Supporting Information for:

Asymmetric Catalysis with Organic Azides and Diazo Compounds Initiated by Photoinduced Electron Transfer

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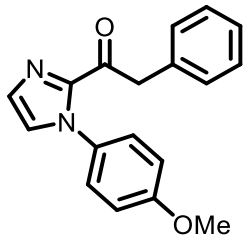
1. General Information

All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. Catalytic reactions were performed in a Schlenk tube (10 mL). A 21 W compact fluorescent lamp (CFL) served as light source. The catalysts Δ-**IrS**,[1] Δ-**RhO**,[2] and Δ/Λ-**RhS**[3] were synthesized according to our published procedures. Solvents were distilled under nitrogen from calcium hydride (CH_3CN, CH_2Cl_2), sodium/benzophenone (THF). HPLC grade of acetone was used without further purification. Dry DMSO was bought from Sigma-Aldrich. Reagents that were purchased from commercial suppliers were used without further purification. Flash column chromatography was performed with silica gel 60 M from Macherey-Nagel (irregular shaped, 230-400 mesh, pH 6.8, pore volume: 0.81 mL × g^{-1}, mean pore size: 66 Å, specific surface: 492 m^2 × g^{-1}, particle size distribution: 0.5% < 25 μm and 1.7% > 71 μm, water content: 1.6%). ^{1}H NMR, ^{19}F NMR and proton decoupled ^{13}C NMR spectra were recorded on Bruker Avance 300 (300 MHz), or Bruker AM (500 MHz) spectrometers at ambient temperature. NMR standards were used as follows: ^{1}H NMR spectroscopy: δ = 7.26 ppm ($CDCl_3$). ^{19}F NMR spectroscopy: δ = 0 ppm ($CFCl_3$). ^{13}C NMR spectroscopy: δ = 77.0 ppm ($CDCl_3$). 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 using ESI/EI technique. Chiral HPLC chromatography was performed with an Agilent 1200, Agilent 1260 HPLC system or Shimadzu Lc-2030c HPLC system. Optical rotations were measured on a Krüss P8000-T polarimeter with $[\alpha]_D^{22}$ values reported in degrees with concentrations reported in g/100 mL. The EPR spectrometer is from Bruker (model esp300), with a modified Varian rectangular X-band cavity and the modulation frequency was set to 100 kHz, the modulation amplitude was 0.1 mT. Luminescence quenching experiments were recorded on a Spectra Max M5 microplate reader in a 10.0 mm quartz cuvette.

2. Synthesis of Substrates

2-Acyl imidazoles **1** were synthesized according to our recently published procedures.[4] The experimental data of **1a-b, 1e-q** are in accord with our previous reports.[4] The data of **1c-d** are shown below.



1-(1-(4-Methoxyphenyl)-1*H*-imidazol-2-yl)-2-phenylethan-1-one (1c)

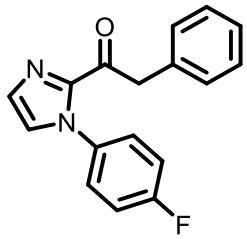
A white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.18 (m, 6H), 7.18-7.10 (m, 3H), 6.94-6.87 (m, 2H), 4.44 (s, 2H), 3.82 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.5, 159.7, 142.9, 134.5, 131.1, 129.9, 129.5, 128.4, 127.7, 126.9, 126.7, 114.1, 55.5, 45.6.

IR (film): ν (cm^{-1}) 3105, 3030, 2914, 1685, 1592, 1494, 1452, 1390, 1340, 1307, 1208, 1147, 1079, 1023, 991, 958, 912, 887, 840, 789, 761, 721, 696, 590, 542, 512, 480, 454.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{17}N_2O_2$ $[M+H]^+$: 293.1285, found: 293.1286.



1-(1-(4-Fluorophenyl)-1*H*-imidazol-2-yl)-2-phenylethan-1-one (1d)

A white solid.

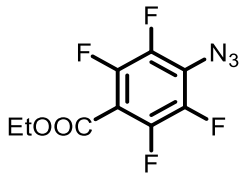
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.17 (m, 9H), 7.16-7.08 (m, 2H), 4.48 (s, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6, 162.5 (d, J = 247.5 Hz), 142.9, 134.3, 134.2, 129.91, 129.86, 128.5, 127.7 (d, J = 8.8 Hz), 127.4, 126.8, 115.9 (d, J = 23.0 Hz), 45.6.

IR (film): ν (cm^{-1}) 3159, 3077, 1683, 1508, 1449, 1399, 1219, 1147, 1027, 962, 911, 842, 793, 727, 701, 623, 537.

HRMS (EI, *m*/*z*) calcd for $C_{17}H_{13}FN_2O$ $[M]^+$: 280.1012, found: 280.1004.

Azides **2a-b**[5], **2d**[5], **2e**[6] were synthesized according to reported procedures. The experimental data are in accord with the literatures. The synthesis of **2c**, **2f**, **2g**, and **2h** are shown below.



Ethyl 4-azido-2,3,5,6-tetrafluorobenzoate (2c)

2c was synthesized by SNAr from corresponding ethyl 2,3,4,5,6-pentafluorobenzoate according to literature[7] as a yellow liquid.

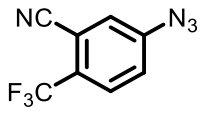
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.43 (q, J = 7.0 Hz, 2H), 1.39 (t, J = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.3, 146.4-146.1 (m), 144.3-144.0 (m), 141.6-141.3 (m), 139.6-139.3 (m), 123.2-123.0 (m), 108.3-107.9 (m), 62.7, 14.0.

^{19}F NMR (282 MHz, $CDCl_3$) δ –139.41 - –139.57 (m, 2F), –151.45 - –151.60 (m, 2F).

IR (film): ν (cm^{-1}) 2990, 2170, 2126, 1733, 1645, 1484, 1419, 1368, 1325, 1250, 1201, 993, 915, 864, 748.

HRMS (ESI, *m*/*z*) calcd for $C_9H_5F_4N_3O_2Na$ $[M+Na]^+$: 286.0210, found: 286.0210.



5-Azido-2-(trifluoromethyl)benzonitrile (2f)

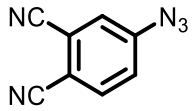
2f was synthesized by diazotization-azidation from corresponding aniline according to literature[5] as a grey solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 8.4 Hz, 1H), 7.38 (d, J = 2.1 Hz, 1H), 7.30 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 145.6, 136.3, 135.3 (q, J = 33.4 Hz), 122.3, 121.8 (q, J = 272.6 Hz), 117.7 (q, J = 5.2 Hz), 115.0, 105.7 (q, J = 1.7 Hz).

IR (film): ν (cm^{-1}) 2387, 2226, 2113, 1606, 1493, 1432, 1314, 1262, 1178, 1124, 1044, 905, 839, 733, 675, 634, 548.

HRMS (ESI, *m*/*z*) calcd for $C_8H_3F_3N_4Na$ $[M+Na]^+$: 235.0202, found: 235.0202.



4-Azidophthalonitrile (2g)

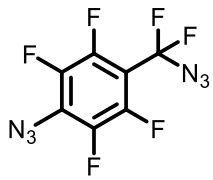
2g was synthesized by diazotization-azidation from corresponding aniline according to literature[5] as a grey solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 1.8 Hz, 1H), 7.35 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.0, 135.1, 123.8, 123.3, 117.7, 115.0, 114.5, 111.3.

IR (film): v (cm^{-1}) 2233, 2122, 1764, 1589, 1558, 1483, 1413, 1306, 1263, 1212, 1173, 1131, 890, 843, 753, 605, 521.

HRMS (ESI, m/z) calcd for $C_8H_3N_5Na$ $[M+Na]^+$: 192.0281, found: 192.0281.



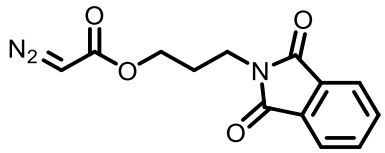
1-(Azidodifluoromethyl)-2,3,4,5,6-pentafluorobenzene (2h)

2h was synthesized by SN from corresponding perfluoro benzylic iodide according to literature[8] as a yellow liquid.

^{19}F NMR (282 MHz, $CDCl_3$) δ –64.19 - –64.92 (m, 2F), –139.56 - –140.22 (m, 2F), –149.90 - –150.93 (m, 2F).

IR (film): v (cm^{-1}) 2126, 1651, 1490, 1426, 1334, 1250, 1164, 1054, 999, 975, 848, 782.

Diazo compounds **3** were synthesized according to reported literature.[9] The experimental data of **3c**, **3e-h** are in accord with the literatures.[9] The data of **3b** and **3d** are shown below.



3-(1,3-Dioxoisoindolin-2-yl)propyl 2-diazoacetate (3b)

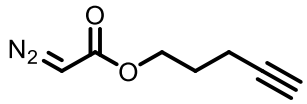
A yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.81 (m, 2H), 7.75-7.68 (m, 2H), 4.69 (s, 1H), 4.21 (t, J = 6.2 Hz, 2H), 3.80 (t, J = 6.9 Hz, 2H), 2.11-2.00 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.2, 134.0, 132.0, 123.3, 62.2, 46.2, 34.9, 27.7. (Missing one ^{13}C signal)

IR (film): v (cm^{-1}) 3104, 2955, 2110, 1771, 1703, 1616, 1464, 1441, 1395, 1362, 1240, 1184, 1048, 986, 899, 794, 718, 526, 501.

HRMS (ESI, m/z) calcd for $C_{13}H_{11}N_3O_4Na$ $[M+Na]^+$: 296.0642, found: 296.0642.



Pent-4-yn-1-yl 2-diazoacetate (3d)

A yellow liquid.

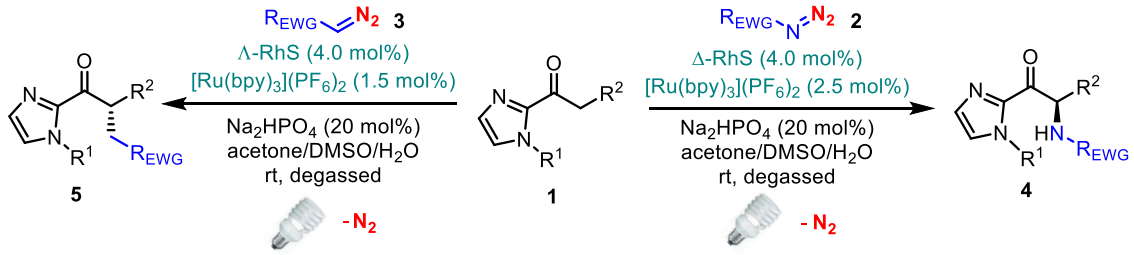
^{1}H NMR (300 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.25 (t, J = 6.2 Hz, 2H), 2.27 (td, J_1 = 7.2 Hz, J_2 = 2.7 Hz, 2H), 1.96 (t, J = 2.7 Hz, 1H), 1.91-1.82 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.6, 82.8, 69.0, 63.3, 46.0, 27.7, 15.1.

IR (film): v (cm^{-1}) 3296, 3114, 2961, 2107, 1682, 1443, 1396, 1359, 1296, 1239, 1179, 1086, 1035, 992, 738, 635, 556, 479.

HRMS (ESI, m/z) calcd for $C_7H_8N_2O_2Na$ $[M+Na]^+$: 175.0478, found: 175.0478.

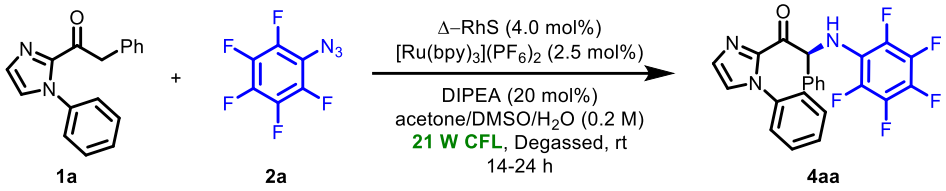
3. General Procedure



A dried 10 mL Schlenk tube was charged with 2-acyl imidazole **1** (0.10 mmol), Δ/Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol% or 1.3 mg, 1.5 mol%) and Na_2HPO_4 (2.8 mg, 20 mol%). The tube was purged with nitrogen. Then acetone/DMSO (9:1, 0.5 mL, 0.2 M) was added via syringe, followed by H_2O (36.0 mg, 20 equiv). Azide **2** or diazo compound **3** (3.0 equiv) was added under nitrogen atmosphere with stirring. The reaction mixture was degassed via freeze-pump-thaw for three cycles. After the mixture was thoroughly degassed, the vial was sealed and positioned approximately 5 cm from a 21 W compact fluorescent lamp. The reaction was stirred at room temperature for the indicated time (monitored by TLC) under nitrogen atmosphere. Afterwards, the mixture was diluted with CH_2Cl_2. The combined organic layers were concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (*n*-hexane/EtOAc) to afford the products **4** or **5**. Racemic samples were obtained by carrying out the reactions with *rac*-**RhS**. The enantiomeric excess was determined by chiral HPLC analysis.

4. Screening of Reaction Conditions

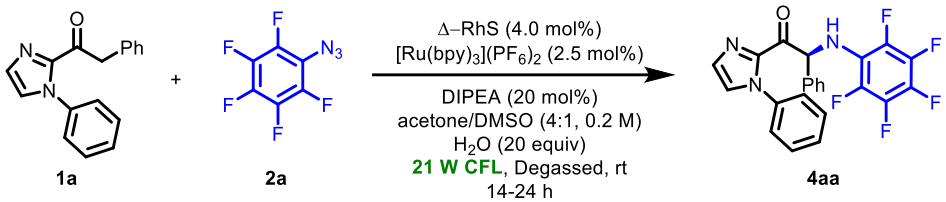
Table S1. Effect of Solvent Ratio[a]



entry	acetone/DMSO	H_2O (equiv)	result
1	4:1	0	61% yield; 97.1% ee
2	4:1	5	64% yield; 97.7% ee
3	4:1	20	70% yield; 97.7% ee
4	4:1	50	68% yield; 97.9% ee
5	1:0	20	65% yield; 96.9% ee
6	**9:1**	**20**	**77% yield; 98.1% ee**
7	1:1	20	71% yield; 96.0 % ee

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), Δ-**RhS** (4.0 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), DIPEA (20 mol%) and H_2O in acetone/DMSO (0.2 M) were stirred at room temperature for 14-24 h with visible light.

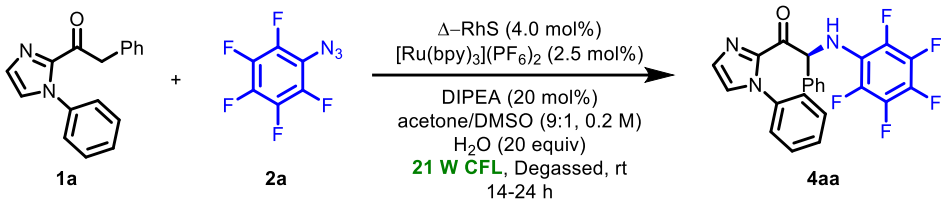
Table S2. Effect of Photoredox Catalysts[a]



entry	photoredox catalyst	result
1	**$[Ru(bpy)_3](PF_6)_2$**	**70% yield; 97.7% ee**
2	$[Ir(ppy)_2(dtbbpy)](PF_6)$	62% yield; 97.8% ee
3	*fac*-$Ir(ppy)_3$	37% yield; 89% ee
4[b]	Δ–IrS	0% yield

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), Δ-**RhS** (4.0 mol%), photoredox catalyst (2.5 mol%), DIPEA (20 mol%) and H_2O in acetone/DMSO (0.2 M) were stirred at room temperature for 14-24 h with visible light. [b]Without **RhS**.

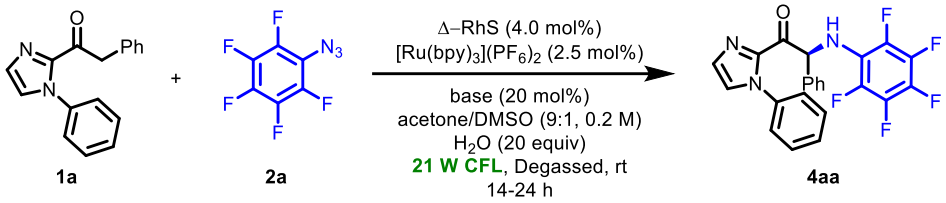
Table S3. Effect of the Amount of Azide[a]



entry	**2a** (equiv)	result
1	1.2	51% yield; 97.8% ee
2	2.0	65% yield; 97.9% ee
3	**3.0**	**77% yield; 98.1% ee**

[a]Reaction conditions: **1a** (0.10 mmol), **2a**, Δ-**RhS** (4.0 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), DIPEA (20 mol%) and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature for 14-24 h with visible light.

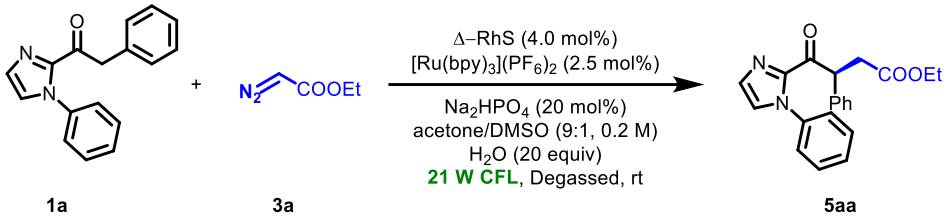
Table S4. Effect of Different Bases[a]



entry	base (20 mol%)	result
1	DIPEA	77% yield; 98.1% ee
2	2,6-lutidine	73% yield; 98.0% ee
3	**Na_2HPO_4**	**82% yield; 98.4% ee**
4[b]	NaOAc	< 10% yield
5[c]	Na_2CO_3	< 5%
6[c]	K_3PO_4	0%

[a]Reaction conditions: **1a** (0.10 mmol), **2a** (0.30 mmol), Δ-**RhS** (4.0 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), base (20 mol%) and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature for 14-24 h with visible light. [b]Low conversion. [c]Full conversion with the decomposition of **4aa**.

Table S5. Control Experiments of Alkylation[a]



1a **3a** **5aa**

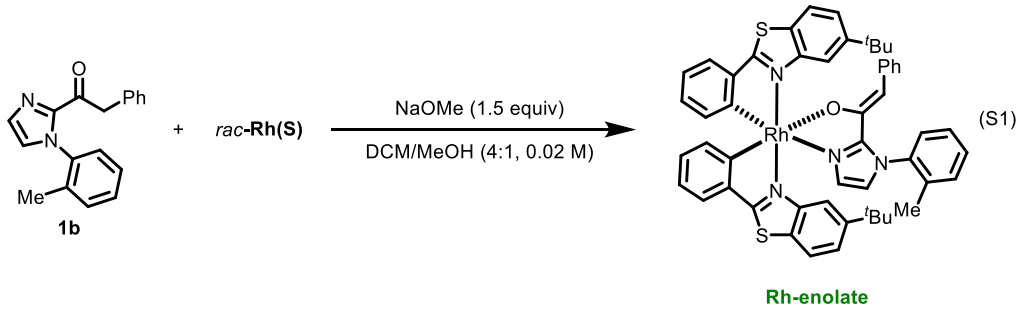
entry	variation	results
1	none	6 h, 93% yield, 92% ee
2	without $[Ru(bpy)_3](PF_6)_2$	No reaction
3	without **21 W CFL**	No reaction

[a]Reaction conditions: **1a** (0.10 mmol), **3a** (0.30 mmol), Δ-**RhS** (4.0 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol%), Na_2HPO_4 (20 mol%) and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature for 15 h with visible light.

5. Mechanistic Studies

5.1 Identification of Rh-enolate Intermediate

5.1.1 Synthesis

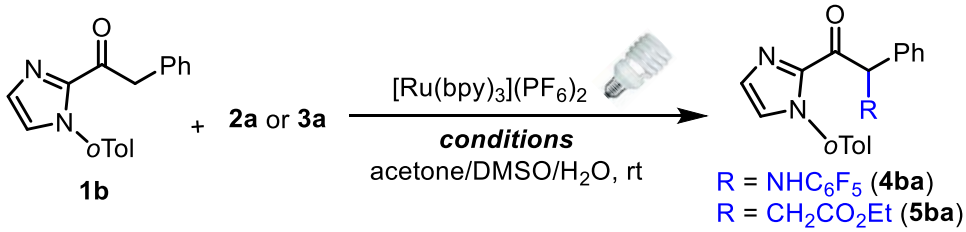


(S1)

As shown in eq S1: MeOH (0.4 mL) and DCM (1.6 mL) were added to a mixture of *rac*-**RhS** (86 mg, 0.1 mmol), imidazole **1b** (33.1mg, 0.12 mmol) and NaOMe (8.1 mg, 0.15 mmol) under N_2 atmosphere. The mixture was stirred at room temperature overnight. Then solvents were removed in vacuo and the mixture was filtered through a short silica column with EA/*n*-hexane. The yellow elution fraction was collected, evaporated and the obtained yellow solid was recrystallized by DCM/*n*-hexane giving pure **Rh-enolate**, which was characterized by X-ray diffraction (see part 9).

5.1.2 Catalytic behavior

Table S6. Catalytic Behavior of **Rh-enolate**



entry	reagent	*conditions*	products
1[a]	**2a**	**RhS** + Na_2HPO_4	**4ba**, 79%
2[b]	**2a**	**Rh-enolate**	**4ba**, 74%
3[a]	**3a**	**RhS** + Na_2HPO_4	**5ba**, 99%
4[b]	**3a**	**Rh-enolate**	**5ba**, 99%

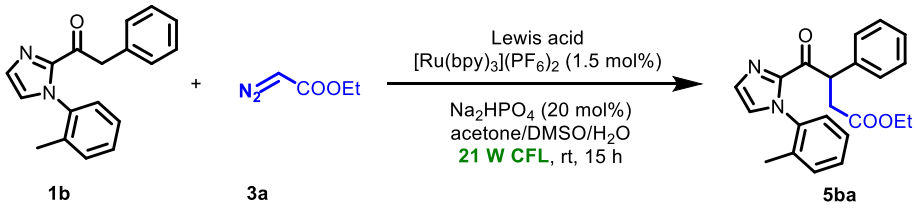
[a]Reaction conditions: **1b** (0.10 mmol), **2a/3a** (0.30 mmol), **RhS** (4.0 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol% for entry 1, 1.5 mol% for entry 3), Na_2HPO_4 (20 mol%) and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature with visible light. [b]Reaction conditions: **1b** (0.096 mmol), **2a/3a** (0.30 mmol), **Rh-enolate** (0.004 mmol), $[Ru(bpy)_3](PF_6)_2$ (2.5 mol% for entry 2, 1.5 mol% for entry 4), **Na_2HPO_4 (0 mol%)** and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature with visible light.

As shown in Table S6, comparable yields to **RhS**/base were observed with rhodium-enolate as the catalyst in the absence of any base, providing alternative base-free conditions for these amination/alkylation. These results support that the rhodium-enolate serves as a key intermediate in these transformations.

5.1.3 Superiority of Rh-base Lewis acid

As shown in Table S7, chiral-at-metal Rh complex shows unique reactivity in this transformation. Other Lewis acid, such as $Sc(OTf)_3$, $FeCl_3$, and $Cu(OAc)_2$ could not catalyze the reaction.

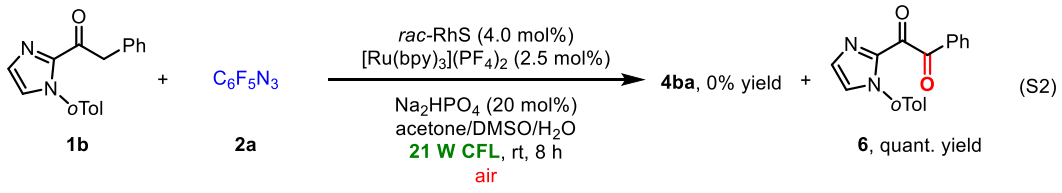
Table S7. Comparison of Lewis Acid[a]

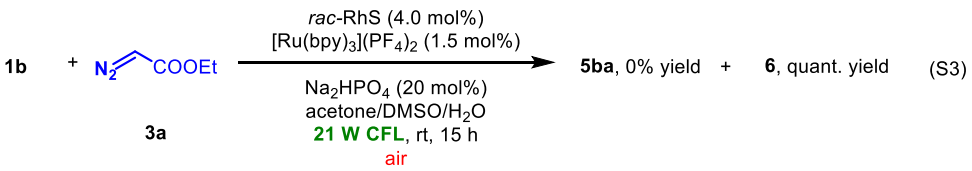


entry	**Lewis acid**	results
1	**RhS (4.0 mol%)**	99% yield; 97% ee
2	$Sc(OTf)_3$ (20 mol%)	No reaction
3	$Zn(OTf)_2$ (20 mol%)	20% yield
4	$FeCl_3$ (20 mol%)	No reaction
5	$Cu(OAc)_2$ (20 mol%)	No reaction

[a]Reaction conditions: **1b** (0.10 mmol), **3a** (0.30 mmol), Lewis acid, $[Ru(bpy)_3](PF_6)_2$ (1.5 mol%), Na_2HPO_4 (20 mol%) and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature for 15 h with visible light.

5.2 Trapping Experiments with Air





As shown in eqs S2-S3, when the reaction was conducted under air atmosphere, no target molecules **4ba** or **5ba** was formed, respectively. Quantitative yield of diketone **6** was obtained, which implies that α-carbonyl carbon radical might be involved.

1-Phenyl-2-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethane-1,2-dione (6)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.67-7.58 (m, 1H), 7.53-7.20 (m, 8H), 2.14 (s, 3H).

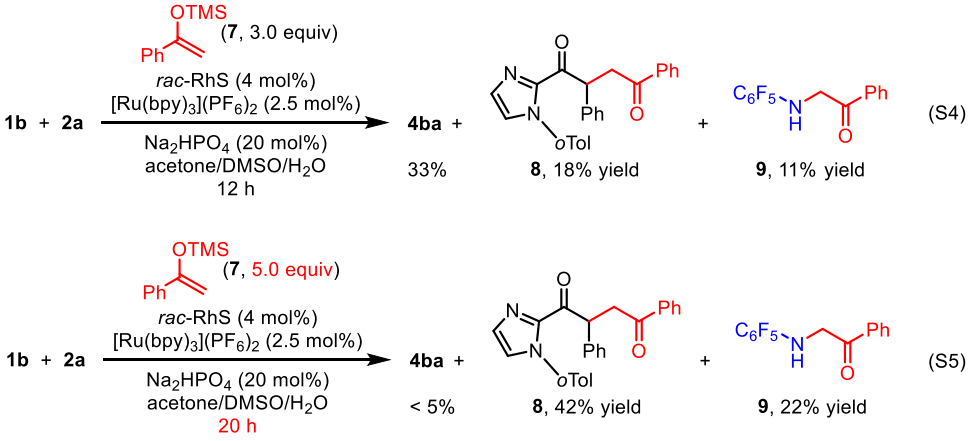
^{13}C NMR (125 MHz, $CDCl_3$) δ 192.5, 183.6, 141.4, 136.5, 134.6, 134.5, 132.7, 132.3, 131.0, 129.8, 129.7, 128.9, 127.4, 126.9, 126.5, 17.3.

IR (film): ν (cm^{-1}) 3125, 3059, 2921, 1671, 1587, 1498, 1452, 1394, 1311, 1262, 1149, 1071, 860, 794, 761, 720, 663, 551, 527, 453.

HRMS (ESI, *m*/*z*) calcd for $C_{18}H_{15}N_2O_2$ $[M+H]^+$: 291.1128, found: 291.1128.

5.3 Trapping Experiments with TMS-enolate

5.3.1 Trapping with amination reaction



When the TMS-enolate **7** (3.0 equiv) was added to the reaction of **1b** with **2a**, the C-C and C-N bond formation products **8** (18% yield) and **9** (11% yield) were isolated, respectively (eq S4). When 5.0 equiv of **7** was employed, **8** and **9** were isolated with improved yields (42%, 22% respectively) (eq S5). These results indicate the intermediate formation of an α-carbonyl carbon radical and aminyl radical.

2,4-Diphenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butane-1,4-dione (8)

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.96-7.90 (m, 2H), 7.57-7.17 (m, 13H), 7.06-7.03 (m, 1H), 6.95 (d, *J* = 7.8 Hz, 1H, the other rotamer), 6.84-5.75 (m, 1H), 4.13-4.00 (m, 1H), 3.42-3.30 (m, 1H), 2.08 (s,

3H), 1.62 (s, 3H, the other rotamer).

^{13}C NMR (75 MHz, $CDCl_3$) δ 197.5, 189.6, 189.5, 143.2, 143.1, 138.3, 138.2, 138.1, 138.0, 136.53, 136.49, 135.2, 134.3, 133.0, 130.6, 130.4, 130.2, 128.9, 128.8, 128.7, 128.4, 128.0, 127.2, 127.1, 126.7, 126.5, 126.3, 126.21, 126.19, 126.1, 48.10, 48.06, 43.2, 42.7, 17.1, 16.5. (Mixture of two rotation isomers).

IR (film): ν (cm^{-1}) 3060, 3031, 2913, 1679, 1591, 1495, 1451, 1403, 1360, 1306, 1247, 1203, 1150, 1015, 989, 944, 907, 759, 726, 692, 591, 552, 523, 456.

HRMS (EI, *m*/*z*) calcd for $C_{26}H_{23}N_2O_2$ $[M+H]^+$: 395.1754, found: 395.1756.

2-((Perfluorophenyl)amino)-1-phenylethan-1-one (9)

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00-7.94 (m, 2H), 7.69-7.61 (m, 1H), 7.56-7.47 (m, 2H), 4.96 (br s, 1H), 4.83 (br s, 2H).

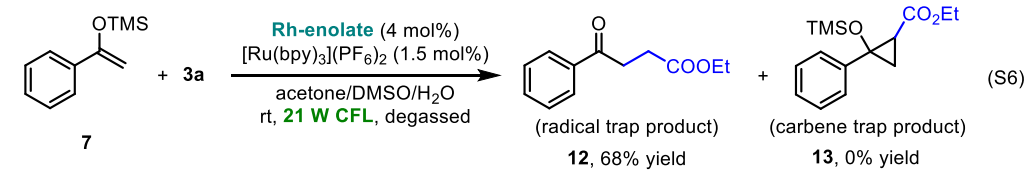
^{13}C NMR (75 MHz, $CDCl_3$) δ 194.5, 134.3, 134.2, 129.0, 127.8, 52.0-51.7 (m).

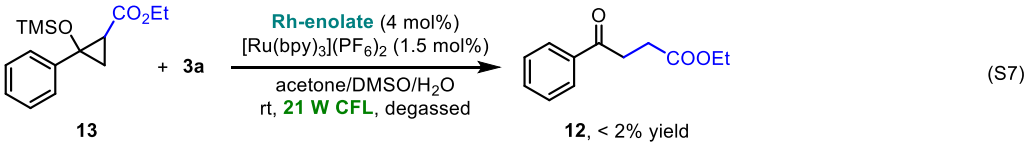
^{19}F NMR (282 MHz, $CDCl_3$) δ –160.78 - –160.95 (m, 2F), –165.05 - –165.26 (m, 2F), –172.40 (tt, J_1 = 21.15 Hz, J_2 = 6.49 Hz, 1F).

IR (film): ν (cm^{-1}) 3401, 2956, 2923, 2852, 1686, 1518, 1439, 1344, 1266, 1229, 1188, 1118, 995, 950, 755, 684, 606, 583, 558, 473.

HRMS (EI, *m*/*z*) calcd for $C_{14}H_8F_5NO$ $[M]^+$: 301.0526, found: 301.0517.

5.3.2 Trapping with diazo compound



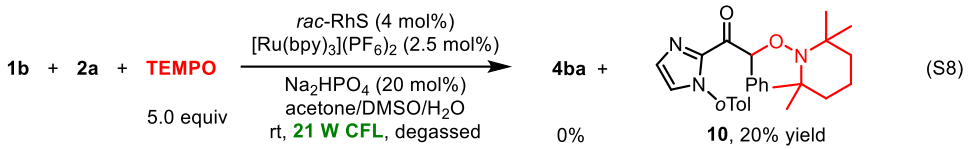


As shown in eq S6, when the TMS-enolate **7** was stirred with **3a** under current conditions, 68% of the radical addition product **12** was detected, instead of the cyclopropanation product **13**. Furthermore, **13** cannot be converted into **12** under these reaction conditions (eq S7). These results exclude the

possibility of carbene intermediates. **13** was synthesized according to literature report.[10] All spectroscopic data of **12**[11] and **13**[10] are in agreement with previous reports.

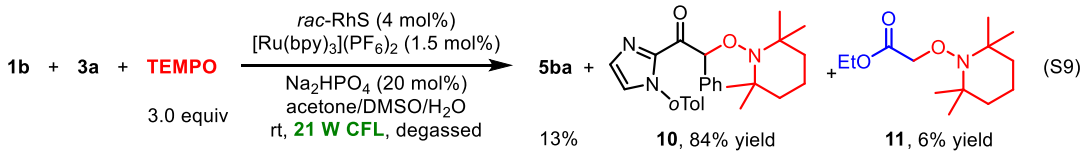
5.4 Trapping Experiments with TEMPO

5.4.1 Trapping with amination reaction



As shown in eq S8, when the TEMPO (5.0 equiv) was added to the reaction mixture of **1b** with **2a** under current conditions, the TEMPO adduct **10** was isolated in 20% yield and the formation of **4ba** was totally inhibited, indicating that α-carbonyl carbon radicals might be involved in amination reaction. All spectroscopic data of **10** are in agreement with our previous report.[4c]

5.4.2 Trapping with alkylation reaction



When the TEMPO (3.0 equiv) was added to the reaction mixture of **1b** with **3a** under current conditions, the TEMPO adducts **10** (84% yield) and **11** (6% yield) were isolated, respectively, being indicative for two types of intermediate α-carbonyl carbon radicals (eq S9). All spectroscopic data of **11** are in agreement with literature report.[12]

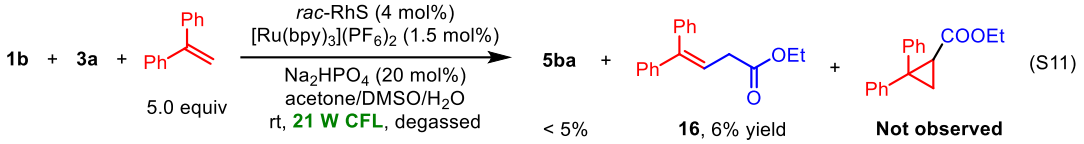
5.5 Trapping Experiments with Alkenes

5.5.1 Trapping with amination reaction

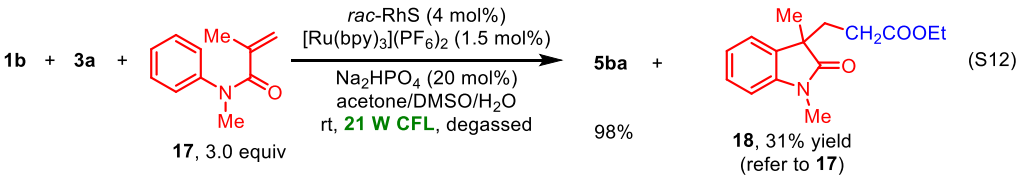
When the styrene (5.0 equiv) was added to the reaction mixture of **1b** with **2a** under current conditions, the amination product **4ba** was detected in 80% yield, while aziridination product was not observed

(S10). These results imply nitrene intermediate might not be involved in this transformation, which is thus distinct from Yoon's recent report.[13]

5.5.2 Trapping with alkylation reaction



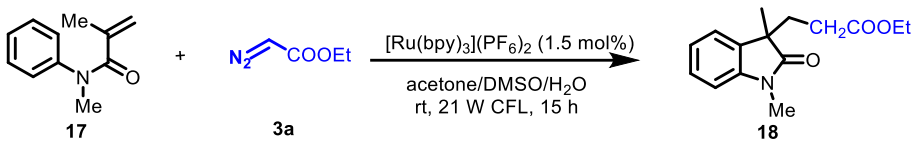
As shown in eq S11, when the 1,1-diphenylethene (5.0 equiv) was added to the reaction mixture of **1b** with **3a** under current conditions, the alkylation was totally inhibited. And **16**[14] was obtained in 6% yield via radical addition and subsequent oxidation processes, while cyclopropanation product was not observed. These results indicate that a radical process rather than a carbene insertion pathway is involved.



When the alkene **17** (3.0 equiv) was added to the reaction mixture of **1b** with **3a** under current conditions, the alkylation product **5ba** was detected in 98% yield, together with the formation of radical cycloaddition product **18** (eq S12). These results support that an α-ester carbon radical derived from diazo compound **3a** was formed during the alkylation reaction. All spectroscopic data of **18** are in agreement with literature report.[15]

Substrate **3a** with the relatively highly negative reduction potential (E_p^{red} = -1.97 V, vs Fc/Fc^+, see Figure S5) cannot quench the excited state of $[Ru(bpy)_3]^{2+}$ ($E_{1/2}^{III/*II}$ = -0.81 V, vs SCE in MeCN) via an oxidative quenching cycle. Therefore, the reaction of **17** and **3a** under conditions listed in entry 1, Table S8, cannot deliver any product. When a catalytic amount of DIPEA or **Rh-enolate** was added as a reductive quencher, **18** can be observed in 20% NMR yield (Table S8, entries 2-3). However, *fac*-$Ir(ppy)_3$, which is a very strong SET reductant in excited state [Ir(IV)/Ir(III)* = -1.73 V], failed to catalyze this reaction (entry 4). All these results support the conclusion that the **Rh-enolate** intermediate acts as a **reductive quencher**.

Table S8. Investigation of **Rh-enolate** as a Reductive Quencher[a]



entry	additive	NMR yield of **17** (%)
1	Na_2HPO_4 (20 mol%)	0
2	DIPEA (20 mol%)	20
3	Rh-enolate (4 mol%)	20
4[b]	*fac*-Ir(ppy)$_3$ (1.5 mol%)	0

[a]Reaction conditions: **17** (0.10 mmol), **3a** (0.30 mmol), $[Ru(bpy)_3](PF_6)_2$ (1.5 mol%), additives and H_2O (20 equiv) in acetone/DMSO (9:1, 0.2 M) were stirred at room temperature for 15 h with visible light; [b]Without $[Ru(bpy)_3](PF_6)_2$, THF as solvent.

5.6 EPR Experiments

EPR spectra were recorded at room temperature using DMPO as free radical spin trapping agent. As shown in Figure S1, according to general procedure, the reaction of **1b** and **3a** was stirred under standard conditions for 60 min. Then a portion of the reaction mixture was added to DMPO solution and measured by EPR. Signals with 6 lines (g=2.006; α_N = 15.9 G, α_H^{β} = 22.5 G) were observed and identified as EPR signals of adducts **14**, which are in good agreement with literature (Figure S1).[16] All these results support the formation of an ethyl acetate α-carbon radical through single electron reduction of the diazo compound **3a**.

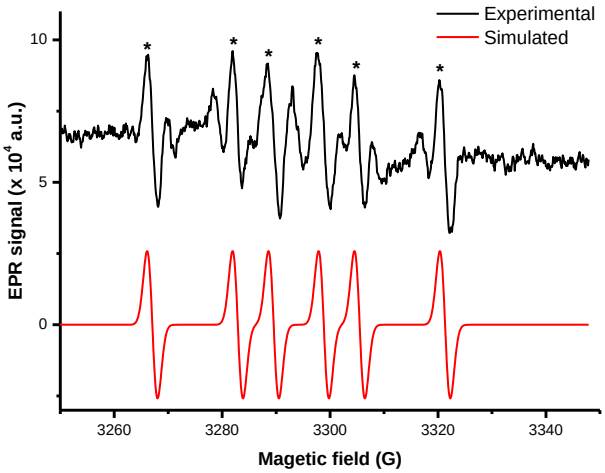


Figure S1. EPR experiments (X band, r.t.). After 60 min of irradiation, a portion of the reaction mixture was added to DMPO solution and then measured by EPR.

5.7 Stern-Volmer Quenching Experiments

5.7.1 UV-Vis absorption spectra and luminescence emission spectra

As shown in Figure S2, **Rh-enolate** solution absorb light with wavelength < 475 nm. In order to stimulate the reaction conditions, the luminescence quenching experiments were performed with the photoredox sensitizer $[Ru(bpy)_3]^{2+}$ alone and with the mixture of $[Ru(bpy)_3]^{2+}$ and **Rh-enolate** in a ratio of 1.5 : 4.0, respectively. Also in the luminescence quenching experiments with the $[Ru(bpy)_3]^{2+}$ alone, different exciting light wavelengths were chosen.

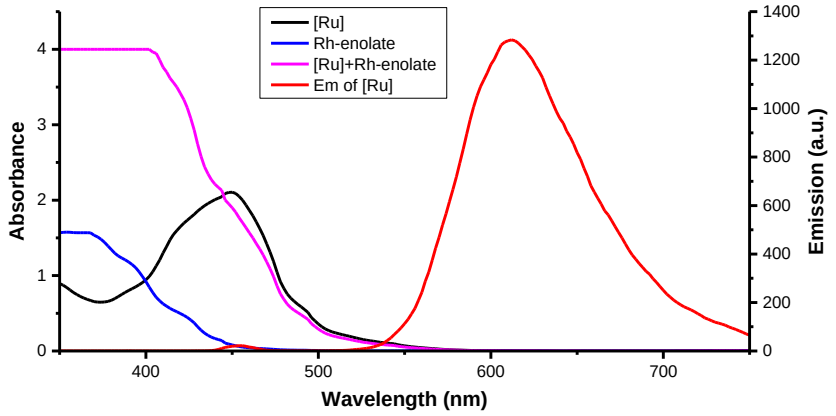


Figure S2. UV-Vis absorption spectra and luminescence emission spectra. [Ru] = $[Ru(bpy)_3]^{2+}$; Concentration in solution of acetone/DMSO/H_2O (9:1:0.72): [Ru] = 0.05 mM, **Rh-enolate** = 0.05 mM, [Ru]+**Rh-enolate** = 0.1 mM/0.27 mM, Em of [Ru] = 0.10 mM.

5.7.2 Quenching experiments with the mixture of $[Ru(bpy)_3]^{2+}$ and Rh-enolate

The solutions of $[Ru(bpy)_3]^{2+}$ and **Rh-enolate** (0.1 mM and 0.27 mM in acetone/DMSO/H_2O, respectively) were excited at λ = 470 nm and the emission was measured at 610 nm (emission maximum). For each quenching experiment, after degassed with a nitrogen stream for 5 minutes, the emission intensity of the solution (1 mL) of $[Ru(bpy)_3]^{2+}$ and **Rh-enolate** with different concentration of quencher (0, 0.5, 1.0, 2.0, 4.0 mM) in a screw-top 10.0 mm quartz cuvette was collected.

Results: imidazole **1b**, azide **2a**, diazo compound **3a**, and TMS-enolate **7** could not quench the luminescence.

5.7.3 Quenching experiments with $[Ru(bpy)_3]^{2+}$ alone

The solutions of $[Ru(bpy)_3]^{2+}$ in acetone/DMSO/H_2O were excited at λ = 470 nm and the emission

was measured at 610 nm (emission maximum). For each quenching experiment, after degassed with a nitrogen stream for 5 minutes, the emission intensity of the solution (1 mL) of $[Ru(bpy)_3]^{2+}$ with different concentration of quencher (0, 0.5, 1.0, 2.0, 4.0 mM) in a screw-top 10.0 mm quartz cuvette was collected.

Results: imidazole **1b**, azide **2a**, diazo compound **3a**, and TMS-enolate **7** and *rac*-**RhS** could not quench the luminescence. Only **Rh-enolate** was capable of quenching the excited state of $[Ru(bpy)_3]^{2+}$. In order to exclude the effect of competitive absorption by **Rh-enolate**, the solutions of $[Ru(bpy)_3]^{2+}$ with different concentration of **Rh-enolate** (0, 0.5, 1.0, 2.0, 4.0 mM) were excited at λ = 470 nm, 510 nm, and 530 nm, respectively. At the same time, the absorbance of the mixture was measured as well. As shown in Figure S3, the absorption of the mixture kept constant with the increment of **Rh-enolate** indicating there is no competitive absorption by **Rh-enolate** in 530 nm. And only the intermediate **Rh-enolate**, but not the catalyst **RhS** or the TMS-enolate **7**, can quench the excited state of the $[Ru(bpy)_3]^{2+}$. Furthermore, the quenching effect of **Rh-enolate** was similar in different exciting light wavelengths (Figure S4).

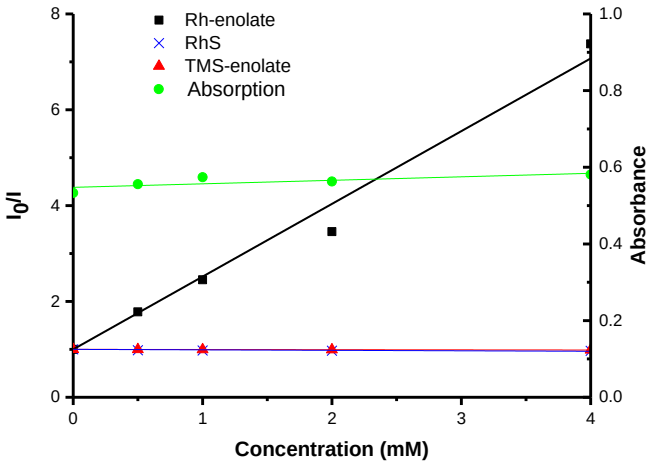


Figure S3. Stern-Volmer plots. I_0 and I are respective luminescence intensities in the absence and presence of the indicated concentrations of the corresponding quencher. [Ru] = 0.5 mM, Ex = 530 nm, Absorption refer to the absorbance of the solutions of $[Ru(bpy)_3]^{2+}$ with different concentration of **Rh-enolate**.

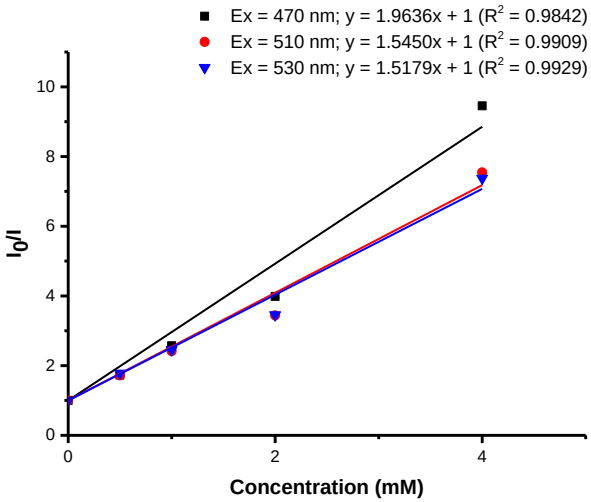


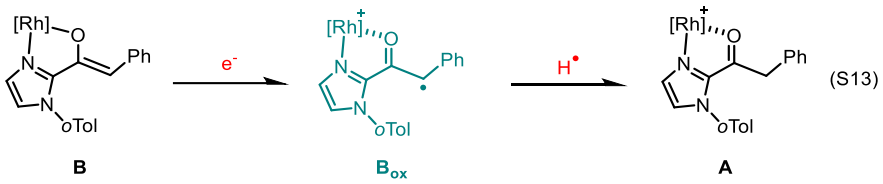
Figure S4. Quenching effect of **Rh-enolate** with different exciting light wavelengths.

5.8 Cyclic Voltammetry

Experiment details: Voltammetric experiments were conducted with a computer controlled Eco Chemie Autolab PGSTAT302N potentiostat in a Metrohm electrochemical cell containing 1 mm diameter planar platinum and glassy carbon (GC) disk electrodes (eDAQ), a platinum wire auxiliary electrode (Metrohm) and a silver wire miniature reference electrode (eDAQ) that was connected to the test solution via a salt bridge containing 0.5 M nBu$_4$NPF$_6$ in CH$_3$CN. Accurate potentials were referenced to the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple, which was used as an internal standard. All solutions used for the voltammetric experiments were deoxygenated by purging with high purity argon gas and measurements were performed in a Faraday cage at room temperature (22 ± 2 ^{o}C). HPLC purity acetonitrile (CH$_3$CN) was purchased from Macron. The supporting electrolyte, tetrabutylammonium hexafluorophosphate (nBu$_4$NPF$_6$), was prepared by reacting equal molar amounts of nBu$_4$NOH (40%, Alfa Aesar) and HPF$_6$ (65%, Fluka), washing the precipitate with ultrapure water and recrystallizing three times with hot ethanol followed by drying under vacuum at 140 °C for 6 hours.

Results and discussion: As shown in Figure S5, both **RhS** and **Rh-enolate** were able to undergo an oxidation process in a chemically irreversible way at positive potentials between ~ 1.0 - 1.4 V vs Fc/Fc$^+$. Importantly, **Rh-enolate** has an additional chemically irreversible oxidation peak at approximately +0.08 V *vs.* Fc/Fc$^+$, which means it could be easily oxidized at a relative low potential

(~0.08 V vs Fc/Fc^+) to form a new compound that is itself further oxidized at more positive potentials. Different from **RhS**, which could be reduced in a chemically irreversible process at ~ –1.8 - –2.1 V vs Fc/Fc^+, no reduction process is seen for **Rh-enolate** unless the potential is first scanned in the positive direction past 0.08 V vs Fc/Fc^+. Therefore, it is likely that **Rh-enolate** undergoes SET oxidation at the enolate (E_p^{ox} = 0.078 V, vs Fc/Fc^+), generating Rh-coordinated radical intermediate $\mathbf{B}_{ox}$. And the subsequent gain of a hydrogen atom forms a Rh-coordinated substrate intermediate **A**, which then can become reduced (eq S13).



(S13)

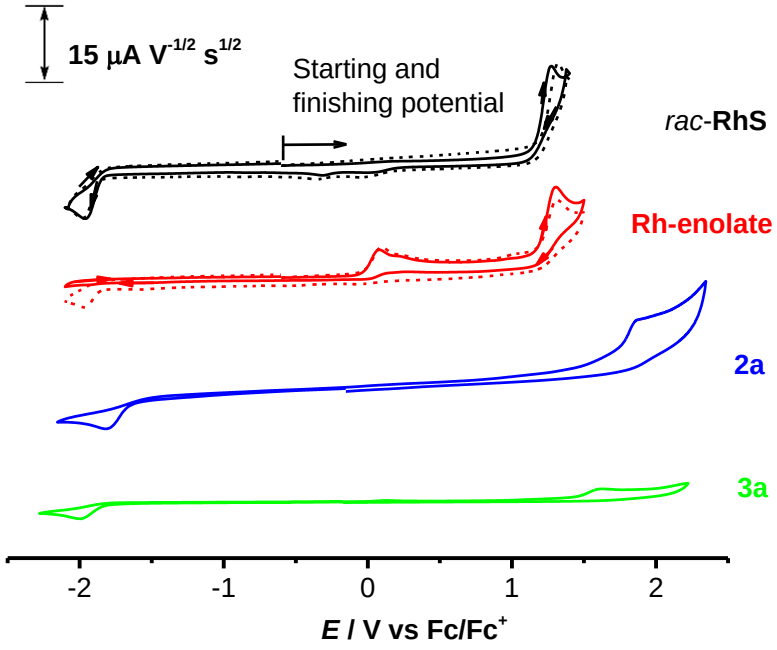


Figure S5. Cyclic voltammograms of **RhS**, **Rh-enolate**, **2a** and **3a**. Recorded in CH_3CN containing 0.1 M *n*-Bu_4NPF_6 at 22 ± 2 °C at a 1 mm diameter GC electrode for 1 mM solutions of the analytes. (–) Scan rate = 0.1 V s^{-1}, and (⋯) scan rate = 1 V s^{-1}. The current data were normalised by dividing by the square root of the scan rate.

The compounds **2a** and **3a** can both be reduced in a chemically irreversible way at relatively negative potentials that are similar to the other compound. As shown in Figure S5, **2a** has a chemically

irreversible reduction peak at -1.82 V vs Fc/Fc^+, while **3a** at -1.97 V vs Fc/Fc^+. These results, in consistence with quenching experiments, demonstrate that the excited state of $[Ru(bpy)_3]^{2+}$ ($E_{1/2}^{III/*II}$ = –0.81 V, vs SCE in MeCN)[17a] cannot reduce azide **2a** or diazo compound **3a**. On the contrary, the SET process from the strongly reducing $[Ru(bpy)_3]^+$ ($E_{1/2}^{II/I}$ = –1.33V, vs SCE in MeCN; < –1.7 V, vs Fc/Fc^+)[17], which could be formed via reductive quenching of [Ru]* by **Rh-enolate** as demonstrated above, to the organic azide or diazo reagent is more feasible.

In summary, **Rh-enolate** (E_p^{ox} = 0.078 V, vs Fc/Fc^+ in MeCN) has a significantly lower oxidative potential than **RhS** (E_p^{red} = 1.25 V, vs Fc/Fc^+ of MeCN). All these results, in combination with other mechanistic studies, strongly suggest that SET oxidation of **Rh-enolate** by excited $[Ru^{II}]$* ($E_{1/2}^{*II/I}$ = +0.77 V, vs SCE in MeCN) is the key step of the photoredox cycle. A SET reduction of **2a** or **3a** by hereby generated $[Ru(bpy)_3]^+$ is also feasible.

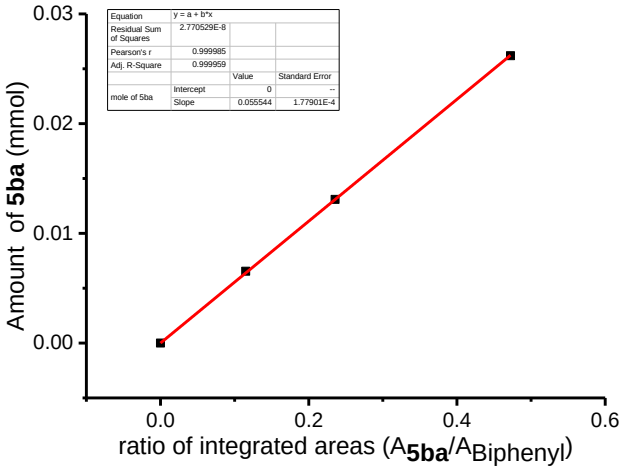
5.9 Quantum Yield Measurement

5.9.1 General information

All the light sensitive operations were processed in the darkroom under red light. A 150 W xenon lamp (50% of light intensity, 420 ± 5 nm bandpass filter) was used as the light source. The measured method was designed according to a published procedure with slight modifications.[18] Photon flux of the spectrophotometer was determined as 7.32×10^{-10} einstein/s by standard ferrioxalate actinometry.

5.9.2 Determination of response factor for GC analysis

Biphenyl was chosen as the internal standard, the amount of which remained constant for every GC measurement (FID detector, column: HP-5). The amount of product **5ba** is related to the ratios of integrated areas (see figure below).



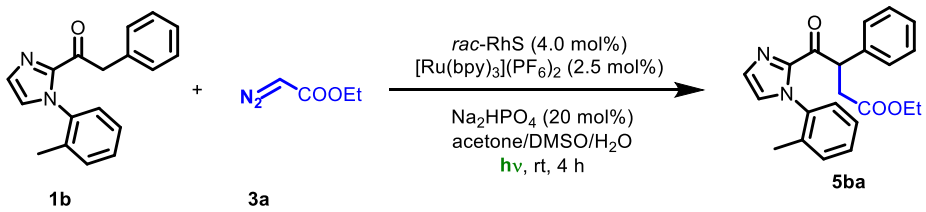
The relation formula was yielded as:

$y = 5.554 \times 10^{-2}x$

Where y is the amount of product **5ba (**mmol), x is the ratio of integrated areas.

5.9.3 Measurement of quantum yield

Model reaction:



The Newport instrument for quantum yield determination was set up at a fixed position in a dark room (red light). A screw-top cuvette (10.0 mm) was charged with **1b** (55.2 mg, 0.2 mmol), **3a** (68.4 mg, 3.0 equiv), *rac*-**RhS** (6.9 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (4.4 mg, 2.5 mol%), Na_2HPO_4 (5.6 mg, 20 mol%) and H_2O (72.0 mg, 20 equiv) in acetone/DMSO (9:1, 1.0 mL, 0.2 M) and a small magnetic stir bar. The cuvette was degassed with an nitrogen stream for 10 min. After the mixture was thoroughly degassed, the vial was sealed and fixed at the same position as the measurement of photon flux. The reaction mixture was stirred and irradiated for 4 h. After irradiation, the reaction mixture was diluted with ethyl acetate. Then, Biphenyl was added and analyzed by GC.

5.9.4 Results and discussion

The amount of **5ba** formed was measured by GC analysis as 1.046×10^{-6} mol.

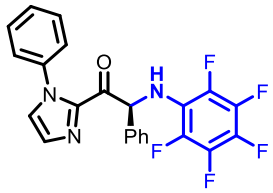
Therefore, the quantum yield was calculated according to the following equation:

$$\Phi = \frac{\text{moles of product}}{\text{moles of absorbed photons}} = \frac{\text{moles of product}}{\text{flux} * t * f} = (1.046 \times 10^{-6}\,\text{mol}) / (7.32 \times 10^{-10} \times 14\,400 \times 1) = 0.099$$

Absorbance of at 420 nm is >3 demonstrating that the fraction of light absorbed is > 0.999 ($f = 1 - 10^{-A}$).

The photoredox sensitizer absorbs only a fraction of the overall light at 420 nm due to the competitive light absorption from present rhodium-enolate intermediate (inner filter effect, see Figure S2). Thus, the quantum yield with respect to the photoredox sensitizer $[Ru(bpy)_3](PF_6)_2$ at 420 nm is > 0.099. This value presents overall quantum yield and does not take into account that there is no chain process in this system.

6. Experimental and Characterization Data of Products



(*S*)-2-((Perfluorophenyl)amino)-2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (4aa)

According to the general procedure, the reaction of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl) ethan-1-one **1a** (26.2 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 8 hours, afforded 36.3 mg (82%) of **4aa** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 98% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 5.7 min, t_r (minor) = 4.9 min). $[\alpha]_D^{22}$ = +150.0° (*c* 1.0, CH_2Cl_2).

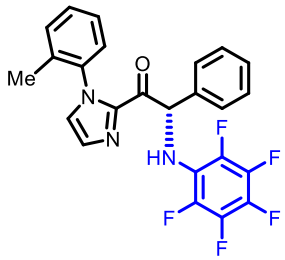
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.54 (m, 5H), 7.33 (d, *J* = 1.0 Hz, 1H), 7.32-7.27 (m, 2H), 7.26-7.21 (m, 1H), 7.18 (d, *J* = 0.5 Hz, 1H), 7.14-7.11 (m, 2H), 6.74 (d, *J* =9.0 Hz, 1H), 5.36 (d, *J* = 9.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.1, 140.8, 137.7, 136.8, 130.5, 129.11, 129.07, 128.8, 128.4, 128.1, 127.7, 125.5, 63.4-63.2 (m).

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.35 - –157.51 (m, 2F), –164.25 - –164.46 (m, 2F), –170.41 (tt, J_1 = 22.28 Hz, J_2 = 5.92 Hz, 1F).

IR (film): *v* (cm^{-1}) 3367, 1688, 1596, 1517, 1449, 1398, 1346, 1305, 1263, 1188, 1154, 1107, 1072, 1021, 976, 911, 839, 761, 732, 694, 625, 585, 548, 526, 498, 461.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{14}F_5N_3ONa$ $[M+ Na]^+$: 466.0949, found: 466.0946.



(*S*)-2-((Perfluorophenyl)amino)-2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4ba)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2- yl)ethan-1-one **1b** (27.6 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 13 hours, afforded 36.1 mg (79%) of **4ba** as a white solid . Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.1% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 7.5 min, t_r (minor) = 6.8 min). $[\alpha]_D^{22}$ = +156.4° (*c* 1.0, CH_2Cl_2).

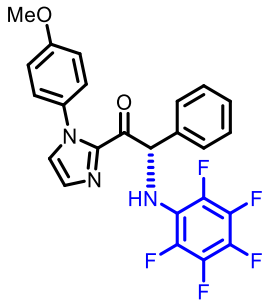
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.31 (m, 5H), 7.30-7.18 (m, 5H), 7.09 (d, *J* = 1.0 Hz, 1H), 6.78 (d, *J* = 8.0 Hz, 1H, other rotamer), 6.76-6.68 (m, 1H), 5.41-5.28 (m, 1H), 2.04 (s, 3H, other rotamer), 1.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 185.9, 141.3, 141.2, 137.2, 137.1, 136.7, 134.7, 134.2, 130.81, 130.78, 130.7, 129.5, 129.4, 128.8, 128.7, 128.4, 128.3, 128.1, 128.0, 127.18, 127.16 126.7, 126.6, 126.4, 126.0, 63.3 (t, *J* = 3.4 Hz), 63.0 (t, *J* = 3.7 Hz), 17.2, 16.1. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.30 - –157.68 (m, 2F), –164.31 - –164.51 (m, 2F), –170.31 - –170.69 (m, 1F).

IR (film): ν (cm^{-1}) 3370, 2923, 1300, 1686, 1515, 1459, 1400, 1023, 980, 959, 768, 700, 673, 647, 618, 558.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{16}F_5N_3ONa$ $[M+Na]^+$: 480.1106, found: 480.1102.



(*S*)-1-(1-(4-Methoxyphenyl)-1*H*-imidazol-2-yl)-2-((perfluorophenyl)amino)-2-phenylethan-1-one (4ca)

According to the general procedure, the reaction of 1-(1-(4-methoxyphenyl)-1*H*-imidazol-2-yl)-2-phenylethan-1-one **1c** (29.2 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0

equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 6 hours, afforded 37.7 mg (80%) of **4ca** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 99% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 6.3 min, t_r (minor) = 5.3 min). $[\alpha]_D^{22}$ = +173.0° (*c* 1.0, CH_2Cl_2).

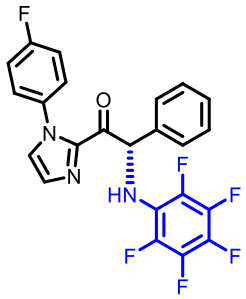
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.44 (m, 2H), 7.32-7.27 (m, 3H), 7.25-7.20 (m, 1H), 7.14 (d, *J* = 1.0 Hz, 1H), 7.07-7.02 (m, 2H), 6.97-6.91 (m, 2H), 6.73 (d, *J* = 9.0 Hz, 1H), 5.36 (d, *J* = 9.0 Hz, 1H), 3.86 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 159.8, 140.8, 136.8, 130.4, 128.8, 128.3, 128.10, 128.06 126.6, 114.2, 63.2 (t, *J* = 3.5 Hz), 55.5. (Missing one ^{13}C signal)

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.74 - –157.90 (m, 2F), –164.67 - –164.89 (m, 2F), –170.85 (tt, J_1 = 22.00 Hz, J_2 = 5.78 Hz, 1F).

IR (film): *v* (cm^{-1}) 3367, 2964, 2791, 1687, 1608, 1515, 1453, 1397, 1346, 1298, 1249, 1177, 1109, 1071, 1020, 976, 911, 836, 779, 732, 698, 675, 625, 585, 499.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{16}F_5N_3O_2Na$ $[M+Na]^+$: 496.1055, found: 496.1054.



(*S*)-1-(1-(4-Fluorophenyl)-1*H*-imidazol-2-yl)-2-((perfluorophenyl)amino)-2-phenylethan-1-one (4da)

According to the general procedure, the reaction of 1-(1-(4-fluorophenyl)-1*H*-imidazol-2-yl)-2-phenylethan-1-one **1d** (28.0 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 14 hours, afforded 34.9 mg (76%) of **4da** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98% (HPLC: AD-H, 254 nm, *n*-

hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 7.0 min, t_r (minor) = 5.4 min). $[\alpha]_D^{22}$ = +150.0° (*c* 1.0, CH_2Cl_2).

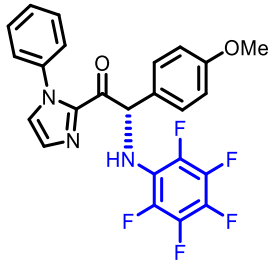
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.32 (d, *J* = 1.0 Hz, 1H), 7.31-7.27 (m, 2H), 7.26-7.21 (m, 1H), 7.16-7.09 (m, 5H), 6.72 (d, *J* = 9.5 Hz, 1H), 5.32 (d, *J* = 9.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.2, 162.6 (d, *J* = 249.3), 140.9, 136.7, 133.6 (d, *J* = 3.3 Hz), 130.7, 128.9, 128.4, 128.1, 127.5, 127.4 (d, *J* = 8.4 Hz), 116.1 (d, *J* = 22.9 Hz), 63.3 (t, *J* = 3.3 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ –111.60 (s, 1F), –157.36 - –157.51 (m, 2F), –164.17 - –164.38 (m, 2F), –170.23 (tt, J_1 = 21.86 Hz, J_2 = 6.06 Hz, 1F).

IR (film): *v* (cm^{-1}) 3368, 1687, 1514, 1452, 1399, 1345, 1310, 1227, 1154, 1099, 1070, 1023, 978, 914, 842, 784, 735, 699, 625, 585, 545, 464, 423.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{14}F_6N_3O$ $[M+H]^+$: 462.1036, found: 462.1031.



(*S*)-2-(4-Methoxyphenyl)-2-((perfluorophenyl)amino)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (4ea)

According to the general procedure, the reaction of 2-(4-methoxyphenyl)-1-(1-phenyl-1*H*- imidazol-2-yl)ethan-1-one **4e** (29.2 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), DIPEA (2.6 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 17 hours, afforded 33.6 mg (71%) of **4ea** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.1% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 10.1 min, t_r (minor) = 8.6 min). $[\alpha]_D^{22}$ = +202.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.42 (m, 3H), 7.39-7.34 (m, 2H), 7.32-7.30 (m, 1H), 7.18-7.10 (m, 1H), 7.15-7.10 (m, 2H), 6.84-6.78 (m, 2H), 6.67 (br s, 1H), 5.30 (br s, 1H), 3.75 (s, 3H).

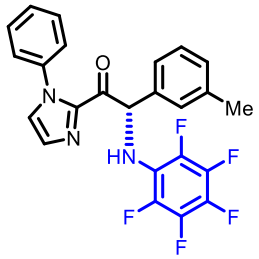
^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 159.5, 140.8, 137.7, 130.5, 129.4, 129.11, 129.06, 128.6, 127.6,

125.6, 114.3, 62.6 (t, J = 3.3 Hz), 55.1.

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.30 - –157.47 (m, 2F), –164.32 - –164.55 (m, 2F), –170.46 (tt, J_1 = 22.00 Hz, J_2 = 5.78 Hz, 1F).

IR (film): ν (cm^{-1}) 3353, 2931, 2963, 1670, 1603, 1512, 1468, 1446, 1399, 1306, 1258, 1175, 1098, 1023, 979, 956, 913, 818, 786, 761, 731, 691, 573.

HRMS (EI, m/z) calcd for $C_{24}H_{16}F_5N_3O_2$ $[M]^+$: 473.1163, found: 473.1173.



(*S*)-2-((Perfluorophenyl)amino)-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(*m*-tolyl)ethan-1-one (4fa)

According to the general procedure, the reaction of 1-(1-phenyl-1*H*-imidazol-2-yl)-2-(*m*-tolyl) ethan-1-one **1f** (27.6 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 7 hours, afforded 35.1 mg (77%) of **4fa** as a brown solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 6.4 min, t_r (minor) = 4.7 min). $[\alpha]_D^{22}$ = +177.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.40 (m, 3H), 7.32 (d, J = 1.5 Hz, 1H), 7.29-7.27 (m, 2H), 7.26-2.24 (m, 2H, other rotamer), 7.23-2.18 (m, 1H), 7.18 (d, J = 1.5 Hz, 1H), 7.17-7.10 (m, 2H), 7.07-7.06 (m, 1H), 7.05-7.03 (m, 1H, other rotamer), 6.69 (d, J = 14.5, 1H), 5.32-5.26 (m, 1H), 2.31 (s, 3H).

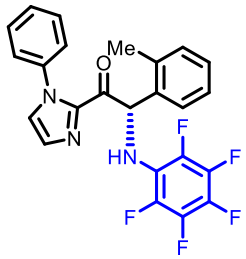
^{13}C NMR (125 MHz, $CDCl_3$) δ 186.2, 140.9, 138.6, 137.7, 136.6, 130.5, 129.2, 129.10, 129.05, 128.7, 127.7, 125.6, 125.2, 63.3 (t, J = 5.9 Hz), 21.4. (Missing one ^{13}C signal)

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.36 - –157.52 (m, 2F), –164.30 - –164.52 (m, 2F), –170.53 (tt, J_1 = 22.00 Hz, J_2 = 5.78 Hz, 1F).

IR (film): ν (cm^{-1}) 3371, 1682, 1519, 1447, 1395, 1306, 1025, 980, 957, 915, 843, 768, 727, 697, 670,

637, 591, 555, 516, 460.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{16}F_5N_3ONa$ $[M+Na]^+$: 480.1106, found: 480.1106.



(*S*)-2-((Perfluorophenyl)amino)-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(*o*-tolyl)ethan-1-one (4ga)

According to the general procedure, the reaction of 1-(1-phenyl-1*H*-imidazol-2-yl)-2-(*o*-tolyl) ethan-1-one **1g** (27.6 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 10 hours, afforded 25.0 mg (55%) of **4ga** as a white solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 98% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 6.0 min, t_r (minor) = 4.6 min). $[\alpha]_D^{22}$ = +214.2° (*c* 1.0, CH_2Cl_2).

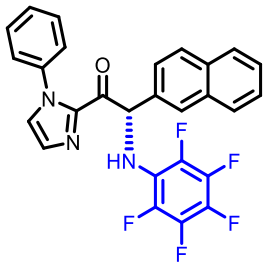
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.41 (m, 3H), 7.25 (d, *J* = 0.5 Hz, 1H), 7.24-7.18 (m, 3H), 7.17-7.14 (m, 2H), 7.14-7.11 (m, 2H), 6.90 (br s, 1H), 4.86 (br s, 1H), 2.72 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 187.3, 141.4, 138.3, 137.7, 135.0, 131.5, 130.3, 129.1, 129.0, 128.6, 127.5, 126.6, 126.4, 125.5, 60.4 (t, *J* = 3.6 Hz), 19.4.

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.40 - –157.56 (m, 2F), –164.25 - –164.47 (m, 2F), –170.29 (tt, J_1 = 22.00 Hz, J_2 = 5.64 Hz, 1F).

IR (film): ν (cm^{-1}) 3366, 3128, 2923, 2855, 1692, 1597, 1514, 1464, 1402, 1351, 1307, 1247, 1211, 1152, 1120, 1086, 1011, 964, 912, 875, 844, 787, 761, 733, 691, 653, 625, 579, 561, 508.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{16}F_5N_3ONa$ $[M+Na]^+$: 480.1106, found: 480.1105.



(*S*)-2-(Naphthalen-2-yl)-2-((perfluorophenyl)amino)-1-(1-phenyl-1*H*-imidazol-2-yl)ethan-1-one (4ha)

According to the general procedure, the reaction of 2-(naphthalen-2-yl)-1-(1-phenyl-1H-imidazol- 2-yl)ethan-1-one **1h** (31.2 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 17 hours, afforded 24.8 mg (50%) of **4ha** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 95% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 8.3 min, t_r (minor) = 6.4 min). $[\alpha]_D^{22}$ = +260.2° (*c* 1.0, CH_2Cl_2).

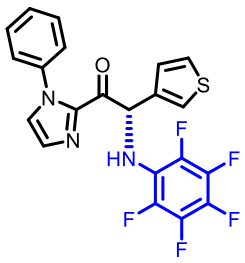
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.85-7.81 (m, 1H), 7.80-7.76 (m, 2H), 7.55 (dd, J_1 = 8.5 Hz, J_2 = 1.5 Hz, 1H), 7.50-7.41 (m, 5H), 7.33 (d, J = 1.0 Hz, 1H), 7.16 (d, J = 1.0 Hz, 1H), 7.14-7.10 (m, 2H), 6.93-6.88 (m, 1H) 5.50-5.45 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.8, 140.8, 137.6, 134.2, 133.3, 133.1, 130.6, 129.1, 128.8, 128.21, 128.16, 127.8, 127.6, 126.5, 126.3, 125.6, 125.0, 63.3 (t, J = 3.6 Hz). (Missing one ^{13}C signal)

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.32 - –157.49 (m, 2F), –164.18 - –164.39 (m, 2F), –170.29 (tt, J_1 = 22.00 Hz, J_2 = 5.92 Hz, 1F).

IR (film): ν (cm^{-1}) 3367, 1687, 1597, 1517, 1448, 1398, 1305, 1266, 1180, 1154, 1123, 1099, 1022, 971, 909, 843, 813, 734, 691, 668, 641, 610, 544, 503, 474.

HRMS (ESI, *m*/*z*) calcd for $C_{27}H_{16}F_5N_3ONa$ $[M+Na]^+$: 516.1106, found: 516.1106.



(*S*)-2-((Perfluorophenyl)amino)-1-(1-phenyl-1*H*-imidazol-2-yl)-2-(thiophen-3-yl)ethan-1-one (4ia)

According to the general procedure, the reaction of 1-(1-phenyl-1*H*-imidazol-2-yl)-2-(thiophen-3-yl)ethan-1-one **1i** (26.8 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), DIPEA (2.6 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 40 hours, afforded 19.0 mg (42%) of **4ia** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 93% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 7.8 min, t_r (minor) = 6.2 min). $[\alpha]_D^{22}$ = +123.8° (*c* 0.4, CH_2Cl_2).

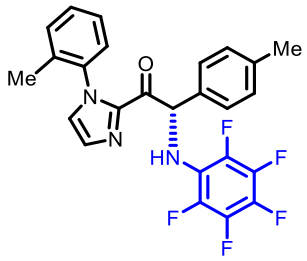
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.44 (m, 3H), 7.38-7.35 (m, 1H), 7.34 (d, J = 1.0 Hz, 1H), 7.23 (dd, J_1 = 5.0 Hz, J_2 = 3.0 Hz, 1H), 7.21 (d, J = 1.0 Hz, 1H), 7.18-7.14 (m, 2H), 7.07 (dd, J_1 = 5.0 Hz, J_2 = 1.0 Hz, 1H), 6.83 (d, J = 9.5 Hz, 1H), 5.21 (d, J = 9.5 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.5, 140.7, 137.6, 137.5, 130.6, 129.2, 129.1, 127.8, 126.5, 126.3, 125.6, 124.6, 59.3 (t, J = 3.9 Hz).

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.70 - –157.86 (m, 2F), –164.51 - –164.72 (m, 2F), –170.50 (tt, J_1 = 22.14 Hz, J_2 = 5.50 Hz, 1F).

IR (film): ν (cm^{-1}) 3364, 1687, 1599, 1515, 1448, 1397, 1348, 1305, 1260, 1182, 1151, 1098, 1021, 972, 912, 840, 763, 731, 693, 664, 546, 460.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{12}F_5N_3OSNa$ $[M+Na]^+$: 472.0513, found: 472.0510.



(*S*)-2-((Perfluorophenyl)amino)-2-(*p*-tolyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4ja)

According to the general procedure, the reaction of 2-(*p*-tolyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1j** (29.0 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), DIPEA (2.6 mg, 20 mol%)

and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 12 hours, afforded 37.5 mg (80%) of **4ja** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 7.1 min, t_r (minor) = 6.0 min). $[\alpha]_D^{22}$ = +241.0° (*c* 1.0, CH_2Cl_2).

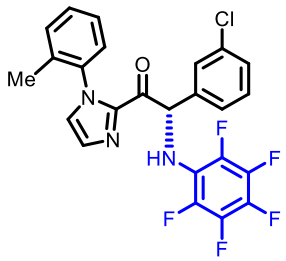
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.27 (m, 5H), 7.26-7.19 (m, 2H), 7.10-7.03 (m, 3H), 6.80 (d, *J* = 8.0 Hz, 1H, other rotamer), 6.71-6.64 (m, 1H), 5.40-5.23 (m, 1H), 2.27 (s, 3H, other rotamer), 2.25 (s, 3H), 2.03 (s, 3H, other rotamer), 1.46 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.1, 186.0, 141.4, 141.3, 138.2, 138.1, 137.3, 137.2, 134.7, 134.3, 133.7, 130.83, 130.76, 130.73, 130.68, 129.6, 129.5, 129.43, 129.37, 128.00, 127.9, 127.1, 126.7, 126.6, 126.5, 126.1, 63.0 (t, *J* = 3.3 Hz), 62.8 (t, *J* = 3.9 Hz), 21.11, 21.08, 17.2, 16.3. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.51 - –157.75 (m, 2F), –164.54 - –164.75 (m, 2F), –170.61 - –170.96 (m, 1F).

IR (film): *v* (cm^{-1}) 3368, 2925, 2857, 1687, 1517, 1453, 1400, 1346, 1303, 1262, 1186, 1153, 1095, 1021, 967, 912, 851, 803, 765, 727, 653, 616, 555, 496, 455.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{18}F_5N_3ONa$ $[M+Na]^+$: 494.1262, found: 494.1263.



(*S*)-2-(3-Chlorophenyl)-2-((perfluorophenyl)amino)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4ka)

According to the general procedure, the reaction of 2-(3-chlorophenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1k** (31.1 mg, 0.10 mmol), 1-azido-2,3,4,5,6-pentafluorobenzene **2a** (62.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 48 hours, afforded 23.3 mg (47%) of **4ka** as a white solid. Enantiomeric excess was

established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 7.7 min, t_r (minor) = 6.9 min). $[\alpha]_D^{22}$ = +162.0° (*c* 1.0, CH_2Cl_2).

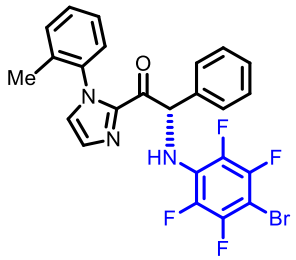
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47-7.43 (m, 1H), 7.43-7.32 (m, 4H), 7.28-7.18 (m, 4H), 7.13-7.10 (m, 1H), 6.83 (d, *J* = 8.0 Hz, 1H, other rotamer), 6.72-6.64 (m, 1H), 5.40-5.28 (m, 1H), 2.03 (s, 3H, other rotamer), 1.48 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.3, 185.2, 141.0, 140.9, 139.0, 138.9, 137.03, 136.95, 134.7, 134.64, 134.60, 134.2, 131.0, 130.94, 130.86, 130.1, 130.0, 129.6, 129.5, 128.63, 128.58, 128.2, 128.1, 127.50, 127.48, 126.8, 126.7, 126.4, 126.2, 126.0, 62.6 (t, *J* = 3.8 Hz), 62.4 (t, *J* = 3.5 Hz), 17.2, 16.2. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –157.89 - –158.16 (m, 2F), –164.29 - –164.51 (m, 2F), –170.25 - –170.61 (m, 1F).

IR (film): *v* (cm^{-1}) 3366, 1684, 1517, 1446, 1397, 1303, 1187, 1155, 1081, 1024, 981, 956, 911, 846, 765, 723, 696, 664, 630, 585, 554, 453.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{15}ClF_5N_3ONa$ $[M+Na]^+$: 514.0716, found: 514.0715.



(*S*)-2-((4-Bromo-2,3,5,6-tetrafluorophenyl)amino)-2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4bb)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2- yl)ethan-1-one **1b** (27.6 mg, 0.10 mmol), 1-azido-4-bromo-2,3,5,6-tetrafluorobenzene **2b** (80.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 5 hours, afforded 46.5 mg (90%) of **4bb** as a white solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 99.4% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 8.3 min, t_r (minor) = 7.4 min).

$[\alpha]_D^{22}$ = +150.8° (*c* 1.0, CH_2Cl_2).

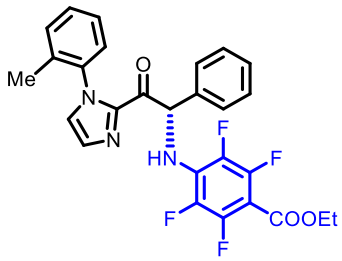
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.43 (m, 2H), 7.42-7.19 (m, 8H), 7.11-7.09 (m, 1H), 6.86-6.81 (m, 1H, other rotamer), 6.81-6.75 (m, 1H), 5.67-5.61 (m, 1H), 5.60-5.56 (m, 1H, other rotamer), 2.04 (s, 3H, other rotamer), 1.41 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.8, 185.7, 146.2-145.8 (m), 144.3-144.0 (m), 141.4-141.0 (m), 139.2-138.7 (m), 137.3-136.9 (m), 136.8, 134.7, 134.3, 130.82, 130.80, 130.77, 130.7, 129.5, 129.4, 128.84, 128.76, 128.38, 128.35 128.1, 128.0, 127.21, 127.18 126.7, 126.6, 126.4, 126.0, 62.5 (t, *J* = 3.7 Hz), 62.2 (t, *J* = 3.8 Hz), 17.2, 16.0. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –136.00 - –136.20 (m, 2F), –156.03 - –156.31 (m, 2F).

IR (film): *v* (cm^{-1}) 3350, 2923, 2856, 1688, 1641, 1495, 1455, 1404, 1299, 1148, 1074, 1026, 981, 948, 913, 858, 762, 736, 702, 675, 619, 579, 494, 454.

HRMS (ESI, *m*/*z*) calcd for $C_{24}H_{16}BrF_4N_3ONa$ $[M+Na]^+$: 540.0305, found: 540.0305.



Ethyl (*S*)-2,3,5,6-tetrafluoro-4-((2-oxo-1-phenyl-2-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethyl)amino) benzoate (4bc)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2- yl)ethan-1-one **1b** (27.6 mg, 0.10 mmol), ethyl 4-azido-2,3,5,6-tetrafluorobenzoate **2c** (78.9 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 6 hours, afforded 41.3 mg (81%) of **4bc** as a white solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 99.6% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 8.7 min, t_r (minor) = 5.3 min). $[\alpha]_D^{22}$ = +101.0° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.44 (m, 2H), 7.43-7.18 (m, 8H), 7.12-7.09 (m, 1H), 6.92-6.82 (m, 1H), 6.77 (d, *J* = 7.8 Hz, 1H, other rotamer), 5.94-5.81 (m, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.04 (s,

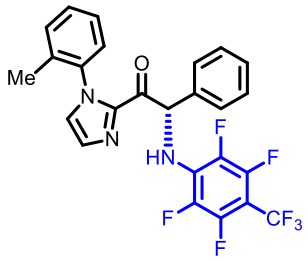
3H, other rotamer), 1.40 (s, 3H), 1.34 (t, J = 7.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.4, 185.2, 160.6-160.4 (m), 147.0-147.3 (m), 145.3-145.0 (m), 141.1, 140.9, 138.1-137.7 (m), 137.04, 136.98, 136.7, 136.1-135.8 (m), 134.7, 134.2, 130.9, 130.81, 130.80, 130.77, 129.5, 129.4, 129.12, 129.09, 129.06, 129.03, 129.00, 128.9, 128.8, 128.5, 128.4, 128.1, 128.0, 127.31, 127.28, 126.7, 126.6, 126.4, 126.0, 62.6 (t, J = 3.8 Hz), 62.3 (t, J = 3.8 Hz), 61.6, 17.2, 16.0, 14.1. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –140.71 - –140.86 (m, 2F), –158.78 - –156.97 (m, 2F).

IR (film): ν (cm^{-1}) 3349, 2973, 2932, 1718, 1687, 1651, 1533, 1495, 1452, 1399, 1371, 1310, 1233, 1154, 1022, 986, 957, 913, 842, 789, 759, 699, 624, 561.

HRMS (ESI, m/z) calcd for $C_{27}H_{21}F_4N_3O_3Na$ $[M+Na]^+$: 534.1411, found: 534.1416.



(*S*)-2-Phenyl-2-((2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)amino)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4bd)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2- yl)ethan-1-one **1b** (27.6 mg, 0.10 mmol), 1-azido-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene **2d** (77.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 6 hours, afforded 35.6 mg (70%) of **4bd** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 99% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 5.1 min, t_r (minor) = 4.1 min). $[\alpha]_D^{22}$ = +127.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51-7.44 (m, 2H), 7.43-7.19 (m, 8H), 7.12-7.09 (m, 1H), 6.91-6.87 (m, 1H), 6.87-6.82 (m, 1H, other rotamer), 6.77 (d, J = 8.0 Hz, 1H, other rotamer), 5.97-5.91 (m, 1H), 5.89-5.83 (m, 1H, other rotamer), 2.04 (s, 3H, other rotamer), 1.39 (s, 3H).

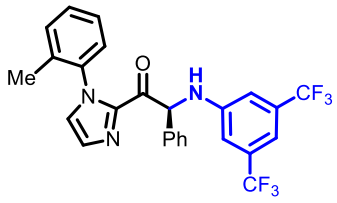
^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2, 185.1, 141.1, 140.8, 137.02, 136.96, 136.6, 134.7, 134.2,

130.93, 130.85, 130.8, 129.53, 129.47, 129.0, 128.9, 128.6, 128.5, 128.1, 128.0, 127.38, 127.36 126.8, 126.7, 126.4, 126.0, 63.0 (t, *J* = 3.6 Hz), 62.7 (t, *J* = 3.9 Hz), 17.2, 16.1. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –55.1 (t, *J* = 20.87, 3F), –143.25 - –143.50 (m, 2F), –158.28 - –158.50 (m, 2F).

IR (film): ν (cm^{-1}) 3373, 1688, 1655, 1539, 1505, 1457, 1400, 1330, 1304, 1235, 1179, 1130, 1078, 1025, 983, 957, 911, 884, 835, 764, 734, 703, 672, 626, 560, 494.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{16}F_7N_3ONa$ $[M+Na]^+$: 530.1074, found: 530.1075.



(*S*)-2-((3,5-Bis(trifluoromethyl)phenyl)amino)-2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4be)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), 1-azido-3,5-bis(trifluoromethyl)benzene **2e** (76.6 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 7 hours, afforded 29.8 mg (59%) of **4be** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 8.5 min, t_r (minor) = 7.0 min). $[\alpha]_D^{22}$ = +97.0° (*c* 1.0, CH_2Cl_2).

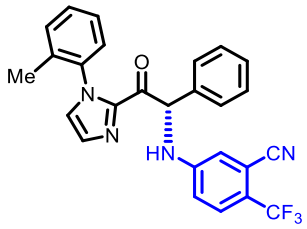
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.53 (m, 2H), 7.43-7.16 (m, 8H), 7.13-7.09 (m, 2H), 6.98-6.94 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H, other rotamer), 6.56-6.49 (m, 1H), 5.79 (d, *J* =7.2 Hz, 1H), 5.73 (d, *J* =7.2 Hz, 1H, other rotamer), 2.00 (s, 3H, other rotamer), 1.40 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 186.0, 185.9, 146.5, 146.4, 141.4, 141.3, 137.1, 137.0, 136.1, 134.6, 134.2, 132.3 (q, *J* = 97.5 Hz) 130.80, 130.78, 130.72, 130.7, 129.43, 129.37, 129.0, 128.9, 128.39, 128.38, 128.2, 128.1, 127.4, 126.0, 123.4 (q, *J* = 271.1 Hz), 112.61, 112.58, 110.6-110.4 (m), 61.9, 61.7, 17.2, 16.0 (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.40 (6F), –63.40 (other rotamer).

IR (film): ν (cm^{-1}) 3381, 3066, 2927, 1674, 1624, 1501, 1450, 1394, 1274, 1172, 1126, 1028, 996, 969, 927, 867, 762, 726, 690, 644, 606, 529, 405.

HRMS (EI, *m*/*z*) calcd for $C_{26}H_{19}F_6N_3O$ $[M]^+$: 503.1432, found: 503.1447.



(*S*)-5-((2-Oxo-1-phenyl-2-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethyl)amino)-2-(trifluoromethyl)benzonitrile (4bf)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2- yl)ethan-1-one **1b** (27.6 mg, 0.10 mmol), 5-azido-2-(trifluoromethyl)benzonitrile **2f** (63.6 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 6 hours, afforded 33.9 mg (74%) of **4bf** as a yellow solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 96% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 80:20, flow rate 1 mL/min, 25 °C, t_r (major) = 8.9 min, t_r (minor) = 16.0 min). $[\alpha]_D^{22}$ = +114.4° (*c* 1.0, CH_2Cl_2).

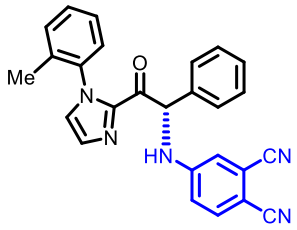
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57-7.50 (m, 2H), 7.48-7.45 (m, 1H), 7.43-7.17 (m, 8H), 7.15-7.13 (m, 1H), 6.89 (dd, J_1 = 7.5 Hz, J_2 = 2.0 Hz, 1H), 6.75 (d, J = 8.0 Hz, 1H, other rotamer), 6.70-6.65 (m, 1H), 6.53 (d, J = 6.5 Hz, 1H), 6.49 (d, J = 6.5 Hz, 1H, other rotamer), 6.14-6.10 (m, 1H), 2.00 (s, 3H, other rotamer), 1.37 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 185.2, 185.1, 148.8, 148.7, 141.1, 141.0, 136.9, 136.8, 136.1, 135.60, 135.57, 134.6, 134.24, 134.15, 134.0, 130.9, 130.83, 130.79, 129.5, 129.4, 129.1, 129.0, 128.6, 128.2, 128.0, 127.6, 126.72, 126.67, 126.3, 126.0, 123.5, 121.3, 116.9, 114.6, 111.2, 96.2, 61.6, 61.3, 17.2, 16.0. (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –63.097 (3F), –63.102 (3F, other rotamer).

