Supporting Information

Rh(II)-Catalyzed Formation of Pyrrolo[2,3-b]quinolines from Azide-MCPs and Isonitriles

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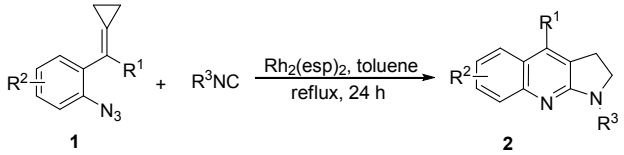
CONTENTS

General remarks

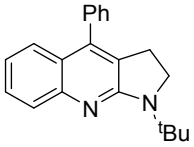
Dichloromethane was freshly distilled from calcium hydride; THF, Et_2O and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrophotometers. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm-1. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by EI, and HRMS were measured on a HP-5989 instrument.

General procedure for the synthesis of compounds 2

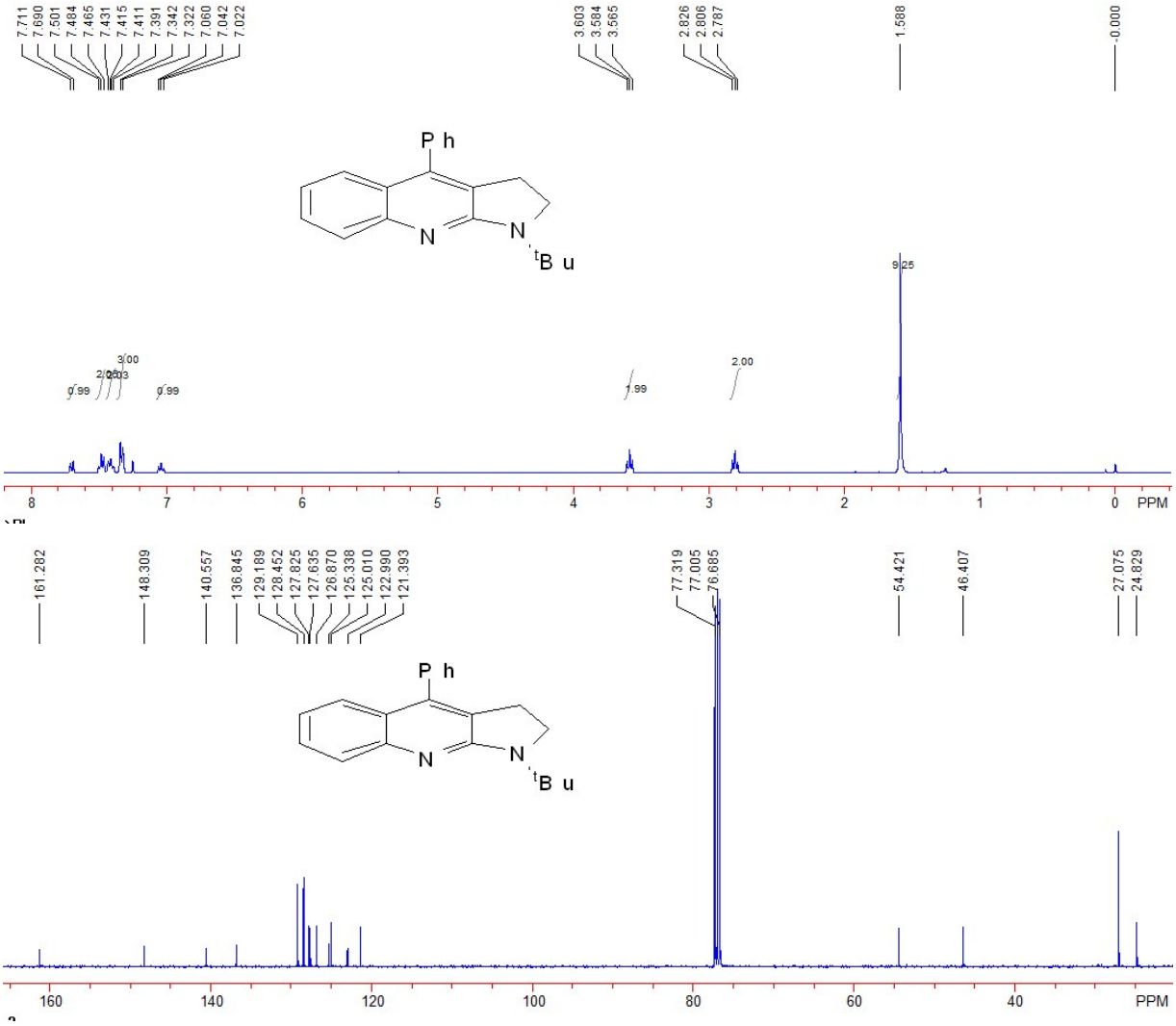


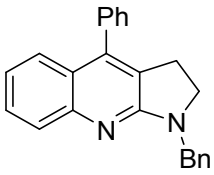
A solution of compound **1** (0.2 mmol), isonitrile (1.0 mmol) and $Rh_2(esp)_2$ (4.5 mg, 0.006 mmol) in dry toluene (2 mL) was stirred at 110 ^oC for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product **2** in moderate to high yield.

Spectroscopic data for all products 2

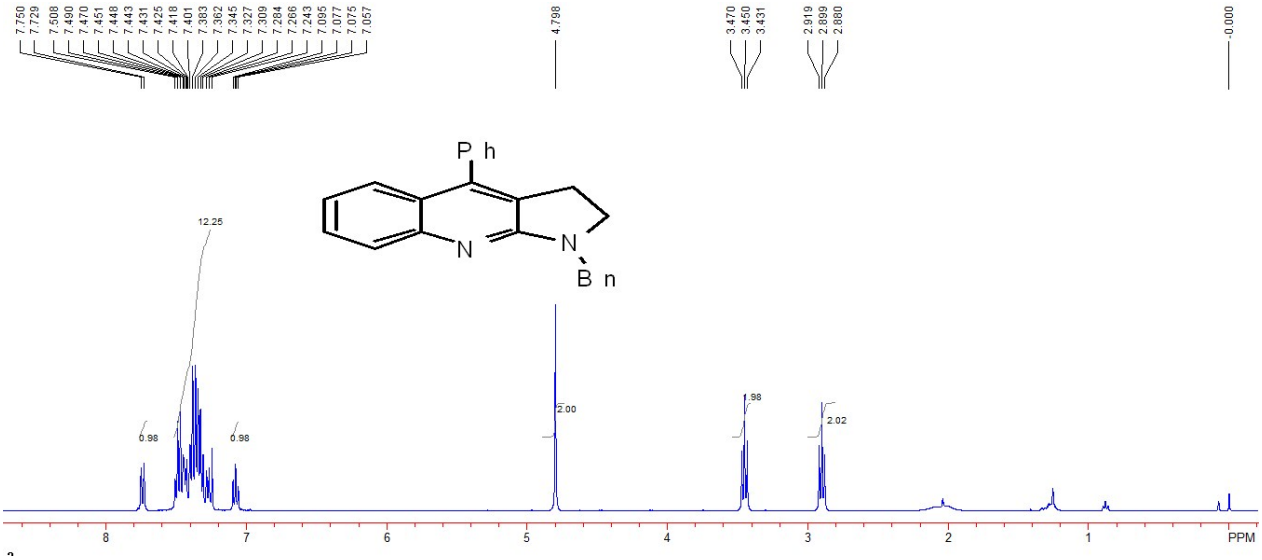


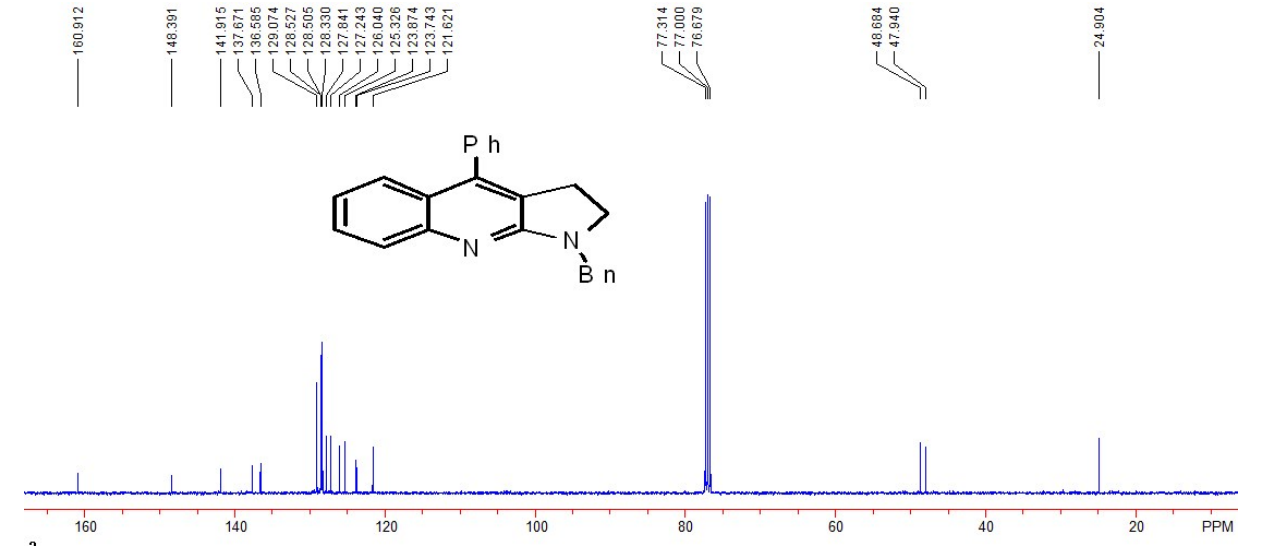
Compound 2a: 48 mg, 80%, A yellow solid, m.p. 144-146 ^{o}C; IR (CH_2Cl_2): ν 3060, 2971, 1628, 1429, 1312, 762, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.59 (s, 9H), 2.81 (t, J = 7.6 Hz, 2H), 3.58 (t, J = 7.6 Hz, 2H), 7.04 (dd, J_1 = J_2 = 7.6 Hz, 1H), 7.33 (d, J = 8.0 Hz, 3H), 7.39-7.43 (m, 2H), 7.47-7.50 (m, 2H), 7.70 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.8, 27.1, 46.4, 54.4, 121.4, 123.0, 125.0, 125.3, 126.9, 127.6, 127.8, 128.5, 129.2, 136.8, 140.6, 148.3, 161.3; MS (ESI) *m/z*: 303.2 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{21}H_{23}N_2^{+}$ requires: 303.1856, found: 303.1856.

