Electronic Supplementary Information

Copper catalyzed pyrrole synthesis from 3,6-dihydro-1,2-oxazines

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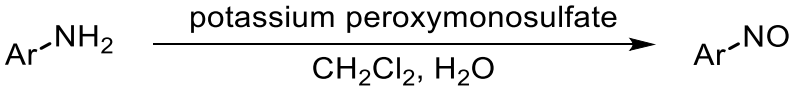
Contents

1. General Information.

10% Pd/C, 10% Pt/C, 10% Rh/C, 10% Ru/C, 10% Ni/C, 10% Ir/C, 10% Au/C, 10% Ag/C and 10% Cu/C was supplied by N. E. Chemcat Corporation (Tokyo, Japan). Cu powder, CuBr, $CuBr_2$, H_2O, MeOH, EtOH, MeCN, DMF, THF, toluene, CH_2Cl_2 and acetic acid were purchased from commercial sources and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). ^{1}H and ^{13}C NMR spectra were recorded on a ECA 500 spectrometer at room temperature in $CDCl_3$ and DMSO-d_6 as a solvent and internal standard (^{1}H NMR: δ= 7.26; ^{13}C NMR: δ= 77.0 for $CDCl_3$, ^{1}H NMR: δ= 2.49 for DMSO-d_6) with tetramethylsilane as an internal standard. IR spectra were recorded by a Bruker FT-IR ALPHA. ESI high resolution mass spectra (HRMS) were measured by a Shimadzu hybrid IT-TOF mass spectrometer. Elemental analyses were carried out using J Science LaboJM10. Melting points were measured by a SANSYO SMP-300 melting point apparatus. Substrates (**1a**, **2n**, **2o**) are commercially available. The substrate (**1c**) was prepared according to reference 1. Substrates (**2a**–**2e**, **2g**, **2i**–**2l**) were prepared according to reference 2.

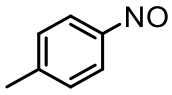
2. Preparation of substrates.

2-1. Synthesis of nitrosobenzene derivatives (1)[1)]



To a solution of aniline derivative (5.0 mmol) in CH_2Cl_2 (11 mL) was added a solution of potassium peroxymonosulfate [oxone® (molecular weight; 307.4 g/mol); 6.15 g, 20.0 mmol] in water (42 mL). The reaction mixture was stirred under argon at room temperature until the TLC monitoring indicated the complete consumption of the starting material. The reaction mixture was extracted with CH_2Cl_2 (30 mL × 2) and washed with water (50 mL × 2). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding nitrosobenzene derivative (**1**).

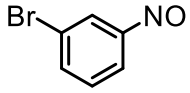
4-Methyl-nitrosobenzene (1b)



4-Toluidine (2.22 g, 20.0 mmol) was used as a substrate and **1b** (0.52 g, 4.3 mmol) was obtained in 22% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 2.45 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 3.

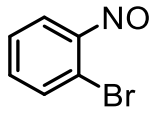
3-Bromo-nitrosobenzene (1d)



3-Bromoaniline (1.72 g, 10.0 mmol) was used as a substrate and **1d** (1.33 g, 7.2 mmol) was obtained in 72% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (ddd, J = 2.0, 2.0, 8.0 Hz, 1H), 7.84 (ddd, J = 2.0, 2.0, 8.0 Hz, 1H), 7.77 (dd, J = 2.0, 2.0 Hz, 1H), 7.57 (dd, J = 8.0, 8.0 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 4.

2-Bromo-nitrosobenzene (1e)

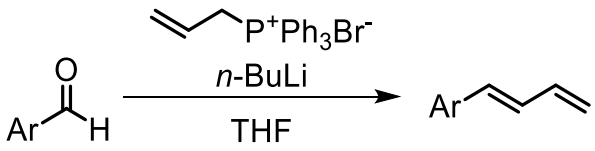


2-Bromoaniline (0.95 g, 5.5 mmol) was used as a substrate and **1e** (1.04 g, 5.5 mmol) was obtained in quantitative yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00 (dd, J = 1.5, 7.5 Hz, 1H), 7.54 (ddd, J = 1.5, 7.5, 7.5 Hz, 1H), 7.28 (ddd, J = 1.5, 7.5, 7.5 Hz, 1H), 6.22 (dd, J = 1.5, 7.5 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 4.

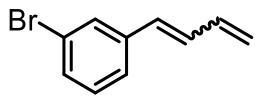
2-2. Synthesis of 1,3-butadienes (2)

2-2-1. Genaral procedure[2)]



To a suspension of allytriphenylphosphonium bromide (6.13 g, 16.0 mmol) in THF (90 mL, 0.17 M) was added *n*-BuLi (6.34 mL: 2.6 M in *n*-hexane, 18.0 mmol) at 0 ºC under argon. After stirring for 15 min, the benzaldehyde derivative (2.37 g, 15.0 mmol) was added. The reaction mixture was warmed up to room temperature and the progress of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was quenched with sat. NH_4Cl aq. (40 mL) and extracted with AcOEt (50 mL × 2). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give the corresponding 1-aryl-1,3-butadiene derivative (**1**).

(*E* or *Z*)-1-(Buta-1,3-dienyl)-3-bromobenzene (2f)

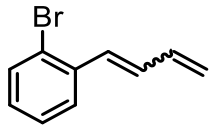


3-Bromobenzaldehyde (2.37 g, 15.0 mmol) was used as a substrate and **2f** (1.56 g, 7.5 mmol) was obtained in 50% yield after purification by silica-gel column chromatography using *n*-hexane. *E*/*Z* mixture was obtained. *E*/*Z* ratio = 52/48.

Colorless solid; ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 7.55 (s, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.25–7.16 (m, 1H), 6.78–6.75 (m, 1H), 6.53–6.46 (m, 2H), 5.37 (d, J =17.5 Hz, 1H), 5.22 (d, J =10.5 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those

reported in reference 5. ^{1}H NMR of *Z* isomer (500 MHz, $CDCl_3$): δ 7.46 (s, 1H), 7.37 (d, J = 6.5 Hz, 1H), 7.25–7.16 (m, 2H), 6.85–6.80 (m, 1H), 6.37 (d, J = 11.5 Hz, 1H), 6.29 (dd, J = 11.5 11.5 Hz, 1H), 5.40 (d, J = 19.5 Hz, 1H), 5.27 (d, J = 10.5 Hz, 1H). *Z* isomer is unknown compound but the two isomers were inseparable.

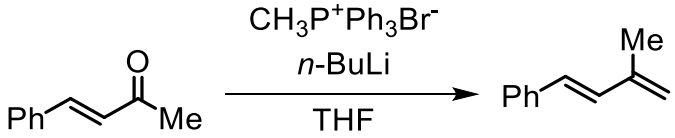
(*E* or *Z*)-1-(Buta-1,3-dienyl)-2-bromobenzene (2h)



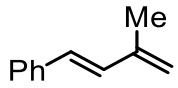
2-Bromoaldehyde (2.37 g, 15.0 mmol) was used as s substrate and **2h** (1.04 g, 5.0 mmol) was obtained in 33% yield after purification by silica-gel column chromatography using *n*-hexane. *E*/*Z* mixture was obtained. *E*/*Z* ratio = 34/66.

Colorless solid; ^{1}H NMR of *E* isomer (500 MHz, $CDCl_3$): δ 7.60–7.54 (m, 2H), 7.29 (dd, J = 7.5, 7.5 Hz, 1H), 7.09, (ddd, J = 1.0, 7.5, 7.5 Hz, 1H), 6.92 (d, J = 15.0 Hz, 1H), 6.76–6.50 (m, 2H), 5.39 (d, J = 16.5 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 6. ^{1}H NMR of *Z* isomer (500 MHz, $CDCl_3$): δ 7.60 (dd, J = 8.0, 8.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 1H), 7.29 (dd, J = 8.0, 8.0 Hz, 1H), 7.13, (d, J = 8.0 Hz, 1H), 6.76–6.50 (m, 2H), 6.35 (dd, J = 11.5, 11.5 Hz, 1H), 5.42 (d, J = 16.0 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H). *Z* isomer is unknown compound but the two isomers were inseparable.

2-2-2. Synthetic procedures of (*E*)-3-methylbuta-1,3-dien-1-yl]benzene (2m)



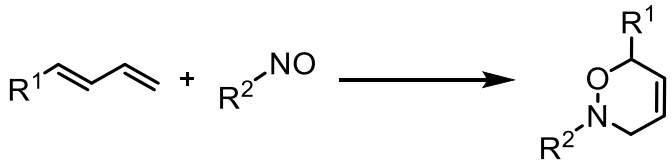
To a suspension of methyltriphenylphosphonium bromide (3.75 g, 10.5 mmol) in THF (60 mL, 0.17 M) was added *n*-BuLi (4.2 mL: 2.6 M in *n*-hexane, 11.0 mmol) at 0 °C under argon. After stirring for 15 min, benzalacetone (1.46 g, 10.0 mmol) was added. The reaction mixture was warmed at room temperature. After stirring for 15 h, the reaction mixture was quenched with sat. NH_4Cl aq. (30 mL) and extracted with AcOEt (40 mL × 2). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography using only *n*-hexane as an eluent to give [(*E*)-3-methylbuta-1,3-dien-1-yl]benzene (**2m**: 1.00 g, 6.6 mmol) in 66% yield.



Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 7.5 Hz, 2H), 7.33 (dd, J = 1.5, 7.5 Hz,

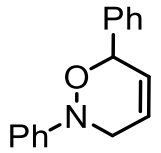
2H), 7.23 (dt, *J* = 1.5, 7.5 Hz, 1H), 6.93 (d, *J* = 16.0 Hz, 1H) 6.54 (d, *J* = 16.0 Hz, 1H), 5.12 (s, 1H), 5.08 (s, 1H), 1.98 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 7.

2-3. Synthesis of 3,6-dihydro-2*H*-[1,2]oxazine derivative (3)



1,3-Butadiene derivative (0.39 g, 3.0 mmol) and nitrosobenzene derivative (0.39 g, 3.6 mmol) were added to a round bottomed flask at room temperature under argon and the progress of the reaction was monitored by TLC. After the reaction was completed, the residue was purified by silica-gel column chromatography to give the corresponding 3,6-dihydro-[1,2]-oxazine derivative (**3**).

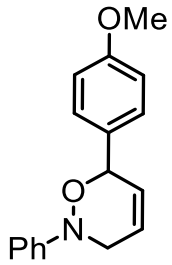
2,6-Diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (3aa)



1a (0.39 g, 3.6 mmol) and **2a** (0.39 g, 3.0 mmol) were used as substrates and **3aa** (0.55 g, 2.3 mmol) was obtained in 77% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Colorless solid; M. p. 81–83 ^{o}C; IR (ATR) cm^{-1}: 3061, 3038, 2927, 2861, 2819, 1599, 1492, 1453, 1431, 1385, 1338, 1298, 1265, 1212, 1178, 1156, 1112, 1097, 1068, 1008; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, *J* = 7.5 Hz, 2H), 7.38 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.16–6.07 (m, 2H), 5.62–5.61 (m, 1H), 4.00–3.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.32, 138.89, 128.99, 128.73, 128.44, 128.37, 128.14, 128.82, 122.15, 115.77, 79.86, 51.55; ESI-HRMS m/z: 238.1256 ([M+H^{+}]); Calcd for $C_{16}H_{16}NO$: 238.1226.

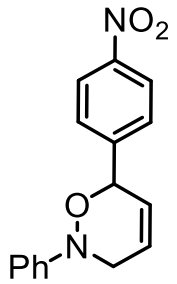
6-(4-Methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ab)



1a (0.13 g, 1.2 mmol) and **2b** (0.16 g, 1.0 mmol) were used as substrates and **3ab** (0.18 g, 0.61 mmol) was obtained in 61% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; M. p. 78–79 °C; IR (ATR) cm^{-1}: 3046, 2996, 2947, 2834, 1598, 1511, 1490, 1453, 1302, 1246, 1212, 1173, 1033; ^1H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 7.5 Hz, 2H), 7.26 (dd, J = 7.5, 7.5 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.95 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.15–6.11 (m, 1H), 6.08–6.04 (m, 1H), 5.56–5.55 (m, 1H), 3.99–3.86 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.67, 150.32, 130.99, 129.66, 129.14, 128.70, 123.81, 122.05, 115.73, 113.77, 79.46, 55.26, 51.42; ESI-HRMS m/z: 290.1154 ([M+Na^+]); Calcd for $C_{17}H_{17}NO_2Na$: 290.1152.

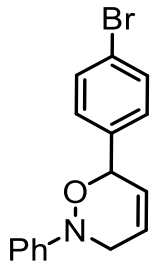
6-(4-Nitrophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ac)



1a (0.13 g, 1.2 mmol) and **2c** (0.18 g, 1.0 mmol) were used as substrates and **3ac** (0.20 g, 0.68 mmol) was obtained in 68% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (5/1).

Yiellow solid; M. p. 88–90 °C; IR (ATR) cm^{-1}: 3071, 2923, 2858, 2822, 1598, 1519, 1490, 1454, 1430, 1348, 1265, 1213, 1109, 1073, 1044, 1009; ^1H NMR (500 MHz, $CDCl_3$): δ 8.22 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 2H), 7.28 (dd, J = 7.5, 7.5 Hz, 2H), 7.07 (d, J = 7.5 Hz, 2H), 7.01 (t, J = 7.5 Hz, 1H), 6.22–6.19 (m, 1H), 6.10–6.08 (m, 1H), 5.66 (m, 1H), 3.95 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.02, 147.68, 146.45, 128.86, 128.70, 127.35, 125.01, 123.63, 122.70, 115.87, 78.56, 51.86; ESI-HRMS m/z: 283.1077 ([M+H^+]); Calcd for $C_{16}H_{15}N_2O_3$: 283.1077.

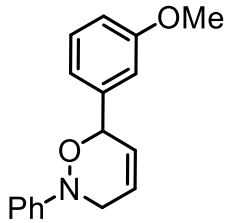
6-(4-Bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ad)



1a (0.39 g, 3.6 mmol) and **2d** (0.63 g, 3.0 mmol) were used as substrates and **3ad** (0.26 g, 0.8 mmol) was obtained in 27% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; M. p. 71–73 °C; IR (ATR) cm^{-1}: 3041, 2860, 2818, 1596, 1488, 1453, 1429, 1405, 1323, 1295, 1212, 1094, 1070, 1043, 1011; ^1H NMR (500 MHz, $CDCl_3$): δ 7.50 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.5 Hz, 2H), 7.28 (dd, J = 8.0, 8.0 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 8.0 Hz, 1H), 6.17–6.13 (m, 1H), 6.06–6.02 (m, 1H), 5.56–5.55 (m, 1H), 3.97–3.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.18, 138.01, 131.55, 129.87, 128.77, 128.32, 124.29, 122.38, 122.34, 115.78, 79.11, 51.58; ESI-HRMS m/z: 316.0336 ([M+H^+]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

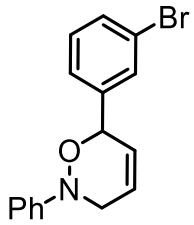
6-(3-Methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ae)



1a (0.19 g, 1.8 mmol) and **2e** (0.24 g, 1.5 mmol) were used as substrates and **3ae** (0.09 g, 0.3 mmol) was obtained in 20% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow oil; IR (ATR) cm^{-1}: 3041, 2937, 2860, 2834, 1599, 1489, 1454, 1434, 1385, 1319, 1269, 1213, 1153, 1097, 1071, 1043, 1008; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31–7.26 (m, 3H), 7.11 (d, J = 7.5 Hz, 2H), 7.05 (d, J = 7.5 Hz, 1H), 7.01 (dd, J = 1.5, 1.5 Hz, 1H), 6.97 (t, J = 7.5 Hz, 1H), 6.87 (dd, J = 1.5, 8.0 Hz, 1H), 6.14–6.11 (m, 1H), 6.09–6.06 (m, 1H), 5.60–5.59 (m, 1H), 3.99–3.88 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.61, 150.30, 140.47, 129.45, 128.95, 128.73, 123.81, 122.16, 120.37, 115.78, 113.82, 113.55, 79.71, 55.23, 51.56; ESI-HRMS m/z: 268.1332 ([M+H^+]); Calcd for $C_{17}H_{18}NO_2$: 268.1332.

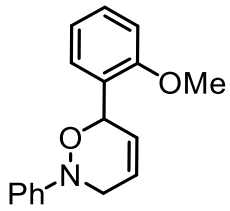
6-(3-Bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3af)



1a (0.39 g, 3.6 mmol) and **2f** (0.63 g, 3.0 mmol) were used as substrates and **3af** (0.26 g, 0.8 mmol) was obtained in 27% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; M. p. 58–60 ºC; IR (ATR) cm^{-1}: 3060, 2860, 2819, 1657, 1598, 1569, 1490, 1475, 1453, 1427, 1384, 1320, 1295, 1212, 1192, 1111, 1097, 1071, 1043, 1008; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (s, 1H), 7.46 (d, J = 7.5 Hz, 1H), 7.40 (d, J = 7.5 Hz, 1H), 7.30–7.22 (m, 3H), 7.09 (d, J = 8.0 Hz, 2H), 6.99 (t, J = 8.0 Hz, 1H), 6.17–6.14 (m, 1H), 6.05–6.03 (m, 1H), 5.56 (d, J = 2.0 Hz, 1H), 3.98–3.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.14, 141.21, 131.41, 131.17, 130.01, 128.77, 128.21, 126.78, 124.40, 122.46, 122.39, 115.85, 79.10, 51.60; ESI-HRMS m/z: 316.0331 ([M+H$^+$]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

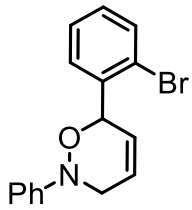
6-(2-Methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ag)



1a (0.19 g, 1.8 mmol) and **2g** (0.24 g, 1.5 mmol) were used as substrates and **3ag** (0.08 g, 0.3 mmol) was obtained in 20% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow oil; IR (ATR) cm^{-1}: 3040, 2935, 2835, 1599, 1489, 1462, 1437, 1384, 1333, 1286, 1242, 1212, 1162, 1109, 1096, 1071, 1048, 1028, 1008; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (dd, J = 1.5, 8.0 Hz, 1H), 7.30–7.25 (m, 3H), 7.11 (d, J = 7.5 Hz, 2H), 6.97–6.92 (m, 3H), 6.09–6.05 (m, 3H), 3.95–3.90 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.02, 150.43, 129.23, 129.19, 128.68, 128.52, 127.21, 123.27, 121.85, 120.42, 115.62, 110.49, 73.75, 55.52, 51.23; ESI-HRMS m/z: 268.1333 ([M+H$^+$]); Calcd for $C_{17}H_{18}NO_2$: 268.1332.

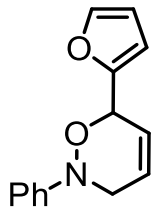
6-(2-Bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ah)



1a (0.39 g, 3.6 mmol) and **2h** (0.63 g, 3.0 mmol) were used as substrates and **3ah** (0.13 g, 0.4 mmol) was obtained in 13% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow oil; IR (ATR) cm^{-1}: 3059, 2861, 2817, 1599, 1567, 1491, 1469, 1453, 1436, 1384, 1318, 1274, 1212, 1122, 1110, 1095, 1072, 1044, 1025, 1008; ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.0 Hz, 1H), 7.30–7.28 (m, 3H), 7.19 (dd, J = 8.0, 8.0 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 8.0 Hz, 1H), 6.21–6.17 (m, 1H), 6.11–6.08 (m, 1H), 6.02–6.02 (m, 1H), 3.99–3.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.09, 137.79, 132.90, 130.00, 129.82, 128.75, 127.97, 127.32, 124.49, 124.26, 122.15, 115.67, 78.50, 51.13; ESI-HRMS m/z: 316.0333 ([M+H^+]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

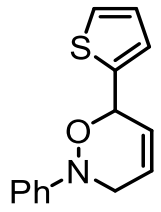
6-Furyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ai)



1a (0.19 g, 1.8 mmol) and **2i** (0.18 g, 1.5 mmol) were used as substrates and **3ai** (0.23 g, 1.0 mmol) was obtained in 67% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (15/1).

Yellow oil; IR (ATR) cm^{-1}: 3052, 2861, 2818, 1597, 1489, 1454, 1429, 1380, 1348, 1315, 1292, 1212, 1176, 1142, 1111, 1096, 1070, 1041, 1004; ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (d, J = 1.5 Hz, 1H), 7.28 (dd, J = 8.0, 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 8.0 Hz, 1H), 6.40 (d, J = 3.0 Hz, 1H), 6.37 (dd, J = 1.5, 3.0 Hz, 1H), 6.19–6.16 (m, 1H), 6.13–6.10 (m, 1H), 5.62–5.61 (m, 1H), 3.91–3.90 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.18, 150.04, 142.88, 128.71, 125.80, 125.30, 122.23, 115.83, 110.38, 109.71, 72.85, 51.02; ESI-HRMS m/z: 228.1015 ([M+H^+]); Calcd for $C_{14}H_{14}NO_2$:228.1019.

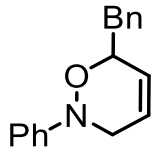
2-Phenyl-6-thienyl-3,6-dihydro-2*H*-[1,2]oxazine (3aj)



1a (0.26 g, 2.4 mmol) and **2j** (0.27 g, 2.0 mmol) were used as substrates and **3aj** (0.08 g, 0.34 mmol) was obtained in 17% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Brown Solid; M p. 90–91 ºC; IR (ATR) cm^{-1}:3040, 2859, 2817, 1599, 1490, 1453, 1430, 1385, 1348, 1279, 1212, 1177, 1095, 1069, 1037, 1005; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32–7.27 (m, 3H), 7.13 (d, J = 3.5 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.01–6.96 (m, 2H), 6.17–6.11 (m, 2H), 5.79 (m, 1H), 3.96–3.88 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.05, 142.18, 128.72, 128.42, 126.53, 126.46, 126.39, 124.18, 122.27, 115.90, 75.02, 51.18; ESI-HRMS m/z: 266.0613([M+Na^+]); Calcd for $C_{14}H_{13}NOSNa$:266.0613.

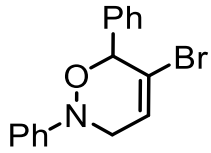
6-Benzyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ak)



1a (0.26 g, 2.4 mmol) and **2k** (0.29 g, 2.0 mmol) were used as substrates and **3ak** (0.17 mg, 0.67 mmol) was obtained in 34% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (15/1).

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.24 (m, 6H), 7.05 (dd, J = 1.0, 8.5 Hz, 2H), 6.98 (t, J = 7.5 Hz, 1H), 5.98–5.95 (m, 1H), 5.92–5.90 (m, 1H), 4.82–4.79 (m, 1H), 3.89–3.79 (m, 2H), 3.12 (dd, J = 8.0, 14.0 Hz, 1H), 2.92 (dd, J = 6.0, 14.0 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 8.

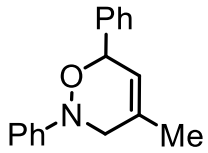
5-Bromo-2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (3al)



1a (0.19 g, 1.8 mmol) and **2l** (0.31 g, 1.5 mmol) were used as substrates and **3al** (0.36 g, 1.1 mmol) was obtained in 73% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Colorless solid; M. p. 103–104 ^{o}C; IR (ATR) cm^{-1}: 3265, 3062, 3030, 2920, 2869, 1662, 1602, 1496, 1454, 1305, 1209, 1144, 1075, 1028; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.49 (dd, J = 2.0, 7.5 Hz, 2H), 7.42–7.37 (m, 3H), 7.24 (dd, J = 8.0, 8.0 Hz, 2H), 6.98–6.96 (m, 3H), 6.52–6.50 (m, 1H), 5.51–5.51 (m, 1H), 4.07–3.99 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.29, 136.51, 129.38, 129.02, 128.76, 128.34, 126.25, 122.72, 116.78, 84.16, 53.55; ESI-HRMS m/z: 316.0336 ([M+H^{+}]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

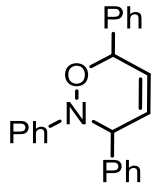
4-Methyl-2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (3am)



1a (0.13 g, 1.2 mmol) and **2m** (0.14 g, 1.0 mmol) were used as substrates and **3am** (0.04 g, 0.16 mmol) was obtained in 16% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (15/1).

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.45 (d, J = 8.0 Hz, 2H), 7.39–7.27 (m, 5H), 7.12 (d, J = 8.0 Hz, 2H), 6.97 (t, J = 8.0 H`z, 1H), 5.77–5.76 (m, 1H), 5.55–5.54 (m, 1H), 3.83–3.75 (m, 2H), 1.90 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 9.

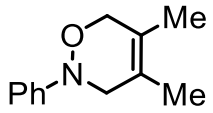
2,3,6-Triphenyl-3,6-dihydro-2*H*-[1,2]oxazine (3an)



1a (0.64 g, 6.0 mmol) and **2n** (1.03 g, 5.0 mmol) were used as substrates and **3an** (1.40 g, 4.4 mmol) was obtained in 88% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (15/1).

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.54 (d, J = 7.0 Hz, 2H), 7.46–7.37 (m, 5H), 7.25–7.14 (m, 5H), 6.99 (dd, J = 1.5, 8.5 Hz, 2H), 6.85 (dt, J = 1.0, 7.0 Hz, 1H), 6.23–6.15 (m, 2H), 5.62 (m, 1H), 5.19–5.18 (m, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 10.

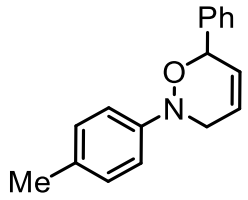
4,5-Dimethyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ao)



1a (0.32 g, 3.0 mmol) and **2o** (0.49 g, 6.0 mmol) were used as substrates and **3ao** (0.36 g, 1.9 mmol) was obtained in 32% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J = 7.5, 7.5 Hz, 2H), 7.13 (dd, J = 1.5, 7.5, 2H), 7.00 (dt, J = 1.5, 7.5, 1H), 4.33 (s, 2H), 3.67 (s, 2H), 1.74 (s, 3H), 1.65 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 10.

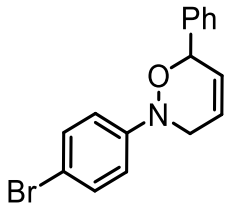
2-(4-Methylphenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ba)



1b (0.15 g, 1.2 mmol) and **2a** (0.13 g, 1.0 mmol) were used as substrates and **3ba** (0.17 g, 0.7 mmol) was obtained in 70% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; M. p. 63–64 ºC; IR (ATR) cm^{-1}: 3031, 2920, 2860, 2817, 1654, 1614, 1509, 1454, 1430, 1385, 1347, 1300, 1264, 1218, 1205, 1125, 1090, 1043, 1008; ^{1}H NMR (500 MHz, $CDCl_3$):δ 7.46 (d, J = 8.0 Hz, 2H), 7.38 (dd, J = 6.5, 6.5 Hz, 2H), 7.33 (t, J = 6.5 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 6.5 Hz, 2H), 6.14─6.06 (m, 2H), 5.61 (m, 1H), 3.95–3.85 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 139.0, 131.8, 129.3, 129.0, 128.4, 128.3, 128.1, 123.9, 116.2, 79.8, 52.0, 20.6; ESI-HRMS m/z: 252.1374 ([M+H$^+$]); Calcd for $C_{17}H_{18}NO$: 252.1374.

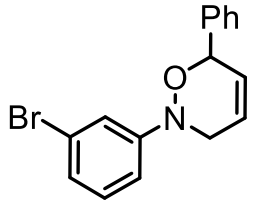
2-(4-Bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ca)



1c (0.22 g, 1.2 mmol) and **2a** (0.13 g, 1.0 mmol) were used as substrates and **3ca** (0.22 g, 0.68 mmol) was obtained in 68% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; M. p. 78–79 °C; IR (ATR) cm^{-1}: 3031, 2862, 2819, 1588, 1486, 1454, 1431, 1402, 1386, 1347, 1298, 1266, 1213, 1180, 1121, 1075, 1042, 1003; ^1H NMR (500 MHz, $CDCl_3$): δ 7.44 (dd, J = 1.5, 8.5 Hz, 2H), 7.39–7.33 (m, 5H), 6.96 (dd, J = 2.0, 7.0 Hz, 2H), 6.14–6.06 (m, 2H), 5.59 (dd, J = 2.0, 2.0 Hz, 1H), 3.95–3.91 (m, 1H), 3.88–3.83 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.4, 138.6, 131.6, 128.9, 128.5, 128.1, 123.5, 117.3, 114.6, 79.9, 51.3; ESI-HRMS m/z: 316.0330 ([M+H$^+$]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

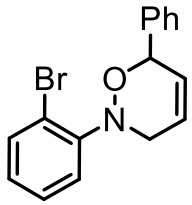
2-(3-Bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3da)



1d (0.22 g, 1.2 mmol) and **2a** (0.13 g, 1.0 mmol) were used as substrates and **3da** (0.19 g, 0.6 mmol) was obtained in 60% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow oil; IR (ATR) cm^{-1}: 3031, 2862, 2819, 1589, 1566, 1493, 1474, 1453, 1428, 1385, 1348, 1303, 1264, 1213, 1176, 1105, 1081, 1042, 1011; ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (dd, J = 2.0, 7.5 Hz, 2H), 7.42–7.35 (m, 3H), 7.27 (d, J = 2.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.08 (dd, J = 1.5, 7.0 Hz, 1H), 6.98 (dd, J = 1.5, 7.0 Hz, 1H), 6.15–6.07 (m, 2H), 5.61 (dd, J = 2.0, 2.0 Hz, 1H), 3.99–3.87 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.56, 138.48, 130.02, 128.97, 128.56, 128.51, 128.17, 124.77, 123.39, 122.75, 118.47, 114.05, 80.04, 51.07; ESI-HRMS m/z: 316.0323 ([M+H$^+$]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

2-(2-Bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3ea)

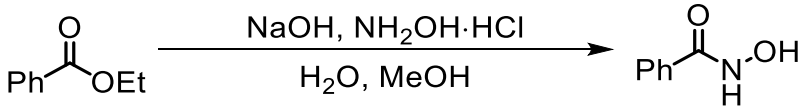


1e (0.22 g, 1.2 mmol) and **2a** (0.13 g, 1.0 mmol) were used as substrates and **3ea** (0.23 g, 0.7 mmol) was obtained in 70% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (30/1).

Yellow solid; M. p. 54–55 °C; IR (ATR) cm^{-1}: 3061, 3033, 2863, 2818, 1654, 1585, 1493, 1469, 1454, 1439, 1384, 1338, 1303, 1208, 1172, 1123, 1088, 1052, 1029; ^1H NMR (500 MHz, $CDCl_3$): δ 7.57 (dd, J = 1.0, 8.0 Hz, 1H), 7.47–7.43 (m, 3H), 7.38–7.27 (m, 4H), 7.00 (dt, J = 2.0, 8.0 Hz,

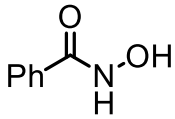
1H), 6.17–6.13 (m, 1H), 6.08–6.05 (m, 1H), 5.83 (s, 1H), 3.88 (dd, J = 2.0, 3.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.30, 138.48, 133.36, 129.06, 128.50, 128.44, 128.29, 128.05, 126.38, 124.12, 120.53, 117.85, 80.75, 52.46; ESI-HRMS m/z: 316.0332 ([M+H$^+$]); Calcd for $C_{16}H_{15}NOBr$: 316.0332.

