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Supporting Information

Asymmetric [3+2] Photocycloadditions of Cyclopropanes with Alkenes or Alkynes through Visible-Light Excitation of Catalyst-Bound Substrates

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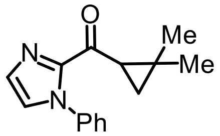
1. General Information

All catalytic reactions were performed in a Schlenk tube (10 mL) with magnetic stirring. A 24 W blue LEDs lamp served as light source (Hongchangzhaoming from Chinese Taobao, https://hongchang-led.taobao.com; for emission spectrum, see Figure S1). The catalyst Δ/Λ-**RhS** was synthesized according to our published procedures.[1] HPLC grade of acetone, THF, CH_2Cl_2, MeCN, DMF and PhCl were used without further purification. Reagents that were purchased from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230-400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 × g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR, proton decoupled ^{13}C NMR and ^{19}F NMR spectra were recorded on Bruker Avance 300 (300 MHz) or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR yields were determined using 1,1,2,2-tetrachloroethane as internal standard. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), 2.50 ppm ($(CD_3)_2SO$); ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$), 39.52 ppm ($(CD_3)_2SO$); ^{19}F NMR spectroscopy: δ = 0 ppm ($CFCl_3$). IR spectra were recorded on a Bruker Alpha FT-IR spectrophotometer. High-resolution mass spectra were recorded on a Bruker En Apex Ultra 7.0 TFT-MS instrument. Chiral HPLC chromatography was performed with an Agilent 1200 or Agilent 1260 HPLC system. Optical rotations were measured on a Krüss P8000-T polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL. UV/Vis absorbance spectra were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette.

2. Synthesis of Substrates

Cyclopropyl ketones **1** were prepared via the well-established Weinreb ketone synthesis.[2] All cyclopropanes are used in racemic. The data of new starting materials are shown below.



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

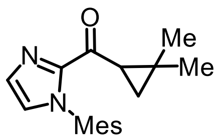
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.40 (m, 3H), 7.30-7.22 (m, 3H), 7.16-7.10 (m, 1H), 3.16 (dd, J_1 = 7.8 Hz, J_2 = 6.0 Hz, 1H), 1.35-1.29 (m, 4H), 1.12 (s, 3H), 0.98 (dd, J_1 = 7.8 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.9, 144.6, 138.8, 129.4, 128.9, 128.5, 126.5, 125.9, 32.4, 28.5, 27.3, 24.1, 18.1.

IR (film): v (cm^{-1}) 3100, 3067, 2996, 2955, 2870, 1663, 1494, 1441, 1410, 1370, 1298, 1093, 1024, 971, 894, 784, 760, 689, 642.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{17}N_2O$ $[M+H]^+$: 241.1335, found: 241.1330.



(2,2-Dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone (1b)

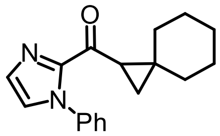
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.35 (m, 1H), 6.97-6.91 (m, 3H), 3.17 (dd, J_1 = 7.8 Hz, J_2 = 5.7 Hz, 1H), 2.32 (s, 3H), 1.89 (s, 3H), 1.84 (s, 3H), 1.34-1.29 (m, 4H), 1.06 (s, 3H), 0.94 (dd, J_1 = 7.8 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 144.5, 138.2, 135.3, 134.0, 133.9, 130.1, 128.9, 128.8, 125.1, 32.2, 28.2, 27.2, 23.6, 21.1, 18.0, 17.3, 17.2.

IR (film): v (cm^{-1}) 3132, 3107, 2978, 2947, 2921, 2869, 1659, 1483, 1412, 1373, 1328, 1280, 1091, 1019, 974, 891, 850, 816, 775, 743, 585.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$: 283.1805, found: 283.1797.



(1-Phenyl-1*H*-imidazol-2-yl)(spiro[2.5]octan-1-yl)methanone (1c)

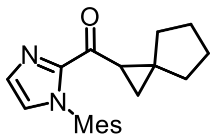
A colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.41 (m, 3H), 7.30-7.28 (m, 1H), 7.28-7.22 (m, 2H), 7.17-7.14 (m, 1H), 3.16 (dd, J_1 = 7.8 Hz, J_2 = 5.7 Hz, 1H), 1.73-1.38 (m, 9H), 1.33 (dd, J_1 = 5.7 Hz, J_2 = 3.9 Hz, 1H), 1.28-1.12 (m, 1H), 0.96 (dd, J_1 = 7.5 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 144.4, 138.9, 129.4, 128.9, 128.6, 126.4, 125.9, 37.8, 36.5, 31.7, 28.0, 26.2, 26.1, 25.9, 22.6.

IR (film): ν (cm^{-1}) 3109, 3063, 2923, 2850, 1666, 1596, 1495, 1442, 1411, 1330, 1305, 1208, 1147, 1107, 1057, 1034, 966, 891, 868, 758, 690, 638, 513.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{21}N_2O$ $[M+H]^+$: 281.1648, found: 281.1641.



(1-Mesityl-1*H*-imidazol-2-yl)(spiro[2.4]heptan-1-yl)methanone (1d)

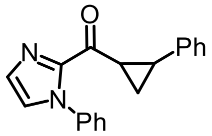
A colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.34 (m, 1H), 6.96-6.91 (m, 3H), 3.33 (dd, J_1 = 7.8 Hz, J_2 = 6.0 Hz, 1H), 2.32 (s, 3H), 1.89 (s, 3H), 1.85 (s, 3H), 1.88-1.80 (m, 1H), 1.75-1.45 (m, 7H), 1.43 (dd, J_1 = 5.7 Hz, J_2 = 3.9 Hz, 1H), 1.17 (dd, J_1 = 8.1 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.0, 144.4, 138.2, 135.2, 133.9, 130.1, 128.9, 128.8, 125.1, 39.3, 37.1, 31.9, 29.7, 26.0, 25.9, 23.0, 21.1, 17.3, 17.2. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3109, 2950, 2862, 1665, 1485, 1441, 1410, 1377, 1321, 1281, 1146, 1058, 982, 938, 894, 851, 819, 766, 738, 581.

HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{25}N_2O$ $[M+H]^+$: 309.1961, found: 309.1956.



(1-Phenyl-1*H*-imidazol-2-yl)(2-phenylcyclopropyl)methanone (1e)

<u>*Trans*-**1e**</u>: A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.44 (m, 3H), 7.35-7.24 (m, 5H), 7.23-7.14 (m, 4H), 3.67-3.58 (m, 1H), 2.68-2.58 (m, 1H), 1.78-1.70 (m, 1H), 1.56-1.46 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.9, 143.5, 140.4, 138.5, 129.9, 128.9, 128.8, 128.4, 127.1, 126.4, 126.2, 126.0, 29.7, 29.4, 20.2.

IR (film): ν (cm^{-1}) 3108, 3061, 3031, 1667, 1598, 1495, 1437, 1409, 1311, 1149, 1043, 966, 910, 869, 832, 756, 692, 660, 560, 525.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{17}N_2O$ [M+H]$^+$: 289.1335, found: 289.1328.

<u>*Cis*-**1e**</u>: A white solid. *Cis*-**1e** was synthesized from the corresponding *cis*-cyclopropyl carboxylic acid.[3]

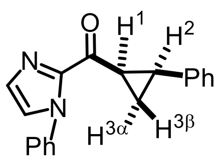
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.20 (m, 9H), 7.14-7.10 (m, 1H), 6.80-6.73 (m, 2H), 3.84-3.74 (m, 1H), 3.03-2.91 (m, 1H), 2.06-1.97 (m, 1H), 1.52-1.42 (m, 1H).

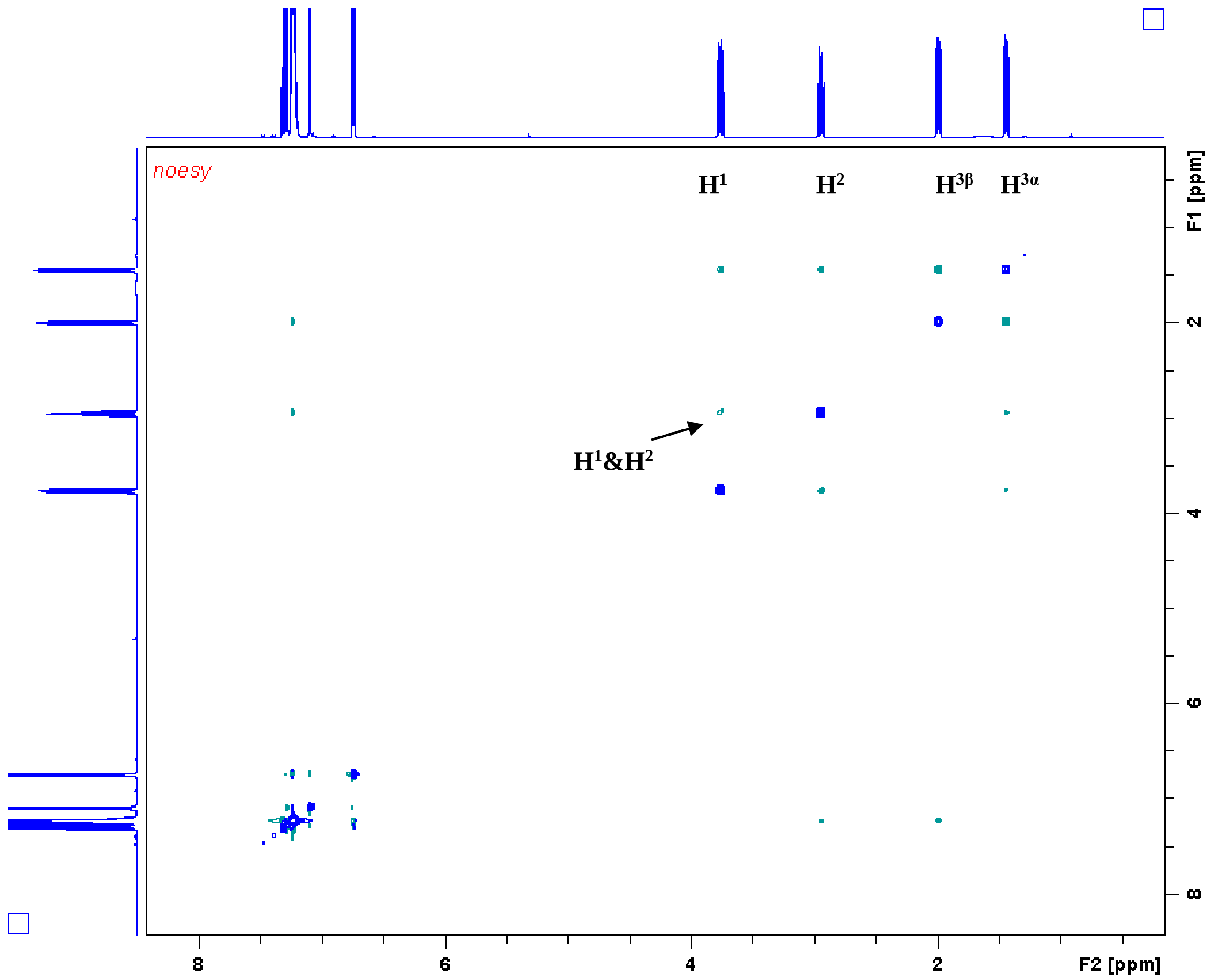
^{13}C NMR (75 MHz, $CDCl_3$) δ 186.0, 144.2, 138.1, 136.0, 129.6, 129.5, 128.7, 128.2, 127.8, 126.4, 126.3, 125.3, 29.8, 27.4, 11.1.

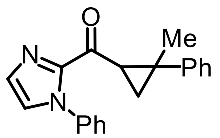
IR (film): ν (cm^{-1}) 3117, 3052, 3013, 1663, 1596, 1495, 1448, 1413, 1336, 1306, 1206, 1147, 1105, 1080, 1030, 970, 918, 883, 806, 759, 724, 692, 550, 509.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{16}N_2ONa$ [M+Na]$^+$: 311.1155, found: 311.1163.

NOE spectrum of *cis*-**1e**:







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

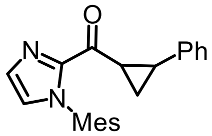
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.43 (m, 5H), 7.38-7.27 (m, 5H), 7.26-7.17 (m, 2H), 3.36 (dd, J_1 = 7.8 Hz, J_2 = 6.0 Hz, 1H), 1.65 (dd, J_1 = 6.3 Hz, J_2 = 4.2 Hz, 1H), 1.49 (dd, J_1 = 8.1 Hz, J_2 = 4.2 Hz, 1H), 1.41 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.3, 146.3, 144.5, 138.7, 129.7, 128.9, 128.6, 128.5, 127.6, 126.7, 126.4, 126.0, 35.3, 32.8, 21.9, 19.4.

IR (film): ν (cm^{-1}) 3058, 2987, 2928, 1666, 1594, 1493, 1410, 1369, 1337, 1300, 1068, 1031, 957, 906, 851, 760, 696, 658, 541.

HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{19}N_2O$ $[M+H]^+$: 303.1492, found: 303.1485.



(1-Mesityl-1*H*-imidazol-2-yl)(2-phenylcyclopropyl)methanone (1g)

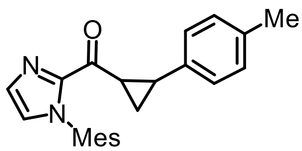
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.36 (m, 1H), 7.32-7.23 (m, 2H), 7.22-7.12 (m, 3H), 7.02-7.00 (m, 1H), 6.96 (br s, 2H), 3.64-3.57 (m, 1H), 2.64-2.56 (m, 1H), 2.34 (s, 3H), 1.90 (s, 3H), 1.88 (s, 3H), 1.74-1.66 (m, 1H), 1.51-1.43 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.8, 143.5, 140.5, 138.5, 134.9, 134.1, 133.9, 130.5, 128.9, 128.4, 126.4, 126.2, 125.7, 29.5, 29.1, 21.1, 20.2, 17.34, 17.32. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3112, 3027, 2919, 2859, 1664, 1604, 1487, 1411, 1380, 1319, 1282, 1147, 1083, 1038, 969, 936, 910, 855, 767, 737, 698, 669, 533.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{23}N_2O$ [M+H]$^+$: 331.1805, found: 331.1797.



(1-Mesityl-1*H*-imidazol-2-yl)(2-(*p*-tolyl)cyclopropyl)methanone (1h)

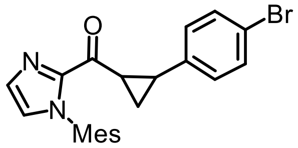
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.36 (m, 1H), 7.12-7.02 (m, 4H), 7.02-7.00 (m, 1H), 6.97 (br s, 2H), 3.63-3.53 (m, 1H), 2.63-2.53 (m, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 1.91 (s, 3H), 1.89 (s, 3H), 1.74-1.65 (m, 1H), 1.50-1.41 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.9, 143.5, 138.4, 137.4, 135.9, 134.9, 134.1, 133.9, 130.5, 129.0, 128.9, 126.1, 125.6, 29.3, 29.0, 21.1, 20.9, 20.1, 17.31, 17.28. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3144, 3114, 3013, 2948, 2920, 2860, 1664, 1487, 1439, 1410, 1378, 1322, 1047, 970, 943, 918, 872, 804, 771, 741, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{25}N_2O$ [M+H]$^+$: 345.1961, found: 345.1953.



(2-(4-Bromophenyl)cyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone (1i)

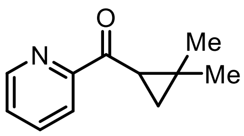
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.34 (m, 3H), 7.05-6.97 (m, 3H), 6.96 (br s, 2H), 3.60-3.52 (m, 1H), 2.59-2.50 (m, 1H), 2.34 (s, 3H), 1.89 (s, 3H), 1.88 (s, 3H), 1.74-1.65 (m, 1H), 1.47-1.38 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.4, 143.4, 139.6, 138.5, 134.8, 134.1, 133.9, 131.4, 130.6, 129.0, 128.0, 125.8, 120.1, 29.0, 28.7, 21.1, 20.0, 17.34, 17.32. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3063, 2959, 2916, 2855, 1664, 1484, 1412, 1374, 1314, 1037, 1007, 968, 913, 857, 841, 806, 777, 751, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{22}BrN_2O$ $[M+H]^+$: 409.0910, found: 409.0900.



(2,2-Dimethylcyclopropyl)(pyridin-2-yl)methanone (1j)

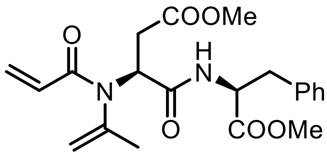
A grey solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.73-8.68 (m, 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.81 (td, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.44 (ddd, J_1 = 7.2 Hz, J_2 = 4.8 Hz, J_3 = 1.2 Hz, 1H), 3.38 (dd, J_1 = 7.5 Hz, J_2 = 5.7 Hz, 1H), 1.49 (dd, J_1 = 5.7 Hz, J_2 = 3.9 Hz, 1H), 1.33 (s, 3H), 1.18 (s, 3H), 1.08 (dd, J_1 = 7.5 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 199.3, 154.8, 148.9, 136.7, 126.5, 121.5, 30.5, 28.9, 27.3, 25.0, 18.2.

IR (film): ν (cm^{-1}) 3058, 2994, 2943, 2870, 1667, 1575, 1443, 1384, 1312, 1273, 1211, 1116, 1089, 1038, 996, 910, 834, 797, 758, 711, 678, 646, 616.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{14}NO$ $[M+H]^+$: 176.1070, found: 176.1070.



Methyl (*S*)-4-(((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-4-oxo-3-(*N*-(prop-1-en-2-yl) acrylamido)butanoate (2t)

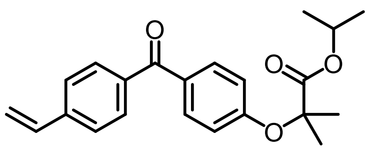
A white solid. **2t** was isolated as a minor product in the tandem esterification/acylation reaction of **aspartame** following a published procedure.[4]

^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 8.04 (d, *J* = 7.8 Hz, 1H), 7.27-7.21 (m, 2H), 7.21-7.18 (m, 1H), 7.18-7.14 (m, 2H), 6.43 (dd, J_1 = 16.8 Hz, J_2 = 10.3 Hz, 1H), 6.22 (dd, J_1 = 16.8 Hz, J_2 = 2.0 Hz, 1H), 5.73 (dd, J_1 = 10.3 Hz, J_2 = 2.3 Hz, 1H), 5.25 (t, *J* = 7.4 Hz, 1H), 5.12-5.10 (m, 1H), 4.63 (s, 1H), 4.49-4.42 (m, 1H), 3.61 (s, 3H), 3.57 (s, 3H), 3.03 (dd, J_1 = 13.9 Hz, J_2 = 5.1 Hz, 1H), 2.92 (dd, J_1 = 13.8 Hz, J_2 = 9.4 Hz, 1H), 2.87 (dd, J_1 = 16.6 Hz, J_2 = 8.0 Hz, 1H), 2.56 (dd, J_1 = 16.6 Hz, J_2 = 6.8 Hz, 1H), 1.58 (s, 3H).

^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 171.5, 170.6, 169.3, 164.4, 141.6, 137.1, 129.1, 128.9, 128.3, 127.9, 126.6, 118.1, 53.8, 53.3, 52.0, 51.6, 36.3, 33.5, 22.1.

IR (film): ν (cm^{-1}) 3380, 2956, 1738, 1678, 1644, 1610, 1516, 1448, 1413, 1369, 1314, 1237, 1167, 1128, 1024, 986, 929, 897, 824, 750, 703, 548, 497, 392.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{26}N_2O_6Na$ $[M+Na]^+$: 425.1683, found: 425.1678.



Isopropyl 2-methyl-2-(4-(4-vinylbenzoyl)phenoxy)propanoate (2u)

A white solid. **2u** was synthesized through a Suzuki cross coupling of **fenofibrate** with potassium vinyltrifluoroborate according to a published procedure.[5]

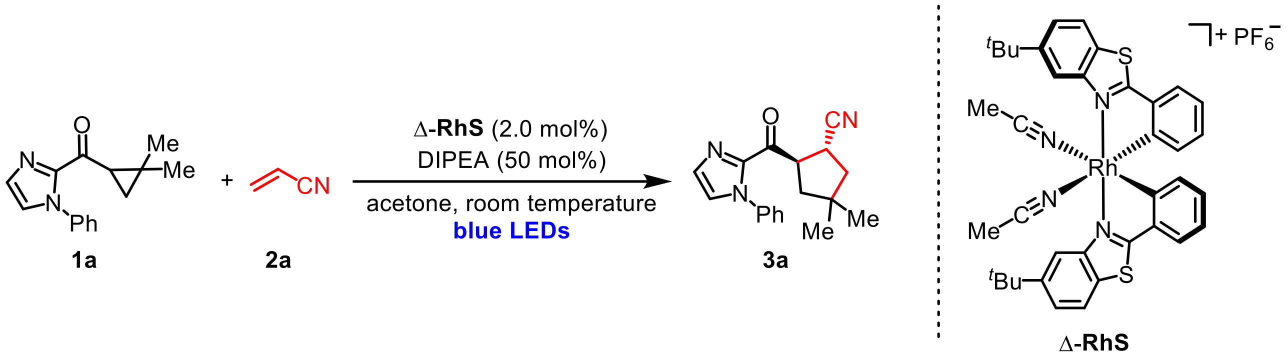
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.70 (m, 4H), 7.52-7.46 (m, 2H), 6.90-6.83 (m, 2H), 6.78 (dd, J_1 = 17.4 Hz, J_2 = 10.8 Hz, 1H), 5.88 (d, *J* = 17.7 Hz, 1H), 5.39 (d, *J* = 10.8 Hz, 1H), 5.09 (sept, *J* = 6.0 Hz, 1H), 1.66 (s, 6H), 1.22 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.0, 173.2, 159.5, 141.1, 137.3, 136.1, 131.9, 130.8, 130.2, 126.0, 117.2, 116.3, 79.4, 69.3, 25.4, 21.5.

IR (film): ν (cm^{-1}) 3082, 2983, 2938, 2877, 1718, 1641, 1599, 1570, 1281, 1247, 1174, 1148, 1103, 971, 923, 854, 775, 669, 594.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{24}O_4Na$ $[M+Na]^+$: 375.1567, found: 375.1556.

3. Typical Procedure

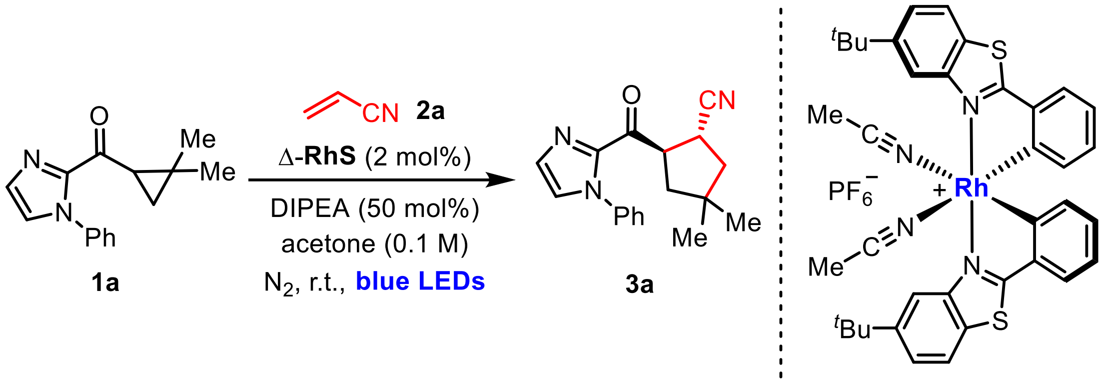


An oven-dried 10 mL Schlenk tube was charged with cyclopropane **1a** (24.0 mg, 0.10 mmol) and Δ-**RhS** (1.7 mg, 2 mol%). The tube was purged with nitrogen. Then, acetone (1.0 mL, 0.1 M) was added via syringe, followed by acrylonitrile **2a** (13.3 mg, 2.5 equiv) and DIPEA (6.5 mg, 0.5 equiv) under nitrogen atmosphere with stirring. The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned at approximately 10 cm away from a 24 W blue LEDs lamp. After stirring for the indicated time (monitored by TLC), the mixture was diluted with CH_2Cl_2. The combined mixture was concentrated under reduced pressure. The crude residue was subjected to ^{1}H NMR to determine the d.r. value. Then, all the mixture was collected and purified by flash chromatography on silica gel (*n*-hexane/EtOAc) to afford the product **3a**. The enantiomeric excess was determined by HPLC analysis on a chiral stationary phase.

Racemic samples were obtained by carrying out the reactions with *rac*-**RhS**.

4. Additional Information for Condition Screening and Substrate Scope

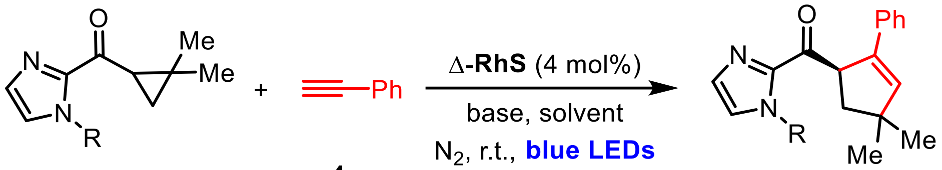
Table S1: Control experiments for [3+2] cycloadditions with alkenes.[a]



Entry	Derivation from conditions	Yield [%][b]	D.r.[c]	Ee [%][c]
1	none	98	> 20:1	99
2	without **RhS**	0	n.a.	n.a.
3	without DIPEA	0	n.a.	n.a.
4	without light	0	n.a.	n.a.
5	under air	0	n.a.	n.a.

[a] Reaction conditions: **1a** (0.10 mmol), **2a** (0.25 mmol), Δ-**RhS** (2.0 mol%) and DIPEA (0.05 mmol) in acetone (1.0 mL) were stirred at room temperature under an atmosphere of nitrogen with irradiation of blue LEDs (24 W). [b] Isolated yield. [c] Only one diastereoisomer was observed as judged by ^{1}H NMR and enantiomeric excess was determined by HPLC analysis on a chiral stationary phase. n.a. = not applicable.

Table S2: Conditions optimization for [3+2] cycloadditions with alkynes.[a]



1a (R = Ph)
1b (R = Mes)

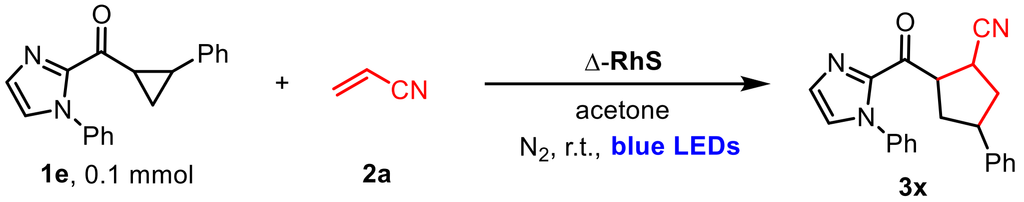
4a

5a (R = Ph)
5b (R = Mes)

Entry	Base (2.0 equiv)	Solvent	Yield [%][b]	Ee [%][c]
1	DIPEA	acetone	57 (**5a**)	87
2	Et_3N	acetone	73 (**5a**)	88
3	2,6-Lutidine	acetone	0 (**5a**)	n.a.
4	K_2CO_3	acetone	0 (**5a**)	n.a.
5	Et_3N	CH_2Cl_2	82 (**5a**)	81
6	Et_3N	MeCN	57 (**5a**)	77
7	Et_3N	DMF	55 (**5a**)	88
8	Et_3N	PhCl	97 (**5a**)	88
9	Et_3N	THF	95 (**5a**)	89
10[d]	Et_3N	THF	99 (95) (**5b**)	98

[a] Reaction conditions: **1** (0.05 mmol), **4a** (0.25 mmol), Δ-**RhS** (4.0 mol%) and base (0.1 mmol) in solvent (0.5 mL) were stirred at room temperature under an atmosphere of nitrogen with irradiation of blue LEDs (24 W). [b] NMR yields. [c] Enantiomeric excess was determined by HPLC analysis on a chiral stationary phase. [d] **1b** was employed and isolated yield is provided in parenthesis. n.a. = not applicable.

Table S3: Effect of DIPEA on the formation of cyclopentane **3x**.[a]

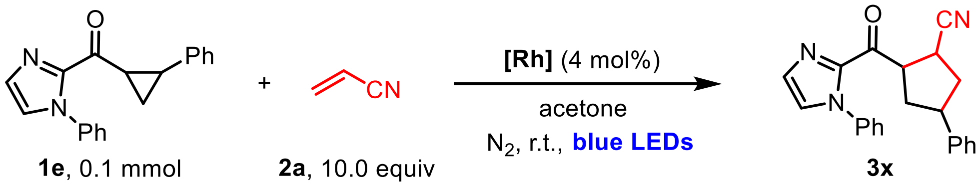


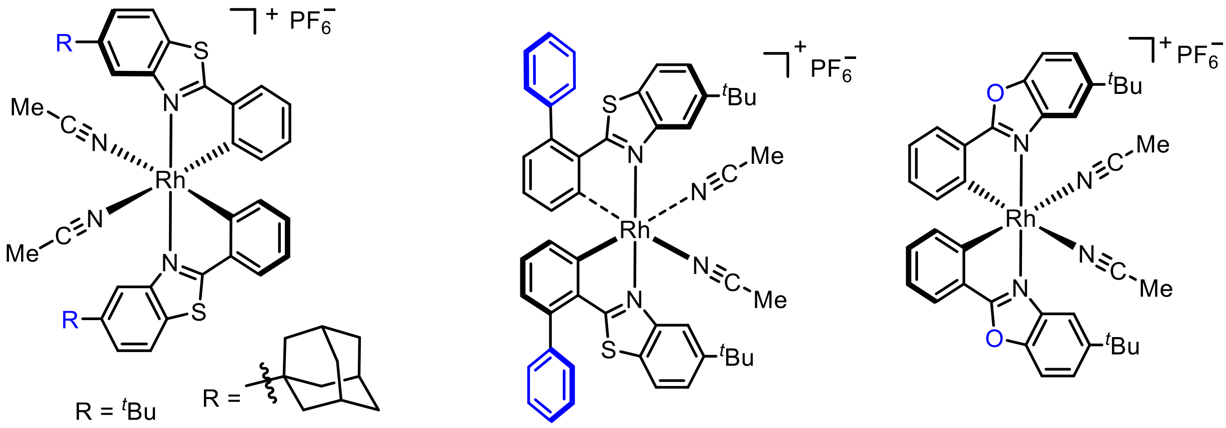
Entry	DIPEA	Conditions	Results
1	none	4.0 mol% of **RhS**; 10.0 equiv of **2a**; acetone (0.2 M)	quant. yield 2.1:1 d.r. 95% ee, 95% ee
2	50 mol%	2.0 mol% of **RhS**; 2.5 equiv of **2a**; acetone (0.1 M)	quant. yield 2.1:1 d.r. 97% ee, 99% ee

[a] Reaction conditions: **1e** (0.10 mmol), **2a** and Δ-**RhS** in acetone were stirred at room temperature under an atmosphere of nitrogen with irradiation of blue LEDs (24 W) for 16 h; NMR yields; diastereomeric ratio determined by ^{1}H NMR of the crude product; enantiomeric excess determined by HPLC analysis on a chiral stationary phase.

Note: Different from **1a** (see Table S1), **1e** bearing an aromatic substituent on cyclopropyl ring could undergo cycloadditions directly without a reductive initiator, which might be interpreted by the enhanced life time of excited states for cyclopropanes with aromatic system. It is reported that electronically excited cyclopropanes could undergo ring opening.[6] Since the addition of 50 mol% of DIPEA has positive effect, we decided to use the conditions with DIPEA for the reactions generating **3x-ab** (see Figure 4 in main text).

Table S4: Effect of catalysts on the diastereoselectivity of cyclopentane **3x**.[a]

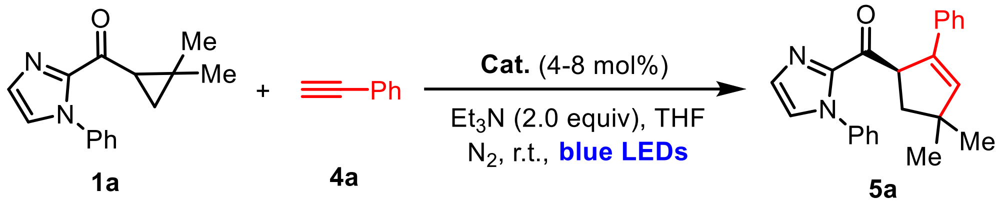




Δ-RhS	Δ-RhS(Adm)[b]	*rac*-RhS(Ph)[c]	Λ-RhO[d]
quant. yield	quant. yield	quant. yield	quant. yield
2.1:1 d.r.	2.4:1 d.r.	1.8:1 d.r.	1.5:1 d.r.
95% ee, 95% ee	98% ee, 98% ee		87% ee, 95% ee

[a] Reaction conditions: **1e** (0.10 mmol), **2a** and **Rh** based catalyst in acetone were stirred at room temperature under an atmosphere of nitrogen with irradiation of blue LEDs (24 W) for 16 h; NMR yields; diastereomeric ratio determined by ^{1}H NMR of the crude product; enantiomeric excess determined by HPLC analysis on a chiral stationary phase. [b] See ref. S7. [c] See ref. S8. [d] See ref. S9.

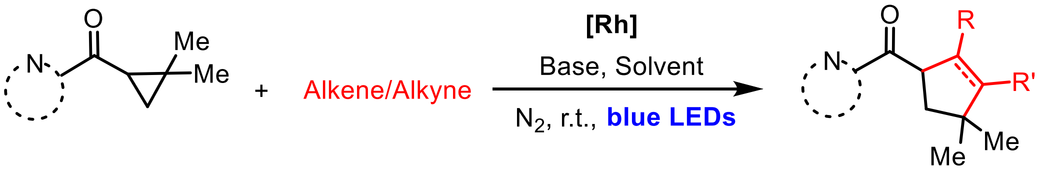
Table S5: Effect of catalyst on the formation of **5a**.[a]

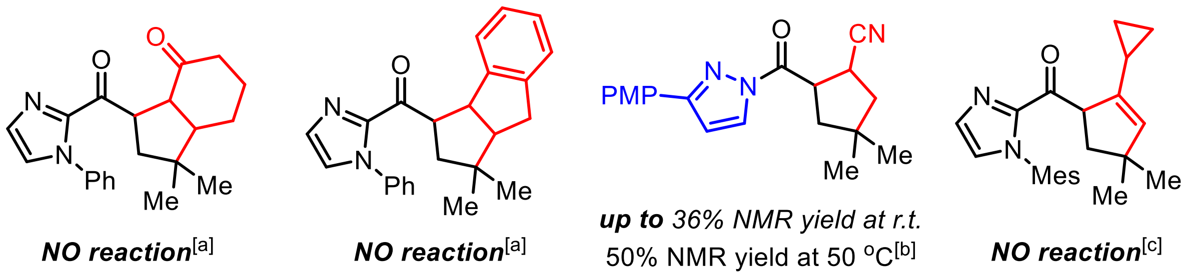


Entry	Cat.	Results
1	**RhS** (8.0 mol%)	91% yield, 91% ee
2	**RhS** (4.0 mol%)	93% yield, 89% ee
3	**RhO** (4.0 mol%)	97% yield, 63% ee
4	**RhS(Adm)** (4.0 mol%)	75% yield, 93% ee
5	**IrS**[b] (4.0 mol%)	< 10% yield, 81% ee

[a] Reaction conditions: **1a** (0.05 mmol), **4a** (0.25 mmol), Et_3N (0.10 mmol) and the catalyst in THF were stirred at room temperature under an atmosphere of nitrogen with irradiation of blue LEDs (24 W) for 24 h; NMR yields; enantiomeric excess determined by HPLC analysis on a chiral stationary phase. [b] See ref. S10.

Table S6: Limitations on the substrate scope.[a]





[a] Reaction conditions see Table S1, entry 1. [b] Reaction conditions: the corresponding cyclopropane (0.10 mmol), **2a** (0.50 mmol), *N*,*N*-dimethylaniline (0.20 mmol) and 8.0 mol% of a modified racemic octahedral **Rh**-based catalyst bearing two cyclometalated ligands, namely (5-(*tert*-butyl)-2-(2,4-dimethoxypheny)benzo[*d*]thiazole), in acetone (0.1 M) were stirred at under an atmosphere of nitrogen with irradiation of blue LEDs (24 W) for 48 h. [c] Reaction conditions see Table S2, entry 10.

5. Mechanistic Studies

5.1 Absorption/Emission Spectra

Figure S1 shows the emission spectrum of the Blue LEDs lamp used in this study.

Figure S2 shows the absorption spectra of **1a**, **RhS-1a** and **RhS-3a**. **RhS-1a** and **RhS-3a** were prepared according to our previously developed well-documented method.[12] Free substrate **1a**, which has a maximum absorption at around 280 nm, can not be excited by visible light. In contrast, strong absorption of **RhS-1a** appears at near UV and visible-light region. These results support the role of **RhS** for the direct visible light excitation of catalyst bound cyclopropanes. Otherwise to reach the excited state of a cyclopropane needs a high energy UV-light. To be mentioned, addition of DIPEA (25 equiv) to the solution of **RhS-1a** (0.02 mM in CH_2Cl_2) has little influence on the absorption spectra in near UV/visible-light region indicating the absence of EDA complex between **RhS-1a** and DIPEA. In addition, the absorption of product bound rhodium complex **RhS-3a** has no significant difference compared with **RhS-1a**.

Figure S3 shows the phosphorescence spectra of the **RhS-1a** and **RhS** which were recorded at 77 K in a quartz tube. In order to obtain a transparent rigid matrix at 77 K, a mixture of CH_2Cl_2/$CHCl_3$ (1:1 v/v) was employed as the solvents. The emission maximum of **RhS-1a** centered at 507 nm, which corresponds to 2.45 eV. Compared with **RhS**, the peaks in emission spectrum of **RhS-1a** shift to shorter wavelength which is in consistent with the coordination of a electron-deficient ligand. This indicates the involvement of substrate **1a** in the excited state of **RhS-1a**.

Figure S4 shows the phosphorescence intensity decay of **RhS-1a** which was monitored at 507 nm, 548 nm, 594 nm and 650 nm recorded at 77 K. In all cases, a monoexponential decay was observed, with a lifetime of 0.12 ms

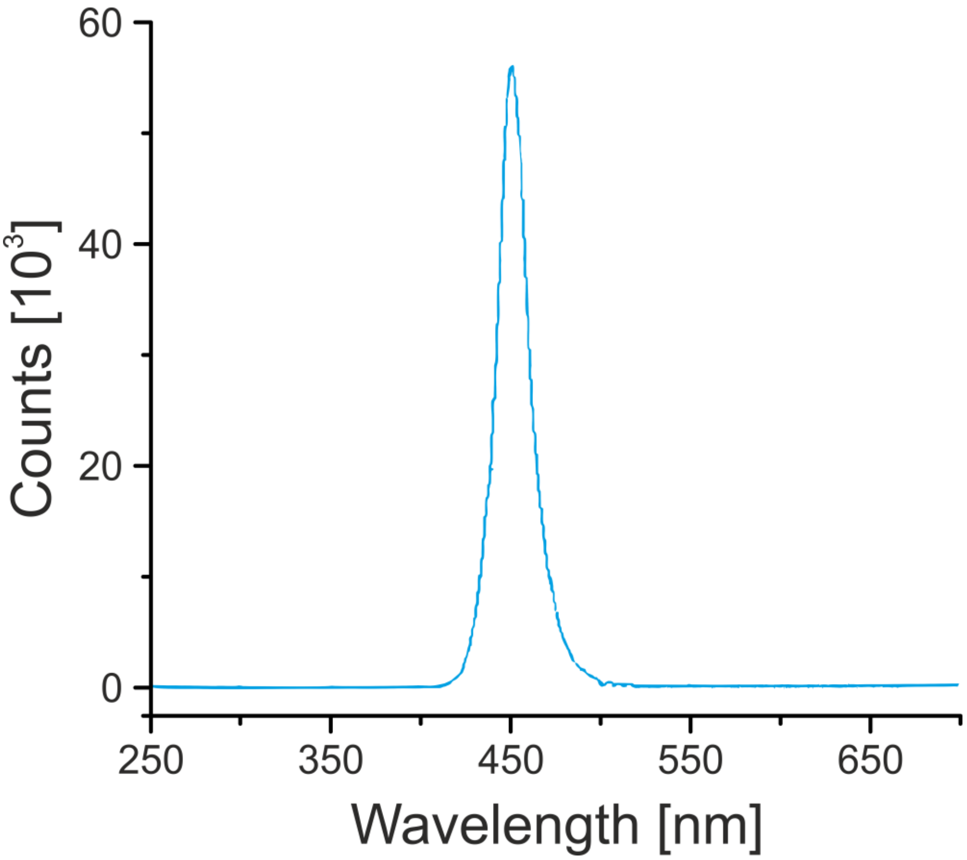


Figure S1. Emission spectrum of the 24 W Blue LEDs lamp.

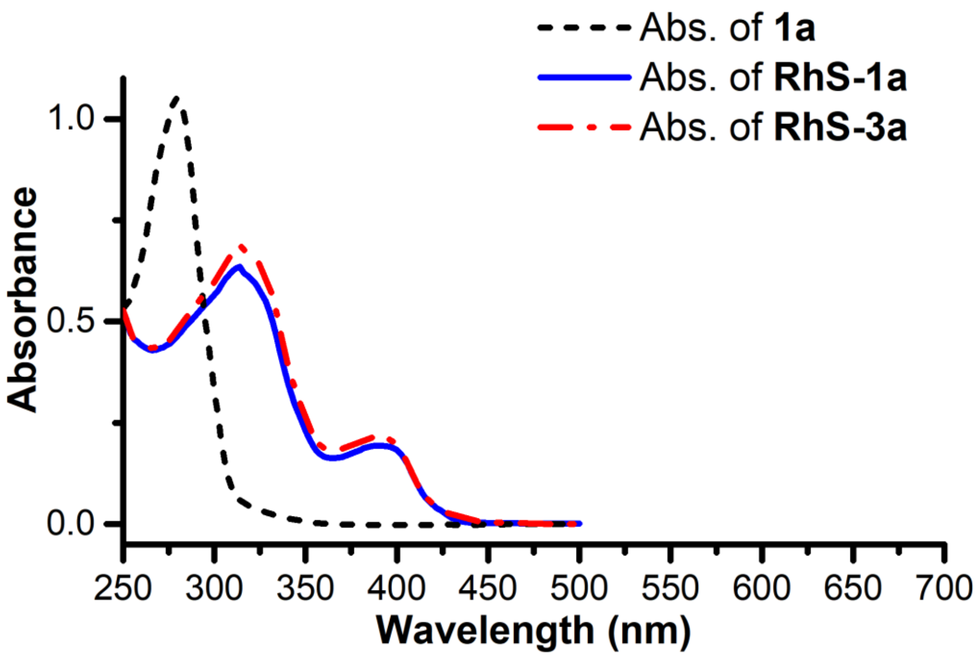


Figure S2. UV/Vis absorption spectra of **1a** (0.2 mM), **RhS-1a** (0.02 mM) and **RhS-3a** (0.02 mM). Recorded in CH_2Cl_2.

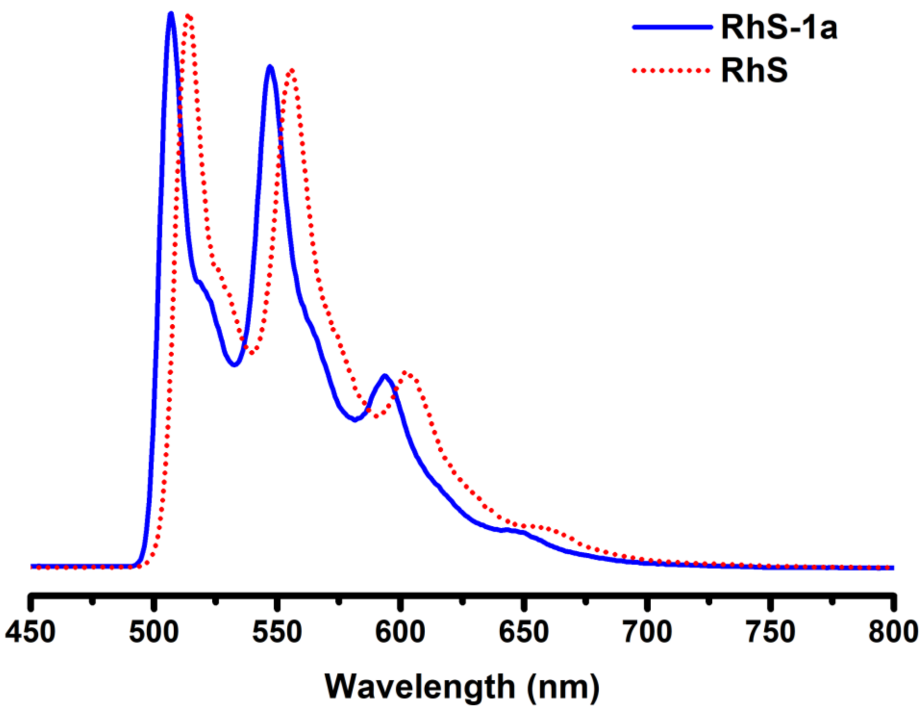


Figure S3. Phosphorescence spectrum of **RhS-1a** (blue solid line, excited at 400 nm, setup parameters: slits 5-5 nm, delay time 0.01 ms, gate time 0.5 ms) and **RhS** (red dot line, excited at 350 nm, setup parameters: slits 5-5 nm, delay time 0.05 ms, gate time 0.5 ms). Recorded in $CH_2Cl_2/CHCl_3$ (1:1 v/v) at 77 K. The intensity was normalized.

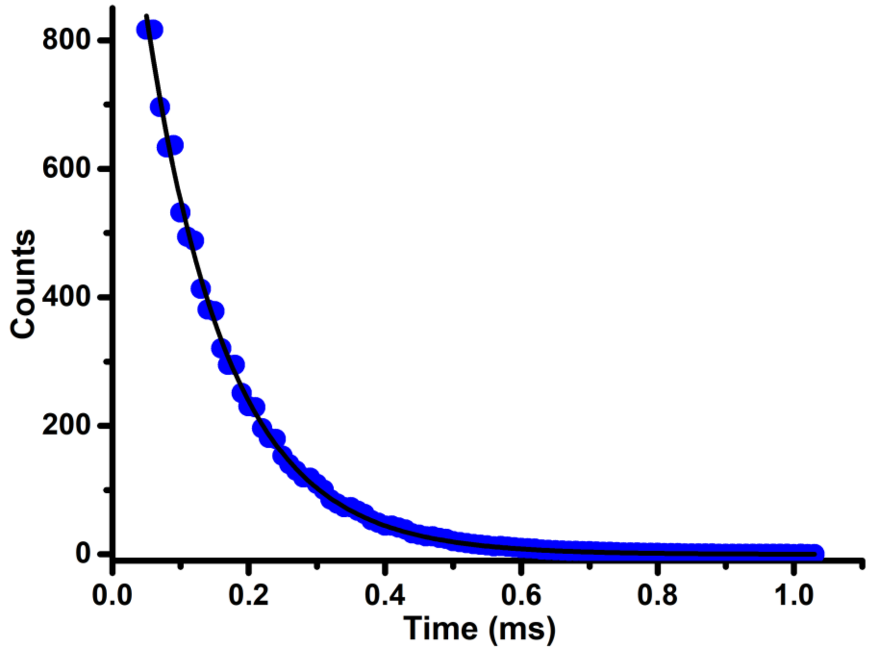


Figure S4. Emission intensity decay at 77 K of **RhS-1a**. (Blue dots, setup parameters: λ_{ex} 400 nm, λ_{em} 507 nm, slits 5-5-nm, integration time 0.1 s, cycle time 20 ms, first delay time 0.05 ms, gate time 0.5 ms, delay time interval 0.01 ms). The black curve represents the mathematical fit of the experimental data.

5.2 Cyclic Voltammetry

Voltammetric experiments were conducted with a computer controlled Eco Chemie Autolab PGSTAT204 potentiostat in a Metrohm electrochemical cell containing a 1 mm diameter planar platinum electrode, a Pt wire electrode and a Ag/AgCl/KCl(3 M) reference electrode. All solution used for the voltammetric experiment was deoxygenated by nitrogen gas and measurement was performed at room temperature (22 ± 2 °C).

As shown in Figure S5, the free substrate **1a** could be reduced at approximately –2.5 V versus Ag/AgCl,[11] while after coordination, the reduction potential of **RhS-1a** is significantly decreased to –1.2 V. According to the triplet energy of 2.5 eV that is calculated according to the emission of **RhS-1a** (Figure S3), excited state reduction potential of **RhS-1a** could be estimated as +1.3 V vs. Ag/AgCl. Besides, DIPEA could be oxidized at +1.0 V (E_{pa} vs Ag/AgCl, see Figure S6), which means DIPEA is feasible to reduce the excited **RhS-1a**. Compared with **RhS-1a**, the reduction potential for **RhS** is a little bit more negative (E_{pc} = –1.3 V vs Ag/AgCl, Figure S5). In combination with the reactivity, this implies that the SET reduction of the **RhS-1a** complex is ligand centered.

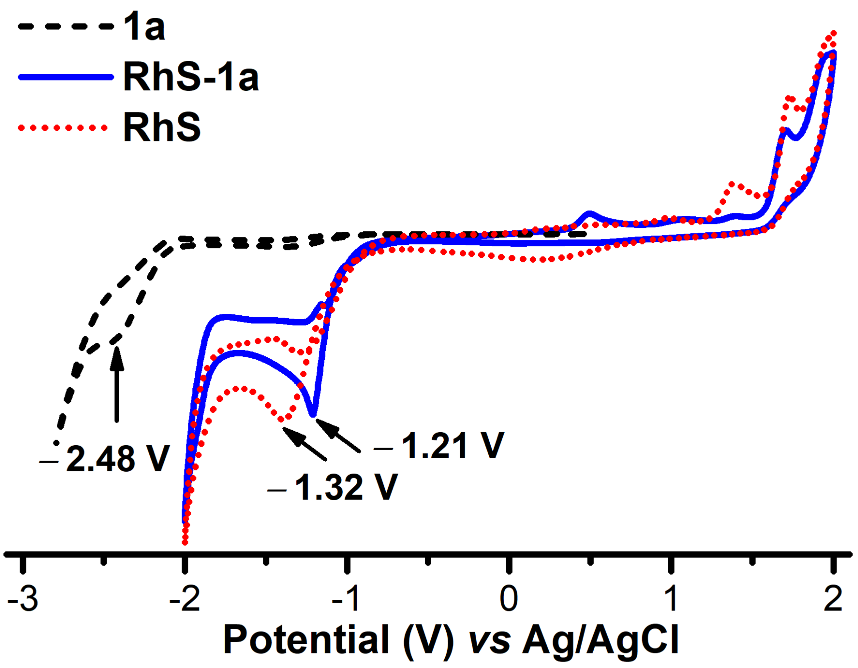


Figure S5. Cyclic voltammograms of **1a**, **RhS** and **RhS-1a**. Recorded in CH_2Cl_2 containing 0.1 M $n$$Bu_4NPF_6$ at a scan rate = 0.1 V/s. The current is normalized.

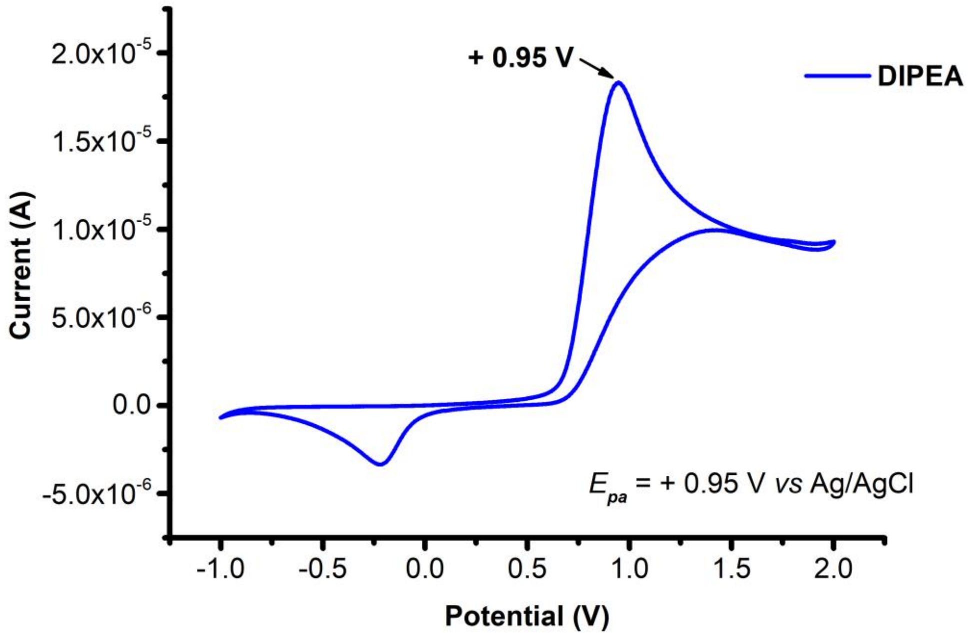


Figure S6. Cyclic voltammograms of DIPEA. Recorded in CH_2Cl_2 containing 0.1 M $n$$Bu_4NPF_6$ at a scan rate = 0.1 V/s.

5.3 Quantum Yield Measurement

The quantum yield was measured following our recently reported procedures.[12] A 400 nm LED was employed as light source. A Powermeter was used as detector. The measurement was accomplished in a dark room with a 1.1 W red LEDs. The [3+2] cycloaddition **1a** + **2a** → **3a** was chosen as model reaction.

Step 1: The radiant power of light transmitted by the cuvette with a blank solution was measured as P_{blank} = 34.37 mW.

Step 2: The reaction mixture of **1a** (48.0 mg, 0.20 mmol), **2a** (26.6 mg, 2.5 equiv), *rac*-**RhS** (3.5 mg, 2 mol%) and DIPEA (13.0 mg, 0.5 equiv) in acetone (2.0 mL, 0.1 M) was filled into a fluorescence cuvette with a stirring bar and septum and degassed by bubbling with nitrogen (10 min). Then, the cuvette was put into the setups and illuminated with the 400 nm LED. The transmitted radiant power P_{sample} = 1.04 mW was noted. The transmitted radiant power was monitored during the irradiation and remained constant.

Step 3: After illumination for 2 hours ($t = 2 \times 3600$ s), the amount of the formed **3a** was determined as 7.881×10^{-5} mol ($n_{product}$) by ^{1}H NMR.

Step 4: The overall quantum yield can be calculated as following:

$$\text{Quantum Yield} = \frac{N_{product}}{N_{photon}} = \frac{N_A \times n_{product}}{\frac{P_{absorbed} \times \mathrm{t}}{\frac{h \times c}{\lambda}}} = \frac{h \times \mathrm{c} \times N_A \times n_{product}}{(P_{blank} - P_{sample}) \times \mathrm{t} \times \lambda}$$

$$= \frac{6.626 \times 10^{-34}\mathrm{Js} \times 2.998 \times 10^{8}\mathrm{ms}^{-1} \times 6.022 \times 10^{23}\mathrm{mol}^{-1} \times 7.881 \times 10^{-5}\mathrm{mol}}{(34.37 - 1.04) \times 10^{-3}\mathrm{Js}^{-1} \times 2 \times 3600\mathrm{s} \times 400 \times 10^{-9}\mathrm{m}} = 0.098$$

where $N_{product}$ is the number of product **3a** formed; N_{photon} is the number of photons absorbed; N_A is Avogadro's constant; $n_{product}$ is the molar amount of product **3a** formed; $P_{absorbed}$ is the radiant power absorbed; *t* is the irradiation time; *h* is the Planck's constant; *c* is the speed of light; λ is the wavelength of light source, P_{blank} is the radiant power transmitted by the cuvette with a blank solution; P_{sample} is the radiant power transmitted by the cuvette with reaction mixture.

Steps 1-4 were repeated leading to the following result:

$$\text{Quantum Yield of second exp.} = \frac{N_{product}}{N_{photon}} = \frac{N_A \times n_{product}}{\frac{P_{absorbed} \times \mathrm{t}}{\frac{h \times c}{\lambda}}} = \frac{h \times \mathrm{c} \times N_A \times n_{product}}{(P_{blank} - P_{sample}) \times \mathrm{t} \times \lambda}$$

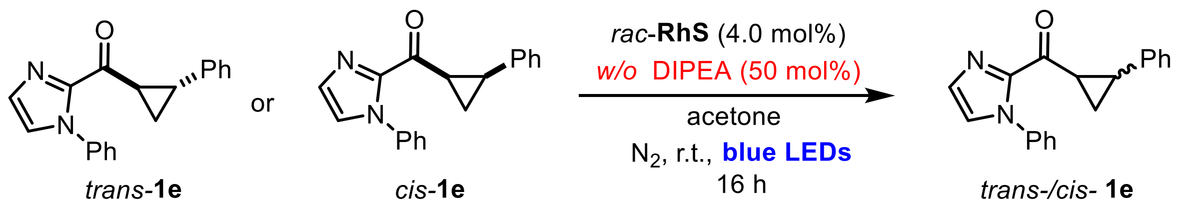
$$= \frac{6.626 \times 10^{-34}\mathrm{Js} \times 2.998 \times 10^{8}\mathrm{ms}^{-1} \times 6.022 \times 10^{23}\mathrm{mol}^{-1} \times 9.773 \times 10^{-5}\mathrm{mol}}{(34.07 - 1.21) \times 10^{-3}\mathrm{Js}^{-1} \times 2 \times 3600\mathrm{s} \times 400 \times 10^{-9}\mathrm{m}} = 0.124$$

Therefore, the average quantum yield for the reaction **1a** + **2a** → **3a** was determined as 0.11.

5.4 Ring Opening with Diastereomeric Substrates

As mentioned in Table S3, cyclopropanes bearing an aromatic ring (**1e-i**) could undergo the [3+2] photocycloadditions in the presence or absence of an amine. To further confirm that the aryl substituted cyclopropanes could undergo ring opening upon direct excitation, *cis*-**1e** was synthesized[3] and irradiated under different conditions. As shown in Table S7, *cis*- to *trans*-isomerization of the cyclopropane was observed in the presence or absence of an amine. There results indicate that the aryl substituted cyclopropanes could undergo reversible ring opening/closure upon direct photoexcitation.

Table S7: *Cis*- to *trans*- Isomerization of cyclopropane **1e**.[a]



Entry	Starting **1e**	DIPEA	Ratio of *trans/cis* of the recovered **1e**[b]
1	*trans*-**1e**	none	> 25:1
2	*trans*-**1e**	50 mol%	> 25:1
3	*cis*-**1e**	none	> 25:1
4	*cis*-**1e**	50 mol%	> 25:1

[a] Reaction conditions: **1e** (0.05 mmol), *rac*-**RhS** (4.0 mol%), and DIPEA (0 or 50 mol%) in acetone (0.1 M) were stirred at room temperature under an atmosphere of nitrogen with irradiation of blue LEDs (24 W) for 16 h. [b] Ratios were determined by crude ^{1}H NMR and in all entries > 90% of **1e** was recovered.

5.5 Competitive Coordination of Substrate and Product to RhS

In order to gain information about the coordination rate of substrate/product with **RhS**, two NMR experiments were done.

(1) Mix *rac*-**RhS** (0.02 mmol, 1.0 equiv), **1a** (0.02 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (0.02 mmol, internal standard), and CD_2Cl_2 (1.0 mL) in a NMR tube. After mixing for 10 minutes, the mixture was measured with ^{1}H NMR (Figure S7)

(2) Mix *rac*-**RhS** (0.01 mmol, 1.0 equiv), **3a** (0.015 mmol, 1.5 equiv), 1,3,5-trimethoxybenzene (0.02 mmol, internal standard), and CD_2Cl_2 (0.5 mL) in a NMR tube. After mixing for 10 minutes, the mixture was measured with ^{1}H NMR (Figure S8)

Conclusion: as shown in (Figures S7-8) both **1a** and **3a** could bind to **RhS** quickly. These results are inconsistent with our previous observation that this bis-cyclometalated rhodium catalyst is coordinatively very labile.

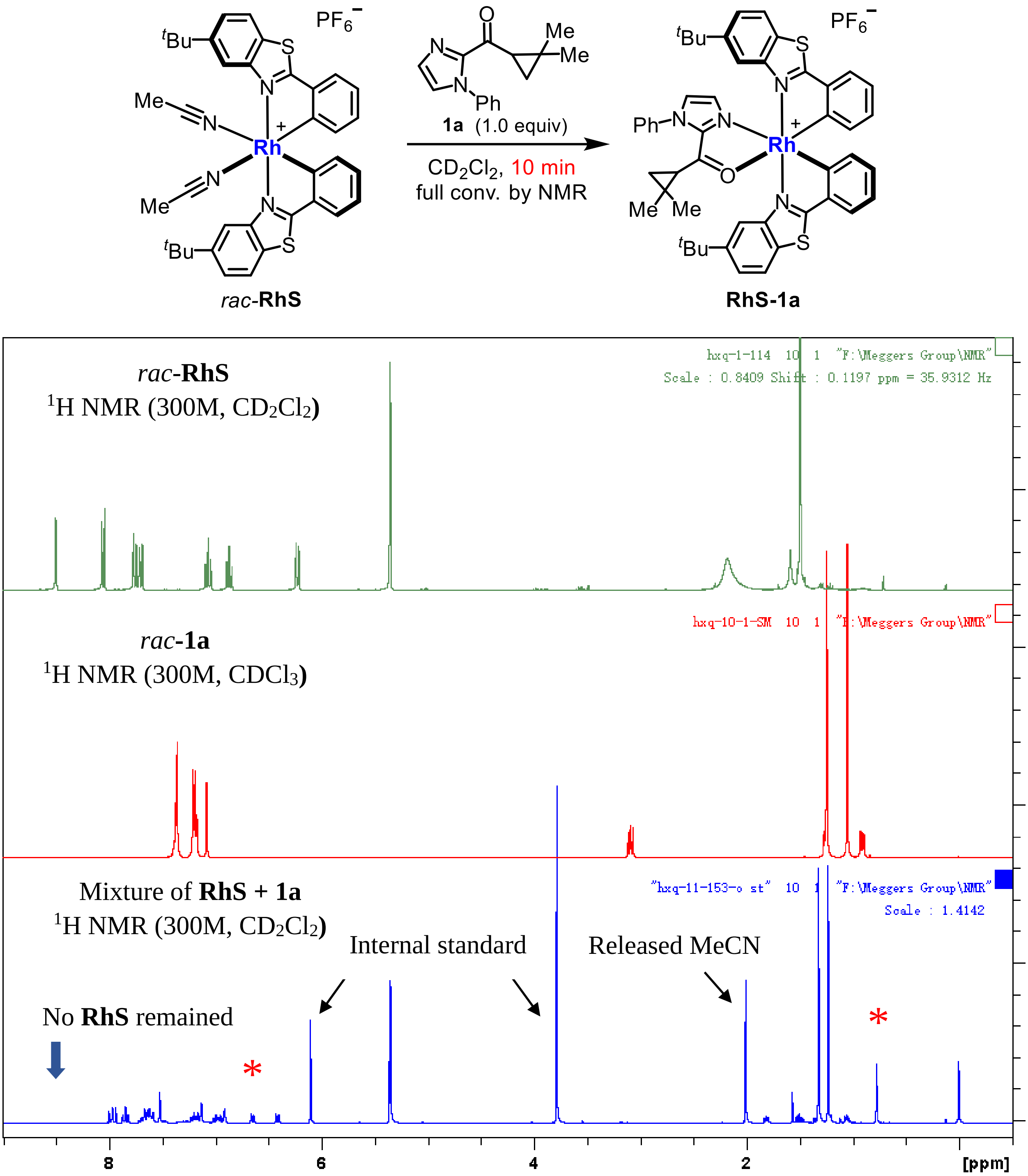


Figure S7. Fast coordination of **1a** to **RhS** as demonstrated by ^{1}H NMR experiment. *Down:* mix *rac*-**RhS** (0.02 mmol, 1.0 equiv), **1a** (0.02 mmol, 1.0 equiv), 1,3,5-trimethoxybenzene (0.02 mmol, internal standard), and CD_2Cl_2 (1.0 mL) in a NMR tube for 10 minutes. Red * refers to typical peaks of **RhS-1a**.

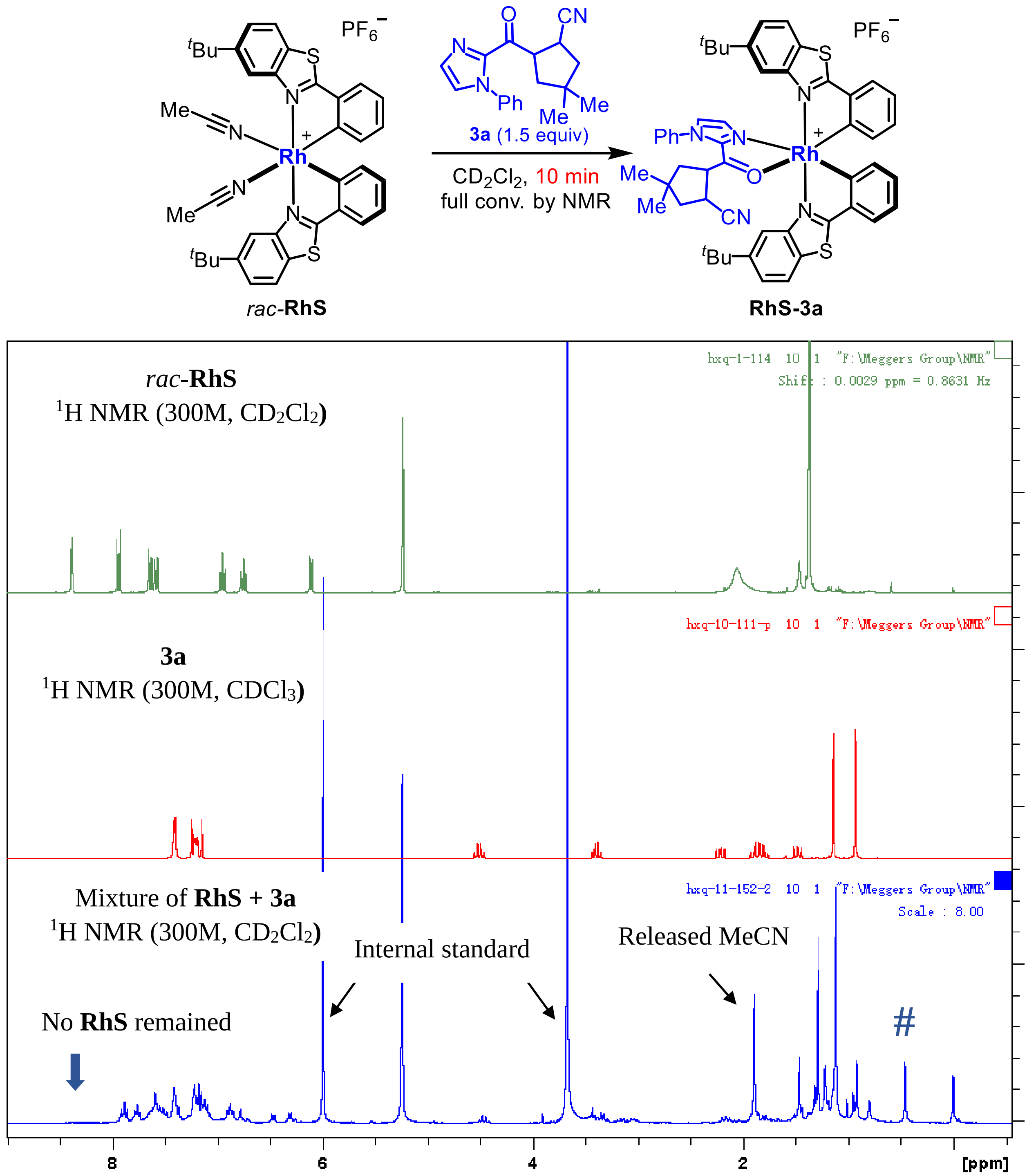


Figure S8. Fast coordination of **3a** to **RhS** as demonstrated by [1]H NMR experiment. *Down:* mix *rac*-**RhS** (0.01 mmol, 1.0 equiv), **3a** (0.015 mmol, 1.5 equiv), 1,3,5-trimethoxybenzene (0.02 mmol, internal standard), and CD_2Cl_2 (0.5 mL) in a NMR tube for 10 minutes. Blue # refers to typical peaks of **RhS-3a**.

In order to differ the coordination affinity of substrate/product with **RhS**, the following experiments were done:

(1) Mix **1a** (0.02 mmol, 1.0 equiv), **3a** (an oil, difficult to weight accurately, around 0.017 mmol), 1,3,5-trimethoxybenzene (0.02 mmol, internal standard), and CD_2Cl_2 (2.0 mL) in a NMR tube. Then the mixture was recorded by ^{1}H NMR. According to spectrum (Figure S9, upper), the ratio of **1a**:**2a** was determined as **1:0.8**.

(2) Add *rac*-**RhS** (0.02 mmol, 1.0 equiv) to the above mixture. After mixing for 30 minutes, the mixture was measured by ^{1}H NMR.

Results: as shown in Figure S9, only the substrate coordinated Rh complex (**RhS-1a**) was formed in the mixture of **RhS**/**1a**/**3a** (1:1:0.8) while all **3a** remained free without the formation of **RhS-3a**.

Conclusion: compared with the product, the substrate have a much higher coordination constant with **RhS**. We attribute this with the higher steric bulk of the product which leads to steric crowding and a reduction of the binding constant. Besides, only the substrate-coordinated Rh complexes would undergo the following transformation leading to continuoue consumption of substrate. Therefore, good conversions without significant catalyst inhibition by product are reasonable in current system.

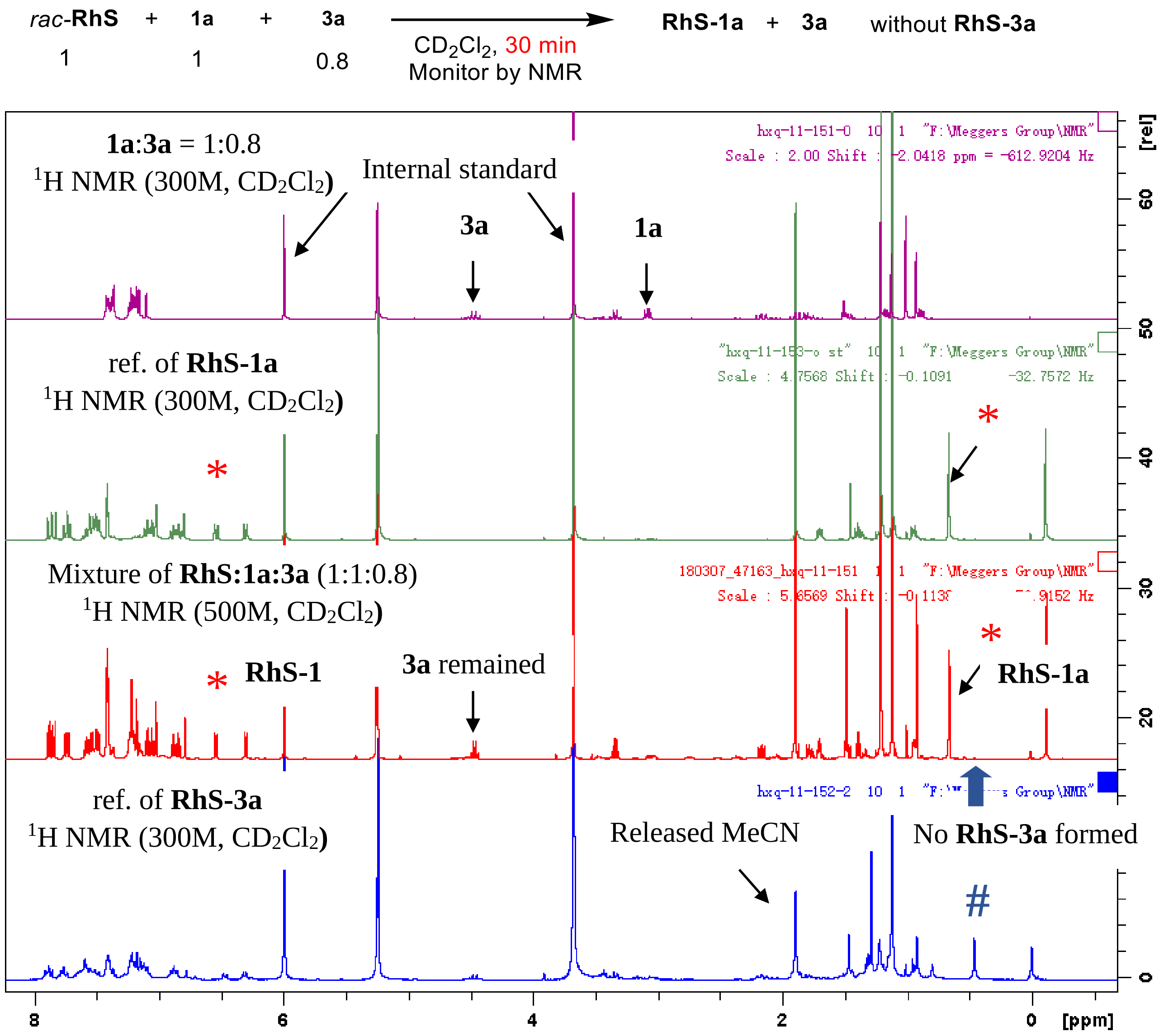
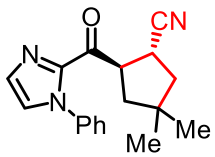


Figure S9. Competitive coordination of **1a** and **3a** to **RhS** as demonstrated by ^{1}H NMR experiment. *The third spectrum:* mix *rac*-**RhS** (0.02 mmol), **1a** (0.02 mmol) and **3a** (ratio of **1a**:**3a** = **1:0.8** as determined by the first spectrum), 1,3,5-trimethoxybenzene (0.02 mmol, internal standard), and CD_2Cl_2 (2.0 mL) in a NMR tube for 30 minutes. Red * refers to typical peaks of **RhS-1a**. Blue # refers to typical peaks of **RhS-3a**.

6. Experimental and Characterization Data of Products



((1*R*,2*R*)-4,4-Dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carbonitrile (3a)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 28.8 mg (98% yield) of **3a** as a colorless oil.

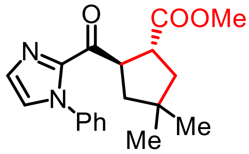
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 99% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 40 °C, t_r (major) = 8.0 min, t_r (minor) = 10.7 min). $[\alpha]_D^{22}$ = –86.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.37 (m, 3H), 7.26-7.23 (m, 1H), 7.22-7.18 (m, 2H), 7.16-7.13 (m, 1H), 4.51 (q, J = 9.2 Hz, 1H), 3.39 (q, J = 8.5 Hz, 1H), 2.21 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 1.89 (dd, J_1 = 12.9 Hz, J_2 = 9.0 Hz, 1H), 1.80 (dd, J_1 = 12.9 Hz, J_2 = 8.1 Hz, 1H), 1.48 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.14 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 142.0, 138.1, 130.3, 129.03, 128.97, 127.7, 125.9, 122.4, 52.1, 46.2, 45.2, 40.3, 28.64, 28.55, 27.9.

IR (film): ν (cm^{-1}) 3112, 2957, 2868, 2239, 1681, 1596, 1496, 1448, 1402, 1337, 1305, 1150, 1069, 1033, 978, 910, 836, 797, 763, 731, 692, 659, 535.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{20}N_3O$ $[M+H]^+$: 294.1601, found: 294.1593.



Methyl

(1*R*,2*R*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carboxylate (3b)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-

imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), methyl acrylate **2b** (21.5 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 22 hours, afforded 32.5 mg (99% yield) of **3b** as a colorless oil.

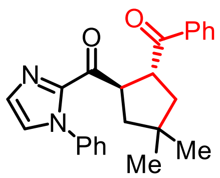
The d.r. value was determined through ^{1}H NMR of crude materials as 15:1; enantiomeric excess of the major diastereoisomer was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 25 °C, t_r (major) = 12.4 min, t_r (minor) = 15.4 min). $[\alpha]_D^{22}$ = –63.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50-7.42 (m, 3H), 7.31-7.25 (m, 3H), 7.20-7.17 (m, 1H), 4.56 (q, *J* = 9.0 Hz, 1H), 3.62 (s, 3H, the corresponding peak of the minor diastereoisomer at 3.27), 4.48 (q, *J* = 9.0 Hz, 1H), 2.18 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.89-1.82 (m, 2H), 1.61 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 1.13 (s, 3H), 1.02 (s, 3H, the corresponding peak of minor diastereoisomer at 1.05).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 175.3, 142.9, 138.5, 129.8, 128.9, 128.7, 127.0, 125.8, 51.7, 50.4, 45.9, 44.9, 44.0, 39.5, 29.11, 29.09.

IR (film): v (cm^{-1}) 3134, 3110, 2952, 2867, 1730, 1681, 1597, 1504, 1493, 1445, 1404, 1369, 1306, 1247, 1196, 1172, 1150, 1041, 1003, 982, 905, 849, 806, 760, 693, 660, 535.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{22}N_2O_3Na$ $[M+Na]^+$: 349.1523, found: 349.1520.



(1*R*,2*R*)-2-Bnzoyl-4,4-dimethylcyclopentyl)(1-phenyl-1*H*-imidazol-2-yl)methanone (3c)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-phenylprop-2-en-1-one **2c** (33.1 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 28.5 mg (77% yield) of the major diastereoisomer of **3c** as a yellow solid.

The d.r. value was determined through ^{1}H NMR of crude materials as 12:1, therefore the total yield is estimated as 83%. Enantiomeric excess of the major diastereoisomer was established by HPLC analysis using a Chiralpak AD-H column, ee = 91% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol

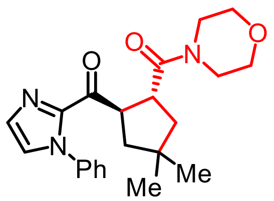
= 85:15, flow rate 1 mL/min, 40 °C, t_r (major) = 9.1 min, t_r (minor) = 15.0 min). $[\alpha]_D^{22}$ = –65.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.94-7.88 (m, 2H), 7.54-7.46 (m, 1H), 7.45-7.36 (m, 5H), 7.29-7.27 (m, 1H), 7.24-7.18 (m, 2H), 7.14-7.12 (m, 1H), 4.86 (q, *J* = 9.3 Hz, 1H), 4.41 (q, *J* = 9.0 Hz, 1H), 2.31 (dd, J_1 = 12.3 Hz, J_2 = 9.3 Hz, 1H), 2.02 (dd, J_1 = 12.6 Hz, J_2 = 9.9 Hz, 1H), 1.77-1.66 (m, 2H), 1.12 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 201.2, 192.3, 142.8, 138.5, 136.8, 132.7, 129.9, 128.9, 128.6, 128.4, 126.9, 125.9, 125.8, 49.5, 48.0, 46.2, 45.8, 40.2, 29.4, 29.0.

IR (film): *ν* (cm^{-1}) 3055, 2951, 2930, 2864, 1672, 1504, 1491, 1446, 1411, 1375, 1307, 1228, 1207, 1049, 873, 812, 786, 770, 705, 694, 661, 536.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_2O_2Na$ $[M+Na]^+$: 395.1730, found: 395.1728.



(1*R*,2*R*)-4,4-Dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentyl)(morpholino) methanone (3d)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-morpholinoprop-2-en-1-one **2d** (35.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 33.1 mg (87% yield) of **3d** as a colorless oil.

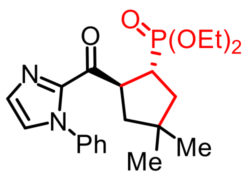
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 91% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 40:60, flow rate 1 mL/min, 40 °C, t_r (major) = 9.5 min, t_r (minor) = 20.7 min). $[\alpha]_D^{22}$ = –38.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.48-7.41 (m, 3H), 7.32-7.29 (m, 1H), 7.28-7.22 (m, 2H), 7.16-7.13 (m, 1H), 4.81 (q, *J* = 9.0 Hz, 1H), 3.68-3.45 (m, 9H), 2.32 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.79 (dd, J_1 = 12.3 Hz, J_2 = 9.0 Hz, 1H), 1.68 (dd, J_1 = 12.3 Hz, J_2 = 9.6 Hz, 1H), 1.60 (dd, J_1 = 12.6 Hz, J_2 = 9.6 Hz, 1H), 1.17 (s, 3H), 1.02 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 173.0, 142.8, 138.6, 130.0, 128.9, 128.6, 126.9, 125.8, 66.9, 66.8, 51.0, 46.1, 46.0, 45.1, 42.3, 41.6, 39.8, 29.5, 29.4.

IR (film): ν (cm^{-1}) 2954, 2928, 2861, 1677, 1635, 1597, 1503, 1493, 1443, 1402, 1304, 1269, 1231, 1211, 1113, 1069, 1046, 911, 870, 806, 762, 728, 693, 536.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{27}N_3O_3Na$ $[M+Na]^+$: 404.1945, found: 404.1942.



Diethyl ((1*R*,2*S*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentyl)phosphonate (3e)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), diethyl vinylphosphonate **2e** (41.0 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 37.5 mg (93% yield, total yield) of **3e** as a colorless oil as a mixture of two diastereosiomers.

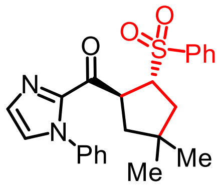
The d.r. value was determined through ^1H NMR of crude materials as 8:1; enantiomeric excess of the major diastereoisomer was established by HPLC analysis using a Chiralpak IG column, ee = 98% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 1 mL/min, 40 °C, t_r (major) = 7.4 min, t_r (minor) = 24.1 min). $[\alpha]_D^{22}$ = –33.4° (*c* 1.0, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$) δ 7.50-7.41 (m, 3H), 7.31-7.25 (m, 3H), 7.20-7.15 (m, 1H), 4.64-4.46 (m, 1H), 4.11-3.90 (m, 4H), 3.16-2.97 (m, 1H), 2.23-2.11 (m, 1H), 1.89-1.78 (m, 2H), 1.61 (dd, J_1 = 12.9 Hz, J_2 = 8.1 Hz, 1H), 1.26-1.16 (m, 6H), 1.15 (s, 3H), 0.99 (s, 3H, the corresponding peak of the minor diastereoisomer at 1.05).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4 (d, *J* = 2.3 Hz), 142.8, 138.5, 129.8, 128.9, 128.6, 127.0, 125.7, 61.6 (d, *J* = 5.4 Hz), 61.5, (d, *J* = 6.5 Hz), 48.1, 47.1 (d, *J* = 11.9 Hz), 41.6 (d, *J* = 2.3 Hz), 40.2 (d, *J* = 12.7 Hz), 36.2 (d, *J* = 146.4 Hz), 29.0, 28.6, 16.4 (d, *J* = 1.5 Hz), 16.3 (d, *J* = 1.9 Hz).

IR (film): ν (cm^{-1}) 2954, 2868, 1683, 1504, 1493, 1445, 1404, 1237, 1053, 1020, 955, 900, 810, 761, 730, 693, 663, 564, 549, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{29}N_2O_4PNa$ $[M+Na]^+$: 427.1757, found: 427.1755.



((1*S*,2*R*)-4,4-Dimethyl-2-(phenylsulfonyl)cyclopentyl)(1-phenyl-1*H*-imidazol-2-yl)methanone (3f)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), (vinylsulfonyl)benzene **2f** (42.1 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 20 hours, afforded 40.1 mg (98% yield) of **3f** as a yellow sold.

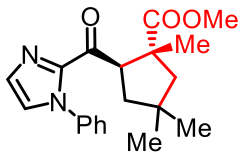
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 1 mL/min, 40 °C, t_r (major) = 10.4 min, t_r (minor) = 20.7 min). $[\alpha]_D^{22}$ = –13.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.83 (m, 2H), 7.60-7.52 (m, 1H), 7.48-7.38 (m, 5H), 7.31-7.28 (m, 1H), 7.16-7.13 (m, 1H), 7.23-7.06 (m, 2H), 4.80 (q, J = 8.7 Hz, 1H), 4.35 (q, J = 9.0 Hz, 1H), 2.24 (dd, J_1 = 12.9 Hz, J_2 = 9.9 Hz, 1H), 2.10 (dd, J_1 = 13.2 Hz, J_2 = 9.0 Hz, 1H), 1.85 (dd, J_1 = 13.2 Hz, J_2 = 9.3 Hz, 1H), 1.61 (dd, J_1 = 12.6 Hz, J_2 = 8.1 Hz, 1H), 1.13 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.5, 142.0, 138.5, 138.1, 133.3, 130.0, 128.9, 128.8, 128.7, 127.3, 125.7, 64.8, 47.8, 46.7, 40.9, 40.0, 28.7, 28.5. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3124, 3062, 2952, 2868, 1685, 1496, 1450, 1407, 1340, 1294, 1144, 1080, 1033, 987, 916, 885, 808, 755, 716, 690, 601, 561, 496, 417.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}N_2O_3SNa$ $[M+Na]^+$: 431.1400, found: 431.1397.



Methyl (1*R*,2*R*)-1,4,4-trimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carboxylate (3g)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), methyl methacrylate **2g** (25.0 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 32.9 mg (97% yield) of **3g** as a yellow solid.

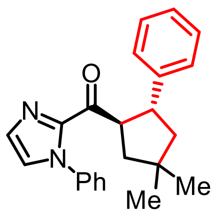
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 25 °C, t_r (major) = 6.4 min, t_r (minor) = 8.3 min). $[\alpha]_D^{22}$ = –60.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.22-7.16 (m, 2H), 7.15-7.12 (m, 1H), 7.08-7.05 (m, 1H), 4.70 (dd, J_1 = 12.6 Hz, J_2 = 6.6 Hz, 1H), 3.62 (s, 3H, the corresponding peak of the minor diastereoisomer at 3.41), 2.20 (d, J = 13.5 Hz, 1H), 1.99 (t, J = 12.6 Hz, 1H), 1.56 (dd, J_1 = 12.9 Hz, J_2 = 6.3 Hz, 1H), 1.42 (d, J = 13.5 Hz, 1H), 1.09 (s, 3H), 1.03 (s, 3H), 1.01 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 177.7, 143.7, 138.5, 129.5, 128.9, 128.6, 127.0, 125.9, 53.9, 53.5, 53.1, 52.1, 42.2, 37.1, 31.1, 30.2, 21.5.

IR (film): ν (cm^{-1}) 2938, 2868, 1728, 1679, 1495, 1444, 1404, 1333, 1302, 1253, 1175, 1144, 1113, 1067, 1018, 994, 968, 899, 860, 823, 765, 688, 536.

HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{24}N_2O_3Na$ $[M+Na]^+$: 363.1679, found: 363.1677.



((1*R*,2*R*)-4,4-Dimethyl-2-phenylcyclopentyl)(1-phenyl-1*H*-imidazol-2-yl)methanone (3h)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), styrene **2h** (26.1 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 28.0 mg (81% yield) of **3h** as a colorless oil.

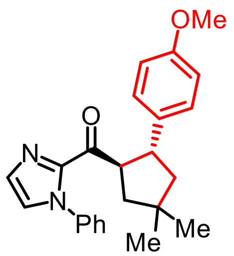
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 25 °C, t_r (major) = 5.4 min, t_r (minor) = 6.2 min). $[\alpha]_D^{22}$ = –171.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.31 (m, 3H), 7.23-7.11 (m, 5H), 7.10-7.02 (m, 3H), 7.02-6.99 (m, 1H), 4.47-4.34 (q, J = 9.8 Hz, 1H), 3.64 (td, J_1 = 11.4 Hz, J_2 = 7.6 Hz, 1H), 2.16 (dd, J_1 = 12.8 Hz, J_2 = 9.6 Hz, 1H), 1.89 (dd, J_1 = 12.6 Hz, J_2 = 7.6 Hz, 1H), 1.71 (t, J = 12.1 Hz, 1H), 1.62 (dd, J_1 = 12.8 Hz, J_2 = 9.3 Hz, 1H), 1.13 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 143.6, 143.4, 138.4, 129.5, 128.9, 128.6, 128.2, 127.5, 126.8, 126.0, 125.7, 54.6, 50.2, 47.1, 46.8, 38.5, 30.7, 30.2.

IR (film): ν (cm^{-1}) 3060, 3029, 2949, 2863, 1679, 1596, 1495, 1447, 1403, 1304, 1149, 1069, 1032, 979, 894, 816, 756, 693, 663, 528.

HRMS (ESI, *m/z*) calcd for $C_{23}H_{25}N_2O$ $[M+H]^+$: 345.1961, found: 345.1953.



((1*R*,2*R*)-2-(4-Methoxyphenyl)-4,4-dimethylcyclopentyl)(1-phenyl-1*H*-imidazol-2-yl) methanone (3i)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-methoxy-4-vinylbenzene **2i** (33.6 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere **at 50 ºC** with blue LEDs for 36 hours, afforded 26.3 mg (70% yield) of **3i** as a colorless oil.

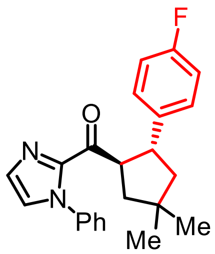
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 90% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 10.1 min, t_r (minor) = 12.0 min). $[\alpha]_D^{22}$ = –92.4° (*c* 0.5, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.46 (m, 3H), 7.21 (d, J = 1.0 Hz, 1H), 7.20-7.17 (m, 2H), 7.16-7.12 (m, 2H), 7.10 (d, J = 1.1 Hz, 1H), 6.75-6.75 (m, 2H), 4.47-4.39 (m, 1H), 3.74 (s, 3H), 3.66 (td, J_1 = 12.7 Hz, J_2 = 7.5 Hz, 1H), 2.21 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.93 (dd, J_1 = 12.6 Hz, J_2 = 9.6 Hz, 1H), 1.74 (t, J = 12.3 Hz, 1H), 1.67 (dd, J_1 = 12.9 Hz, J_2 = 9.4 Hz, 1H), 1.19 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 193.0, 157.8, 143.3, 138.4, 135.6, 129.5, 128.9, 128.6, 128.4, 126.9, 125.7, 113.6, 55.2, 54.8, 50.3, 46.7, 46.4, 38.3, 30.8, 30.3.

IR (film): ν (cm^{-1}) 3062, 2948, 2863, 1678, 1605, 1506, 1447, 1403, 1304, 1244, 1177, 1149, 1032, 978, 891, 827, 761, 692, 662, 536.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{27}N_2O_2$ $[M+H]^+$: 375.2067, found: 375.2063.



((1*R*,2*R*)-2-(4-Fluorophenyl)-4,4-dimethylcyclopentyl)(1-phenyl-1*H*-imidazol-2-yl)methanone (3j)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-fluoro-4-vinylbenzene **2j** (30.5 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 26 hours, afforded 23.8 mg (66% yield) of **3j** as a colorless oil.

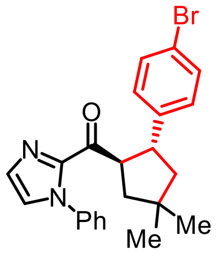
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 7.7 min, t_r (minor) = 9.2 min). $[\alpha]_D^{22}$ = –97.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.40 (m, 3H), 7.25-7.18 (m, 3H), 7.18-7.13 (m, 2H), 7.12-6.99 (m, 1H), 6.96-6.85 (m, 2H), 4.43 (q, J = 10.5 Hz, 1H), 3.68 (td, J_1 = 11.7 Hz, J_2 = 7.5 Hz, 1H), 2.23 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.95 (dd, J_1 = 12.6 Hz, J_2 = 7.5 Hz, 1H), 1.74 (t, J = 12.0 Hz, 1H), 1.69 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.20 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.7, 161.3 (d, J = 242.0), 143.3, 139.2 (d, J = 2.9 Hz), 138.4, 129.6, 128.9, 128.8 (d, J = 7.5 Hz), 128.7, 127.0, 125.7, 114.9 (d, J = 20.6 Hz), 54.8, 50.3, 46.6, 46.4, 38.4, 30.7, 30.2.

IR (film): ν (cm^{-1}) 3112, 3047, 2950, 2864, 1679, 1599, 1503, 1447, 1403, 1304, 1222, 1154, 1070, 1033, 979, 893, 833, 760, 732, 692, 661, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}FN_2O$ $[M+H]^+$: 363.1867, found: 363.1865.



((1*R*,2*R*)-2-(4-Bromophenyl)-4,4-dimethylcyclopentyl)(1-phenyl-1*H*-imidazol-2-yl)methanone (3k)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-bromo-4-vinylbenzene **2k** (45.8 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 26 hours, afforded 31.2 mg (74% yield) of **3k** as a white solid.

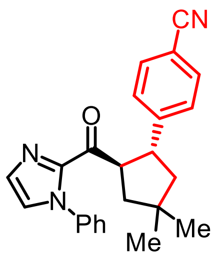
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 5.9 min, t_r (minor) = 6.5 min). $[\alpha]_D^{22}$ = –123.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.40 (m, 3H), 7.36-7.30 (m, 2H), 7.23-7.20 (m, 1H), 7.19-7.10 (m, 5H), 4.44 (q, J = 9.8 Hz, 1H), 3.67 (td, J_1 = 11.4 Hz, J_2 = 7.8 Hz, 1H), 2.24 (dd, J_1 = 12.9 Hz, J_2 = 9.9 Hz, 1H), 1.95 (dd, J_1 = 12.3 Hz, J_2 = 7.5 Hz, 1H), 1.73 (t, J = 12.0 Hz, 1H), 1.68 (dd, J_1 = 13.5 Hz, J_2 = 9.6 Hz, 1H), 1.20 (s, 3H), 1.10 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.5, 143.2, 142.6, 138.4, 131.3, 129.6, 129.3, 128.9, 128.7, 127.1, 125.7, 119.7, 54.5, 50.1, 46.7, 46.4, 38.5, 30.7, 30.2.

IR (film): ν (cm^{-1}) 3121, 3046, 2947, 2925, 2859, 1680, 1491, 1451, 1405, 1369, 1303, 1074, 1035, 1006, 893, 818, 763, 693, 654, 528.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}BrN_2O$ $[M+H]^+$: 423.1067, found: 423.1063.



4-((1*R*,2*R*)-4,4-Dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentyl)benzonitrile (3l)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 4-vinylbenzonitrile **2l** (32.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 20 hours, afforded 35.9 mg (97% yield) of **3l** as a colorless oil.

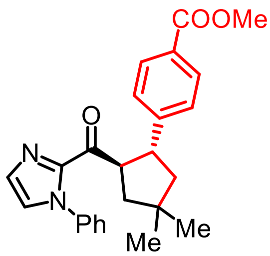
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 15.1 min, t_r (minor) = 21.3 min). $[\alpha]_D^{22}$ = –185.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53-7.48 (m, 2H), 7.47-7.41 (m, 3H), 7.39-7.34 (m, 2H), 7.23-7.21 (m, 1H), 7.19-7.14 (m, 2H), 7.14-7.12 (m, 1H), 4.47 (q, J = 9.8 Hz, 1H), 3.76 (td, J_1 = 11.4 Hz, J_2 = 7.5 Hz, 1H), 2.27 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.98 (dd, J_1 = 12.6 Hz, J_2 = 7.5 Hz, 1H), 1.75 (t, J = 12.0 Hz, 1H), 1.70 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 1.21 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 149.4, 142.9, 138.2, 132.1, 129.7, 129.0, 128.8, 128.3, 127.2, 125.7, 119.0, 109.9, 54.4, 49.8, 46.8, 46.7, 38.6, 30.6, 30.0.

IR (film): *v* (cm^{-1}) 3113, 3062, 2951, 2865, 2226, 1679, 1602, 1497, 1447, 1403, 1304, 1149, 1070, 1032, 895, 832, 763, 730, 692, 657, 558.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{24}N_3O$ $[M+H]^+$: 370.1914, found: 370.1912.



Methyl 4-((1*R*,2*R*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentyl)benzoate (3m)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), methyl 4-vinylbenzoate **2m** (40.6 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 20 hours, afforded 39.9 mg (99% yield) of **3m** as a white solid.

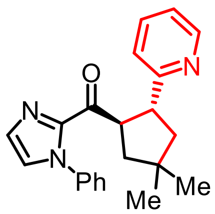
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 9.0 min, t_r (minor) = 12.1 min). $[\alpha]_D^{22}$ = –184.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93-7.86 (m, 2H), 7.46-7.40 (m, 3H), 7.37-7.30 (m, 2H), 7.22-7.19 (m, 1H), 7.18-7.12 (m, 2H), 7.12-7.09 (m, 1H), 4.50 (q, J = 9.8 Hz, 1H), 3.86 (s, 3H), 3.76 (td, J_1 = 11.1 Hz, J_2 = 7.5 Hz, 1H), 2.25 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.98 (dd, J_1 = 12.9 Hz, J_2 = 7.5 Hz, 1H), 1.79 (t, J = 12.0 Hz, 1H), 1.71 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.21 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 167.1, 149.2, 143.1, 138.3, 129.7, 129.6, 128.9, 128.7, 128.0, 127.5, 127.1, 125.7, 54.4, 51.9, 49.8, 47.1, 46.7, 38.6, 30.6, 30.1.

IR (film): ν (cm^{-1}) 3137, 2951, 2862, 1706, 1681, 1602, 1492, 1446, 1410, 1366, 1276, 1180, 1151, 1100, 1038, 1015, 984, 961, 896, 854, 788, 756, 699, 660, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{27}N_2O_3$ $[M+H]^+$: 403.2016, found: 403.2013.



((1*R*,2*R*)-4,4-Dimethyl-2-(pyridin-2-yl)cyclopentyl)(1-phenyl-1*H*-imidazol-2-yl)methanone (3n)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 2-vinylpyridine **2n** (26.3 mg, 2.5 equiv), Δ-**RhS**

(1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 28.2 mg (82% yield) of **3n** as a colorless oil.

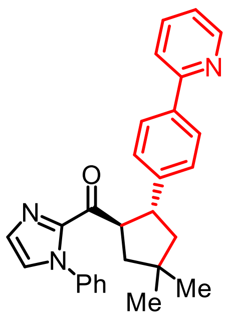
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 98% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 25 °C, t_r (major) = 9.2 min, t_r (minor) = 11.7 min). $[\alpha]_D^{22}$ = –81.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.48 (d, J = 4.5 Hz, 1H), 7.50 (td, J_1 = 7.5 Hz, J_2 = 1.8 Hz, 1H), 7.46-7.40 (m, 3H), 7.29-7.23 (m, 2H), 7.22 (br s, 1H), 7.16 (d, J = 8.1 Hz, 1H), 7.12 (br s, 1H), 7.02 (dd, J_1 = 7.2 Hz, J_2 = 5.4 Hz, 1H), 4.66 (q, J = 9.6 Hz, 1H), 3.99-3.87 (m, 1H), 2.29 (dd, J_1 = 12.9 Hz, J_2 = 9.9 Hz, 1H), 2.03-1.94 (m, 2H), 1.75 (dd, J_1 = 12.9 Hz, J_2 = 9.0 Hz, 1H), 1.21 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 162.9, 149.1, 143.5, 138.6, 135.9, 129.5, 128.9, 128.5, 126.6, 125.7, 122.2, 121.0, 53.3, 48.7, 48.1, 46.3, 38.9, 30.3, 30.0.

IR (film): ν (cm^{-1}) 3060, 2950, 2864, 1679, 1591, 1497, 1442, 1404, 1305, 1148, 1072, 1034, 991, 900, 806, 757, 692, 661, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{24}N_3O$ $[M+H]^+$: 346.1914, found: 346.1911.



((1*R*,2*R*)-4,4-Dimethyl-2-(4-(pyridin-2-yl)phenyl)cyclopentyl)(1-phenyl-1*H*-imidazol-2-yl) methanone (3o)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 2-(4-vinylphenyl)pyridine **2o** (45.4 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 20 hours, afforded 41.1 mg (98% yield) of **3o** as a colorless oil.

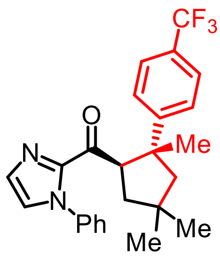
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 96% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 13.2 min, t_r (minor) = 15.6 min). $[\alpha]_D^{22}$ = –200.8° (*c* 1.0, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$) δ 8.67-8.62 (m, 1H), 7.89-7.83 (m, 2H), 7.74-7.64 (m, 2H), 7.45-7.35 (m, 5H), 7.22-7.13 (m, 4H), 7.10-7.08 (m, 1H), 4.54 (q, J = 9.8 Hz, 1H), 3.77 (td, J_1 = 11.4 Hz, J_2 = 7.5 Hz, 1H), 2.26 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 2.00 (dd, J_1 = 12.6 Hz, J_2 = 7.5 Hz, 1H), 1.83 (t, J = 12.3 Hz, 1H), 1.72 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 1.23 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.8, 157.4, 149.5, 144.6, 143.3, 138.4, 137.2, 136.6, 129.6, 128.9, 128.6, 127.9, 127.0, 126.8, 125.7, 121.7, 120.2, 54.5, 50.2, 47.1, 46.8, 38.5, 30.7, 30.2.

IR (film): ν (cm^{-1}) 3056, 2950, 2863, 1678, 1586, 1497, 1461, 1440, 1403, 1302, 1150, 1069, 1034, 982, 896, 819, 765, 731, 692, 663, 561, 507.

HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{28}N_3O$ $[M+H]^+$: 422.2227, found: 422.2226.



(1-Phenyl-1*H*-imidazol-2-yl)((1*R*,2*R*)-2,4,4-trimethyl-2-(4-(trifluoromethyl)phenyl)cyclopentyl)methanone (3p)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-(prop-1-en-2-yl)-4-(trifluoromethyl)benzene **2p** (46.6 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 26 hours, afforded 40.5 mg (95% yield) of **3p** as a colorless oil.

The d.r. value was determined through ^1H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = > 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 4.4 min, t_r (minor) = 5.4 min). $[\alpha]_D^{22}$ = –108.8° (*c* 1.0, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$) δ 7.61-7.55 (m, 2H), 7.54-7.48 (m, 2H), 7.47-7.42 (m, 3H), 7.23-7.17

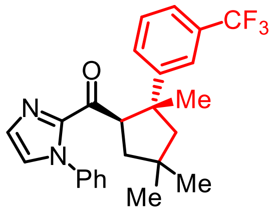
(m, 2H), 7.09-7.06 (m, 2H), 4.90 (dd, J_1 = 12.0 Hz, J_2 = 6.9 Hz, 1H), 2.22-2.11 (m, 2H), 1.93-1.82 (m, 2H), 1.35 (s, 3H), 1.20 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 153.6, 143.8, 138.5, 129.3, 129.0, 128.7, 127.8 (q, J = 29.8 Hz), 127.0, 126.6, 125.9, 124.9 (q, J = 3.9 Hz), 124.4 (q, J = 269.9 Hz), 58.1, 54.7, 51.9, 44.4, 36.7, 31.7, 31.4, 25.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.34 (s, 3F).

IR (film): ν (cm^{-1}) 2954, 2870, 1678, 1617, 1497, 1447, 1404, 1323, 1163, 1116, 1072, 1014, 968, 910, 877, 826, 762, 691, 661, 605, 541, 524.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{26}F_3N_2O$ $[M+H]^+$: 427.1992, found: 427.1986.



(1-Phenyl-1*H*-imidazol-2-yl)((1*R*,2*R*)-2,4,4-trimethyl-2-(3-(trifluoromethyl)phenyl)cyclopentyl)methanone (3q)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), 1-(prop-1-en-2-yl)-3-(trifluoromethyl)benzene **2q** (40.5 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 28 hours, afforded 26.7 mg (63% yield) of **3q** as a colorless oil.

The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 4.0 min, t_r (minor) = 4.5 min). $[\alpha]_D^{22}$ = –159.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71-7.64 (m, 2H), 7.49-7.42 (m, 3H), 7.41-7.36 (m, 2H), 7.23-7.16 (m, 2H), 7.08-7.04 (m, 2H), 4.88 (dd, J_1 = 12.3 Hz, J_2 = 6.9 Hz, 1H), 2.24-2.13 (m, 2H), 1.91-1.81 (m, 2H), 1.34 (s, 3H), 1.20 (s, 3H), 1.15 (s, 3H).

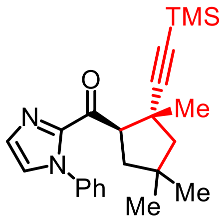
^{13}C NMR (75 MHz, $CDCl_3$) δ 192.4, 150.3, 143.9, 138.5, 130.1 (q, J = 34.5 Hz), 129.9 (q, J = 1.0 Hz), 129.3, 129.0, 128.7, 128.4, 127.0, 125.9, 124.4 (q, J = 270.1 Hz), 123.0 (q, J = 3.8 Hz), 122.5

(q, J = 3.9 Hz), 57.9, 54.9, 51.9, 44.2, 36.6, 31.8, 31.5, 25.3.

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.37 (s, 3F).

IR (film): ν (cm^{-1}) 3067, 2954, 2870, 1678, 1596, 1496, 1443, 1404, 1326, 1161, 1120, 1074, 969, 902, 823, 799, 763, 695, 661, 541.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{26}F_3N_2O$ [M+H]$^+$: 427.1992, found: 427.1990.



(1-Phenyl-1*H*-imidazol-2-yl)((1*R*,2*R*)-2,4,4-trimethyl-2-((trimethylsilyl)ethynyl)cyclopentyl) methanone (3r)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), trimethyl(3-methylbut-3-en-1-yn-1-yl)silane **2r** (34.6 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 28 hours, afforded 37.4 mg (98% yield) of **3r** as a colorless oil.

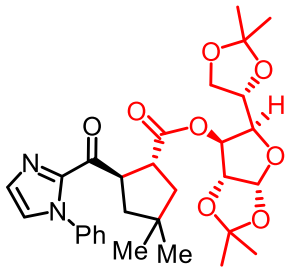
The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = > 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 4.7 min, t_r (minor) = 5.1 min). $[\alpha]_D^{22}$ = –135.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.42 (m, 3H), 7.30-7.24 (m, 3H), 7.19-7.16 (m, 1H), 4.73 (dd, J_1 = 11.1 Hz, J_2 = 7.2 Hz, 1H), 2.04-1.90 (m, 2H), 1.75-1.64 (m, 2H), 1.19 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H), 0.07 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.1, 144.5, 138.6, 129.5, 129.0, 128.6, 126.9, 125.9, 114.4, 84.2, 56.9, 55.3, 42.30, 42.27, 37.4, 31.2, 31.1, 24.8, 0.12.

IR (film): ν (cm^{-1}) 2955, 2868, 2160, 1679, 1497, 1445, 1406, 1309, 1248, 1049, 967, 907, 838, 759, 693, 663, 533.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{31}N_2OSi$ [M+H]$^+$: 379.2200, found: 379.2198.



(3a*R*,5*R*,6*S*,6a*R*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (1*R*,2*R*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carboxylate ((1*R*,2*R*)-3s)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), the corresponding **glucofuranose** derived alkene **2s** (39.3 mg, 1.25 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 55.0 mg (99% yield) of (1*R*,2*R*)-**3s** as a colorless oil.

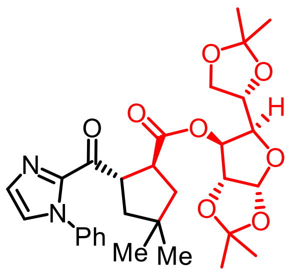
Only a single isomer was formed as determined through ^{1}H NMR of crude materials (> 20:1 d.r.). $[\alpha]_D^{22}$ = –67.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.34 (m, 3H), 7.25-7.17 (m, 3H), 7.13-7.10 (m, 1H), 5.71 (d, J = 3.6 Hz, 1H), 5.16 (d, J = 3.0 Hz, 1H), 4.51 (q, J = 9.3 Hz, 1H), 4.36 (d, J = 3.6 Hz, 1H), 4.08 (dd, J_1 = 7.8 Hz, J_2 = 3.0 Hz, 1H), 4.02-3.94 (m, 1H), 3.88-3.82 (m, 2H), 3.46 (q, J = 9.3 Hz, 1H), 2.09 (dd, J_1 = 12.6 Hz, J_2 = 9.6 Hz, 1H), 1.79 (d, J = 9.0 Hz, 2H), 1.53 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 1.42 (s, 3H), 1.30 (s, 3H), 1.21 (s, 6H), 1.04 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 191.4, 173.4, 142.7, 138.4, 129.8, 129.0, 128.8, 127.2, 125.9, 112.2, 109.3, 105.1, 83.2, 80.1, 76.0, 72.3, 67.3, 50.3, 46.0, 45.0, 43.6, 39.7, 28.9, 26.8, 26.2, 25.1.