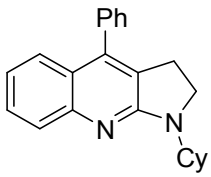




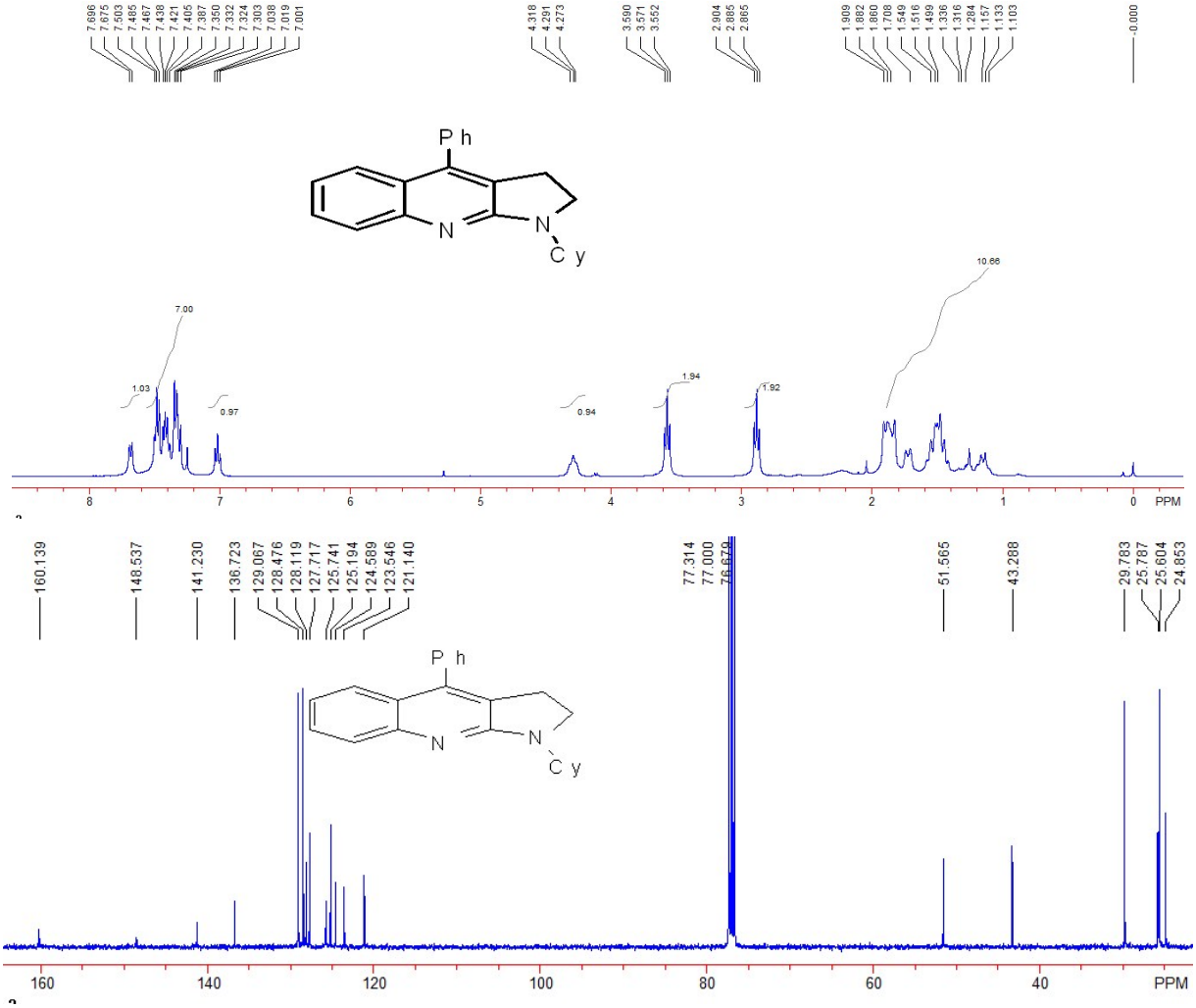
Compound 2b: 48 mg, 71%, A yellow solid, m.p. 147-149 ^{o}C; IR (CH_2Cl_2): ν 3061, 2924, 1629, 1576, 1443, 1311, 763, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 2.90 (t, *J* = 7.6 Hz, 2H), 3.45 (t, *J* = 7.6 Hz, 2H), 4.80 (s, 2H), 7.06-7.10 (m, 1H), 7.27-7.51 (m, 12H), 7.74 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.9, 47.9, 48.7, 121.6, 123.7, 123.9, 125.3, 126.0, 127.2, 127.8, 128.3, 128.51, 128.53, 129.1, 136.6, 137.7, 141.9, 148.4, 160.9; MS (ESI) *m/z*: 337.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{24}H_{21}N_2^+$ requires: 337.1699, found: 337.1699.

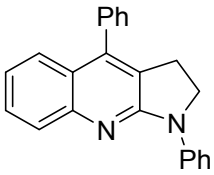




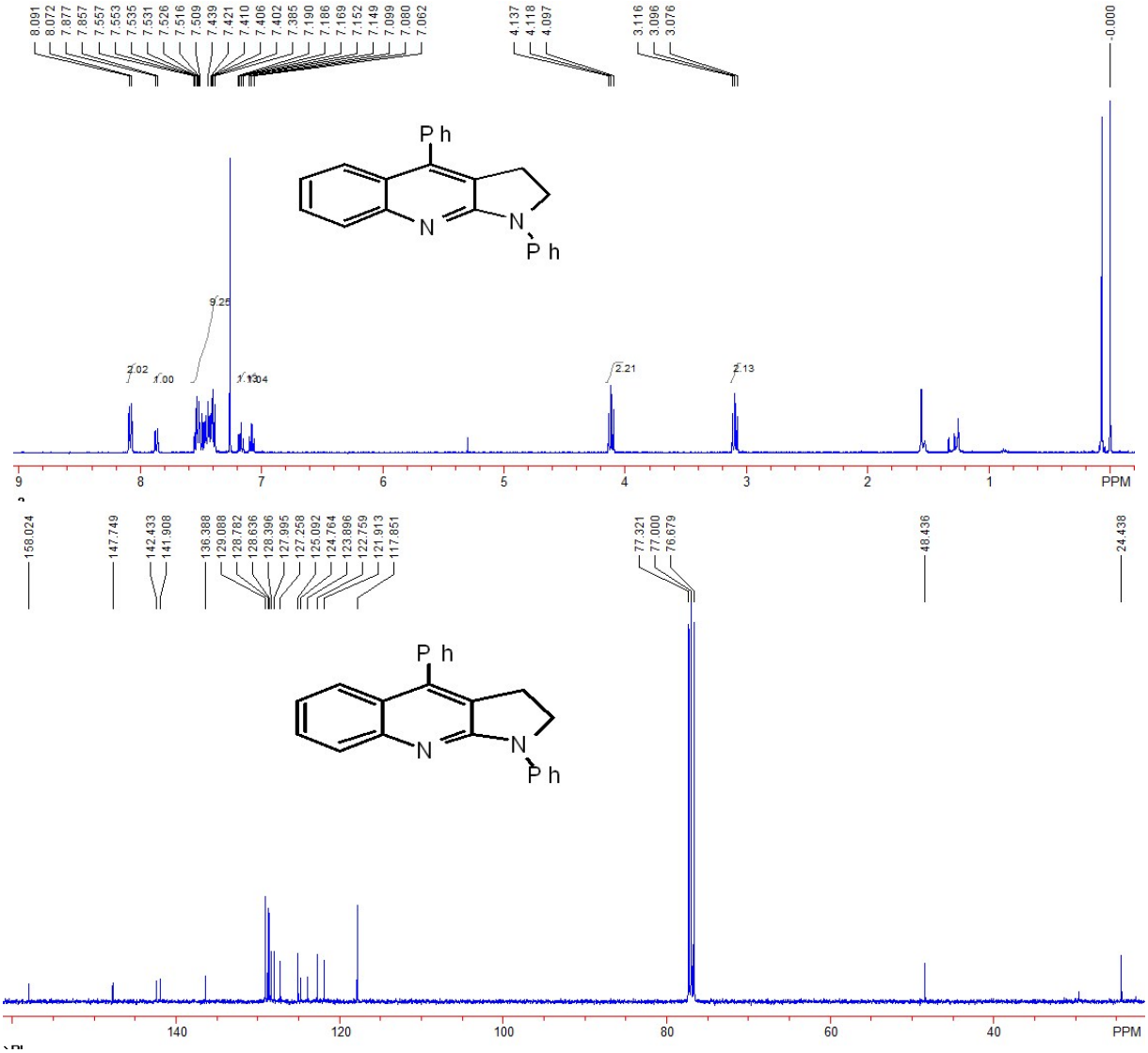


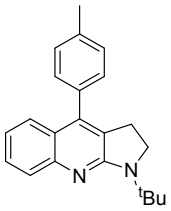
Compound 2c: 48 mg, 73%, A yellow solid, m.p. 192-194 ^{o}C; IR (CH_2Cl_2): ν 2925, 2852, 1726, 1630, 1440, 1311, 761, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.13-1.91 (m, 10H), 2.89 (t, J = 7.6 Hz, 2H), 3.57 (t, J = 7.6 Hz, 2H), 4.27-4.32 (m, 1H), 7.02 (dd, $J_1 = J_2$ = 7.2 Hz, 1H), 7.30-7.50 (m, 7H), 7.69 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.9, 25.6, 25.8, 29.8, 43.3, 51.6, 121.1, 123.5, 124.6, 125.2, 125.7, 127.7, 128.1, 128.5, 129.1, 136.7, 141.2, 148.5, 160.1; MS (ESI) *m/z*: 329.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{25}N_2^+$ requires: 329.2012, found: 329.2016.



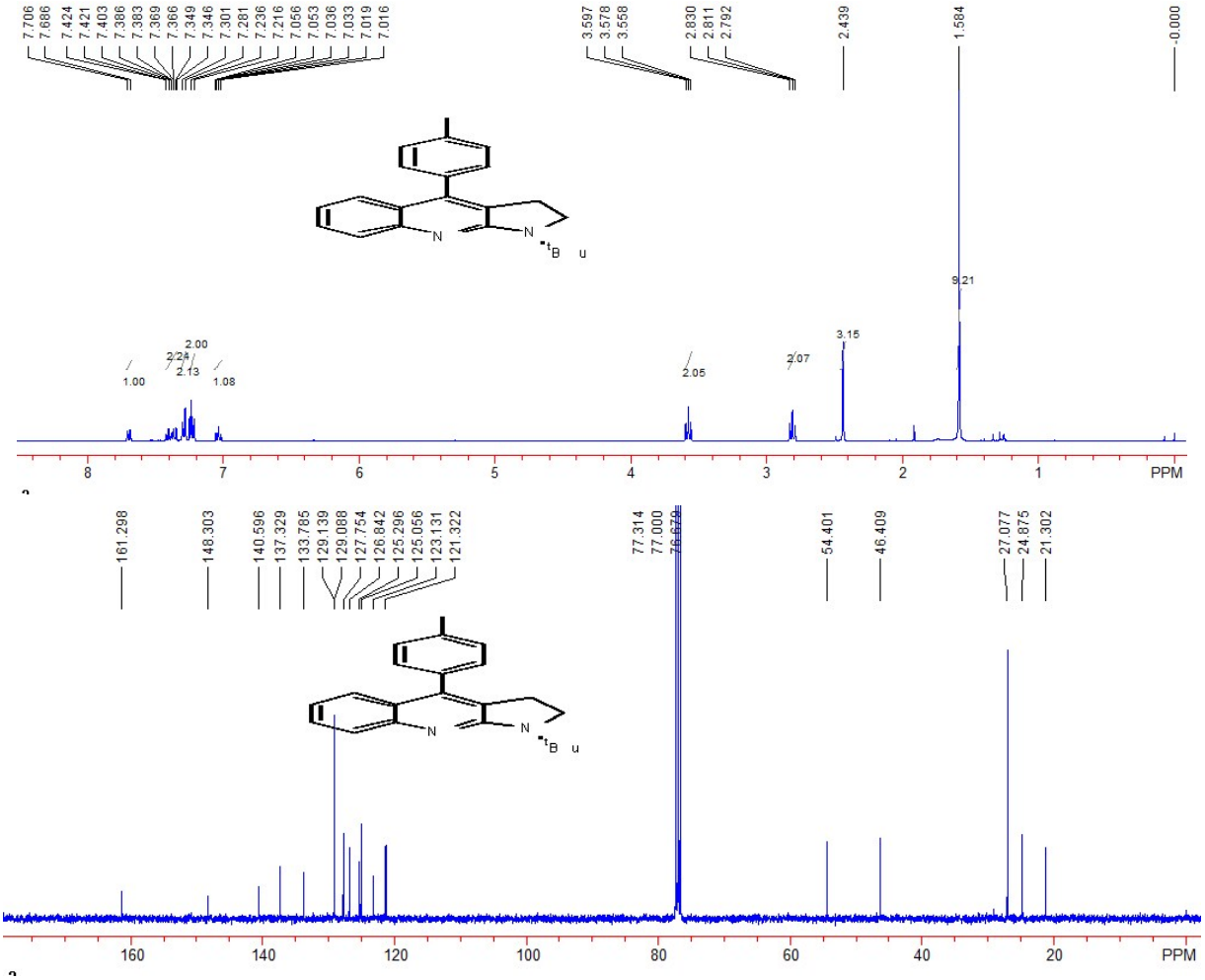


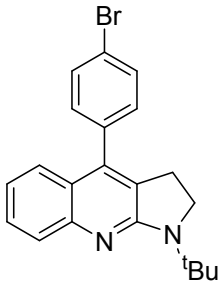
Compound 2d: 36 mg, 56%, A yellow solid, m.p. 186-188 ^{o}C; IR (CH_2Cl_2): ν 3062, 2923, 1596, 1499, 1318, 753, 702 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.10 (t, J = 8.0 Hz, 2H), 4.12 (t, J = 8.0 Hz, 2H), 7.08 (dd, $J_1 = J_2$ = 7.2 Hz, 1H), 7.15-7.19 (m, 1H), 7.39-7.55 (m, 9H), 7.87 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.4, 48.4, 117.9, 121.9, 122.8, 123.9, 124.8, 125.1, 127.3, 128.0, 128.4, 128.6, 128.8, 129.1, 136.4, 141.9, 142.4, 147.7, 158.0; MS (ESI) *m/z*: 323.2 (M+H$^+$, 100); HRMS (ESI) Calcd. for $C_{23}H_{19}N_2^+$ requires: 323.1543, found: 323.1544.



