nature catalysis

SUPPLEMENTARY INFORMATION

https://doi.org/10.1038/s41929-018-0198-y

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Electricity-driven asymmetric Lewis acid catalysis

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Supplementary Information

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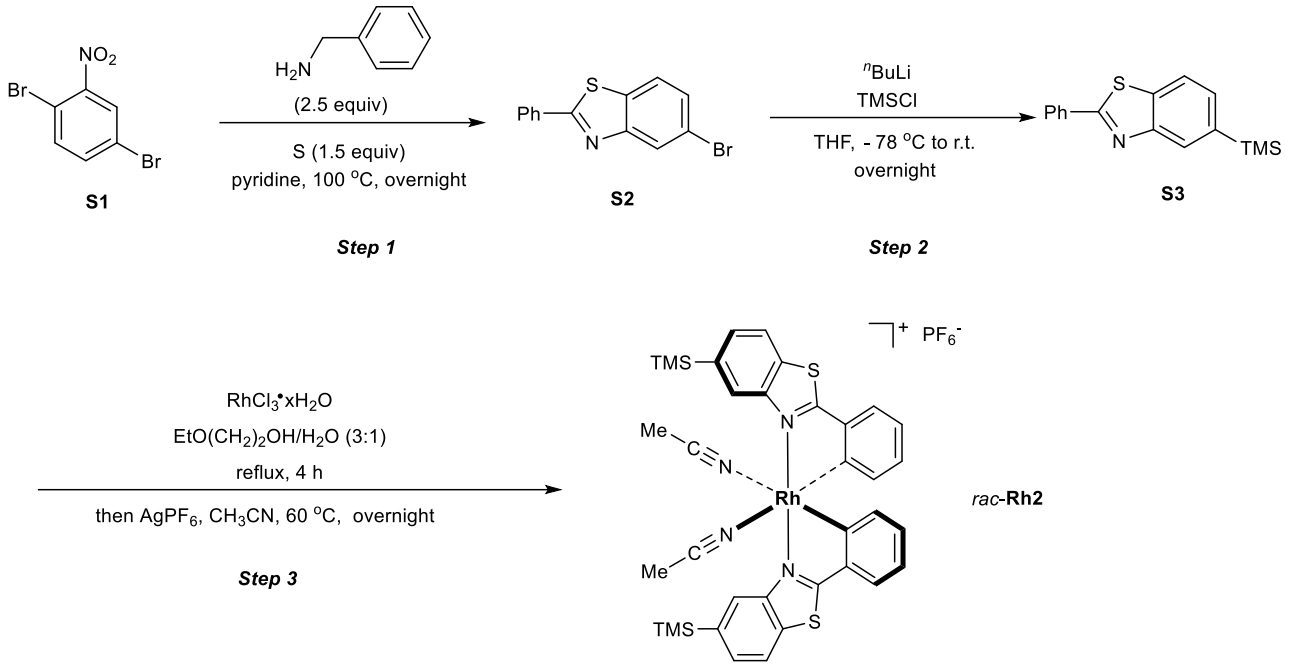
Supplementary Methods

1. General Information

All catalytic reactions were performed in a 5 mL vial using the ElectraSyn 2.0.[1] The typical procedure is descripted in the main text Method section. The chiral-at-metal **Ir**/**Rh** catalysts were synthesized according to our published procedures.[2] Anhydrous THF (dried by Na/benzophenone), MeOH (dried by Mg/I_2), MeCN (dried by CaH_2), and CH_2Cl_2 (dried by CaH_2) were used. 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 $m^2 \times g^{-1}$, 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 250 (250 MHz), Bruker Avance 300 (300 MHz) or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR yields were determined using 1,3,5-trimethoxybenzene as internal standard. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$), 5.32 ppm (CD_2Cl_2); ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$), 53.8 ppm (CD_2Cl_2); ^{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. CD spectra were recorded on a JASCO J-810 CD spectropolarimeter (600-200 nm, 1 nm bandwidth, 50 nm/min scanning speed, accumulation of 3 scans). 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. Chiral HPLC chromatography was performed with an Agilent 1200 or Agilent 1260 HPLC system with a Daicel Chiralpak OD-H, IG, IC, or AS-H column (250 × 4.6 mm) using *n*-hexane/isopropanol as a mobile phase. 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 Ag 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 ^{o}C).

2. Synthesis of Enantiopure Δ-Rh2 and Λ-Rh2

2.1 Synthesis of racemic Rh2



Step 1. To a 50-mL round-bottom flask with a stirring bar, 1,4-dibromo-2-nitrobenzene **S1** (5.65 g, 20.0 mmol), sulfur (0.96 g, 30.0 mmol) and benzyl amine (9.15 g, 50.0 mmol) were added. Then, pyridine (20 mL) was added slowly via a syringe. The mixture was heated at 100 °C under N_2 atmosphere. After 20 h (as indicated by TLC), the mixture was quenched with aqueous NH_4Cl solution and extracted with EtOAc for three time. All the organic layer was collected, evaporated to dryness and purified by column chromatography on silica gel (EtOAc/*n*-Pentane = 20:1) to give 5-bromo-2-phenylbenzo[*d*]thiazole **S2** (4.90 g, 17.4 mmol, 87% yield) as a dark yellow solid. All characteristic date of **S2** are in consistent with the literature report.[3]

Step 2. To a solution of **S2** (4.90 mg, 17.4 mmol) in anhydrous THF (30 mL), ^{n}BuLi (7.66 mL, 2.5 M in *n*-hexane, 1.1 equiv) was added dropwise at –78 °C under nitrogen atmosphere. The mixture was stirred at –78 °C for 1 hour, and then at room temperature for another 1 hour. After that the mixture was cooled down to –78 °C again and chlorotrimethylsilane (2.63 ml, 20.8 mmol) was added dropwise. The mixture was allowed to slowly warm to room temperature. After 20 h (as monitored by TLC), the mixture was quenched with aqueous NH_4Cl solution and extracted with EtOAc for three time. All the organic layer was collected, evaporated to dryness and purified by column chromatography on silica gel (EtOAc/*n*-Pentane = 20:1) to give 2-phenyl-5-(trimethylsilyl)

benzo[*d*]thiazole **S3** (4.08 g, 14.4 mmol, 83% yield) as a yellow solid.

The characteristic data of **S3** are shown below:

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27 (s, 1H), 8.14-8.07 (m, 2H), 7.91 (d, J = 7.8 Hz, 1H), 7.55-7.47 (m, 4H), 0.35 (s, 9H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.8, 153.8, 138.7, 135.6, 133.6, 131.0, 129.8, 129.0, 128.2, 127.6, 121.1, –1.0.

IR (film): ν (cm^{-1}) 2955, 1507, 1475, 1441, 1397, 1303, 1248, 1092, 1061, 965, 909, 831, 753, 687, 626.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{18}NSSi$ $[M+H]^+$: 284.0924, found: 284.0920.

Step 3. According to our previous procedure,[2] **S3** (2.54 g, 8.95 mmol) and $RhCl_3$•xH_2O (1.09 g, 4.26 mmol) in 2-ethoxyethanol and water (v/v 3:1, 89 mL) was heated at 120 °C for 4 h under an atmosphere of nitrogen. Afterwards, the solvent was removed on a rotary evaporator using a water bath set at 60 °C and a vacuum pressure gradient of 50–5 mbar. After removing most of the solvent, keep the flask on the rotary evaporator under vacuum for another 30 min and then dry the mixture using an oil vacuum pump to get rid of the residual water thoroughly. To the obtained mixture, CH_3CN (90 mL) and $AgPF_6$ (1.08 g, 4.26 mmol) were added. Then the reaction mixture was stirred at 60 °C overnight. After cooled to room temperature, the mixture was filtered. The filtrate was collected, evaporated to dryness and purified by column chromatograph on silica gel (100% CH_2Cl_2 to CH_2Cl_2/CH_3CN = 20:1) to give *rac*-**Rh2** (1.24 g, 1.39 mmol, 33% yield for two steps) as a pale yellow solid.

Characteristic data of **Rh2** are shown below:

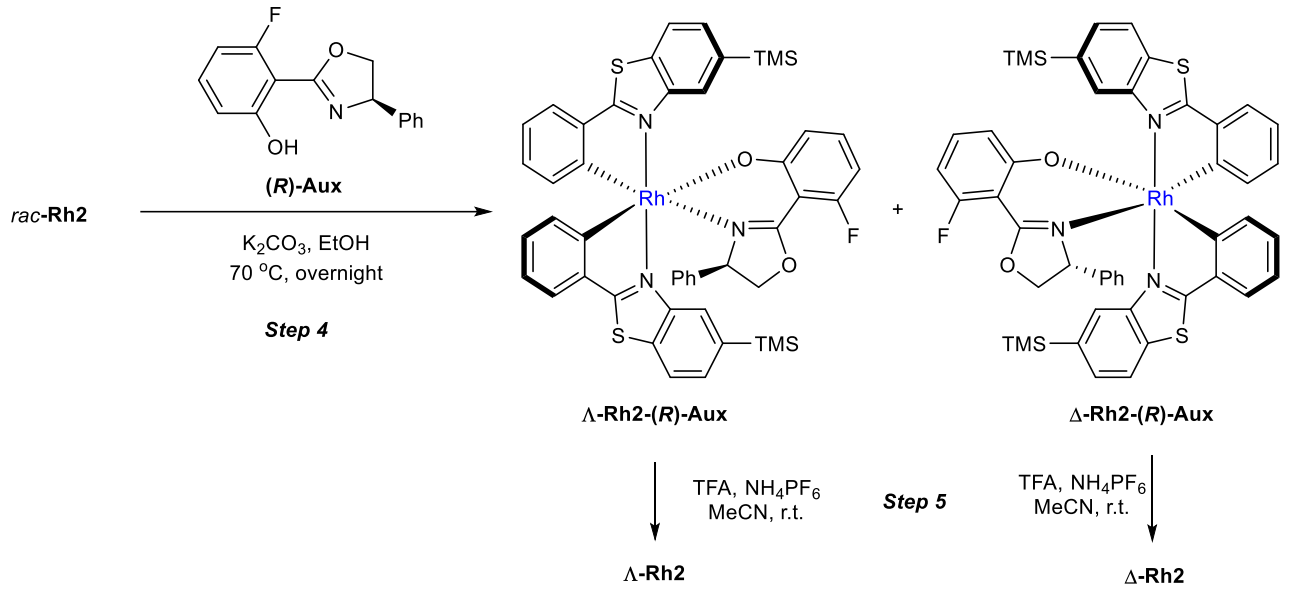
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.58 (s, 2H), 8.11 (d, J = 7.8 Hz, 2H), 7.77 (d, J = 7.8 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.04 (t, J = 7.4 Hz, 2H), 6.84 (t, J = 7.2 Hz, 2H), 6.20 (d, J = 7.5 Hz, 2H), 2.17 (s, 6H), 0.39 (s, 18H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 176.52, 176.48, 160.4, 149.4, 141.9, 140.2, 133.4, 132.7, 131.6, 131.4, 126.4, 125.1, 124.6, 123.0, 3.7, –0.9.

IR (film): ν (cm^{-1}) 2954, 2283, 1583, 1480, 1443, 1397, 1287, 1246, 1164, 1096, 1027, 995, 922, 833, 753, 725, 634, 583, 555.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{32}N_2RhS_2Si_2$ $[M–2(MeCN)–(PF_6^-)]^+$: 667.0595, found: 667.0578.

2.2 Resolution and synthesis of enantiopure catalyst



Step 4. The mixture of racemic rhodium catalyst *rac*-**Rh2** (895 mg, 1.00 mmol), K_2CO_3 (152 mg, 1.10 mmol), and (*R*)-3-fluoro-2-(4-phenyl-4,5-dihydrooxazol-2-yl)phenol (**(*R*)-Aux**, 309 mg, 1.20 mmol) was added absolute ethanol (20 mL) and then heated at 70 °C overnight. Afterwards, the reaction mixture was cooled to room temperature and concentrated to dryness. The residue was filtered by a thin pad of silica gel, washed with CH_2Cl_2, and the filtrate was evaporated to give the mixture of two diastereoisomers. The mixture was subjected to the flash chromatography on silica gel washed by *n*-hexane/CH_2Cl_2/EtOAc (100:10:1 to 20:2:1) to give the Δ-**Rh2-(*R*)-Aux** (278 mg, 0.30 mmol, 30% yield) as a yellow solid. The other rhodium auxiliary complex Λ-**Rh2-(*R*)-Aux** (240 mg, 0.26 mmol, 26% yield) was obtained as a yellow solid from the same silica gel chromatography (*n*-hexane/CH_2Cl_2/EtOAc = 20:2:1 to 10:2:1).

Δ-Rh2-(*R*)-Aux:

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.92 (s, 1H), 8.08 (s, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.61 (dd, J_1= 7.6 Hz, J_2= 1.0 Hz, 1H), 7.58 (dd, J_1= 8.0 Hz, J_2= 1.0 Hz, 1H), 7.50 (dd, J_1= 8.0 Hz, J_2= 1.1 Hz, 1H), 7.43 (dd, J_1= 7.6 Hz, J_2= 1.0 Hz, 1H), 7.41-7.30 (m, 1H), 6.98 (td, J_1= 7.3 Hz, J_2= 0.9 Hz, 1H), 6.94 (td, J_1= 7.4 Hz, J_2= 1.0 Hz, 1H), 6.86-6.70 (m, 5H), 6.65-6.55 (m, 1H), 6.35 (d, J = 8.7 Hz, 1H), 6.31 (d, J =7.4 Hz, 2H), 5.93 (d, J = 7.9 Hz, 1H), 5.77 (ddd, J_1= 12.6 Hz, J_2= 7.9 Hz, J_3 = 1.1 Hz, 1H), 4.88-4.79 (m, 2H), 4.03 (dd, J_1 = 7.2 Hz, J_2 = 3.3 Hz, 1H), 0.39 (s, 9H), 0.20 (s, 9H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.84, 176.82, 175.2, 175.1, 175.0, 174.9, 170.9, 170.7, 168.4, 168.1, 166.0, 165.9, 164.6, 162.5, 150.64, 150.59, 141.5, 141.4, 140.9, 140.2, 140.1, 135.4, 133.2, 132.9, 132.8, 132.4, 130.3, 130.2, 129.9, 129.7, 129.2, 127.9, 127.5, 126.1, 124.4, 123.1, 122.5, 122.4, 121.5, 120.40, 120.38, 101.31, 101.26, 98.7, 98.5, 75.6, 69.4, –0.8, –1.0. (^{13}C-^{19}F coupling can not be identified.)

IR (film): ν (cm^{-1}) 3054, 2954, 2922, 1647, 1616, 1582, 1527, 1468, 1437, 1371, 1308, 1278, 1241, 1211, 1157, 1122, 1093, 1058, 1030, 990, 948, 918, 836, 798, 752, 727, 695, 626.

HRMS (ESI, *m*/*z*) calcd for $C_{47}H_{43}FN_3O_2RhS_2Si_2Na$ $[M+Na]^+$: 946.1267, found: 946.1272.

CD (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 412 (+21), 365 (–31), 343 (–34), 299 (+42), 273 (–7), 264 (–4), 245 (–34), 233 (+7), 216 (–47).

Λ-Rh2-(*R*)-Aux：

^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.24 (s, 1H), 8.66 (s, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.65 (d, J = 7.6 Hz, 1H), 7.59 (d, J = 8.1 Hz, 1H), 7.18 (d, J = 7.6 Hz, 1H), 6.98 (t, J = 7.4 Hz, 1H), 6.96-6.86 (m, 5H), 6.83-6.75 (m, 2H), 6.57 (t, J = 7.4 Hz, 1H), 6.41 (t, J = 7.6 Hz, 1H), 6.35-6.29 (m, 2H), 6.17 (d, J = 7.8 Hz, 1H), 5.84 (dd, J_1 = 11.5 Hz, J_2= 8.1 Hz, 1H), 4.42 (t, J = 8.9 Hz, 1H), 4.11 (dd, J_1 = 12.6 Hz, J_2 = 9.8 Hz, 1H), 3.97 (dd, J_1 = 12.7 Hz, J_2 = 8.7 Hz, 1H), 0.41 (s, 9H), 0.23 (s, 9H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 176.13, 176.11, 176.08, 176.05, 174.89, 174.87, 169.3, 169.1, 169.0, 168.9, 167.0, 164.1, 162.0, 150.6, 150.4, 141.5, 140.9, 140.4, 139.9, 138.7, 135.1, 133.4, 132.9, 132.8, 132.4, 132.3, 130.7, 130.5, 130.2, 129.6, 129.2, 128.2, 127.7, 127.3, 127.1, 126.9, 126.1, 125.9, 125.6, 123.1, 122.2, 122.12, 122.06, 119.19, 119.17, 104.0, 103.9, 98.7, 98.5, 75.0, 70.5, –0.82, –0.83, –1.2 (^{13}C-^{19}F coupling can not be identified.)

IR (film): ν (cm^{-1}) 3050, 2953, 1708, 1619, 1581, 1531, 1444, 1373, 1306, 1278, 1249, 1223, 1156, 1123, 1093, 1028, 987, 954, 917, 838, 796, 752, 726, 694, 626, 582, 526.

HRMS (ESI, *m*/*z*) calcd for $C_{47}H_{43}FN_3O_2RhS_2Si_2Na$ $[M+Na]^+$: 946.1267, found: 946.1272.

CD (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 421 (–24), 373 (+8), 361 (+6), 335 (+22), 299 (–40), 276 (+15), 266 (+10), 253 (+24), 235 (–16), 207 (+49).

Step 5. To a suspension of Δ-**Rh2-(*R*)-Aux** (278 mg, 0.30 mmol) in CH_3CN (5 mL) was added TFA (0.138 mL, 1.80 mmol) in one portion, then stirred at room temperature for 1 h in the dark. The reaction mixture was evaporated to dryness, dissolved in CH_2Cl_2, and subjected to the column chromatography on silica gel. Elute the column with 200 mL of CH_2Cl_2/CH_3CN/TFA (100:1:0.1) firstly. And then, with CH_2Cl_2/CH_3CN (20:1) until the purple band (auxiliary) was gone completely. Afterward, NH_4PF_6 (489 mg, 3.00 mmol) was added to the top of the sea sand and use CH_2Cl_2/CH_3CN (50:50) to elute the residual pale-yellow band on the column. Remove the solvent by the rotary evaporator and filtrate the excess salts to give the enantiopure catalyst Δ-**Rh2** (230 mg, 86% yield) as a yellow solid.

Accordingly, starting from the corresponding Λ-**Rh2-(*R*)-Aux**, Λ-**Rh2** could be obtained by the same procedure in 92% yield.

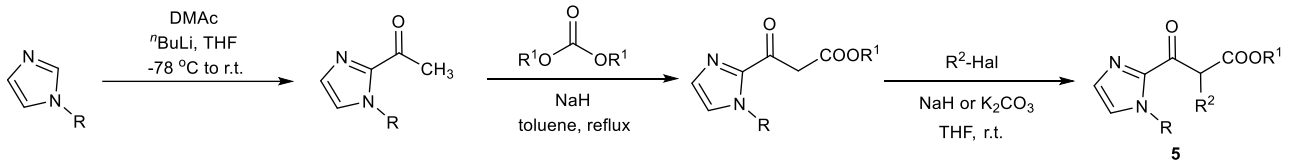
CD of Δ-**Rh2** (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 407 (+34), 366 (–57), 300 (+77), 266 (–23), 259 (–25), 244 (–47), 227 (+14), 214 (–89).

CD of Λ-**Rh2** (CH_2Cl_2): λ, nm (Δε, $M^{-1}cm^{-1}$) 407 (–35), 366 (+58), 300 (–77), 266 (+25), 259 (+26), 244 (+48), 227 (–14), 214 (+91).

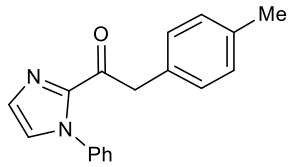
For CD spectra, see Supplementary Figures 39-40.

3. Synthesis of Substrates

Acyl imidazoles **1** were prepared via the well-established Weinreb ketone synthesis.[4] Silyl enol ethers **2** used in this paper are all reported, which were prepared according to well-developed methods[5] and subjected to the reaction after simple extraction without further distillation. Racemic imidazoles **5** were synthesized according to the following route.



The data of new starting materials are shown below:



1-(1-Phenyl-1*H*-imidazol-2-yl)-2-(*p*-tolyl)ethan-1-one (1c)

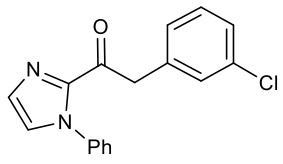
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45-7.39 (m, 3H), 7.34-7.32 (m, 1H), 7.27-7.18 (m, 5H), 7.15-7.08 (m, 2H), 4.42 (s, 2H), 2.32 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.7, 142.8, 138.3, 136.3, 131.2, 129.8, 129.7, 129.1, 128.9, 128.6, 127.3, 125.8, 45.2, 21.0.

IR (film): ν (cm^{-1}) 3055, 2899, 1686, 1593, 1490, 1447, 1398, 1306, 1209, 1139, 1092, 1028, 960, 910, 852, 815, 763, 729, 689, 565, 504, 474, 404.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{16}N_2ONa$ $[M+Na]^+$: 299.1155, found: 299.1153.



2-(3-Chlorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (1e)

A white solid.

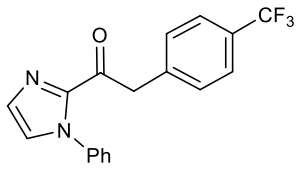
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47-7.40 (m, 3H), 7.34-7.31 (m, 2H), 7.28-7.17 (m, 6H), 4.44 (s,

2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.7, 142.6, 138.2, 136.3, 134.2, 130.1, 129.8, 129.6, 129.0, 128.8, 128.2, 127.7, 127.0, 125.9, 45.1.

IR (film): ν (cm^{-1}) 3115, 1679, 1592, 1489, 1449, 1392, 1344, 1309, 1213, 1172, 1143, 1085, 1028, 960, 909, 764, 687, 591, 535, 502, 444, 411.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{13}ClN_2ONa$ $[M+Na]^+$: 319.0609, found: 319.0606.



1-(1-Phenyl-1*H*-imidazol-2-yl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one (1h)

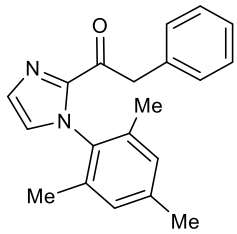
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.52 (m, 2H), 7.48-7.41 (m, 5H), 7.36-7.33 (m, 1H), 7.29-7.21 (m, 3H), 4.53 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.5, 142.5, 138.5, 138.1, 130.3, 130.0, 129.1 (q, J = 31.8 Hz), 129.0, 128.8, 127.7, 125.8, 125.3 (q, J = 4.0 Hz), 124.2 (q, J = 269.7 Hz), 45.3.

IR (film): ν (cm^{-1}) 3062, 2921, 1690, 1600, 1496, 1449, 1400, 1320, 1152, 1101, 1063, 1018, 959, 913, 866, 819, 766, 692, 638, 591, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{13}F_3N_2ONa$ $[M+Na]^+$: 353.0872, found: 353.0869.



1-(1-Mesityl-1*H*-imidazol-2-yl)-2-phenylethan-1-one (1j)

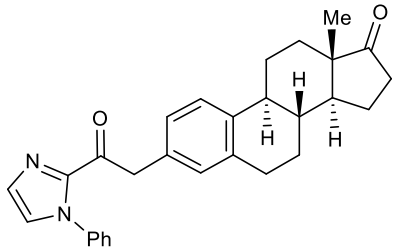
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.38 (m, 1H), 7.31-7.15 (m, 5H), 7.01-6.98 (m, 1H), 6.90 (br s, 2H), 4.42 (s, 2H), 2.29 (s, 3H), 1.78 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.4, 143.0, 138.4, 134.6, 134.4, 134.0, 130.3, 129.8, 128.9, 128.4, 126.7, 126.0, 45.4, 21.0, 17.1.

IR (film): ν (cm^{-1}) 3133, 2915, 1667, 1601, 1488, 1449, 1396, 1324, 1284, 1184, 1141, 1095, 1045, 976, 936, 911, 853, 801, 768, 733, 694, 625, 576, 518, 462, 438, 402.

HRMS (ESI, *m*/*z*) calcd for $C_{20}H_{20}N_2ONa$ $[M+Na]^+$: 327.1468, found: 327.1466.



(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(2-oxo-2-(1-phenyl-1*H*-imidazol-2-yl)ethyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (1o)

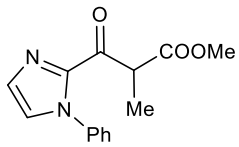
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43-7.38 (m, 3H), 7.33-7.30 (m, 1H), 7.27-7.20 (m, 3H), 7.20-7.18 (m, 1H), 7.09 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H), 7.03 (br s, 1H), 4.40 (s, 2H), 2.92-2.84 (m, 2H), 2.49 (dd, J_1 = 17.7 Hz, J_2 = 7.8 Hz, 1H), 2.45-1.90 (m, 6H), 1.70-1.30 (m, 6H), 0.89 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.7, 142.8, 138.32, 138.25, 136.5, 131.7, 130.5, 129.7, 128.9, 128.7, 127.41, 127.35, 125.9, 125.4, 50.5, 48.0, 45.0, 44.3, 38.1, 35.8, 31.6, 29.3, 26.5, 25.6, 21.6, 13.8. (^{13}C signal of carbonyl in estrone motif (expected at ~ 220 ppm) is beyond the range of the measurement)

IR (film): ν (cm^{-1}) 2924, 2860, 1734, 1684, 1597, 1496, 1447, 1398, 1340, 1307, 1257, 1147, 1080, 1047, 1010, 969, 910, 763, 728, 692, 647, 554, 519, 439.

HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{30}N_2O_2Na$ $[M+Na]^+$: 461.2199, found: 461.2196.



Methyl 2-methyl-3-oxo-3-(1-phenyl-1*H*-imidazol-2-yl)propanoate (5a)

A colorless oil. Racemic.

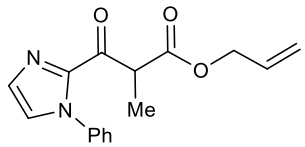
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49-7.42 (m, 3H), 7.33-7.27 (m, 3H), 7.22-7.19 (m, 1H), 4.78 (q, J = 7.5 Hz, 1H), 3.71 (s, 3H), 1.44 (d, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 186.7, 171.7, 142.2, 138.0, 130.0, 129.0, 128.8, 127.4, 125.7, 52.3,

48.3, 13.1.

IR (film): ν (cm^{-1}) 3113, 2992, 2948, 1736, 1687, 1596, 1497, 1447, 1400, 1311, 1203, 1173, 1083, 1028, 973, 940, 909, 858, 762, 691, 551, 515.

HRMS (ESI, *m*/*z*) calcd for $C_{14}H_{14}N_2O_3Na$ $[M+Na]^+$: 281.0897, found: 281.0895.



Allyl 2-methyl-3-oxo-3-(1-phenyl-1*H*-imidazol-2-yl)propanoate (5b)

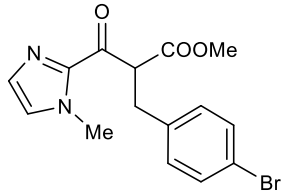
A colorless oil. Racemic.

^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.42 (m, 3H), 7.34-7.27 (m, 3H), 7.22-7.19 (m, 1H), 5.93-5.78 (m, 1H), 5.30-5.15 (m, 2H), 4.80 (q, J = 7.2 Hz, 1H), 4.64-4.57 (m, 2H), 1.45 (d, J = 6.9 Hz, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 186.7, 170.9, 142.3, 138.0, 131.9, 130.0, 129.0, 128.8, 127.3, 125.7, 118.1, 65.6, 48.4, 13.0.

IR (film): ν (cm^{-1}) 3113, 2988, 2940, 1735, 1688, 1650, 1596, 1497, 1449, 1401, 1310, 1214, 1177, 1081, 1024, 1005, 939, 908, 761, 691, 549, 514.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{16}N_2O_3Na$ $[M+Na]^+$: 307.1053, found: 307.1051.



Methyl 2-(4-bromobenzyl)-3-(1-methyl-1*H*-imidazol-2-yl)-3-oxopropanoate (5c)

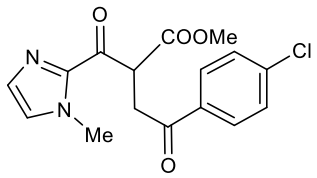
A white solid. Racemic.

^1H NMR (300 MHz, $CDCl_3$) δ 7.38-7.33 (m, 2H), 7.18-7.12 (m, 3H), 7.03 (br s, 1H), 5.08 (t, J = 7.4 Hz, 1H), 3.96 (s, 3H), 3.66 (s, 3H), 3.29 (dd, J_1 = 14.1 Hz, J_2 = 7.5 Hz, 1H), 3.22 (dd, J_1 = 14.1 Hz, J_2 = 7.8 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 186.3, 170.1, 142.3, 137.5, 131.4, 130.8, 129.9, 127.7, 120.4, 55.1, 52.4, 36.1, 33.9.

IR (film): ν (cm^{-1}) 3108, 2951, 1721, 1680, 1581, 1479, 1442, 1401, 1331, 1279, 1234, 1196, 1161, 1099, 1068, 1011, 936, 904, 869, 820, 784, 744, 717, 687, 638, 613, 579, 530.

HRMS (ESI, *m*/*z*) calcd for $C_{15}H_{15}BrN_2O_3Na$ $[M+Na]^+$: 373.0158, found: 373.0156.



Methyl 4-(4-chlorophenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxobutanoate (5d)

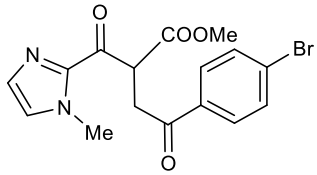
A white solid. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95-7.88 (m, 2H), 7.46-7.40 (m, 2H), 7.23-7.20 (m, 1H), 7.07 (br s, 1H), 5.40 (dd, J_1 = 8.4 Hz, J_2 = 5.7 Hz, 1H), 4.00 (s, 3H), 3.81 (dd, J_1 = 17.7 Hz, J_2 = 8.1 Hz, 1H), 3.73 (s, 3H), 3.63 (dd, J_1 = 17.7 Hz, J_2 = 5.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.4, 186.4, 170.4, 142.3, 139.8, 134.5, 130.0, 129.6, 128.9, 127.5, 52.7, 49.2, 38.0, 36.1.

IR (film): ν (cm^{-1}) 3135, 2958, 1738, 1674, 1587, 1469, 1441, 1406, 1364, 1319, 1268, 1242, 1167, 1087, 991, 950, 908, 823, 788, 689, 648, 607, 529, 490, 458, 403.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{15}ClN_2O_4Na$ $[M+Na]^+$: 357.0613, found: 357.0610.



Methyl 4-(4-bromophenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxobutanoate (5e)

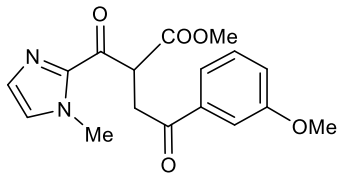
A white solid. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87-7.80 (m, 2H), 7.63-7.56 (m, 2H), 7.21 (br s, 1H), 7.06 (br s, 1H), 5.39 (dd, J_1 = 8.4 Hz, J_2 = 5.7 Hz, 1H), 3.99 (s, 3H), 3.79 (dd, J_1 = 18.3 Hz, J_2 = 8.4 Hz, 1H), 3.72 (s, 3H), 3.63 (dd, J_1 = 17.7 Hz, J_2 = 5.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.6, 186.4, 170.4, 142.3, 134.5, 131.9, 130.0, 129.7, 128.6, 127.5, 52.7, 49.2, 38.0, 36.0.

IR (film): ν (cm^{-1}) 3137, 2956, 1735, 1674, 1580, 1476, 1405, 1363, 1319, 1266, 1167, 1093, 1067, 991, 949, 908, 821, 785, 756, 685, 648, 613, 531, 495, 450, 408.

HRMS (ESI, *m*/*z*) calcd for $C_{16}H_{15}BrN_2O_4Na$ $[M+Na]^+$: 401.0107, found: 401.0105.



Methyl 4-(3-methoxyphenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxobutanoate (5f)

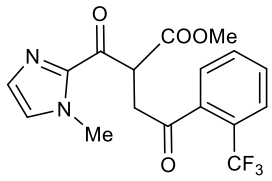
A colorless oil. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz, 1H), 7.51-7.46 (m, 1H), 7.36 (t, J = 9.3 Hz, 1H), 7.21 (br s, 1H), 7.14-7.08 (m, 1H), 7.06 (br s, 1H), 5.41 (dd, J_1 = 8.4 Hz, J_2 = 5.4 Hz, 1H), 4.00 (s, 3H), 3.85 (dd, J_1 = 17.7 Hz, J_2 = 8.7 Hz, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.66 (dd, J_1 = 18.3 Hz, J_2 = 5.7 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 196.4, 186.6, 170.5, 159.8, 142.4, 137.5, 129.9, 129.6, 127.4, 120.9, 120.1, 112.2, 55.4, 52.6, 49.2, 38.2, 36.0.

IR (film): v (cm^{-1}) 3111, 2954, 2839, 1736, 1676, 1589, 1459, 1402, 1359, 1326, 1260, 1158, 1086, 1012, 956, 905, 867, 782, 739, 685, 611, 571, 500.

HRMS (ESI, m/z) calcd for $C_{17}H_{18}N_2O_5Na$ $[M+Na]^+$: 353.1108, found: 353.1106.



Methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-4-(2-(trifluoromethyl)phenyl)butanoate (5g)

A white solid. Racemic.

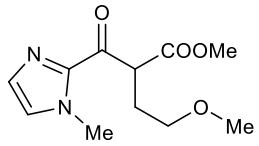
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74-7.54 (m, 4H), 7.22 (br s, 1H), 7.06 (br s, 1H), 5.38 (dd, J_1 = 8.4 Hz, J_2 = 6.3 Hz, 1H), 4.00 (s, 3H), 3.73 (s, 3H), 3.67 (dd, J_1 = 18.6 Hz, J_2 = 8.4 Hz, 1H), 3.49 (dd, J_1 = 18.3 Hz, J_2 = 6.0 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 200.4, 185.9, 170.2, 142.2, 139.3 (q, J = 1.7 Hz), 131.8, 130.3, 130.0, 127.6, 127.5, 127.1 (q, J = 32.3 Hz), 126.6 (q, J = 5.1 Hz), 123.4 (q, J = 272.1 Hz), 52.7, 49.6, 41.8, 36.0.

IR (film): v (cm^{-1}) 3031, 2955, 2917, 1736, 1706, 1674, 1402, 1308, 1279, 1162, 1135, 1064, 1030,

994, 946, 906, 774, 660, 564.

HRMS (ESI, *m*/*z*) calcd for $C_{17}H_{15}F_3N_2O_4Na$ $[M+Na]^+$: 391.0876, found: 391.0872.



Methyl 4-methoxy-2-(1-methyl-1*H*-imidazole-2-carbonyl)butanoate (5h)

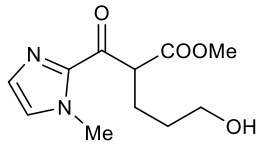
A colorless oil. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.16 (m, 1H), 7.04 (br s, 1H), 4.87 (t, J = 7.1 Hz, 1H), 4.00 (s, 3H), 3.70 (s, 3H), 3.50-3.40 (m, 2H), 3.23 (s, 3H), 2.37-2.16 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.4, 170.8, 142.6, 129.6, 127.4, 70.2, 58.4, 52.4, 51.1, 36.0, 28.9.

IR (film): ν (cm^{-1}) 3113, 2951, 2874, 2819, 1737, 1676, 1510, 1438, 1402, 1331, 1287, 1245, 1196, 1163, 1115, 1087, 978, 912, 846, 780, 693, 610, 524.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{16}N_2O_4Na$ $[M+Na]^+$: 263.1002, found: 263.1001.



Methyl 5-hydroxy-2-(1-methyl-1*H*-imidazole-2-carbonyl)pentanoate (5i)

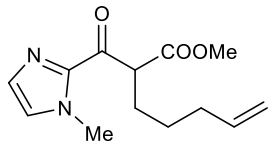
A colorless oil. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (br s, 1H), 7.06 (br s, 1H), 4.81 (t, J = 6.9 Hz, 1H), 4.01 (s, 3H), 3.77-3.65 (m, 2H), 3.72 (s, 3H), 2.64 (br s, 1H), 2.22-2.00 (m, 2H), 1.80-1.52 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.7, 170.7, 142.2, 129.7, 127.6, 61.8, 53.1, 52.3, 36.2, 30.1, 25.3.

IR (film): ν (cm^{-1}) 3383, 2955, 2880, 1733, 1674, 1401, 1281, 1236, 1202, 1159, 1059, 1003, 957, 913, 778, 691.

HRMS (ESI, *m*/*z*) calcd for $C_{11}H_{16}N_2O_4Na$ $[M+Na]^+$: 263.1002, found: 263.1000.



Methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)hept-6-enoate (5j)

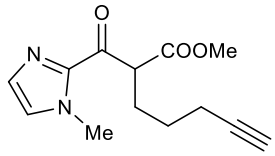
A colorless oil. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (br s, 1H), 7.05 (br s, 1H), 5.86-5.70 (m, 1H), 5.05-4.90 (m, 2H), 4.74 (t, J = 7.4 Hz, 1H), 4.01 (s, 3H), 3.69 (s, 3H), 2.14-2.04 (m, 2H), 2.04-1.94 (m, 2H), 1.55-1.38 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.6, 170.9, 142.6, 138.2, 129.7, 127.6, 114.9, 53.6, 52.3, 36.1, 33.5, 28.3, 26.8.

IR (film): ν (cm^{-1}) 3113, 2949, 2858, 1737, 1675, 1440, 1402, 1336, 1283, 1235, 1202, 1160, 990, 961, 912, 872, 774, 692.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{18}N_2O_3Na$ $[M+Na]^+$: 273.1210, found: 273.1208.



Methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)hept-6-ynoate (5k)

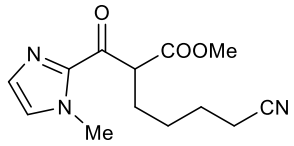
A colorless oil. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.15 (m, 1H), 7.05 (br s, 1H), 4.75 (t, J = 7.4 Hz, 1H), 4.01 (s, 3H), 3.69 (s, 3H), 2.23 (td, J_1 = 6.9 Hz, J_2 = 2.7 Hz, 2H), 2.09 (q, J = 7.5 Hz, 2H), 1.93 (t, J = 2.7 Hz, 1H), 1.68-1.50 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.3, 170.7, 142.5, 129.8, 127.6, 83.7, 68.7, 53.2, 52.3, 36.1, 27.9, 26.3, 18.3.

IR (film): ν (cm^{-1}) 3288, 2952, 1735, 1674, 1440, 1402, 1335, 1283, 1201, 1155, 1086, 994, 961, 913, 873, 777, 637, 512.

HRMS (ESI, *m*/*z*) calcd for $C_{13}H_{16}N_2O_3Na$ $[M+Na]^+$: 271.1053, found: 271.1051.



Methyl 6-cyano-2-(1-methyl-1*H*-imidazole-2-carbonyl)hexanoate (5l)

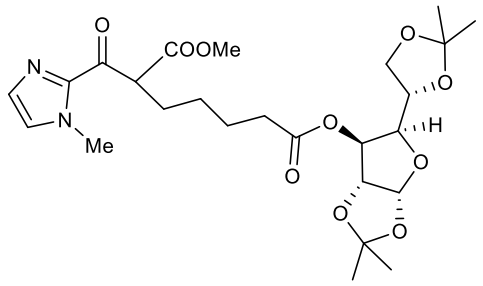
A colorless oil. Racemic.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.19-7.16 (m, 1H), 7.07 (br s, 1H), 4.75 (t, J = 7.8 Hz, 1H), 4.01 (s, 3H), 3.70 (s, 3H), 2.34 (t, J = 7.2 Hz, 2H), 2.01 (q, J = 7.5 Hz, 2H), 1.79-1.65 (m, 2H), 1.60-1.44 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.2, 170.6, 142.4, 129.8, 127.8, 119.4, 53.2, 52.4, 36.1, 27.8, 26.5, 25.1, 16.9.

IR (film): v (cm^{-1}) 2950, 2278, 1736, 1674, 1458, 1402, 1263, 1200, 1155, 1085, 1002, 957, 909, 845, 782, 692.

HRMS (ESI, m/z) calcd for $C_{13}H_{17}N_3O_3Na$ $[M+Na]^+$: 286.1162, found: 286.1160.



7-((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-methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)heptanedioate (5m)

A colorless oil. Mixture of two diastereoisomers.

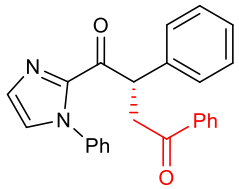
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.15 (m, 1H), 7.05 (br s, 1H), 5.88-5.84 (m, 1H), 5.25-5.22 (m, 1H), 4.72 (t, J = 7.1 Hz, 1H), 4.47 (d, J = 3.6 Hz, 1H), 4.22-4.12 (m, 2H), 4.10-4.03 (m, 1H), 4.02-3.96 (m, 1H), 4.01 (s, 3H), 3.68 (s, 3H), 2.34 (t, J = 7.5 Hz, 2H), 1.98 (q, J = 7.8 Hz, 2H), 1.72-1.61 (m, 2H), 1.51 (s, 3H), 1.48-1.35 (m, 2H), 1.39 (s, 3H), 1.30 (s, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 187.4, 172.0, 170.7, 142.5, 142.4, 129.7, 127.6, 112.2, 109.3, 105.1, 83.4, 79.9, 75.9, 72.4, 67.2, 53.4, 52.3, 36.1, 33.8, 28.3, 26.9, 26.8, 26.7, 26.2, 25.2, 24.59, 24.57.

IR (film): v (cm^{-1}) 2987, 2944, 2869, 1739, 1677, 1458, 1405, 1376, 1211, 1154, 1071, 1017, 952, 910, 884, 846, 782, 735, 512.

HRMS (ESI, m/z) calcd for $C_{25}H_{36}N_2O_{10}Na$ $[M+Na]^+$: 547.2262, found: 547.2260.

4. Experimental and Characterization Data of Products



(*S*)-2,4-Diphenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3a)

According to the typical procedure (in main text), electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 30.1 mg (79% yield) of **3a** as a yellow solid after electricity consumption of 2.4 F/mol.

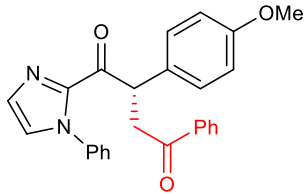
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 60:40, flow rate 1 mL/min, 40 °C, t_r (major) = 19.3 min, t_r (minor) = 13.9 min). $[\alpha]_D^{22}$ = +218.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.98-7.92 (m, 2H), 7.61-7.52 (m, 1H), 7.49-7.39 (m, 7H), 7.38-7.30 (m, 2H), 7.29-7.20 (m, 4H), 7.20-7.17 (m, 1H), 5.69 (dd, J_1 = 11.1 Hz, J_2 = 3.6 Hz, 1H), 4.03 (dd, J_1 = 18.0 Hz, J_2 = 11.1 Hz, 1H), 3.37 (dd, J_1 = 18.3 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 189.9, 143.1, 138.99, 138.96, 136.9, 133.5, 130.1, 129.20, 129.15, 129.1, 128.9, 128.8, 128.4, 127.6, 127.5, 126.1, 48.9, 43.4.

IR (film): ν (cm^{-1}) 3060, 2910, 1678, 1592, 1495, 1448, 1401, 1360, 1307, 1247, 1204, 1149, 1098, 1074, 1023, 992, 939, 907, 867, 755, 691, 587, 522, 435.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{20}N_2O_2Na$ $[M+Na]^+$: 403.1417, found: 403.1415.



(*S*)-2-(4-Methoxyphenyl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3b)

According to the typical procedure, electrolysis of the reaction mixture of 2-(4-methoxyphenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1b** (29.2 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 28.0 mg (68% yield) of **3b** as a yellow oil after electricity consumption of 2.4 F/mol.

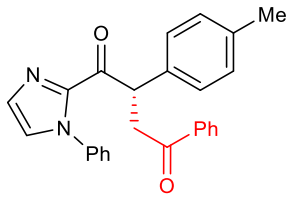
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 20:80, flow rate 1 mL/min, 40 °C, t_r (major) = 19.8 min, t_r (minor) = 15.0 min). $[\alpha]_D^{22}$ = +268.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.97-7.91 (m, 2H), 7.60-7.52 (m, 1H), 7.49-7.34 (m, 7H), 7.29-7.26 (m, 1H), 7.24-7.16 (m, 3H), 6.90-6.84 (m, 2H), 5.62 (dd, J_1 = 10.8 Hz, J_2 = 3.9 Hz, 1H), 3.99 (dd, J_1 = 18.0 Hz, J_2 = 10.8 Hz, 1H), 3.77 (s, 3H), 3.33 (dd, J_1 = 18.0 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.4, 190.1, 159.3, 143.2, 139.0, 137.0, 133.5, 130.7, 130.1, 130.0, 129.2, 128.9, 128.8, 128.4, 127.4, 126.1, 114.5, 55.6, 48.0, 43.3.

IR (film): *v* (cm^{-1}) 3060, 2907, 2837, 1678, 1601, 1504, 1447, 1401, 1356, 1305, 1248, 1204, 1178, 1149, 1106, 1076, 1027, 992, 940, 907, 874, 834, 763, 734, 690, 655, 574, 535, 422.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}N_2O_3Na$ $[M+H]^+$: 433.1523, found: 433.1519.



(*S*)-4-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(*p*-tolyl)butane-1,4-dione (3c)

According to the typical procedure, electrolysis of the reaction mixture of 1-(1-phenyl-1*H*-imidazol-2-yl)-2-(*p*-tolyl)ethan **1c** (27.6 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 34.6 mg (88% yield) of **3c** as a yellow solid after electricity consumption of 2.4 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 16.2 min, t_r (minor) = 12.8 min). $[\alpha]_D^{22}$ = +238.0° (*c* 1.0, CH_2Cl_2).

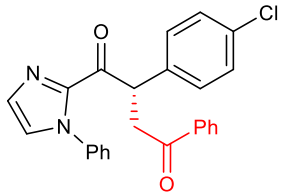
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.97-7.91 (m, 2H), 7.60-7.52 (m, 1H), 7.50-7.40 (m, 5H), 7.37-7.30 (m, 2H), 7.24-7.27 (m, 1H), 7.25-7.20 (m, 2H), 7.19-7.12 (m, 3H), 5.64 (dd, J_1 = 10.5 Hz, J_2 = 3.3 Hz, 1H), 4.01 (dd, J_1 = 18.0 Hz, J_2 = 10.8 Hz, 1H), 3.34 (dd, J_1 = 17.7 Hz, J_2 = 3.3 Hz, 1H), 2.32 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.3, 190.0, 143.1, 139.0, 137.4, 137.0, 135.8, 133.5, 130.3, 130.0, 129.8, 129.2, 128.9, 128.8, 128.4, 127.5, 126.1, 48.5, 43.4, 21.1.

IR (film): *v* (cm^{-1}) 3062, 2914, 1718, 1676, 1592, 1498, 1449, 1406, 1352, 1320, 1295, 1247, 1193,

1176, 1146, 1108, 1077, 1021, 992, 943, 908, 827, 767, 689, 655, 570, 534, 494.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}N_2O_2Na$ $[M+Na]^+$: 417.1573, found: 417.1571.



(*S*)-2-(4-Chlorophenyl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3d)

According to the typical procedure, electrolysis of the reaction mixture of 2-(4-chlorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1d** (29.7 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 28.5 mg (67% yield) of **3d** as a yellow solid after electricity consumption of 2.0 F/mol.

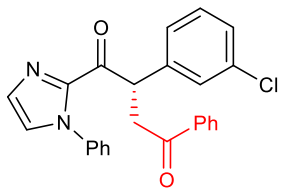
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 95% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 15.0 min, t_r (minor) = 10.8 min). $[\alpha]_D^{22}$ = +229.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.97-7.92 (m, 2H), 7.62-7.53 (m, 1H), 7.50-7.39 (m, 7H), 7.34-7.27 (m, 3H), 7.26-7.18 (m, 3H), 5.69 (dd, J_1 = 10.8 Hz, J_2 = 3.9 Hz, 1H), 4.00 (dd, J_1 = 18.0 Hz, J_2 = 10.8 Hz, 1H), 3.36 (dd, J_1 = 18.0 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.0, 189.5, 142.9, 138.9, 137.5, 136.8, 133.6, 133.4, 130.6, 130.2, 129.24, 129.21, 129.0, 128.9, 128.4, 127.7, 126.1, 48.2, 43.2.

IR (film): ν (cm^{-1}) 3063, 2919, 2852, 1676, 1593, 1490, 1449, 1406, 1351, 1316, 1249, 1203, 1177, 1147, 1081, 1006, 992, 942, 910, 834, 807, 772, 689, 561, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{19}ClN_2O_2Na$ $[M+Na]^+$: 437.1027, found: 437.1023.



(*S*)-2-(3-Chlorophenyl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3e)

According to the typical procedure, electrolysis of the reaction mixture of 2-(3-chlorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1e** (29.7 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)

oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 36.4 mg (88% yield) of **3e** as a yellow solid after electricity consumption of 2.4 F/mol.

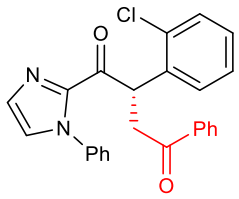
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 20:80, flow rate 1 mL/min, 40 °C, t_r (major) = 14.9 min, t_r (minor) = 12.0 min). $[\alpha]_D^{22}$ = +172.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.98-7.91 (m, 2H), 7.62-7.53 (m, 1H), 7.50-7.35 (m, 7H), 7.33-7.20 (m, 6H), 5.68 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.01 (dd, J_1 = 18.0 Hz, J_2 = 11.1 Hz, 1H), 3.37 (dd, J_1 = 18.3 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 197.9, 189.3, 143.0, 141.1, 138.9, 136.8, 134.7, 133.6, 130.4, 130.2, 129.2, 129.1, 129.0, 128.9, 128.4, 127.8, 127.7, 127.5, 126.1, 48.4, 43.2.

IR (film): ν (cm^{-1}) 3061, 2911, 1679, 1592, 1496, 1445, 1400, 1354, 1306, 1243, 1204, 1149, 1077, 1023, 992, 940, 906, 763, 732, 689, 662, 601, 559, 527, 507.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{19}ClN_2O_2Na$ $[M+Na]^+$: 437.1027, found: 437.1023.



(*S*)-2-(2-Chlorophenyl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3f)

According to the typical procedure, electrolysis of the reaction mixture of 2-(2-chlorophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1f** (29.7 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 31.4 mg (76% yield) of **3f** as a yellow solid after electricity consumption of 2.2 F/mol.

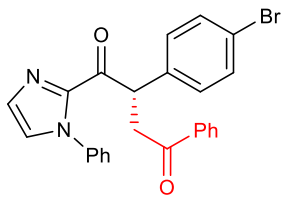
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 94% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 12.7 min, t_r (minor) = 10.2 min). $[\alpha]_D^{22}$ = +283.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.97-7.90 (m, 2H), 7.61-7.52 (m, 1H), 7.50-7.41 (m, 6H), 7.33-7.26 (m, 2H), 7.25-7.17 (m, 5H), 6.06 (dd, J_1 = 10.8 Hz, J_2 = 3.3 Hz, 1H), 3.86 (dd, J_1 = 18.3 Hz, J_2 = 11.1 Hz, 1H), 3.31 (dd, J_1 = 18.0 Hz, J_2 = 3.3 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 197.8, 189.5, 143.1, 138.9, 137.2, 136.8, 134.3, 133.6, 130.6, 130.3, 129.3, 129.1, 128.94, 128.92, 128.8, 128.4, 127.7, 127.5, 126.2, 45.8, 42.1.

IR (film): ν (cm^{-1}) 3060, 2909, 1679, 1592, 1497, 1445, 1401, 1353, 1304, 1244, 1205, 1150, 1097, 1078, 1039, 1011, 990, 938, 906, 845, 754, 690, 540, 485.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{19}ClN_2O_2Na$ $[M+Na]^+$: 437.1027, found: 437.1024.



(*S*)-2-(4-Bromophenyl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3g)

According to the typical procedure, electrolysis of the reaction mixture of 2-(4-bromophenyl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1g** (34.1 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 38.2 mg (83% yield) of **3g** as a yellow solid after electricity consumption of 2.2 F/mol.

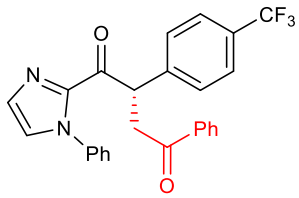
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 16.9 min, t_r (minor) = 11.5 min). $[\alpha]_D^{22}$ = +194.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (250 MHz, CD_2Cl_2) δ 7.97-7.90 (m, 2H), 7.60-7.52 (m, 1H), 7.52-7.31 (m, 9H), 7.31-7.16 (m, 4H), 5.66 (dd, J_1 = 10.6 Hz, J_2 = 3.4 Hz, 1H), 3.99 (dd, J_1 = 18.0 Hz, J_2 = 10.9 Hz, 1H), 3.36 (dd, J_1 = 17.9 Hz, J_2 = 3.4 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.0, 189.4, 142.9, 138.9, 138.1, 136.8, 133.6, 132.2, 130.9, 130.2, 129.2, 129.0, 128.9, 128.4, 127.7, 126.1, 121.5, 48.2, 43.1.

IR (film): ν (cm^{-1}) 3063, 2922, 2854, 1675, 1592, 1486, 1449, 1406, 1353, 1315, 1247, 1202, 1073, 1005, 943, 909, 832, 770, 720, 685, 558, 528.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{19}BrN_2O_2Na$ $[M+Na]^+$: 481.0522, found: 481.0518.



(*S*)-4-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(4-(trifluoromethyl)phenyl)butane-1,4-dione (3h)

According to the typical procedure, electrolysis of the reaction mixture of 1-(1-phenyl-1*H*-imidazol-2-yl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one **1h** (33.0 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 39.0 mg (87% yield) of **3h** as a yellow solid after electricity consumption of 2.2 F/mol.

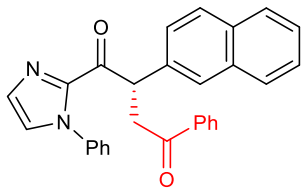
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 95% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 11.2 min, t_r (minor) = 7.0 min). $[\alpha]_D^{22}$ = +193.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.97-7.93 (m, 2H), 7.65-7.55 (m, 5H), 7.51-7.40 (m, 5H), 7.30 (d, J = 1.0 Hz, 1H), 7.26-7.22 (m, 2H), 7.21 (d, J = 1.0 Hz, 1H), 5.79 (dd, J_1 = 11.0 Hz, J_2 = 4.0 Hz, 1H), 4.04 (dd, J_1 = 18.0 Hz, J_2 = 10.5 Hz, 1H), 3.40 (dd, J_1 = 18.0 Hz, J_2 = 4.0 Hz, 1H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 197.7, 189.1, 143.2, 142.7, 138.7, 136.6, 133.7, 130.2, 129.52, 129.50 (q, J = 32.0 Hz), 129.2, 128.94, 128.90, 128.3, 127.8, 126.1, 125.9 (q, J = 3.9 Hz), 124.6 (q, J = 270.3 Hz), 48.6, 43.1.

IR (film): ν (cm^{-1}) 2919, 2853, 1679, 1593, 1496, 1449, 1407, 1321, 1250, 1159, 1112, 1066, 1013, 992, 944, 910, 845, 766, 688, 605, 557, 527.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{19}F_3N_2O_2Na$ $[M+Na]^+$: 471.1291, found: 471.1288.



(*S*)-2-(Naphthalen-2-yl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3i)

According to the typical procedure, electrolysis of the reaction mixture of 2-(naphthalen-2-yl)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1i** (33.0 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 27.1 mg (63% yield) of **3i** as a yellow solid after electricity consumption of 2.4 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 23.5 min, t_r (minor) = 16.2 min). $[\alpha]_D^{22}$ = +286.8° (*c* 1.0, CH_2Cl_2).

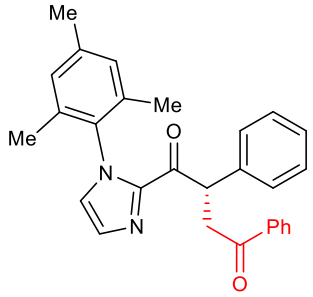
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.00-7.94 (m, 2H), 7.91 (br s, 1H), 7.87-7.80 (m, 3H), 7.62 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 1H), 7.58-7.51 (m, 1H), 7.51-7.38 (m, 7H), 7.29 (d, J = 0.9 Hz, 1H), 7.25-7.19

(m, 2H), 7.17 (d, J = 0.9 Hz, 1H), 5.86 (dd, J_1 = 11.1 Hz, J_2 = 3.9 Hz, 1H), 4.14 (dd, J_1 = 18.3 Hz, J_2 = 10.8 Hz, 1H), 3.46 (dd, J_1 = 18.3 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 189.7, 143.1, 139.0, 136.9, 136.4, 134.0, 133.6, 133.0, 130.1, 129.2, 129.0, 128.847, 128.753, 128.4, 128.1, 127.9, 127.8, 127.6, 127.2, 126.6, 126.3, 126.2, 49.0, 43.4.

IR (film): v (cm^{-1}) 3056, 2908, 1678, 1593, 1497, 1447, 1402, 1349, 1310, 1264, 1211, 1149, 1097, 1075, 992, 939, 906, 858, 820, 759, 735, 690, 654, 567, 534, 478.

HRMS (ESI, m/z) calcd for $C_{29}H_{22}N_2O_2Na$ $[M+Na]^+$: 453.1573, found: 453.1570.



(*S*)-1-(1-Mesityl-1*H*-imidazol-2-yl)-2,4-diphenylbutane-1,4-dione (3j)

According to the typical procedure, electrolysis of the reaction mixture of 1-(1-mesityl-1*H*-imidazol- 2-yl)-2-phenylethan-1-one **1j** (30.4 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 21.3 mg (50% yield) of **3j** as a colorless oil after electricity consumption of 2.2 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99.6% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C, t_r (major) = 16.6 min, t_r (minor) = 9.5 min). $[\alpha]_D^{22}$ = +153.8° (*c* 1.0, CH_2Cl_2).

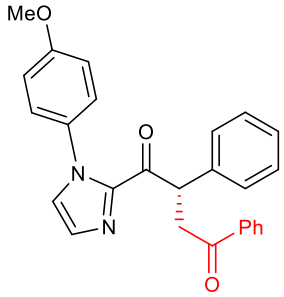
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.95-7.88 (m, 2H), 7.60-7.51 (m, 1H), 7.49-7.35 (m, 5H), 7.33-7.18 (m, 3H), 6.97 (br s, 1H), 6.94 (br s, 1H), 6.89 (br s, 1H), 5.68 (dd, J_1 = 11.1 Hz, J_2 = 3.6 Hz, 1H), 3.99 (dd, J_1 = 18.0 Hz, J_2 = 10.8 Hz, 1H), 3.32 (dd, J_1 = 18.3 Hz, J_2 = 3.9 Hz, 1H), 2.31 (s, 3H), 1.94 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.1, 189.9, 143.2, 139.1, 138.7, 137.0, 135.4, 135.2, 134.5, 133.4, 130.8, 129.1, 129.0, 128.93, 128.89, 128.3, 127.5, 126.2, 48.6, 43.1, 21.1, 17.4, 16.9. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): v (cm^{-1}) 3059, 3029, 2918, 2859, 1679, 1598, 1488, 1449, 1403, 1361, 1326, 1283, 1247,

1203, 1149, 1084, 1013, 989, 959, 933, 907, 849, 736, 693, 561, 522.

HRMS (ESI, *m*/*z*) calcd for $C_{28}H_{26}N_2O_2Na$ $[M+Na]^+$: 445.1886, found: 445.1882.



(*S*)-1-(1-(4-Methoxyphenyl)-1*H*-imidazol-2-yl)-2,4-diphenylbutane-1,4-dione (3k)

According to the typical procedure, electrolysis of the reaction mixture of 1-(1-(4-methoxyphenyl)-1*H*-imidazol-2-yl)-2-phenylethan-1-one **1k** (29.2 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 22.5 mg (55% yield) of **3k** as a white solid after electricity consumption of 2.4 F/mol.

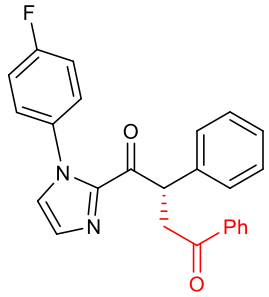
Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 40 °C, t_r (major) = 12.4 min, t_r (minor) = 10.8 min). $[\alpha]_D^{22}$ = +237.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.96-7.92 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.41 (m, 4H), 7.36-7.30 (m, 2H), 7.27-7.22 (m, 2H), 7.15-7.11 (m, 3H), 6.93-6.88 (m, 2H), 5.66 (dd, J_1 = 11.0 Hz, J_2 = 4.0 Hz, 1H), 4.02 (dd, J_1 = 18.0 Hz, J_2 = 11.0 Hz, 1H), 3.82 (s, 3H), 3.35 (dd, J_1 = 18.0 Hz, J_2 = 3.5 Hz, 1H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 198.2, 189.8, 159.9, 143.1, 138.9, 136.8, 133.5, 131.7, 129.8, 129.1, 129.0, 128.9, 128.3, 127.8, 127.5, 127.1, 114.1, 55.8, 48.7, 43.4.

IR (film): ν (cm^{-1}) 3060, 2911, 2839, 1678, 1592, 1513, 1450, 1400, 1360, 1332, 1297, 1246, 1207, 1176, 1149, 1103, 1076, 1030, 998, 940, 907, 834, 735, 693, 623, 523, 402.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}N_2O_3Na$ $[M+Na]^+$: 433.1523, found: 433.1519.



(*S*)-1-(1-(4-Fluorophenyl)-1*H*-imidazol-2-yl)-2,4-diphenylbutane-1,4-dione (3l)

According to the typical procedure, electrolysis of the reaction mixture of 1-(1-(4-fluorophenyl)-1*H*-imidazol-2-yl)-2-phenylethan-1-one **1l** (28.0 mg, 0.10 mmol) and trimethyl((1-phenylvinyl) oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 20.8 mg (52% yield) of **3l** as a white solid after electricity consumption of 2.2 F/mol.

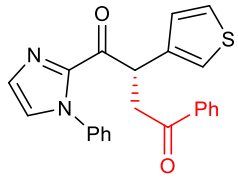
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 20:80, flow rate 1 mL/min, 40 °C, t_r (major) = 10.5 min, t_r (minor) = 9.4 min). $[\alpha]_D^{22}$ = +130.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.98-7.92 (m, 2H), 7.61-7.53 (m, 1H), 7.50-7.42 (m, 4H), 7.37-7.30 (m, 2H), 7.29-7.19 (m, 4H), 7.18-7.16 (m, 1H), 7.15-7.06 (m, 2H), 5.67 (dd, J_1 = 11.1 Hz, J_2 = 3.6 Hz, 1H), 4.03 (dd, J_1 = 18.0 Hz, J_2 = 11.1 Hz, 1H), 3.38 (dd, J_1 = 18.3 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.3, 190.1, 162.7 (d, J = 246.1), 143.2, 138.9, 136.9, 135.0 (d, J = 3.2 Hz), 133.6, 130.2, 129.2, 129.1, 129.0, 128.4, 128.0 (d, J = 8.7 Hz), 127.63, 127.57, 116.4 (d, J = 23.0 Hz), 48.8, 43.5.

IR (film): ν (cm^{-1}) 3062, 2910, 1678, 1598, 1508, 1449, 1402, 1360, 1323, 1220, 1152, 1095, 1020, 989, 940, 907, 840, 814, 735, 693, 621, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{19}FN_2O_2Na$ $[M+Na]^+$: 421.1323, found: 421.1320.



(*S*)-4-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(thiophen-3-yl)butane-1,4-dione (3n)

According to the typical procedure, electrolysis of the reaction mixture of 1-(1-phenyl-1*H*-imidazol-2-yl)-2-(thiophen-3-yl)ethan-1-one **1n** (26.8 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)

silane **2a** (115.4 mg, 6.0 equiv) afforded 16.2 mg (42% yield) of **3n** as a yellow solid after electricity consumption of 2.2 F/mol.

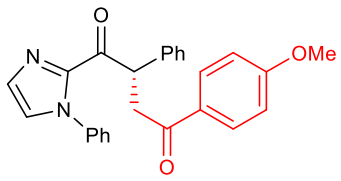
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 98% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 13.2 min, t_r (minor) = 10.5 min). $[\alpha]_D^{22}$ = +162.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.98-7.92 (m, 2H), 7.62-7.53 (m, 1H), 7.50-7.38 (m, 5H), 7.33-7.20 (m, 6H), 7.17 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 5.81 (dd, J_1 = 11.1 Hz, J_2 = 3.6 Hz, 1H), 4.02 (dd, J_1 = 18.3 Hz, J_2 = 11.1 Hz, 1H), 3.41 (dd, J_1 = 18.3 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 189.5, 143.1, 138.99, 138.97, 136.9, 133.6, 130.1, 129.2, 129.0, 128.8, 128.4, 128.2, 127.6, 126.2, 126.1, 123.0, 44.2, 42.9.

IR (film): ν (cm^{-1}) 3105, 3061, 2912, 1678, 1592, 1495, 1446, 1402, 1353, 1309, 1252, 1217, 1147, 1076, 991, 939, 907, 848, 810, 761, 733, 690, 654, 540, 510, 408.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{18}N_2O_2SNa$ $[M+Na]^+$: 409.0981, found: 409.0978.



(*S*)-4-(4-Methoxyphenyl)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3o)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and ((1-(4-methoxyphenyl)vinyl)oxy)trimethylsilane **2b** (133.4 mg, 6.0 equiv) afforded 37.3 mg (91% yield) of **3o** as a yellow oil after electricity consumption of 2.2 F/mol.

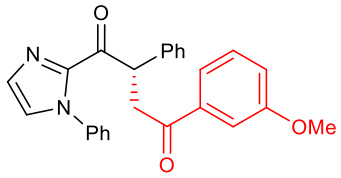
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 94% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 20:80, flow rate 1 mL/min, 40 °C, t_r (major) = 24.9 min, t_r (minor) = 19.7 min). $[\alpha]_D^{22}$ = +168.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.97-7.90 (m, 2H), 7.49-7.39 (m, 5H), 7.38-7.30 (m, 2H), 7.29-7.20 (m, 4H), 7.20-7.17 (m, 1H), 6.97-6.89 (m, 2H), 5.66 (dd, J_1 = 11.1 Hz, J_2 = 3.9 Hz, 1H), 3.98 (dd, J_1 = 17.7 Hz, J_2 = 10.8 Hz, 1H), 3.85 (s, 3H), 3.32 (dd, J_1 = 18.3 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 196.6, 190.0, 164.0, 143.2, 139.1, 139.0, 130.6, 130.047, 129.979, 129.2, 129.12, 129.07, 128.8, 127.54, 127.49, 126.1, 114.1, 55.9, 48.9, 43.2.

IR (film): ν (cm^{-1}) 3060, 2908, 2841, 1673, 1598, 1499, 1449, 1402, 1360, 1310, 1250, 1212, 1169, 1105, 1075, 1023, 988, 939, 908, 836, 761, 734, 694, 588, 525.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}N_2O_3Na$ $[M+Na]^+$: 433.1523, found: 433.1518.



(*S*)-4-(3-Methoxyphenyl)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3p)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and ((1-(3-methoxyphenyl)vinyl)oxy)trimethylsilane **2c** (133.4 mg, 6.0 equiv) afforded 31.4 mg (76% yield) of **3p** as a yellow oil after electricity consumption of 2.4 F/mol.

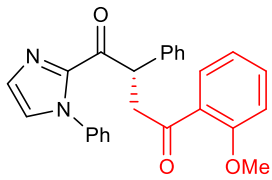
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 20:80, flow rate 1 mL/min, 40 °C, t_r (major) = 19.1 min, t_r (minor) = 12.3 min). $[\alpha]_D^{22}$ = +181.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.57-7.52 (m, 1H), 7.49-7.40 (m, 6H), 7.40-7.30 (m, 3H), 7.29-7.20 (m, 4H), 7.20-7.17 (m, 1H), 7.11 (ddd, J_1 = 8.4 Hz, J_2 = 2.7 Hz, J_3 = 1.2 Hz, 1H), 5.69 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.01 (dd, J_1 = 18.3 Hz, J_2 = 11.1 Hz, 1H), 3.83 (s, 3H), 3.36 (dd, J_1 = 18.0 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.0, 189.9, 160.3, 143.1, 139.0, 138.9, 138.3, 130.1, 130.0, 129.2, 129.146, 129.070, 128.8, 127.6, 127.5, 126.1, 121.0, 119.8, 112.8, 55.8, 48.9, 43.5.

IR (film): ν (cm^{-1}) 3060, 2913, 2839, 1679, 1590, 1492, 1449, 1402, 1311, 1259, 1166, 1077, 1023, 940, 908, 850, 761, 736, 692, 585, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}N_2O_3Na$ $[M+Na]^+$: 433.1523, found: 433.1519.



(*S*)-4-(2-Methoxyphenyl)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3q)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and ((1-(2-methoxyphenyl)vinyl)oxy)trimethylsilane **2d** (133.4 mg, 6.0 equiv) afforded 32.8 mg (80% yield) of **3q** as a yellow solid after electricity consumption of 2.2 F/mol.

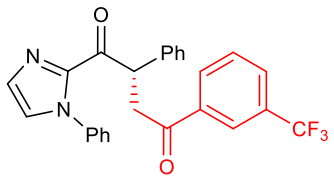
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 94% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 17.4 min, t_r (minor) = 12.1 min). $[\alpha]_D^{22}$ = +134.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.68 (dd, J_1 = 7.8 Hz, J_2 = 1.8 Hz, 1H), 7.52-7.40 (m, 6H), 7.37-7.28 (m, 2H), 7.28-7.20 (m, 4H), 7.20-7.17 (m, 1H), 7.02-6.94 (m, 2H), 5.64 (dd, J_1 = 11.1 Hz, J_2 = 3.9 Hz, 1H), 4.01 (dd, J_1 = 18.6 Hz, J_2 = 11.1 Hz, 1H), 3.86 (s, 3H), 3.43 (dd, J_1 = 18.6 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 199.9, 190.3, 159.5, 143.3, 139.3, 139.1, 134.1, 130.7, 130.0, 129.2, 129.1, 129.0, 128.7, 127.8, 127.4, 126.1, 120.8, 112.1, 55.9, 49.2, 48.7. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): ν (cm^{-1}) 3131, 3059, 2961, 2840, 1668, 1592, 1487, 1454, 1402, 1348, 1306, 1281, 1240, 1186, 1156, 1109, 1061, 1013, 991, 938, 909, 880, 845, 808, 755, 694, 665, 578, 539, 505.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{22}N_2O_3Na$ $[M+Na]^+$: 433.1523, found: 433.1519.



(*S*)-2-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-4-(3-(trifluoromethyl)phenyl)butane-1,4-dione (3r)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and trimethyl((1-(3-(trifluoromethyl)phenyl)vinyl)oxy)silane **2e** (156.2 mg, 6.0 equiv) afforded 21.2 mg (47% yield) of **3r** as a yellow oil after electricity consumption of 2.2 F/mol.

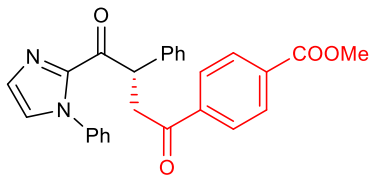
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 98% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 9.6 min, t_r (minor) = 6.8 min). $[\alpha]_D^{22}$ = +152.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.20 (s, 1H), 8.14 (d, J = 7.9 Hz, 1H), 7.82 (d, J = 7.8 Hz, 1H), 7.61 (t, J = 7.8 Hz, 1H), 7.47-7.40 (m, 5H), 7.37-7.32 (m, 2H), 7.29-7.24 (m, 2H), 7.23-7.18 (m, 3H), 5.70 (dd, J_1 = 10.9 Hz, J_2 = 3.5 Hz, 1H), 4.04 (dd, J_1 = 18.2 Hz, J_2 = 11.0 Hz, 1H), 3.36 (dd, J_1 = 18.2 Hz, J_2 = 3.7Hz, 1H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 197.0, 189.5, 142.9, 138.8, 138.6, 137.3, 131.7, 131.2 (q, J = 32.4 Hz), 130.1, 129.9 (q, J = 3.7 Hz), 129.7, 129.2, 129.0, 128.8, 127.7, 127.6, 126.0, 125.2 (q, J = 2.4 Hz), 124.2 (q, J = 270.7 Hz), 48.7, 43.4. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): v (cm^{-1}) 3062, 2908, 1683, 1605, 1496, 1446, 1403, 1365, 1323, 1241, 1168, 1125, 1071, 1026, 940, 905, 809, 761, 737, 691, 585, 529, 407.

HRMS (ESI, m/z) calcd for $C_{26}H_{19}F_3N_2O_2Na$ $[M+Na]^+$: 471.1291, found: 471.1287.



Methyl (*S*)-4-(4-oxo-3-phenyl-4-(1-phenyl-1*H*-imidazol-2-yl)butanoyl)benzoate (3s)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and ethyl 4-(1-((trimethylsilyl)oxy)vinyl)benzoate **2f** (150.2 mg, 6.0 equiv) afforded 32.1 mg (73% yield) of **3s** as a yellow solid after electricity consumption of 2.2 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 98% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 20:80, flow rate 1 mL/min, 40 °C, t_r (major) = 24.6 min, t_r (minor) = 16.9 min). $[\alpha]_D^{22}$ = +174.8° (*c* 1.0, CH_2Cl_2).

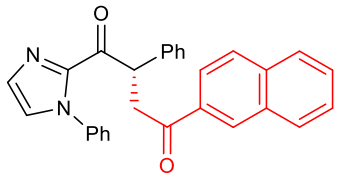
^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.09 (d, J = 8.4 Hz, 2H), 7.99 (d, J = 8.7 Hz, 2H), 7.48-7.40 (m, 5H), 7.38-7.31 (m, 2H), 7.30-7.17 (m, 5H), 5.69 (dd, J_1 = 10.8 Hz, J_2 = 3.6 Hz, 1H), 4.04 (dd, J_1 = 18.6 Hz, J_2 = 11.1 Hz, 1H), 3.91 (s, 3H), 3.37 (dd, J_1 = 18.3 Hz, J_2 = 3.9 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 197.9, 189.7, 166.4, 143.0, 140.0, 138.9, 138.7, 134.5, 130.1, 130.0, 129.2, 129.0, 128.8, 128.4, 127.7, 127.6, 126.1, 52.7, 48.8, 43.6. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): v (cm^{-1}) 3059, 2952, 1722, 1681, 1597, 1496, 1444, 1402, 1362, 1276, 1195, 1150, 1107,

991, 939, 909, 858, 760, 733, 693, 530.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{22}N_2O_4Na$ $[M+Na]^+$: 461.1472, found: 461.1467.



(*S*)-4-(Naphthalen-2-yl)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3t)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and trimethyl((1-(naphthalen-2-yl)vinyl)oxy)silane **2g** (145.4 mg, 6.0 equiv) afforded 30.9 mg (72% yield) of **3t** as a yellow solid after electricity consumption of 2.2 F/mol.

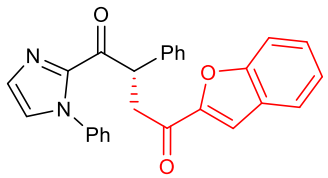
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 25.8 min, t_r (minor) = 15.8 min). $[\alpha]_D^{22}$ = +218.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.51 (s, 1H), 8.00 (dd, J_1 = 8.4 Hz, J_2 = 1.5 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 7.93-7.86 (m, 2H), 7.65-7.48 (m, 4H), 7.46-7.33 (m, 5H), 7.32-7.22 (m, 4H), 7.21-7.18 (m, 1H), 5.75 (dd, J_1 = 10.8 Hz, J_2 = 3.3 Hz, 1H), 4.17 (dd, J_1 = 18.0 Hz, J_2 = 11.1 Hz, 1H), 3.51 (dd, J_1 = 18.0 Hz, J_2 = 3.6 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.1, 189.9, 143.2, 139.03, 139.00, 136.0, 134.2, 132.9, 130.2, 130.1, 129.9, 129.20, 129.18, 129.1, 128.9, 128.8, 128.7, 128.1, 127.62, 127.56, 127.2, 126.1, 124.1, 49.0, 43.5.

IR (film): ν (cm^{-1}) 3058, 2908, 1675, 1628, 1594, 1495, 1447, 1401, 1363, 1309, 1265, 1217, 1178, 1124, 1076, 1025, 940, 905, 860, 822, 734, 694, 587, 529, 475.

HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{22}N_2O_2Na$ $[M+Na]^+$: 453.1573, found: 453.1570.



(*S*)-4-(Benzofuran-2-yl)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3u)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and ((1-(benzofuran-2-yl)vinyl)oxy)trimethylsilane **2h** (139.4 mg, 6.0 equiv) afforded 32.5 mg (77% yield) of **3u** as a yellow oil after electricity consumption of 2.4 F/mol.

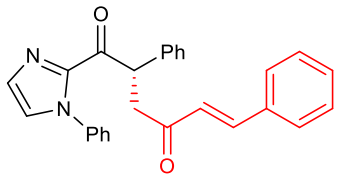
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 26.7 min, t_r (minor) = 17.6 min). $[\alpha]_D^{22}$ = +169.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, J = 7.8 Hz, 1H), 7.48-7.36 (m, 5H), 7.36-7.30 (m, 3H), 7.29-7.12 (m, 7H), 7.07-7.04 (m, 1H), 5.69 (dd, J_1 = 10.8 Hz, J_2 = 4.2 Hz, 1H), 3.95 (dd, J_1 = 18.0 Hz, J_2 = 10.8 Hz, 1H), 3.33 (dd, J_1 = 18.0 Hz, J_2 = 4.2 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 189.3, 188.9, 155.6, 152.2, 142.6, 138.4, 138.1, 130.0, 128.9, 128.8, 128.7, 128.6, 128.1, 127.3, 127.00, 126.97, 125.7, 123.8, 123.2, 112.7, 112.4, 48.0, 43.0.

IR (film): ν (cm^{-1}) 3060, 2913, 1676, 1594, 1555, 1495, 1448, 1400, 1369, 1337, 1308, 1265, 1192, 1140, 1103, 1075, 1018, 935, 909, 874, 833, 735, 694, 537, 499.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{20}N_2O_3Na$ $[M+Na]^+$: 443.1366, found: 443.1362.



(*S*,*E*)-2,6-Diphenyl-1-(1-phenyl-1*H*-imidazol-2-yl)hex-5-ene-1,4-dione (3v)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and (*E*)-trimethyl((4-phenylbuta-1,3-dien-2-yl)oxy)silane **2i** (131.0 mg, 6.0 equiv) afforded 31.2 mg (77% yield) of **3v** as a yellow oil after electricity consumption of 2.4 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 96% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 30:70, flow rate 1 mL/min, 40 °C, t_r (major) = 19.4 min, t_r (minor) = 14.0 min). $[\alpha]_D^{22}$ = +271.8° (*c* 1.0, CH_2Cl_2).

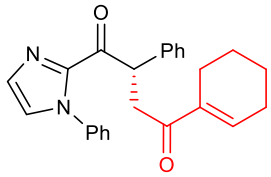
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.58-7.52 (m, 3H), 7.45-7.41 (m, 5H), 7.41-7.37 (m, 3H), 7.35-7.32 (m, 2H), 7.27-7.20 (m, 4H), 7.18 (d, J = 1.1 Hz, 1H), 6.72 (d, J = 16.3 Hz, 1H), 5.59 (dd, J_1 = 10.9 Hz, J_2 = 3.9 Hz, 1H), 3.72 (dd, J_1 = 17.9 Hz, J_2 = 10.9 Hz, 1H), 3.08 (dd, J_1 = 17.9 Hz, J_2 = 4.0 Hz,

1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 189.8, 143.1, 143.0, 138.9, 134.9, 130.8, 130.0, 129.24, 129.15, 129.1, 128.9, 128.8, 128.6, 127.5, 126.2, 126.0, 48.7, 44.9. (Missing two ^{13}C signal because the resolution of NMR spectrometer is not enough)

IR (film): ν (cm^{-1}) 3058, 2904, 1681, 1606, 1495, 1448, 1401, 1363, 1308, 1260, 1174, 1103, 1064, 1026, 976, 939, 909, 843, 735, 693, 585, 529.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{22}N_2O_2Na$ $[M+Na]^+$: 429.1573, found: 429.1570.



(*S*)-4-(Cyclohex-1-en-1-yl)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3w)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and ((1-(cyclohex-1-en-1-yl)vinyl)oxy)trimethylsilane **2j** (117.8 mg, 6.0 equiv) afforded 31.6 mg (82% yield) of **3w** as a yellow oil after electricity consumption of 2.0 F/mol.

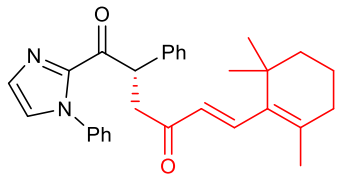
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 95% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 1 mL/min, 40 °C, t_r (major) = 14.5 min, t_r (minor) = 10.9 min). $[\alpha]_D^{22}$ = +232.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.46-7.37 (m, 5H), 7.35-7.27 (m, 2H), 7.26-7.18 (m, 4H), 7.17-7.14 (m, 1H), 6.96-6.90 (m, 1H), 5.52 (dd, J_1 = 11.1 Hz, J_2 = 3.6 Hz, 1H), 3.68 (dd, J_1 = 17.7 Hz, J_2 = 11.1 Hz, 1H), 3.04 (dd, J_1 = 17.7 Hz, J_2 = 3.9 Hz, 1H), 2.28-2.12 (m, 4H), 1.68-1.53 (m, 4H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 199.0, 190.2, 143.2, 140.7, 139.2, 139.1, 139.0, 130.0, 129.2, 129.04, 129.02, 128.8, 127.43, 127.38, 126.1, 48.8, 42.2, 26.4, 23.4, 22.3, 21.9.

IR (film): ν (cm^{-1}) 3058, 2930, 2861, 1682, 1660, 1596, 1495, 1447, 1401, 1309, 1266, 1240, 1188, 1146, 1076, 1023, 992, 942, 907, 843, 760, 734, 695, 586, 525.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{24}N_2O_2Na$ $[M+Na]^+$: 407.1730, found: 407.1727.



(*S*,*E*)-2-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-6-(2,6,6-trimethylcyclohex-1-en-1-yl)hex-5-ene-1,4-dione (3x)

According to the typical procedure, electrolysis of the reaction mixture of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one **1a** (26.2 mg, 0.10 mmol) and (*E*)-trimethyl((4-(2,6,6-trimethylcyclohex-1-en-1-yl)buta-1,3-dien-2-yl)oxy)silane **2k** (158.7 mg, 6.0 equiv) afforded 37.0 mg (82% yield) of **3x** as a yellow oil after electricity consumption of 2.2 F/mol.

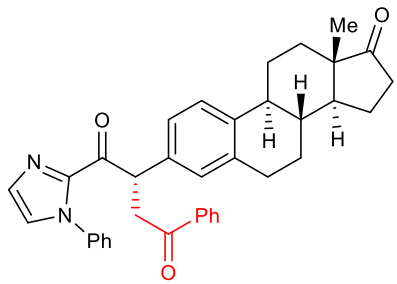
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 97% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 1 mL/min, 40 °C, t_r (major) = 8.9 min, t_r (minor) = 7.4 min). $[\alpha]_D^{22}$ = +167.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.48-7.38 (m, 5H), 7.36-7.19 (m, 7H), 7.18-7.15 (m, 1H), 6.10 (d, J = 16.5 Hz, 1H), 5.55 (dd, J_1 = 11.1 Hz, J_2 = 3.9 Hz, 1H), 3.61 (dd, J_1 = 18.0 Hz, J_2 = 10.8 Hz, 1H), 3.01 (dd, J_1 = 17.7 Hz, J_2 = 4.2 Hz, 1H), 2.07 (t, J = 6.0 Hz, 2H), 1.74 (s, 3H), 1.68-1.55 (m, 2H), 1.52-1.44 (m, 2H), 1.05 (s, 6H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 189.9, 143.2, 142.8, 139.1, 139.0, 136.7, 136.3, 130.5, 130.0, 129.2, 129.07, 129.03, 128.8, 127.5, 126.1, 48.8, 44.8, 40.2, 34.4, 33.9, 28.9, 21.9, 19.3. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): ν (cm^{-1}) 2929, 2863, 1682, 1593, 1496, 1449, 1402, 1363, 1309, 1260, 1174, 1148, 1100, 1062, 1027, 977, 940, 909, 843, 761, 734, 694, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{32}N_2O_2Na$ $[M+Na]^+$: 475.2356, found: 475.2351.



(*S*)-2-((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta

[*a*]phenanthren-3-yl)-4-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butane-1,4-dione (3y)

According to the typical procedure, electrolysis of the reaction mixture of estrone derived acyl imidazole **1o** (43.9 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 26.7 mg (48% yield) of **3y** as a white solid after electricity consumption of 2.4 F/mol.

Diastereoselectivity was determined by ^{1}H NMR analysis of the crude mixture as > 20:1. $[\alpha]_D^{22}$ = +213.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.96-7.91 (m, 2H), 7.59-7.53 (m, 1H), 7.48-7.40 (m, 5H), 7.29-7.16 (m, 6H), 7.14 (br s, 1H), 5.58 (dd, J_1 = 11.0 Hz, J_2 = 3.5 Hz, 1H), 3.98 (dd, J_1 = 18.2 Hz, J_2 = 11.0 Hz, 1H), 3.31 (dd, J_1 = 18.1 Hz, J_2 = 3.6 Hz, 1H), 2.95-2.85 (m, 2H), 2.46 (dd, J_1 = 19.9 Hz, J_2 = 9.4 Hz, 1H), 2.43-2.36 (m, 1H), 2.32-2.24 (m, 1H), 2.14-1.98 (m, 3H), 1.93-1.86 (m, 1H), 1.65-1.36 (m, 6H), 0.88 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 220.6, 198.2, 189.9, 143.1, 139.4, 138.9, 137.6, 136.8, 136.1, 133.5 130.0, 129.3, 129.1, 128.9, 128.8, 128.3, 127.5, 126.3, 126.2, 126.1, 50.8, 48.3, 48.2, 44.7, 43.6, 38.4, 36.1, 32.0, 29.8, 26.8, 26.1, 21.8, 14.0.

IR (film): ν (cm^{-1}) 3059, 2925, 2861, 1734, 1680, 1595, 1496, 1447, 1402, 1349, 1308, 1257, 1209, 1148, 1080, 1044, 1008, 941, 906, 821, 764, 732, 692, 560, 514.

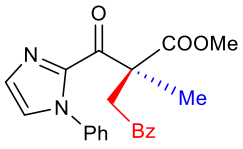
HRMS (ESI, *m*/*z*) calcd for $C_{37}H_{36}N_2O_3Na$ $[M+Na]^+$: 579.2618, found: 579.2612.

One-pot procedure and cleavege of imidazolyl group:

In a 5 mL ElectraSyn vial with a stirring bar, to the solution of acetophenone (72.0 mg, 0.60 mmol) and 2,6-lutidine (74.9 mg, 0.70 mmol) in anhydrous THF (1.0 mL), TMSOTf (111.1 mg, 0.5 mmol) was added dropwise at 0 °C. After stirring at the same temperature for 0.5 hour, MeOH (2.0 mL), $TBAPF_6$ (116.2 mg, 0.30 mmol), Δ-**Rh2** (4.5 mg, 0.005 mmol), and 2-acyl imidazole **1a** (26.2 mg, 0.10 mmol) were added in sequence. Following the typical procedure, the mixture was electrolyzed at a constant current of 0.6 mA with the consumption of 2.4 F/mol of electricity, to give product **3a** in 56% yield (21.2 mg) with 95% ee.

Methyl (*S*)-4-oxo-2,4-diphenylbutanoate (4)

According to our previously reported procedure,[6] the reaction of **3a** (30 mg, 0.079 mmol, 95% ee) afforded 17.9 mg (80% yield) of **4** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AS-H column, ee = 94% (HPLC: AS-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 40 °C, t_r (major) = 12.8 min, t_r (minor) = 15.7 min). $[\alpha]_D^{22}$ = +94.4° (*c* 1.0, CH_2Cl_2). Optical rotation and NMR spectra are in accord with literature report.[7]



Methyl (*S*)-2-methyl-4-oxo-4-phenyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)butanoate (6a)

According to the typical procedure, electrolysis of the reaction mixture of methyl 2-methyl-3-oxo-3-(1-phenyl-1*H*-imidazol-2-yl)propanoate **5a** (25.8 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 31.2 mg (83% yield) of **6a** as a yellow solid after electricity consumption of 2.2 F/mol.

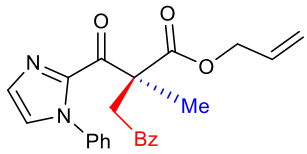
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 96% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C, t_r (major) = 7.9 min, t_r (minor) = 10.2 min). $[\alpha]_D^{22}$ = –5.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.00-7.94 (m, 2H), 7.62-7.41 (m, 8H), 7.14-7.11 (m, 2H), 4.56 (d, *J* = 18.3 Hz, 1H), 3.93 (d, *J* = 18.3 Hz, 1H), 3.67 (s, 3H), 1.53 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 186.6, 173.5, 141.8, 139.0, 137.3, 133.7, 129.3, 129.0, 128.8, 128.5, 126.6, 126.0, 55.5, 52.8, 46.3, 21.0. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): *v* (cm^{-1}) 3060, 2946, 2917, 1737, 1686, 1591, 1448, 1405, 1351, 1228, 1180, 1095, 1029, 955, 897, 855, 753, 689, 580, 539.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{20}N_2O_4Na$ $[M+Na]^+$: 399.1315, found: 399.1311.



Allyl (*S*)-2-methyl-4-oxo-4-phenyl-2-(1-phenyl-1*H*-imidazole-2-carbonyl)butanoate (6b)

According to the typical procedure, electrolysis of the reaction mixture of allyl 2-methyl-3-oxo-3-(1-phenyl-1*H*-imidazol-2-yl)propanoate **5b** (28.4 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy) silane **2a** (115.4 mg, 6.0 equiv) afforded 30.2 mg (75% yield) of **6b** as a yellow oil after electricity consumption of 2.4 F/mol.

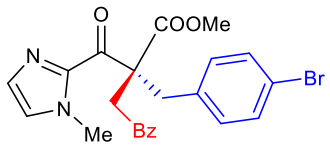
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 40 °C, t_r (major) = 9.0 min, t_r (minor) = 13.1 min). $[\alpha]_D^{22}$ = –10.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.00-7.94 (m, 2H), 7.62-7.40 (m, 8H), 7.14-7.11 (m, 2H), 5.90-5.74 (m, 1H), 5.26-5.12 (m, 2H), 4.64-4.55 (m, 3H), 3.94 (d, *J* = 18.0 Hz, 1H), 1.55 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 186.5, 172.7, 141.8, 139.0, 137.3, 133.7, 132.5, 129.30, 129.27, 129.0, 128.8, 128.5, 126.6, 126.1, 118.0, 66.2, 55.6, 46.3, 21.1.

IR (film): *v* (cm^{-1}) 3063, 2928, 1736, 1688, 1593, 1497, 1449, 1401, 1350, 1302, 1225, 1181, 1101, 960, 901, 852, 757, 690, 580, 535.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{22}N_2O_4Na$ $[M+Na]^+$: 425.1472, found: 425.1469.



Methyl (*S*)-2-(4-bromobenzyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-4-phenylbutanoate (6c)

According to the typical procedure, electrolysis of the reaction mixture of methyl 2-(4-bromobenzyl)-3-(1-methyl-1*H*-imidazol-2-yl)-3-oxopropanoate **5c** (36.8 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 39.6 mg (84% yield) of **6c** as a white solid after electricity consumption of 2.2 F/mol.

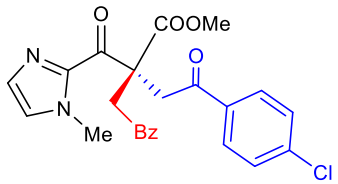
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 93% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C, t_r (major) = 12.6 min, t_r (minor) = 10.4 min). $[\alpha]_D^{22}$ = –165.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.86-7.80 (m, 2H), 7.60-7.52 (m, 1H), 7.46-7.38 (m, 2H), 7.36-7.30 (m, 2H), 7.02-6.95 (m, 2H), 6.86-6.80 (m, 2H), 4.36 (d, *J* = 18.6 Hz, 1H), 3.95 (s, 3H), 3.69 (d, *J* = 18.6 Hz, 1H), 3.63 (s, 3H), 3.49 (d, *J* = 14.1 Hz, 1H), 3.40 (d, *J* = 13.8 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.3, 186.9, 171.5, 142.0, 137.0, 136.3, 133.8, 132.4, 131.7, 128.9, 128.8, 128.4, 126.8, 121.2, 60.2, 52.7, 42.4, 38.0, 36.2.

IR (film): *v* (cm^{-1}) 3058, 2952, 2923, 1736, 1683, 1483, 1443, 1399, 1357, 1216, 1180, 1076, 1044, 1006, 941, 906, 848, 739, 690, 542, 509.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{21}BrN_2O_4Na$ $[M+Na]^+$: 491.0577, found: 491.0573.



Methyl (*R*)-4-(4-chlorophenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-2-(2-oxo-2-phenylethyl)butanoate (6d)

According to the typical procedure, electrolysis of the reaction mixture of 4-(4-chlorophenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxobutanoate **5d** (33.5 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 41.2 mg (91% yield) of **6d** as a yellow solid after electricity consumption of 2.4

F/mol. The reaction *catalyzed by Δ-**Rh2** (4.5 mg, 5 mol%)* formed **6d** in 46% with 87% ee.

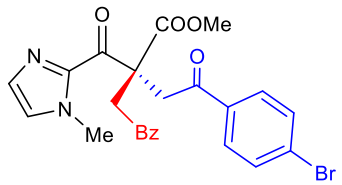
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 96% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 60:40, flow rate 1 mL/min, 40 °C, t_r (major) = 14.2 min, t_r (minor) = 17.1 min). $[\alpha]_D^{22}$ = +4.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.96-7.85 (m, 4H), 7.60-7.42 (m, 1H), 7.49-7.39 (m, 4H), 7.01-6.97 (m, 2H), 4.47 (d, *J* = 18.3 Hz, 1H), 4.42 (d, *J* = 17.7 Hz, 1H), 4.11 (d, *J* = 18.0 Hz, 1H), 4.10 (d, *J* = 18.0 Hz, 1H), 3.99 (s, 3H), 3.64 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 197.2, 187.3, 171.4, 142.0, 139.9, 137.2, 135.7, 133.7, 130.0, 129.2, 128.9, 128.6, 128.5, 126.8, 59.1, 52.9, 43.3, 43.2, 36.5.

IR (film): *v* (cm^{-1}) 2920, 2853, 1739, 1684, 1591, 1456, 1378, 1283, 1215, 1091, 1001, 908, 815, 757, 716, 529.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{21}ClN_2O_5Na$ $[M+Na]^+$: 475.1031, found: 475.1025.



Methyl (*R*)-4-(4-bromophenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-2-(2-oxo-2-phenylethyl)butanoate (6e)

According to the typical procedure, electrolysis of the reaction mixture of methyl 4-(4-bromophenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxobutanoate **5e** (37.9 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 34.9 mg (70% yield) of **6e** as a white solid after electricity consumption of 2.4 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 93% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 1 mL/min, 40 °C, t_r (major) = 12.3 min, t_r (minor) = 14.6 min). $[\alpha]_D^{22}$ = +3.0° (*c* 1.0, CH_2Cl_2).

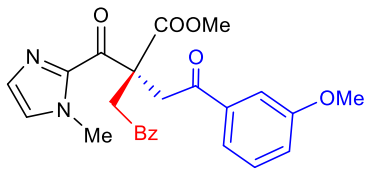
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.95-7.89 (m, 2H), 7.83-7.77 (m, 2H), 7.62-7.53 (m, 3H), 7.48-7.40 (m, 2H), 7.01-6.97 (m, 2H), 4.46 (d, *J* = 18.0 Hz, 1H), 4.41 (d, *J* = 17.7 Hz, 1H), 4.11 (d, *J* = 18.0 Hz, 1H), 4.09 (d, *J* = 18.0 Hz, 1H), 3.99 (s, 3H), 3.64 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 197.5, 187.3, 171.4, 142.0, 137.2, 136.1, 133.7, 132.2, 130.1,

128.9, 128.6, 128.5, 126.8, 59.1, 52.9, 43.3, 43.2, 36.5. (Missing one ^{13}C signal because the resolution of NMR spectrometer is not enough.)

IR (film): ν (cm^{-1}) 2953, 2921, 2851, 1739, 1679, 1584, 1443, 1397, 1352, 1214, 1182, 1072, 998, 967, 942, 907, 813, 757, 734, 690, 599, 561, 530.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{21}BrN_2O_5Na$ $[M+Na]^+$: 519.0526, found: 519.0521.



Methyl (*R*)-4-(3-methoxyphenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-2-(2-oxo-2-phenylethyl)butanoate (6f)

According to the typical procedure, electrolysis of the reaction mixture of methyl 4-(3-methoxyphenyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxobutanoate **5f** (33.0 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 36.5 mg (81% yield) of **6f** as a white solid after electricity consumption of 2.2 F/mol.

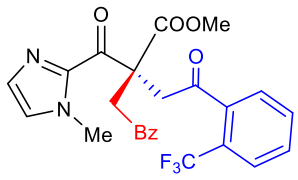
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 1 mL/min, 40 °C, t_r (major) = 15.1 min, t_r (minor) = 13.3 min). $[\alpha]_D^{22}$ = –55.0° (*c* 1.0, CH_2Cl_2).

^1H NMR (300 MHz, CD_2Cl_2) δ 7.96-7.89 (m, 2H), 7.60-7.50 (m, 2H), 7.49-7.40 (m, 3H), 7.35 (t, J = 8.0 Hz, 1H), 7.09 (ddd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, J_3 = 0.9 Hz, 8.1 Hz, 1H), 7.01-6.97 (m, 2H), 4.45 (d, J = 18.0 Hz, 1H), 4.44 (d, J = 18.0 Hz, 1H), 4.12 (d, J = 17.7 Hz, 1H), 4.11 (d, J = 18.0 Hz, 1H), 4.00 (s, 3H), 3.82 (s, 3H), 3.65 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.3, 198.1, 187.4, 171.5, 160.3, 142.1, 138.6, 137.2, 133.6, 129.9, 128.9, 128.6, 128.5, 126.8, 121.1, 119.9, 112.8, 59.1, 55.8, 52.8, 43.5, 43.3, 36.5.

IR (film): ν (cm^{-1}) 3063, 3003, 2951, 2839, 1739, 1678, 1589, 1438, 1399, 1350, 1258, 1210, 1084, 1043, 1003, 969, 943, 907, 782, 734, 689, 594, 563, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{24}N_2O_6Na$ $[M+Na]^+$: 471.1527, found: 471.1523.



Methyl (*R*)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-2-(2-oxo-2-(2-(trifluoromethyl) phenyl)ethyl)-4-phenylbutanoate (6g)

According to the typical procedure, electrolysis of the reaction mixture of methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-4-(2-(trifluoromethyl)phenyl)butanoate **5g** (36.8 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%)*, afforded 38.4 mg (79% yield) of **6g** as a white solid after electricity consumption of 2.2 F/mol.

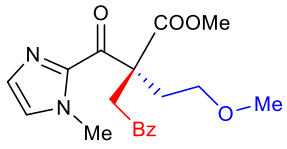
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 93% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C, t_r (major) = 12.6 min, t_r (minor) = 9.7 min). $[\alpha]_D^{22}$ = –12.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.98-7.92 (m, 2H), 7.70-7.53 (m, 5H), 7.52-7.43 (m, 2H), 7.06-7.03 (m, 1H), 7.03-7.01 (m, 1H), 4.444 (d, *J* = 18.9 Hz, 1H), 4.436 (d, *J* = 17.7 Hz, 1H), 4.18 (d, *J* = 18.0 Hz, 1H), 4.06 (d, *J* = 19.2 Hz, 1H), 3.99 (s, 3H), 3.68 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 202.0, 198.2, 187.0, 171.2, 142.0, 139.8 (q, *J* = 2.1 Hz), 137.2, 133.7, 132.3, 130.7, 129.0, 128.7, 128.5, 128.1, 127.1 (q, *J* = 31.5 Hz), 127.0 (q, *J* = 5.1 Hz), 126.9, 124.0 (q, *J* = 272.0 Hz), 58.9, 52.9, 47.9, 43.0, 36.5.