IR (film): ν (cm^{-1}) 3336, 2922, 2223, 1697, 1608, 1522, 1497, 1447, 1402, 1352, 1274, 1172, 1131, 1025, 842, 768, 738, 701, 673, 557, 454.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{19}F_3N_4ONa$ $[M+Na]^+$: 483.1403, found: 483.1405.



(*S*)-4-((2-Oxo-1-phenyl-2-(1-(o-tolyl)-1*H*-imidazol-2-yl)ethyl)amino)phthalonitrile (4bg)

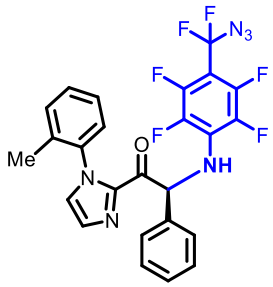
According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2- yl)ethan-1-one **1b** (27.6 mg, 0.10 mmol), 4-azidophthalonitrile **2g** (50.7 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 6 hours, afforded 37.0 mg (89%) of **4bg** as a yellow solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak AD-H column, ee = 99% (HPLC: AD-H, 254 nm, *n*-hexane/isopropanol = 60:40, flow rate 1 mL/min, 25 °C, t_r (major) = 8.2 min, t_r (minor) = 17.3 min). $[\alpha]_D^{22}$ = +111.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56-7.50 (m, 2H), 7.44-7.37 (m, 2H), 7.37-7.23 (m, 5H), 7.22-7.16 (m, 2H), 7.15-7.13 (m, 1H), 6.86-6.83 (m, 1H), 6.78-6.72 (m, 1H), 6.78-6.72 (m, 1H, other rotamer), 6.50 (d, *J* = 6.5 Hz, 1H), 6.46 (d, *J* = 6.5 Hz, 1H, other rotamer), 6.21-6.15 (m, 1H), 2.01 (s, 3H, other rotamer), 1.36 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 184.9, 184.8, 148.9, 148.8, 141.0, 140.9, 136.9, 136.8, 135.3, 135.2, 134.6, 134.5, 134.1, 130.94, 130.86, 130.82, 130.79, 129.5, 129.4, 129.14, 129.10, 128.7, 128.1, 128.0, 127.7, 126.70, 126.66, 126.3, 126.0, 117.0, 116.6, 116.4, 115.8, 102.2, 61.5, 61.3, 17.2, 15.9. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 3366, 3063, 2923, 2220, 1685, 1596, 1514, 1454, 1398, 1346, 1304, 1257, 1023, 968, 910, 832, 764, 731, 703, 673, 521, 492, 453,

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{19}N_5ONa$ $[M+Na]^+$: 440.1482, found: 440.1482.



(*S*)-2-((4-(Azidodifluoromethyl)-2,3,5,6-tetrafluorophenyl)amino)-2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one (4bh)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), 1-azido-4-(azidodifluoromethyl)-2,3,5,6-tetrafluorobenzene **2h** (84.6 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 11 hours, afforded 25.5 mg (48%) of **4bh** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 8.8 min, t_r (minor) = 7.6 min). $[\alpha]_D^{22}$ = +128.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.43 (m, 2H), 7.42-7.18 (m, 8H), 7.11-7.09 (m, 1H), 6.90-6.85 (m, 1H), 6.85-6.81 (m, 1H, other rotamer), 6.76 (d, *J* = 8.0 Hz, 1H, other rotamer), 5.90-5.85 (m, 1H), 5.83-5.78 (m, 1H, other rotamer), 2.03 (s, 3H, other rotamer), 1.39 (s, 3H).

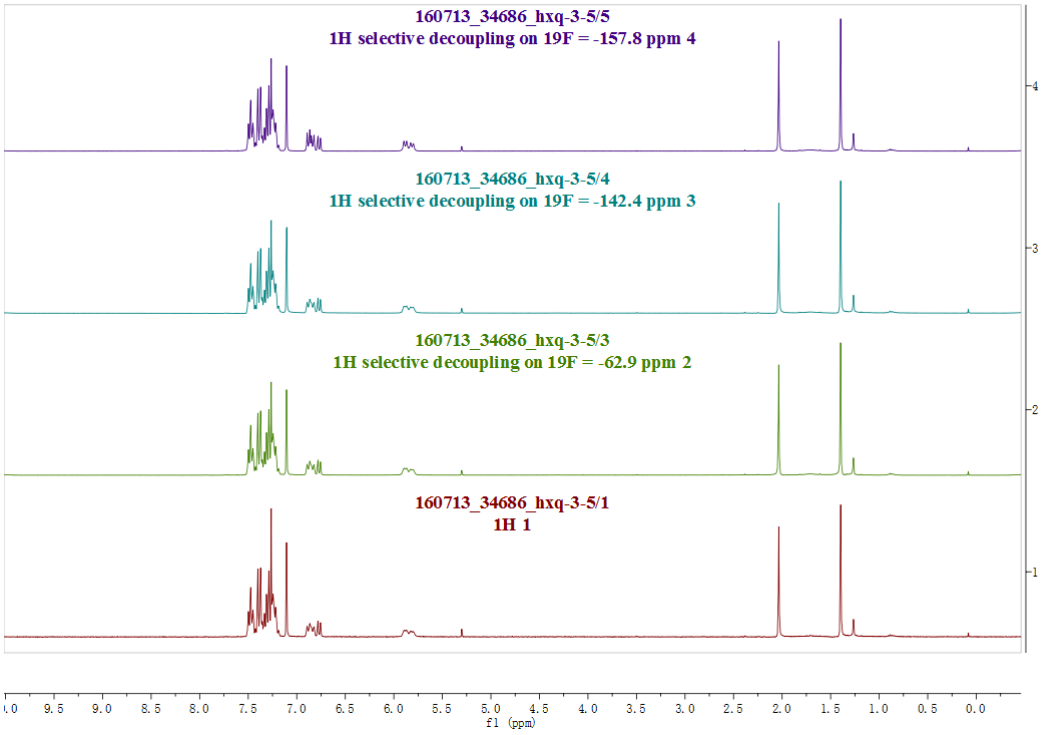
^{13}C NMR (125 MHz, $CDCl_3$) δ 185.3, 185.2, 141.1, 140.9, 137.05, 136.98, 136.7, 134.7, 134.2, 130.9, 130.84, 130.81, 129.52, 129.46, 128.94, 128.85, 128.1, 128.0, 127.4, 127.3, 126.75, 126.65, 126.4, 126.0, 62.6 (t, *J* = 3.4 Hz), 62.2 (t, *J* = 3.7 Hz), 17.2, 16.0 (Mixture of two rotation isomers).

^{19}F NMR (282 MHz, $CDCl_3$) δ –62.93 (t, *J* = 24.82, 2F), –142.24 - –142.54 (m, 2F), –157.67 - –157.90 (m, 2F).

IR (film): *v* (cm^{-1}) 3373, 2962, 2927, 2145, 1689, 1655, 1536, 1500, 1456, 1428, 1400, 1320, 1275, 1229, 1148, 1028, 979, 953, 912, 865, 786, 763, 730, 697, 670, 626, 562, 488, 454, 393.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{16}F_6N_6ONa$ $[M+Na]^+$: 553.1182, found: 553.1182.

The structure of **4bh** was further confirmed by ^{1}H-{^{19}F} NMR shown below: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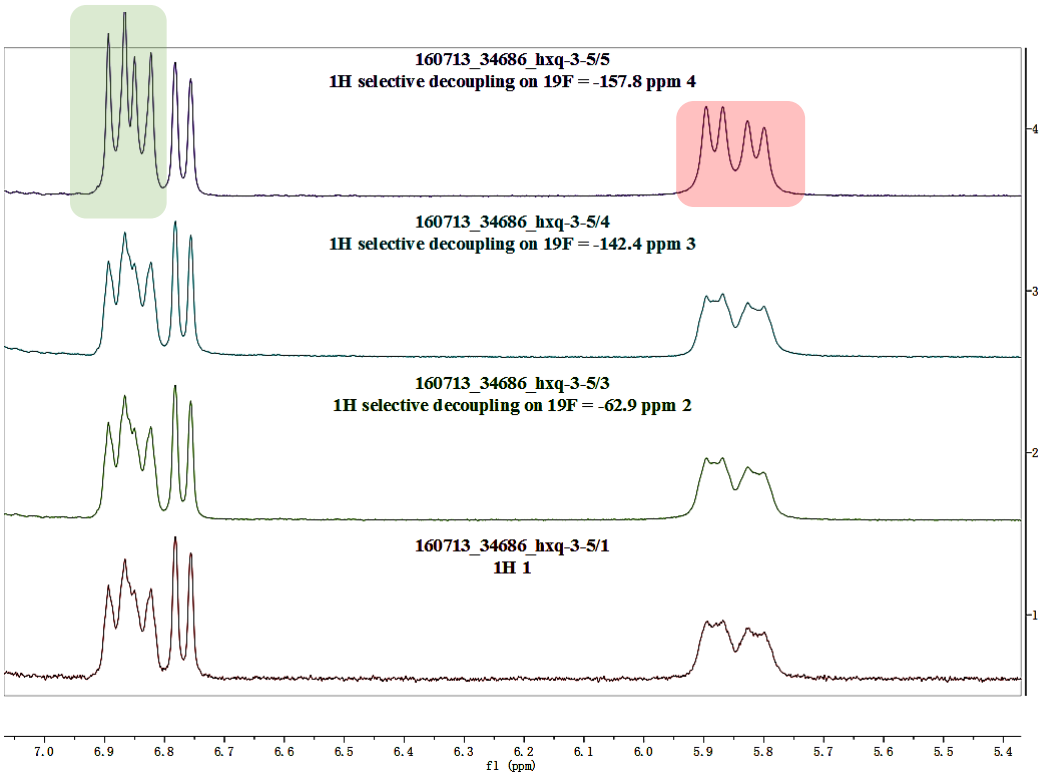
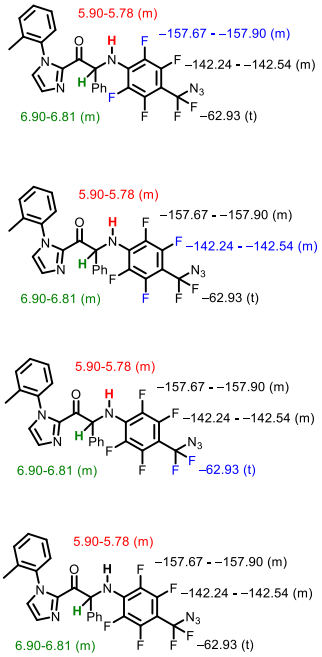
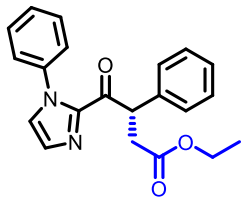
1H selective decoupling on 19F = -142.4 ppm 3
160713_34686_hxq-3-5/3
1H selective decoupling on 19F = -62.9 ppm 2
160713_34686_hxq-3-5/1
1H 1
f1 (ppm)


160713_34686_hxq-3-5/5
1H selective decoupling on 19F = -157.8 ppm 4
160713_34686_hxq-3-5/4
1H selective decoupling on 19F = -142.4 ppm 3
160713_34686_hxq-3-5/3
1H selective decoupling on 19F = -62.9 ppm 2
160713_34686_hxq-3-5/1
1H 1
f1 (ppm)


5.90-5.78 (m)
−157.67 - −157.90 (m)
−142.24 - −142.54 (m)
6.90-6.81 (m)
−62.93 (t)



Ethyl (S)-4-oxo-3-phenyl-4-(1-phenyl-1*H*-imidazol-2-yl)butanoate (5aa)

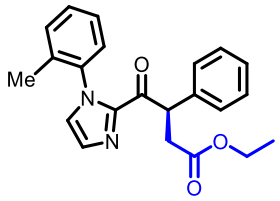
According to the general procedure, the reaction of 2-phenyl-1-(1-phenyl-1*H*-imidazol-2-yl) ethan-1-one **1a** (26.2 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Δ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 15 hours, afforded 32.7 mg (94%) of **5aa** as a yellow solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 92% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 15.0 min, t_r (minor) = 11.1 min). $[\alpha]_D^{22}$ = +213.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44-7.39 (m, 5H), 7.32-7.27 (m, 2H), 7.27 (d, J = 1.5 Hz, 1H), 7.25-7.21 (m, 1H), 7.19-7.15 (m, 2H), 7.11 (d, J = 1.0 Hz, 1H), 5.60 (dd, J_1 = 10.5 Hz, J_2 = 5.0 Hz, 1H), 4.07 (qd, J_1 = 7.0 Hz, J_2 = 1.0 Hz, 2H), 3.30 (dd, J_1 = 17.0 Hz, J_2 = 10.5 Hz, 1H), 2.70 (dd, J_1 = 17.0 Hz, J_2 = 5.0 Hz, 1H), 1.16 (t, J = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 171.8, 142.4, 138.3, 137.6, 129.9, 128.9, 128.7, 128.6, 127.3, 127.0, 125.6, 60.6, 48.8, 37.4, 14.1. (Missing one ^{13}C signal)

IR (film): ν (cm^{-1}) 2980, 2930, 1722, 1678, 1495, 1449, 1401, 1373, 1329, 1302, 1245, 1187, 1152, 1097, 1029, 939, 906, 756, 694, 585, 530.

HRMS (ESI, *m*/*z*) calcd for $C_{21}H_{21}N_2O_3$ $[M+H]^+$: 349.1547, found: 349.1548.



Ethyl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5ba)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20

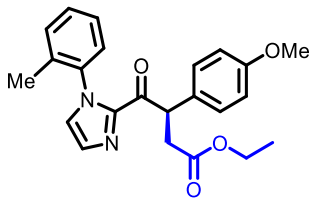
equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 15 hours, afforded 35.9 mg (99%) of **5ba** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 97% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 9.8 min, t_r (minor) = 11.7 min). $[\alpha]_D^{22}$ = –238.4° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.18 (m, 10H), 7.03 (d, *J* = 1.0 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H, other rotamer), 5.65-5.58 (m, 1H), 4.10-4.03 (m, 2H), 3.34-3.25 (m, 1H), 2.74-2.64 (m, 1H), 2.04 (s, 3H), 1.55 (s, 3H, other rotamer), 1.20-1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.35, 189.25, 171.6, 142.9, 142.8, 137.84, 137.80, 137.7, 137.6, 134.9, 134.3, 130.6, 130.5, 130.2, 130.1, 129.0, 128.9, 128.7, 128.61, 128.56, 128.5, 127.23, 127.19, 126.5, 126.41, 126.38, 126.1, 60.5, 48.61, 48.58, 37.4, 37.0, 17.1, 16.4, 14.05, 14.02. (Mixture of two rotation isomers)

IR (film): *v* (cm^{-1}) 3111, 3061, 2981, 2931, 1729, 1682, 1594, 1495, 1453, 1403, 1375, 1305, 1243, 1178, 1093, 1026, 941, 909, 848, 762, 699, 670, 587, 529, 455.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{22}N_2O_3Na$ $[M+Na]^+$: 385.1523, found: 385.1525



Ethyl (*R*)-3-(4-methoxyphenyl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5la)

According to the general procedure, the reaction of 2-(4-methoxyphenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1l** (30.6 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 15 hours, afforded 38.1 mg (97%) of **5la** as a yellow solid. 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, 25 °C, t_r (major) = 13.1 min, t_r (minor) = 14.8 min). $[\alpha]_D^{22}$ = –239.4° (*c* 1.0, CH_2Cl_2).

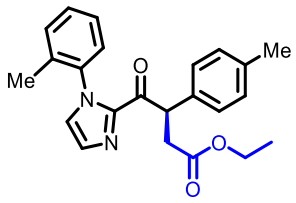
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.26 (m, 5H), 7.25-7.18 (m, 2H), 7.03-7.01 (m, 1H), 6.89 (d, *J* = 8.0 Hz, 1H, other rotamer), 6.84-6.78 (m, 2H), 5.58-5.51 (m, 1H), 4.09-4.02 (m, 2H), 3.76 (s, 3H),

3.29-3.20 (m, 1H), 2.71-2.61 (m, 1H), 2.03 (s, 3H), 1.57 (s, 3H, other rotamer), 1.20-1.13 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 189.4, 171.7, 158.8, 143.0, 142.9, 137.9, 134.9, 134.3, 130.6, 130.08, 130.06, 129.7, 129.6, 129.0, 128.9, 126.5, 126.44, 126.39, 126.33, 126.31, 126.1, 114.1, 114.0, 60.5, 55.2, 47.83, 47.76, 37.4, 37.1, 17.2, 16.5, 14.1, 14.0. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2971, 2933, 1728, 1674, 1606, 1507, 1452, 1340, 1302, 1243, 1178, 1106, 1091, 1024, 940, 906, 848, 766, 719, 536.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}N_2O_4Na$ $[M+Na]^+$: 415.1628, found: 415.1629.



Ethyl (*R*)-4-oxo-3-(*p*-tolyl)-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5ja)

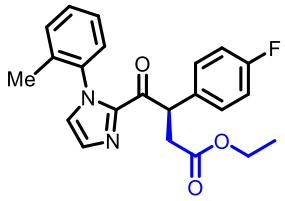
According to the general procedure, the reaction of 2-(*p*-tolyl)-1-(1-(*o*-tolyl)-1*H*-imidazol- 2-yl)ethan-1-one **1j** (29.0 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 2.0 mL, 0.05 M) under nitrogen atmosphere with visible light for 24 hours, afforded 35.5 mg (94%) of **5ja** as a yellow solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 10.5 min, t_r (minor) = 13.2 min). $[\alpha]_D^{22}$ = –272.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.21 (m, 7H), 7.12-7.06 (m, 2H), 7.03-7.01 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H, other rotamer), 5.60-5.53 (m, 1H), 4.10-4.02 (m, 2H), 3.31-3.24 (m, 1H), 2.71-2.62 (m, 1H), 2.30 (s, 3H), 2.29 (s, 3H, other rotamer), 2.04 (s, 3H), 1.59 (s, 3H, other rotamer), 1.21-1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 189.4, 171.7, 142.3, 142.8, 137.9, 137.8, 136.8, 134.9, 134.6, 134.5, 134.3, 130.6, 130.5, 130.11, 130.09, 129.4, 129.3, 128.95, 128.89, 128.4, 126.5, 126.41, 126.35, 126.30, 126.29, 126.1, 60.4, 48.21, 48.20, 37.4, 37.1, 21.0, 17.2, 16.6, 14.05, 14.01. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 3172, 2981, 2924, 1731, 1680, 1500, 1445, 1405, 1373, 1321, 1179, 1032, 942, 907, 767, 717, 534.

HRMS (ESI, *m*/*z*) calcd for $C_{23}H_{24}N_2O_3Na$ $[M+Na]^+$: 399.1679, found: 399.1677.



Ethyl (*R*)-3-(4-fluorophenyl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5ma)

According to the general procedure, the reaction of 2-(4-fluorophenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1m** (29.4 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 1.0 mL, 0.1 M) under nitrogen atmosphere with visible light for 16 hours, afforded 36.5 mg (96%) of **5ma** as a yellow solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 98% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 7.6 min, t_r (minor) = 8.7 min). $[\alpha]_D^{22}$ = –205.8° (*c* 1.0, CH_2Cl_2).

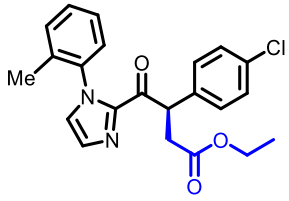
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.26 (m, 5H), 7.25-7.17 (m, 2H), 7.04-7.02 (m, 1H), 6.99-6.92 (m, 2H), 6.90 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H, other rotamer), 5.62-5.54 (m, 1H), 4.08-4.01 (m, 2H), 3.28-3.20 (m, 1H), 2.71-2.60 (m, 1H), 2.02 (s, 3H), 1.56 (s, 3H, other rotamer), 1.19-1.12 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 189.1, 171.51, 171.49, 163.0, 161.0, 142.7, 142.6, 137.79, 137.75, 134.9, 134.2, 133.41, 133.39, 133.35, 133.32, 130.7, 130.6, 130.23, 130.21, 130.16, 130.1, 129.1, 129.0, 126.6, 126.5, 126.4, 126.0, 115.64, 115.59, 115.5, 115.4, 60.6, 47.8, 47.7, 37.4, 37.0, 17.1, 16.5, 14.1, 14.0. (Mixture of two rotation isomers)

^{19}F NMR (282 MHz, $CDCl_3$) δ –115.32 (1F), –115.39 (1F, other rotamer).

IR (film): ν (cm^{-1}) 3119, 2985, 2926, 1723, 1683, 1502, 1454, 1403, 1376, 1313, 1225, 1185, 1159, 1096, 1022, 941, 908, 842, 803, 766, 716, 544, 492, 454.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{21}FN_2O_3Na$ $[M+Na]^+$: 403.1428, found: 403.1425.



Ethyl (*R*)-3-(4-chlorophenyl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5na)

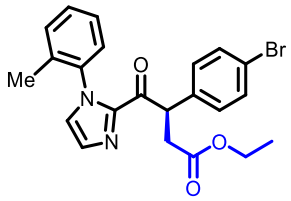
According to the general procedure, the reaction of 2-(4-chlorophenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1n** (31.1 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 2.0 mL, 0.05 M) under nitrogen atmosphere with visible light for 22 hours, afforded 39.0 mg (98%) of **5na** as a white solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 25 °C, t_r (major) = 7.3 min, t_r (minor) = 8.7 min). $[\alpha]_D^{22}$ = –208.4 ° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5H), 7.26-7.17 (m, 4H), 7.04-7.03 (m, 1H), 6.91 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H, other rotamer), 5.61-5.54 (m, 1H), 4.08-4.01 (m, 2H), 3.16-3.06 (m, 1H), 2.72-2.62 (m, 1H), 2.04 (s, 3H), 1.81 (s, 3H, other rotamer), 1.20-1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 188.9, 171.3, 171.2, 142.80, 142.77, 137.83, 137.81, 136.1, 135.9, 135.0, 134.2, 134.1, 134.0, 130.7, 130.6, 130.45, 130.41, 130.2, 129.1, 129.0, 128.6, 128.5, 128.43, 128.40, 126.9, 126.8, 126.7, 126.55, 126.50, 126.43, 126.37, 126.1, 60.6, 45.7, 45.6, 36.7, 36.5, 17.2, 16.9, 14.03, 14.00. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2974, 2925, 1731, 1682, 1493, 1458, 1401, 1374, 1254, 1185, 1148, 1087, 1035, 943, 906, 769, 717, 531.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{21}ClN_2O_3Na$ $[M+Na]^+$: 419.1133, found: 419.1131.



Ethyl (*R*)-3-(4-bromophenyl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5oa)

According to the general procedure, the reaction of 2-(4-bromophenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1o** (35.5 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 2.0 mL, 0.05 M) under nitrogen atmosphere with visible light for 38 hours, afforded 41.0 mg (93%) of **5oa** as a white solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, *n*-hexane/isopropanol =

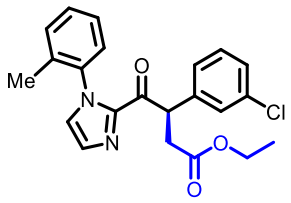
85:15, flow rate 1 mL/min, 25 °C, t_r (major) = 7.8 min, t_r (minor) = 9.1 min). $[\alpha]_D^{22}$ = –183.2° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.17 (m, 9H), 7.05-7.02 (m, 1H), 6.91 (d, *J* = 8.0 Hz, 1H, other rotamer), 5.60-5.53 (m, 1H), 4.08-4.02 (m, 2H), 3.27-3.19 (m, 1H), 2.70-2.61 (m, 1H), 2.01 (s, 3H), 1.59 (s, 3H, other rotamer), 1.19-1.12 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.9, 188.8, 171.43, 171.41, 142.6, 142.5, 137.74, 137.71, 136.20, 136.17, 134.9, 134.2, 133.20, 133.19, 130.7, 130.6, 130.24, 130.21, 130.0, 129.12, 129.06, 128.9, 128.8, 126.7, 126.63, 126.58, 126.5, 126.4, 126.0, 60.6, 47.97, 47.95, 37.2, 36.9, 17.1, 16.6, 14.1, 14.0. (Mixture of two rotation isomers)

IR (film): *v* (cm^{-1}) 2980, 2929, 1730, 1683, 1491, 1454, 1403, 1374, 1309, 1240, 1178, 1014, 941, 909, 766, 722, 532.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{21}BrN_2O_3Na$ $[M+Na]^+$: 463.0628, found: 463.0624.



Ethyl (*R*)-3-(3-chlorophenyl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5ka)

According to the general procedure, the reaction of 2-(3-chlorophenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1k** (31.1 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 26 hours, afforded 36.5 mg (92%) of **5ka** as a yellow oil. 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, 25 °C, t_r (major) = 7.1 min, t_r (minor) = 12.2 min). $[\alpha]_D^{22}$ = –223.0° (*c* 1.0, CH_2Cl_2).

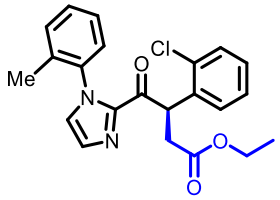
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.18 (m, 9H), 7.06-7.04 (m, 1H), 6.31 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H, other rotamer), 5.61-5.55 (m, 1H), 4.09-4.02 (m, 2H), 3.28-3.21 (m, 1H), 2.71-2.62 (m, 1H), 2.02 (s, 3H), 1.62 (s, 3H, other rotamer), 1.20-1.13 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 188.70, 188.65, 171.4, 171.3, 142.7, 142.6, 139.72, 139.69, 137.73, 137.69, 134.7, 134.40, 134.38, 134.2, 130.7, 130.34, 130.31, 129.91, 129.88, 129.12, 129.06, 128.64,

128.59, 127.5, 126.88, 126.85, 126.69, 126.67, 126.6, 126.5, 126.4, 126.1, 60.6, 48.22, 48.20, 37.3, 36.9, 17.1, 16.5, 14.1, 14.0. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2982, 2930, 1730, 1683, 1454, 1402, 1376, 1304, 1241, 1180, 1088, 1025, 942, 908, 766, 724, 690, 454.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{21}ClN_2O_3Na$ $[M+Na]^+$: 419.1133, found: 419.1131.



Ethyl (*R*)-3-(2-chlorophenyl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5pa)

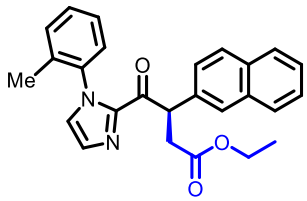
According to the general procedure, the reaction of 2-(2-chlorophenyl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1p** (31.1 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 15 hours, afforded 32.2 mg (81%) of **5pa** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 97% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 25 °C, t_r (major) = 12.9 min, t_r (minor) = 15.6 min). $[\alpha]_D^{22}$ = –309.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.21 (m, 6H), 7.20-7.08 (m, 3H), 7.04-7.02 (m, 1H), 7.01 (d, *J* = 8.0 Hz, 1H, other rotamer), 6.03-5.95 (m, 1H), 4.50-4.03 (m, 2H), 3.16-3.06 (m, 1H), 2.72-2.62 (m, 1H), 2.04 (s, 3H), 1.81 (s, 3H, other rotamer), 1.20-1.14 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.0, 188.9, 171.3, 171.2, 142.80, 142.77, 137.83, 137.81, 136.1, 135.9, 135.0, 134.2, 134.1, 134.0, 130.7, 130.6, 130.45, 130.41, 130.2, 129.1, 129.0, 128.6, 128.5, 128.43, 128.40, 126.9, 126.8, 126.7, 126.55, 126.50, 126.43, 126.37, 126.1, 60.6, 45.7, 45.6, 36.7, 36.5, 17.2, 16.9, 14.03, 14.00. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2982, 2929, 1731, 1683, 1451, 1403, 1375, 1299, 1242, 1180, 1033, 940, 909, 759, 727, 458.

HRMS (ESI, *m*/*z*) calcd for $C_{22}H_{22}ClN_2O_3$ $[M+H]^+$: 397.1313, found: 397.1315.



Ethyl (*R*)-3-(naphthalen-2-yl)-4-oxo-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5qa)

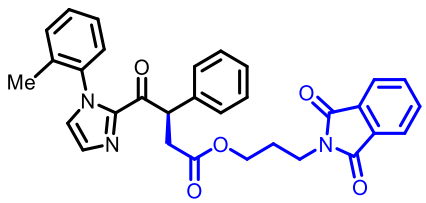
According to the general procedure, the reaction of 2-(naphthalen-2-yl)-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)ethan-1-one **1q** (32.6 mg, 0.10 mmol), ethyl 2-diazoacetate **3a** (34.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 15 hours, afforded 35.4 mg (86%) of **5qa** as a colorless oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 95% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 25 °C, t_r (major) = 15.3 min, t_r (minor) = 17.7 min). $[\alpha]_D^{22}$ = –297.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 12.5 Hz, 1H), 7.79-7.74 (m, 3H), 7.56-7.50 (m, 1H), 7.46-7.40 (m, 2H), 7.38-7.27 (m, 3H), 7.24-7.17 (m, 2H), 7.01-6.98 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H, other rotamer), 5.80-5.73 (m, 1H), 4.10-4.03 (m, 2H), 3.41-3.32 (m, 1H), 2.81-2.72 (m, 1H), 2.05 (s, 3H), 1.52 (s, 3H, other rotamer), 1.20-1.13 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2 189.1, 171.7, 171.6, 142.9, 142.8, 137.8, 135.2, 134.9, 134.3, 133.4, 132.5, 130.61, 130.58, 130.22, 130.16, 129.1, 129.0, 128.40, 128.35, 127.9, 127.8, 127.6, 127.5, 126.6, 126.52, 126.46, 126.4, 126.1, 126.0, 125.87, 125.85, 60.6, 48.80, 48.77, 37.5, 37.2, 17.2, 16.6, 14.09, 14.05. (Mixture of two rotation isomers)

IR (film): *v* (cm^{-1}) 3056, 2981, 2929, 1729, 1682, 1498, 1453, 1403, 1376, 1262, 1241, 1178, 1154, 1024, 941, 908, 816, 763, 728, 479.

HRMS (ESI, *m*/*z*) calcd for $C_{26}H_{24}N_2O_3Na$ $[M+Na]^+$: 435.1679, found: 435.1678.



3-(1,3-Dioxoisoindolin-2-yl)propyl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5bb)

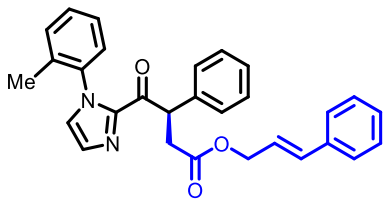
According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), 3-(1,3-dioxoisoindolin-2-yl)propyl 2-diazoacetate **3b** (82.0 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 16 hours, afforded 51.3 mg (98%) of **5bb** as a white solid. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 96% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 50:50, flow rate 0.5 mL/min, 25 °C, t_r (major) = 58.0 min, t_r (minor) = 50.5 min). $[\alpha]_D^{22}$ = –106.8° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.80 (m, 2H), 7.75-7.66 (m, 2H), 7.38-7.23 (m, 7H), 7.23-7.17 (m, 3H), 7.01-7.00 (m, 1H), 6.87 (d, *J* = 7.5 Hz, 1H, other rotamer), 5.61-5.54 (m, 1H), 4.09-3.98 (m, 2H), 3.76-3.67 (m, 2H), 3.29-3.19 (m, 1H), 2.68-2.59 (m, 1H), 2.01 (s, 3H), 1.98-1.90 (m, 2H), 1.52 (s, 3H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 189.1, 171.6,1 171.60, 168.2, 142.9, 142.8, 137.83, 137.80, 137.6, 137.5, 134.9, 134.3, 134.1, 133.9, 132.0, 130.65, 130.56, 130.1, 129.02, 128.96, 128.70, 128.66, 128.6, 127.3, 127.2, 126.54, 126.50, 126.44, 126.39, 126.1, 123.3, 62.0, 48.59, 48.55, 37.2, 36.7, 35.0, 34.9, 27.5, 17.2, 16.5. (Mixture of two rotation isomers)

IR (film): *v* (cm^{-1}) 2953, 2928, 1771, 1708, 1683, 1496, 1445, 1398, 1243, 1172, 1086, 1046, 941, 907, 765, 717, 524, 466.

HRMS (ESI, *m*/*z*) calcd for $C_{31}H_{27}N_3O_5Na$ $[M+Na]^+$: 544.1843, found: 544.1848.



Cinnamyl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5bc)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), cinnamyl 2-diazoacetate **3c** (60.7 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 10 hours, afforded 26.3 mg (58%) of **5bc** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak IC column, ee = 98% (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15,

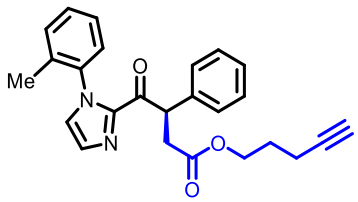
flow rate 1 mL/min, 25 °C, t_r (major) = 14.9 min, t_r (minor) = 17.8 min). $[\alpha]_D^{22}$ = –168.6° (*c* 1.0, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.36 (m, 2H), 7.36-7.29 (m, 6H), 7.29-7.24 (m, 4H), 7.24-7.17 (m, 3H), 7.17-7.14 (m, 1H, other rotamer), 7.00 (dd, J_1 = 3.5 Hz, J_2 = 1.0 Hz, 1H), 6.89 (dd, J_1 = 8.0 Hz, J_2 = 1.0 Hz, 1H, other rotamer), 6.57 (d, J = 15.5 Hz, 1H), 6.56 (d, J = 15.5 Hz, 1H, other rotamer), 6.21-6.12 (m, 1H), 5.67-5.60 (m, 1H), 4.72-4.61 (m, 2H), 3.39-3.30 (m, 1H), 2.79-2.70 (m, 1H), 1.98 (s, 3H), 1.54 (s, 3H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.27, 189.18, 171.5, 171.4, 142.9, 142.8, 137.84, 137.79, 137.6, 137.5, 136.2, 134.9, 134.3, 133.93, 133.85, 130.61, 130.55, 130.21, 130.20, 129.0, 128.9, 128.73, 128.68, 128.59, 128.57, 128.51, 128.48, 128.0, 127.30, 127.27, 126.6, 126.52, 126.46, 126.44, 126.42, 126.39, 126.0, 123.1, 123.0, 65.13, 65.12, 48.7, 48.6, 37.41, 37.0, 17.1, 16.5. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 3059, 3030, 2927, 1732, 1682, 1495, 1451, 1404, 1308, 1242, 1161, 1091, 965, 939, 907, 759, 732, 695, 546, 454.

HRMS (ESI, *m*/*z*) calcd for $C_{29}H_{26}N_2O_3Na$ $[M+Na]^+$: 473.1836, found: 473.1837.



Pent-4-yn-1-yl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5bd)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), pent-4-yn-1-yl 2-diazoacetate **3d** (45.7 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 18 hours, afforded 36.0 mg (90%) of **5bd** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 12.2 min, t_r (minor) = 14.6 min). $[\alpha]_D^{22}$ = –201.4° (*c* 1.0, CH_2Cl_2).

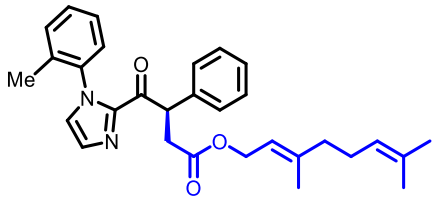
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.26 (m, 7H), 7.25-7.19 (m, 3H), 7.04-7.03 (m, 1H), 6.89 (d, J = 7.5 Hz, 1H, other rotamer), 5.65-5.57 (m, 1H), 4.17-4.07 (m, 2H), 3.36-3.29 (m, 1H), 2.75-2.66 (m,

1H), 2.22-2.13 (m, 2H), 2.04 (s, 3H), 1.97-1.93 (m, 1H), 1.80-1.73 (m, 2H), 1.55 (s, 3H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.2, 189.1 171.6, 171.5, 142.8, 142.7, 137.78, 137.76, 137.6, 137.4, 134.8, 134.3, 130.6, 130.5, 130.2, 130.1, 129.0, 128.9, 128.70, 128.66, 128.5, 127.29, 127.25, 126.51, 126.48, 126.43, 126.40, 126.39, 126.0, 83.0, 68.9, 63.1, 63.0, 48.64, 48.56, 37.3, 36.9, 27.42, 27.38, 17.2, 16.4, 15.05, 15.00. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 3289, 2959, 2927, 1731, 1682, 1495, 1453, 1403, 1362, 1306, 1243, 1170, 1089, 1026, 941, 908, 763, 700, 639, 525.

HRMS (ESI, *m*/*z*) calcd for $C_{25}H_{24}N_2O_3Na$ $[M+Na]^+$: 423.1679, found: 423.1679.



(*E*)-3,7-Dimethylocta-2,6-dien-1-yl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5be)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), (*E*)-3,7-dimethylocta-2,6-dien-1-yl 2-diazoacetate **3e** (66.7 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 24 hours, afforded 38.6 mg (82%) of **5be** as a yellow oil. Enantiomeric excess was established by HPLC analysis using a Chiralpak OD-H column, ee = 96% (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 90:10, flow rate 1 mL/min, 25 °C, t_r (major) = 7.7 min, t_r (minor) = 9.1 min). $[\alpha]_D^{22}$ = –170.2° (*c* 0.4, CH_2Cl_2).

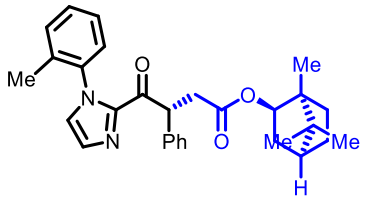
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.24 (m, 7H), 7.24-7.17 (m, 3H), 7.03-7.01 (m, 1H), 6.89 (d, *J* = 7.5 Hz, 1H, other rotamer), 5.64-5.57 (m, 1H), 5.27-5.22 (m, 1H), 5.10-5.05 (m, 1H), 4.55-4.49 (m, 2H), 3.35-3.26 (m, 1H), 2.75-2.65 (m, 1H), 2.11-1.97 (m, 4H), 2.04 (s, 3H), 1.69 (s, 3H), 1.65 (s, 3H), 1.64 (s, 3H, other rotamer), 1.61 (s, 3H), 1.55 (s, 3H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 189.3, 171.7, 143.0, 142.8, 142.1, 142.0, 137.9, 137.8, 137.7, 137.6, 134.9, 134.3, 131.8, 130.60, 130.56, 130.2, 130.1, 129.0, 128.9, 128.7, 128.63, 128.59, 128.58, 127.23, 127.20, 126.5, 126.45, 126.39, 126.37, 126.1, 123.7, 118.2, 118.1, 61.50, 48.65, 48.62, 39.5,

37.4, 37.0, 26.2, 25.7, 17.7, 17.2, 16.5, 16.4. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2968, 2922, 2858, 1731, 1685, 1496, 1451, 1405, 1310, 1240, 1167, 940, 908, 763, 738, 700, 547.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{34}N_2O_3Na$ $[M+Na]^+$: 493.2462, found: 493.2462.



(1*S*,2*R*,4*S*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl)butanoate (5bf)

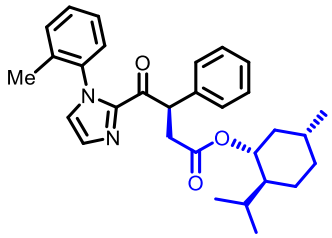
According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), (1*S*,2*R*,4*S*)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 2-diazoacetate **3f** (66.7 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 24 hours, afforded 43.4 mg (92%) of **5bf** as a yellow solid. Diasteromer ratio was established by ^1H NMR and HPLC analysis using a Chiralpak OD-H column, d.r. > 98:2 (HPLC: OD-H, 254 nm, *n*-hexane/isopropanol = 99:1, flow rate 1 mL/min, 25 °C, t_r (major) = 17.8 min, t_r (minor) = 25.5 min). $[\alpha]_D^{22}$ = –180.0° (*c* 1.0, CH_2Cl_2).

^1H NMR (500 MHz, $CDCl_3$) δ 7.44-7.17 (m, 10H), 7.04-7.01 (m, 1H), 6.86 (d, *J* = 8.0 Hz, 1H, other rotamer), 5.67-5.50 (m, 1H), 4.87-4.76 (m, 1H), 3.39-3.25 (m, 1H), 2.79-2.70 (m, 1H), 2.32-2.21 (m, 1H), 2.05 (s, 3H), 1.89-1.60 (m, 3H), 1.52 (s, 3H, other rotamer), 1.30-1.06 (m, 2H), 1.51 (s, 3H, other rotamer), 0.95-0.83 (m, 7H), 0.72 (s, 3H), 0.70 (s, 3H, other rotamer).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 189.2, 171.9, 171.8, 142.89, 142.87, 137.81, 137.79, 137.6, 137.5, 134.8, 134.3, 130.6, 130.5, 130.13, 130.09, 129.0, 128.9, 128.8, 128.7, 128.62, 128.60, 128.58, 127.22, 127.19, 126.5, 126.42, 126.35, 126.1, 80.2, 48.8, 48.61, 48.59, 48.5, 47.70, 47.66, 44.74, 44.73, 37.5, 37.1, 36.45, 36.35, 27.82, 27.77, 27.0, 26.9, 19.6, 18.7, 17.2, 16.4, 13.3, 13.28. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2953, 2878, 1728, 1684, 1495, 1453, 1404, 1306, 1253, 1181, 1155, 1022, 942, 910, 763, 731, 703, 549.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{34}N_2O_3Na$ $[M+Na]^+$: 493.2462, found: 493.2462.



(1*R*,2*S*,5*R*)-2-Isopropyl-5-methylcyclohexyl (*R*)-4-oxo-3-phenyl-4-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) butanoate (5bg)

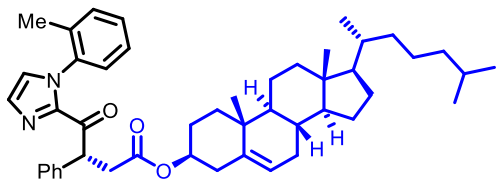
According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (27.6 mg, 0.10 mmol), (1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 2-diazoacetate **3g** (67.2 mg, 3.0 equiv), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (1.3 mg, 1.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 0.5 mL, 0.2 M) under nitrogen atmosphere with visible light for 13 hours, afforded 44.2 mg (93%) of **5bg** as a colorless oil. Diasteromer ratio was established by ^{1}H NMR and HPLC analysis using a Chiralpak IC column, d.r. > 99:1 (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 98:2, flow rate 1 mL/min, 25 °C, t_r (major) = 30.4 min, t_r (minor) = 22.0 min). $[\alpha]_D^{22}$ = –220.6° (*c* 0.4, CH_2Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.16 (m, 10H), 7.03-7.00 (m, 1H), 6.84 (d, *J* = 7.5 Hz, 1H, other rotamer), 5.62-5.54 (m, 1H), 4.62-4.53 (m, 1H), 3.30-3.17 (m, 1H), 2.74-2.65 (m, 1H), 2.03 (s, 3H), 1.88-1.83 (m, 1H), 1.66-1.60 (m, 2H), 1.51 (s, 3H, other rotamer), 1.47-1.23 (m, 3H), 1.02-0.75 (m, 9H), 0.66-0.60 (m, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.3, 171.3, 171.3, 143.0, 142.9, 137.8, 137.6, 137.5, 134.9, 134.3, 130.6, 130.14, 130.10, 129.03, 128.96, 128.68, 128.66, 128.6, 127.3, 127.2, 126.47, 126.45, 126.40, 126.37, 126.1, 74.49, 74.47, 49.0, 48.8, 46.8, 46.7, 40.7, 37.7, 37.3, 34.2, 31.3, 26.03, 25.97, 23.33, 23.26, 21.99, 21.95, 20.73, 20.68, 17.3, 16.4, 16.21, 16.15. (Mixture of two rotation isomers)

IR (film): *v* (cm^{-1}) 2954, 2926, 2867, 1726, 1684, 1496, 1454, 1405, 1373, 1306, 1246, 1178, 1153, 1091, 980, 941, 909, 763, 730, 702, 549.

HRMS (ESI, *m*/*z*) calcd for $C_{30}H_{36}N_2O_3Na$ $[M+Na]^+$: 495.2618, found: 495.2619.



(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)-

2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthren-3-yl (*R*)-4-oxo-3-phenyl-4-(1-(*o*- tolyl)-1*H*-imidazol-2-yl)butanoate (5bh)

According to the general procedure, the reaction of 2-phenyl-1-(1-(*o*-tolyl)-1*H*-imidazol-2-yl) ethan-1-one **1b** (41.4 mg, 0.15 mmol), cholesteryl 2-diazoacetate **3h** (45.4 mg, 0.10 mmol), Λ-**RhS** (3.5 mg, 4 mol%), $[Ru(bpy)_3](PF_6)_2$ (2.2 mg, 2.5 mol%), Na_2HPO_4 (2.8 mg, 20 mol%) and H_2O (36.0 mg, 20 equiv) in acetone/DMSO (9:1, 2.0 mL, 0.05 M) under nitrogen atmosphere with visible light for 60 hours, afforded 58.1 mg (83%) of **5bh** as a white solid. Diasteromer ratio was established by ^{1}H NMR and HPLC analysis using a Chiralpak IC column, d.r. > 97:3 (HPLC: IC, 254 nm, *n*-hexane/isopropanol = 85:15, flow rate 1 mL/min, 25 °C, t_r (major) = 15.5 min, t_r (minor) = 8.9 min). $[\alpha]_D^{22}$ = –116.6° (*c* 0.4, CH_2Cl_2).

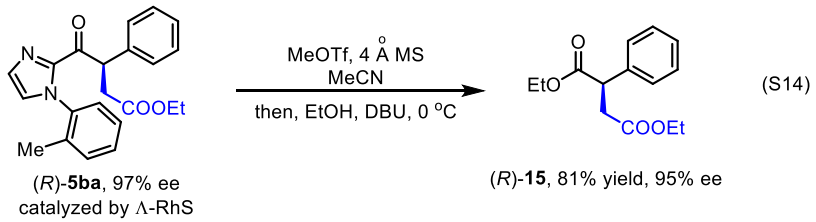
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.17 (m, 10H), 7.03-7.01 (m, 1H), 6.88 (d, *J* = 7.5 Hz, 1H, other rotamer), 5.62-5.56 (m, 1H), 5.35-5.31 (m, 1H), 4.56-4.57 (m, 1H), 3.30-3.22 (m, 1H), 2.73-2.62 (m, 1H), 2.25-2.17 (m, 2H), 2.04 (s, 3H), 2.03-1.90 (m, 2H), 1.88-1.70 (m, 3H), 1.60-0.98 (m, 21H), 1.54 (s, 3H, other rotamer), 0.98 (s, 3H), 0.97 (s, 3H, other rotamer), 0.91 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H), 0.67 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.4, 189.3, 171.1, 171.0, 142.9, 142.8, 139.7, 139.6, 137.85, 137.83, 137.7, 137.6, 134.9, 134.3, 130.61, 130.59, 130.10, 130.07, 129.02, 128.96, 128.7, 128.6, 127.23, 127.20, 126.5, 126.4, 126.1, 122.50, 122.46, 74.25, 74.23, 56.6, 56.1, 49.93, 49.92, 48.7, 48.6, 42.3, 39.7, 39.5, 37.92, 37.87, 37.8, 37.4, 36.9, 36.52, 36.50, 36.1, 35.8, 31.9, 31.84, 31.79, 28.20, 28.0, 27.6, 27.5, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 17.3, 16.5, 11.8. (Mixture of two rotation isomers)

IR (film): ν (cm^{-1}) 2939, 2864, 1730, 1685, 1496, 1458, 1406, 1373, 1245, 1176, 1007, 940, 909, 763, 730, 703, 547.

HRMS (ESI, *m*/*z*) calcd for $C_{47}H_{62}N_2O_3Na$ $[M+Na]^+$: 725.4653, found: 725.4666.

7. Removal of Directing Group



(*R*)-**5ba**, 97% ee
catalyzed by Λ-RhS

(*R*)-**15**, 81% yield, 95% ee

(S14)

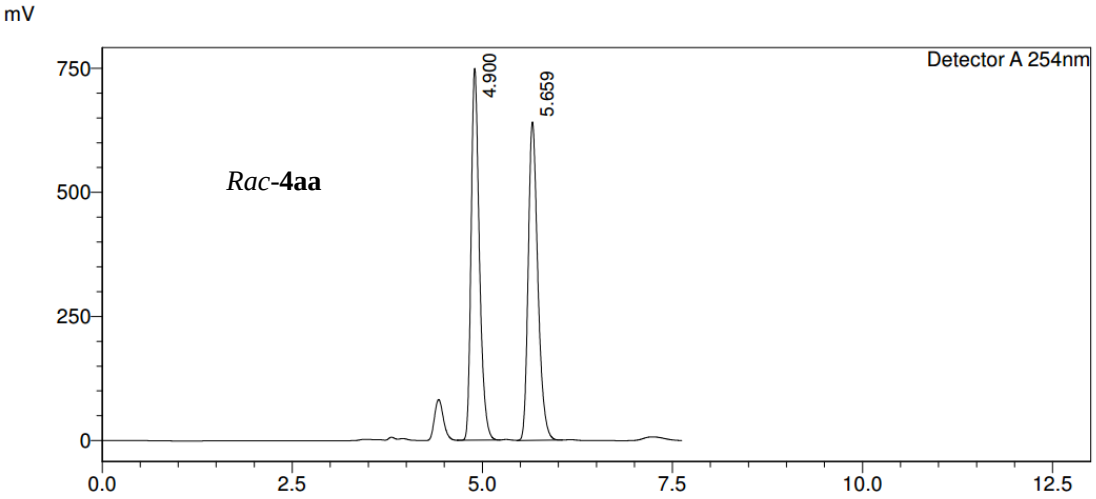
The directing imidazole moiety was cleaved according to our previous report with slight modification.[19] 4 Å MS (169 mg, 100 mg/0.1 mmol of **5ba**) was added to a solution of (*R*)-**5ba** (61 mg, 0.169 mmol) in CH_3CN (0.1 M) under nitrogen atmosphere. The suspension was stirred vigorously under a positive pressure of nitrogen for 3 h at 0 °C. Then methyl trifluoromethansulfonate (30.5 mg, 0.186 mmol, 1.1 equiv) was added dropwise at 0 °C. After being stirred at 0 °C for 6 h, EtOH (1.0 mL) and DBU (28.3 mg, 0.186 mmol, 1.1 equiv) were subsequently added to the reaction mixture at 0 °C. After being stirred at 0 °C for 60 min, 10 mL of saturated $NaHCO_3$ aqueous solution was added. And the mixture was extracted with DCM, washed with $NaHCO_3$ aqueous solution, water. The organic layer was dried and the solvent was evaporated and the residue was purified by flash chromatography on silica gel (EtOAc/*n*-hexane = 1:50) to give 34.1 mg (*R*)-**15** (81%) as a colorless oil.

Enantiomeric excess of (*R*)-**15** was established by HPLC analysis using a Chiralpak AD-H column, 95% ee (HPLC: AD-H, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, 25 °C, t_r (major) = 7.0 min, t_r (minor) = 8.0 min). $[\alpha]_D^{22}$ = –97.6° (*c* 1.0, CH_2Cl_2).

Literature report[20] for (*S*)-**15**: 77% ee (HPLC: AD-H, *n*-hexane/isopropanol = 95:5, flow rate 1 mL/min, Retention times: 6.69 min [(*R*)-enantiomer], 7.68 min [(*S*)-enantiomer]. $[\alpha]_D^{29}$ = +51.25 (c 1.19, $CHCl_3$). All other spectroscopic data of **15** are in agreement with literature report.[20]

8. Enantioselectivities as Determined by Chiral HPLC

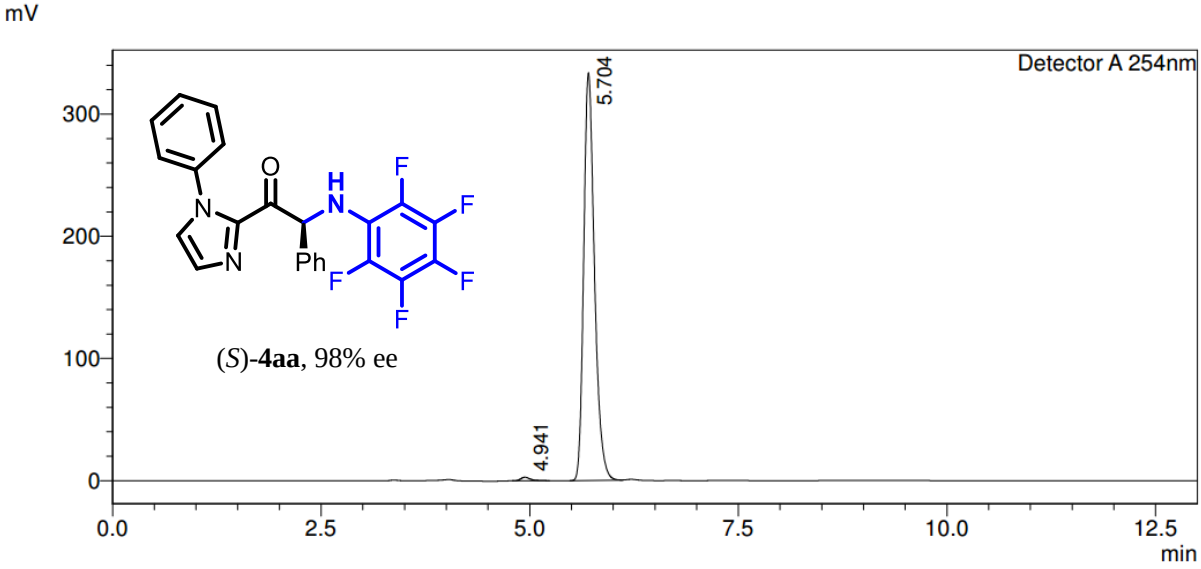
Enantiomeric purities of the reaction products were determined with a Daicel Chiralpak AD-H, OD-H, IC (250 × 4.6 mm) HPLC column on an Agilent 1200 or 1260 Series or Shimadzu Lc-2030c HPLC System using *n*-hexane/isopropanol as a mobile phase. The column temperature was 25 °C and UV-absorption was measured at 254 nm.



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	4.900	5655784	50.042
2	5.659	5646309	49.958
Total		11302093	100.000

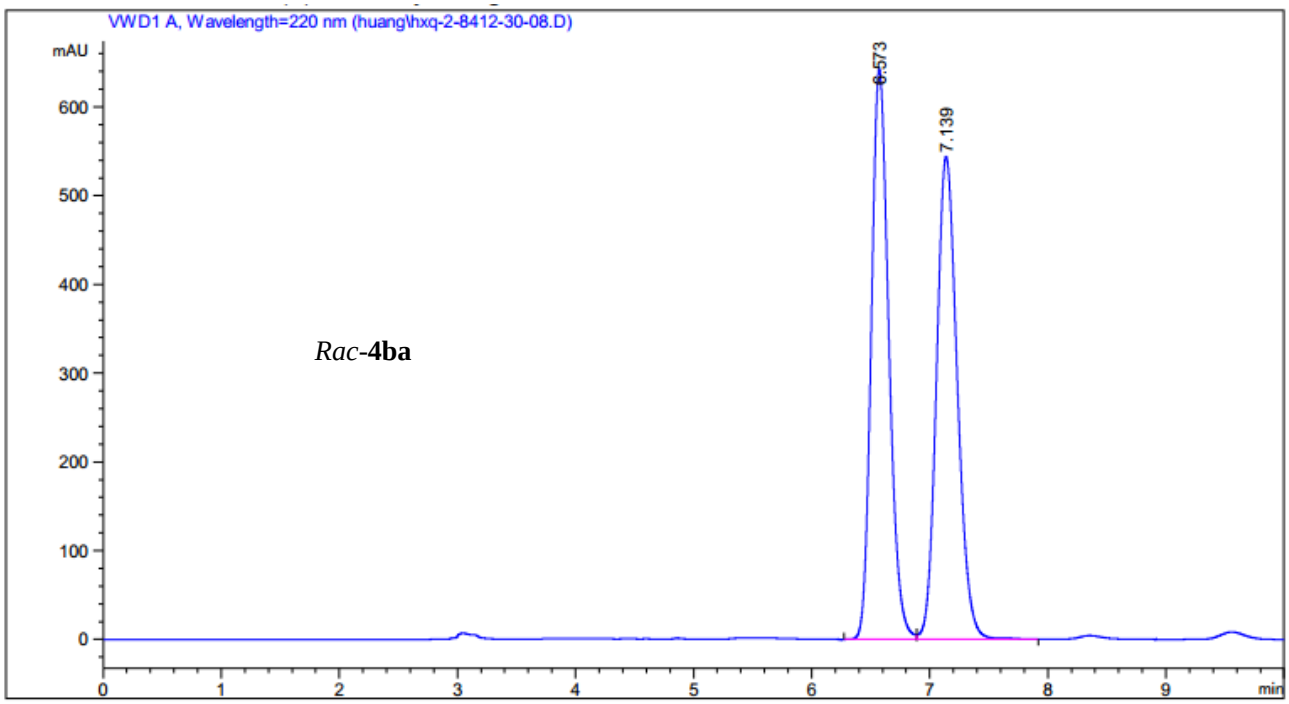


(*S*)-**4aa**, 98% ee

Detector A 254nm

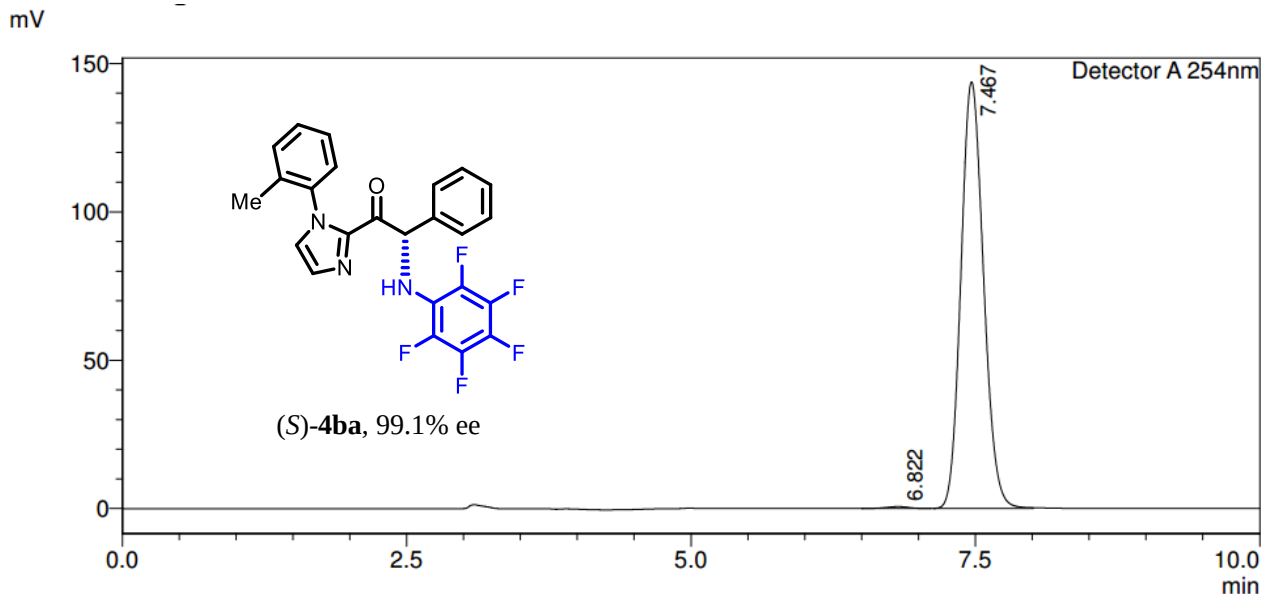
Peak#	Ret. Time	Area	Area%
1	4.941	23510	0.780
2	5.704	2991241	99.220
Total		3014751	100.000

Figure S6. HPLC traces of *rac*-**4aa** (reference) and (*S*)-**4aa**.



Rac-**4ba**

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.573	BV	0.1594	6602.59326	642.30603	49.8664
2	7.139	VV R	0.1893	6637.96484	544.12408	50.1336



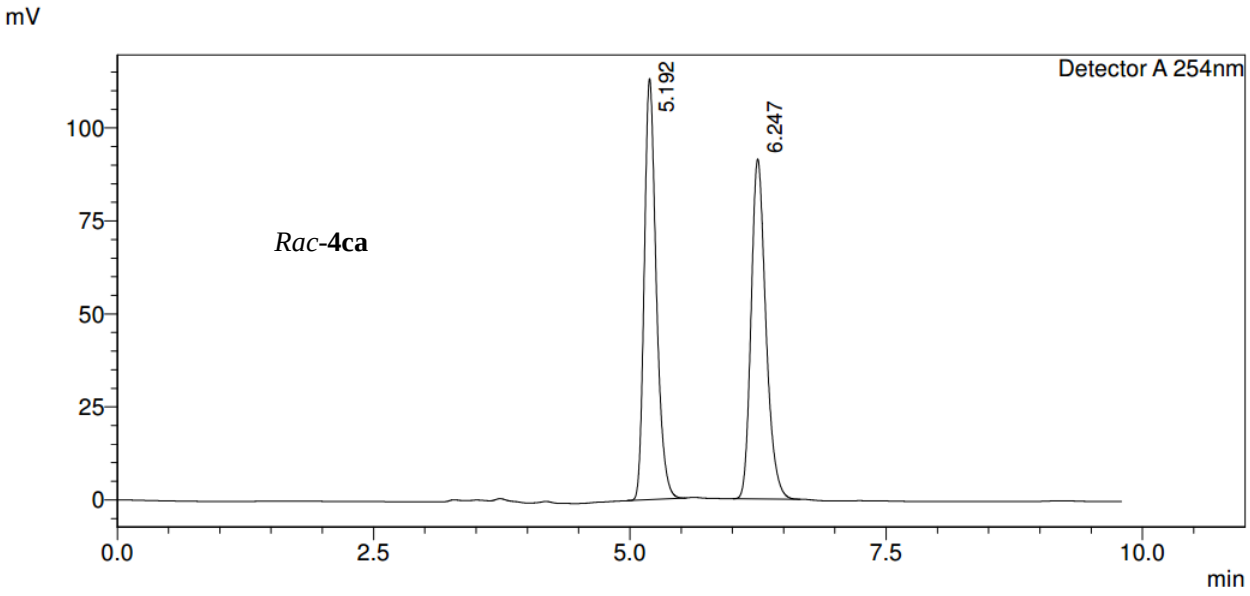
(*S*)-**4ba**, 99.1% ee

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	6.822	8758	0.439
2	7.467	1986670	99.561
Total		1995428	100.000

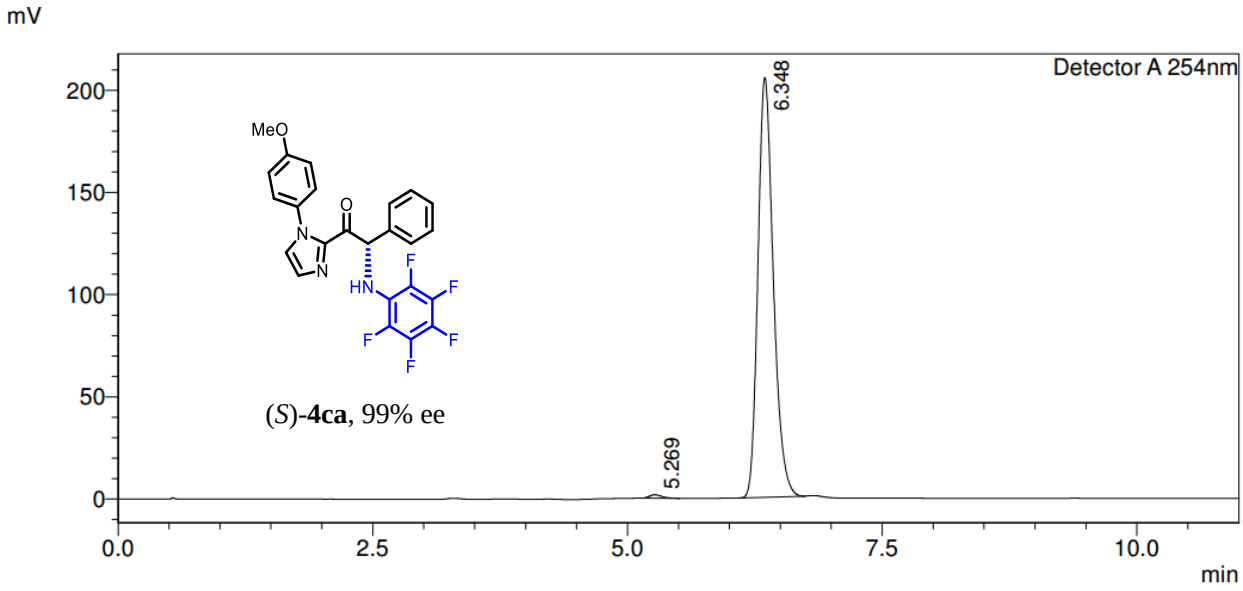
Figure S7. HPLC traces of *rac*-**4ba** (reference) and (*S*)-**4ba**.



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	5.192	923178	50.150
2	6.247	917651	49.850
Total		1840829	100.000

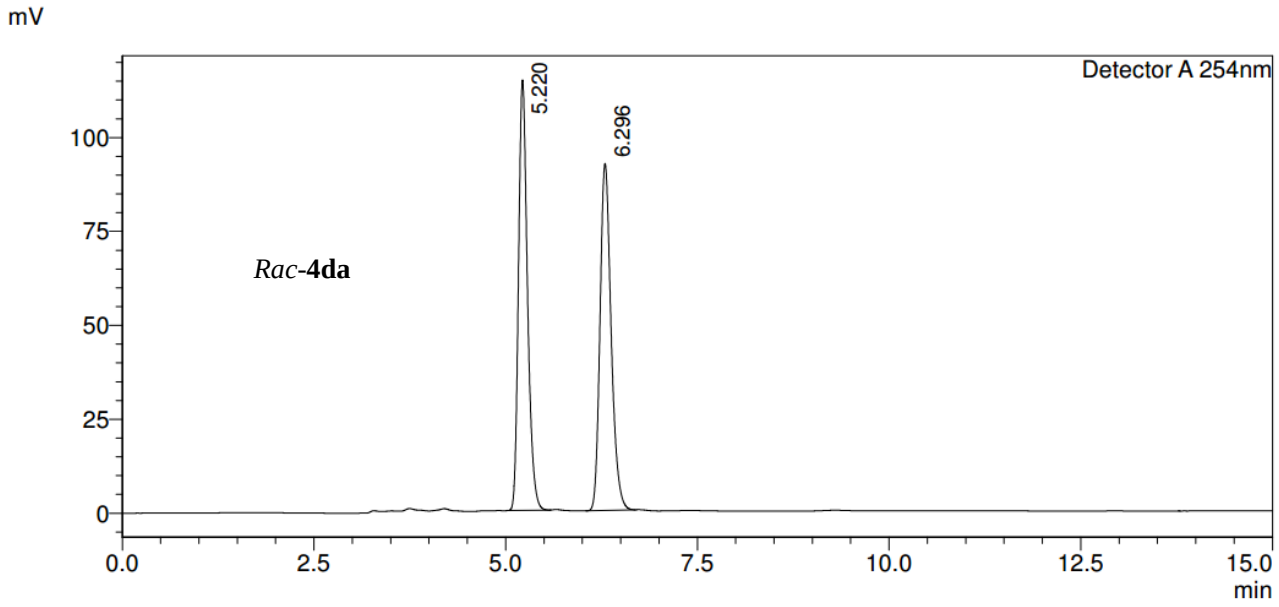


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	5.269	14044	0.646
2	6.348	2161068	99.354
Total		2175112	100.000

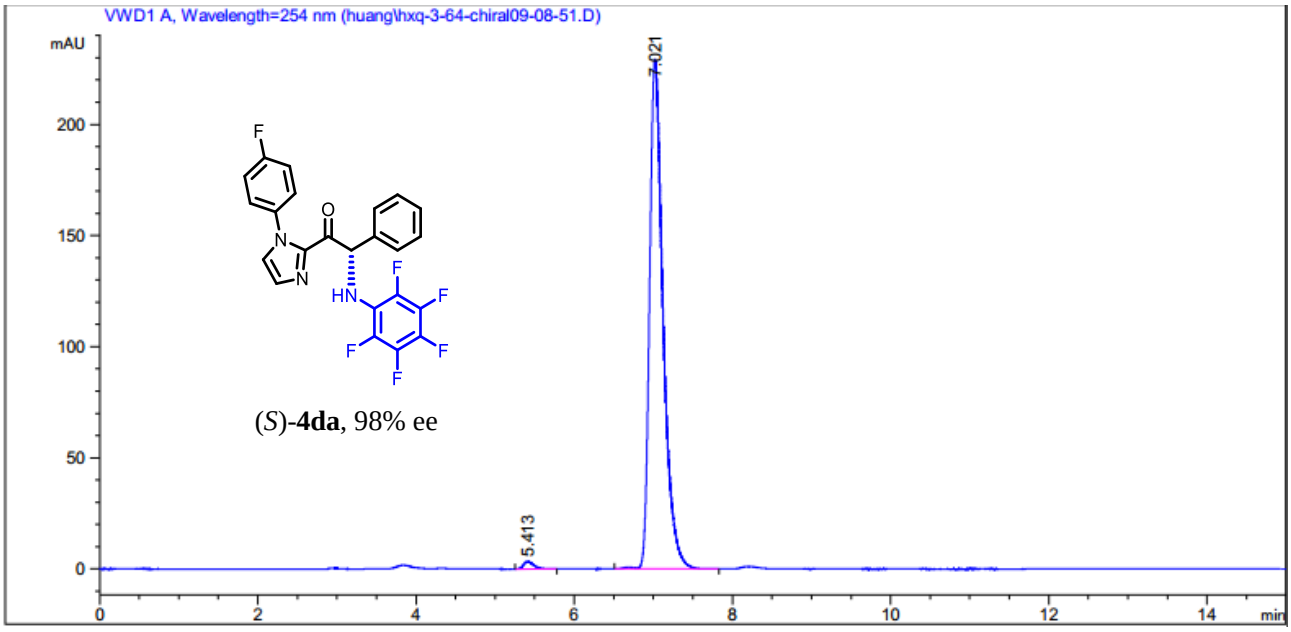
Figure S8. HPLC traces of *rac*-**4ca** (reference) and (*S*)-**4ca**.



<Peak Table>

Detector A 254nm

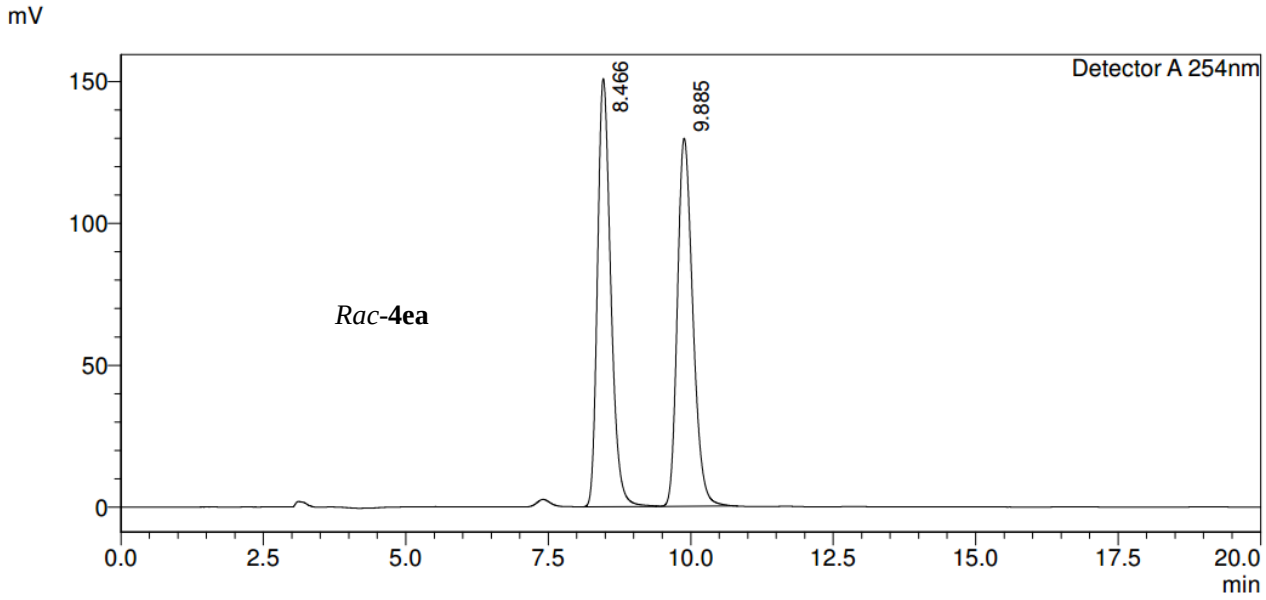
Peak#	Ret. Time	Area	Area%
1	5.220	932942	50.121
2	6.296	928434	49.879
Total		1861376	100.000



(*S*)-**4da**, 98% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.413	BV R	0.1148	30.64151	3.40977	1.1178
2	7.021	VV R	0.1770	2710.66138	229.21643	98.8822
Totals :				2741.30289	232.62620	

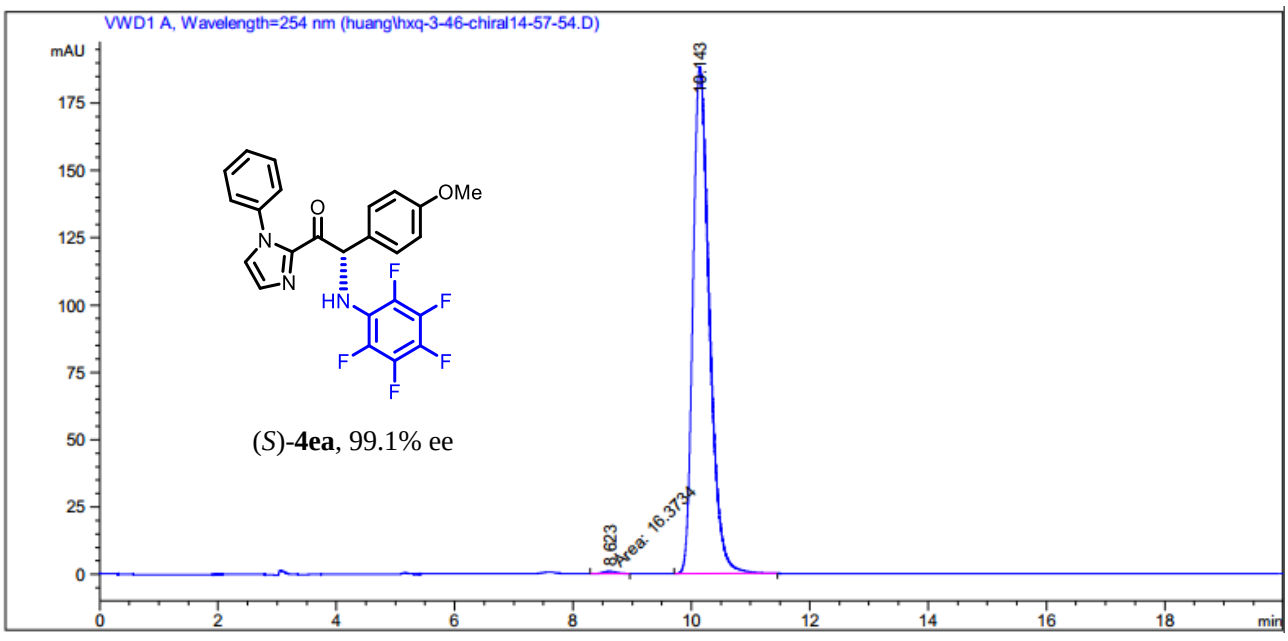
Figure S9. HPLC traces of *rac*-**4da** (reference) and (*S*)-**4da**.



<Peak Table>

Detector A 254nm

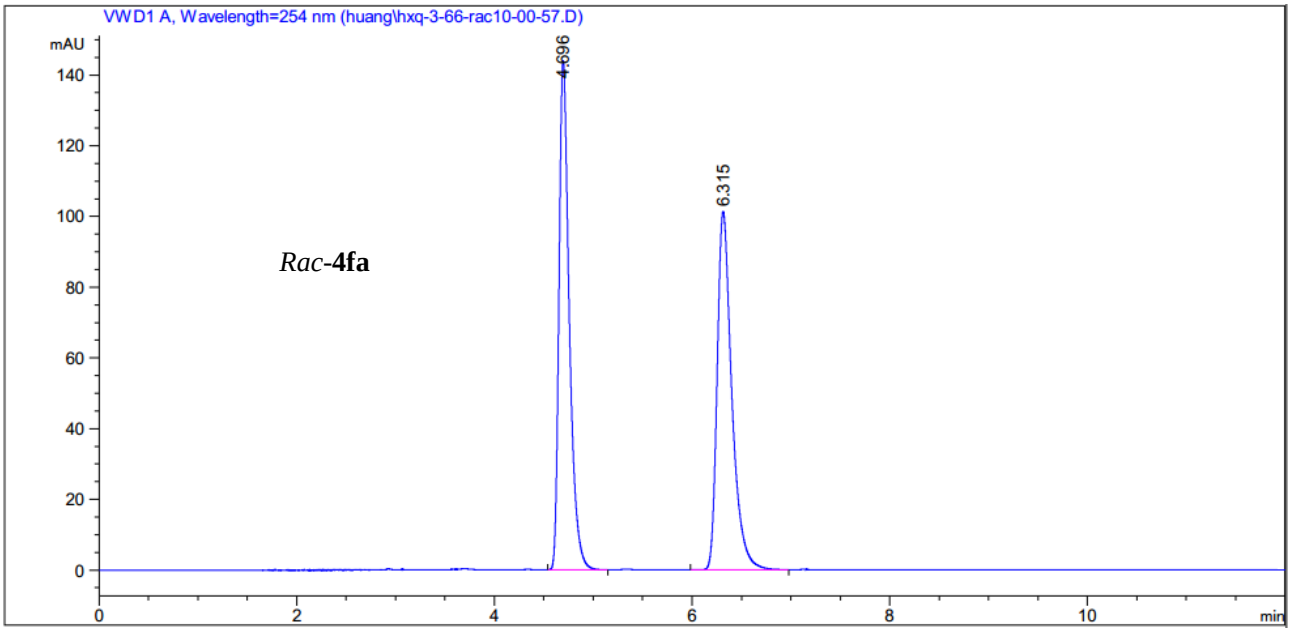
Peak#	Ret. Time	Area	Area%
1	8.466	2447131	49.962
2	9.885	2450820	50.038
Total		4897951	100.000



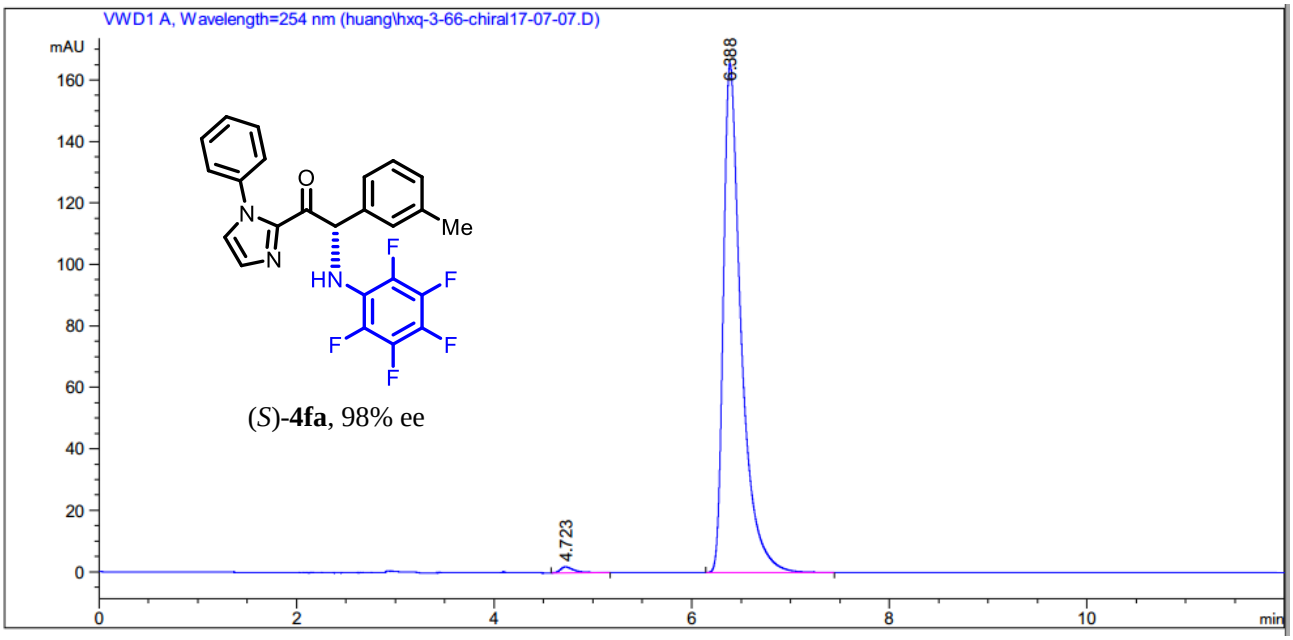
(*S*)-**4ea**, 99.1% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.623	MM	0.2815	16.37341	9.69304e-1	0.4489
2	10.143	BB	0.2945	3631.01636	188.30353	99.5511
Totals :				3647.38976	189.27283	

Figure S10. HPLC traces of *rac*-**4ea** (reference) and (*S*)-**4ea**.

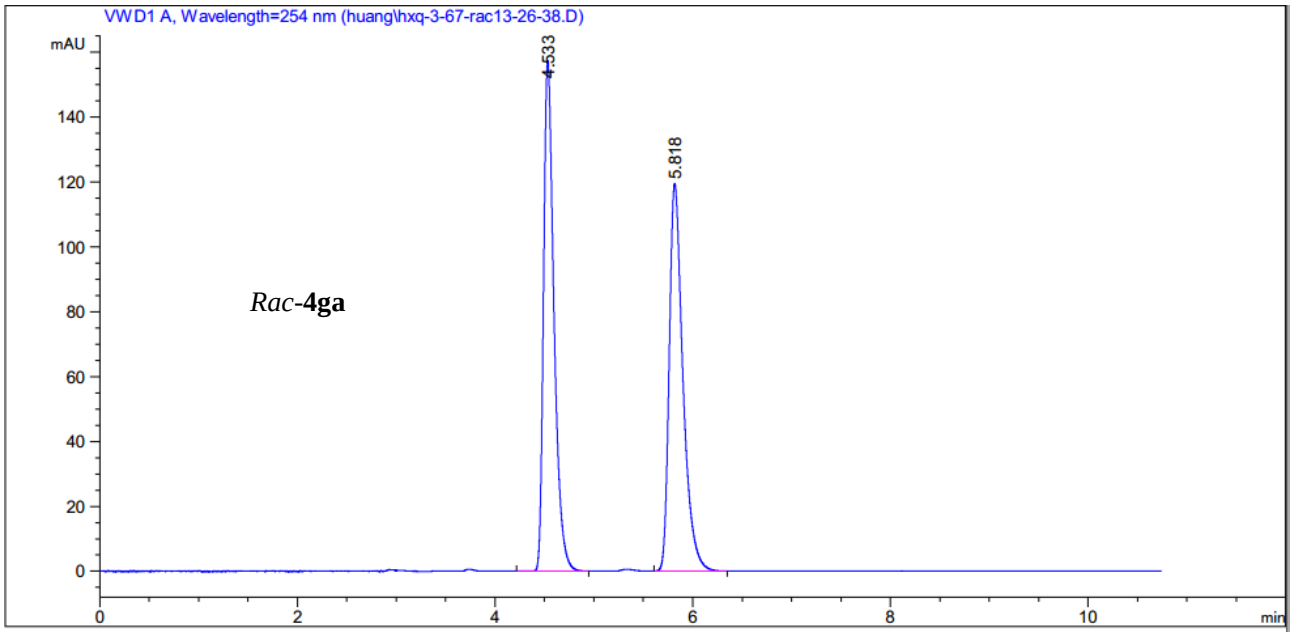


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.696	BB	0.1090	1042.27026	143.95796	50.0022
2	6.315	BB	0.1549	1042.17859	101.36533	49.9978
Totals :				2084.44885	245.32330	

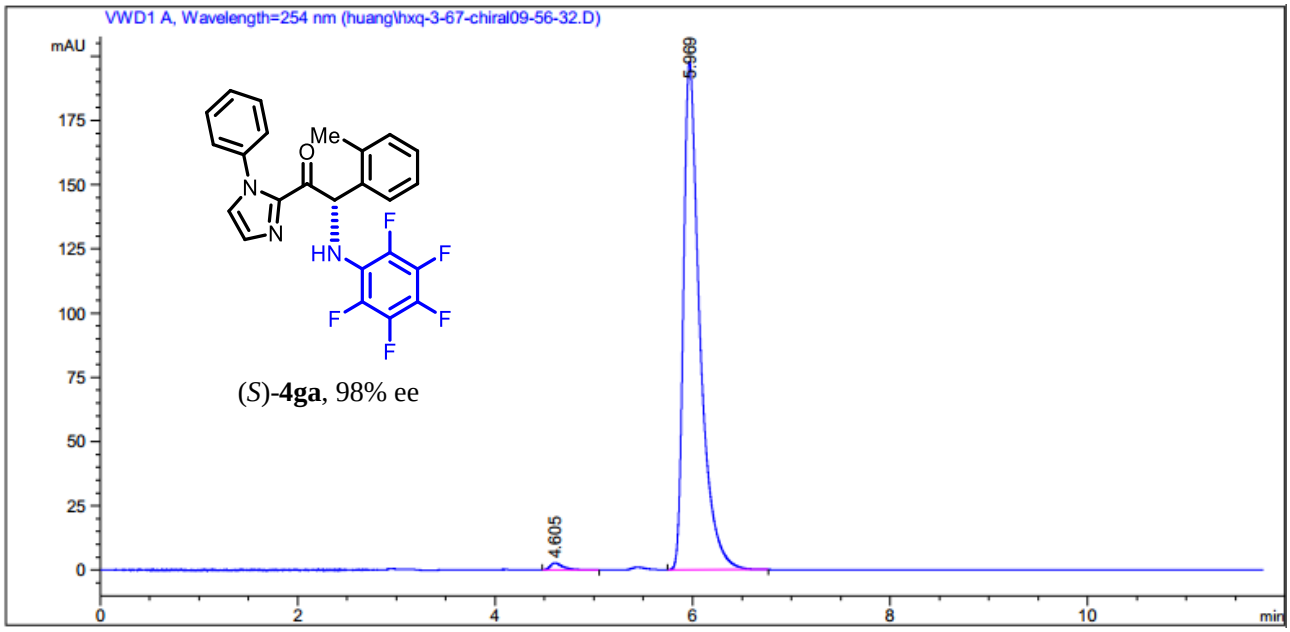


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.723	BB	0.1183	18.82629	1.92084	0.8981
2	6.388	BB	0.1863	2077.33789	165.65442	99.1019

Figure S11. HPLC traces of *rac*-**4fa** (reference) and (*S*)-**4fa**.

