.37; found: C 86.59, H 6.15, N 3.41.

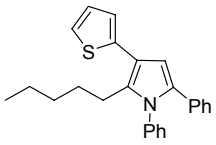
Data are in accordance with previously reported results.[3]



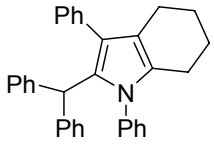
3-(2-Methoxyphenyl)-2-pentyl-1,5-diphenyl-1*H*-pyrrole(5ha): A yellow oil; Yield: 89 % (0.175 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.37 (m, 4H), 7.24-7.29 (m, 3H), 7.05-7.13 (m, 5H), 6.96-7.02 (m, 2H), 6.51 (s, 1H), 3.85 (s, 3H), 2.56 (t, J = 8.0 Hz, 2H), 1.09-1.16 (m, 2H), 0.96-1.01 (m, 4H), 0.65 (t, J = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1, 139.8, 134.1, 133.6, 133.3, 131.8, 129.1, 129.0, 128.1, 127.9, 127.6, 127.5, 126.4, 125.6, 120.6, 118.8, 111.4, 111.0, 55.6, 31.6, 29.1, 25.8, 22.1, 13.9 ppm; IR (film):1493, 1595, 3031 cm^{-1}; MS (ESI): m/z (%): 396 (100) [M + H^{+}]; elemental analysis calcd (%) for $C_{28}H_{29}NO$: C 85.02, H 7.39, N 3.54; found: C 85.13, H 7.27, N 3.58.



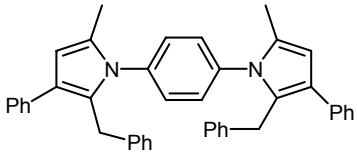
2-Methyl-3-(naphthalen-1-yl)-1,5-diphenyl-1*H*-pyrrole(5ia): A yellow solid, m.p. 115-116 ^{o}C; Yield: 79 % (0.142 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19-8.21 (m, 1H), 7.89-7.91 (m, 1H), 7.81 (dd, J = 6.8 and 2.8Hz, 1H), 7.47-7.55 (m, 4H), 7.34-7.43 (m, 3H), 7.29-7.31 (m, 2H),7.08-7.19 (m, 5H), 6.59 (s, 1H), 2.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.7, 135.1, 134.1, 133.5, 133.4, 132.8, 129.5, 129.2, 128.8, 128.4, 128.2, 127.9(2), 127.6, 127.0, 126.8, 125.9, 125.7(2), 125.6, 121.1, 111.8, 12.3 ppm; IR (film):1493, 1591, 3039 cm^{-1}; MS (ESI): m/z (%): 360 (100) [M + H^{+}]; elemental analysis calcd (%) for $C_{27}H_{21}N$: C 90.21, H 5.89, N 3.90; found: C 90.26, H 6.00, N 3.92.



2-Pentyl-1,5-diphenyl-3-(thiophen-2-yl)-1*H*-pyrrole(5ja): A yellow oil; Yield: 83 % (0.154 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.39 (m, 3H), 7.18-7.23 (m, 3H), 7.05-7.15 (m, 7H), 6.58 (s, 1H), 2.69 (t, *J* = 8.0 Hz, 2H), 1.33-1.41 (m, 2H), 1.12-1.16 (m, 4H), 0.75 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.5, 139.1, 134.1, 133.5, 133.0, 129.1(2), 128.1(2), 128.0, 127.4, 126.2, 122.7(2), 115.8, 109.3, 31.7, 29.6, 25.7, 22.2, 14.0 ppm; IR (film):1493, 1602, 3031, 3063 cm^{-1}; MS (ESI): m/z (%): 372 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{25}H_{25}NS$: C 80.82, H 6.78, N 3.77; found: C 80.73, H 6.81, N 3.69.



2-Benzhydryl-1,3-diphenyl-4,5,6,7-tetrahydro-1*H*-indole(6aa): A yellow oil; Yield: 61 % (0.134 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16-7.23 (m, 3H),7.04-7.06 (m, 9H), 6.91-6.95 (m, 4H), 6.86-6.88 (m, 4H), 5.51 (s, 1H), 2.38 (t, *J* = 4.8 Hz, 2H), 2.22 (t, *J* = 5.2 Hz, 2H), 1.71-1.77 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.9, 138.9, 136.8, 130.4, 129.6, 129.4, 129.2, 128.7, 128.5, 127.7, 127.5(2), 125.8, 125.3, 122.7, 116.9, 48.6, 23.8, 23.5, 22.9, 22.3 ppm; IR (film):1493, 1599, 3020 cm^{-1}; MS (ESI): m/z (%): 440 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{33}H_{29}N$: C 90.16, H 6.65, N 3.19; found: C 90.08, H 6.69, N 3.21.

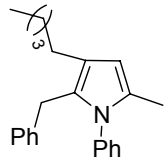


2-Benzyl-1-(4-(2-benzyl-5-methyl-3-phenyl-1*H*-pyrrol-1-yl)phenyl)-5-methyl-3-phenyl-1*H*-pyrrole(5dj): To a 10-mL flask, propargylic acetate **1d** (1.0 mmol), enoxysilane **2b** (2.0 mmol), chlorobenzene (4.0 mL) and $ZnCl_2$ (0.20 mmol) were successively added. The reaction was allowed to stir at 75 °C for 0.3 h, followed by the addition of primary amine **3i** (0.4 mmol). The reaction mixture was heated to reflux temperature for an additional 10 h until completion by TLC. Upon cooling to room temperature, the reaction mixture was then quenched with 1M HCl (2 mL), the organic and aqueous layers were separated, and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/100) to afford substituted pyrrole **5dj**. A yellow solid, m.p. 200-201 °C; yield 64 % (0.146 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (d, *J* = 7.2 Hz, 4H), 7.31-7.35 (m, 4H), 7.18-7.22 (m, 2H), 7.05 (s, 6H), 6.78-6.83 (m, 8H), 6.22 (s, 2H), 3.94 (s, 4H), 2.03 (s, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 138.0, 137.1, 129.5, 129.1, 128.6, 128.2, 128.1, 128.0, 127.4, 125.9, 125.7, 123.4, 107.2, 31.5, 12.9 ppm; IR (film):1516, 1598, 3023 cm^{-1}; MS (ESI): m/z (%): 569 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{42}H_{36}N_2$: C 88.69, H 6.38, N 4.93; found:

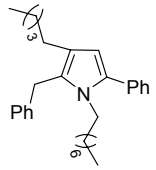
C 88.75, H 6.26, N 4.88.

General Procedure for the Synthesis of Substituted Pyrroles (5la-5ma)

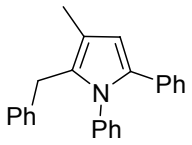
To a 10-mL flask, propargylic acetates **1** (0.5 mmol), enoxysilanes **2** (1.0 mmol), nitromethane (2.0 mL) and $ZnCl_2$ (0.05 mmol) were successively added. The reaction was allowed to stir at r.t. for 1 h, nitromethane was removed in vacuo, followed by the addition of chlorobenzene (2 mL) and amine **3** (1.0 mmol) was added directly to the reaction. The reaction mixture was heated to reflux temperature for an additional 3-10 h until completion by TLC. Upon cooling to room temperature, the reaction mixture was then quenched with 1M HCl (2 mL), the organic and aqueous layers were separated, and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/100) to afford corresponding substituted pyrroles.



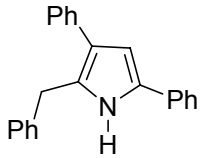
2-Benzyl-5-methyl-3-pentyl-1-phenyl-1*H*-pyrrole(5la): A yellow oil; Yield: 72 % (0.114 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.24-7.29 (m, 3H), 7.04-7.15 (m, 3H), 6.96-6.99 (m, 2H), 6.80-6.82 (m, 2H), 5.90 (s, 1H), 3.74 (s, 2H), 2.43 (t, *J* = 8.0 Hz, 2H), 1.54-1.62 (m, 2H), 1.32-1.36 (m, 4H), 1.26 (s, 3H), 0.89 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.0, 139.2, 128.8(2), 128.4, 128.2, 128.1, 127.6, 127.2, 125.6, 121.3, 106.7, 32.2, 31.2, 30.9, 26.5, 22.8, 14.2, 13.0 ppm; IR (film):1497, 1602, 3027 cm^{-1}; MS (ESI): m/z (%): 318 (100) [*M* + H$^+$]; elemental analysis calcd (%) for $C_{23}H_{27}N$: C 87.02, H 8.57, N 4.41; found: C 87.00, H 8.52, N 4.45.



2-Benzyl-1-octyl-3-pentyl-5-phenyl-1*H*-pyrrole(5lb): A yellow oil; Yield: 63 % (0.131 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32-7.37 (m, 4H), 7.23-7.29 (m, 3H), 7.13-7.19 (m, 3H), 6.08 (m, 1H), 4.01 (s, 2H), 3.69 (t, *J* = 7.8 Hz, 2H), 2.45 (t, *J* = 7.6 Hz, 2H), 1.55-1.61 (m, 2H), 1.18-1.34 (m, 8H), 0.93-1.13 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 3H), 0.84 (t, *J* = 7.6 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.6, 134.7, 133.4, 128.9, 128.6, 128.4, 128.1, 127.7, 126.5, 126.1, 122.3, 108.9, 44.6, 32.1, 31.8, 31.3, 31.1, 30.8, 29.1, 29.0, 26.7, 26.5, 22.7, 14.2 ppm; IR (film):1489, 1606, 3024 cm^{-1}; MS (ESI): m/z (%): 416 (100) [*M* + H$^+$]; elemental analysis calcd (%) for $C_{30}H_{41}N$: C 86.69, H 9.94, N, 3.37; found: C 86.72, H 9.83, N 3.31.



2-Benzyl-3-methyl-1,5-diphenyl-1*H*-pyrrole(5ma): A yellow oil; Yield: 71 % (0.115 g); ^{1}H NMR (400 MHz, $CDCl_3$,): δ = 7.15-7.24 (m, 5H), 7.08-7.12 (m, 3H), 7.02-7.05 (m, 3H), 6.89-6.95 (m, 4H), 6.33 (s, 1H), 3.84 (s, 2H), 2.16 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.4, 139.6, 133.5(2), 130.7, 129.0, 128.8, 128.3, 128.2, 128.0, 127.8, 127.5, 125.8, 125.7, 117.2, 110.9, 30.9, 11.7 ppm; IR (film):1493, 1595, 3027 cm^{-1}; MS (ESI): m/z (%): 324 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{24}H_{21}N$: C 89.12, H 6.54, N 4.33; found: C 89.08, H 6.52, N 4.37.



2-Benzyl-3,5-diphenyl-1*H*-pyrrole(7aa): Sodium hydride in mineral oil (60 %, 24 mg, 0.6 mmol) was added to a stirred solution of **5dk** (0.186 g, 0.5 mmol) in dry acetonitrile (3.0 mL) maintained in a nitrogen atmosphere. The solution was heated at 50 ^{o}C for 2 h and 6 M hydrochloric acid (0.84 mL, 5 mmol) was added dropwise. After an additional 6 h, a solution of sodium acetate (494 mg, 6 mmol) in water (1.0 mL) was added and the solution was heated at reflux temperture for 0.5 h. Upon cooling to room temperature, the solution was extracted with ether (3×5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/10) to afford N-H pyrrole **7aa**. A white solid, m.p. 85-86 ^{o}C; yield 61% (0.113 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.02 (s, 1H), 7.46-7.48 (m, 2H), 7.30-7.41 (m, 8H), 7.21-7.27 (m, 4H), 7.13-7.18 (m, 1H), 6.67 (d, J = 2.8 Hz, 1H), 4.19 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.3, 136.7, 132.6, 131.1, 129.0(2), 128.8, 128.6, 127.9, 127.7, 126.8, 126.3, 125.9, 124.2, 123.7, 106.6, 32.8 ppm; IR (film):1489, 1599, 3023, 3423 cm^{-1}; MS (ESI): m/z (%): 310 (100) [M + H$^+$]; elemental analysis calcd (%) for $C_{23}H_{19}N$: C 89.28, H 6.19, N 4.53; found: C 89.40, H 6.09, N 4.49.

General Procedure for the Synthesis of *N*-bridgehead Pyrroles (8aa-8ea)

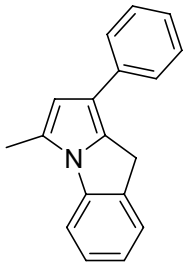
A. the synthesis of the γ-alkynyl ketone 4

To a 10-mL flask, propargylic acetates **1** (0.5 mmol), enoxysilanes **2** (1.0 mmol), chlorobenzene (2.0 mL) and $ZnCl_2$ (0.05 mmol) were successively added. The reaction was allowed to stir at 75 ^{o}C for 0.3 h. The solvent was removed under reduced pressure by an aspirator, and then the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/20) to afford the γ-alkynyl ketone **4**.

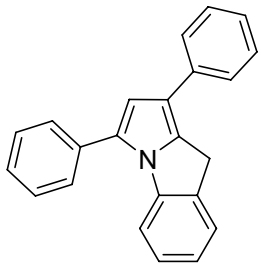
B. the synthesis of *N*-bridgehead pyrroles 8

To a stirred solution of $Pd(PPh_3)_4$ (0.025 mmol) , CuI (0.025 mmol) in anhydrous Et_3N (3 mL), amines **3** (0.5 mmol) and the γ-alkynyl ketone **4** (0.5 mmol) in Et_3N (2 mL) and THF (1 mL) were added. The reaction mixture was heated at reflux temperature under argon atmosphere for 2 h and then the solvent was removed under reduced pressure, followed by the addition of chlorobenzene (2.0 mL) and $ZnCl_2$ (0.05 mmol). The reaction was sitred at reflux until completion by TLC.

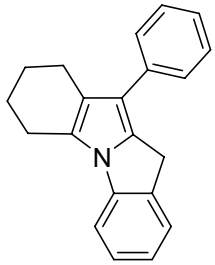
Upon cooling to room temperature, the reaction mixture was then quenched with 1M HCl (2 mL), the organic and aqueous layers were separated, and the aqueous layer was extracted with Et_2O (3×5 mL). The combined organic layers were dried over $MgSO_4$ and filtered. The filtrate was concentrated in vacuo, and then the residue was purified by silica gel column chromatography (EtOAc/hexane = 1/100) to afford corresponding *N*-bridgehead pyrroles.



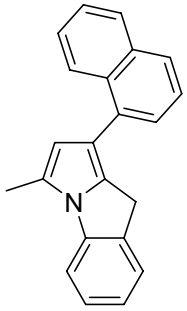
3-Methyl-1-phenyl-9*H*-pyrrolo[1,2-*a*]indole(8aa): A yellow solid, m.p. 145-146 ^{o}C ; Yield: 63 % (0.077g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.53-7.55 (m, 2H), 7.36-7.45 (m, 4H), 7.28-7.32 (m, 1H), 7.14-7.18 (m, 1H), 7.08-7.10 (m, 1H), 6.38 (d, *J* = 0.8 Hz, 1H), 4.03 (s, 2H), 2.61 (d, *J* = 0.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 135.9, 135.0, 131.0, 128.8, 127.6, 126.1, 125.1, 125.0, 123.7, 122.9, 116.3, 110.8, 109.7, 30.4, 13.5 ppm; IR (film):1489, 1602, 3027 cm^{-1}; MS (ESI): m/z (%): 246 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{18}H_{15}N$: C 88.13, H 6.16, N 5.71; found: C 88.19, H 6.09, N 5.66.



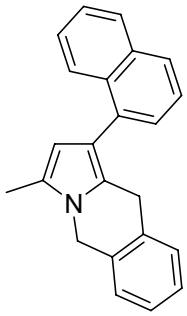
1,3-Diphenyl-9*H*-pyrrolo[1,2-*a*]indole(8ba): A white solid, m.p. 171-172 ^{o}C; Yield: 61 % (0.094 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.59-7.63 (m, 4H), 7.38-7.49 (m, 6H), 7.19-7.25 (m, 1H), 7.07-7.15 (m, 3H), 6.68 (s, 1H), 4.14 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ=141.4, 135.5, 135.1, 133.3, 133.0, 129.2, 128.9, 128.5, 127.7, 127.3, 125.9, 125.4, 125.3, 123.3, 117.7, 112.1, 112.0, 30.4 ppm; IR (film):1487, 1602, 3023 cm^{-1}; MS (ESI): m/z (%): 308 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{23}H_{17}N$: C 89.87, H 5.57, N 4.56; found: C 89.81, H 5.63, N 4.51.



11-Phenyl-2,3,4,10-tetrahydro-1*H*-indolo[1,2-*a*]indole(8ca): A yellow solid, m.p. 160-161 ^{o}C; Yield: 59 % (0.084 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* =7.6 Hz, 2H), 7.38-7.41 (m, 3H), 7.25-7.34 (m, 2H), 7.27 (dd, *J* = 7.2 and 7.6 Hz, 1H), 7.05 (dd, *J* = 7.2 and 7.6 Hz, 1H), 4.01 (s, 2H), 3.02 (t, *J* = 6.0 Hz, 2H), 2.78 (t, *J* = 6.0 Hz, 2H), 1.94-1.98 (m, 2H), 1.81-1.86 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 141.7, 136.4, 134.6, 130.9, 128.6, 127.5, 127.0, 125.9, 125.1, 122.8, 122.5, 120.7, 115.6, 110.5, 29.9, 24.4, 23.8, 23.2, 23.1 ppm; IR (film):1491, 1603, 3031 cm^{-1}; MS (ESI): 286 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{21}H_{19}N$: C 88.38, H 6.71, N 4.91; found: C 88.27, H 6.80, N 4.78.



3-Methyl-1-(naphthalen-1-yl)-9*H*-pyrrolo[1,2-*a*]indole(8da): A yellow oil; Yield: 65 % (0.096 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ=8.21(dd, *J* = 7.2 and 2.4 Hz, 1H), 7.89 (dd, *J* = 8.0 and 2.4 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.45-7.55 (m, 5H), 7.29-7.37 (m, 2H), 7.06-7.10 (m, 1H), 6.31 (d, *J* = 0.8 Hz, 1H), 3.82 (s, 2H), 2.68 (d, *J* = 0.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 142.1, 135.1, 134.6, 134.1, 132.4, 131.7, 128.5, 127.5, 126.6(2), 126.3, 126.1, 125.7, 123.0, 122.8, 115.8, 113.7, 110.8, 29.5, 13.5 ppm; IR (film):1486, 1599, 3034 cm^{-1}; MS (ESI): m/z (%): 296 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{22}H_{17}N$: C 89.46, H 5.80, N 4.74; found: C 89.39, H 5.84, N 4.75.



3-Methyl-1-(naphthalen-1-yl)-5,10-dihydropyrrolo[1,2-*b*]isoquinoline(8ea): A yellow oil; Yield: 63 % (0.097 g); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.39-7.53 (m, 4H), 7.29-7.31 (m, 1H), 7.19-7.26 (m, 2H),7.13-7.15 (m, 1H), 6.17 (d, *J* = 0.8 Hz, 1H), 5.06 (s, 2H), 3.94 (s, 2H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 135.3, 134.1, 133.9, 132.6, 132.4, 128.5, 128.3, 127.5, 127.4, 127.1, 126.5, 126.4(2), 126.1, 125.7, 124.3, 116.7, 109.0, 45.8, 28.3, 12.1 ppm; IR (film):1488, 1589, 3039 cm^{-1}; MS (ESI): m/z (%): 310 (100) [$M + H^+$]; elemental analysis calcd (%) for $C_{23}H_{19}N$: C 89.28, H 6.19, N 4.53; found: C 89.33, H 6.03, N 4.51.