2-4. Synthesis of 2-benzyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3fa)

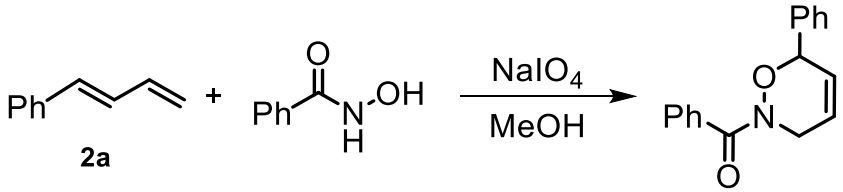


To a suspension of hydroxylamine hydrochloride (2.78 g, 40 mmol) in H_2O (50 mL) was added NaOH (3.2 mg, 80 mmol) at 0 ºC under argon. After stirring for 10 min, ethyl benzoate (3.0 g, 20.0 mmol) in MeOH (50 mL) was added. The reaction mixture was warmed up to room temperature and the reaction progress was monitored by TLC. After the reaction was completed, the solution was acidified with 5% HCl aq to pH 5.5. The solvent was removed in vacuo to yield a mixture of the product and sodium chloride, which was then redissolved in MeOH. The sodium chloride was removed by filtration. The methanol was removed in vacuo to give the corresponding product, which then recrystallized from hot water to give *N*-hydroxybenzamide (0.74 g, 5.4 mmol) in 27% yield.[11)]

***N*-Hydroxybenzamide**



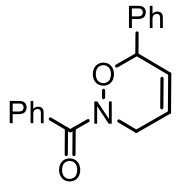
Colorless solid; ^{1}H NMR (500 MHz, DMSO-d_6): δ 11.25 (s, 1H), 9.07 (s, 1H), 7.78 (d, J = 7.5 Hz, 2H), 7.56 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.5 Hz, 2H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 11.



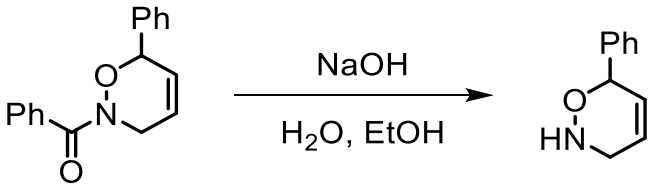
To a suspension of **2a** (0.39 g, 3.0 mmol) and $NaIO_4$ (0.60 g, 3 mmol) in MeOH (15 mL) was added *N*-hydroxybenzamide (0.41 g, 3 mmol) in MeOH (15 mL) at room temperature under argon. The reaction mixture was warmed up to room temperature. After stirring for 18 h, the reaction

mixture was concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-AcOEt (3/1) to give 2-benzoyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (0.54g, 1.72 mmol) in 57% yield.[11)]

2-Benzoyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine

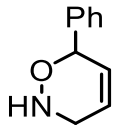


Colorless liquid; IR (ATR) cm^{-1}: 3060, 2845, 1762, 1662, 1638, 1601, 1578, 1492, 1448, 1402, 1377, 1237, 1221, 1182, 1157, 1076, 1039; ^1H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, J = 7.0 Hz, 2H), 7.36 (t, J = 7.0 Hz, 1H), 7.29–7.22 (m, 5H), 7.14 (t, J = 7.0 Hz, 2H), 6.12–6.08 (m, 1H), 5.98–5.95 (m, 1H), 5.35 (s, 1H), 4.59–4.55 (m, 1H), 4.40–4.36 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 169.98, 136.11, 133.51, 130.51, 129.16, 128.67, 128.53, 128.51, 127.62, 126.40, 123.45, 80.96, 42.74; ESI-HRMS m/z: 266.1157 ([M+H^+]); Calcd for $C_{17}H_{16}NO_2$: 266.1176.

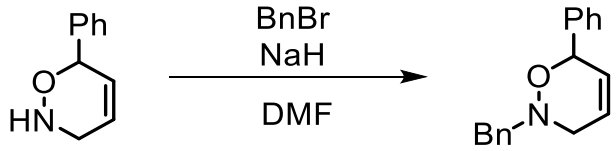


To a suspension of 2-benzoyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (0.66 g, 2.5 mmol) in EtOH (5 mL) and H_2O (5 mL) was added NaOH (100 mg, 2.5 mmol) at 80 ºC. After stirring for 15 h, the reaction mixture was warmed at 100 ºC. After stirring for 18 h, the reaction mixture concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-AcOEt (1/1) to give 6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (0.23 g, 1.0 mmol) in 40% yield.

6-Phenyl-3,6-dihydro-2*H*-[1,2]oxazine

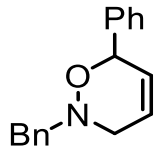


Yellow oil; IR (ATR) cm^{-1}: 3293, 3033, 2832, 1680, 1598, 1493, 1452, 1426, 1383, 1269, 1176, 1092, 1027, 1002; ^1H NMR (500 MHz, $CDCl_3$): δ 7.42–7.33 (m, 5H), 6.13–6.11 (m, 1H), 6.03–6.01 (m, 1H), 5.32–5.30 (m, 1H), 3.73–3.69 (m, 1H), 3.60–3.56 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 138.91, 128.53, 128.45, 128.16, 127.73, 125.13, 77.71, 46.95; ESI-HRMS m/z: 184.0746 ([M+Na^+]); Calcd for $C_{10}H_{11}NONa$: 184.0733.



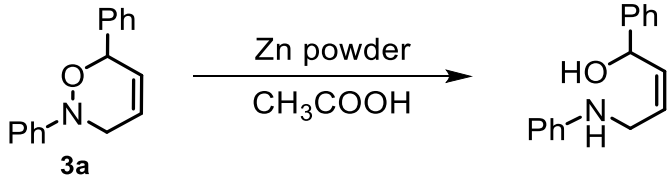
To a suspension of 6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (0.16 g, 1.0 mmol) in DMF (3 mL, 0.33 M) was added NaH (60% oil suspension, 90 mg, 1.1 mmol) at 0 °C under argon. After stirring for 30 min, the benzyl bromide (2.37 g, 15.0 mmol) was added. The reaction mixture was warmed up to room temperature. After stirring for 15 h, the reaction mixture was quenched with H_2O (5 mL) and extracted with AcOEt (5 mL × 2). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-AcOEt (15/1) to give 2-benzyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3fa**, 0.20 g, 0.76 mmol) in 76% yield.

2-Benzyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (3fa)

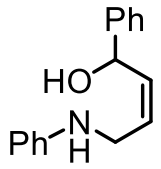


Yellow oil; IR (ATR) cm^{-1}: 3062, 3030, 2920, 2849, 2805, 1603, 1494, 1453, 1432, 1390, 1370, 1337, 1304, 1271, 1211, 1174, 1068, 1030, 1002; ^1H NMR (500 MHz, $CDCl_3$): δ 7.32–7.23 (m, 10H), 6.02–5.96 (m, 2H), 5.44 (m, 1H), 4.08 (d, J = 13.0 Hz, 1H), 3.86 (d, J = 13.0 Hz, 1H), 3.41–3.36 (m, 2H); ^{13}C NMR (125 MHz, $CHCl_3$): δ 139.40, 136.87, 128.97, 128.72, 128.30, 128.14, 128.01, 127.10, 124.37, 79.29, 62.76, 54.27; ESI-HRMS m/z: 252.1387 ([M+H^+]); Calcd for $C_{17}H_{18}NO$: 252.1383.

2-5. Synthesis of 5-phenylamino-*cis*-3-hexen-2-ol (5)[12)]

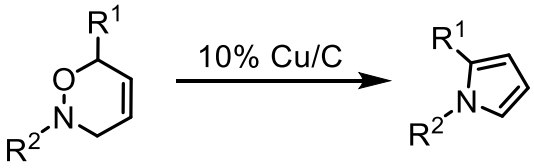


Zinc dust (0.98 g, 3 mmol) was added slowly to a stirred solution of **3aa** in 5 mL of acetic acid. The reaction mixture was heated at 50 °C and stirred overnight. After stirring for 24 h, the reaction mixture was quenched with 7 M NaOH aq (12.5 mL) and extracted with toluene (15 mL× 3). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-AcOEt (5/1) to give 5-phenylamino-*cis*-3-hexen-2-ol (**5**, 0.24 g, 1.02 mmol) in 34% yield.



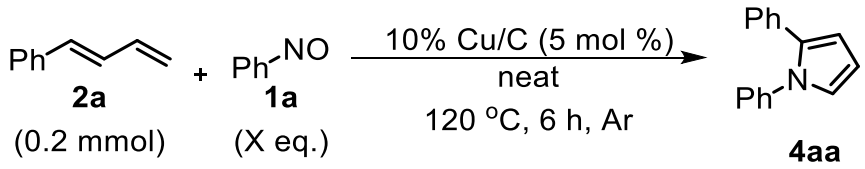
Colorless liquid; IR (ATR) cm^{-1}: 3356, 3023, 2853, 1600, 1502, 1451, 1430, 1314, 1253, 1180, 1155, 1071, 1024; ^1H NMR (500 MHz, $CDCl_3$): δ 7.42–7.36 (m, 4H), 7.31 (t, J = 7.0 Hz, 1H), 7.19 (dd, J = 7.5, 7.5 Hz, 2H), 6.75 (dd, J = 1.0, 7.5 Hz, 1H), 6.63 (dd, J = 1.0, 7.5 Hz, 2H), 5.88–5.84 (m, 1H), 5.77–5.73 (m, 1H), 5.60 (d, J = 8.0 Hz, 1H), 3.98 (dd, J = 7.0, 14.5 Hz, 1H), 3.86 (dd, J = 7.0, 14.5Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.75, 143.13, 134.82, 129.26, 128.69, 128.66, 127.78, 126.00, 118.01, 113.22, 70.09, 41.48; ESI-HRMS m/z: 240.1385 ([M+H^+]); Calcd for $C_{16}H_{18}NO$: 240.1383.

3. Typical procedures in Cu/C-catalyzed pyrrole synthesis.



3,6-Dihydro-2*H*-[1,2]oxazine derivative (**3**: 0.20 mmol) and 10% Cu/C (6.4 mg, 0.005 mmol) were added to a 17 mL sealded (septum) test tube with stirring bar. The air inside was replaced with argon (balloon) by three vacuum/argon cycles. The test tube was placed on a personal organic synthesizer, ChemiStation (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was refluxed (120 ^oC; temperature of the extrenal aluminum heating block). After stirring for 6 h, the reaction mixture was cooled to room temperature and passed through a membrane filter (Millipore, Millex-LH, 0.20 μm) using AcOEt to remove Cu/C. The filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography using *n*-hexane-AcOEt to give pyrrole derivative (**4**).

4. Optimization of Cu/C-catalyzed pyrrole synthesis in a one-pot manner.

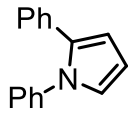


X	Yield (%)
	4aa
1.2	44
1.5	60
2.0	38
1.5 [a]	58

[a] 0 °C (6 h) then 120 °C (6 h).

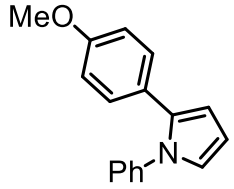
5. Spectroscopic data of the synthesized products.

1,2-Diphenylpyrrole (4aa)



3aa (47.4 mg, 0.20 mmol) was used as a substrate and **4aa** (36.8 mg, 0.17 mmol) was obtained in 84% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33–7.13 (m, 10H), 6.95 (dd, J = 2.0, 3.5 Hz, 1H), 6.45 (dd, J = 2.0, 3.5 Hz, 1H), 6.37 (dd, J = 3.5, 3.5 Hz, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 13.

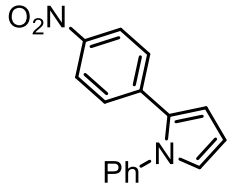
2-(4-Methoxyphenyl)-1-phenylpyrrole (4ab)



3ab (53.5 mg, 0.2 mmol) was used as a substrate and **4ab** (36.8 mg, 0.14 mmol) was obtained in 72% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J = 7.5, 7.5 Hz, 2H), 7.25 (t, J = 7.5 Hz,

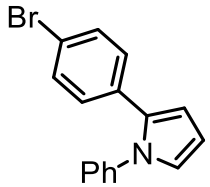
1H), 7.16 (d, J = 7.5 Hz, 2H), 7.06 (d, J = 8.5 Hz, 2H), 6.91 (dd, J = 1.5, 3.0 Hz, 1H), 6.75 (d, J = 8.5 Hz, 2H), 6.36–6.34 (m, 2H), 3.76 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 14.

2-(4-Nitrophenyl)-1-phenylpyrrole (4ac)



3ac (56.5 mg, 0.20 mmol) was used as a substrate and **4ac** (43.6 mg, 0.15 mmol) was obtained in 77% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.05 (d, J = 8.5 Hz, 2H), 7.40–7.35 (m, 3H), 7.23 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 7.0 Hz, 2H), 7.02 (s, 1H), 6.64 (s, 1H), 6.42 (s, 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 15.

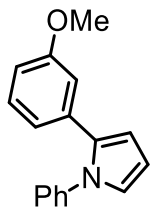
2-(4-Bromophenyl)-1-phenylpyrrole (4ad)



3ad (31.6 mg, 0.10 mmol) was used as a substrate and **4ad** (25.3 mg, 0.08 mmol) was obtained in 79% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

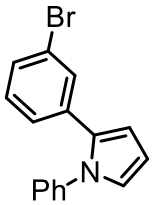
Brown solid; M. p. 107–108 ºC; IR (ATR) cm^{-1}: 3064, 2923, 2851, 1687, 1596, 1562, 1541, 1498, 1488, 1459, 1451, 1422, 1390, 1343, 1319, 1256, 1187, 1098, 1073, 1053, 1037, 1009; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37–7.28 (m, 5H), 7.17 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 6.95 (dd, J = 2.0, 3.0 Hz, 1H), 6.45 (dd, J = 2.0, 3.0 Hz, 1H), 6.37 (dd, J = 3.0, 3.0 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.19, 132.52, 131.85, 131.19, 129.65, 129.14, 126.84, 125.69, 124.83, 120.24, 110.97, 109.38; ESI-HRMS m/z: 298.0231([M+H$^+$]); Calcd for $C_{16}H_{13}NBr$: 298.0226.

2-(3-Methoxyphenyl)-1-phenylpyrrole (4ae)



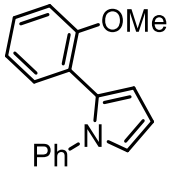
3ae (26.7 mg, 0.10 mmol) was used as a substrate and **4ae** (16.9 mg, 0.07 mmol) was obtained in 67% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Brown solid; M. p. 66–68 °C; IR (ATR) cm^{-1}: 3064, 2930, 2833, 1599, 1541, 1498, 1473, 1454, 1342, 1319, 1287, 1225, 1214, 1169, 1102, 1073, 1038; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, J = 8.0, 8.0 Hz, 2H), 7.26 (dd, J = 8.0, 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 8.0 Hz, 1H), 6.96–6.95 (m, 1H), 6.75–6.71 (m, 2H), 6.67 (s, 1H), 6.47 (dd, J = 1.5, 3.5 Hz, 1H), 6.37 (dd, J = 3.5, 3.5 Hz, 1H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.11, 140.51, 134.17, 133.63, 129.00, 128.97, 126.64, 125.76, 124.42, 120.78, 113.38, 112.31, 110.67, 109.16, 54.97; ESI-HRMS m/z: 250.1228 ([M+H^+]); Calcd for $C_{17}H_{16}NO$: 250.1226.

2-(3-Bromophenyl)-1-phenylpyrrole (4af)



3af (63.2 mg, 0.20 mmol) was used as a substrate and **4af** (50.3 mg, 0.16 mmol) was obtained in 80% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Colorless oil; IR (ATR) cm^{-1}: 3061, 2922, 1594, 1560, 1496, 1479, 1461, 1447, 1395, 1342, 1319, 1187, 1102, 1089, 1074, 1057, 1037; ^1H NMR (500 MHz, $CDCl_3$): δ 7.38–7.35 (m, 3H), 7.33–7.28 (m, 2H), 7.18 (d, J = 8.0 Hz, 2H), 7.04 (t, J = 8.0 Hz, 1H), 6.97–6.96 (m, 2H), 6.48 (dd, J = 2.0, 3.5 Hz, 1H), 6.38 (dd, J = 3.5, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.08, 134.94, 132.07, 130.84, 129.42, 129.11, 129.06, 126.91, 126.67, 125.68, 124.99, 122.08, 111.35, 109.40; ESI-HRMS m/z: 298.0224 ([M+H^+]); Calcd for $C_{16}H_{13}NBr$: 298.0226.

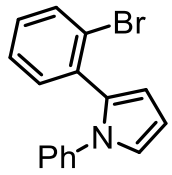
2-(2-Methoxyphenyl)-1-phenylpyrrole (4ag)



3ag (26.7 mg, 0.10 mmol) was used as a substrate and **4ag** (15.5 mg, 0.06 mmol) was obtained in 61% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Brown solid; M. p. 61–62 °C; IR (ATR) cm^{-1}: 3061, 2923, 1685, 1591, 1574, 1545, 1482, 1465, 1429, 1335, 1255, 1186, 1105, 1089, 1070, 1036; ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (dd, J = 2.0, 7.5 Hz, 1H), 7.27–7.22 (m, 3H), 7.18–7.17 (m, 1H), 7.11 (d, J = 7.5 Hz, 2H), 7.00 (dd, J = 2.0, 2.0 Hz, 1H), 6.94 (t, J = 7.5 Hz, 1H), 6.70 (d, J = 7.5 Hz, 1H), 6.39 (d, J = 2.0 Hz, 2H), 3.29

(s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.40, 141.47, 131.50, 130.42, 128.79, 128.50, 125.78, 124.01, 122.68, 122.60, 120.43, 111.23, 110.74, 108.99, 54.61; ESI-HRMS m/z: 250.1224 ([M+H$^+$]); Calcd for $C_{17}H_{16}NO$: 250.1226.

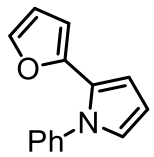
2-(2-Bromophenyl)-1-phenylpyrrole (4ah)



3ah (63.2 mg, 0.20 mmol) was used as a substrate and **4ah** (46.3 mg, 0.15 mmol) was obtained in 76% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Colorless solid; M. p. 118–119 ^{o}C; IR (ATR) cm^{-1}: 3056, 2920, 1597, 1560, 1546, 1546, 1496, 1479, 1458, 1443, 1414, 1340, 1321, 1261, 1187, 1158, 1100, 1074, 1024; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (d, J = 7.0 Hz, 1H), 7.26–7.17 (m, 5H), 7.12–7.09 (m, 3H), 7.01 (dd, J = 2.0, 2.5 Hz, 1H), 6.43–6.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.21, 134.53, 132.87, 132.79, 131.80, 128.92, 128.76, 126.83, 126.19, 124.84, 122.73, 112.11, 108.79; Anal. Calcd for $C_{17}H_{15}NO$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.10; H, 4.08; N, 4.70.

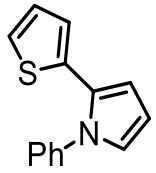
2-Furyl-1-phenylpyrrole (4ai)



3ai (45.8 mg, 0.20 mmol) was used as a substrate and **4ai** (28.1 mg, 0.13 mmol) was obtained in 65% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

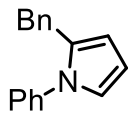
Brown oil; IR (ATR) cm^{-1}: 3116, 3065, 2924, 1598, 1528, 1500, 1455, 1440, 1416, 1371, 1344, 1319, 1257, 1221, 1189, 1157, 1099, 1075, 1036, 1013; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.37 (m, 3H), 7.32–7.30 (m, 3H), 6.87 (dd, J = 2.0, 3.5 Hz, 1H), 6.61 (dd, J = 2.0, 3.5 Hz, 1H), 6.35 (dd, J = 2.5, 3.5 Hz, 1H), 6.26 (dd, J = 2.5, 3.5 Hz, 1H), 5.66 (dd, J = 3.5, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 147.36, 140.91, 140.35, 128.97, 127.53, 126.21, 125.19, 124.30, 110.75, 109.73, 109.18, 105.51; ESI-HRMS m/z: 210.0912 ([M+H$^+$]); Calcd for $C_{14}H_{12}NO$: 210.0913.

1-Phenyl-2-thienyl-pyrrole (4aj)



3aj (24.3 mg, 0.10 mmol) was used as a substrate and **4aj** (20.1 mg, 0.09 mmol) was obtained in 88% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Green solid; M. p. 55–56 ºC; IR (ATR) cm^{-1}: 3099, 3064, 2924, 2854, 1593, 1561, 1496, 1462, 1427, 1403, 1350, 1324, 1303, 1227, 1161, 1093, 1081, 1047, 1034, 1013; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.41–7.34 (m, 3H), 7.29–7.27 (m, 2H), 7.11 (dd, J = 1.5, 5.0 Hz, 1H), 6.91 (dd, J = 1.5, 3.5 Hz, 1H), 6.86 (dd, J = 3.5, 5.0 Hz, 1H), 6.58 (dd, J = 1.5, 3.5 Hz, 1H), 6.50 (dd, J = 1.5, 3.5 Hz, 1H), 6.34 (dd, J = 3.5, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.04, 134.92, 128.95, 127.39, 126.94, 126.55, 124.85, 124.41, 124.12, 110.88, 109.13; ESI-HRMS m/z: 226.0680 ([M+H$^+$]); Calcd for $C_{14}H_{12}NS$: 226.0685.

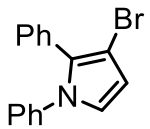
2-Benzyl-1-phenylpyrrole (4ak)



3ak (50.3 mg, 0.20 mmol) was used as a substrate and **4ak** (27.2 mg, 0.12 mmol) was obtained in 58% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Colorless oil; IR (ATR) cm^{-1}: 3062, 3027, 2917, 2849, 1598, 1563, 1555, 1536, 1497, 1470, 1453, 1423, 1324, 1262, 1232, 1173, 1141, 1094, 1073, 1032, 1004; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, J = 7.5, 7.5 Hz, 2H), 7.34 (t, J = 7.5 Hz, 1H), 7.24–7.21 (m, 4H), 7.16 (t, J = 7.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 2H), 6.80 (dd, J = 1.5, 3.0 Hz, 1H), 6.25 (dd, J = 3.0, 3.0 Hz, 1H), 6.05–6.00 (m, 1H), 3.91 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.17, 139.84, 132.28, 128.95, 128.57, 128.20, 127.14, 126.29, 125.95, 122.05, 108.96, 108.00, 33.03; ESI-HRMS m/z: 234.1277 ([M+H$^+$]); Calcd for $C_{17}H_{16}N$: 234.1277.

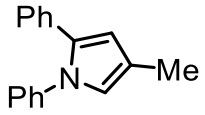
3-Bromo-1,2-diphenylpyrrole (4al)



3al (63.2 mg, 0.20 mmol) was used as a substrate and **4al** (46.1 mg, 0.16 mmol) was obtained in 77% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1). Colorless oil; IR (ATR) cm^{-1}: 3058, 2923, 1596, 1536, 1493, 1467, 1439, 1320, 1282, 1226, 1175,

1157, 1088, 1070, 1027; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30–7.22 (m, 8H), 7.08 (dd, J = 1.5, 8.0 Hz, 2H), 6.91 (d, J = 3.5 Hz, 1H), 6.45 (d, J = 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.11, 130.74, 130.67, 130.40, 128.97, 127.91, 127.29, 126.81, 125.40, 122.95, 112.21, 98.07; ESI-HRMS m/z: 298.0223 ([M+H$^+$]); Calcd for $C_{16}H_{13}NBr$: 298.0226.

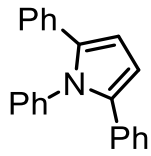
4-Methyl-1,2-diphenylpyrrole (4am)



3am (18.8 mg, 0.08 mmol) was used as a substrate and **4am** (15.8 mg, 0.06 mmol) was obtained in 78% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Brown oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, J = 7.5, 7.5 Hz, 2H), 7.21–7.09 (m, 8H), 6.71 (s, 1H), 6.28 (s, 1H), 2.17 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 16.

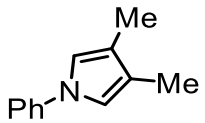
1,2,5-Triphenylpyrrole (4an)



3an (62.7 mg, 0.20 mmol) was used as a substrate and **4an** (29.2 mg, 0.01 mmol) was obtained in 49% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26–7.23 (m, 5H), 7.19–7.14 (m, 5H), 7.07–7.03 (m, 5H), 6.49 (s, 2H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 17.

3,4-Dimethyl-1-phenylpyrrole (4ao)

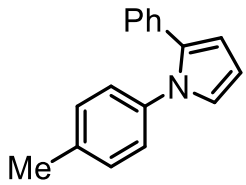


3ao (37.9 mg, 0.20 mmol) was used as a substrate and **4ao** (11.4 mg, 0.06 mmol) was obtained in 35% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Brown solid; M. p. 62–63 ^{o}C; IR (ATR) cm^{-1}:3045, 2921, 2859, 1599, 1529, 1504, 1461, 1397, 1364, 1237, 1185, 1153, 1078, 1049; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38 (dd, J = 7.5, 7.5 Hz,

2H), 7.32 (d, J = 7.5 Hz, 2H), 7.17 (t, J = 7.5 Hz, 1H), 6.85 (s, 2H), 2.09 (s, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.72, 129.40, 124.57, 120.75, 119.45, 116.71, 10.14; ESI-HRMS m/z: 194.0965 ([M+Na^+]); Calcd for $C_{12}H_{13}NNa$: 194.0940.

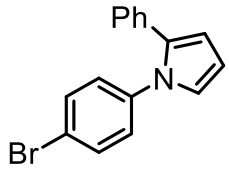
1-(4-Methylphenyl)-2-phenylpyrrole (4ba)



3ba (63.2 mg, 0.20 mmol) was used as a substrate and **4ba** (40.9 mg, 0.14 mmol) was obtained in 71% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25–7.22 (m, 2H), 7.20–7.13 (m, 5H), 7.08 (dd, J = 2.0, 8.5 Hz, 2H), 6.94 (dd, J = 1.5, 3.0 Hz 1H), 6.46 (dd, J = 1.5, 3.0 Hz 1H), 6.39–6.37 (m, 1H), 2.38 (s, 3H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 18.

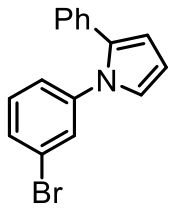
1-(4-Bromophenyl)-2-phenylpyrrole (4ca)



3ca (63.2 mg, 0.20 mmol) was used as a substrate and **4ca** (40.9 mg, 0.14 mmol) was obtained in 66% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Brown solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.5 Hz, 2H), 7.24–7.17 (m, 3H), 7.12 (d, J = 6.5 Hz 2H), 7.03 (d, J = 8.5 Hz 2H), 6.92 (dd, J = 1.5, 3.5 Hz 1H), 6.45 (dd, J = 1.5, 2.5 Hz 1H), 6.39 (dd, J = 2.5, 3.5 Hz 1H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 18.

1-(3-Bromophenyl)-2-phenylpyrrole (4da)

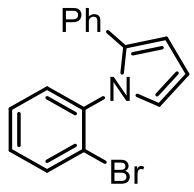


3da (63.2 mg, 0.20 mmol) was used as a substrate and **4da** (63.2 mg, 0.20 mmol) was obtained in 66% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt

(50/1).

Brown solid; M. p. 92–94 °C; IR (ATR) cm^{-1}: 3052, 2932, 2833, 1636, 1599, 1579, 1559, 1542, 1450, 1464, 1436, 1414, 1341, 1323, 1259, 1243, 1181, 1161, 1117, 1100, 1060, 1027; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.40 (m, 2H), 7.27–7.15 (m, 6H), 7.05–7.03 (m, 1H), 6.95 (dd, J = 2.0, 3.5 Hz, 1H), 6.46 (dd, J = 2.0, 3.5 Hz, 1H), 6.40 (dd, J = 3.5, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.69, 133.81, 132.48, 130.12, 129.59, 128.36, 128.31, 128.17, 126.56, 124.51, 124.15, 122.34, 111.15, 109.76; ESI-HRMS m/z: 298.0217 ([M+H$^+$]); Calcd for $C_{16}H_{13}NBr$: 298.0226.

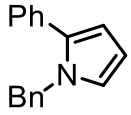
1-(2-Bromophenyl)-2-phenylpyrrole (4ea)



3ea (63.2 mg, 0.20 mmol) was used as a substrate and **4ea** (20.8 mg, 0.07 mmol) was obtained in 34% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (50/1).

Brown solid; M. p. 83–84 °C; IR (ATR) cm^{-1}: 3061, 2926, 2849, 1601, 1586, 1484, 1462, 1441, 1340, 1253, 1186, 1105, 1064, 1028; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.65 (dd, J = 1.5, 8.0 Hz, 1H), 7.32–7.12 (m, 8H), 6.85 (dd, J = 2.0, 3.5 Hz, 1H), 6.50 (dd, J = 2.0, 3.5 Hz, 1H), 6.42 (dd, J = 3.5, 3.5 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 139.92, 134.86, 133.45, 132.71, 130.09, 129.29, 128.06, 127.98, 127.64, 126.28, 124.56, 122.30, 109.29, 109.15; ESI-HRMS m/z: 298.0226 ([M+H$^+$]); Calcd for $C_{16}H_{13}NBr$: 298.0226.

1-Benzyl-2-phenyl-1*H*-pyrrole(4fa)



3fa (25.1 mg, 0.1 mmol) was used as a substrate and **4fa** (5.3 mg, 0.032 mmol) was obtained in 10% yield after purification by silica-gel column chromatography using *n*-hexane-AcOEt (15/1).

Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34–7.23 (m, 8H), 7.02 (d, J = 7.5 Hz, 2H), 6.76 (dd, J = 2.5, 2.5 Hz, 1H), 6.29 (d, J = 2.5 Hz, 2H), 5.16 (s, 2H). Spectroscopic data of ^{1}H NMR was identical to those reported in reference 19.

6. Reuse test.

2,6-Diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3aa**: 47.4 mg, 0.20 mmol) and 10% Cu/C (6.4 mg,

0.005 mmol), were added to a 17 mL sealded (septum) test tube with stirring bar. The air inside was replaced with argon (balloon) by three vacuum/argon cycles. The test tube was placed on a personal organic synthesizer, ChemiStation (EYELA, Tokyo Rikakikai Co., Ltd., Tokyo, Japan), and the mixture was refluxed (120 ^{o}C; temperatureof the extrenal aluminum heating block). After stirring for 6 h, the reaction mixture was cooled to room temperature. The reaction mixture was passed through a filter paper [Kiriyama, No. 5C (1 μm), diameter = 40 mm]. The filtrated catalyst was washed with H_2O (10 mL × 5) and MeOH (10 mL × 5) and dried in a desiccator under vacuum overnight, then the recovered catalyst was used for the next run.

