Asymmetric Hydroalkylation of Alkynes and Allenes with Imidazolidinone Derivatives: α-Alkenylation of α-Amino Acids

Farhad Panahi,[a] Hormoz Khosravi,[a] Felix Bauer[a] and Bernhard Breit[a,*]

[a] Institut für Organische Chemie, Albert-Ludwigs-Universität Freiburg Albertstraße 21, 79104 Freiburg im Breisgau (Germany)

Outline

1. General methods and materials

■Chemicals were purchased from commercial suppliers and used without further purification, unless mentioned. Alkynes were either commercially available or synthesized according tothe reported procedures. Allenes were synthesized according to the reportedprocedures.

■Toluene was freshly distilled over Sodium/Benzophenone and degassed with argon prior to use. THF was freshly distilled over Na and collected under Argon. DMF was purchased from Acros and used as received. Other solvents for optimization study were purchased in p.a. grade and used without further purification. Solvents employed for work-up and column chromatography were purified prior to use by evaporation on a rotary evaporator.

■All reactions were performed using Schlenk technique in flame dried glassware under argon (Argon 5.0, Sauerstoffwerk Friedrichshafen).

■Reactions were monitored by TLC analysis which was performed on aluminum platespre-coated with silica gel (MERCK, 60 F-254), and visualized by UV fluorescence (λ_{max} = 254 nm) and/or by staining with 1% w/v $KMnO_4$ in 0.5 M aqueous K_2CO_3.

■FCC (Flash Column Chromatography) was accomplished using MACHEREY-NAGEL silica gel 60® (230-400 mesh).

■ NMR (Nuclear Magnetic Resonance) spectra were acquired on a Bruker Avance 400 spectrometer (400 MHz and 101 MHz for ^{1}H and ^{13}C respectively) and/or on a Bruker DRX 500 (500 MHz and 126 MHz for ^{1}H and ^{13}C respectively).

■All ^{1}H-NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signal at 7.26 ppm ($CHCl_3$).

■All ^{13}C-NMR spectra are reported in ppm relative to residual $CHCl_3$ (77.16 ppm) and were obtained with 1H-decoupling.

■Data for ^{1}H-NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; quin, quintet; sx, sextet; sept, septet; m, multiplet; mc, centered multiplet, app, apparent; br, broad signal), coupling constant (Hz), integration.

■Data for ^{13}C-NMR spectra are described in terms of chemical shift (δ in ppm).

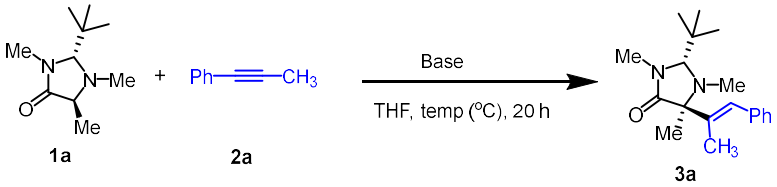
■High-resolution mass spectra (HR-MS) were obtained on a Thermo Scientific Advantage and a Thermo Scientific Exactive instrument (APCI/MeOH: spray voltage 4-5 kV, ion transfer tube: 250-300 °C, vaporizer: 300-400 °C).

■Chiral HPLC were performed on a Merck Hitachi HPLC apparatus (pump: L-7100, UV detector: L-7400, auto sampler: L-7200 oven: L-7360) a Varian Pro Star (pump: 230, UV detector: 310, auto sampler: 410, oven: 510) and a Hitachi Primade (pump: 1100, DAD detector: 1430, auto sampler: 1210, oven: 1310). Used columns: Dr. MaischReprosil AM-3. Diacel Chiralpak AS, AD-H, AD-3, OB-H, OD-3, OJ-H, IC. Phenomenex Lux LA-1, LA-2, LC-1, LC-2, LC-3, LC-4.

■Melting points were measured with a Bibby Scientific Limited Stuart smp10.

2. Optimization of reaction condition

Table 1S. Screening of base

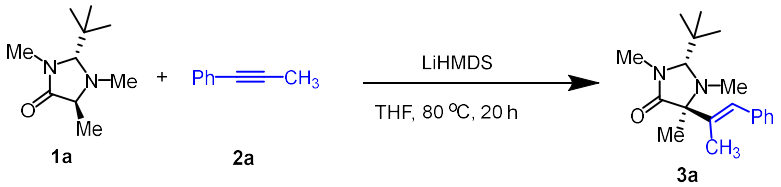


entry	base (eq)	temp (°C)	yield of **3a** (%)[b]	dr[c]	**er**[d]
1	NaOH (2.0)	100	0	-	-
2	NaH (2.0)	100	0	-	-
3	K_3PO_4 (2.0)	100	0	-	-
4	K_2CO_3 (2.0)	100	0	-	-
5	Cs_2CO_3 (2.0)	100	0	-	-
6	KtOBu (2.0)	100	0	-	-
7	LiHMDS (2.0)	80	91	>99:1	>99:1
8	NaHMDS (2.0)	80	82	>99:1	56:44
9	KHMDS (2.0)	80	79	>99:1	68:32
10	LDA (2.0)	80	75	95:5	95:5
11	n-BuLi (2.0)	80	71	92:8	90:10

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), base (0.4 mmol), THF (2.0 mL, 0.08M).

[b]NMR yield with 1,3,5-trimethoxybenzene(TMB) as reference. [c]dr were determined using ^{1}HNMR.[d] er was determined by chiral HPLC.

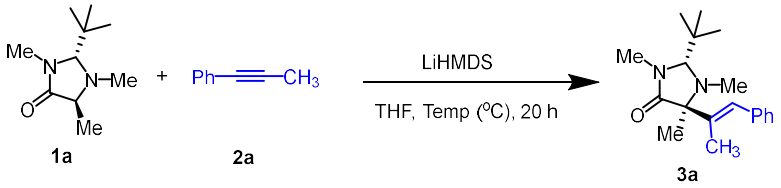
Table 2S. Screening of solvent



entry	base (eq)	Solvent	yield of **3a** (%)[b]	dr[c]
1	LiHMDS (2.0)	THF	91	>99:1
2	LiHMDS (2.0)	Toluene	84	>99:1
3	LiHMDS (2.0)	DMF	55	91:9
4	LiHMDS (2.0)	DCE	trace	ND
5	LiHMDS (2.0)	1,4-dioxane	73	>99:1
6	LiHMDS (2.0)	Benzene	83	>99:1
7	LiHMDS (2.0)	CH_3CN	25	ND
8	LiHMDS (2.0)	CH_2Cl_2	trace	ND

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), LiHMDS (0.4 mL, 1.0 M in THF), solvent (2.0 mL, 0.08M).
[b]NMR yield with 1,3,5-trimethoxybenzene(TMB) as reference. [c]dr were determined using ^{1}HNMR.