References

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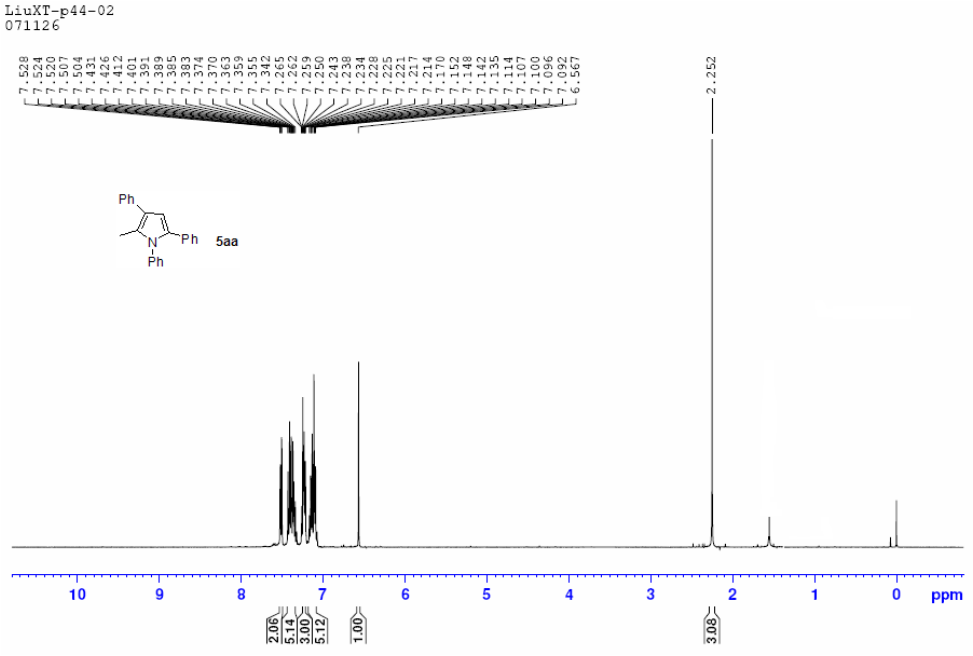
3 Y.-J. Bian, X.-Y. Liu, K.-G. Ji, X.-Z. Shu, L.-N. Guo and Y.-M. Liang, *Tetrahedron* 2009, **57**, 1424-1429.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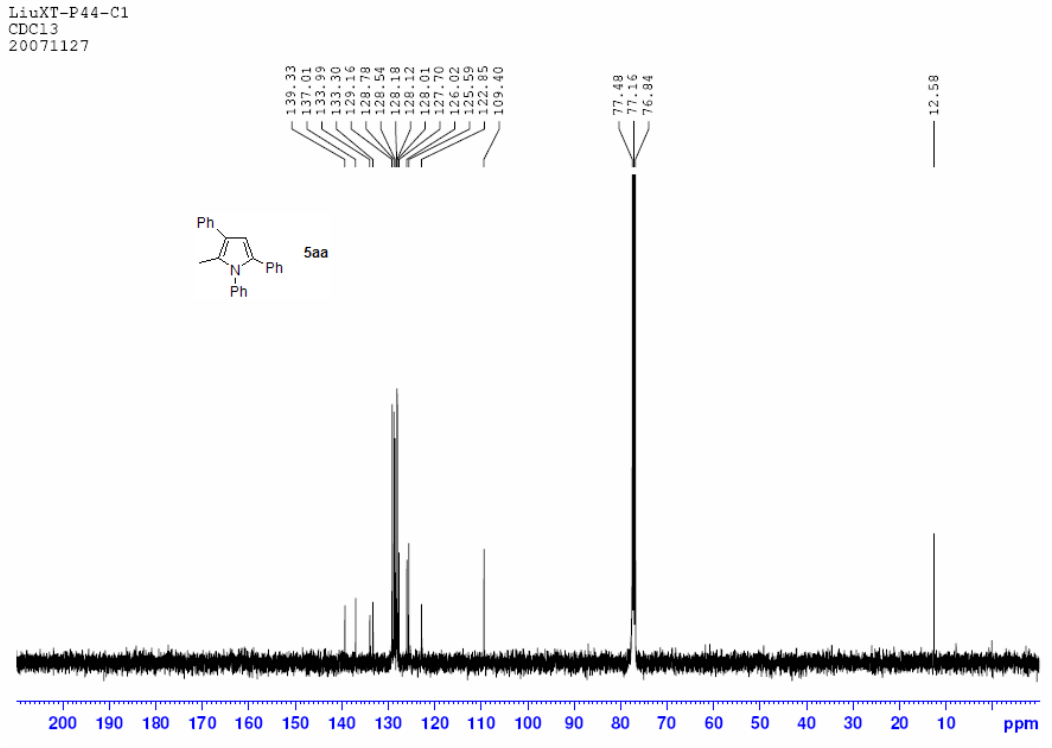
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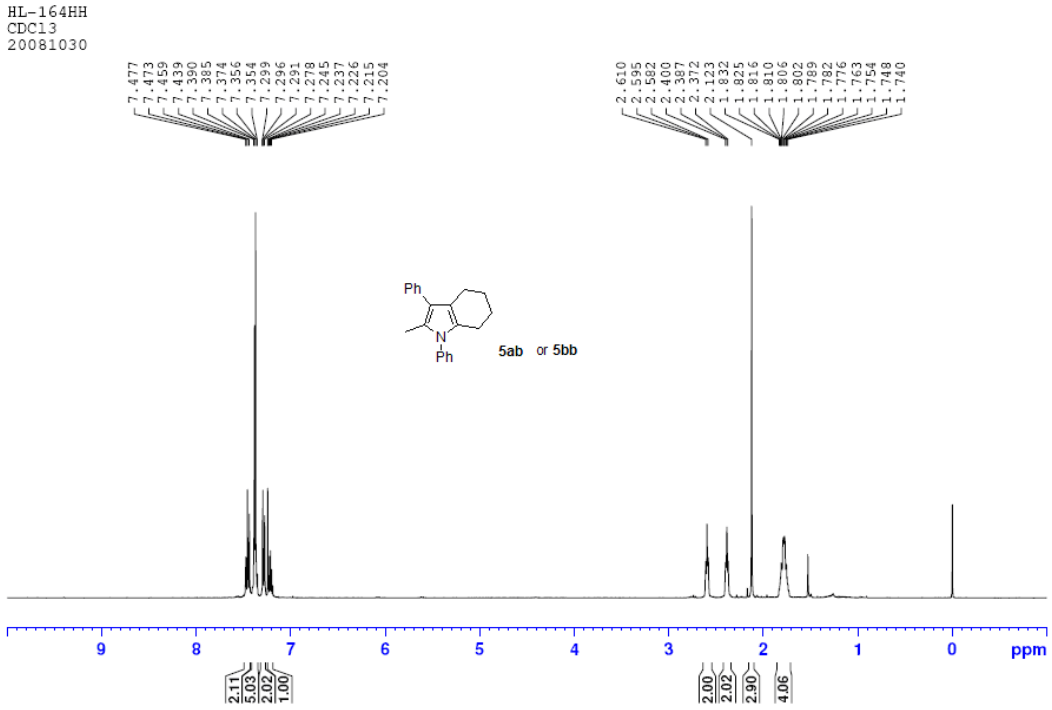
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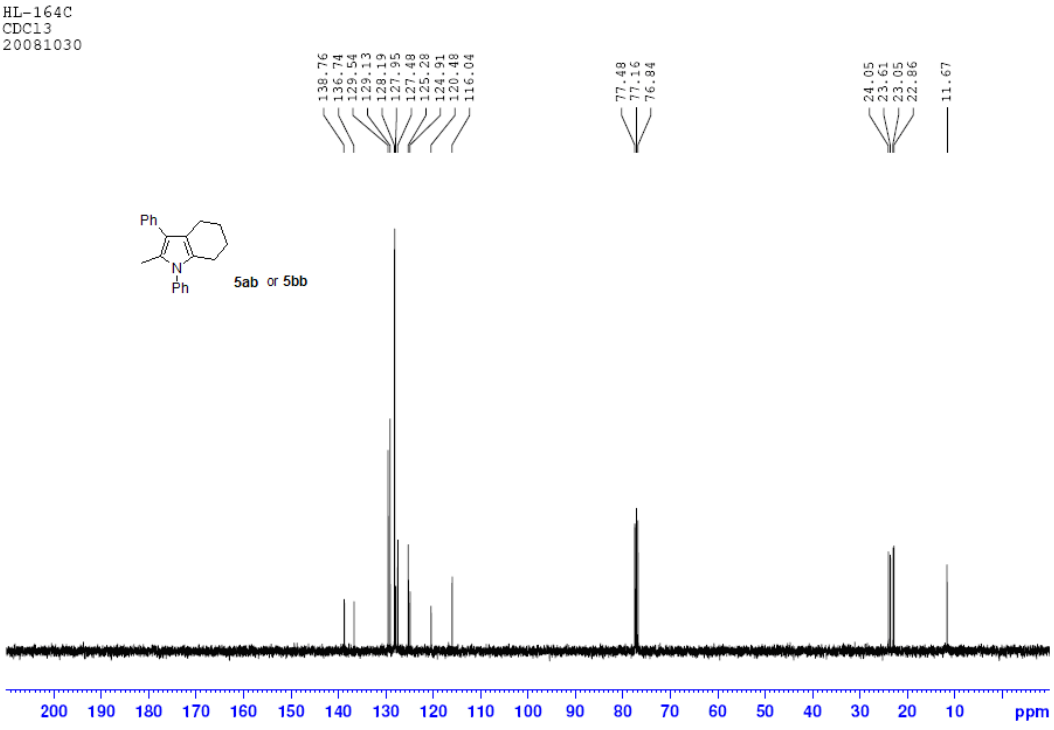
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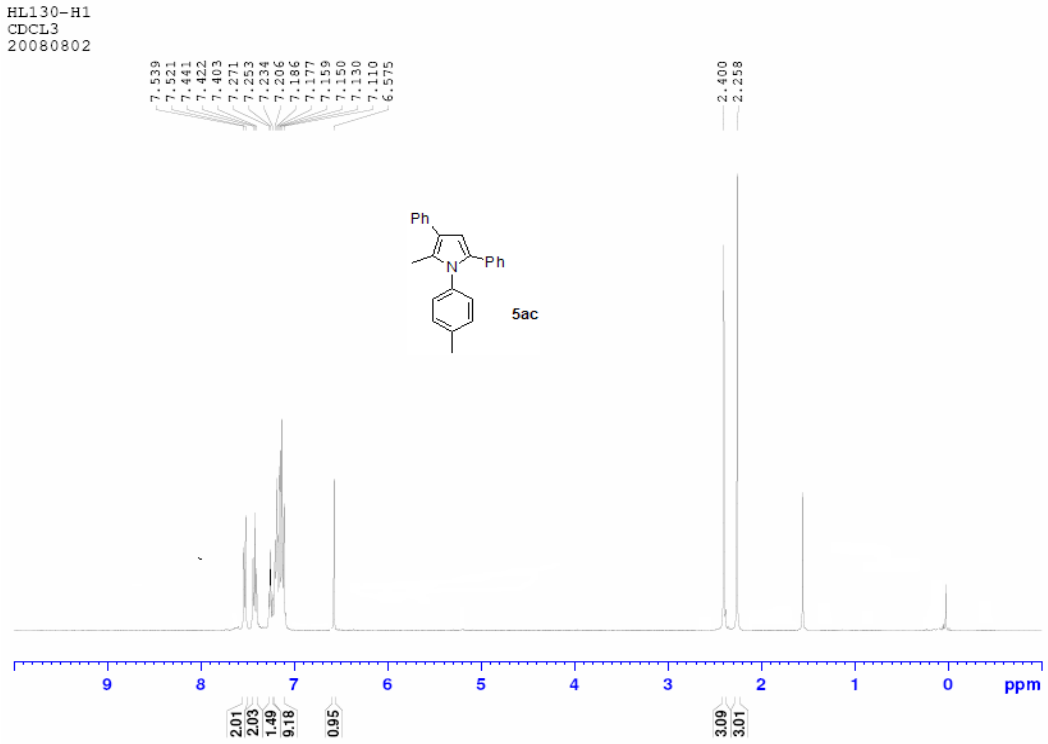
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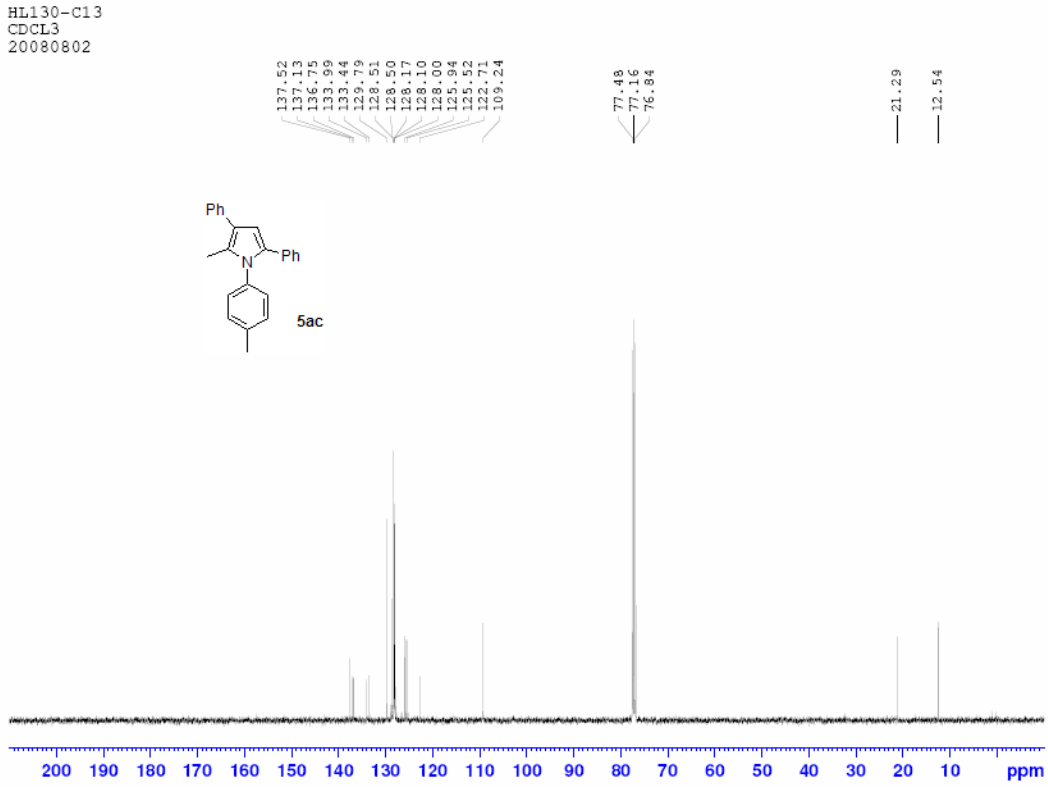
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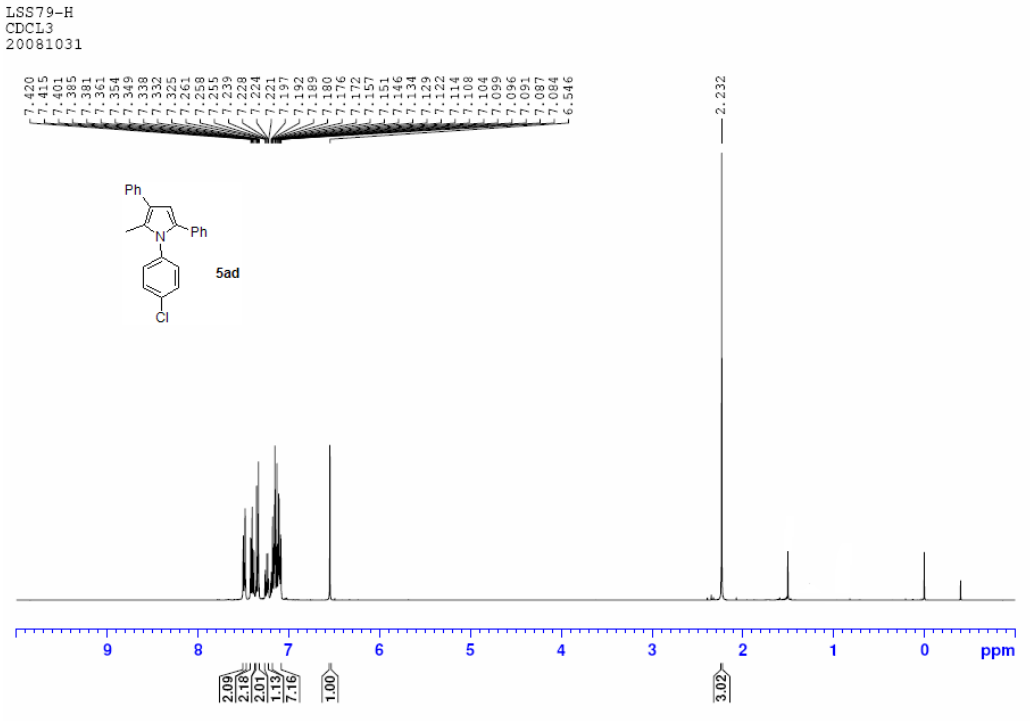
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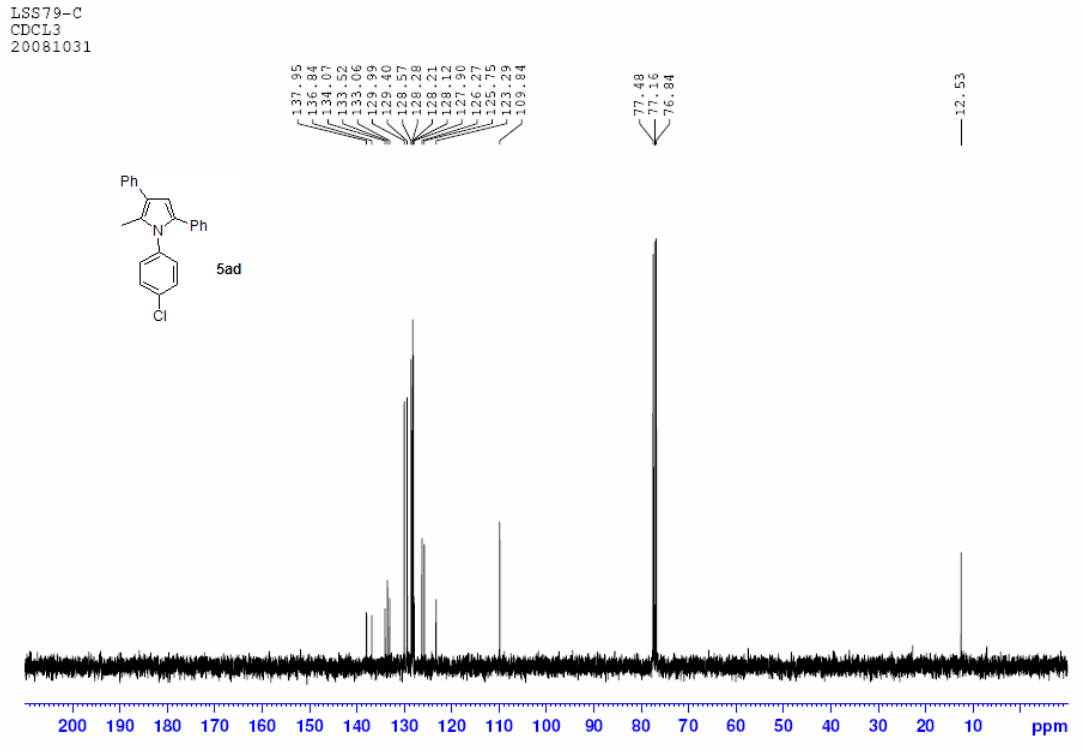
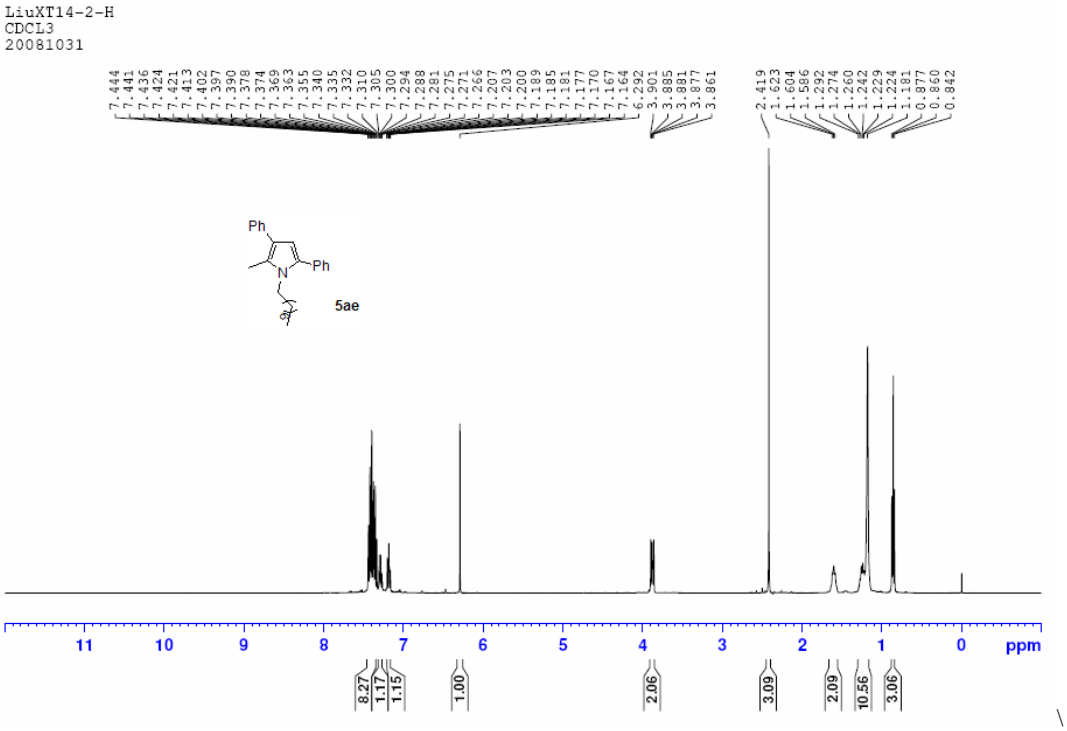
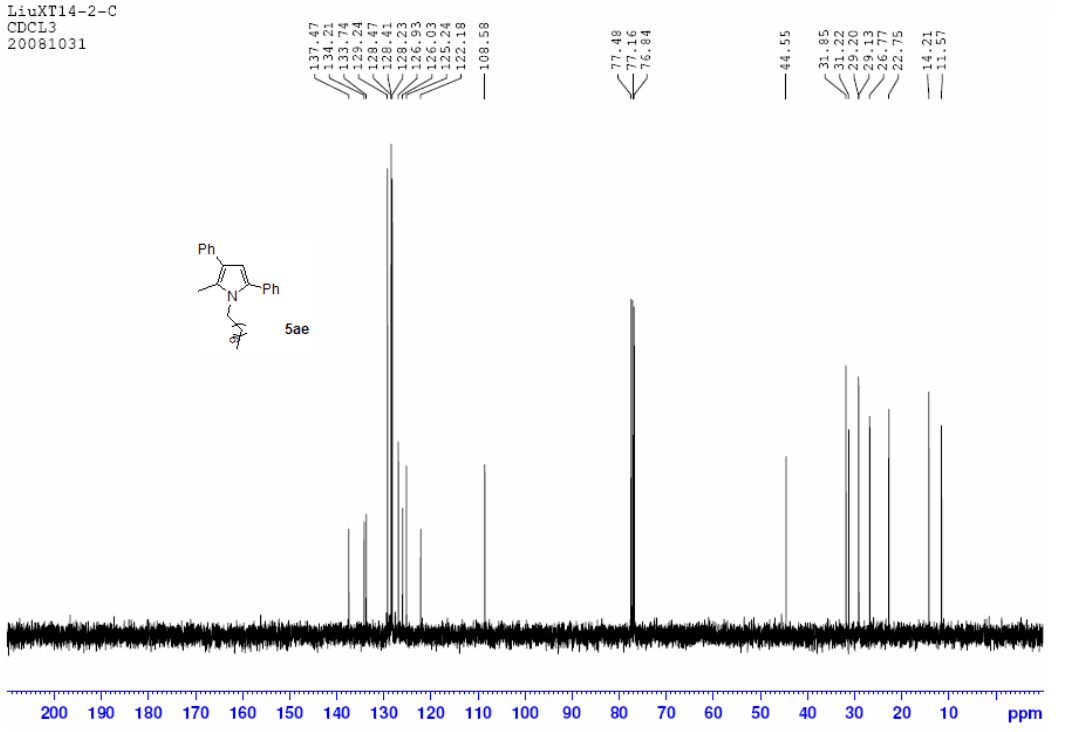
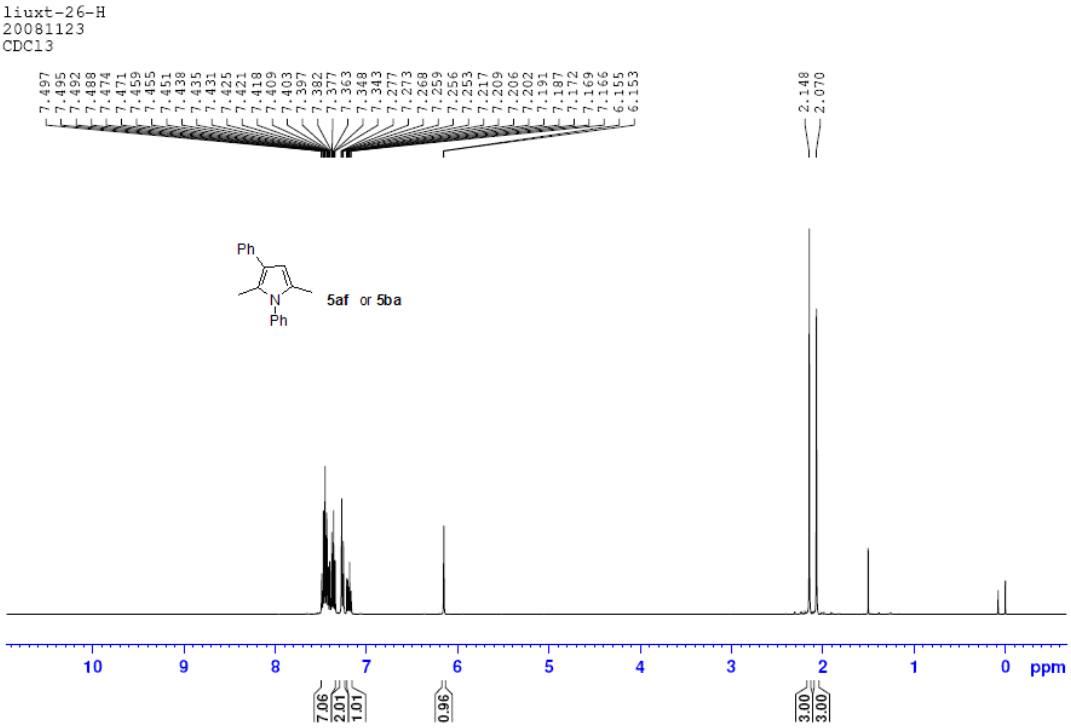
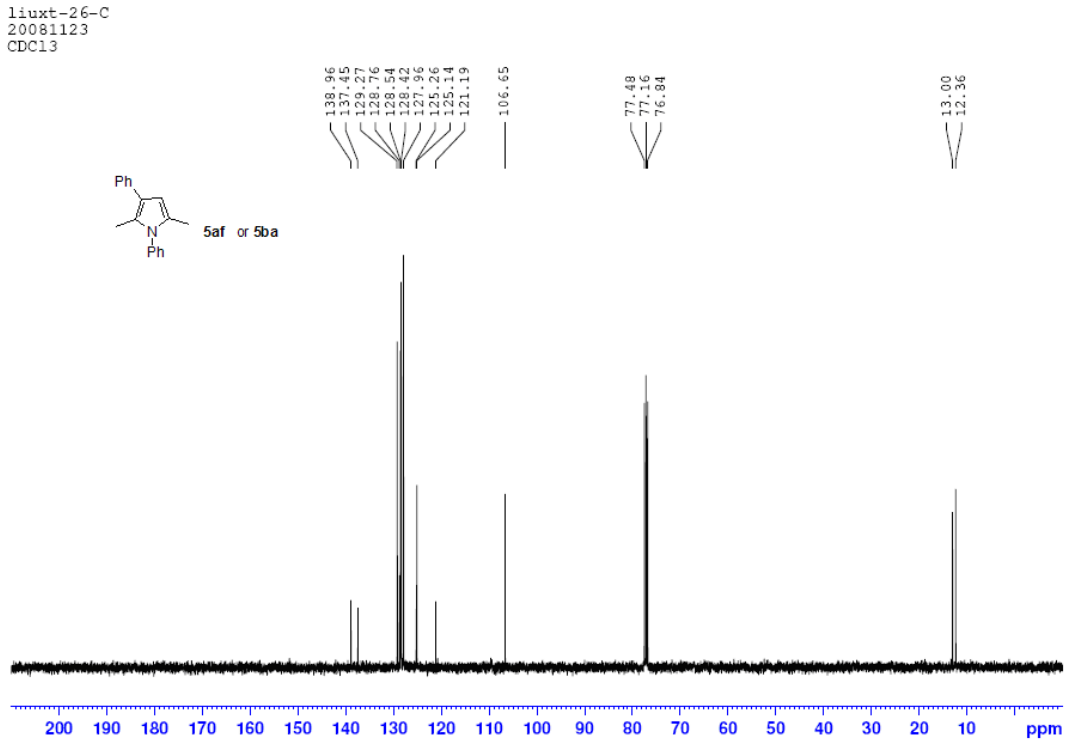
3
2
1
0
ppm
2.09
2.18
2.01
1.13
7.16
1.00
3.02

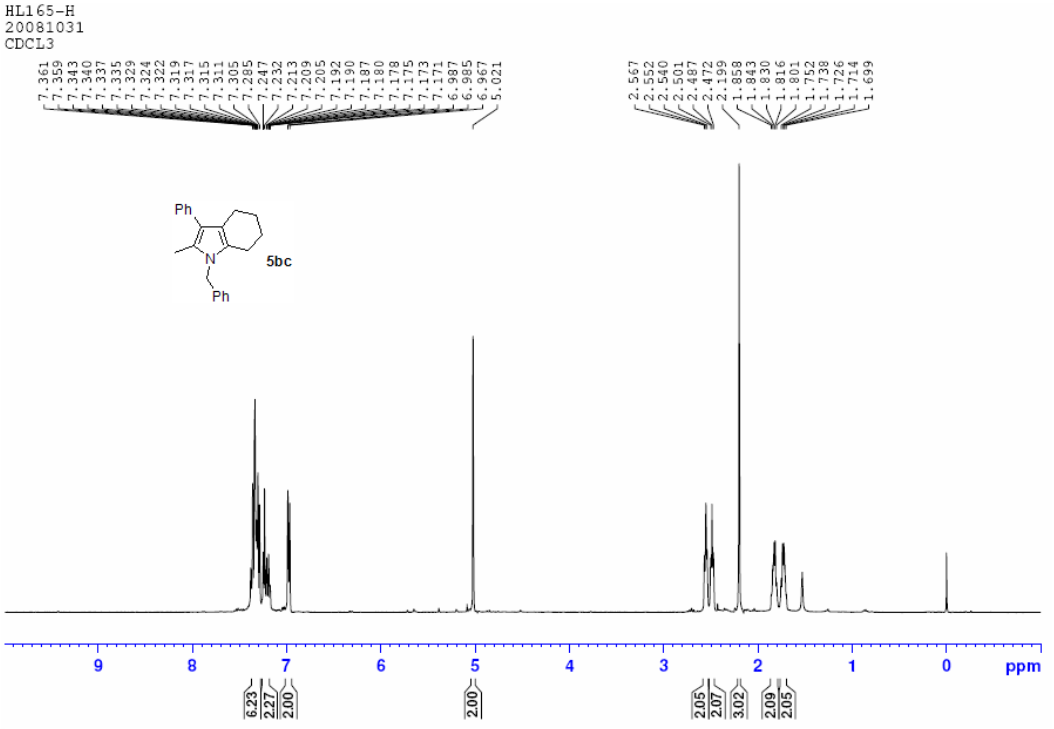

LSS79-C
CDCL3
20081031
137.95
136.84
134.07
133.52
133.06
129.99
129.40
128.57
128.28
128.21
128.12
127.90
126.27
125.75
123.29
109.84
77.48
77.16
76.84
12.53
Ph
Ph
N
Cl
5ad
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

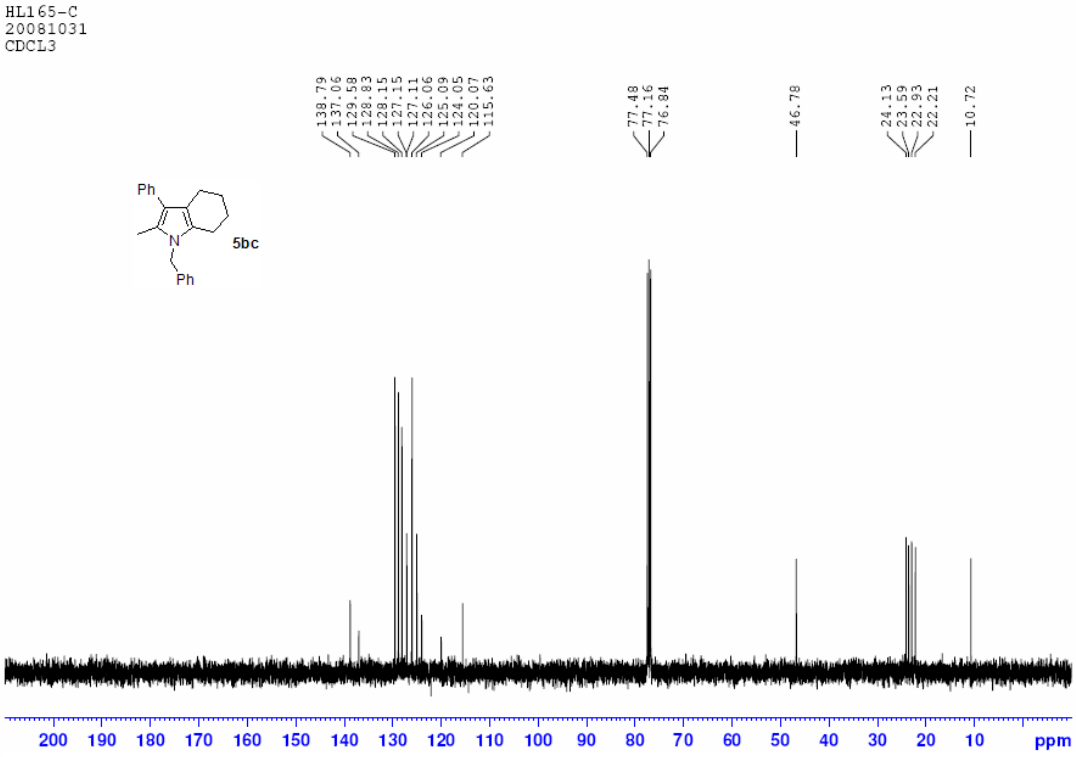

LiuXT14-2-H
CDCL3
20081031
7.444
7.441
7.436
7.424
7.421
7.413
7.402
7.397
7.390
7.378
7.374
7.369
7.363
7.355
7.340
7.335
7.332
7.310
7.305
7.300
7.294
7.288
7.281
7.275
7.271
7.266
7.207
7.203
7.200
7.189
7.185
7.181
7.177
7.170
7.167
7.164
6.292
3.901
3.885
3.881
3.877
3.861
2.419
1.623
1.604
1.586
1.292
1.274
1.260
1.242
1.229
1.224
1.181
0.877
0.860
0.842
Ph
Ph
N
5ae
11
10
9
8
7
6
5
4
3
2
1
0
ppm
8.27
1.17
1.15
1.00
2.06
3.09
2.09
10.56
3.06


LiuXT14-2-C
CDCL3
20081031
137.47
134.21
133.74
129.24
128.47
128.41
128.23
126.93
126.03
125.24
122.18
108.58
77.48
77.16
76.84
44.55
31.85
31.22
29.20
29.13
26.77
22.75
14.21
11.57
Ph
Ph
N
5ae
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