7. References.

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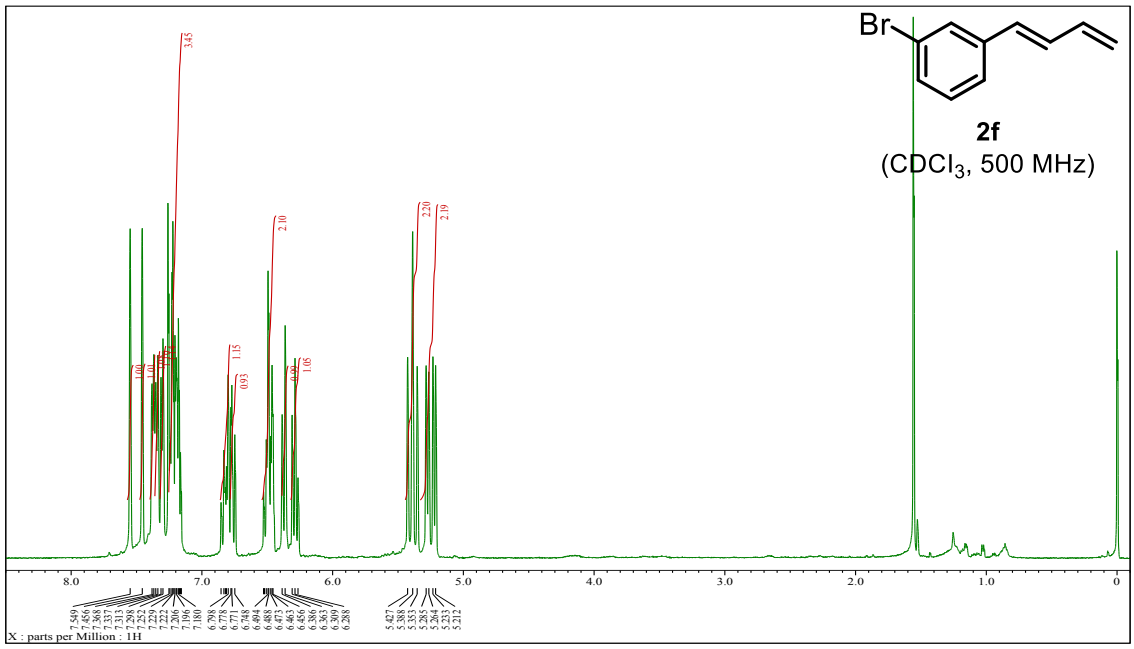
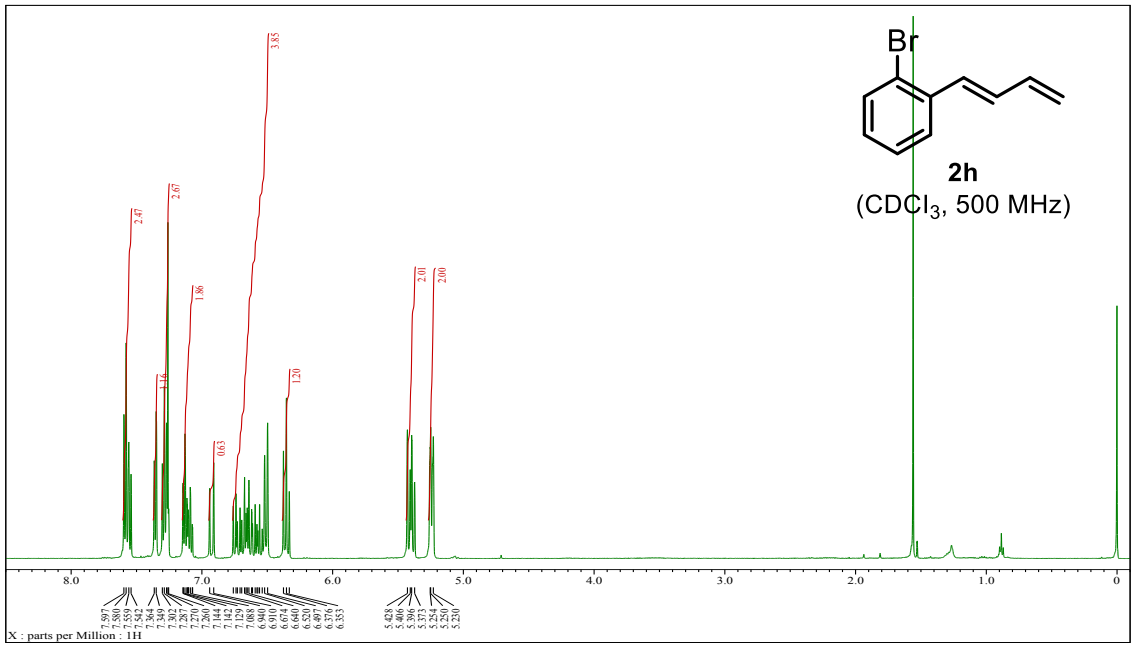
8. ^{1}H and ^{13}C NMR spectra of the newly synthesized substrates and products.

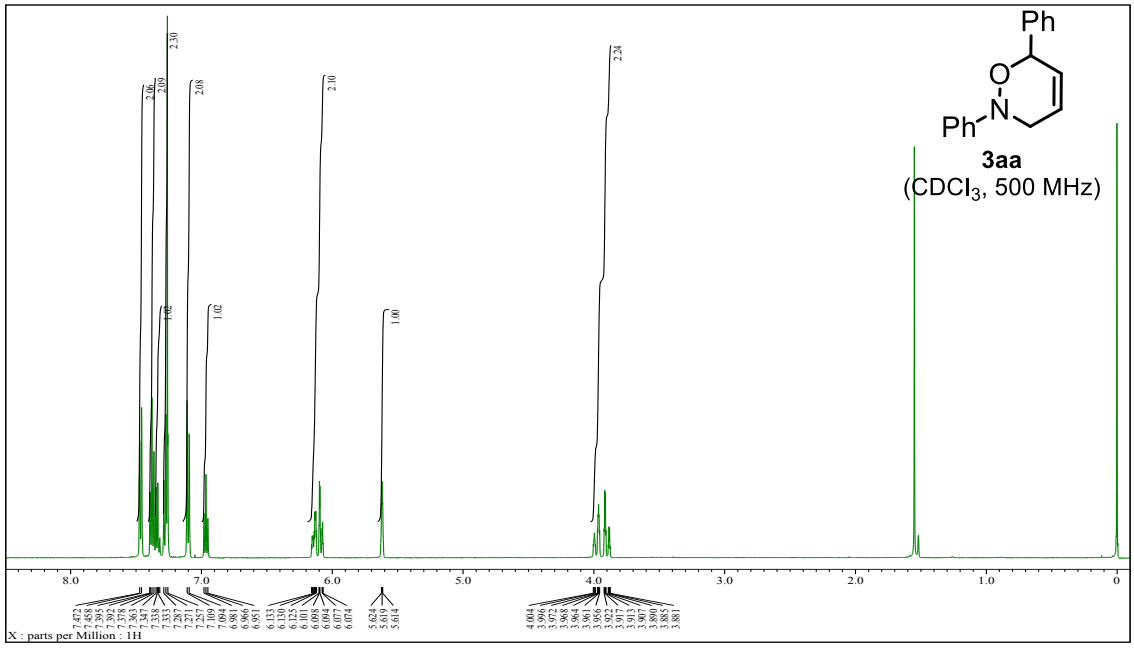
^{1}H NMR of (*E* or *Z*)-1-(buta-1,3-dienyl)-3-bromobenzene (**2f**)



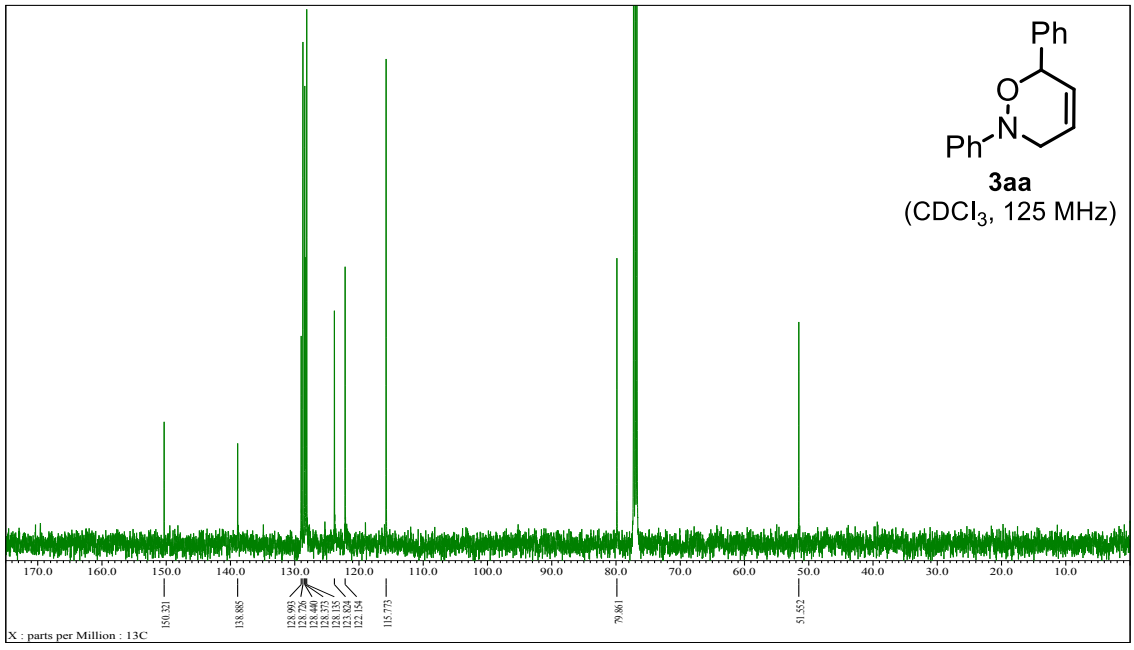
^{1}H NMR of (*E* or *Z*)-1-(buta-1,3-dienyl)-2-bromobenzene (**2h**)



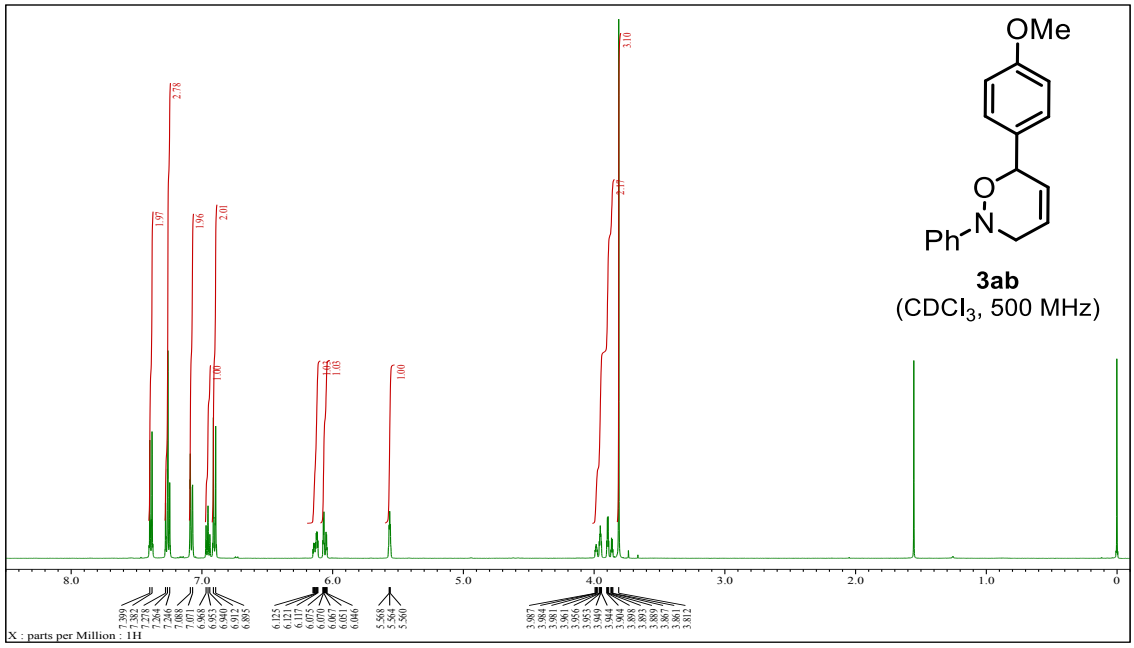
^{1}H NMR of 2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3aa**)



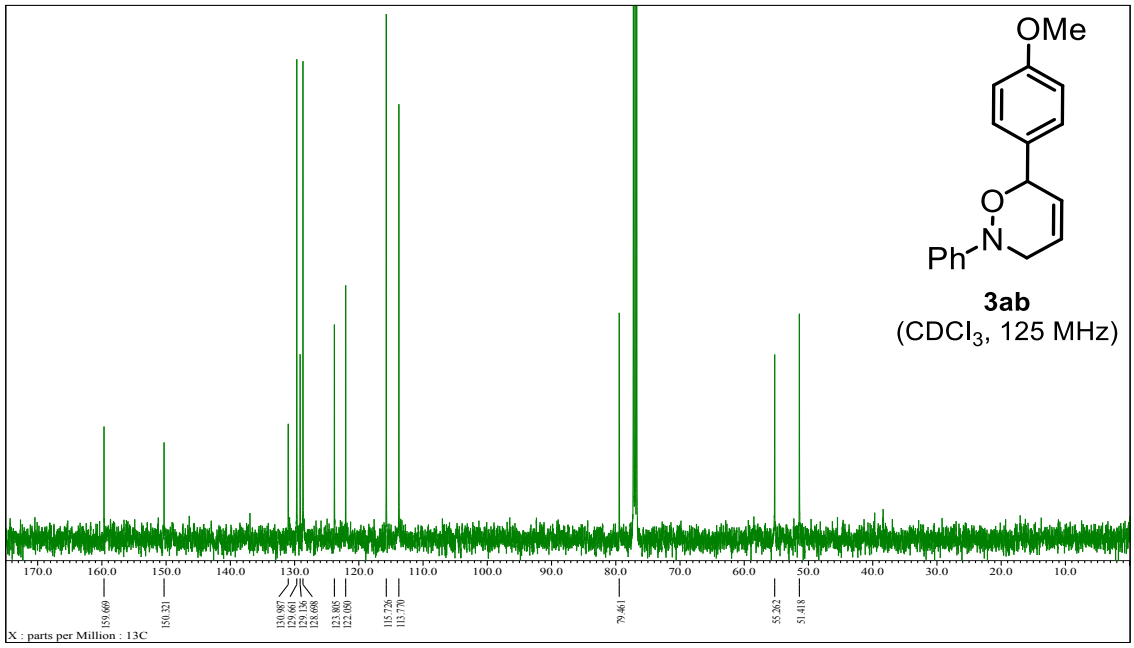
^{13}C NMR of 2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3aa**)



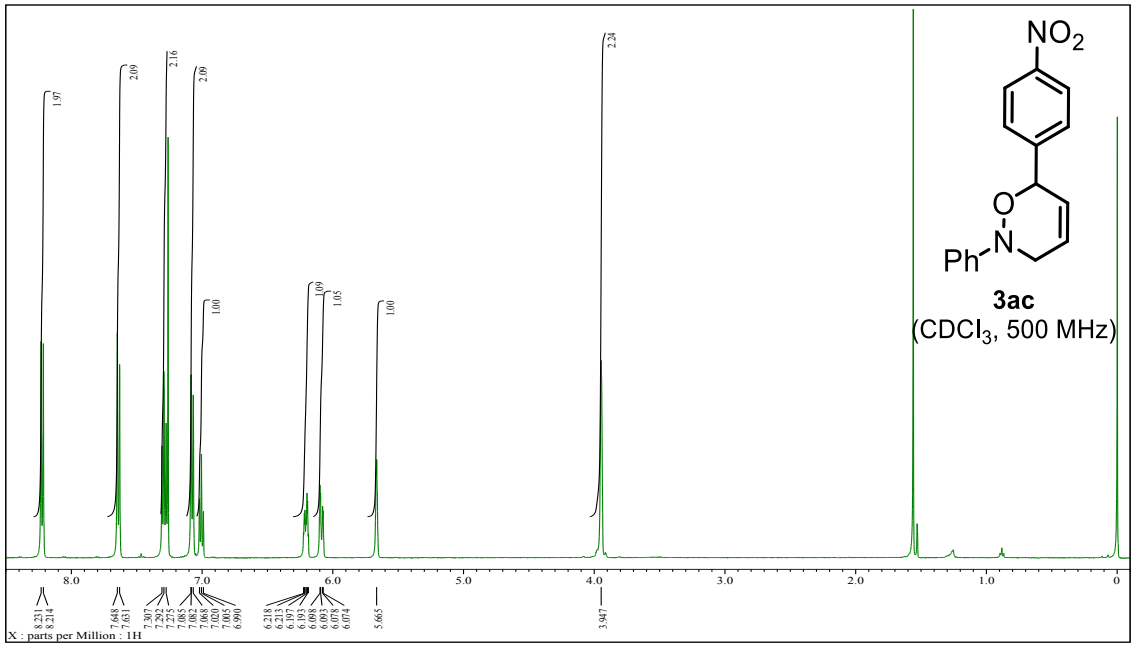
^{1}H NMR of 6-(4-methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ab**)



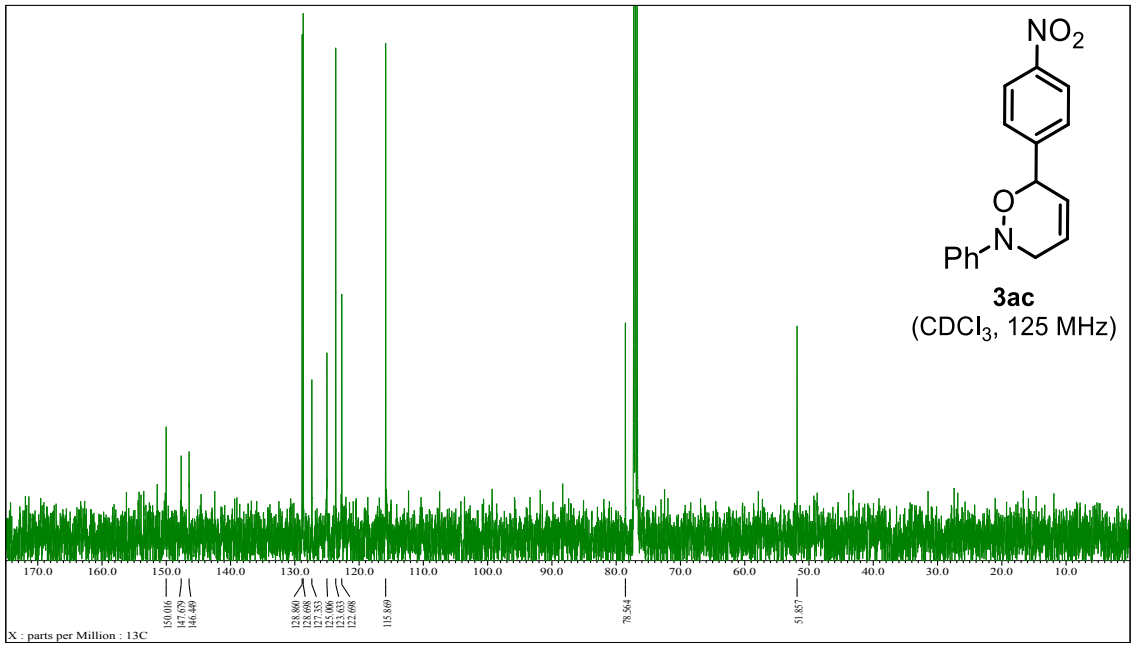
^{13}C NMR of 6-(4-methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ab**)



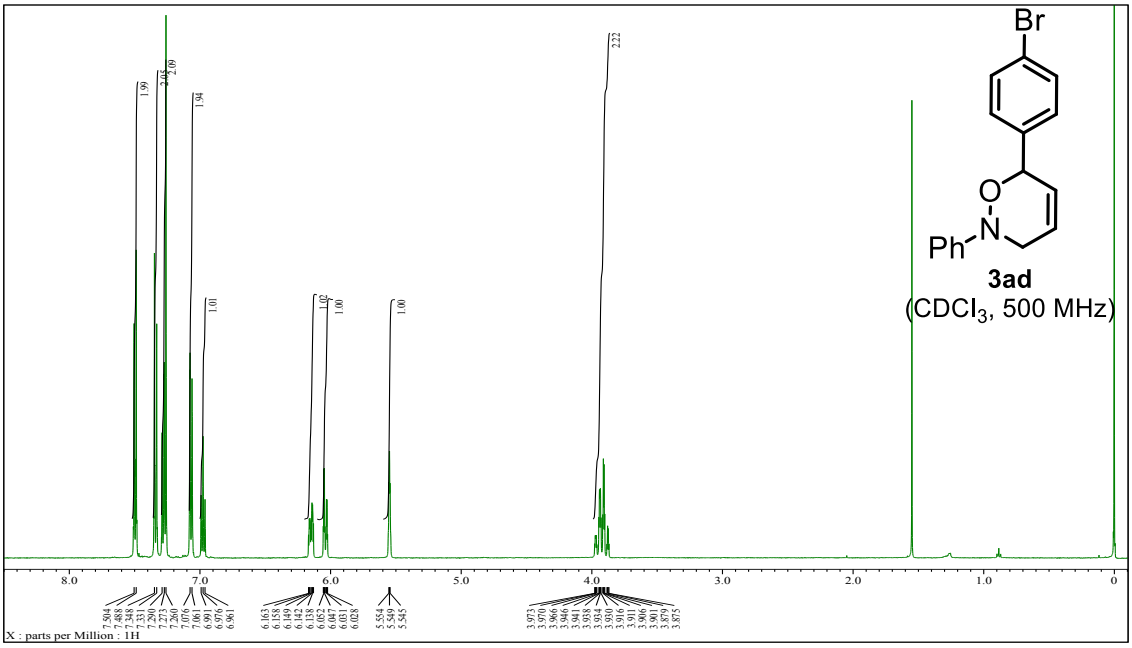
^{1}H NMR of 6-(4-nitrophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ac**)



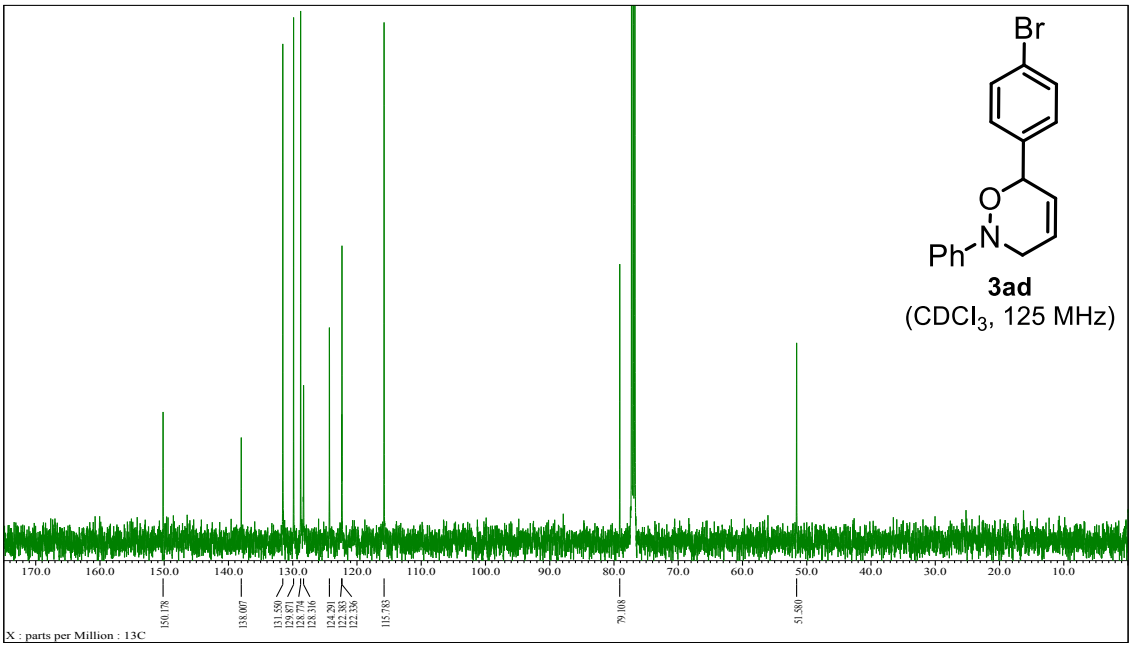
^{13}C NMR of 6-(4-nitrophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ac**)



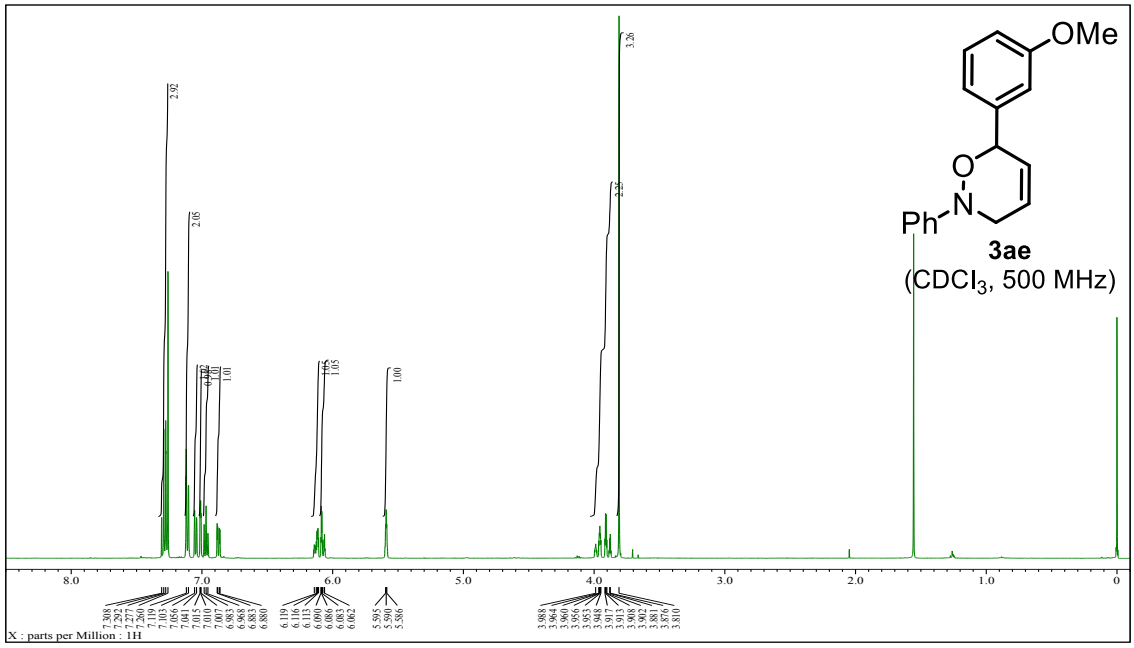
^{1}H NMR of 6-(4-bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ad**)



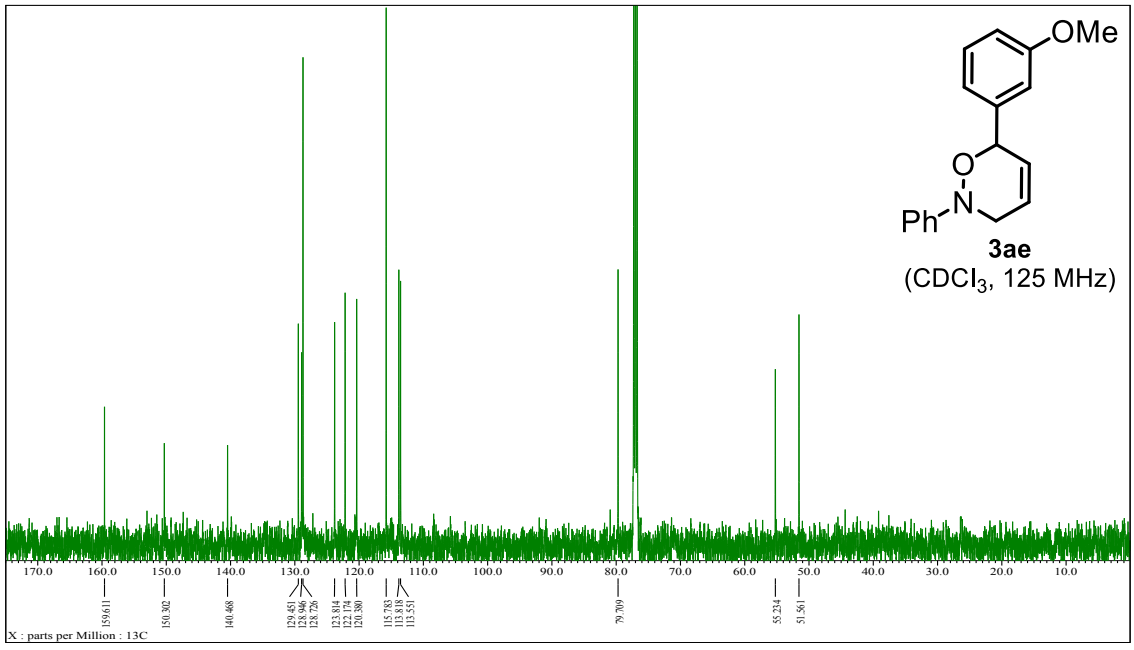
^{13}C NMR of 6-(4-bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ad**)



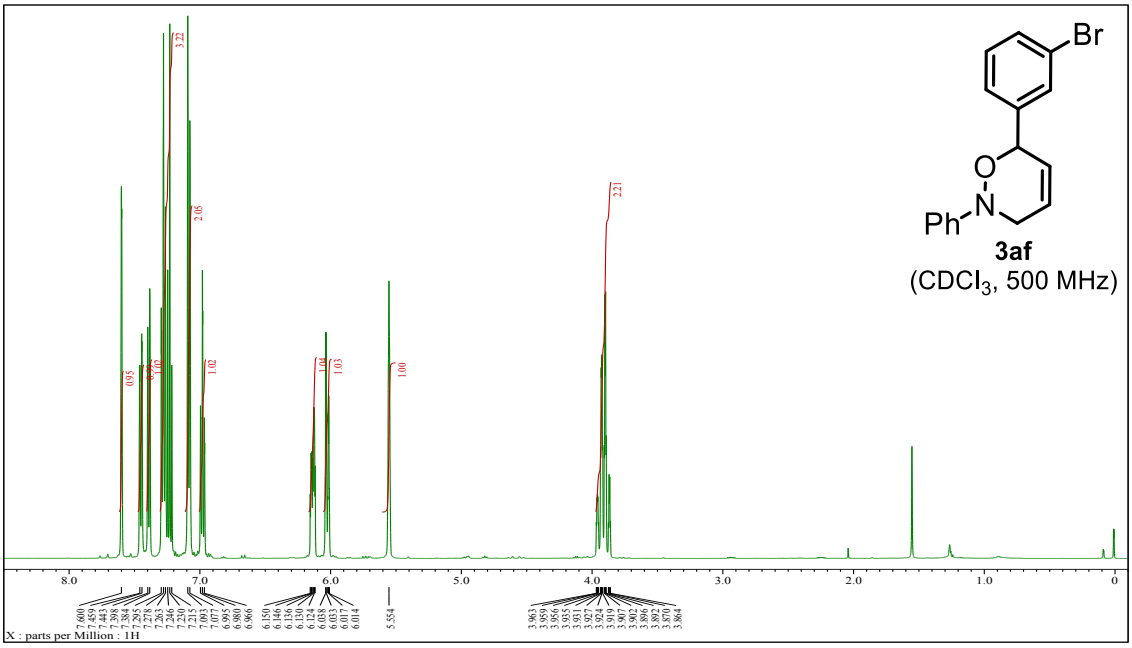
^{1}H NMR of 6-(3-methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ae**)