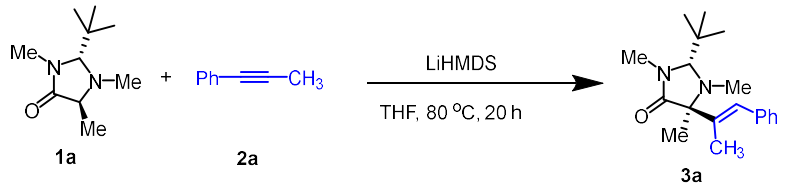
Table 3S. Screening of temperature



entry	base (eq)	Temp (°C)	yield of **3a** (%)[b]	dr[c]
1	LiHMDS (2.0)	rt	30	>99:1
2	LiHMDS (2.0)	50	48	>99:1
3	LiHMDS (2.0)	60	85	>99:1
4	LiHMDS (2.0)	70	87	>99:1
5	LiHMDS (2.0)	80	91	>99:1
6	LiHMDS (2.0)	90	86	97:3
7	LiHMDS (2.0)	100	80	95:5
8	LiHMDS (2.0)	110	68	90:10

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), base (0.4 mmol), THF (2.0 mL, 0.08M).
[b]NMR yield with 1,3,5-trimethoxybenzene(TMB) as reference. [c]dr were determined using ^{1}HNMR.

Table 4S. Screening of ratio of 1a, 2a and base



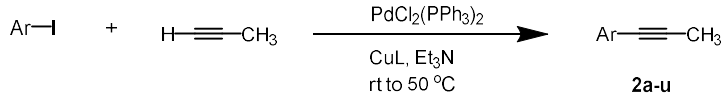
entry	**1a**:**2a**:LiHMDS	yield of **3a** (%)[b]	dr[c]
1	1:1:2	91	>99:1
2	1:1.5:2.5	85	98:2
3	1:1.2:2.2	90	98:2
4	1:1:2.2	92	98:2
5	1:1:1	23	>99:1
6	1:1:1.5	58	>99:1
7	1:1:0.5	trace	ND
8	1.5:1:2.5	62	>99:1

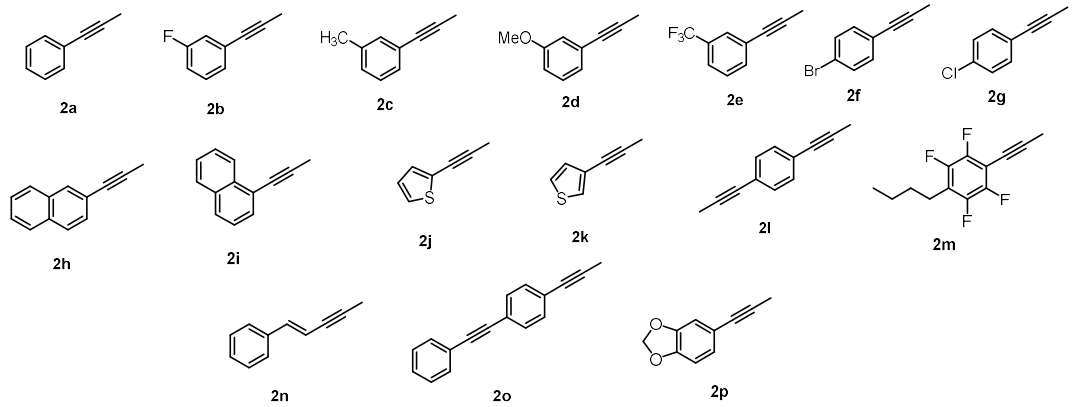
[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), base (0.4 mmol), THF (2.0 mL, 0.08M).

[b]NMR yield with 1,3,5-trimethoxybenzene(TMB) as reference. [c] dr were determined using ^{1}HNMR.

3. Synthesized substrates for this protocol

3.1. Aryl-methyl alkynes



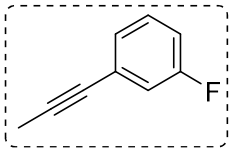


3.1.1. General procedure for the synthesis of alkynes

To a solution of iodobenzene derivative (5.0 mmol, 1.0 equiv), $PdCl_2(PPh_3)_2$ (2.0 mol %) and CuI (4.0 mol %) was added 15.0 mL of triethylamine. The reaction mixture was stirred under argon at room temperature to 50 °C for 5 minutes. Then, propyne (ca. 5% in tetrahydrofuran, ca. 1.0 mol/L, purchased from TCI) was added in one portion to the reaction mixture. The reaction solution was stirred between 5 hours to 24 hours (depends to the aryl halide used). To monitor the complete of the reaction TLC was used. After completion of the reaction it was cooled to room temperature and dilutedby ethyl acetate (60.0 mL). Filtration of the reaction mixture through a plug of Celite afforded an organic phase without precipitate. This obtained organic phase was washed with water and brine and it was dried over anhydrous Na_2SO_4. After collection of organic layer, it was concentrated in in vacuo and the residue was purified by flash chromatography on silica gel with pentane to obtain the pure products (**2b-u**).

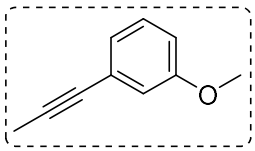
3.1.2. Spectral data for the synthesized aryl-methyl alkynes derivative

3.1.2.1. 1-Fluoro-3-(prop-1-yn-1-yl)benzene (2b)



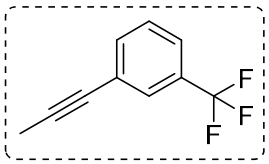
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.19 (m, 1H), 7.17 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.09 (ddd, *J* = 9.6, 2.6, 1.4 Hz, 1H), 7.02 – 6.94 (m, 1H), 2.05 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.5 (d, *J* = 245.8 Hz), 129.8 (d, *J* = 9.0 Hz), 127.5 (d, *J* = 3.2 Hz), 126.0 (d, *J* = 9.4 Hz), 118.4 (d, *J* = 22.7 Hz), 114.9 (d, *J* = 21.2 Hz), 87.1, 78.8 (d, *J* = 3.4 Hz), 4.4; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -113.40, -113.41.

3.1.2.2. 1-Methoxy-3-(prop-1-yn-1-yl)benzene (2d)



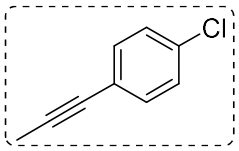
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.15 (m, 1H), 7.00 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.95 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.84 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 3.79 (s, 3H), 2.05 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.4, 129.3, 125.2, 124.1, 116.6, 114.2, 85.7, 79.8, 55.3, 4.3.