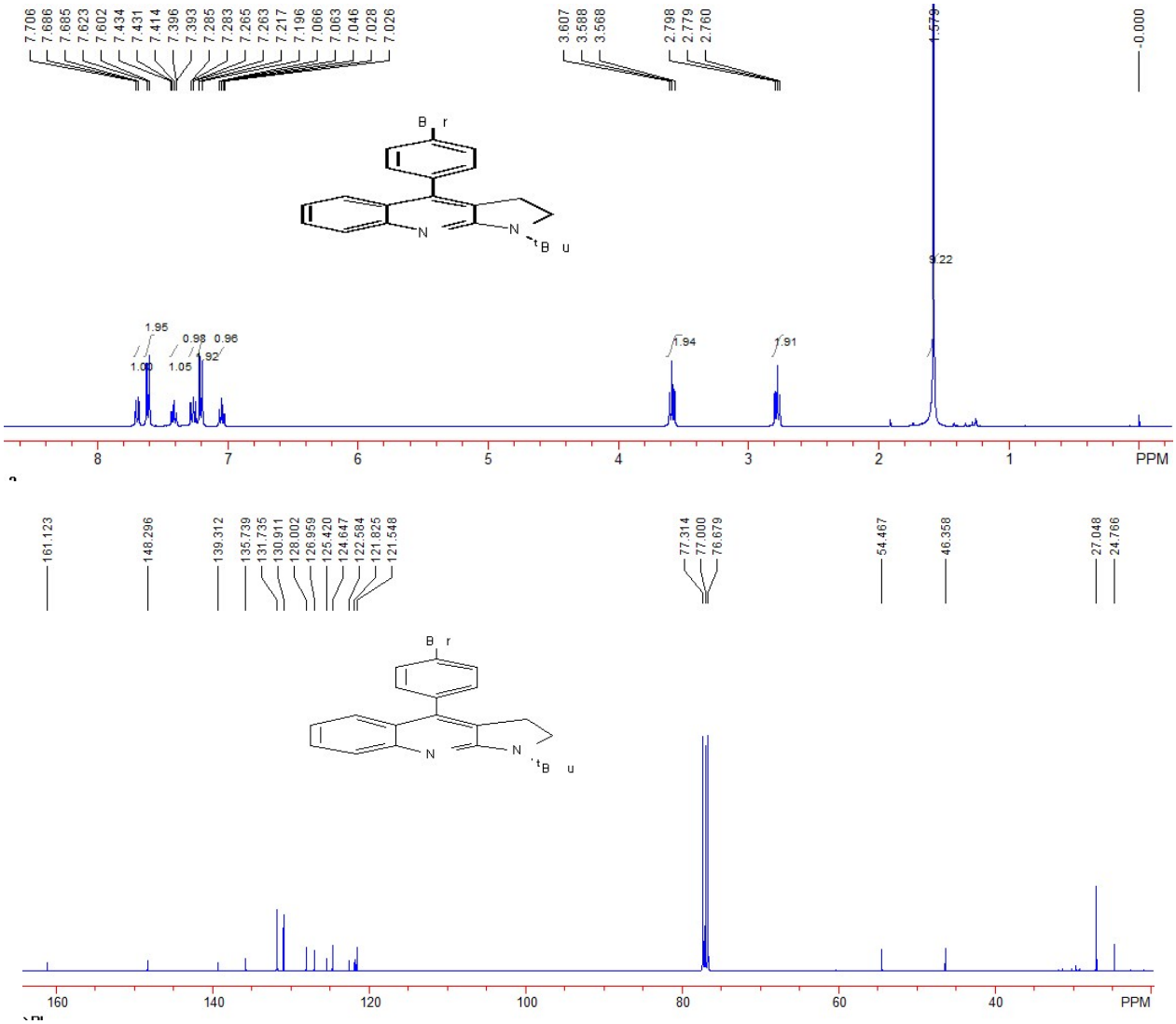


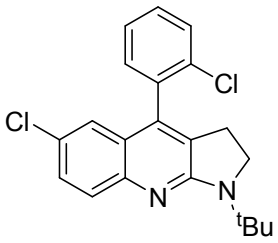
Compound 2e: 39 mg, 62%, A yellow solid, m.p. 143-145 ^{o}C; IR (CH_2Cl_2): ν 2968, 2922, 2852, 1627, 1429, 1315, 816, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.58 (s, 9H), 2.44 (s, 3H), 2.81 (t, *J* = 7.6 Hz, 2H), 3.58 (t, *J* = 7.6 Hz, 2H), 7.02-7.06 (m, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.35-7.42 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 21.3, 24.9, 27.1, 46.4, 54.4, 121.3, 123.1, 125.1, 125.3, 126.8, 127.8, 129.09, 129.14, 133.8, 137.3, 140.6, 148.3, 161.3; MS (ESI) m/z: 317.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{25}N_2^+$ requires: 317.2012, found: 317.2013.



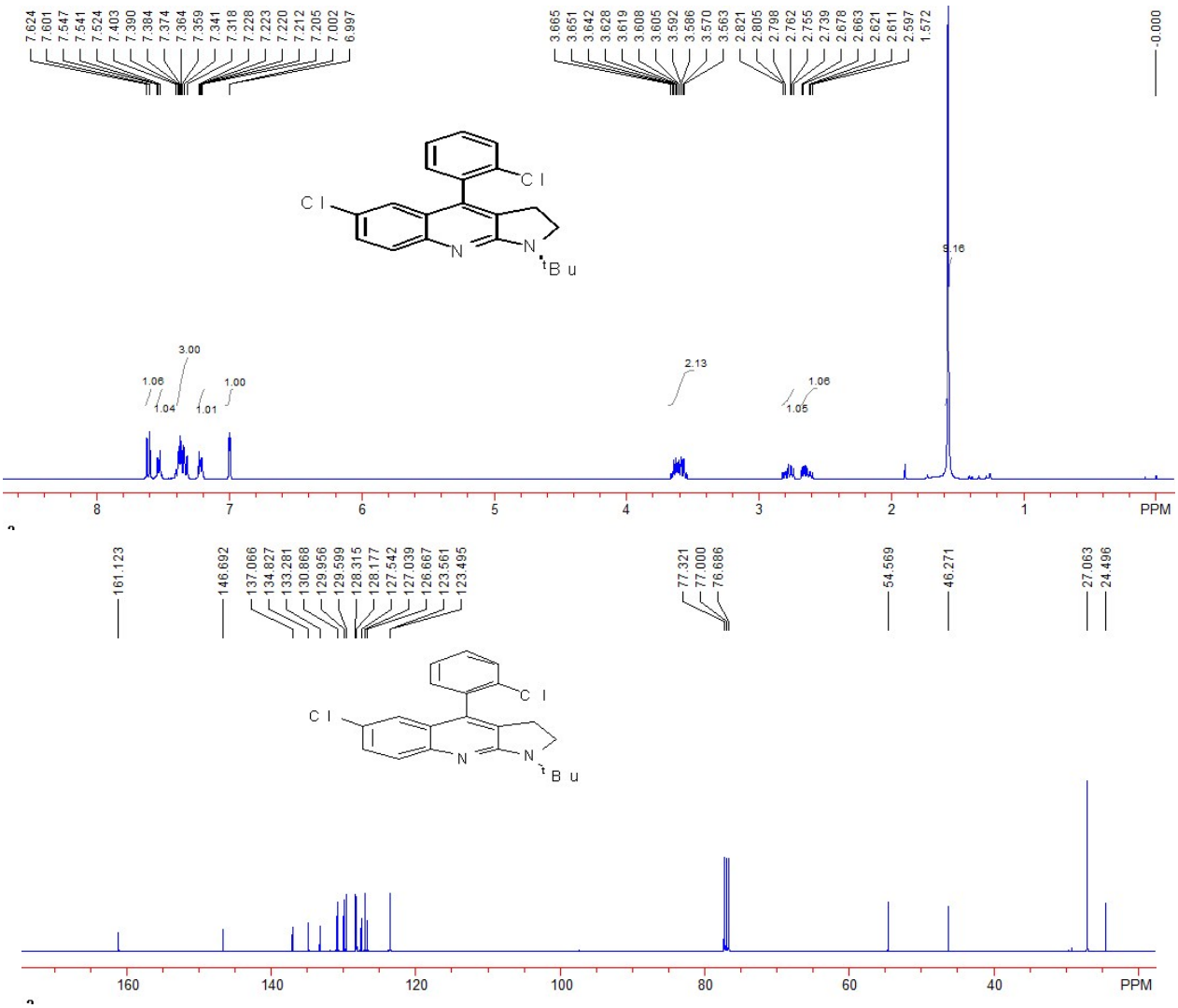


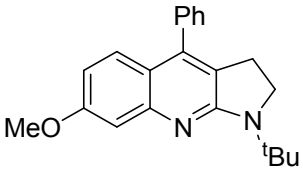
Compound 2f: 61 mg, 80%, A yellow solid, m.p. 196-198 °C; IR (CH_2Cl_2): ν 3062, 2971, 1630, 1571, 1429, 1313, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.58 (s, 9H), 2.78 (t, *J* = 7.6 Hz, 2H), 3.59 (t, *J* = 7.6 Hz, 2H), 7.03-7.07 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.39-7.43 (m, 1H), 7.61 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.8, 27.0, 46.4, 54.5, 121.5, 121.8, 122.6, 124.6, 125.4, 127.0, 128.0, 130.9, 131.7, 135.7, 139.3, 148.3, 161.1; MS (ESI) *m/z*: 381.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{22}BrN_2^+$ requires: 381.0961, found: 381.0961.



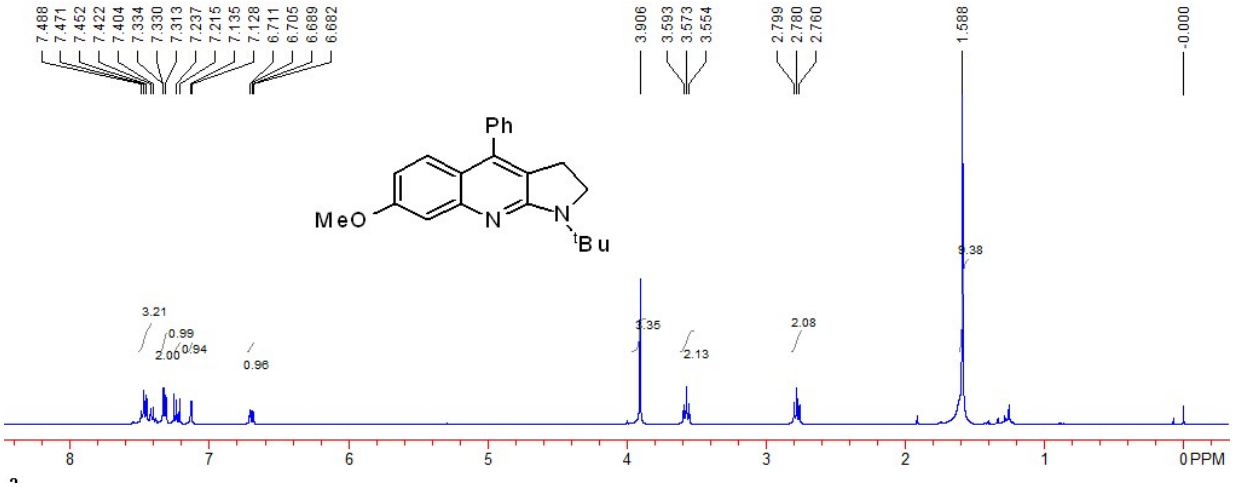


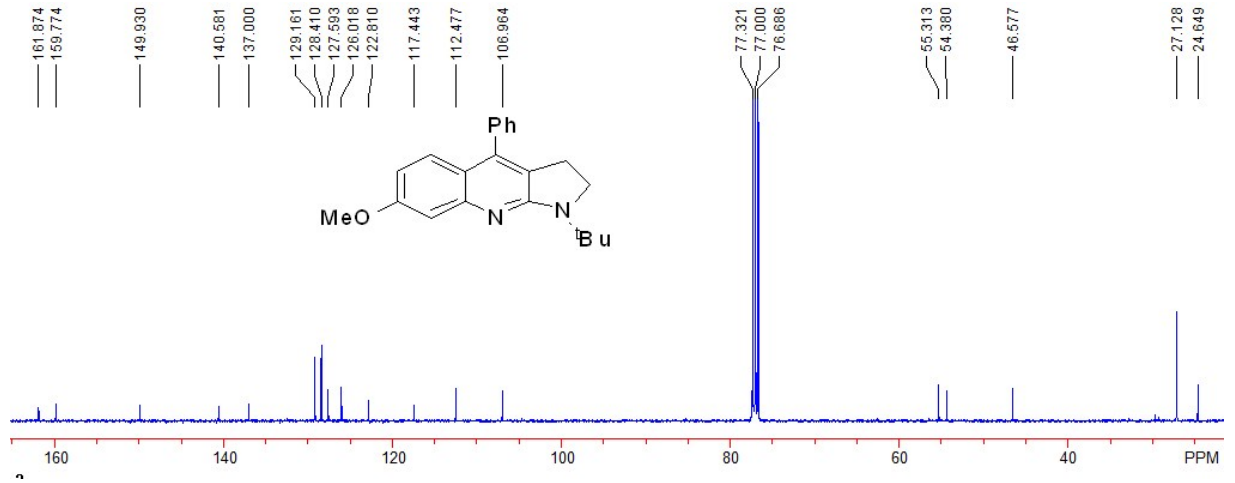
Compound 2g: 57 mg, 77%, A yellow solid, m.p. 150-152 ^{o}C; IR (CH_2Cl_2): ν 2973, 1636, 1566, 1421, 1221, 1082, 735 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.57 (s, 9H), 2.60-2.68 (m, 1H), 2.74-2.82 (m, 1H), 3.56-3.65 (m, 2H), 7.00 (d, *J* = 2.0 Hz, 1H), 7.21-7.24 (m, 1H), 7.32-7.40 (m, 3H), 7.52-7.55 (m, 1H), 7.61 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.5, 27.1, 46.3, 54.6, 123.5, 123.6, 126.7, 127.0, 127.5, 128.2, 128.3, 129.6, 130.0, 130.9, 133.3, 134.8, 137.1, 146.7, 161.1; MS (ESI) *m/z*: 371.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{21}Cl_2N_2^+$ requires: 371.1076, found: 371.1079.