IR (film): *v* (cm^{-1}) 2954, 2923, 1740, 1679, 1589, 1445, 1399, 1351, 1312, 1275, 1215, 1168, 1129, 1066, 1038, 966, 941, 763, 692, 649, 598, 563, 409.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{21}F_3N_2O_5Na$ $[M+Na]^+$: 509.1295, found: 509.1292.



Methyl (*S*)-2-(2-methoxyethyl)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-4-oxo-4-phenylbutanoate (6h)

According to the typical procedure, electrolysis of the reaction mixture of methyl 4-methoxy-2-(1-methyl-1*H*-imidazole-2-carbonyl)butanoate **5h** (24.0 mg, 0.10 mmol) and trimethyl((1-

phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 26.8 mg (75% yield) of **6h** as a colorless oil after electricity consumption of 2.2 F/mol.

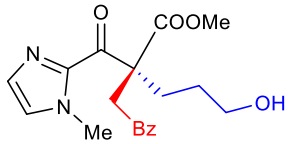
Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 40 °C, t_r (major) = 9.4 min, t_r (minor) = 8.8 min). $[\alpha]_D^{22}$ = –78.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.93-7.86 (m, 2H), 7.58-7.50 (m, 1H), 7.47-7.38 (m, 2H), 6.99-6.96 (m, 1H), 6.96-6.94 (m, 1H), 4.43 (d, *J* = 18.0 Hz, 1H), 4.08 (d, *J* = 18.0 Hz, 1H), 3.96 (s, 3H), 3.63 (s, 3H), 3.44 (t, *J* = 5.7 Hz, 2H), 3.06 (s, 3H), 2.37 (t, *J* = 5.7 Hz, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.1, 187.8, 172.4, 142.3, 137.3, 133.4, 128.8, 128.5, 128.4, 126.4, 69.1, 58.4, 57.8, 52.7, 43.9, 36.1, 33.3.

IR (film): *v* (cm^{-1}) 2925, 2872, 2811, 1736, 1683, 1591, 1443, 1399, 1356, 1290, 1217, 1188, 1111, 1001, 972, 907, 820, 757, 691, 571.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{22}N_2O_5Na$ $[M+Na]^+$: 381.1421, found: 381.1419.



Methyl (*S*)-5-hydroxy-2-(1-methyl-1*H*-imidazole-2-carbonyl)-2-(2-oxo-2-phenylethyl) pentanoate (6i)

According to the typical procedure, electrolysis of the reaction mixture of methyl 5-hydroxy-2-(1-methyl-1*H*-imidazole-2-carbonyl)pentanoate **5i** (24.0 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 24.7 mg (69% yield) of **6i** as a colorless oil after electricity consumption of 2.2 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 70:30, flow rate 1 mL/min, 40 °C, t_r (major) = 6.3 min, t_r (minor) = 7.3 min). $[\alpha]_D^{22}$ = –22.8° (*c* 1.0, CH_2Cl_2).

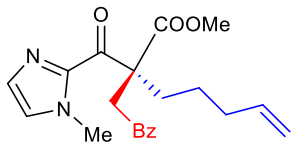
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.90-7.85 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.40 (m, 2H), 6.99-6.98 (m, 1H), 6.97-6.95 (m, 1H), 4.40 (d, *J* = 18.0 Hz, 1H), 3.94 (d, *J* = 18.0 Hz, 1H), 3.93 (s, 3H), 3.63 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 2H), 2.26-2.07 (m, 2H), 1.61 (br s, 1H), 1.58-1.42 (m, 2H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 198.1, 187.9, 172.4, 142.1, 137.1, 133.6, 128.9, 128.6, 128.3, 126.5,

62.9, 58.9, 52.6, 43.1, 36.2, 29.5, 28.1.

IR (film): ν (cm^{-1}) 3523, 2926, 2865, 1733, 1682, 1592, 1446, 1398, 1356, 1220, 1183, 1091, 1053, 1005, 942, 905, 757, 691, 565.

HRMS (ESI, *m*/*z*) calcd for $C_{19}H_{22}N_2O_5Na$ $[M+Na]^+$: 381.1421, found: 381.1419.



Methyl (*S*)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-2-(2-oxo-2-phenylethyl)hept-6-enoate (6j)

According to the typical procedure, electrolysis of the reaction mixture of methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)hept-6-enoate **5j** (25.0 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 20.3 mg (55% yield) of **6j** as a colorless oil after electricity consumption of 2.4 F/mol.

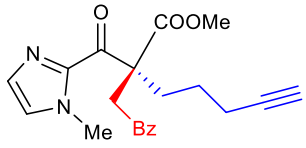
Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 94% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 40 °C, t_r (major) = 11.9 min, t_r (minor) = 11.2 min). $[\alpha]_D^{22}$ = –23.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.91-7.85 (m, 2H), 7.59-7.51 (m, 1H), 7.46-7.39 (m, 2H), 6.99-6.97 (m, 1H), 6.96-6.94 (m, 1H), 5.82-5.65 (m, 1H), 5.01-4.87 (m, 2H), 4.40 (d, *J* = 18.0 Hz, 1H), 3.945 (d, *J* = 18.0 Hz, 1H), 3.941 (s, 3H), 3.63 (s, 3H), 2.21-1.98 (m, 4H), 1.46-1.18 (m, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.2, 188.0, 172.4, 142.3, 138.7, 137.3, 135.6, 128.9, 128.6, 128.4, 126.5, 114.9, 59.2, 52.6, 43.1, 36.2, 34.2, 32.6, 24.2.

IR (film): ν (cm^{-1}) 3069, 2950, 2925, 2856, 1736, 1683, 1591, 1444, 1400, 1355, 1291, 1220, 1085, 996, 907, 758, 691, 565, 400.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{24}N_2O_4Na$ $[M+Na]^+$: 391.1628, found: 391.1622.



Methyl (*S*)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-2-(2-oxo-2-phenylethyl)hept-6-ynoate (6k)

According to the typical procedure, electrolysis of the reaction mixture of methyl 2-(1-methyl-1*H*-imidazole-2-carbonyl)hept-6-ynoate **5k** (24.8 mg, 0.10 mmol) and trimethyl((1-

phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv) afforded 25.1 mg (69% yield) of **6k** as a colorless oil after electricity consumption of 2.2 F/mol.

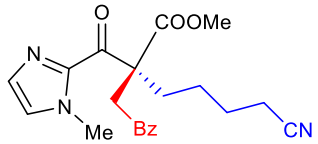
Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 90% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 34.9 min, t_r (minor) = 33.1 min). $[\alpha]_D^{22}$ = –37.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.92-7.87 (m, 2H), 7.59-7.52 (m, 1H), 7.47-7.39 (m, 2H), 7.00-6.97 (m, 1H), 6.97-6.94 (m, 1H), 4.43 (d, *J* = 18.0 Hz, 1H), 3.95 (s, 3H), 3.93 (d, *J* = 18.0 Hz, 1H), 3.64 (s, 3H), 2.31-2.07 (m, 4H), 1.92 (t, *J* = 5.4 Hz, 1H), 1.60-1.35 (m, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.1, 187.7, 172.3, 142.2, 137.3, 133.6, 128.9, 128.6, 128.4, 126.5, 84.1, 68.7, 59.0, 52.7, 43.2, 36.2, 32.4, 24.2, 19.0.

IR (film): *v* (cm^{-1}) 3289, 2950, 1735, 1683, 1591, 1445, 1399, 1355, 1293, 1218, 1179, 1085, 998, 937, 905, 758, 690, 640, 566, 523, 481.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{22}N_2O_4Na$ $[M+Na]^+$: 389.1472, found: 389.1469.



Methyl (*S*)-6-cyano-2-(1-methyl-1*H*-imidazole-2-carbonyl)-2-(2-oxo-2-phenylethyl)hexanoate (6l)

According to the typical procedure, electrolysis of the reaction mixture of methyl 6-cyano-2-(1-methyl-1*H*-imidazole-2-carbonyl)hexanoate **5l** (26.3 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 21.0 mg (55% yield) of **6l** as a colorless oil after electricity consumption of 2.2 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 91% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 40 °C, t_r (major) = 14.8 min, t_r (minor) = 19.6 min). $[\alpha]_D^{22}$ = –59.2° (*c* 1.0, CH_2Cl_2).

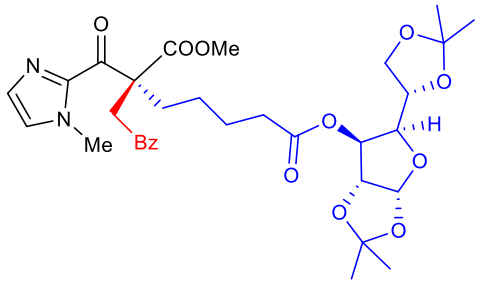
^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.92-7.85 (m, 2H), 7.61-7.52 (m, 1H), 7.47-7.39 (m, 2H), 7.01-6.98 (m, 1H), 6.98-6.95 (m, 1H), 4.42 (d, *J* = 18.0 Hz, 1H), 3.93 (s, 3H), 3.92 (d, *J* = 17.7 Hz, 1H), 3.64 (s, 3H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.25-2.03 (m, 2H), 1.70-1.56 (m, 2H), 1.51-1.25 (m, 2H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 198.1, 187.7, 172.3, 142.1, 137.2, 133.7, 128.9, 128.7, 128.4, 126.7,

119.9, 59.1, 52.7, 43.1, 36.2, 32.3, 26.0, 24.0, 17.2.

IR (film): ν (cm^{-1}) 2950, 2870, 2246, 1736, 1683, 1591, 1450, 1400, 1356, 1286, 1220, 1174, 1091, 1044, 1001, 944, 906, 852, 759, 692, 567.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{23}N_3O_4Na$ $[M+Na]^+$: 404.1581, found: 404.1578.



7-((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-methyl (*S*)-2-(1-methyl-1*H*-imidazole-2-carbonyl)-2-(2-oxo-2-phenylethyl) heptanedioate (6m)

According to the typical procedure, electrolysis of the reaction mixture of glucofuranose derived acyl imidazole **5m** (52.5 mg, 0.10 mmol) and trimethyl((1-phenylvinyl)oxy)silane **2a** (115.4 mg, 6.0 equiv), *catalyzed by Δ-**Rh1** (4.3 mg, 5 mol%),* afforded 38.7 mg (60% yield) of **6m** as a yellow solid after electricity consumption of 2.0 F/mol.

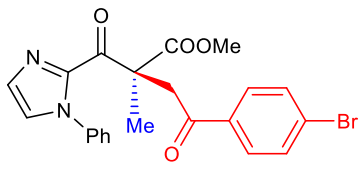
Diastereoselectivity was determined by HPLC analysis using a Chiralpak IC column, de = 94% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 40 °C, t_r (major) = 39.2 min, t_r (minor) = 34.7 min). $[\alpha]_D^{22}$ = –32.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.90-7.85 (m, 2H), 7.58-7.53 (m, 1H), 7.46-7.40 (m, 2H), 6.99-6.98 (m, 1H), 6.97-6.95 (m, 1H), 5.86 (d, *J* = 3.7 Hz, 1H), 5.14 (d, *J* = 2.7 Hz, 1H), 4.45 (d, *J* = 3.8 Hz, 1H), 4.39 (d, *J* = 18.0 Hz, 1H), 4.22-4.14 (m, 2H), 4.05-4.01 (m, 1H), 3.98-3.93 (m, 1H), 3.93 (s, 3H), 3.91 (d, *J* = 18.0 Hz, 1H), 3.62 (s, 3H), 2.30 (t, *J* = 7.6 Hz, 2H), 2.19-2.00 (m, 2H), 1.64-1.56 (m, 2H), 1.49 (s, 3H), 1.37 (s, 3H), 1.35-1.20 (m, 2H), 1.29 (s, 3H), 1.28 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 198.1, 187.8, 172.4, 172.3, 142.0, 137.1, 133.6, 128.9, 128.6, 128.3, 126.5, 112.4, 109.4, 105.5, 83.7, 80.0, 76.2, 72.8, 67.2, 59.0, 52.6, 43.0, 36.2, 34.1, 32.5, 26.79, 26.77, 26.3, 25.30, 25.27, 24.3.

IR (film): ν (cm^{-1}) 2987, 2942, 2871, 1739, 1685, 1596, 1509, 1453, 1401, 1377, 1214, 1157, 1071, 1018, 945, 903, 846, 759, 734, 692, 565, 512.

HRMS (ESI, *m*/*z*) calcd for $C_{33}H_{42}N_2O_{11}Na$ $[M+Na]^+$: 665.2681, found: 665.2679.



Methyl (*S*)-4-(4-bromophenyl)-2-methyl-4-oxo-2-(1-phenyl-1*H*-imidazole-2-carbonyl) butanoate (6n)

According to the typical procedure, electrolysis of the reaction mixture of methyl 2-methyl-3-oxo-3-(1-phenyl-1*H*-imidazol-2-yl)propanoate **5a** (25.8 mg, 0.10 mmol) and ((1-(4-bromophenyl)vinyl)oxy)trimethylsilane **2l** (162.7 mg, 6.0 equiv) afforded 37.2 mg (82% yield) of **6a** as a yellow solid after electricity consumption of 2.4 F/mol.

Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 40 °C, t_r (major) = 12.2 min, t_r (minor) = 14.0 min). $[\alpha]_D^{22}$ = –42.6° (*c* 1.0, CH_2Cl_2).

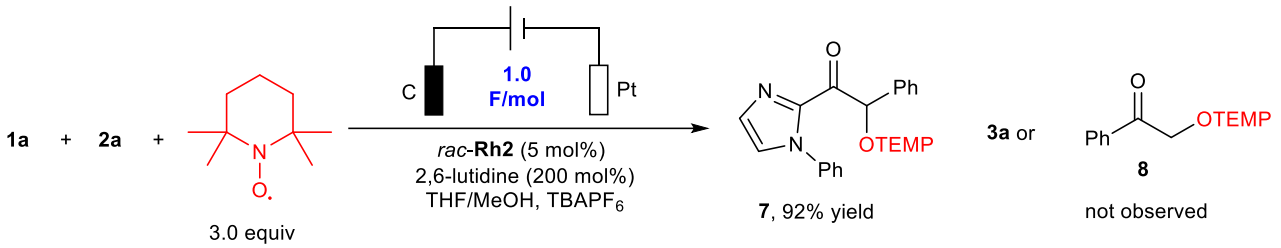
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.86-7.82 (m, 2H), 7.64-7.59 (m, 2H), 7.54-7.45 (m, 3H), 7.44-7.39 (m, 2H), 7.15-7.11 (m, 2H), 4.51 (d, *J* = 18.2 Hz, 1H), 3.88 (d, *J* = 18.2 Hz, 1H), 3.66 (s, 3H), 1.52 (s, 3H).

^{13}C NMR (125 MHz, CD_2Cl_2) δ 197.2, 186.3, 173.4, 141.5, 138.8, 135.9, 132.2, 130.0, 129.30, 129.26, 128.8, 128.7, 126.6, 125.9, 55.4, 52.8, 46.2, 21.0.

IR (film): *v* (cm^{-1}) 2922, 2851, 1736, 1690, 1583, 1495, 1449, 1398, 1347, 1300, 1232, 1180, 1101, 1070, 1028, 1002, 958, 903, 855, 813, 760, 691, 527, 453.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{19}BrN_2O_4Na$ $[M+Na]^+$: 479.0403, found: 479.0394.

5. Mechanistic Studies



According to the typical procedure, 3.0 equiv of 2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO) was added to the reaction mixture of **1a** and **2a**. After electrolysis of *1.0 F/mol*, the reaction afforded compound **7** in 92% yield (92% current efficiency) as a white solid. **3a** or compound **8** was not observed. This result is consistent with the cyclic voltammograms (Fig. 4a in the main text), indicating that the intermediate rhodium enolate complex is the first species to be oxidized under the presented electrochemical conditions.

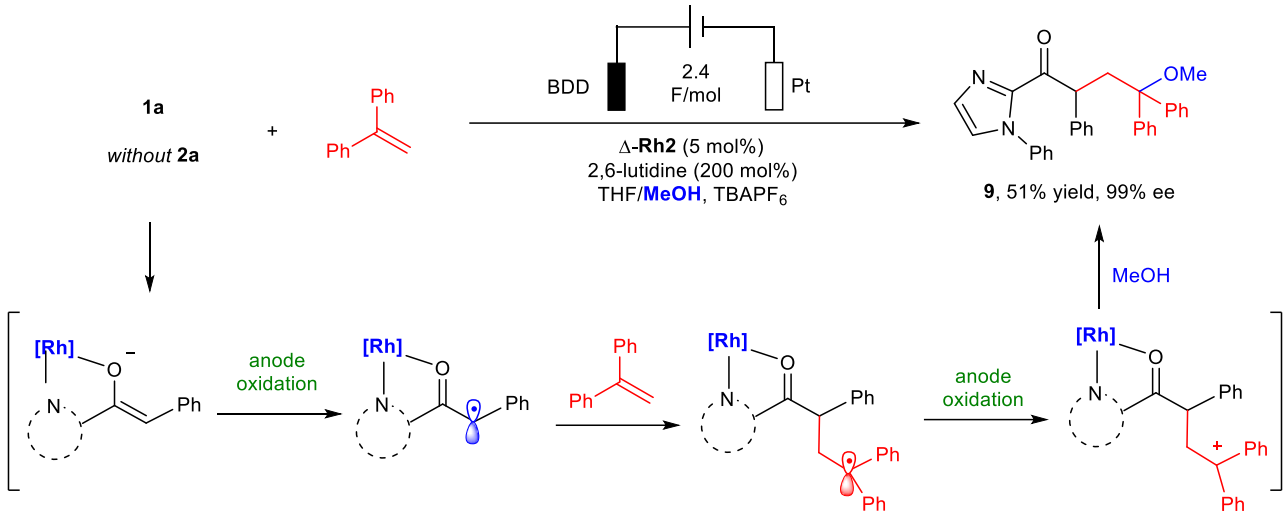
2-Phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)-2-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)ethan-1-one (7)

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.54-7.48 (m, 2H), 7.45-7.35 (m, 3H), 7.32-7.21 (m, 4H), 7.19-7.16 (m, 1H), 7.05-6.99 (m, 2H), 6.64 (s, 1H), 1.60-1.22 (m, 6H), 1.18 (s, 3H), 1.06 (s, 6H), 0.77 (s, 3H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 189.2, 142.7, 138.5, 138.4, 130.1, 129.2, 128.9, 128.51, 128.45, 127.9, 127.6, 125.8, 89.9, 60.2, 59.9, 40.5, 34.0, 33.5, 20.2, 17.5.

IR (film): ν (cm^{-1}) 2968, 2930, 2873, 1693, 1595, 1496, 1448, 1397, 1304, 1241, 1136, 1054, 1020, 956, 918, 881, 828, 788, 759, 694, 621, 553, 524.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{32}N_3O_2Na$ $[M+H]^+$: 418.2489, found: 418.2487.



According to the typical procedure, the reaction of **1a** with 6.0 equiv 1,1-diphenyl ethylene in the absence of **2a** furnished a three-component product **9** in 51% yield with 99% ee. The formation of **9** was assumed to go through the trapping of rhodium bound radical intermediate by 1,1-diphenyl ethylene, followed by further oxidation and methanol trapping. This result is indicative of intermediate rhodium bound radical cation **[Rh2-1a]**$^{\cdot+}$.

4-Methoxy-2,4,4-triphenyl-1-(1-phenyl-1*H*-imidazol-2-yl)butan-1-one (9)

Enantiomeric excess was established by HPLC analysis using a Chiralpak IG column, ee = 99% (HPLC: IG, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 40 °C, t_r (major) = 6.4 min, t_r (minor) = 7.6 min). $[\alpha]_D^{22}$ = +157.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.42-7.21 (m, 14H), 7.20-7.09 (m, 5H), 7.05-7.03 (m, 1H), 7.02-6.96 (m, 2H), 5.31 (dd, J_1 = 9.3 Hz, J_2 = 1.5 Hz, 1H), 3.59 (dd, J_1 = 14.4 Hz, J_2 = 9.3 Hz, 1H), 2.91 (s, 3H), 2.57 (dd, J_1 = 14.4 Hz, J_2 = 1.5 Hz, 1H).

^{13}C NMR (75 MHz, CD_2Cl_2) δ 188.8, 145.3, 144.7, 142.5, 141.1, 138.6, 129.3, 128.6, 128.5, 128.3, 127.9, 127.5, 127.4, 127.2, 127.1, 126.8, 126.6, 126.0, 82.4, 50.4, 47.3, 38.2.

IR (film): ν (cm^{-1}) 3058, 2928, 1683, 1596, 1493, 1446, 1399, 1311, 1261, 1152, 1073, 1030, 956, 908, 859, 758, 696, 618, 582, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{32}H_{28}N_2O_2Na$ $[M+Na]^+$: 495.2043, found: 495.2037.

6. Single Crystal X-Ray Diffraction

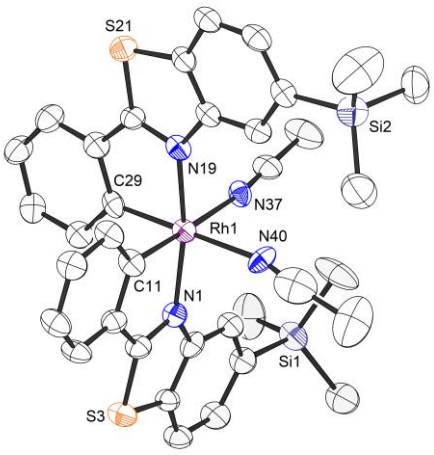
6.1 Single-crystal X-ray analysis of Λ-Rh2

Single crystals of Λ-**Rh2** suitable for X-ray diffraction were obtained by slow diffusion of a solution of Λ-**Rh2** (20 mg) in CH_2Cl_2 (0.5 mL) layered with Et_2O (1.0 mL) at room temperature for several days in a NMR tube.

Data was collected with an STOE STADIVARI diffractometer equipped with 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 100(2) K. Data were collected on one crystal with two different orientaions to maximize completion. Absorption effects were corrected semi-empirical using multiscanned reflexions (STOE LANA, absorption correction by scaling of reflection intensities). XPREP was used to get a combined scaled data set.

Cell constants were refined using 68239 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-2018/3 (Sheldrick, 2018). 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. Absolute structure was determined: The Flack parameter refined to -0.014(7). The structure is shown below:



Crystal data and structure refinement for Λ-**Rh2** are listed below:

Crystal data		
Identification code	RHSTMS_scaled	
Habitus, colour	prism, light yellow	
Crystal size	0.16 x 0.10 x 0.03 mm^3	
Crystal system	Triclinic	
Space group	P1	Z = 2
Unit cell dimensions	a = 12.4889(2) Å	α = 103.445(1)°.
	b = 13.5038(2) Å	β = 103.530(1)°.
	c = 14.5543(2) Å	γ = 90.419(1)°.
Volume	2316.08(6) $Å^3$	
Cell determination	68239 peaks with Theta 3.2 to 76.1°.	
Empirical formula	C_{38} H_{42} Cl_4 F_6 N_4 P Rh S_2 Si_2	
Moiety formula	C_{36} H_{38} N_4 Rh S_2 Si_2, F_6 P, 2(C H_2 Cl_2)	
Formula weight	1064.73	
Density (calculated)	1.527 Mg/m^3	
Absorption coefficient	7.266 mm^{-1}	
F(000)	1080	

Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54186 Å
Temperature	100(2) K
Theta range for data collection	3.218 to 75.747°.
Index ranges	-15<=h<=15, -16<=k<=16, -18<=l<=18
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016)[8]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[9]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[10]
	X-Area LANA 1.68.2.0 (STOE, 2016)[11]
	XPREP (BRUKER, 2014)[12]

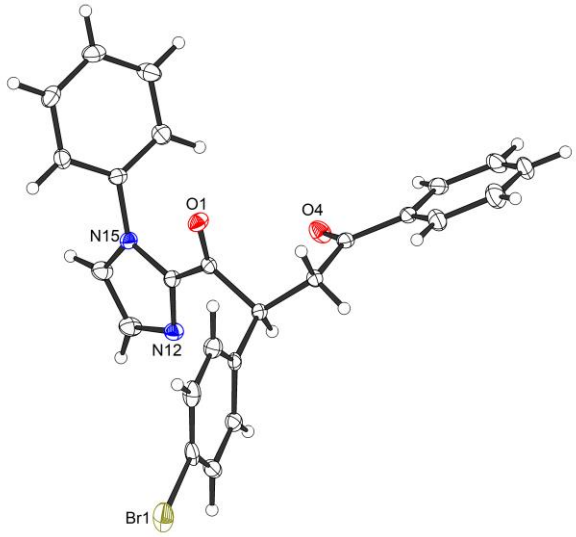
Solution and refinement:

Reflections collected	134932
Independent reflections	16790 [R(int) = 0.0670]
Completeness to theta = 67.686°	100.0 %
Observed reflections	13116[I > 2σ(I)]
Reflections used for refinement	16790
Absorption correction	Semi-empirical from equivalents[11]
Max. and min. transmission	1.0000 and 0.1769
Flack parameter (absolute struct.)	-0.014(7)[13]
Largest diff. peak and hole	0.743 and -0.555 $e.Å^{-3}$
Solution	intrinsic phases[14]
Refinement	Full-matrix least-squares on F^2 [15]
Treatment of hydrogen atoms	Calculated positions, constr ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[14]
	SHELXL-2018/3 (Sheldrick, 2018)[14]
	DIAMOND (Crystal Impact)[16]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[17]
Data / restraints / parameters	16790 / 103 / 1117
Goodness-of-fit on F^2	0.932
R index (all data)	wR2 = 0.0952
R index conventional [I>2sigma(I)]	R1 = 0.0442

6.2 Single-crystal X-ray analysis of 3g

Single crystals of **3g** suitable for X-ray diffraction were obtained by slow diffusion of a solution of **3g** (30 mg) in CH_2Cl_2 (0.5 mL) layered with *n*-hexane (1.0 mL) at room temperature for several days in a NMR tube.

Data was collected with an STOE STADIVARI diffractometer equipped with 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 100(2) K. Absorption effects were corrected semi-empirical using multiscanned reflexions (STOE LANA, absorption correction by scaling of reflection intensities.). Cell constants were refined using 35530 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-2018/3 (Sheldrick, 2018). 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. The absolute configuration of the molecule in the crystal could be determined: The Flack parameter refined to -0.016(4). The structure is shown below:



Crystal data and structure refinement for **3g** are listed below:

Crystal data

Identification code	hxqL160R	
Habitus, colour	nugget, colourless	
Crystal size	0.49 x 0.36 x 0.21 mm^3	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	Z = 4
Unit cell dimensions	a = 12.1520(2) Å	α = 90°.
	b = 12.7735(3) Å	β = 90°.
	c = 13.4315(2) Å	γ = 90°.
Volume	2084.89(7) $Å^3$	
Cell determination	35530 peaks with Theta 3.3 to 76.2°.	
Empirical formula	C_{25} H_{19} Br N_2 O_2	
Moiety formula	C_{25} H_{19} Br N_2 O_2	
Formula weight	459.33	
Density (calculated)	1.463 Mg/m^3	
Absorption coefficient	2.881 mm^{-1}	
F(000)	936	

Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54186 Å
Temperature	100(2) K
Theta range for data collection	4.908 to 75.603°.
Index ranges	-15<=h<=12, -13<=k<=15, -15<=l<=16
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016)[8]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[9]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[10]
	X-Area LANA 1.68.2.0 (STOE, 2016)[11]

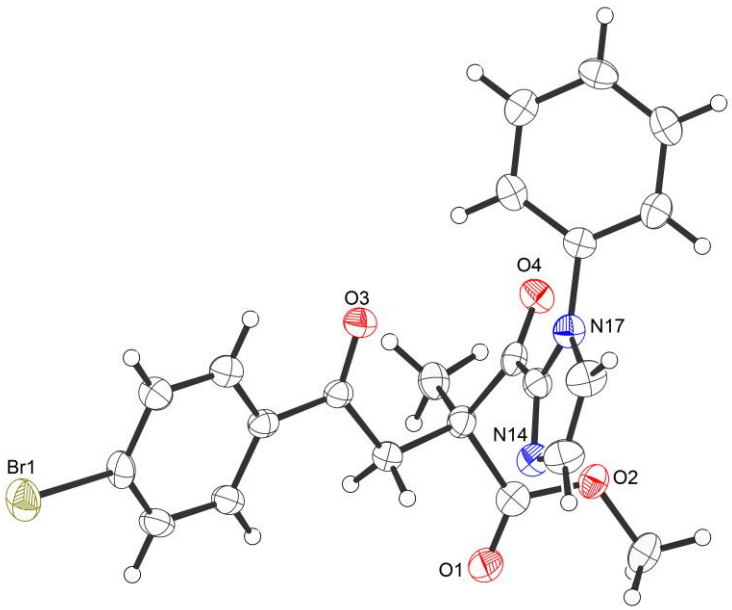
Solution and refinement:

Reflections collected	20804
Independent reflections	4273 [R(int) = 0.0193]
Completeness to theta = 67.686°	99.9 %
Observed reflections	4266[I > 2σ(I)]
Reflections used for refinement	4273
Absorption correction	Semi-empirical from equivalents[11]
Max. and min. transmission	0.5407 and 0.2622
Flack parameter (absolute struct.)	-0.016(4)[13]
Largest diff. peak and hole	0.302 and -0.757 $e.Å^{-3}$
Solution	intrinsic phases[14]
Refinement	Full-matrix least-squares on F^2 [15]
Treatment of hydrogen atoms	Calculated positions, constr. ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[14]
	SHELXL-2018/3 (Sheldrick, 2018)[15]
	DIAMOND (Crystal Impact)[16]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[17]
Data / restraints / parameters	4273 / 0 / 271
Goodness-of-fit on F^2	1.104
R index (all data)	wR2 = 0.0590
R index conventional [I>2sigma(I)]	R1 = 0.0228

6.3 Single-crystal X-ray analysis of 6n

Single crystals of **6n** suitable for X-ray diffraction were obtained by slow diffusion of a solution of **6n** (30 mg) in CH_2Cl_2 (0.5 mL) layered with *n*-hexane (1.0 mL) at –20 ^oC for several days in a NMR tube.

Data was collected with an STOE STADIVARI diffractometer equipped with with CuK_a radiation, a graded multilayer mirror monochromator (l = 1.54186 Å) and DECTRIS PILATUS 300K detector using an oil-coated shock-cooled crystal at 100(2) K. Absorption effects were corrected semi-empirical using multiscanned reflexions (STOE LANA, absorption correction by scaling of reflection intensities.). Cell constants were refined using 20187 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-2018/3 (Sheldrick, 2018). 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. The absolute configuration of the molecule in this crystal was established: The Flack parameter refined to -0.032(12). The structure is shown below:



Crystal data and structure refinement for **6n** are listed below:

Crystal data

Identification code	hxqM124	
Habitus, colour	needle, colourless	
Crystal size	0.24 x 0.03 x 0.02 mm^3	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	Z = 4
Unit cell dimensions	a = 7.0991(3) Å	α = 90°.
	b = 14.6639(9) Å	β = 90°.
	c = 19.2121(9) Å	γ = 90°.
Volume	1999.99(18) $Å^3$	
Cell determination	20187 peaks with Theta 3.8 to 75.4°.	
Empirical formula	C_{22} H_{19} Br N_2 O_4	
Moiety formula	C_{22} H_{19} Br N_2 O_4	
Formula weight	455.30	
Density (calculated)	1.512 Mg/m^3	
Absorption coefficient	3.070 mm^{-3}	
F(000)	928	

Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54186 Å
Temperature	100(2) K
Theta range for data collection	3.792 to 75.320°.
Index ranges	-8<=h<=8, -16<=k<=18, -13<=l<=23
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016)[8]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[9]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[10]
	X-Area LANA 1.68.2.0 (STOE, 2016)[11]

Solution and refinement:

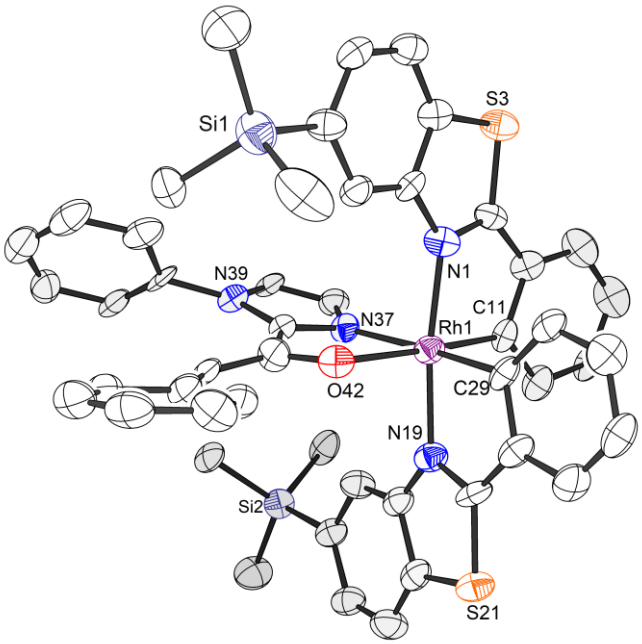
Reflections collected	18971
Independent reflections	4044 [R(int) = 0.0506]
Completeness to theta = 67.686°	99.6 %
Observed reflections	3407[I > 2σ(I)]
Reflections used for refinement	4044
Absorption correction	Semi-empirical from equivalents[11]
Max. and min. transmission	0.6496 and 0.1848
Flack parameter (absolute struct.)	-0.032(12)[13]
Largest diff. peak and hole	0.545 and -0.312 $e.Å^{-3}$
Solution	intrinsic phases[14]
Refinement	Full-matrix least-squares on F^2 [15]
Treatment of hydrogen atoms	Calculated positions, constr. ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[14]
	SHELXL-2018/3 (Sheldrick, 2018)[15]
	DIAMOND (Crystal Impact)[16]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[17]
Data / restraints / parameters	4044 / 0 / 264
Goodness-of-fit on F^2	1.006
R index (all data)	wR2 = 0.0994
R index conventional [I>2sigma(I)]	R1 = 0.0402

6.4 Single-crystal X-ray analysis of Rh2-1a

Rh2-1a was synthesized according to our previous method but employing a higher temperature.[6] Single crystals of **Rh2-1a** suitable for X-ray diffraction were obtained by slow diffusion of a solution of **Rh2-1a** (20 mg) in CH_2Cl_2 (0.5 mL) layered with Et_2O (1.0 mL) at room temperature for several days in a NMR tube.

Data was collected with an STOE STADIVARI diffractometer equipped with 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 100(2) K. A "twin integration" was performed. Absorption effects were corrected semi-empirical using multiscanned reflexions (STOE LANA, absorption correction by scaling of reflection intensities.). Cell constants were refined using 28713 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-2018/3 (Sheldrick, 2018) as a two component twin. 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.

The structure is shown below:



Crystal data and structure refinement for **Rh2-1a** are listed below:

Crystal data

Identification code	hxqM39_5	
Habitus, colour	neeedle, pale yellow	
Crystal size	0.23 x 0.04 x 0.04 mm^3	
Crystal system	Triclinic	
Space group	P-1	Z = 4
Unit cell dimensions	a = 11.8377(5) Å	α = 81.120(3)°.
	b = 19.7310(7) Å	β = 81.221(3)°.
	c = 19.8024(8) Å	γ = 78.747(3)°.
Volume	4446.0(3) $Å^3$	
Cell determination	28713 peaks with Theta 3.8 to 75.5°.	
Empirical formula	C_{49} H_{45} N_4 O Rh S_2 Si_2	
Moiety formula	C_{49} H_{45} N_4 O Rh S_2 Si_2	
Formula weight	929.10	
Density (calculated)	1.388 Mg/m^3	
Absorption coefficient	4.823 mm^{-1}	
F(000)	1920	

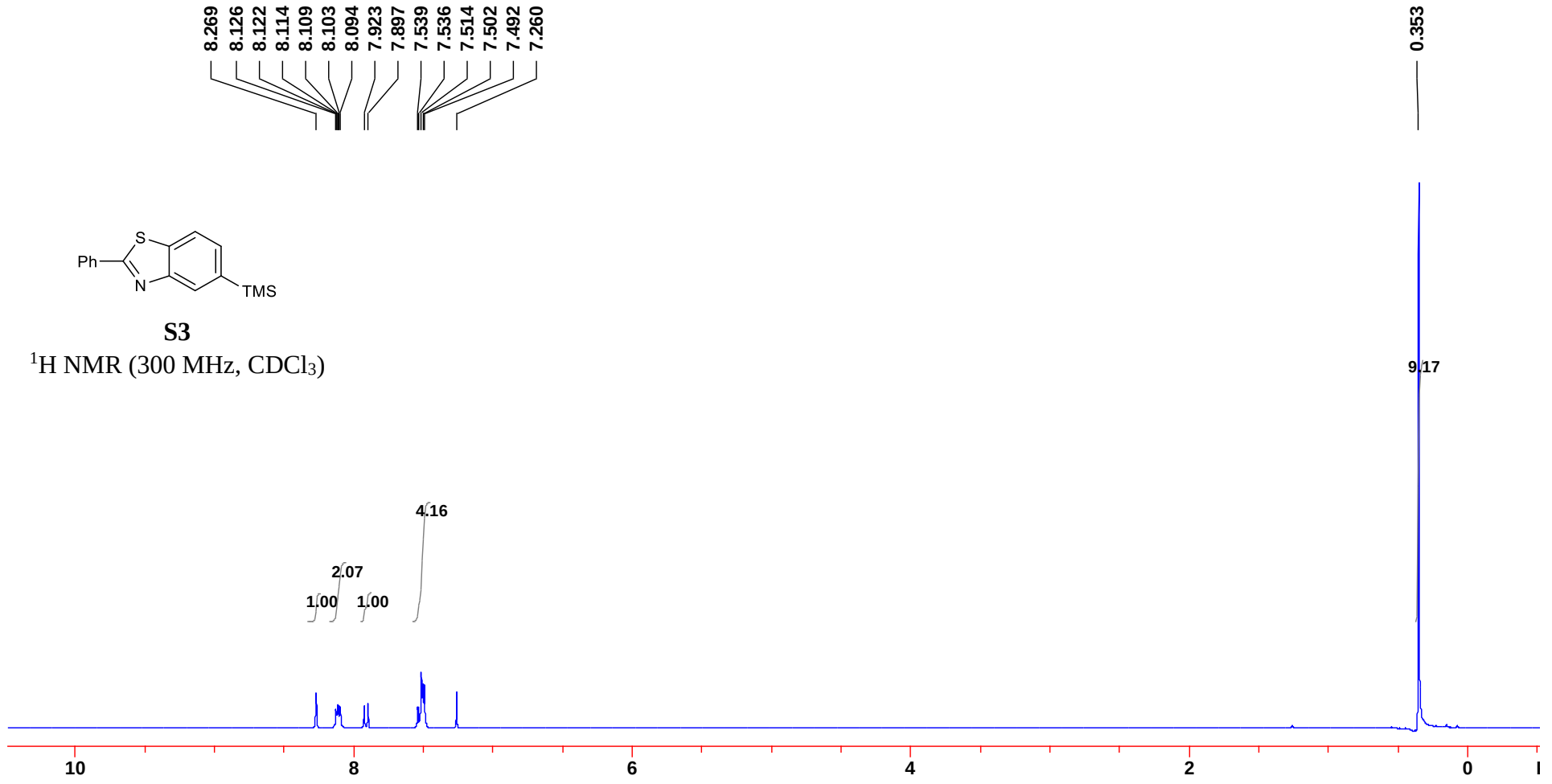
Data collection:

Diffractometer type	STOE STADIVARI
Wavelength	1.54186 Å
Temperature	100(2) K
Theta range for data collection	3.023 to 75.866°.
Index ranges	-10<=h<=14, -24<=k<=24, -24<=l<=24
Data collection software	X-Area Pilatus3_SV 1.31.127.0 (STOE, 2016)[8]
Cell refinement software	X-Area Recipe 1.33.0.0 (STOE, 2015)[9]
Data reduction software	X-Area Integrate 1.71.0.0 (STOE, 2016)[10]
	X-Area LANA 1.68.2.0 (STOE, 2016)[11]

Solution and refinement:

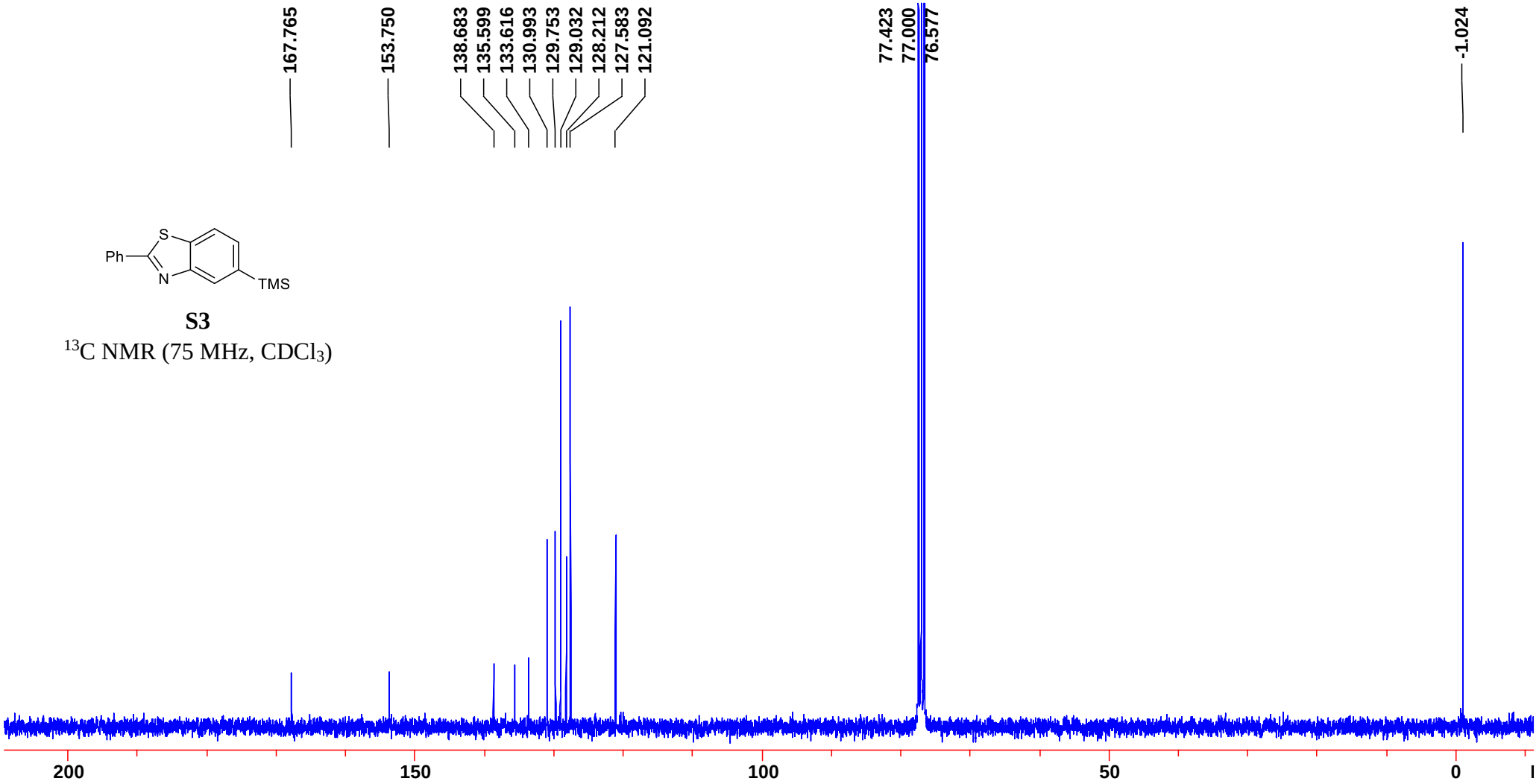
Reflections collected	87185
Independent reflections	28982 [R(int) = 0.0895]
Completeness to theta = 67.686°	92.3 %
Observed reflections	15724[I > 2σ(I)]
Reflections used for refinement	28982
Absorption correction	Semi-empirical from equivalents[11]
Max. and min. transmission	0.87 and 0.38
Largest diff. peak and hole	1.331 and -1.224 e.$Å^{-3}$
Solution	intrinsic phases[14]
Refinement	Full-matrix least-squares on F^2 [15]
Treatment of hydrogen atoms	Calculated positions, constr. ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[14]
	SHELXL-2018/3 (Sheldrick, 2018)[15]
	DIAMOND (Crystal Impact)[16]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[17]
Data / restraints / parameters	28982 / 1302 / 1076
Goodness-of-fit on F^2	0.928
R index (all data)	wR2 = 0.1938
R index conventional [I>2sigma(I)]	R1 = 0.0726

7. NMR Spectra of New Compounds



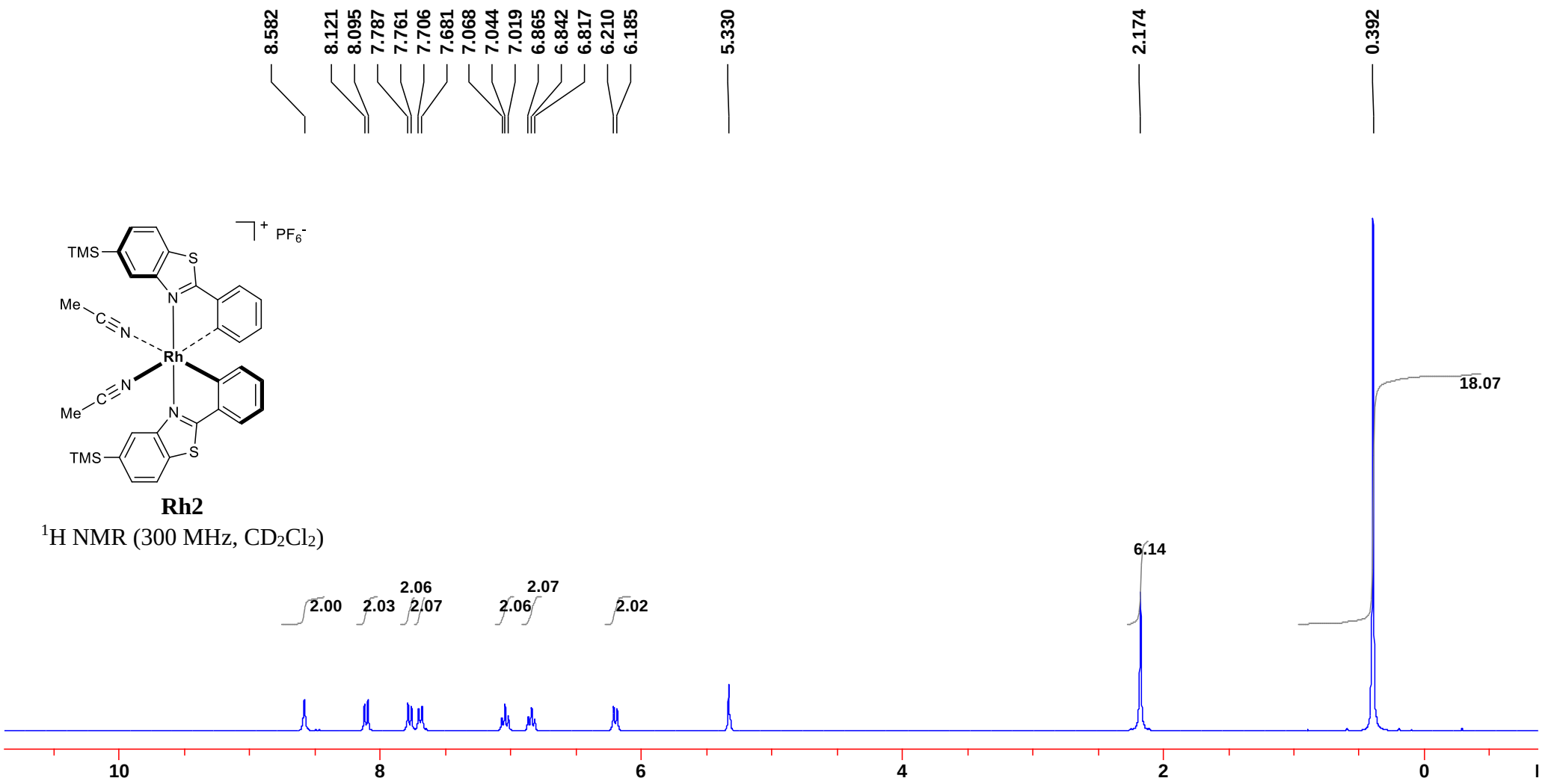
S3

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



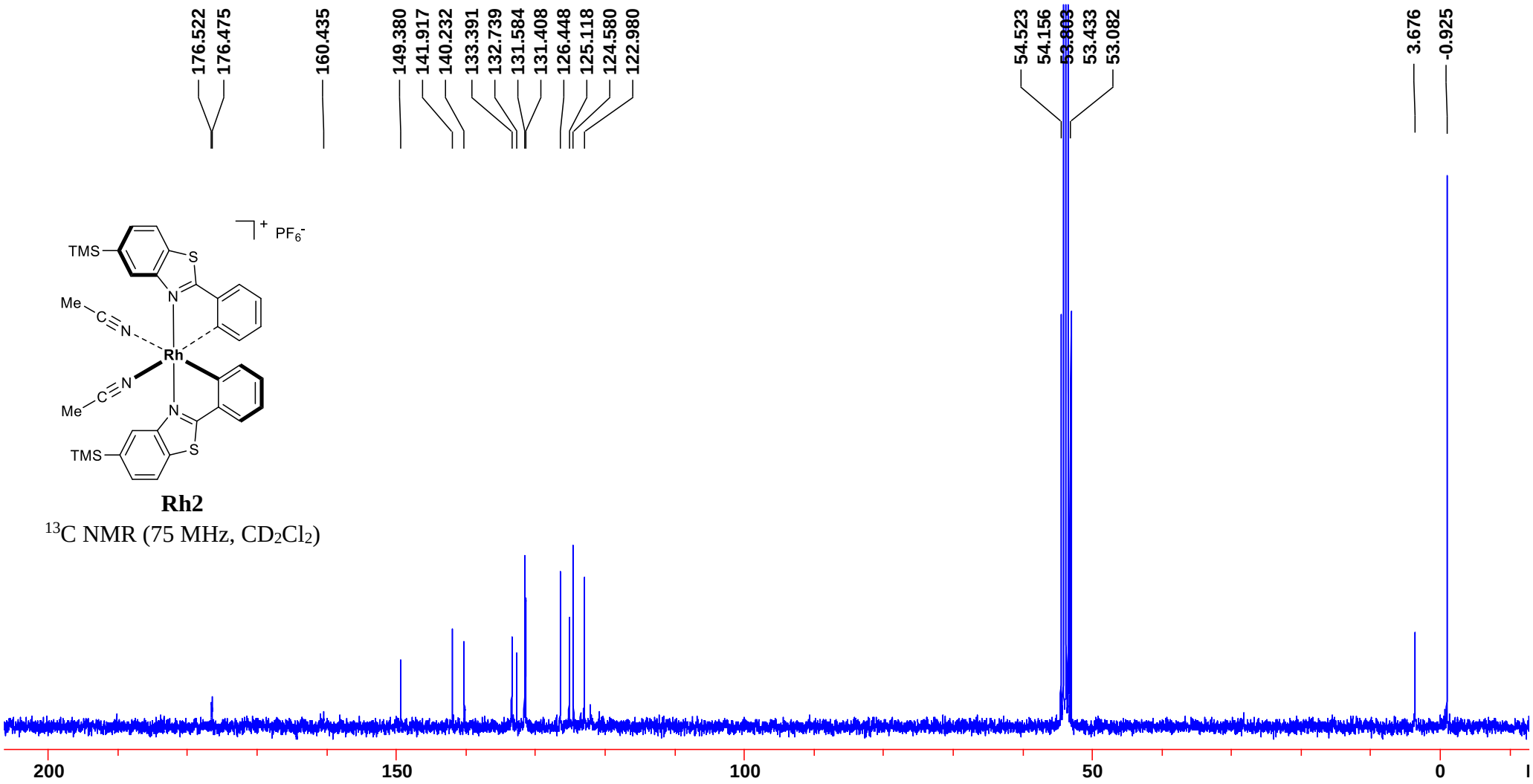
S3

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



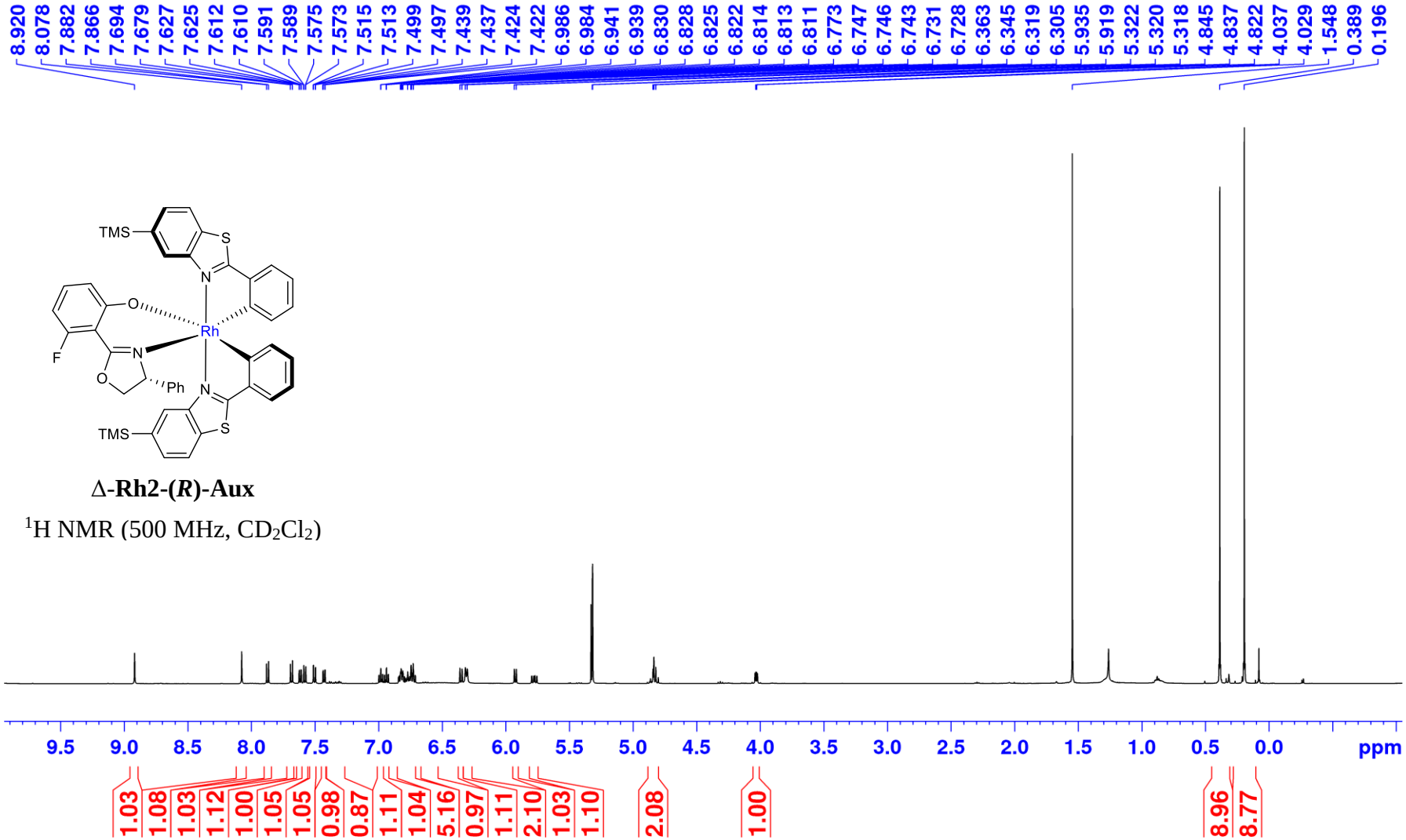
Rh2

^{1}H NMR (300 MHz, CD_2Cl_2)



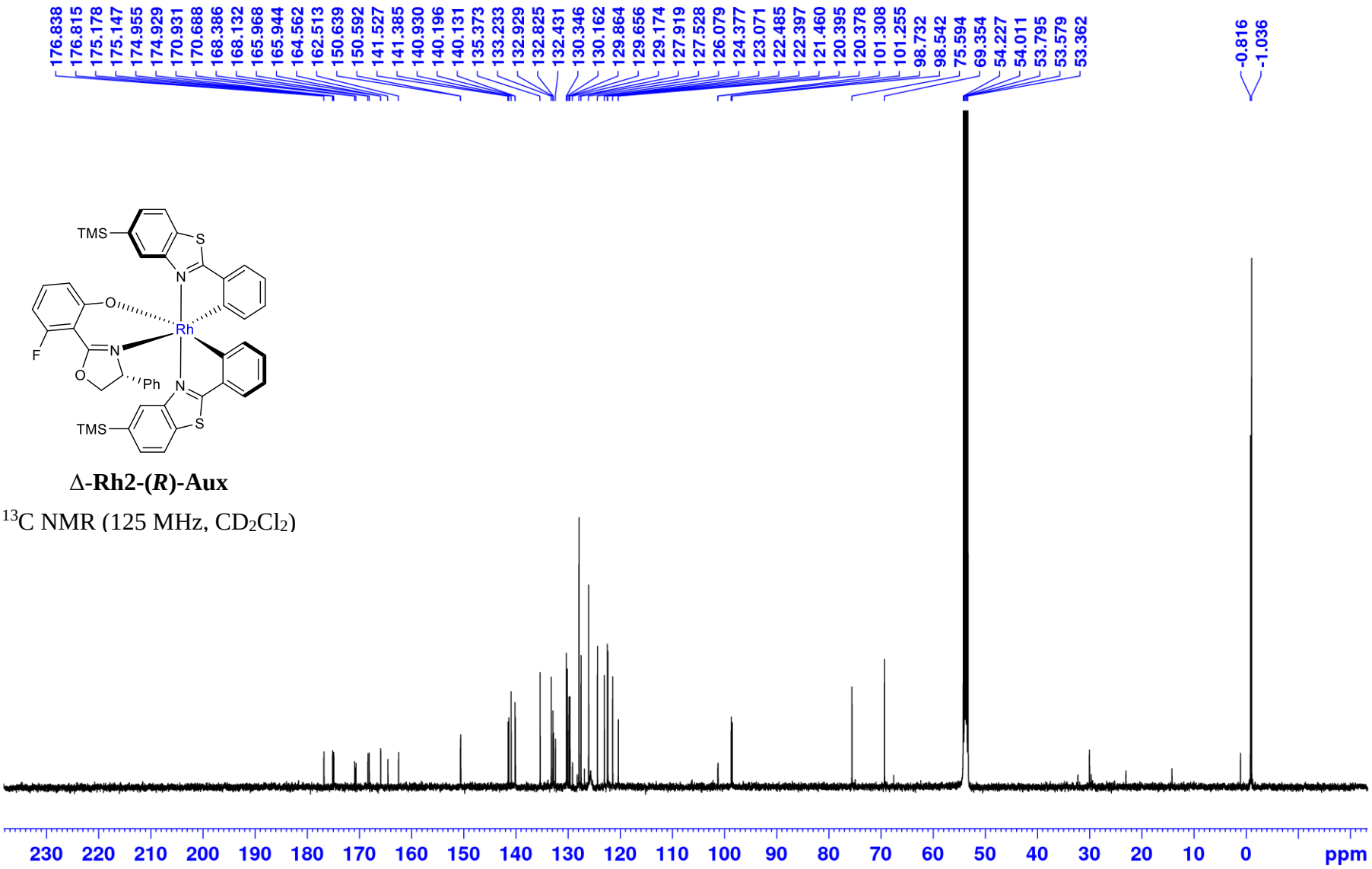
Rh2

^{13}C NMR (75 MHz, CD_2Cl_2)



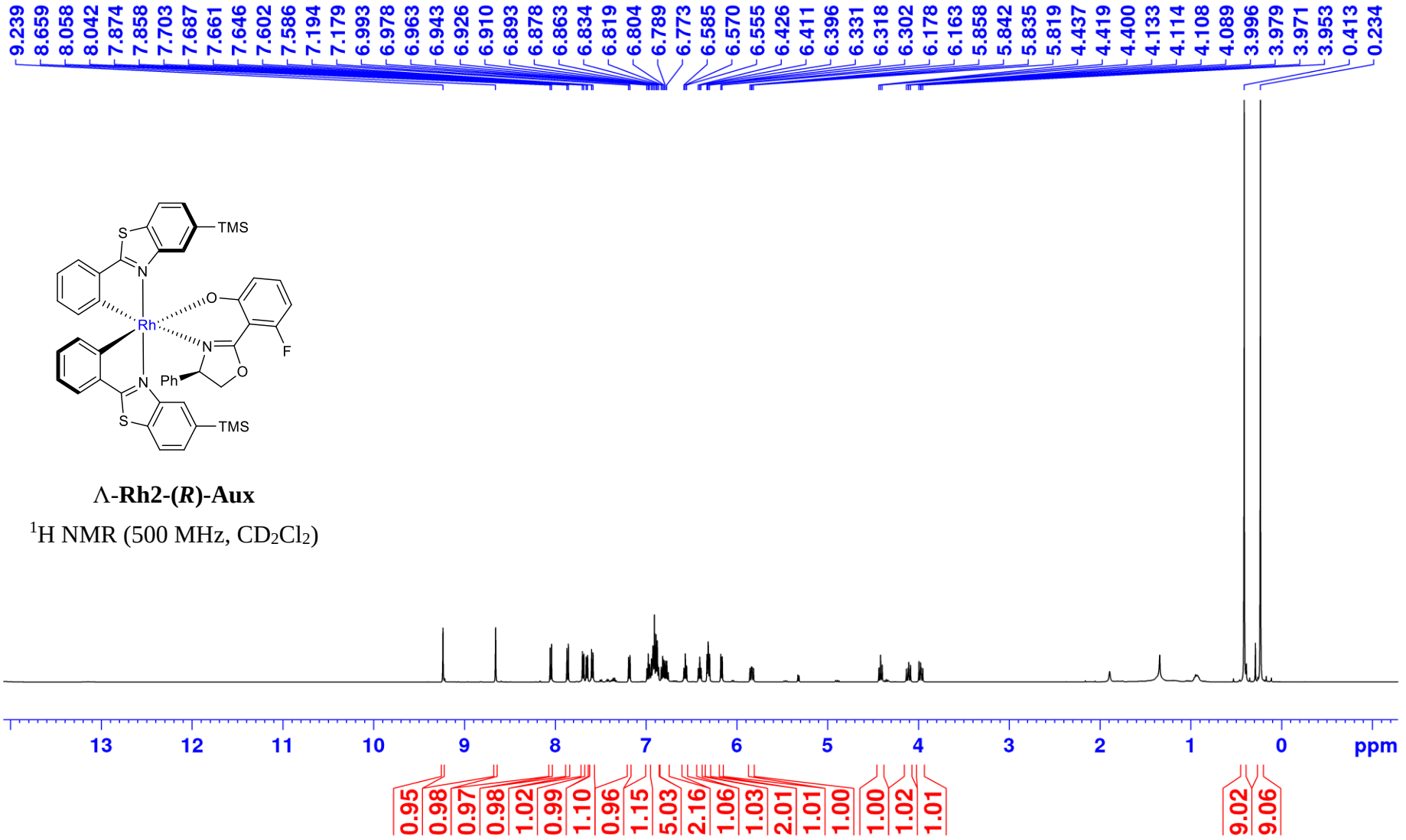
Δ-Rh2-(*R*)-Aux

^{1}H NMR (500 MHz, CD_2Cl_2)



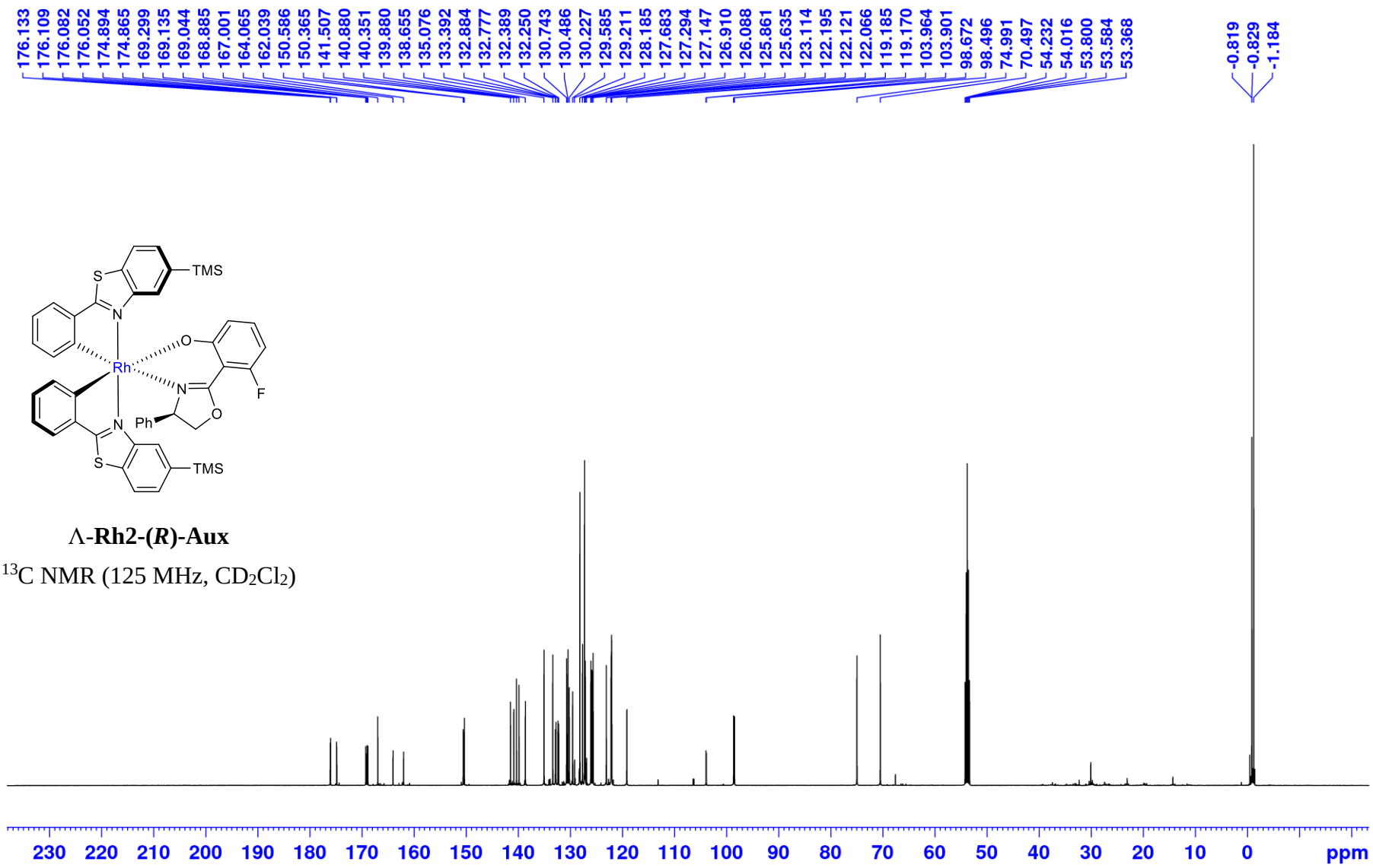
Δ-Rh2-(*R*)-Aux

^{13}C NMR (125 MHz, CD_2Cl_2)



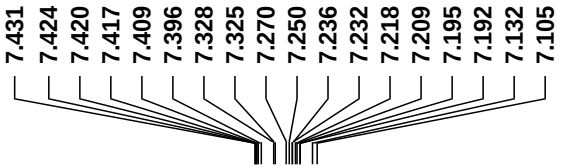
Λ-Rh2-(*R*)-Aux

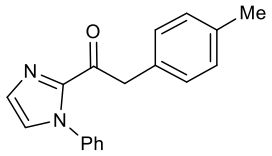
^{1}H NMR (500 MHz, CD_2Cl_2)



Λ-Rh2-(*R*)-Aux

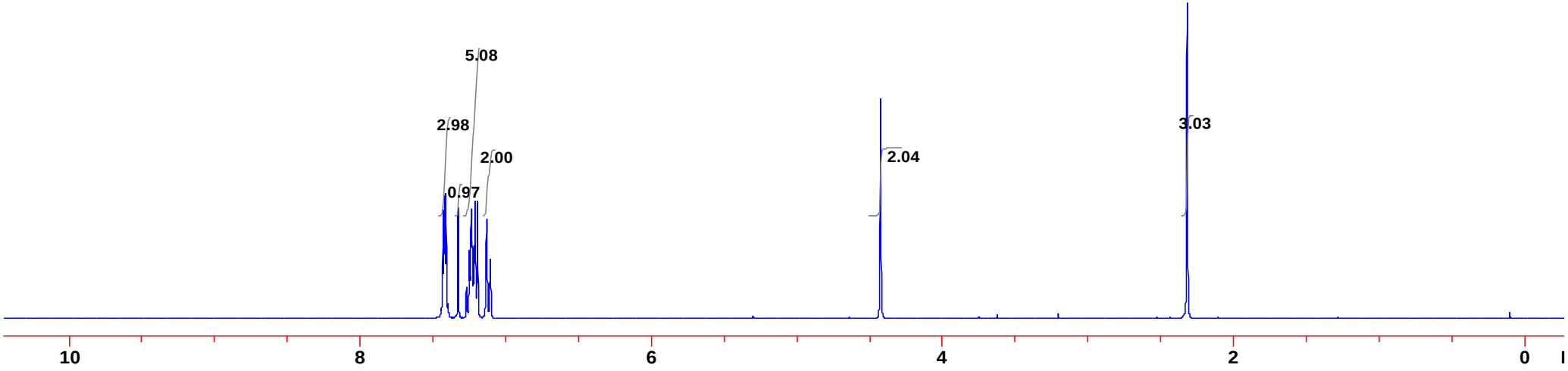
^{13}C NMR (125 MHz, CD_2Cl_2)

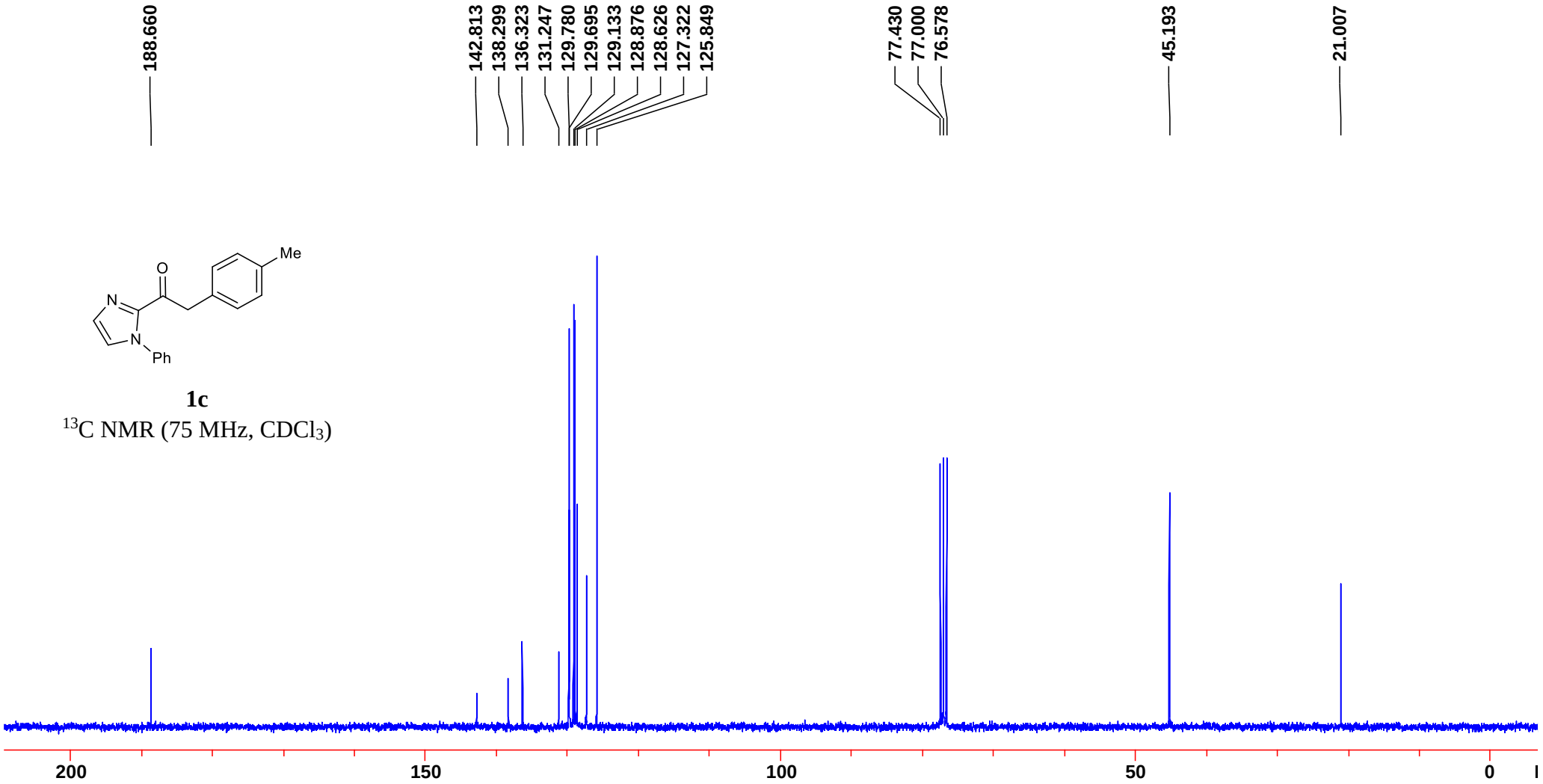




1c

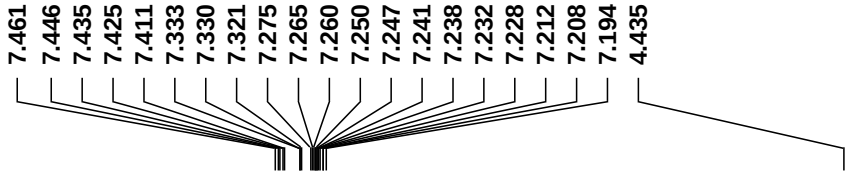
^{1}H NMR (300 MHz, $CDCl_3$)

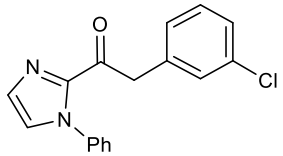




1c

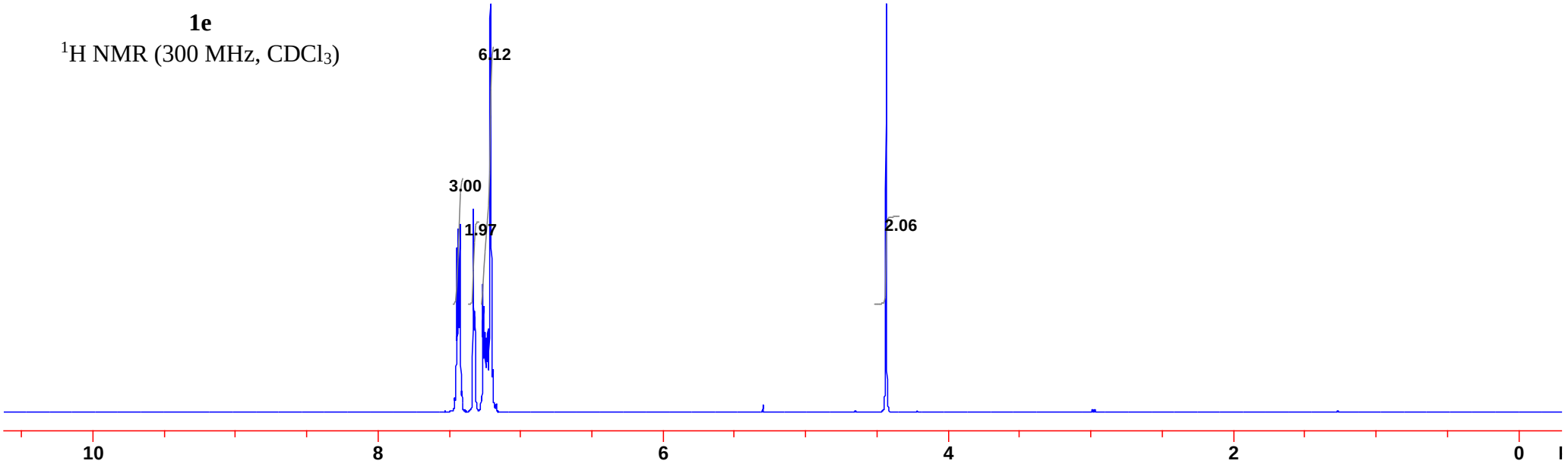
^{13}C NMR (75 MHz, $CDCl_3$)

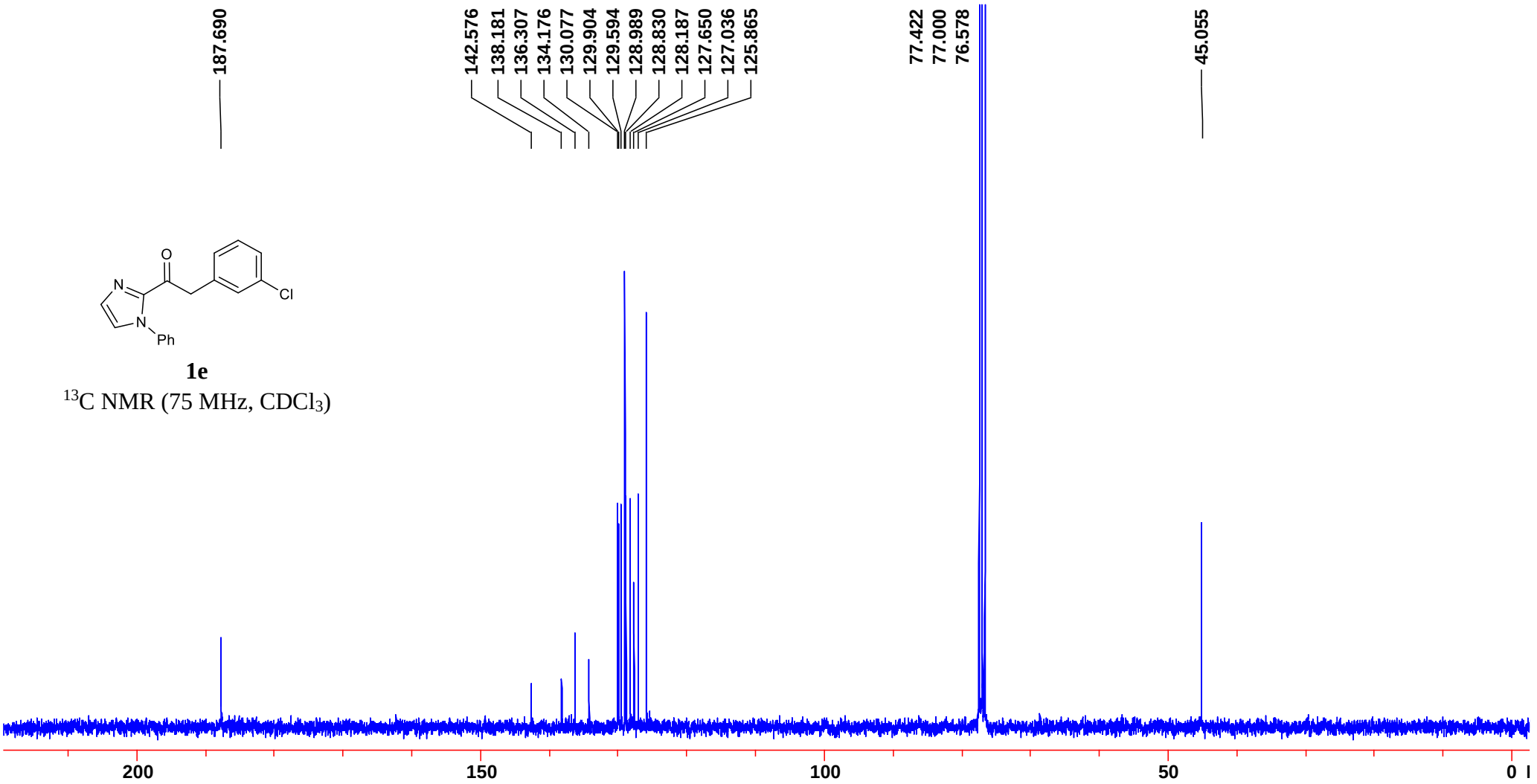




1e

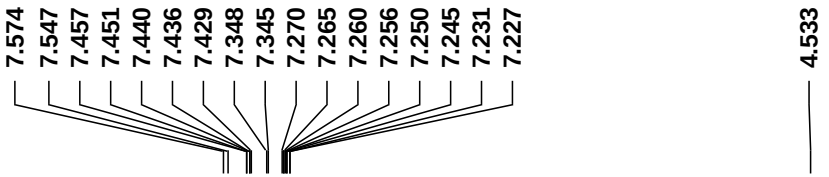
^{1}H NMR (300 MHz, $CDCl_3$)

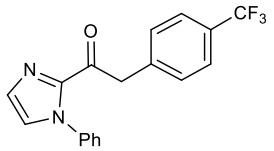




1e

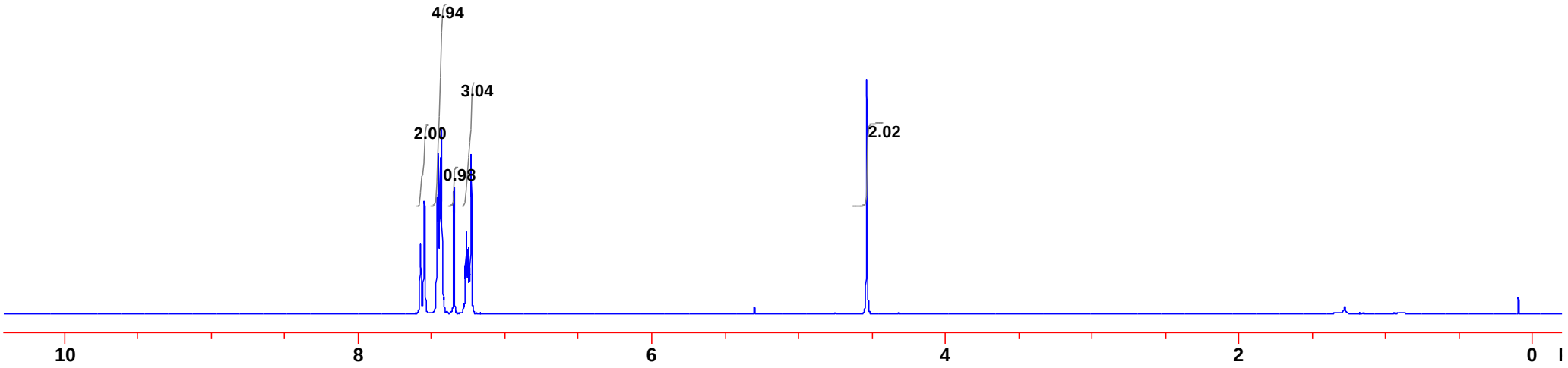
^{13}C NMR (75 MHz, $CDCl_3$)

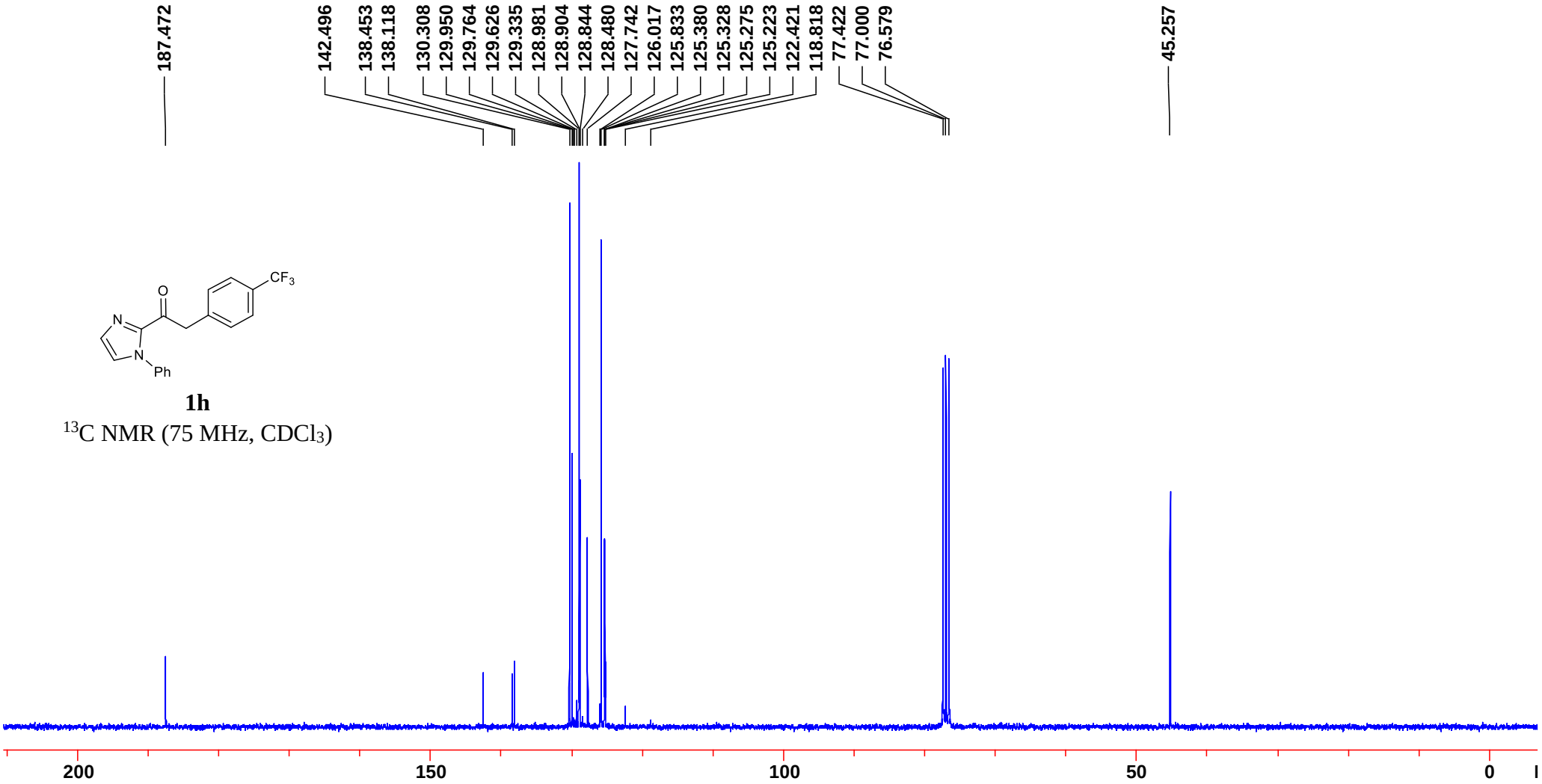




1h

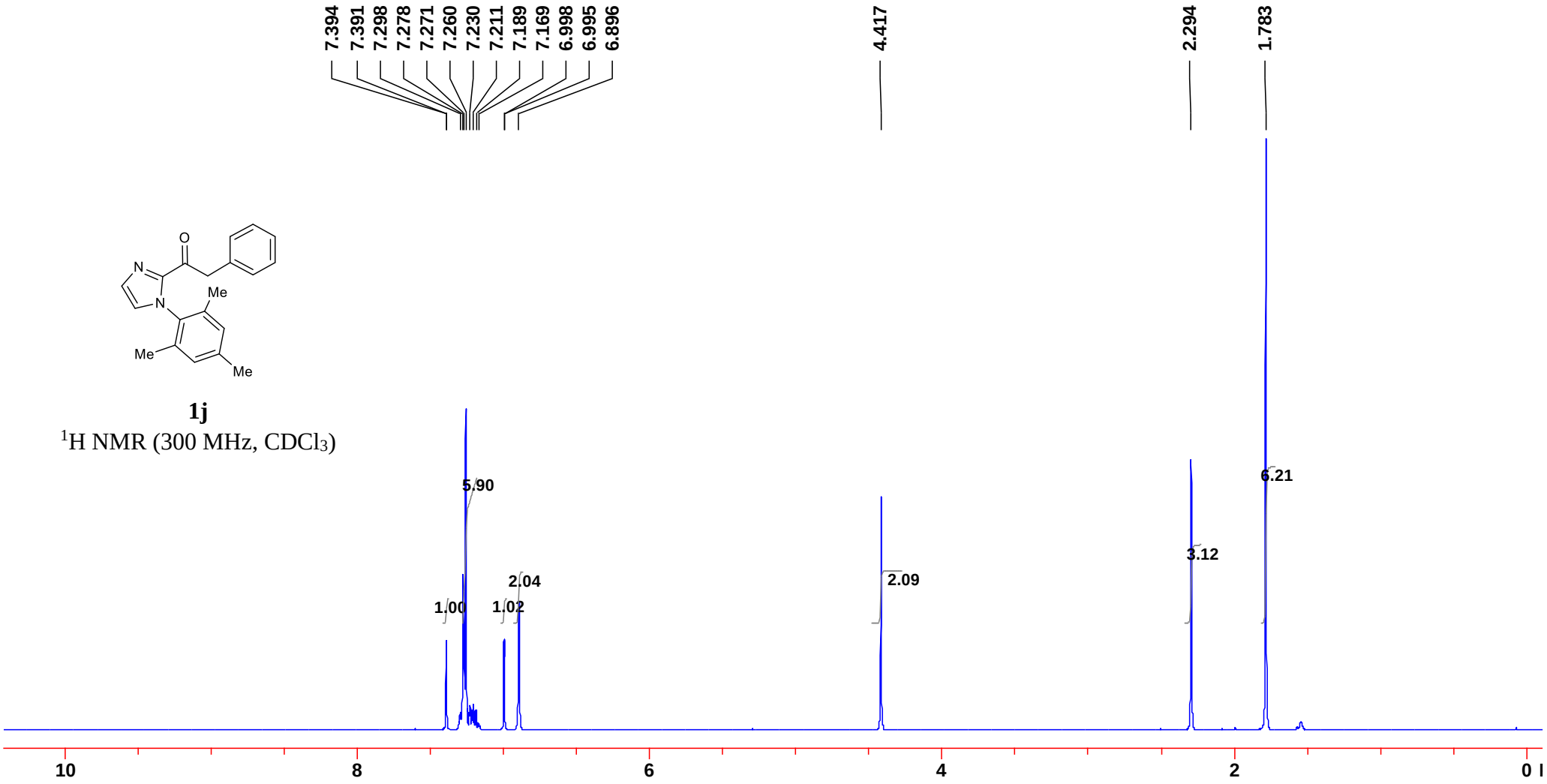
^{1}H NMR (300 MHz, $CDCl_3$)

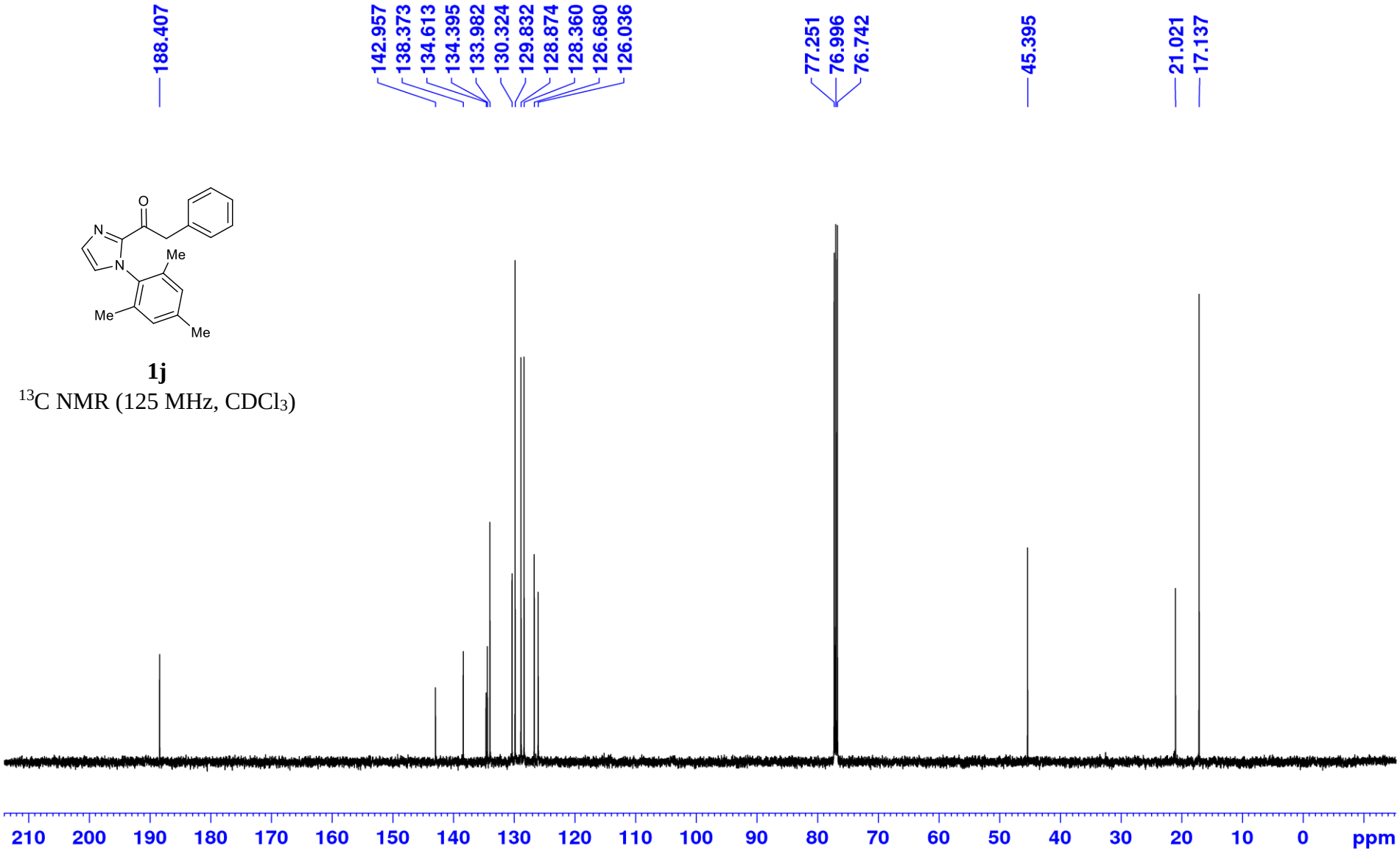




1h

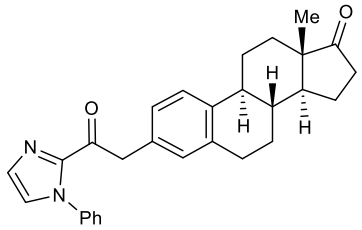
^{13}C NMR (75 MHz, $CDCl_3$)


7.394
7.391
7.298
7.278
7.271
7.260
7.230
7.211
7.189
7.169
6.998
6.995
6.896
4.417
2.294
1.783
O
N
N
Me
Me
Me
1j
1H NMR (300 MHz, CDCl3)
5.90
1.00
1.02
2.04
2.09
3.12
6.21
10
8
6
4
2
0



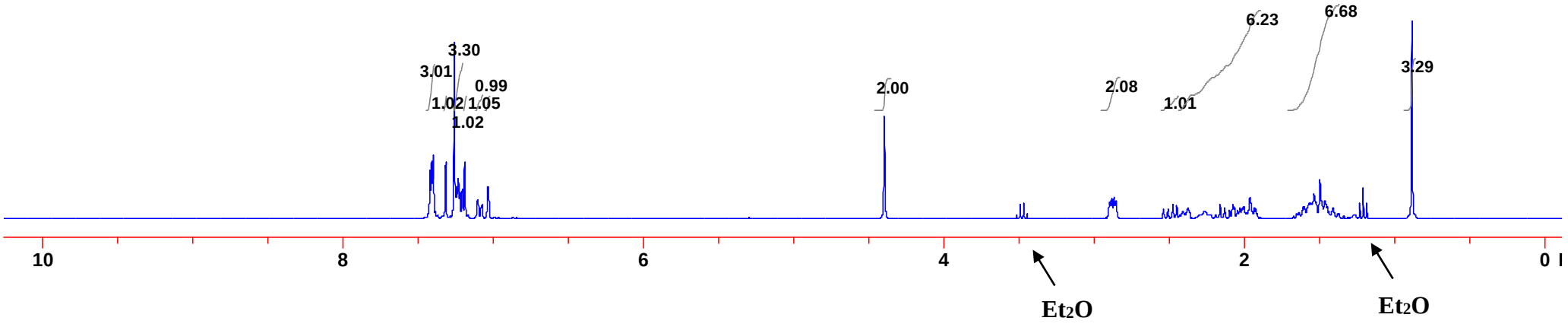
1j

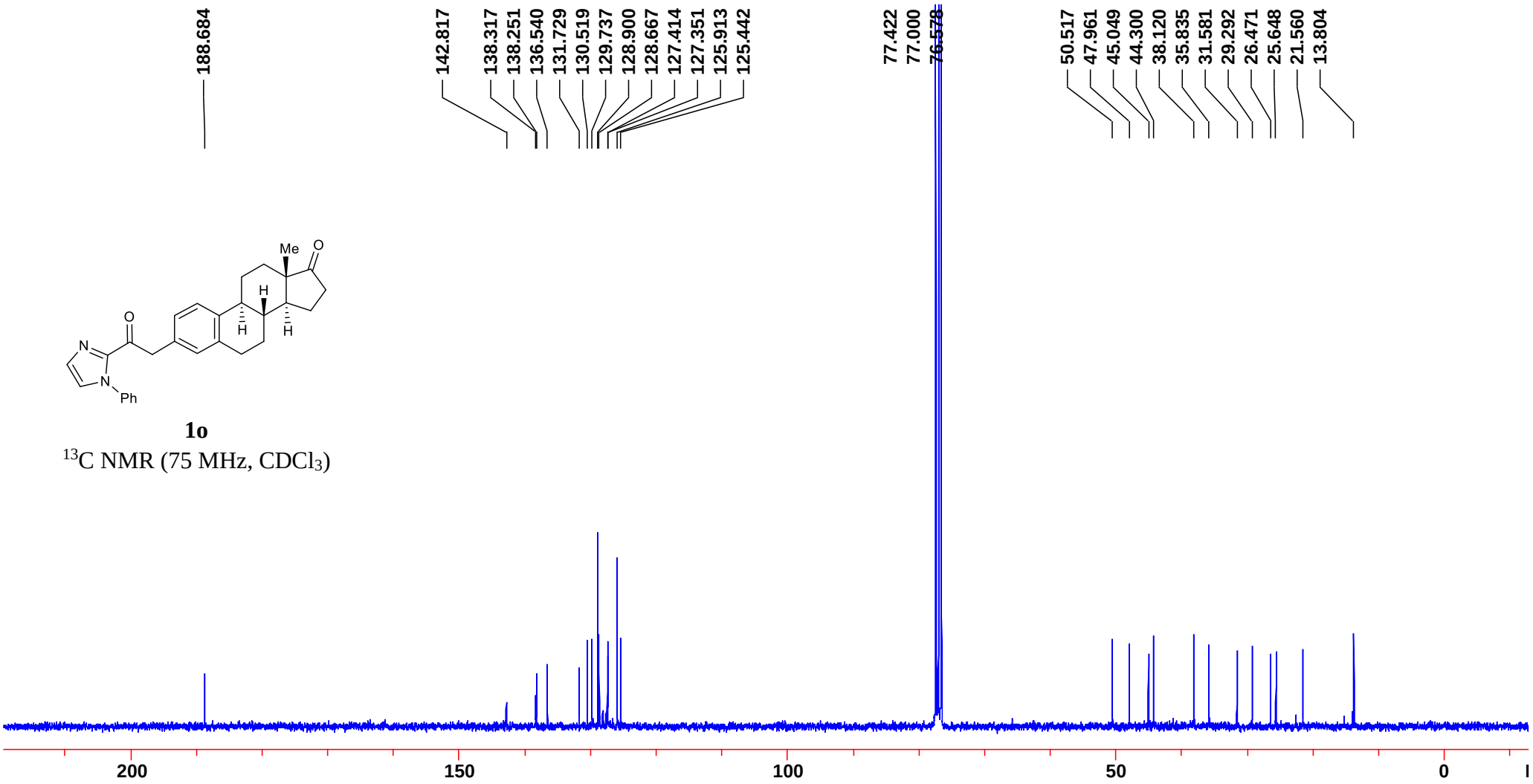
^{13}C NMR (125 MHz, $CDCl_3$)