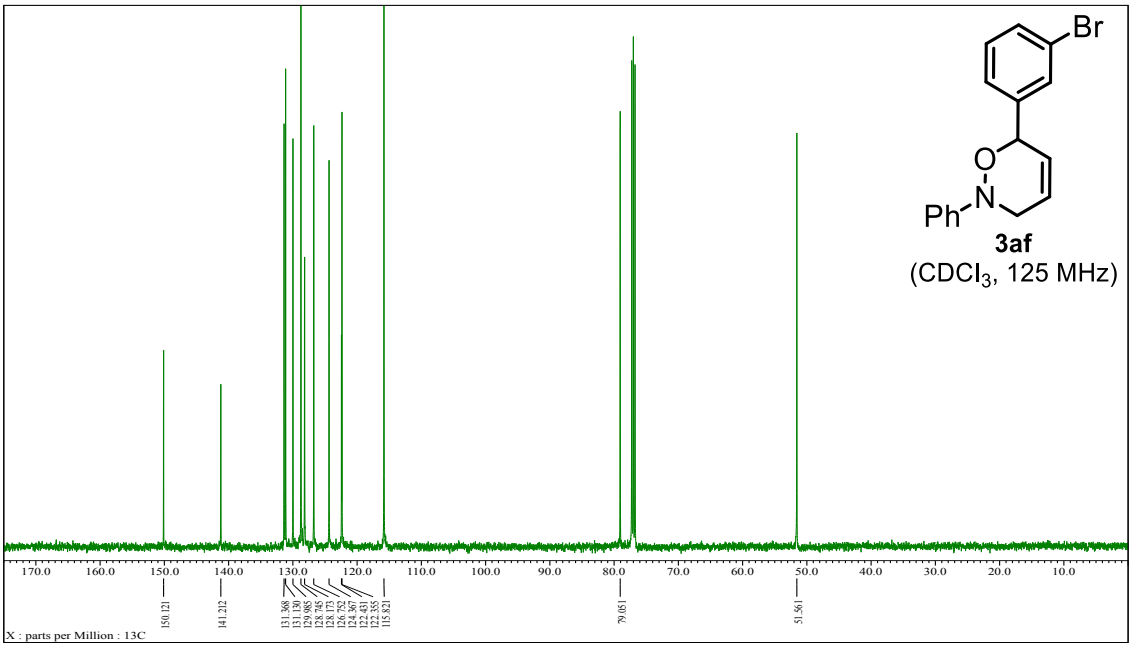
^{13}C NMR of 6-(3-methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ae**)



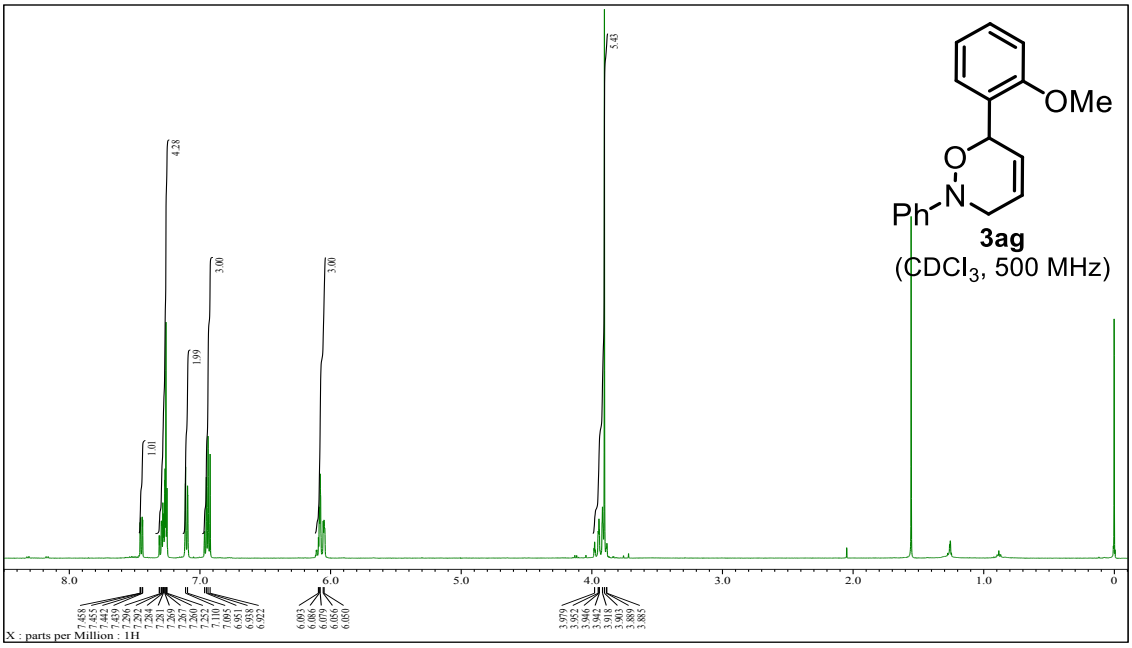
^{1}H NMR of 6-(3-bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3af**)



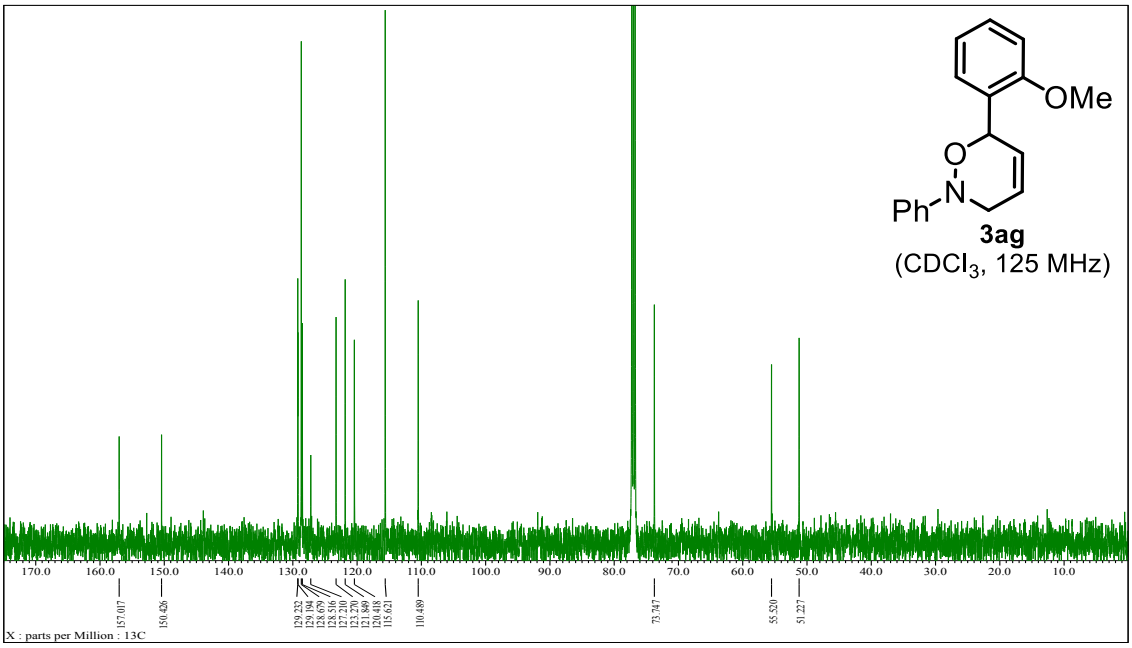
^{13}C NMR of 6-(3-bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3af**)



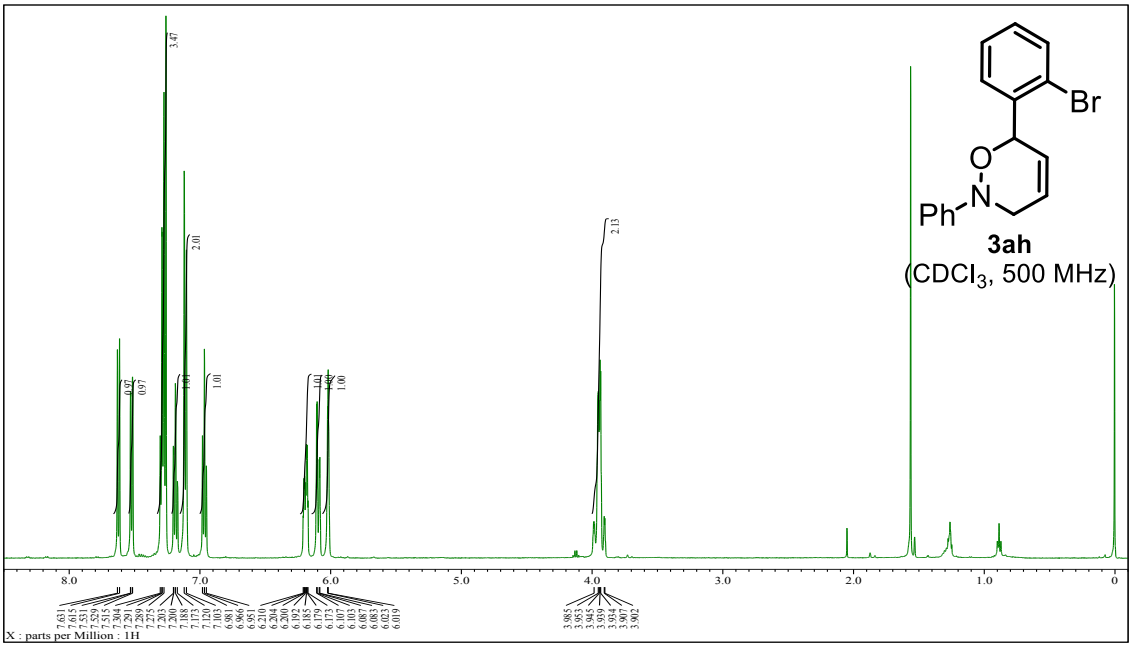
^{1}H NMR of 6-(2-methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ag**)



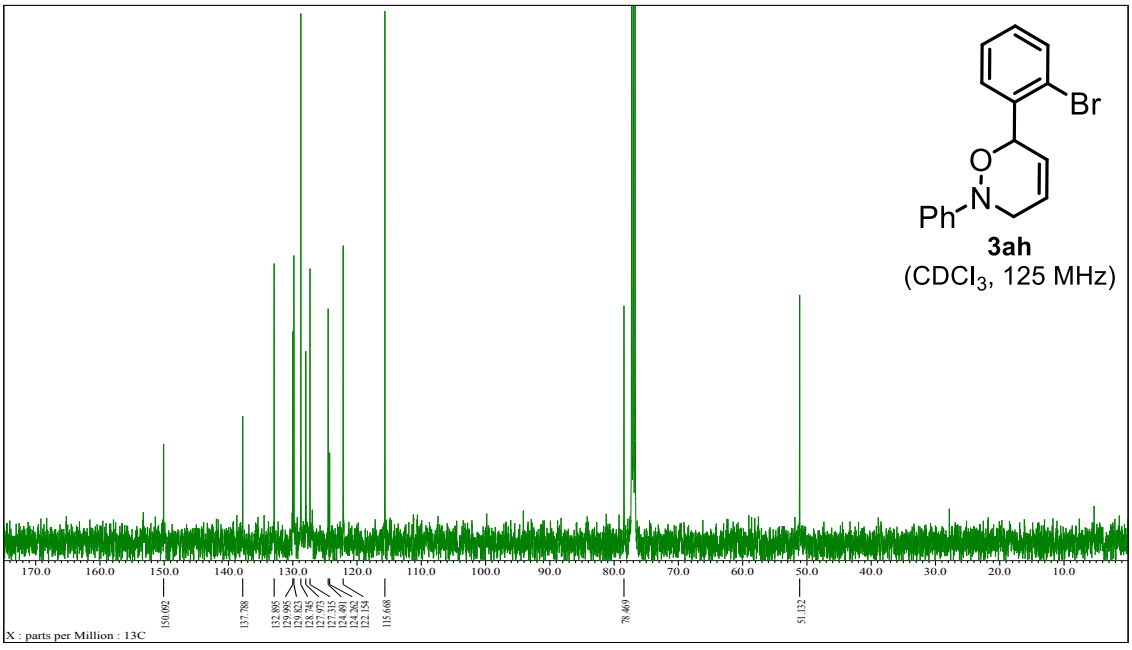
^{13}C NMR of 6-(2-methoxyphenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ag**)



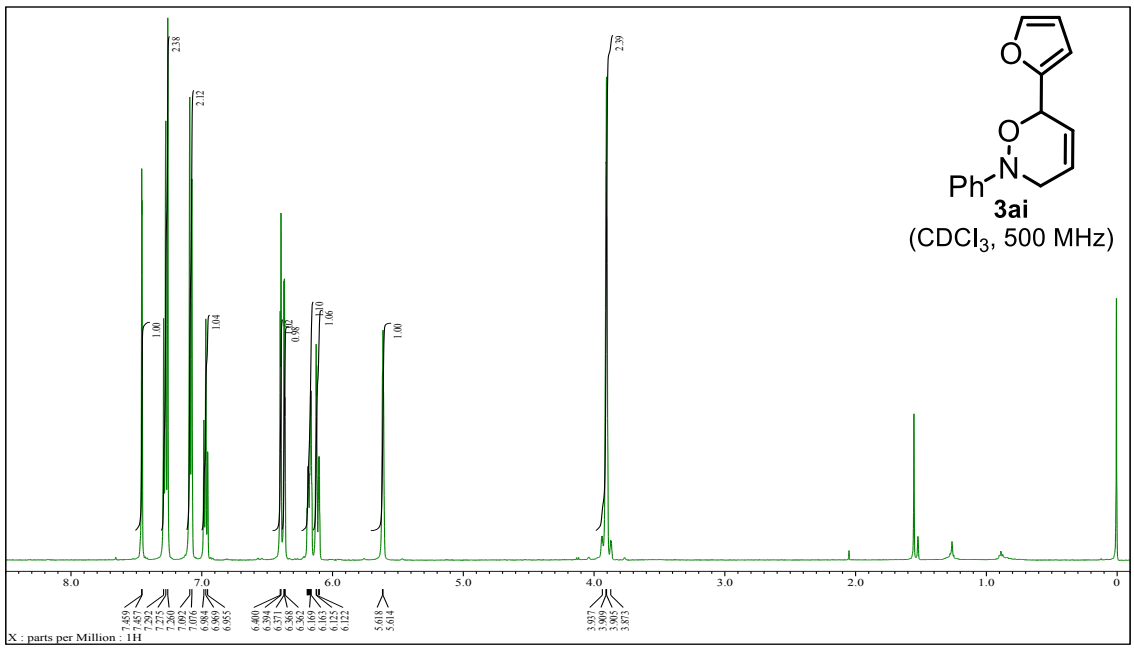
^{1}H NMR of 6-(2-bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ah**)



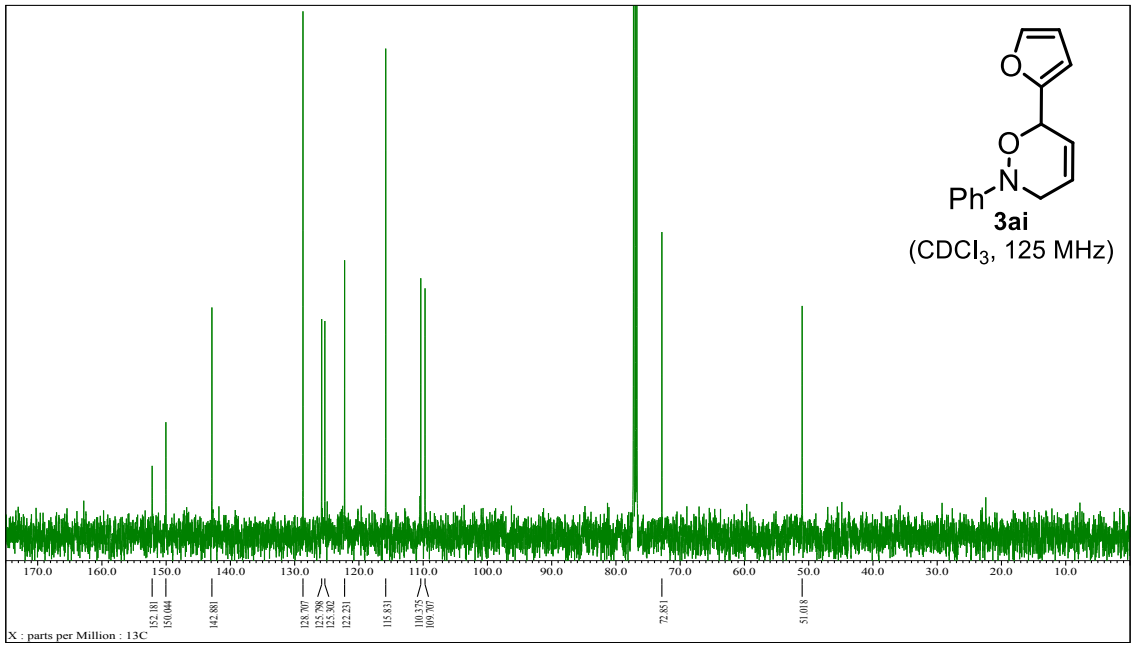
^{13}C NMR of 6-(2-bromophenyl)-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ah**)



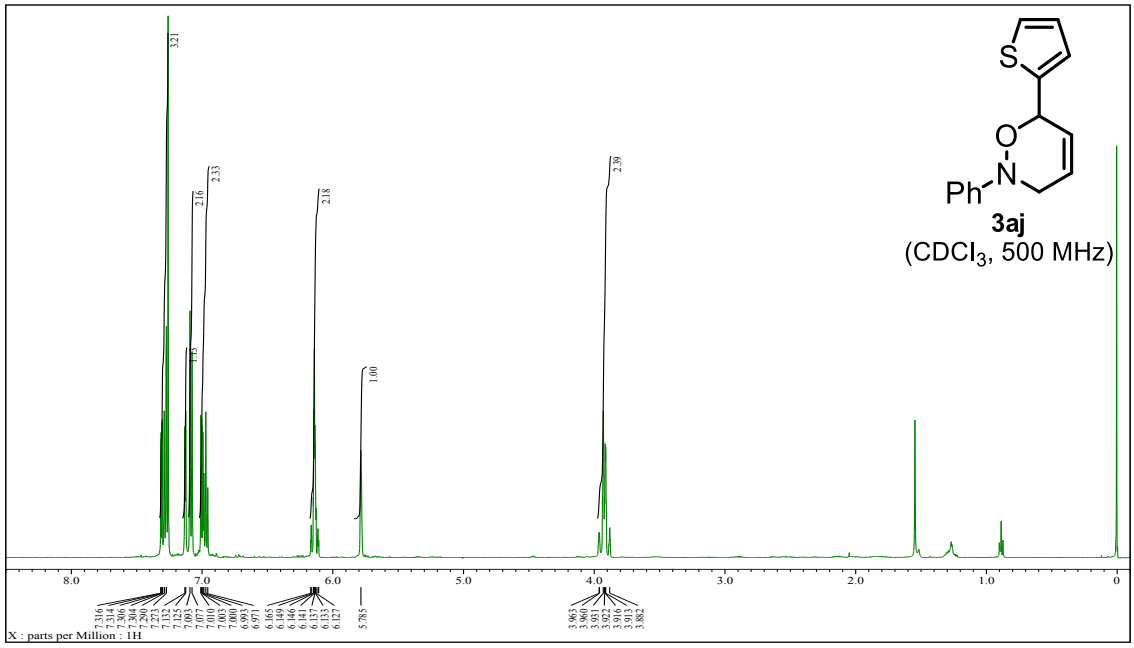
^{1}H NMR of 6-furyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ai**)



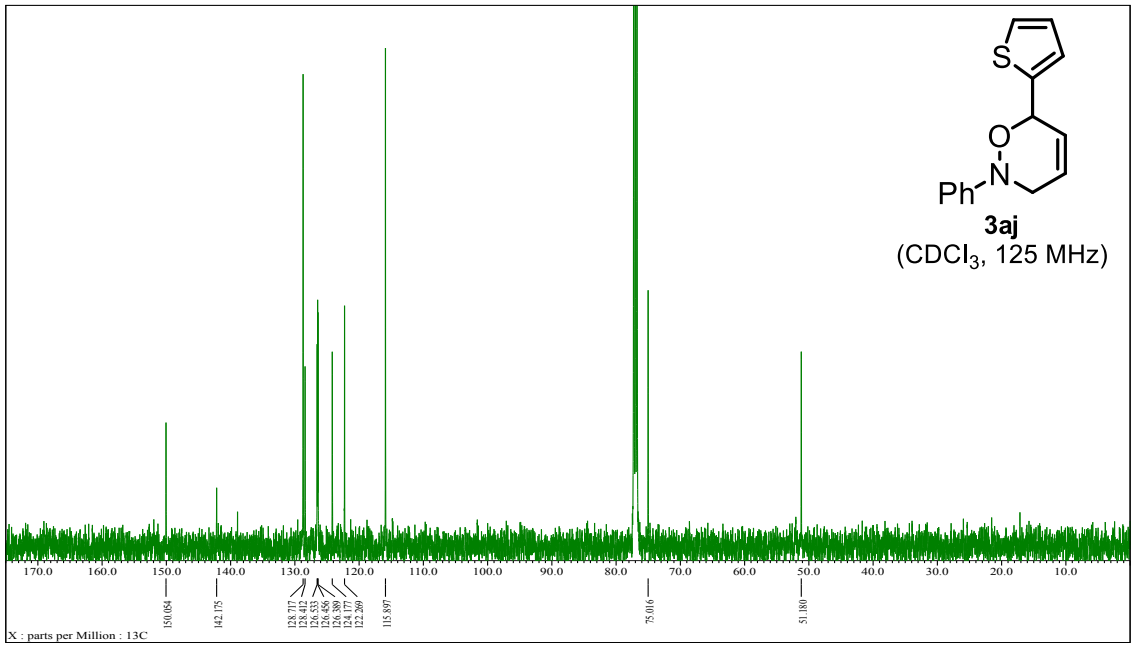
^{13}C NMR of 6-furyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ai**)



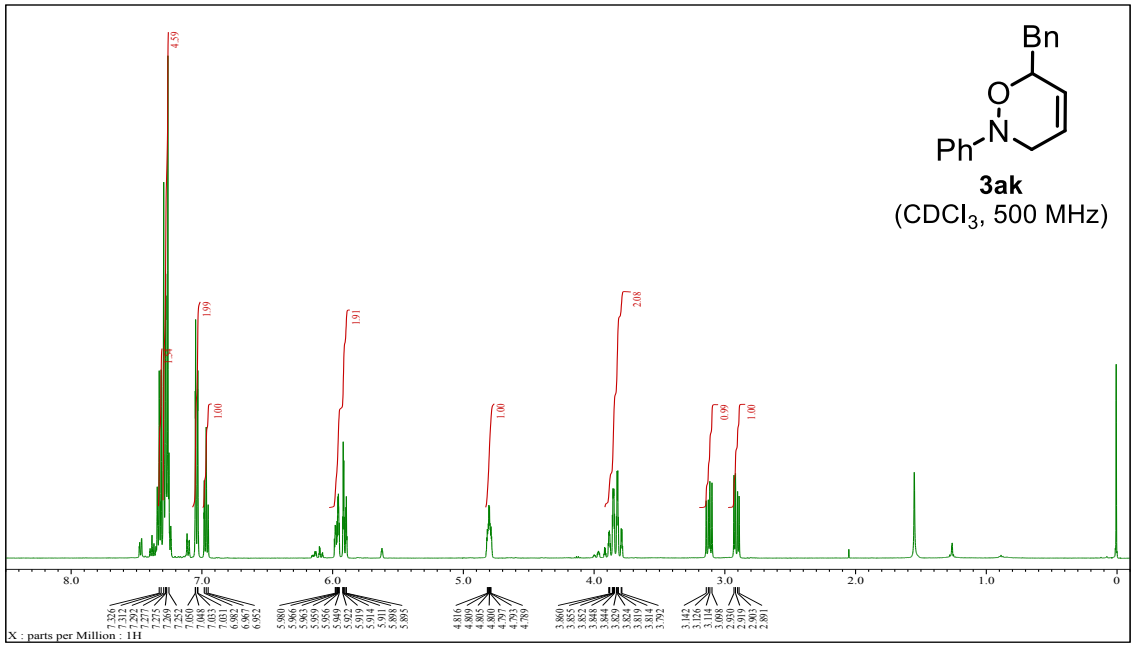
^{1}H NMR of 2-phenyl-6-thienyl-3,6-dihydro-2*H*-[1,2]oxazine (**3aj**)



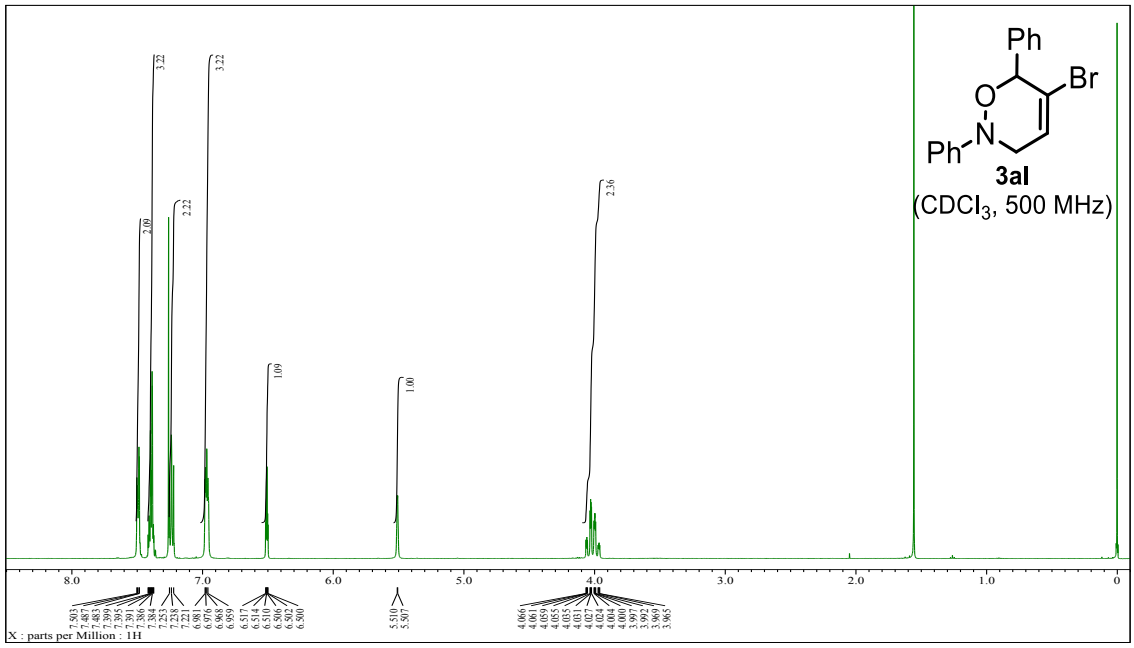
^{13}C NMR of 2-phenyl-6-thienyl-3,6-dihydro-2*H*-[1,2]oxazine (**3aj**)



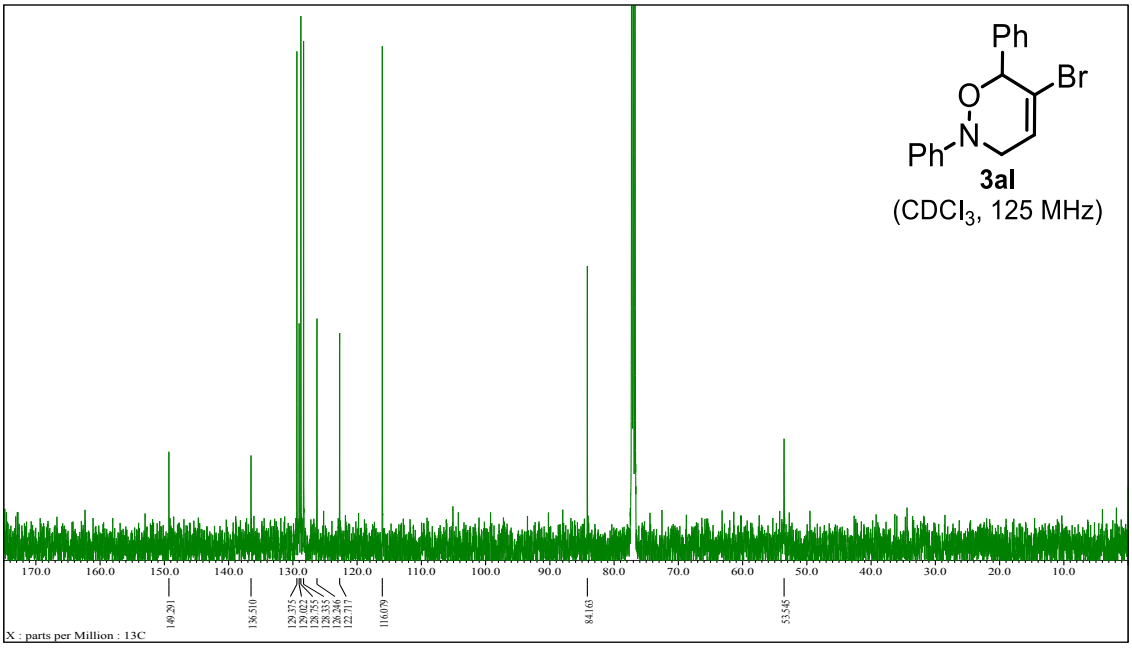
^{1}H NMR of 6-benzyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ak**)



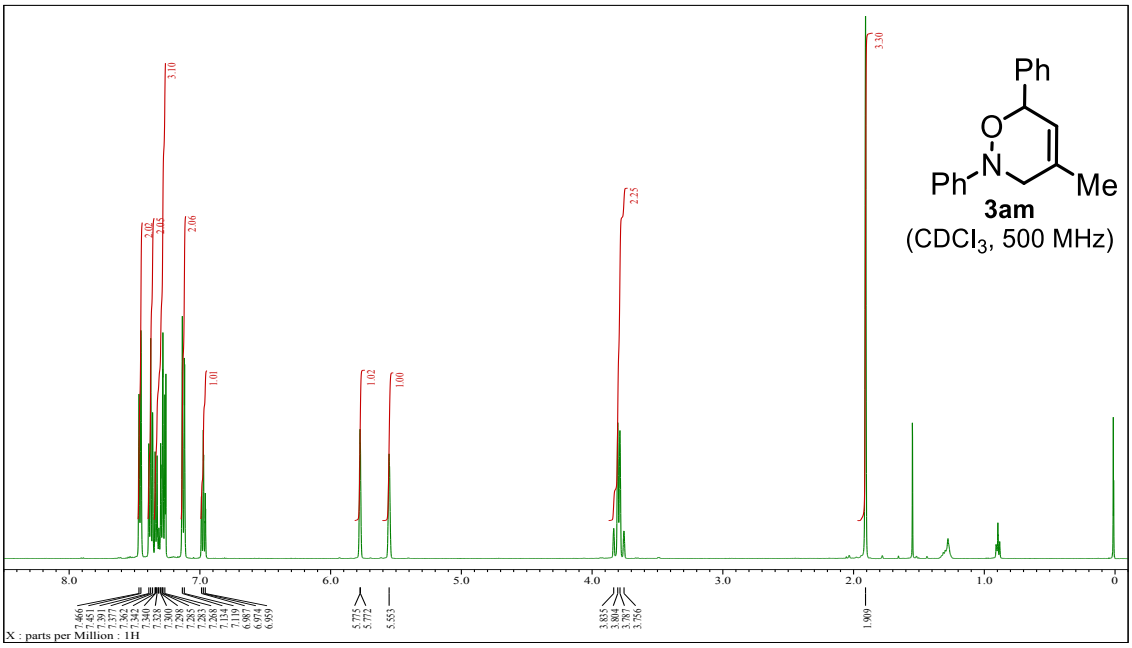
^{1}H NMR of 5-bromo-2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3al**)