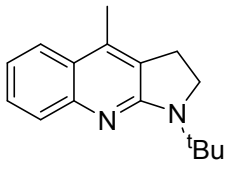




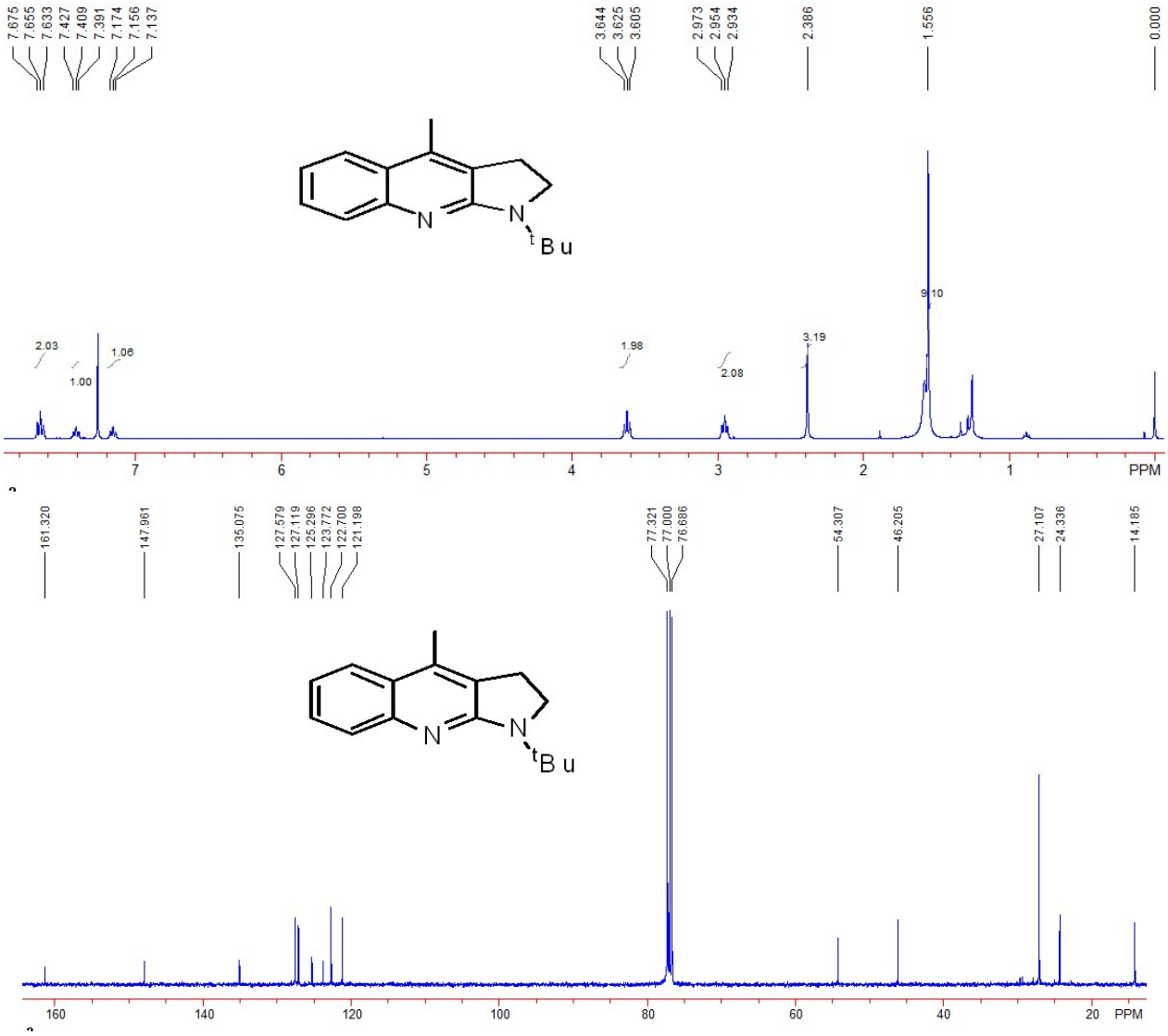
Compound 2h: 40 mg, 60%, A yellow solid, m.p. 140-142 °C; IR (CH_2Cl_2): ν 3057, 2957, 1613, 1410, 1107, 1034, 761, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.59 (s, 9H), 2.78 (t, *J* = 7.6 Hz, 2H), 3.57 (t, *J* = 7.6 Hz, 2H), 3.91 (s, 3H), 6.70 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 7.13 (d, *J* = 2.8 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.31-7.33 (m, 2H), 7.39-7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.6, 27.1, 46.6, 54.4, 55.3, 107.0, 112.5, 117.4, 122.8, 126.0, 127.6, 128.4, 129.2, 137.0, 140.6, 149.9, 159.8, 161.9; MS (ESI) *m/z*: 333.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{22}H_{25}N_2O^+$ requires: 333.1961, found: 333.1965.

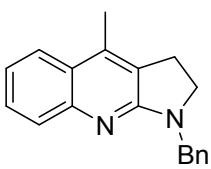






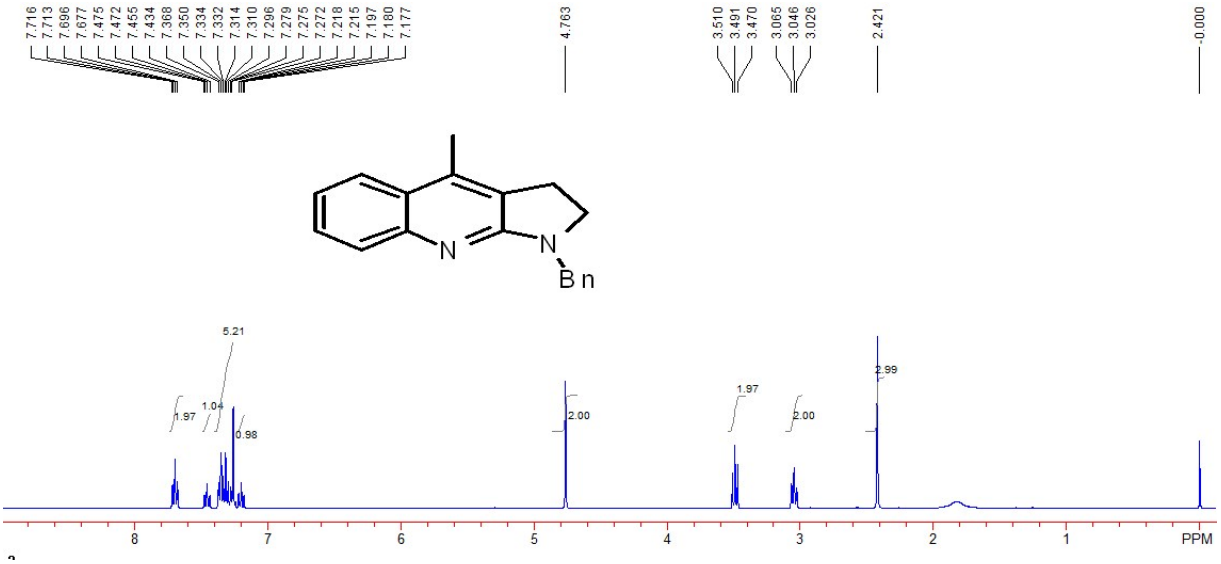
Compound 2i: 33 mg, 70%, A yellow solid, m.p. 108-110 °C; IR (CH_2Cl_2): ν 2952, 1716, 1640, 1571, 1274, 1228, 752 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.56 (s, 9H), 2.39 (s, 3H), 2.95 (t, J = 7.6 Hz, 2H), 3.63 (t, J = 7.6 Hz, 2H), 7.16 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.41 (dd, $J_1 = J_2$ = 7.6 Hz, 1H), 7.66 (dd, $J_1 = J_2$ = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.2, 24.3, 27.1, 46.2, 54.3, 121.2, 122.7, 123.8, 125.3, 127.1, 127.6, 135.1, 148.0, 161.3; MS (ESI) *m/z*: 241.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{16}H_{21}N_2^+$ requires: 241.1699, found: 241.1702.

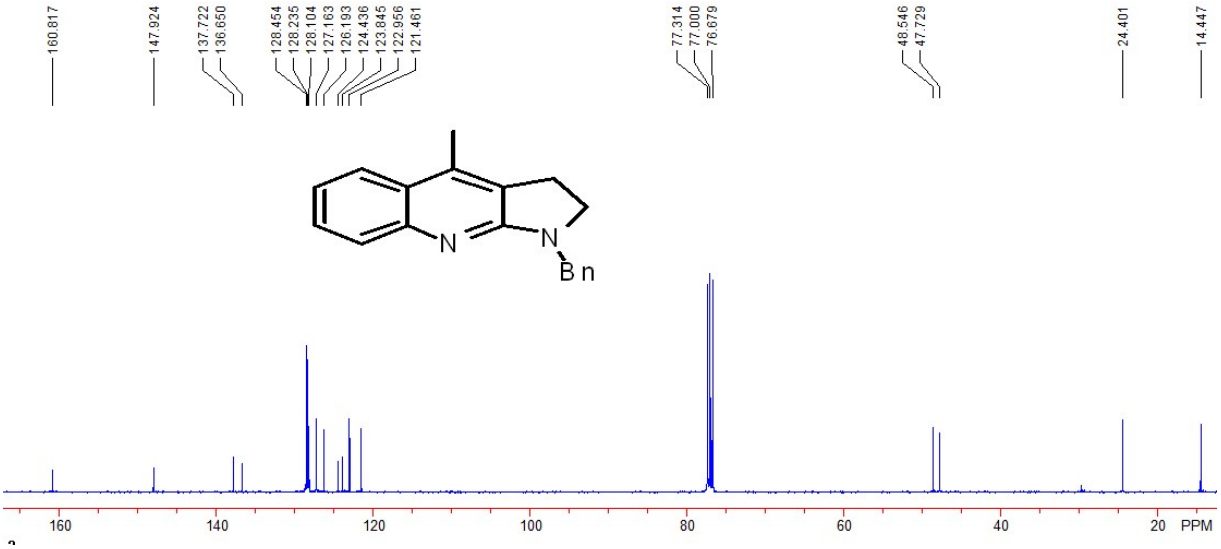


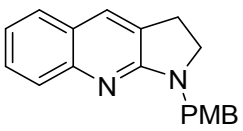


Compound 2j: 35 mg, 64%, A yellow solid, m.p. 143-145 °C; IR (CH_2Cl_2): ν 3063, 2872, 1639, 1575, 1496, 1443, 746, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.42 (s, 3H), 3.05 (t, J = 7.6 Hz, 2H), 3.49 (t, J = 7.6 Hz, 2H), 4.76 (s, 2H), 7.18-7.22 (m, 1H), 7.27-7.37 (m, 5H), 7.43-

7.48 (m, 1H), 7.68-7.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 14.4, 24.4, 47.7, 48.5, 121.5, 123.0, 123.8, 124.4, 126.2, 127.2, 128.1, 128.2, 128.5, 136.7, 137.7, 147.9, 160.8; MS (ESI) *m/z*: 275.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{19}N_2^+$ requires: 275.1543, found: 275.1542.