3.1.2.3.1-(Prop-1-yn-1-yl)-3-(trifluoromethyl)benzene (2e)



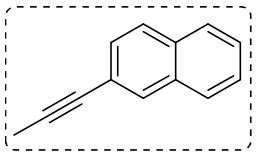
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.57 – 7.49 (m, 2H), 7.42 – 7.35 (m, 1H), 2.06 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 130.9 (q, *J* = 32.5 Hz), 128.4 (q, *J* = 4.0 Hz), 125.3, 125.1, 124.2 (q, *J* = 3.9 Hz), 122.6, 87.8, 78.6, 4.3; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -63.02.

3.1.2.4. 1-Chloro-4-(prop-1-yn-1-yl)benzene (2g)



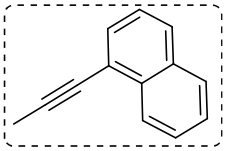
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 1H), 7.27 – 7.23 (m, 1H), 2.04 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.6, 132.8, 128.6, 122.7, 87.0, 78.8, 4.4.

3.1.2.5.2-(Prop-1-yn-1-yl)naphthalene (2h)



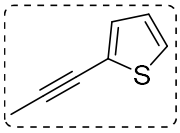
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (s, 1H), 7.84 – 7.74 (m, 3H), 7.52 – 7.43 (m, 3H), 2.12 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 133.2, 132.6, 131.1, 128.8, 127.9, 127.8, 127.7, 126.5, 126.4, 121.47, 86.3, 80.2, 4.5.

3.1.2.6.1-(Prop-1-yn-1-yl)naphthalene(2i)



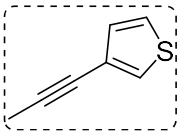
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (ddd, *J* = 9.1, 1.8, 0.8 Hz, 1H), 7.90 – 7.85 (m, 1H), 7.81 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 7.1, 1.1 Hz, 1H), 7.60 (ddd, *J* = 8.3, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.1, 6.8, 1.4 Hz, 1H), 7.44 (dd, *J* = 8.3, 7.1 Hz, 1H), 2.25 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 133.7, 133.3, 130.1, 128.3, 128.0, 126.5, 126.4, 126.3, 125.3, 121.9, 90.9, 77.9, 4.7.

3.1.2.7. 2-(Prop-1-yn-1-yl)thiophene (2j)



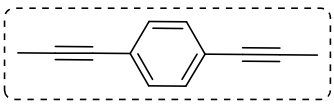
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.12 (ddd, *J* = 3.6, 1.1, 0.5 Hz, 1H), 6.94 (dd, *J* = 5.2, 3.6 Hz, 1H), 2.08 (d, *J* = 0.5 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 130.9, 126.8, 125.9, 124.3, 90.0, 73.0, 4.6.

3.1.2.8. 3-(Prop-1-yn-1-yl)thiophene (2k)



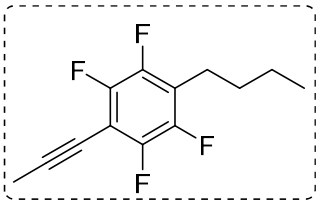
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 3.0, 1.1 Hz, 1H), 7.23 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.07 (dd, *J* = 5.0, 1.2 Hz, 1H), 2.03 (s, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 130.0, 127.6, 125.0, 123.1, 85.4, 74.9, 4.3.

3.1.2.9. 1,4-Di(prop-1-yn-1-yl)benzene (2l)



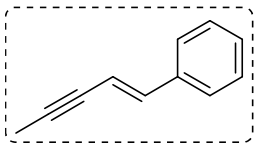
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 2.05 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.4, 123.3, 87.4, 79.7, 4.5.

3.1.2.10. 1-Butyl-2,3,5,6-tetrafluoro-4-(prop-1-yn-1-yl)benzene (2m)



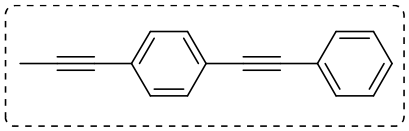
^{1}H NMR (500 MHz, $CDCl_3$) δ 4.45 (t, *J* = 9.4 Hz, 1H), 2.98 (ddd, *J* = 10.0, 1.8, 0.9 Hz, 1H), 2.72 (ddd, *J* = 7.7, 3.1, 1.5 Hz, 1H), 1.78 (s, 1H), 1.65 – 1.49 (m, 2H), 1.38 (dq, *J* = 14.7, 7.4 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 2H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.0,146.1 (ddd, *J* = 12.2, 8.5, 4.1 Hz), 144.9 (ddd, *J* = 15.0, 6.2, 3.6 Hz), 144.2 (ddd, *J* = 14.2, 8.0, 3.7 Hz), 143.0 (ddd, *J* = 14.7, 6.4, 3.4 Hz), 118.5 (t, *J* = 18.9 Hz), 113.2 (t, *J* = 18.0 Hz), 96.1 (t, *J* = 2.5 Hz), 69.6, 33.4, 31.6, 29.8, 22.6, 22.5, 13.8, 13.2, 13.2, 13.1; **^{19}F NMR** (377 MHz, $CDCl_3$) δ -141.08 (dd, *J* = 22.5, 12.1 Hz), -146.23 (dd, *J* = 22.6, 12.0 Hz).

3.1.2.11. (*E*)-Pent-1-en-3-yn-1-ylbenzene (2n)



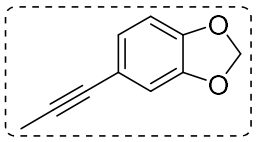
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.22 (m, 8H), 6.86 (d, *J* = 16.4 Hz, 1H), 6.13 (dq, *J* = 16.2, 2.4 Hz, 1H), 2.01 (dd, *J* = 2.4, 0.6 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.2, 136.7, 128.8, 128.4, 126.2, 109.0, 88.4, 79.1, 4.6, 1.2.

3.1.2.12. 1-(Phenylethynyl)-4-(prop-1-yn-1-yl)benzene (2o)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.46 – 7.42 (m, 1H), 7.39 – 7.33 (m, 1H), 2.07 (s, 1H);**^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.7, 131.6, 131.6, 128.5, 124.1, 123.3, 122.5, 90.9, 89.3, 88.0, 79.7, 4.5.

