Electronic Supplementary Information

Enantioselective rhodium/ruthenium photoredox catalysis en route to chiral 1,2-aminoalcohols

Jiajia Ma, Klaus Harms and Eric Meggers*

*Email: meggers@chemie.uni-marburg.de

1. General Information S2

2. Synthesis of Substrates S3

2.1. Synthesis of 2-Acyl Imidazoles S3

2.2. Synthesis of Aniline Derivatives S13

3. Rhodium-Catalyzed Photoredox Reactions S16

4. Chiral Chromatography S37

5. Mechanistic Studies S58

6. Single Crystal X-Ray Diffraction Studies S61

7. References S64

8. NMR Spectra S65

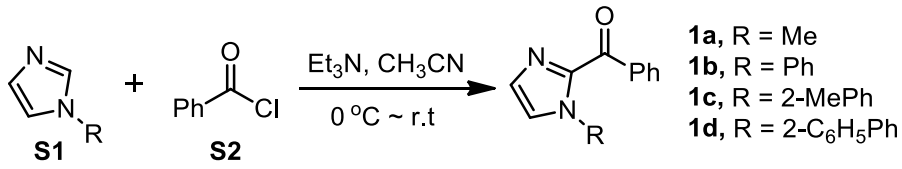
1. General Information

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. Catalytic reactions were performed by using standard Schlenk glassware techniques. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2), sodium/benzophenone (THF, Et_2O). The N,N-dimethylacetamide (DMAC) was purchased from Aldrich and used without further purification. ^1H NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^1H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), δ = 5.32 ppm (CD_2Cl_2), δ = 7.16 ppm (C_6D_6).$^{13}C\{^1H\}$ NMR spectroscopy: δ = 77.1 ppm ($CDCl_3$), δ = 53.8 ppm (CD_2Cl_2), δ = 128.0 ppm (C_6D_6). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer or on a Nicolet Avatar 330 FT-IR spectrophotometer. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (600-200 nm, 1 nm band width, 50 nm/min scanning speed, accumulation of 3 scans). High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument using ESI technique. Chiral HPLC chromatography was performed with an Agilent 1200, 1260 or Shimadzu Lc-2030c HPLC system. Optical rotations were measured with a Perkin-Elmer 241 or 341 polarimeter at concentrations of 1.0 g/100 mL. The anilines **2a**[1], **2d-g**[1], and **2h-i**[2] were prepared according to published procedures. All other reagents were commercially available and used without further purification.

2. Synthesis of Substrates

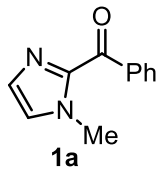
2.1. Synthesis of 2-Acyl Imidazoles

Method A



General procedure for the preparation of 1a-d with method A. To a mixture of **S1** (2.0 mmol) in CH_3CN (8 mL) was added **S2** (348 μL, 3.0 mmol) dropwise at 0 °C, followed by the addition of Et_3N (420 μL, 3.0 mmol), then stirred at room temperature for 12h. Afterwards, the reaction mixture was poured into H_2O (50 mL), extracted by EtOAc (3 × 20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, filtered, then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:3).

(1-Methyl-1*H*-imidazol-2-yl)(phenyl)methanone (1a)



1-Methyl-1*H*-imidazole was converted to 2-acyl imidazole **1a** (316 mg, 1.70 mmol, 85% yield) as a pale yellow oil.

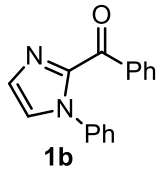
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23-8.21 (m, 2H), 7.50 (tt, J = 7.3, 2.3 Hz, 1H), 7.43-7.39 (m, 2H), 7.15 (d, J = 0.6 Hz, 1H), 7.01 (s, 1H), 3.96 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 183.9, 142.9, 137.1, 132.4, 130.5, 129.0, 127.8, 126.6, 36.1.

IR (film): ν (cm^{-1}) 3107, 3063, 2956, 1706, 1639, 1597, 1507, 1448, 1393, 1292, 1257, 1165, 1077, 999, 935, 897, 770, 735, 681, 651, 618, 554.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{11}N_2O^+$ $[M+H]^+$: 187.0866, found: 187.0866.

Phenyl(1-phenyl-1*H*-imidazol-2-yl)methanone (1b)



1b

1-Phenyl-1*H*-imidazole was converted to 2-acyl imidazole **1b** (456 mg, 1.84 mmol, 92% yield) as a pale yellow oil.

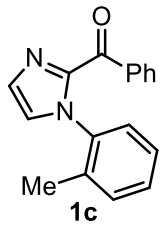
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28-8.25 (m, 2H), 7.59 (tt, *J* = 7.3, 2.4 Hz, 1H), 7.51-7.45 (m, 5H), 7.36 (d, *J* = 0.9 Hz, 1H), 7.35-7.32 (m, 2H), 7.28 (d, *J* = 0.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.9, 143.2, 138.5, 136.8, 133.0, 130.8, 129.6, 129.1, 128.5, 128.1, 126.3, 125.6.

IR (film): *v* (cm^{-1}) 3061, 1647, 1594, 1494, 1445, 1395, 1337, 1302, 1240, 1162, 1100, 1073, 1001, 928, 893, 759, 687, 656, 576, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{13}N_2O^+$ $[M+H]^+$: 249.1022, found: 249.1023.

Phenyl(1-(*o*-tolyl)-1*H*-imidazol-2-yl)methanone (1c)



1c

1-(*o*-Tolyl)-1*H*-imidazole was converted to 2-acyl imidazole **1c** (424 mg, 1.62 mmol, 81% yield) as a colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32-8.28 (m, 2H), 7.57 (tt, *J* = 7.4, 2.4 Hz, 1H), 7.50-7.44 (m, 2H), 7.40 (d, *J* = 1.0 Hz, 1H), 7.39-7.27 (m, 3H), 7.22 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.17 (d, *J* = 1.0 Hz, 1H).

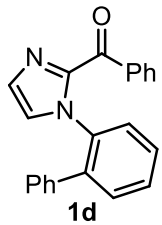
^{13}C NMR (75 MHz, $CDCl_3$) δ 182.6, 143.7, 138.2, 136.7, 134.5, 132.9, 130.9, 130.8, 129.9, 129.0,

128.2, 126.6, 126.4, 126.1, 17.4.

IR (film): *v* (cm^{-1}) 3062, 2922, 1646, 1592, 1494, 1447, 1395, 1334, 1300, 1243, 1203, 1161, 1087, 1038, 1002, 930, 894, 762, 688, 658, 551, 458.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{15}N_2O^+$ $[M+H]^+$: 263.1179, found: 263.1180.

(1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazol-2-yl)(phenyl)methanone (1d)



1d

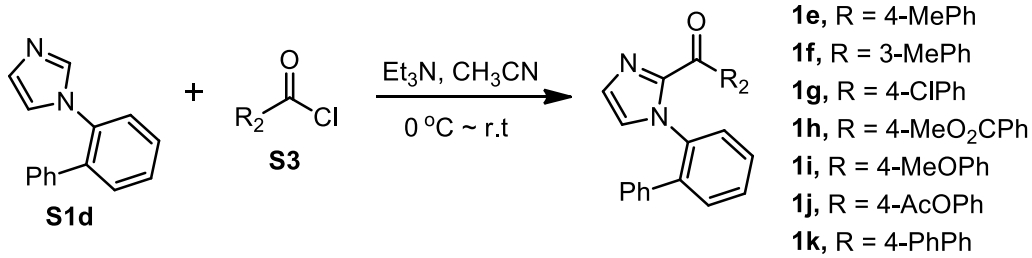
1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazole was converted to 2-acyl imidazole **1d** (640 mg, 1.98 mmol, 99% yield) as a white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2H), 7.57-7.47 (m, 5H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.24 (br, 1H), 7.19 (br, 1H), 7.15-7.08 (m, 3H), 7.00-6.96 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 183.1, 144.1, 138.5, 137.8, 136.4, 136.3, 132.7, 130.9, 130.5, 129.5, 129.0, 128.4, 128.3, 128.2, 127.8, 127.5, 126.4, 126.2.

IR (film): *v* (cm^{-1}) 3131, 3061, 1732, 1650, 1590, 1480, 1440, 1402, 1302, 1237, 1159, 1080, 1002, 930, 893, 763, 690, 653, 574, 523, 465.

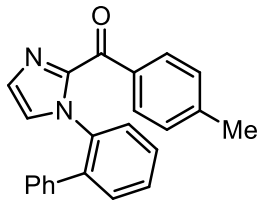
HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{16}N_2NaO^+$ $[M+Na]^+$: 347.1155, found: 347.1156.



General procedure for the preparation of 1e-g with method A. To a mixture of **S1d** (220 mg, 1.0

mmol) in CH_3CN (4 mL) was added **S3** (1.5 mmol) portionwise at 0 °C, followed by the addition of Et_3N (210 μL, 1.5 mmol), then stirred at room temperature for 12 h. Afterwards, the reaction mixture was poured into H_2O (25 mL), extracted by EtOAc (3 × 20 mL). The organic layer was collected and dried over anhydrous Na_2SO_4, filtered, then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 3:1).

(1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazol-2-yl)(*p*-tolyl)methanone (1e)



1e

4-Methylbenzoyl chloride was converted to 2-acyl imidazole **1e** (275 mg, 0.82 mmol, 82% yield) as a white solid.

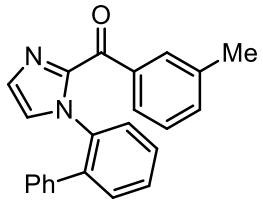
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77-7.73 (m, 2H), 7.56-7.40 (m, 4H), 7.22 (d, J = 1.1 Hz, 1H), 7.18-7.08 (m, 6H), 7.02-7.00 (m, 2H), 2.38 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.7, 144.2, 143.4, 138.3, 137.8, 136.4, 133.7, 130.7, 130.6, 129.2, 128.9, 128.4, 128.2 (2C), 128.1, 127.4, 126.4, 126.0, 21.6.

IR (film): ν (cm^{-1}) 3131, 3076, 3028, 1650, 1605, 1570, 1503, 1482, 1455, 1434, 1411, 1334, 1304, 1267, 1253, 1182, 1162, 1090, 994, 898, 832, 792, 778, 761, 735, 697, 658, 555, 482, 433.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{18}N_2NaO^+$ $[M+Na]^+$: 361.1311, found: 361.1311.

(1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazol-2-yl)(*m*-tolyl)methanone (1f)



1f

3-Methylbenzoyl chloride was converted to 2-acyl imidazole **1f** (326 mg, 0.97 mmol, 97% yield) as a white solid.

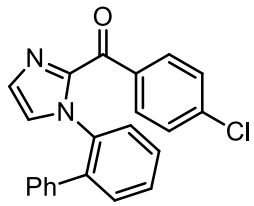
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (d, J = 7.6 Hz, 1H), 7.43-7.36 (m, 3H), 7.35-7.30 (m, 2H), 7.19 (d, J = 8.0 Hz, 1H), 7.14-7.10 (m, 2H), 7.06 (d, J = 1.1 Hz, 1H), 7.04-6.96 (m, 3H), 6.89-6.85 (m, 2H), 2.23 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 183.5, 144.3, 138.5, 137.9, 137.4, 136.4 (2C), 133.6, 131.0, 130.9, 129.4, 129.1, 128.4, 128.3 (2C), 127.8, 127.5, 126.5, 126.1, 21.3.

IR (film): ν (cm^{-1}) 3129, 3113, 1646, 1582, 1481, 1456, 1443, 1304, 1271, 1261, 1204, 1151, 1134, 1089, 1010, 942, 833, 778, 766, 736, 706, 698, 674, 584, 560, 536, 430.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{19}N_2O^+$ $[M+H]^+$: 339.1492, found: 339.1491.

(1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazol-2-yl)(4-chlorophenyl)methanone (1g)



1g

4-Chlorobenzoyl chloride was converted to 2-acyl imidazole **1g** (304 mg, 0.85 mmol, 85% yield) as a pale yellow solid.

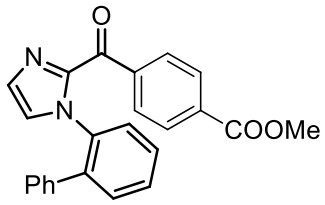
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.57-7.50 (m, 2H), 7.48-7.42 (m, 2H), 7.31 (dt, J = 8.8, 2.0 Hz, 2H), 7.24 (d, J = 1.1 Hz, 1H), 7.22 (d, J = 1.1 Hz, 1H), 7.15-7.07 (m, 3H), 7.00-6.93 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.6, 143.8, 139.2, 138.4, 137.8, 136.2, 134.6, 131.9, 130.9, 129.6, 129.1, 128.4, 128.3, 128.2, 128.1, 127.5, 126.4, 126.3.

IR (film): ν (cm^{-1}) 3094, 3059, 1656, 1584, 1504, 1482, 1448, 1434, 1409, 1393, 1235, 1168, 1143, 1083, 1007, 926, 899, 870, 827, 795, 734, 697, 683, 655, 592, 538, 499, 477.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{15}ClN_2NaO^+$ $[M+Na]^+$: 381.0765, found: 381.0766.

Methyl 4-(1-([1,1'-biphenyl]-2-yl)-1H-imidazole-2-carbonyl)benzoate (1h)



1h

Methyl 4-(chlorocarbonyl)benzoate was converted to 2-acyl imidazole **1h** (305 mg, 0.80 mmol, 80% yield) as a white solid.

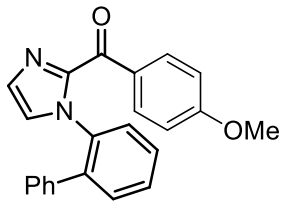
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.5 Hz, 2H), 7.59-7.53 (m, 2H), 7.51-7.45 (m, 2H), 7.28 (d, J = 2.4 Hz, 2H), 7.19-7.08 (m, 3H), 6.99-6.95 (m, 2H), 3.95 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.3, 166.4, 143.7, 139.8, 138.5, 137.8, 136.2, 133.3, 130.9, 130.3, 129.8, 129.2, 128.9, 128.5, 128.4, 128.2, 127.6, 126.6, 126.3, 52.3.

IR (film): v (cm^{-1}) 3120, 3060, 2948, 1712, 1655, 1569, 1506, 1481, 1436, 1409, 1276, 1231, 1168, 1101, 1007, 924, 895, 865, 820, 776, 743, 700, 647, 613, 534, 495, 462.

HRMS (ESI, m/z) calcd for $C_{24}H_{18}N_2NaO_3^+$ $[M+Na]^+$: 405.1210, found: 405.1212.

(1-([1,1'-Biphenyl]-2-yl)-1H-imidazol-2-yl)(4-methoxyphenyl)methanone (1i)



1i

4-Methoxybenzoyl chloride was converted to 2-acyl imidazole **1i** (258 mg, 0.73 mmol, 73% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, J = 9.0 Hz, 2H), 7.54-7.40 (m, 4H), 7.20 (d, J = 0.8 Hz, 1H), 7.14-7.06 (m, 4H), 7.00-6.97 (m, 2H), 6.84 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H).

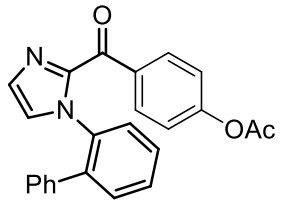
^{13}C NMR (75 MHz, $CDCl_3$) δ 181.7, 163.5, 144.4, 138.4, 137.9, 136.5, 133.0, 130.8, 129.2 (2C),

129.0, 128.4, 128.3 (2C), 127.5, 126.5, 125.9, 113.2, 55.4 .

IR (film): *v* (cm^{-1}) 3061, 2906, 2935, 1643, 1595, 1507, 1481, 1444, 1399, 1306, 1249, 1154, 1026, 923, 898, 843, 763, 730, 695, 652, 619, 579, 562, 517.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{18}N_2NaO_2^+$ $[M+Na]^+$: 377.1260, found: 377.1262.

4-(1-([1,1'-Biphenyl]-2-yl)-1H-imidazole-2-carbonyl)phenyl acetate (1j)



1j

4-(Chlorocarbonyl)phenyl acetate was converted to 2-acyl imidazole **1j** (263 mg, 0.70 mmol, 70% yield) as a pale yellow solid.

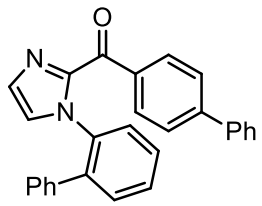
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.7 Hz, 2H), 7.55-7.40 (m, 4H), 7.20 (d, *J* = 10.7 Hz, 2H), 7.13-7.07 (m, 5H), 6.97-6.94 (m, 2H), 2.29 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 181.6, 168.6, 154.2, 143.9, 138.4, 137.7, 136.3, 133.7, 132.2, 130.9, 129.4, 129.0, 128.4, 128.3, 128.2, 127.6, 126.4, 126.3, 120.9, 21.1..

IR (film): *v* (cm^{-1}) 3120, 3060, 2948, 1712,1655, 1506, 1481, 1436, 1276, 1231, 1168, 1101, 1007, 924, 896, 866, 821, 777, 744, 700, 647, 613, 534, 495, 462.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{18}N_2NaO_3^+$ $[M+Na]^+$: 405.1210, found: 405.1212.

(1-([1,1'-Biphenyl]-2-yl)-1H-imidazol-2-yl)([1,1'-biphenyl]-4-yl)methanone (1k)



1k

[1,1'-Biphenyl]-4-carbonyl chloride was converted to 2-acylimidazole **1k** (293 mg, 0.73 mmol, 73% yield) as a white solid.

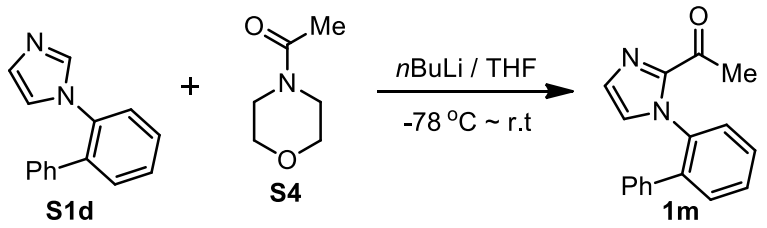
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (dt, J = 8.5, 1.8 Hz, 2H), 7.66-7.58 (m, 4H), 7.56-7.45 (m, 6H), 7.41 (dt, J = 6.1, 1.4 Hz, 1H), 7.27 (d, J = 1.1 Hz, 1H), 7.21 (d, J = 1.1 Hz, 1H), 7.18-7.10 (m, 3H), 7.04-7.00 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 182.6, 145.3, 144.2, 140.2, 138.4, 137.8, 136.4, 135.1, 131.0, 130.8, 129.4, 128.9, 128.8, 128.3 (2C), 128.2, 128.0, 127.5, 127.2, 126.5, 126.4, 126.2.

IR (film): ν (cm^{-1}) 1648, 1598, 1480, 1443, 1402, 1305, 1238, 1166, 1143, 1002, 929, 897, 847, 751, 727, 692, 655, 587, 558, 528, 490.

HRMS (ESI, m/z) calcd for $C_{28}H_{21}N_2O^+$ $[M+H]^+$: 401.1648, found: 401.1651.

Method B



Preparation of 1h with method B. To a solution of **S1d** (220 mg, 1.0 mmol) in THF (4 mL) was added *n*BuLi (0.48 mL, 2.5 M in *n*-hexane, 1.2 mmol) at -78 °C dropwise. After stirred at this temperature for 1 h, **S4** (0.13 mL, 1.1 mmol) was added slowly. The reaction mixture was warmed to room temperature gradually, then stirred for another 15 h. Afterwards, the mixture was poured into saturated aqueous solution of NH_4Cl and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:1) to give **1m** (197 mg, 0.75 mmol, 75% yield) as a white solid.

1-(1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazol-2-yl)ethanone (1m)

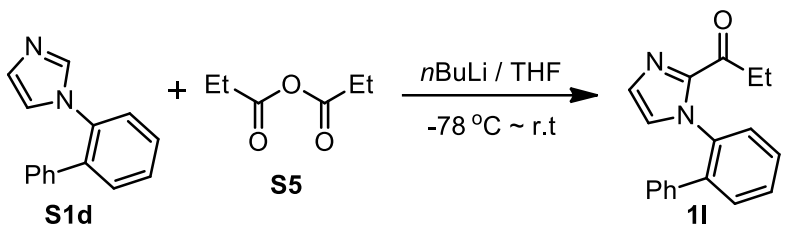
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.32 (m, 3H), 7.32-7.29 (m, 1H), 7.23-7.20 (m, 3H), 7.13 (d, J = 0.9 Hz, 1H), 7.05 (d, J = 0.9 Hz, 1H), 7.00-6.94 (m, 2H), 2.31 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.8, 143.9, 138.6, 137.8, 136.2, 130.7, 129.3, 129.0, 128.1 (2C), 127.4, 126.8, 126.4, 26.6.

IR (film): ν (cm^{-1}) 3032, 2921, 2851, 1682, 1504, 1483, 1447, 1434, 1403, 1357, 1337, 1304, 1267, 1224, 1158, 1145, 1128, 1101, 1085, 1017, 763, 714, 702, 680, 610 , 563, 430.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{15}N_2O^+$ $[M+H]^+$: 263.1179, found: 263.1180.

Method C



Preparation of 1i with method C. To a solution of **S1d** (220 mg, 1.0 mmol) in THF (4 mL) was added *n*BuLi (0.48 mL, 2.5 M in *n*-hexane, 1.2 mmol) at -78 °C dropwise. After stirred at this temperature for 1 h, **S5** (0.16 mL, 1.2 mmol) was added slowly. The reaction mixture was warmed to room temperature gradually, then stirred for another 15 h. Afterwards, the mixture was poured into saturated aqueous solution of Na_2CO_3 and extracted with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:1) to give **1l** (180 mg, 0.66 mmol, 66% yield) as a colorless oil.

1-(1-([1,1'-Biphenyl]-2-yl)-1*H*-imidazol-2-yl)propan-1-one (1l)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54-7.42 (m, 3H), 7.34-7.30 (m, 1H), 7.23-7.18 (m, 3H), 7.13 (d, J = 1.0 Hz, 1H), 7.07 (d, J = 1.1 Hz, 1H), 6.98-6.94 (m, 2H), 2.99-2.85 (m, 1H), 2.63-2.50 (m, 1H), 0.93 (t, J = 7.3 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 143.7, 138.7, 138.0, 136.4, 130.7, 129.2, 129.0, 128.2 (2C), 127.4, 126.5, 126.4, 32.0, 7.7.

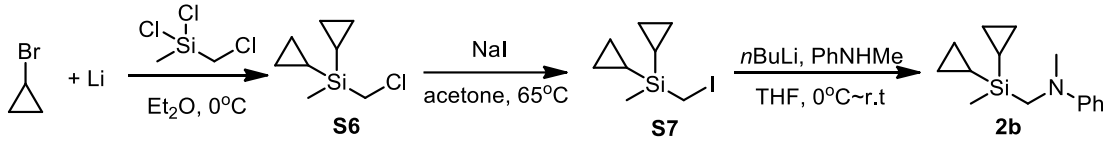
IR (film): ν (cm^{-1}) 2975, 2936, 1683, 1505, 1482, 1455, 1446, 1378, 1324, 1303, 1210, 1145, 1075, 1021, 1009, 938, 909, 803, 763, 735, 699, 645, 611, 573, 554, 505.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{17}N_2O^+$ $[M+H]^+$: 277.1335, found: 277.1335.

2.2. Synthesis of Aniline Derivatives

The anilines **2a**[1], **2d-g**[1], and **2h-i**[2] were prepared according to the published procedure.

Preparation of 2b:



Procedure for the preparation of (chloromethyl)dicyclopropyl(methyl)silane (S6). To a stirred suspension of granular lithium (278 mg, 40 mmol) in diethyl ether (10 mL) at 0 °C was added a solution of bromocyclopropane (1.60 mL, 20 mmol) in diethyl ether (10 mL) dropwise within 10 min, and the resulting mixture was stirred at 0 °C for another 60 min. Afterwards, a solution of dichloro(chloromethyl)methylsilane (1.31 mL, 10 mmol) in diethyl ether (5 mL) was added dropwise with 10 min at 0 °C. Subsequently, the reaction mixture was stirred at this temperature for another 45 min, then poured into water (30 mL). The organic phase was separated and the aqueous layer was extracted with diethyl ether (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to furnish **S6** (1.40 g, 8.0 mmol, 80% yield, > 95% purity judged by ^{1}H NMR) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.83 (s, 2H), 0.63-0.57 (m, 4H), 0.35-0.30 (m, 4H), –0.11 (s, 3H), –0.39 (tt, J = 9.8, 6.9 Hz, 2H).

All spectroscopic data was in agreement with the literature.[3]

Procedure for the preparation of dicyclopropyl(iodomethyl)(methyl)silane (S7). A suspension of **S6** (1.40 g, 8.0 mmol) and NaI (6.01 g, 40 mmol) in acetone (15 mL) was heated at 65 °C for 6h. Afterwards, the reaction mixture was poured into water (100 mL), extracted with diethyl ether (3 × 30 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to furnish **S7** (1.75 g, 6.56 mmol, 82% yield, >95% purity judged by ^{1}H-NMR) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 2.03 (s, 2H), 0.65-0.58 (m, 4H), 0.34-0.28 (m, 4H), –0.10 (s, 3H), –0.38 (tt, J = 9.8, 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 1.3, 1.1, –7.3, –7.7, –15.2.

IR (film): ν (cm^{-1}) 3070, 2997, 1287, 1252, 1186, 1099, 1078, 1053, 1032, 896, 822, 790, 773, 784, 722, 690, 661, 516.

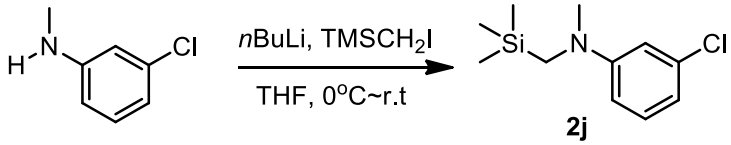
Procedure for the preparation of *N*-((dicyclopropyl(methyl)silyl)methyl)-*N*-methylaniline (2b). To a stirred solution of *N*-methylaniline (0.43 mL, 4.0 mmol) in THF (10 mL) at 0 °C was added *n*BuLi (2.4 mL, 2.5 M in *n*-hexane, 6.0 mmol) dropwise. After stirred at 0 °C for 2 h, **S7** (1.28 g, 4.80 mmol) was added to the mixture slowly, and the resulting solution was stirred for another 15 h. The reaction was then quenched by slow addition of a saturated solution of NH_4Cl (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:30) to give **2b** (785 mg, 3.20 mmol, 80% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.40 (m, 2H), 6.96-6.93 (m, 2H), 6.85 (tt, J = 7.3, 0.8 Hz, 1H), 3.22 (s, 3H), 3.17 (s, 2H), 0.83-0.77 (m, 4H), 0.53-0.50 (m, 4H), 0.00 (s, 3H), –0.23 (tt, J = 9.8, 6.9 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 150.7, 128.8, 115.0, 111.9, 42.2, 40.2, 1.4, 1.0, –7.1, –8.5.

IR (film): ν (cm^{-1}) 3068, 2996, 2925, 2802, 1597, 1504, 1365, 1286, 1251, 1233, 1192, 1097, 1032, 989, 897, 821, 799, 772, 743, 689, 631, 512, 400.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{24}NSi^+$ $[M+H]^+$: 246.1673, found: 246.1673.



2j

Procedure for the preparation of 3-chloro-*N*-methyl-*N*-((trimethylsilyl)methyl)aniline (2j). To a stirred solution of 3-Chloro-*N*-methylaniline (0.61 mL, 5.0 mmol) in THF (12 mL) at 0 °C was

added *n*BuLi (2.4 mL, 2.5 M in *n*-hexane, 6.0 mmol) dropwise. After stirred at 0 °C for 2 h, (Iodomethyl)trimethylsilane (1.11 mL, 7.50 mmol) was added to the mixture slowly, and the resulting solution was stirred for another 15 h. The reaction was then quenched by slow addition of a saturated solution of NH_4Cl (15 mL) and extracted with EtOAc (3 × 20 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:30) to give **2j** (830 mg, 3.64 mmol, 73% yield) as a pale yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (t, J = 8.0 Hz, 2H), 6.60-6.48 (m, 3H), 2.94 (s, 3H), 2.87 (s, 2H), 0.11 (s, 9H).

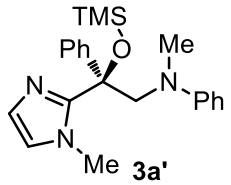
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.2, 134.9, 129.8, 114.8, 111.4, 109.8, 43.9, 40.1, –1.2.

IR (film): ν (cm^{-1}) 2953, 2894, 2809, 1591, 1557, 1493, 1366, 1247, 1232, 1195, 1099, 986, 837, 753, 680, 661, 443.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{19}ClNSi^+$ $[M+H]^+$: 228.0970, found: 228.0970.

3. Rhodium-Catalyzed Photoredox Reactions

General procedure for entries 1-6 of Table 1. A dried 10 mL Schlenk tube was charged with the catalyst Λ-**RhO** (4 mol%) (entries 1-5) or Λ-**IrO** (4 mol%) (entry 6), the photosensitizer $[Ru(bpy)_3](PF_6)_2$ (0.86 mg, 0.001 mmol, 1 mol%) and the corresponding 2-acyl imidazoles (0.10 mmol, 1.0 eq.). A solution of **2a** (29.0 mg, 0.15 mmol, 1.5 eq.) in MeCN/DMAC (v/v = 4:1, 1 mL) was added in one portion. The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was redissolved in THF (2 mL), and then TBAF (0.5 mL, 1.0 M in THF, 0.5 mmol) was added (except entry 1). The mixture was stirred at room temperature for another 0.5 h and quenched by the addition of saturated aqueous solution of NH_4Cl, extracted by EtOAc (3 × 10 mL). The combined organic layers were concentrated and subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:7 to 1:4) to afford the products **3a'-d**. Racemic samples were obtained by carrying out the reactions with *rac*-**RhO**. The enantiomeric excess was determined by chiral HPLC analysis.



3a'

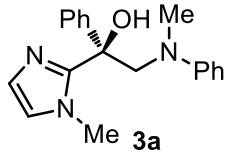
As for entry 1, starting from **1a** (18.6 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure without treating with TBAF to give **3a'** as a pale yellow oil (27.0 mg, 0.68 mmol, 68% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 41% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 9.6 min, t_r (major) = 11.2 min); $[\alpha]_D^{20}$ = +38.0° (*c* 1.0, CH_2Cl_2)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.28-7.23 (m, 2H), 7.19-7.07 (m, 3H), 7.00 (d, *J* = 1.2 Hz, 1H), 6.97-6.90 (m, 2H), 6.82 (d, *J* = 1.1 Hz, 1H), 6.50-6.44 (m, 3H), 4.76 (d, *J* = 15.1 Hz, 1H), 4.02 (d, *J* = 15.1 Hz, 1H), 2.97 (s, 6H), 0.02 (s, 9H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 151.0, 149.5, 144.0, 128.5, 127.9, 127.2, 126.7, 126.4, 123.3, 116.1, 112.8, 79.7, 62.6, 39.4, 34.7.

IR (film): ν (cm^{-1}) 3060, 3025, 2953, 2897, 1598, 1505, 1448, 1403, 1368, 1343, 1279, 1262, 1251, 1195, 1125, 1088, 1064, 1016, 992, 959, 883, 840, 744, 725, 690, 582, 462.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{30}N_3OSi^+$ $[M+H]^+$: 380.2153, found: 380.2158.



3a

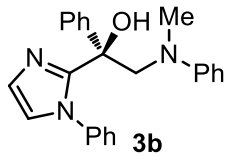
As for entry 2, starting from **1a** (18.6 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure to give **3a** as a pale yellow oil (22.4 mg, 0.729 mmol, 73% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 41% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 20.4 min, t_r (major) = 15.2 min); $[\alpha]_D^{20}$ = +50.4° (*c* 1.0, CH_2Cl_2)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.32 (m, 4H), 7.30-7.19 (m, 3H), 7.01 (d, *J* = 1.2 Hz, 1H), 6.94-6.90 (m, 2H), 6.83-6.78 (m, 2H), 4.82 (d, *J* = 14.9 Hz, 1H), 3.96 (br, 1H), 3.74 (d, *J* = 14.9 Hz, 1H), 3.41 (s, 3H), 2.76 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 152.0, 149.4, 144.3, 129.2, 128.7, 127.5, 126.0, 125.2, 123.1, 118.8, 114.5, 74.7, 65.1, 39.8, 34.4.

IR (film): ν (cm^{-1}) 3059, 2952, 2870, 2758, 1597, 1503, 1448, 1407, 1346, 1279, 1256, 1174, 1145, 1123, 1092, 1064, 1031, 991, 966, 938, 900, 745, 730, 696, 645, 589, 562, 470.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{22}N_3O^+$ $[M+H]^+$: 308.1757, found: 308.1753.



3b

As for entry 3, starting from **1b** (24.8 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure to give **3b** as a white solid (27.0 mg, 0.740 mmol, 74%

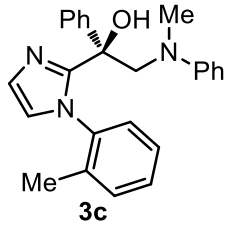
yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak AD-H column, ee = 82% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 14.0 min, t_r (major) = 9.9 min); $[\alpha]_D^{20}$ = +56.6° (*c* 1.0, CH_2Cl_2)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.26-7.18 (m, 6H), 7.17-7.12 (m, 4H), 7.11 (d, *J* = 1.2 Hz, 1H), 6.97 (d, *J* = 1.3 Hz, 1H), 6.89-6.83 (m, 4H), 6.73 (tt, *J* = 7.3, 0.8 Hz, 1H) 4.78 (d, *J* = 14.9 Hz, 1H), 3.75 (d, *J* = 14.9 Hz, 1H), 3.54 (br, 1H), 2.70 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.3, 150.4, 145.2, 139.2, 129.2, 128.5, 128.4, 128.2, 127.7, 127.3, 126.7, 125.6, 124.4, 118.4, 114.4, 75.6, 65.5, 39.7.

IR (film): *v* (cm^{-1}) 3059, 3025, 2870, 2729, 1597, 1496, 1446, 1352, 1302, 1253, 1175, 1138, 1122, 1096, 1065, 1031, 990, 937, 897, 746, 727, 689, 595, 538, 514.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{23}N_3NaO^+$ $[M+Na]^+$: 392.1733, found: 392.1732.



3c

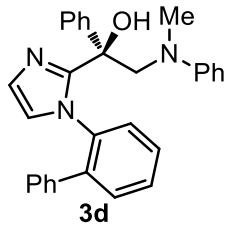
As for entry 4, starting from **1c** (26.2 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure to give **3c** as a white solid (28.0 mg, 0.73 mmol, 73% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 88% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 12.3 min, t_r (major) = 13.7 min); $[\alpha]_D^{20}$ = +70.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 7.32-7.28 (m, 1H), 7.57 (tt, *J* = 7.3, 1.3 Hz, 0.8 H), 7.47 (tt, *J* = 7.7, 1.4 Hz, 0.2 H, other rotamer), 7.42-7.30 (m, 1H), 7.36-7.25 (m, 1H), 7.24-7.21 (m, 2H), 7.20-7.18 (m, 3H), 7.17-7.15 (m, 2H), 7.15-7.12 (m, 1H), 6.92-6.83 (m, 2H), 6.82-6.74 (m, 2H), 6.12 (d, *J* = 7.8 Hz, 0.8 H, other rotamer), 4.92 (d, *J* = 14.7 Hz, 0.8 H), 4.78 (d, *J* = 14.7 Hz, 0.2 H, other rotamer), 3.83 (d, *J* = 2.7 Hz, 0.8 H), 3.78 (d, *J* = 2.8 Hz, 0.2 H, other rotamer), 2.56 (br, 0.8 H), 2.51 (br, 0.2 H, other rotamer), 2.72 (s, 2.4 H), 2.64 (s, 0.6 H, other rotamer), 2.08 (s, 2.4 H), 2.06 (s, 0.6 H, other rotamer).

^{13}C NMR (125 MHz, CD_2Cl_2, mixture of rotamers) δ 152.4 (2C), 150.3, 150.2, 145.4, 144.3, 138.5, 138.0, 136.5, 135.8, 130.5, 130.3, 129.9, 129.2, 128.8 (2C), 128.5, 128.2, 128.1, 127.5, 127.1, 126.9, 126.7, 125.9, 125.7, 123.8, 123.6, 118.7, 118.5, 114.6, 115.5, 75.5, 75.2, 66.0, 65.4, 39.6, 17.6, 17.0.

IR (film): ν (cm^{-1}) 3058, 3025, 2924, 2855, 1598, 1495, 1446, 1351, 1301, 1253, 1175, 1139, 1120, 1093, 1064, 1032, 991, 938, 848, 747, 721, 693, 674, 645, 602, 547, 516, 456.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{26}N_3O^+$ $[M+H]^+$: 384.2070, found: 384.2071.



3d

As for entry 5, starting from **1d** (32.4 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure to give **3d** as a white solid (32.0 mg, 0.072 mmol, 72% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 93% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 15.8 min, t_r (major) = 13.3 min).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.26 (m, 9H), 7.24-7.16 (m, 3H), 7.12-6.98 (m, 3H), 6.87-6.74 (m, 4H), 6.67 (d, *J* = 1.1 Hz, 1H), 6.39 (d, *J* = 7.8 Hz, 1H), 4.70 (d, *J* = 14.8 Hz, 1H), 3.72 (d, *J* = 14.8 Hz, 1H), 3.50 (br, 1H), 2.66 (s, 3H).

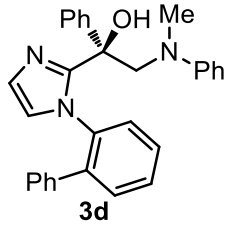
^{13}C NMR (75 MHz, $CDCl_3$) δ 151.6, 149.8, 145.0, 138.8, 138.7, 137.1, 130.3, 128.9, 128.6, 128.3 (2C), 128.2, 128.1, 127.3, 127.2, 127.1, 126.3, 125.0, 124.2, 118.4,114.2, 75.4, 65.2, 39.1.

IR (film): ν (cm^{-1}) 3060, 3020, 1596, 1572, 1502, 1485, 1447, 1436, 1356, 1341, 1327, 1255, 1182, 1097, 1068, 1031, 1008, 992, 958, 940, 909, 767, 751, 732, 699, 672, 547, 463.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{27}N_3NaO^+$ $[M+Na]^+$: 468.2046, found: 468.2047.

General procedure for entries 7 and 10 of Table 1. A dried 10 mL Schlenk tube was charged with the catalyst Λ-IrO (3.70 mg, 0.004 mmol, 4 mol%) (entry 7) or Λ-**RhS** (3.50 mg, 0.004 mmol, 4 mol%) (entry 10) and the 2-acyl imidazole **1d** (32.4 mg, 0.10 mmol, 1.0 eq.). A solution of **2a** (29.0

mg, 0.15 mmol, 1.5 eq.) in MeCN/DMAC (v/v = 4:1, 1 mL) was added in one portion. The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at room temperature for 24 h or 20 h under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was redissolved in THF (2 mL), then TBAF (0.5 mL, 1.0 M in THF, 0.5 mmol) was added. The mixture was stirred at room temperature for another 0.5 h and quenched by the addition of saturated aqueous solution of NH_4Cl, extracted by EtOAc (3 × 10 mL). The combined organic layers were concentrated. The conversion was determined by the crude ^1H NMR analysis.

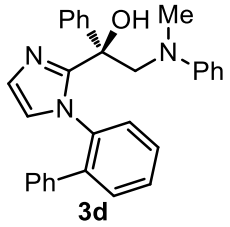


3d

As for entry 7, starting from **1d** (32.4 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure to give **3d** as a white solid (19.0 mg, 0.430 mmol, 43% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 3% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 15.1 min, t_r (major) = 13.3 min).

General procedure for entries 8-9 and 11-12 of Table 1. A dried 10 mL Schlenk tube was charged with the catalyst Λ-**RhS** (3.50 mg, 0.004 mmol, 4 mol%), the photosensitizer $[Ru(bpy)_3](PF_6)_2$ (0.86 mg, 0.001 mmol, 1 mol%) and 2-acyl imidazole **1d** (32.4 mg, 0.10 mmol, 1.0 eq.). A solution of **2a-c** (0.15 mmol, 1.5 eq.) in MeCN/DMAC (v/v = 4:1, 1 mL) was added in one portion. The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp (the catalytic reaction of entry 8 was conducted in the dark). The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was redissolved in THF (2 mL), then TBAF (0.5 mL, 1.0 M in THF, 0.5 mmol) was added. The mixture was stirred at room temperature for another 0.5 h and quenched by the addition of saturated aqueous solution of NH_4Cl, extracted by EtOAc (3 × 10 mL). The combined organic layers were concentrated. The

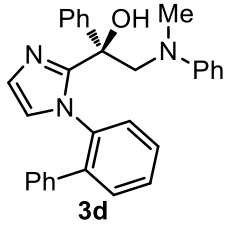
conversion was determined by the crude ^{1}H NMR analysis. If the product was detected in the crude ^{1}H NMR, the residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:7 to 1:4) to afford the products **3d**. The enantiomeric excess was determined by chiral HPLC analysis.



3d

As for entry 8, starting from **1d** (32.4 mg, 0.10 mmol) and **2a** (29.0 mg, 0.15 mmol) according to the general procedure to give **3d** as a white solid (33.8 mg, 0.760 mmol, 76% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 15.1 min, t_r (major) = 13.3 min); $[\alpha]_D^{20}$ = –6.6° (*c* 1.0, CH_2Cl_2).

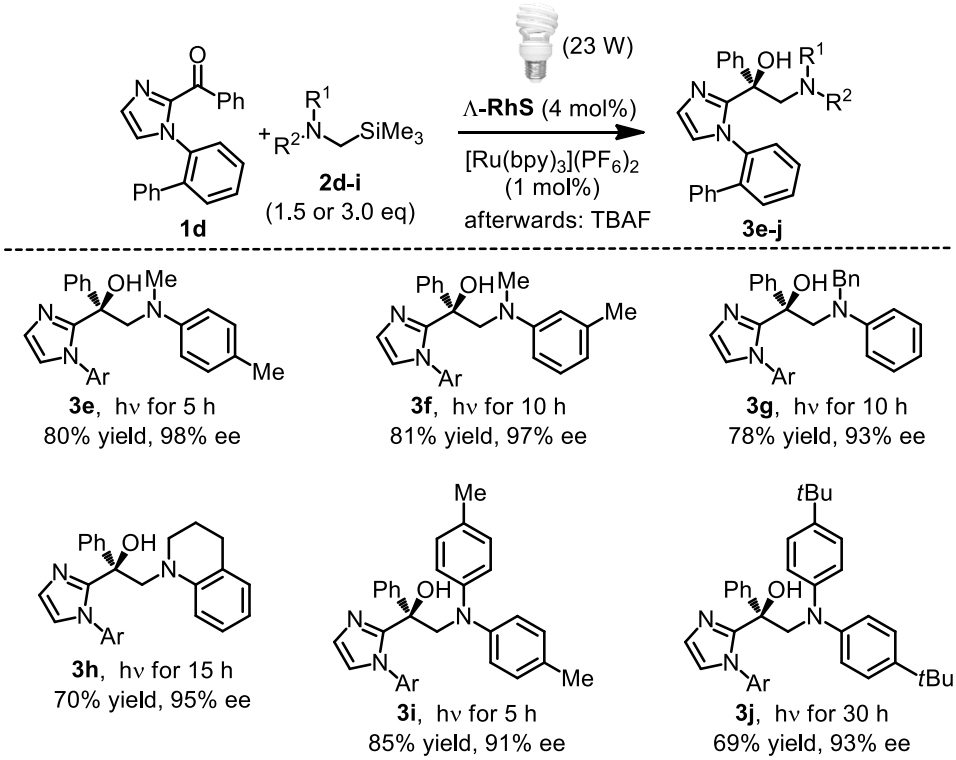
All other spectroscopic data was in agreement with former.

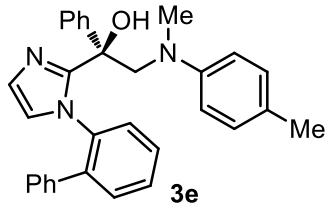


3d

As for entry 11, starting from **1d** (32.4 mg, 0.10 mmol) and **2b** (36.8 mg, 0.15 mmol) according to the general procedure to give **3d** as a white solid (3.0 mg, 0.070 mmol, 7% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 79% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 15.1 min, t_r (major) = 13.3 min).

General procedure for Figure 2. A dried 10 mL Schlenk tube was charged with the catalyst Λ-**RhS** (5.2 mg, 0.0060 mmol, 4 mol%), the photosensitizer $[Ru(bpy)_3](PF_6)_2$ (1.30 mg, 0.0015 mmol, 1 mol%) and 2-acyl imidazole **1d** (48.6 mg, 0.150 mmol, 1.0 eq.). A solution of **2d** (0.45 mmol, 3.0 eq.) or **2e-i** (0.225 mmol, 1.5 eq.) in MeCN/DMAC (v/v = 4:1, 1.5 mL) was added in one portion. The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was redissolved in THF (2 mL), then TBAF (1.0 mL, 1.0 M in THF, 1.0 mmol) was added. The mixture was stirred at room temperature for another 0.5 h and quenched by the addition of saturated aqueous solution of NH_4Cl, extracted by EtOAc (3 × 10 mL). The combined organic layers were concentrated. The residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:7 to 1:4) to afford the products **3e-j**. The enantiomeric excess was determined by chiral HPLC analysis.





3e

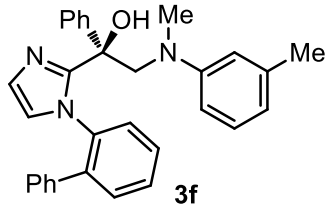
Starting from **1d** (48.9 mg, 0.15 mmol) and **2d** (93.2 mg, 0.45 mmol) with Λ-**RhS** for 5 h according to the general procedure to give **3e** as a pale yellow oil (55.0 mg, 0.120 mmol, 80% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak AD-H column, ee = 98% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 9.9 min, t_r (major) = 6.0 min); $[\alpha]_D^{20}$ = –24.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.42-7.32 (m, 6H), 7.30-7.22 (m, 6H), 7.07 (td, *J* = 8.3, 2.3 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.91 (d, *J* = 0.8 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 2H), 6.63 (d, *J* = 1.0 Hz, 1H), 6.35 (d, *J* = 7.9 Hz, 1H), 4.63 (d, *J* = 14.7 Hz, 1H), 3.73 (br, 1H), 3.58 (d, *J* = 14.7 Hz, 1H), 2.62 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 150.2, 145.8, 139.2, 139.0, 137.5, 130.6, 129.7, 128.8, 128.7, 128.6, 128.5 (2C), 128.2, 128.1, 127.6, 127.5, 126.4, 125.8, 125.4, 124.5, 114.9, 75.5, 66.4, 39.4, 20.3.

IR (film): *v* (cm^{-1}) 3059, 3028, 2924, 2860, 1615, 1599, 1517, 1483, 1446, 1352, 1303, 1252, 1177, 1139, 1117, 1097, 1068, 806, 765, 739, 699, 526, 514, 450, 410, 391.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{30}N_3O^+$ $[M+H]^+$: 460.2383, found: 460.2385.



3f

Starting from **1d** (48.9 mg, 0.15 mmol) and **2g** (46.6 mg, 0.225 mmol) with Λ-**RhS** for 10 h according to the general procedure to give **3f** as a pale yellow oil (56.0 mg, 0.122 mmol, 81% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak AD-H column, ee = 97% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 6.8 min, t_r (major) = 6.0 min); $[\alpha]_D^{20}$ = –30.4° (*c* 1.0, CH_2Cl_2).

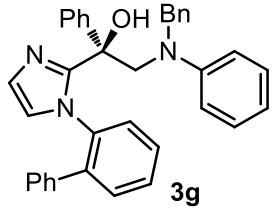
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.41-7.33 (m, 6H), 7.31-7.23 (m, 6H), 7.08-7.06 (m, 1H), 7.04 (d, *J*

= 7.8 Hz, 1H), 6.92 (d, *J* = 1.0 Hz, 1H), 6.64-6.60 (m, 3H), 6.58 (d, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 7.7 Hz, 1H), 4.65 (d, *J* = 14.7 Hz, 1H), 3.66 (d, *J* = 14.7 Hz, 1H), 3.56 (s, 1H), 2.64 (s, 3H), 2.25 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 152.2, 150.1, 145.7, 139.1, 139.0, 138.9, 137.5, 130.6, 129.0, 128.8, 128.7, 128.6, 128.5, 127.6, 127.5 (2C), 126.4, 125.4, 124.5, 119.6, 115.3, 111.7, 75.8, 65.8, 39.4, 21.9.

IR (film): *v* (cm^{-1}) 3058, 2922, 2859, 2811, 1601, 1581, 1494, 1482, 1352, 1303, 1257, 1172, 1139, 1095, 1067, 1030, 1009, 995, 961, 945, 841, 764, 737, 698, 675, 610, 559, 446.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{30}N_3O^+$ $[M+H]^+$: 460.2383, found: 460.2386.



3g

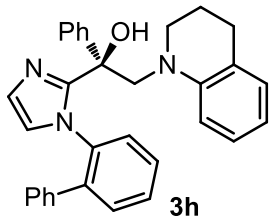
Starting from **1d** (48.9 mg, 0.15 mmol) and **2f** (60.6 mg, 0.225 mmol) with Λ-**RhS** for 10 h according to the general procedure to give **3g** as a pale white solid (61.0 mg, 0.117 mmol, 78% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 93% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 11.2 min, t_r (major) = 10.0 min); $[\alpha]_D^{20}$ = –5.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.42 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.38-7.36 (m, 2H), 7.32-7.28 (m, 6H), 7.24-7.21 (m, 5H), 7.19-7.18 (m, 1H), 7.12 (t, *J* = 7.3 Hz, 2H), 7.07 (td, *J* = 7.9, 1.7 Hz, 1H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.97 (s, 1H), 6.79 (d, *J* = 8.2 Hz, 2H), 6.67 (d, *J* = 1.0 Hz, 1H), 6.35 (d, *J* = 7.7 Hz, 1H), 4.89 (d, *J* = 15.0 Hz, 1H), 4.47 (d, *J* = 17.3 Hz, 1H), 4.09 (d, *J* = 17.3 Hz, 1H), 4.04 (d, *J* = 15.0 Hz, 1H), 3.31 (br, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 149.7 (2C), 144.9, 138.9, 138.6, 137.7, 136.8, 130.4, 128.9, 128.7, 128.4, 128.3 (2C), 128.1, 127.4, 127.3, 127.2, 126.7, 126.4, 126.3, 125.3, 125.1, 124.2, 118.1, 114.5, 76.1, 62.3, 53.5.

IR (film): ν (cm^{-1}) 3060, 3027, 2930, 1964, 1598, 1503, 1483, 1450, 1384, 1450, 1384, 1360, 1303, 1265, 1231, 1197, 1138, 1070, 990, 767, 748, 728, 697, 675, 608, 557, 535, 512, 458.

HRMS (ESI, *m*/*z*) calcd for $C_{36}H_{32}N_3O^+$ $[M+H]^+$: 522.2540, found: 522.2545.



3h

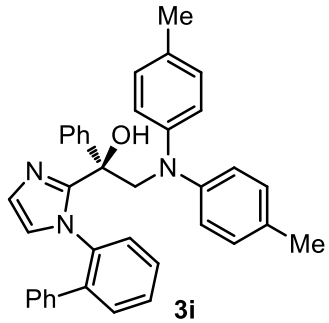
Starting from **1d** (48.9 mg, 0.15 mmol) and **2g** (49.4 mg, 0.225 mmol) with Λ-**RhS** for 15 h according to the general procedure to give **3h** as a pale yellow oil (49.0 mg, 0.105 mmol, 70% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 12.0 min, t_r (major) = 8.8 min); $[\alpha]_D^{20}$ = –17.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.43-7.33 (m, 6H), 7.32-7.23 (m, 6H), 7.04 (td, *J* = 7.8, 1.7 Hz, 1H), 6.94-6.90 (m, 3H), 6.70 (d, *J* = 8.5 Hz, 1H), 6.66-6.60 (m, 2H), 6.27 (d, *J* = 7.9 Hz, 1H), 4.69 (d, *J* = 14.8 Hz, 1H), 3.64 (d, *J* = 14.8 Hz, 1H), 3.59 (br, 1H), 3.19-3.14 (m, 1H), 3.00-2.82 (m, 1H), 2.77-2.66 (m, 2H), 1.84-1.77 (m, 1H), 1.75-1.70 (m, 1H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 149.9, 147.5, 145.6, 138.8, 138.5, 137.0, 130.3, 129.3, 128.5, 128.3 (2C), 128.2, 128.1, 127.3, 127.2, 127.1, 126.7, 126.0, 125.0, 124.1 (2C), 117.8, 114.0, 75.2, 64.7, 51.1, 28.0, 22.0.