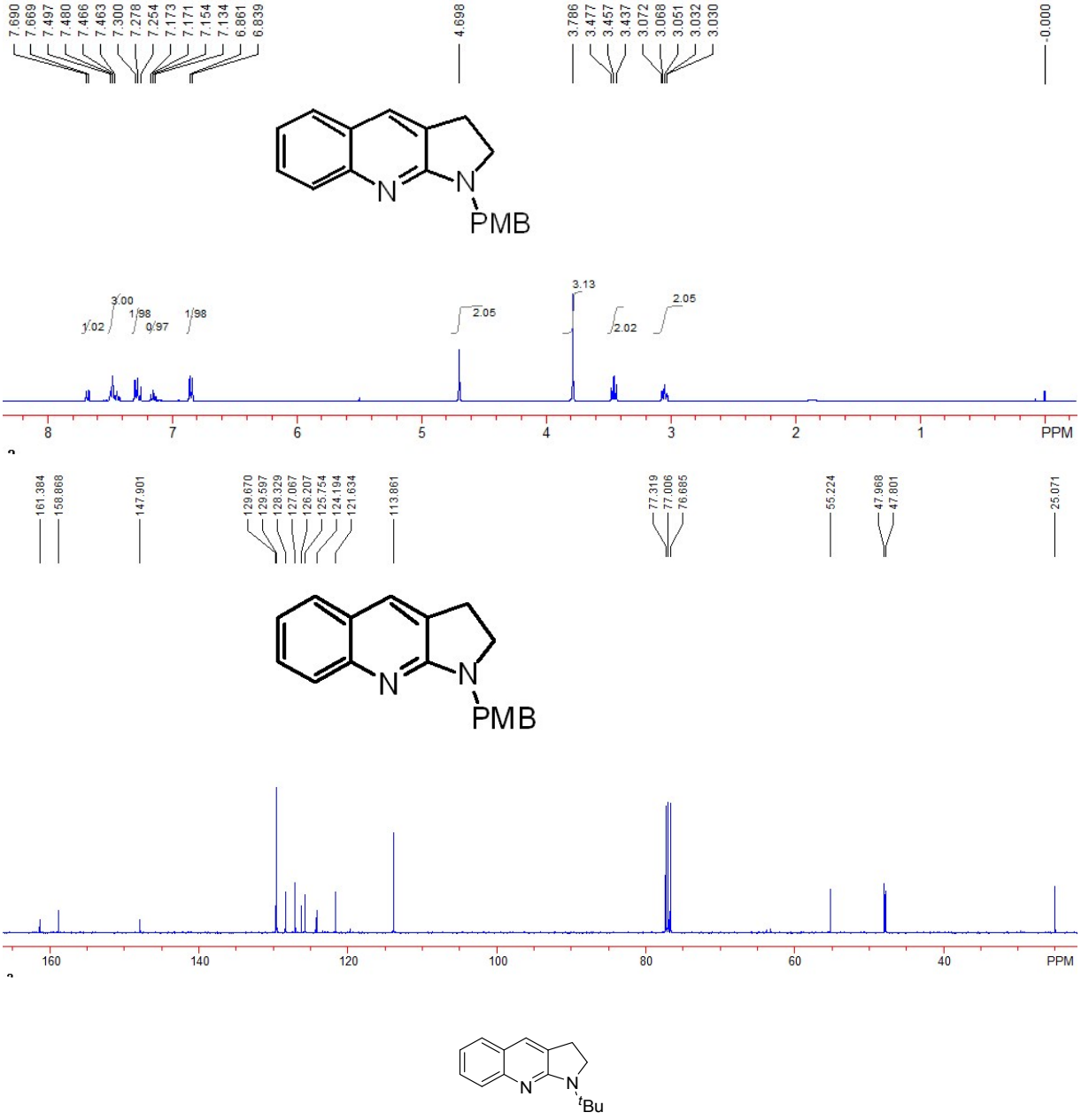




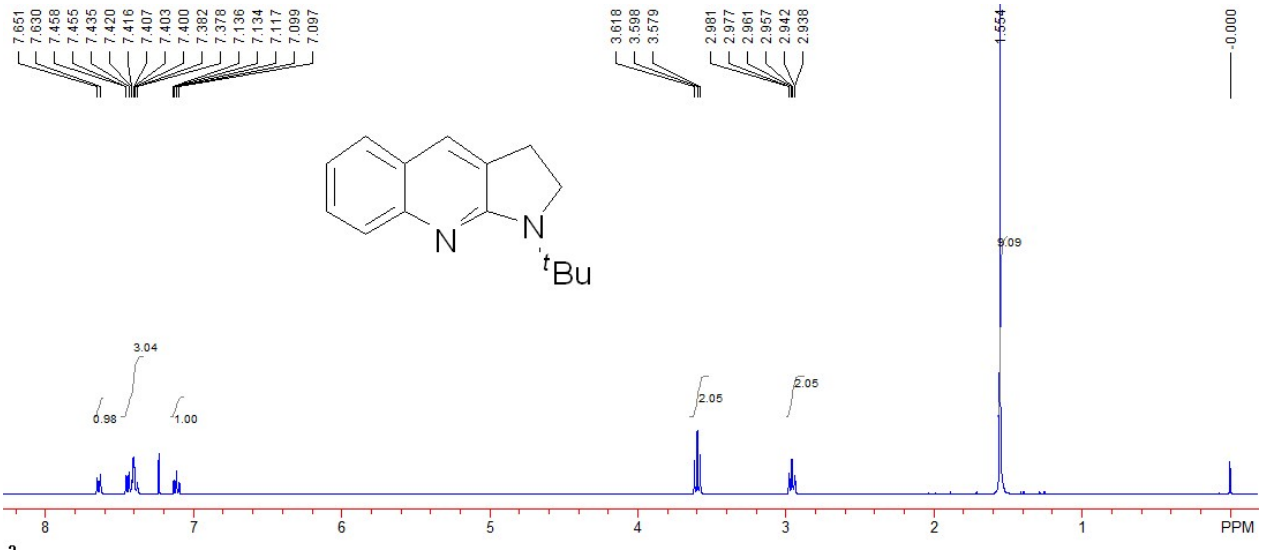


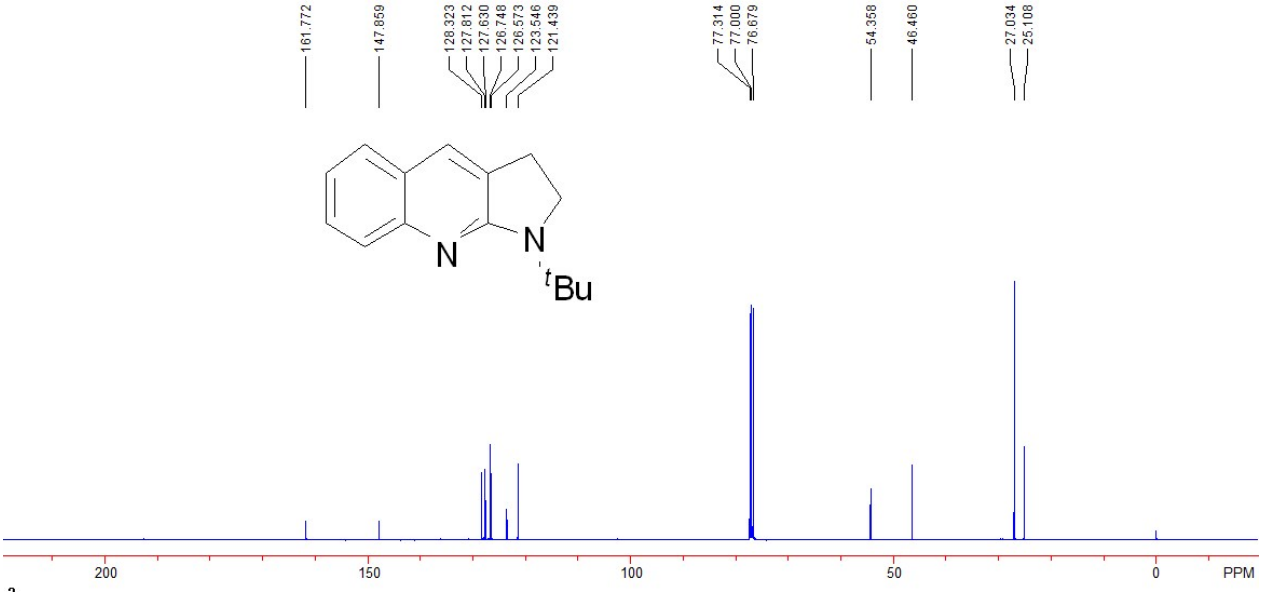
Compound 2k: 41 mg, 71%, A yellow solid, m.p. 88-90 ^{o}C; IR (CH_2Cl_2): ν 3055, 2928, 1641, 1571, 1511, 1244, 754 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.03-3.07 (m, 2H), 3.46 (t, J = 8.0 Hz, 2H), 3.79 (s, 3H), 4.70 (s, 2H), 6.85 (d, J = 8.8 Hz, 2H), 7.13-7.17 (m, 1H), 7.25-7.30 (m, 2H), 7.46-7.50 (m, 3H), 7.68 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.1,

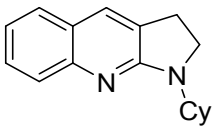
47.8, 48.0, 55.2, 113.9, 121.6, 124.2, 125.8, 126.2, 127.1, 128.3, 129.6, 129.7, 147.9, 158.9, 161.4; MS (ESI) *m/z*: 291.1 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{19}H_{19}N_2O^+$ requires: 291.1492, found: 291.1492.



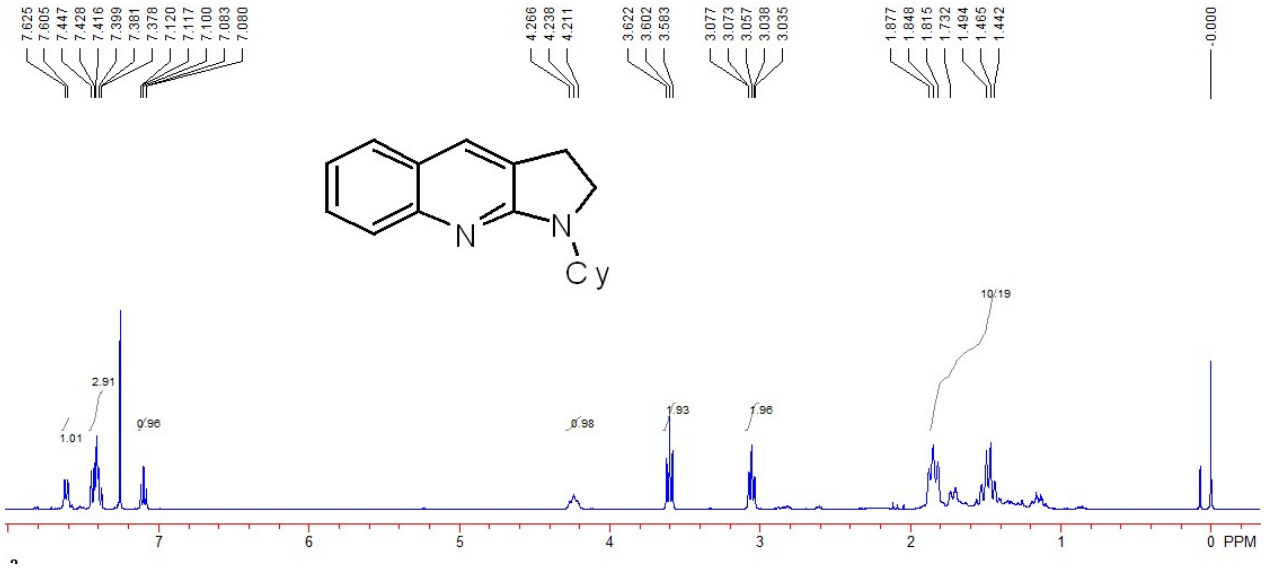
Compound 2l: 35 mg, 77%, A yellow solid, m.p. 99-101 ^oC; IR (CH_2Cl_2): ν 2971, 2854, 1643, 1570, 1428, 1223, 753 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.55 (s, 9H), 2.96 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 3.46 (t, J = 8.0 Hz, 2H), 7.10-7.14 (m, 1H), 7.38-7.46 (m, 3H), 7.64 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.1, 27.0, 46.5, 54.4, 121.4, 123.5, 126.6, 126.7, 127.6, 127.8, 128.3, 147.9, 161.8; MS (ESI) *m/z*: 227.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{15}H_{19}N_2^+$ requires: 227.1543, found: 227.1543.