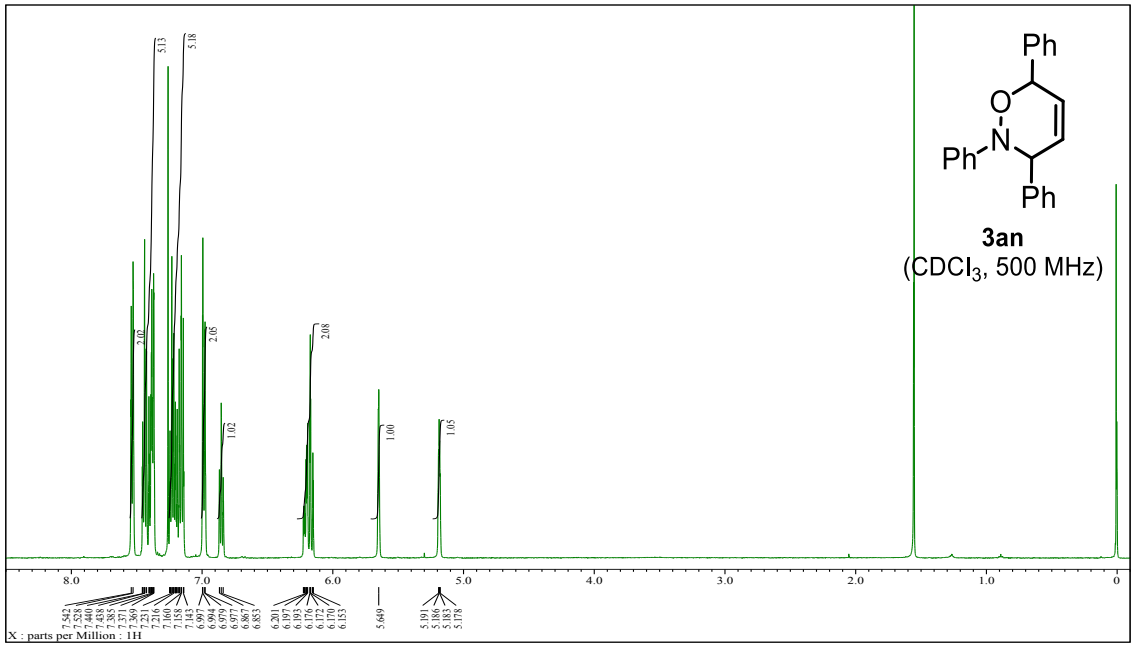
^{13}C NMR of 5-bromo-2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3al**)



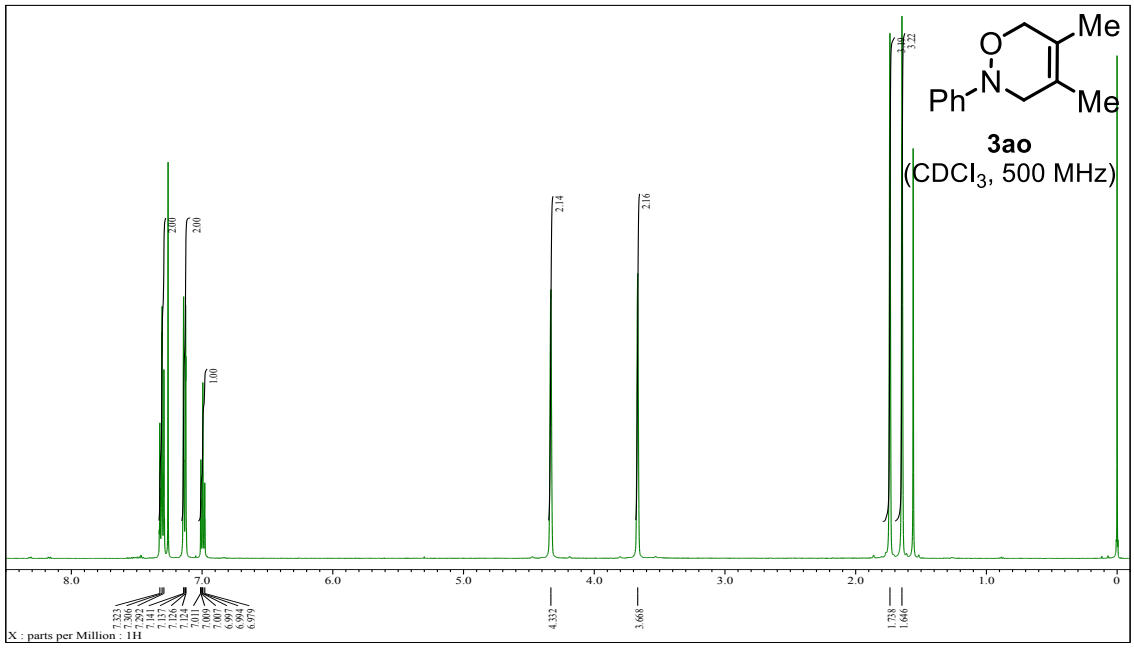
^{1}H NMR of 4-methyl-2,6-diphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3am**)



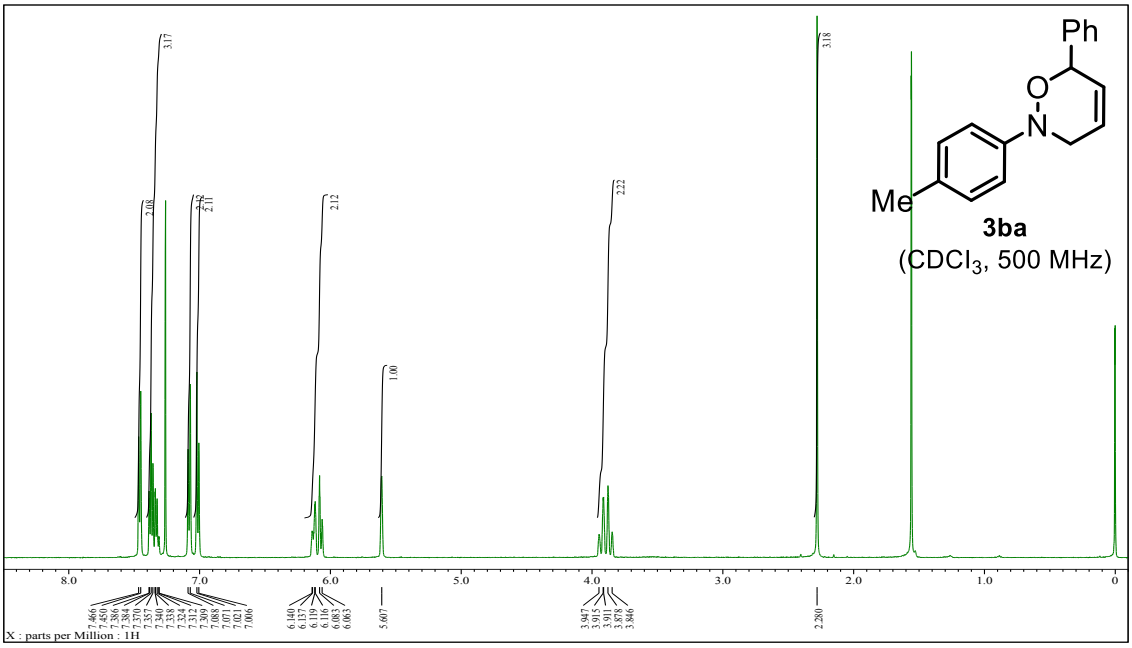
^{1}H NMR of 2,3,6-triphenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3an**)



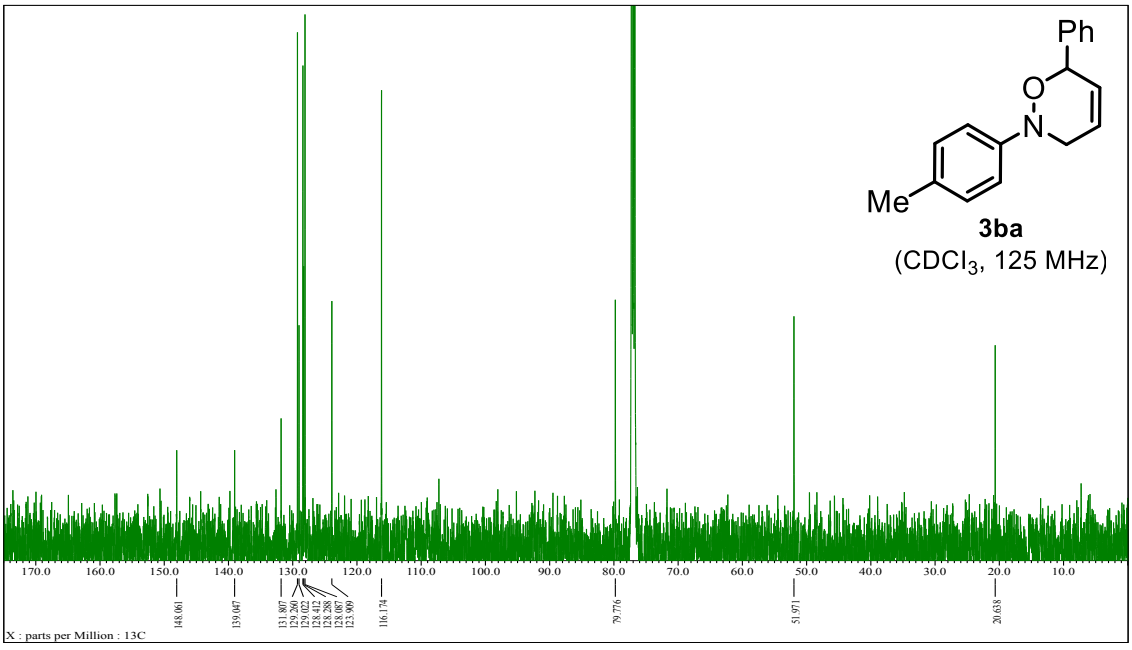
^{1}H NMR of 4,5-dimethyl-2-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ao**)



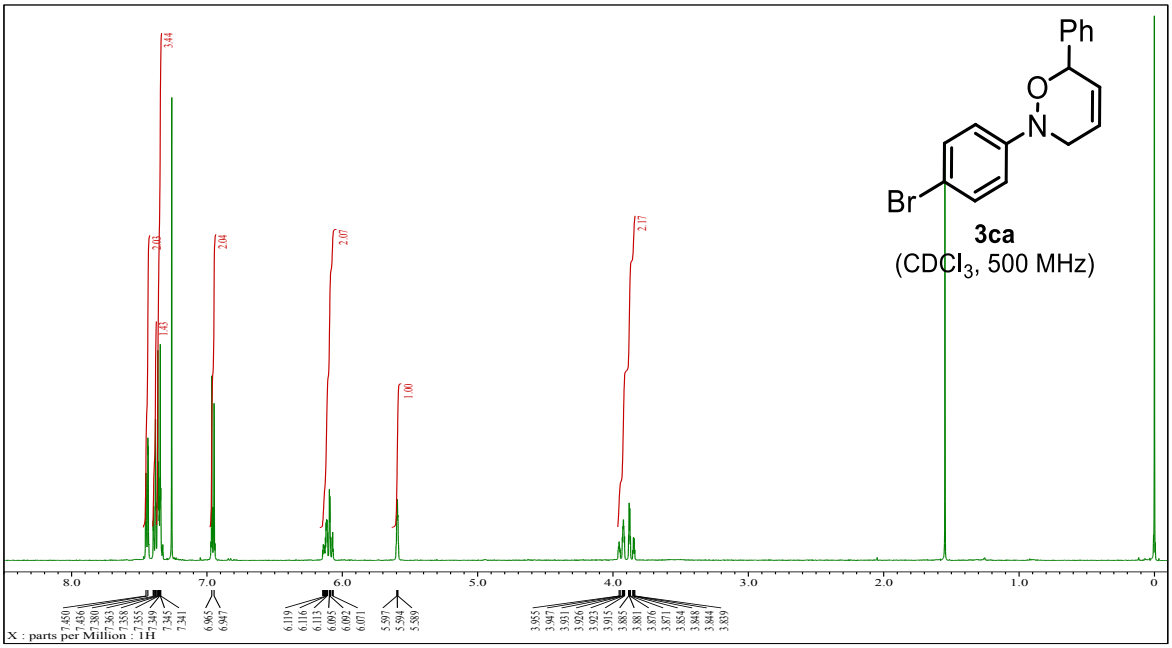
^{1}H NMR of 2-(4-methylphenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ba**)



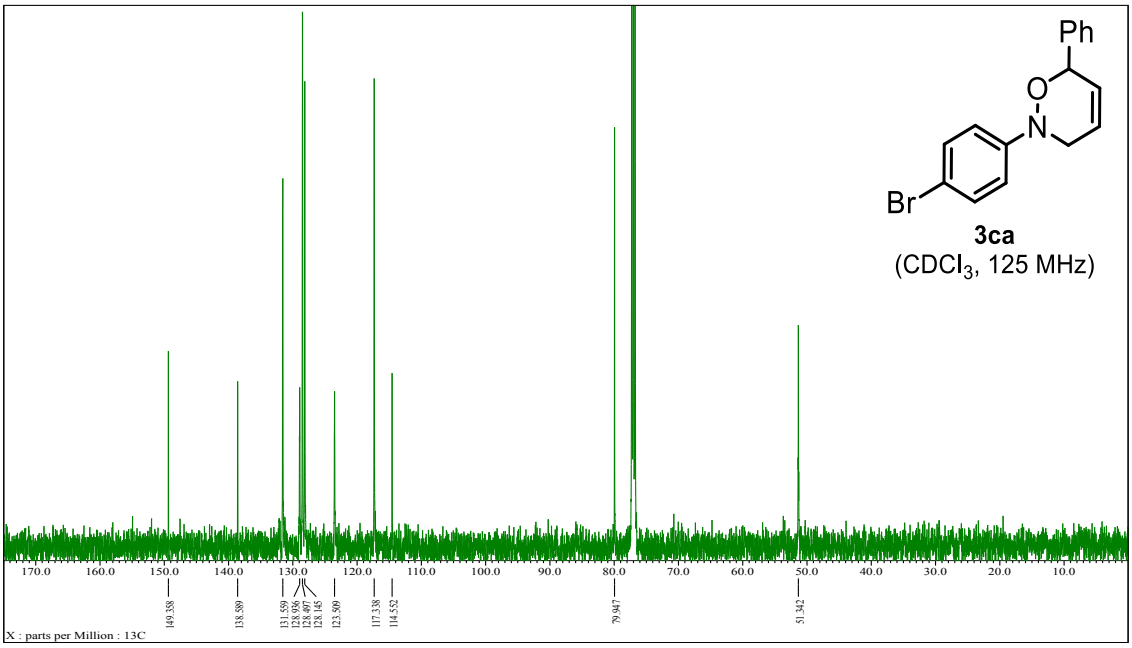
^{13}H NMR of 2-(4-methylphenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ba**)



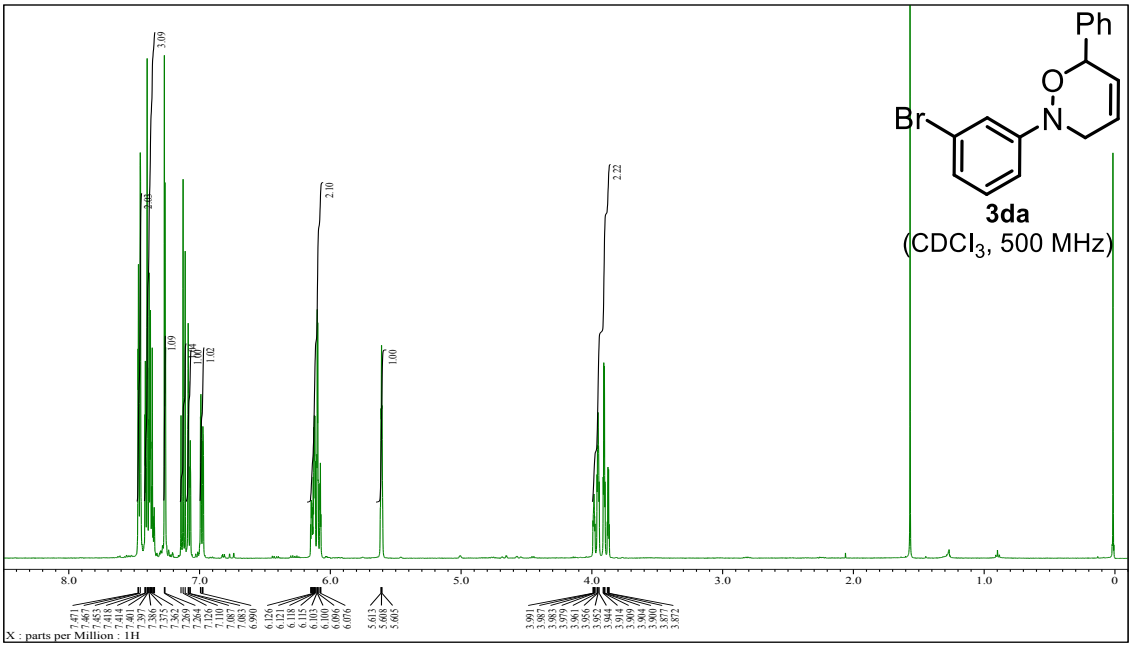
^{1}H NMR of 2-(4-bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ca**)



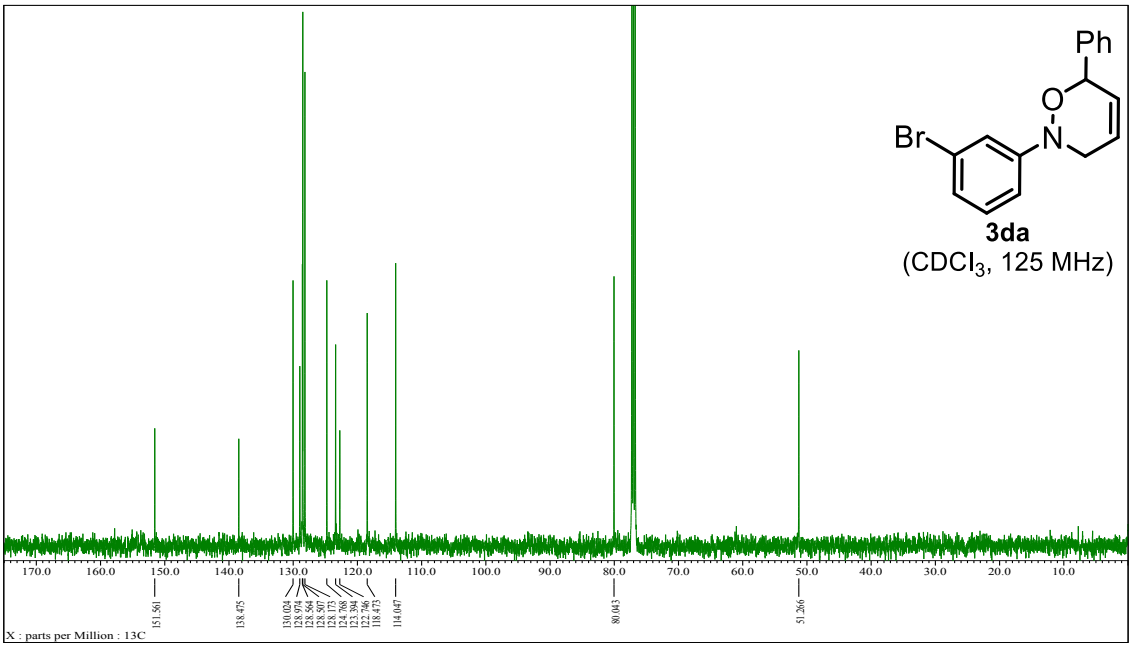
^{13}C NMR of 2-(4-bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ca**)



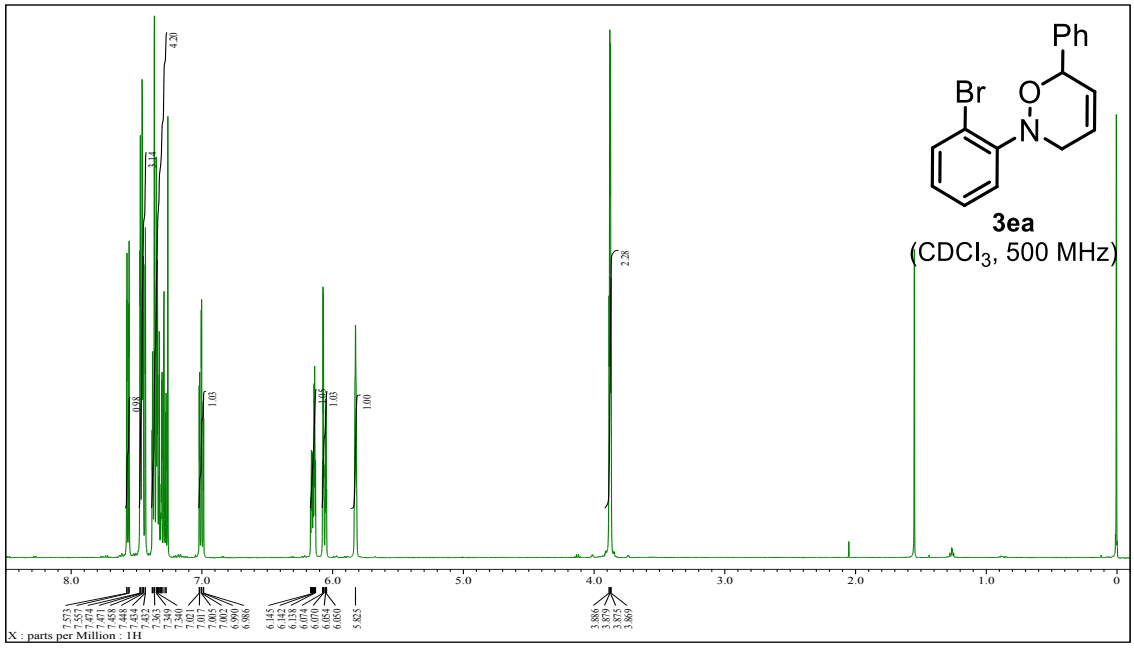
^{1}H NMR of 2-(3-bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3da**)



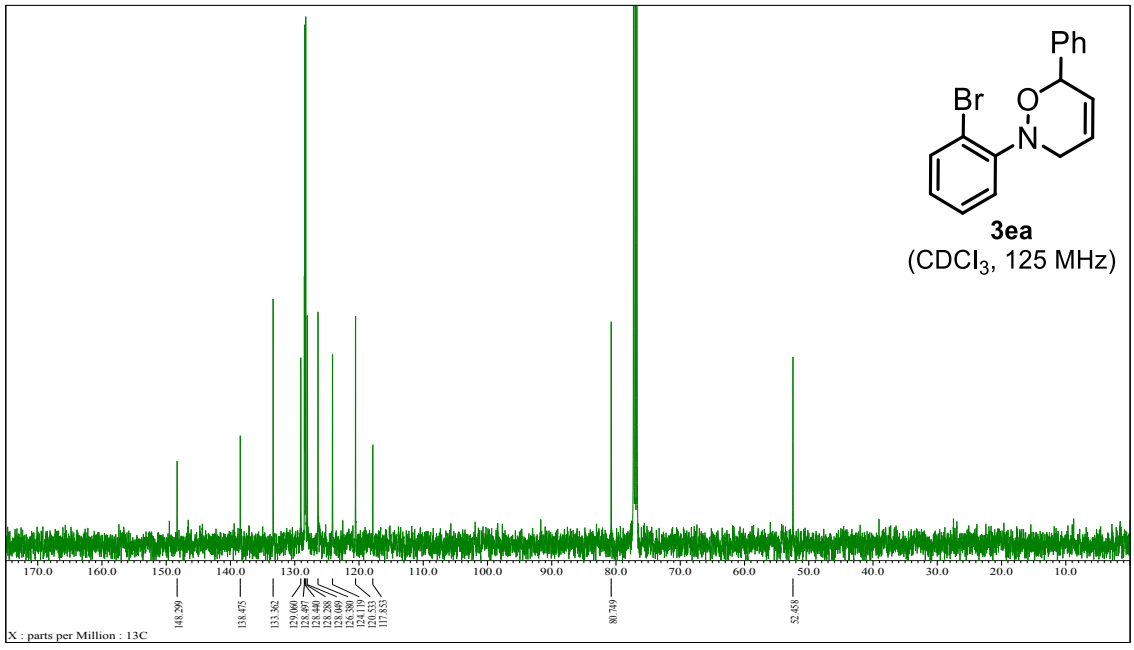
^{13}C NMR of 2-(3-bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3da**)



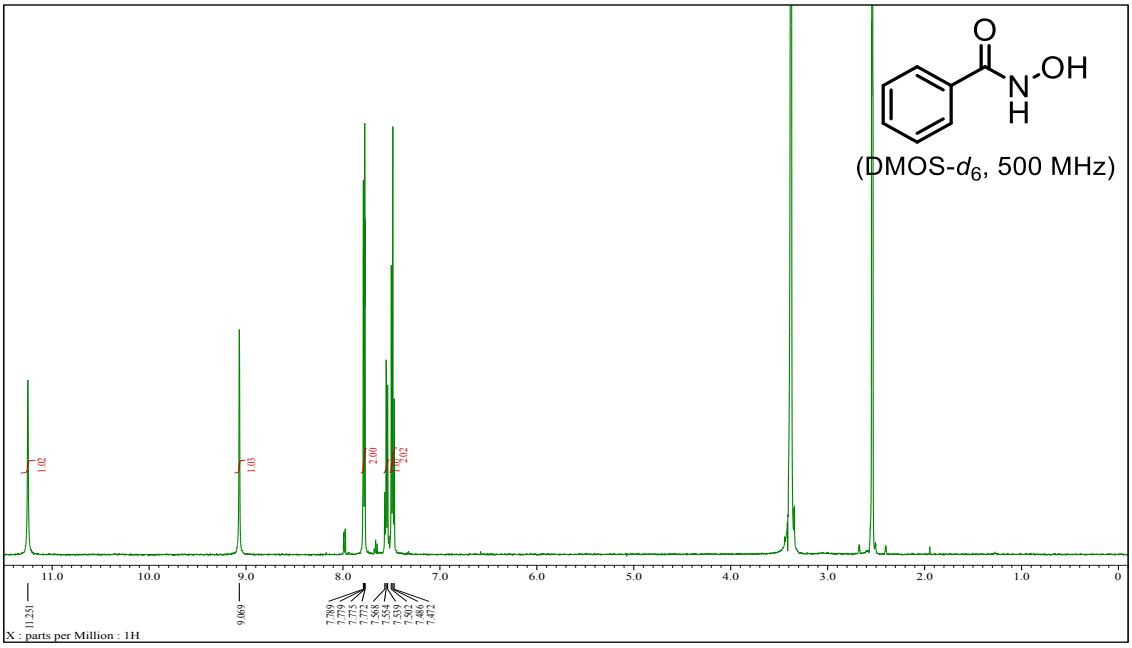
^{1}H NMR of 2-(2-bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ea**)



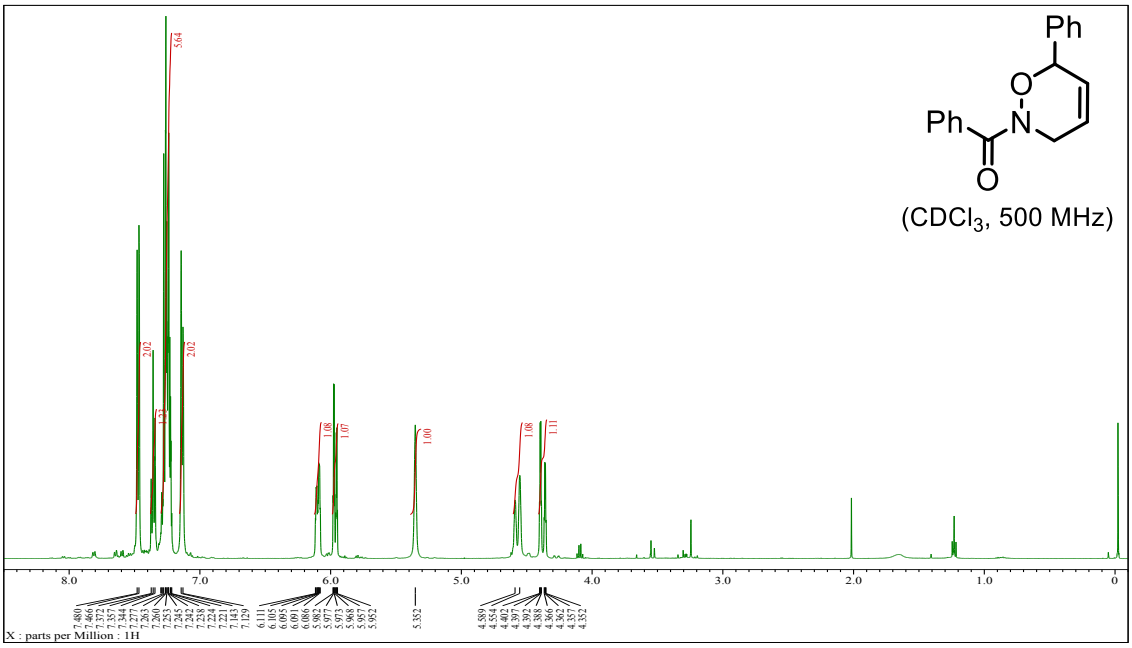
^{13}C NMR of 2-(2-bromophenyl)-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3ea**)