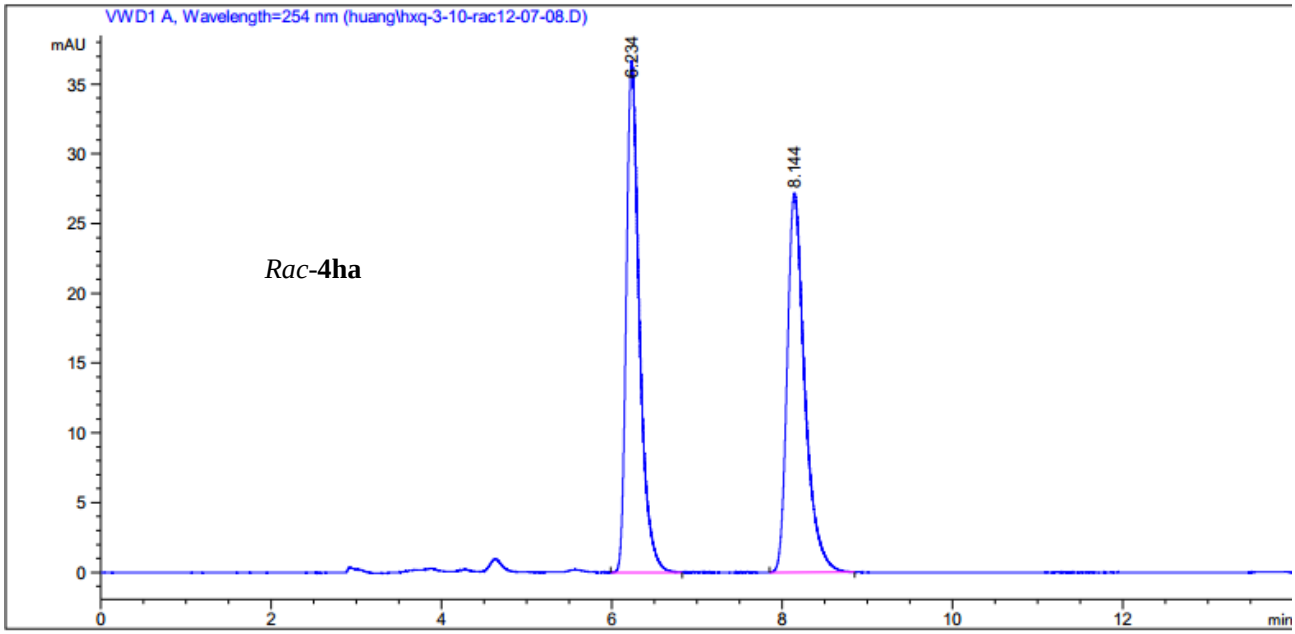


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.533	VB R	0.1106	1154.15881	157.31387	50.0763
2	5.818	BB	0.1434	1150.64209	119.41300	49.9237

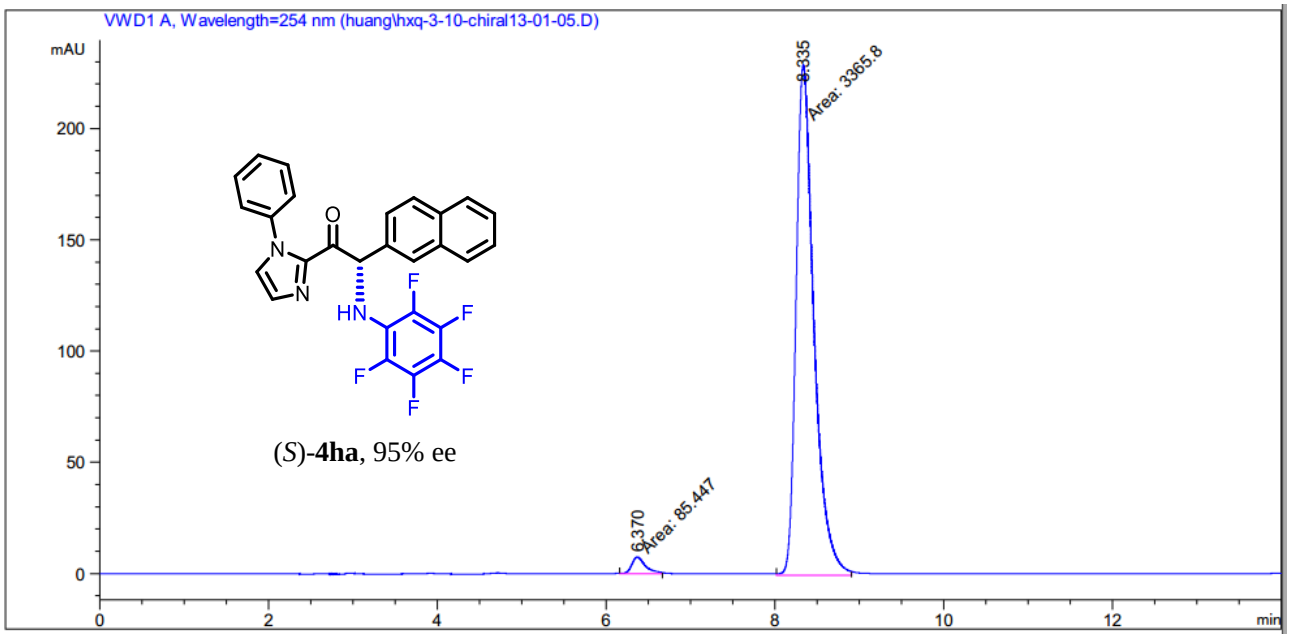


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.605	BB	0.1123	24.39757	2.70437	1.0616
2	5.969	BV R	0.1696	2273.75488	197.77589	98.9384

Figure S12. HPLC traces of *rac*-**4ga** (reference) and (*S*)-**4ga**.

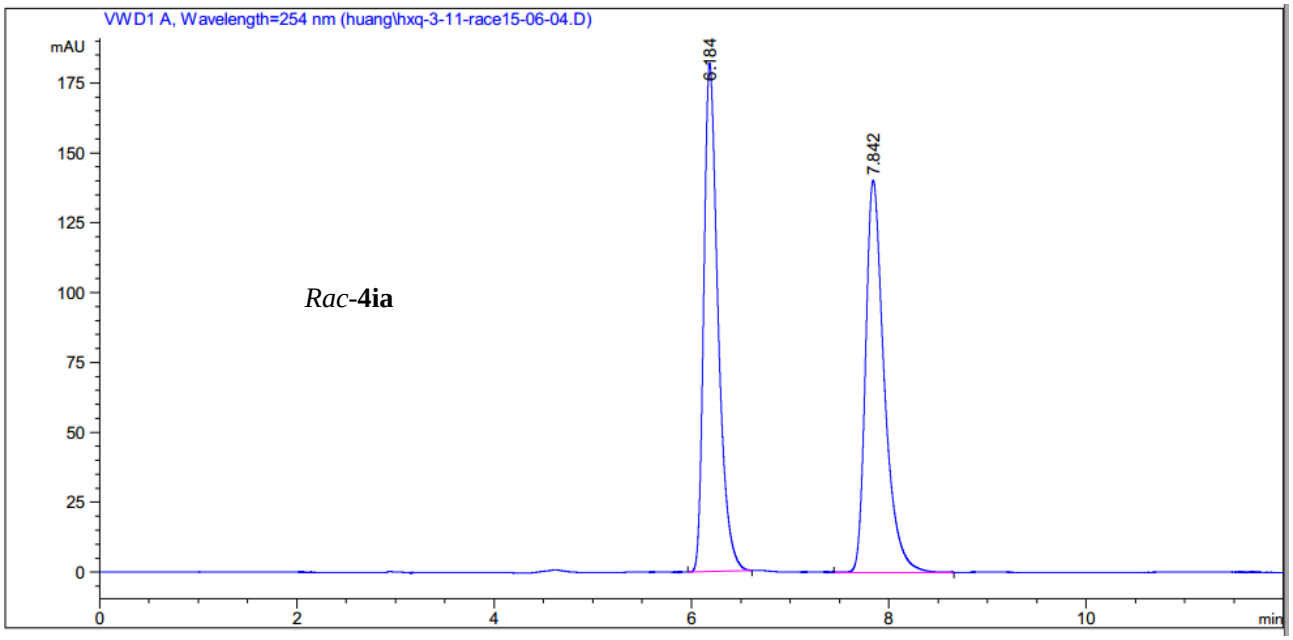


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.234	BB	0.1570	391.23090	36.67200	50.1275
2	8.144	BB	0.2051	389.24060	27.17608	49.8725

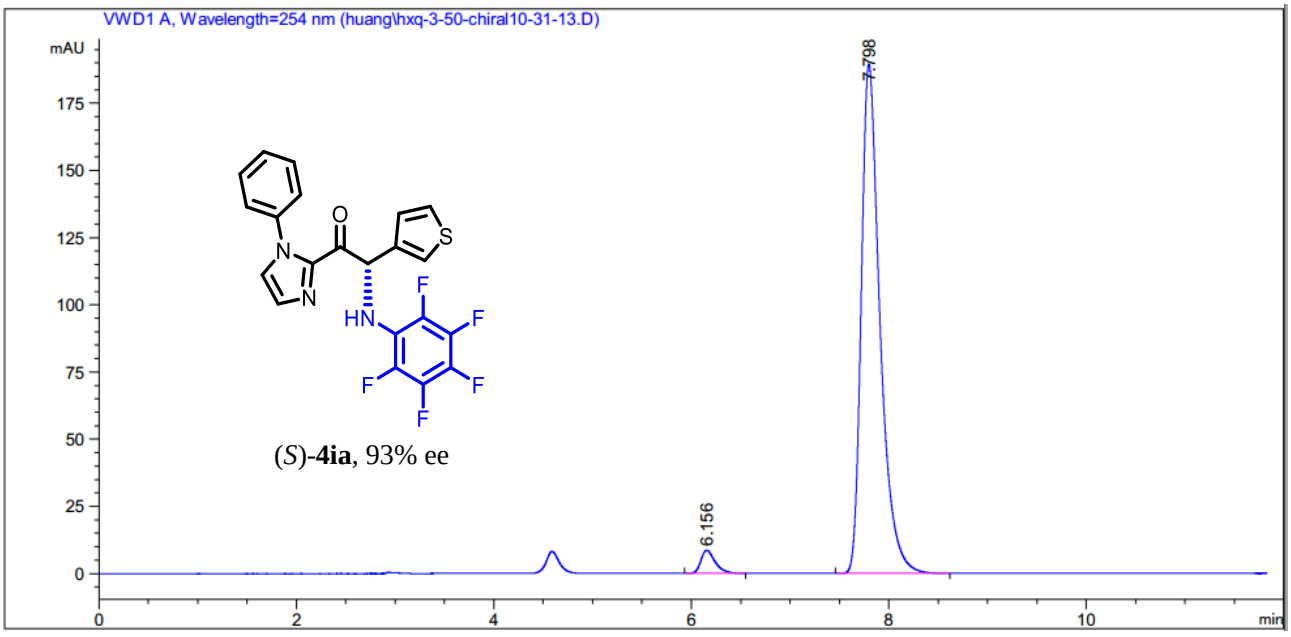


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.370	MM	0.1895	85.44697	7.51552	2.4758
2	8.335	MM	0.2446	3365.80078	229.34956	97.5242

Figure S13. HPLC traces of *rac*-**4ha** (reference) and (*S*)-**5ha**.

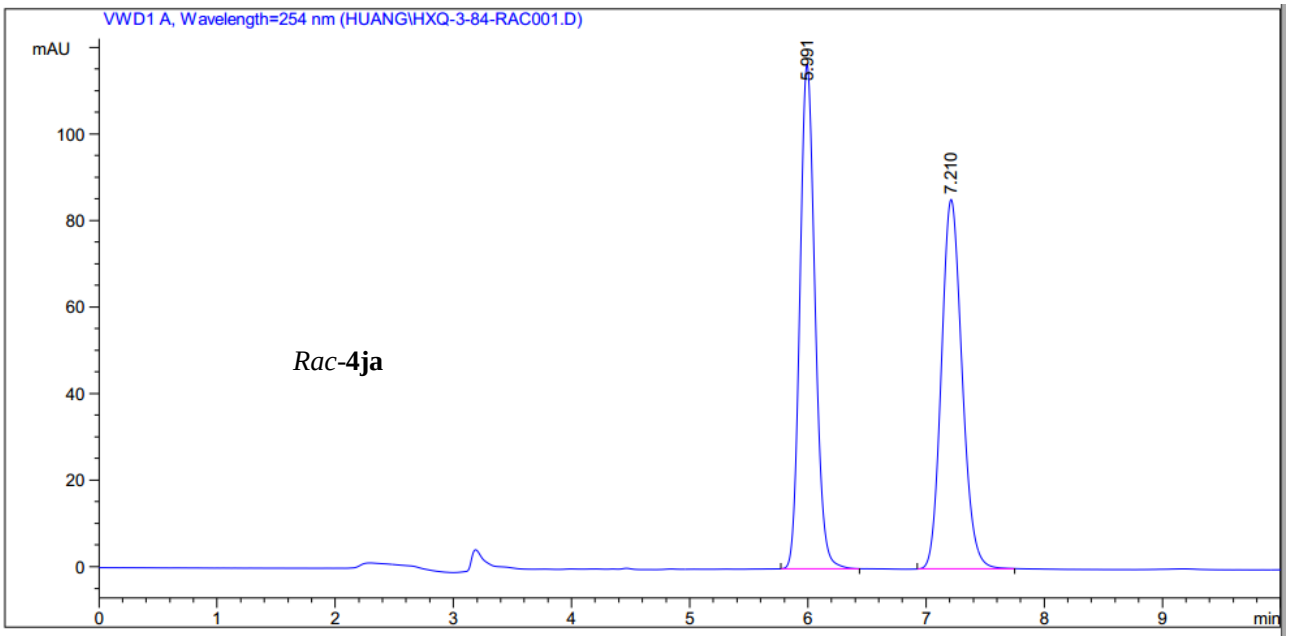


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.184	BB	0.1521	1824.24597	181.81285	49.7816
2	7.842	BB	0.1965	1840.25415	140.31100	50.2184

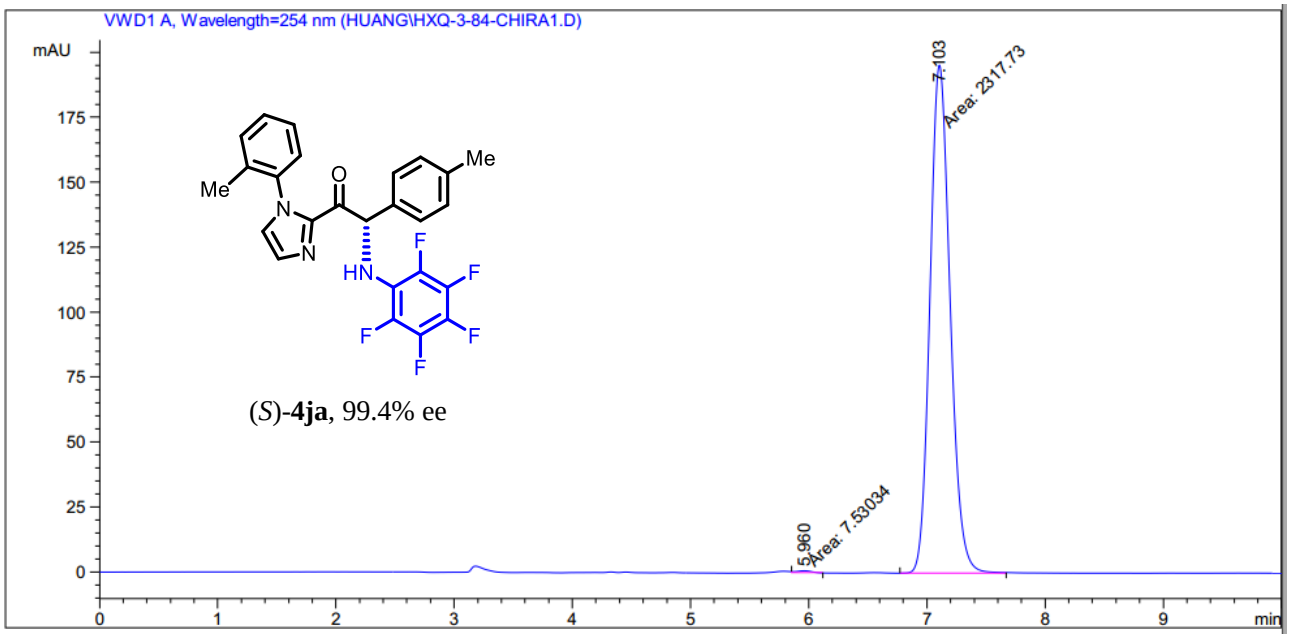


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.156	BB	0.1419	86.60161	8.60934	3.3564
2	7.798	BB	0.1955	2493.58569	189.56358	96.6436

Figure S14. HPLC traces of *rac*-**4ia** (reference) and (*S*)-**4ia**.

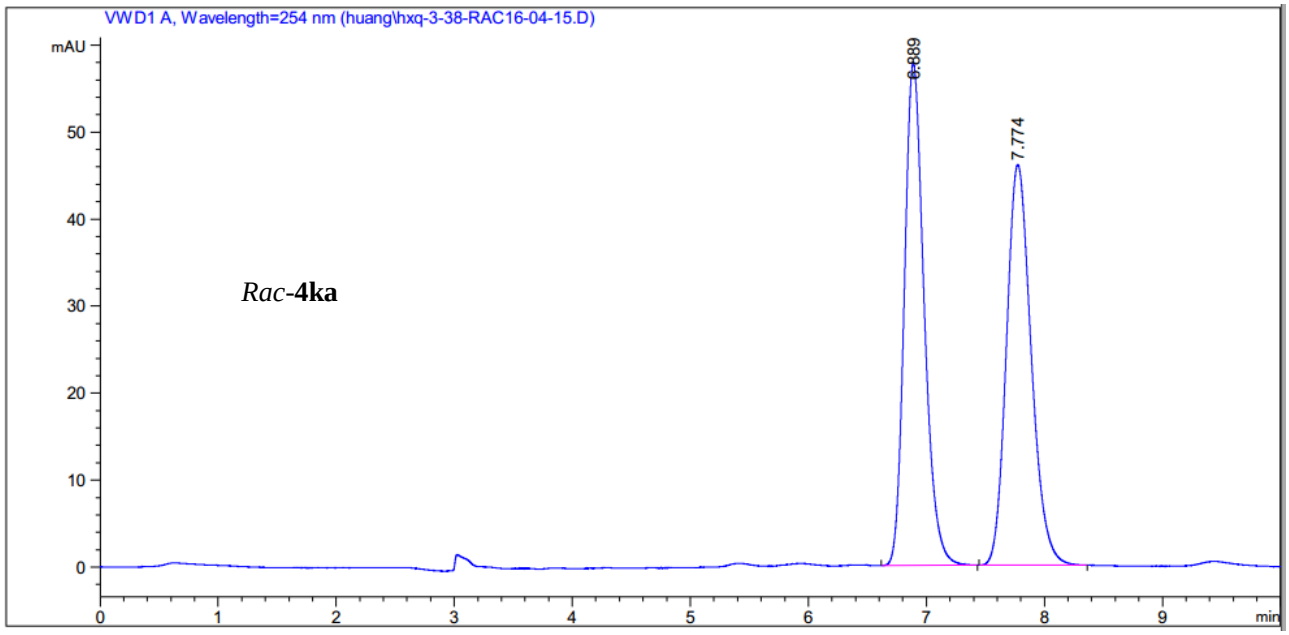


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.991	BB	0.1374	1039.11853	116.68845	50.0166
2	7.210	BB	0.1885	1038.42822	85.39353	49.9834

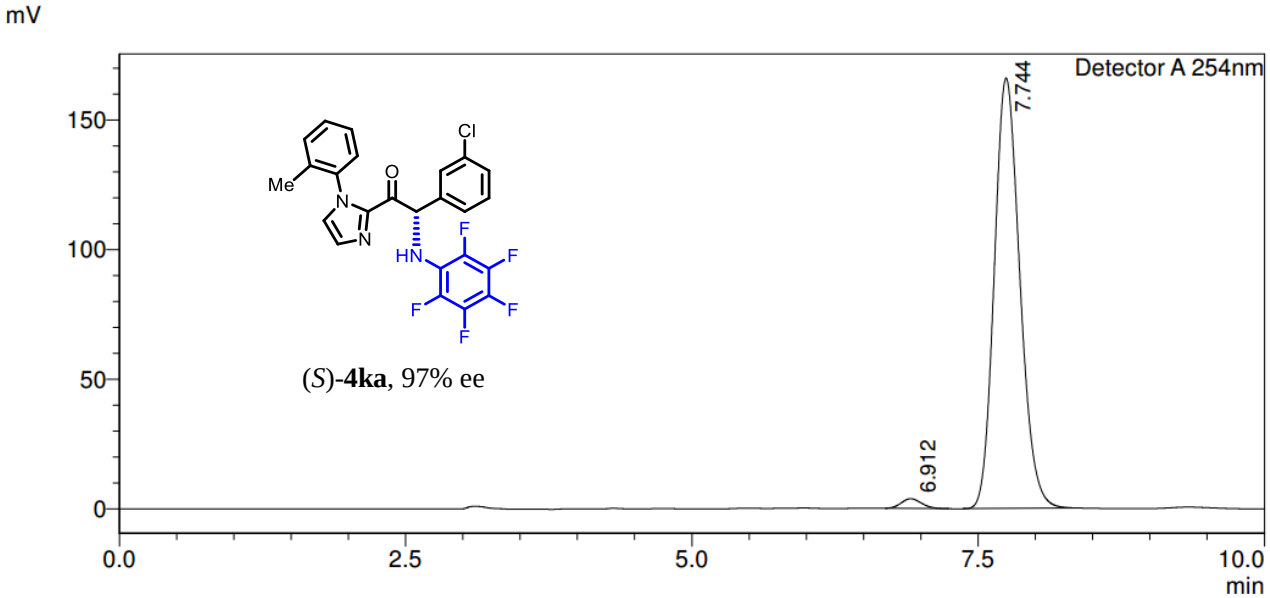


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.960	FM	0.1528	7.53034	8.21494e-1	0.3238
2	7.103	MM	0.1974	2317.72754	195.66428	99.6762

Figure S15. HPLC traces of *rac*-**4ja** (reference) and (*S*)-**4ja**.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.889	BB	0.1769	670.94501	57.79842	50.0413
2	7.774	BV R	0.2167	669.83807	46.06023	49.9587

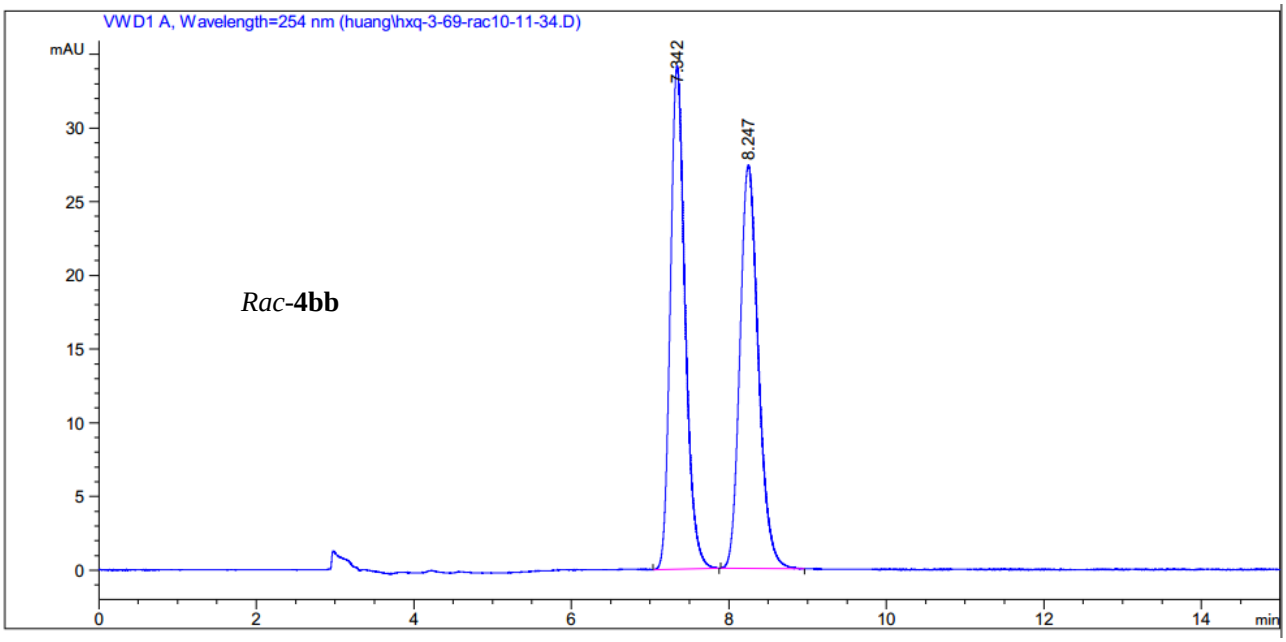


<Peak Table>

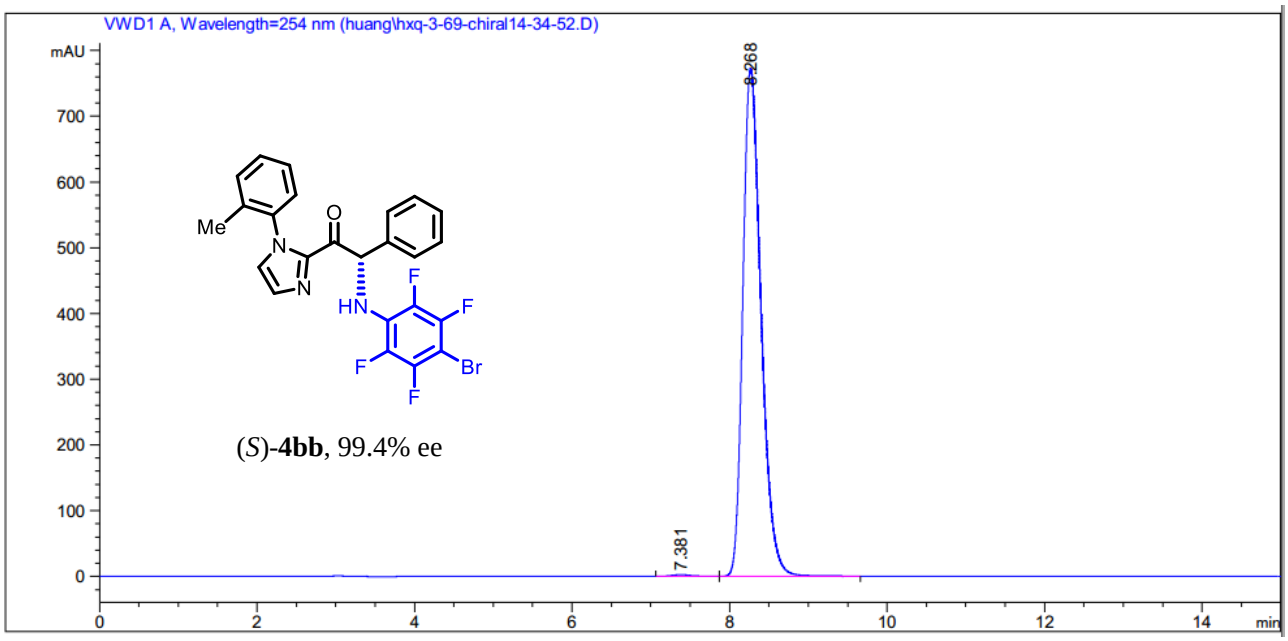
Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	6.912	45760	1.745
2	7.744	2576344	98.255
Total		2622103	100.000

Figure S16. HPLC traces of *rac*-**4ka** (reference) and (*S*)-**4ka**.

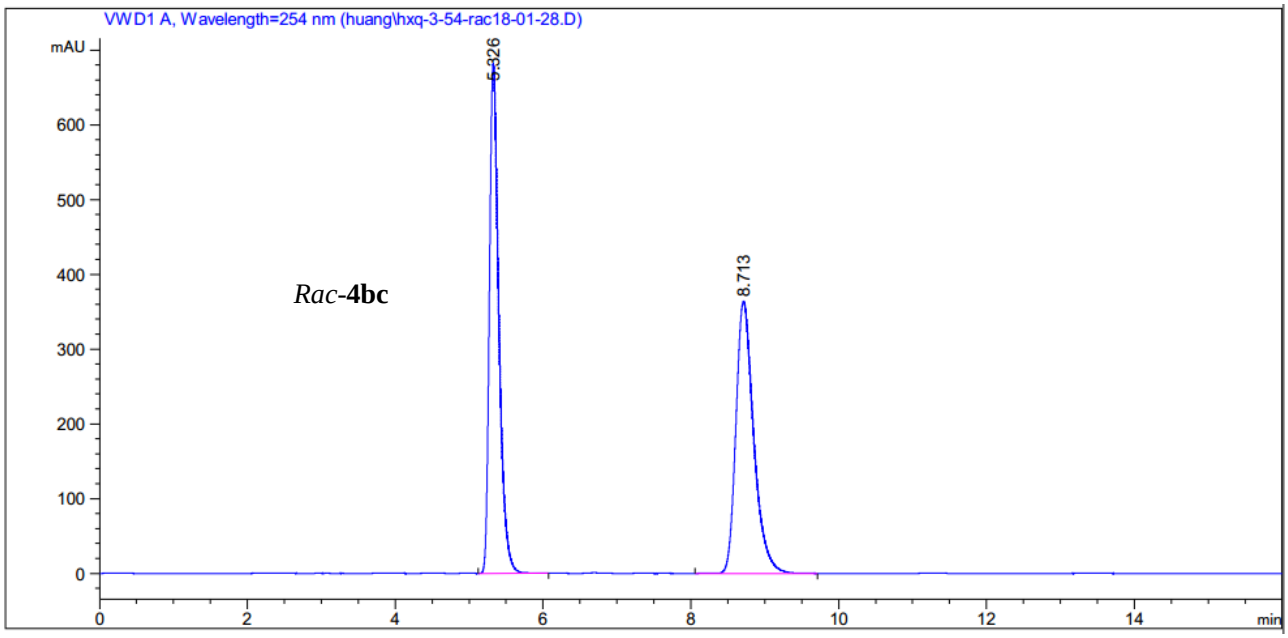


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.342	BB	0.1945	444.79471	34.13875	50.0546
2	8.247	BB	0.2218	443.82416	27.35356	49.9454

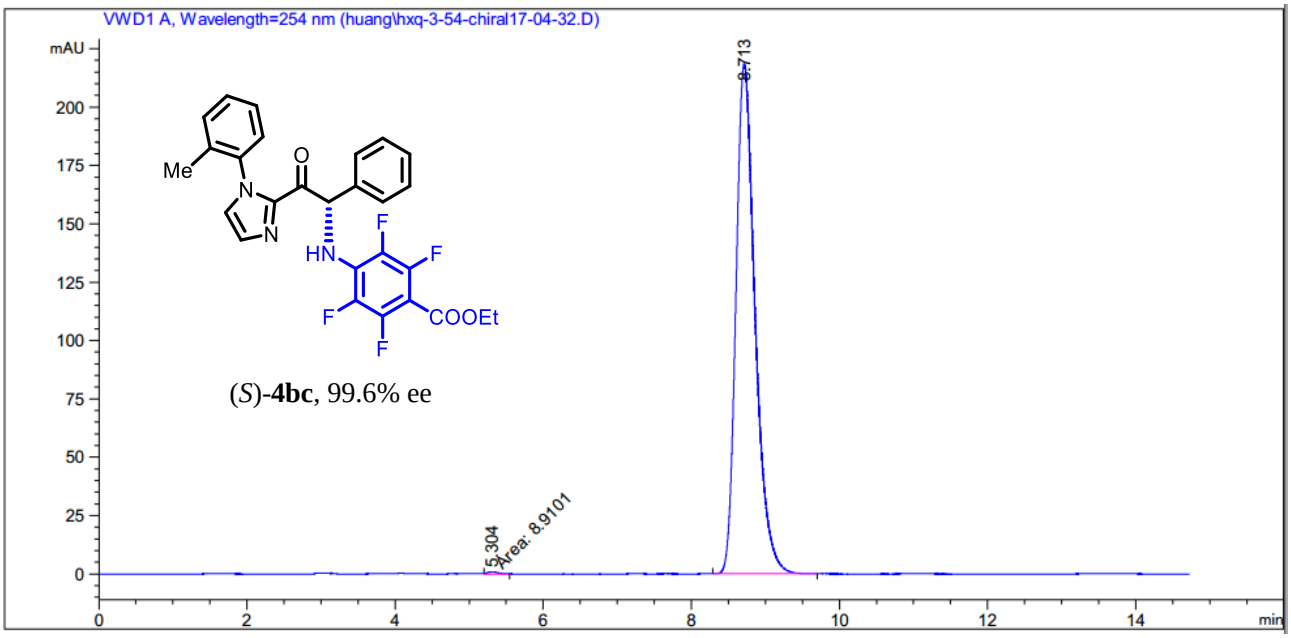


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.381	BB	0.1804	38.32401	2.49974	0.3084
2	8.268	BB	0.2470	1.23873e4	772.74170	99.6916

Figure S17. HPLC traces of *rac*-**4bb** (reference) and (*S*)-**4bb**.

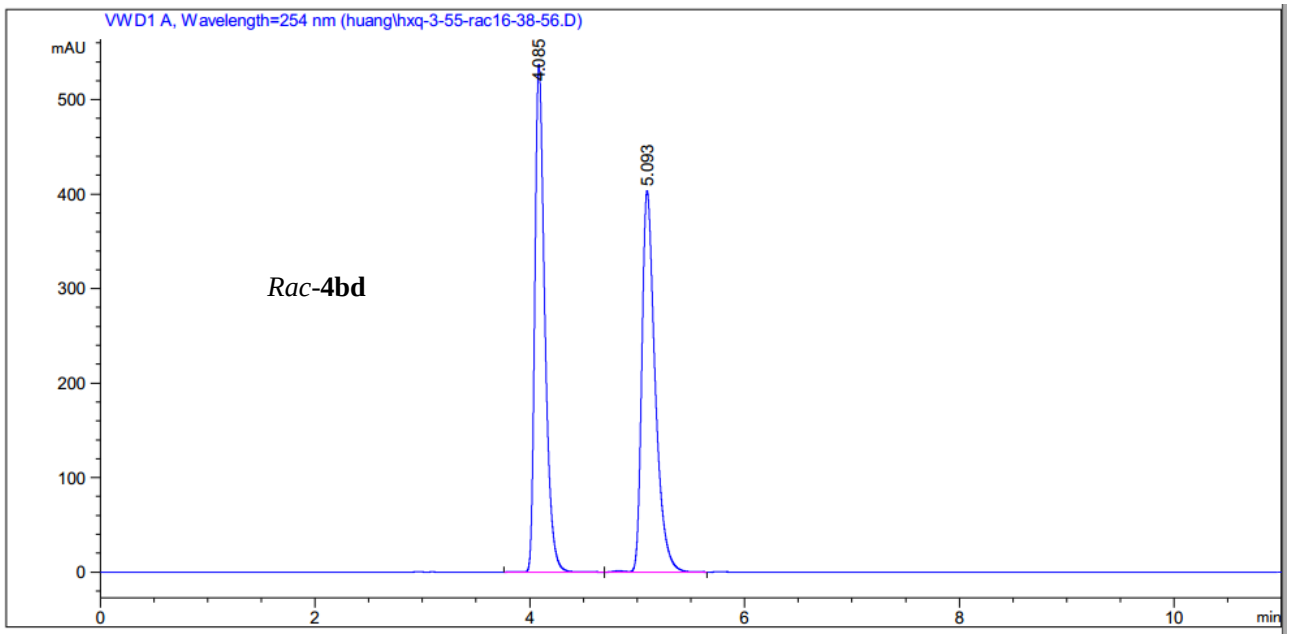


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.326	BB	0.1323	6035.45459	681.91357	49.8877
2	8.713	VB R	0.2519	6062.61719	363.91815	50.1123

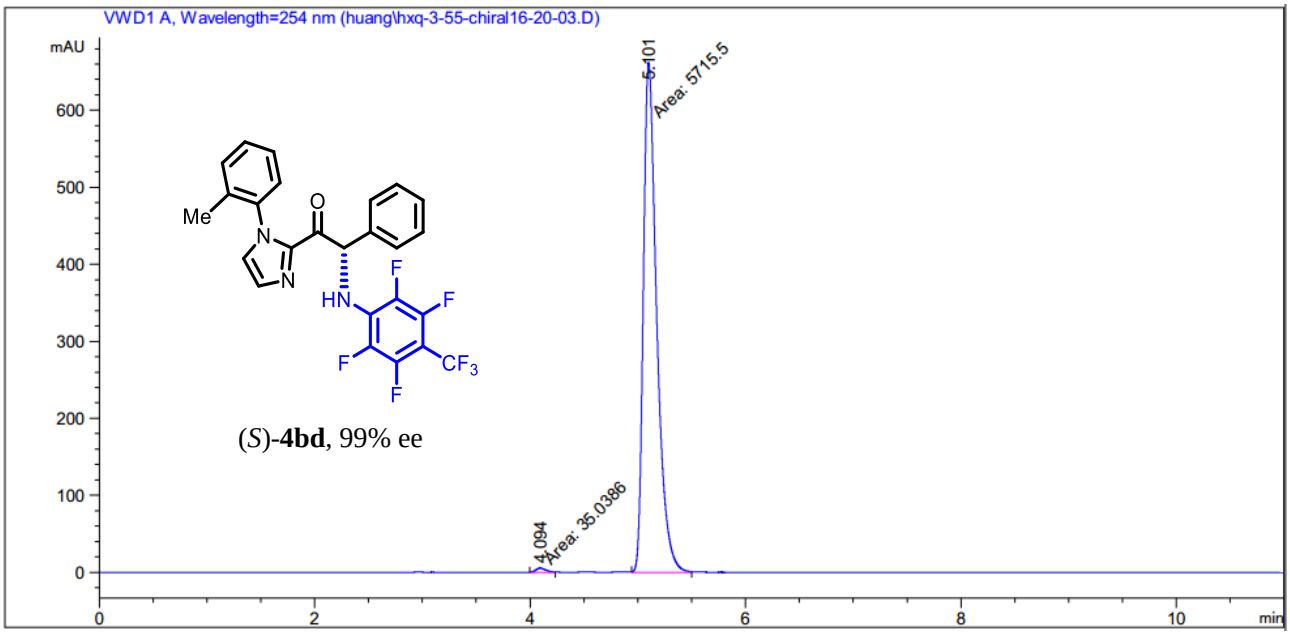


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.304	MM	0.1718	8.91010	8.64277e-1	0.2278
2	8.713	BV R	0.2725	3902.89868	218.41608	99.7722

Figure S18. HPLC traces of *rac*-**4bc** (reference) and (*S*)-**4bc**.

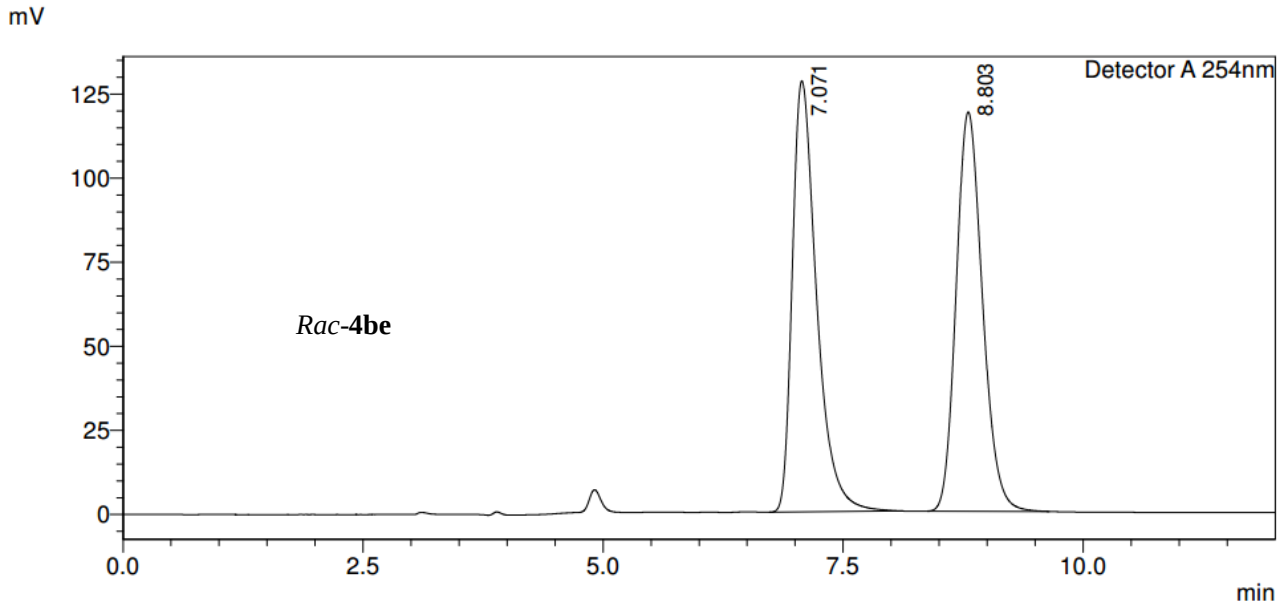


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.085	VV R	0.0981	3479.11646	537.23145	49.9747
2	5.093	VB R	0.1297	3482.63818	403.46780	50.0253



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.094	MM	0.1054	35.03857	5.53997	0.6093
2	5.101	MM	0.1439	5715.50049	662.07043	99.3907

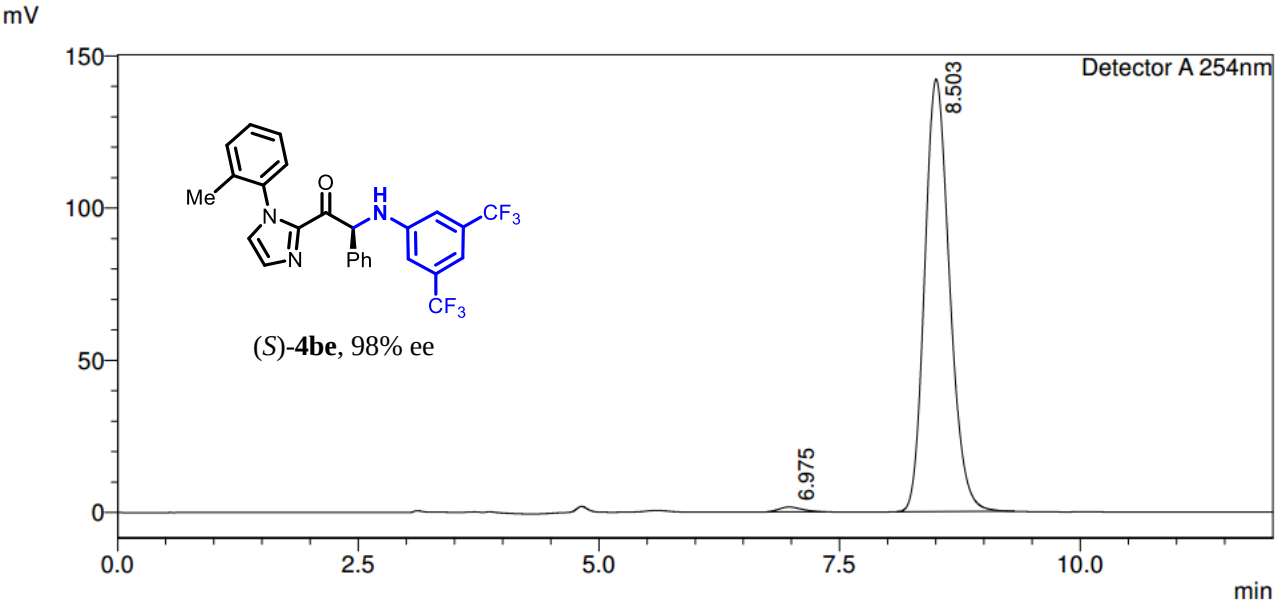
Figure S19. HPLC traces of *rac*-**4bd** (reference) and (*S*)-**4bd**.



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	7.071	2257837	49.931
2	8.803	2264107	50.069
Total		4521944	100.000



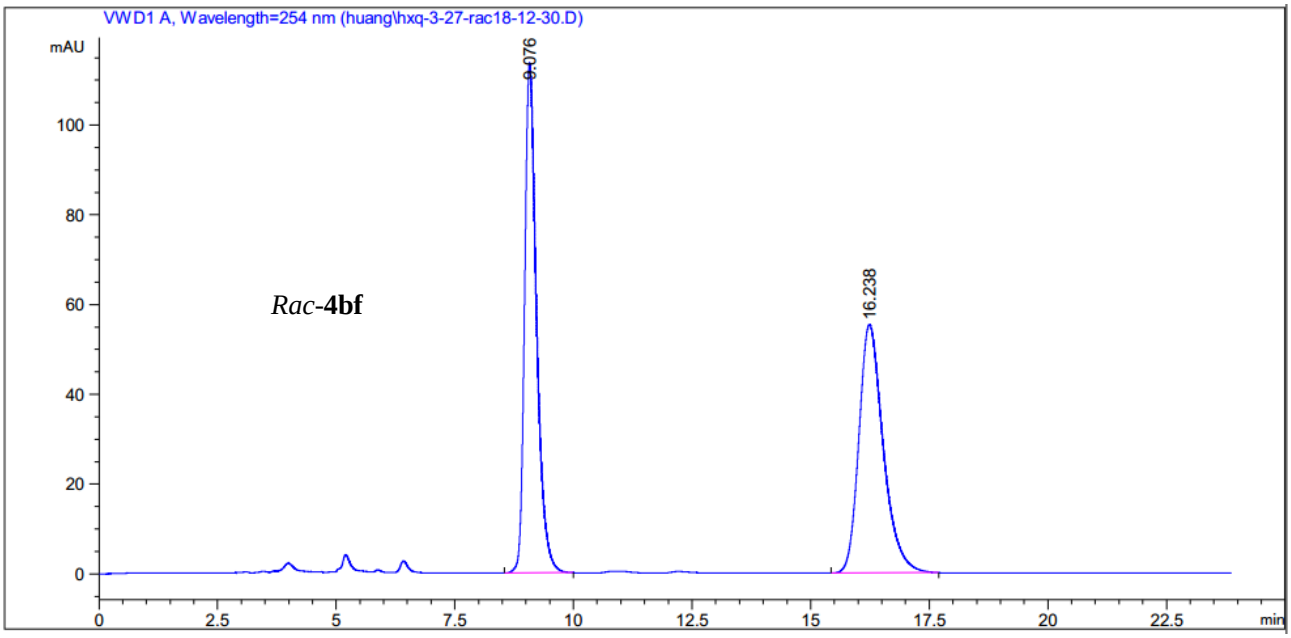
(*S*)-**4be**, 98% ee

<Peak Table>

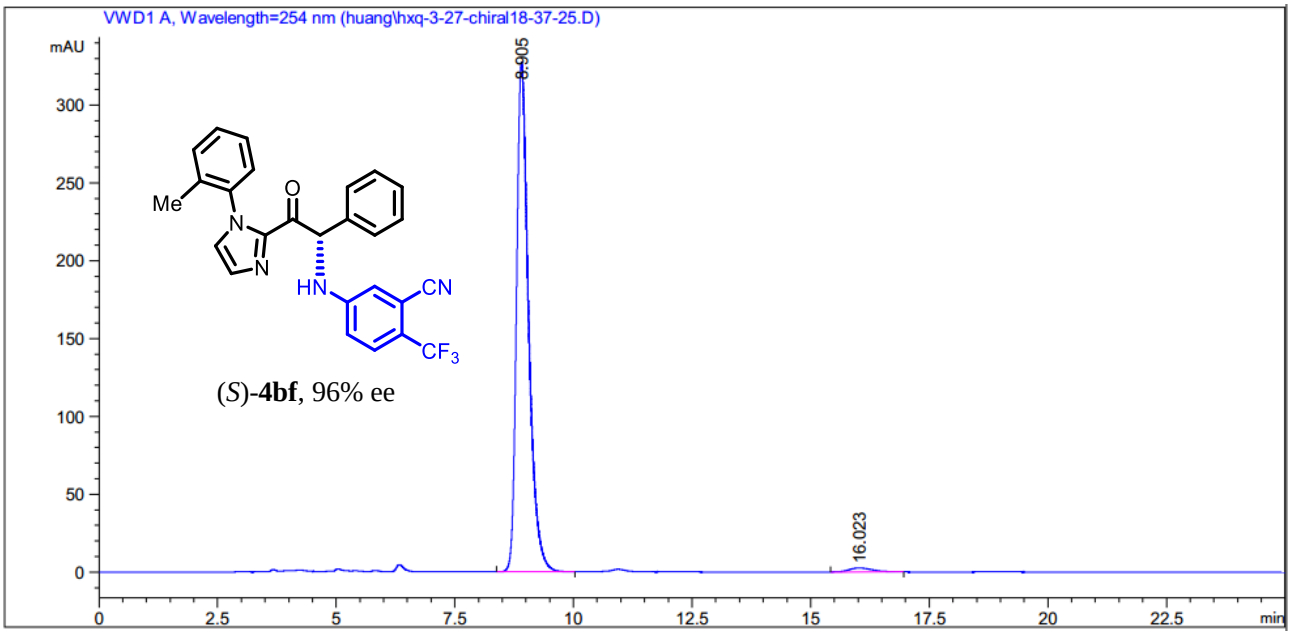
Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	6.975	25835	1.000
2	8.503	2558683	99.000
Total		2584518	100.000

Figure S20. HPLC traces of *rac*-**4be** (reference) and (*S*)-**4be**.

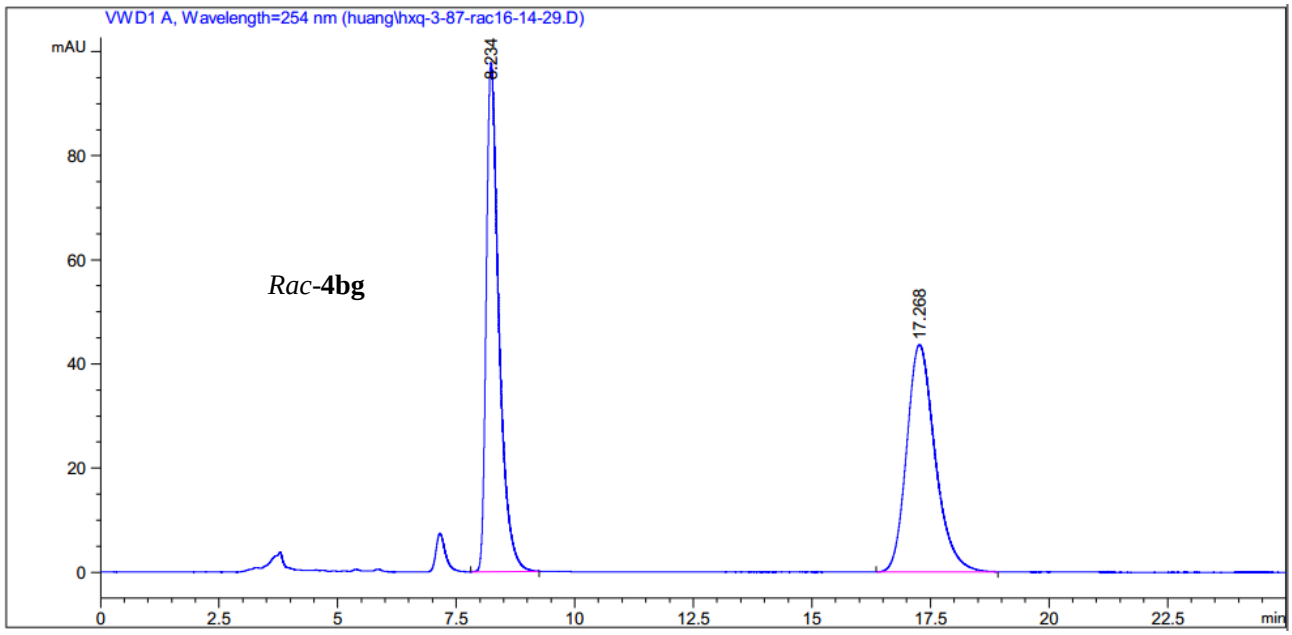


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.076	BB	0.2583	1980.06104	113.62733	50.1121
2	16.238	BB	0.4188	1971.20325	55.37199	49.8879

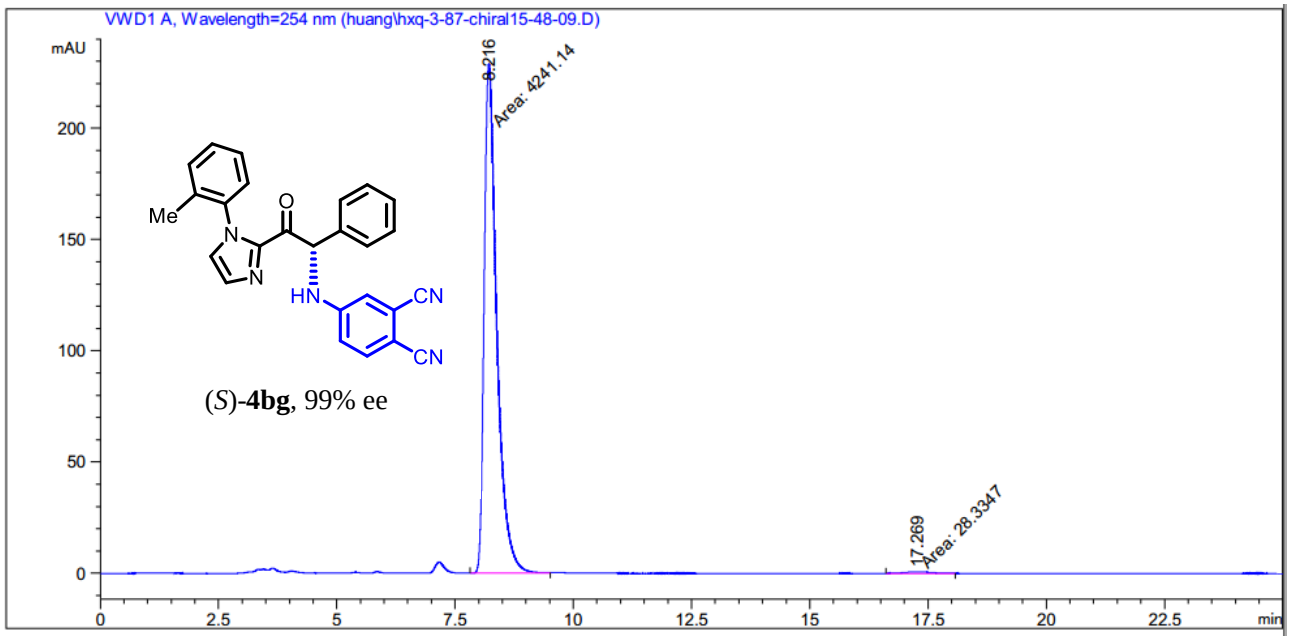


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.905	BB	0.2624	5761.10889	327.18430	98.4889
2	16.023	BB	0.4061	88.39083	2.56802	1.5111

Figure S21. HPLC traces of *rac*-**4bf** (reference) and (*S*)-**4bf**.

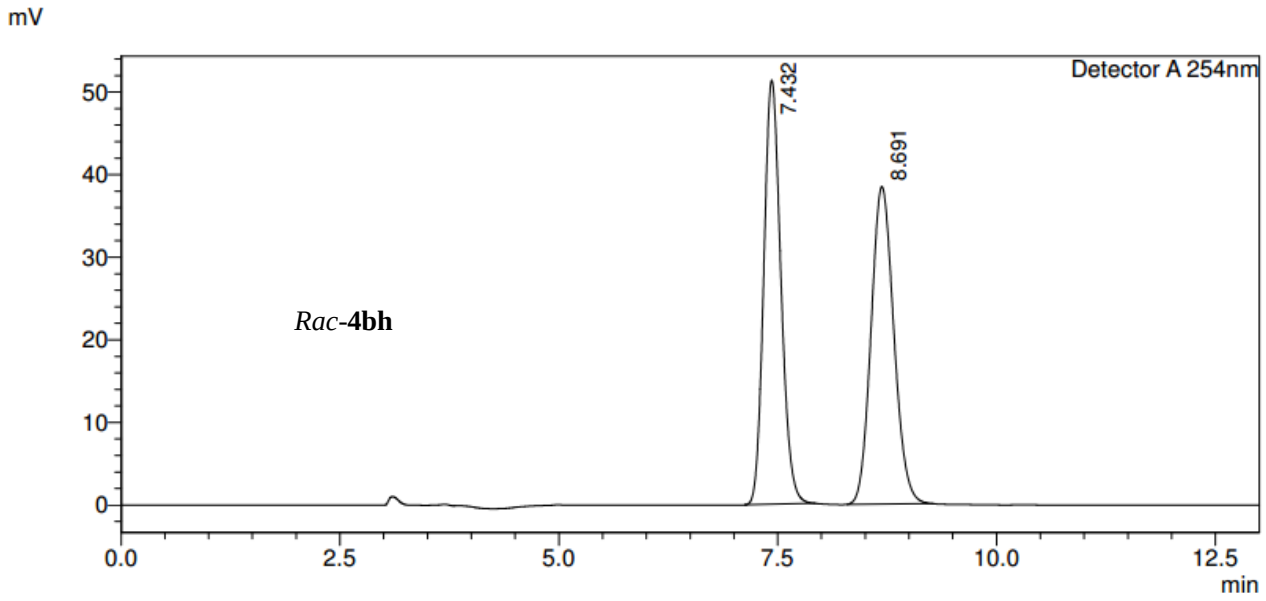


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.234	BB	0.2693	1811.85742	97.74931	49.9649
2	17.268	BB	0.4871	1814.40271	43.67960	50.0351



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.216	MM	0.3089	4241.13770	228.83850	99.3363
2	17.269	MM	0.6724	28.33471	7.02330e-1	0.6637

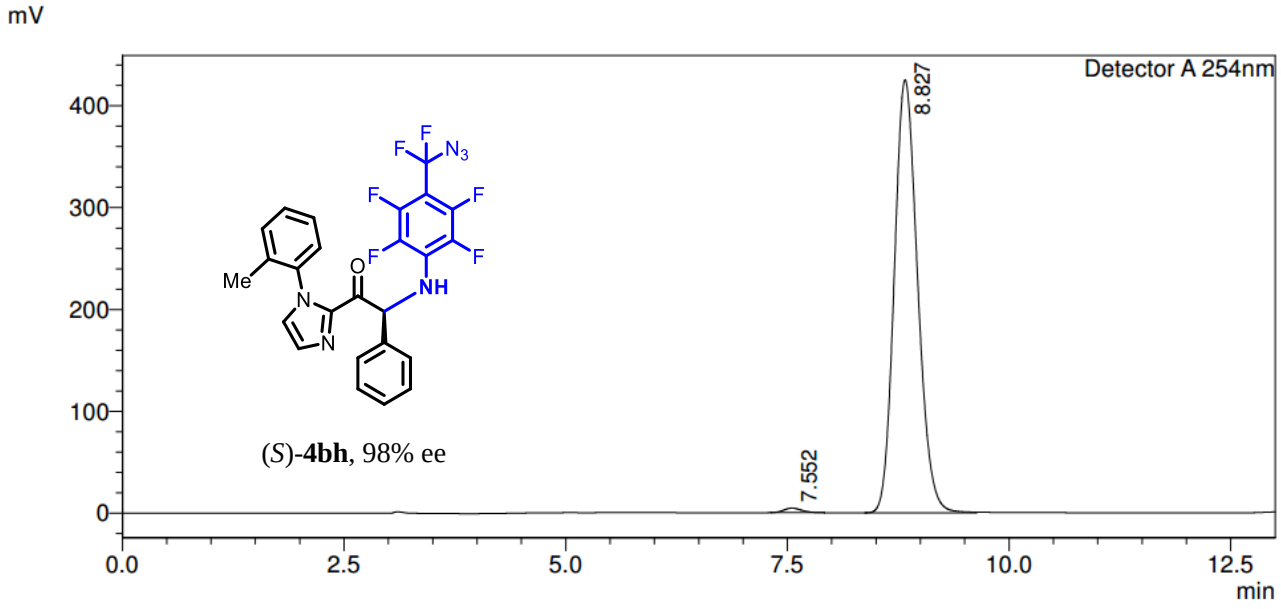
Figure S22. HPLC traces of *rac*-**4bg** (reference) and (*S*)-**4bg**.



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	7.432	696315	50.044
2	8.691	695077	49.956
Total		1391392	100.000



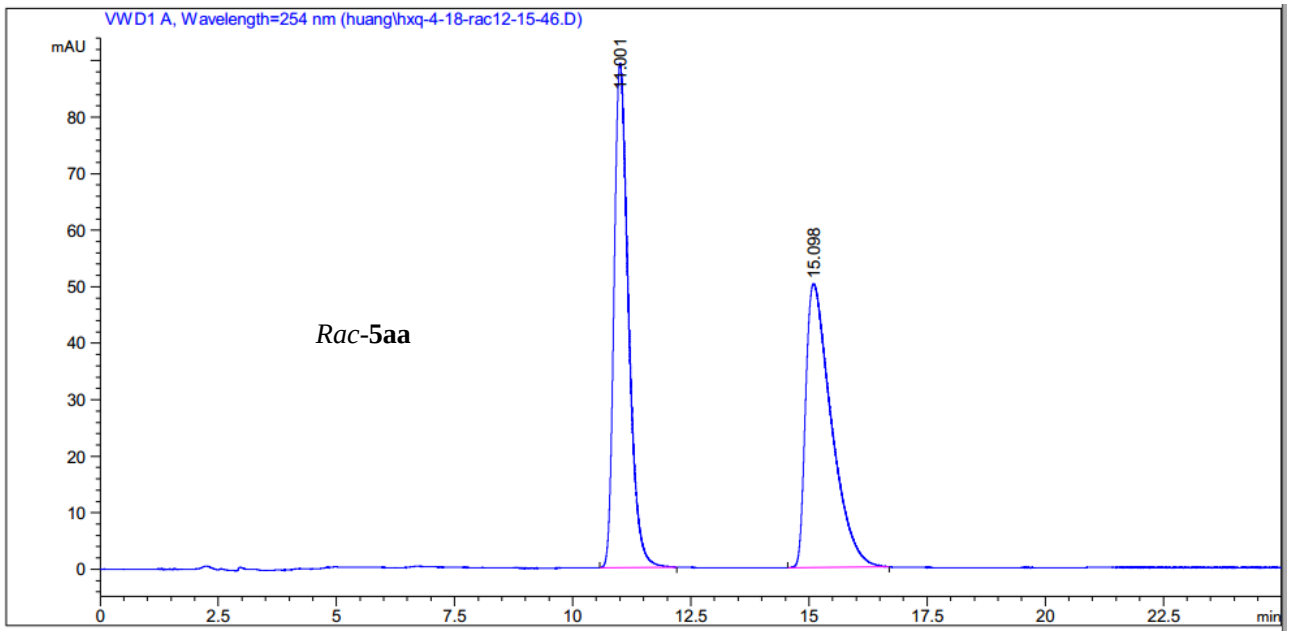
(*S*)-**4bh**, 98% ee

<Peak Table>

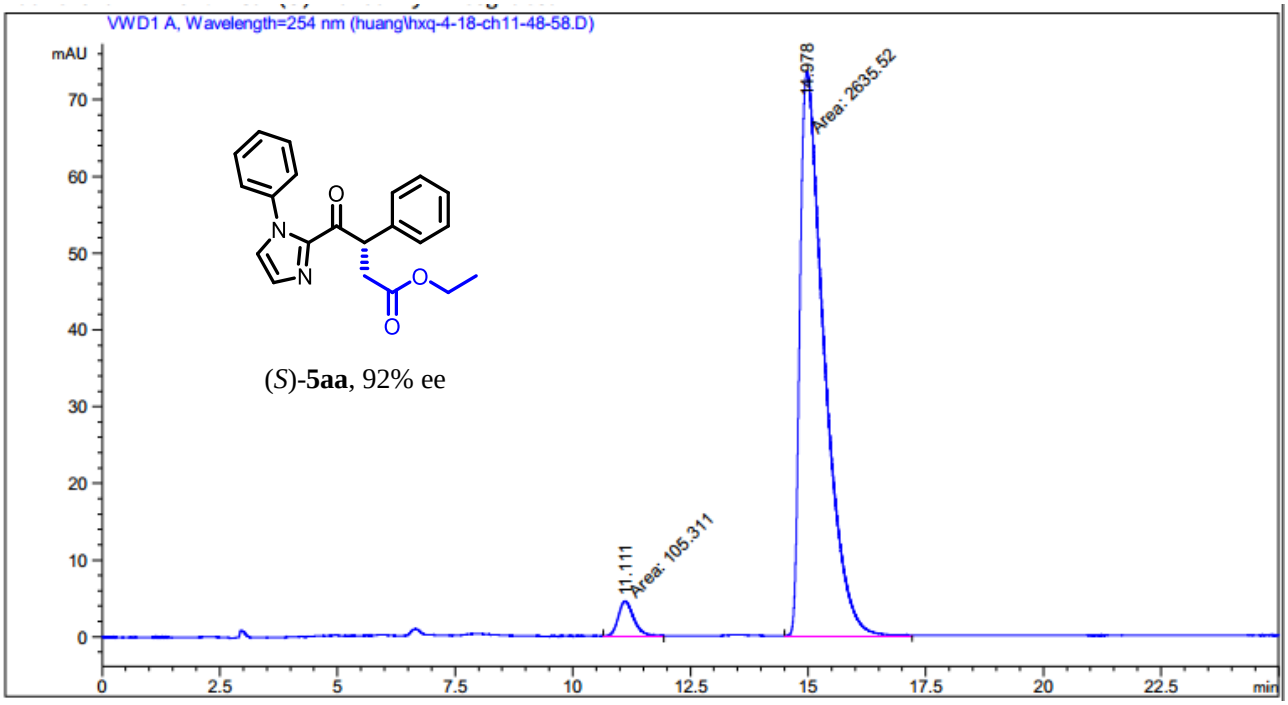
Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	7.552	62340	0.797
2	8.827	7762066	99.203
Total		7824406	100.000

Figure S23. HPLC traces of *rac*-**4bh** (reference) and (*S*)-**4bh**.



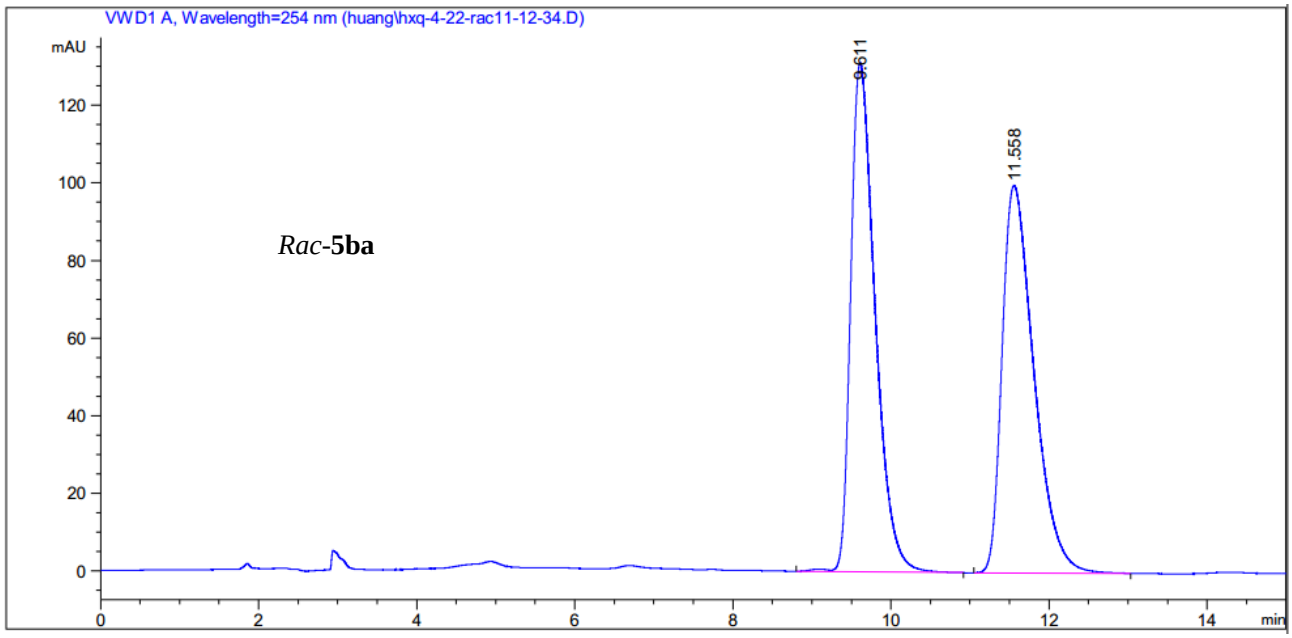
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.001	BB	0.3176	1891.01514	89.28069	49.9996
2	15.098	BV R	0.4421	1891.04675	50.23932	50.0004



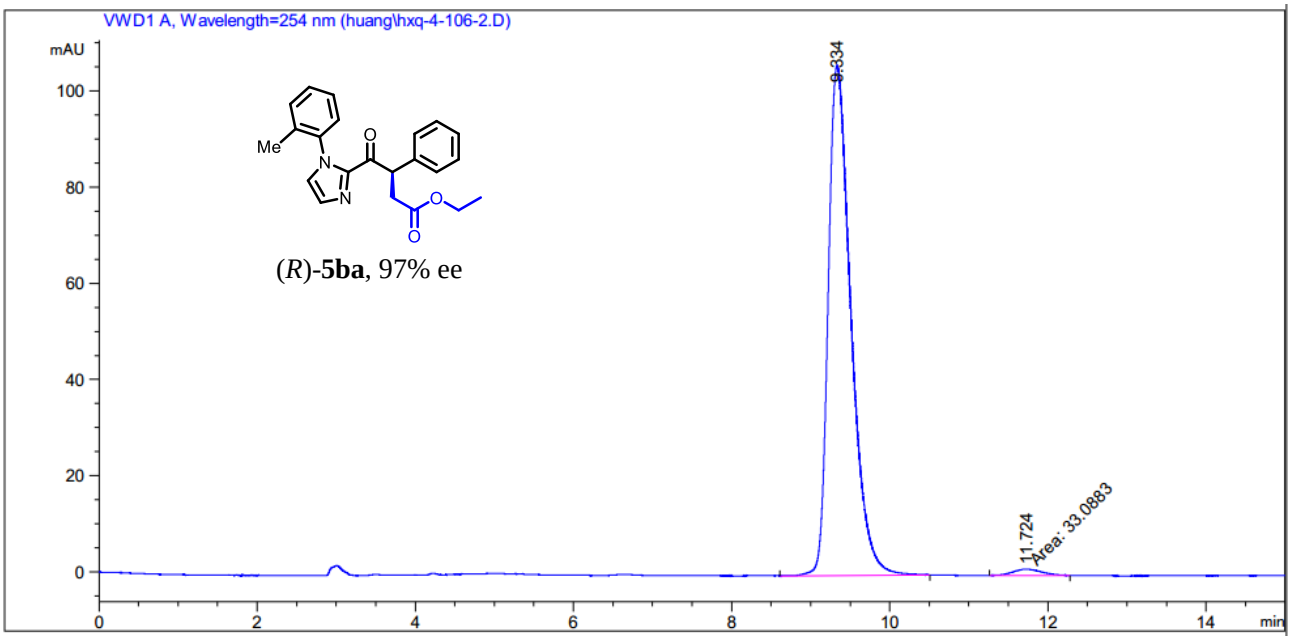
(*S*)-**5aa**, 92% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.111	MM	0.3841	105.31077	4.56942	3.8423
2	14.978	MM	0.5969	2635.52051	73.59348	96.1577

Figure S24. HPLC traces of *rac*-**5aa** (reference) and (*S*)-**5aa**.

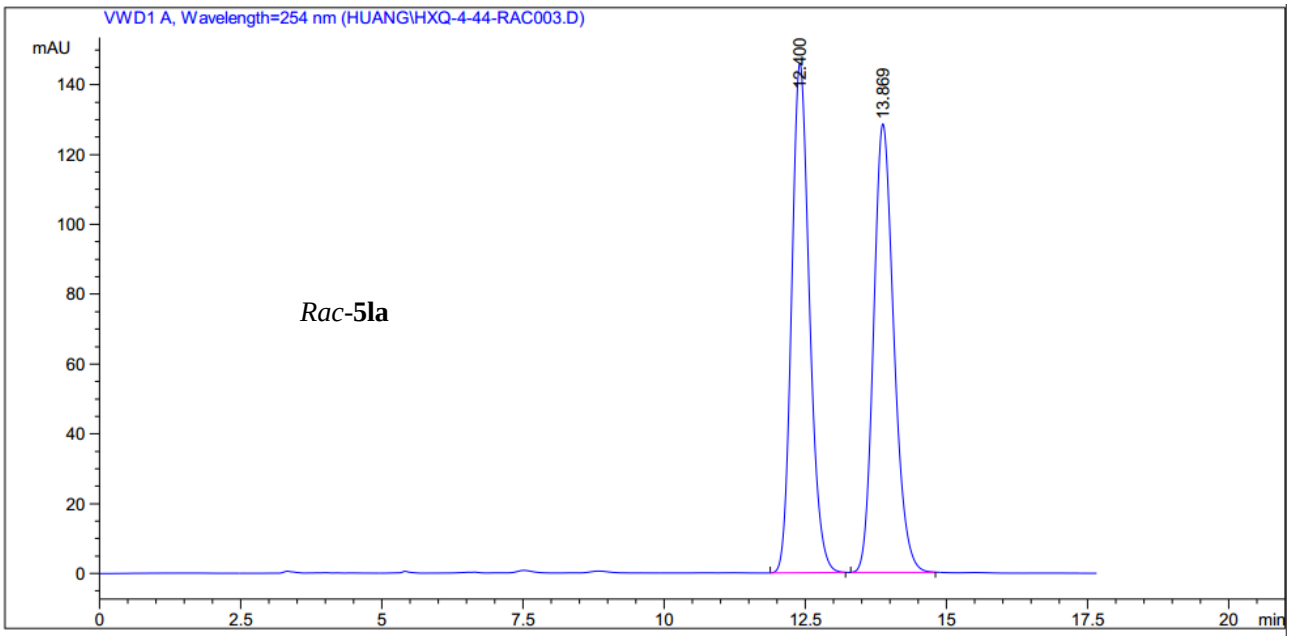


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.611	VB R	0.3189	2804.89648	131.21301	50.1553
2	11.558	BB	0.3881	2787.52124	99.89500	49.8447

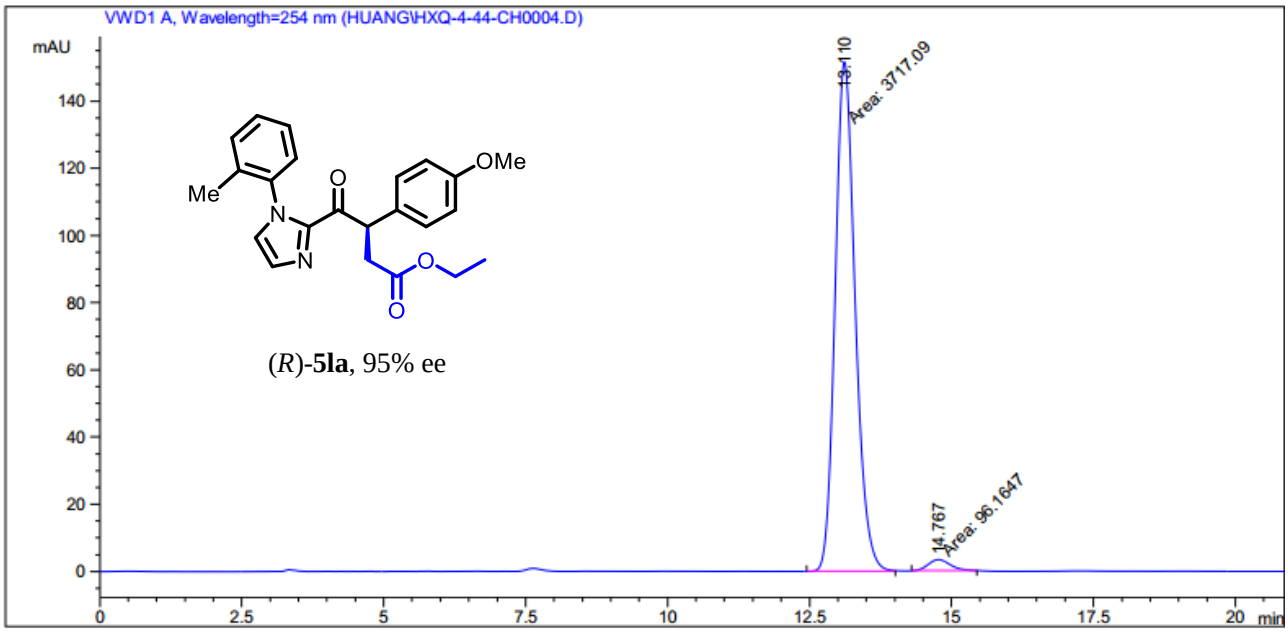


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.334	BB	0.2910	2108.03979	106.02441	98.4546
2	11.724	MM	0.4251	33.08827	1.29725	1.5454

Figure S25. HPLC traces of *rac*-**5ba** (reference) and (*R*)-**5ba**.

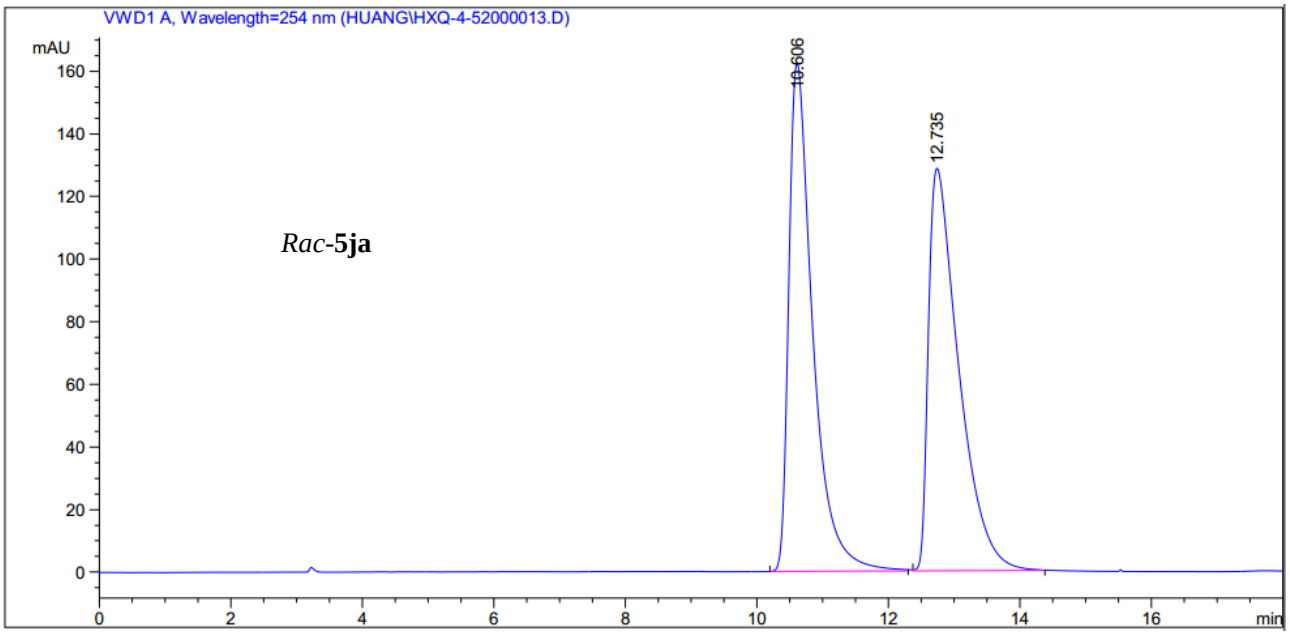


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.400	BB	0.3376	3207.41748	146.11475	50.0114
2	13.869	BB	0.3840	3205.95483	128.59326	49.9886

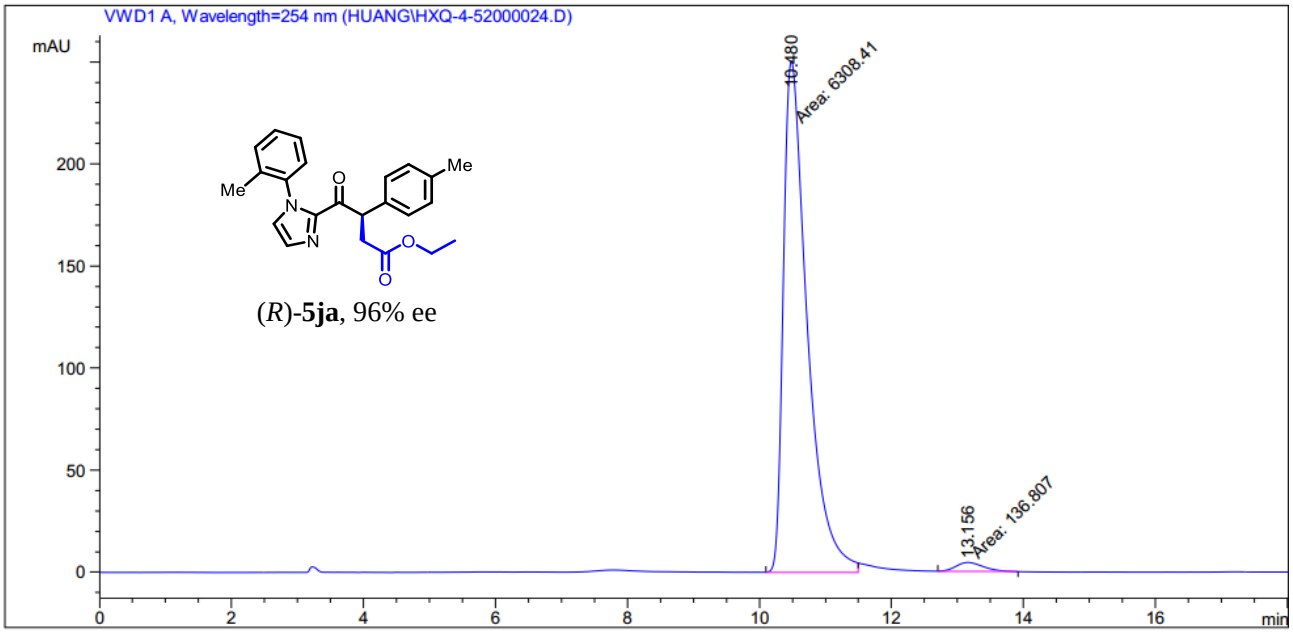


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.110	MM	0.4085	3717.08862	151.67430	97.4781
2	14.767	MM	0.4745	96.16473	3.37791	2.5219

Figure S26. HPLC traces of *rac*-**5la** (reference) and (*R*)-**5la**.

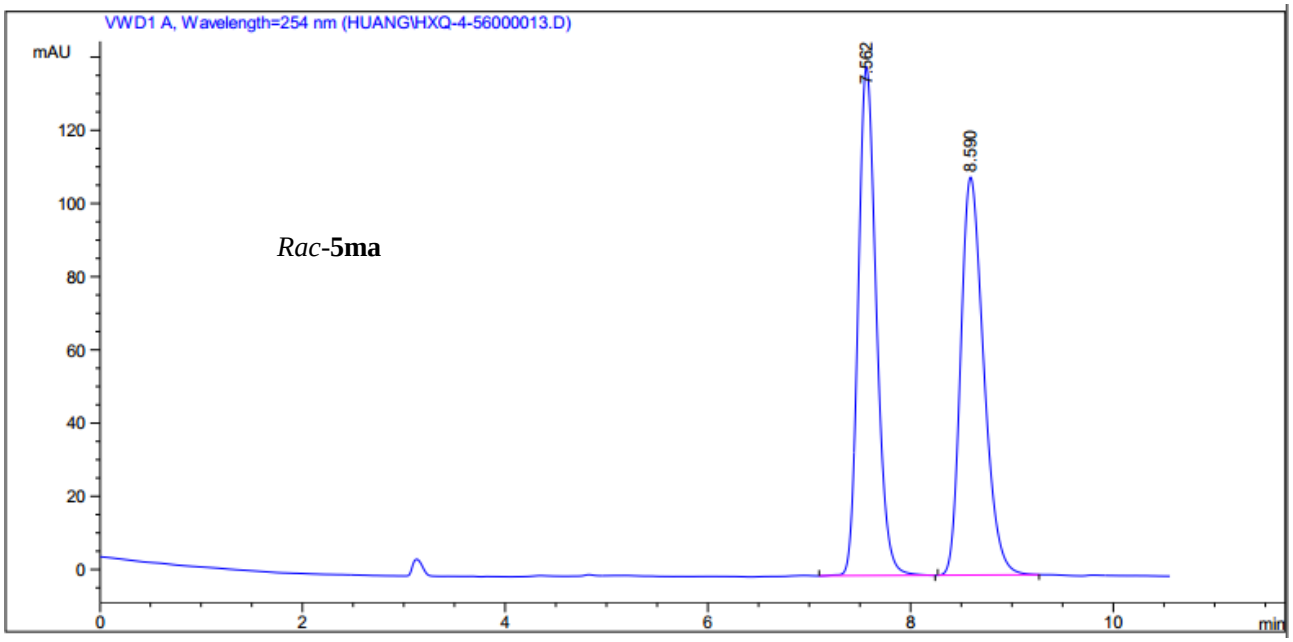


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.606	BB	0.3766	4109.04541	162.49393	49.9851
2	12.735	BB	0.4706	4111.49854	128.58272	50.0149



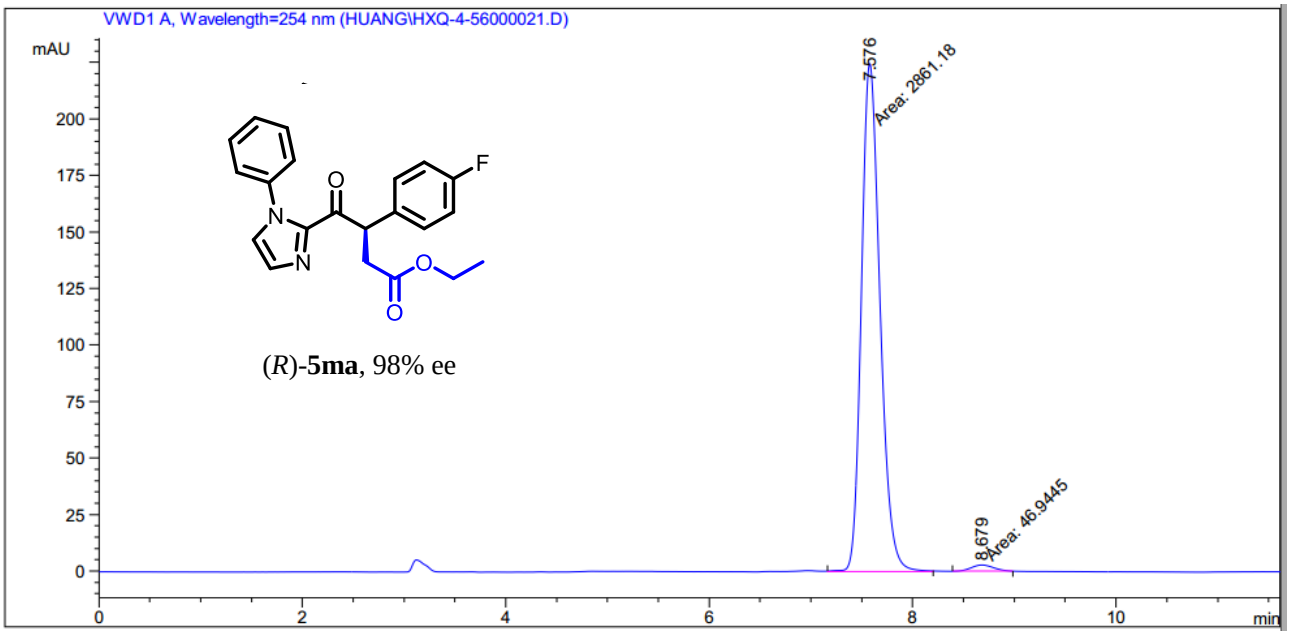
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.480	MF	0.4193	6308.40918	250.73100	97.8774
2	13.156	MM	0.5030	136.80702	4.53341	2.1226

Figure S27. HPLC traces of *rac*-**5ja** (reference) and (*R*)-**5ja**.



Rac-**5ma**

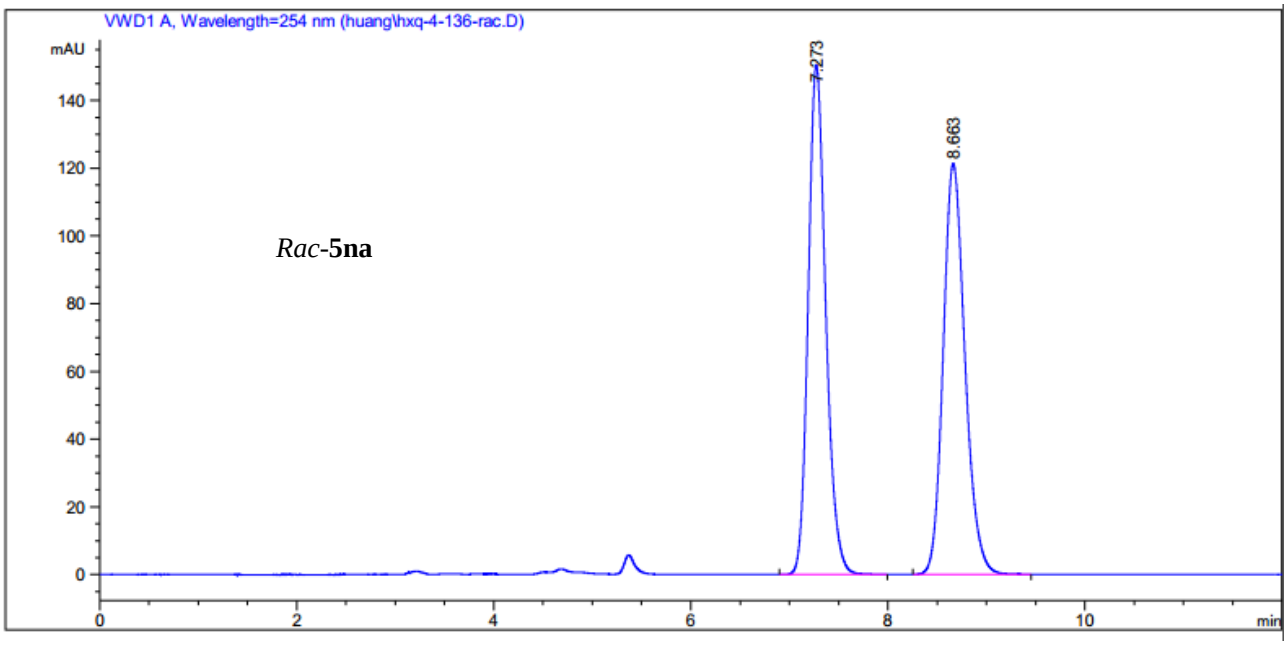
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.562	VB	0.1915	1728.82495	139.16643	50.2247
2	8.590	BB	0.2434	1713.35339	108.80094	49.7753



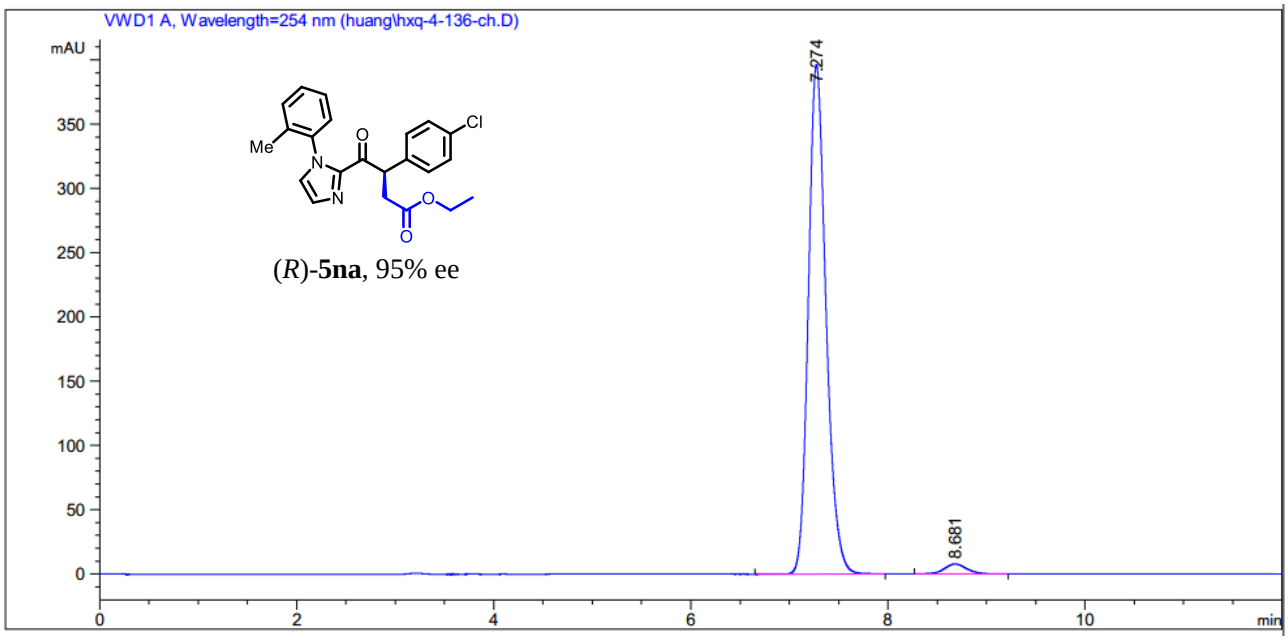
(*R*)-**5ma**, 98% ee

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.576	MM	0.2121	2861.18140	224.84807	98.3857
2	8.679	MM	0.2713	46.94451	2.88356	1.6143

Figure S28. HPLC traces of *rac*-**5ma** (reference) and (*R*)-**5ma**.