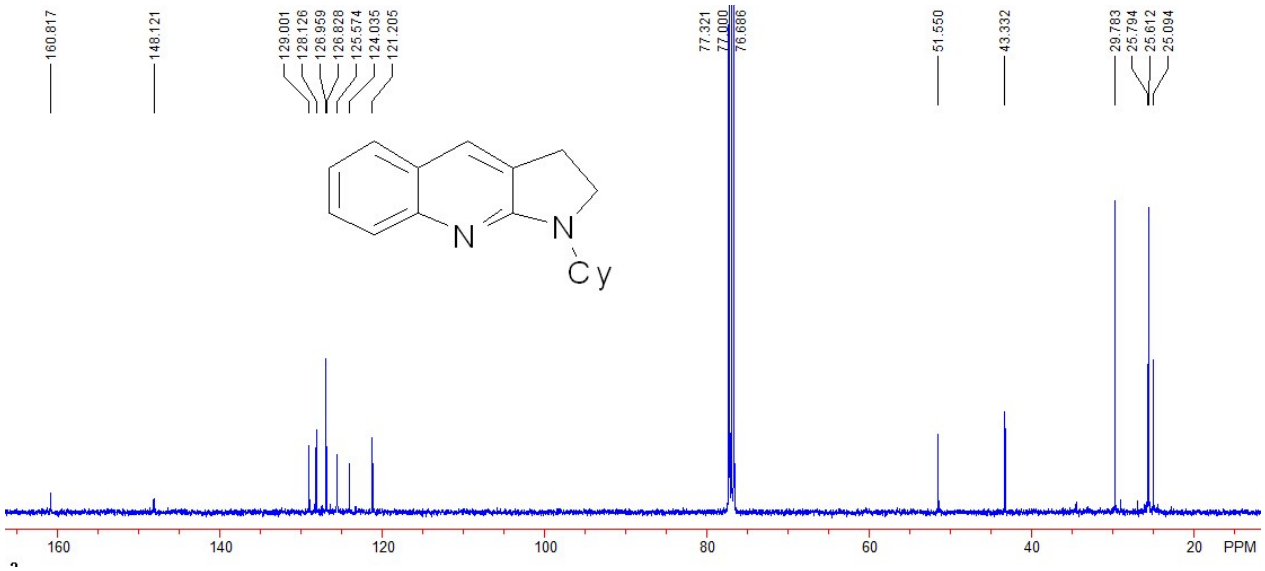




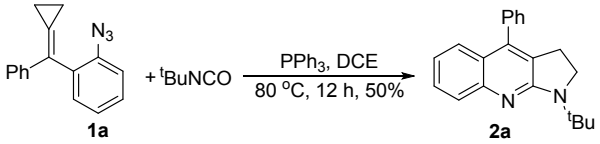


Compound 2m: 36 mg, 72%, A yellow solid, m.p. 152-154 ^{o}C; IR (CH_2Cl_2): ν 2929, 2853, 1641, 1573, 1495, 1438, 1309, 752 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.44-1.88 (m, 10H), 3.04-3.08 (m, 2H), 3.60 (t, *J* = 8.0 Hz, 2H), 4.21-4.27 (m, 1H), 7.08-7.12 (m, 1H), 7.38-7.45 (m, 3H), 7.62 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 25.1, 25.6, 25.8, 29.8, 43.3, 51.6, 121.2, 124.0, 125.6, 126.8, 127.0, 128.1, 129.0, 148.1, 160.8; MS (ESI) *m/z*: 253.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{17}H_{21}N_2^+$ requires: 253.1699, found: 253.1699.


7.625
7.605
7.447
7.428
7.416
7.399
7.381
7.378
7.120
7.117
7.100
7.083
7.080
4.266
4.238
4.211
3.622
3.602
3.583
3.077
3.073
3.057
3.038
3.035
1.877
1.848
1.815
1.732
1.494
1.465
1.442
0.000
N
N
Cy
10.19
2.91
1.01
0.96
0.98
1.93
1.96
7
6
5
4
3
2
1
0 PPM


160.817
148.121
129.001
128.126
126.959
126.828
125.574
124.035
121.205
77.321
77.000
76.686
51.550
43.332
29.783
25.794
25.612
25.094
N
N
Cy
160
140
120
100
80
60
40
20 PPM

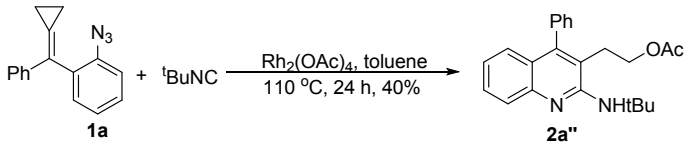
Typical procedure for the synthesis of compound 2a from Staudinger reduction



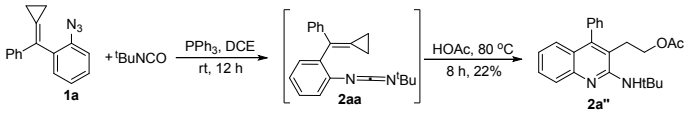
1a **2a**

A solution of compound **1a** (0.1 mmol), PPh_3 (39 mg, 0.15 mmol) and ^tBuNCO (35 μL, 0.3 mmol) in dry DCE (1 mL) was stirred at 80 ^oC for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product in 50% yield.

Control experiment on how to get compounds 2a' and 2a''

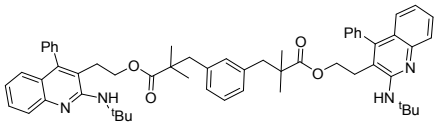


A solution of compound **1a** (0.2 mmol), isonitrile (1.0 mmol) and $Rh_2(OAc)_4$ (28 mg, 0.1 mmol) in dry toluene (2 mL) was stirred at 110 °C for 24 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product in 40% yield.

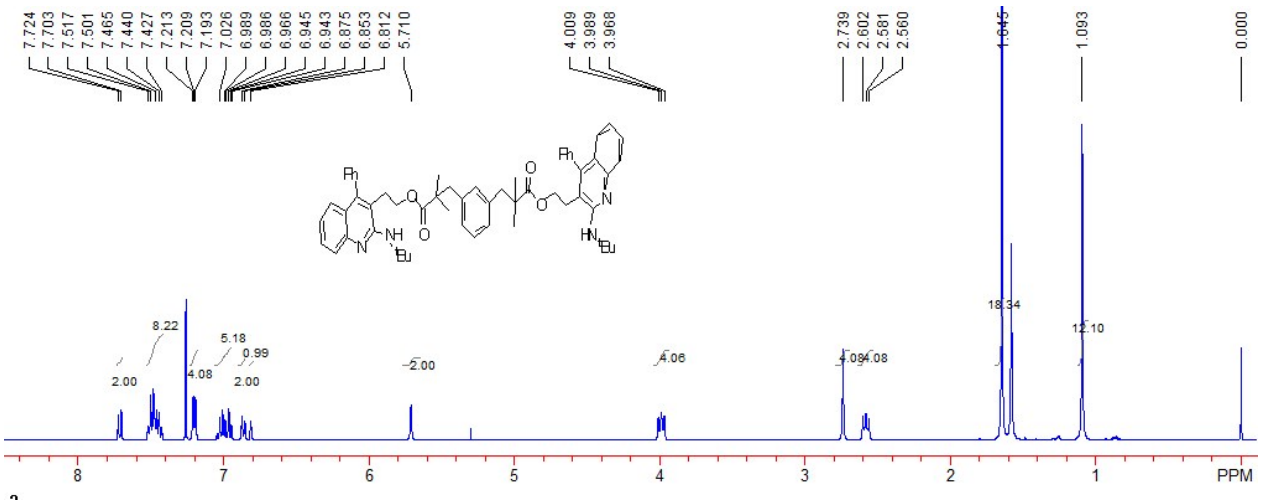


A solution of compound **1a** (0.1 mmol), PPh_3 (39 mg, 0.15 mmol) and ^{t}BuNCO (35 μL, 0.3 mmol) in dry DCE (1 mL) was stirred at room temperature for 12 h. Then HOAc (6 μL, 0.1 mmol) was added and the mixture was heated at 80 °C for another 8 h before the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product in 22% yield.

This control experiment illustrated that the byproducts **2a'** and **2a''** were obtained by the reaction between the carbodiimide intermediates and the acids derived from Rh(II) catalysts.



Compound 2a': 4 mg, 4%, A yellow solid, m.p. 176-178 °C; IR (CH_2Cl_2): ν 3407, 2966, 1716, 1589, 1414, 1124, 760 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 1.09 (s, 12H), 1.65 (s, 18H), 2.58 (t, *J* = 8.4 Hz, 4H), 2.74 (s, 4H), 3.99 (t, *J* = 8.4 Hz, 4H), 5.71 (s, 2H), 6.81 (s, 1H), 6.85-6.88 (m, 2H), 6.96-7.03 (m, 5H), 7.19-7.21 (m, 4H), 7.44-7.50 (m, 8H), 7.71 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.9, 28.0, 29.3, 43.4, 45.8, 52.0, 62.5, 116.1, 121.4, 122.9, 126.2, 126.5, 127.5, 127.7, 128.3, 128.5, 129.0, 132.3, 137.2, 137.8, 146.8, 147.5, 154.8, 178.0; MS (ESI) *m/z*: 442.3 ($M+2H^{2+}$, 100); HRMS (ESI) Calcd. for $C_{58}H_{68}N_4O_4^+$ requires: 442.2615, found: 442.2629.


7.724
7.703
7.517
7.501
7.465
7.440
7.427
7.213
7.209
7.193
7.026
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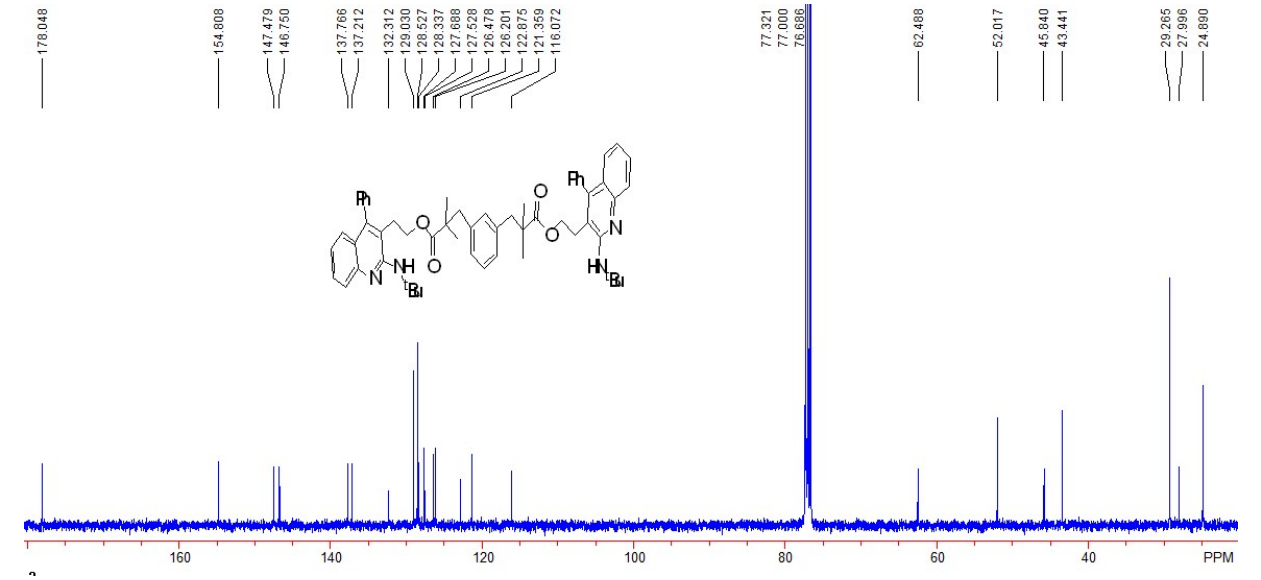
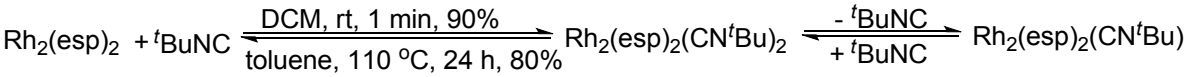
6.986
6.966
6.945
6.943
6.875
6.853
6.812
5.710
4.009
3.989
3.968
2.739
2.602
2.581
2.560
1.845
1.093
0.000
Ph
O
O
O
N
NH
tBu
Ph
N
HN
tBu
8.22
5.18
0.99
2.00
4.08
2.00
2.00
4.06
4.08
4.08
18.34
12.10
8
7
6
5
4
3
2
1
PPM


178.048
154.808
147.479
146.750
137.766
137.212
132.312
129.030
128.527
128.337
127.688
127.528
126.478
126.201
122.875
121.359
116.072
77.321
77.000
76.686
62.488
52.017
45.840
43.441
29.265
27.996
24.890
Ph
O
O
O
N
NH
tBu
Ph
N
HN
tBu
160
140
120
100
80
60
40
PPM

Typical procedure for the synthesis of catalysts $Rh_2(esp)_2(CN^tBu)_2$ and $Rh_2(esp)_2(CN^tBu)$



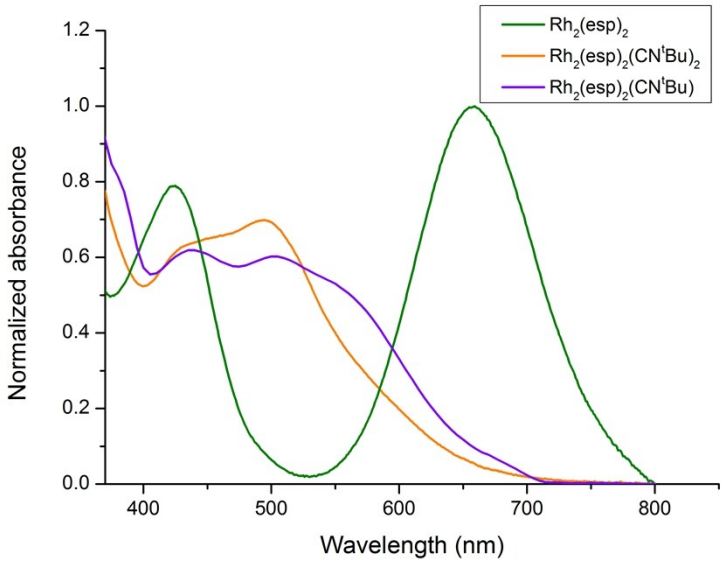
Compound $Rh_2(esp)_2$ (0.01 mmol) and ^{t}BuNC (22 μL, 0.2 mmol) were mixed in dry DCM (1 mL) at room temperature for 1 min. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 5 / 1) to afford the product $Rh_2(esp)_2(CN^tBu)_2$ in 90% yield. Heated in toluene at 110 °C for 24 h, $Rh_2(esp)_2(CN^tBu)_2$ could be transformed back to $Rh_2(esp)_2$ in 80% yield. Interestingly, $Rh_2(esp)_2(CN^tBu)_2$ could be easily transformed to a more stable $Rh_2(esp)_2(CN^tBu)$ once put in air for 24 h.