1o

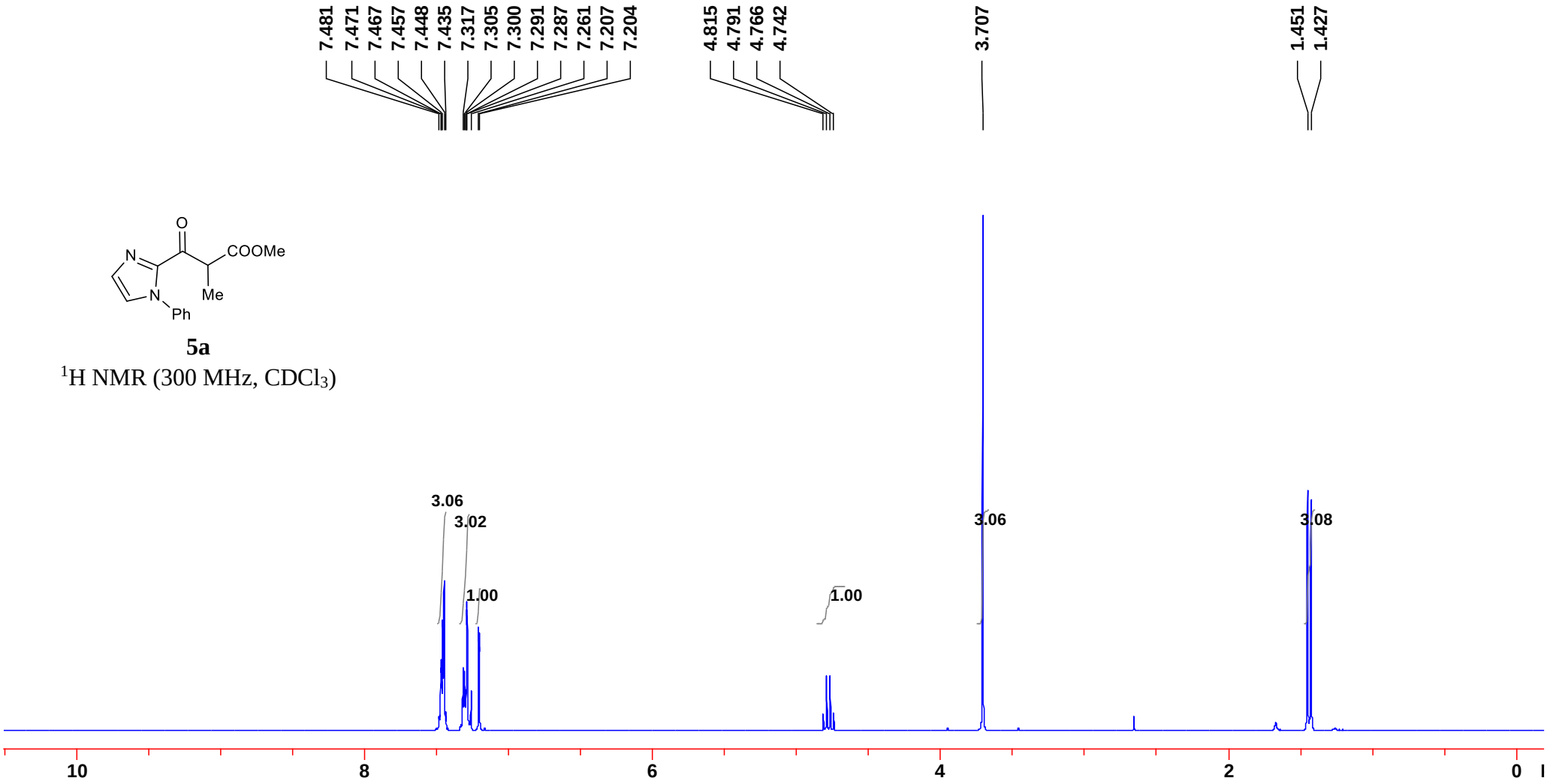
^{1}H NMR (300 MHz, $CDCl_3$)





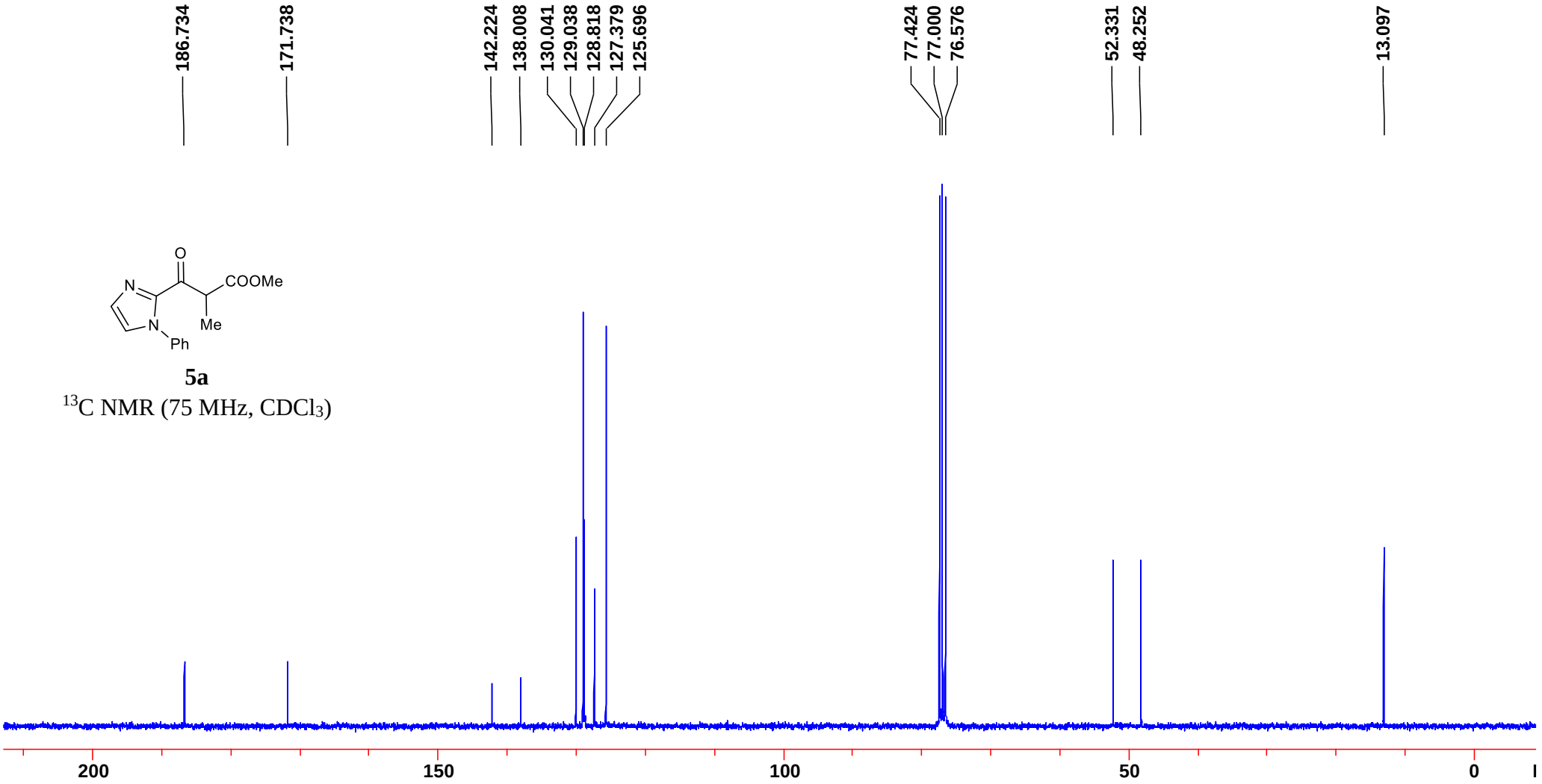
1o

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



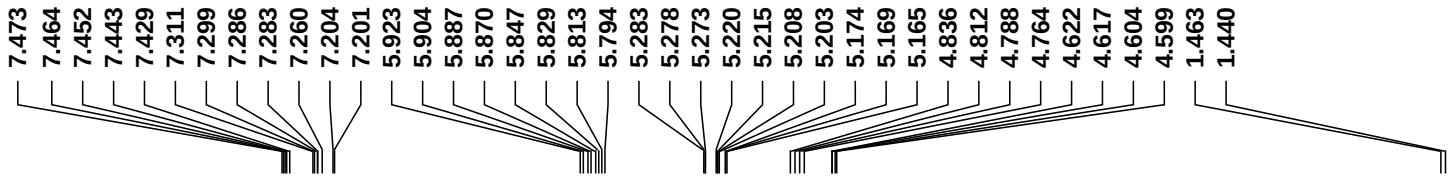
5a

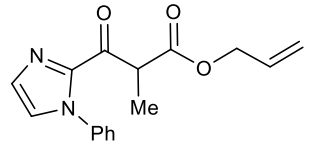
^{1}H NMR (300 MHz, $CDCl_3$)



5a

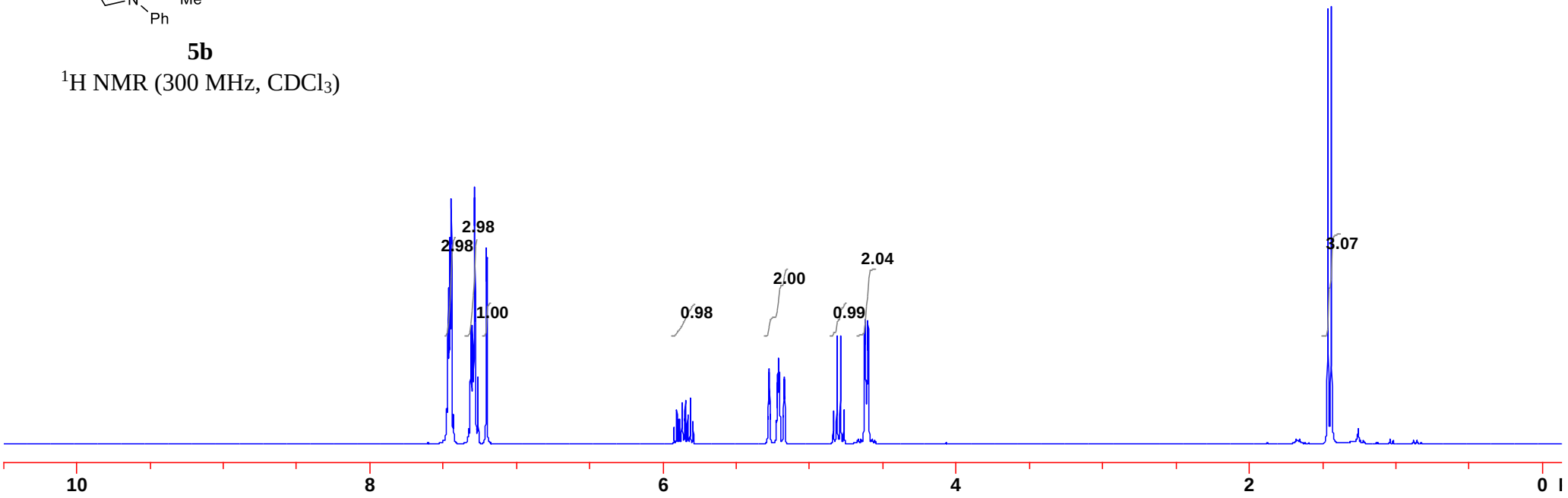
^{13}C NMR (75 MHz, $CDCl_3$)

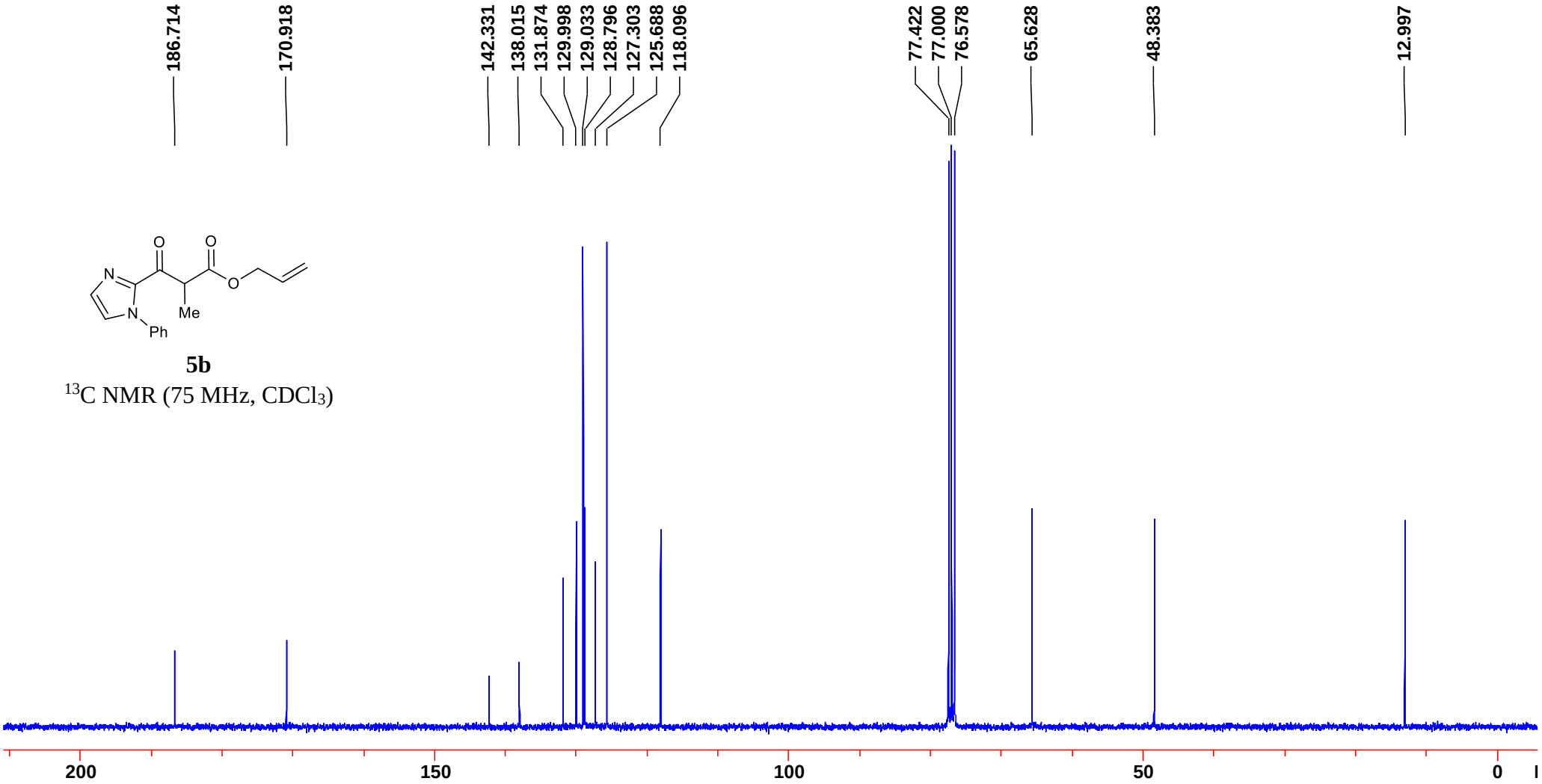




5b

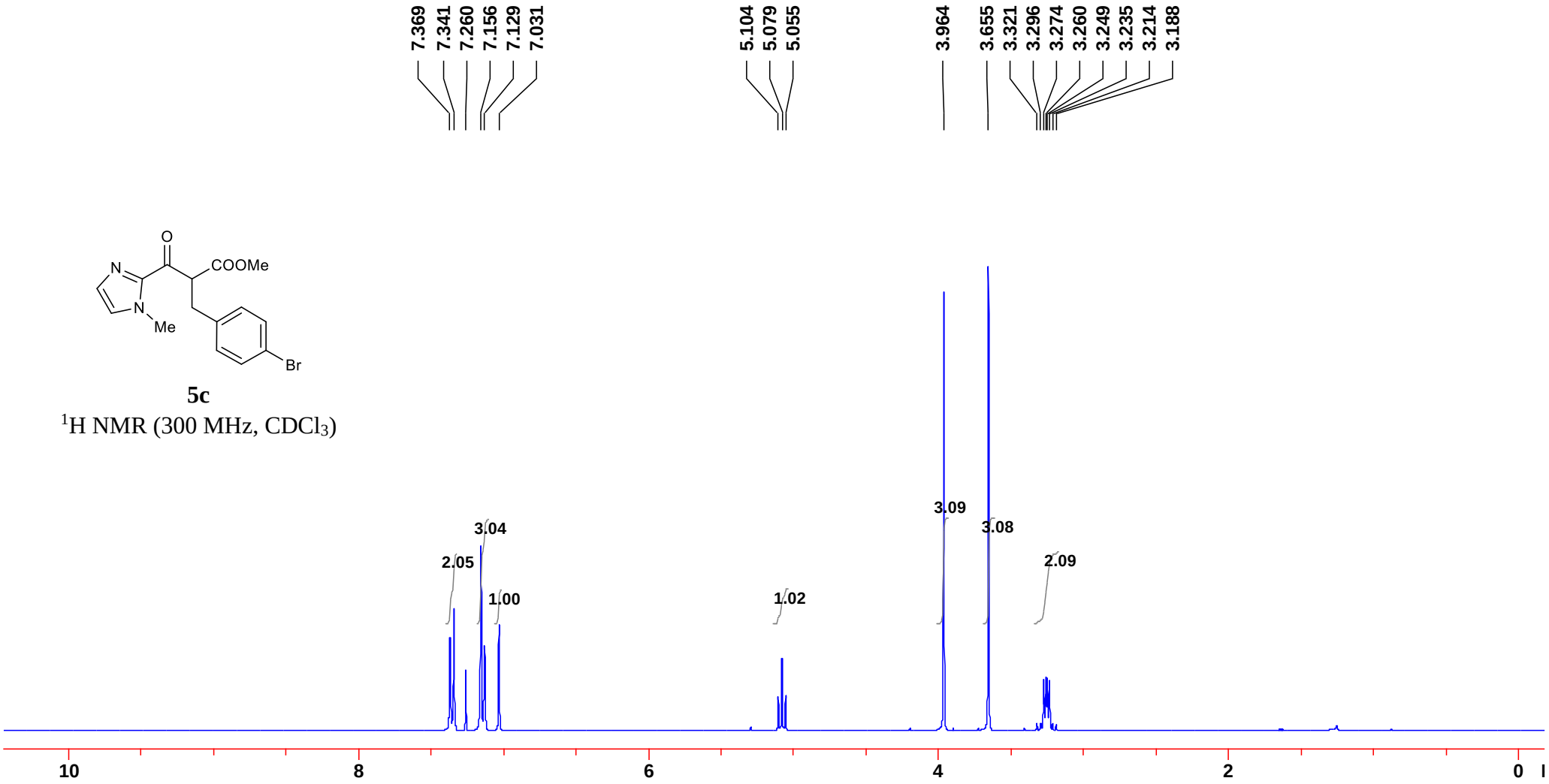
^{1}H NMR (300 MHz, $CDCl_3$)





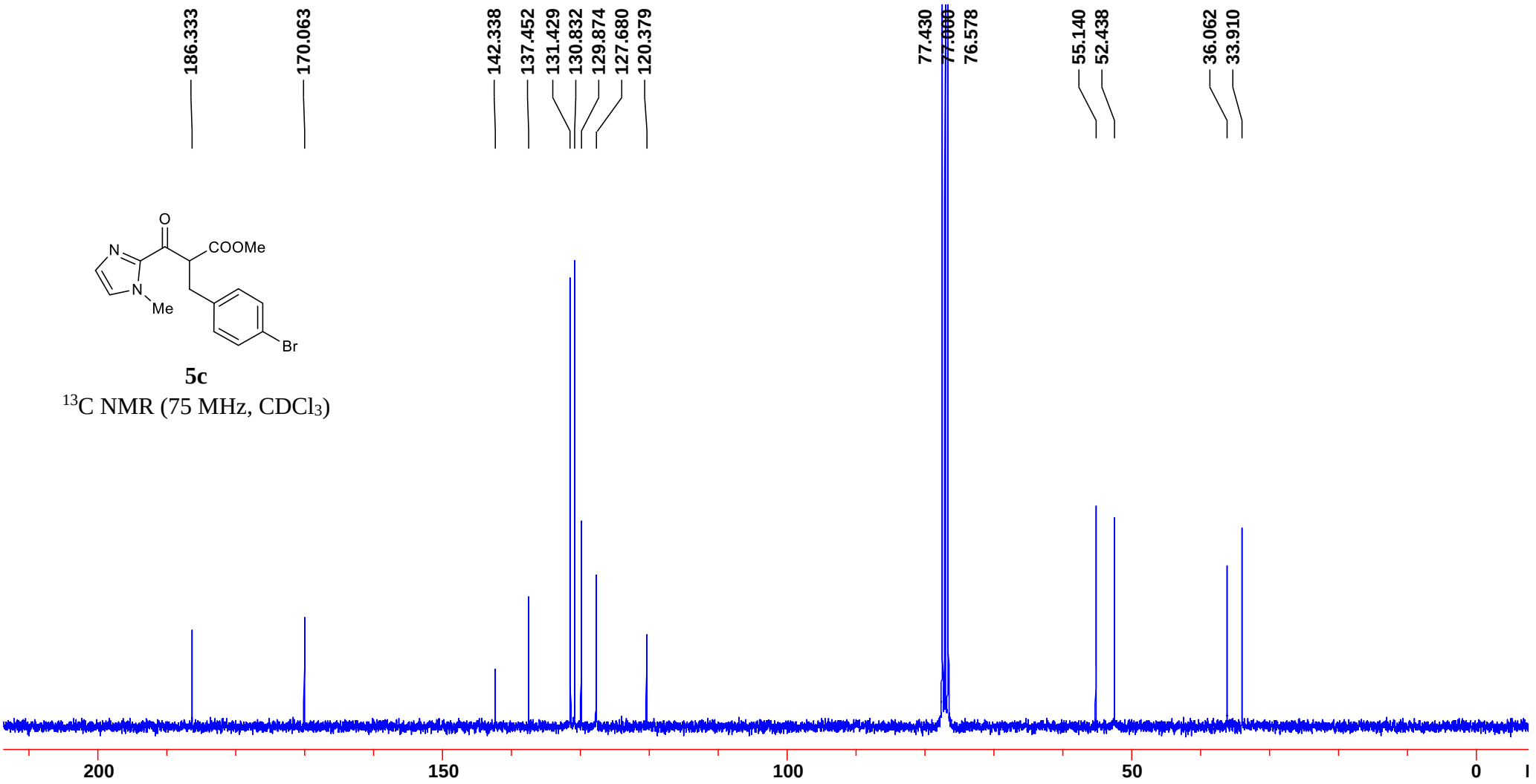
5b

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



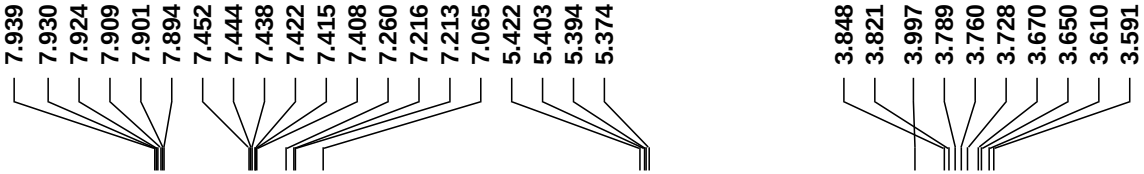
5c

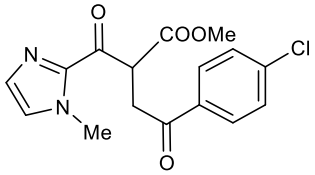
^{1}H NMR (300 MHz, $CDCl_3$)



5c

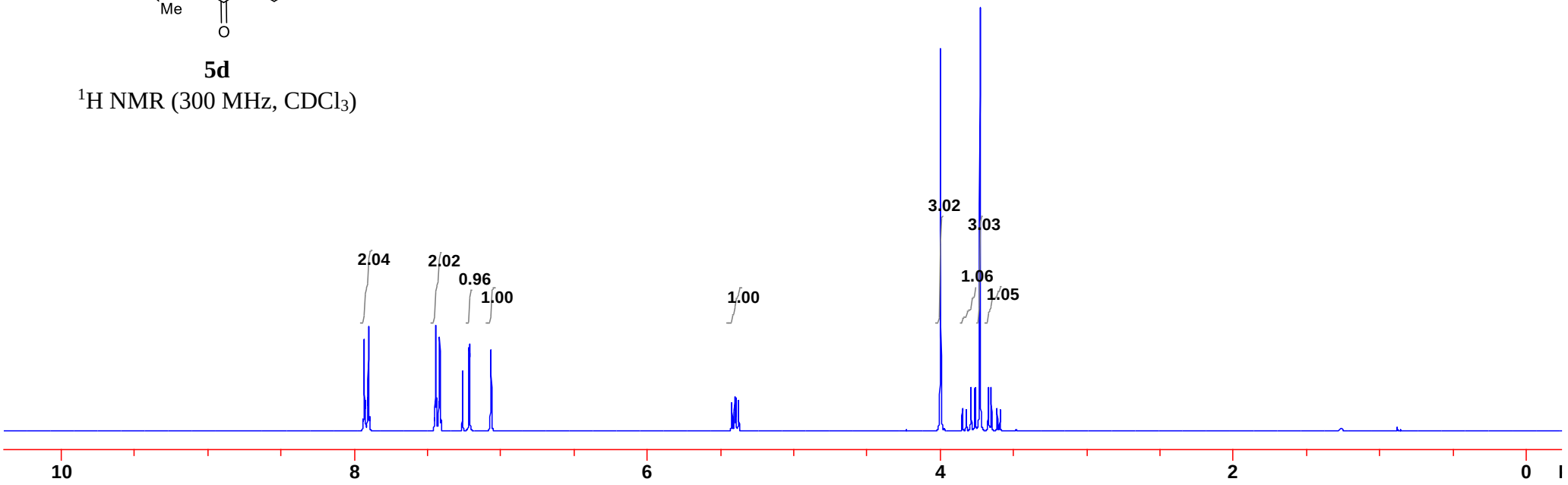
^{13}C NMR (75 MHz, $CDCl_3$)

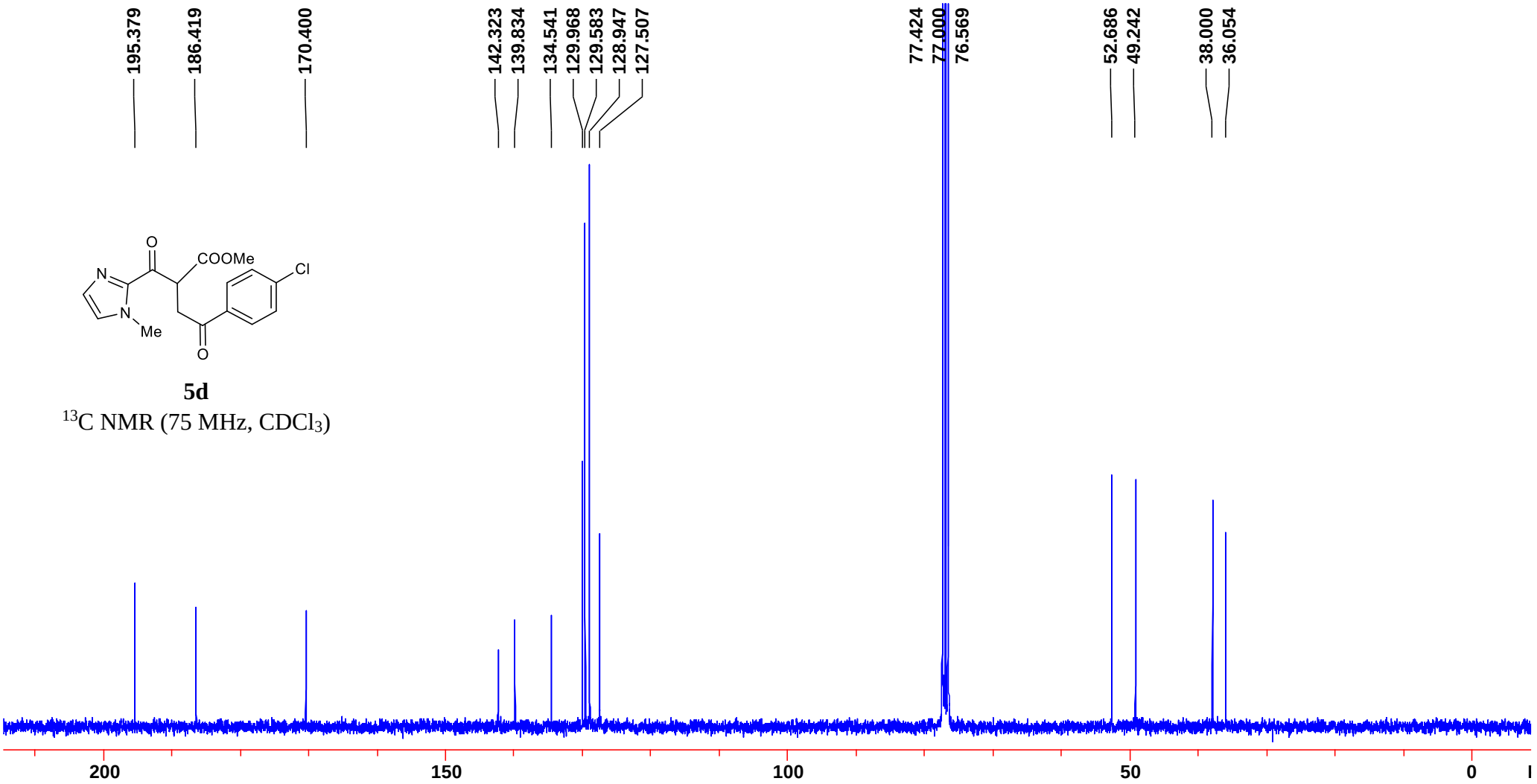




5d

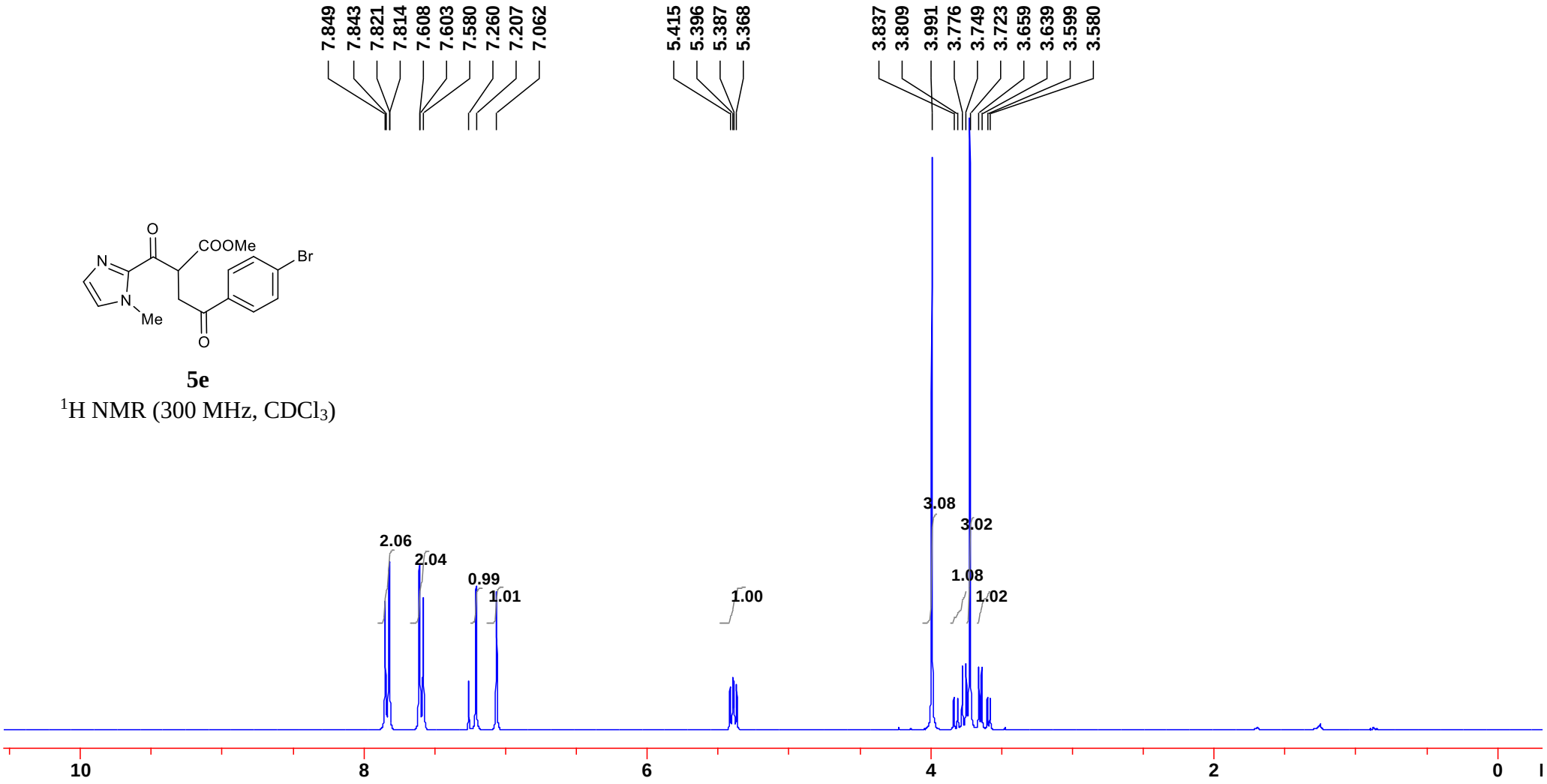
^{1}H NMR (300 MHz, $CDCl_3$)





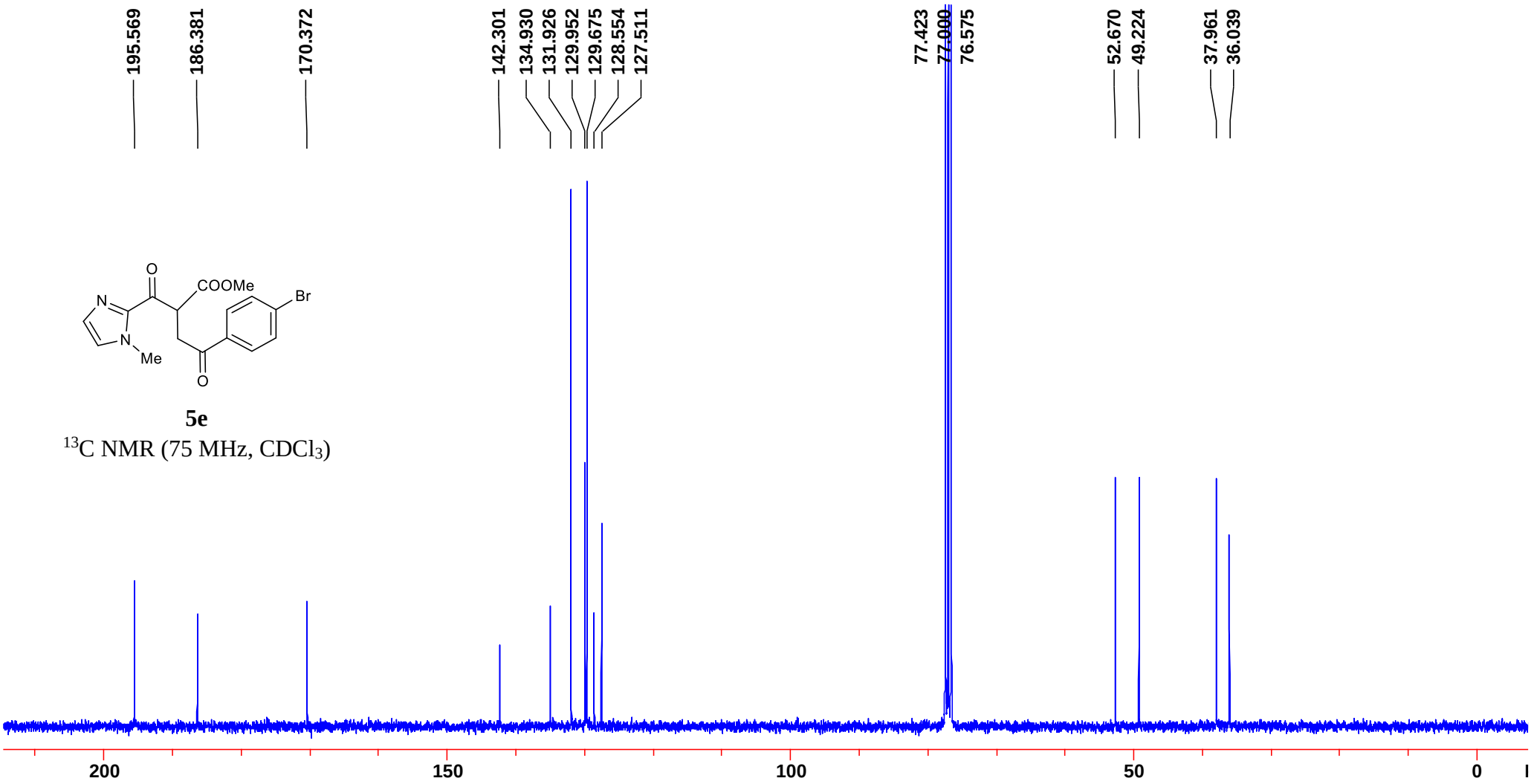
5d

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



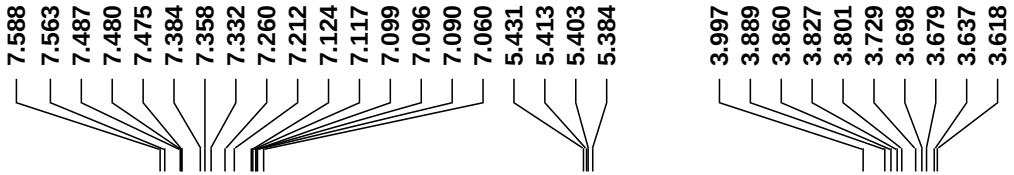
5e

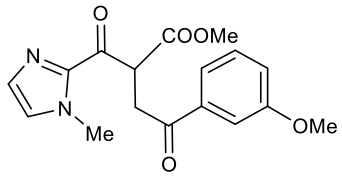
^{1}H NMR (300 MHz, $CDCl_3$)



5e

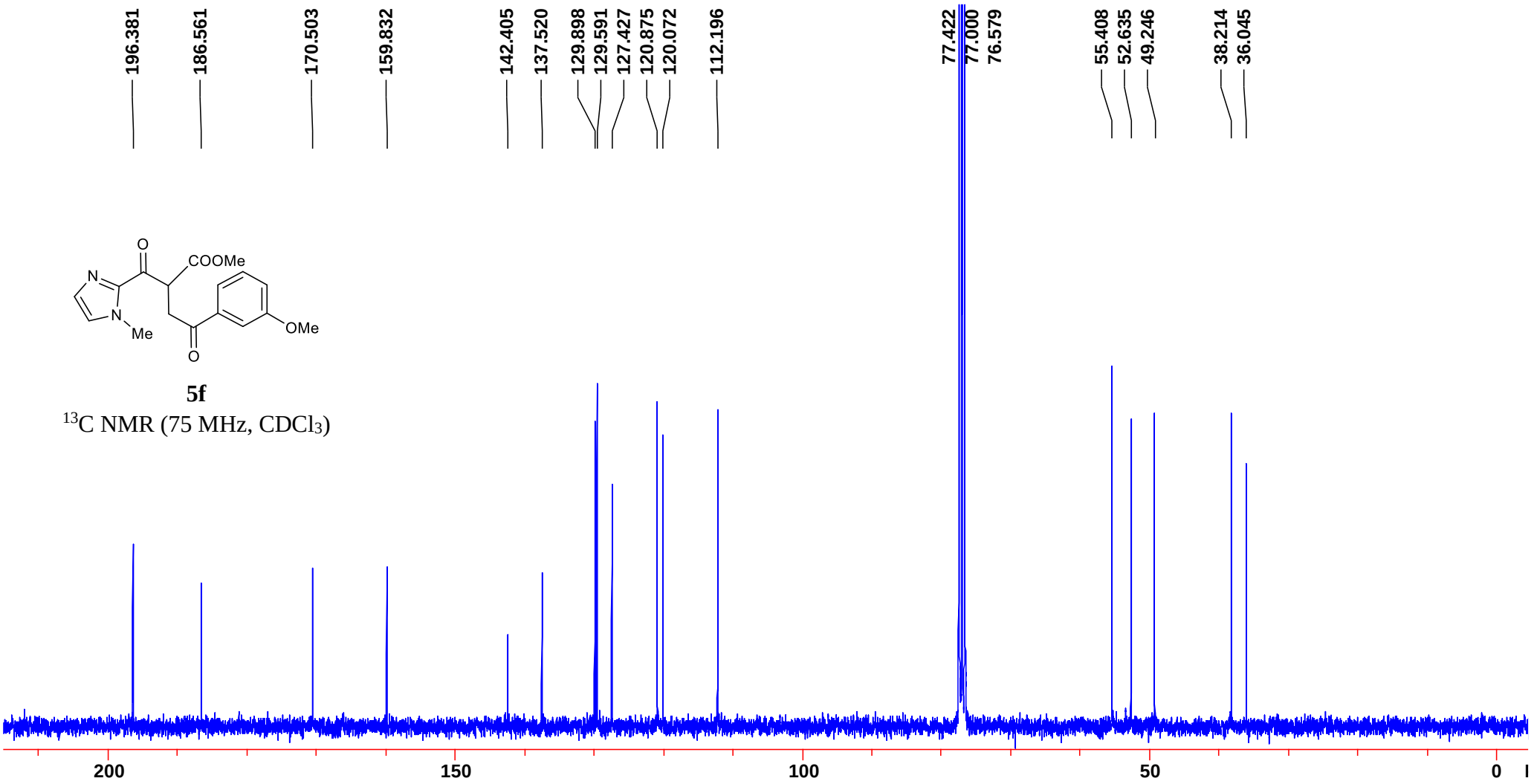
^{13}C NMR (75 MHz, $CDCl_3$)





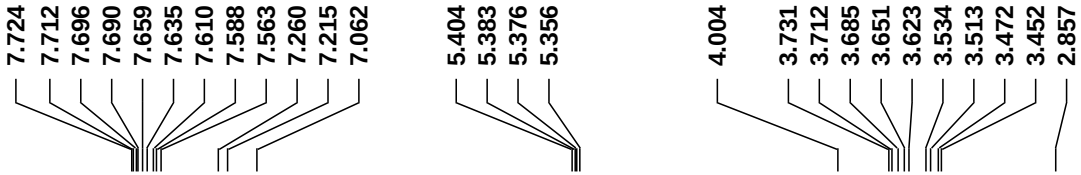
5f

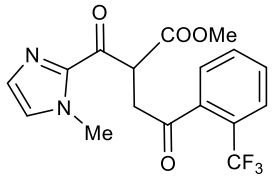
^{1}H NMR (300 MHz, $CDCl_3$)



5f

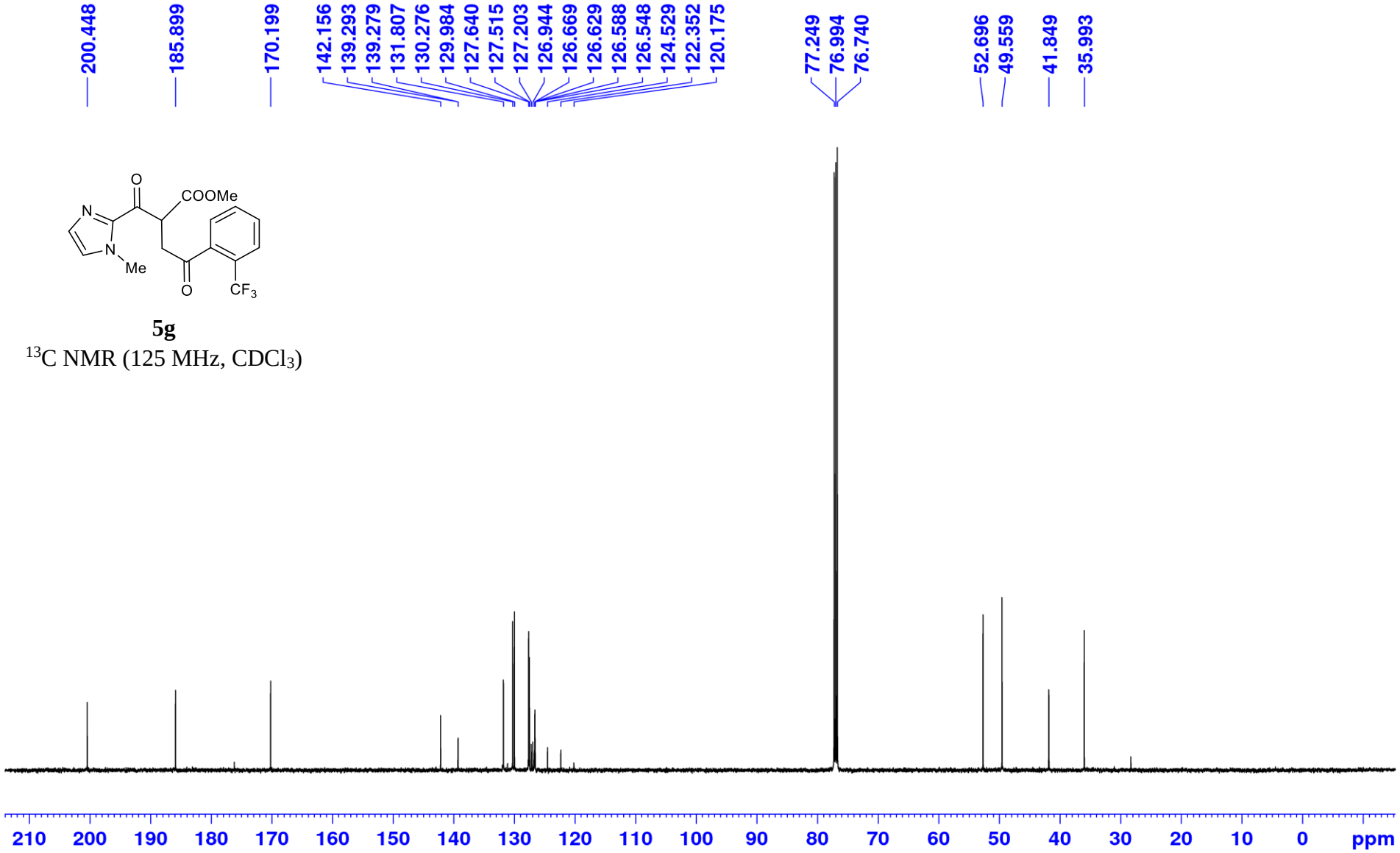
^{13}C NMR (75 MHz, $CDCl_3$)





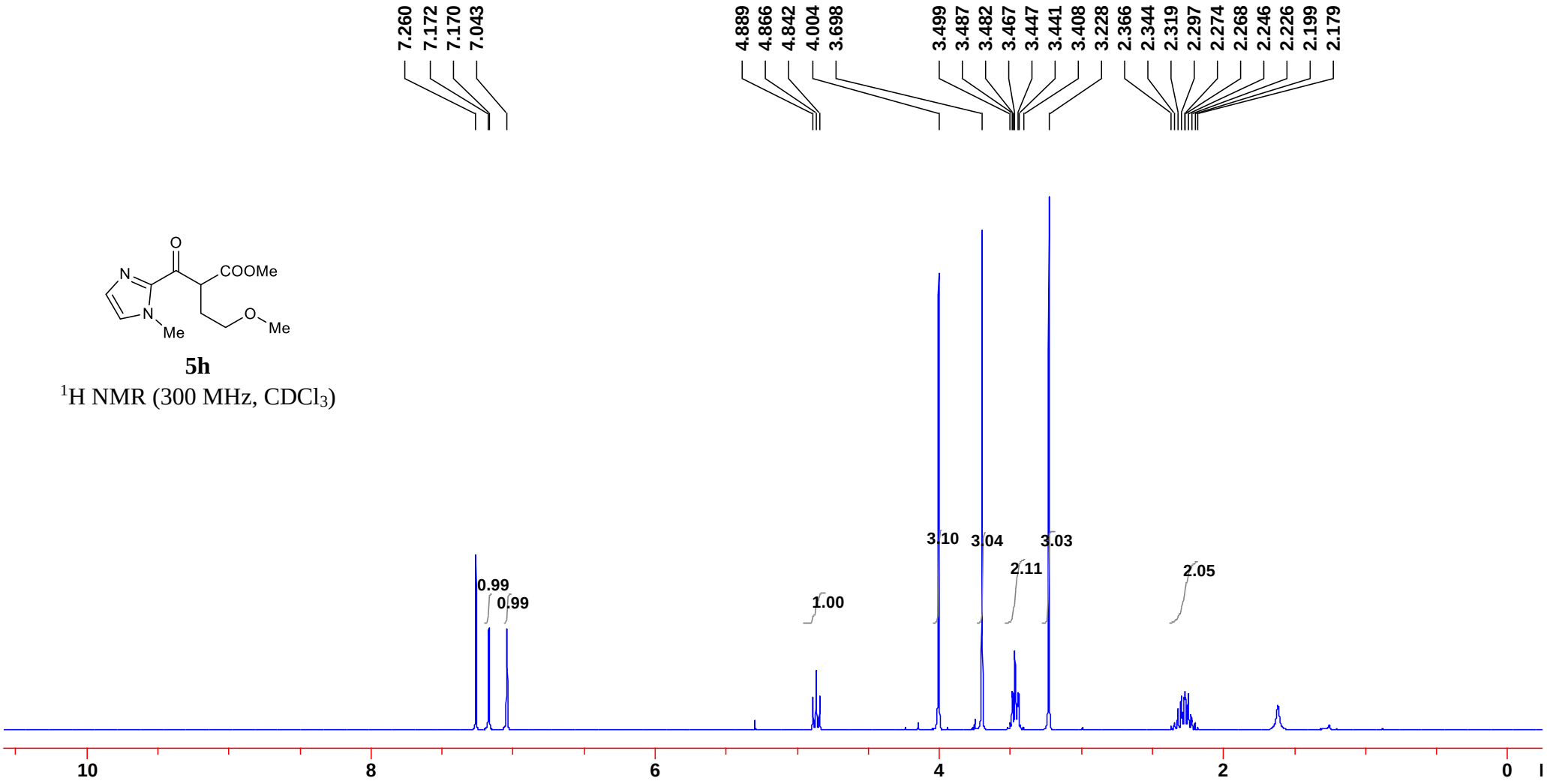
5g

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



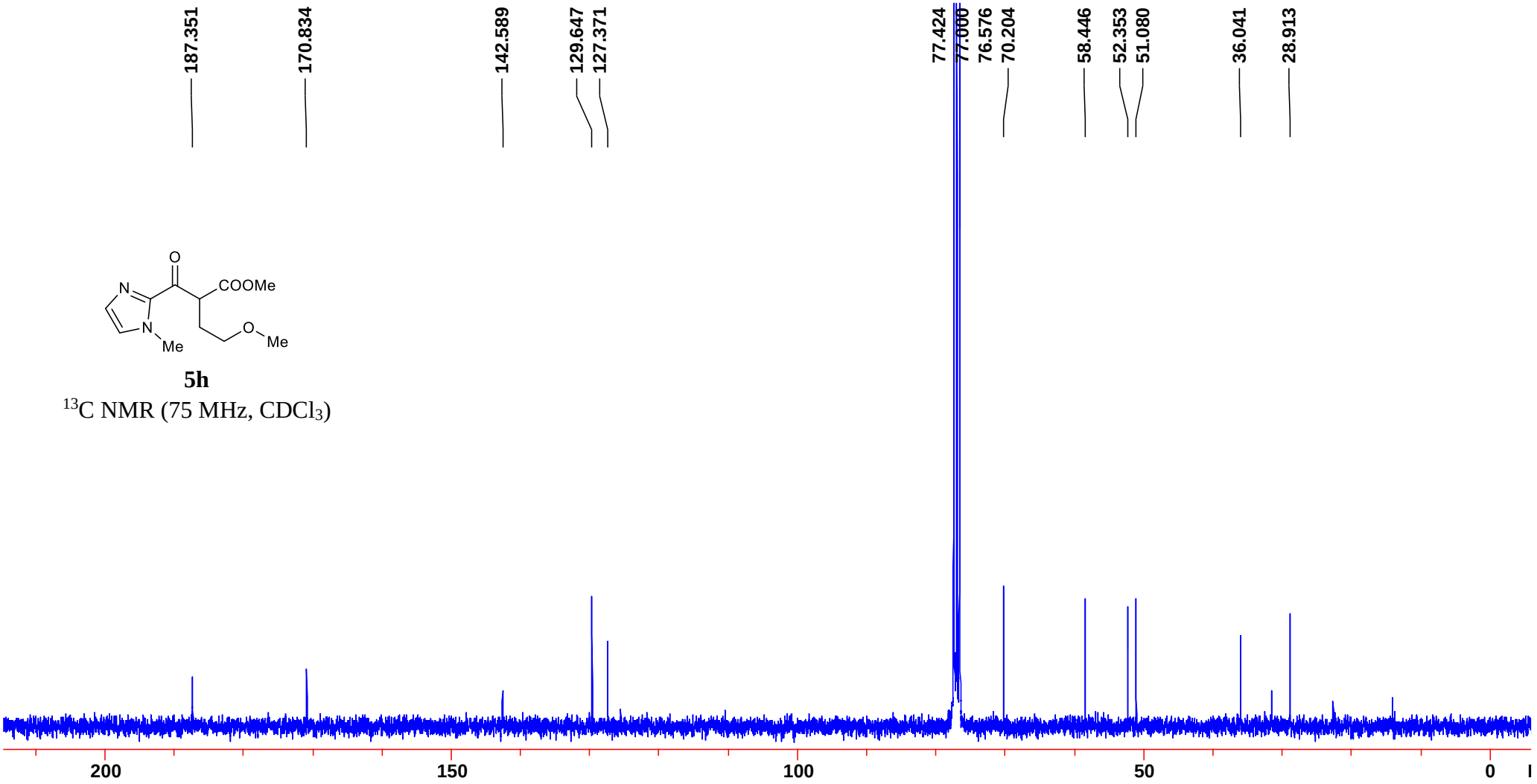
5g

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



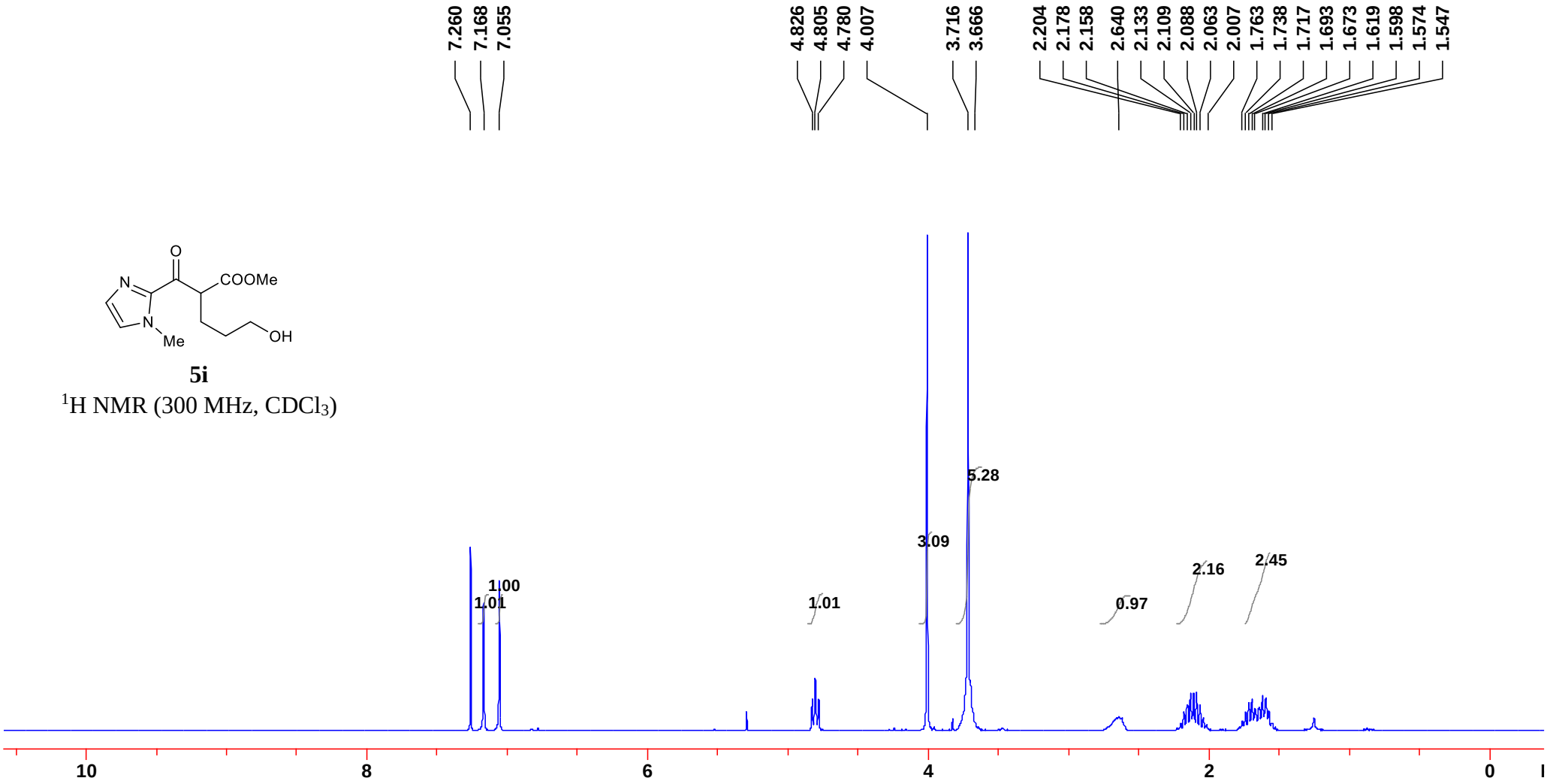
5h

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



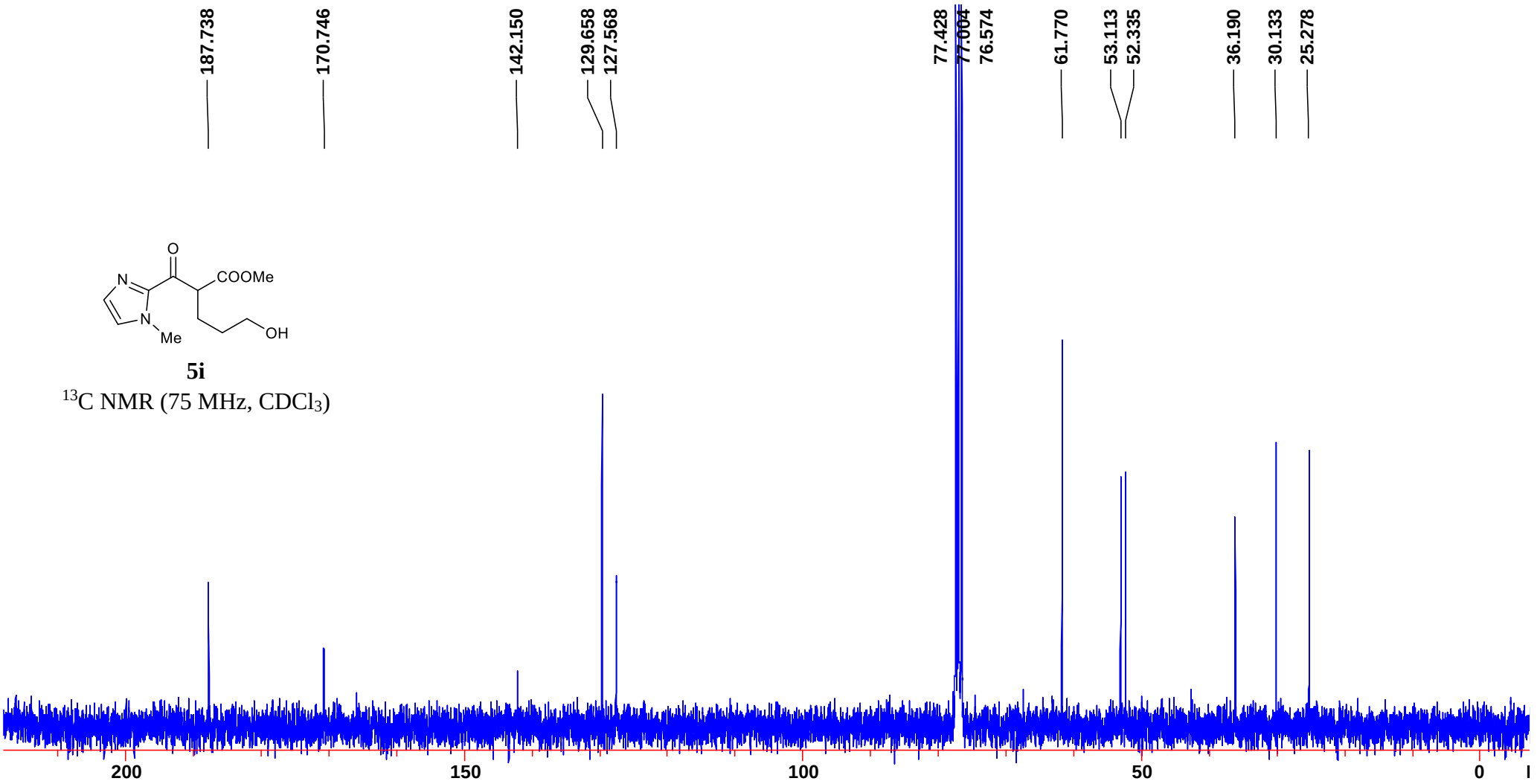
5h

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



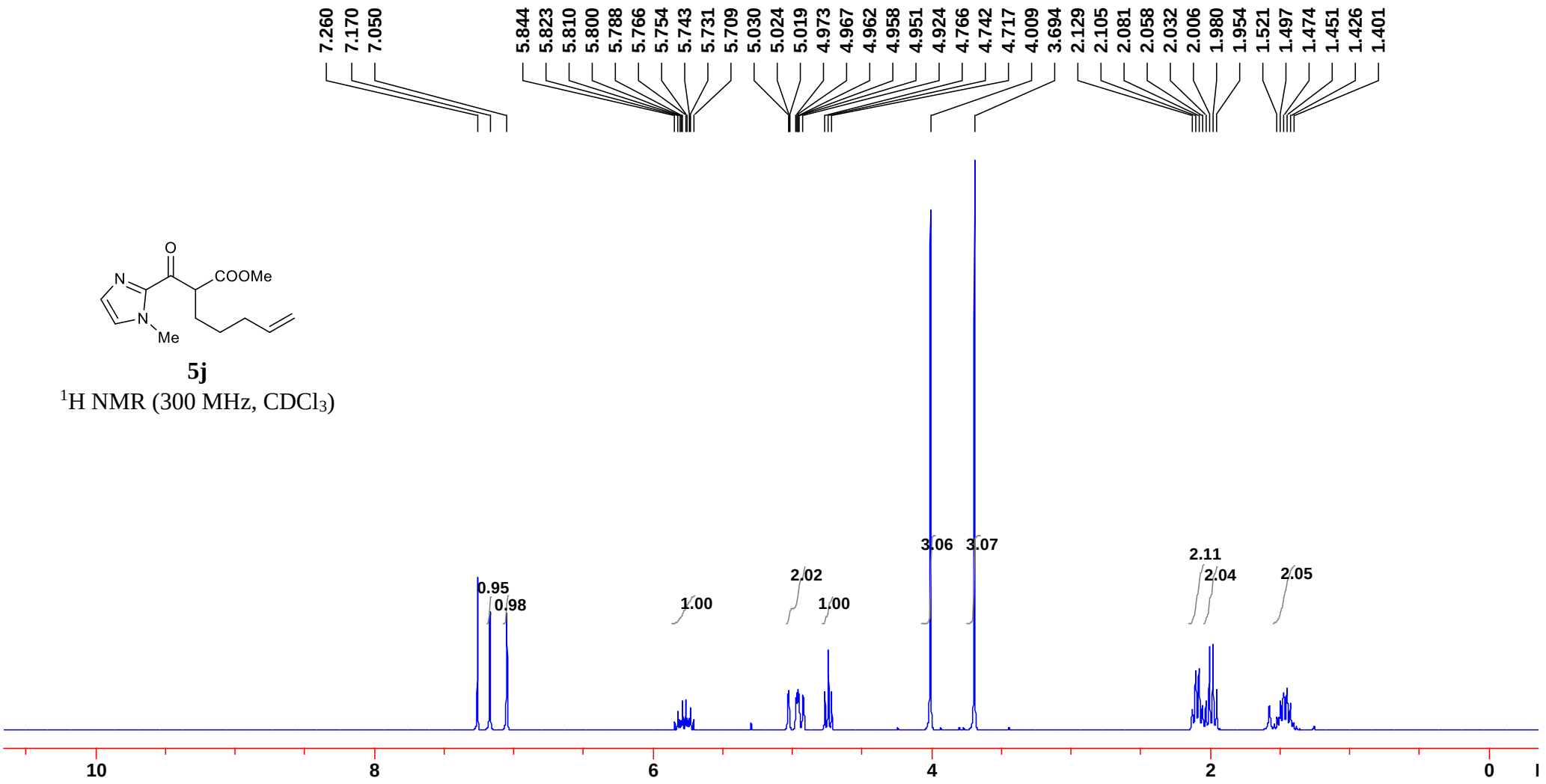
5i

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



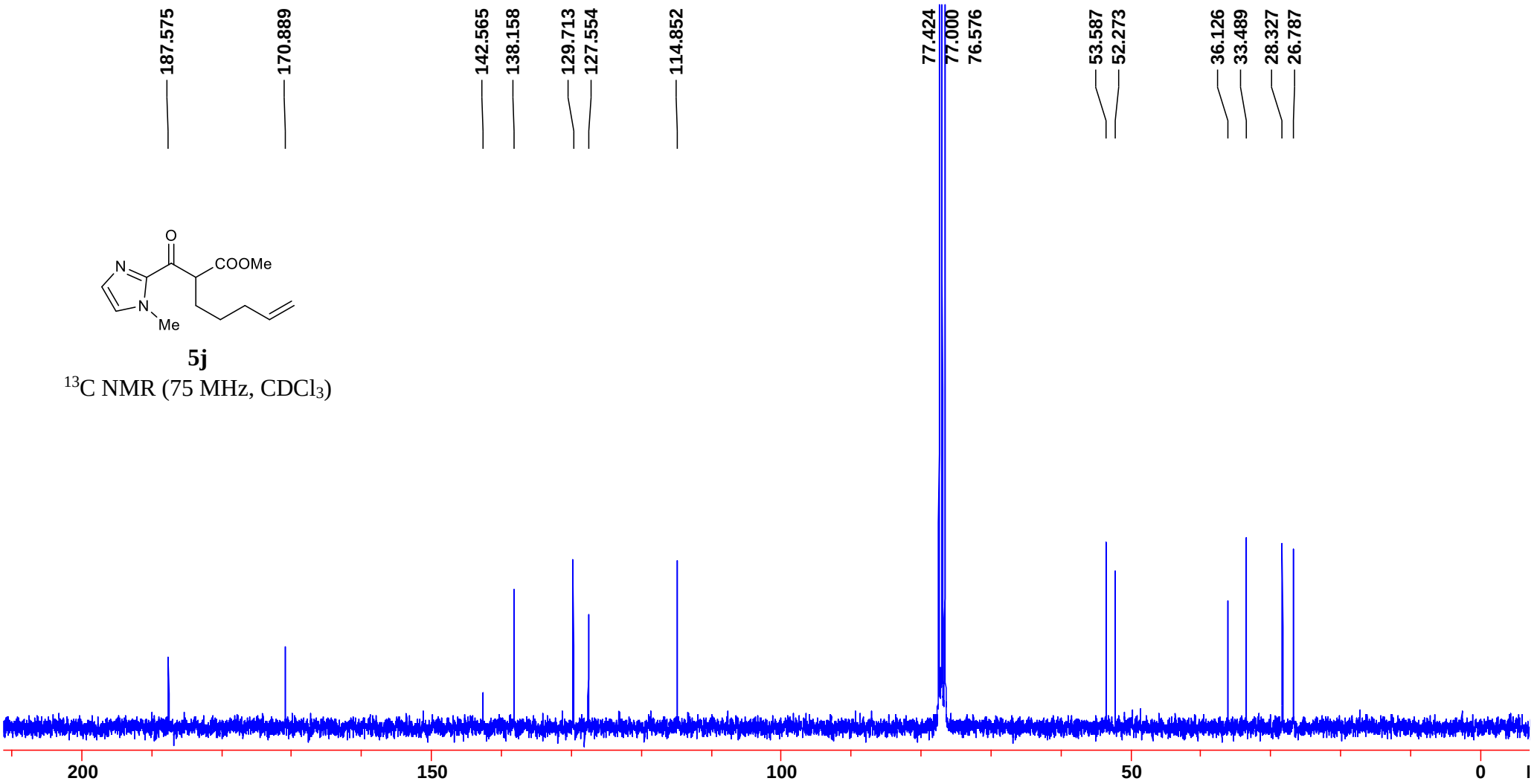
5i

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



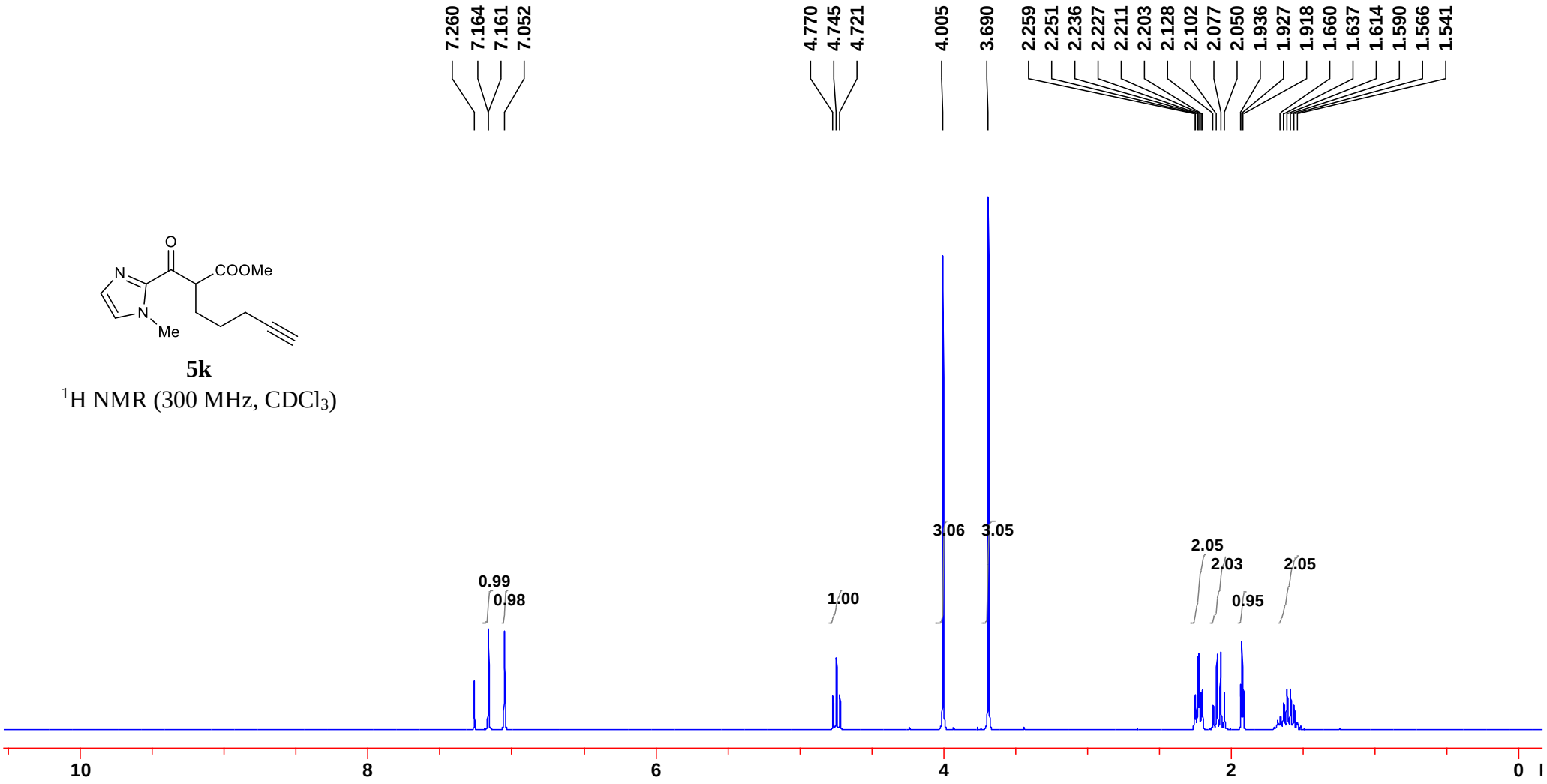
5j

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



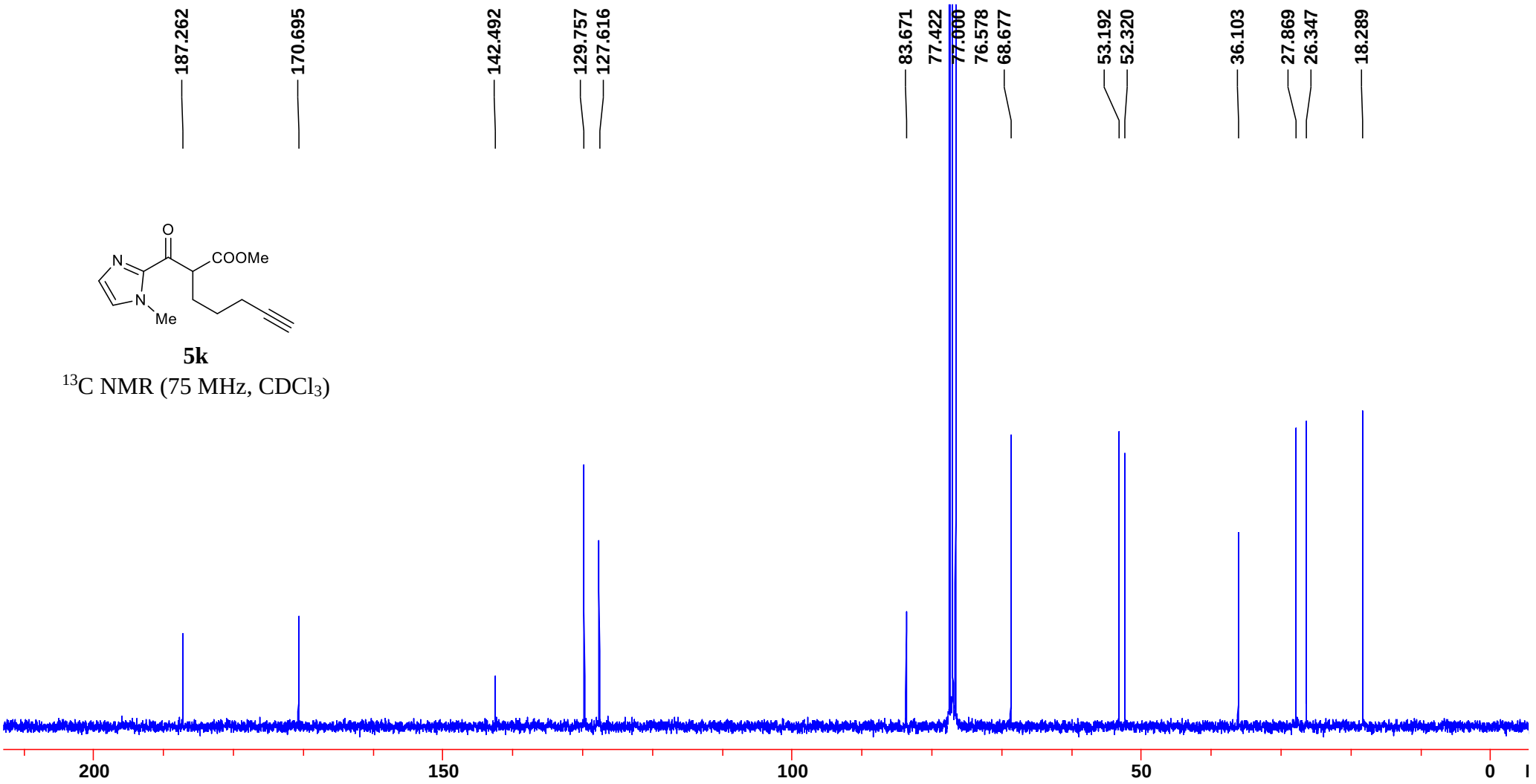
5j

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



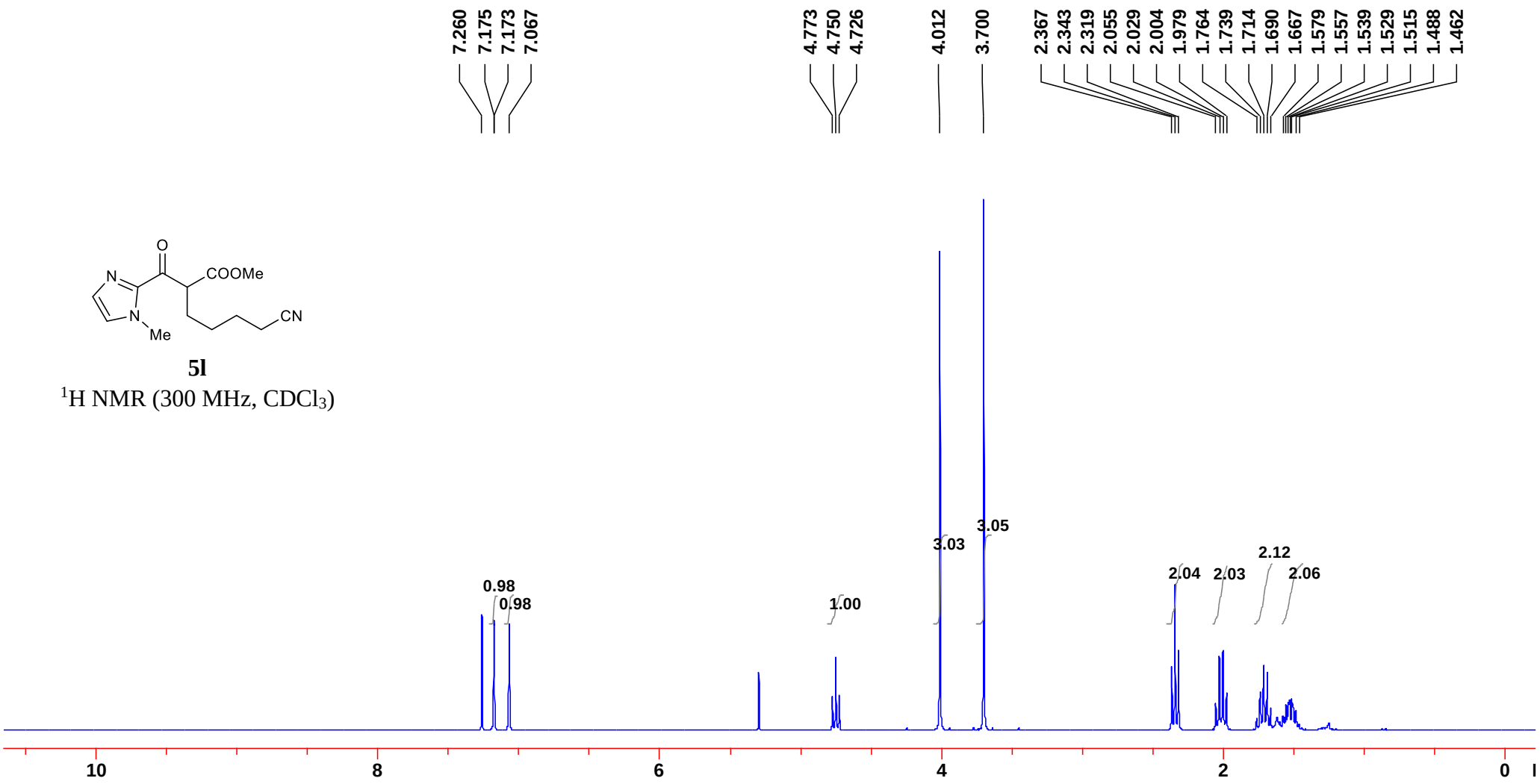
5k

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



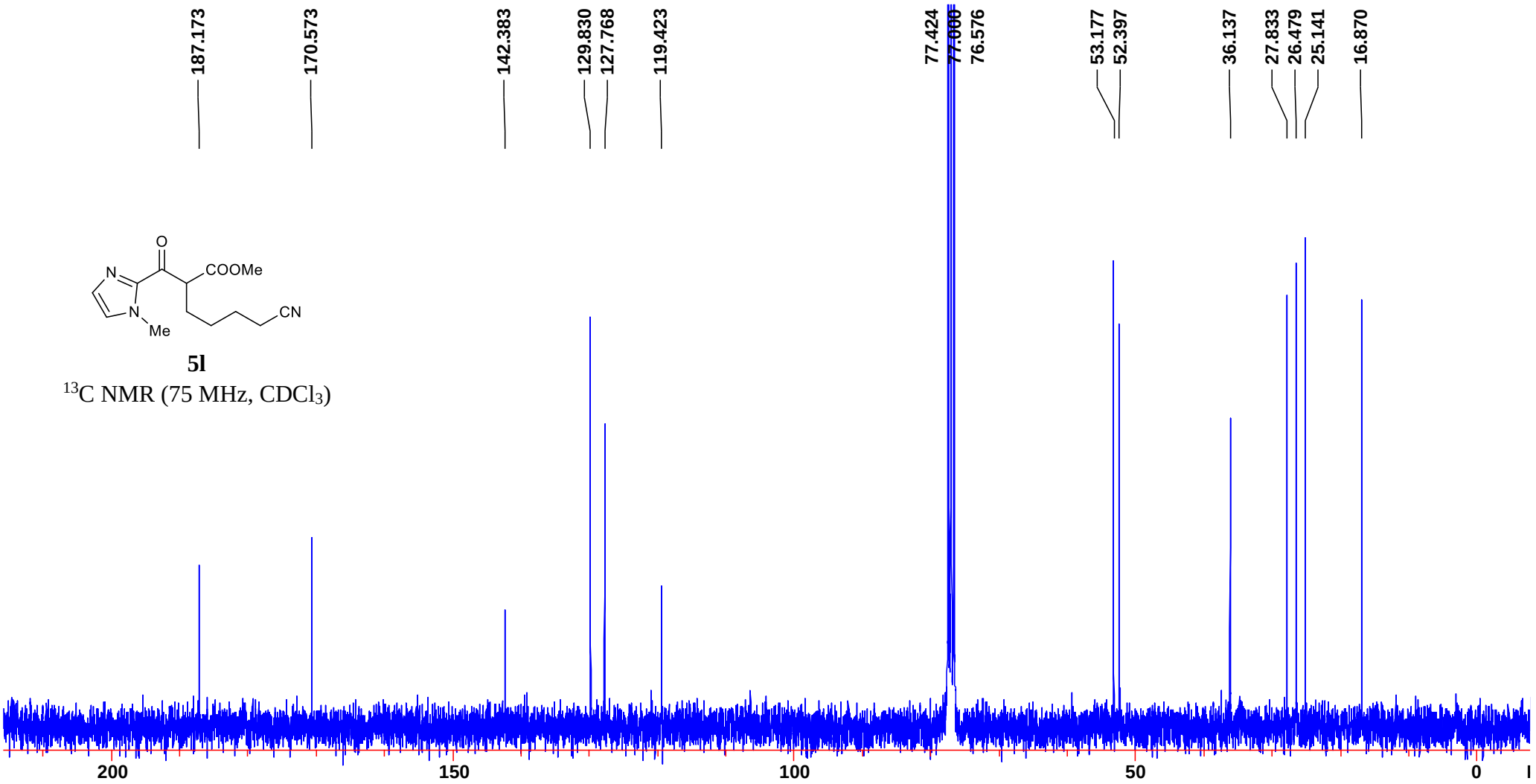
5k

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



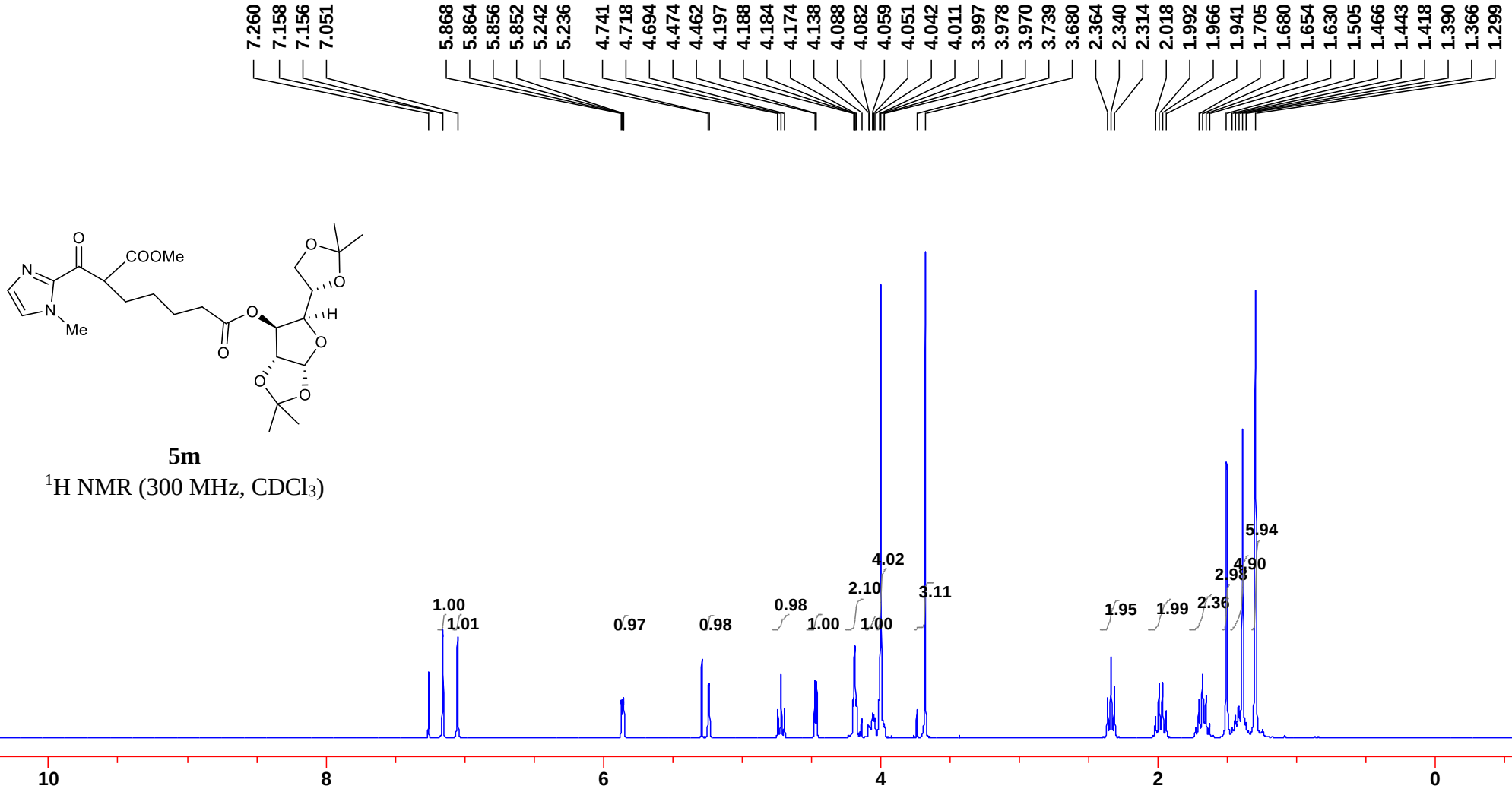
5l

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



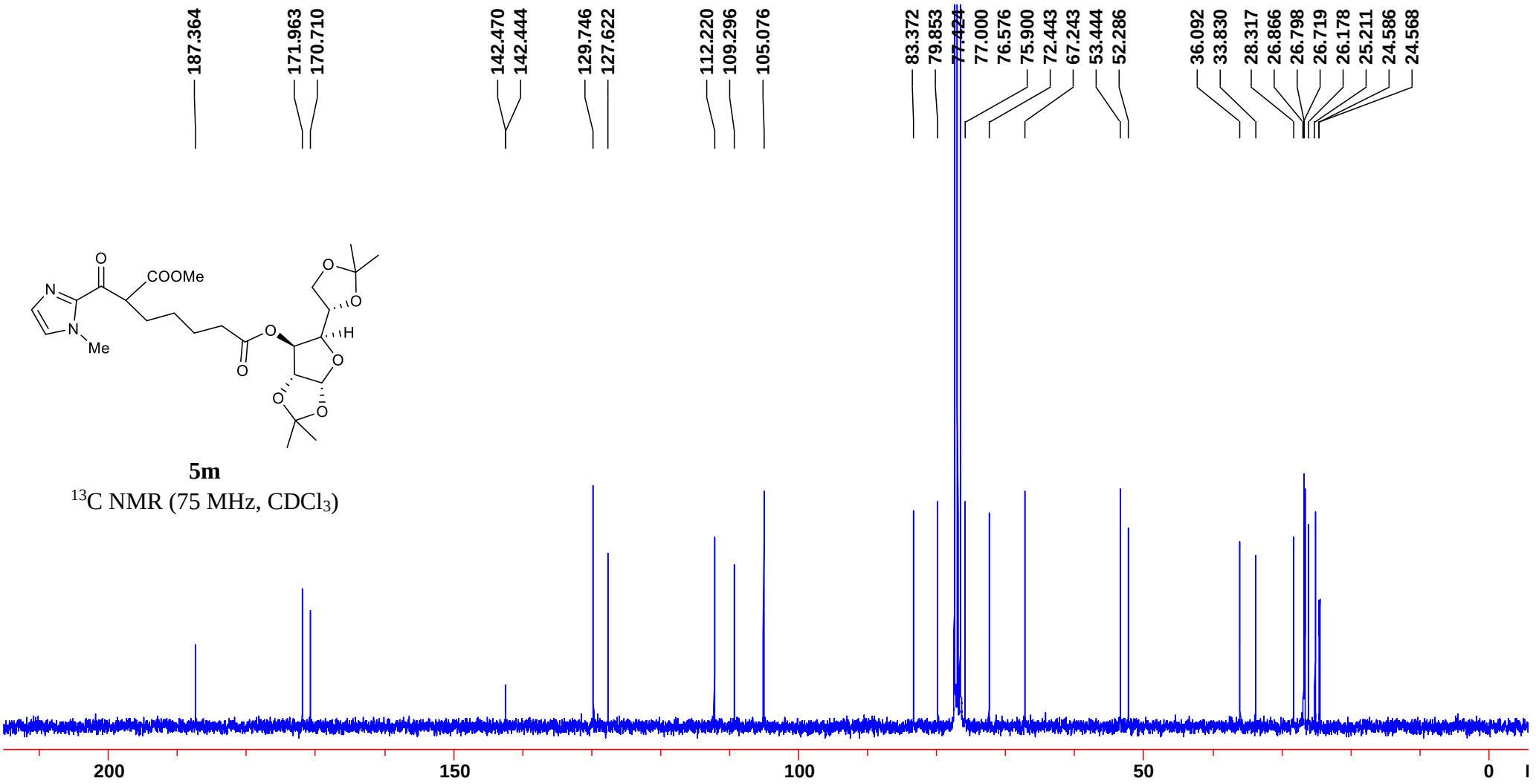
5l

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



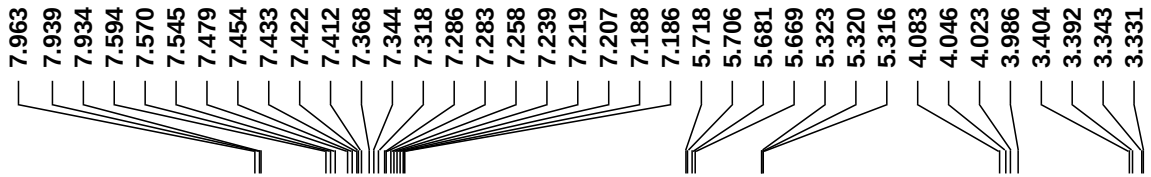
5m

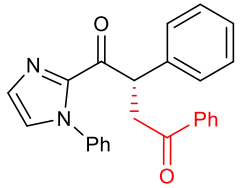
^{1}H NMR (300 MHz, $CDCl_3$)



5m

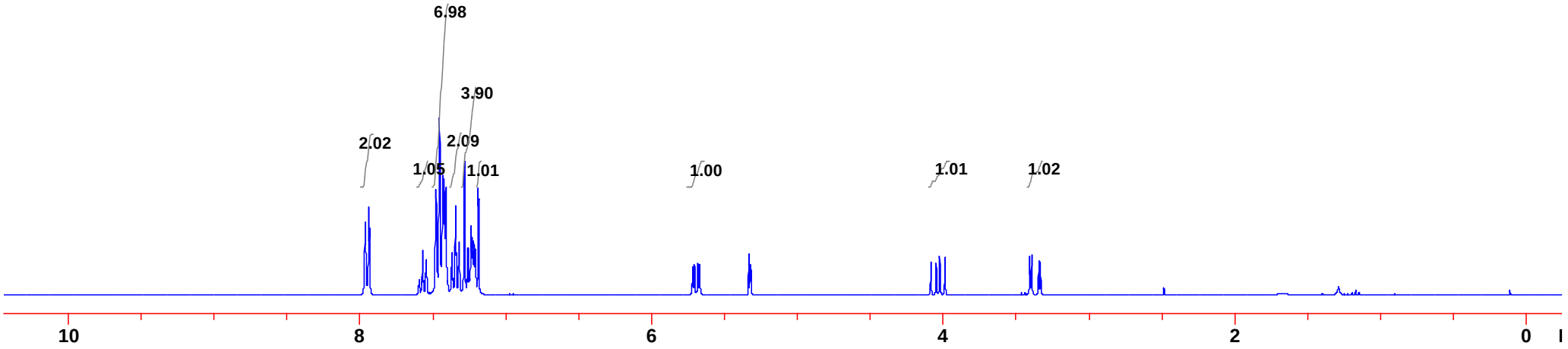
^{13}C NMR (75 MHz, $CDCl_3$)

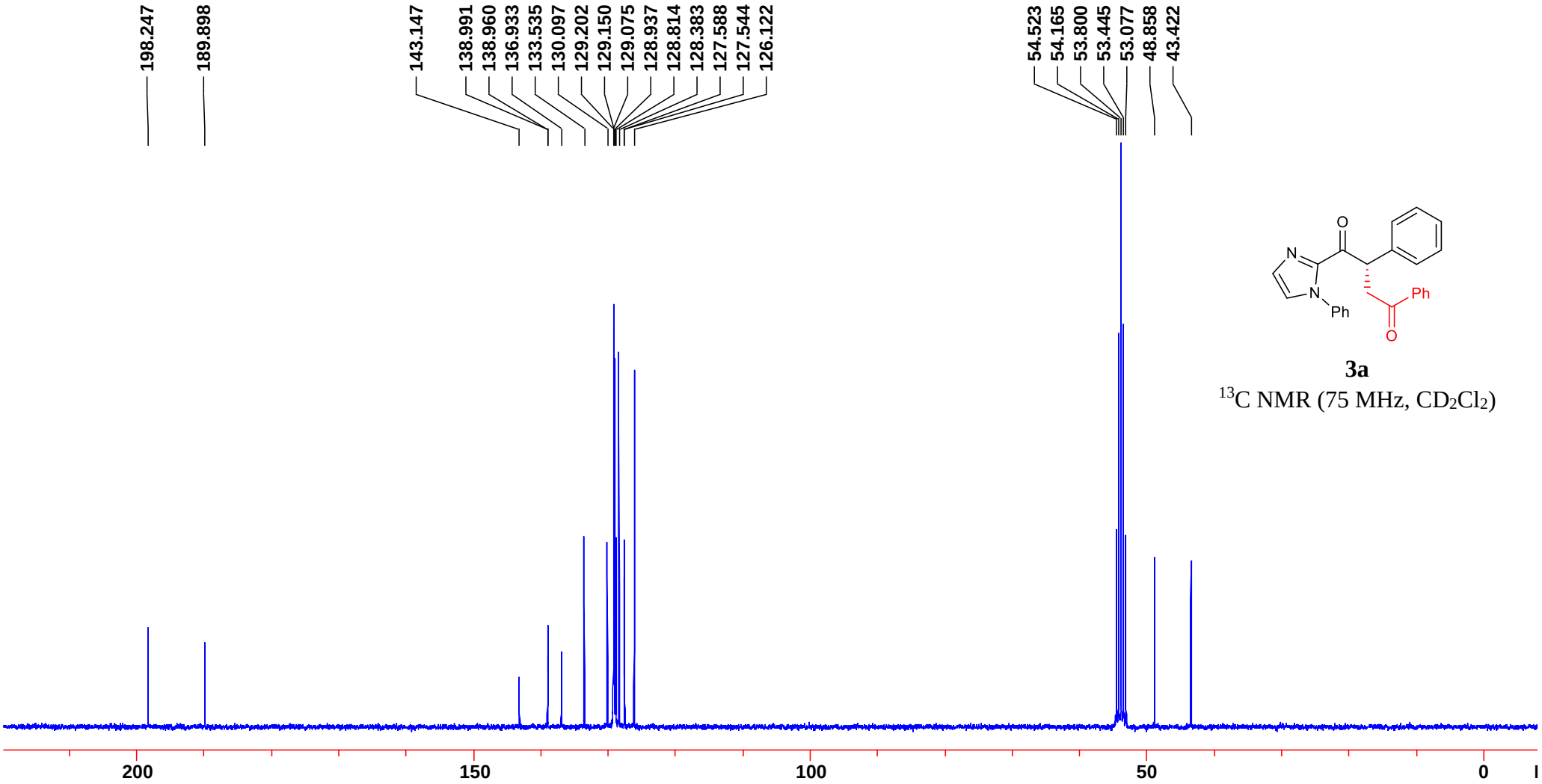




3a

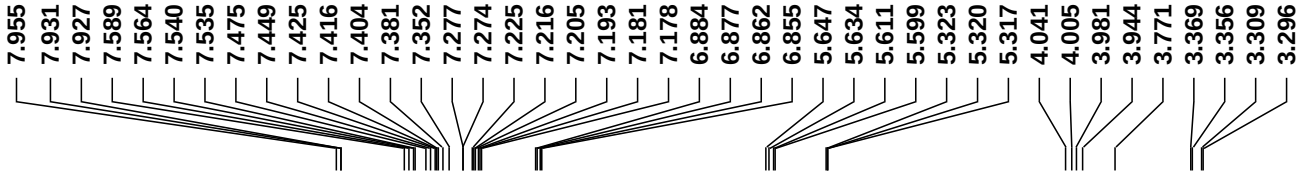
^{1}H NMR (300 MHz, CD_2Cl_2)