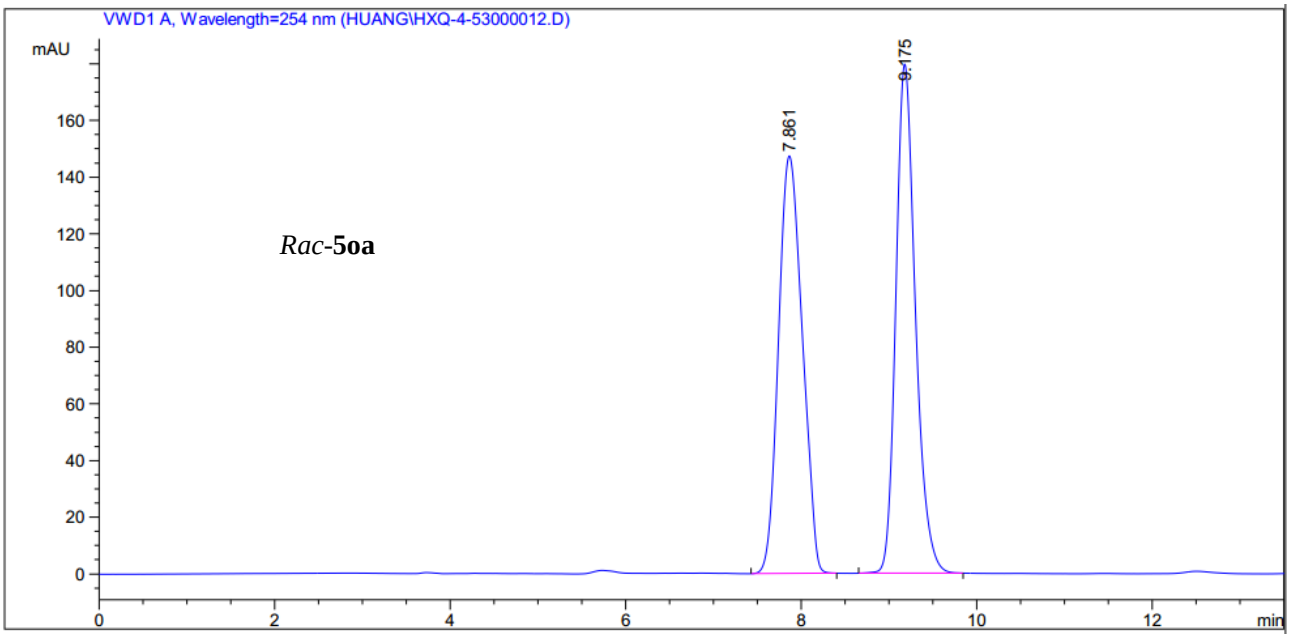


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.273	BV R	0.1884	1862.09949	150.48218	50.0039
2	8.663	BV R	0.2330	1861.81116	121.31923	49.9961

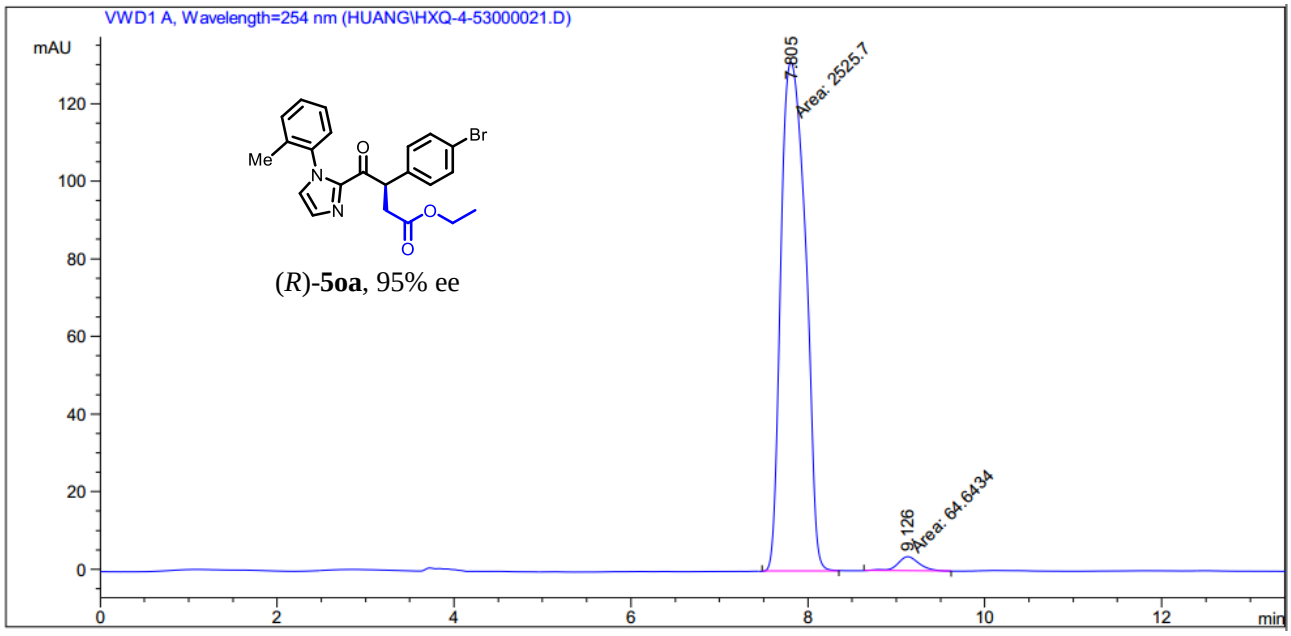


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.274	VB R	0.1888	4917.85059	396.19290	97.5658
2	8.681	BB	0.1922	122.69769	7.72764	2.4342

Figure S29. HPLC traces of *rac*-**5na** (reference) and (*R*)-**5na**.

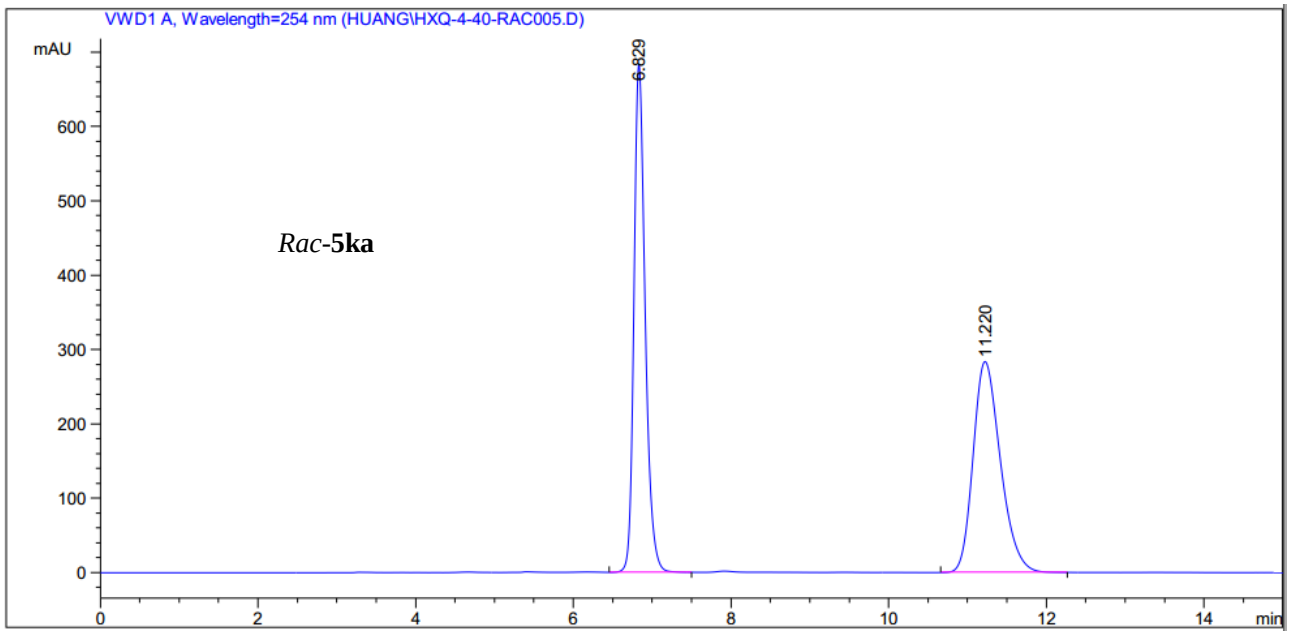


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.861	BB	0.2925	2774.74512	147.32872	49.9547
2	9.175	BB	0.2358	2779.78247	179.67154	50.0453



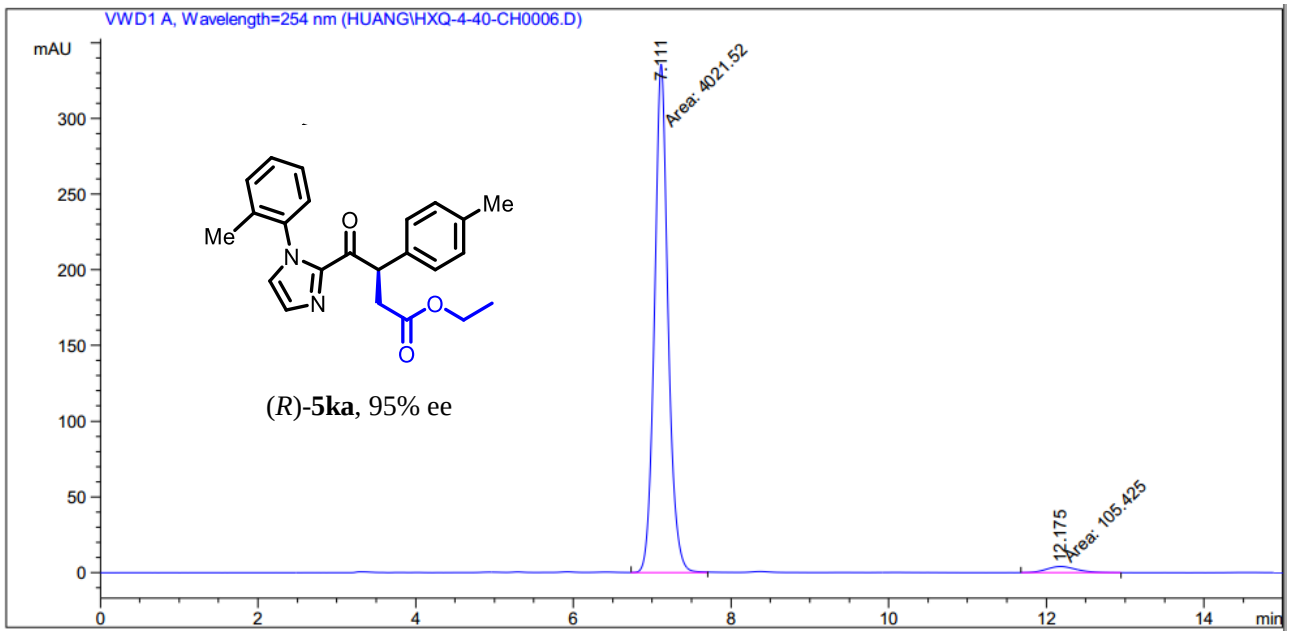
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.805	MM	0.3211	2525.69629	131.09987	97.5044
2	9.126	MM	0.2925	64.64340	3.68310	2.4956

Figure S30. HPLC traces of *rac*-**5oa** (reference) and (*R*)-**5oa**.



Rac-**5ka**

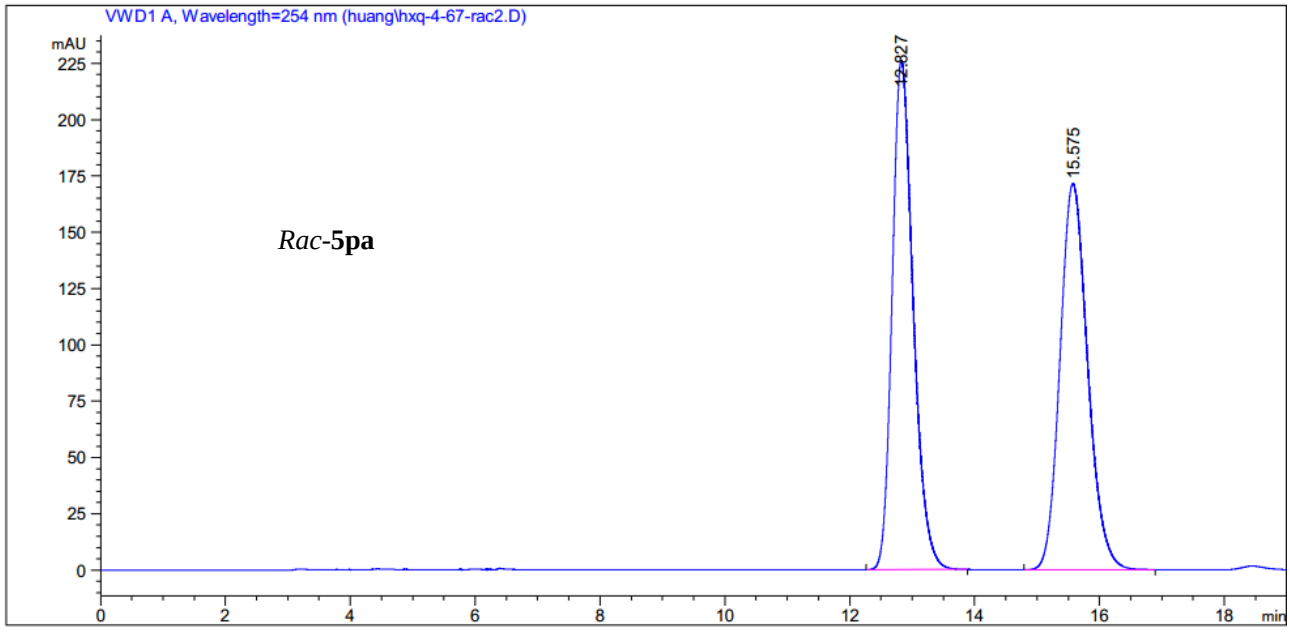
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.829	VB	0.1522	6784.99561	683.86713	49.8325
2	11.220	BB	0.3696	6830.61182	283.77704	50.1675



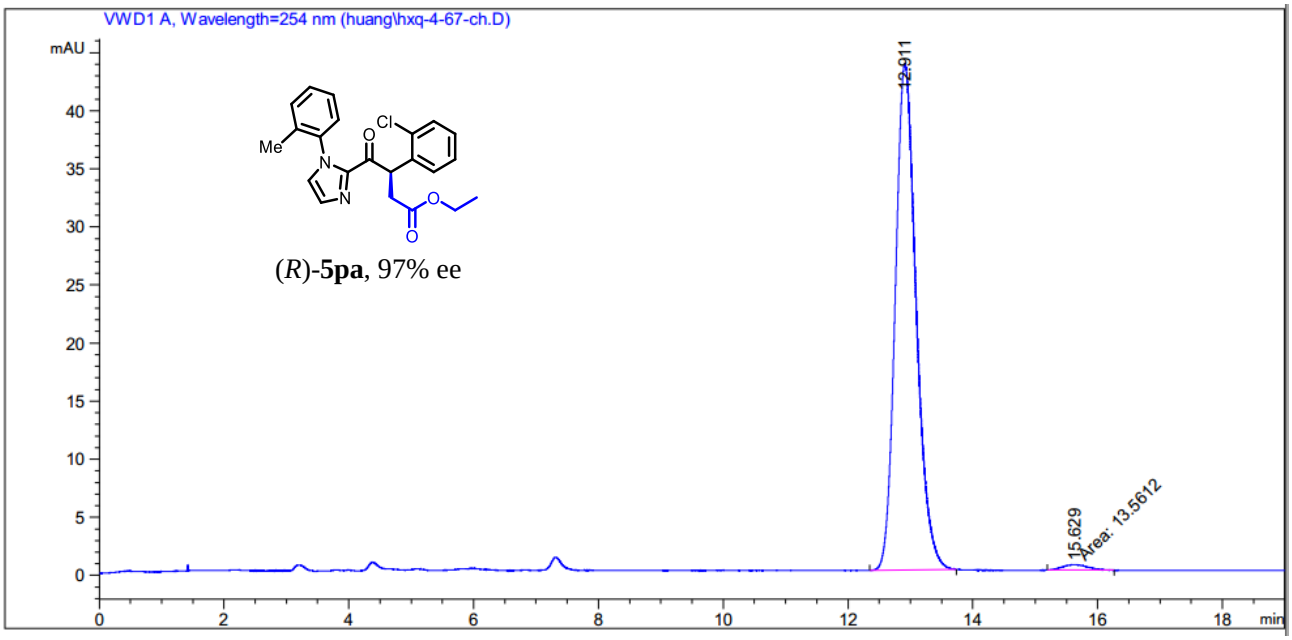
(*R*)-**5ka**, 95% ee

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.111	MM	0.1994	4021.51636	336.17990	97.4454
2	12.175	MM	0.4376	105.42550	4.01525	2.5546

Figure S31. HPLC traces of *rac*-**5ka** (reference) and (*R*)-**5ka**.



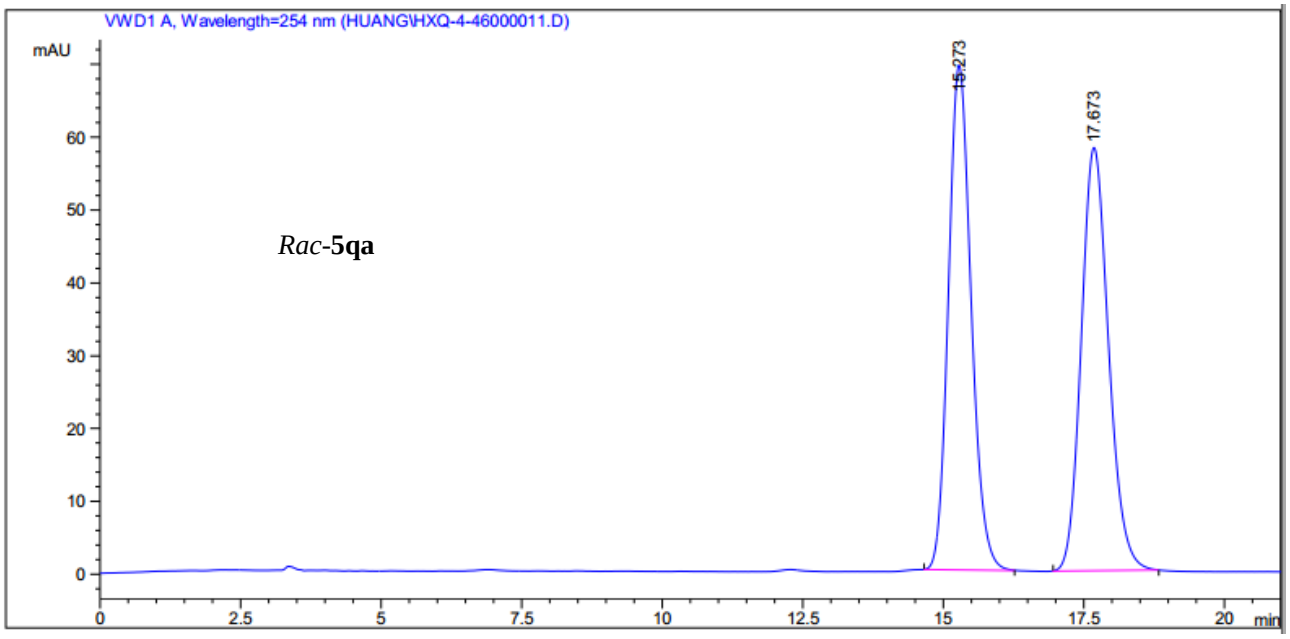
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.827	BB	0.3490	5271.27588	226.06474	49.9784
2	15.575	BV R	0.4534	5275.83545	171.48004	50.0216



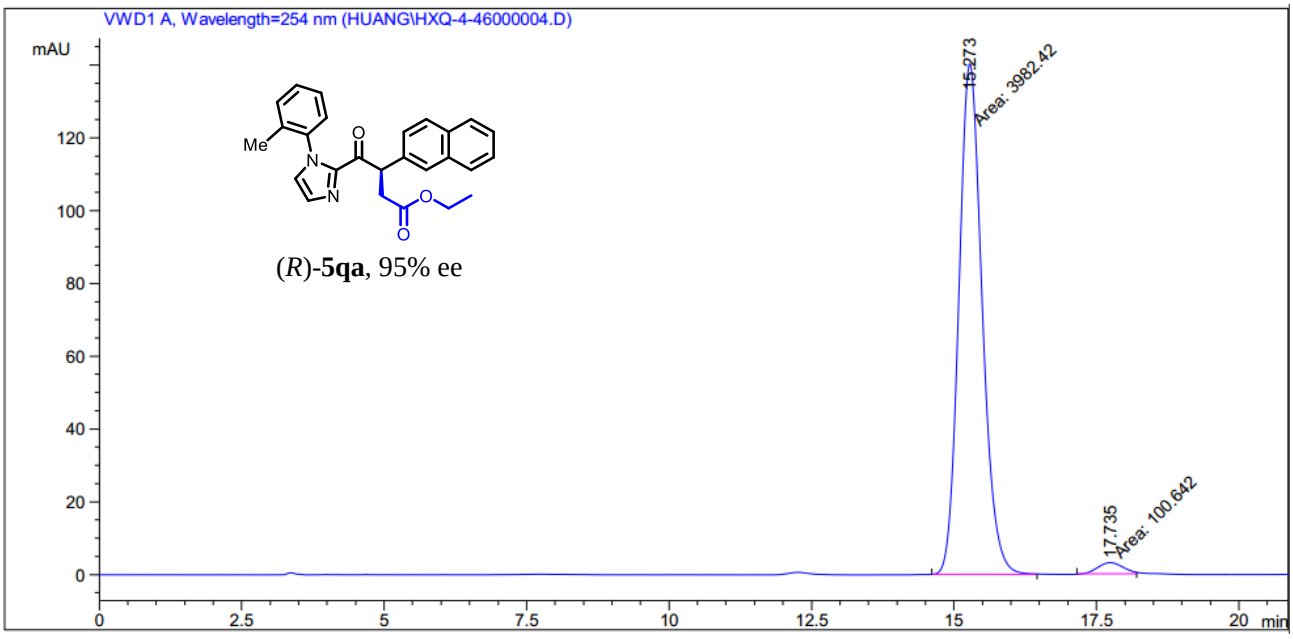
(*R*)-**5pa**, 97% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.911	BB	0.3086	1010.60754	43.57258	98.6759
2	15.629	MM	0.4727	13.56121	4.78110e-1	1.3241

Figure S32. HPLC traces of *rac*-**5pa** (reference) and (*R*)-**5pa**.

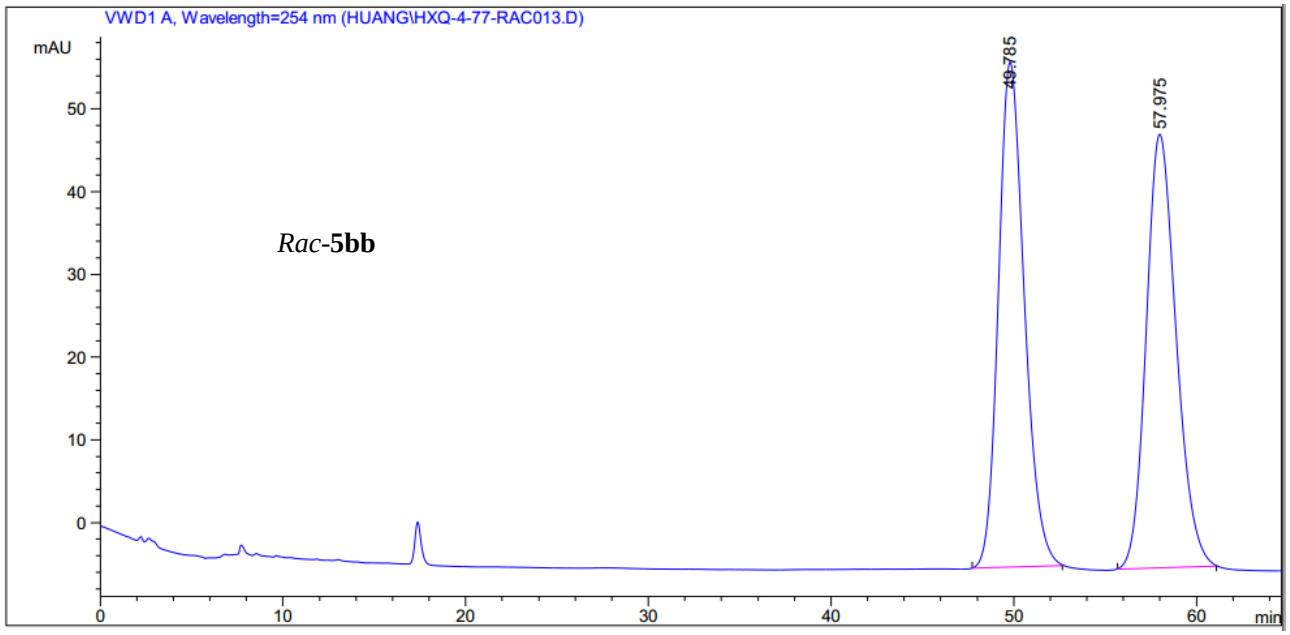


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.273	BB	0.4324	1944.91565	69.27367	49.7955
2	17.673	BB	0.5205	1960.88843	58.08216	50.2045

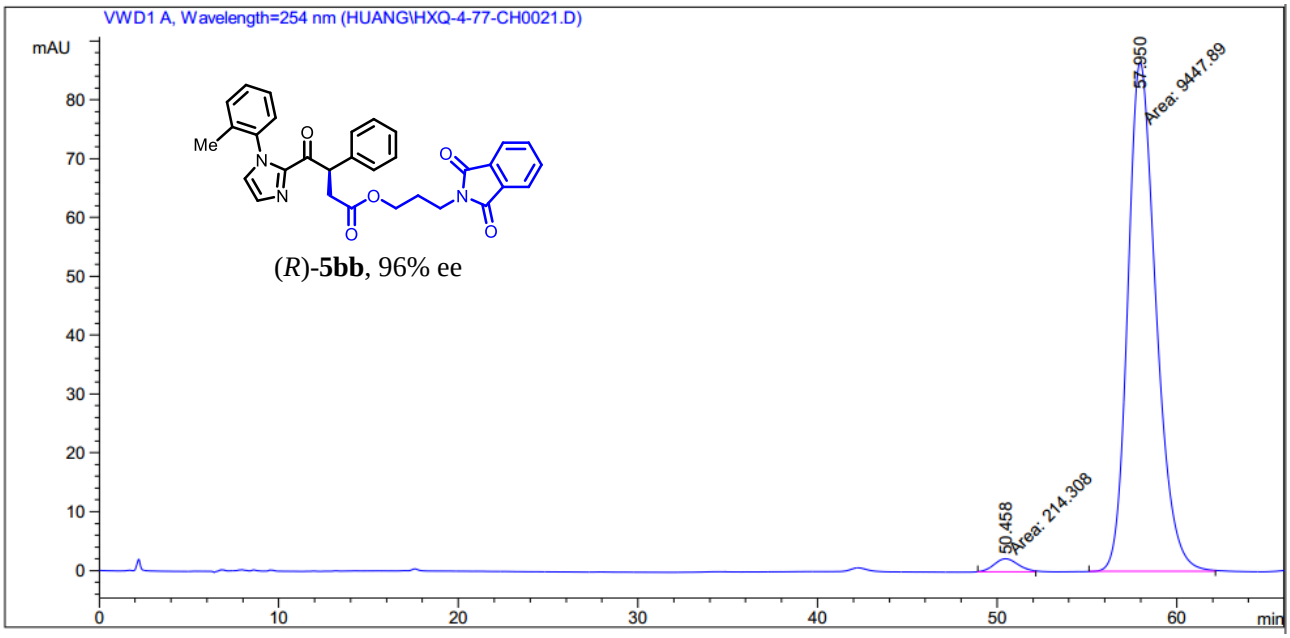


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.273	MM	0.4732	3982.42261	140.27773	97.5351
2	17.735	MM	0.5311	100.64239	3.15806	2.4649

Figure S33. HPLC traces of *rac*-**5qa** (reference) and (*R*)-**5qa**.

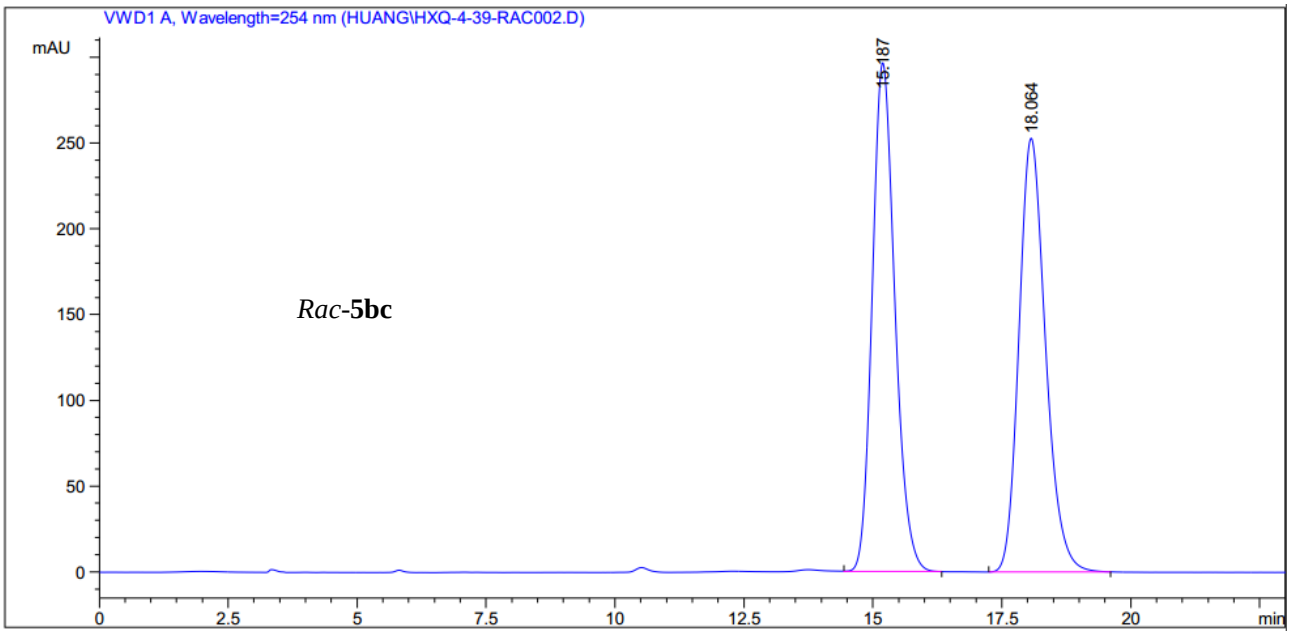


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	49.785	BB	1.4602	6017.85547	61.04536	50.1291
2	57.975	BB	1.6621	5986.86523	52.45432	49.8709

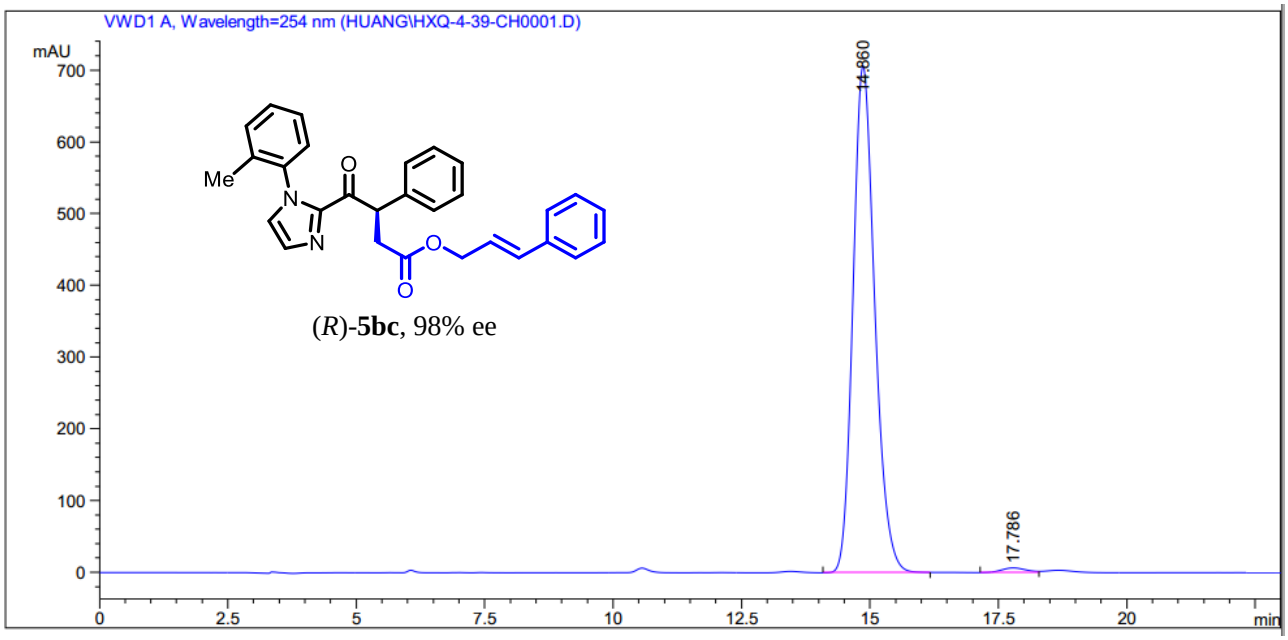


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	50.458	MM	1.5806	214.30838	2.25984	2.2180
2	57.950	MM	1.8200	9447.89453	86.51817	97.7820

Figure S34. HPLC traces of *rac*-**5bb** (reference) and (*R*)-**5bb**.

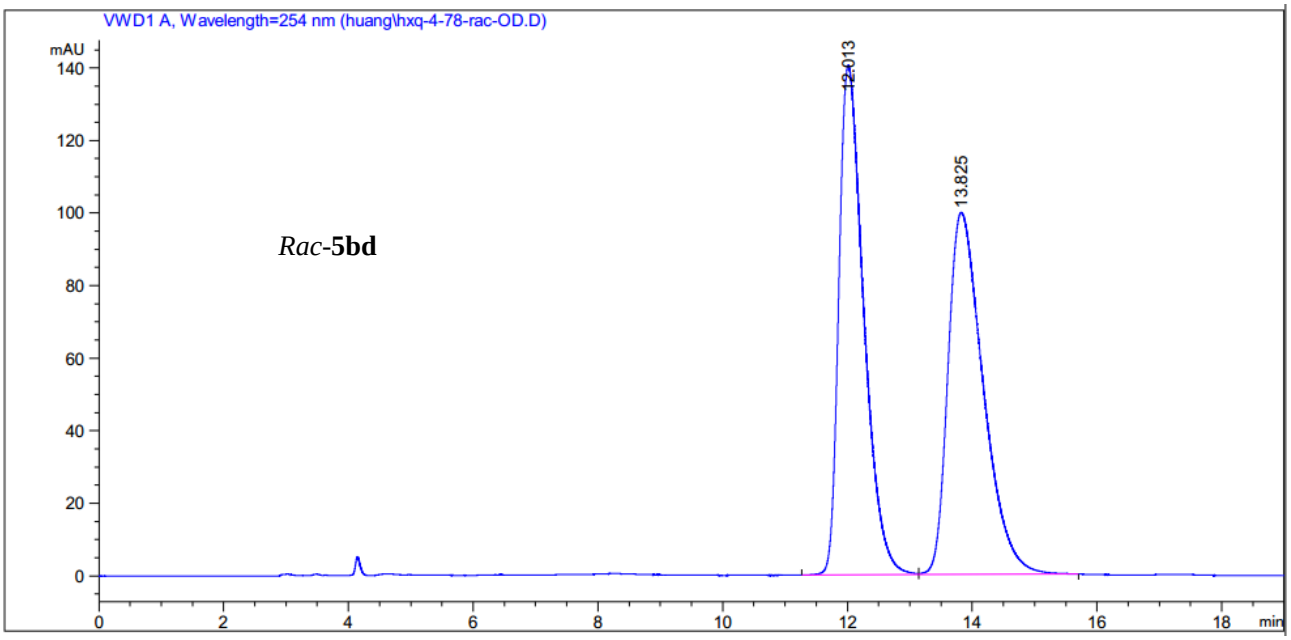


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.187	VB	0.4693	9047.49121	296.71277	49.9689
2	18.064	BB	0.5504	9058.75977	252.89378	50.0311

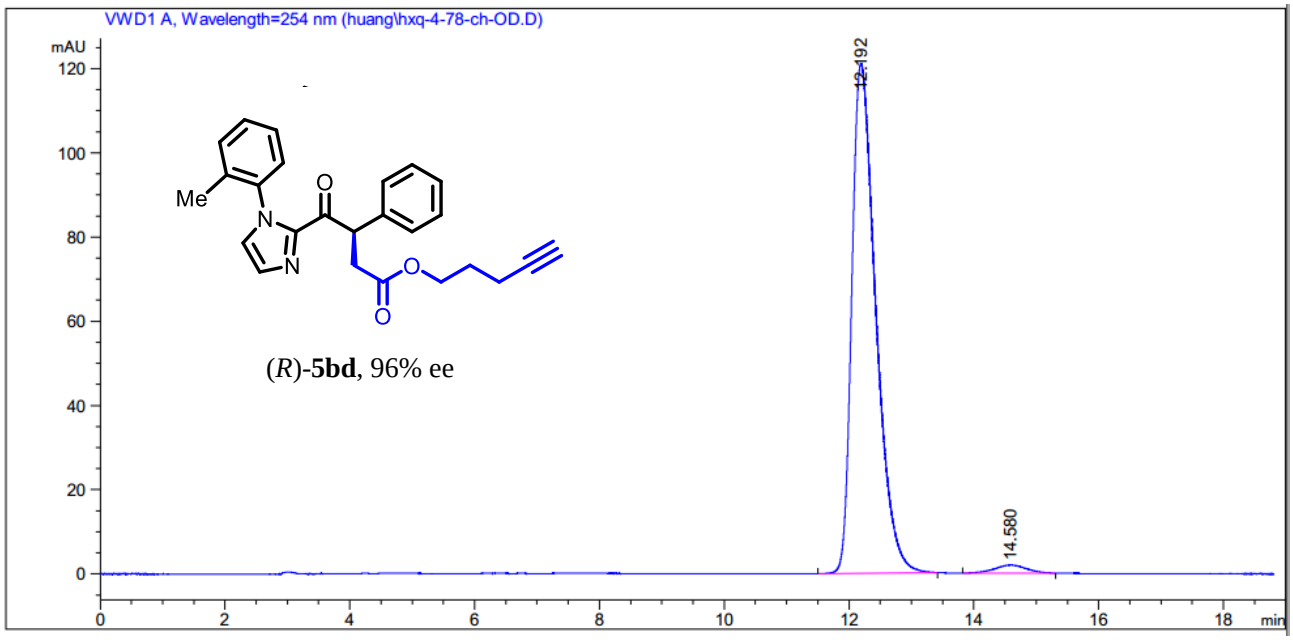


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.860	VB	0.4525	2.07813e4	706.21075	98.9366
2	17.786	BV	0.5198	223.35866	6.55629	1.0634

Figure S35. HPLC traces of *rac*-**5bc** (reference) and (*R*)-**5bc**.



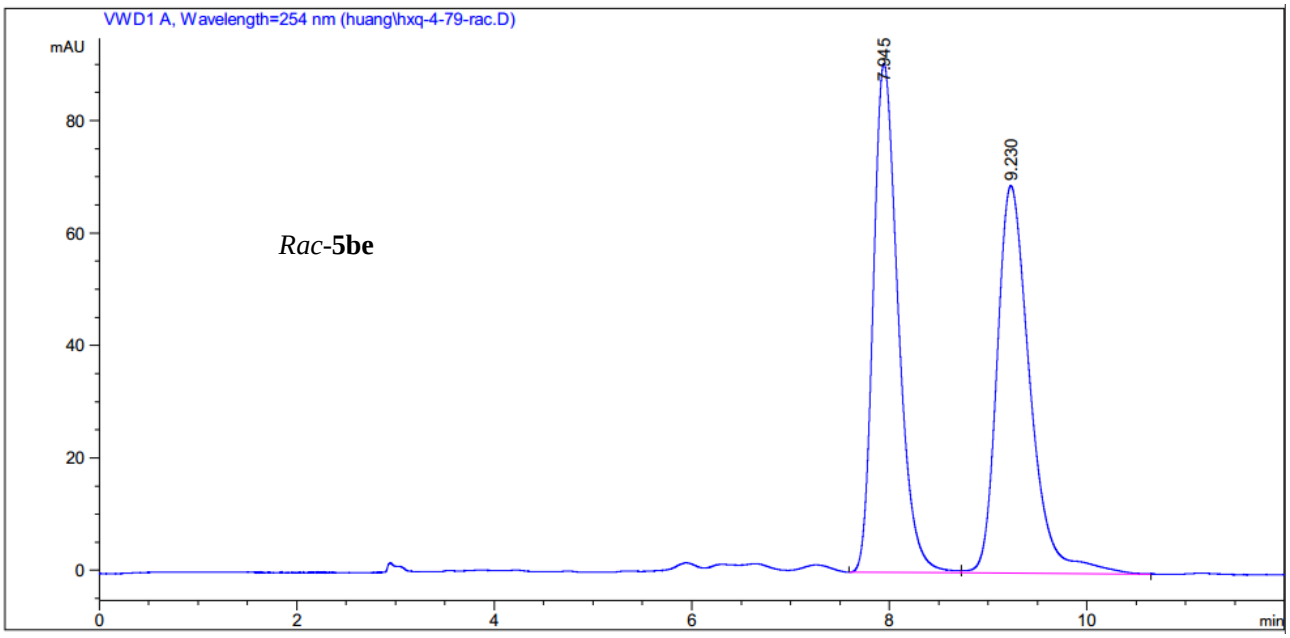
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.013	BV	0.3909	3875.29980	140.46620	49.7713
2	13.825	VV R	0.5076	3910.91748	99.83010	50.2287



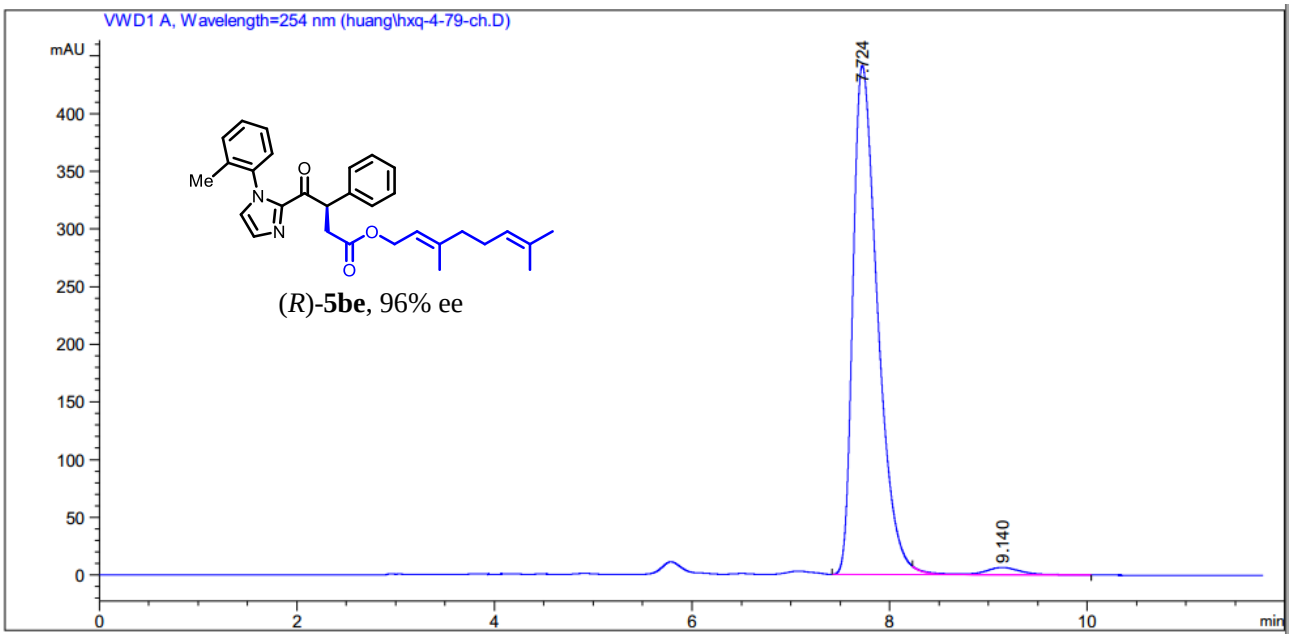
(*R*)-**5bd**, 96% ee

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.192	BB	0.3782	3214.28809	121.08460	97.8778
2	14.580	BV R	0.4175	69.69202	1.95207	2.1222

Figure S36. HPLC traces of *rac*-**5bd** (reference) and (*R*)-**5bd**.

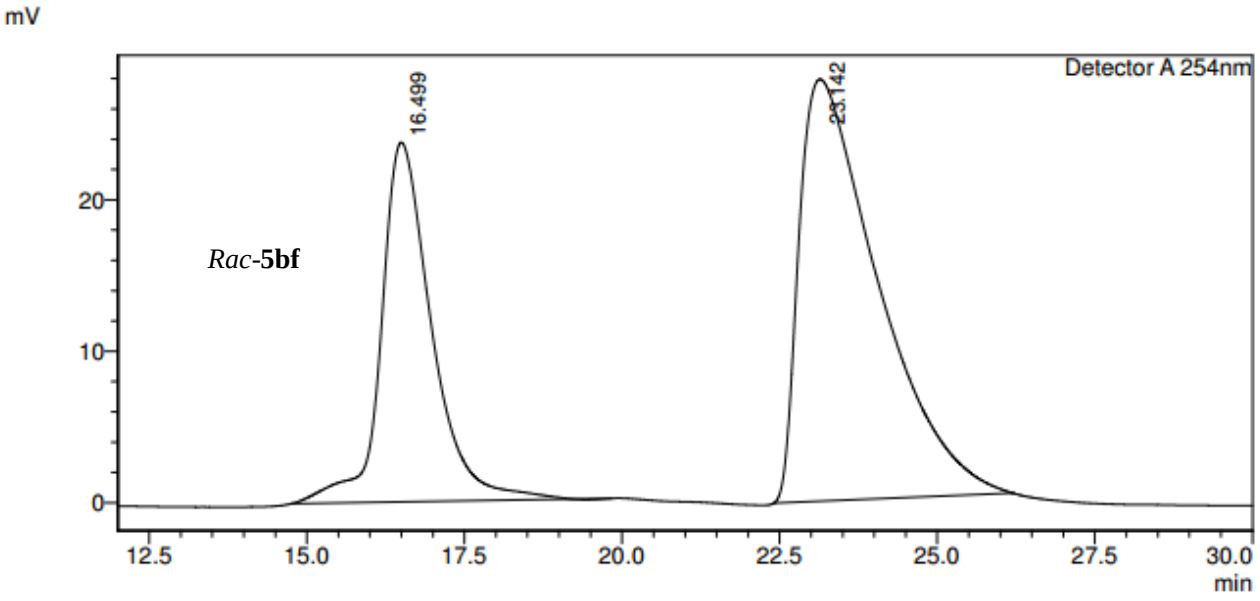


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.945	BV	0.2586	1575.56812	90.52299	49.7323
2	9.230	VB	0.3345	1592.53113	68.93356	50.2677



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.724	BV R	0.2609	7640.43457	441.47693	97.7742
2	9.140	VB E	0.3204	173.93202	6.35338	2.2258

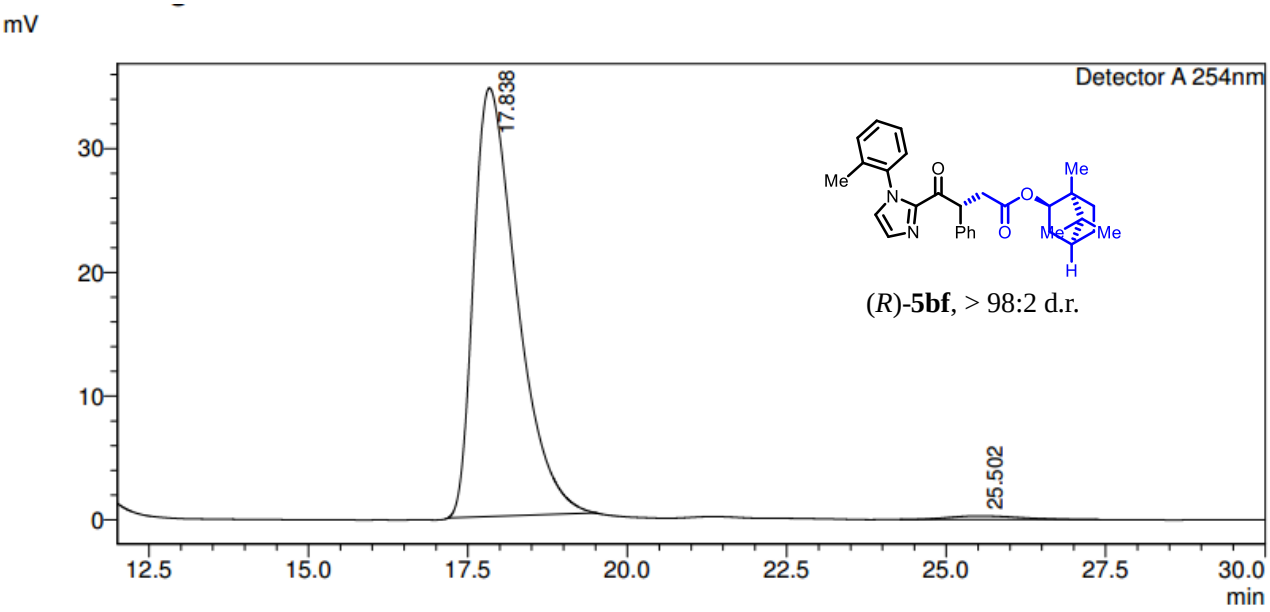
Figure S37. HPLC traces of *rac*-**5be** (reference) and (*R*)-**5be**.



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	16.499	1326110	35.416
2	23.142	2418227	64.584
Total		3744337	100.000



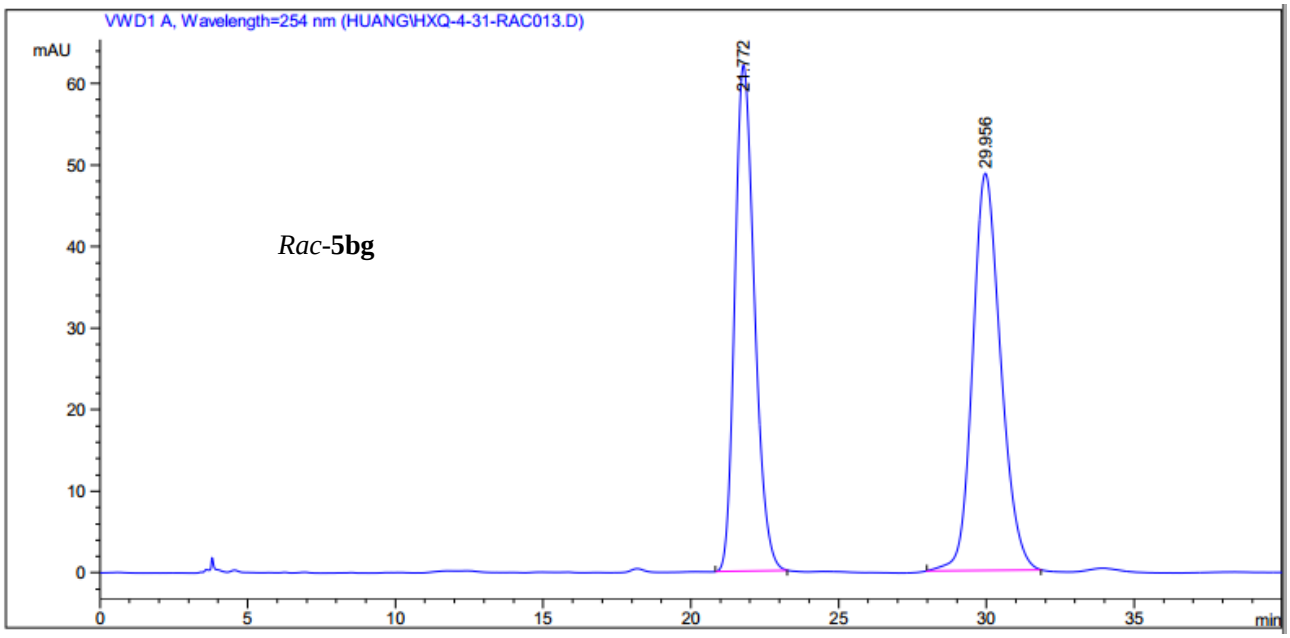
(*R*)-**5bf**, > 98:2 d.r.

<Peak Table>

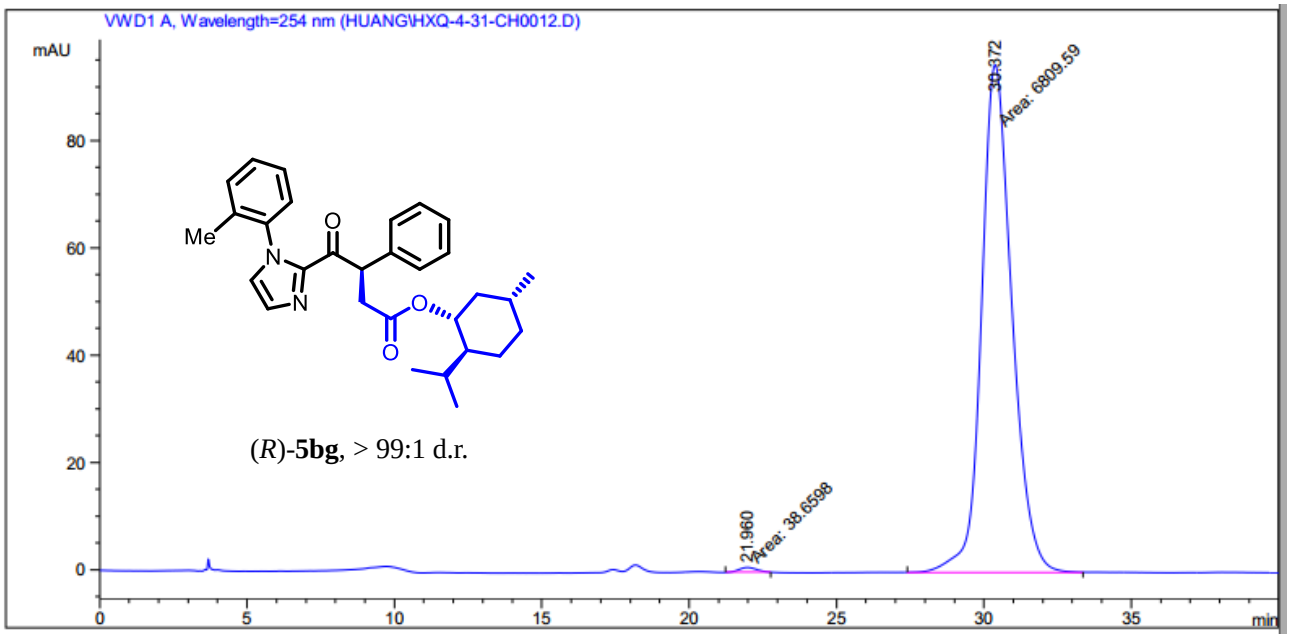
Detector A 254nm

Peak#	Ret. Time	Area	Area%
1	17.838	1636703	98.593
2	25.502	23359	1.407
Total		1660063	100.000

Figure S38. HPLC traces of *rac*-**5bf** (reference) and (*R*)-**5bf**.

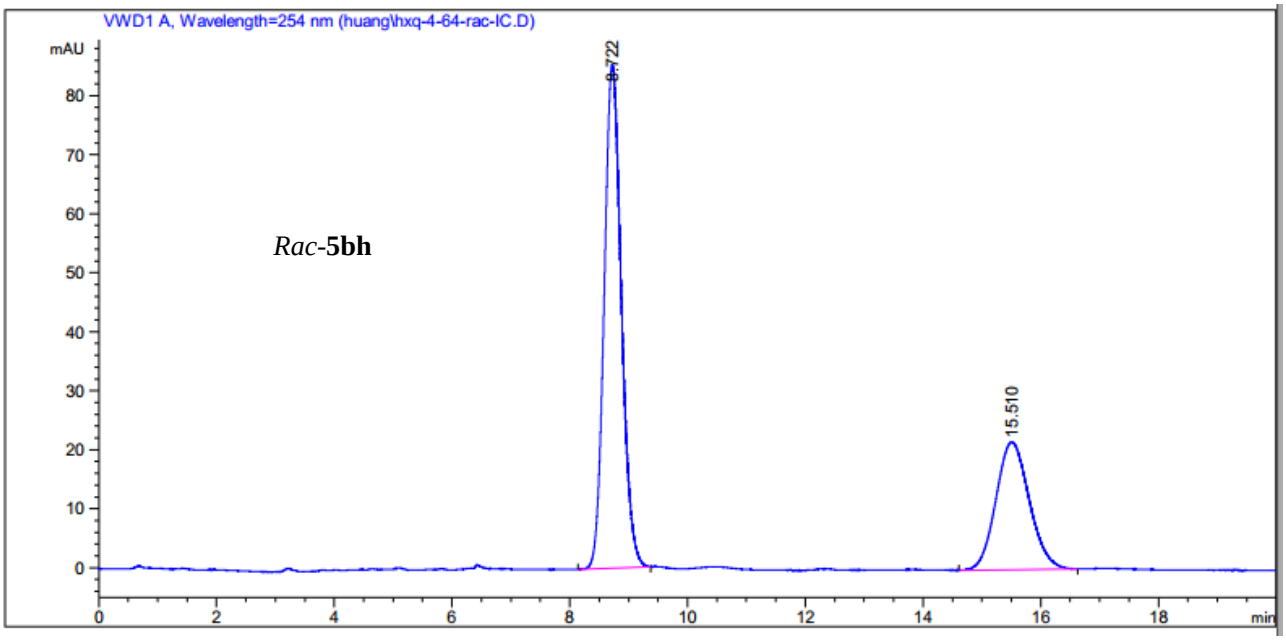


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.772	BB	0.7154	2877.98120	62.09925	47.1401
2	29.956	BB	0.9892	3227.19092	48.75308	52.8599



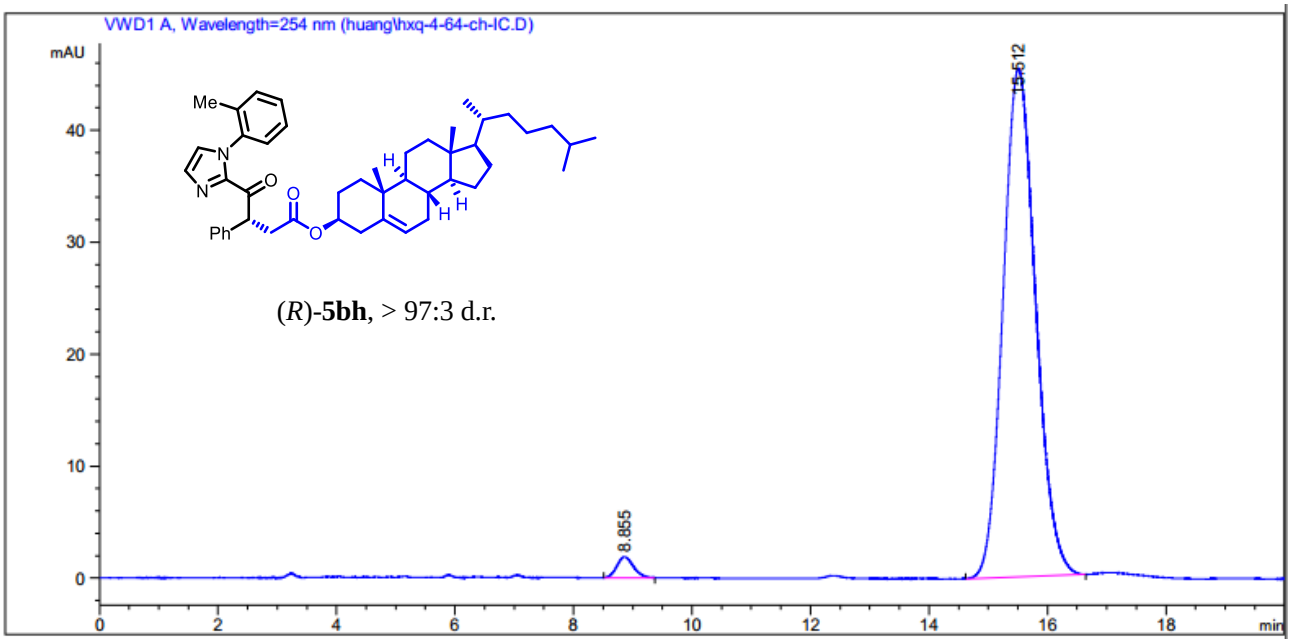
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.960	MM	0.7129	38.65981	9.03790e-1	0.5645
2	30.372	MM	1.2000	6809.59131	94.57644	99.4355

Figure S39. HPLC traces of *rac*-**5bg** (reference) and (*R*)-**5bg**.



Rac-**5bh**

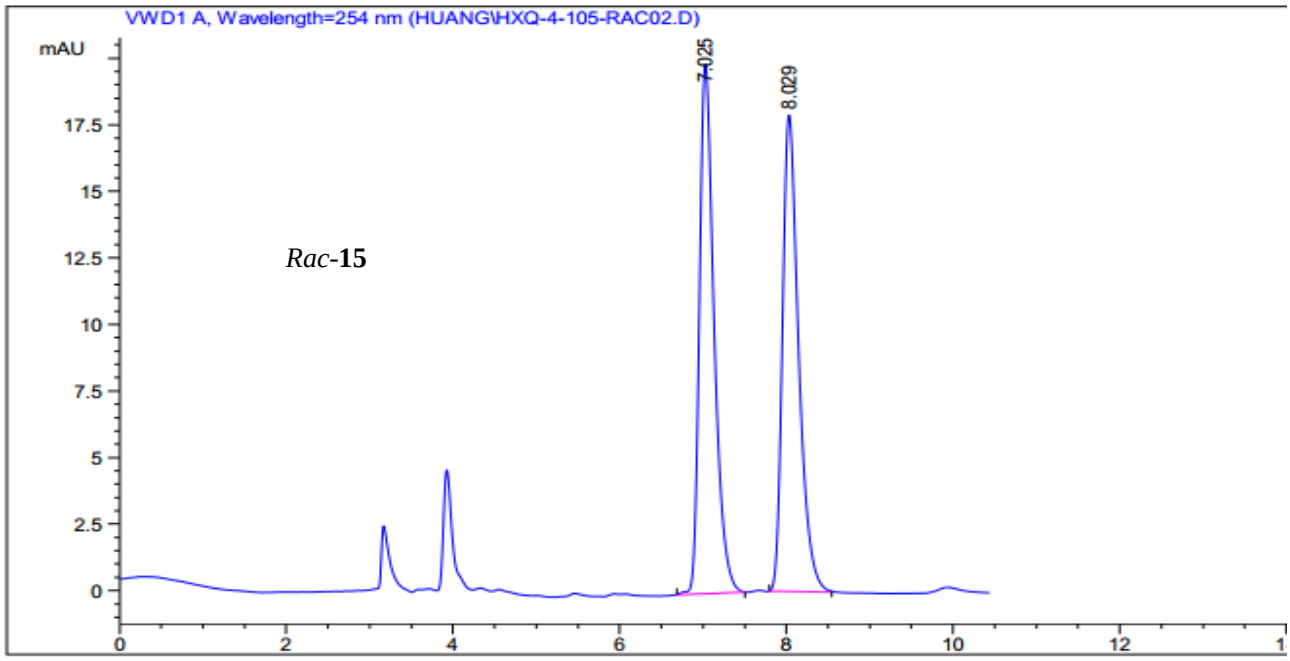
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.722	BB	0.2801	1718.35535	85.28737	66.8744
2	15.510	BB	0.4613	851.17047	21.61997	33.1256



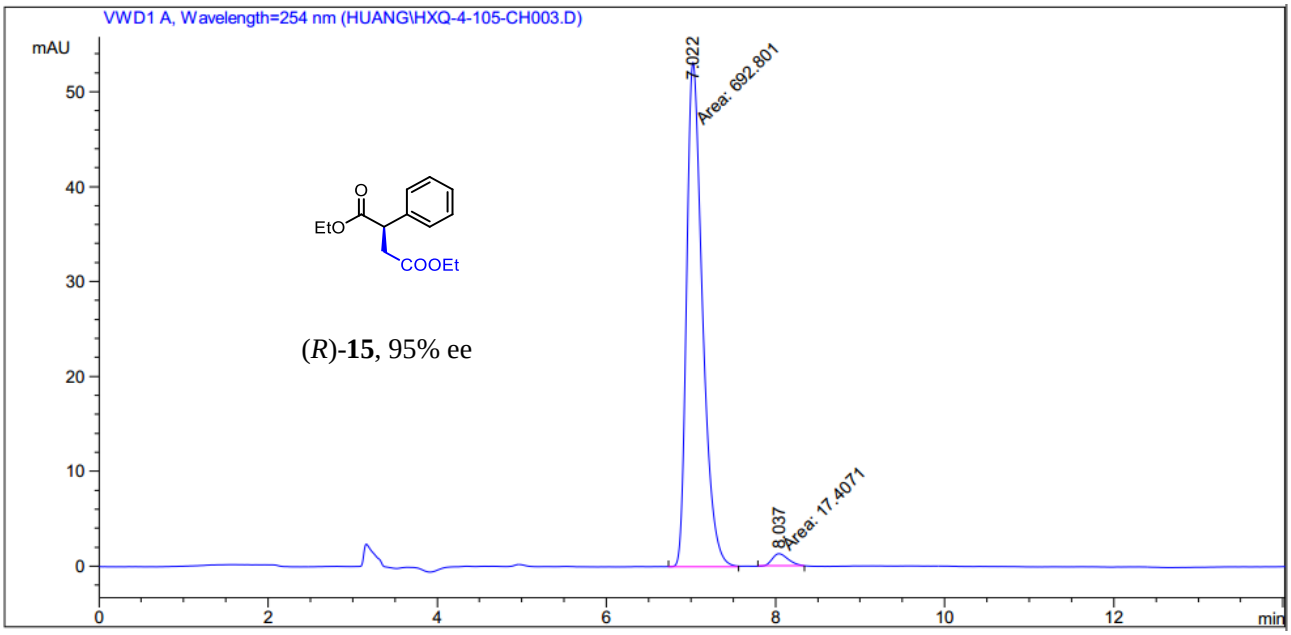
(*R*)-**5bh**, > 97:3 d.r.

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.855	BB	0.2281	36.35423	1.87150	2.0567
2	15.512	BB	0.4464	1731.21362	45.39298	97.9433

Figure S40. HPLC traces of *rac*-**5bh** (reference) and (*R*)-**5bh**.



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.025	BB	0.1831	242.83606	19.90819	50.2670
2	8.029	BB	0.2032	240.25670	17.89603	49.7330



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.022	MM	0.2172	692.80115	53.16166	97.5490
2	8.037	MM	0.2230	17.40712	1.30107	2.4510

Figure S41. HPLC traces of *rac*-**15** (reference) and (*R*)-**15**.

9. Single-Crystal X-Ray Diffraction Studies

Single crystals of **Rh-enolate** suitable for X-ray diffraction were obtained by slow diffusion from a solution of **Rh-enolate** (20 mg) in DCM (1.0 mL) layered with *n*-hexane (0.5 mL) at room temperature for several days in a NMR tube.

Single crystals of **5oa** suitable for X-ray diffraction were obtained by slow diffusion from a solution of **5oa** (30 mg) in DCM (0.5 mL) layered with *n*-hexane (0.5 mL) at - 20 ^{o}C for several days in a NMR tube.

X-ray data were collected with a Bruker 3 circuit D8 Quest diffractometer with MoKα radiation (microfocus tube with multilayer optics) and Photon 100 CMOS detector at 100 K. Scaling and absorption correction was performed by using the SADABS[21Error! Bookmark not defined.] software package of Bruker. Structures were solved using direct methods in SHELXT[22] and refined using the full matrix least squares procedure in SHELXL-2014[23]. The hydrogen atoms were placed in calculated positions and refined as riding on their respective C atom, and Uiso(H) was set at 1.2 Ueq(Csp^2) and 1.5 Ueq(Csp^3). Disorder was refined using restraints for both the geometry and the anisotropic displacement factors. The absolute configuration of **5oa** has been determined.[24]

Crystal structure, data and details of the structure determination for **Rh-enolate** are presented in the Figure S42 and Table S9.

Crystal structure, data and details of the structure determination for **5oa** are presented in the Figure S43 and Table S10.

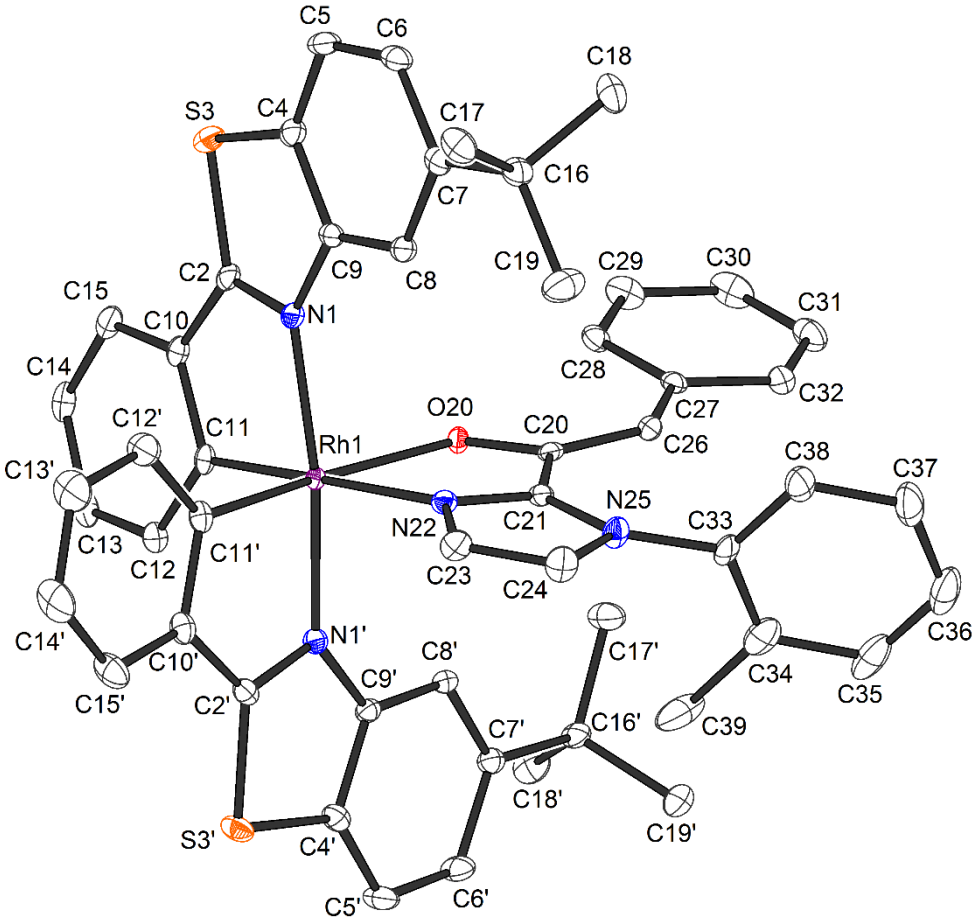


Figure S42. Crystal structure of **Rh-enolate**. ORTEP drawing with 30% probability thermal ellipsoids.

Table S9. Crystal Data and Structure Refinement for **Rh-enolate**

Crystal data

Identification code	hxqC31_0m	
Habitus, colour	nugget, light green	
Crystal size	0.23 x 0.13 x 0.10 mm^3	
Crystal system	Monoclinic	
Space group	$P2_1/n$	Z = 4
Unit cell dimensions	a = 11.6759(5) Å	α= 90°.
	b = 23.0296(9) Å	β= 92.6600(10)°.
	c = 16.4573(7) Å	γ = 90°.
Volume	4420.5(3) $Å^3$	
Cell determination	9634 peaks with Theta 2.4 to 27.5°.	
Empirical formula	C_{52} H_{47} N_4 O Rh S_2	
Moiety formula	C_{52} H_{47} N_4 O Rh S_2	
Formula weight	910.96	
Density (calculated)	1.369 Mg/m^3	
Absorption coefficient	0.524 mm^{-1}	
F(000)	1888	

Data collection:

Diffractometer type	Bruker D8 QUEST area detector
Wavelength	0.71073 Å
Temperature	100(2) K
Theta range for data collection	2.159 to 27.558°.
Index ranges	-15<=h<=15, -29<=k<=29, -21<=l<=21
Data collection software	APEX3 (Bruker AXS Inc., 2015)[25]
Cell refinement software	SAINT V8.35A (Bruker AXS Inc., 2015)[26]
Data reduction software	SAINT V8.35A (Bruker AXS Inc., 2015)

Solution and refinement:

Reflections collected	155552
Independent reflections	10199 [R(int) = 0.0382]
Completeness to theta = 25.242°	99.9 %
Observed reflections	9143[I > 2(I)]
Reflections used for refinement	10199
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.95 and 0.90
Largest diff. peak and hole	0.413 and -0.701 e.$Å^{-3}$
Solution	Direct methods
Refinement	Full-matrix least-squares on F^2
Treatment of hydrogen atoms	Calculated positions, constr. ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[27]
	SHELXL-2014/7 (Sheldrick, 2014)[28]
	DIAMOND (Crystal Impact)[29]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[30]
Data / restraints / parameters	10199 / 303 / 583
Goodness-of-fit on F^2	1.052
R index (all data)	wR2 = 0.0556
R index conventional [I>2sigma(I)]	R1 = 0.0227

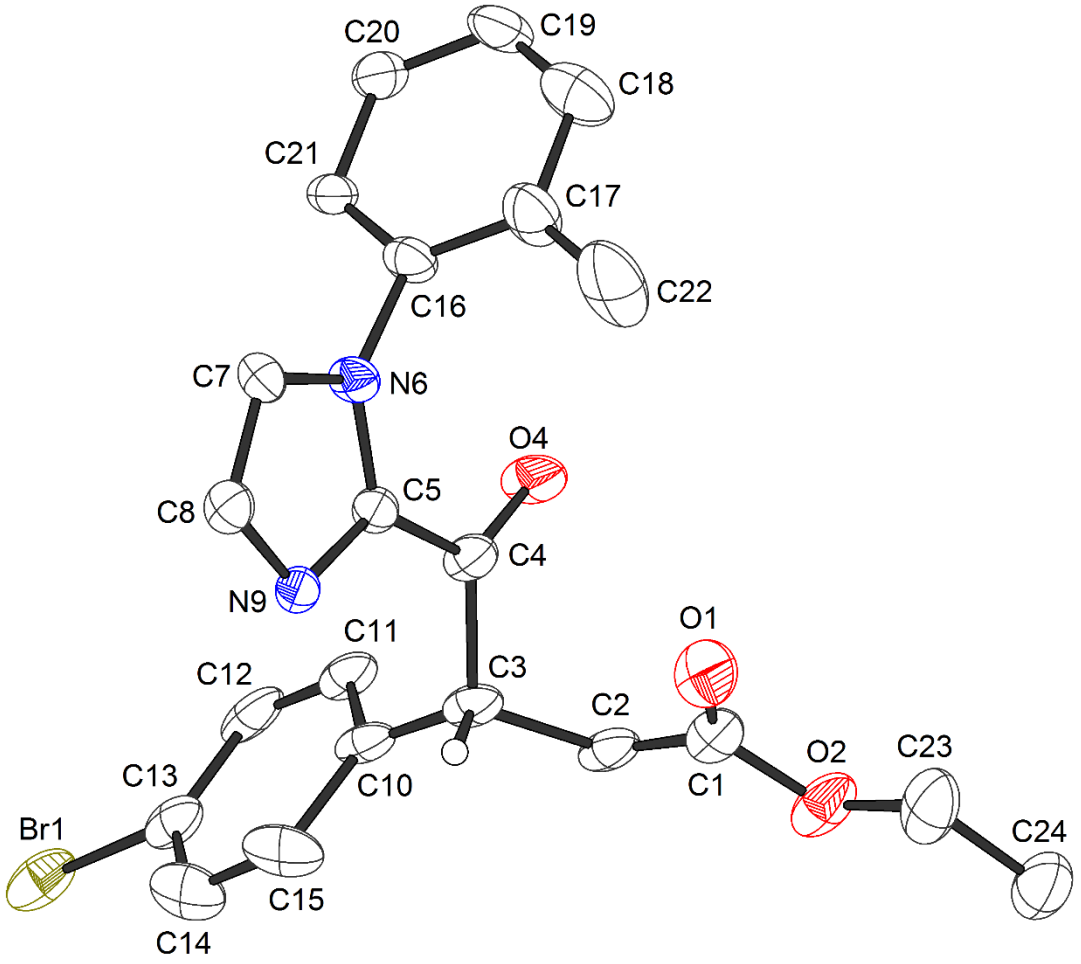


Figure S43. Crystal structure of **5oa**. ORTEP drawing with 30% probability thermal ellipsoids.