3.1.2.13. 5-(Prop-1-yn-1-yl)benzo[d][1,3]dioxole (2p)

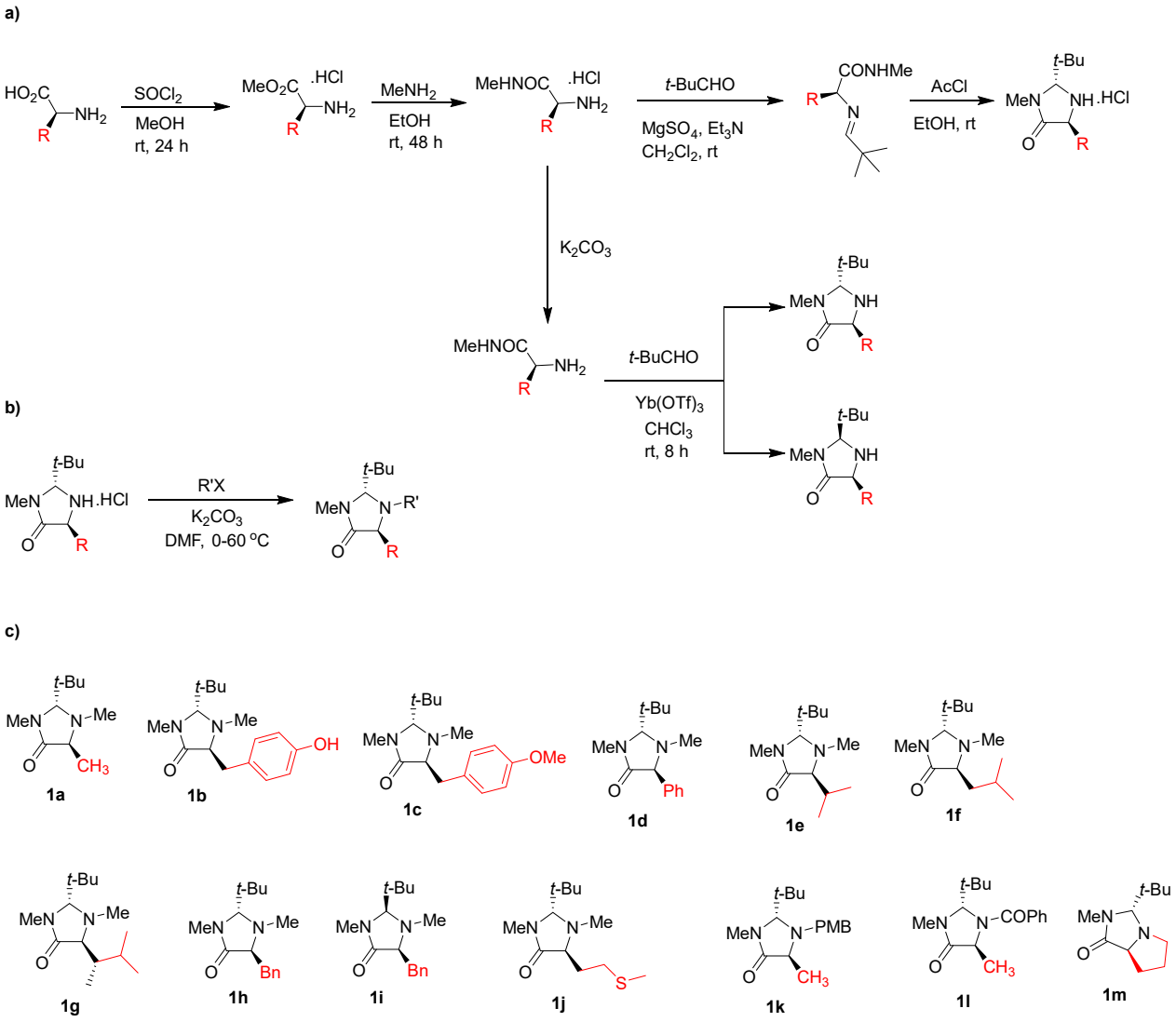


^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.84 (d, *J* = 1.6 Hz, 1H), 6.74 – 6.69 (m, 1H), 5.94 (s, 1H), 2.01 (s, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 147.3, 125.9, 117.5, 111.7, 108.4, 101.2, 84.0, 79.6, 4.3.

3.2. Synthesis of imidazolidinone derivatives

3.2.1. Synthetic pathway toward synthesis of imidazolidinone derivatives starting from amino acids

To synthesize imidazolidinone derivatives a known synthetic route in the literature was used (Scheme 1S).[1,2]



Scheme S1. Synthetic route to prepare imidazolidinone derivatives starting from amino acids

[1] Naef, R.; Seebach, D. *Helv. Chim. Acta* **1985**, 68, 135-143.
[2] Leonard, D.J.; Ward, J.W.; Clayden, J. *Nature* **2018**, 562, 105-109.

3.2.2. General Procedure A: Imine amide formation

***N*-Methylamide**: To an amino acid methyl esters hydrochloride (1.0 eq.) was added $MeNH_2$ (33% w/w solution in EtOH, 7.0 eq.). The mixture was left to stir at room temperature for 48 h andconcentrated in vacuo. The solid was suspendedin toluene and concentrated again. Thetitled product was used without any further purification.

Imine amide: To a solution of *N*-methylamide (10 mmol, 1.0 eq.) and $MgSO_4$ (1.90 g)in anhydrous CH_2Cl_2 (1.5 M) was added pivaldehyde (1.18 mL, 10.8 mmol, 1.1 equiv) at 0 °C. The reaction mixture was left to stir at room temperature for 24 h before addedadditional $MgSO_4$ (0.20 g) and pivaldehyde (1.18 mL, 10.8 mmol, 1.10 equiv) and stirring for 5 h.The reaction mixture was diluted with Et_2O to induce precipitation. The solids were filtered off and the filtrate was concentrated under reduced pressure. The crude product was used immediately without any further purification.[3]

3.2.3. General Procedure B: Imidazolidinone synthesis

Toanhydrous EtOH (2.0 M) was added dropwise Acetyl Chloride (1.1 eq) at 0 ºC. Imine amide (1.0 eq.) was added and solution stirred for 15 min at 0 °C and 30 min at 75 °C. mixture was stirred at room temperature for addition 4h. the solid was filter off and washed with small portion of cold EtOH. The filtrate was concentrated and precipitate was fitter off again. After drying under vacuum the desired product was obtained.[3]

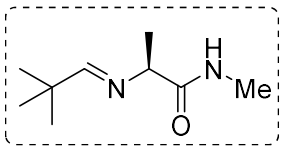
3.2.4. General Procedure C: (5*S*)-2-(*tert*-butyl)-5-alkyl-2,3-dimethylimidazolidin-4-one

To solution of Imidazolidinone (1.0 eq.) and K_2CO_3 (2.0- 2.5 eq.) in anhydrous DMF (0.6 M) at 0 °C was added methyl iodide (1.5 eq.) during 5 min. The mixture was heated at 60 °C for 12 hours. After the reaction time, the mixture diluted with water and extracted with ethyl acetate (×3). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and subjected to silica gel chromatography (pet. ether/EtOAc 4:1).