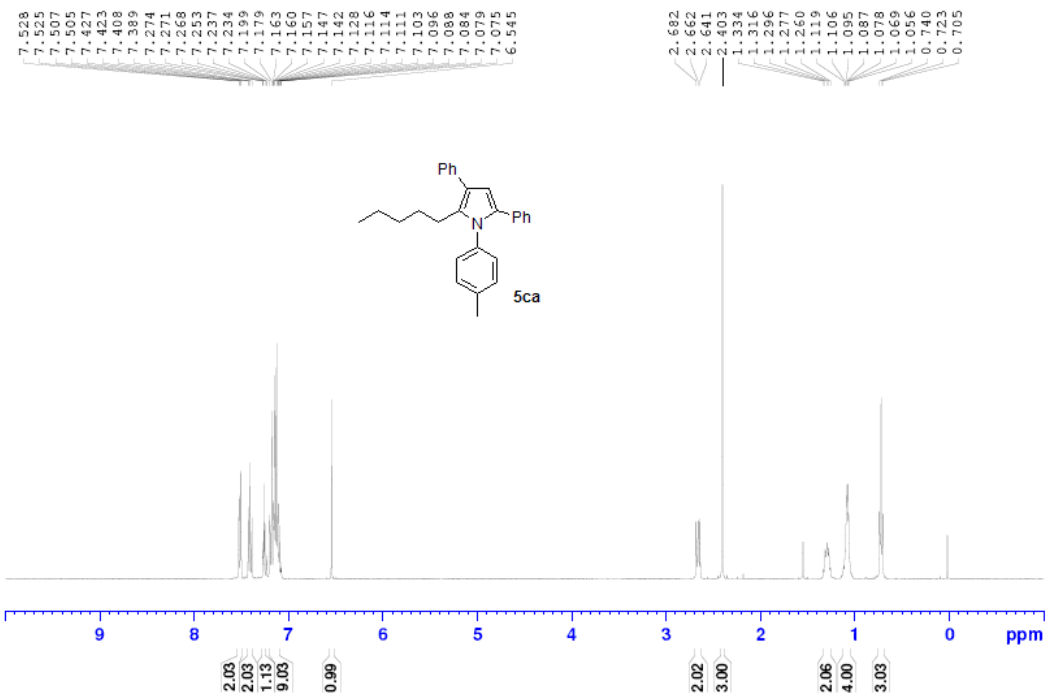

liuxt-26-H
20081123
CDCl3
7.497
7.495
7.492
7.488
7.474
7.471
7.459
7.455
7.451
7.438
7.435
7.431
7.425
7.421
7.418
7.409
7.403
7.397
7.382
7.377
7.363
7.348
7.343
7.277
7.273
7.268
7.259
7.256
7.253
7.217
7.209
7.206
7.202
7.191
7.187
7.172
7.169
7.166
6.155
6.153
2.148
2.070
Ph
N
Ph
5af or 5ba
10
9
8
7
6
5
4
3
2
1
0
ppm
7.06
2.01
1.01
0.96
3.00
3.00


liuxt-26-C
20081123
CDCl3
138.96
137.45
129.27
128.76
128.54
128.42
127.96
125.26
125.14
121.19
106.65
77.48
77.16
76.84
13.00
12.36
Ph
N
Ph
5af or 5ba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

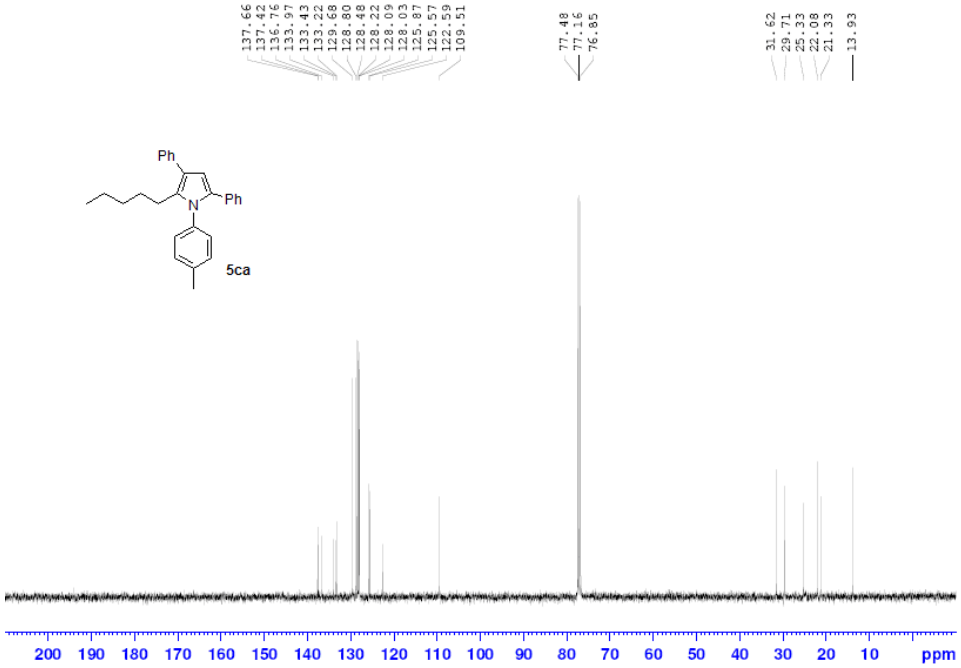

HL165-H
20081031
CDCL3
7.361
7.359
7.343
7.340
7.337
7.335
7.329
7.324
7.322
7.319
7.317
7.315
7.311
7.305
7.285
7.247
7.232
7.213
7.209
7.205
7.192
7.190
7.187
7.180
7.178
7.175
7.173
7.171
6.987
6.985
6.967
5.021
2.567
2.552
2.540
2.501
2.497
2.472
2.199
1.858
1.843
1.830
1.816
1.801
1.752
1.738
1.726
1.714
1.699
Ph
N
Ph
5bc
9
8
7
6
5
4
3
2
1
0
ppm
6.23
2.27
2.00
2.00
2.05
2.07
3.02
2.09
2.05

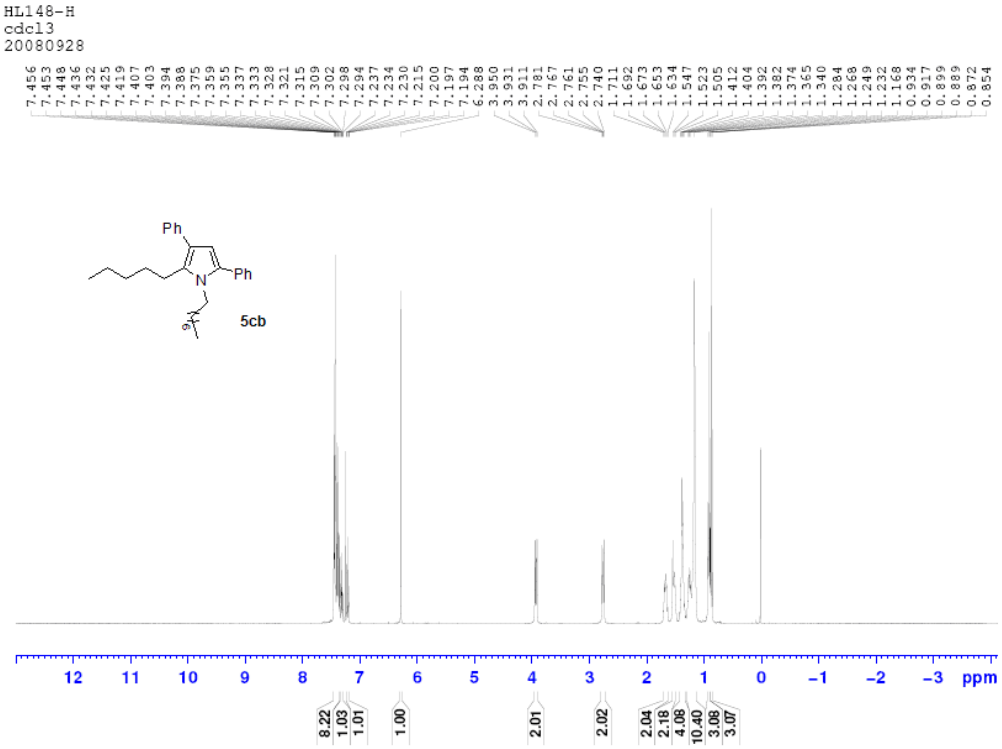

HL165-C
20081031
CDCL3
138.79
137.06
129.58
128.83
128.15
127.15
127.11
126.06
125.09
124.05
120.07
115.63
77.48
77.16
76.84
46.78
24.13
23.59
22.93
22.21
10.72
Ph
N
Ph
5bc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

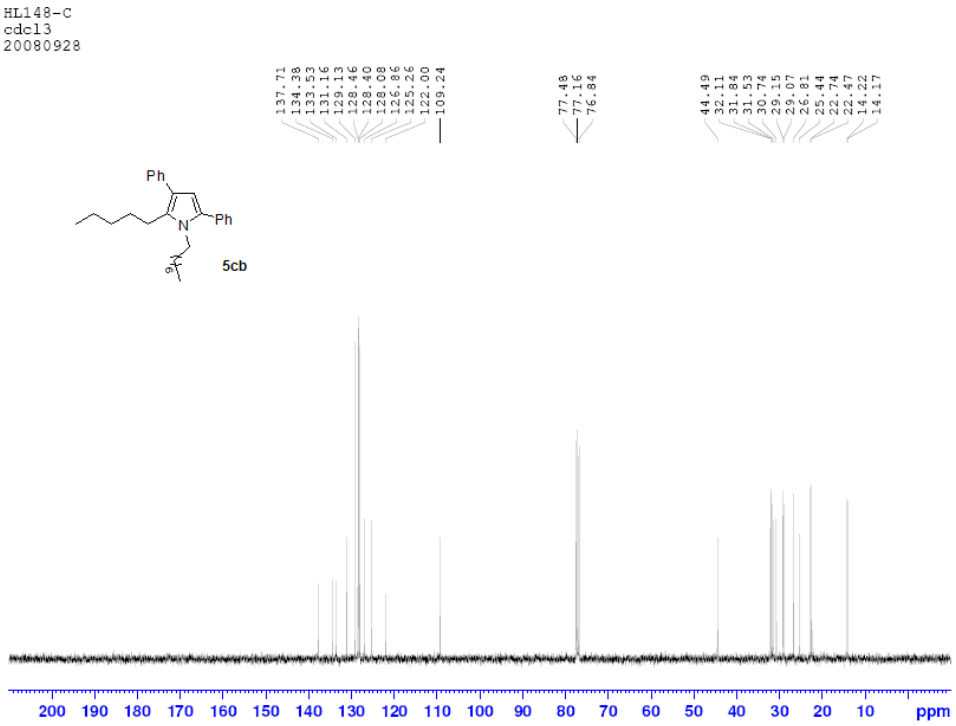
HL135-H1
20080901
CDCL3

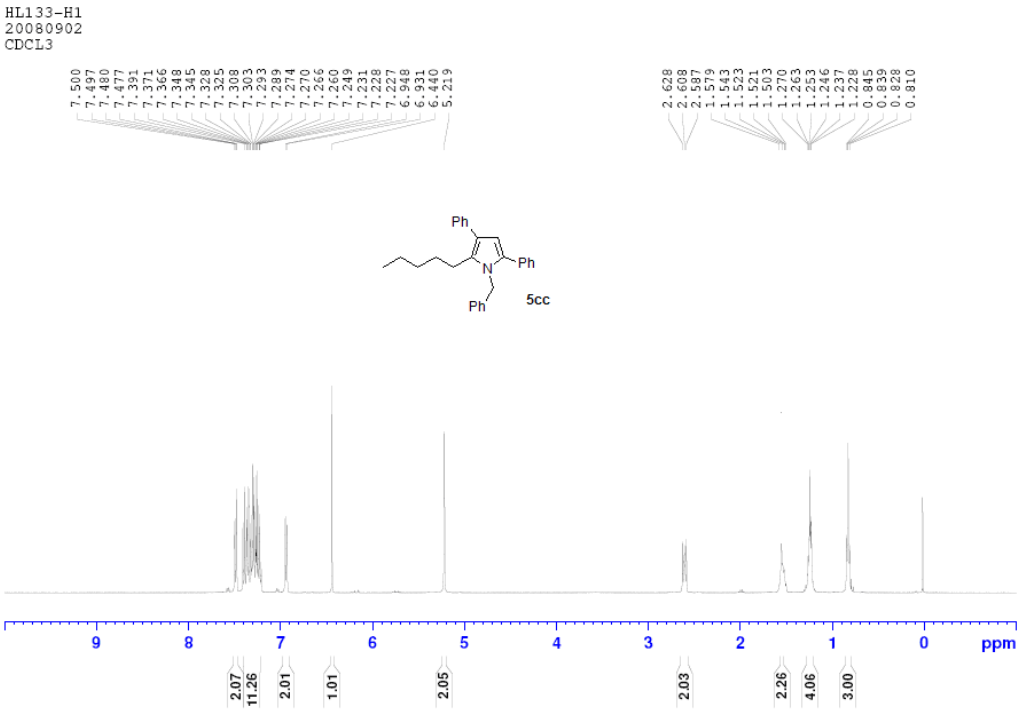


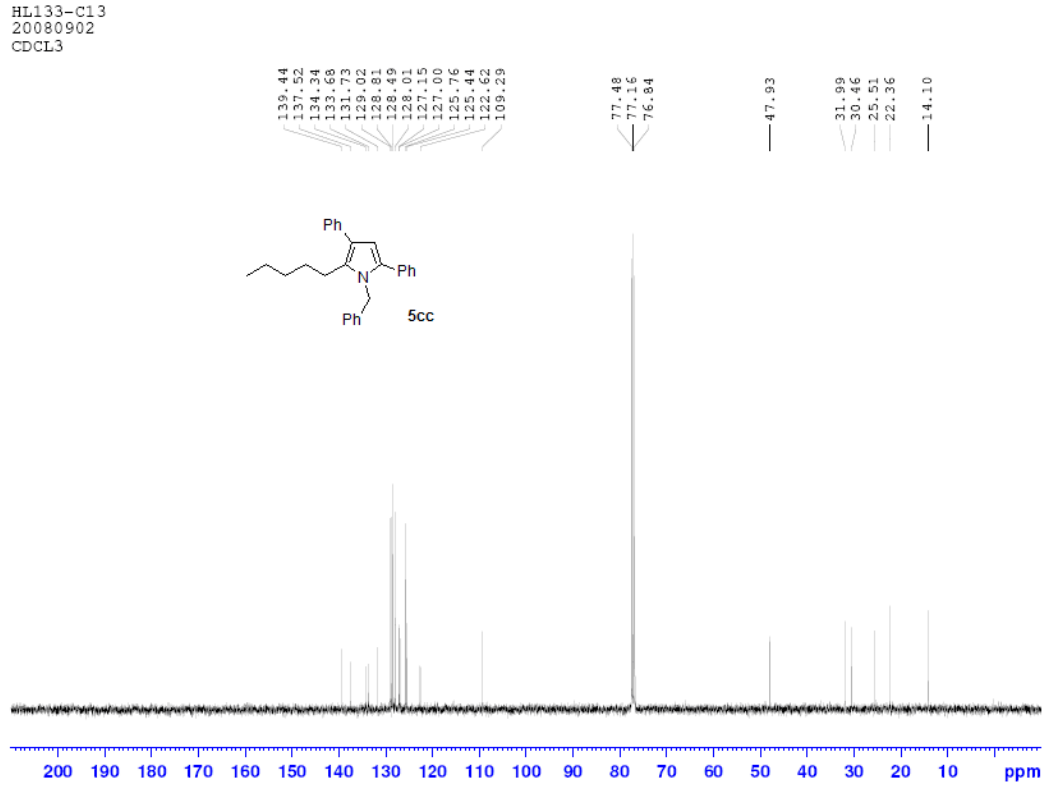
HL135-C13
20080901
CDCL3

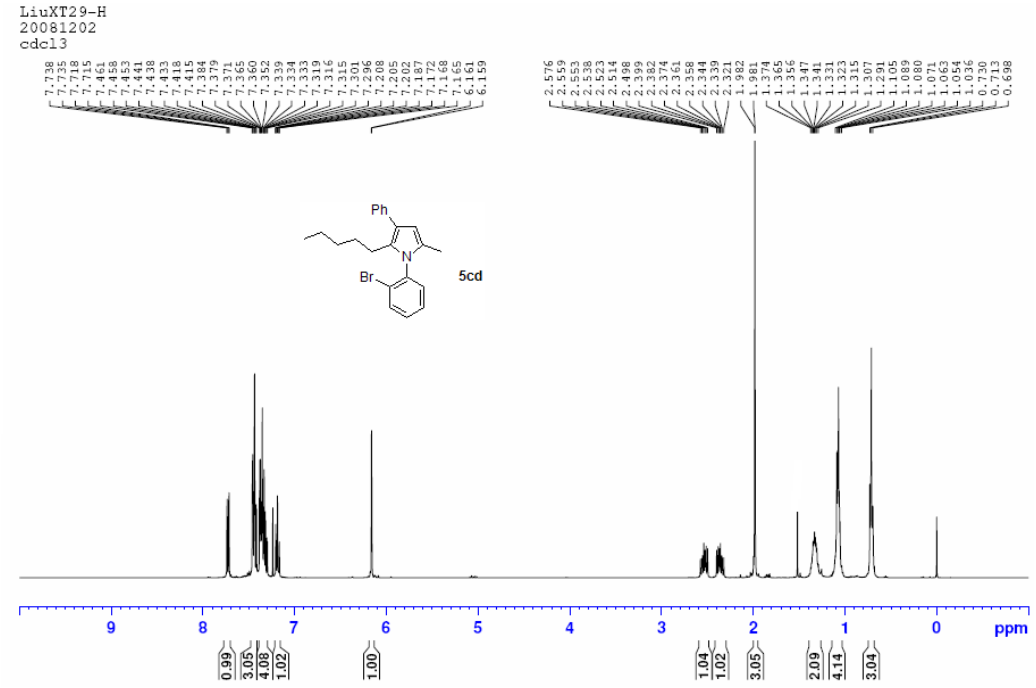


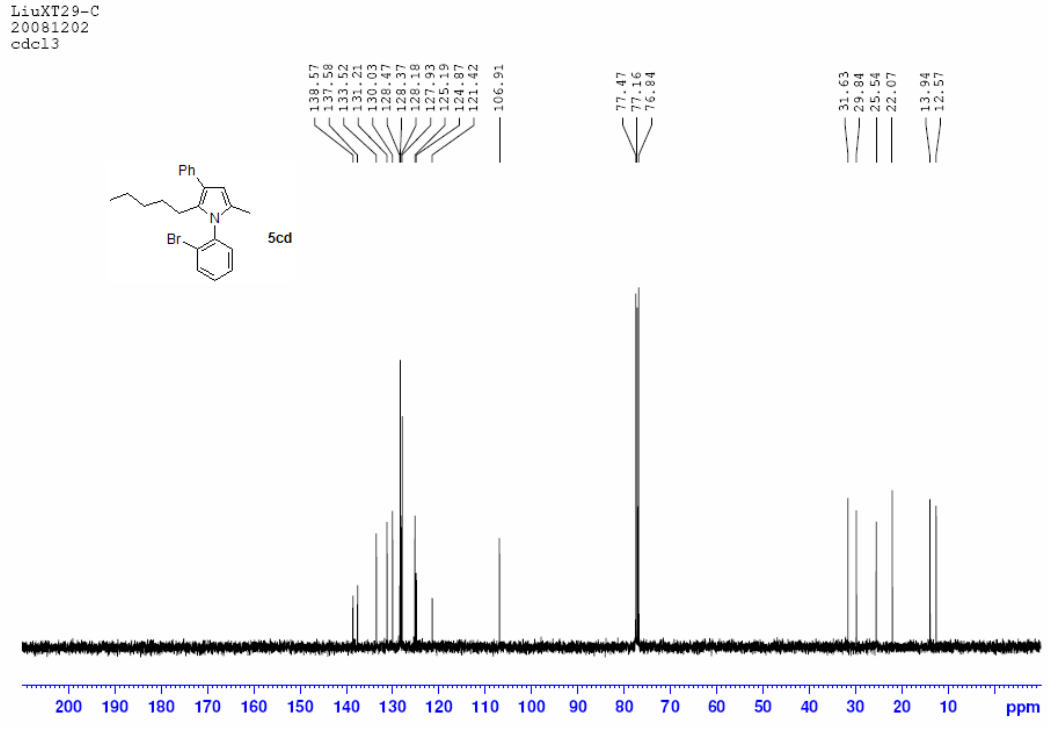

HL148-H
cdcl3
20080928
Ph
Ph
5cb
ppm

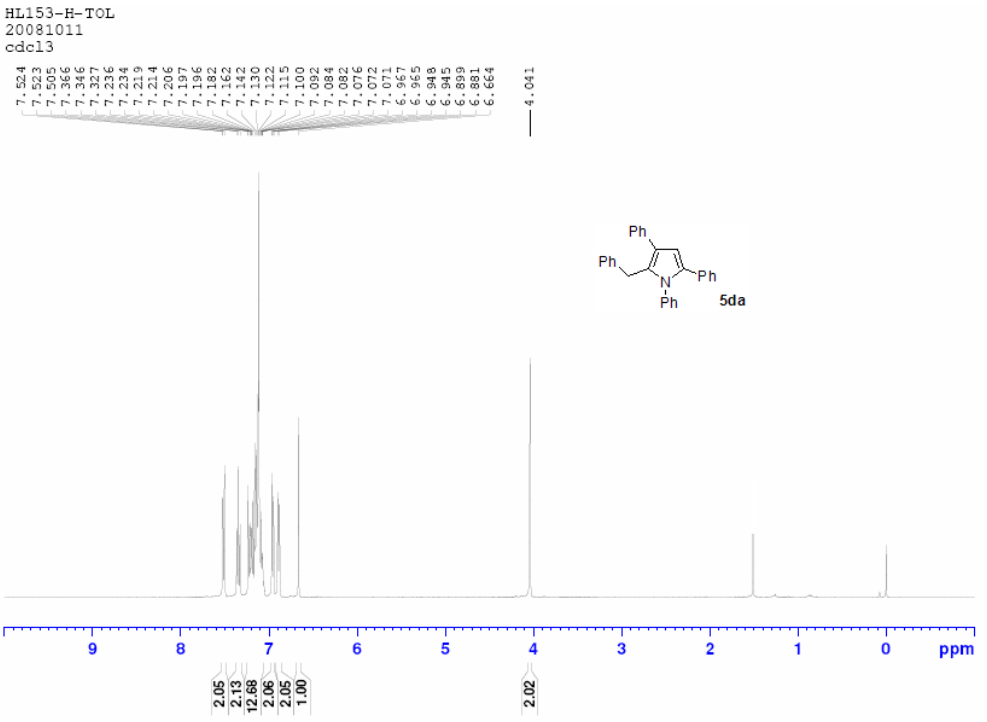

HL148-C
cdcl3
20080928
Ph
Ph
5cb
ppm

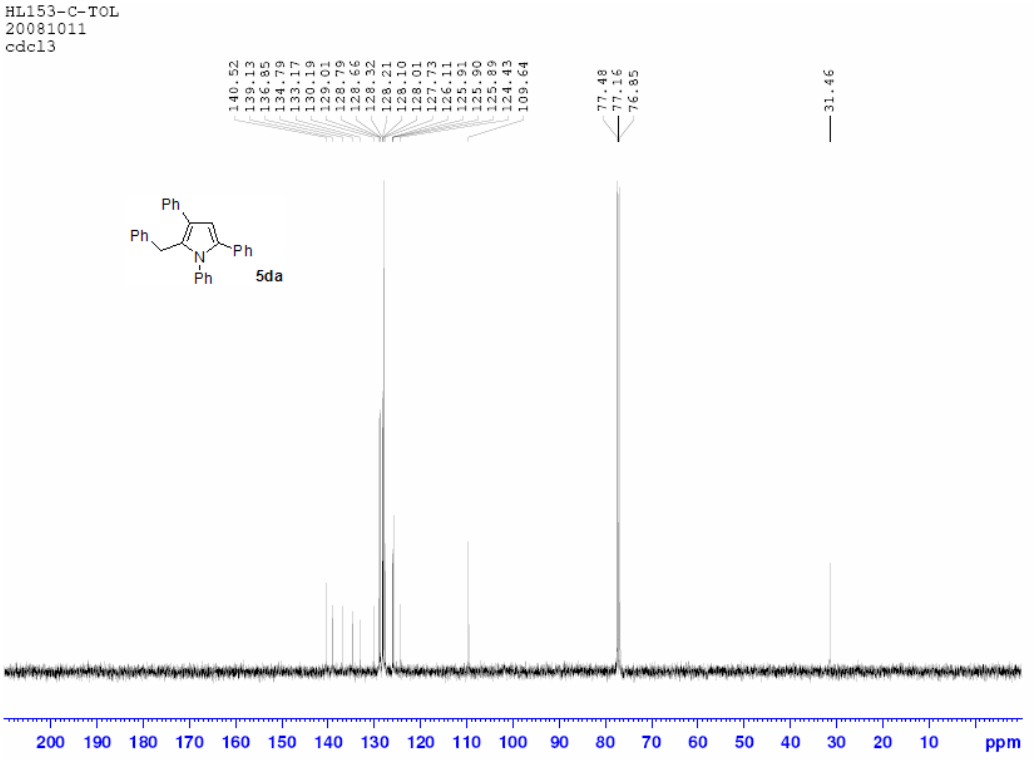

HL133-H1
20080902
CDCL3
7.500
7.497
7.480
7.477
7.391
7.371
7.366
7.348
7.345
7.328
7.325
7.308
7.303
7.293
7.289
7.274
7.270
7.266
7.260
7.249
7.231
7.228
7.227
6.948
6.931
6.440
5.219
2.628
2.608
2.587
1.579
1.543
1.523
1.521
1.503
1.270
1.263
1.253
1.246
1.237
1.228
0.845
0.839
0.828
0.810
Ph
Ph
N
Ph
5cc
9
8
7
6
5
4
3
2
1
0
ppm
2.07
11.26
2.01
1.01
2.05
2.03
2.26
4.06
3.00

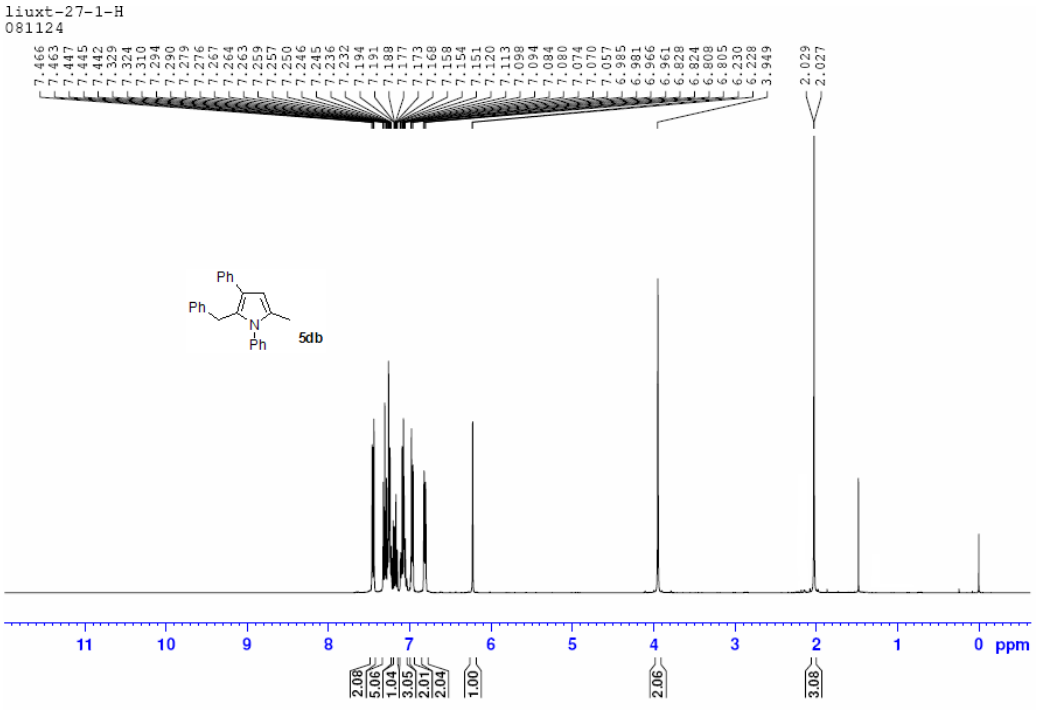

HL133-C13
20080902
CDCL3
139.44
137.52
134.34
133.68
131.73
129.02
128.81
128.49
128.01
127.15
127.00
125.76
125.44
122.62
109.29
77.48
77.16
76.84
47.93
31.99
30.46
25.51
22.36
14.10
Ph
Ph
N
Ph
5cc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