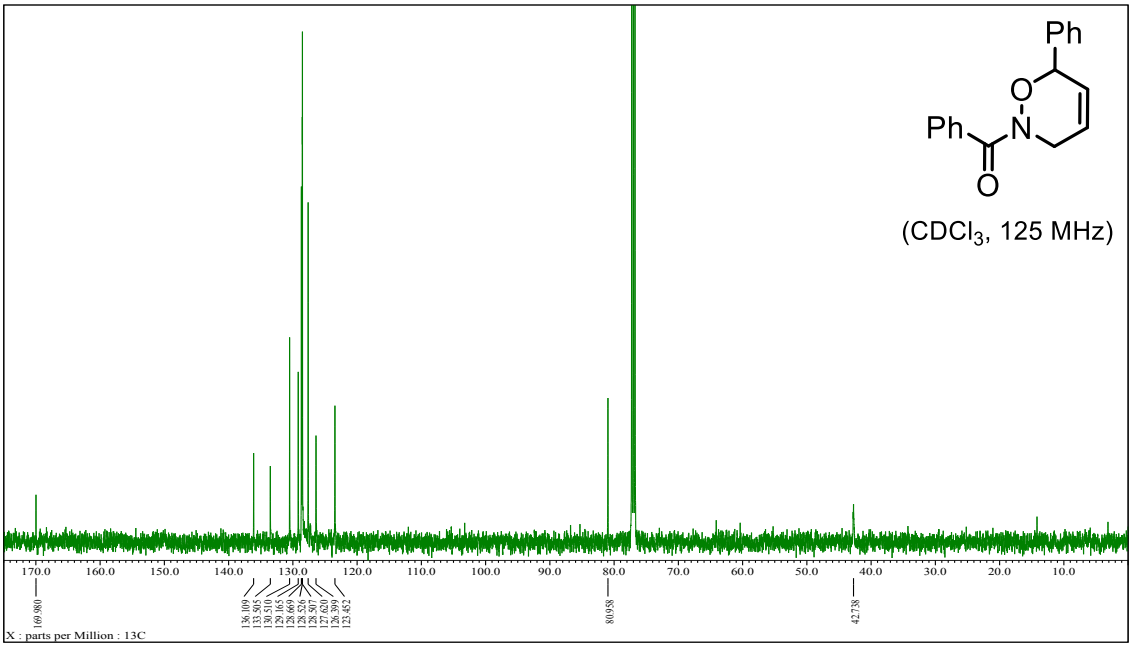
^{1}H NMR of *N*-hydroxybenzamide



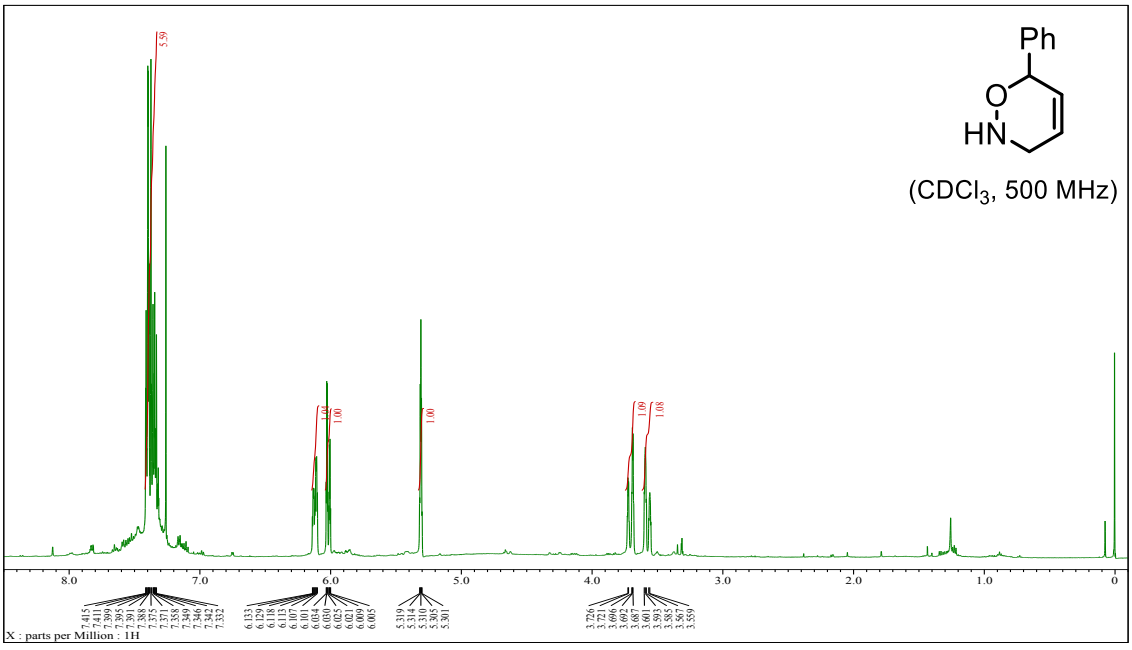
^{1}H NMR of 6-phenyl-2-benzoyl-3,6-dihydro-2*H*-[1,2]oxazine



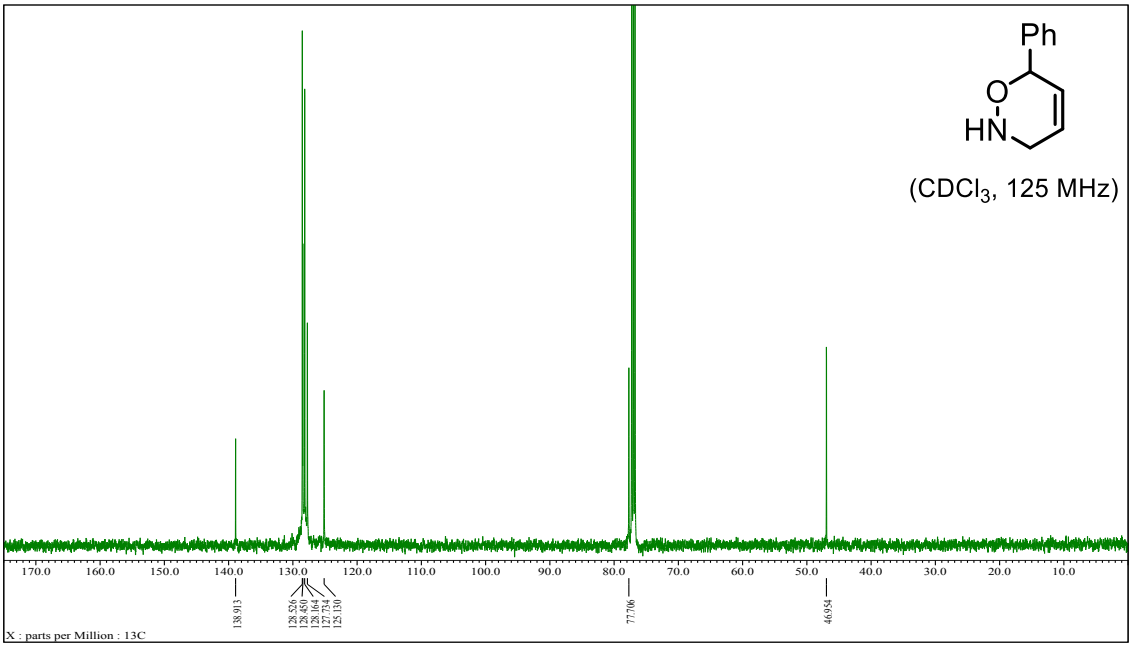
^{13}C NMR of 6-phenyl-2- benzoyl-3,6-dihydro-2*H*-[1,2]oxazine



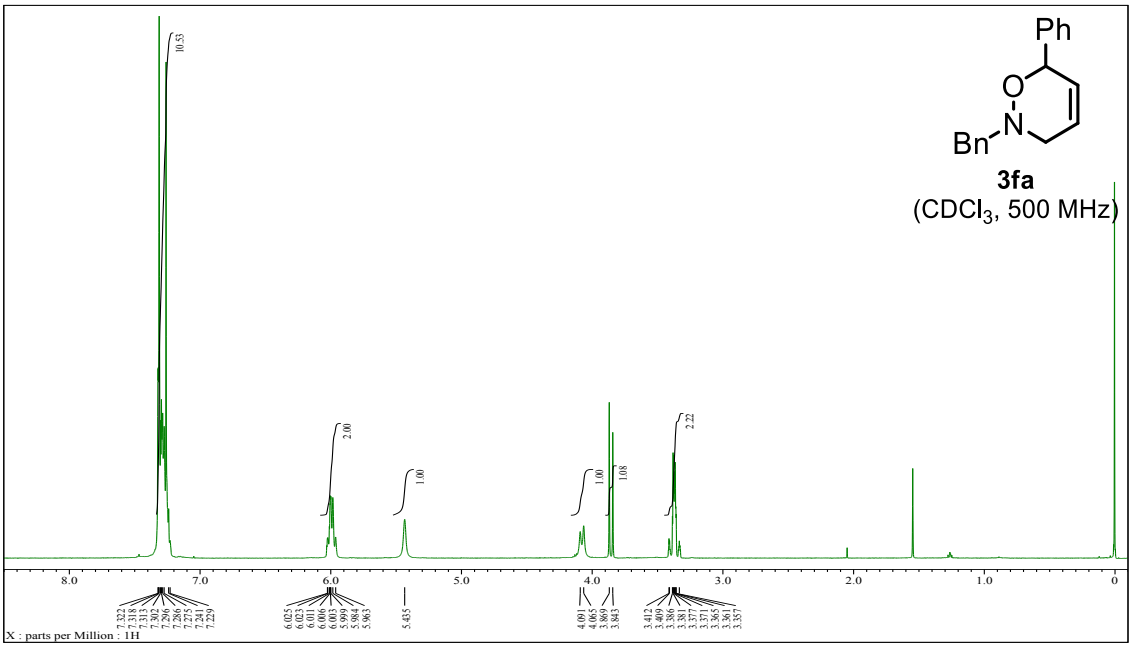
^{1}H NMR of 6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine



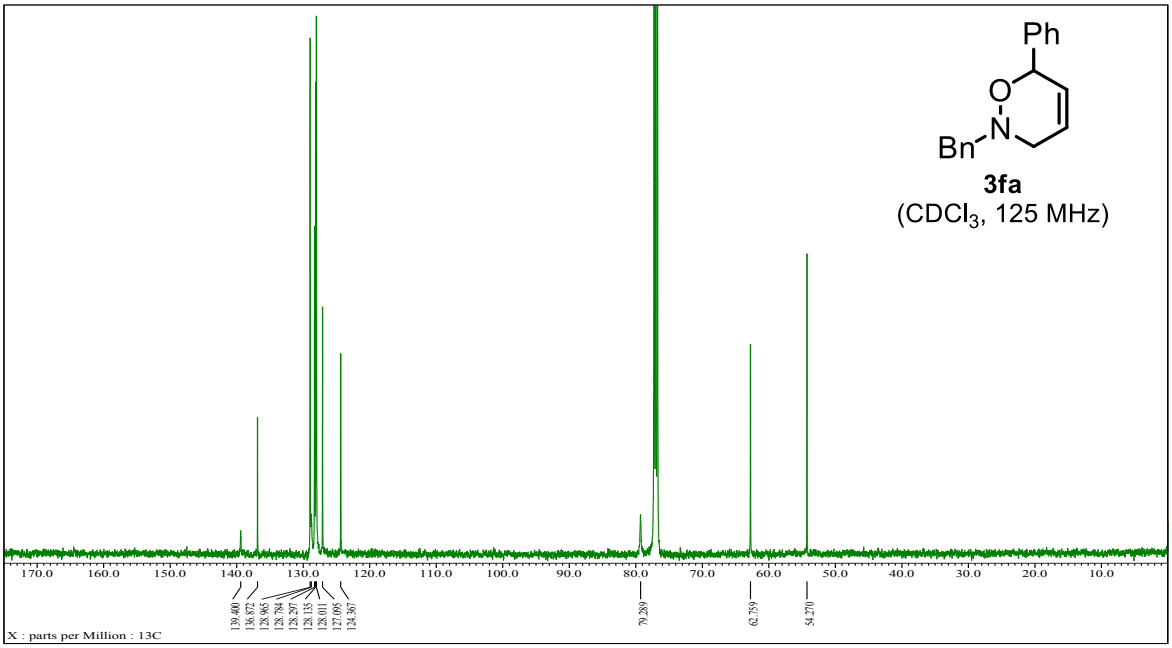
^{13}C NMR of 6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine



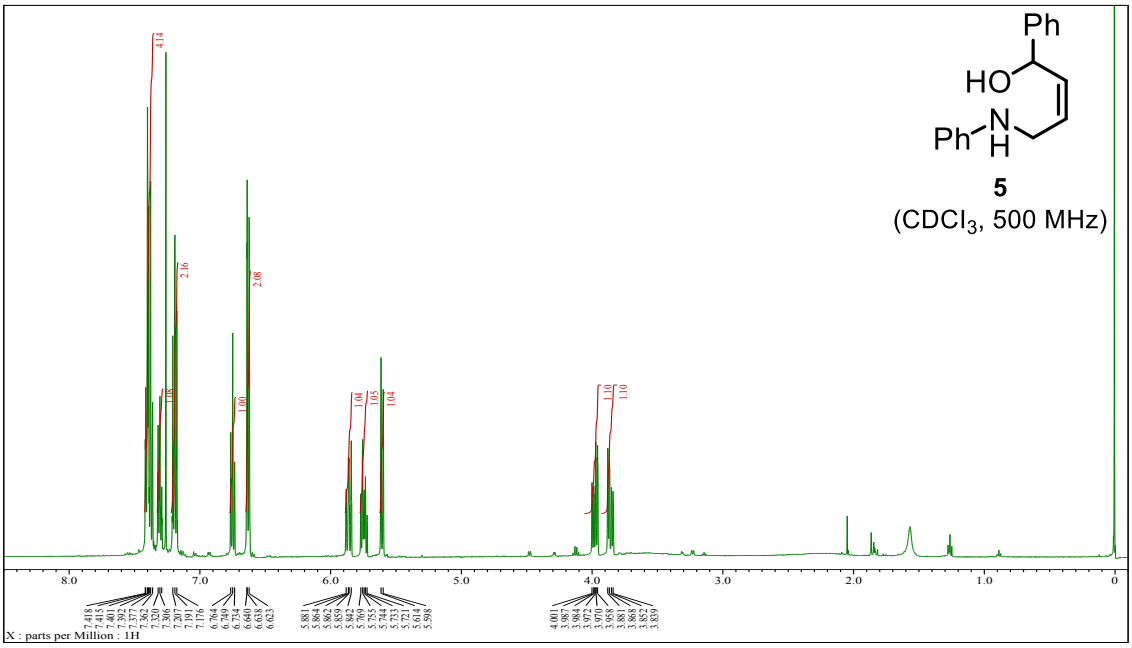
^{1}H NMR of 2-benzyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3fa**)



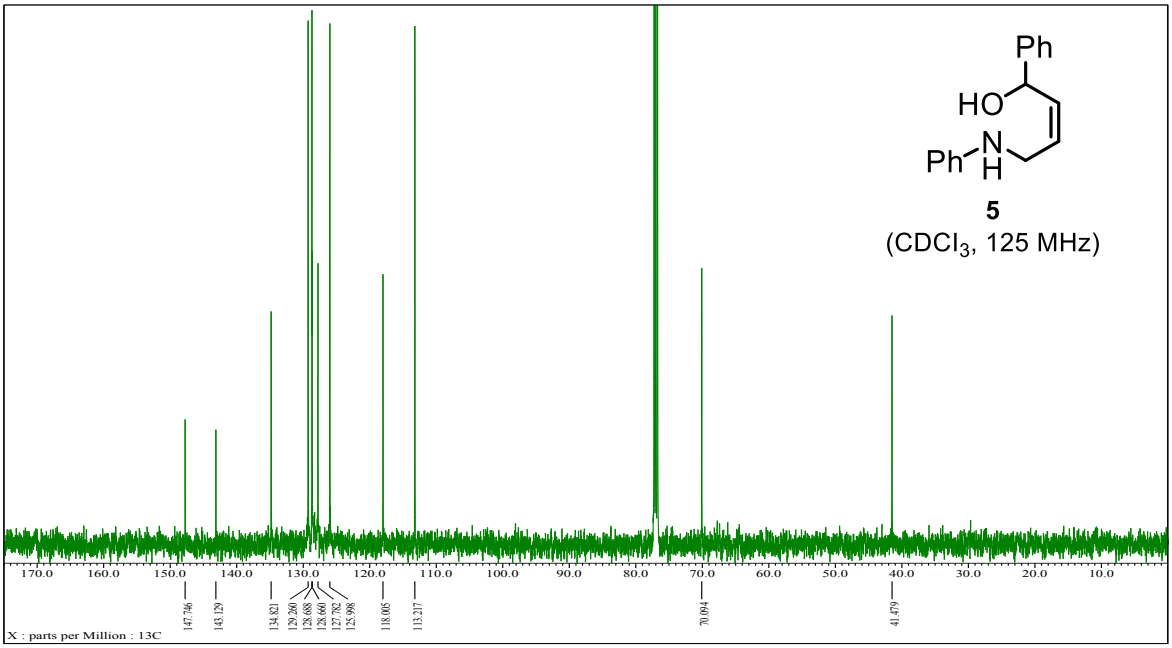
^{13}C NMR of 2-benzyl-6-phenyl-3,6-dihydro-2*H*-[1,2]oxazine (**3fa**)



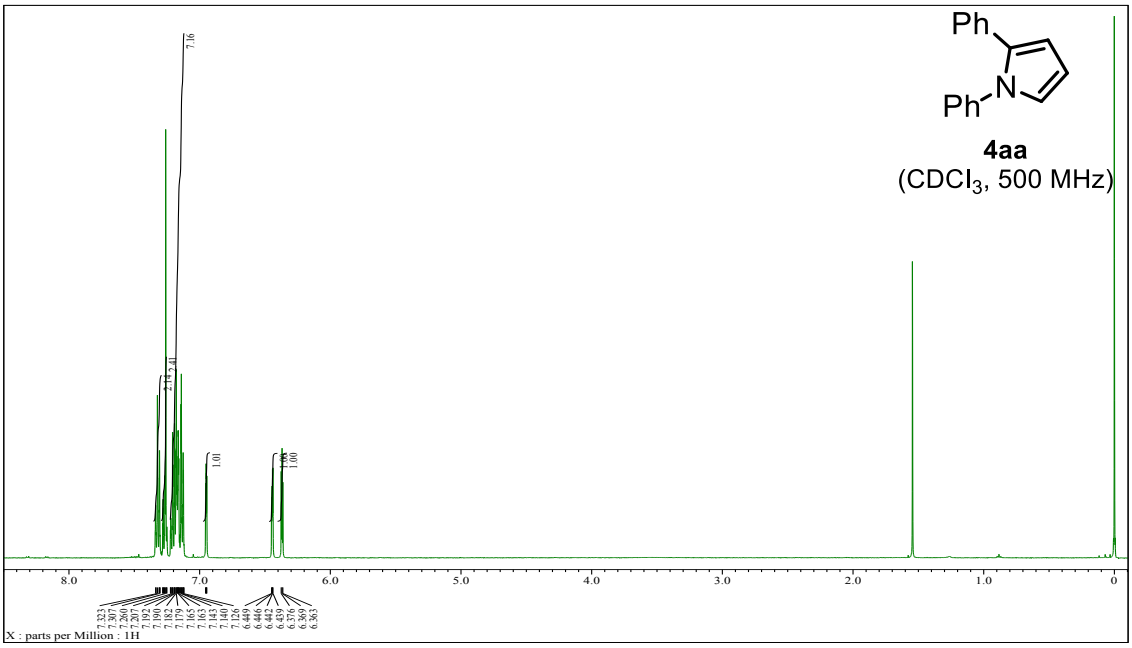
^{1}H NMR of 5-phenylamino-*cis*-3-hexen-2-ol (**5**)



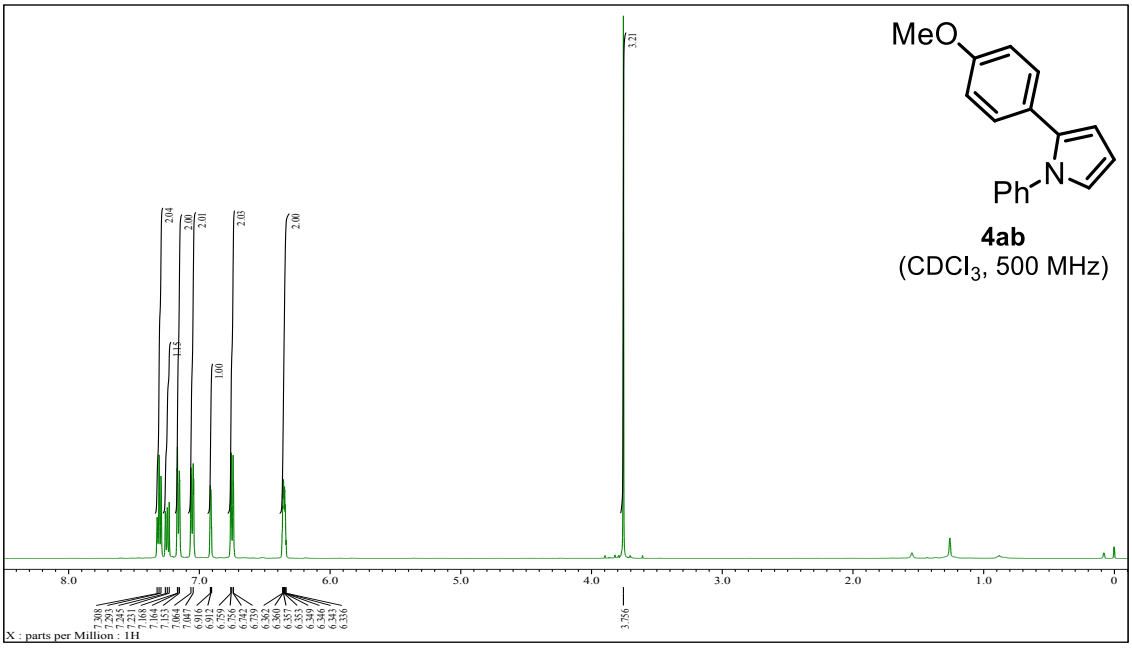
^{13}C NMR of 5-phenylamino-*cis*-3-hexen-2-ol (**5**)



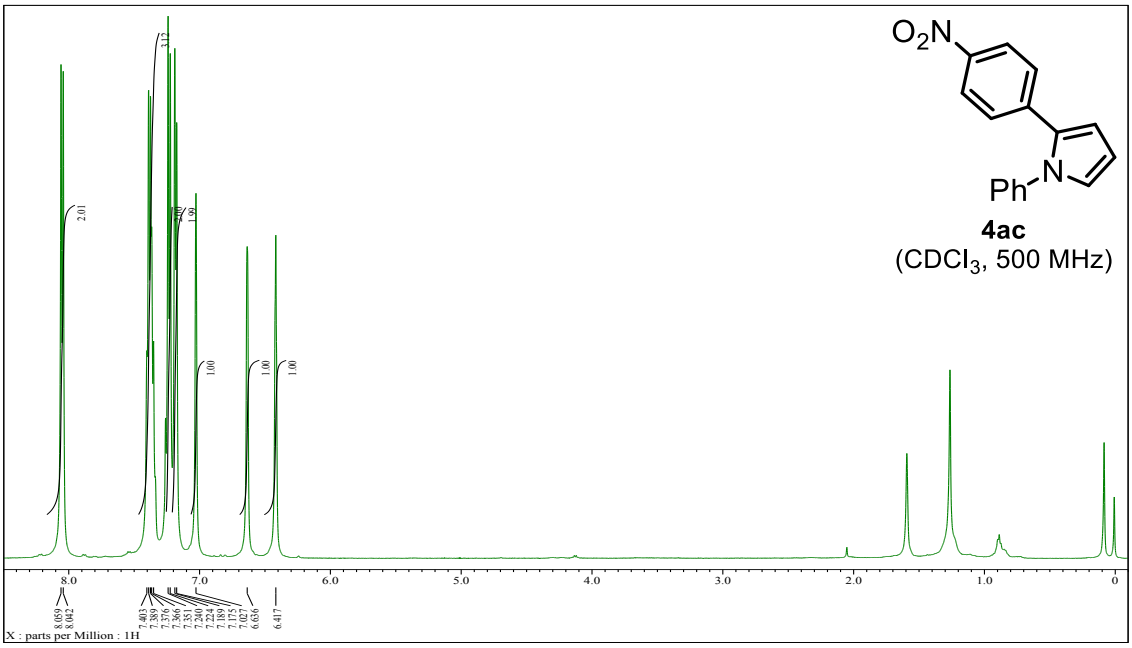
^{1}H NMR of 1,2-diphenylpyrrole (**4aa**)



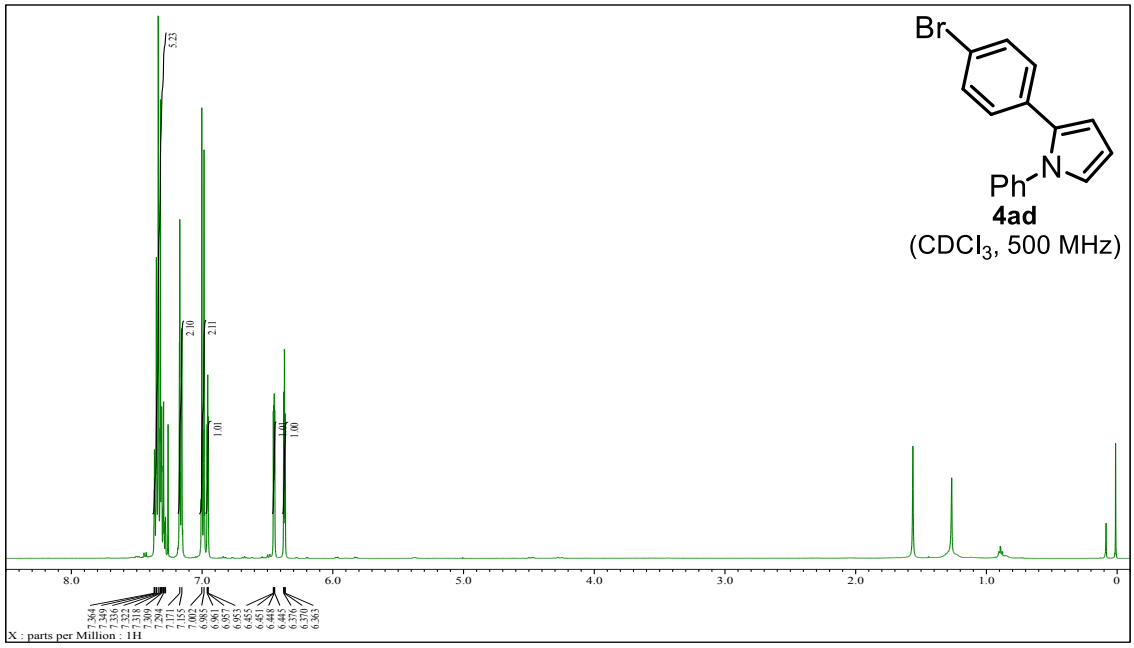
^{1}H NMR of 2-(4-methoxyphenyl)-1-phenyl pyrrole (**4ab**)



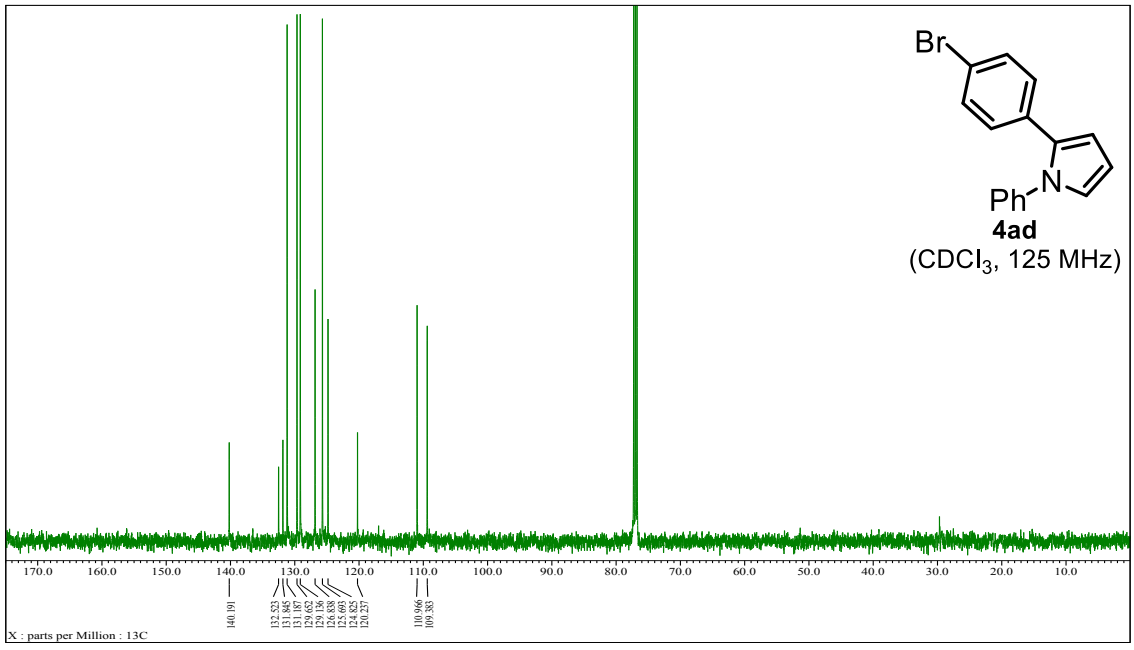
^{1}H NMR of 2-(4-nitrophenyl)-1-phenyl pyrrole (**4ac**)



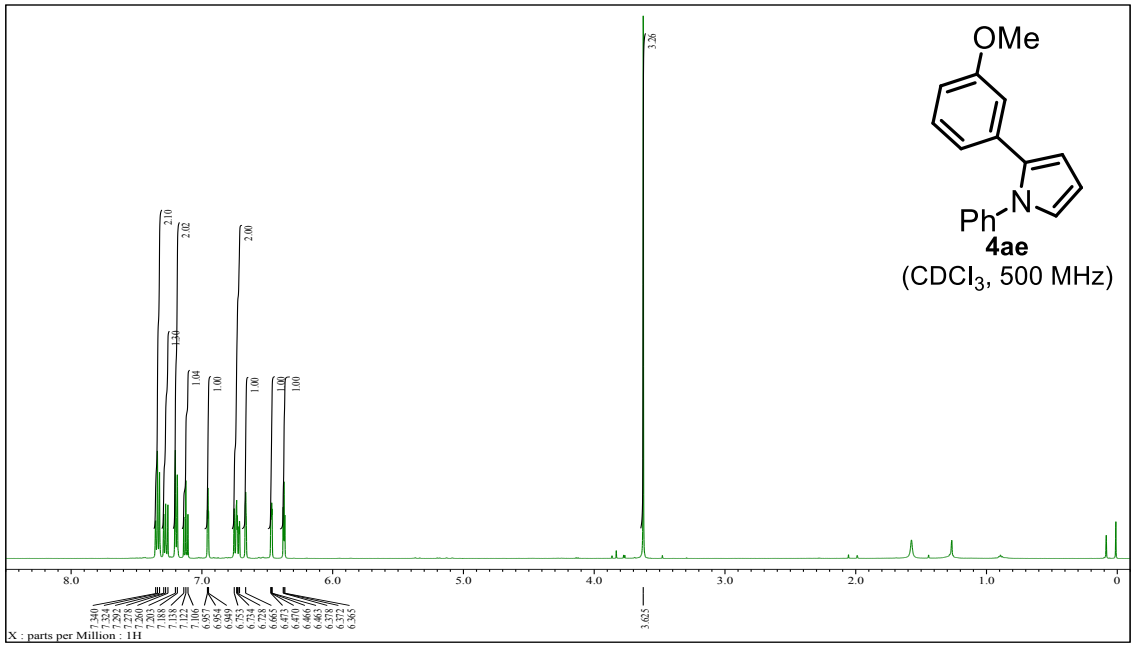
^{1}H NMR of 2-(4-bromophenyl)-1-phenyl pyrrole (**4ad**)



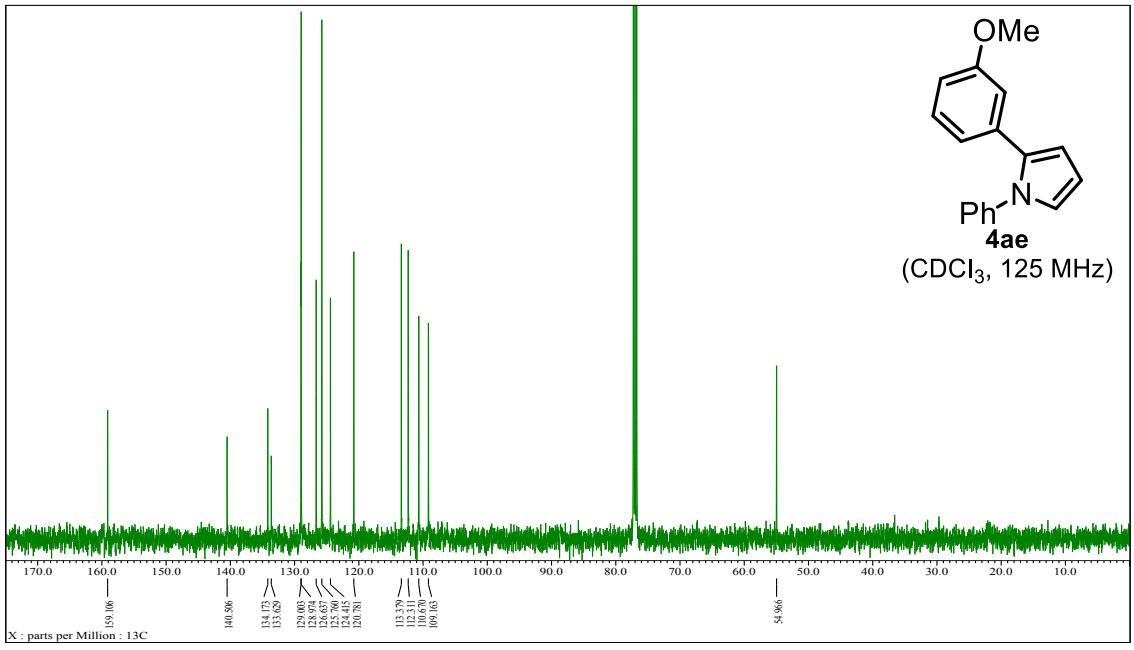
^{13}C NMR of 2-(4-bromophenyl)-1-phenyl pyrrole (**4ad**)