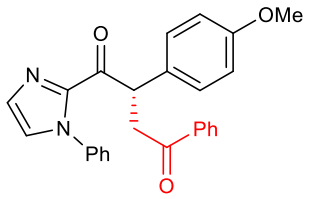




3a

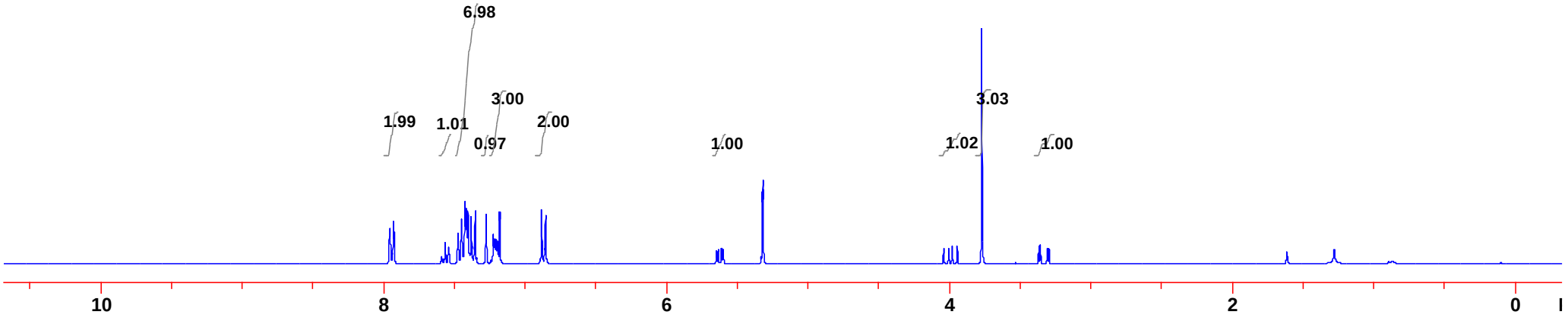
^{13}C NMR (75 MHz, CD_2Cl_2)

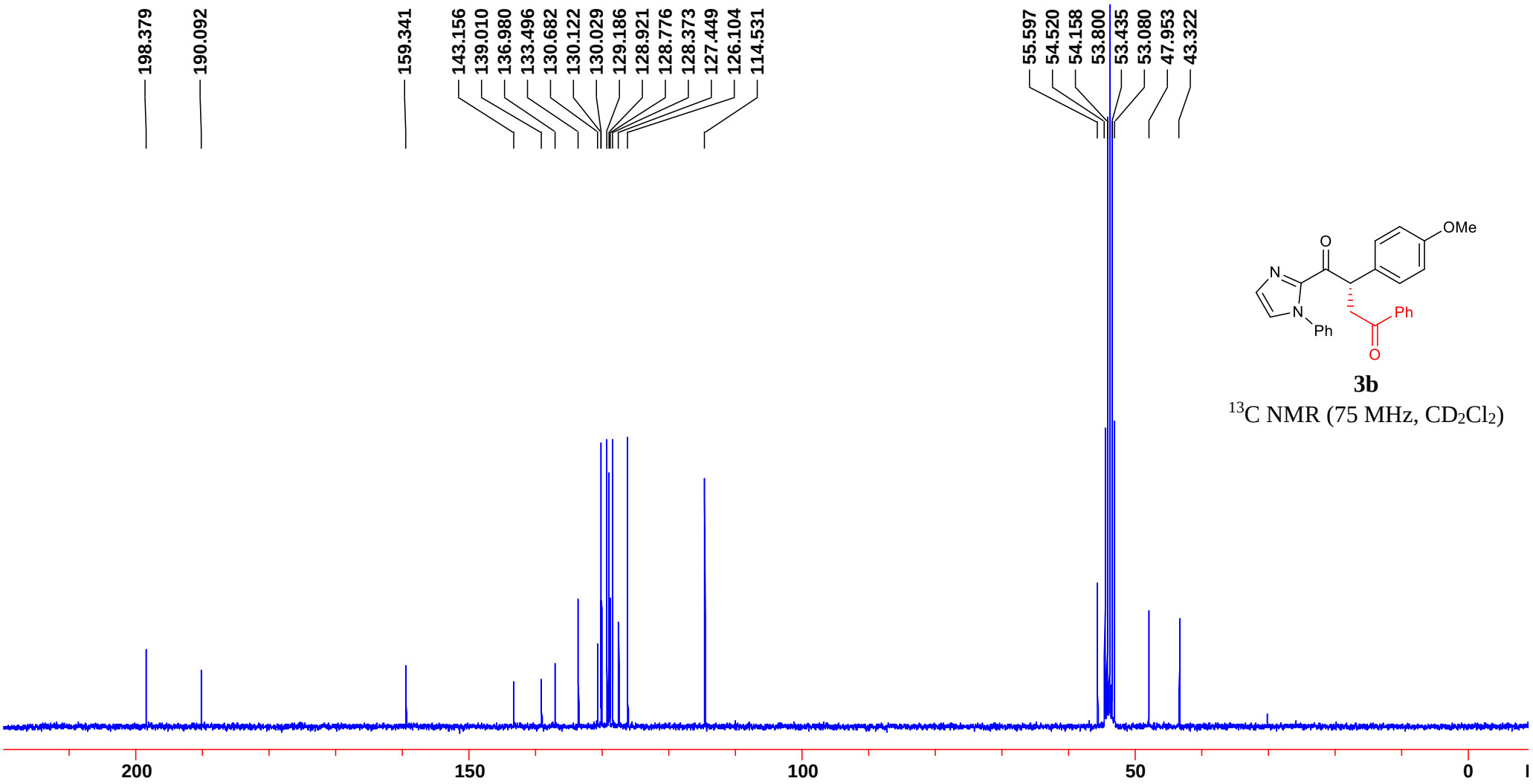




3b

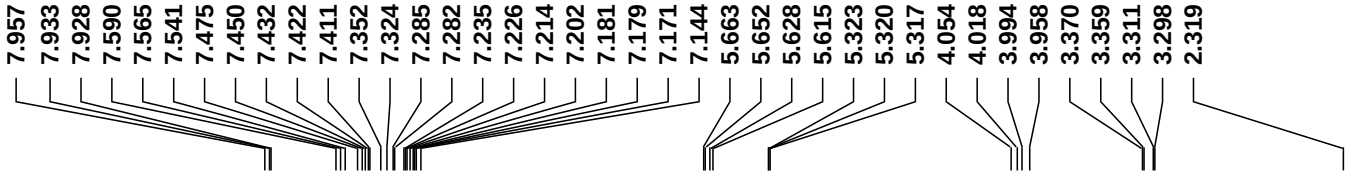
^{1}H NMR (300 MHz, CD_2Cl_2)

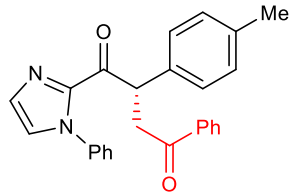




3b

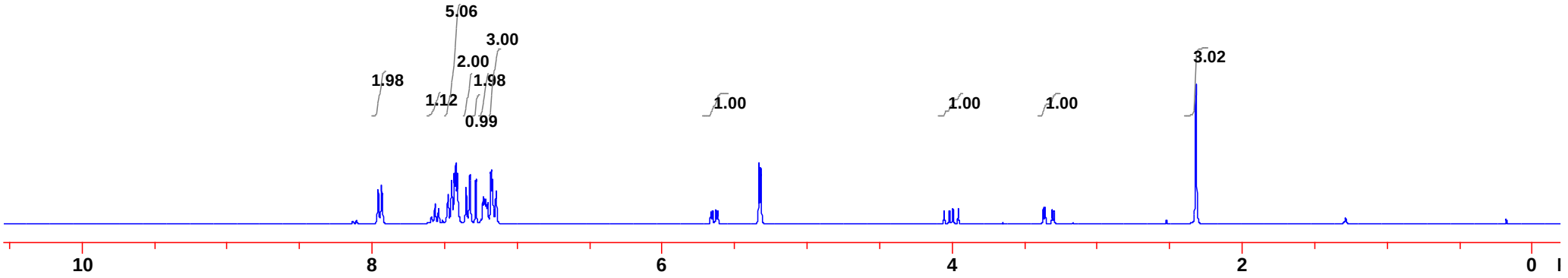
^{13}C NMR (75 MHz, CD_2Cl_2)

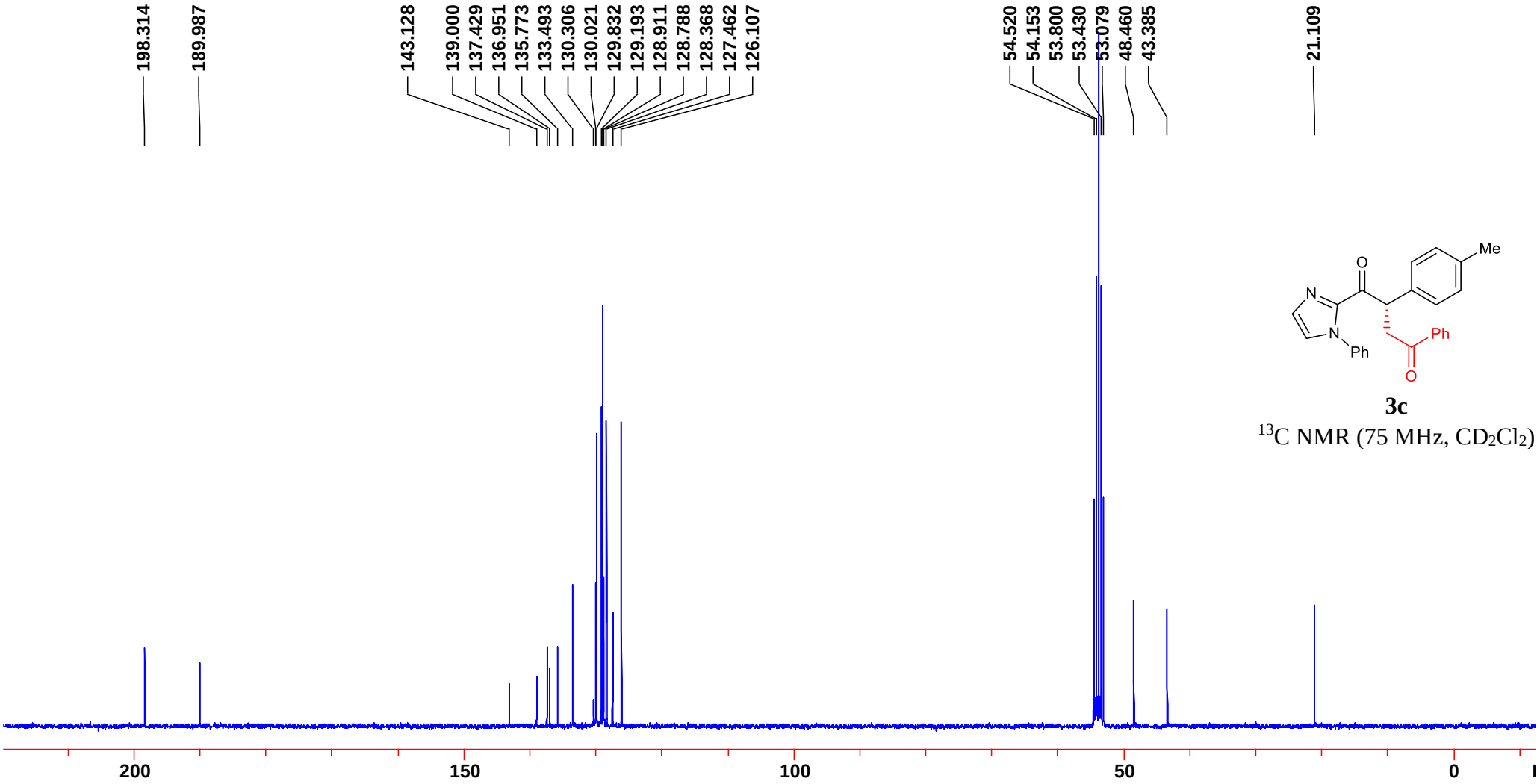




3c

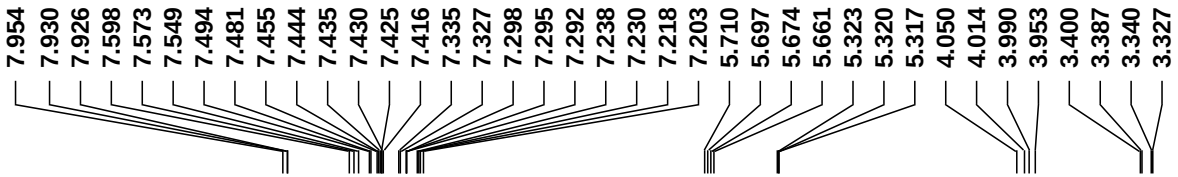
^{1}H NMR (300 MHz, CD_2Cl_2)

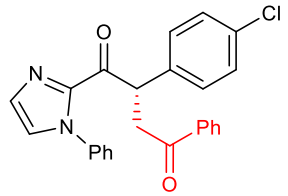




3c

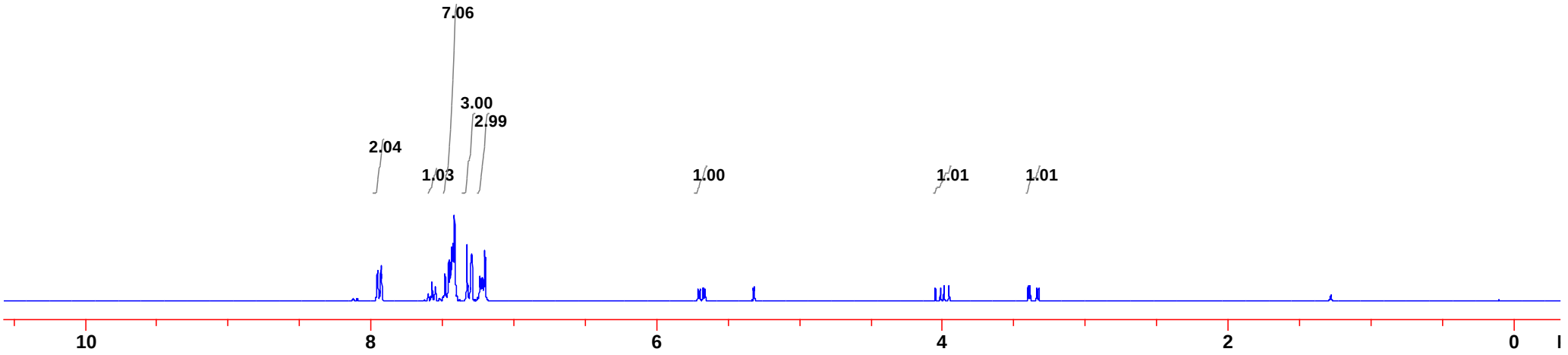
^{13}C NMR (75 MHz, CD_2Cl_2)

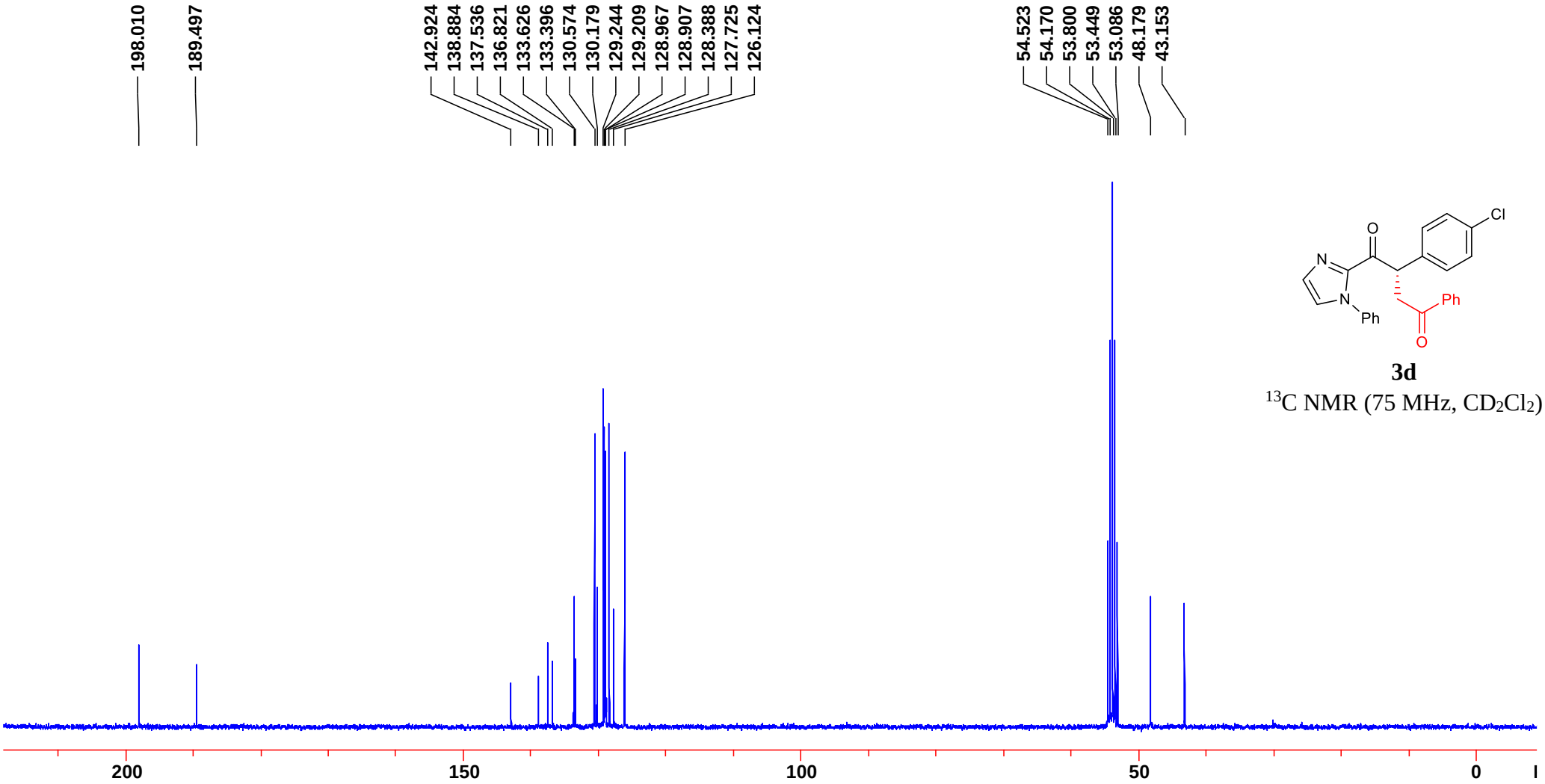




3d

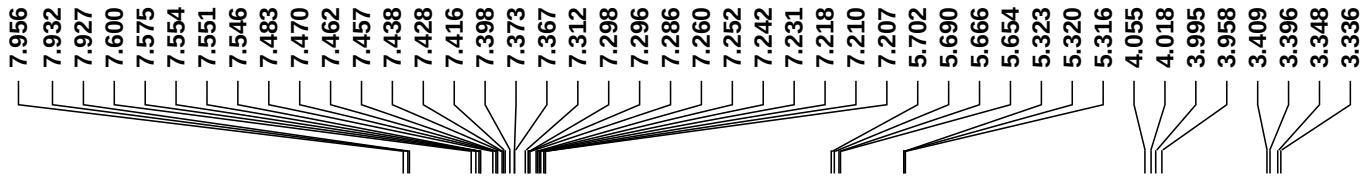
^{1}H NMR (300 MHz, CD_2Cl_2)

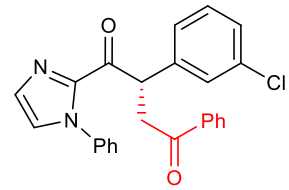




3d

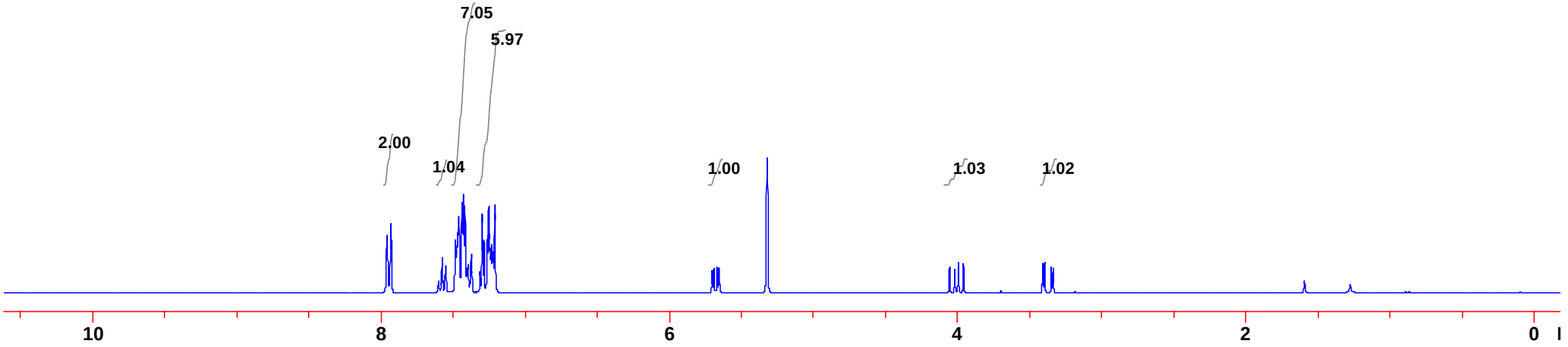
^{13}C NMR (75 MHz, CD_2Cl_2)

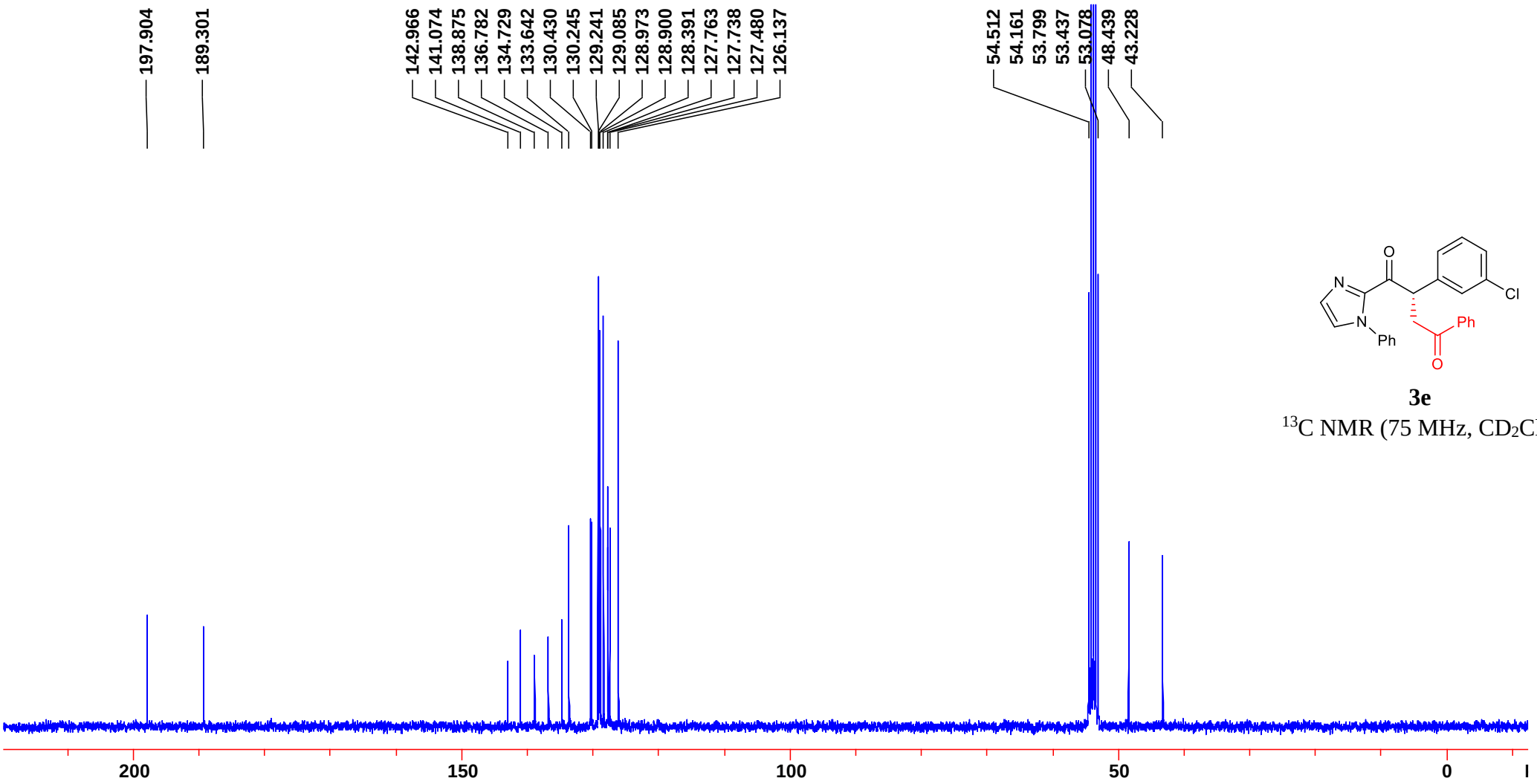




3e

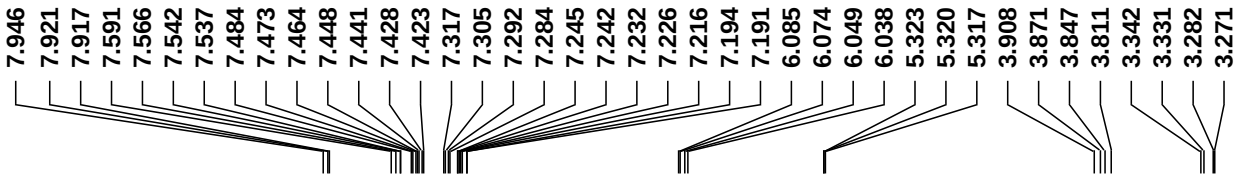
^{1}H NMR (300 MHz, CD_2Cl_2)

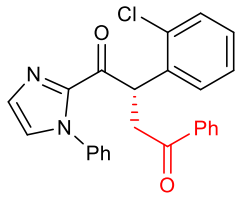




3e

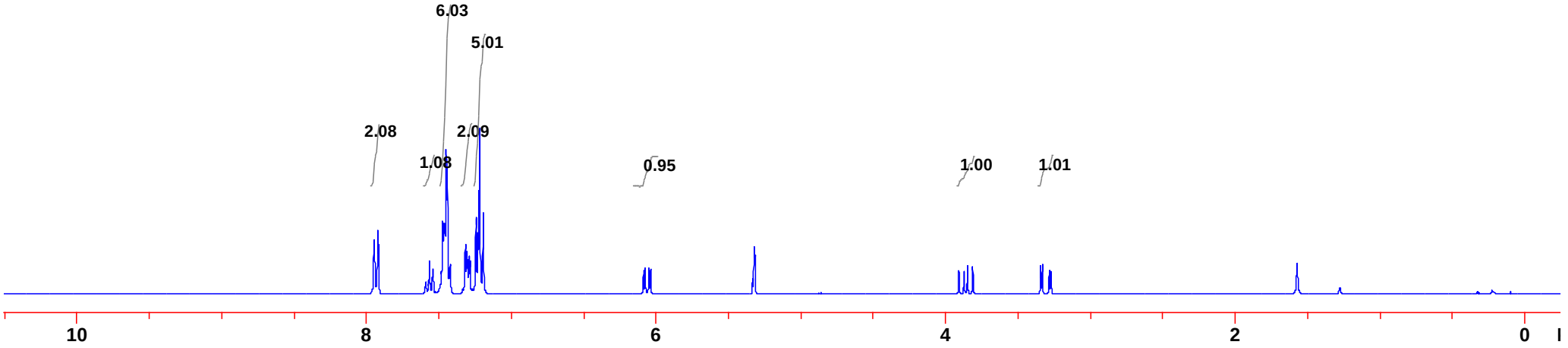
^{13}C NMR (75 MHz, CD_2Cl_2)

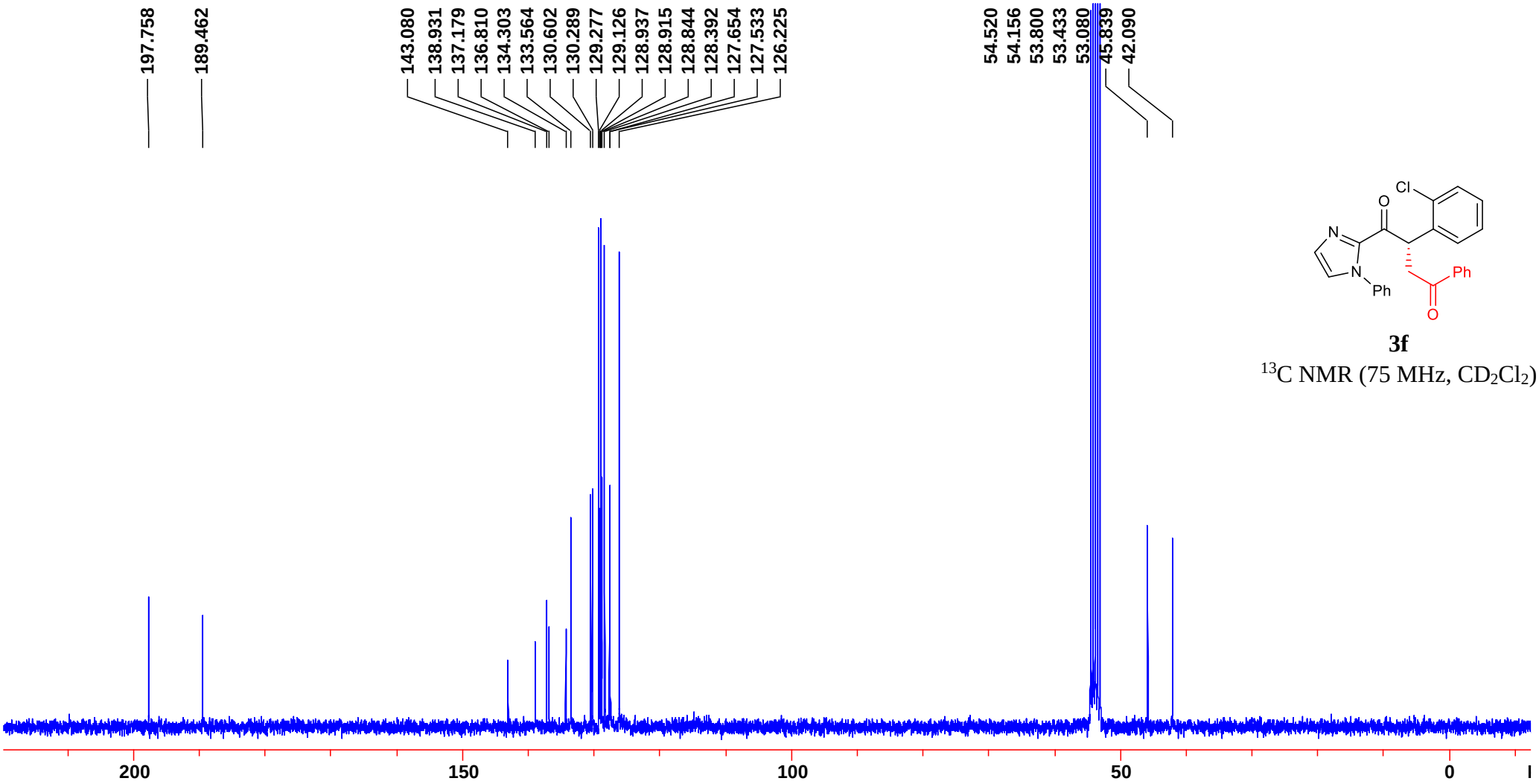




3f

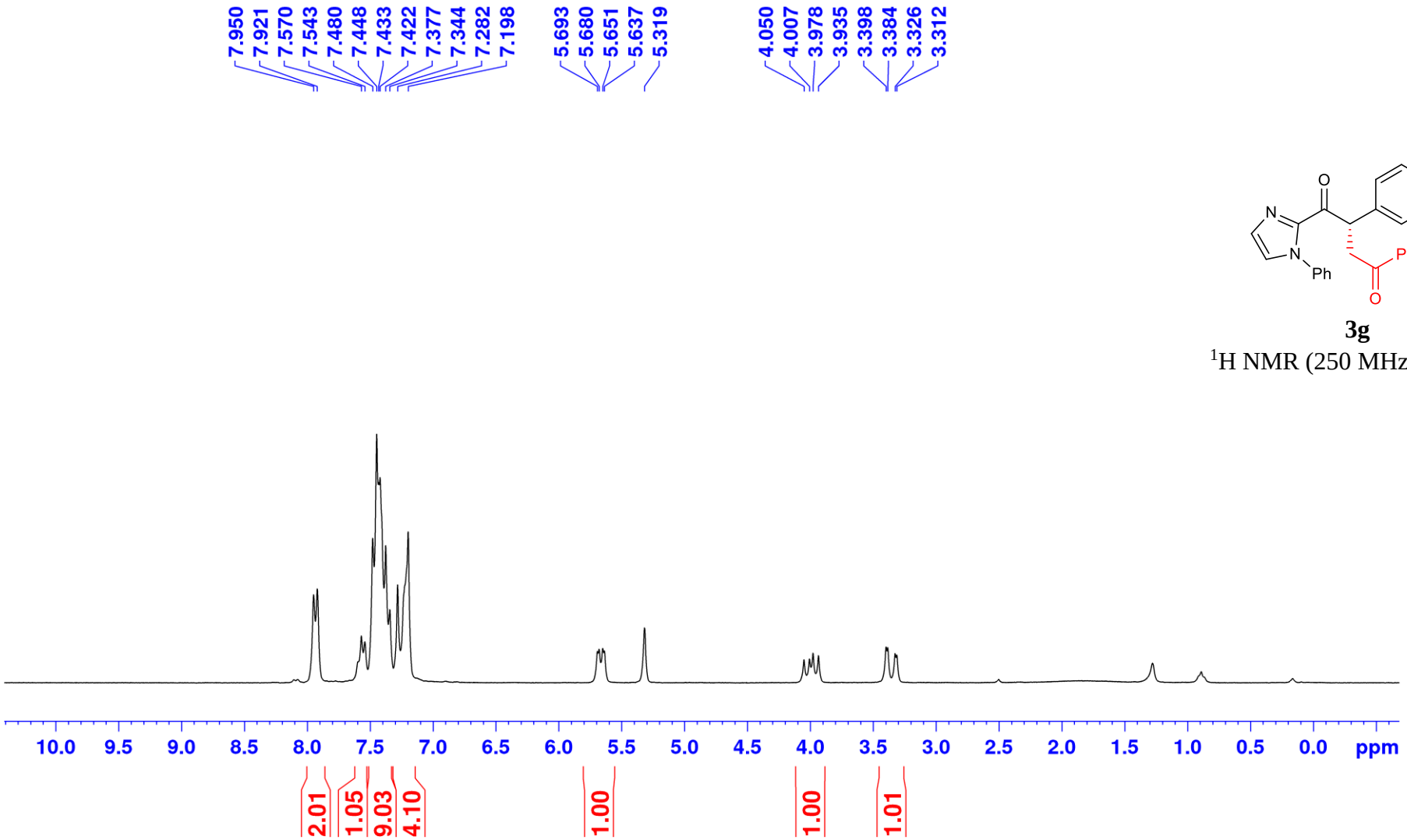
^{1}H NMR (300 MHz, CD_2Cl_2)





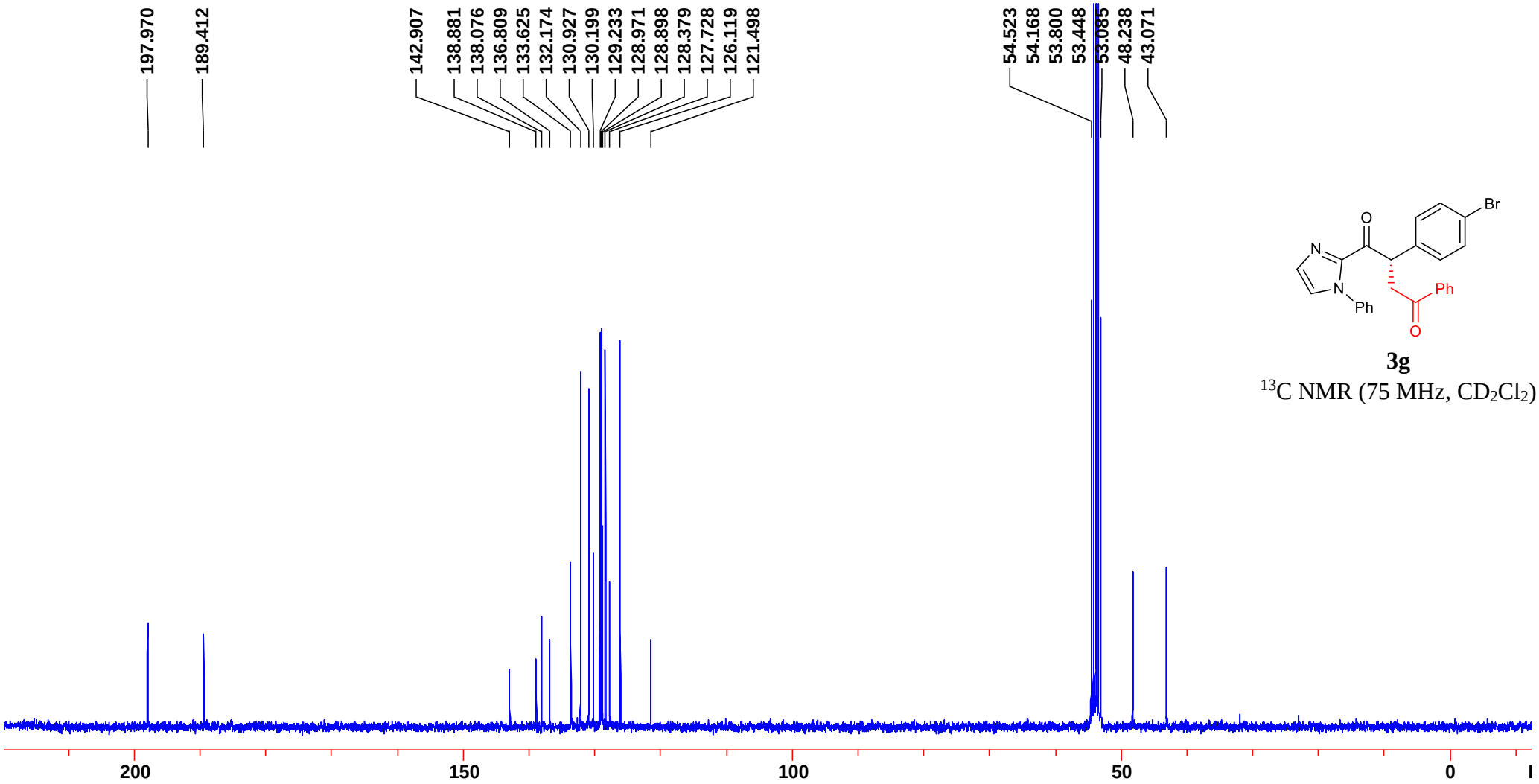
3f

^{13}C NMR (75 MHz, CD_2Cl_2)



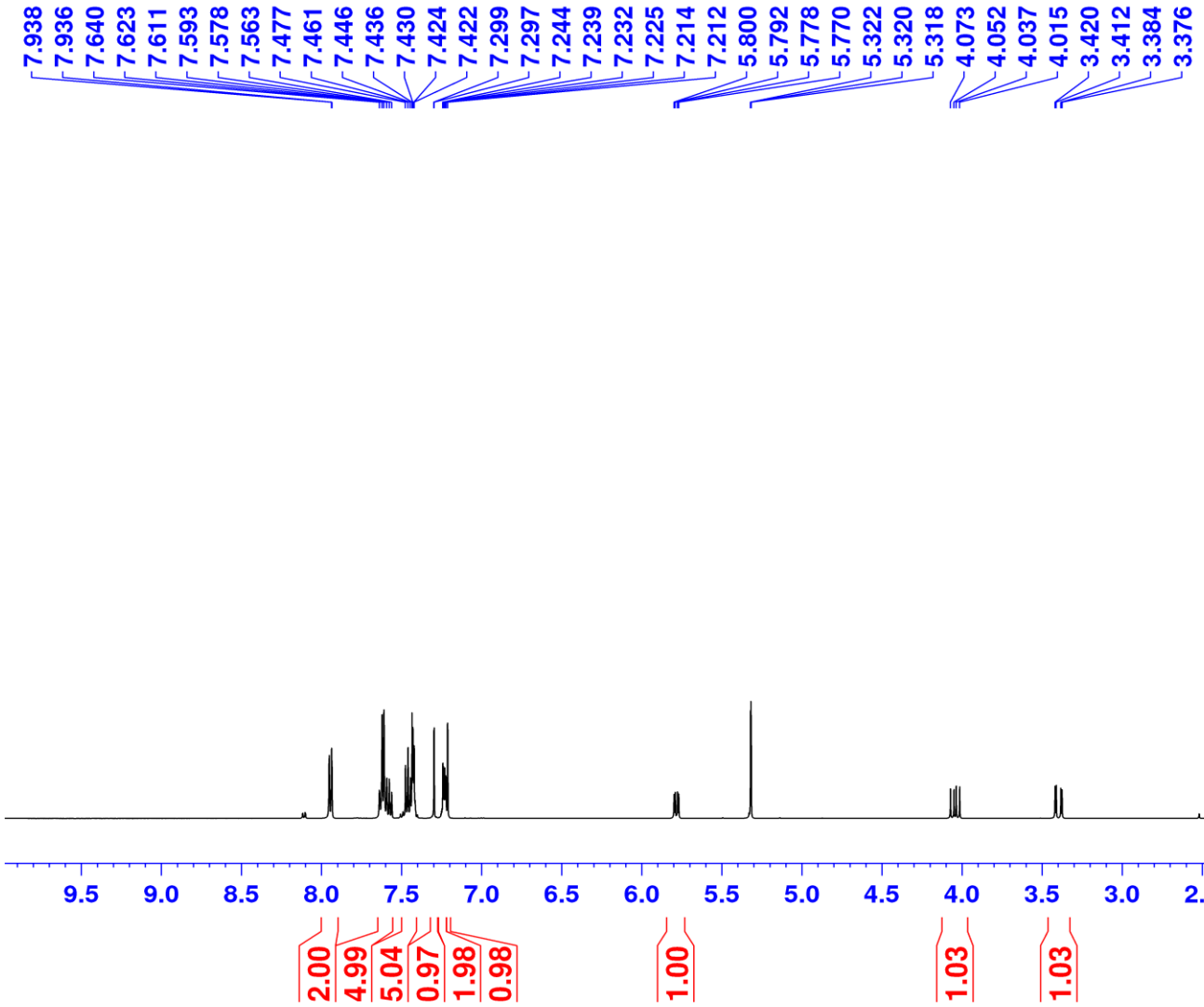
3g

^{1}H NMR (250 MHz, CD_2Cl_2)



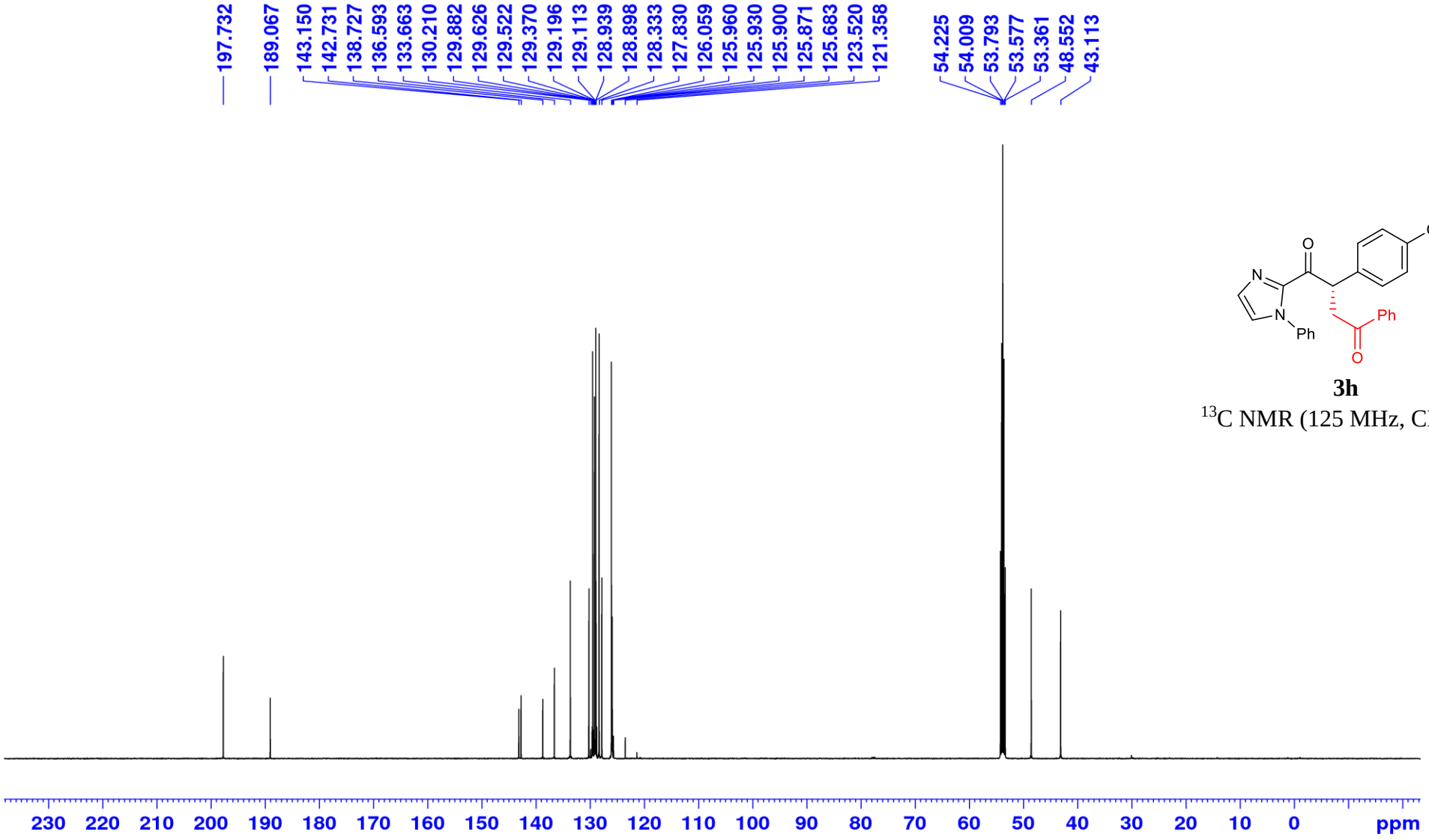
3g

^{13}C NMR (75 MHz, CD_2Cl_2)



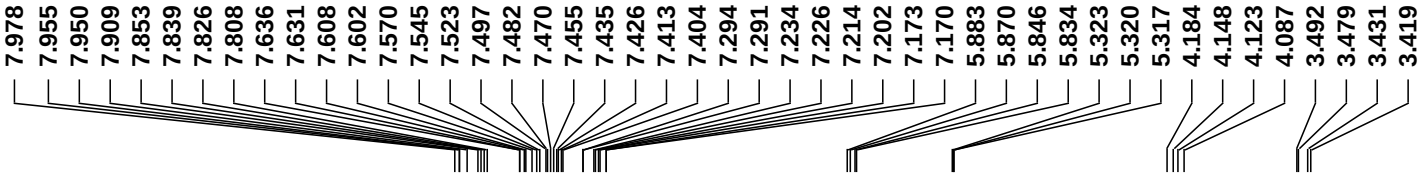
3h

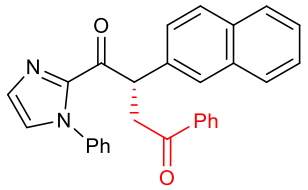
^{1}H NMR (500 MHz, CD_2Cl_2)



3h

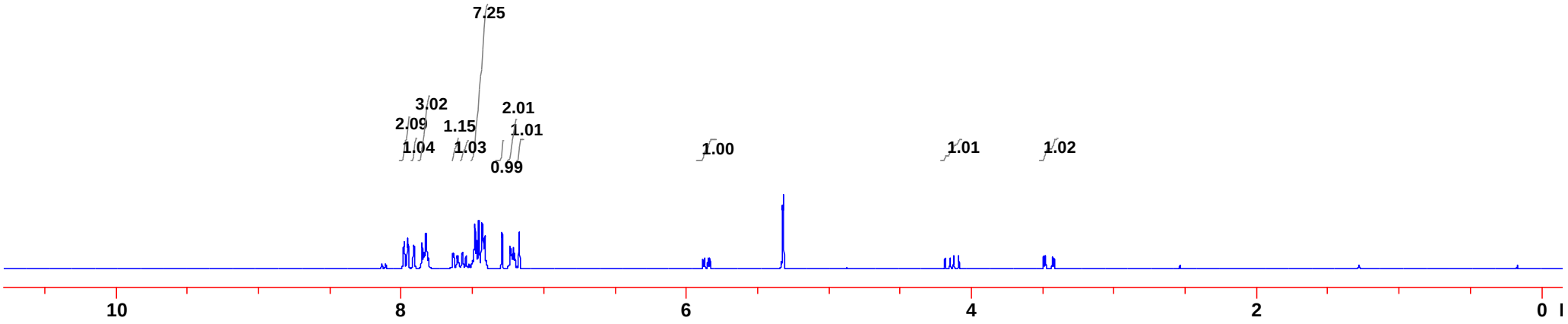
^{13}C NMR (125 MHz, CD_2Cl_2)

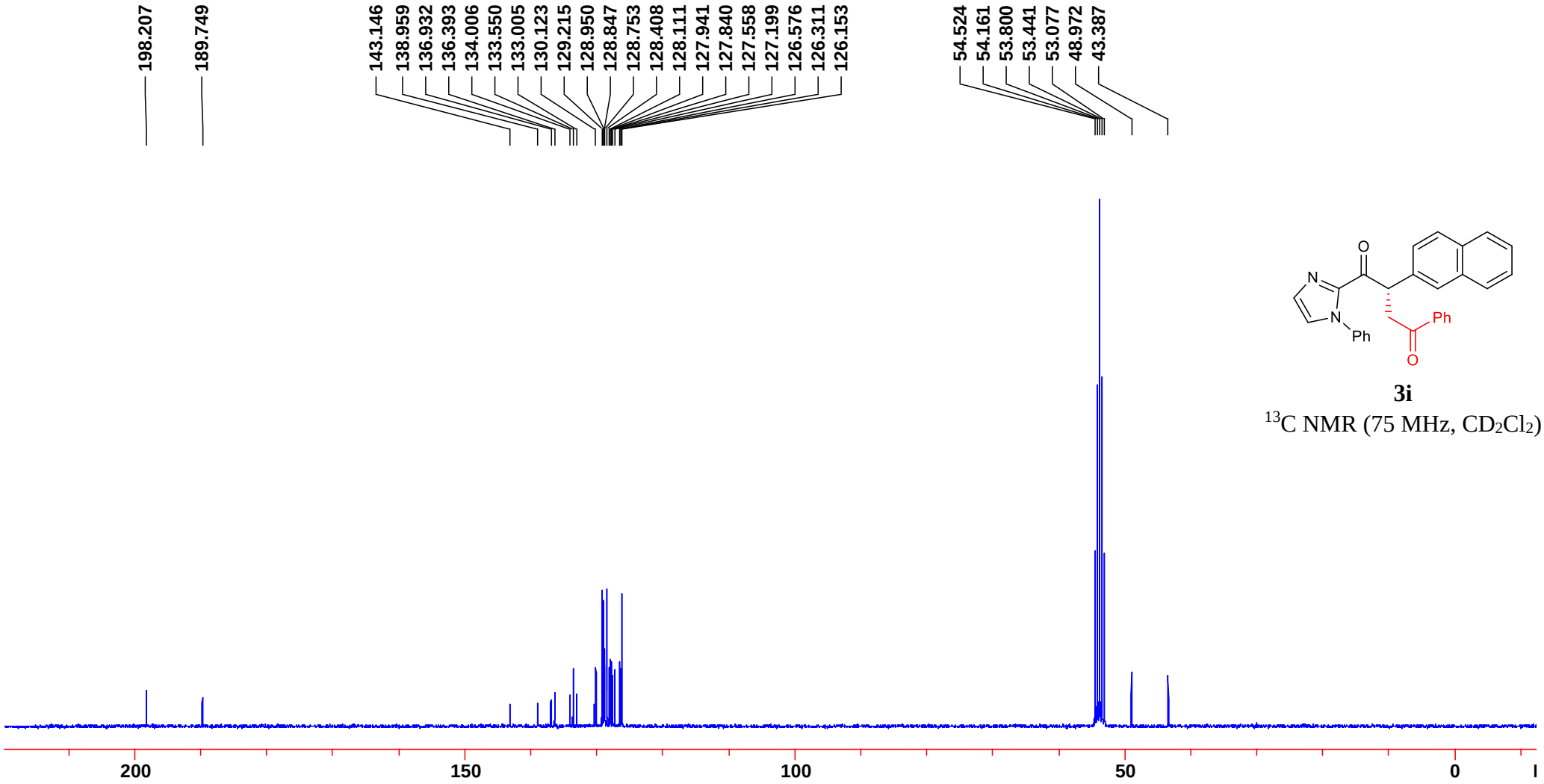




3i

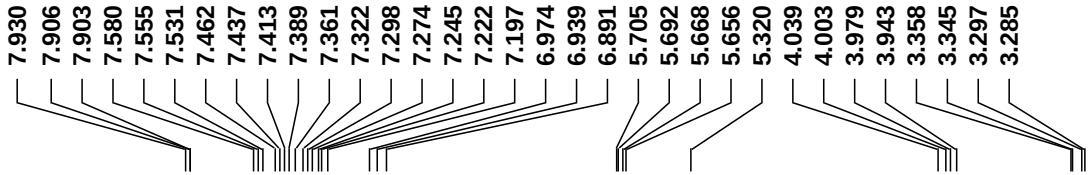
^{1}H NMR (300 MHz, CD_2Cl_2)

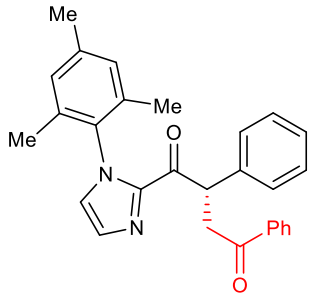




3i

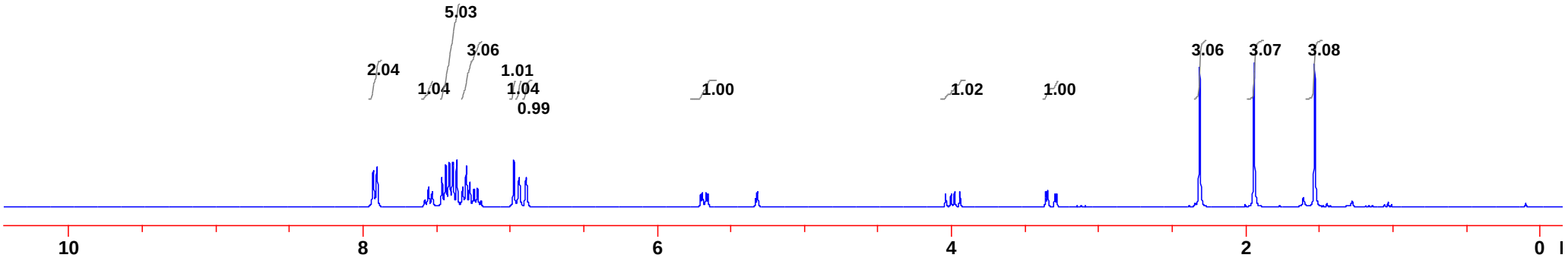
^{13}C NMR (75 MHz, CD_2Cl_2)

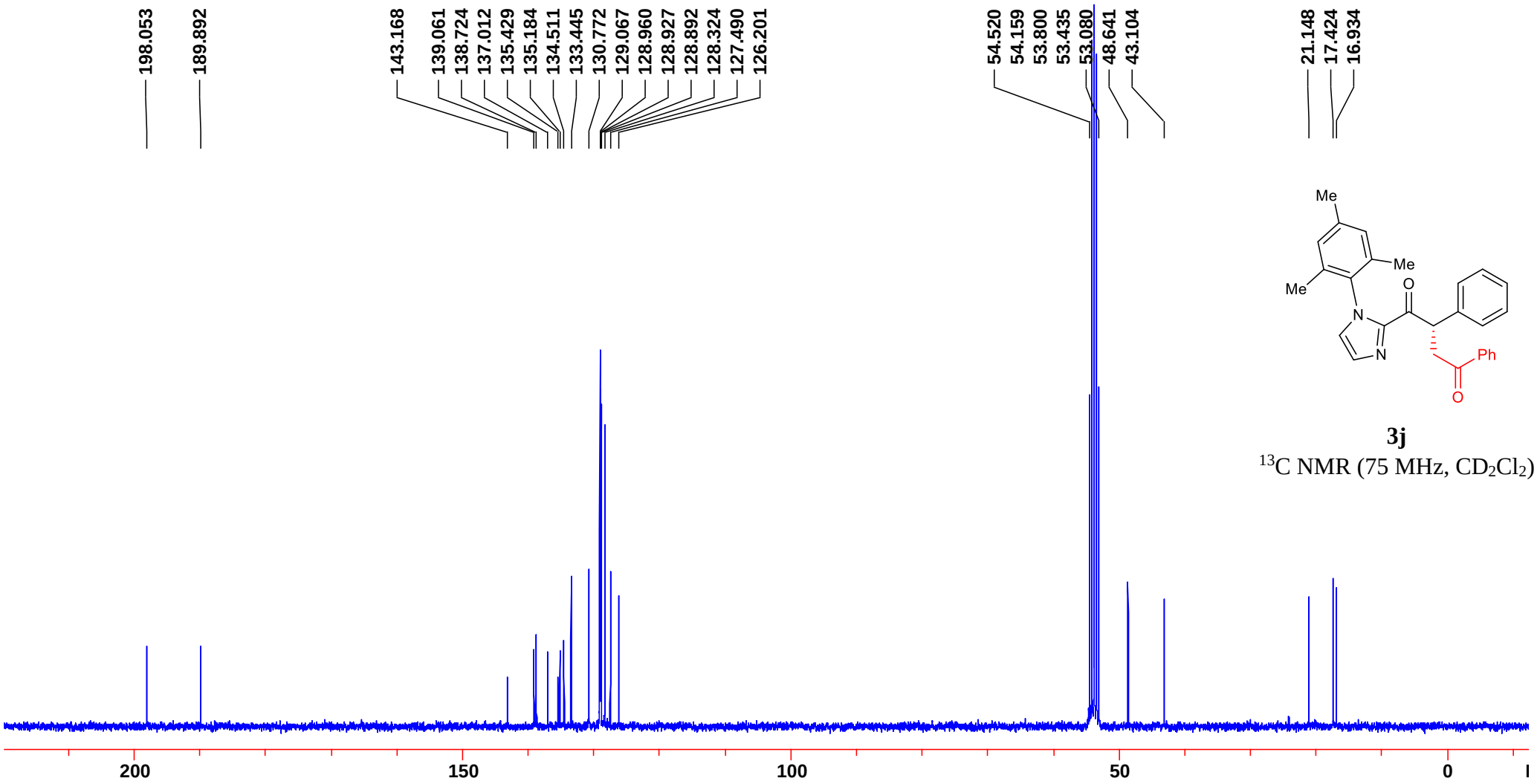




3j

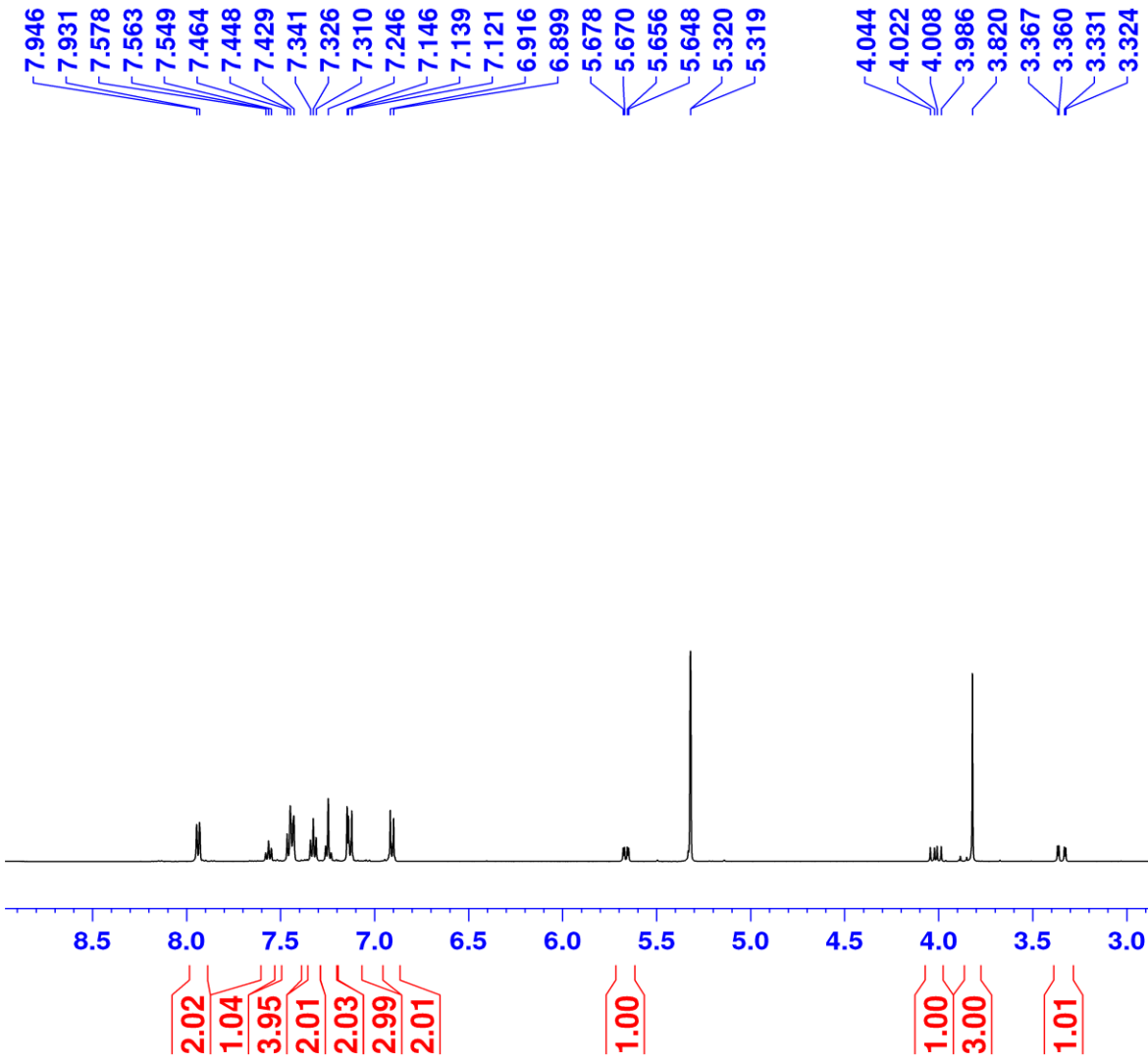
^{1}H NMR (300 MHz, CD_2Cl_2)

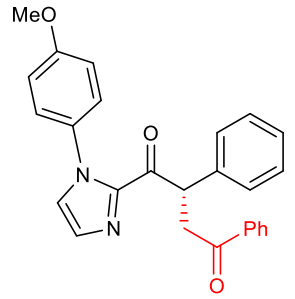




3j

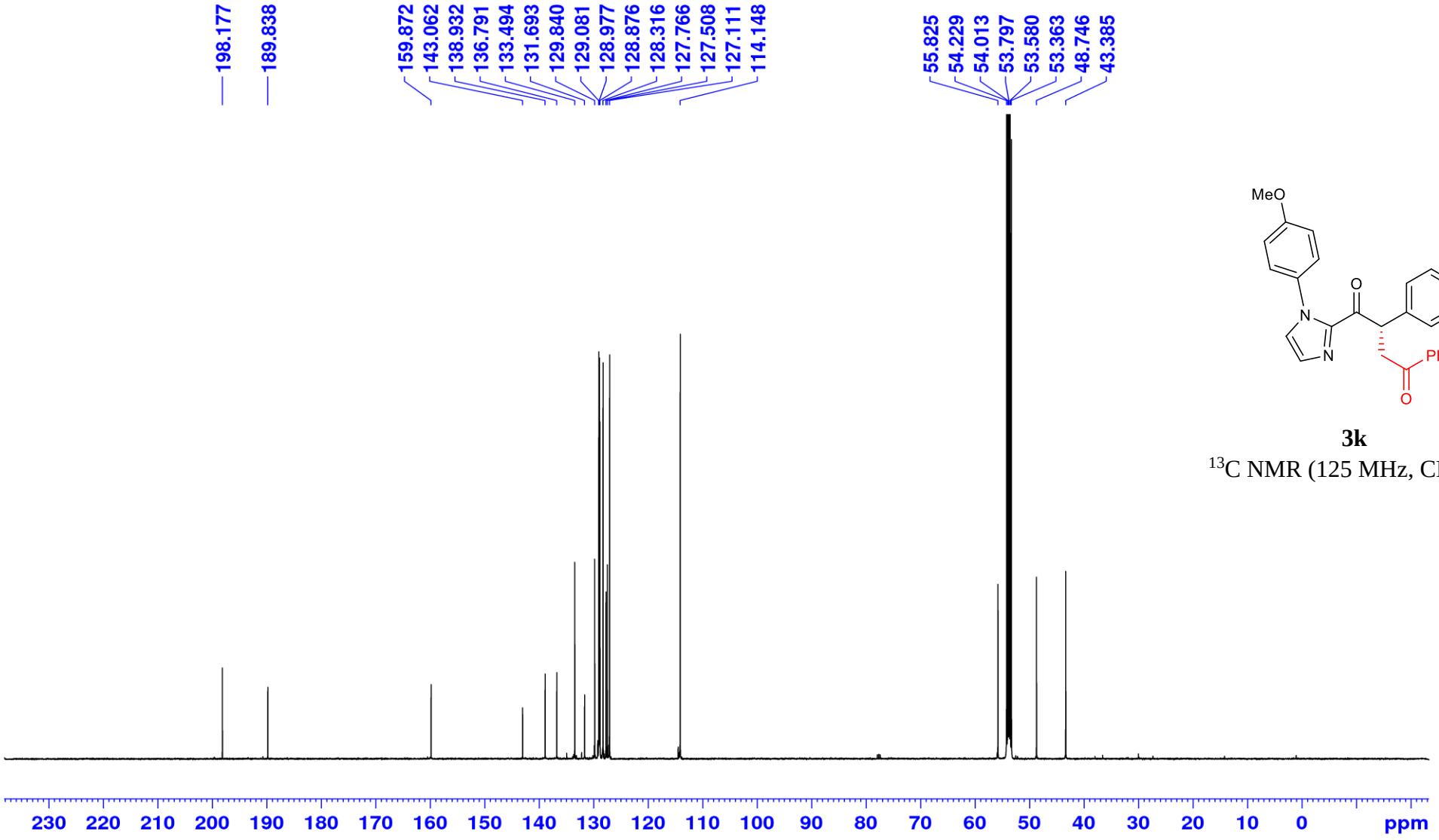
^{13}C NMR (75 MHz, CD_2Cl_2)





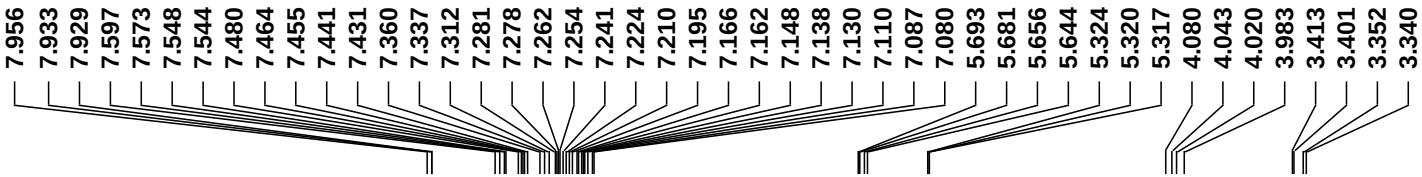
3k

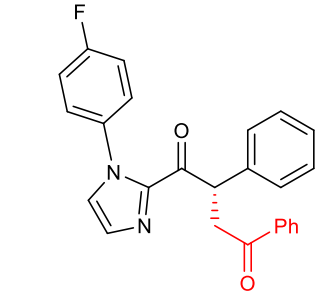
^{1}H NMR (500 MHz, CD_2Cl_2)



3k

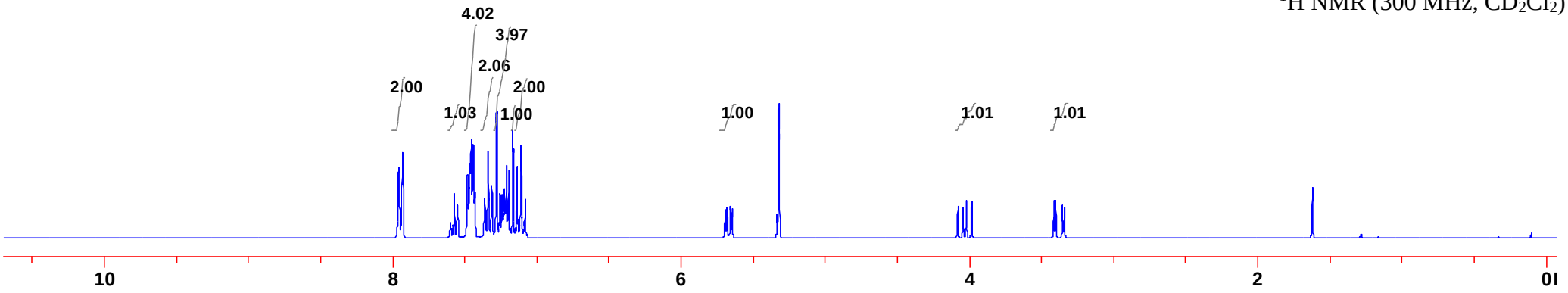
^{13}C NMR (125 MHz, CD_2Cl_2)

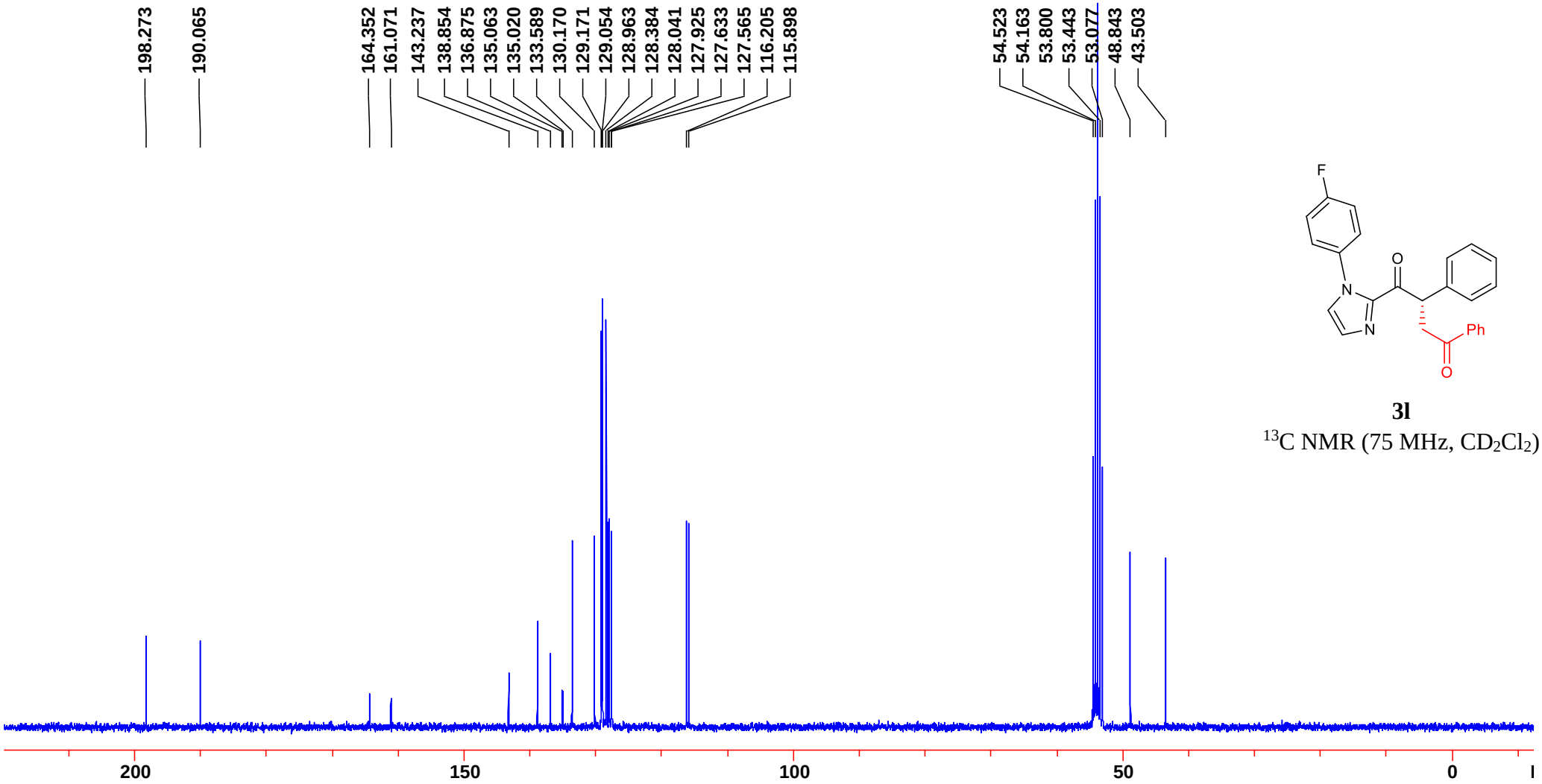




3l

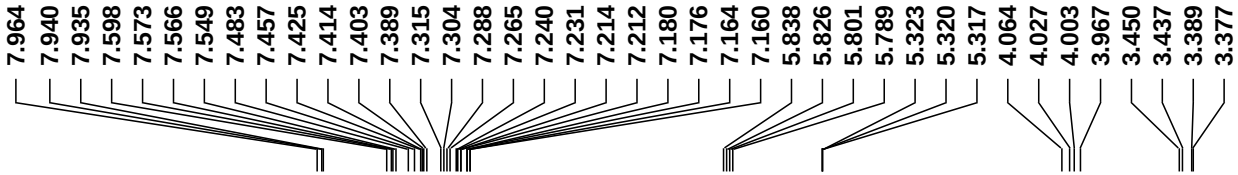
^{1}H NMR (300 MHz, CD_2Cl_2)

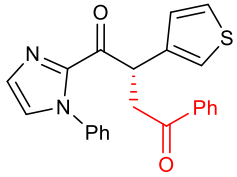




3l

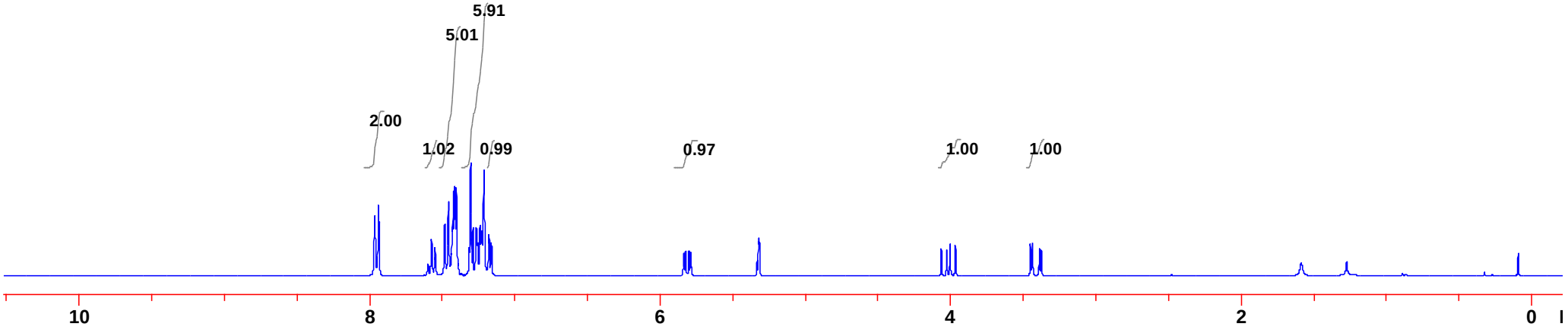
^{13}C NMR (75 MHz, CD_2Cl_2)

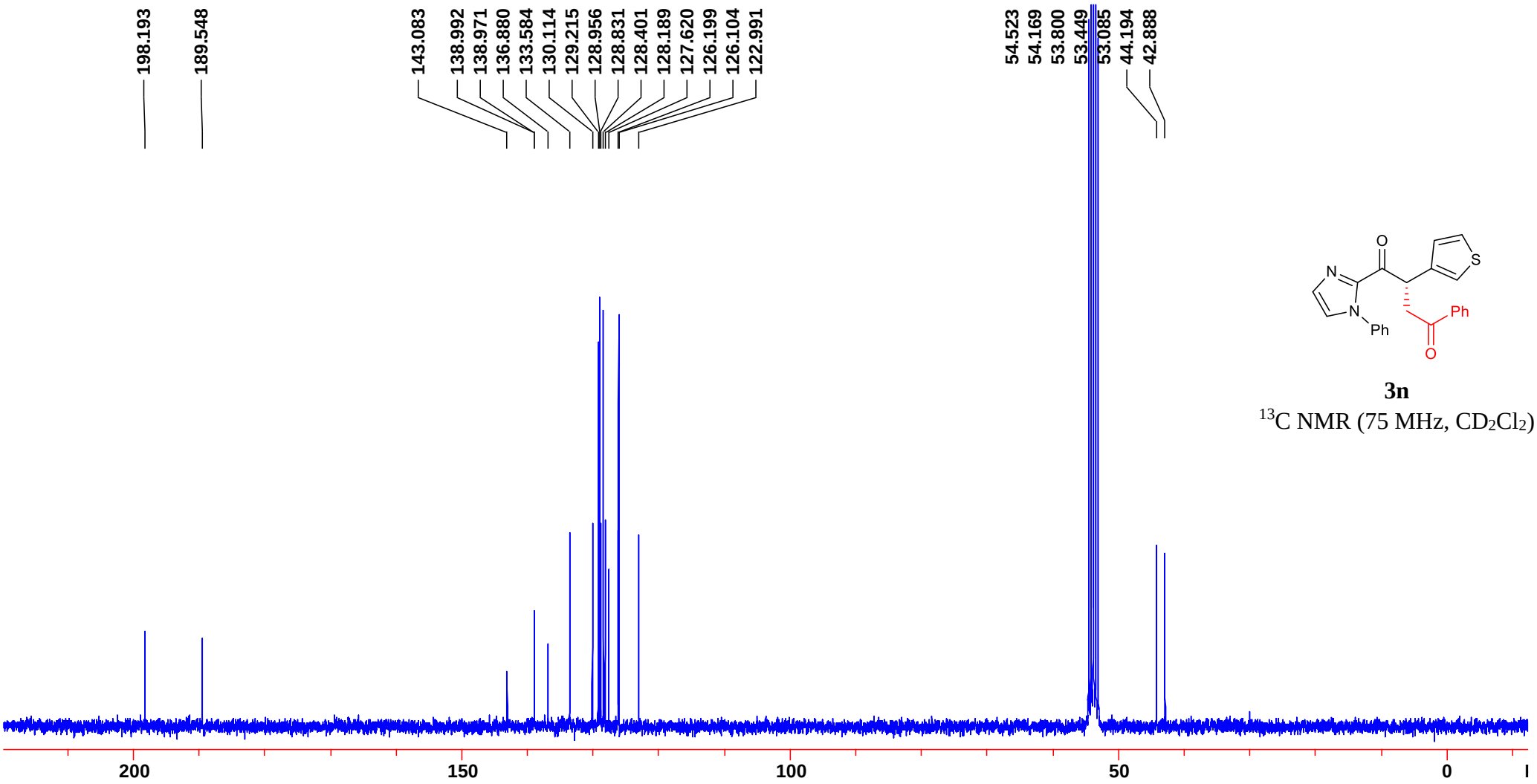




3n

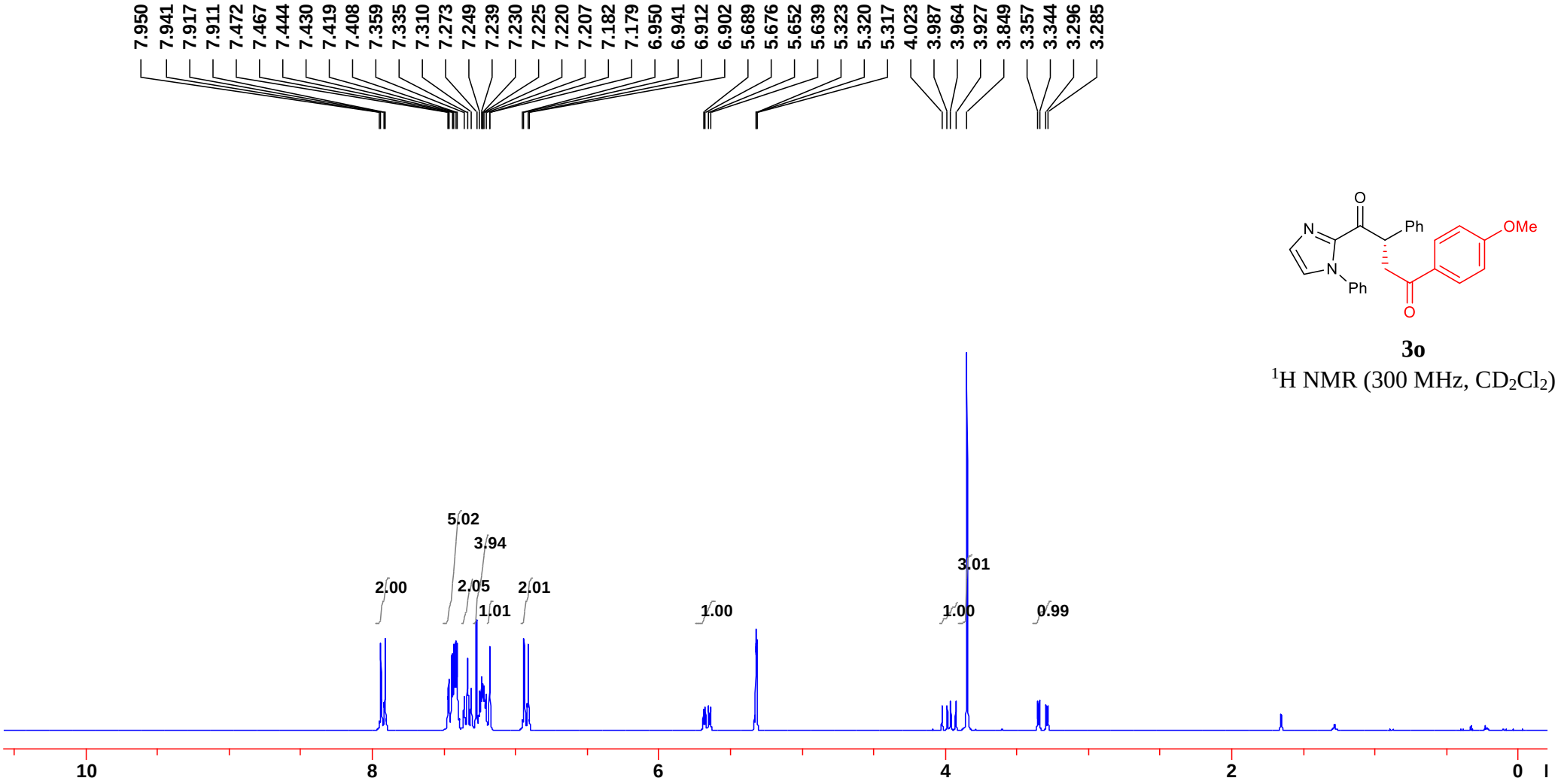
^{1}H NMR (300 MHz, CD_2Cl_2)





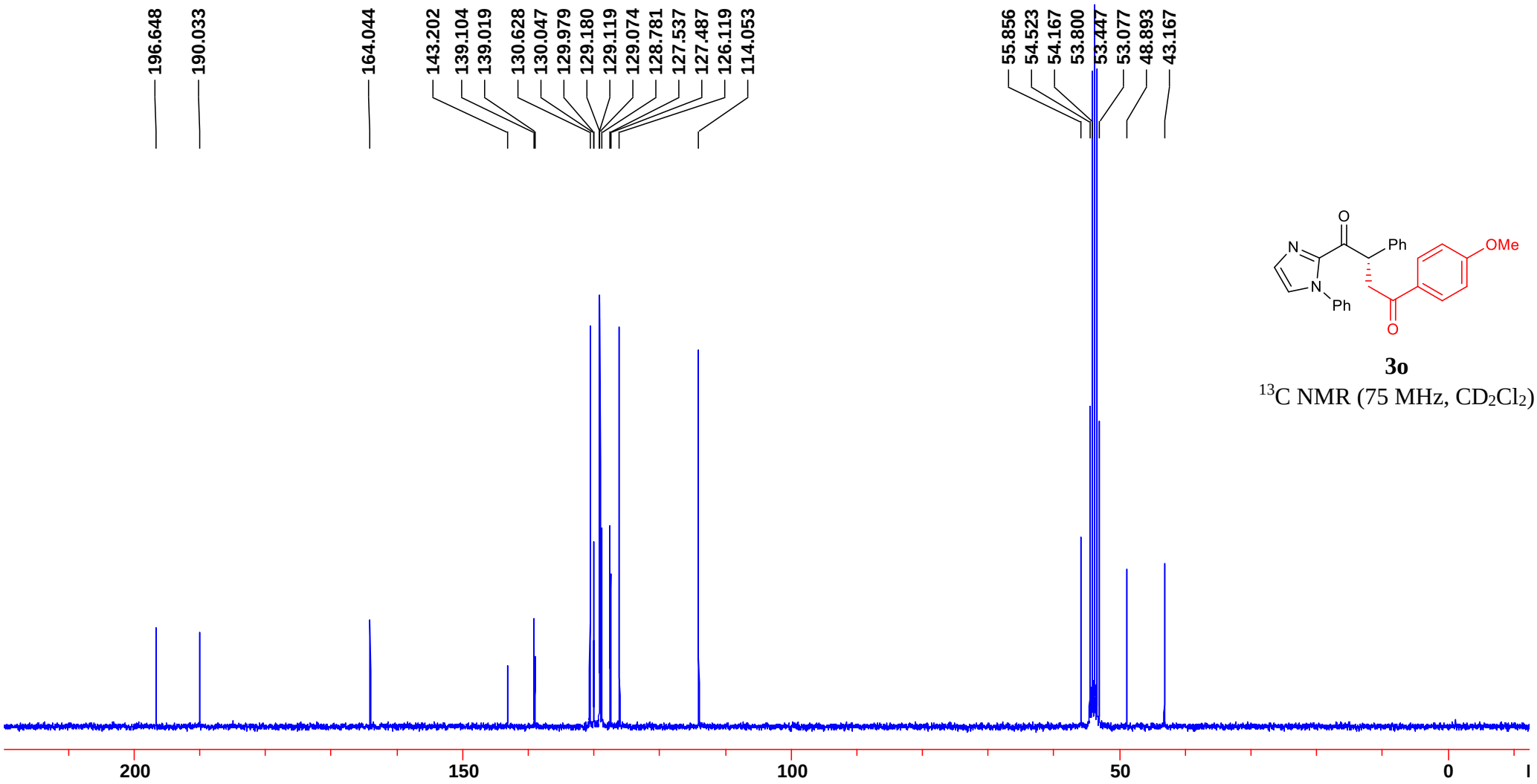
3n

^{13}C NMR (75 MHz, CD_2Cl_2)



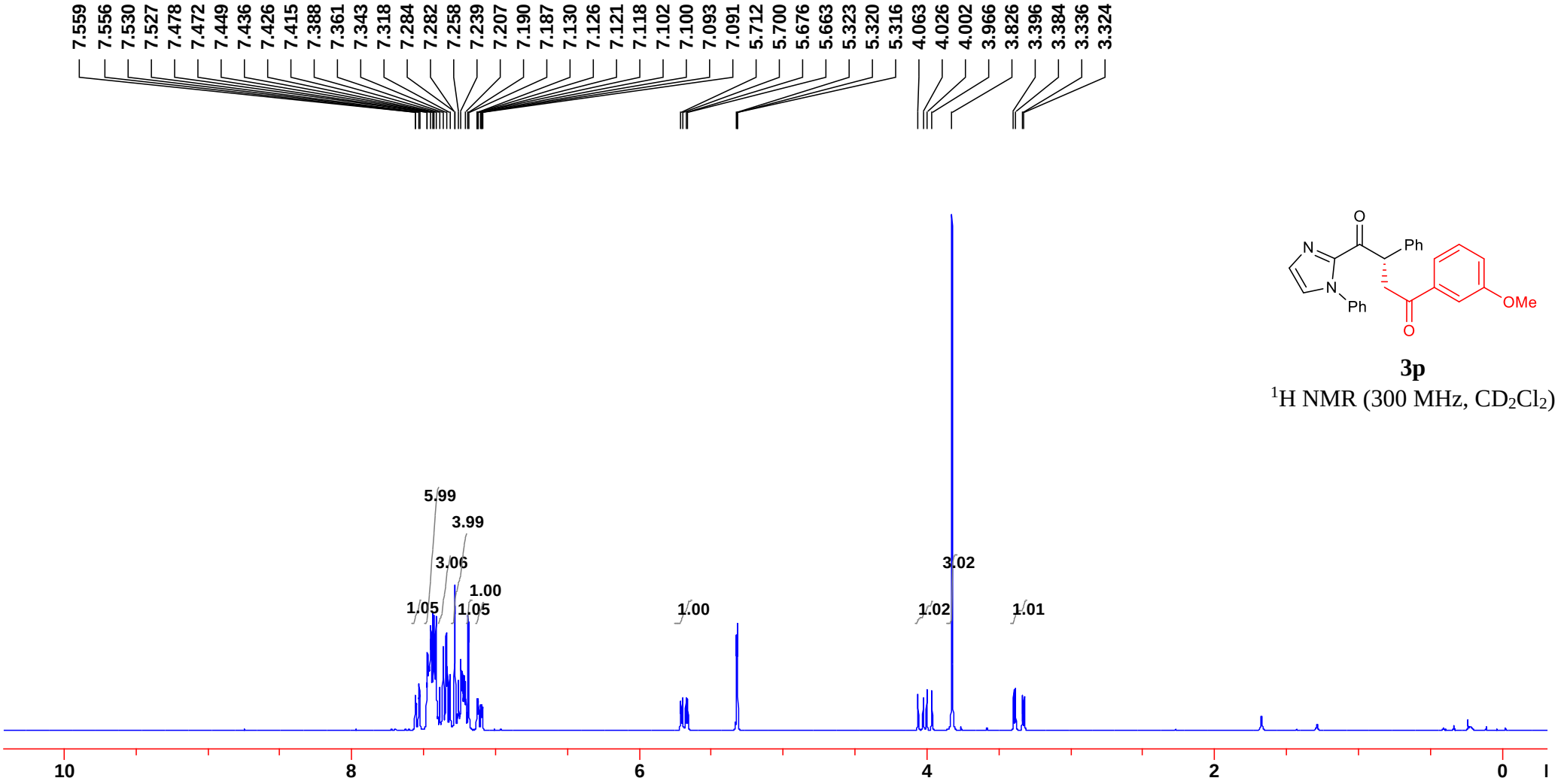
3o

^{1}H NMR (300 MHz, CD_2Cl_2)



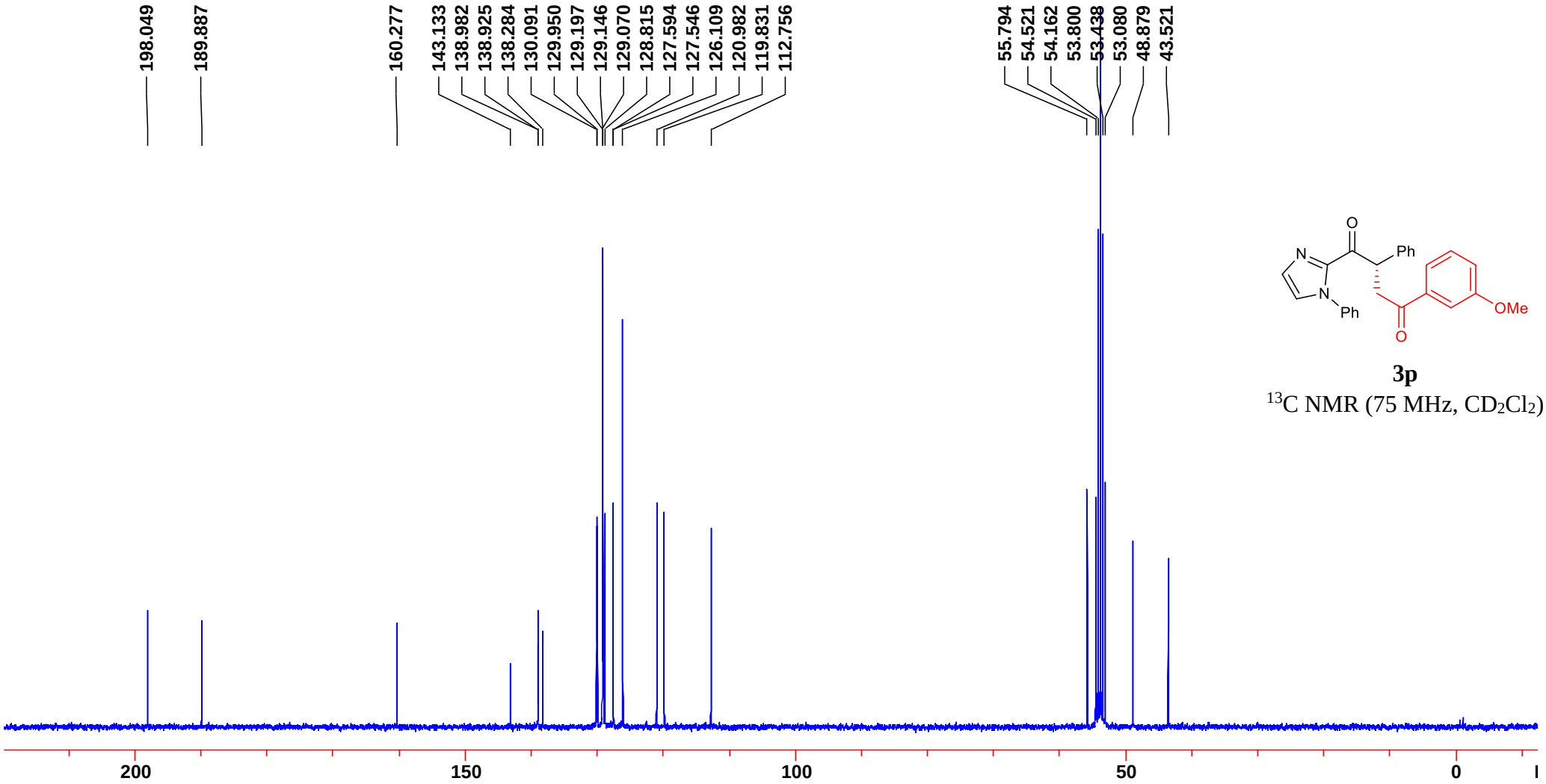
3o

^{13}C NMR (75 MHz, CD_2Cl_2)



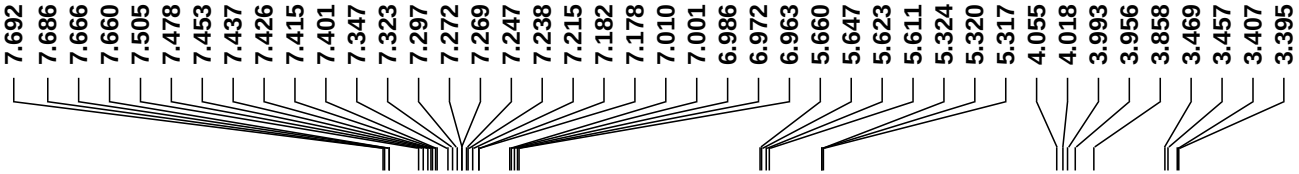
3p

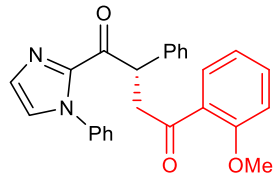
^{1}H NMR (300 MHz, CD_2Cl_2)



3p

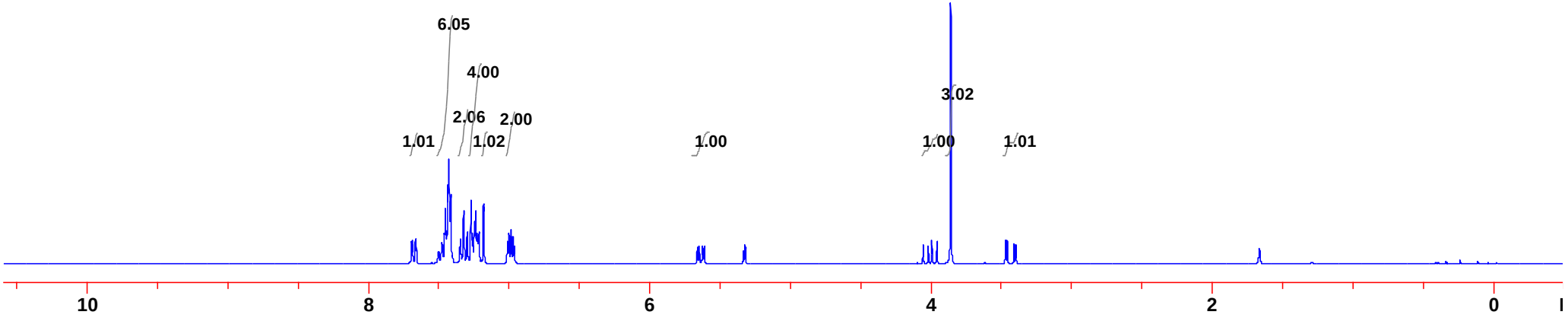
^{13}C NMR (75 MHz, CD_2Cl_2)