IR (film): ν (cm^{-1}) 3060, 3023, 2929, 2841, 1671, 1600, 1575, 1493, 1482, 1444, 1343, 1326, 1301, 1191, 1171, 1137, 1097, 1063, 763, 739, 697, 675, 647,563, 440.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{30}N_3O^+$ $[M+H]^+$: 472.2383, found: 472.2386.



3i

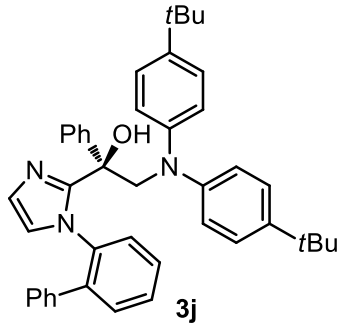
Starting from **1d** (48.9 mg, 0.15 mmol) and **2h** (63.9 mg, 0.225 mmol) with Λ-**RhS** for 5 h according to the general procedure to give **3i** as a pale yellow solid (68.0 mg, 0.128 mmol, 85% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 91% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 8.9 min, t_r (major) = 8.4 min); $[\alpha]_D^{20}$ = +11.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.40-7.34 (m, 2H), 7.31-7.24 (m, 5H), 7.23-7.19 (m, 5H), 7.00 (td, *J* = 8.1, 2.0 Hz, 1H), 6.91 (d, *J* = 8.3 Hz, 4H), 6.77 (d, *J* = 0.9 Hz, 1H), 6.60 (d, *J* = 8.3 Hz, 4H), 6.57 (d, *J* = 0.8 Hz, 1H), 6.19 (d, *J* = 7.8 Hz, 1H), 4.98 (d, *J* = 15.2 Hz, 1H), 4.40 (d, *J* = 15.2 Hz, 1H), 3.39 (s, 1H), 2.22 (s, 6H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 149.3, 147.2, 144.6, 138.6, 138.5, 136.5, 131.2, 130.1, 129.3, 129.2, 128.3, 128.1, 127.9, 127.7, 127.1, 126.8, 126.7, 125.7, 125.1, 123.6, 121.7, 76.1, 64.0, 20.0.

IR (film): *v* (cm^{-1}) 3057, 3026, 2977, 2858, 1687, 1507, 1482, 1439, 1341, 1302, 1264, 1172, 1137, 1101, 1069, 1010, 880, 811, 764, 736, 697, 676, 581, 565, 530, 444.

HRMS (ESI, *m*/*z*) calcd for $C_{37}H_{34}N_3O^+$ $[M+H]^+$: 536.2696, found: 536.2699.



3j

Starting from **1d** (48.9 mg, 0.15 mmol) and **2i** (82.6 mg, 0.225 mmol) with Λ-**RhS** for 30 h according to the general procedure to give **3j** as a white solid (64.0 mg, 0.104 mmol, 69% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak IA

column, ee = 93% (HPLC: IA, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.3 mL/min, 25 °C, t_r (minor) = 18.3 min, t_r (major) = 20.3 min); $[\alpha]_D^{20}$ = +24.6° (*c* 1.0, CH_2Cl_2).

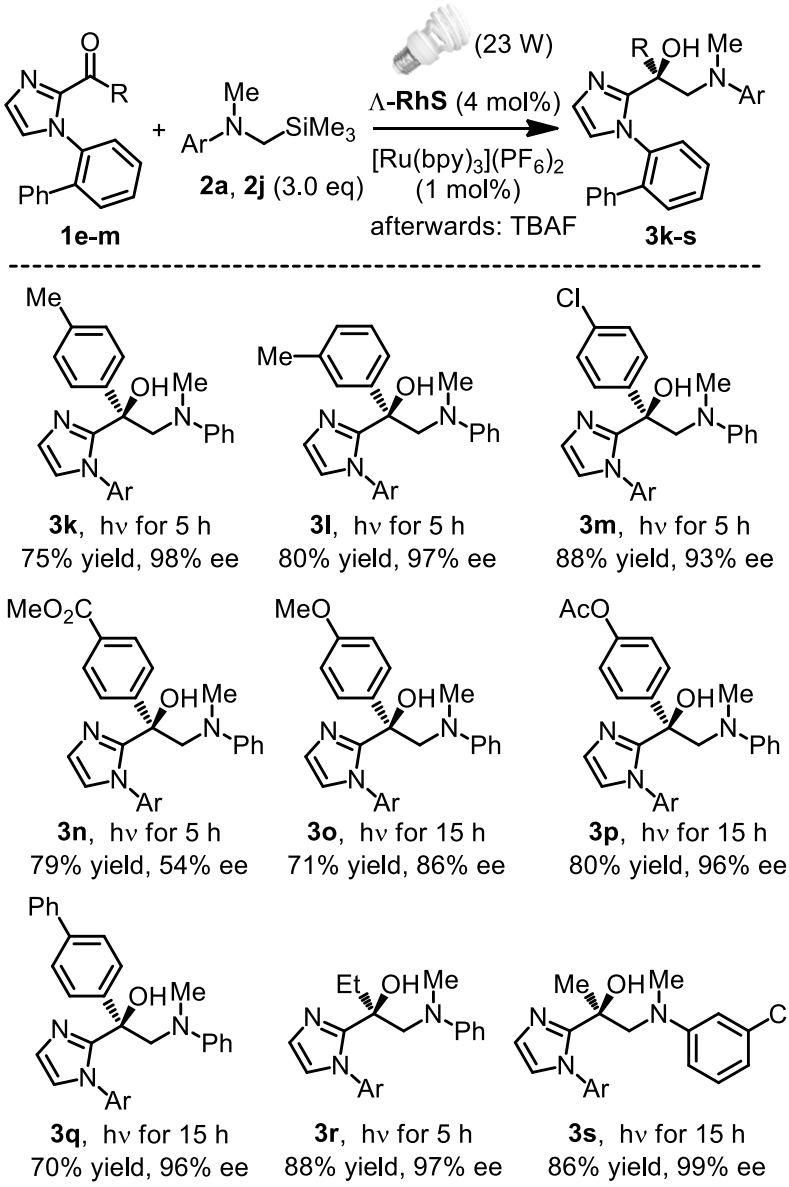
^{1}H NMR (300 MHz, $CDCl_3$, mixture of two rotamers) δ 7.45-7.35 (m, 2H), 7.33-7.24 (m, 4H), 7.23-7.11 (m, 7H), 7.10 (br, 2H), 7.04-6.95 (m, 2H), 6.78 (d, *J* = 1.2 Hz, 1H), 6.75-6.66 (m, 4H), 6.58 (br, 1H), 6.19 (d, *J* = 7.6 Hz, 1H), 5.02 (d, *J* = 15.4 Hz, 0.2 H), 4.92 (d, *J* = 15.1 Hz, 0.8 H, other rotamer), 4.47 (d, *J* = 15.1 Hz, 0.8 H), 4.15 (d, *J* = 14.8 Hz, 0.2 H, other rotamer), 3.44 (br, 0.8 H), 3.27 (br, 0.2 H, other rotamer), 1.17 (s, 18H).

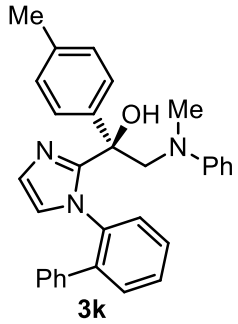
^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 146.9, 144.7, 144.5, 138.9, 138.7, 136.7, 130.3, 128.6, 128.5, 128.4, 128.1, 127.8, 127.7, 127.6, 127.3, 126.9 126.8, 126.5, 126.1, 126.0, 125.7, 125.4, 123.7, 121.5, 75.9, 64.3, 34.0, 31.4.

IR (film): *v* (cm^{-1}) 3058, 2959, 2902, 2865, 1603, 1509, 1483, 1445, 1393, 1363, 1303, 1266, 1201, 1172, 1138, 1100, 1068, 1011, 882, 826, 766, 736, 697, 677, 656, 609, 583, 571, 556.

HRMS (ESI, *m*/*z*) calcd for $C_{43}H_{46}N_3O^+$ $[M+H]^+$: 620.3635, found: 620.3643.

General procedure for Figure 3. A dried 10 mL Schlenk tube was charged with the catalyst Λ-**RhS** (5.20 mg, 0.0060 mmol, 4 mol%), the photosensitizer $[Ru(bpy)_3](PF_6)_2$ (1.30 mg, 0.0015 mmol, 1 mol%) and 2-acyl imidazole **1e-m** (0.150 mmol, 1.0 eq.). A solution of **2a** (87.0 mg, 0.450 mmol, 3.0 eq.) or **2j** (103 mg, 0.450 mmol, 3.0 eq.) in MeCN/DMAC (v/v = 4:1, 1 mL) was added in one portion. The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. The residue was redissolved in THF (2 mL), then TBAF (1.0 mL, 1.0 M in THF, 1.0 mmol) was added. The mixture was stirred at room temperature for another 0.5 h and quenched by the addition of saturated aqueous solution of NH_4Cl, extracted by EtOAc (3 × 10 mL). The combined organic layers were concentrated. The residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:7 to 1:4) to afford the products **3k-s**. The enantiomeric excess was determined by chiral HPLC analysis.





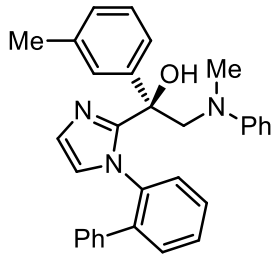
Starting from **1e** (50.7 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 5h according to the general procedure to give **3k** as a white solid (51.6 mg, 0.113 mmol, 75% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 14.8 min, t_r (major) = 10.6 min); $[\alpha]_D^{20}$ = –40.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2, mixture of rotamers) δ 7.41-7.37 (m, 2H), 7.30-7.20 (m, 6H), 7.19-7.14 (m, 4H), 7.10-7.07 (m, 1H), 6.92 (d, *J* = 1.0 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 0.9 Hz, 1H), 6.41 (d, *J* = 7.8 Hz, 1H), 4.63 (d, *J* = 14.7 Hz, 0.8 H), 4.46 (d, *J* = 14.7 Hz, 0.2 H, other rotamer), 3.64 (d, *J* = 14.7 Hz, 1H), 3.42 (br, 0.8 H), 3.32 (br, 0.2 H, other rotamer), 2.66 (s, 2.4 H), 2.56 (s, 0.6 H, other rotamer), 2.36 (s, 2.4 H), 2.28 (s, 0.6 H, other rotamer).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 152.2, 150.2, 142.6, 139.1, 139.0, 137.6, 137.3, 130.6, 129.3, 129.1, 128.8, 128.7, 128.6, 128.5, 127.6, 127.5, 126.4, 125.3, 124.5, 118.5, 114.4, 75.9, 65.7, 39.2, 21.1.

IR (film): *v* (cm^{-1}) 3059, 3026, 2921, 2867, 2813, 1598, 1503, 1482, 1438, 1411, 1351, 1303, 1252, 1172, 1139, 1113, 1088, 1034, 992, 952, 927, 915, 816, 765, 735, 695, 559, 469.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{30}N_3O^+$ $[M+H]^+$: 460.2383, found: 460.2387.



3l

Starting from **1f** (50.7 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 5h according to the general procedure to give **3l** as a white solid (55.0 mg, 0.12 mmol, 80% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 11.7 min, t_r (major) = 10.3 min); $[\alpha]_D^{20}$ = –18.2° (*c* 1.0, CH_2Cl_2).

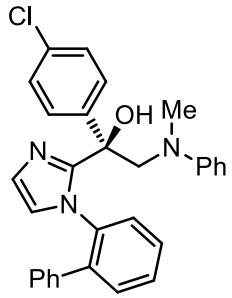
^{1}H NMR (500 MHz, CD_2Cl_2, mixture of rotamers) δ 7.40-7.38 (m, 2H), 7.28-7.20 (m, 5H), 7.18-7.04 (m, 6H), 6.92 (d, *J* = 0.7 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 0.9 Hz, 1H), 6.38 (d, *J* = 7.9 Hz, 1H), 4.65 (d, *J* = 14.8 Hz, 0.8 H), 4.52 (d, *J* = 14.3 Hz, 0.2 H, other rotamer), 3.67 (d, *J* = 14.7 Hz, 1H), 3.46 (br, 0.8 H), 3.43 (br, 0.2 H, other rotamer), 2.66 (s, 2.4 H), 2.56 (s, 0.6 H, other rotamer), 2.33 (s, 2.4 H), 2.21 (s, 0.6 H, other rotamer).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 152.2, 150.1, 145.5, 139.1, 139.0, 138.4, 137.5, 130.6, 129.1, 128.9,

128.7, 128.6, 128.5 (2C),128.3, 128.1, 127.6, 127.4, 126.4, 126.0, 124.5, 122.5, 118.5, 114.4, 75.8, 65.7, 39.3, 21.7.

IR (film): *v* (cm^{-1}) 3055, 3025, 2920, 2861, 1598, 1503, 1482, 1438, 1350, 1303, 1256, 1180, 1034, 992, 942, 788, 747, 736, 695, 676, 649, 609, 556, 514, 438.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{30}N_3O^+$ $[M+H]^+$: 460.2383, found: 460.2386.



3m

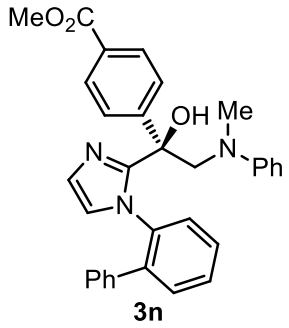
Starting from **1g** (53.8 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 5h according to the general procedure to give **3m** as a white solid (63.2 mg, 0.13 mmol, 88% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 93% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 6.5 min, t_r (major) = 5.0 min); $[\alpha]_D^{20}$ = + 11.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.44-7.43 (m, 2H), 7.37-7.31 (m, 4H), 7.29-7.23 (m, 5H), 7.22-7.19 (m, 3H), 7.17-7.12 (m, 1H), 7.01 (d, *J* = 1.2 Hz, 1H), 6.82-6.80 (m, 3H), 6.72 (d, *J* = 1.2 Hz, 1H), 6.45 (d, *J* = 7.8 Hz, 1H), 4.67 (d, *J* = 14.8 Hz, 1H), 3.63 (d, *J* = 14.8 Hz, 1H), 3.54 (s, 1H), 2.64 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.5, 149.3, 143.5, 138.8, 138.6, 136.9, 133.1, 130.4, 129.0 (2C), 128.8, 128.4, 128.3, 128.0, 127.4, 127.2, 126.5, 126.4, 124.4, 118.7, 114.3, 75.0, 65.2, 39.0.

IR (film): *v* (cm^{-1}) 3137, 2923, 2853, 1652, 1583, 1568, 1504, 1481, 1445, 1434, 1395, 1341, 1305, 1280, 1256, 1233, 1165, 1141, 1084, 1011, 928, 872, 794, 755, 737, 721, 695, 653, 612, 593, 550, 497, 427.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{27}ClN_3O^+$ $[M+H]^+$: 480.1837, found: 480.1835.



3n

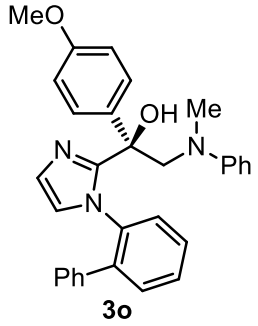
Starting from **1h** (57.3 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 5h according to the general procedure to give **3n** as a white solid (59.1 mg, 0.118 mmol, 79% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 54% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 6.1 min, t_r (major) = 4.8 min); $[\alpha]_D^{20}$ = -6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2, mixture of rotamers) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 2H, other rotamer), 7.48 (d, *J* = 8.4 Hz, 2H), 7.43-7.38 (m, 2H), 7.37-7.31 (m, 1H), 7.23-7.20 (m, 3H), 7.19-7.16 (m, 2H), 7.09-7.06 (m, 1H), 7.02 (br, 1H), 6.81 (t, *J* = 8.2 Hz, 1H), 6.82-6.76 (m, 3H), 6.70 (br, 1H), 6.34 (d, *J* = 7.8 Hz, 1H), 4.71 (d, *J* = 15.0 Hz, 0.8 H), 4.51 (d, *J* = 14.8 Hz, 0.2 H, other rotamer), 3.93 (s, 3H), 3.65 (d, *J* = 14.6 Hz, 1H), 3.60 (br, 1H), 2.60 (s, 2.4 H), 2.57 (s, 0.6 H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.0, 151.6, 149.2, 139.0, 138.7, 136.9, 130.5, 129.8, 129.3, 129.1, 129.0, 128.4 (2C), 128.0, 127.5, 127.4, 126.5, 125.5, 125.2, 124.6, 118.9, 114.4, 75.3, 65.2, 52.2, 39.2.

IR (film): *v* (cm^{-1}) 2953, 2897, 2807, 1722, 1599, 1504, 1441, 1410, 1362, 1275, 1246, 1186, 1106, 846, 743, 693, 516.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{29}N_3NaO_3^+$ $[M+Na]^+$: 526.2101, found: 526.2101.



3o

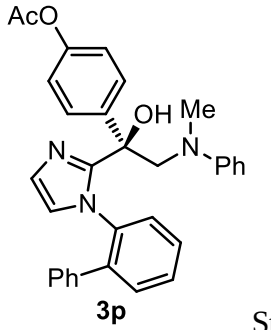
Starting from **1i** (53.1 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 15h according to the general procedure to give **3o** as a white solid (50.5 mg, 0.106 mmol, 71% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 86% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 7.5 min, t_r (major) = 5.8 min); $[\alpha]_D^{20}$ = –33° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2, mixture of rotamers) δ 7.44-7.38 (m, 2H), 7.33-7.22 (m, 6H), 7.17 (dd, *J* = 7.3, 1.3 Hz, 2H), 7.11-7.08 (m, 1H), 7.00-6.90 (m, 3H), 6.83-6.80 (m, 3H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 0.9 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 4.66 (d, *J* = 14.8 Hz, 0.8 H), 4.52 (d, *J* = 14.4 Hz, 0.2 H, other rotamer), 3.76 (s, 2.4 H), 3.67 (d, *J* = 14.8 Hz, 1H), 3.65 (s, 0.6 H, other rotamer), 3.50 (br, 1H), 2.66 (s, 2.4 H), 2.58 (s, 0.6 H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.8, 151.8, 149.7, 146.9, 138.8, 137.1, 130.3, 129.3, 128.8, 128.5, 128.3, 128.2, 127.3, 127.1, 126.1, 124.2, 118.3, 117.4, 114.1, 112.7, 110.5, 75.3, 65.3, 55.2, 38.9.

IR (film): *v* (cm^{-1}) 3059, 2925, 2862, 1599, 1503, 1445, 1413, 1352, 1301, 1246, 1172, 1085, 1031, 951, 828, 737, 695, 559, 521, 470.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{29}N_3NaO_2^+$ $[M+Na]^+$: 498.2152, found: 498.2148.



3p

Starting from **1j** (57.3 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 15h according to the general procedure to give **3p** as a pale yellow oil (60.4 mg, 0.120

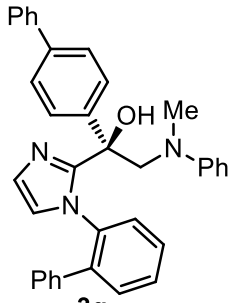
mmol, 80% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 9.4 min, t_r (major) = 7.2 min); $[\alpha]_D^{20}$ = –40° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$, mixture of rotamers) 7.44-7.40 (m, 3H), 7.34-7.32 (m, 1H), 7.28-7.19 (m, 6H), 7.16-7.10 (m, 1H), 7.09-7.06 (m, 2H), 7.00 (br, 1H), 6.88-6.74 (m, 4H), 6.70 (d, *J* = 1.1 Hz, 1H), 6.45 (d, *J* = 7.9 Hz, 1H), 4.70 (d, *J* = 14.7 Hz, 0.75 H), 4.45 (d, *J* = 14.1 Hz, 0.25 H, other rotamer), 3.67 (d, *J* = 14.8 Hz, 1H), 3.57 (br, 1H), 2.66 (s, 2.25 H), 2.60 (s, 0.75 H, other rotamer), 2.34 (s, 2.25 H), 2.31 (s, 0.75 H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 151.6, 149.9, 149.6, 138.8, 138.7, 130.3, 129.0 (2C), 128.8, 128.3 (2C),128.2, 128.0, 127.4, 127.3, 126.5, 126.2, 124.4, 121.4, 118.7, 114.3, 75.1, 65.2, 39.0, 21.2.

IR (film): *v* (cm^{-1}) 3059, 2925, 2869, 1757, 1598, 1499, 1443, 1363, 1304, 1256, 1195, 1116, 1084, 1012, 954, 909, 845, 737, 695, 554, 521.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{29}N_3NaO_3^+$ $[M+Na]^+$: 526.2101, found: 526.2098.



3q

Starting from **1k** (60.0 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 15 h according to the general procedure to give **3q** as a white solid (46.4 mg, 0.105 mmol, 70% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 16.5 min, t_r (major) = 11.5 min); $[\alpha]_D^{20}$ = –26.2° (*c* 1.0, CH_2Cl_2).

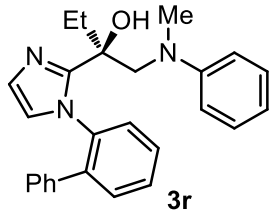
^{1}H NMR (500 MHz, CD_2Cl_2, mixture of rotamers) δ 7.69 (d, *J* = 7.7 Hz, 2H), 7.64 (d, *J* = 8.4, 2H), 7.51-7.43 (m, 5H), 7.42-7.27 (m, 6H), 7.22 (t, *J* = 8.7 Hz, 2H), 7.16-7.12 (m, 1H), 7.00 (d, *J* =1.1

Hz, 1H) 6.87 (d, *J* =8.4 Hz, 2H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.72 (d, *J* = 1.0, 1H), 6.51 (d, *J* = 8.0, 1H), 4.74 (d, *J* = 14.8 Hz, 0.8 H), 4.51 (d, *J* = 14.8 Hz, 0.2 H, other rotamer), 3.74 (d, *J* = 14.7 Hz, 1H), 3.57 (br, 0.8 H), 3.43 (br, 0.2 H, other rotamer), 2.72 (s, 2.4 H), 2.63 (s, 0.6 H, other rotamer).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 152.2, 150.0, 144.6, 140.9, 140.2, 139.1 (2C), 137.5, 130.7, 129.2, 129.1, 128.9, 128.7, 128.6 (2C), 127.7, 127.6, 127.3, 127.2, 126.6, 125.9, 124.6, 118.6, 114.5, 75.8, 65.7, 39.3.

IR (film): *v* (cm^{-1}) 3383, 3060, 2967, 2878, 1597, 1494, 1446, 1366, 1303, 1268, 1193, 1161, 1132, 1104, 1070, 951, 740, 696, 608, 533, 457.

HRMS (ESI, *m*/*z*) calcd for $C_{36}H_{32}N_3O^+$ $[M+H]^+$: 522.2540, found: 522.2543.



3r

Starting from **1l** (40.8 mg, 0.15 mmol) and **2a** (87.4 mg, 0.45 mmol) with Λ-**RhS** for 5h according to the general procedure to give **3r** as a white solid (52.4 mg, 0.132 mmol, 88% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25 °C, t_r (minor) = 19.2 min, t_r (major) = 15.9 min); $[\alpha]_D^{20}$ = +19.2° (*c* 1.0, CH_2Cl_2).

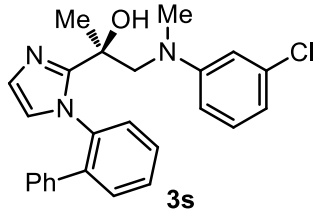
^{1}H NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 7.52-7.46 (m, 1H), 7.44-7.32 (m, 2H), 7.30-7.24 (m, 2H), 7.23-7.18 (m, 2H), 7.17-7.11 (m, 4H), 7.09 (d, *J* = 1.1 Hz, 1H), 7.03 (d, *J* = 1.1 Hz, 1H, other rotamer), 6.95-6.91 (m, 1H), 6.70 (dd, *J* = 12.5, 6.9 Hz, 1H), 6.62 (d, *J* = 8.3 Hz, 1H), 6.51 (d, *J* = 8.3 Hz, 1H), 3.64 (d, *J* = 14.8 Hz, 0.4 H), 3.55 (d, *J* = 14.9 Hz, 0.6 H, other rotamer), 3.47 (d, *J* = 14.8 Hz, 0.4 H), 3.39 (d, *J* = 14.9 Hz, 0.6 H, other rotamer), 2.70 (br, 0.4 H), 2.62 (s, 1.8 H), 2.42 (s, 1.2 H, other rotamer), 2.26 (br, 0.6 H, other rotamer), 1.86-1.73 (m, 1.2 H), 1.58-1.48 (m, 0.8 H, other rotamer), 0.67 (t, *J* = 7.5 Hz, 1.2 H), 0.40 (t, *J* = 7.4 Hz, 1.8 H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$, mixture of rotamers) δ 151.5, 150.8, 150.6, 150.3, 139.7 (2C), 138.6,

138.5, 137.7, 137.4, 130.9, 130.6, 129.1, 129.0 (2C), 128.8, 128.7, 128.6, 128.5, 128.4, 127.9, 127.7, 127.6, 127.5, 127.0, 126.7, 124.9, 124.6, 117.4, 117.2, 113.4, 112.8, 78.2, 64.5, 64.3, 39.8, 39.1, 33.7, 31.3, 8.0, 6.8.

IR (film): *v* (cm^{-1}) 3060, 2965, 2932, 2874, 1598, 1504, 1481, 1439, 1371, 1330, 1303, 1277, 1256, 1213, 1191, 1166, 1129, 1118, 1100, 1025, 989, 926, 879, 761, 700, 692, 610, 556, 526, 484.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{28}N_3O^+$ $[M+H]^+$: 398.2227, found: 398.2226.



3s

Starting from **1m** (39.3 mg, 0.15 mmol) and **2j** (103 mg, 0.45 mmol) with Λ-**RhS** for 15h according to the general procedure to give **3s** as a white solid (54.2 mg, 0.130 mmol, 86% yield). Enantiomeric excess established by HPLC analysis by using a Chiralpak OD-H column, ee = 99% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90: 10, flow rate 1.0 mL/min, 25 °C, t_r (minor) = 8.3 min, t_r (major) = 7.4 min); $[\alpha]_D^{20}$ = –8.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$, mixture of rotamers) δ 7.58-7.47 (m, 2H), 7.46-7.27 (m, 3H), 7.26-7.09 (m, 4H), 7.07-7.01 (m, 1H), 6.99 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.92 (dd, *J* = 13.2, 1.2 Hz, 1H), 6.62 (dt, *J* = 7.8, 1.8 Hz, 1H), 6.56 (dt, *J* = 12.2, 2.4 Hz, 1H), 6.47 (qd, *J* = 17.7, 8.5, 2.4 Hz, 1H), 3.60-3.50 (m, 1H), 3.48-3.28 (m, 1H), 3.00 (br, 0.6 H), 2.65 (s, 1.8 H), 2.60 (s, 1.2 H, other rotamer), 2.30 (br, 0.4 H, other rotamer), 1.23 (s, 1.2 H), 1.13 (s, 1.8 H, other rotamer).

^{13}C NMR (75 MHz, CD_2Cl_2, mixture of rotamers) δ 152.4, 152.2, 151.7, 151.3, 140.1, 140.0, 138.8, 138.7, 137.8, 137.6, 135.1, 134.9, 131.4, 131.0, 130.2, 130.1, 129.8, 129.6, 129.0, 128.8 (3C), 128.3 (2C), 128.2, 128.1, 127.4, 126.8, 125.3, 124.8, 116.9, 116.7, 112.9, 112.8, 111.4, 111.3, 75.7, 74.8, 64.8, 63.4, 40.0 (2C), 26.5, 26.3.

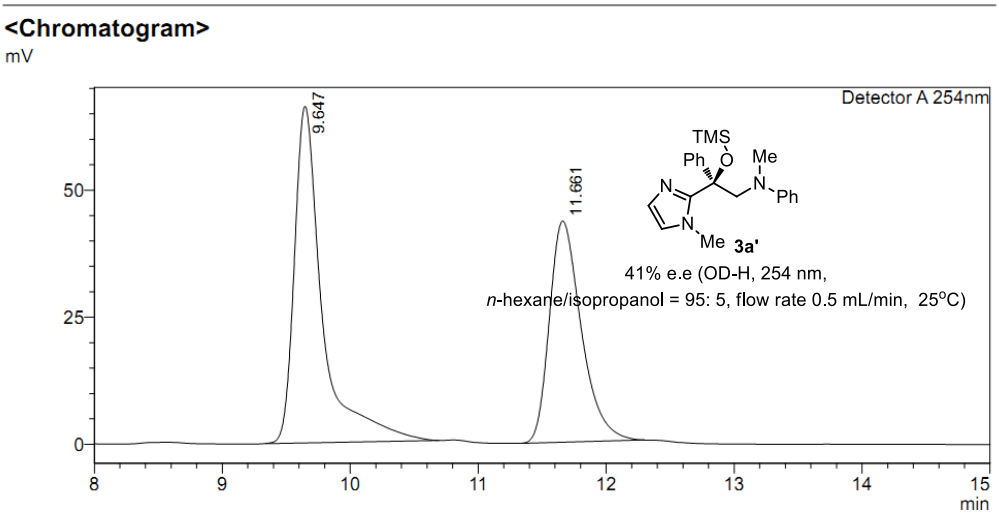
IR (film): *v* (cm^{-1}) 2971, 2918, 2849, 1594, 1558, 1497, 1481, 1373, 1339, 1308, 1263, 1195, 1179, 1126, 1098, 1080, 1001, 988, 979, 948, 921, 819, 773, 762, 752, 732, 699, 675, 603, 572, 546, 499, 442.

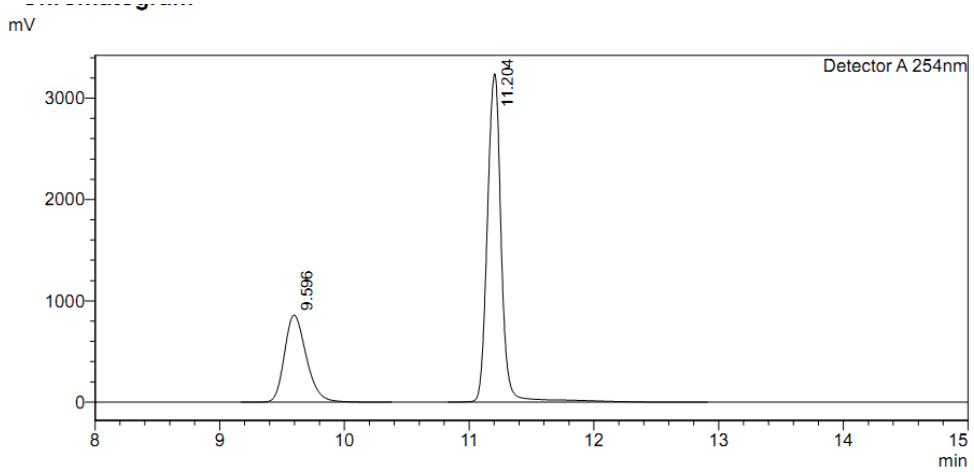
HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{25}ClN_3O^+$ $[M+H]^+$: 418.1681, found: 418.1684.

4. Chiral Chromatography

Enantiomeric purities of the compounds **3a-s** were determined with a Daicel Chiralpak IA, OD-H or AD-H (250 × 4.6 mm) HPLC column on an Agilent 1200, 1260 or Shimadzu Lc-2030c HPLC system by using *n*-hexane/isopropanol as mobile phase, column temperature = 25 °C, UV-absorption was measured at 254 nm.

4.1. Enantioselectivities of Catalytic Reactions in Table 1



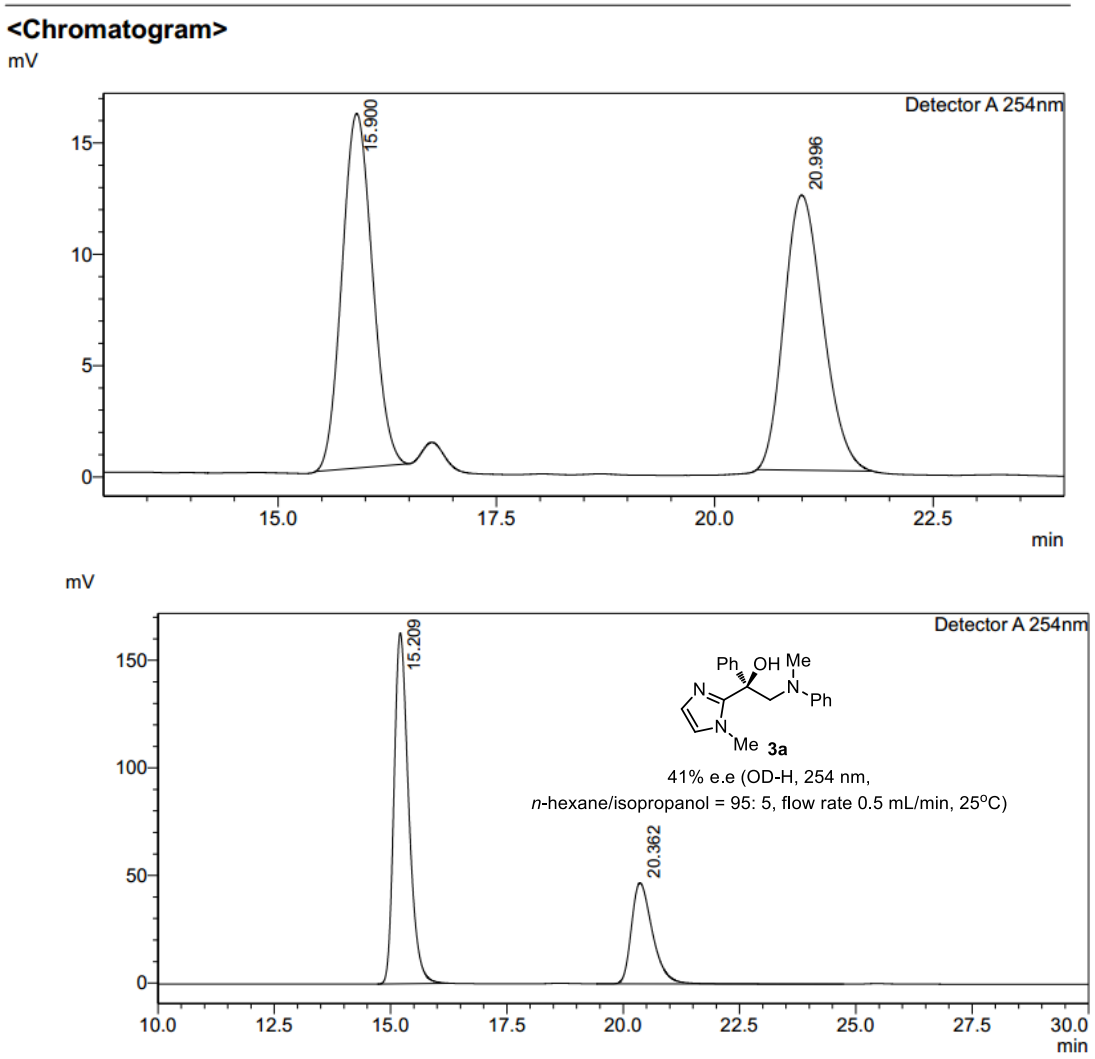


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area%	Height%
1	9.596	29.371	20.946
2	11.204	70.629	79.054
Total		100.000	100.000

Figure S1. HPLC traces of *rac*-**3a'** (reference) and (*S*)-**3a'** for entry 1 (Table 1). Area integration = 70.6:29.4 (41.2% ee).

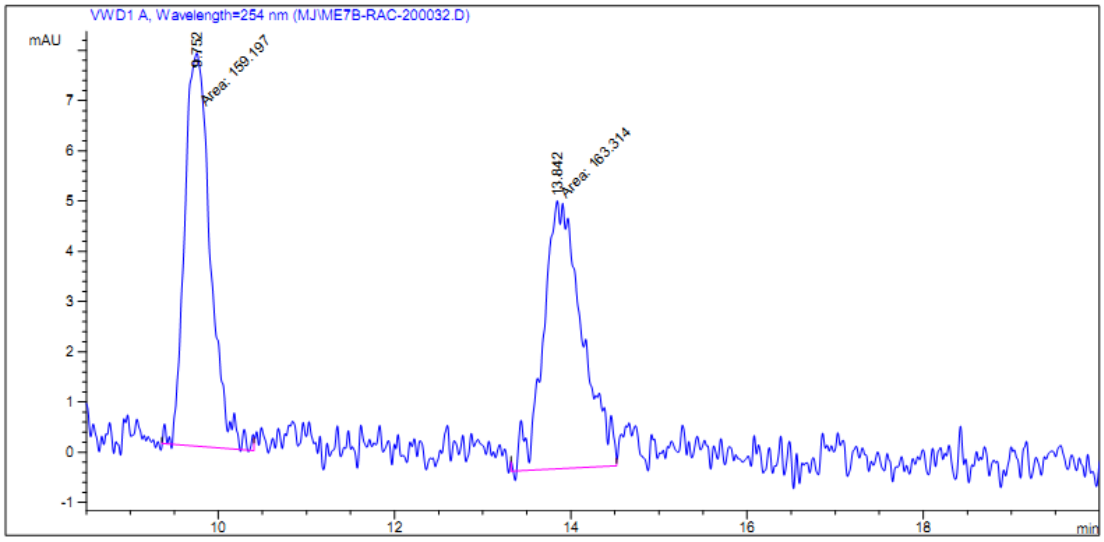


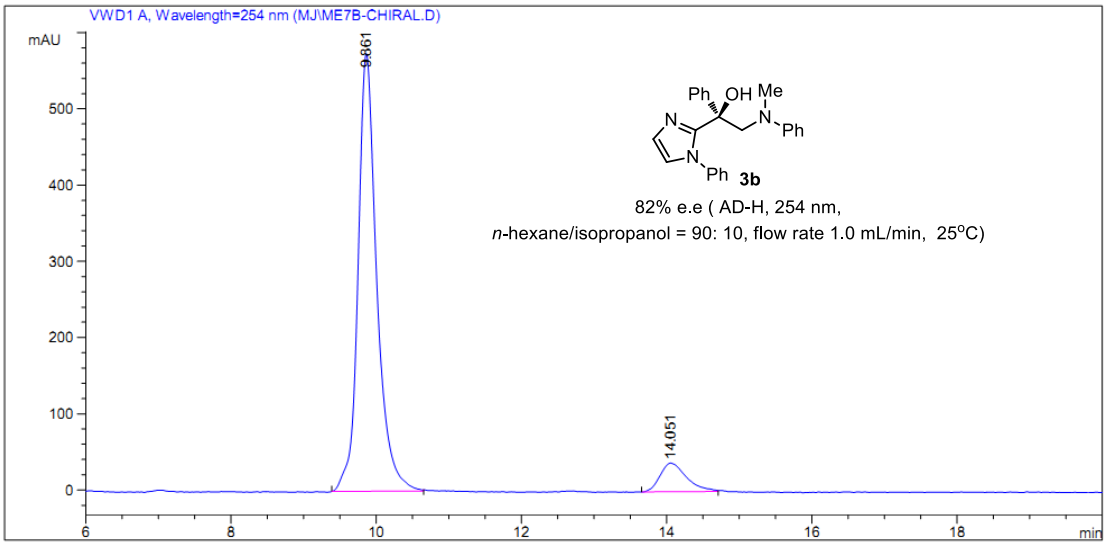
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Height	Area%
1	15.209	162937	70.663
2	20.362	46930	29.337
Total		209867	100.000

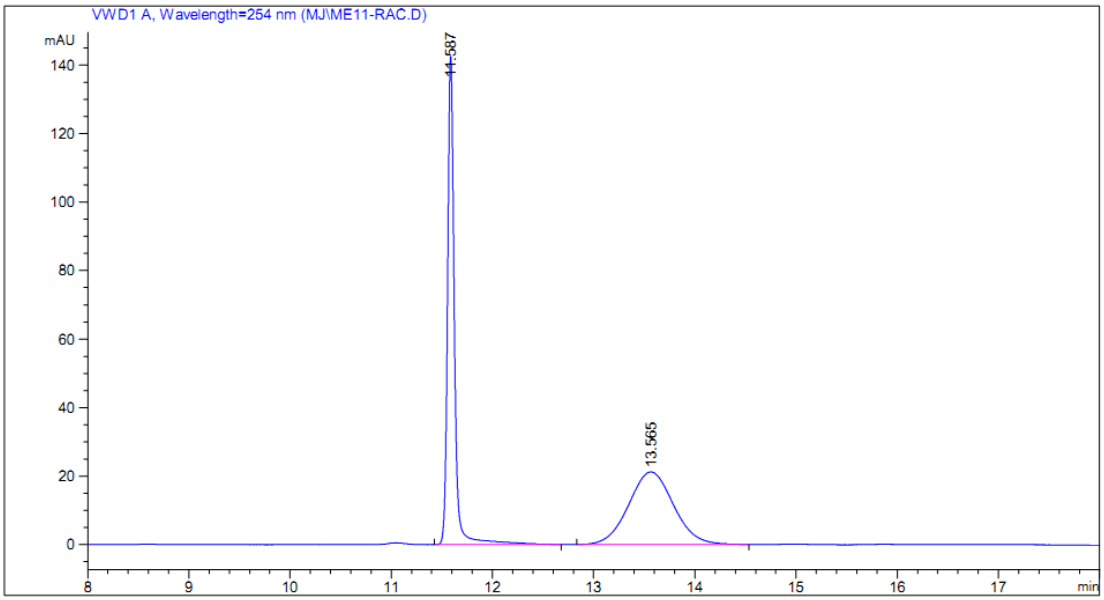
Figure S2. HPLC traces of *rac*-**3a** (reference) and (*S*)-**3a** for entry 2 (Table 1). Area integration = 70.7:29.3 (41.4% ee).

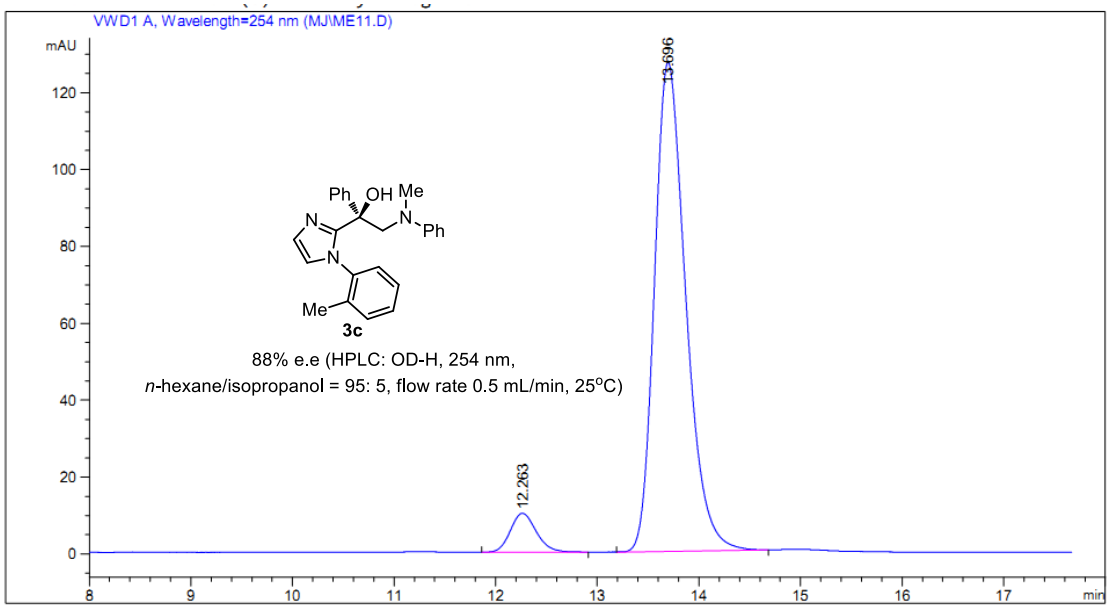




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.861	BB	0.2660	1.03046e4	574.54633	90.9323
2	14.051	MM	0.4476	1027.56458	38.26324	9.0677

Figure S3. HPLC traces of *rac*-**3b** (reference) and (*S*)-**3b** for entry 3 (Table 1). Area integration = 90.9:9.1 (81.8% ee).

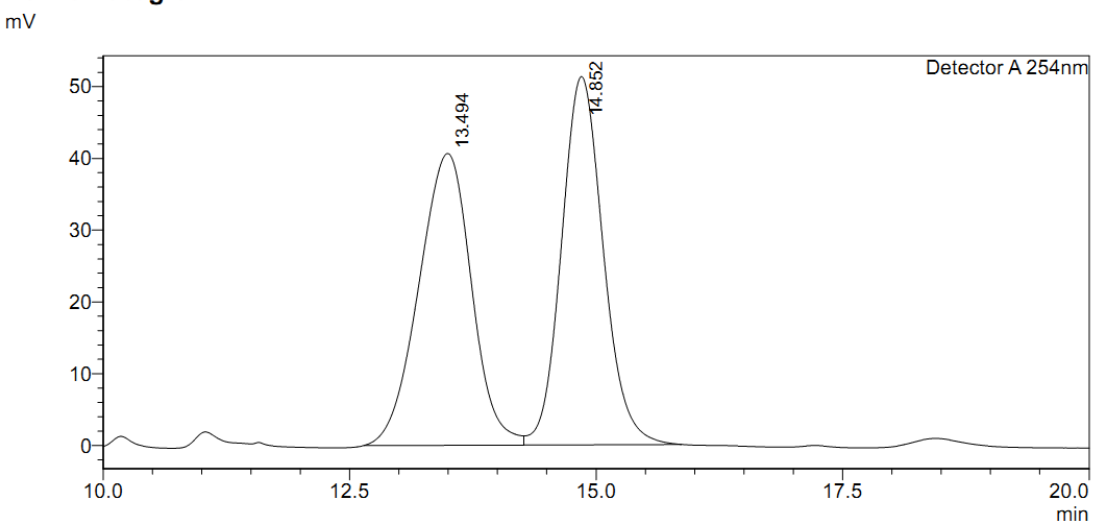


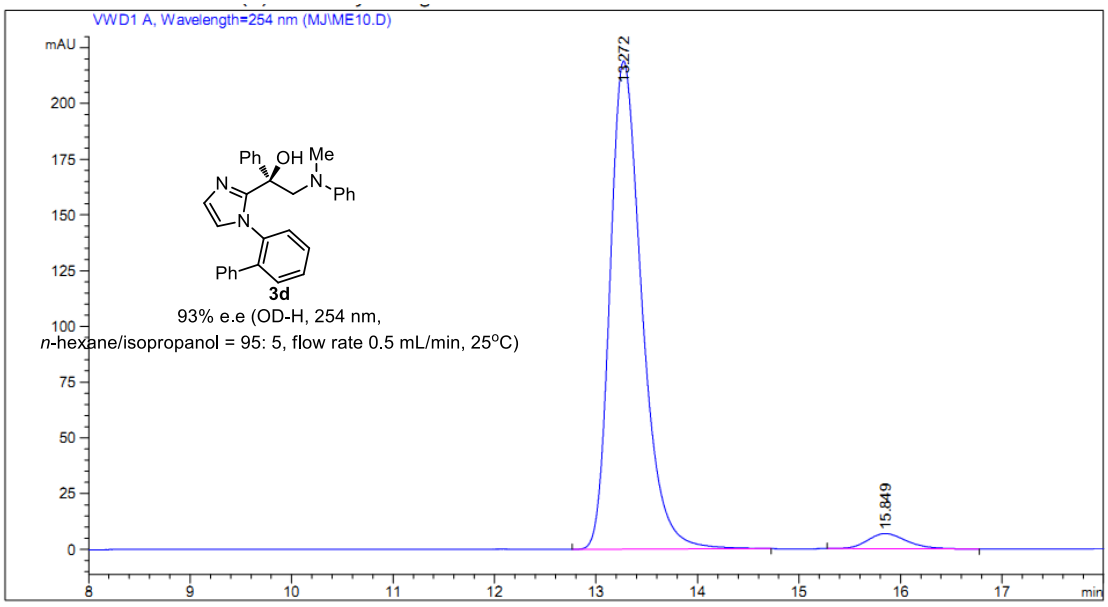


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.263	BB	0.2140	179.30820	10.13283	6.1965
2	13.696	BV R	0.3174	2714.38672	127.20956	93.8035

Figure S4. HPLC traces of *rac*-**3c** (reference) and (*S*)-**3c** for entry 4 (Table 1). Area integration = 93.8:6.2 (87.6% ee).

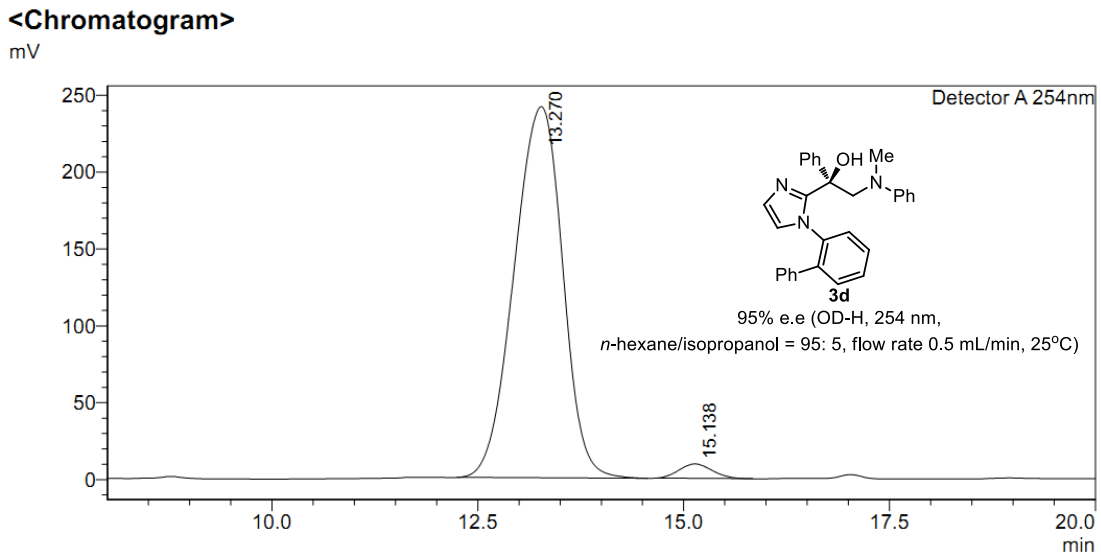
<Chromatogram>





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.272	BB	0.3314	4766.38721	219.01707	96.2819
2	15.849	BB	0.3159	184.06299	6.81893	3.7181

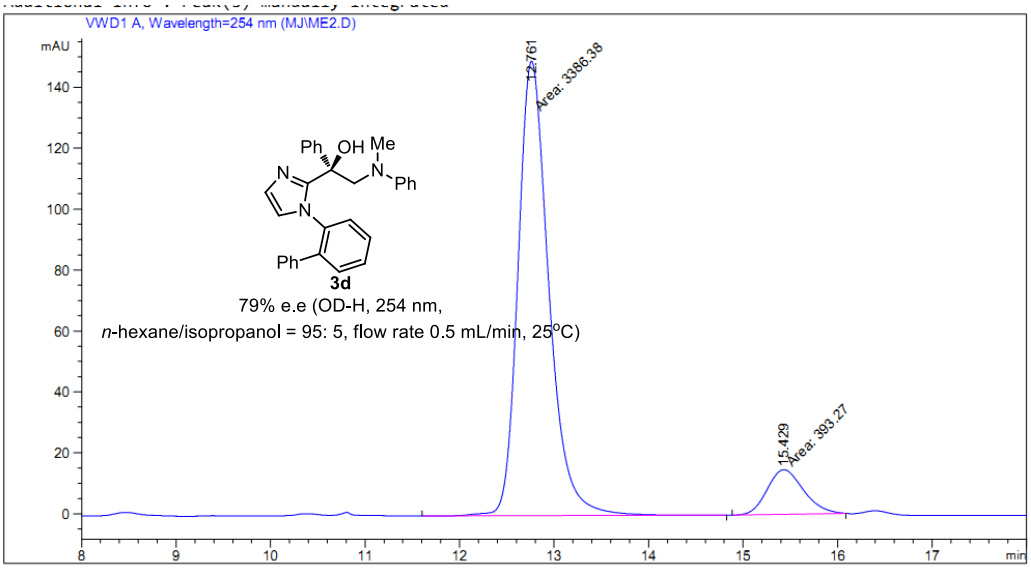
Figure S5. HPLC traces of *rac*-**3d** (reference) and (*S*)-**3d** for entry 5 (Table 1). Area integration = 96.3:3.7 (92.6% ee).



Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.270	9890583	241364	97.402
2	15.138	263857	9359	2.598
Total		10154440	250723	100.000

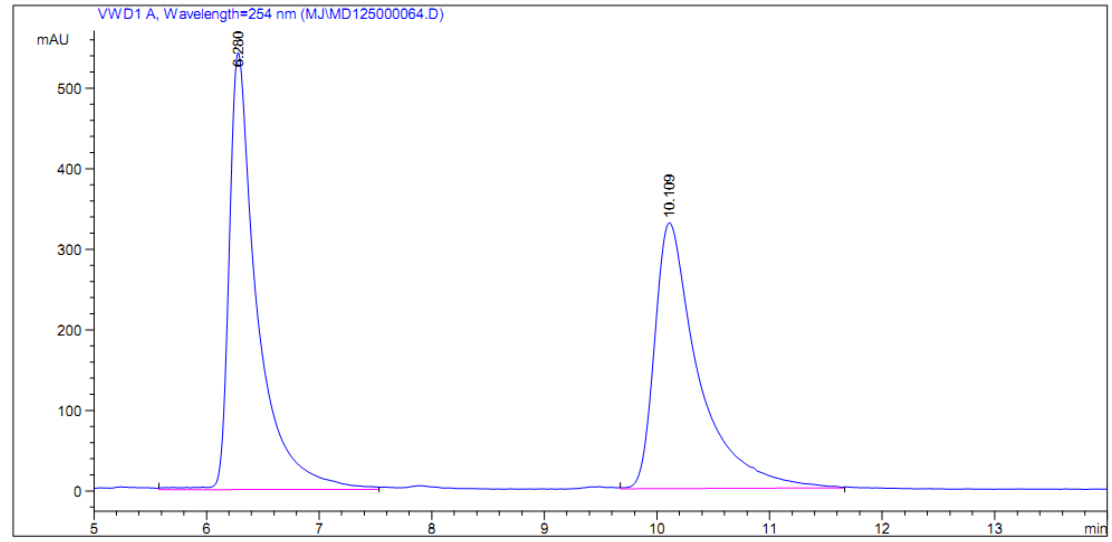
Figure S6. HPLC traces of (*S*)-**3d** for entry 8 (Table 1). Area integration = 97.4:2.6 (94.8% ee).

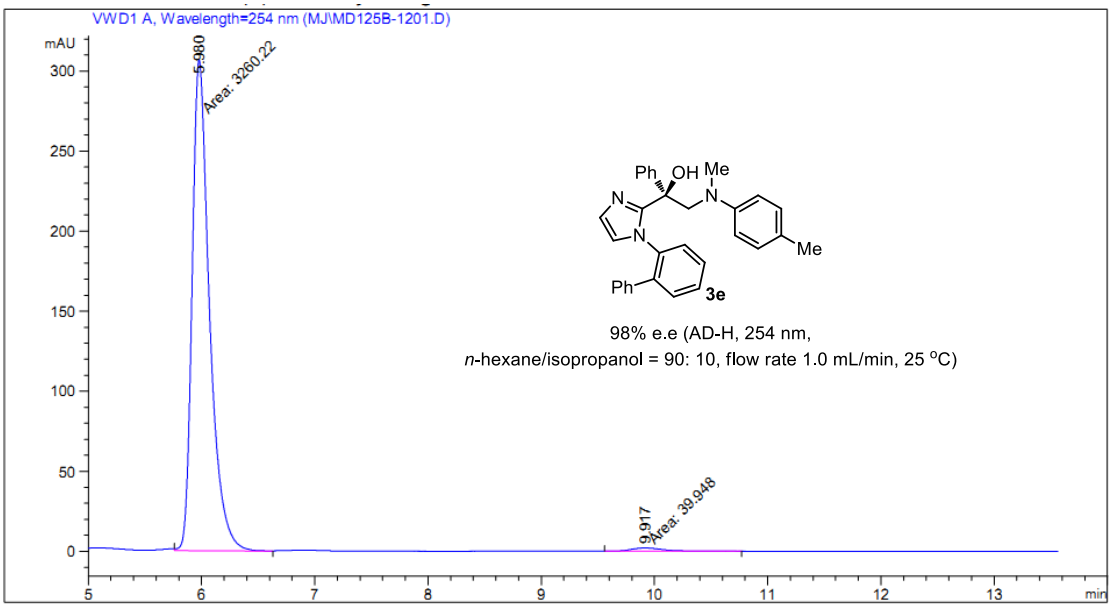


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.761	MM	0.3782	3386.37866	149.22783	89.5951
2	15.429	MM	0.4466	393.27032	14.67682	10.4049

Figure S7. HPLC traces of (*S*)-**3d** for entry 11 (Table 1). Area integration = 89.6:10.4 (79% ee).

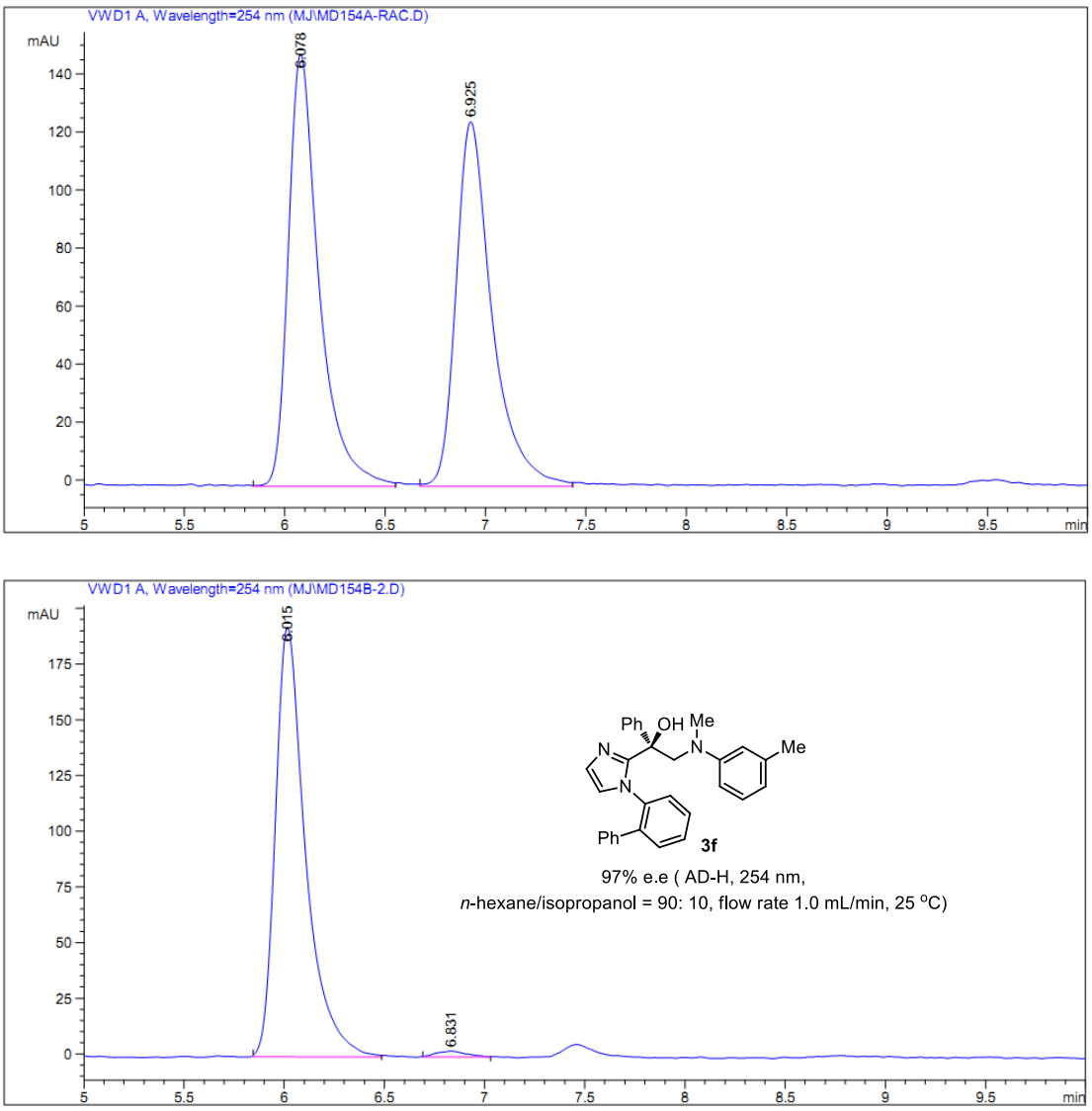
4.2. Enantioselectivities of Catalytic Reactions in Figure 2





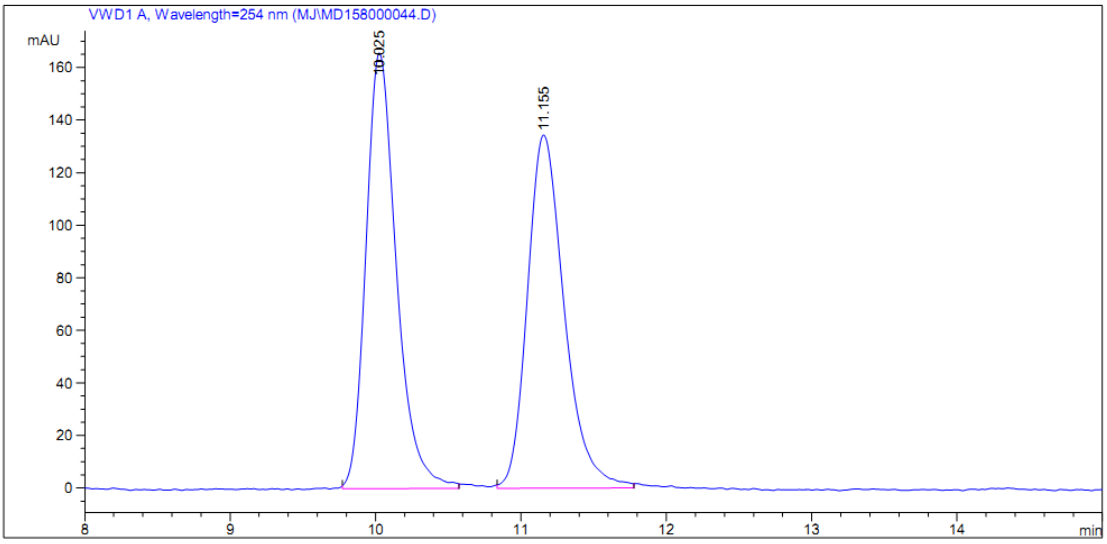
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.980	FM	0.1774	3260.22437	306.32999	98.7895
2	9.917	MM	0.3193	39.94799	2.08492	1.2105

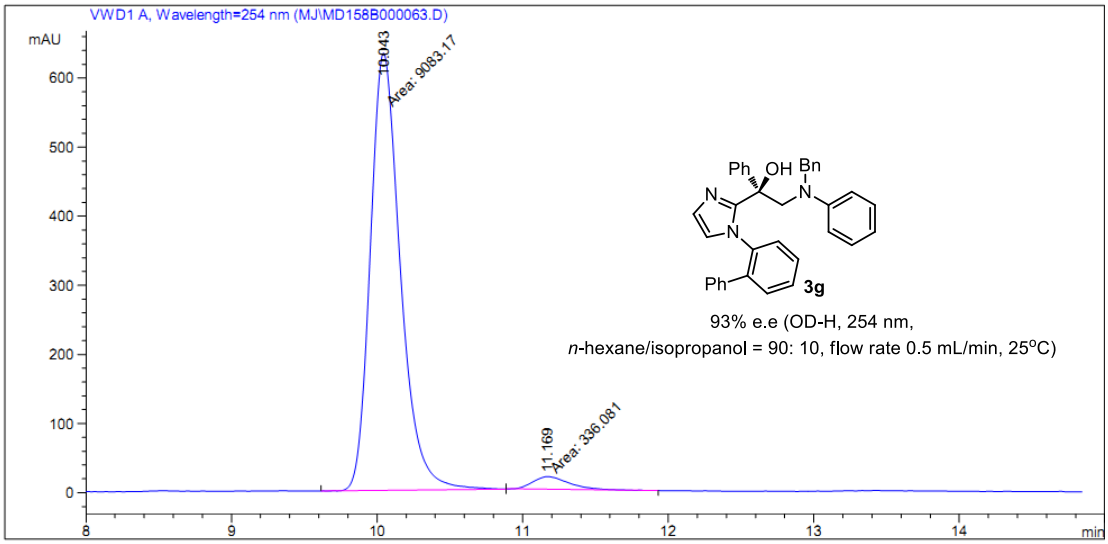
Figure S8. HPLC traces of *rac*-**3e** (reference) and (*S*)-**3e**. Area integration = 98.8:1.2 (97.6% ee).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.015	BB	0.1547	2029.23083	193.00230	98.4628
2	6.831	BB	0.1502	31.68109	2.84675	1.5372

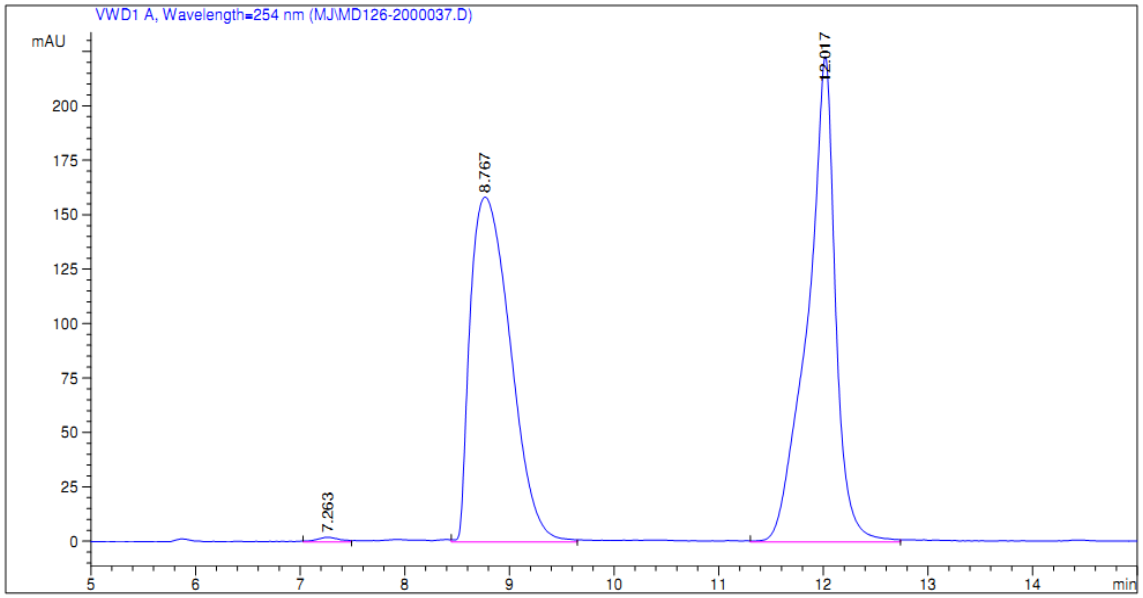
Figure S9. HPLC traces of *rac*-**3f** (reference) and (*S*)-**3f**. Area integration = 98.5:1.5 (97.0% ee).

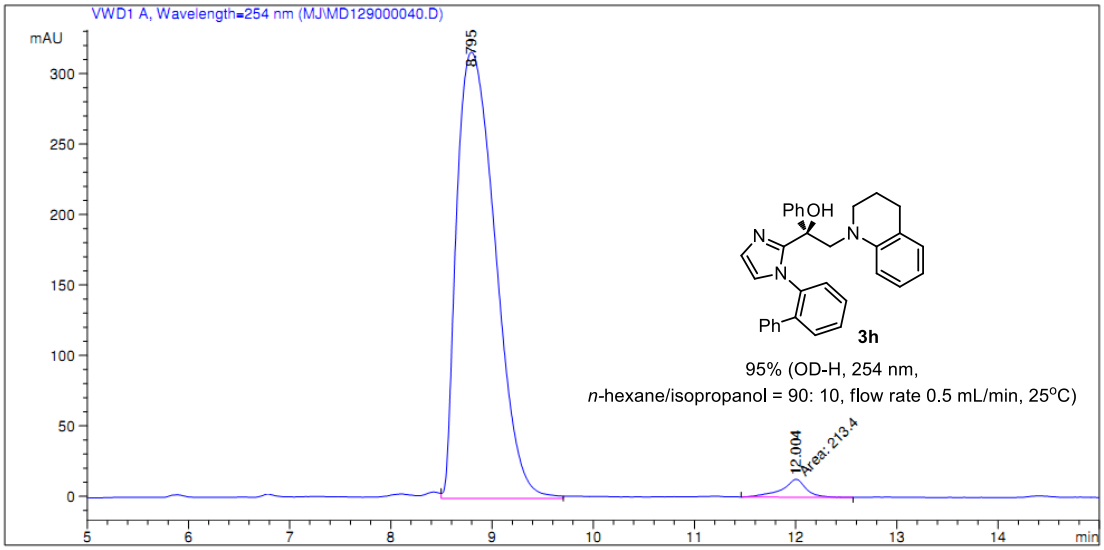




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.043	MM	0.2391	9083.17383	633.03650	96.4320
2	11.169	MM	0.2989	336.08112	18.74218	3.5680

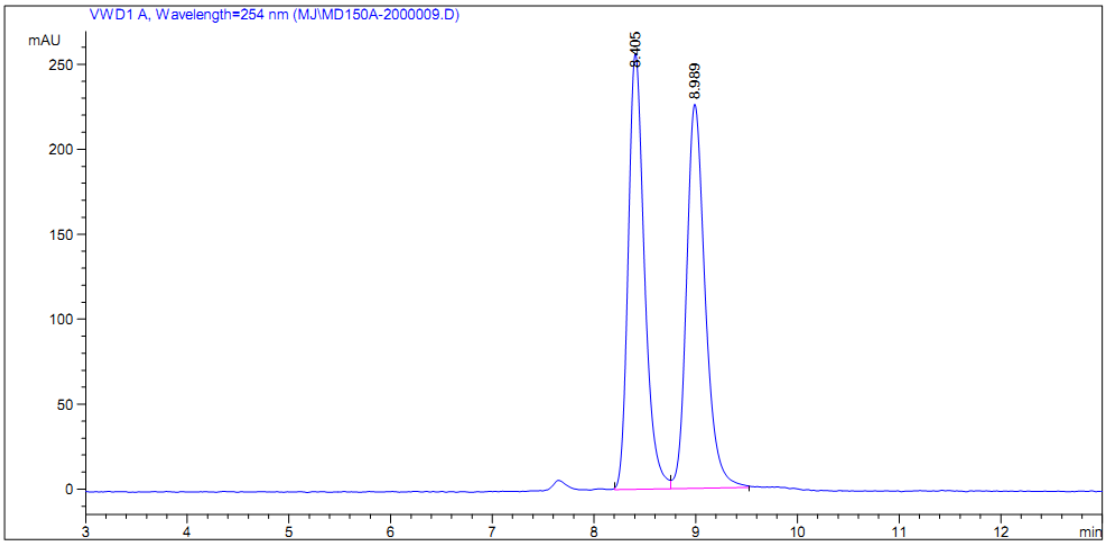
Figure S10. HPLC traces of *rac*-**3g** (reference) and (*S*)-**3g.** Area integration = 96.4:3.6 (92.8% ee).

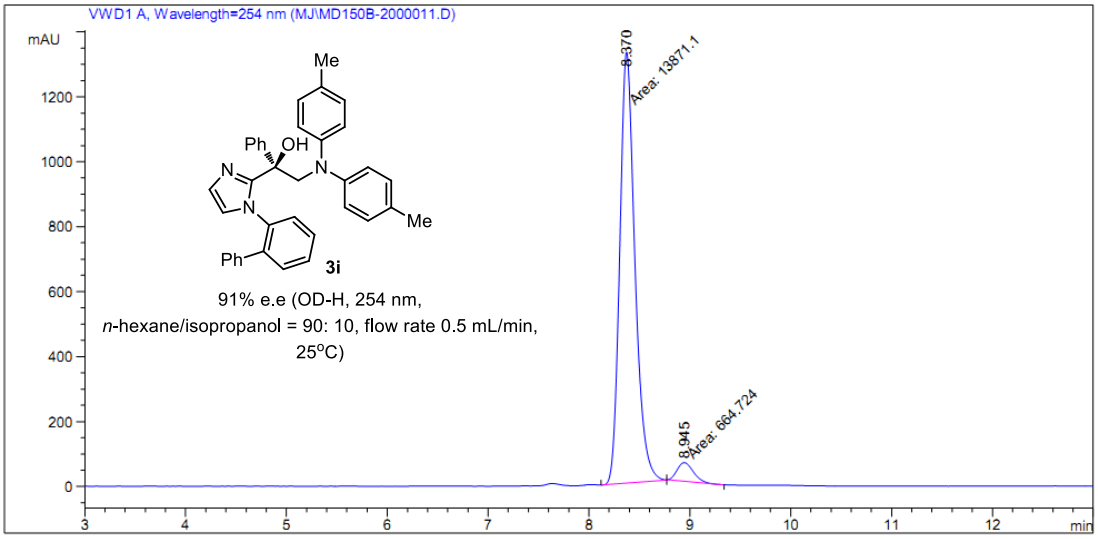




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.795	VV	0.4384	8384.35840	316.73041	97.5180
2	12.004	MM	0.2793	213.39981	12.73467	2.4820

Figure S11. HPLC traces of *rac*-**3h** (reference) and (*S*)-**3h**. Area integration = 97.5:2.5 (95% ee).

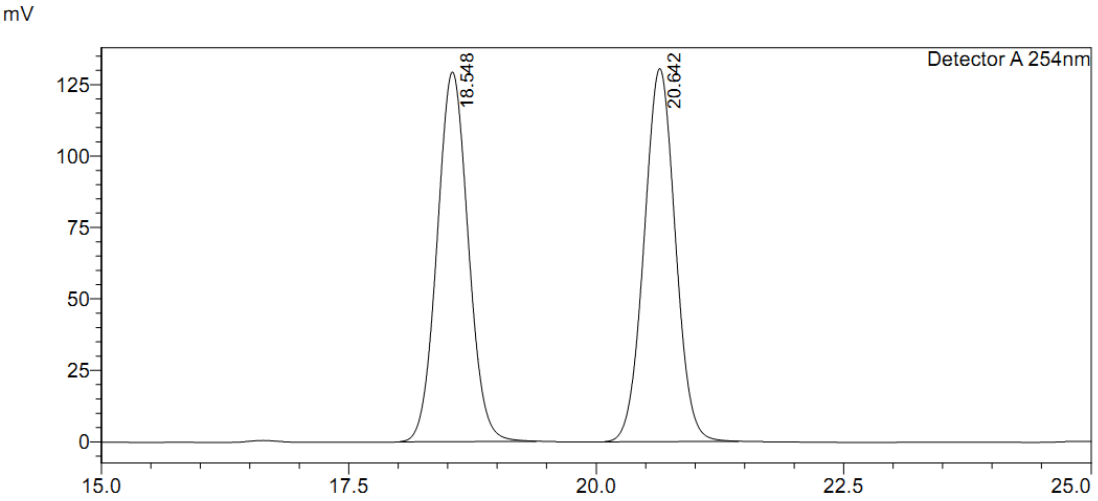




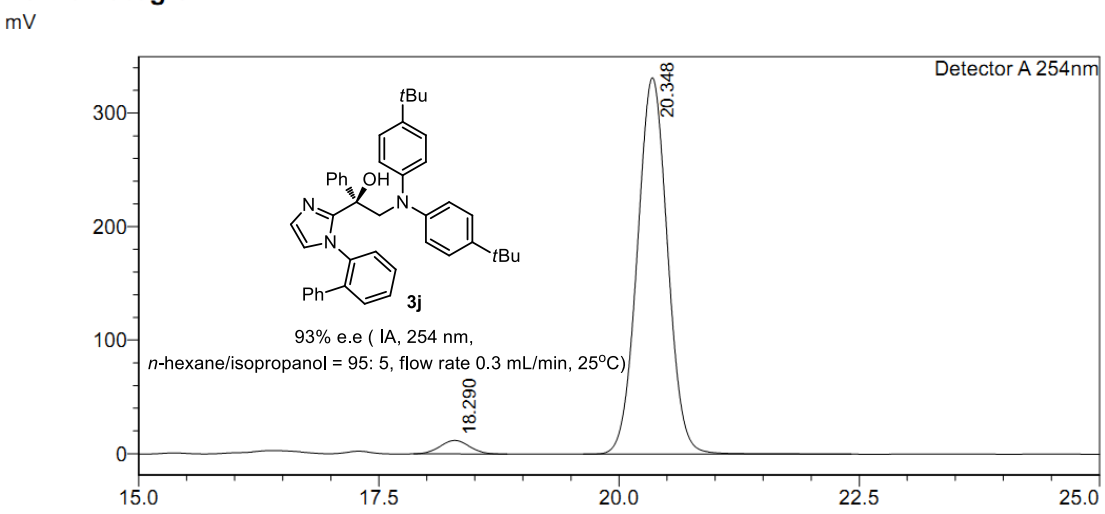
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.370	MM	0.1740	1.38711e4	1328.44141	95.4270
2	8.945	MM	0.1901	664.72369	58.27687	4.5730

Figure S12. HPLC traces of *rac*-**3i** (reference) and (*S*)-**3i**. Area integration = 95.4:4.6 (90.8% ee).

<Chromatogram>



<Chromatogram>

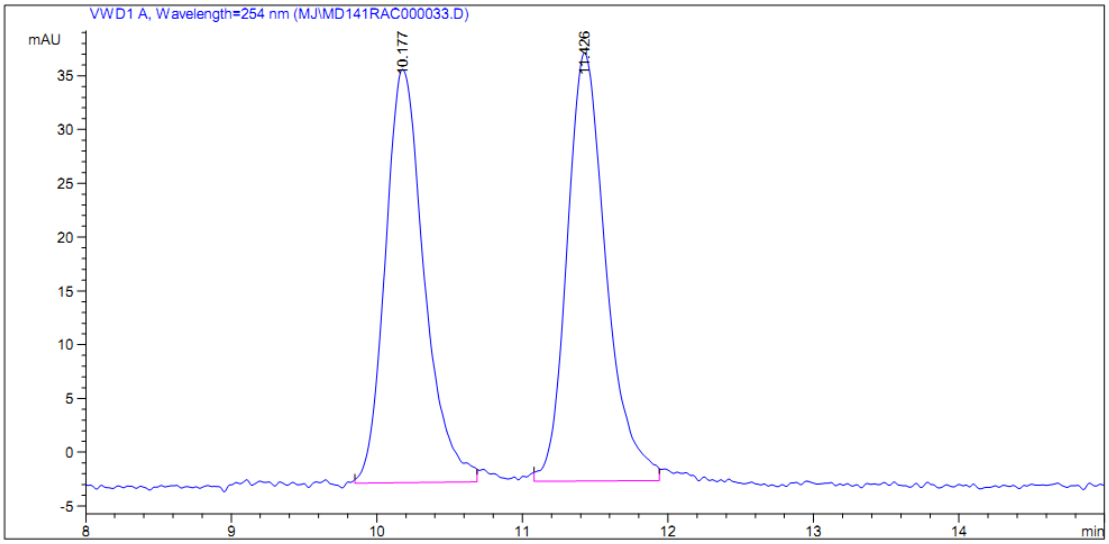


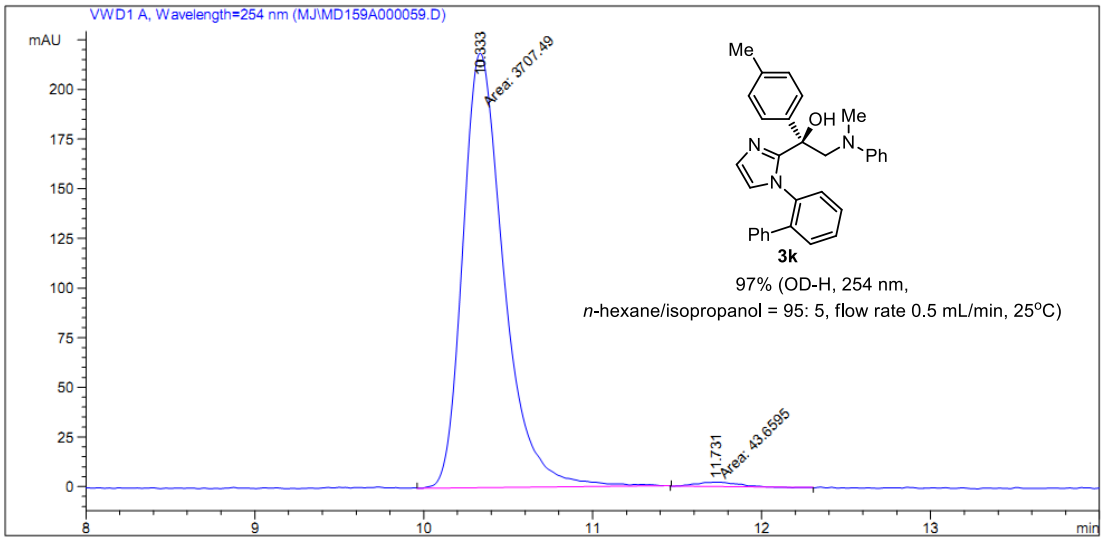
Detector A 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.290	254320	11956	3.378
2	20.348	7273575	331402	96.622
Total		7527895	343358	100.000

Figure S13. HPLC traces of *rac*-**3j** (reference) and (*S*)-**3j**. Area integration = 96.6:3.4 (93.2% ee).

4.3. Enantioselectivities of Catalytical Reactions in Figure 3



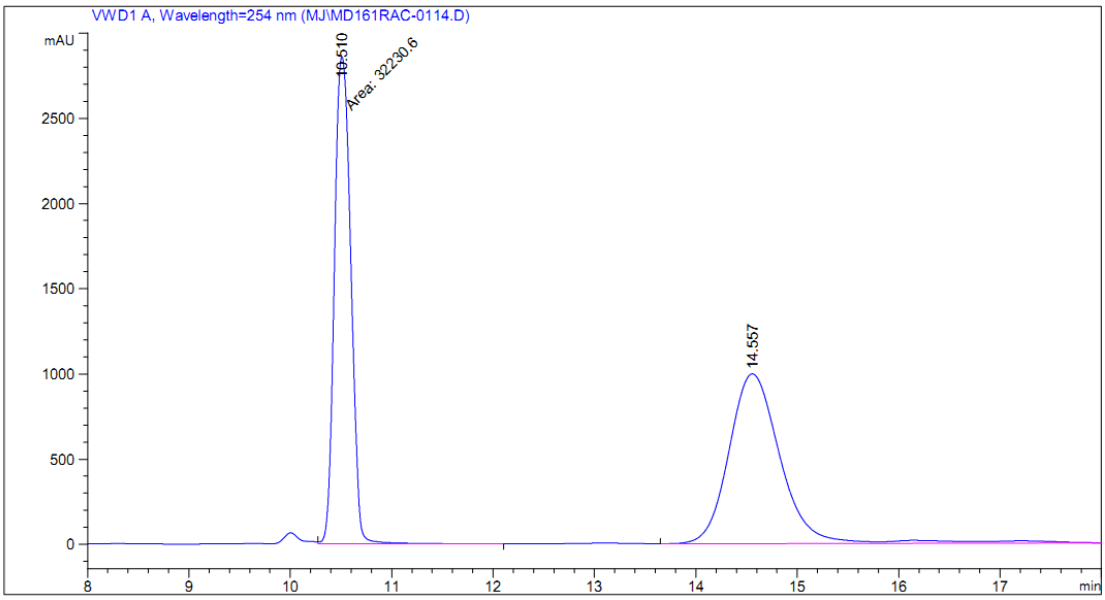


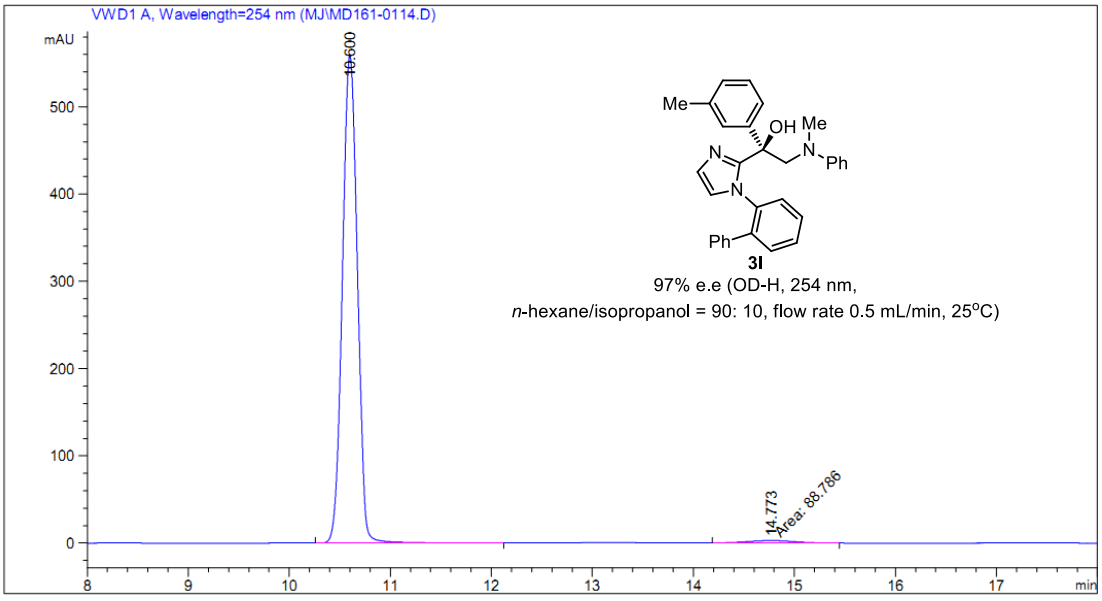
3k

97% (OD-H, 254 nm,
n-hexane/isopropanol = 95: 5, flow rate 0.5 mL/min, 25°C)

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.333	MM	0.2822	3707.48926	218.97369	98.8361
2	11.731	MM	0.3151	43.65955	2.30919	1.1639

Figure S14. HPLC traces of *rac*-**3k** (reference) and (*S*)-**3k**. Area integration = 98.8:1.2 (97.6% ee).





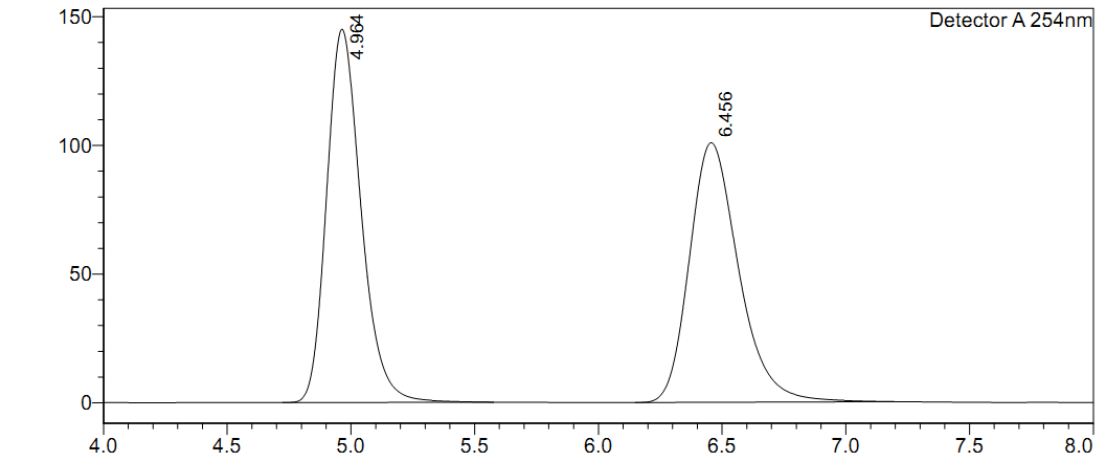
3l

97% e.e (OD-H, 254 nm,
n-hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25°C)

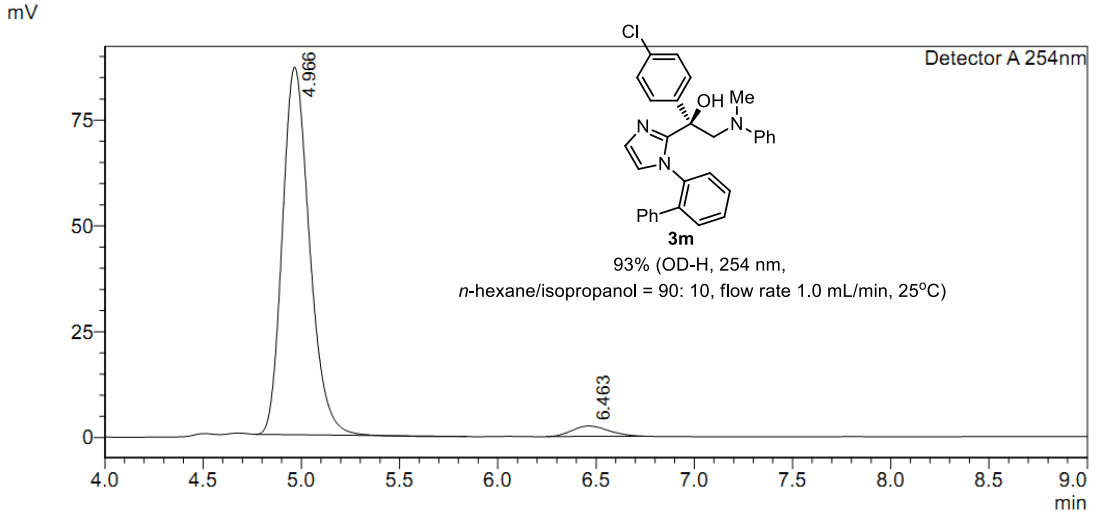
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.600	BB	0.1646	5755.83105	556.66669	98.4809
2	14.773	MM	0.5538	88.78605	2.67200	1.5191

Figure S15. HPLC traces of *rac*-**3l** (reference) and (*S*)-**3l**. Area integration = 98.5:1.5 (97.0% ee).

<Chromatogram>



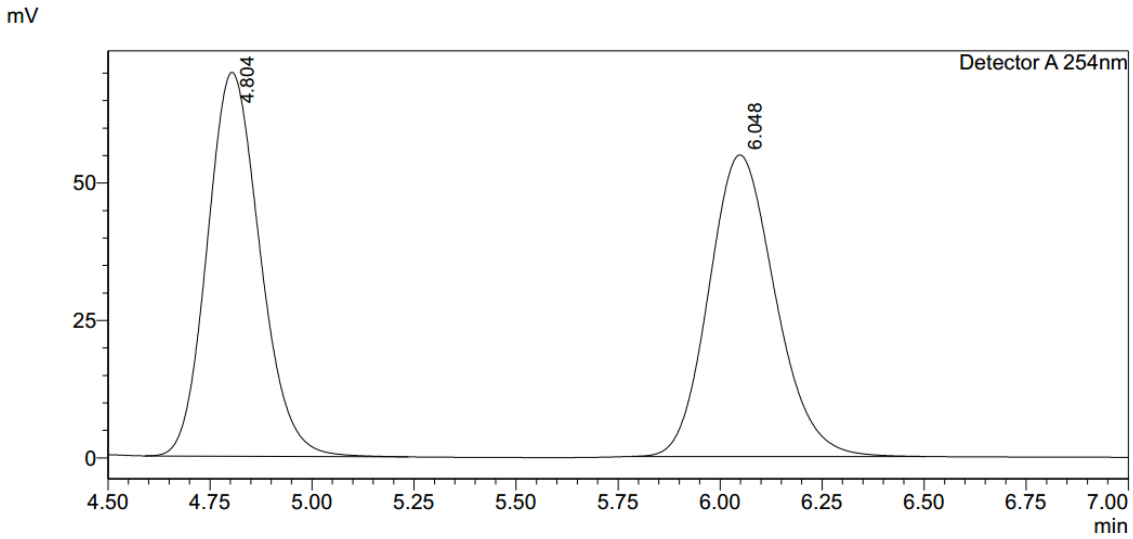
<Chromatogram>

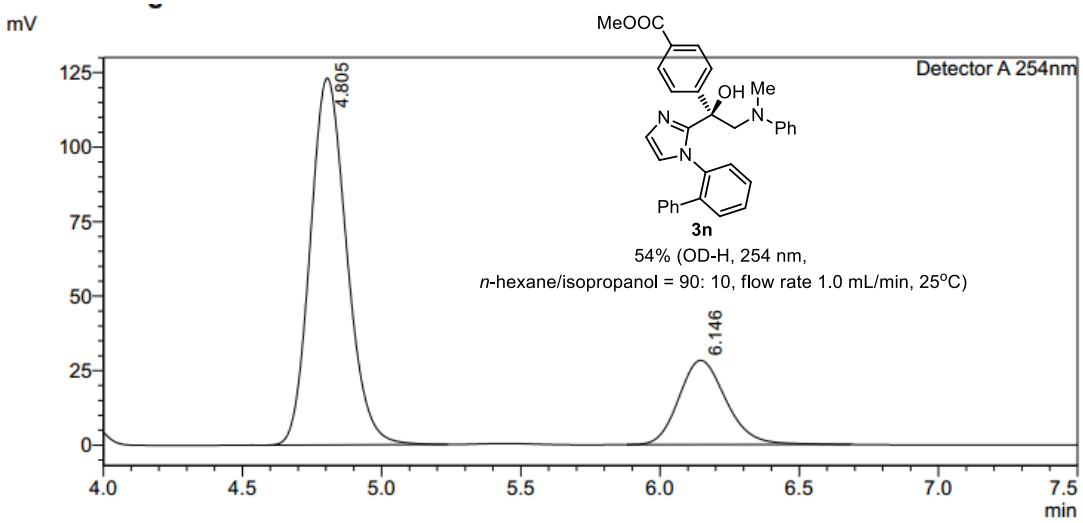


Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	4.966	834381	96.258
2	6.463	32437	3.742
Total		866818	100.000

Figure S16. HPLC traces of *rac*-**3m** (reference) and (*S*)-**3m**. Area integration = 96.3:3.7 (92.6% ee).



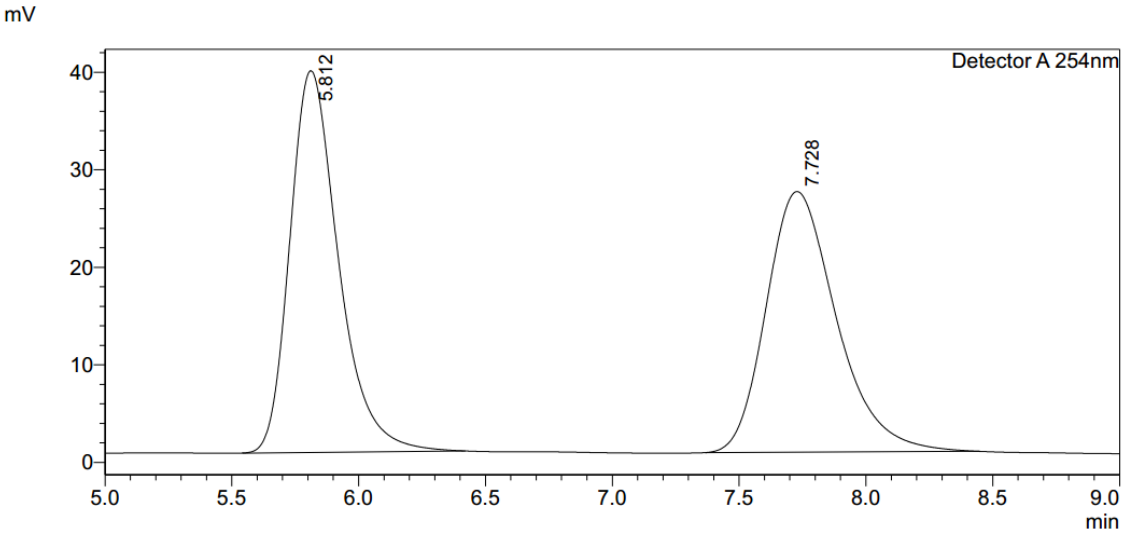


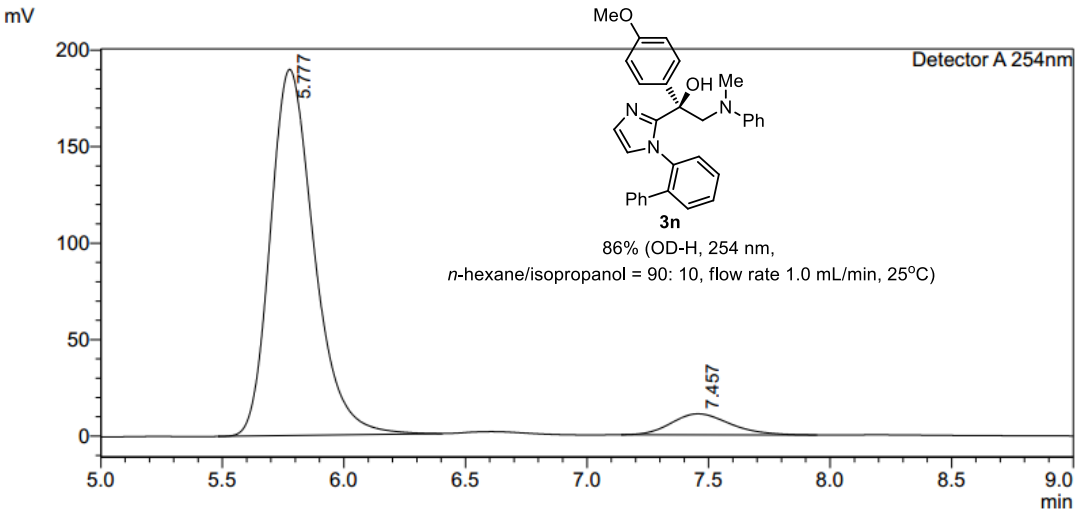
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	4.805	1119561	77.019
2	6.146	334063	22.981
Total		1453624	100.000

Figure S17. HPLC traces of *rac*-**3n** (reference) and (*S*)-**3n**. Area integration = 77:23 (54% ee).



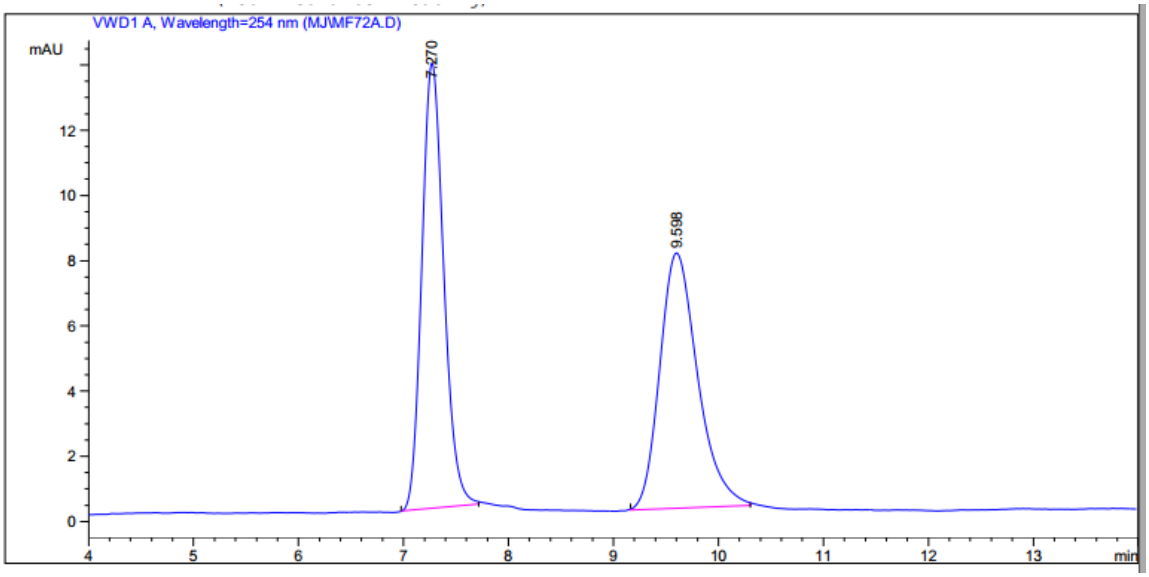


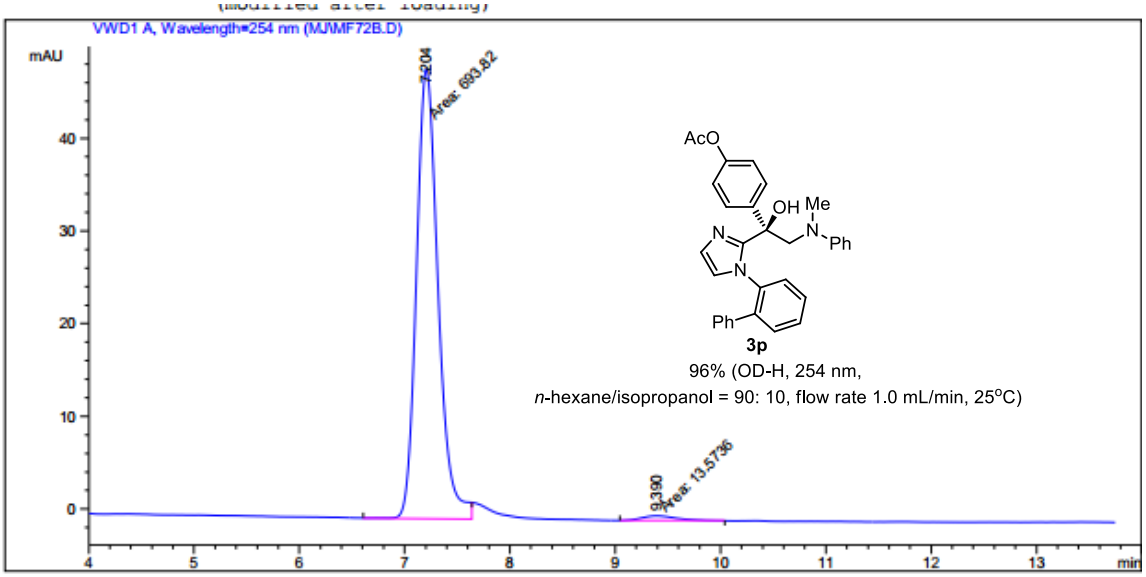
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	5.777	2376310	92.861
2	7.457	182679	7.139
Total		2558989	100.000

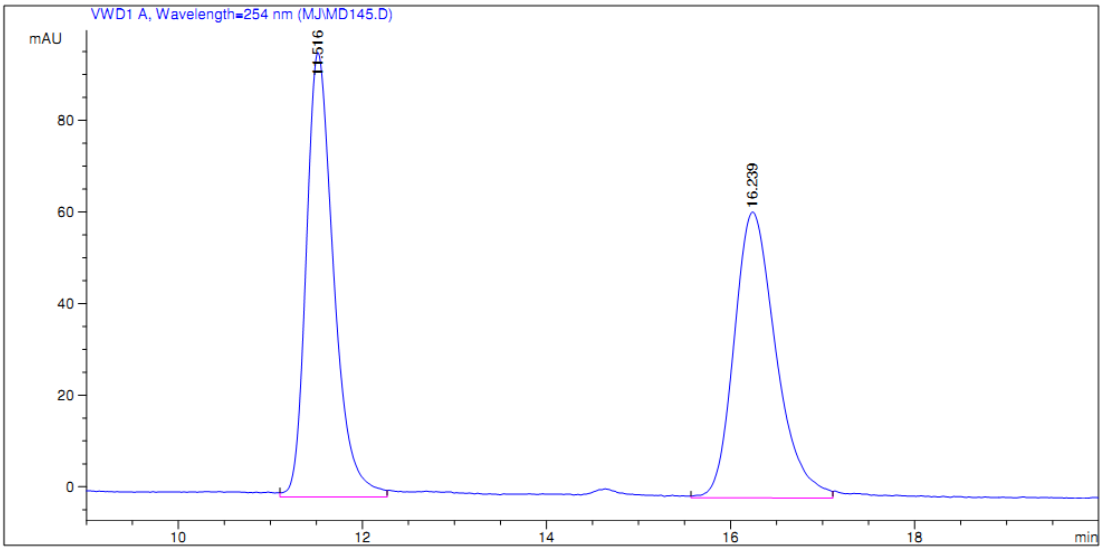
Figure S18. HPLC traces of *rac*-**3o** (reference) and (*S*)-**3o**. Area integration = 92.9: 7.1 (85.8% ee).