The colour of $Rh_2(esp)_2$ is green.

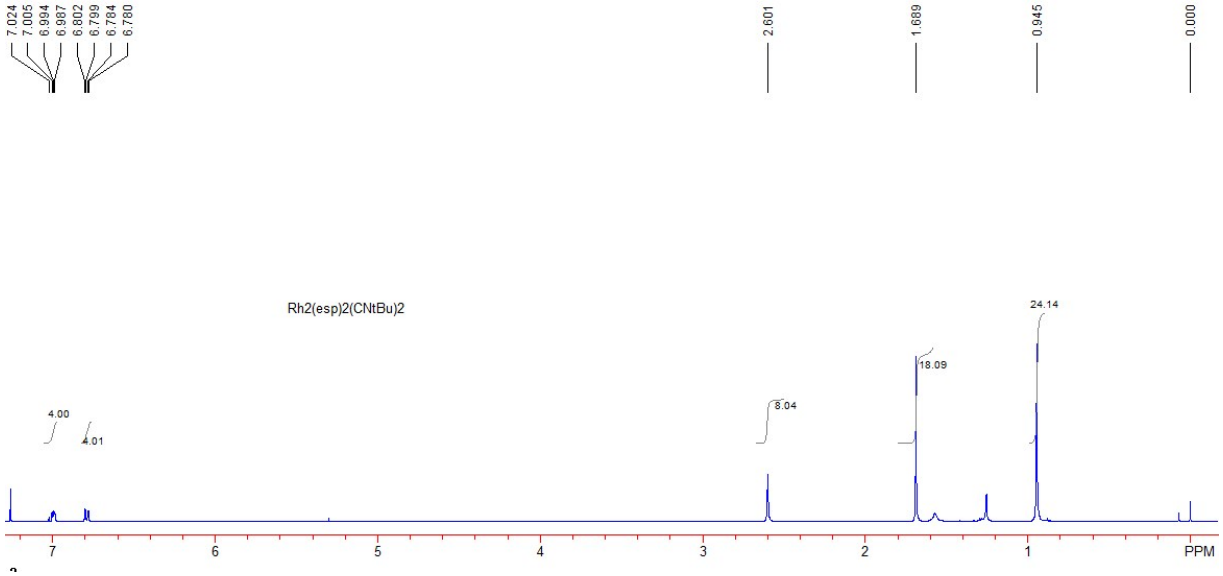
The colour of $Rh_2(esp)_2(CN^tBu)_2$ is orange.

The colour of $Rh_2(esp)_2(CN^tBu)$ is purple.

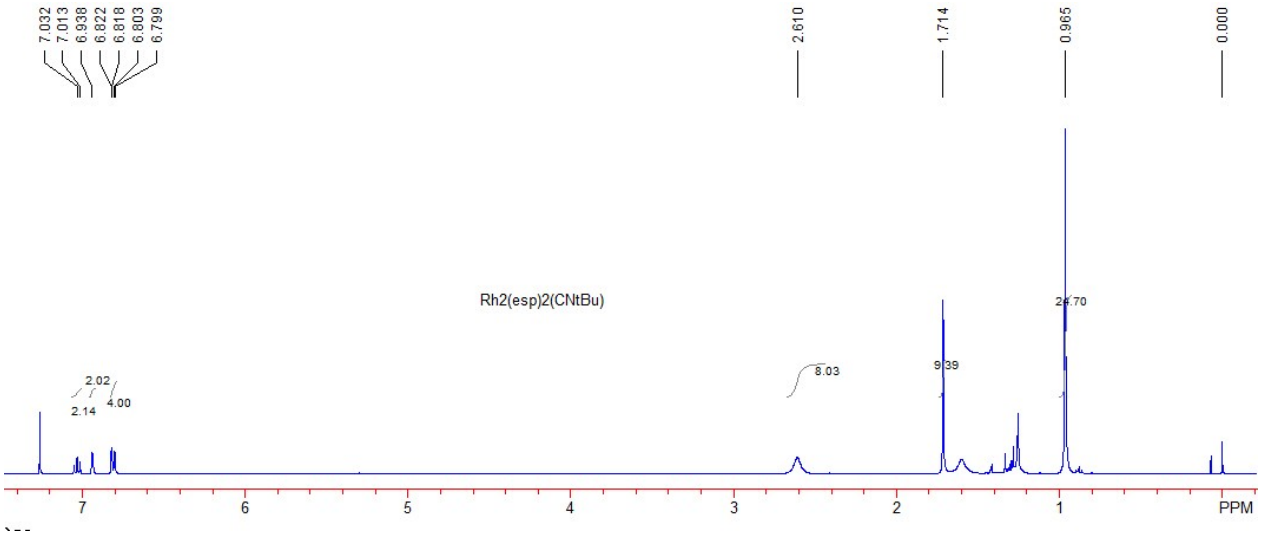
The UV/visible spectroscopy of these three catalysts:



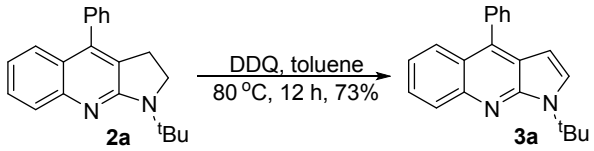
$Rh_2(esp)_2(CN^tBu)_2$:^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.95 (s, 24H), 1.69 (s, 18H), 2.60 (s, 8H), 6.79 (dd, J = 7.6 Hz, J = 1.6 Hz, 4H), 6.99-7.02 (m, 4H); HRMS (MALDI) Calcd. for $C_{42}H_{59}N_2O_8Rh_2^+$ requires: 925.2376, found: 925.2403.



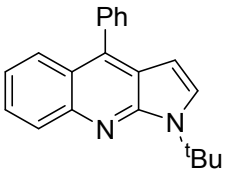
$Rh_2(esp)_2(CN^tBu)$: ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 0.97 (s, 24H), 1.71 (s, 9H), 2.61 (s, 8H), 6.81 (dd, J = 7.6 Hz, J = 1.2 Hz, 4H), 6.94 (s, 2H), 7.04 (d, J = 7.6 Hz, 2H); HRMS (MALDI) Calcd. for $C_{37}H_{50}NO_8Rh_2^+$ requires: 842.1641, found: 842.1694.



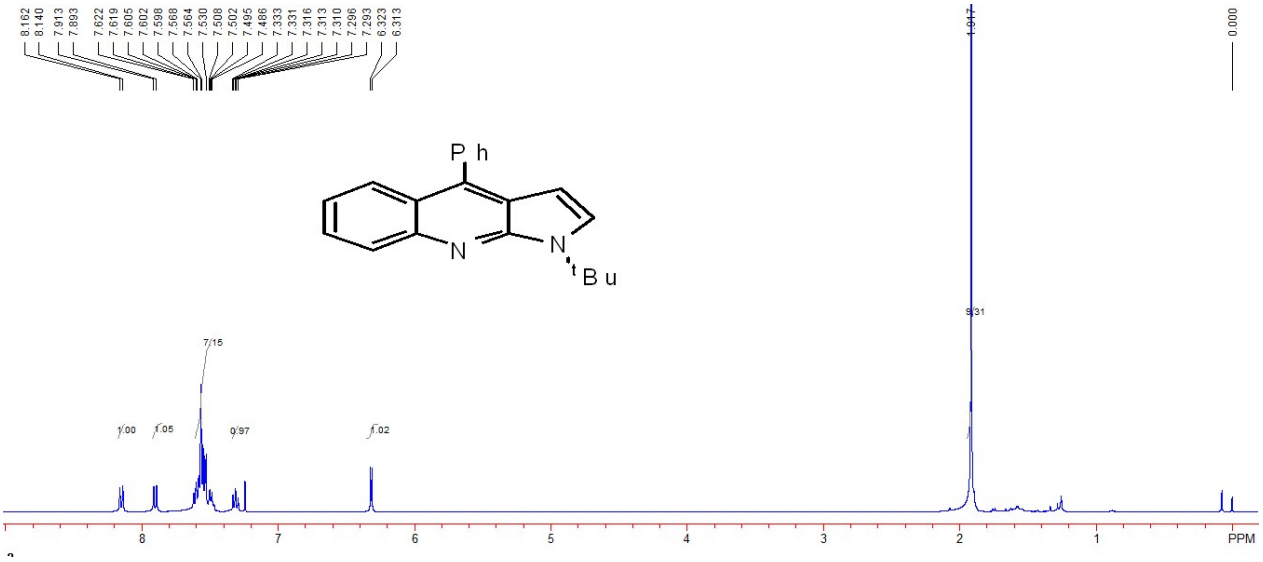
Transformation of compounds 2a and 2k

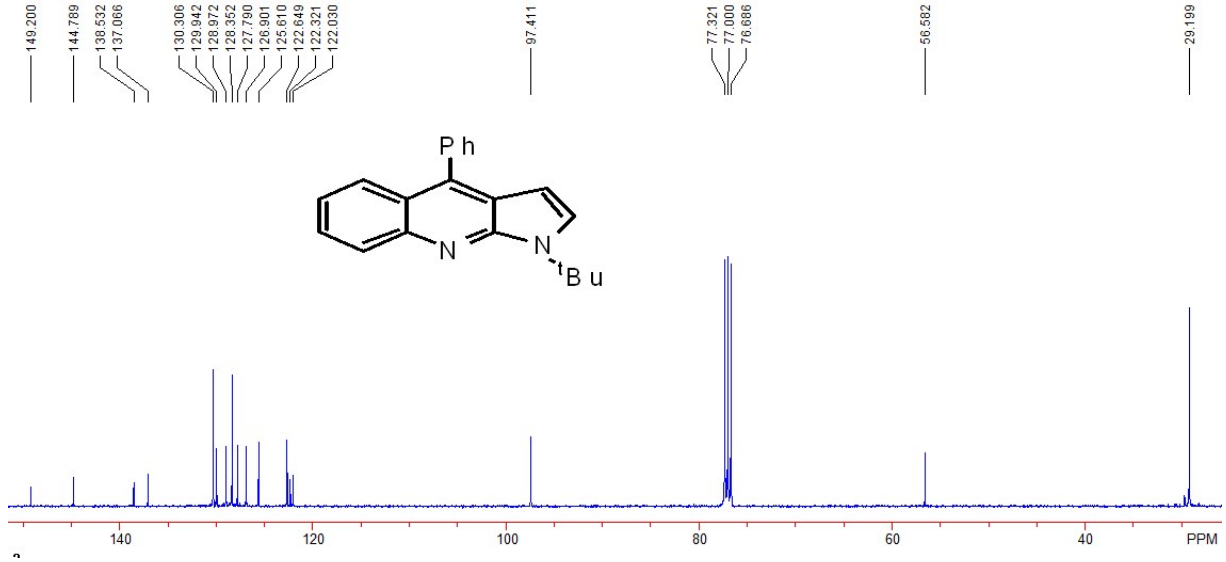


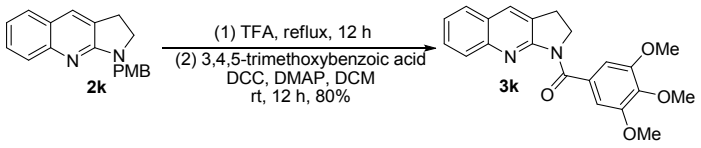
A solution of compound **2a** (30 mg, 0.1 mmol) and DDQ (44 mg, 0.2 mmol) in dry toluene (1 mL) was stirred at 80 °C for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 30 / 1) to afford the product **3a** in 73% yield.