Table S10. Crystal Data and Structure Refinement for **5oa**

Crystal data

Identification code	hxqD53_0m	
Habitus, colour	nugget, colourless	
Crystal size	0.27 x 0.22 x 0.15 mm^3	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	Z = 4
Unit cell dimensions	a = 9.8543(4) Å	α = 90°.
	b = 13.1873(6) Å	β = 90°.
	c = 15.4684(7) Å	γ = 90°.
Volume	2010.14(15) $Å^3$	
Cell determination	9961 peaks with Theta 2.5 to 25.3°.	
Empirical formula	C_{22} H_{21} Br N_2 O_3	
Moiety formula	C_{22} H_{21} Br N_2 O_3	
Formula weight	441.32	
Density (calculated)	1.458 Mg/m^3	
Absorption coefficient	2.070 mm^{-1}	
F(000)	904	

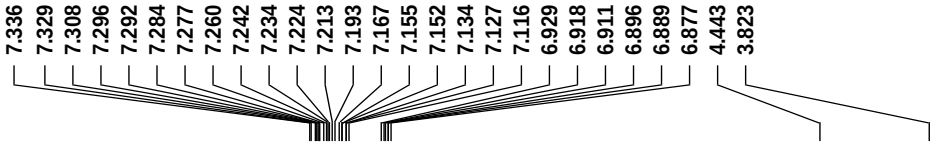
Data collection:

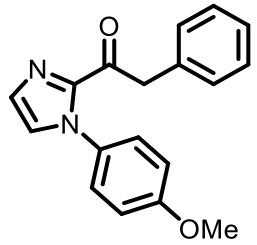
Diffractometer type	Bruker D8 QUEST area detector
Wavelength	0.71073 Å
Temperature	100(2) K
Theta range for data collection	2.451 to 25.288°.
Index ranges	-11<=h<=11, -13<=k<=15, -18<=l<=18
Data collection software	APEX3 (Bruker AXS Inc., 2015)[25]
Cell refinement software	SAINT V8.35A (Bruker AXS Inc., 2015)[26]
Data reduction software	SAINT V8.35A (Bruker AXS Inc., 2015)

Solution and refinement:

Reflections collected	29129
Independent reflections	3633 [R(int) = 0.0358]
Completeness to theta = 25.242°	100.0 %
Observed reflections	3507[I > 2(I)]
Reflections used for refinement	3633
Extinction coefficient	X = 0.0018(4)
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.75 and 0.65
Flack parameter (absolute struct.)	0.005(4)[31]
Largest diff. peak and hole	0.720 and -0.920 e.$Å^{-3}$
Solution	Direct methods
Refinement	Full-matrix least-squares on F^2
Treatment of hydrogen atoms	Calculated positions, constr. ref.
Programs used	XT V2014/1 (Bruker AXS Inc., 2014)[27]
	SHELXL-2014/7 (Sheldrick, 2014)[28]
	DIAMOND (Crystal Impact)[29]
	ShelXle (Hübschle, Sheldrick, Dittrich, 2011)[30]
Data / restraints / parameters	3633 / 756 / 366
Goodness-of-fit on F^2	1.152
R index (all data)	wR2 = 0.0787
R index conventional [I>2sigma(I)]	R1 = 0.0376

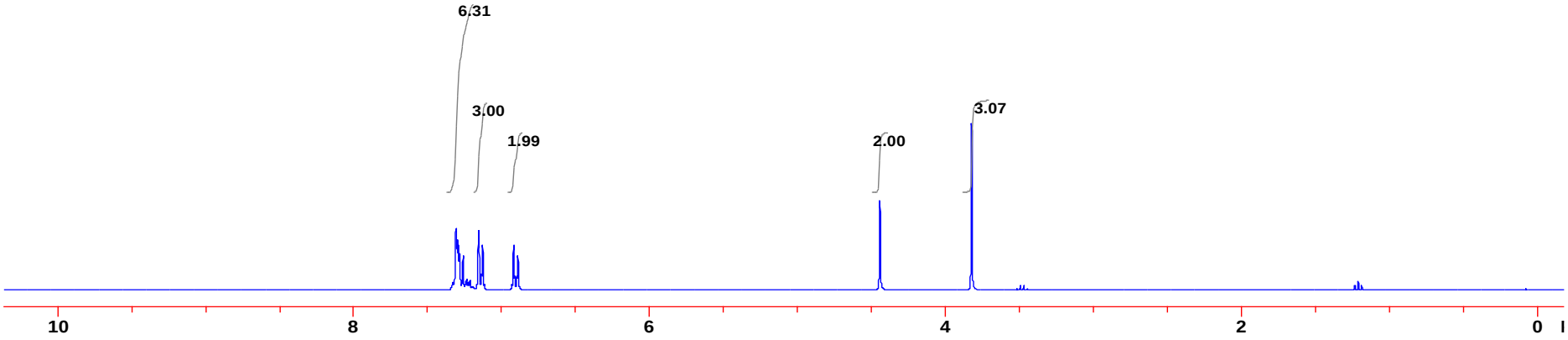
10. NMR Spectra of New Compounds

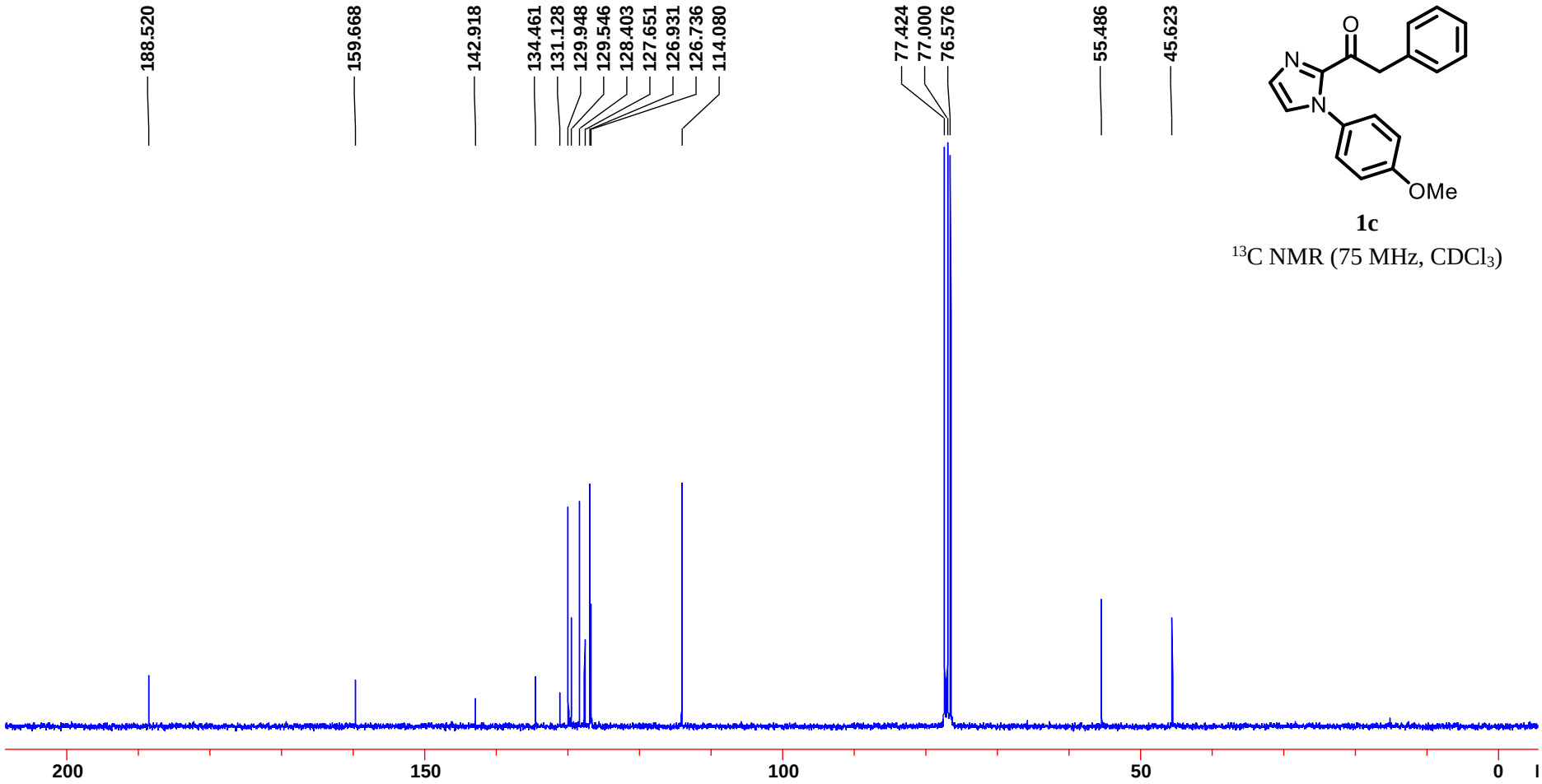




1c

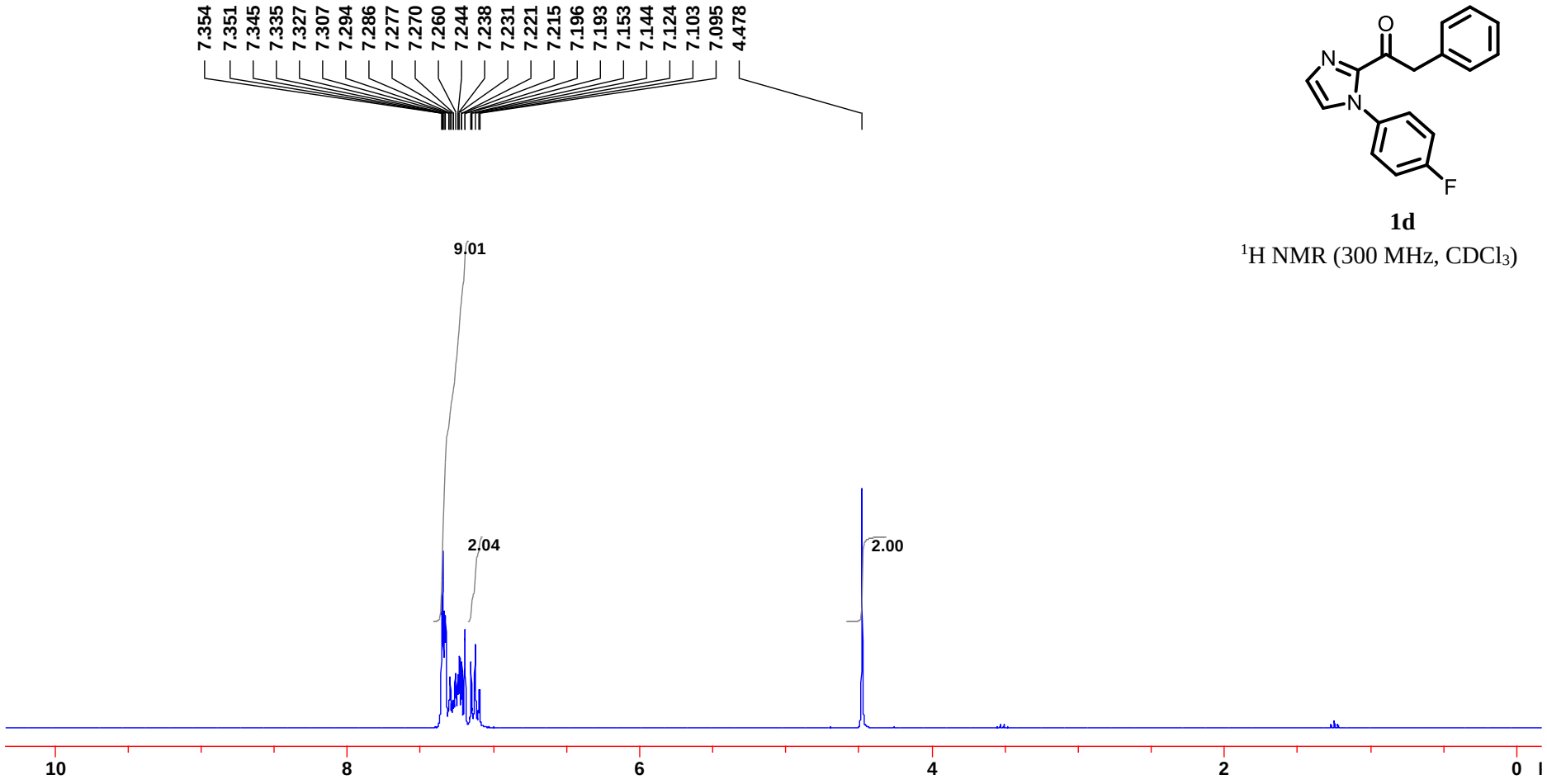
^{1}H NMR (300 MHz, $CDCl_3$)





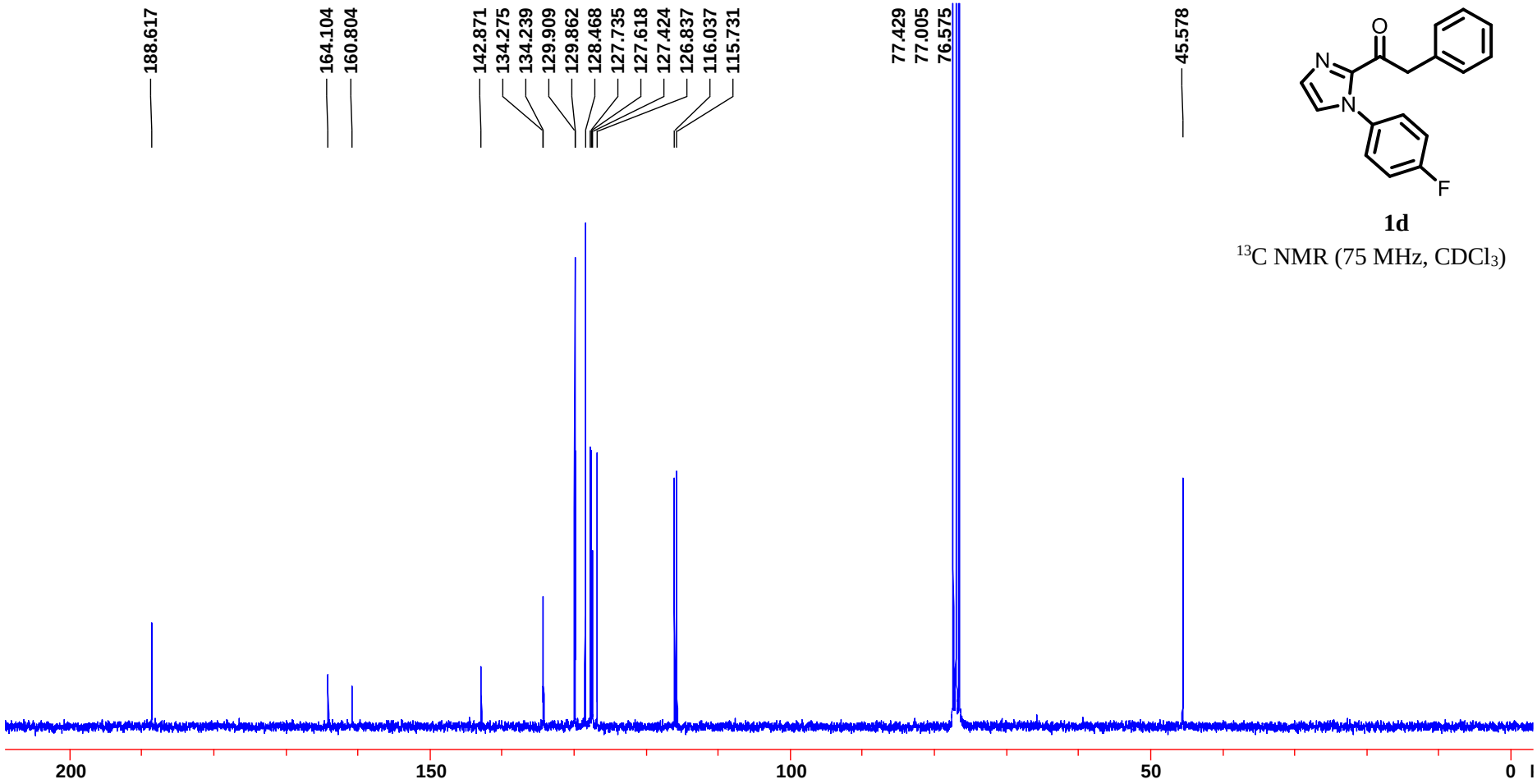
1c

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



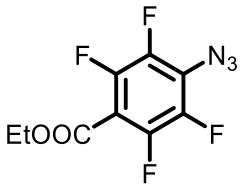
1d

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



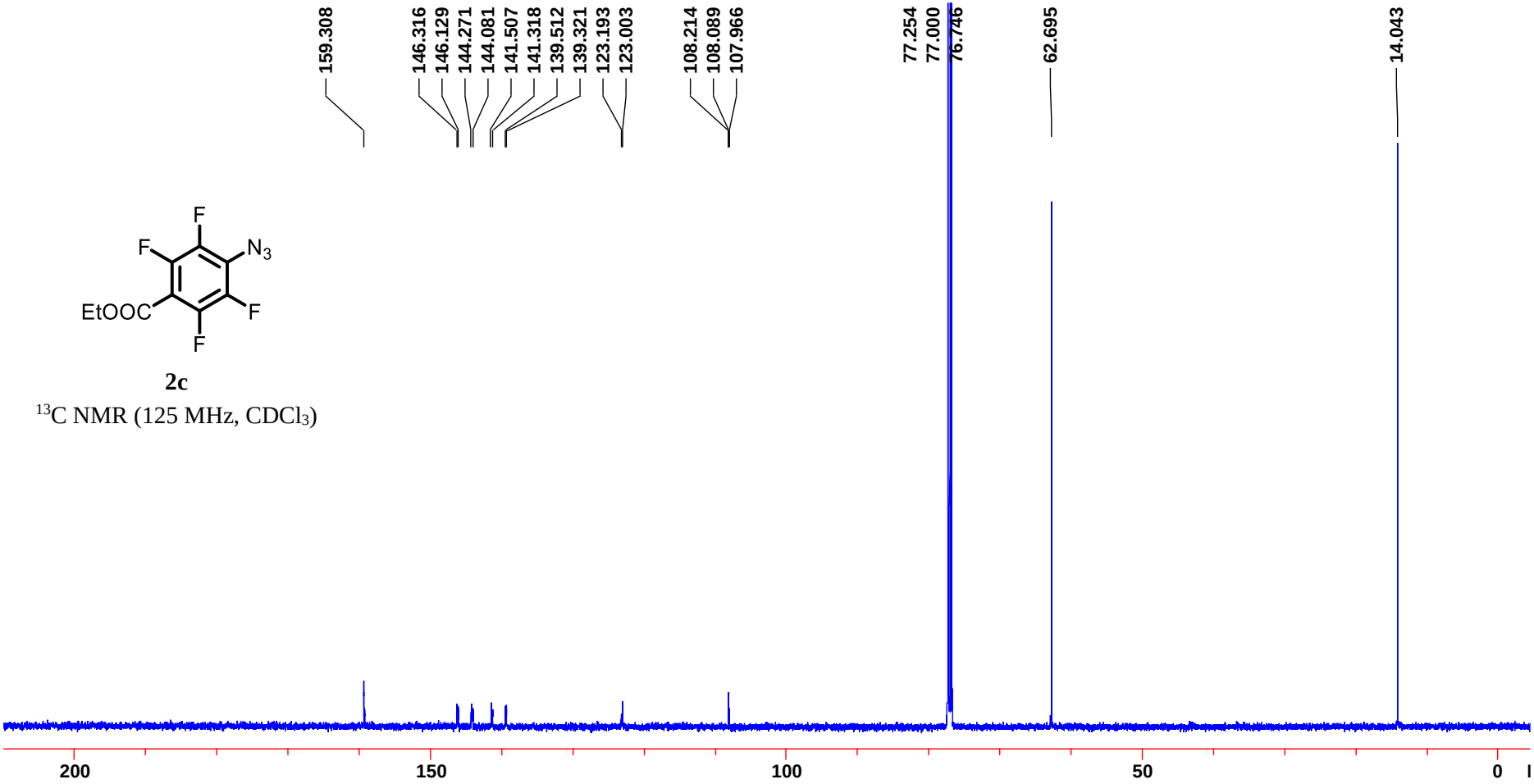
1d

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



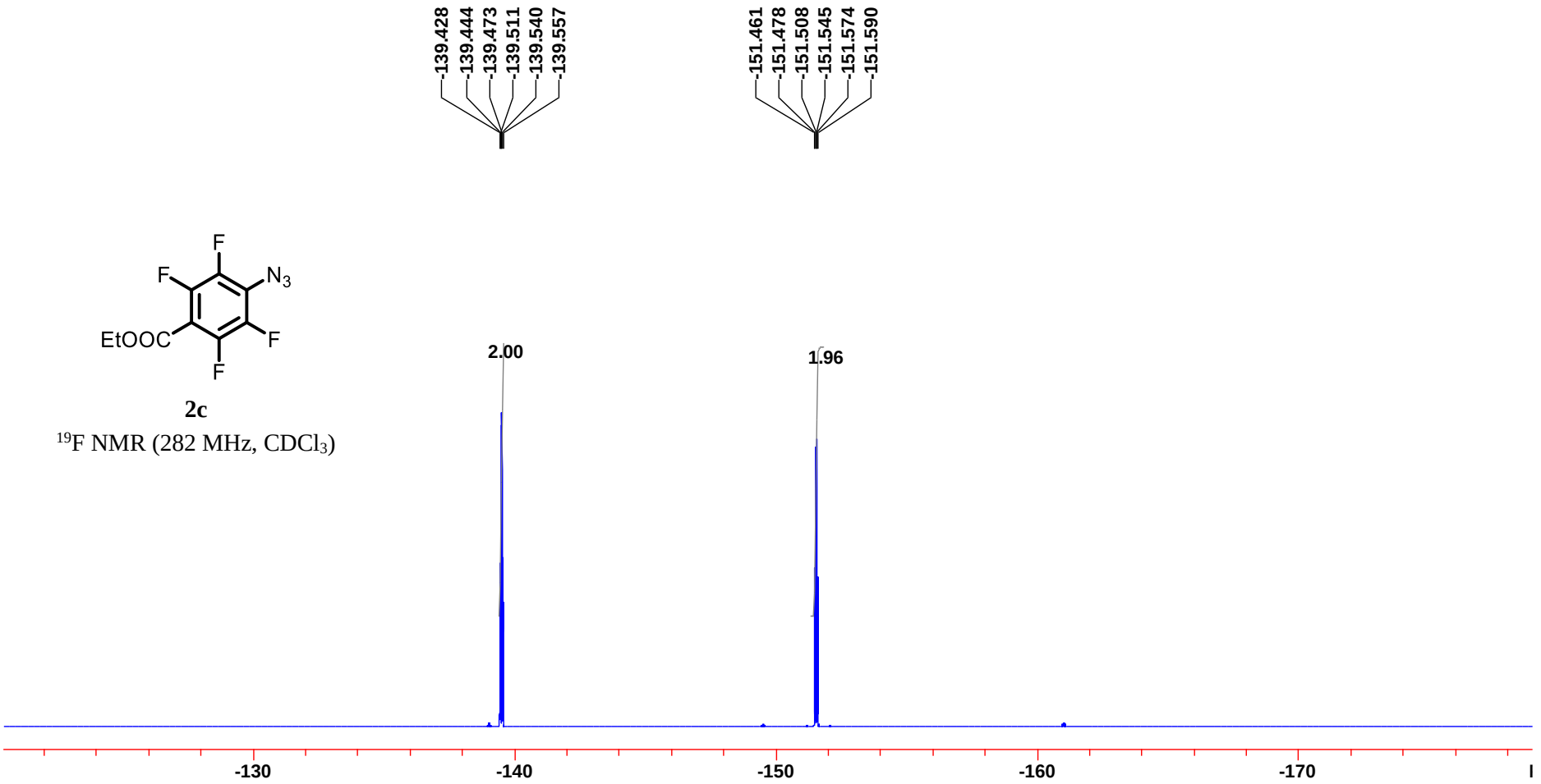
2c

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



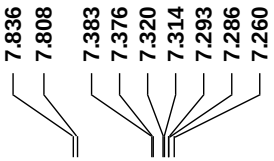
2c

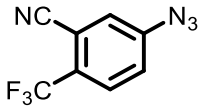
^{13}C NMR (125 MHz, $CDCl_3$)



2c

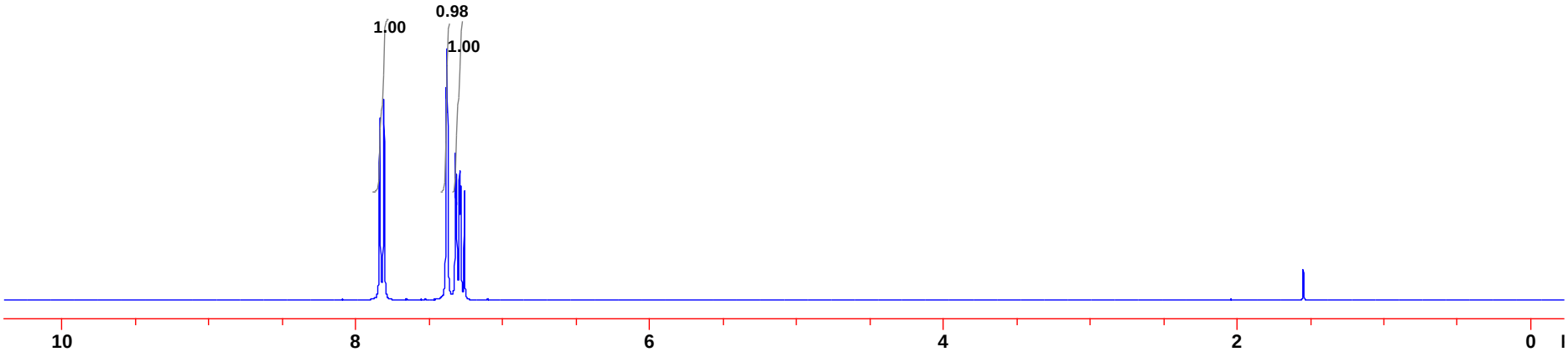
^{19}F NMR (282 MHz, $CDCl_3$)

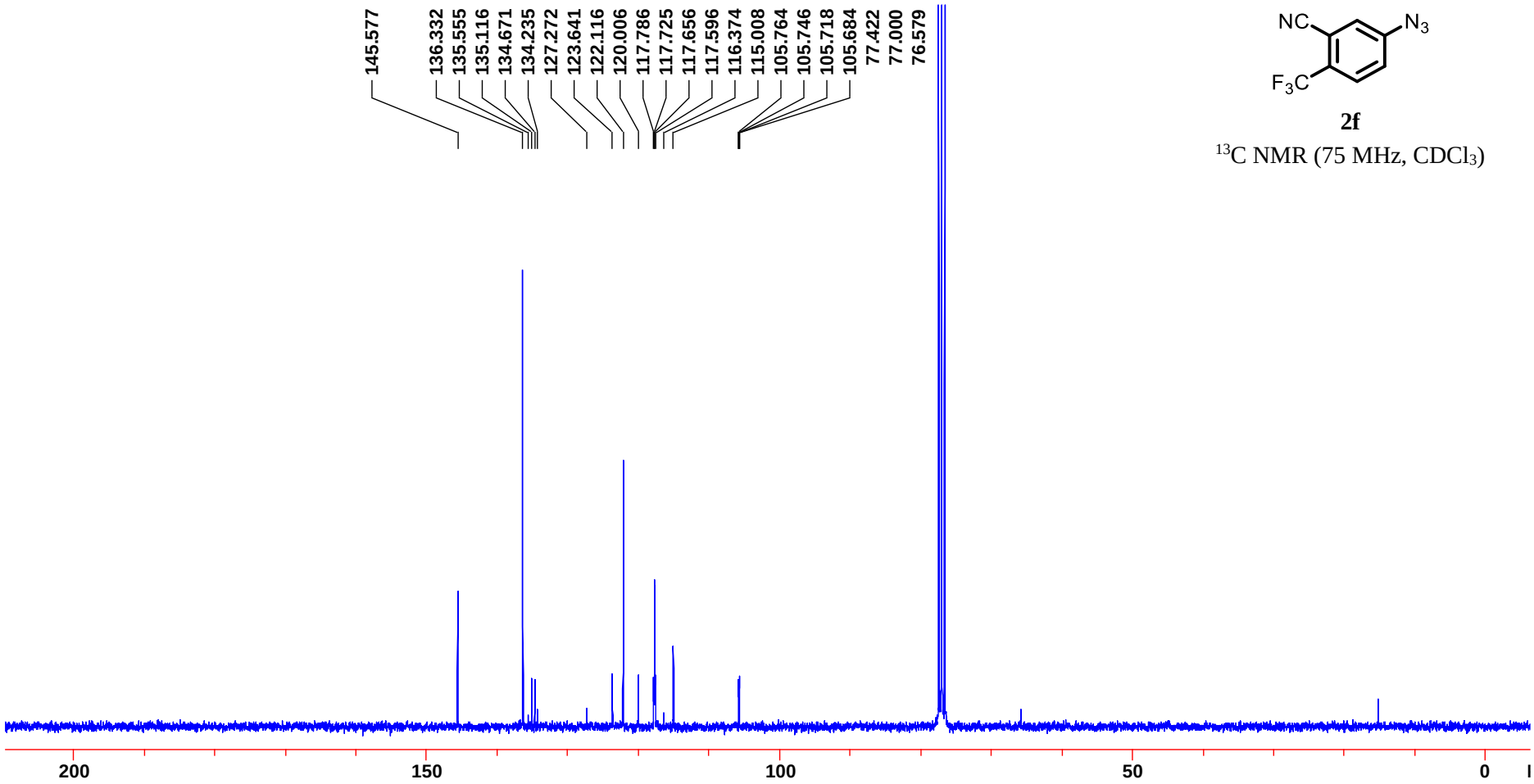




2f

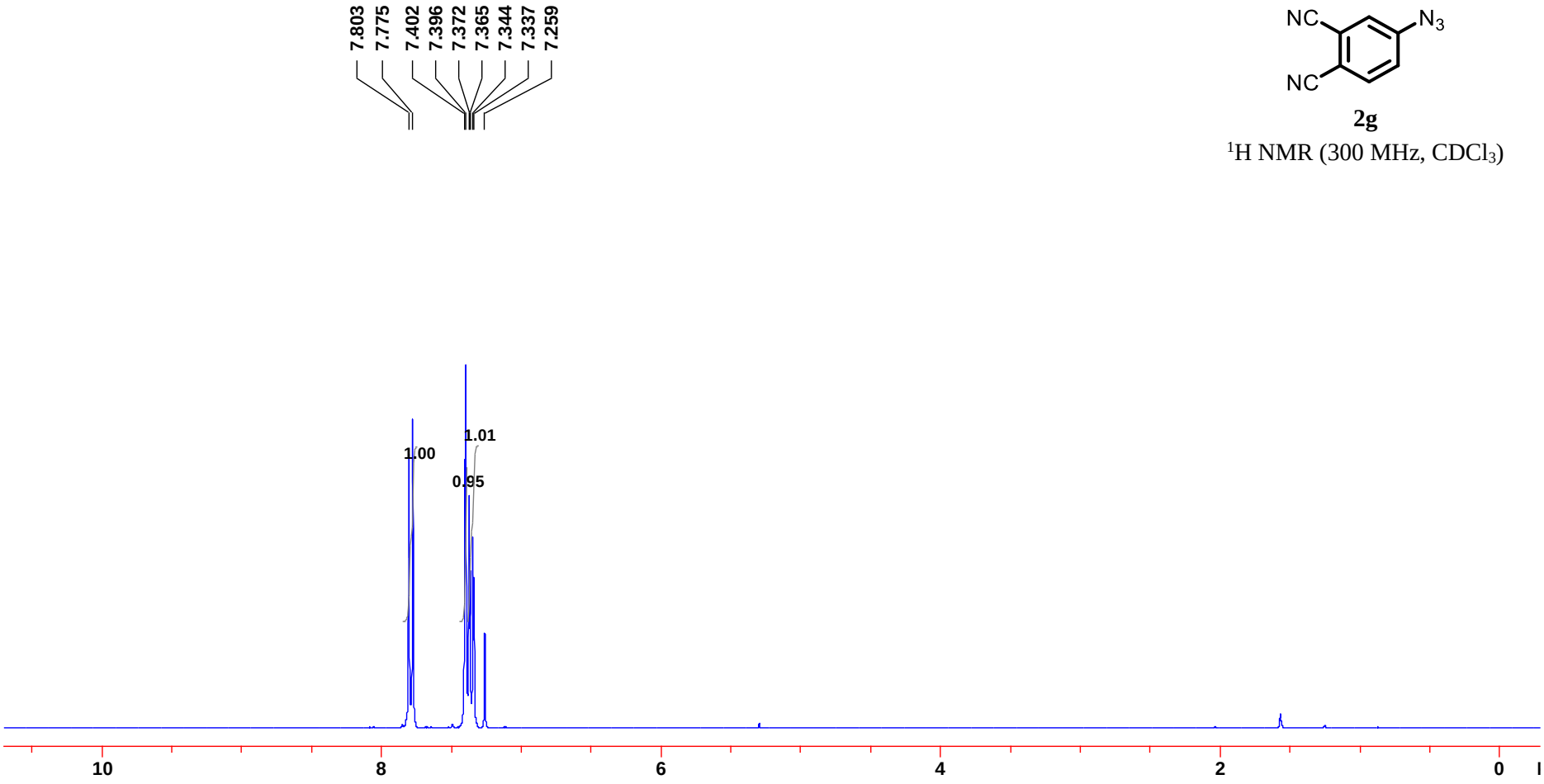
^{1}H NMR (300 MHz, $CDCl_3$)

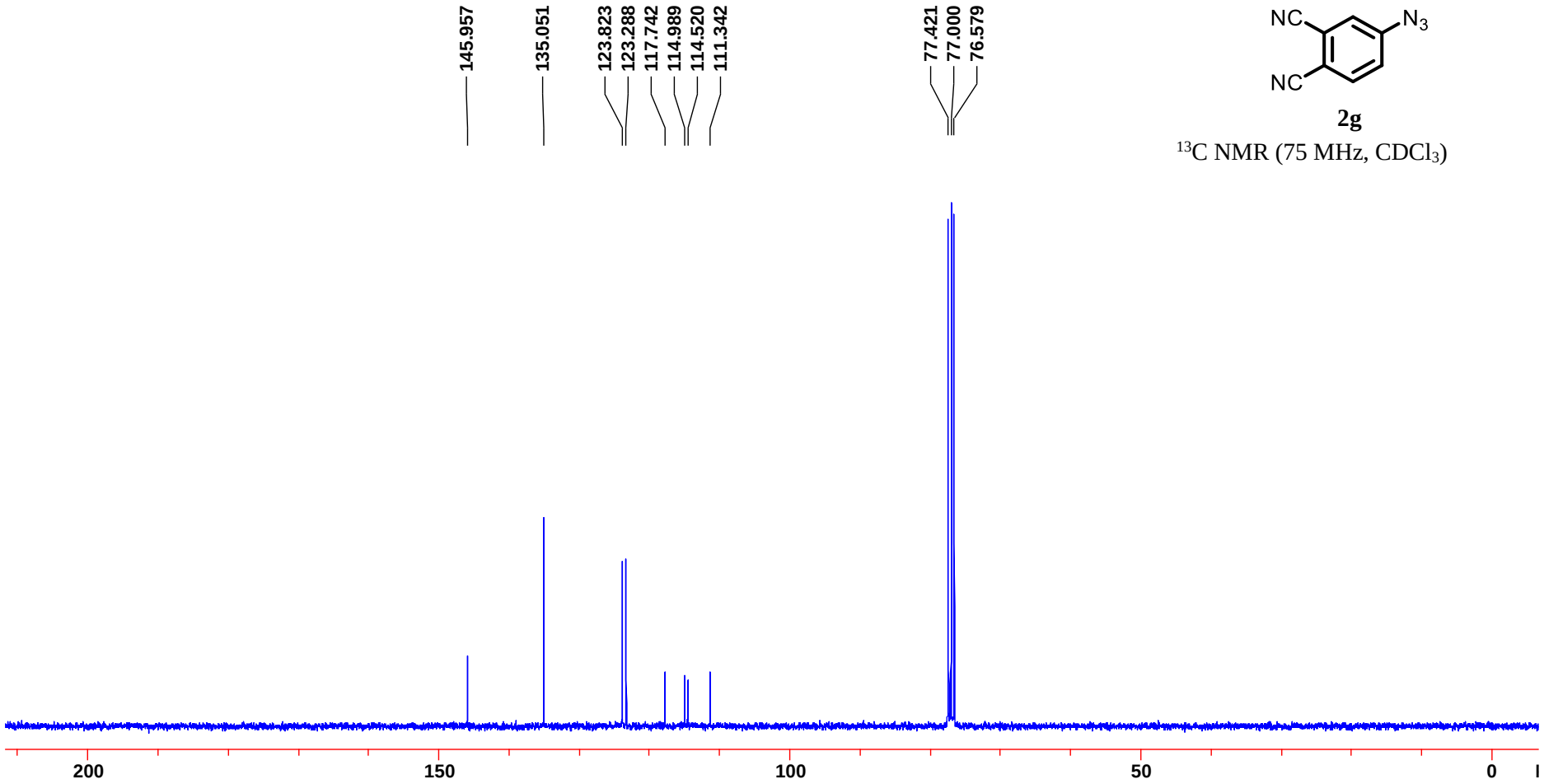




2f

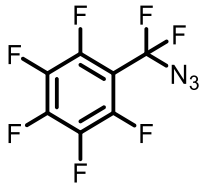
^{13}C NMR (75 MHz, $CDCl_3$)


7.803
7.775
7.402
7.396
7.372
7.365
7.344
7.337
7.259
NC
N3
NC
2g
1H NMR (300 MHz, CDCl3)
1.00
1.01
0.95
10
8
6
4
2
0



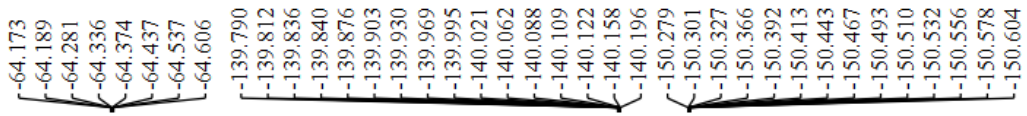
2g

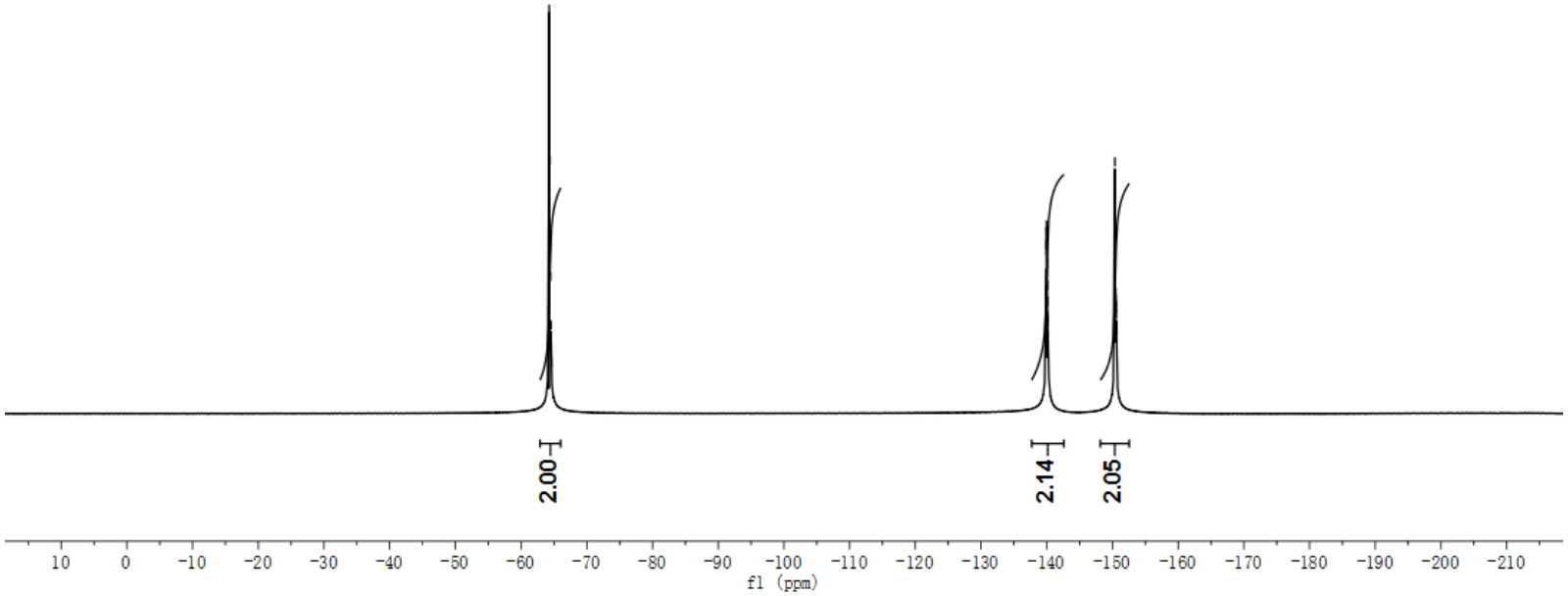
^{13}C NMR (75 MHz, $CDCl_3$)

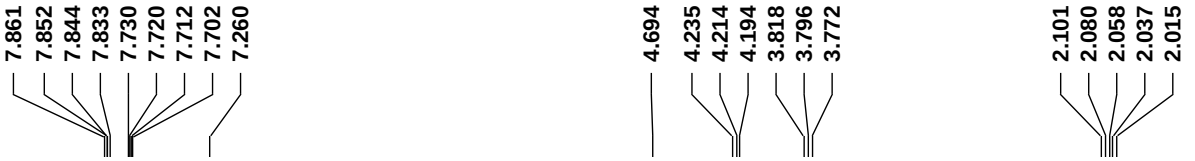


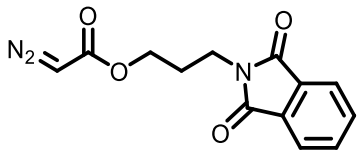
2h

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



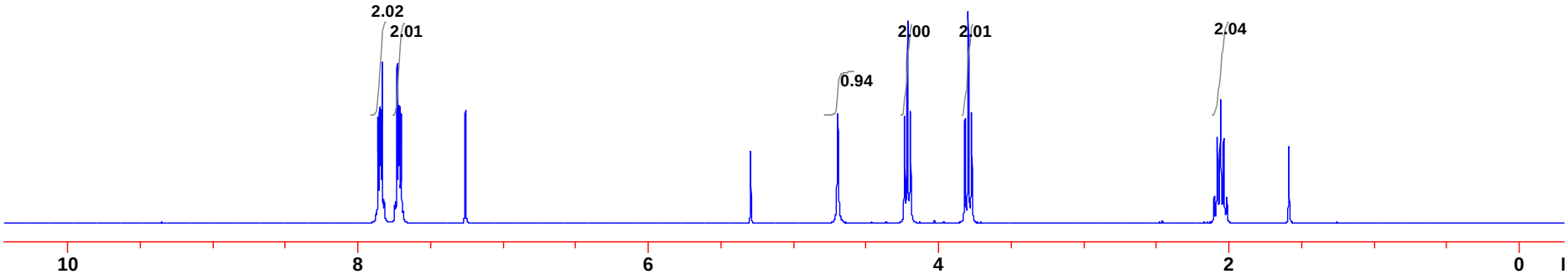


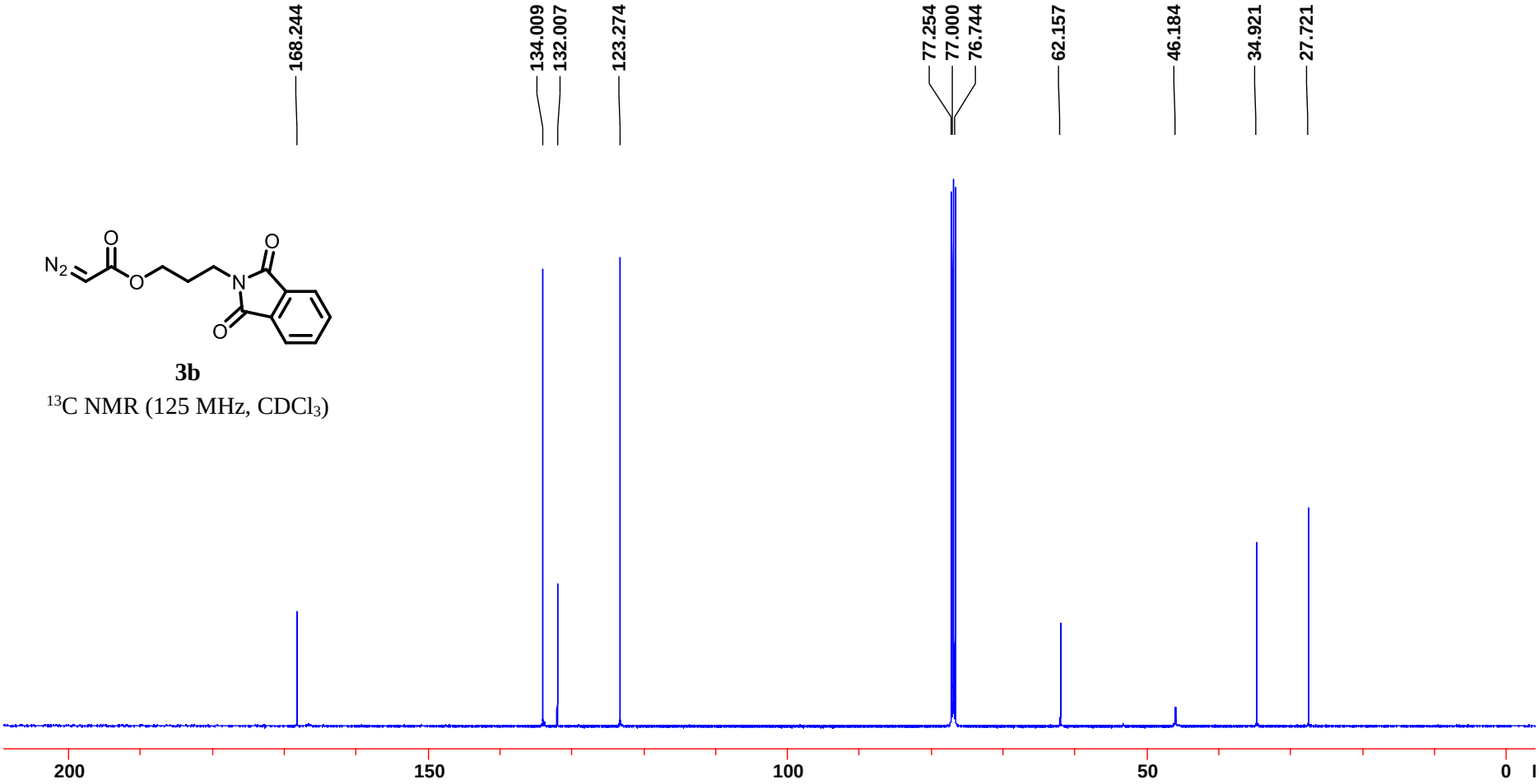




3b

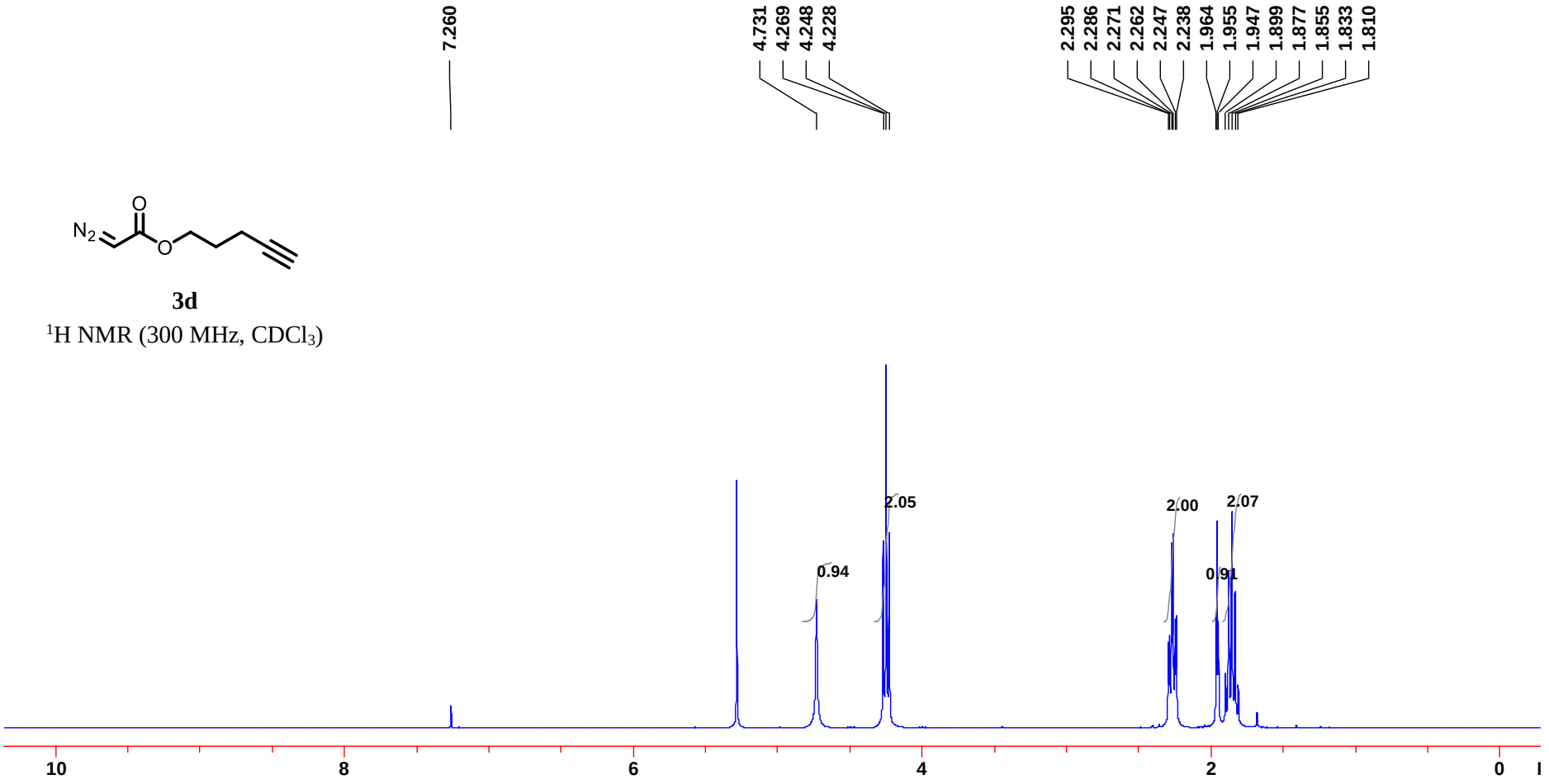
^{1}H NMR (300 MHz, $CDCl_3$)





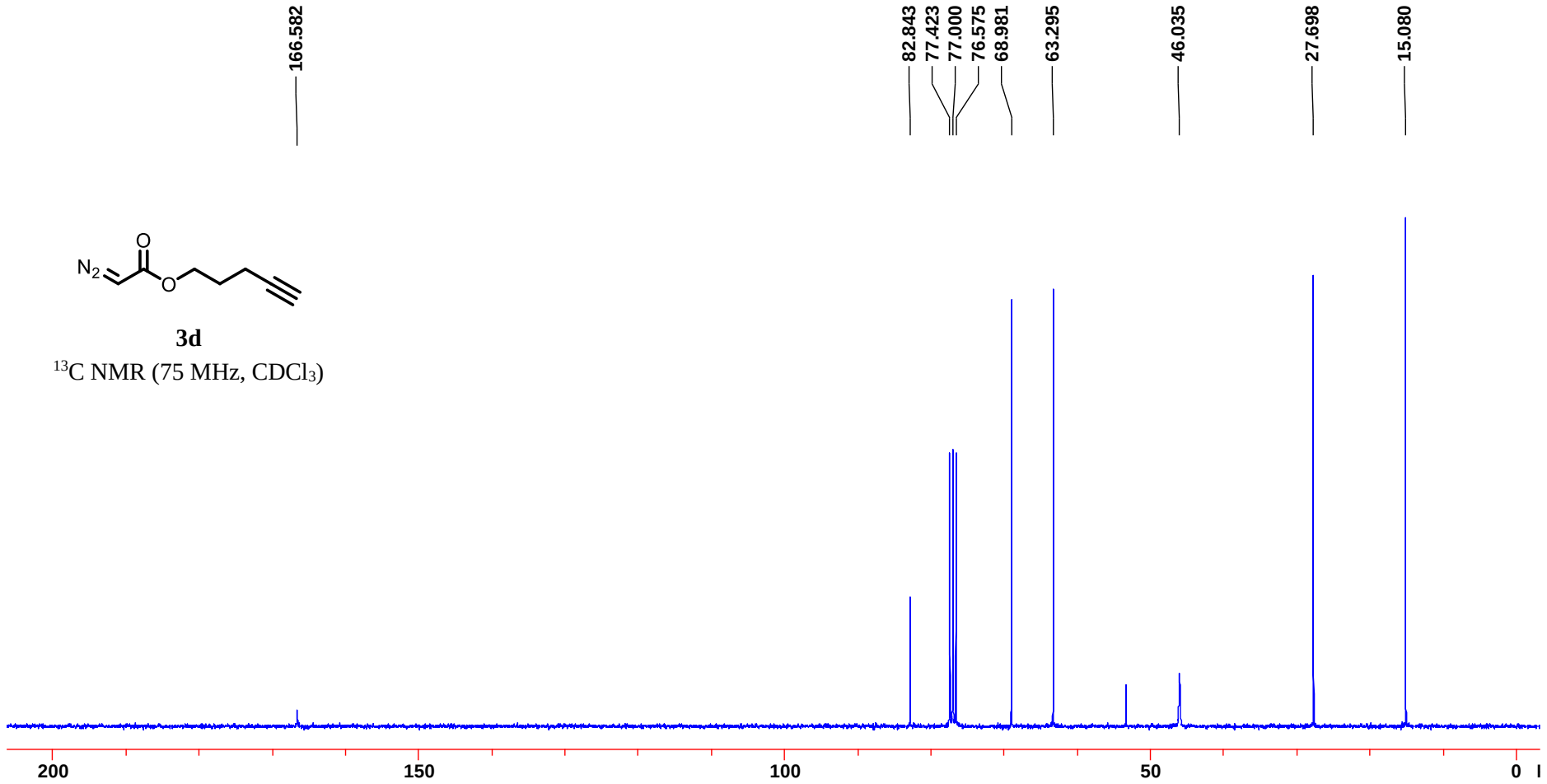
3b

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



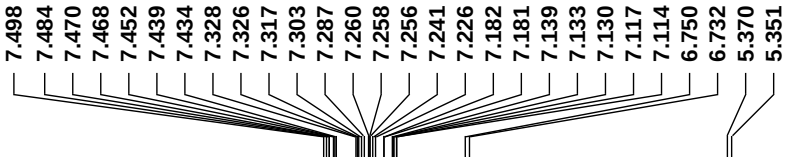
3d

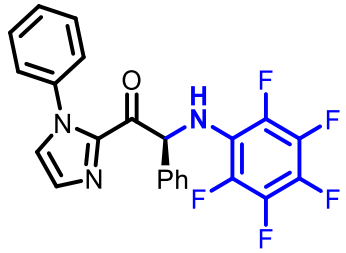
^{1}H NMR (300 MHz, $CDCl_3$)



3d

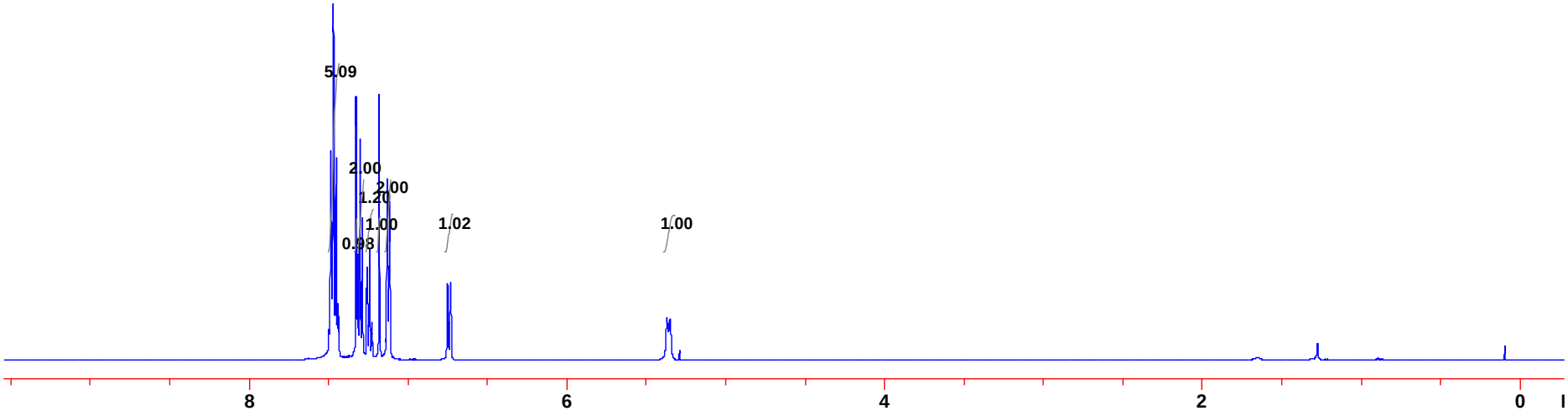
^{13}C NMR (75 MHz, $CDCl_3$)

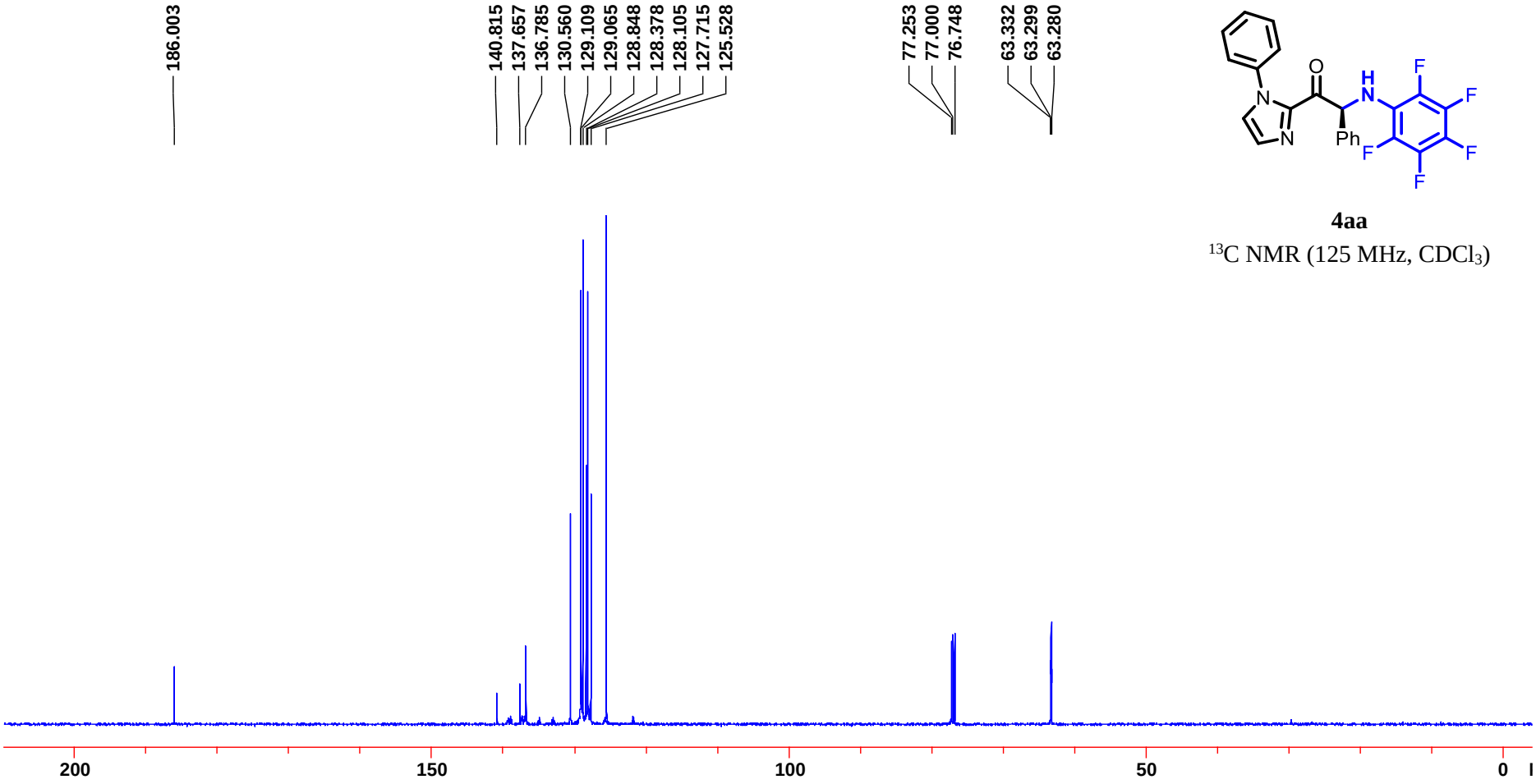




4aa

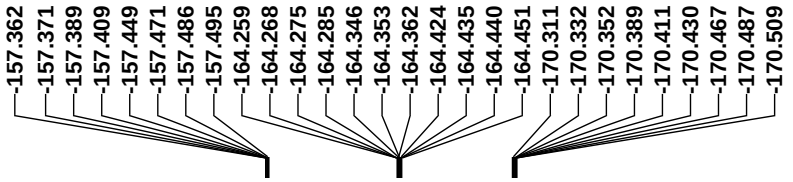
^{1}H NMR (500 MHz, $CDCl_3$)

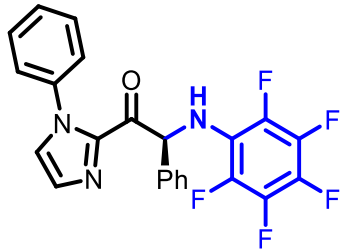




4aa

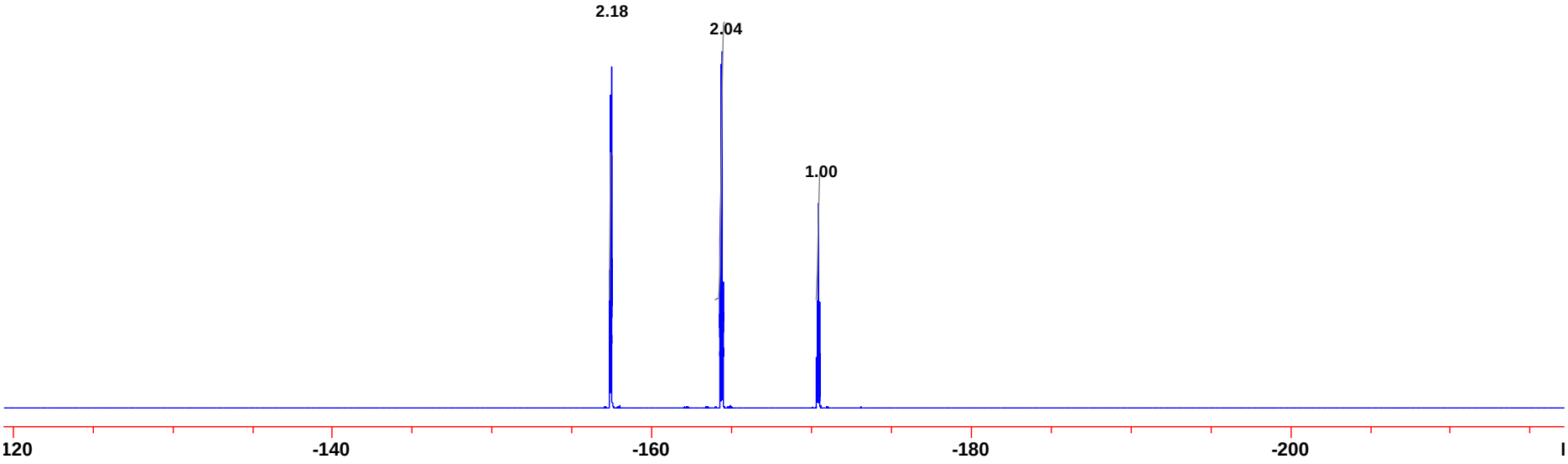
^{13}C NMR (125 MHz, $CDCl_3$)

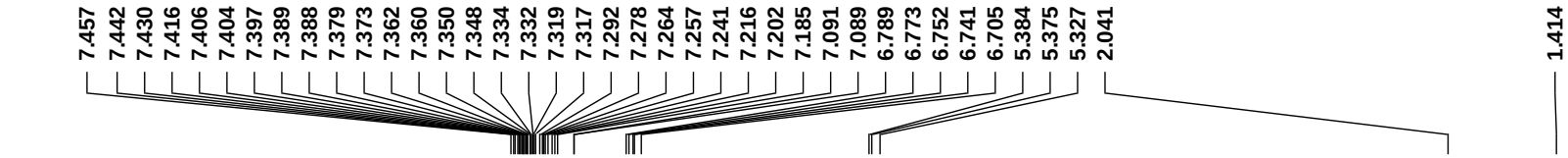


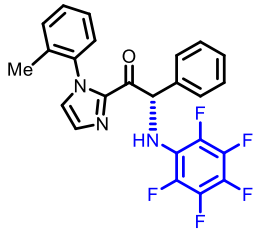


4aa

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

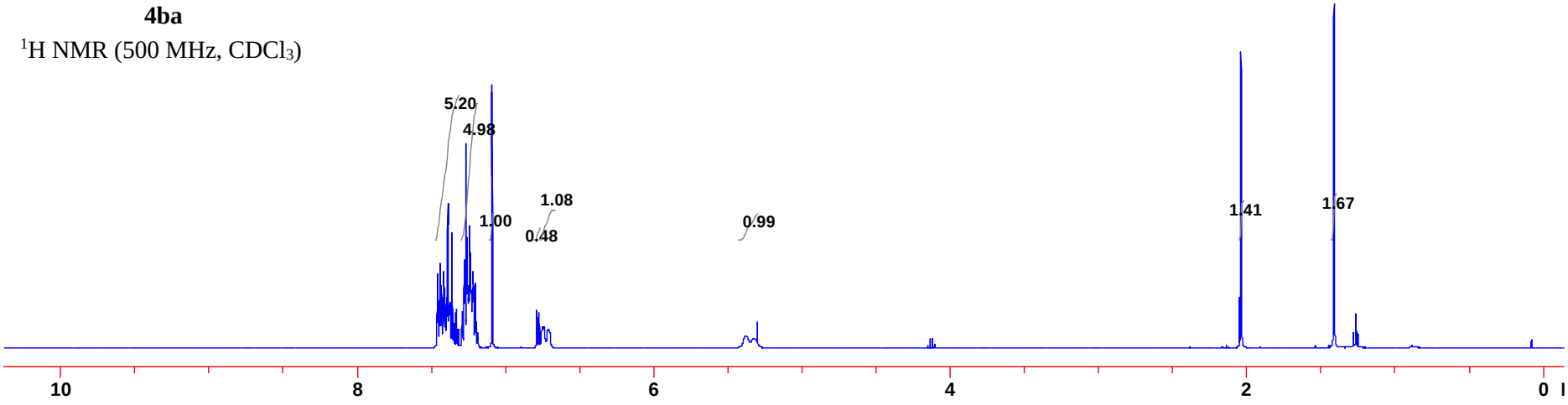


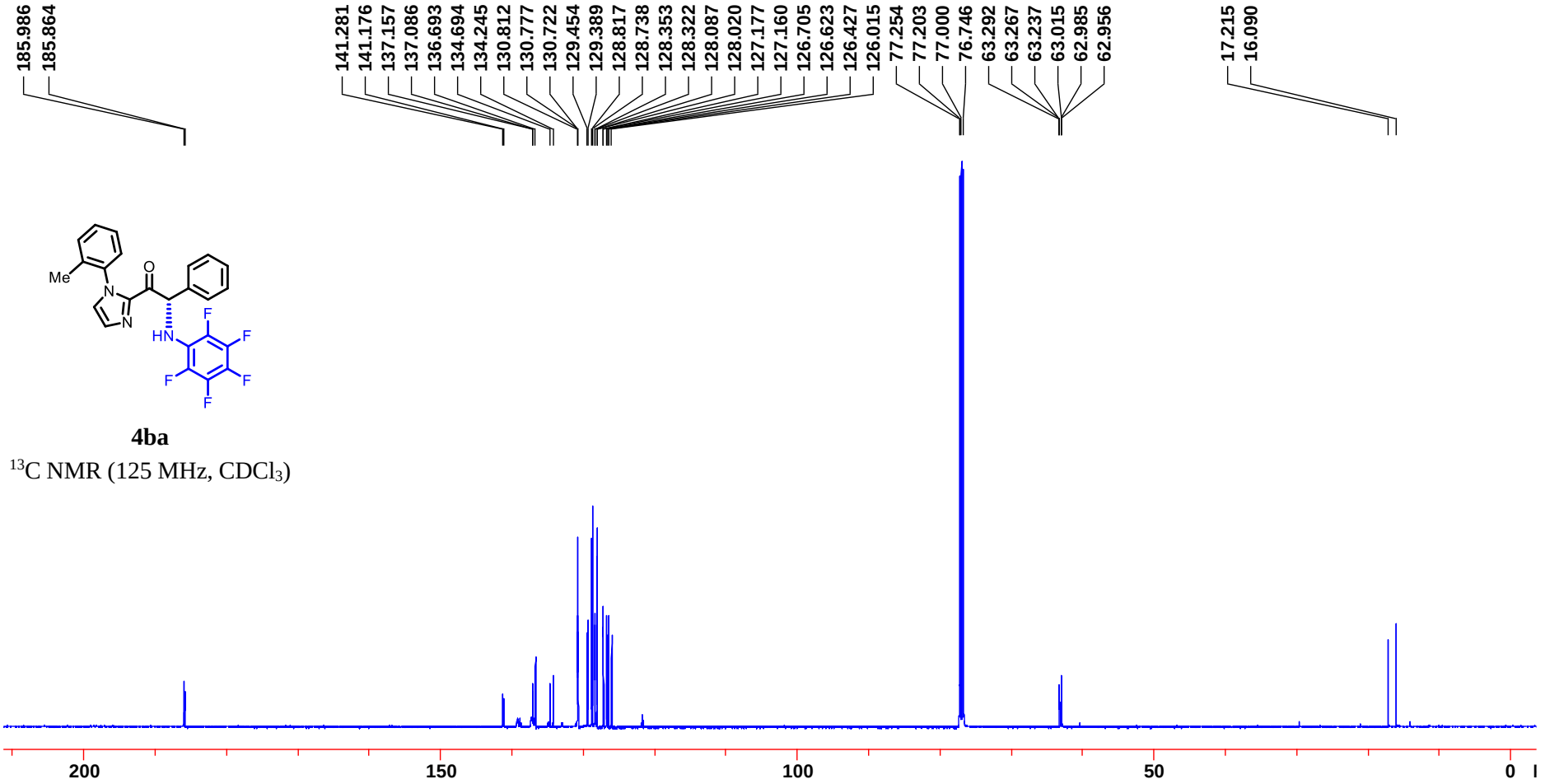




4ba

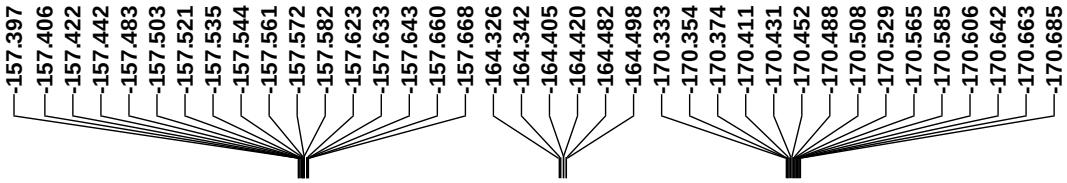
^{1}H NMR (500 MHz, $CDCl_3$)

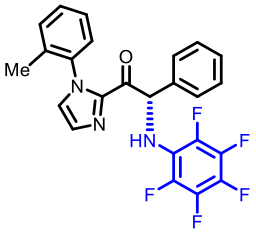




4ba

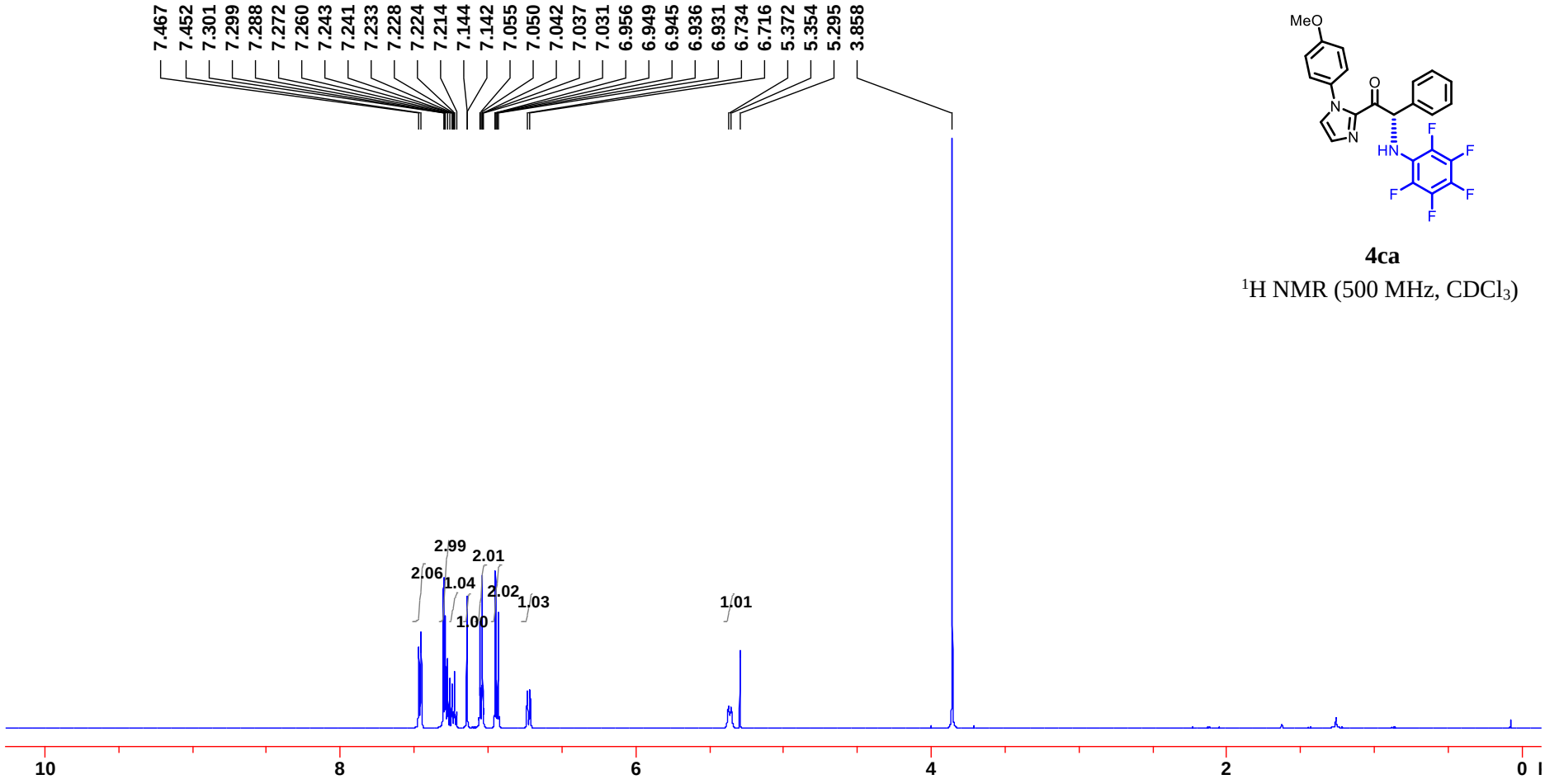
^{13}C NMR (125 MHz, $CDCl_3$)





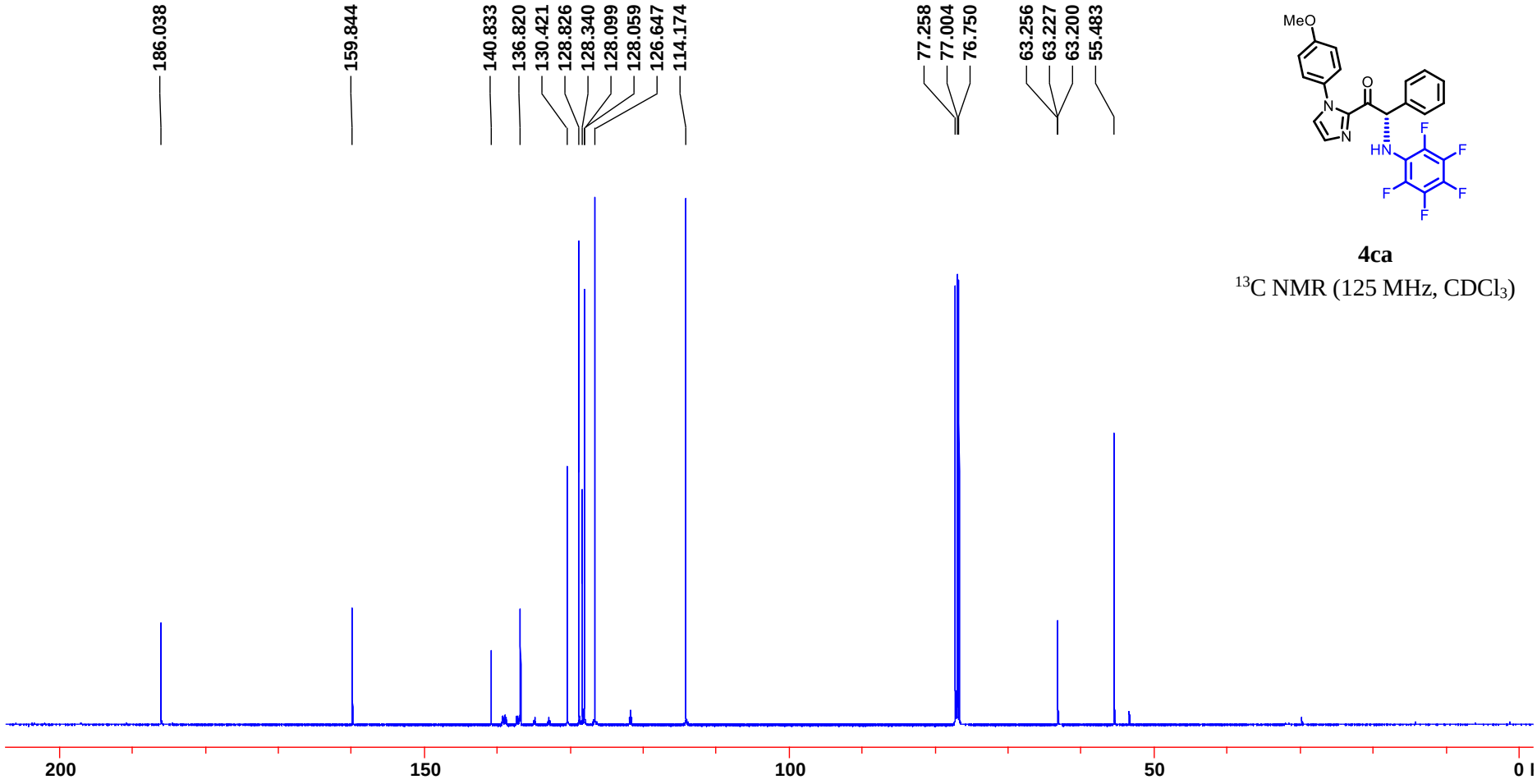
4ba

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



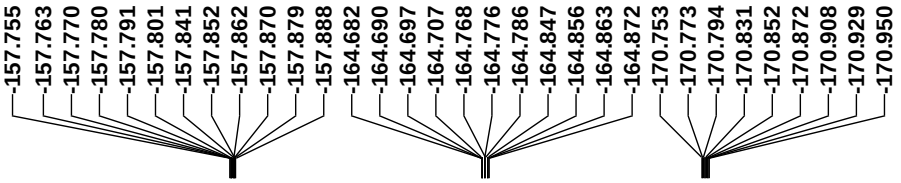
4ca

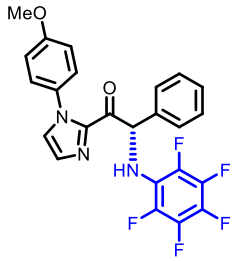
^{1}H NMR (500 MHz, $CDCl_3$)



4ca

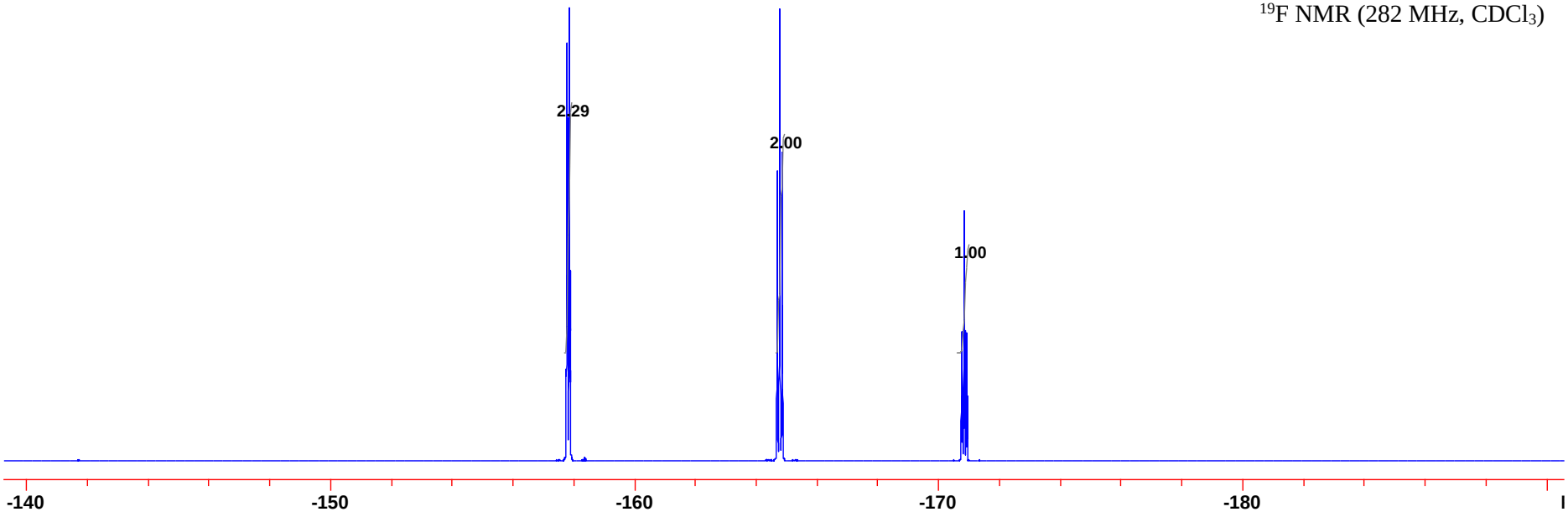
^{13}C NMR (125 MHz, $CDCl_3$)

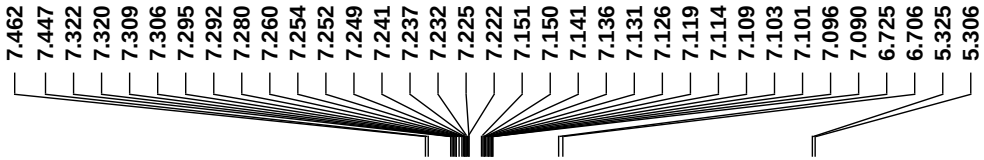


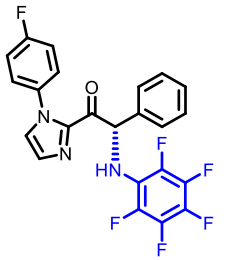


4ca

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

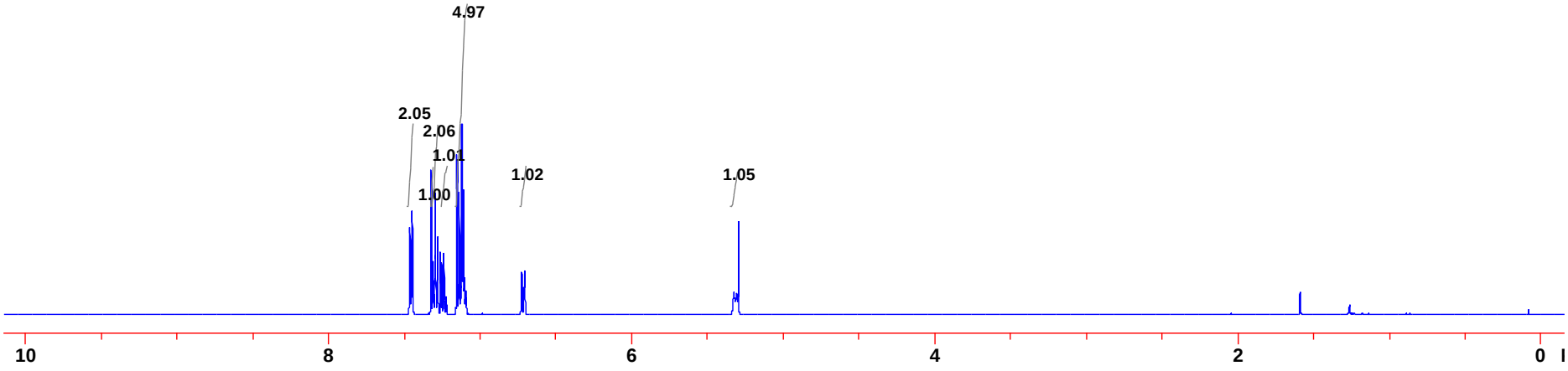


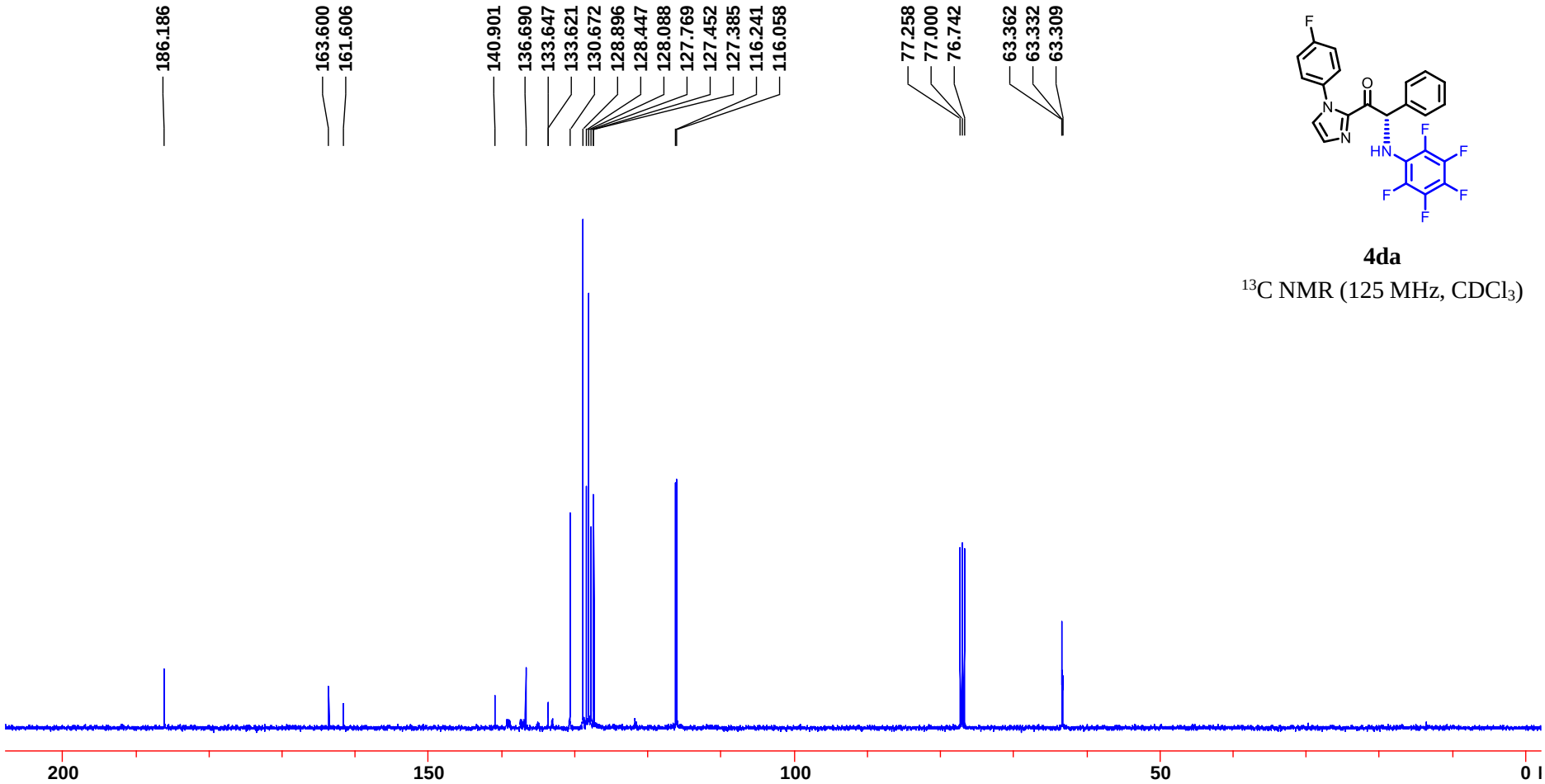




4da

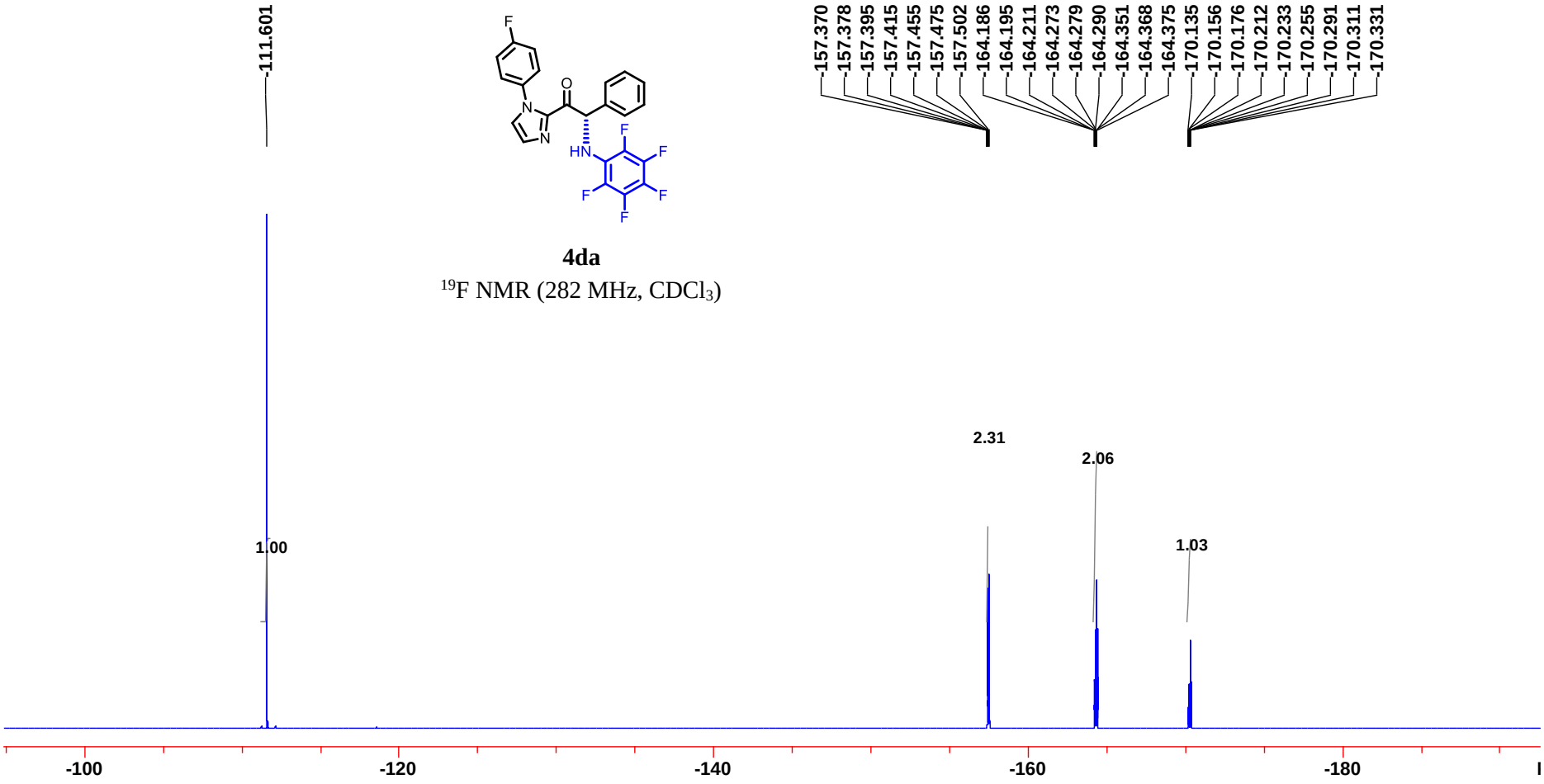
^{1}H NMR (500 MHz, $CDCl_3$)





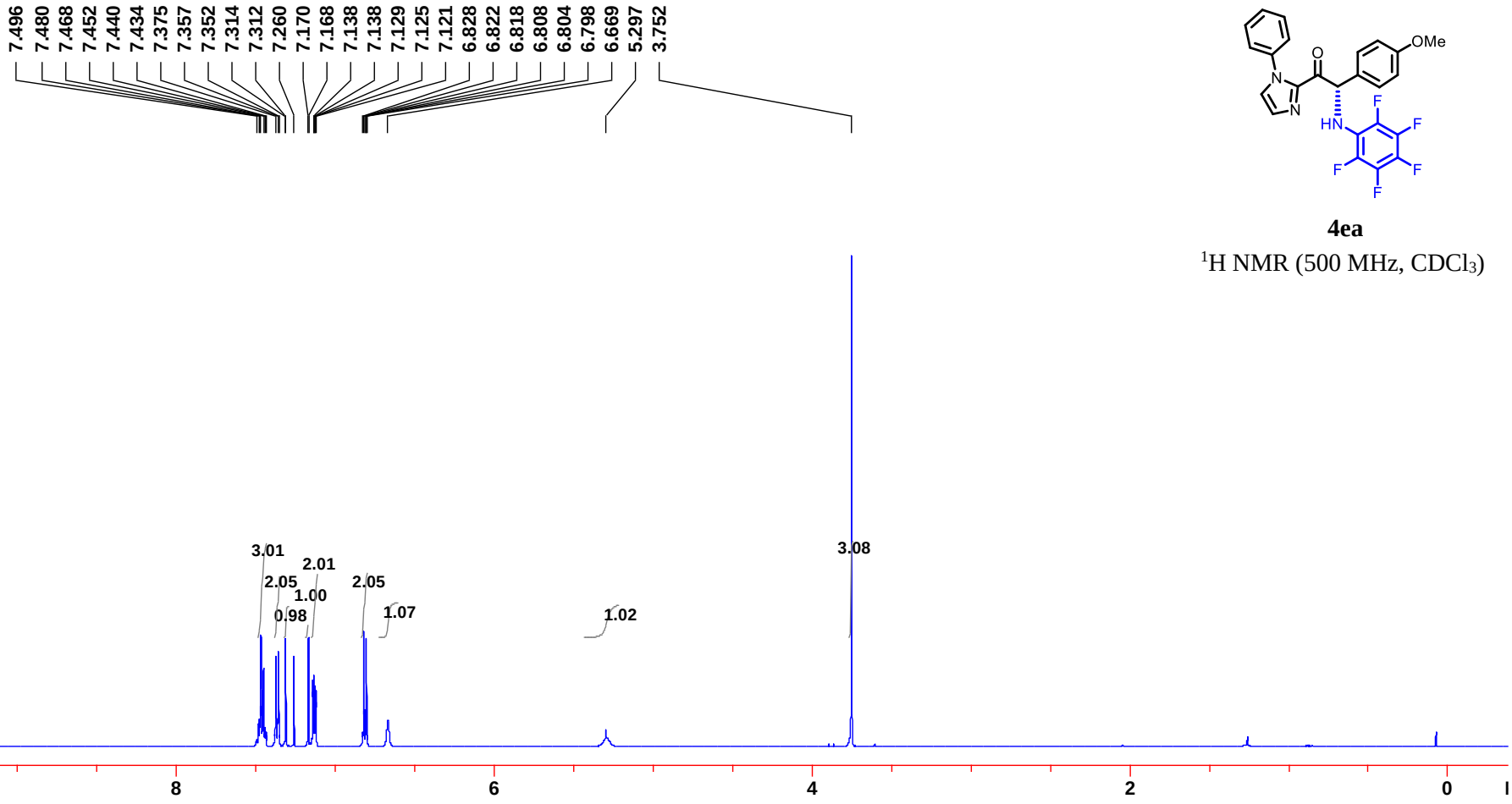
4da

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



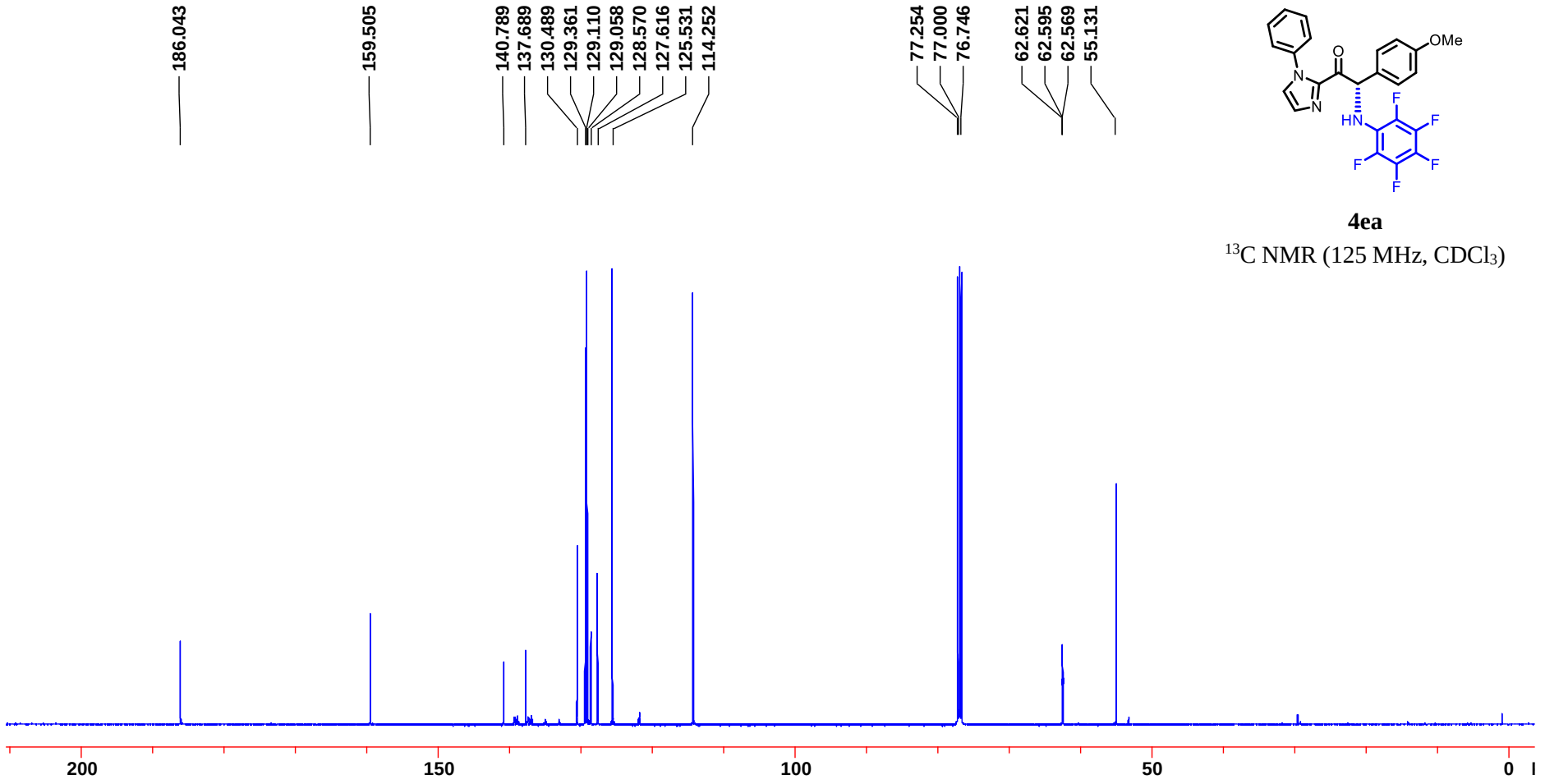
4da

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



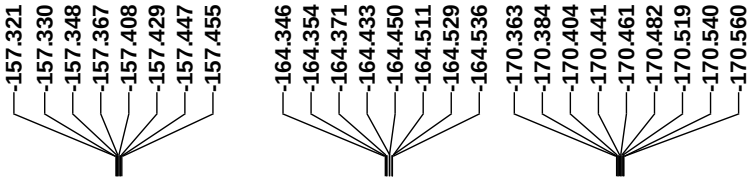
4ea

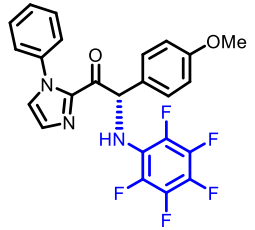
^{1}H NMR (500 MHz, $CDCl_3$)