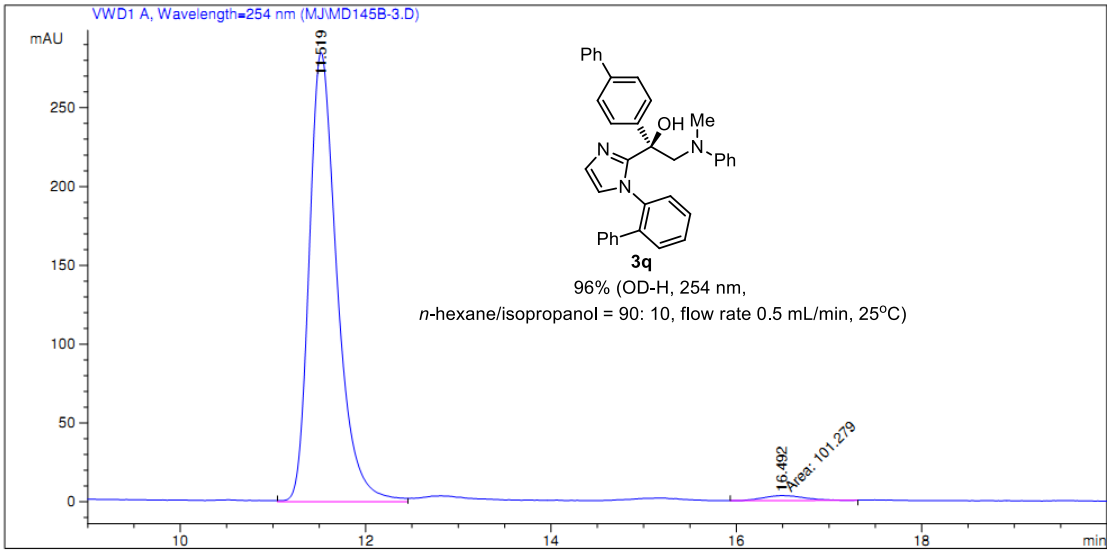




Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.204	MF	0.2382	693.82043	48.54126	98.0812
2	9.390	MM	0.4197	13.57364	5.39016e-1	1.9188

Figure S19. HPLC traces of *rac*-**3p** (reference) and (*S*)-**3p**. Area integration = 98:2 (96% ee).





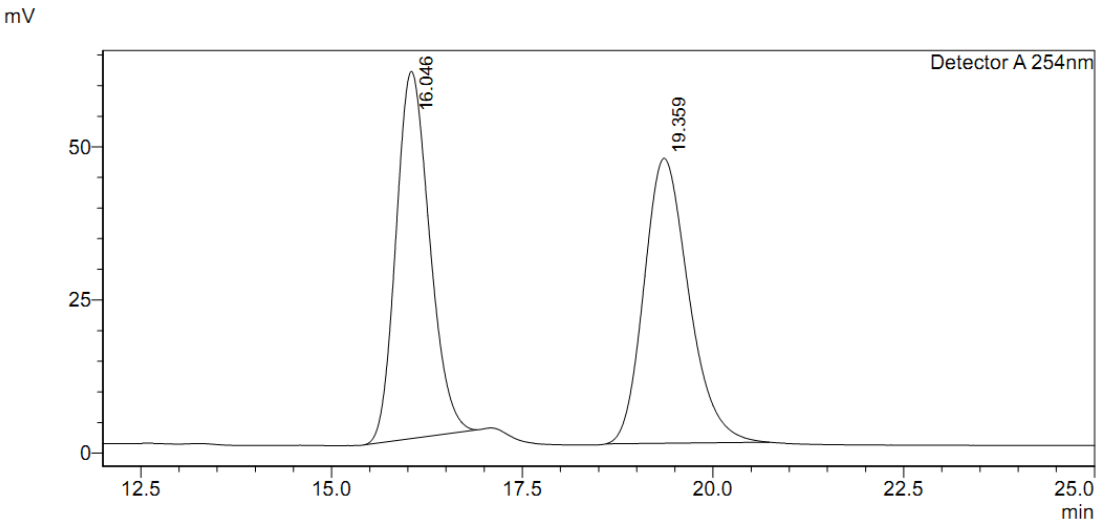
3q

96% (OD-H, 254 nm,
n-hexane/isopropanol = 90: 10, flow rate 0.5 mL/min, 25°C)

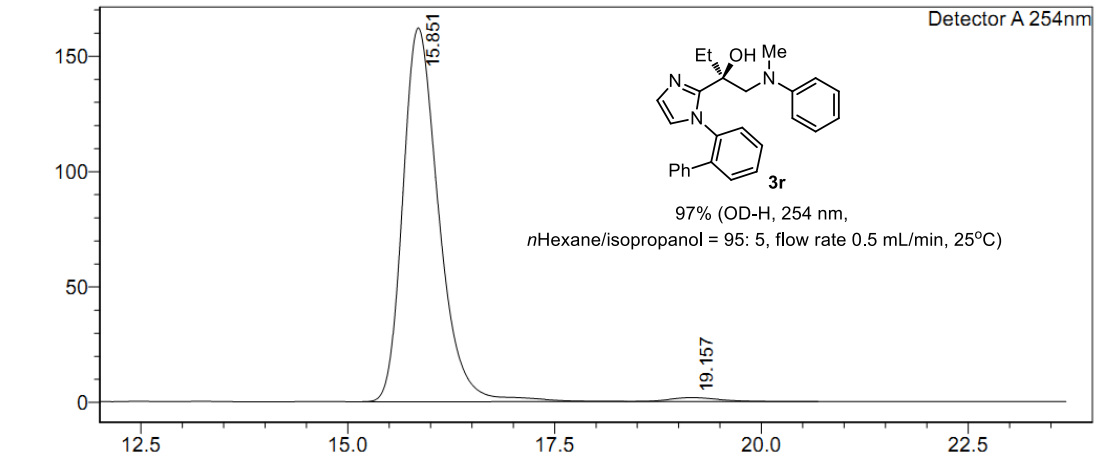
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.519	VV	0.3146	5945.34229	285.11261	98.3250
2	16.492	MM	0.5240	101.27905	3.22156	1.6750

Figure S20. HPLC traces of *rac*-**3q** (reference) and (*S*)-**3q**. Area integration = 98.3:1.7 (96.6% ee).

<Chromatogram>



<Chromatogram>



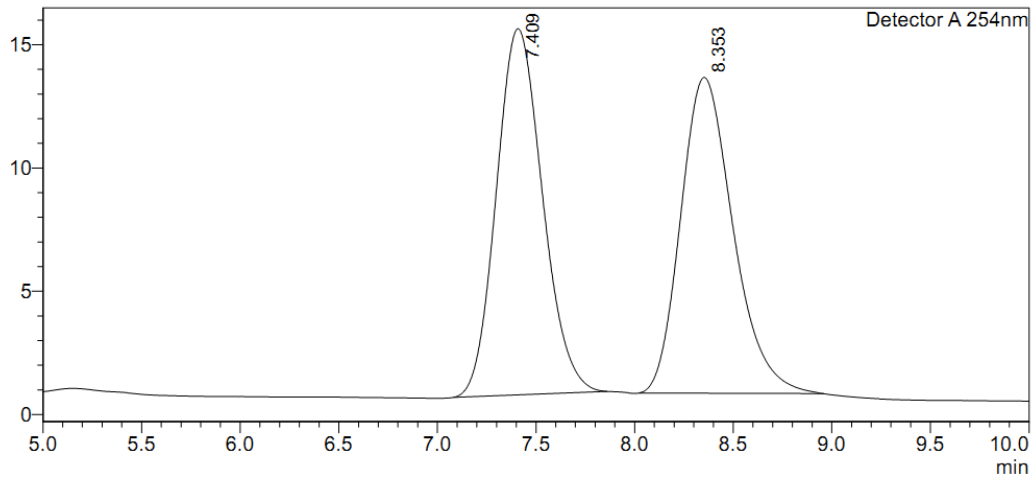
Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	15.851	4882967	98.579
2	19.157	70398	1.421
Total		4953365	100.000

Figure S21. HPLC traces of *rac*-**3r** (reference) and (*S*)-**3r**. Area integration = 98.6:1.4 (97.2% ee).

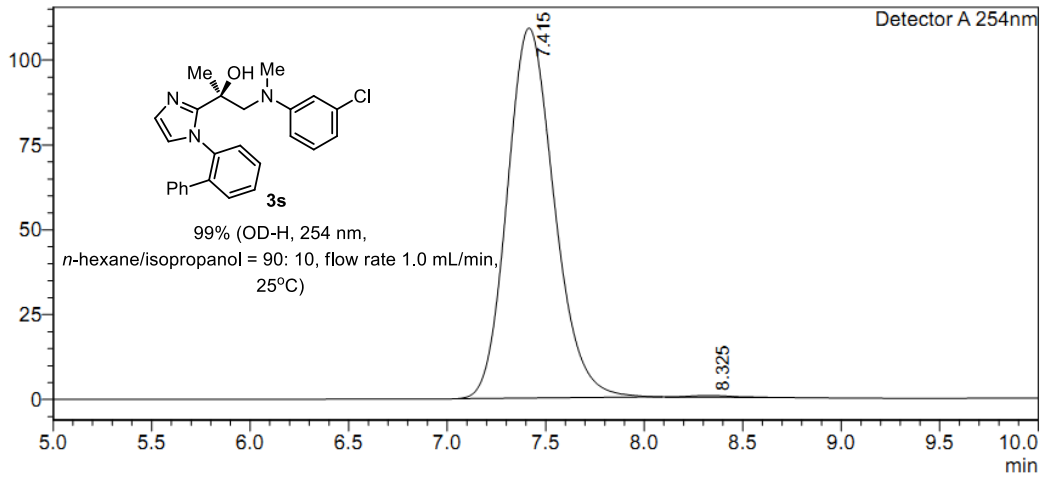
<Chromatogram>

mV



<Chromatogram>

mV



<Peak Table>

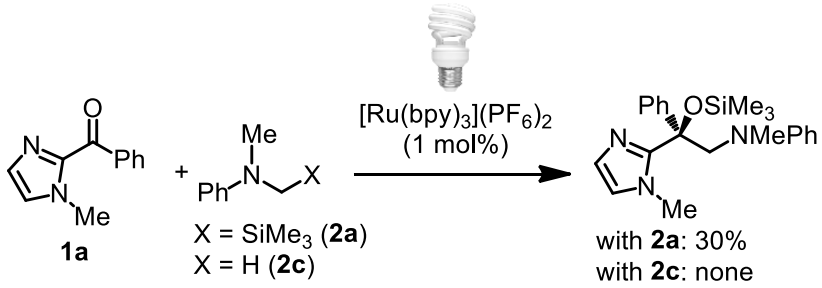
Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	7.415	1812156	99.610
2	8.325	7102	0.390
Total		1819258	100.000

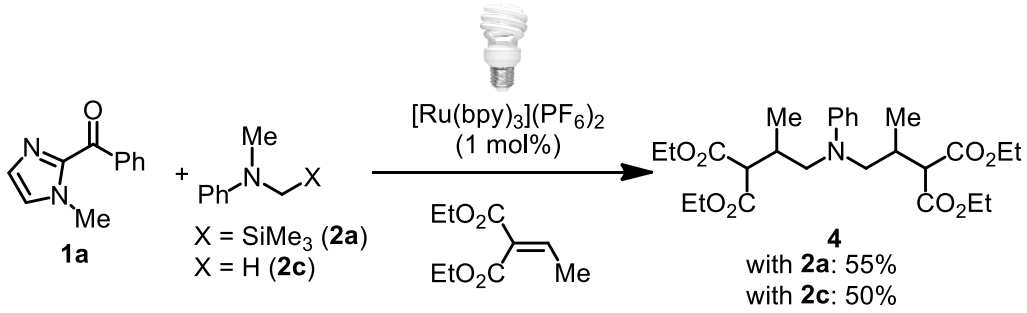
Figure S22. HPLC traces of *rac*-**3s** (reference) and (*S*)-**3s**. Area integration = 99.6:0.4 (99.2% ee).

5. Mechanistic Studies

5.1 α-Amino Radical Trapping Experiments



A dried 10 mL Schlenk tube was charged with the photosensitizer $[Ru(bpy)_3](PF_6)_2$ (0.86 mg, 0.001 mmol, 1 mol%) and the 2-acyl imidazole **1a** (0.10 mmol, 1.0 eq.). A solution of **2a** (58.0 mg, 0.30 mmol, 3.0 eq.) or **2c** (36.4 mg, 0.30 mmol, 3.0 eq.) in MeCN/DMAC (v/v = 4:1, 1 mL) was added in one portion. The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at room temperature for 15h under nitrogen atmosphere. Afterwards, the mixture was concentrated under reduced pressure. With **2a**, the residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:20 to 1:10) to afford the product **3a'** (11.3 mg, 0.030 mmol, 30% yield). With **2c**, no product was formed.



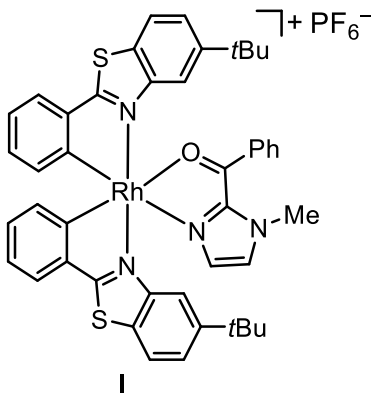
A dried 10 mL Schlenk tube was charged with the photosensitizer $[Ru(bpy)_3](PF_6)_2$ (0.86 mg, 0.001 mmol, 1 mol%) and the 2-acyl imidazole **1a** (0.10 mmol, 1.0 eq.). A solution of **2a** (58.0 mg, 0.30 mmol, 3.0 eq.) or **2c** (36.4 mg, 0.30 mmol, 3.0 eq.) in MeCN/DMAC (v/v = 4:1, 1 mL) was added

in one portion, followed by the addition of Diethyl 2-ethylidenemalonate (18 µL, 0.1 mmol, 1 eq.). The reaction mixture was degassed *via* freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 23 W compact fluorescent lamp. The reaction was stirred at room temperature for 15h under nitrogen atmosphere. Afterwards, the reaction was quenched by the addition of saturated aqoues NH_4Cl solution, then extracted by EtOAc (3 × 10 mL). The organic layer was collected and concentrated under reduced pressure. The residue was subjected to a flash chromatography on silica gel (EtOAc/*n*-hexane = 1:20 to 1:10) to afford the product **4** (with **2a**: 27.0 mg, 0.055 mmol, 55% yield; with **2c**: 24.6 mg, 0.050 mmol, 50% yield).

^{1}H NMR (300 MHz, C_6D_6) δ 7.28-7.21 (m, 2H), 7.10-7.00 (m, 2H), 6.76-6.70 (m, 1H), 4.02-3.86 (m, 8H), 3.81 (dd, J = 14.3, 5.1 Hz, 1H), 3.68 (dd, J = 14.6, 6.9 Hz, 1H), 3.43 (d, J = 6.5 Hz, 1H), 3.36 (d, J = 6.8 Hz, 1H,), 3.32 (dd, J = 14.6, 8.1 Hz, 1H), 3.13 (dd, J = 14.3, 9.2 Hz, 1H), 3.05-2.93 (m, 2H), 1.021 (d, J = 7.0 Hz, 3H), 1.017 (d, J = 6.8 Hz, 3H), 0.94-0.87 (m, 12H).

All spectroscopic data were in agreement with the literature.[4]

5.2 Synthesis of the Intermediate Complex I



I

The racemic complex **I** was obtained by reacting substrate **2a** (13.0 mg, 0.049 mmol) with *rac*-**RhS** (40.0 mg, 0.043 mmol) at room temperature for 10 min in CH_2Cl_2 (1.0 mL). After the slow addition of *n*-hexane (5.0 mL), crystals were collected after several days (32.2 mg, yield: 68%).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.92 (dd, J = 8.5, 0.4 Hz, 1H), 7.86 (d, J = 8.7 Hz, 1H), 7.81 (dd, J = 7.7, 0.2 Hz, 1H), 7.78 (dd, J = 7.7, 0.4 Hz, 1H), 7.72 (tt, J = 7.1, 1.5 Hz, 1H), 7.58-7.50 (m, 8H), 7.16 (dd, J = 7.5, 1.0 Hz, 1H), 7.12 (dd, J = 7.5, 1.0 Hz, 1H), 7.09 (d, J = 1.1 Hz, 1H), 6.95-6.90 (m, 3H), 6.47 (dt, J = 7.9, 0.9 Hz, 1H), 6.40 (d, J = 7.5 Hz, 1H), 3.67 (s, 3H), 1.20 (s, 9H), 1.15 (s, 9H).

^{13}C NMR (125 MHz, CD_2Cl_2) 190.0, 178.2 (2C), 174.9, 174.8, 163.3, 163.0, 159.5, 159.2, 152.5, 152.3, 149.4, 149.1, 145.8, 141.2, 139.6, 135.9, 135.1, 134.6, 134.3, 132.5, 131.7, 131.4, 131.3, 130.0, 129.6, 126.8, 126.5, 125.3, 124.8, 124.7, 124.5, 123.2, 123.1, 115.6, 115.4, 38.7, 35.2 (2C), 31.5, 31.4.

6. Single Crystal X-Ray Diffraction Studies

Crystals of **3s** and complex **I** were obtained by slow diffusion from a solution of the compounds in CH_2Cl_2 layered with *n*-hexane at room temperature for several days.

Crystal data and details of the structure determination are presented in Table S1. X-ray data were collected with a Bruker 3 circuit D8 Quest diffractometer with MoKa radiation (microfocus tube with multilayer optics) and Photon 100 CMOS detector at 115 K. Scaling and absorption correction was performed by using the SADABS[5] software package of Bruker. Structures were solved using direct methods in SHELXT[6] and refined using the full matrix least squares procedure in SHELXL-2014[7]. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C atom, and Uiso(H) was set at 1.2 Ueq(Csp^2) and 1.5 Ueq(Csp^3). Disorder of PF_6 ions, solvent molecules or phenyl and *tert*-butyl groups was refined using restraints for both the geometry and the anisotropic displacement factors.

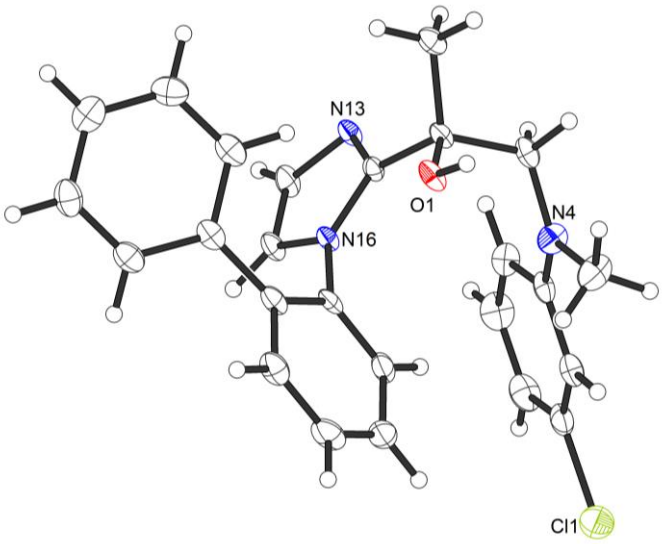


Figure S23. Crystal structure of **3s.** ORTEP drawing with 50 % probability thermal ellipsoids.

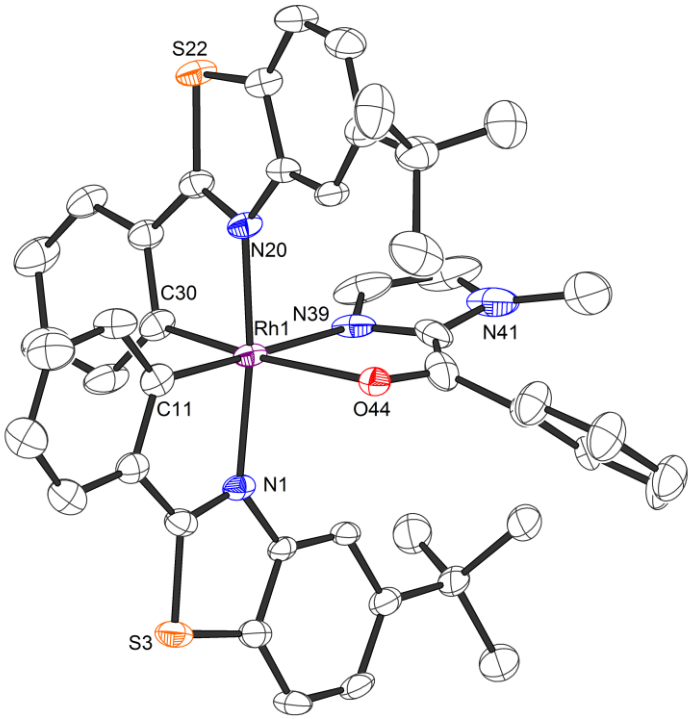


Figure S24. One of the two independent ions of complex **I** in the asymmetric unit. The hexafluorophosphate counteranion and the solvent molecules (hexane and DCM) are omitted for clarity. No disorder shown. ORTEP drawing with 50 % probability thermal ellipsoids.

Table S1. Crystal data and details of the structure determination.

	3s	complex **I**
Empiric formula	C_{25} H_{24} Cl N_3 O	$C_{48.4}$ $H_{49.6}$ Cl_2 F_6 N_4 O P Rh S_2
Formula weight	417.92	1086.22
Crystal system, space group	Orthorhombic, $P2_12_12_1$	Triclinic, P-1
a, *b*, *c* (Å)	10.3206(4), 11.6585(5), 18.3971(8)	17.1583(11), 17.7095(11), 18.8292(12)
α, β, γ (°)	90, 90, 90	66.918(2), 69.054(2), 76.796(2)
V (Å^3)	2213.59(16)	4889.7(5)
Z	4	4
μ (mm^{-1})	0.194	0.640
Crystal size (mm)	0.43 x 0.09 x 0.04	0.37 x 0.37 x 0.03
T_{min}, T_{max}	0.92, 0.99	0.98, 0.86
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12569, 4006, 3552	112817, 17855, 13904
R_{int}	0.0336	0.0533
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.0352, 0.0736, 1.060	0.0565, 0.1437, 1.039
No. of used reflections	4006	17855
No. of parameters	277	1548
No. of restraints	0	582
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.148, -0.212	1.691, -0.833
Absolute structure parameter	0.08(3)	-
CCDC	1480694	1480695

7. References

1) L. Ruiz Espelt, I. S. McPherson, E. M. Wiensch and T. P. Yoon, *J. Am. Chem. Soc.*, 2015, **137**, 2452-2455.

2) C. Wang, Y. Zheng, H. Huo, P. Röse, L. Zhang, K. Harms, G. Hilt and E. Meggers, *Chem. Eur. J.*, 2015, **21**, 7355-7359.

3) A. Sunderkötter, S. Lorenzen, R. Tacke and P. Kraft, *Chem. Eur. J.*, 2010, **16**, 7404-7421.

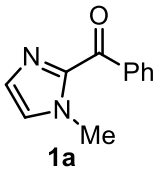
4) Y. Miyake, K. Nakajima and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2012, **134**, 3338-3341.

5) *SADABS. Bruker AXS area detector scaling and absorption correction*, Bruker AXS Inc., Madison, Wisconsin, USA, 2014.

6) G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.

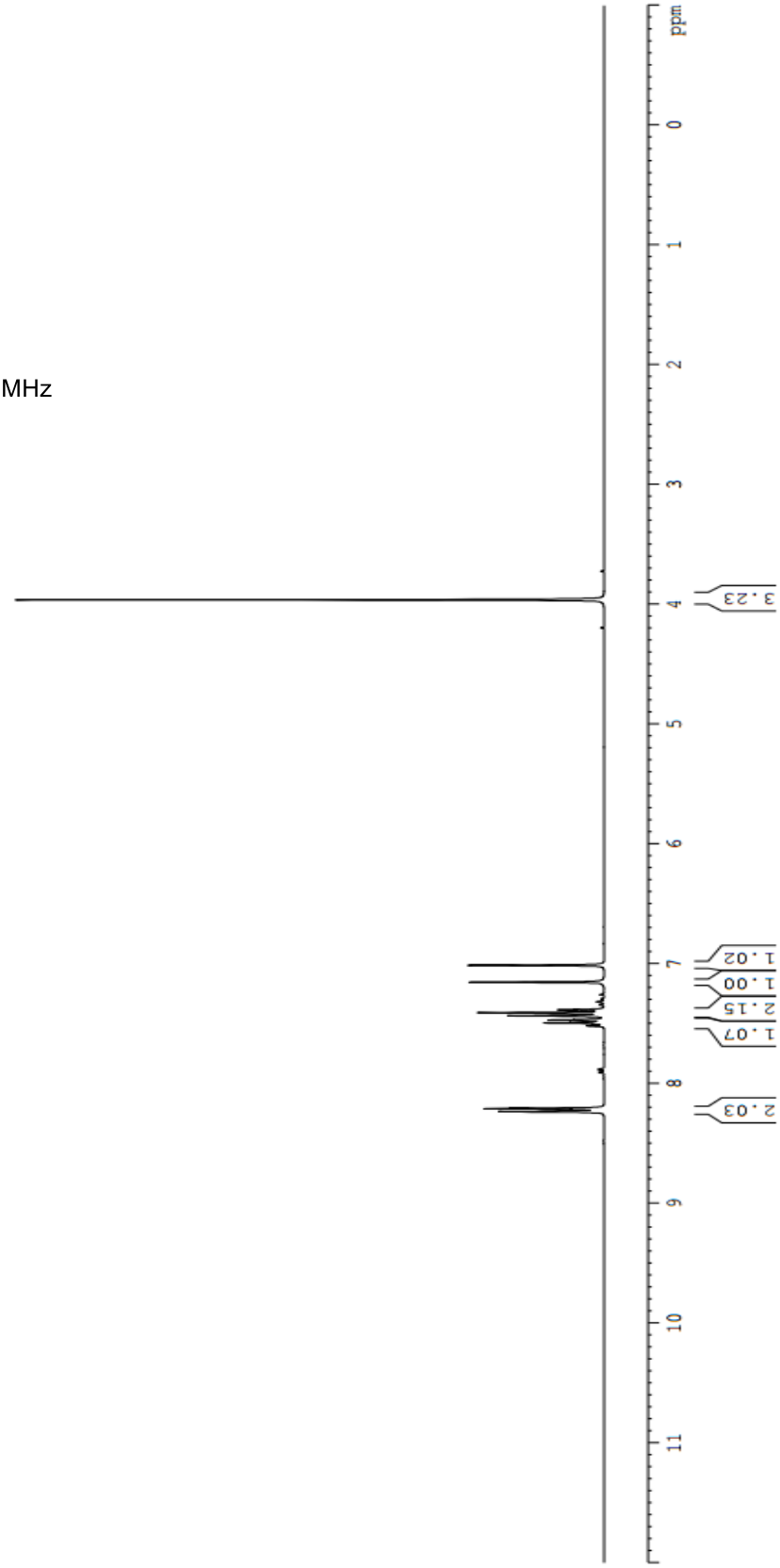
7) G. M. Sheldrick, *SHELXT*, Universität Göttingen, Göttingen, Germany, 2014.

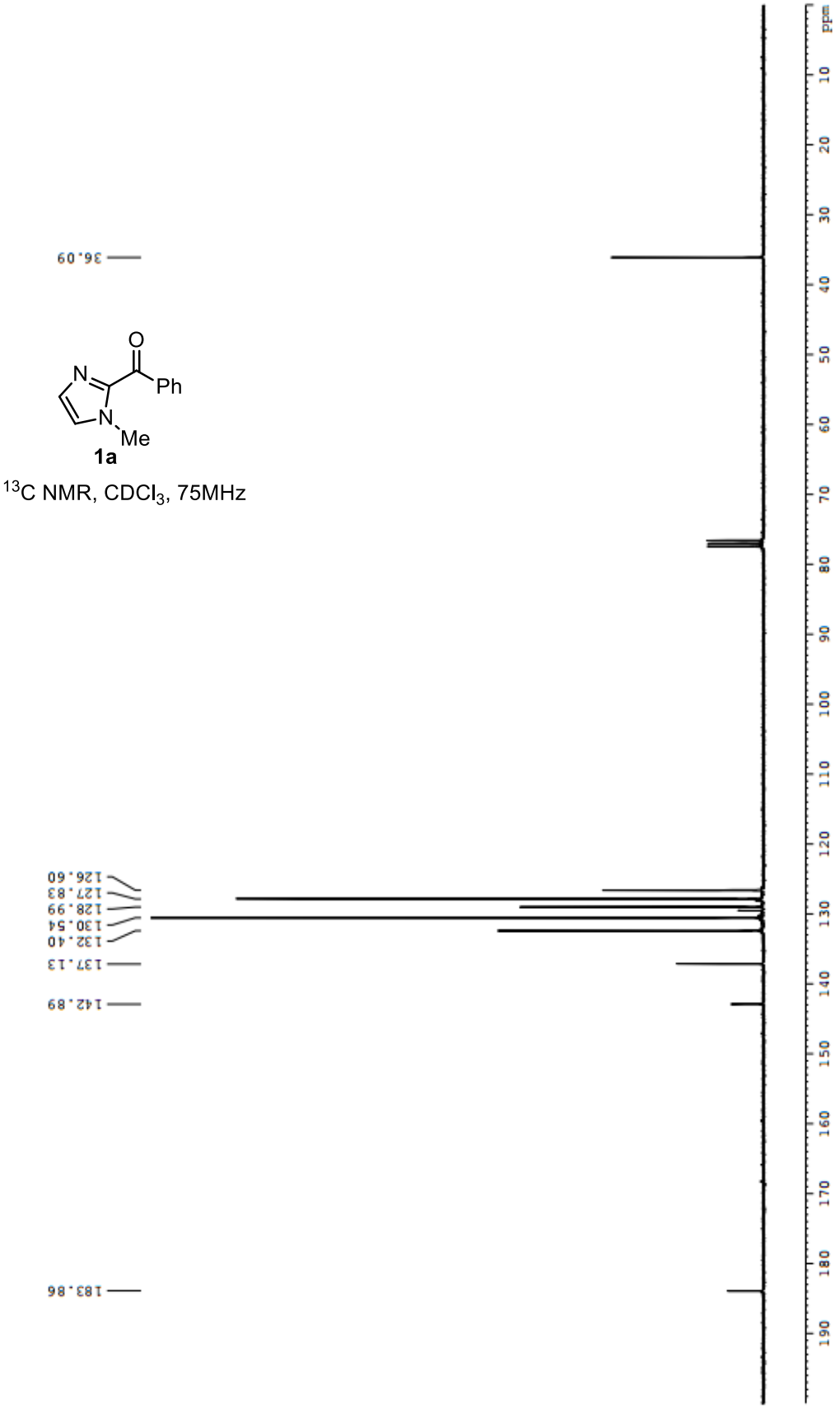
8. NMR Spectra



1a

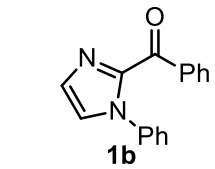
^{1}H NMR, $CDCl_3$, 300MHz





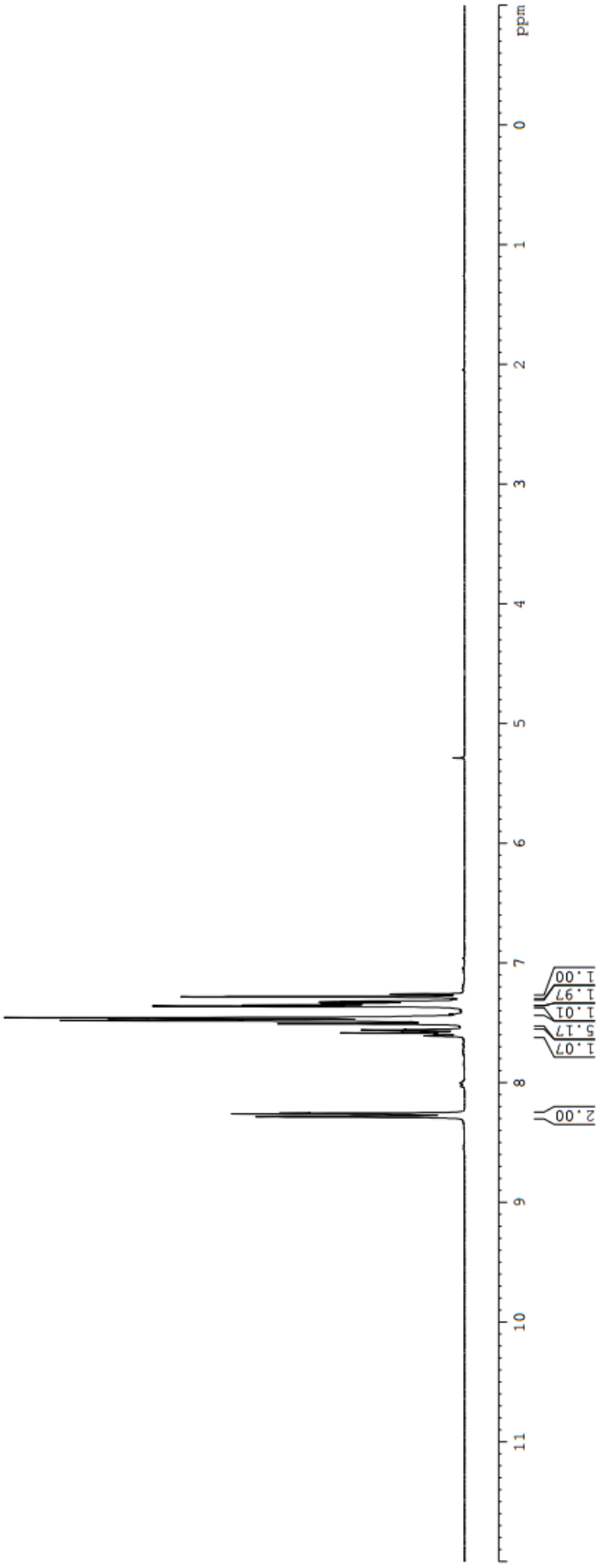
1a

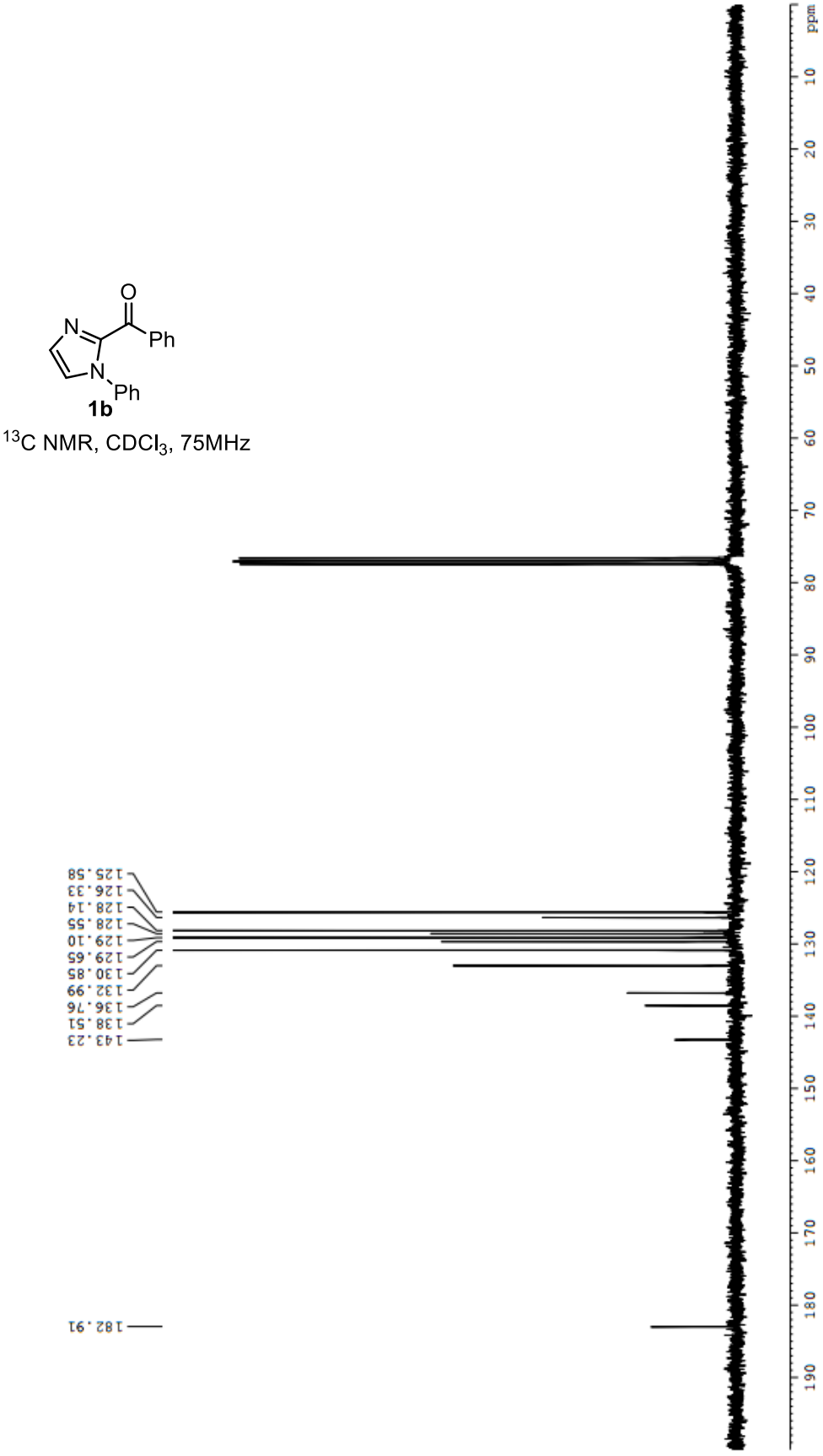
^{13}C NMR, $CDCl_3$, 75MHz

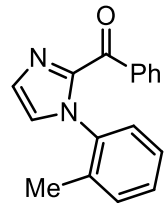


1b

^{1}H NMR, $CDCl_3$, 300MHz

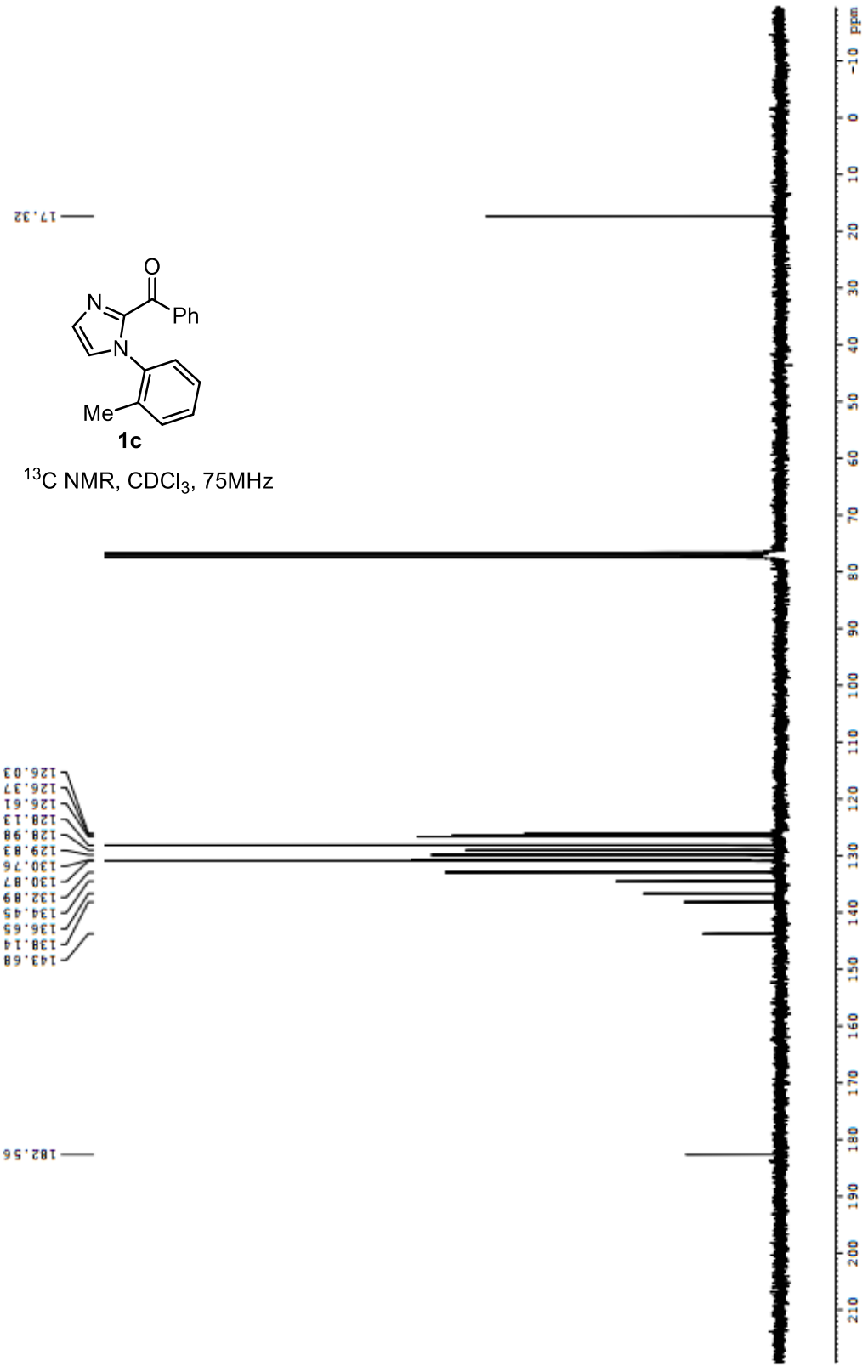


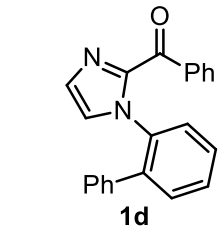

O
N
Ph
N
Ph
1b
13C NMR, CDCl3, 75MHz
182.91
143.23
138.51
136.76
132.99
130.85
129.65
129.10
128.55
128.14
126.33
125.58
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190



1c

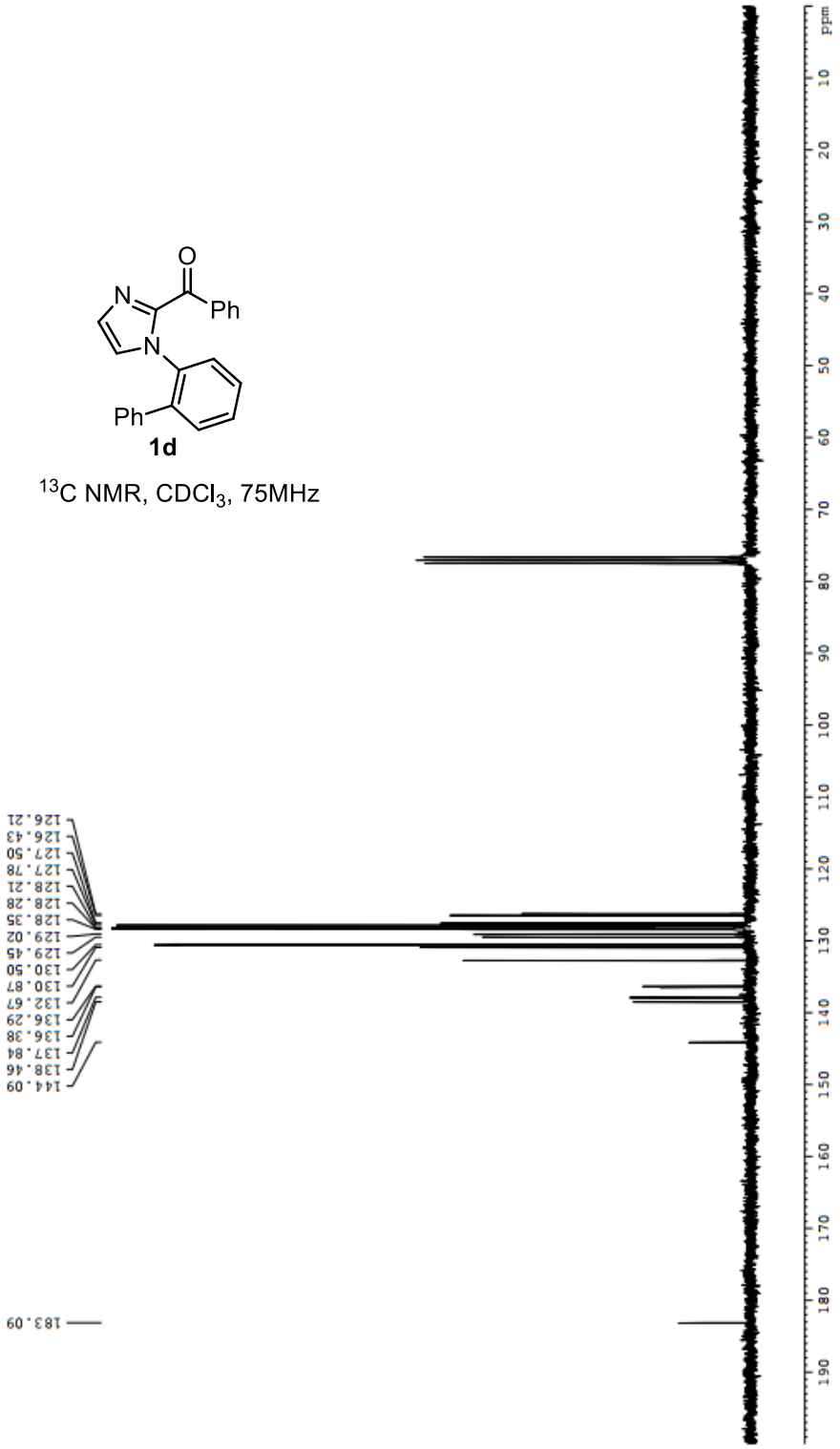
^{1}H NMR, $CDCl_3$, 300MHz

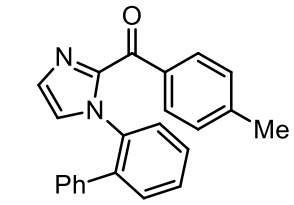

17.32
126.03
126.37
126.61
128.13
128.98
129.83
130.76
130.87
132.89
134.45
136.65
138.14
143.68
182.56
O
N
Ph
N
Me
1c
^{13}C NMR, $CDCl_3$, 75MHz
ppm



1d

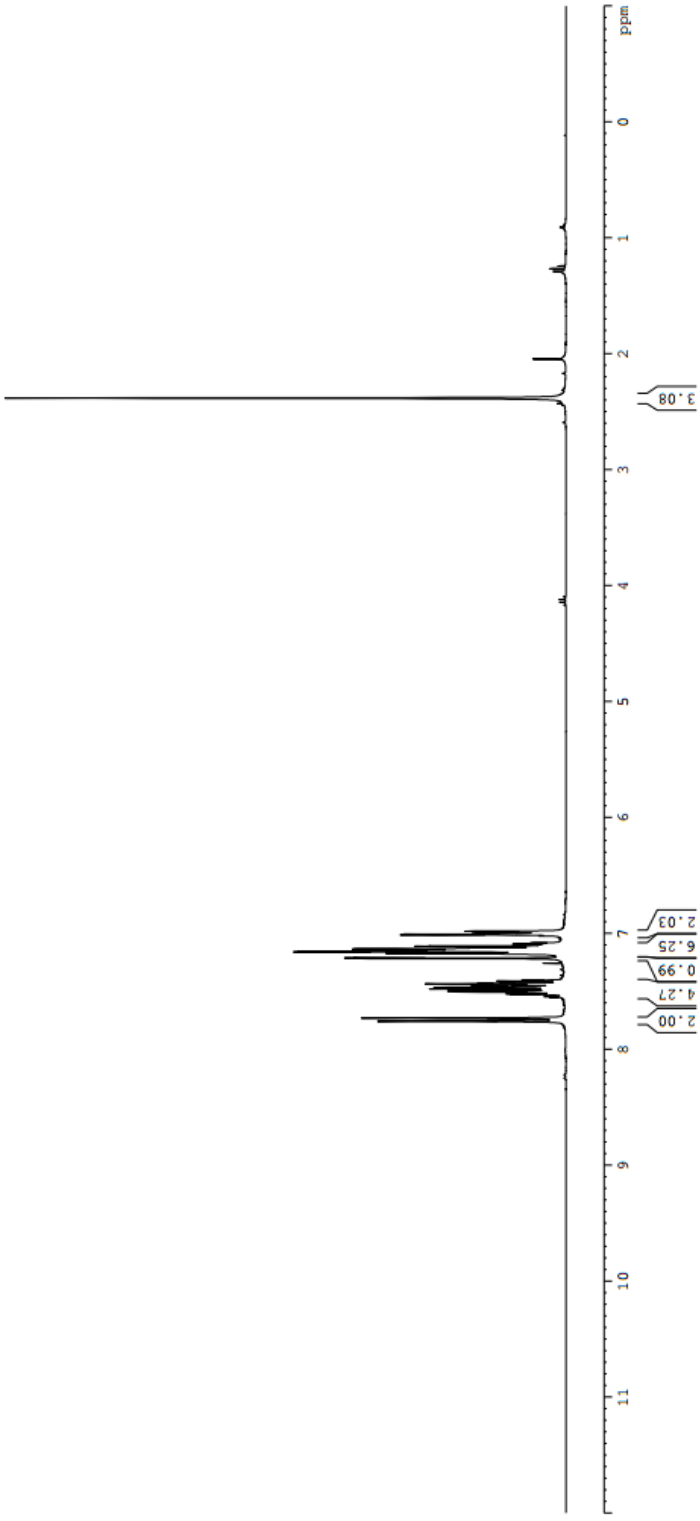
^{1}H NMR, $CDCl_3$, 300MHz

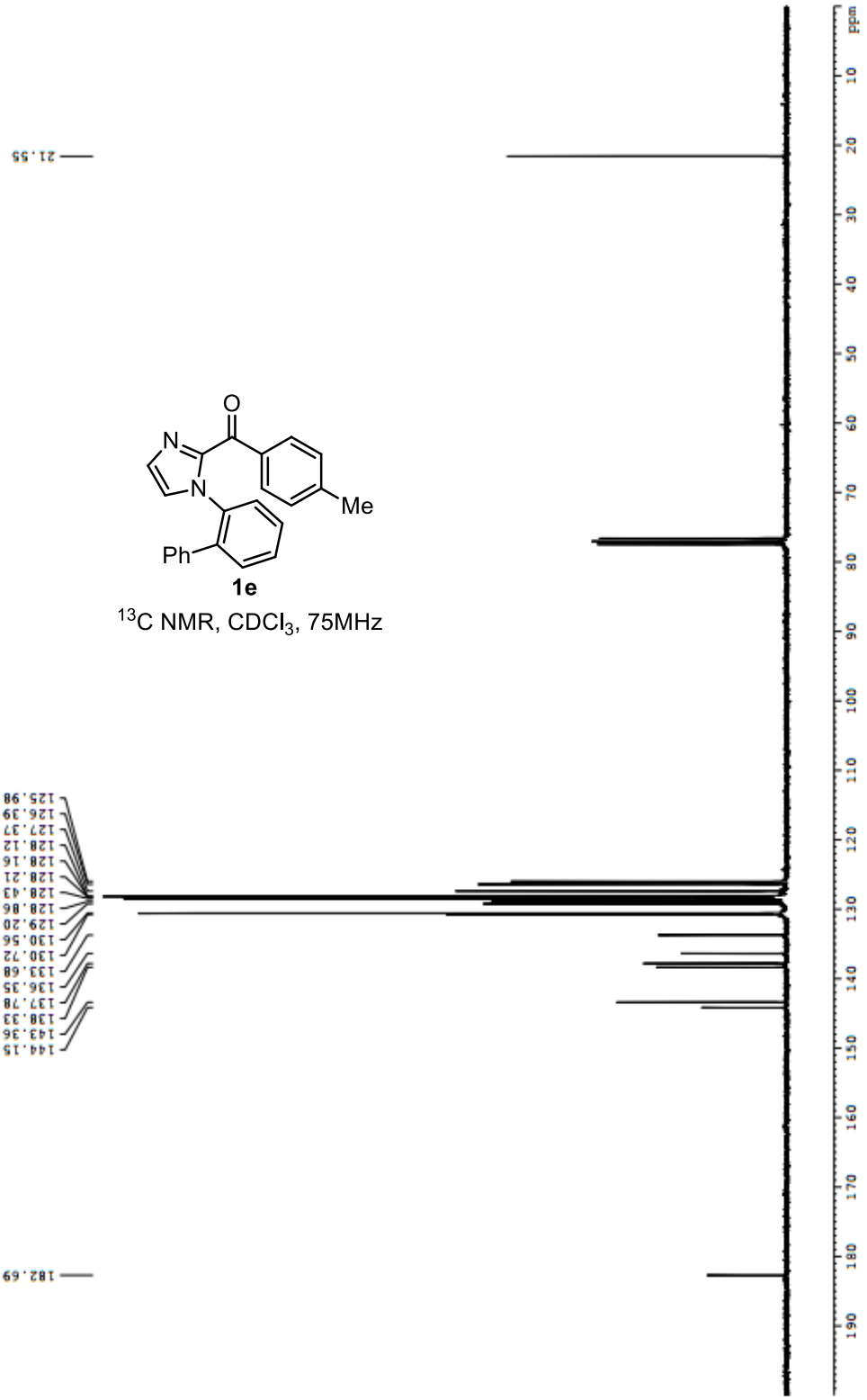

O
N
Ph
N
Ph
1d
13C NMR, CDCl3, 75MHz
126.21
126.43
127.50
127.78
128.21
128.28
128.35
129.02
129.45
130.50
130.87
132.67
136.29
136.38
137.84
138.46
144.09
183.09
ppm
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190