IR (film): ν (cm^{-1}) 2984, 2954, 2871, 1740, 1684, 1497, 1449, 1407, 1376, 1306, 1252, 1213, 1154, 1071, 1020, 912, 886, 848, 803, 763, 732, 694, 659, 538, 511.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{38}N_2O_8Na$ $[M+Na]^+$: 577.2520, found: 577.2516.



(3a*R*,5*R*,6*S*,6a*R*)-5-((*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yl (1*S*,2*S*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carboxylate ((1*S*,2*S*)-3s)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), the corresponding **glucofuranose** derived alkene **2s** (39.3 mg, 1.25 equiv), ***Λ*-RhS (3.5 mg, 4 mol%)** and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 54.6 mg (98% yield) of ***(1S,2S)*-3s** as a colorless oil.

Only a single isomer was formed as determined through ^{1}H NMR of crude materials (> 20:1 d.r.). $[\alpha]_D^{22}$ = +28.8° (*c* 1.0, CH_2Cl_2).

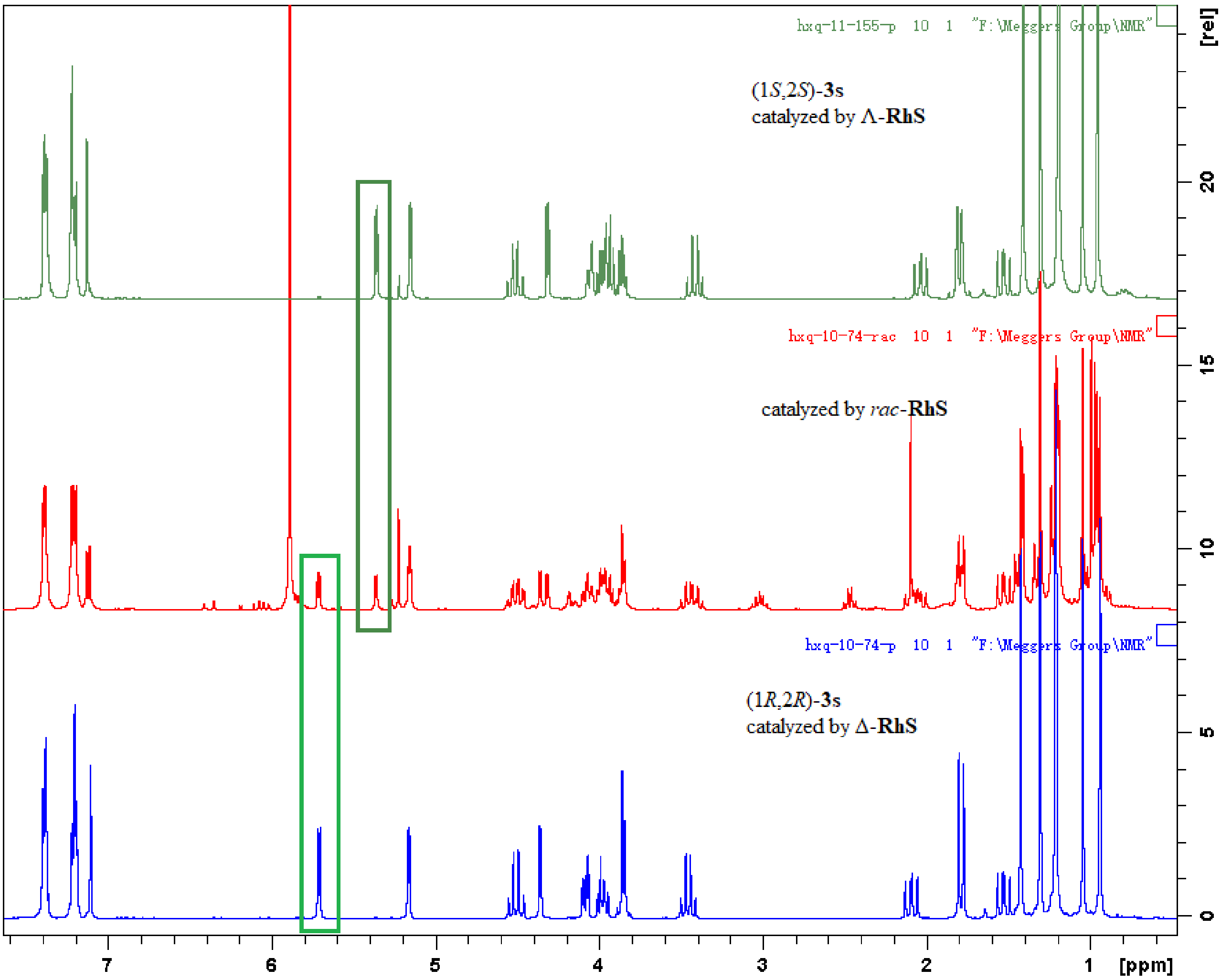
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.39 (m, 3H), 7.28-7.22 (m, 3H), 7.18-7.15 (m, 1H), 5.40 (d, J = 3.9 Hz, 1H), 5.19 (d, J = 2.7 Hz, 1H), 4.53 (q, J = 9.4 Hz, 1H), 4.36 (d, J = 3.6 Hz, 1H), 4.10 (dd, J_1 = 7.8 Hz, J_2 = 3.0 Hz, 1H), 4.06-3.86 (m, 3H), 3.45 (q, J = 9.2 Hz, 1H), 2.08 (dd, J_1 = 12.6 Hz, J_2 = 9.0 Hz, 1H), 1.88-1.80 (m, 2H), 1.57 (dd, J_1 = 12.6 Hz, J_2 = 9.9 Hz, 1H), 1.45 (s, 3H), 1.34 (s, 3H), 1.24 (s, 3H), 1.23 (s, 3H), 1.09 (s, 3H), 1.00 (s, 3H).

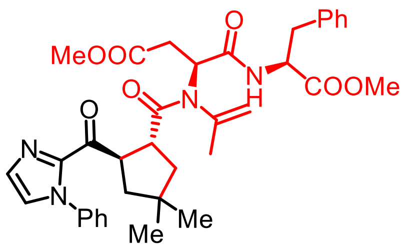
^{13}C NMR (75 MHz, $CDCl_3$) δ 191.7, 173.2, 142.8, 138.4, 129.7, 128.9, 128.8, 127.5, 125.9, 112.1, 109.2, 105.0, 83.2, 80.0, 75.8, 72.3, 67.3, 50.0, 46.0, 45.5, 43.3, 39.6, 29.2, 26.8, 26.7, 26.2, 25.2.

IR (film): ν (cm^{-1}) 2950, 2870, 1743, 1683, 1598, 1497, 1450, 1406, 1376, 1306, 1251, 1214, 1156, 1073, 1020, 911, 848, 802, 765, 731, 694, 646, 511, 421.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{38}N_2O_8Na$ $[M+Na]^+$: 577.2520, found: 577.2536.

The spectra of ((1*R*,2*R*)-**3s** and ((1*S*,2*S*)-**3s** are compared with the crude ^{1}H NMR of the corresponding reaction mixture catalyzed by *rac*-**RhS** which shown a 1:1 mixture of ((1*R*,2*R*)-**3s** and ((1*S*,2*S*)-**3s**. See below:





Methyl (*S*)-3-((1*R*,2*R*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)-*N*-(prop-1-en-2-yl) cyclopentane-1-carboxamido)-4-(((*S*)-1-methoxy-1-oxo-3-phenylpropan-2-yl)amino)-4-oxobutanoate (3t)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), the corresponding **aspartame** derived alkene **2t** (50.3 mg, 1.25 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 56.7 mg (88% yield) of **3t** as a yellow solid.

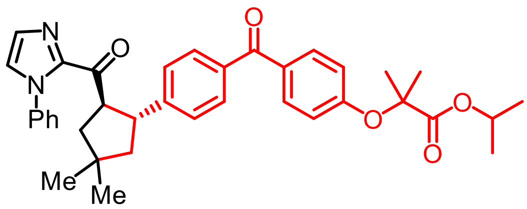
Only a single isomer was formed as determined through ^{1}H NMR of crude materials. $[\alpha]_D^{22}$ = –135.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $(CD_3)_2SO$) δ 8.12 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 1.0 Hz, 1H), 7.47-7.43 (m, 3H), 7.31-7.27 (m, 3H), 7.27-7.22 (m, 2H), 7.21-7.17 (m, 3H), 5.14 (dd, J_1 = 8.3 Hz, J_2 = 6.1 Hz, 1H), 4.92 (s, 1H), 4.52 (q, J = 9.2 Hz, 1H), 4.44-4.36 (m, 2H), 3.58 (s, 3H), 3.52 (s, 3H), 3.41 (q, J = 9.1 Hz, 1H), 2.98 (dd, J_1 = 13.8 Hz, J_2 = 5.1 Hz, 1H), 2.89 (dd, J_1 = 13.8 Hz, J_2 = 9.5 Hz, 1H), 2.82 (dd, J_1 = 16.5 Hz, J_2 = 8.7 Hz, 1H), 2.46 (dd, J_1 = 16.3 Hz, J_2 = 5.8 Hz, 1H), 2.04 (dd, J_1 = 12.5 Hz, J_2 = 9.4 Hz, 1H), 1.60-1.50 (m, 3H), 1.57 (s, 3H), 1.12 (s, 3H), 0.93 (s, 3H).

^{13}C NMR (125 MHz, $(CD_3)_2SO$) δ 191.5, 173.2, 171.7, 170.6, 169.2, 142.1, 141.7, 138.1, 137.2, 129.6, 129.0, 128.9, 128.4, 128.3, 128.1, 126.5, 125.6, 117.6, 54.9, 54.0, 51.9, 51.4, 50.9, 46.0, 45.3, 43.1, 39.3, 36.3, 33.8, 29.3, 29.0, 22.2.

IR (film): ν (cm^{-1}) 3423, 3332, 3112, 2952, 2865, 1738, 1678, 1499, 1442, 1399, 1306, 1209, 1169, 1036, 912, 845, 760, 696, 535, 508.

HRMS (ESI, *m*/*z*) calcd for $C_{36}H_{42}N_4O_7Na$ $[M+Na]^+$: 665.2946, found: 665.2947.



Isopropyl 2-(4-(4-((1*R*,2*R*)-4,4-dimethyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentyl) benzoyl)phenoxy)-2-methylpropanoate (3u)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (24.0 mg, 0.10 mmol), the corresponding **fenofibrate** derived alkene **2u** (44.1 mg, 1.25 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 22 hours, afforded 58.8 mg (99% yield) of **3u** as a colorless oil.

The d.r. value was determined through ^{1}H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C, t_r (major) = 10.3 min, t_r (minor) = 13.2

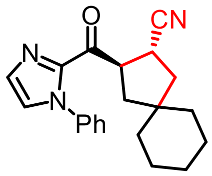
min). $[\alpha]_D^{22}$ = –129.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.74-7.68 (m, 2H), 7.65-7.59 (m, 2H), 7.46-7.49 (m, 3H), 7.39-7.32 (m, 2H), 7.23-7.20 (m, 1H), 7.20-7.14 (m, 2H), 7.13-7.10 (m, 1H), 6.87-6.80 (m, 2H), 5.08 (sept, *J* = 6.3 Hz, 1H), 4.52 (q, *J* = 10.5 Hz, 1H), 3.86-3.73 (m, 1H), 2.27 (dd, J_1 = 13.2 Hz, J_2 = 9.6 Hz, 1H), 2.01 (dd, J_1 = 12.6 Hz, J_2 = 7.8 Hz, 1H), 1.81 (t, *J* = 12.3 Hz, 1H), 1.72 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 1.65 (s, 6H), 1.22 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) *δ* 195.2, 192.4, 173.1, 159.3, 148.3, 143.1, 138.3, 136.0, 131.9, 130.9, 129.9, 129.7, 128.9, 128.7, 127.3, 127.1, 125.7, 117.1, 79.3, 69.2, 54.5, 50.0, 46.9, 46.7, 38.6, 30.6, 30.1, 25.3, 21.5.

IR (film): *ν* (cm^{-1}) 2949, 2866, 1730, 1680, 1651, 1599, 1499, 1449, 1406, 1282, 1247, 1175, 1146, 1101, 1033, 974, 922, 848, 817, 763, 730, 691, 636, 522.

HRMS (ESI, *m*/*z*) calcd for $C_{37}H_{41}N_2O_5$ $[M+H]^+$: 593.3010, found: 593.3008.



(2*R*,3*R*)-3-(1-Phenyl-1*H*-imidazole-2-carbonyl)spiro[4.5]decane-2-carbonitrile (3v)

According to the typical procedure, the reaction of (1-phenyl-1*H*-imidazol-2-yl)(spiro[2.5]octan-1-yl)methanone **1c** (28.0 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 40 hours, afforded 19.1 mg (a colorless oil) of the major diastereoisomer and 2.5 mg of the minor diastereoisomer of **3v** (65% total yield).

The d.r. value was determined through ^{1}H NMR of crude materials as 7:1.

The major diastereoisomer: enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 70:10, flow rate 1 mL/min, 25 °C, t_r (major) = 16.2 min, t_r (minor) = 27.0 min). $[\alpha]_D^{22}$ = –62.6° (*c* 1.0, CH_2Cl_2).

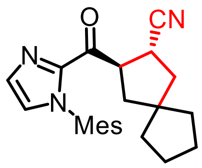
^{1}H NMR (300 MHz, $CDCl_3$) *δ* 7.52-7.44 (m, 3H), 7.34-7.32 (m, 1H), 7.32-7.25 (m, 2H), 7.24-7.21 (m, 1H), 4.52 (q, *J* = 9.3 Hz, 1H), 3.35 (q, *J* = 9.0 Hz, 1H), 2.34 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 2.03 (dd, J_1 = 12.9 Hz, J_2 = 8.7 Hz, 1H), 1.88 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 1.58-1.46 (m, 5H), 1.45-1.25 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.4, 142.1, 138.1, 130.3, 129.03, 128.96, 127.7, 125.9, 122.1, 51.5, 43.64, 43.58, 42.8, 37.9, 27.8, 25.8, 23.35, 23.32. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3113, 3062, 2924, 2852, 2239, 1682, 1596, 1496, 1447, 1403, 1339, 1307, 1149, 1066, 1033, 962, 912, 841, 762, 731, 692, 661, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{24}N_3O$ $[M+H]^+$: 334.1914, found: 334.1906.

The minor diastereoisomer: ^1H NMR (300 MHz, $CDCl_3$) δ 7.50-7.43 (m, 3H), 7.39-7.32 (m, 2H), 7.30-7.27 (m, 1H), 7.24-7.20 (m, 1H), 4.49-4.36 (m, 1H), 3.62-3.51 (m, 1H), 2.09-1.78 (m, 4H), 1.55-1.30 (m, 10H).



(2*R*,3*R*)-3-(1-Mesityl-1*H*-imidazole-2-carbonyl)spiro[4.4]nonane-2-carbonitrile (3w)

According to the typical procedure, the reaction of (1-phenyl-1*H*-imidazol-2-yl)(spiro[2.4]heptan-1-yl)methanone **1d** (30.8 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 32.9 mg of **3w** (91% yield) as a white solid.

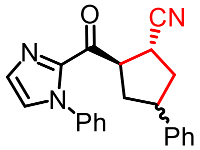
The d.r. value was determined through ^1H NMR of crude materials as > 20:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 17.1 min, t_r (minor) = 14.0 min). $[\alpha]_D^{22}$ = –35.4° (*c* 1.0, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.38 (m, 1H), 7.05-7.01 (m, 1H), 6.99 (br s, 1H), 6.95 (br s, 1H), 4.53 (q, J = 8.9 Hz, 1H), 3.42 (q, J = 8.3 Hz, 1H), 2.36 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 2.34 (s, 3H), 2.03 (dd, J_1 = 12.6 Hz, J_2 = 8.7 Hz, 1H), 1.95 (dd, J_1 = 12.6 Hz, J_2 = 7.8 Hz, 1H), 1.91 (s, 3H), 1.83 (s, 3H), 1.70-1.52 (m, 7H), 1.46-1.35 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.2, 142.1, 138.7, 134.5, 134.2, 133.7, 130.9, 129.1, 128.9, 126.3, 122.4, 51.9, 51.4, 44.4, 43.3, 38.7, 38.6, 27.8, 24.4, 24.3, 21.1, 17.3, 17.1.

IR (film): ν (cm^{-1}) 3108, 2949, 2921, 2859, 2238, 1681, 1485, 1448, 1402, 1314, 1282, 1218, 1155, 1030, 979, 912, 866, 818, 781, 737, 665, 562.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{28}N_3O$ $[M+H]^+$: 362.2227, found: 362.2225.



(1*R*,2*R*)-4-Phenyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carbonitrile (3x)

According to the typical procedure, the reaction of (1-phenyl-1*H*-imidazol-2-yl)(2-phenylcyclopropyl)methanone **1e** (28.8 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 16 hours, afforded 33.0 mg of **3x** (97% yield, a colorless oil) as a mixture of two diastereosiomers.

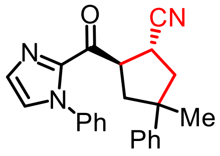
The d.r. value was determined through ^{1}H NMR of crude materials as 2.1:1; enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee [major] = 97% (t_r (major) = 10.3 min, t_r (minor) = 8.0 min), ee [minor] = 99% (t_r (major) = 22.0 min, t_r (minor) = 9.9 min) (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C). $[\alpha]_D^{22}$ = –19.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.48 (m, 3H), 7.38-7.36 (m, 1H), 7.36-7.54 (m, 4H), 7.25-7.23 (m, 1H), 7.23-7.18 (m, 3H), 4.74-4.68 (m, 0.33H, minor), 4.67-4.61 (m, 0.67H, major), 3.64-3.58 (m, 0.67H, major), 3.58-3.46 (m, 1H), 3.15-3.05 (m, 0.33H, minor), 2.93-2.85 (m, 0.67H, major), 2.64-2.56 (m, 0.33H, minor), 2.53-2.43 (m, 1H), 2.37-2.30 (m, 0.33H, minor), 2.20-2.08 (m, 1H), 1.84-1.75 (m, 0.67H, major). (Mixture of two diastereosiomers)

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 188.6, 141.8, 141.75, 141.68, 141.6, 138.00, 137.96, 130.4, 129.06, 129.05, 128.61, 128.58, 127.89, 127.87, 126.89, 126.88, 126.85, 126.80, 126.78, 125.88, 125.86, 122.5, 121.7, 52.3, 50.9, 45.3, 44.2, 40.2, 39.4, 38.6, 38.2, 28.6. (Mixture of two diastereosiomers)

IR (film): ν (cm^{-1}) 3394, 3067, 2238, 1670, 1627, 1577, 1494, 1449, 1417, 1333, 1312, 1283, 1220, 1073, 977, 911, 846, 766, 708, 681, 589, 541, 480.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{20}N_3O$ $[M+H]^+$: 342.1601, found: 342.1600.

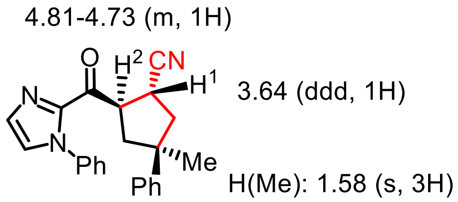


(1*R*,2*R*)-4-Methyl-4-phenyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carbonitrile (3y)

According to the typical procedure, the reaction of (2-methyl-2-phenylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1f** (30.2 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 29.8 mg of **3y** (84% total yield) as two separable diastereoisomers.

The d.r. value was determined through ^{1}H NMR of crude materials as 2.2:1.

<u>The major diastereoisomer:</u>



(1*R*,2*R*,4*R*)

Eenantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [major] = 95% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 40 °C, t_r (major) = 16.2 min, t_r (minor) = 25.4 min). $[\alpha]_D^{22}$ = –86.8° (*c* 1.0, CH_2Cl_2).

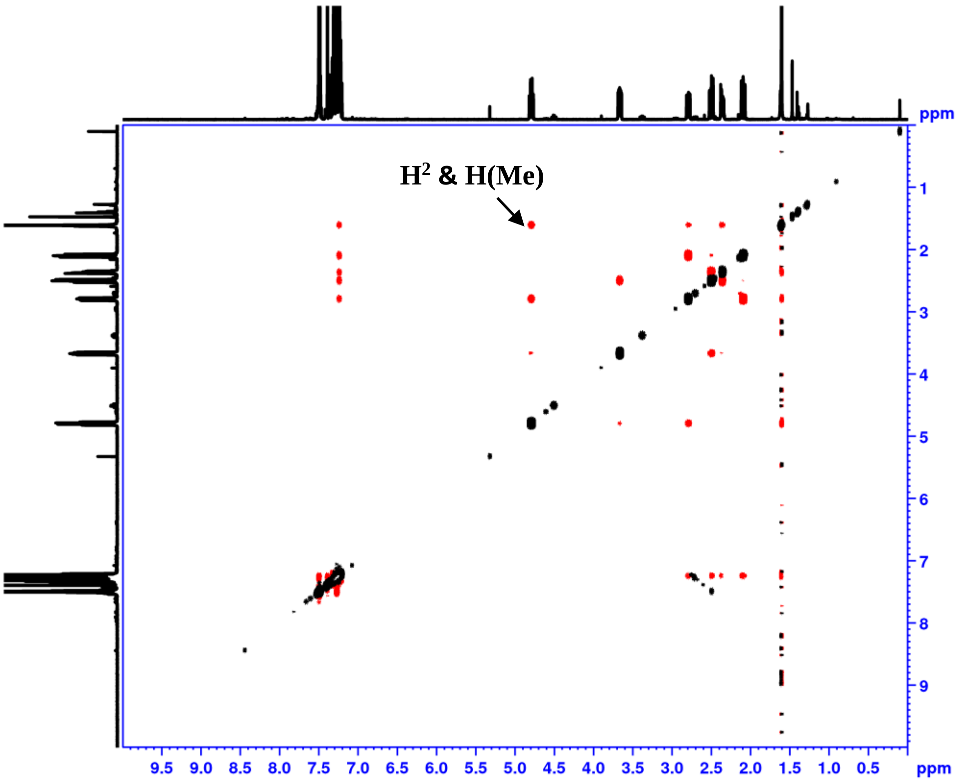
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 3H), 7.37-7.36 (m, 1H), 7.31-7.26 (m, 2H), 7.26-7.23 (m, 3H), 7.23-7.17 (m, 3H), 4.81-4.73 (m, 1H), 3.64 (ddd, J_1 = 12.2 Hz, J_2 = 7.5 Hz, J_3 = 4.8 Hz, 1H), 2.77 (ddd, J_1 = 12.6 Hz, J_2 = 8.2 Hz, J_3 = 1.6 Hz, 1H), 2.48 (dd, J_1 = 13.3 Hz, J_2 = 10.5 Hz, 1H), 2.34 (ddd, J_1 = 13.3 Hz, J_2 = 4.8 Hz, J_3 = 1.6 Hz, 1H), 2.07 (dd, J_1 = 12.5 Hz, J_2 = 11.0 Hz, 1H), 1.58 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.6, 148.2, 141.8, 138.0, 130.4, 129.0, 128.5, 127.8, 126.2, 125.8, 125.4, 123.0, 51.7, 48.4, 45.3, 43.5, 29.7, 26.9. (Missing one ^{13}C signal)

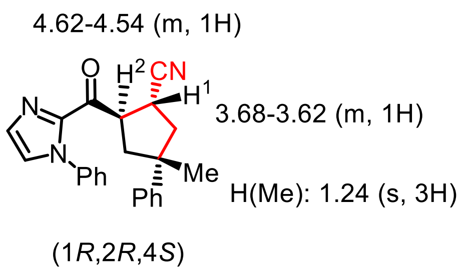
IR (film): ν (cm^{-1}) 3112, 3058, 2964, 2871, 2239, 1682, 1597, 1496, 1447, 1402, 1338, 1305, 1220, 1150, 1103, 1068, 1029, 974, 909, 834, 801, 762, 730, 695, 659, 539.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{22}N_3O$ $[M+H]^+$: 356.1757, found: 356.1755.

NOE spectrum:



The minor diastereoisomer:



Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [minor] = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 40 °C, t_r (major) = 16.9 min, t_r (minor) = 22.9 min). $[\alpha]_D^{22}$ = +13.6° (*c* 0.5, CH_2Cl_2).

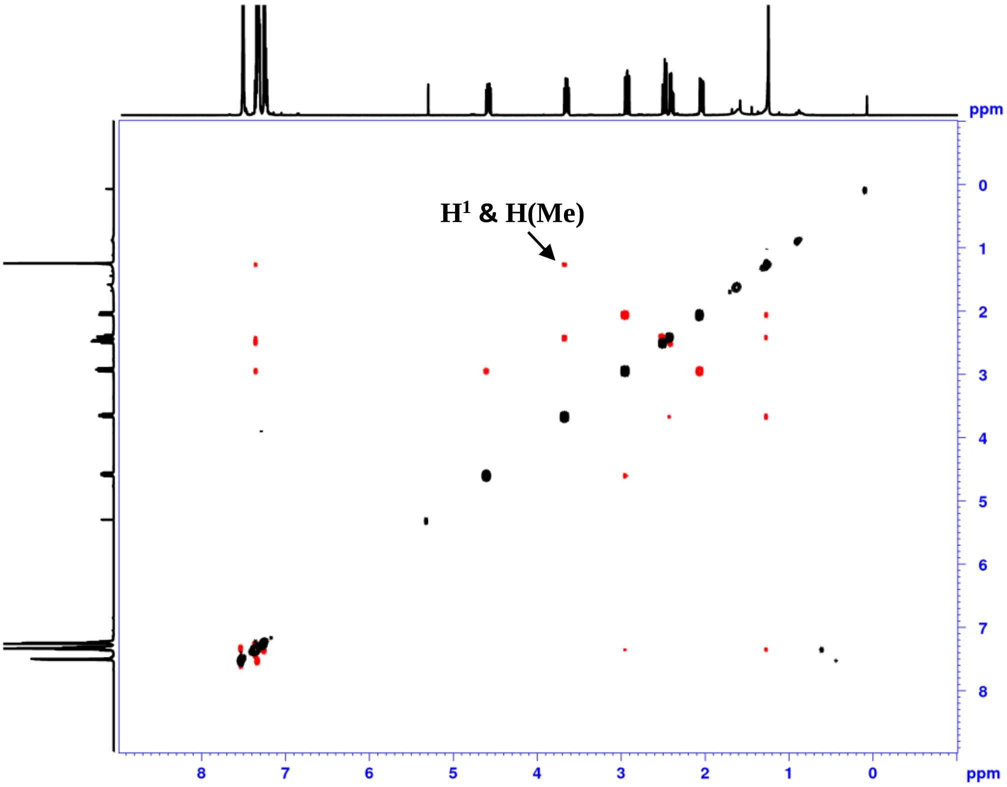
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53-7.48 (m, 3H), 7.37-7.30 (m, 7H), 7.25-7.21 (m, 2H), 4.62-4.54 (m, 1H), 3.68-3.62 (m, 1H), 2.93 (dd, J_1 = 13.5 Hz, J_2 = 11.3 Hz, 1H), 2.48 (dd, J_1 = 12.5 Hz, J_2 = 10.5 Hz, 1H), 2.40 (ddd, J_1 = 12.5 Hz, J_2 = 7.7 Hz, J_3 = 0.8 Hz, 1H), 2.07 (ddd, J_1 = 13.6 Hz, J_2 = 7.2 Hz, J_3 = 1.1 Hz, 1H), 1.24 (s, 3H).

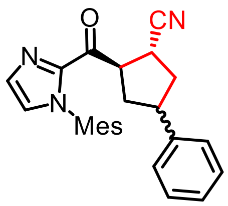
^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 148.2, 141.9, 138.0, 130.4, 129.09, 129.06, 128.5, 127.8, 126.3, 125.9, 125.6, 121.6, 51.4, 47.2, 44.5, 44.1, 30.0, 27.6.

IR (film): ν (cm^{-1}) 3105, 3057, 2929, 2877, 2241, 1683, 1597, 1496, 1450, 1406, 1304, 1241, 1145, 1103, 1069, 1031, 983, 910, 839, 801, 767, 694, 544.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}N_3ONa$ $[M+Na]^+$: 378.1577, found: 378.1573.

NOE spectrum:





(1*R*,2*R*)-2-(1-Mesityl-1*H*-imidazole-2-carbonyl)-4-phenylcyclopentane-1-carbonitrile (3z)

According to the typical procedure, the reaction of (1-mesityl-1*H*-imidazol-2-yl)(2-phenylcyclopropyl)methanone **1g** (33.0 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 38.0 mg of **3z** (99% yield, a yellow oil) as a mixture of two diastereosiomers.

The d.r. value was determined through ^{1}H NMR of crude materials as 1.9:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee [major] = 99% (t_r (major) = 24.6 min, t_r (minor) = 19.5 min), ee [minor] = 99% (t_r (major) = 30.6 min, t_r (minor) = 21.6 min) (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 40 °C). $[\alpha]_D^{22}$ = +6.4° (*c* 1.0,

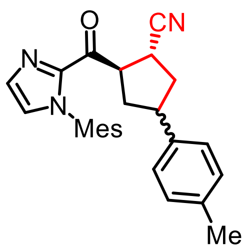
CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.41 (m, 1H), 7.35-7.26 (m, 2H), 7.25-7.15 (m, 3H), 7.08-7.05 (m, 1H), 7.02 (br s, 1H), 6.97 (br s, 1H), 4.78-4.58 (m, 1H), 3.64-3.43 (m, 1H), 3.64-3.43 (m, 0.67H, major), 3.14-3.00 (m, 0.33H, minor), 2.95-2.83 (m, 0.67H, major), 2.65-2.54 (m, 0.33H, minor), 2.52-2.40 (m, 1H), 2.36 (s, 3H), 2.32-2.22 (m, 0.33H, minor), 2.22-2.05 (m, 1H), 1.94 (s, 3H), 1.86 (s, 1H, minor), 1.83 (s, 2H, major), 1.77-1.62 (m, 0.67H, major). (Mixture of two diastereosiomers)

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 188.6, 141.9, 141.8, 141.7, 138.8, 134.44, 134.40, 134.2, 133.70, 133.68, 131.1, 129.2, 129.0, 128.64, 128.61, 126.9, 126.85, 126.80, 126.6, 126.5, 122.4, 121.6, 52.3, 50.9, 45.4, 44.2, 40.4, 39.5, 38.8, 38.2, 28.5, 28.4, 21.1, 17.4, 17.1. (Mixture of two diastereosiomers)

IR (film): *ν* (cm^{-1}) 3028, 2923, 2865, 2241, 1680, 1603, 1487, 1450, 1404, 1339, 1315, 1281, 1149, 1083, 1027, 976, 909, 851, 773, 731, 698, 580, 519.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{25}N_3ONa$ $[M+Na]^+$: 406.1890, found: 406.1887.



(1*R*,2*R*)-2-(1-Mesityl-1*H*-imidazole-2-carbonyl)-4-(*p*-tolyl)cyclopentane-1-carbonitrile (3aa)

According to the typical procedure, the reaction of (1-mesityl-1*H*-imidazol-2-yl)(2-(*p*-tolyl)cyclopropyl)methanone **1h** (34.5 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 37.1 mg of **3aa** (93% yield, a yellow oil) as a mixture of two diastereosiomers.

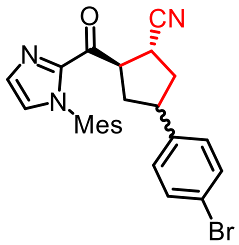
The d.r. value was determined through ^{1}H NMR of crude materials as 1.5:1; enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [major] = 98% (t_r (major) = 19.9 min, t_r (minor) = 17.8 min), ee [minor] = 99% (t_r (major) = 23.0 min, t_r (minor) = 18.7 min) (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C). $[\alpha]_D^{22}$ = +22.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42-7.40 (m, 1H), 7.14-7.04 (m, 5H), 7.01 (br s, 1H), 6.97 (br s, 1H), 4.76-4.58 (m, 1H), 3.63-3.55 (m, 0.6H, major), 3.55-3.42 (m, 1H), 3.10-2.95 (m, 0.4H, minor), 2.92-2.80 (m, 0.6H, major), 2.62-2.51 (m, 0.4H, minor), 2.49-2.38 (m, 1H), 2.36 (s, 3H), 2.32 (s, 1.2H, minor), 2.31 (s, 1.8H, major), 2.28-2.19 (m, 0.4H, minor), 2.18-2.04 (m, 1H), 1.94 (s, 3H), 1.85 (s, 1.2H, minor), 1.82 (s, 1.8H, major), 1.75-1.60 (m, 0.6H, major). (Mixture of two diastereosiomers)

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 188.7, 142.0, 141.9, 138.80, 138.77, 138.6, 136.44, 136.40, 134.45, 134.41, 134.2, 133.7, 131.0, 129.30, 129.27, 129.2, 129.1, 128.974, 128.965, 126.8, 126.7, 126.52, 126.49, 122.5, 121.7, 52.3, 50.9, 45.0, 43.8, 40.5, 39.6, 38.8, 38.3, 28.41, 28.39, 21.1, 20.9, 17.4, 17.1. (Mixture of two diastereosiomers)

IR (film): ν (cm^{-1}) 3112, 3016, 2922, 2866, 2240, 1680, 1511, 1484, 1450, 1404, 1341, 1315, 1281, 1148, 1083, 1025, 976, 909, 851, 811, 780, 729, 672, 649, 578, 523, 443.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{27}N_3ONa$ $[M+Na]^+$: 420.2046, found: 420.2044.

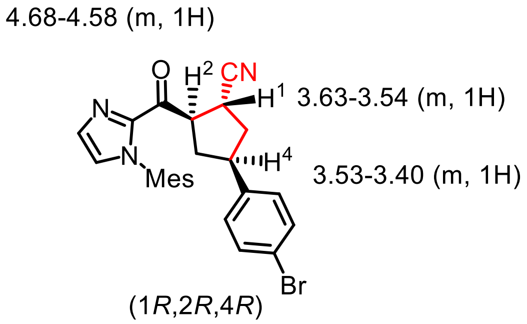


(1*R*,2*R*)-4-(4-Bromophenyl)-2-(1-mesityl-1*H*-imidazole-2-carbonyl)cyclopentane-1-carbonitrile (3ab)

According to the typical procedure, the reaction of (2-(4-bromophenyl)cyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1i** (40.9 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (1.7 mg, 2 mol%) and DIPEA (6.5 mg, 0.5 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 38.0 mg of **3ab** (90% total yield) as two separable diastereoisomers.

The d.r. value was determined through ^{1}H NMR of crude materials as 1.3:1.

<u>The major diastereoisomer:</u>



Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [major] = 98% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 25 °C, t_r (major) = 16.7 min, t_r (minor) = 12.8 min). $[\alpha]_D^{22}$ = +25.4° (*c* 1.0, CH_2Cl_2).

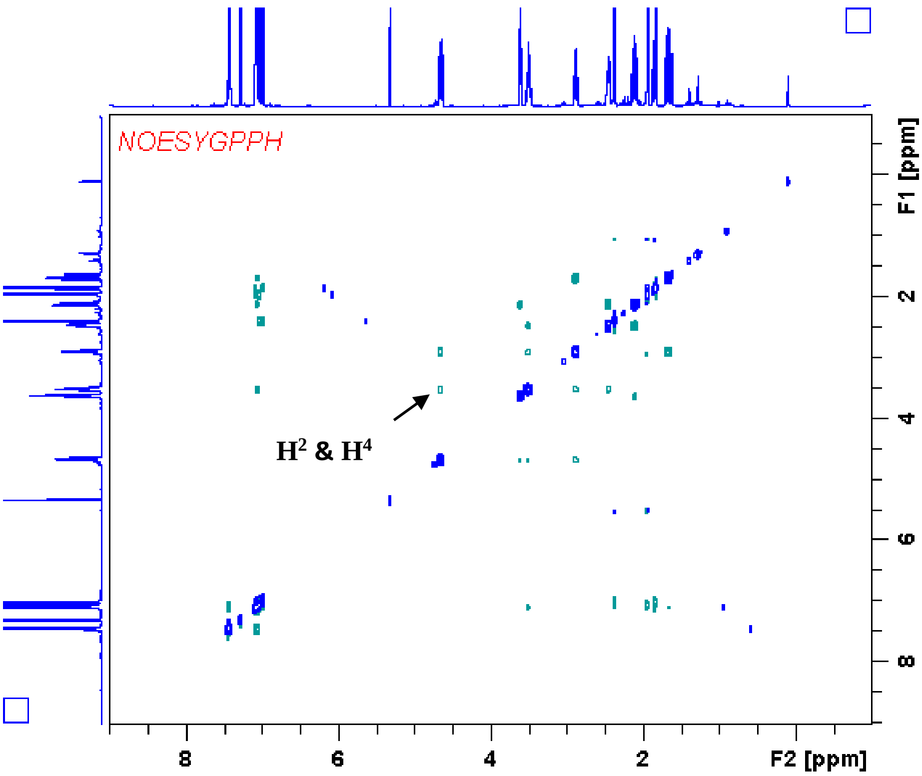
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.37 (m, 3H), 7.08-7.02 (m, 3H), 7.03 (br s, 1H), 6.97 (br s, 1H), 4.68-4.58 (m, 1H), 3.63-3.54 (m, 1H), 3.53-3.40 (m, 1H), 2.92-2.80 (m, 1H), 2.48-2.38 (m, 1H), 2.36 (s, 3H), 2.15-2.02 (m, 1H), 1.92 (s, 3H). 1.82 (s, 3H), 1.72-1.58 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.5, 141.9, 140.8, 138.9, 134.4, 134.2, 133.7, 131.7, 131.1, 129.2, 129.0, 128.6, 126.7, 122.2, 120.6, 52.1, 44.8, 40.2, 38.1, 28.6, 21.1, 17.4, 17.2.

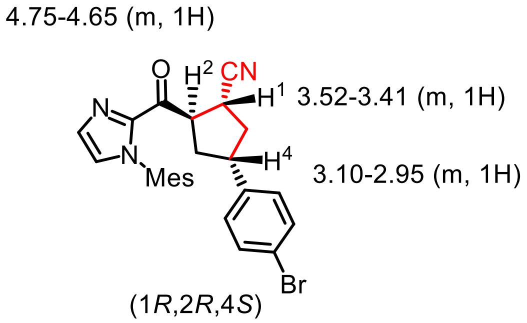
IR (film): *v* (cm^{-1}) 3114, 2923, 2863, 2241, 1680, 1487, 1451, 1403, 1340, 1314, 1282, 1149, 1078, 1034, 1011, 976, 909, 851, 819, 781, 730, 672, 650, 581, 519.

HRMS (ESI, *m/z*) calcd for $C_{25}H_{25}BrN_3O$ [M+H]$^+$: 462.1176, found: 462.1175.

NOE spectrum:



The minor diastereoisomer:



(1*R*,2*R*,4*S*)

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [minor] = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 25 °C, t_r (major) = 18.6 min, t_r (minor) = 13.8 min). $[\alpha]_D^{22}$ = +74.2° (*c* 1.0, CH_2Cl_2).

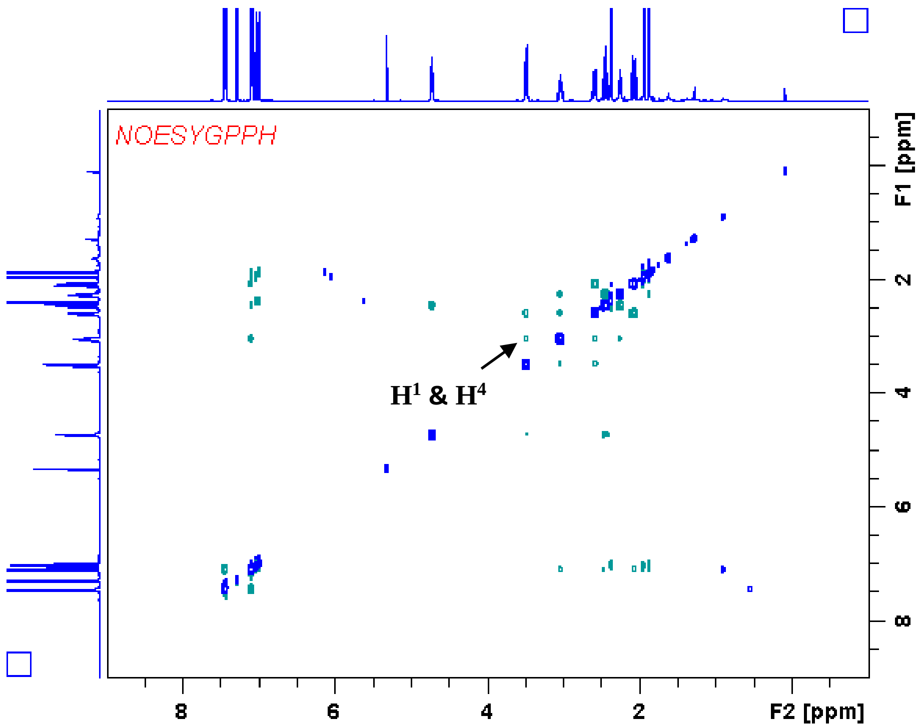
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.40 (m, 3H), 7.10-7.04 (m, 3H), 7.01 (br s, 1H), 6.98 (br s, 1H), 4.75-4.65 (m, 1H), 3.52-3.41 (m, 1H), 3.10-2.95 (m, 1H), 2.62-2.51 (m, 1H), 2.50-2.37 (m, 1H), 2.36 (s, 3H), 2.29-2.18 (m, 1H), 2.12-1.98 (m, 1H), 1.92 (s, 3H). 1.85 (s, 3H).

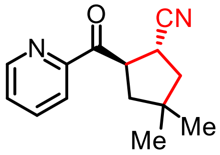
^{13}C NMR (75 MHz, $CDCl_3$) δ 189.1, 141.8, 140.7, 138.9, 134.4, 134.2, 133.7, 131.8, 131.1, 129.2, 129.0, 128.6, 126.6, 121.4, 120.6, 50.8, 43.6, 39.3, 38.6, 28.5, 21.1, 17.4, 17.2.

IR (film): *v* (cm^{-1}) 2916, 2858, 2240, 1676, 1486, 1448, 1403, 1320, 1279, 1145, 1075, 1011, 977, 912, 848, 818, 787, 737, 660, 585, 551, 513.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{25}BrN_3O$ $[M+H]^+$: 462.1176, found: 462.1176.

NOE spectrum:





((1*R*,2*R*)-4,4-Dimethyl-2-picolinoylcyclopentane-1-carbonitrile (3ac)

According to the typical procedure, the mixture of (2,2-dimethylcyclopropyl)(pyridin-2-yl) methanone **1j** (17.5 mg, 0.10 mmol), acrylonitrile **2a** (13.3 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and DIPEA (25.8 mg, 2.0 equiv) in acetone/MeCN (1:1 v/v, 1.0 mL, 0.1 M) were stirred under nitrogen atmosphere with blue LEDs for 24 hours; then, another portion of Δ-**RhS** (3.5 mg, 4 mol%) was added and the mixture was continued to stir for another 20 hours. The reaction afforded 12.4 mg (54% yield) of the major diastereoisomer of **3ac** as a colorless oil.

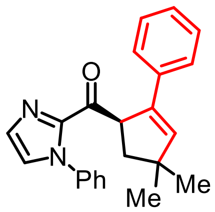
The d.r. value was determined through ^{1}H NMR of crude materials as 6:1, therefore the total yield is estimated as 63%. Enantiomeric excess of the major diastereoisomer was established by HPLC analysis using a Chiralpak IG column, ee = 94% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 19.4 min, t_r (minor) = 20.4 min). $[\alpha]_D^{22}$ = –106.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75-8.71 (m, 1H), 8.12-8.08 (m, 1H), 7.88 (td, J_1 = 7.7 Hz, J_2 = 1.8 Hz, 1H), 7.52 (ddd, J_1 = 7.6 Hz, J_2 = 4.7 Hz, J_3 = 1.2 Hz, 1H), 4.76 (q, J = 9.0 Hz, 1H), 3.66 (q, J = 8.5 Hz, 1H), 2.28 (dd, J_1 = 13.0 Hz, J_2 = 9.8 Hz, 1H), 2.06 (dd, J_1 = 12.9 Hz, J_2 = 8.9 Hz, 1H), 1.96 (ddd, J_1 = 12.9 Hz, J_2 = 8.2 Hz, J_3 = 0.5 Hz, 1H), 1.51 (dd, J_1 = 13.0 Hz, J_2 = 9.0 Hz, 1H), 1.25 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 199.9, 152.1, 149.2, 136.9, 127.5, 122.8, 122.7, 50.6, 45.5, 45.2, 40.4, 28.6, 28.4, 28.0.

IR (film): ν (cm^{-1}) 2957, 2869, 2239, 1694, 1579, 1461, 1441, 1365, 1298, 1220, 1018, 850, 797, 744, 685, 615.

HRMS (ESI, *m/z*) calcd for $C_{14}H_{16}N_2ONa$ $[M+Na]^+$: 251.1155, found: 251.1155.



(*R*)-(4,4-Dimethyl-2-phenylcyclopent-2-en-1-yl)(1-phenyl-1*H*-imidazol-2-yl)methanone (5a)

According to the typical procedure, as shown in Table 2, entry 9, the reaction of (2,2-dimethylcyclopropyl)(1-phenyl-1*H*-imidazol-2-yl)methanone **1a** (12.0 mg, 0.05 mmol), ethynylbenzene **4a** (25.6 mg, 5.0 equiv), Δ-**RhS** (1.7 mg, 4 mol%) and Et_3N (10.1 mg, 2.0 equiv) in THF (0.5 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 15.8 mg (92% yield, 95% NMR yield) of **5a** as a colorless oil.

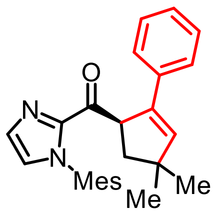
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 89% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 8.9 min, t_r (minor) = 8.3 min). $[\alpha]_D^{22}$ = +90.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36-7.29 (m, 6H), 7.25-7.12 (m, 4H), 7.10-7.04 (m, 2H), 6.09 (d, *J* = 1.5 Hz, 1H), 5.62 (ddd, J_1 = 9.6 Hz, J_2 = 6.3 Hz, J_3 = 1.8 Hz, 1H), 2.39 (dd, J_1 = 12.9 Hz, J_2 = 9.3 Hz, 1H), 1.96 (dd, J_1 = 12.9 Hz, J_2 = 6.0 Hz, 1H), 1.19 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 143.5, 140.5, 138.8, 138.2, 135.9, 129.7, 128.9, 128.5, 128.2, 127.1, 126.9, 126.1, 125.5, 53.4, 45.4, 44.6, 29.1, 28.9.

IR (film): ν (cm^{-1}) 3057, 3030, 2953, 2862, 1683, 1596, 1496, 1445, 1398, 1309, 1045, 906, 828, 757, 691, 554, 516.

HRMS (ESI, *m/z*) calcd for $C_{23}H_{23}N_2O$ $[M+H]^+$: 343.1805, found: 343.1813.



(*R*)-(4,4-Dimethyl-2-phenylcyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl)methanone (5b)

According to the typical procedure, as shown in Table 2, entry 10, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (14.1 mg, 0.05 mmol), ethynylbenzene **4a** (25.6 mg, 5.0 equiv), Δ-**RhS** (1.7 mg, 4 mol%) and Et_3N (10.1 mg, 2.0 equiv) in THF (0.5 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 22 hours, afforded 18.3 mg (95% yield, 99% NMR yield) of **5b** as a colorless oil.

The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) =

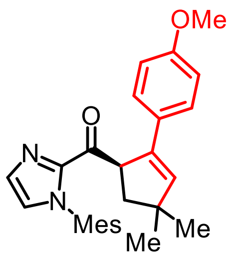
6.1 min, t_r (minor) = 5.7 min). $[\alpha]_D^{22}$ = +62.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.32-7.27 (m, 2H), 7.19-7.07 (m, 3H), 7.01-6.98 (m, 1H), 6.88 (br s, 1H), 6.80 (br s, 1H), 6.05 (d, *J* = 1.5 Hz, 1H), 5.65 (ddd, J_1 = 9.3 Hz, J_2 = 6.0 Hz, J_3 = 1.5 Hz, 1H), 2.37 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 2.25 (s, 3H), 1.90 (dd, J_1 = 12.9 Hz, J_2 = 6.3 Hz, 1H), 1.85 (s, 3H), 1.60 (s, 3H), 1.18 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 143.3, 140.3, 138.9, 138.2, 135.8, 134.8, 134.1, 133.7, 130.3, 128.9, 128.7, 128.1, 126.8, 126.0, 52.9, 45.4, 44.8, 29.1, 28.8, 21.0, 17.2, 16.9. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3027, 2954, 2926, 2862, 1681, 1488, 1447, 1399, 1316, 1283, 1147, 1039, 906, 849, 761, 692, 577.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{29}N_2O$ $[M+H]^+$: 385.2274, found: 385.2266.



(*R*)-(1-Mesityl-1*H*-imidazol-2-yl)(2-(4-methoxyphenyl)-4,4-dimethylcyclopent-2-en-1-yl) methanone (5c)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-ethynyl-4-methoxybenzene **4b** (66.1 mg, 5.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in THF (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 39.2 mg (95% yield) of **5c** as an oil.

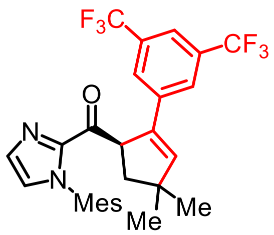
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 8.5 min, t_r (minor) = 5.8 min). $[\alpha]_D^{22}$ = +36.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (m, 1H), 7.26-7.20 (m, 2H), 7.01-6.99 (m, 1H), 6.88 (br s, 1H), 6.81 (br s, 1H), 6.74-6.76 (m, 2H), 5.93 (d, *J* = 1.8 Hz, 1H), 5.60 (ddd, J_1 = 9.6 Hz, J_2 = 6.3 Hz, J_3 = 1.8 Hz, 1H), 3.74 (s, 3H), 2.35 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 2.26 (s, 3H), 1.88 (dd, J_1 = 12.9 Hz, J_2 = 6.3 Hz, 1H), 1.85 (s, 3H), 1.62 (s, 3H), 1.16 (s, 3H), 1.12 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 158.6, 143.3, 138.5, 138.2, 134.8, 134.1, 133.7, 130.3, 128.9, 128.75, 128.67, 127.2, 126.0, 113.6, 55.2, 53.0, 45.4, 44.8, 29.3, 29.0, 21.0, 17.2, 16.9. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 2951, 2925, 2861, 1682, 1607, 1510, 1487, 1451, 1400, 1288, 1248, 1177, 1035, 906, 829, 777, 730, 582, 555, 522.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_2O_2$ $[M+H]^+$: 415.2380, found: 415.2380.



(*R*)-(2-(3,5-Bis(trifluoromethyl)phenyl)-4,4-dimethylcyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl)methanone (5d)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-ethynyl-3,5-bis(trifluoromethyl)benzene **4c** (59.5 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in acetone (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 35.0 mg (67% yield) of **5d** as an oil.

The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 3.6 min, t_r (minor) = 4.0 min). $[\alpha]_D^{22}$ = +69.8° (*c* 1.0, CH_2Cl_2).

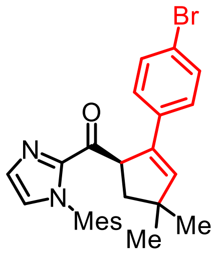
^1H NMR (300 MHz, $CDCl_3$) δ 7.75 (s, 2H), 7.60 (s, 1H), 7.46 (d, J = 1.5 Hz, 1H), 7.42 (d, J = 1.5 Hz, 1H), 6.89 (br s, 1H), 6.82 (br s, 1H), 6.23 (d, J = 1.5 Hz, 1H), 5.72 (ddd, J_1 = 9.6 Hz, J_2 = 6.3 Hz, J_3 = 1.8 Hz, 1H), 2.41 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 2.26 (s, 3H), 1.98 (dd, J_1 = 12.9 Hz, J_2 = 6.6 Hz, 1H), 1.85 (s, 3H), 1.51 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.1, 144.2, 142.8, 138.5, 138.0, 136.8, 134.6, 133.9, 133.6, 131.4 (q, J = 32.8 Hz), 130.7, 129.0, 128.8, 126.5, 126.1-126.0 (m), 123.3 (q, J = 271.2 Hz), 120.4-120.2 (m, 1H), 52.7, 45.7, 44.5, 28.7, 28.6, 21.0, 17.2, 16.5.

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.00 (s, 6F).

IR (film): ν (cm^{-1}) 2958, 2930, 2866, 1681, 1451, 1385, 1275, 1172, 1130, 1035, 899, 857, 777, 735, 680, 579.

HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{27}F_6N_2O$ $[M+H]^+$: 521.2022, found: 521.2013.



(*R*)-(2-(4-Bromophenyl)-4,4-dimethylcyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl) methanone (5e)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-bromo-4-ethynylbenzene **4d** (90.5 mg, 5.0 equiv), Δ-**RhS** (6.9 mg, 8 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 44.8 mg (97% yield) of **5e** as a grey solid.

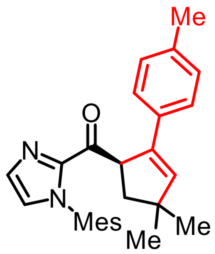
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 7.1 min, t_r (minor) = 6.1 min). $[\alpha]_D^{22}$ = +12.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.41 (m, 1H), 7.32-7.25 (m, 2H), 7.20-7.13 (m, 2H), 7.03-7.00 (m, 1H), 6.89 (br s, 1H), 6.84 (br s, 1H), 6.05 (d, J = 1.5 Hz, 1H), 5.61 (ddd, J_1 = 9.3 Hz, J_2 = 6.0 Hz, J_3 = 1.5 Hz, 1H), 2.37 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 2.27 (s, 3H), 1.90 (dd, J_1 = 12.9 Hz, J_2 = 6.0 Hz, 1H), 1.85 (s, 3H), 1.63 (s, 3H), 1.18 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.7, 143.2, 141.2, 138.3, 137.9, 134.9, 134.7, 134.0, 133.7, 131.2, 130.4, 128.9, 128.8, 127.7, 126.2, 120.6, 52.9, 45.5, 44.7, 29.0, 28.7, 21.0, 17.2, 16.9.

IR (film): ν (cm^{-1}) 3030, 2953, 2926, 2862, 1681, 1485, 1448, 1399, 1319, 1281, 1147, 1071, 1042, 1010, 904, 822, 774, 734, 700, 673, 578, 552, 516, 435.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{28}BrN_2O$ $[M+H]^+$: 463.1380, found: 463.1377.



(*R*)-(4,4-Dimethyl-2-(*p*-tolyl)cyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl)methanone (5f)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-ethynyl-4-methylbenzene **4e** (29.1 mg, 2.5 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in THF (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 28 hours, afforded 34.6 mg (87% yield) of **5f** as an oil.

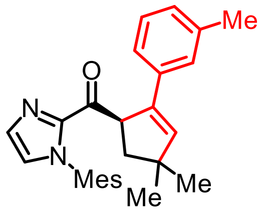
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 6.8 min, t_r (minor) = 5.1 min). $[\alpha]_D^{22}$ = +36.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.19 (d, J = 8.1 Hz, 2H), 7.00 (s, 1H), 6.97 (d, J = 8.1 Hz, 2H), 6.88 (br s, 1H), 6.81 (br s, 1H), 6.00 (d, J = 1.2 Hz, 1H), 5.62 (ddd, J_1 = 9.6 Hz, J_2 = 6.3 Hz, J_3 = 1.5 Hz, 1H), 2.36 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 2.25 (s, 6H), 1.87 (dd, J_1 = 12.9 Hz, J_2 = 6.0 Hz, 1H), 1.85 (s, 3H), 1.62 (s, 3H), 1.17 (s, 3H), 1.13 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 143.3, 139.4, 138.6, 138.2, 136.5, 134.8, 134.1, 133.7, 133.0, 130.2, 128.9, 128.8, 128.7, 126.0, 125.9, 53.0, 45.3, 44.8, 29.2, 28.9, 21.03, 20.98, 17.2, 16.9.

IR (film): ν (cm^{-1}) 3025, 2952, 2925, 2863, 1681, 1508, 1486, 1448, 1399, 1316, 1283, 1041, 906, 848, 816, 775, 729, 578, 516.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_2O$ $[M+H]^+$: 399.2431, found: 399.2431.



(*R*)-(4,4-Dimethyl-2-(*m*-tolyl)cyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl)methanone (5g)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-ethynyl-3-methylbenzene **4f** (58.1 mg, 5.0

equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 22 hours, afforded 39.0 mg (98% yield) of **5g** as an oil.

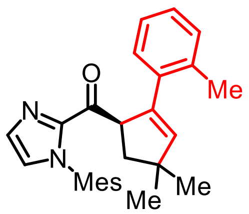
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 95% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 99:1, flow rate 0.6 mL/min, 40 °C, t_r (major) = 8.8 min, t_r (minor) = 9.6 min). $[\alpha]_D^{22}$ = +60.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 0.9 Hz, 1H), 7.14 (br s, 1H), 7.13-7.07 (m, 1H), 7.04 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 0.6 Hz, 1H), 6.95-6.89 (m, 1H), 6.88 (br s, 1H), 6.80 (br s, 1H), 6.04 (d, J = 1.8 Hz, 1H), 5.66 (ddd, J_1 = 9.0 Hz, J_2 = 6.0 Hz, J_3 = 1.5 Hz, 1H), 2.36 (dd, J_1 = 12.6 Hz, J_2 = 9.3 Hz, 1H), 2.26 (s, 3H), 2.21 (s, 3H), 1.90 (dd, J_1 = 12.9 Hz, J_2 = 6.3 Hz, 1H), 1.86 (s, 3H), 1.58 (s, 3H), 1.17 (s, 3H), 1.15 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 143.3, 140.1, 139.0, 138.2, 137.5, 135.7, 134.8, 134.0, 133.7, 130.3, 128.9, 128.7, 128.0, 127.6, 126.8, 126.0, 123.2, 52.9, 45.3, 44.7, 29.1, 28.9, 21.3, 21.0, 17.2, 16.8.

IR (film): ν (cm^{-1}) 3028, 2952, 2925, 2862, 1681, 1604, 1486, 1448, 1399, 1317, 1284, 1147, 1035, 910, 856, 778, 730, 695, 579, 444.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{31}N_2O$ $[M+H]^+$: 399.2431, found: 399.2429.



(*R*)-(4,4-Dimethyl-2-(*o*-tolyl)cyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl)methanone (5h)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-ethynyl-2-methylbenzene **4g** (58.1 mg, 5.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 22 hours, afforded 39.6 mg (99% yield) of **5h** as an oil.

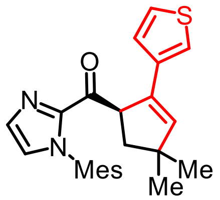
The enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 99% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 99:1, flow rate 0.6 mL/min, 25 °C, t_r (major) = 12.5 min, t_r (minor) = 11.1 min). $[\alpha]_D^{22}$ = +90.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, J = 0.9 Hz, 1H), 7.17-7.12 (m, 1H), 7.07-6.92 (m, 3H), 6.90-6.86 (m, 2H), 6.79 (br s, 1H), 5.66 (ddd, $J_1 = J_2 = 7.8$ Hz, $J_3 = 1.8$ Hz, 1H), 5.63 (d, $J = 1.8$ Hz, 1H), 2.35 (s, 3H), 2.28 (s, 3H), 2.25 (dd, $J_1 = 12.6$ Hz, $J_2 = 8.4$ Hz, 1H), 1.97 (dd, $J_1 = 12.3$ Hz, $J_2 = 8.1$ Hz, 1H), 1.83 (s, 3H), 1.30 (s, 3H), 1.21 (s, 3H), 1.19 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 143.4, 143.1, 139.4, 138.1, 136.5, 135.9, 134.8, 134.1, 133.7, 130.1, 128.8, 128.7, 128.6, 126.5, 125.9, 125.1, 55.0, 45.6, 44.4, 29.0, 28.5, 21.0, 20.8, 17.2, 16.4. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 3020, 2953, 2925, 2862, 1680, 1486, 1450, 1400, 1318, 1282, 1147, 1043, 907, 847, 759, 728, 673, 579, 455.

HRMS (ESI, *m/z*) calcd for $C_{27}H_{31}N_2O$ [M+H]$^+$: 399.2431, found: 399.2431.



(*R*)-(4,4-Dimethyl-2-(thiophen-3-yl)cyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl) methanone (5i)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 3-ethynylthiophene **4h** (54.1 mg, 5.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 33.8 mg (87% yield) of **5i** as an oil.

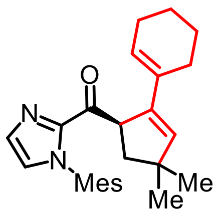
The enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 5.3 min, t_r (minor) = 5.7 min). $[\alpha]_D^{22} = +34.6°$ (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.15-7.10 (m, 2H), 7.03-7.01 (m, 1H), 6.99-6.95 (m, 1H), 6.90 (br s, 1H), 6.84 (br s, 1H), 5.93 (d, $J = 1.5$ Hz, 1H), 5.57 (ddd, $J_1 = 9.9$ Hz, $J_2 = 5.7$ Hz, $J_3 = 1.5$ Hz, 1H), 2.31 (dd, $J_1 = 13.2$ Hz, $J_2 = 9.6$ Hz, 1H), 2.27 (s, 3H), 1.90 (dd, $J_1 = 12.9$ Hz, $J_2 = 5.7$ Hz, 1H), 1.86 (s, 3H), 1.66 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 143.4, 139.6, 138.2, 137.8, 134.8, 134.1, 134.0, 133.7, 130.3, 128.9, 128.8, 126.3, 126.2, 125.1, 120.5, 53.5, 45.5, 44.5, 29.4, 28.9, 21.0, 17.2, 17.0.

IR (film): ν (cm^{-1}) 3028, 2952, 2863, 1680, 1485, 1448, 1398, 1315, 1281, 1147, 1039, 913, 889, 858, 773, 730, 677, 640, 577.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{27}N_2OS$ $[M+H]^+$: 391.1839, found: 391.1838.



(*R*)-(2-(Cyclohex-1-en-1-yl)-4,4-dimethylcyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl) methanone (5j)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), 1-ethynylcyclohex-1-ene **4i** (53.1 mg, 5.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 36.5 mg (94% yield) of **5j** as an oil.

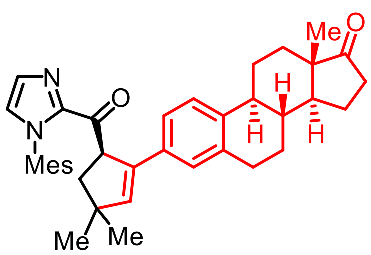
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 4.3 min, t_r (minor) = 4.9 min). $[\alpha]_D^{22}$ = +126.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, J = 0.9 Hz, 1H), 6.99 (d, J = 0.9 Hz, 1H), 6.90 (br s, 2H), 5.60 (s, 1H), 5.47-5.41 (m, 1H), 5.30 (ddd, J_1 = 8.7 Hz, J_2 = 4.5 Hz, J_3 = 0.9 Hz, 1H), 2.30 (s, 3H), 2.23 (dd, J_1 = 12.9 Hz, J_2 = 10.2 Hz, 1H), 2.19-2.11 (m, 2H), 2.08-1.85 (m, 2H), 1.86 (s, 3H), 1.83 (s, 3H), 1.73 (dd, J_1 = 13.2 Hz, J_2 = 4.8 Hz, 1H), 1.66-1.55 (m, 2H), 1.54-1.44 (m, 2H), 1.09 (s, 3H), 1.04 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.5, 143.2, 140.5, 138.2, 137.7, 135.1, 134.0, 133.8, 132.6, 130.2, 128.9, 128.8, 125.8, 125.0, 52.2, 45.2, 44.4, 29.8, 28.8, 26.1, 25.6, 22.6, 22.2, 21.0, 17.2, 17.1.

IR (film): ν (cm^{-1}) 3033, 2926, 2862, 1681, 1486, 1446, 1399, 1316, 1282, 1144, 1039, 899, 855, 805, 772, 729, 576.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{33}N_2O$ $[M+H]^+$: 389.2587, found: 389.2587.



(8*R*,9*S*,13*S*,14*S*)-3-((*R*)-5-(1-Mesityl-1*H*-imidazole-2-carbonyl)-3,3-dimethylcyclopent-1-en-1-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (5k)

According to the typical procedure, the reaction of (2,2-dimethylcyclopropyl)(1-mesityl-1*H*-imidazol-2-yl)methanone **1b** (28.2 mg, 0.10 mmol), the corresponding **estrone** derived alkyne **4j**[13] (34.8 mg, 1.25 equiv), Δ-**RhS** (6.9 mg, 8 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 41.8 mg (75% yield) of **5k** as a white solid.

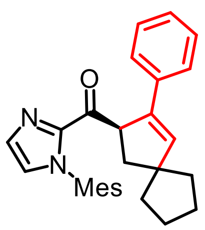
The diasetereoselectivity was established by HPLC analysis using a Chiralpak IG column, d.e. = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 18.7 min, t_r (minor) = 16.3 min). $[\alpha]_D^{22}$ = +28.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (d, J = 0.6 Hz, 1H), 7.09-7.01 (m, 3H), 7.00 (d, J = 0.6 Hz, 1H), 6.88 (br s, 1H), 6.81 (br s, 1H), 6.00 (d, J = 1.2 Hz, 1H), 5.63 (ddd, J_1 = 8.7 Hz, J_2 = 6.3 Hz, J_3 = 1.2 Hz, 1H), 2.90-2.74 (m, 1H), 2.73-2.62 (m, 1H), 2.49 (dd, J_1 = 18.6 Hz, J_2 = 8.7 Hz, 1H), 2.40-2.30 (m, 2H), 2.26 (s, 3H), 2.24-1.86 (m, 5H), 1.85 (s, 3H), 1.70-1.28 (m, 7H), 1.59 (s, 3H), 1.16 (s, 3H), 1.13 (s, 3H), 0.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 193.1, 143.3, 139.7, 138.7, 138.4, 138.2, 135.9, 134.8, 133.9, 133.8, 133.3, 130.2, 128.9, 128.8, 126.6, 126.0, 125.1, 123.6, 52.9, 50.5, 47.9, 45.3, 44.8, 44.3, 38.2, 35.8, 31.6, 29.7, 29.3, 29.0, 28.8, 26.5, 25.7, 21.5, 21.0, 17.2, 16.8, 13.8.

IR (film): ν (cm^{-1}) 2925, 2861, 1736, 1682, 1491, 1450, 1401, 1318, 1285, 1256, 1148, 1086, 1043, 910, 854, 825, 774, 728, 675, 646, 579, 433.

HRMS (ESI, *m*/*z*) calcd for $C_{38}H_{45}N_2O_2$ $[M+H]^+$: 561.3476, found: 561.3475.



(*R*)-(1-Mesityl-1*H*-imidazol-2-yl)(3-phenylspiro[4.4]non-3-en-2-yl)methanone (5l)

According to the typical procedure, the reaction of (1-mesityl-1*H*-imidazol-2-yl)(spiro[2.4]heptan-1-yl)methanone **1d** (30.8 mg, 0.10 mmol), ethynylbenzene **4a** (51.1 mg, 5.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 37.9 mg (92% yield) of **5l** as an oil.

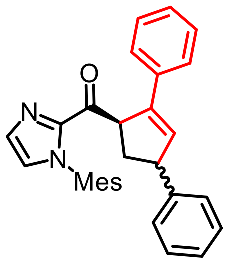
The enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 7.8 min, t_r (minor) = 6.1 min). $[\alpha]_D^{22}$ = +182.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (d, J = 1.2 Hz, 1H), 7.34-7.27 (m, 2H), 7.21-7.06 (m, 3H), 7.00 (d, J = 0.9 Hz, 1H), 6.88 (br s, 1H), 6.80 (br s, 1H), 6.14 (d, J = 1.5 Hz, 1H), 5.61 (ddd, J_1 = 9.6 Hz, J_2 = 5.7 Hz, J_3 = 1.5 Hz, 1H), 2.44 (dd, J_1 = 12.9 Hz, J_2 = 9.6 Hz, 1H), 2.26 (s, 3H), 1.94 (dd, J_1 = 12.9 Hz, J_2 = 5.7 Hz, 1H), 1.86 (s, 3H), 1.73-1.60 (m, 7H), 1.61 (s, 3H), 1.57-1.44 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 192.9, 143.3, 139.2, 138.6, 138.2, 135.8, 134.8, 134.0, 133.7, 130.3, 128.9, 128.7, 128.1, 126.8, 126.00, 125.96, 56.7, 52.7, 43.8, 39.7, 39.5, 24.5, 24.4, 21.0, 17.2, 16.9.

IR (film): ν (cm^{-1}) 3027, 2947, 2861, 1681, 1488, 1446, 1399, 1316, 1283, 1146, 1036, 908, 850, 764, 730, 692, 646, 559.

HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{31}N_2O$ $[M+H]^+$: 411.2431, found: 411.2429.

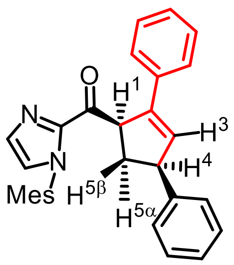


(*R*)-(2,4-Diphenylcyclopent-2-en-1-yl)(1-mesityl-1*H*-imidazol-2-yl)methanone (5m)

According to the typical procedure, the reaction of (1-mesityl-1*H*-imidazol-2-yl)(2-phenylcyclopropyl)methanone **1g** (33.0 mg, 0.10 mmol), ethynylbenzene **4a** (51.1 mg, 5.0 equiv), Δ-**RhS** (6.9 mg, 8 mol%) and Et_3N (20.2 mg, 2.0 equiv) in PhCl (1.0 mL, 0.1 M) under nitrogen atmosphere with blue LEDs for 24 hours, afforded 27.1 mg of **5m** (63% total yield) as two separable diastereoisomers.

The d.r. value was determined through ^{1}H NMR of crude materials as 1.7:1.

<u>The major diastereoisomer:</u>



(1*R*,4*S*)

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [major] = 94% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 40 °C, t_r (major) = 18.5 min, t_r (minor) = 15.0 min). $[\alpha]_D^{22}$ = +109.4° (*c* 1.0, CH_2Cl_2).

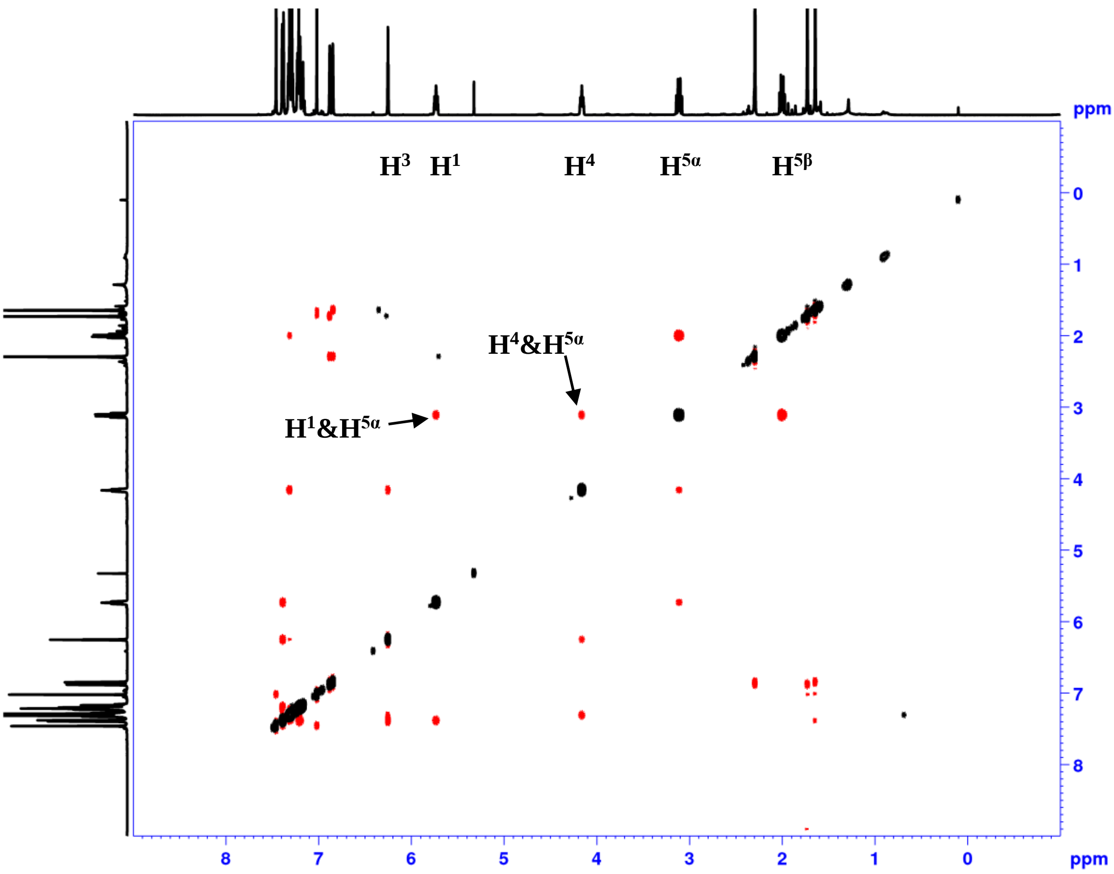
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 1H), 7.38-7.34 (m, 2H), 7.31-7.24 (m, 4H), 7.22-7.17 (m, 3H), 7.16-7.12 (m, 1H), 7.00-6.99 (m, 1H), 6.85 (br s, 1H), 6.82 (br s, 1H), 6.23 (t, J = 2.1 Hz, 1H), 5.71 (tt, J_1 = 8.3 Hz, J_2 = 2.2 Hz, 1H), 4.14 (tt, J_1 = 8.0 Hz, J_2 = 2.3 Hz, 1H), 3.09 (dt, J_1 = 13.1 Hz, J_2 = 6.5 Hz, 1H), 2.27 (s, 3H), 1.98 (dt, J_1 = 13.1 Hz, J_2 = 6.5 Hz, 1H), 1.70 (s, 3H), 1.62 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.6, 145.3, 143.6, 143.2, 138.3, 135.7, 134.7, 134.0, 133.8, 133.2, 130.4, 128.9, 128.8, 128.4, 128.2, 127.9, 127.2, 126.4, 126.3, 126.2, 53.1, 51.1, 40.3, 21.1, 17.2, 17.0.

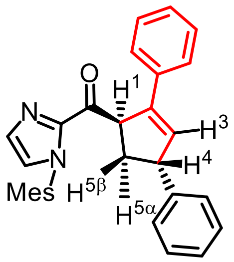
IR (film): ν (cm^{-1}) 3130, 3023, 2924, 2848, 1679, 1602, 1489, 1447, 1398, 1321, 1286, 1147, 1056, 1024, 984, 912, 855, 830, 783, 757, 699, 639, 583, 549, 506, 428.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{29}N_2O$ $[M+H]^+$: 433.2274, found: 433.2274.

NOE spectrum:



The minor diastereoisomer:



(1*R*,4*R*)

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee [minor] = 91% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 6.7 min, t_r (minor) = 11.0 min). $[\alpha]_D^{22}$ = +92.6° (*c* 1.0, CH_2Cl_2).

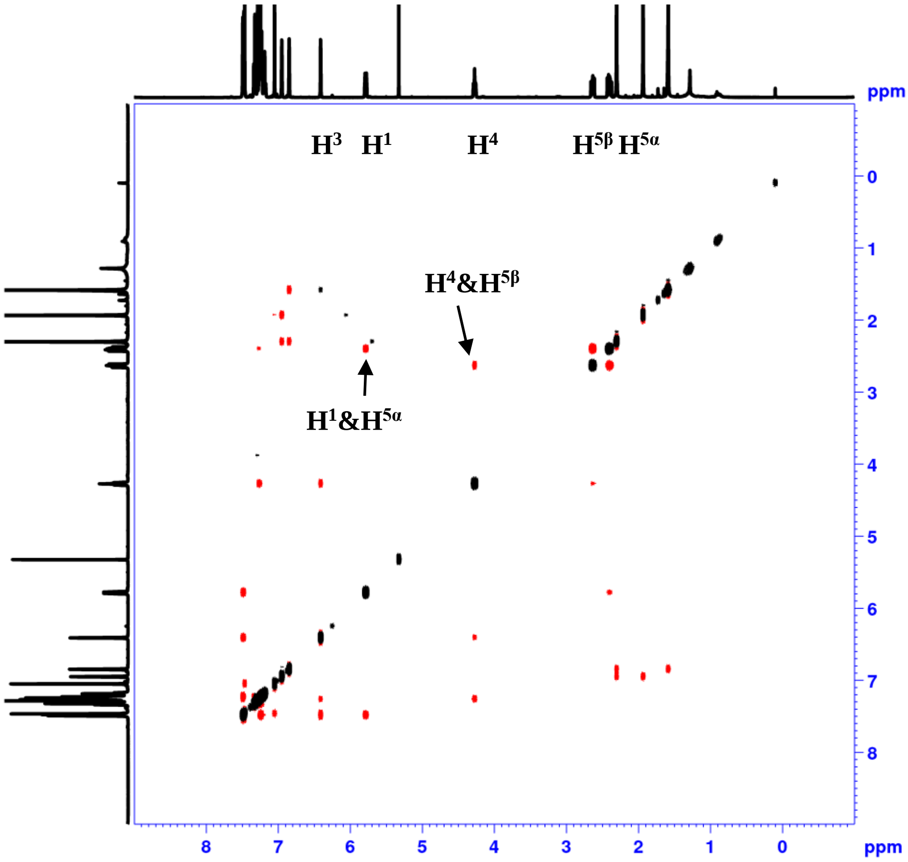
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.46 (m, 3H), 7.35-7.30 (m, 2H), 7.27-7.22 (m, 5H), 7.21-7.16 (m, 1H), 7.06-7.04 (m, 1H), 6.95 (br s, 1H), 6.85 (br s, 1H), 6.41 (dd, J_1 = 2.2 Hz, J_2 = 1.2 Hz, 1H), 5.81-5.76 (m, 1H), 4.27 (tt, J_1 = 8.0 Hz, J_2 = 2.1 Hz, 1H), 2.63 (ttt, J_1 = 13.3 Hz, J_2 = 8.3 Hz, J_2 = 2.9 Hz, 1H), 2.44-2.36 (m, 1H), 2.30 (s, 3H), 1.93 (s, 3H), 1.58 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 192.9, 145.3, 143.0, 142.8, 138.4, 134.9, 134.7, 134.0, 133.8, 133.4, 130.5, 129.0, 128.8, 128.6, 128.3, 127.5, 127.4, 126.4, 126.32, 126.26, 53.0, 51.1, 40.3, 21.1, 17.4, 16.8.

IR (film): ν (cm^{-1}) 3055, 3026, 2924, 2859, 1679, 1601, 1489, 1447, 1398, 1316, 1282, 1149, 1079, 1034, 977, 908, 855, 784, 752, 695, 584, 558, 529.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{29}N_2O$ $[M+H]^+$: 433.2274, found: 433.2274.

NOE spectrum:



7. Stereochemical Assignment via Single Crystal X-Ray Diffraction

Data was collected with an STOE STADIVARI diffractometer equipped with CuK_{α} radiation, a graded multilayer mirror monochromator (λ = 1.54186 Å) and a DECTRIS PILATUS 300K detector using an oil-coated shock-cooled crystal at 230(2) K. Absorption effects were corrected semi-empirical using multiscanned reflexions (X-Area LANA 1.68.2.0 (STOE, 2016)). Cell constants were refined using 20587 of observed reflections of the data collection. The structure was solved by direct methods by using the program XT V2014/1 (Bruker AXS Inc., 2014) and refined by full matrix least squares procedures on F^2 using SHELXL-2017/1 (Sheldrick, 2017). The non-hydrogen atoms have been refined anisotropically, carbon bonded hydrogen atoms were included at calculated positions and refined using the 'riding model' with isotropic temperature factors at 1.2 times (for CH_3 groups 1.5 times) that of the preceding carbon atom. CH_3 groups were allowed to rotate about the bond to their next atom to fit the electron density. Nitrogen or oxygen bonded hydrogen atoms were located and allowed to refine isotropically. Relative and absolute configuration of compound **3k** was determined. The Flack parameter refined to –0.026(6).

Single crystals of **3k** suitable for X-ray diffraction were obtained by slow diffusion from of a solution of **3k** (30 mg) in Et_2O (0.5 mL) layered with *n*-hexane (1.0 mL) at room temperature for several days in a NMR tube. Crystal structure, data and details of the structure determination for **3k** are presented in the Figure S10 and Table S8.

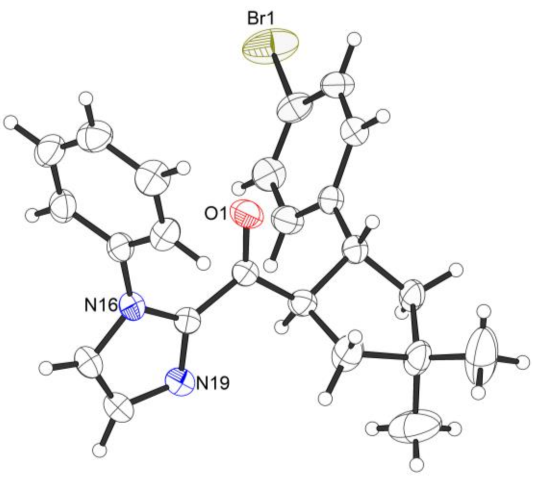


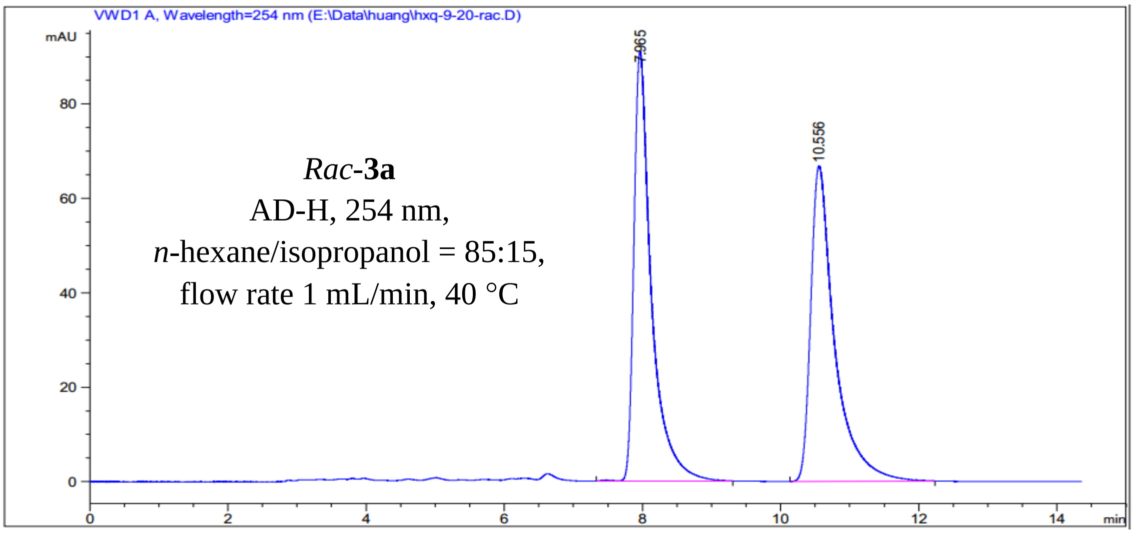
Figure S10. Crystal structure of **3k**.

Table S8: Crystal data and structure refinement for **3k**.

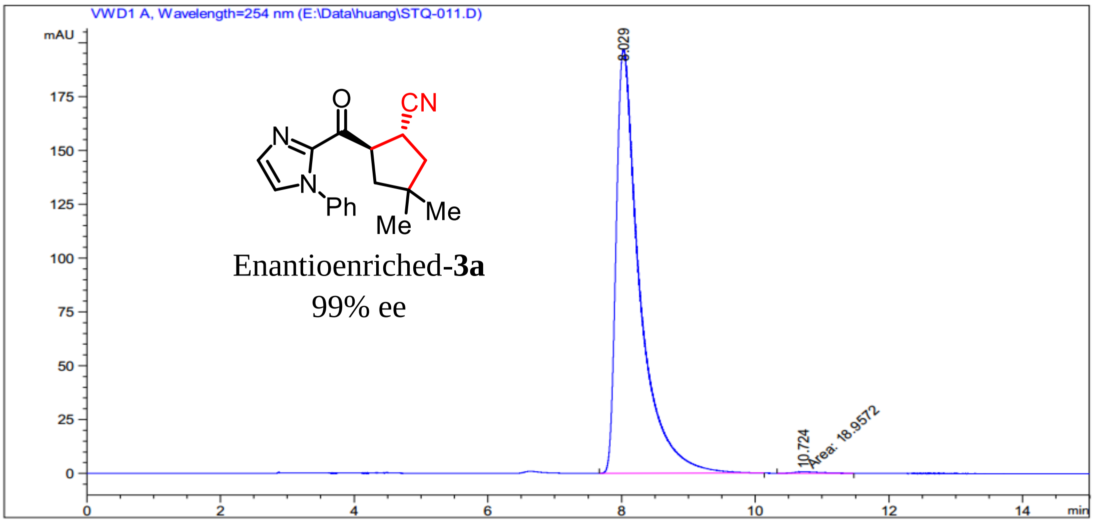
Crystal data		
Identification code	hxqJ27_230k	
Habitus, color	needle, colorless	
Crystal size	0.35 x 0.05 x 0.03 mm^3	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	Z = 4
Unit cell dimensions	a = 6.37310(10) Å	α = 90°.
	b = 9.9779(2) Å	β = 90°.
	c = 32.3962(9) Å	γ = 90°.
Volume	2060.08(8) $Å^3$	
Cell determination	20587 peaks with Theta 2.7 to 72.5°.	
Empirical formula	$C_{23} H_{23} Br N_2 O$	
Moiety formula	$C_{23} H_{23} Br N_2 O$	
Formula weight	423.34	
Density (calculated)	1.365 Mg/m^3	
Absorption coefficient	2.822 mm^{-1}	
F(000)	872	
Data collection:		
Diffractometer type	STOE STADIVARI	
Wavelength	1.54186 Å	
Temperature	230(2) K	
Theta range for data collection	2.728 to 72.236°.	
Index ranges	-7<=h<=6, -10<=k<=12, -38<=l<=39	
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016)[14]	
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[15]	
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[16]	
	X-Area LANA 1.68.2.0 (STOE, 2016)[17]	
Solution and refinement:		
Reflections collected	20724	
Independent reflections	4008 [R(int) = 0.0274]	
Completeness to theta = 67.686°	99.9 %	
Observed reflections	3727[I > 2σ(I)]	
Reflections used for refinement	4008	
Absorption correction	Semi-empirical from equivalents[17]	
Max. and min. transmission	1.0000 and 0.4568	
Flack parameter (absolute struct.)	-0.026(6)	
Largest diff. peak and hole	0.232 and -0.412 $e.Å^{-3}$	
Solution	intrinsic phases[18]	
Refinement	Full-matrix least-squares on F^2 [19]	
Treatment of hydrogen atoms	Calculated positions, constr. ref.	
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[18]	
	SHELXL-2017/1 (Sheldrick, 2017)[19]	
	DIAMOND (Crystal Impact)[20]	
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[21]	
Data / restraints / parameters	4008 / 72 / 294	
Goodness-of-fit on F^2	1.068	
R index (all data)	wR2 = 0.0620	
R index conventional [I>2sigma(I)]	R1 = 0.0245	

8. Enantioselectivities as Determined by Chiral HPLC

Enantiomeric purities of the reaction products were determined with a Daicel Chiralpak AD-H, OD-H, IG, IC column (250 × 4.6 mm) on an Agilent 1200 or 1260 Series HPLC System using *n*-hexane/isopropanol as a mobile phase.

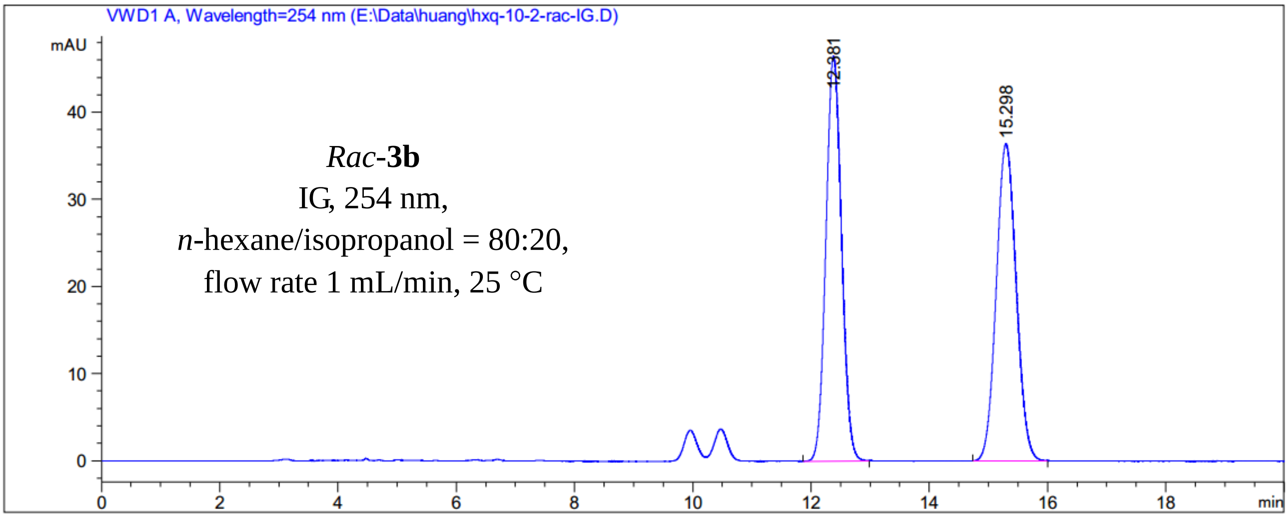


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.965	VB R	0.2529	1602.17981	91.00212	50.0074
2	10.556	BV R	0.3299	1601.70422	66.87949	49.9926

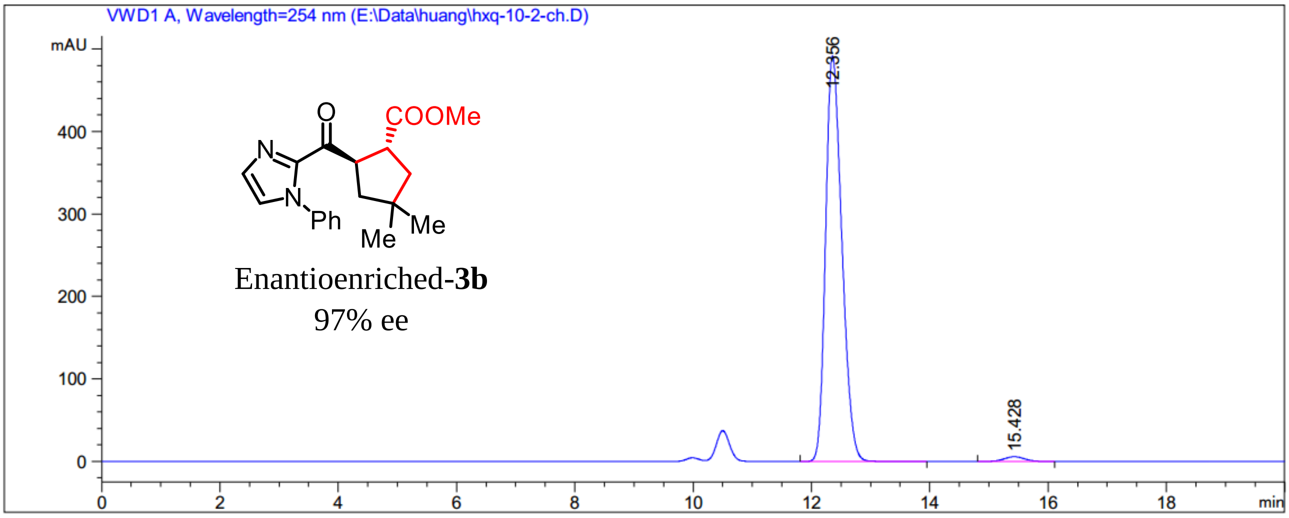


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.029	BV R	0.3477	4803.76270	196.86250	99.6069
2	10.724	MM	0.4386	18.95718	7.20405e-1	0.3931

Figure S11. HPLC traces of *rac*-**3a** (reference) and enantioenriched-**3a**.

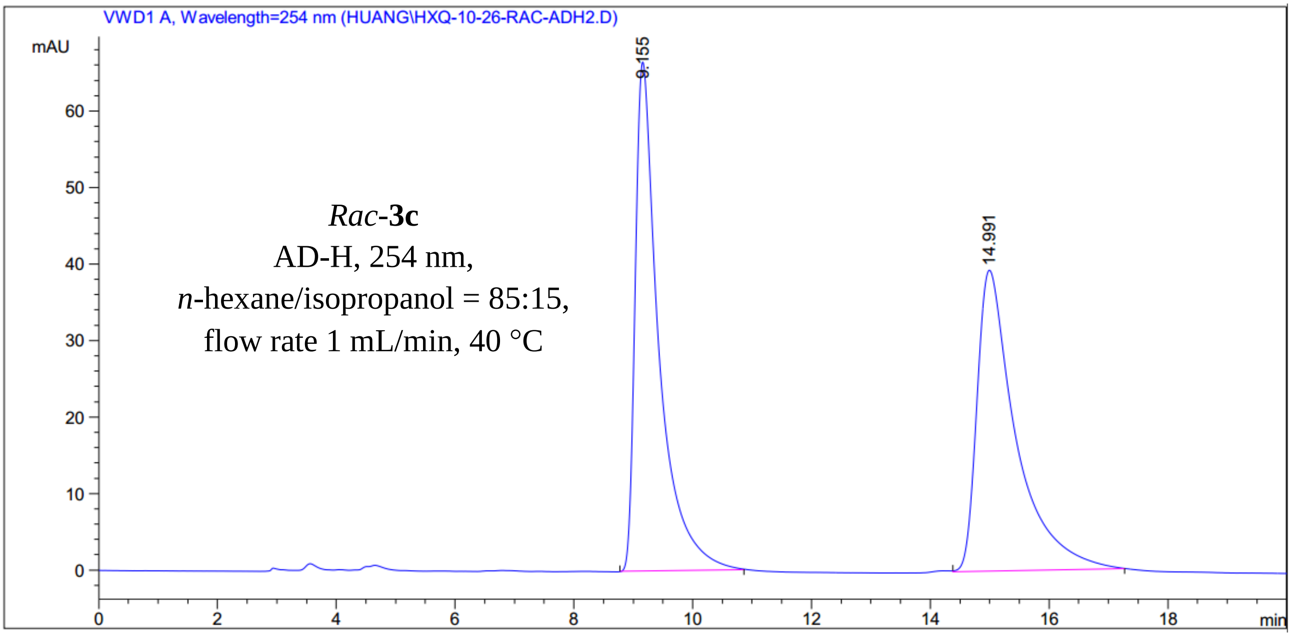


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.381	BB	0.2610	854.68481	46.47641	50.0136
2	15.298	BB	0.2812	854.22095	36.40813	49.9864

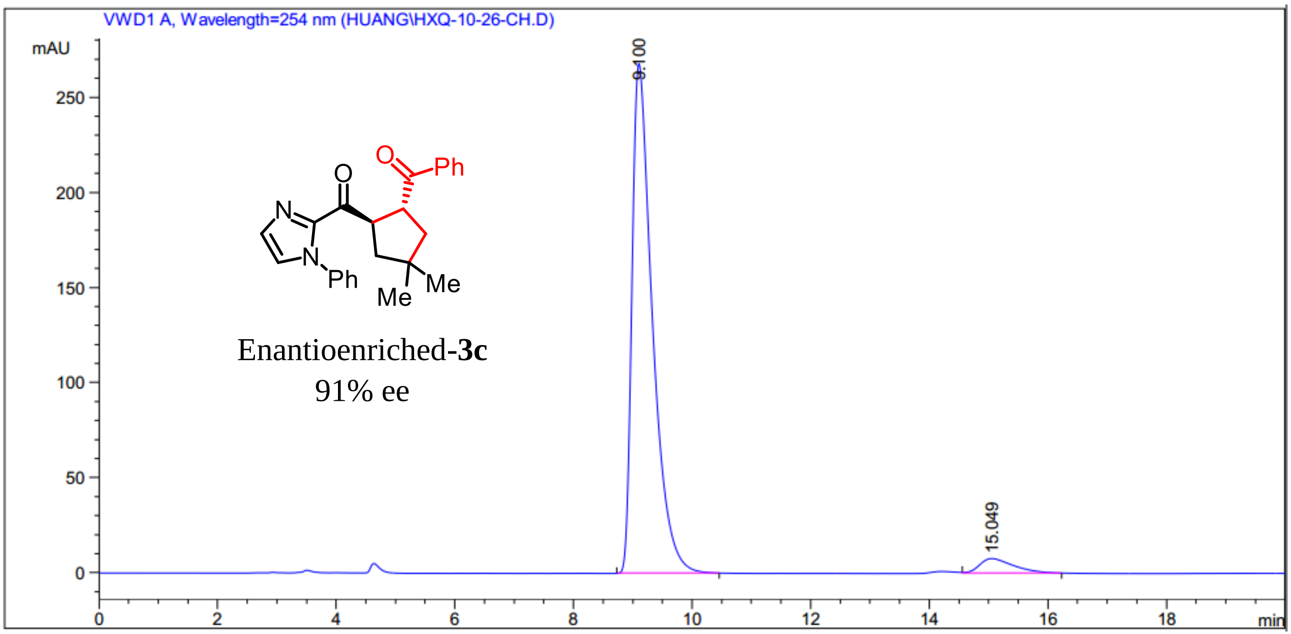


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.356	BB	0.2969	9395.65430	491.68390	98.5862
2	15.428	BB	0.3693	134.73633	5.66834	1.4138

Figure S12. HPLC traces of *rac*-**3b** (reference) and enantioenriched-**3b**.

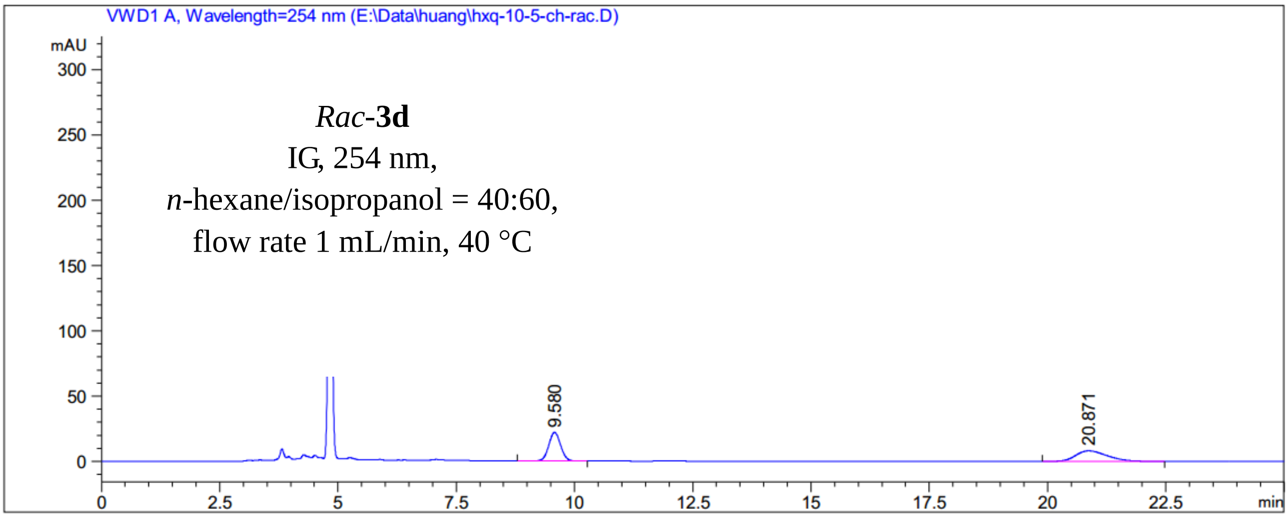


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.155	BB	0.4009	1847.34485	66.57133	50.6809
2	14.991	BB	0.6562	1797.70764	39.39277	49.3191

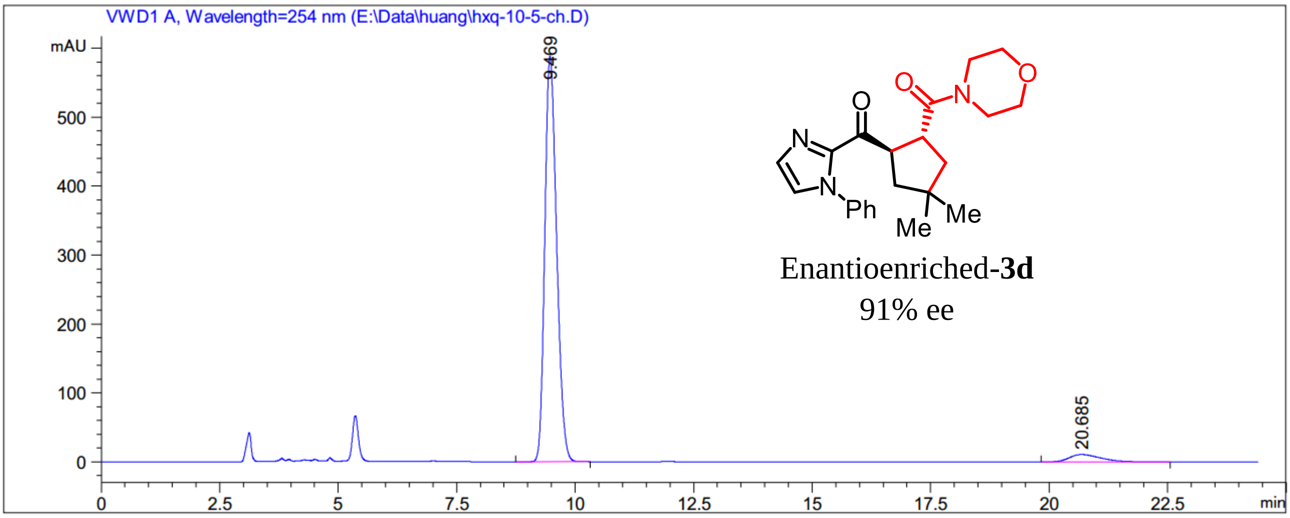


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.100	BB	0.3568	6388.68848	267.92383	95.3115
2	15.049	VB	0.5968	314.26822	7.77545	4.6885

Figure S13. HPLC traces of *rac*-**3c** (reference) and enantioenriched-**3c**.

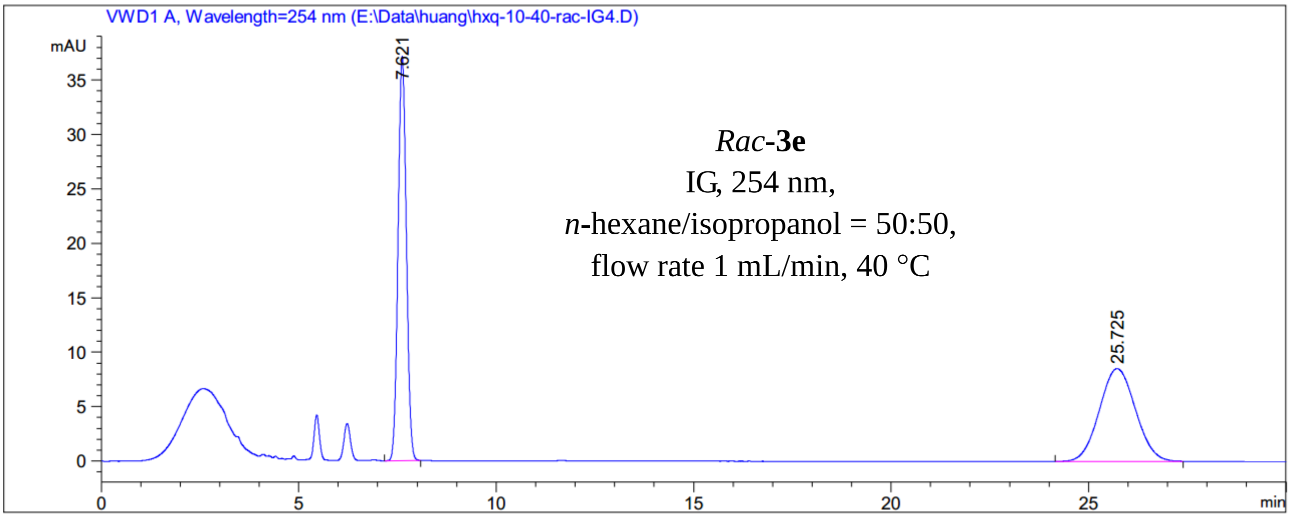


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.580	BB	0.2717	381.99487	21.87920	50.8333
2	20.871	BB	0.6932	369.47089	8.05431	49.1667

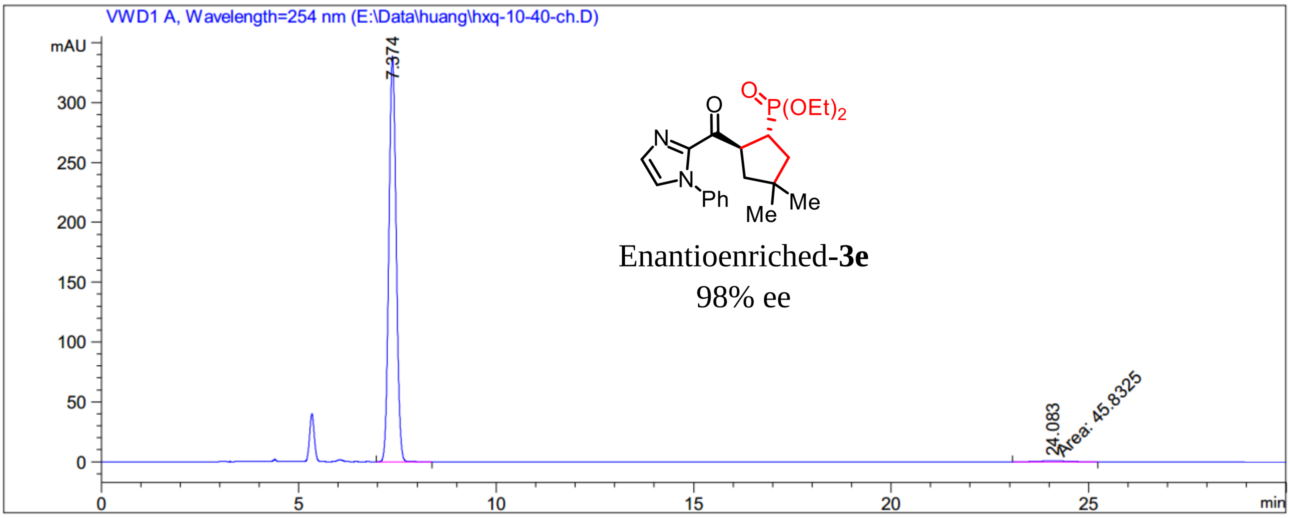


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.469	BB	0.2692	1.01942e4	588.17480	95.3629
2	20.685	BB	0.7026	495.70502	10.71791	4.6371

Figure S14. HPLC traces of *rac*-**3d** (reference) and enantioenriched-**3d**.