4ea

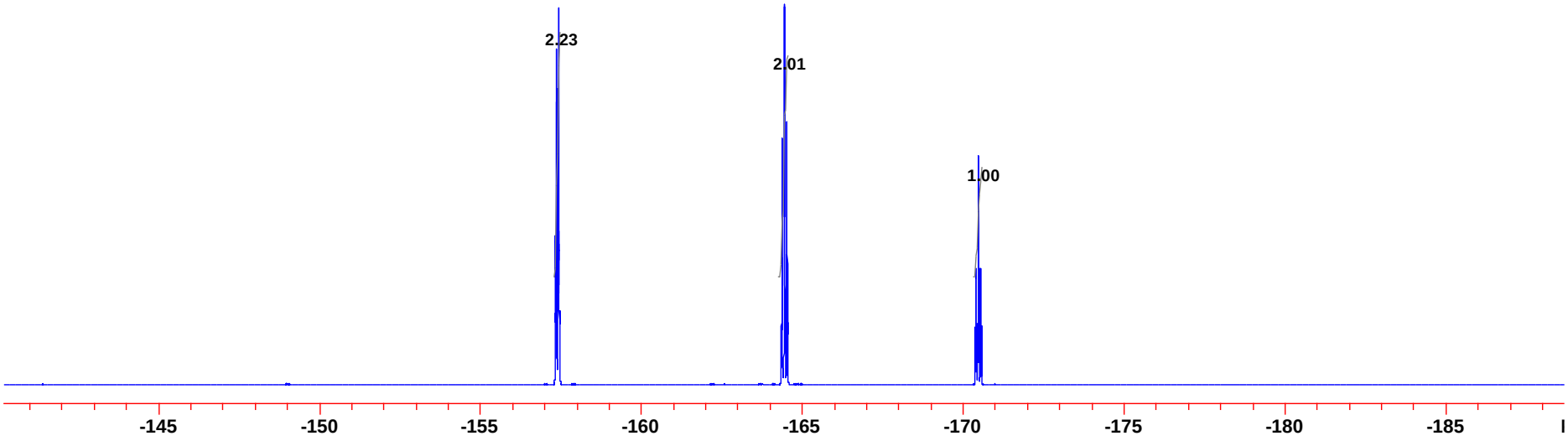
^{13}C NMR (125 MHz, $CDCl_3$)

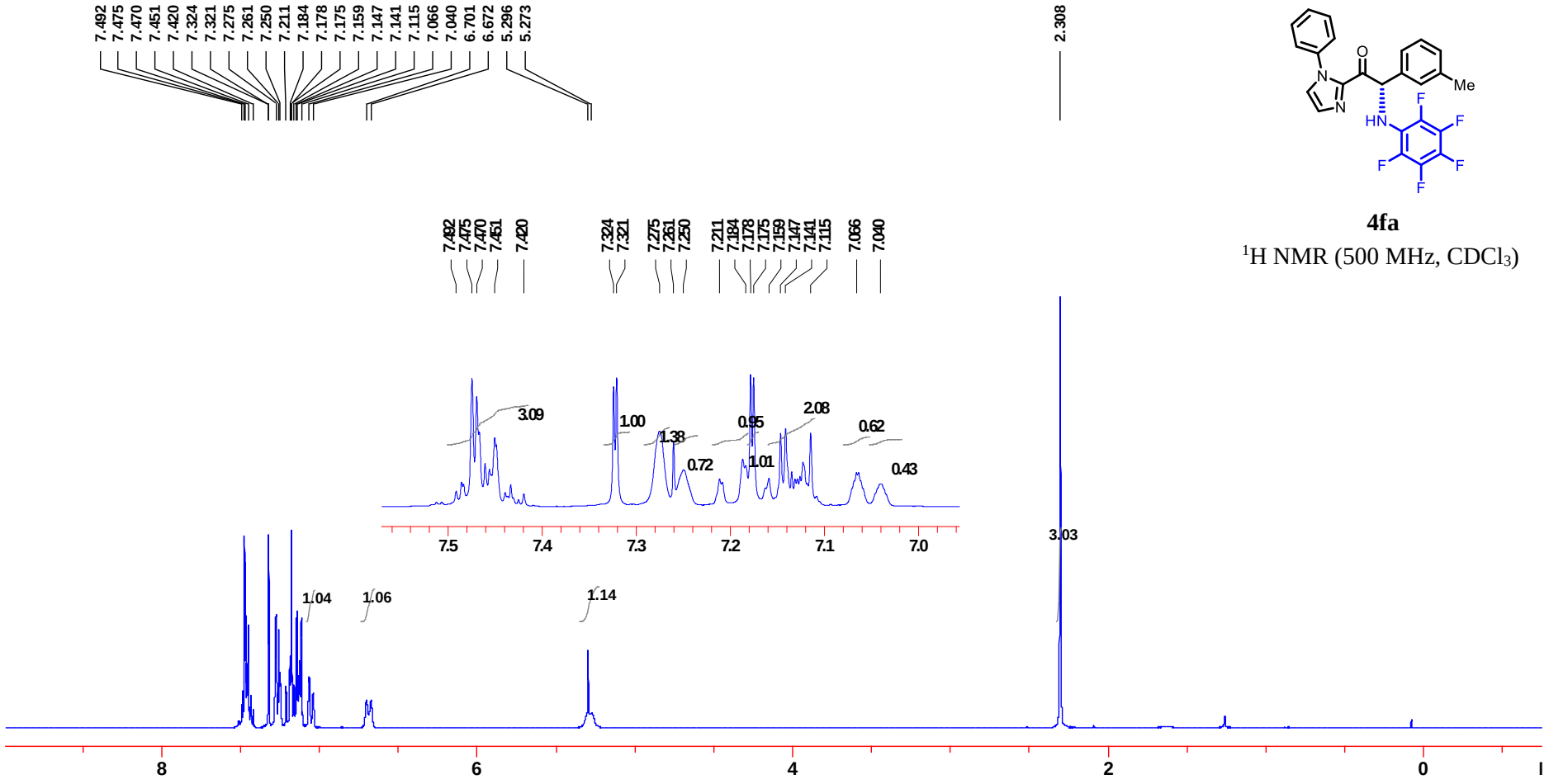




4ea

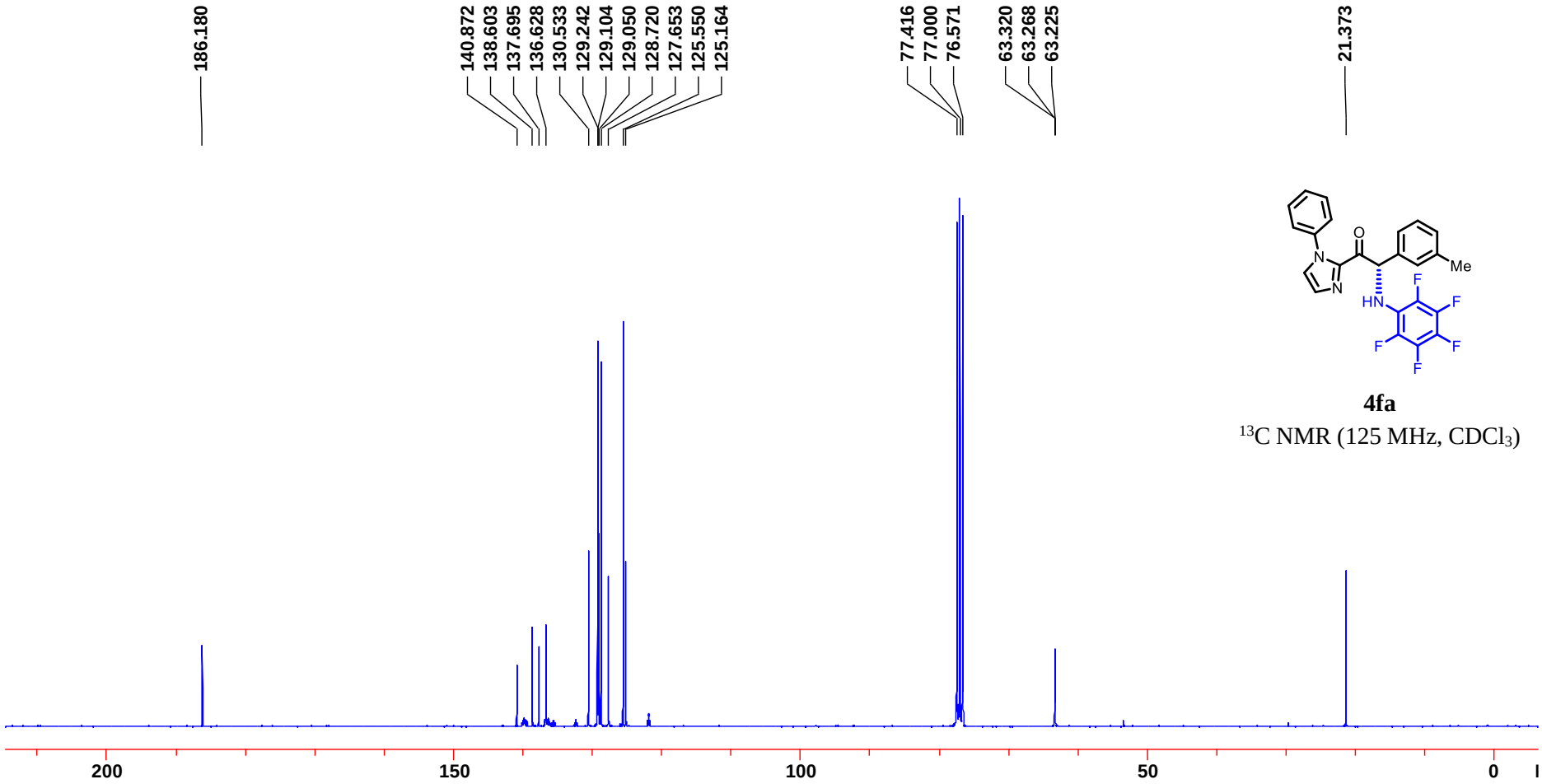
^{19}F NMR (282 MHz, $CDCl_3$)





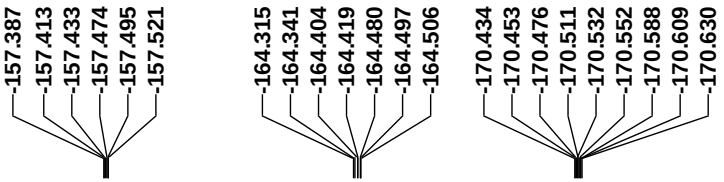
4fa

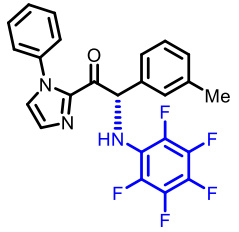
^{1}H NMR (500 MHz, $CDCl_3$)



4fa

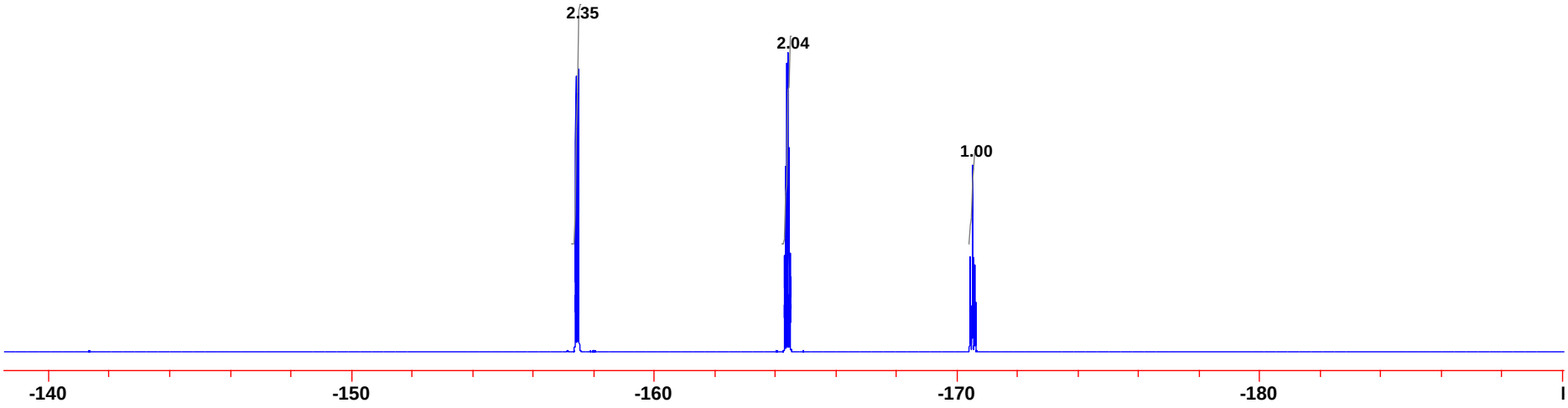
^{13}C NMR (125 MHz, $CDCl_3$)

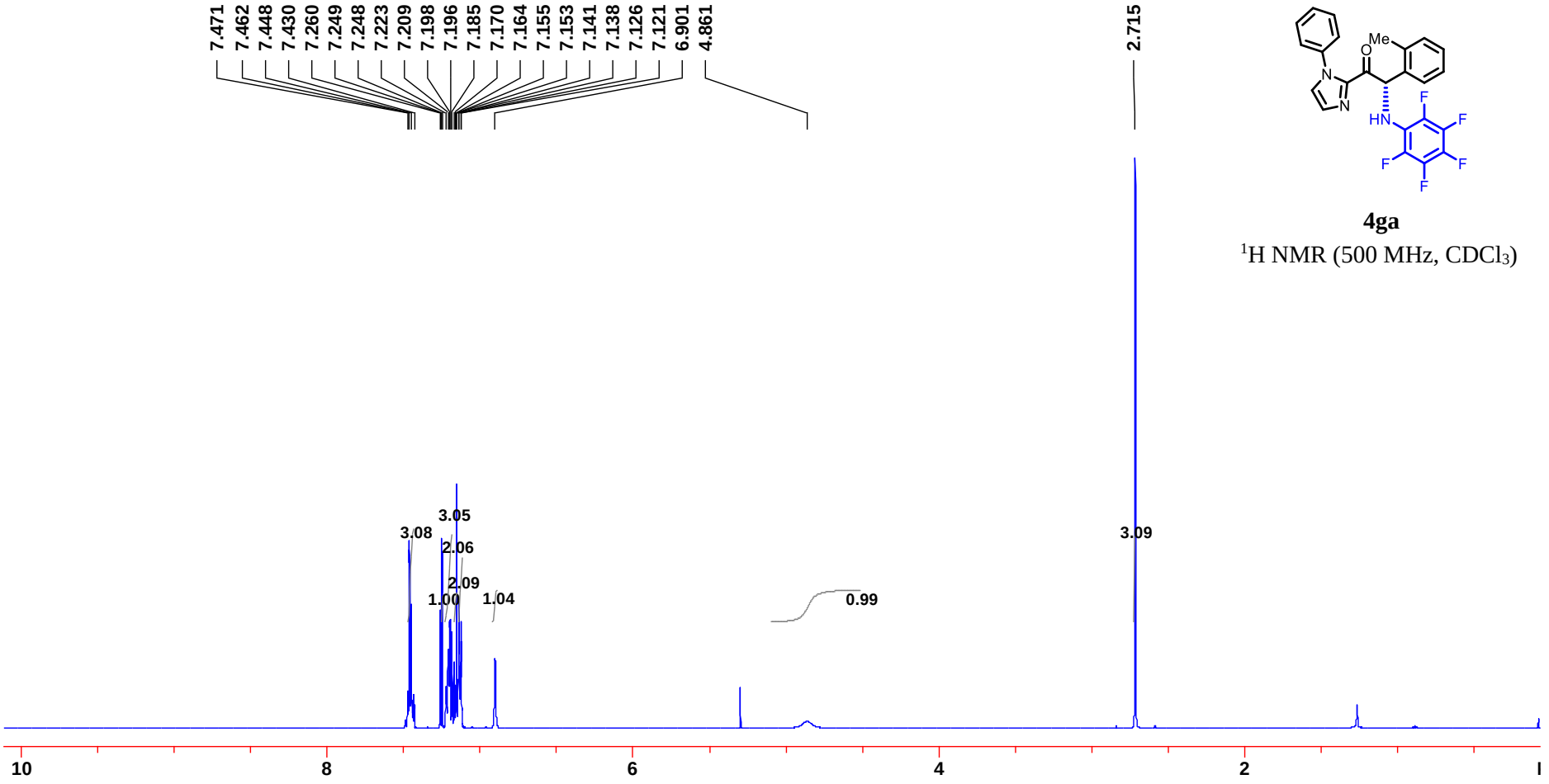




4fa

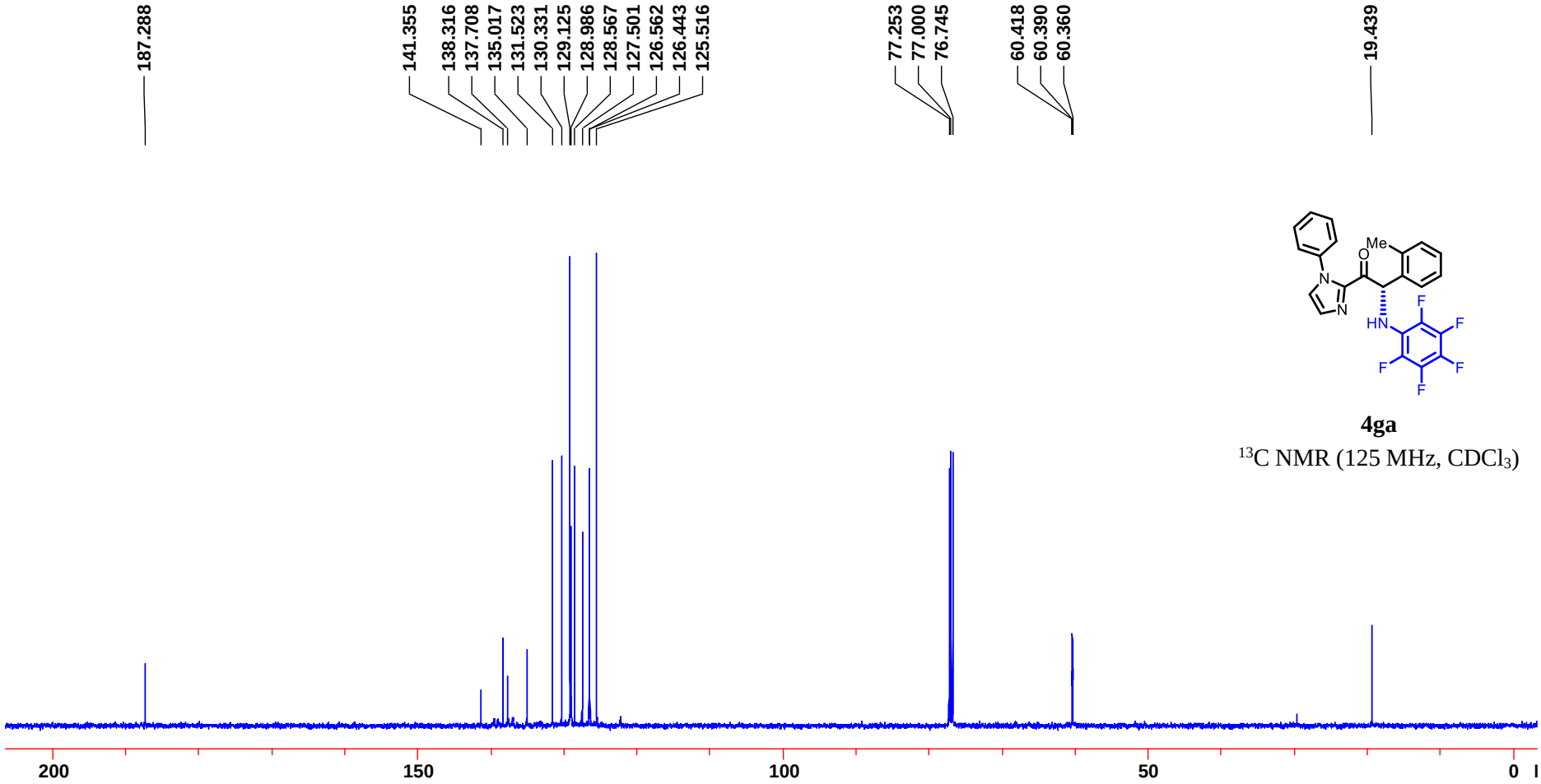
^{19}F NMR (282 MHz, $CDCl_3$)





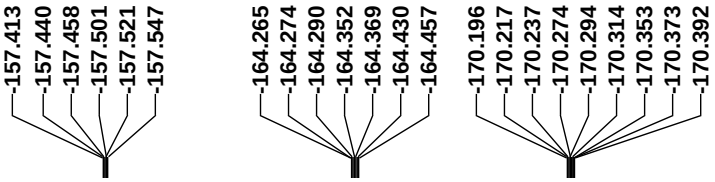
4ga

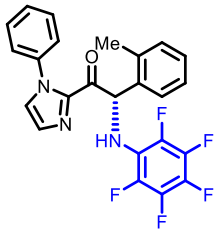
^{1}H NMR (500 MHz, $CDCl_3$)



4ga

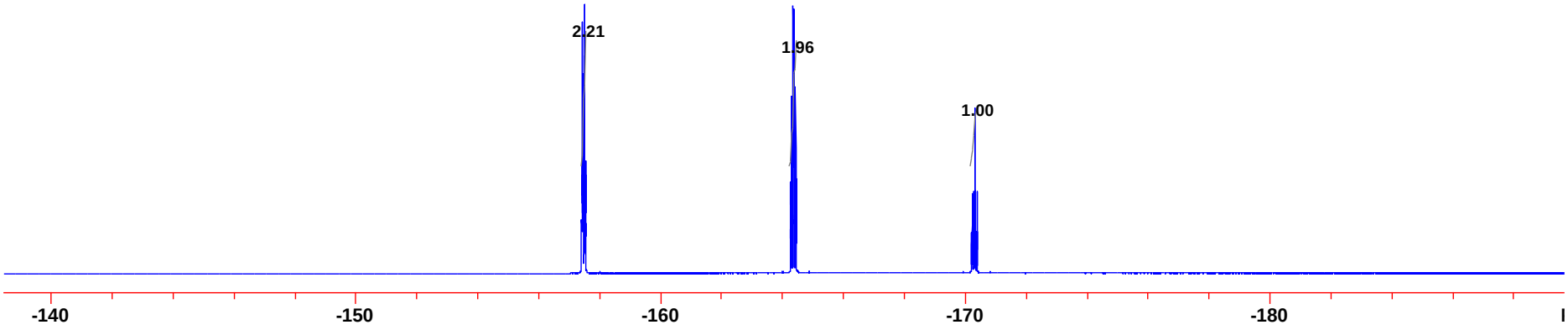
^{13}C NMR (125 MHz, $CDCl_3$)

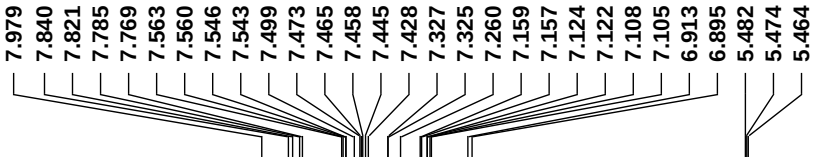


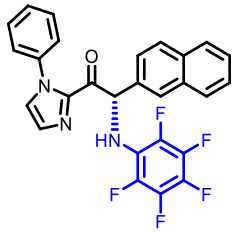


4ga

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

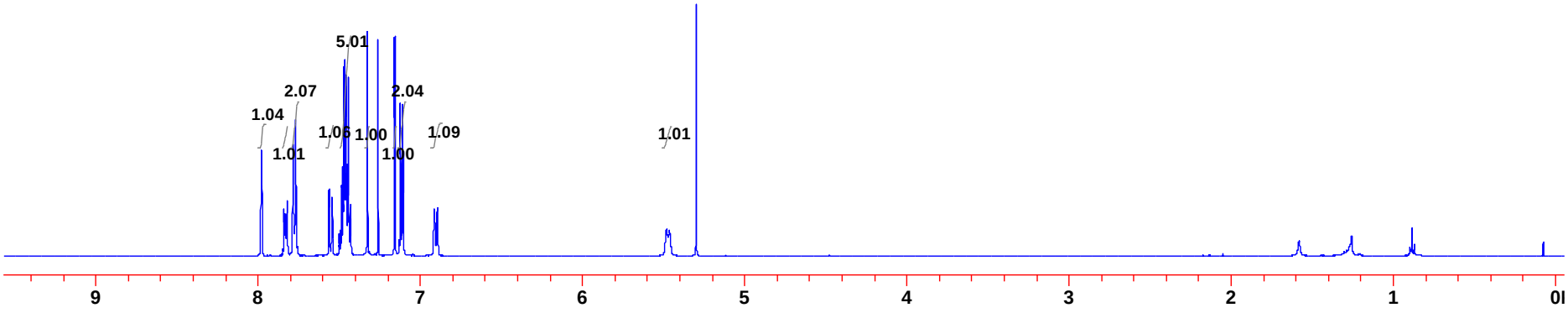


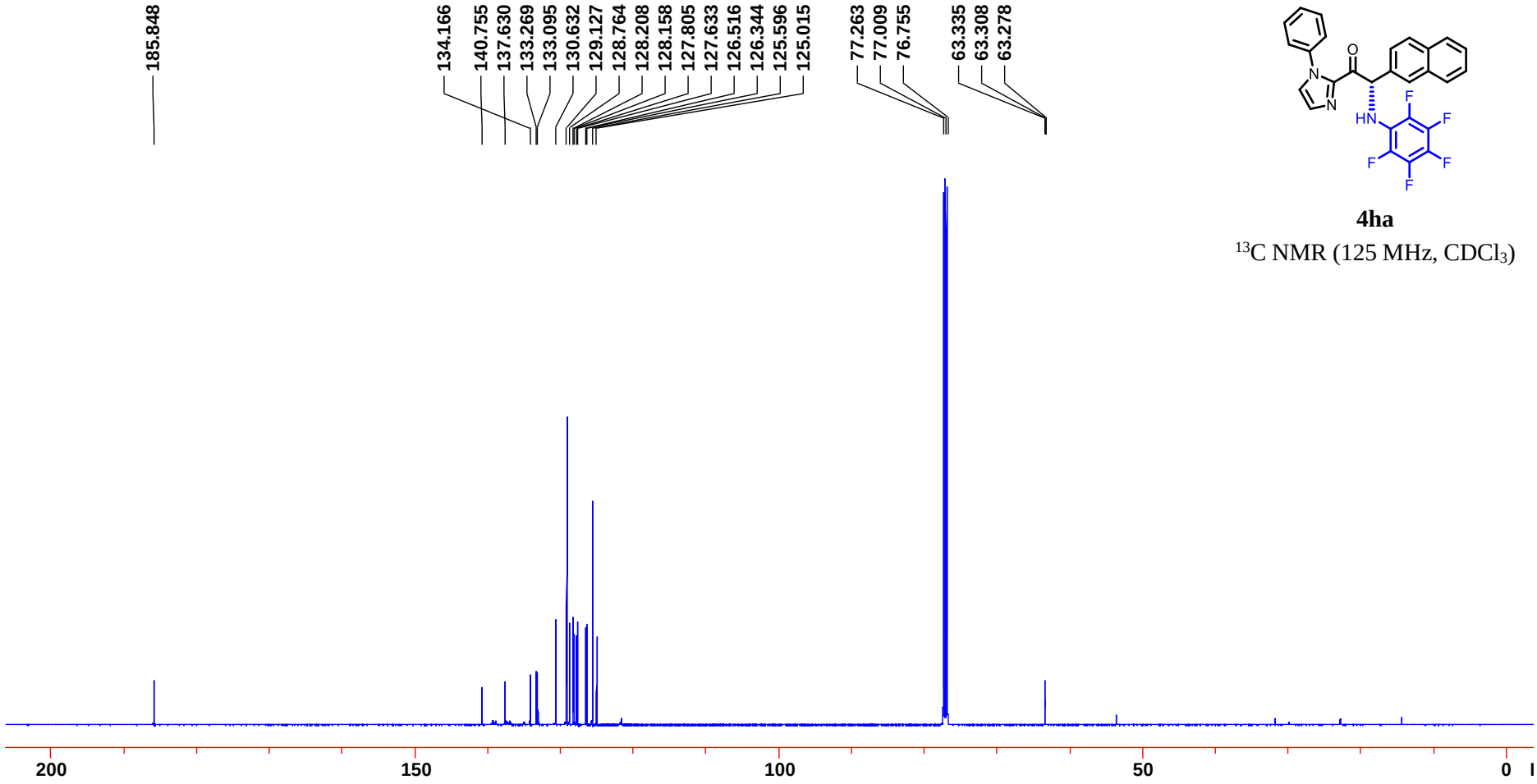




4ha

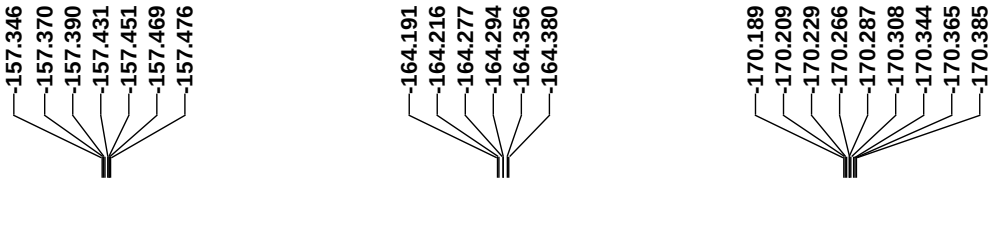
^{1}H NMR (500 MHz, $CDCl_3$)





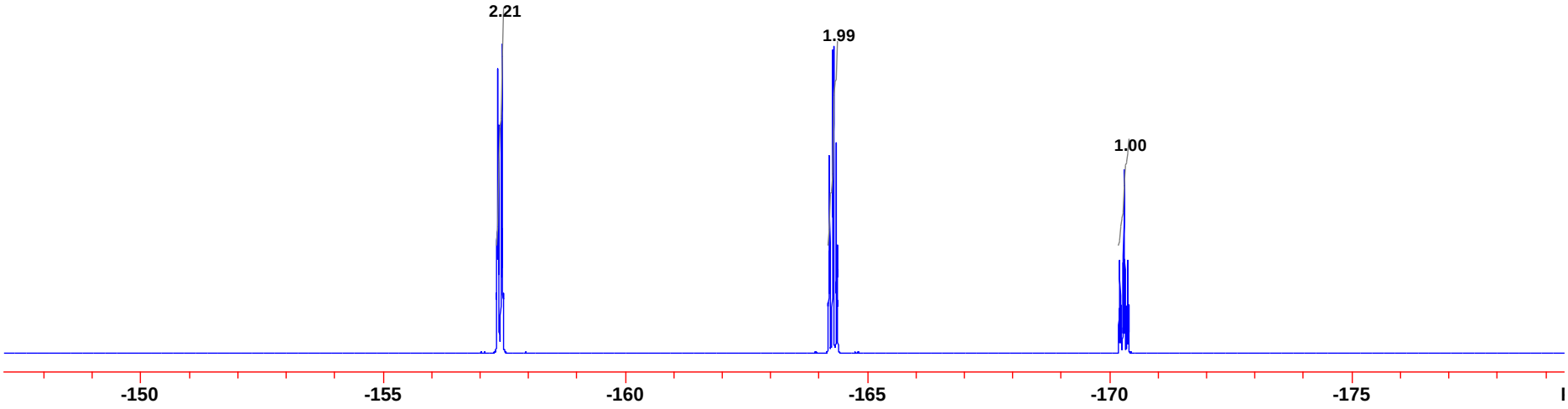
4ha

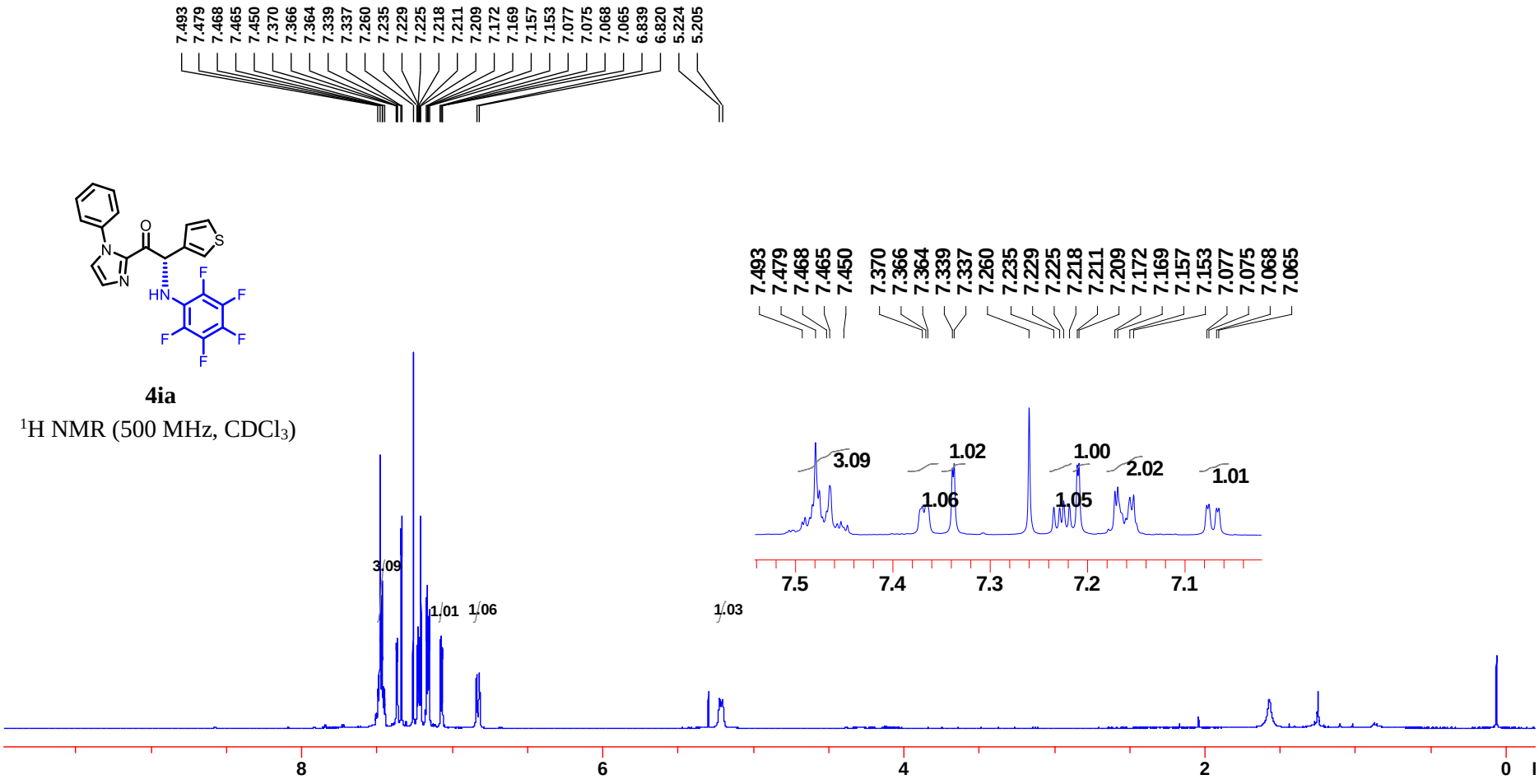
^{13}C NMR (125 MHz, $CDCl_3$)

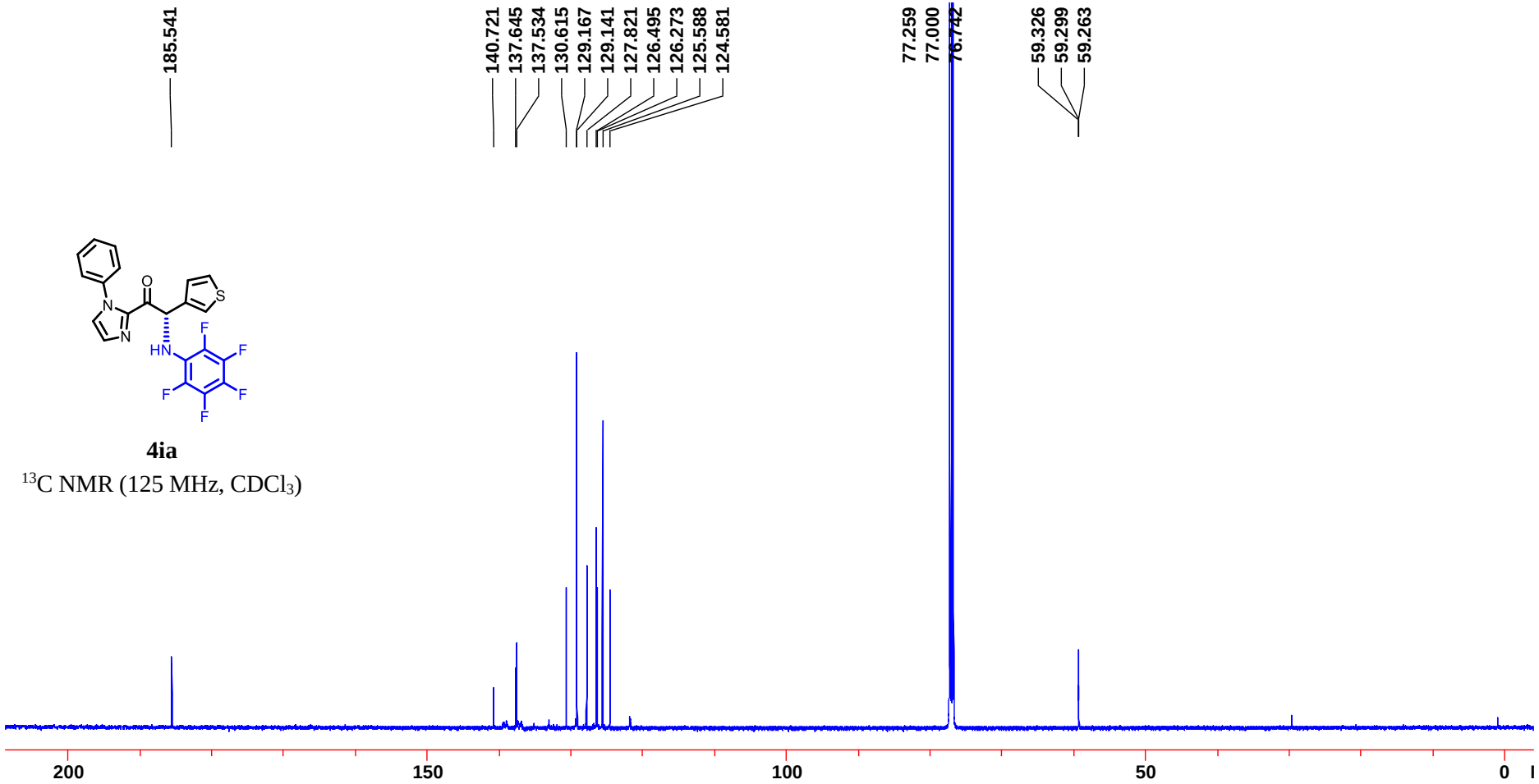


4ha

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

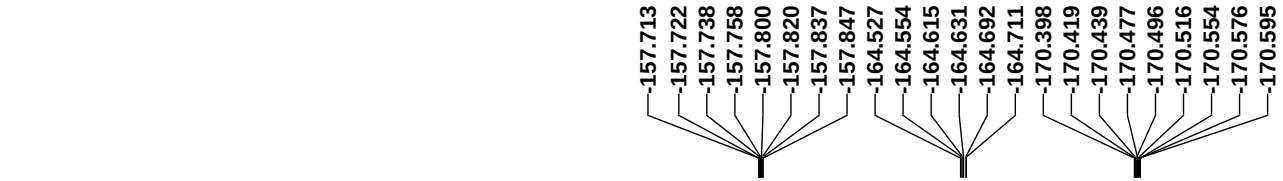


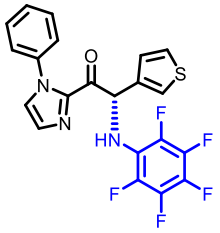

7.493
7.479
7.468
7.465
7.450
7.370
7.366
7.364
7.339
7.337
7.260
7.235
7.229
7.225
7.218
7.211
7.209
7.172
7.169
7.157
7.153
7.077
7.075
7.068
7.065
6.839
6.820
5.224
5.205
O
S
N
N
HN
F
F
F
F
F
4ia
1H NMR (500 MHz, CDCl3)
3.09
1.02
1.00
2.02
1.01
1.06
1.05
7.5
7.4
7.3
7.2
7.1
3.09
1.01
1.06
1.03
8
6
4
2
0



4ia

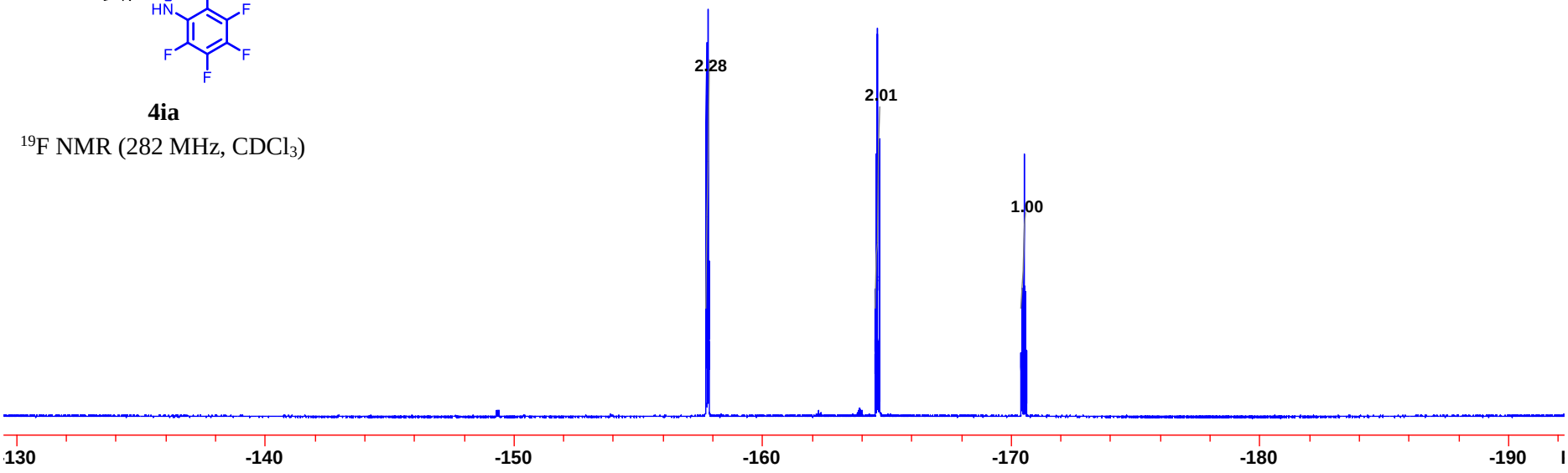
^{13}C NMR (125 MHz, $CDCl_3$)

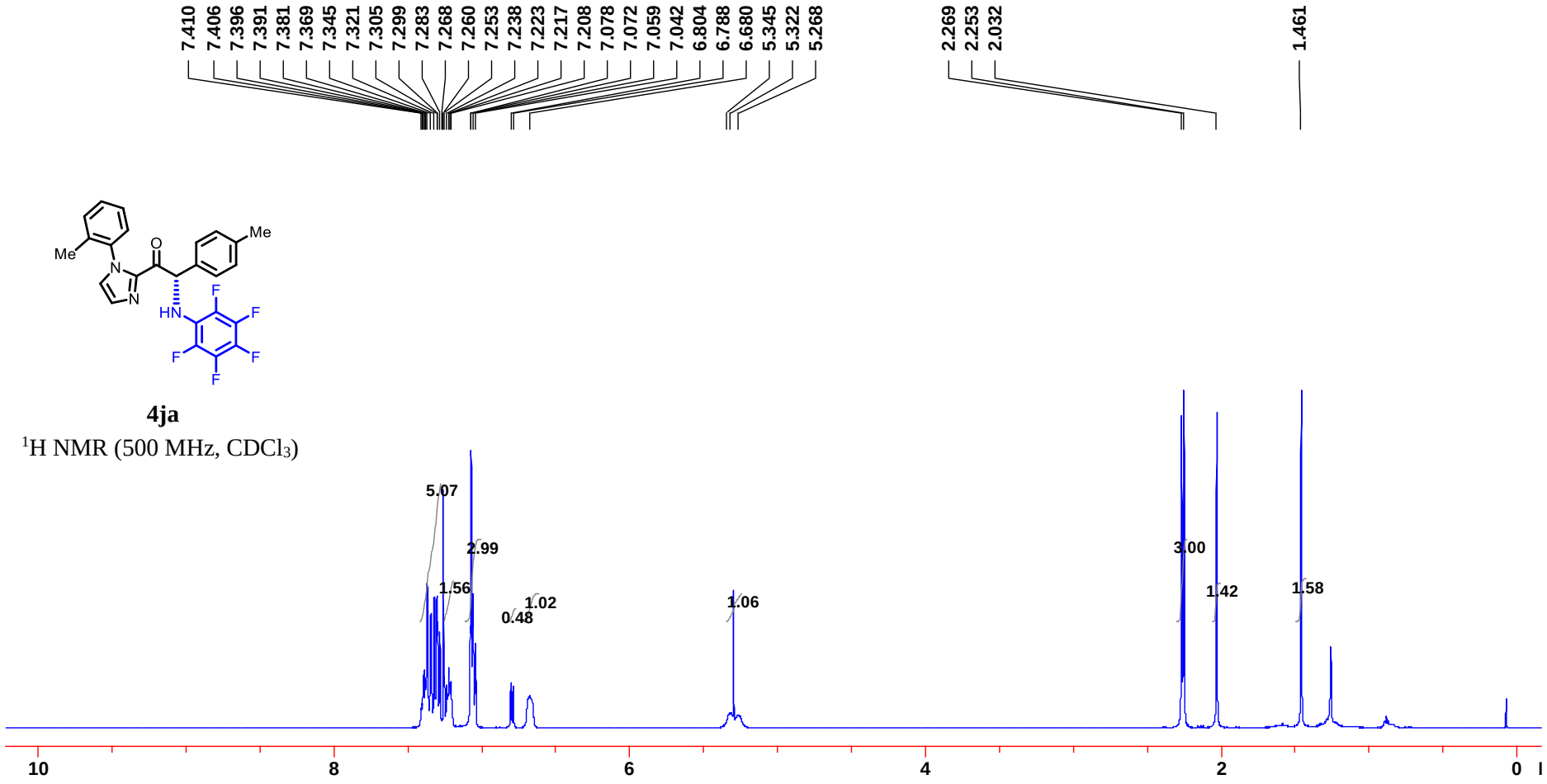


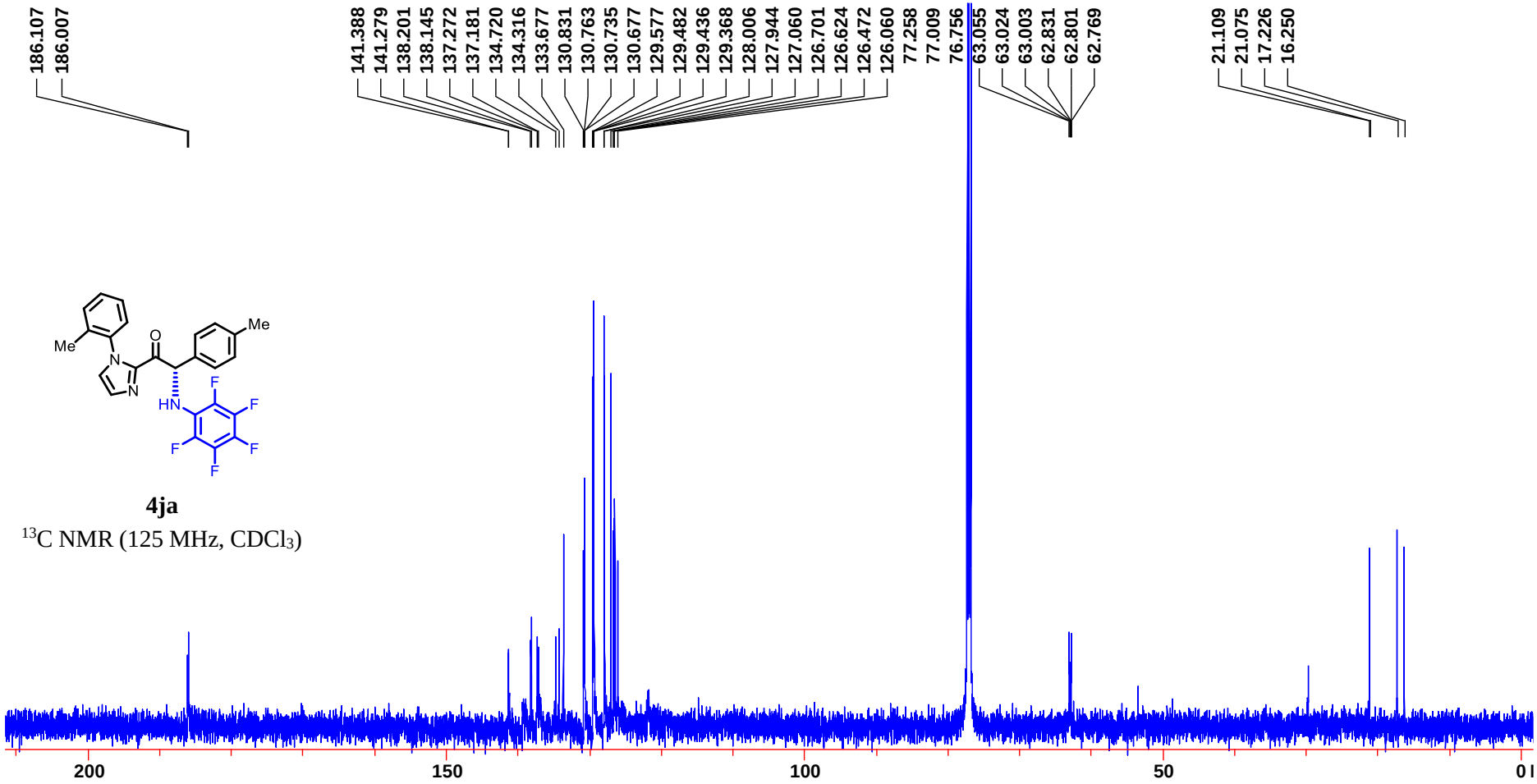


4ia

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

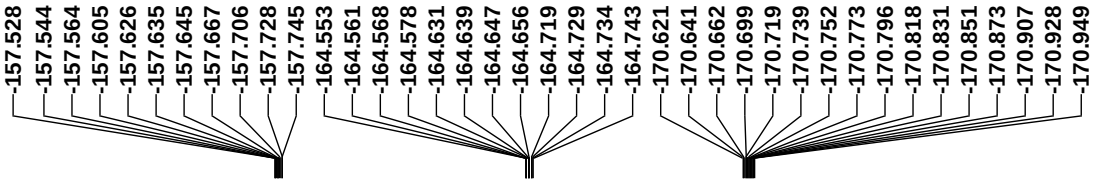


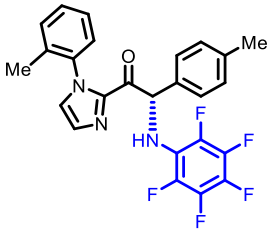

7.410
7.406
7.396
7.391
7.381
7.369
7.345
7.321
7.305
7.299
7.283
7.268
7.260
7.253
7.238
7.223
7.217
7.208
7.078
7.072
7.059
7.042
6.804
6.788
6.680
5.345
5.322
5.268
2.269
2.253
2.032
1.461
Me
Me
O
N
N
HN
F
F
F
F
F
4ja
1H NMR (500 MHz, CDCl3)
5.07
2.99
1.56
1.02
0.48
1.06
3.00
1.42
1.58
10
8
6
4
2
0



4ja

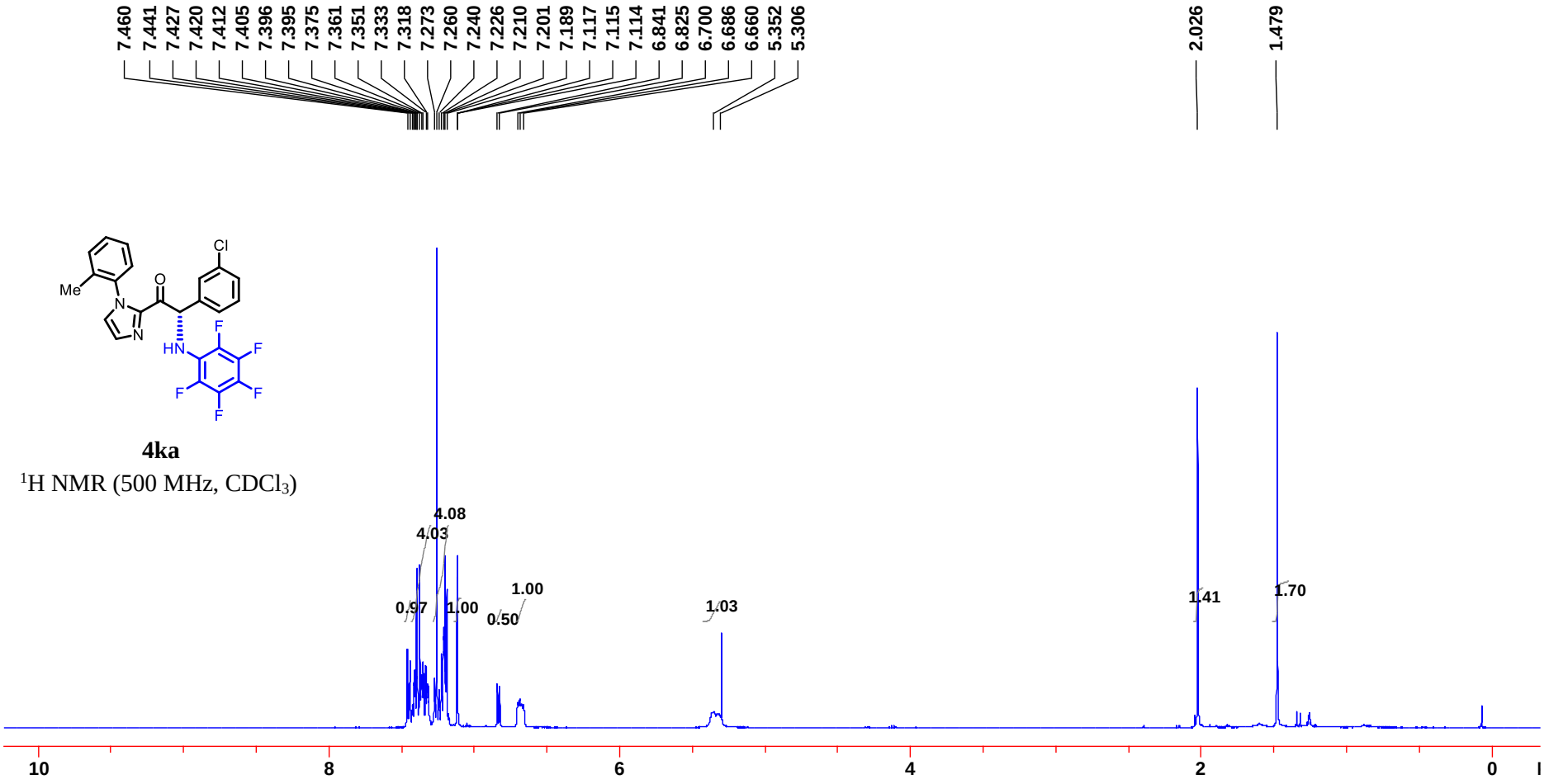
^{13}C NMR (125 MHz, $CDCl_3$)





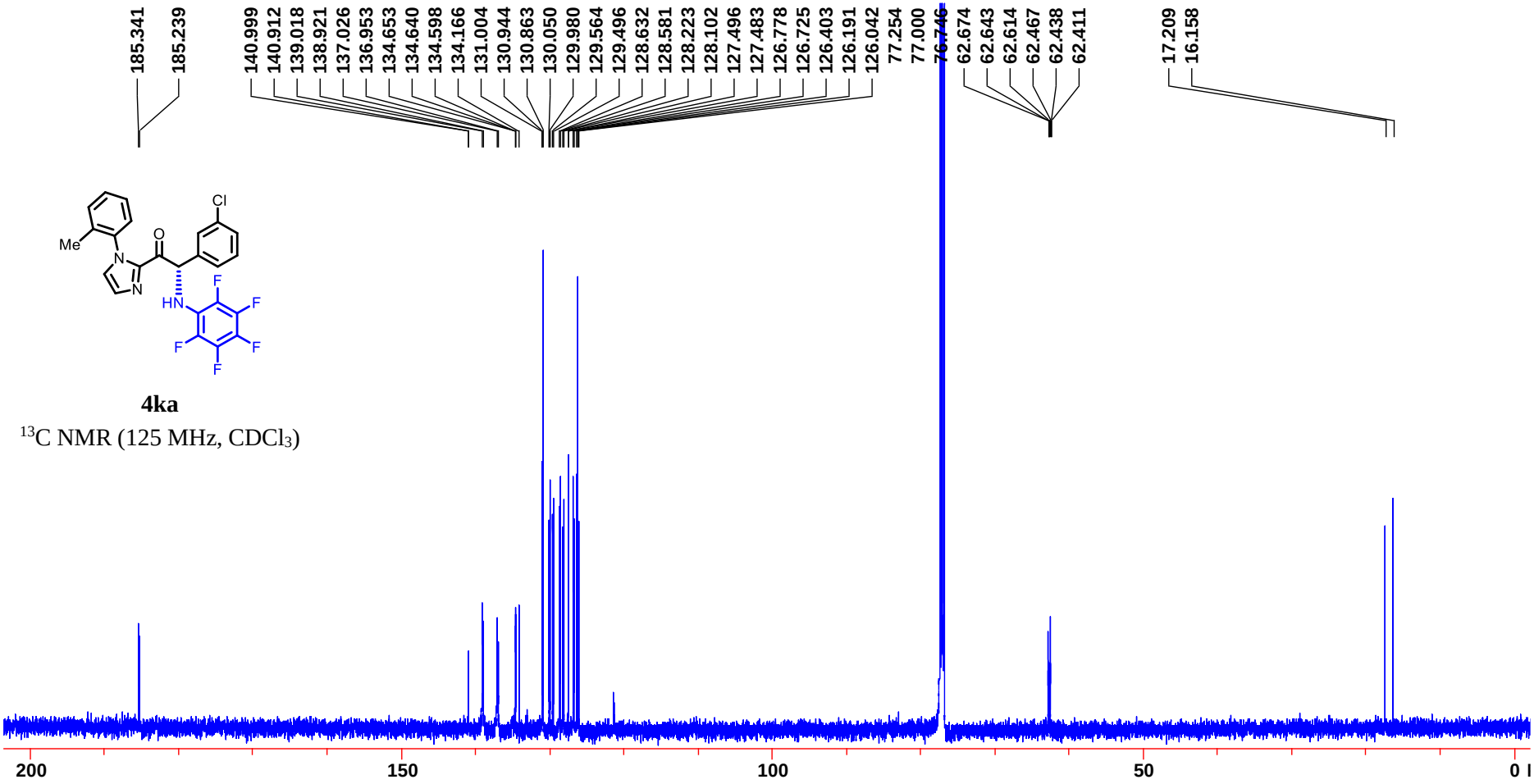
4ja

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



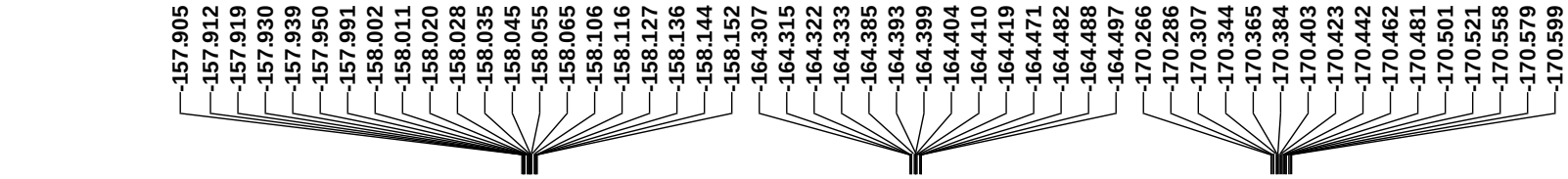
4ka

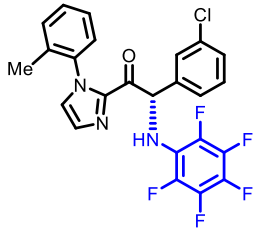
^{1}H NMR (500 MHz, $CDCl_3$)



4ka

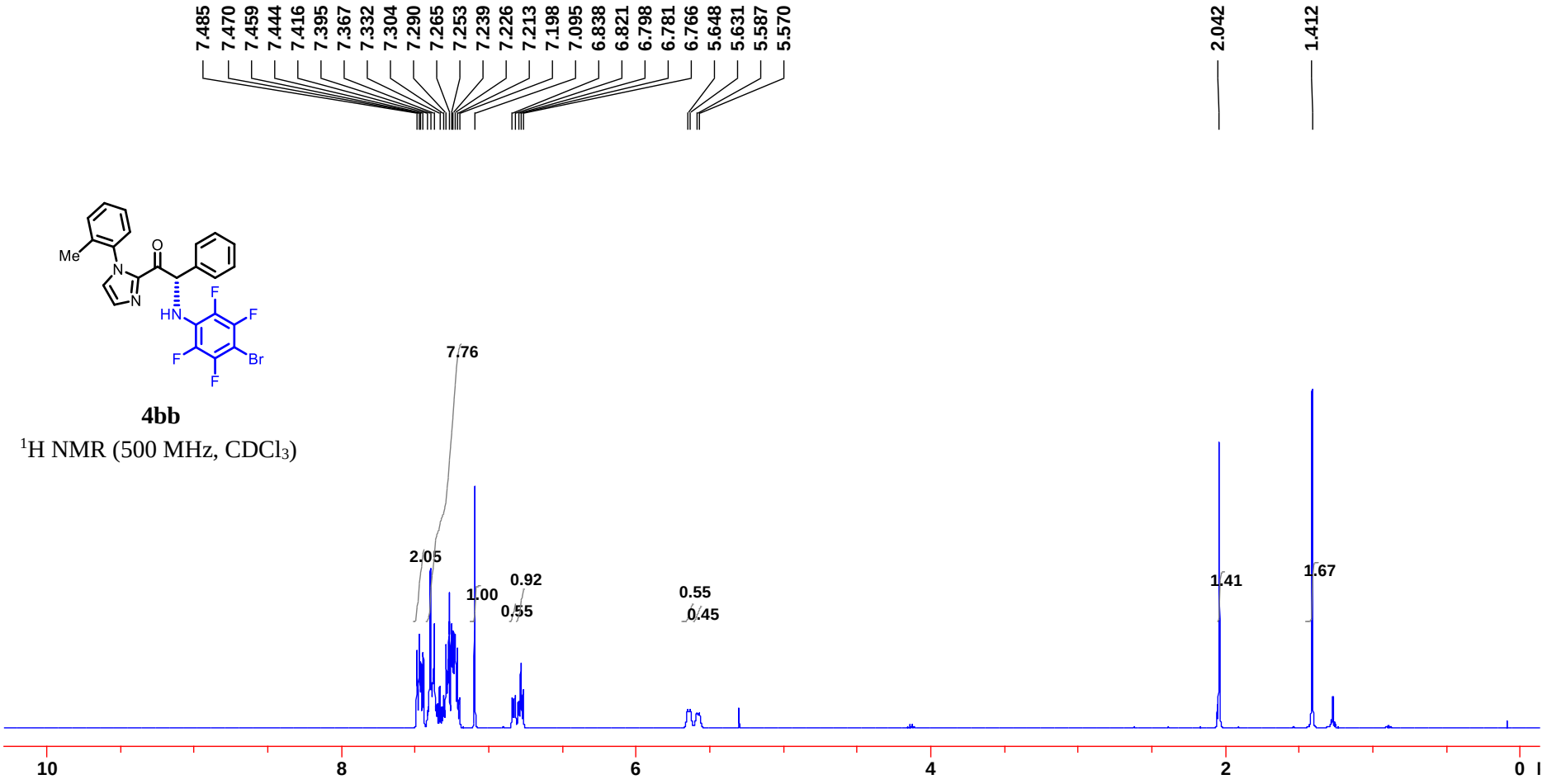
^{13}C NMR (125 MHz, $CDCl_3$)





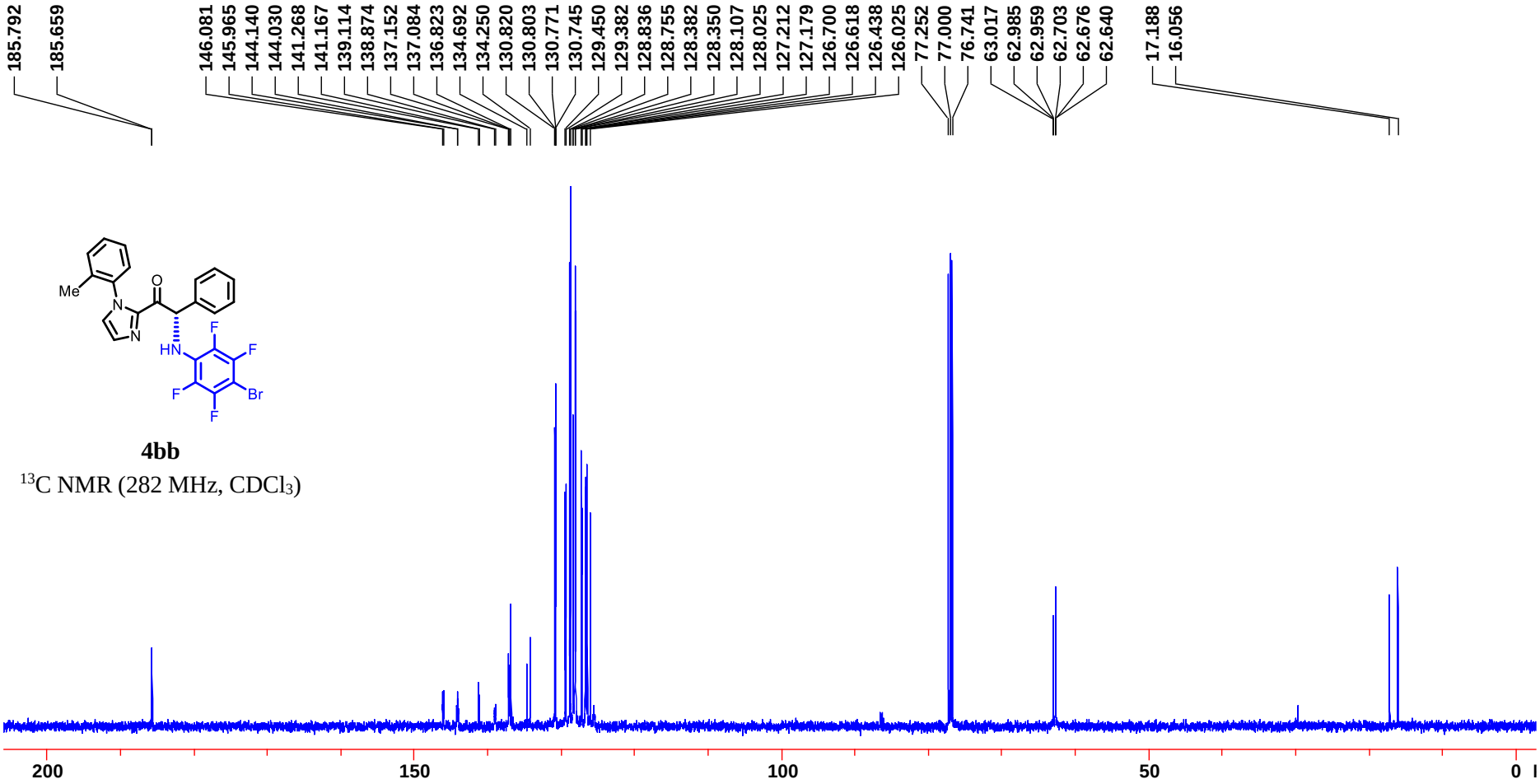
4ka

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



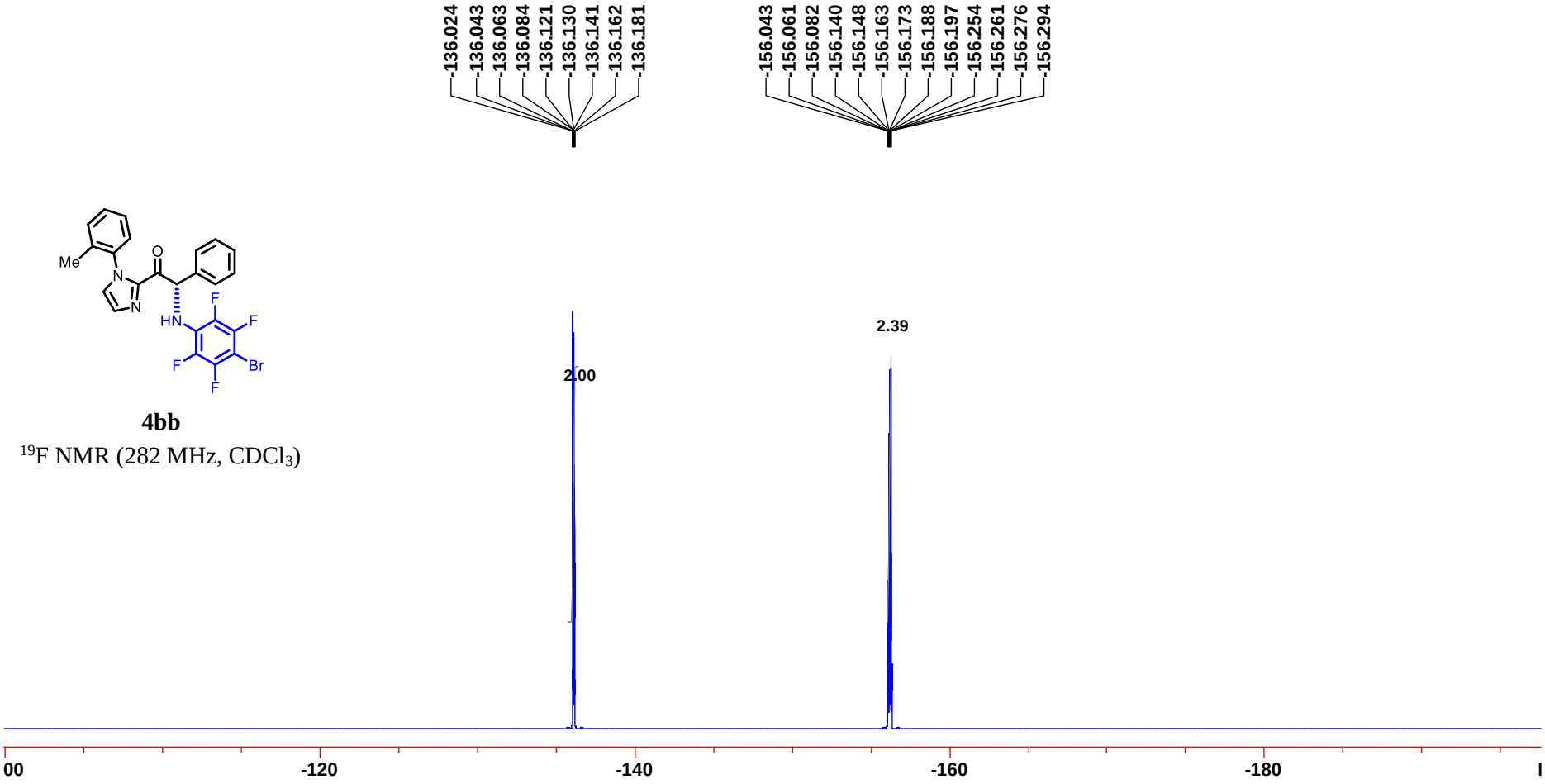
4bb

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



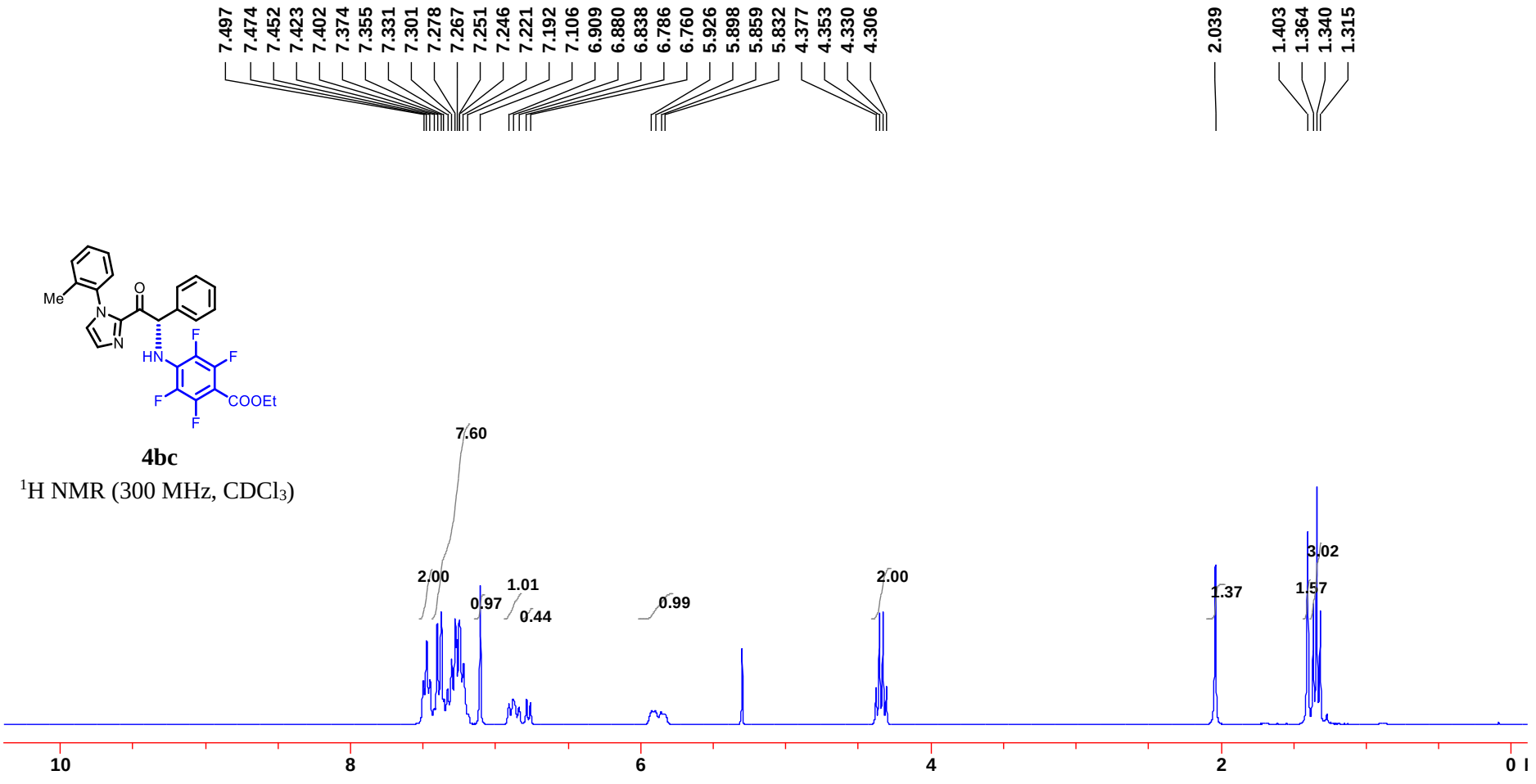
4bb

^{13}C NMR (282 MHz, $CDCl_3$)



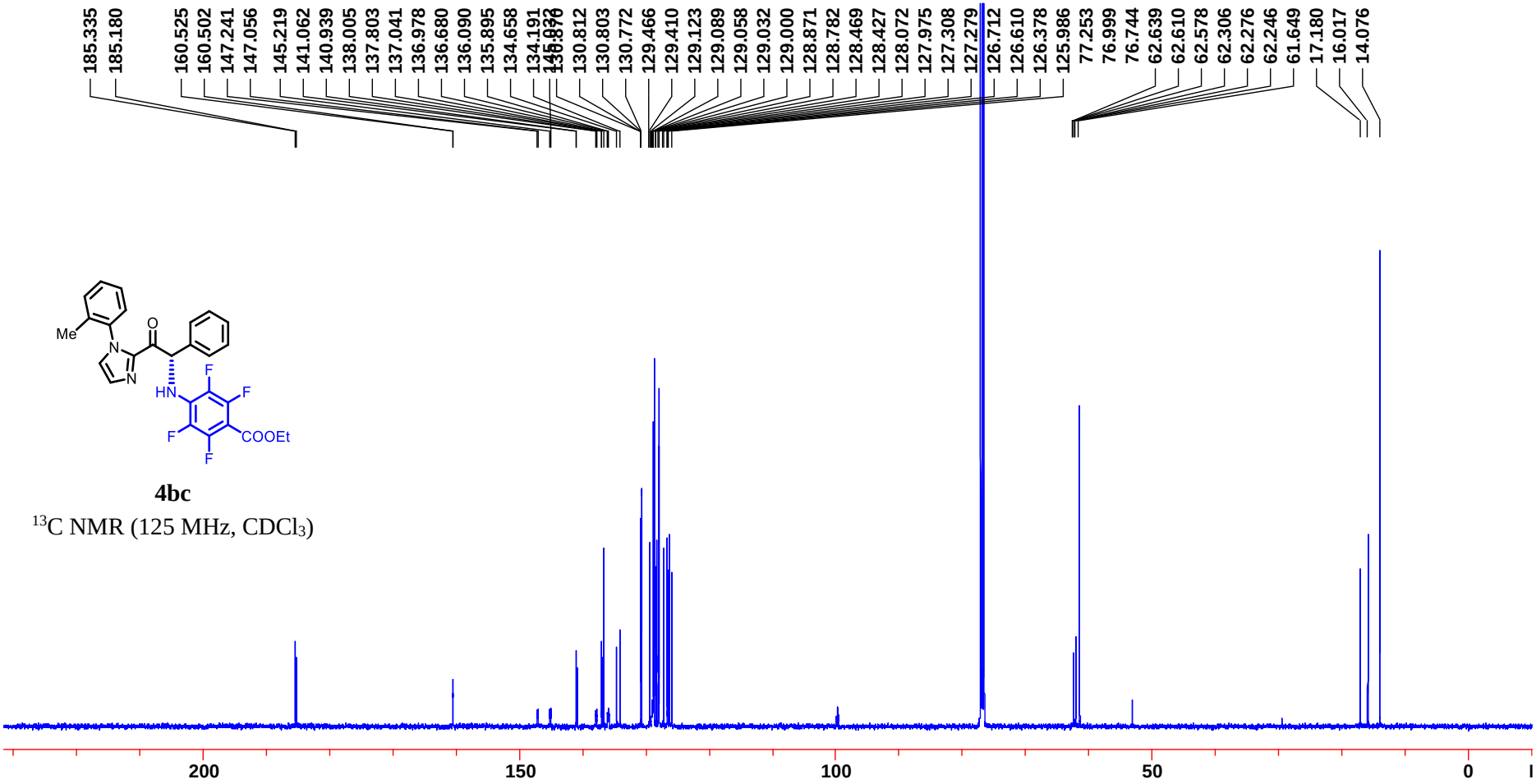
4bb

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



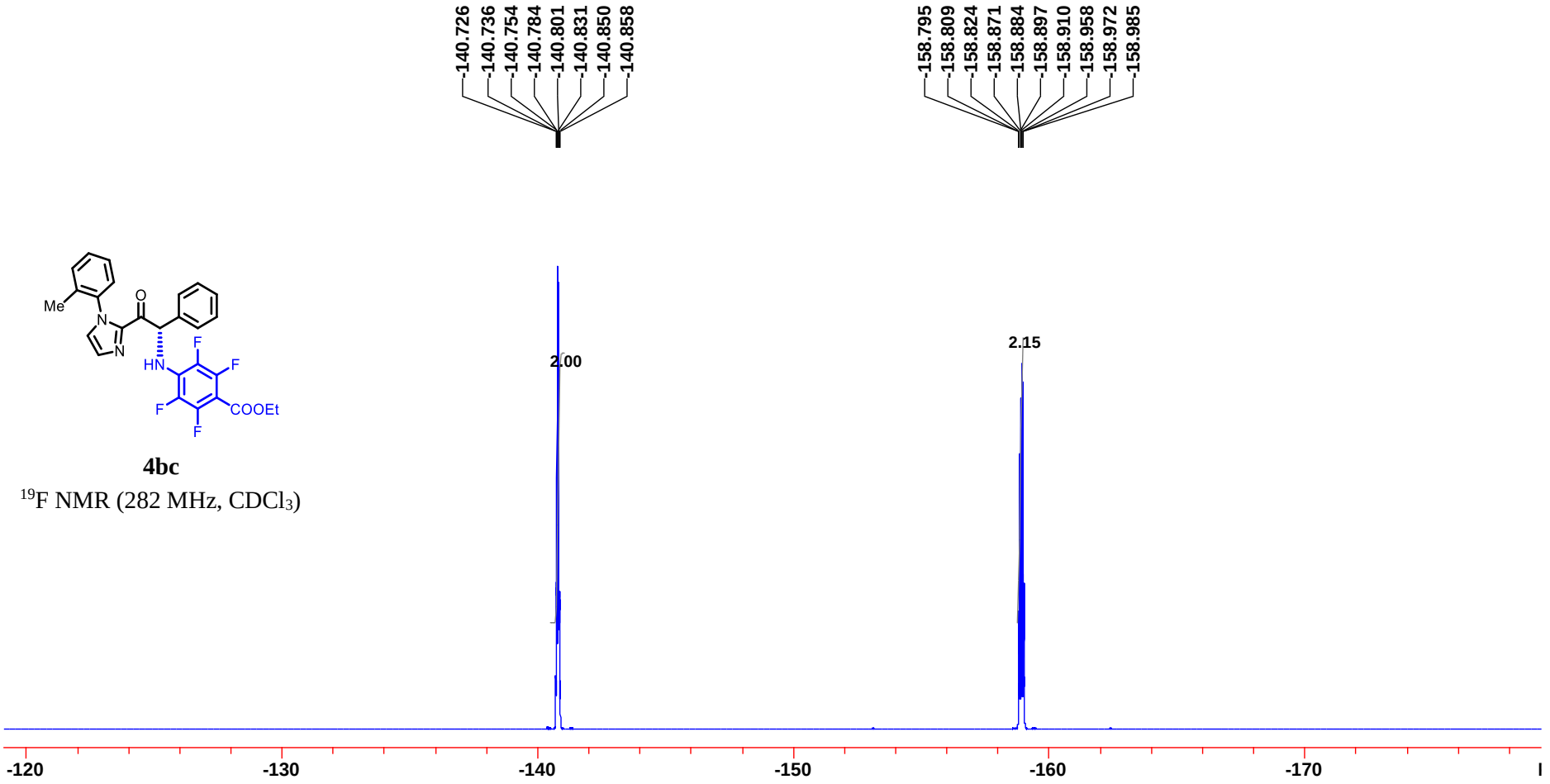
4bc

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



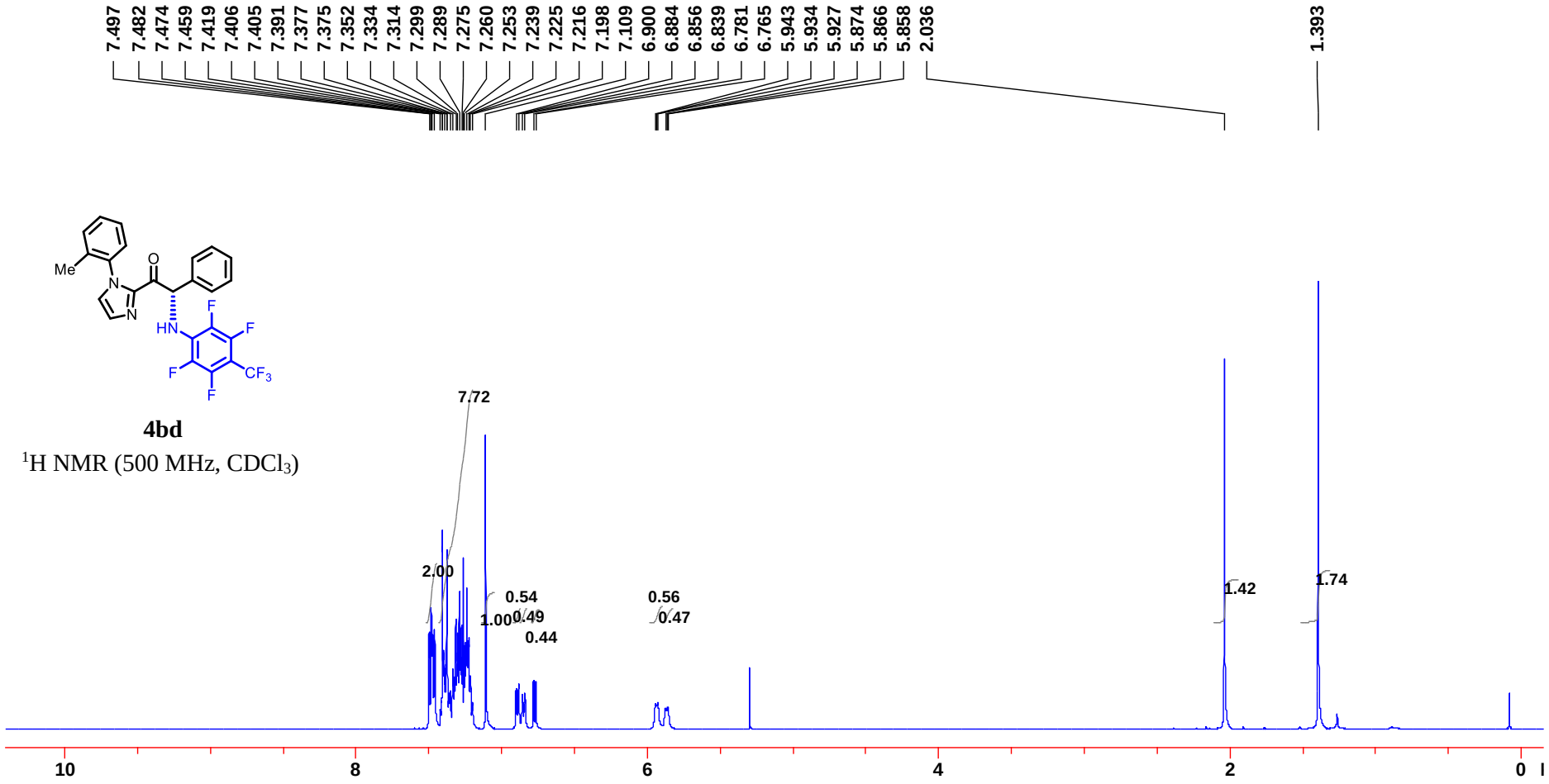
4bc

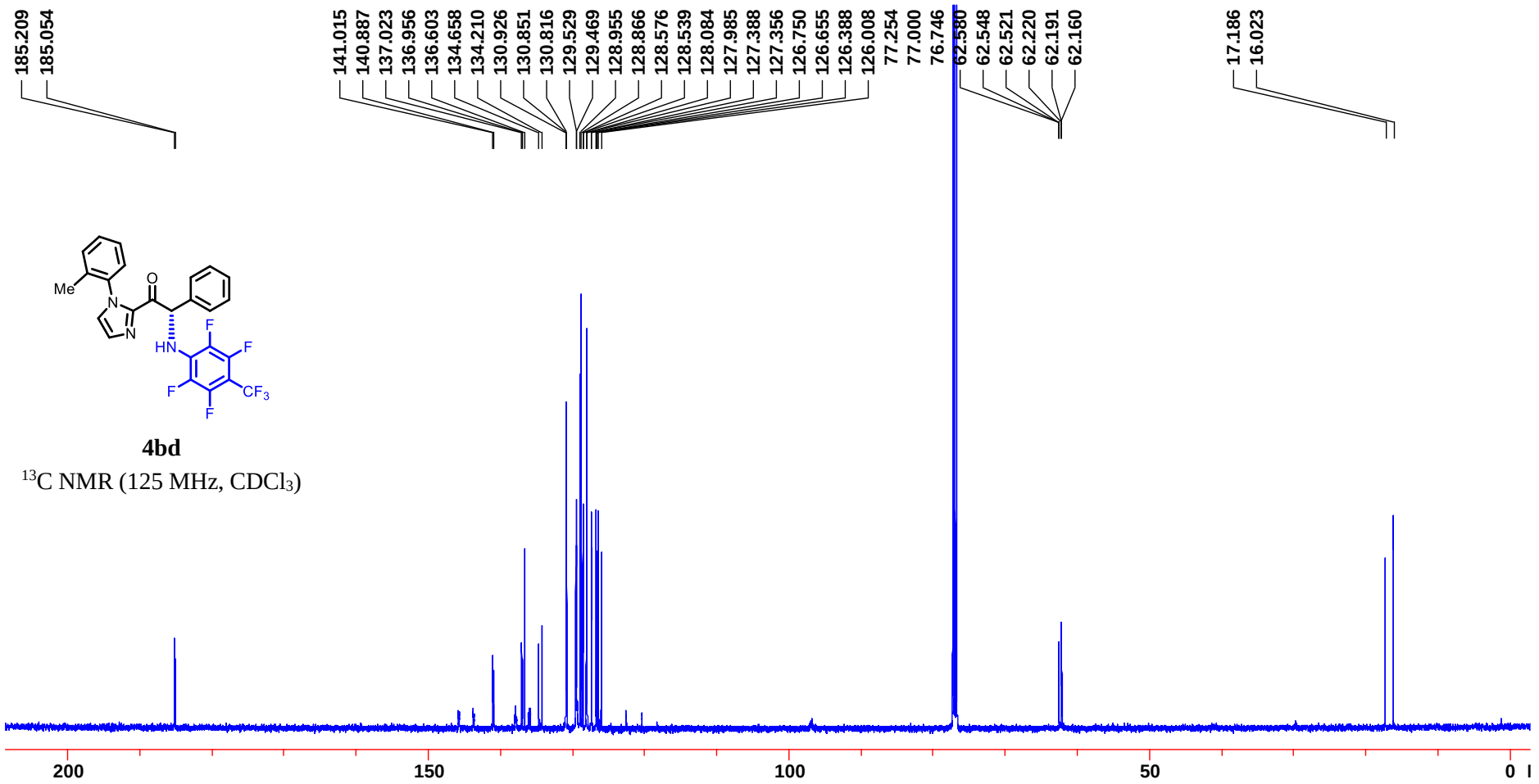
^{13}C NMR (125 MHz, $CDCl_3$)