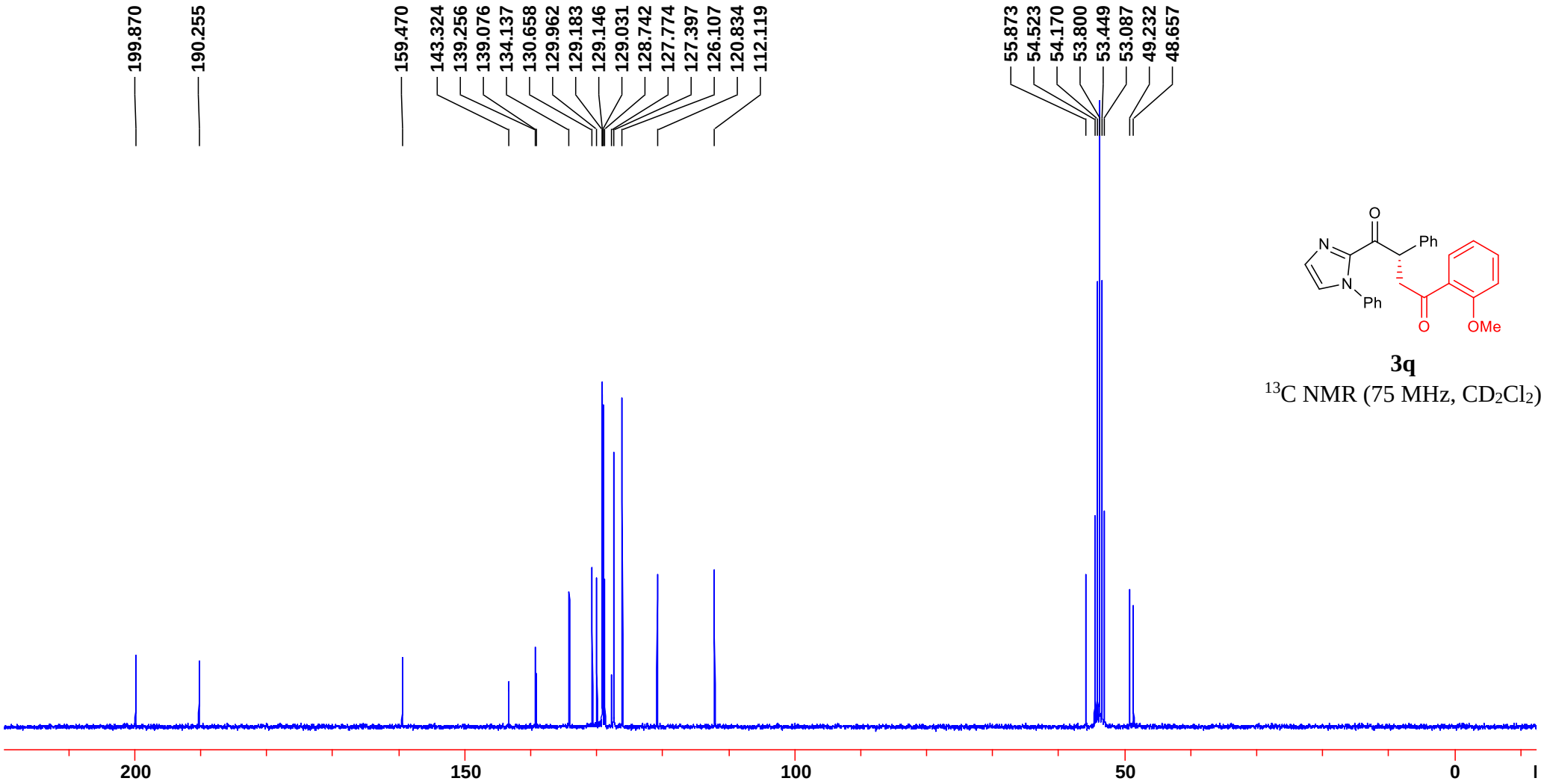




3q

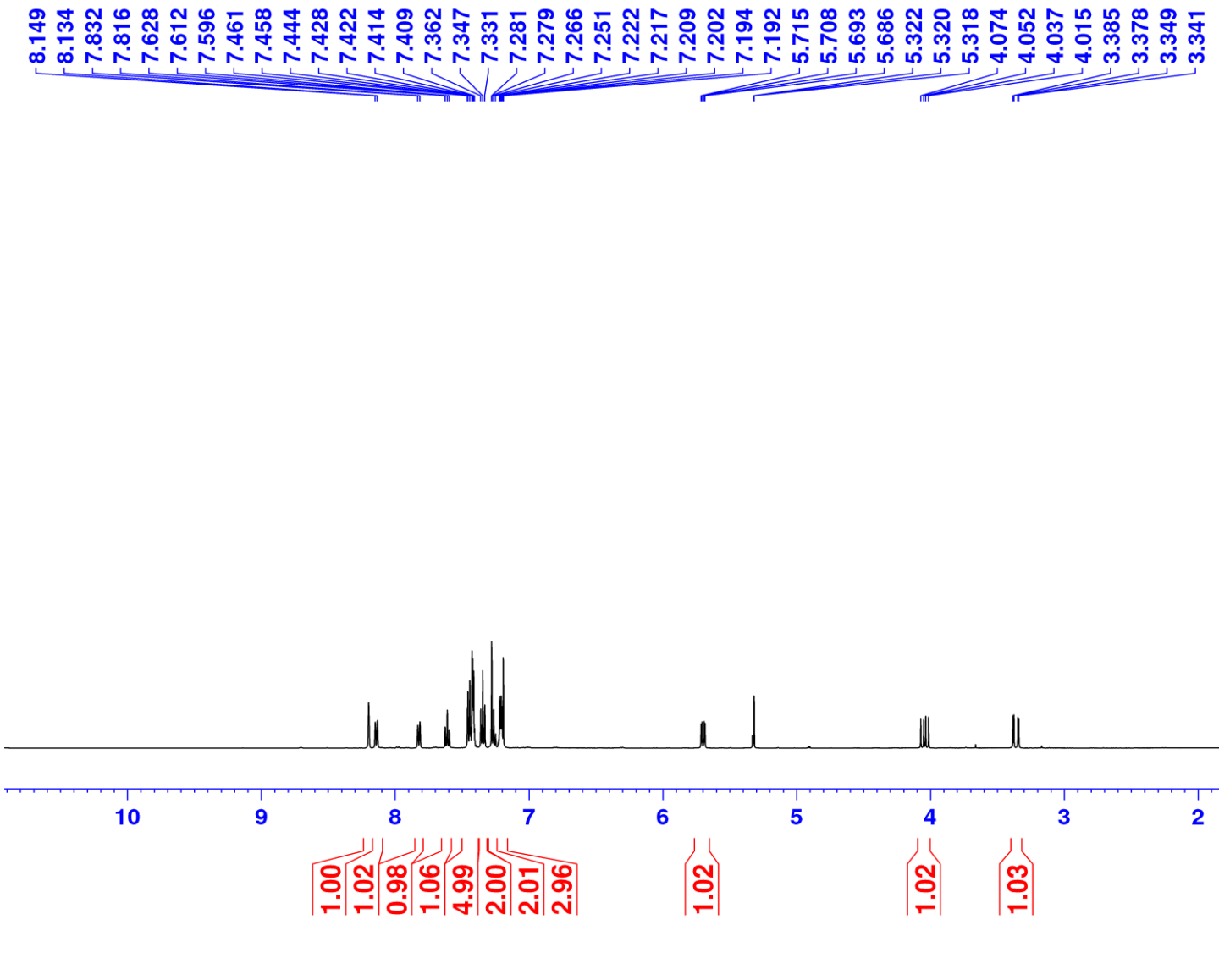
^{1}H NMR (300 MHz, CD_2Cl_2)

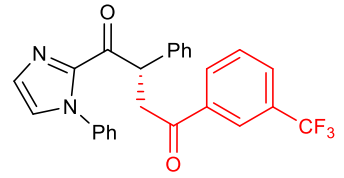




3q

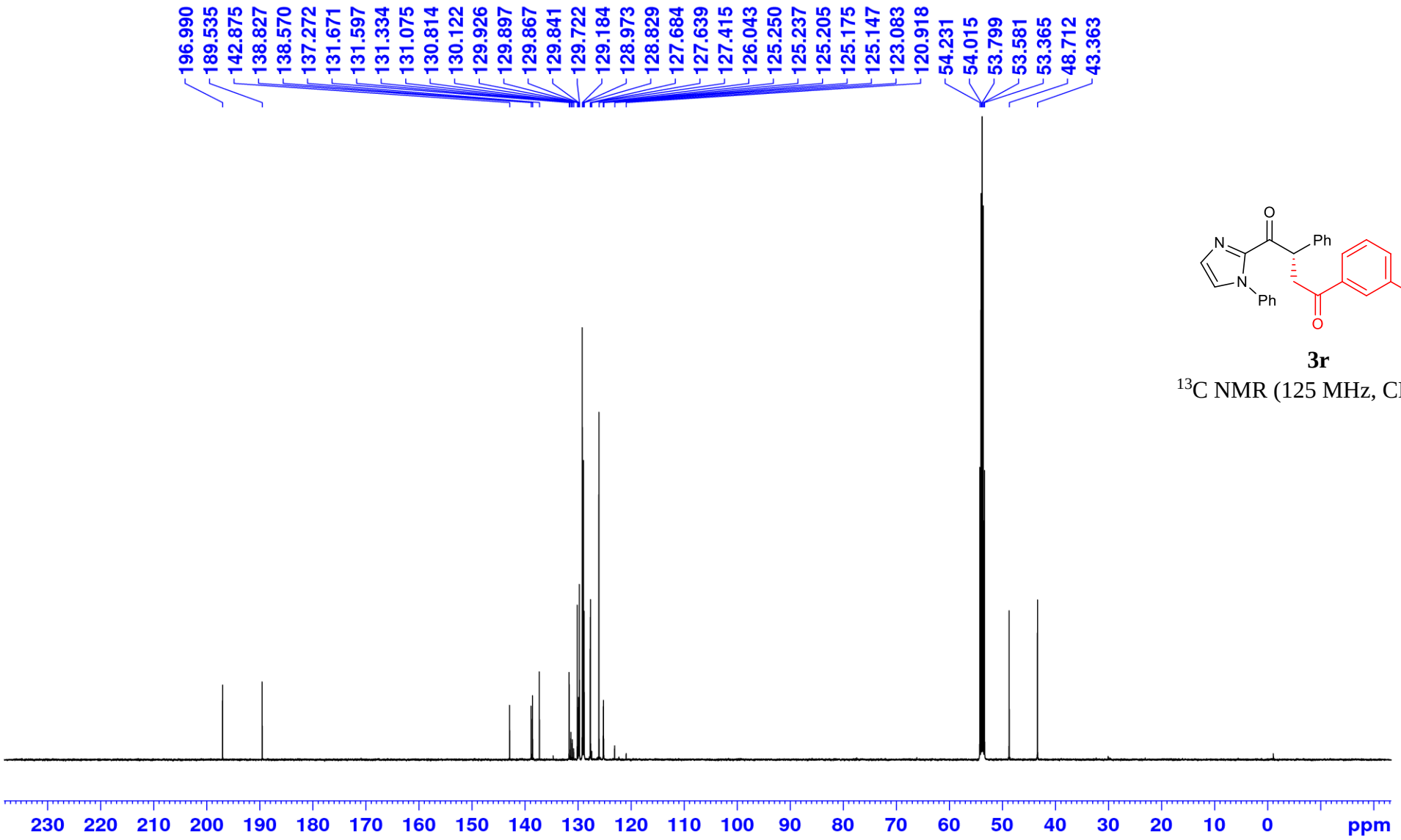
^{13}C NMR (75 MHz, CD_2Cl_2)





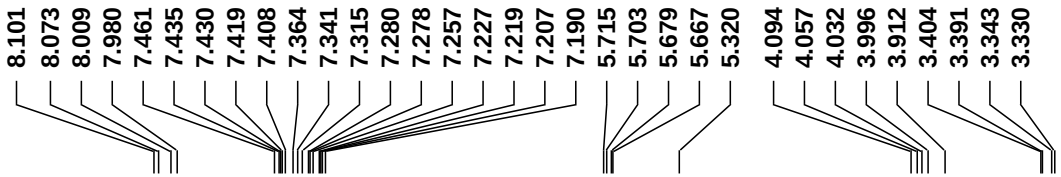
3r

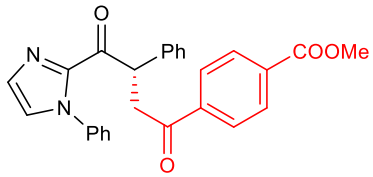
^{1}H NMR (500 MHz, CD_2Cl_2)



3r

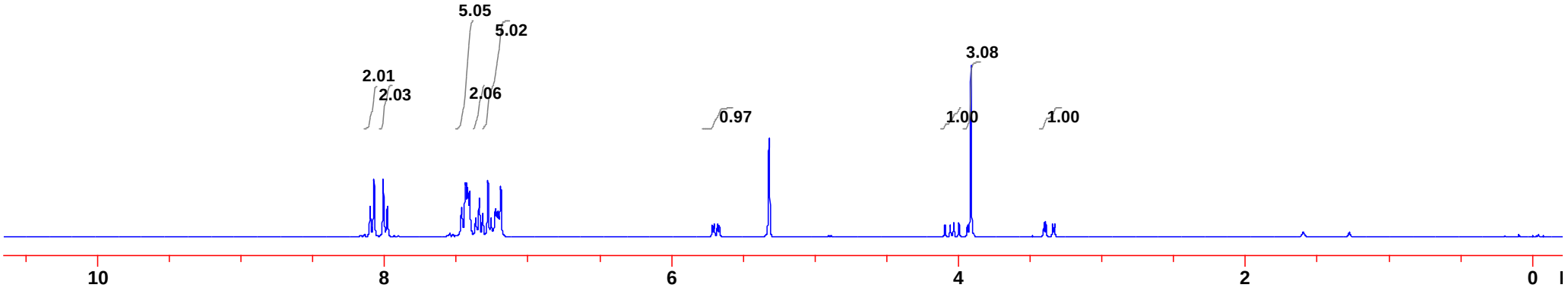
^{13}C NMR (125 MHz, CD_2Cl_2)

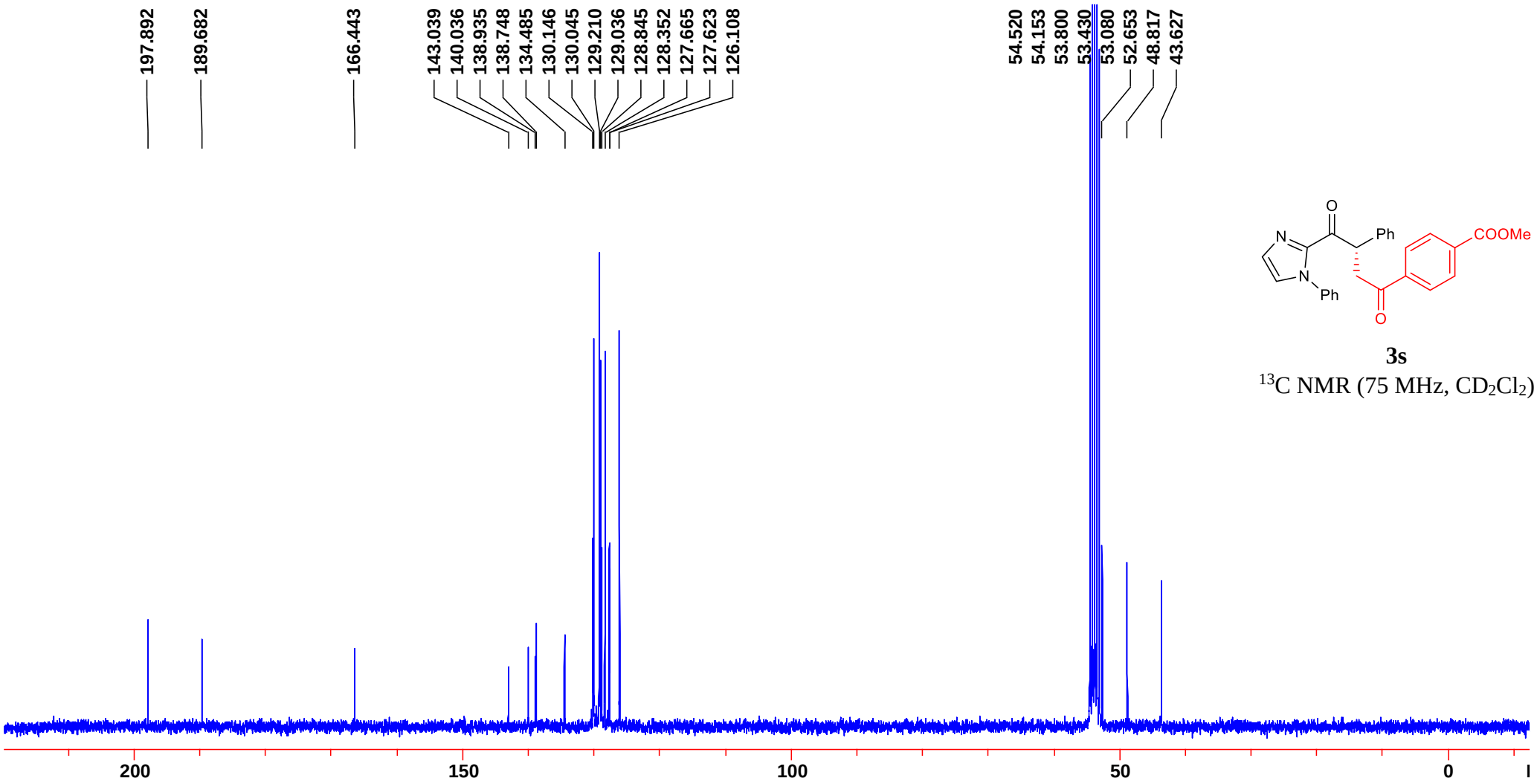




3s

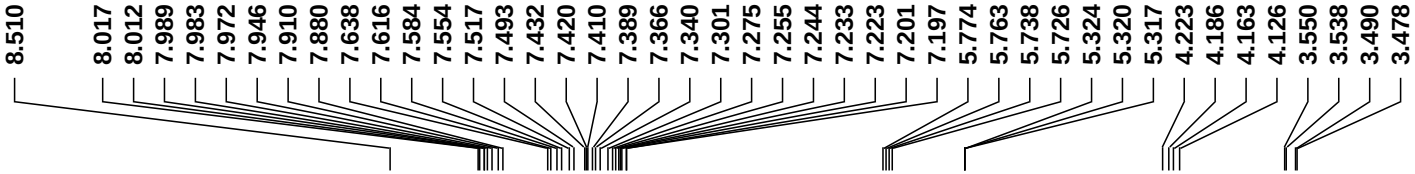
^{1}H NMR (300 MHz, CD_2Cl_2)

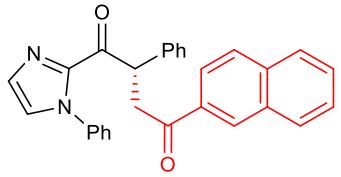




3s

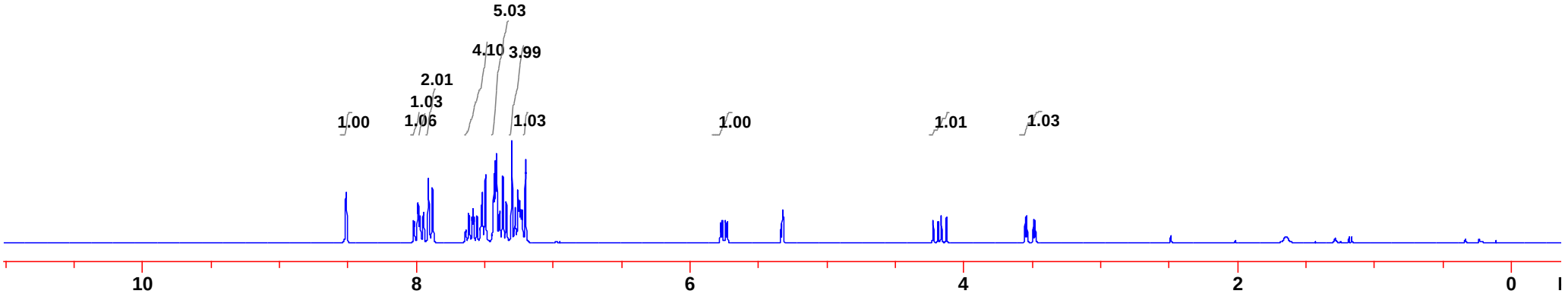
^{13}C NMR (75 MHz, CD_2Cl_2)

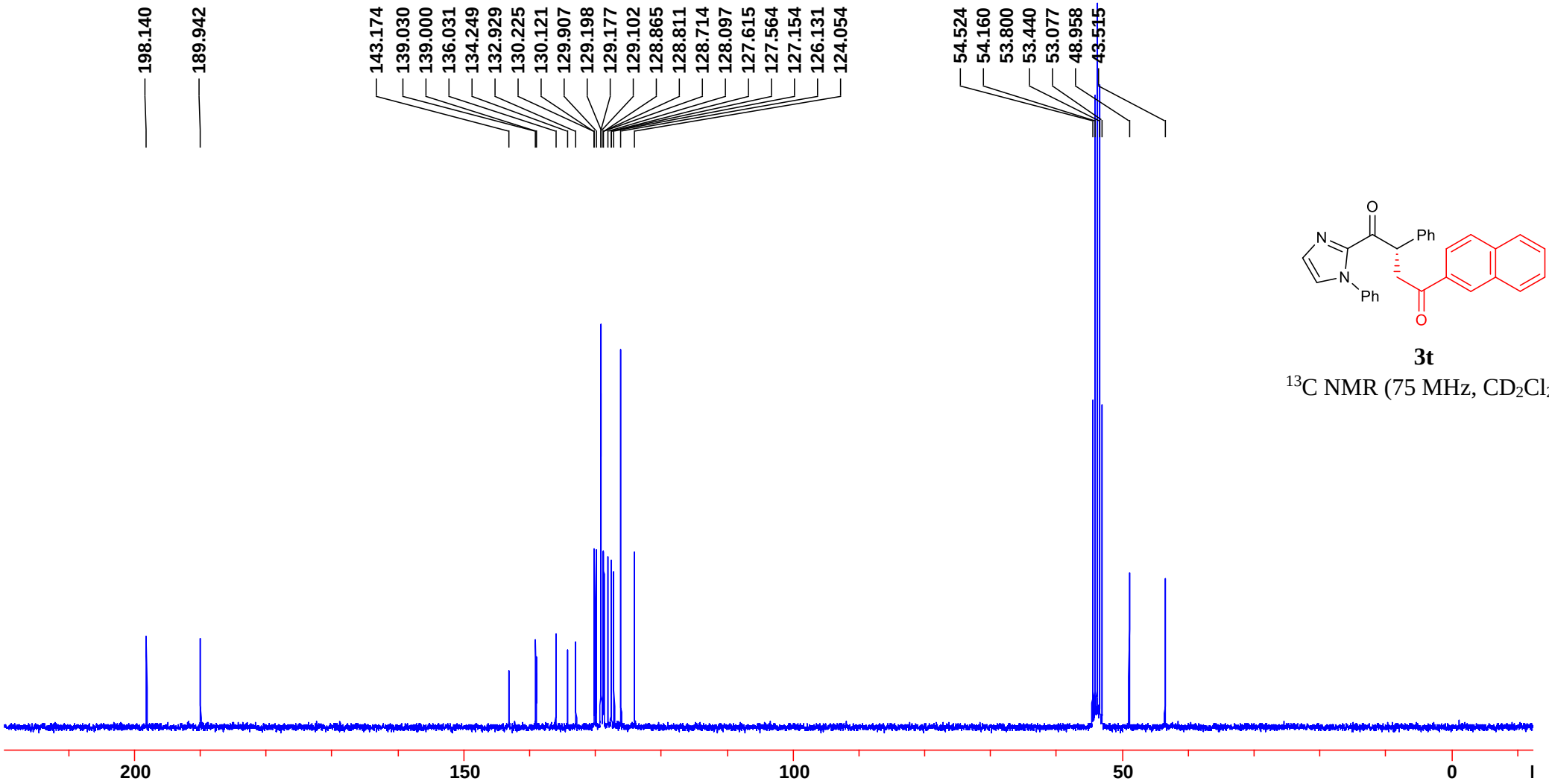




3t

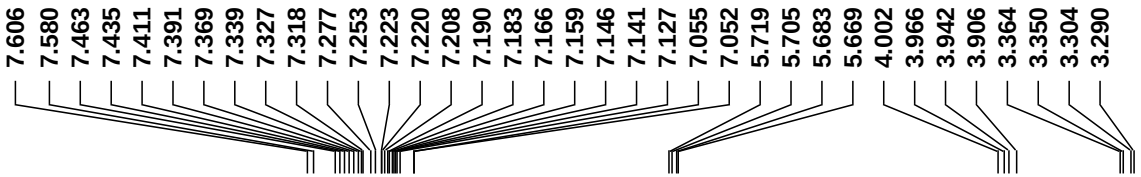
^{1}H NMR (300 MHz, CD_2Cl_2)

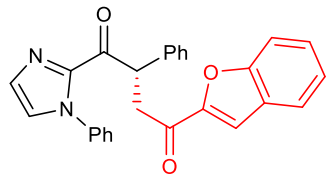




3t

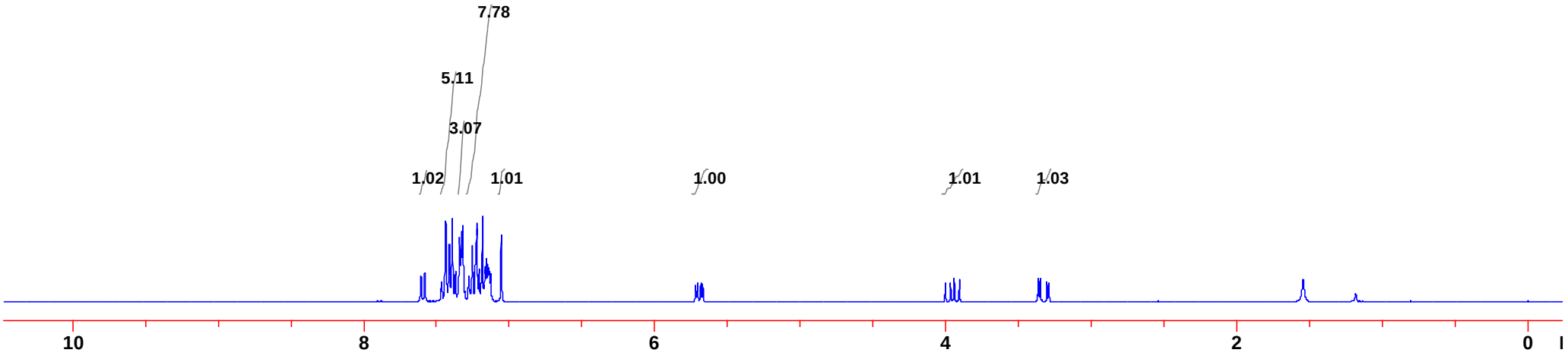
^{13}C NMR (75 MHz, CD_2Cl_2)

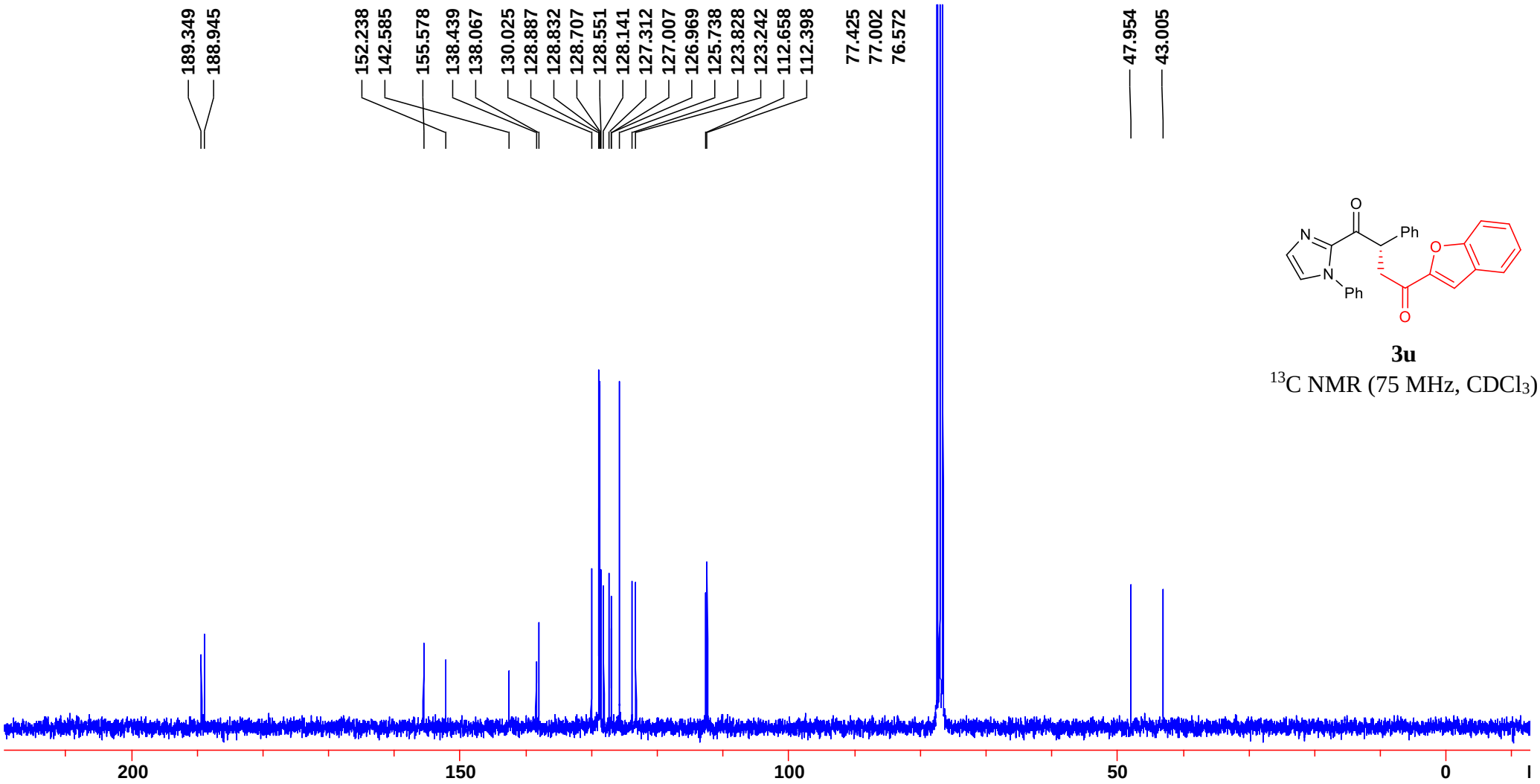




3u

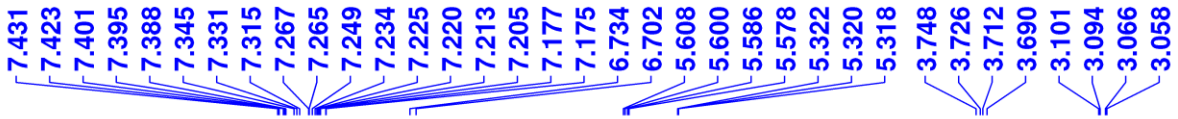
^{1}H NMR (300 MHz, $CDCl_3$)

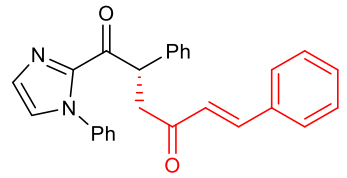




3u

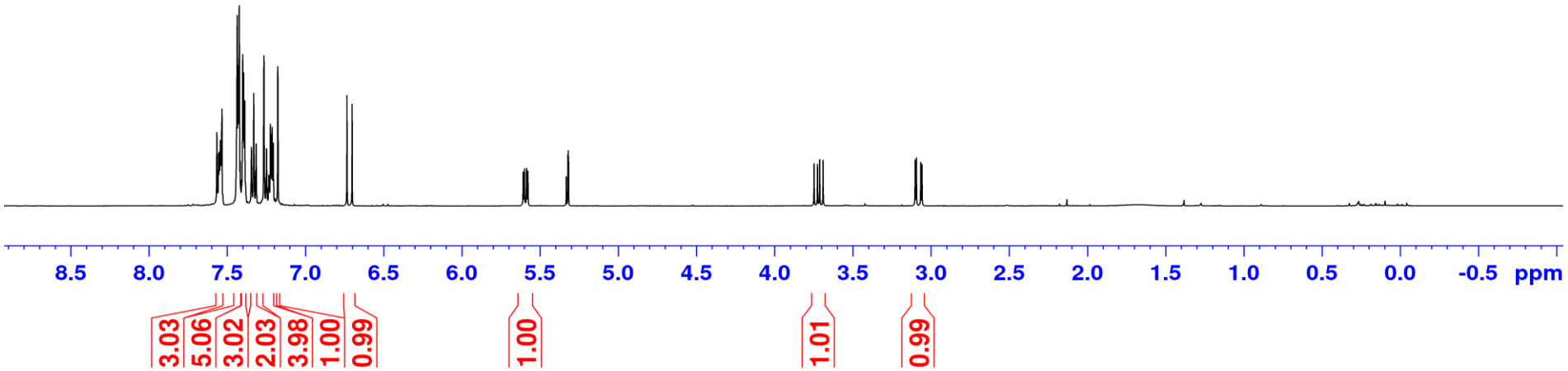
^{13}C NMR (75 MHz, $CDCl_3$)

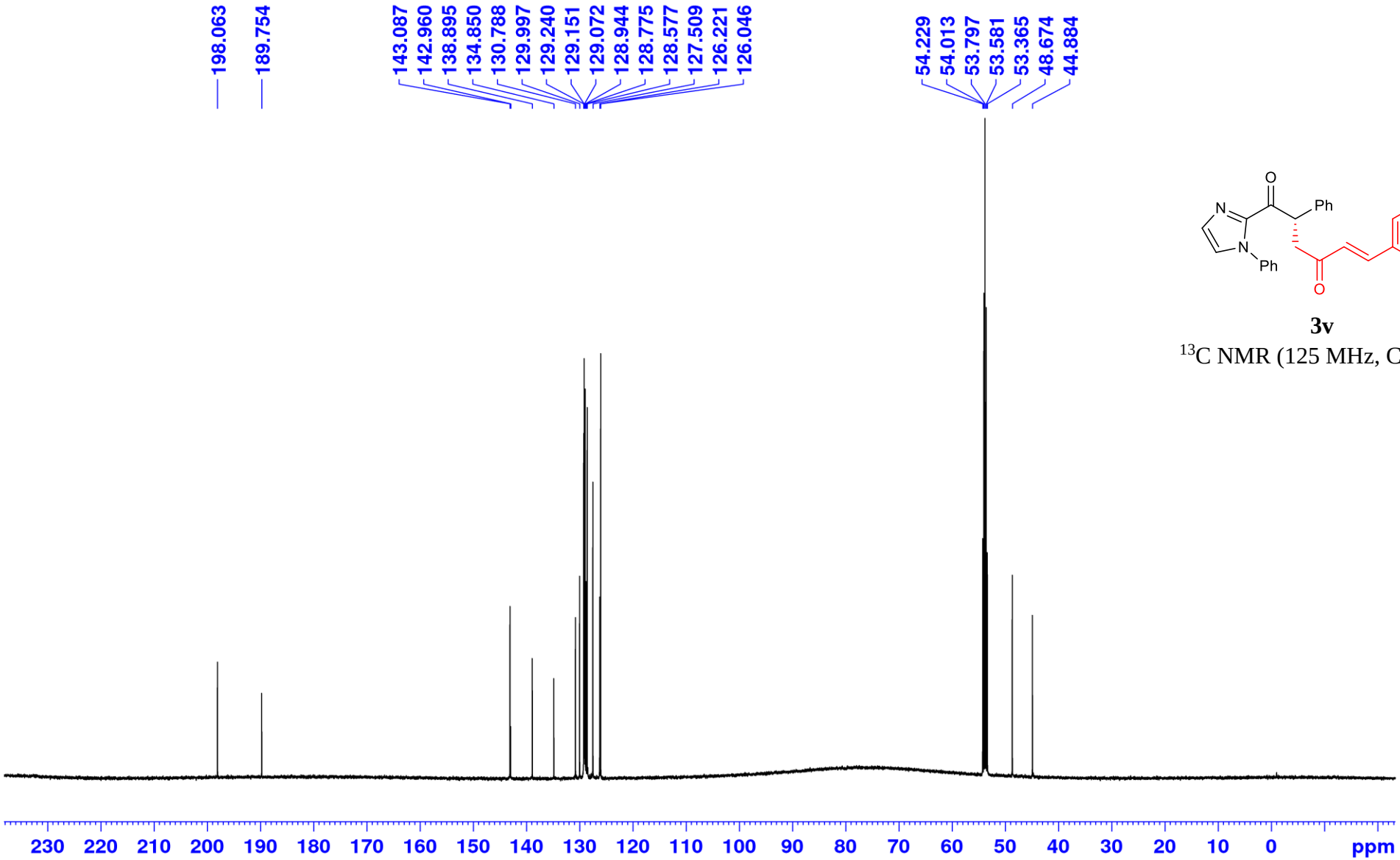




3v

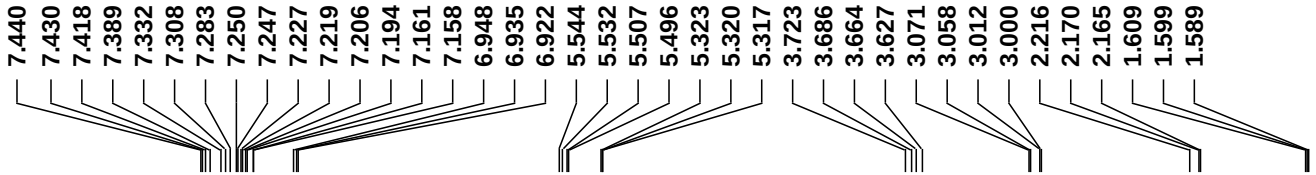
^{1}H NMR (500 MHz, CD_2Cl_2)

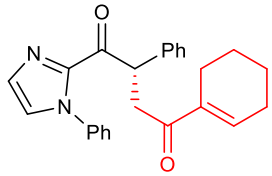




3v

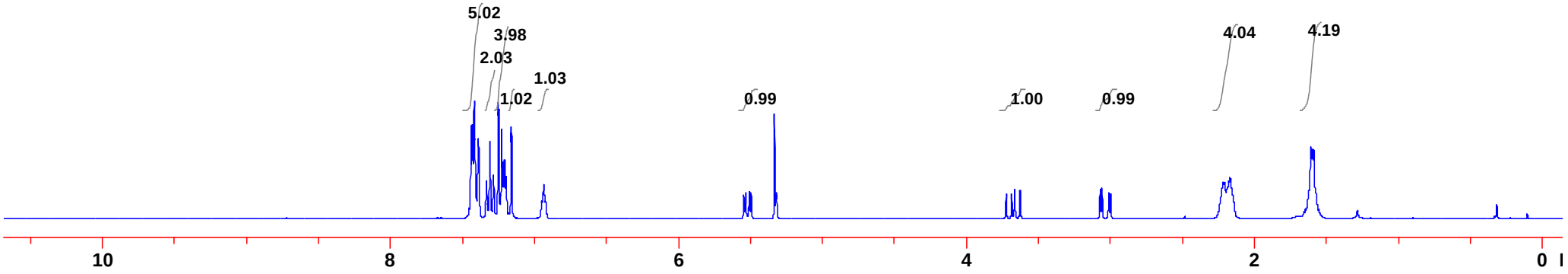
^{13}C NMR (125 MHz, CD_2Cl_2)

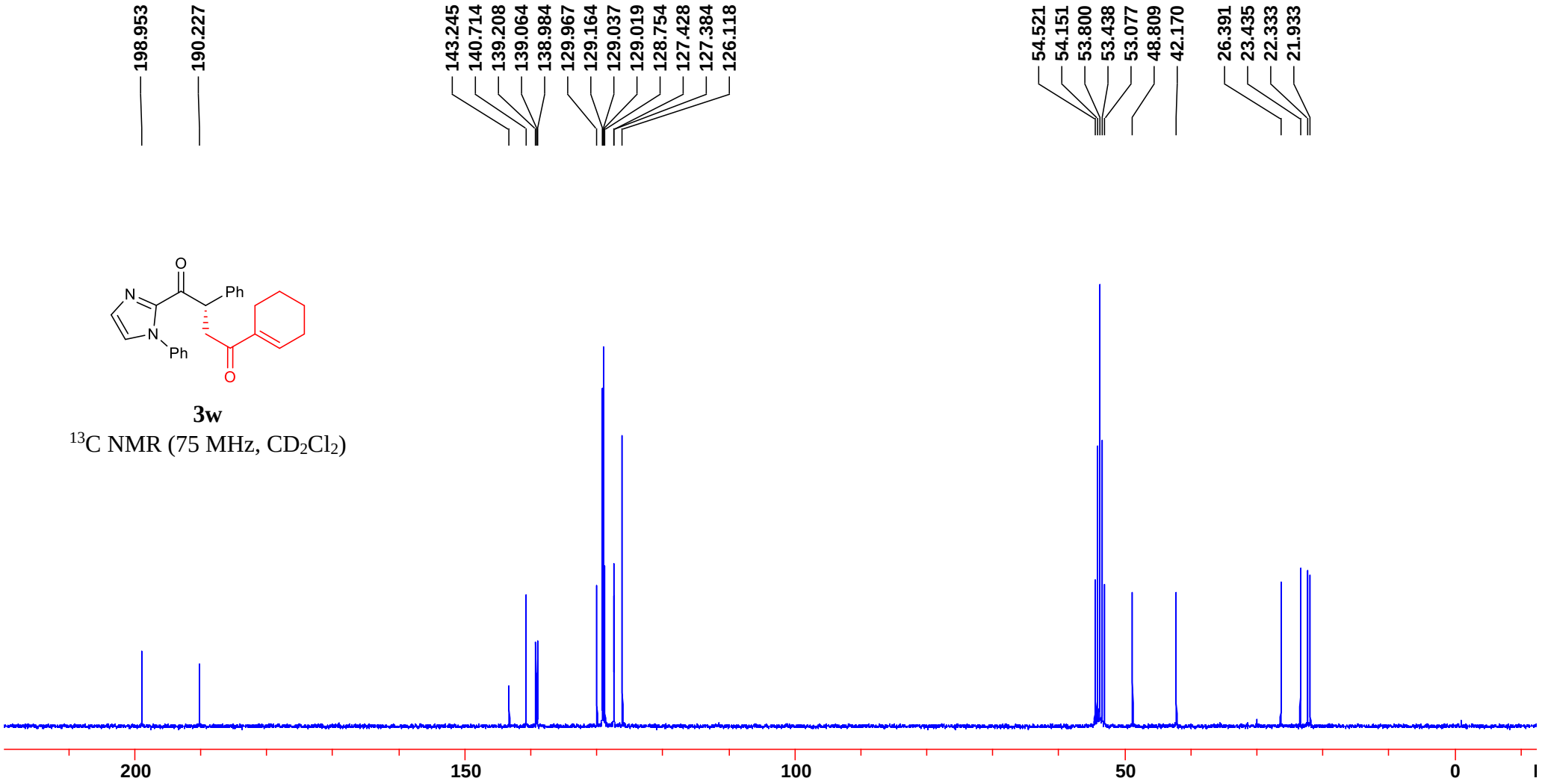




3w

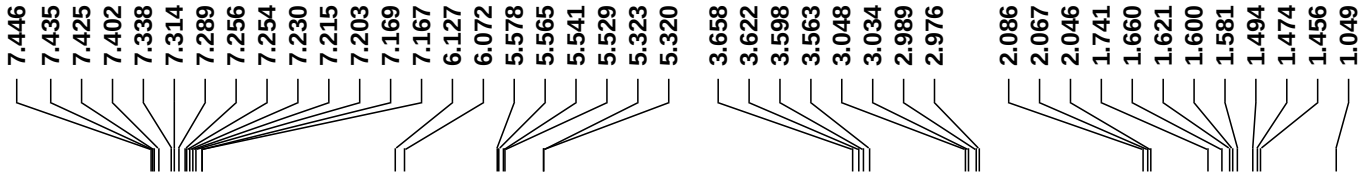
^{1}H NMR (300 MHz, CD_2Cl_2)

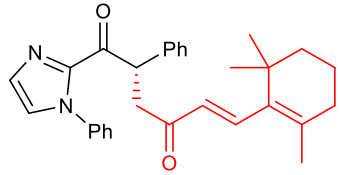




3w

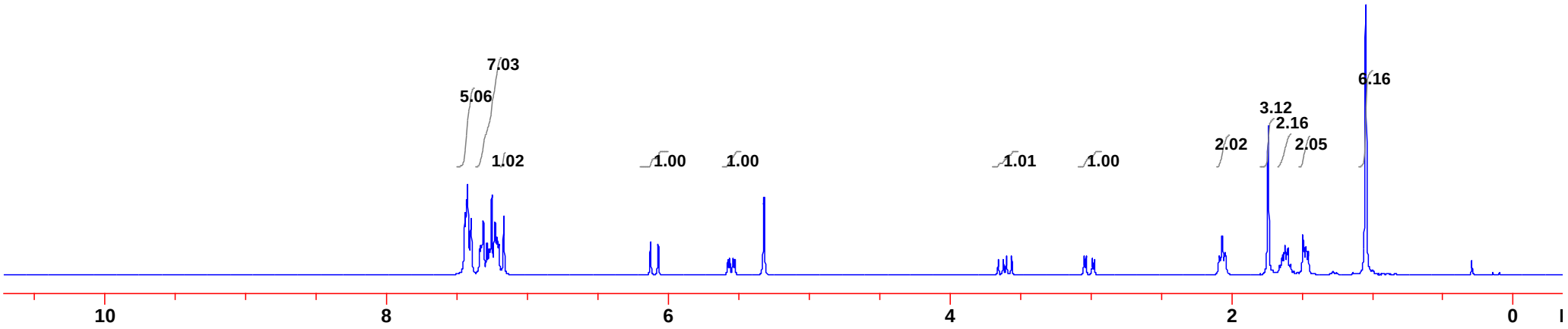
^{13}C NMR (75 MHz, CD_2Cl_2)

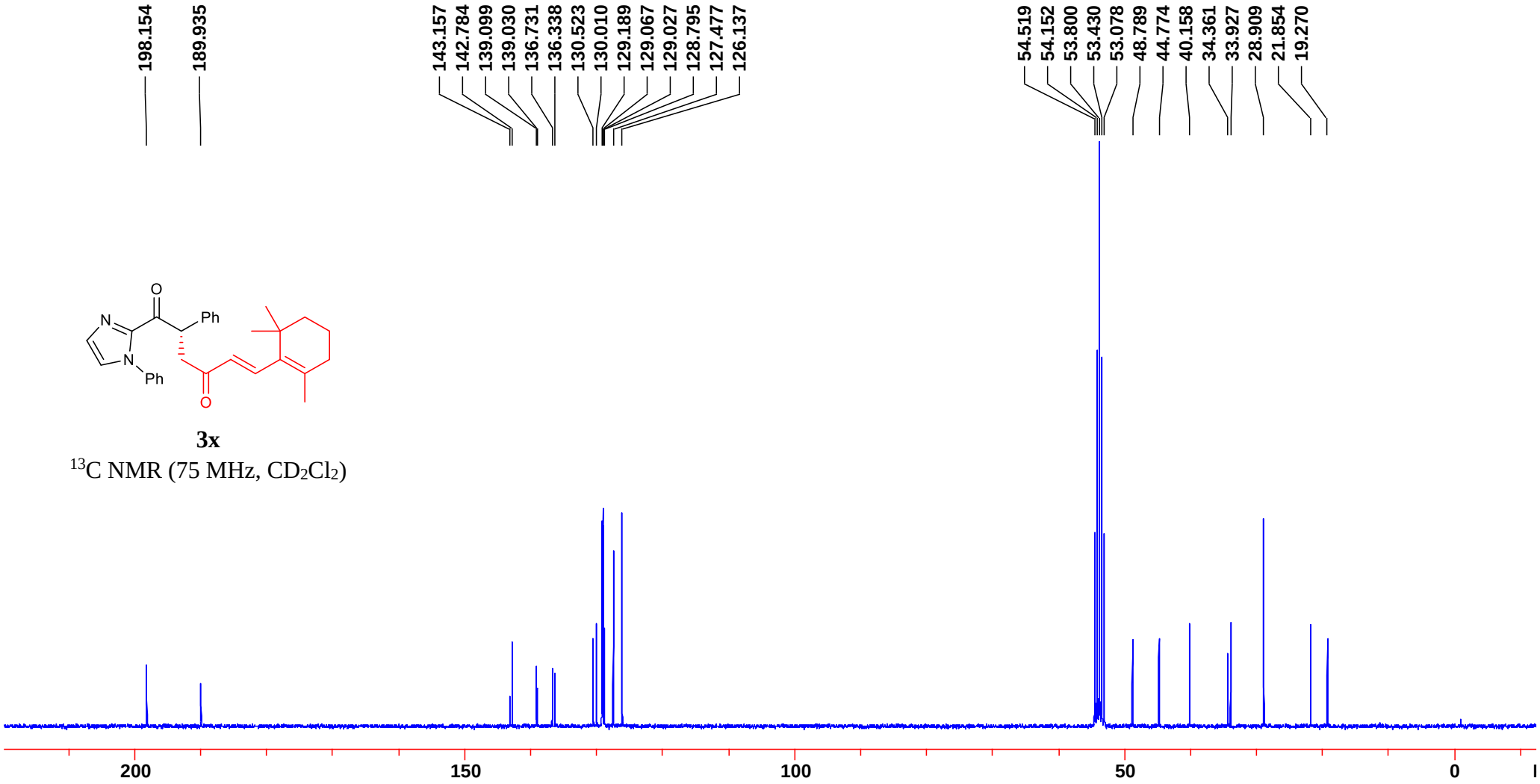




3x

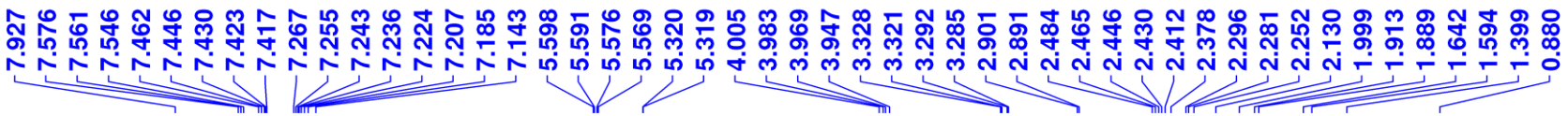
^{1}H NMR (300 MHz, CD_2Cl_2)

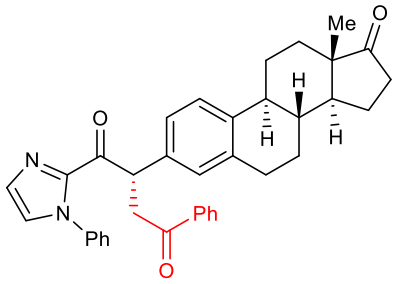




3x

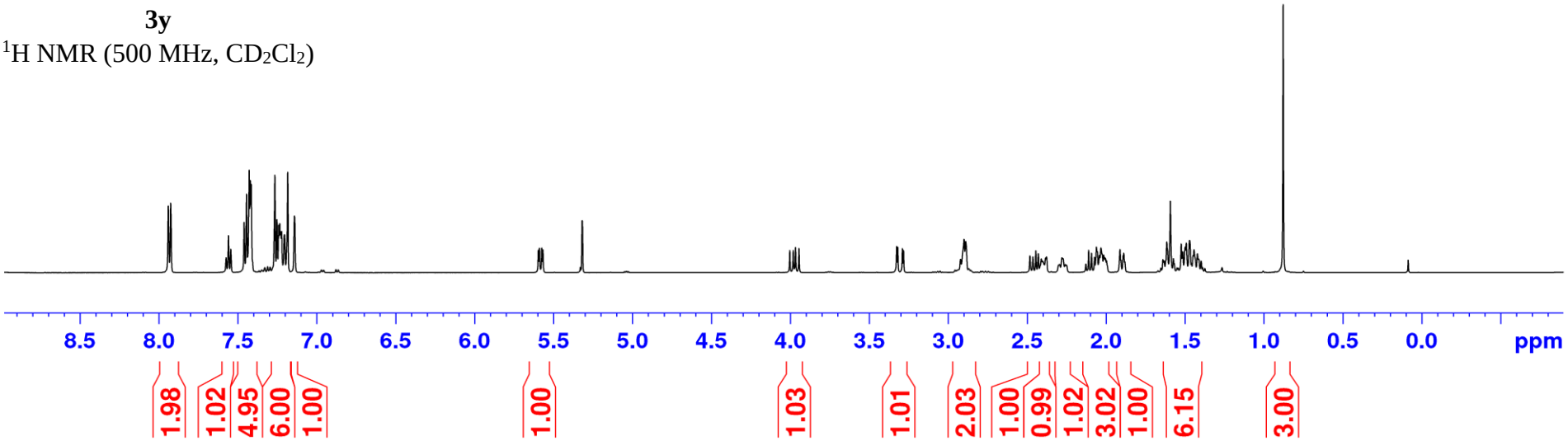
^{13}C NMR (75 MHz, CD_2Cl_2)

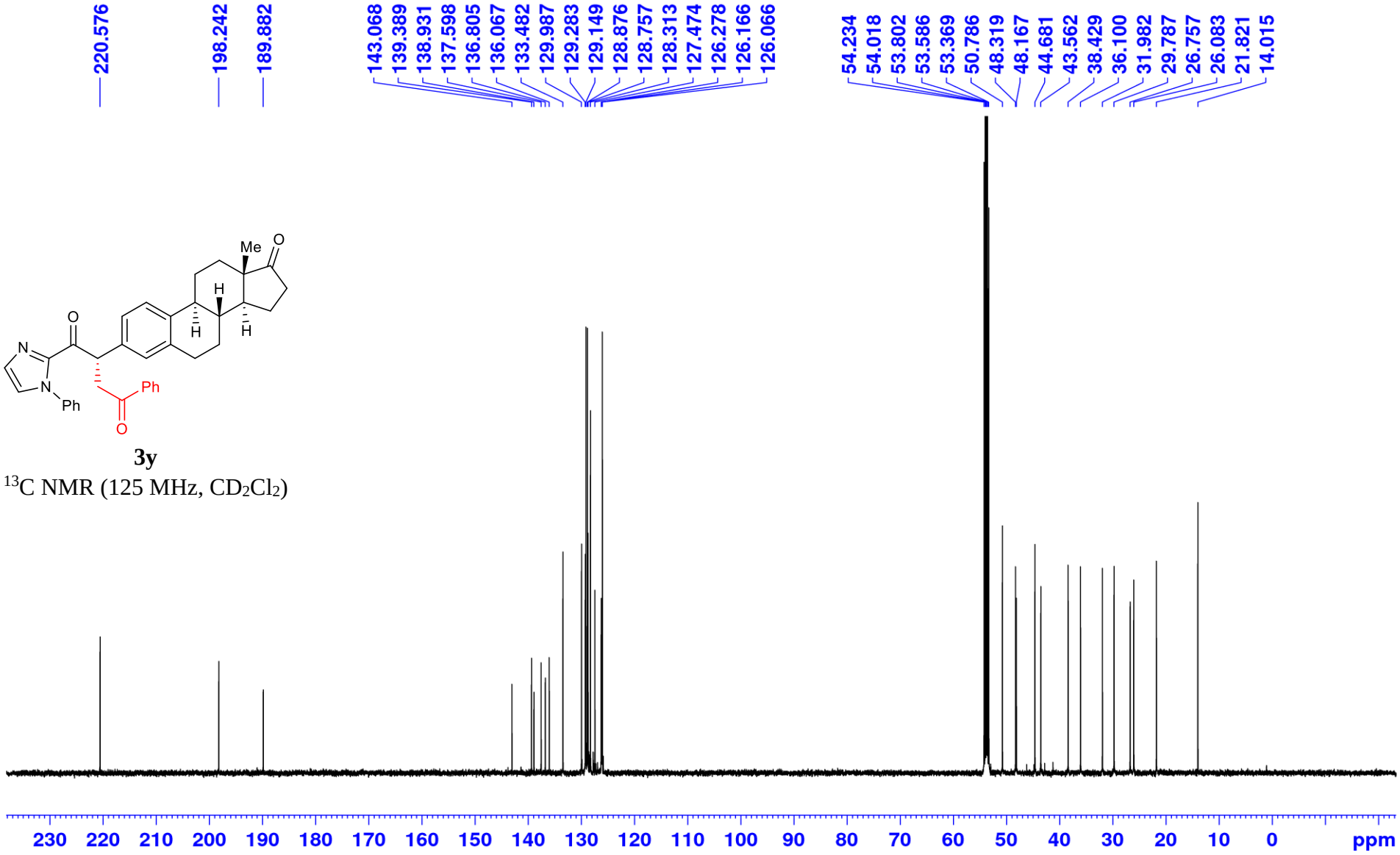




3y

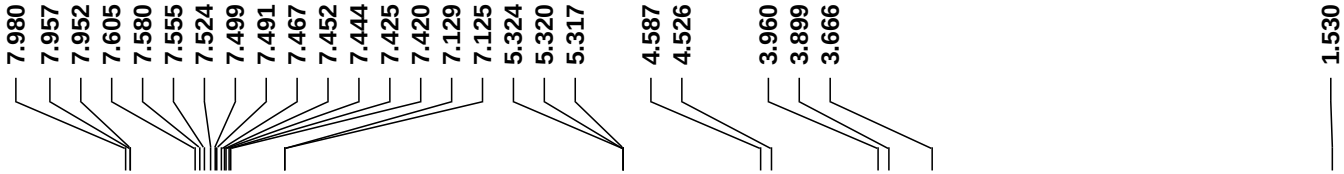
^{1}H NMR (500 MHz, CD_2Cl_2)

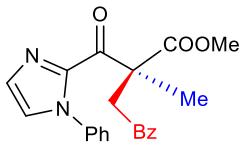




3y

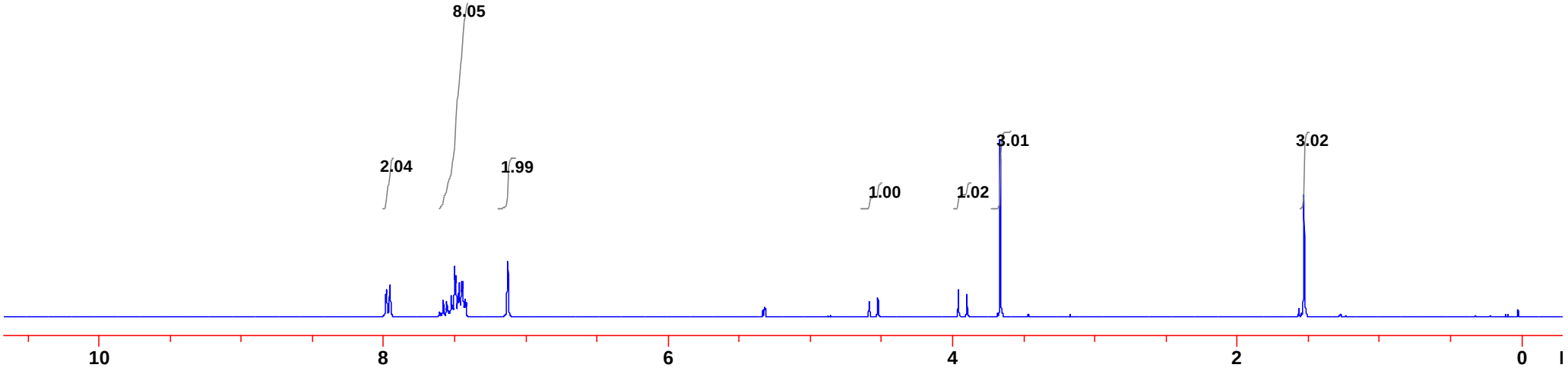
^{13}C NMR (125 MHz, CD_2Cl_2)

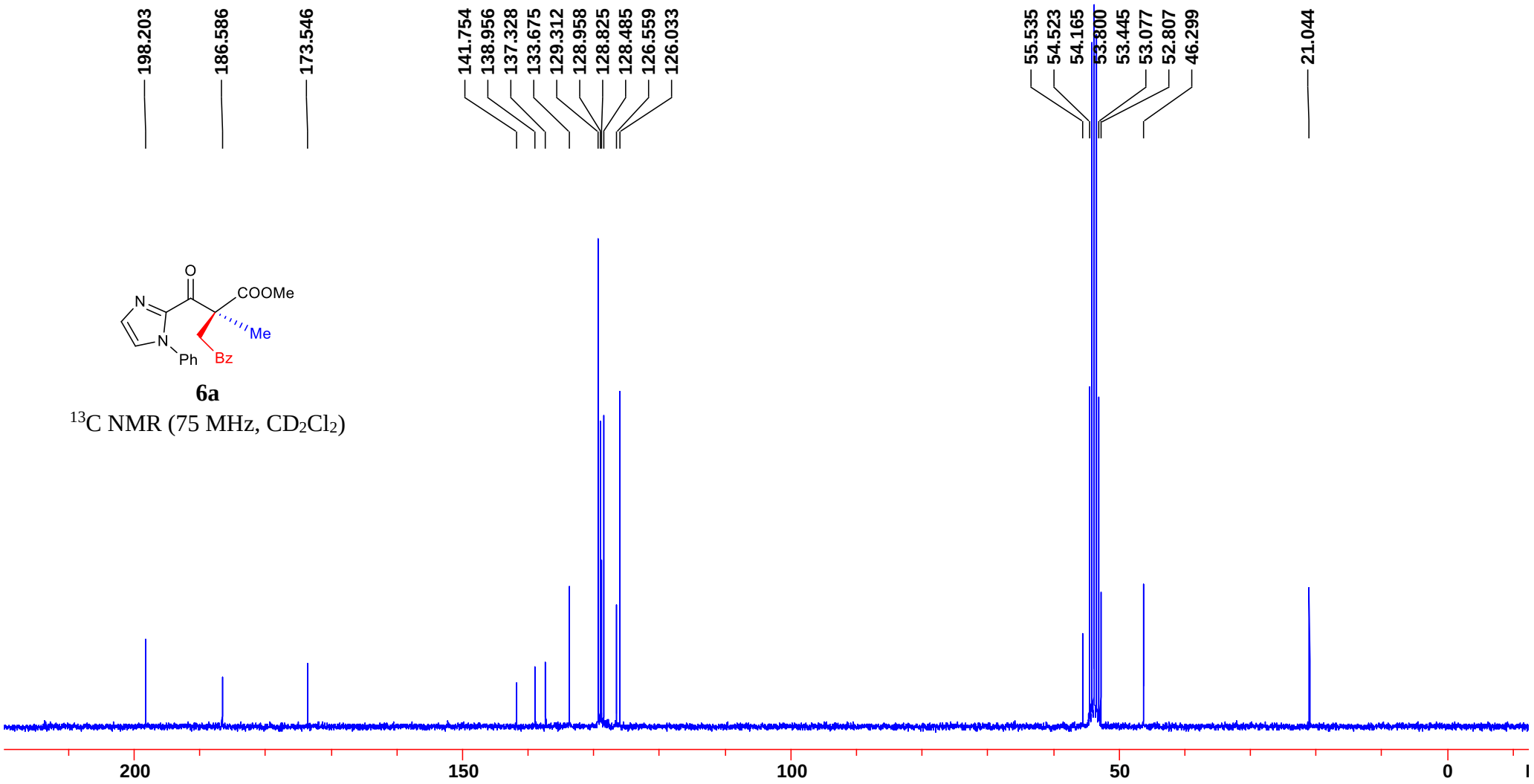




6a

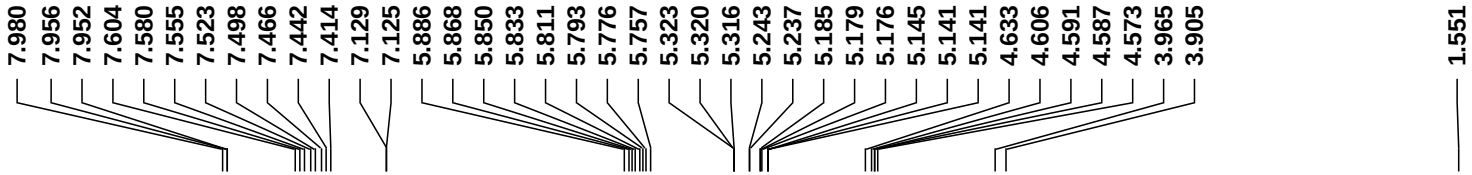
^{1}H NMR (300 MHz, CD_2Cl_2)

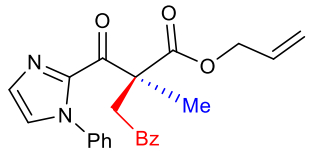




6a

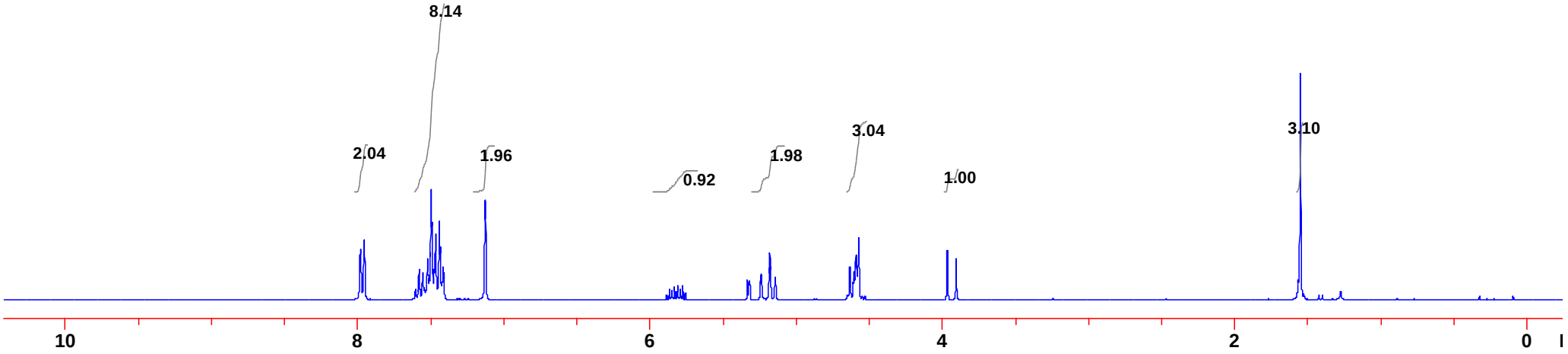
^{13}C NMR (75 MHz, CD_2Cl_2)

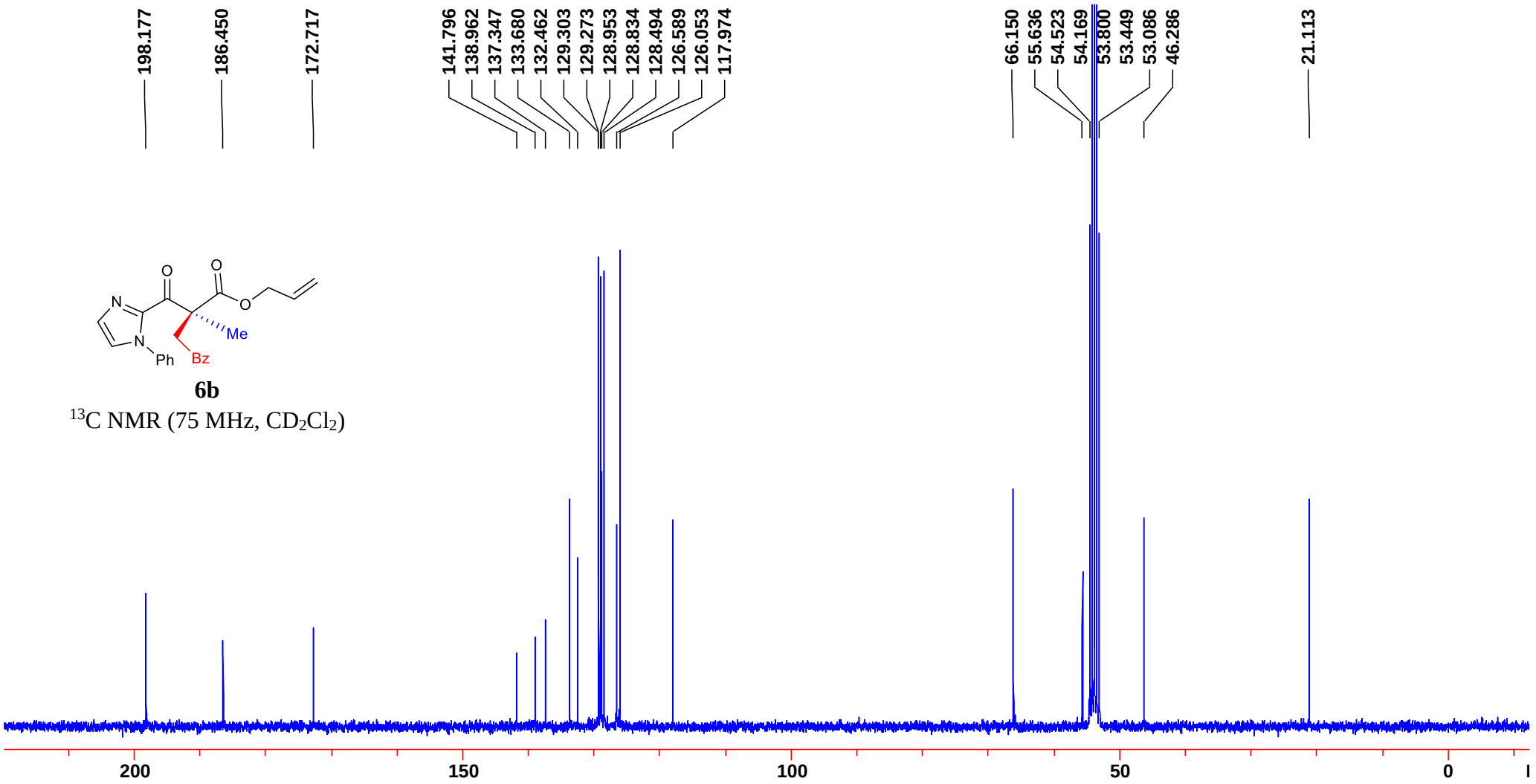




6b

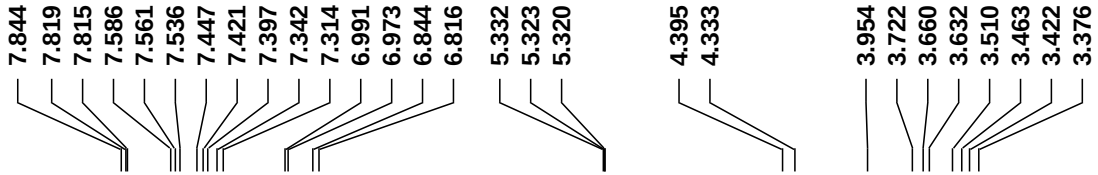
^{1}H NMR (300 MHz, CD_2Cl_2)

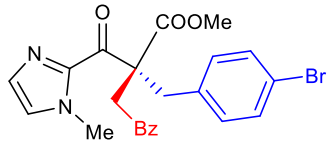




6b

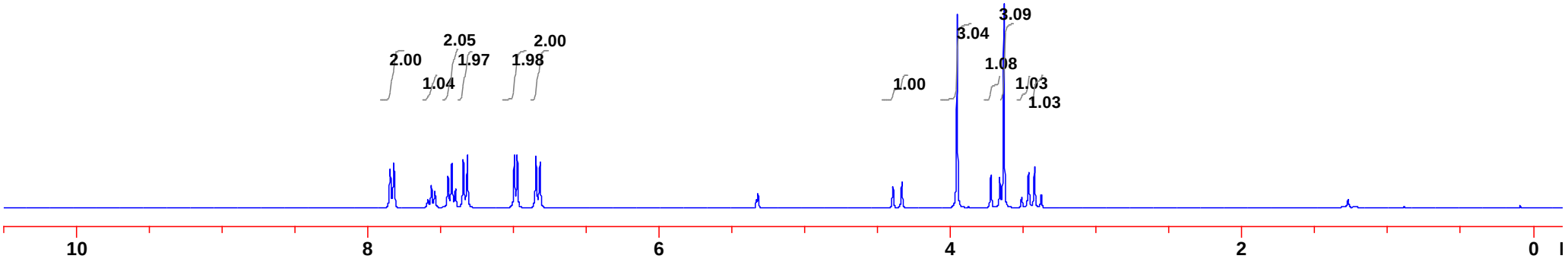
^{13}C NMR (75 MHz, CD_2Cl_2)

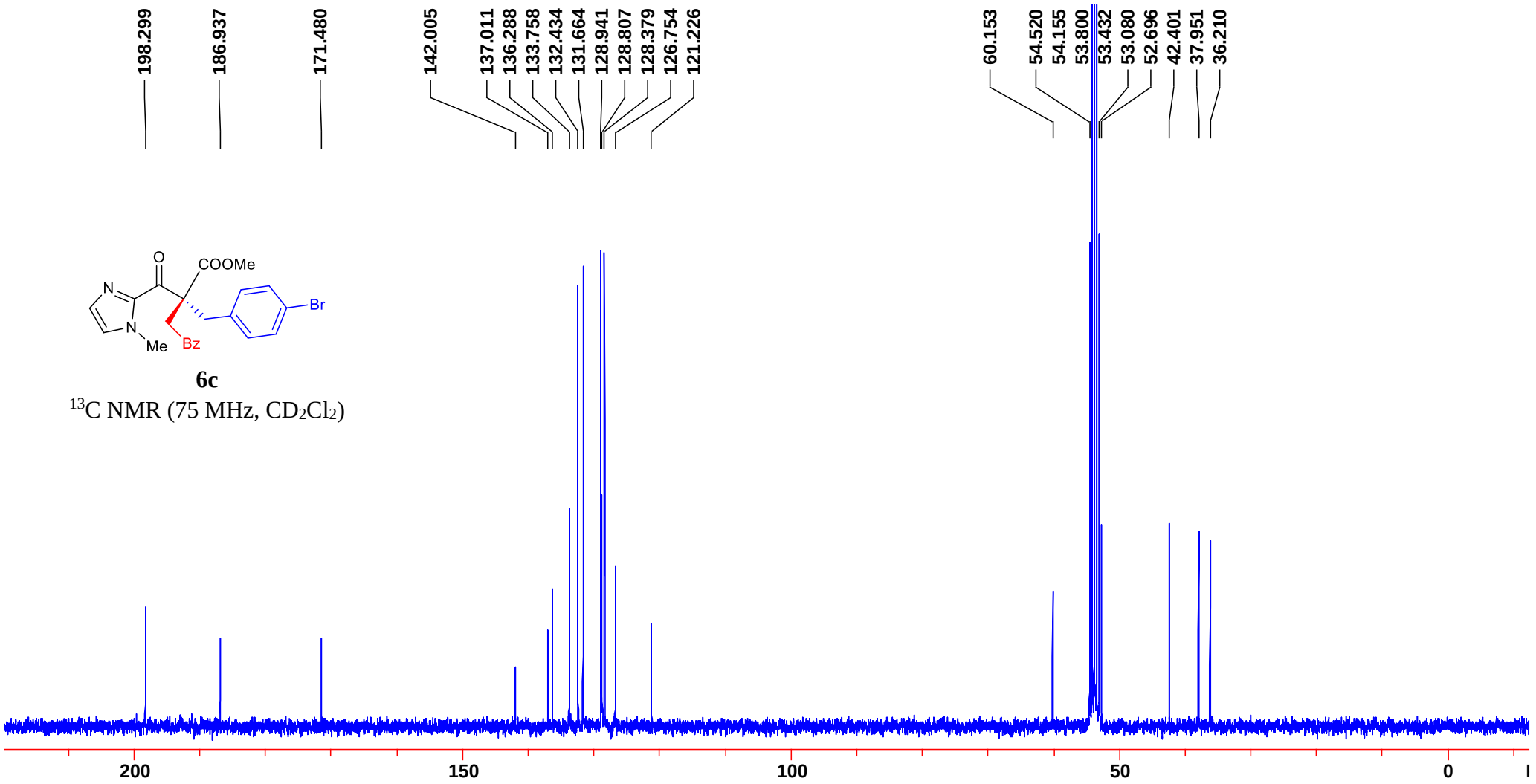




6c

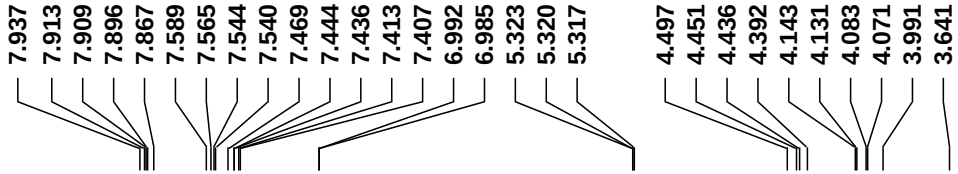
^{1}H NMR (300 MHz, CD_2Cl_2)

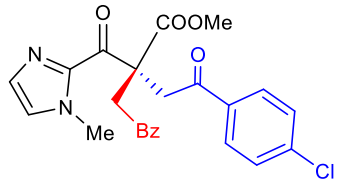




6c

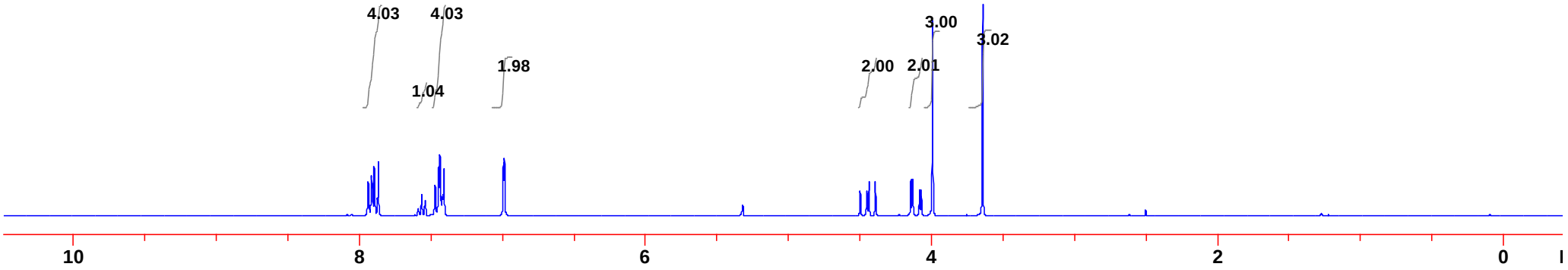
^{13}C NMR (75 MHz, CD_2Cl_2)

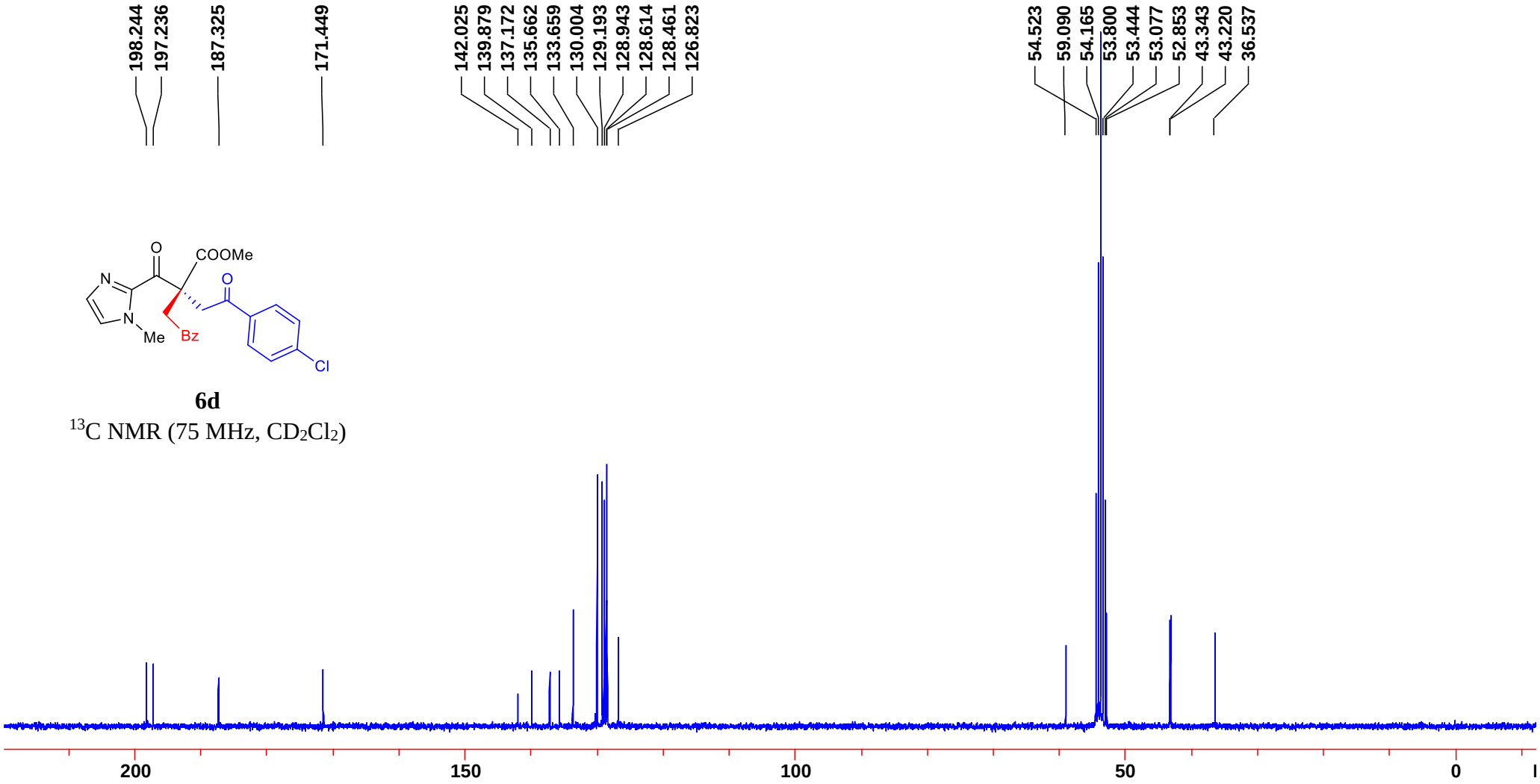




6d

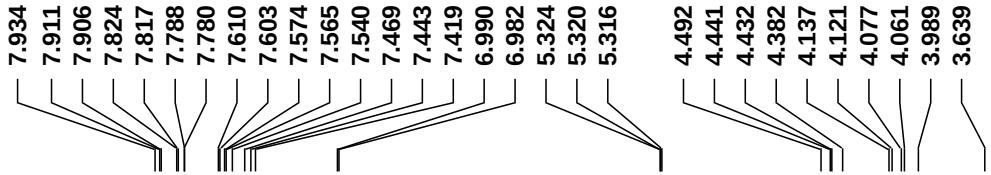
^{1}H NMR (300 MHz, CD_2Cl_2)

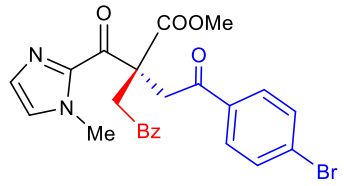




6d

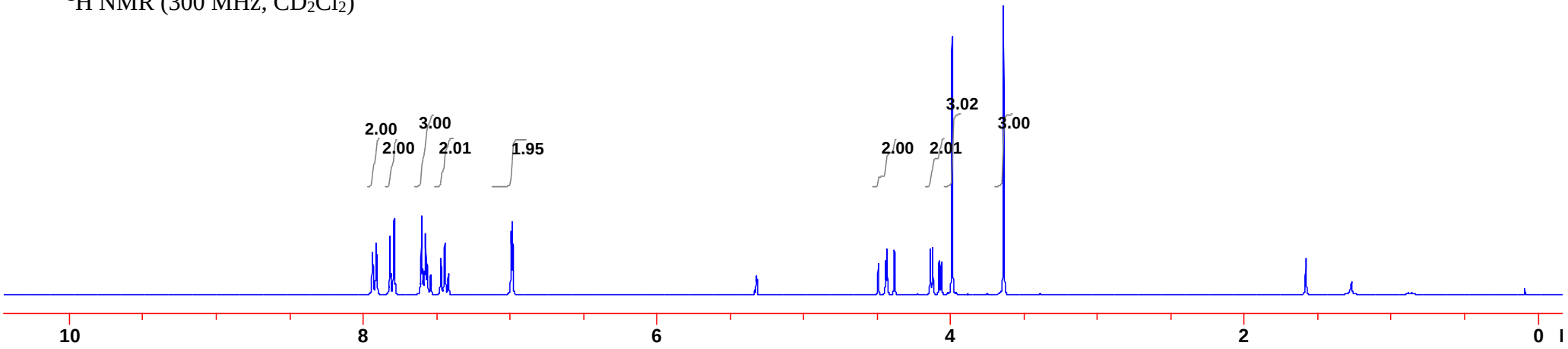
^{13}C NMR (75 MHz, CD_2Cl_2)

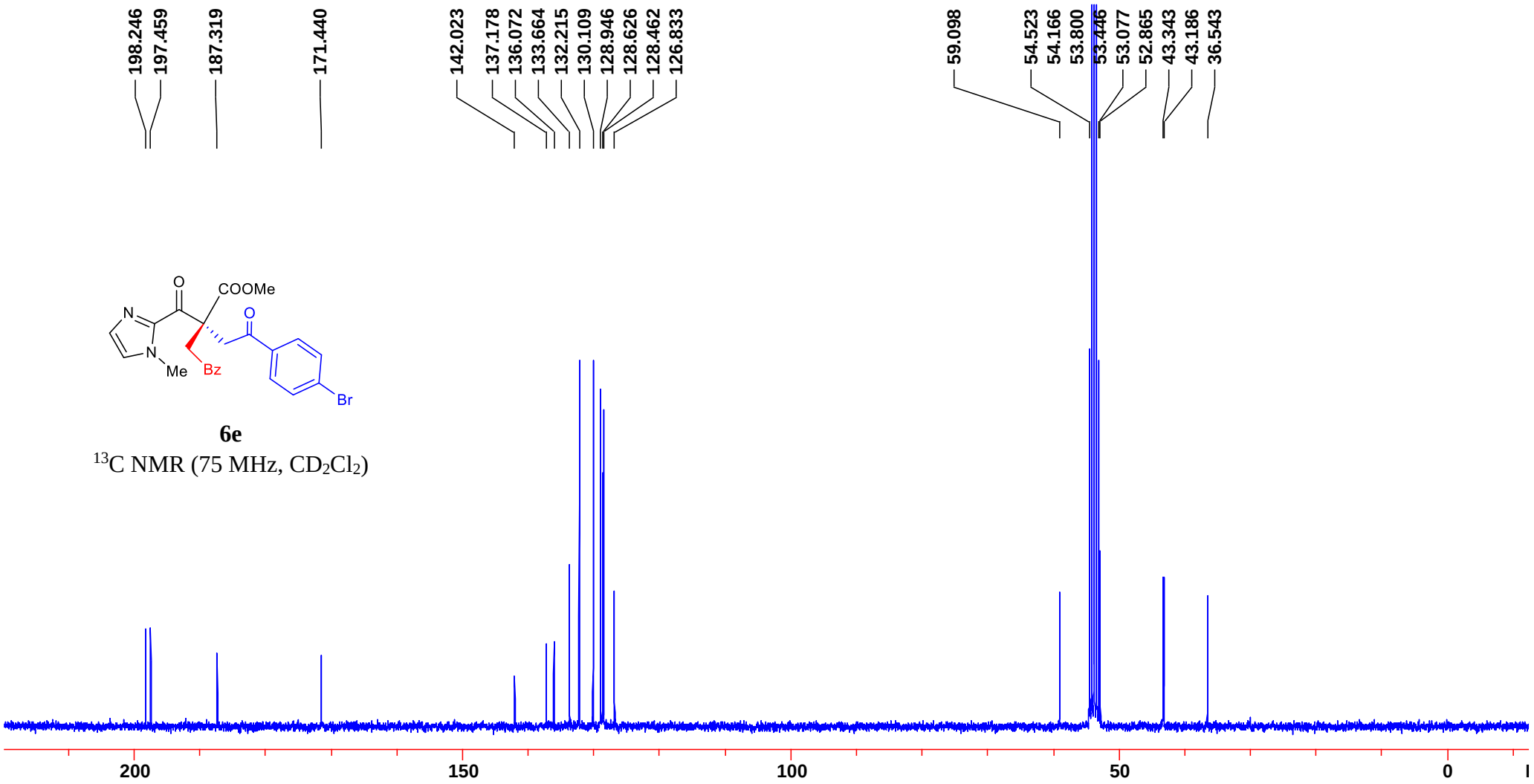




6e

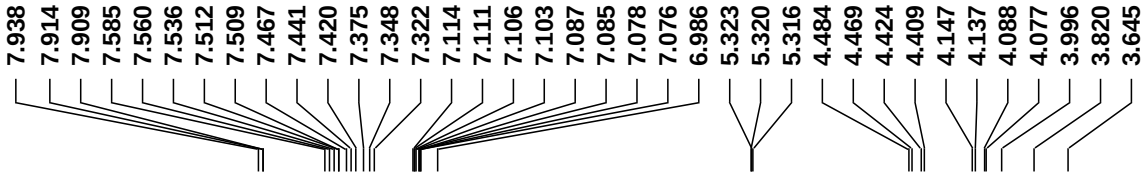
^{1}H NMR (300 MHz, CD_2Cl_2)

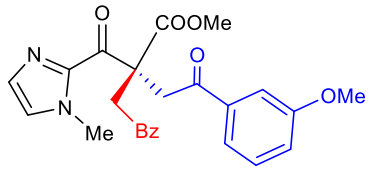




6e

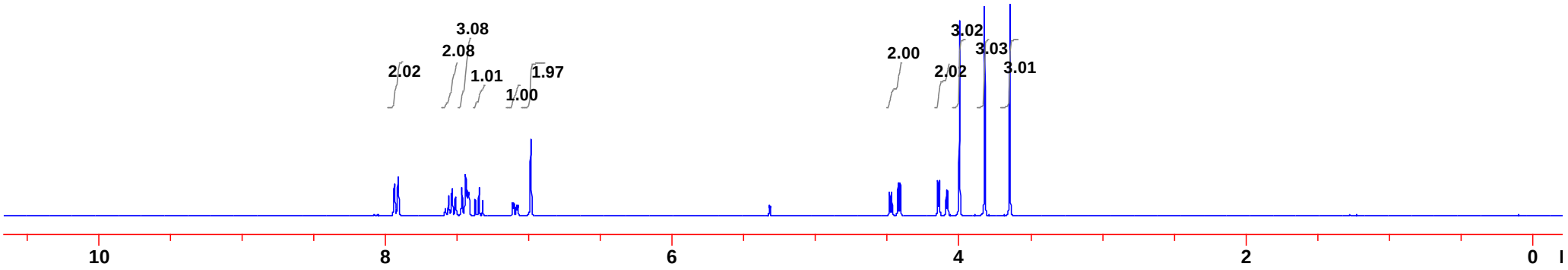
^{13}C NMR (75 MHz, CD_2Cl_2)

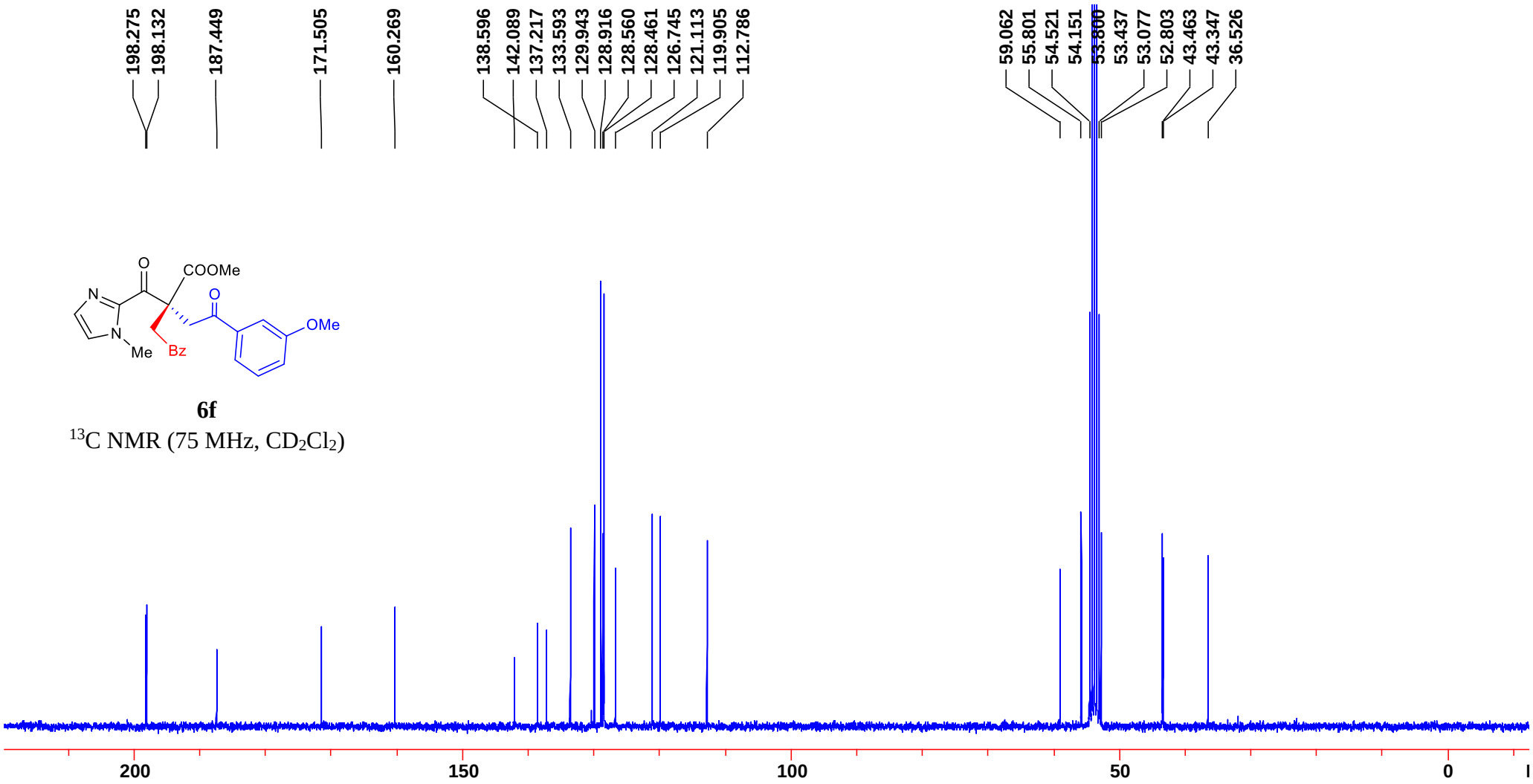




6f

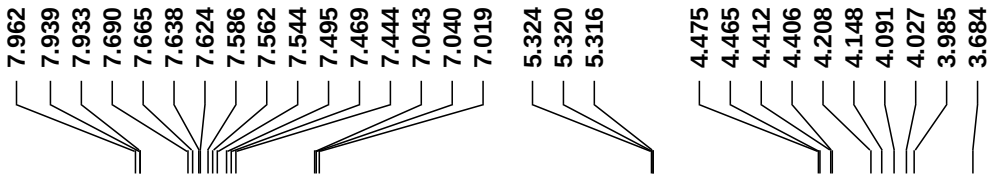
^{1}H NMR (300 MHz, CD_2Cl_2)

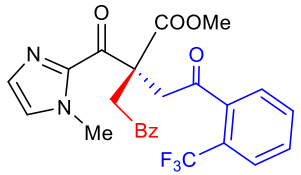




6f

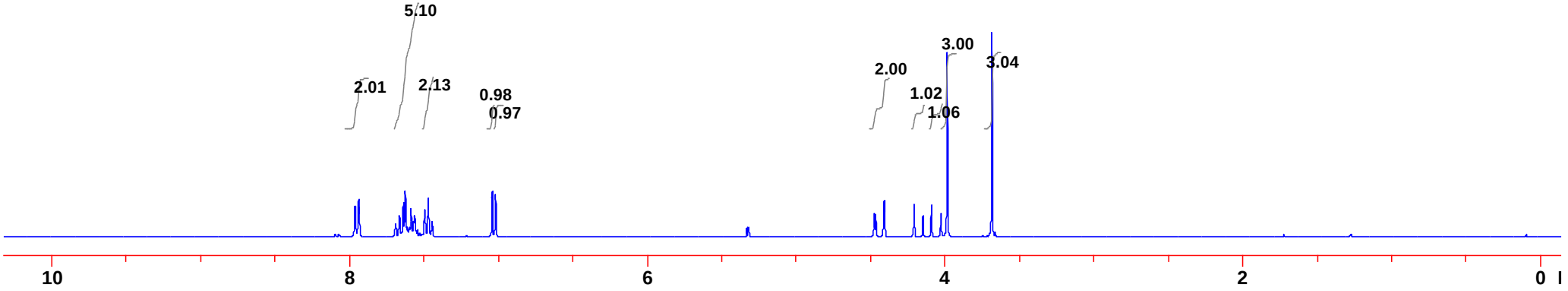
^{13}C NMR (75 MHz, CD_2Cl_2)

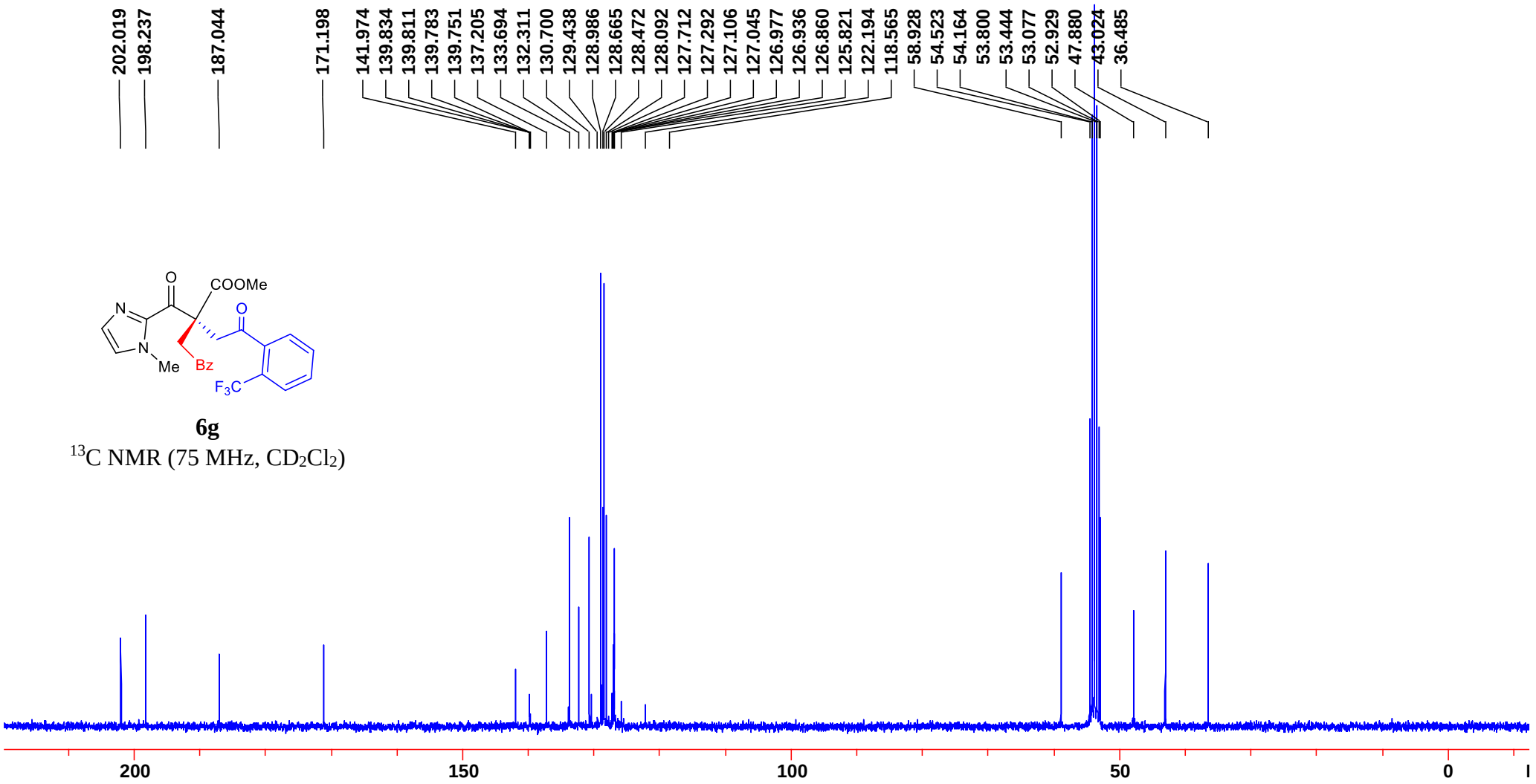




6g

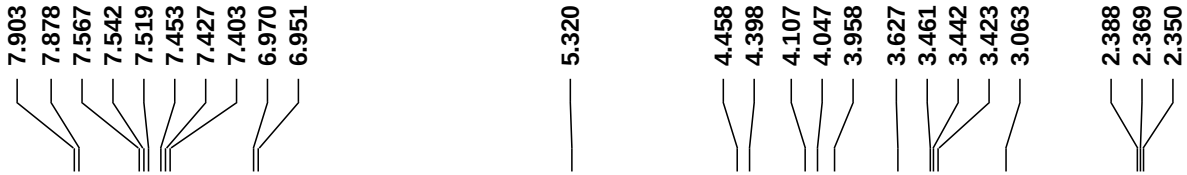
^{1}H NMR (300 MHz, CD_2Cl_2)