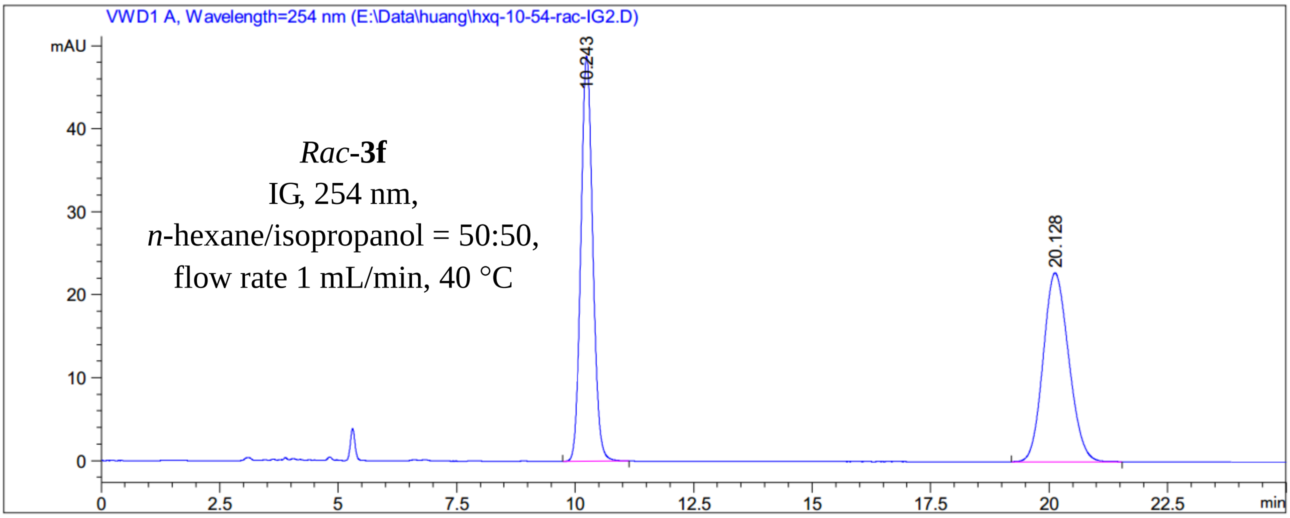


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.621	BB	0.2280	541.31342	37.14006	50.0221
2	25.725	BB	0.9494	540.83435	8.52227	49.9779

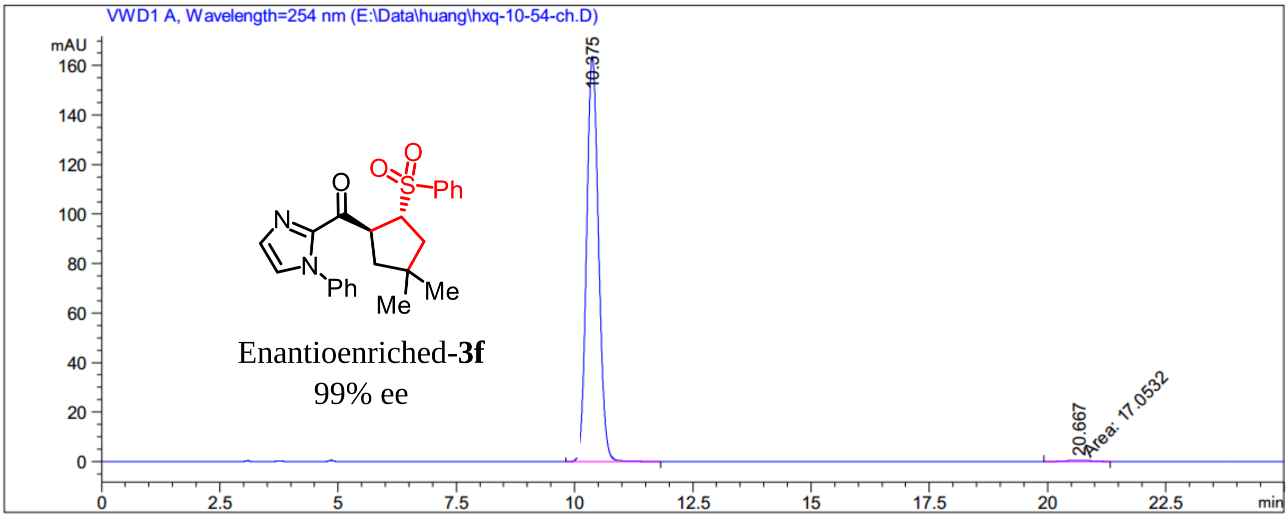


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.374	BB	0.1994	4338.00391	338.70486	98.9545
2	24.083	MM	0.9015	45.83248	8.47352e-1	1.0455

Figure S15. HPLC traces of *rac*-**3e** (reference) and enantioenriched-**3e**.

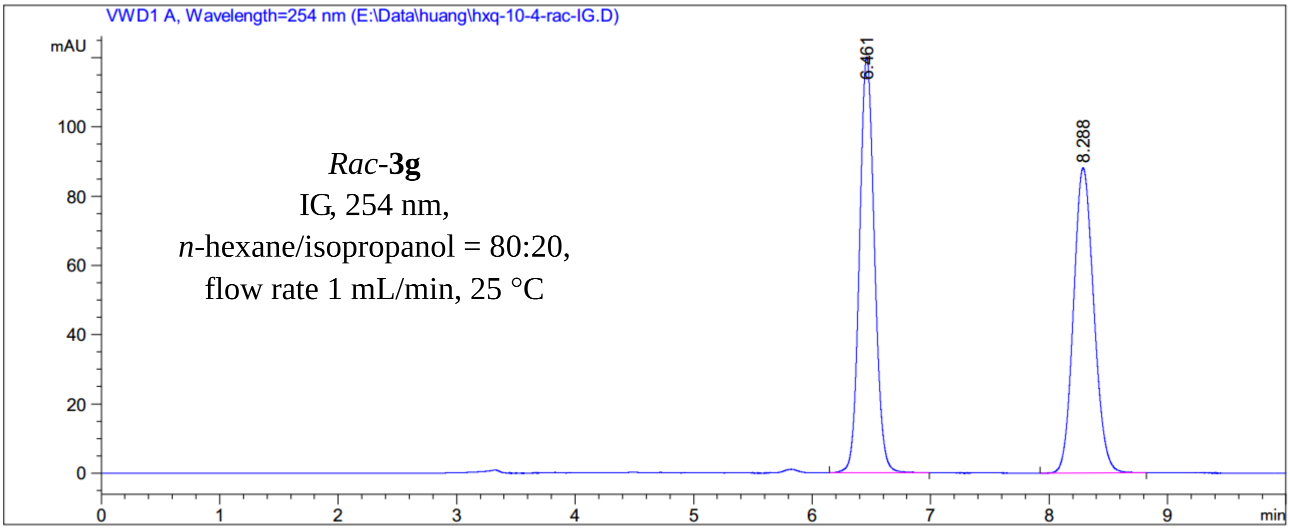


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.243	BB	0.2717	852.33984	48.81604	49.9930
2	20.128	BB	0.5822	852.57751	22.74972	50.0070

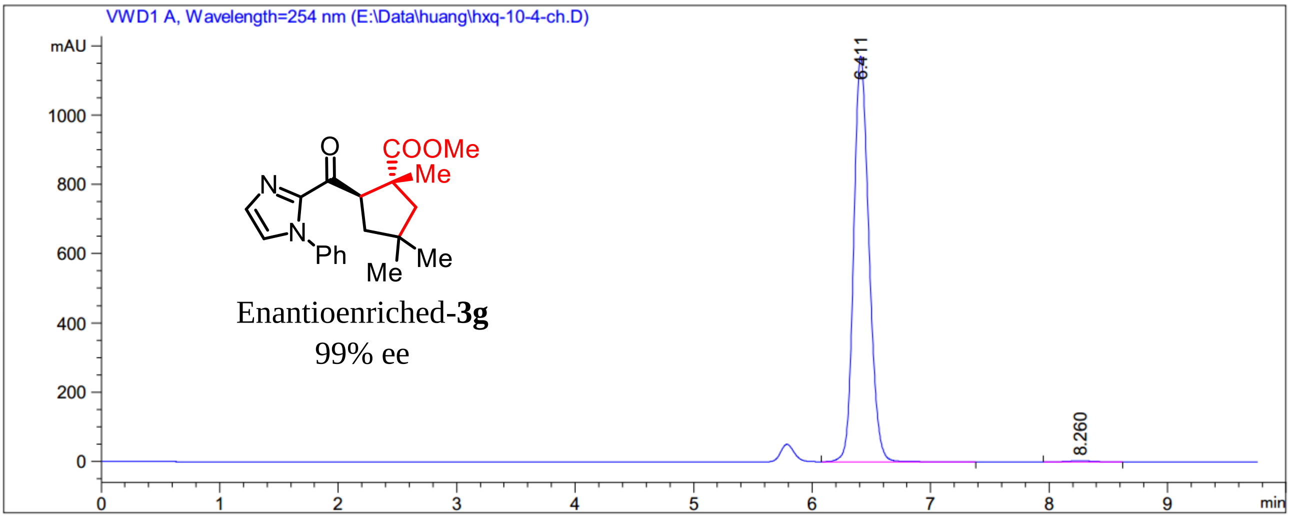


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.375	BB	0.2732	2880.97144	163.77682	99.4116
2	20.667	MM	0.6297	17.05322	4.51359e-1	0.5884

Figure S16. HPLC traces of *rac*-**3f** (reference) and enantioenriched-**3f**.

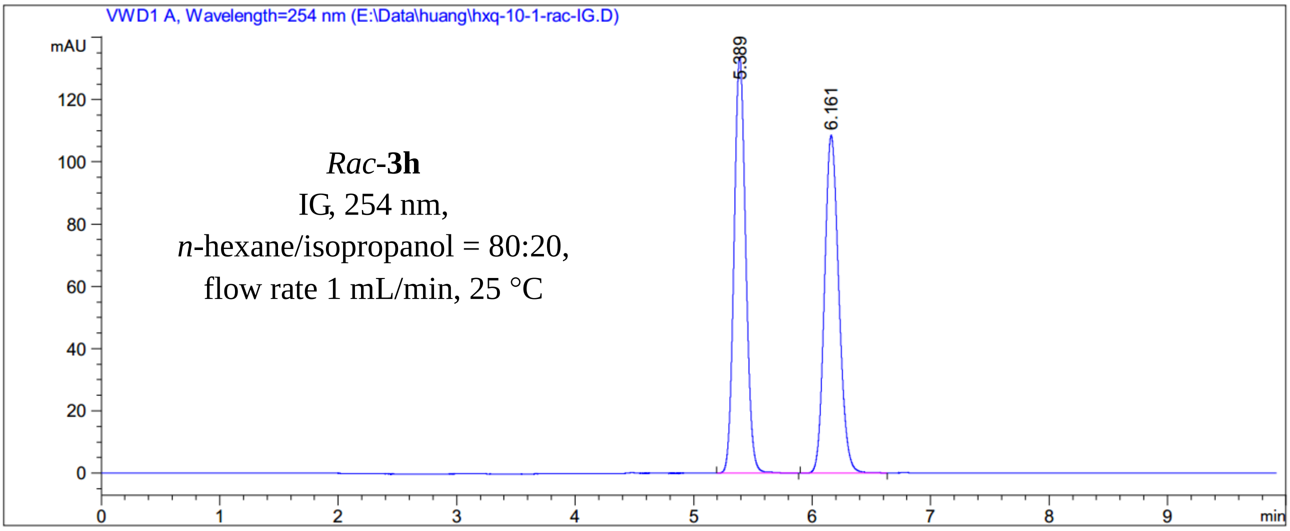


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.461	VB	0.1357	1058.43848	120.20335	50.2266
2	8.288	BB	0.1849	1048.89014	88.08952	49.7734

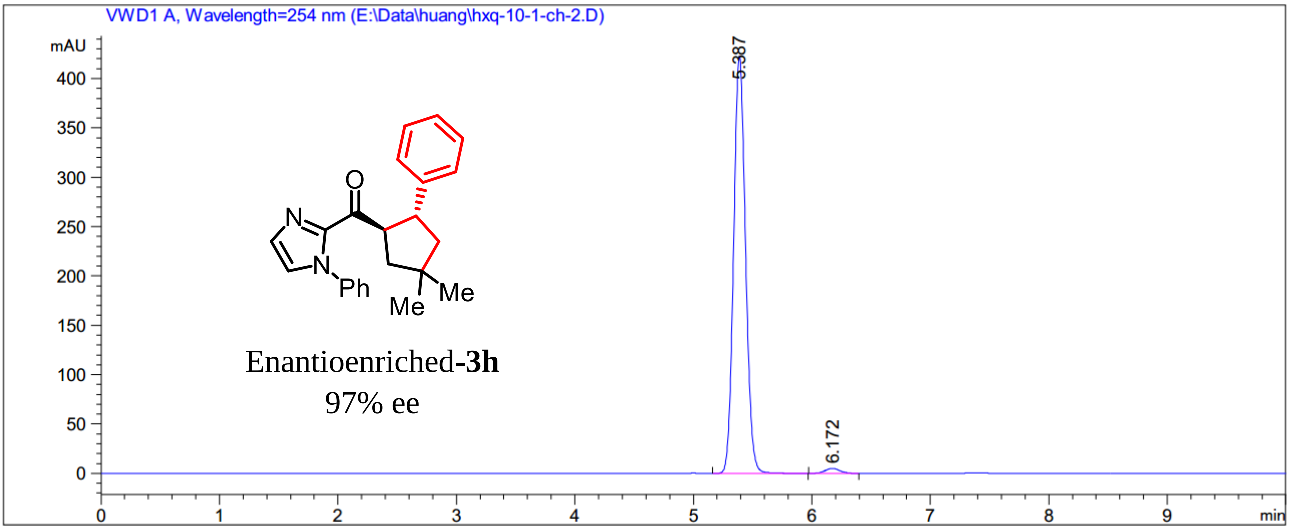


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.411	VB	0.1385	1.04882e4	1170.92444	99.6388
2	8.260	BB	0.1864	38.01778	3.15926	0.3612

Figure S17. HPLC traces of *rac*-**3g** (reference) and enantioenriched-**3g**.

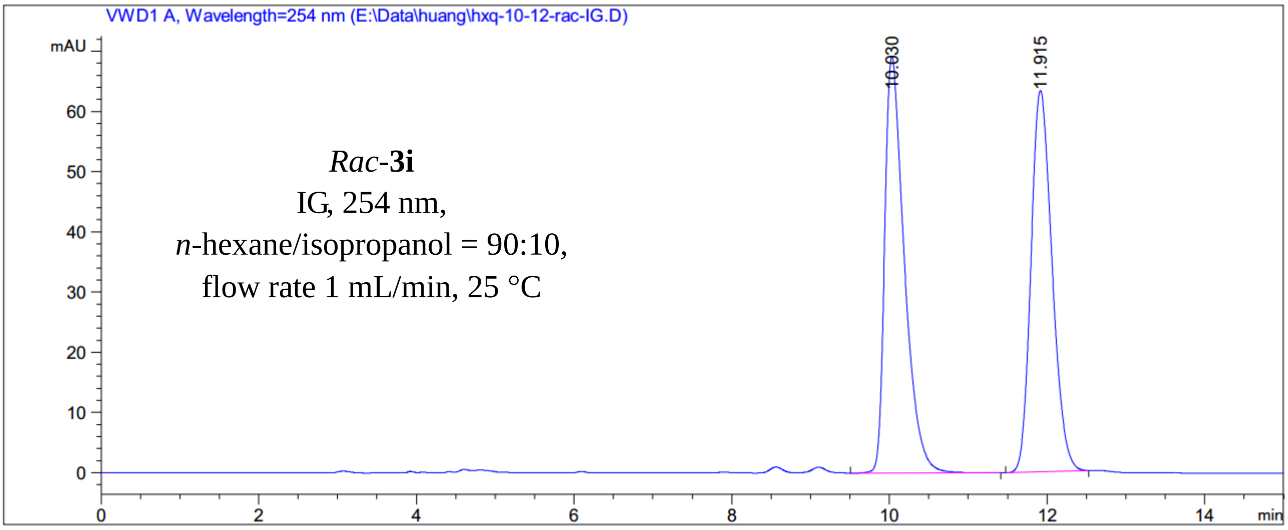


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.389	BV R	0.1069	916.19318	133.74025	50.0873
2	6.161	BV R	0.1307	912.99939	108.48074	49.9127

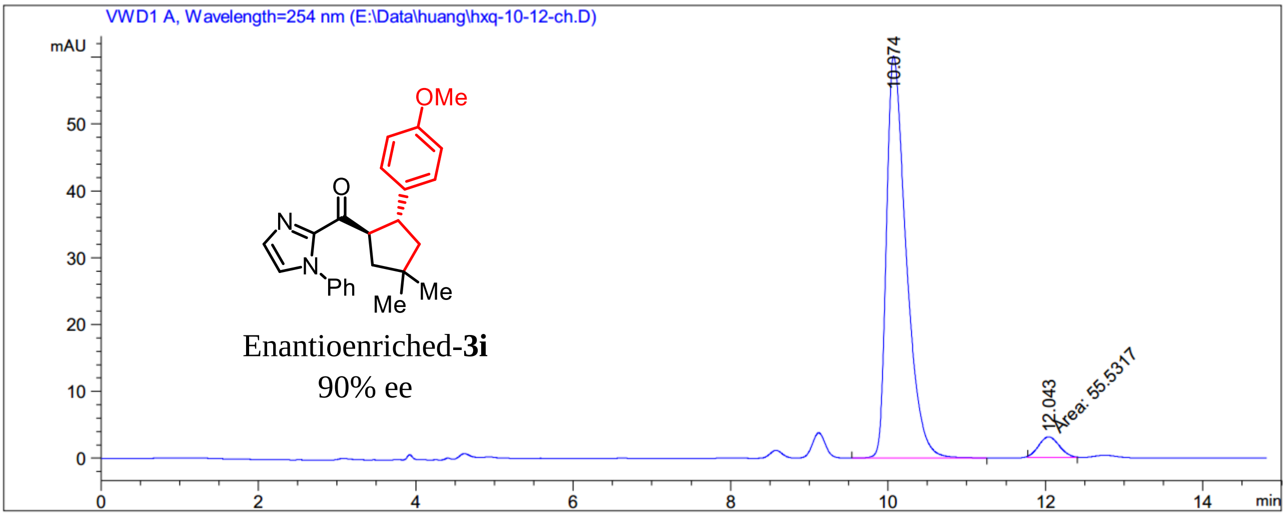


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.387	BB	0.1084	2949.00366	422.64874	98.5857
2	6.172	BB	0.1311	42.30615	5.03289	1.4143

Figure S18. HPLC traces of *rac*-**3h** (reference) and enantioenriched-**3h**.

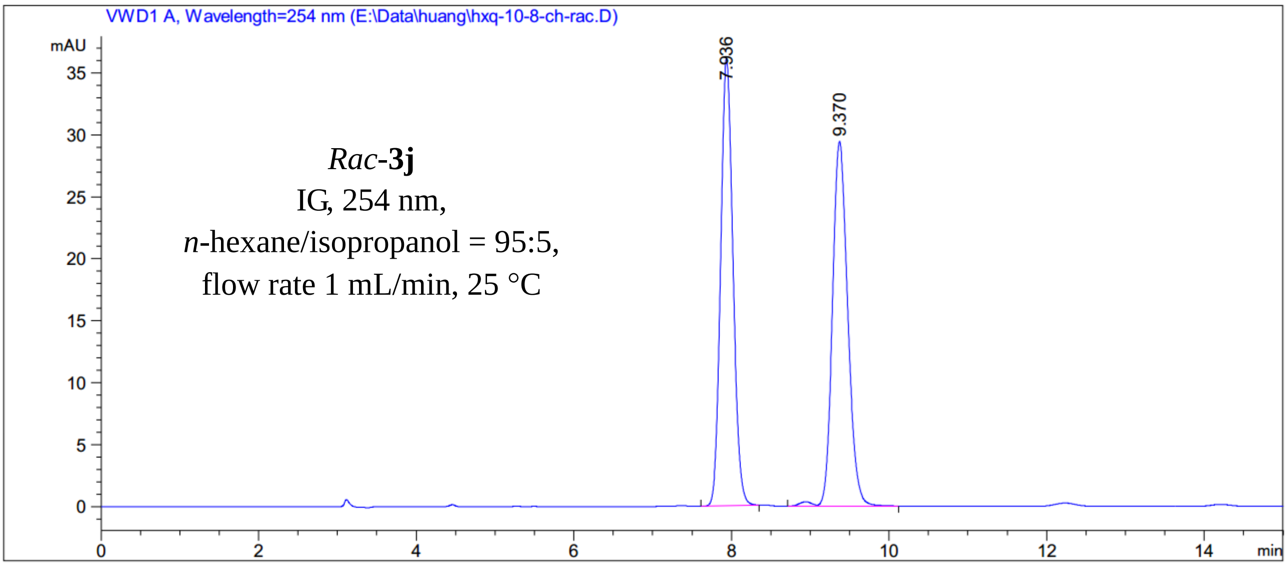


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.030	BB	0.2607	1195.78564	69.15025	50.3794
2	11.915	BB	0.2889	1177.77527	63.35186	49.6206

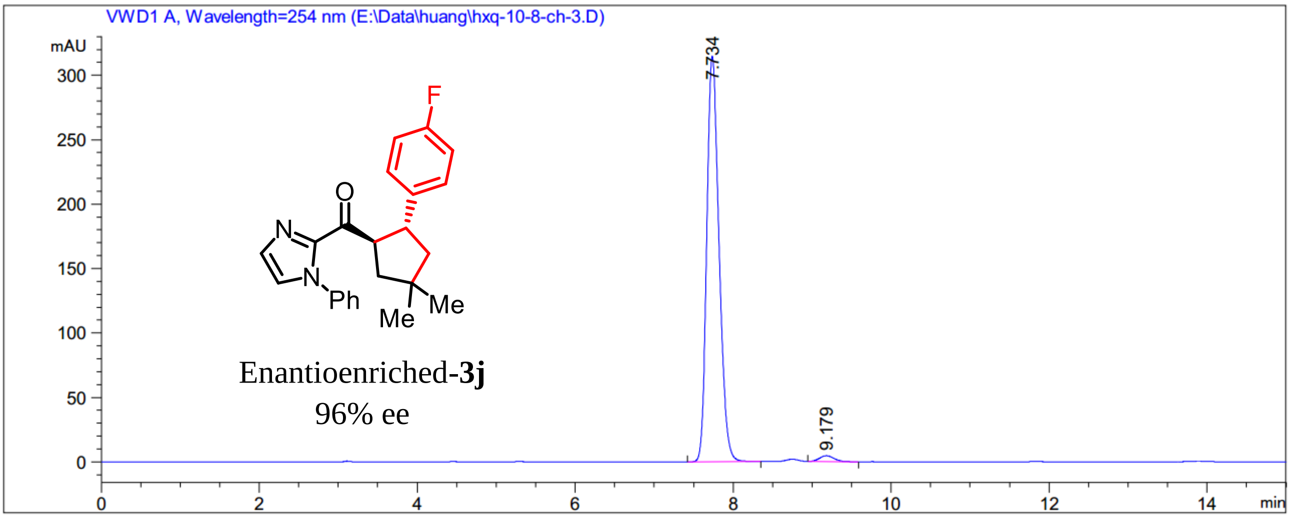


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.074	BB	0.2631	1047.08142	60.15161	94.9636
2	12.043	MM	0.3015	55.53166	3.06955	5.0364

Figure S19. HPLC traces of *rac*-**3i** (reference) and enantioenriched-**3i**.

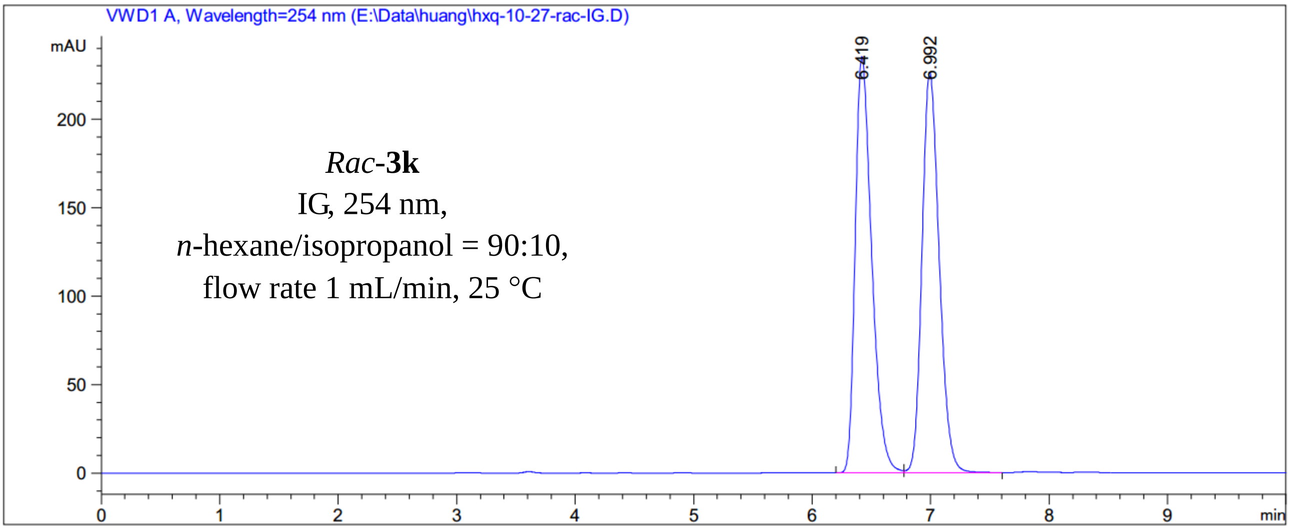


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.936	BB	0.1691	393.25766	36.11168	49.6620
2	9.370	VB R	0.2090	398.61111	29.42678	50.3380

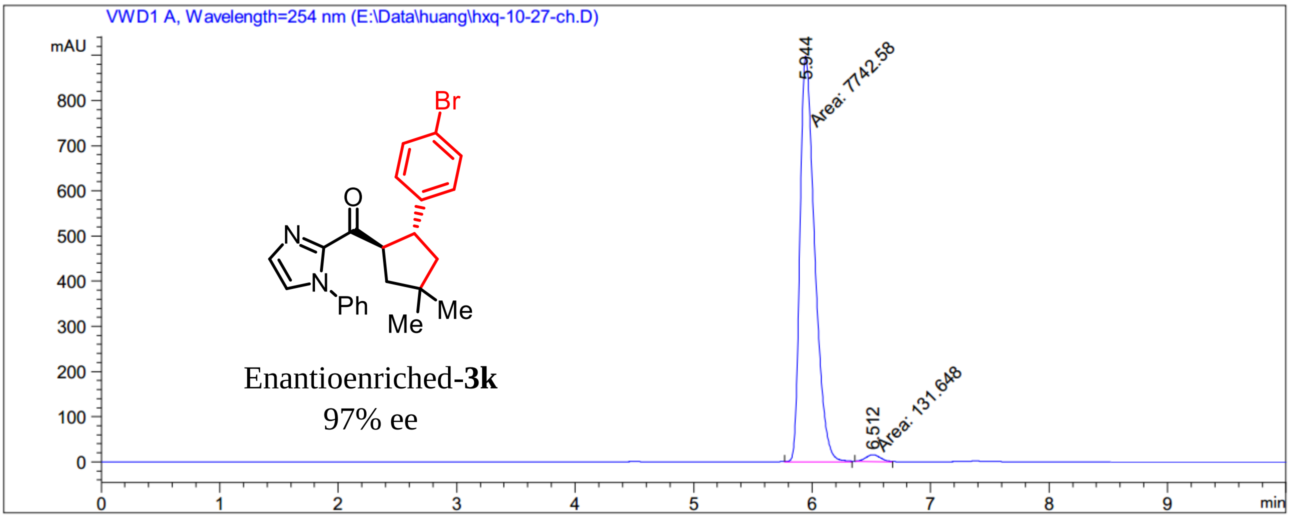


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.734	BB	0.1665	3385.83521	314.71521	98.2343
2	9.179	VB	0.2024	60.85917	4.65864	1.7657

Figure S20. HPLC traces of *rac*-**3j** (reference) and enantioenriched-**3j**.

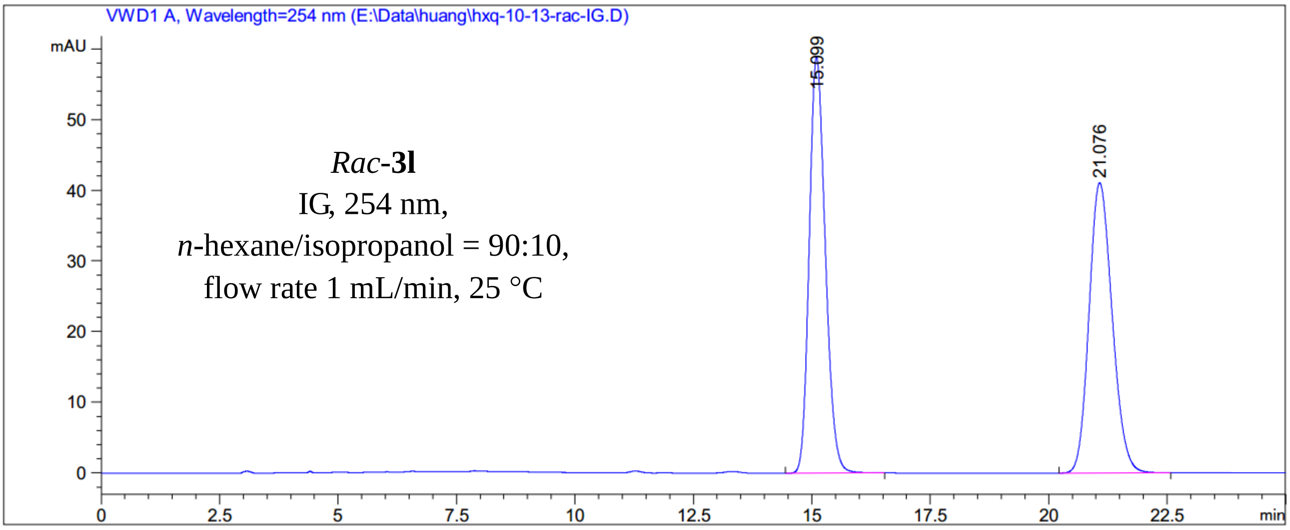


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.419	BV	0.1478	2272.15552	235.10797	49.8474
2	6.992	VB	0.1558	2286.06519	226.35291	50.1526

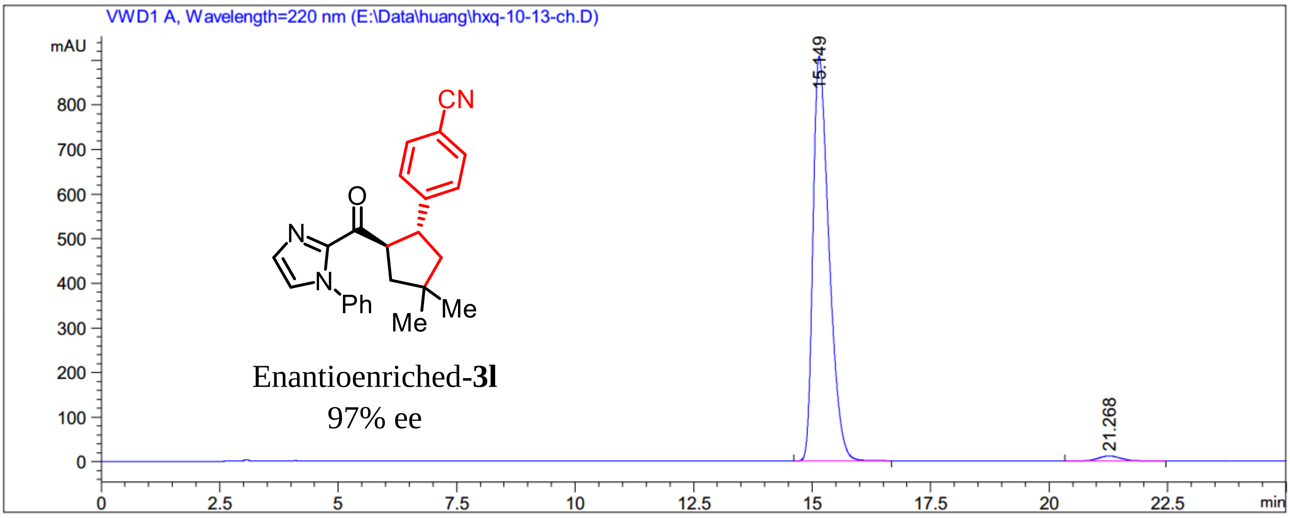


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.944	MM	0.1437	7742.58350	897.70801	98.3281
2	6.512	MM	0.1456	131.64760	15.06856	1.6719

Figure S21. HPLC traces of *rac*-**3k** (reference) and enantioenriched-**3k**.

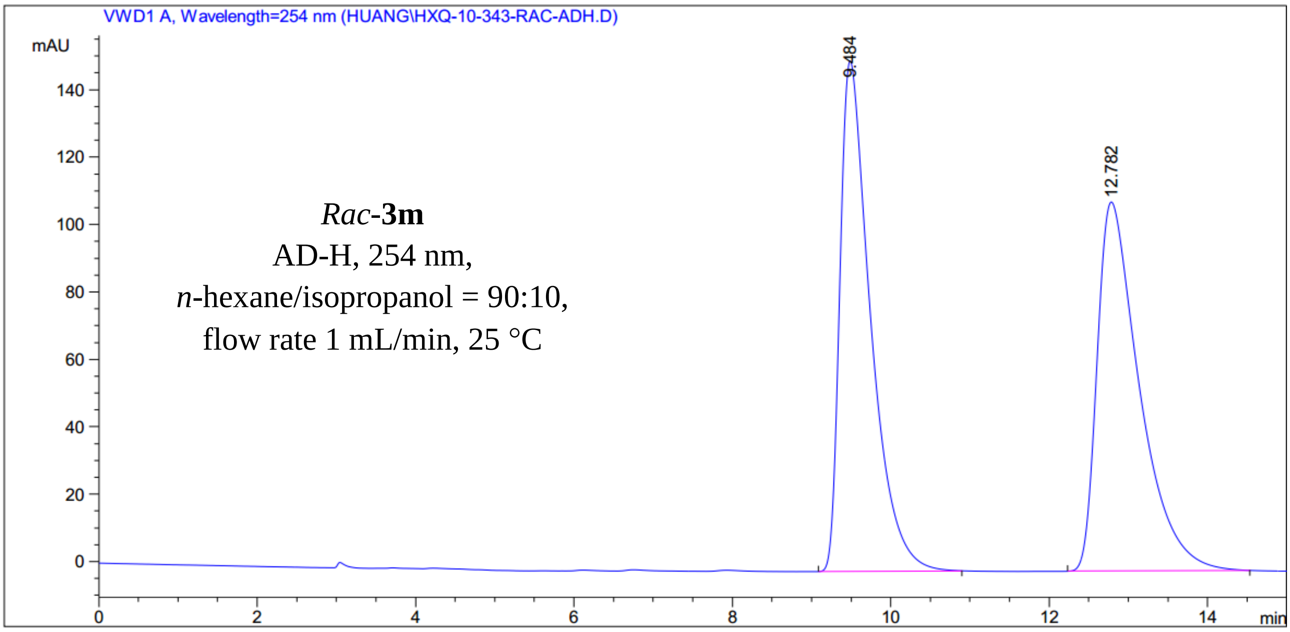


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.099	BB	0.3659	1393.47302	58.91751	50.0042
2	21.076	BB	0.5290	1393.24011	41.05114	49.9958

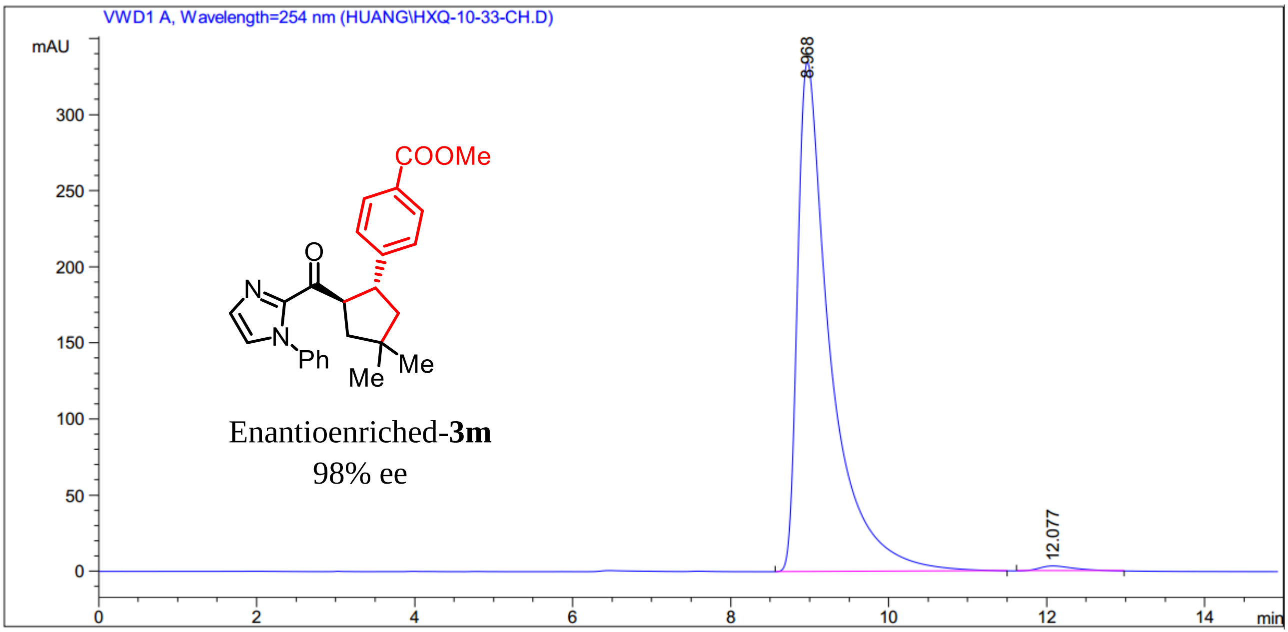


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.149	BB	0.3581	2.13202e4	907.54816	98.3379
2	21.268	BB	0.5048	360.35635	11.06825	1.6621

Figure S22. HPLC traces of *rac*-**3l** (reference) and enantioenriched-**3l**.

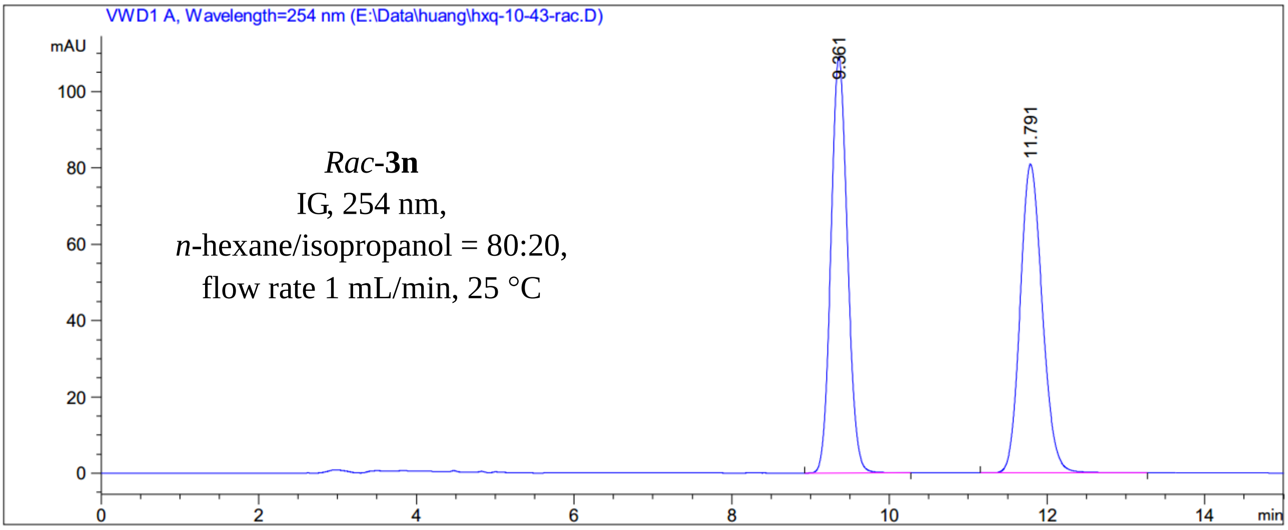


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.484	BB	0.3988	4061.75024	151.44016	49.9977
2	12.782	BB	0.5507	4062.12305	109.51580	50.0023

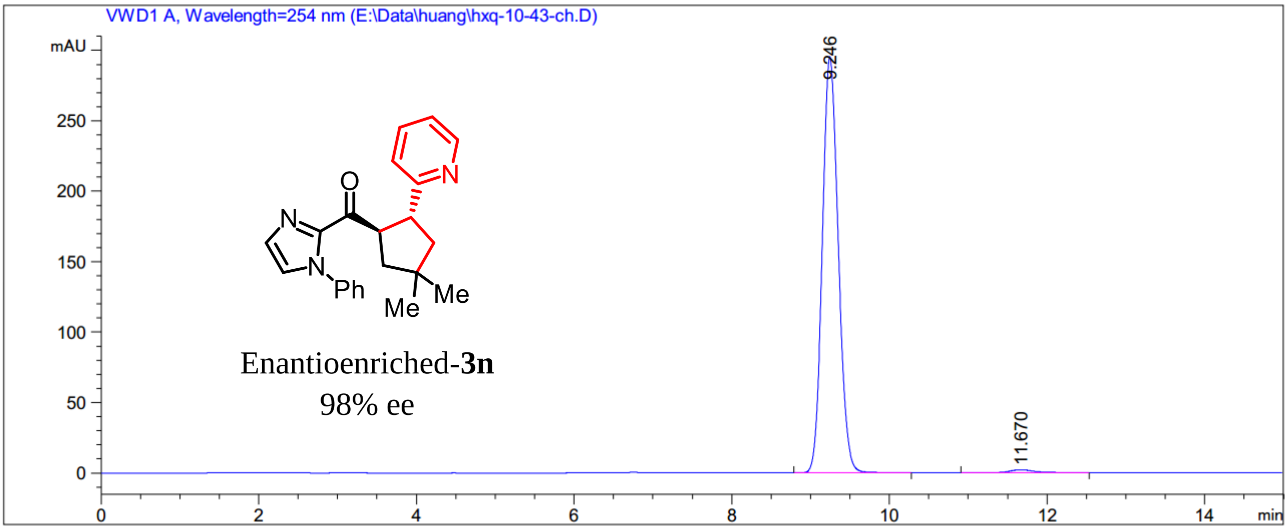


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.968	BB	0.4156	9671.58789	334.89102	98.9212
2	12.077	BB	0.4758	105.47317	3.25303	1.0788

Figure S23. HPLC traces of *rac*-**3m** (reference) and enantioenriched-**3m**.

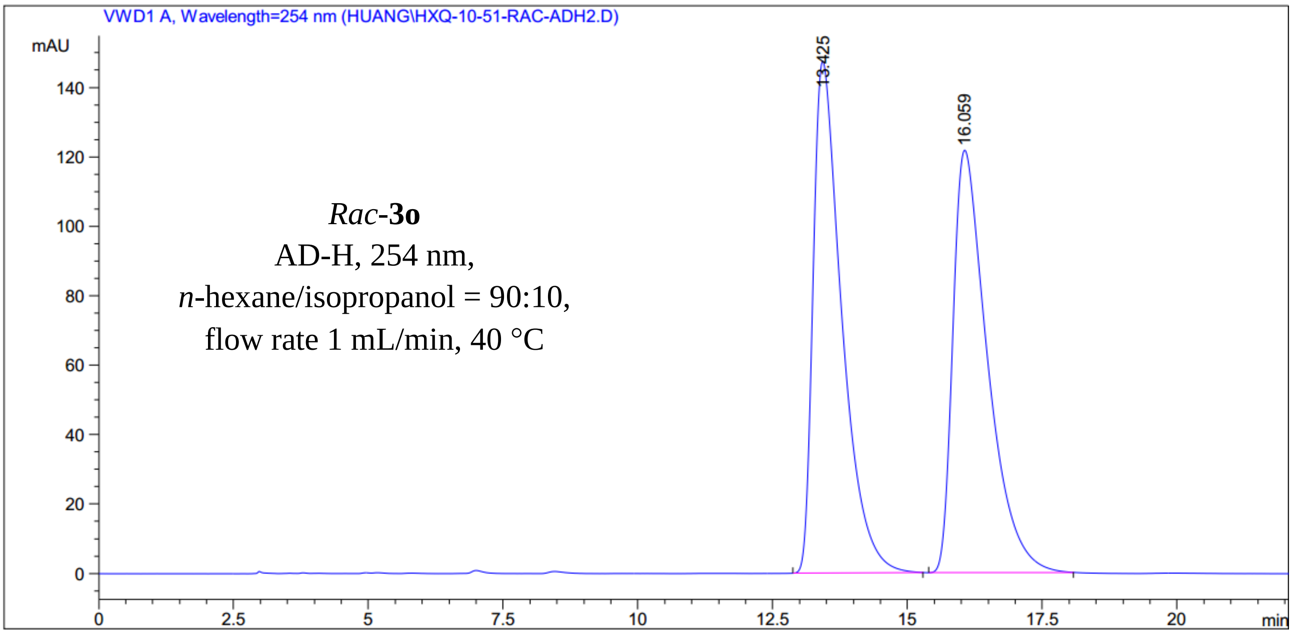


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.361	BB	0.2267	1586.15479	109.05219	50.1623
2	11.791	BB	0.3013	1575.89233	80.89669	49.8377

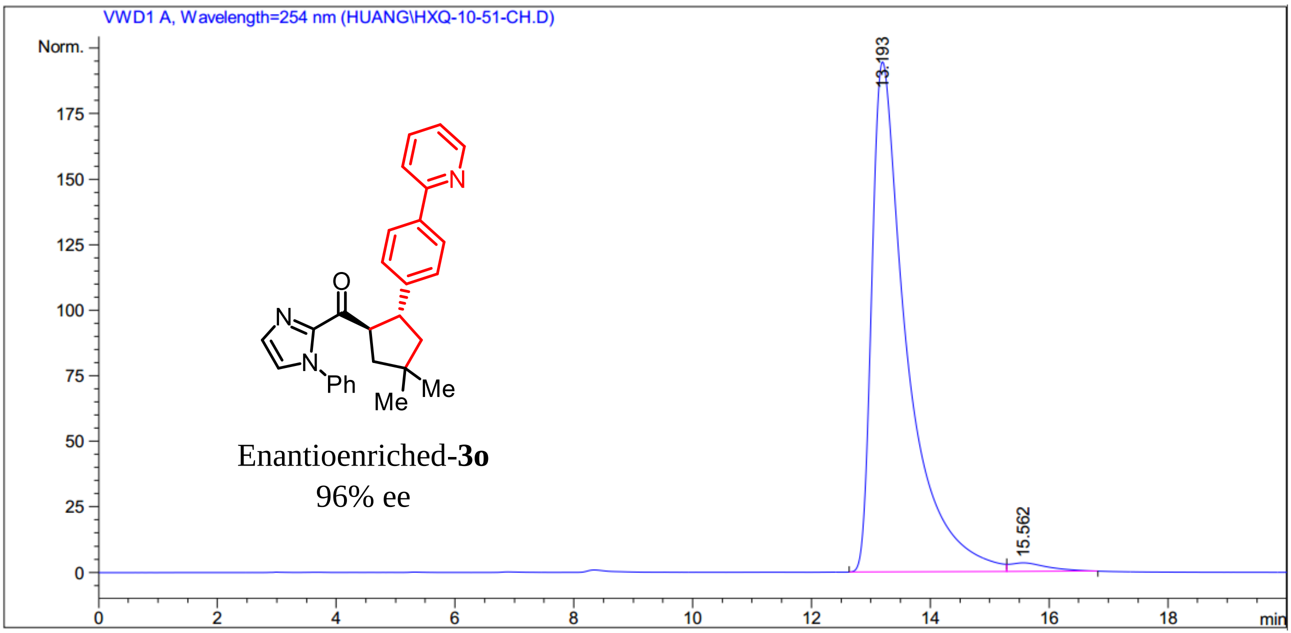


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.246	BB	0.2189	4150.89600	295.43149	98.8479
2	11.670	BB	0.3344	48.37843	2.11859	1.1521

Figure S24. HPLC traces of *rac*-**3n** (reference) and enantioenriched-**3n**.

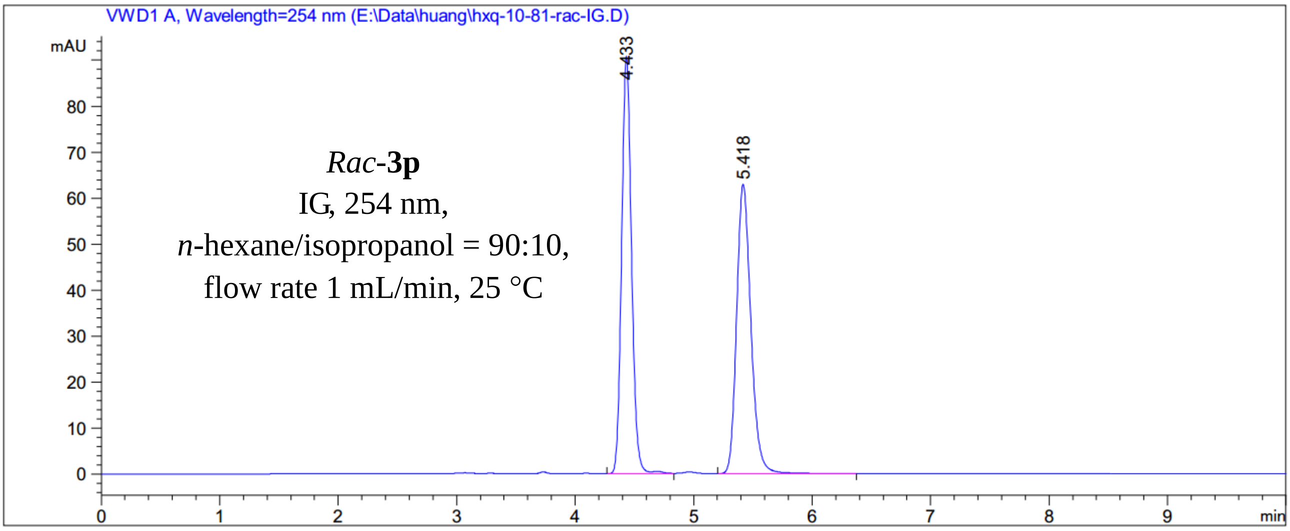


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.425	BB	0.5538	5473.78320	147.49020	50.1713
2	16.059	BB	0.6664	5436.41406	121.78094	49.8287

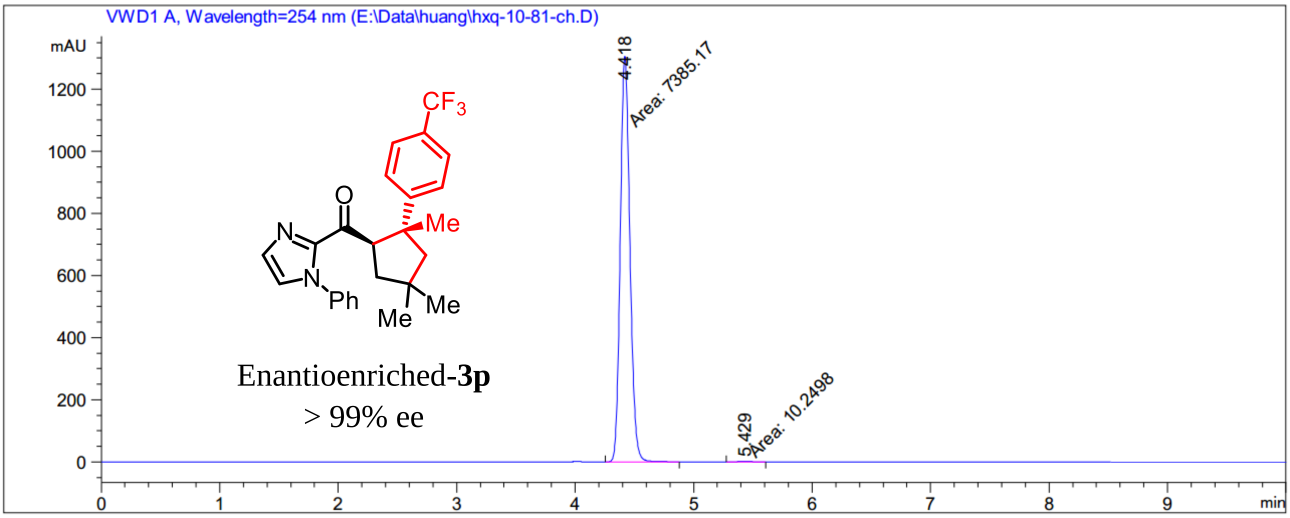


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.193	BB	0.5902	7975.77148	194.62512	98.1508
2	15.562	BB	0.6264	150.26591	3.33354	1.8492

Figure S25. HPLC traces of *rac*-**3o** (reference) and enantioenriched-**3o**.

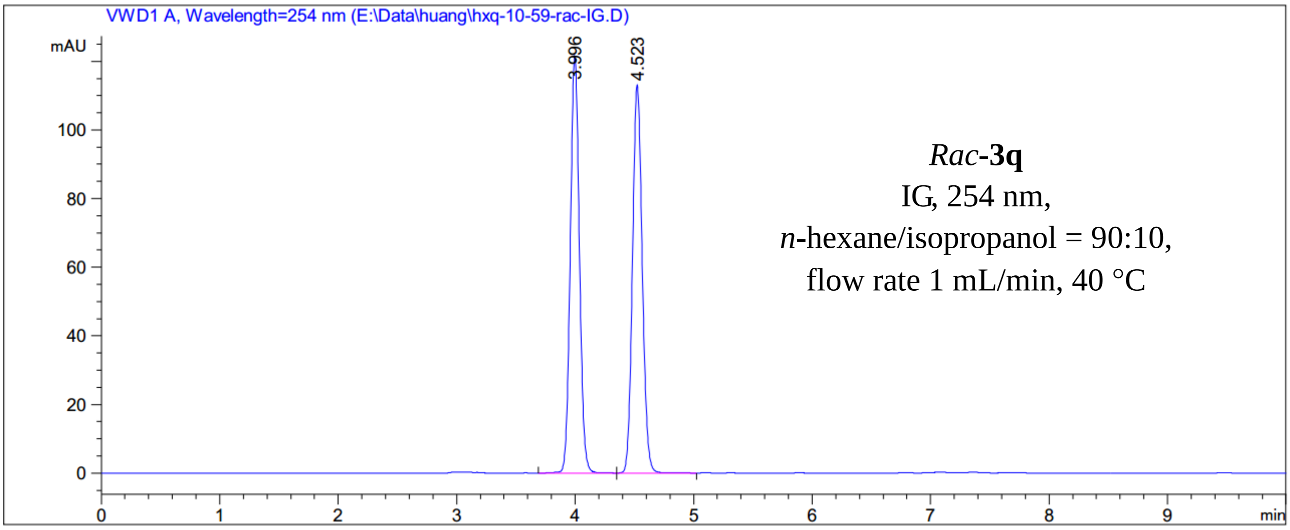


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.433	BV R	0.0896	525.19830	90.62776	50.0368
2	5.418	BB	0.1283	524.42548	62.87243	49.9632

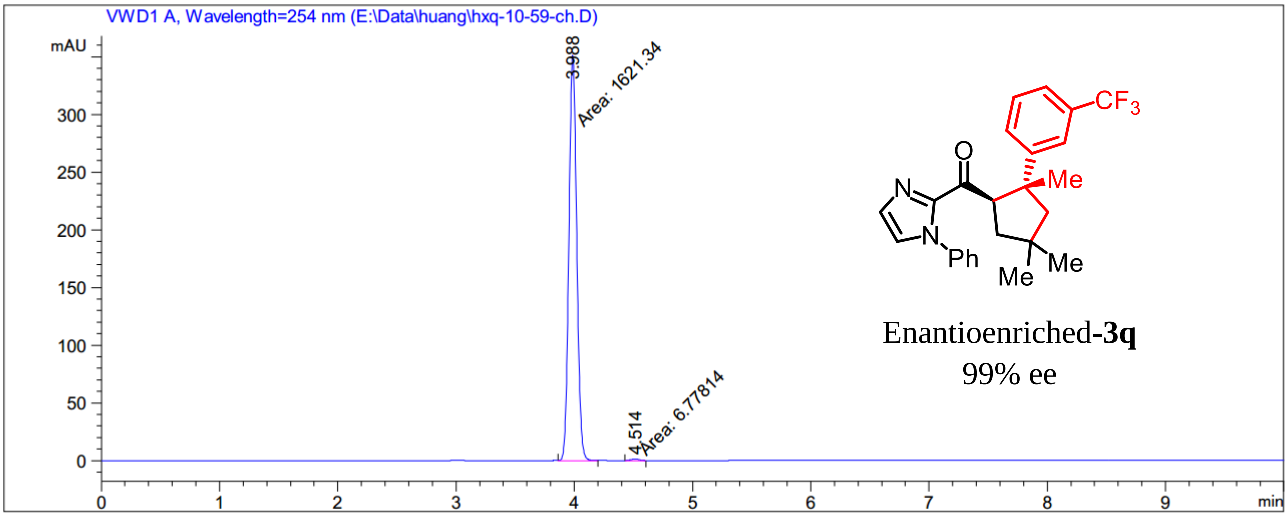


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.418	MF	0.0942	7385.16650	1306.61414	99.8614
2	5.429	MM	0.1416	10.24976	1.20645	0.1386

Figure S26. HPLC traces of *rac*-**3p** (reference) and enantioenriched-**3p**.

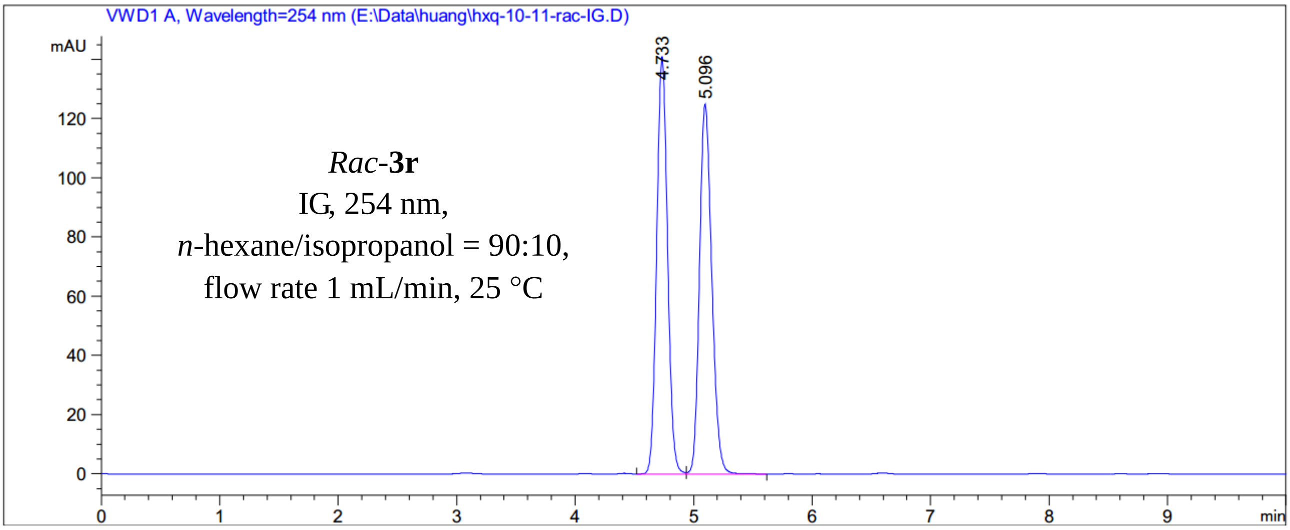


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.996	BB	0.0834	648.36670	121.30615	50.1147
2	4.523	BB	0.0897	645.39862	112.95158	49.8853

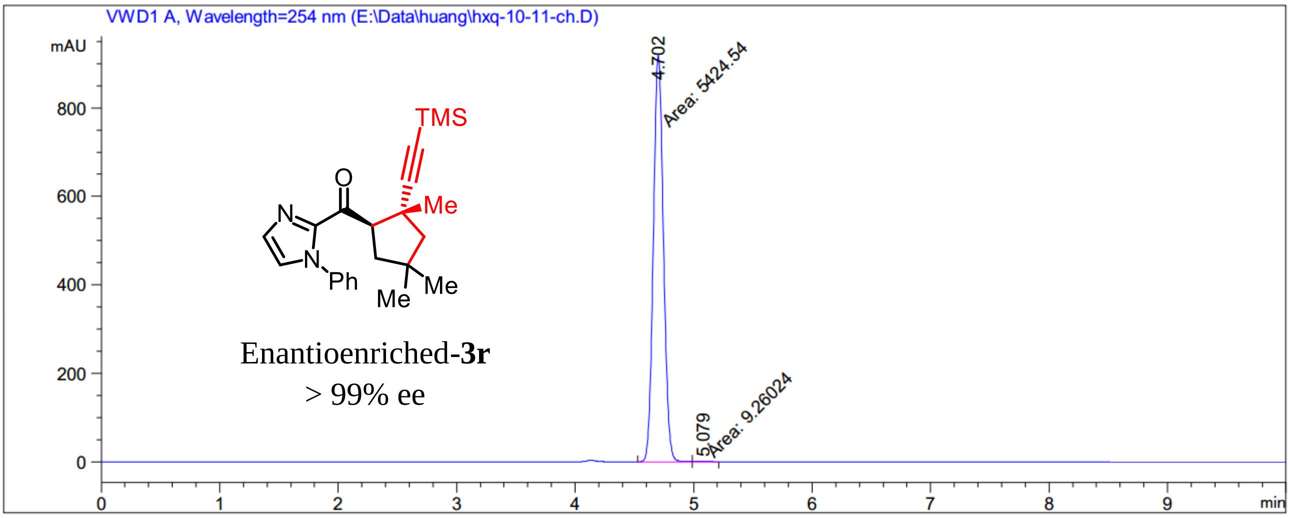


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.988	FM	0.0770	1621.33765	351.01776	99.5837
2	4.514	MM	0.0843	6.77814	1.33997	0.4163

Figure S27. HPLC traces of *rac*-**3q** (reference) and enantioenriched-**3q**.

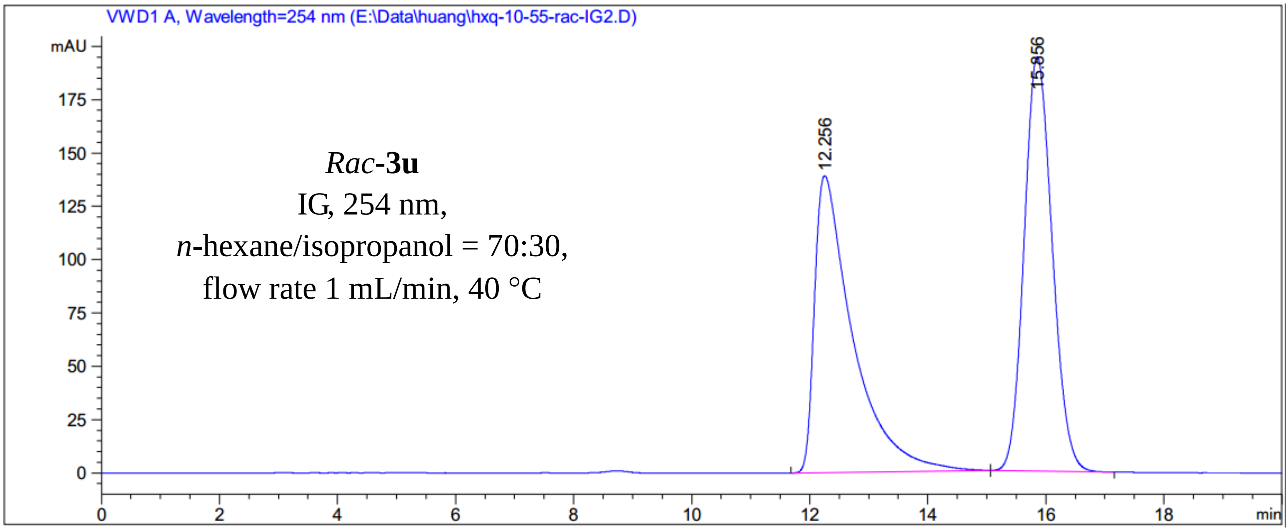


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.733	BV	0.0991	894.65839	140.94907	49.9208
2	5.096	VB	0.1118	897.49890	124.94597	50.0792

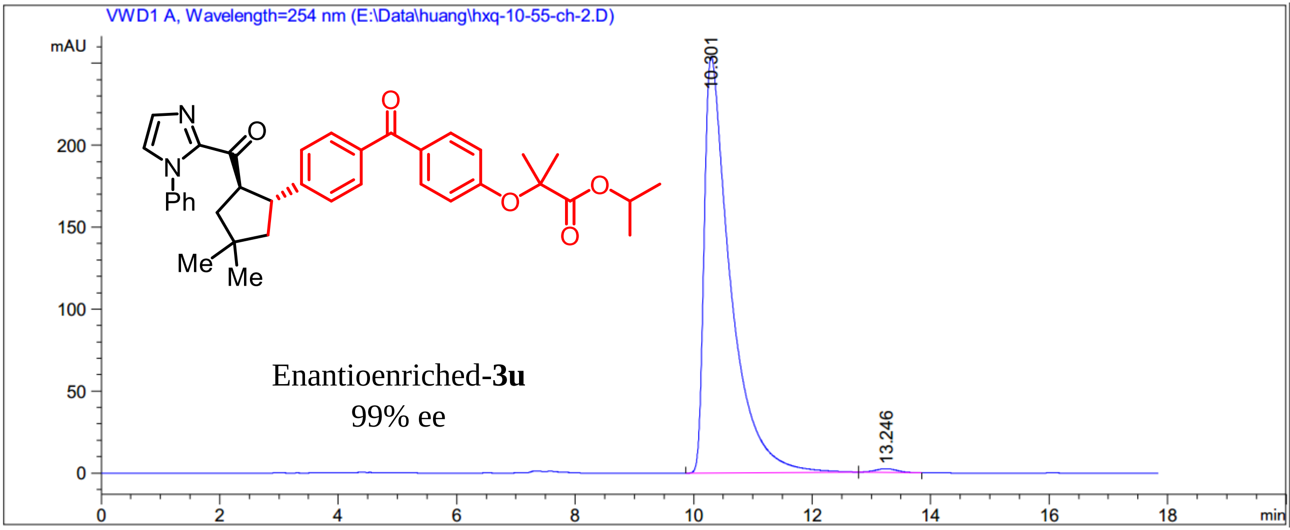


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.702	MF	0.0985	5424.54443	917.73871	99.8296
2	5.079	FM	0.1260	9.26024	1.22483	0.1704

Figure S28. HPLC traces of *rac*-**3r** (reference) and enantioenriched-**3r**.

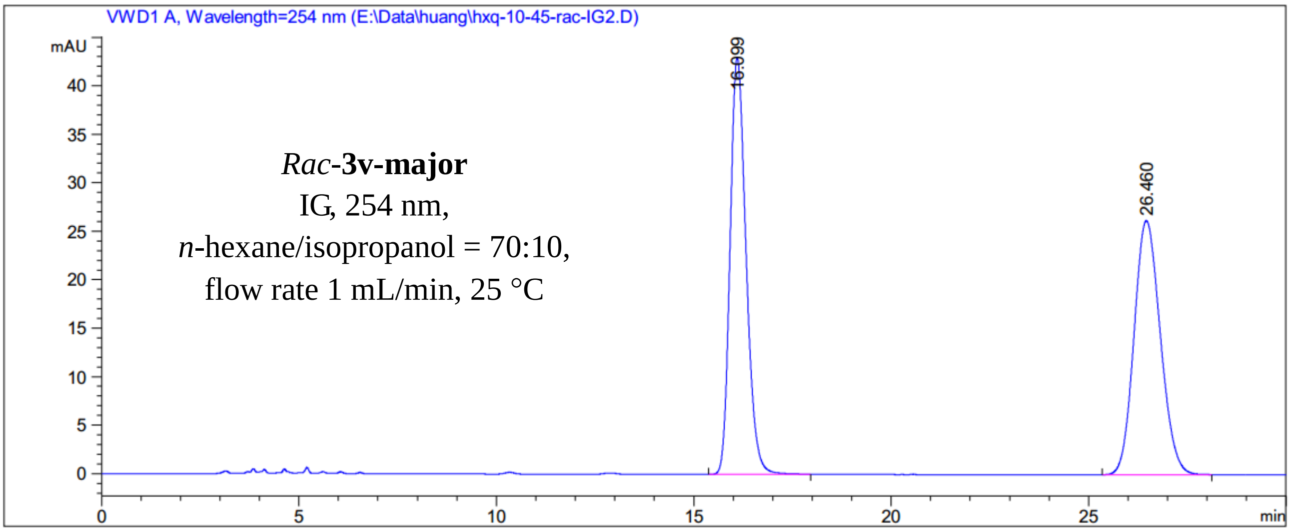


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.256	BB	0.6440	6263.70605	139.20642	49.3181
2	15.856	BB	0.5155	6436.92773	194.27672	50.6819

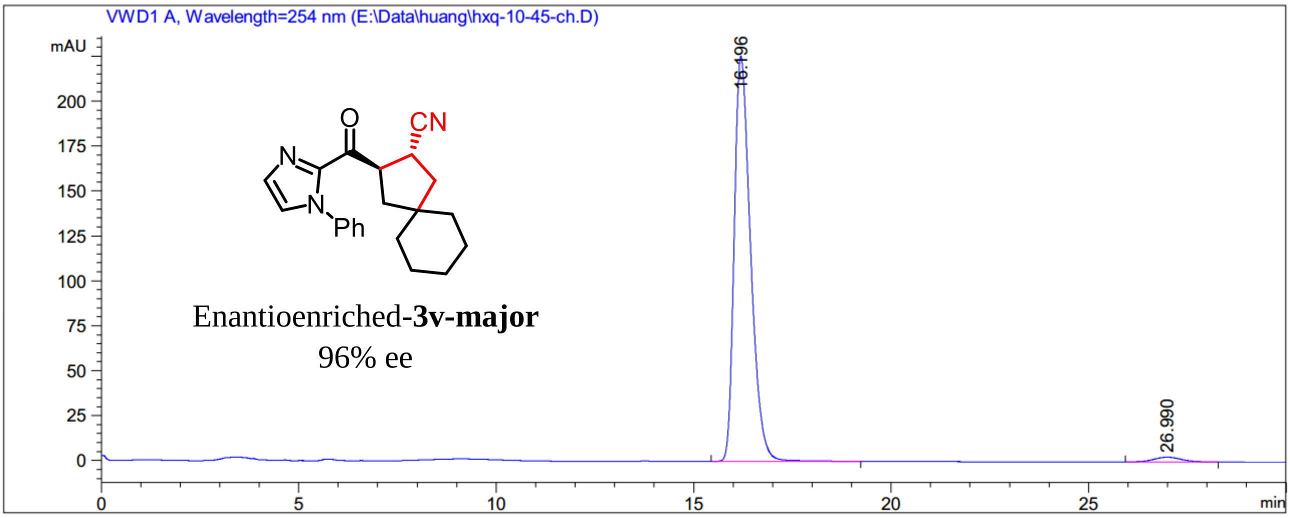


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.301	BB	0.4401	7798.72070	254.07149	99.3046
2	13.246	BB	0.3820	54.60832	2.20456	0.6954

Figure S29. HPLC traces of *rac*-**3u** (reference) and enantioenriched-**3u**.

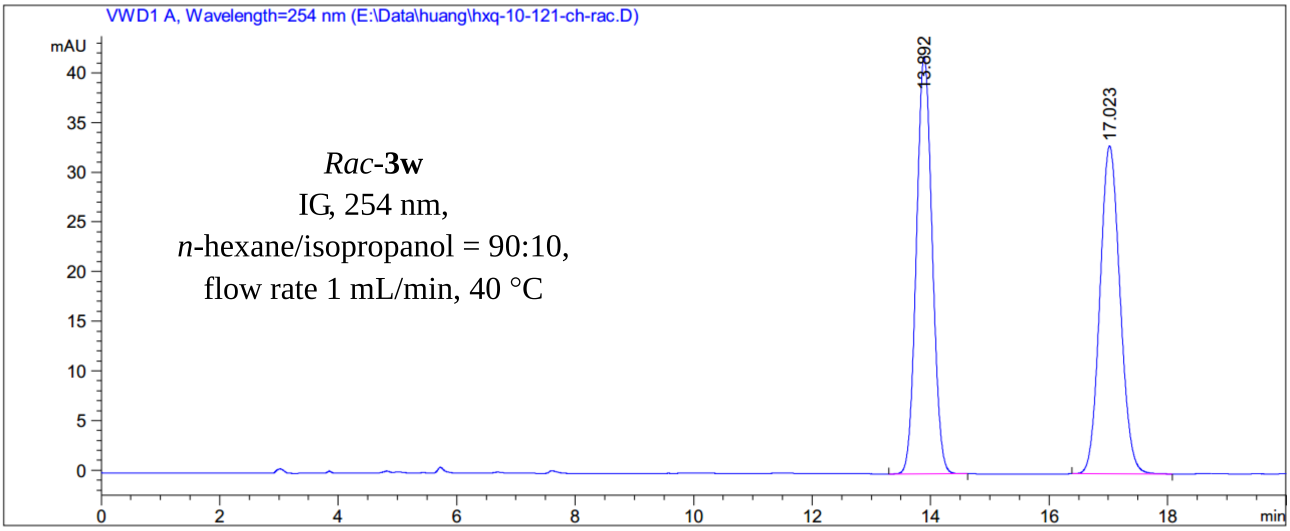


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.099	BB	0.4338	1209.17932	43.03819	49.9616
2	26.460	BB	0.7233	1211.03845	26.19890	50.0384

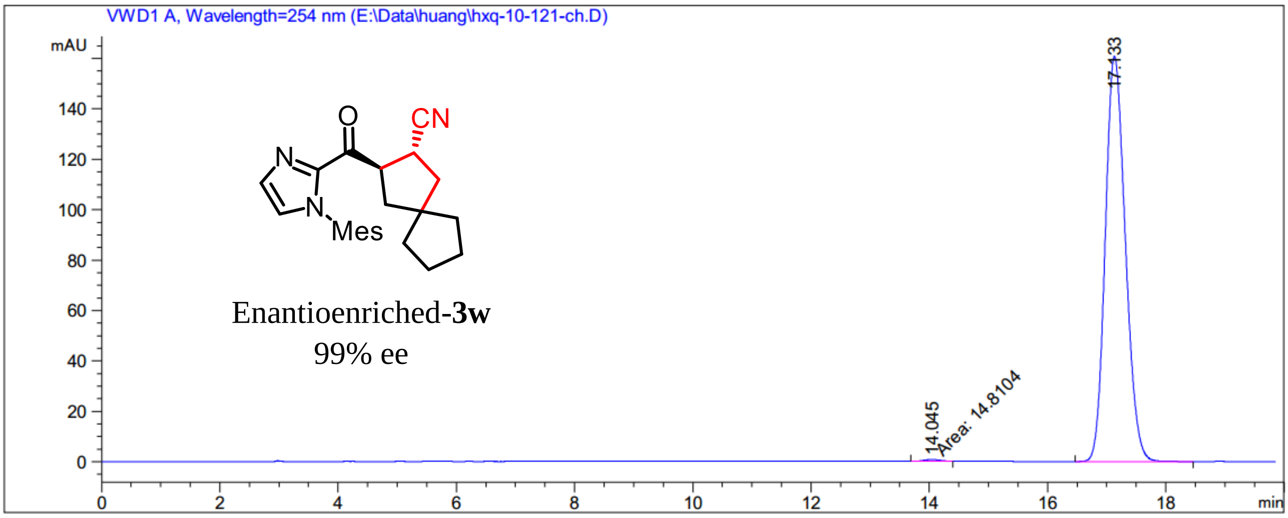


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.196	BB	0.4416	6483.43359	225.36513	98.1150
2	26.990	BB	0.6929	124.55779	2.61884	1.8850

Figure S30. HPLC traces of *rac*-**3v-major** (reference) and enantioenriched-**3v-major**.

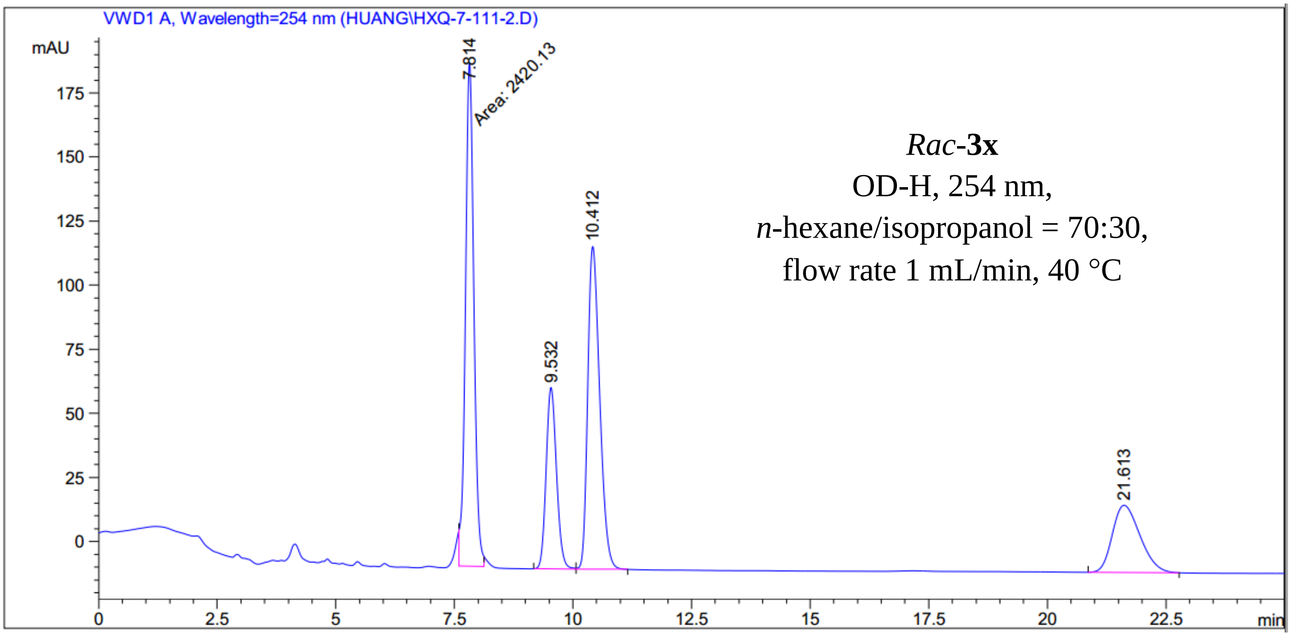


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.892	BB	0.2904	778.88440	41.99063	49.9852
2	17.023	BB	0.3675	779.34583	33.00792	50.0148

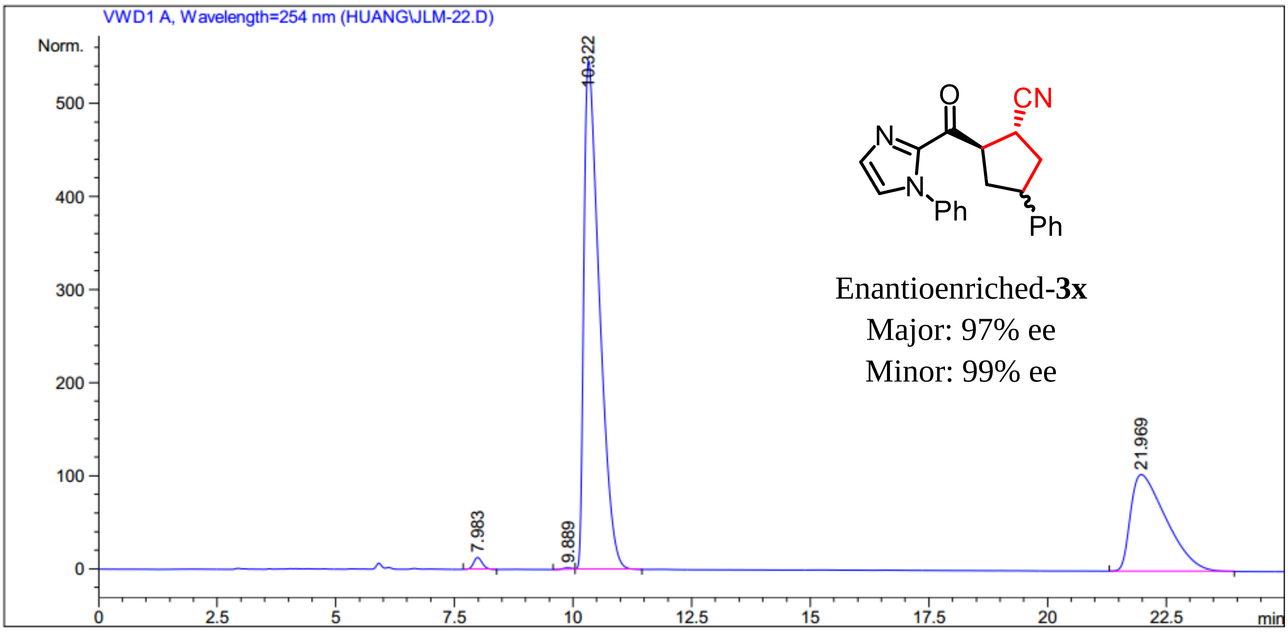


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.045	MM	0.3304	14.81035	7.47117e-1	0.3890
2	17.133	BB	0.3672	3792.13525	160.76515	99.6110

Figure S31. HPLC traces of *rac*-**3w** (reference) and enantioenriched-**3w**.

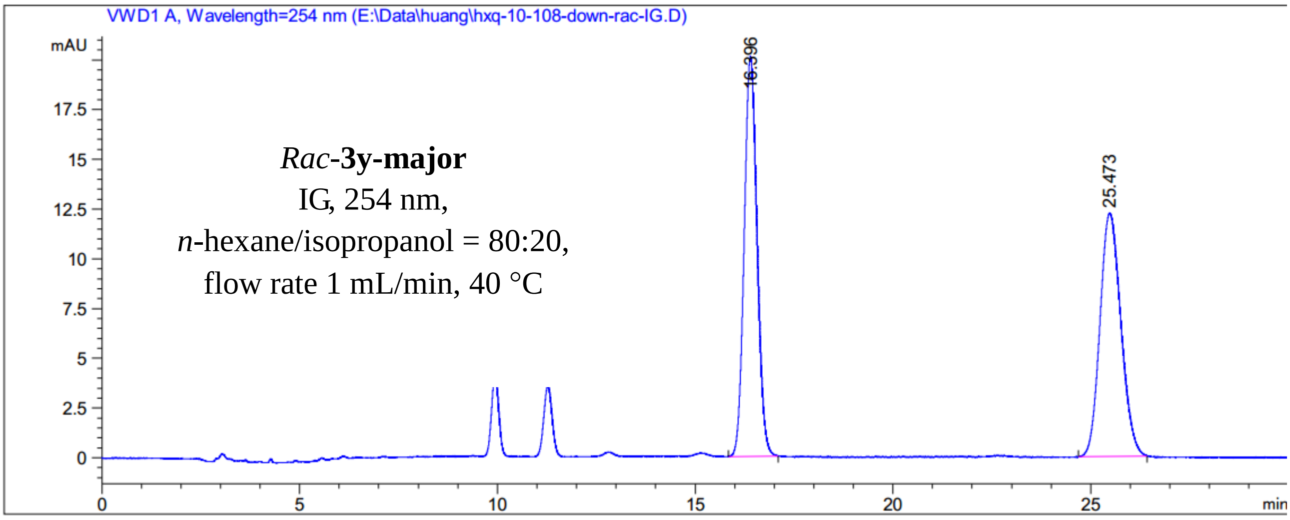


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.814	FM	0.2053	2420.13354	196.44177	35.7286
2	9.532	BV	0.2360	1077.66223	70.73587	15.9096
3	10.412	VB	0.2716	2207.47534	125.88180	32.5891
4	21.613	BB	0.6381	1068.39502	26.24206	15.7728

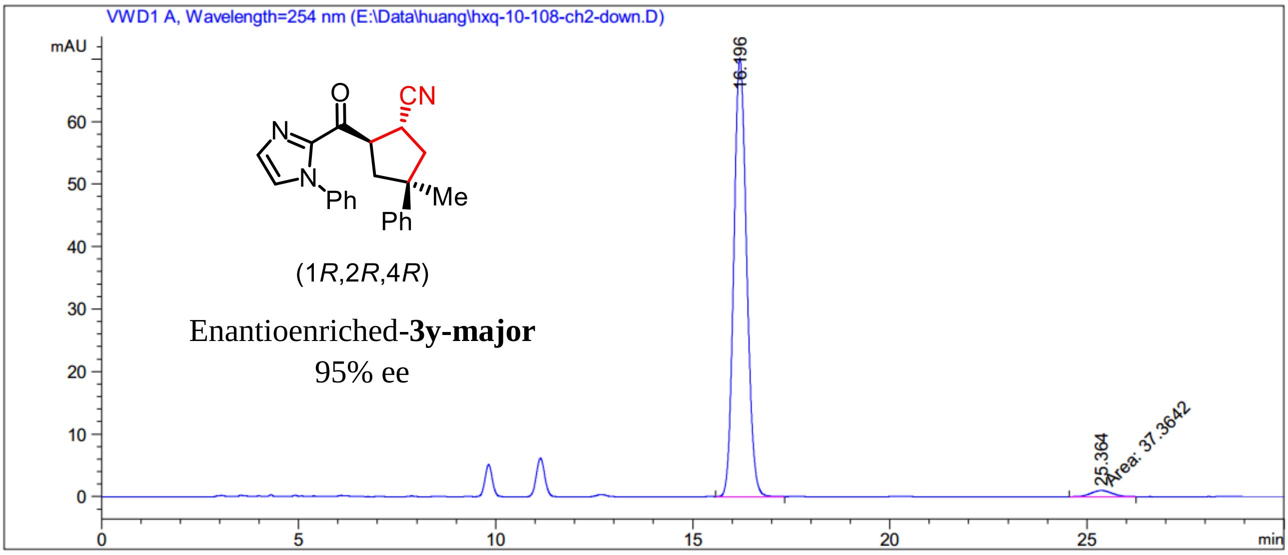


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.983	BB	0.1984	164.77007	12.78825	0.9132
2	9.889	BV	0.2245	26.09563	1.84773	0.1446
3	10.322	VB	0.3443	1.24289e4	545.83160	68.8883
4	21.969	BB	0.7939	5422.36426	103.87320	30.0538

Figure S32. HPLC traces of *rac*-**3x** (reference) and enantioenriched-**3x**.

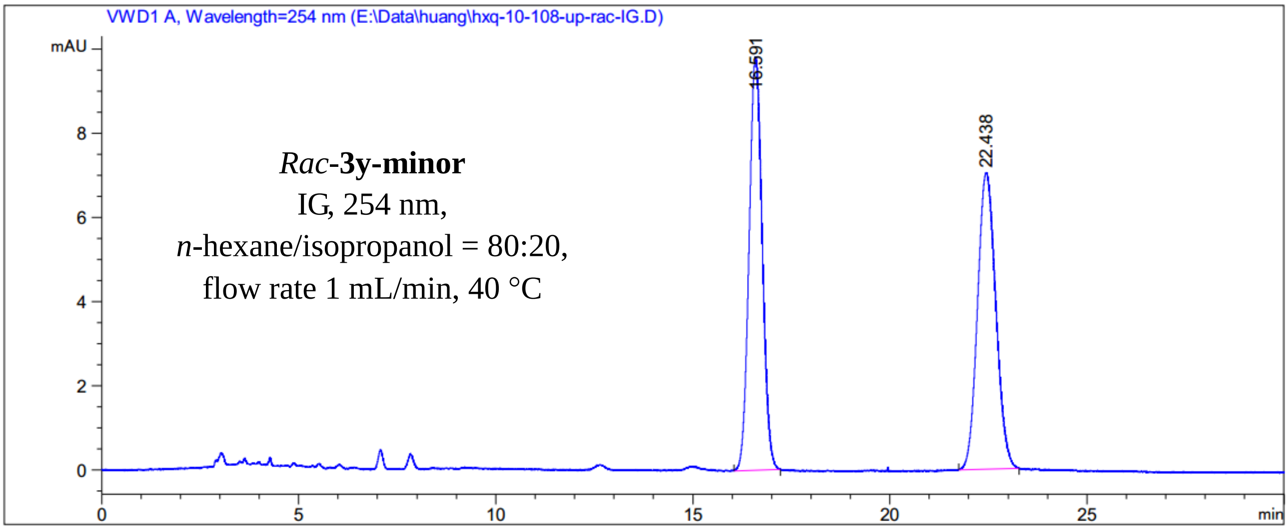


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.396	BV R	0.2660	454.11343	20.10862	50.2922
2	25.473	BV R	0.4292	448.83691	12.24317	49.7078

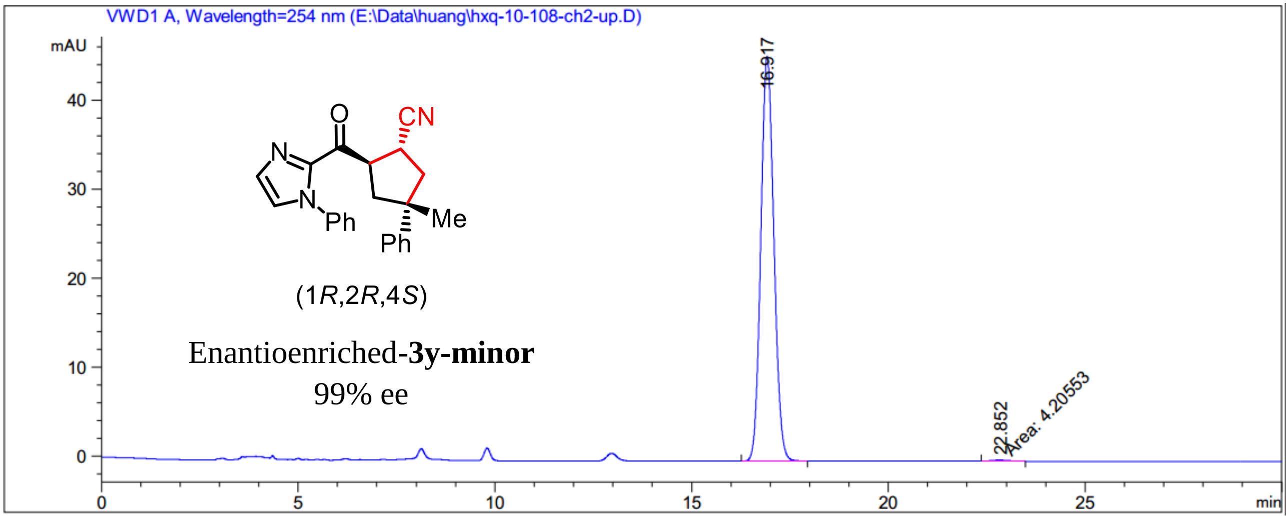


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.196	BB	0.3533	1589.04614	70.14285	97.7027
2	25.364	MM	0.6262	37.36415	9.94408e-1	2.2973

Figure S33. HPLC traces of *rac*-**3y-major** (reference) and enantioenriched-**3y-major**.

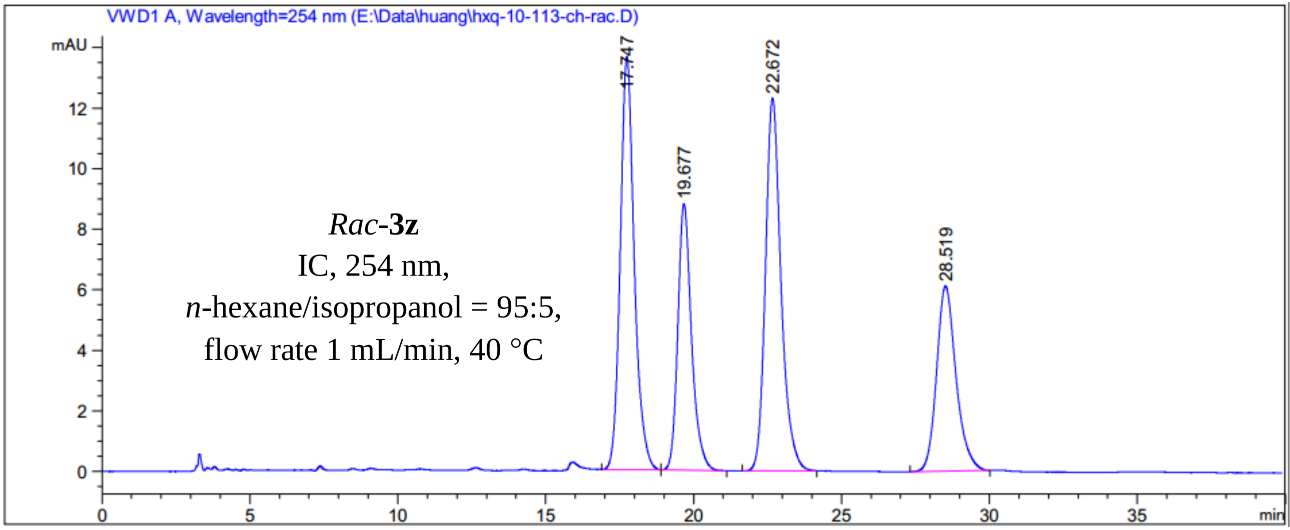


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.591	BB	0.2747	227.52570	9.82230	50.0300
2	22.438	BB	0.3781	227.25291	7.04927	49.9700

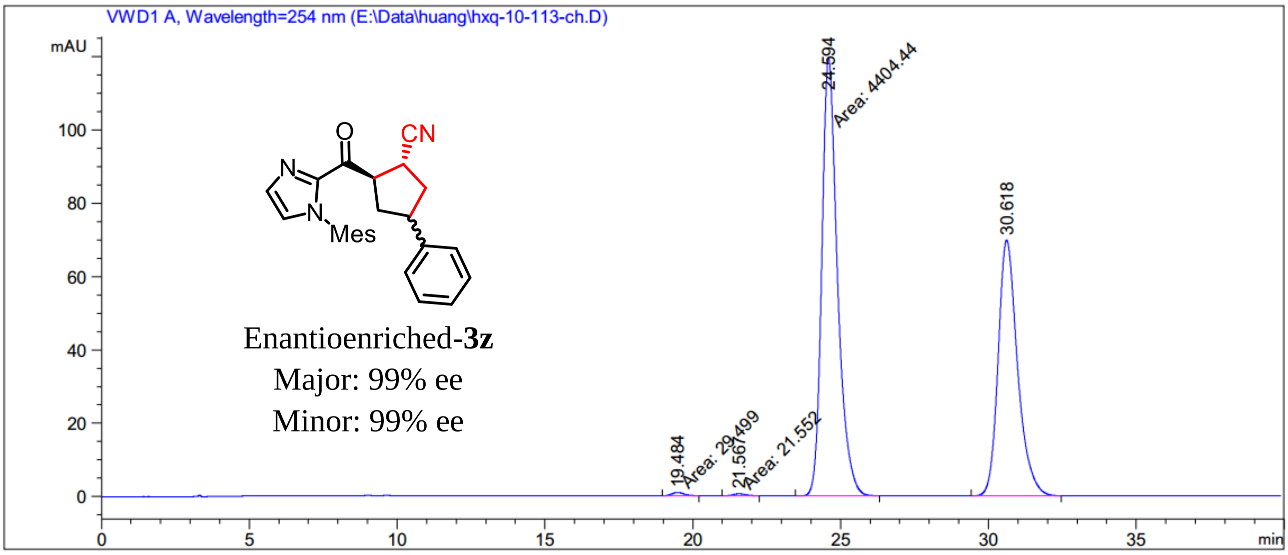


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.917	BB	0.3603	1049.79688	45.48403	99.6010
2	22.852	MM	0.5304	4.20553	1.32142e-1	0.3990

Figure S34. HPLC traces of *rac*-**3y-minor** (reference) and enantioenriched-**3y-minor**.

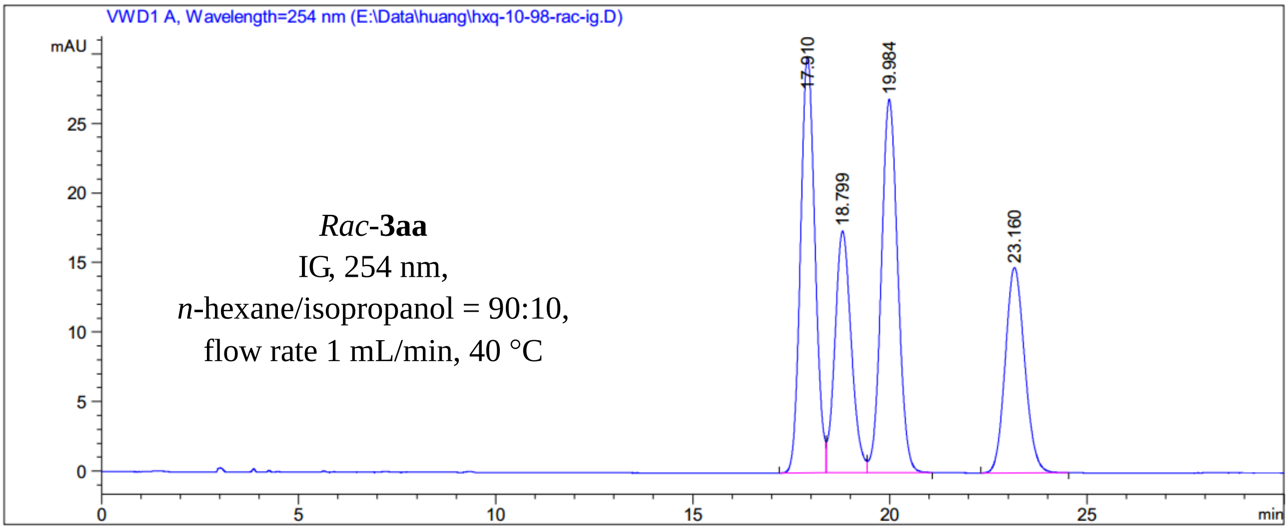


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.747	BB	0.4961	449.23978	13.64692	30.6765
2	19.677	BB	0.4843	283.38278	8.80899	19.3509
3	22.672	BB	0.5529	452.01569	12.32330	30.8661
4	28.519	BB	0.6796	279.80408	6.11798	19.1065

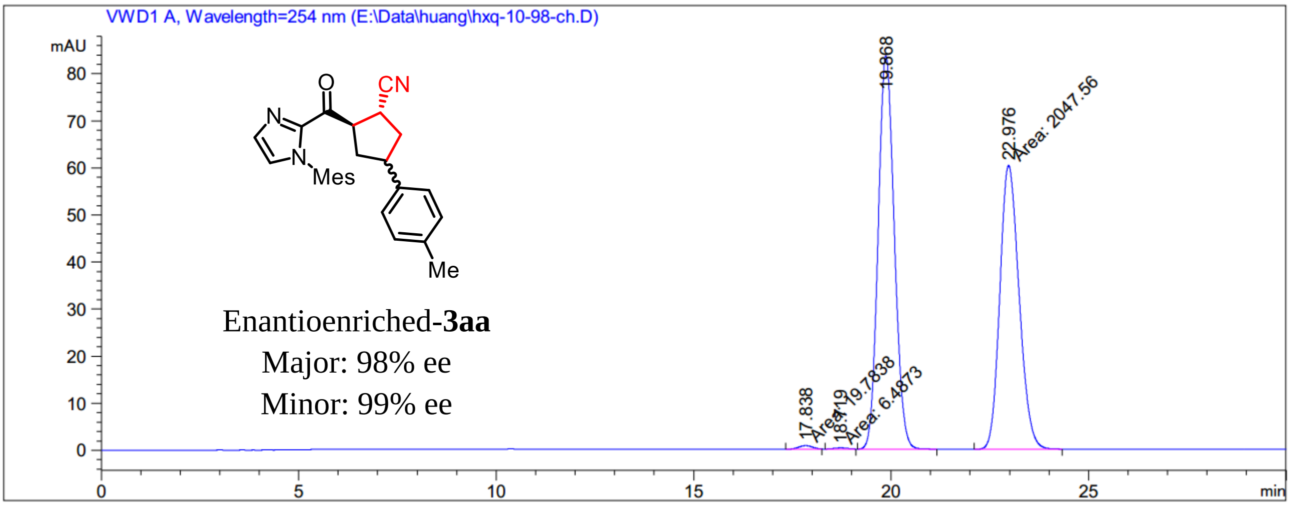


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.484	MM	0.4992	29.49899	9.84925e-1	0.3860
2	21.567	MM	0.5638	21.55196	6.37083e-1	0.2820
3	24.594	MM	0.6150	4404.44336	119.35650	57.6309
4	30.618	BB	0.6909	3187.00366	69.77203	41.7011

Figure S35. HPLC traces of *rac*-**3z** (reference) and enantioenriched-**3z**.

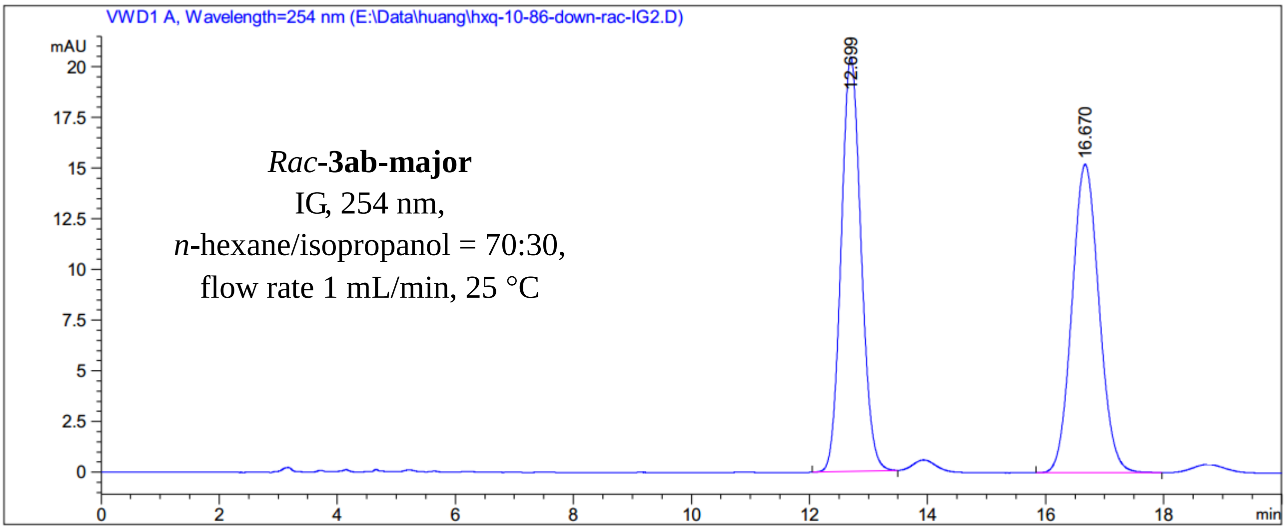


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.910	BV	0.3965	762.94550	29.91999	29.8945
2	18.799	VV	0.4461	502.48816	17.39136	19.6890
3	19.984	VB	0.4508	779.45905	26.83969	30.5416
4	23.160	BB	0.5296	507.23071	14.77066	19.8749

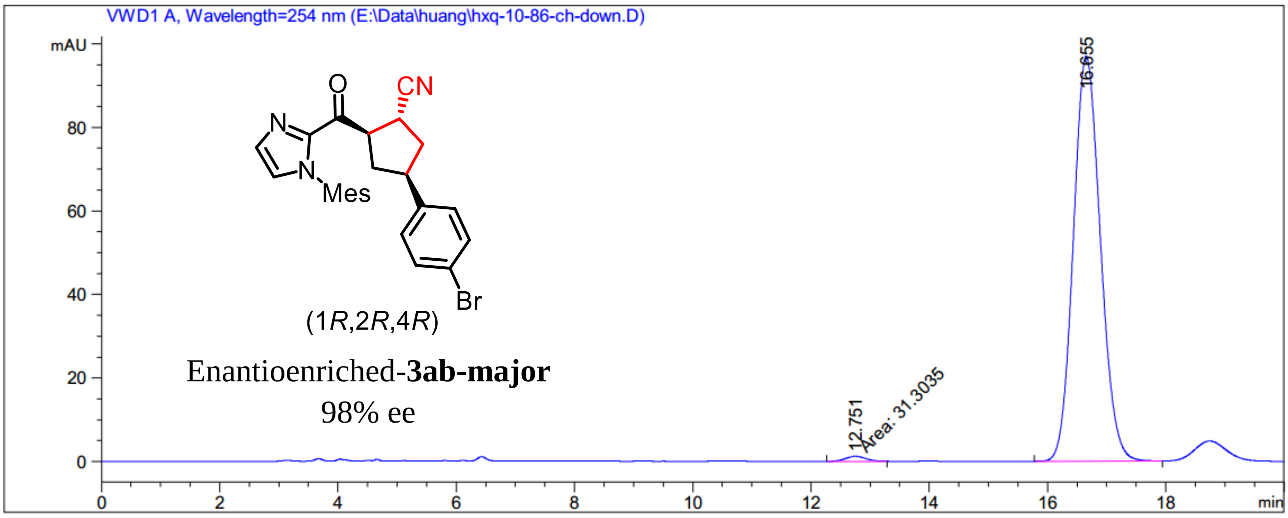


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.838	MM	0.4251	19.78383	7.75675e-1	0.4446
2	18.719	MM	0.4106	6.48730	2.63335e-1	0.1458
3	19.868	BB	0.4438	2376.29834	83.55549	53.3984
4	22.976	MM	0.5660	2047.56116	60.29038	46.0113

Figure S36. HPLC traces of *rac*-**3aa** (reference) and enantioenriched-**3aa**.