[3] Ponath, S.; Menger, M.; Grothues, L.; Weber, M.; Lentz, D.; Strohmann, C.; Christmann*, M. Angew. Chem. Int. Ed.* **2018**, 57, 11683-11687.

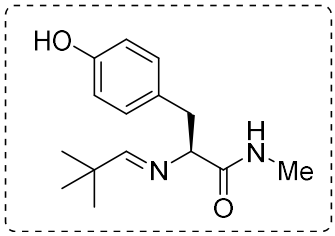
3.2.5. Spectral data for the synthesized imidazolidinone derivatives

3.2.5.1. (S)-2-((2,2-Dimethylpropylidene)amino)-N-methylpropanamide (1´´a)



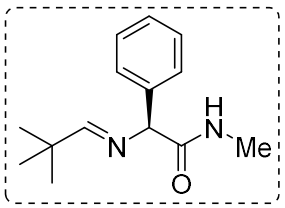
Following general **procedureA**, the title compound (14.13 g, 83%) was yielded as a yellow oil.**^{1}H NMR** (500 MHz, $CDCl_3$): δ_H = 7.58 (s, 1H, $CHC(CH_3)_3$), 6.98 (br. s, 1H, NH), 3.70 (q, J = 7.1, 1H, $CHCH_3$), 2.87(d, J = 4.9, 3H, NMe), 1.32 (d, J = 6.9, 3H, CH_3CH), 1.06 (s, 9H, $C(CH_3)_3$); **HRMS** (ESI^+): m/z calcd. for $C_9H_{19}ON_2$ $[M+H]^+$ 171.1492, found: 171.1494. 233.1649. Data in agreement with reported values.[2]

3.2.5.2. (*S*)-2-((2,2-dimethylpropylidene)amino)-3-(4-hydroxyphenyl)-*N*-methylpropanamide (1´´b)



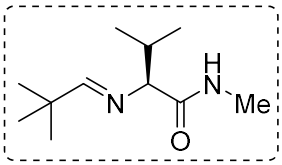
Following general **procedure A**, the title compound (10.04 g, 81%) was yielded as pale yellow oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.08 – 6.99 (m, 1H), 6.87 (d, *J* = 8.5 Hz, 2H), 6.85 (s, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 3.66 (dd, *J* = 10.2, 3.0 Hz, 1H), 3.23 (dd, *J* = 13.5, 3.0 Hz, 1H), 2.86 (d, *J* = 5.0 Hz, 3H), 2.65 (dd, *J* = 13.6, 10.2 Hz, 1H), 0.89 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 174.5 (C=O), 174.5 ($CHC(CH_3)_3$), 155.3 (ArC), 131.1(ArC), 128.5(ArC), 115.3(ArC), 74.3 (CCH_2Ar), 40.2 (CH_2Ar), 36.3 ($C(CH_3)_3$), 26.7 ($(CH_3)_3C$), 26.1(NMe); **HRMS** (ESI^+): m/z calcd. for $C_{15}H_{22}O_2N_2$ $[M+H]^+$263.1754, found: 263.1750.

3.2.5.3. (*S*)-2-((2,2-dimethylpropylidene)amino)-*N*-methyl-2-phenylacetamide (1´´c)



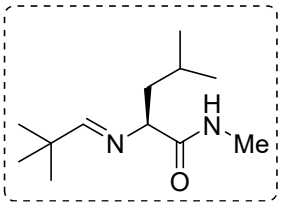
Following general **procedure A**, the title compound (9.86 g, 85%) was yielded as a yellow oil.**^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.58 (s, 1H, $CHC(CH_3)_3$), 7.35 (d, J = 7.1 Hz, 2H, PhH), 7.29 (t, J = 7.4 Hz, 2H, PhH), 7.26 – 7.20 (m, 1H, PhH), 7.00 (br, s, 1H, NH), 4.72 (s, 1H, CHPh), 2.82 (d, J = 5.0 Hz, 3H, NMe), 1.09 (s, 9H, $C(CH_3)_3$); **HRMS** (ESI^+): m/z calcd. for $C_{14}H_{20}ON_2$ $[M+H]^+$ 233.1648, found: 233.1650. Data in agreement with reported values.[2]

3.2.5.4. (*S*)-2-((2,2-dimethylpropylidene)amino)-*N*,3-dimethylbutanamide (1´´d)



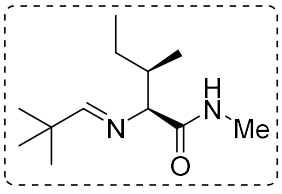
Following general **procedure A**, the title compound (7.83 g, 79%) was yielded as a yellow oil.**^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 7.41 (s, 1H,$CHC(CH_3)_3$), 6.70 (br, s, 1H, NH), 3.36 (d, *J* = 3.8 Hz, 1H, $CHCH(CH_3)_2$), 2.83 (d, *J* = 5.0 Hz, 3H, NMe), 2.21 (pd, *J* = 6.9, 3.8 Hz, 1H, $CH(CH_3)_2$), 1.08 (d, *J* = 0.9 Hz, 9H, $C(CH_3)_3$), 0.82 (t, *J* = 7.1 Hz, 6H, $(CH_3)_2CH$); **HRMS** (ESI^+): m/z calcd. for $C_{11}H_{22}ON_2$ $[M+H]^+$199.1805, found: 199.1805.Data in agreement with reported values.[1]

3.2.5.5. (*S*)-2-((2,2-Dimethylpropylidene)amino)-*N*,4-dimethylpentanamide (1´´e)



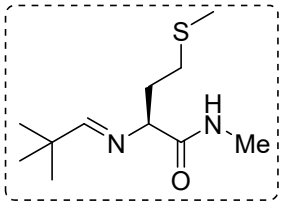
Following general **procedure A**, the title compound (8.69 g, 82%) was yielded as a pale yellow oil.**^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 7.45 (t, *J* = 0.6 Hz, 1H, $CHC(CH_3)_3$), 6.66 (br, s, 1H, NH), 3.62 (dd, *J* = 9.9, 3.9 Hz, 1H, $CHCH_2$), 2.84 – 2.74 (m, 3H, NMe), 1.60 (dddd, *J* = 22.2, 9.8, 4.2, 0.8 Hz, 1H, CH_2CH), 1.46 – 1.35 (m, 1H, $CH(CH_3)_2$), 1.07 (s, 9H, $C(CH_3)_3$), 0.88 (dd, J = 6.7, 0.8 Hz, 3H, $(CH_3)_2CH$), 0.84 (dd, J = 6.6, 0.8 Hz, 3H, $(CH_3)_2CH$); **HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}ON_2$ $[M+H]^+$213.1961, found: 213.1964.Data in agreement with reported values.[2]