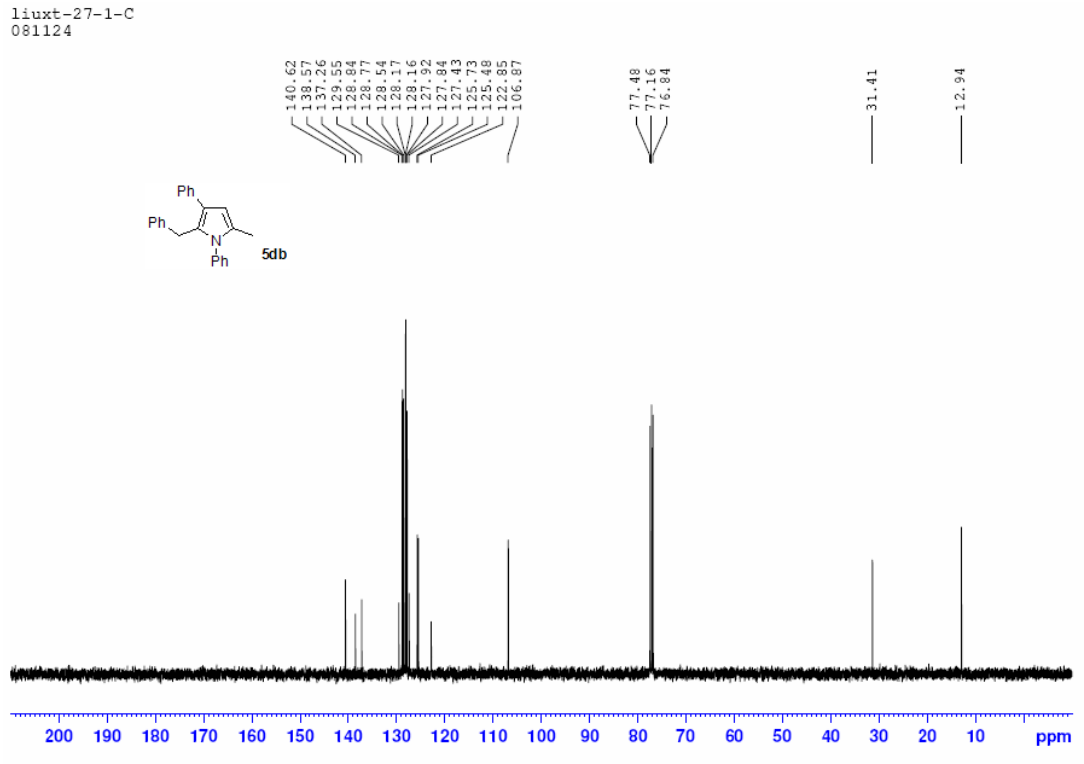

LiuXT29-H
20081202
cdcl3
Ph
Br
5cd
ppm


LiuXT29-C
20081202
cdcl3
Ph
Br
5cd
ppm

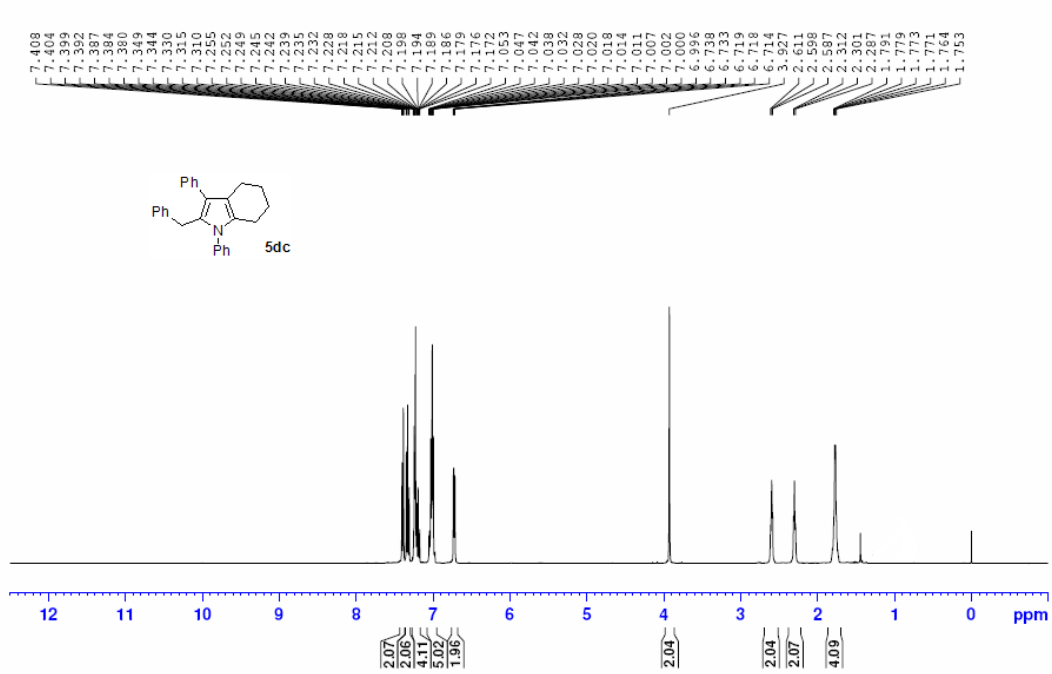

HL153-H-TOL
20081011
cdcl3
7.524
7.523
7.505
7.366
7.346
7.327
7.236
7.234
7.219
7.214
7.206
7.197
7.196
7.182
7.162
7.142
7.130
7.122
7.115
7.100
7.092
7.084
7.082
7.076
7.072
7.071
6.967
6.965
6.948
6.945
6.899
6.881
6.664
4.041
Ph
Ph
Ph
N
Ph
5da
9
8
7
6
5
4
3
2
1
0
ppm
2.05
2.13
12.68
2.06
2.05
1.00
2.02


HL153-C-TOL
20081011
cdcl3
140.52
139.13
136.85
134.79
133.17
130.19
129.01
128.79
128.66
128.32
128.21
128.10
128.01
127.73
126.11
125.91
125.90
125.89
124.43
109.64
77.48
77.16
76.85
31.46
Ph
Ph
Ph
N
Ph
5da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

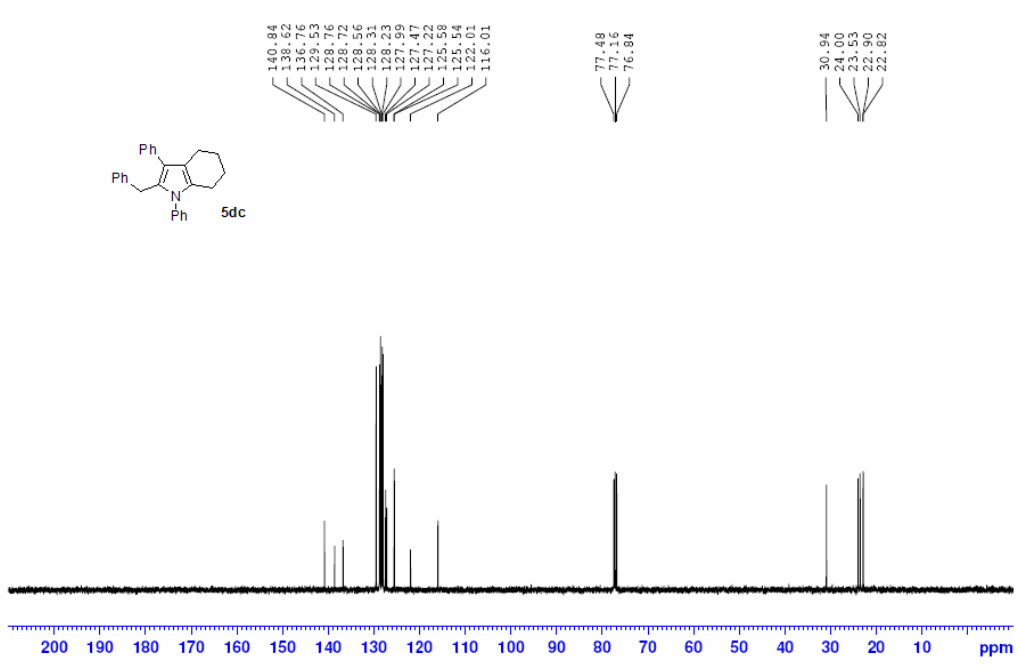

liuxt-27-1-H
081124
7.466
7.463
7.447
7.445
7.442
7.329
7.324
7.310
7.294
7.290
7.279
7.276
7.267
7.264
7.263
7.259
7.257
7.250
7.246
7.245
7.236
7.232
7.194
7.191
7.188
7.177
7.173
7.168
7.158
7.154
7.151
7.120
7.113
7.098
7.094
7.084
7.080
7.074
7.070
7.057
6.985
6.981
6.966
6.961
6.828
6.824
6.808
6.805
6.230
6.228
3.949
2.029
2.027
Ph
Ph
N
Ph
5db
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.06
5.06
1.04
3.05
2.01
2.04
1.00
2.06
3.08

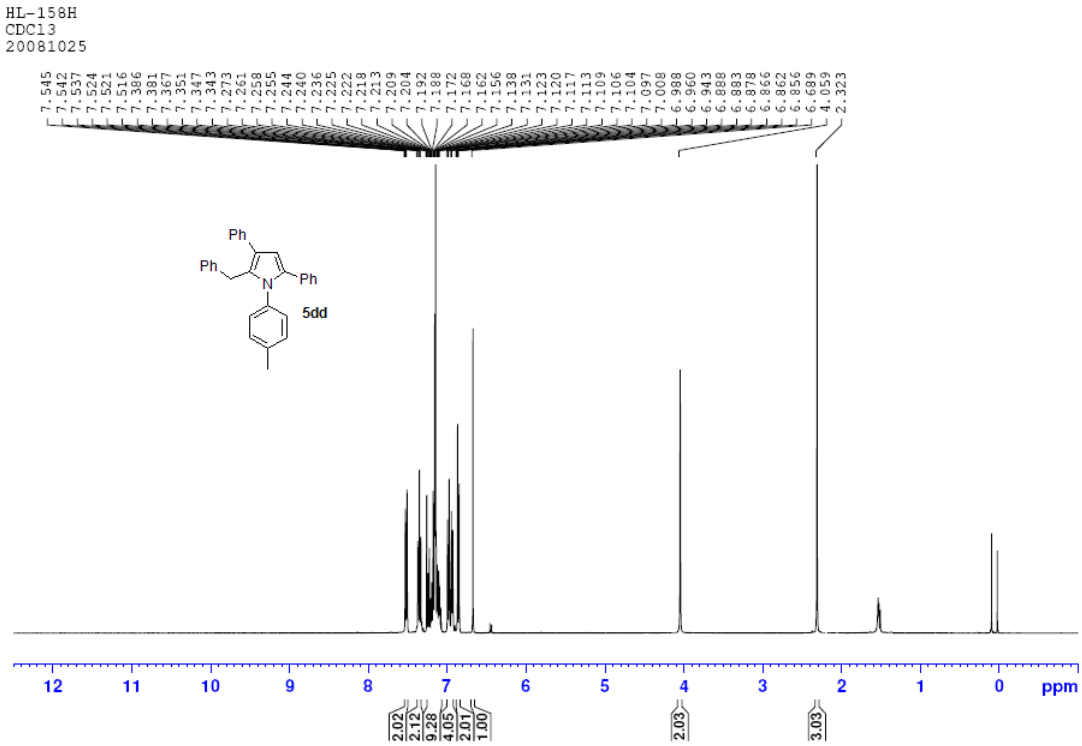

liuxt-27-1-C
081124
140.62
138.57
137.26
129.55
128.84
128.77
128.54
128.17
128.16
127.92
127.84
127.43
125.73
125.48
122.85
106.87
77.48
77.16
76.84
31.41
12.94
Ph
Ph
N
Ph
5db
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

HL-163H
CDCl3
20081030



HL-163C
CDCl3
20081030




HL-158H
CDCl3
20081025
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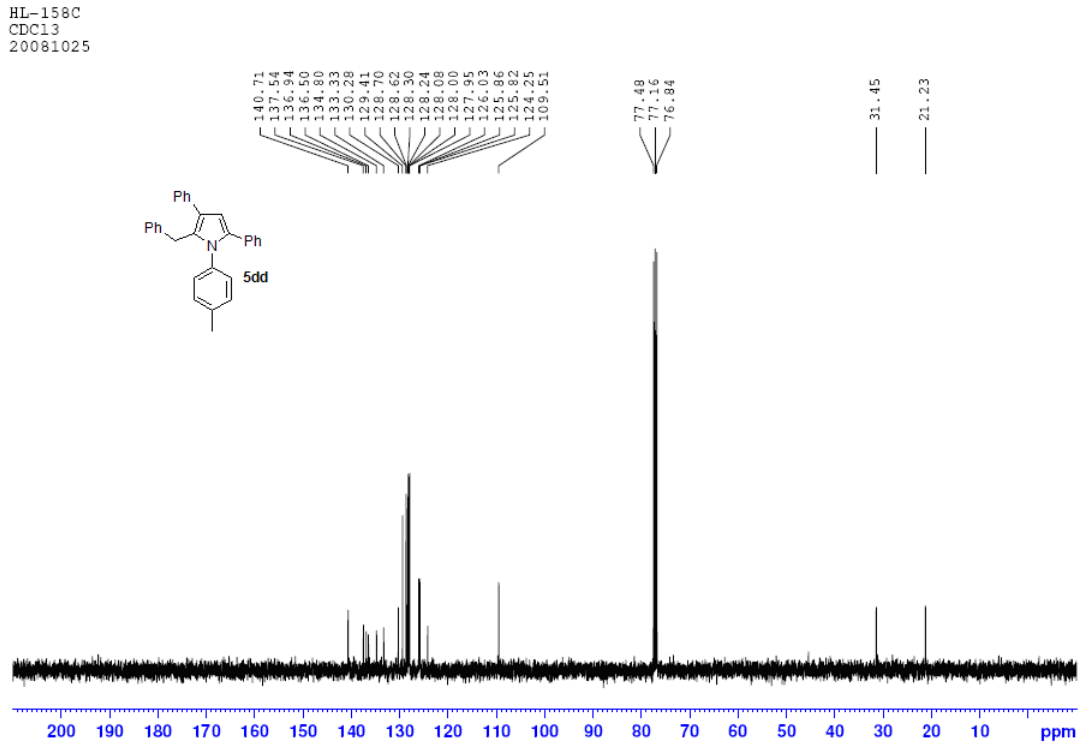
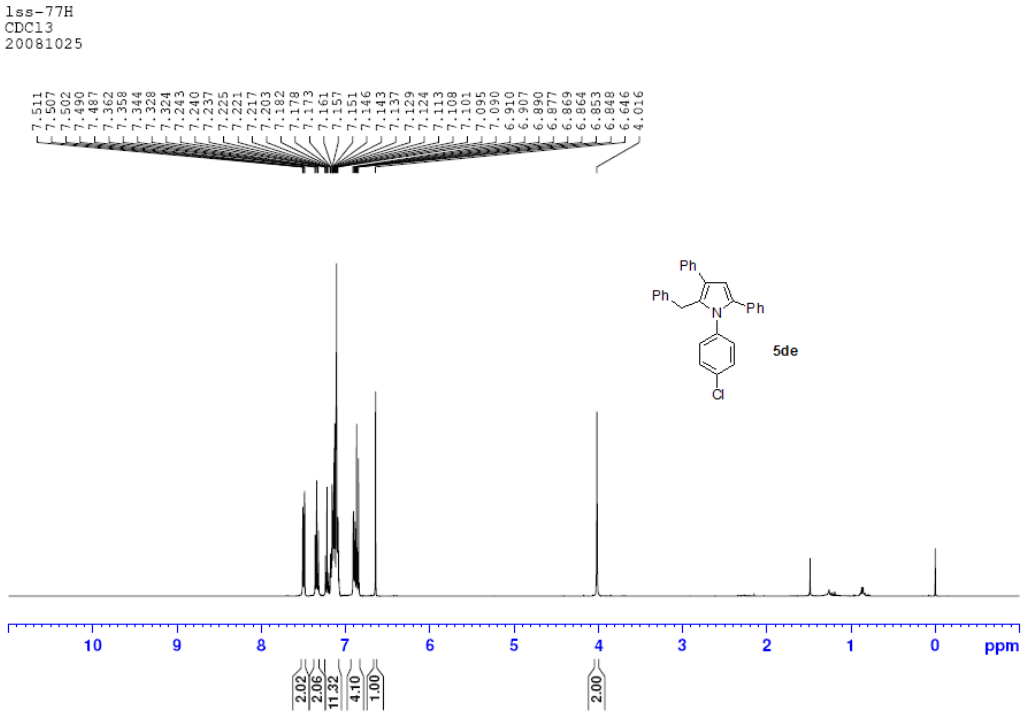
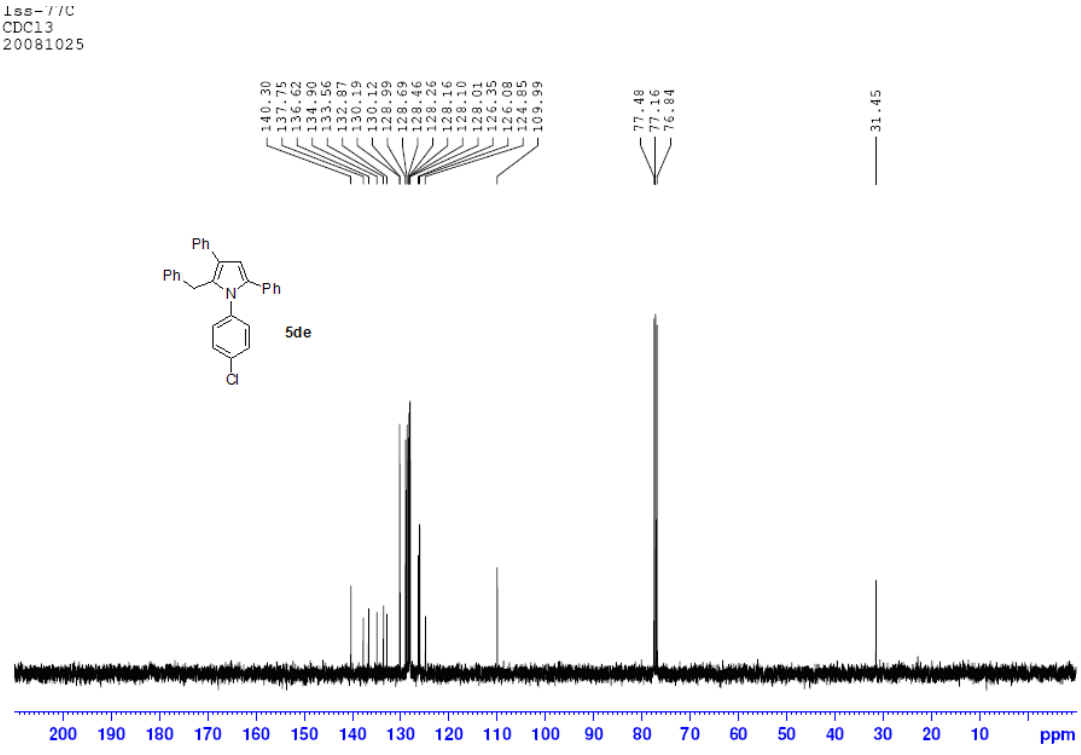
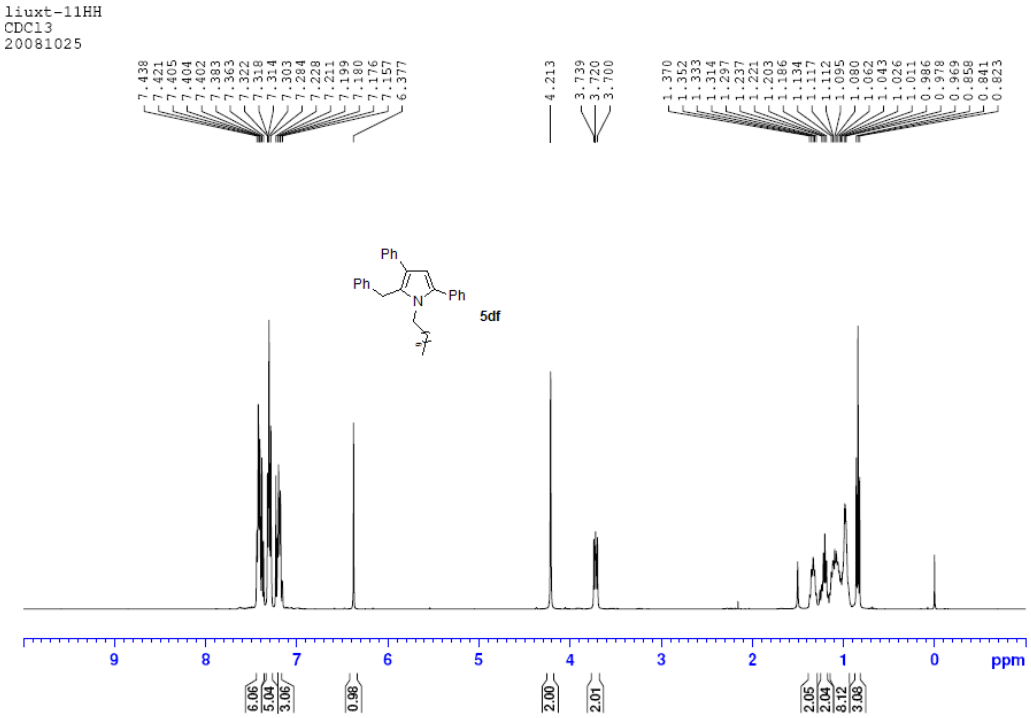
7.542
7.537
7.524
7.521
7.516
7.386
7.381
7.367
7.351
7.347
7.343
7.273
7.261
7.258
7.255
7.244
7.240
7.236
7.225
7.222
7.218
7.213
7.209
7.204
7.192
7.188
7.172
7.168
7.162
7.156
7.138
7.131
7.123
7.120
7.117
7.113
7.109
7.106
7.104
7.097
7.008
6.988
6.960
6.943
6.888
6.883
6.878
6.866
6.862
6.856
6.689
4.059
2.323
Ph
Ph
N
Ph
5dd
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.12
9.28
4.05
2.01
1.00
2.03
3.03


HL-158C
CDCl3
20081025
140.71
137.54
136.94
136.50
134.80
133.33
130.28
129.41
128.70
128.62
128.30
128.24
128.08
128.00
127.95
126.03
125.86
125.82
124.25
109.51
77.48
77.16
76.84
31.45
21.23
Ph
Ph
N
Ph
5dd
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


lss-77H
CDCl3
20081025
7.511
7.507
7.502
7.490
7.487
7.362
7.358
7.344
7.328
7.324
7.243
7.240
7.237
7.225
7.221
7.217
7.203
7.182
7.178
7.173
7.161
7.157
7.151
7.146
7.143
7.137
7.129
7.124
7.113
7.108
7.101
7.095
7.090
6.910
6.907
6.890
6.877
6.869
6.864
6.853
6.848
6.646
4.016
Ph
Ph
Ph
N
Cl
5de
10
9
8
7
6
5
4
3
2
1
0
ppm
2.02
2.06
11.32
4.10
1.00
2.00


lss-77C
CDCl3
20081025
140.30
137.75
136.62
134.90
133.56
132.87
130.19
130.12
128.99
128.69
128.46
128.26
128.16
128.10
128.01
126.35
126.08
124.85
109.99
77.48
77.16
76.84
31.45
Ph
Ph
Ph
N
Cl
5de
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


liuxt-11HH
CDCl3
20081025
7.438
7.421
7.405
7.404
7.402
7.383
7.363
7.322
7.318
7.314
7.303
7.284
7.228
7.211
7.199
7.180
7.176
7.157
6.377
4.213
3.739
3.720
3.700
1.370
1.352
1.333
1.314
1.297
1.237
1.221
1.203
1.186
1.134
1.117
1.112
1.095
1.080
1.062
1.043
1.026
1.011
0.986
0.978
0.969
0.858
0.841
0.823
Ph
Ph
N
Ph
5df
9
8
7
6
5
4
3
2
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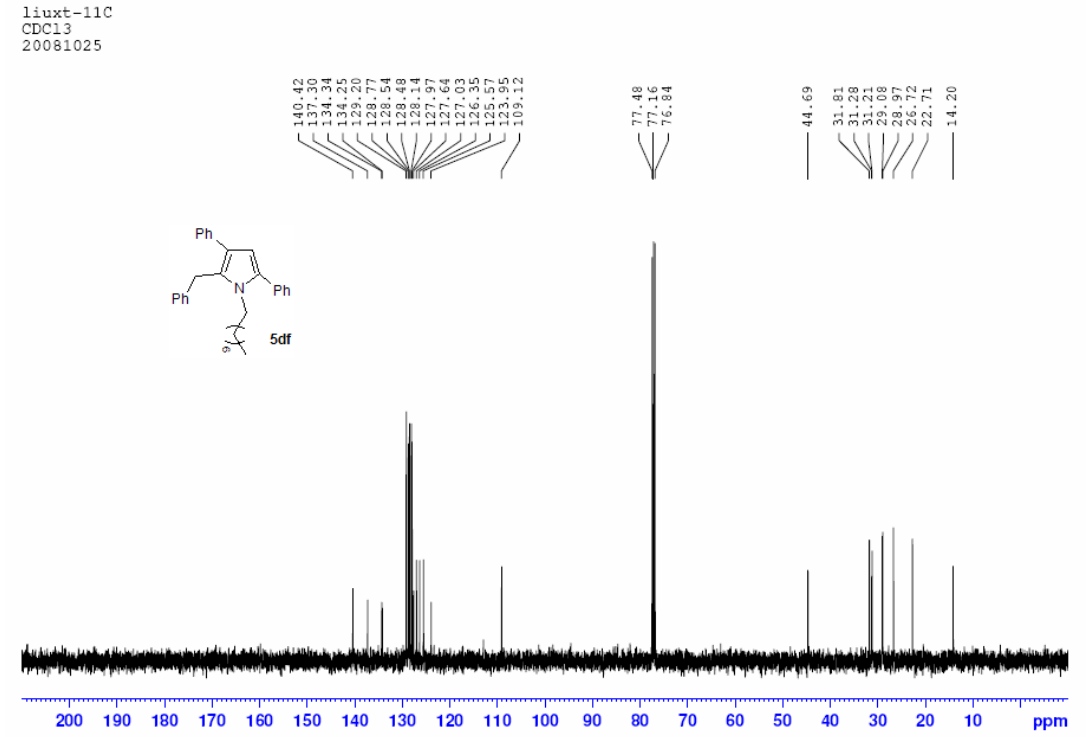
6.06
5.04
3.06
0.98
2.00
2.01
2.05
2.04
8.12
3.08