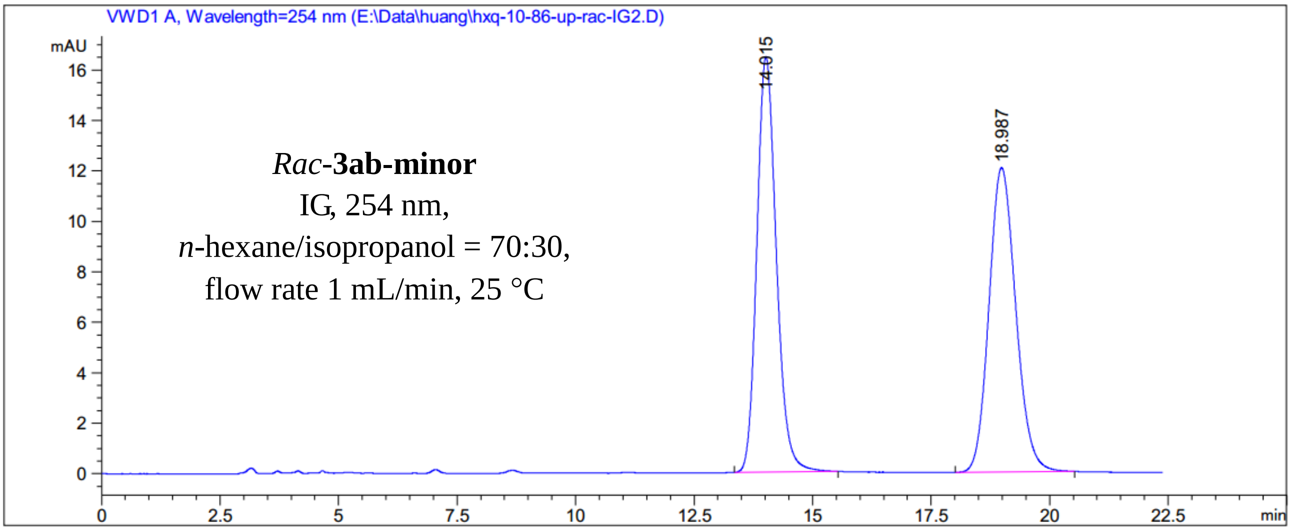


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.699	BB	0.3645	479.08365	20.43833	49.6926
2	16.670	BB	0.4961	485.01077	15.20659	50.3074

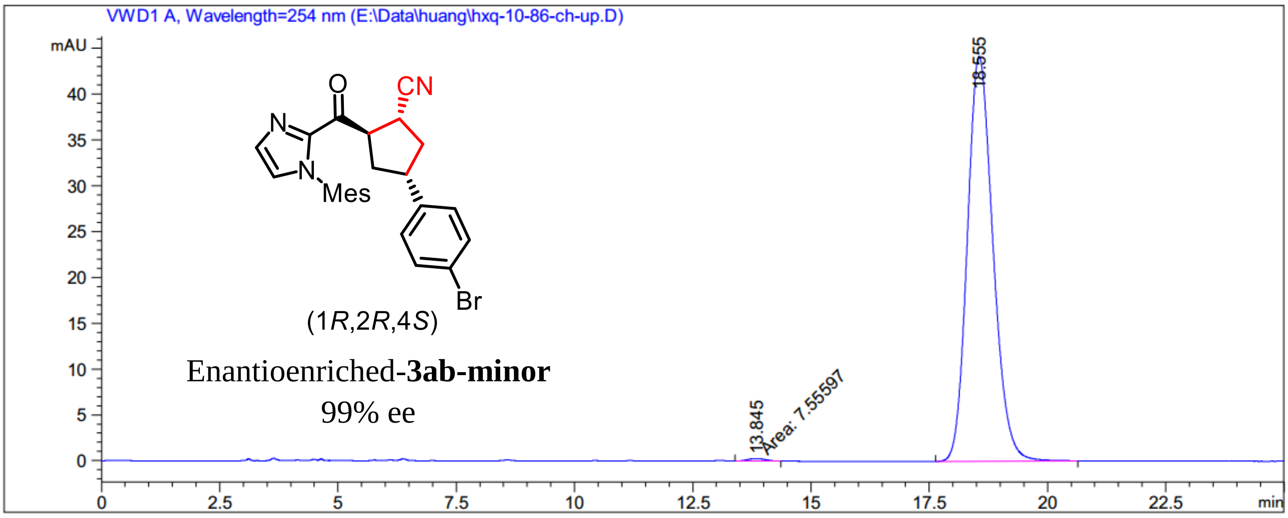


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.751	MM	0.4167	31.30351	1.25219	1.0073
2	16.655	BB	0.4943	3076.40552	96.91998	98.9927

Figure S37. HPLC traces of *rac*-**3ab-major** (reference) and enantioenriched-**3ab-major**.

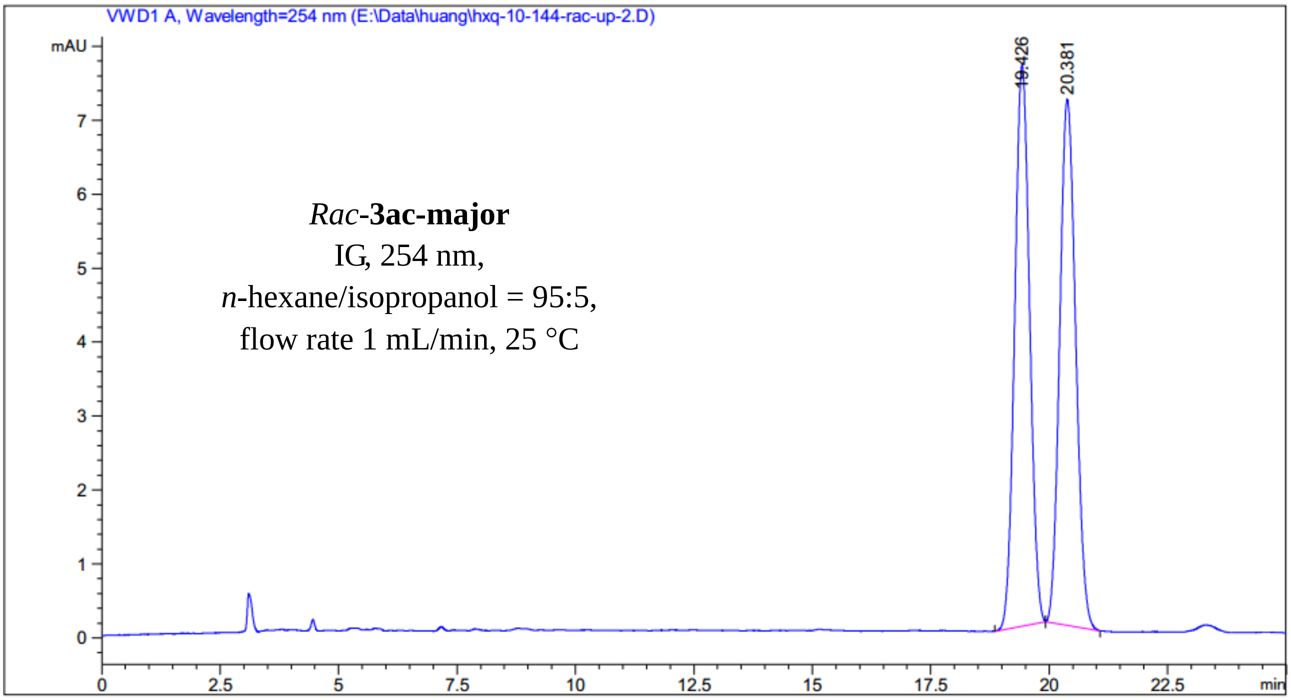


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.015	BB	0.4397	470.96573	16.46689	49.8191
2	18.987	BB	0.5997	474.38660	12.06562	50.1809

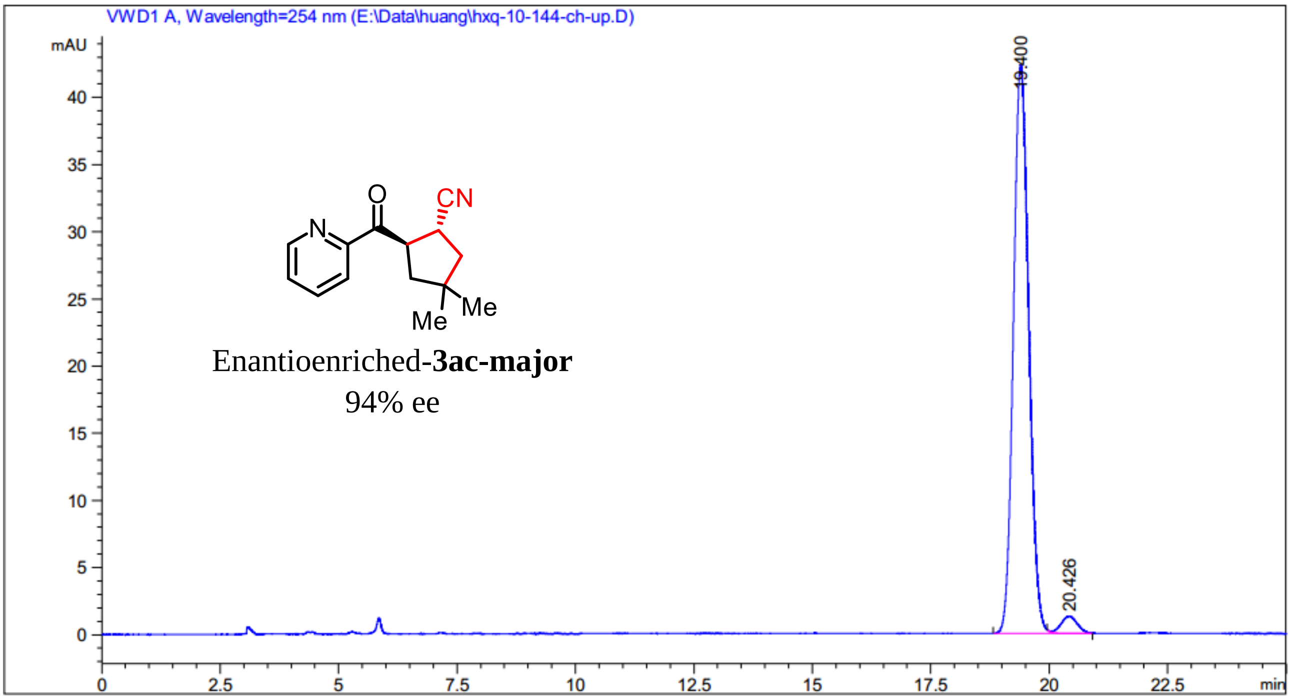


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.845	MM	0.4410	7.55597	2.85580e-1	0.4519
2	18.555	BB	0.5826	1664.38098	44.16864	99.5481

Figure S38. HPLC traces of *rac*-**3ab-minor** (reference) and enantioenriched-**3ab-minor**.

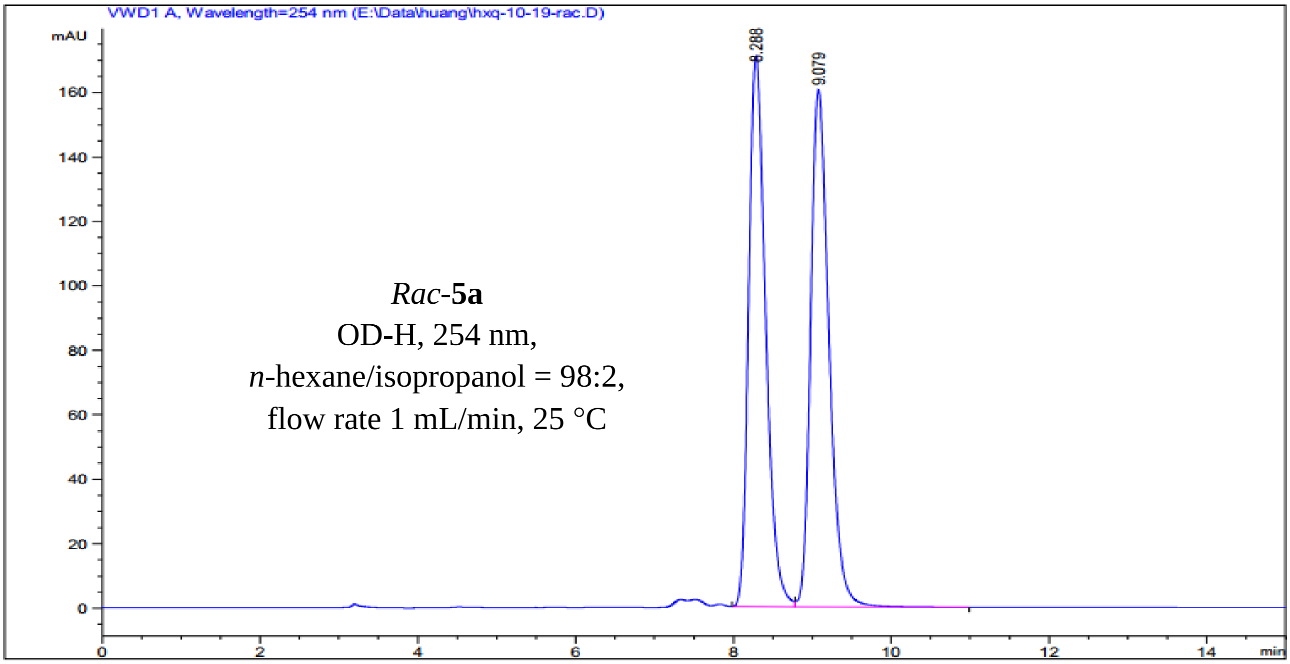


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.426	BB	0.3418	166.39919	7.58879	49.9946
2	20.381	BB	0.3662	166.43530	7.10838	50.0054

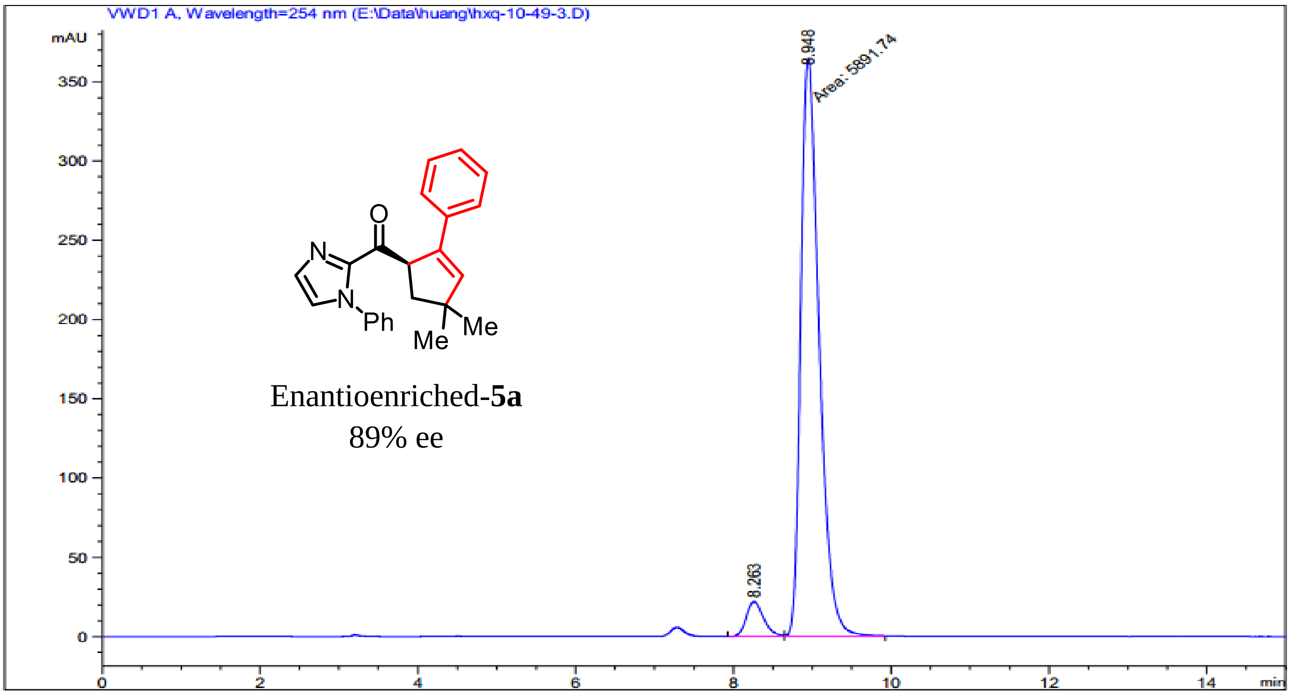


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.400	BV R	0.2743	952.32007	42.35402	96.9413
2	20.426	VB E	0.2771	30.04744	1.26945	3.0587

Figure S39. HPLC traces of *rac*-**3ac-major** (reference) and enantioenriched-**3ac-major**.

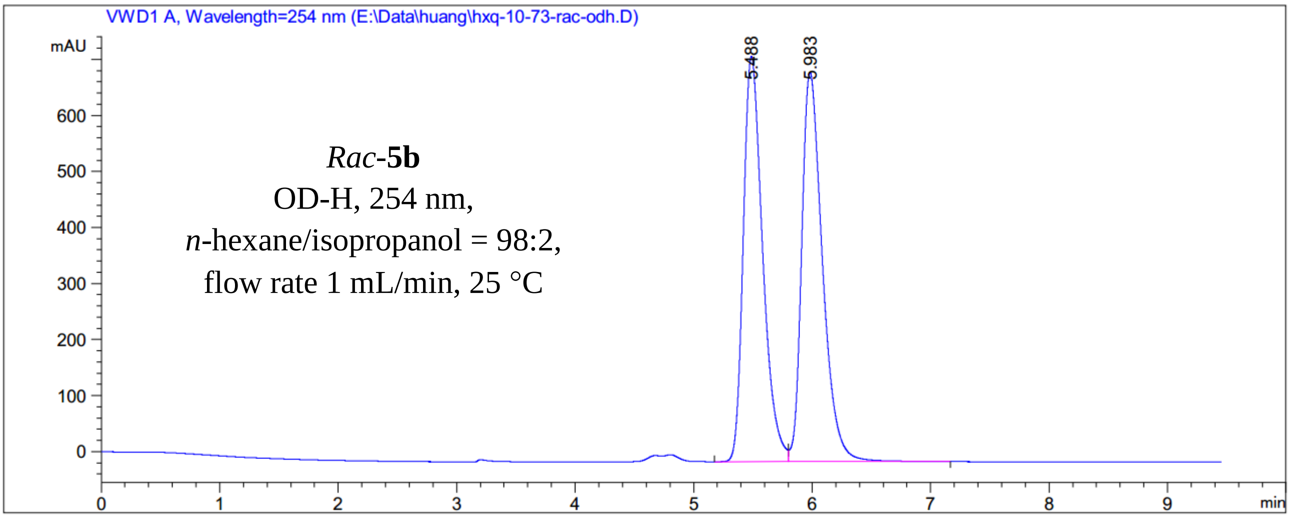


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.288	BV	0.2295	2557.35840	170.93152	49.6341
2	9.079	VB	0.2476	2595.06836	160.50223	50.3659

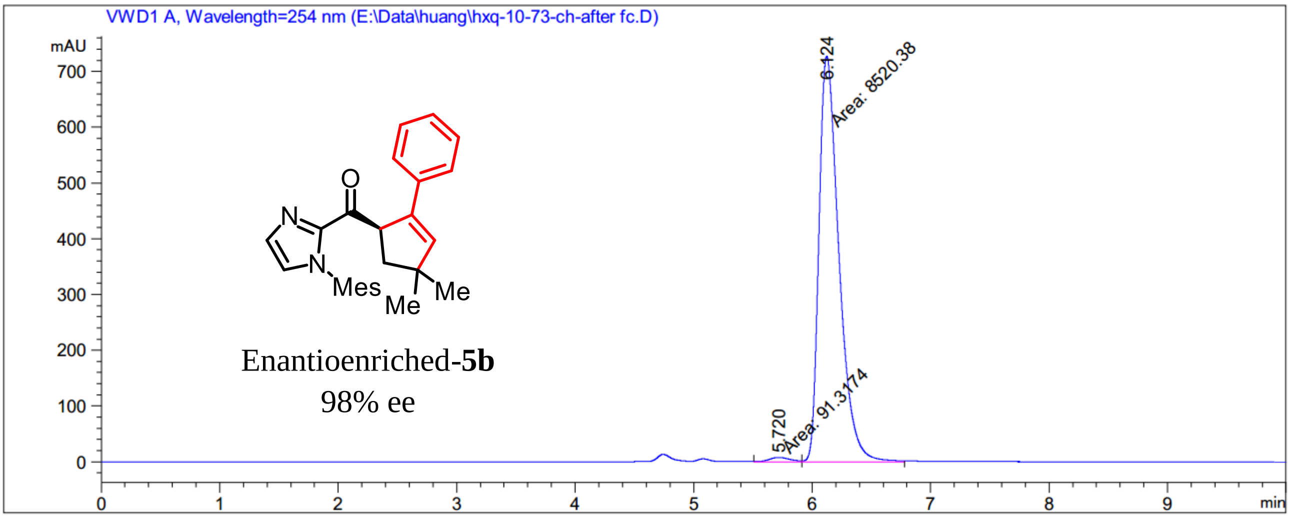


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.263	BV	0.2343	334.98352	21.91302	5.3798
2	8.948	MF	0.2694	5891.73682	364.53094	94.6202

Figure S40. HPLC traces of *rac*-**5a** (reference) and enantioenriched-**5a**.

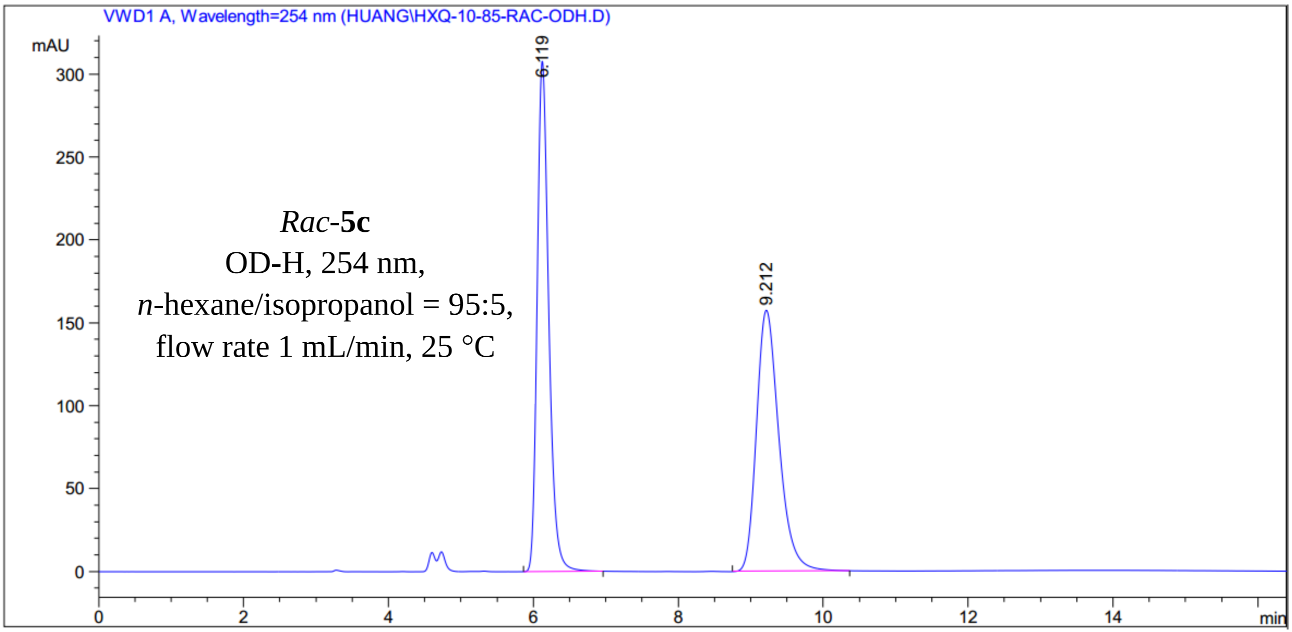


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.488	BV	0.1739	8207.83691	723.50726	49.2402
2	5.983	VV R	0.1830	8461.13477	694.92456	50.7598

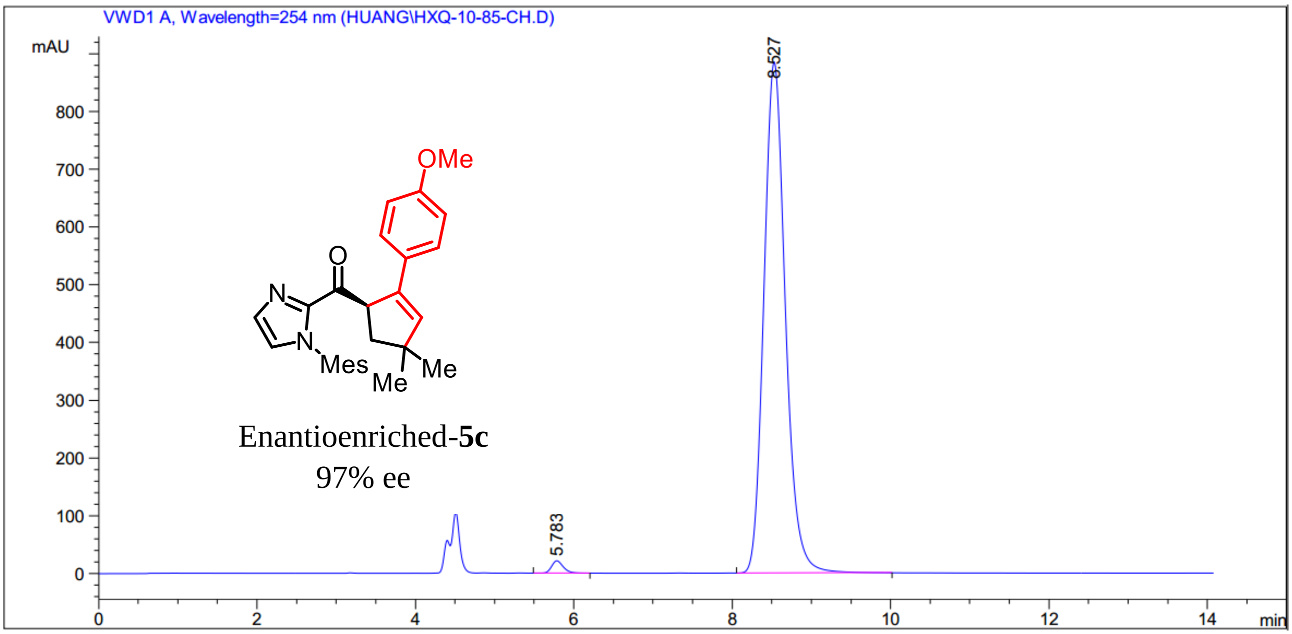


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.720	MF	0.1975	91.31738	7.70432	1.0604
2	6.124	FM	0.1952	8520.37891	727.31006	98.9396

Figure S41. HPLC traces of *rac*-**5b** (reference) and enantioenriched-**5b**.

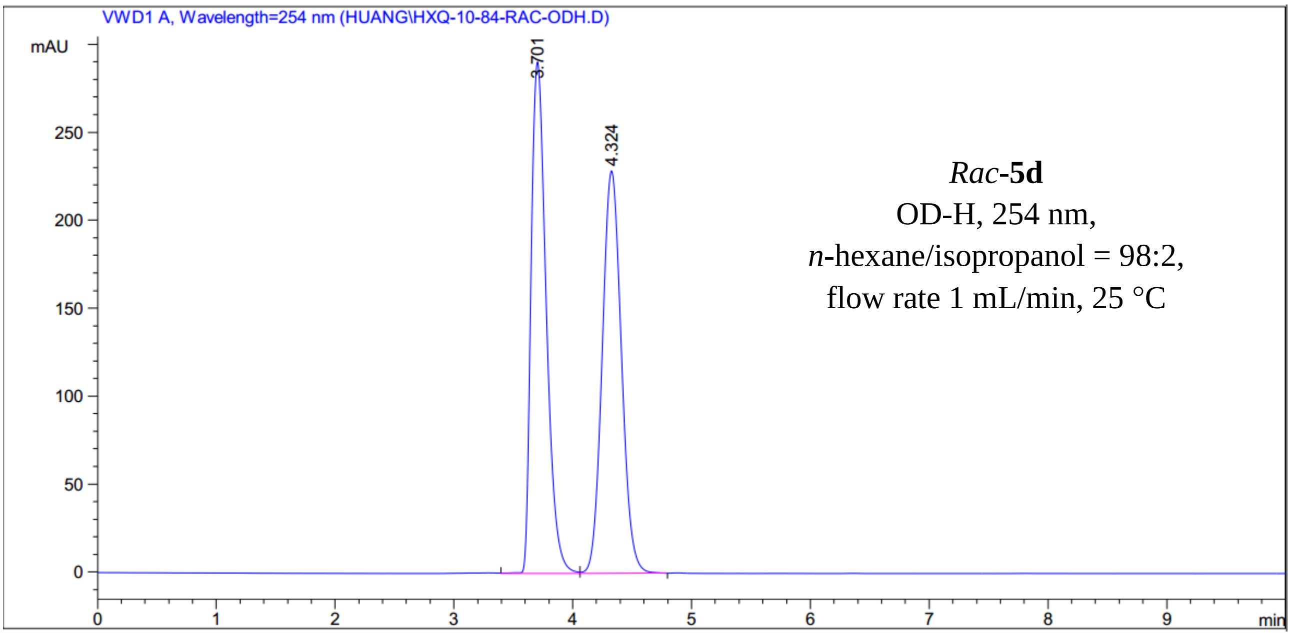


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.119	BB	0.1699	3409.68091	307.97382	50.0980
2	9.212	BB	0.3302	3396.34521	157.51572	49.9020

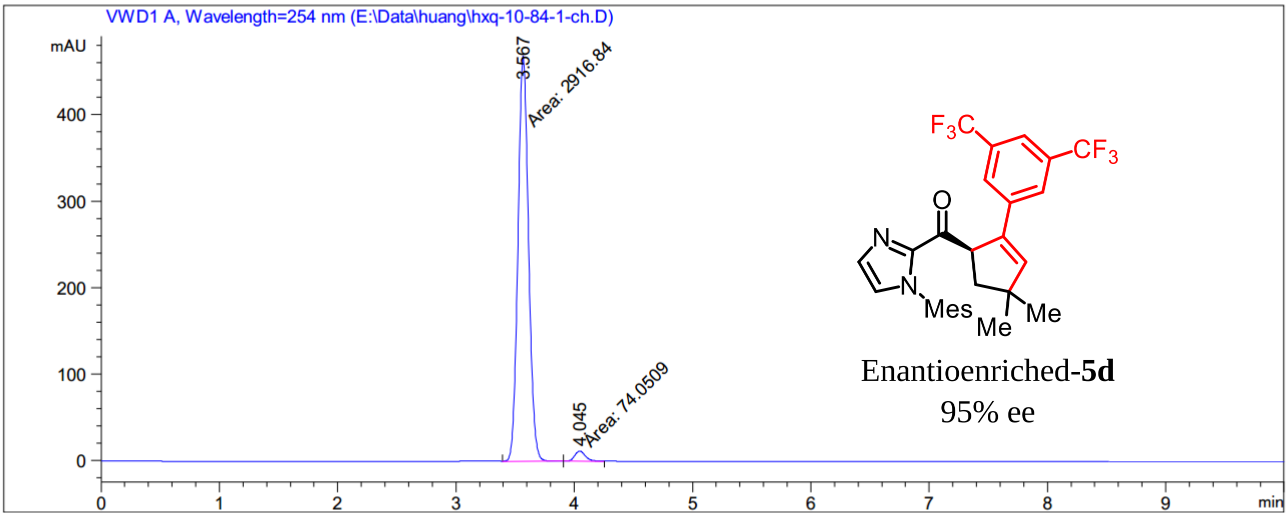


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.783	VB	0.1580	221.08786	21.46333	1.3105
2	8.527	VB	0.2894	1.66496e4	885.03131	98.6895

Figure S42. HPLC traces of *rac*-**5c** (reference) and enantioenriched-**5c**.

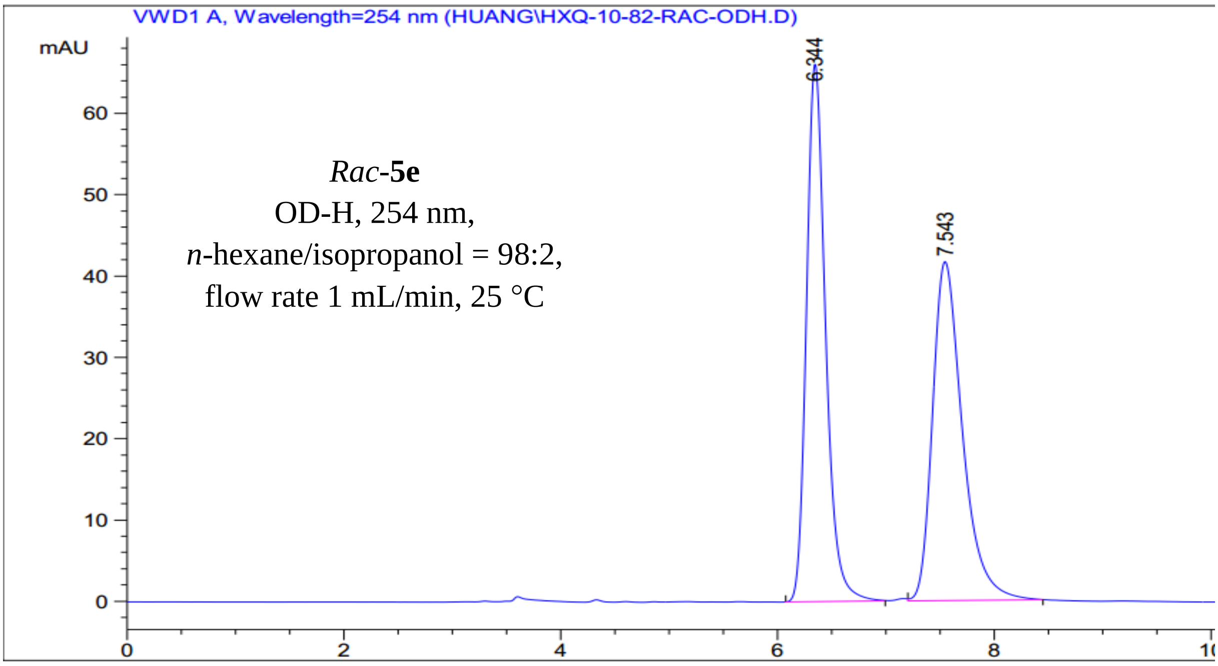


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	3.701	VV	0.1399	2579.30444	290.84387	50.0799
2	4.324	VV	0.1763	2571.07202	228.76311	49.9201

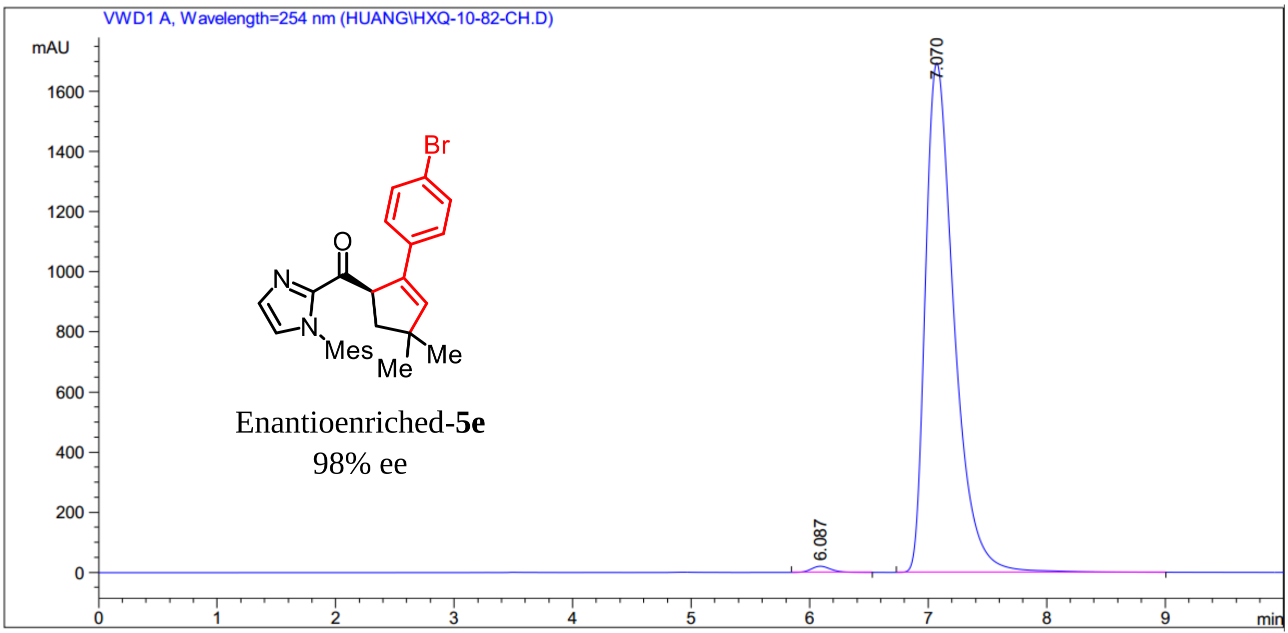


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.567	FM	0.1037	2916.84277	468.80411	97.5241
2	4.045	MF	0.1040	74.05090	11.86971	2.4759

Figure S43. HPLC traces of *rac*-**5d** (reference) and enantioenriched-**5d**.

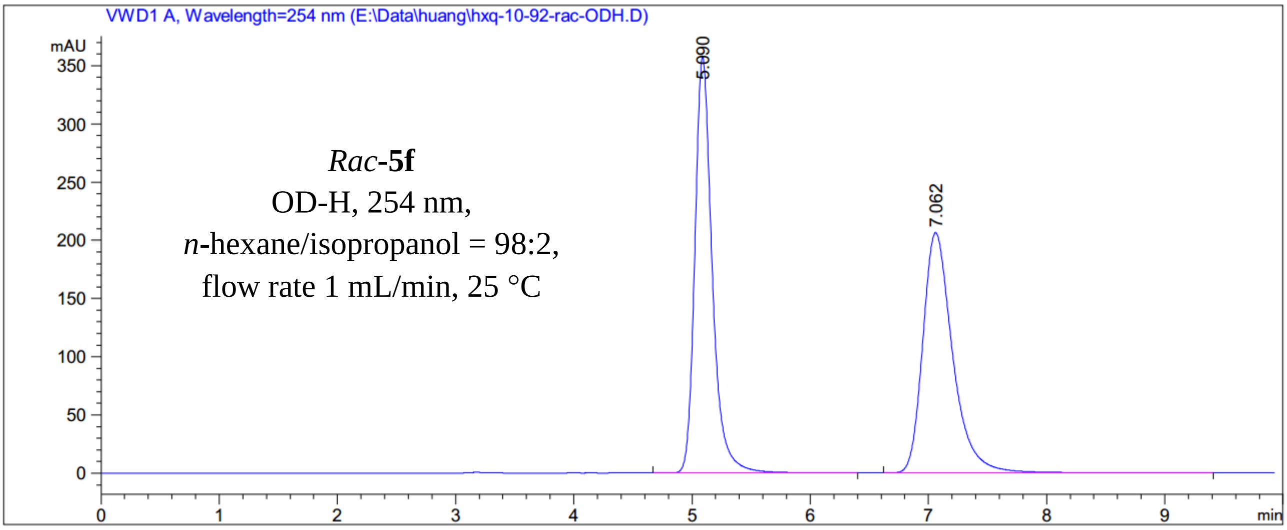


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.344	BB	0.1882	811.03503	66.11780	50.2932
2	7.543	VB	0.2912	801.57813	41.71088	49.7068

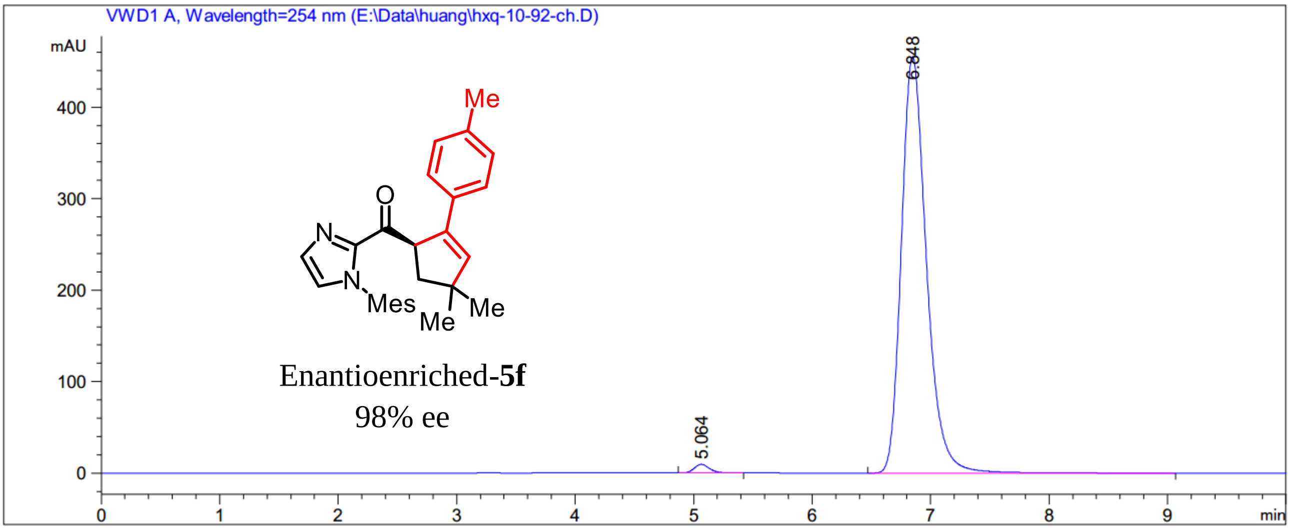


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.087	BB	0.1776	239.04335	20.59402	0.8328
2	7.070	BB	0.2571	2.84646e4	1694.70337	99.1672

Figure S44. HPLC traces of *rac*-**5e** (reference) and enantioenriched-**5e**.

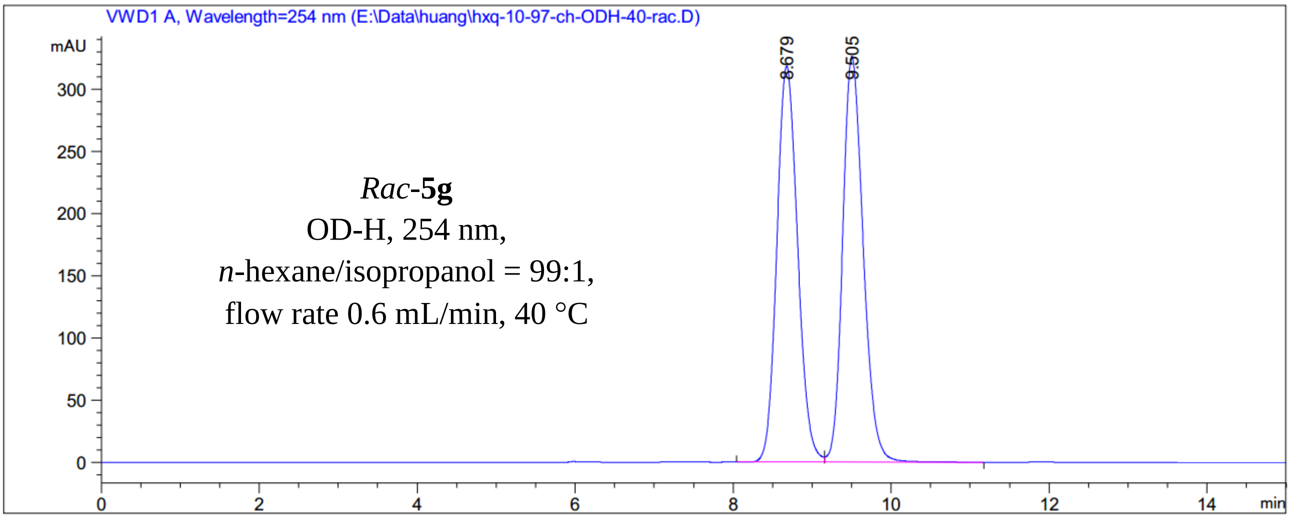


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.090	BB	0.1550	3647.27637	357.53812	50.1045
2	7.062	BB	0.2664	3632.06689	206.30272	49.8955

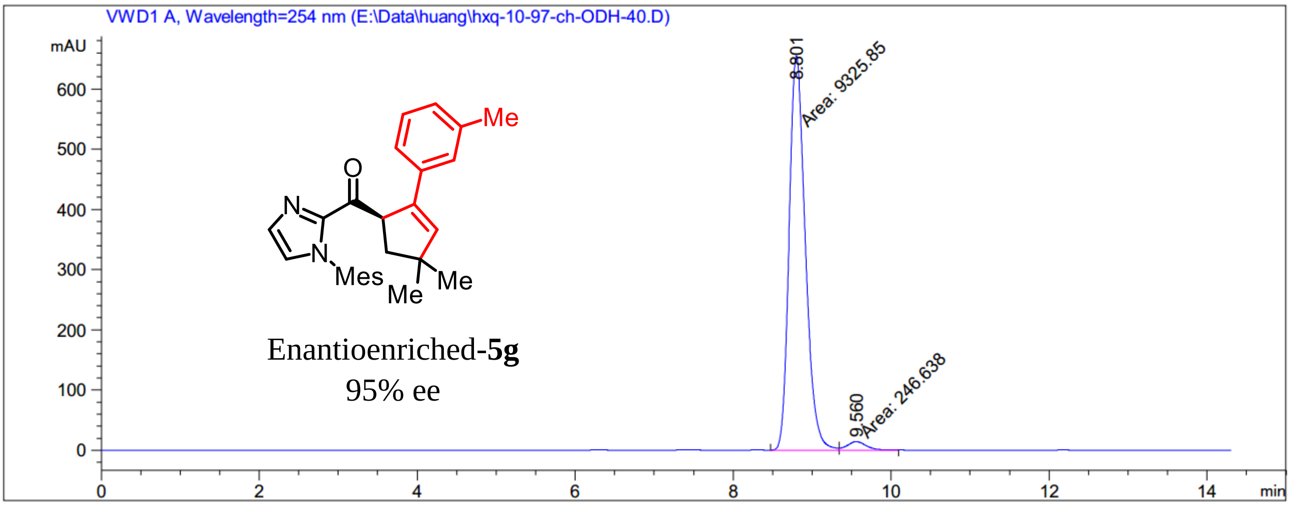


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.064	BB	0.1369	84.21169	9.45357	1.2424
2	6.848	BB	0.2246	6693.78320	455.15359	98.7576

Figure S45. HPLC traces of *rac*-**5f** (reference) and enantioenriched-**5f**.

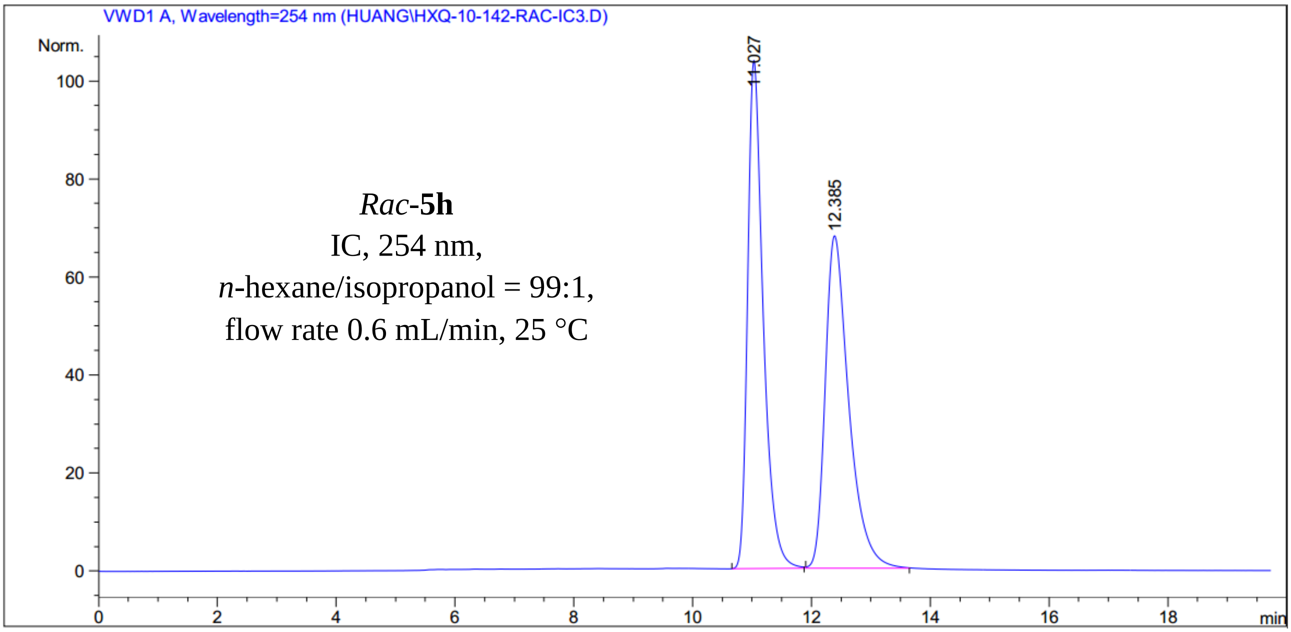


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.679	BV	0.2866	5831.99072	318.48550	49.7295
2	9.505	VB	0.2797	5895.43896	326.45392	50.2705

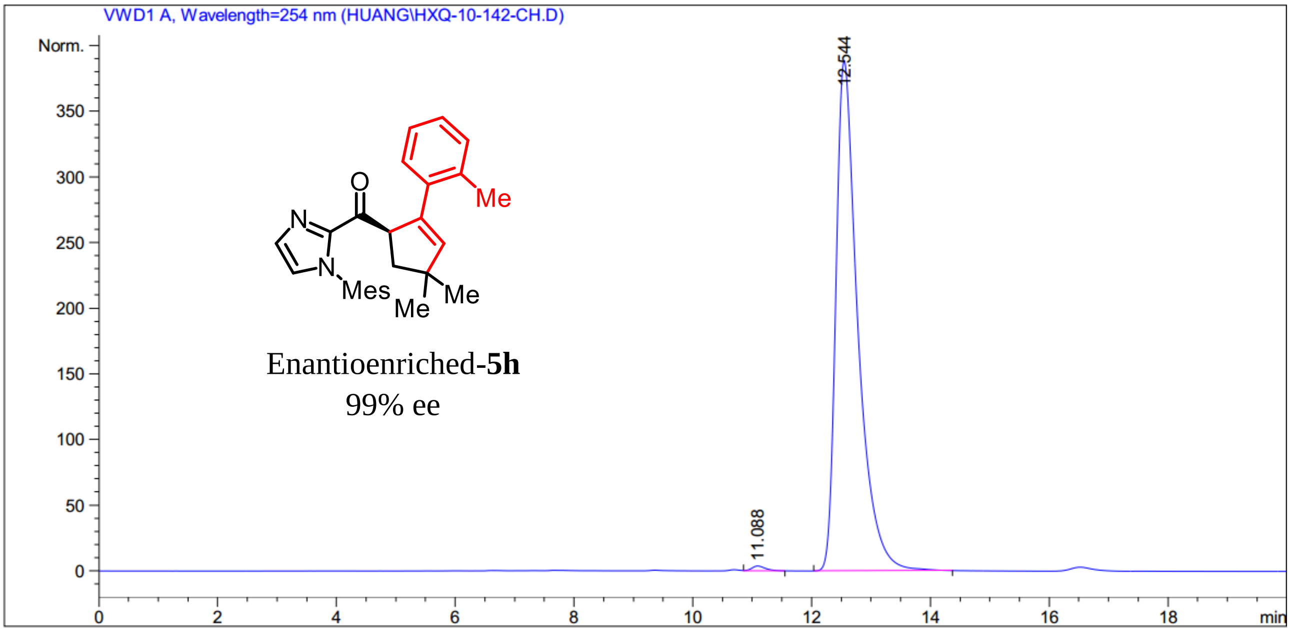


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.801	FM	0.2373	9325.84766	655.06610	97.4235
2	9.560	MF	0.2867	246.63802	14.33699	2.5765

Figure S46. HPLC traces of *rac*-**5g** (reference) and enantioenriched-**5g**.

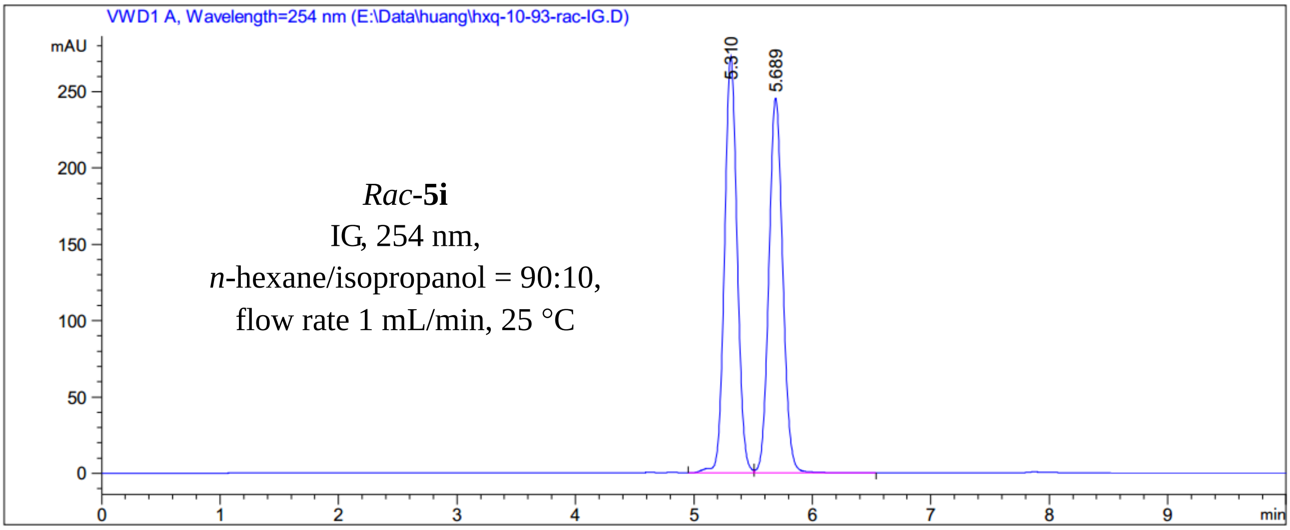


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.027	BB	0.2759	1896.03308	103.68722	50.2584
2	12.385	BB	0.4143	1876.53503	67.87639	49.7416

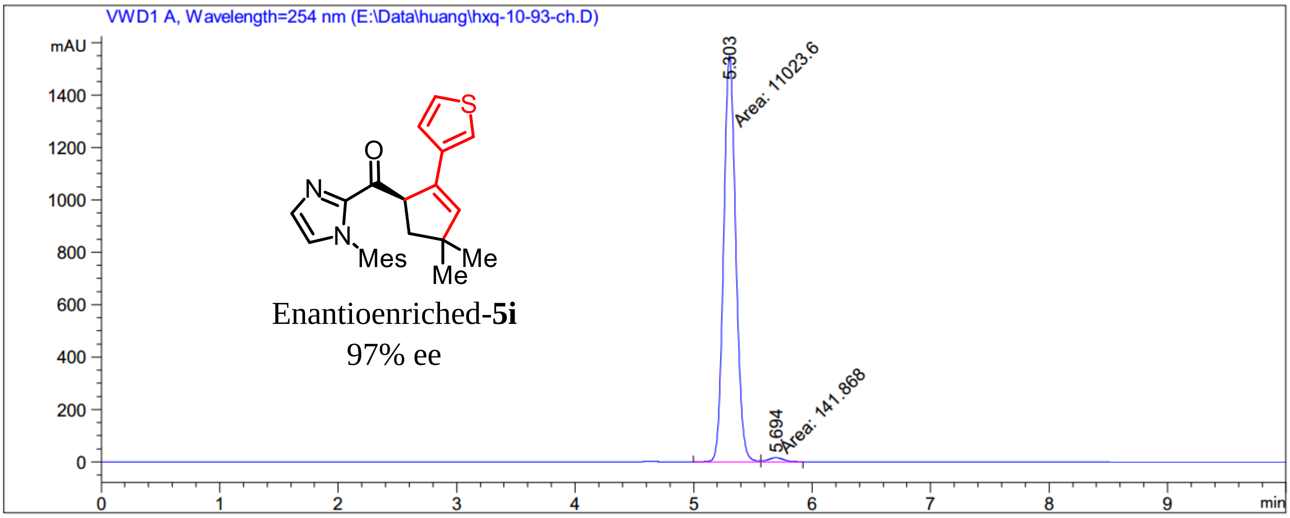


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.088	VB	0.2447	60.87960	3.72177	0.6065
2	12.544	BB	0.3810	9976.93359	388.72577	99.3935

Figure S47. HPLC traces of *rac*-**5h** (reference) and enantioenriched-**5h**.

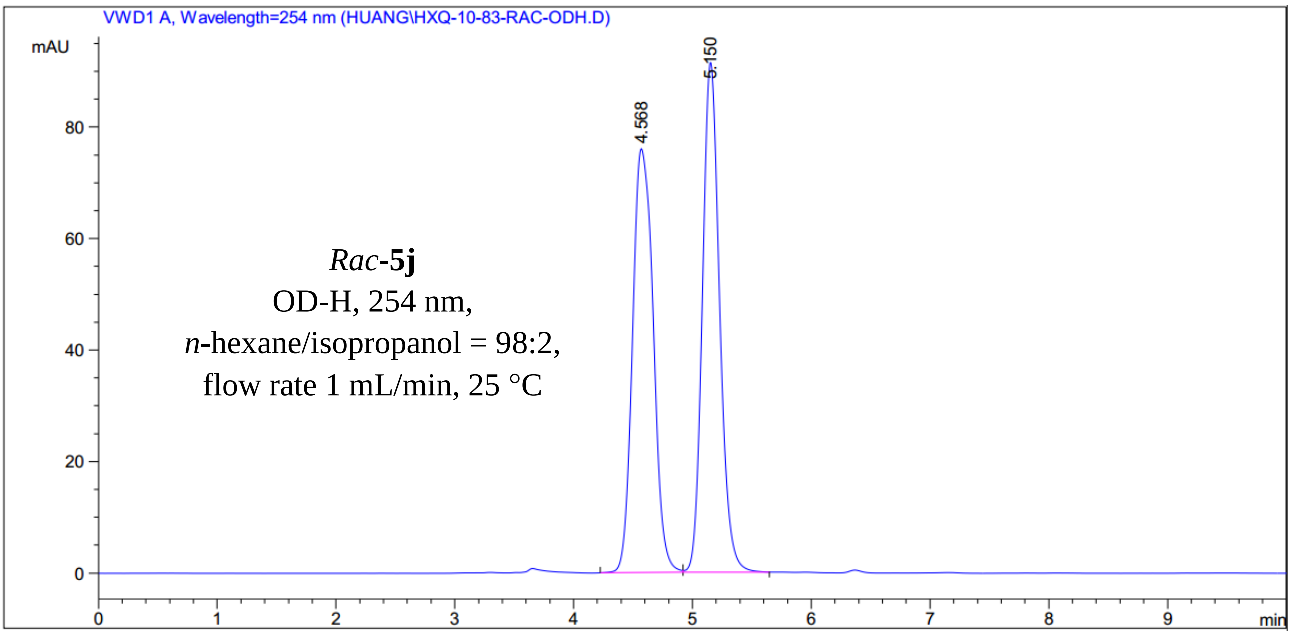


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.310	VV R	0.1146	2024.38123	272.76831	50.3663
2	5.689	VB	0.1257	1994.93762	245.66098	49.6337

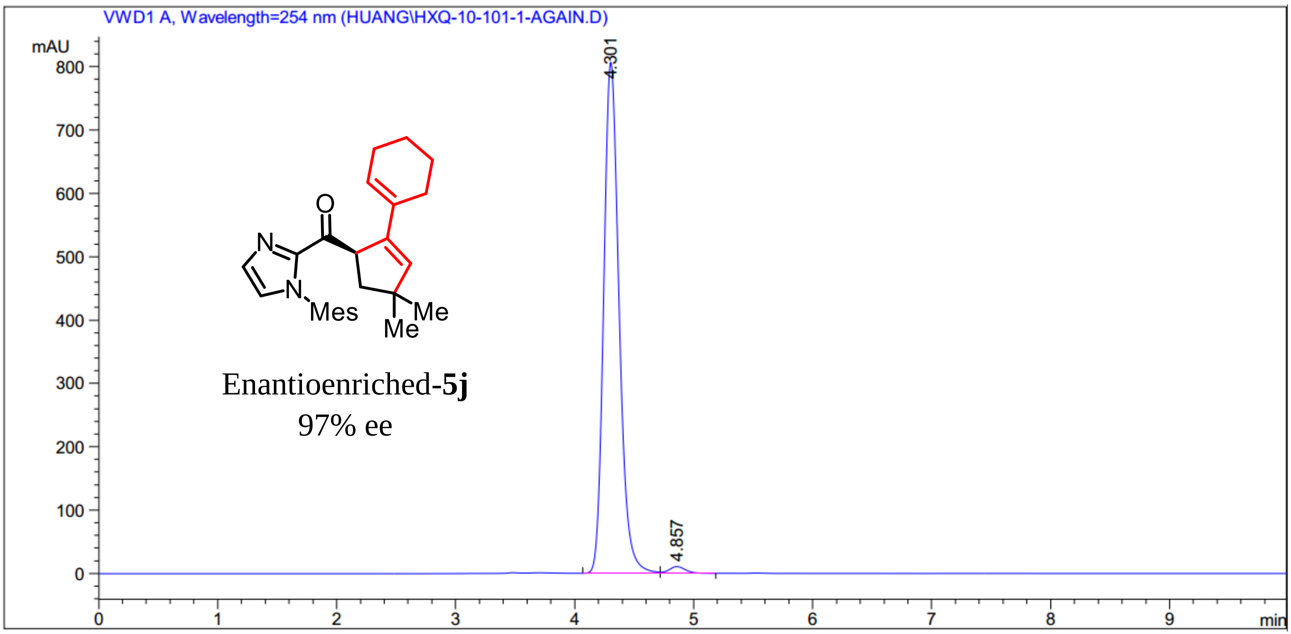


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.303	MF	0.1187	1.10236e4	1547.83289	98.7294
2	5.694	MF	0.1477	141.86844	16.01128	1.2706

Figure S48. HPLC traces of *rac*-**5i** (reference) and enantioenriched-**5i**.

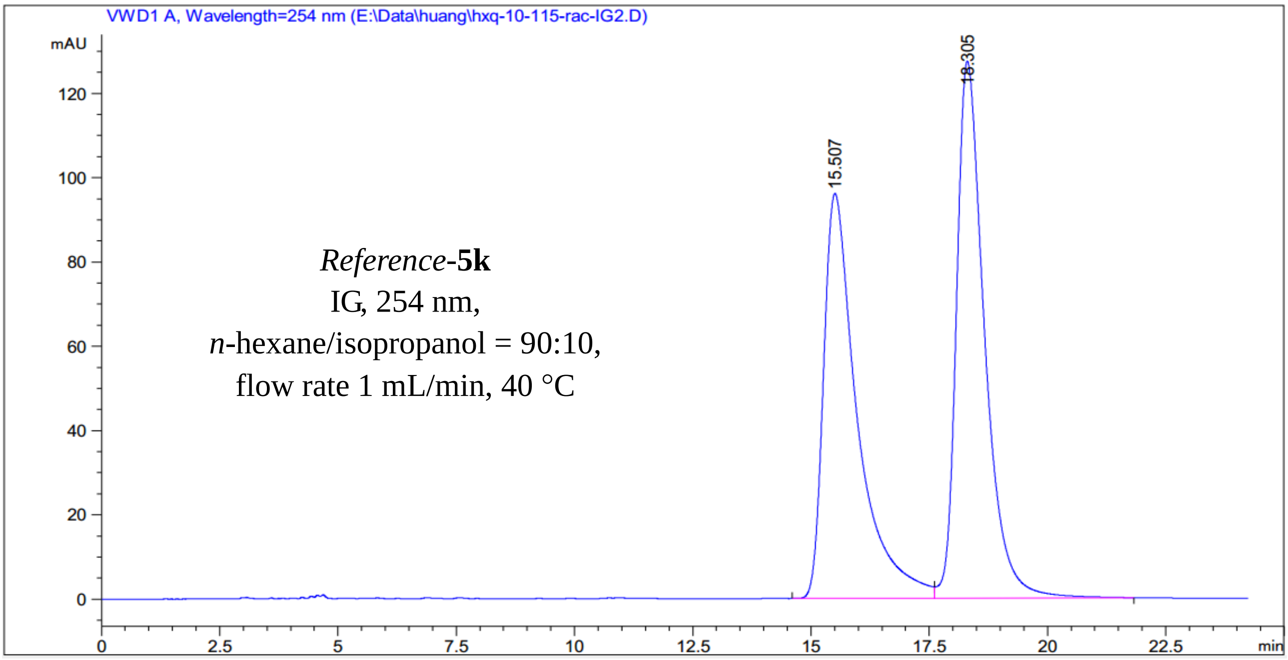


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.568	BV	0.1953	921.63800	76.05346	50.0211
2	5.150	VB	0.1538	920.86212	91.52116	49.9789

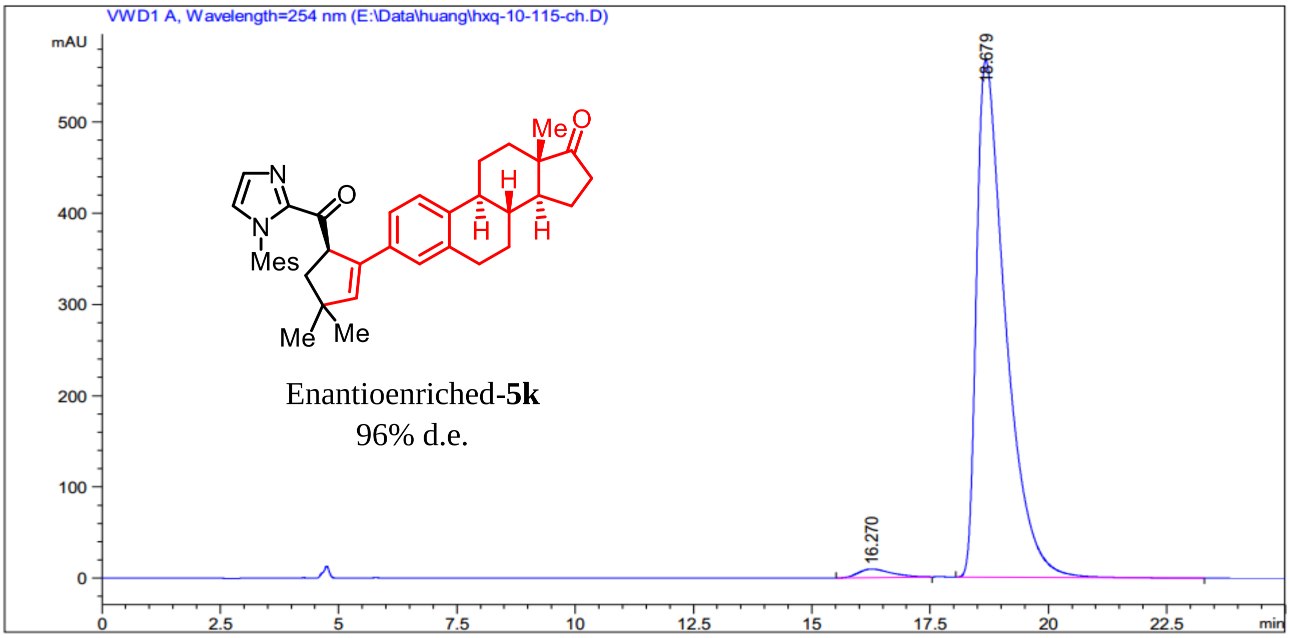


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.301	BV	0.1398	7257.13184	807.35876	98.5996
2	4.857	VB	0.1457	103.07510	10.71280	1.4004

Figure S49. HPLC traces of *rac*-**5j** (reference) and enantioenriched-**5j**.

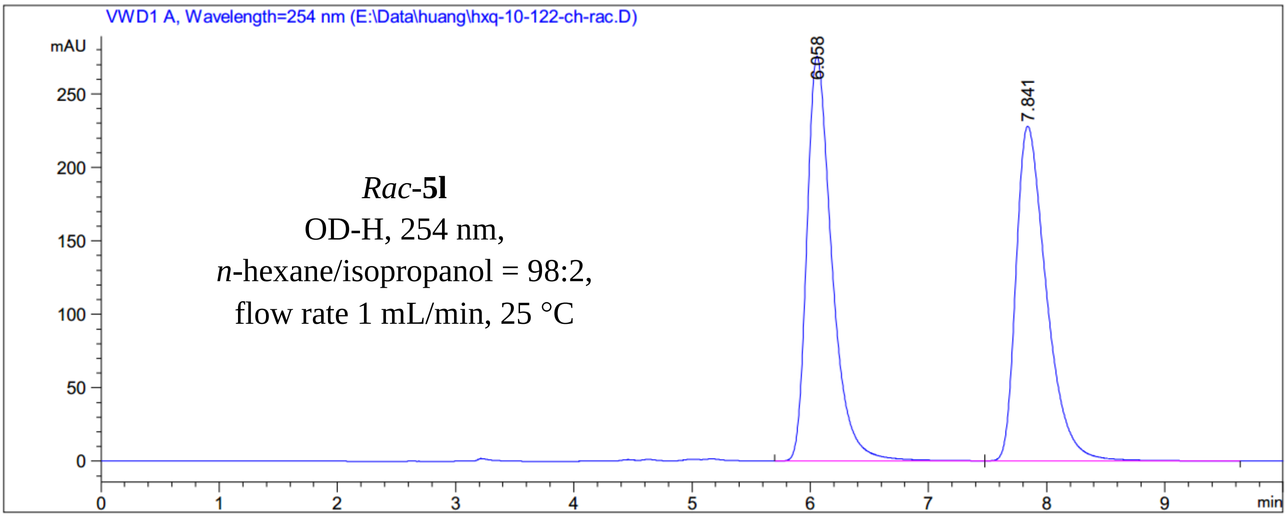


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.507	BV	0.7267	4767.10303	96.10558	47.5792
2	18.305	VB	0.6210	5252.19287	127.40385	52.4208

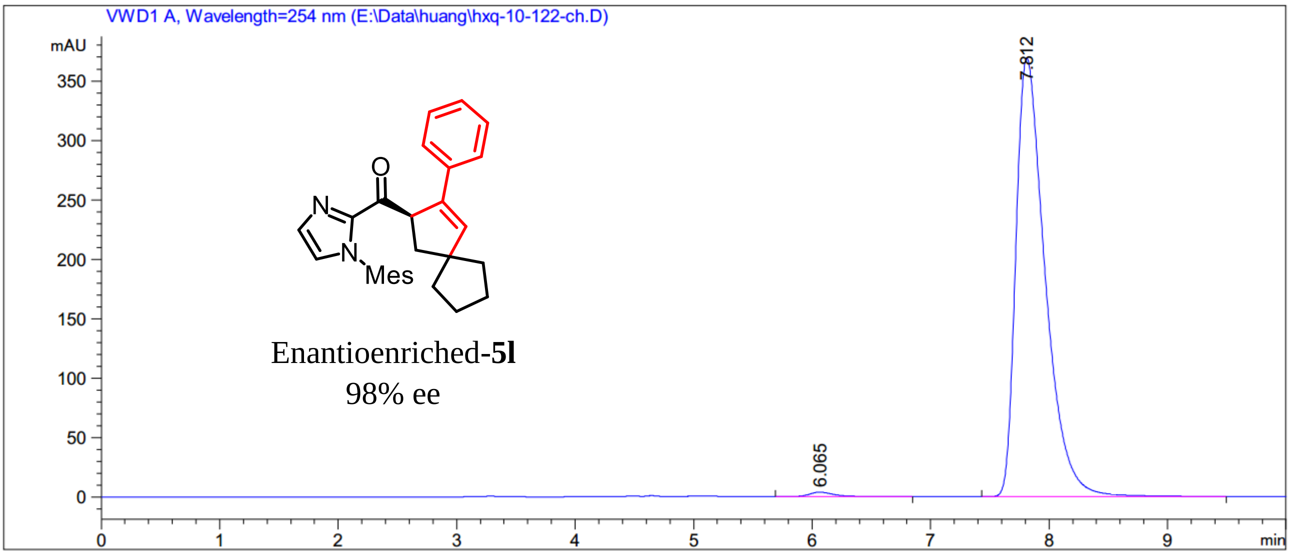


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.270	BB	0.7231	451.50937	9.38876	1.8318
2	18.679	BB	0.6305	2.41973e4	567.38843	98.1682

Figure S50. HPLC traces of *reference*-**5k** and enantioenriched-**5k**.

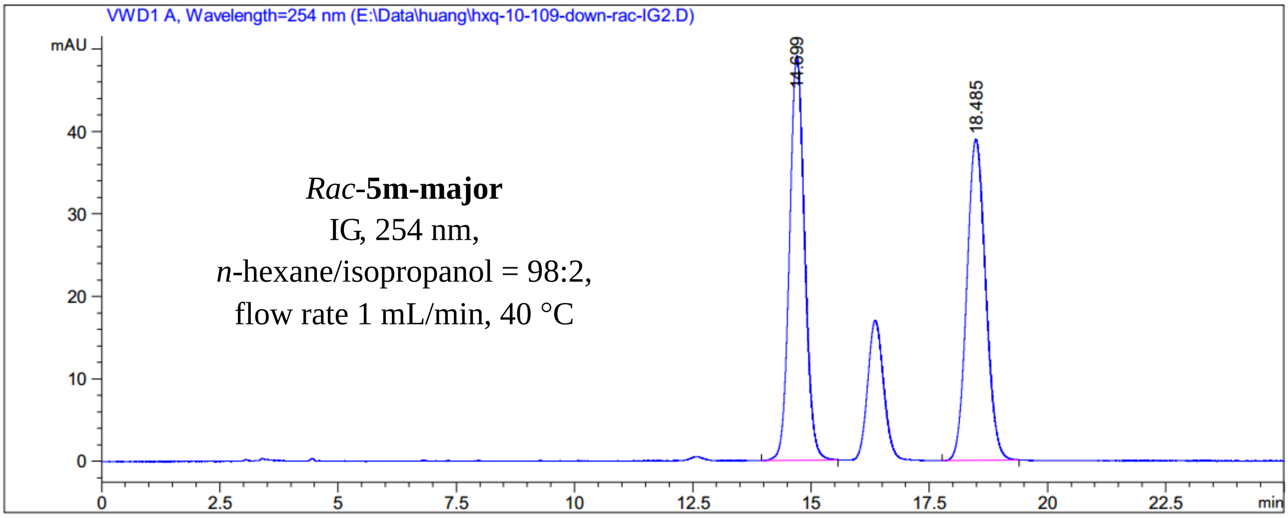


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.058	BB	0.2238	4057.08984	275.55753	49.9780
2	7.841	BB	0.2720	4060.66357	227.71599	50.0220

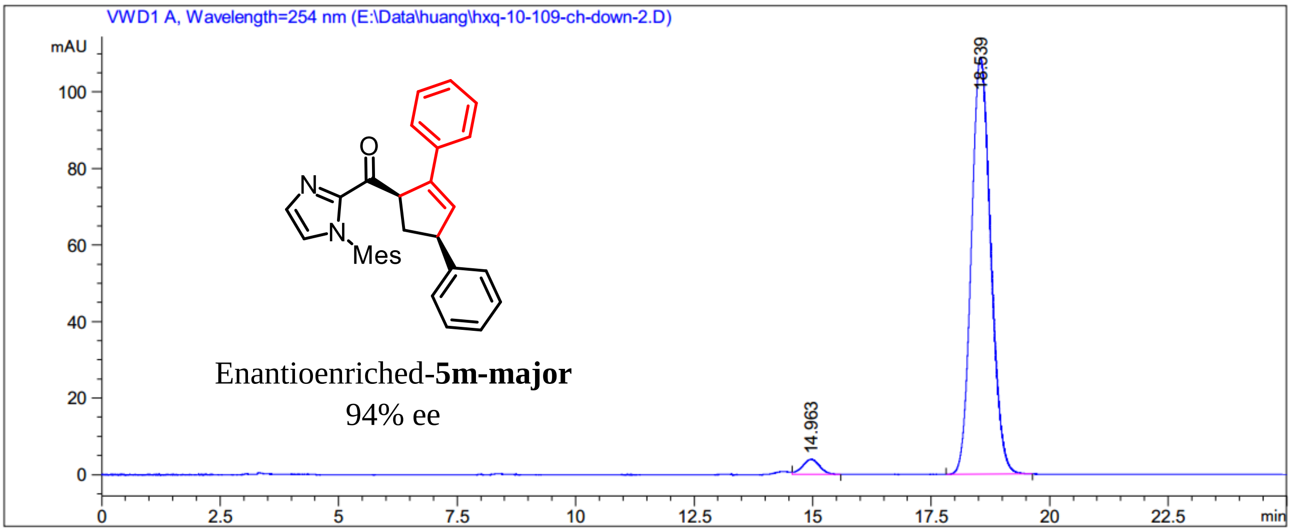


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.065	BB	0.2198	54.18609	3.72350	0.8492
2	7.812	BB	0.2611	6326.59717	368.89365	99.1508

Figure S51. HPLC traces of *rac*-**5l** (reference) and enantioenriched-**5l**.

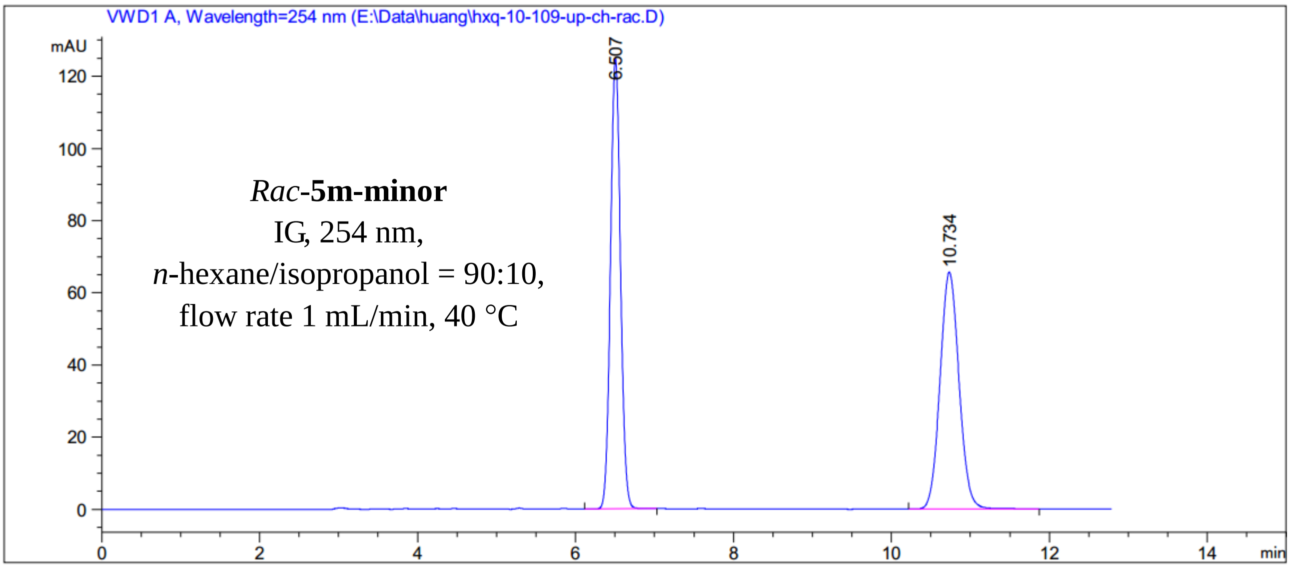


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.699	BV R	0.2926	1088.91260	49.02775	50.2592
2	18.485	BV R	0.3279	1077.68201	38.93514	49.7408

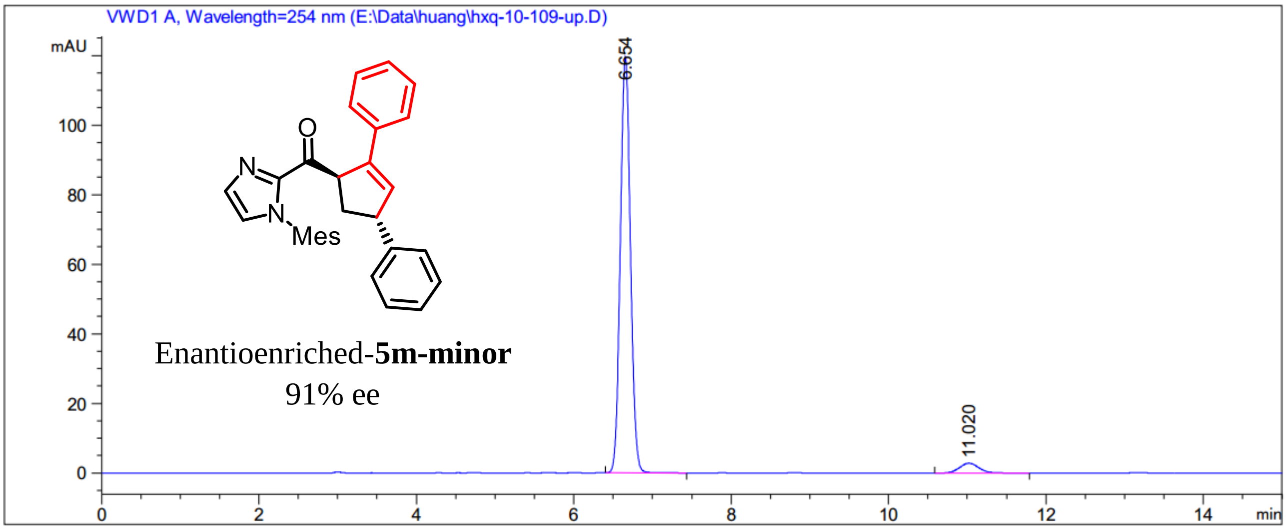


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.963	VB	0.3003	101.34243	3.97652	3.1678
2	18.539	BB	0.3856	3097.83008	109.00040	96.8322

Figure S52. HPLC traces of *rac*-**5m-major** (reference) and enantioenriched-**5m-major**.



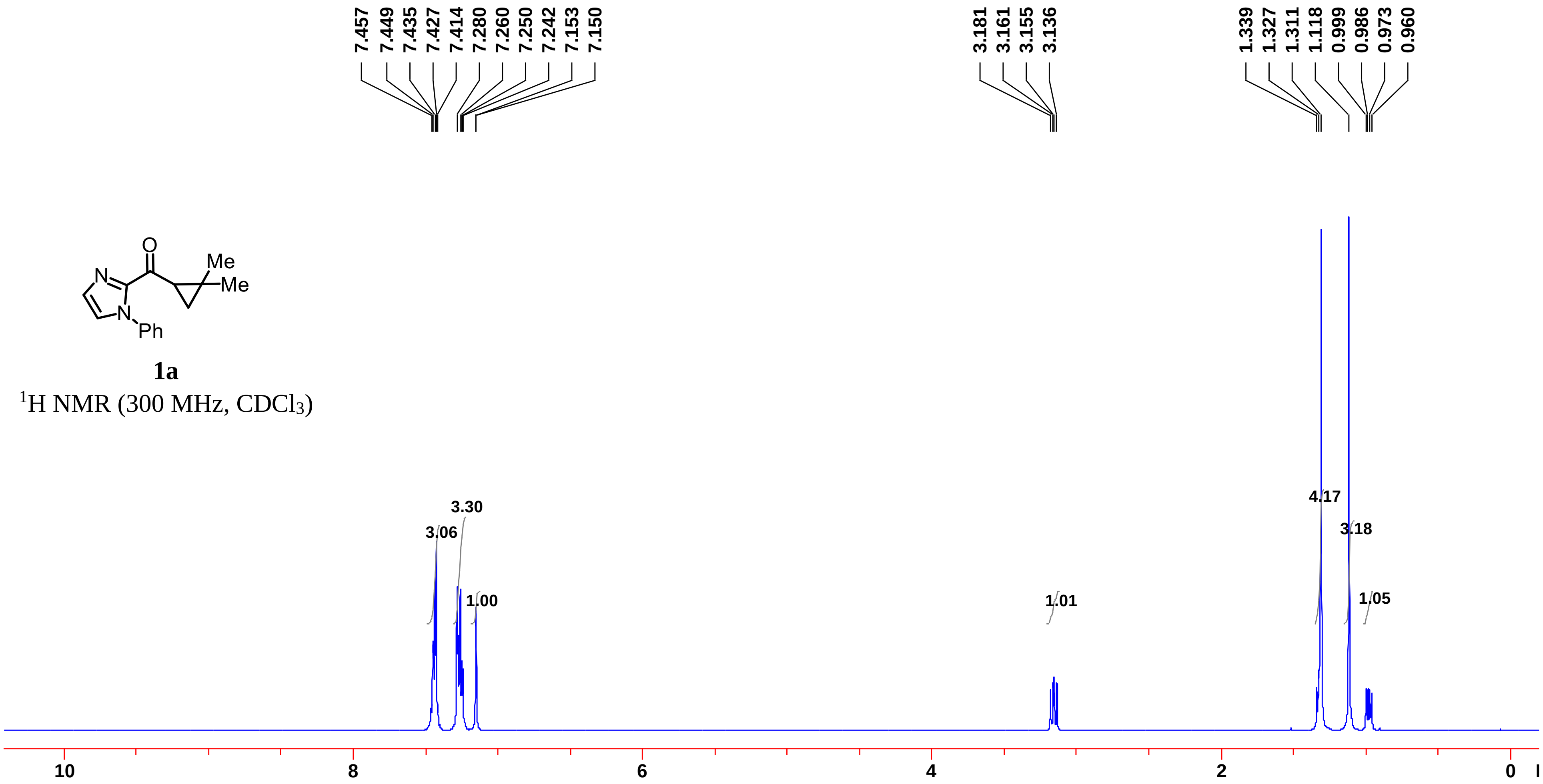
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.507	BB	0.1378	1098.87805	124.67340	50.0027
2	10.734	BB	0.2602	1098.75818	65.67395	49.9973



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.654	BB	0.1391	1067.54651	119.60771	95.6594
2	11.020	BB	0.2643	48.44017	2.83566	4.3406

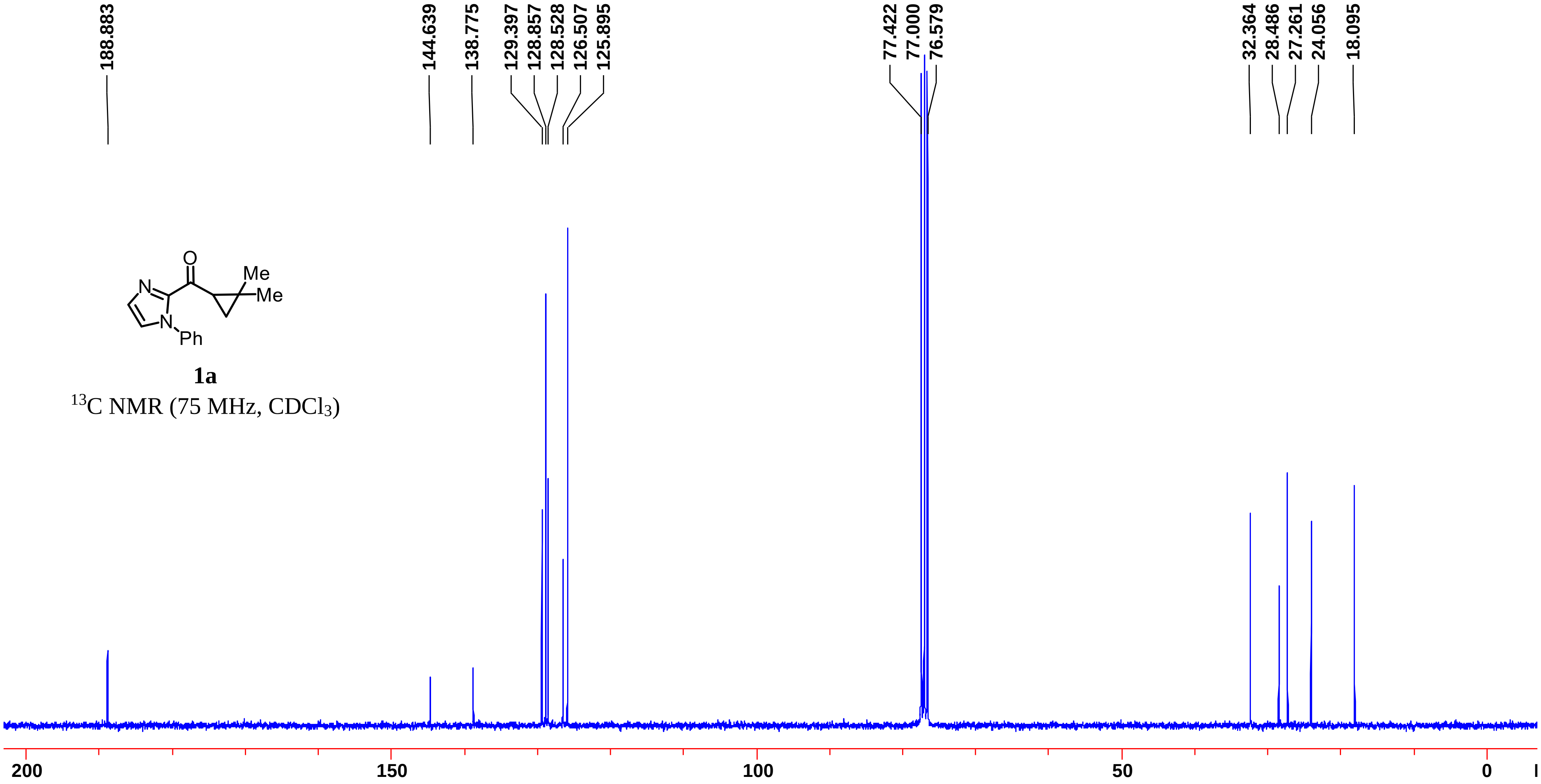
Figure S53. HPLC traces of *rac*-**5m-minor** (reference) and enantioenriched-**5m-minor**.

9. NMR Spectra of New Compounds



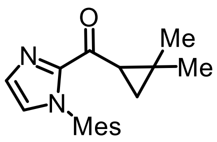
1a

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



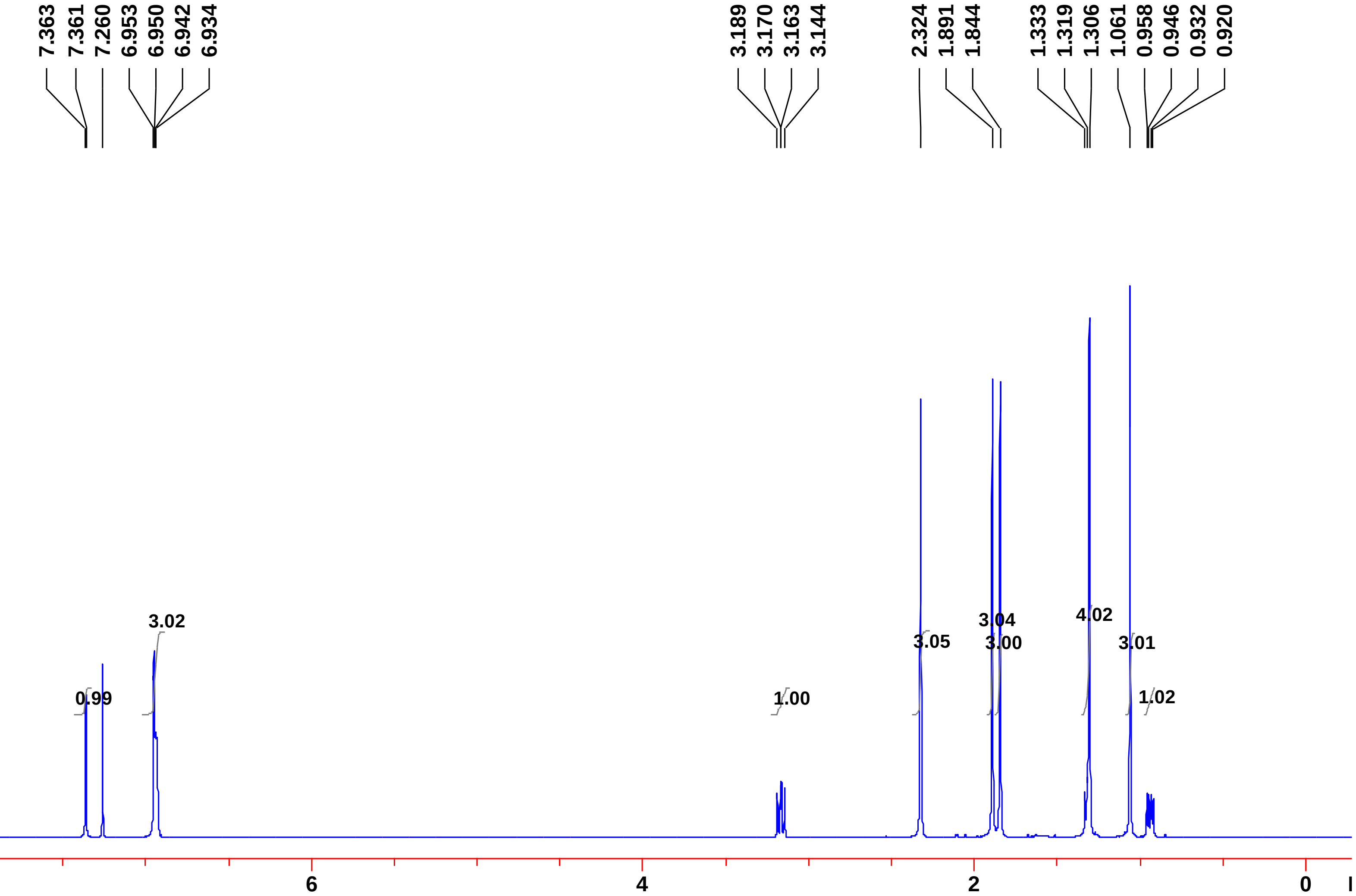
1a

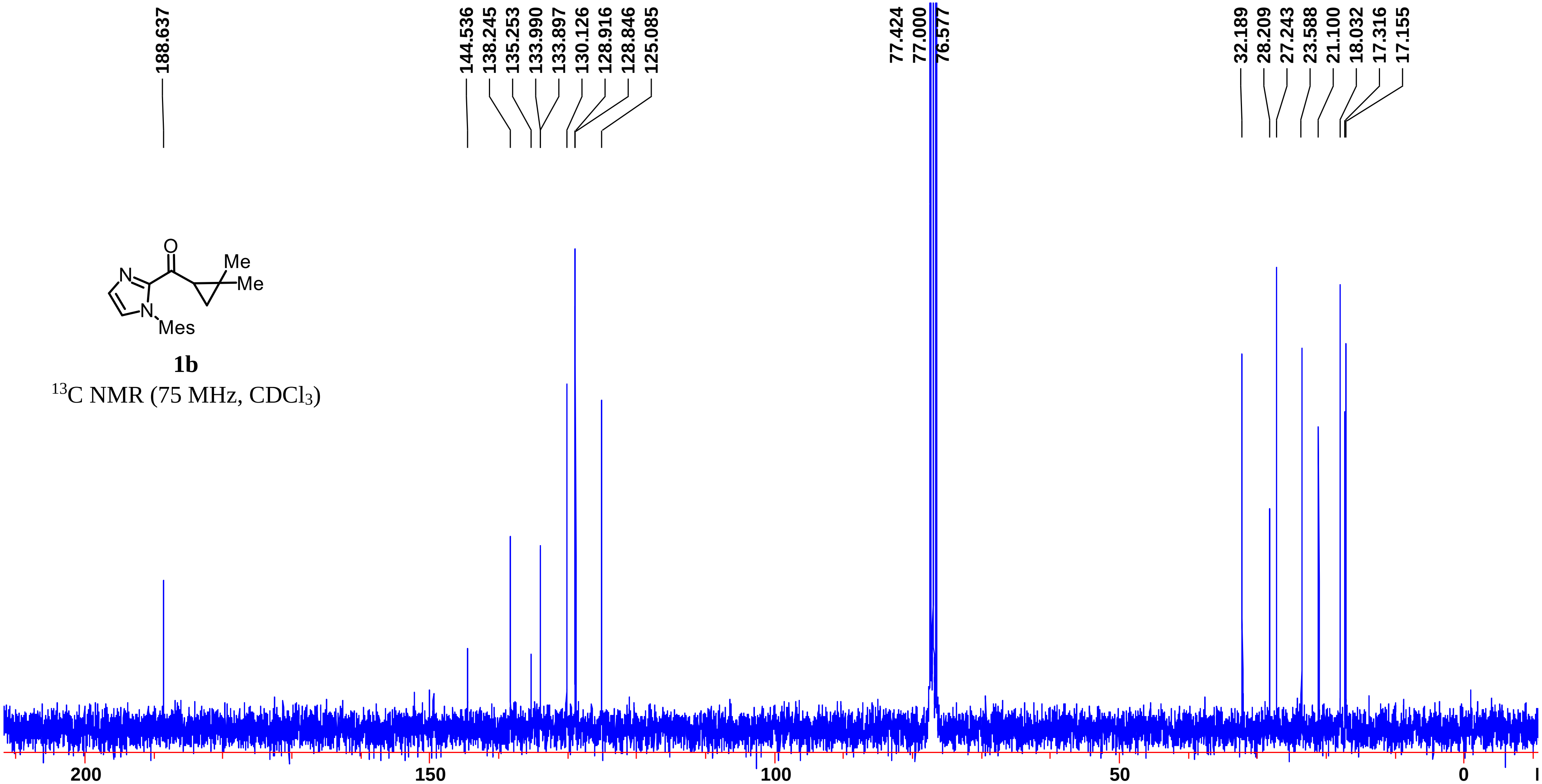
^{13}C NMR (75 MHz, $CDCl_3$)



1b

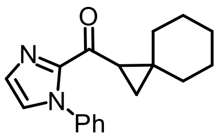
^{1}H NMR (300 MHz, $CDCl_3$)





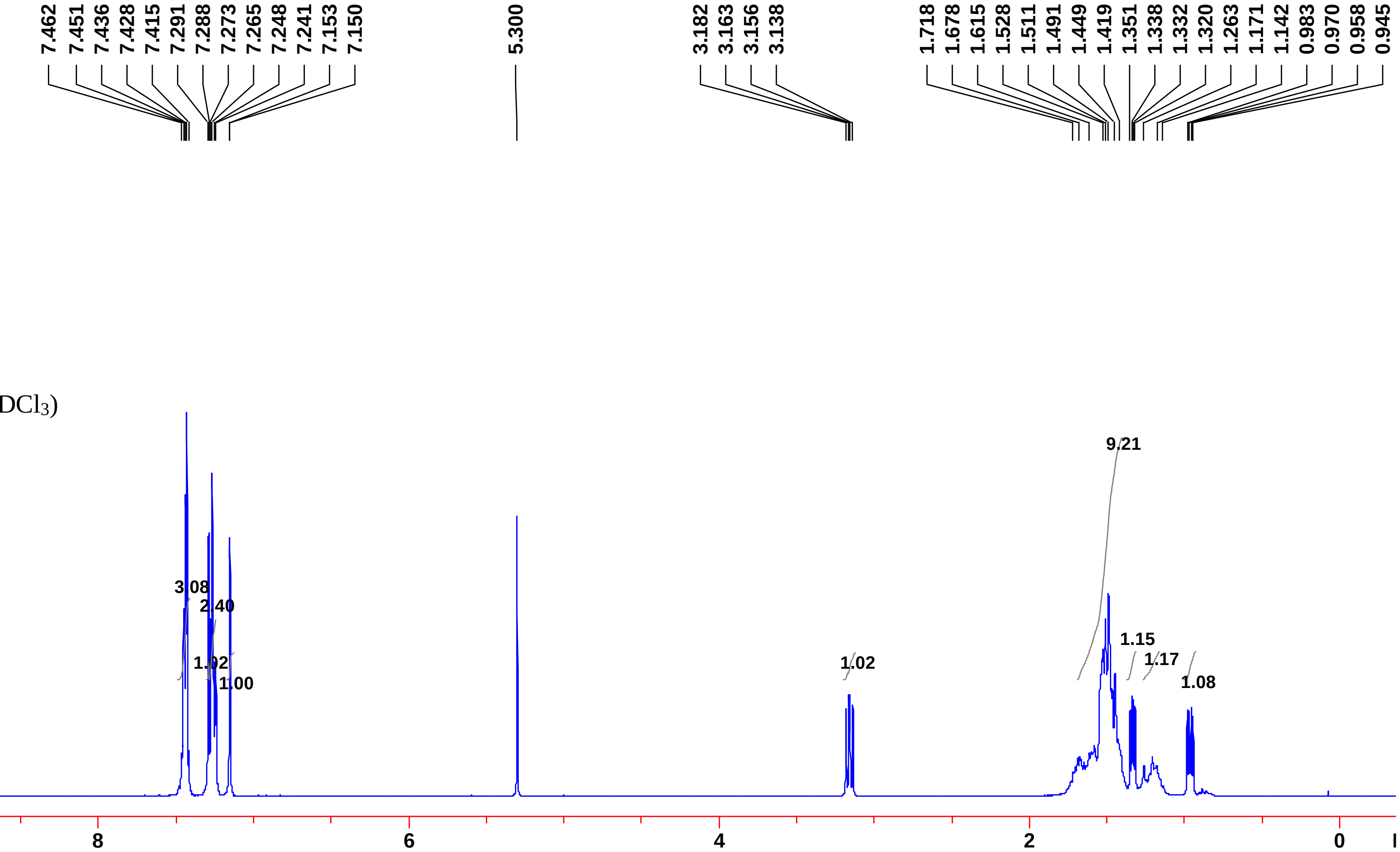
1b

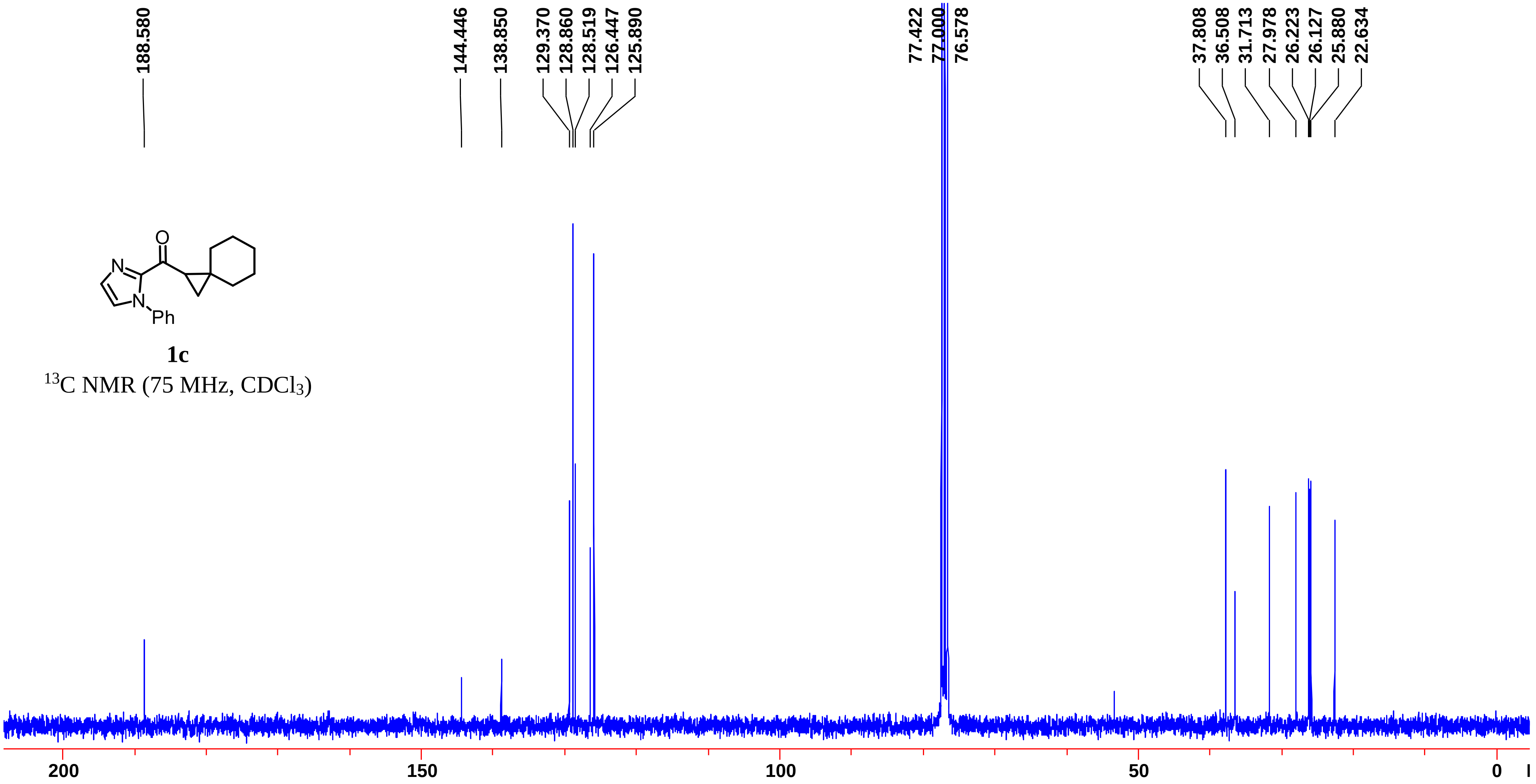
^{13}C NMR (75 MHz, $CDCl_3$)



1c

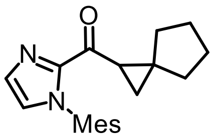
^{1}H NMR (300 MHz, $CDCl_3$)





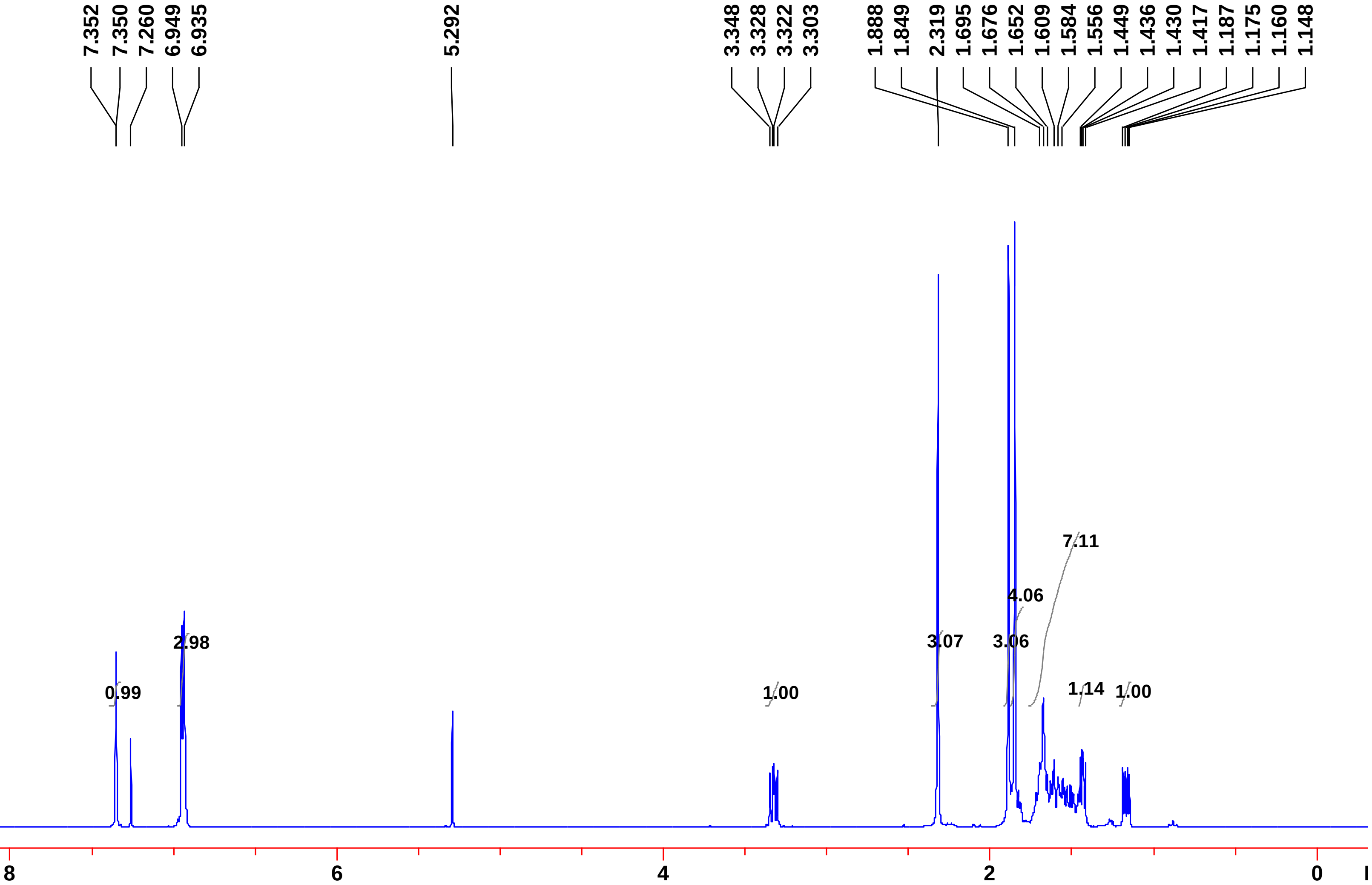
1c

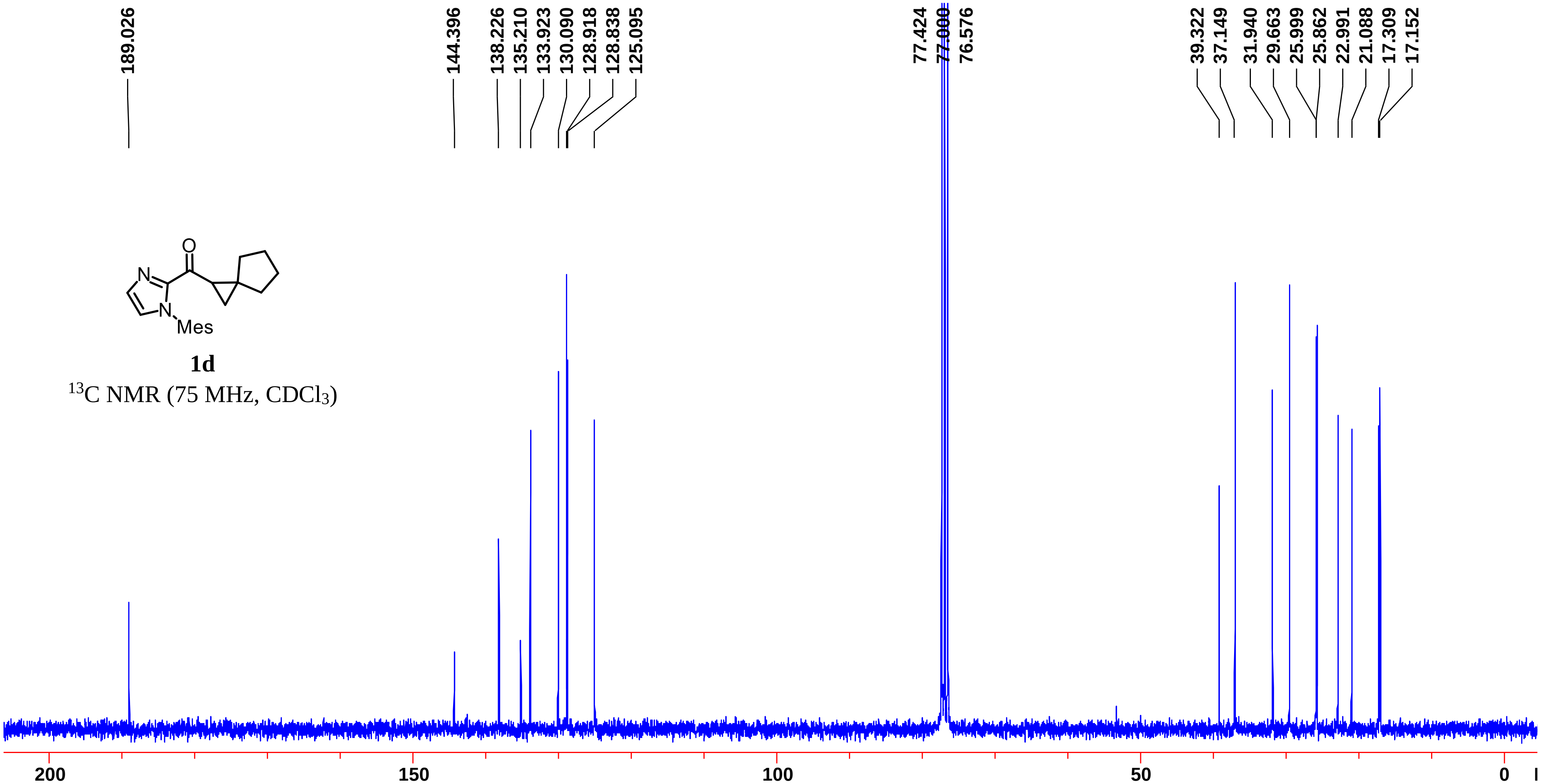
^{13}C NMR (75 MHz, $CDCl_3$)