3.2.5.6. (2*S*,3*R*)-2-((2,2-dimethylpropylidene)amino)-*N*,3-dimethylpentanamide (1´´f)



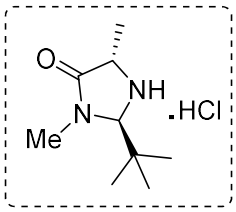
Following general **procedure A**, the title compound (7.95 g, 75%) was yielded as a pale yellow oil.**^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 7.40 (s, 1H, $CHC(CH_3)_3$), 6.68 (br, s, 1H, NH), 3.40 (d, *J* = 3.9 Hz, 1H, $CHCH(CH_3)(CH_2CH_3)$), 2.81 (d, *J* = 5.0 Hz, 3H, NMe), 1.96 – 1.86 (m, 1H, $CH(CH_3)(CH_2CH_3)$), 1.44 (dqt, *J* = 13.7, 7.9, 4.0 Hz, 2H, CH_2CH_3), 1.06 – 1.04 (m, 9H), 0.82 (t, *J* = 7.4 Hz, 3H, CH_3CH_2), 0.78 (d, *J* = 6.9 Hz, 3H, CH_3CH); **HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}ON_2$ $[M+H]^+$213.1961, found: 213.1963. Data in agreement with reported values.[3]

3.2.5.7. (*S*)-2-((2,2-Dimethylpropylidene)amino)-*N*-methyl-4-(methylthio)butanamide (1´´g)



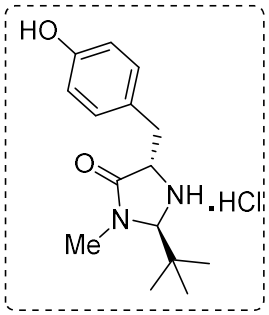
Following general **procedure A**, the title compound (16.56 g, 72%) was yielded as a pale yellow oil.**^{1}H NMR** (500 MHz, $CDCl_3$) δ_C = 7.50 (s, 1H, $CHC(CH_3)_3$), 6.68 (br, s, 1H, NH), 3.68 (dd, *J* = 9.0, 4.0 Hz, 1H, $CHCH_2$), 2.79 (d, *J* = 5.0 Hz, 3H, NMe), 2.39 (ddd, *J* = 13.5, 9.1, 4.7 Hz, 1H, CH_2CH_2), 2.27 (ddd, *J* = 13.1, 8.8, 7.5 Hz, 1H, CH_2CH_2), 2.15 – 2.07 (m, 1H, CH_2CH_2), 2.02 (s, 3H, SMe), 1.86 (dtd, *J* = 13.7, 8.9, 4.7 Hz, 1H, CH_2CH_2), 1.04 (s, 9H, $C(CH_3)_3$); **HRMS** (ESI^+): m/z calcd. for $C_{11}H_{22}ON_2S$ $[M+H]^+$231.1526, found: 231.1525.Data in agreement with reported values.[2]

3.2.5.8. (2*R*,5*S*)-2-(*tert*-butyl)-3,5-dimethylimidazolidin-4-one (1´a)



Following general **procedure B**, the title compound (8.75 g, 85%) was yielded as a white solid.**^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 11.17 (s, 1H, NH), 10.18 (s, 1H, NH), 4.65 (d, *J* = 5.9 Hz, 1H, $CHC(CH_3)_3$), 4.13 (q, *J* = 7.0 Hz, 1H, $CHCH_3$), 3.04 (s, 3H, NMe), 1.71 (d, *J* = 7.1 Hz, 3H, CH_3CH), 1.19 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 169.3 (C=O), 80.6 ($CC(CH_3)_3$), 53.9 (CCH_3), 37.2 ($C(CH_3)_3$), 32.3 (NMe), 25.4 ($(CH_3)_3C$), 15.2 (CH_3CH); **HRMS** (ESI^+): m/z calcd. for $C_9H_{19}ON_2$ $[M+H]^+$171.1492, found: 171.1493.Data in agreement with reported values.[4]

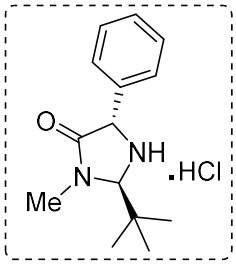
3.2.5.9. (2*R*,5*S*)-2-(*tert*-butyl)-5-(4-hydroxybenzyl)-3-methylimidazolidin-4-one (1´b)



Following general **procedure B**, the title compound (5.98 g, 80%) was yielded as a white solid.**^{1}H NMR** (500 MHz, D_2O) δ_H = 7.21 – 7.09 (m, 2H, ArH), 6.89 – 6.79 (m, 2H, ArH), 4.55 (s, 1H, $CHC(CH_3)_3$), 4.47 (dd, *J* = 7.6, 5.3 Hz, 1H, $CHCH_2$), 3.26 (dd, *J* = 15.0, 5.2 Hz, 1H, CH_2Ar), 3.04 (dd, *J* = 15.1, 7.7 Hz, 1H, CH_2Ar), 2.96 (s, 3H, NMe), 1.00 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, D_2O) δ_C = 170.1 (C=O), 155.2 (ArC), 130.8 (ArC), 125.6 (ArC), 115.9 (ArC), 81.6 ($CC(CH_3)_3$), 59.2 (CCH_2Ar), 35.9 ($C(CH_3)_3$), 33.9 (CH_2Ar), 31.6 (NMe), 24.0 ($C(CH_3)_3$); **HRMS** (ESI^+): m/z calcd. For $C_{15}H_{22}O_2N_2$ $[M+H]^+$ 263.1754, found: 263.1758.