1e

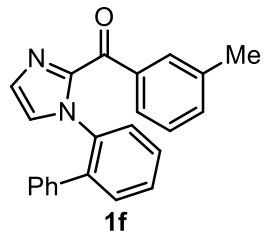
^{1}H NMR, $CDCl_3$, 300MHz





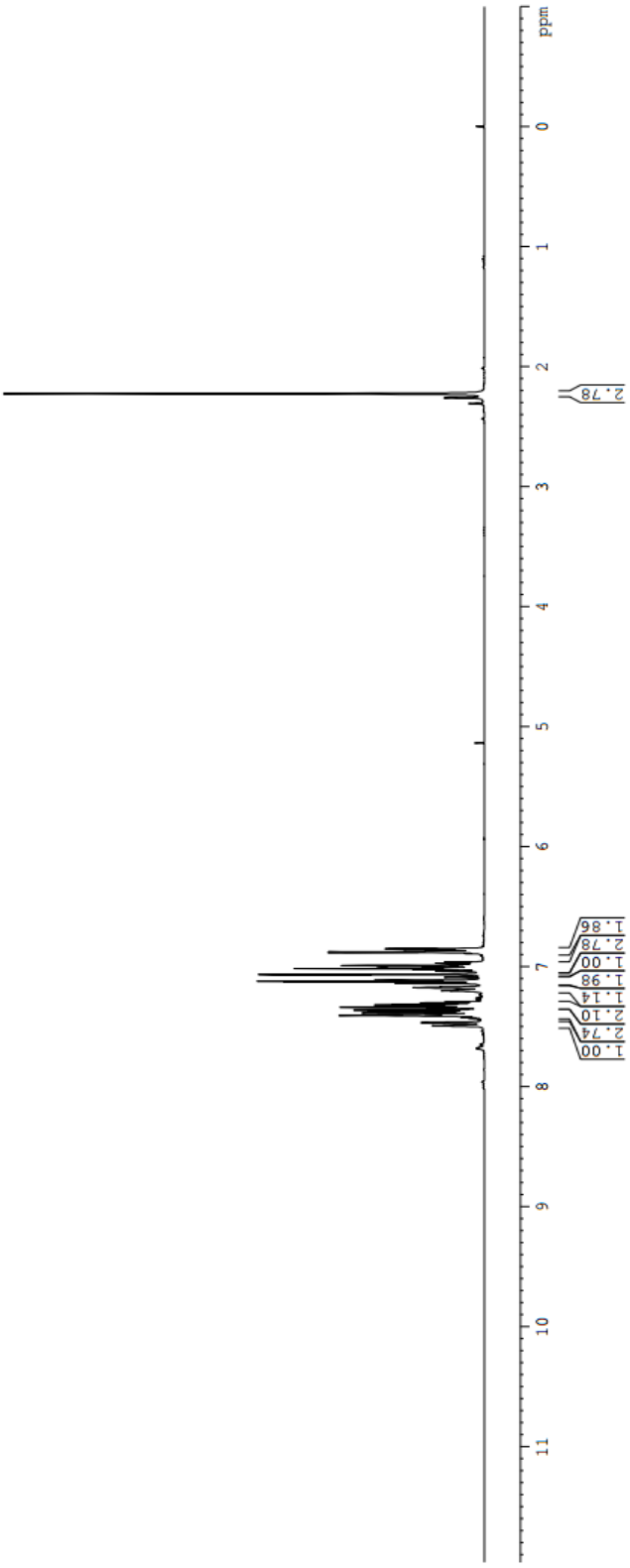
1e

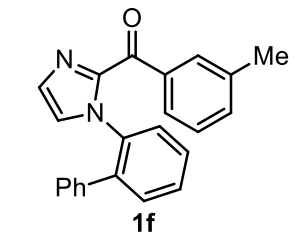
^{13}C NMR, $CDCl_3$, 75MHz



1f

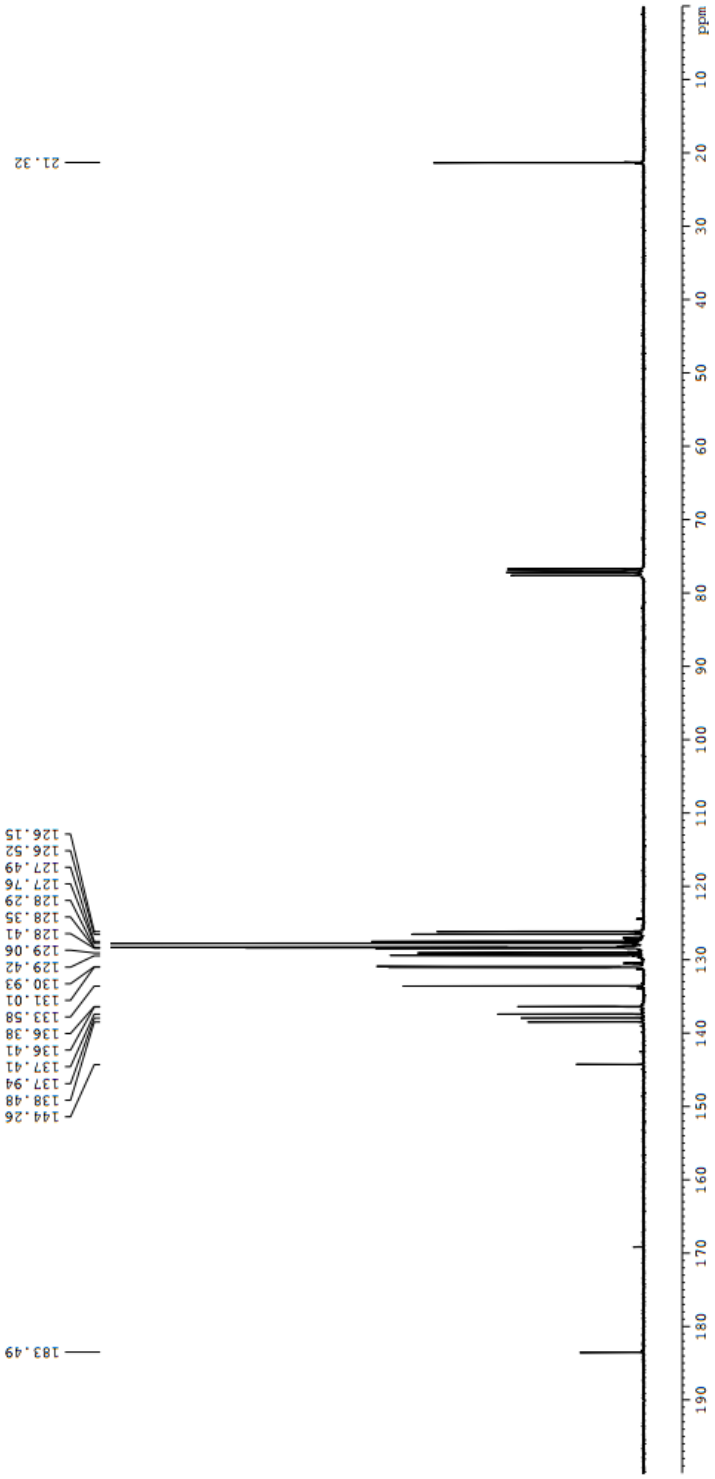
^{1}H NMR, $CDCl_3$, 300MHz

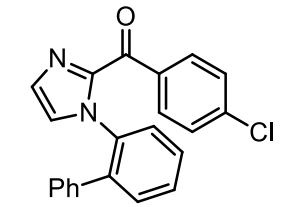




1f

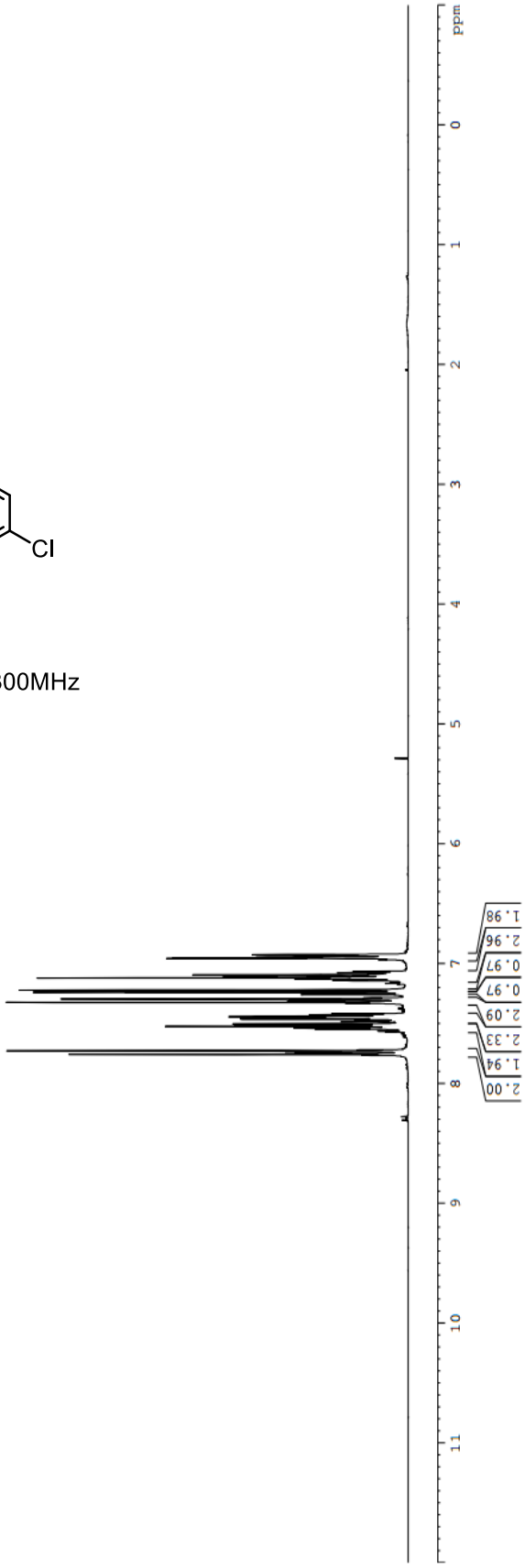
^{13}C NMR, $CDCl_3$, 75MHz

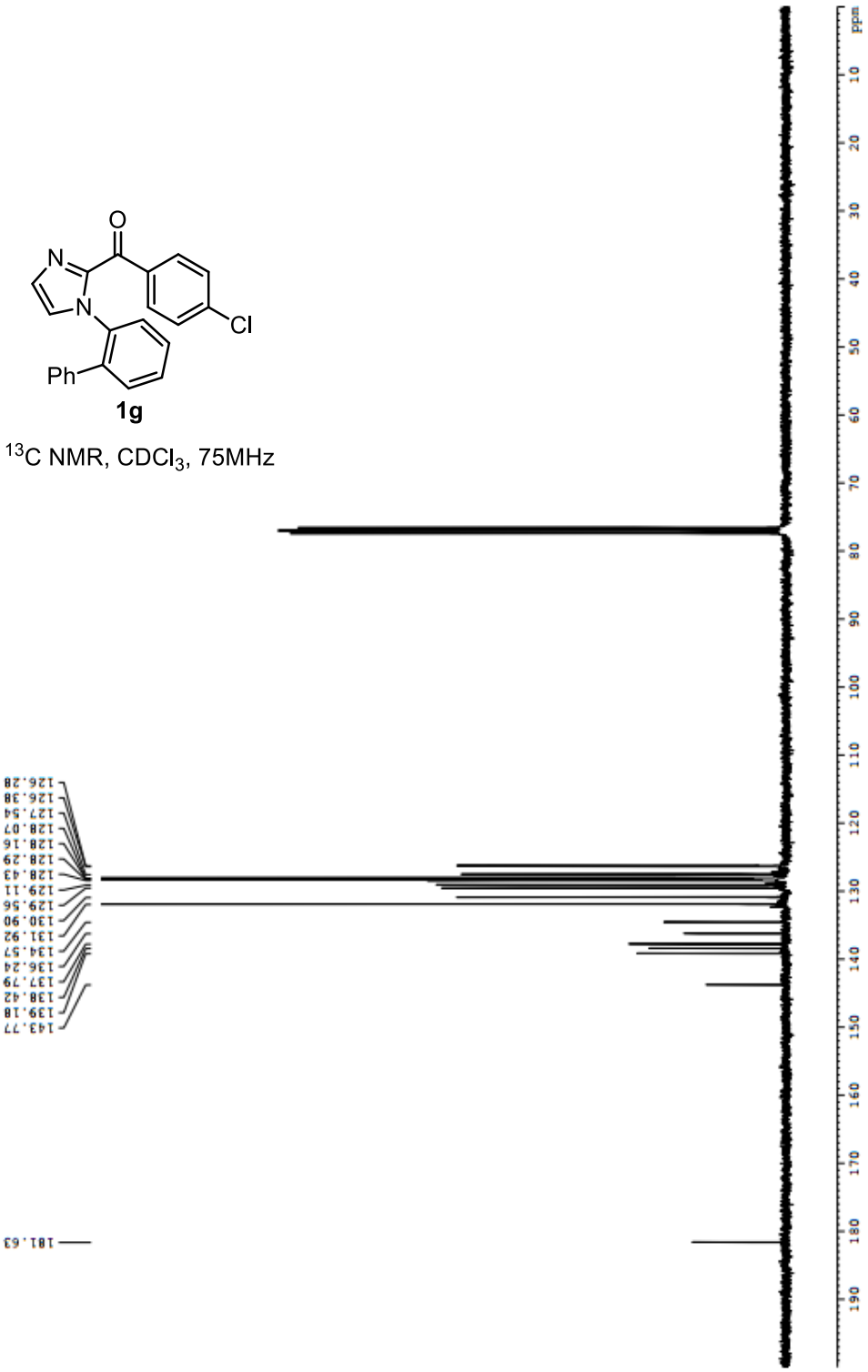


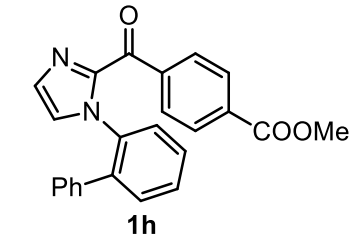


1g

^{1}H NMR, $CDCl_3$, 300MHz

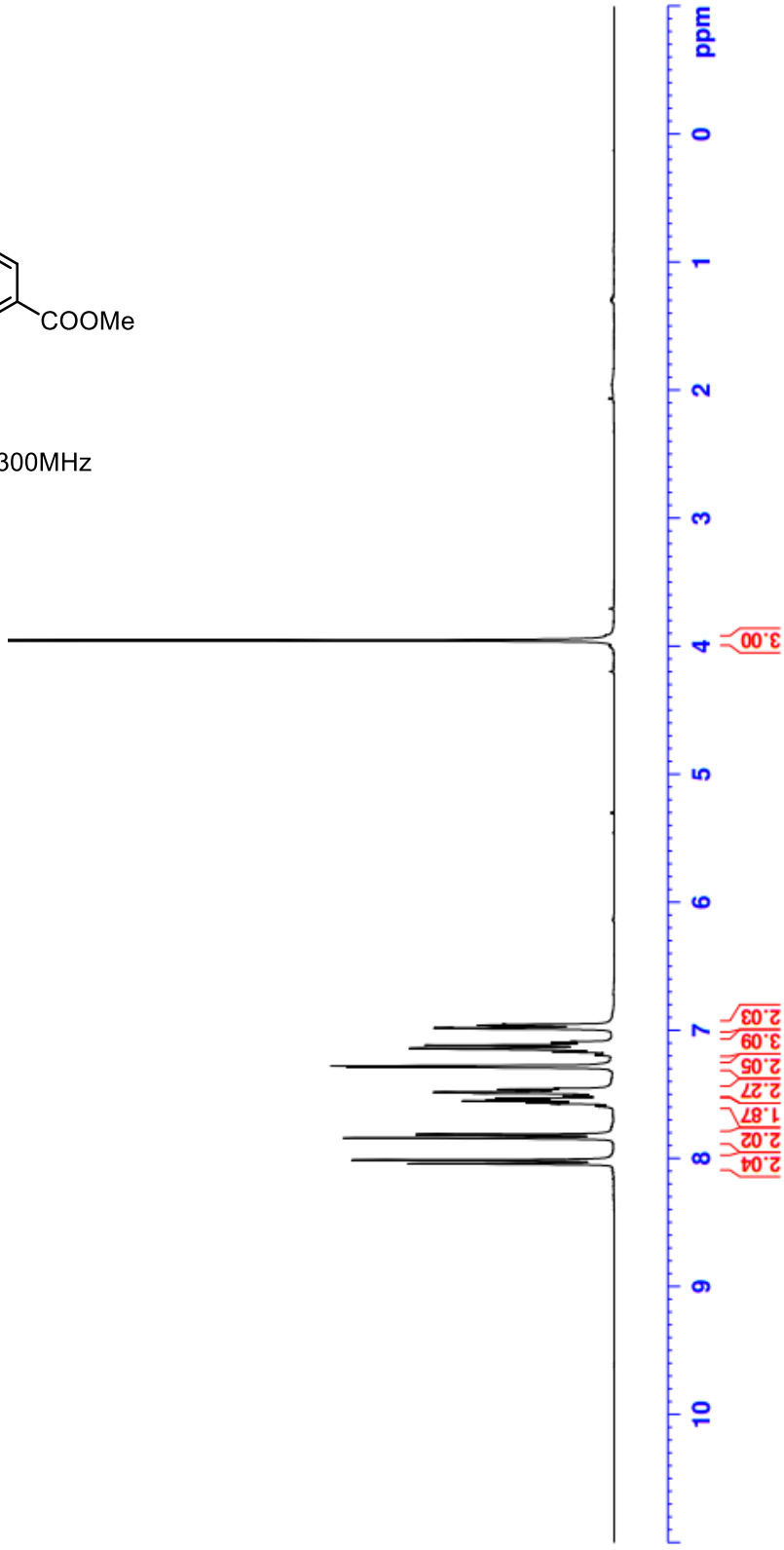


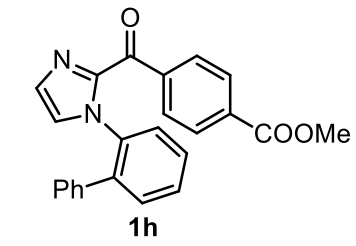

O
N
N
Cl
Ph
1g
13C NMR, CDCl3, 75MHz
181.63
143.77
139.18
138.42
137.79
136.24
134.57
131.92
130.90
129.56
129.11
128.43
128.29
128.16
128.07
127.54
126.38
126.28
ppm