1d

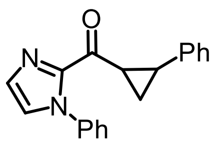
^{1}H NMR (300 MHz, $CDCl_3$)





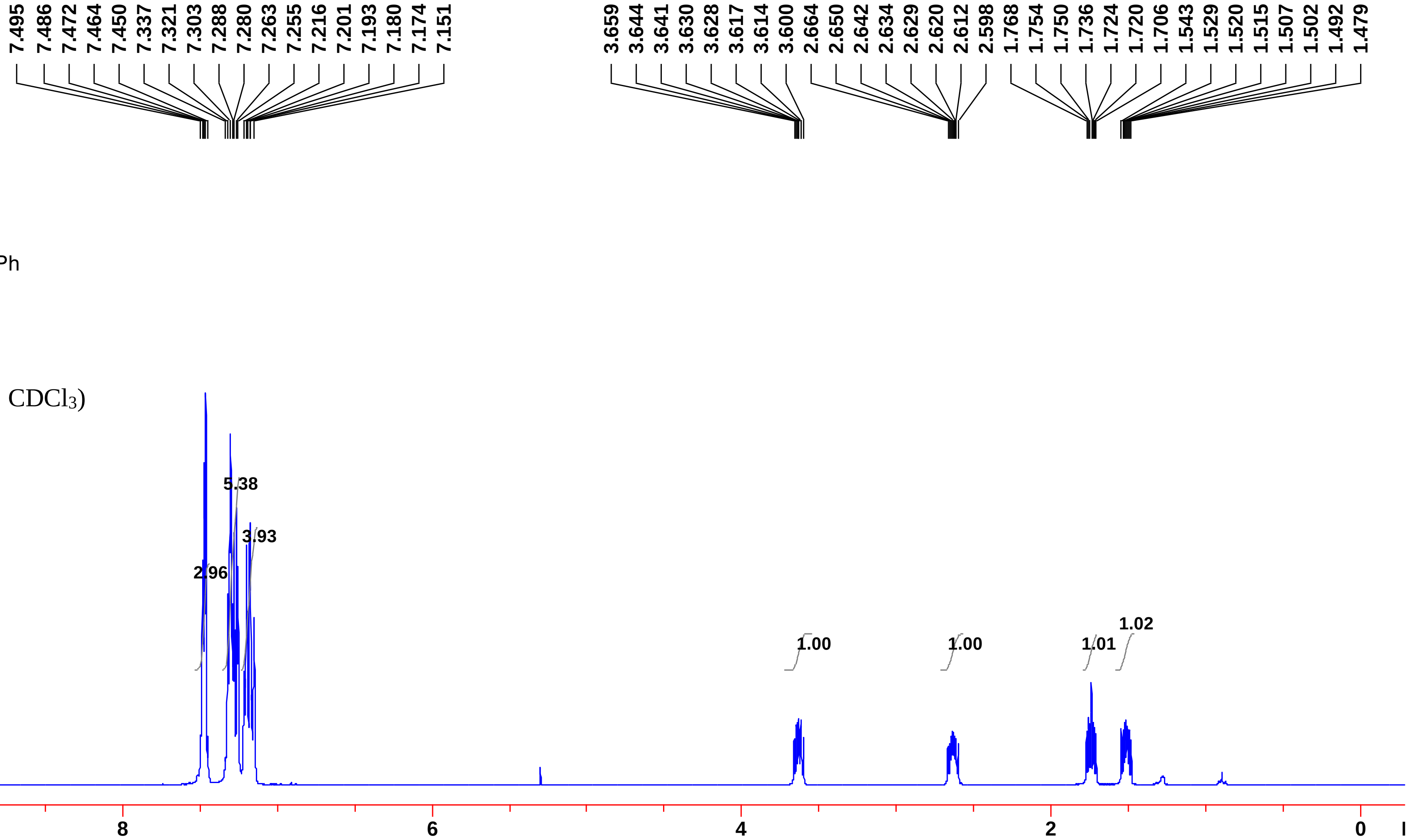
1d

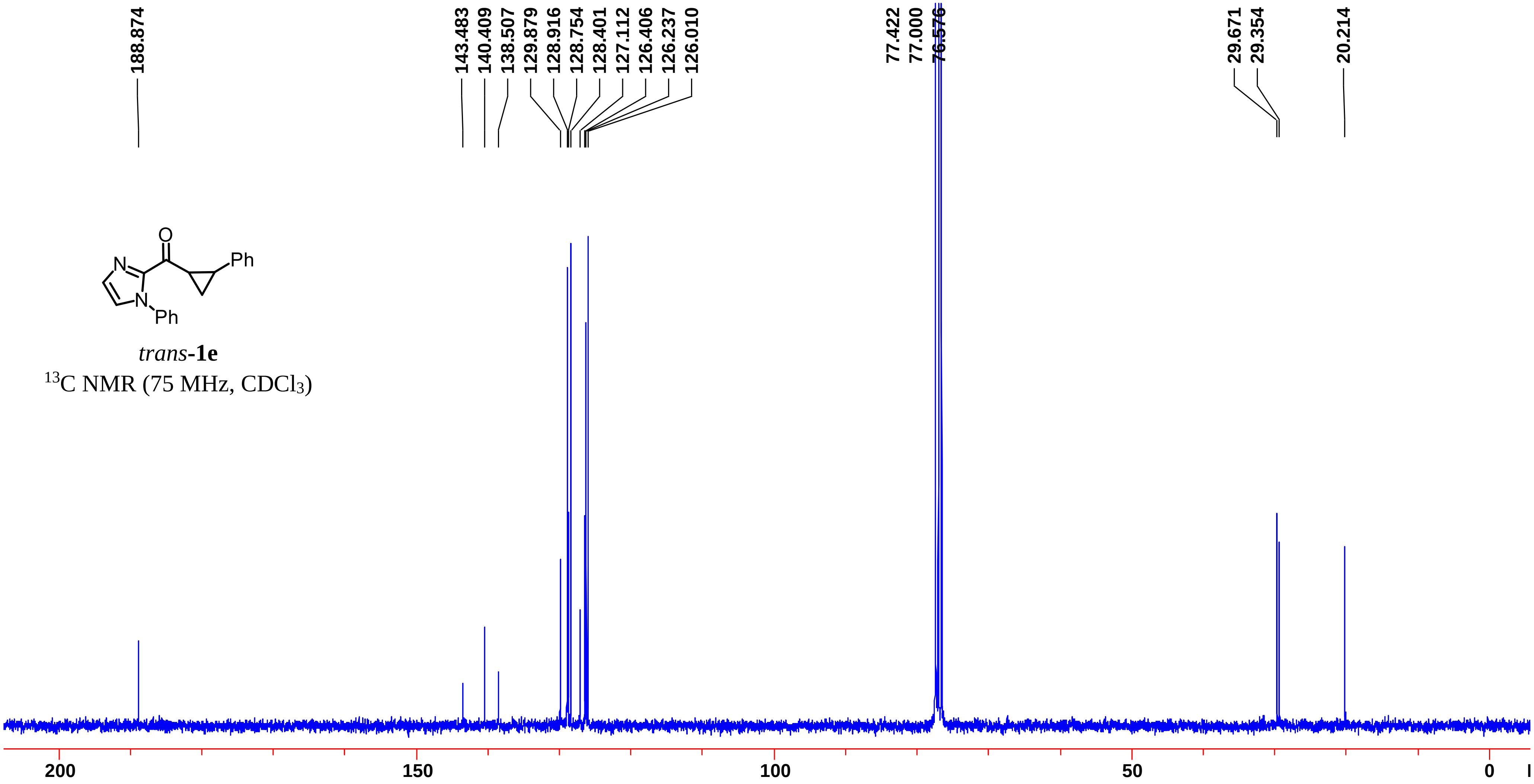
^{13}C NMR (75 MHz, $CDCl_3$)



trans-**1e**

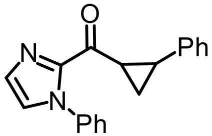
^{1}H NMR (300 MHz, $CDCl_3$)





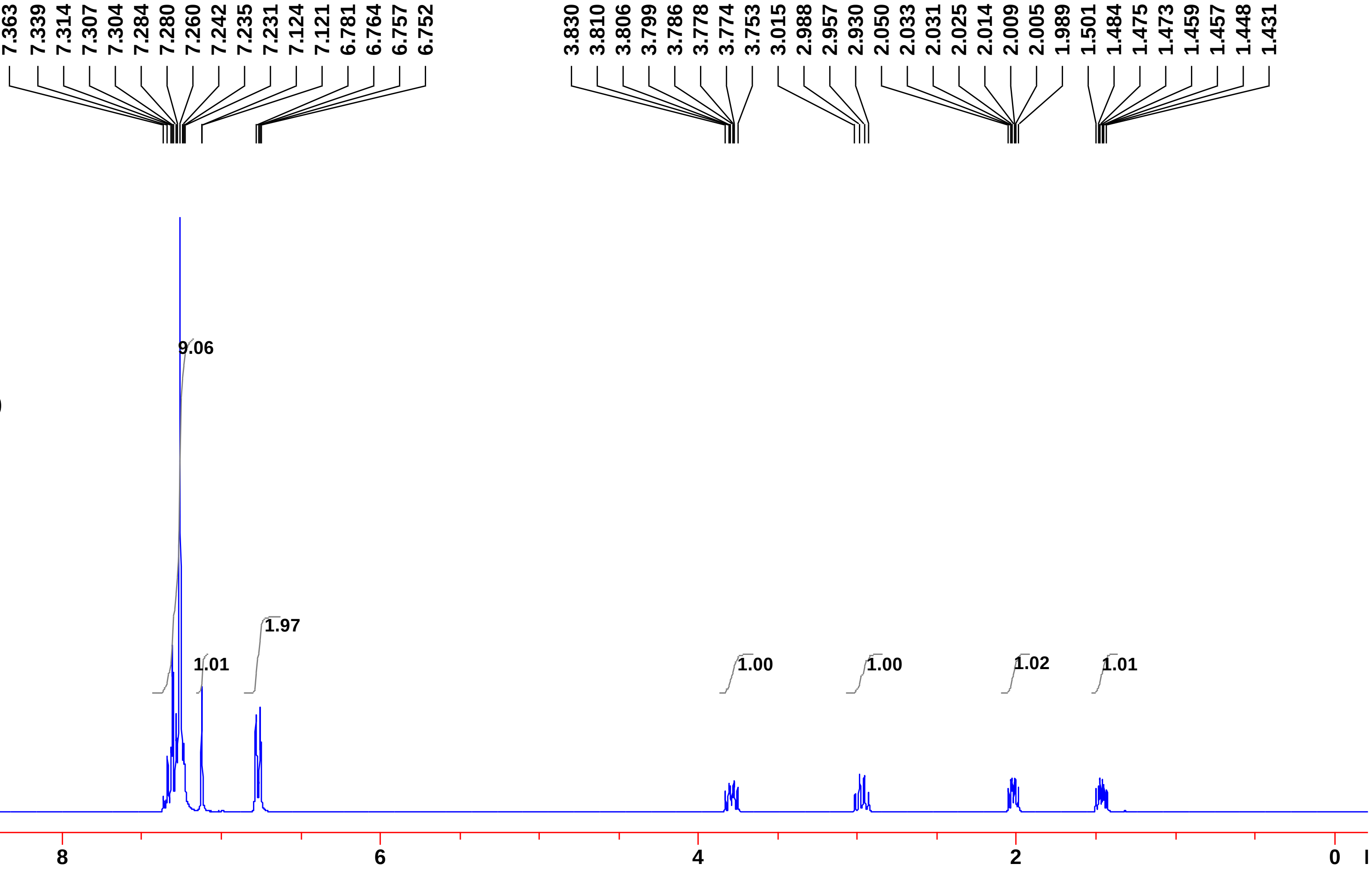
trans-**1e**

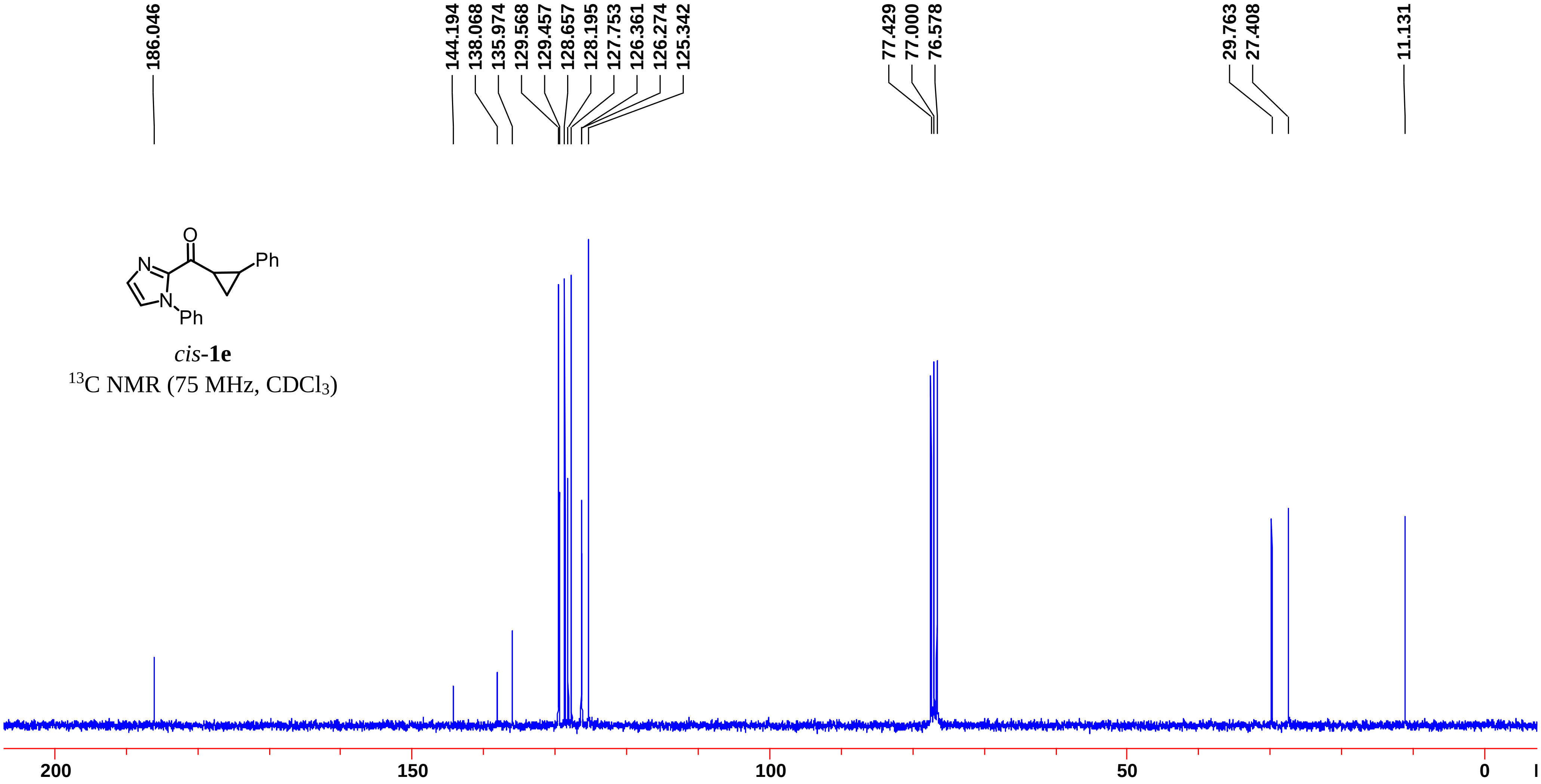
^{13}C NMR (75 MHz, $CDCl_3$)



cis-**1e**

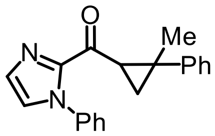
[1]H NMR (300 MHz, $CDCl_3$)





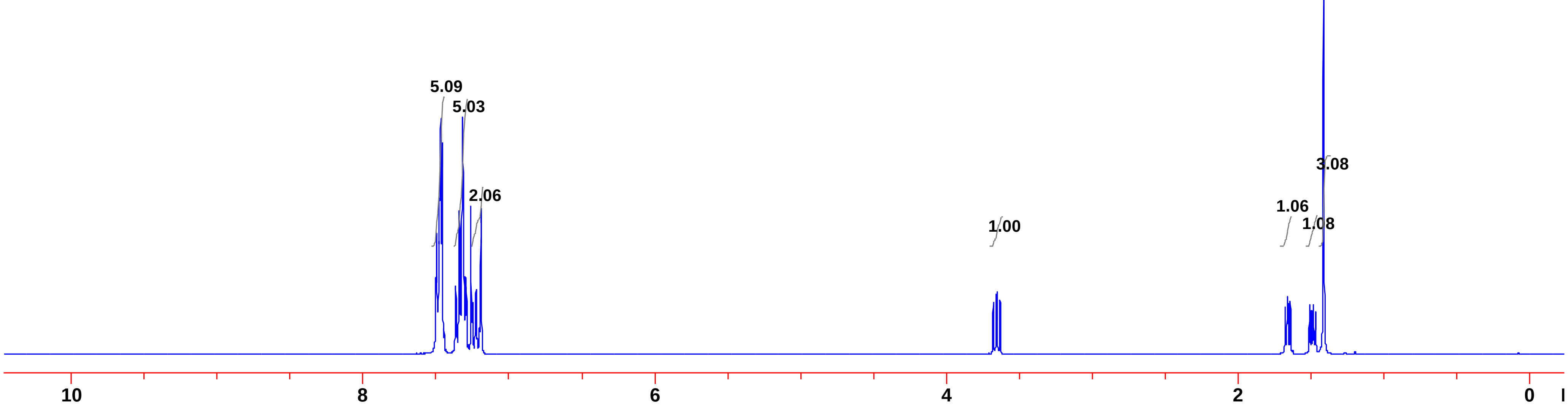
cis-**1e**

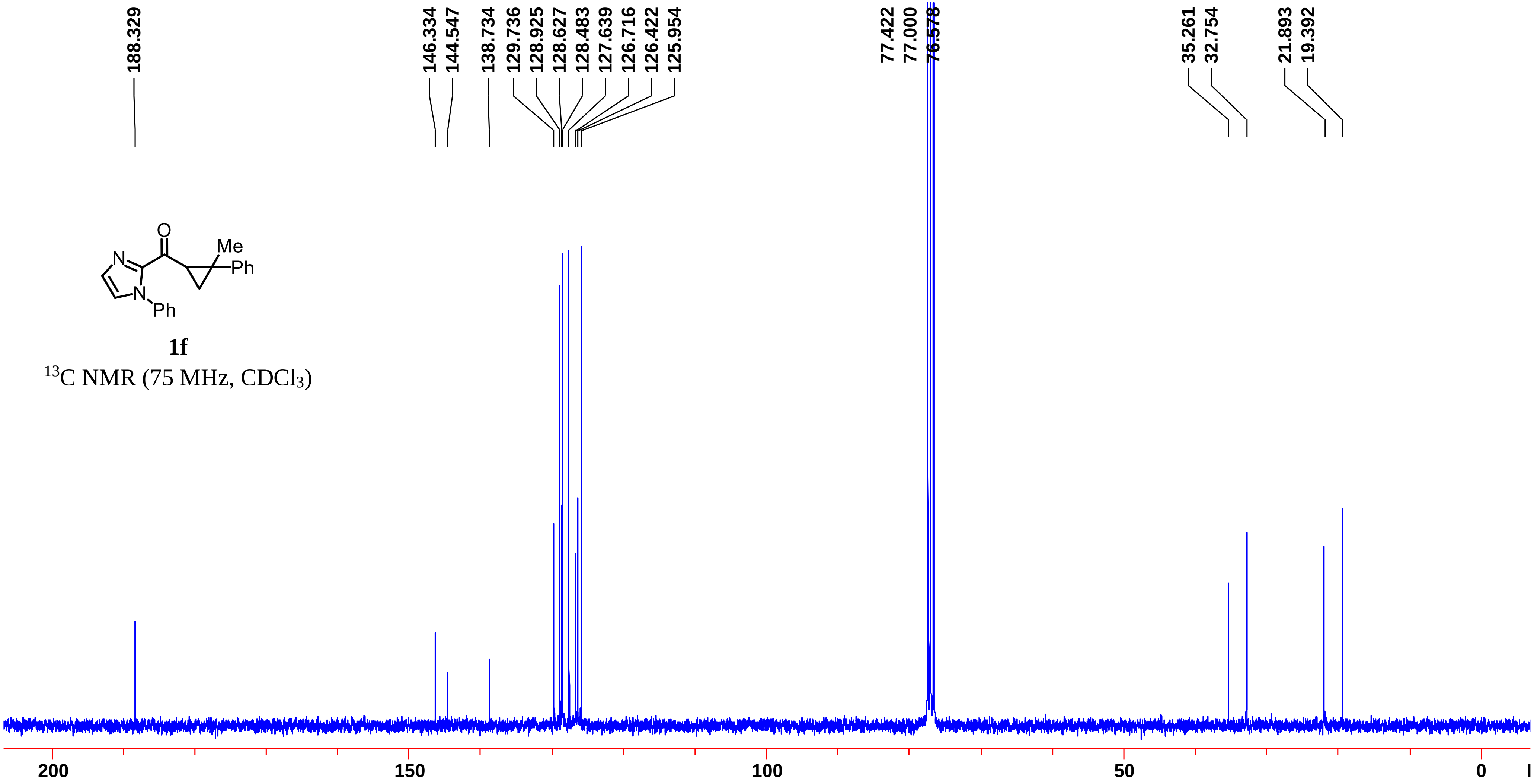
^{13}C NMR (75 MHz, $CDCl_3$)



1f

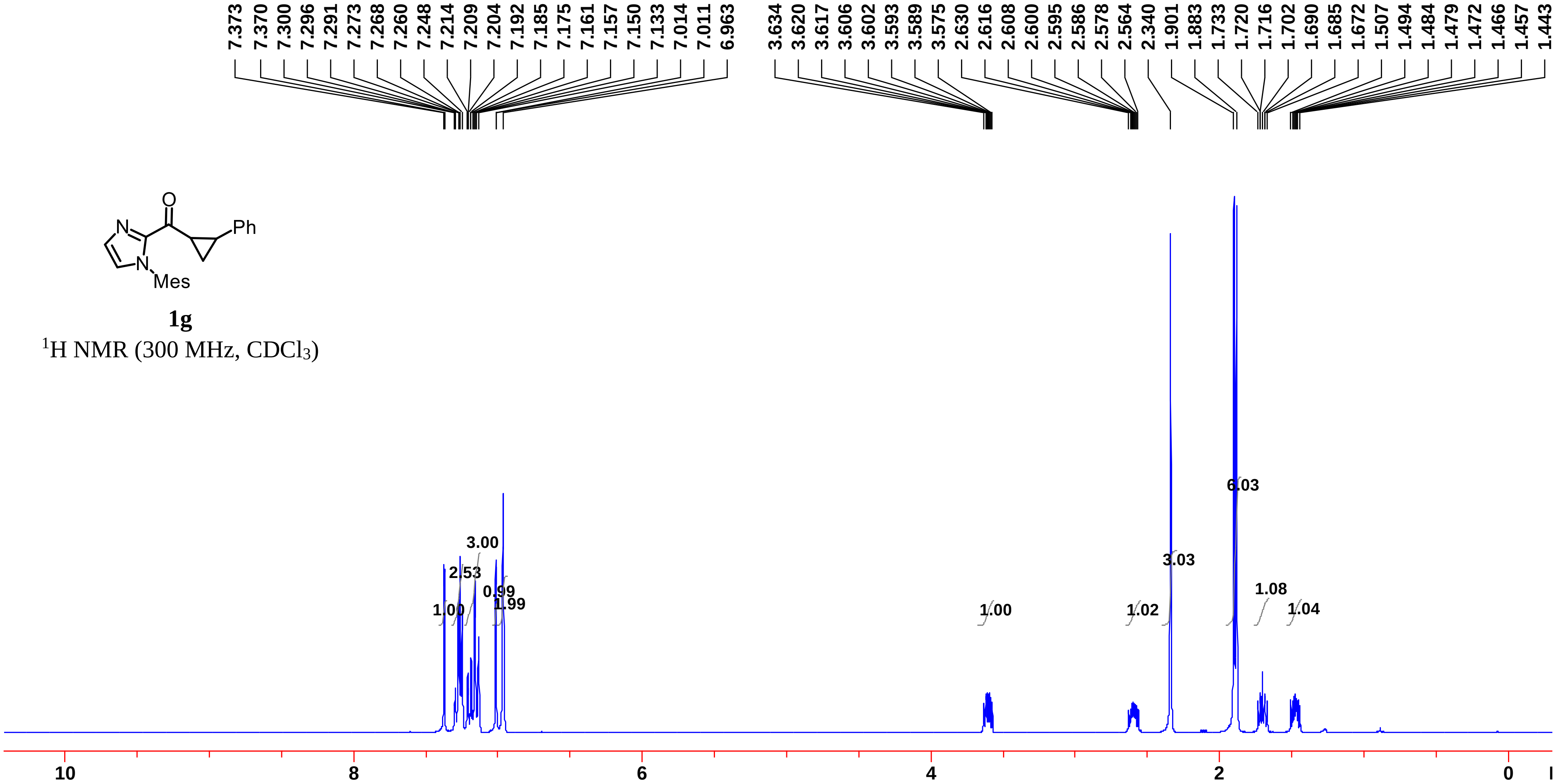
^{1}H NMR (300 MHz, $CDCl_3$)





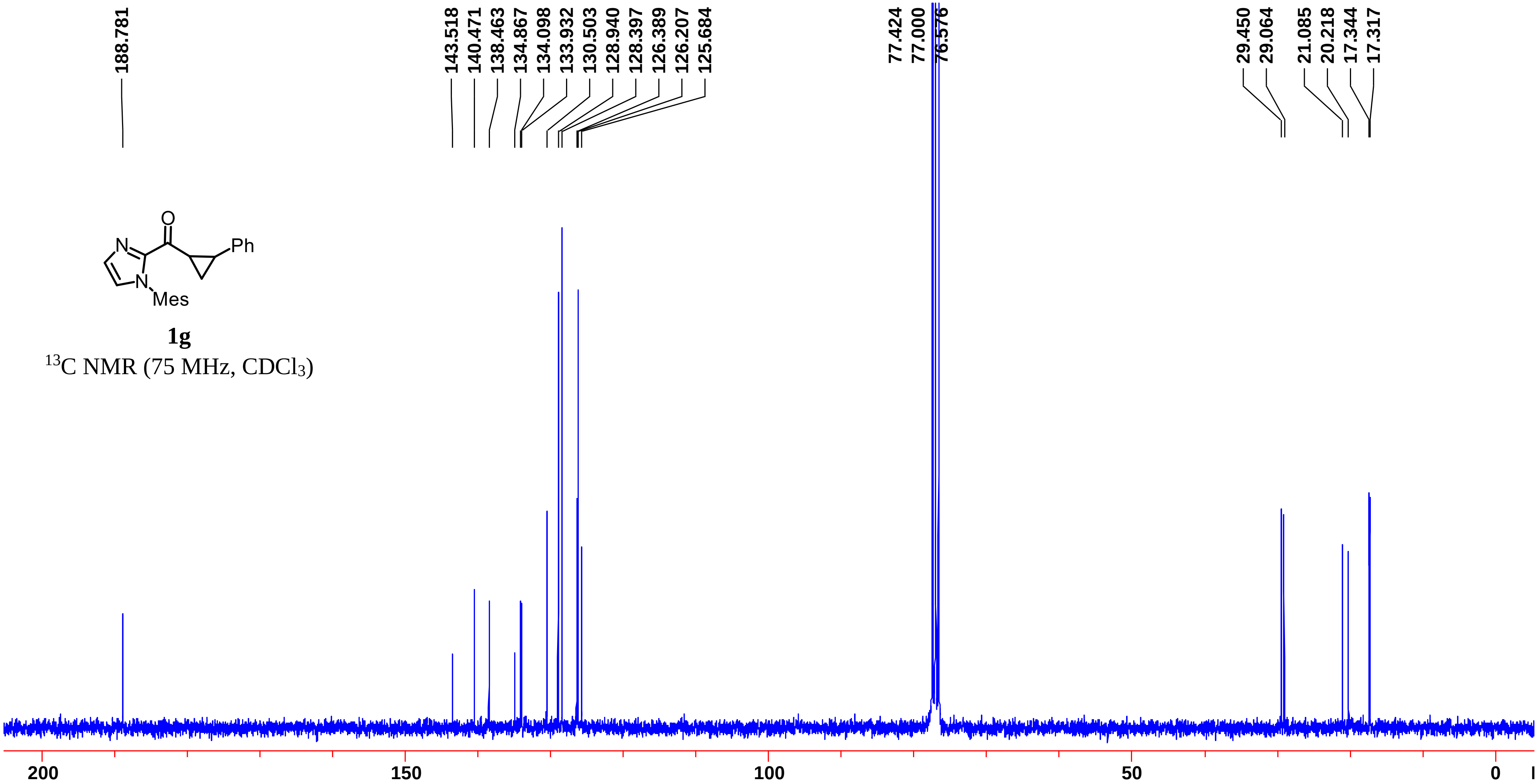
1f

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



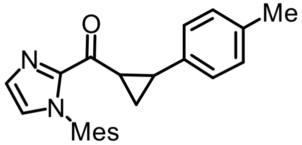
1g

[1]H NMR (300 MHz, $CDCl_3$)



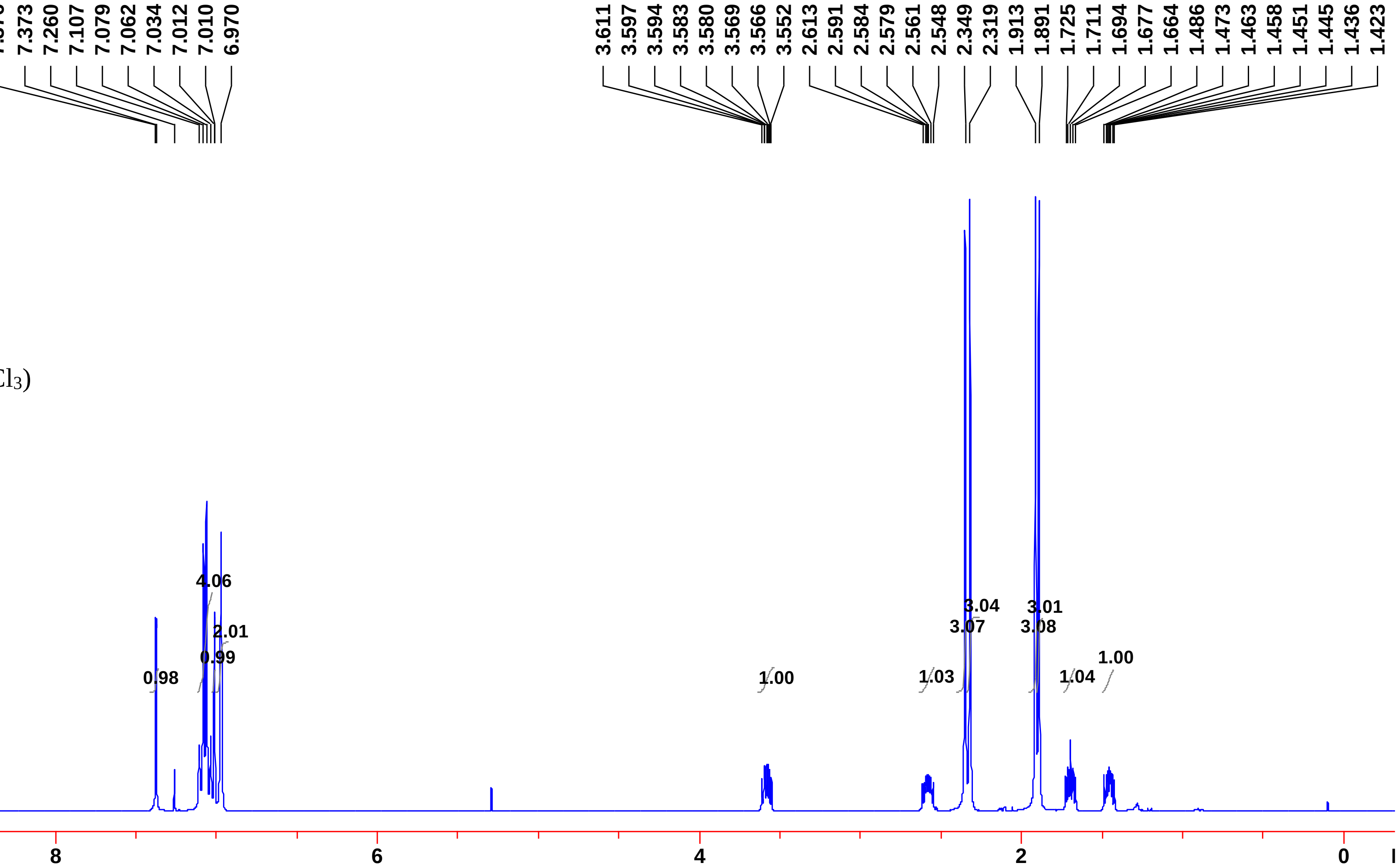
1g

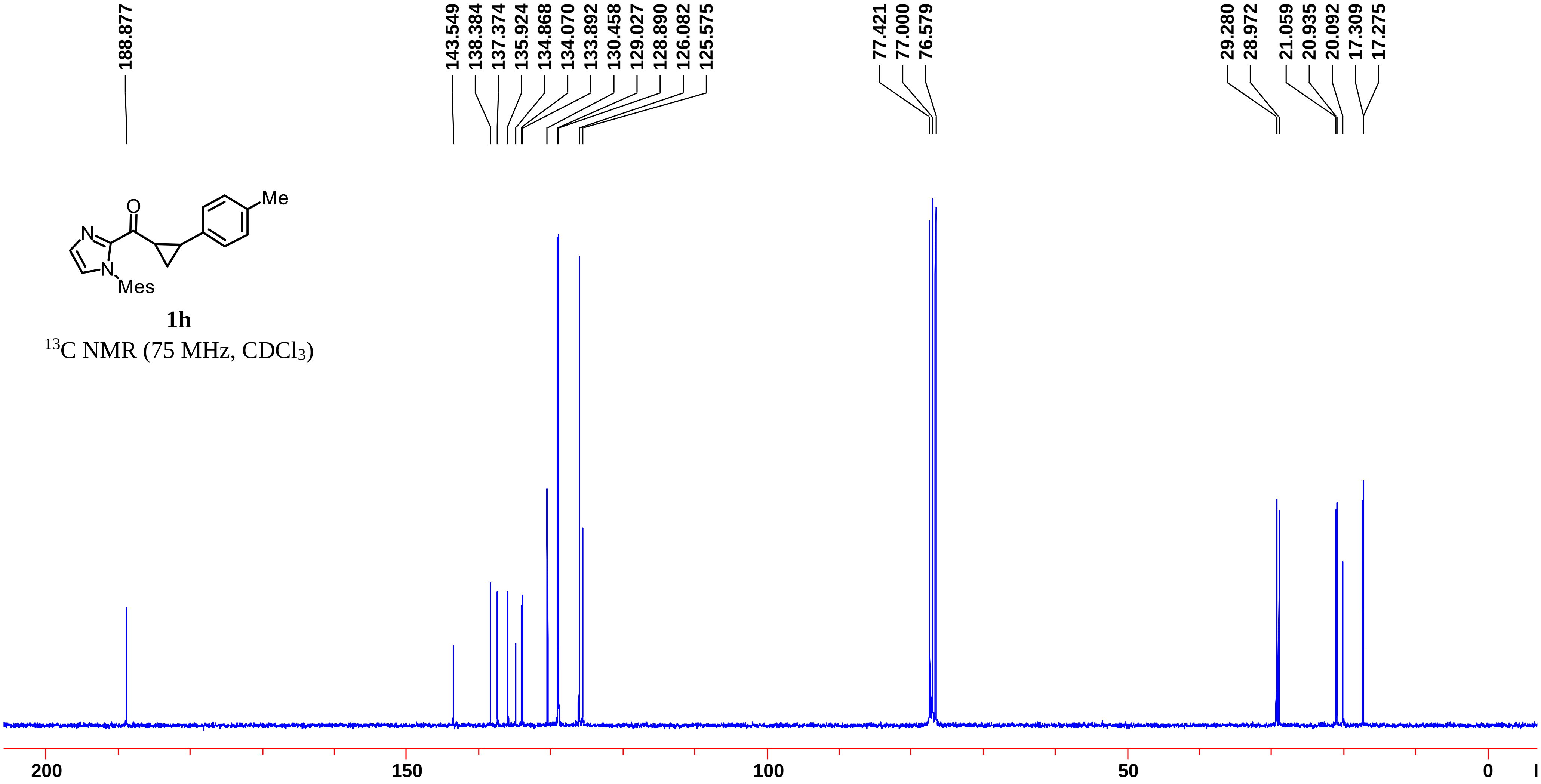
^{13}C NMR (75 MHz, $CDCl_3$)



1h

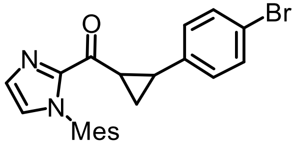
^{1}H NMR (300 MHz, $CDCl_3$)





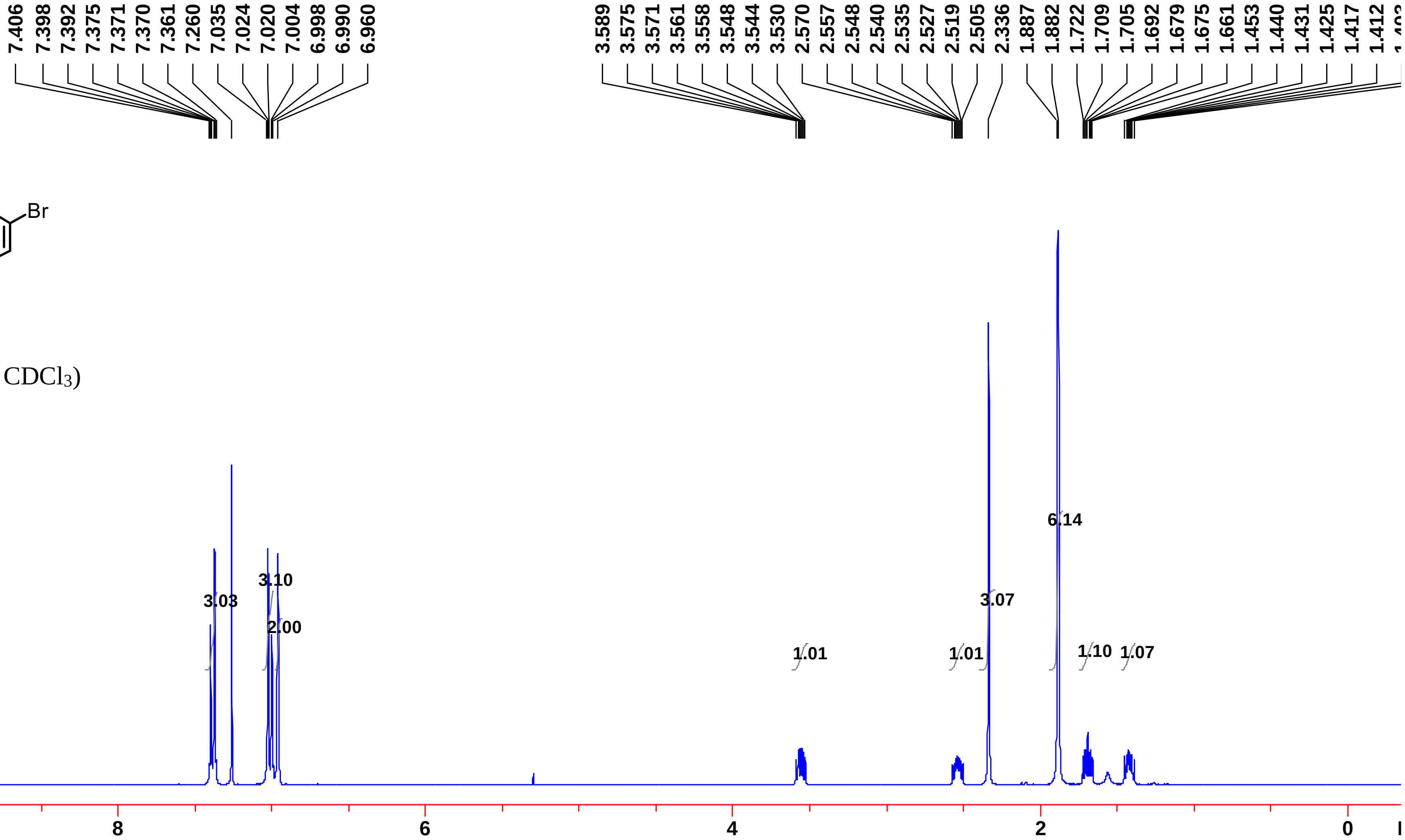
1h

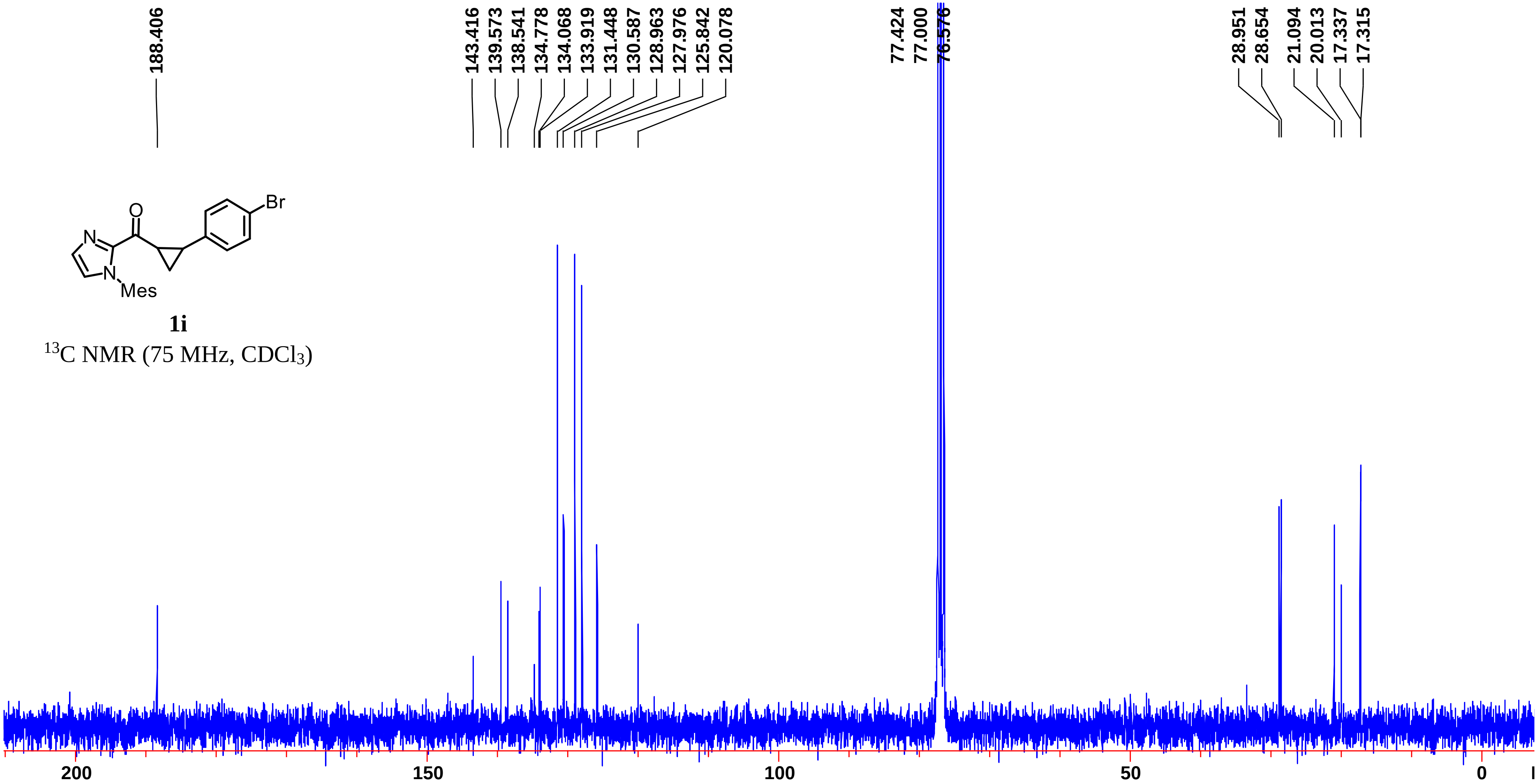
^{13}C NMR (75 MHz, $CDCl_3$)



1i

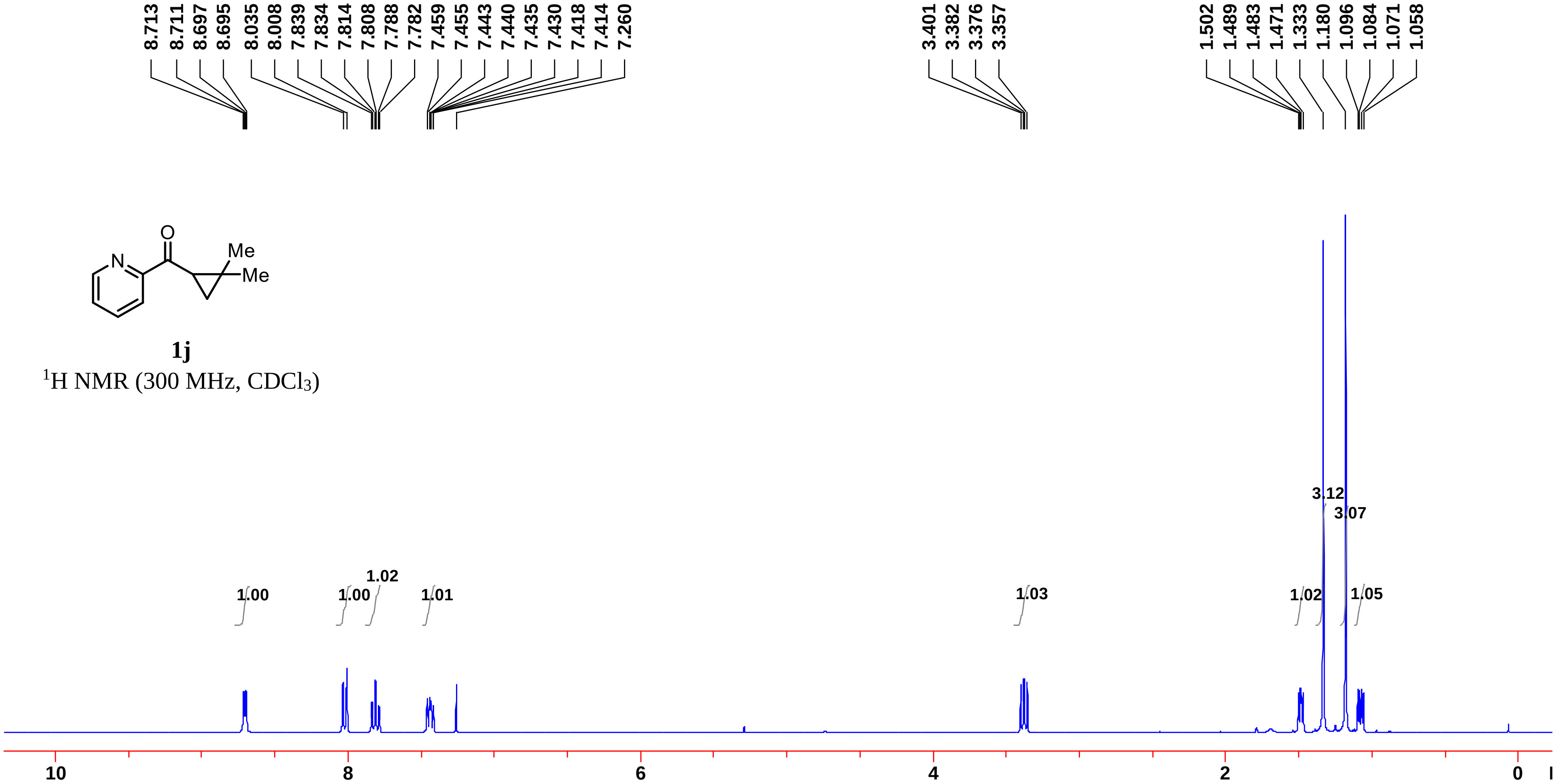
^{1}H NMR (300 MHz, $CDCl_3$)





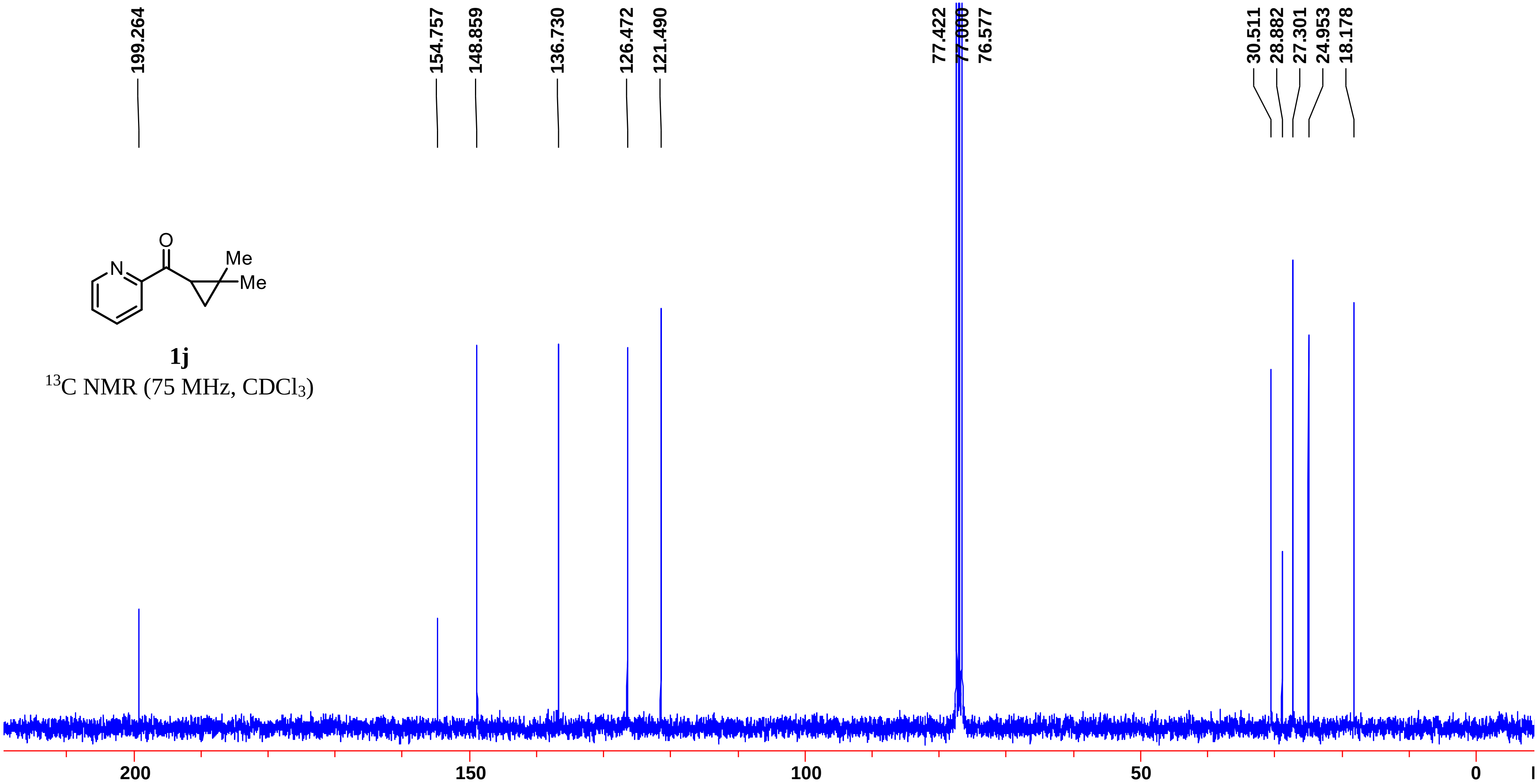
1i

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



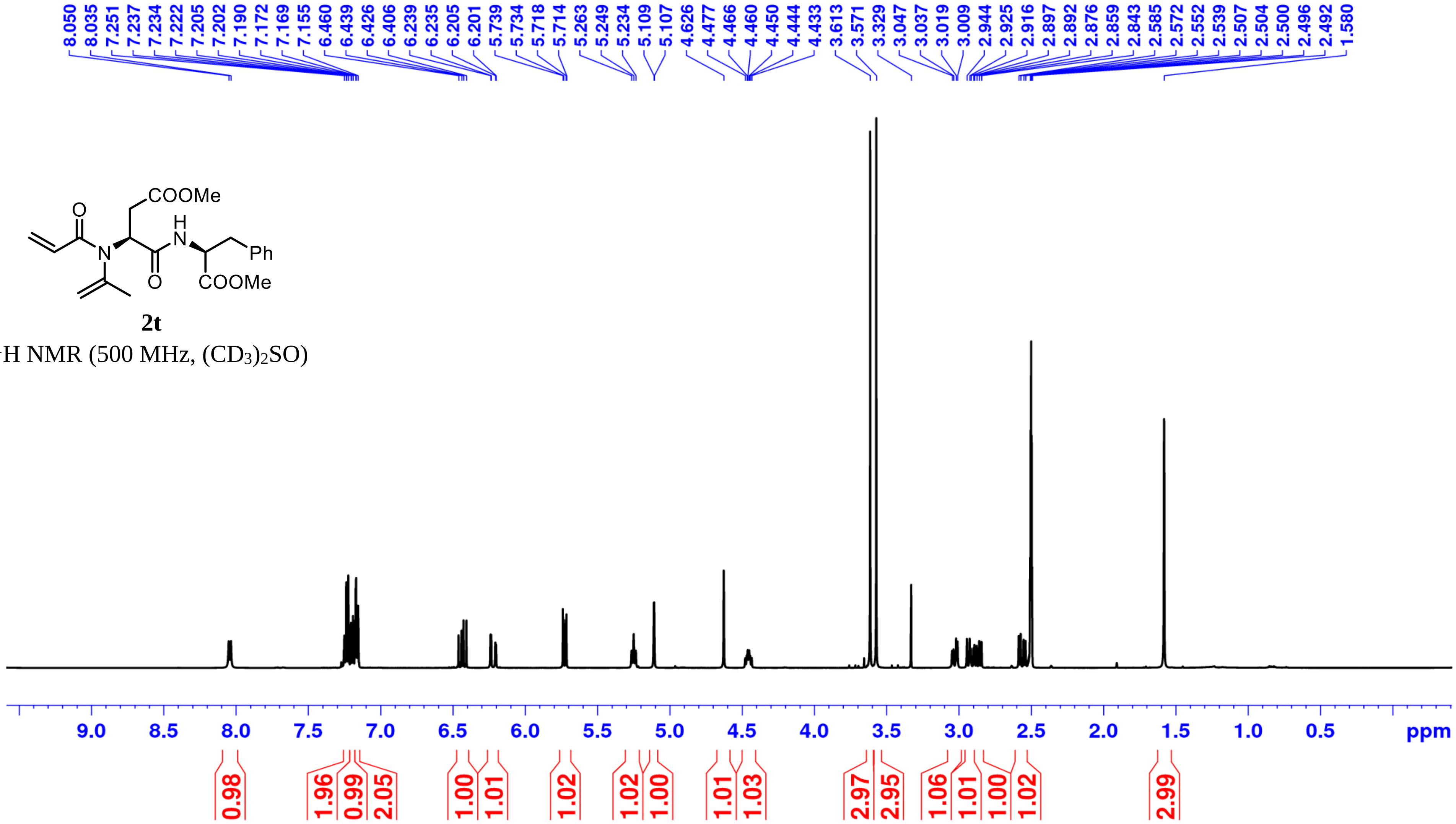
1j

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



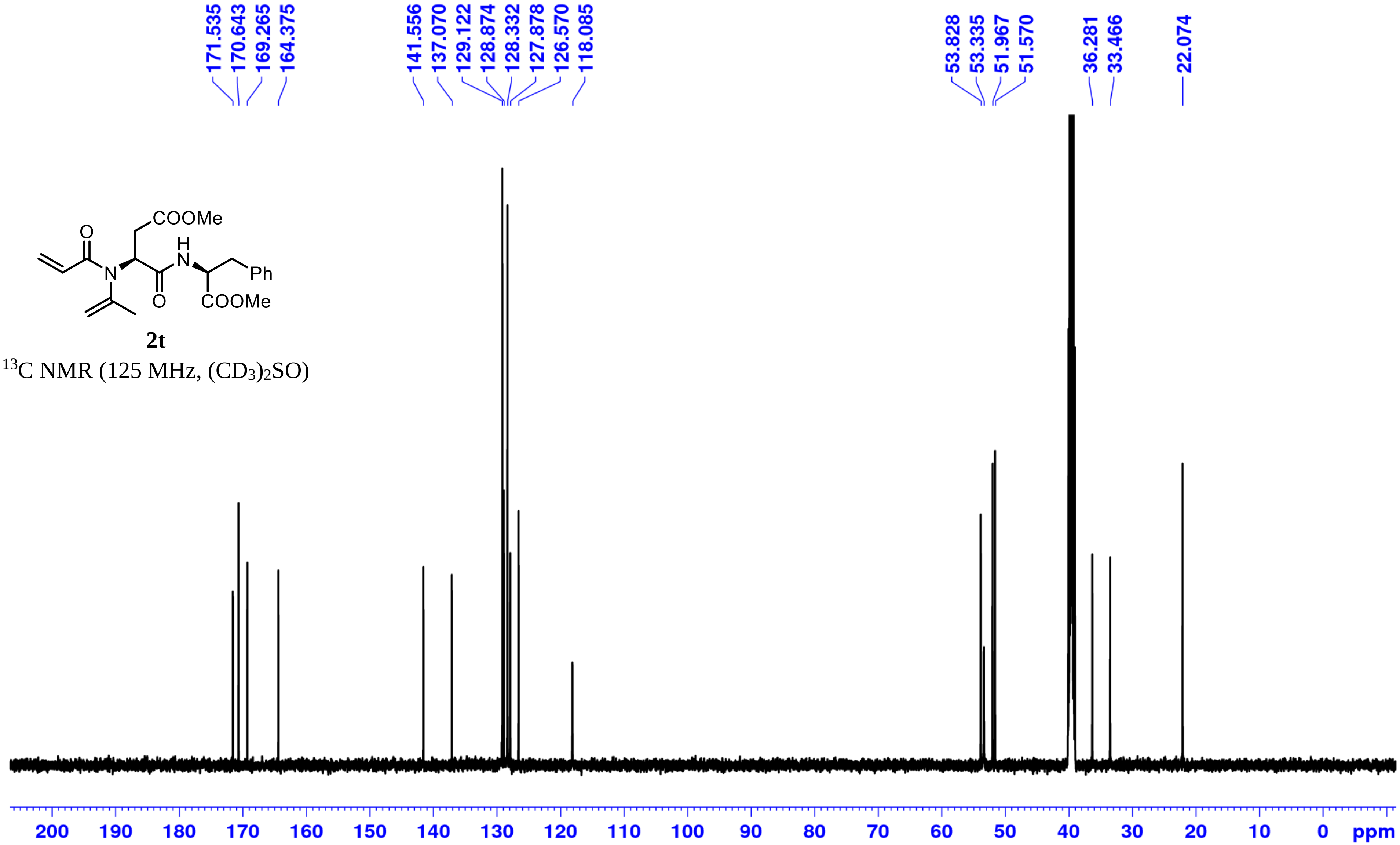
1j

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



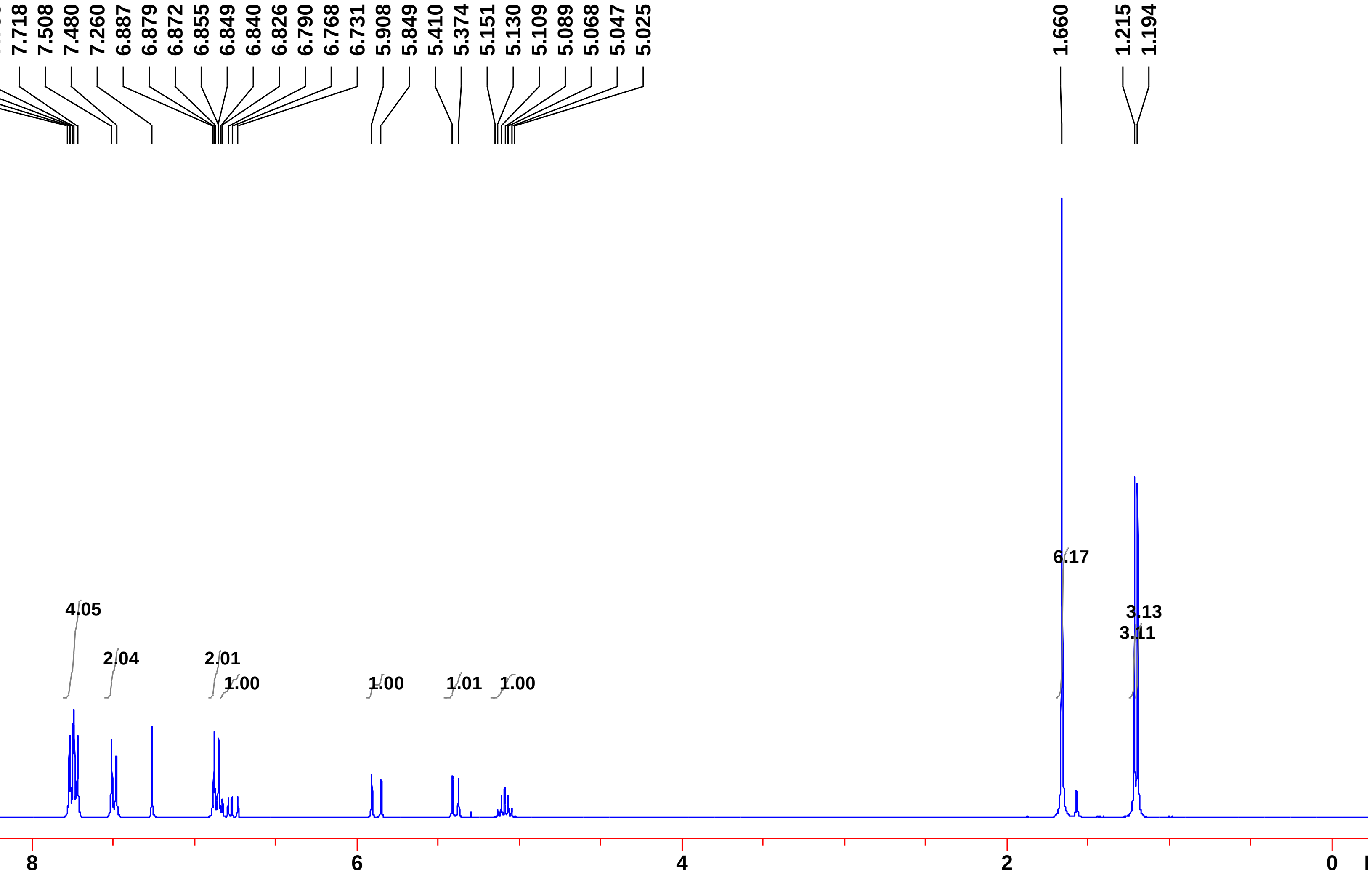
2t

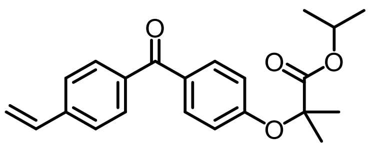
^{1}H NMR (500 MHz, $(CD_3)_2SO$)



2t

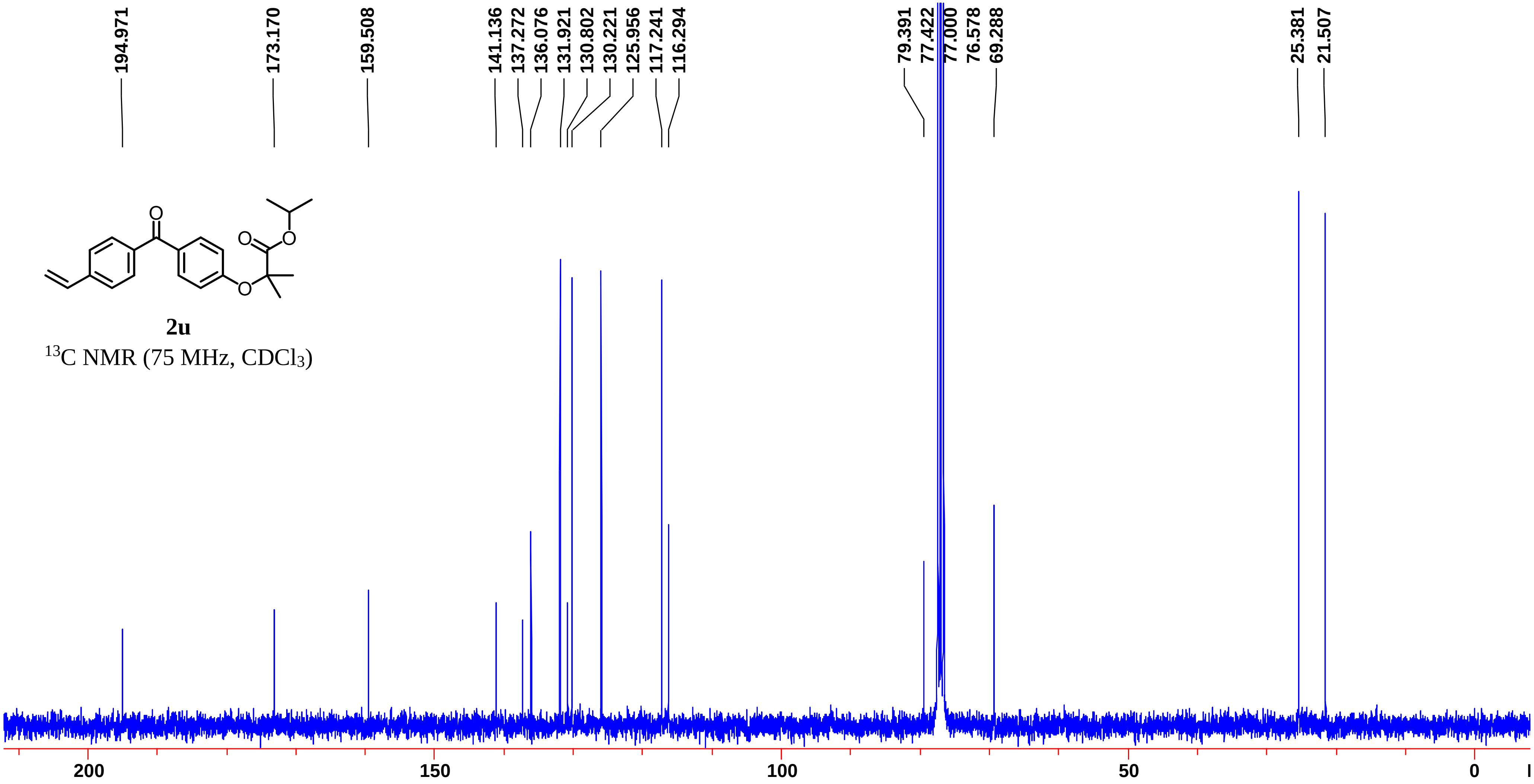
^{13}C NMR (125 MHz, $(CD_3)_2SO$)

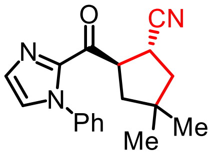




2u

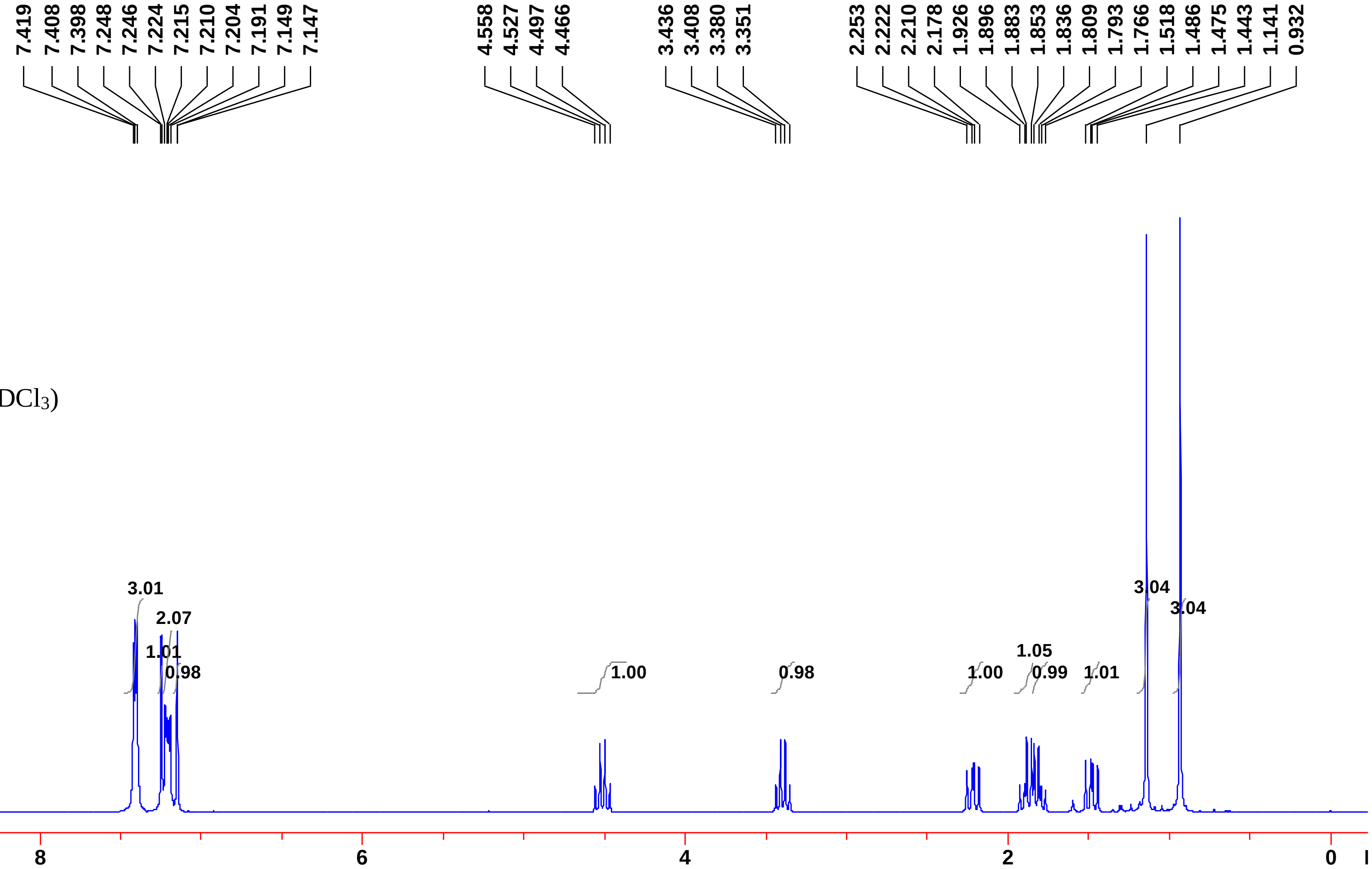
^{1}H NMR (300 MHz, $CDCl_3$)

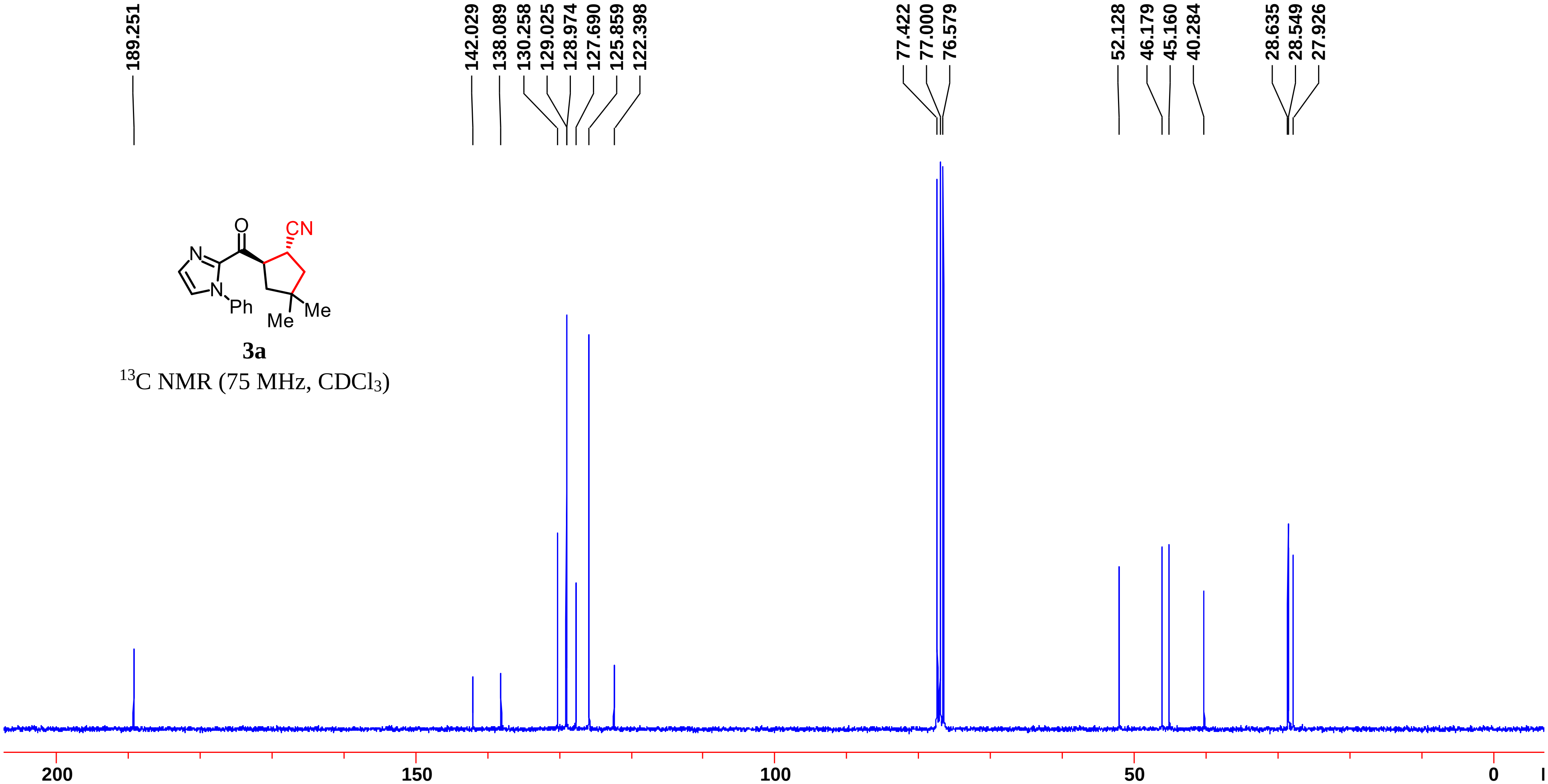

194.971
173.170
159.508
141.136
137.272
136.076
131.921
130.802
130.221
125.956
117.241
116.294
79.391
77.422
77.000
76.578
69.288
25.381
21.507
2u
^{13}C NMR (75 MHz, CDCl$_3$)
200
150
100
50
0

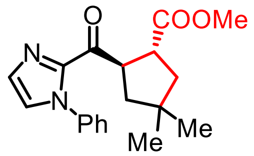


3a

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

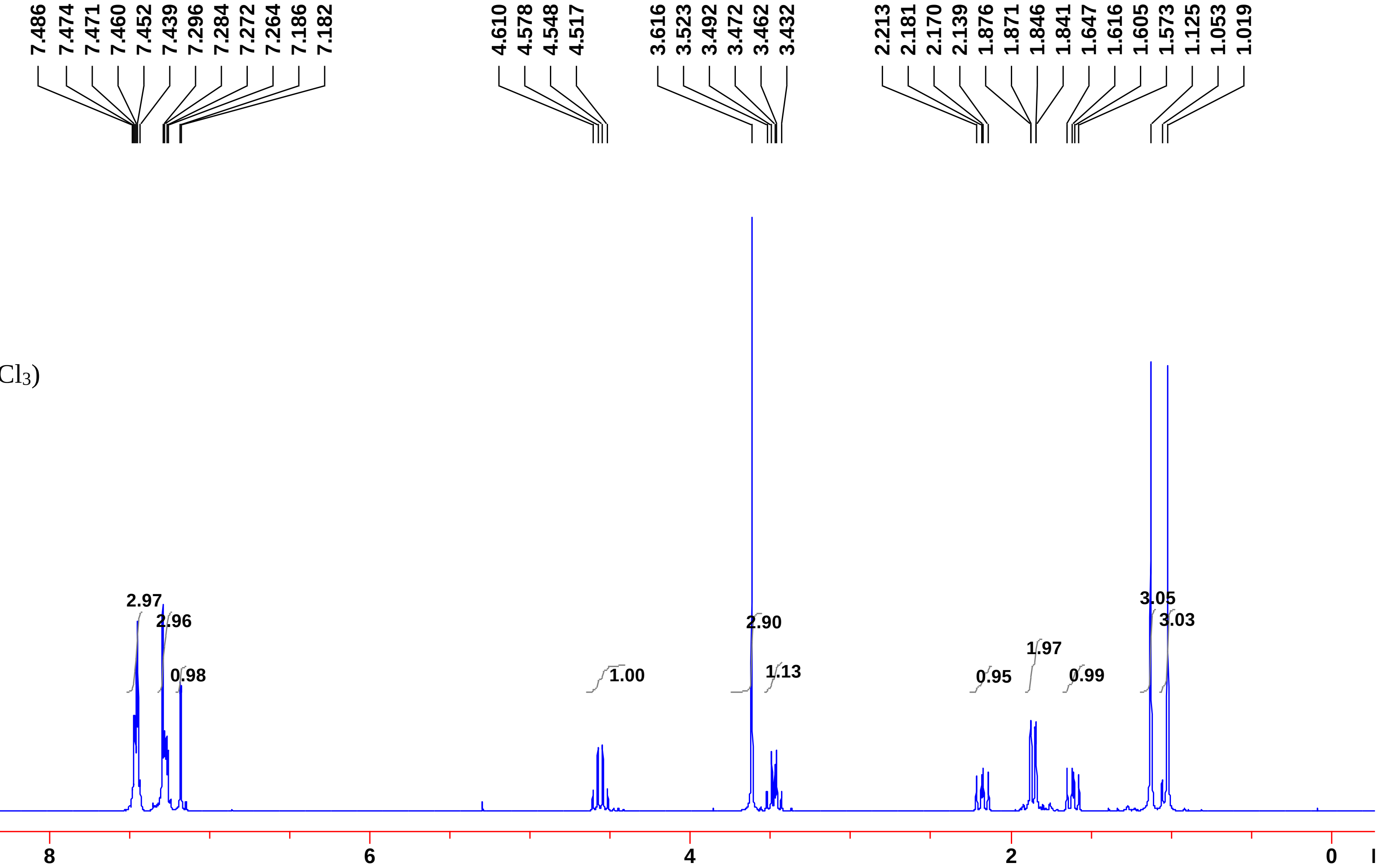


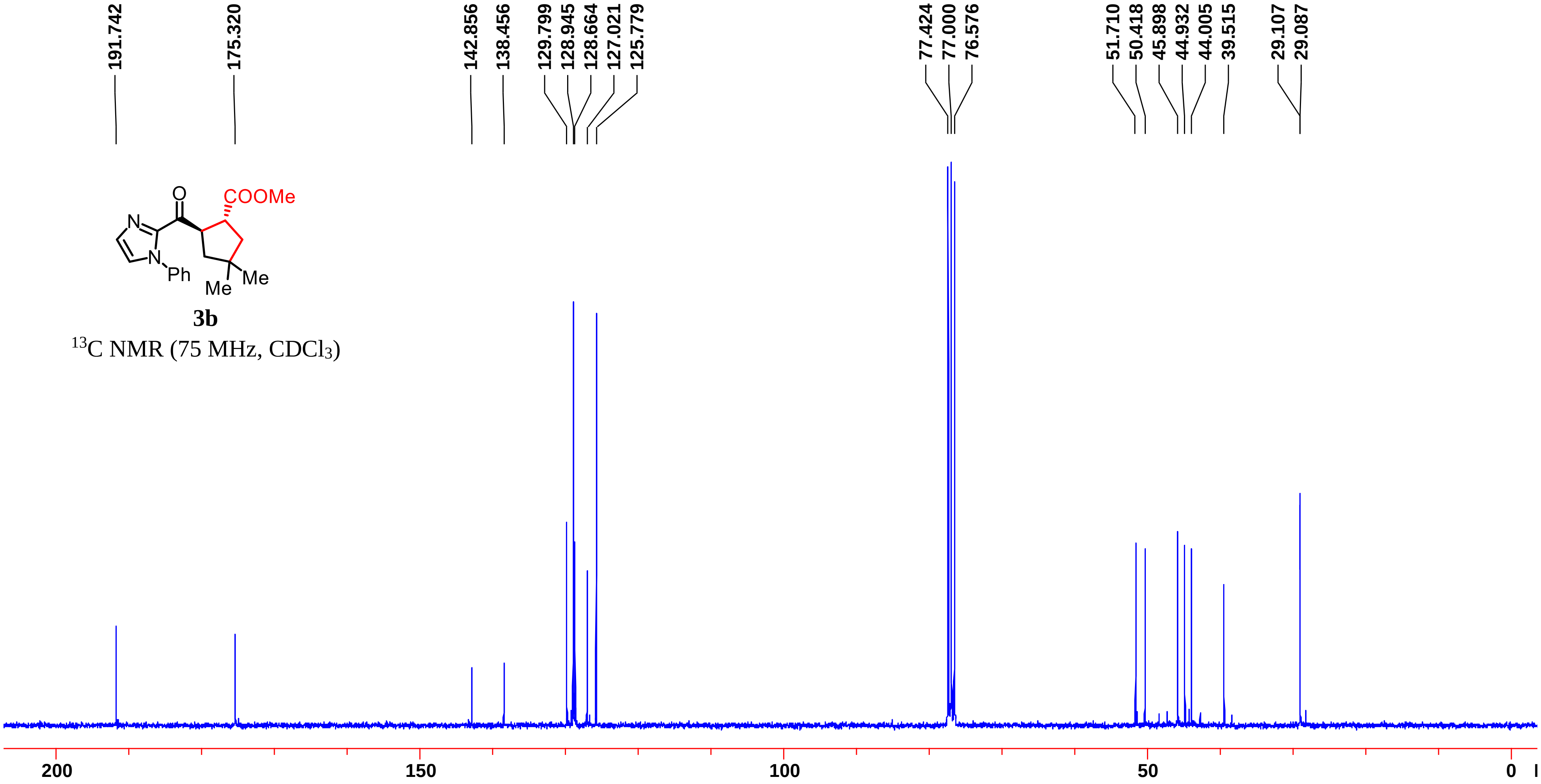

189.251
142.029
138.089
130.258
129.025
128.974
127.690
125.859
122.398
77.422
77.000
76.579
52.128
46.179
45.160
40.284
28.635
28.549
27.926
O
CN
N
N
Ph
Me
Me
3a
^{13}C NMR (75 MHz, $CDCl_3$)
200
150
100
50
0



3b

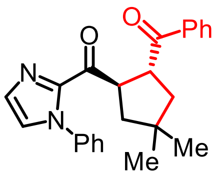
^{1}H NMR (300 MHz, $CDCl_3$)





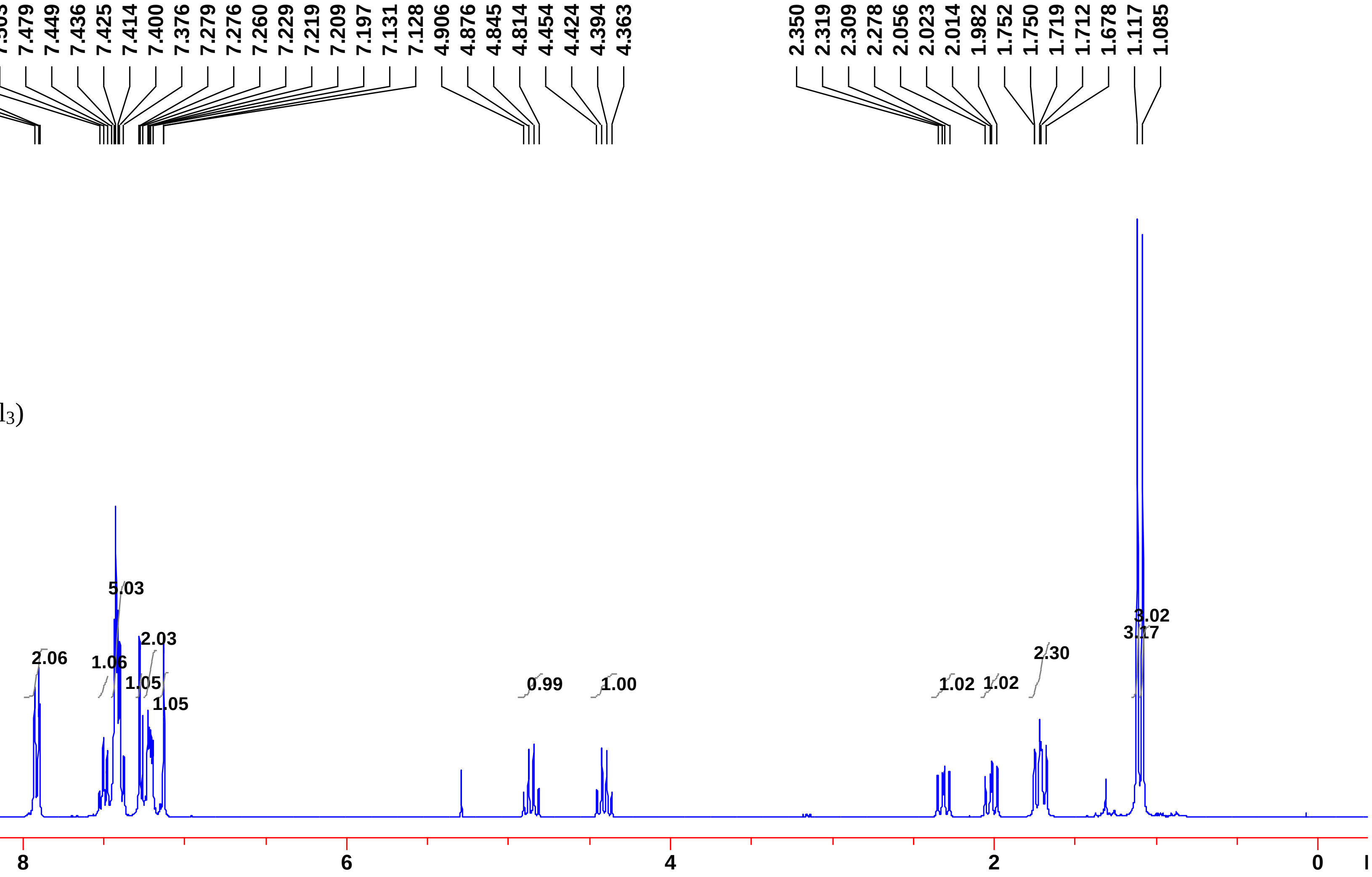
3b

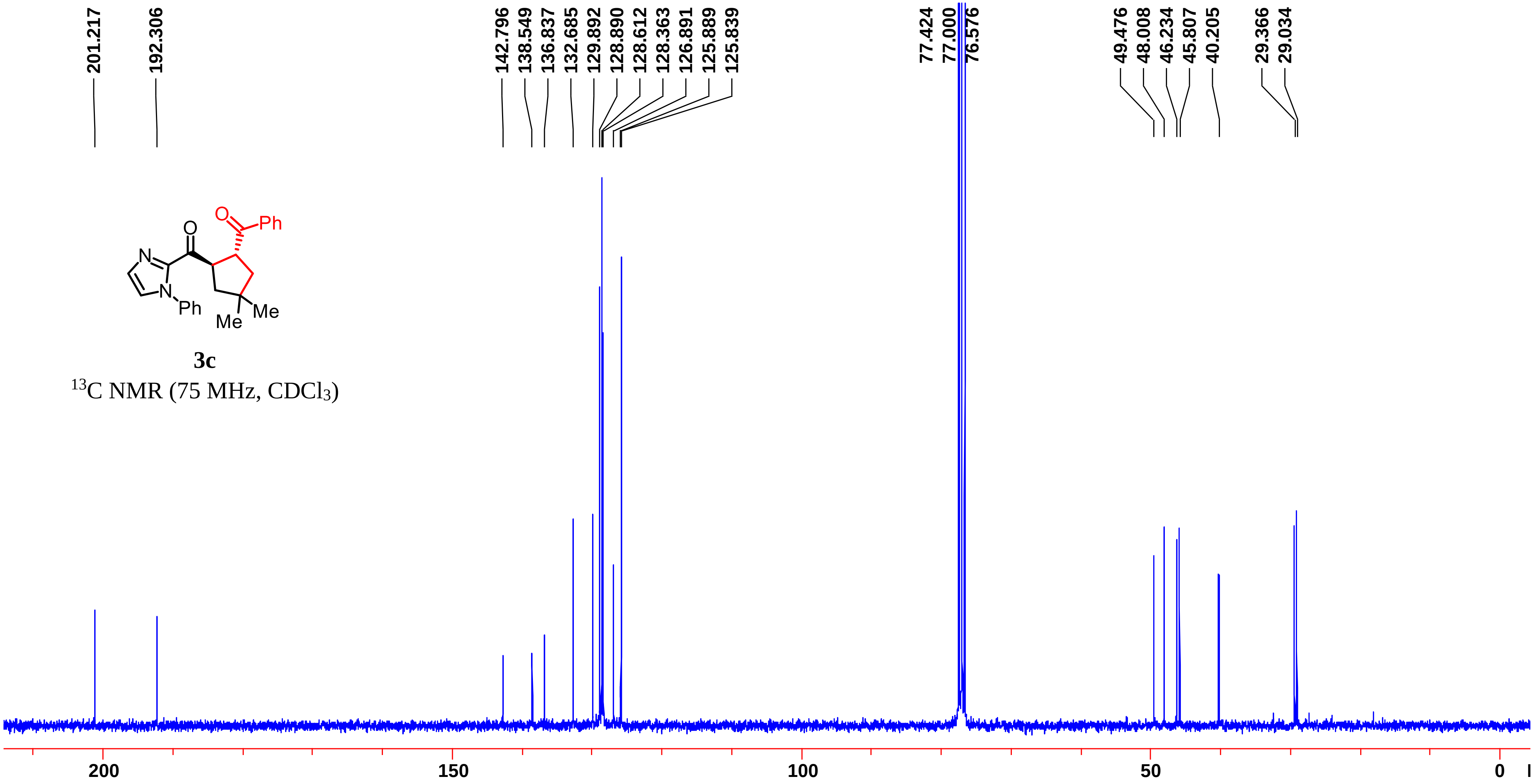
^{13}C NMR (75 MHz, $CDCl_3$)



3c

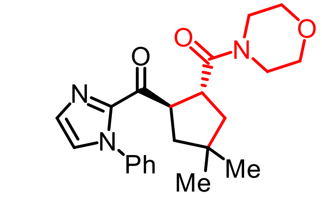
^{1}H NMR (300 MHz, $CDCl_3$)





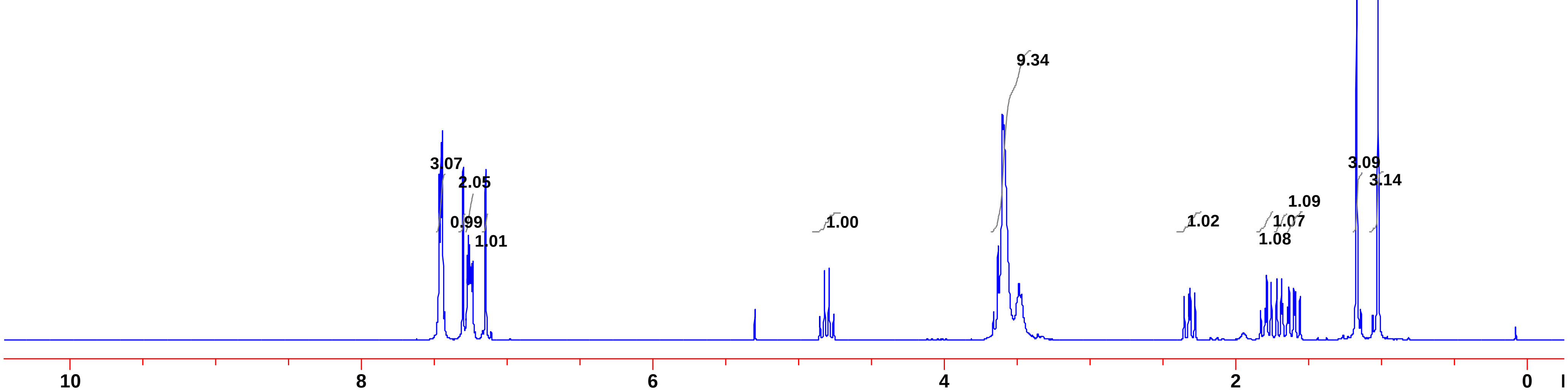
3c

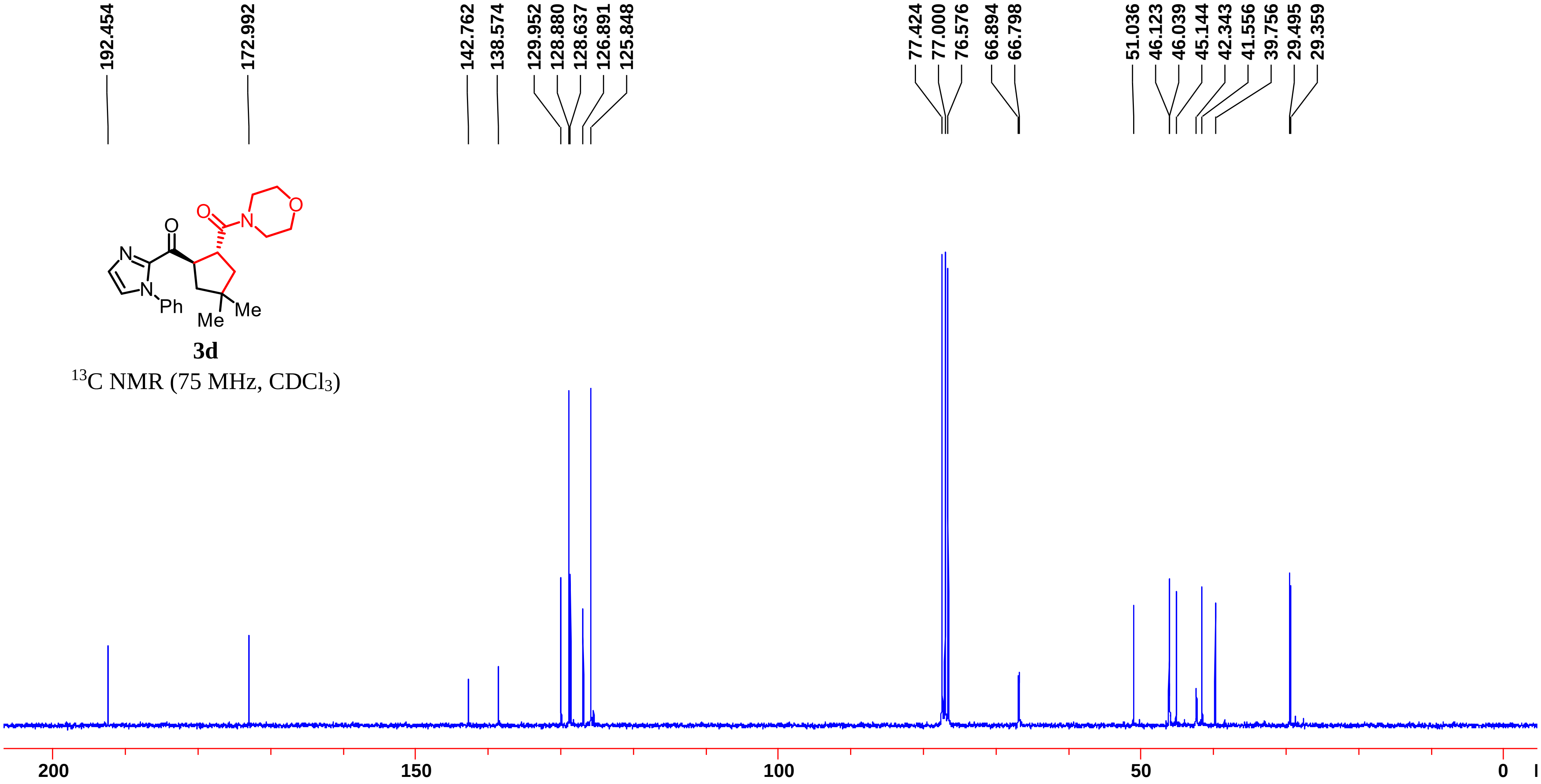
^{13}C NMR (75 MHz, $CDCl_3$)

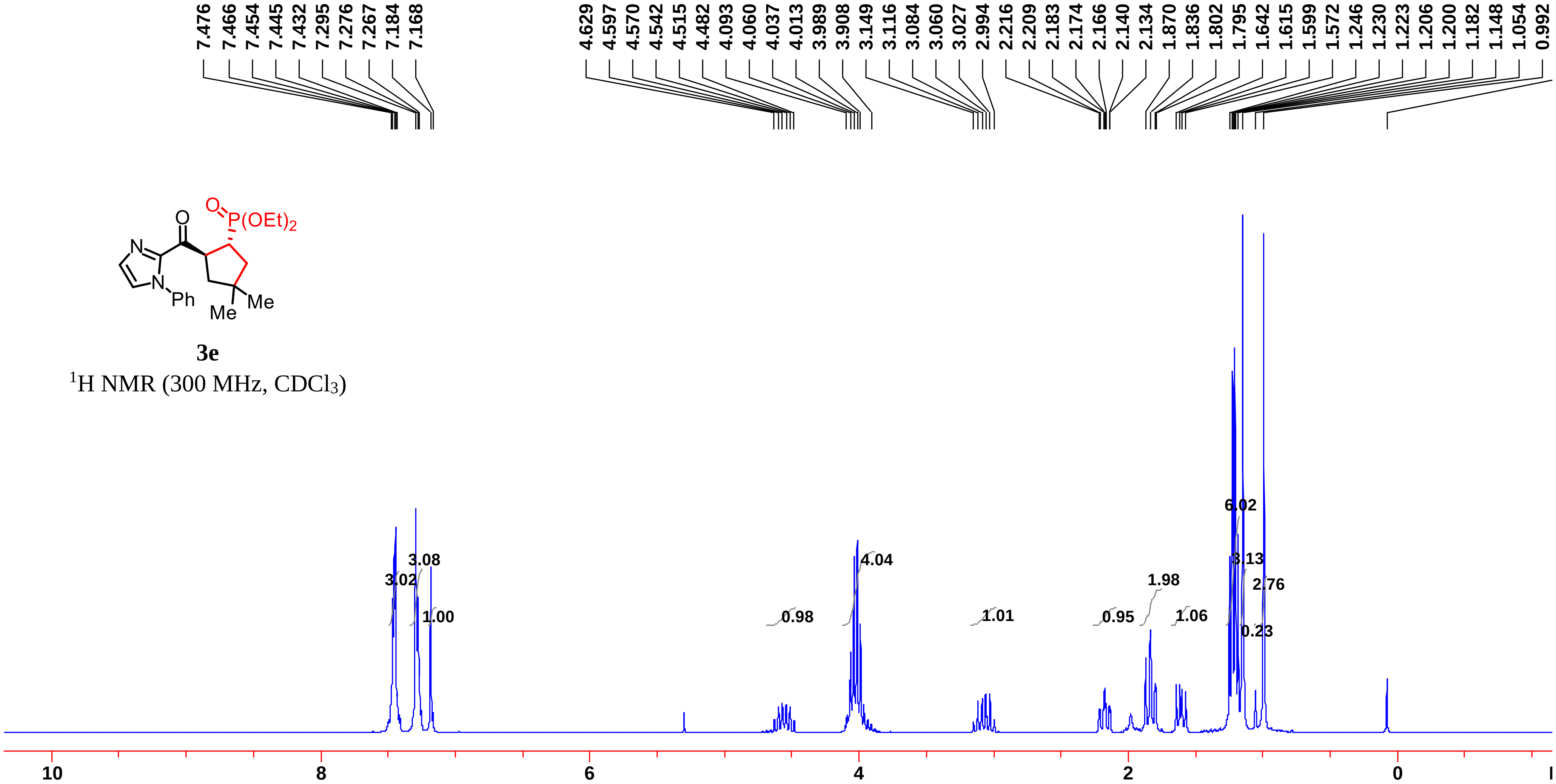


3d

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

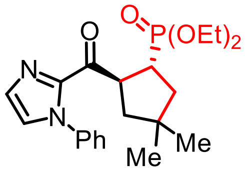



192.454
172.992
142.762
138.574
129.952
128.880
128.637
126.891
125.848
77.424
77.000
76.576
66.894
66.798
51.036
46.123
46.039
45.144
42.343
41.556
39.756
29.495
29.359
O
N
N
Ph
O
N
O
Me
Me
3d
^{13}C NMR (75 MHz, $CDCl_3$)
200
150
100
50
0



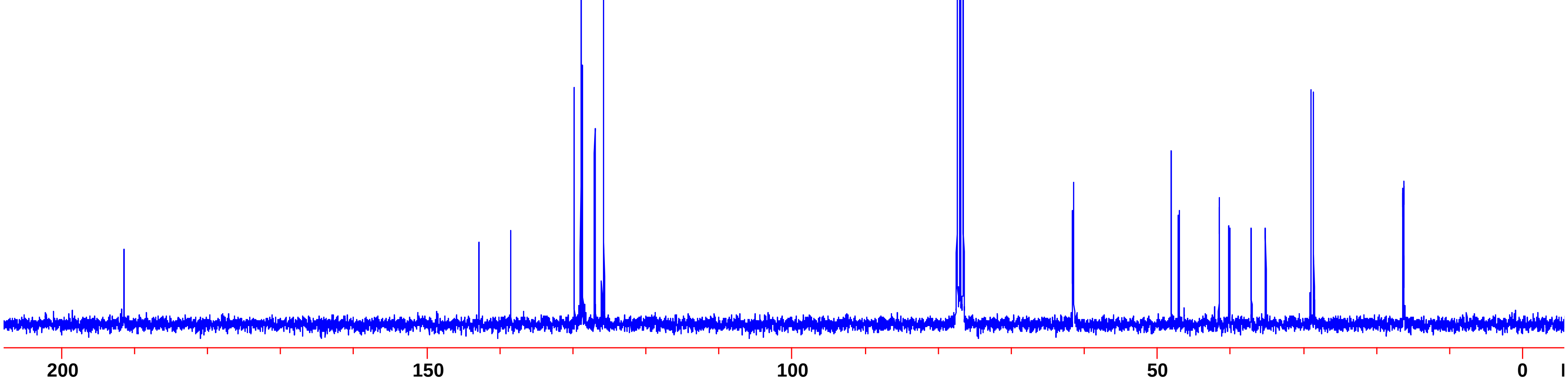
3e

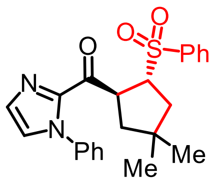
^{1}H NMR (300 MHz, $CDCl_3$)