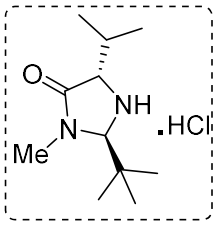
[4] Graham, T. H.; Horning, B. D.; MacMillan, D. W. C. *Org. Synth.* **2003**, 42−53

3.2.5.10. (2*R*,5*S*)-2-(*tert*-butyl)-3-methyl-5-phenylimidazolidin-4-one (1´c)



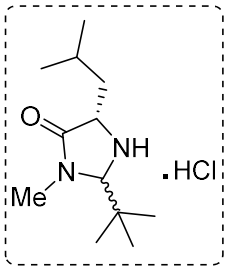
Following general **procedure B**, the title compound (5.04 g, 75%) was yielded as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.47 – 7.33 (m, 5H, PhH), 4.97 (s, 1H, $CHC(CH_3)_3$), 4.72 (s, 1H, CHPh), 3.08 (d, *J* = 0.6 Hz, 3H, NMe), 0.89 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, CDCl3) δ_C = 168.0 (C=O), 130.8 (PhC), 130.2 (PhC), 130.2 (PhC), 129.2 (PhC), 80.9 ($CC(CH_3)_3$), 61.6 (CHPh), 37.3 ($C(CH_3)_3$), 32.6 (NMe), 25.1 ($(CH_3)_3C$), 23.5; **HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}ON_2$ $[M+H]^+$ 233.1648, found: 233.1649.

3.2.5.11. (2*R*,5*S*)-2-(*tert*-butyl)-5-isopropyl-3-methylimidazolidin-4-one (1´d)



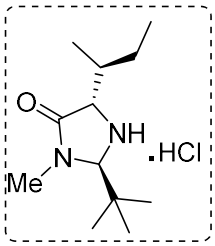
Following general **procedure B**, the title compound (2.53 g, 43%) was yielded as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 10.57 (s, 1H, NH), 10.07 (s, 1H, NH), 4.74 (s, 1H, $CHC(CH_3)_3$), 4.08 (s, 1H, $CHCH(CH_3)_2$), 3.02 (s, 3H, NMe), 2.52 (heptd, *J* = 6.9, 3.3 Hz, 1H, $CH(CH_3)_2$), 1.23 (d, *J* = 7.1 Hz, 3H, CH_3CH), 1.21 (s, 9H, $C(CH_3)_3$), 1.17 (d, *J* = 6.8 Hz, 3H, CH_3CH); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 168.0 (C=O), 81.1 ($CC(CH_3)_3$), 62.4 ($CCH(CH_3)_2$), 37.2 ($C(CH_3)_2$), 31.6, 30.0, 25.4 $(CH_3)_3CCH$), 18.4 ($(CH_3)_2CH$), 17.0 ($(CH_3)_2CH$);**HRMS** (ESI^+): m/z calcd. for $C_{11}H_{22}ON_2$ $[M+H]^+$ 199.1805, found: 199.1805.

3.2.5.12. (5*S*)-2-(*tert*-butyl)-5-isobutyl-3-methylimidazolidin-4-one (1´e)



Following general **procedure B**, the title compound (3.24 g, 52%, 4:1trans:cis) was yielded as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H =11.26 (s, 0.23H, NH $_{(min)}$)10.99 (s, 1H, NH $_{(maj)}$), 10.13 (s, 1H, NH $_{(maj)}$), 8.35 (s, 0.25H, NH $_{(min)}$), 4.73 – 4.65 (s, 1H, $CHC(CH_3)_{3(maj)}$), 4.61 (s, 0.26H, $CHC(CH_3)_3$), 4.04 (m, 1H,$CHCH_{2(maj)}$), 4.00 (m, 0.27H, $CHCH_2$ $_{(min)}$), 3.02 (s, 3H, $NMe_{(maj)}$), 3.00 (s, 0.68H, $NMe_{(min)}$), 2.36 – 2.16 (m, 1.53H), 1.92 (m, , 2.32H), 1.26 (s, 2.07H,$C(CH_3)_{3(min)}$), 1.21 (s, 9H,$C(CH_3)_{3(maj)}$), 0.99 (d, *J* = 6.7 Hz, 7.0H, 2×Me); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C = 169.9 (C=O $_{(min)}$), 169.4 (C=O $_{(maj)}$), 81.2 ($CC(CH_3)_3$ $_{(min)}$), 80.8($CC(CH_3)_3$ $_{(maj)}$), 55.6 (CCH_2 $_{(maj)}$), 55.2 (CCH_2 $_{(min)}$), 39.5$_{(maj)}$, 38.9$_{(min)}$, 37.3$_{(maj)}$, 35.6$_{(min)}$, 32.3 ($NMe_{(maj)}$), 31.7($NMe_{(min)}$), 25.7$_{(min)}$, 25.5$_{(maj)}$, 24.8, 24.1$_{(maj)}$, 22.6$_{(maj)}$, 22.0$_{(maj)}$, 21.9$_{(min)}$;**HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}ON_2$ $[M+H]^+$ 213.1961, found: 213.1964.

3.2.5.13. (2*R*,5*S*)-5-((*S*)-*sec*-butyl)-2-(*tert*-butyl)-3-methylimidazolidin-4-one(1´f)

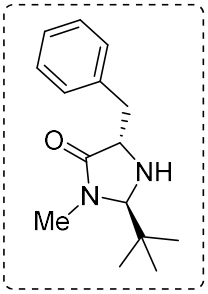


Following general **procedure B**, the title compound (2.74 g, 44%) was yielded as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 10.62 (s, 1H, NH), 10.15 (s, 1H, NH), 4.73 (s, 1H, $CHC(CH_3)_3$), 4.15 (s, 1H, $CHCH(CH_3)(CH_2CH_3)$), 3.01 (s, 3H, NMe), 2.21 (dtq, *J* = 9.7, 6.9, 3.4, 2.9 Hz, 1H,$CH(CH_3)(CH_2CH_3)$), 1.68 (p, *J* = 7.4 Hz, 2H, CH_2CH_3), 1.21 (s, 9H, $C(CH_3)_3$), 1.11 (d, *J* = 6.8 Hz, 3H, CH_3CH), 0.97 (t, *J* = 7.4 Hz, 3H, CH_3CH_2); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C= 167.9 (C=O), 81.1 ($CC(CH_3)_3$), 61.4 ($CCH(CH_3)(CH_2CH_3)$), 37.3, 36.7, 31.6 (NMe), 25.6, 25.4, 13.7, 12.1; **HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}ON_2$ $[M+H]^+$ 213.1961, found: 213.1960.

3.2.5.14. (2*S*,5*S*)-5-Benzyl-2-*tert*-butyl-3-methyl-4-imidazolidinone (1´g) and (2*R*,5*S*)-5-Benzyl-2- *tert*-butyl-3-methyl-4-imidazolidinone (1´h)[5]

The resulting mixture of (S)-2-amino-*N*-methyl-3-phenylpropanamide which was synthesized according to general **procedure A** (2.00 g, 11.2 mmol, 1.00 equiv.), pivaldehyde (1.93 g, 22.4 mmol, 2.00 equiv.) and $Yb(OTf)_3$ (70 mg, 0.11 mmol, 0.01 equiv.) in $CHCl_3$ (100 mL) under an atmosphere of argon was heated at reflux for 8 h. The reaction was allowed to cool to RT and the two diastereomers separated by column chromatography (SiO_2; CH/EtOAc 3:1).