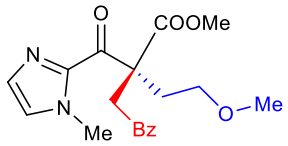




6g

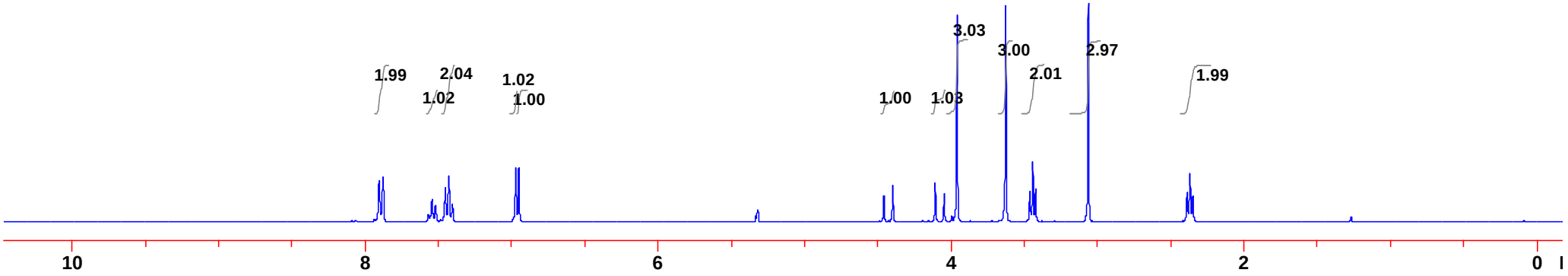
^{13}C NMR (75 MHz, CD_2Cl_2)

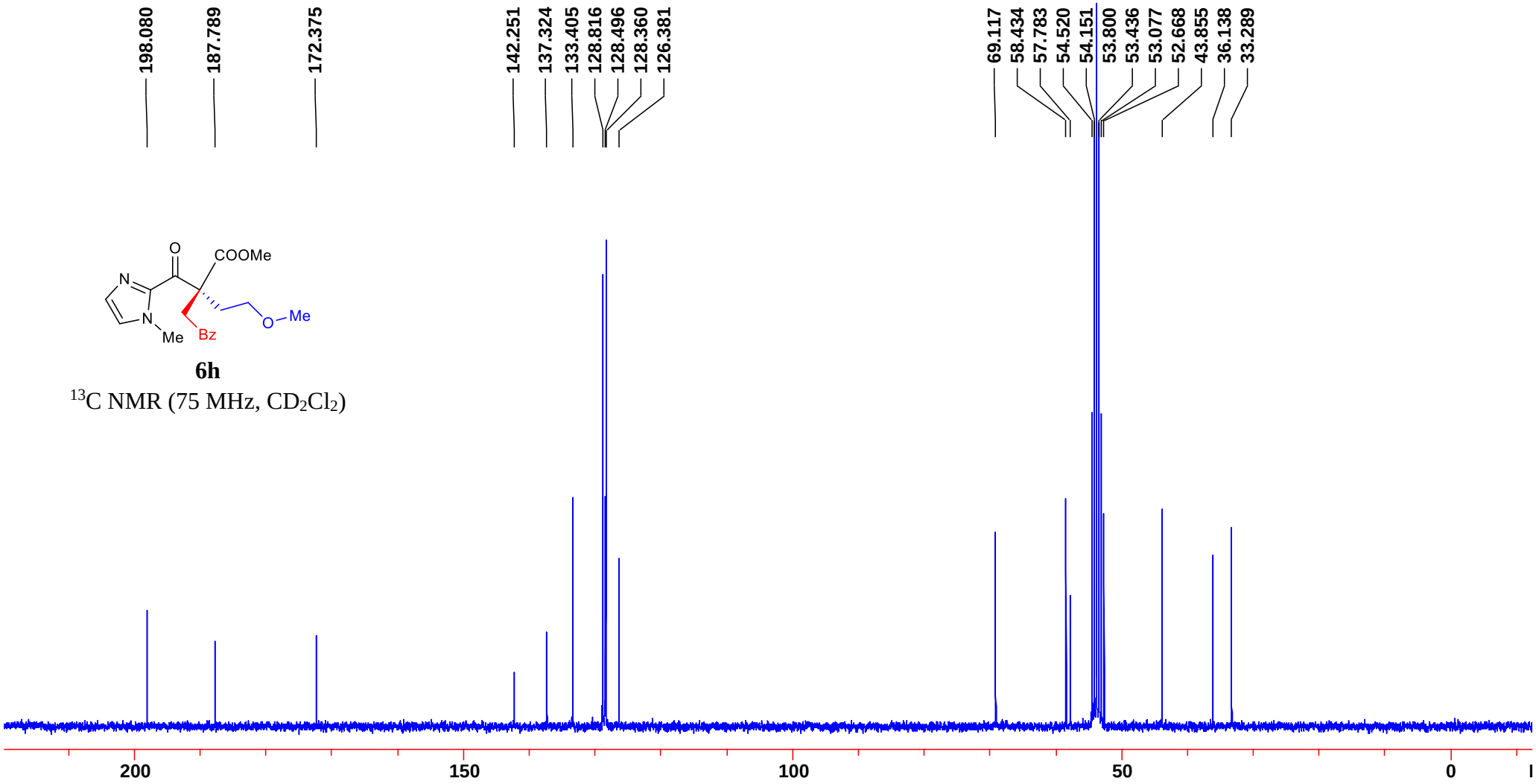




6h

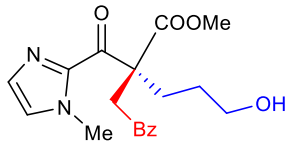
^{1}H NMR (300 MHz, CD_2Cl_2)





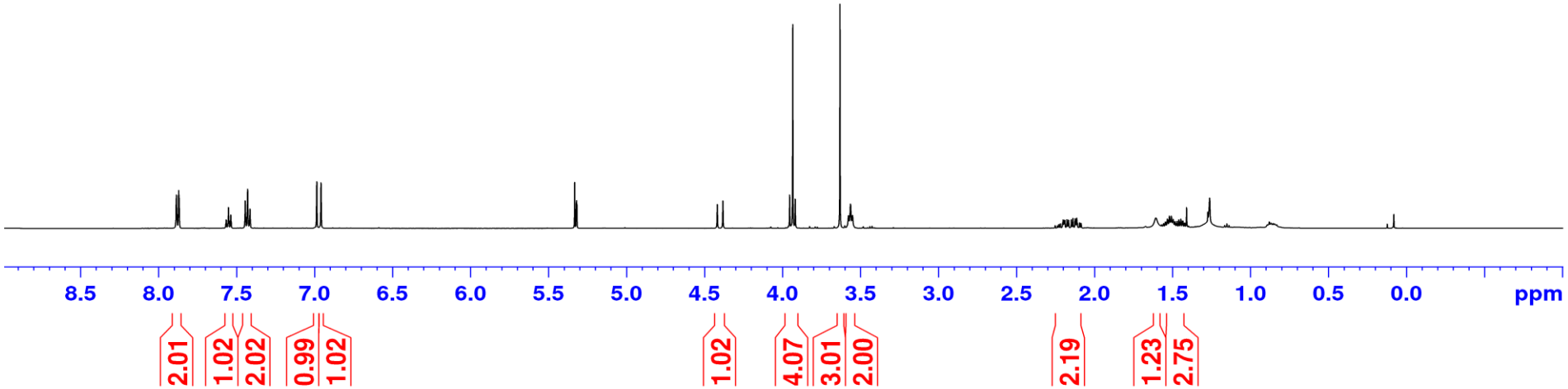
6h

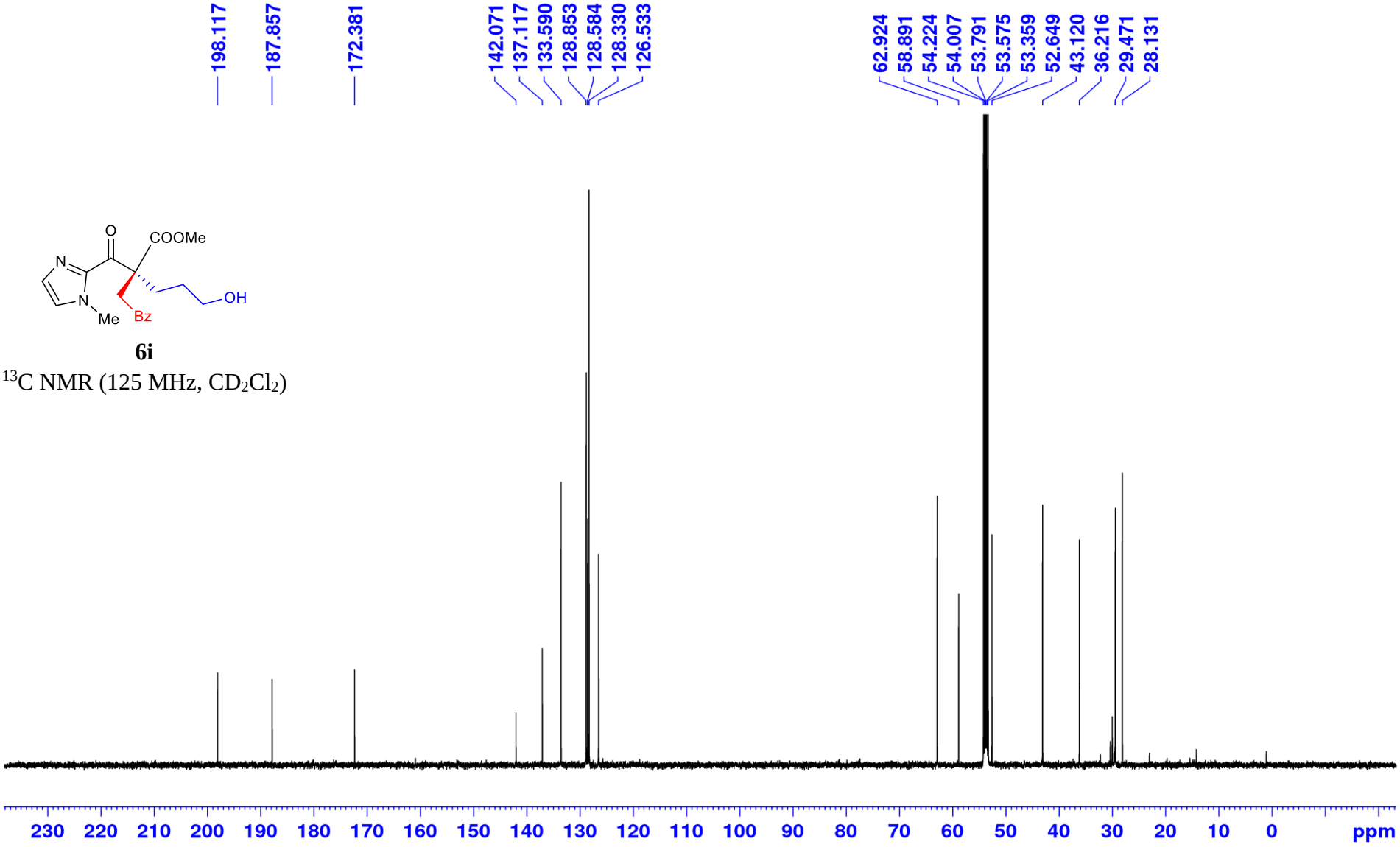
^{13}C NMR (75 MHz, CD_2Cl_2)



6i

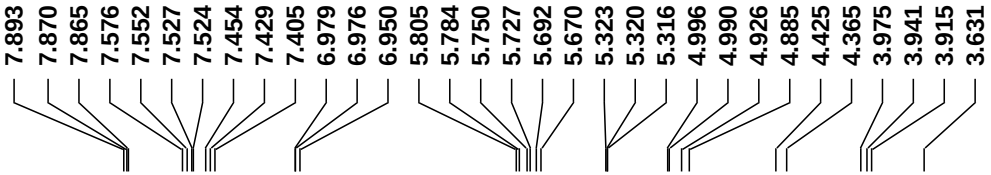
^{1}H NMR (500 MHz, CD_2Cl_2)

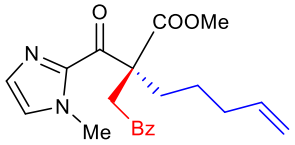




6i

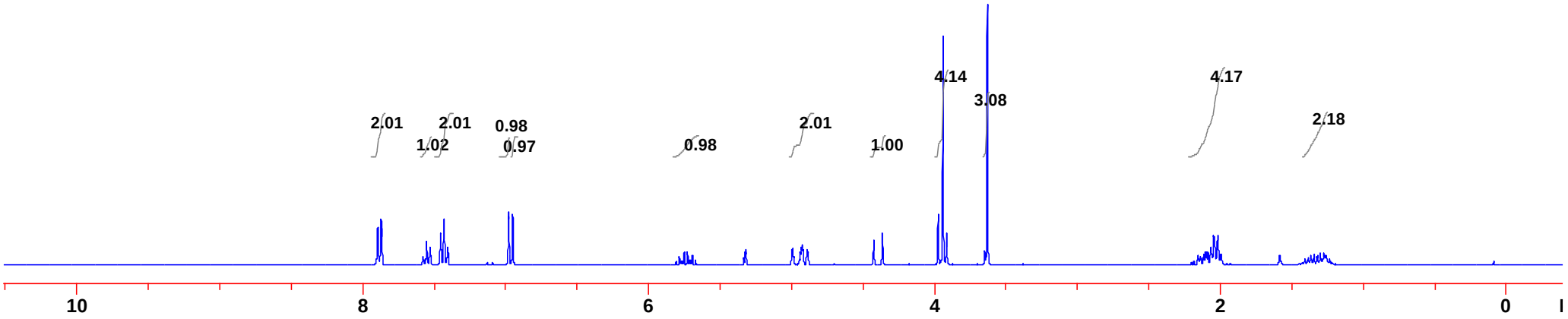
^{13}C NMR (125 MHz, CD_2Cl_2)

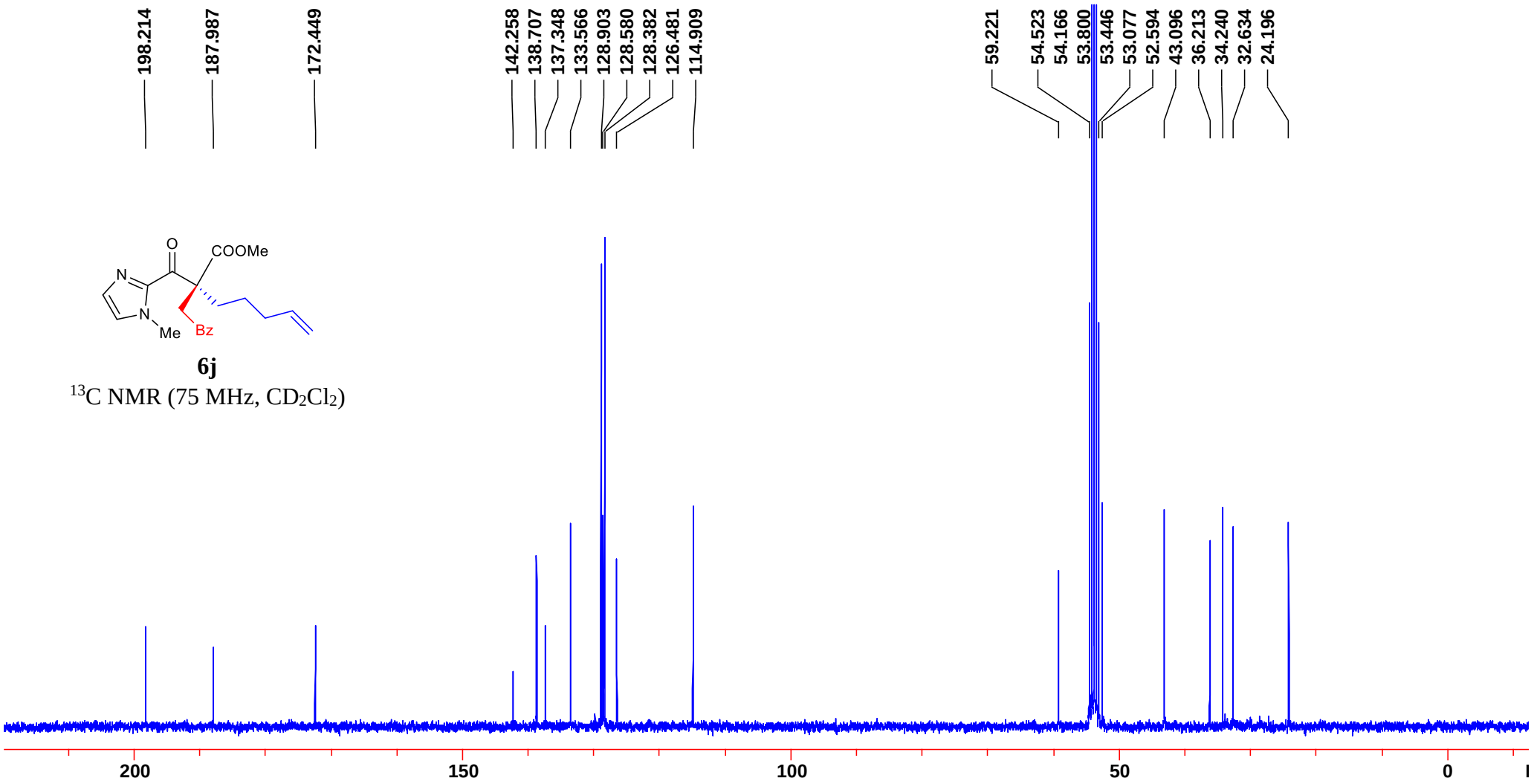




6j

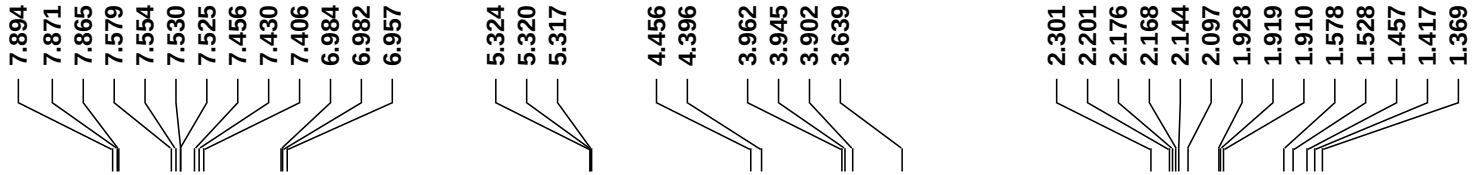
^{1}H NMR (300 MHz, CD_2Cl_2)

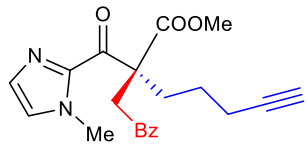




6j

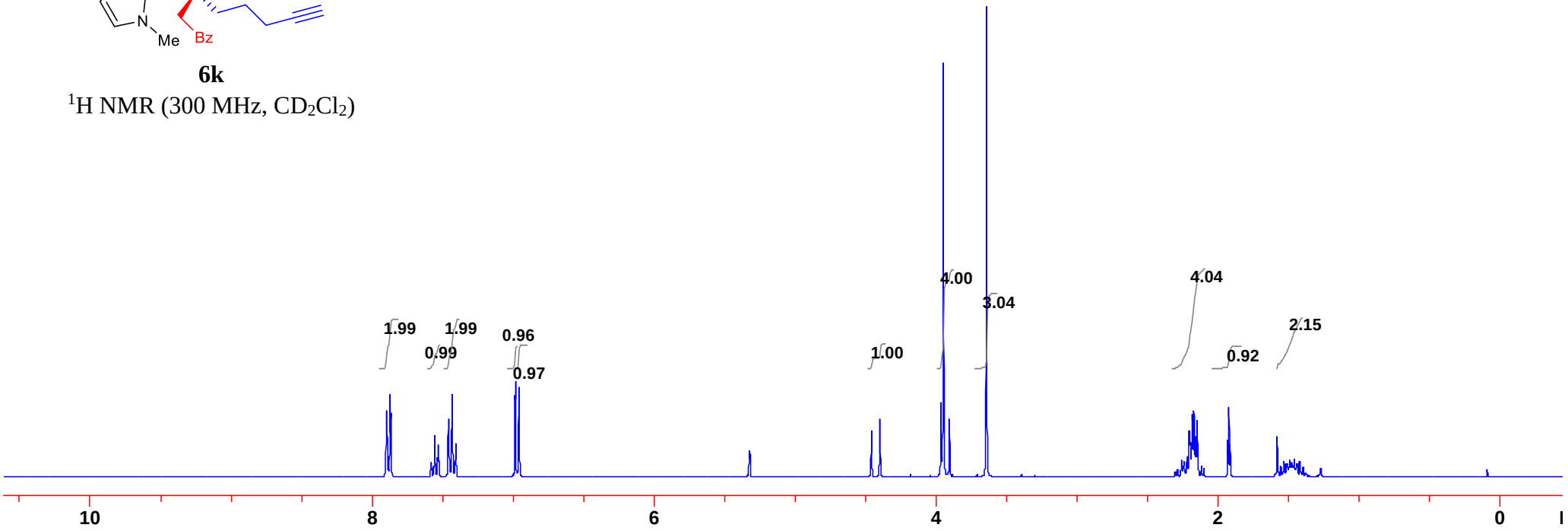
^{13}C NMR (75 MHz, CD_2Cl_2)

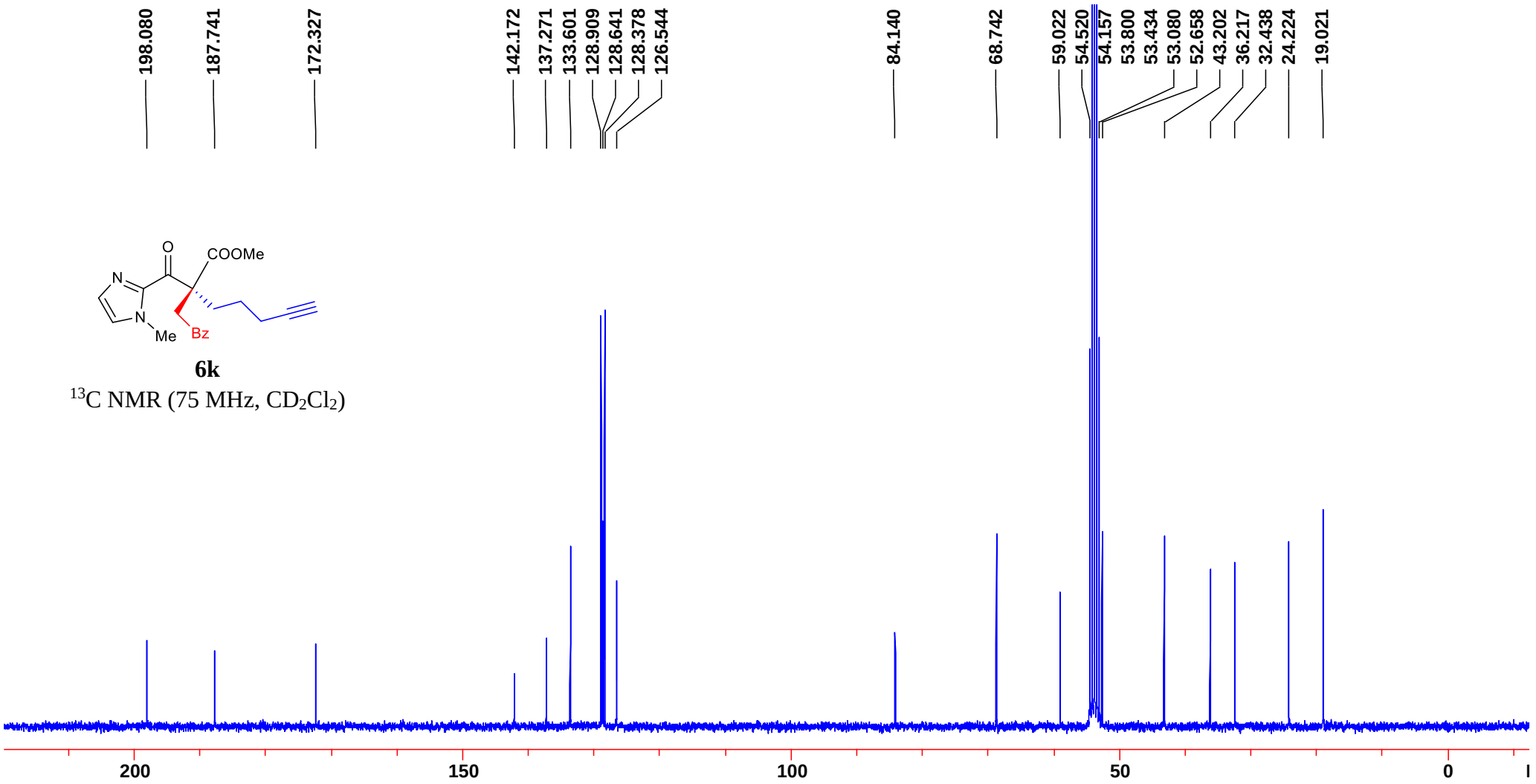




6k

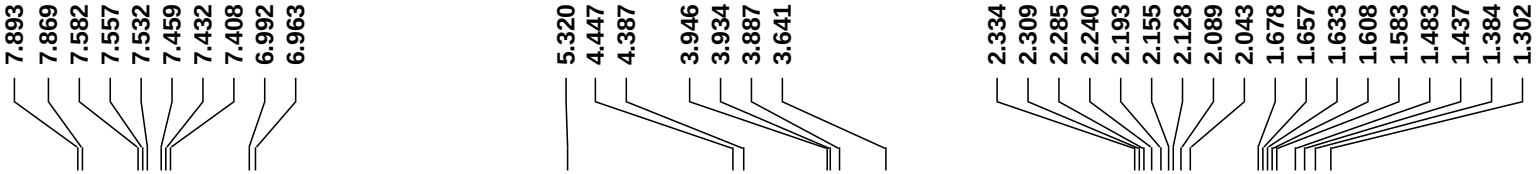
^{1}H NMR (300 MHz, CD_2Cl_2)

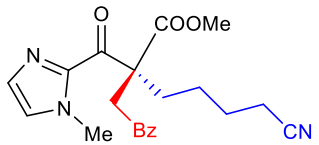




6k

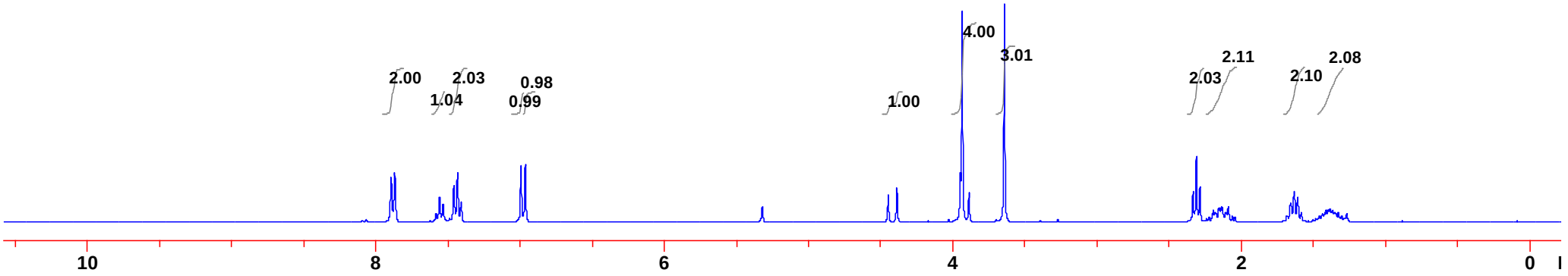
^{13}C NMR (75 MHz, CD_2Cl_2)

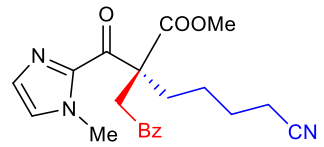




6l

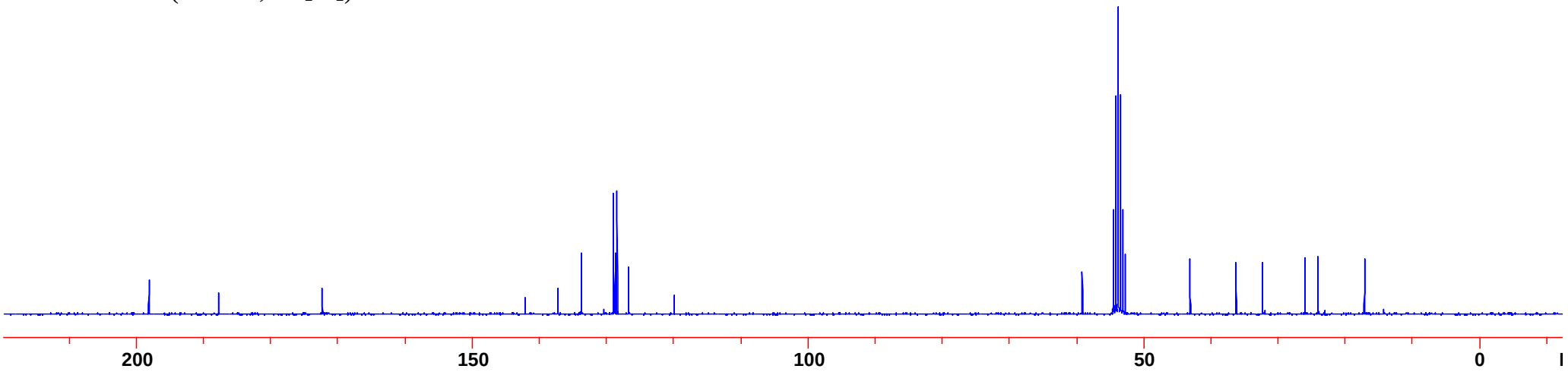
^{1}H NMR (300 MHz, CD_2Cl_2)

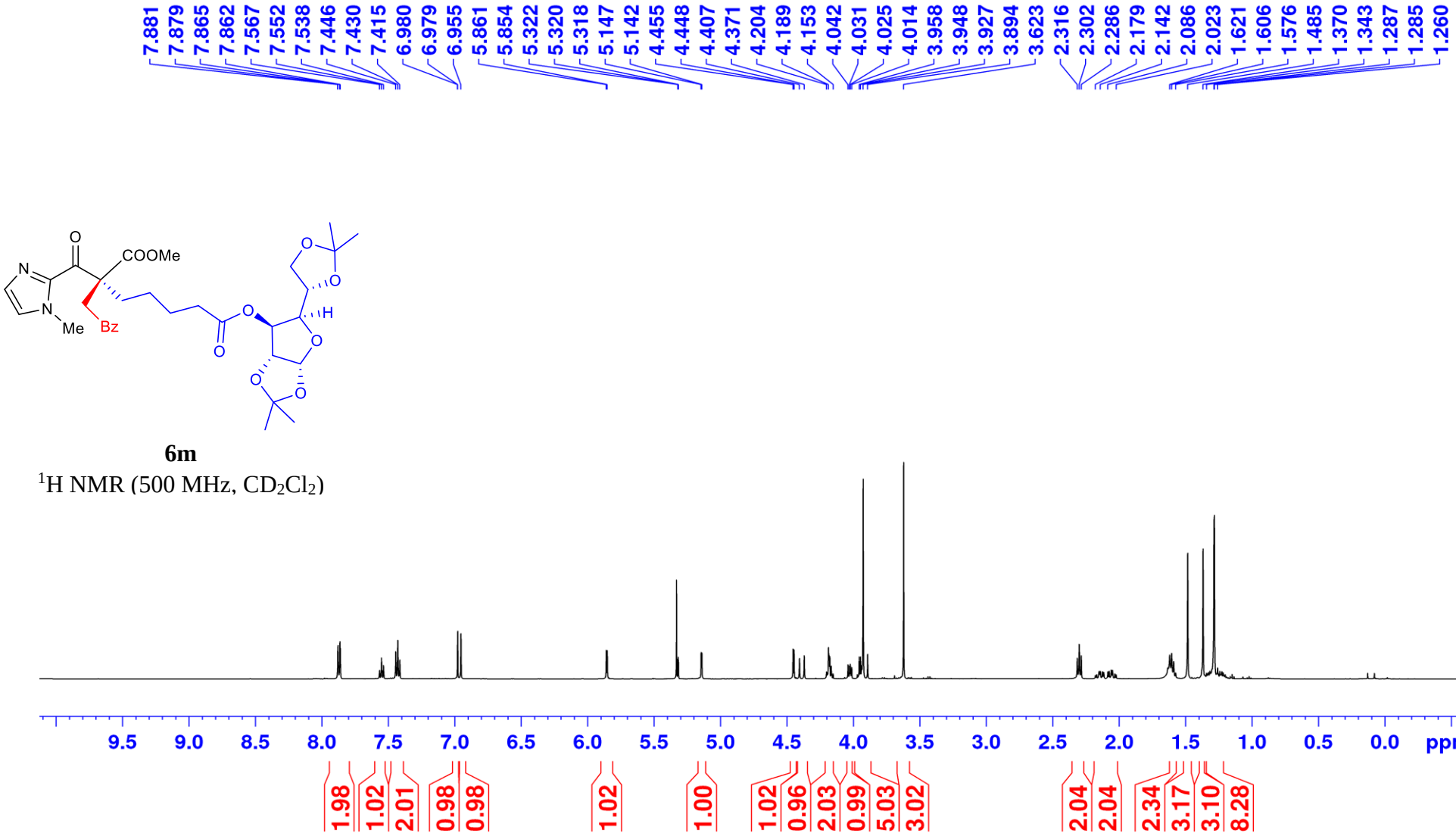




6l

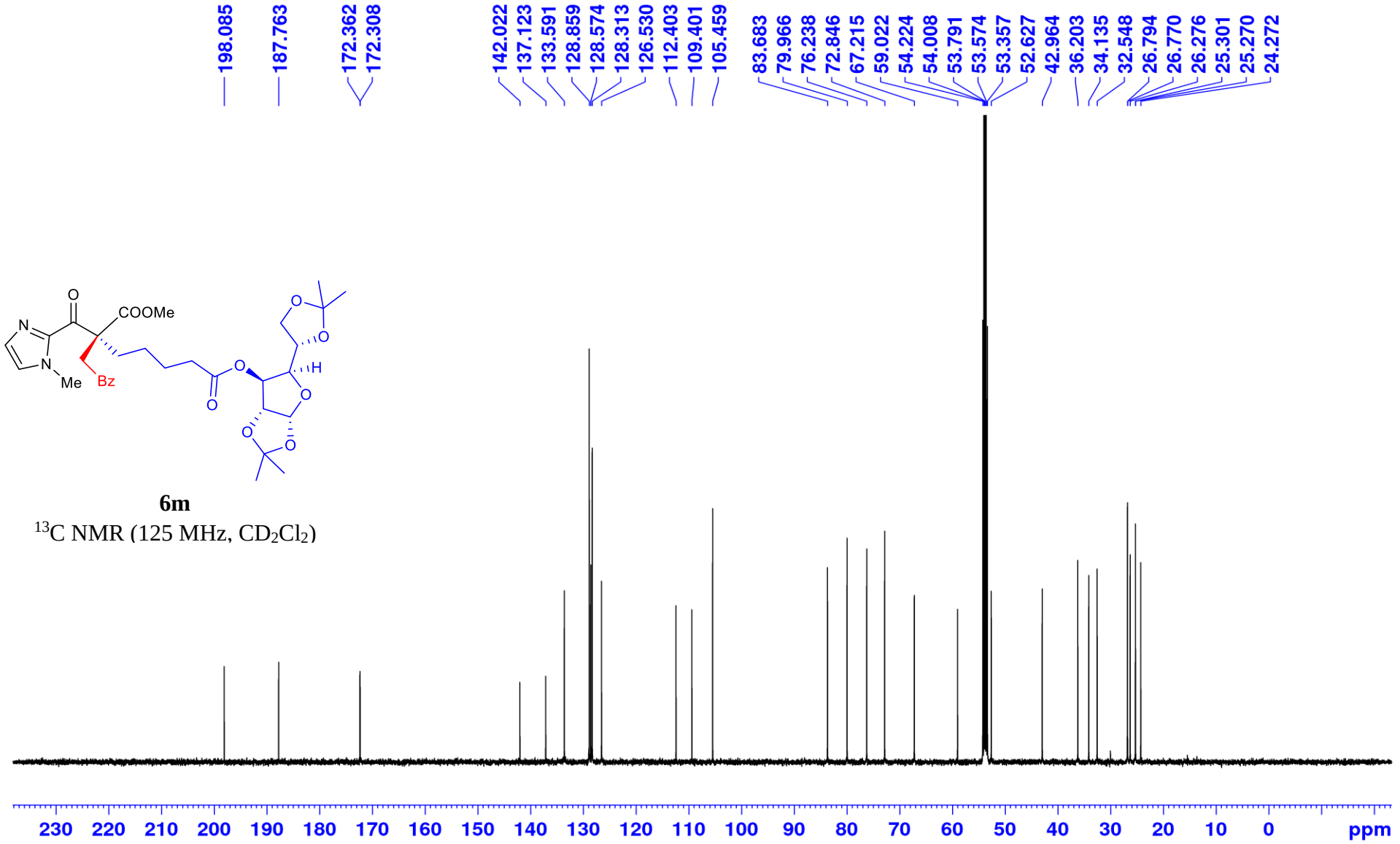
^{13}C NMR (75 MHz, CD_2Cl_2)





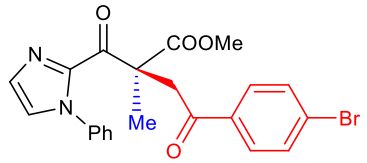
6m

^{1}H NMR (500 MHz, CD_2Cl_2)



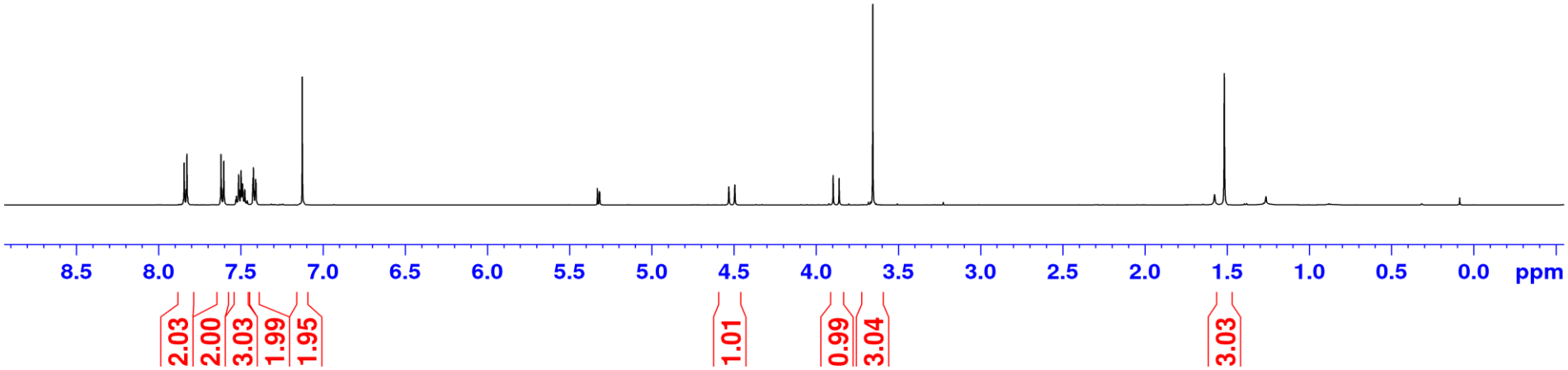
6m

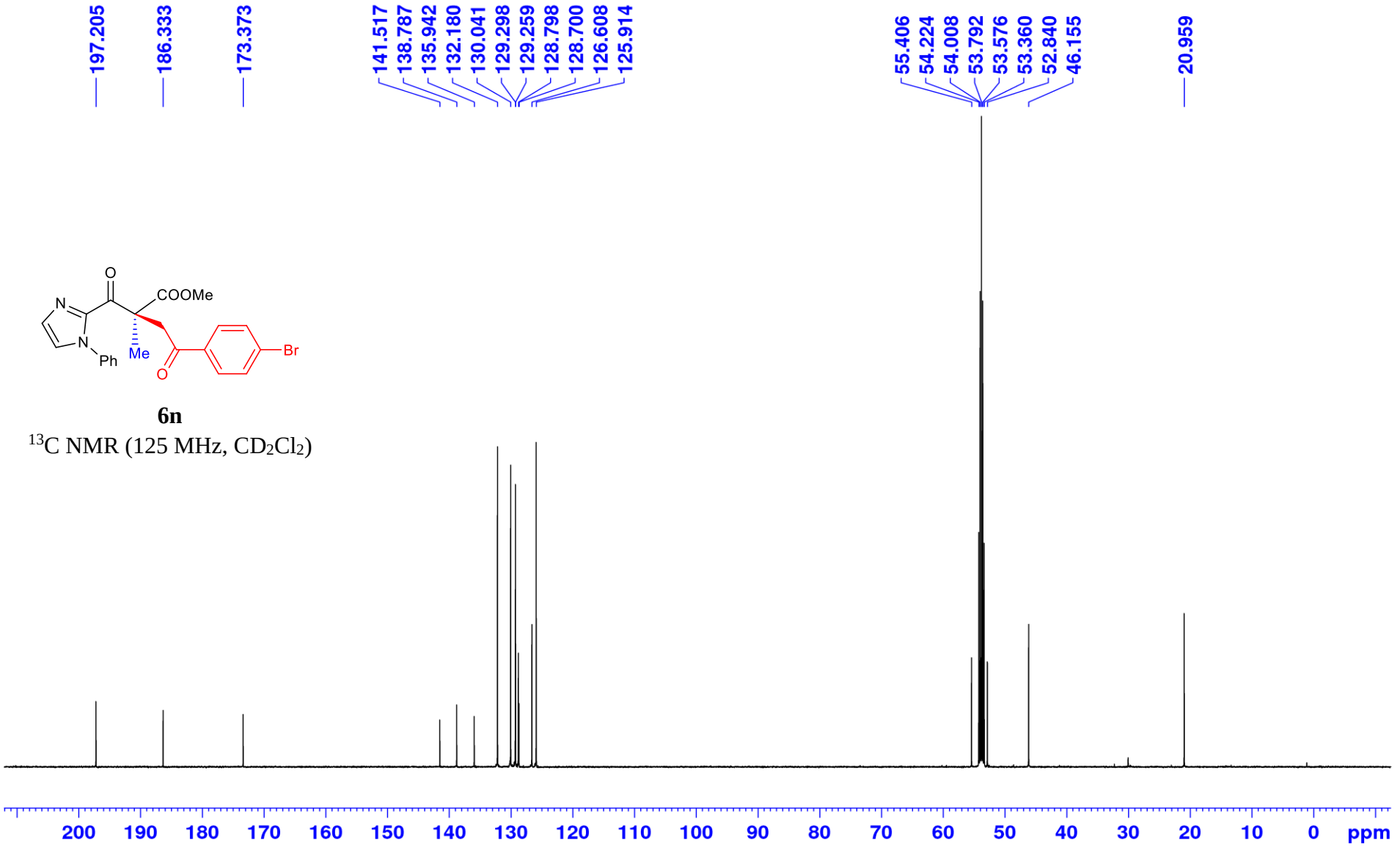
^{13}C NMR (125 MHz, CD_2Cl_2)



6n

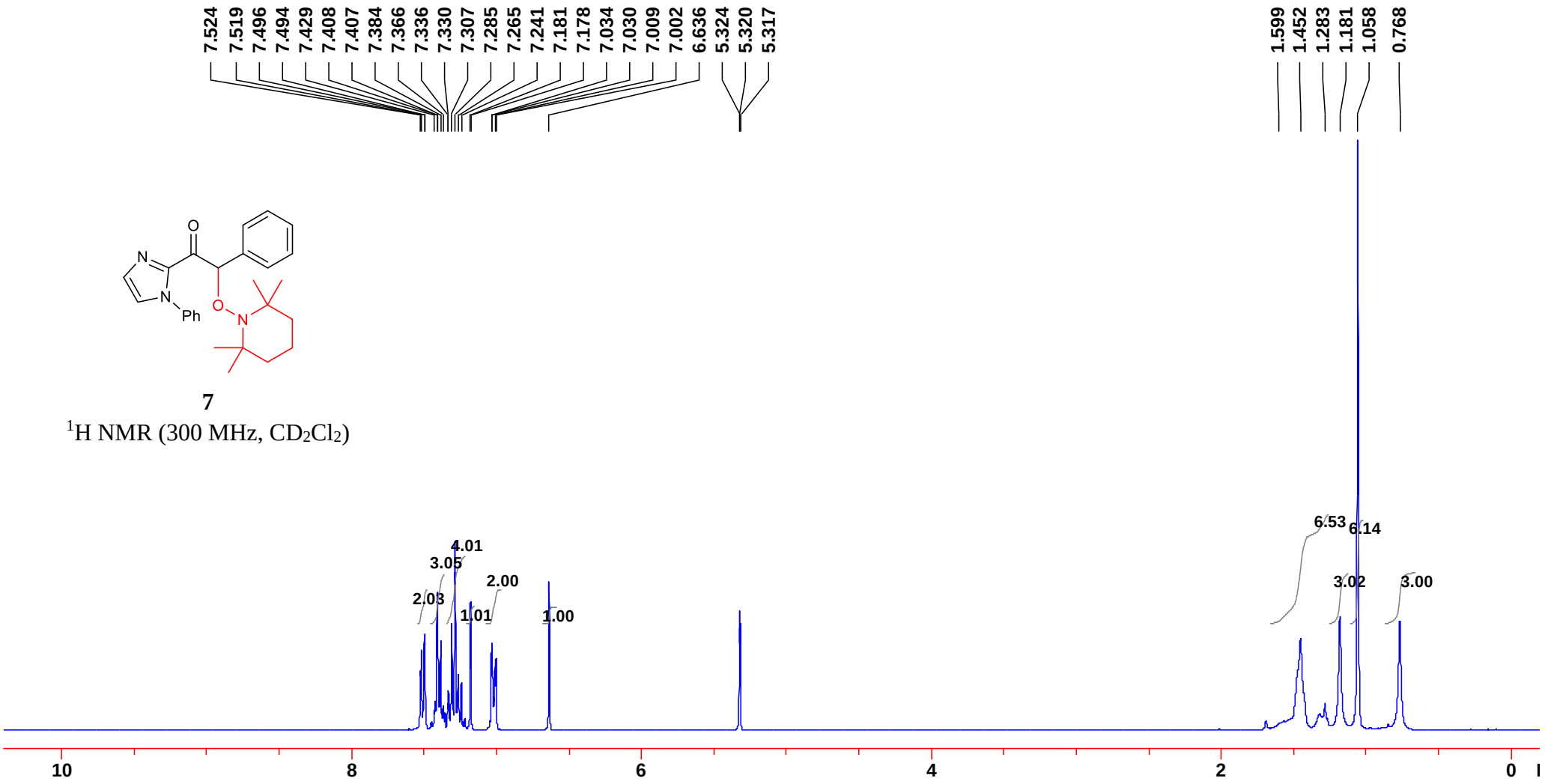
^{1}H NMR (500 MHz, CD_2Cl_2)





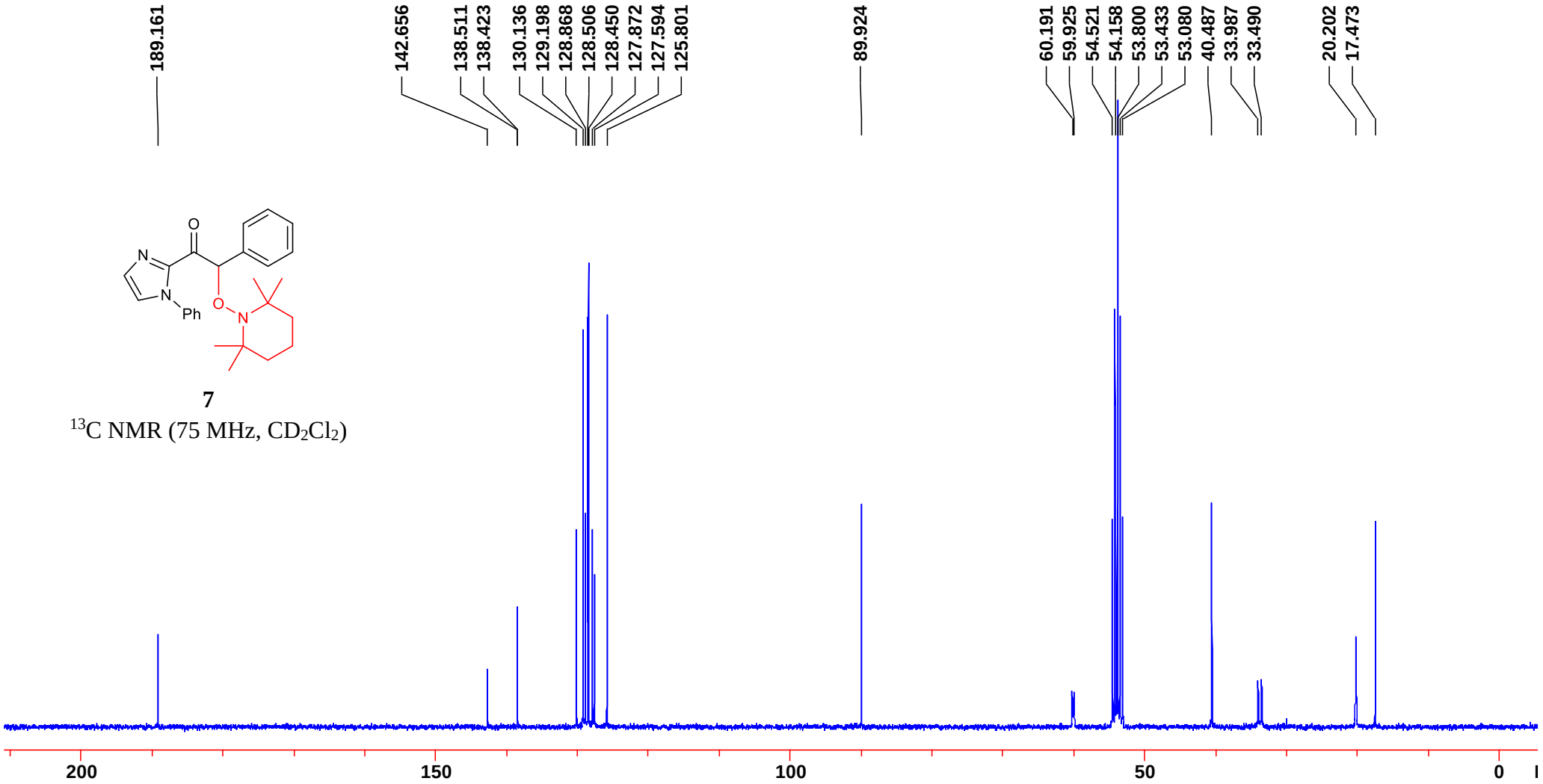
6n

^{13}C NMR (125 MHz, CD_2Cl_2)



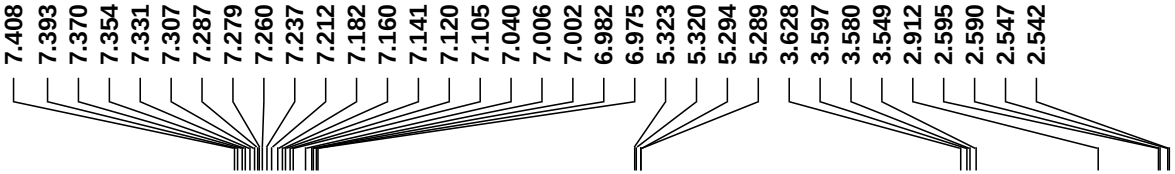
7

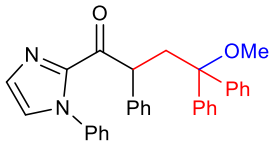
^{1}H NMR (300 MHz, CD_2Cl_2)



7

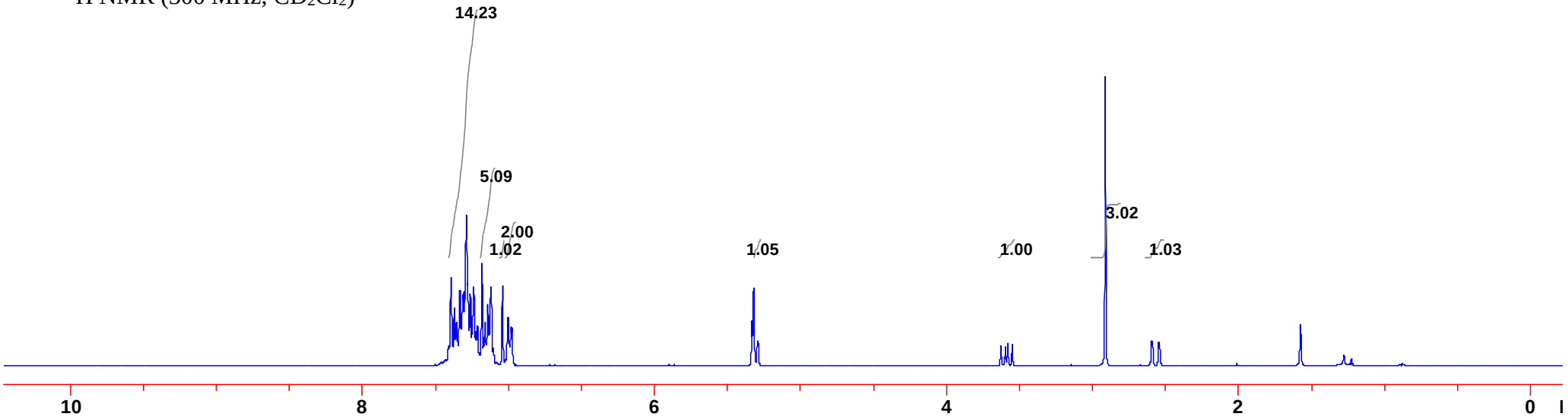
^{13}C NMR (75 MHz, CD_2Cl_2)

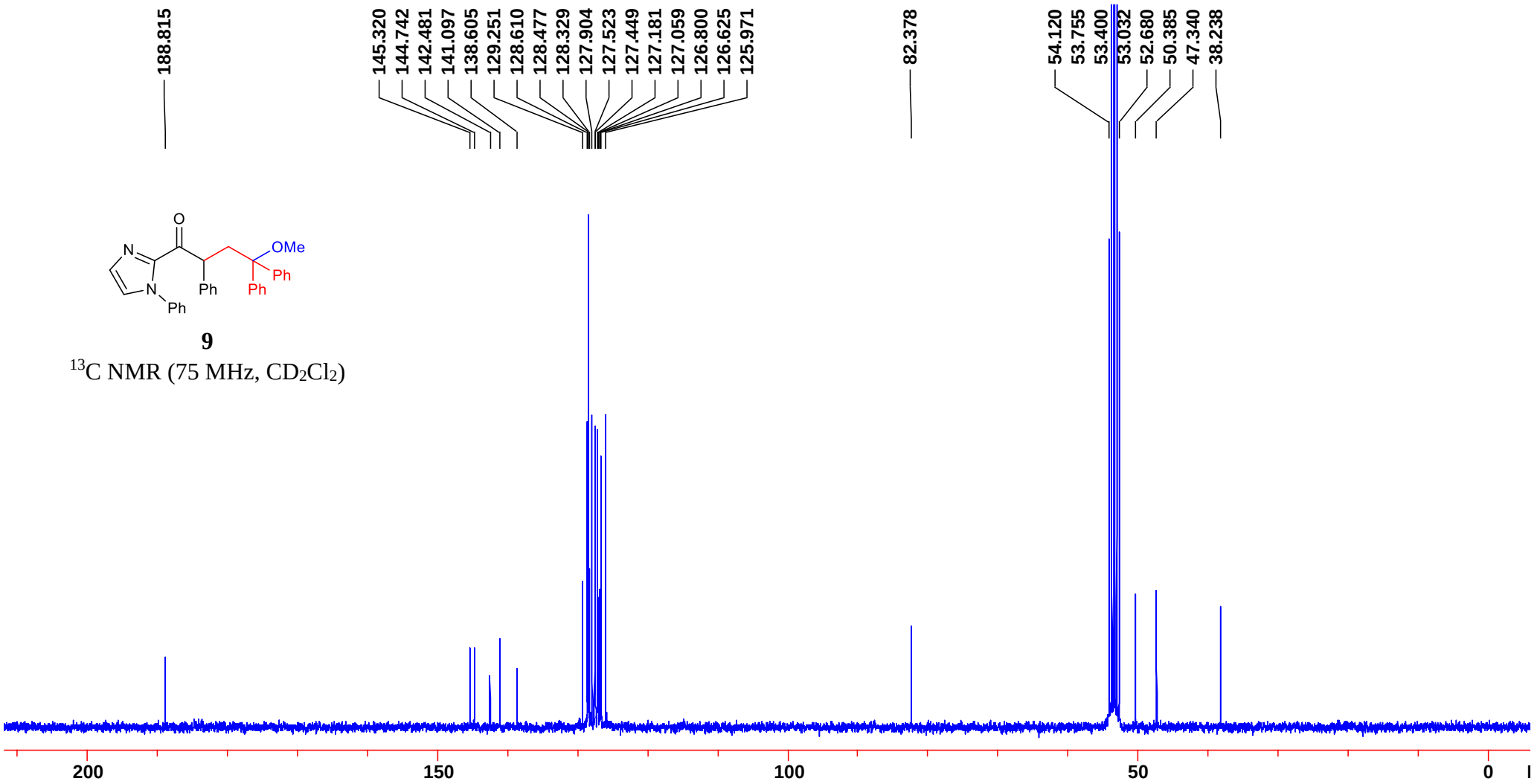




9

^{1}H NMR (300 MHz, CD_2Cl_2)

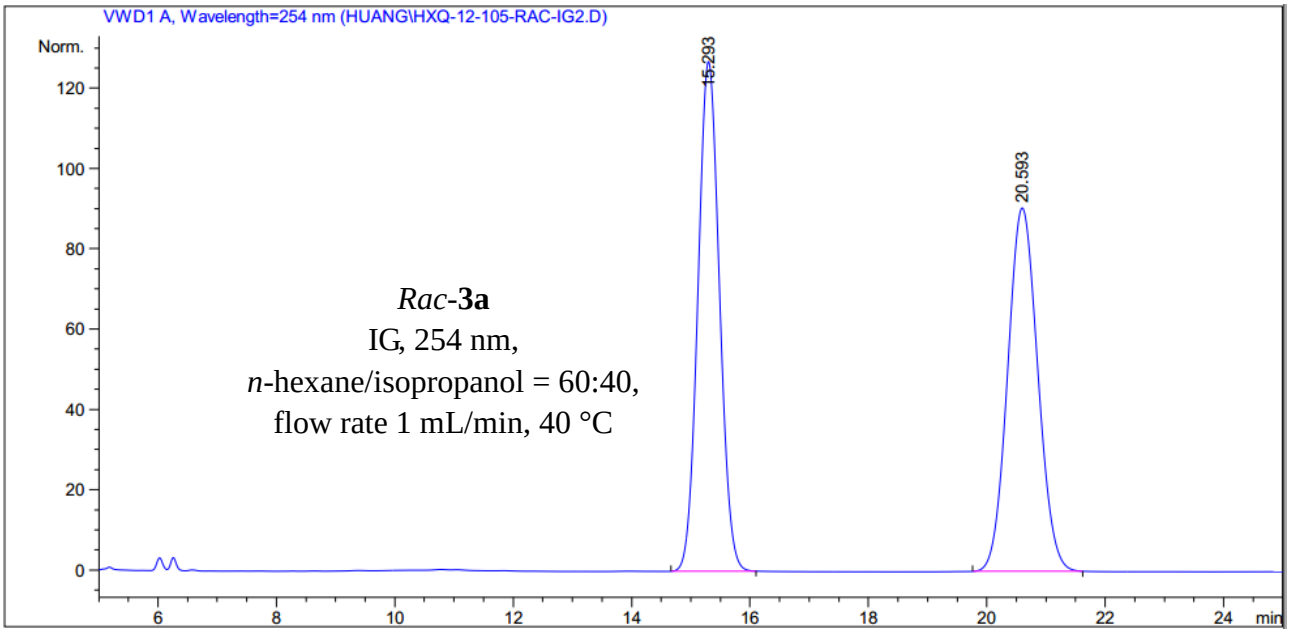




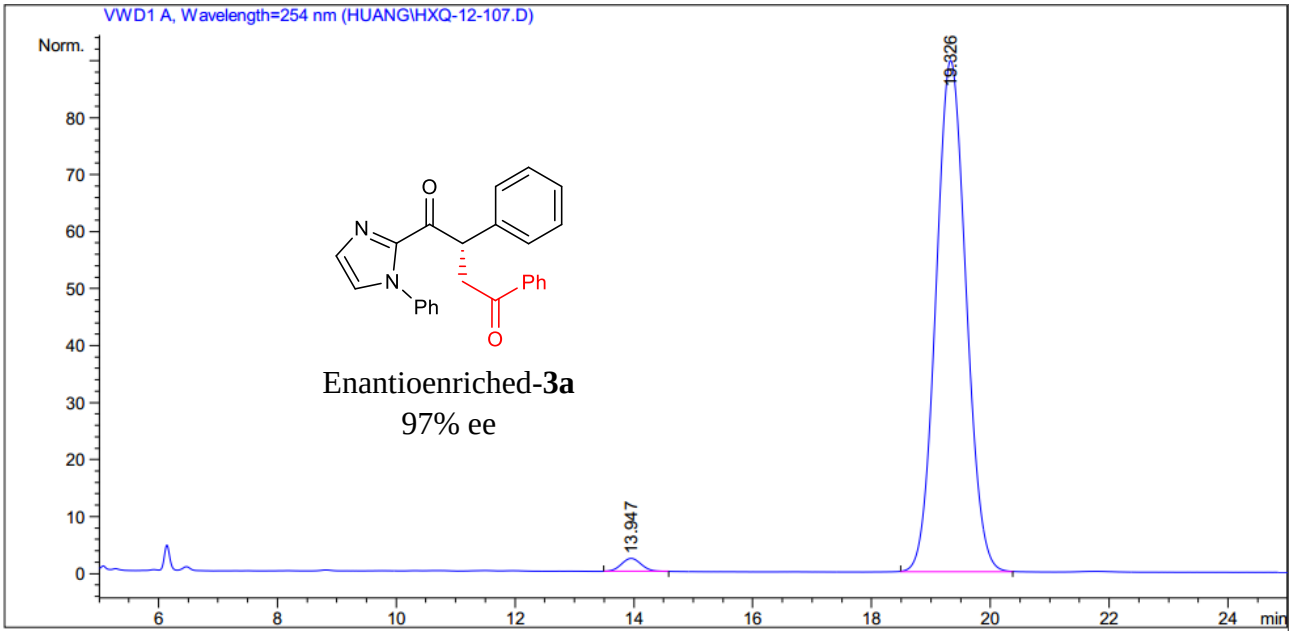
9

^{13}C NMR (75 MHz, CD_2Cl_2)

Supplementary Figures

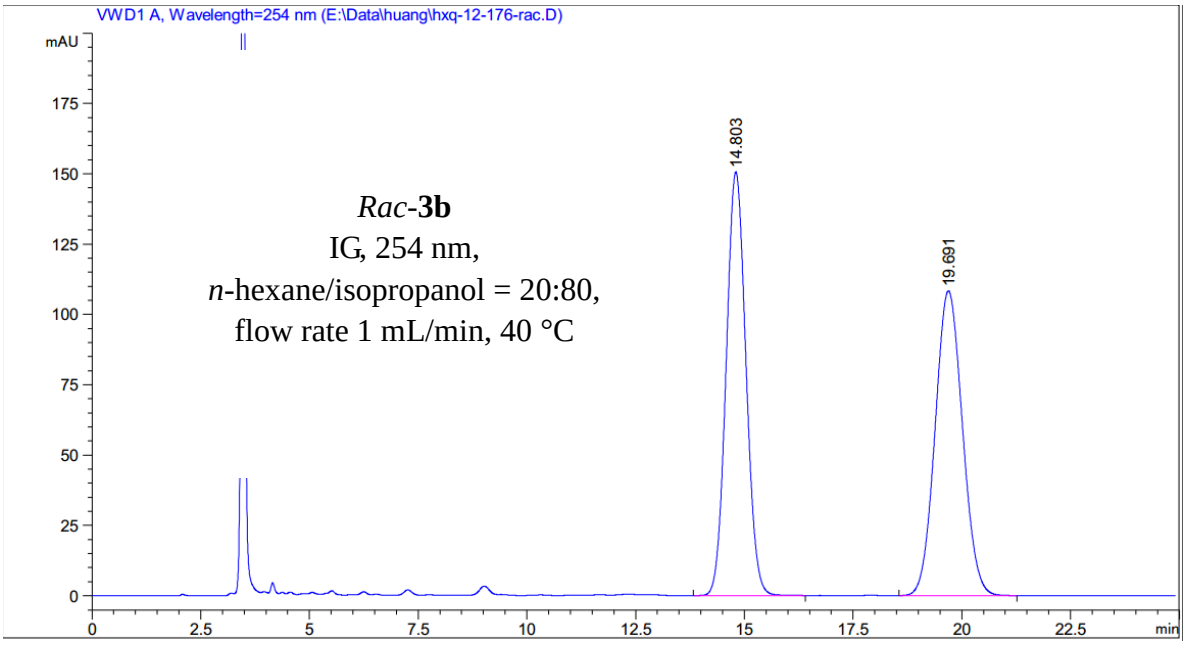


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.293	BB	0.3933	3202.13647	126.93052	50.0041
2	20.593	BB	0.5524	3201.60913	90.52518	49.9959

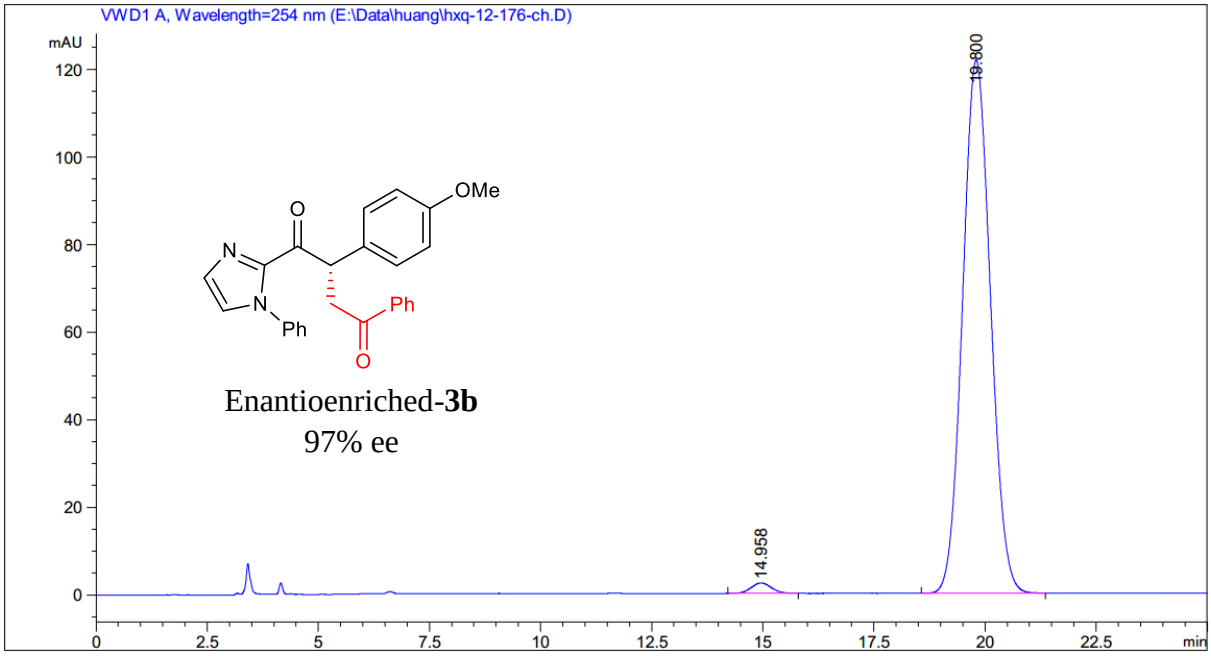


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.947	BB	0.3675	53.16900	2.28542	1.6586
2	19.326	BB	0.5498	3152.53906	89.69482	98.3414

Supplementary Figure 1. HPLC traces of *rac*-**3a** (reference) and enantioenriched-**3a**.

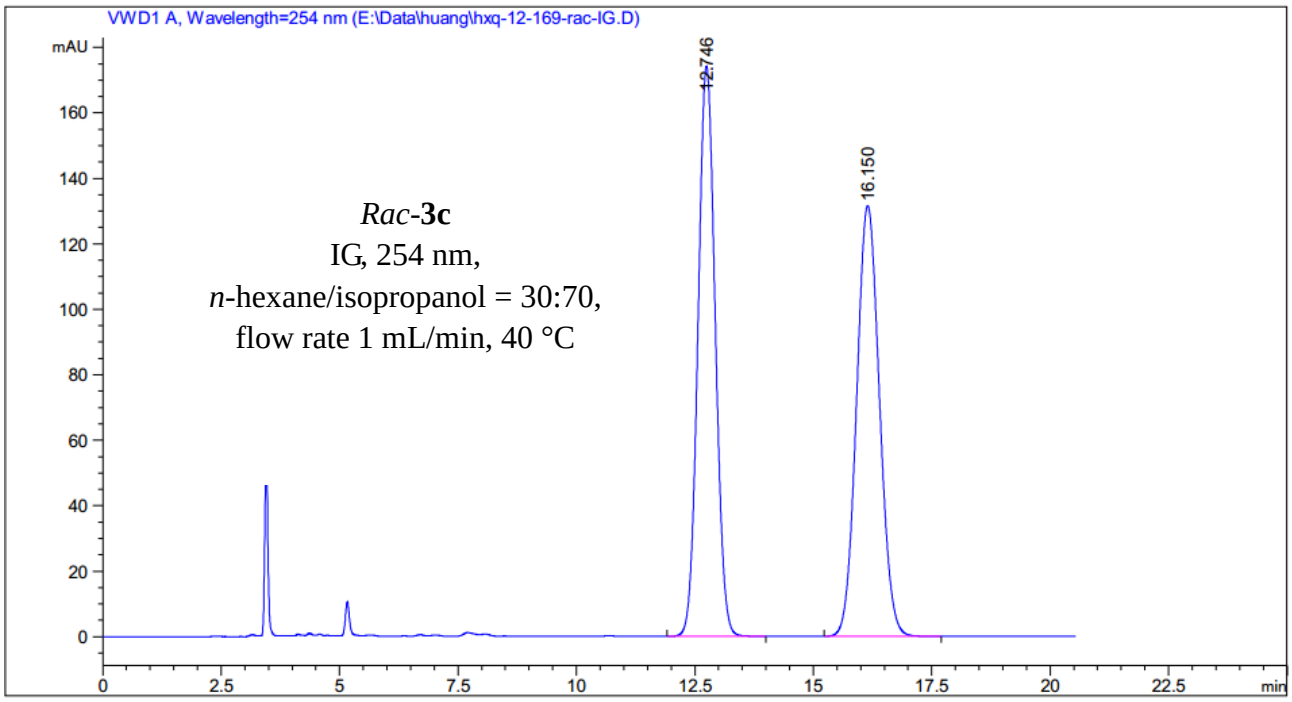


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.803	BB	0.4918	4745.91895	150.53288	50.0939
2	19.691	BB	0.6813	4728.13330	108.30090	49.9061

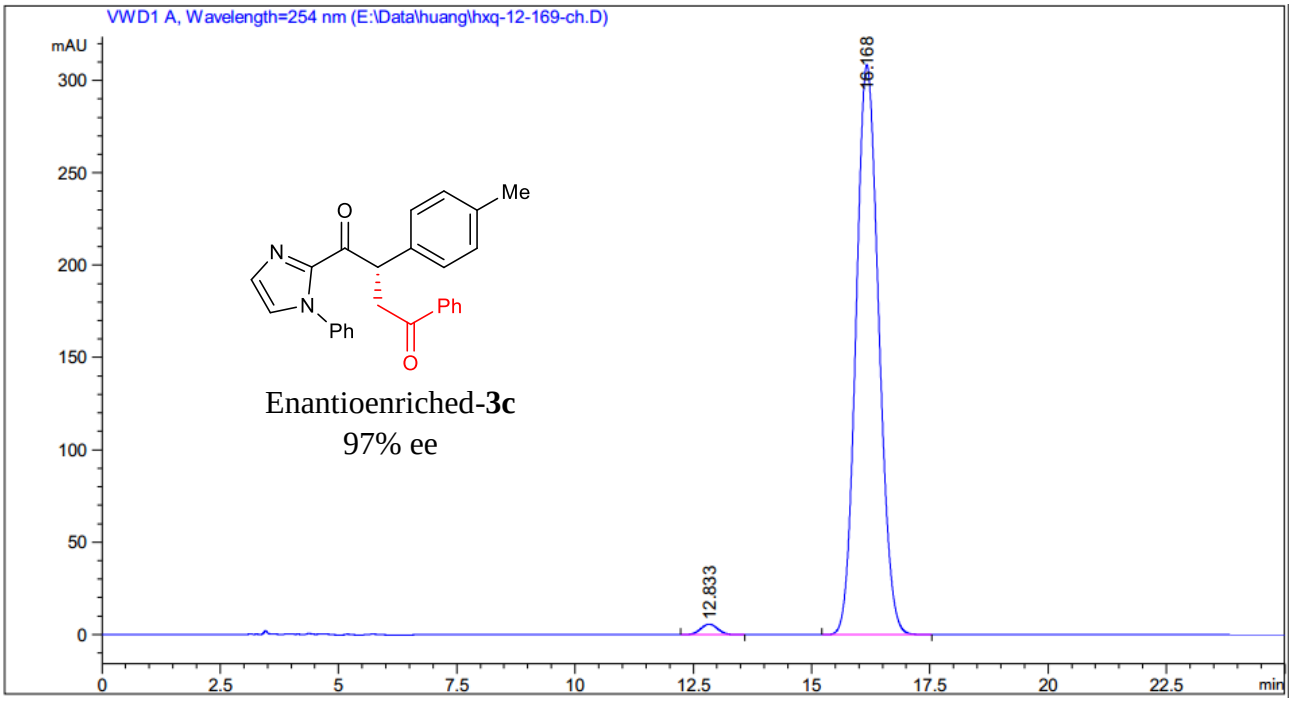


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.958	BB	0.4793	75.34138	2.37346	1.4007
2	19.800	BB	0.6813	5303.47168	121.71532	98.5993

Supplementary Figure 2. HPLC traces of *rac*-**3b** (reference) and enantioenriched-**3b**.

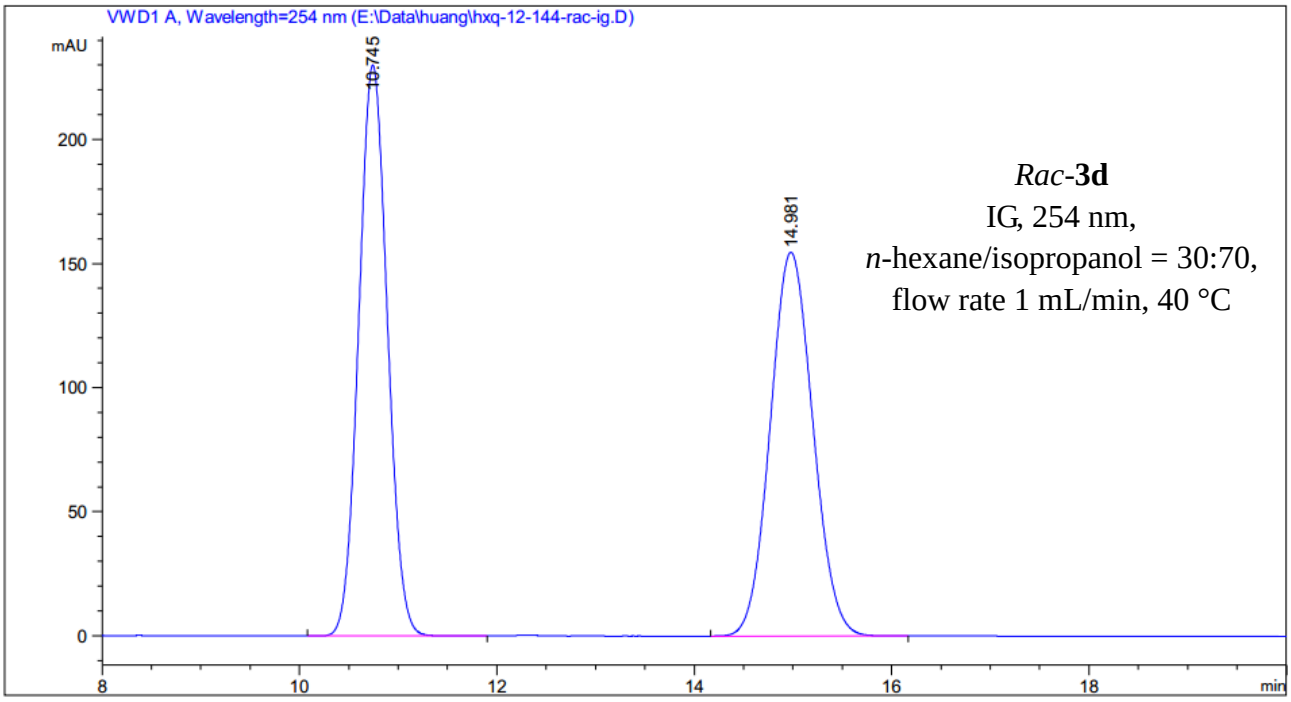


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.746	BB	0.3935	4398.71533	174.25121	49.9467
2	16.150	BB	0.5219	4408.11133	131.54800	50.0533

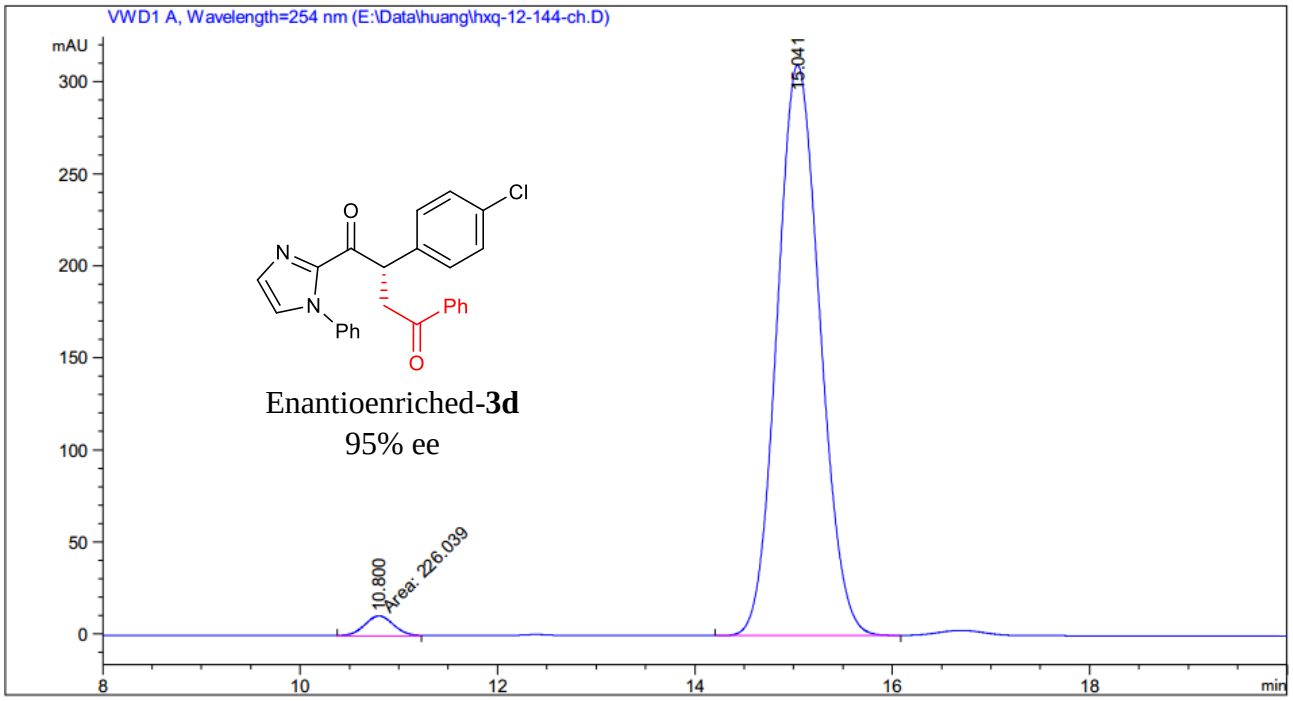


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.833	BB	0.3935	144.54518	5.74555	1.3852
2	16.168	BB	0.5211	1.02903e4	308.50662	98.6148

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

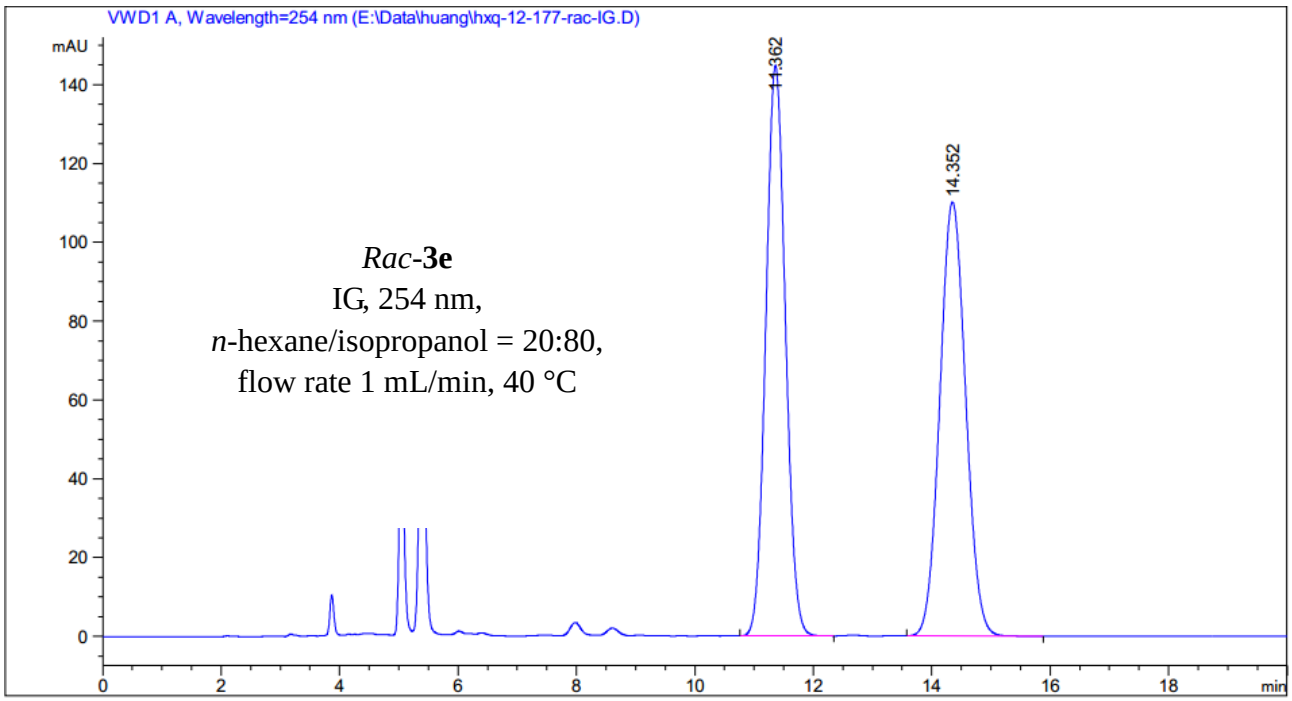


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.745	BB	0.3143	4641.36914	230.13562	49.9670
2	14.981	BB	0.4705	4647.50146	154.70828	50.0330

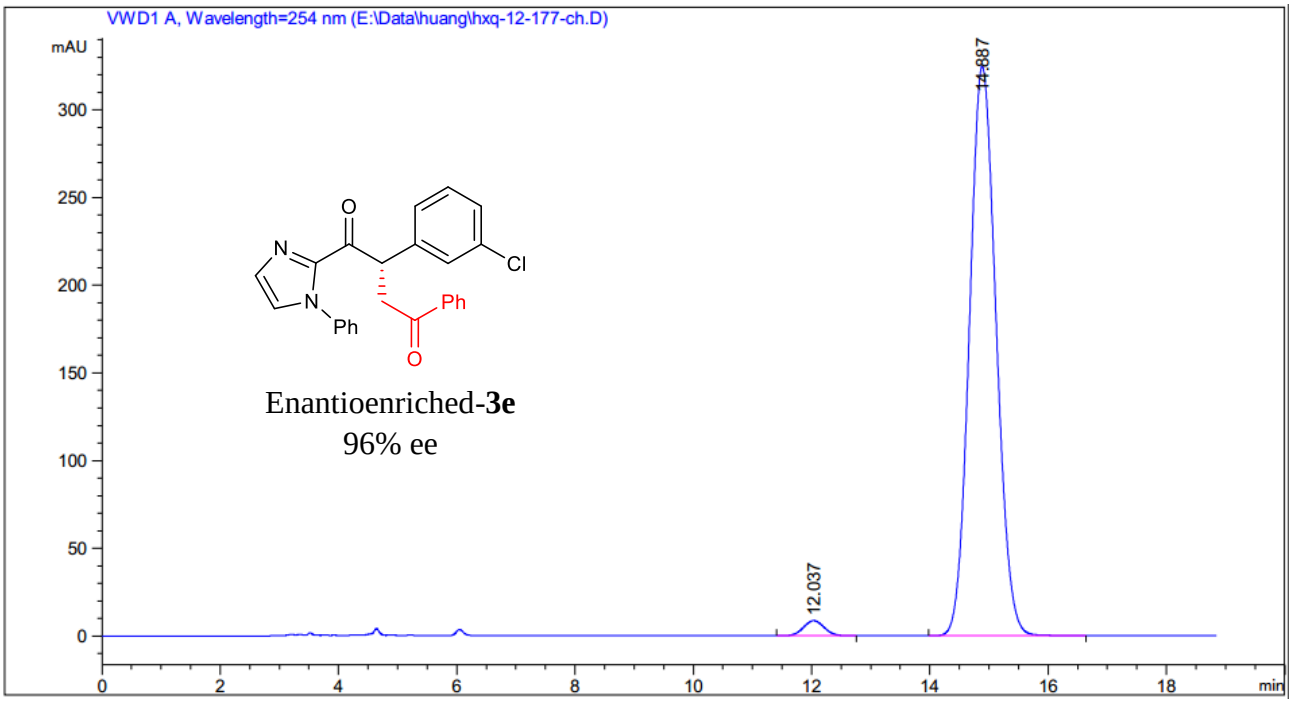


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.800	MM	0.3463	226.03903	10.87988	2.3580
2	15.041	BB	0.4713	9360.21191	309.93100	97.6420

Supplementary Figure 4. HPLC traces of *rac*-**3d** (reference) and enantioenriched-**3d**.

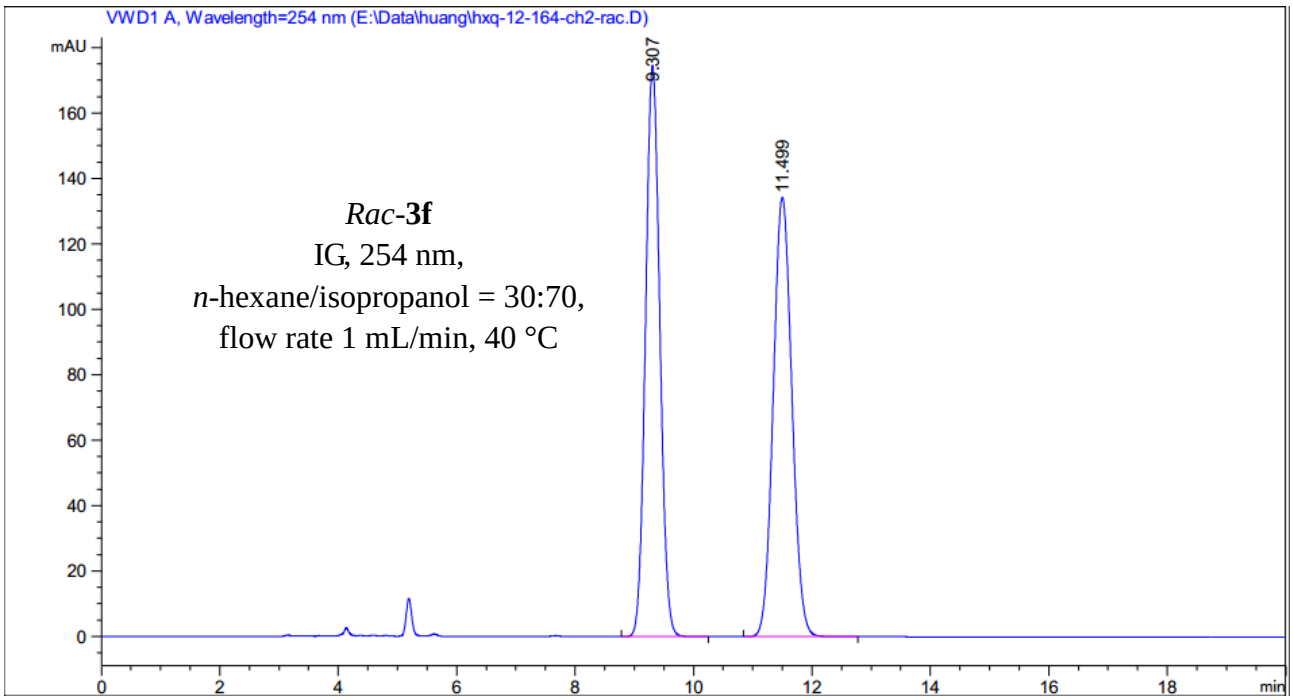


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.362	BB	0.3594	3329.71021	144.75757	49.9719
2	14.352	BB	0.4731	3333.45874	110.12643	50.0281

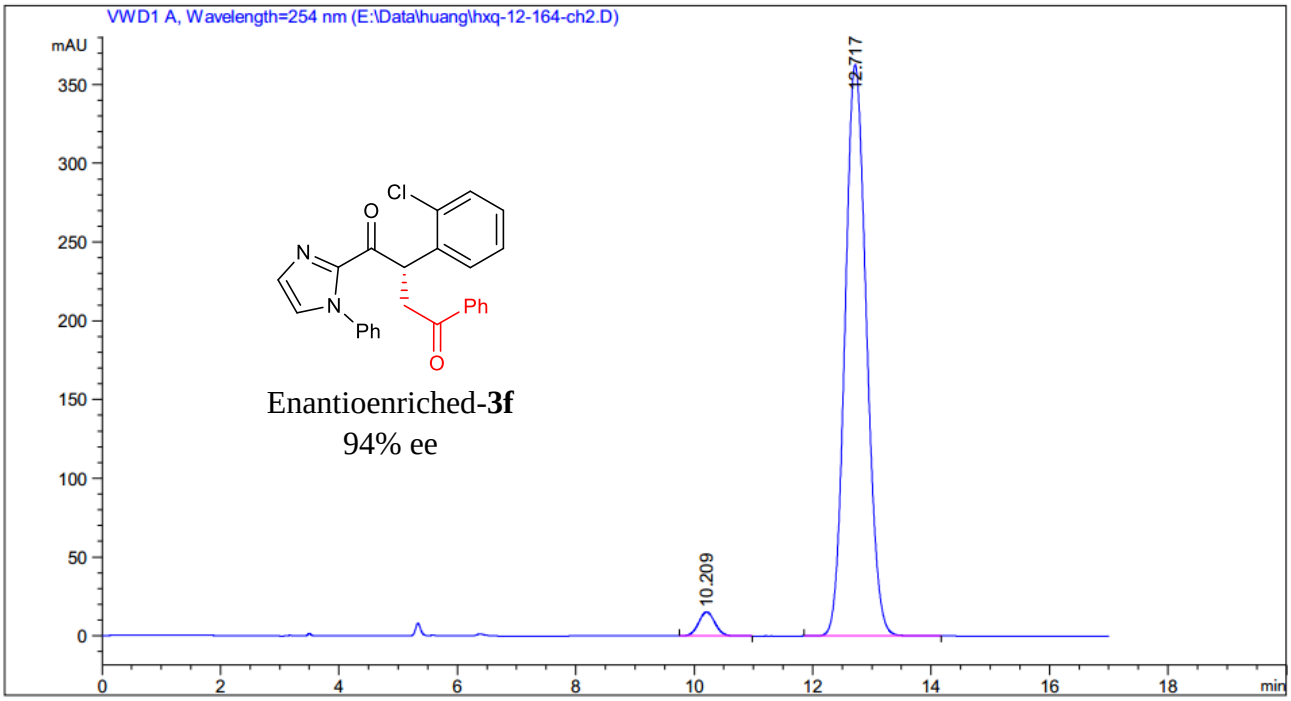


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.037	BB	0.3790	209.22957	8.62624	2.0224
2	14.887	BB	0.4881	1.01365e4	324.82401	97.9776

Supplementary Figure 5. HPLC traces of *rac*-**3e** (reference) and enantioenriched-**3e**.

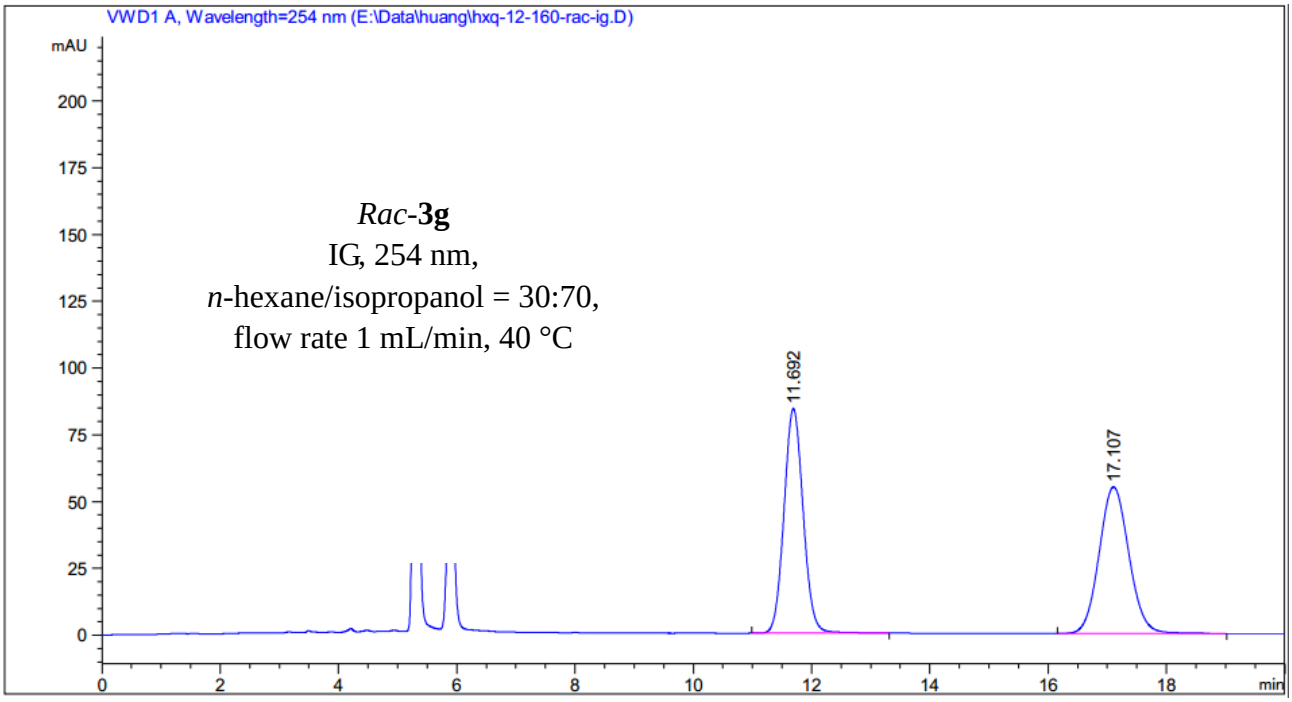


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.307	BB	0.2616	2925.74561	174.54456	49.8989
2	11.499	BB	0.3422	2937.59839	134.30977	50.1011

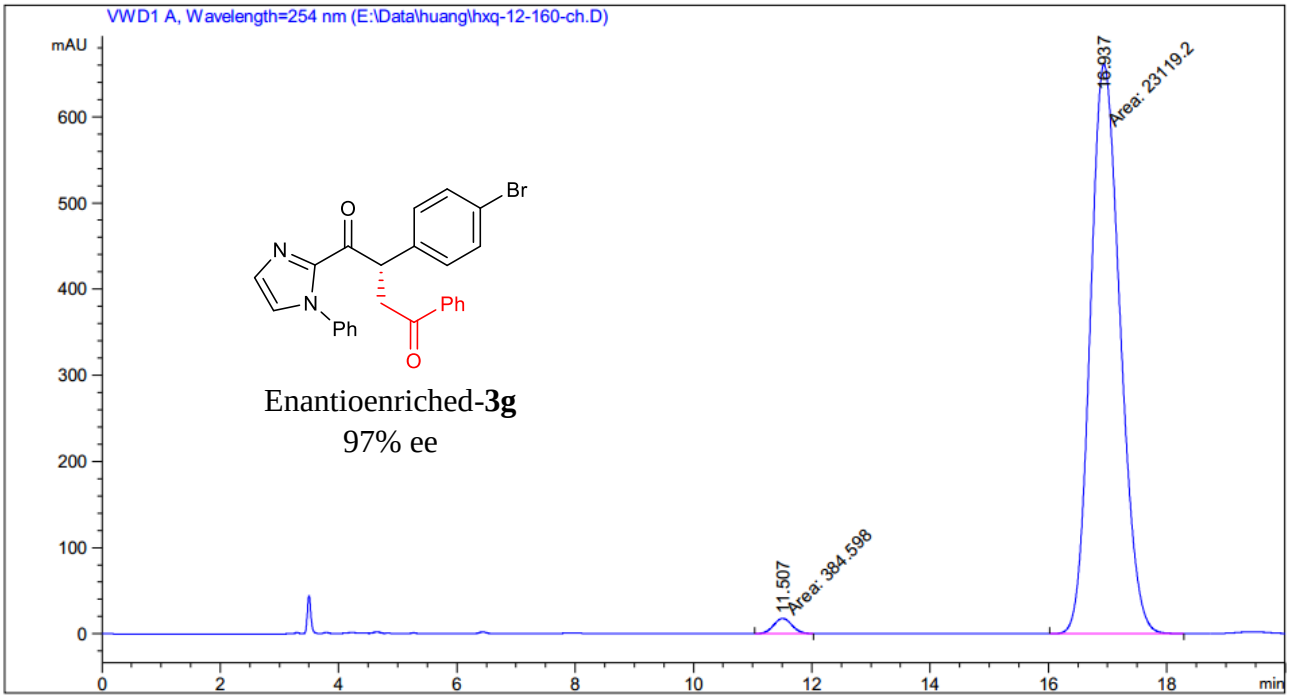


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.209	BB	0.2982	290.10883	15.16438	3.0923
2	12.717	BB	0.3905	9091.58691	362.67413	96.9077

Supplementary Figure 6. HPLC traces of *rac*-**3f** (reference) and enantioenriched-**3f**.