4bc

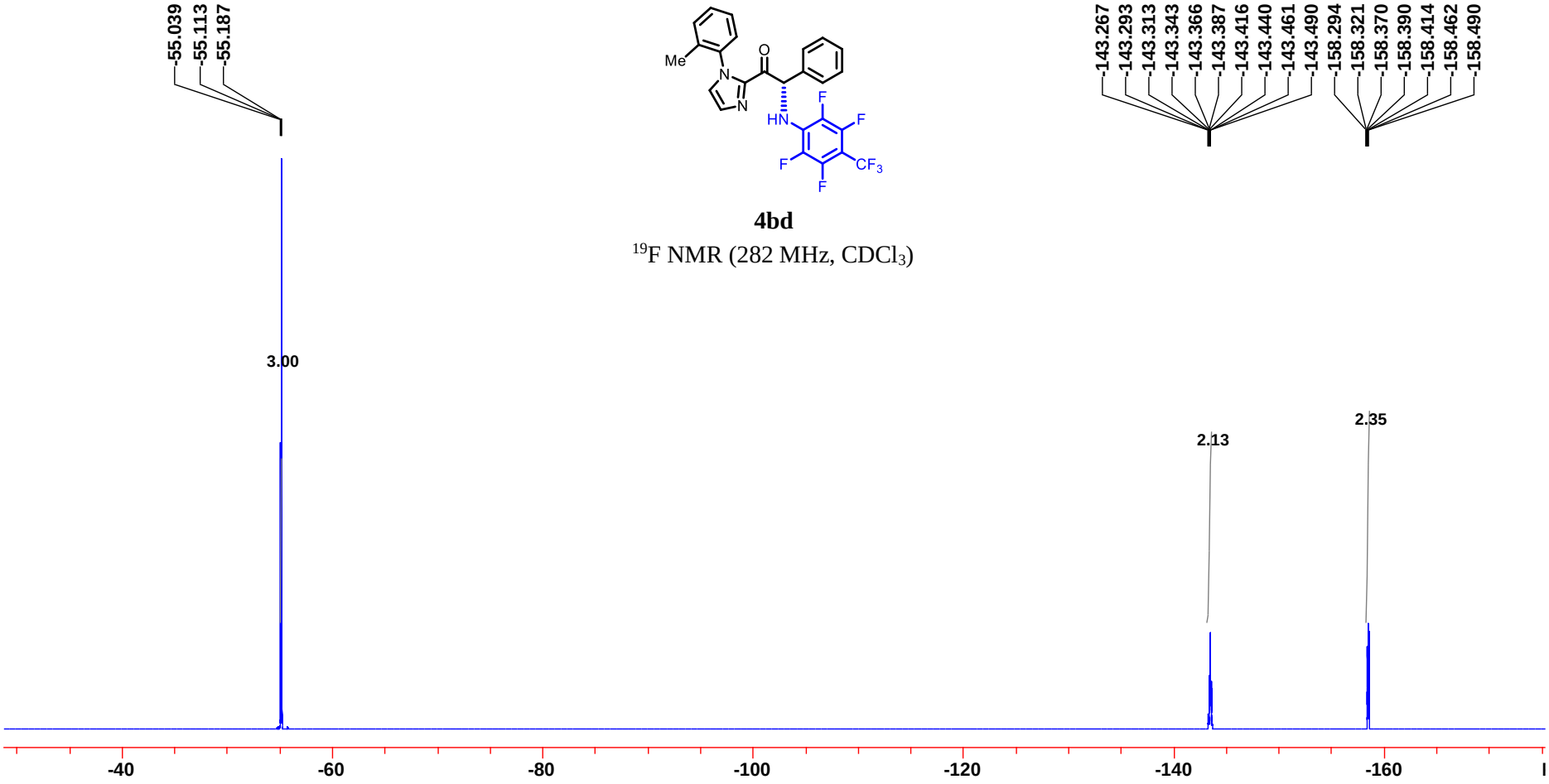
^{19}F NMR (282 MHz, $CDCl_3$)


7.497
7.482
7.474
7.459
7.419
7.406
7.405
7.391
7.377
7.375
7.352
7.334
7.314
7.299
7.289
7.275
7.260
7.253
7.239
7.225
7.216
7.198
7.109
6.900
6.884
6.856
6.839
6.781
6.765
5.943
5.934
5.927
5.874
5.866
5.858
2.036
1.393
Me
O
N
N
HN
F
F
F
F
CF3
4bd
1H NMR (500 MHz, CDCl3)
7.72
2.00
0.54
1.00
0.49
0.44
0.56
0.47
1.42
1.74
10
8
6
4
2
0



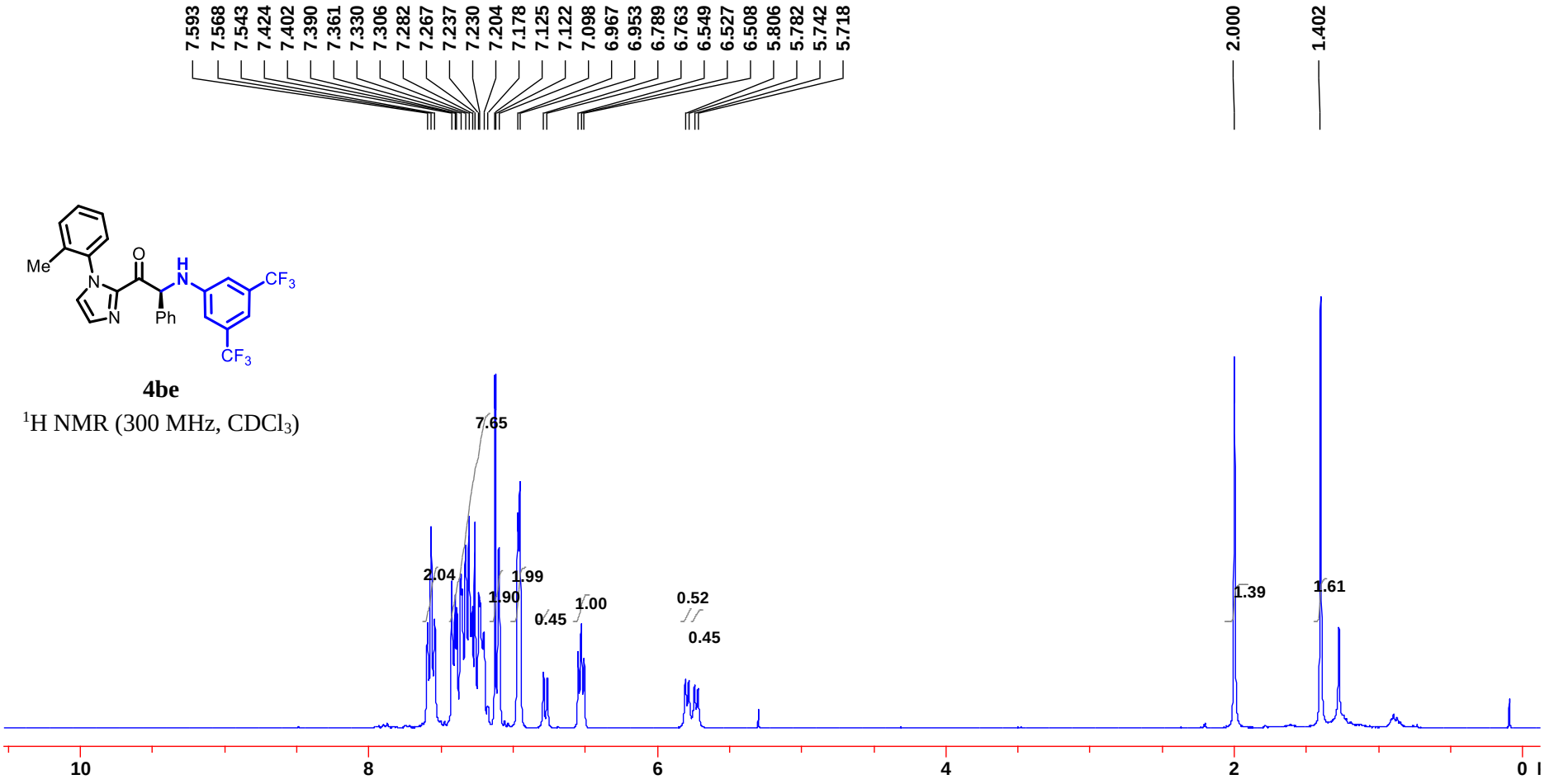
4bd

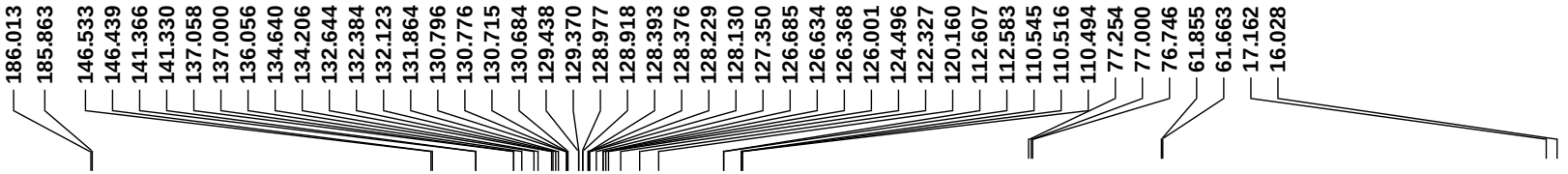
^{13}C NMR (125 MHz, $CDCl_3$)

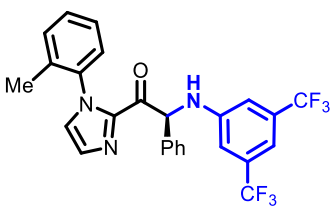


4bd

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

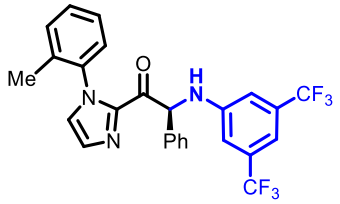

7.593
7.568
7.543
7.424
7.402
7.390
7.361
7.330
7.306
7.282
7.267
7.237
7.230
7.204
7.178
7.125
7.122
7.098
6.967
6.953
6.789
6.763
6.549
6.527
6.508
5.806
5.782
5.742
5.718
2.000
1.402
Me
O
H
N
N
N
Ph
CF3
CF3
4be
1H NMR (300 MHz, CDCl3)
7.65
2.04
1.99
1.90
0.45
1.00
0.52
0.45
1.39
1.61
10
8
6
4
2
0





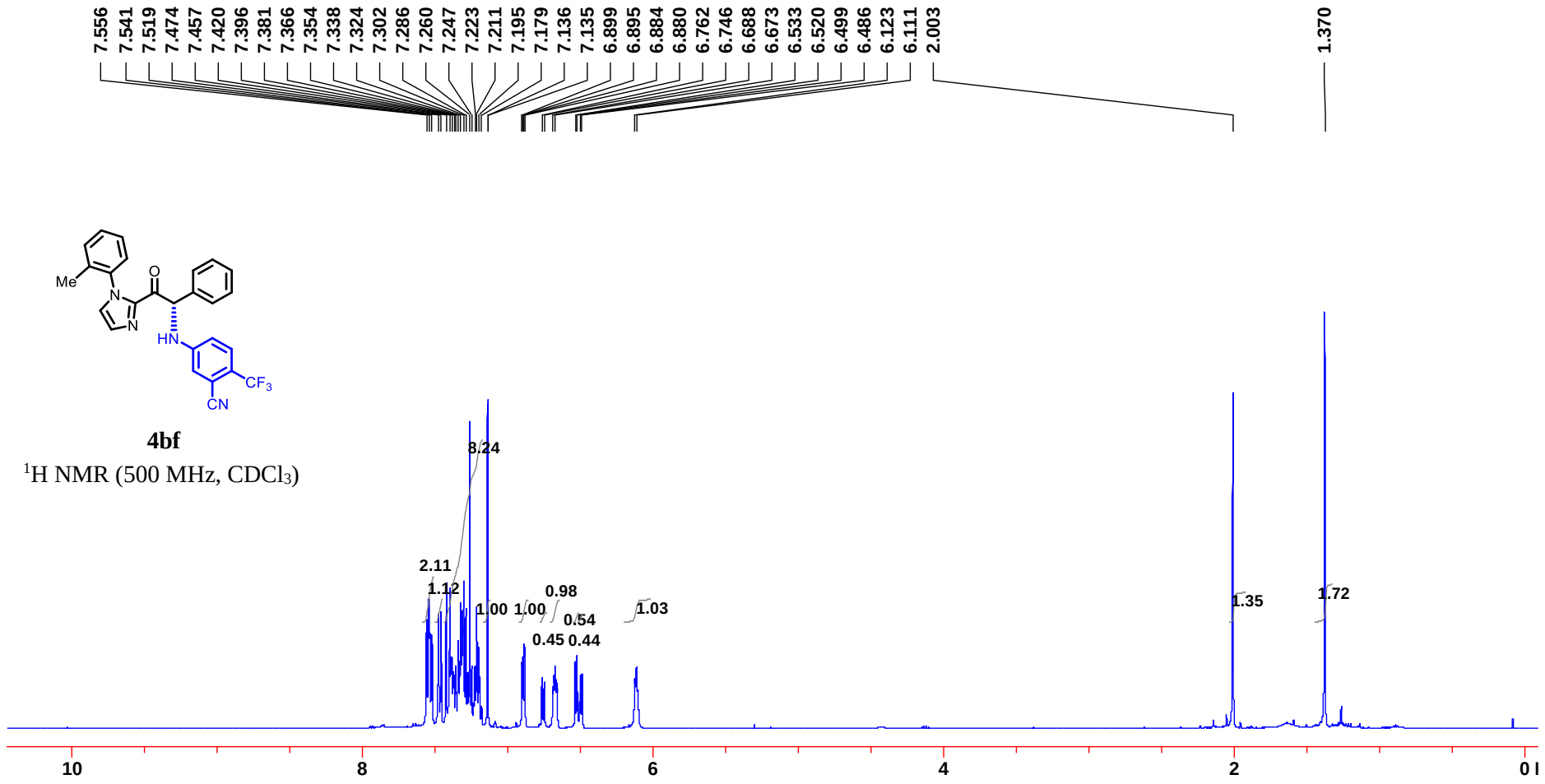
4be

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



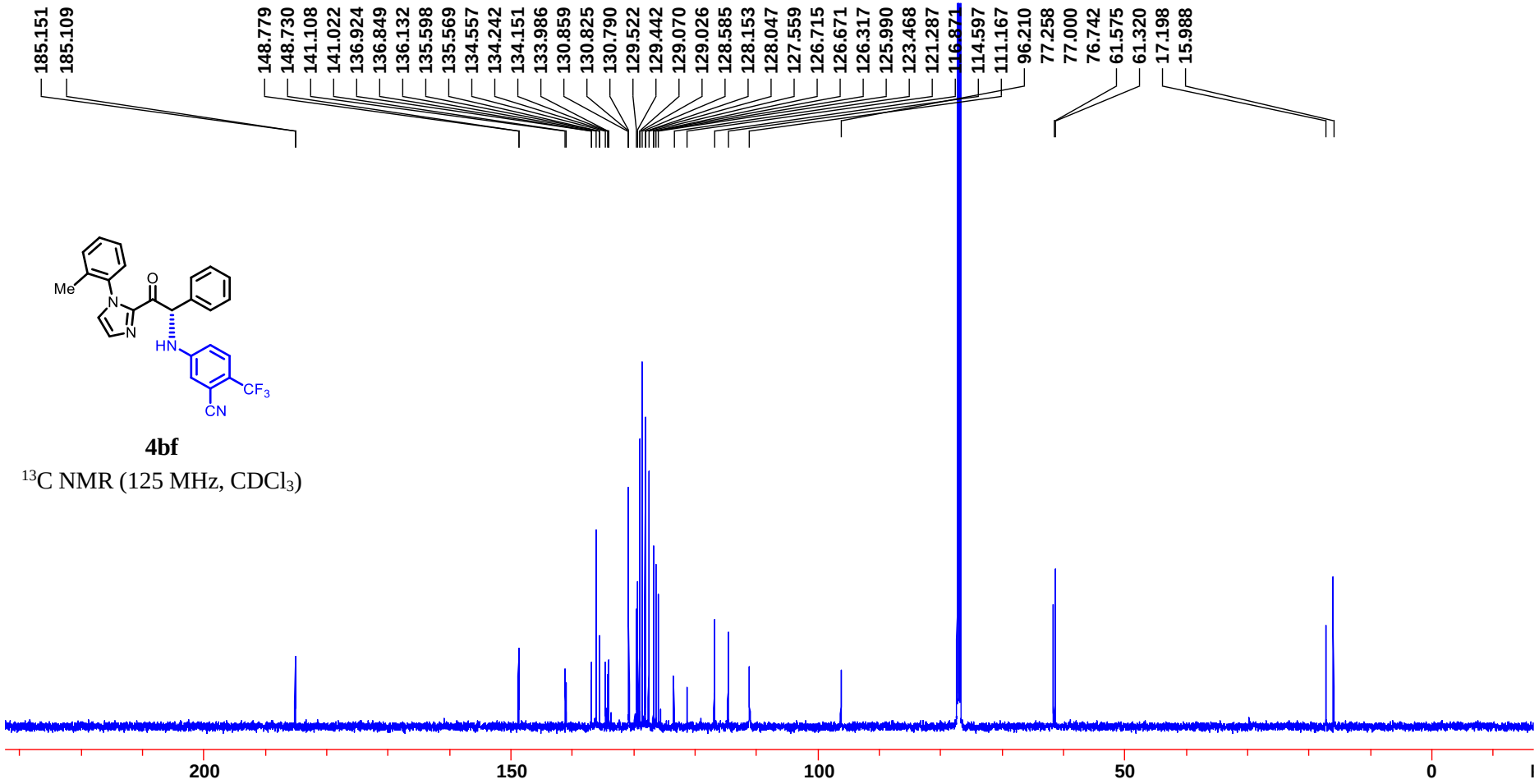
4be

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



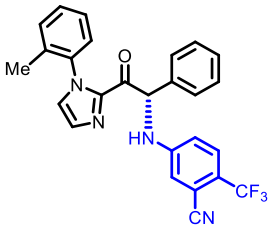
4bf

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



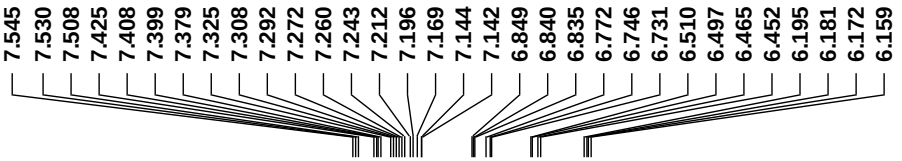
4bf

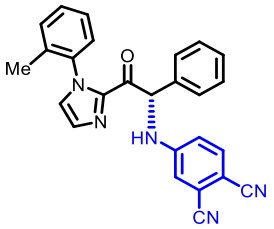
^{13}C NMR (125 MHz, $CDCl_3$)



4bf

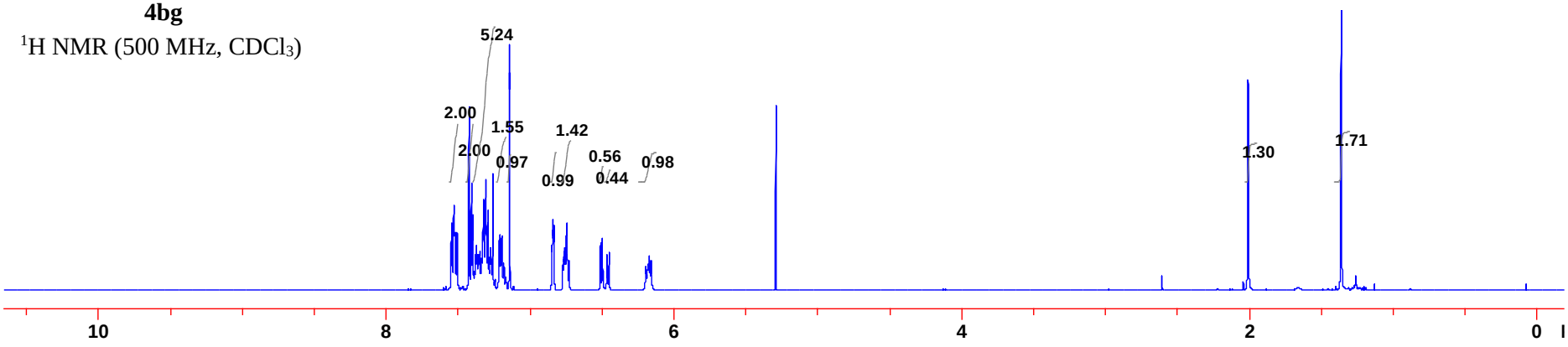
^{19}F NMR (282 MHz, $CDCl_3$)

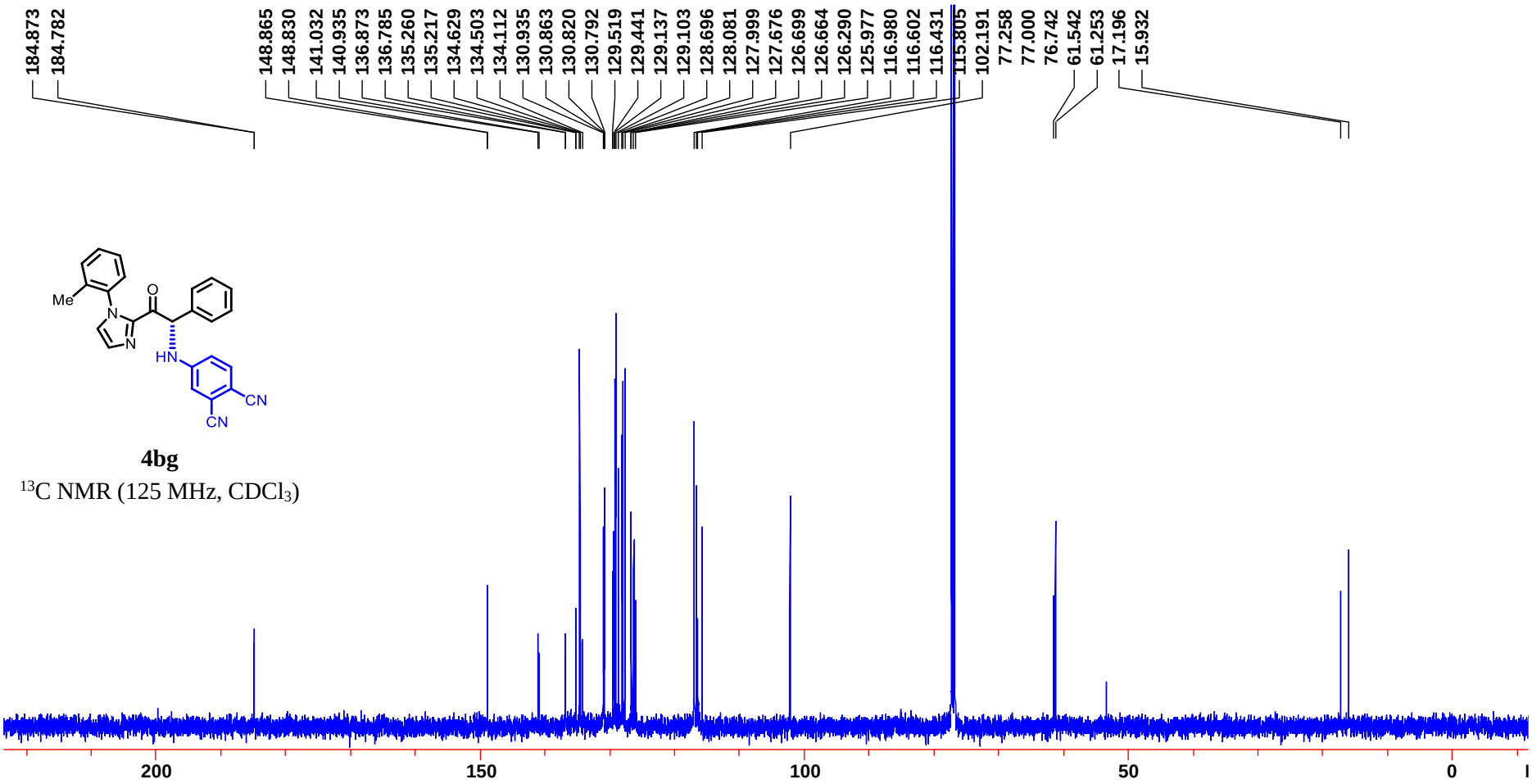




4bg

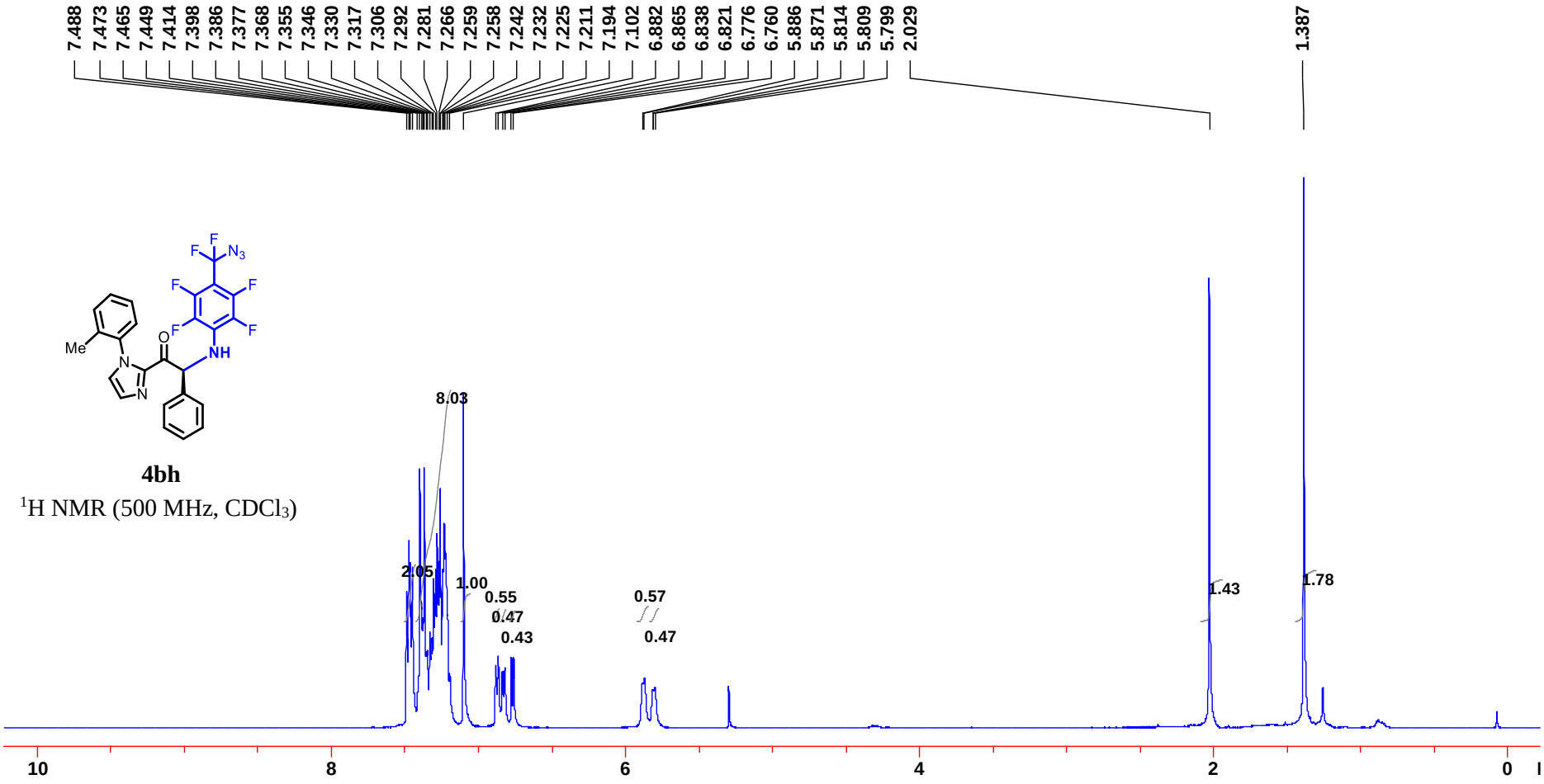
^{1}H NMR (500 MHz, $CDCl_3$)





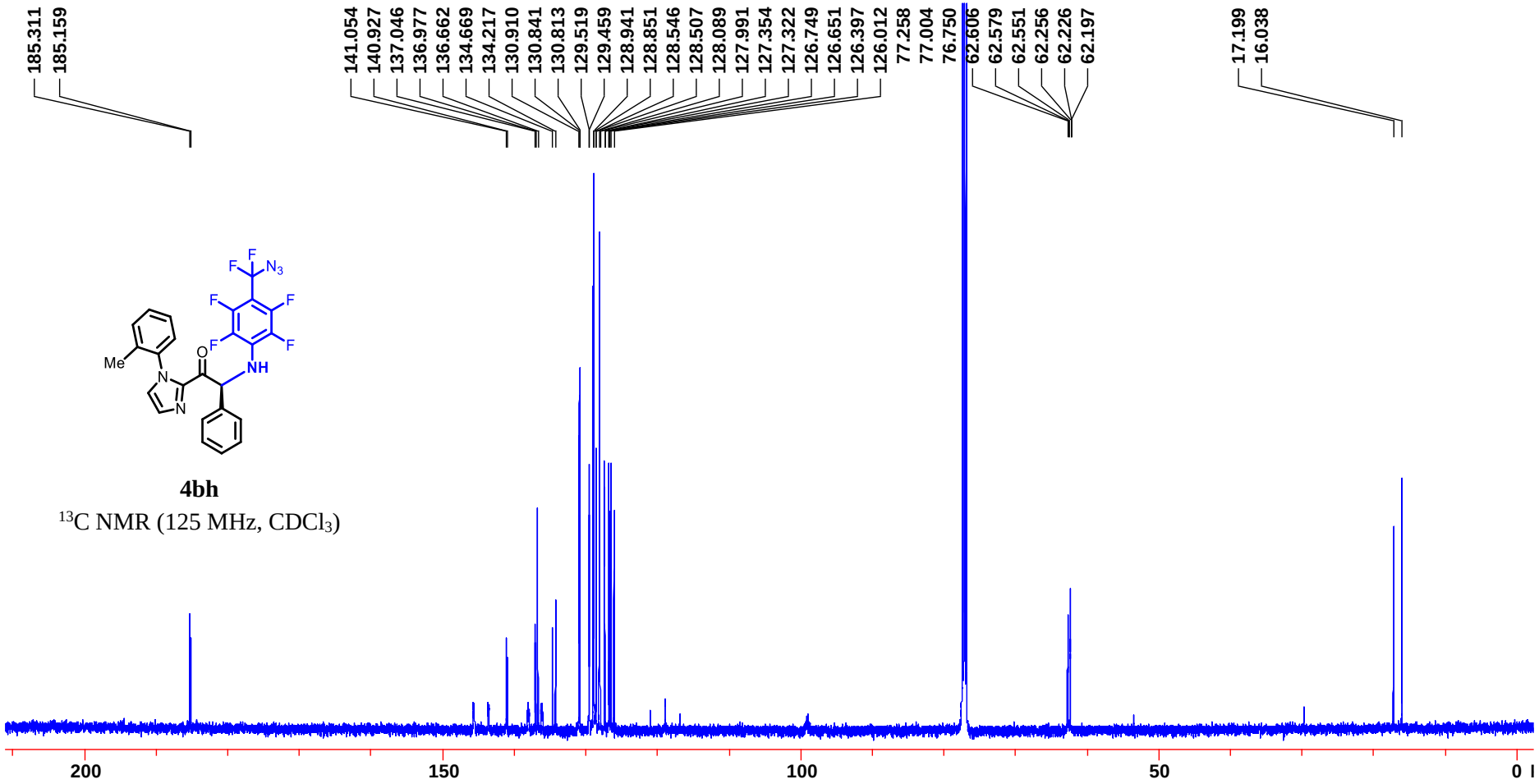
4bg

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



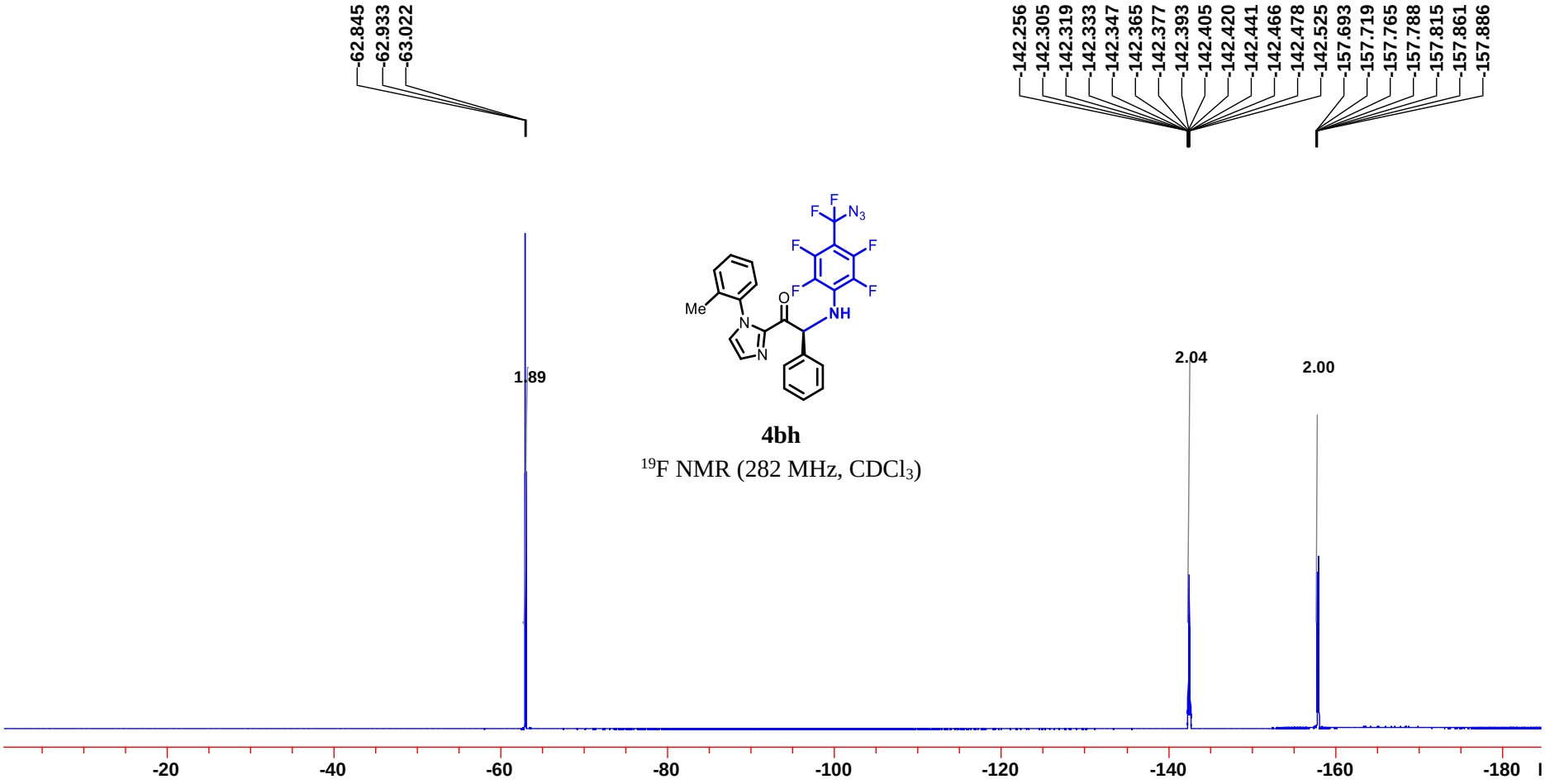
4bh

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



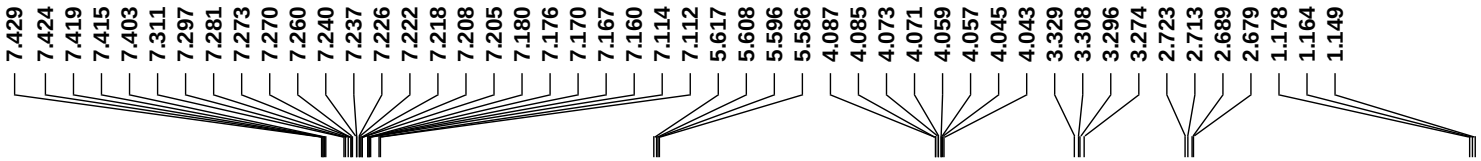
4bh

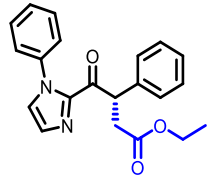
^{13}C NMR (125 MHz, $CDCl_3$)



4bh

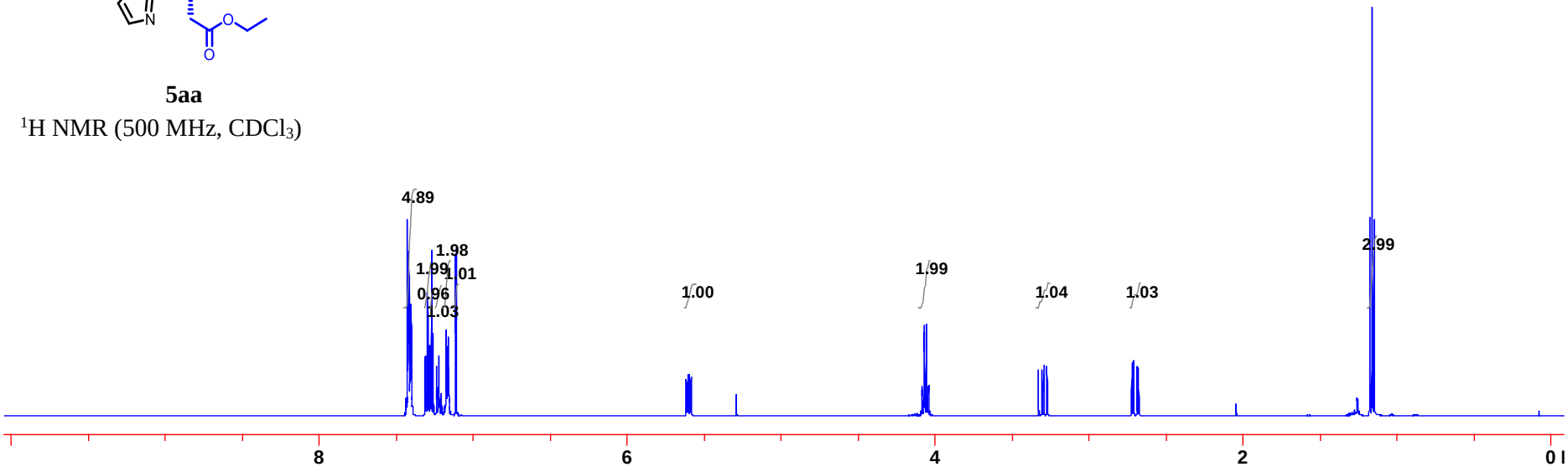
^{19}F NMR (282 MHz, $CDCl_3$)

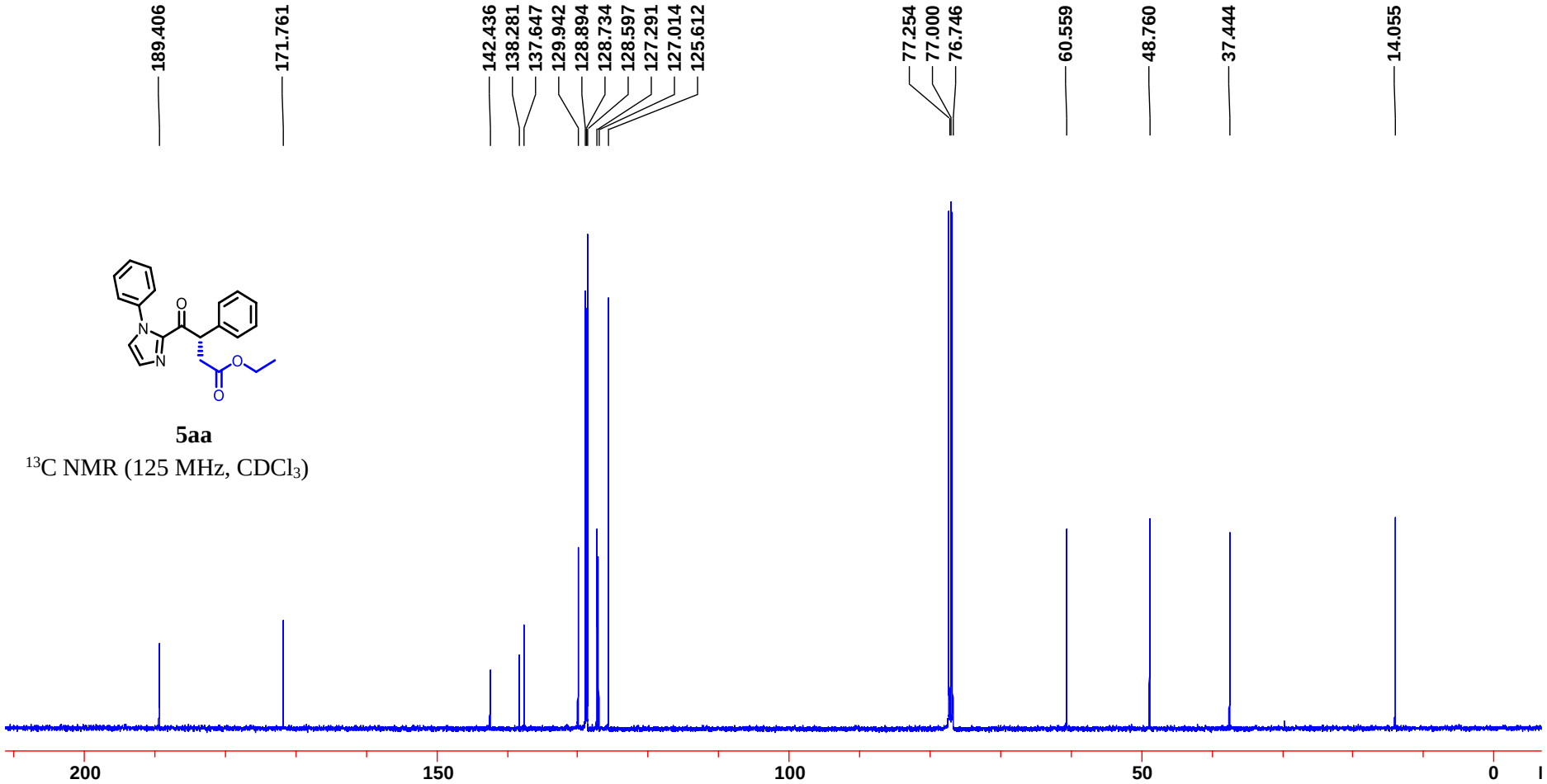




5aa

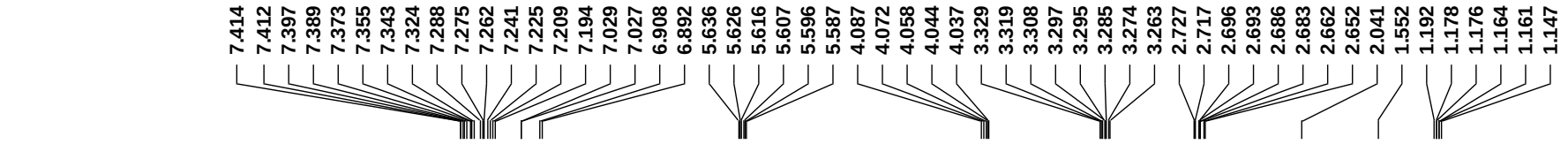
^{1}H NMR (500 MHz, $CDCl_3$)

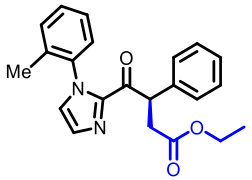




5aa

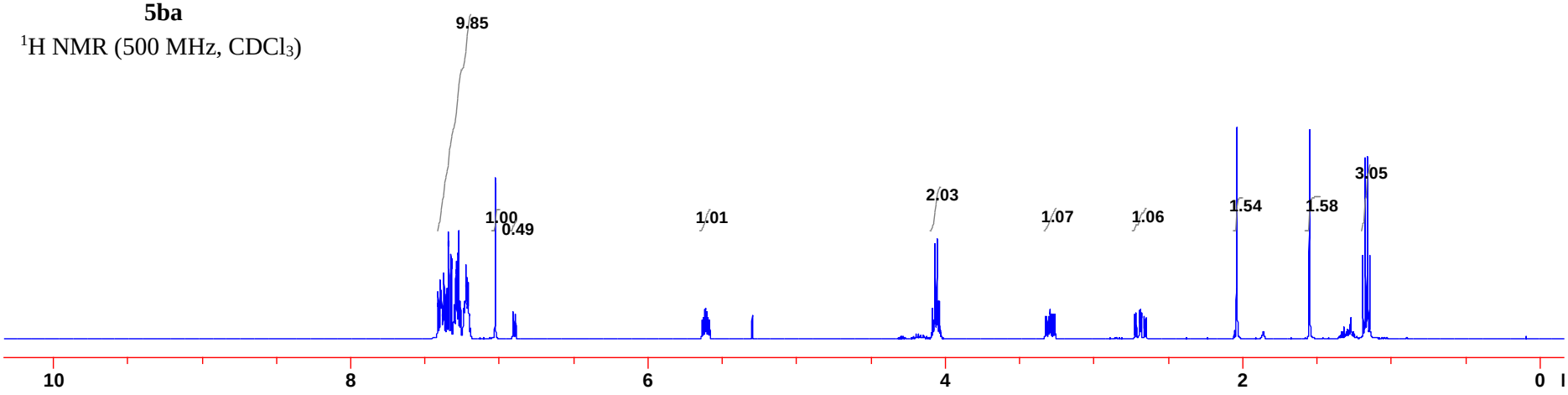
^{13}C NMR (125 MHz, $CDCl_3$)

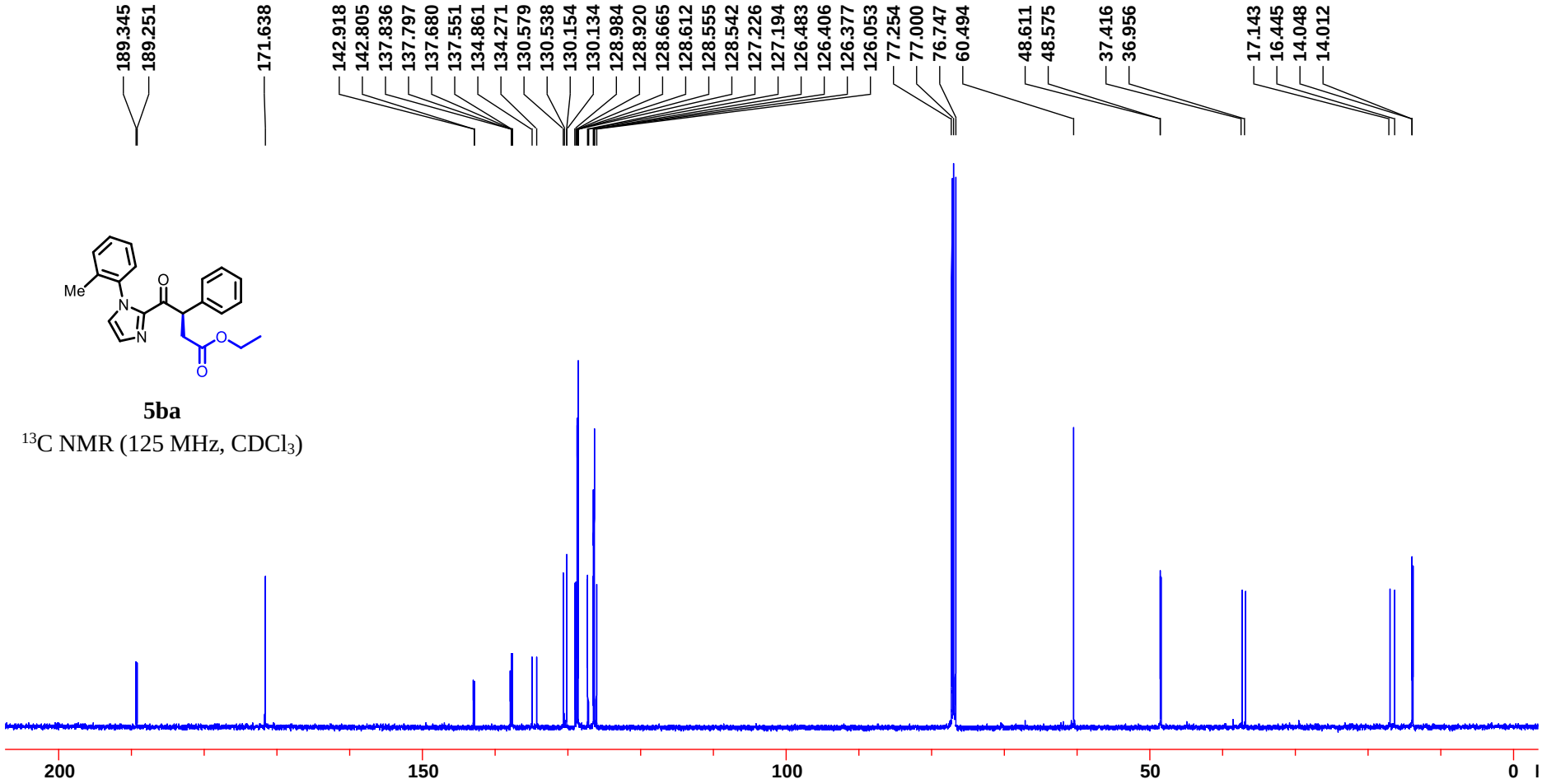




5ba

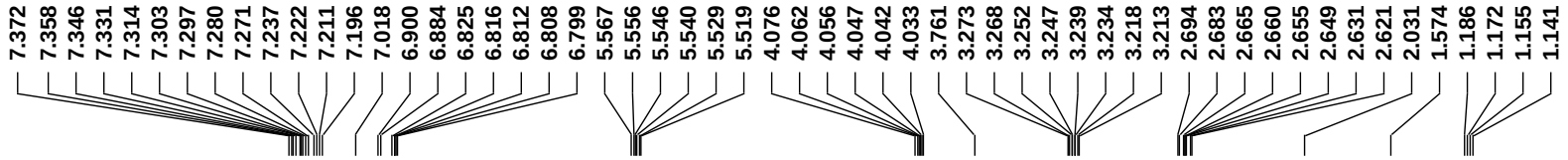
^{1}H NMR (500 MHz, $CDCl_3$)

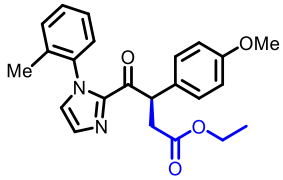




5ba

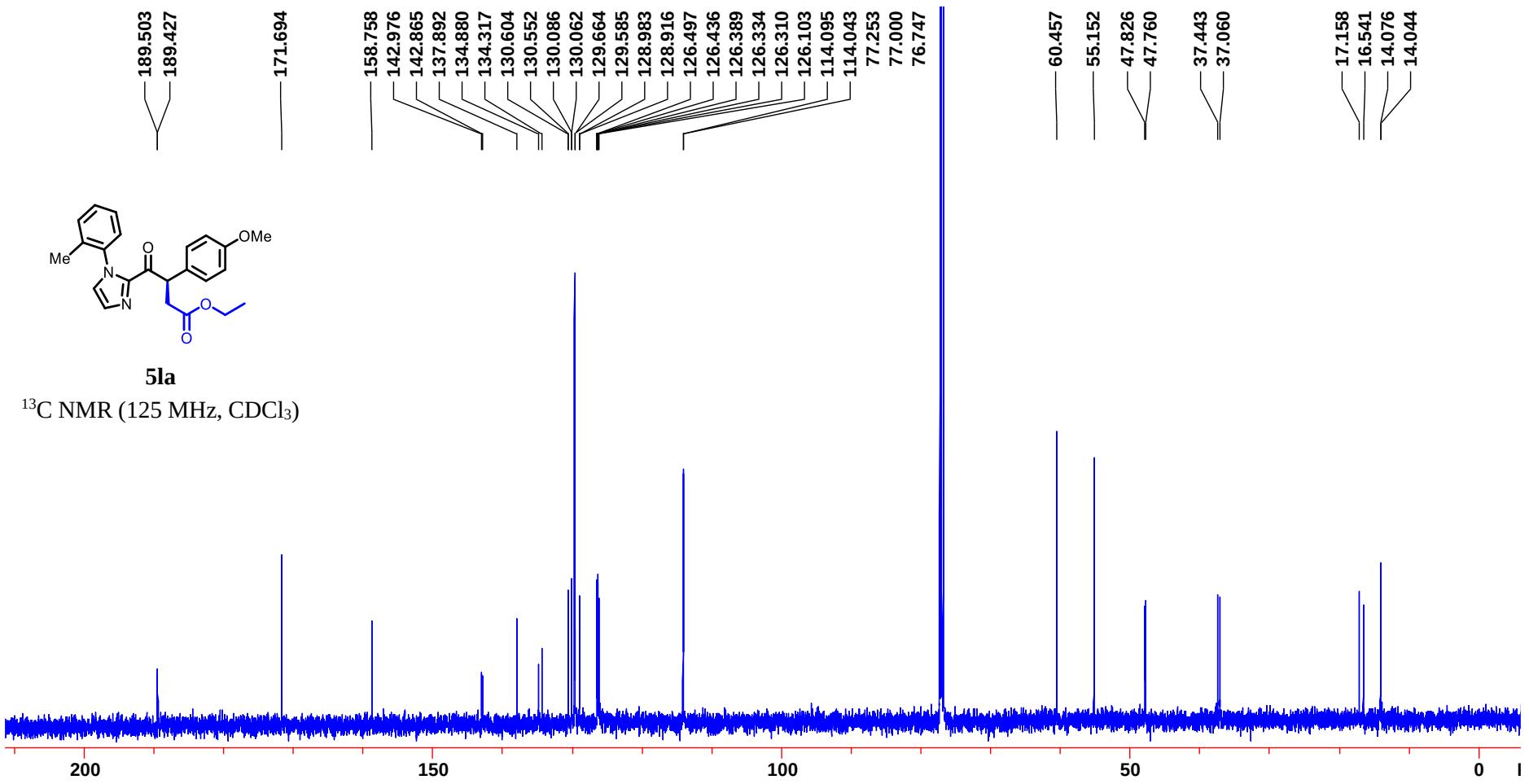
^{13}C NMR (125 MHz, $CDCl_3$)





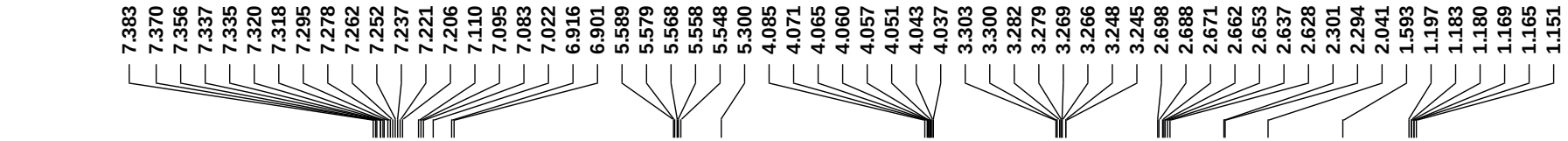
5la

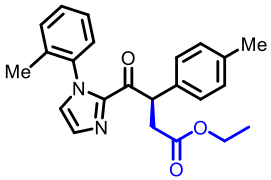
^{1}H NMR (500 MHz, $CDCl_3$)



5la

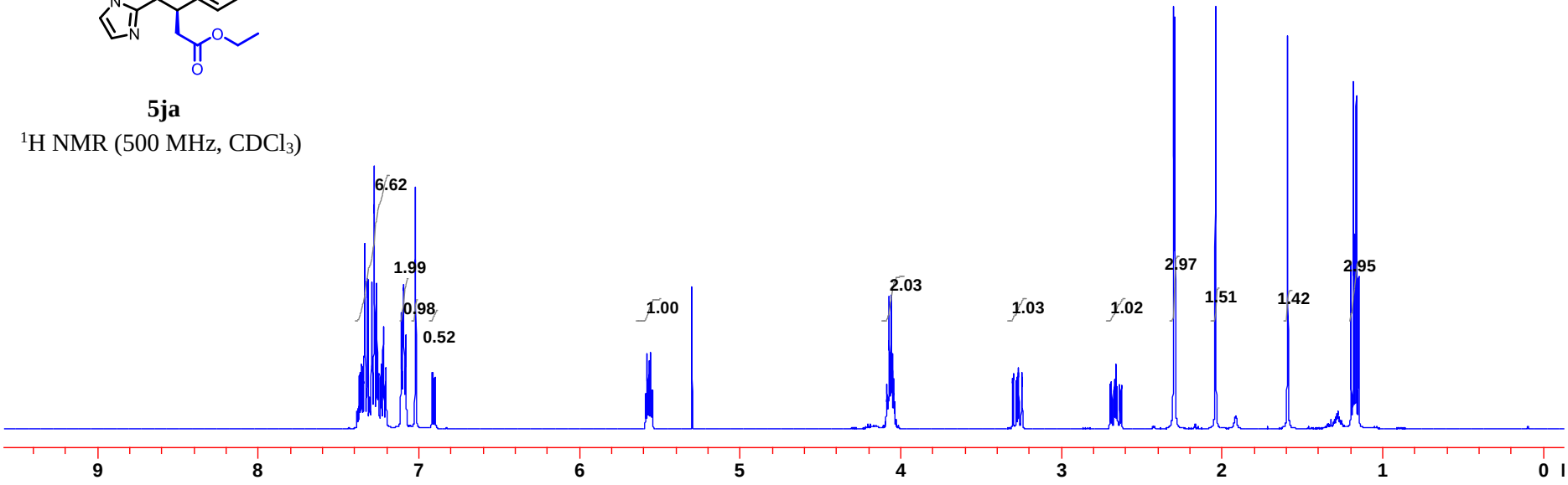
^{13}C NMR (125 MHz, $CDCl_3$)

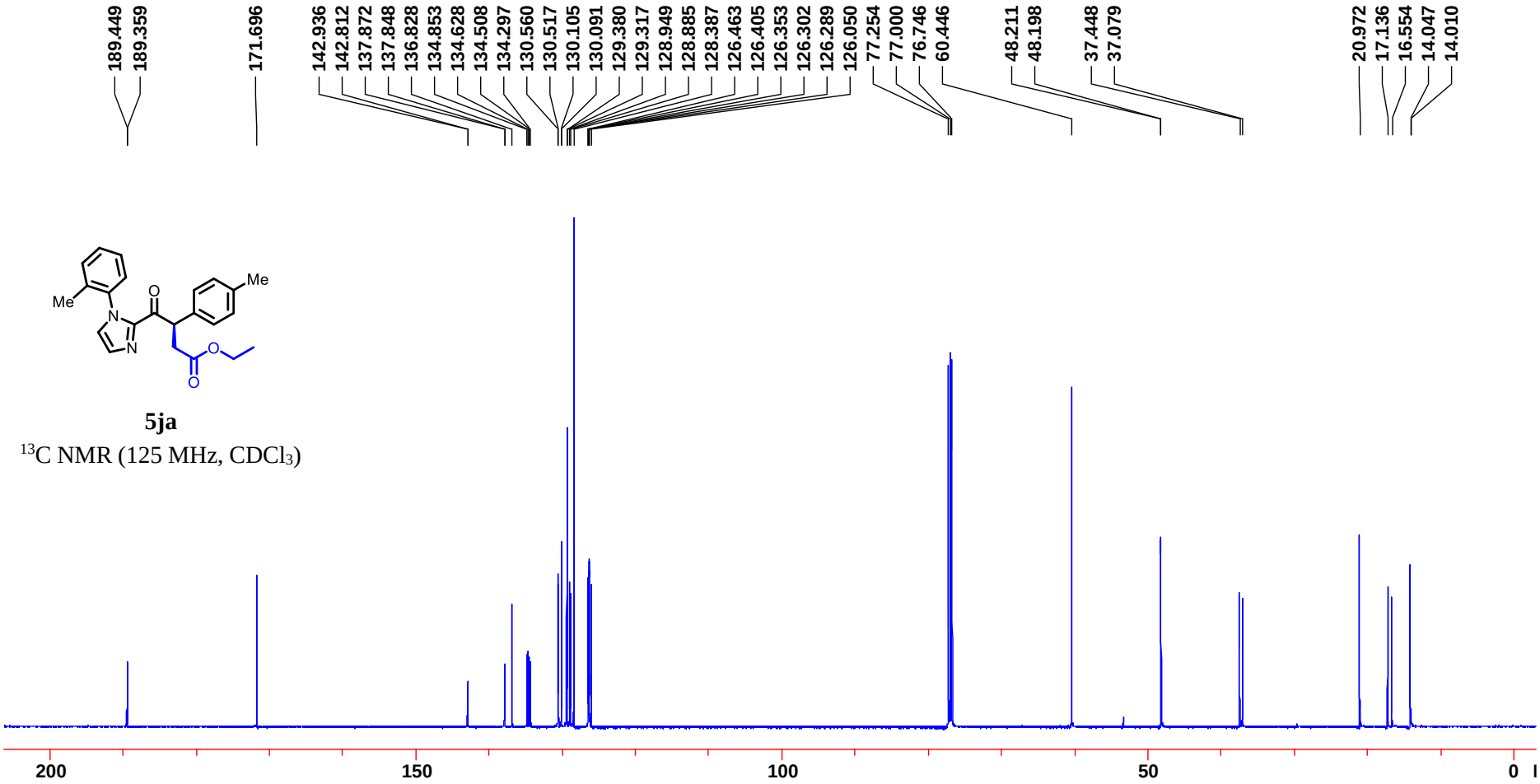




5ja

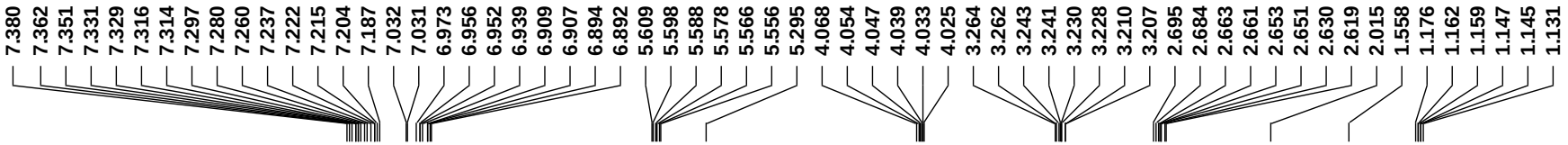
^{1}H NMR (500 MHz, $CDCl_3$)

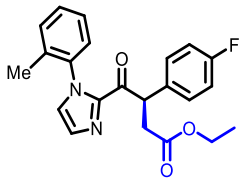




5ja

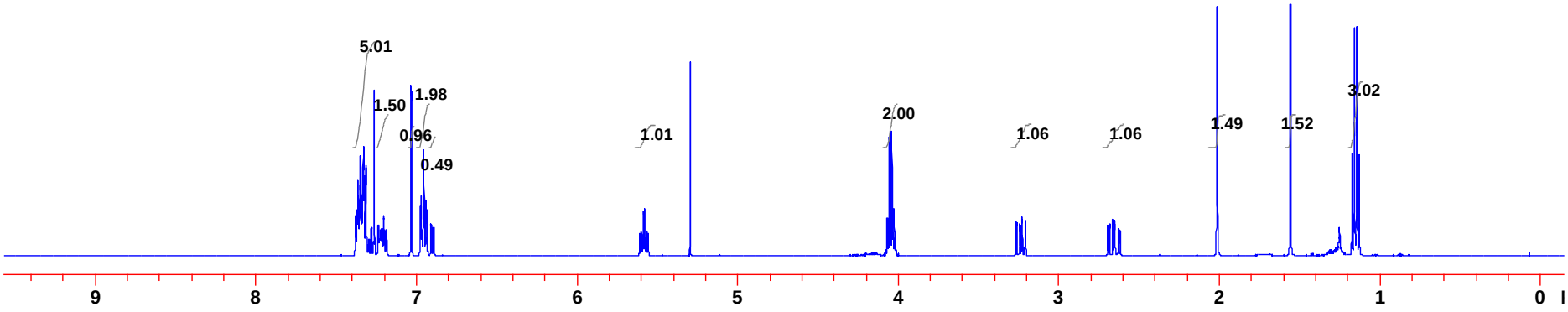
^{13}C NMR (125 MHz, $CDCl_3$)

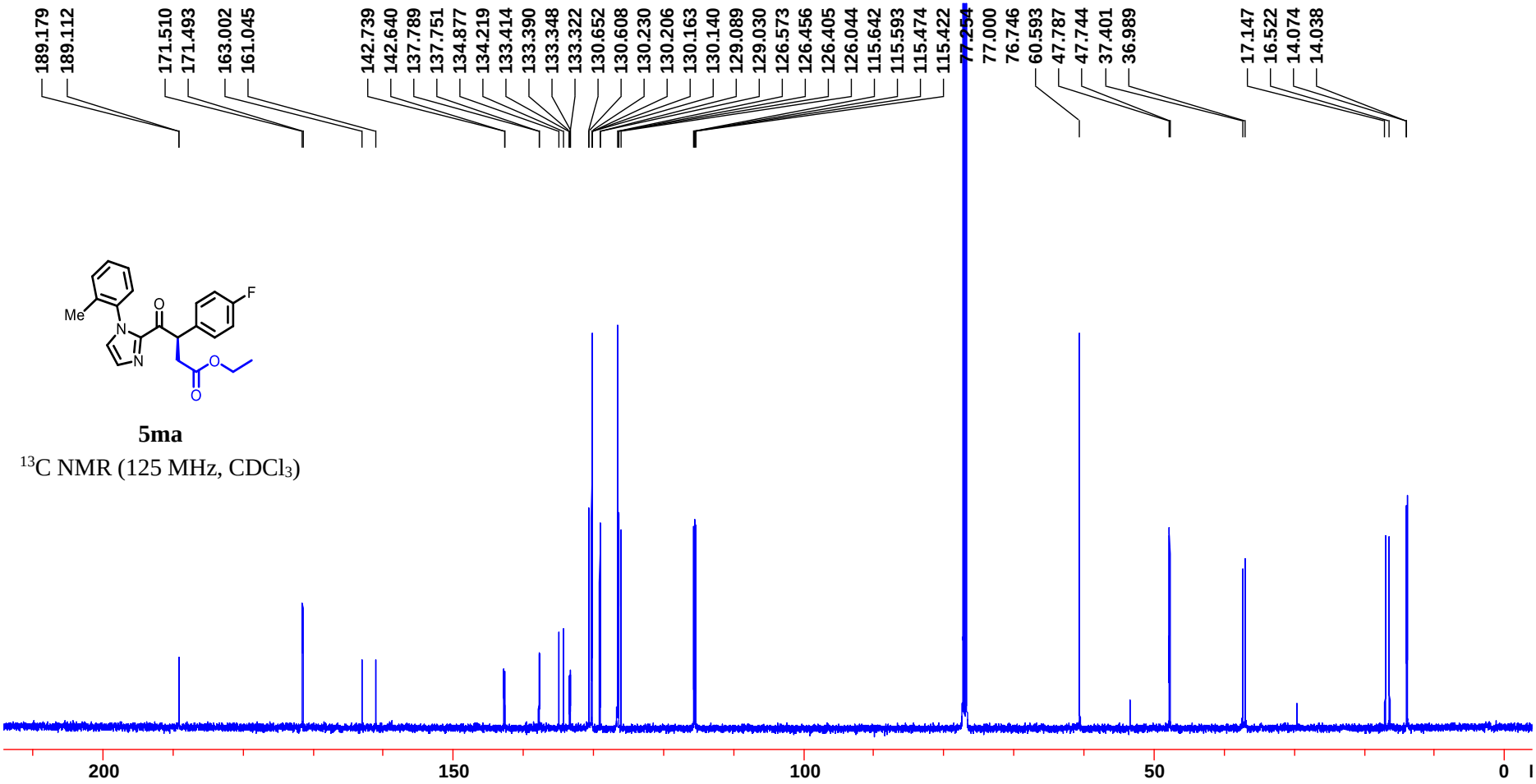




5ma

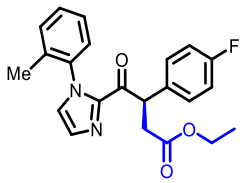
^{1}H NMR (500 MHz, $CDCl_3$)





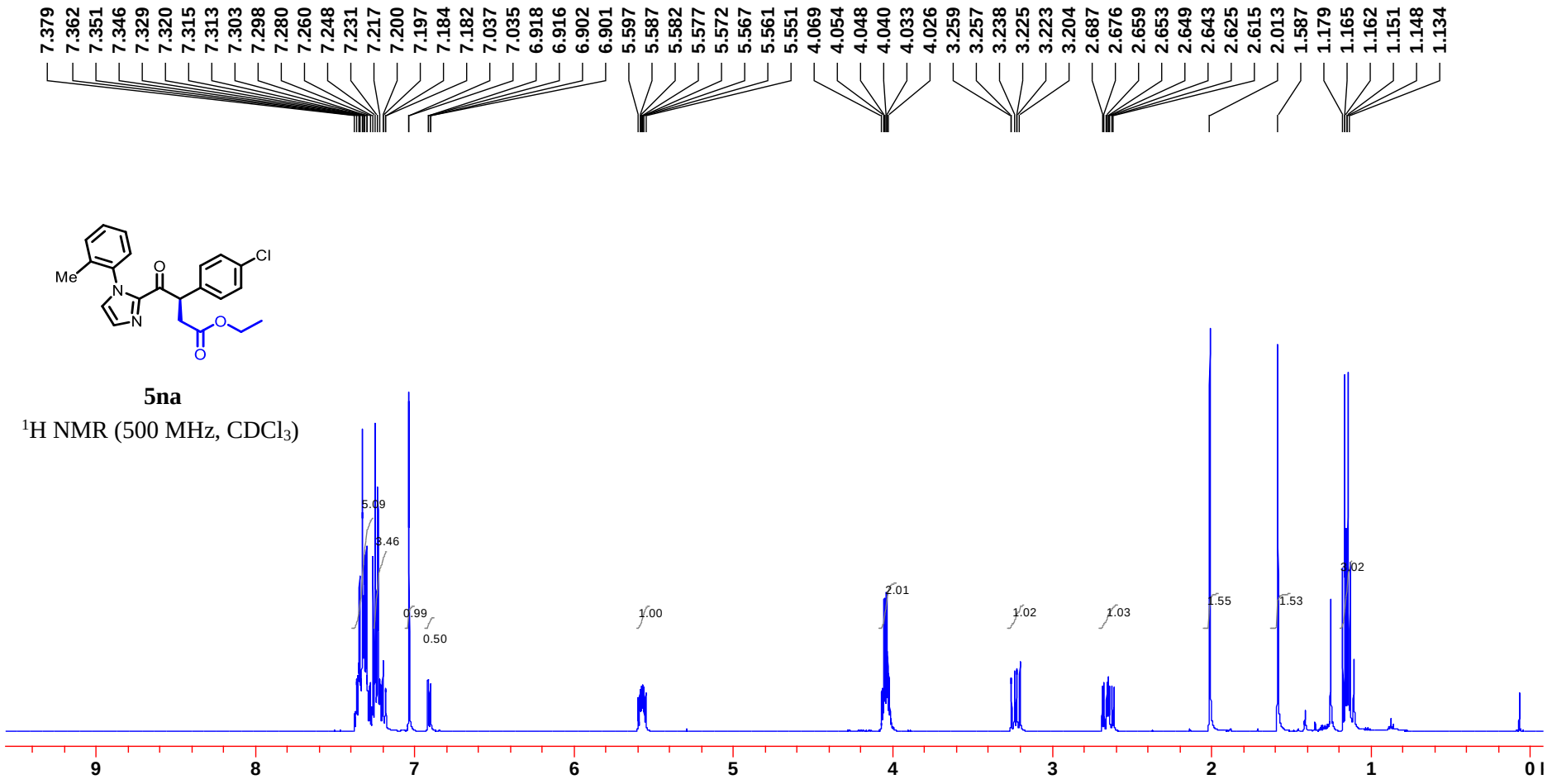
5ma

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



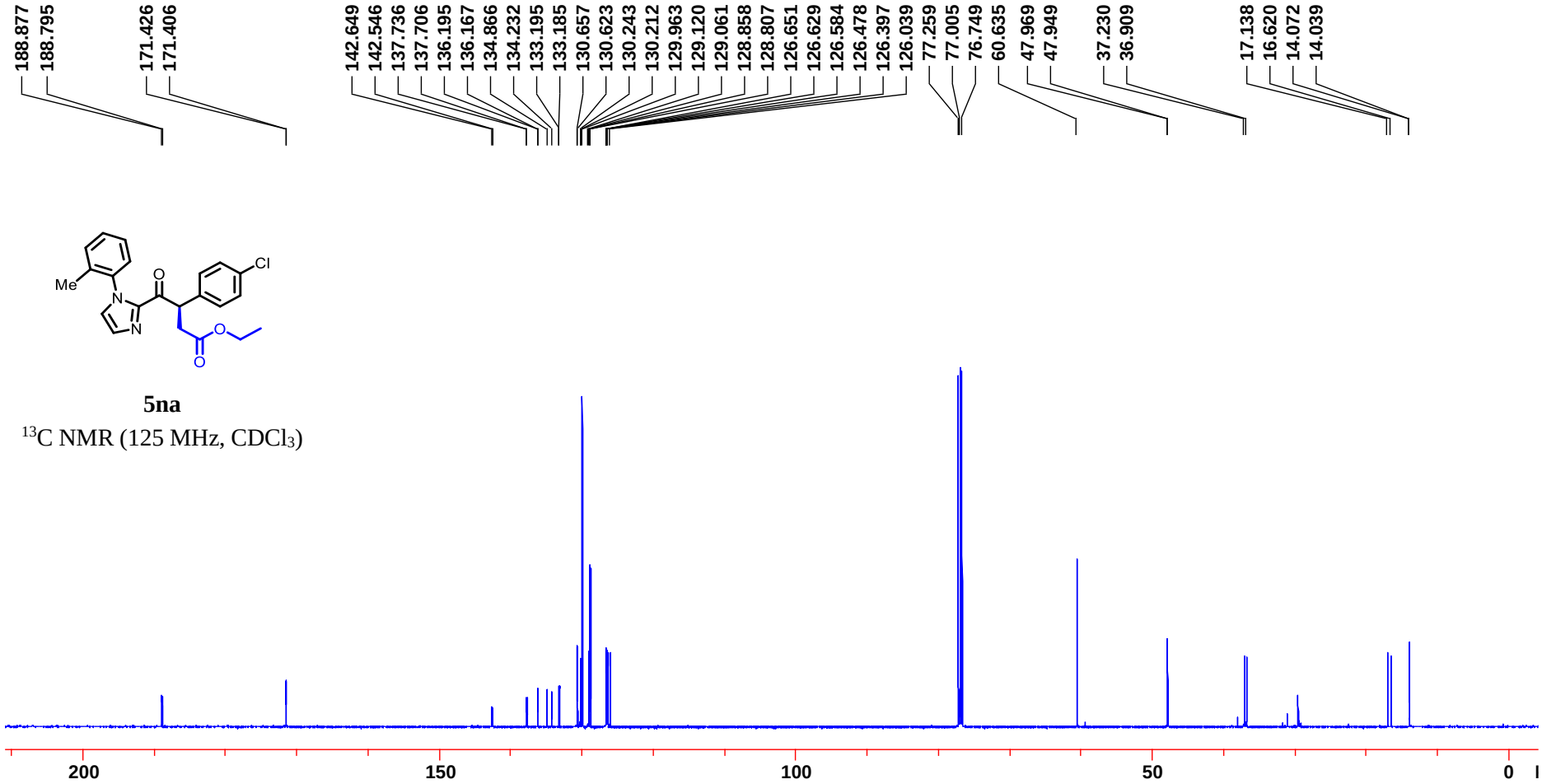
5ma

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



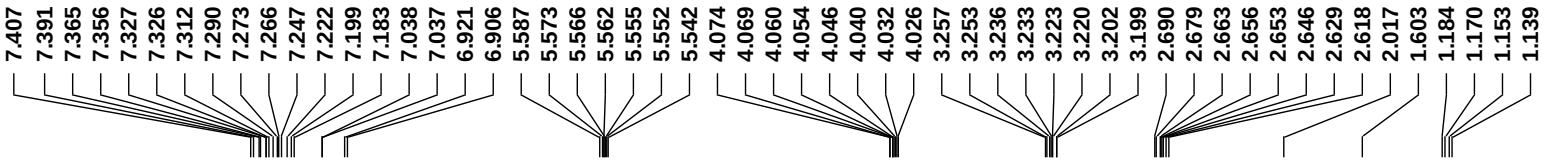
5na

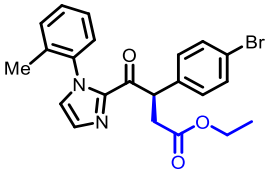
^{1}H NMR (500 MHz, $CDCl_3$)



5na

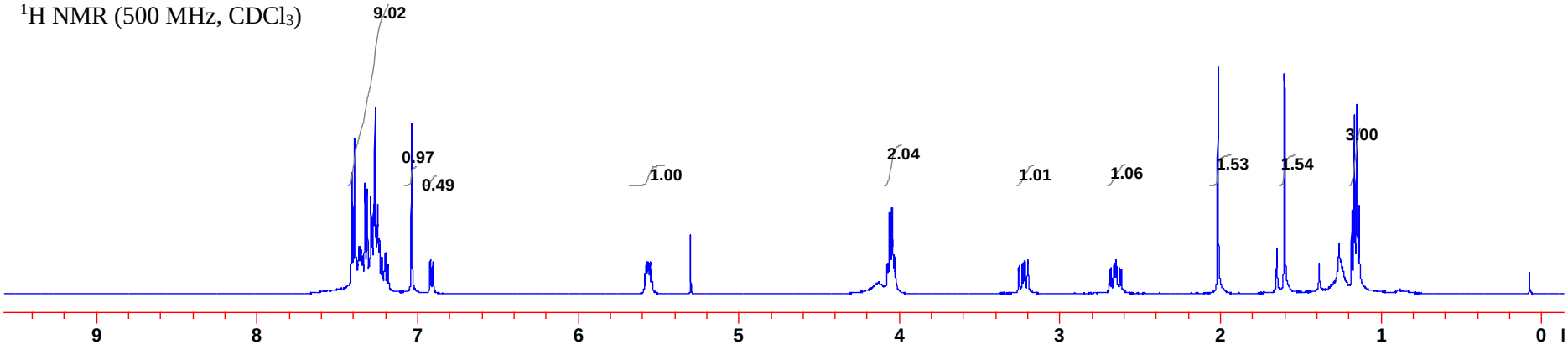
^{13}C NMR (125 MHz, $CDCl_3$)

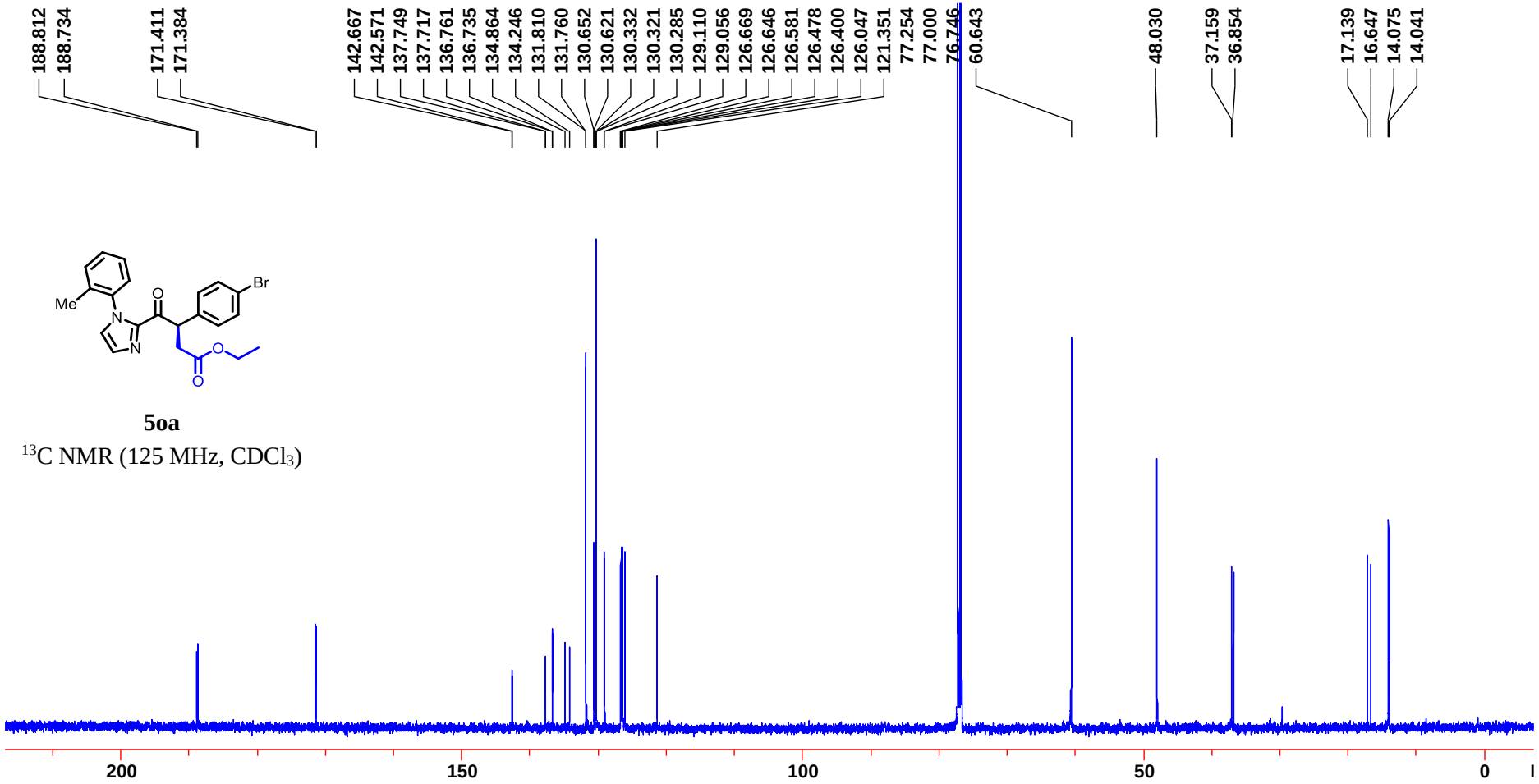




5oa

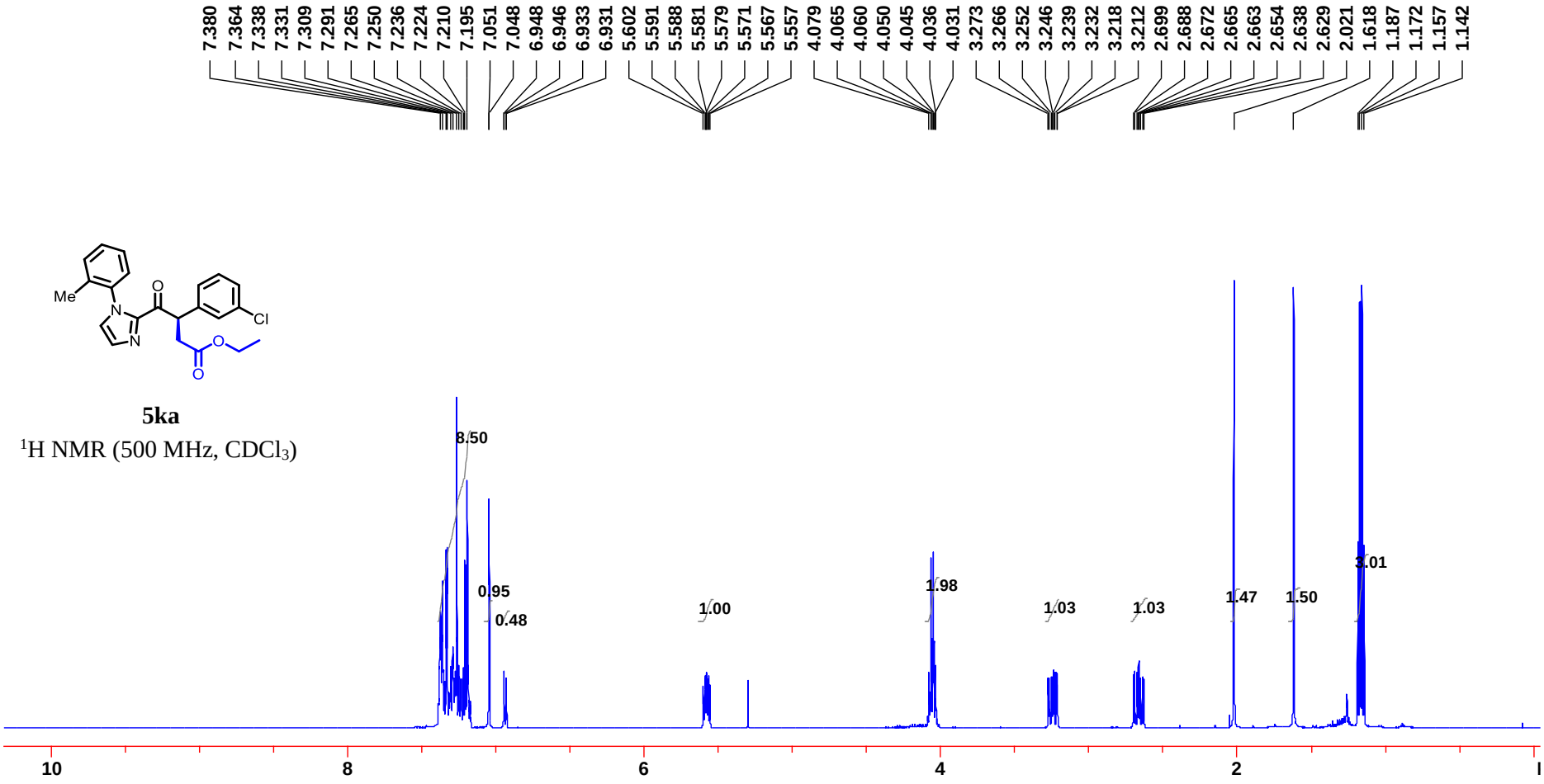
^{1}H NMR (500 MHz, $CDCl_3$)