1h

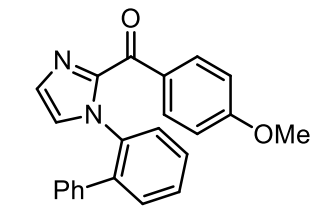
^{1}H NMR, $CDCl_3$, 300MHz





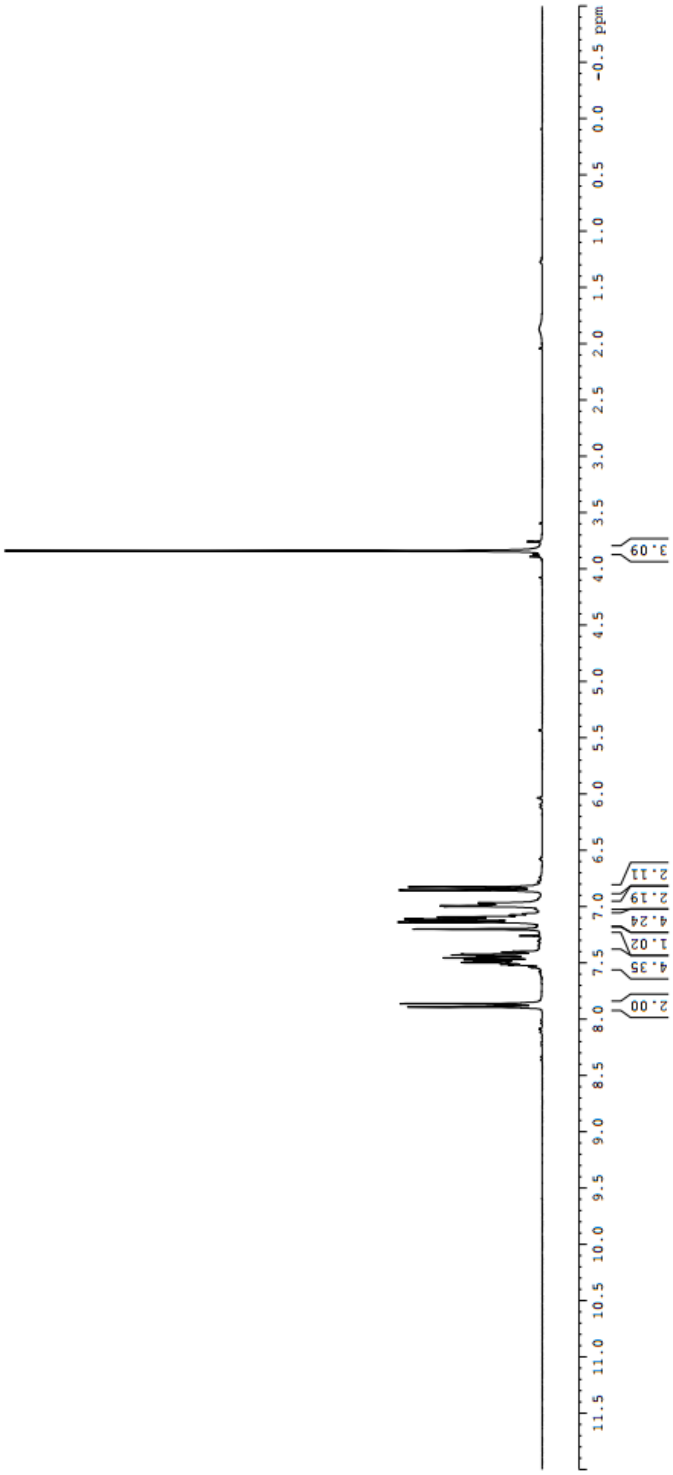
1h

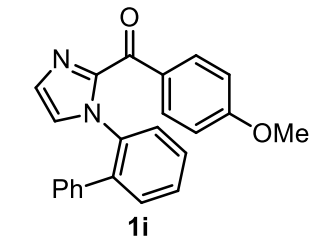
^{13}C NMR, $CDCl_3$, 300MHz



1i

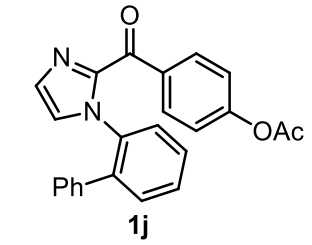
^{1}H NMR, $CDCl_3$, 300MHz





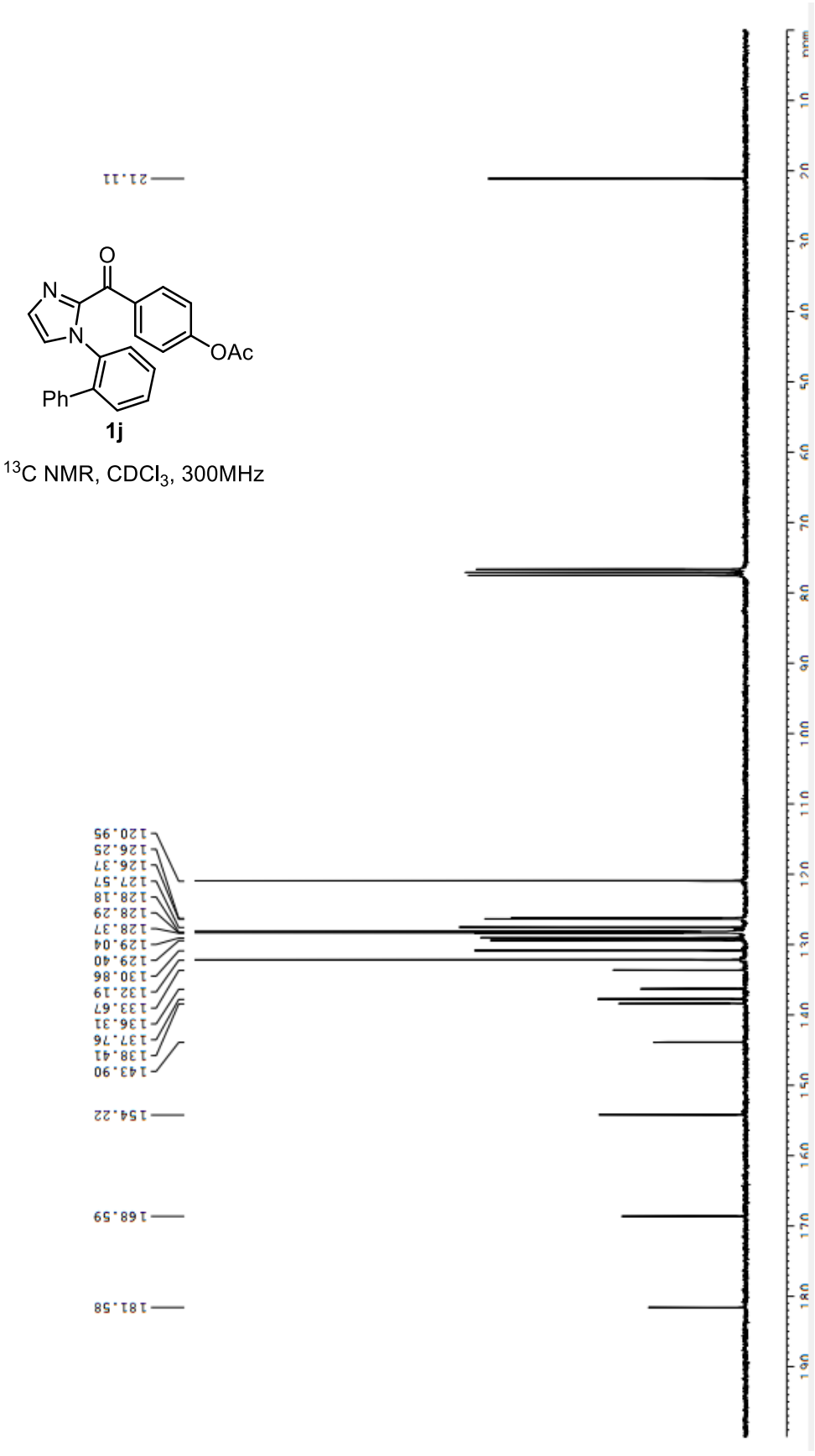
1i

^{13}C NMR, $CDCl_3$, 300MHz



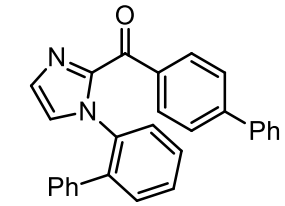
1j

^{1}H NMR, $CDCl_3$, 300MHz



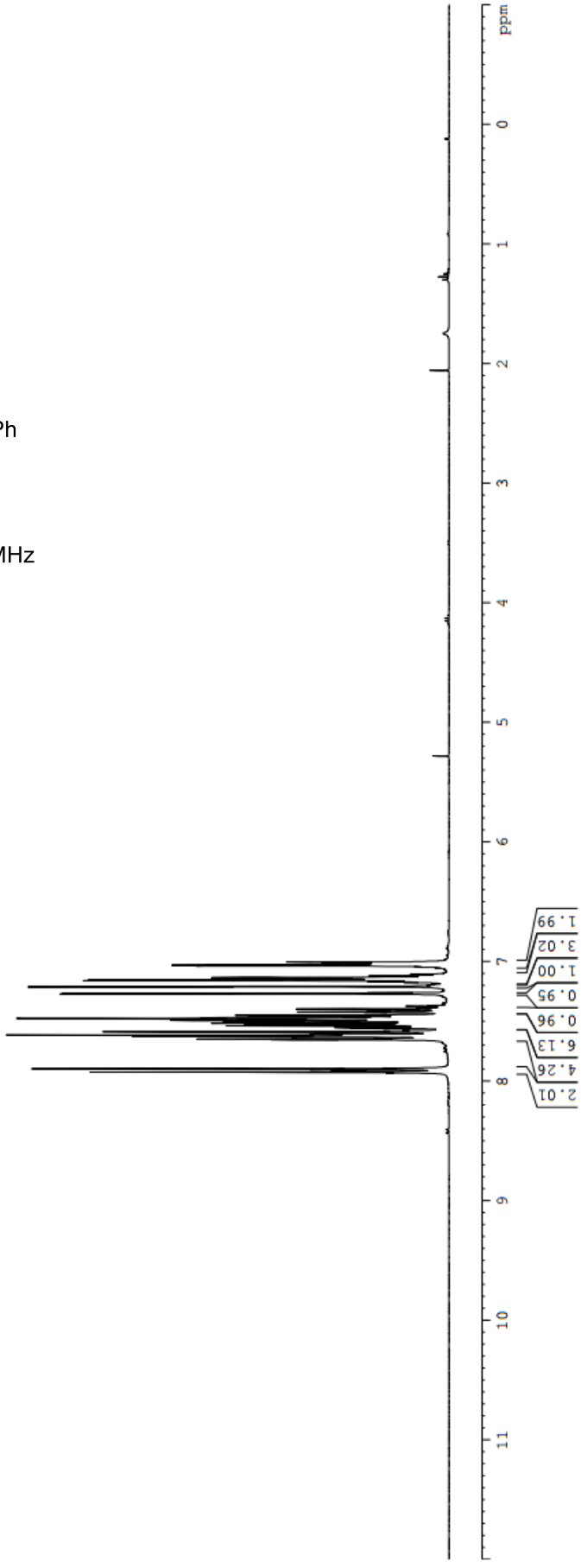
1j

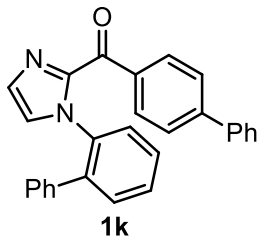
^{13}C NMR, $CDCl_3$, 300MHz



1k

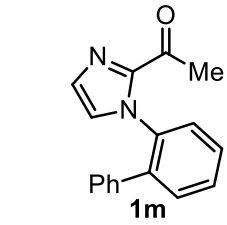
^{1}H NMR, $CDCl_3$, 300MHz





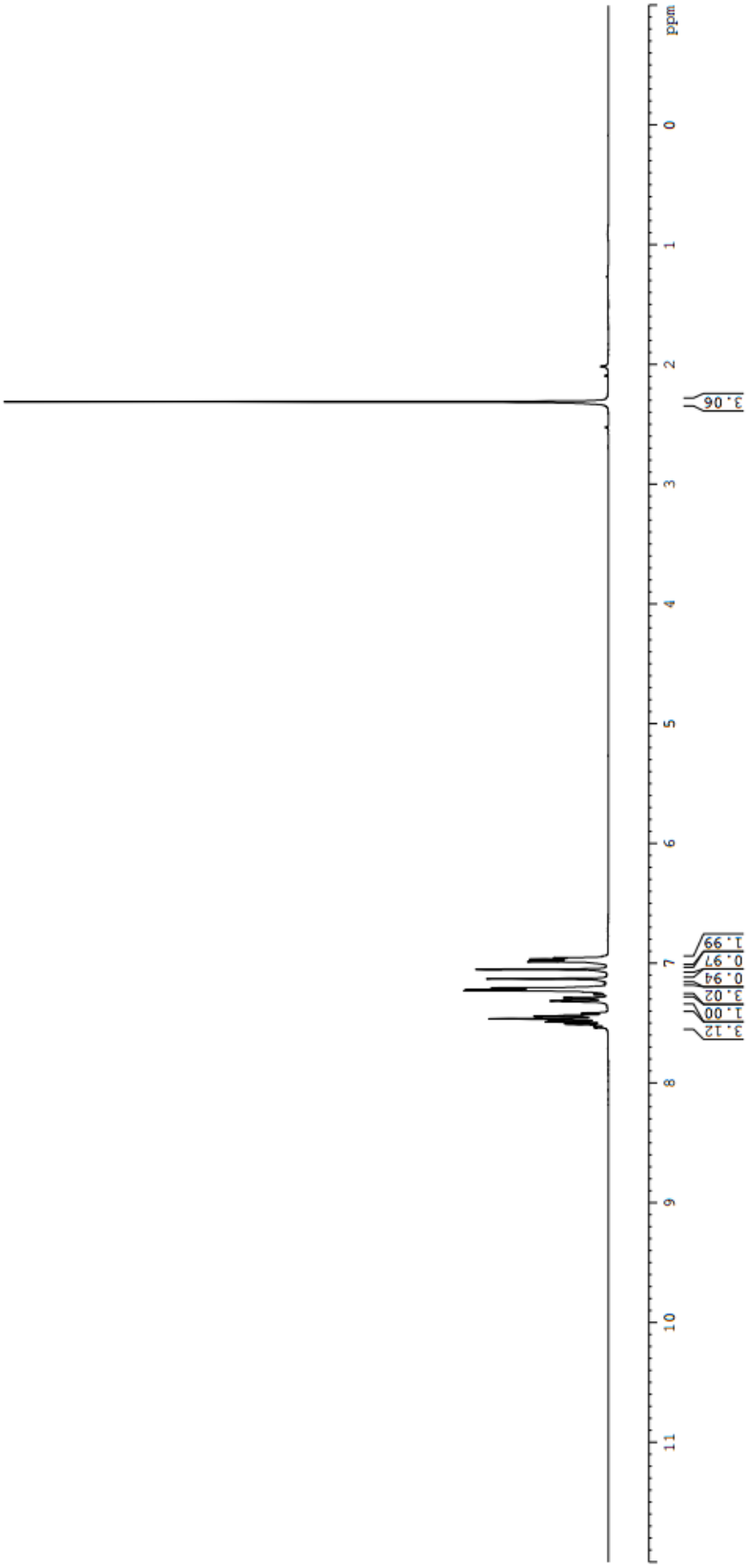
1k

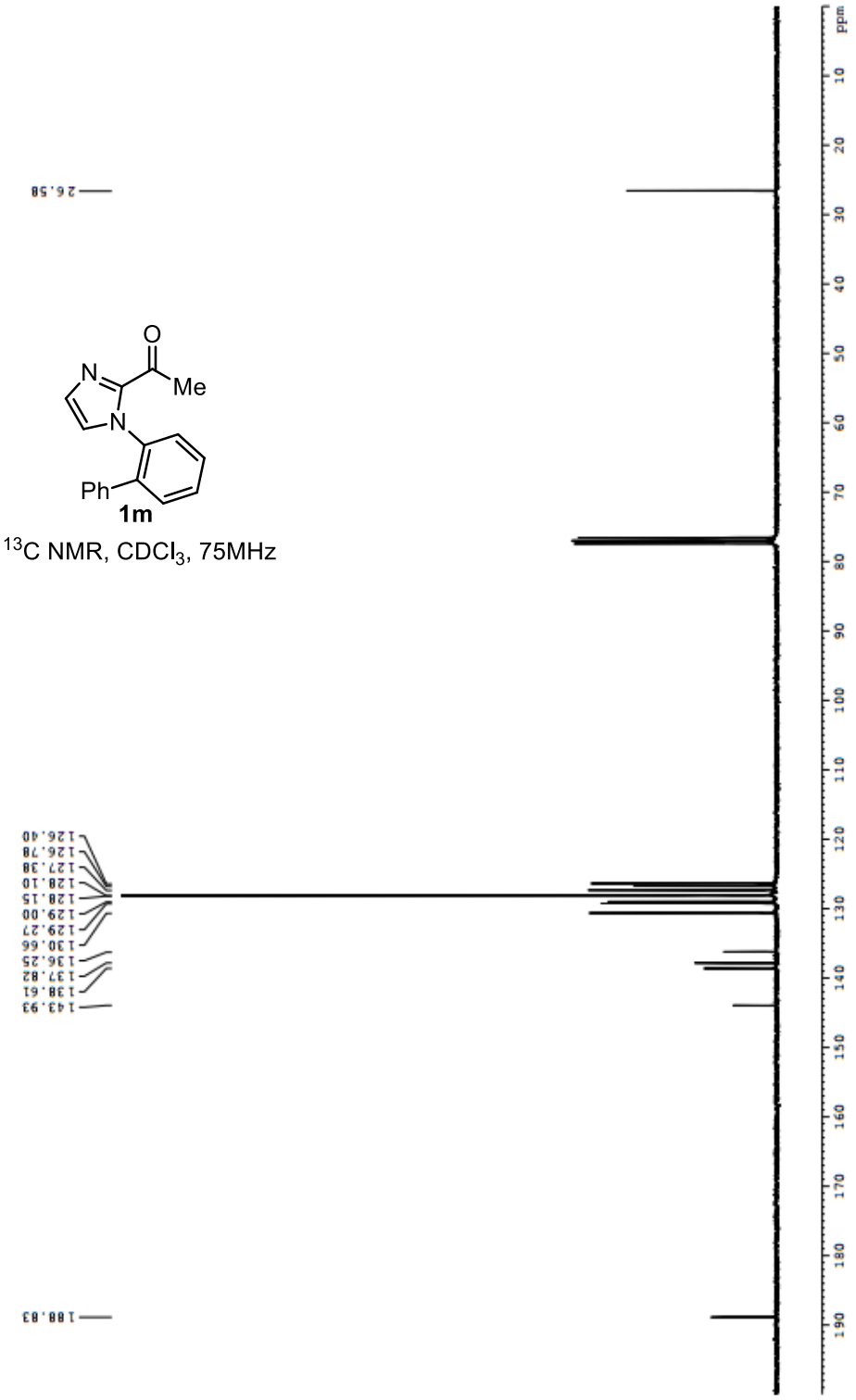
^{13}C NMR, $CDCl_3$, 300MHz



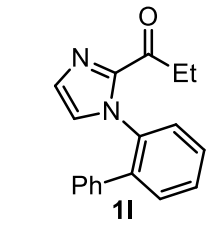
1m

^{1}H NMR, $CDCl_3$, 300MHz



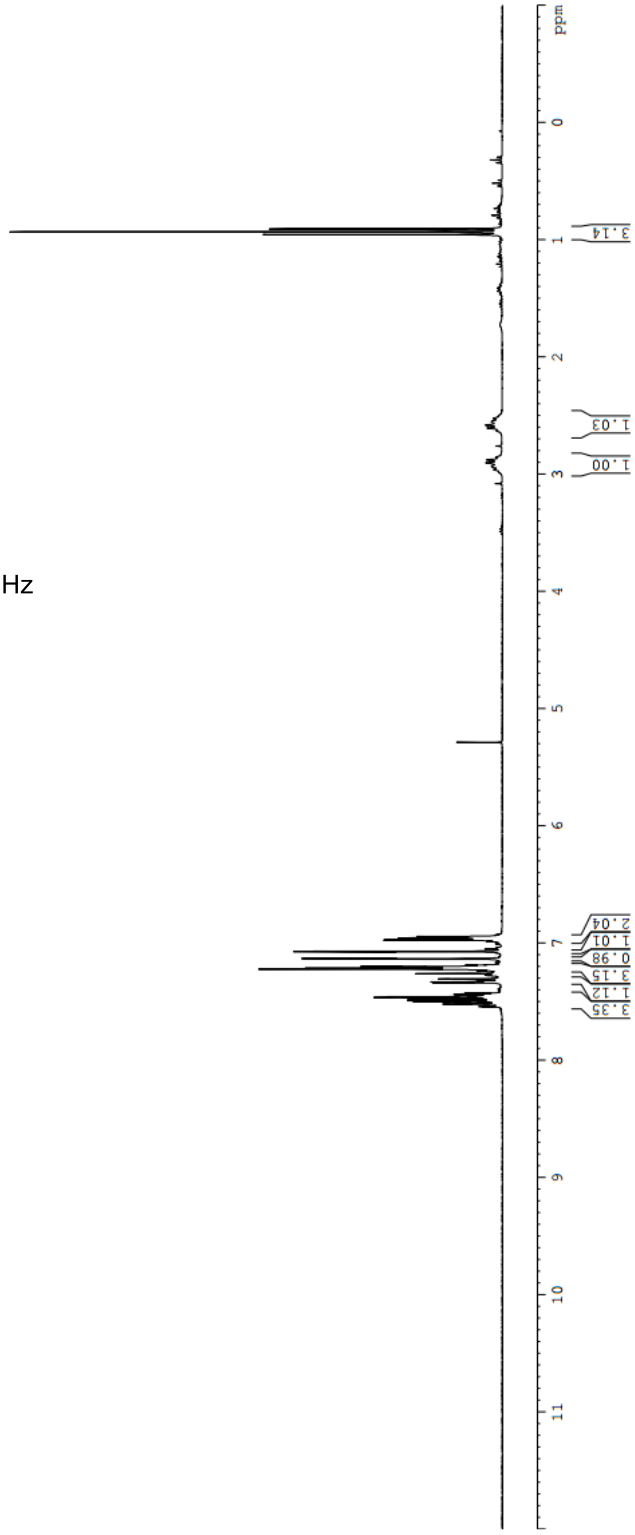


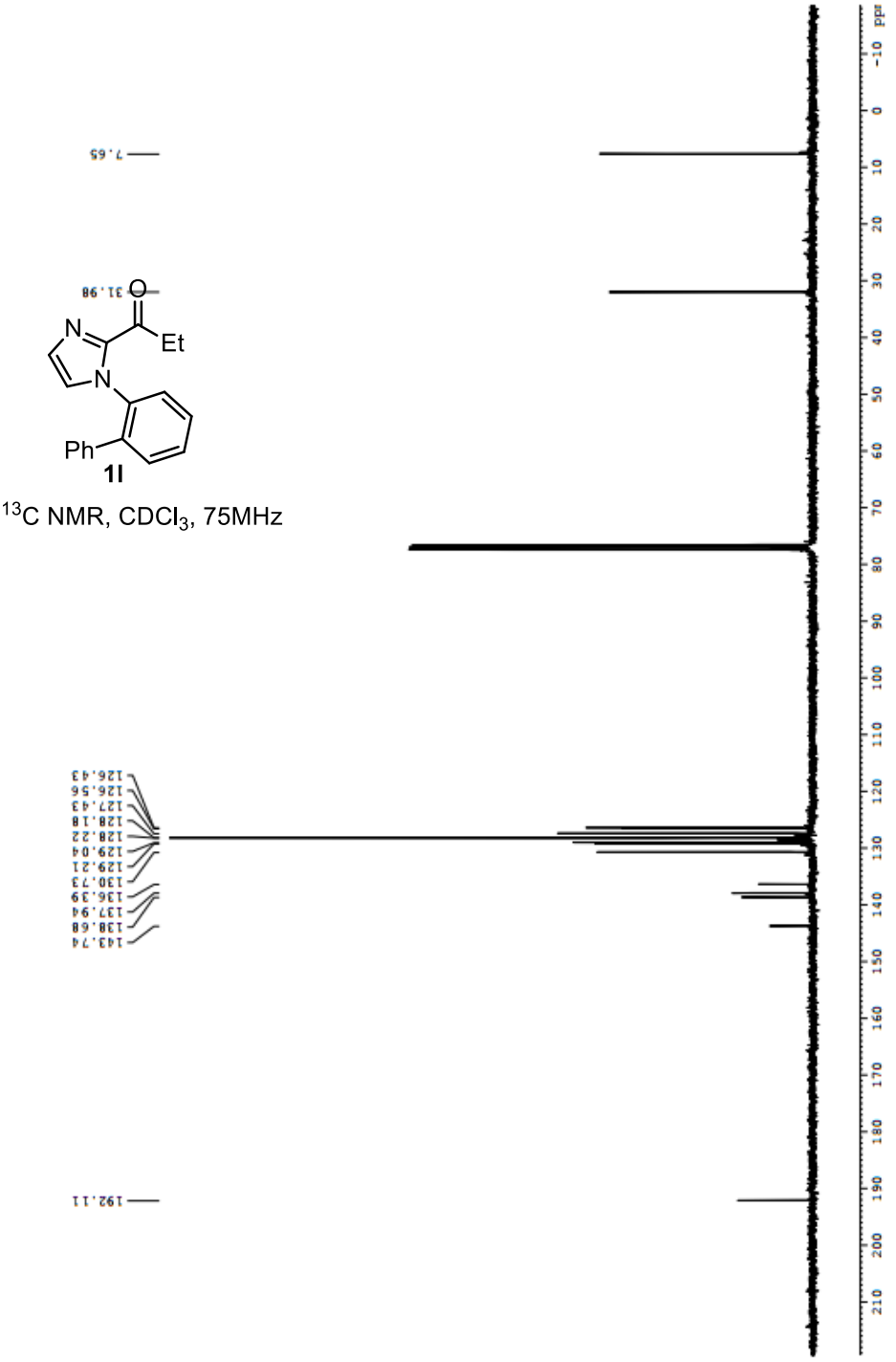
^{13}C NMR, $CDCl_3$, 75MHz



1l

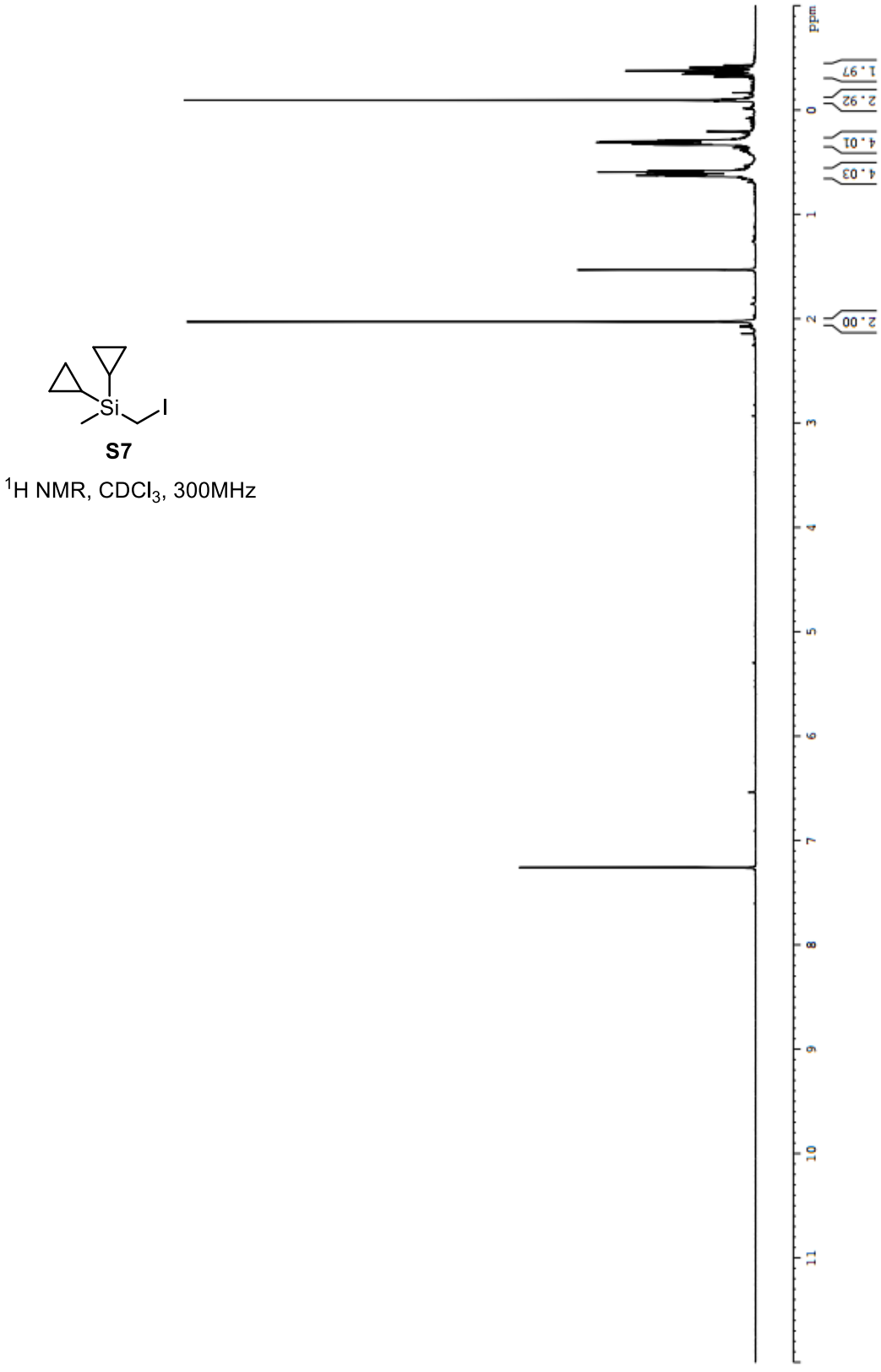
^{1}H NMR, $CDCl_3$, 300MHz





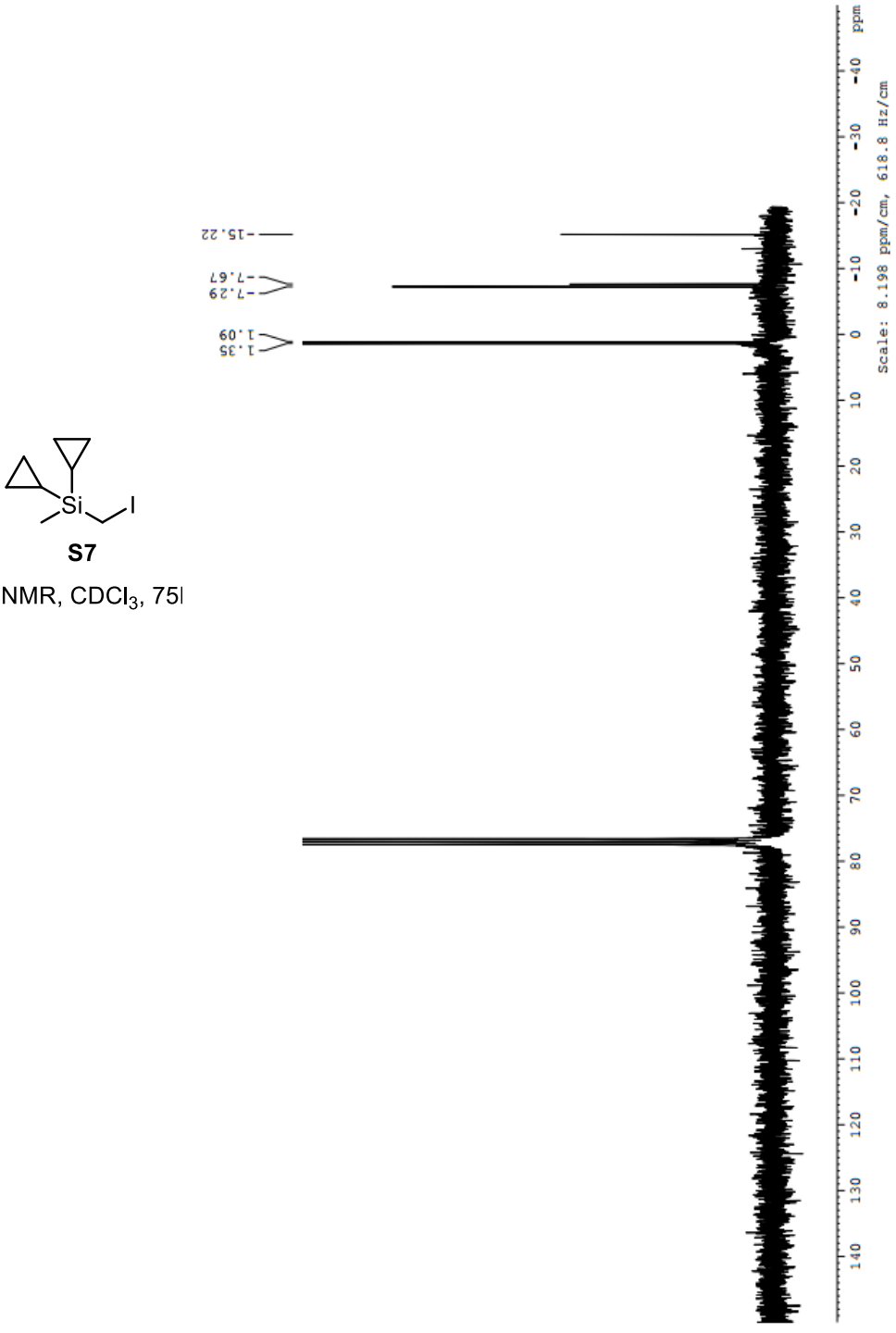
1l

^{13}C NMR, $CDCl_3$, 75MHz



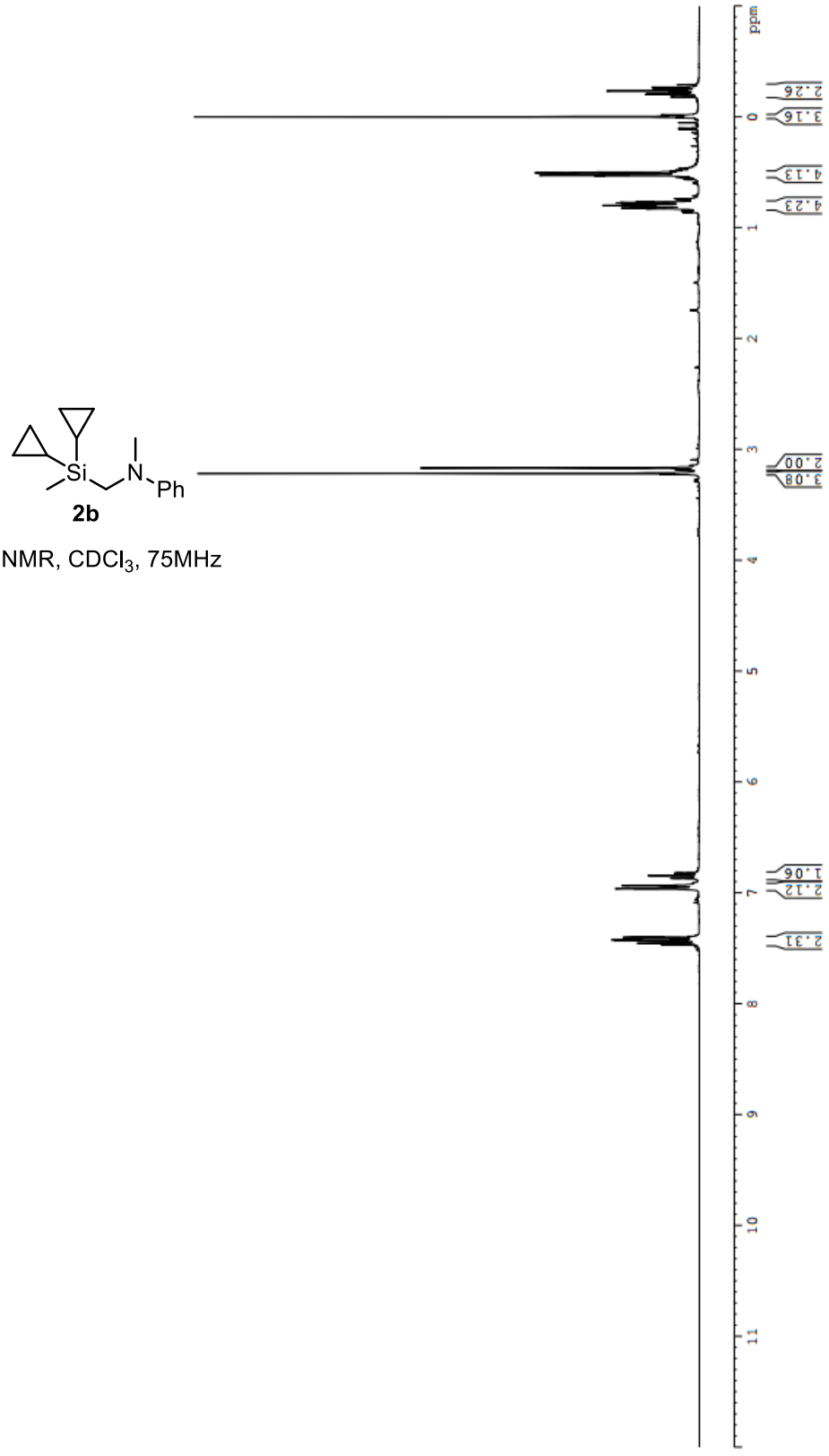
S7

^{1}H NMR, $CDCl_3$, 300MHz



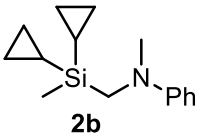
S7

^{13}C NMR, $CDCl_3$, 75I



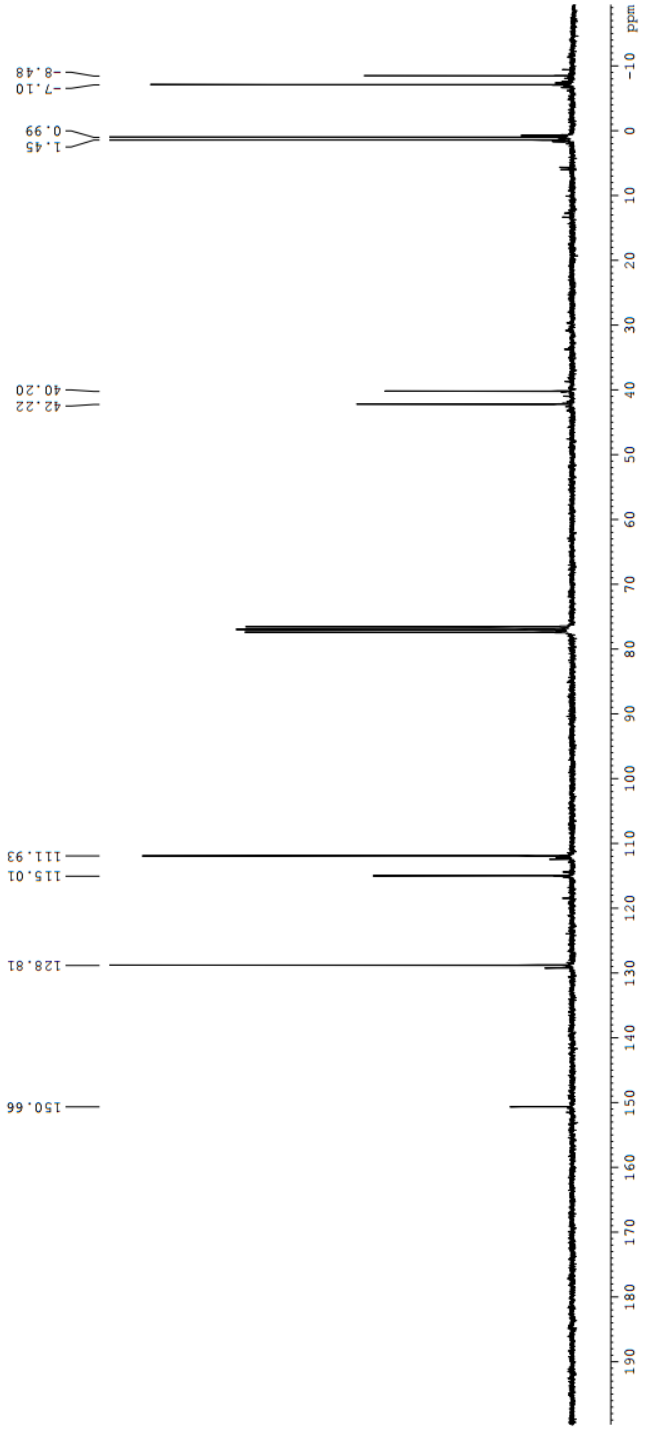
2b

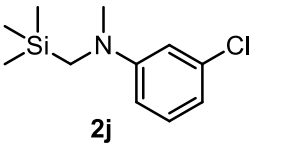
^{13}C NMR, $CDCl_3$, 75MHz



2b

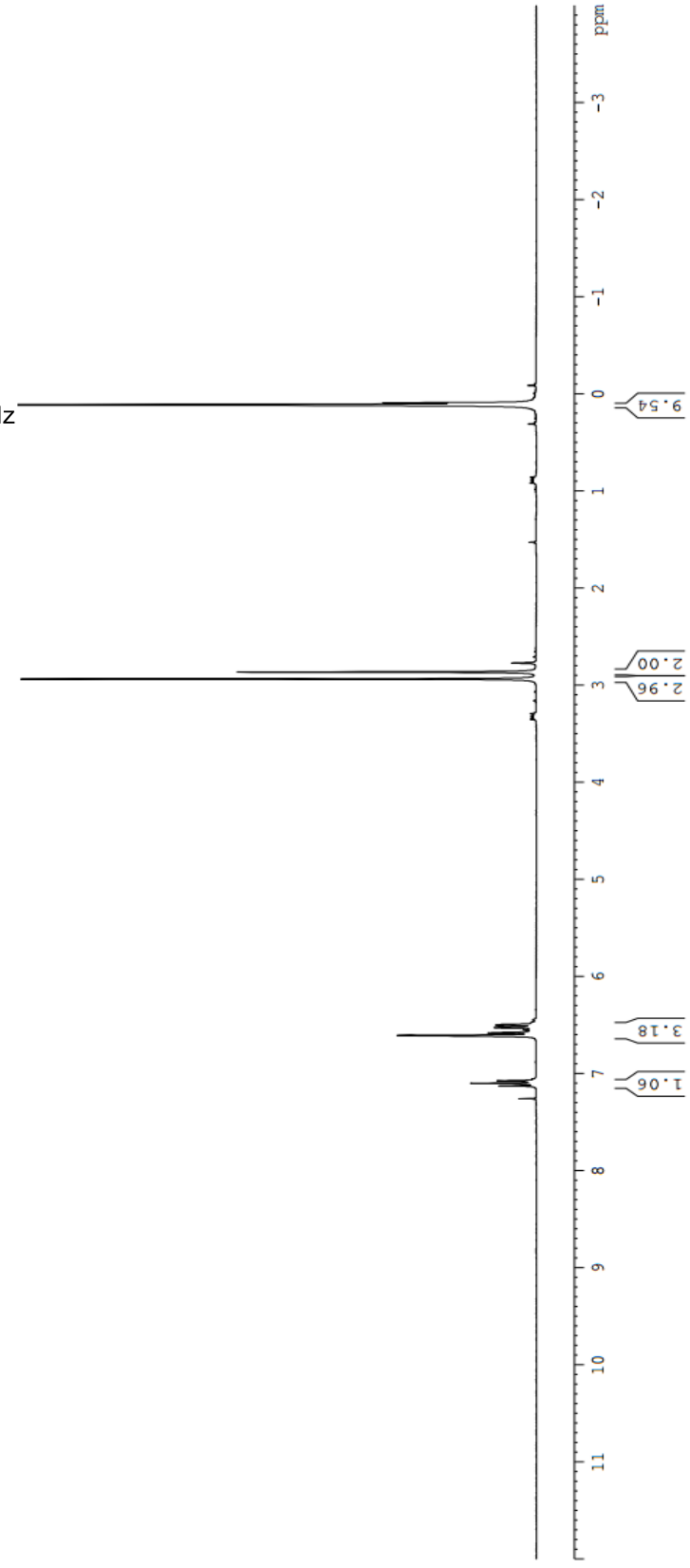
^{1}H NMR, $CDCl_3$, 300MHz

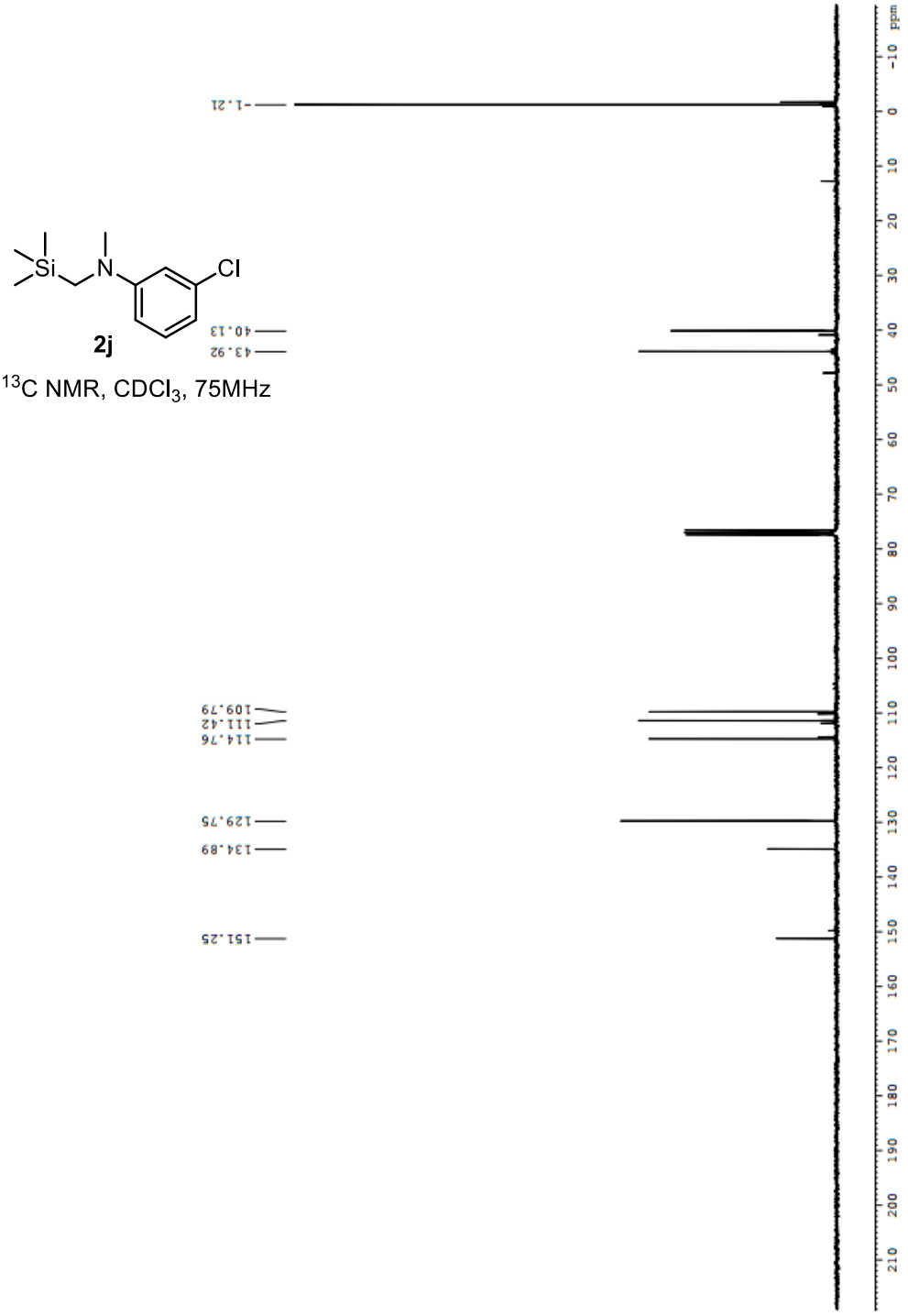




2j

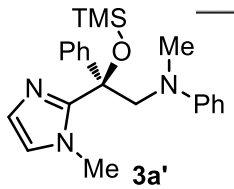
^{1}H NMR, $CDCl_3$, 300MHz





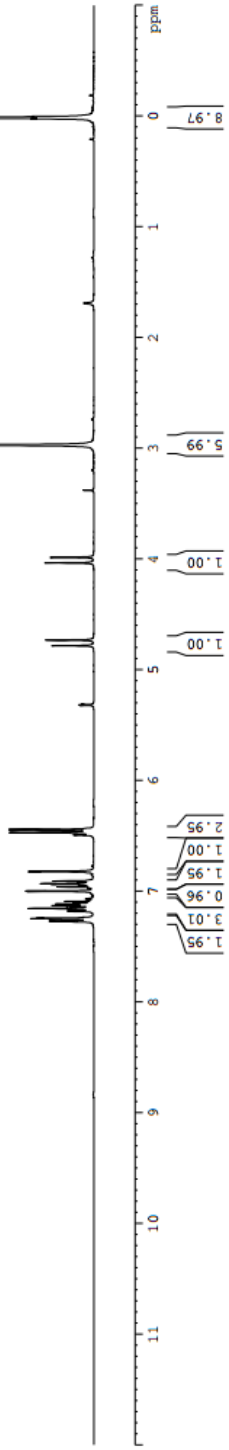
2j

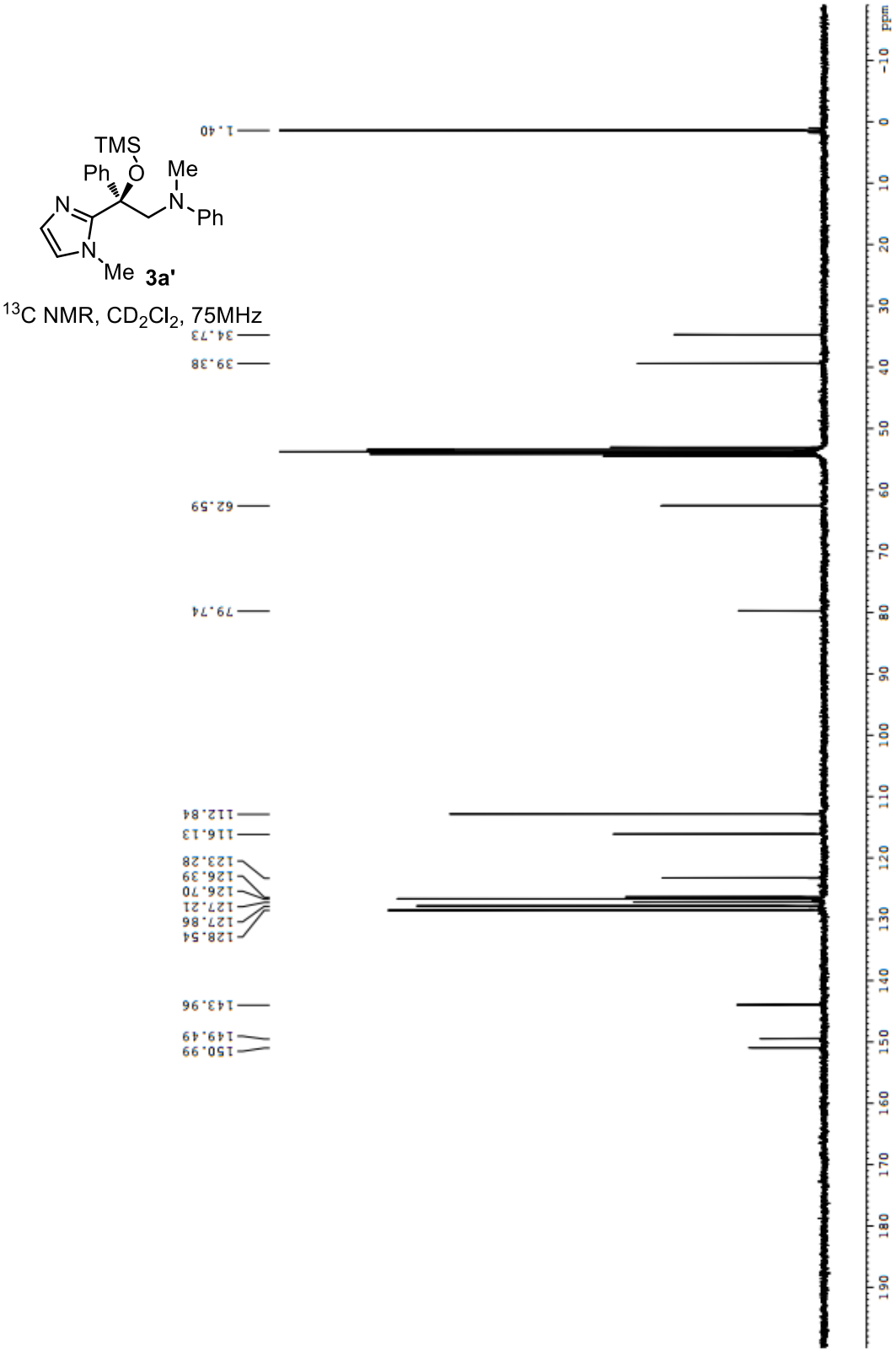
^{13}C NMR, $CDCl_3$, 75MHz

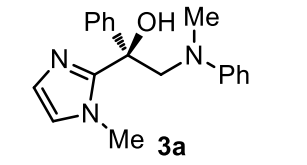


3a'

^{1}H NMR, CD_2Cl_2, 300MHz

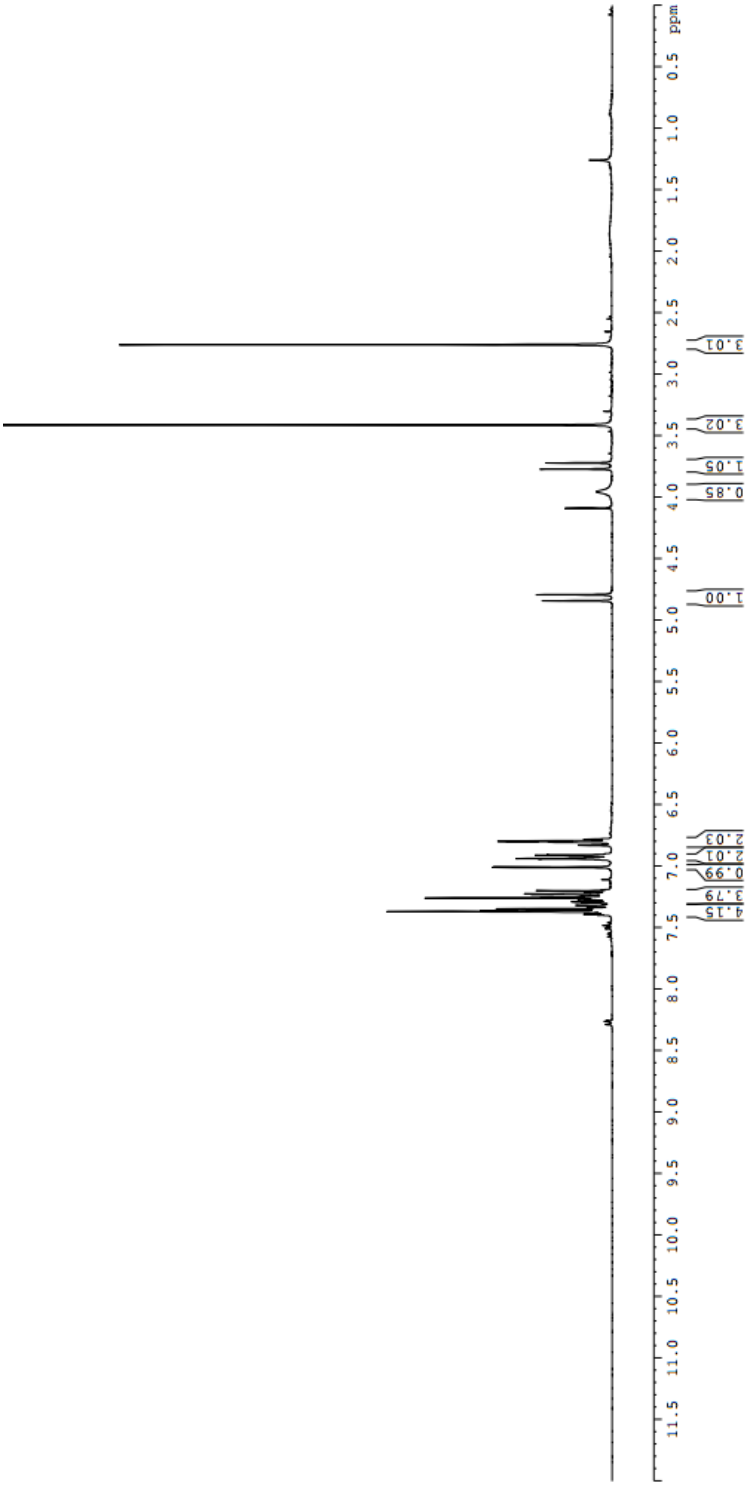


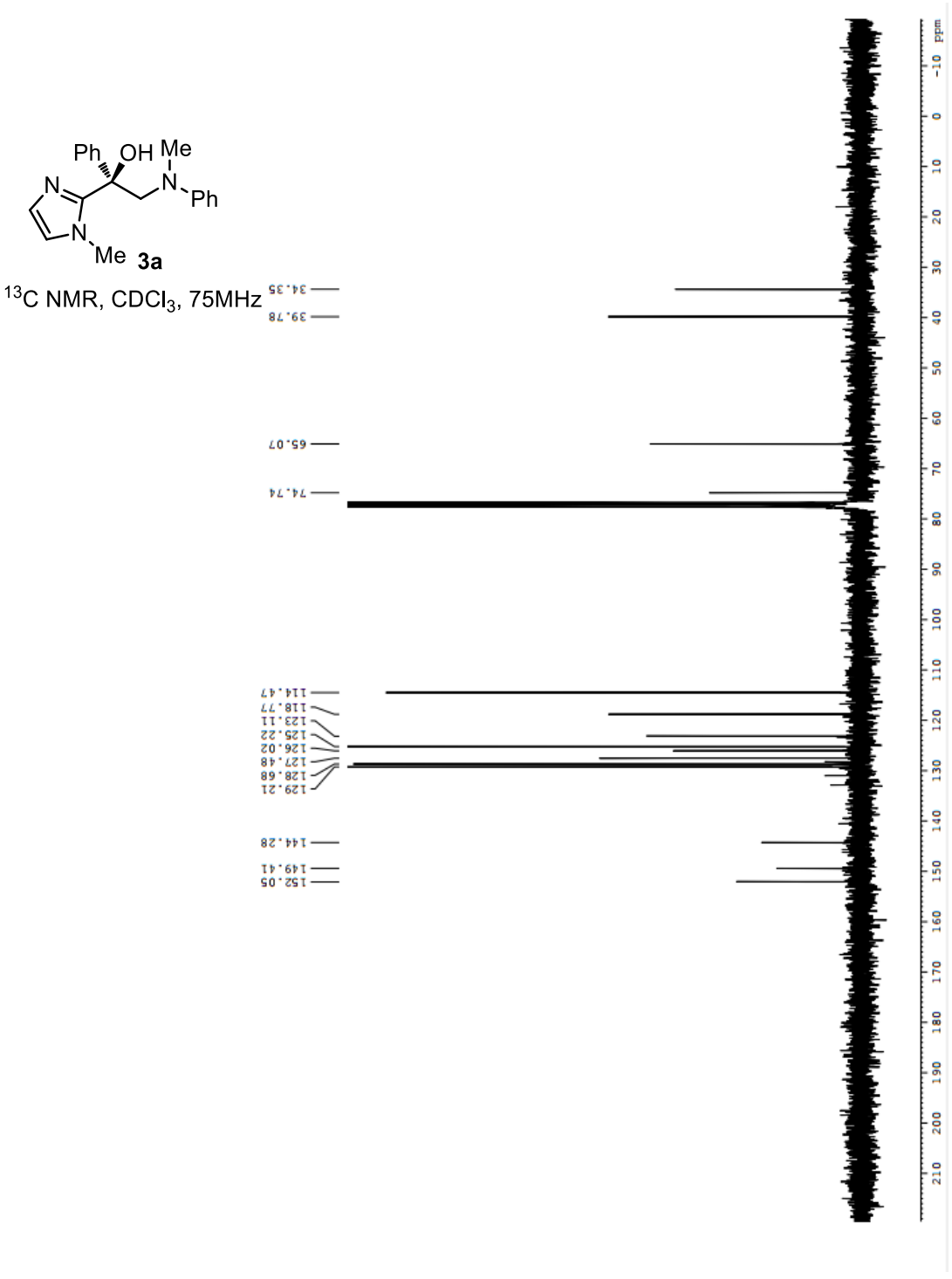

TMS
Ph
O
Me
N
N
Ph
N
Me
3a'
13C NMR, CD2Cl2, 75MHz
1.40
34.73
39.38
62.59
79.74
112.84
116.13
123.28
126.39
126.70
127.21
127.86
128.54
143.96
149.49
150.99
ppm

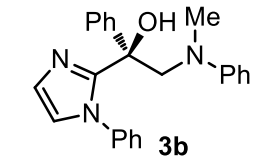


3a

^{1}H NMR, $CDCl_3$, 300MHz

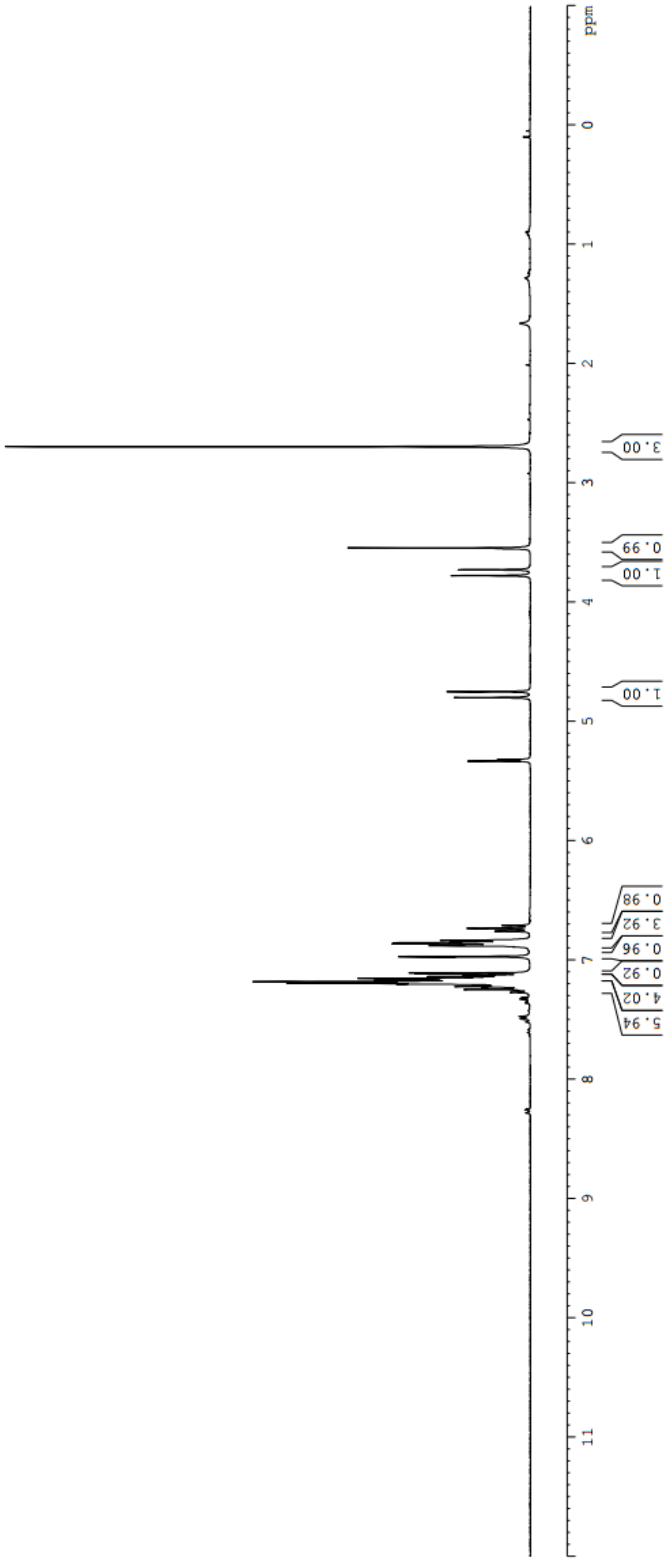


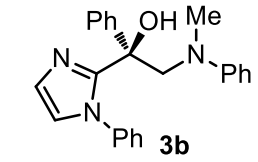

Ph
OH
Me
N
N
Ph
N
Me
3a
^{13}C NMR, CDCl$_3$, 75MHz
34.35
39.78
65.07
74.74
114.47
118.77
123.11
125.22
126.02
127.48
128.68
129.21
144.28
149.41
152.05
ppm