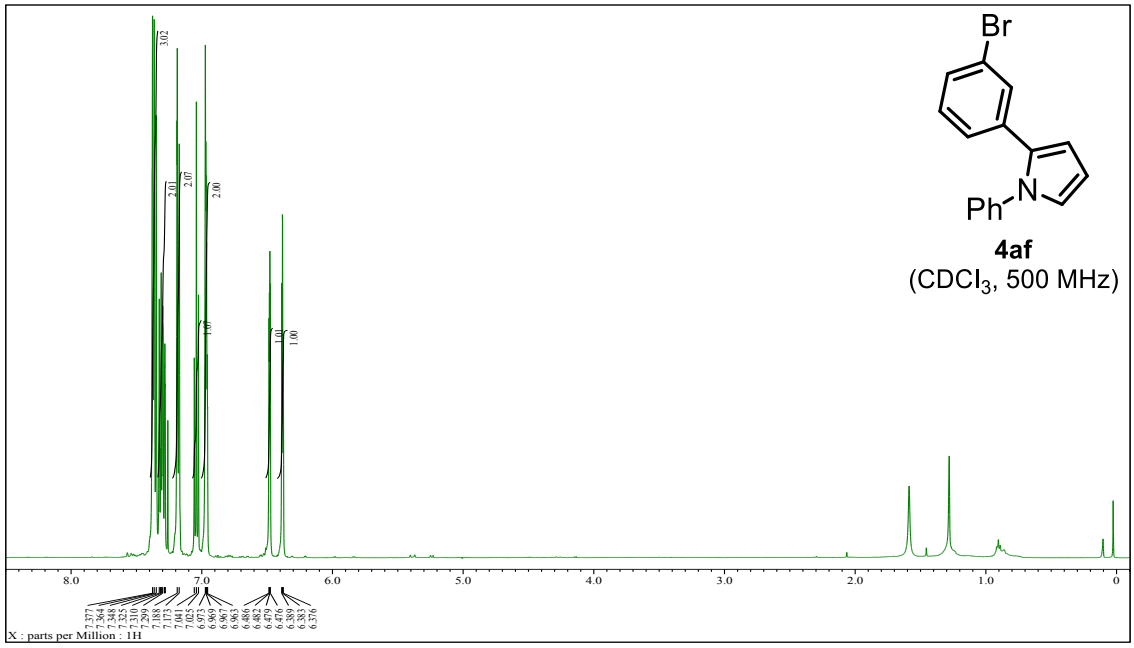
^{1}H NMR of 2-(3-methoxyphenyl)-1-phenyl pyrrole (**4ae**)



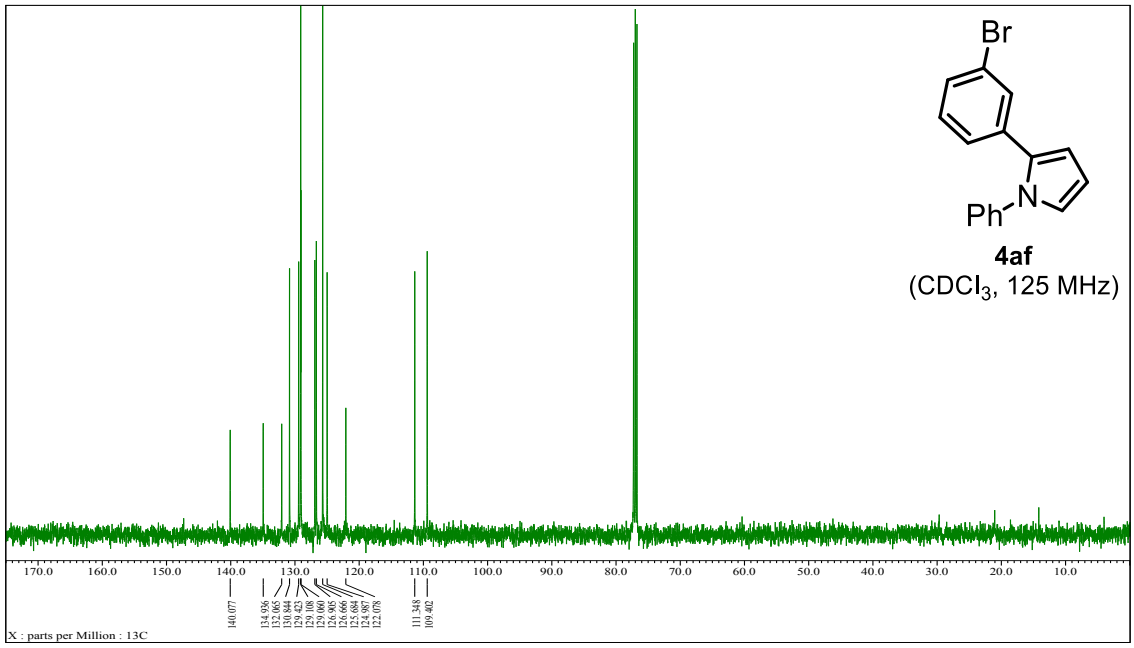
^{13}C NMR of 2-(3-methoxyphenyl)-1-phenyl pyrrole (**4ae**)



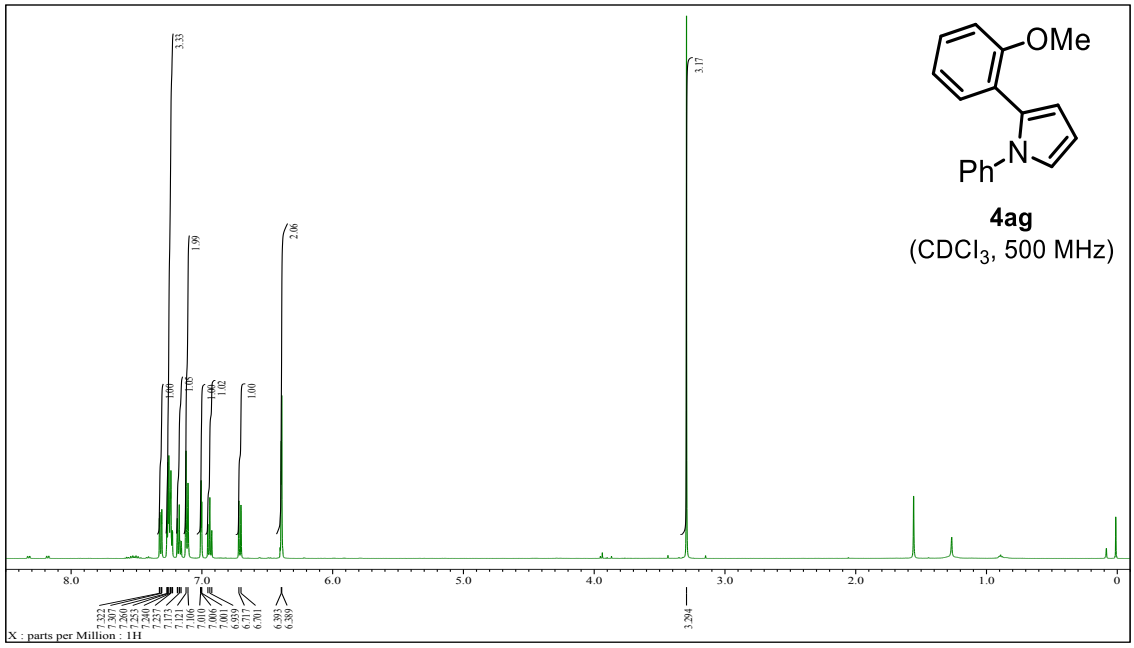
^{1}H NMR of 2-(3-bromophenyl)-1-phenyl pyrrole (**4af**)



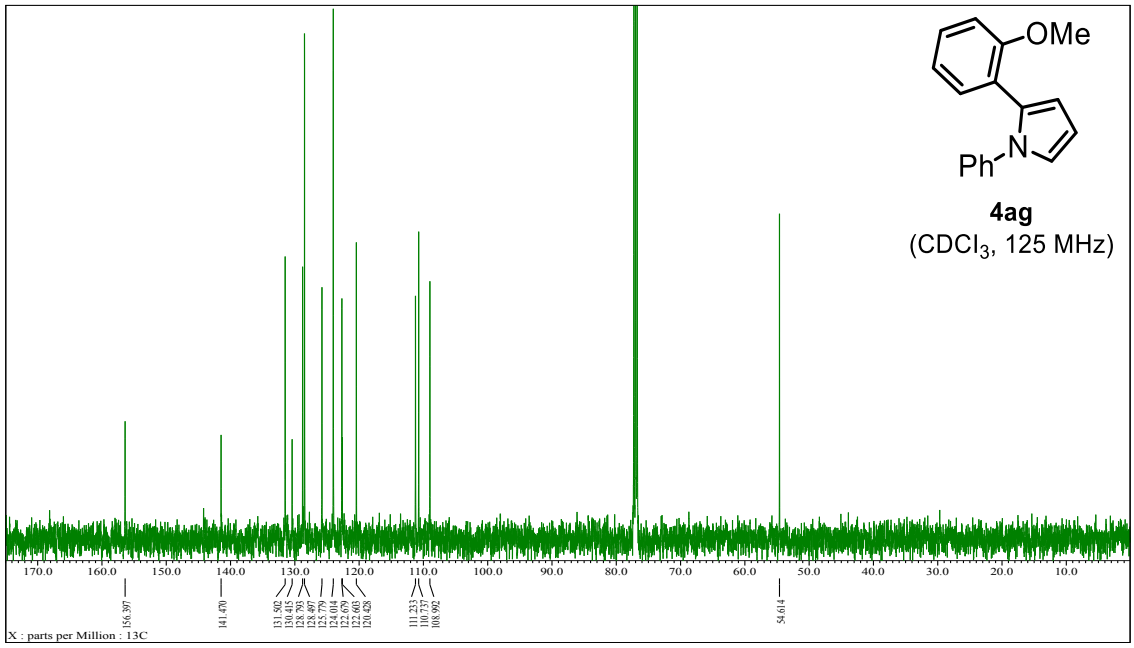
^{13}C NMR of 2-(3-bromophenyl)-1-phenyl pyrrole (**4af**)



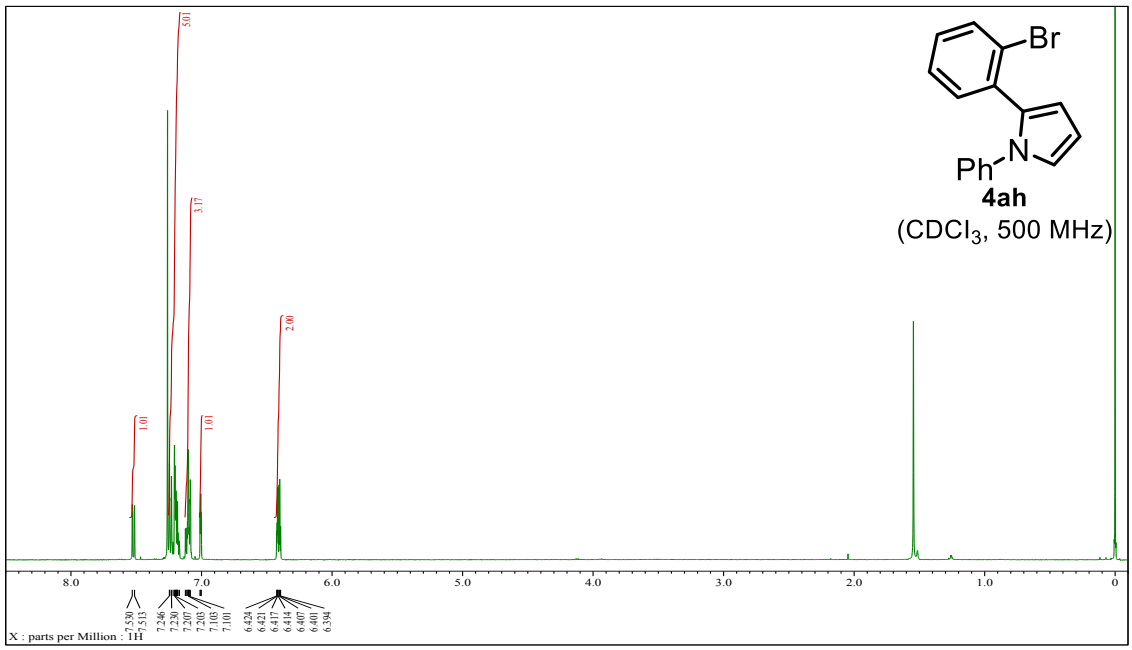
^{1}H NMR of 2-(2-methoxyphenyl)-1-phenyl pyrrole (**4ag**)



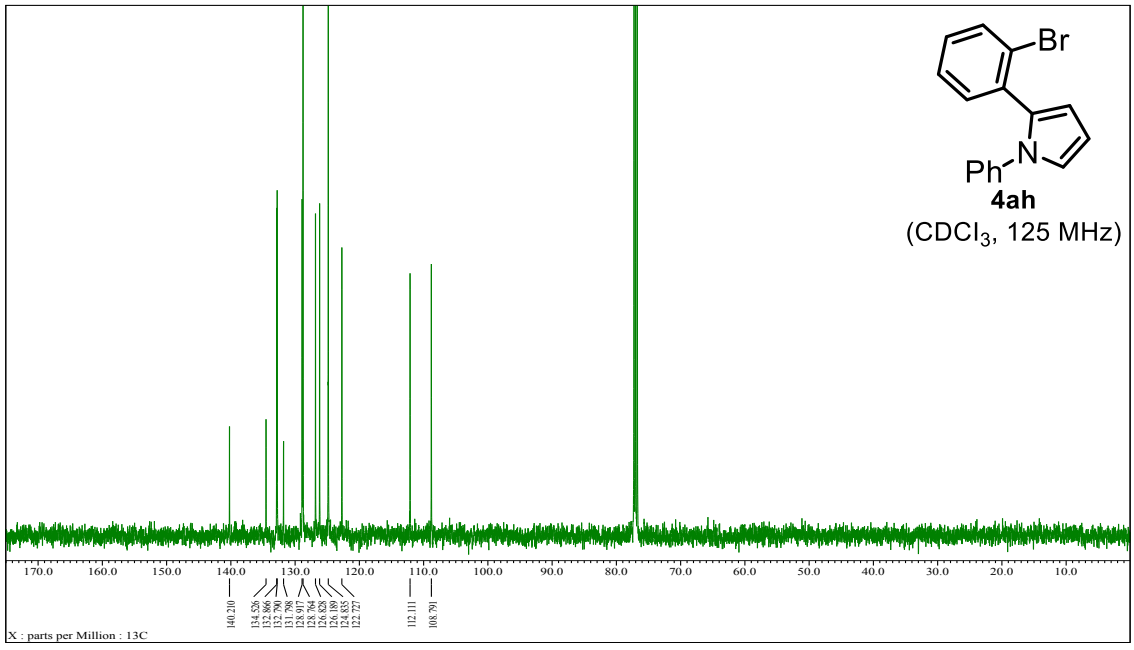
^{13}C NMR of 2-(2-methoxyphenyl)-1-phenyl pyrrole (**4ag**)



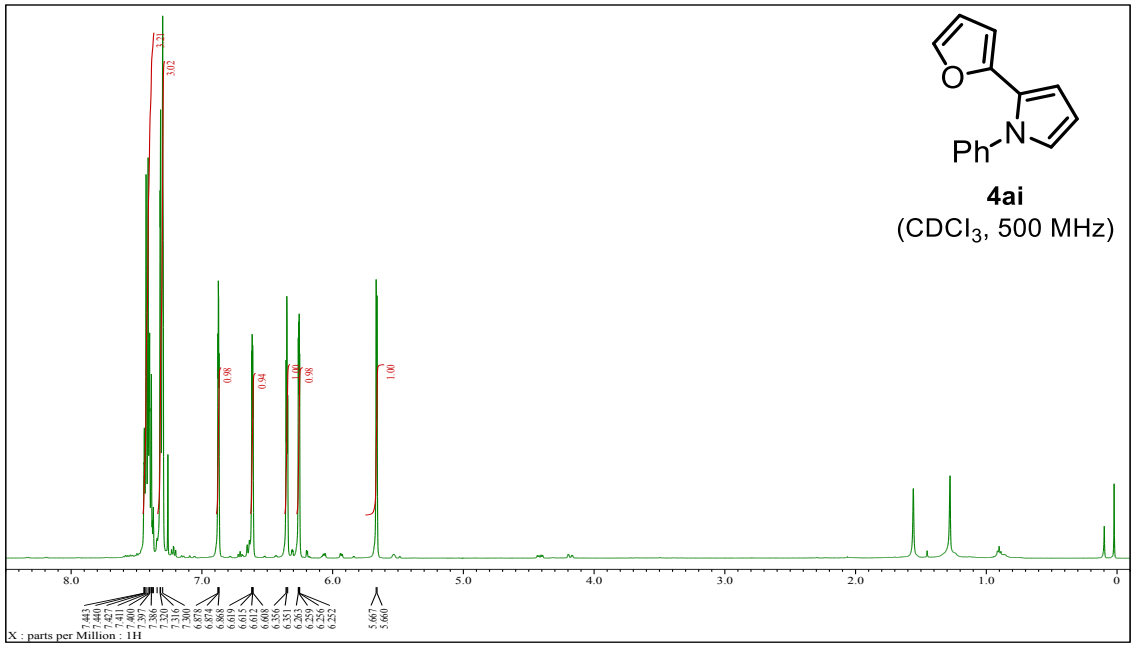
^{1}H NMR of 2-(2-bromophenyl)-1-phenyl pyrrole (**4ah**)



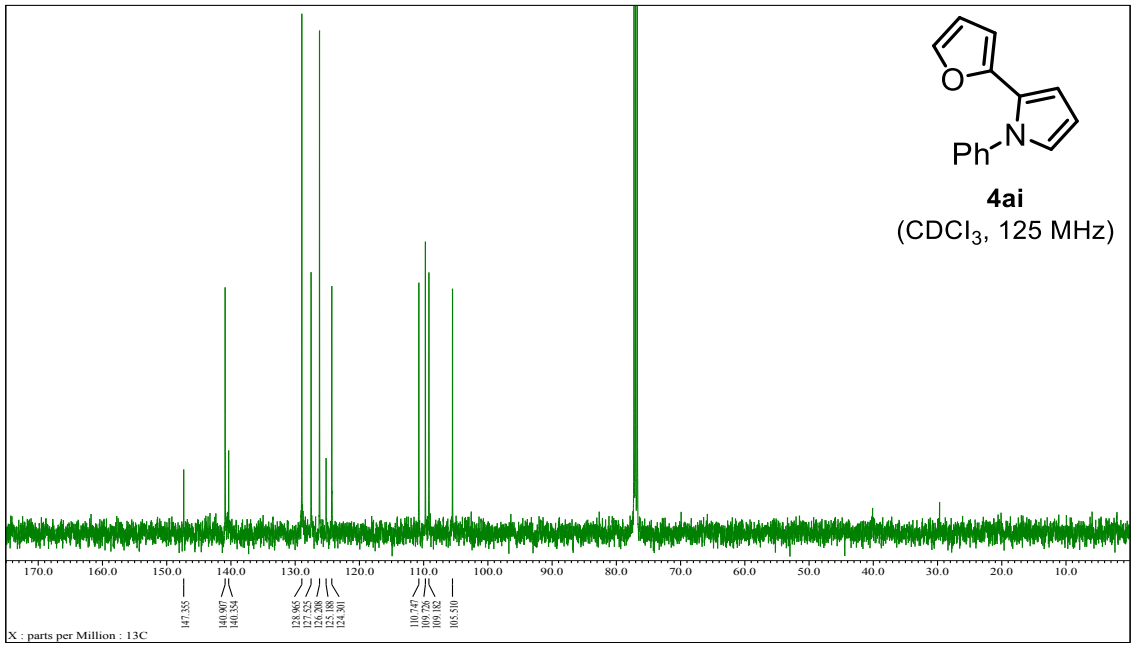
^{13}C NMR of 2-(2-bromophenyl)-1-phenyl pyrrole (**4ah**)



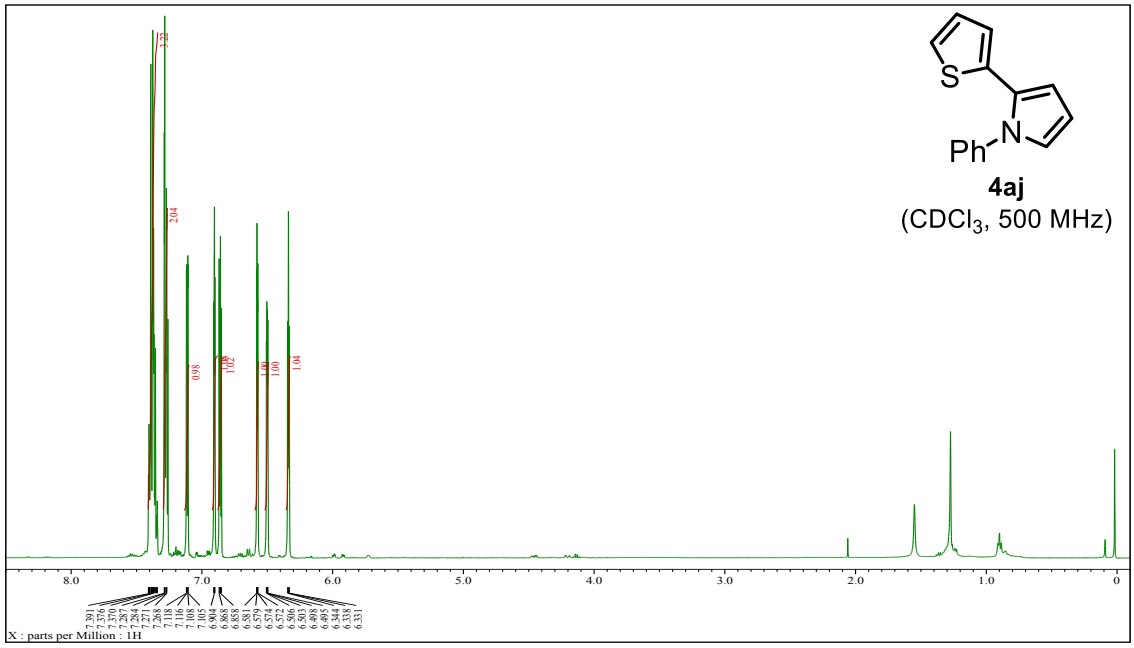
^{1}H NMR of 2-furyl-1-phenylpyrrole (**4ai**)



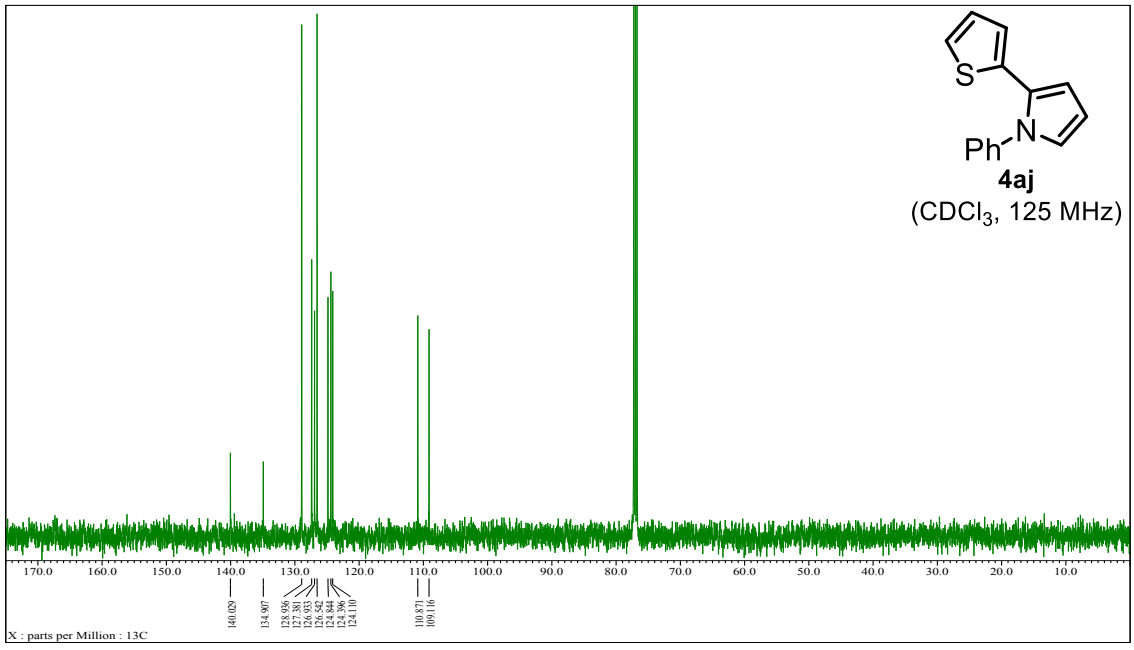
^{13}C NMR of 2-furyl-1-phenylpyrrole (**4ai**)



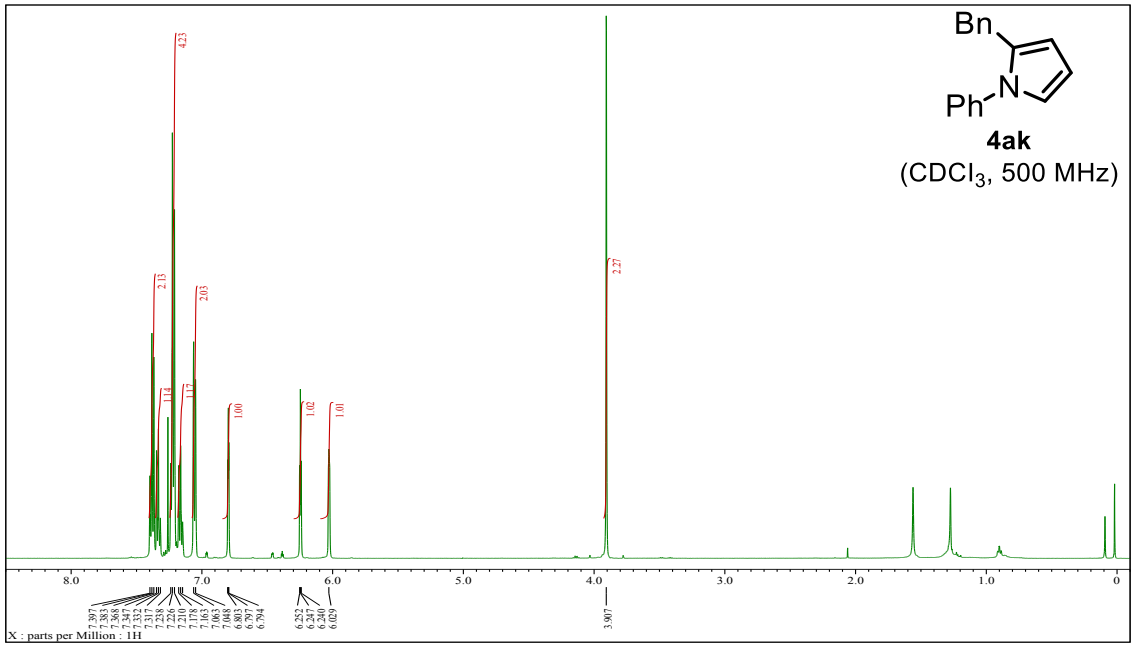
^{1}H NMR of 1-phenyl-2-thienyl-pyrrole (**4aj**)



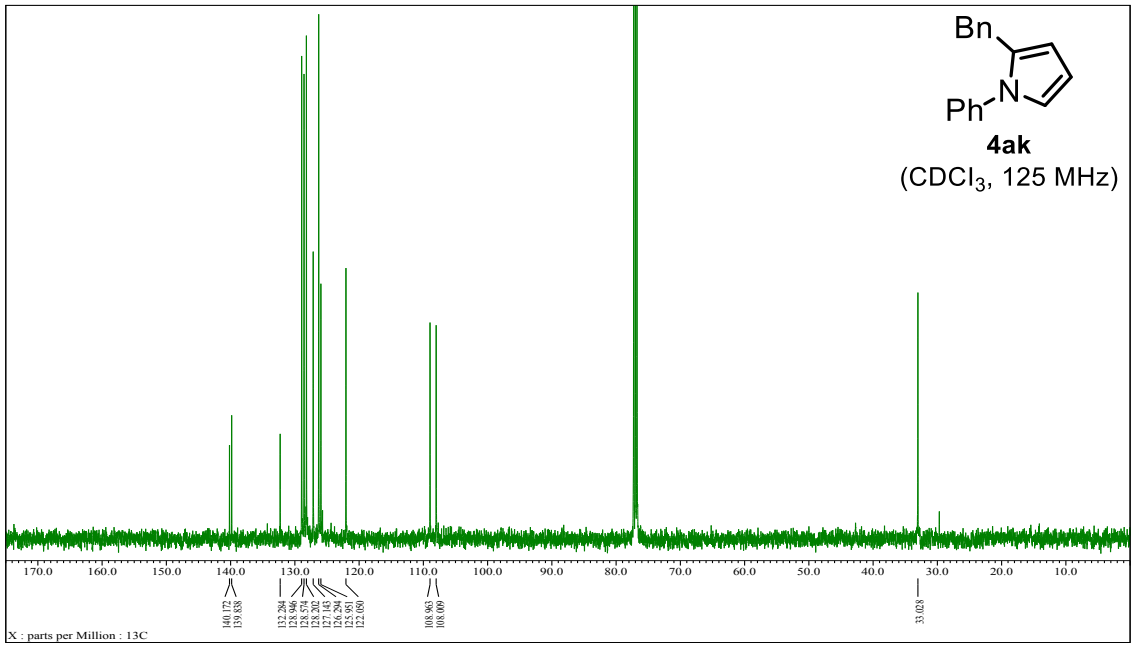
^{13}C NMR of 1-phenyl-2-thienyl-pyrrole (**4aj**)