liuxt-11C
CDCl3
20081025
140.42
137.30
134.34
134.25
129.20
128.77
128.54
128.48
128.14
127.97
127.64
127.03
126.35
125.57
123.95
109.12
77.48
77.16
76.84
44.69
31.81
31.28
31.21
29.08
28.97
26.72
22.71
14.20
Ph
Ph
N
Ph
5df
9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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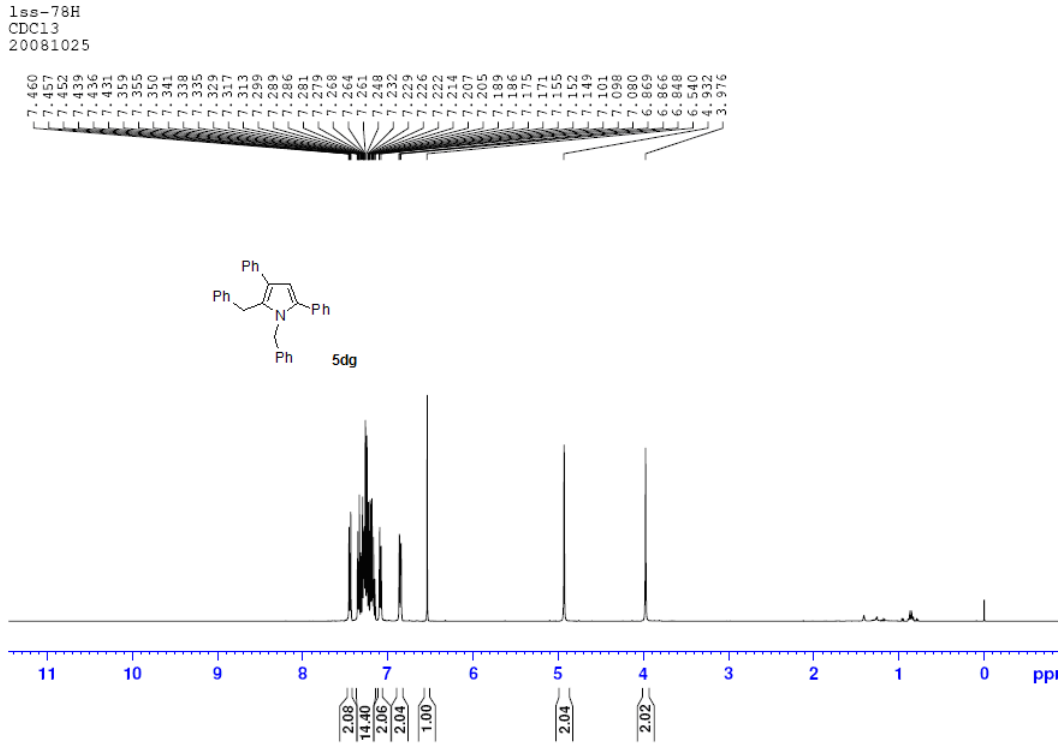
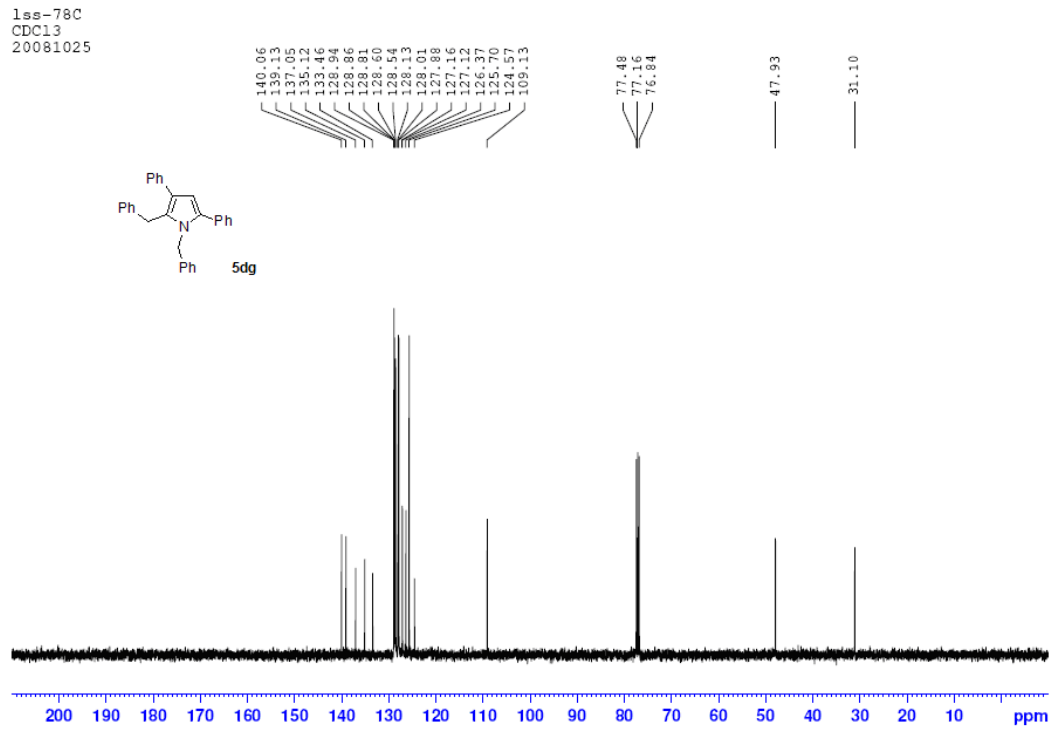
40
30
20
10
ppm


lss-78H
CDCl3
20081025
7.460
7.457
7.452
7.439
7.436
7.431
7.359
7.355
7.350
7.341
7.338
7.335
7.329
7.317
7.313
7.299
7.289
7.286
7.281
7.279
7.268
7.264
7.261
7.248
7.232
7.229
7.226
7.222
7.214
7.207
7.205
7.189
7.186
7.175
7.171
7.155
7.152
7.149
7.101
7.098
7.080
6.869
6.866
6.848
6.540
4.932
3.976
Ph
Ph
N
Ph
Ph
5dg
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.08
14.40
2.06
2.04
1.00
2.04
2.02


lss-78C
CDCl3
20081025
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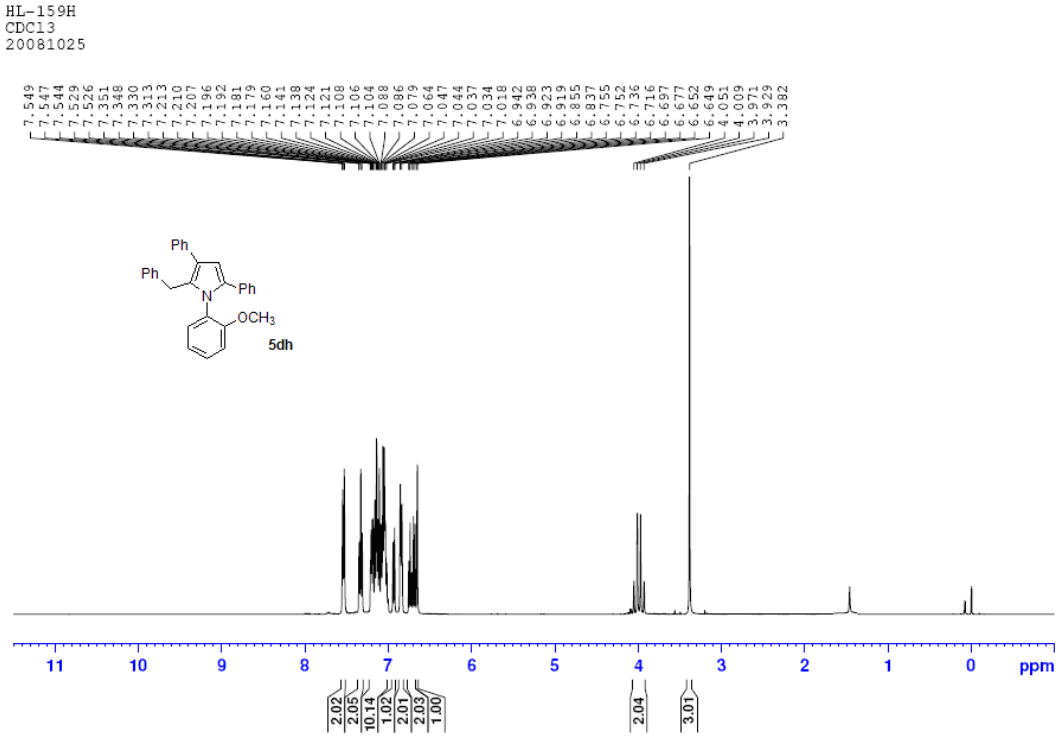
139.13
137.05
135.12
133.46
128.94
128.86
128.81
128.60
128.54
128.13
128.01
127.88
127.16
127.12
126.37
125.70
124.57
109.13
77.48
77.16
76.84
47.93
31.10
Ph
Ph
N
Ph
Ph
5dg
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


HL-159H
CDCl3
20081025
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7.547
7.544
7.529
7.526
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7.348
7.330
7.313
7.213
7.210
7.207
7.196
7.192
7.181
7.179
7.160
7.141
7.138
7.124
7.121
7.108
7.106
7.104
7.088
7.086
7.079
7.064
7.047
7.044
7.037
7.034
7.018
6.942
6.938
6.923
6.919
6.855
6.837
6.755
6.752
6.736
6.716
6.697
6.677
6.652
6.649
4.051
4.009
3.971
3.929
3.382
Ph
Ph
Ph
N
OCH3
5dh
11
10
9
8
7
6
5
4
3
2
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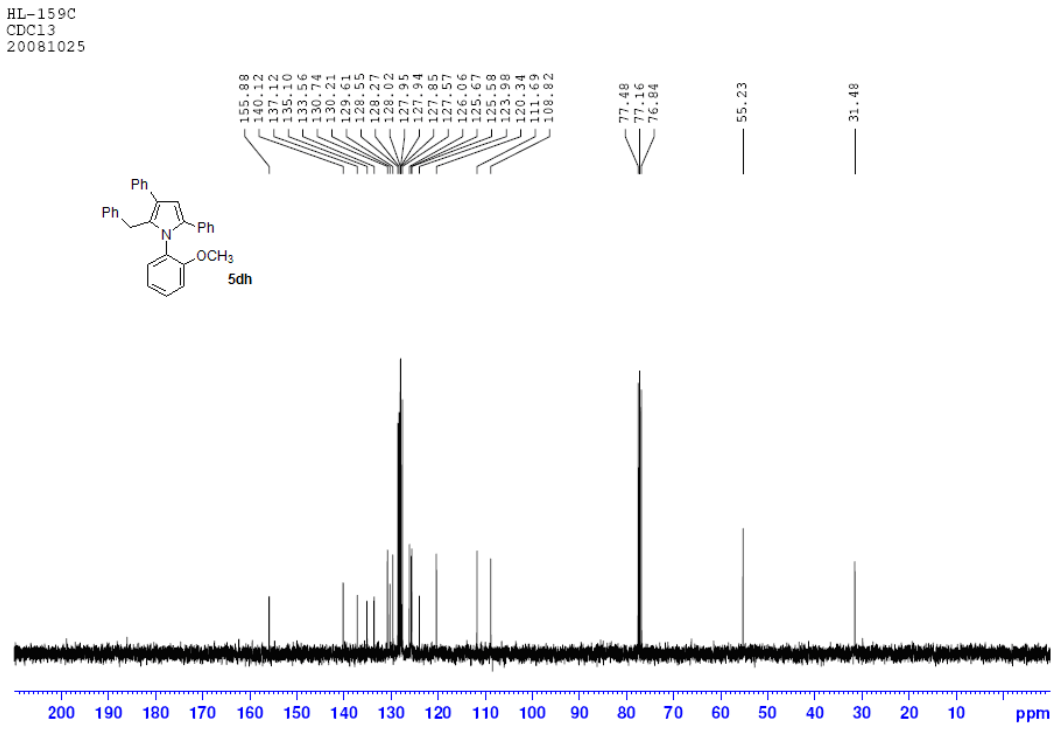
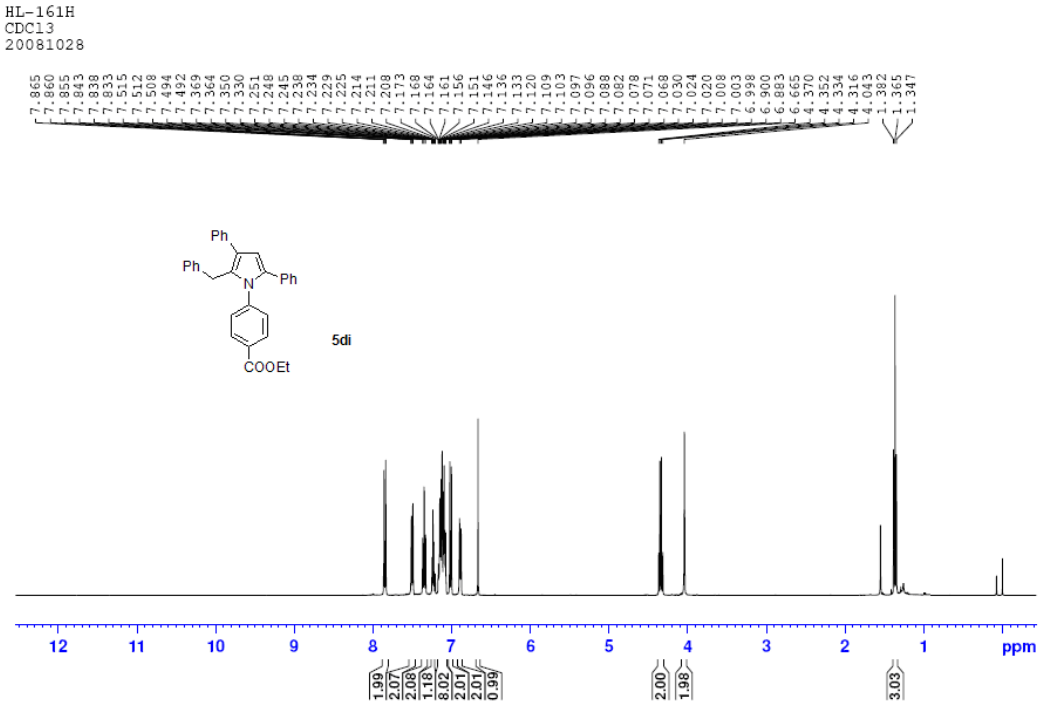
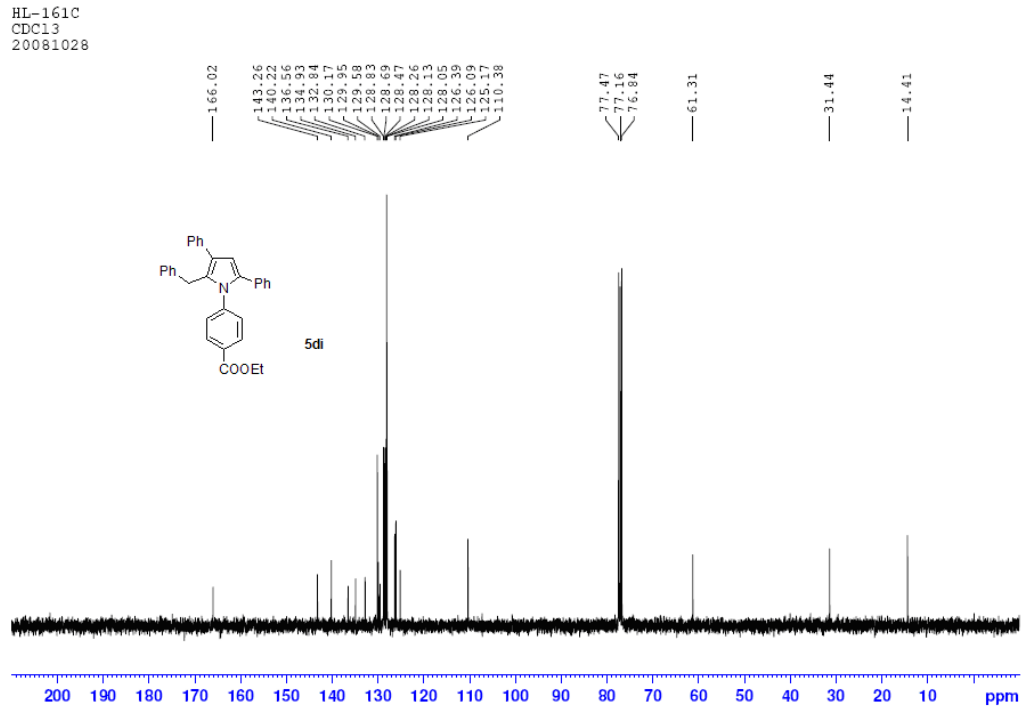
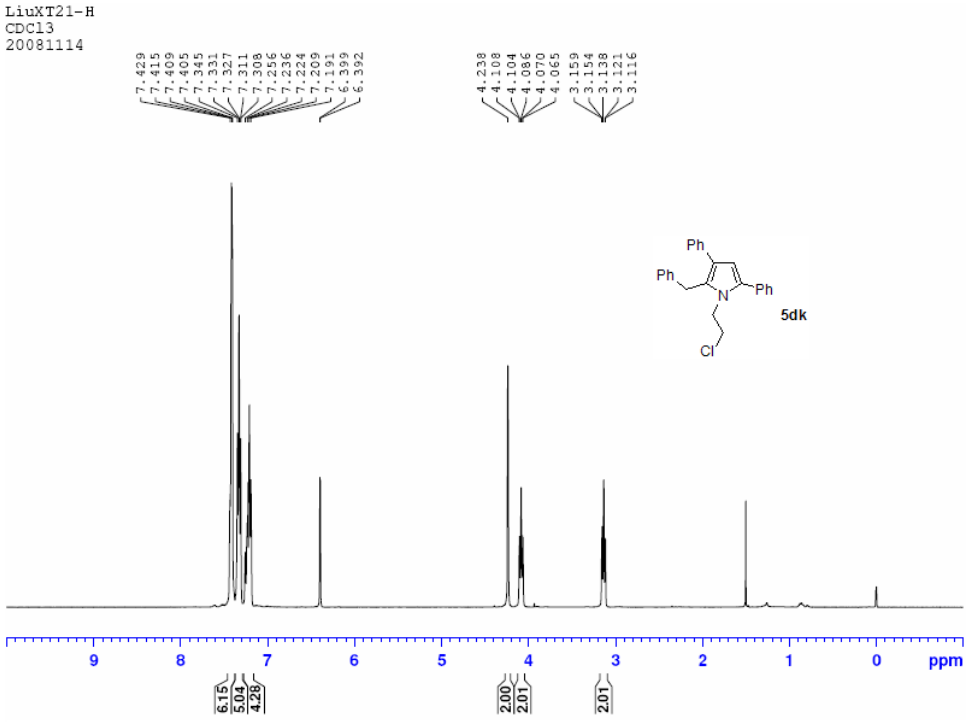
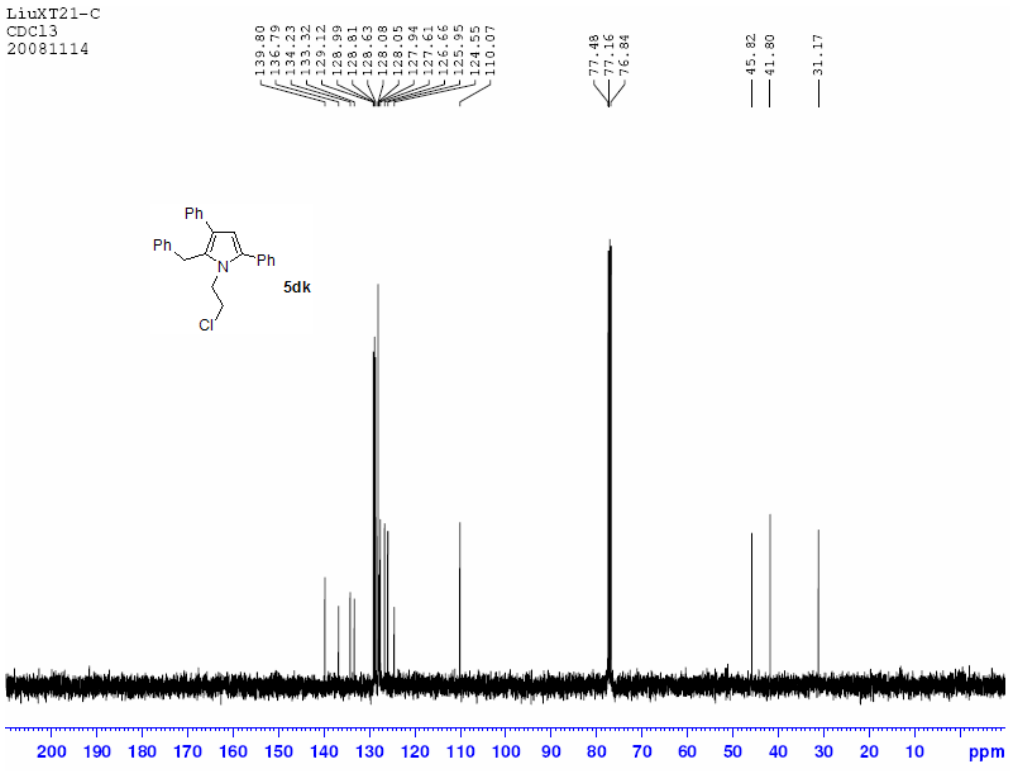
ppm
2.02
2.05
10.14
1.02
2.01
2.03
1.00
2.04
3.01

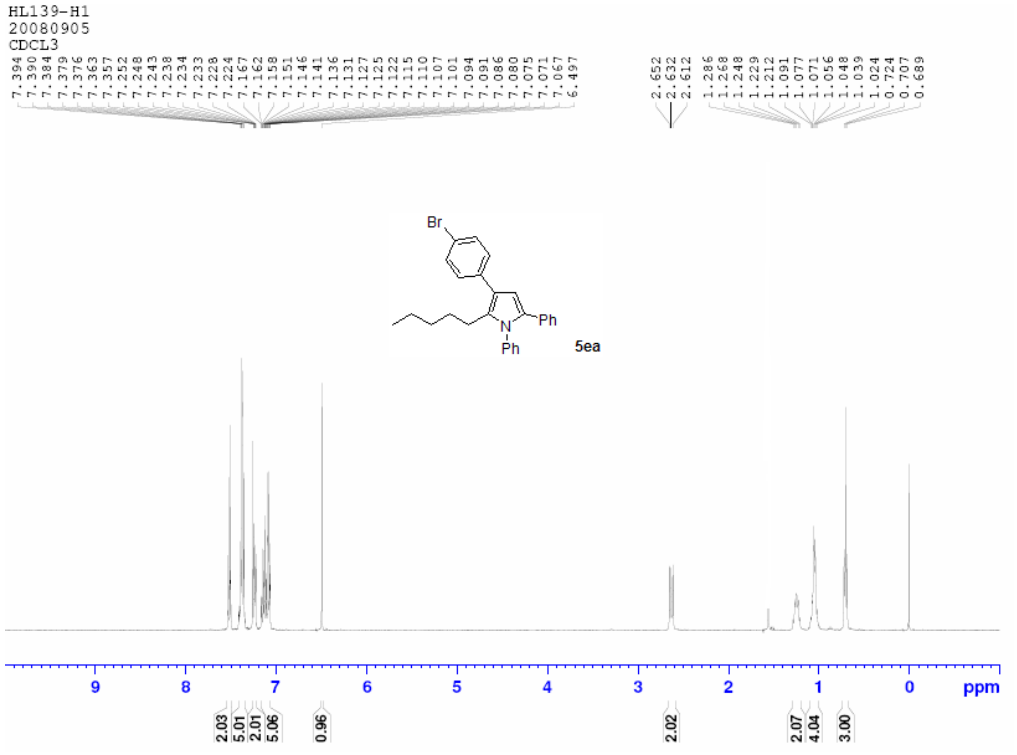

HL-159C
CDCl3
20081025
155.88
140.12
137.12
135.10
133.56
130.74
130.21
129.61
128.55
128.27
128.02
127.95
127.94
127.85
127.57
126.06
125.67
125.58
123.98
120.34
111.69
108.82
77.48
77.16
76.84
55.23
31.48
Ph
Ph
Ph
N
OCH3
5dh
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


HL-161H
CDCl3
20081028
7.865
7.860
7.855
7.843
7.838
7.833
7.515
7.512
7.508
7.494
7.492
7.369
7.364
7.350
7.330
7.251
7.248
7.245
7.238
7.234
7.229
7.225
7.214
7.211
7.208
7.173
7.168
7.164
7.161
7.156
7.151
7.146
7.136
7.133
7.120
7.109
7.103
7.097
7.096
7.088
7.082
7.078
7.071
7.068
7.030
7.024
7.020
7.008
7.003
6.998
6.900
6.883
6.665
4.370
4.352
4.334
4.316
4.043
1.382
1.365
1.347
Ph
Ph
N
Ph
COOEt
5di
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.99
2.07
2.08
1.18
8.02
2.01
2.01
0.99
2.00
1.98
3.03


HL-161C
CDCl3
20081028
166.02
143.26
140.22
136.56
134.93
132.84
130.17
129.95
129.58
128.83
128.69
128.47
128.26
128.13
128.05
126.39
126.09
125.17
110.38
77.47
77.16
76.84
61.31
31.44
14.41
Ph
Ph
N
Ph
COOEt
5di
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


LiuXT21-H
CDCl3
20081114
7.429
7.415
7.409
7.405
7.345
7.331
7.327
7.311
7.308
7.256
7.236
7.224
7.209
7.191
6.399
6.392
4.238
4.108
4.104
4.086
4.070
4.065
3.159
3.154
3.138
3.121
3.116
Ph
Ph
N
Ph
Cl
5dk
9
8
7
6
5
4
3
2
1
0
ppm
6.15
5.04
4.28
2.00
2.01
2.01


LiuXT21-C
CDCl3
20081114
139.80
136.79
134.23
133.32
129.12
128.99
128.81
128.63
128.08
128.05
127.94
127.61
126.66
125.95
124.55
110.07
77.48
77.16
76.84
45.82
41.80
31.17
Ph
Ph
N
Ph
Cl
5dk
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


HL139-H1
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CDCL3
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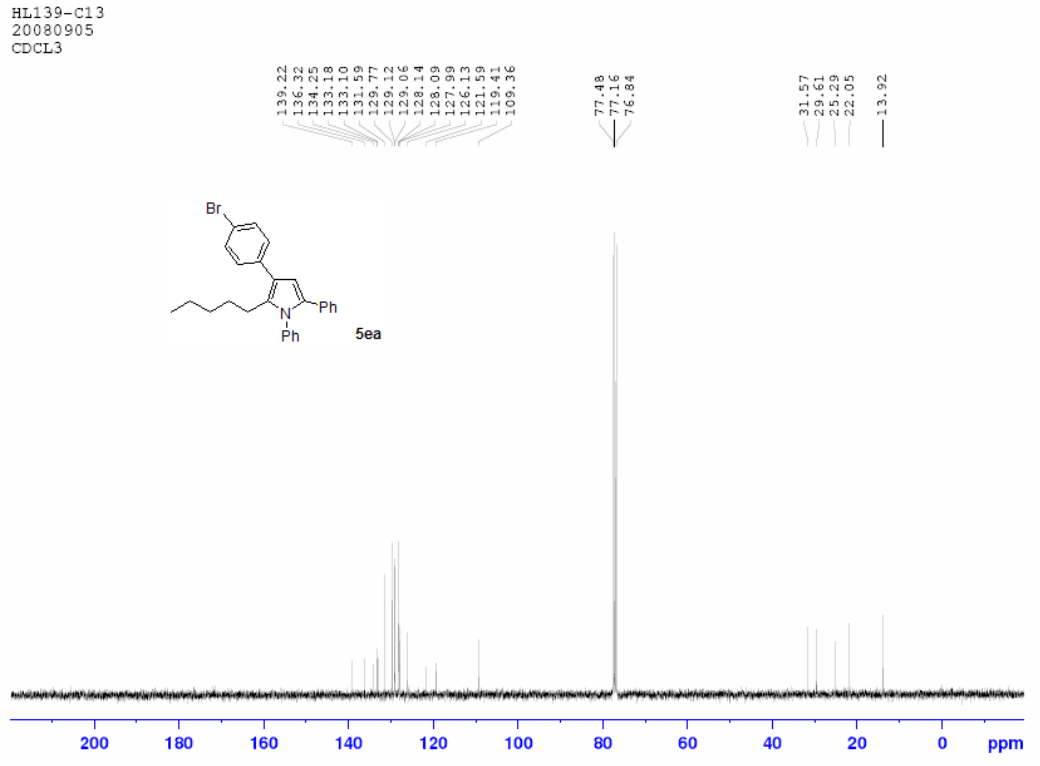
7.384
7.379
7.376
7.363
7.357
7.252
7.248
7.243
7.238
7.234
7.233
7.228
7.224
7.167
7.162
7.158
7.151
7.146
7.141
7.136
7.131
7.127
7.125
7.122
7.115
7.110
7.107
7.101
7.094
7.091
7.086
7.080
7.075
7.071
7.067
6.497
2.652
2.632
2.612
1.286
1.268
1.248
1.229
1.212
1.091
1.077
1.071
1.056
1.048
1.039
1.024
0.724
0.707
0.689
Br
Ph
N
Ph
5ea
9
8
7
6
5
4
3
2
1
0
ppm
2.03
5.01
2.01
5.06
0.96
2.02
2.07
4.04
3.00