3e

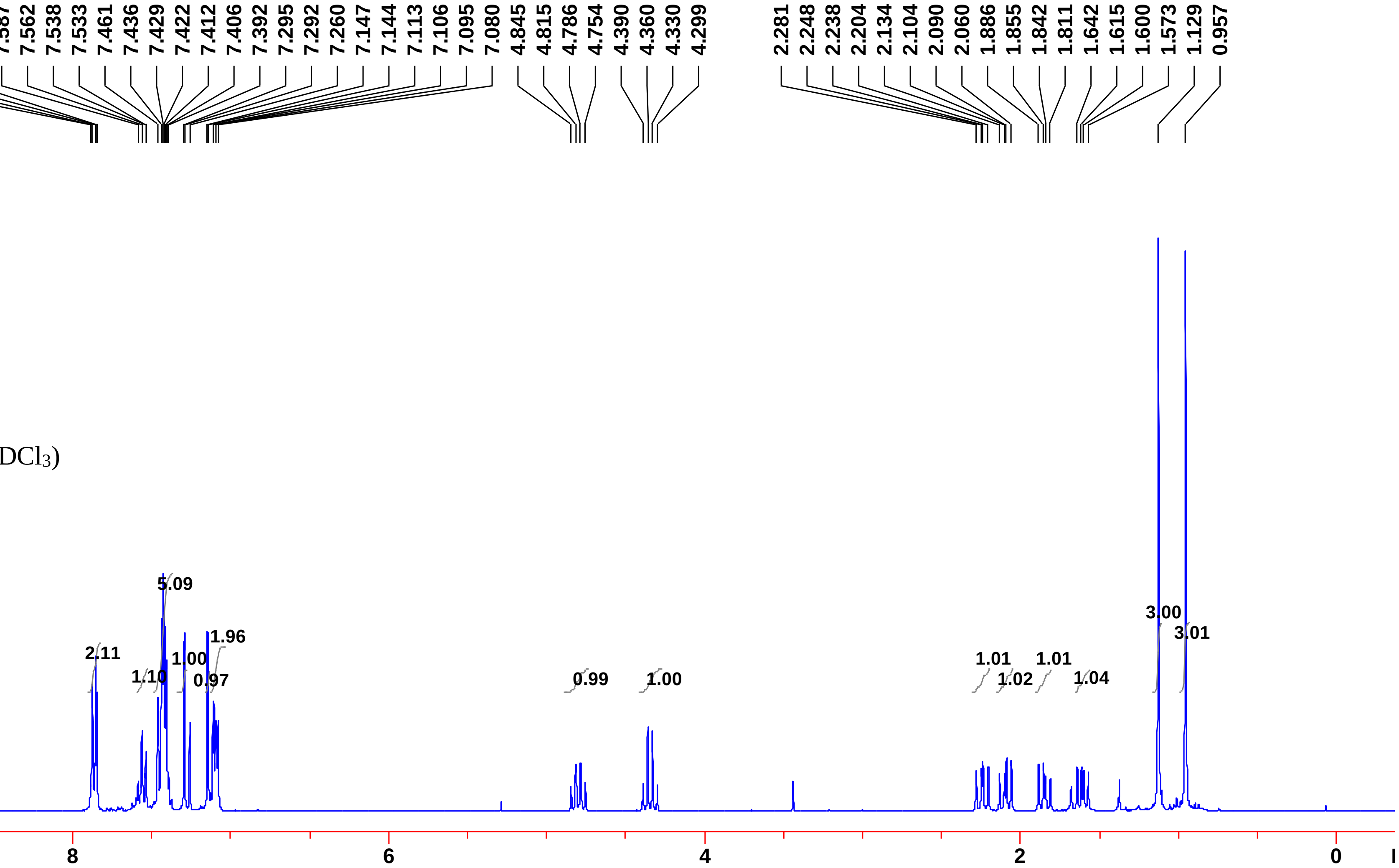
^{13}C NMR (75 MHz, $CDCl_3$)

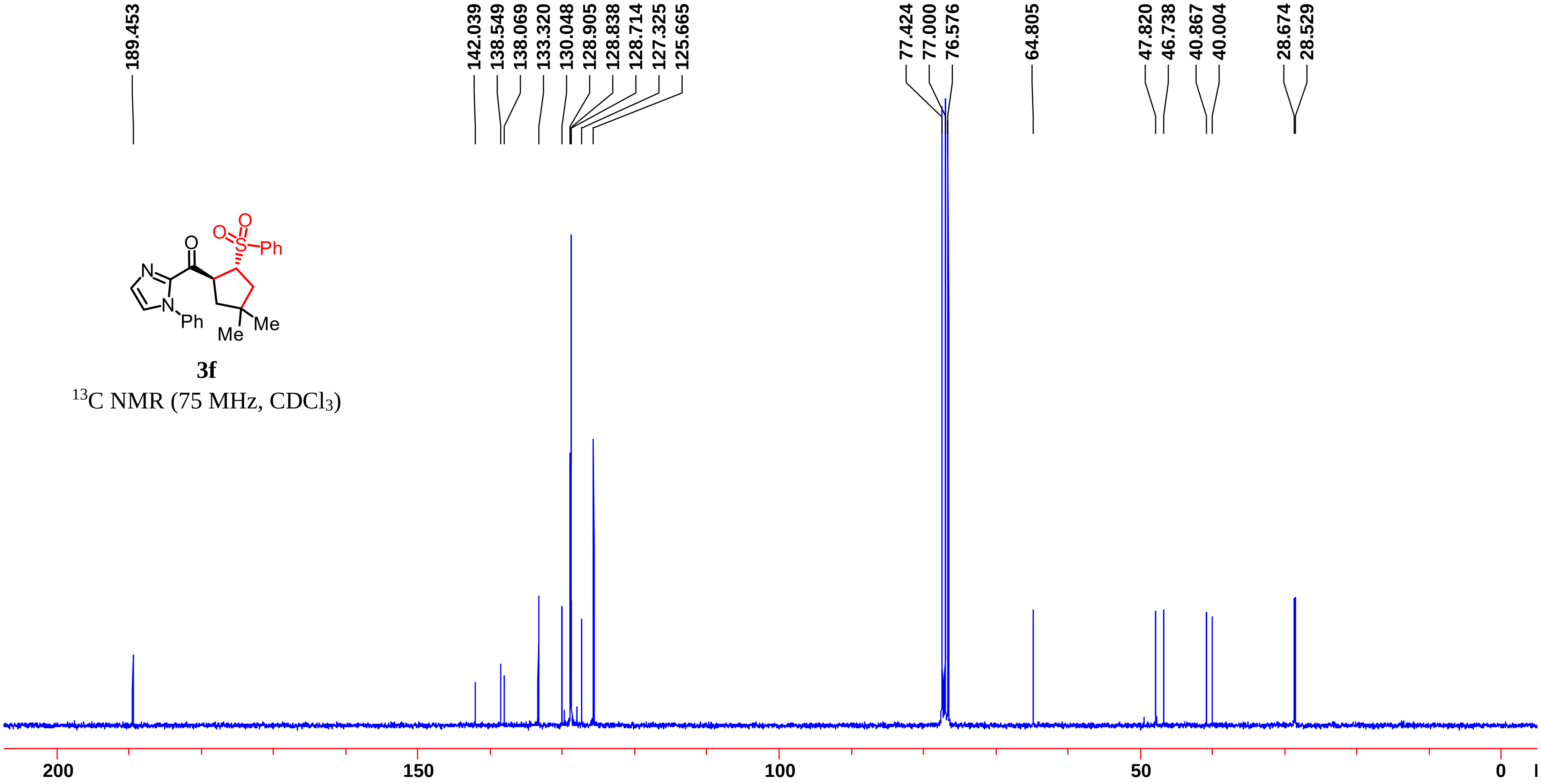




3f

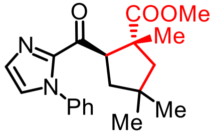
^{1}H NMR (300 MHz, $CDCl_3$)





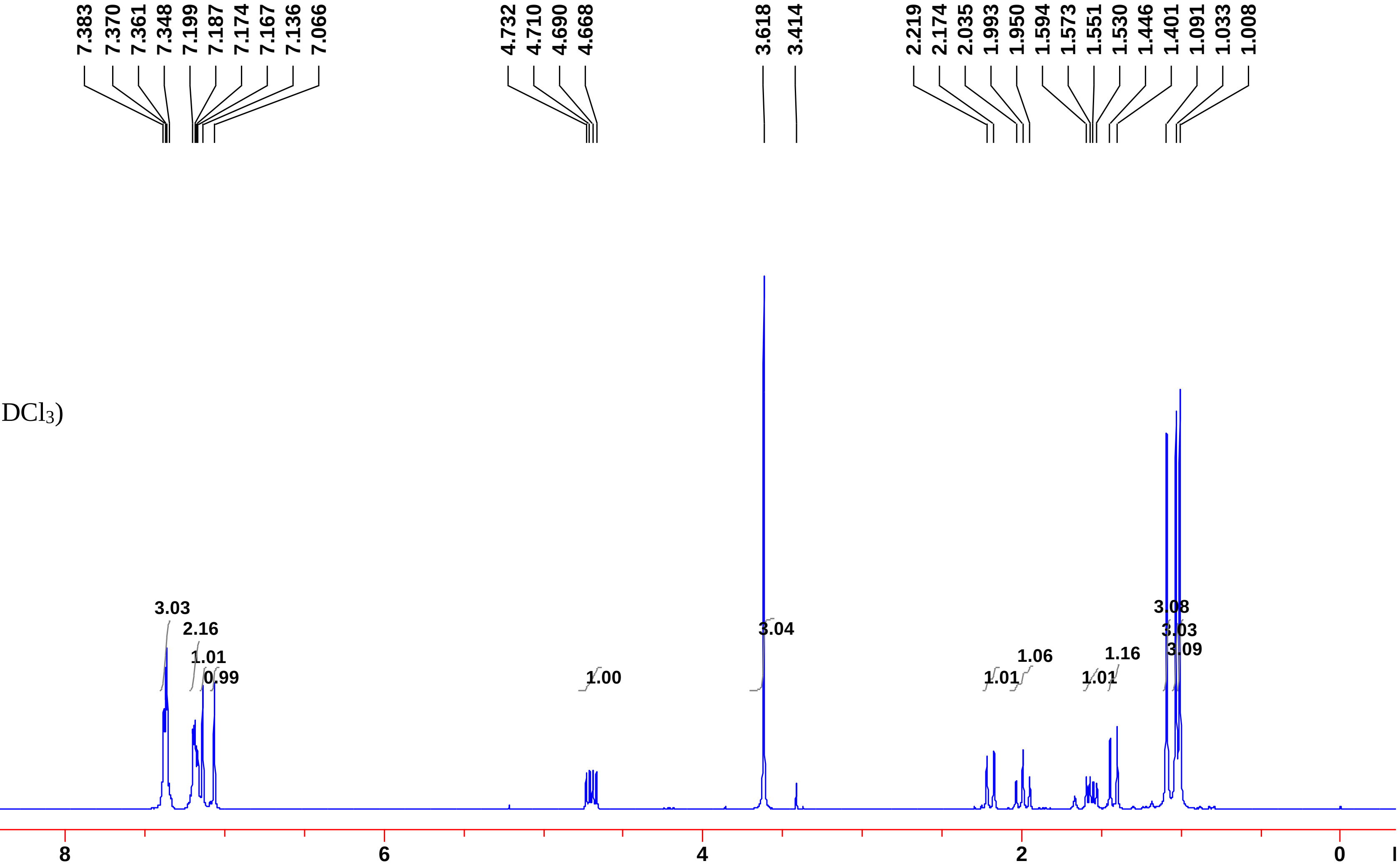
3f

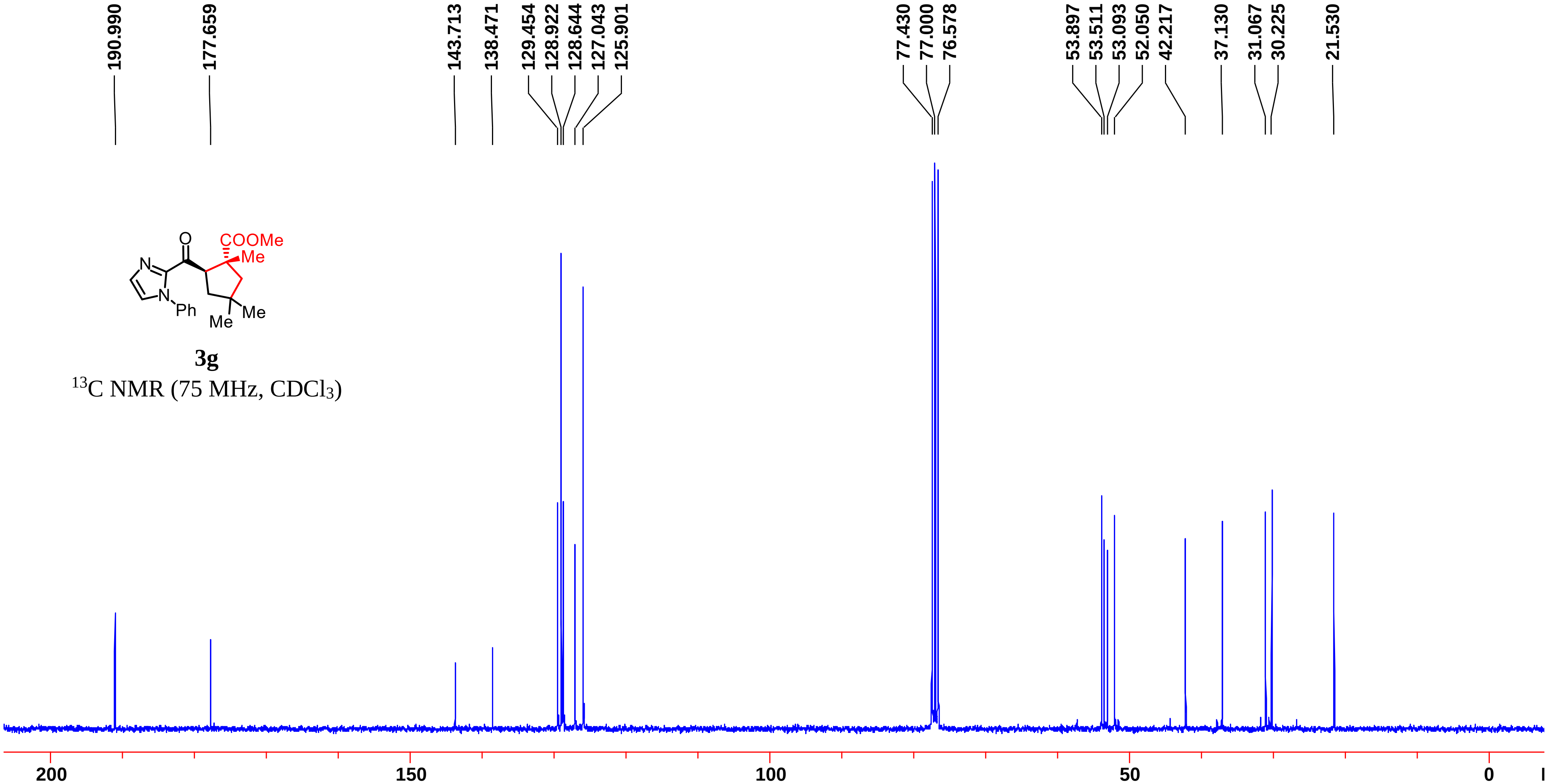
^{13}C NMR (75 MHz, $CDCl_3$)



3g

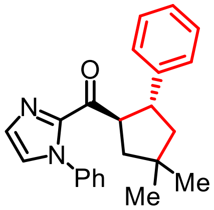
^{1}H NMR (300 MHz, $CDCl_3$)





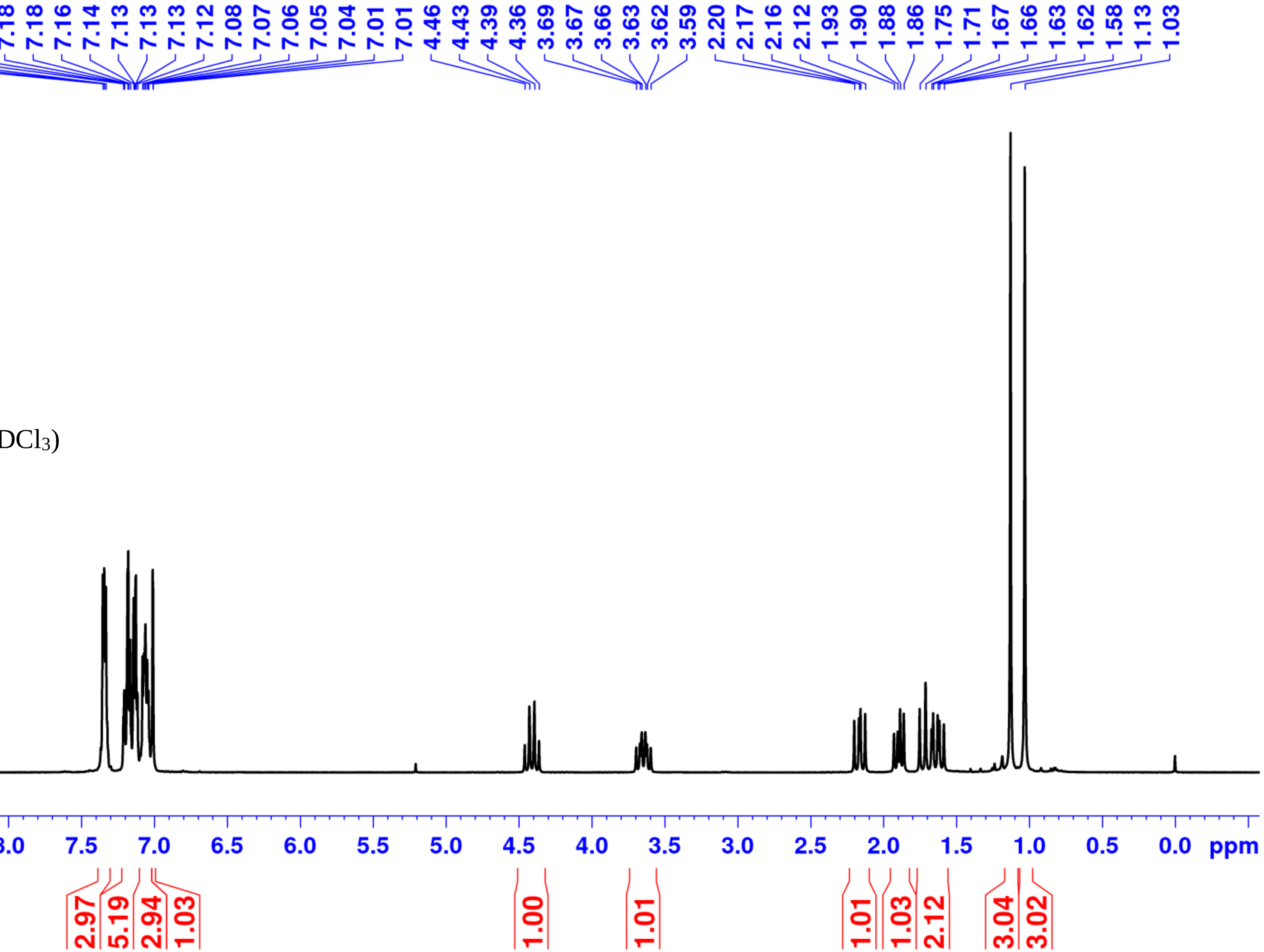
3g

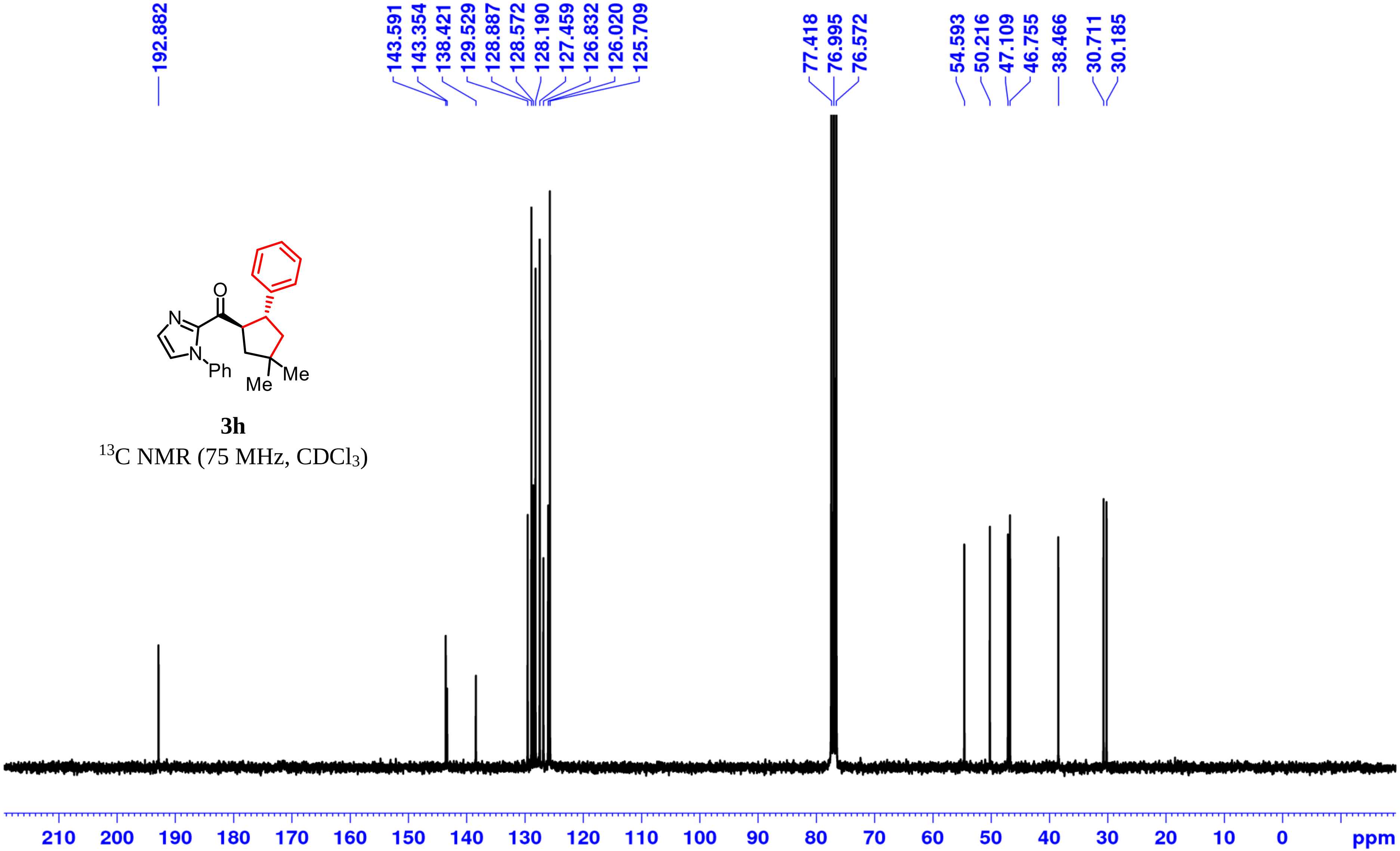
^{13}C NMR (75 MHz, $CDCl_3$)



3h

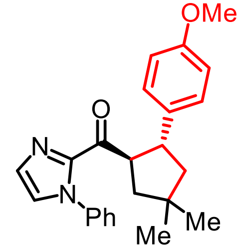
[1]H NMR (300 MHz, $CDCl_3$)





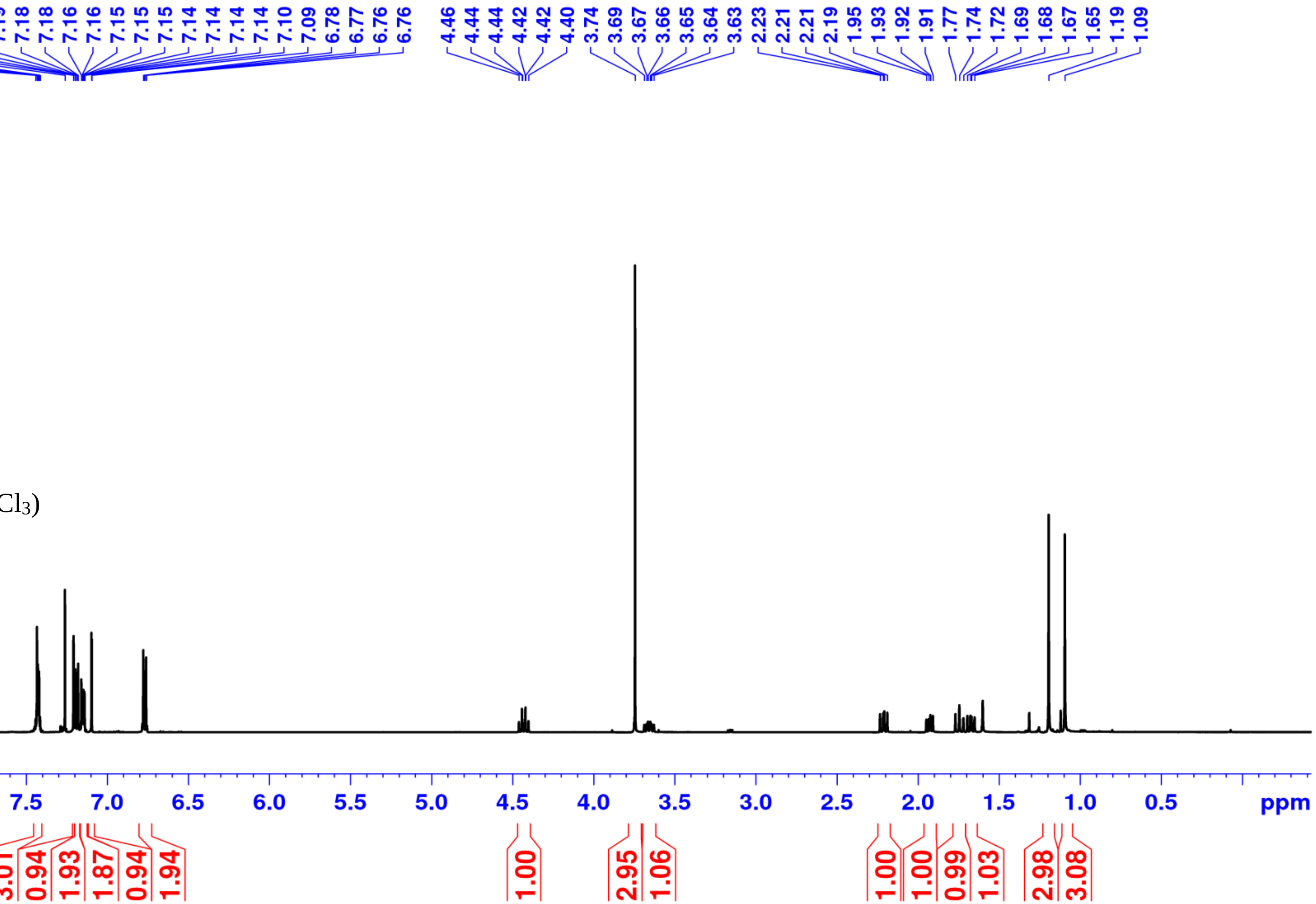
3h

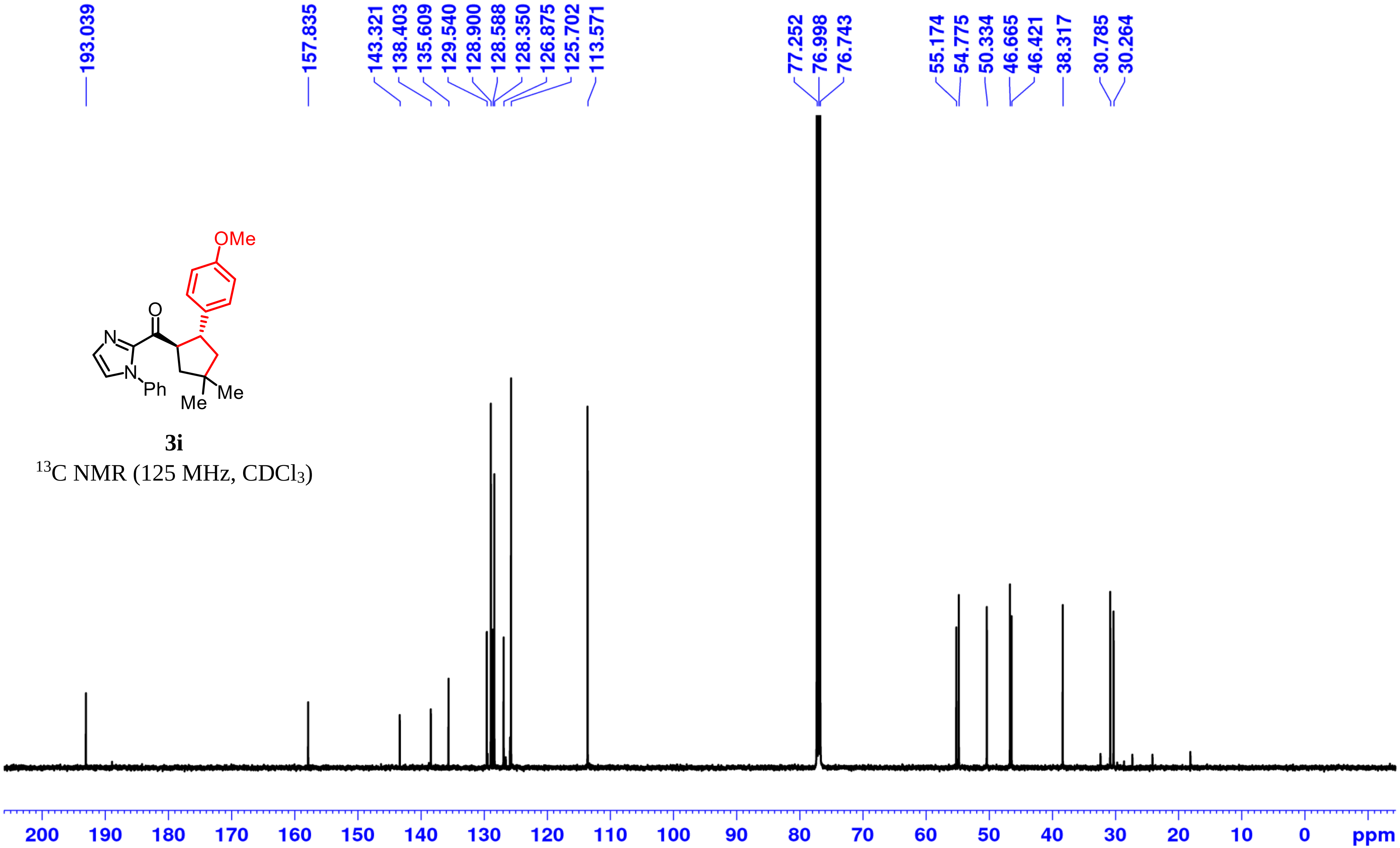
^{13}C NMR (75 MHz, $CDCl_3$)



3i

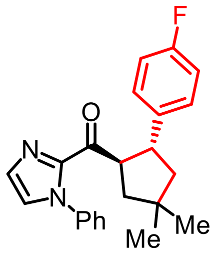
^{1}H NMR (500 MHz, $CDCl_3$)





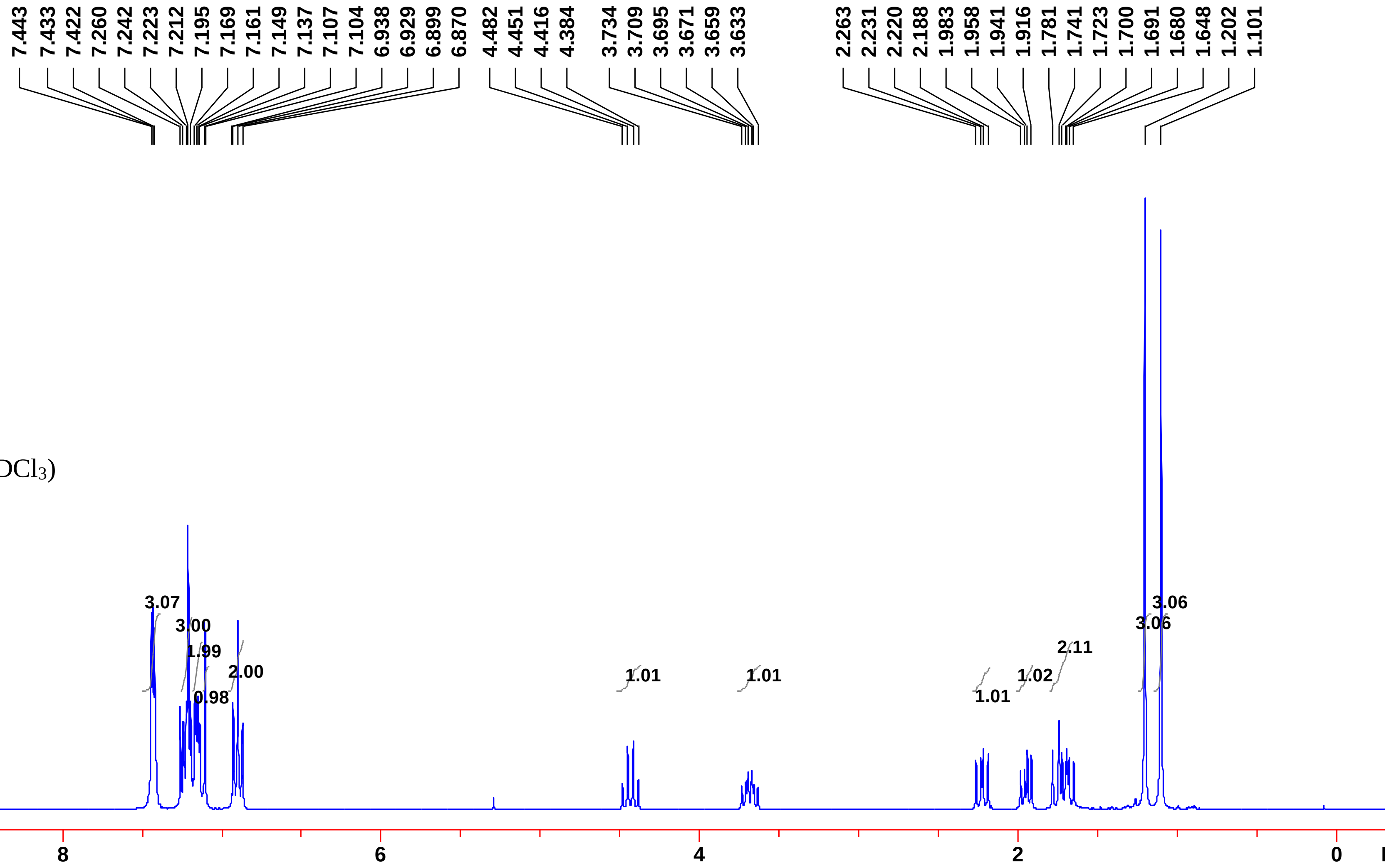
3i

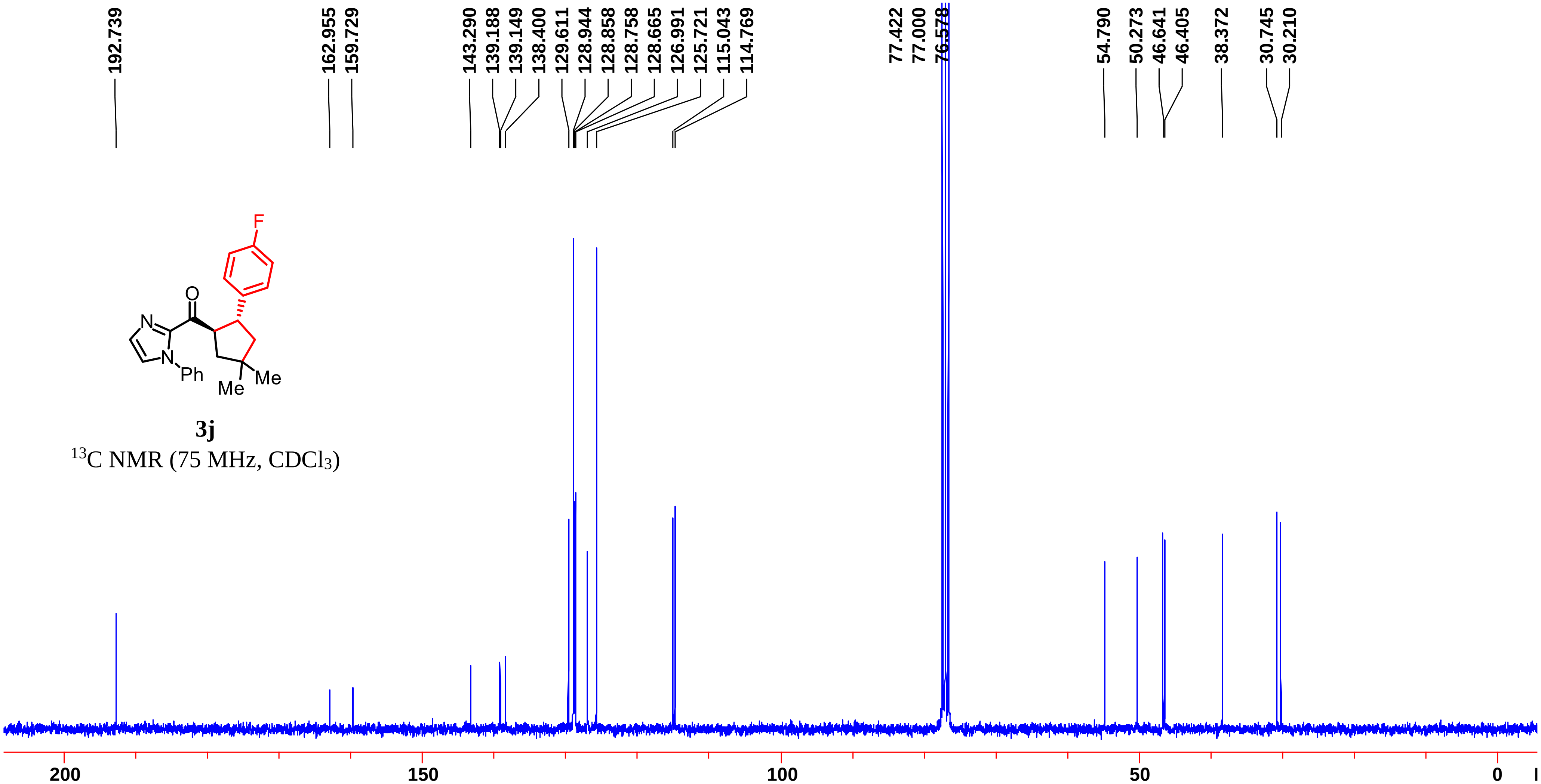
^{13}C NMR (125 MHz, $CDCl_3$)

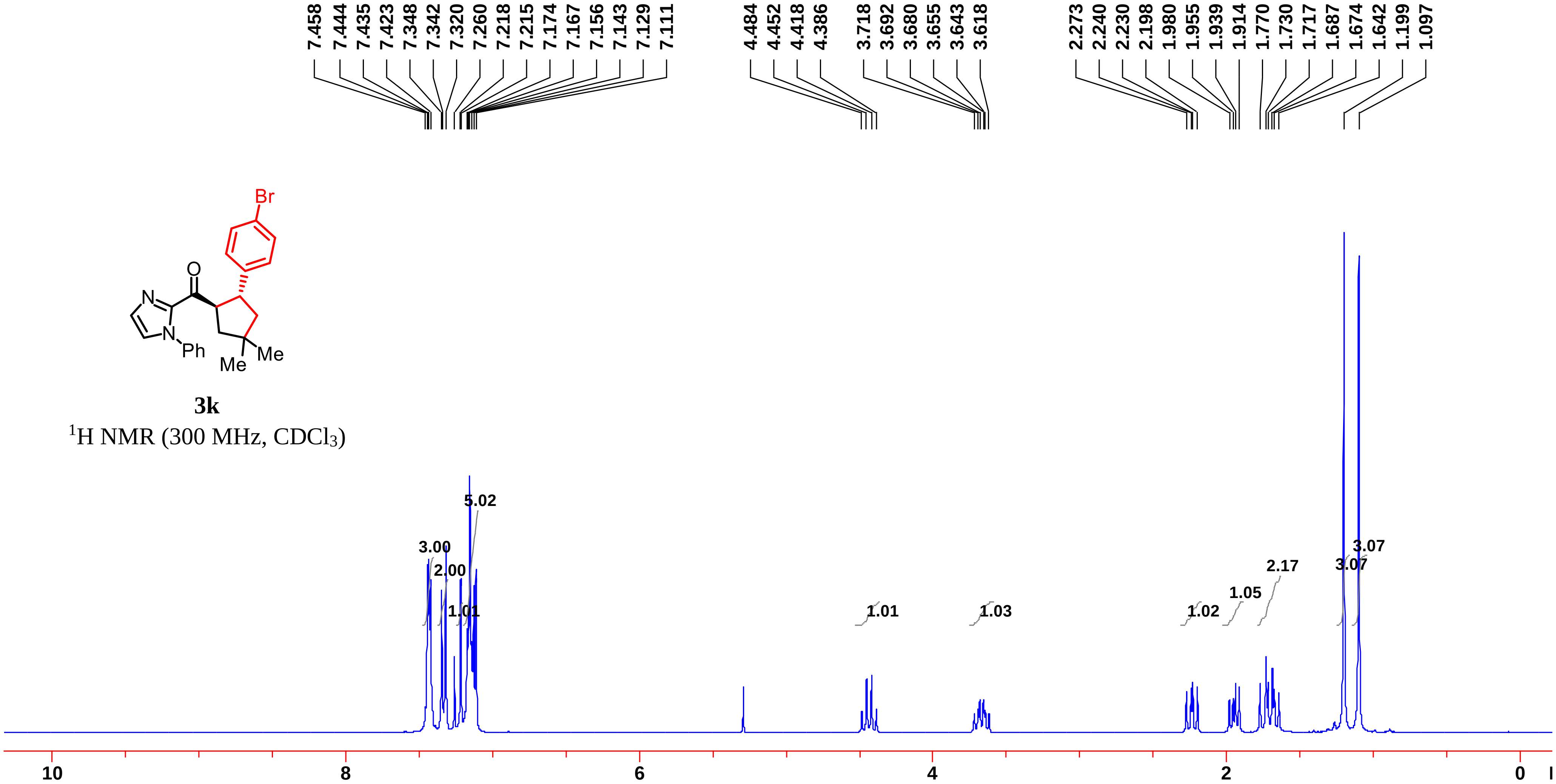


3j

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

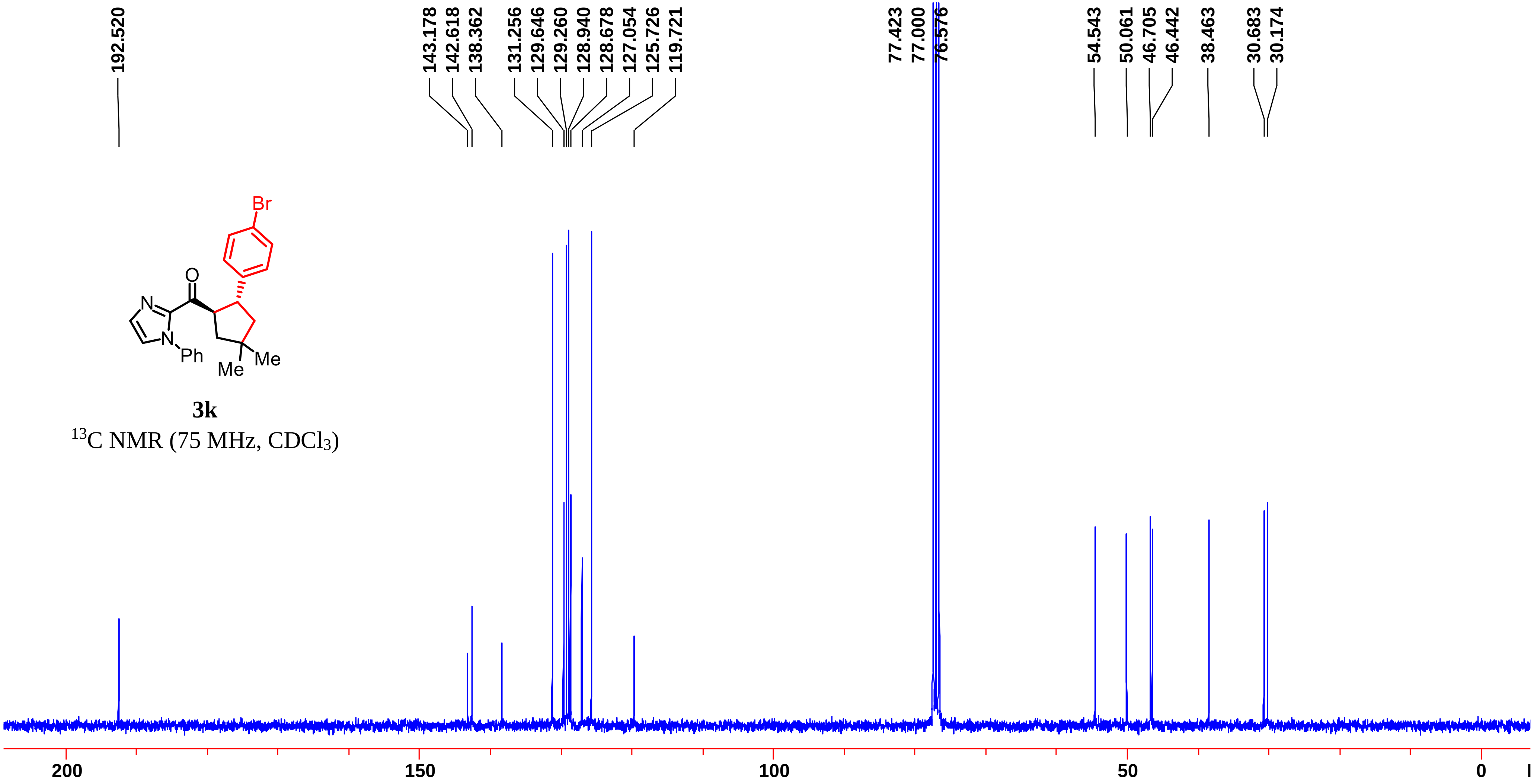



192.739
162.955
159.729
143.290
139.188
139.149
138.400
129.611
128.944
128.858
128.758
128.665
126.991
125.721
115.043
114.769
77.422
77.000
76.578
54.790
50.273
46.641
46.405
38.372
30.745
30.210
F
O
N
N
Ph
Me
Me
3j
^{13}C NMR (75 MHz, CDCl$_3$)
200
150
100
50
0



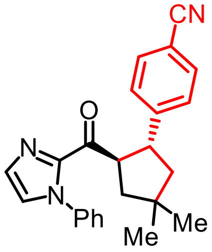
3k

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



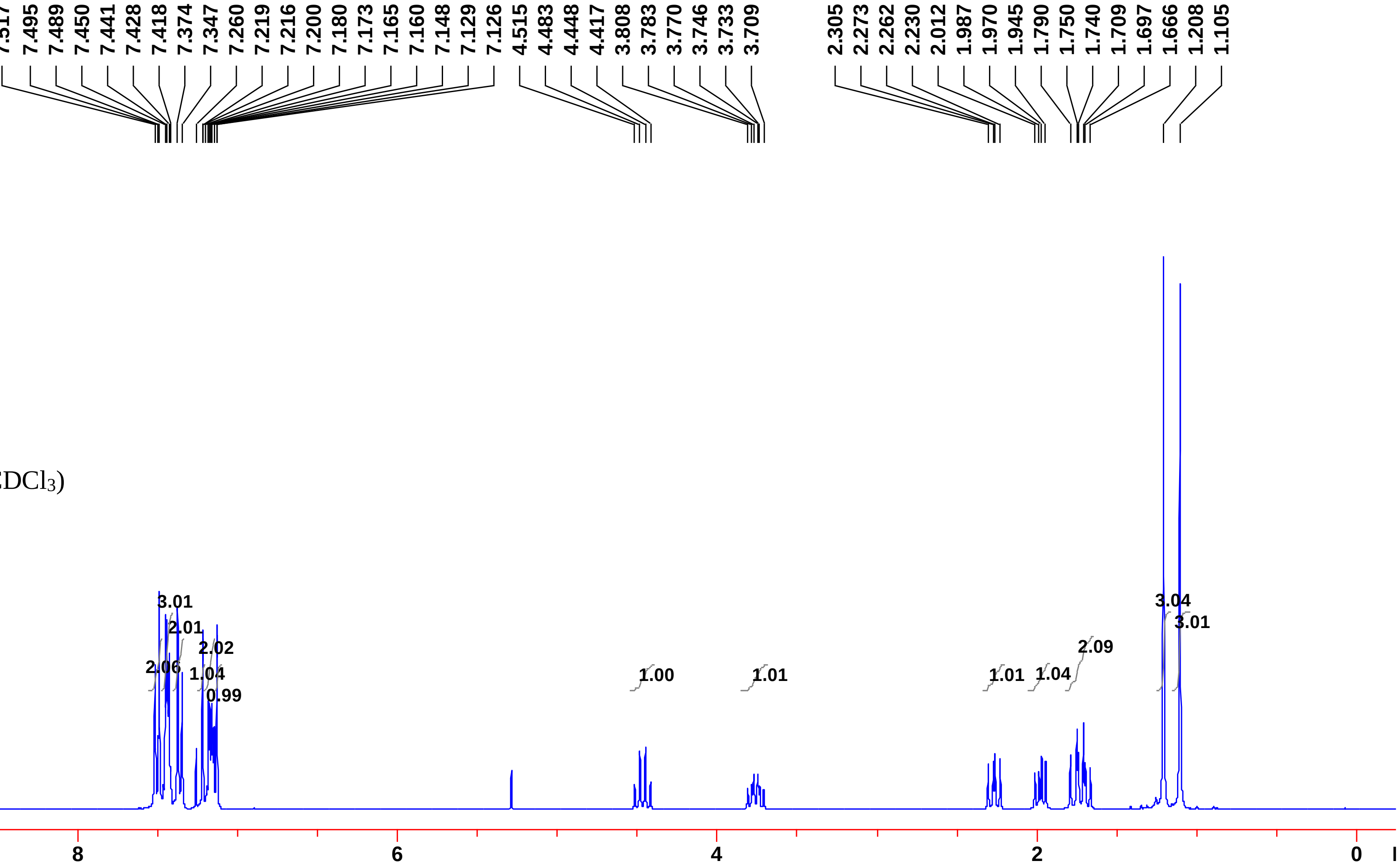
3k

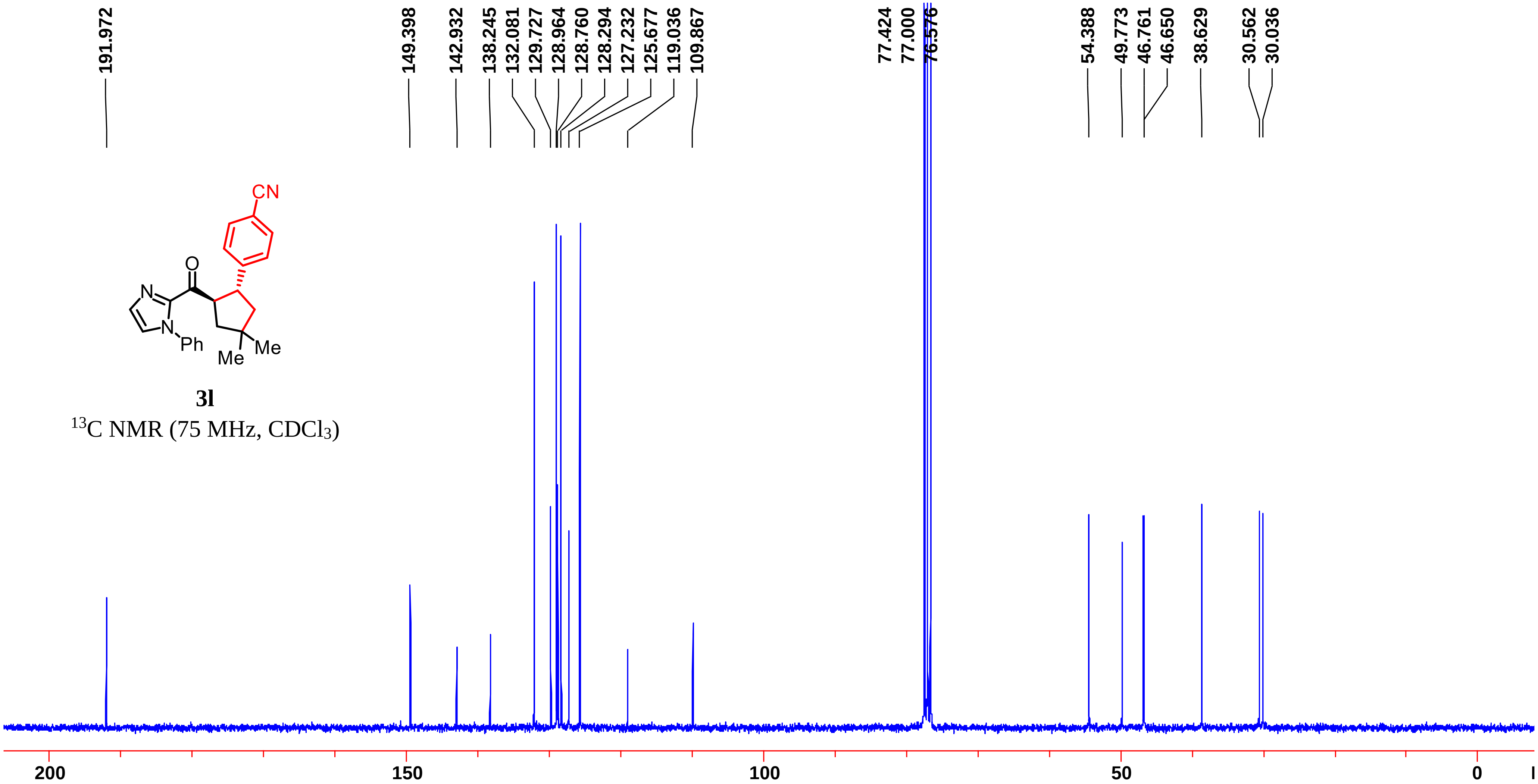
^{13}C NMR (75 MHz, $CDCl_3$)



3l

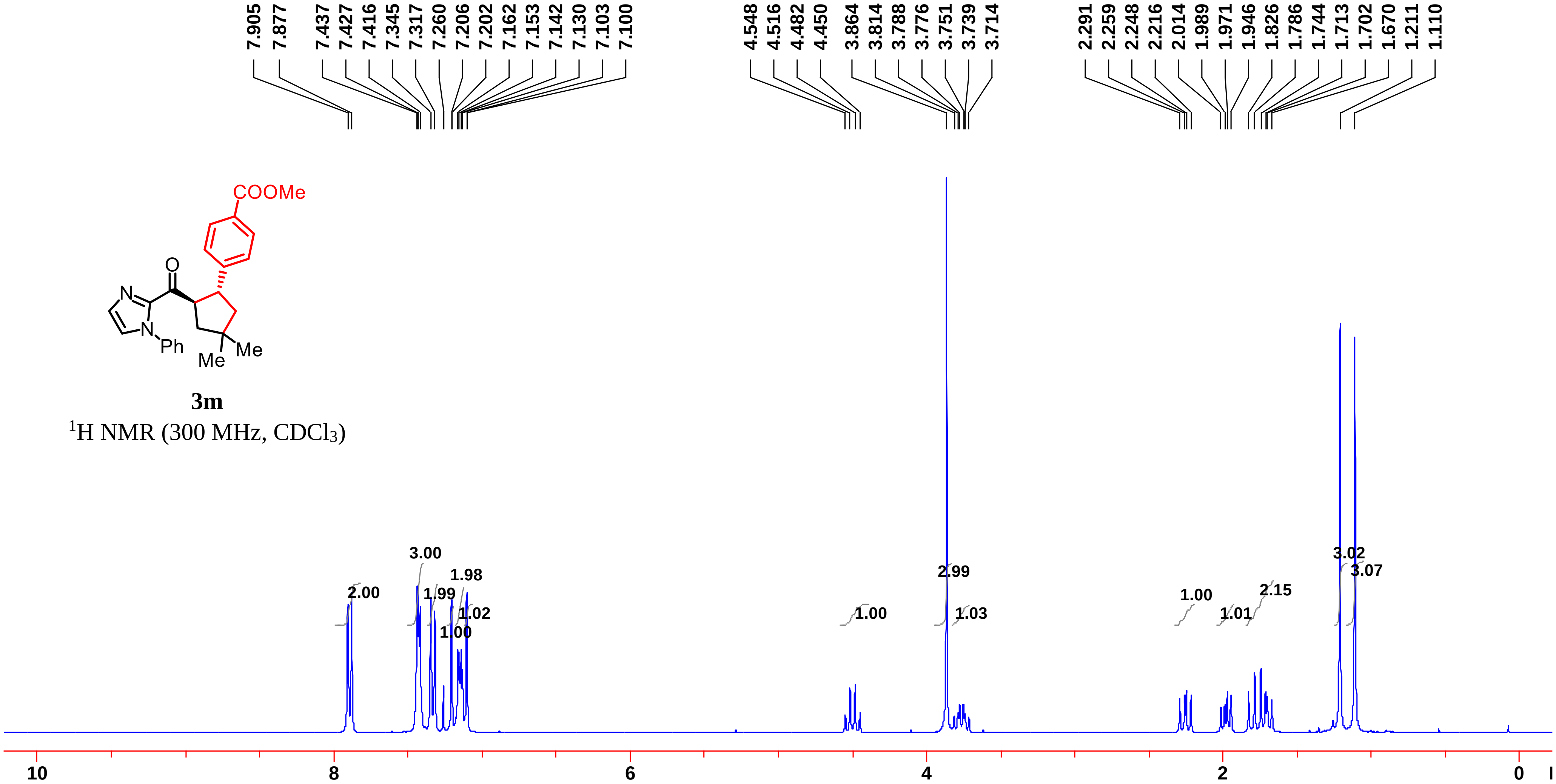
[1]H NMR (300 MHz, $CDCl_3$)





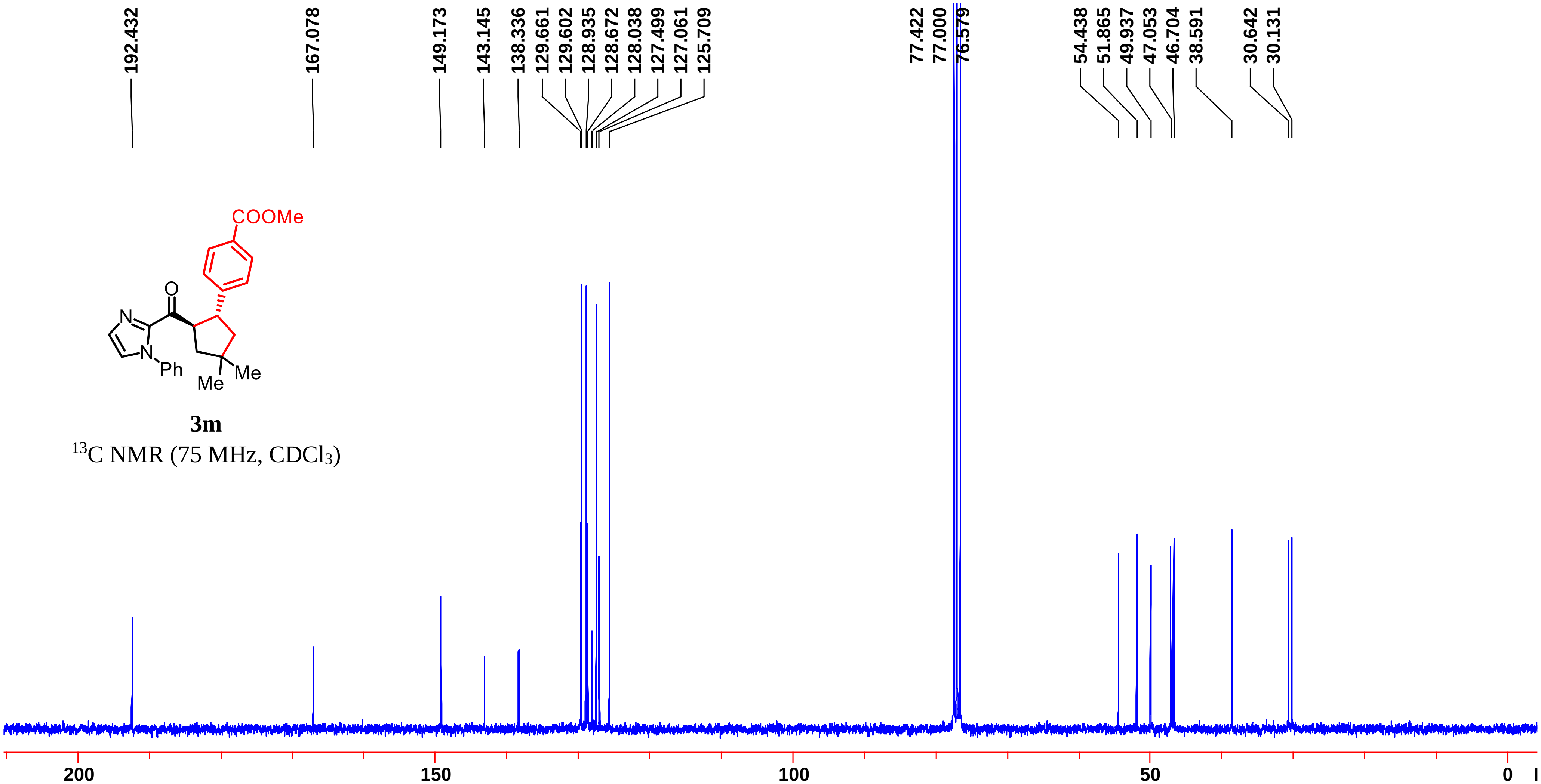
3l

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



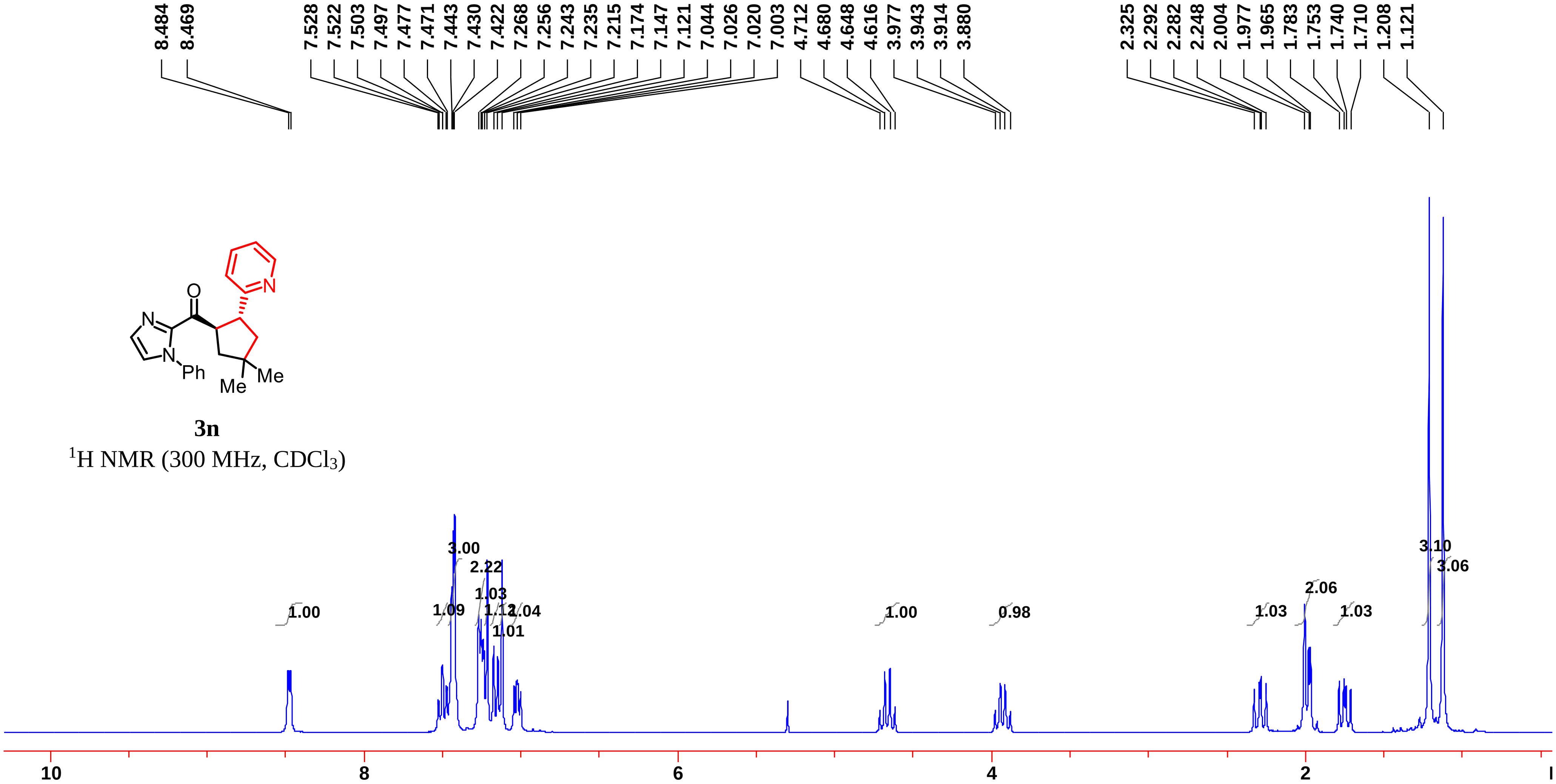
3m

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



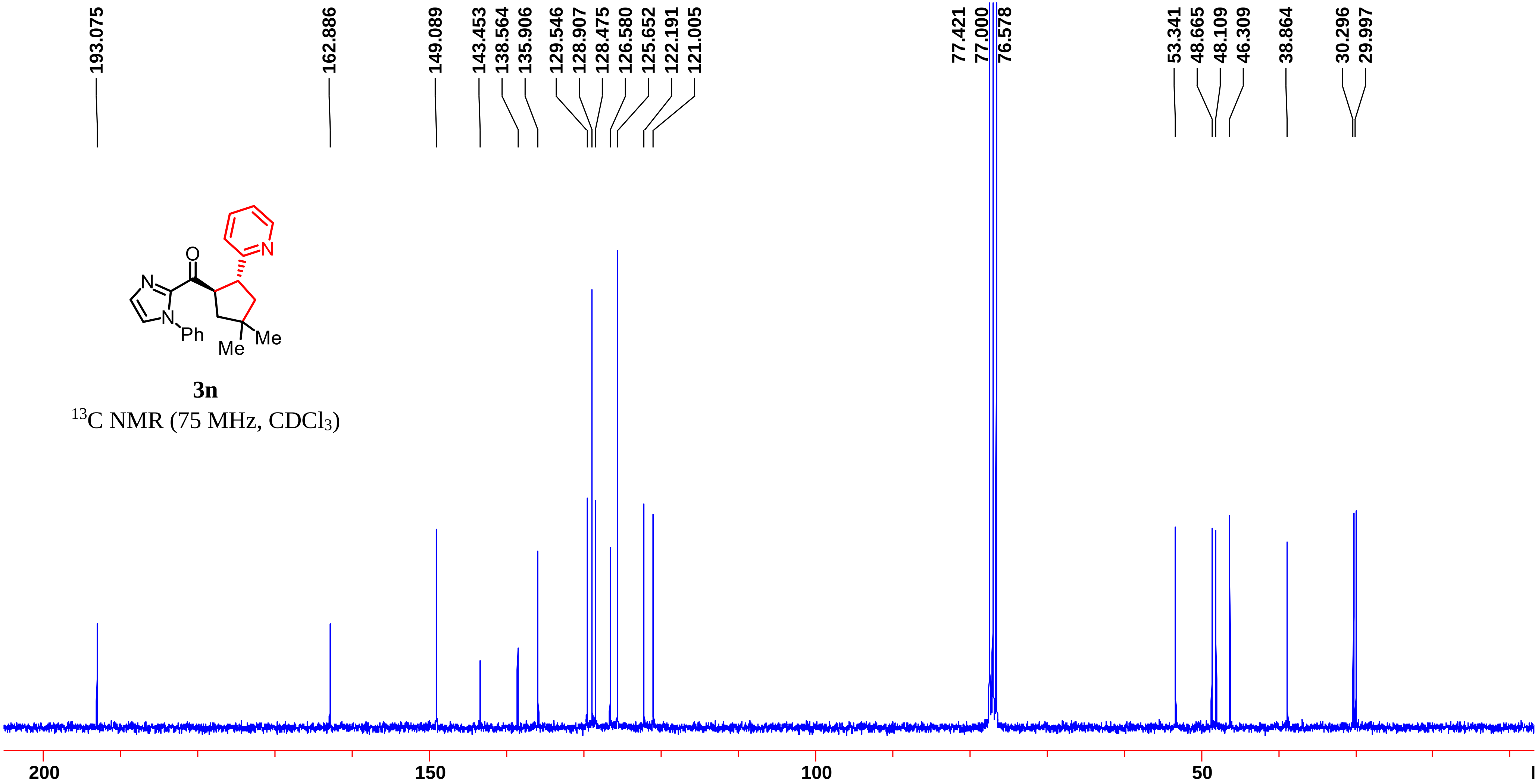
3m

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



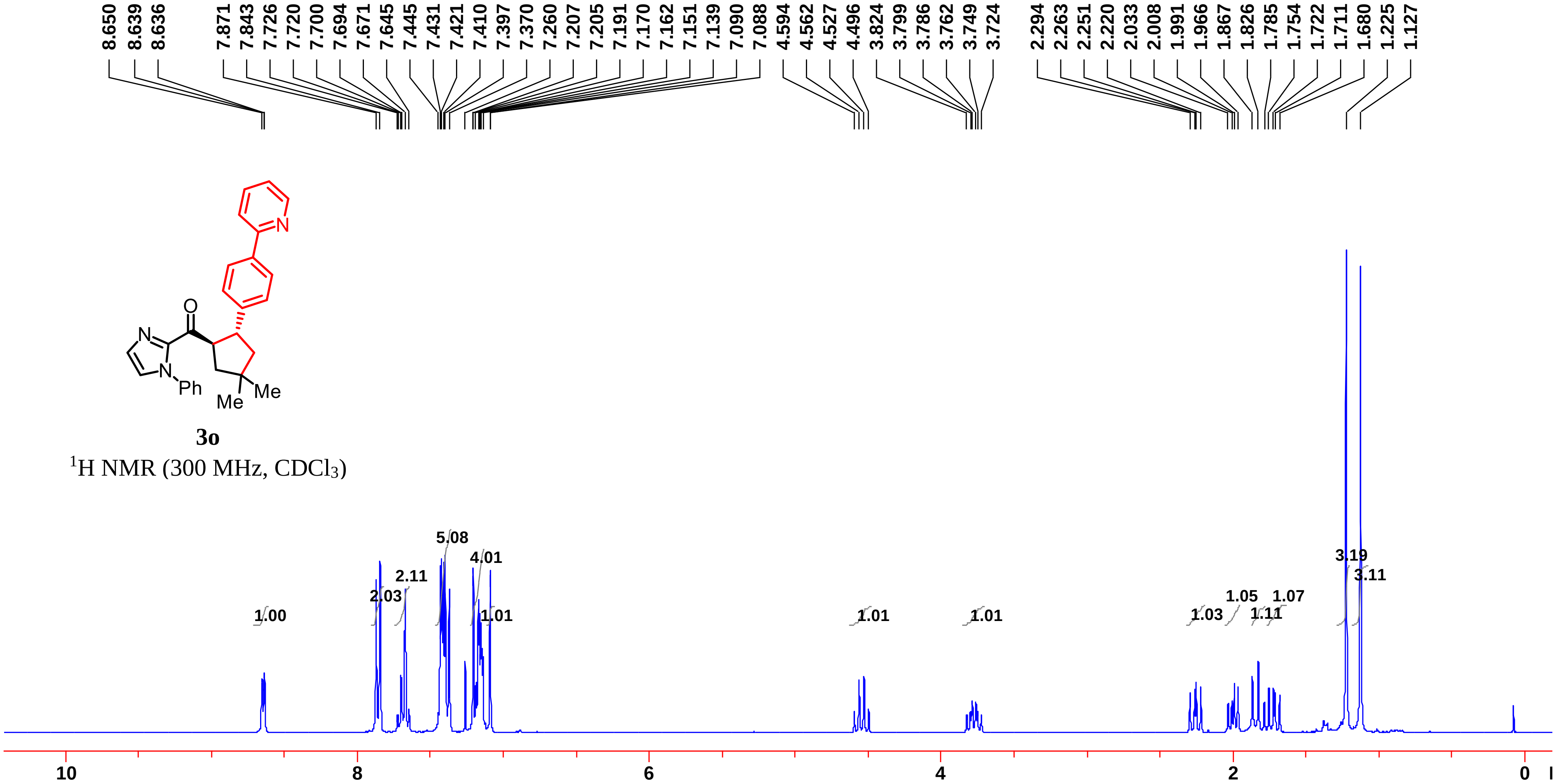
3n

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



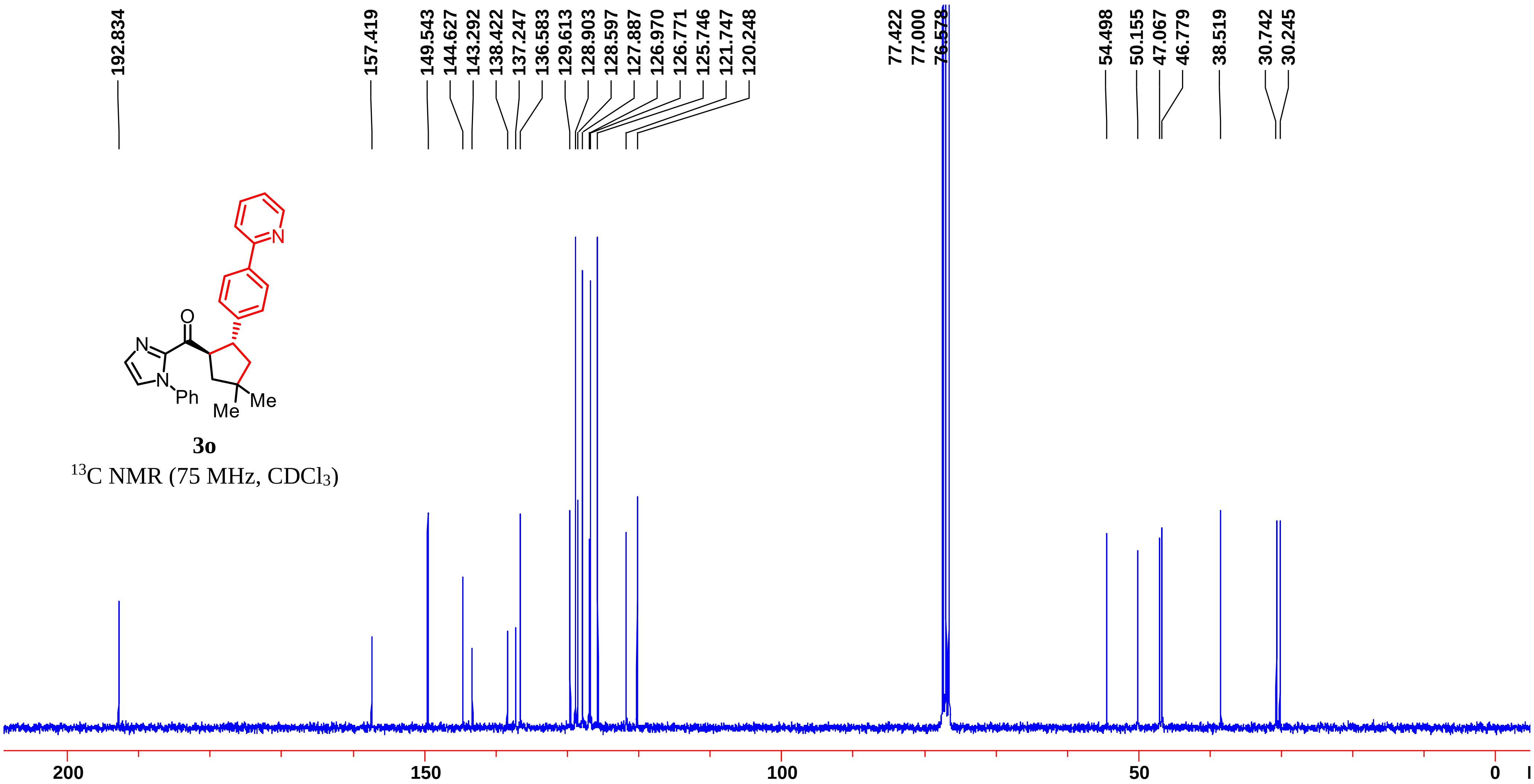
3n

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



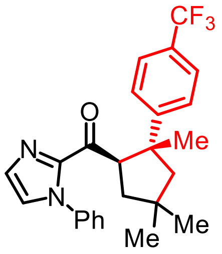
3o

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



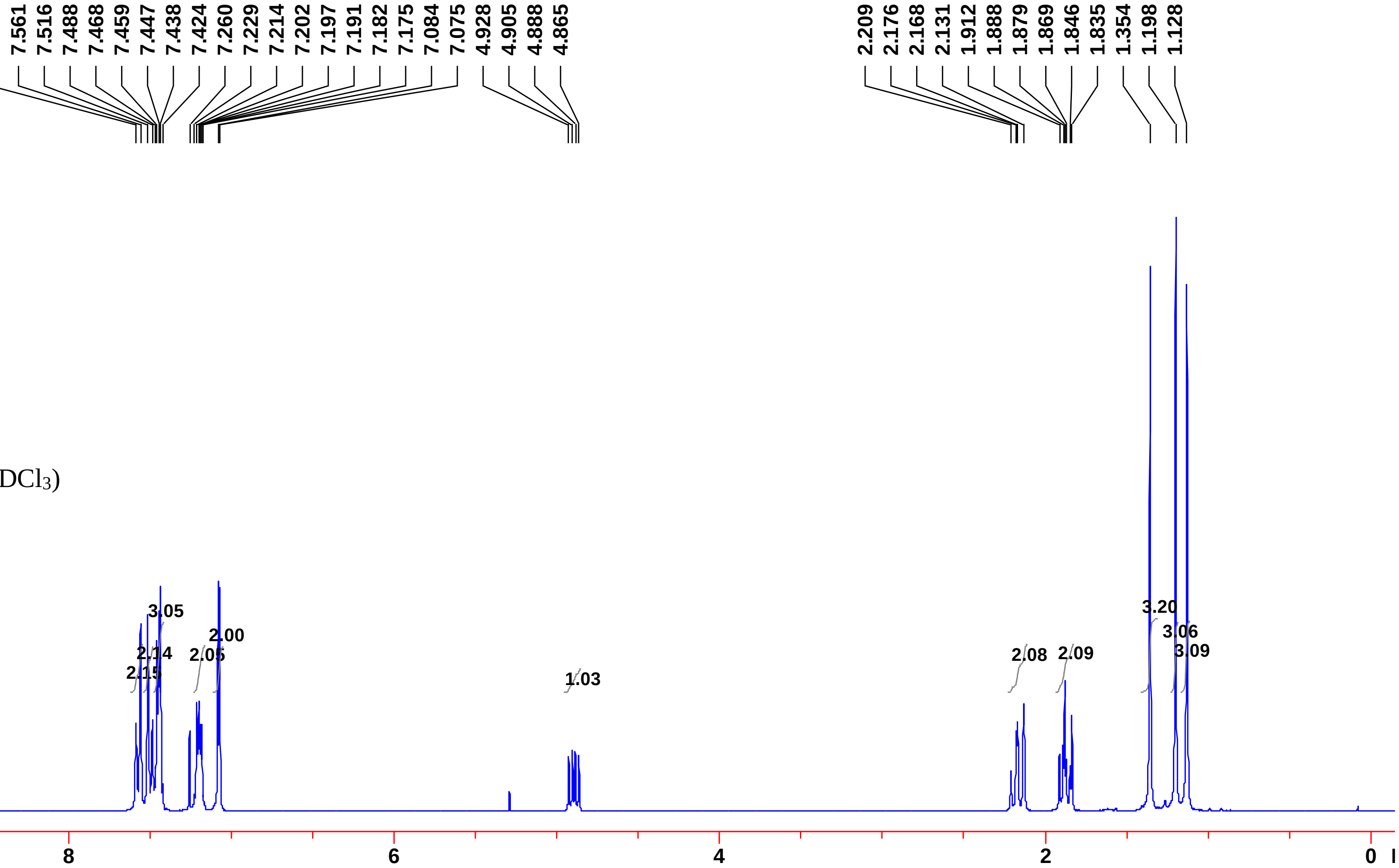
3o

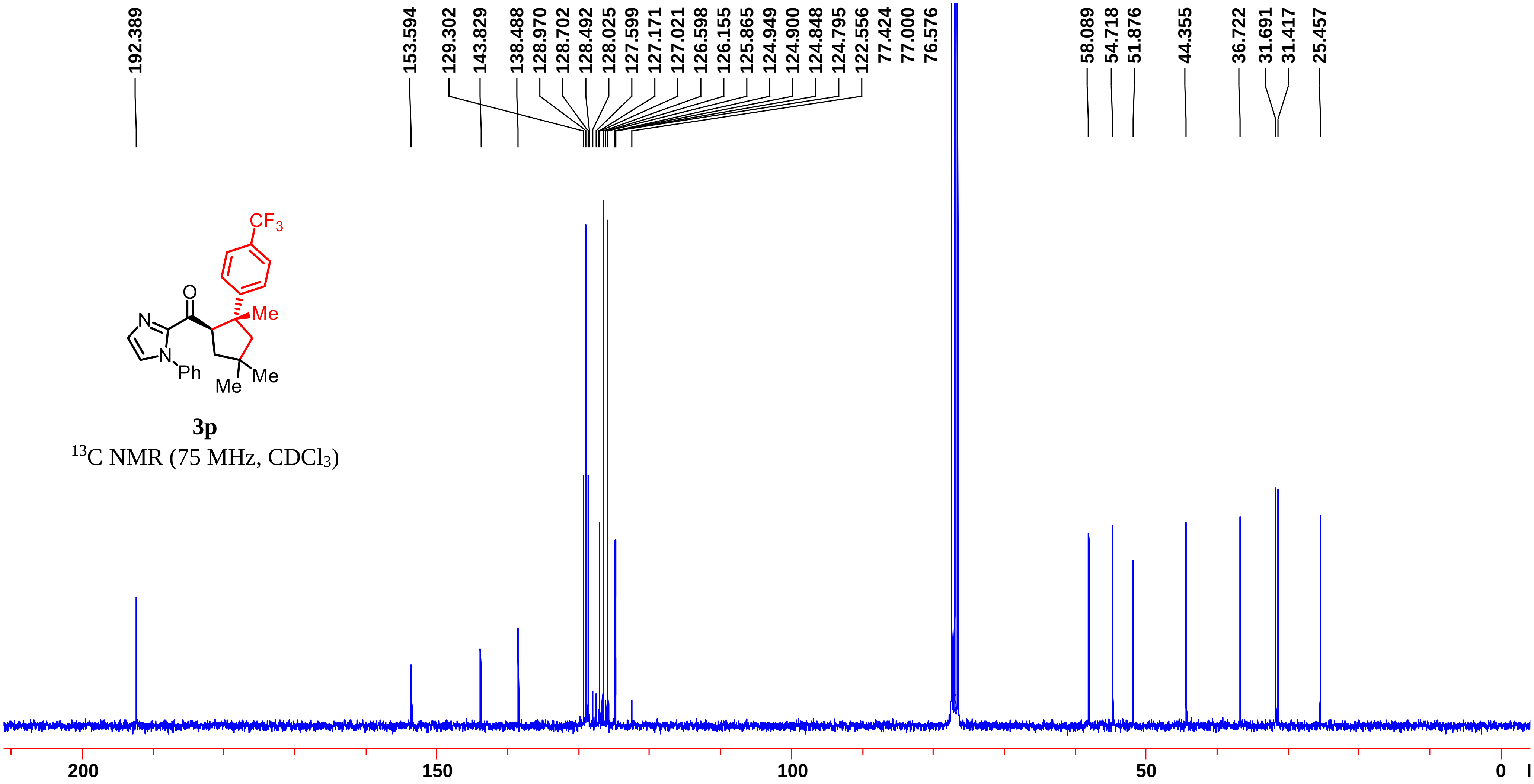
^{13}C NMR (75 MHz, $CDCl_3$)



3p

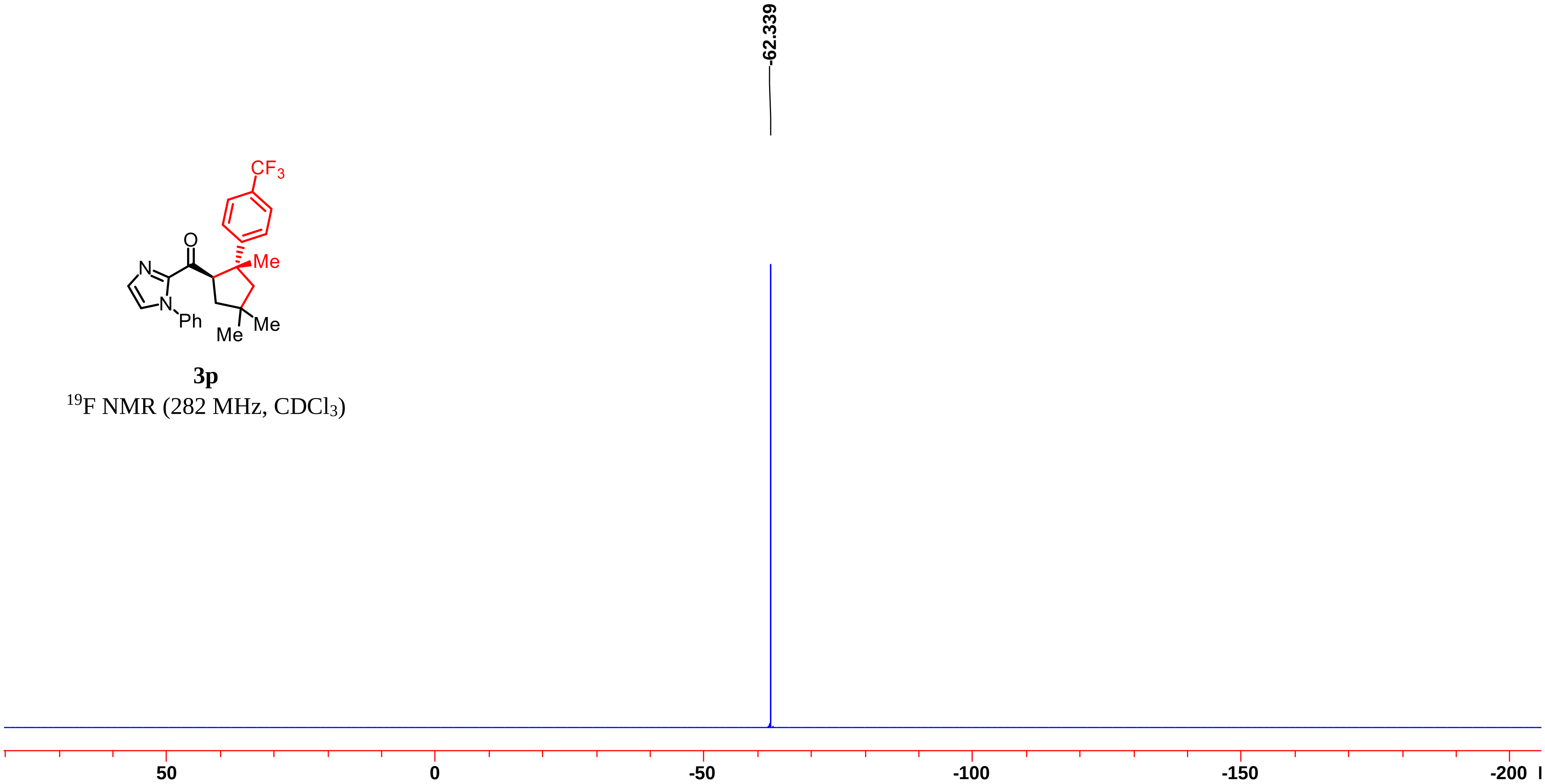
^{1}H NMR (300 MHz, $CDCl_3$)





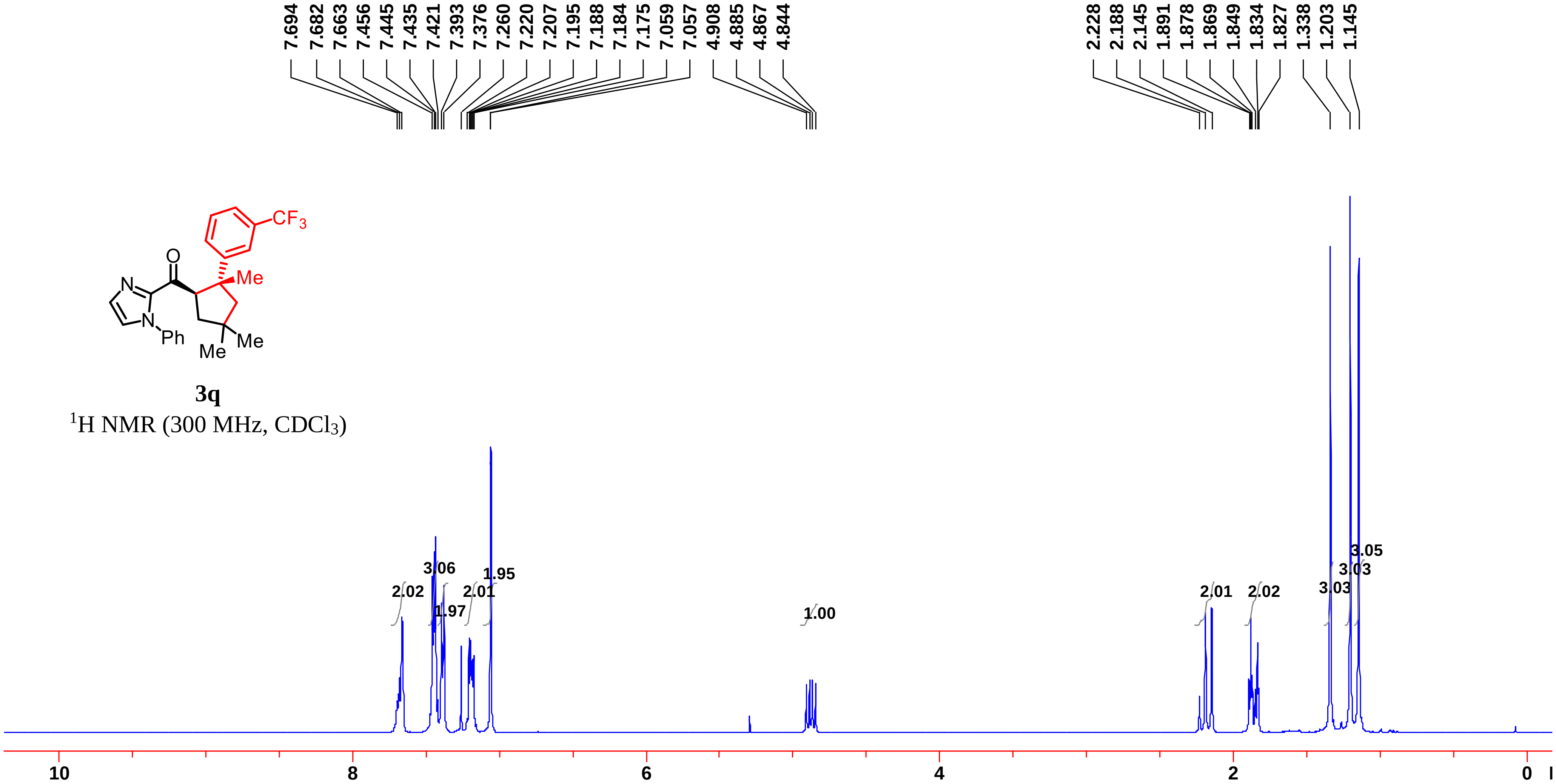
3p

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



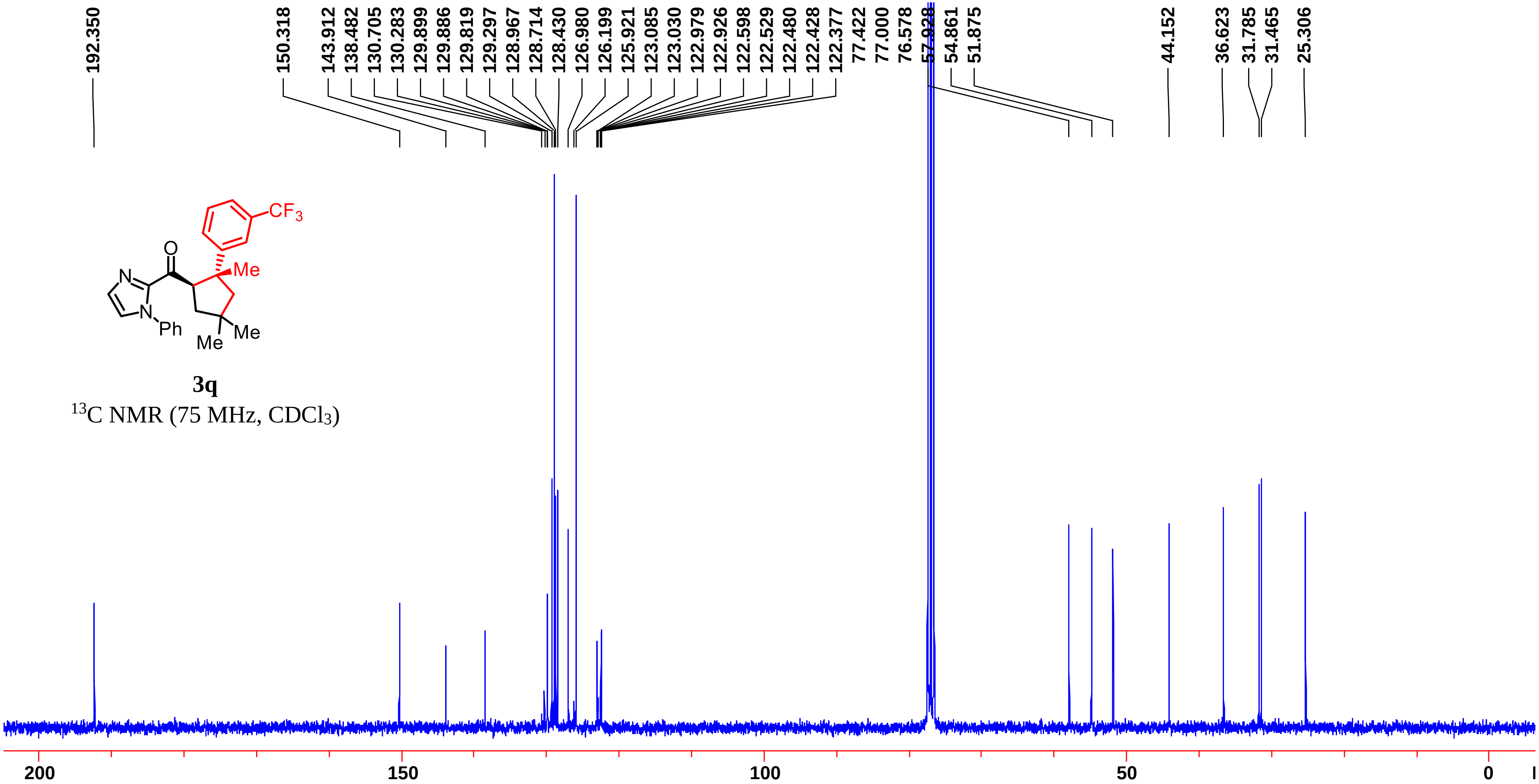
3p

^{19}F NMR (282 MHz, $CDCl_3$)



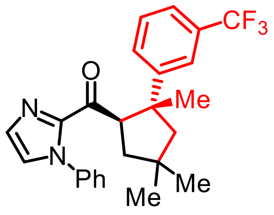
3q

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



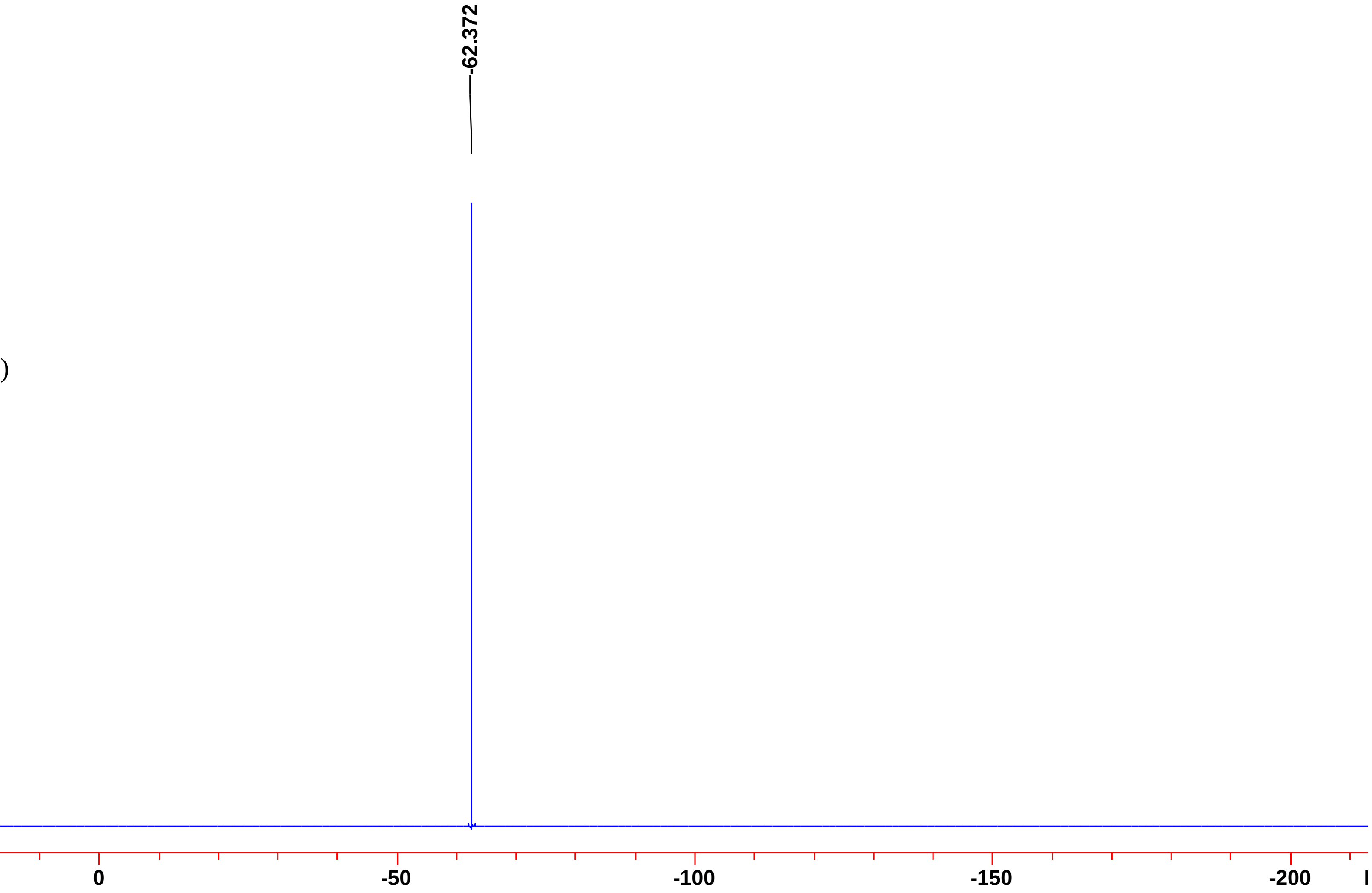
3q

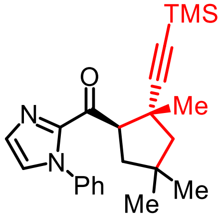
^{13}C NMR (75 MHz, $CDCl_3$)



3q

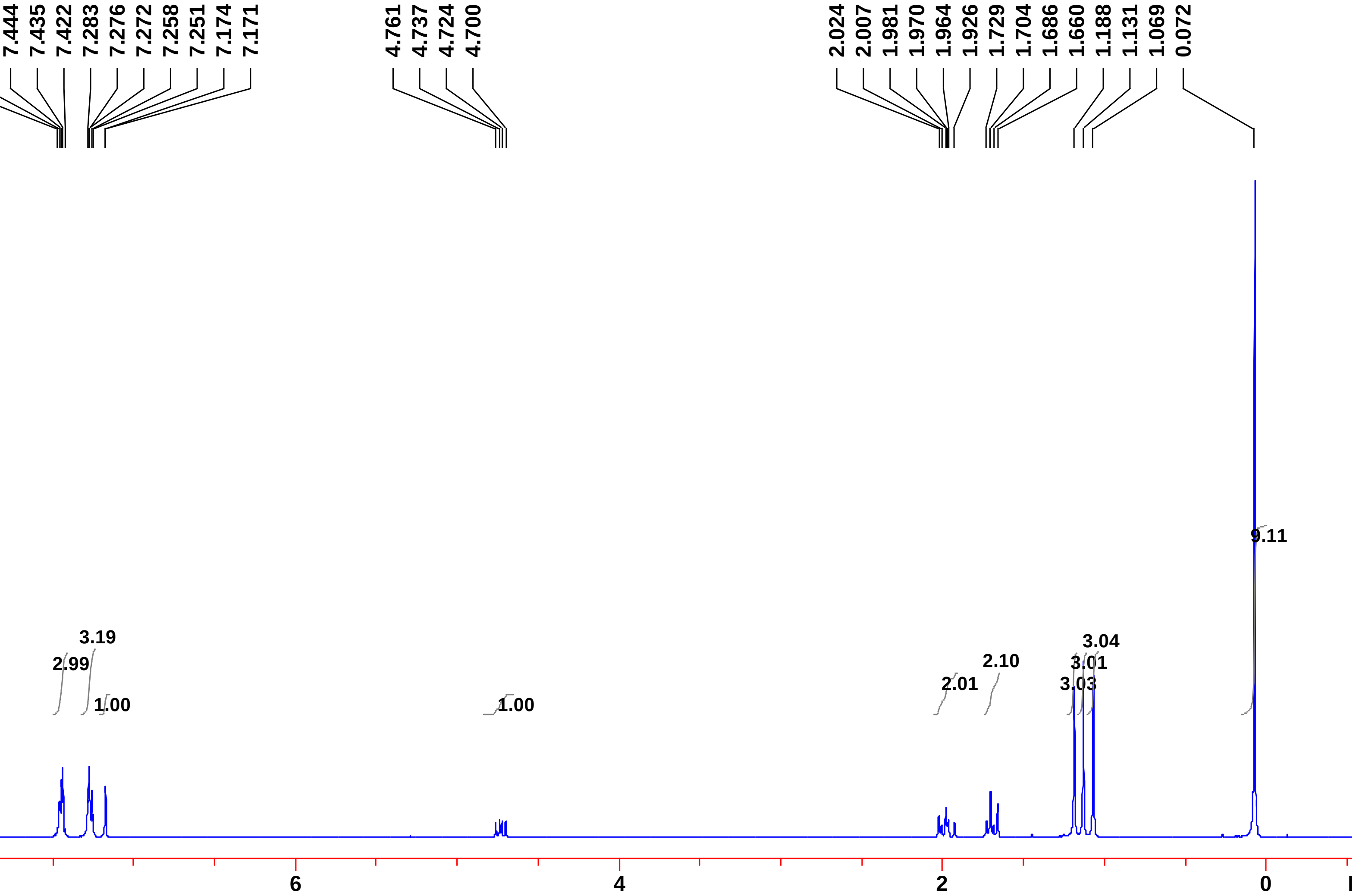
^{19}F NMR (282 MHz, $CDCl_3$)

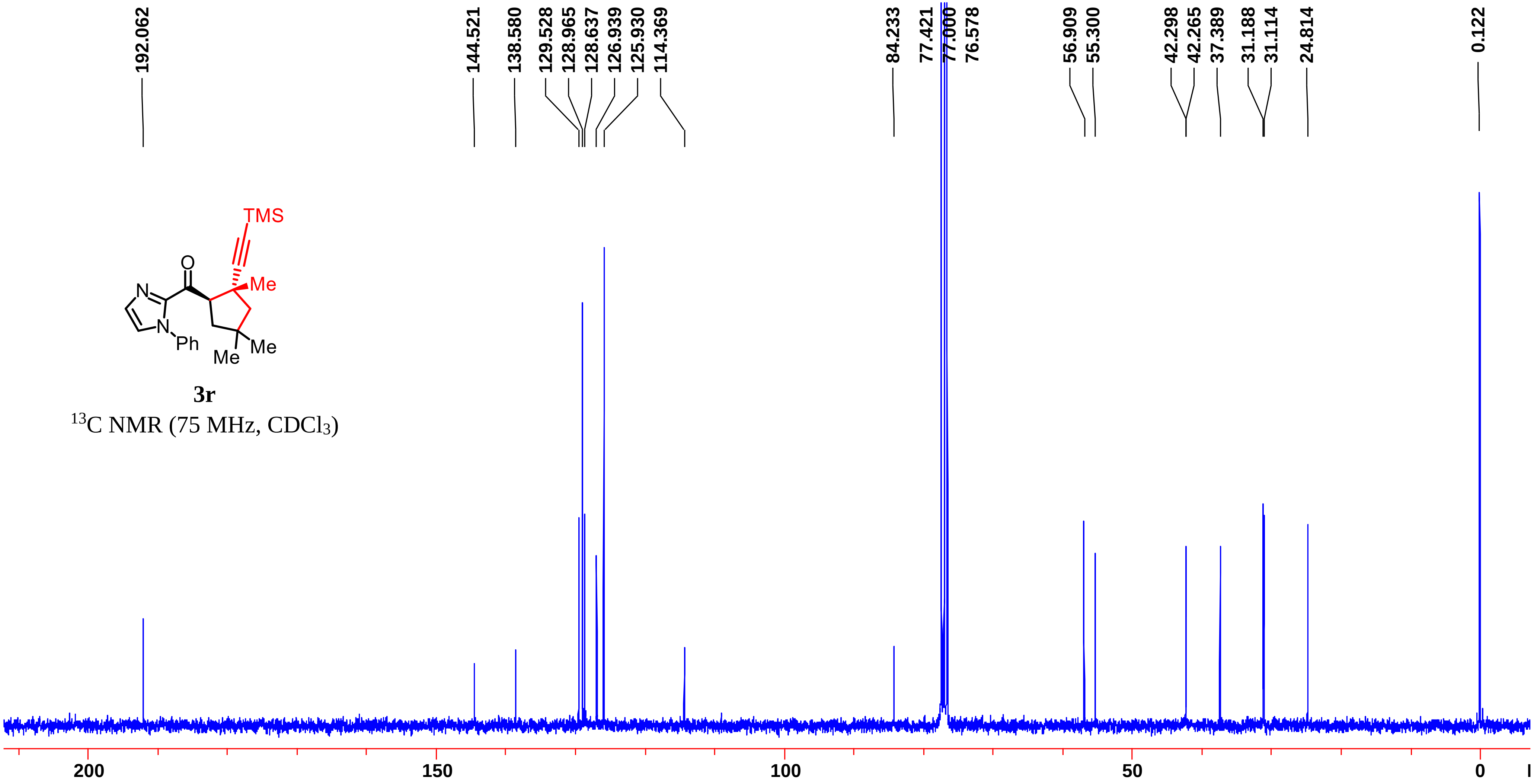




3r

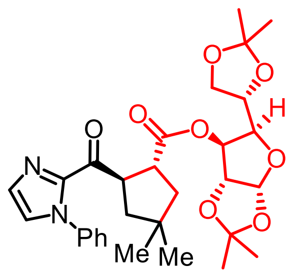
^{1}H NMR (300 MHz, $CDCl_3$)