3b

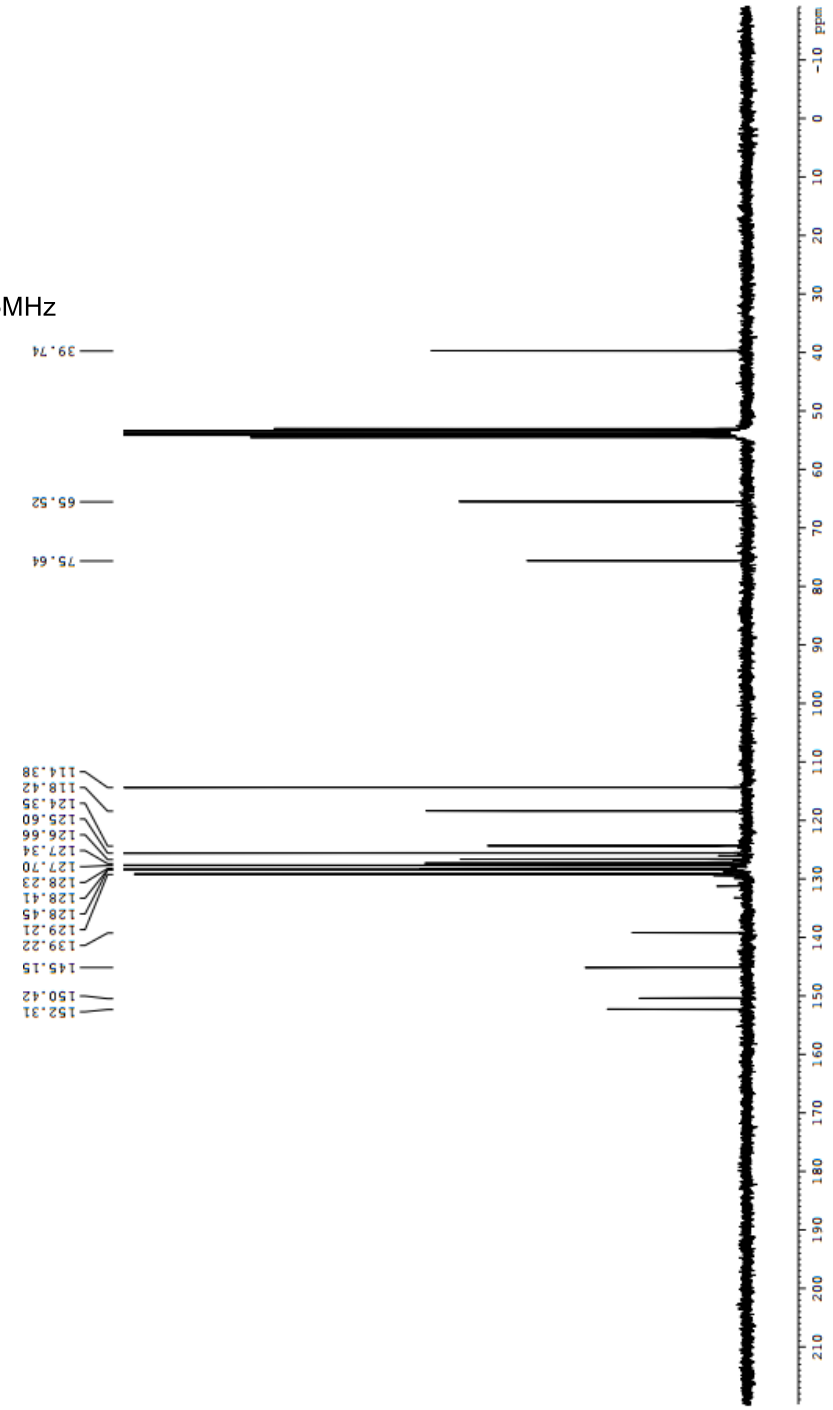
^{1}H NMR, CD_2Cl_2, 300MHz

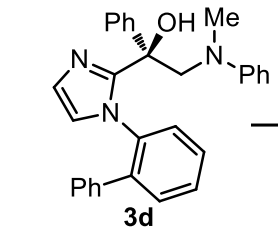




3b

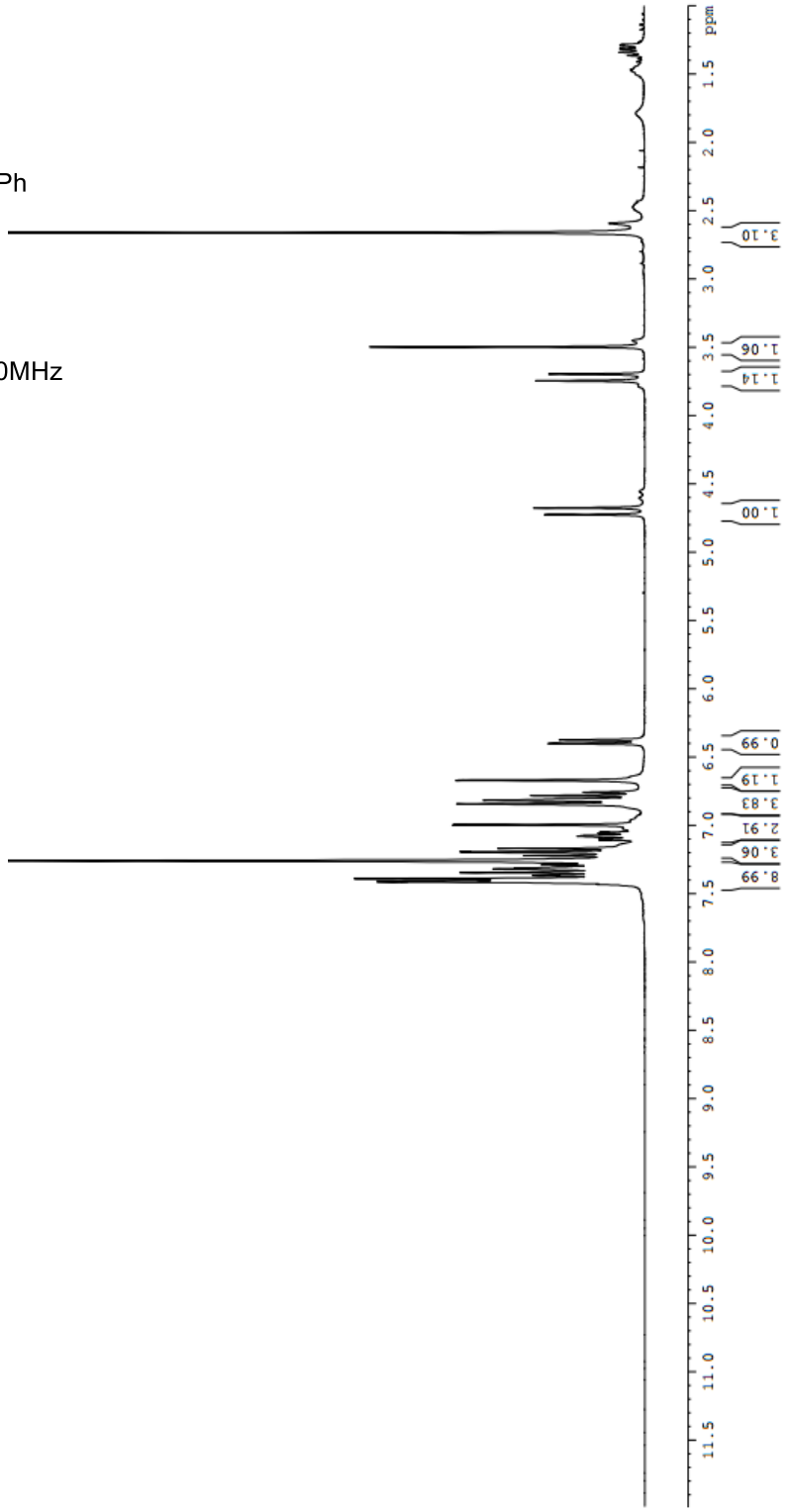
^{13}C NMR, CD_2Cl_2, 75MHz

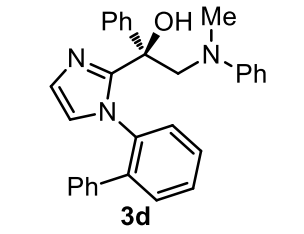




3d

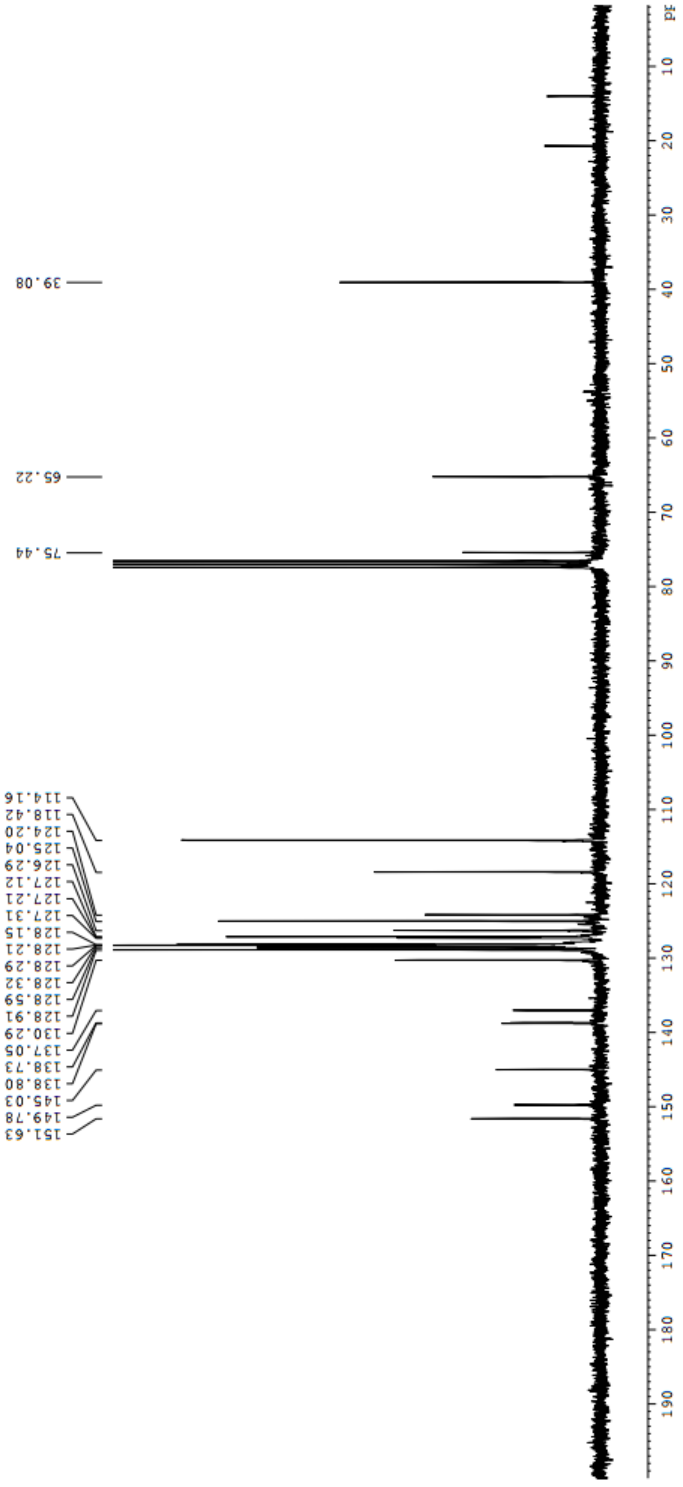
^{1}H NMR, $CDCl_3$, 300MHz

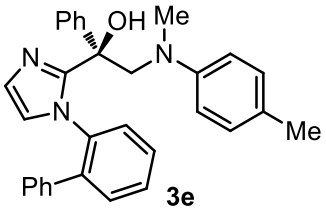




3d

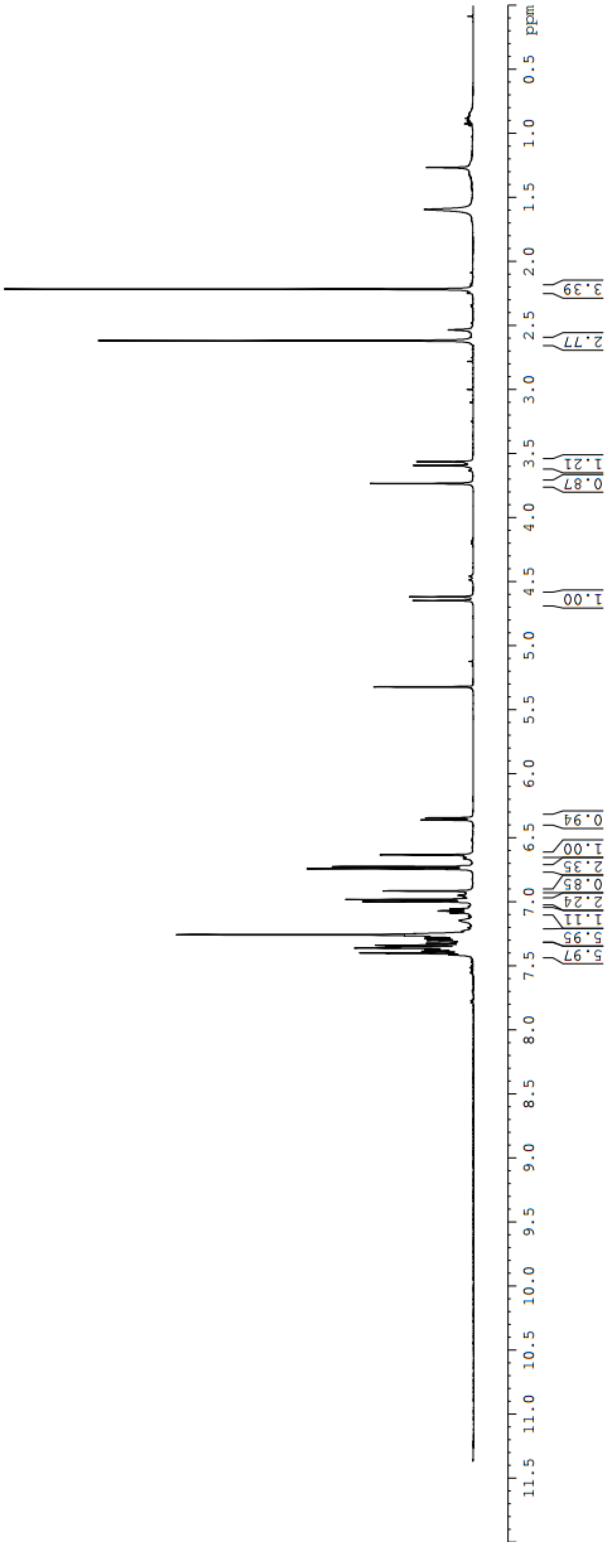
^{13}C NMR, $CDCl_3$, 75MHz

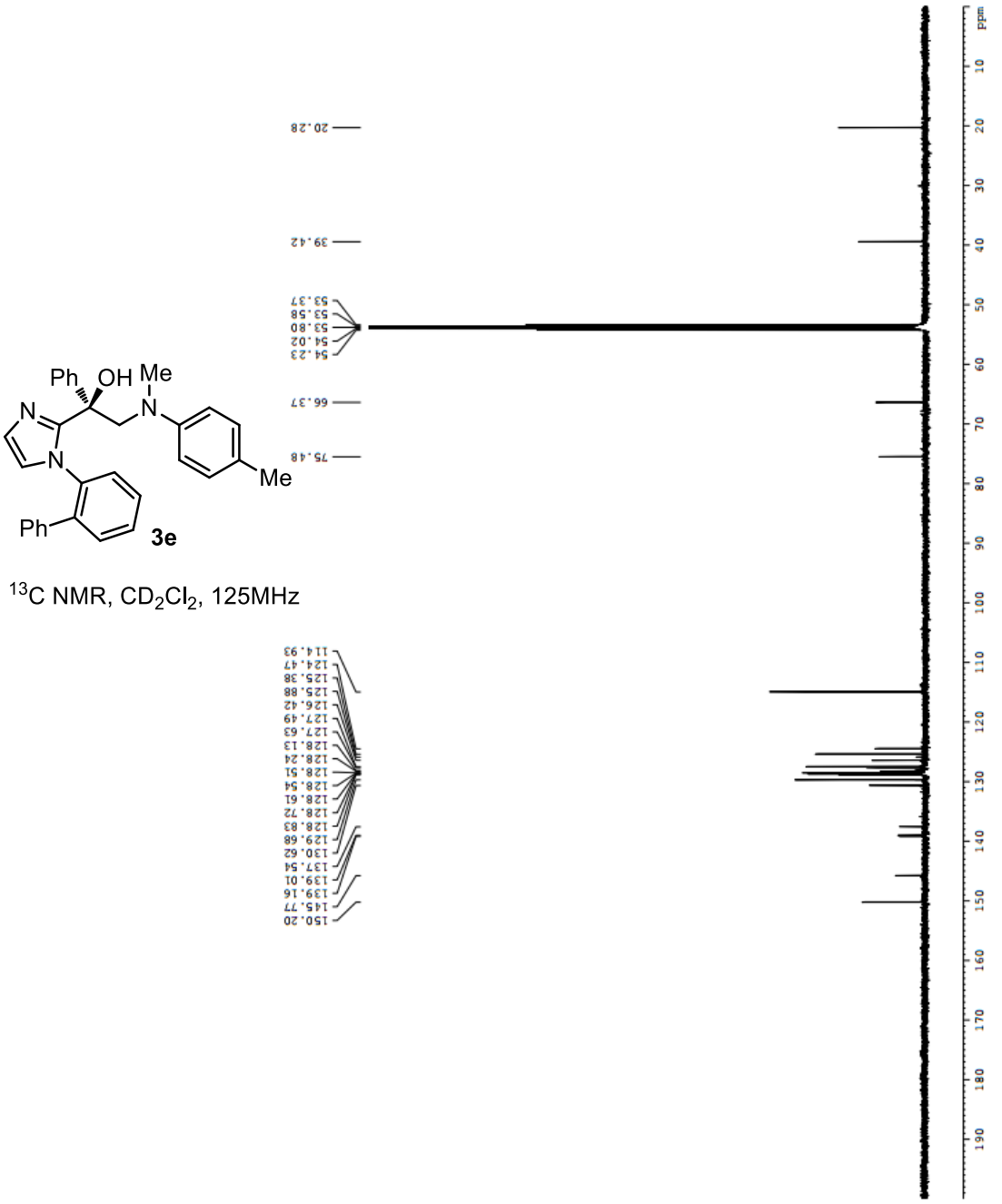




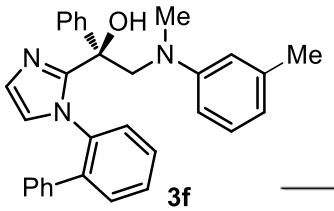
3e

^{1}H NMR, CD_2Cl_2, 500MHz



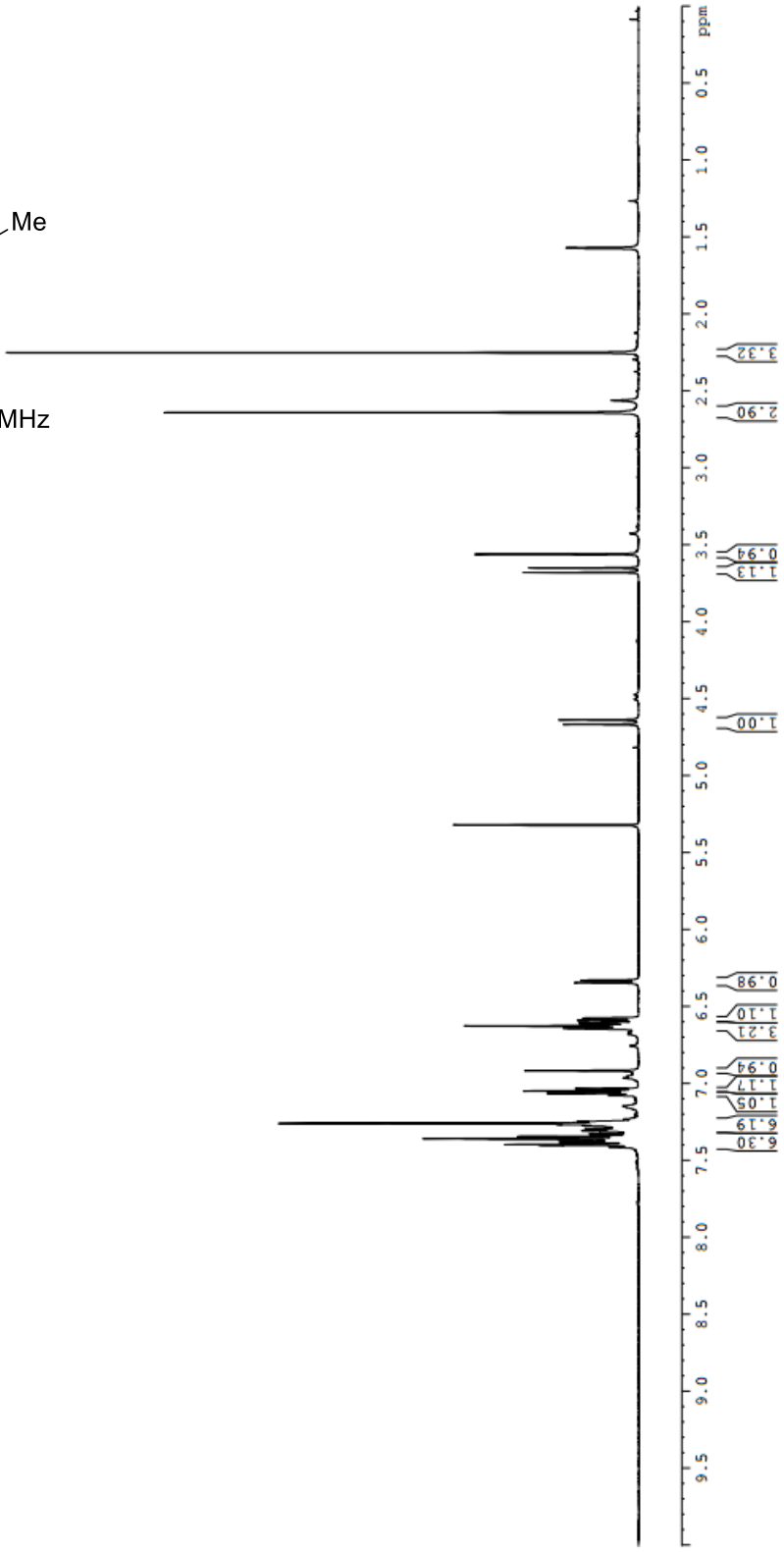


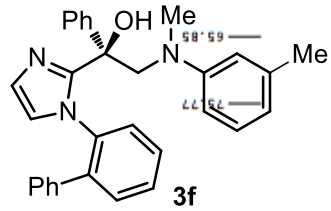
^{13}C NMR, CD_2Cl_2, 125MHz



3f

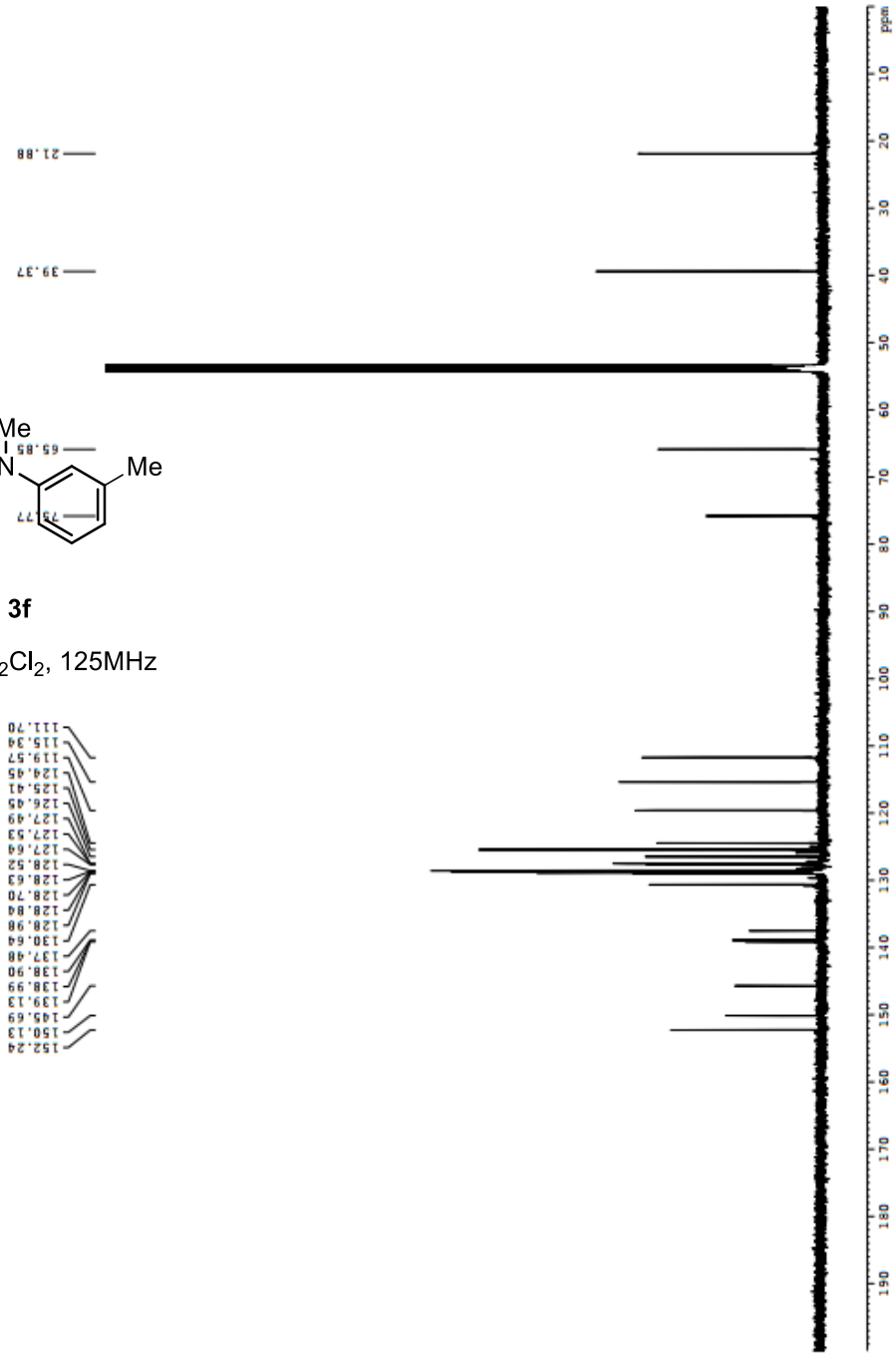
^{1}H NMR, CD_2Cl_2, 500MHz

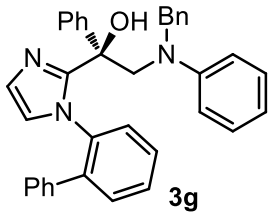




3f

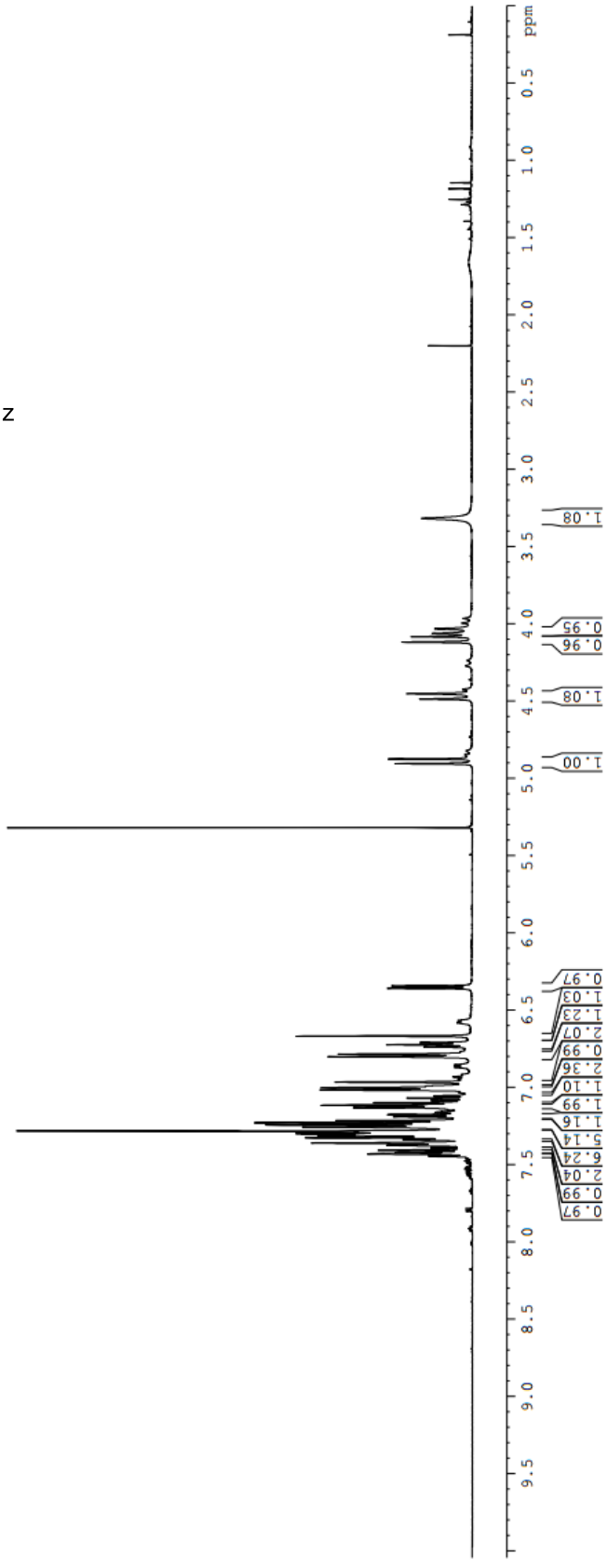
^{13}C NMR, CD_2Cl_2, 125MHz

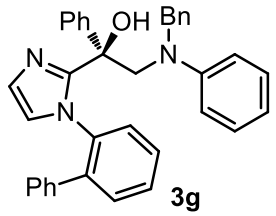




3g

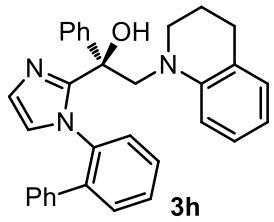
^{1}H NMR, CD_2Cl_2, 500MHz





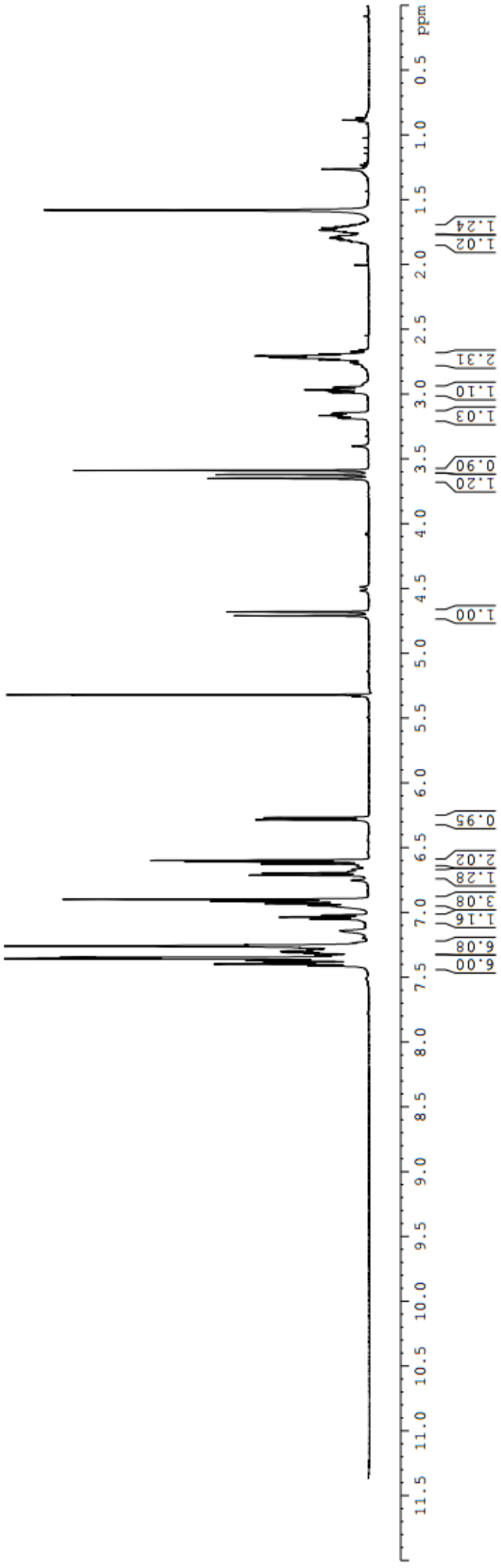
3g

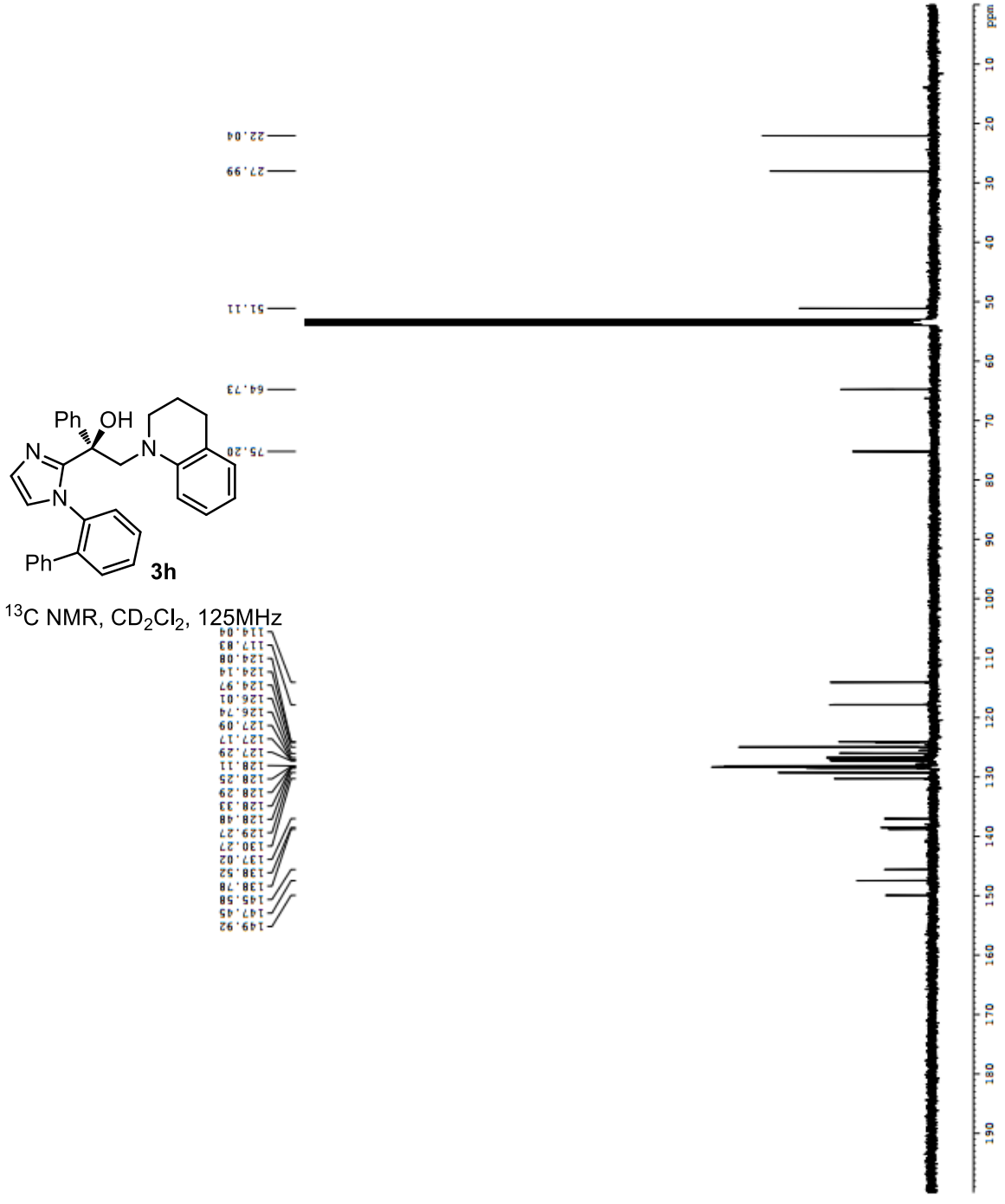
^{13}C NMR, $CDCl_3$, 125MHz

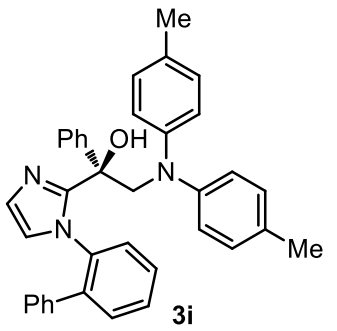


3h

^{1}H NMR, CD_2Cl_2, 500MHz

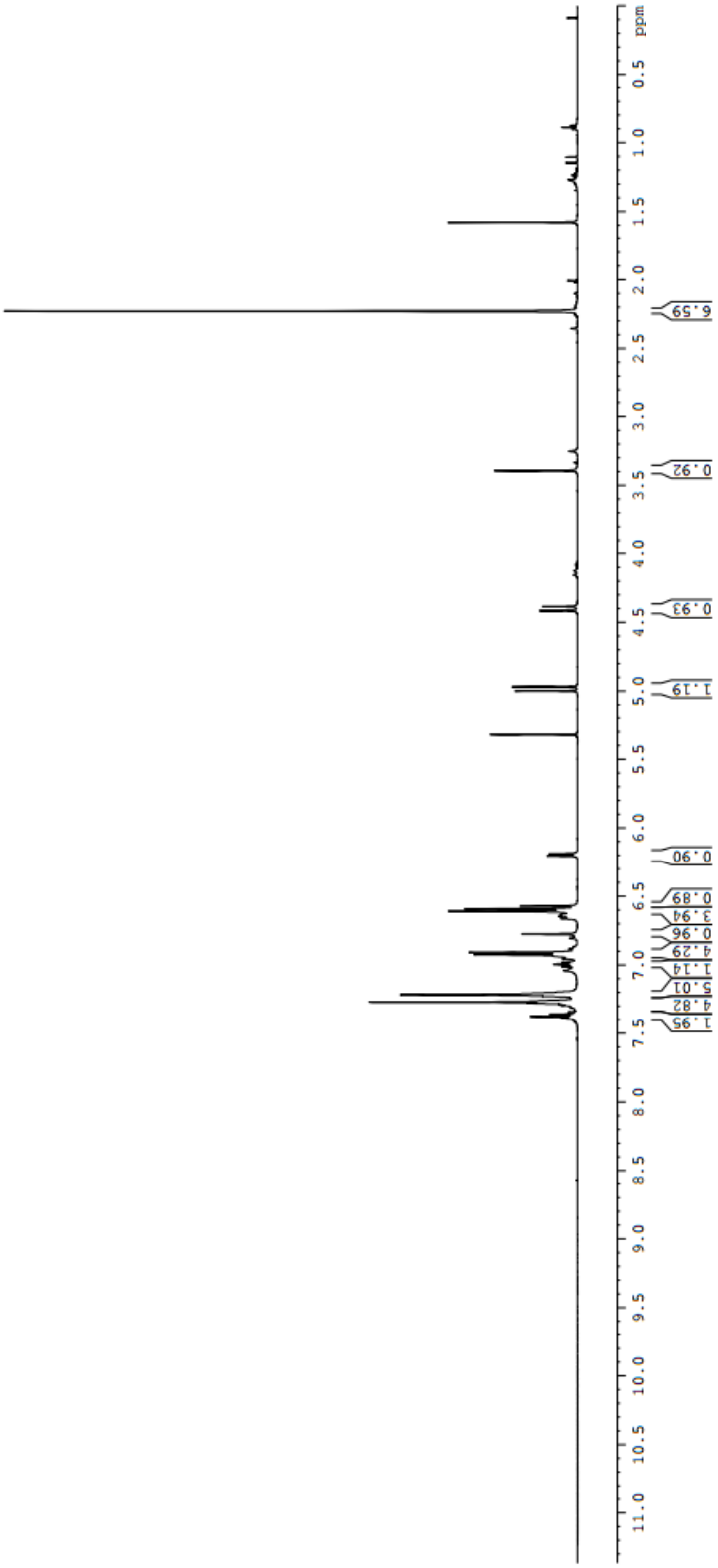


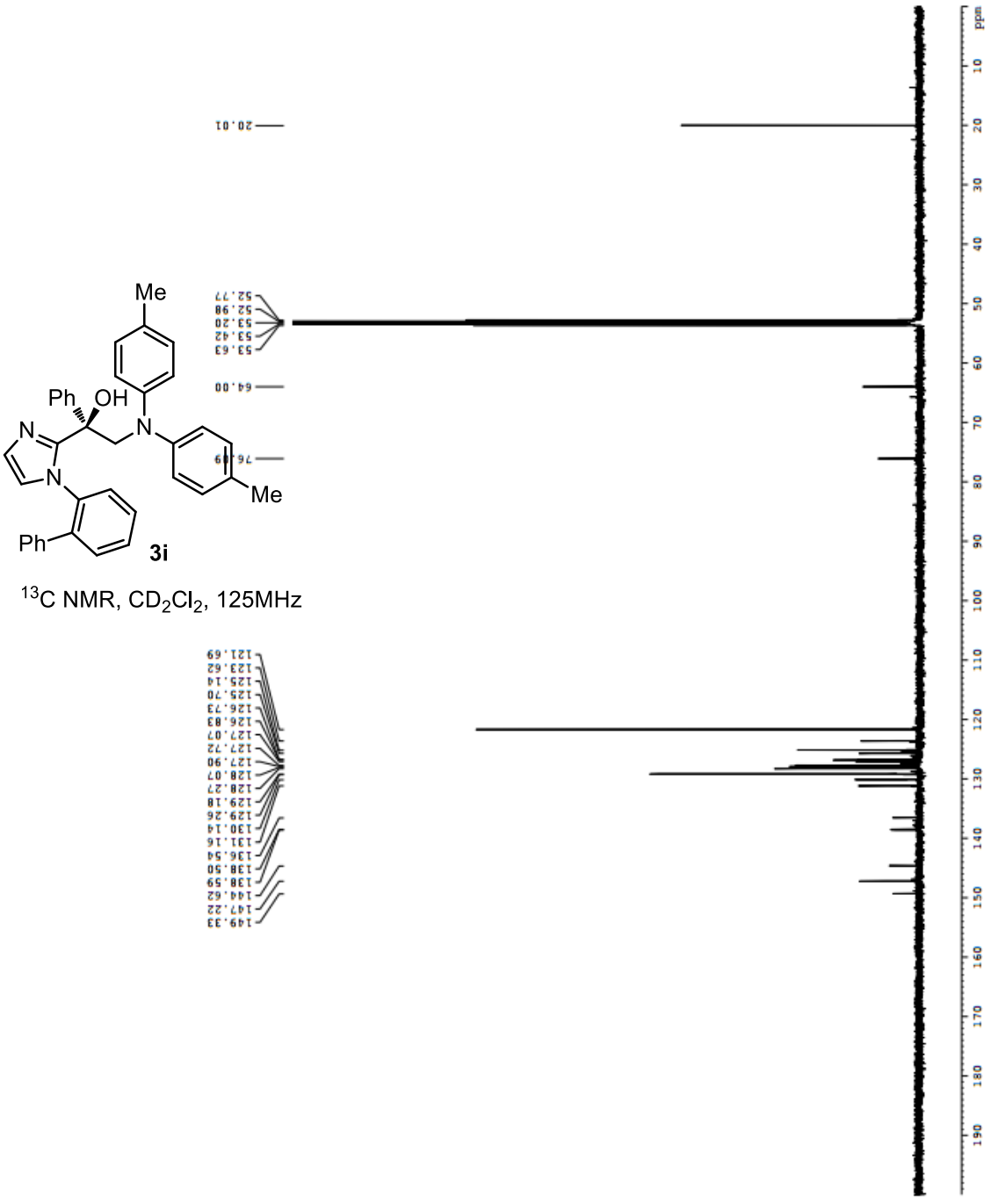

Ph
OH
N
N
N
Ph
3h
^{13}C NMR, CD_2Cl_2, 125MHz
22.04
27.99
51.11
64.73
75.20
114.04
117.83
124.08
124.14
124.97
126.01
126.74
127.09
127.17
127.29
128.11
128.25
128.29
128.33
128.48
129.27
130.27
137.02
138.52
138.78
145.58
147.45
149.92
ppm



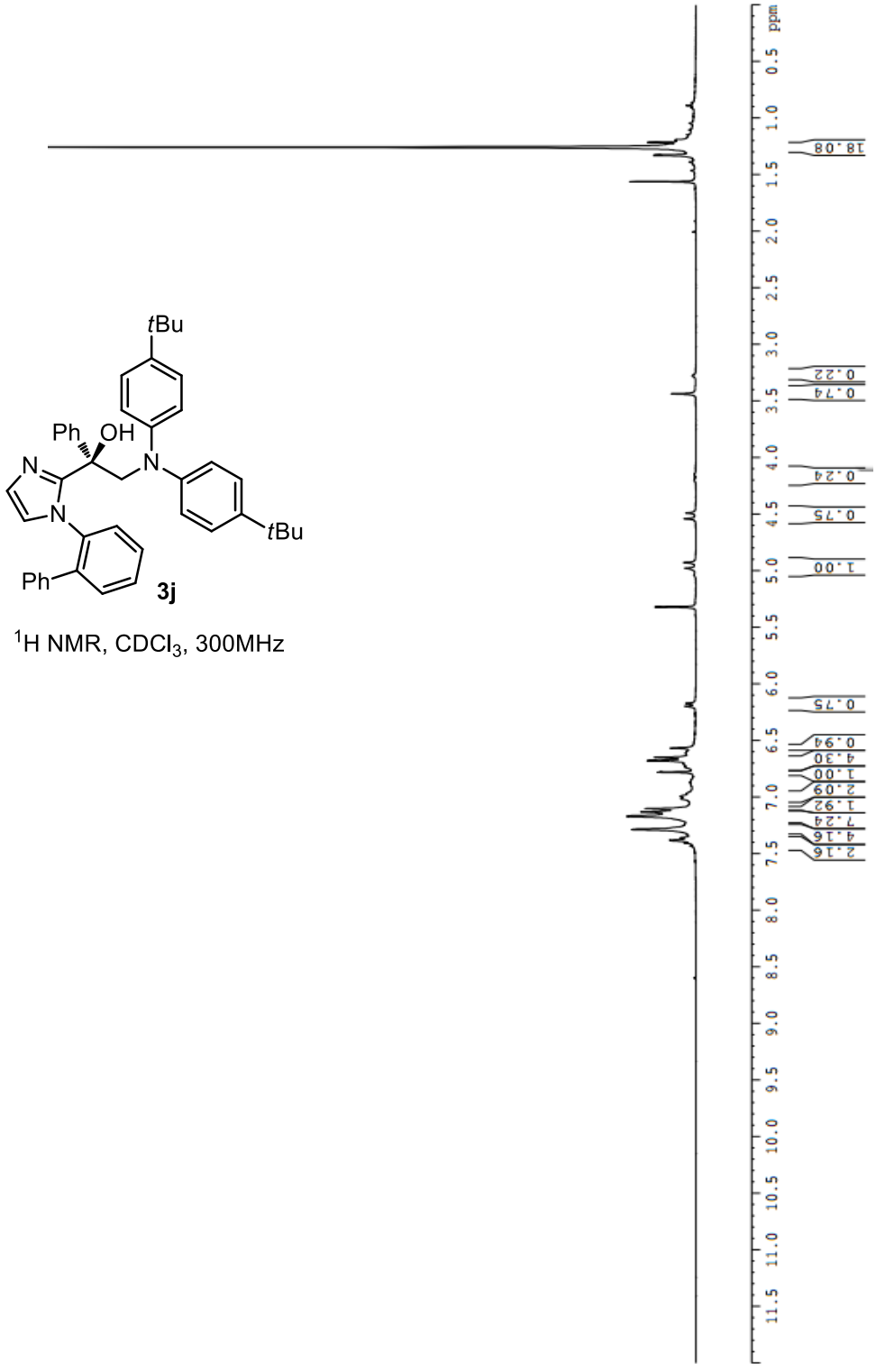
3i

^{1}H NMR, CD_2Cl_2, 500MHz

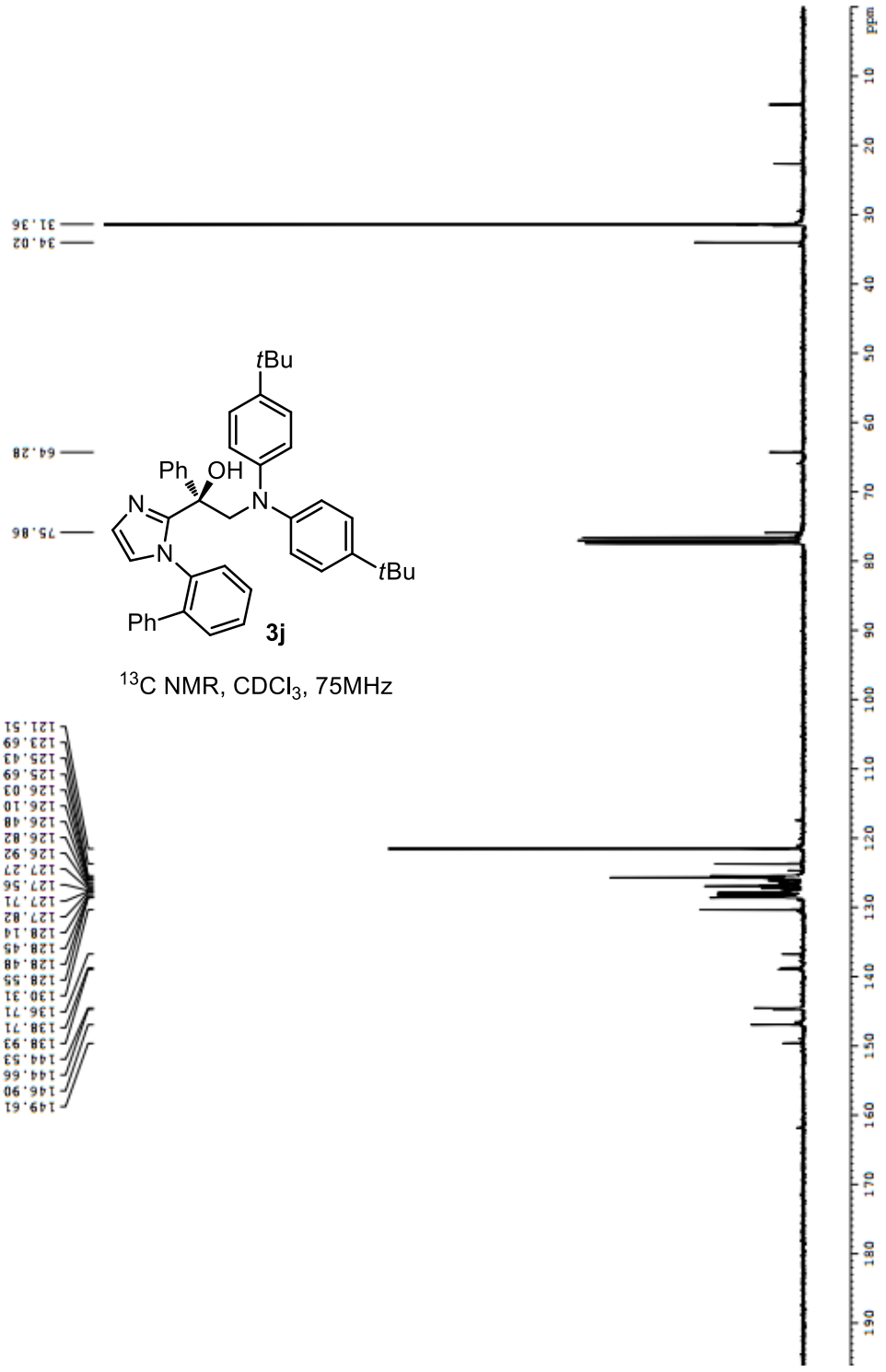




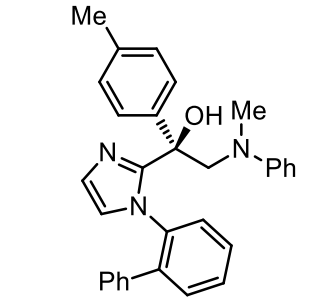
^{13}C NMR, CD_2Cl_2, 125MHz



^{1}H NMR, $CDCl_3$, 300MHz

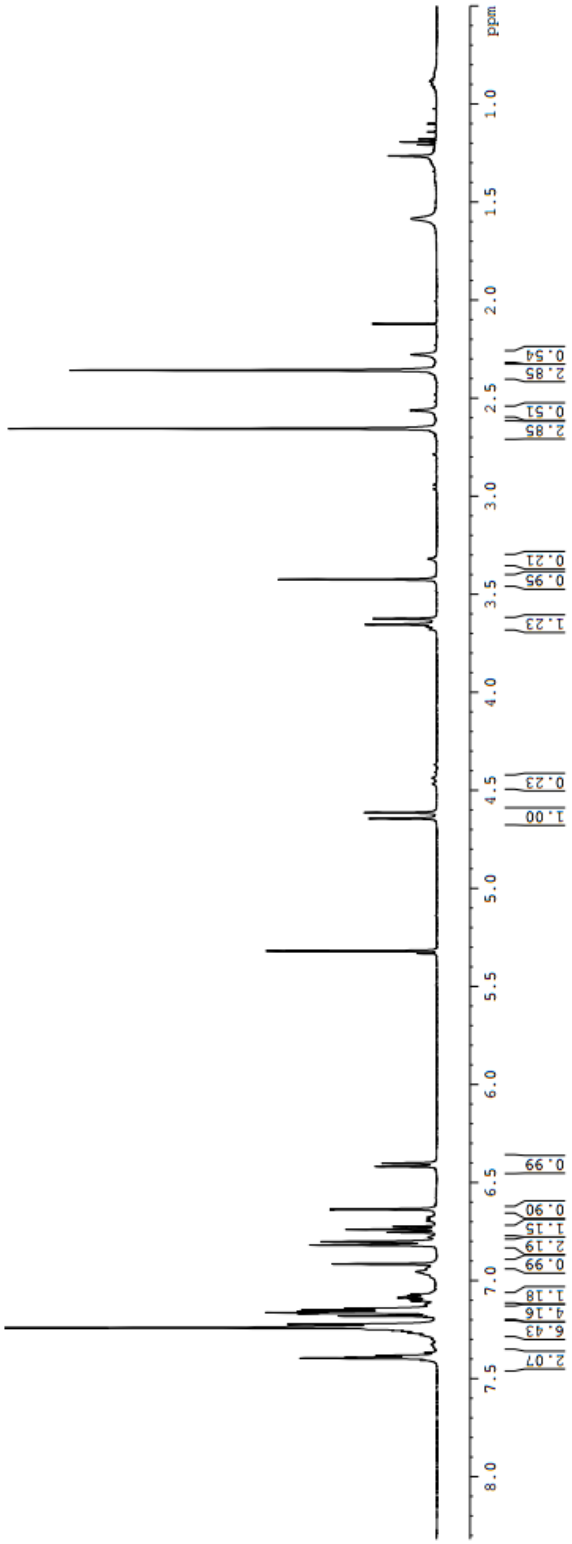


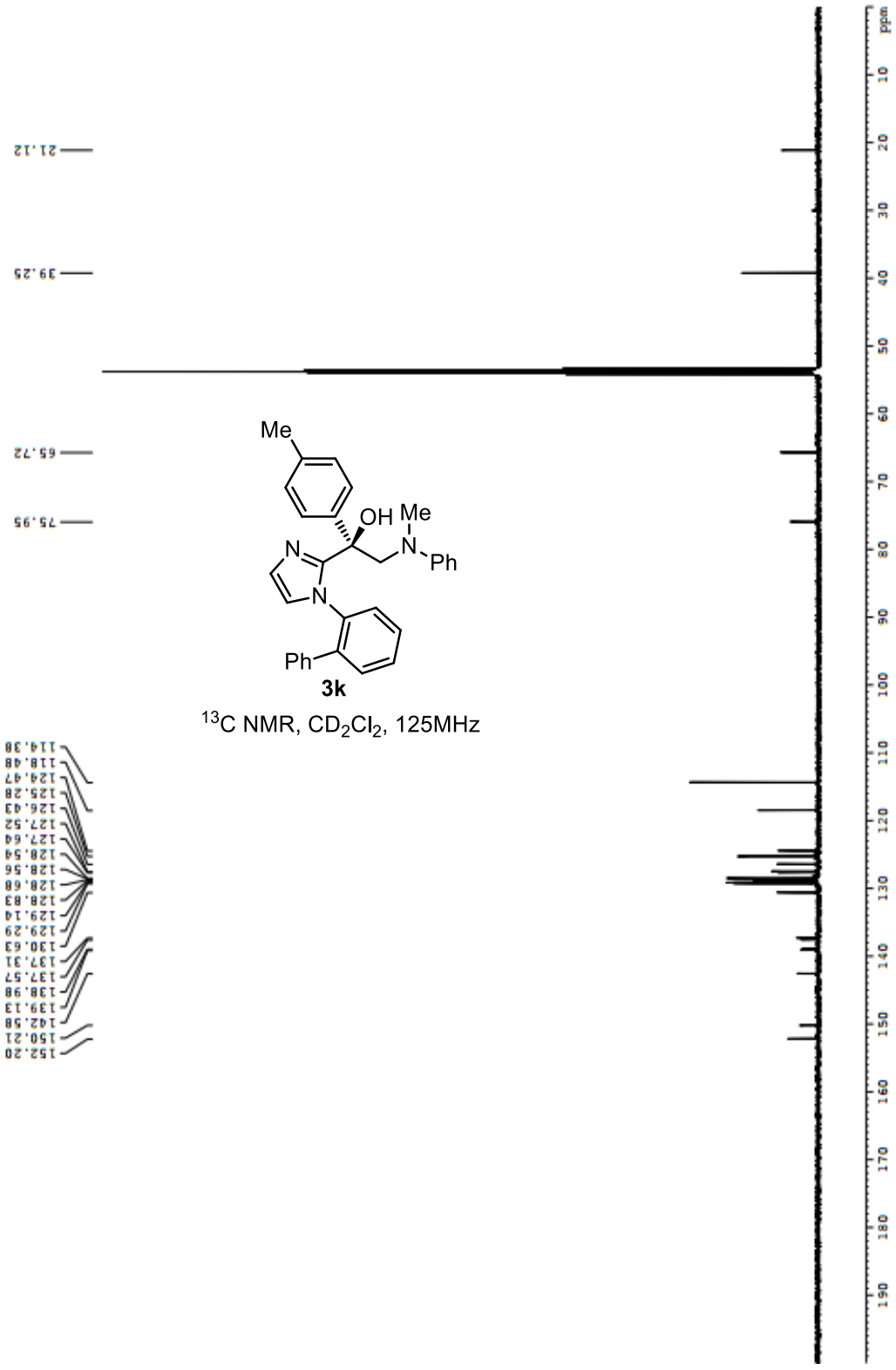
^{13}C NMR, $CDCl_3$, 75MHz

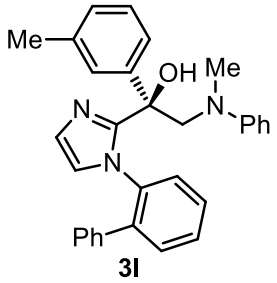


3k

^{1}H NMR, CD_2Cl_2, 500MHz

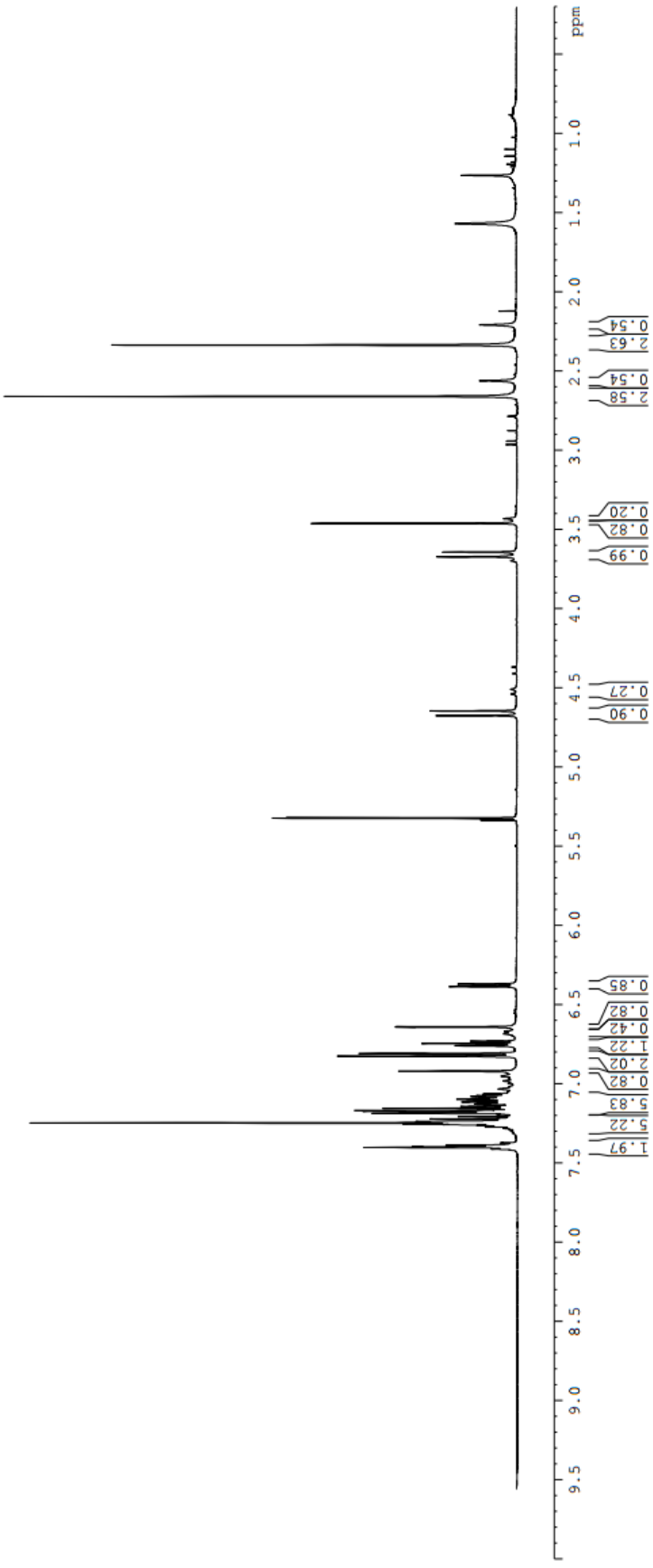


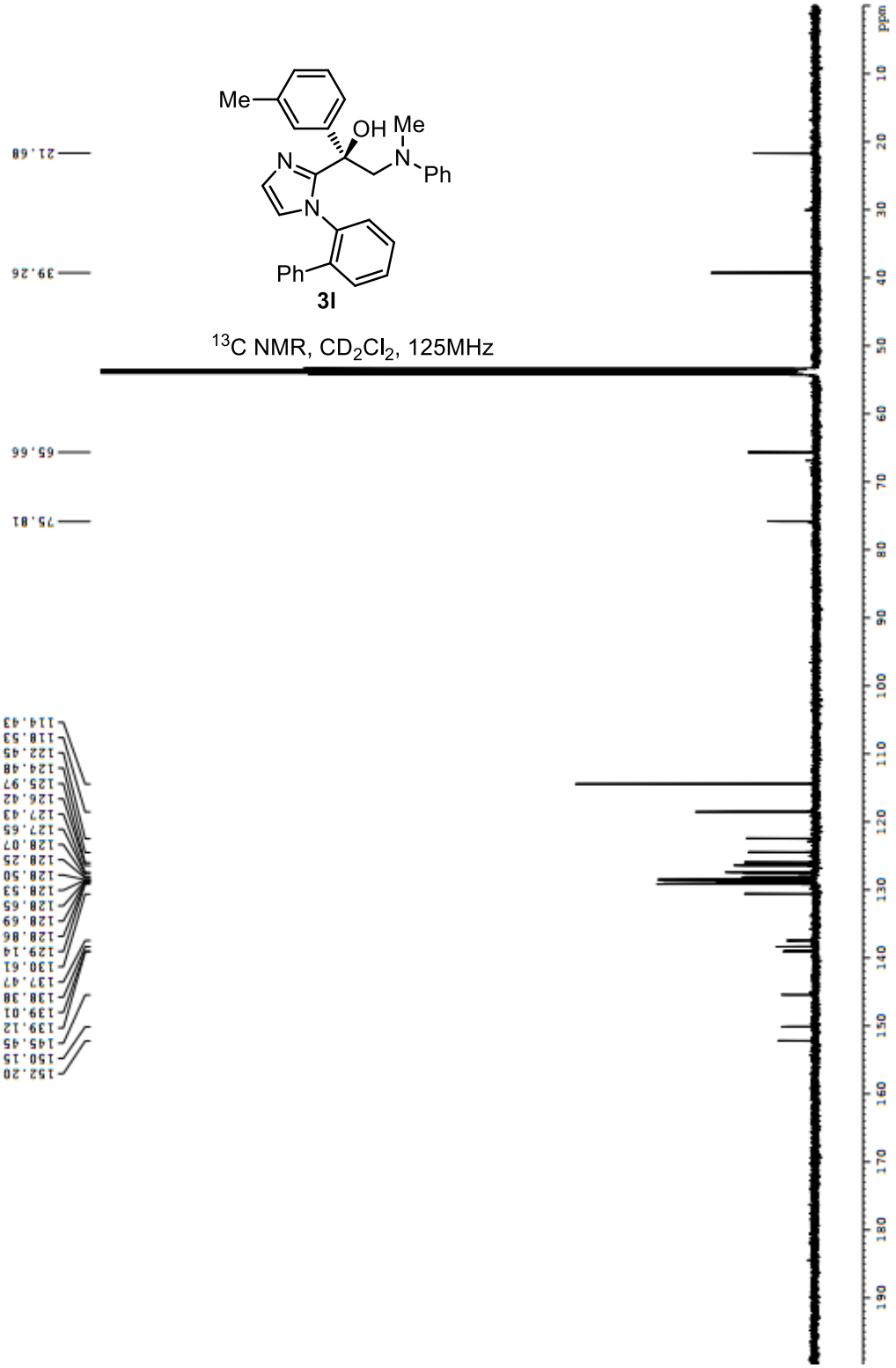

21.12
39.25
65.72
75.95
114.38
118.48
124.47
125.28
126.43
127.52
127.64
128.54
128.56
128.68
128.83
129.14
129.29
130.63
137.31
137.57
138.98
139.13
142.58
150.21
152.20
Me
OH
Me
N
N
Ph
N
Ph
3k
^{13}C NMR, CD_2Cl_2, 125MHz

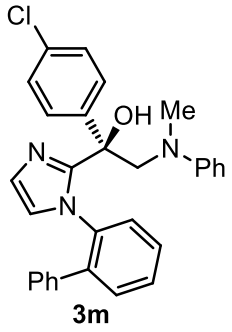


3l

^{1}H NMR, CD_2Cl_2, 500MHz

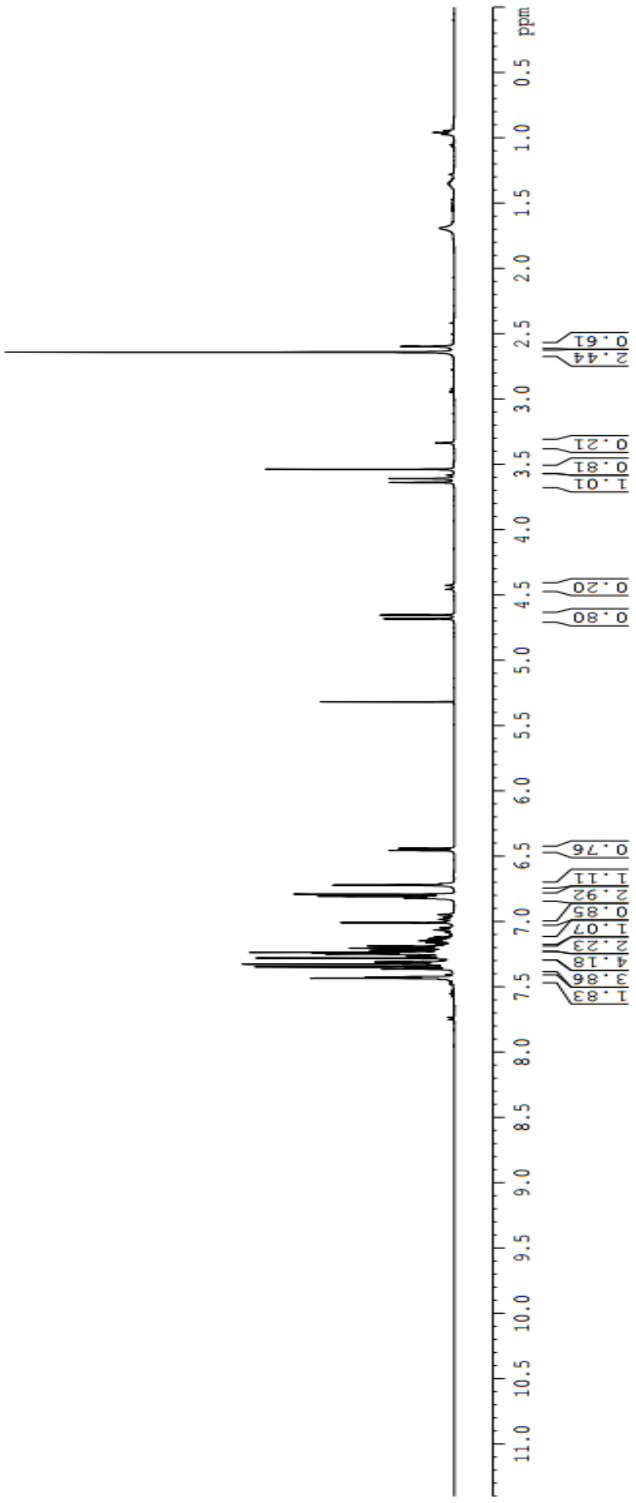


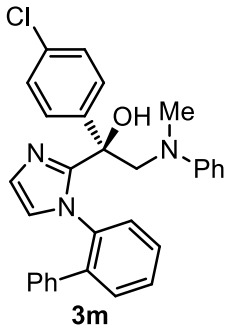

Me
OH
Me
N
N
Ph
N
Ph
3l
^{13}C NMR, CD_2Cl_2, 125MHz
21.68
39.26
65.66
75.81
114.43
118.53
122.45
124.48
125.97
126.42
127.43
127.65
128.07
128.25
128.50
128.53
128.65
128.69
128.86
129.14
130.61
137.47
138.38
139.01
139.12
145.45
150.15
152.20
ppm