HL139-C13
20080905
CDCL3
139.22
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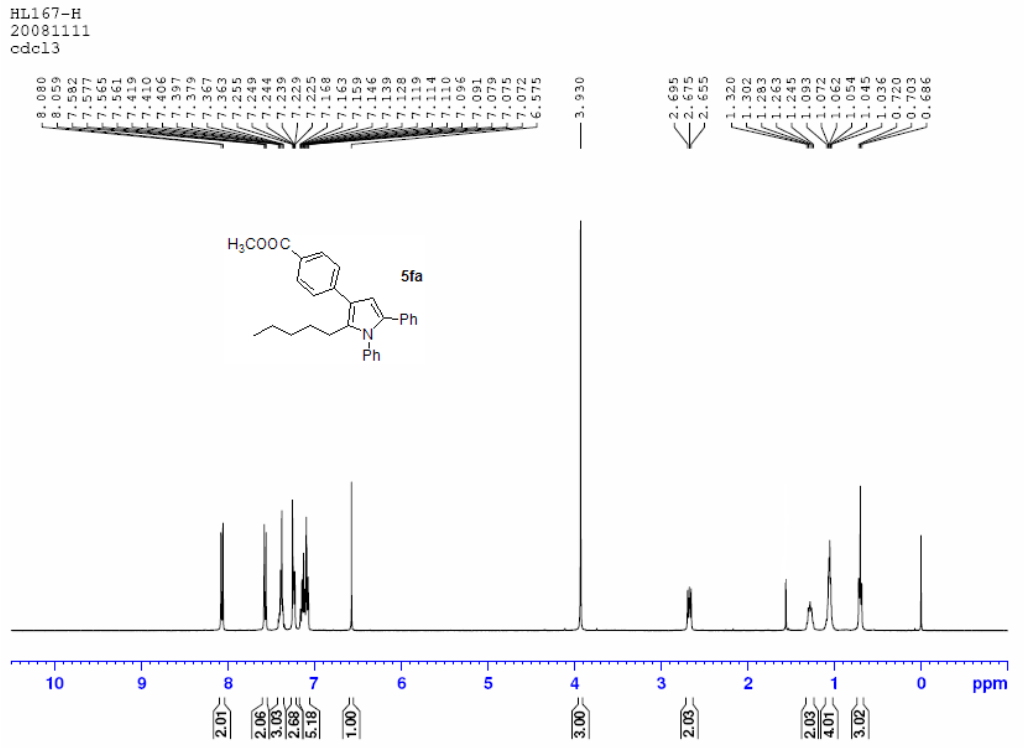
134.25
133.18
133.10
131.59
129.77
129.22
129.06
128.14
128.09
127.99
126.13
121.59
119.41
109.36
77.48
77.16
76.84
31.57
29.61
25.29
22.05
13.92
Br
Ph
N
Ph
5ea
200
180
160
140
120
100
80
60
40
20
0
ppm


HL167-H
20081111
cdcl3
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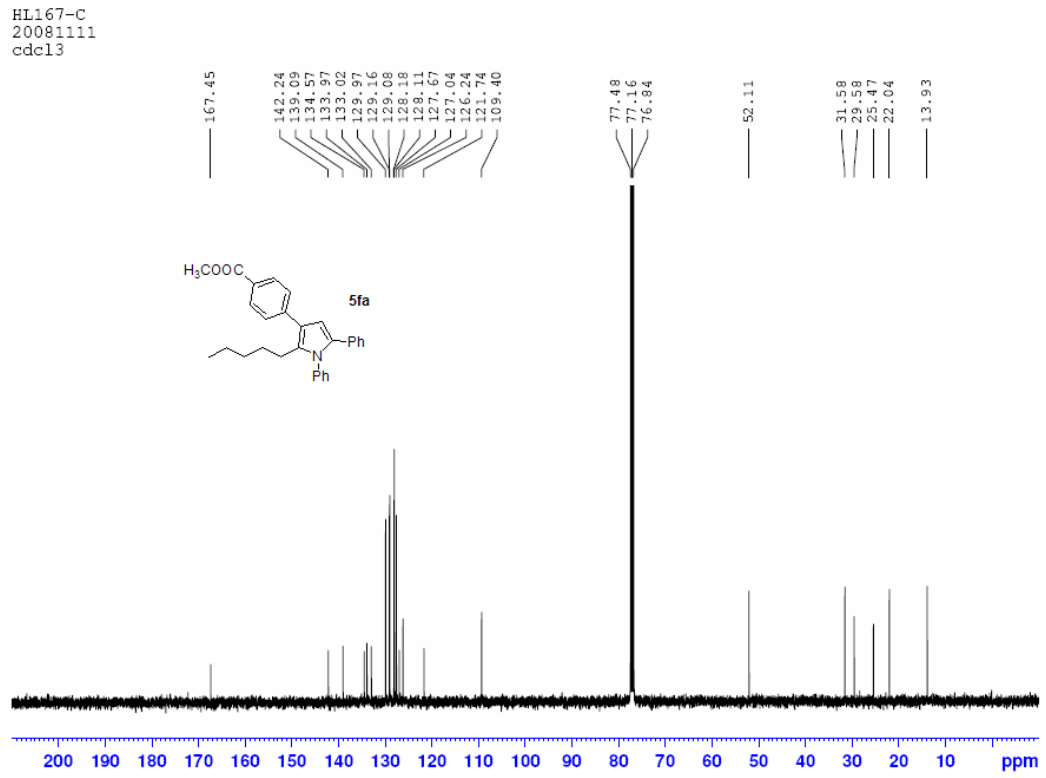
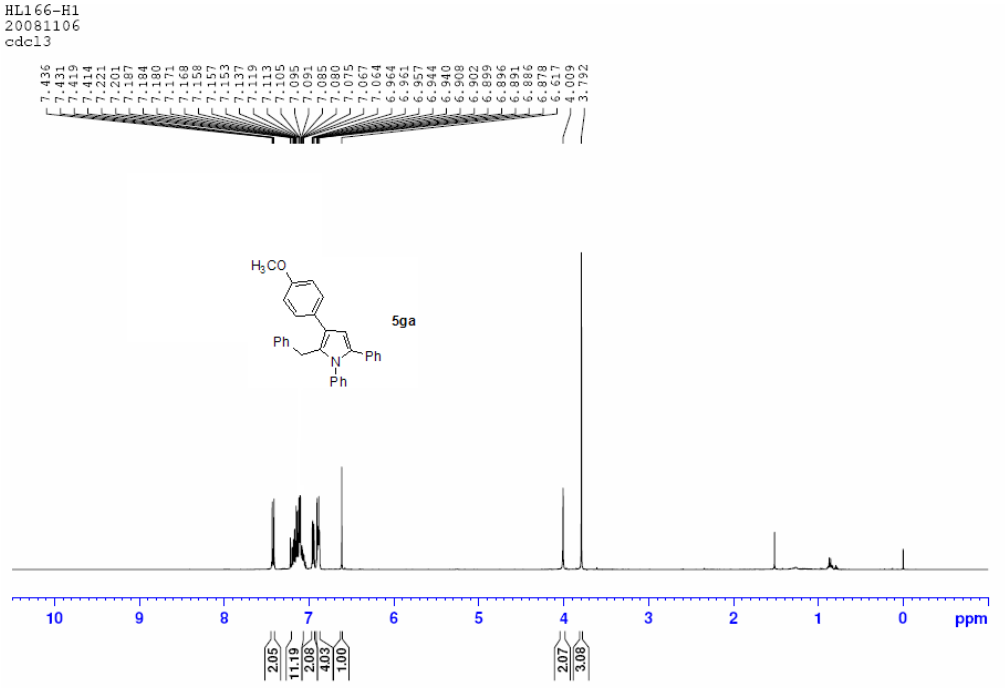
8.059
7.582
7.577
7.565
7.561
7.419
7.410
7.406
7.397
7.379
7.367
7.363
7.255
7.249
7.244
7.239
7.229
7.225
7.168
7.163
7.159
7.146
7.139
7.128
7.119
7.114
7.110
7.096
7.091
7.079
7.075
7.072
6.575
3.930
2.695
2.675
2.655
1.320
1.302
1.283
1.263
1.245
1.093
1.072
1.062
1.054
1.045
1.036
0.720
0.703
0.686
H3COOC
5fa
Ph
N
Ph
10
9
8
7
6
5
4
3
2
1
0
ppm
2.01
2.06
3.03
2.68
5.18
1.00
3.00
2.03
2.03
4.01
3.02


HL167-C
20081111
cdcl3
167.45
142.24
139.09
134.57
133.97
133.02
129.97
129.16
129.08
128.18
128.11
127.67
127.04
126.24
121.74
109.40
77.48
77.16
76.84
52.11
31.58
29.58
25.47
22.04
13.93
H3COOC
5fa
Ph
N
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


HL166-H1
20081106
cdcl3
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7.419
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7.221
7.201
7.187
7.184
7.180
7.171
7.168
7.158
7.157
7.153
7.137
7.119
7.113
7.105
7.095
7.091
7.085
7.080
7.075
7.067
7.064
6.964
6.961
6.957
6.944
6.940
6.908
6.902
6.899
6.896
6.891
6.886
6.878
6.617
4.009
3.792
H3CO
5ga
Ph
Ph
N
Ph
10
9
8
7
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5
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3
2
1
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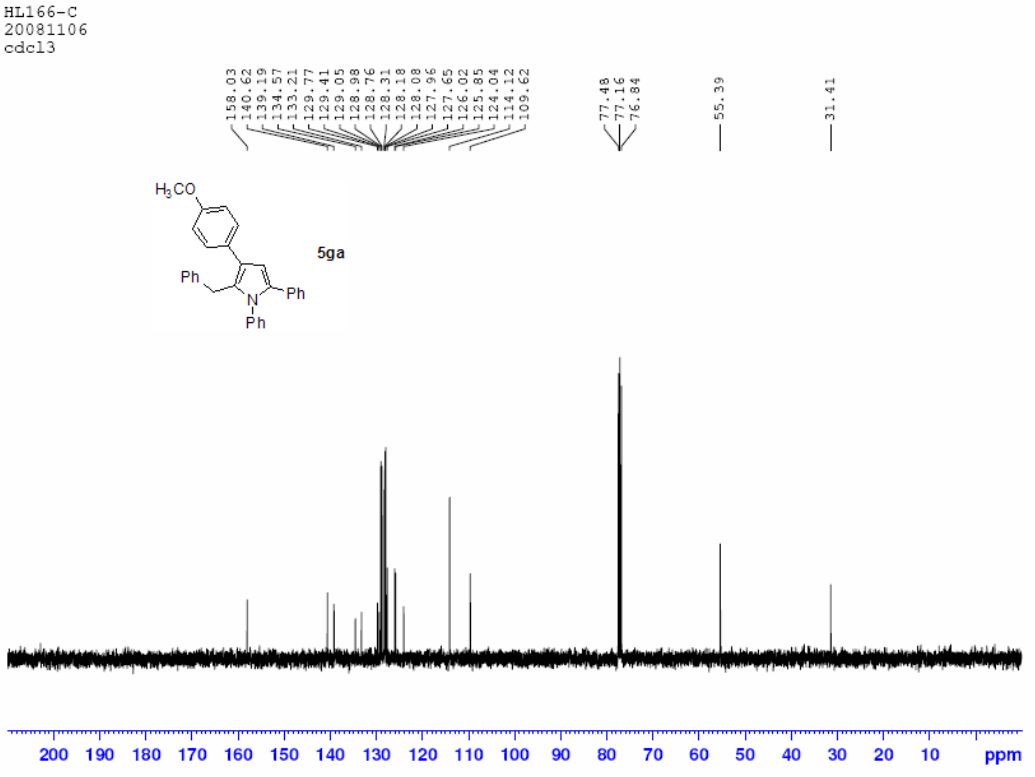
ppm
2.05
11.19
2.08
4.03
1.00
2.07
3.08


HL166-C
20081106
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139.19
134.57
133.21
129.77
129.41
129.05
128.98
128.76
128.31
128.18
128.08
127.96
127.65
126.02
125.85
124.04
114.12
109.62
77.48
77.16
76.84
55.39
31.41
H3CO
5ga
Ph
Ph
N
Ph
200
190
180
170
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150
140
130
120
110
100
90
80
70
60
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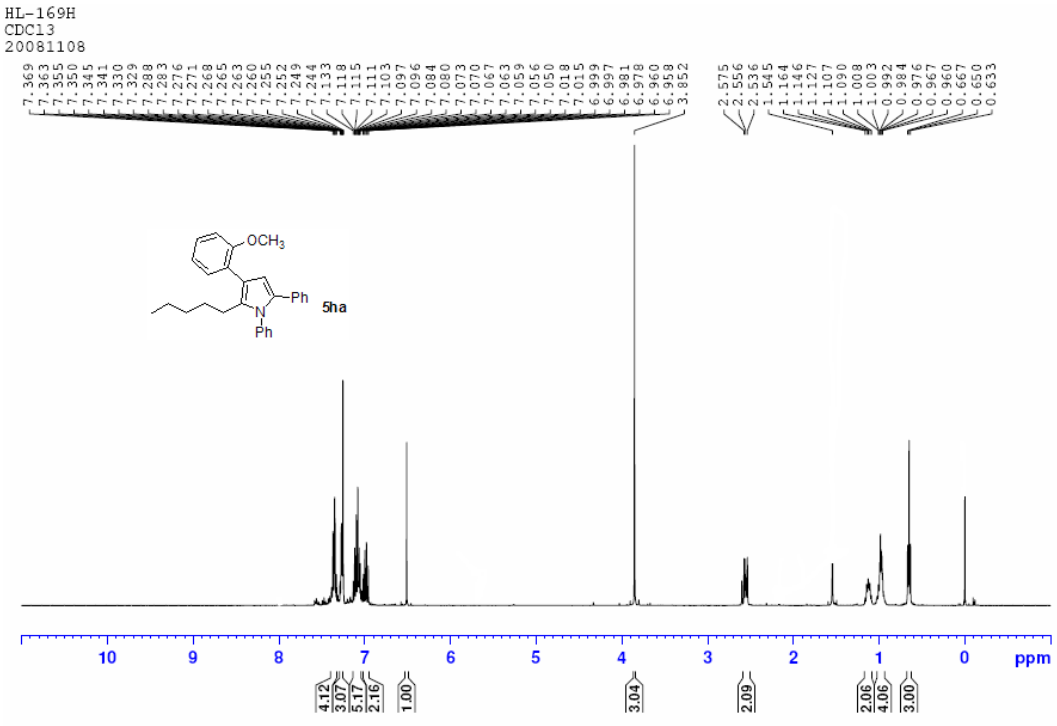
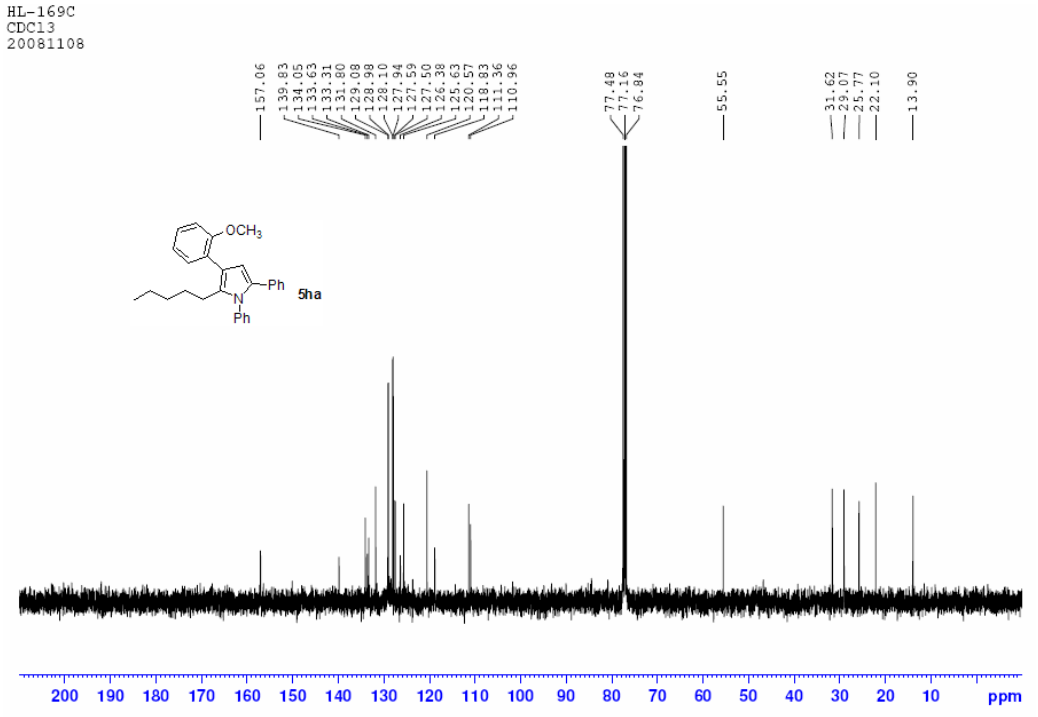
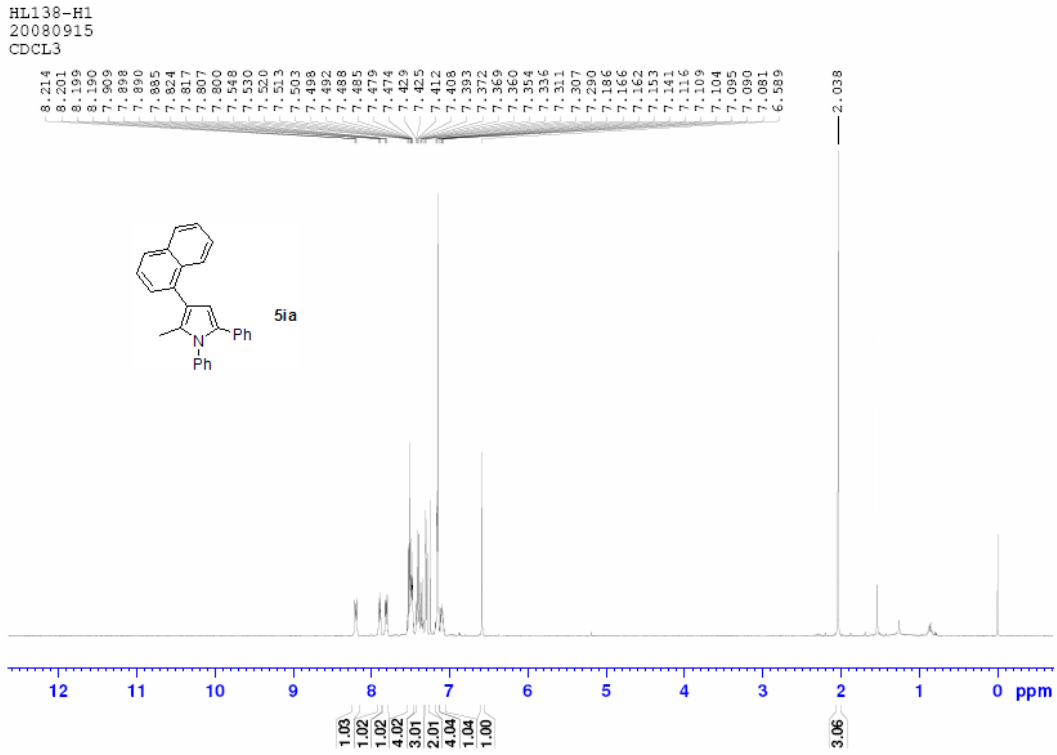
40
30
20
10
ppm


HL-169H
CDCl3
20081108
OCH3
Ph
N
Ph
5ha
ppm


HL-169C
CDCl3
20081108
OCH3
Ph
N
Ph
5ha
ppm


HL138-H1
20080915
CDCL3
8.214
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8.199
8.190
7.909
7.898
7.890
7.885
7.824
7.817
7.807
7.800
7.548
7.530
7.520
7.513
7.503
7.498
7.492
7.488
7.485
7.479
7.474
7.429
7.425
7.412
7.408
7.393
7.372
7.369
7.360
7.354
7.336
7.311
7.307
7.290
7.186
7.166
7.162
7.153
7.141
7.116
7.109
7.104
7.095
7.090
7.081
6.589
2.038
5ia
Ph
N
Ph
12
11
10
9
8
7
6
5
4
3
2
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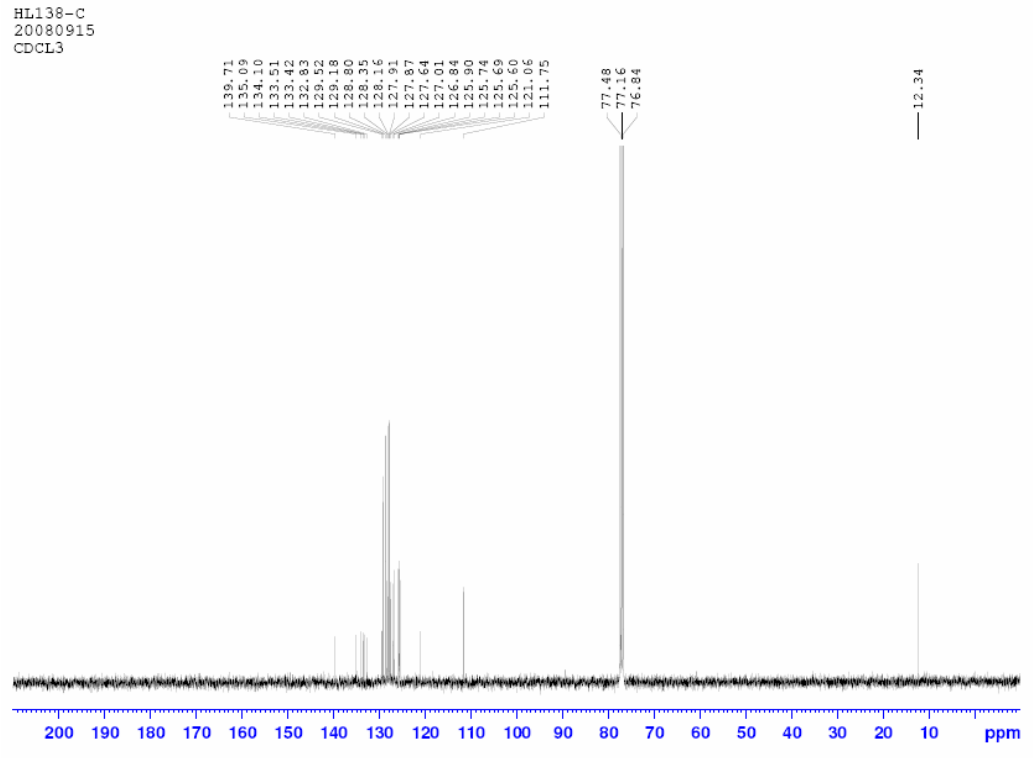
0
ppm
1.03
1.02
1.02
4.02
3.01
2.01
4.04
1.04
1.00
3.06


HL138-C
20080915
CDCL3
139.71
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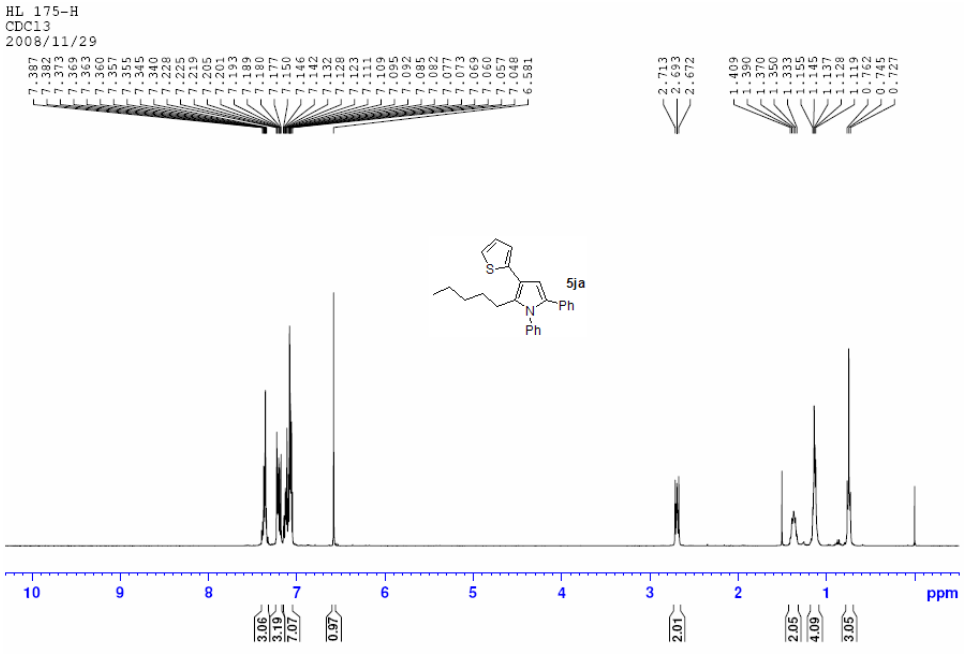
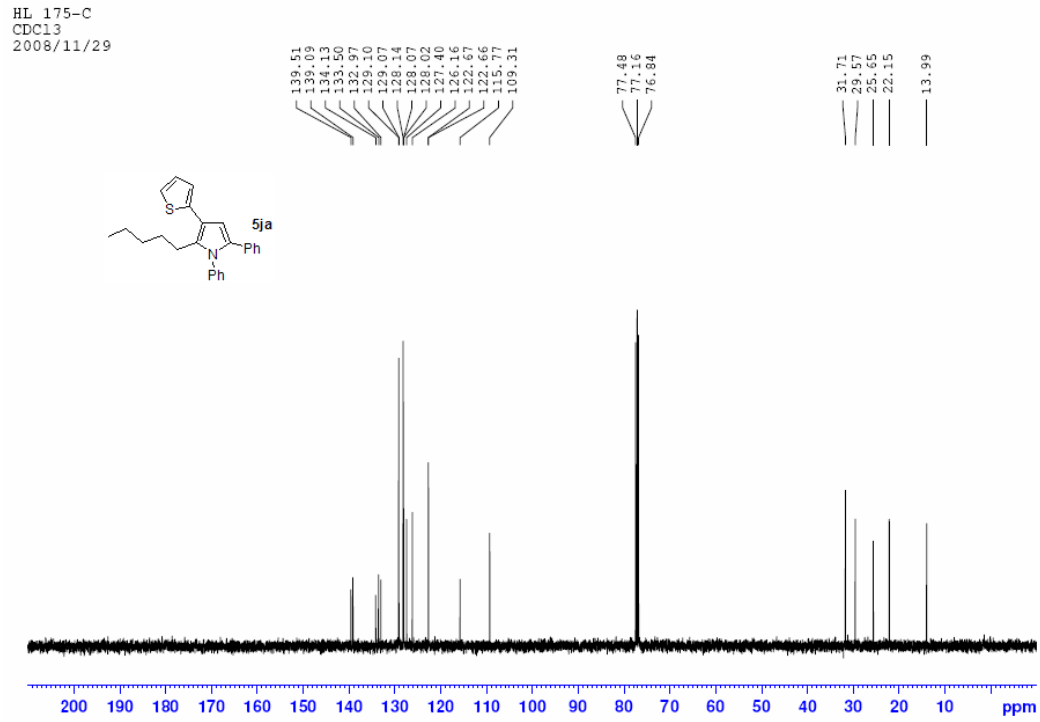
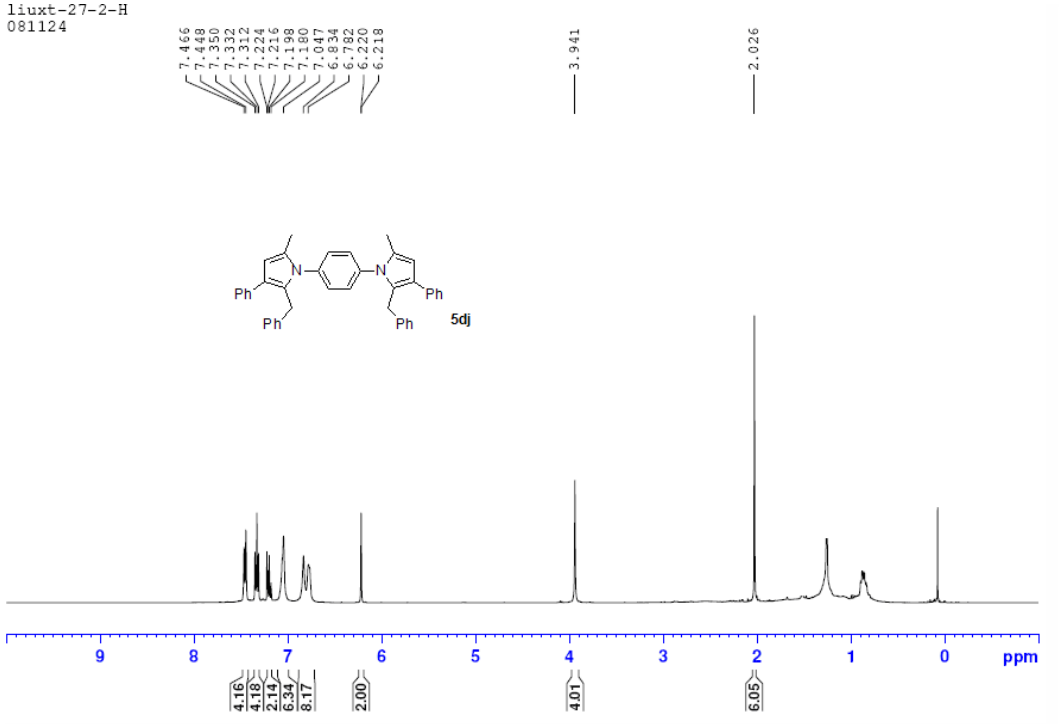
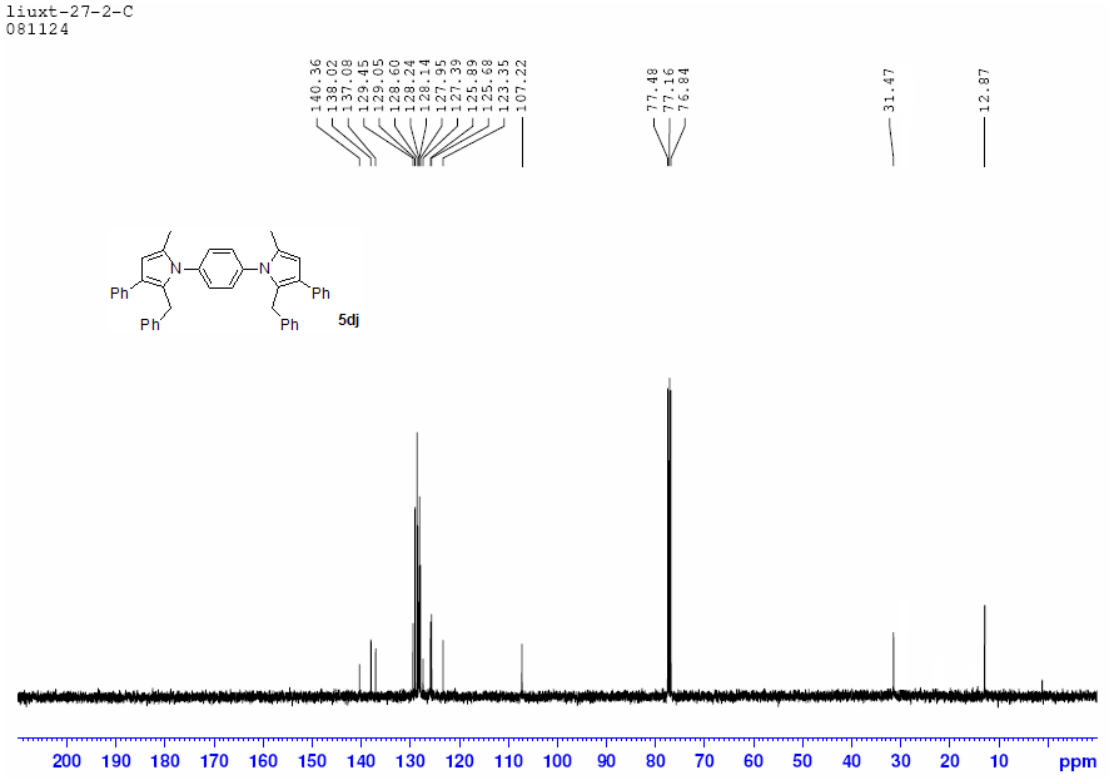
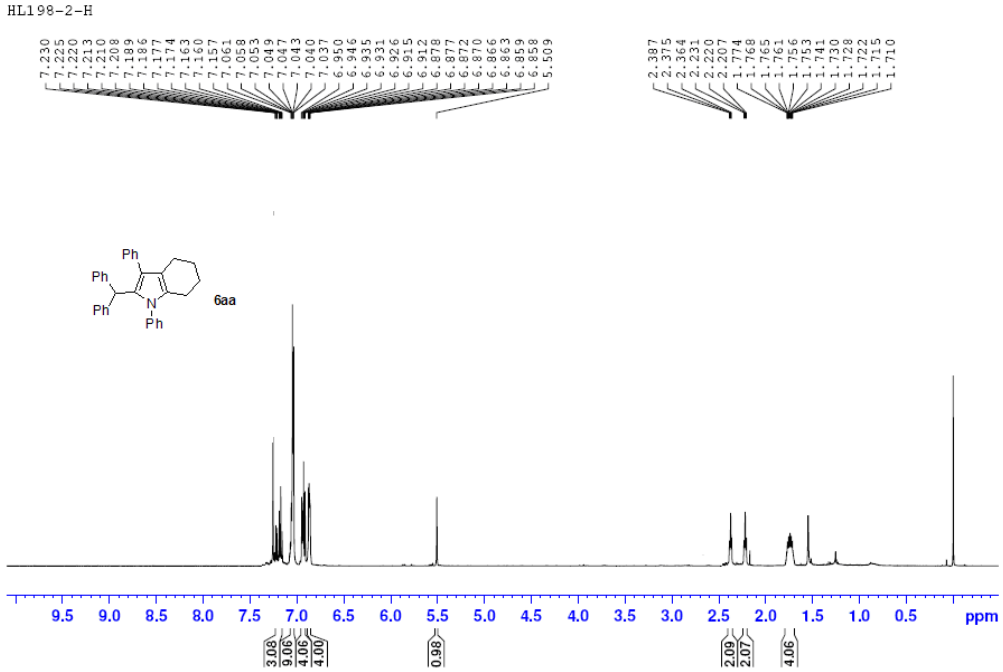
134.10
133.51
133.42
132.83
129.52
129.18
128.80
128.35
128.16
127.91
127.87
127.64
127.01
126.84
125.90
125.74
125.69
125.60
121.06
111.75
77.48
77.16
76.84
12.34
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