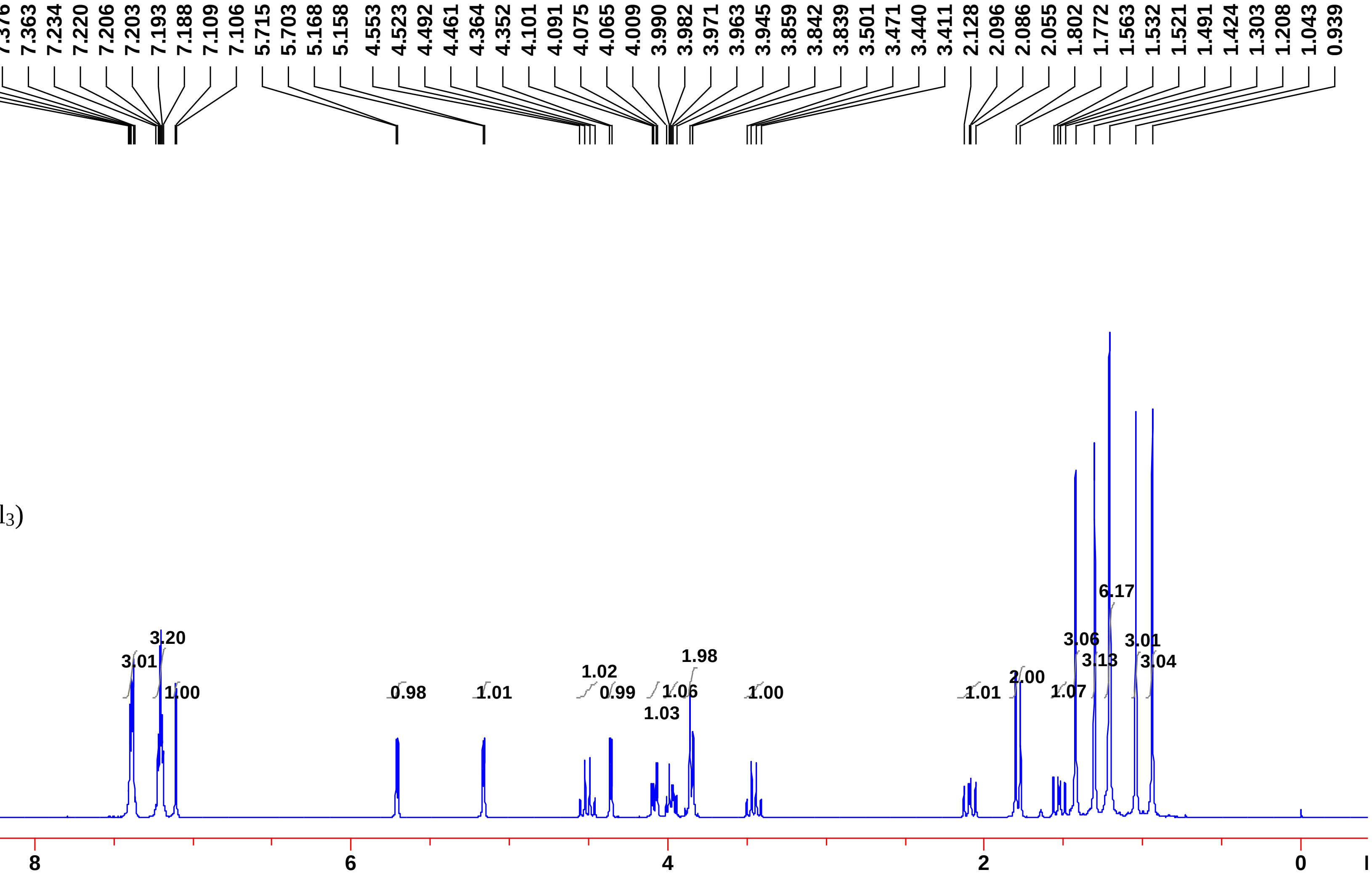


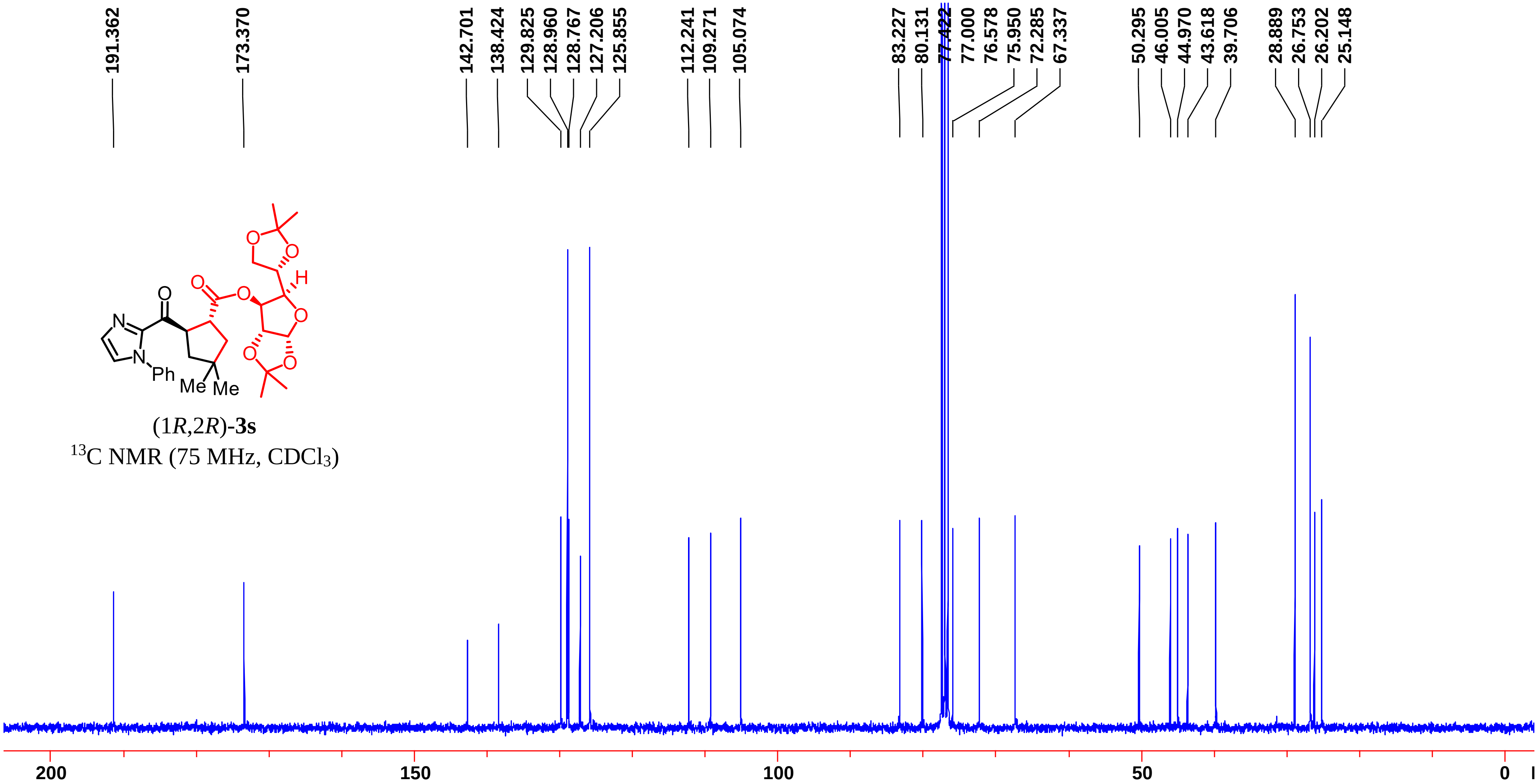
3r

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



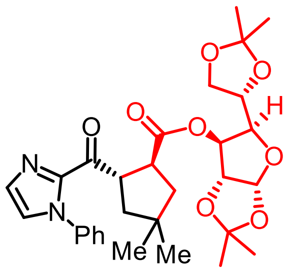
(1*R*,2*R*)-**3s**
[1]H NMR (300 MHz, CDCl3)





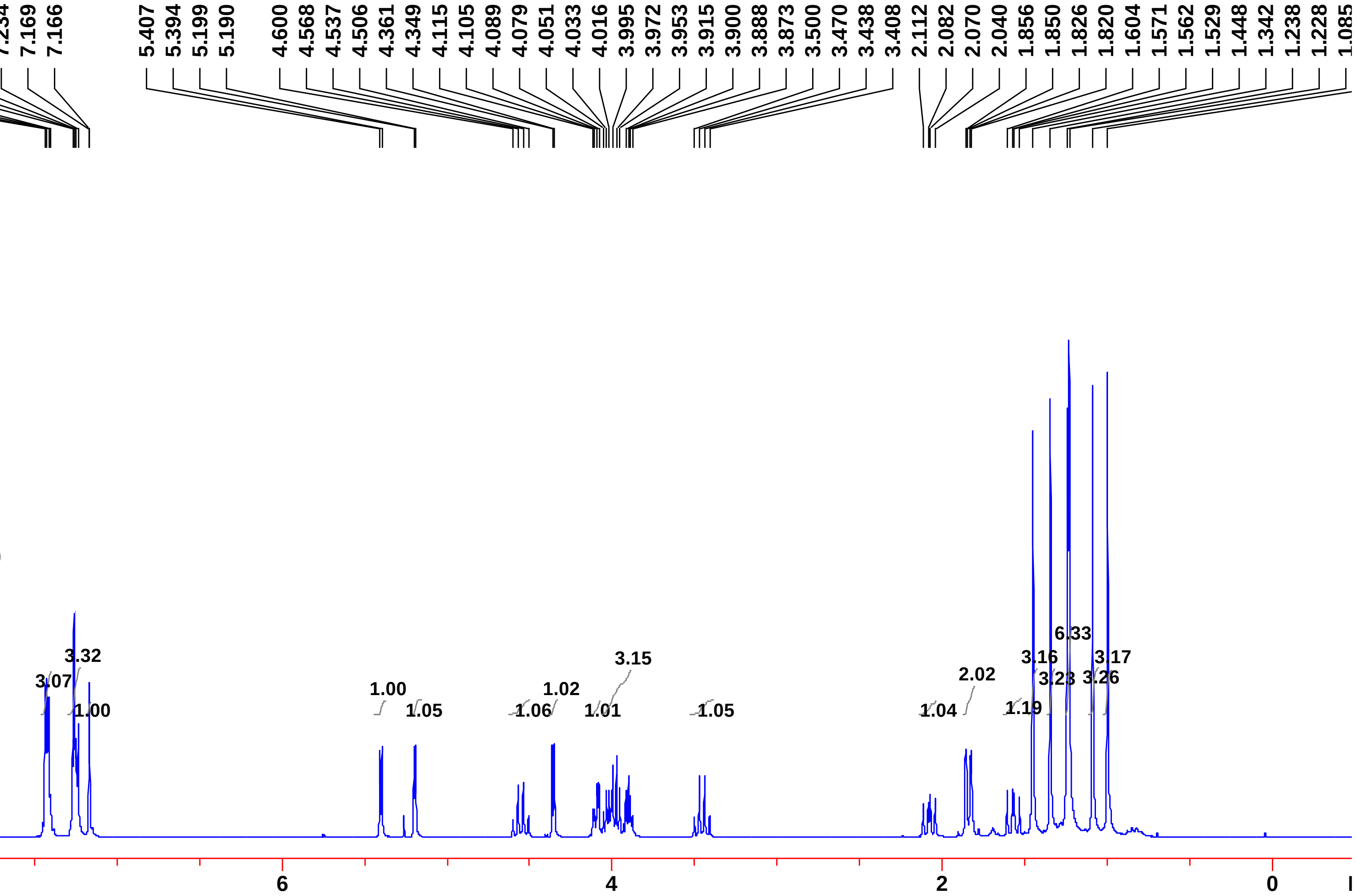
(1*R*,2*R*)-**3s**

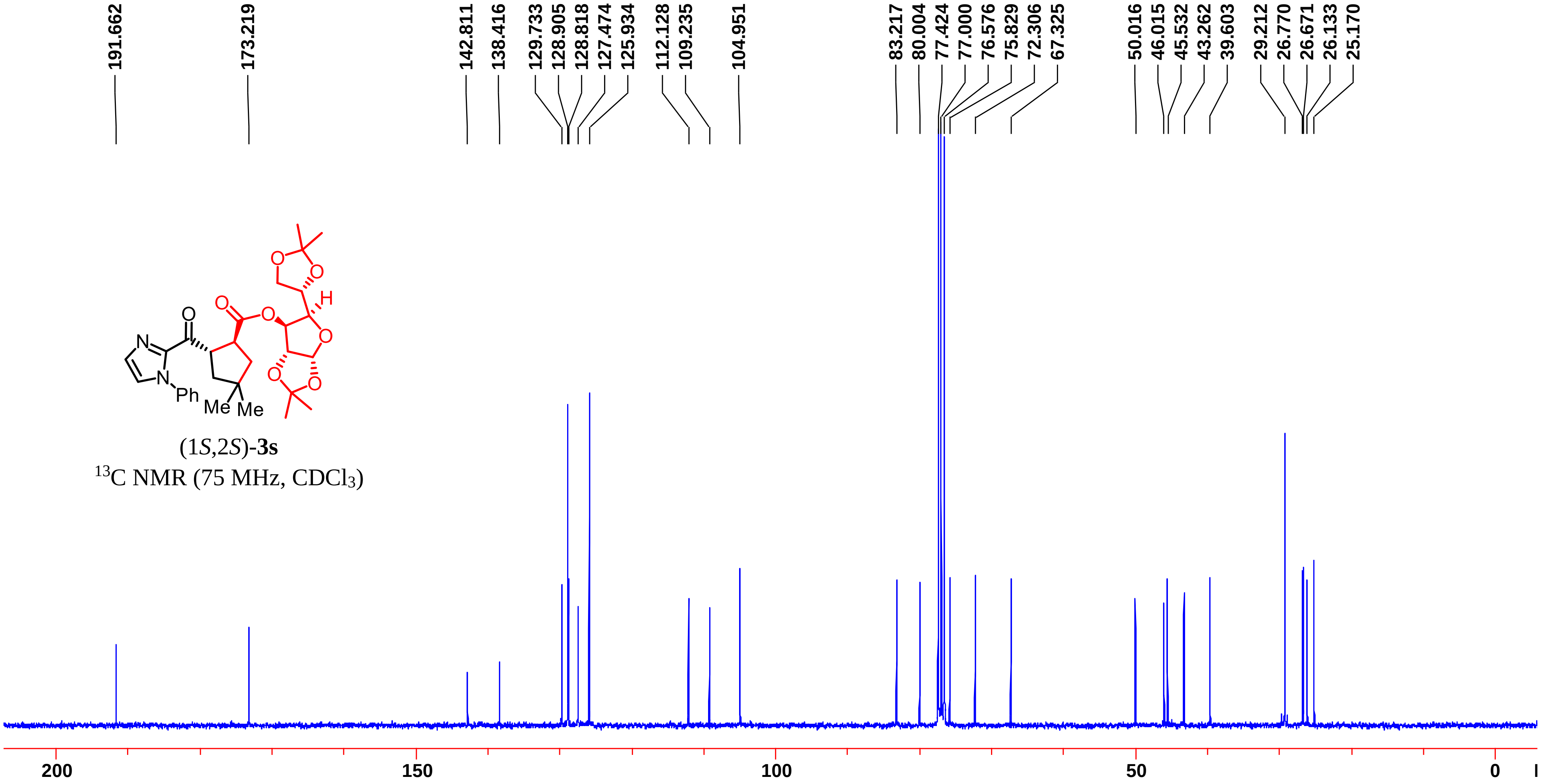
^{13}C NMR (75 MHz, $CDCl_3$)



(1*S*,2*S*)-**3s**

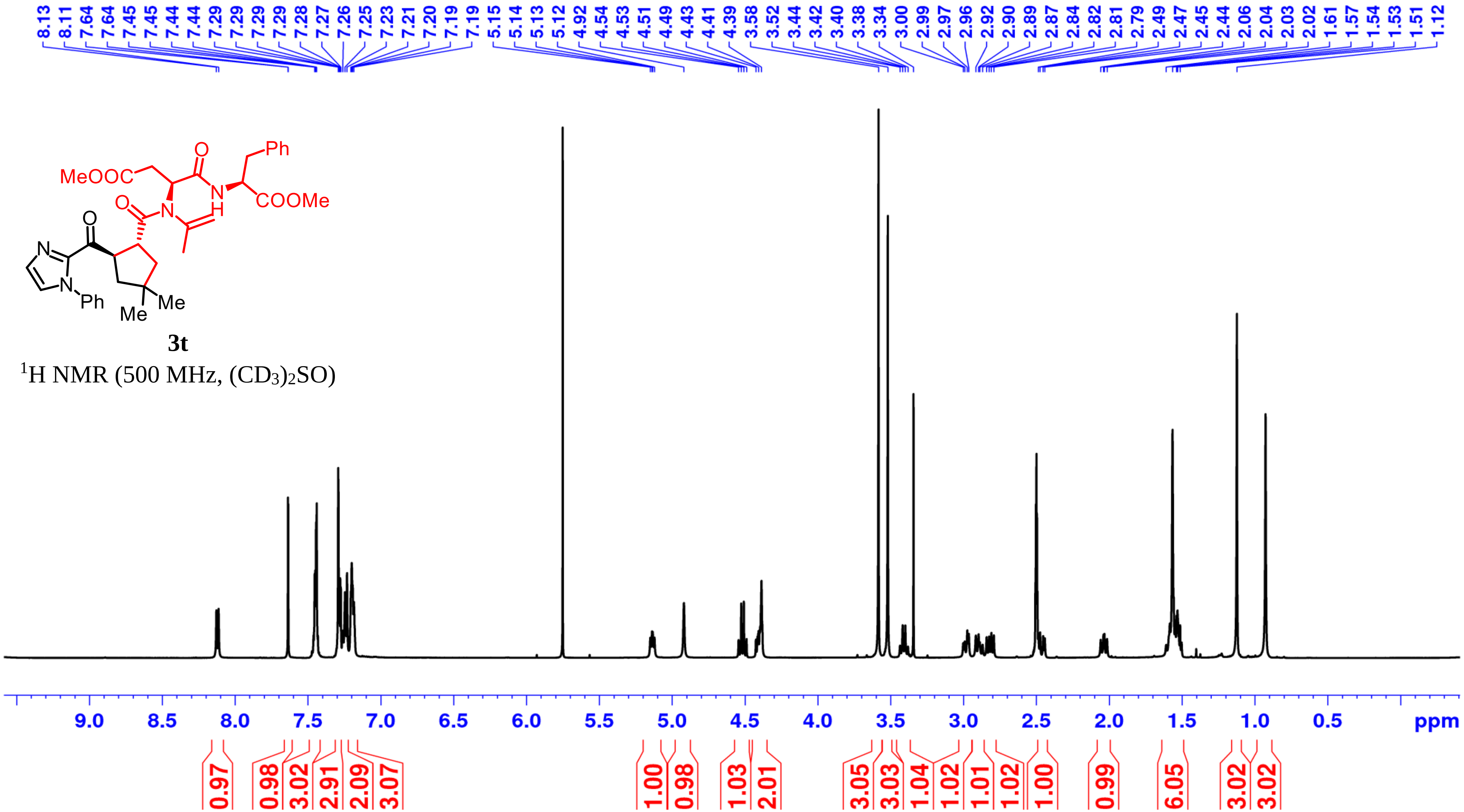
^{1}H NMR (300 MHz, $CDCl_3$)





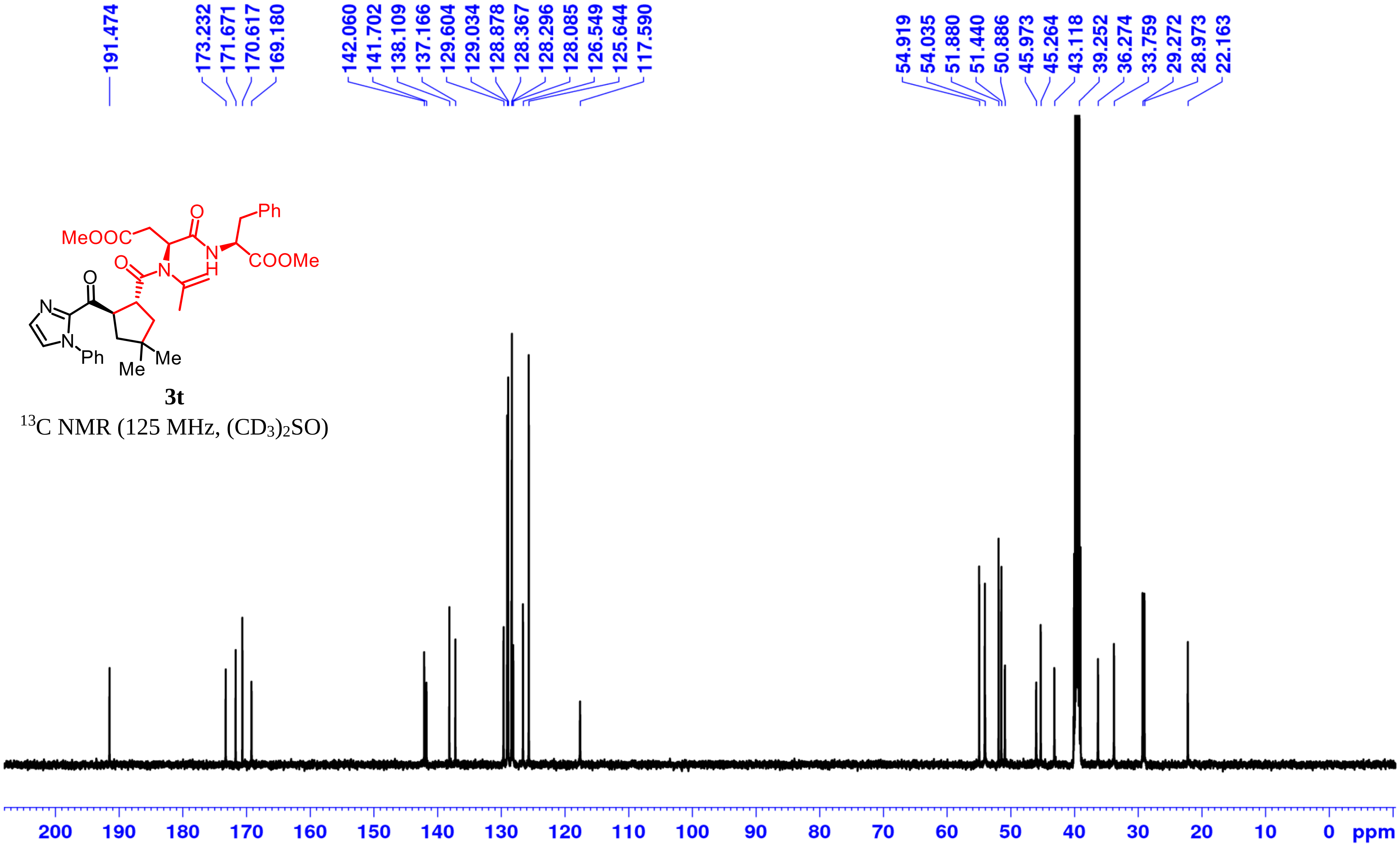
(1*S*,2*S*)-**3s**

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



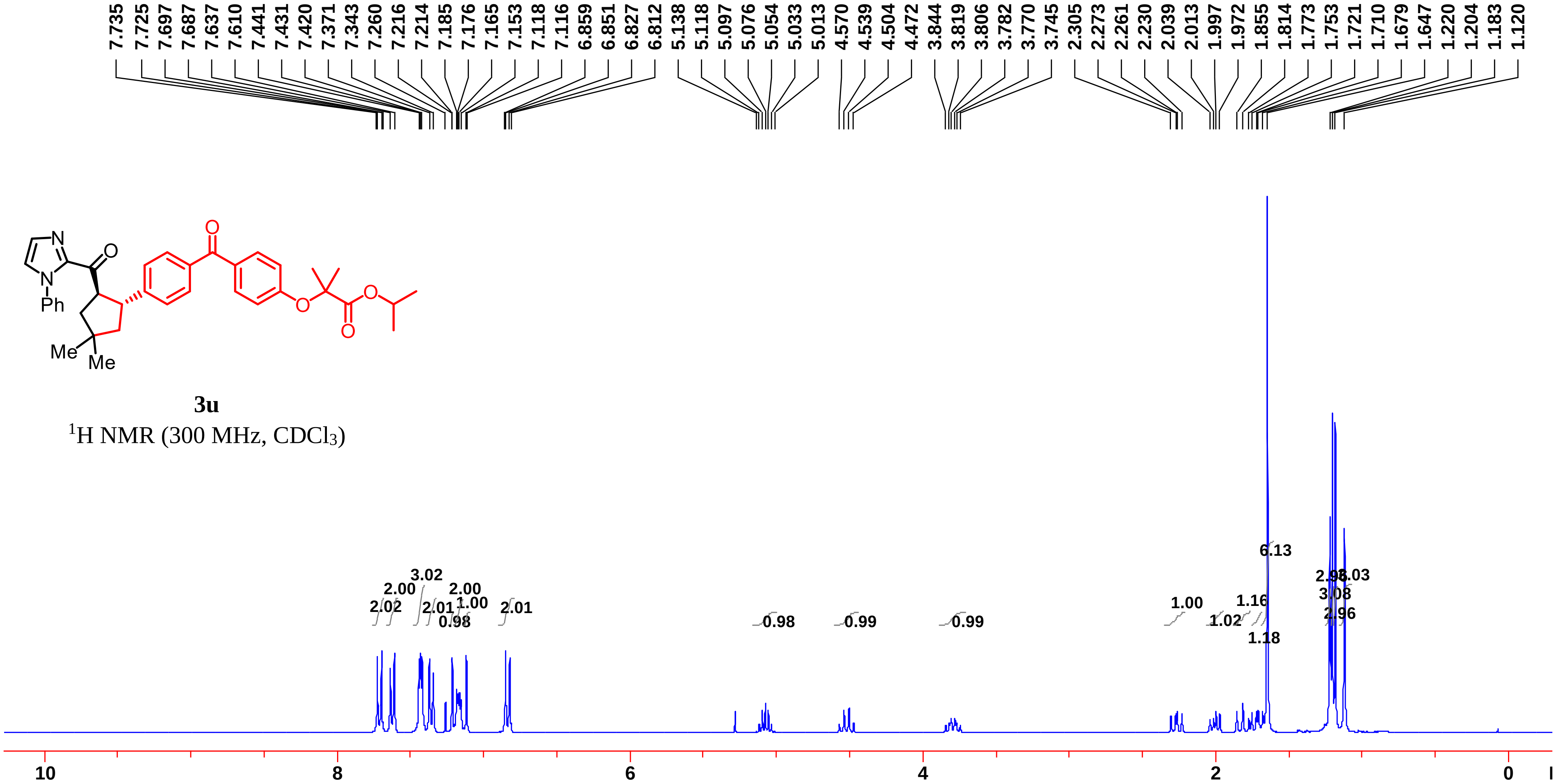
3t

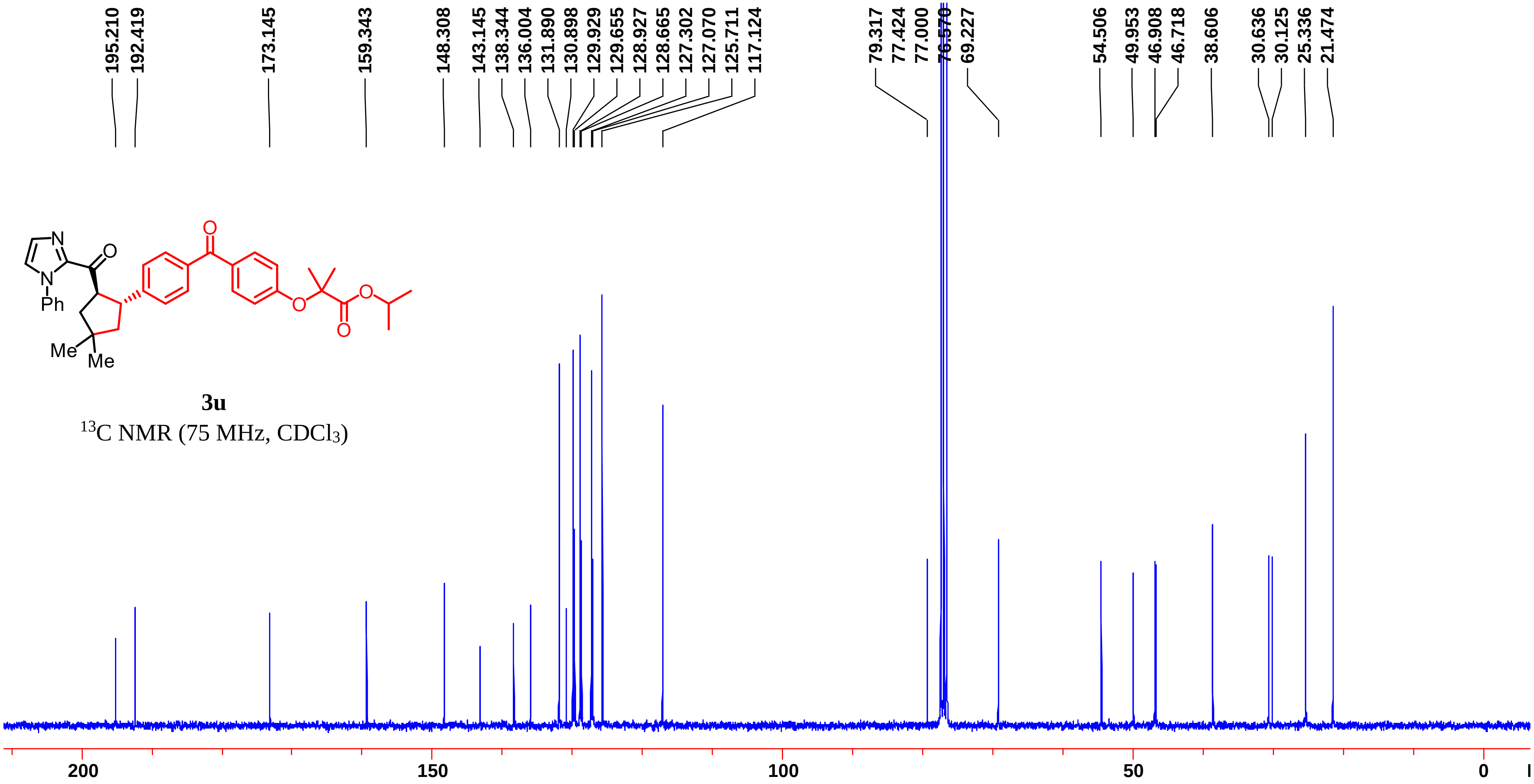
[1]H NMR (500 MHz, $(CD_3)_2SO$)



3t

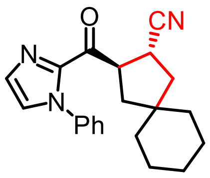
^{13}C NMR (125 MHz, $(CD_3)_2SO$)


7.735
7.725
7.697
7.687
7.637
7.610
7.441
7.431
7.420
7.371
7.343
7.260
7.216
7.214
7.185
7.176
7.165
7.153
7.118
7.116
6.859
6.851
6.827
6.812
5.138
5.118
5.097
5.076
5.054
5.033
5.013
4.570
4.539
4.504
4.472
3.844
3.819
3.806
3.782
3.770
3.745
2.305
2.273
2.261
2.230
2.039
2.013
1.997
1.972
1.855
1.814
1.773
1.753
1.721
1.710
1.679
1.647
1.220
1.204
1.183
1.120
Me
Me
Ph
3u
^{1}H NMR (300 MHz, CDCl$_3$)
10
8
6
4
2
0



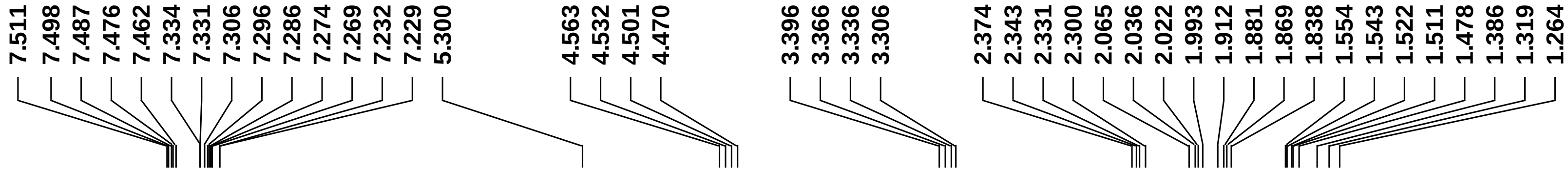
3u

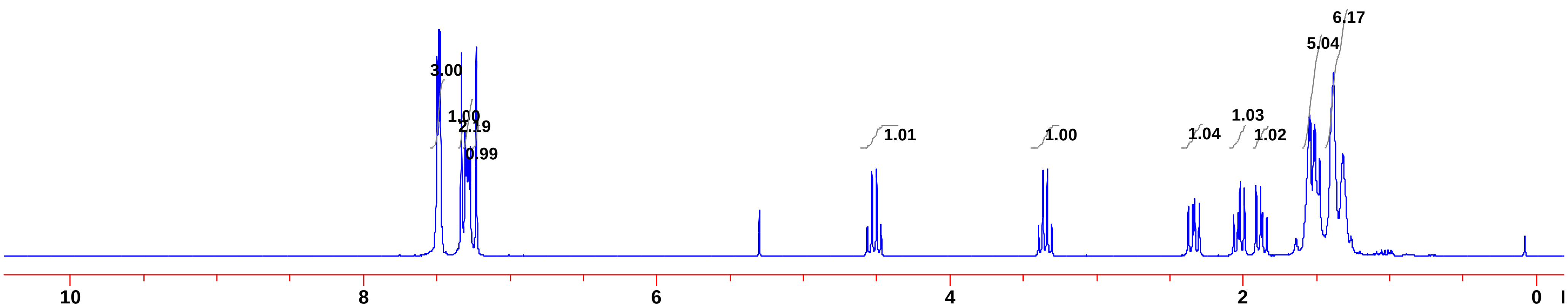
^{13}C NMR (75 MHz, $CDCl_3$)

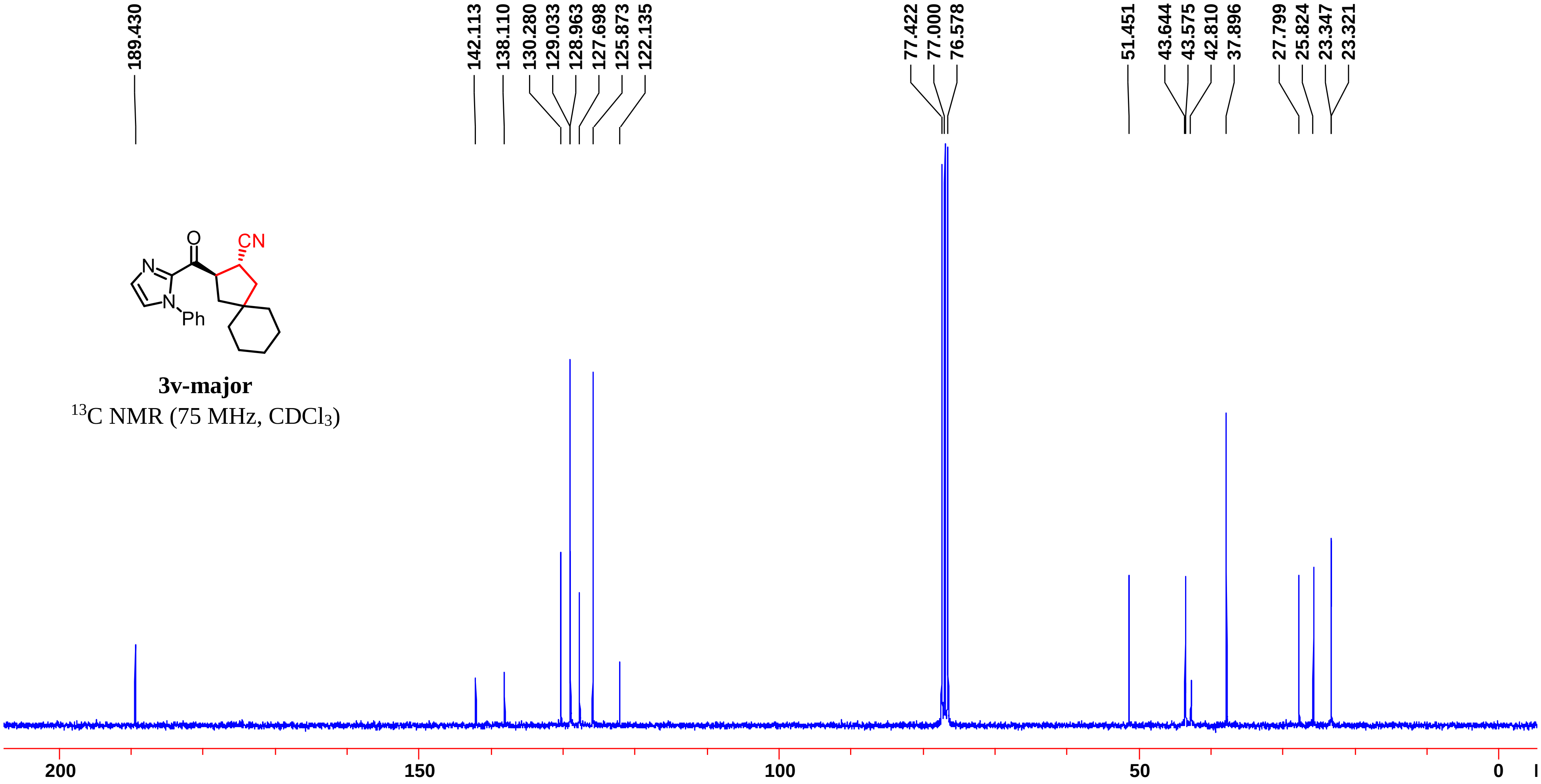


3v-major

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

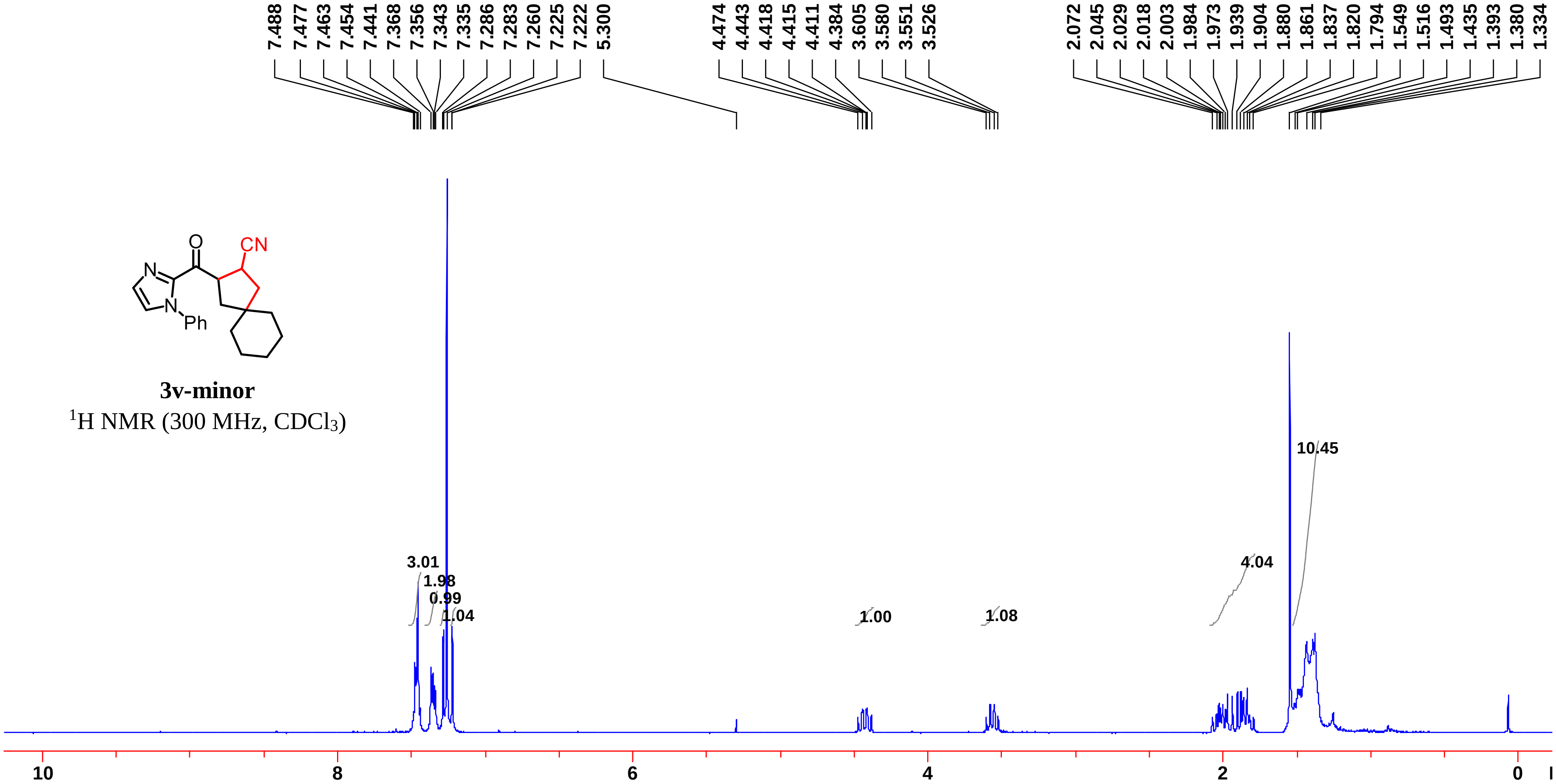






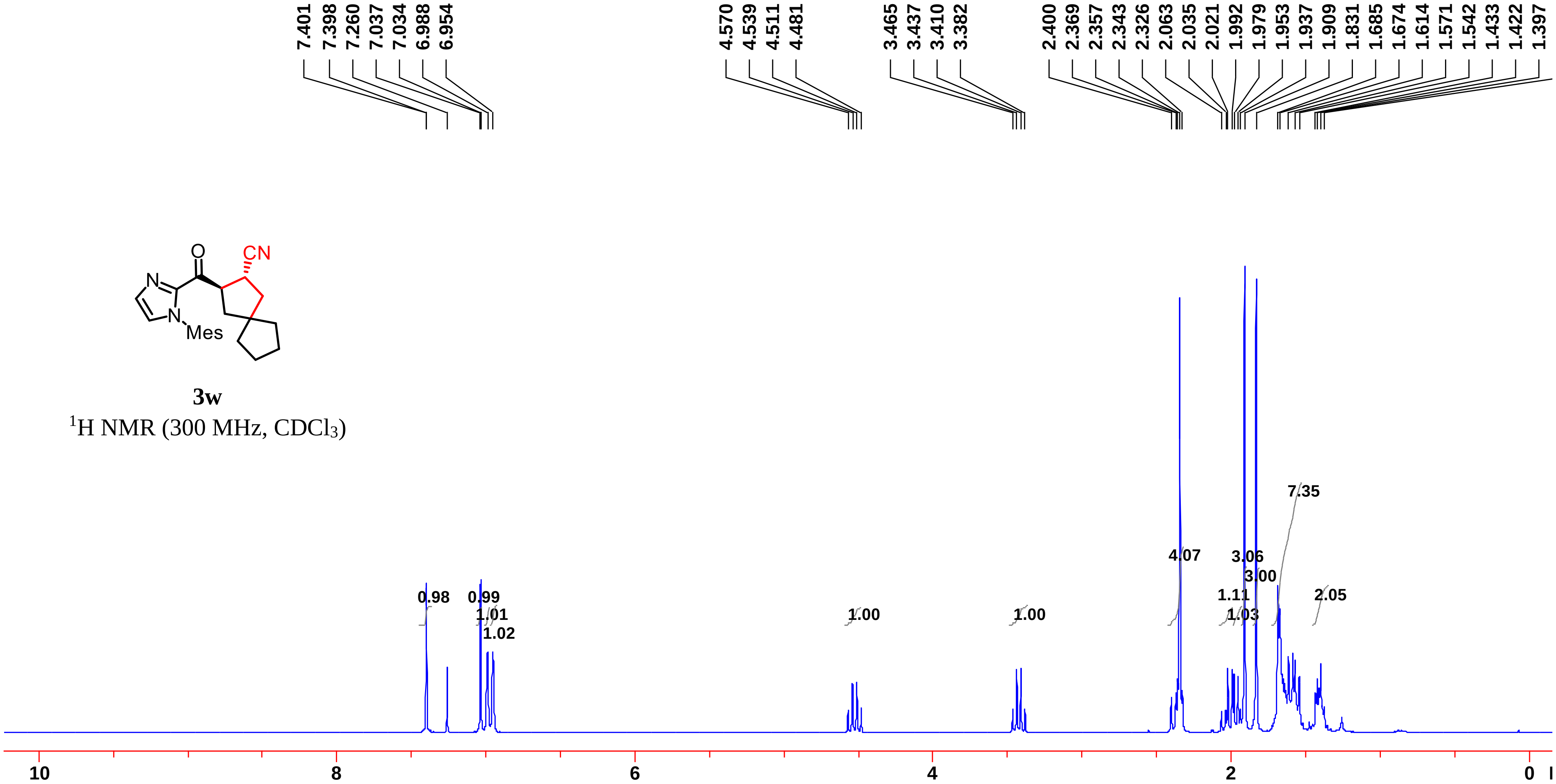
3v-major

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



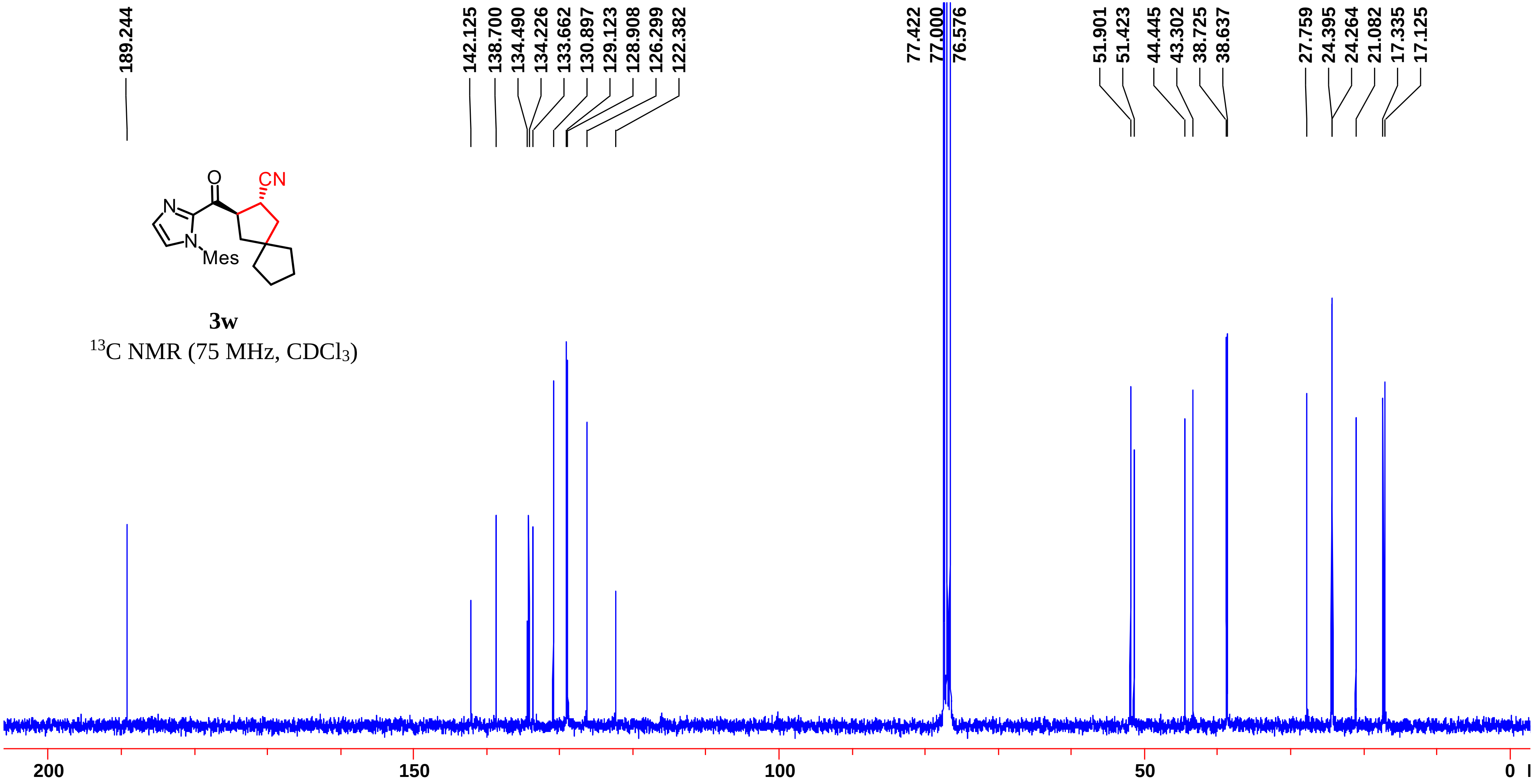
3v-minor

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



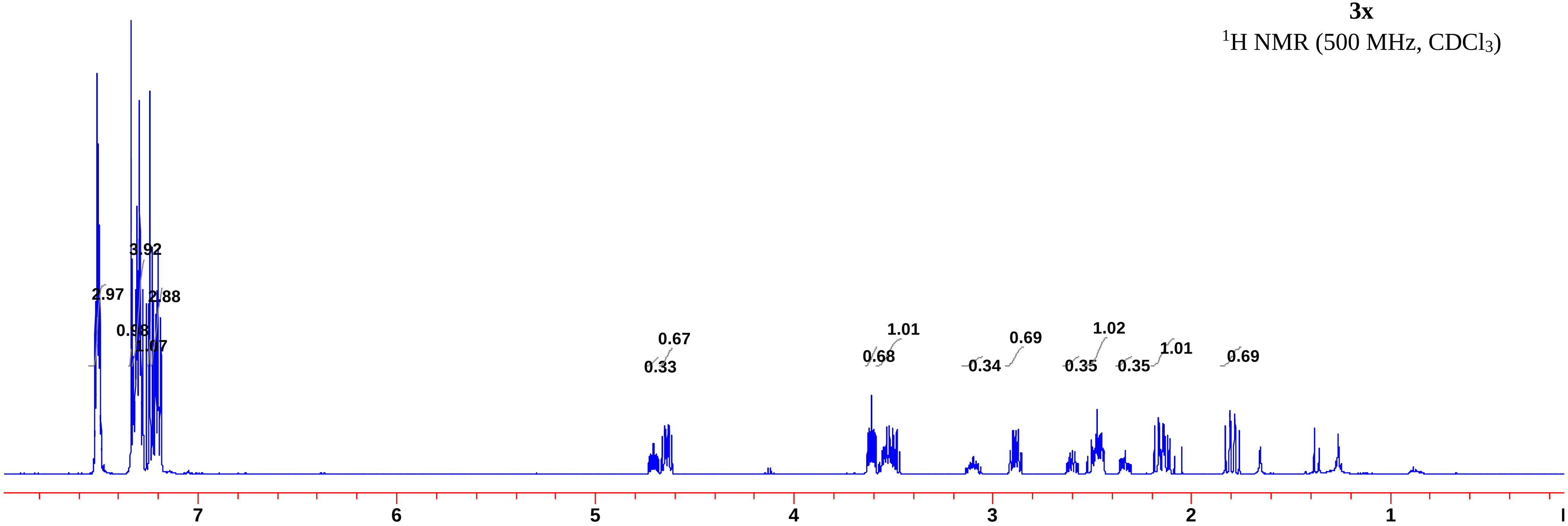
3w

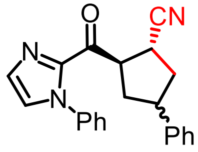
^{1}H NMR (300 MHz, $CDCl_3$)



3w

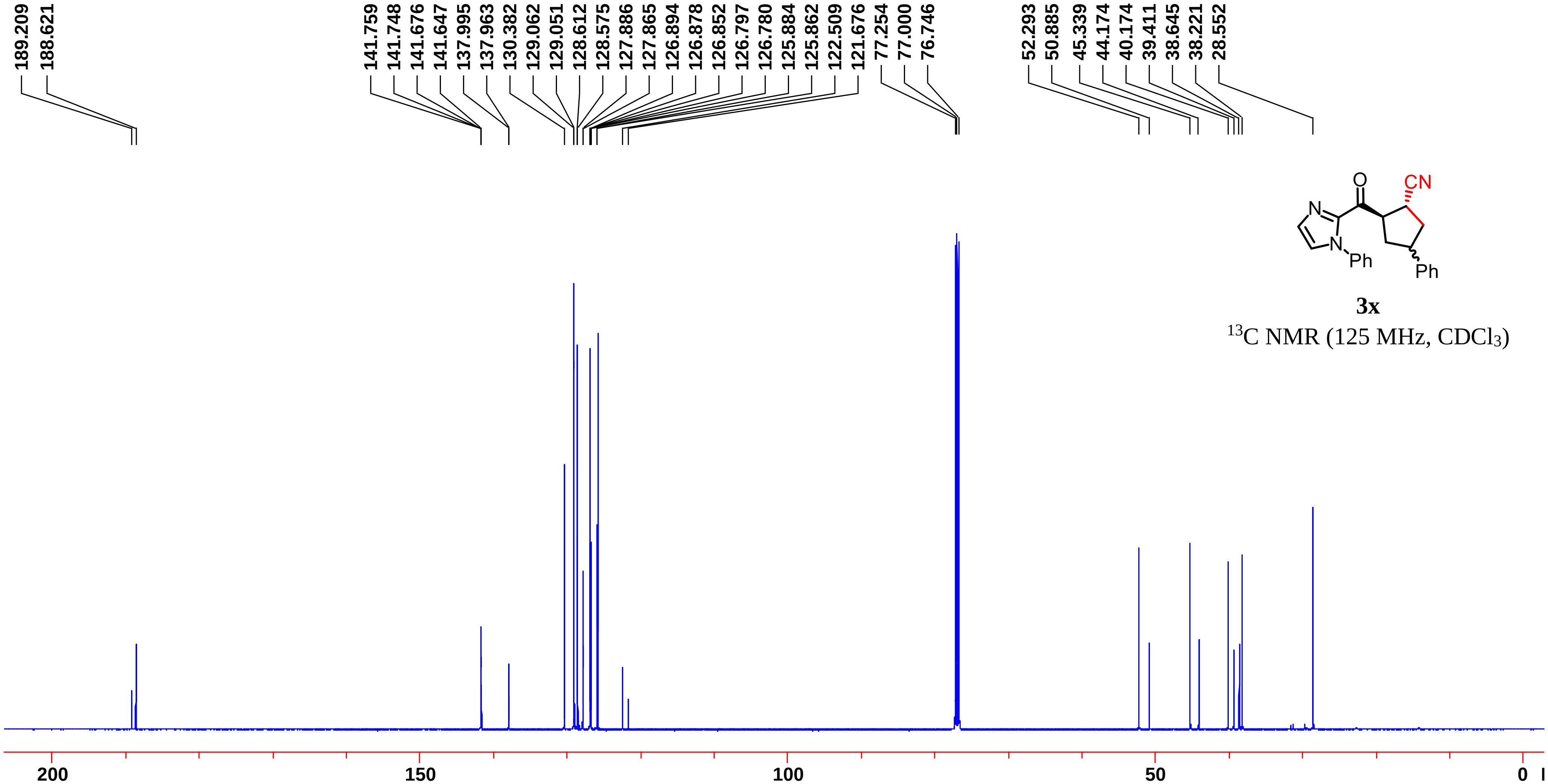
^{13}C NMR (75 MHz, $CDCl_3$)





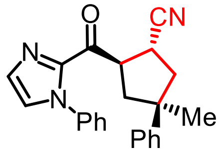
3x

[1]H NMR (500 MHz, $CDCl_3$)



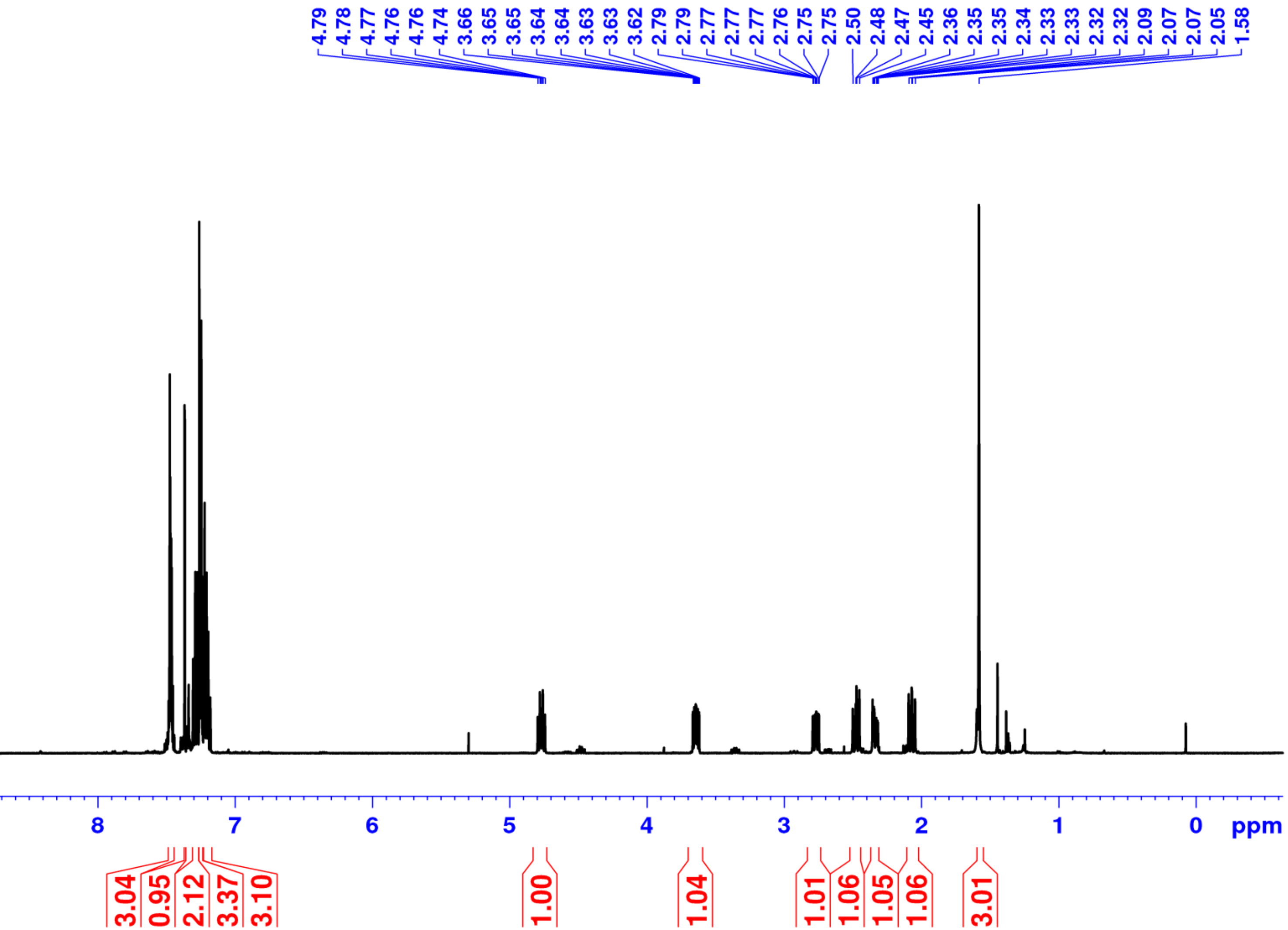
3x

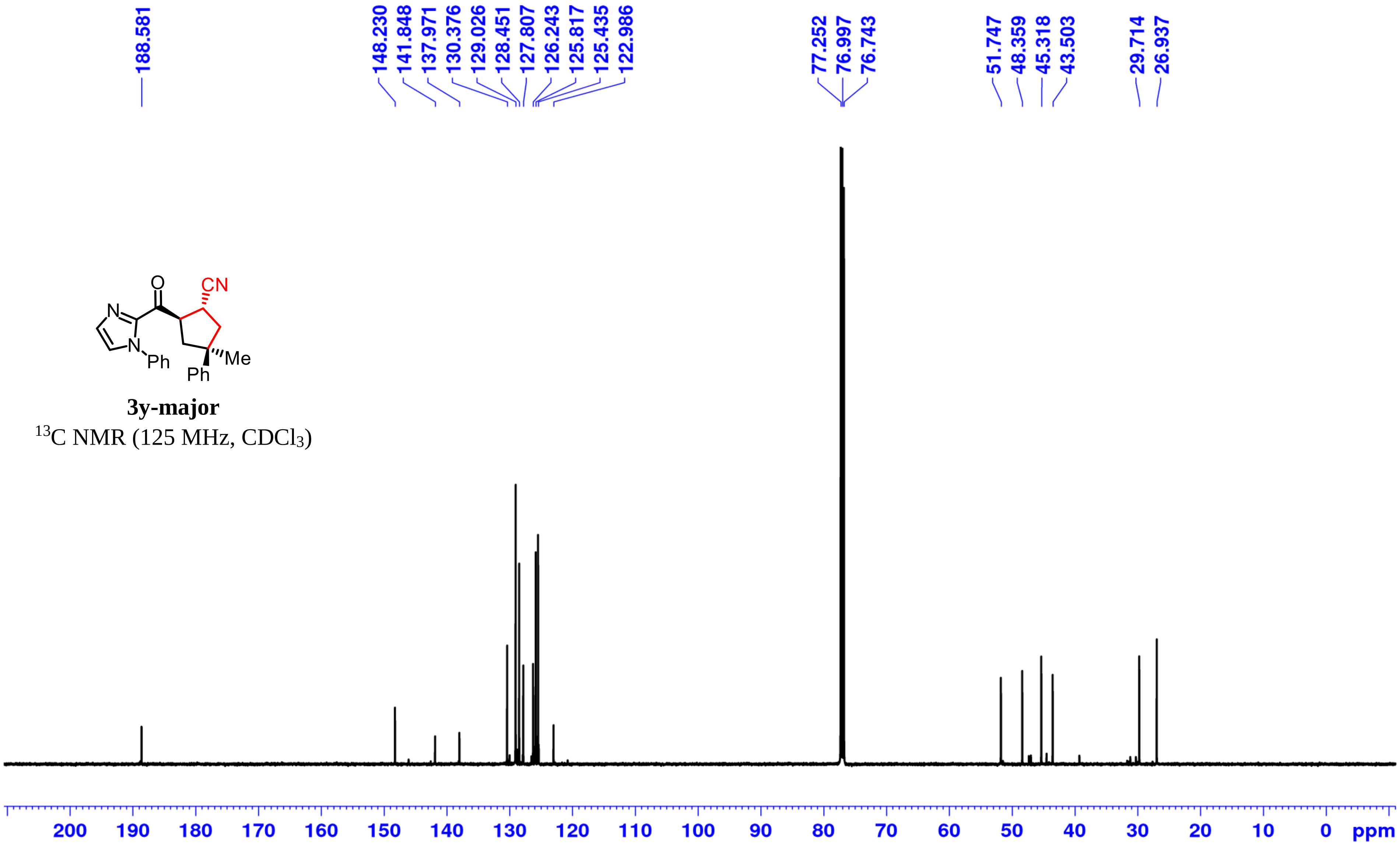
^{13}C NMR (125 MHz, $CDCl_3$)



3y-major

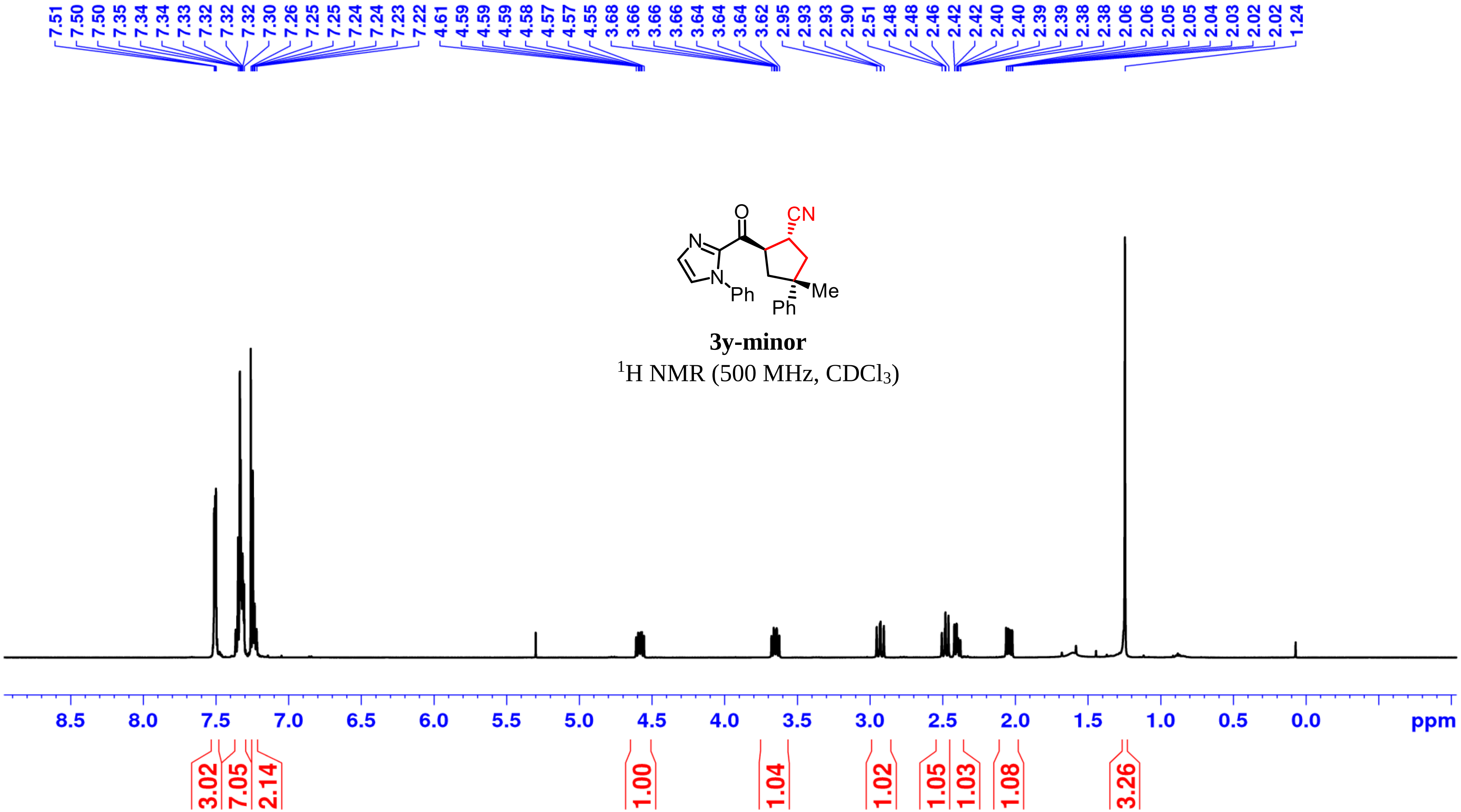
^{1}H NMR (500 MHz, $CDCl_3$)

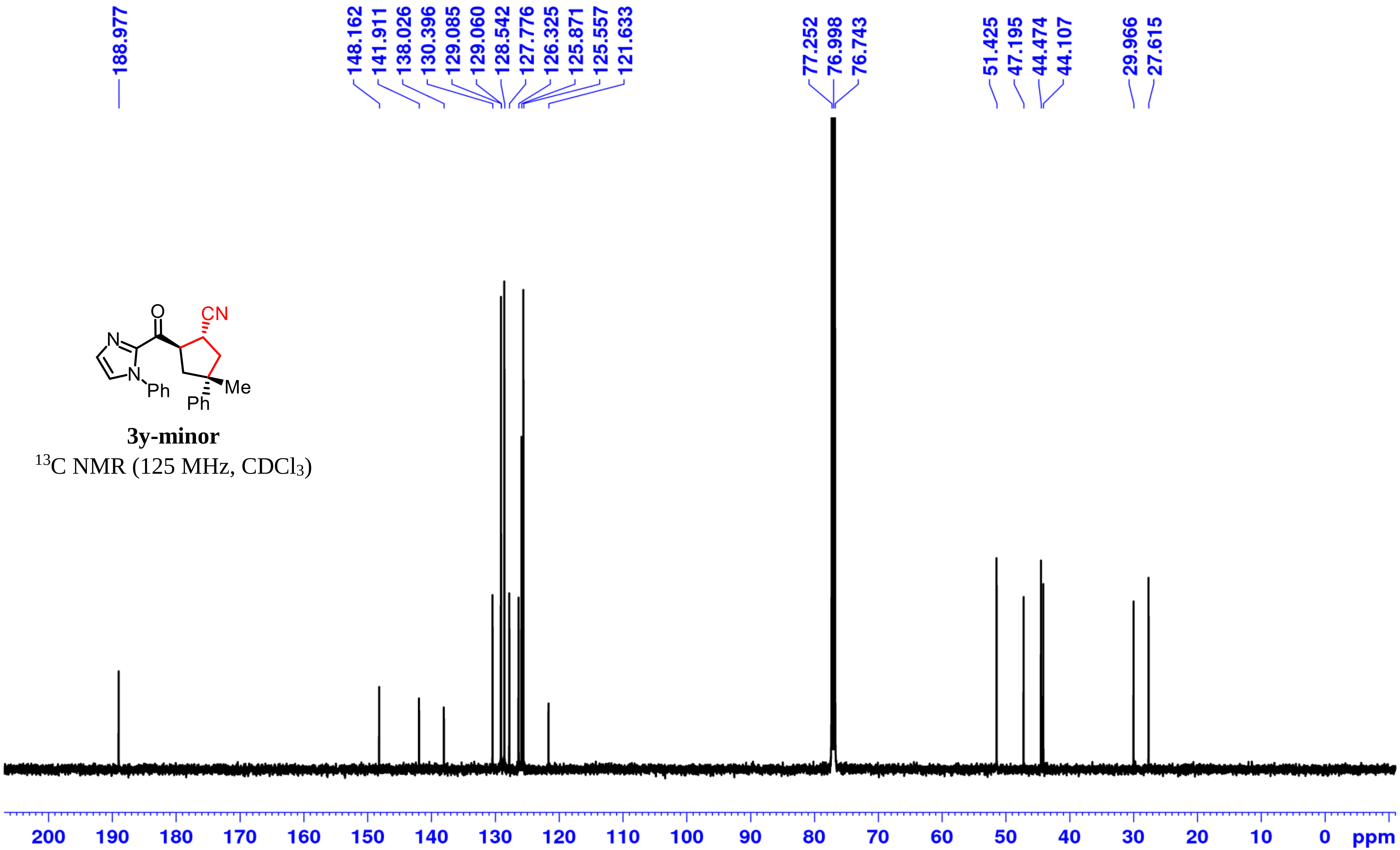




3y-major

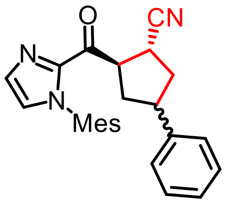
^{13}C NMR (125 MHz, $CDCl_3$)


7.51 7.50 7.50 7.35 7.34 7.34 7.33 7.32 7.32 7.32 7.30 7.26 7.25 7.25 7.24 7.24 7.23 7.22 4.61 4.59 4.59 4.59 4.58 4.57 4.57 4.55 3.68 3.66 3.66 3.64 3.64 3.64 3.62 2.95 2.93 2.93 2.90 2.51 2.48 2.48 2.46 2.42 2.42 2.40 2.40 2.39 2.39 2.38 2.38 2.06 2.06 2.05 2.05 2.04 2.03 2.02 2.02 1.24
O
CN
N
N
Ph
Me
Ph
3y-minor
1H NMR (500 MHz, CDCl3)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
3.02 7.05 2.14 1.00 1.04 1.02 1.05 1.03 1.08 3.26



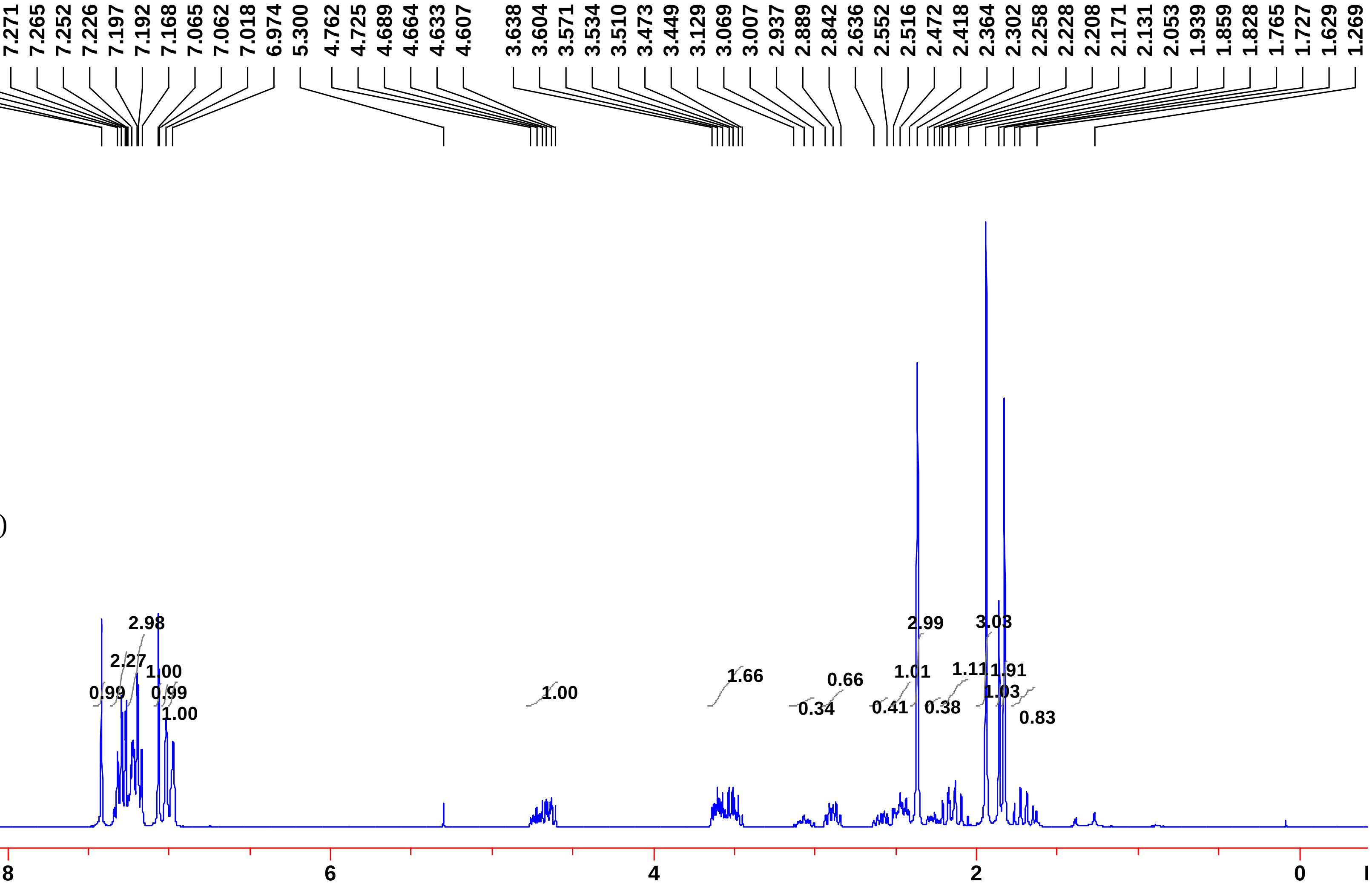
3y-minor

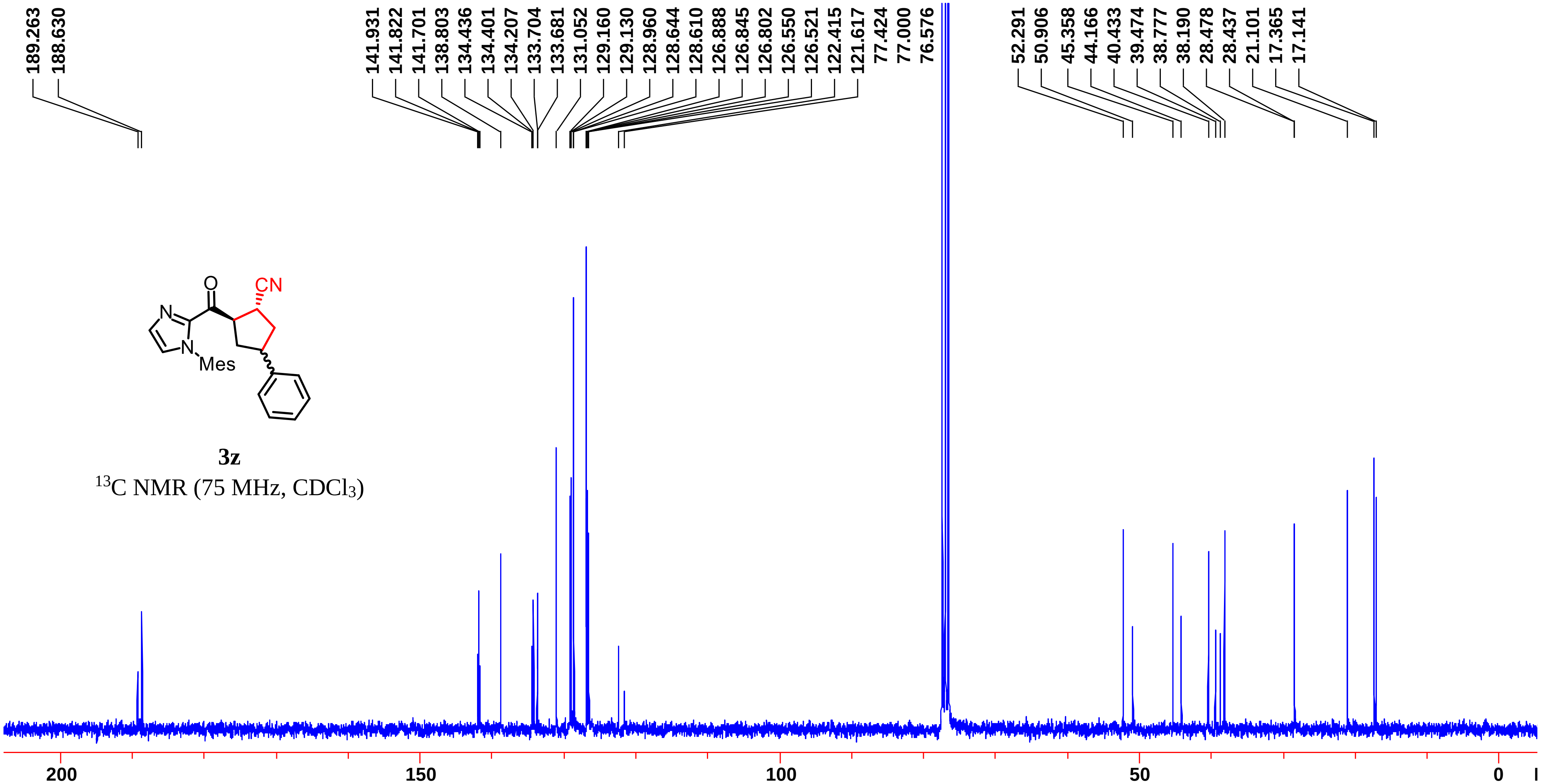
^{13}C NMR (125 MHz, $CDCl_3$)



3z

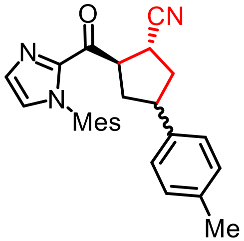
^{1}H NMR (300 MHz, $CDCl_3$)





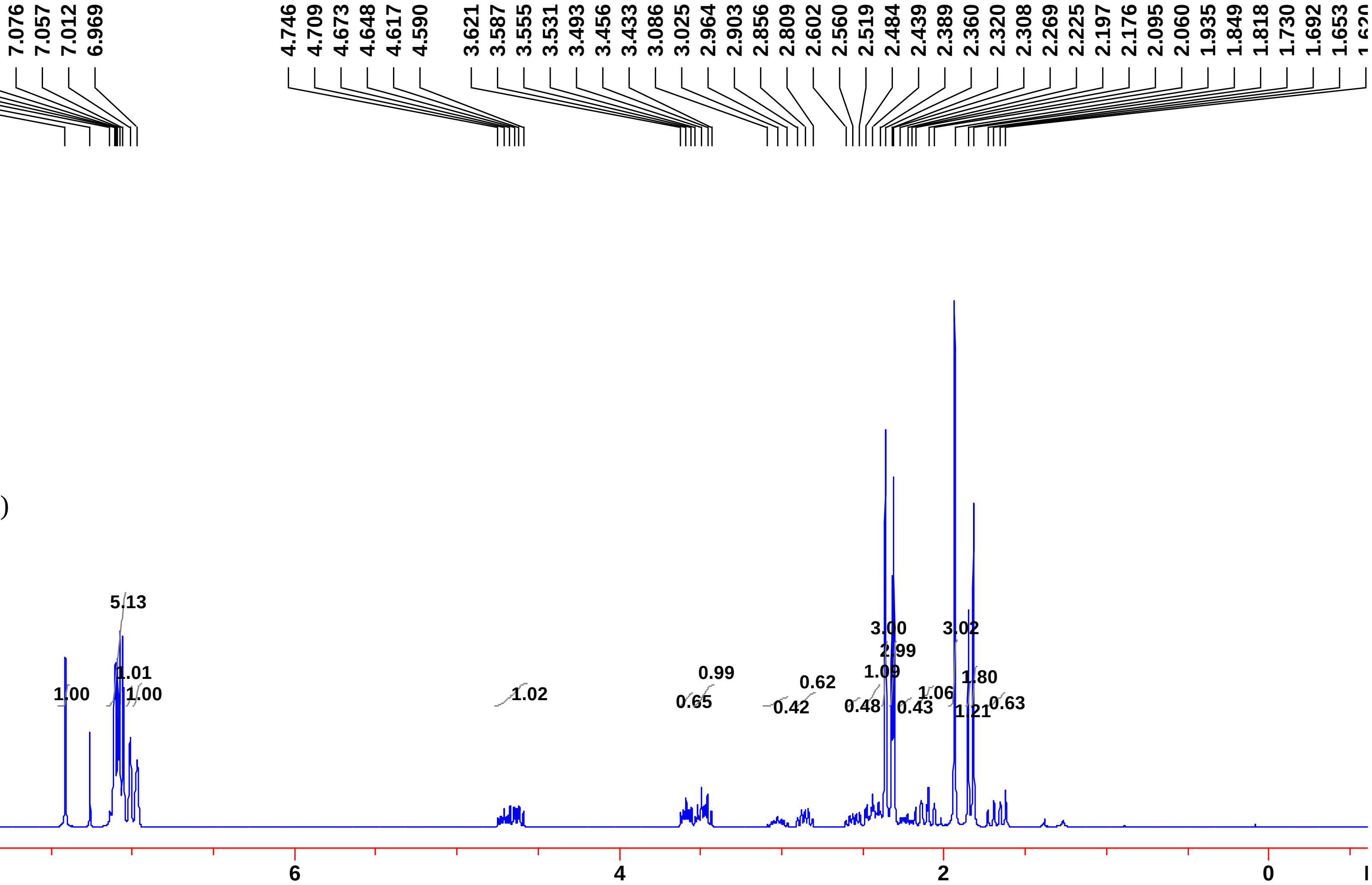
3z

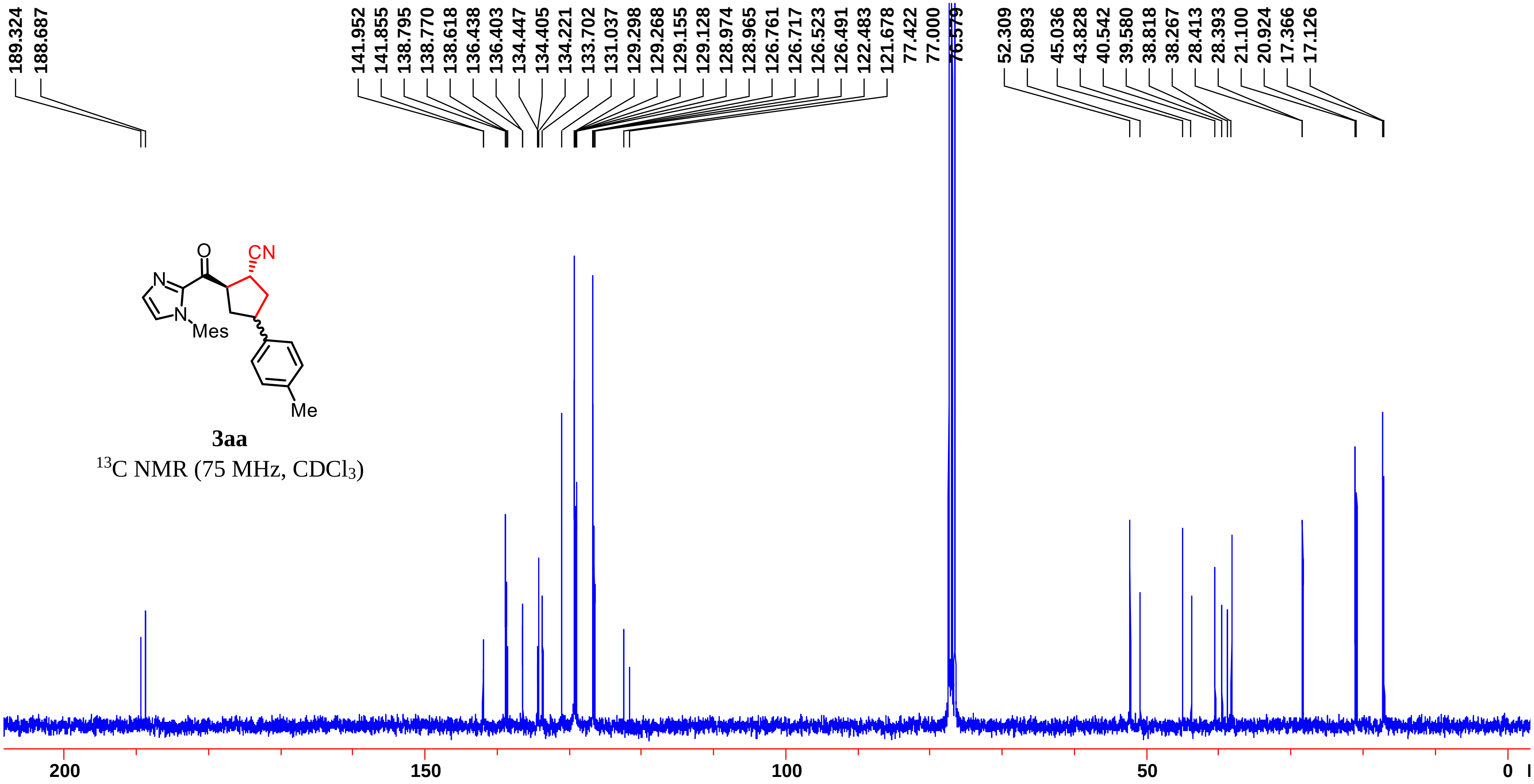
^{13}C NMR (75 MHz, $CDCl_3$)

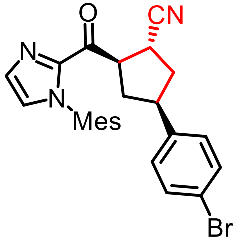


3aa

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

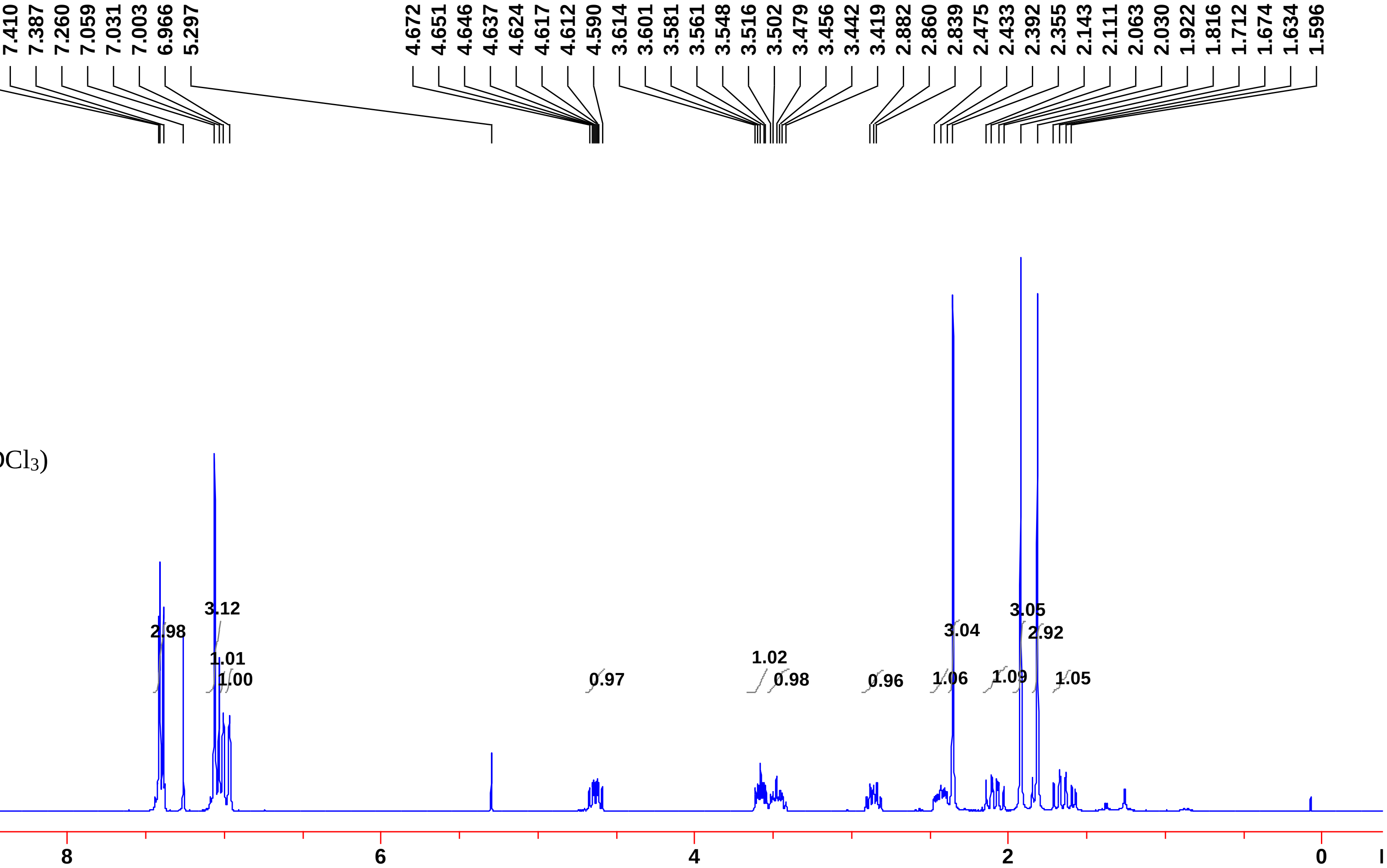


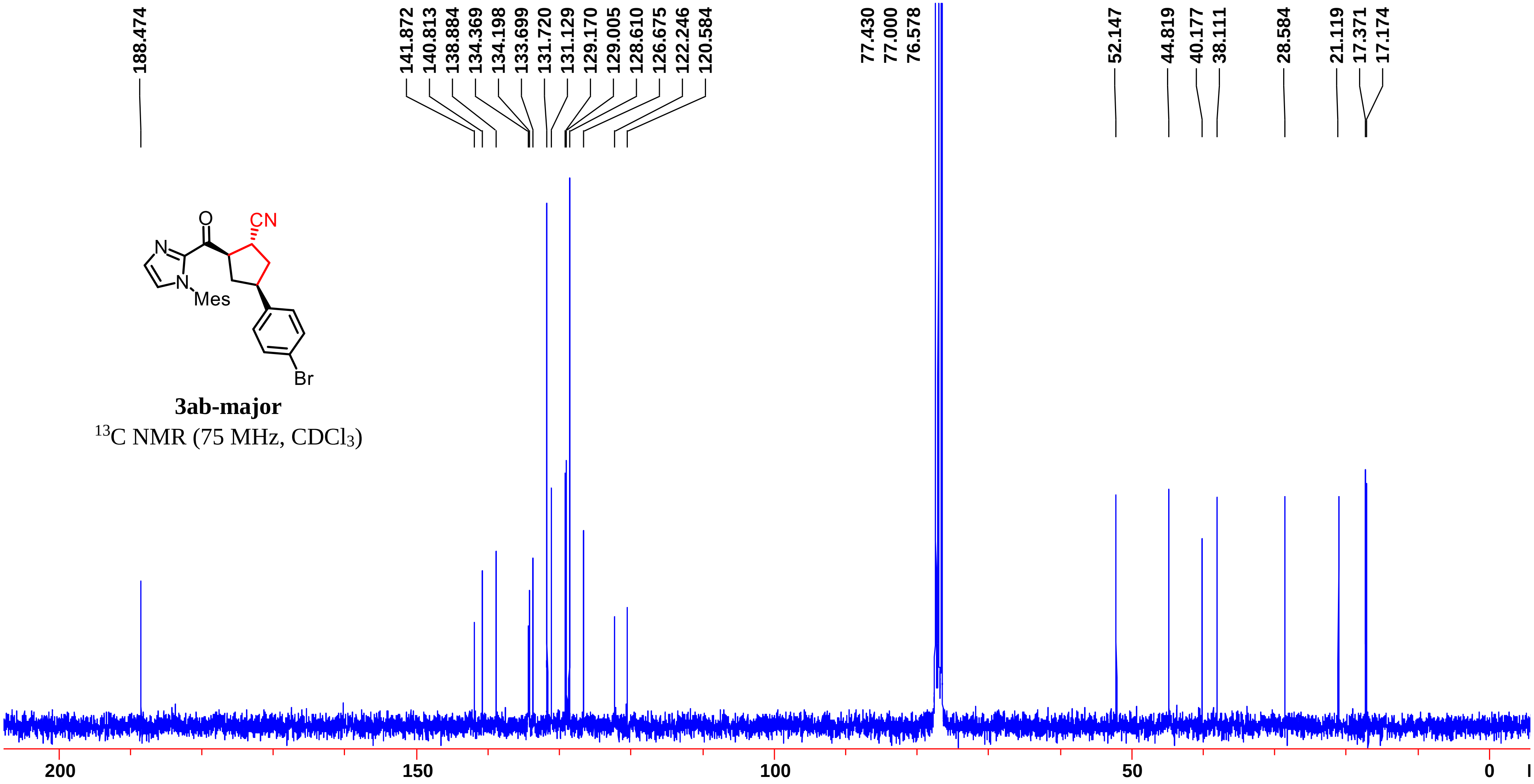

189.324
188.687
141.952
141.855
138.795
138.770
138.618
136.438
136.403
134.447
134.405
134.221
133.702
131.037
129.298
129.268
129.155
129.128
128.974
128.965
126.761
126.717
126.523
126.491
122.483
121.678
77.422
77.000
76.579
52.309
50.893
45.036
43.828
40.542
39.580
38.818
38.267
28.413
28.393
21.100
20.924
17.366
17.126
O
CN
N
N
Mes
Me
3aa
^{13}C NMR (75 MHz, CDCl$_3$)
200
150
100
50
0



3ab-major

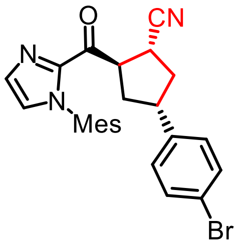
^{1}H NMR (300 MHz, $CDCl_3$)





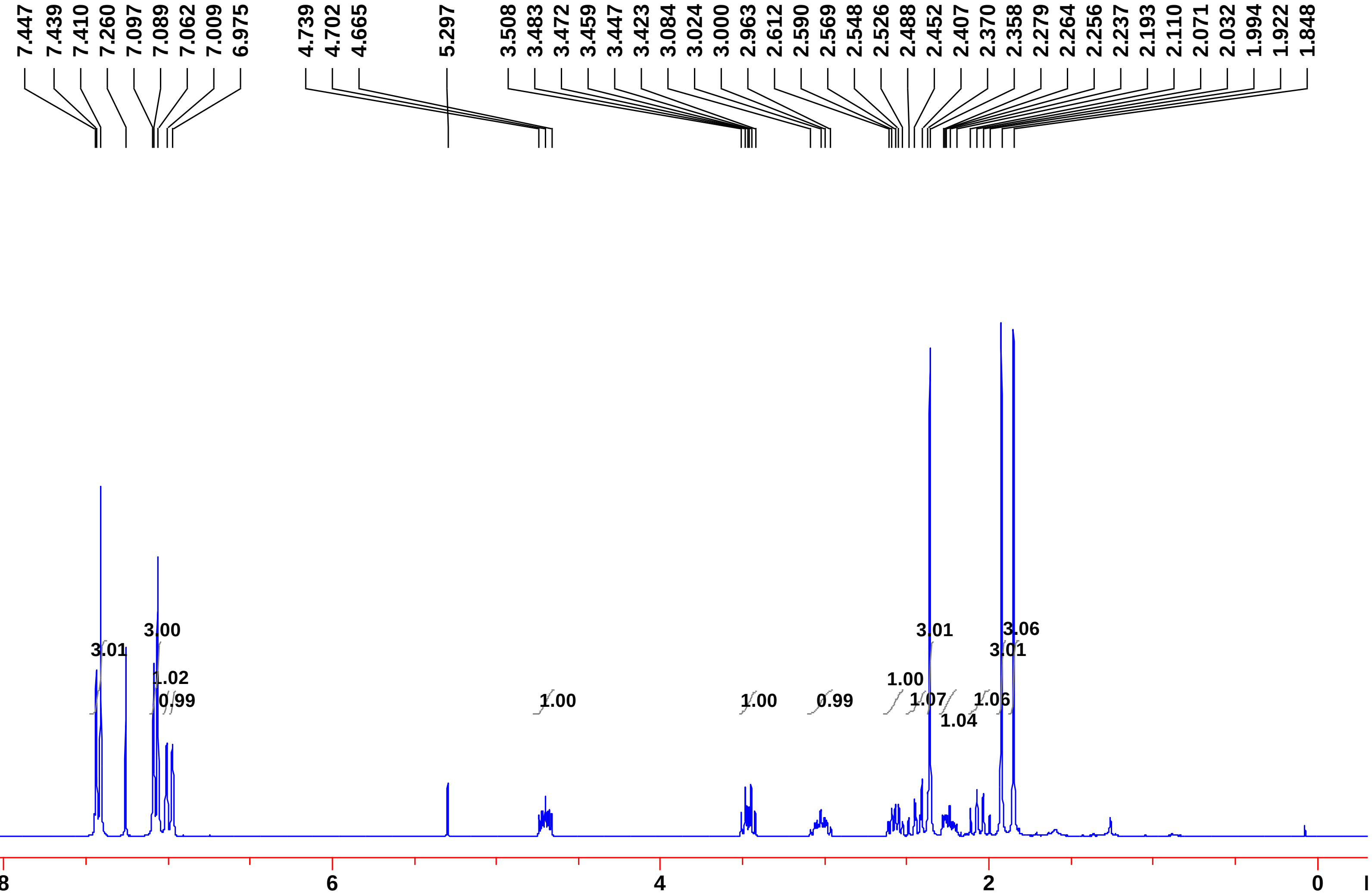
3ab-major

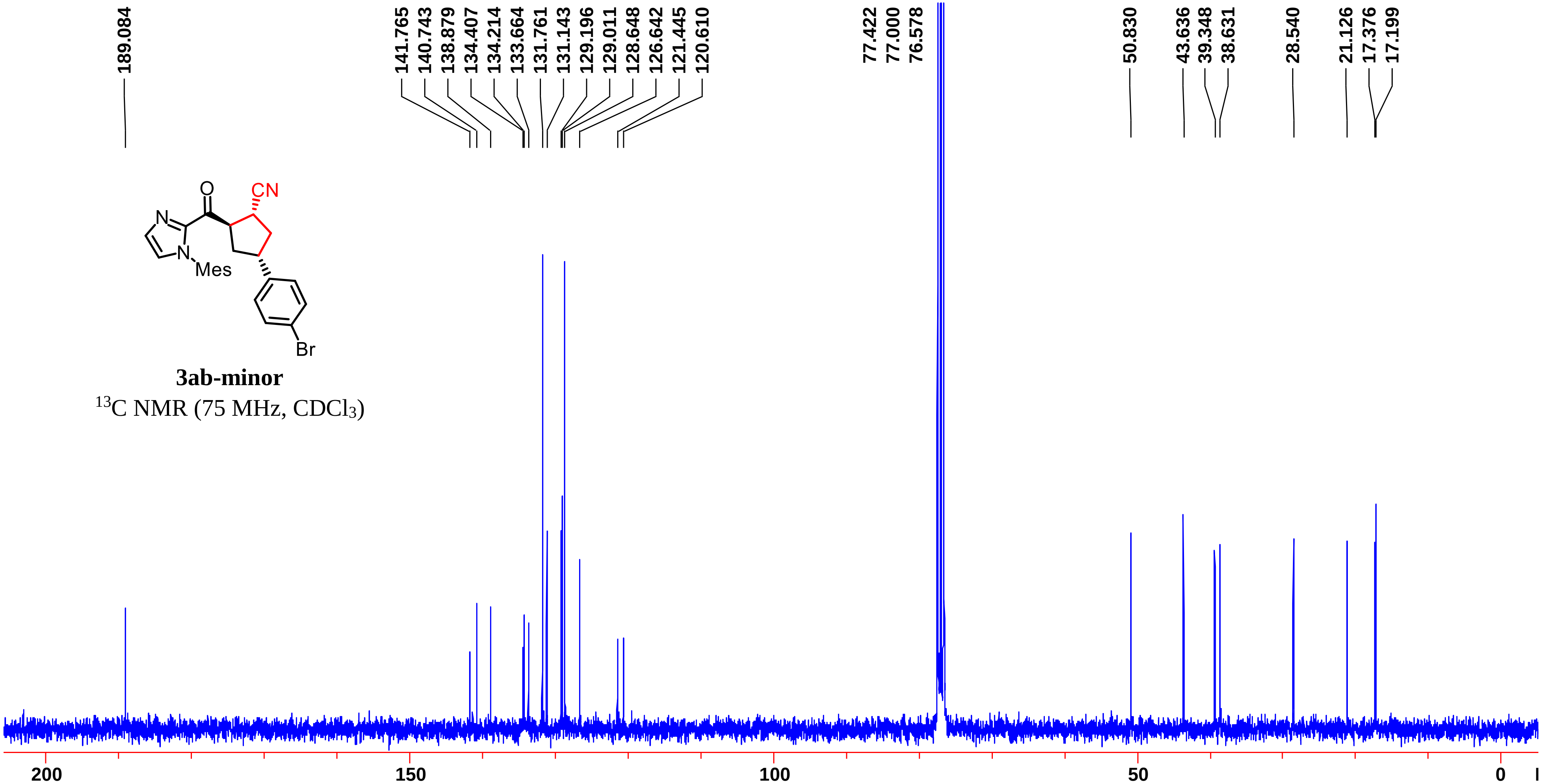
^{13}C NMR (75 MHz, $CDCl_3$)



3ab-minor

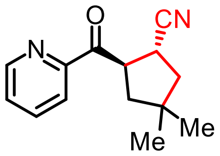
^{1}H NMR (300 MHz, $CDCl_3$)





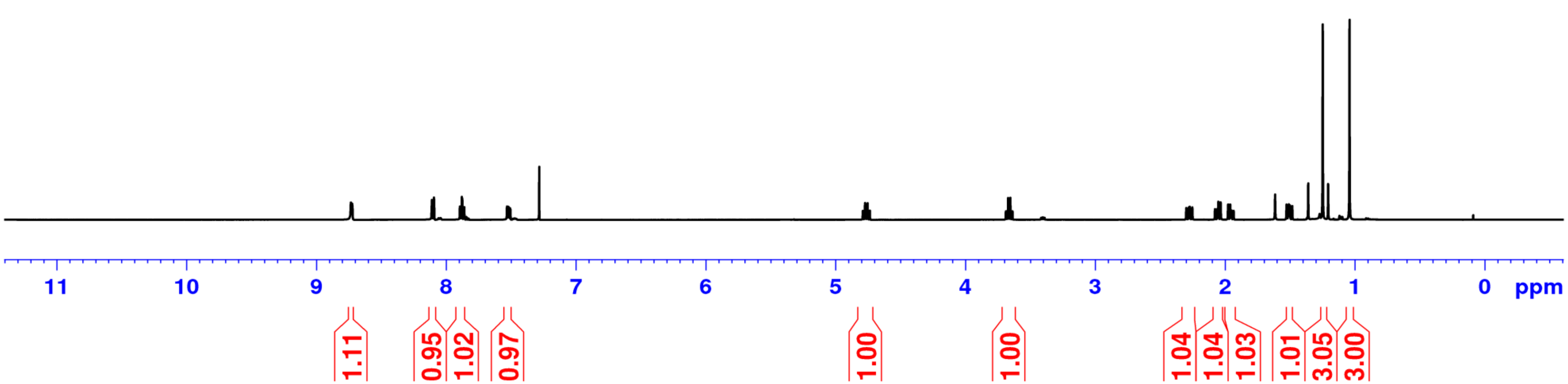
3ab-minor

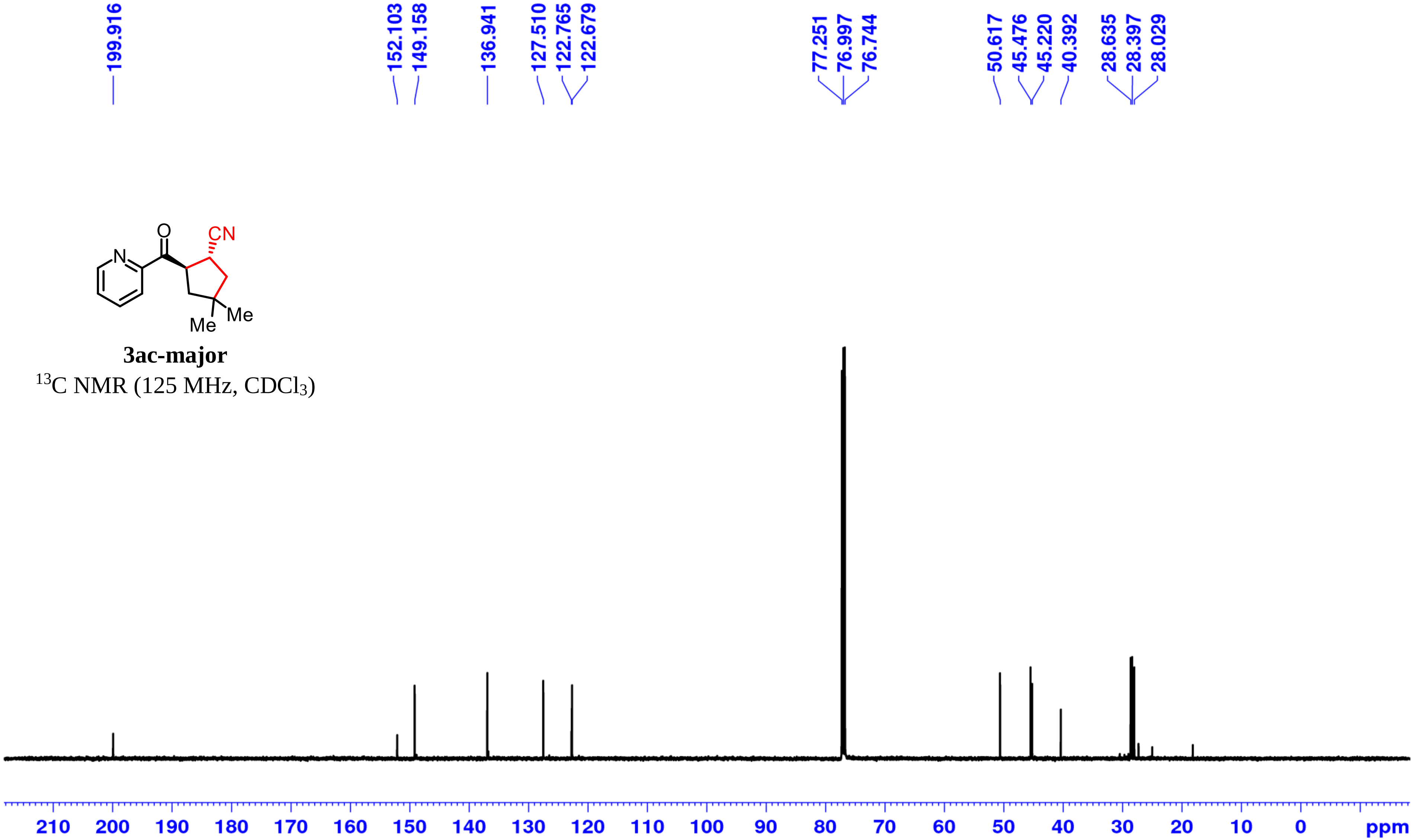
^{13}C NMR (75 MHz, $CDCl_3$)