3m

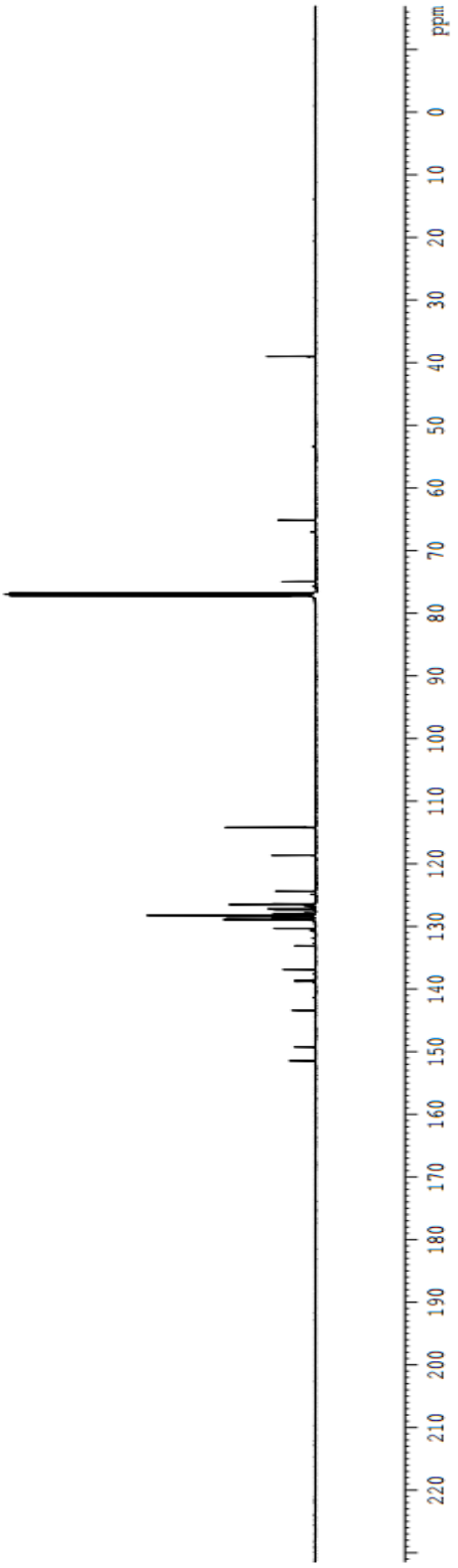
^{1}H NMR, CD_2Cl_2, 500MHz

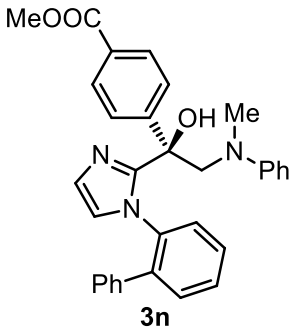




3m

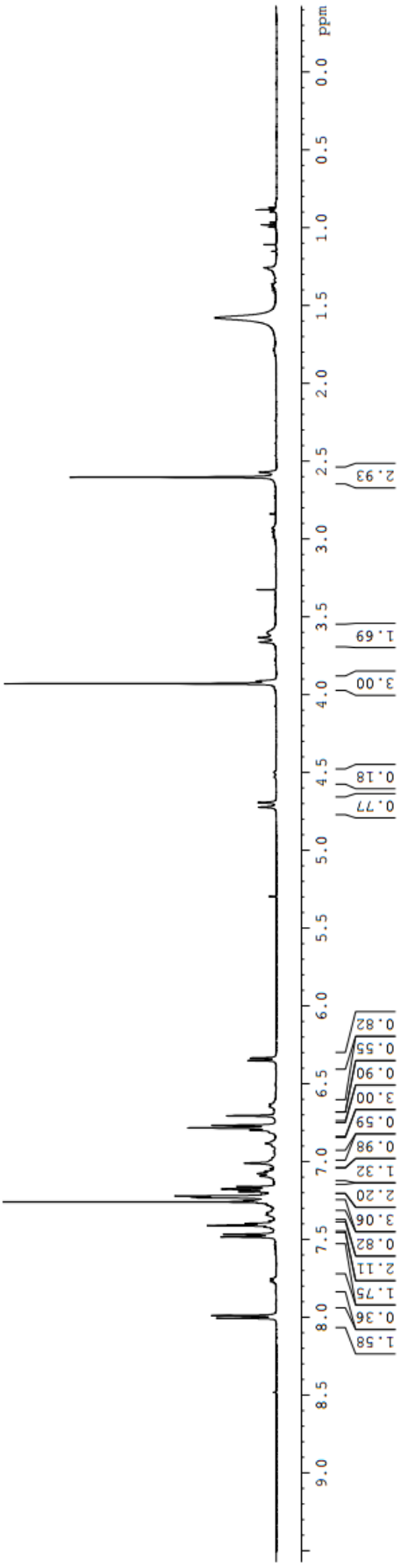
^{13}C NMR, $CDCl_3$, 125MHz

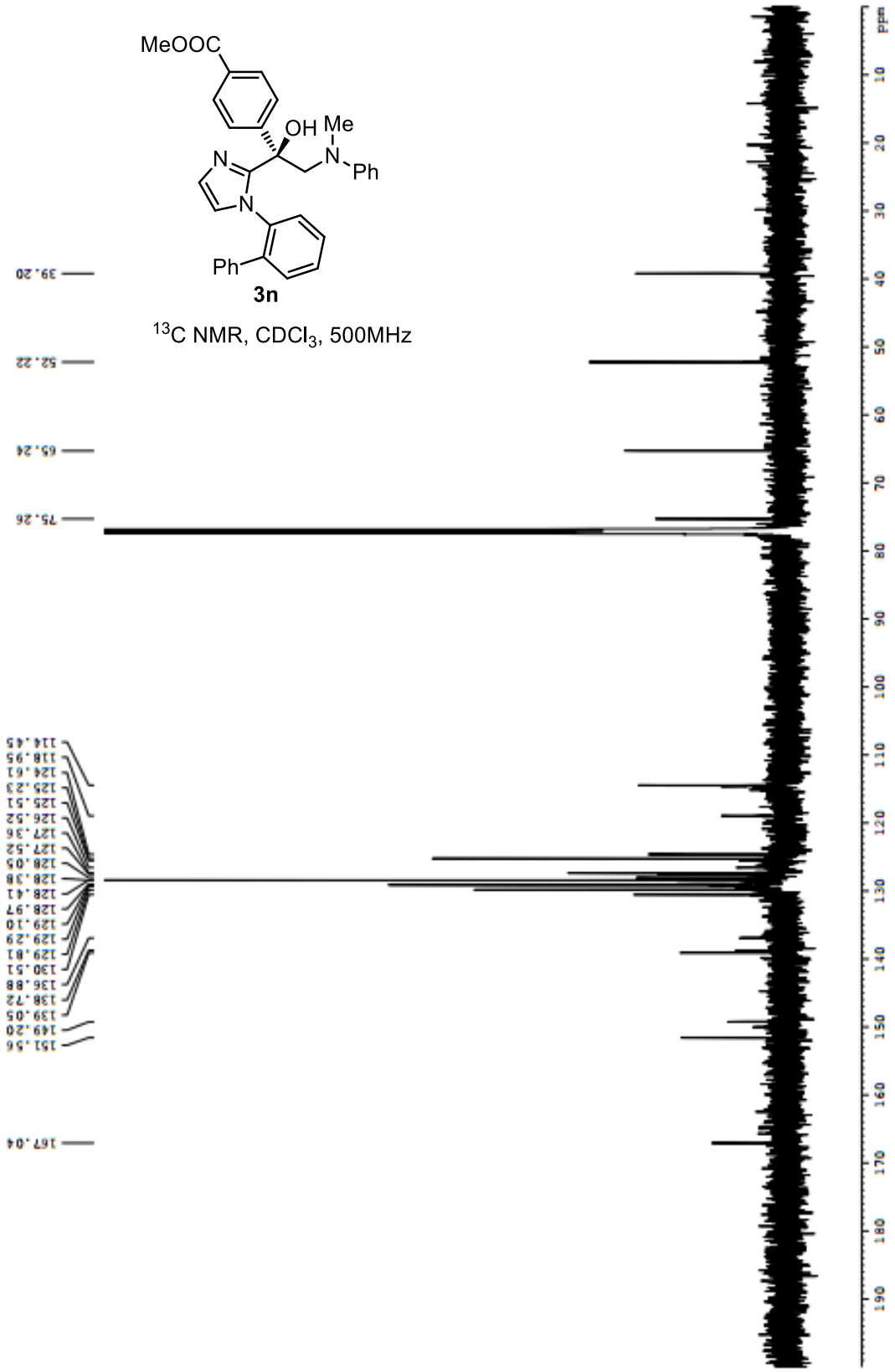


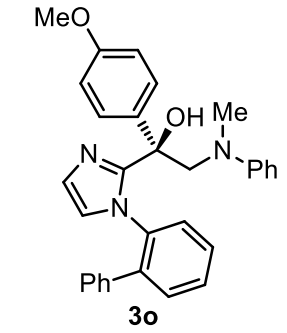


3n

^{1}H NMR, $CDCl_3$, 500MHz

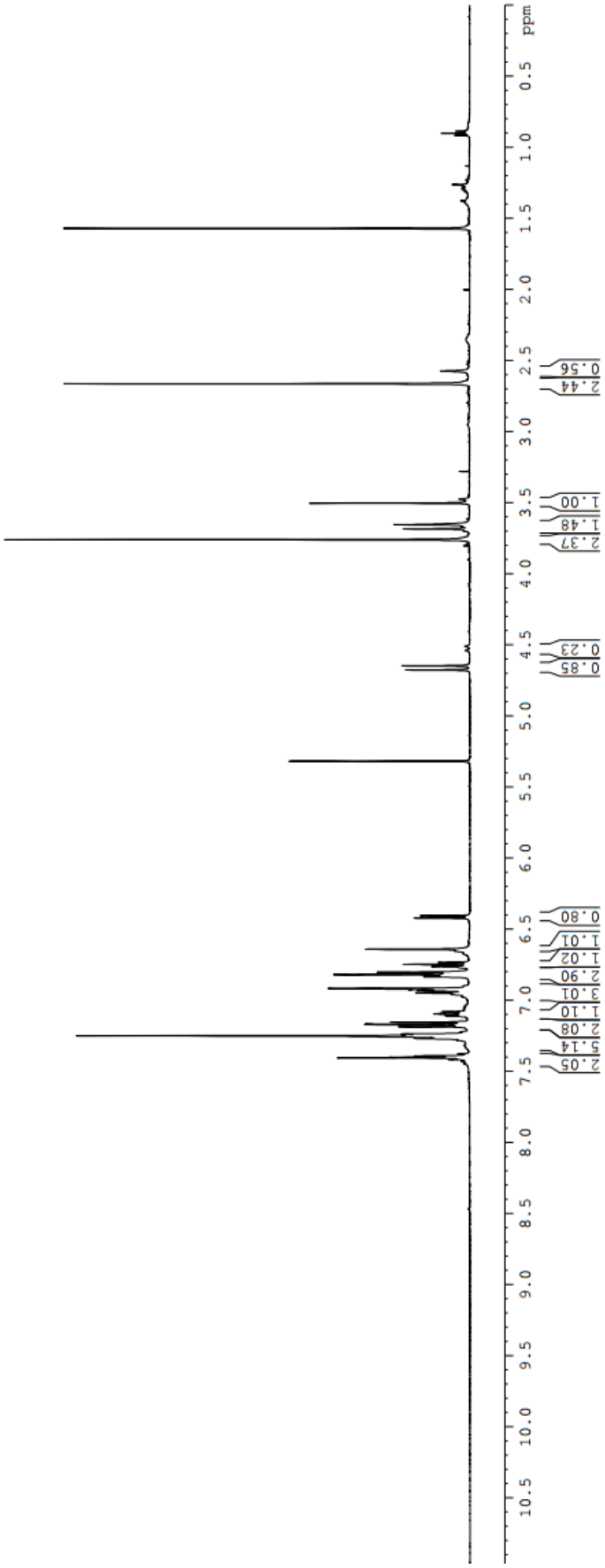


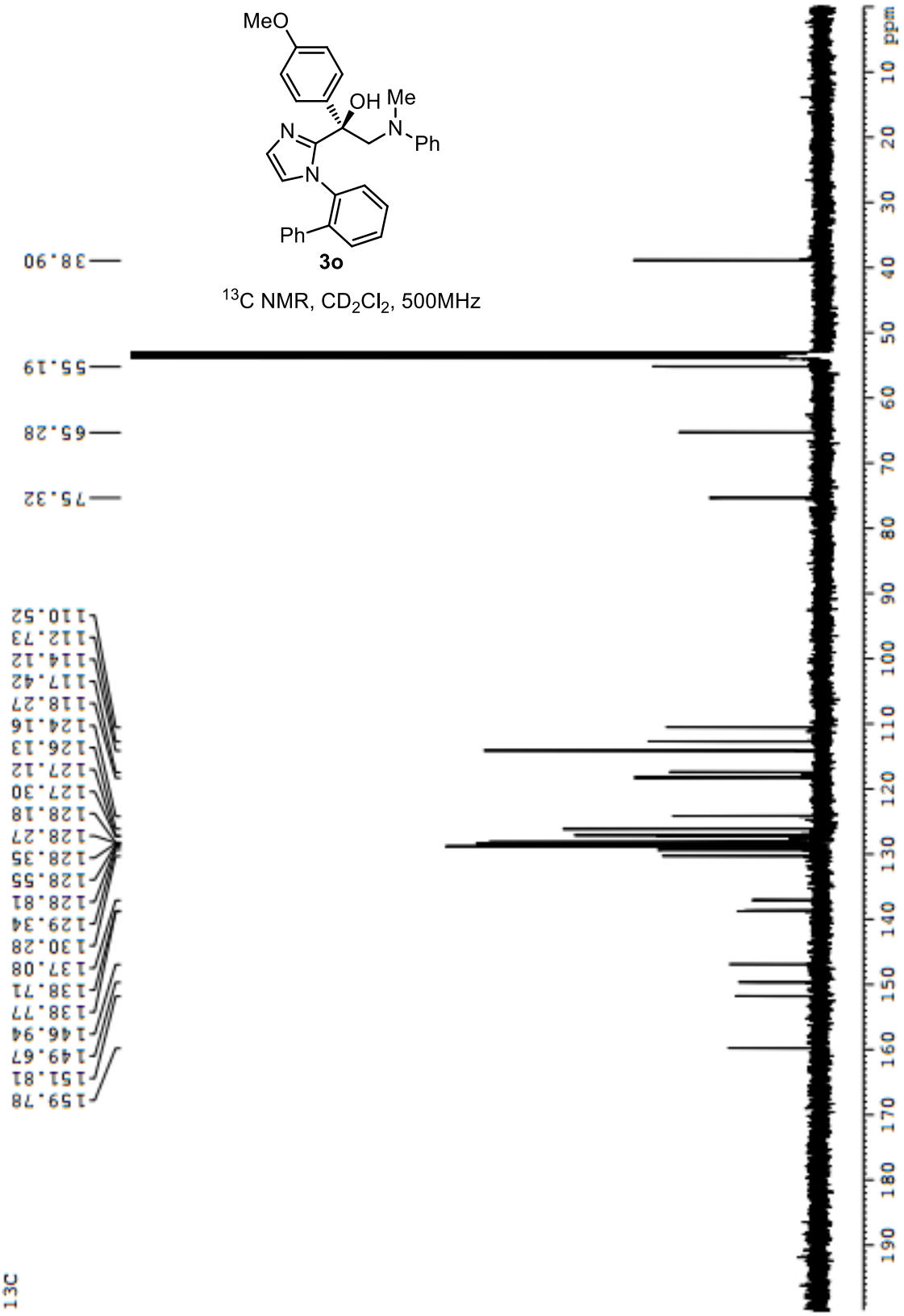

MeOOC
OH
Me
N
N
Ph
N
Ph
3n
^{13}C NMR, $CDCl_3$, 500MHz
39.20
52.22
65.24
75.26
114.45
118.95
124.61
125.23
125.51
126.52
127.36
127.52
128.05
128.38
128.41
128.97
129.10
129.29
129.81
130.51
136.88
138.72
139.05
149.20
151.56
167.04
ppm

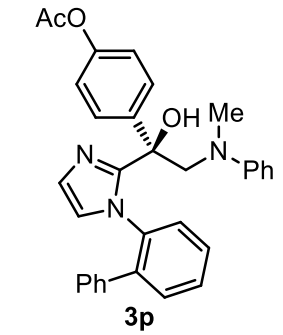


3o

^{1}H NMR, CD_2Cl_2, 500MHz

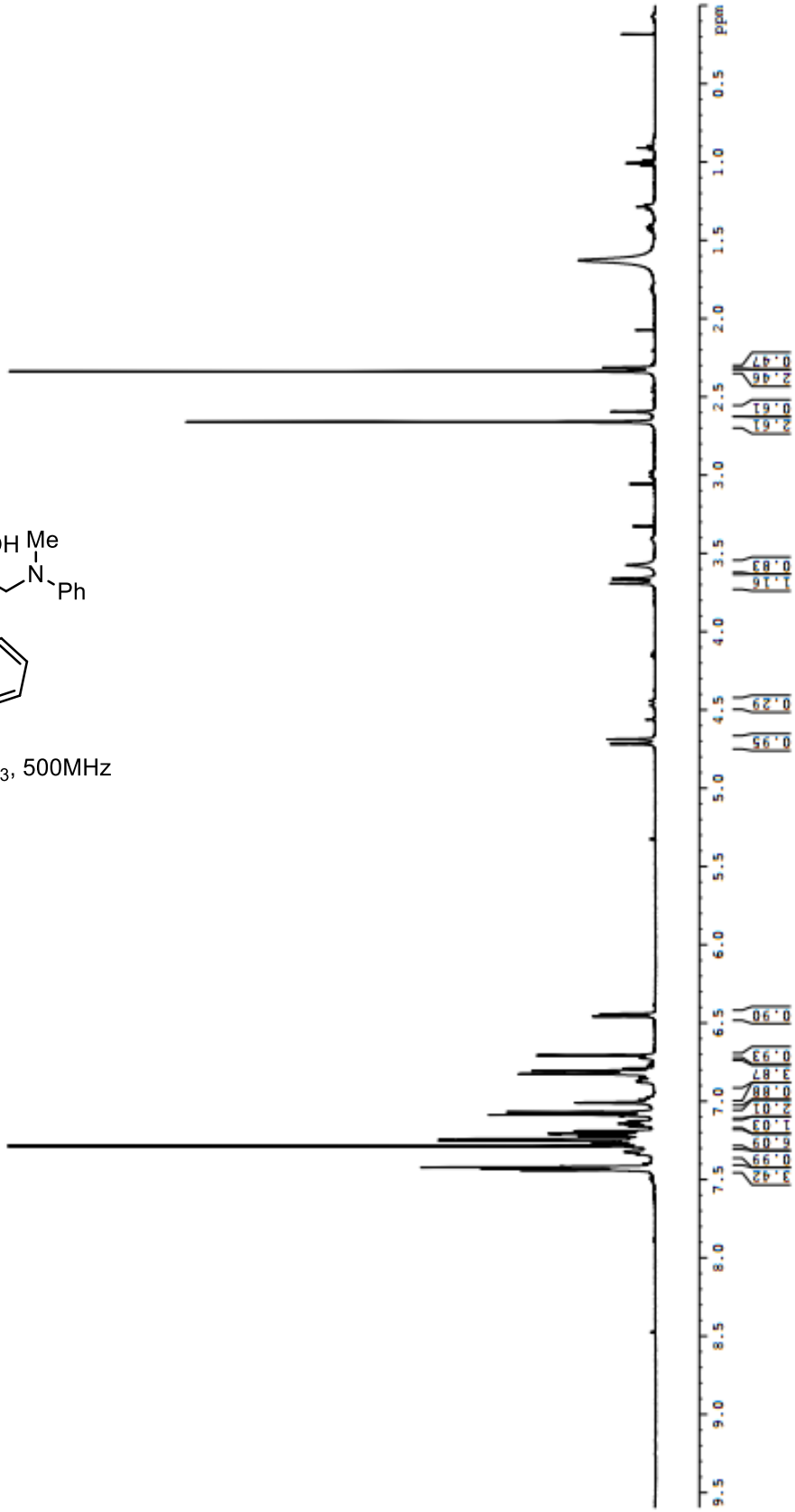


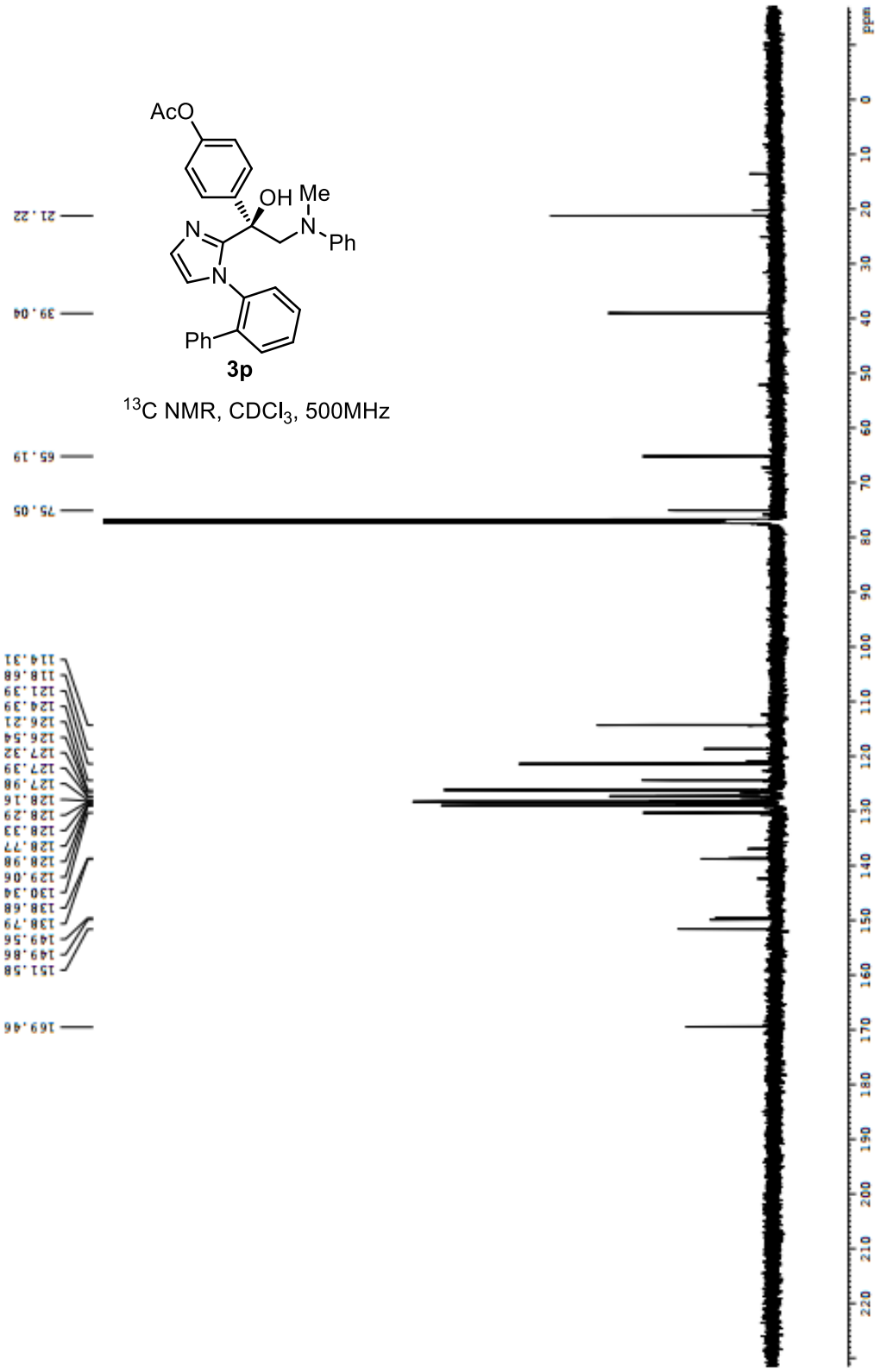

MeO
OH
Me
N
N
Ph
N
Ph
3o
^{13}C NMR, CD_2Cl_2, 500MHz
38.90
55.19
65.28
75.32
110.52
112.73
114.12
117.42
118.27
124.16
126.13
127.12
127.30
128.18
128.27
128.35
128.55
128.81
129.34
130.28
137.08
138.71
138.77
146.94
149.67
151.81
159.78
13C
ppm



3p

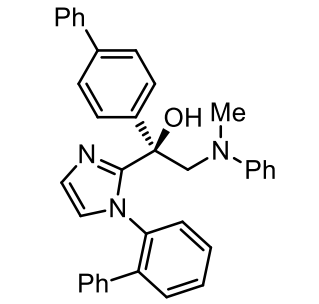
^{1}H NMR, $CDCl_3$, 500MHz





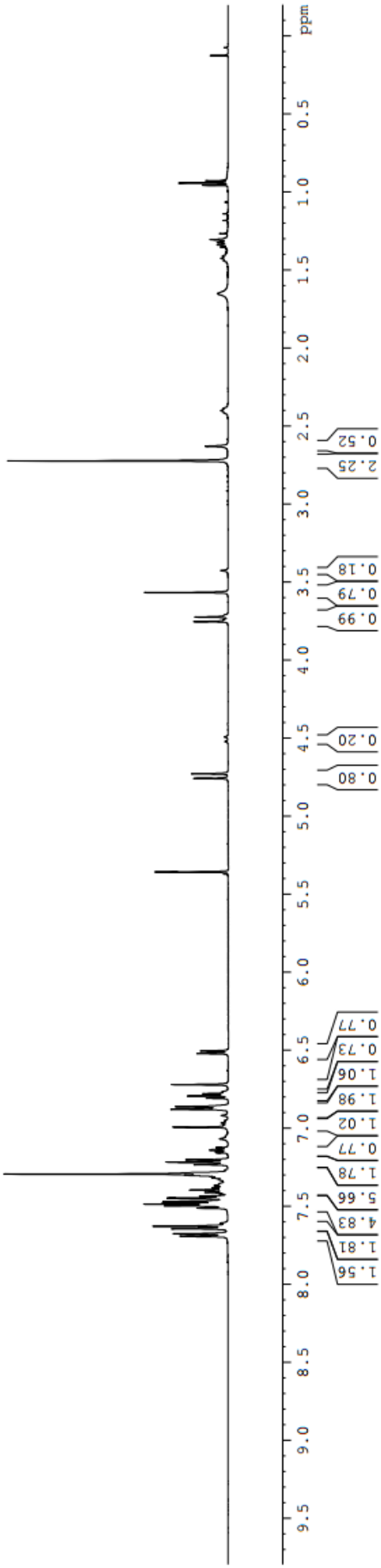
3p

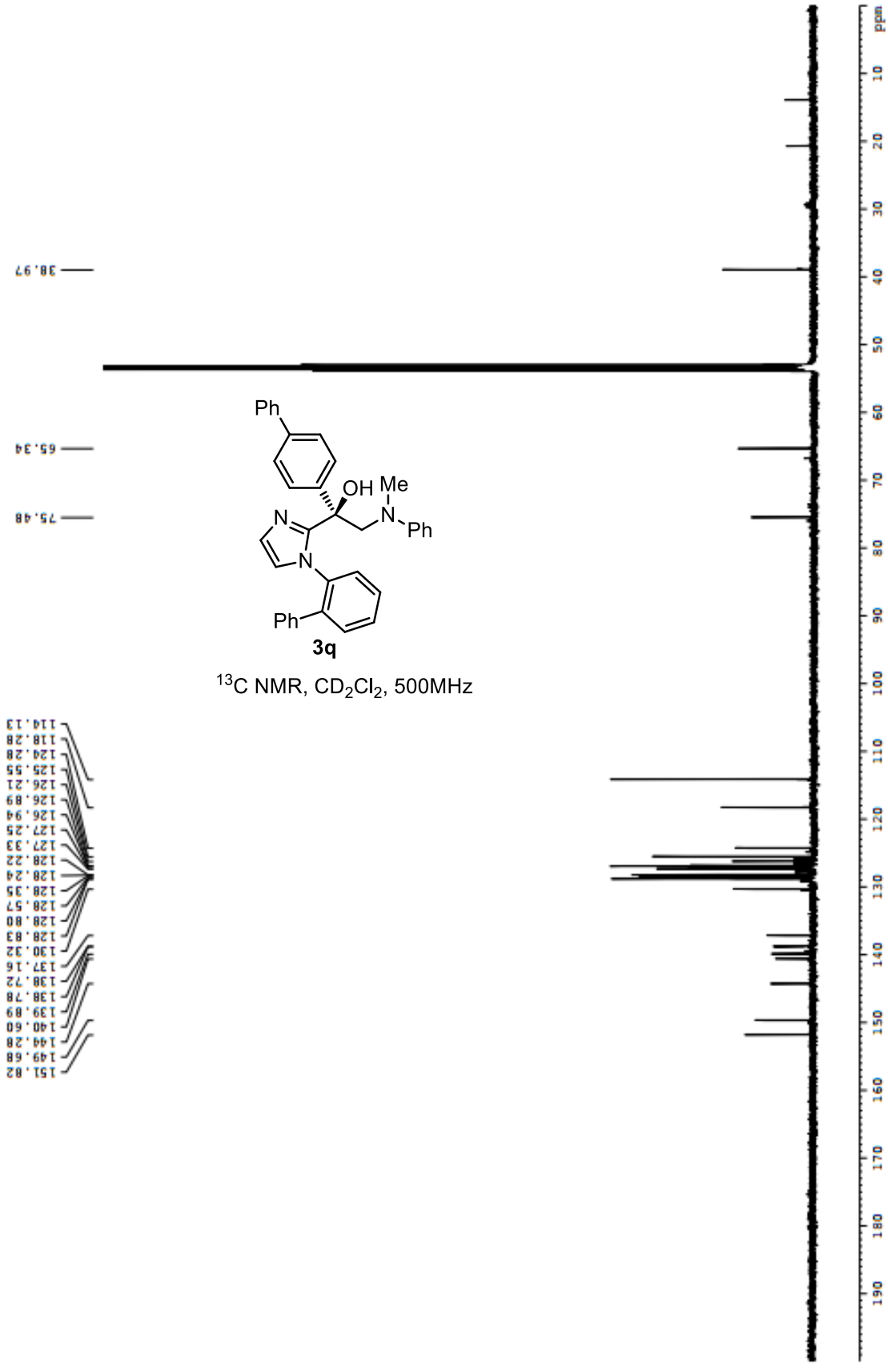
^{13}C NMR, $CDCl_3$, 500MHz

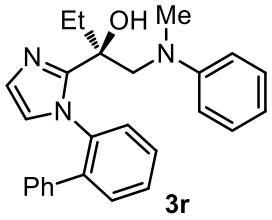


3q

^{1}H NMR, CD_2Cl_2, 500MHz

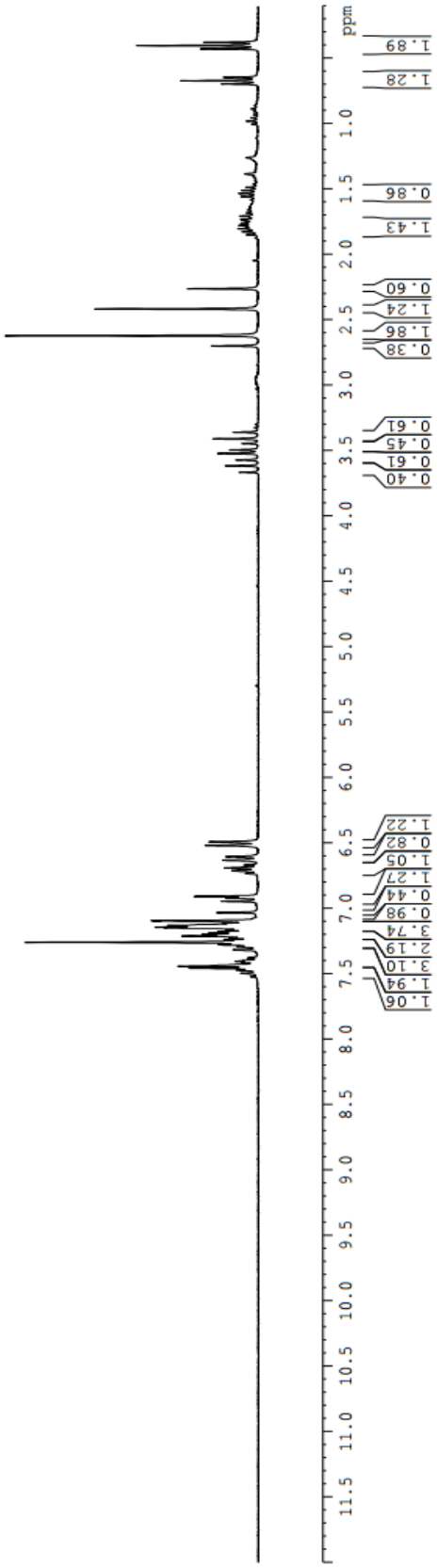


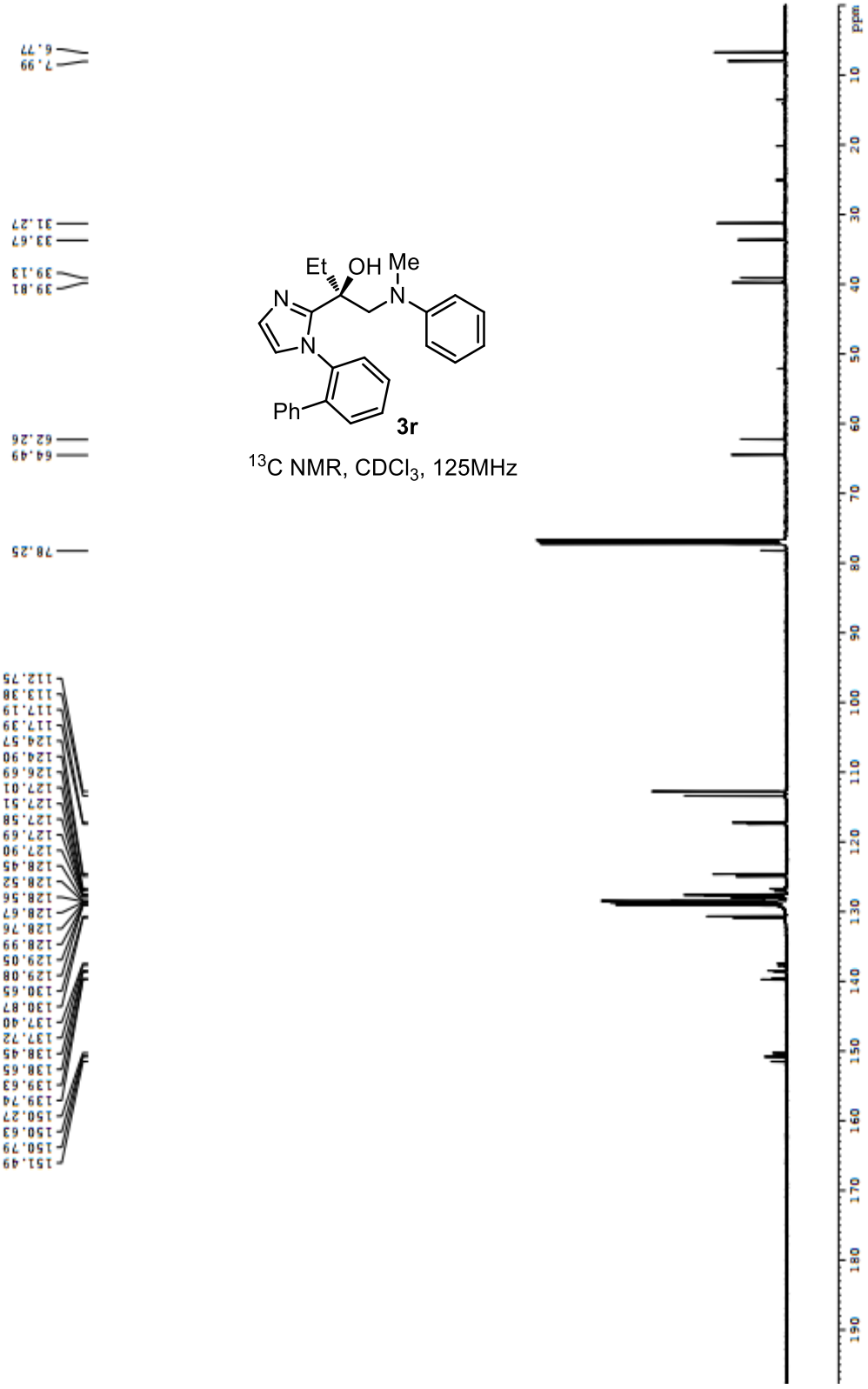

38.97
65.34
75.48
Ph
OH
Me
N
N
Ph
N
Ph
3q
^{13}C NMR, CD_2Cl_2, 500MHz
114.13
118.28
124.28
125.55
126.21
126.89
126.94
127.25
127.33
128.22
128.24
128.35
128.57
128.80
128.83
130.32
137.16
138.72
138.78
139.89
140.60
144.28
149.68
151.82
ppm

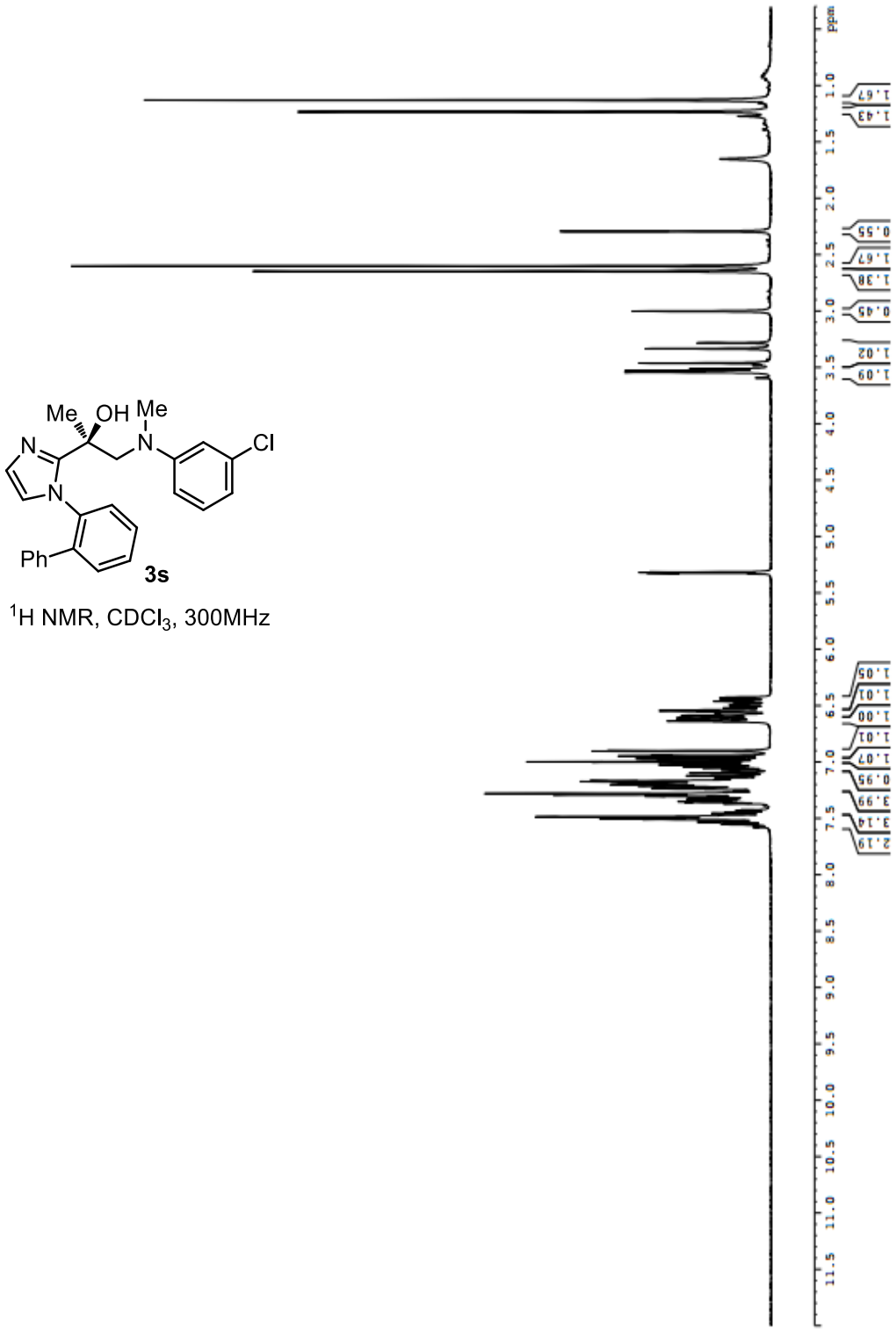


3r

^{1}H NMR, $CDCl_3$, 300MHz

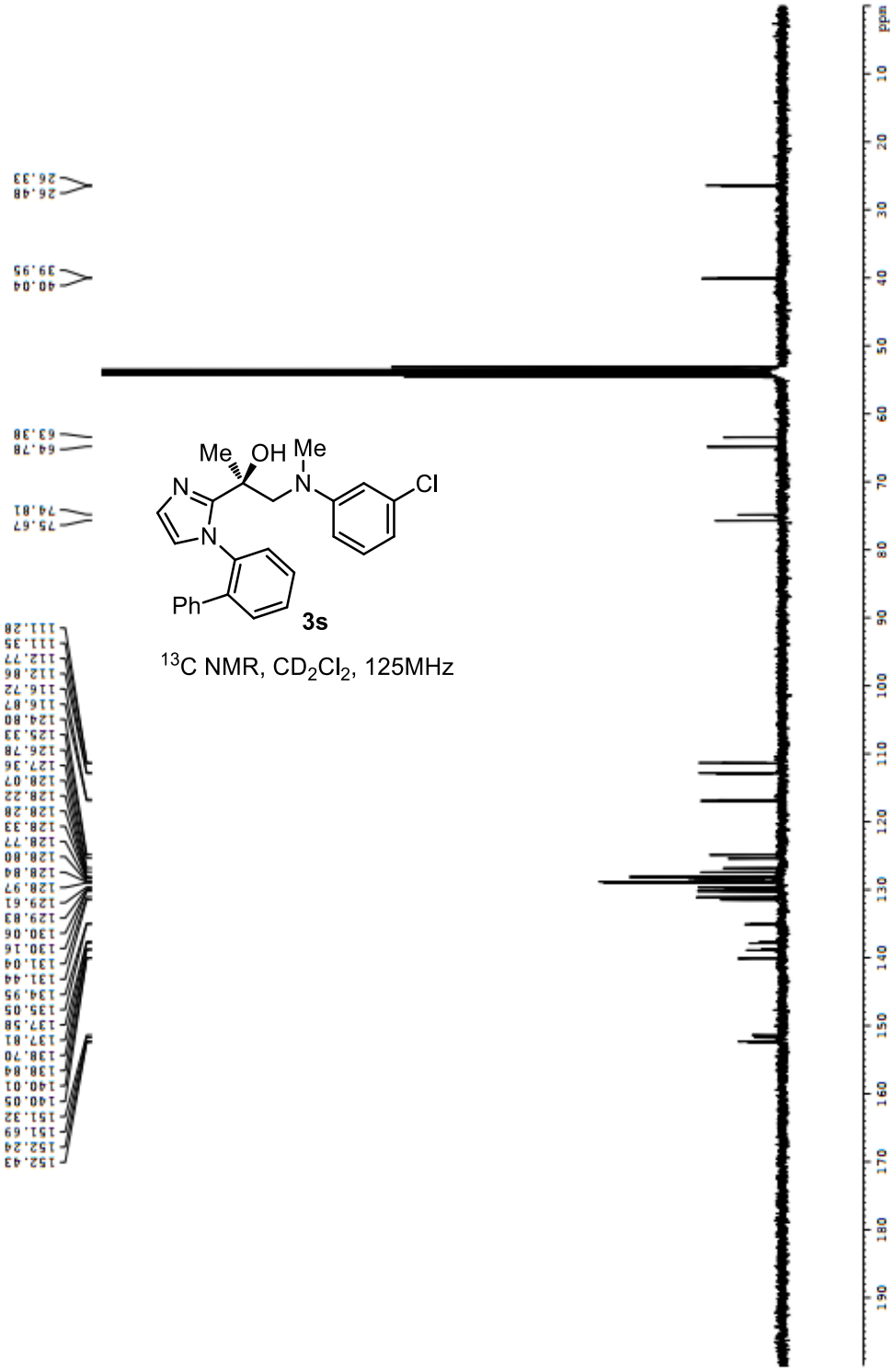



Et
OH
Me
N
N
N
Ph
3r
^{13}C NMR, $CDCl_3$, 125MHz



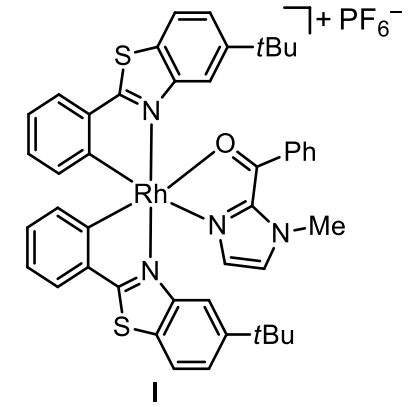
3s

^{1}H NMR, $CDCl_3$, 300MHz



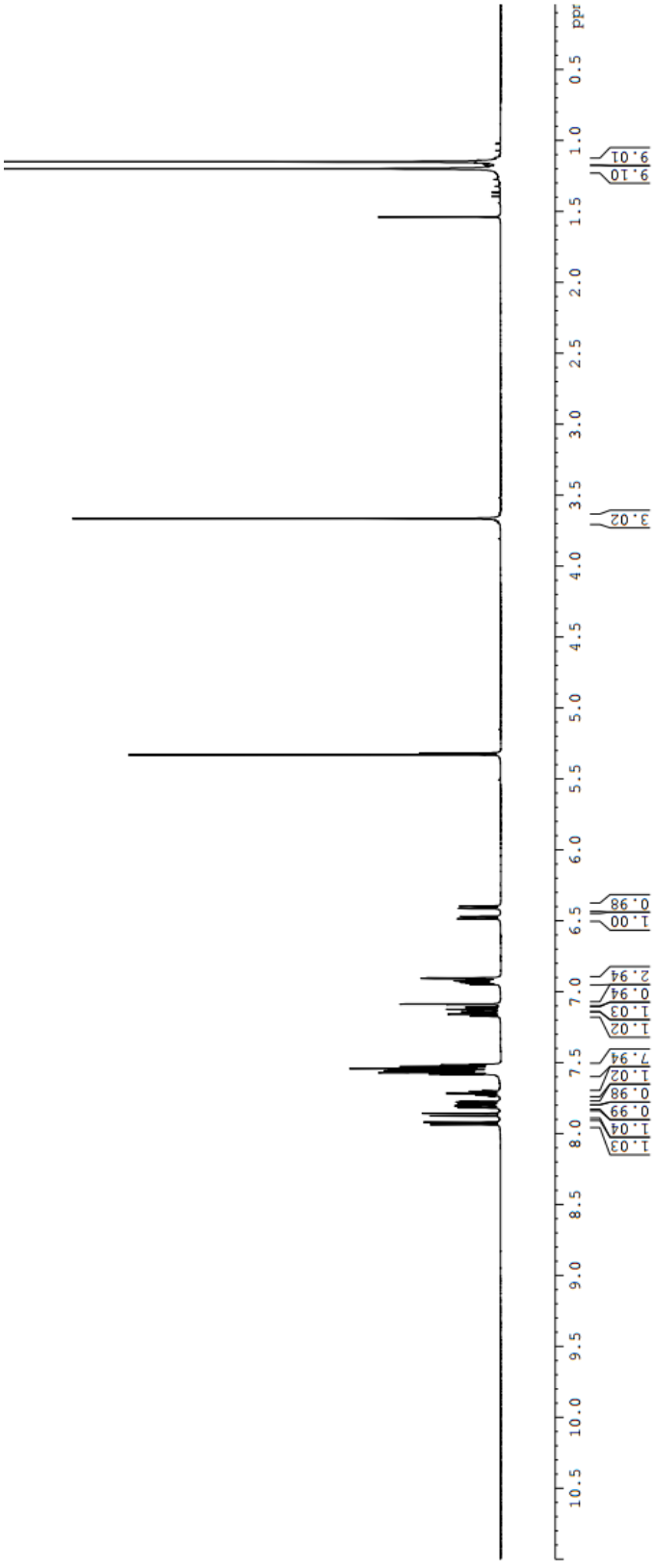
3s

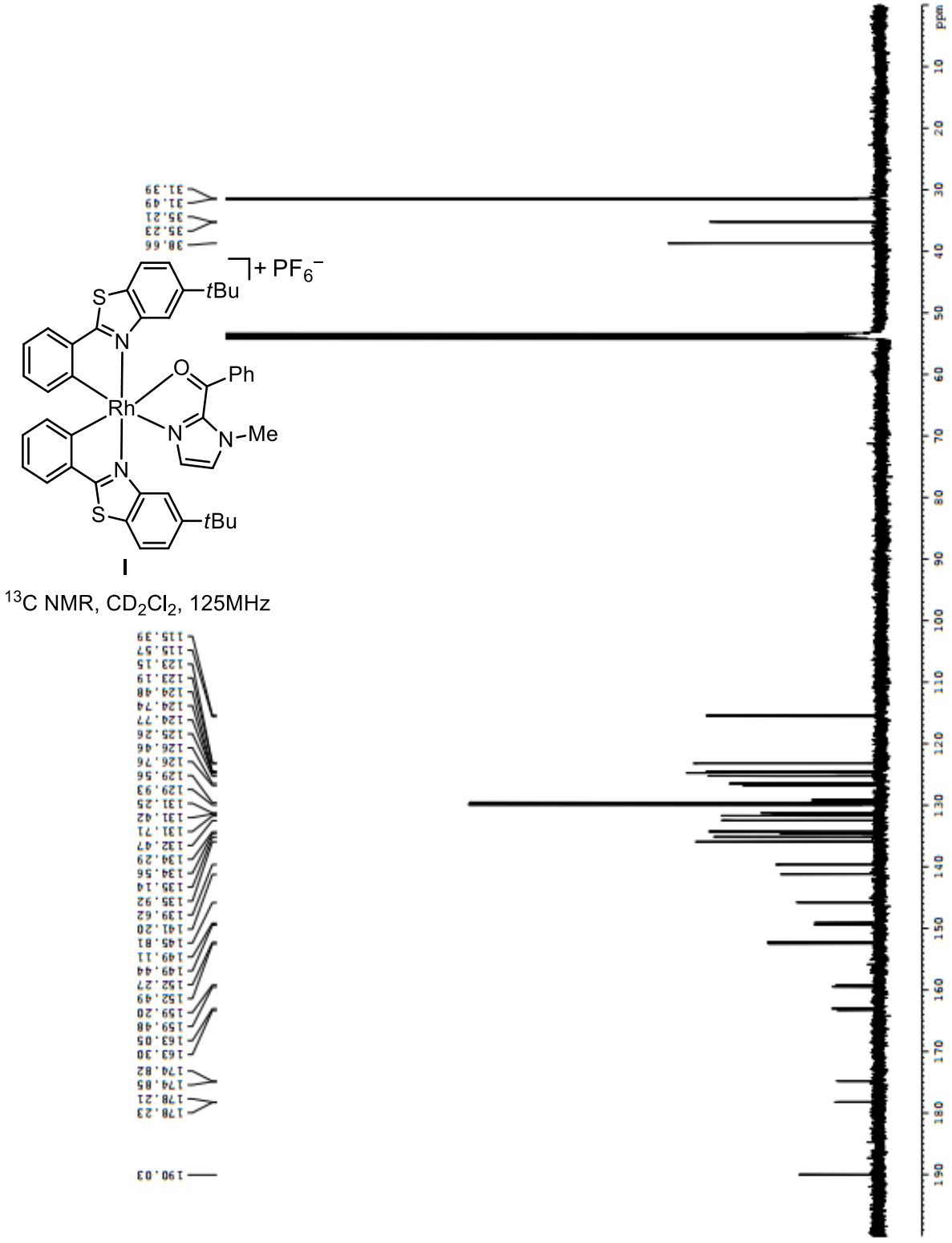
^{13}C NMR, CD_2Cl_2, 125MHz



I

^{1}H NMR, CD_2Cl_2, 500MHz





I

^{13}C NMR, CD_2Cl_2, 125MHz