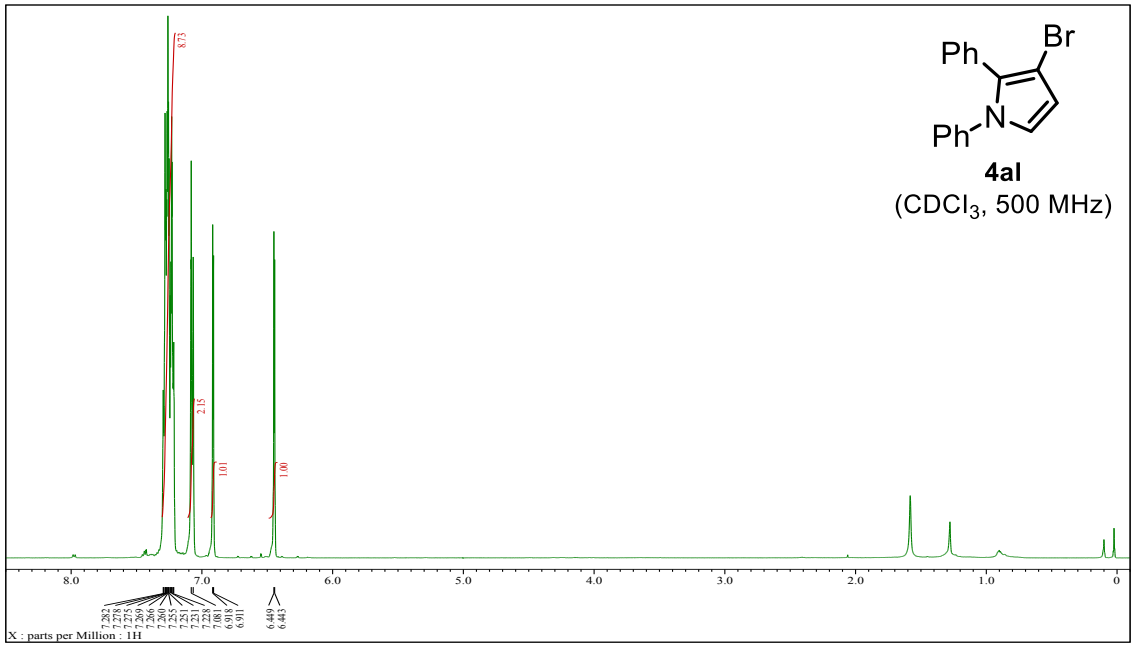
^{1}H NMR of 2-benzyl-1-phenylpyrrole (**4ak**)



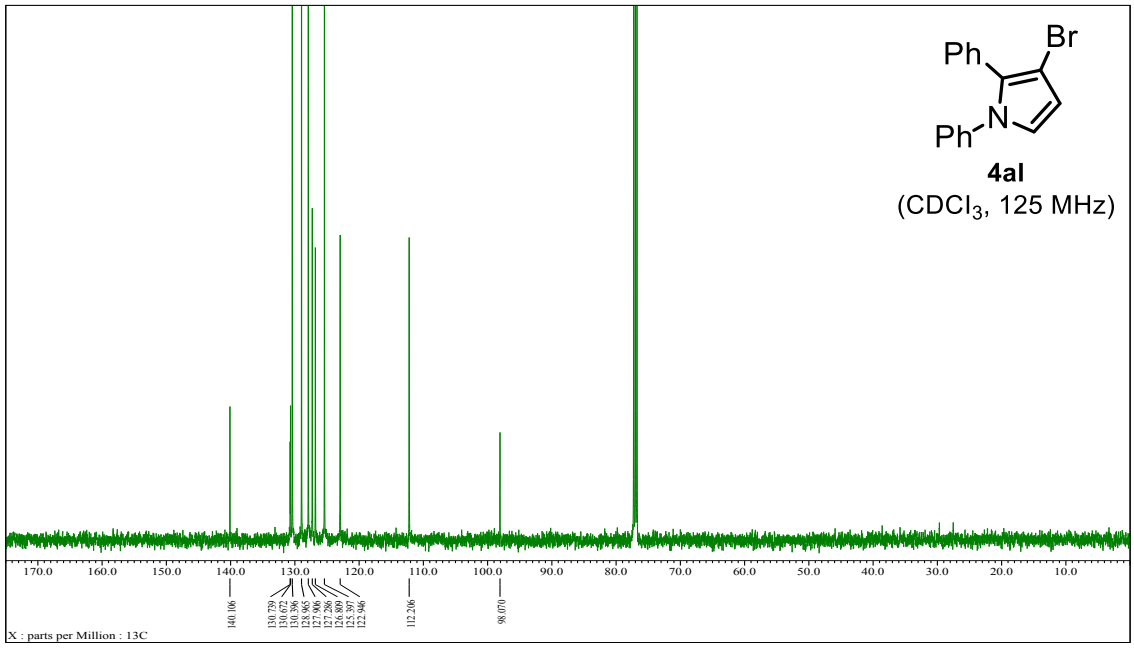
^{13}C NMR of 2-benzyl-1-phenylpyrrole (**4ak**)



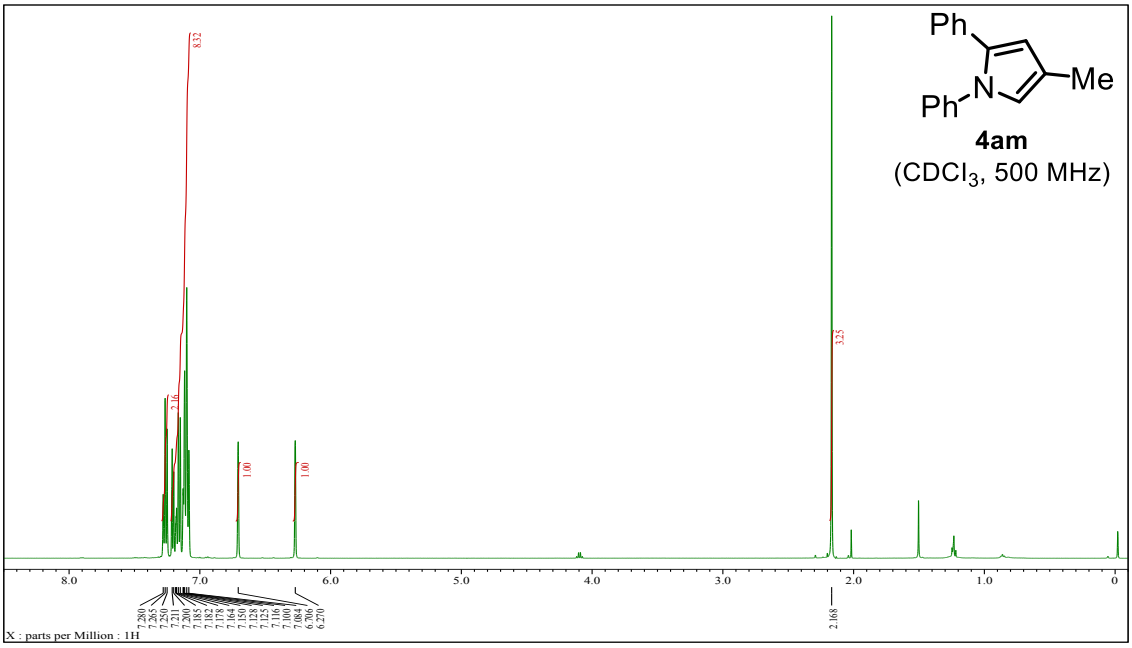
^{1}H NMR of 3-bromo-1,2-diphenylpyrrole (**4al**)



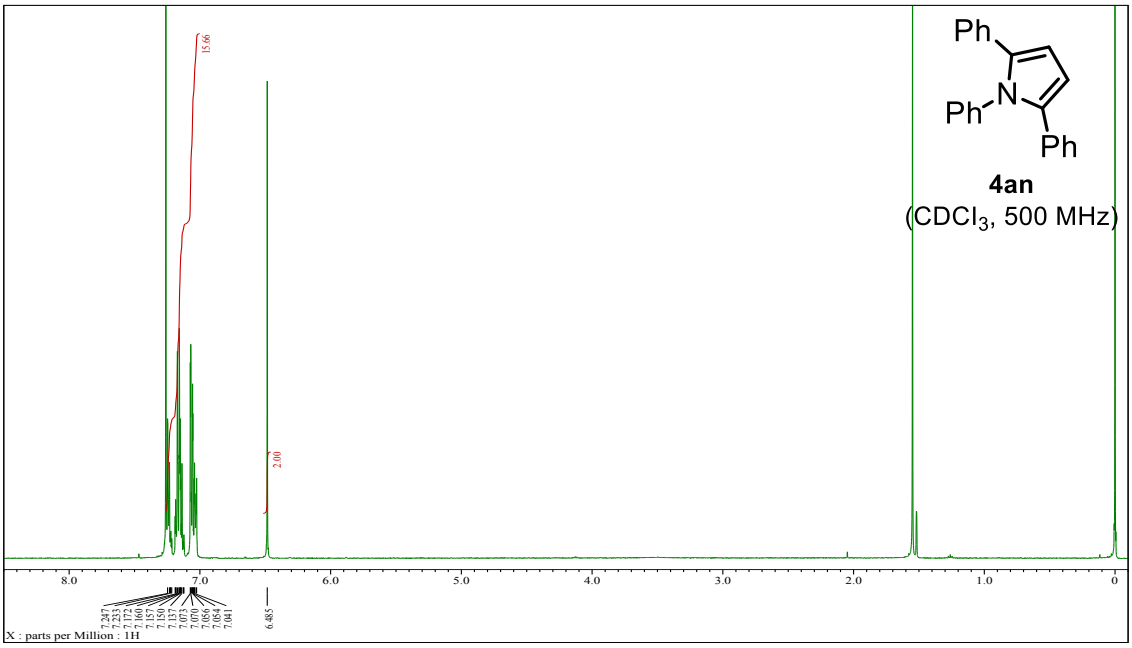
^{13}C NMR of 3-bromo-1,2-diphenylpyrrole (**4al**)



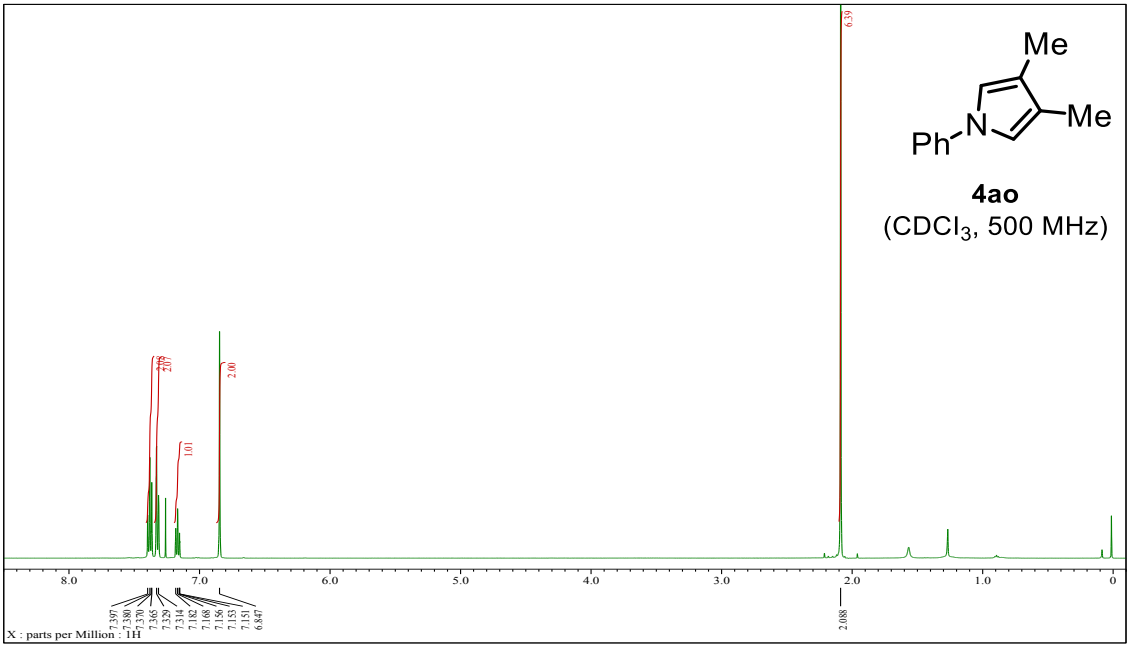
^{1}H NMR of 4-methyl-1,2-diphenylpyrrole (**4am**)



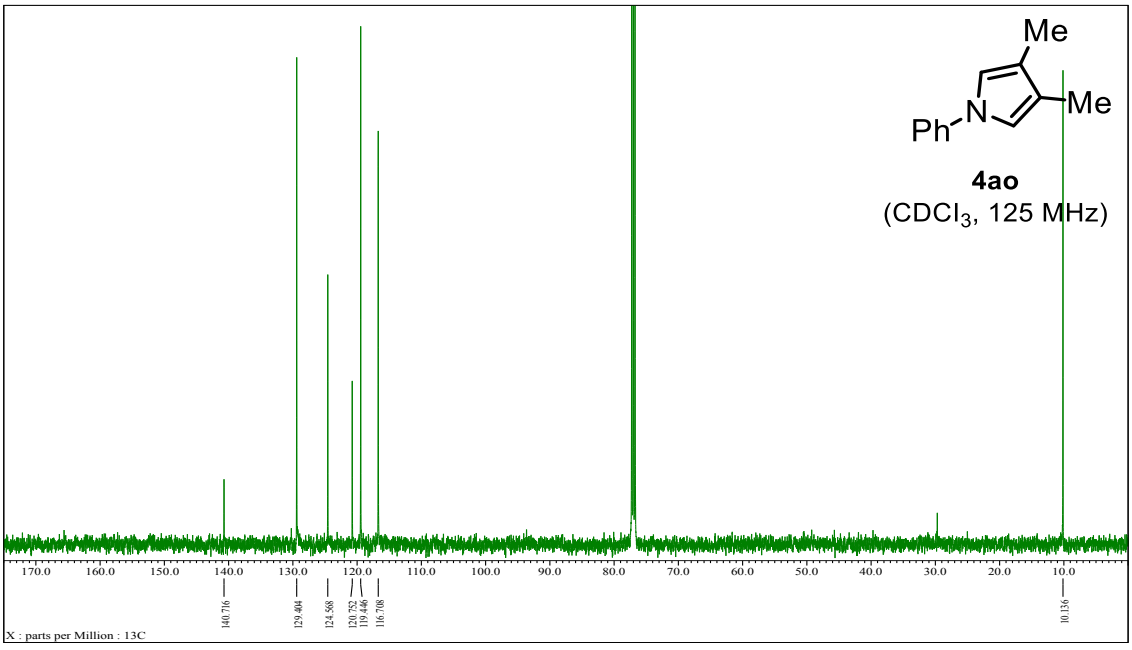
^{1}H NMR of 1,2,5-triphenylpyrrole (**4an**)



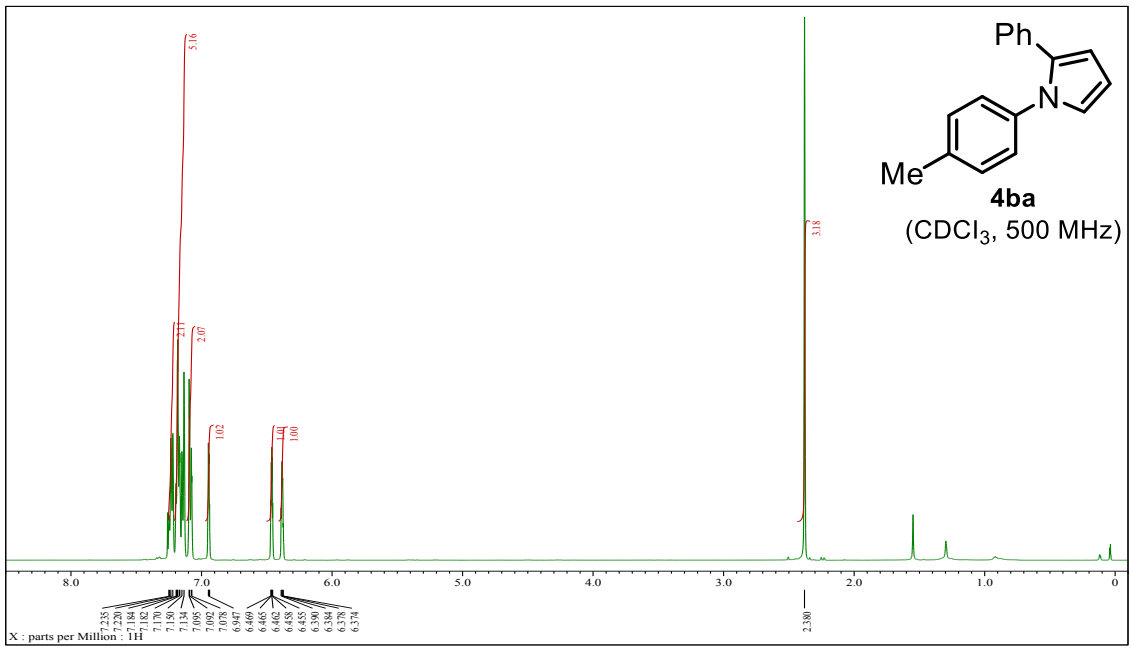
^{1}H NMR of 3,4-dimethyl-1-phenylpyrrole (**4ao**)



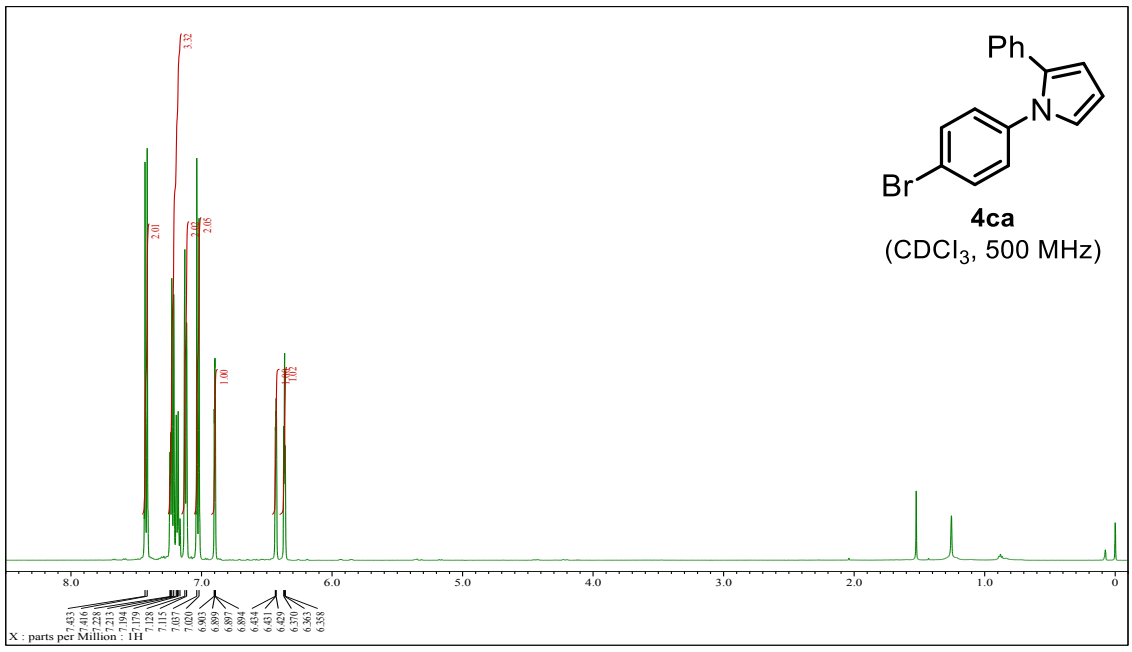
^{13}C NMR of 3,4-dimethyl-1-phenylpyrrole (**4ao**)



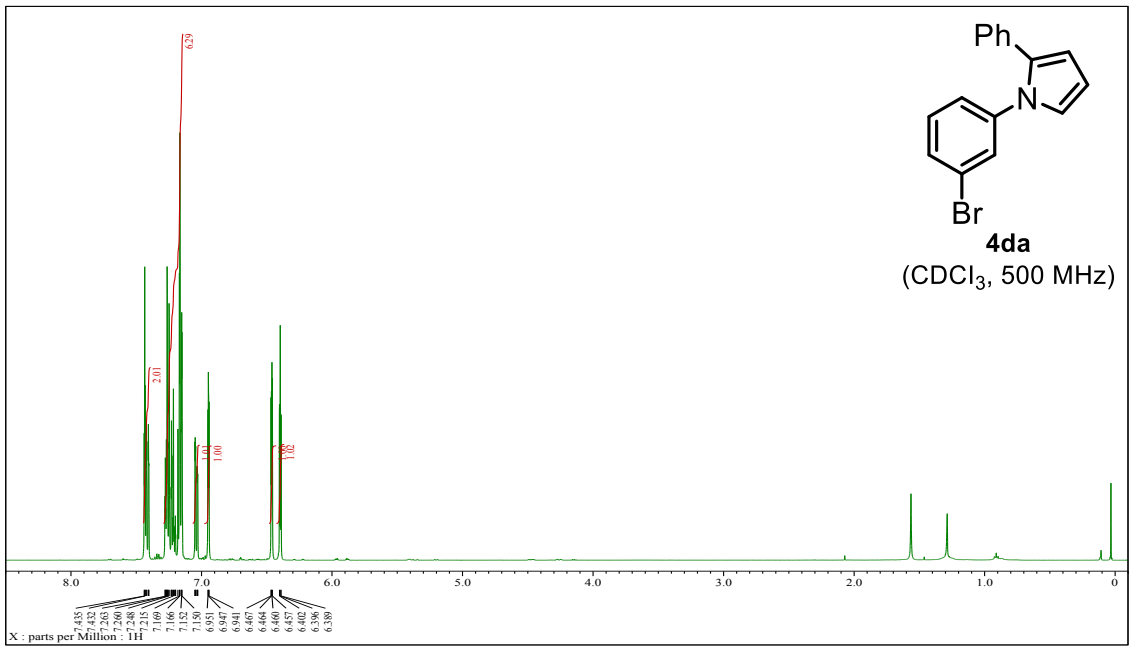
^{1}H NMR of 1-(4-methylphenyl)-2-phenylpyrrole (**4ba**)



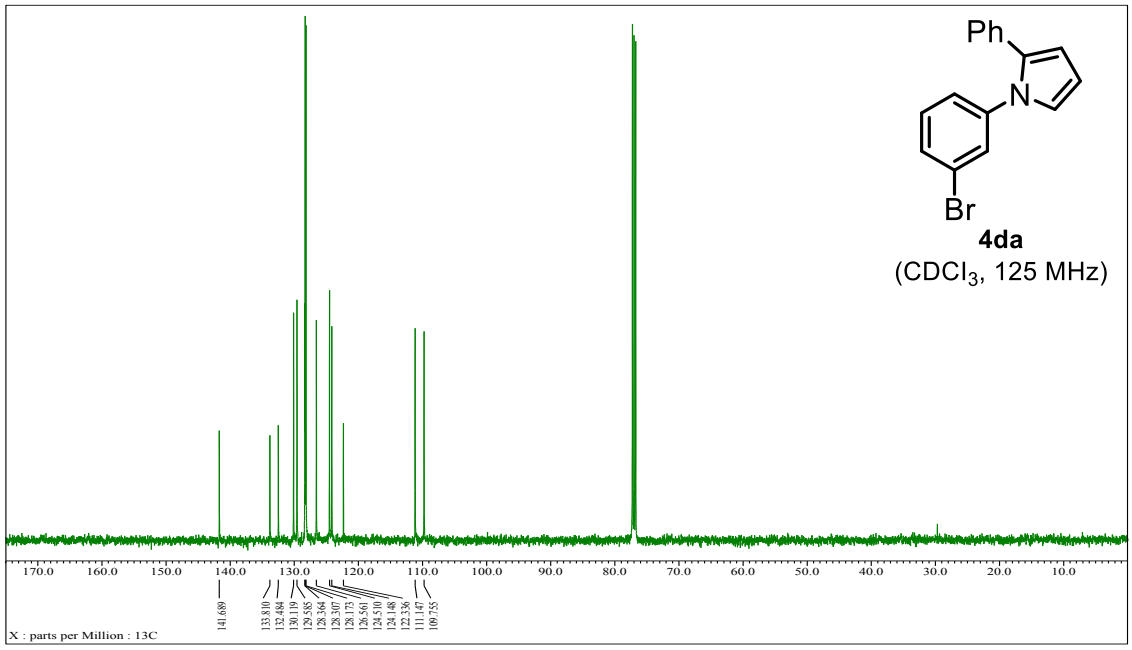
^{1}H NMR of 1-(4-bromophenyl)-2-phenylpyrrole (**4ca**)



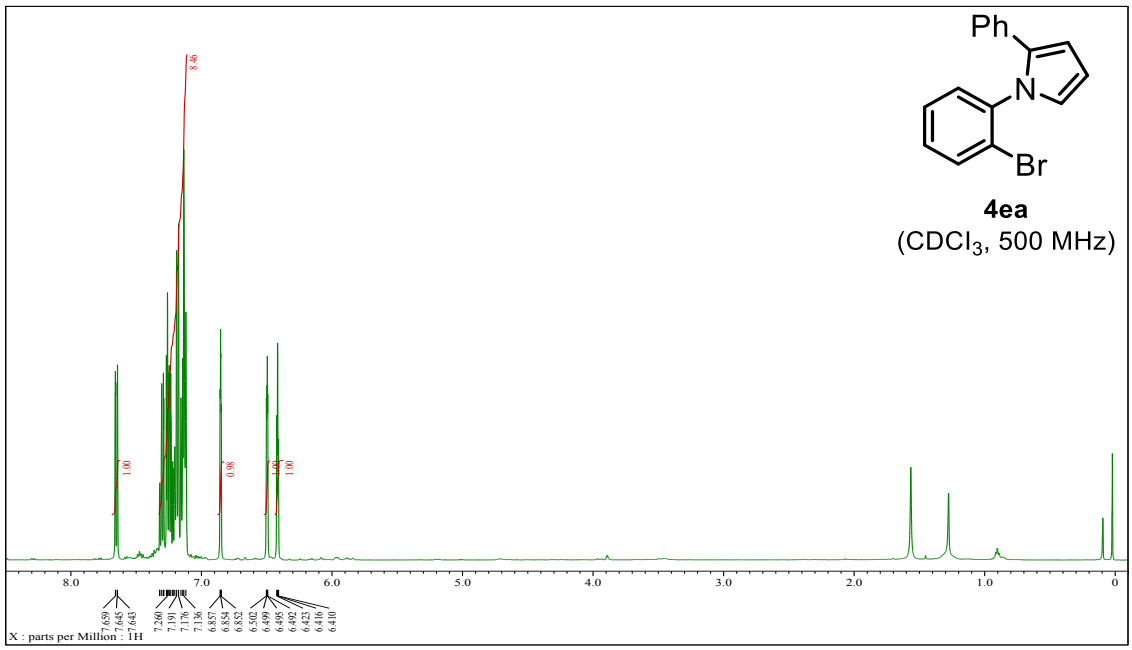
^{1}H NMR of 1-(3-bromophenyl)-2-phenylpyrrole (**4da**)



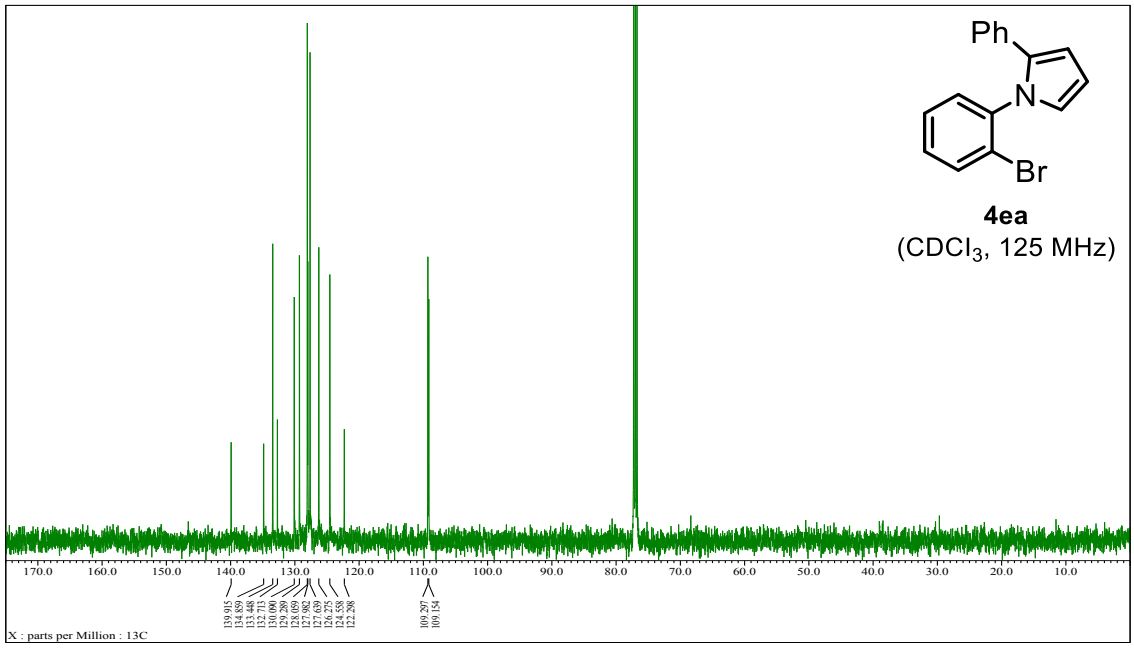
^{13}C NMR of 1-(3-bromophenyl)-2-phenylpyrrole (**4da**)



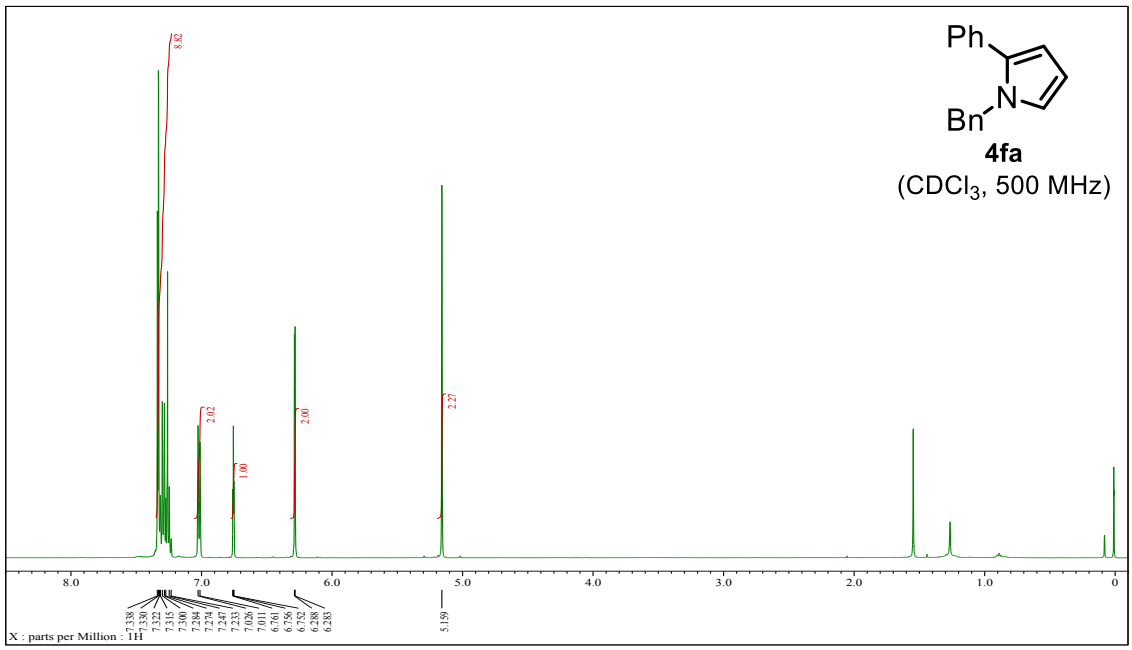
^{1}H NMR of 1-(2-bromophenyl)-2-phenylpyrrole (**4ea**)



^{13}C NMR of 1-(2-bromophenyl)-2-phenylpyrrole (**4ea**)



^{1}H NMR of 1-benzyl-2-phenyl-1H-pyrrole (**4fa**)



^{13}C NMR of 1-benzyl-2-phenyl-1*H*-pyrrole (**4fa**)