5oa

^{13}C NMR (125 MHz, $CDCl_3$)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7.048
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6.931
5.602
5.591
5.588
5.581
5.579
5.571
5.567
5.557
4.079
4.065
4.060
4.050
4.045
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3.232
3.218
3.212
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2.688
2.672
2.665
2.663
2.654
2.638
2.629
2.021
1.618
1.187
1.172
1.157
1.142
Me
N
N
O
Cl
O
O
O
5ka
1H NMR (500 MHz, CDCl3)
8.50
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0.48
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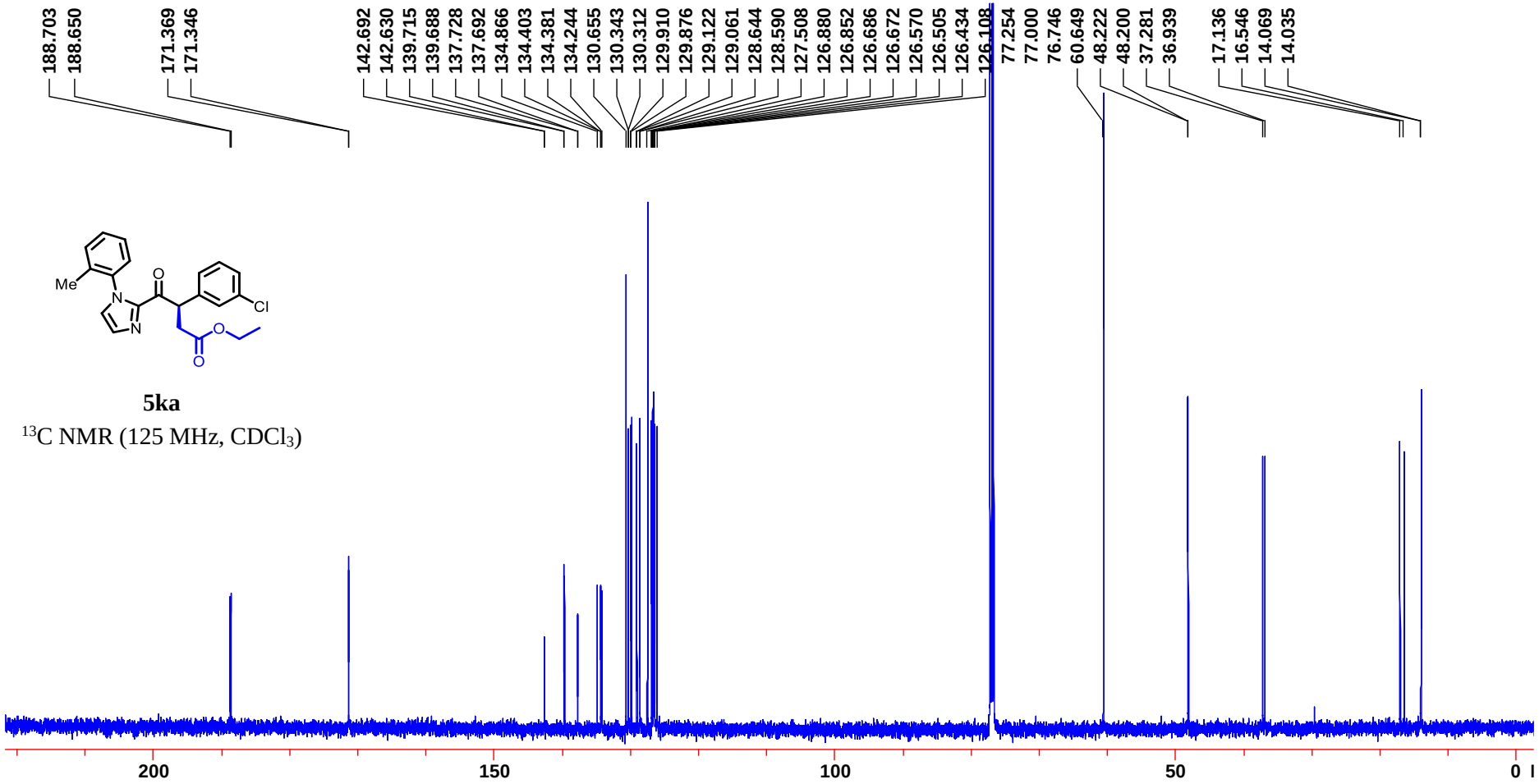
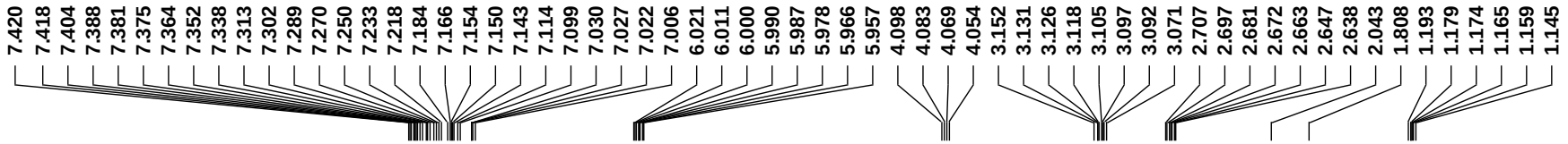
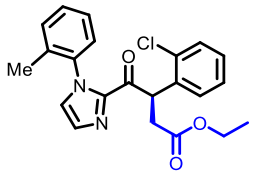
1.98
1.03
1.03
1.47
1.50
3.01
10
8
6
4
2
I



5ka

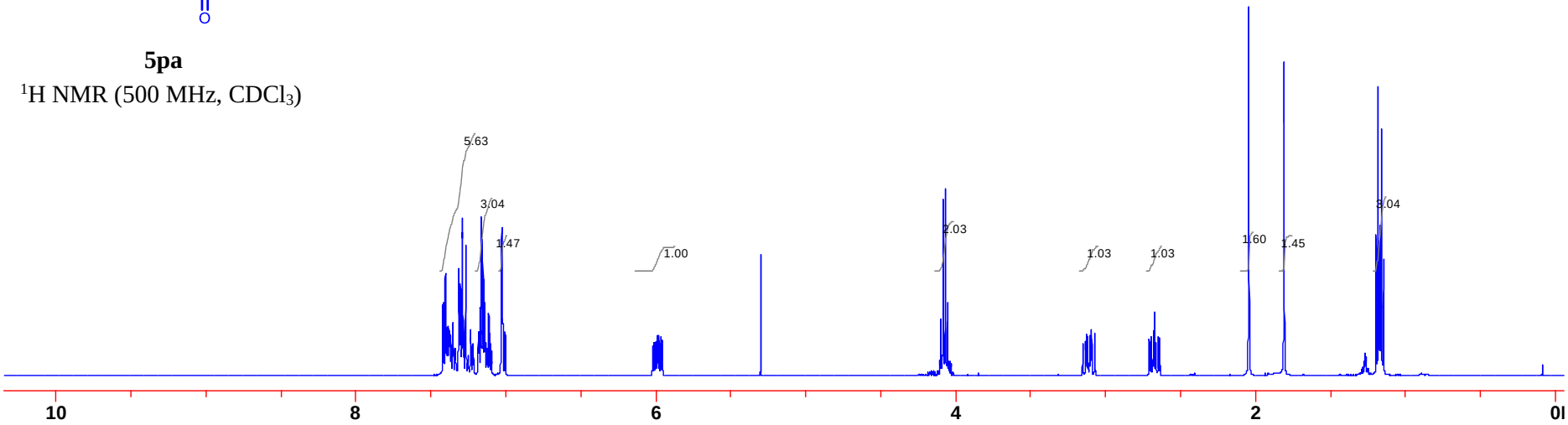
^{13}C NMR (125 MHz, $CDCl_3$)

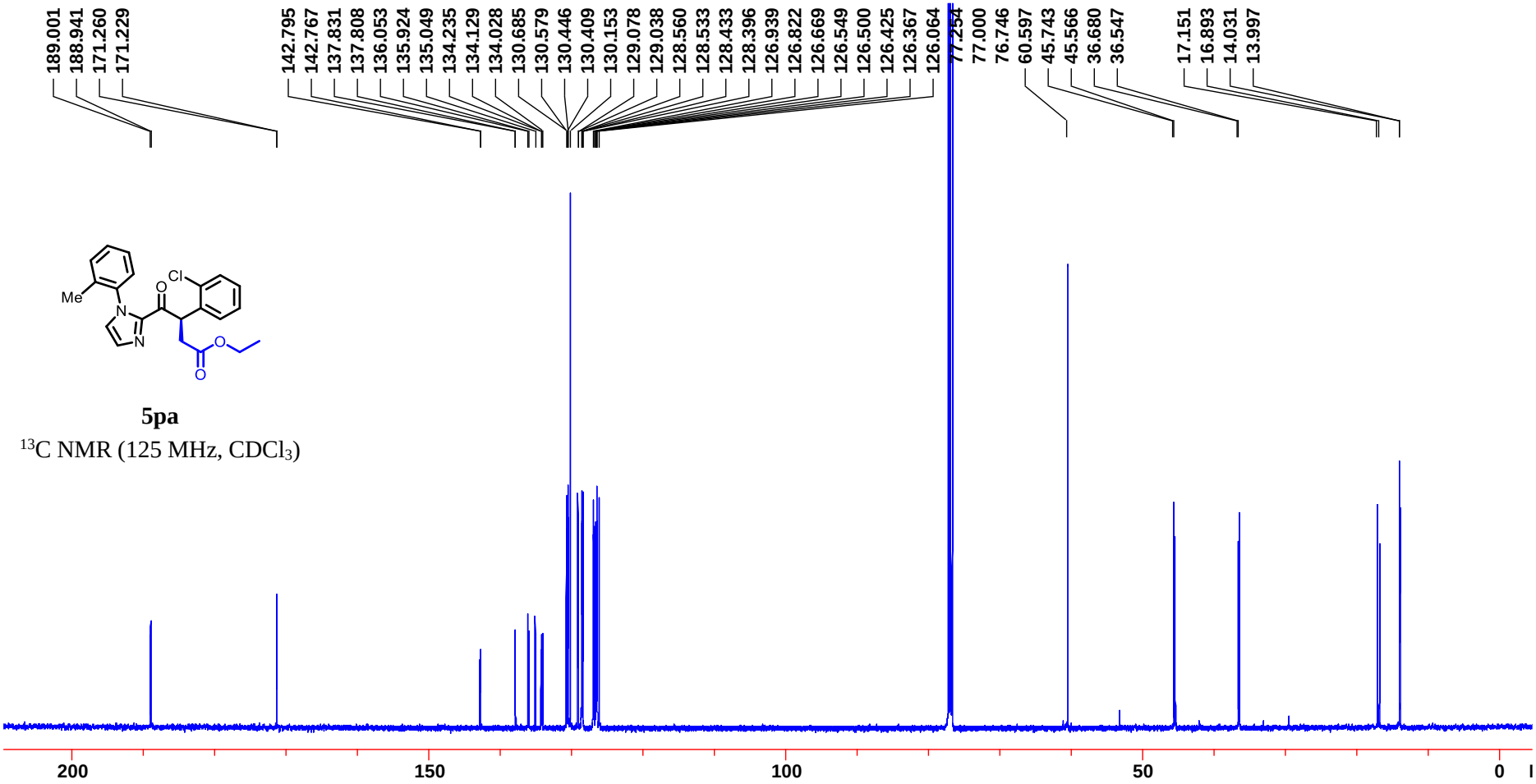




5pa

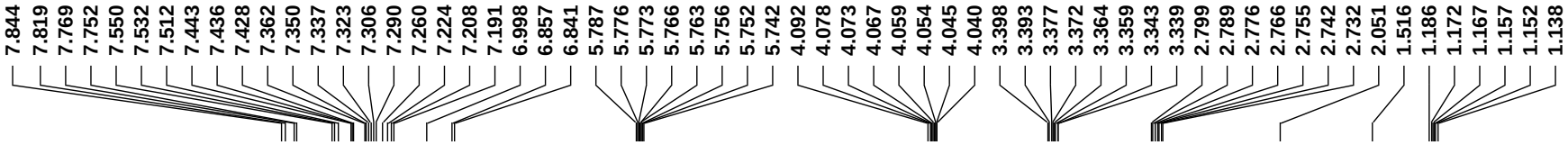
^{1}H NMR (500 MHz, $CDCl_3$)

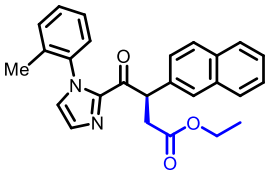




5pa

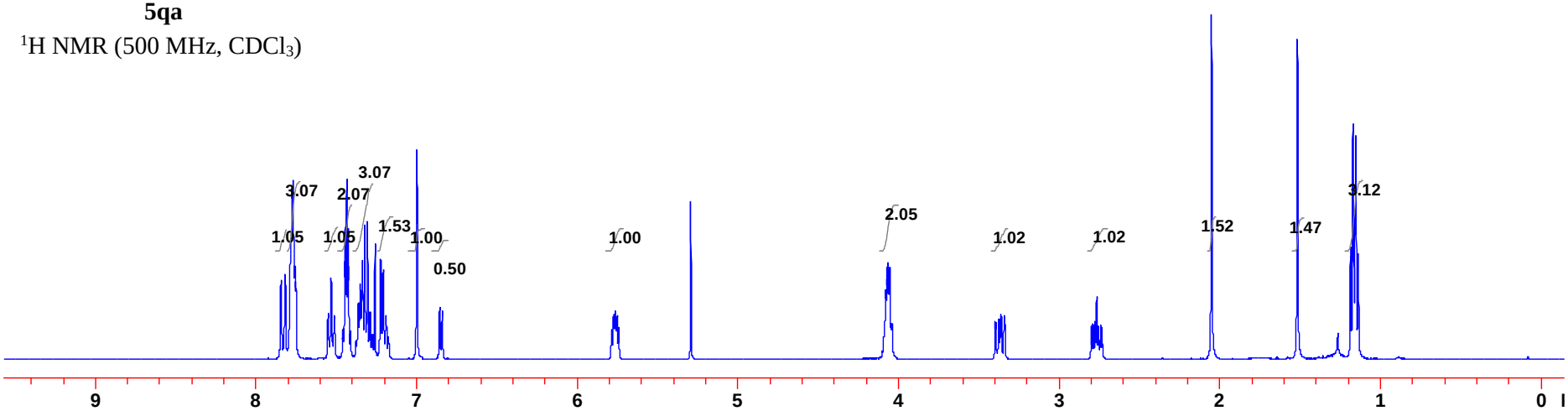
^{13}C NMR (125 MHz, $CDCl_3$)

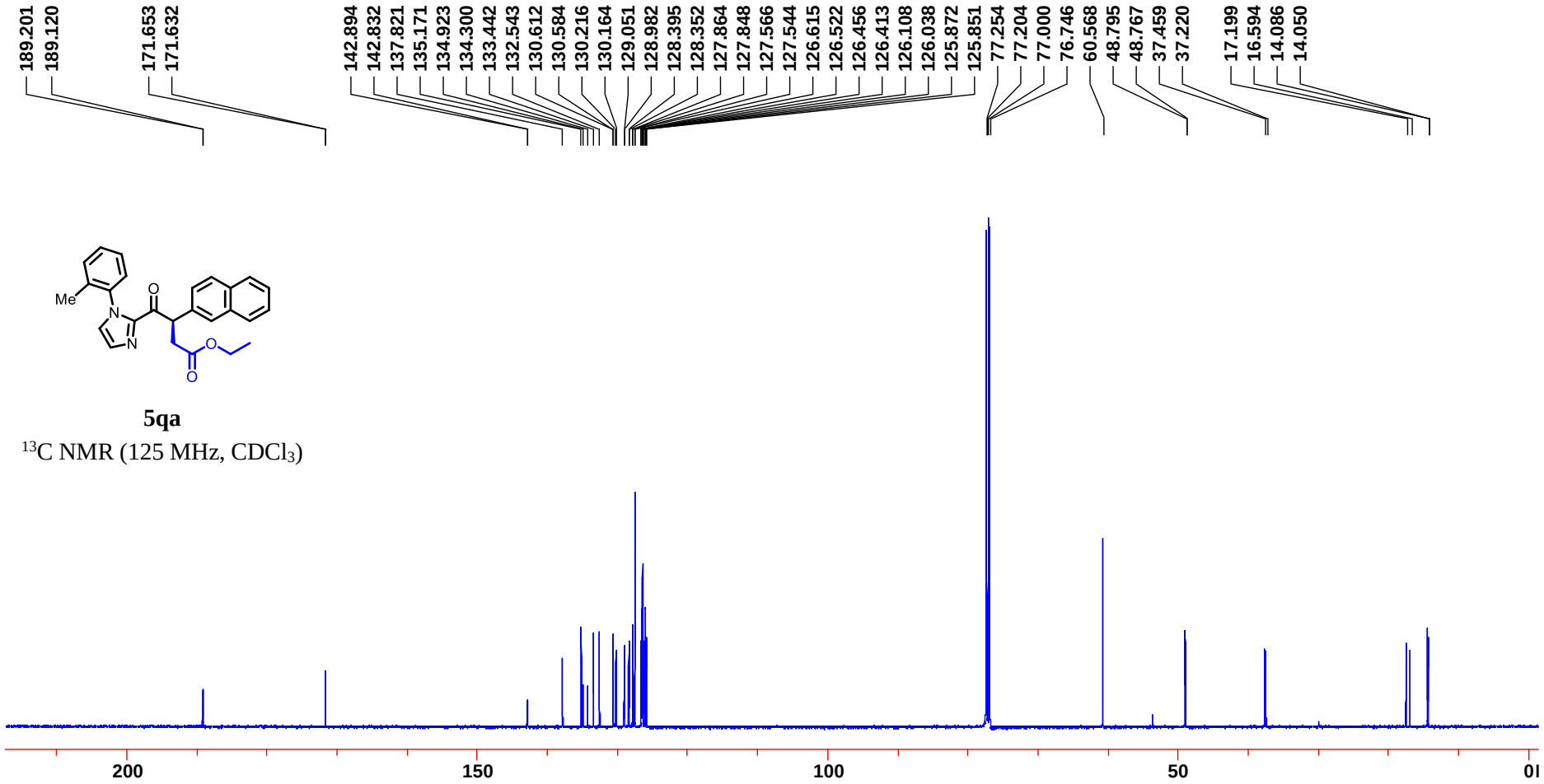




5qa

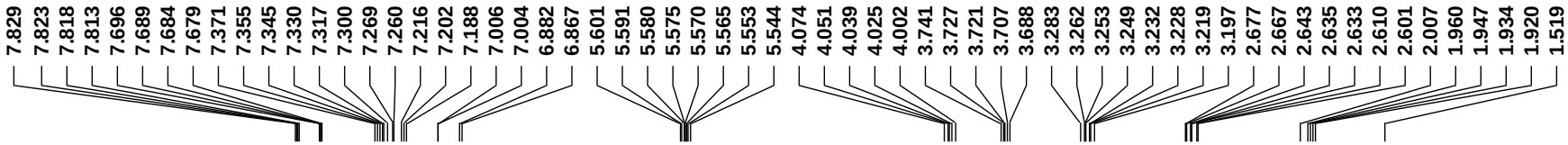
^{1}H NMR (500 MHz, $CDCl_3$)

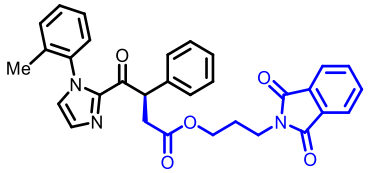




5qa

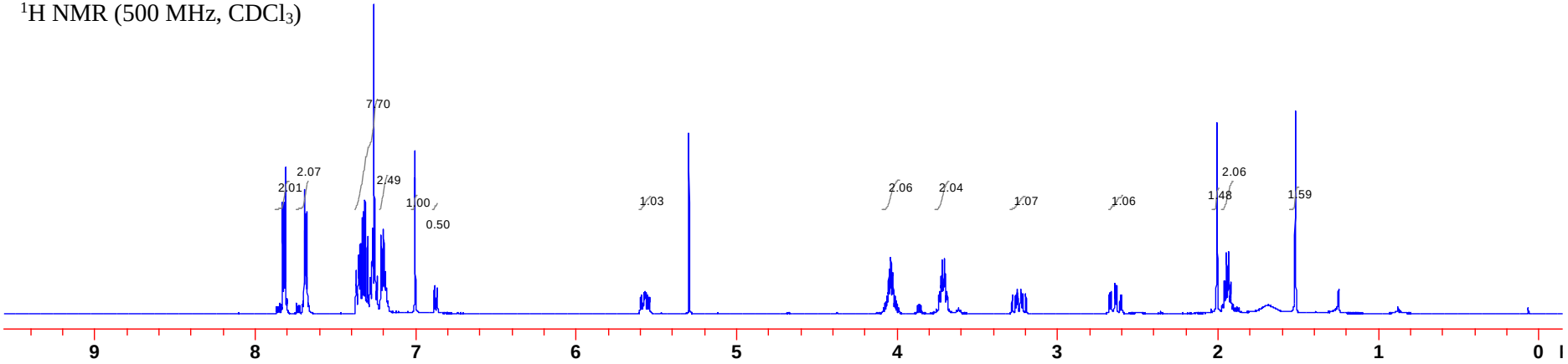
^{13}C NMR (125 MHz, $CDCl_3$)

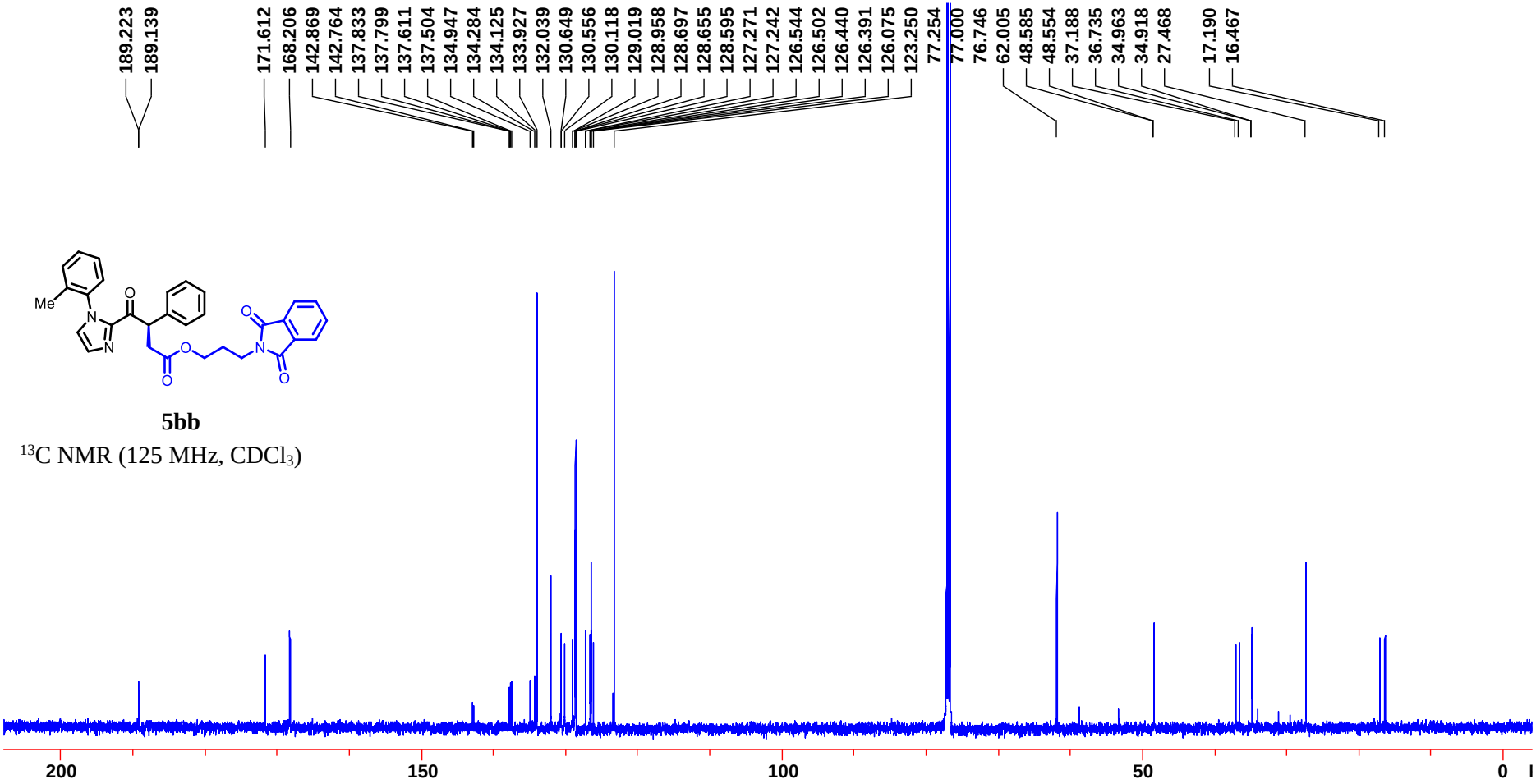




5bb

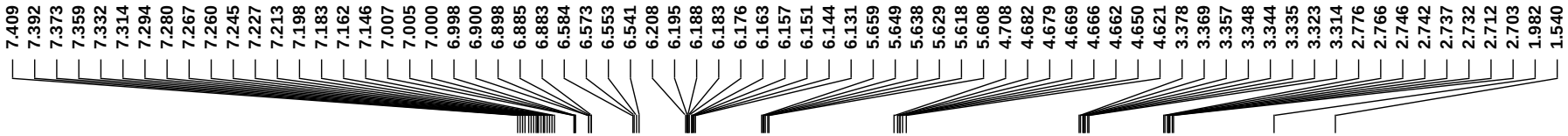
^{1}H NMR (500 MHz, $CDCl_3$)

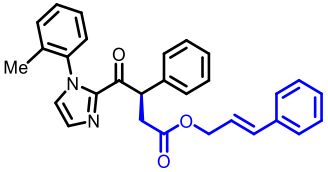




5bb

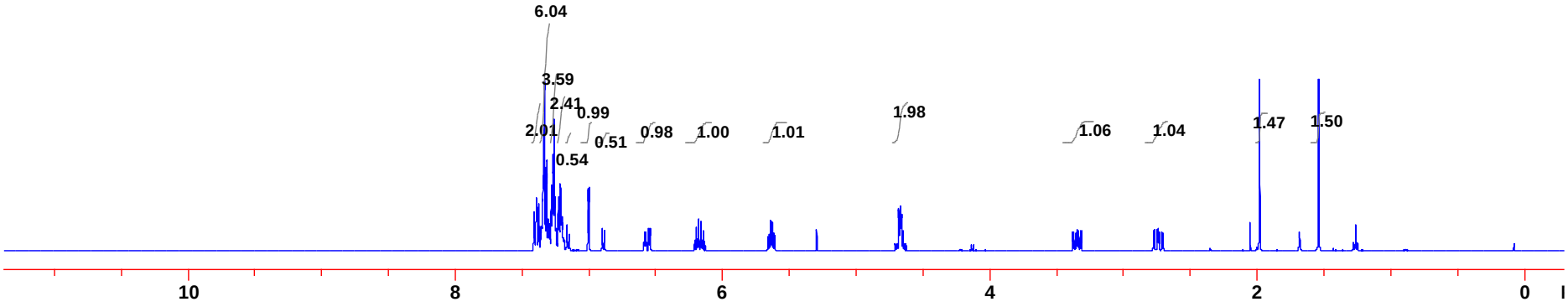
^{13}C NMR (125 MHz, $CDCl_3$)

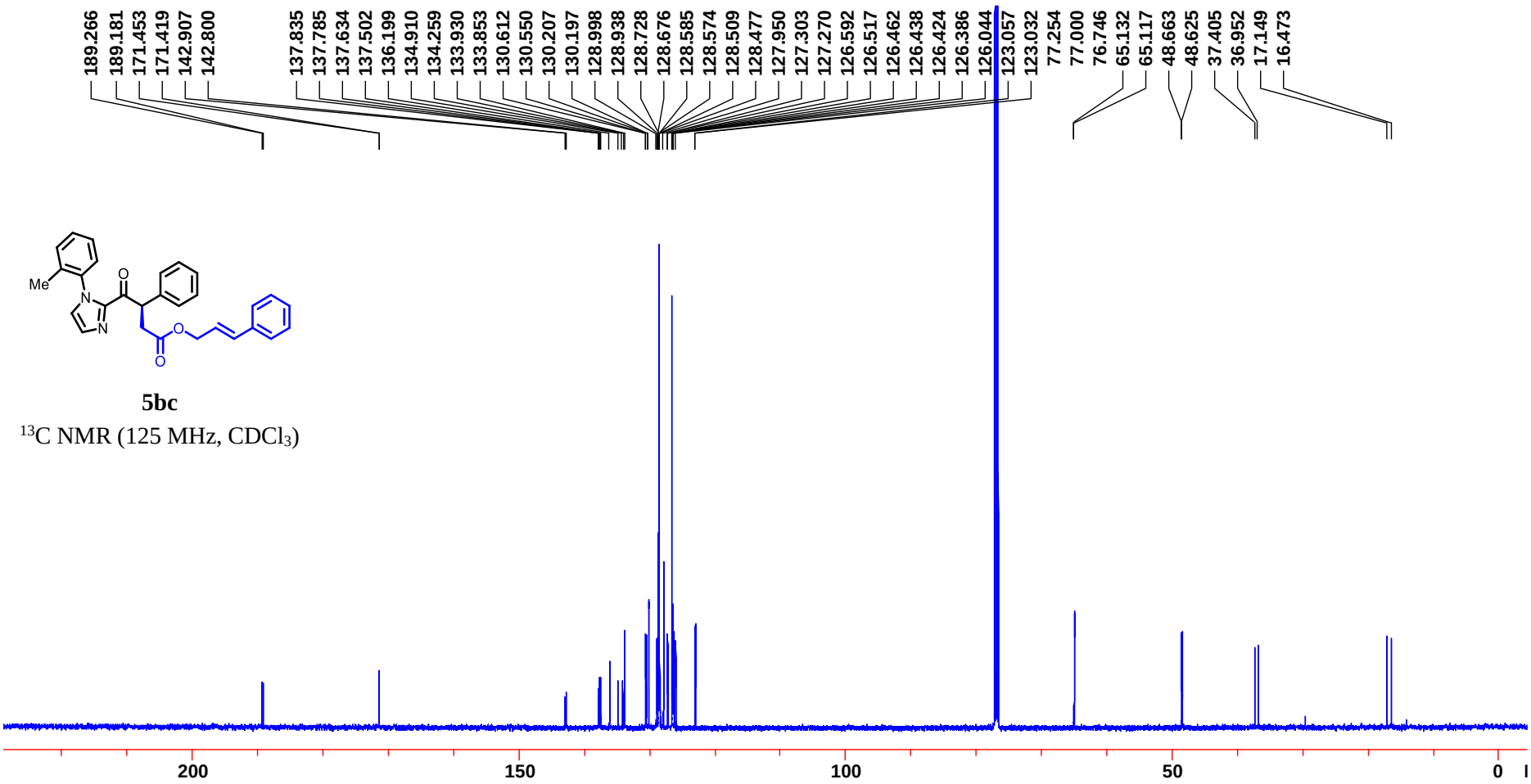




5bc

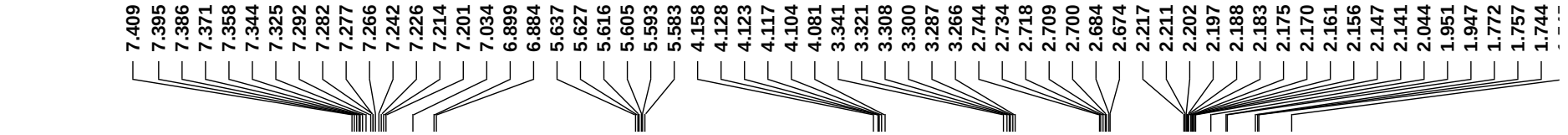
^{1}H NMR (500 MHz, $CDCl_3$)

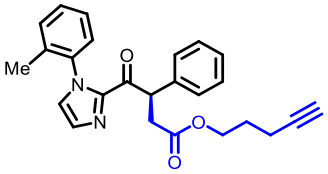




5bc

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





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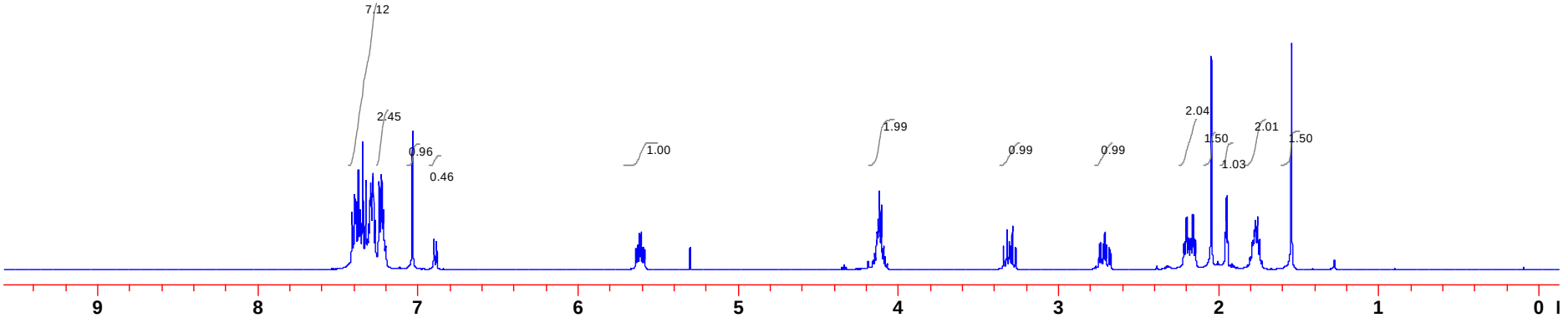
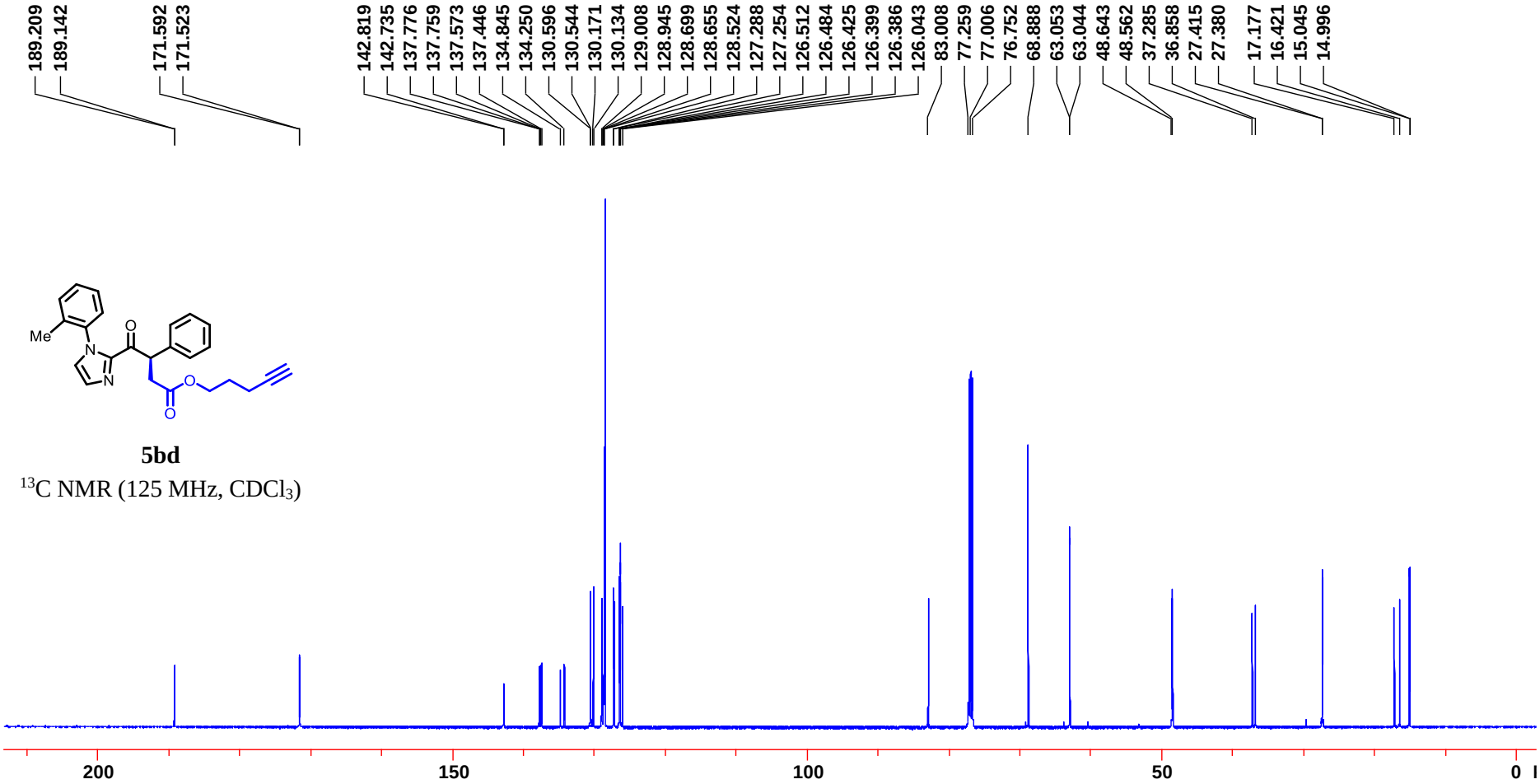
^{1}H NMR (500 MHz, $CDCl_3$)





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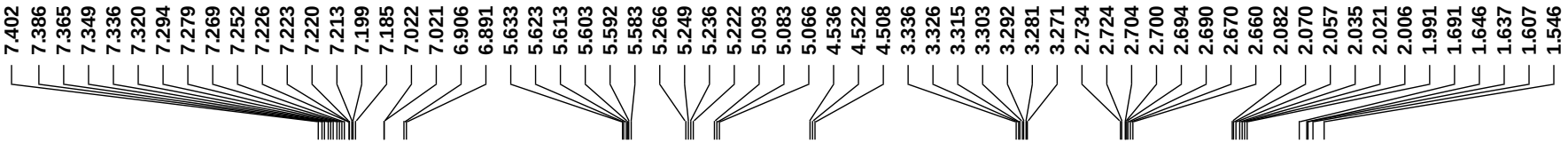
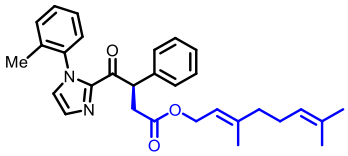
^{13}C NMR (125 MHz, $CDCl_3$)





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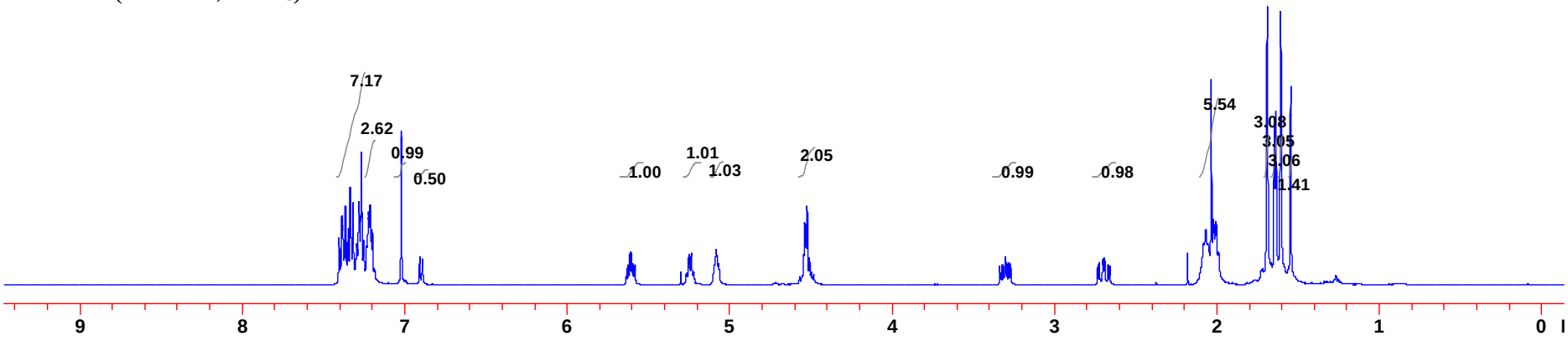
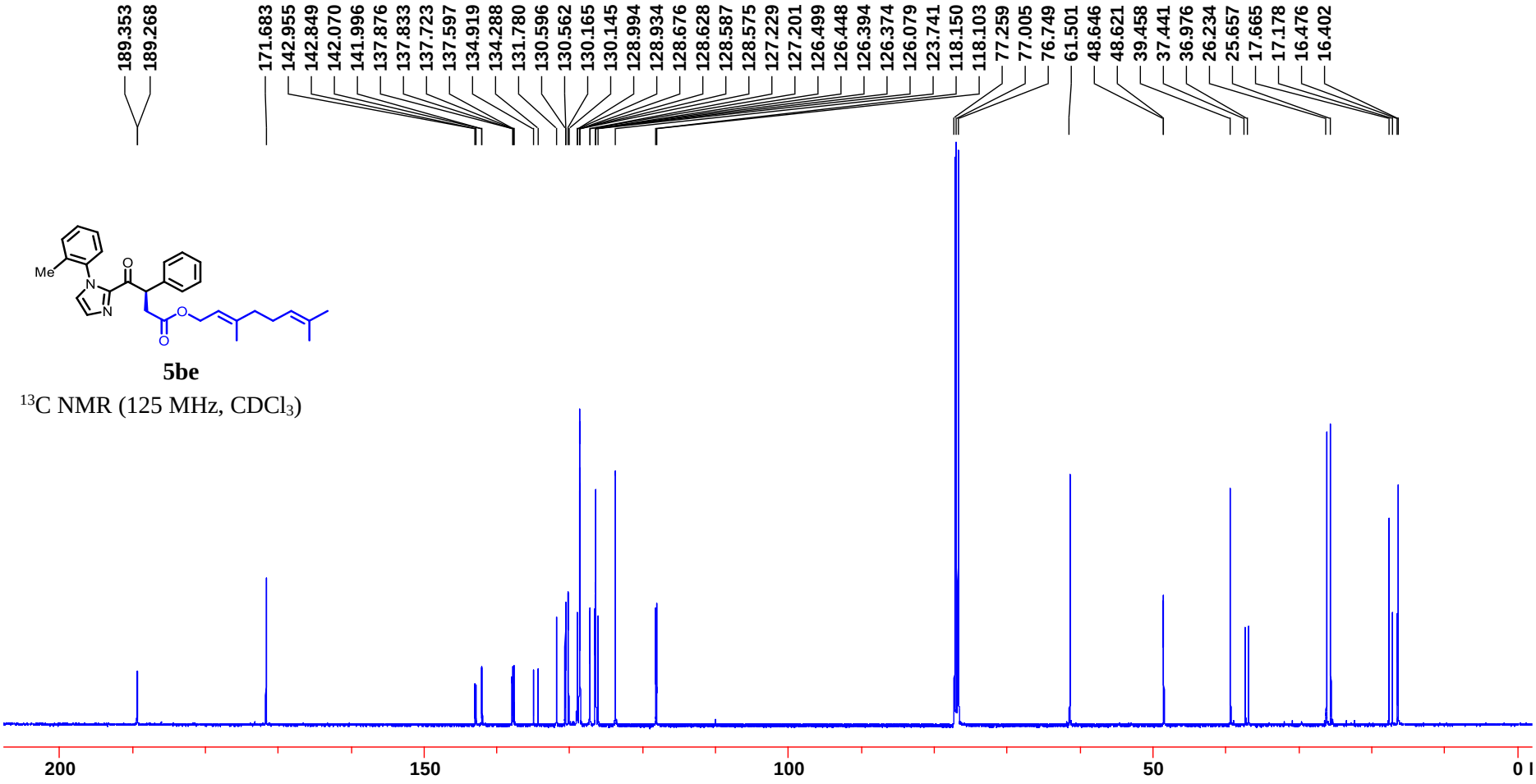
^{1}H NMR (500 MHz, $CDCl_3$)





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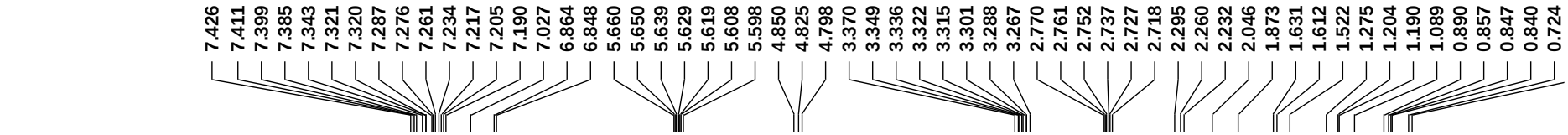
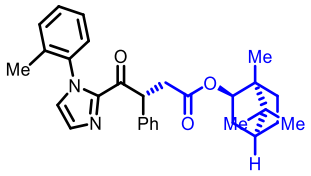
^{13}C NMR (125 MHz, $CDCl_3$)





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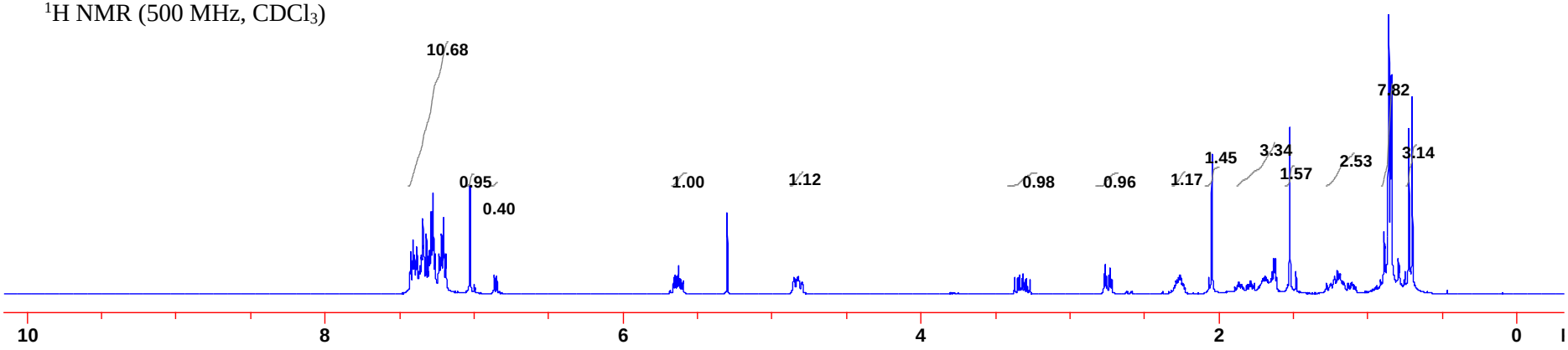
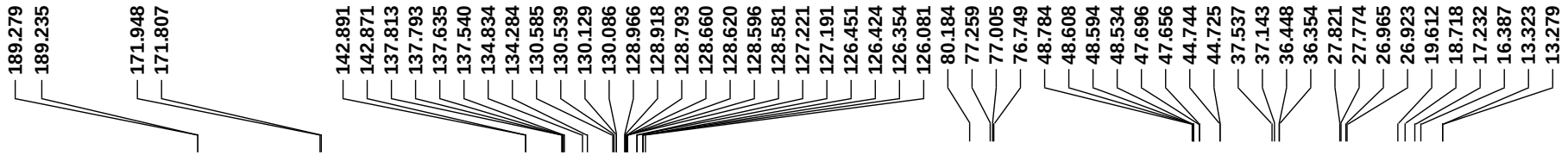
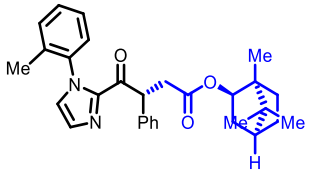
^{1}H NMR (500 MHz, $CDCl_3$)

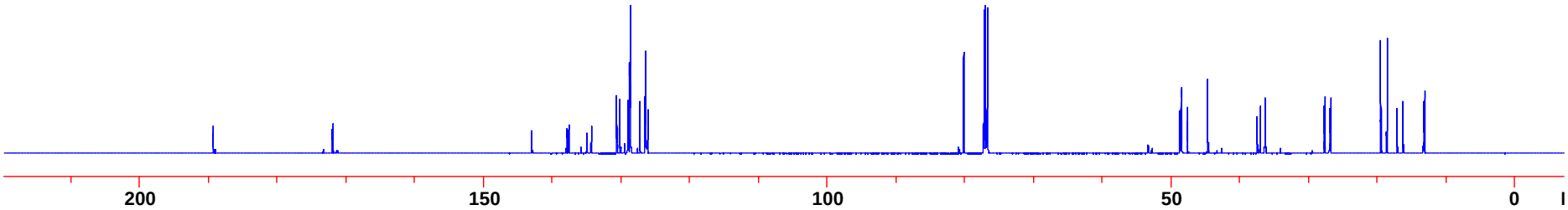


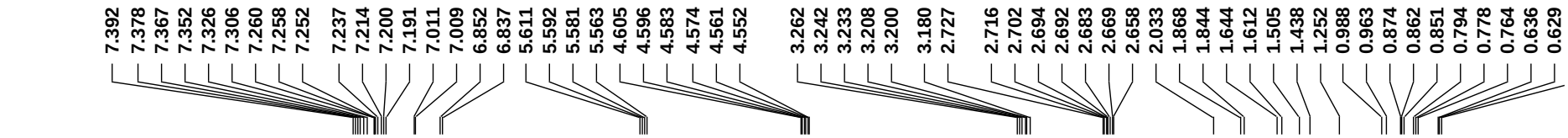


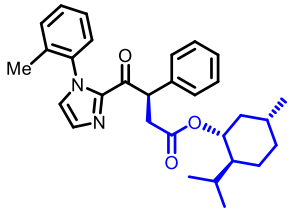


5bf

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

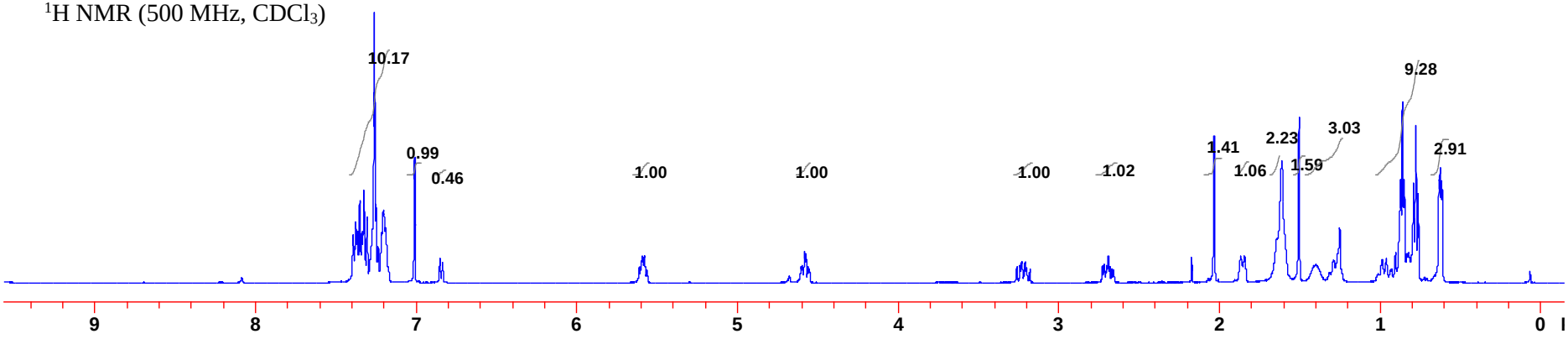


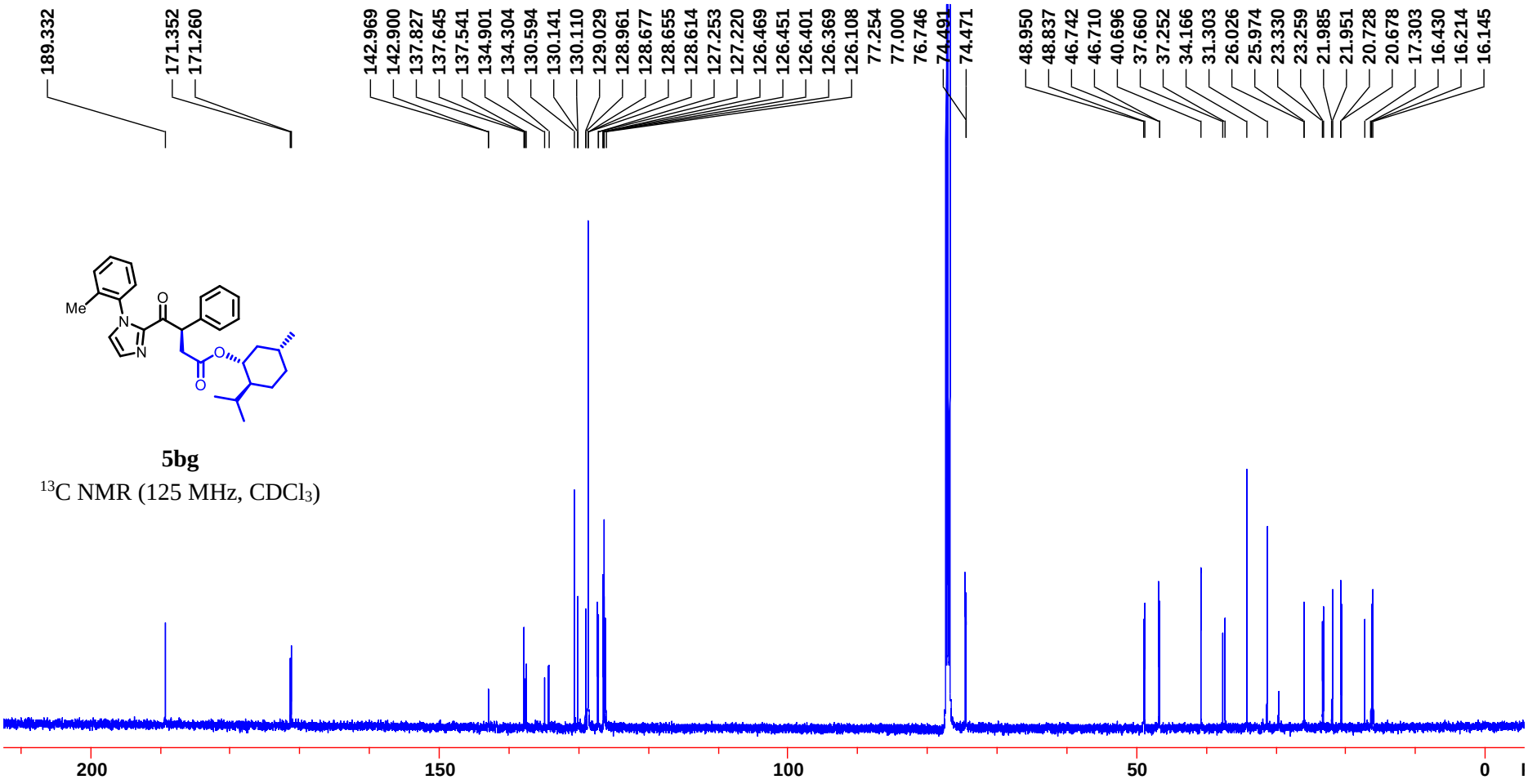




5bg

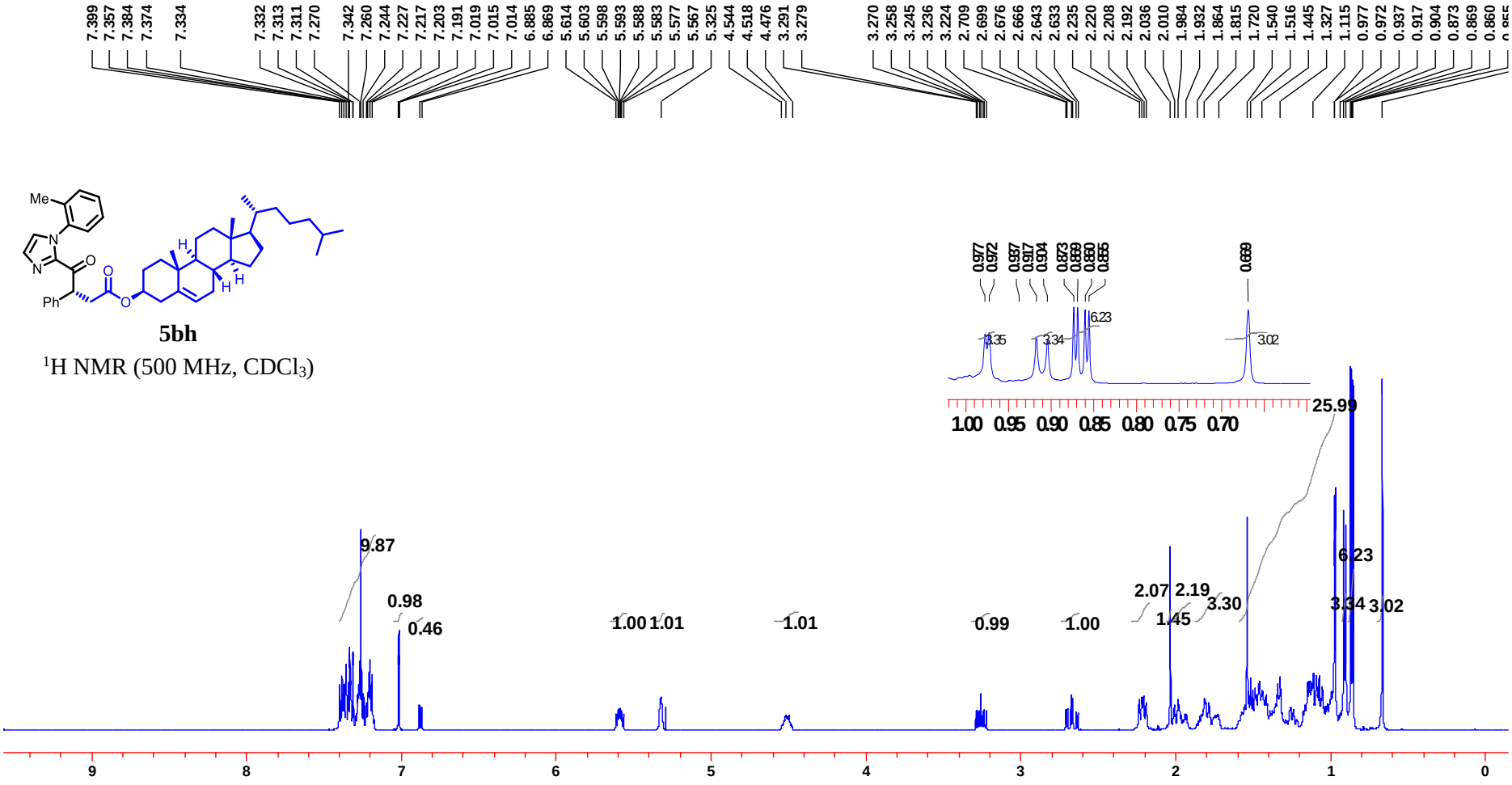
^{1}H NMR (500 MHz, $CDCl_3$)

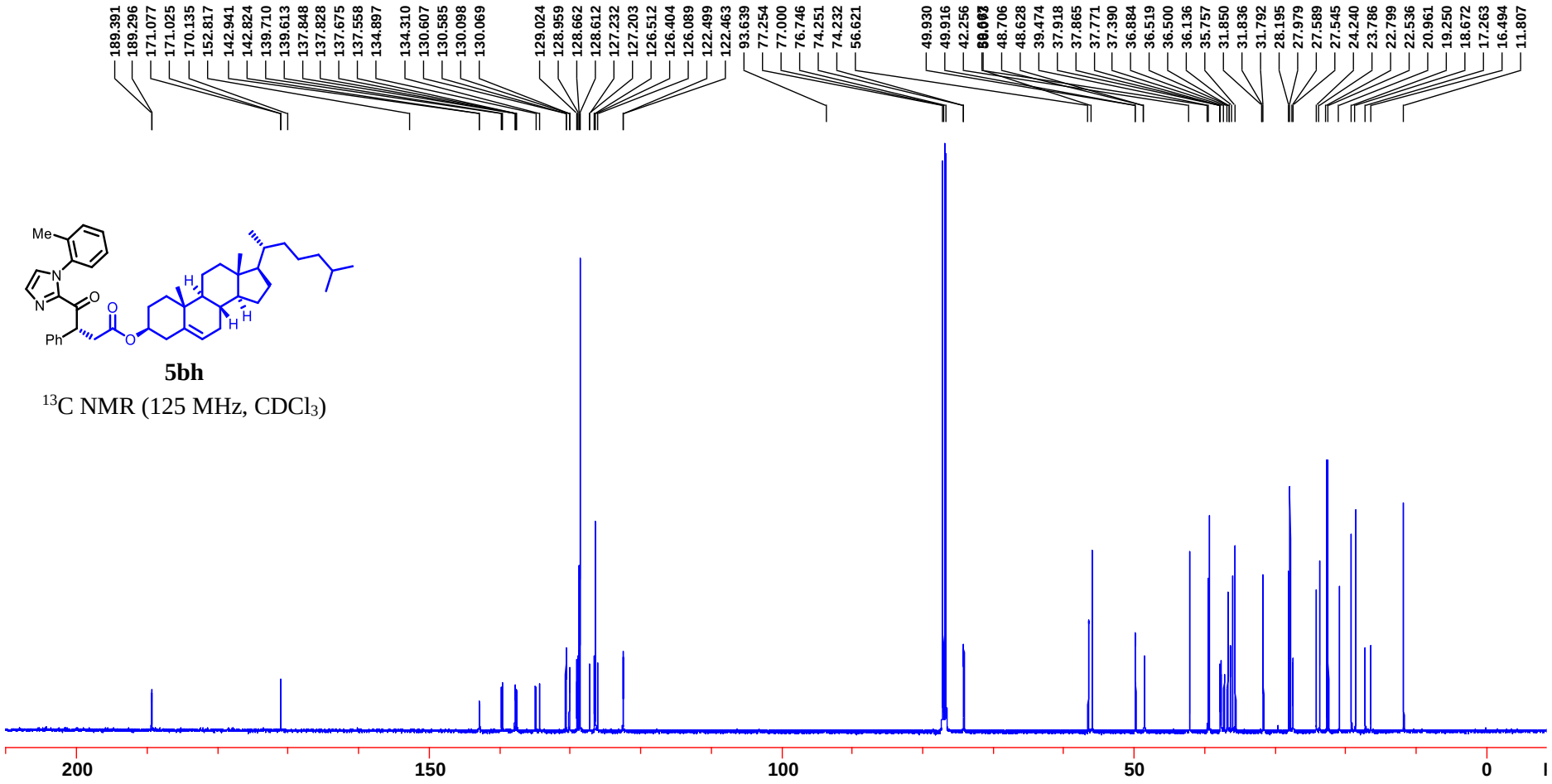




5bg

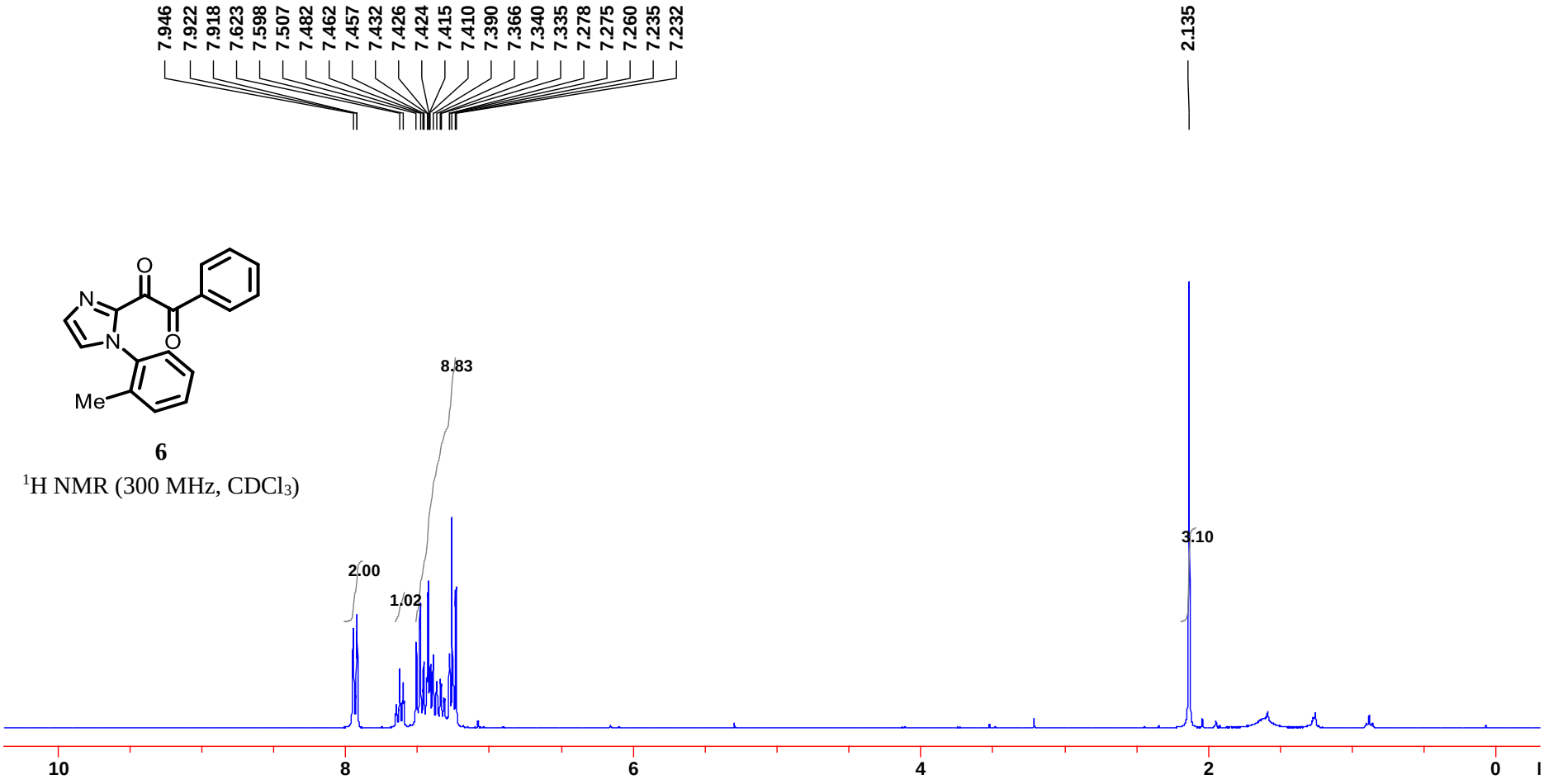
^{13}C NMR (125 MHz, $CDCl_3$)


7.399 7.357 7.384 7.374 7.334 7.332 7.313 7.311 7.270 7.342 7.260 7.244 7.227 7.217 7.203 7.191 7.019 7.015 7.014 6.885 6.869 5.614 5.603 5.598 5.593 5.588 5.583 5.577 5.567 5.325 4.544 4.518 4.476 3.291 3.279 3.270 3.258 3.245 3.236 3.224 2.709 2.699 2.676 2.666 2.643 2.633 2.235 2.220 2.208 2.192 2.036 2.010 1.984 1.932 1.864 1.815 1.720 1.540 1.516 1.445 1.327 1.115 0.977 0.972 0.937 0.917 0.904 0.873 0.869 0.860
Me
N
N
O
O
Ph
O
H
H
H
5bh
1H NMR (500 MHz, CDCl3)
0.977 0.972 0.937 0.917 0.904 0.873 0.869 0.860 0.855 0.669
6.23
3.35
3.34
3.02
1.00 0.95 0.90 0.85 0.80 0.75 0.70
25.99
9.87
0.98
0.46
1.00 1.01
1.01
0.99
1.00
2.07 2.19
1.45
3.30
6.23
3.34 3.02
9 8 7 6 5 4 3 2 1 0



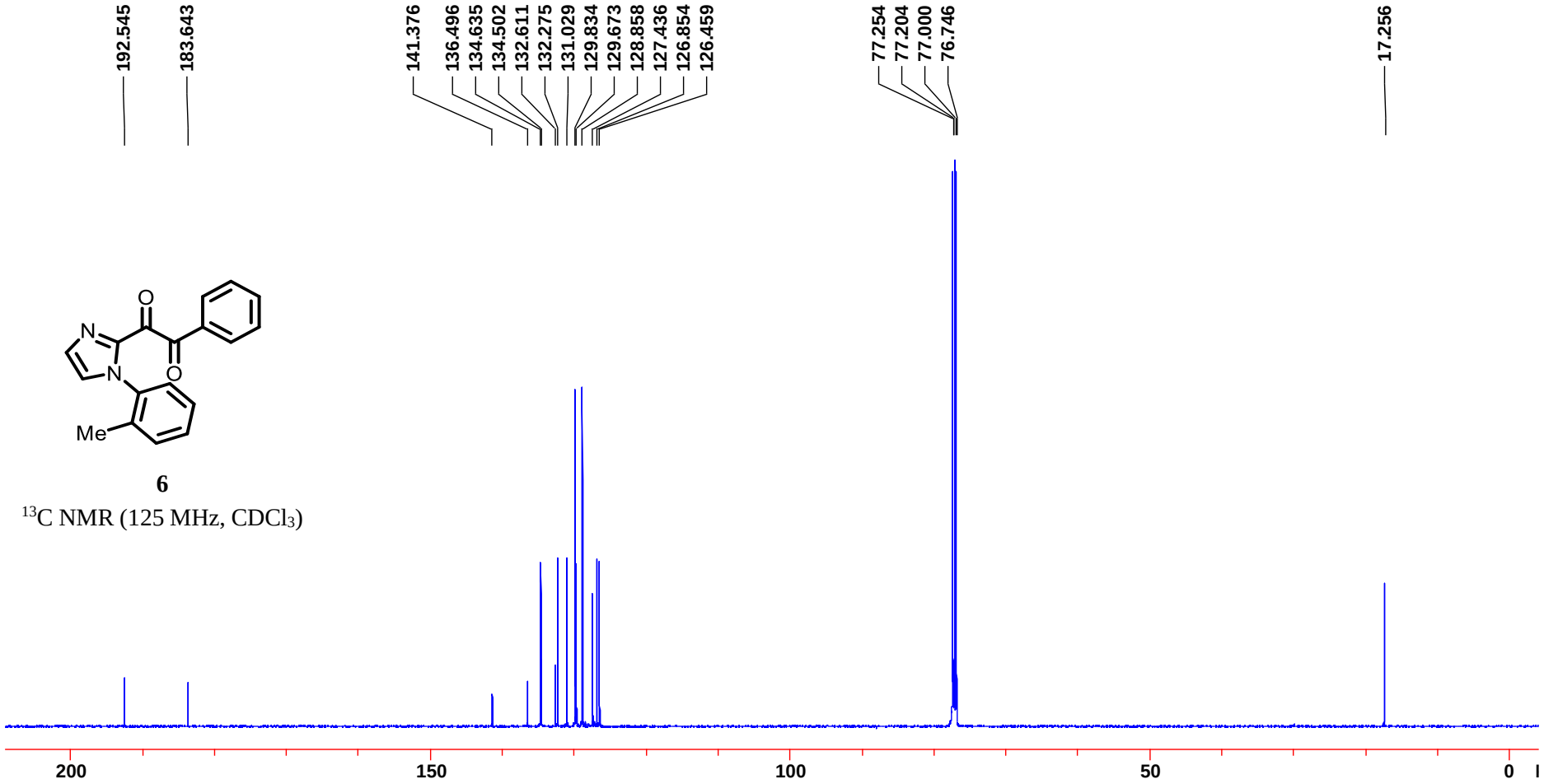
5bh

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



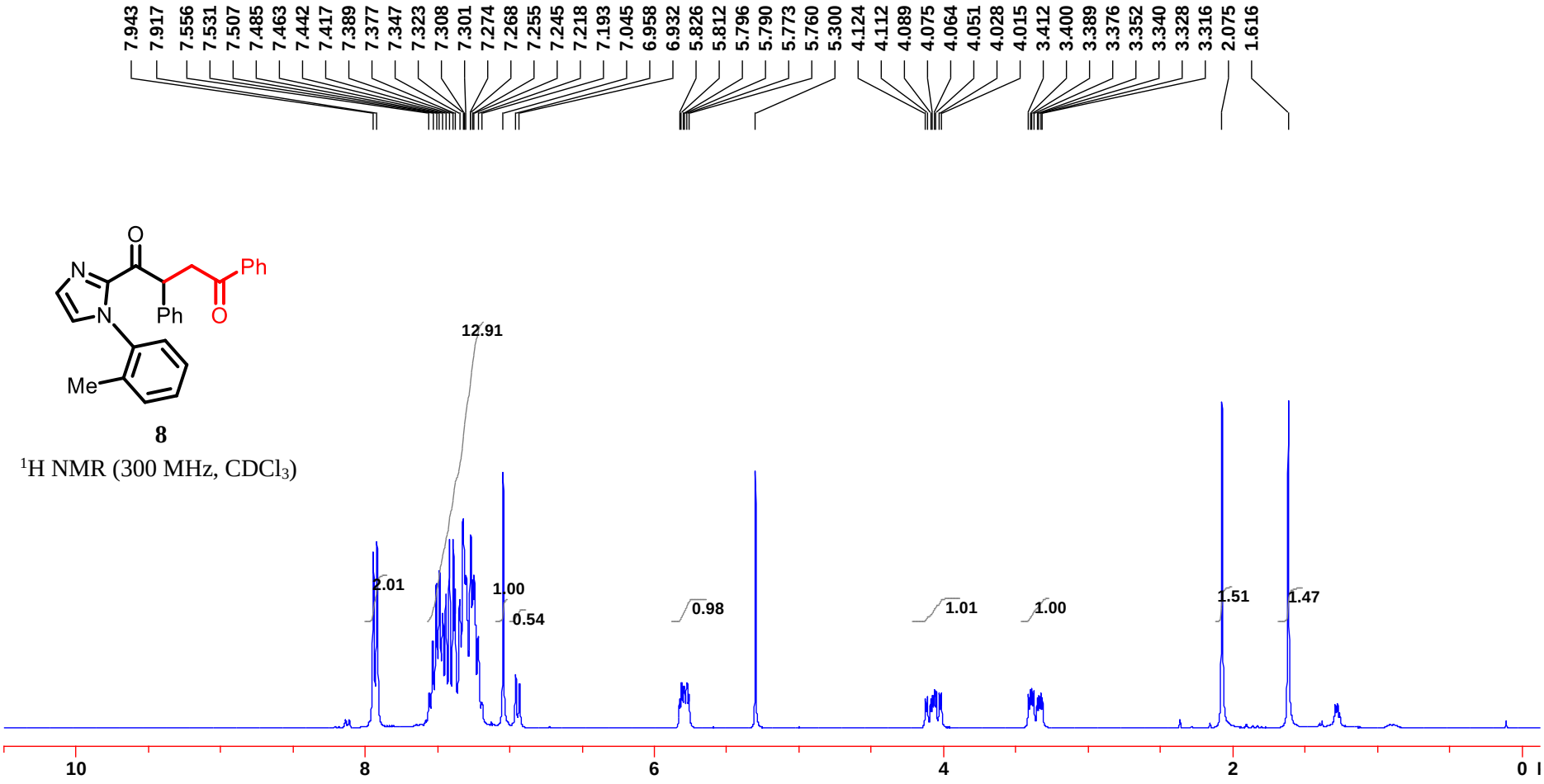
6

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



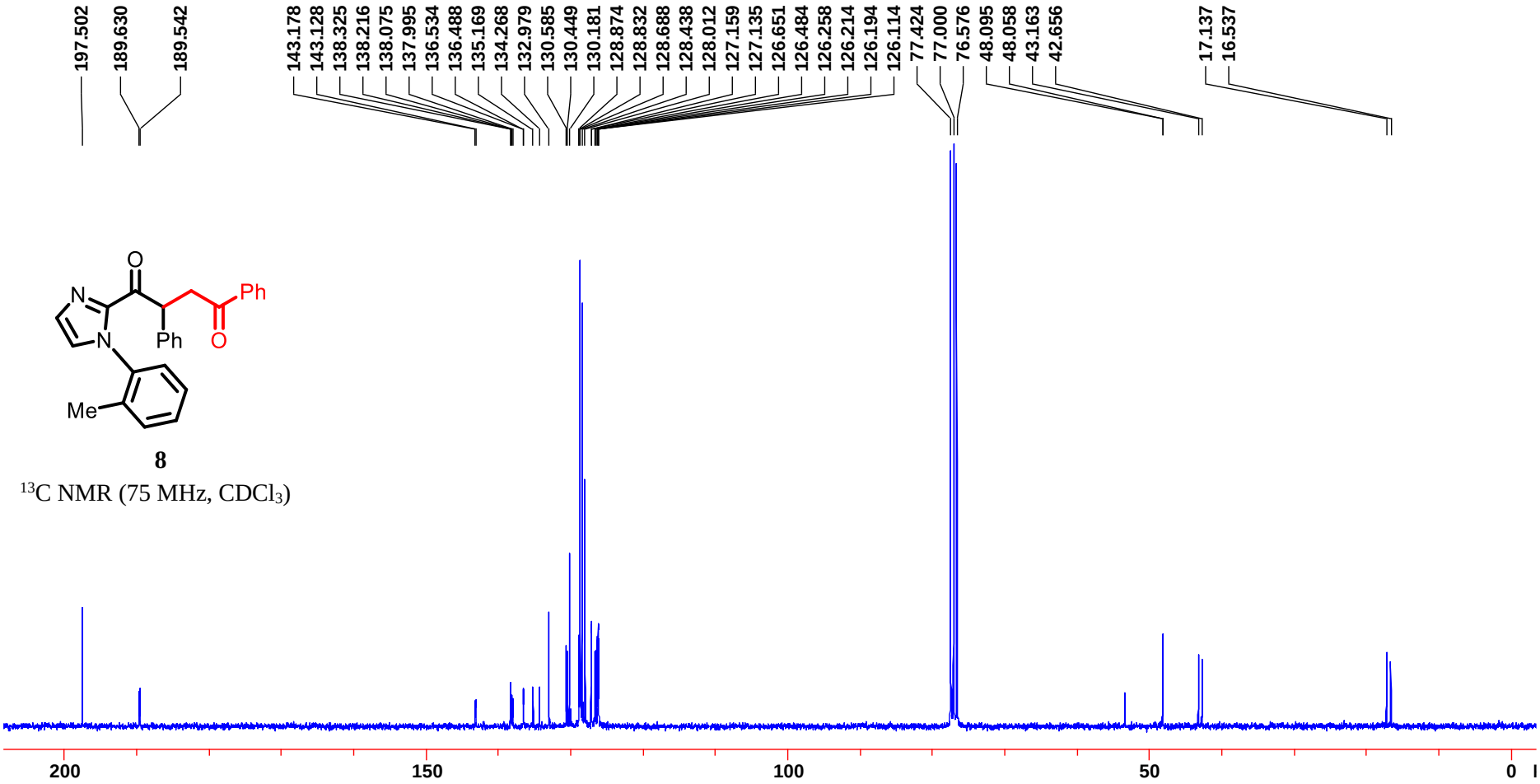
6

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



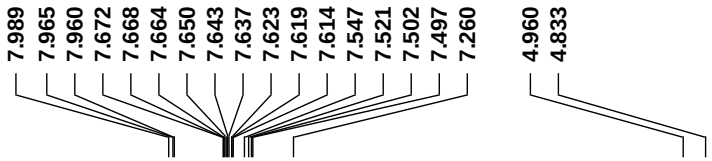
8

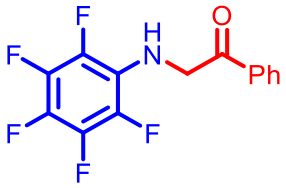
^{1}H NMR (300 MHz, $CDCl_3$)



8

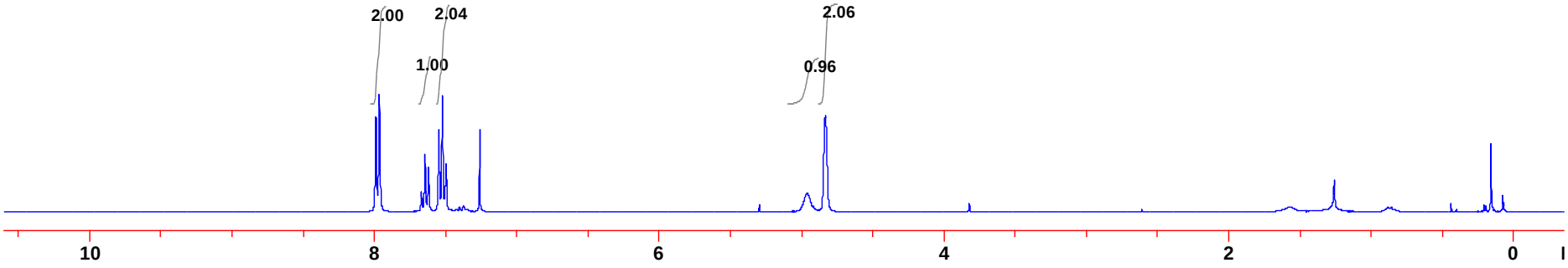
^{13}C NMR (75 MHz, $CDCl_3$)

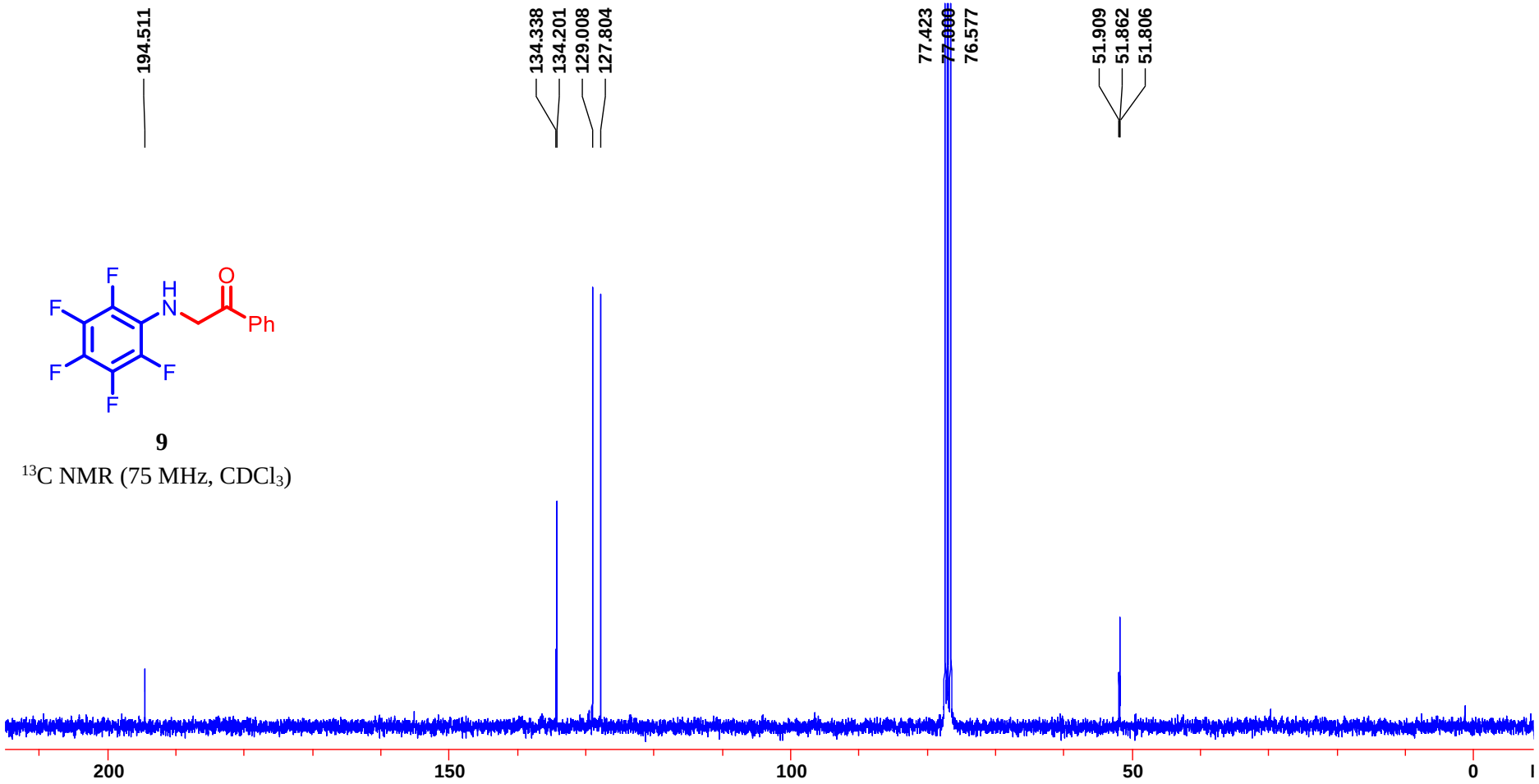




9

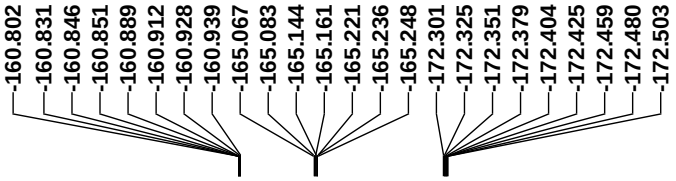
^{1}H NMR (300 MHz, $CDCl_3$)

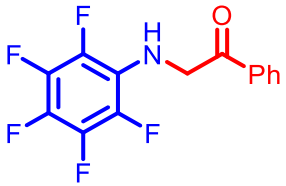




9

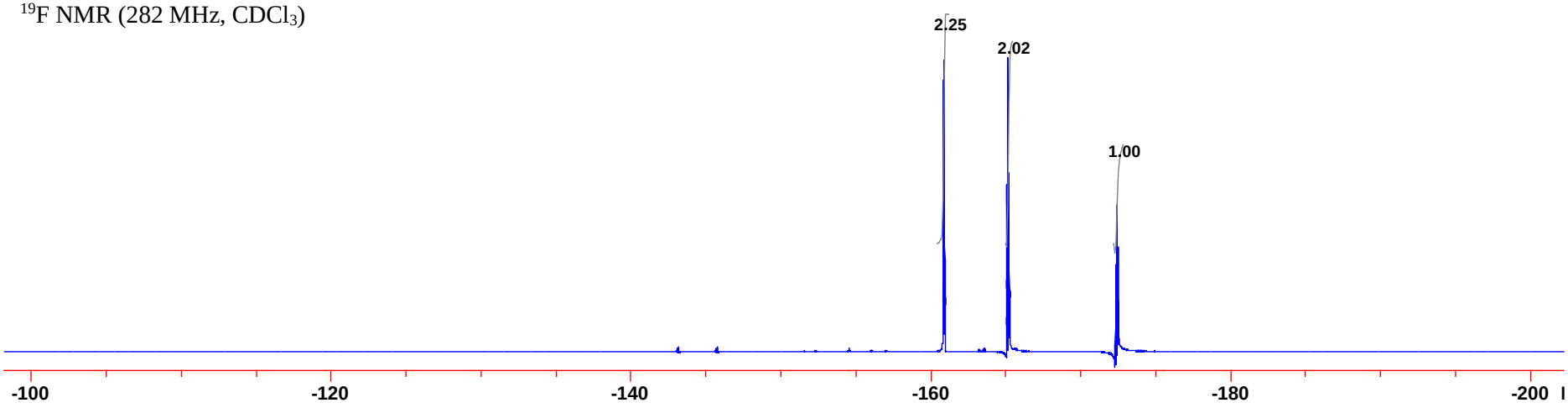
^{13}C NMR (75 MHz, $CDCl_3$)





9

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



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