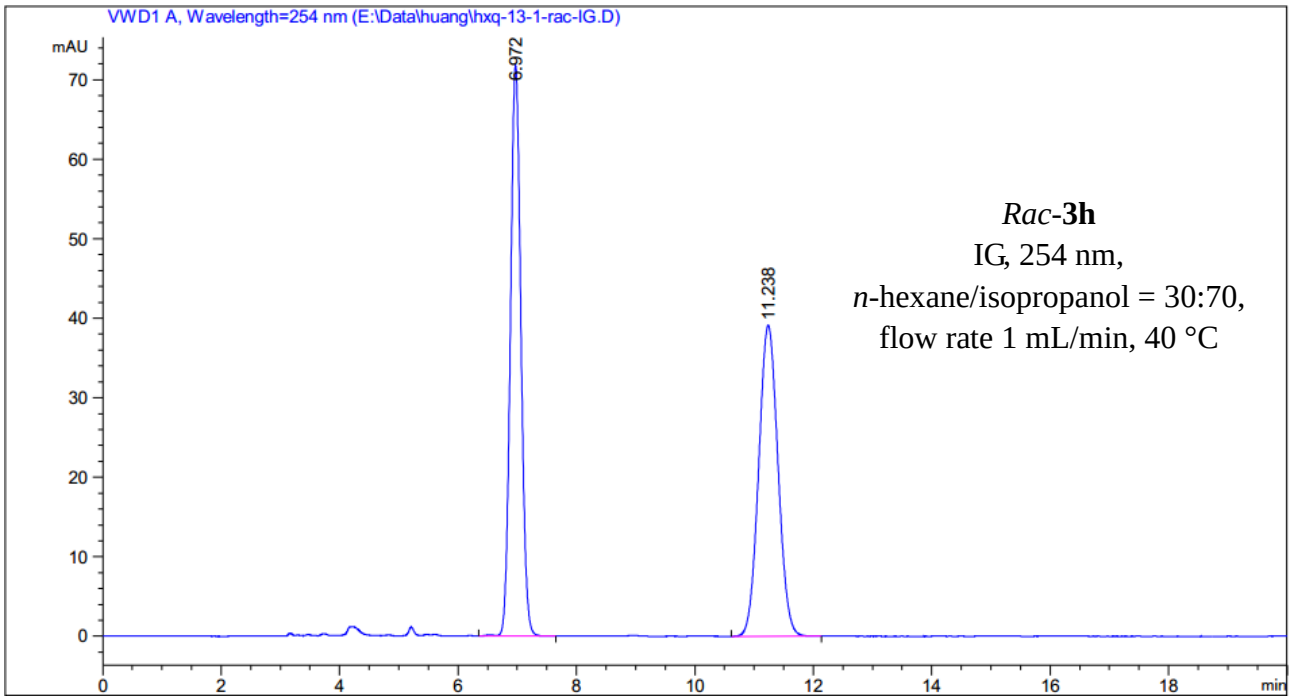


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.692	BB	0.3496	1892.98145	84.09090	49.7277
2	17.107	BB	0.5419	1913.70984	54.87036	50.2723

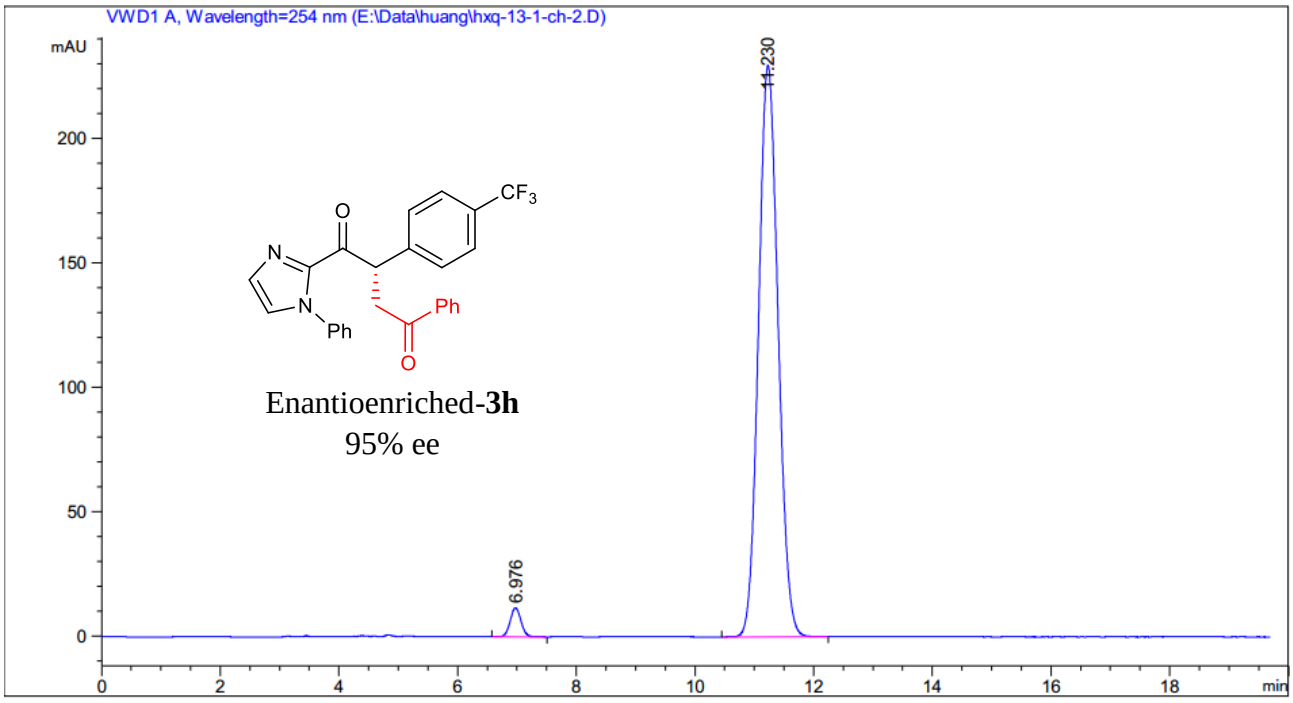


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.507	MM	0.3610	384.59750	17.75468	1.6363
2	16.937	MM	0.5830	2.31192e4	660.91022	98.3637

Supplementary Figure 7. HPLC traces of *rac*-**3g** (reference) and enantioenriched-**3g**.

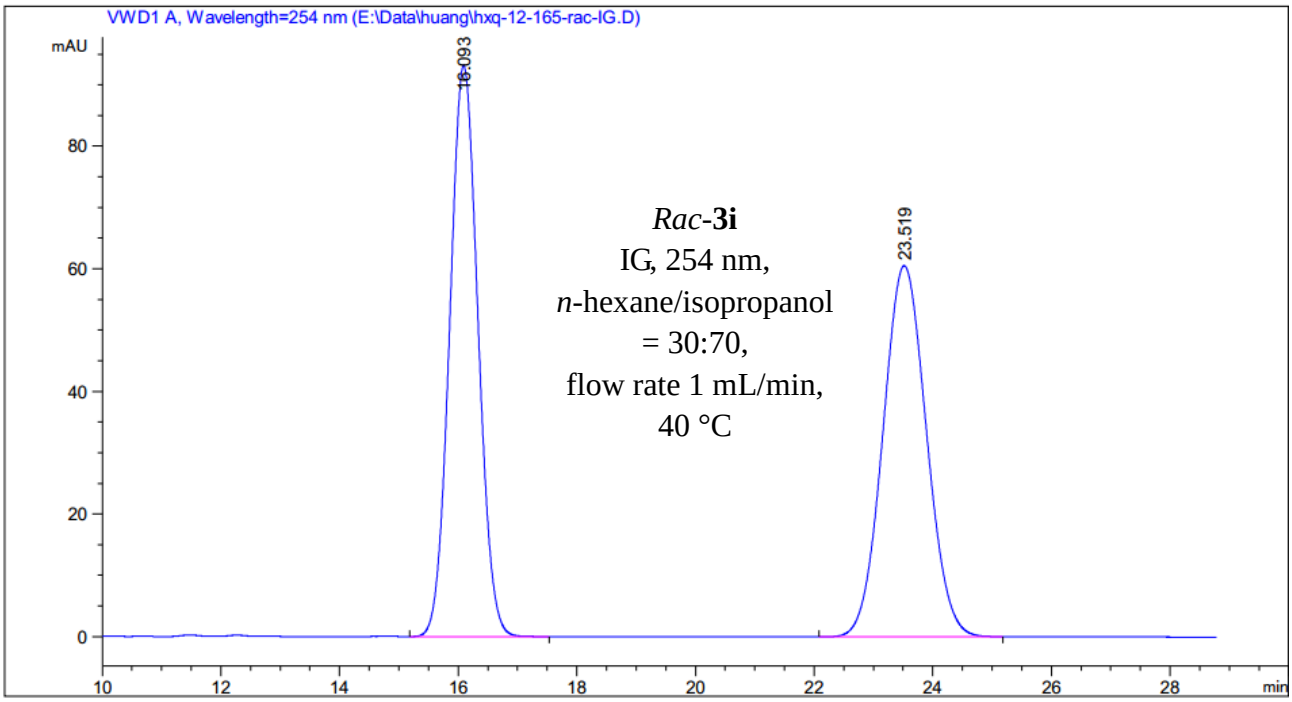


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.972	VB R	0.1919	885.33124	71.78307	50.0408
2	11.238	BB	0.3538	883.88928	39.09276	49.9592

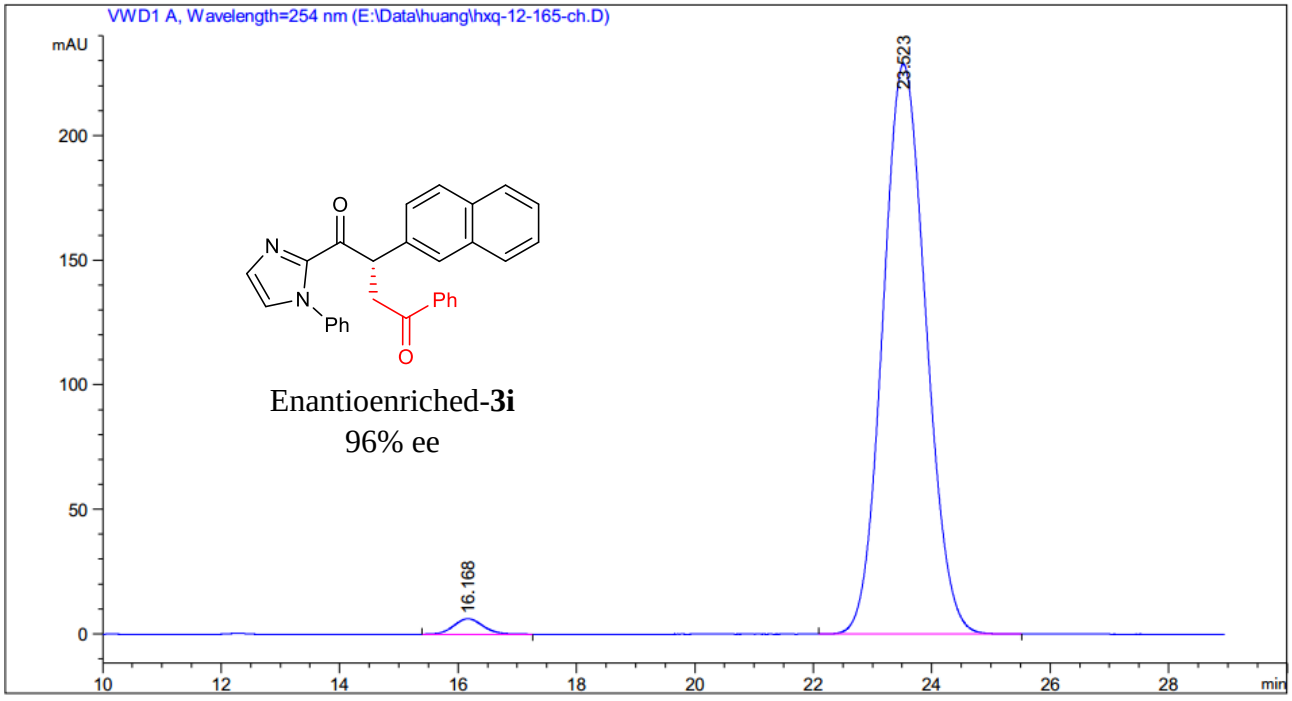


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.976	BB	0.1961	147.38928	11.68661	2.7232
2	11.230	BB	0.3576	5264.91992	229.56715	97.2768

Supplementary Figure 8. HPLC traces of *rac*-**3h** (reference) and enantioenriched-**3h**.

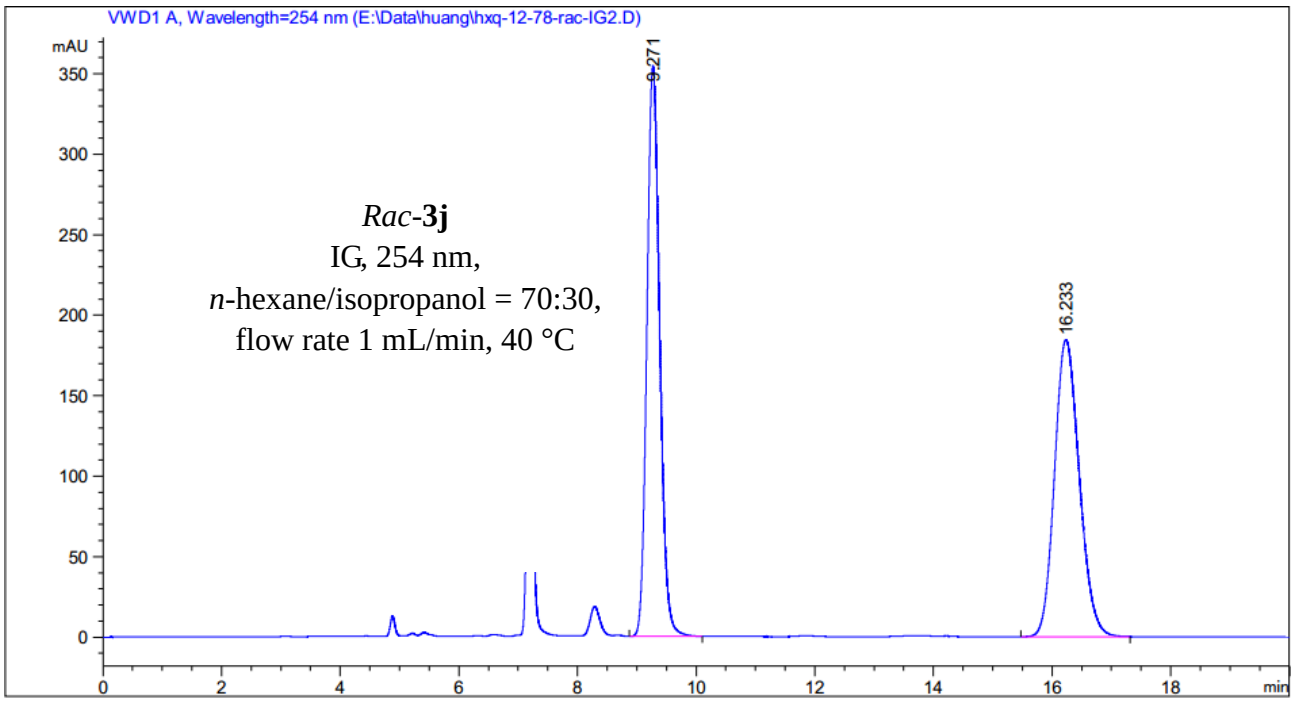


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.093	BB	0.5158	3080.71655	93.17243	50.0113
2	23.519	BB	0.7914	3079.32813	60.53876	49.9887

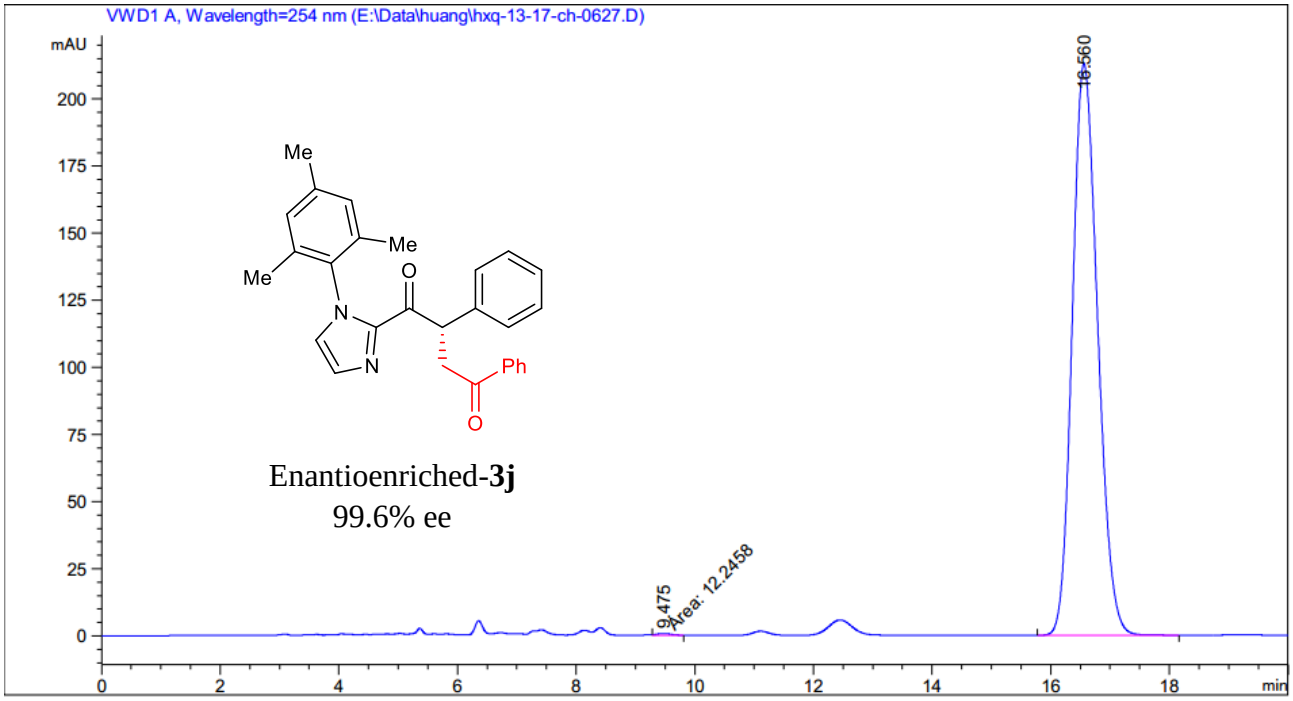


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.168	BB	0.5245	211.31277	6.20129	1.7919
2	23.523	BB	0.7915	1.15811e4	228.82693	98.2081

Supplementary Figure 9. HPLC traces of *rac*-**3i** (reference) and enantioenriched-**3i**.

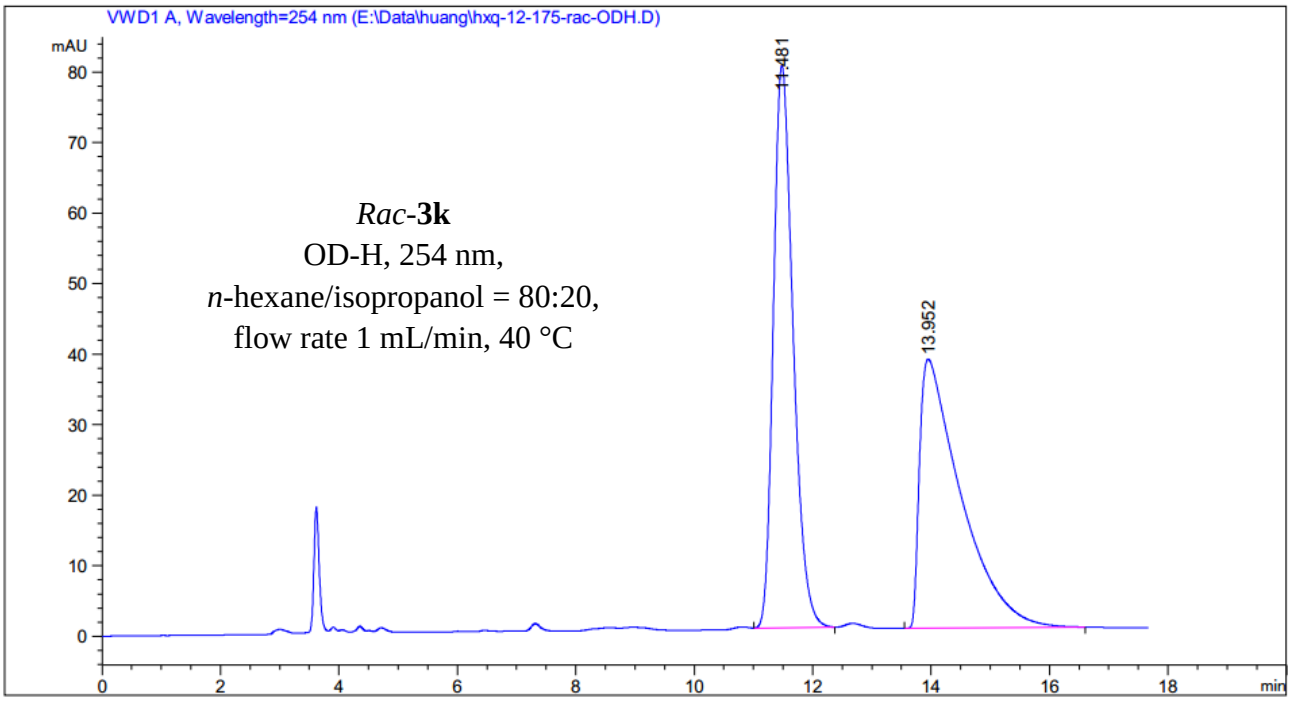


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.271	BB	0.2299	5299.51465	354.46133	49.8135
2	16.233	VV R	0.4063	5339.19385	184.37718	50.1865

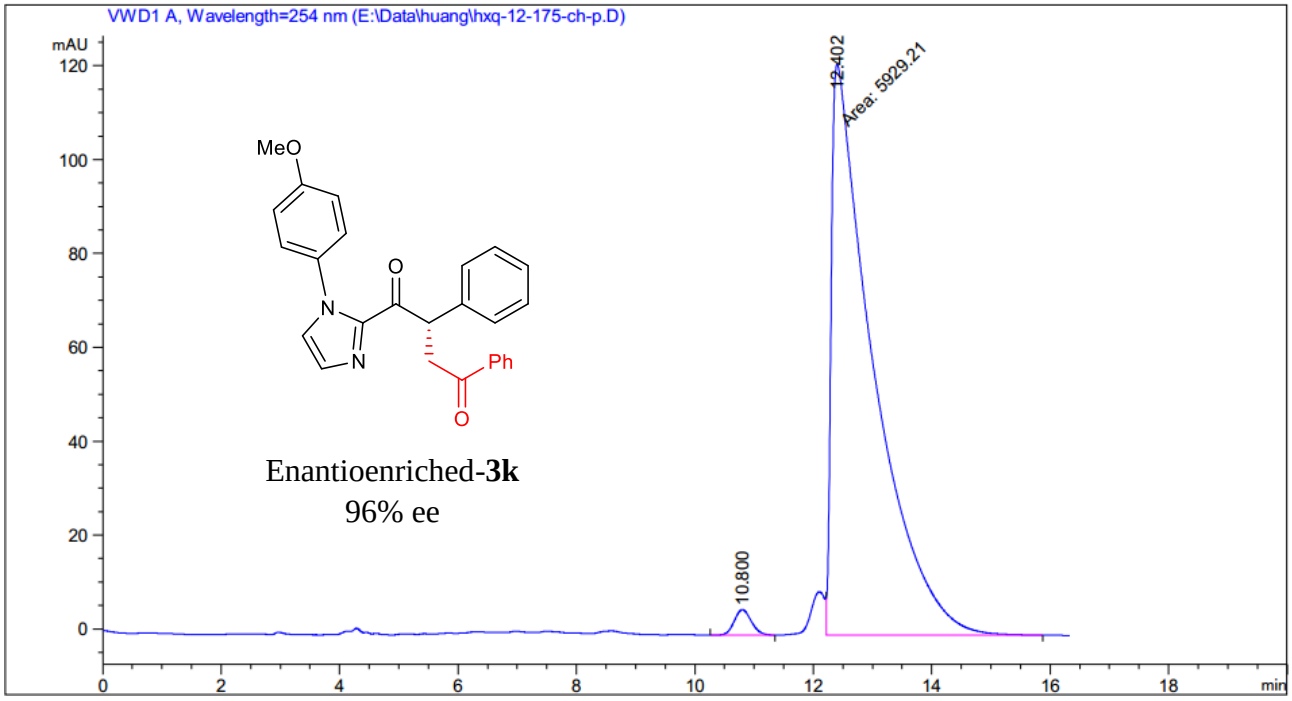


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.475	MM	0.2863	12.24577	7.12835e-1	0.1935
2	16.560	BB	0.4620	6314.89551	212.91115	99.8065

Supplementary Figure 10. HPLC traces of *rac*-**3j** (reference) and enantioenriched-**3j**.



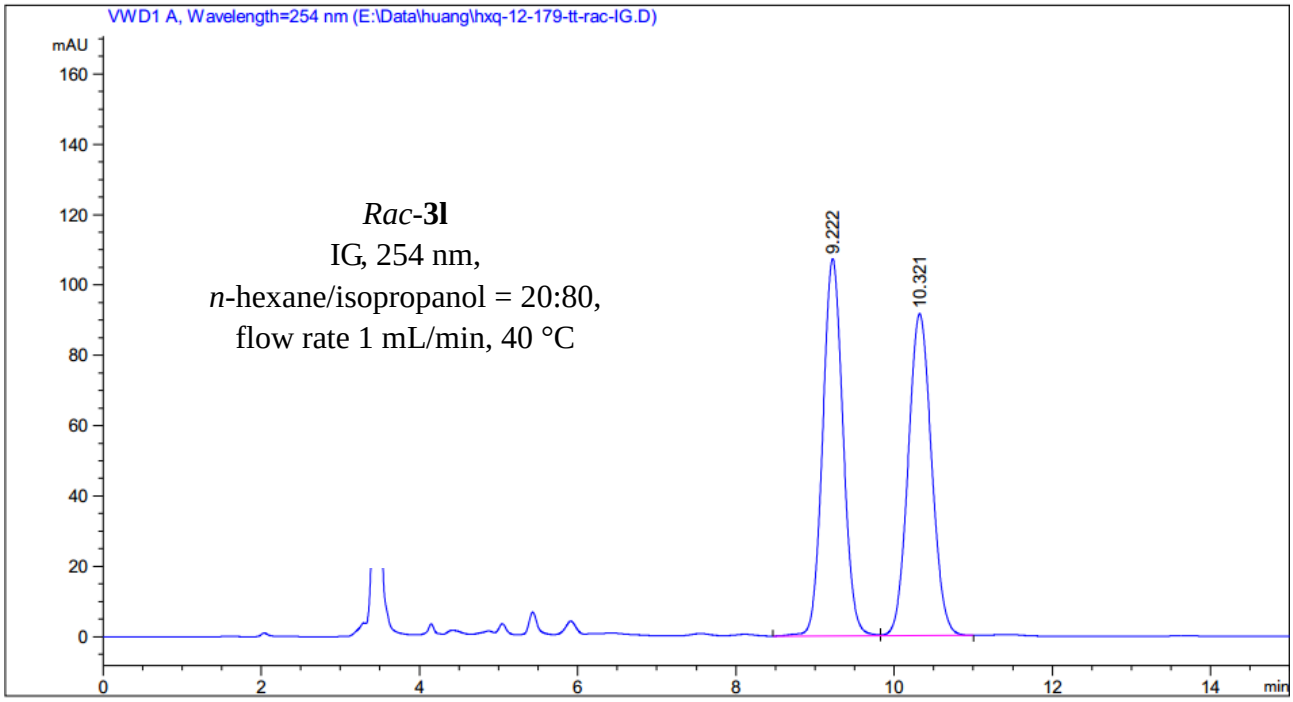
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.481	BB	0.3557	1843.23499	79.74136	49.9731
2	13.952	BB	0.6821	1845.21582	38.16596	50.0269



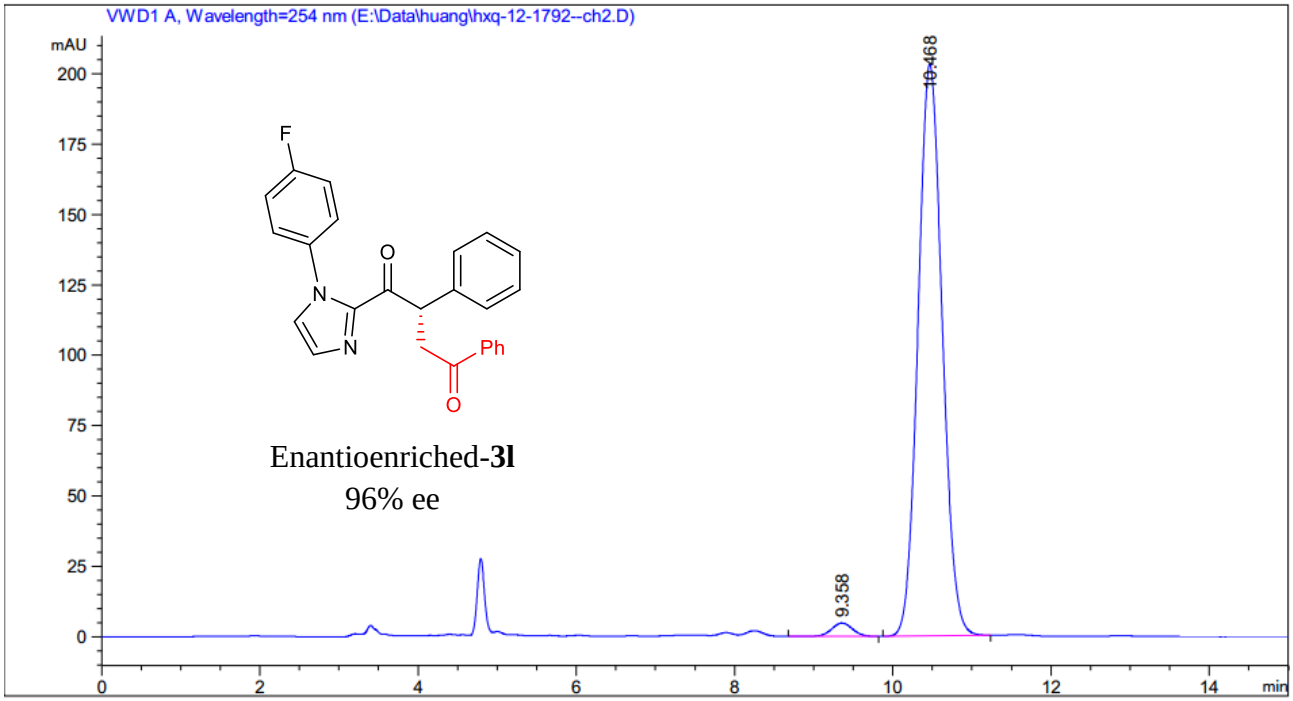
Enantioenriched-**3k**
96% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.800	BB	0.3104	108.97310	5.42469	1.8047
2	12.402	FM	0.8121	5929.21484	121.68423	98.1953

Supplementary Figure 11. HPLC traces of *rac*-**3k** (reference) and enantioenriched-**3k**.

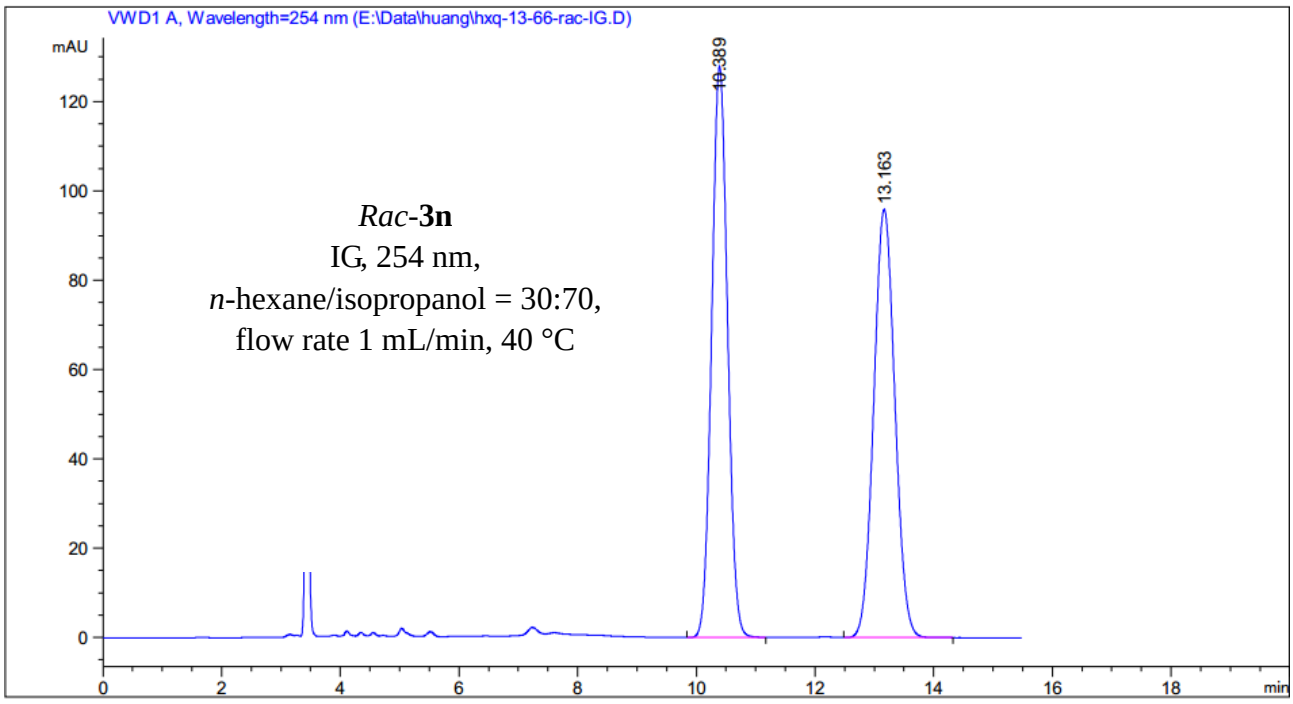


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.222	BV	0.2766	1908.91101	107.27916	50.4581
2	10.321	VB	0.3198	1874.25195	91.58553	49.5419

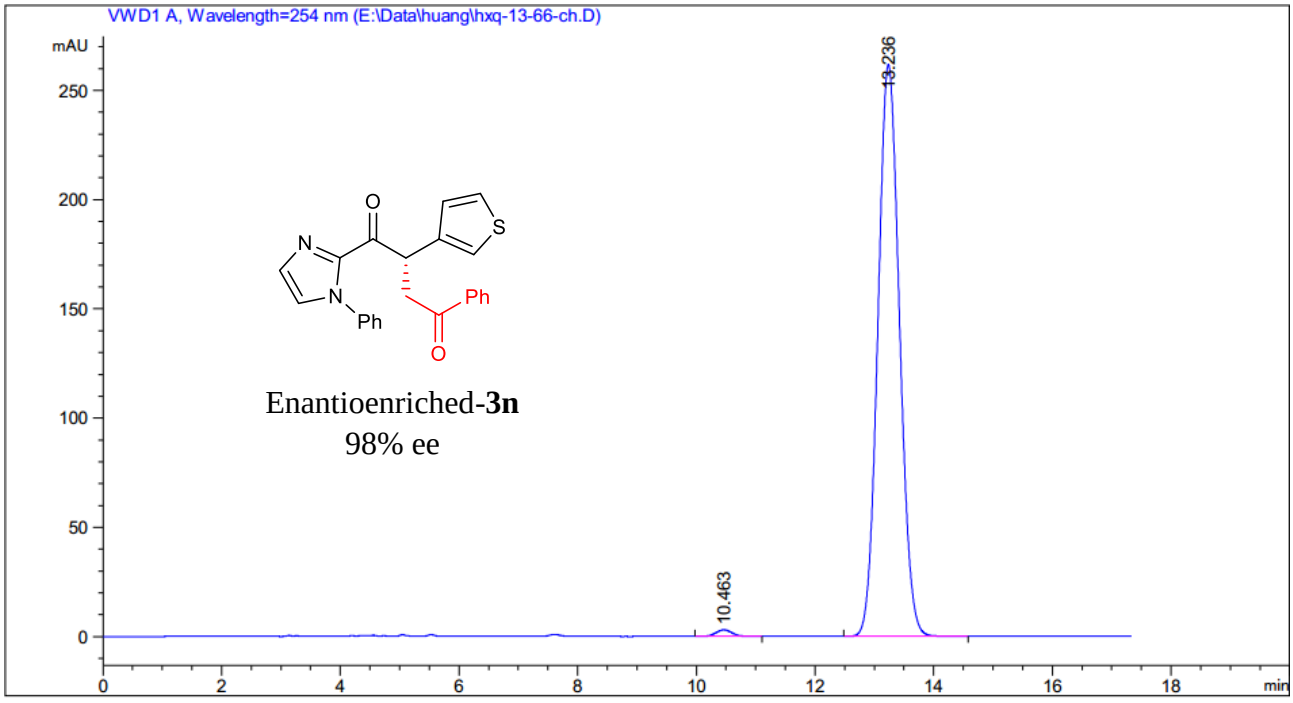


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.358	BB	0.2879	87.36749	4.74388	1.9893
2	10.468	BB	0.3313	4304.56689	203.08650	98.0107

Supplementary Figure 12. HPLC traces of *rac*-**3l** (reference) and enantioenriched-**3l**.

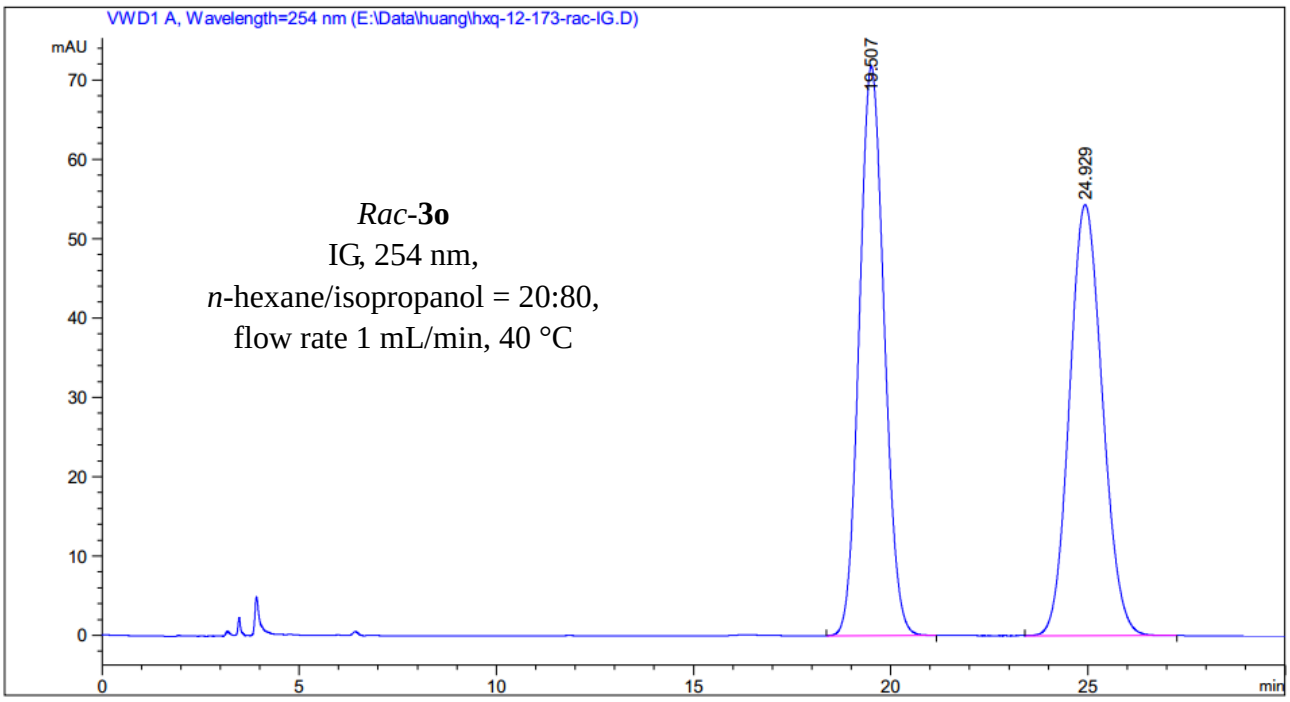


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.389	BB	0.2896	2375.70068	127.94215	50.0202
2	13.163	BB	0.3868	2373.78516	95.89053	49.9798



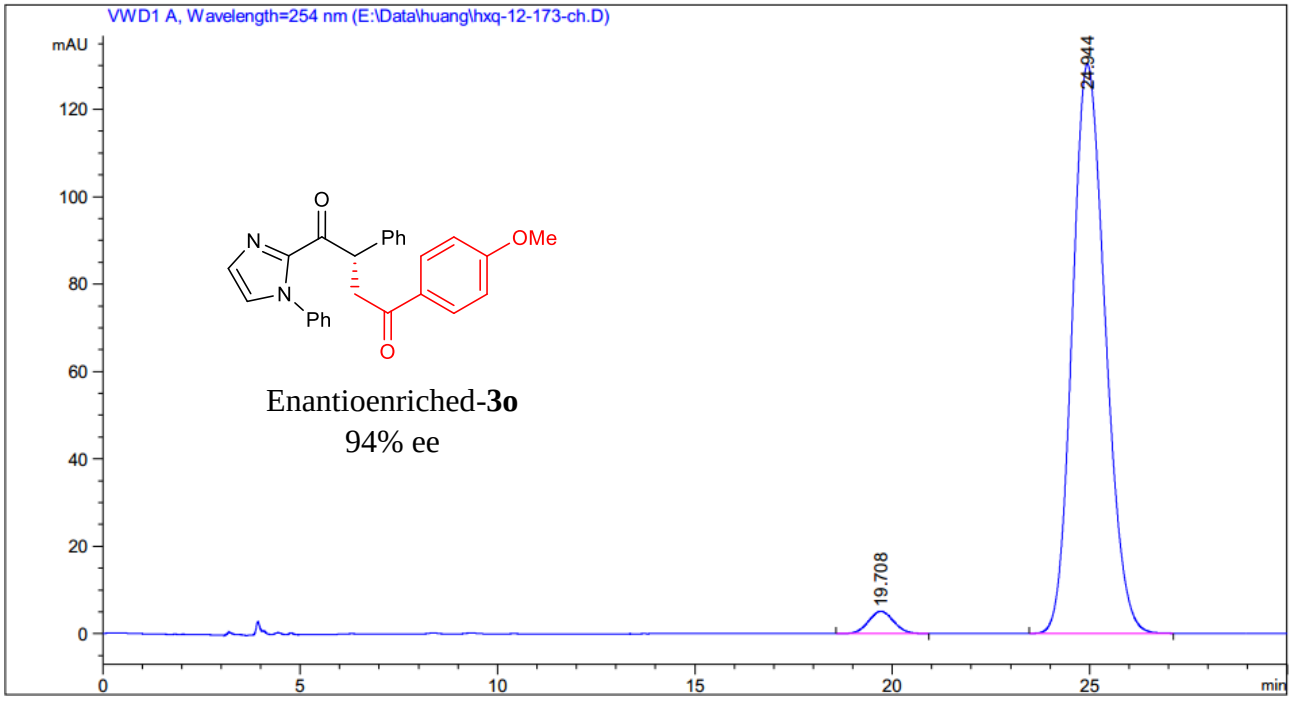
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.463	BB	0.2946	57.39555	3.00858	0.8615
2	13.236	BB	0.3945	6604.83984	261.69019	99.1385

Supplementary Figure 13. HPLC traces of *rac*-**3n** (reference) and enantioenriched-**3n**.



Rac-**3o**
IG, 254 nm,
n-hexane/isopropanol = 20:80,
flow rate 1 mL/min, 40 °C

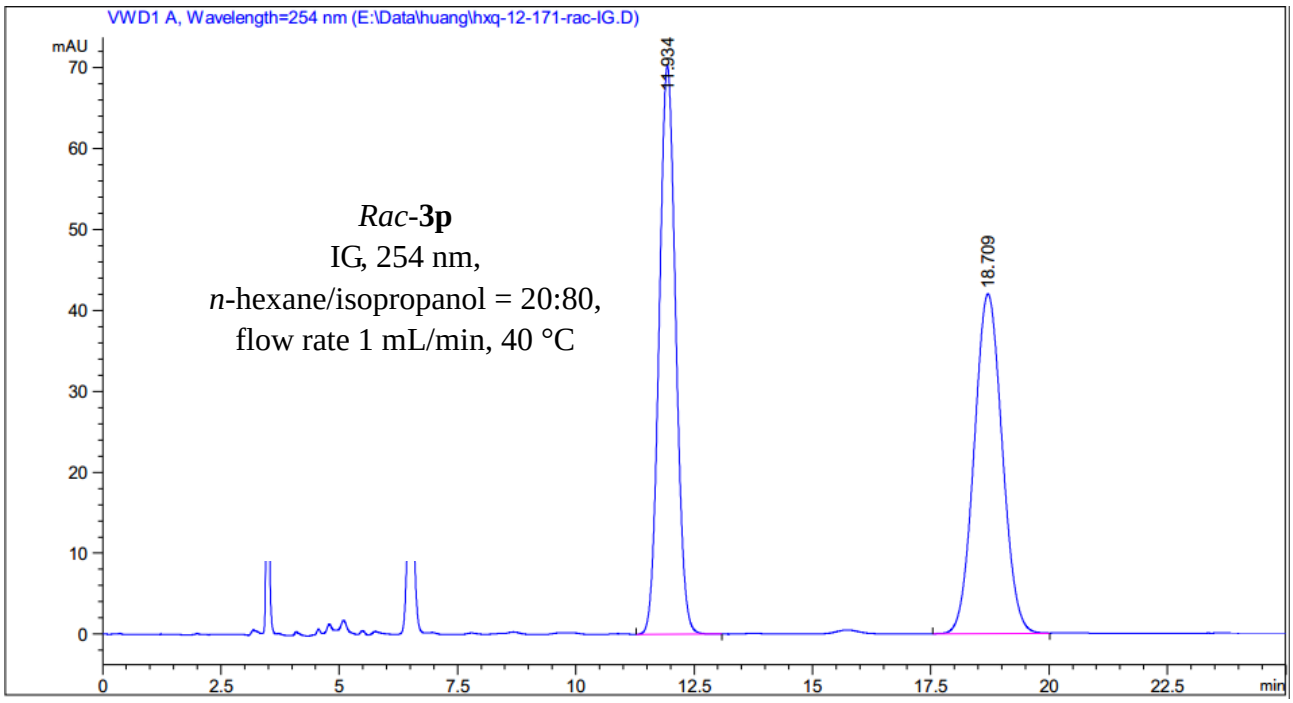
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.507	BB	0.6861	3150.26343	71.76696	49.9433
2	24.929	BB	0.9010	3157.41064	54.33148	50.0567



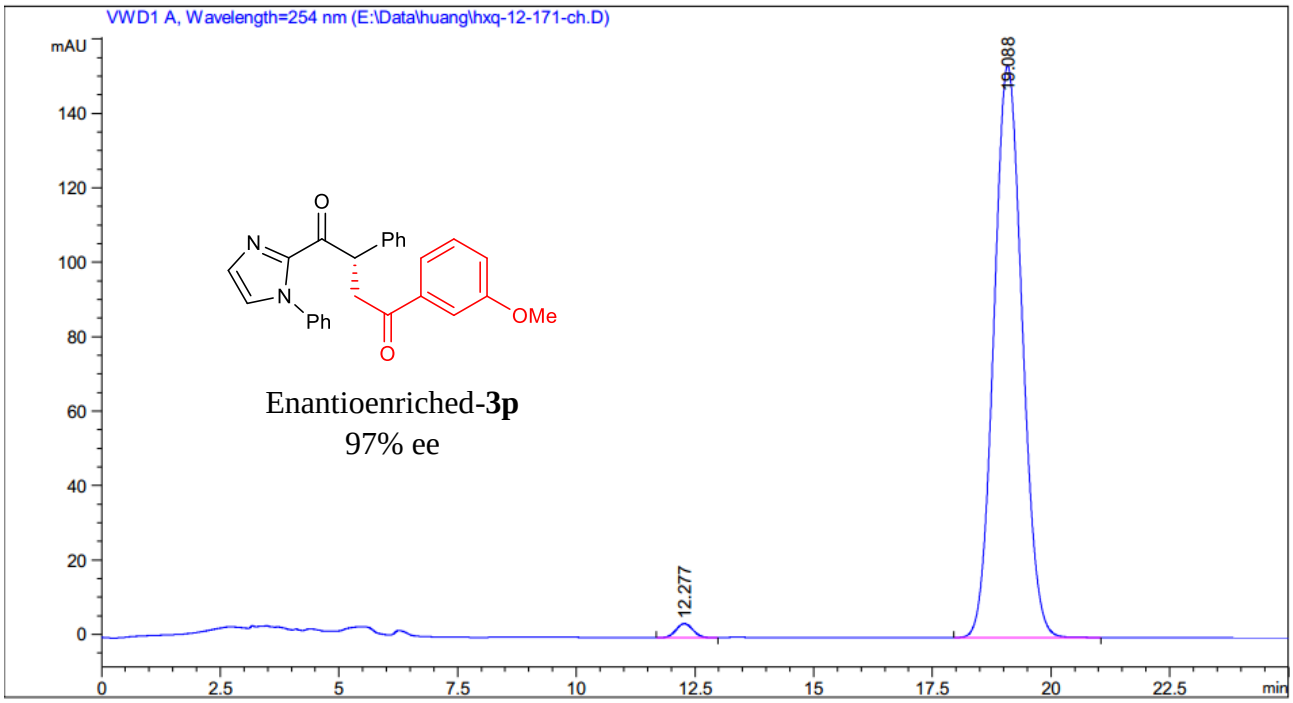
Enantioenriched-**3o**
94% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.708	BB	0.6653	224.81873	5.09032	2.8921
2	24.944	BB	0.9009	7548.76514	130.29802	97.1079

Supplementary Figure 14. HPLC traces of *rac*-**3o** (reference) and enantioenriched-**3o**.

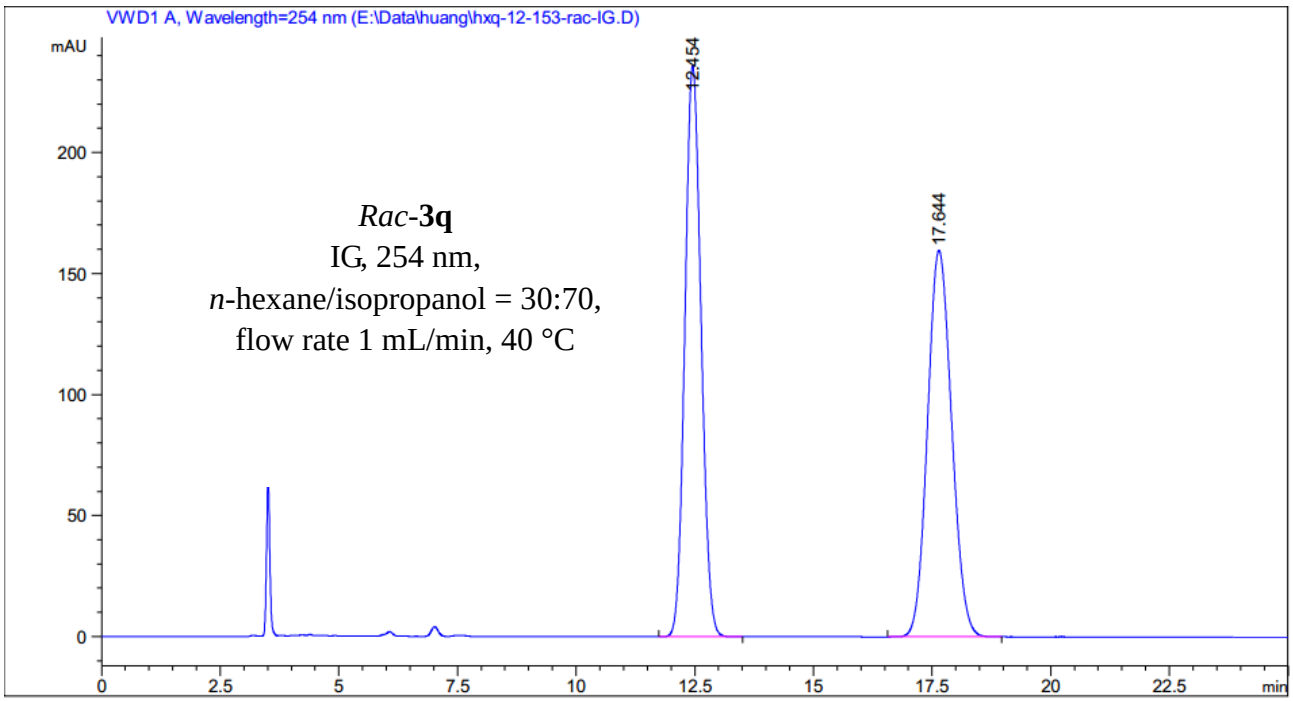


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.934	BB	0.3797	1708.61206	70.25853	49.7827
2	18.709	BB	0.6404	1723.52734	41.94240	50.2173

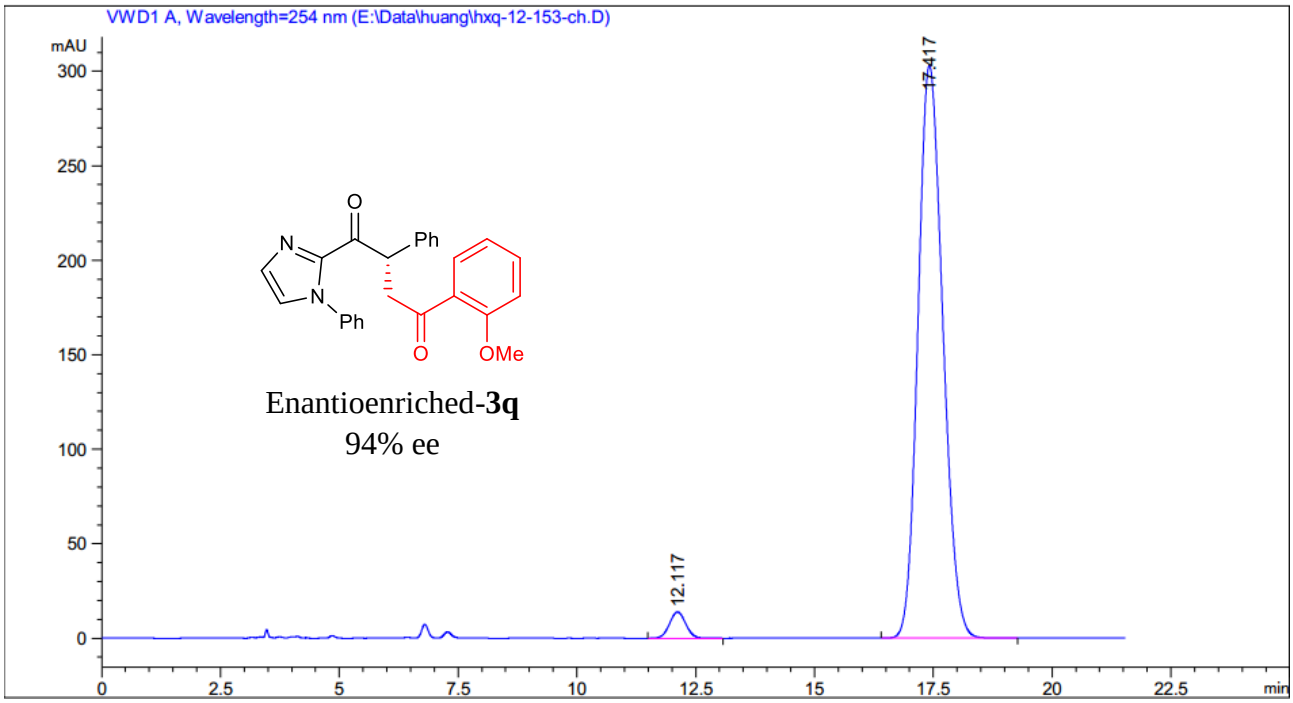


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.277	BB	0.3873	94.21791	3.79970	1.4594
2	19.088	BB	0.6468	6361.88525	153.73997	98.5406

Supplementary Figure 15. HPLC traces of *rac*-**3p** (reference) and enantioenriched-**3p**.

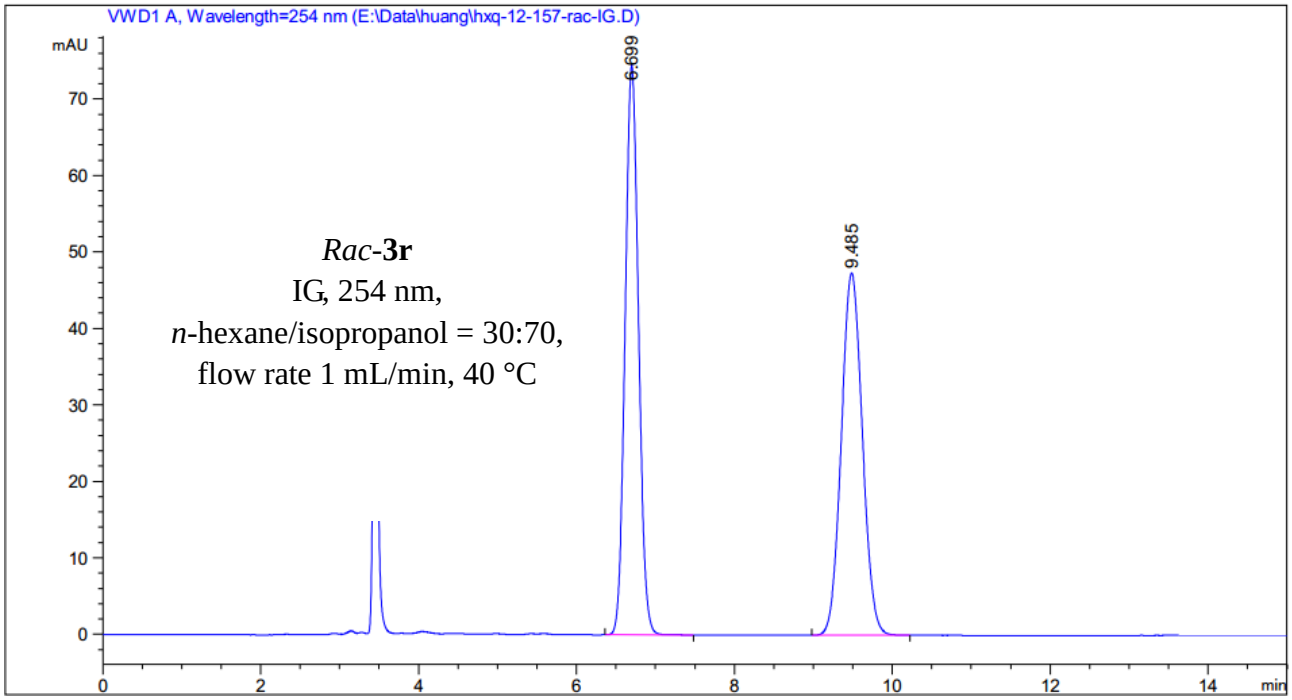


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.454	BB	0.3688	5579.61084	236.01292	49.7160
2	17.644	BB	0.5523	5643.36475	159.67236	50.2840

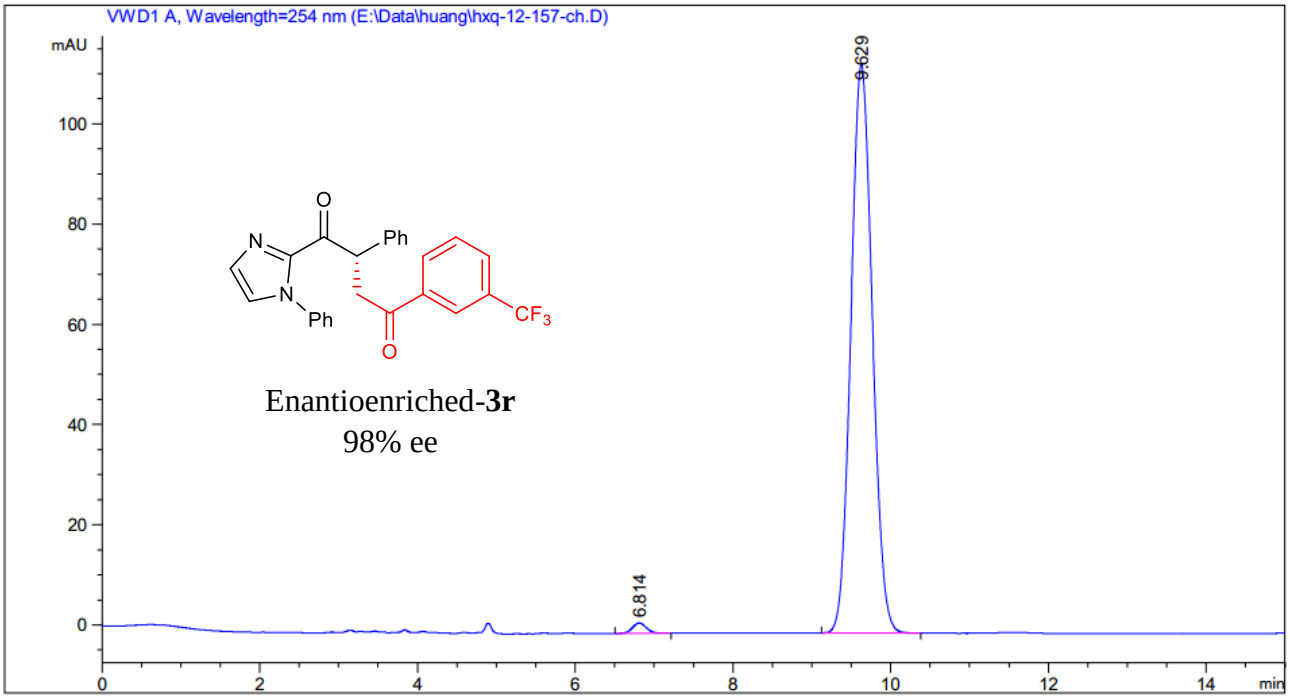


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.117	BB	0.3691	329.77875	13.93288	2.9127
2	17.417	BB	0.5651	1.09921e4	303.08109	97.0873

Supplementary Figure 16. HPLC traces of *rac*-**3q** (reference) and enantioenriched-**3q**.

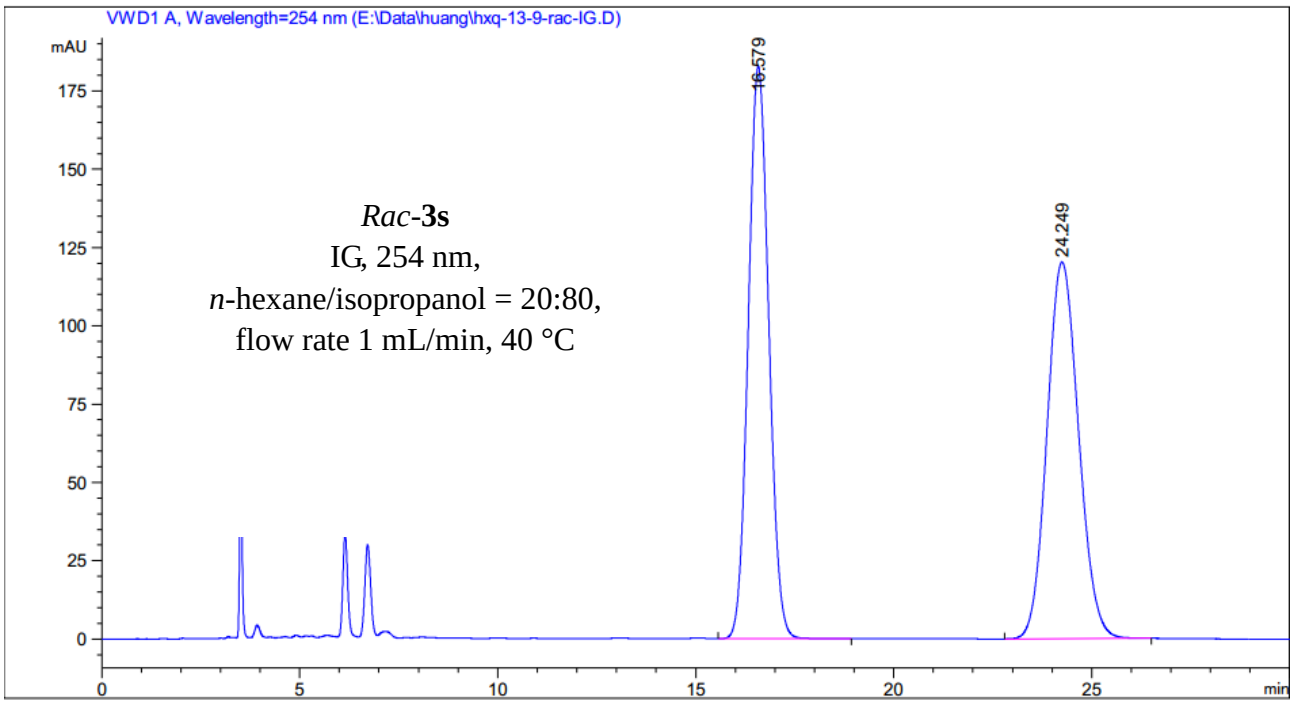


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.699	BB	0.1831	876.87476	74.61463	50.0041
2	9.485	BB	0.2889	876.73193	47.37683	49.9959

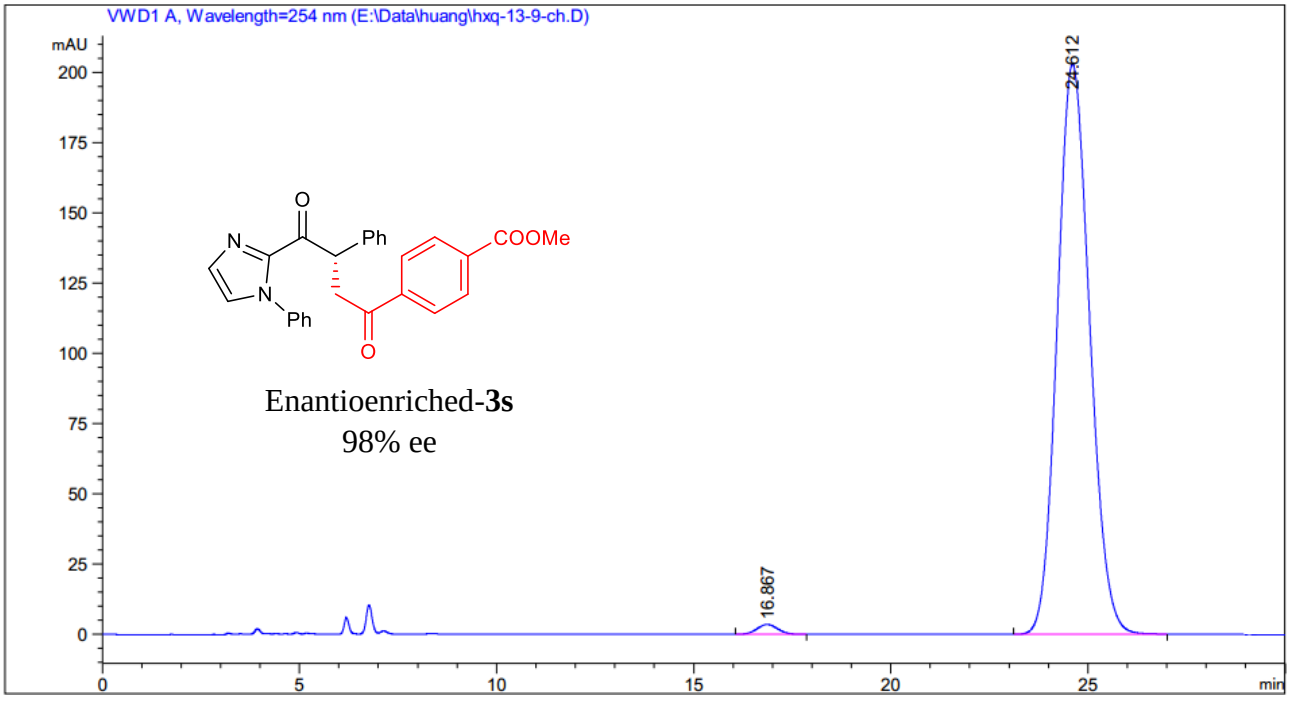


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.814	BB	0.1888	25.08927	2.06437	1.1605
2	9.629	BB	0.2936	2136.93408	113.50898	98.8395

Supplementary Figure 17. HPLC traces of *rac*-**3r** (reference) and enantioenriched-**3r**.

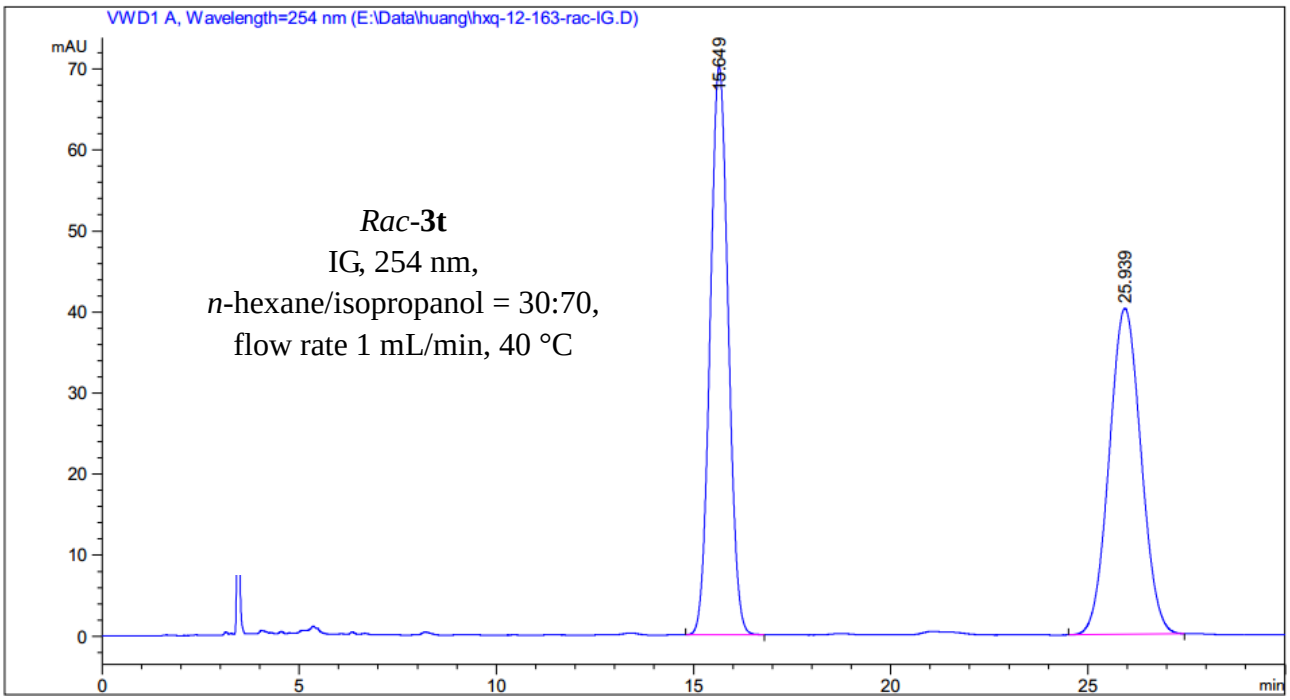


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.579	BB	0.5603	6571.14160	182.83629	49.6248
2	24.249	BB	0.8658	6670.51074	120.31028	50.3752

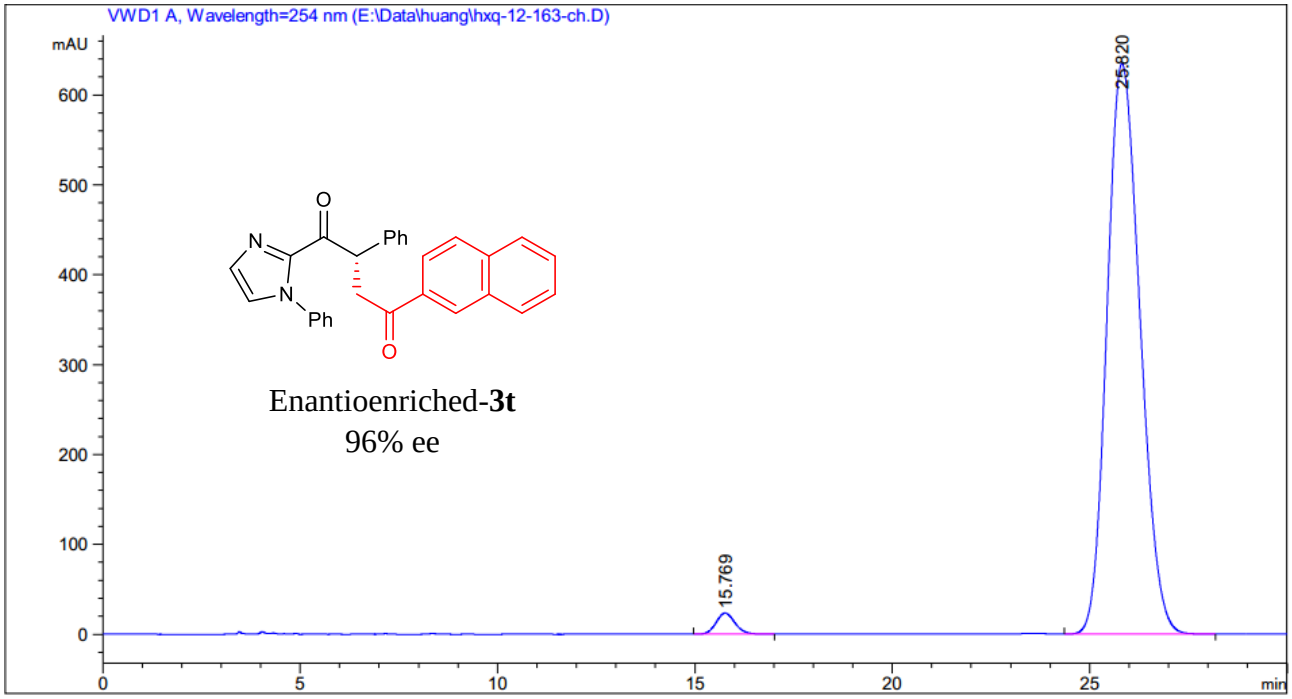


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.867	BB	0.5616	129.66222	3.52916	1.1058
2	24.612	BB	0.8892	1.15963e4	203.07747	98.8942

Supplementary Figure 18. HPLC traces of *rac*-**3s** (reference) and enantioenriched-**3s**.

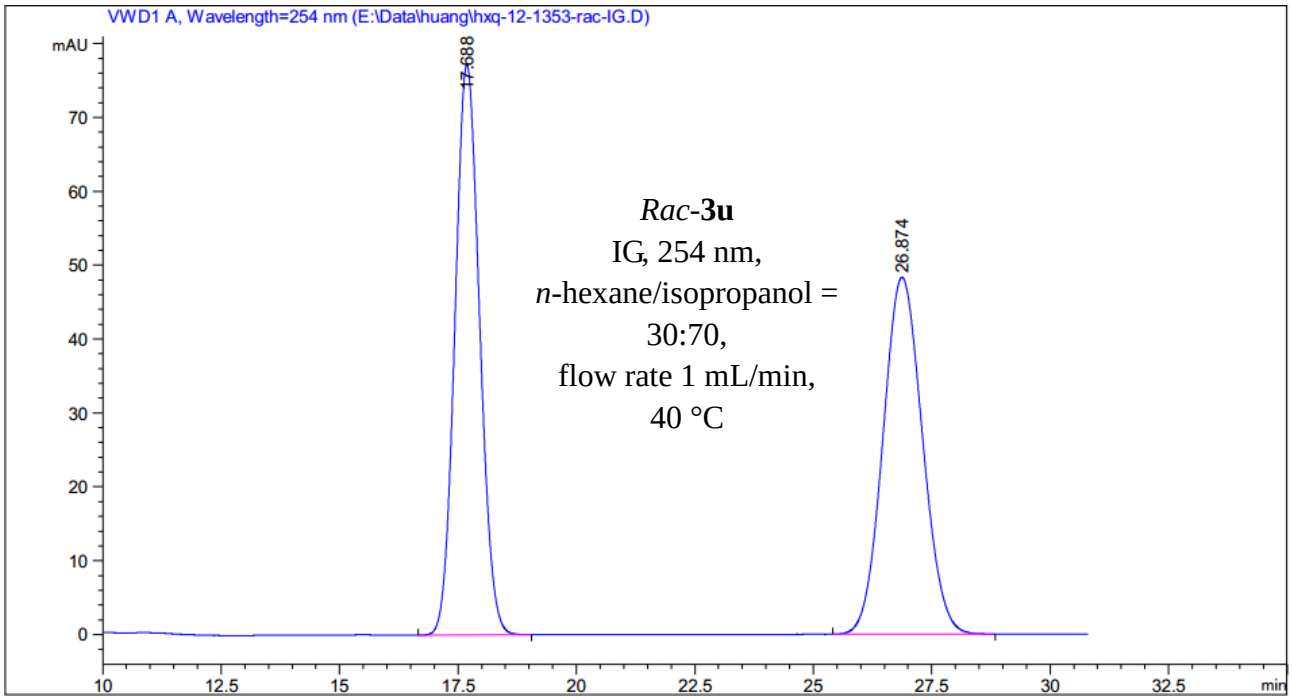


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.649	BB	0.4978	2236.86353	70.19579	49.8292
2	25.939	BB	0.8721	2252.19775	40.23509	50.1708

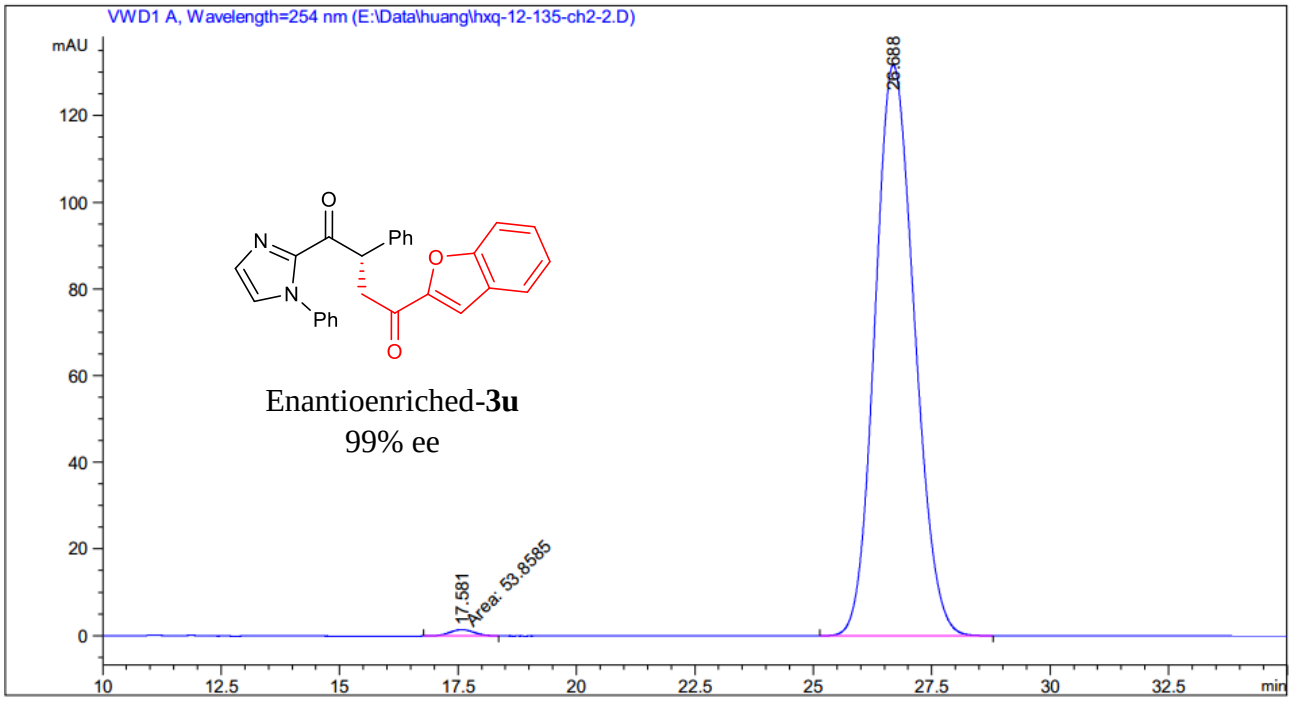


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.769	BB	0.5165	783.40588	23.52313	2.0795
2	25.820	BB	0.9120	3.68897e4	634.73431	97.9205

Supplementary Figure 19. HPLC traces of *rac*-**3t** (reference) and enantioenriched-**3t**.

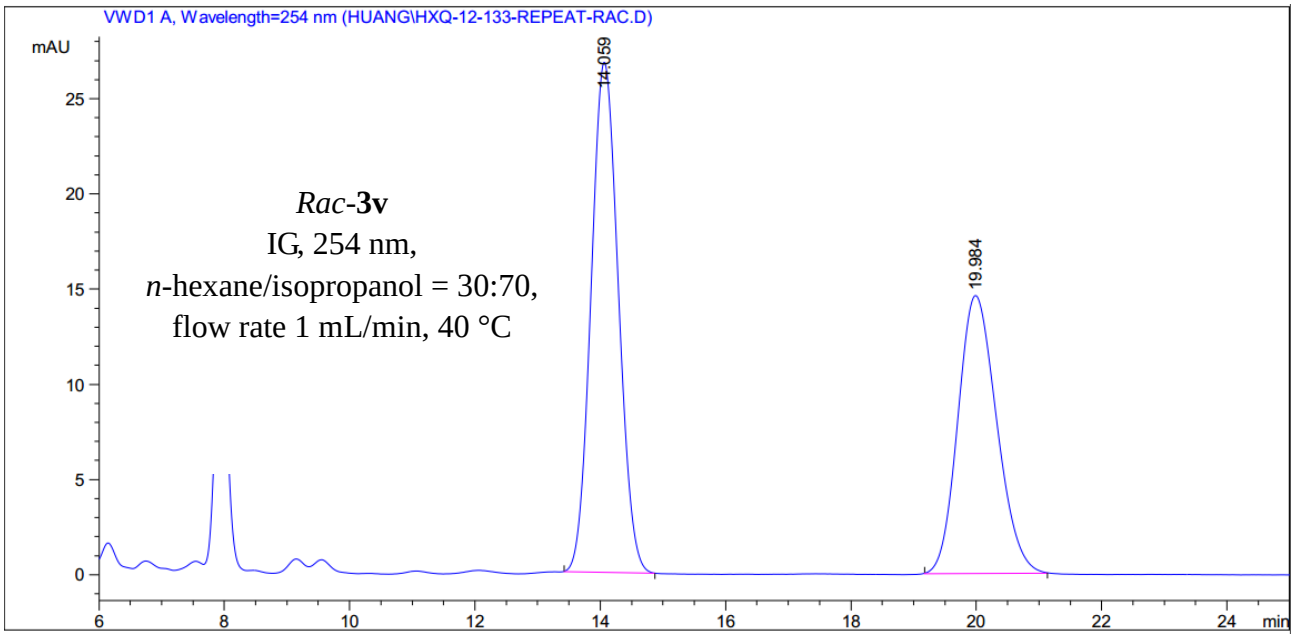


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.688	BB	0.5640	2792.26196	77.20417	49.9808
2	26.874	BB	0.9037	2794.40430	48.32050	50.0192

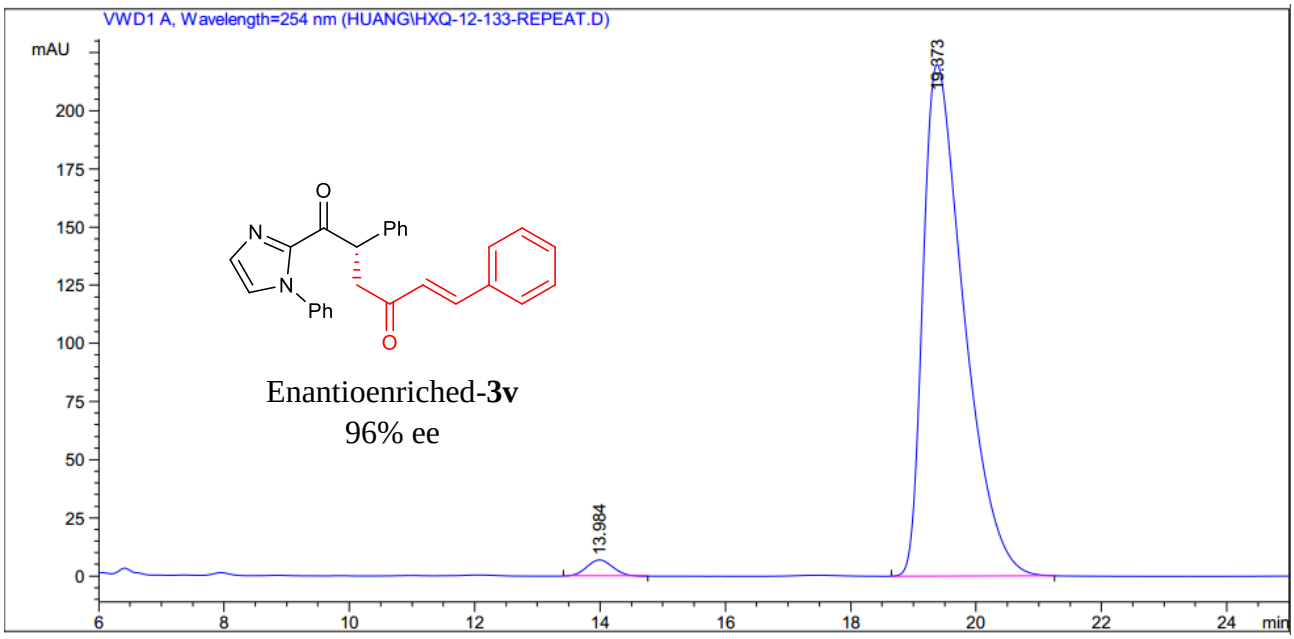


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.581	MM	0.6094	53.85849	1.47298	0.6996
2	26.688	BB	0.9037	7644.19238	131.79387	99.3004

Supplementary Figure 20. HPLC traces of *rac*-**3u** (reference) and enantioenriched-**3u**.

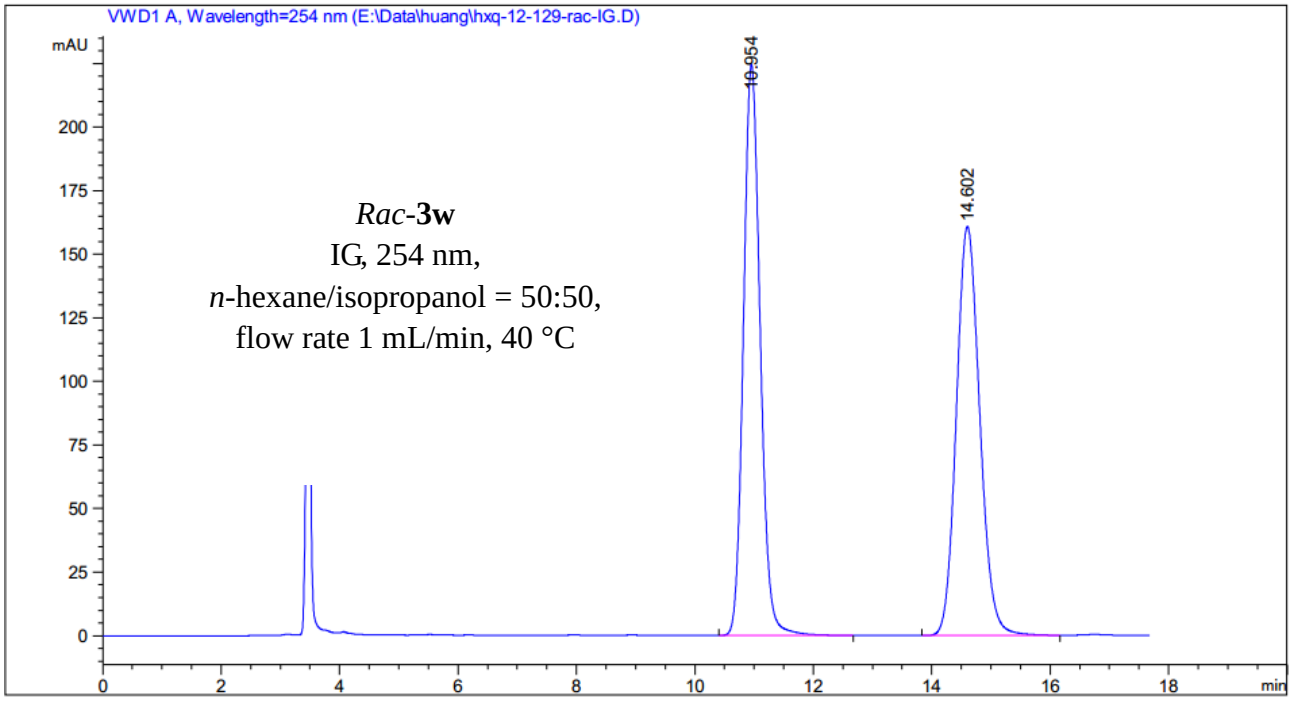


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.059	BB	0.4745	809.24158	26.80564	56.2111
2	19.984	BB	0.6749	630.40479	14.61913	43.7889

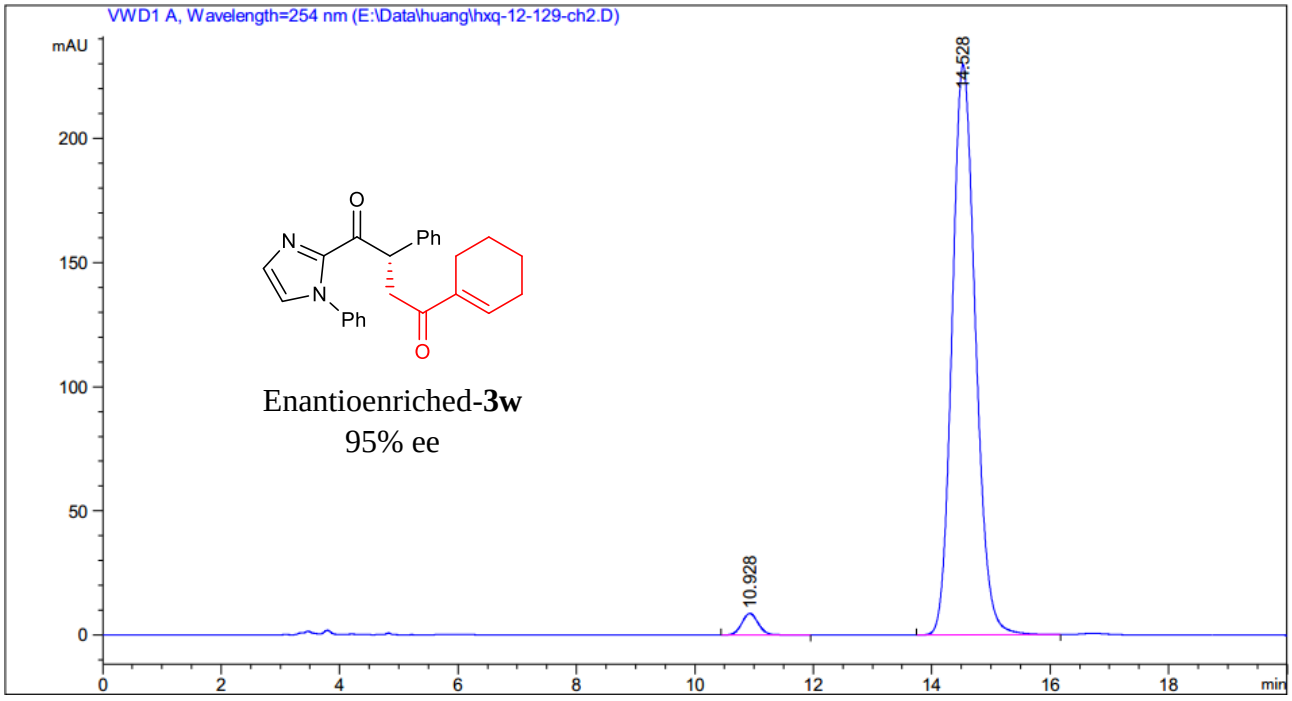


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.984	BB	0.4580	203.13164	6.94013	1.9975
2	19.373	BB	0.6829	9965.96094	219.99080	98.0025

Supplementary Figure 21. HPLC traces of *rac*-**3v** (reference) and enantioenriched-**3v**.

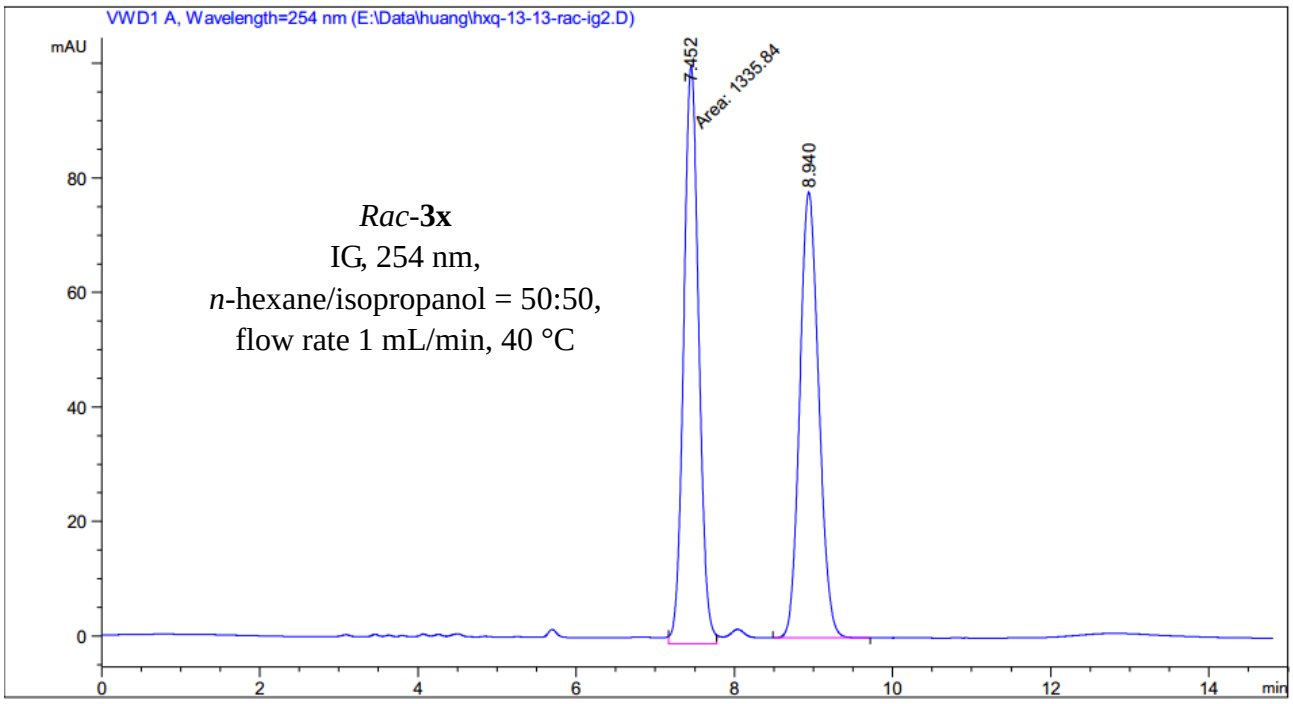


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.954	BB	0.3043	4413.87744	224.54407	49.9817
2	14.602	BB	0.4264	4417.10205	160.81491	50.0183

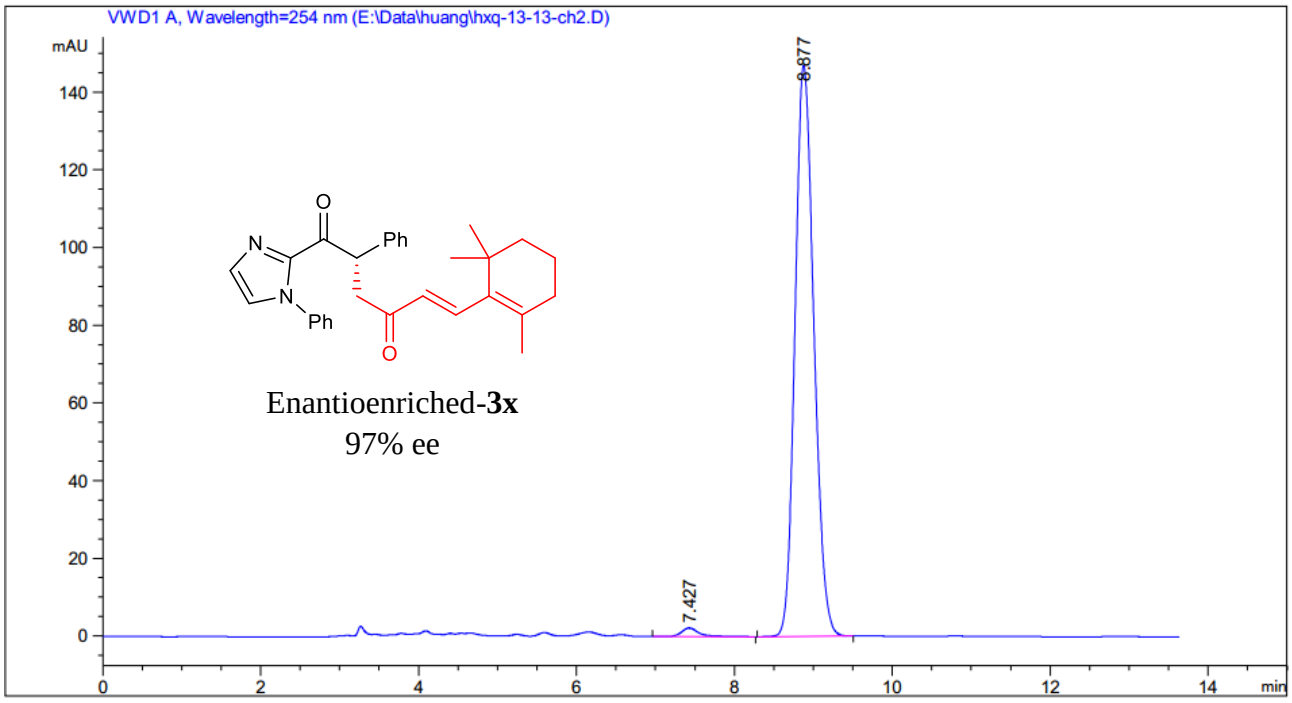


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.928	BB	0.3014	168.44127	8.67943	2.6074
2	14.528	BB	0.4256	6291.58398	229.66879	97.3926

Supplementary Figure 22. HPLC traces of *rac*-**3w** (reference) and enantioenriched-**3w**.