3ac-major

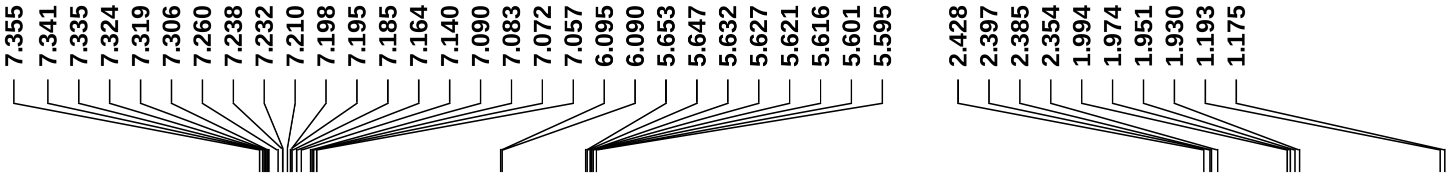
[1]H NMR (500 MHz, $CDCl_3$)

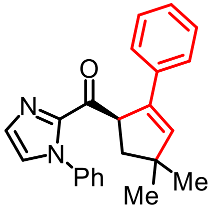




3ac-major

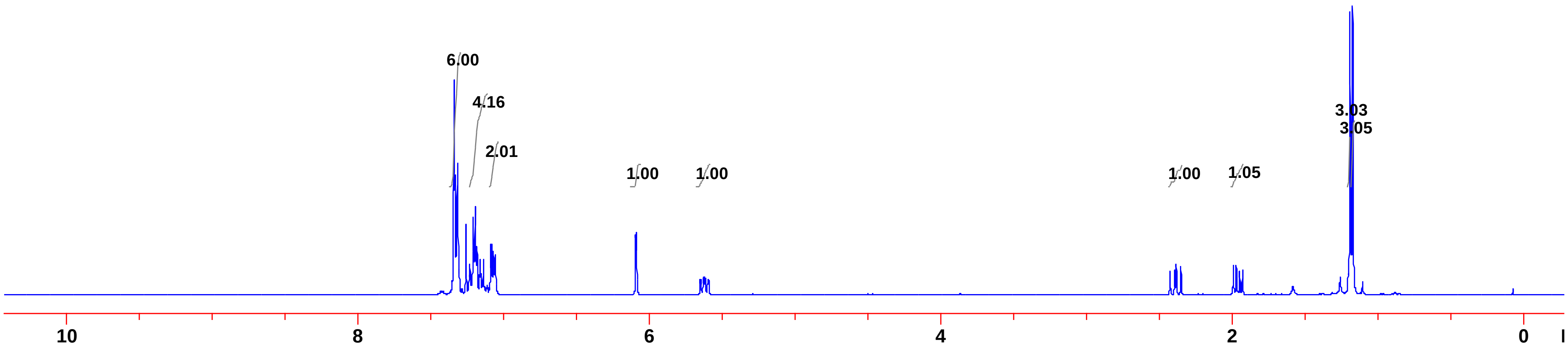
^{13}C NMR (125 MHz, $CDCl_3$)

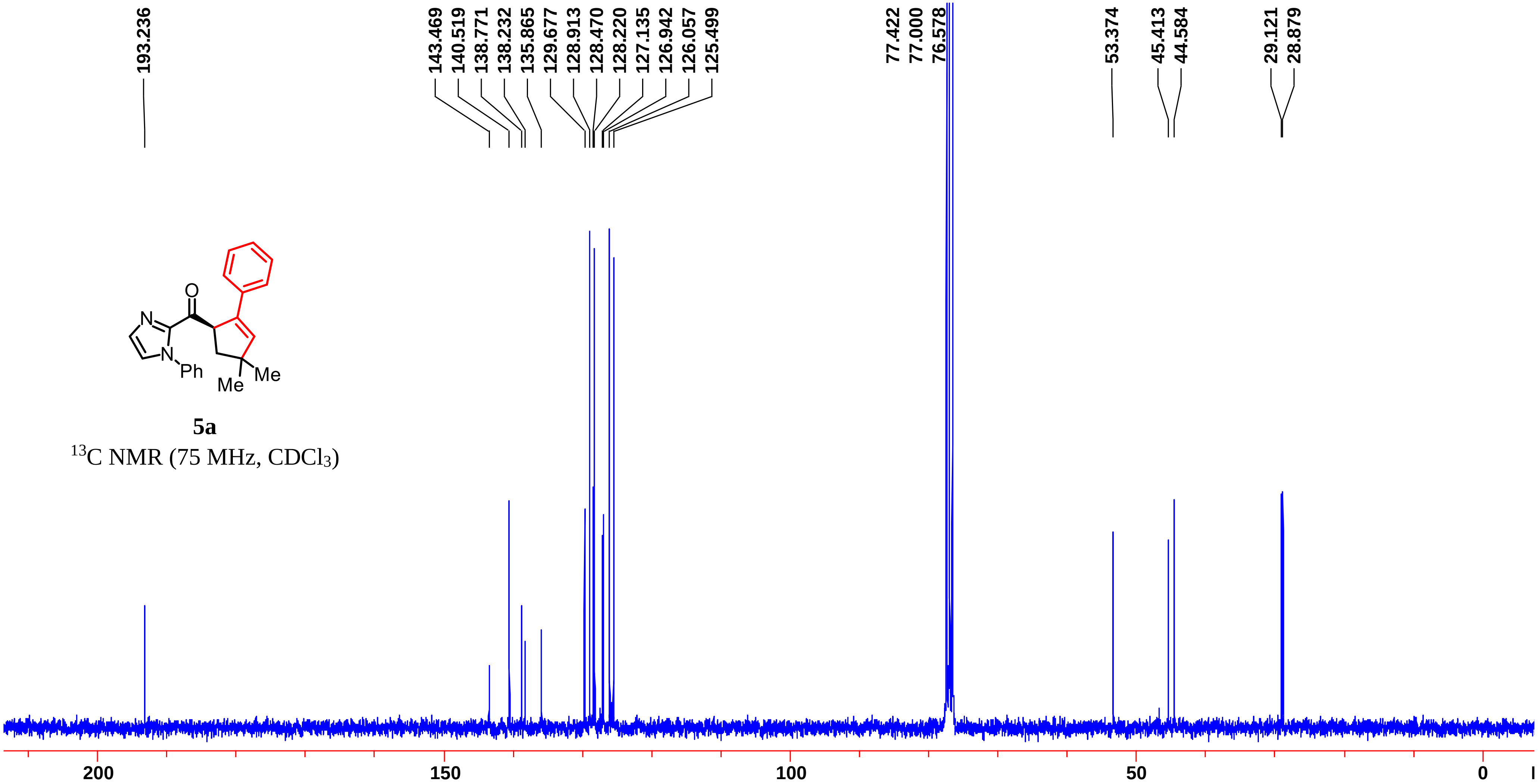




5a

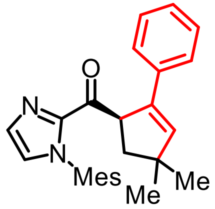
^{1}H NMR (300 MHz, $CDCl_3$)





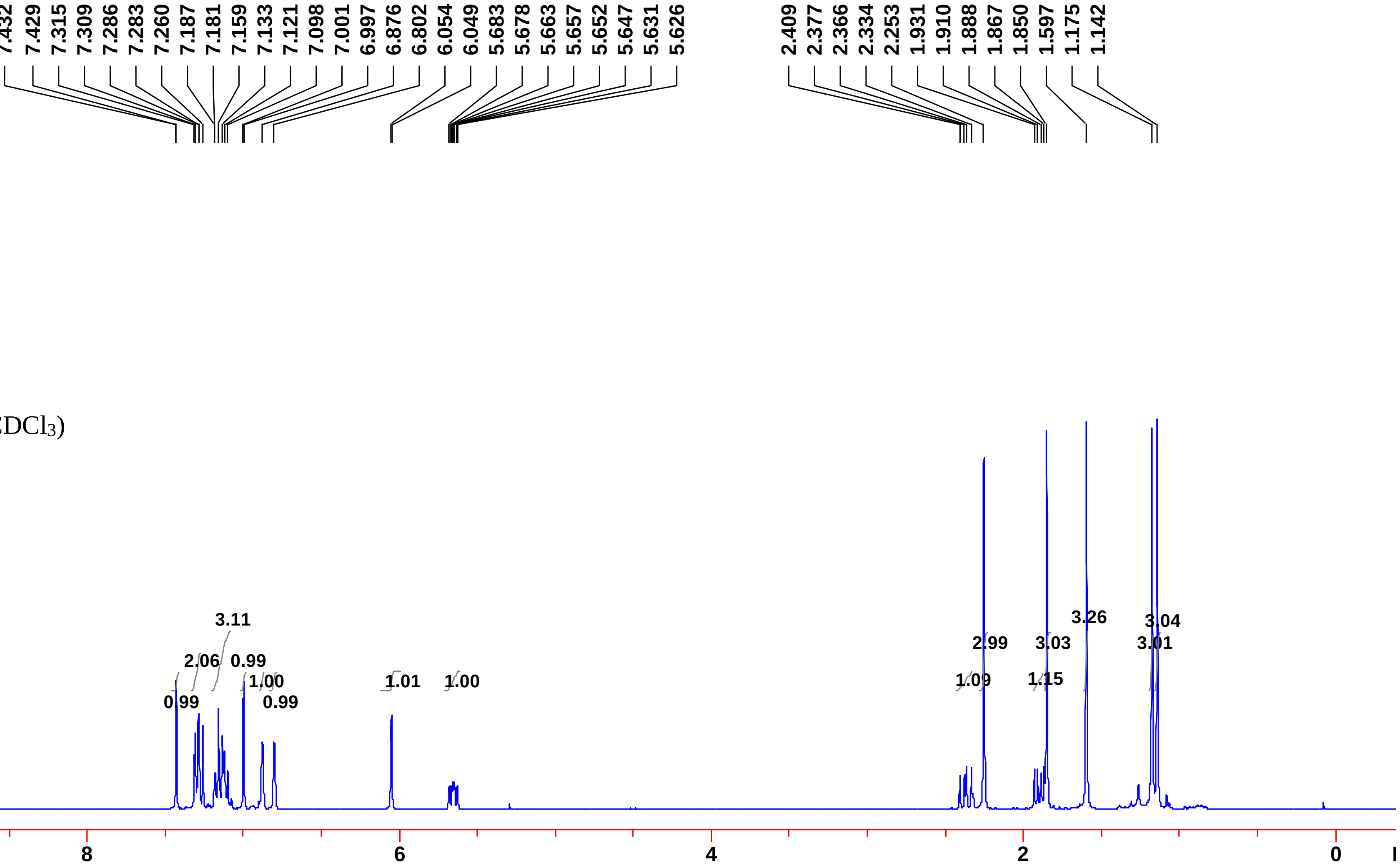
5a

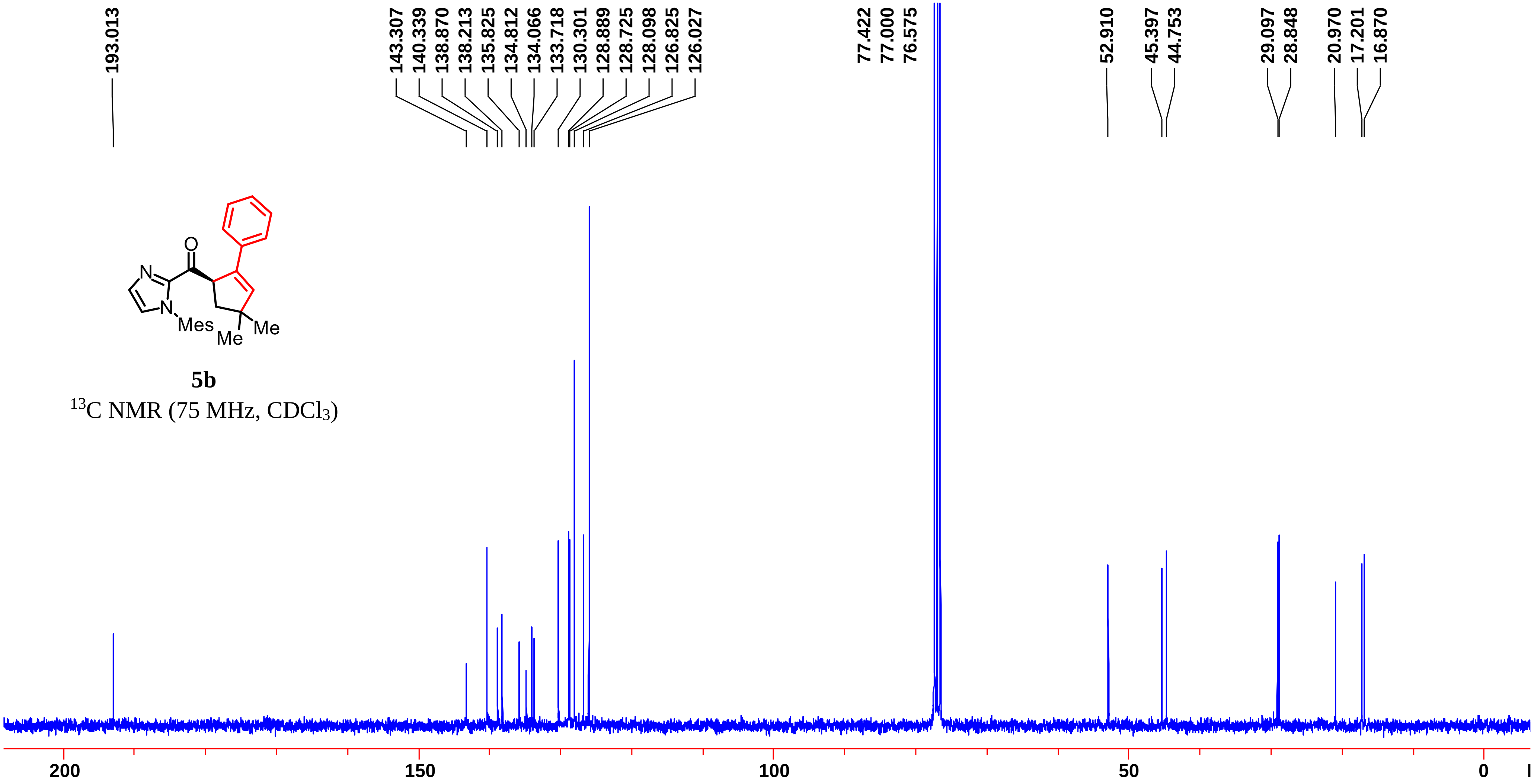
^{13}C NMR (75 MHz, $CDCl_3$)



5b

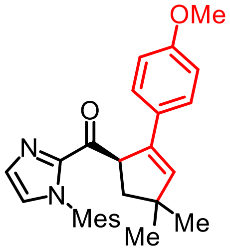
^{1}H NMR (300 MHz, $CDCl_3$)





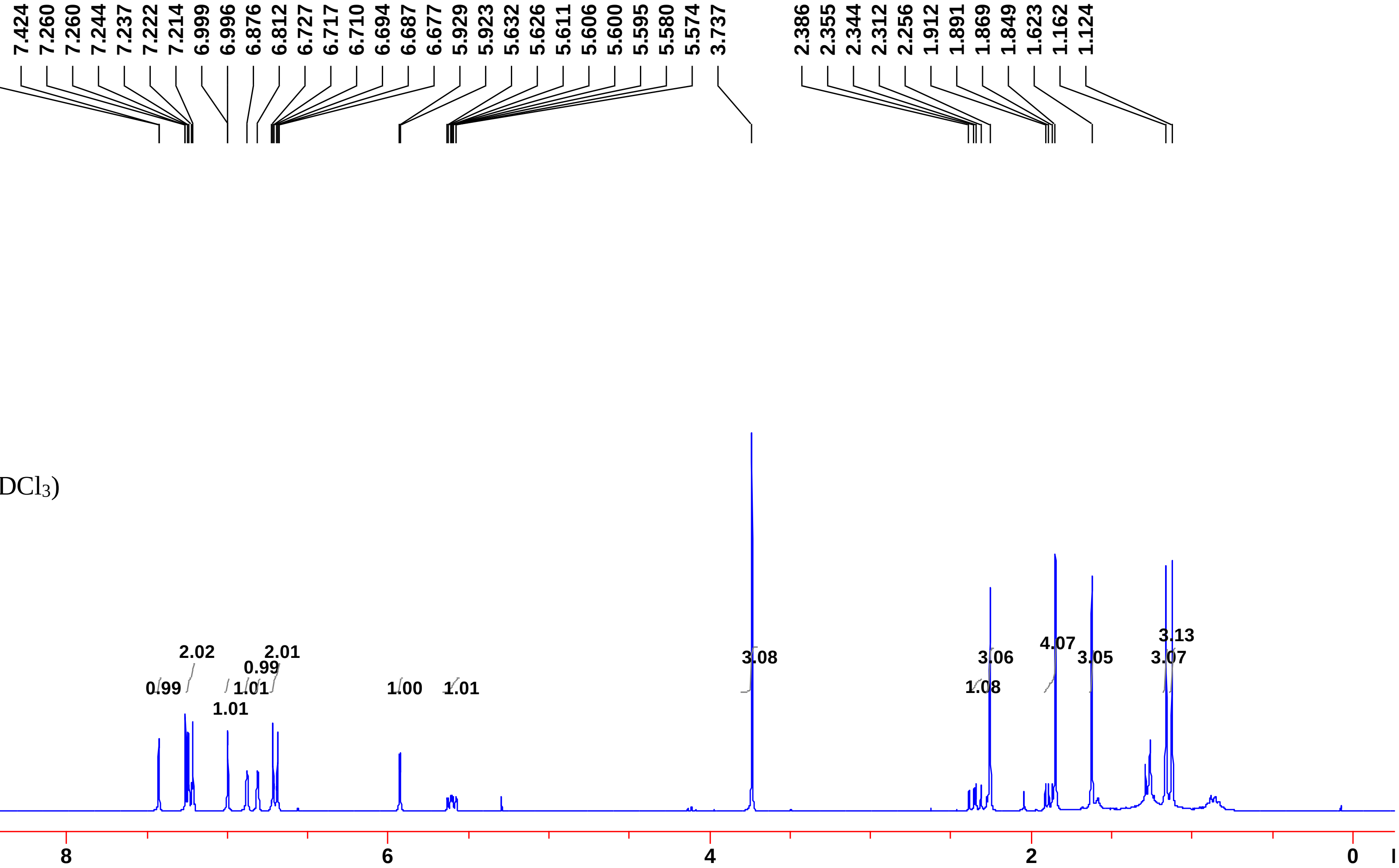
5b

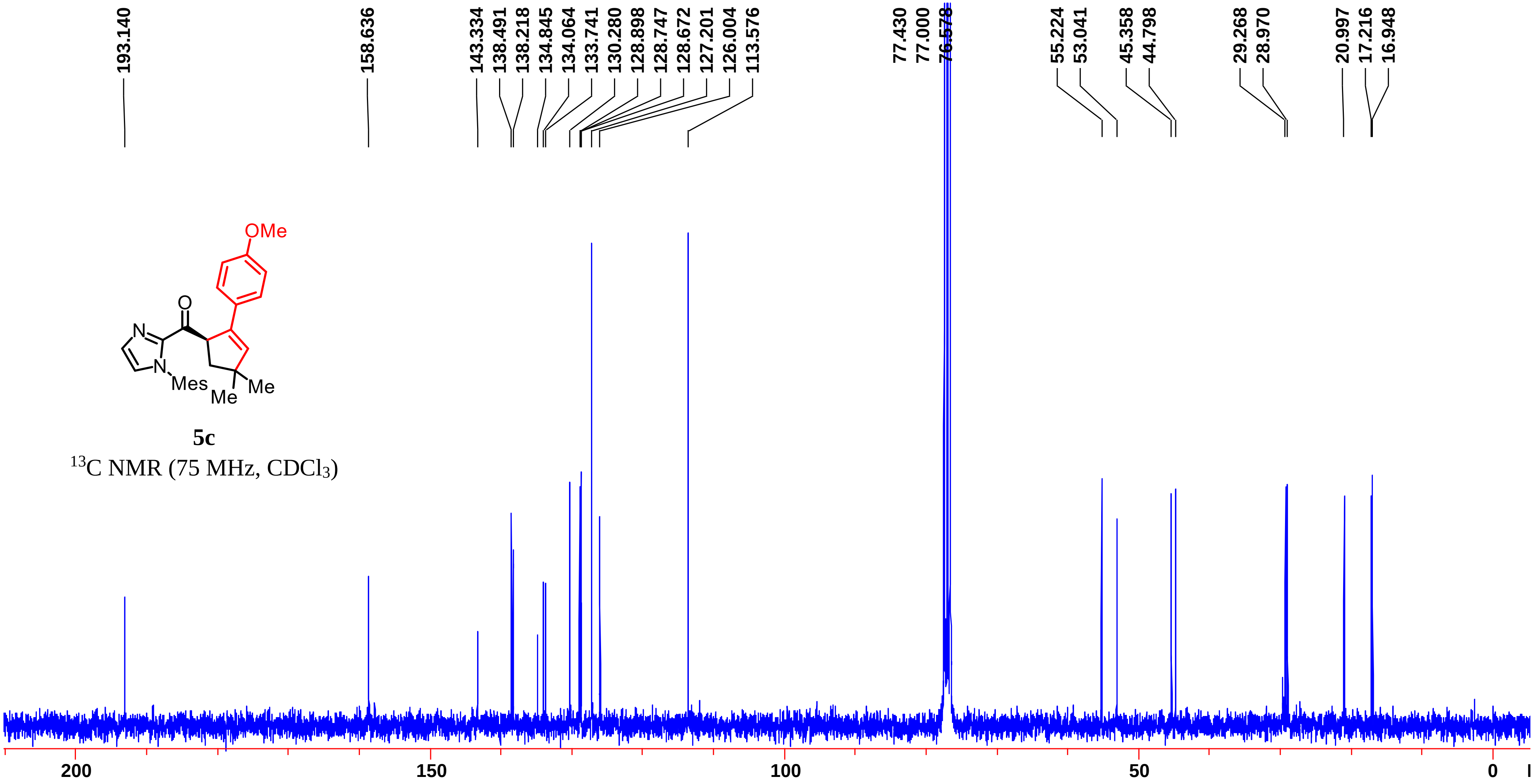
^{13}C NMR (75 MHz, $CDCl_3$)



5c

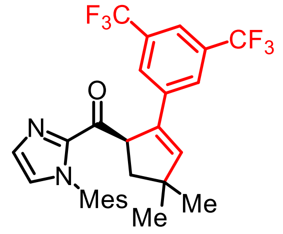
^{1}H NMR (300 MHz, $CDCl_3$)





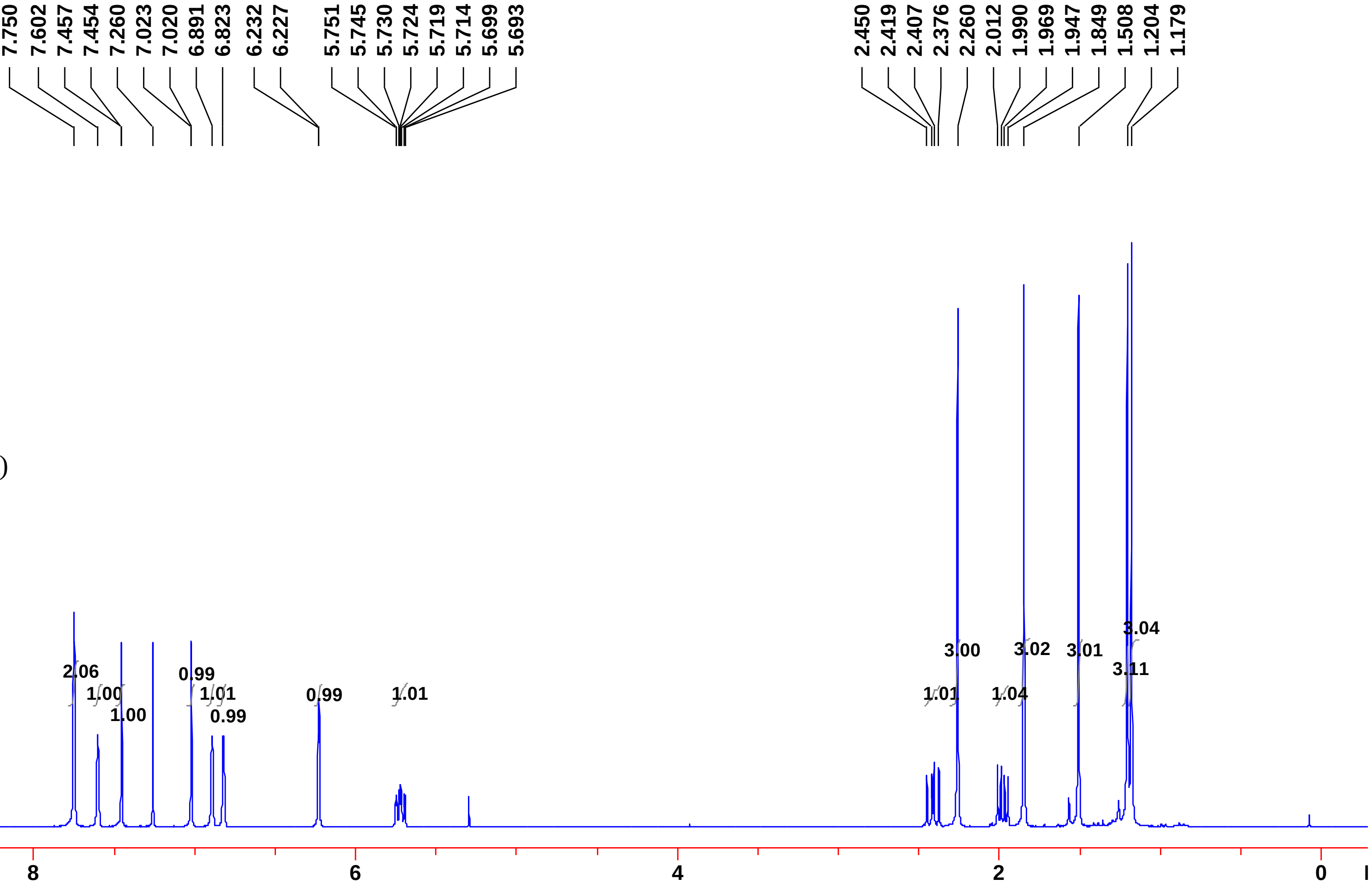
5c

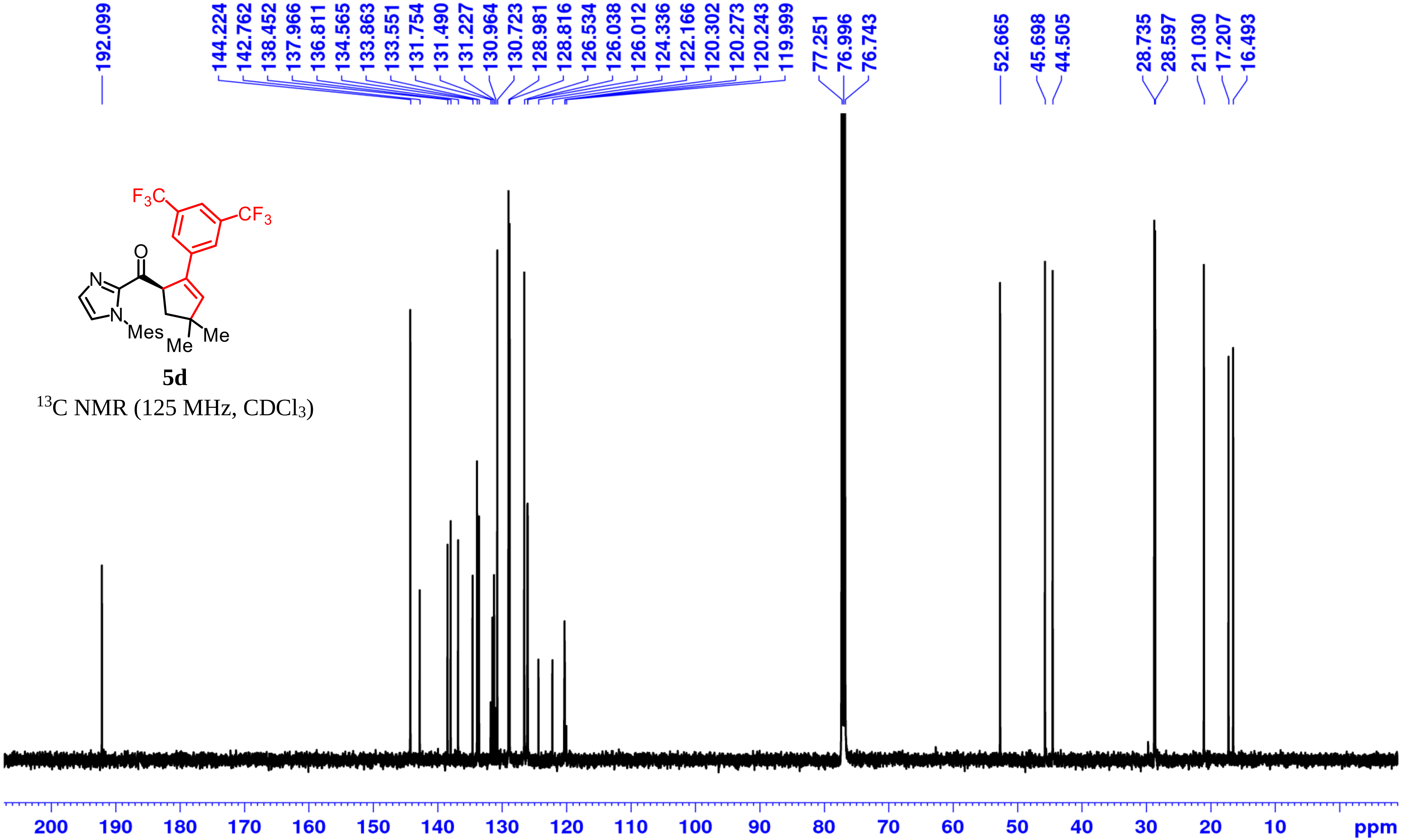
^{13}C NMR (75 MHz, $CDCl_3$)



5d

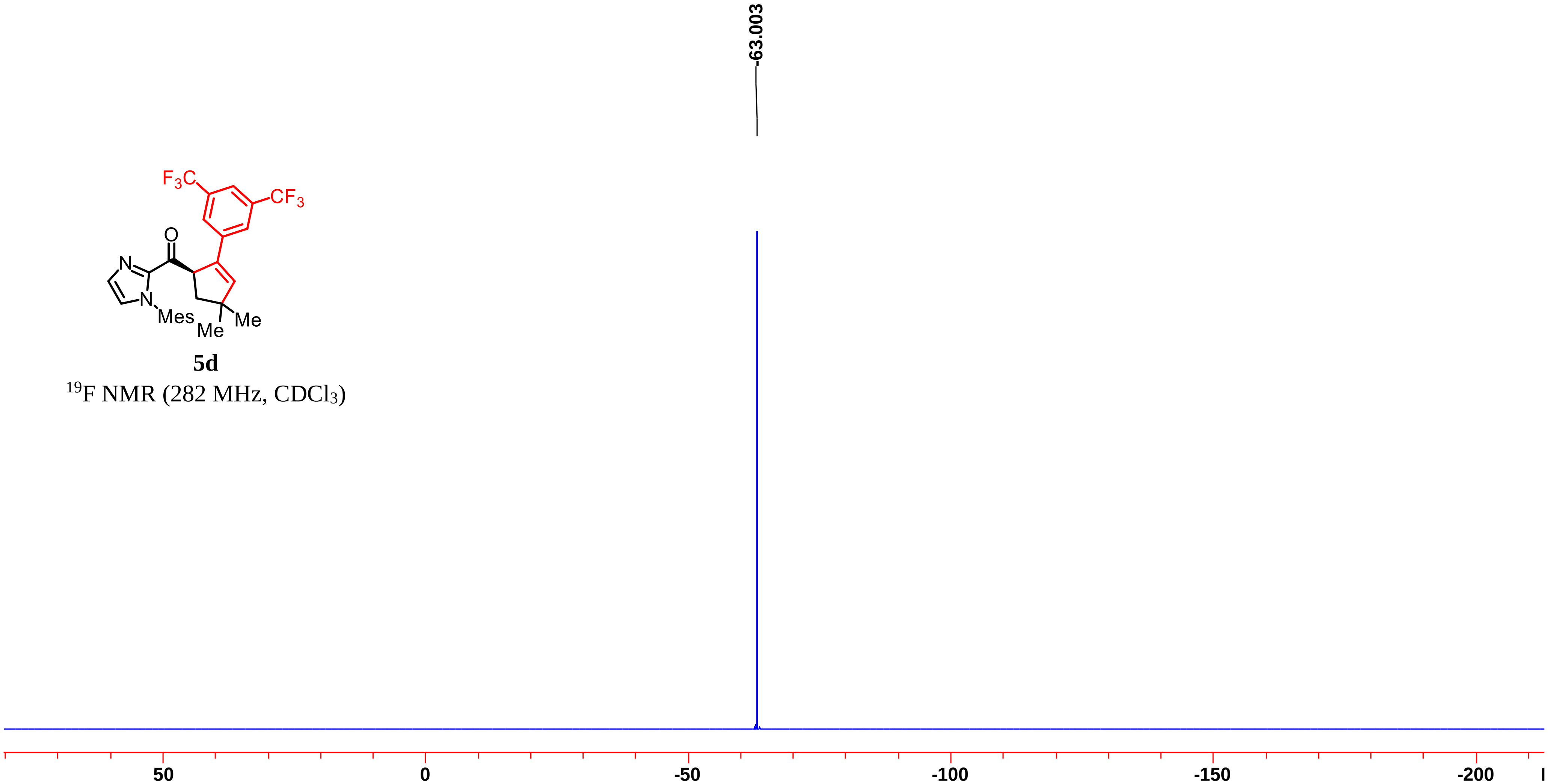
^{1}H NMR (300 MHz, $CDCl_3$)





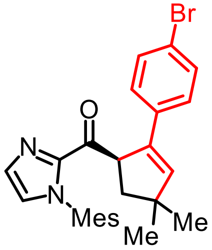
5d

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



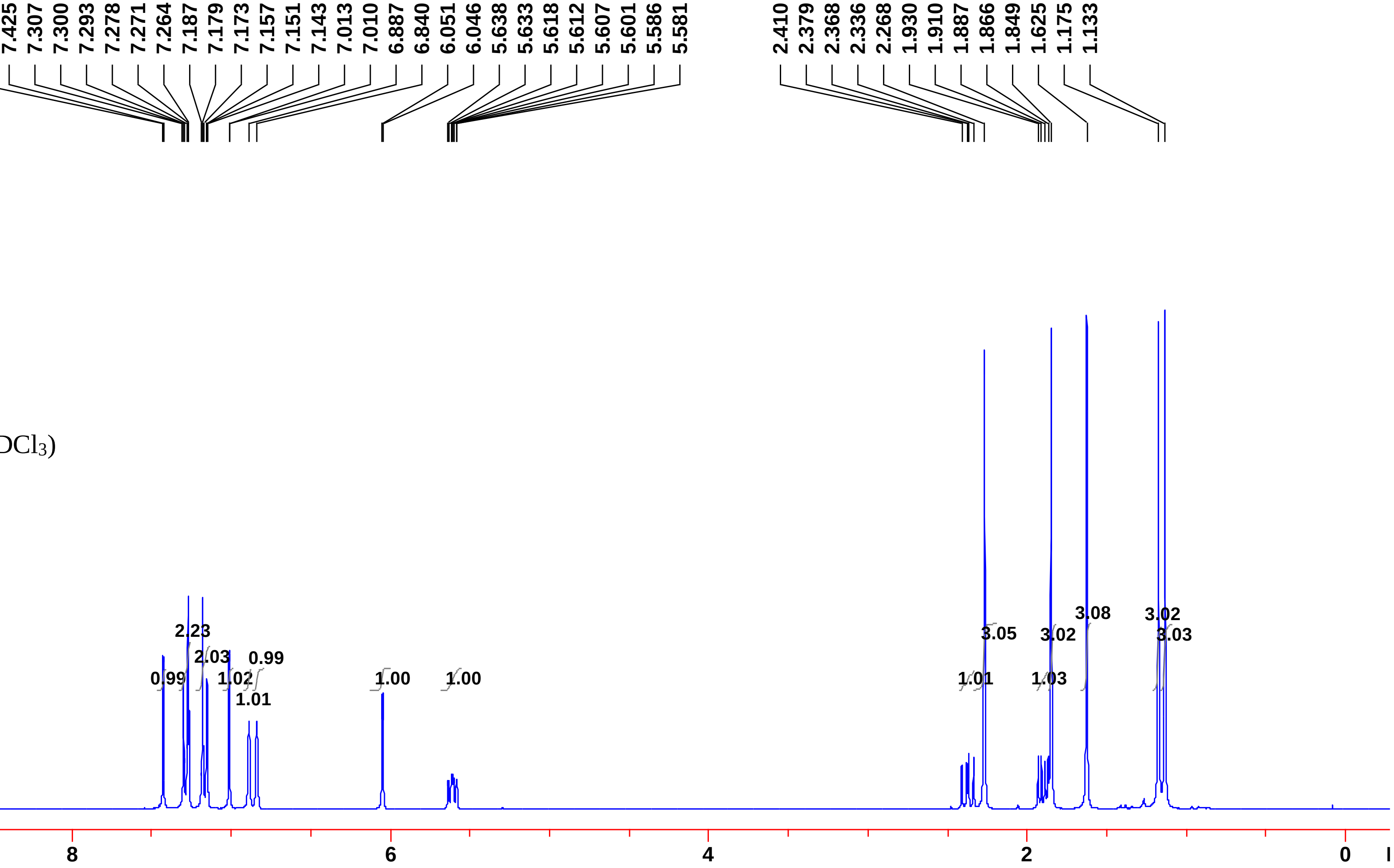
5d

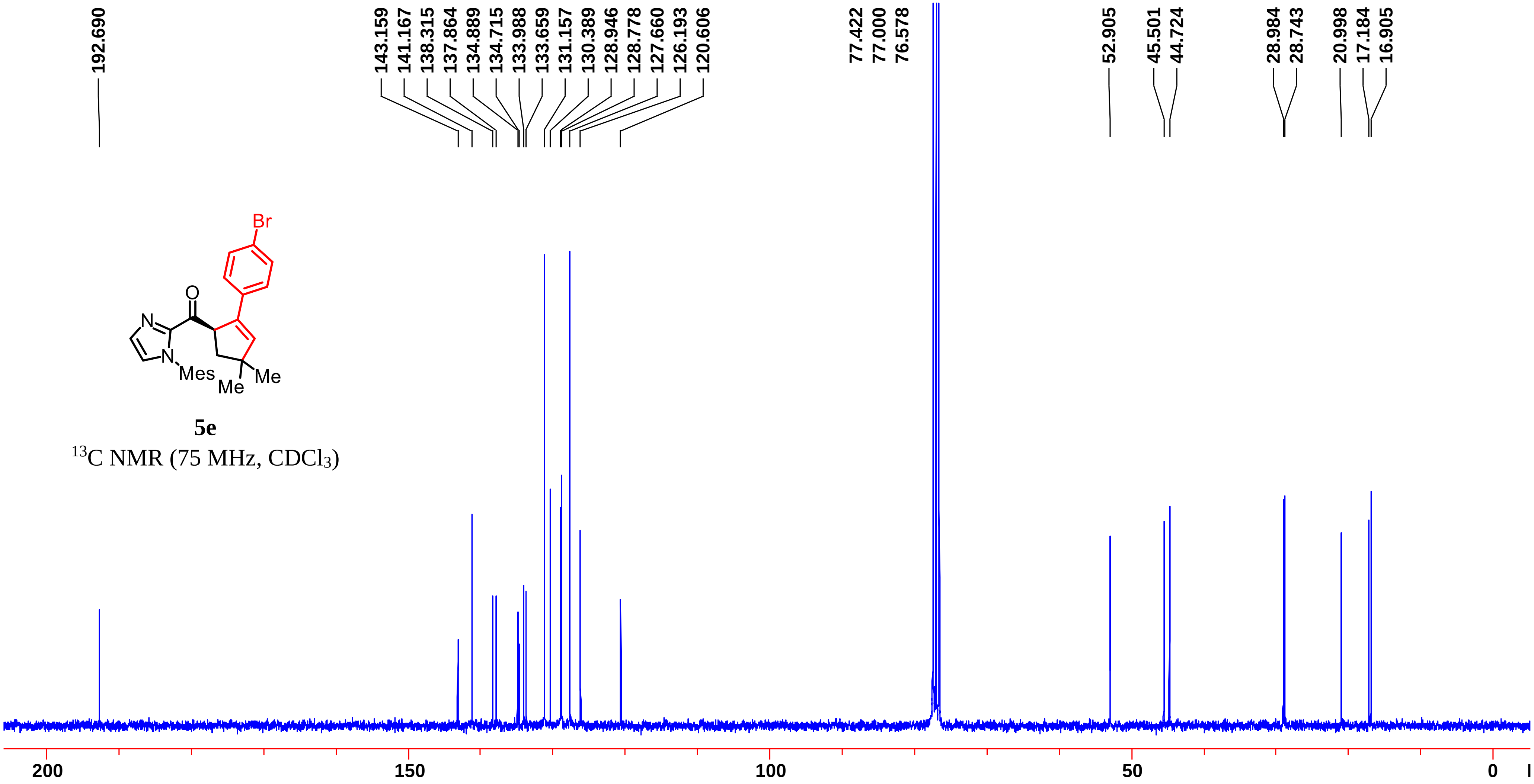
[19]F NMR (282 MHz, $CDCl_3$)



5e

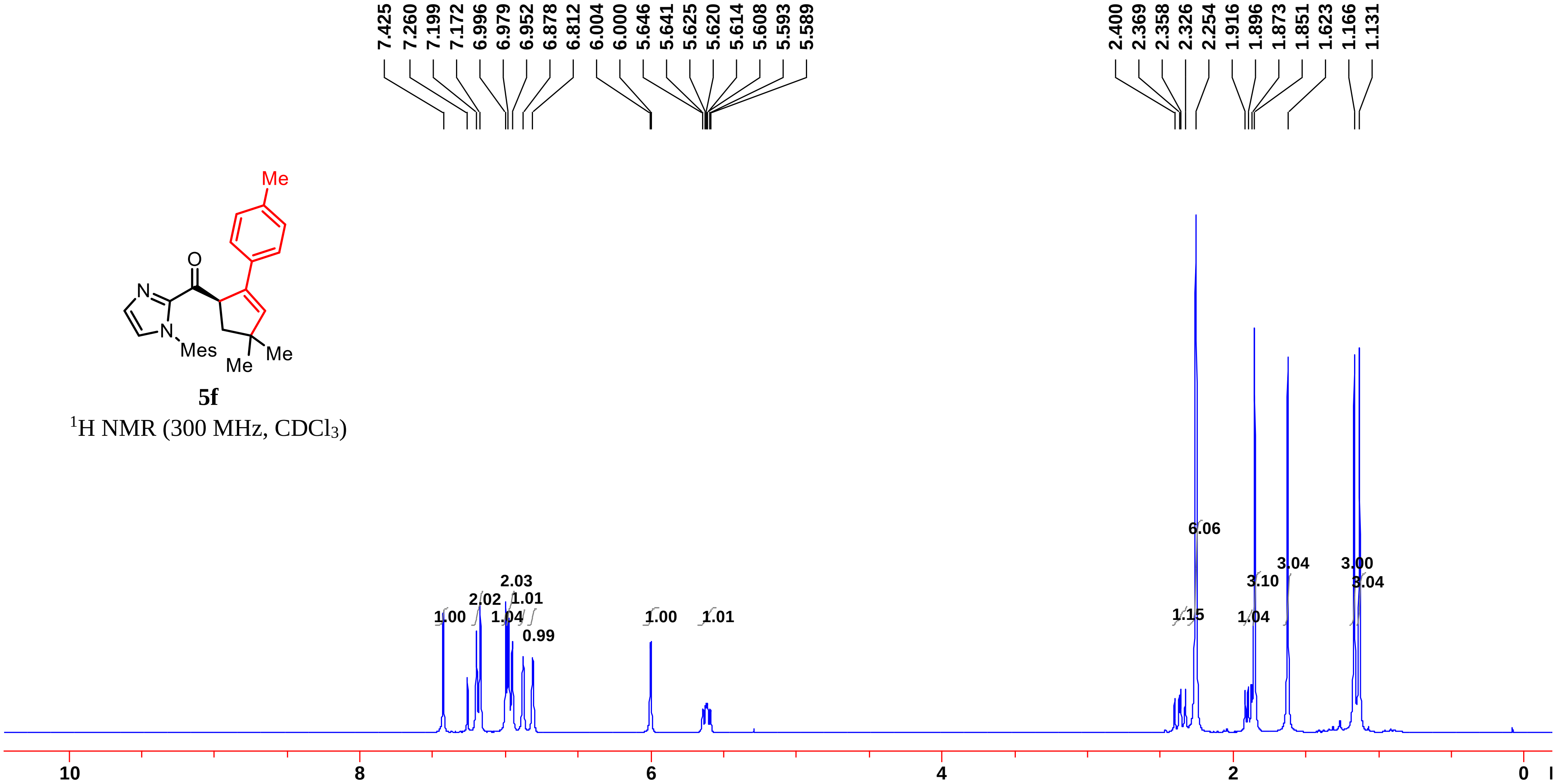
^{1}H NMR (300 MHz, $CDCl_3$)





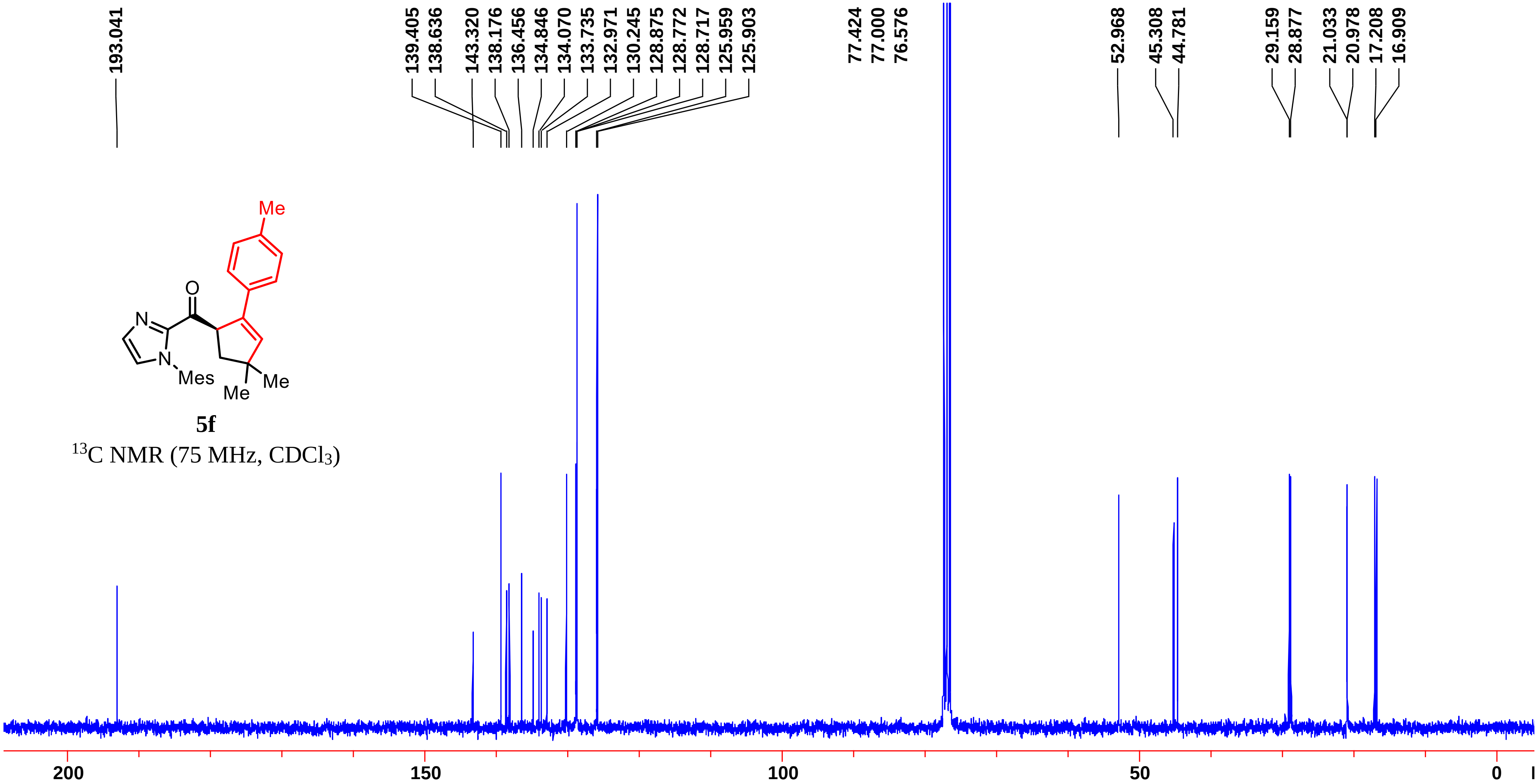
5e

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



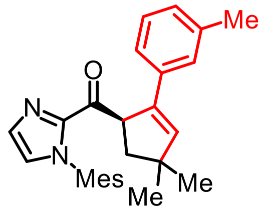
5f

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



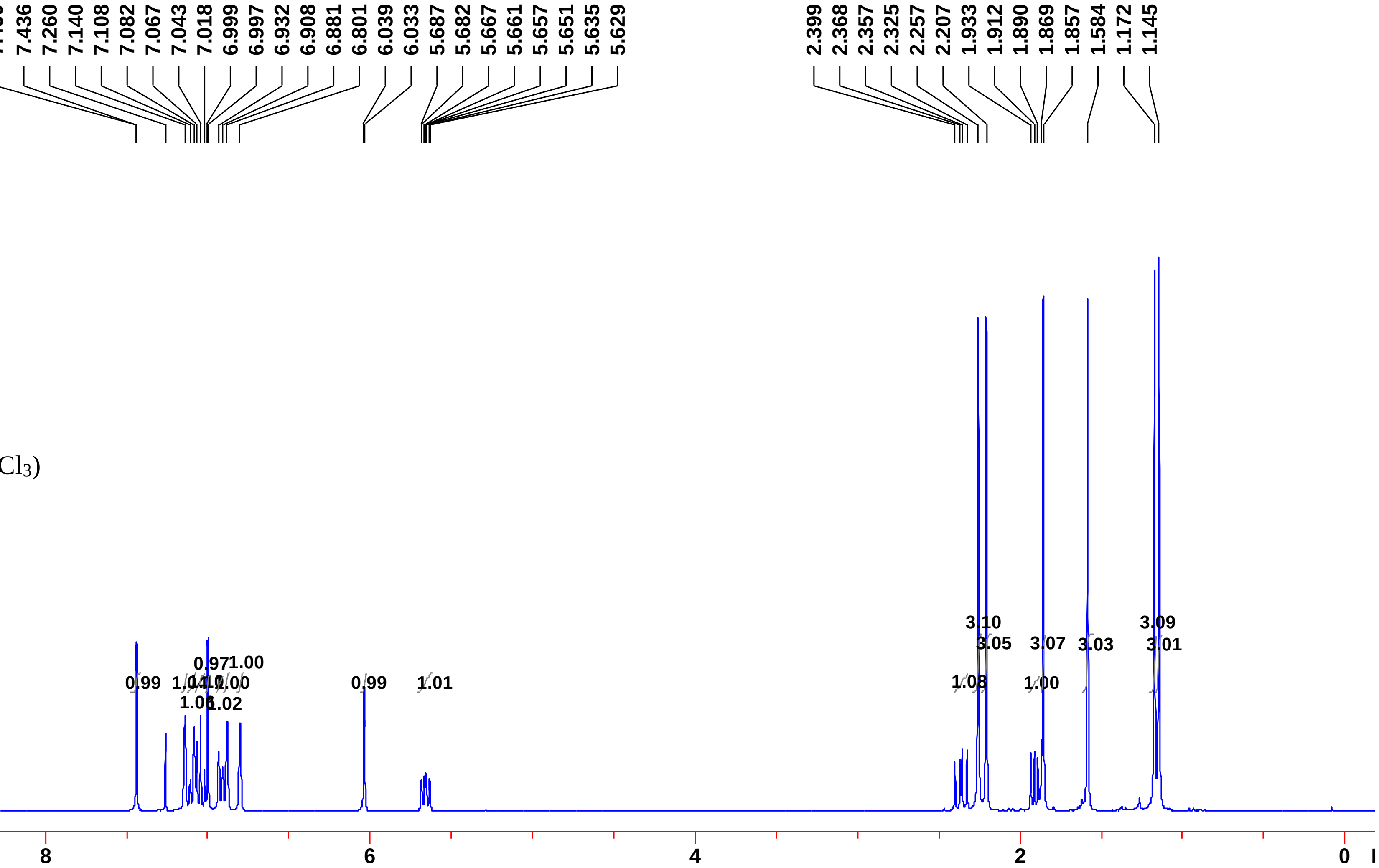
5f

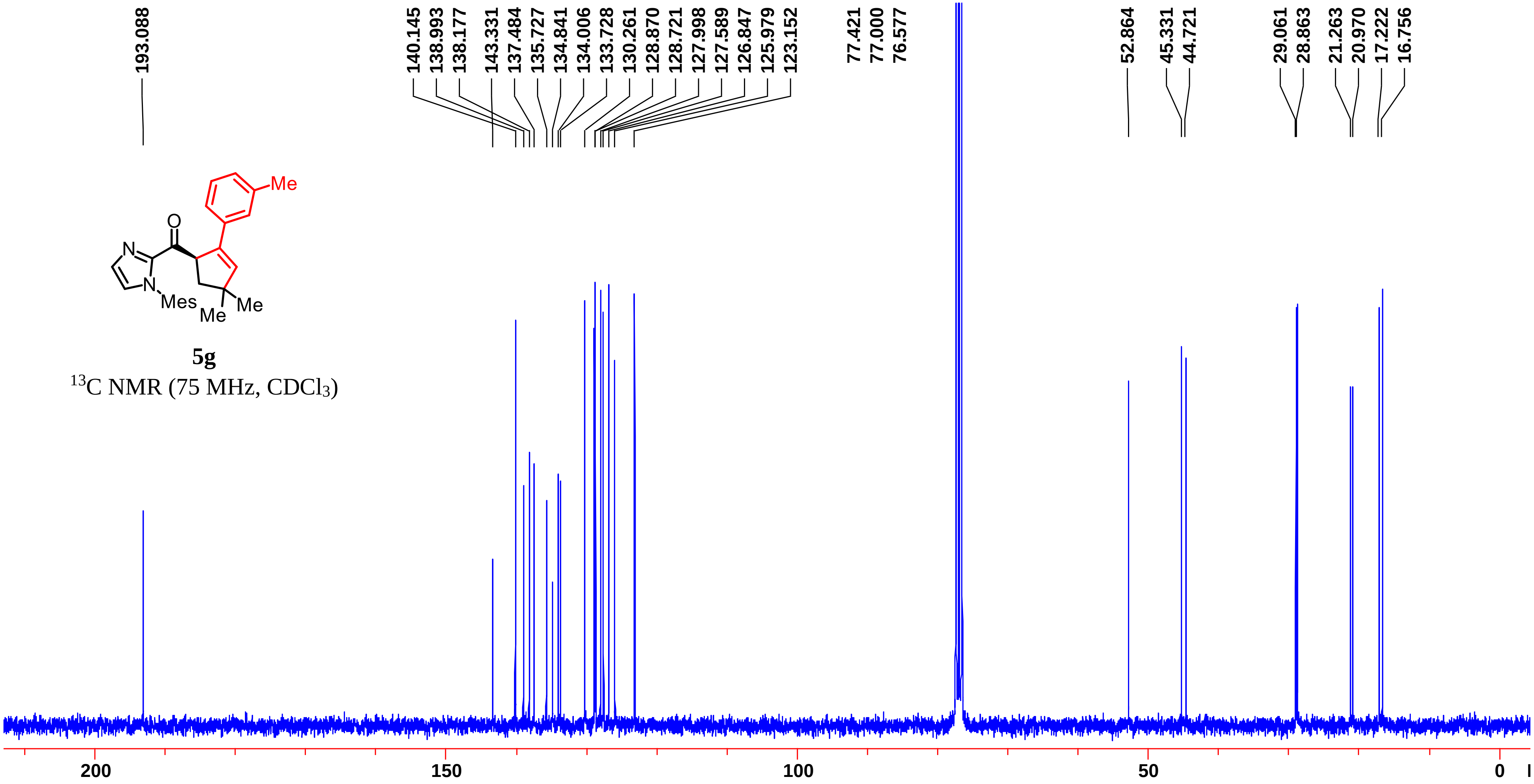
^{13}C NMR (75 MHz, $CDCl_3$)



5g

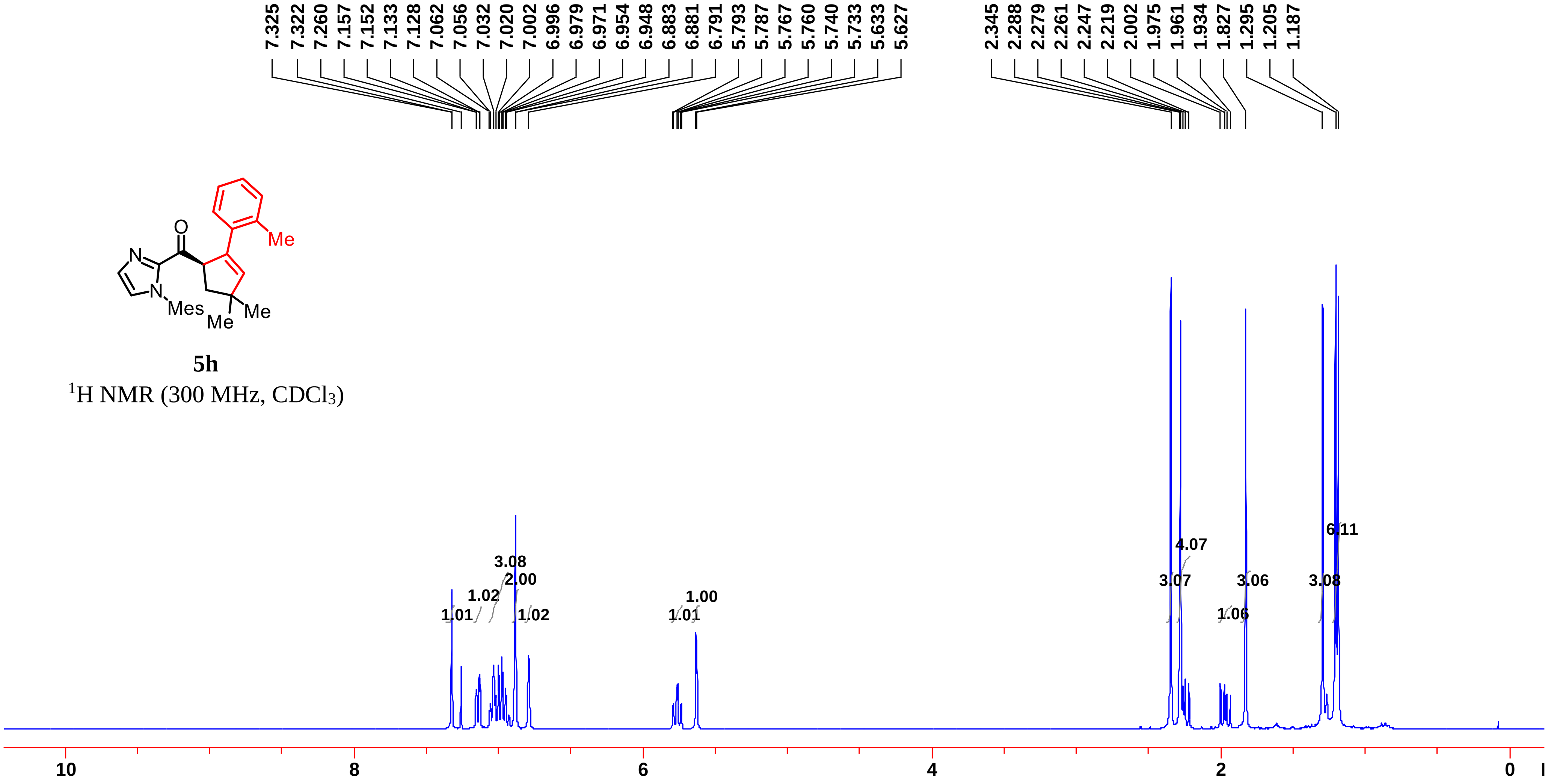
^{1}H NMR (300 MHz, $CDCl_3$)





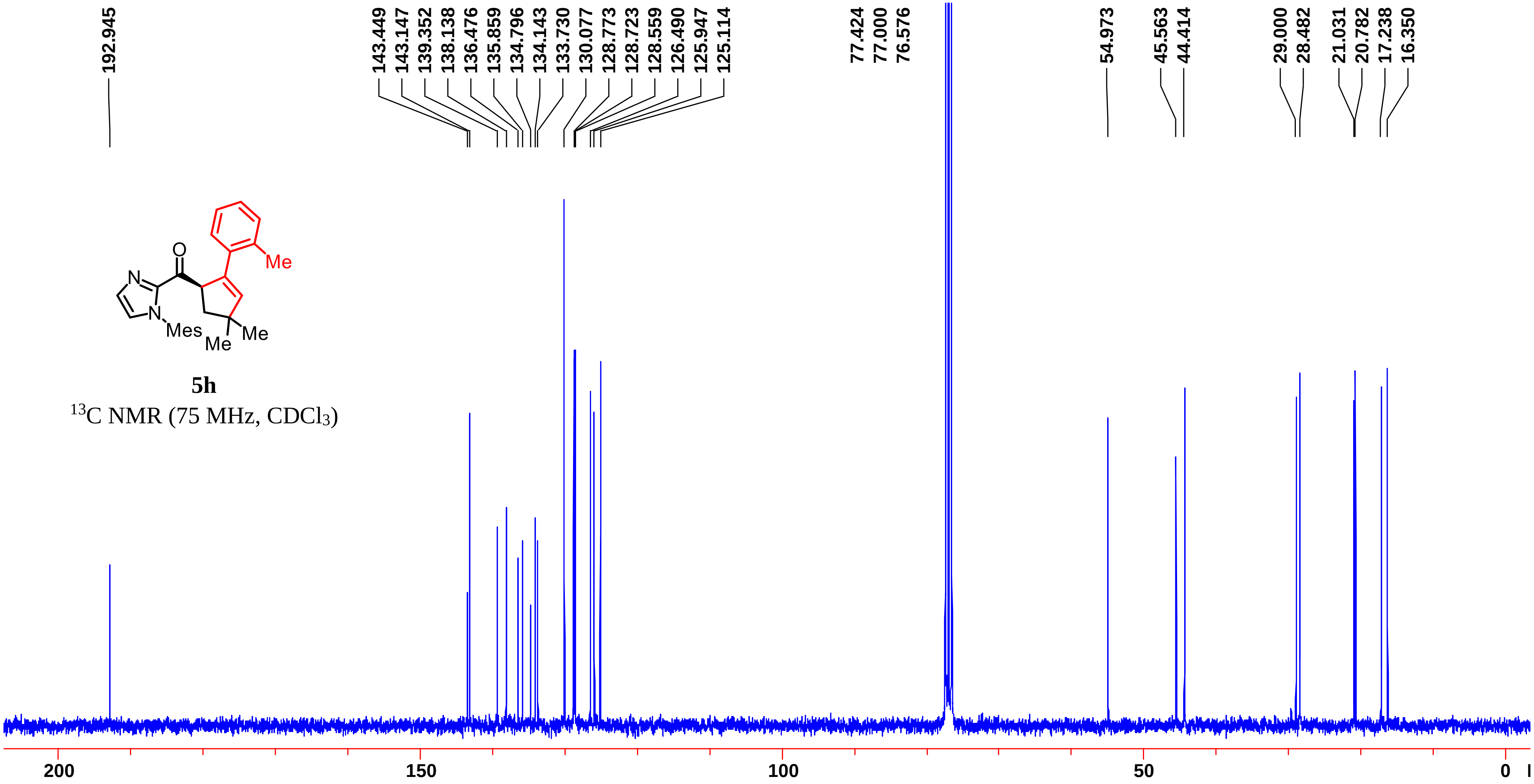
5g

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



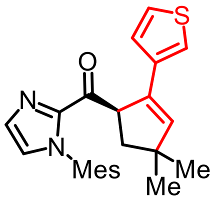
5h

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



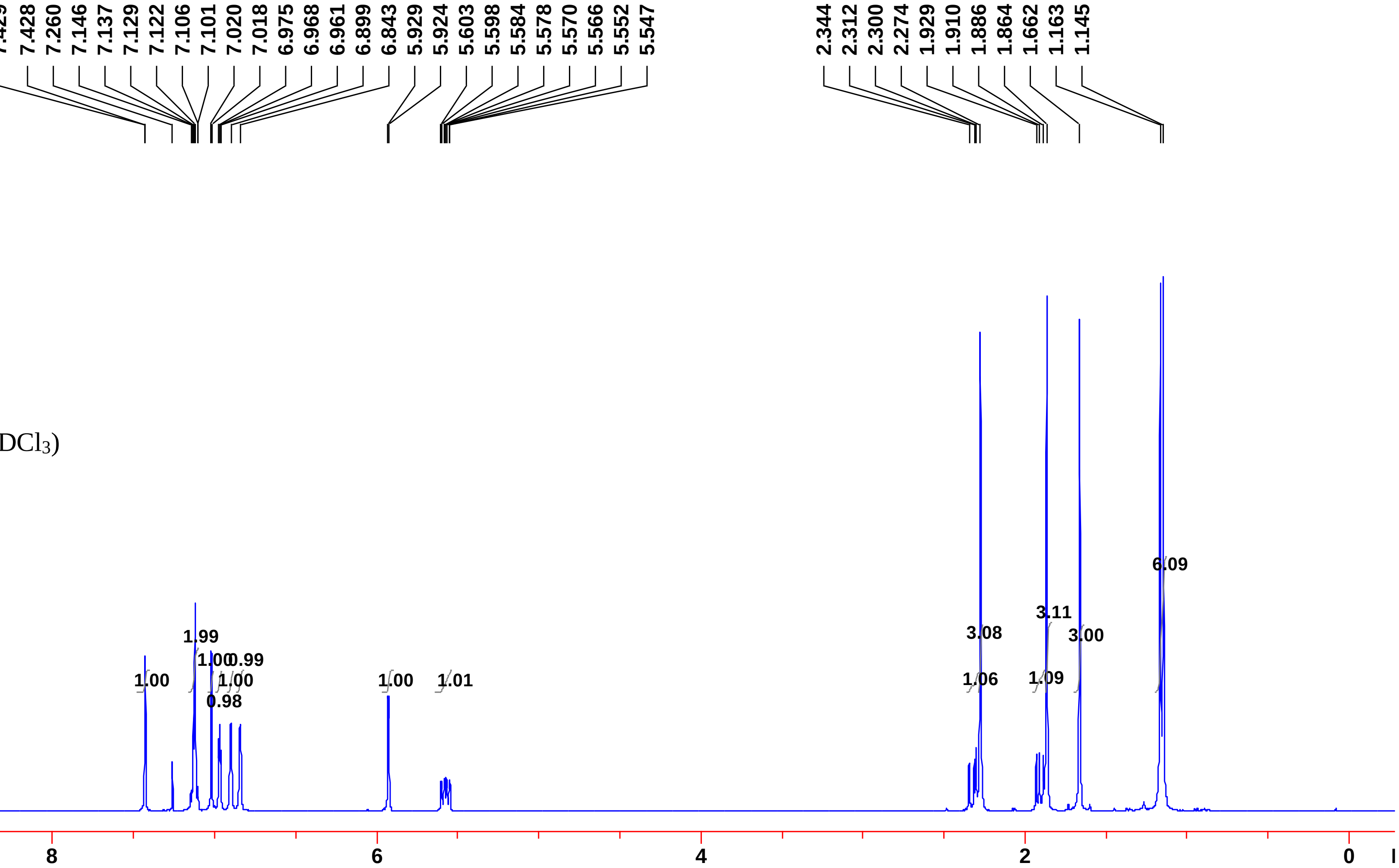
5h

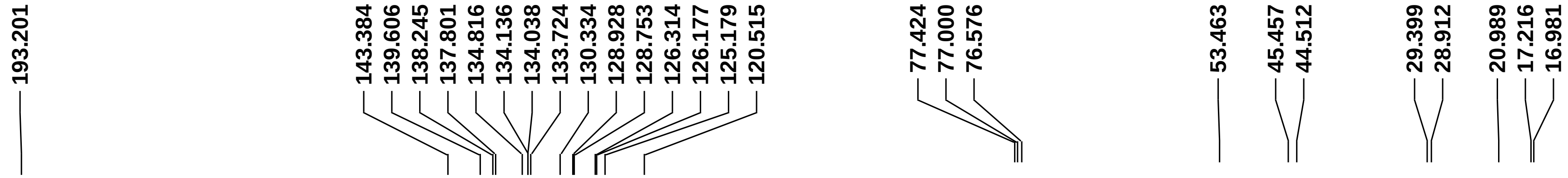
^{13}C NMR (75 MHz, $CDCl_3$)

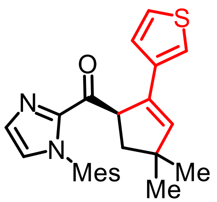


5i

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

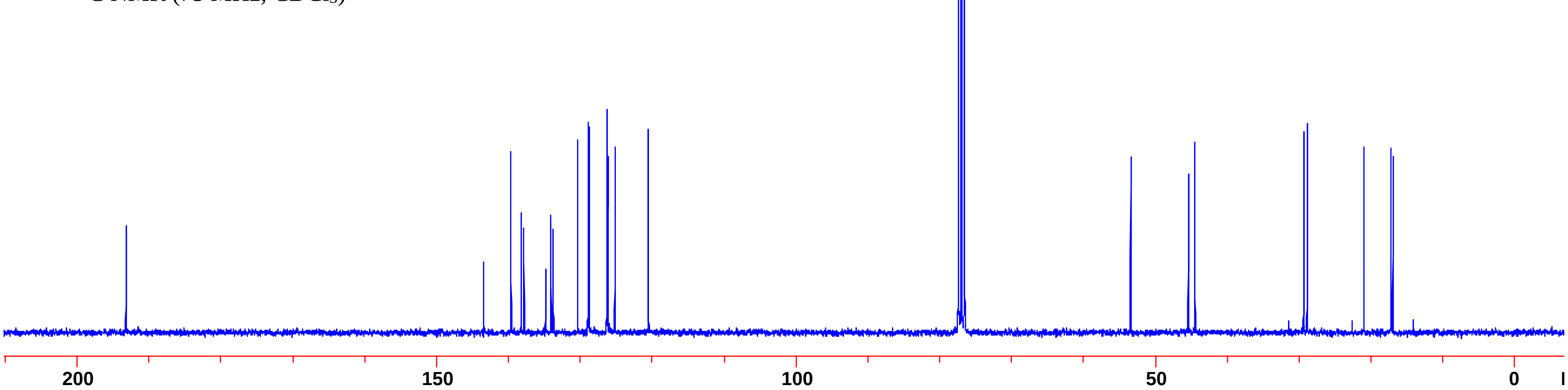


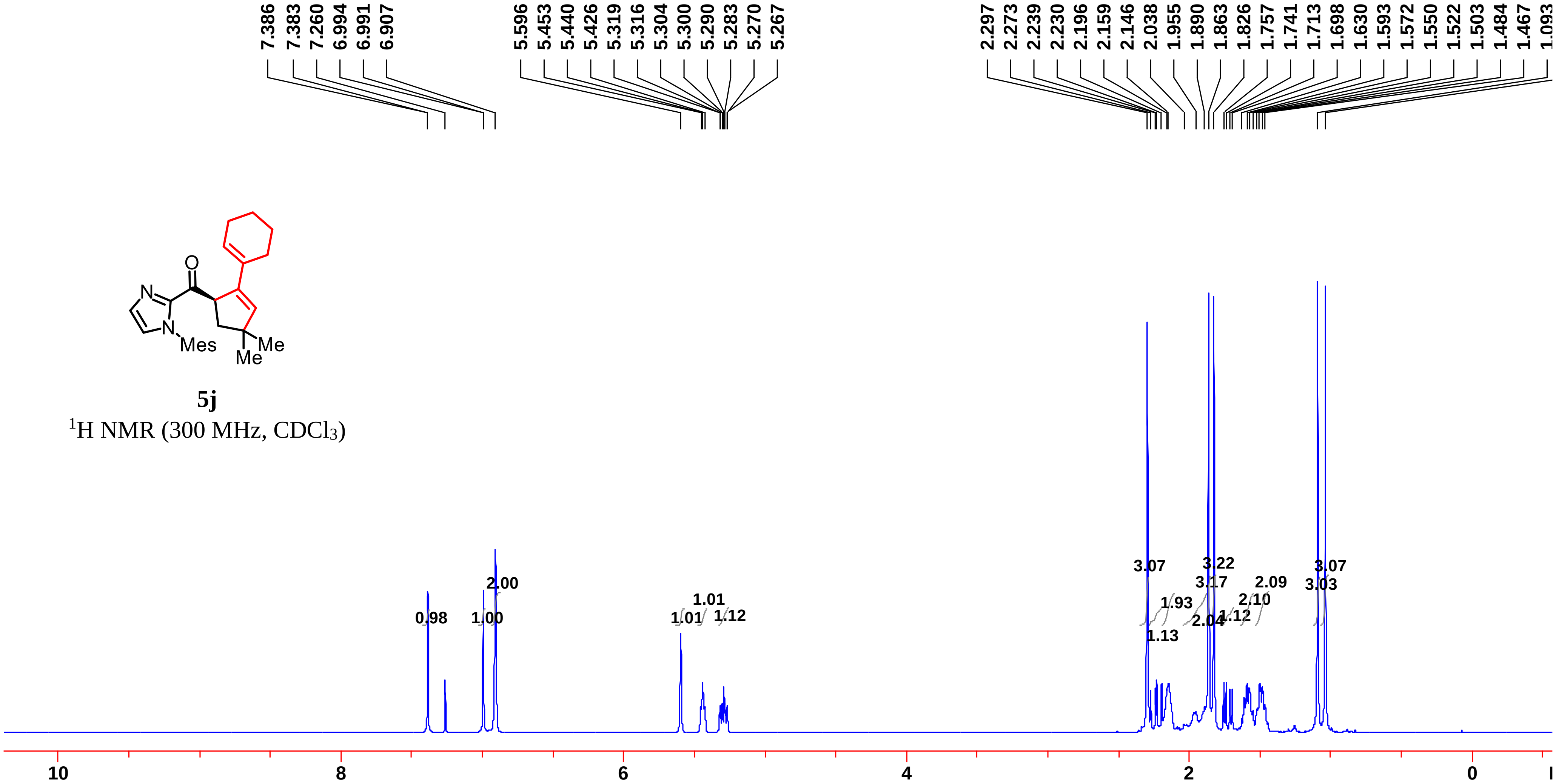




5i

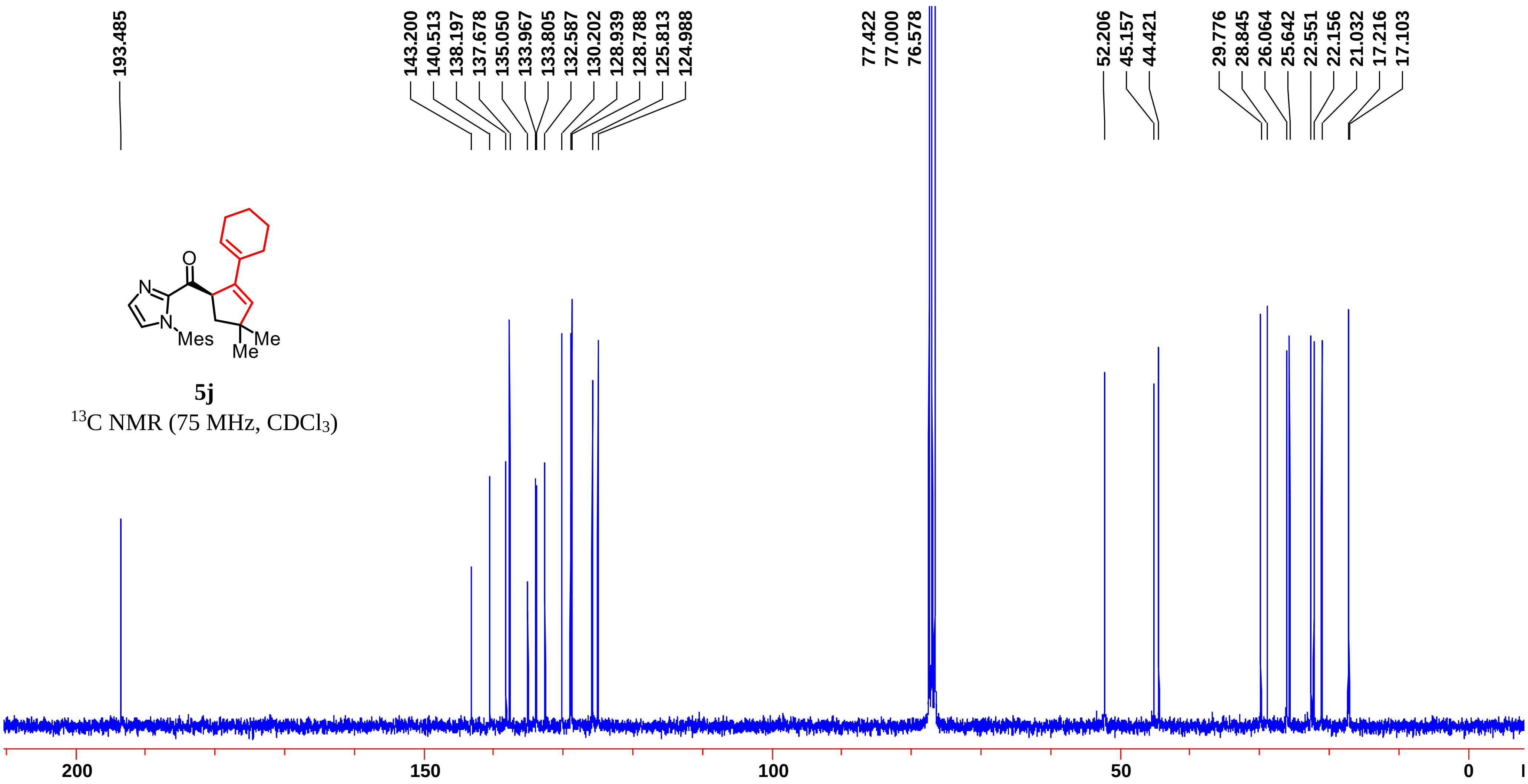
^{13}C NMR (75 MHz, $CDCl_3$)





5j

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



5j

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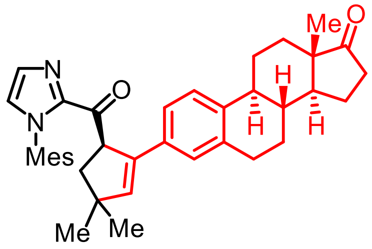
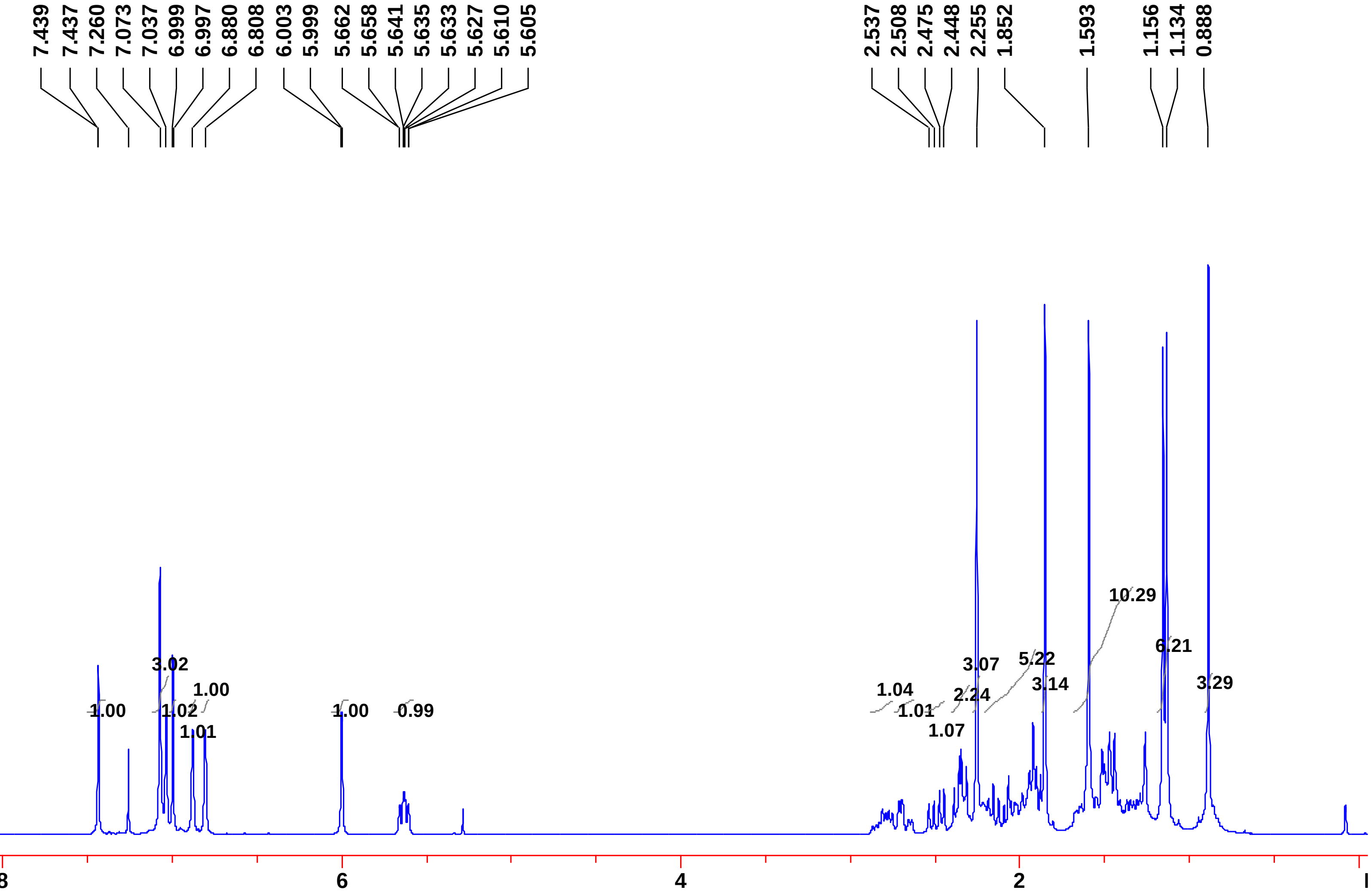
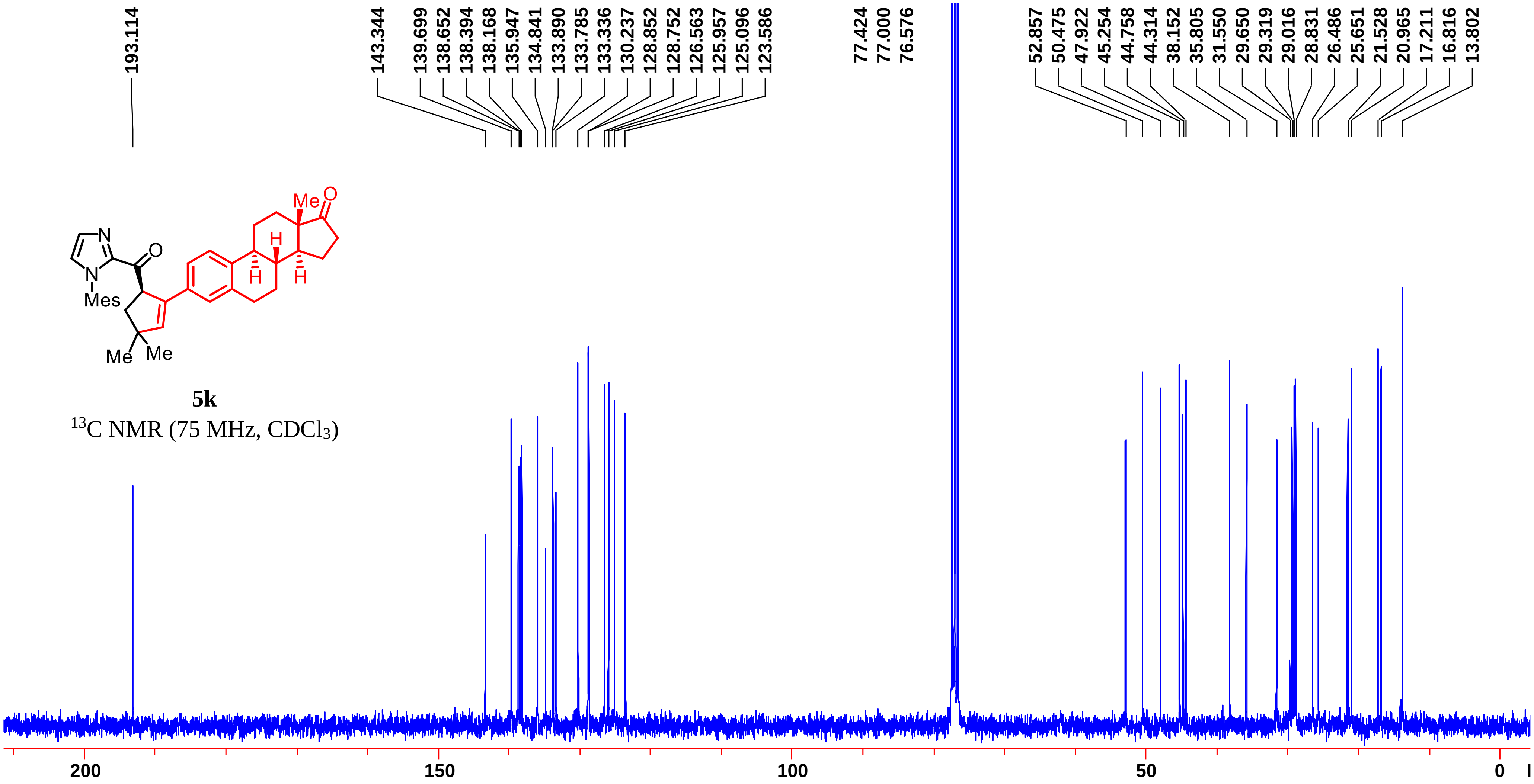
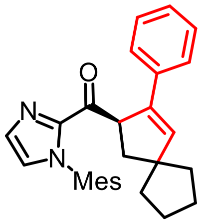


5k

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

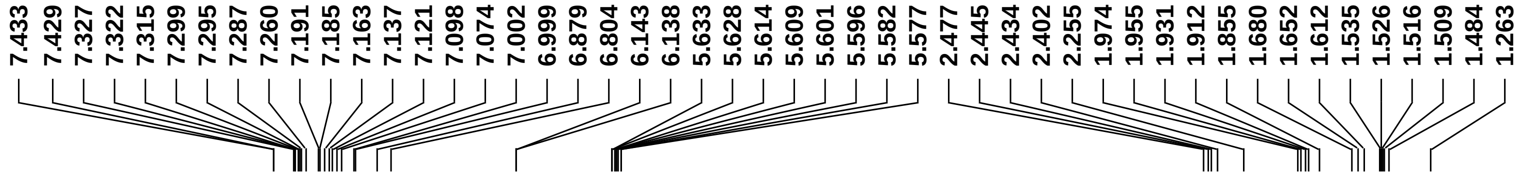


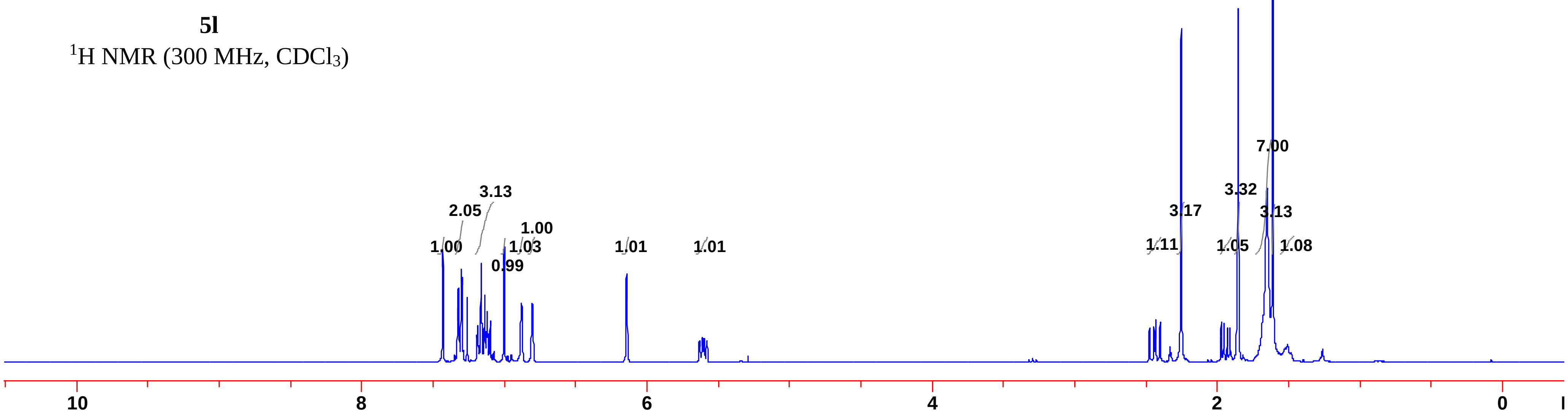

193.114
143.344
139.699
138.652
138.394
138.168
135.947
134.841
133.890
133.785
133.336
130.237
128.852
128.752
126.563
125.957
125.096
123.586
77.424
77.000
76.576
52.857
50.475
47.922
45.254
44.758
44.314
38.152
35.805
31.550
29.650
29.319
29.016
28.831
26.486
25.651
21.528
20.965
17.211
16.816
13.802
N
O
N
Mes
Me
Me
Me
O
H
H
H
5k
13C NMR (75 MHz, CDCl3)
200
150
100
50
0

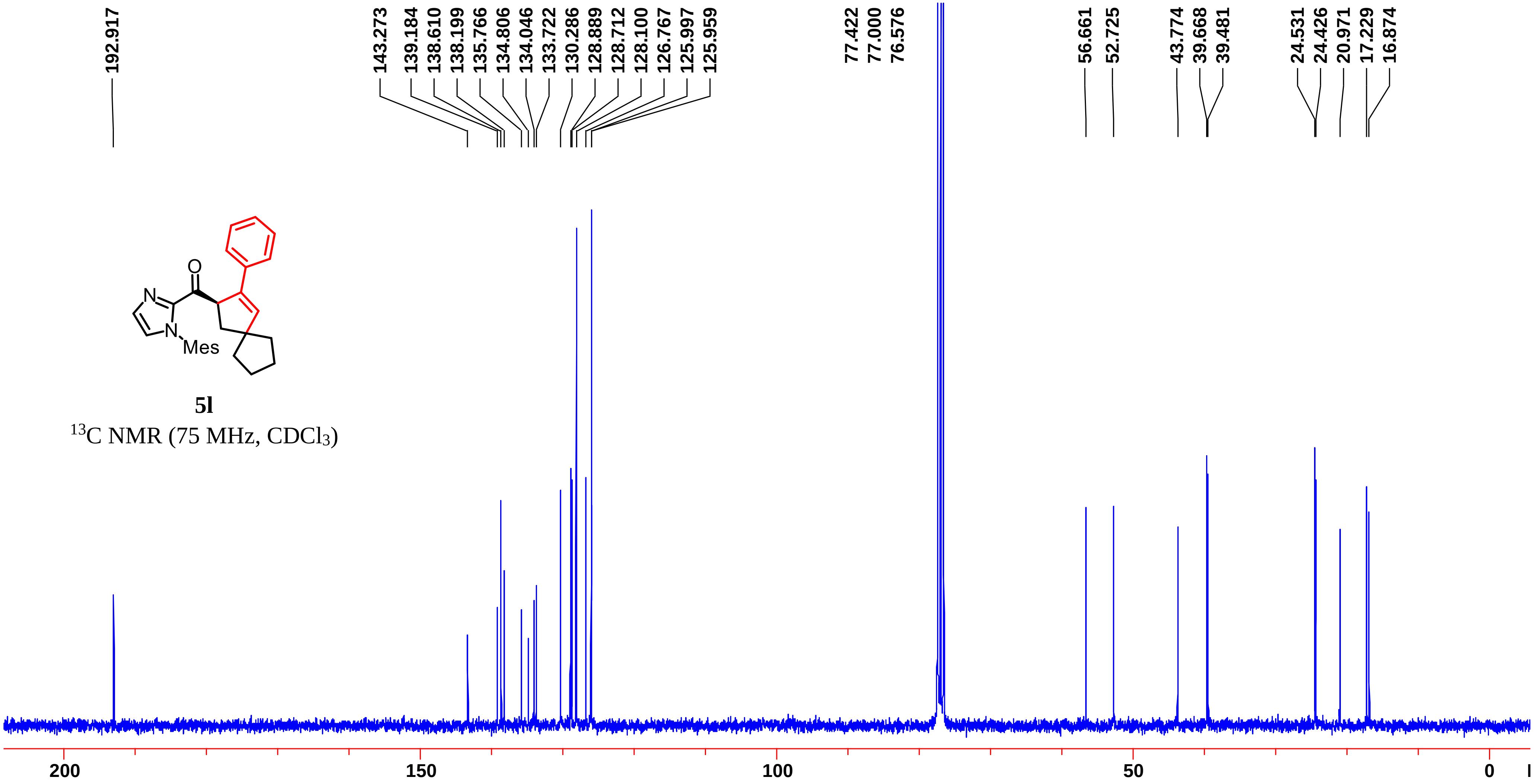


5l

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

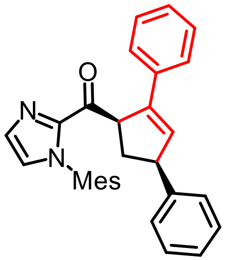






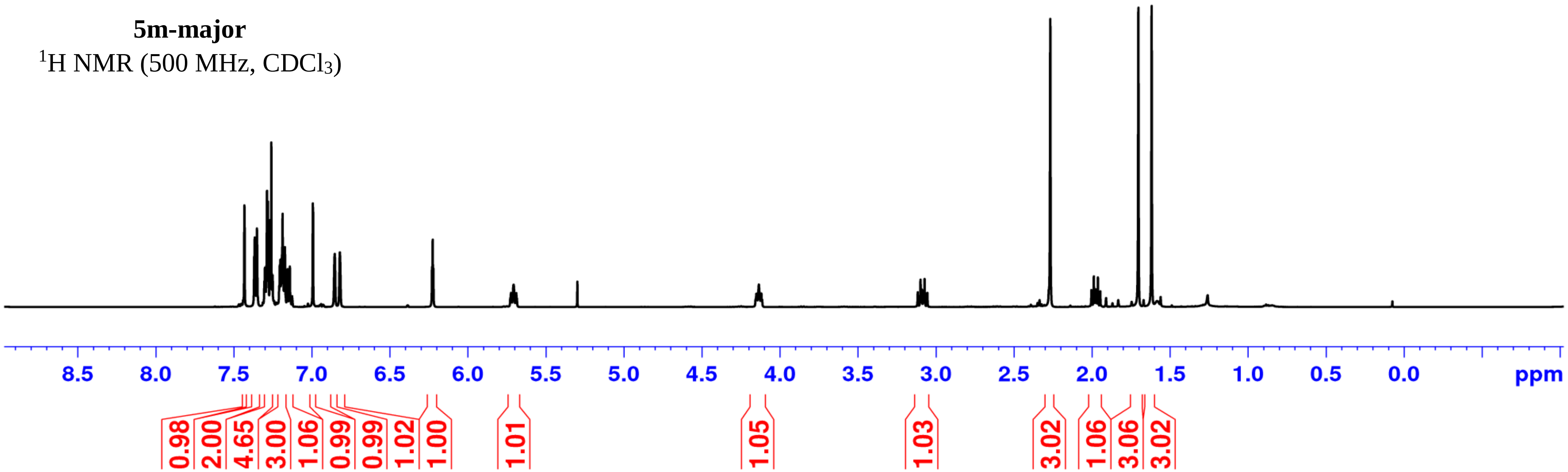
5l

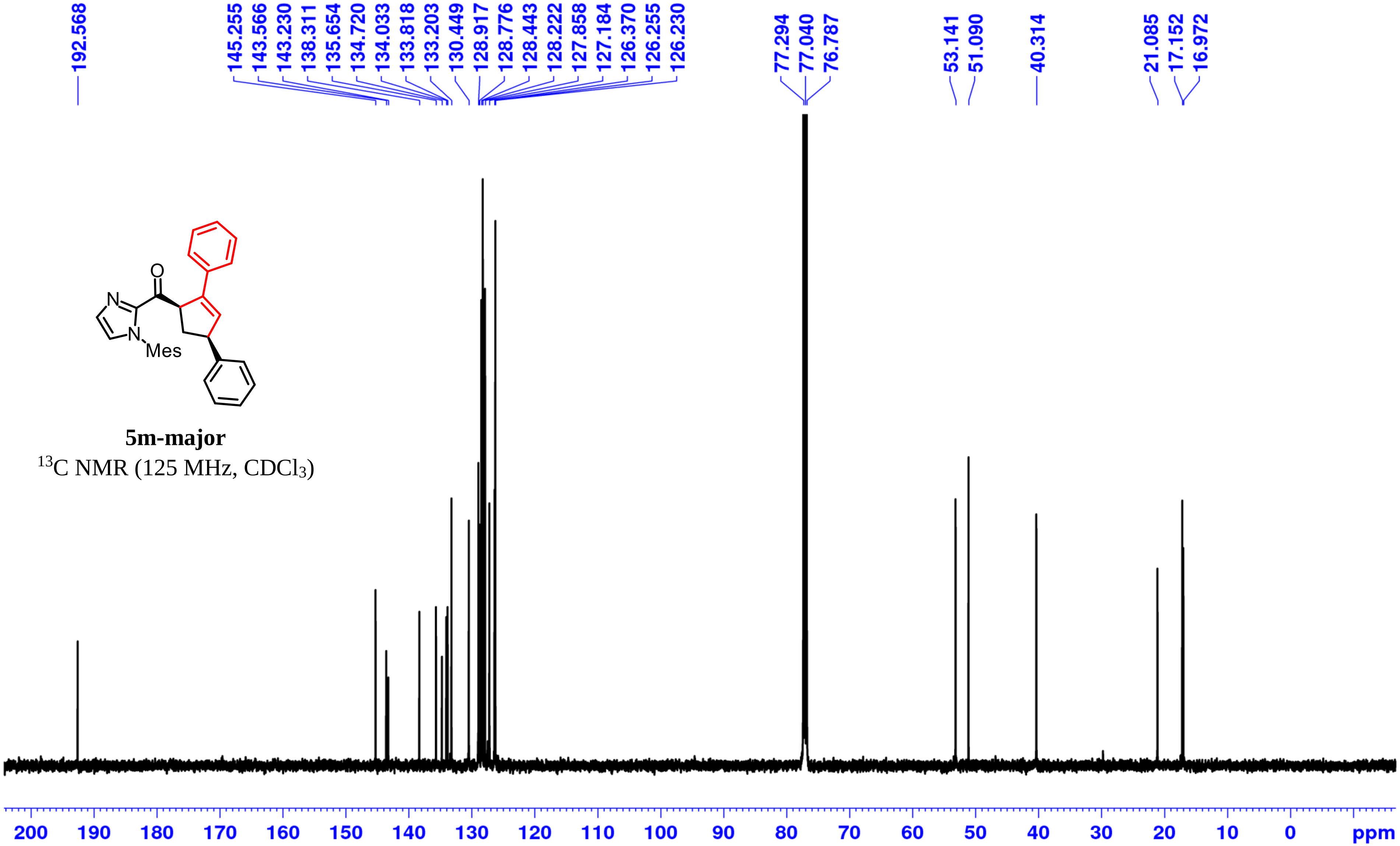
^{13}C NMR (75 MHz, $CDCl_3$)



5m-major

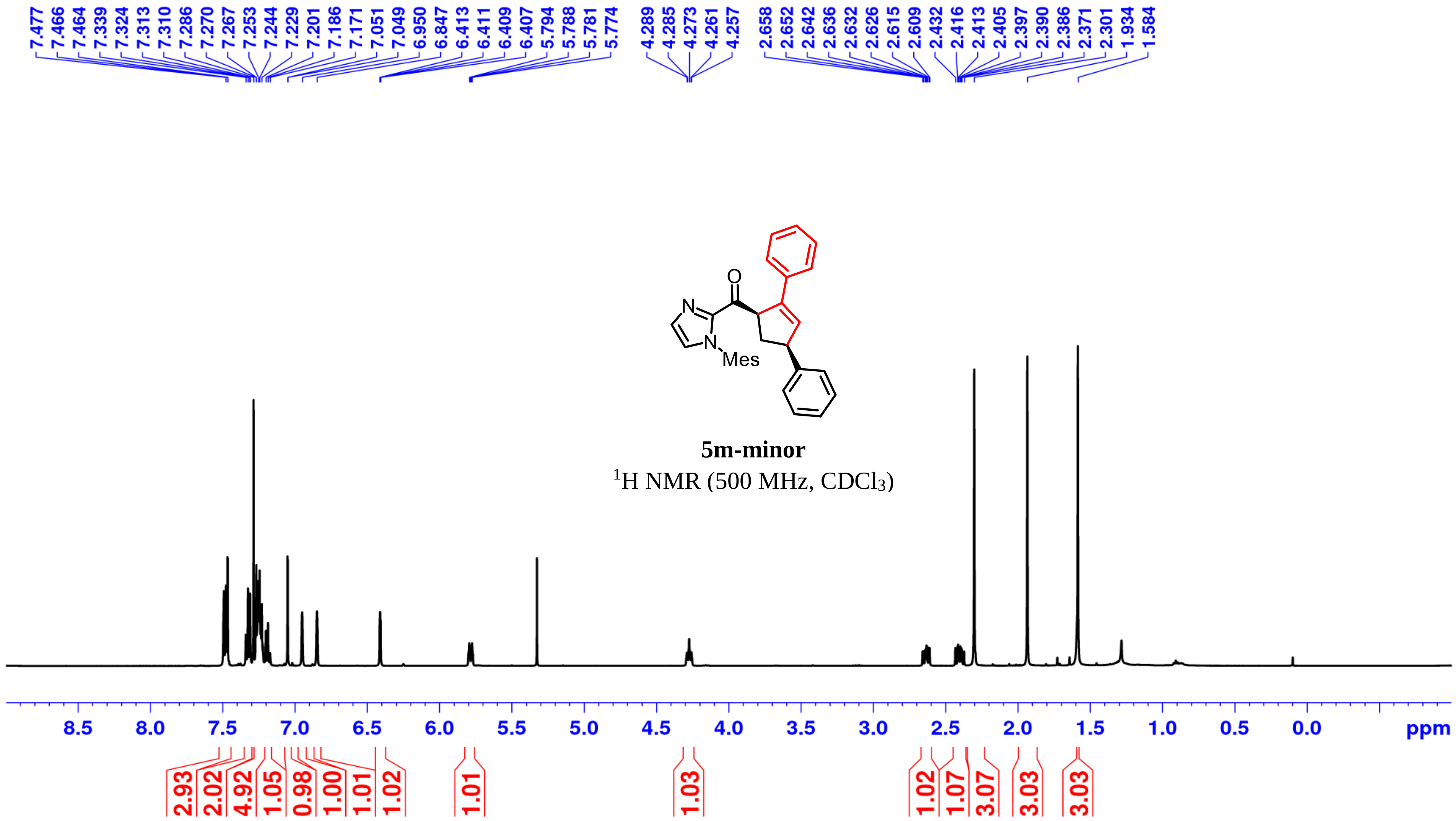
^{1}H NMR (500 MHz, $CDCl_3$)

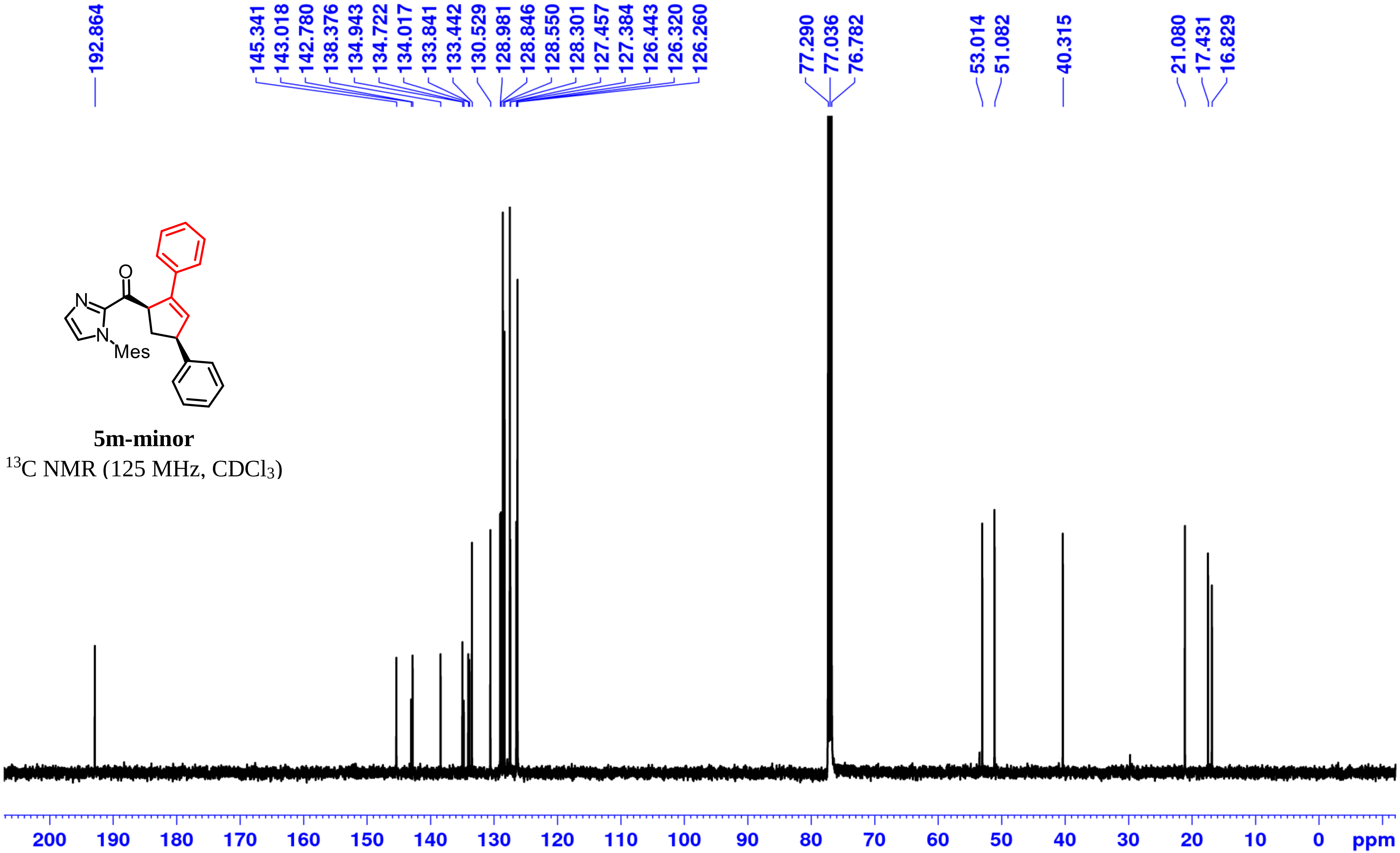




5m-major

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


Mes
5m-minor
^{1}H NMR (500 MHz, CDCl$_3$)
ppm



5m-minor

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

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