Compound 3a: 22 mg, 73%, A yellow solid, m.p. 128-130 °C; IR (CH_2Cl_2): ν 3059, 2922, 1742, 1598, 1390, 1228, 759 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.92 (s, 9H), 6.32 (d, *J* = 4.0 Hz, 1H), 7.29-7.33 (m, 1H), 7.49-7.62 (m, 7H), 7.90 (d, *J* = 8.0 Hz, 1H), 8.15 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 29.2, 56.6, 97.4, 122.0, 122.3, 122.6, 125.6, 126.9, 127.8, 128.4, 129.0, 129.9, 130.3, 137.1, 138.5, 144.8, 149.2; MS (ESI) *m/z*: 301.2 ($M+H^+$, 100); HRMS (ESI) Calcd. for $C_{21}H_{21}N_2^+$ requires: 301.1699, found: 301.1700.

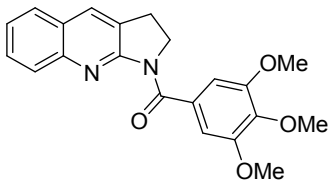




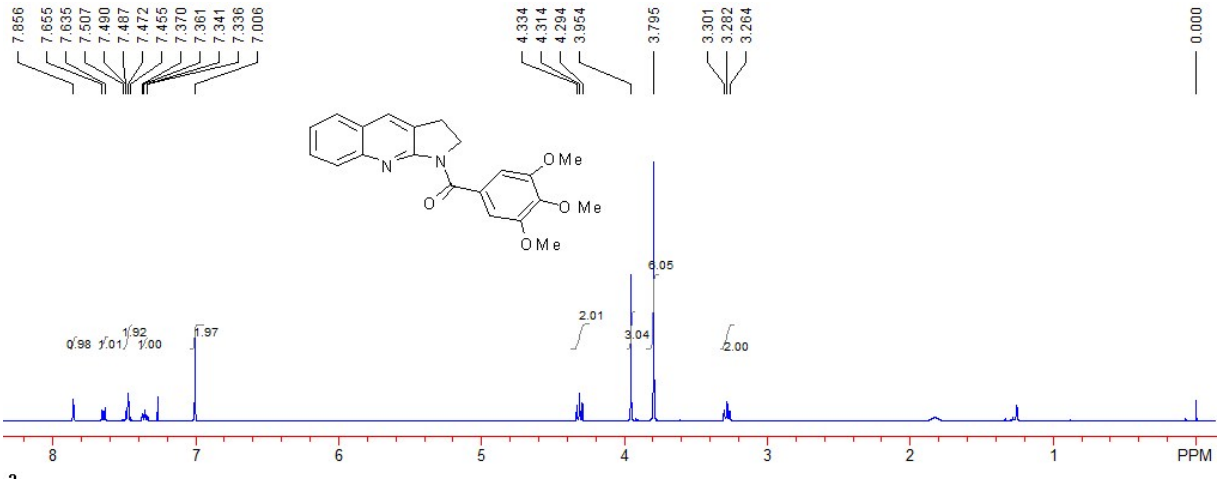


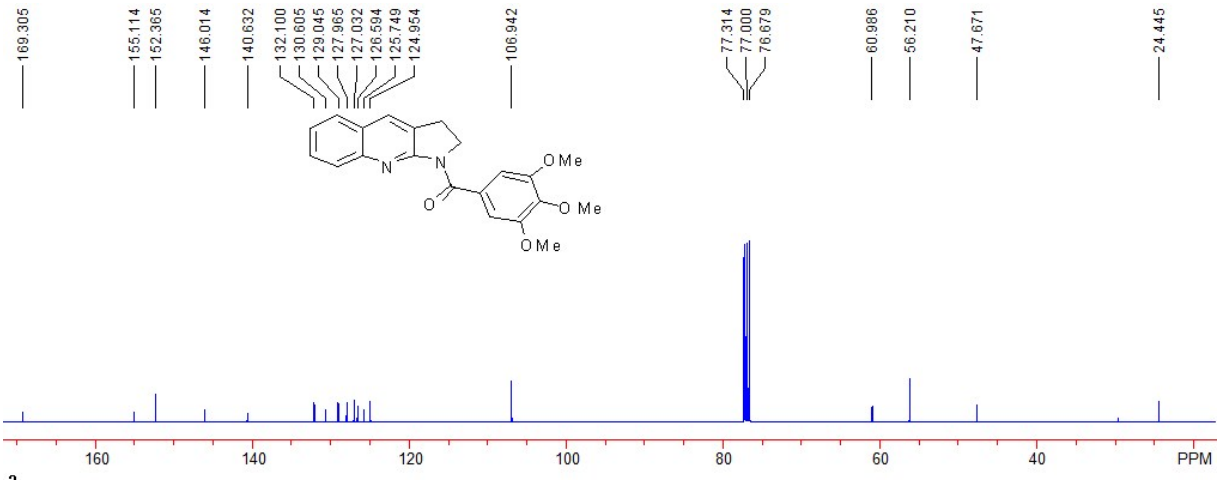
A solution of compound **2k** (45 mg, 0.15 mmol) in TFA (2 mL) was stirred at 75 °C for 12 h. Afterwards the mixture was added in saturated Na_2CO_3 (10 mL), extracted with EtOAc (5 mL x 3), and washed by brine (5 mL). The combined extracts were dried over Na_2SO_4. Then the solvent was removed under reduced pressure and the obtained crude product was used for the next reaction without purification. A mixture of crude product (26 mg, 0.15 mmol), 3,4,5-trimethoxybenzoic acid (64 mg, 0.3 mmol), DCC (62 mg, 0.3 mmol) and DMAP (18 mg, 0.015 mmol) in DCM (2 mL) was stirred at room temperature under an N_2 atmosphere for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash

chromatography (eluent: petroleum ether / ethyl acetate = 5 / 1) to afford the product **3k** in 80% yield.

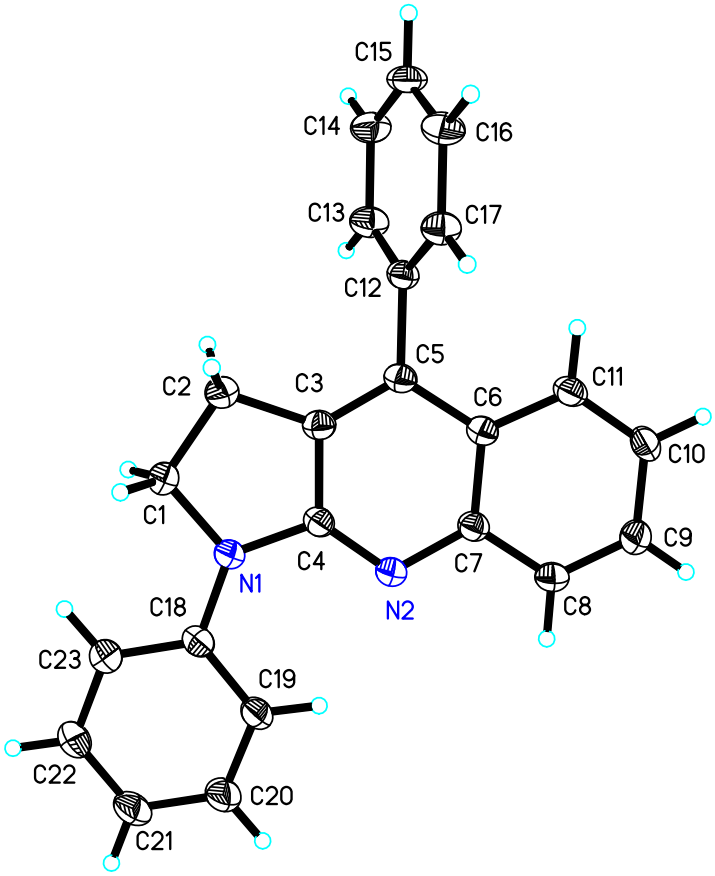


Compound 3k: 44 mg, 80%, A yellow solid, m.p. 152-154 ^{o}C; IR (CH_2Cl_2): ν 3059, 2922, 1742, 1598, 1390, 1228, 759 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 3.28 (t, *J* = 7.6 Hz, 2H), 3.80 (s, 6H), 3.95 (s, 3H), 4.31 (t, *J* = 7.6 Hz, 2H), 7.01 (s, 2H), 7.34-7.37 (m, 1H), 7.46-7.51 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 24.4, 47.7, 56.2, 61.0, 106.9, 125.0, 125.7, 126.6, 127.0, 128.0, 129.0, 130.6, 132.1, 140.6, 146.0, 152.4, 155.1, 169.3; MS (ESI) *m/z*: 365.2 (M+H^{+}, 100); HRMS (ESI) Calcd. for $C_{21}H_{21}N_2O_4^{+}$ requires: 365.1496, found: 365.1502.

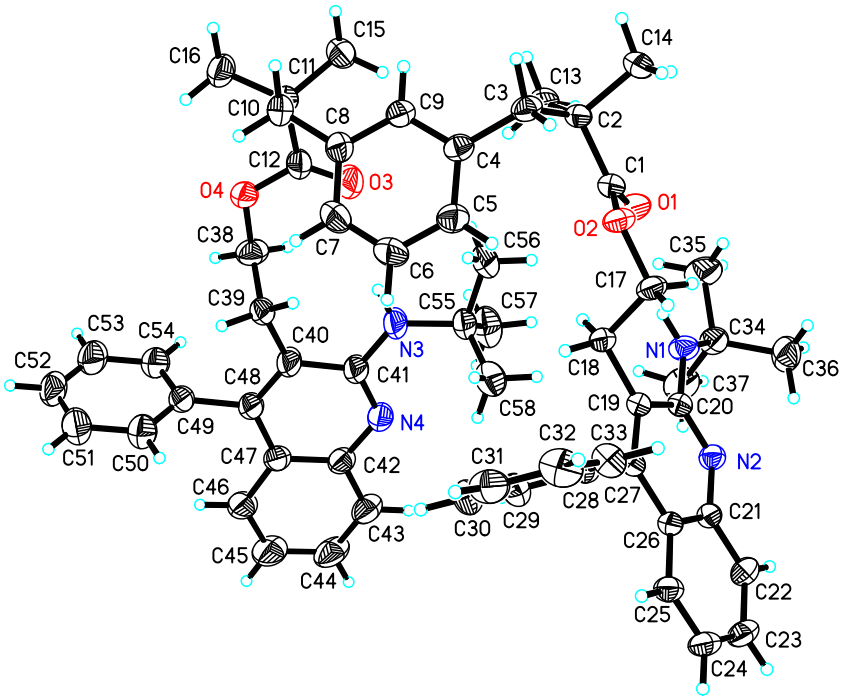




The crystal data of 2d and 2a'



The crystal data of **2d** have been deposited in CCDC with number 1004408. Empirical Formula: Empirical formula $C_{23}H_{19}N_2$, Formula weight: 323.40, Temperature: 293(2)K, Wavelength 0.71073 Å, Crystal system: Triclinic, Space group: P-1, Unit cell dimensions: a = 6.2745(8)Å, α = 109.644(3)°. b = 10.4378(12)Å, β = 97.810(3)°. c = 13.5235(16)Å, γ = 90.942(3)°. Volume: 824.56(17)Å^3, Z: 2, Density (calculated): 1.303 Mg/m^3, F(000): 342, Crystal size: 0.157 x 0.121 x 0.076 mm^3, Final R indices [I>2sigma(I)] R1 = 0.0491, wR2 = 0.1168.



The crystal data of **2a'** have been deposited in CCDC with number 1021020. Empirical Formula: $C_{58}H_{66}N_4O_4$; Formula Weight: 883.14; Crystal Color, Habit: colorless, Crystal Dimensions: 0.165 x 0.112 x 0.056 mm; Crystal System: Triclinic; Lattice Parameters: a = 10.37200(10)Å, b = 14.589(2)Å, c = 18.274(3)Å, α = 81.682(3)°, β = 76.959(4)°, γ = 88.485(4)°, V = 2546.41(4)Å^3; Space group: P-1; Z = 2; D_{calc}= 1.152 g/cm^3; F_{000} = 948; Final R indices [I>2sigma(I)] R1 = 0.0444, wR2 = 0.1255.