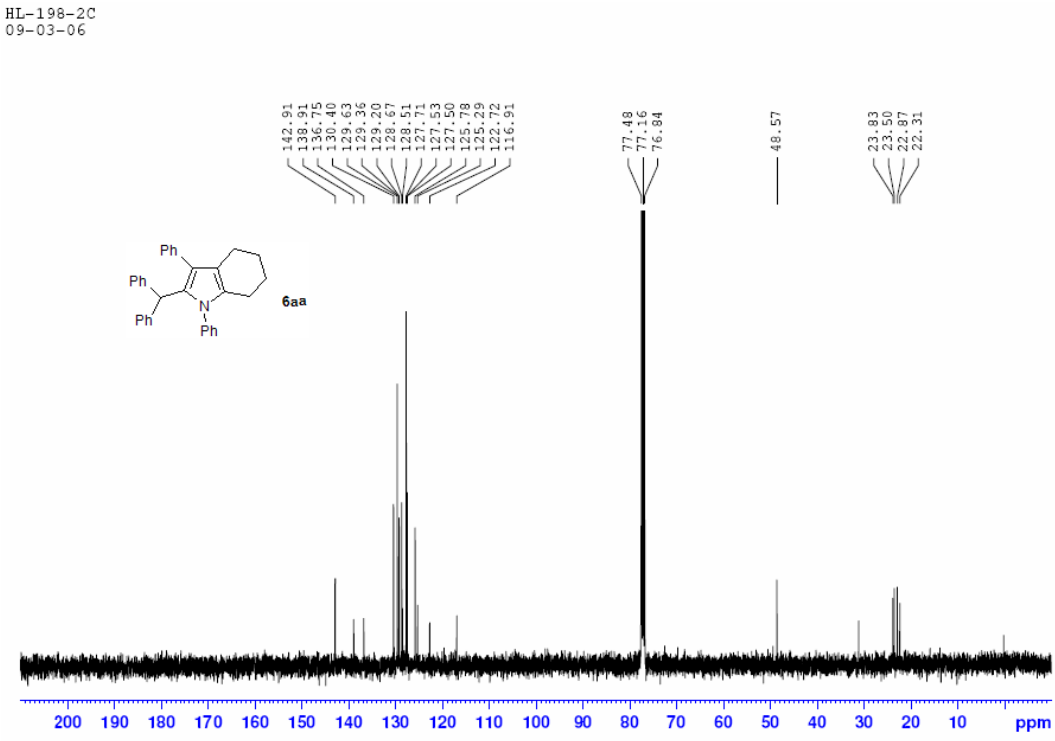

HL 175-H
CDCl3
2008/11/29
7.387
7.382
7.373
7.369
7.363
7.360
7.357
7.355
7.345
7.340
7.228
7.225
7.219
7.205
7.201
7.193
7.188
7.180
7.177
7.150
7.146
7.142
7.132
7.128
7.123
7.111
7.109
7.095
7.092
7.085
7.082
7.077
7.073
7.069
7.060
7.057
7.048
6.581
2.713
2.693
2.672
1.409
1.390
1.370
1.350
1.333
1.155
1.145
1.137
1.128
1.119
0.762
0.745
0.727
5ja
Ph
N
Ph
10
9
8
7
6
5
4
3
2
1
ppm
3.06
3.19
7.07
0.97
2.01
2.05
4.09
3.05


HL 175-C
CDCl3
2008/11/29
139.51
139.09
134.13
133.50
132.97
129.10
129.07
128.14
128.07
128.02
127.40
126.16
122.67
122.66
115.77
109.31
77.48
77.16
76.84
31.71
29.57
25.65
22.15
13.99
5ja
Ph
N
Ph
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

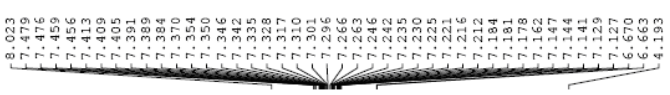

liuxt-27-2-H
081124
7.466
7.448
7.350
7.332
7.312
7.224
7.216
7.198
7.180
7.047
6.834
6.782
6.220
6.218
3.941
2.026
Ph
Ph
Ph
Ph
5dj
9
8
7
6
5
4
3
2
1
0
ppm
4.16
4.18
2.14
6.34
8.17
2.00
4.01
6.05

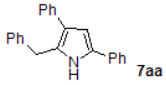

liuxt-27-2-C
081124
140.36
138.02
137.08
129.45
129.05
128.60
128.24
128.14
127.95
127.39
125.89
125.68
123.35
107.22
77.48
77.16
76.84
31.47
12.87
Ph
Ph
Ph
Ph
5dj
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


HL198-2-H
7.230
7.225
7.220
7.213
7.210
7.208
7.189
7.186
7.177
7.174
7.163
7.160
7.157
7.061
7.058
7.053
7.049
7.047
7.043
7.040
7.037
6.950
6.946
6.935
6.931
6.926
6.915
6.912
6.878
6.877
6.872
6.870
6.866
6.863
6.859
6.858
5.509
2.387
2.375
2.364
2.231
2.220
2.207
1.774
1.768
1.765
1.761
1.756
1.753
1.741
1.730
1.728
1.722
1.715
1.710
Ph
Ph
Ph
N
Ph
6aa
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.08
9.06
4.06
4.00
0.98
2.09
2.07
4.06

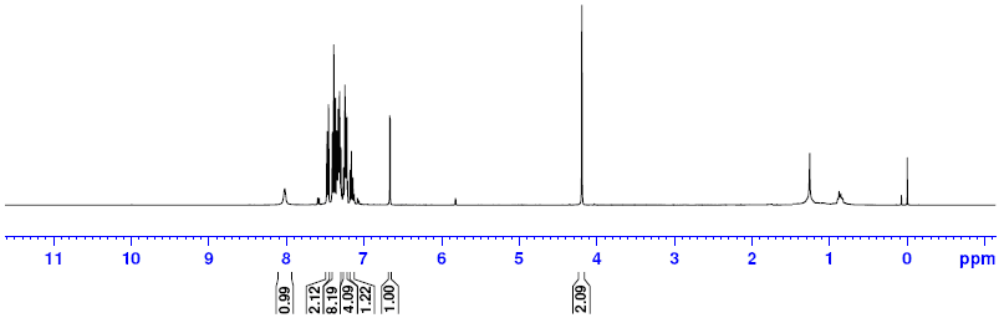

HL-198-2C
09-03-06
142.91
138.91
136.75
130.40
129.63
129.36
129.20
128.67
128.51
127.71
127.53
127.50
125.78
125.29
122.72
116.91
77.48
77.16
76.84
48.57
23.83
23.50
22.87
22.31
Ph
Ph
Ph
N
Ph
6aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Liuxt-22-H
081117



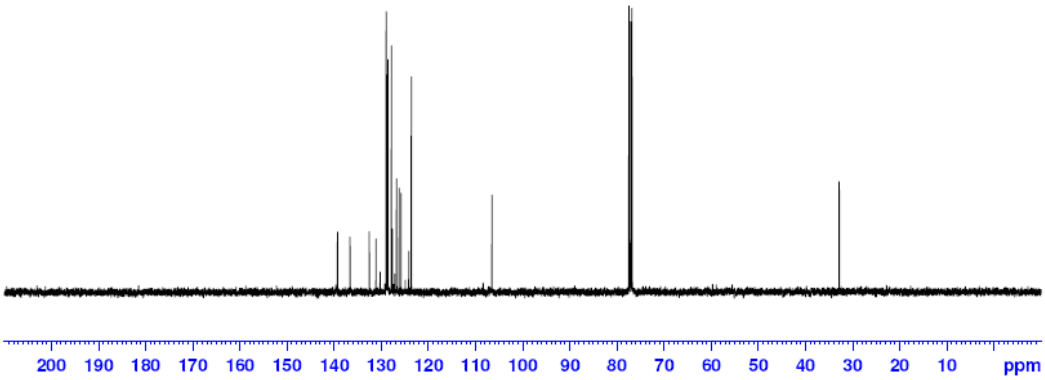


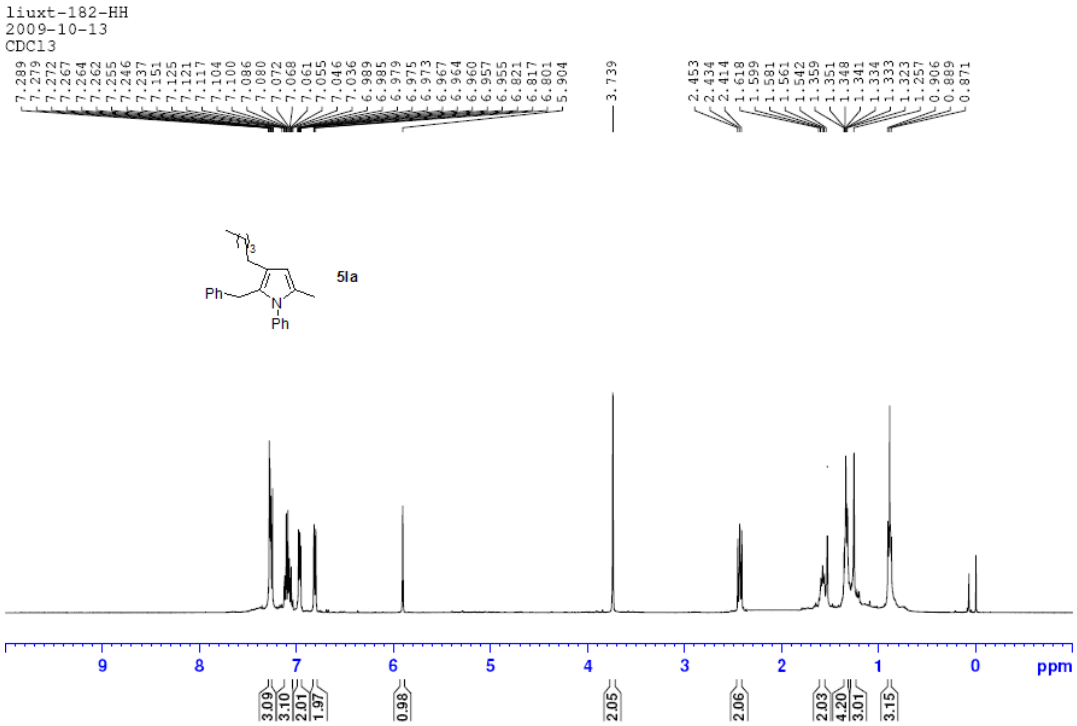
7aa

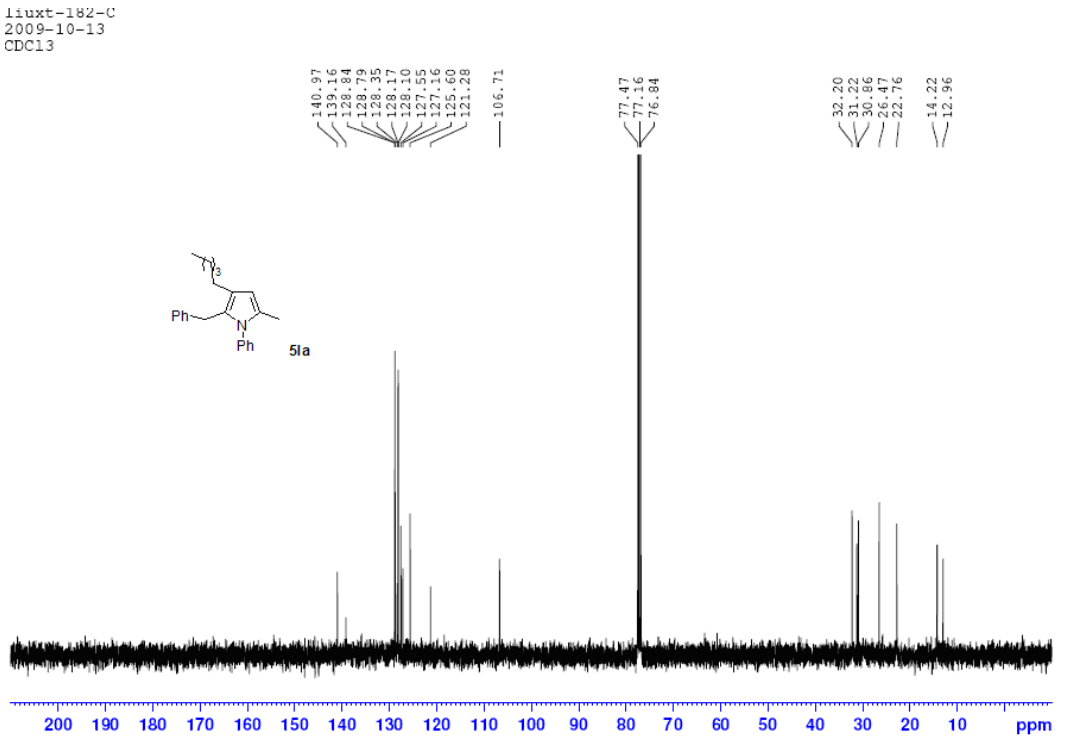


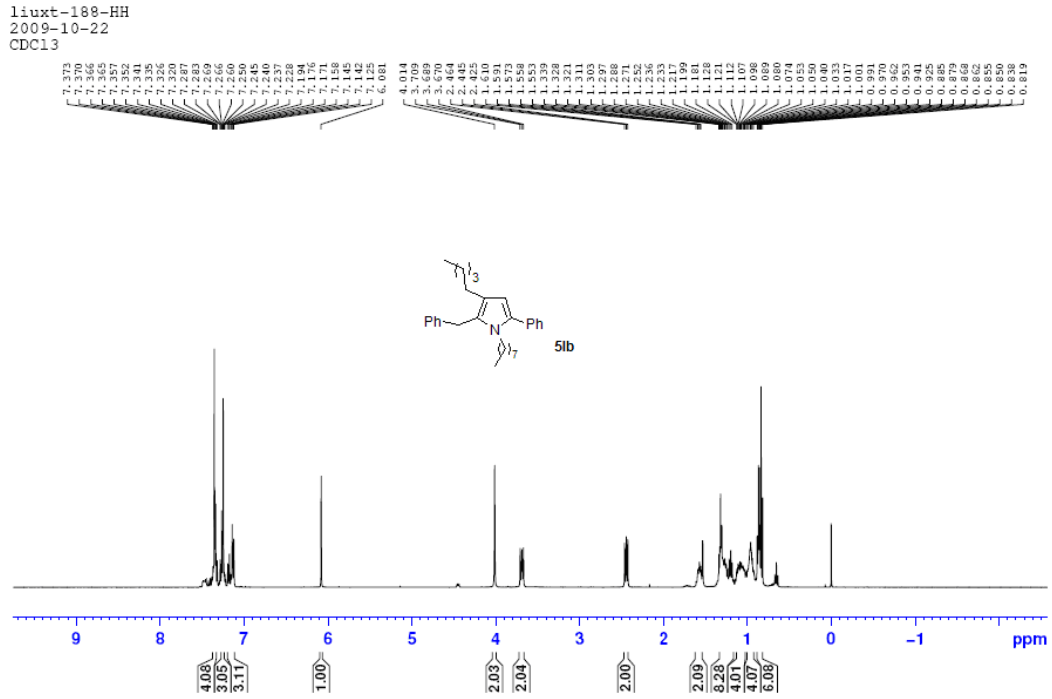
Liuxt-22-C
081117

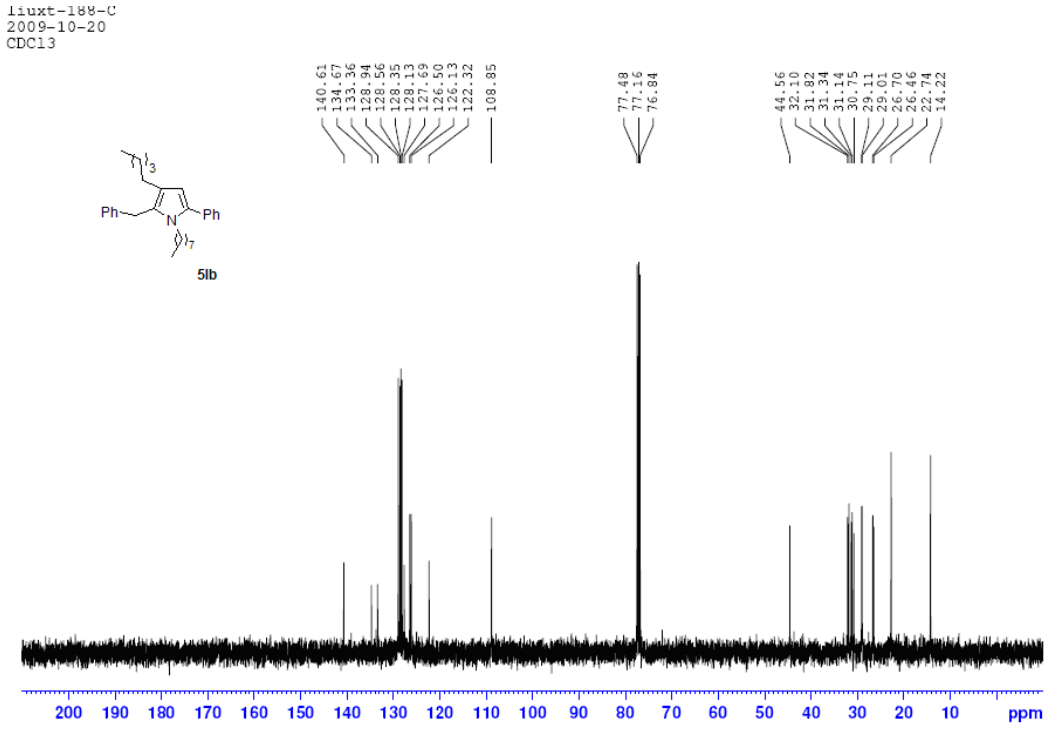
7aa

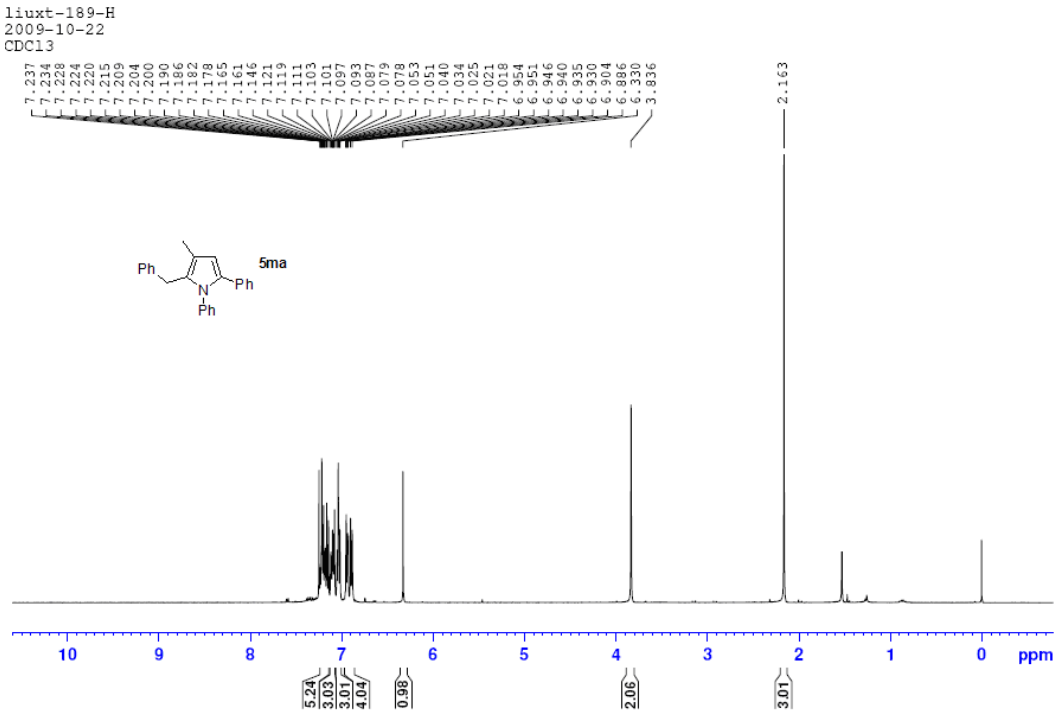


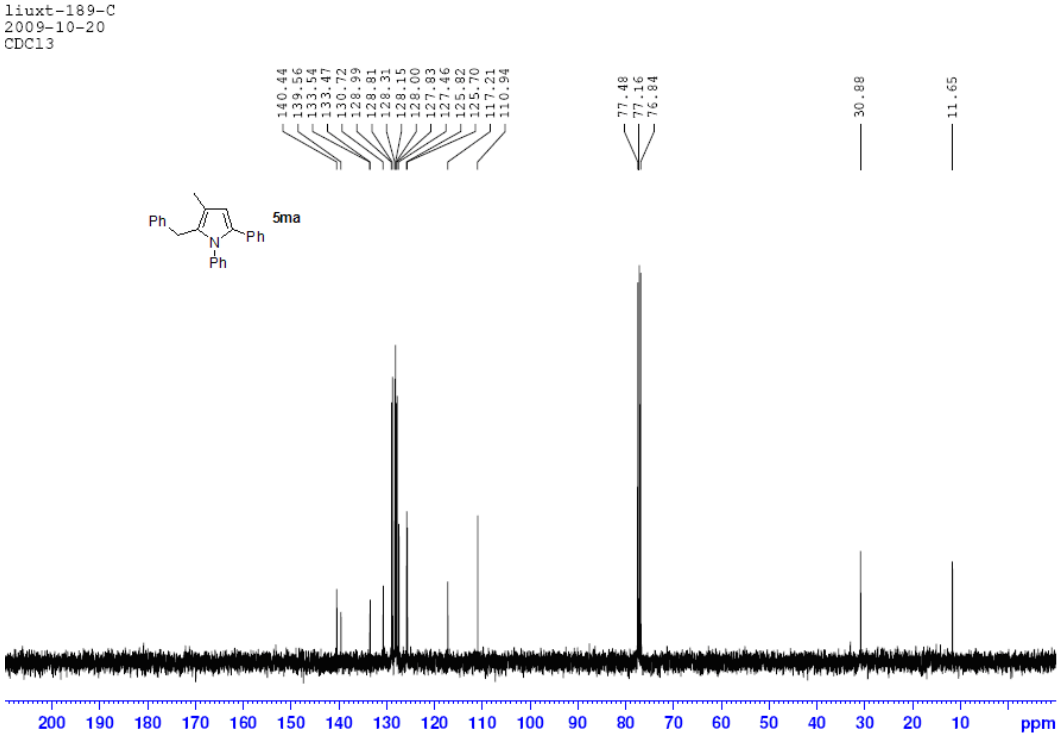

liuxt-182-HH
2009-10-13
CDCl3
7.289
7.279
7.272
7.267
7.264
7.262
7.255
7.246
7.237
7.151
7.125
7.121
7.117
7.104
7.100
7.086
7.080
7.072
7.068
7.061
7.055
7.046
7.036
6.989
6.985
6.979
6.975
6.973
6.967
6.964
6.960
6.957
6.955
6.821
6.817
6.801
5.904
3.739
2.453
2.434
2.414
1.618
1.599
1.581
1.561
1.542
1.359
1.351
1.348
1.341
1.334
1.333
1.323
1.257
0.906
0.889
0.871
Ph
N
Ph
5la
9
8
7
6
5
4
3
2
1
0
ppm
3.09
3.10
2.01
1.97
0.98
2.05
2.06
2.03
4.20
3.01
3.15