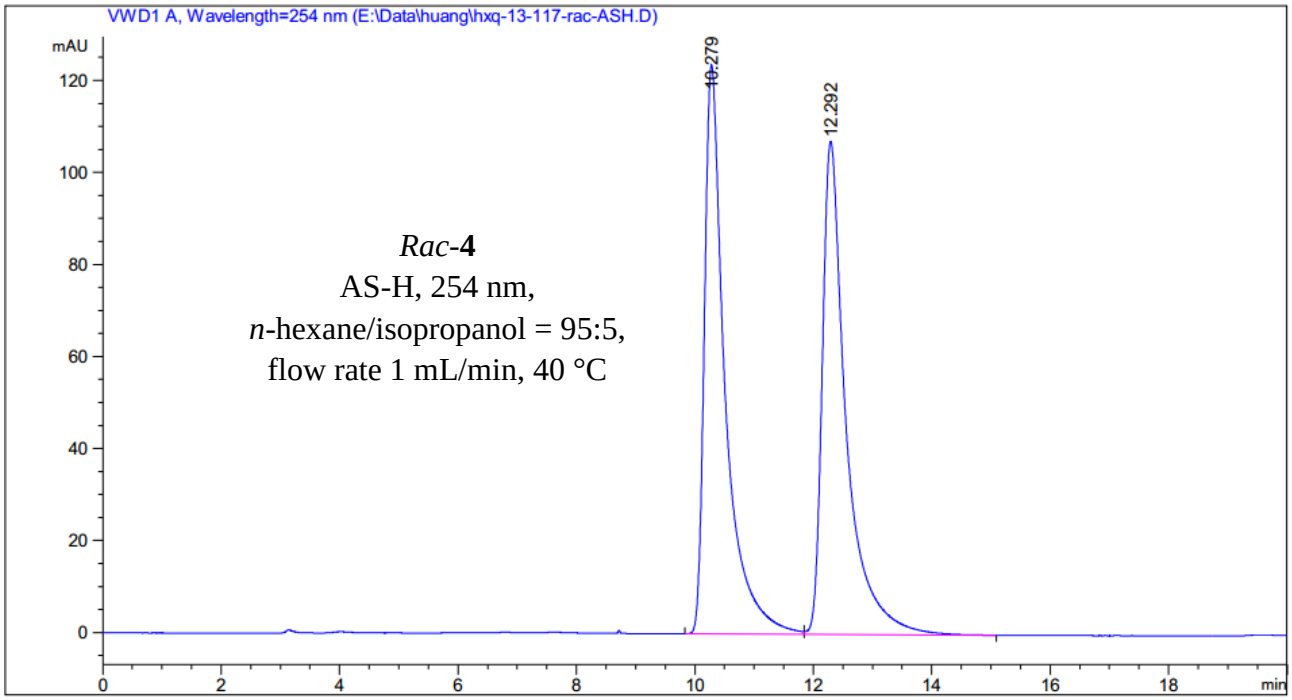


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.452	MM	0.2207	1335.83679	100.89867	50.6923
2	8.940	BB	0.2598	1299.35046	77.82312	49.3077

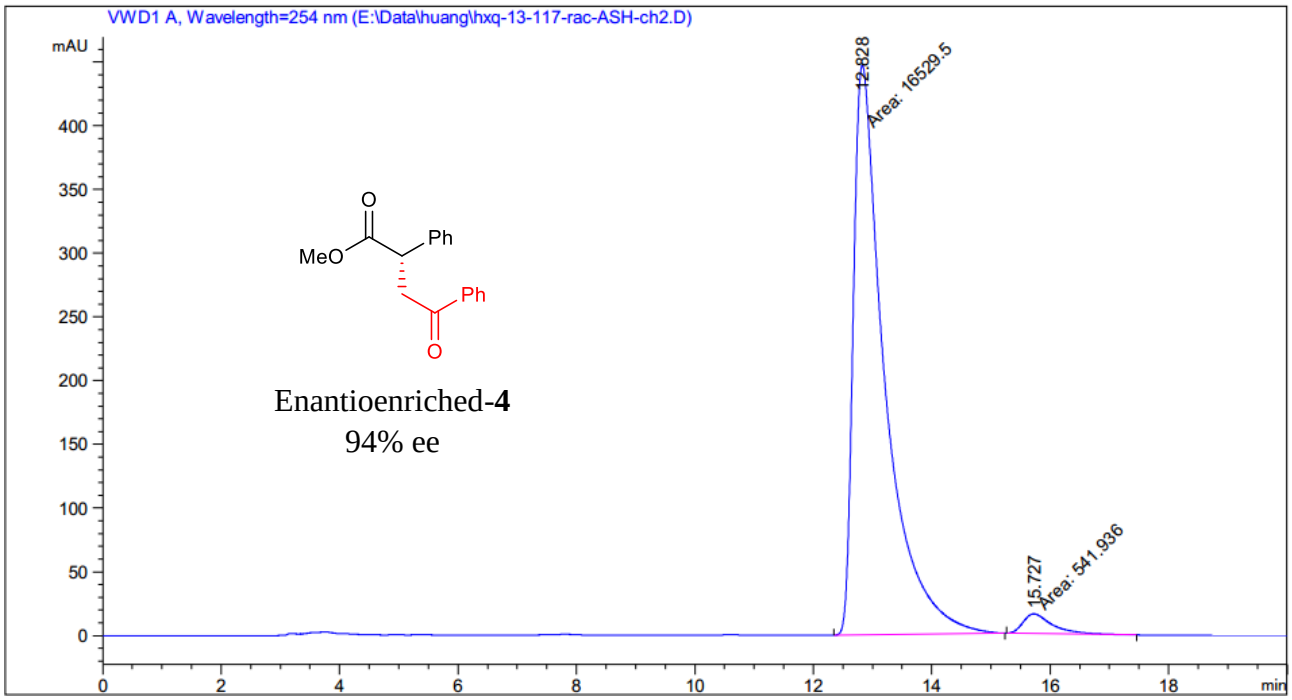


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.427	BB	0.2376	35.74290	2.23484	1.4444
2	8.877	BB	0.2585	2438.89966	147.03490	98.5556

Supplementary Figure 23. HPLC traces of *rac*-**3x** (reference) and enantioenriched-**3x**.

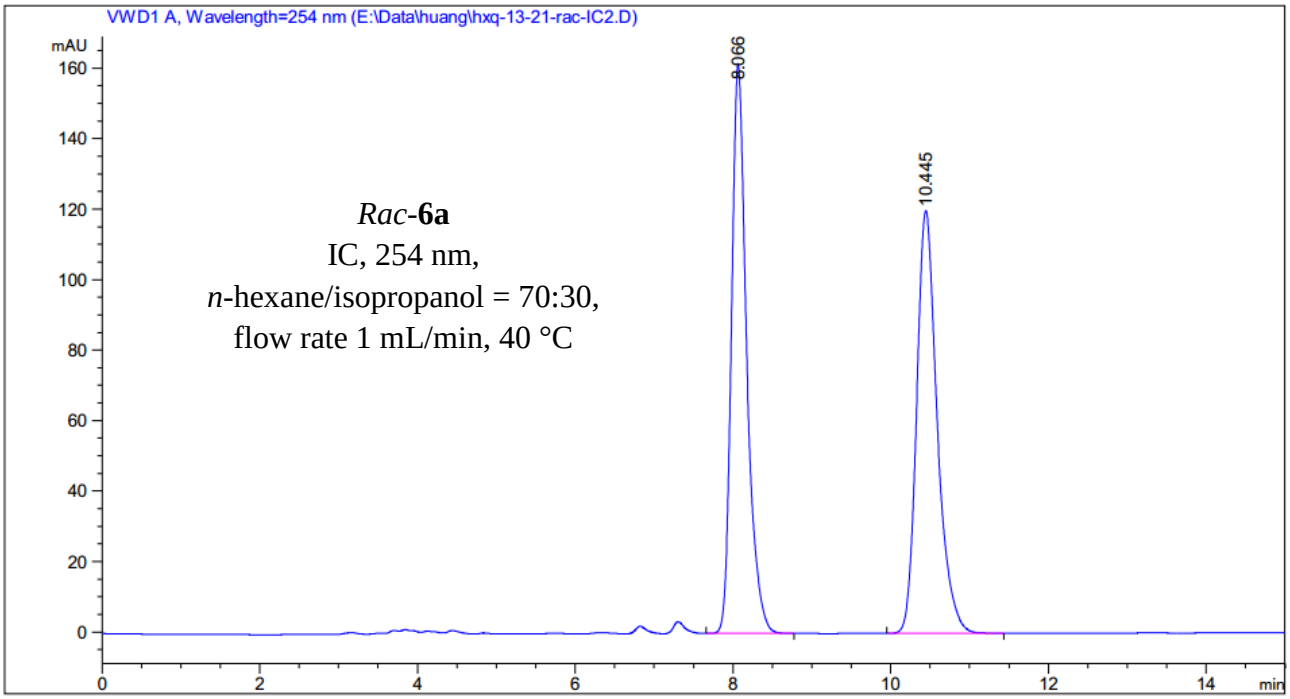


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.279	BV	0.3523	3013.78687	123.68021	50.0609
2	12.292	VB	0.4063	3006.45068	107.15292	49.9391

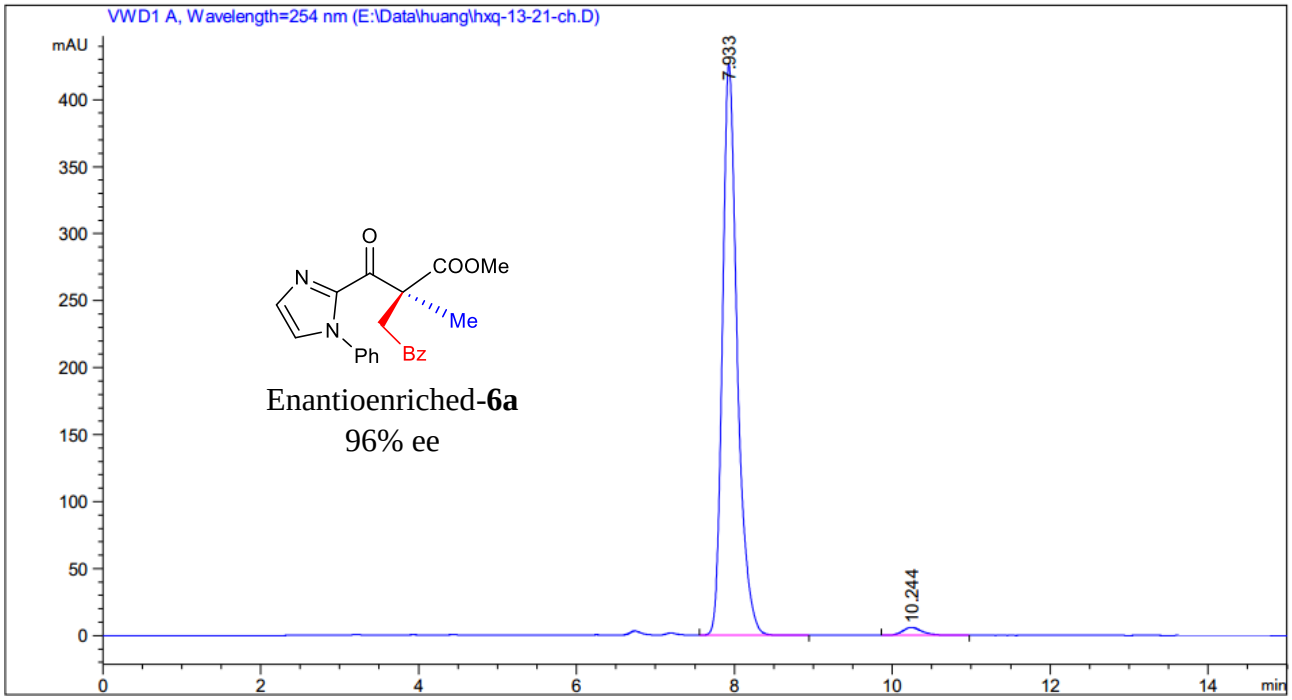


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.828	MM	0.6163	1.65295e4	447.02249	96.8255
2	15.727	MM	0.5814	541.93573	15.53575	3.1745

Supplementary Figure 24. HPLC traces of *rac*-**4** (reference) and enantioenriched-**4**.

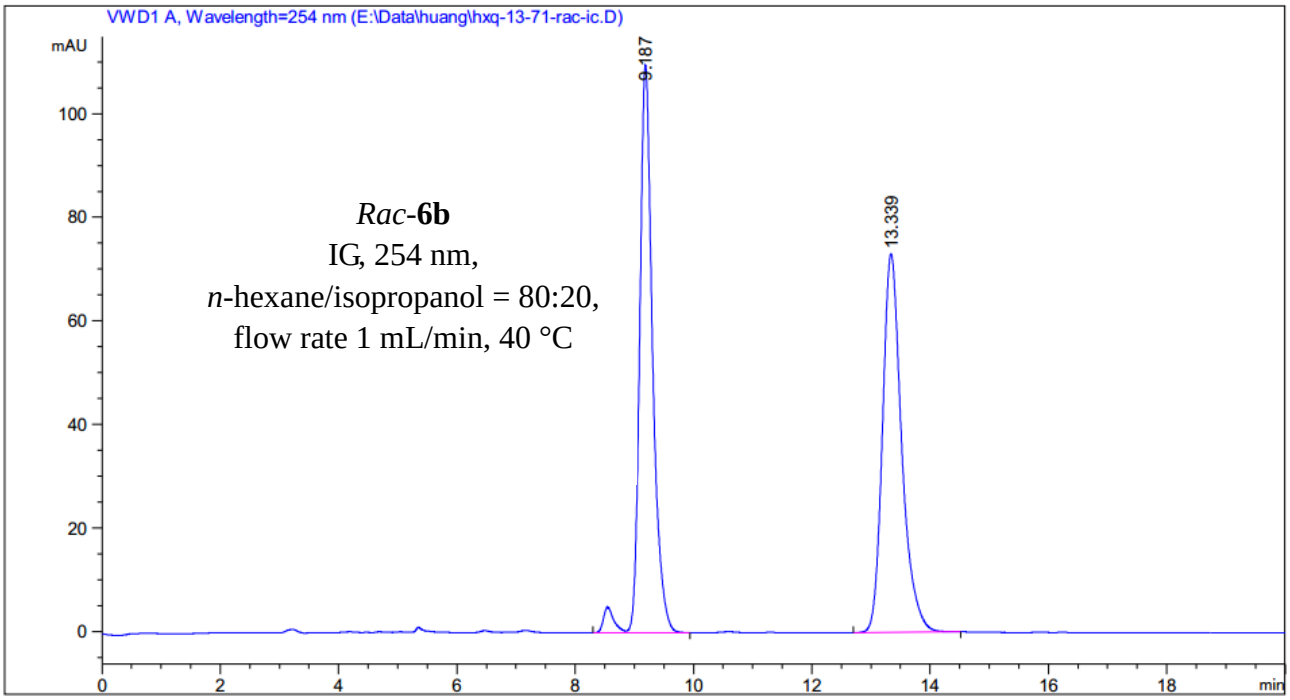


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.066	BB	0.2016	2167.28271	161.44106	50.0309
2	10.445	BB	0.2725	2164.60645	119.95129	49.9691

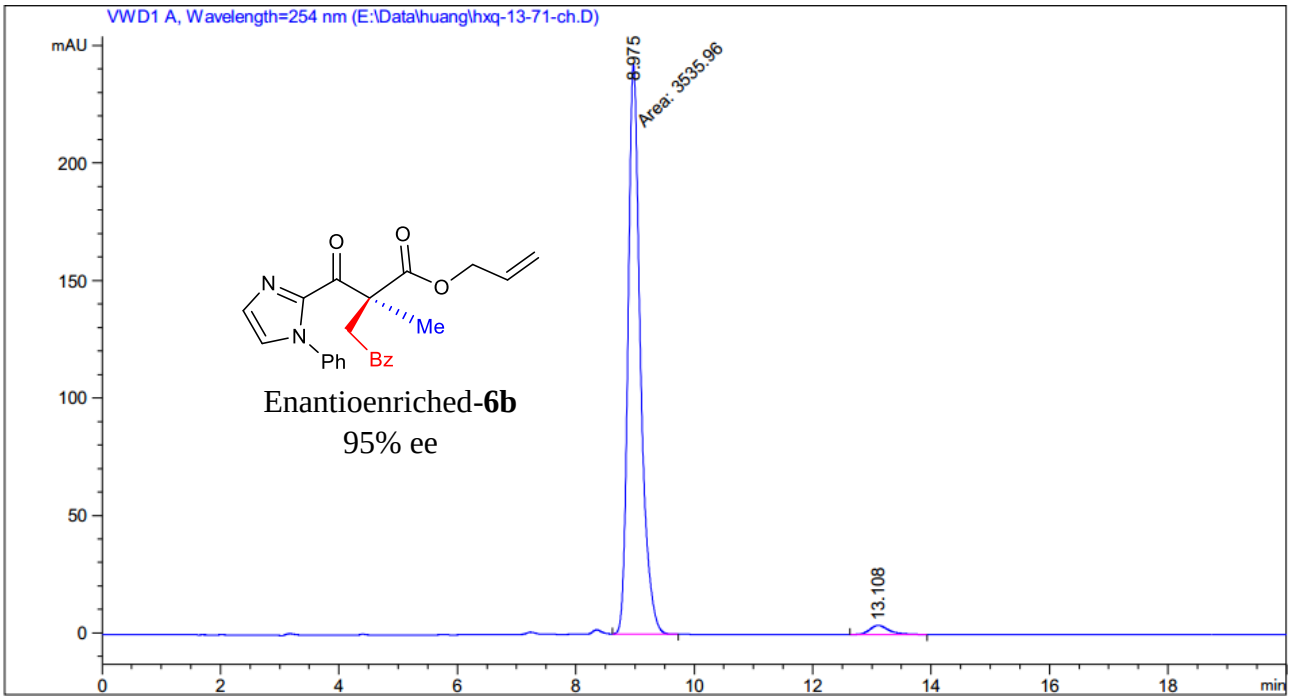


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.933	BB	0.1978	5581.38770	426.19437	98.1764
2	10.244	BB	0.2618	103.67249	5.96381	1.8236

Supplementary Figure 25. HPLC traces of *rac*-**6a** (reference) and enantioenriched-**6a**.

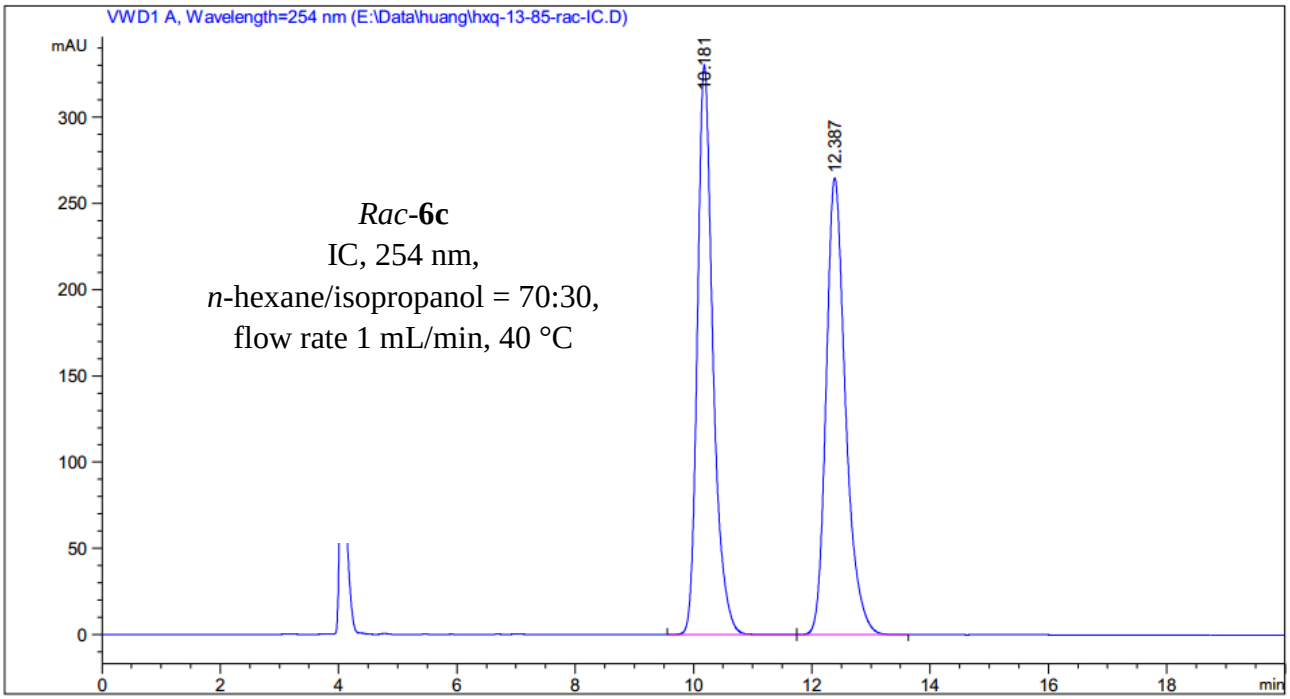


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.187	VB R	0.2247	1702.91382	109.66897	50.8430
2	13.339	BB	0.3396	1646.44556	73.15802	49.1570

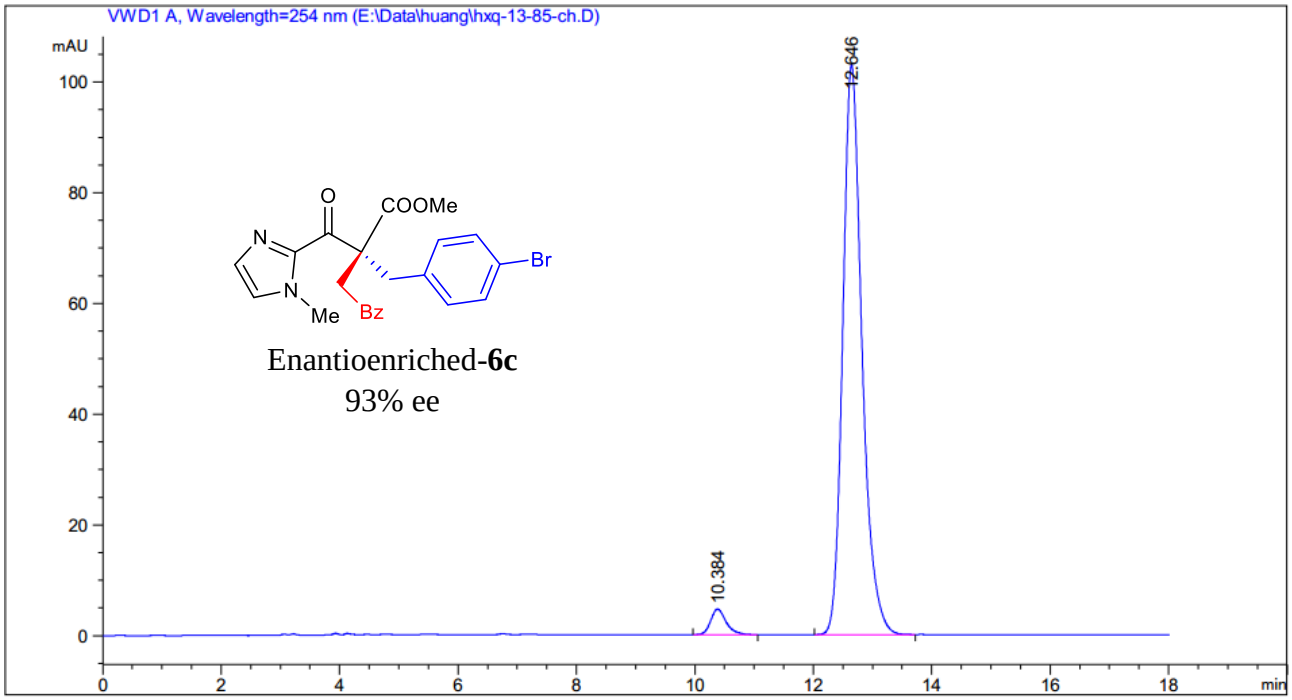


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.975	FM	0.2430	3535.96167	242.48401	97.6027
2	13.108	BB	0.3362	86.84889	3.87851	2.3973

Supplementary Figure 26. HPLC traces of *rac*-**6b** (reference) and enantioenriched-**6b**.

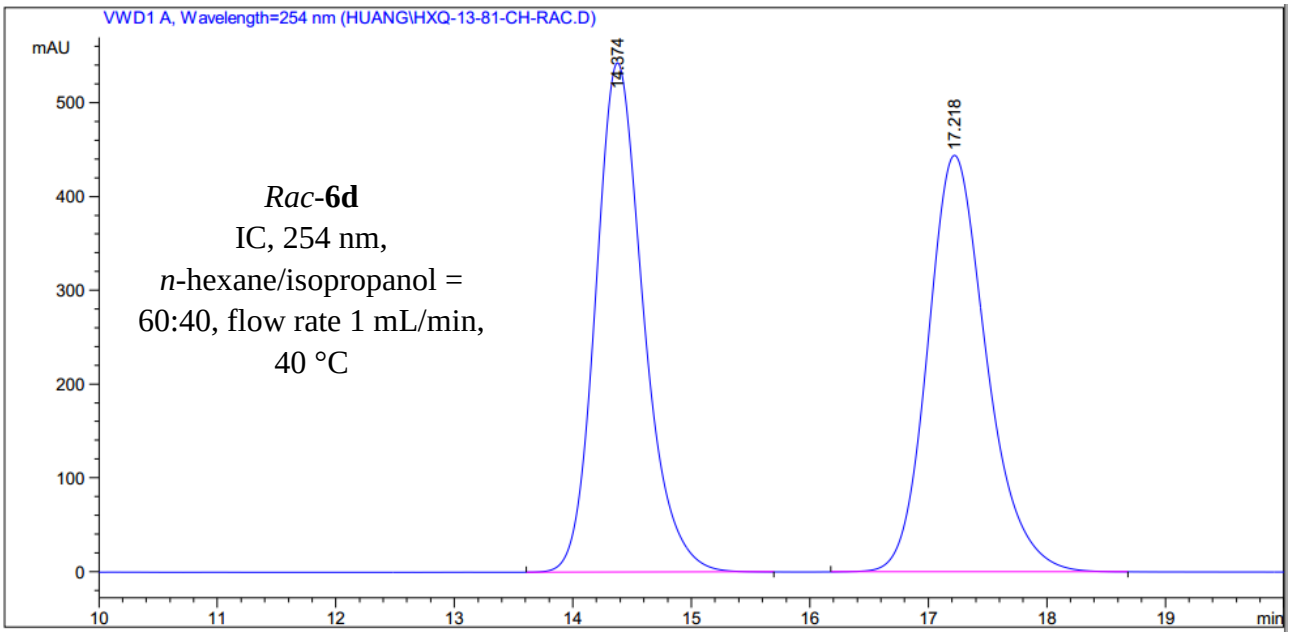


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.181	BB	0.2762	6033.29736	330.19360	49.9922
2	12.387	BB	0.3450	6035.18311	264.68011	50.0078



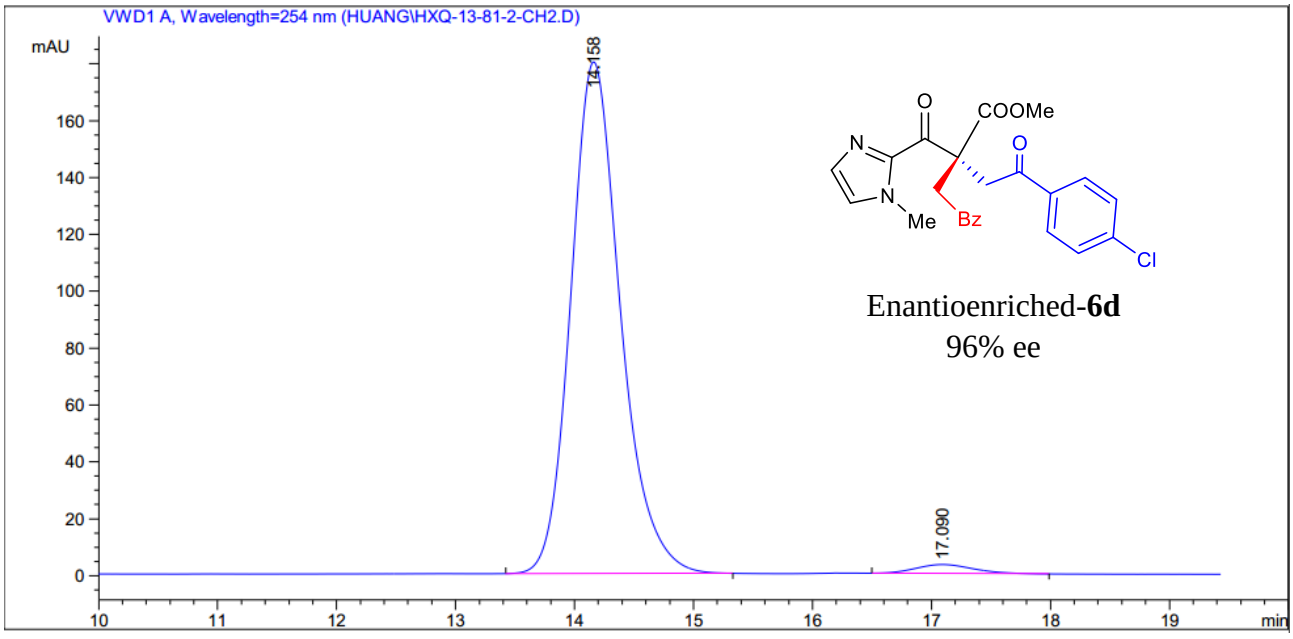
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.384	BB	0.2722	83.77501	4.62681	3.4919
2	12.646	BB	0.3415	2315.37109	102.91091	96.5081

Supplementary Figure 27. HPLC traces of *rac*-**6c** (reference) and enantioenriched-**6c**.



Rac-**6d**
IC, 254 nm,
n-hexane/isopropanol =
60:40, flow rate 1 mL/min,
40 °C

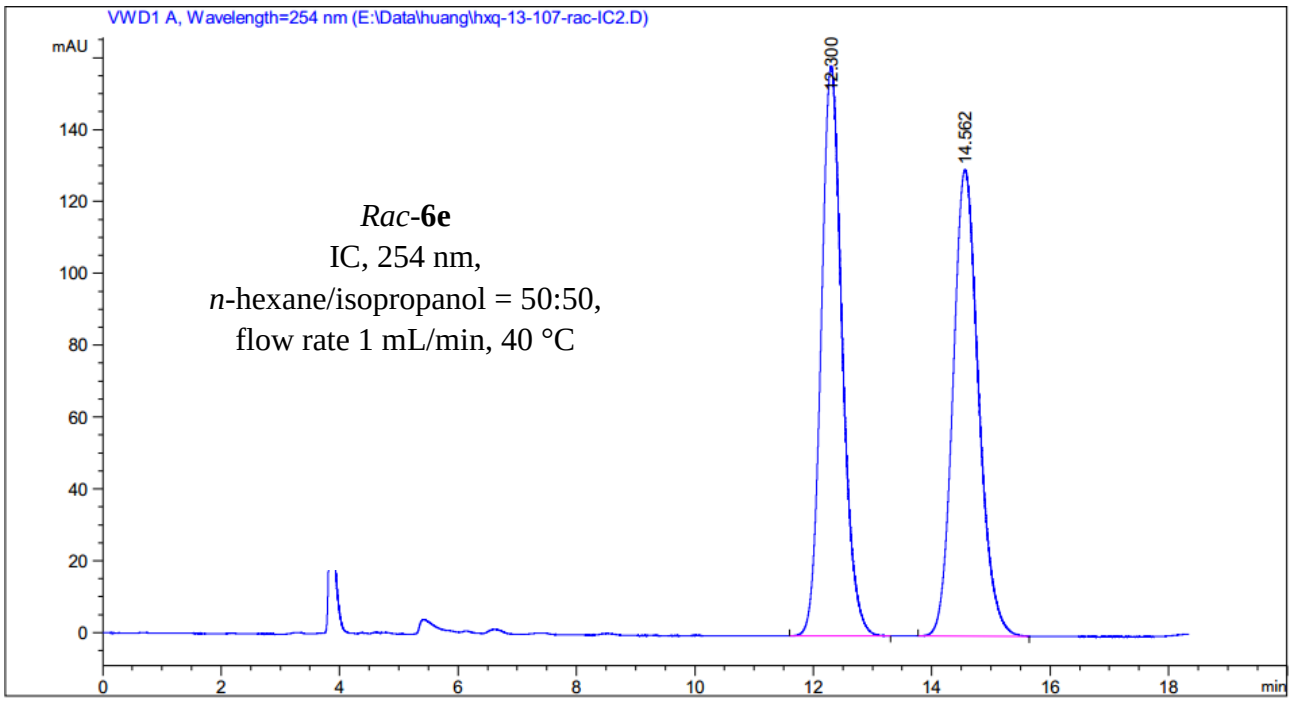
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.374	BB	0.4272	1.52116e4	543.19781	49.8453
2	17.218	BB	0.5242	1.53060e4	444.31485	50.1547



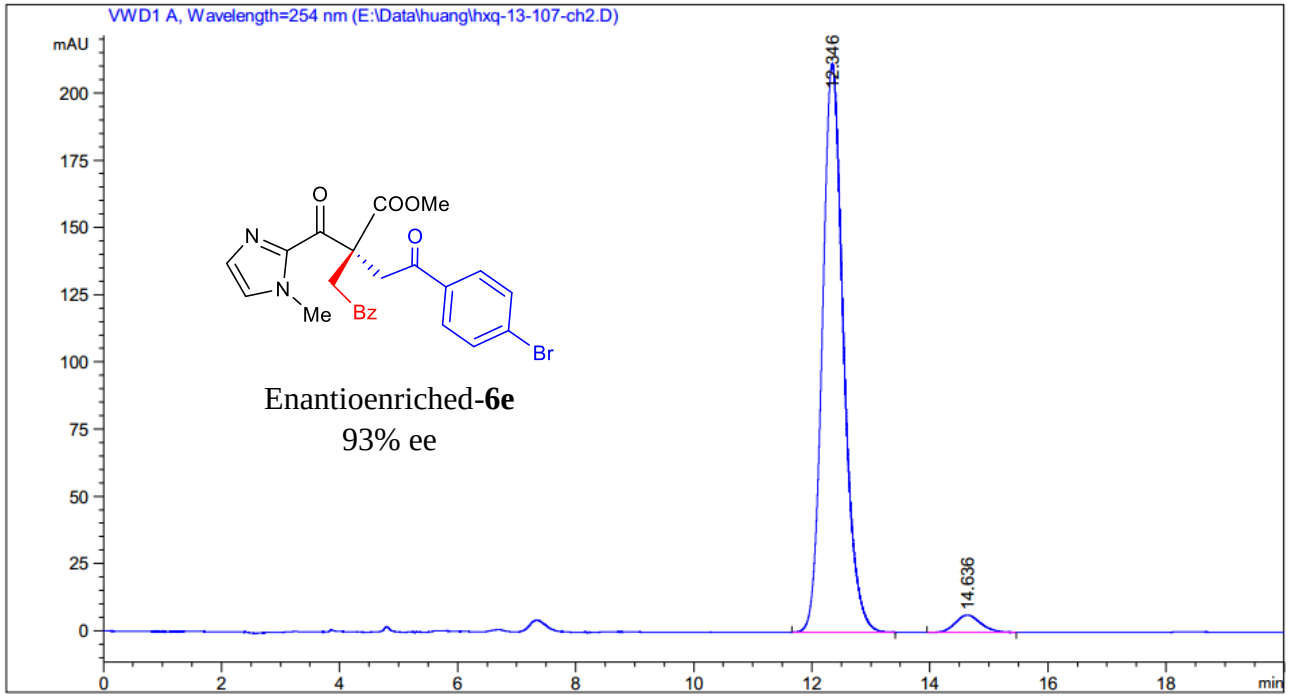
Enantioenriched-**6d**
96% ee

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.158	BB	0.4418	5219.71045	179.93001	97.9980
2	17.090	BB	0.5285	106.63360	3.15348	2.0020

Supplementary Figure 28. HPLC traces of *rac*-**6d** (reference) and enantioenriched-**6d**.

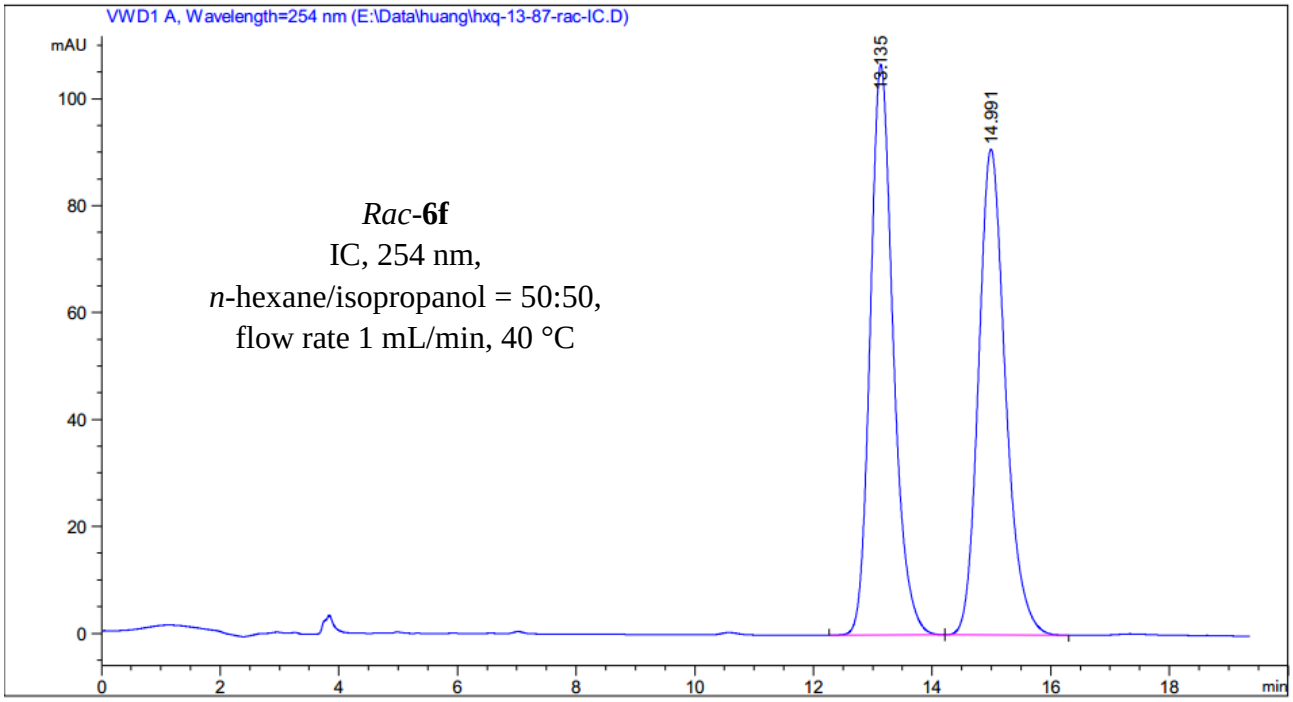


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.300	BV R	0.3548	3895.85327	158.74901	50.0738
2	14.562	VV R	0.3804	3884.37061	129.88875	49.9262

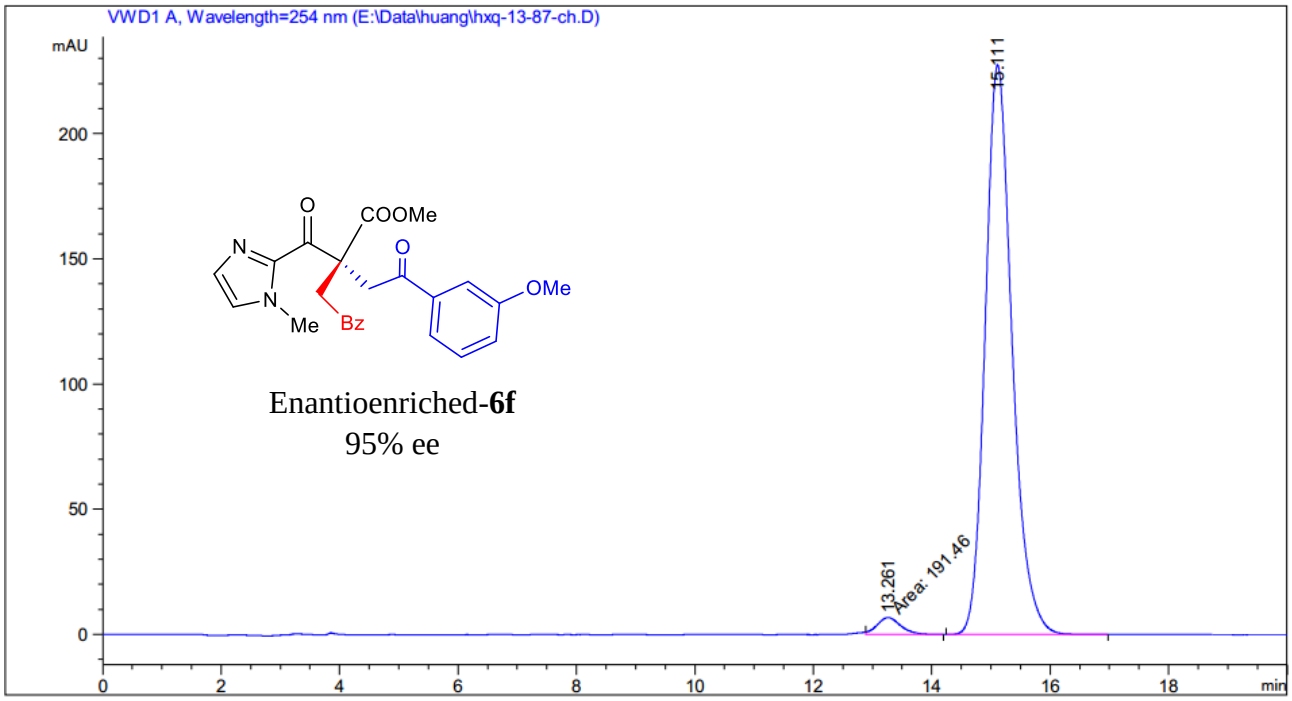


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.346	VV R	0.3411	5223.49268	211.50255	96.4201
2	14.636	VV R	0.3507	193.94064	6.48000	3.5799

Supplementary Figure 29. HPLC traces of *rac*-**6e** (reference) and enantioenriched-**6e**.

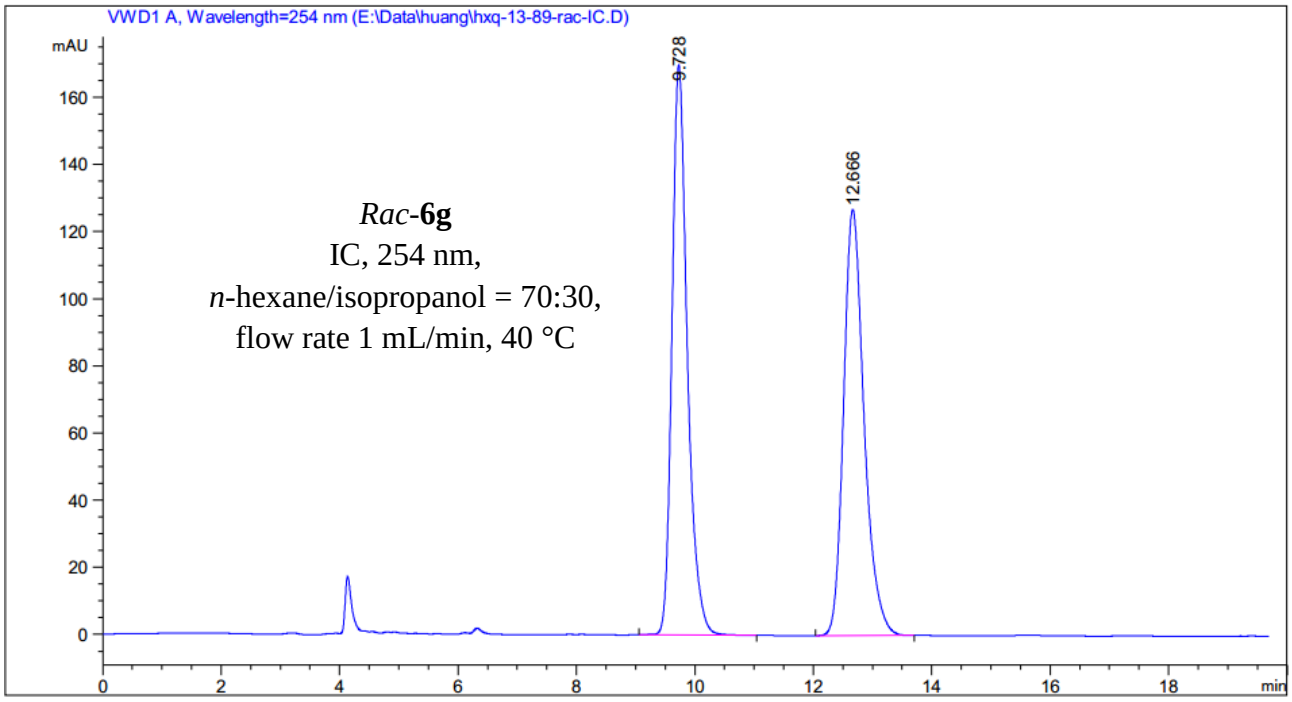


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.135	BB	0.4116	2878.21606	106.74932	50.1027
2	14.991	BB	0.4828	2866.41406	90.91094	49.8973

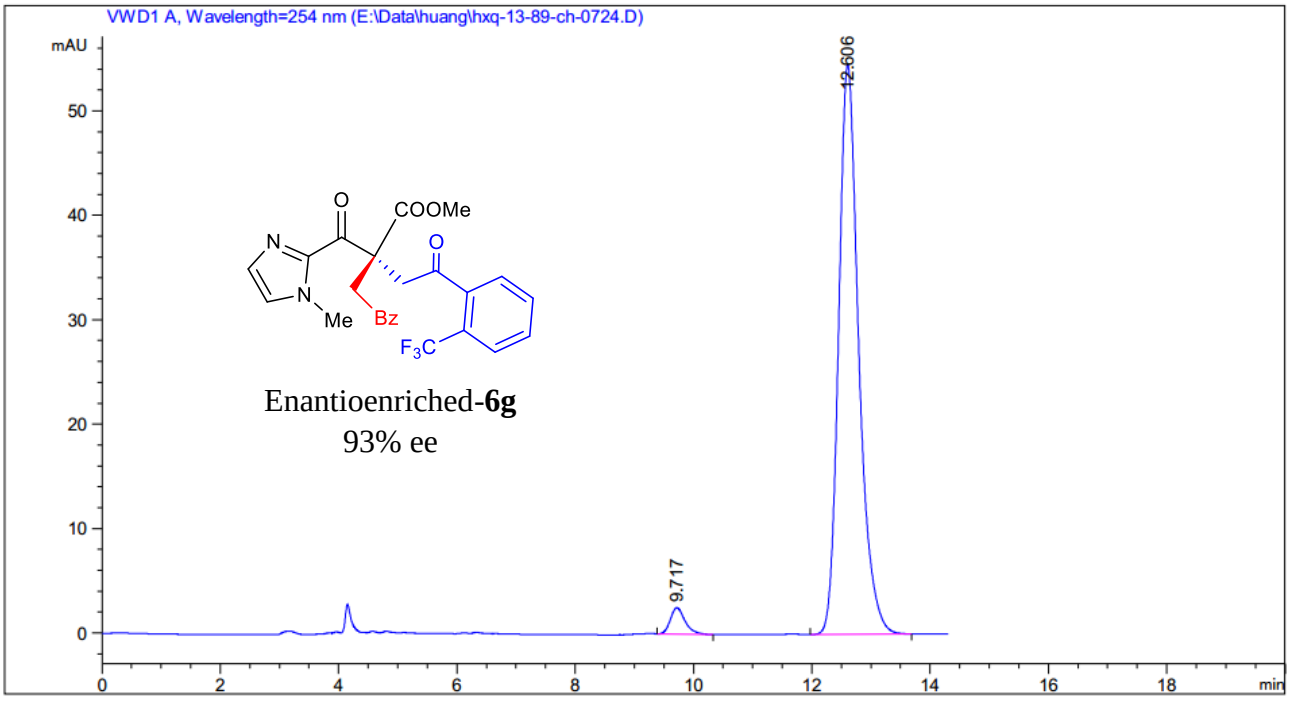


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.261	FM	0.4683	191.45999	6.81426	2.6025
2	15.111	BB	0.4805	7165.28955	227.46152	97.3975

Supplementary Figure 30. HPLC traces of *rac*-**6f** (reference) and enantioenriched-**6f**.

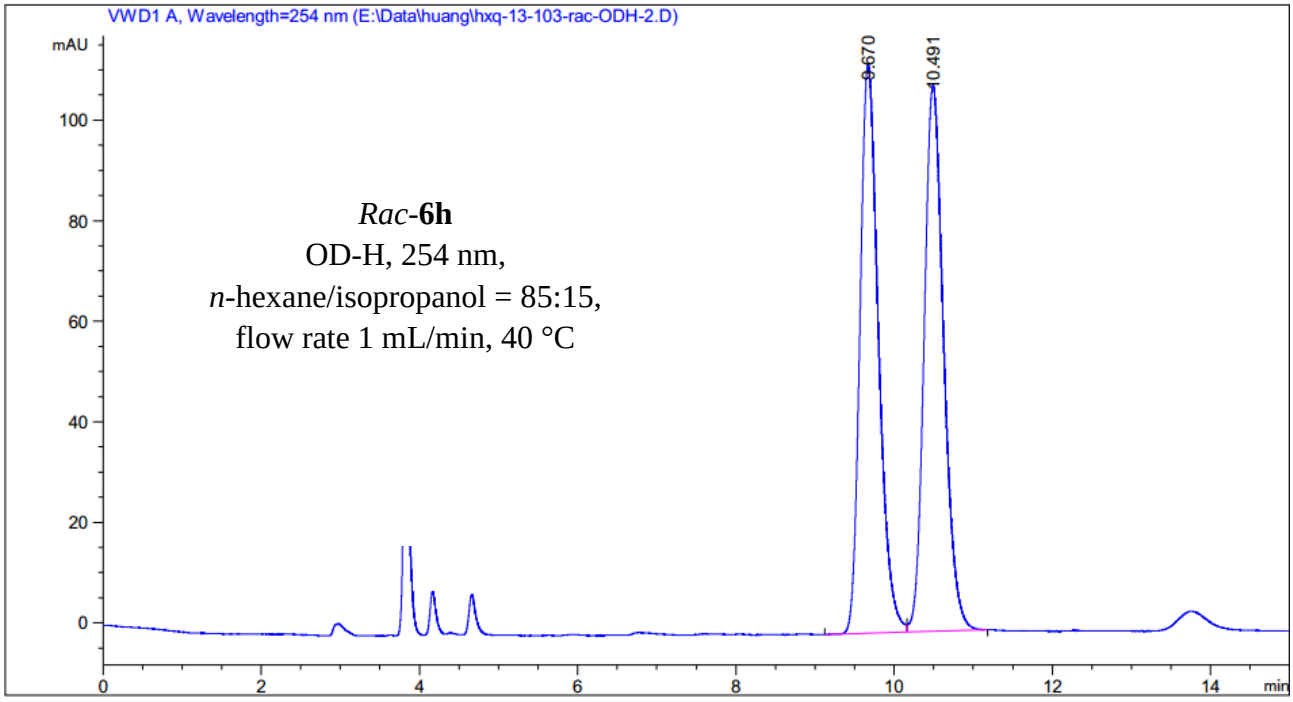


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.728	BB	0.2721	3058.12598	169.82230	50.0964
2	12.666	BB	0.3650	3046.35815	126.91151	49.9036



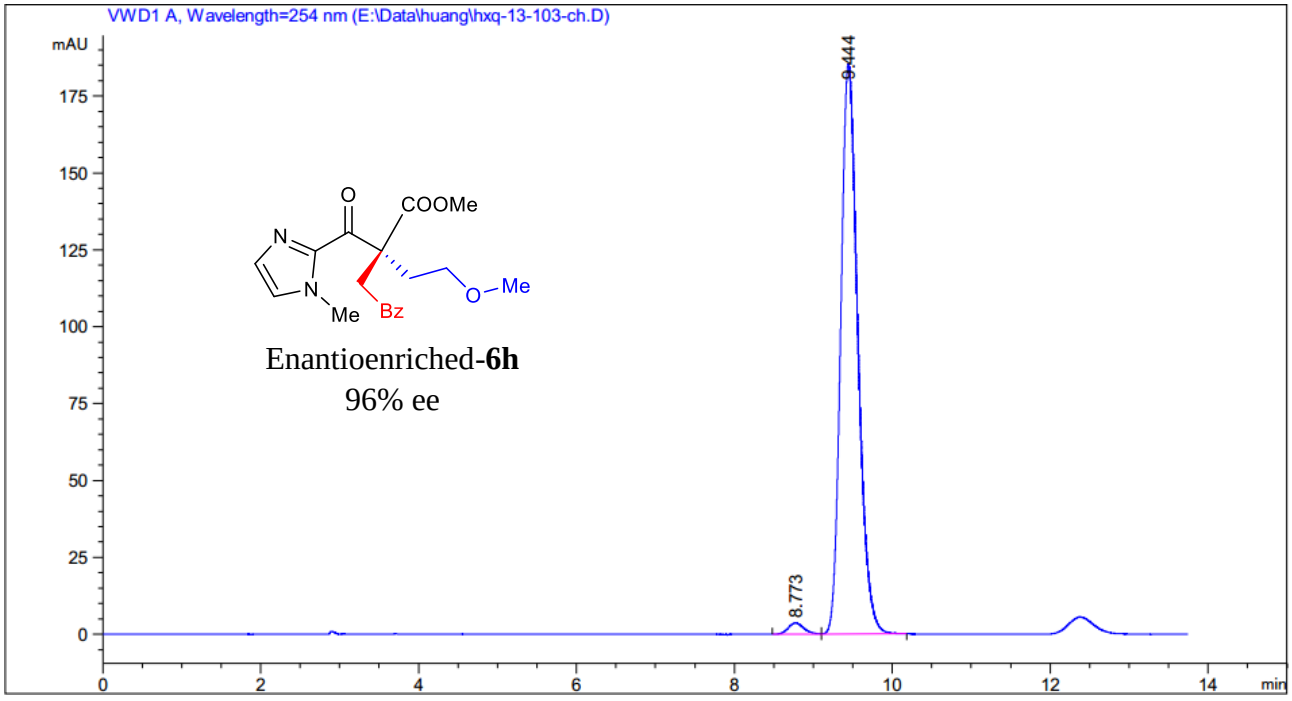
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.717	BB	0.2582	43.30285	2.52317	3.2581
2	12.606	BB	0.3579	1285.77771	54.56317	96.7419

Supplementary Figure 31. HPLC traces of *rac*-**6g** (reference) and enantioenriched-**6g**.



Rac-**6h**
OD-H, 254 nm,
n-hexane/isopropanol = 85:15,
flow rate 1 mL/min, 40 °C

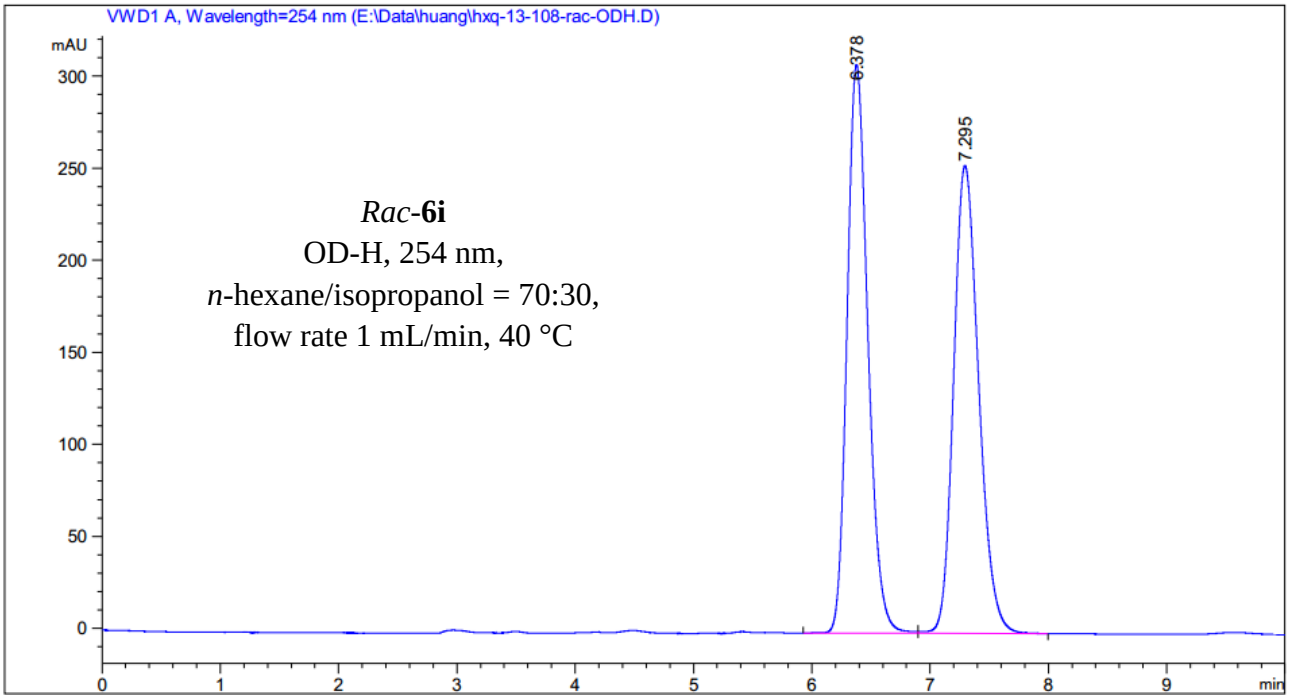
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.670	VV R	0.2440	1834.30017	113.23338	49.6942
2	10.491	VV R	0.2514	1856.87793	108.64541	50.3058



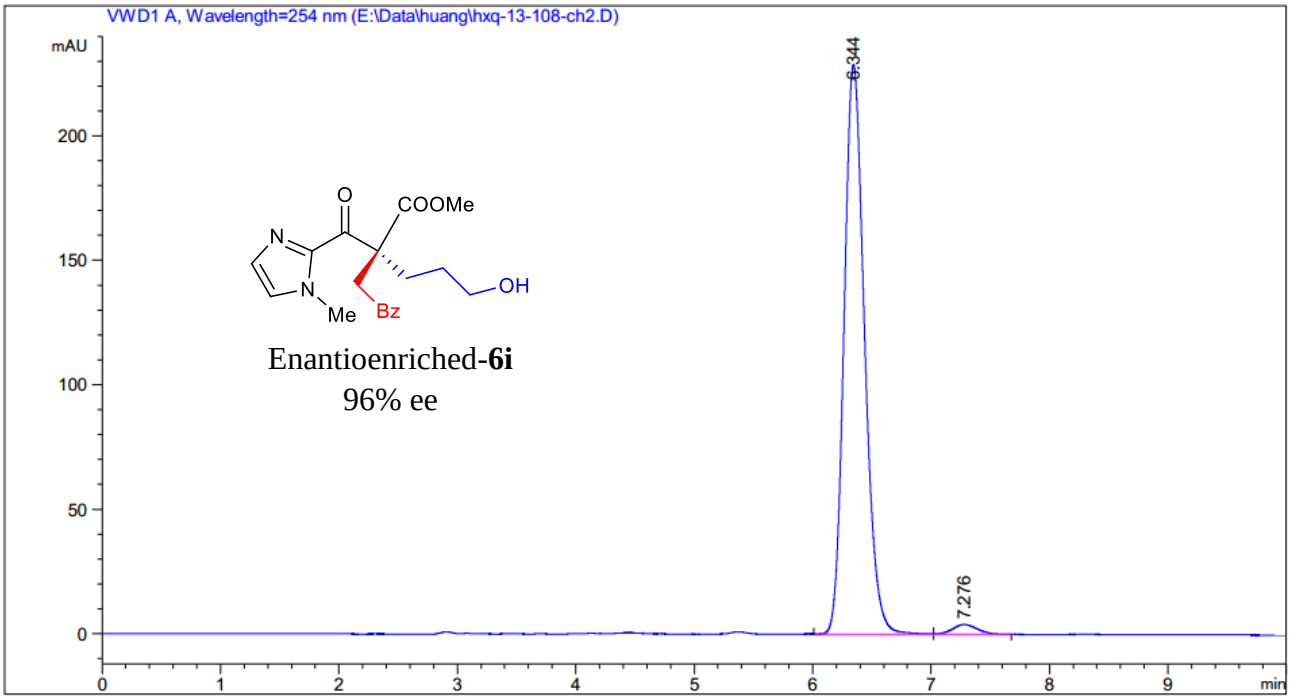
Enantioenriched-**6h**
96% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.773	BV	0.1637	50.88823	3.65925	1.7981
2	9.444	VV R	0.2233	2779.22144	185.47104	98.2019

Supplementary Figure 32. HPLC traces of *rac*-**6h** (reference) and enantioenriched-**6h**.

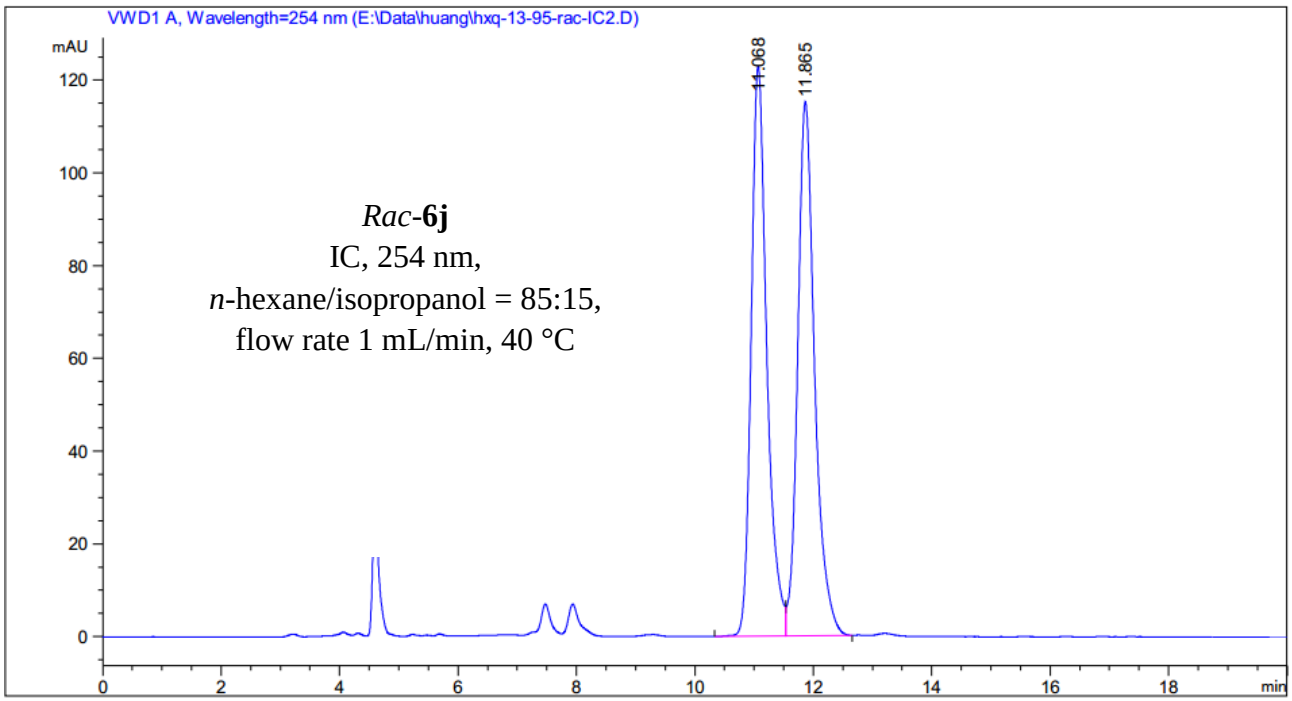


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.378	VV R	0.1882	3767.75732	309.10800	50.2125
2	7.295	VB	0.2229	3735.86963	254.22327	49.7875

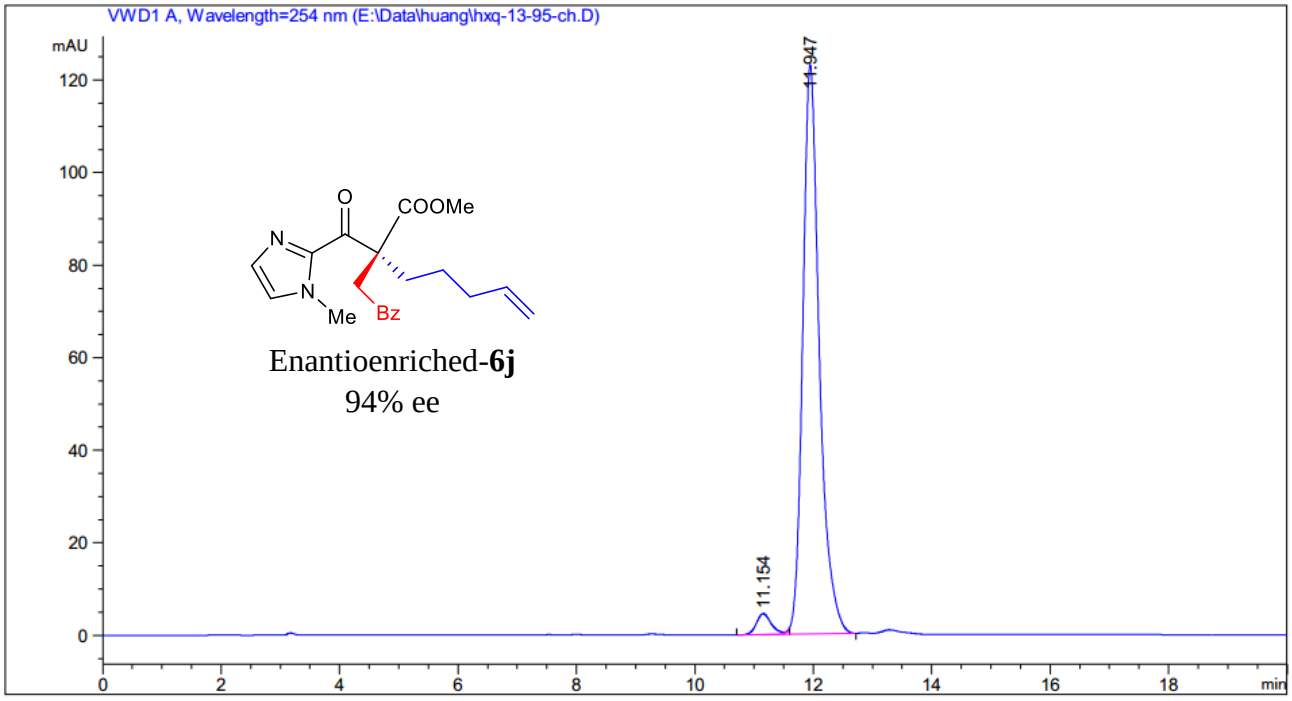


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.344	VV R	0.1847	2737.94678	228.70932	97.9297
2	7.276	VV R	0.1733	57.88220	3.93021	2.0703

Supplementary Figure 33. HPLC traces of *rac*-**6i** (reference) and enantioenriched-**6i**.

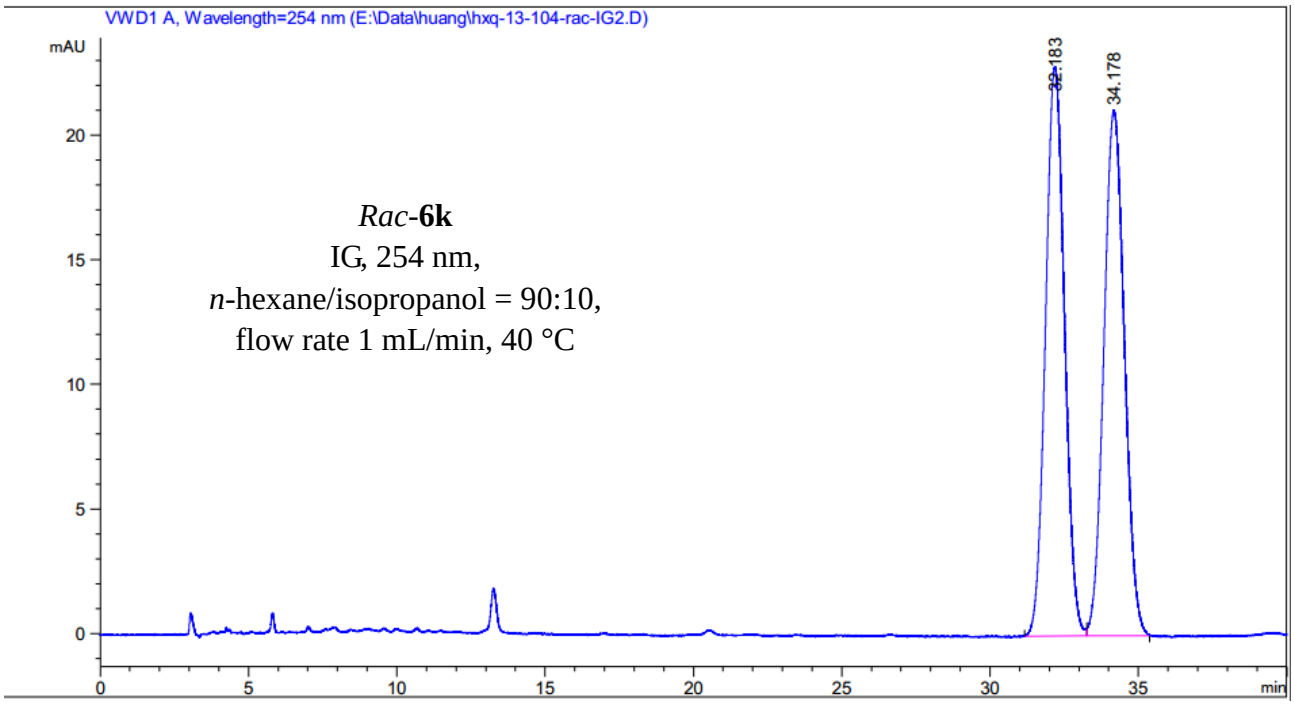


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.068	BV	0.2761	2256.03076	122.95725	49.5486
2	11.865	VB	0.2996	2297.13379	115.20834	50.4514

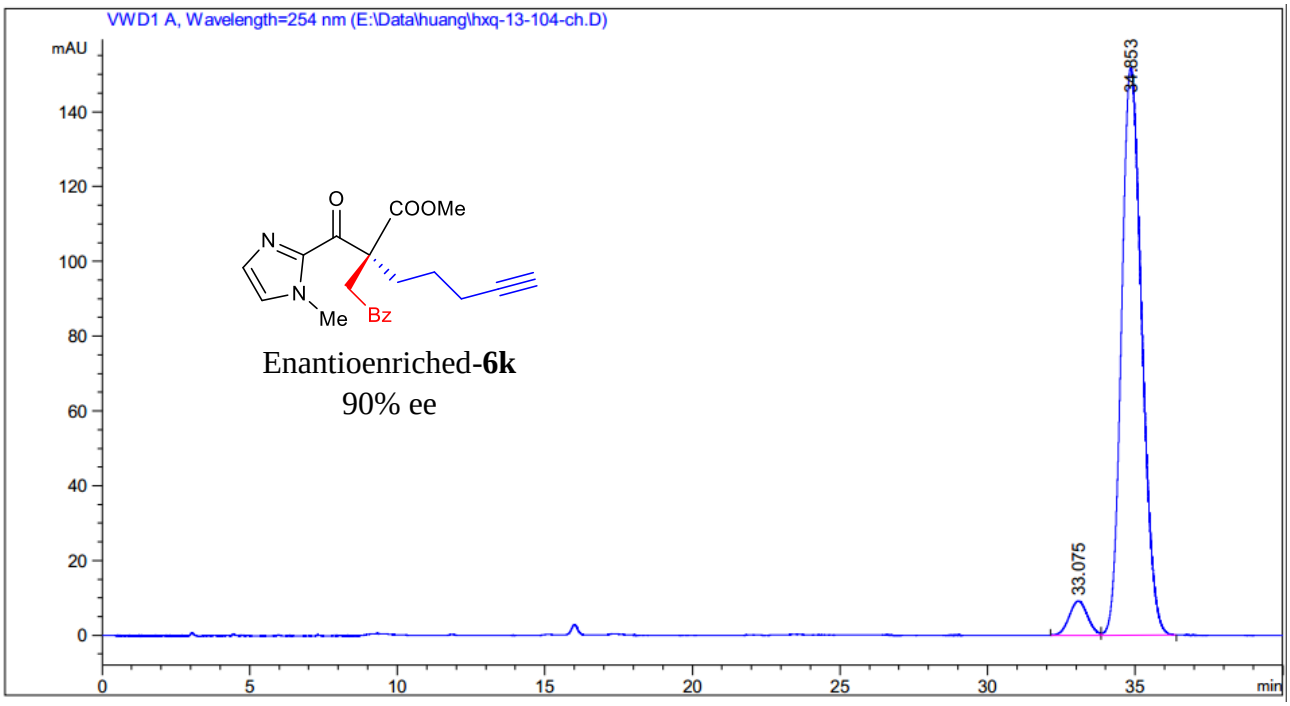


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.154	BV E	0.2619	78.23158	4.52144	3.1617
2	11.947	VB R	0.2932	2396.12183	123.05588	96.8383

Supplementary Figure 34. HPLC traces of *rac*-**6j** (reference) and enantioenriched-**6j**.

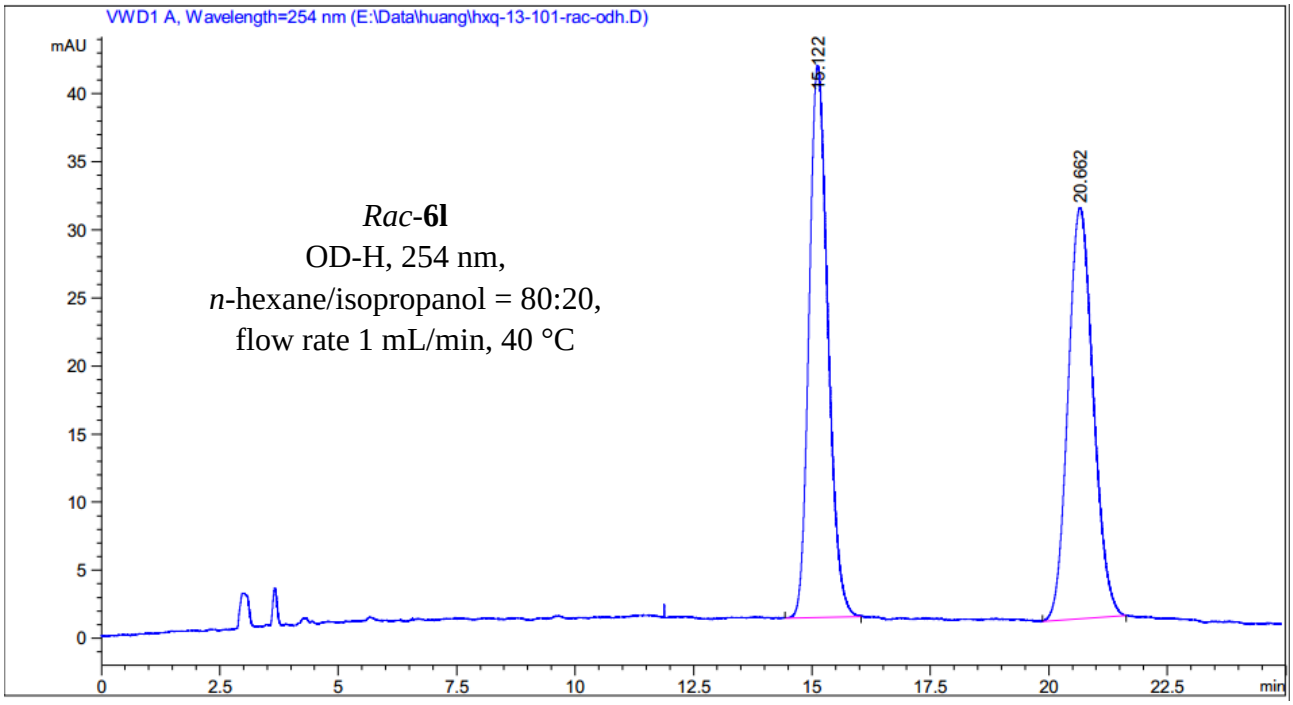


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	32.183	VV R	0.5204	1016.89099	22.86239	50.0601
2	34.178	VV R	0.5647	1014.45111	21.06876	49.9399

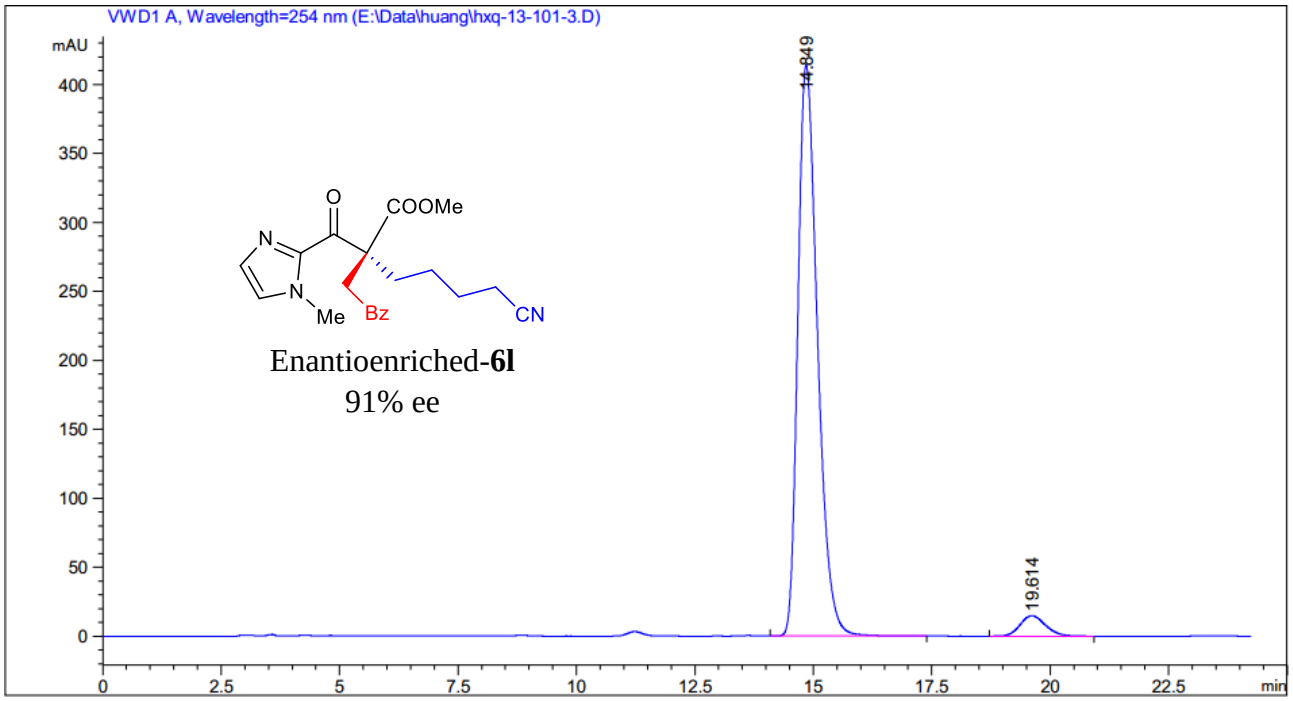


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.075	VV R	0.5022	396.48615	9.22935	5.1912
2	34.853	VV R	0.5601	7241.23047	151.78859	94.8088

Supplementary Figure 35. HPLC traces of *rac*-**6k** (reference) and enantioenriched-**6k**.

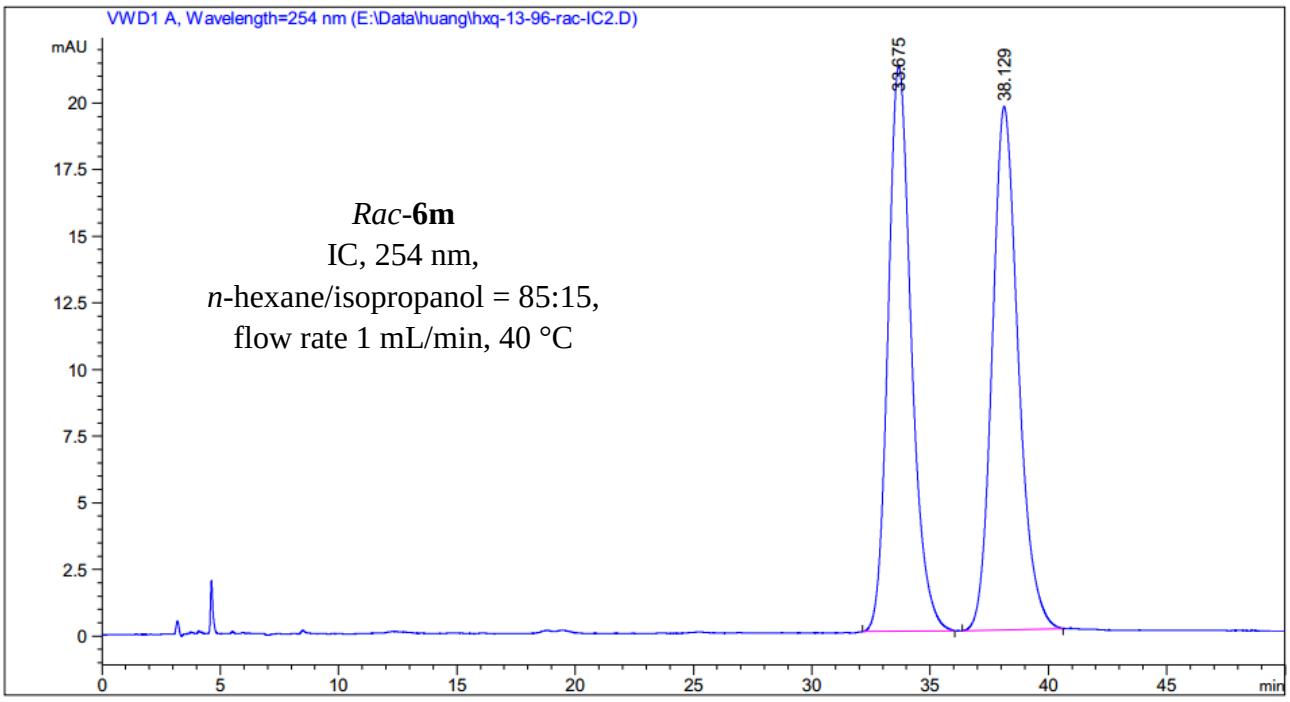


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.122	VV R	0.3232	1118.52246	40.56623	50.0798
2	20.662	VV R	0.4323	1114.95569	30.19180	49.9202

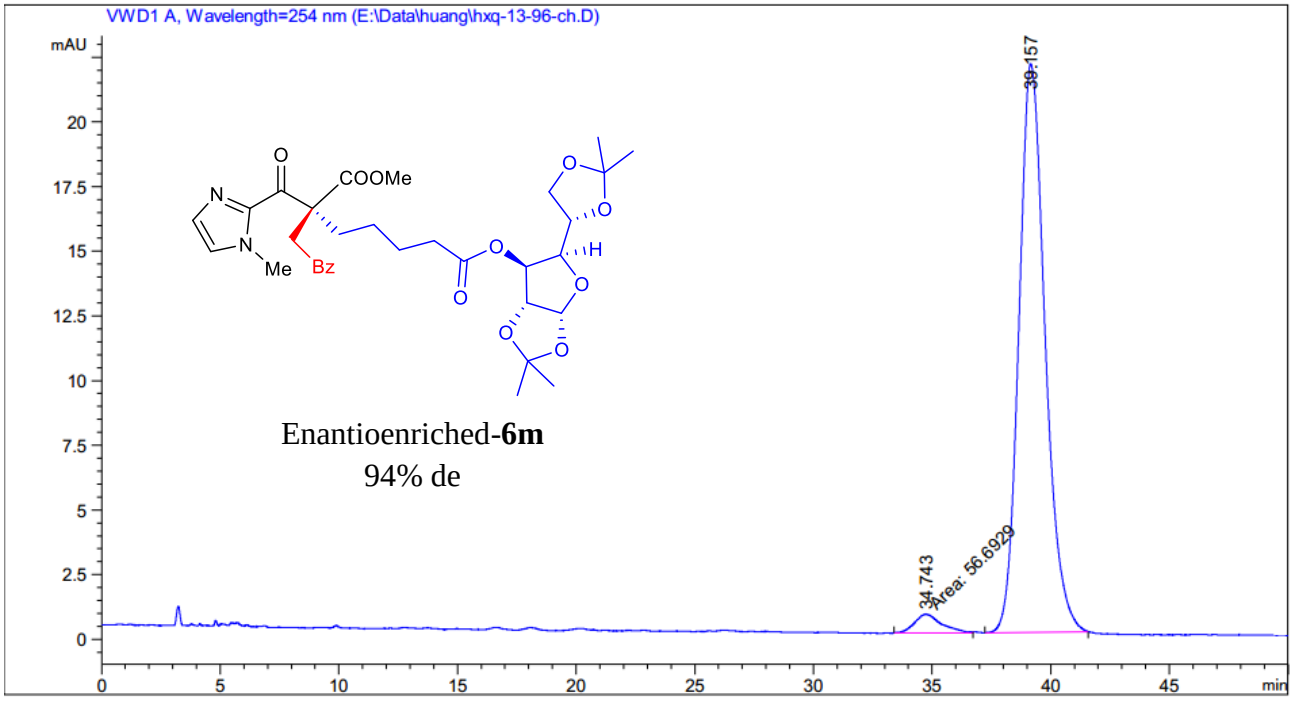


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.849	BB	0.4448	1.19247e4	414.25058	95.5734
2	19.614	BB	0.5761	552.30267	14.81015	4.4266

Supplementary Figure 36. HPLC traces of *rac*-**6l** (reference) and enantioenriched-**6l**.

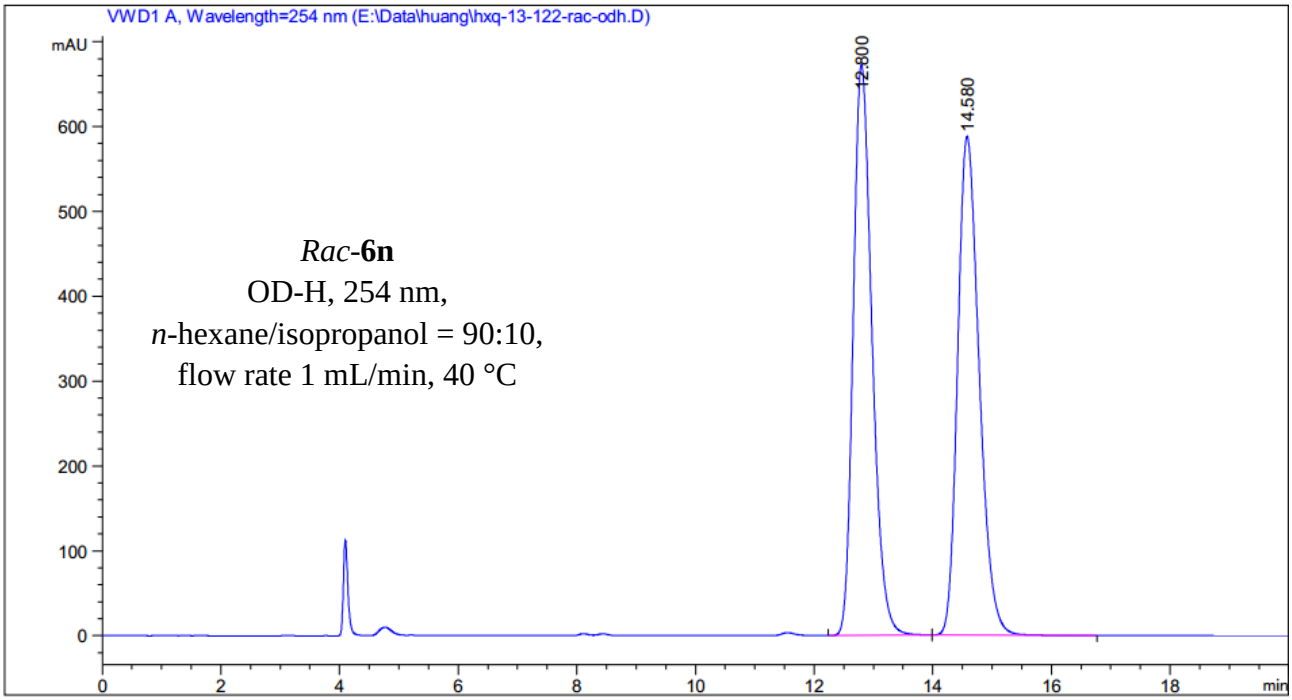


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.675	BB	1.0327	1451.84375	21.20624	49.1773
2	38.129	BB	1.1291	1500.41895	19.64452	50.8227

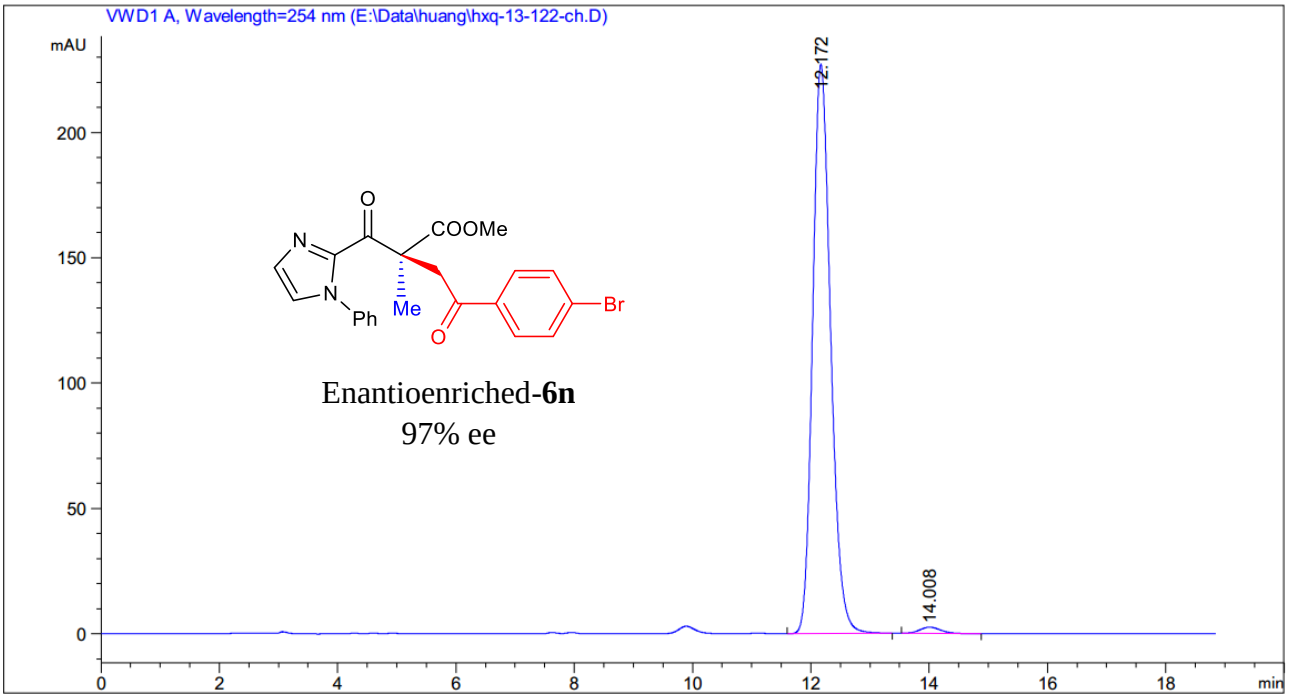


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.743	MM	1.3084	56.69288	7.22170e-1	3.2550
2	39.157	BB	1.1431	1685.01514	21.96205	96.7450

Supplementary Figure 37. HPLC traces of *rac*-**6m** (reference) and enantioenriched-**6m**.

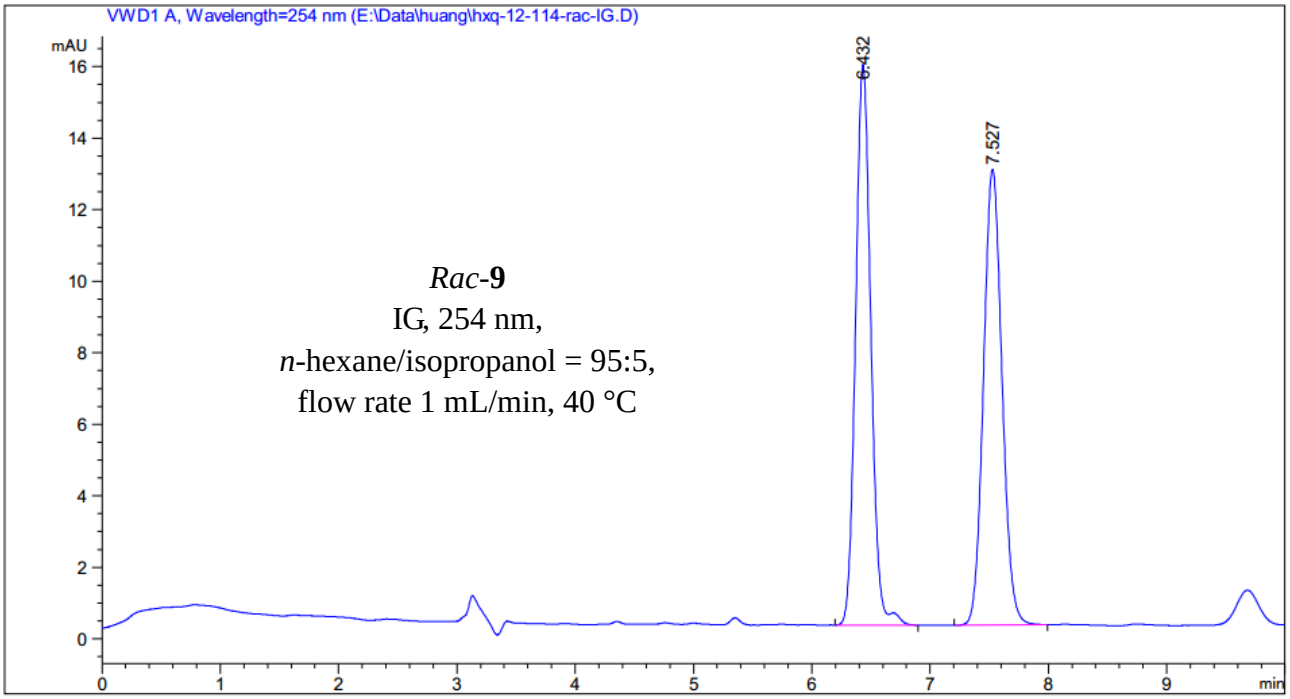


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.800	BB	0.3383	1.47784e4	672.81226	49.9789
2	14.580	BB	0.3896	1.47909e4	587.78522	50.0211

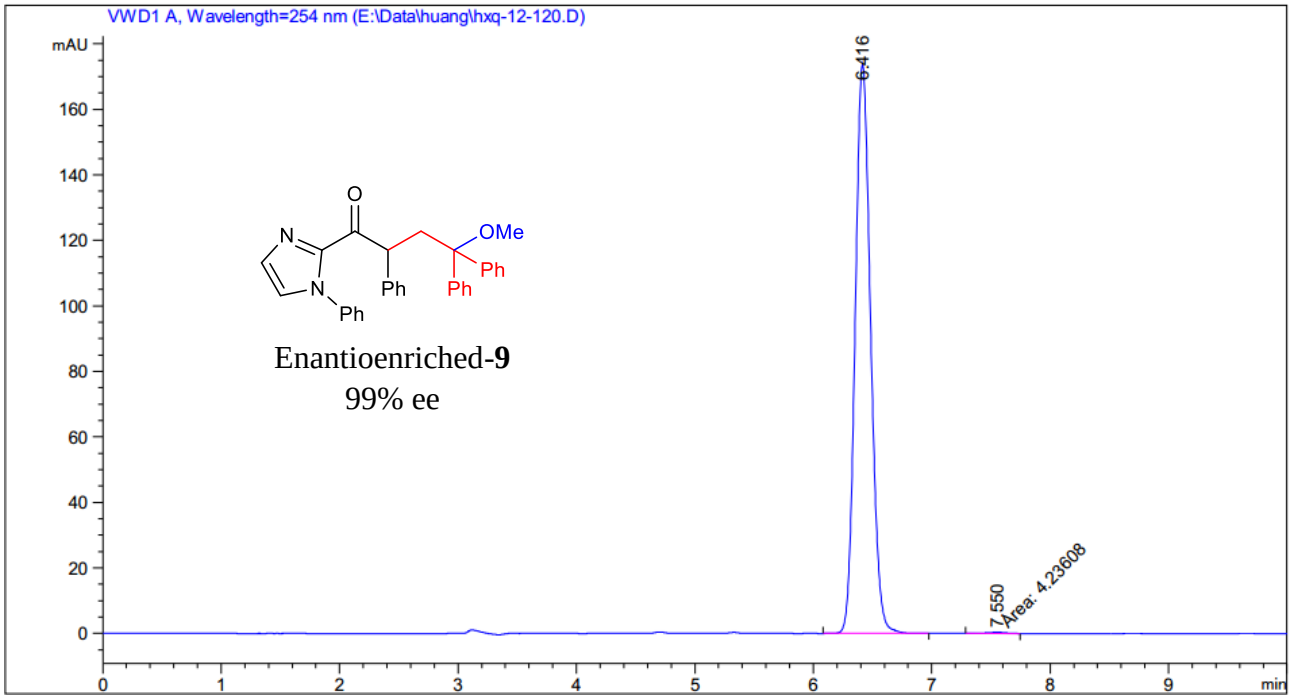


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.172	BB	0.3257	4783.51318	227.09676	98.7490
2	14.008	BB	0.3758	60.60207	2.47351	1.2510

Supplementary Figure 38. HPLC traces of *rac*-**6n** (reference) and enantioenriched-**6n**.

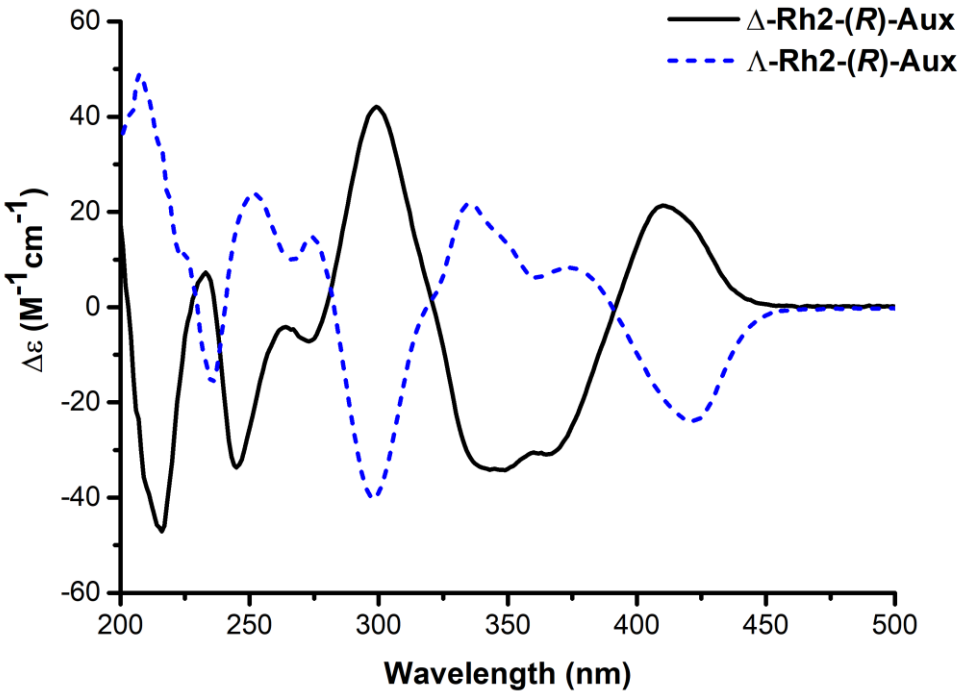


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.432	BV R	0.1387	140.74936	15.67780	50.4266
2	7.527	BB	0.1687	138.36809	12.74264	49.5734

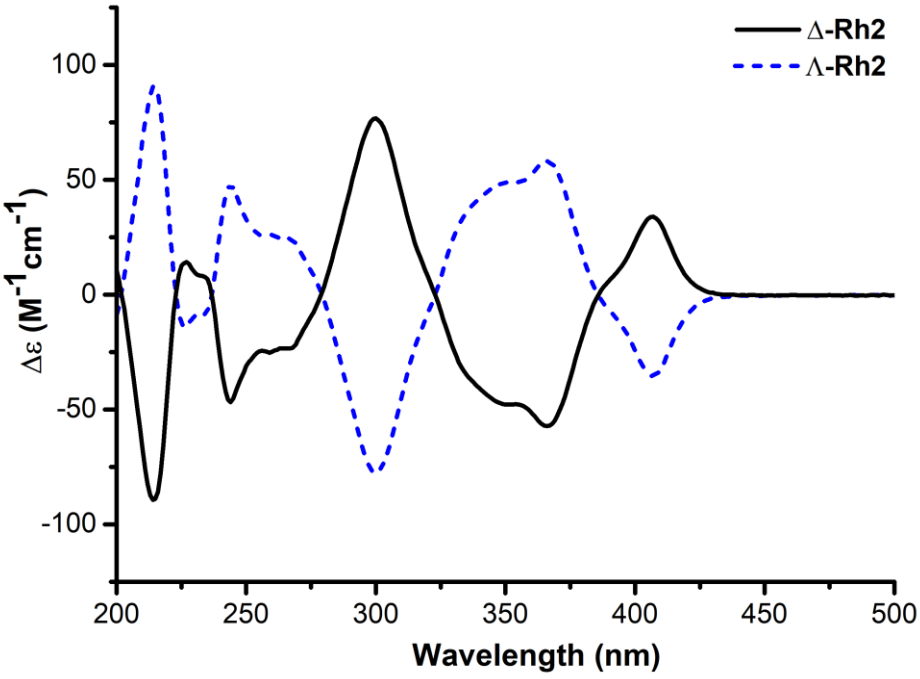


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.416	BB	0.1407	1574.56482	173.83551	99.7317
2	7.550	MM	0.1892	4.23608	3.73172e-1	0.2683

Supplementary Figure 39. HPLC traces of *rac*-**9** (reference) and enantioenriched-**9**.



Supplementary Figure 40. CD spectra of Δ-**Rh2-(*R*)-Aux** and Λ-**Rh2-(*R*)-Aux**. (0.2 mM in CH_3OH).



Supplementary Figure 41. CD spectra of Δ-**Rh2** and Λ-**Rh2**. (0.2 mM in CH_3OH).

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