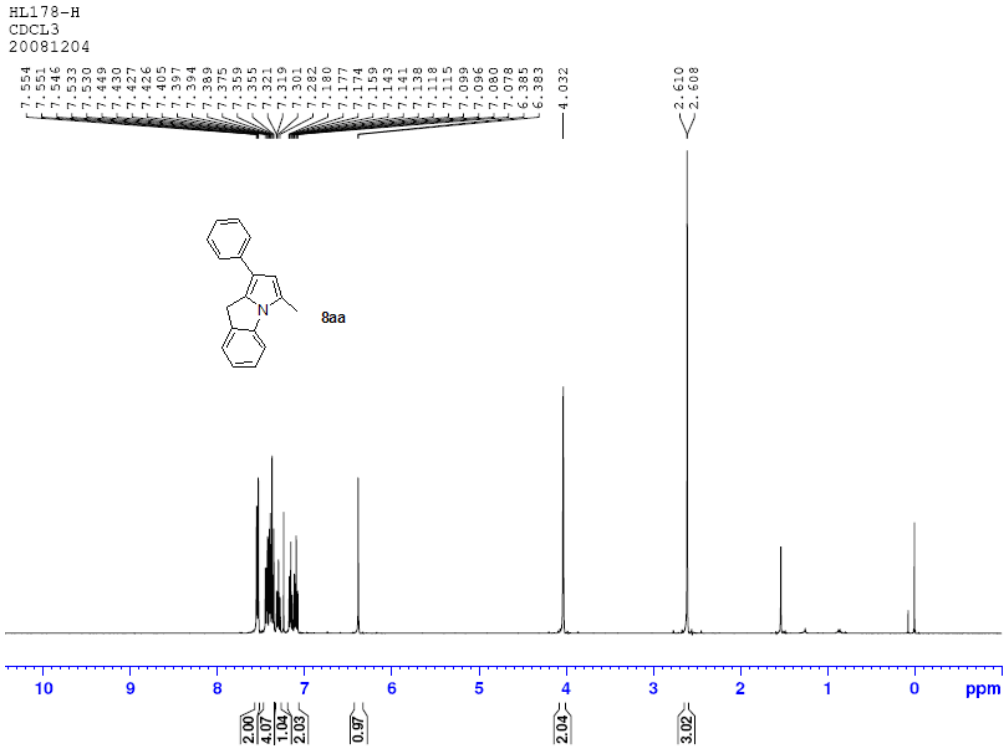

liuxt-182-C
2009-10-13
CDCl3
140.97
139.16
129.84
128.79
128.35
128.17
128.10
127.55
127.16
125.60
121.28
106.71
77.47
77.16
76.84
32.20
31.22
30.86
26.47
22.76
14.22
12.96
Ph
N
Ph
5la
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

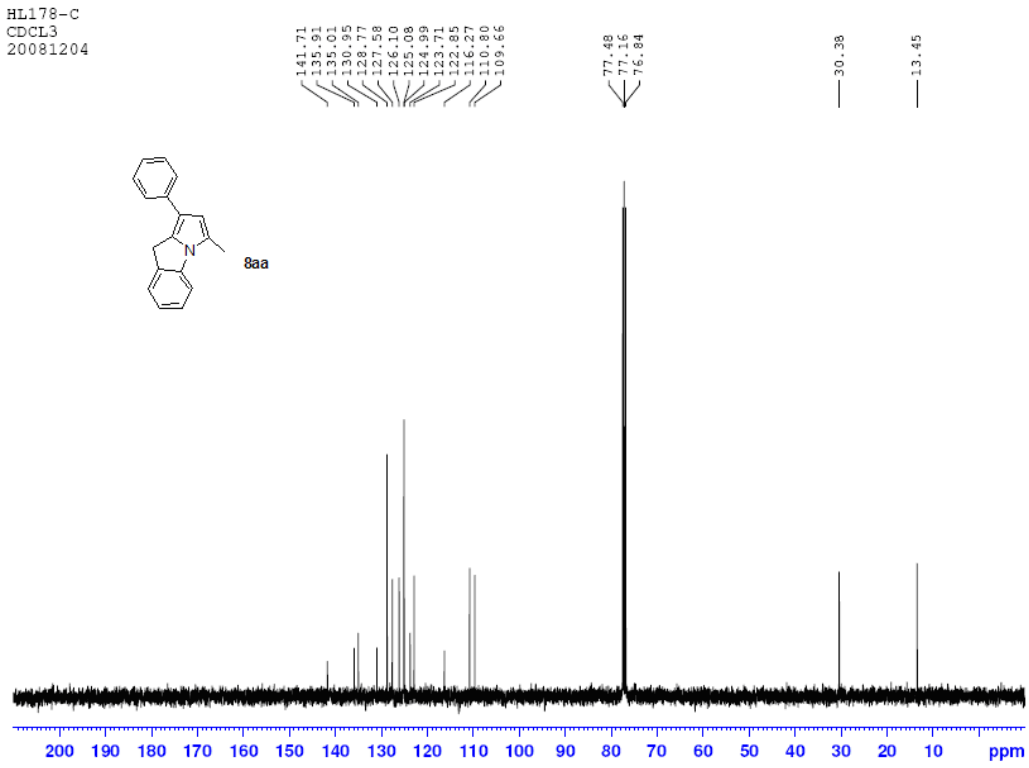

liuxt-188-HH
2009-10-22
CDCl3
5Ib
ppm

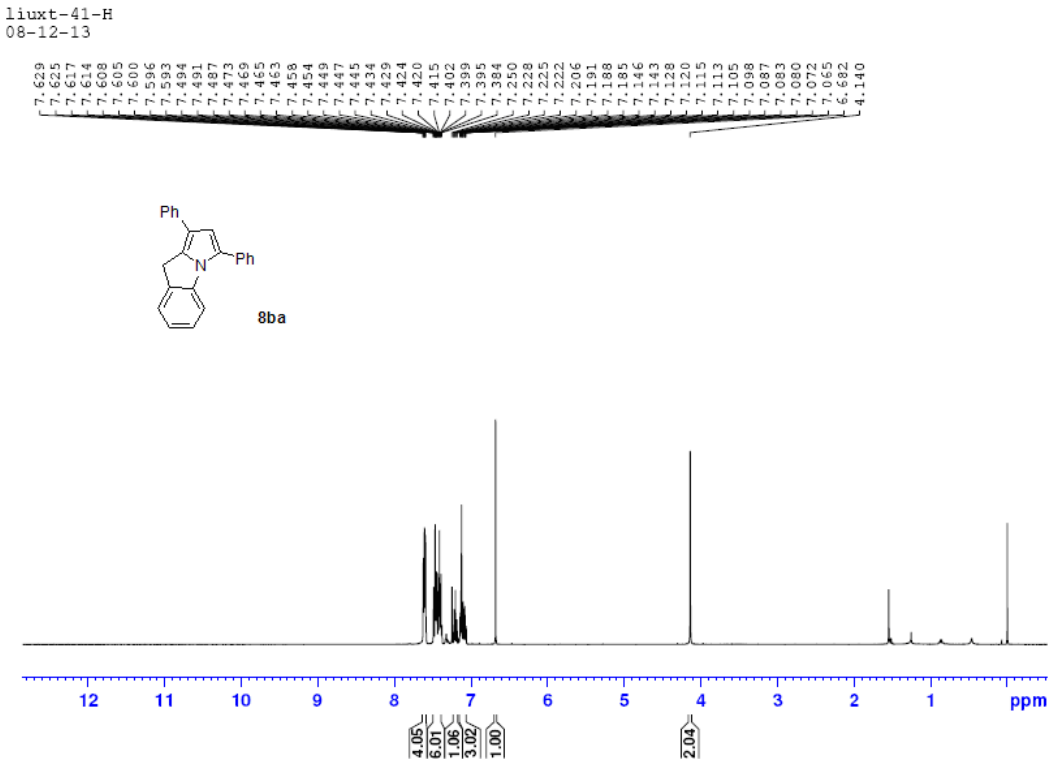

liuxt-188-C
2009-10-20
CDCl3
5Ib
ppm

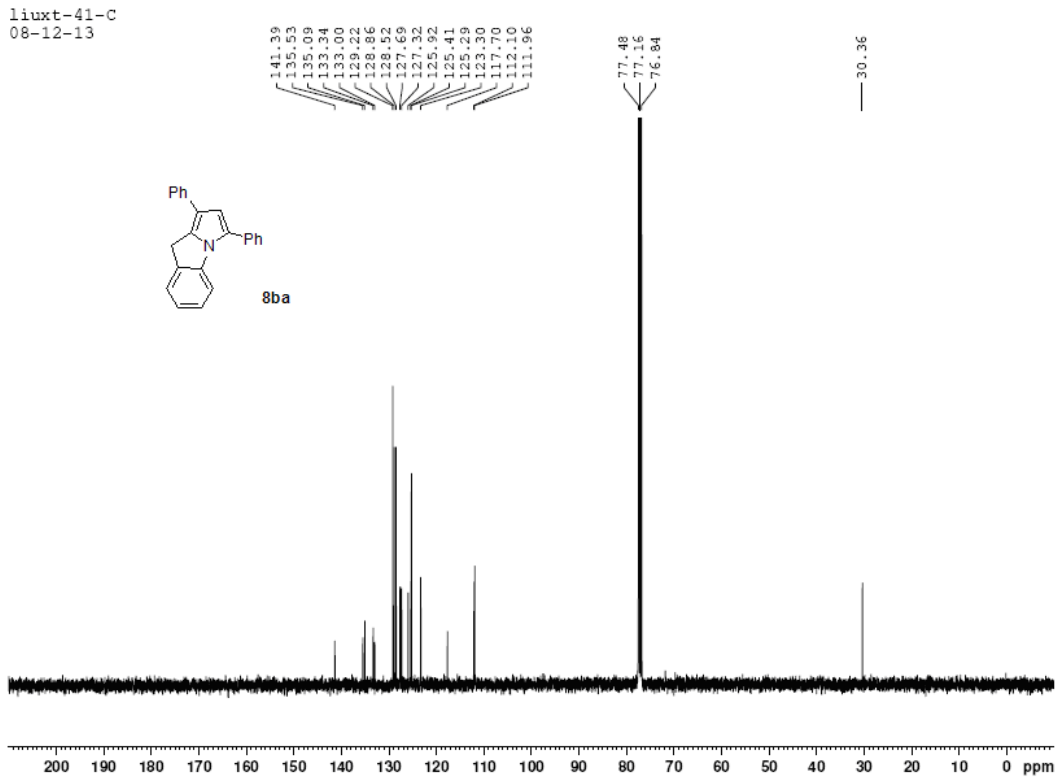

liuxt-189-H
2009-10-22
CDCl3
7.237
7.234
7.228
7.224
7.220
7.215
7.209
7.204
7.200
7.190
7.186
7.182
7.178
7.165
7.161
7.146
7.121
7.119
7.111
7.103
7.101
7.097
7.093
7.087
7.079
7.078
7.053
7.051
7.040
7.034
7.025
7.021
7.018
6.954
6.951
6.946
6.940
6.935
6.930
6.904
6.886
6.330
3.836
2.163
Ph
Ph
N
Ph
5ma
10
9
8
7
6
5
4
3
2
1
0
ppm
5.24
3.03
3.01
4.04
0.98
2.06
3.01

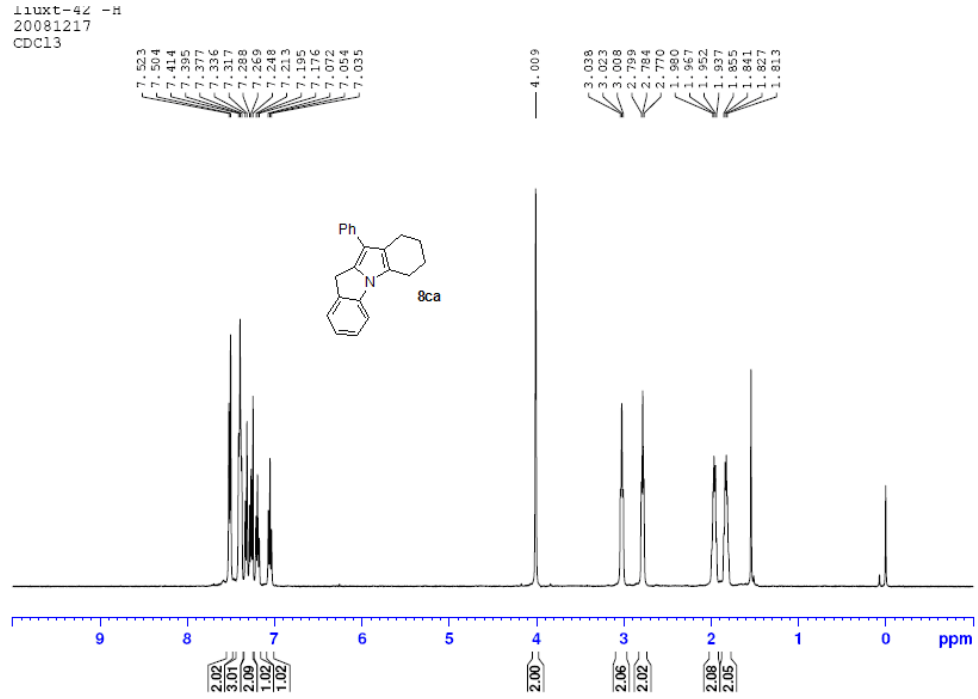

liuxt-189-C
2009-10-20
CDCl3
140.44
139.56
133.54
133.47
130.72
128.99
128.81
128.31
128.15
128.00
127.83
127.46
125.82
125.70
117.21
110.94
77.48
77.16
76.84
30.88
11.65
Ph
Ph
N
Ph
5ma
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

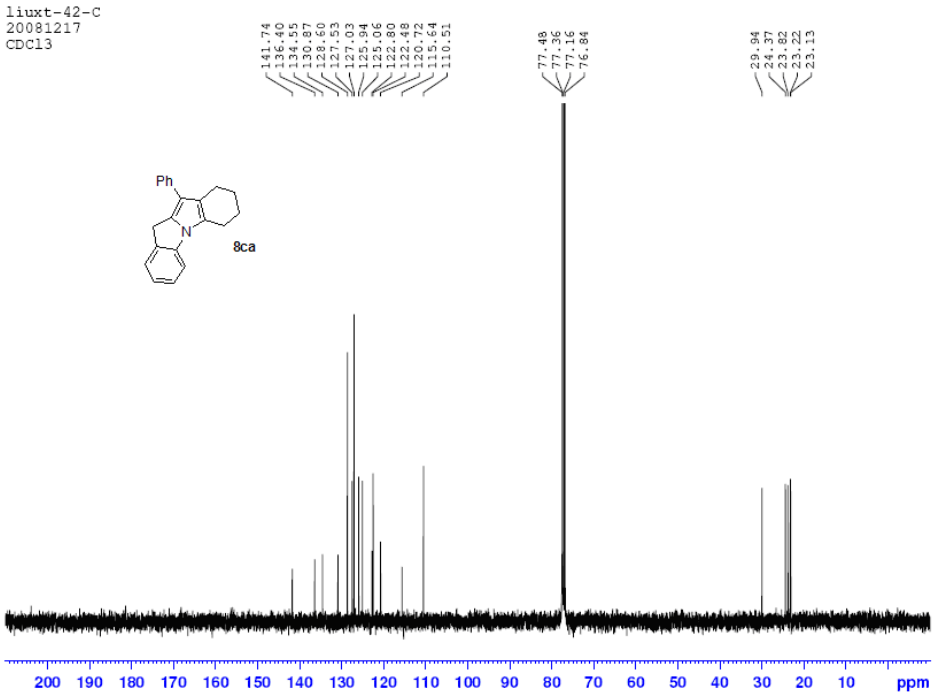

HL178-H
CDCL3
20081204
7.554
7.551
7.546
7.533
7.530
7.449
7.430
7.427
7.426
7.405
7.397
7.394
7.389
7.375
7.359
7.355
7.321
7.319
7.301
7.282
7.180
7.177
7.174
7.159
7.143
7.141
7.138
7.118
7.115
7.099
7.096
7.080
7.078
6.385
6.383
4.032
2.610
2.608
8aa
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
4.07
1.04
2.03
0.97
2.04
3.02

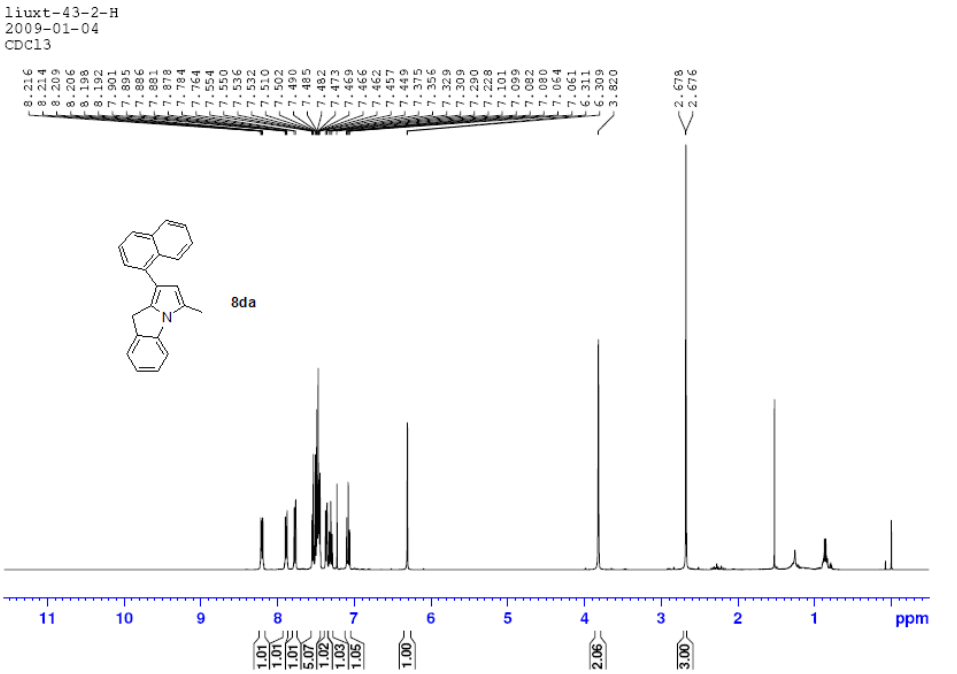

HL178-C
CDCL3
20081204
141.71
135.91
135.01
130.95
128.77
127.58
126.10
125.08
124.99
123.71
122.85
116.27
110.80
109.66
77.48
77.16
76.84
30.38
13.45
8aa
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

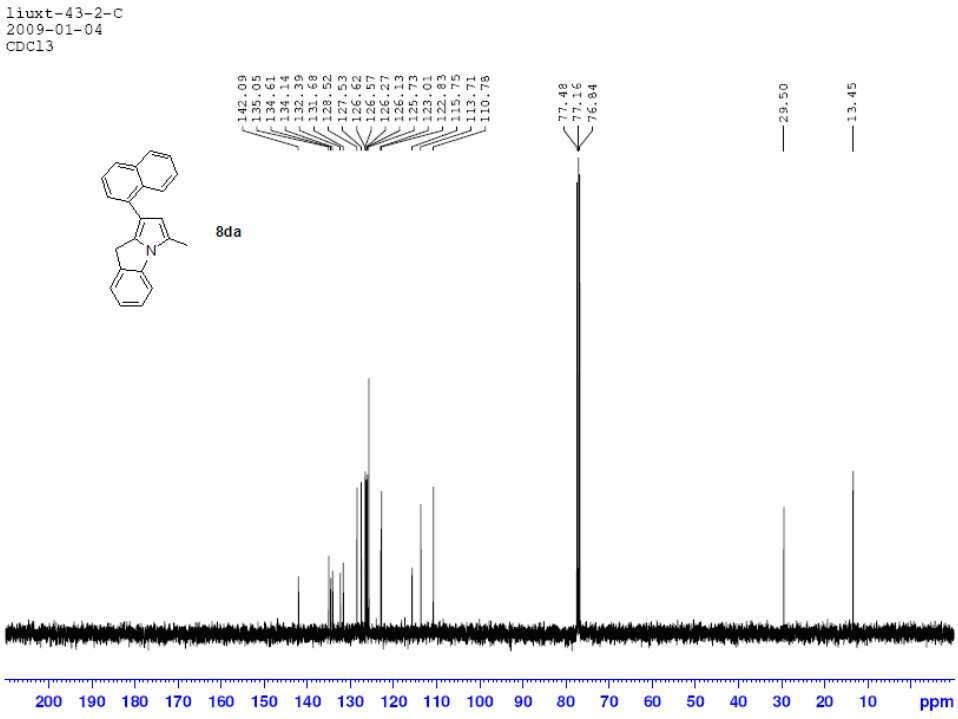

liuxt-41-H
08-12-13
7.629
7.625
7.617
7.614
7.608
7.605
7.600
7.596
7.593
7.494
7.491
7.487
7.473
7.469
7.465
7.463
7.458
7.454
7.449
7.447
7.445
7.434
7.429
7.424
7.420
7.415
7.402
7.399
7.395
7.384
7.250
7.228
7.225
7.222
7.206
7.191
7.188
7.185
7.146
7.143
7.128
7.120
7.115
7.113
7.105
7.098
7.087
7.083
7.080
7.072
7.065
6.682
4.140
Ph
Ph
N
8ba
12
11
10
9
8
7
6
5
4
3
2
1
ppm
4.05
6.01
1.06
3.02
1.00
2.04

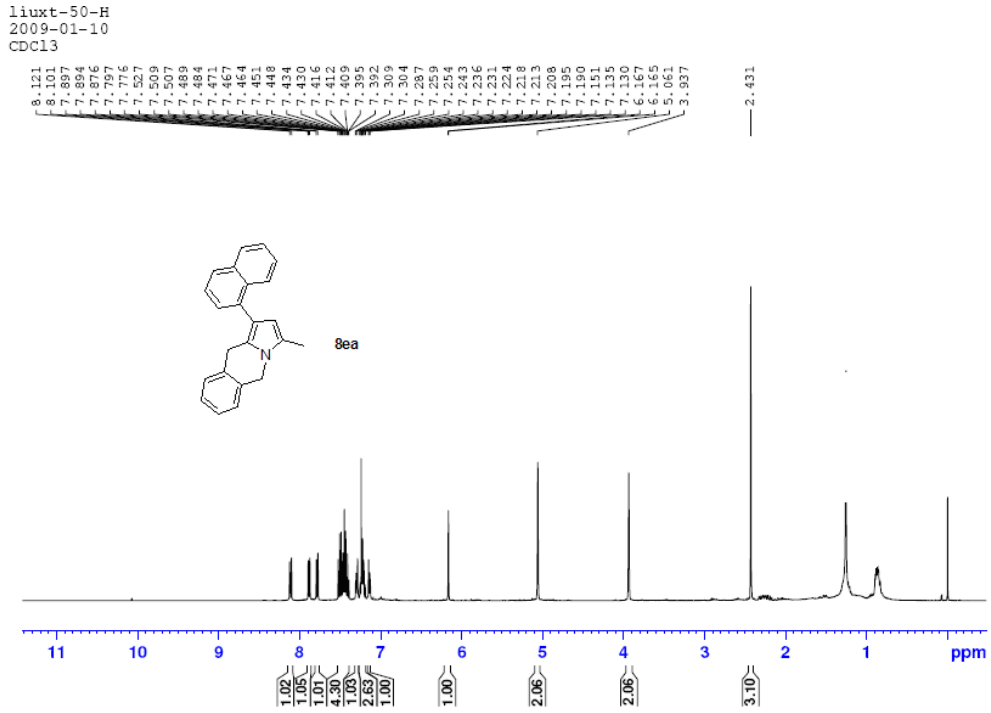

liuxt-41-C
08-12-13
141.39
135.53
135.09
133.34
133.00
129.22
128.86
128.52
127.69
127.32
125.92
125.41
125.29
123.30
117.70
112.10
111.96
77.48
77.16
76.84
30.36
Ph
Ph
N
8ba
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


liuxt-42 -H
20081217
CDCl3
7.523
7.504
7.414
7.395
7.377
7.336
7.317
7.288
7.269
7.248
7.213
7.195
7.176
7.072
7.054
7.035
4.009
3.038
3.023
3.008
2.799
2.784
2.770
1.980
1.967
1.952
1.937
1.855
1.841
1.827
1.813
Ph
N
8ca
9
8
7
6
5
4
3
2
1
0
ppm
2.02
3.01
2.09
1.02
1.02
2.00
2.06
2.02
2.08
2.05


liuxt-42-C
20081217
CDCl3
141.74
136.40
134.55
130.87
128.60
127.53
127.03
125.94
125.06
122.80
122.48
120.72
115.64
110.51
77.48
77.36
77.16
76.84
29.94
24.37
23.82
23.22
23.13
Ph
N
8ca
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


liuxt-43-2-H
2009-01-04
CDCl3
8.216
8.214
8.209
8.206
8.198
8.192
7.901
7.895
7.886
7.881
7.878
7.784
7.764
7.554
7.550
7.536
7.532
7.510
7.502
7.490
7.485
7.482
7.473
7.469
7.466
7.462
7.457
7.449
7.375
7.356
7.329
7.309
7.290
7.228
7.101
7.099
7.082
7.080
7.064
7.061
6.311
6.309
3.820
2.678
2.676
8da
11
10
9
8
7
6
5
4
3
2
1
ppm
1.01
1.01
1.01
5.07
1.02
1.03
1.05
1.00
2.06
3.00


liuxt-43-2-C
2009-01-04
CDCl3
142.09
135.05
134.61
134.14
132.39
131.68
128.52
127.53
126.62
126.57
126.27
126.13
125.73
123.01
122.83
115.75
113.71
110.78
77.48
77.16
76.84
29.50
13.45
8da
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


liuxt-50-H
2009-01-10
CDCl3
8.121
8.101
7.897
7.894
7.876
7.797
7.776
7.527
7.509
7.507
7.489
7.484
7.471
7.467
7.464
7.451
7.448
7.434
7.430
7.416
7.412
7.409
7.395
7.392
7.309
7.304
7.287
7.259
7.254
7.243
7.236
7.231
7.224
7.218
7.213
7.208
7.195
7.190
7.151
7.135
7.130
6.167
6.165
5.061
3.937
2.431
8ea
N
11
10
9
8
7
6
5
4
3
2
1
ppm
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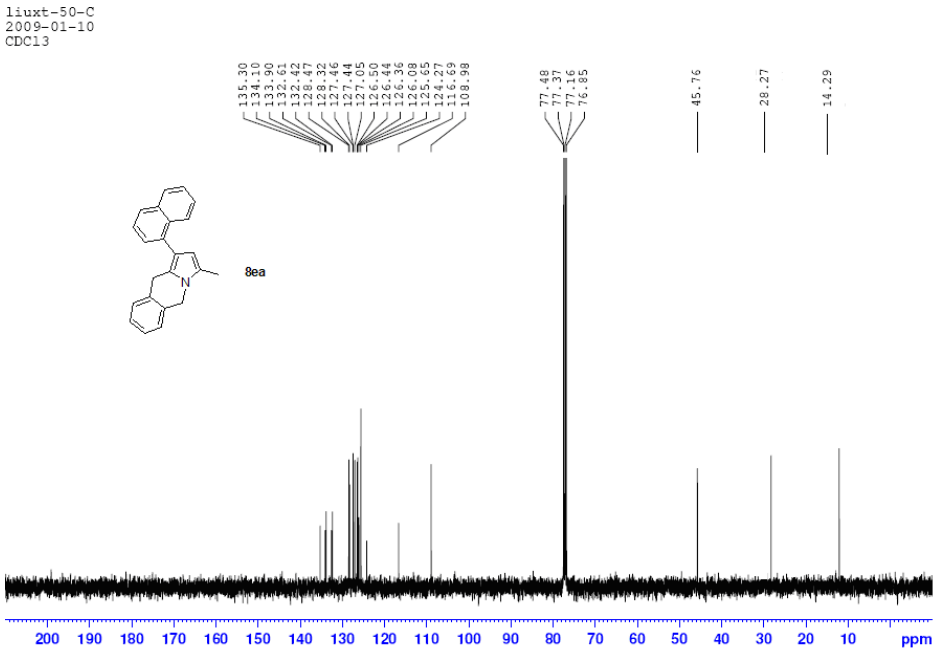
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