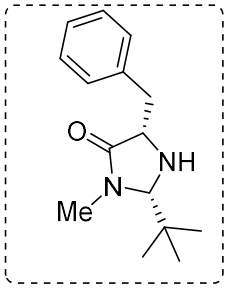
3.2.5.15. (2*R*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-methylimidazolidin-4-one (1´h)



white solid (1.6 g, 58%) R_f = 0.39 (CH/EtOAc 1:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.33 – 7.26 (m, 2H, PhH), 7.25 – 7.20 (m, 3H, PhH), 3.85 (ddd, *J* = 6.6, 4.3, 1.7 Hz, 1H, ($CHCH_2Ph$), 3.80 (d, *J* = 1.8 Hz, 1H, $CHC(CH_3)_3$), 3.11 (dd, *J* = 14.1, 4.2 Hz, 1H, CH_2Ph), 2.94 – 2.84 (m, 1H, CH_2Ph), 2.89 (s, 3H, NMe), 1.81 (s, b, 1H, NH), 0.90 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 175.4 (C=O), 137.6 (PhC), 129.6 (PhC), 128.6 (PhC), 126.7 (PhC), 83.5 ($CC(CH_3)_3$), 59.6 (CCH_2Ph), 38.7 ($C(CH_3)_3$), 37.8 (CH_2Ph), 31.4 (NMe), 25.7 ($(CH_3)_3C$); **HRMS** (ESI^+): m/z calcd. for $C_{15}H_{22}ON_2$ $[M+H]^+$ 247.1805, found: 147.1808.

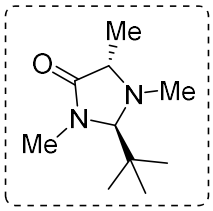
[5]Samulis, L.; Tomkinson, N. C. O. *Tetrahedron***2011**, 67, 4263-4267

3.2.5.16. (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-3-methylimidazolidin-4-one (1´i)



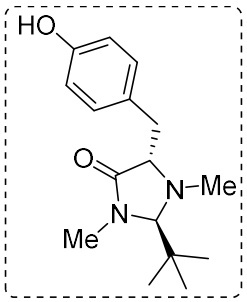
colorless oil (314 mg, 11%), R_f = 0.32 (CH/EtOAc 1:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 5H), 4.06 (d, J = 1.5 Hz, 1H, $CHC(CH_3)_3$), 3.71 (ddd, J = 8.2, 4.0, 1.4 Hz, 1H, $CHCH_2Ph$), 3.16 (dd, J = 13.8, 4.0 Hz, 1H, CH_2Ph), 2.95 (dd, J = 13.8, 7.5 Hz, 1H, CH_2Ph), 2.92 (s, 3H, NMe), 1.66 (s, b, 1H, NH), 0.83 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.3 (C=O), 137.9 (PhC), 129.7 (PhC), 128.7 (PhC), 126.8 (PhC), 82.5 ($CC(CH_3)_3$), 59.5 (CCH_2Ph), 38.2 ($C(CH_3)_3$), 35.1 (CH_2Ph), 30.8 (NMe), 25.4 (($CH_3)_3C$); **HRMS** (ESI^+): m/z calcd. for $C_{15}H_{22}ON_2$ $[M+H]^+$ 247.1805, found: 247.1805.

3.2.5.17. (2*R*,5*S*)-2-(*tert*-butyl)-1,3,5-trimethylimidazolidin-4-one (1a)



Following **procedure C**, Methyl iodide (0.90 mL, 14.56 mmol) was added to solution of K_2CO_3 (2.68 g, 19.4 mmol) and (2R,5S)-2-tert-butyl-3,5-dimethylimidazolidin-4-one (2.0 g, 9.7mmol) to give titlecompound (1.44 g, 81%) as a colorless oil. R_f = 0.30 (pet. ether/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H= 3.66 (q, *J* = 7.4 Hz, 1H, $CHCH_3$), 3.48 (d, *J* = 1.0 Hz, 1H, $CHC(CH_3)_3$), 2.96 (s, 3H, NCH_3), 2.38 (s, 3H, NCH_3), 1.25 (d, *J* = 7.4 Hz, 3H, CCH3), 0.95 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C = 176.1 (C=O), 92.8 ($CHC(CH_3)_3$), 58.1 ($CHCH_3$), 39.9 (NCH_3), 38.9 (NCH_3), 32.0, 26.1 ($C(CH_3)_3$), 12.1 ($CHCH_3$); **HRMS** (ESI^+): m/z calcd. for $C_{10}H_{20}ON_2$ $[M+H]^+$ 185.1651, found: 185.1651.

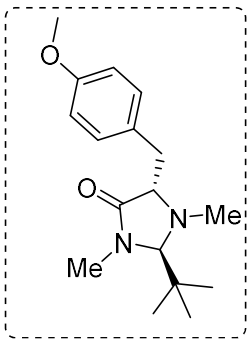
3.2.5.18. (2*R*,5*S*)-2-(*tert*-butyl)-5-(4-hydroxybenzyl)-1,3-dimethylimidazolidin-4-one (1b)



Following **procedure C**, Methyl iodide (187 μL, 3 mmol) was added to solution of K_2CO_3 (0.69 g, 5.0 mmol) and related imidazolidinone (**1´b**) (600mg, 2.0 mmol) to give title compound (385 mg, 65%) as a white solid. R_f = 0.30 (pet. ether/EtOAc 7:3). **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 7.21 – 7.13 (m, 2H, 2×ArH), 6.83 – 6.74 (m, 2H, 2×ArH), 6.03 (s, 1H, OH), 4.00 (dd, J = 11.1, 3.4 Hz, 1H, $CHCH_2$), 3.52 (s, 1H, $CHC(CH_3)_3$), 3.23 (dd, J = 16.7, 3.4 Hz, 1H, CH_2Ar), 3.02 (s, 3H, NMe), 2.85 (dd, J = 16.6, 11.0 Hz, 1H, CH_2Ar), 2.36 (s, 3H, NMe), 1.00 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C = 175.5 (ArC), 154.4 (ArC), 130.6 (ArC), 129.2 (ArC), 115.5 (ArC), 93.1 ($CC(CH_3)_3$), 62.7 (CCH_2), 40.2

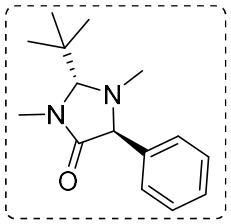
(NMe), 39.1 (NMe), 32.3, 31.0, 26.4; **HRMS** (ESI^+): m/z calcd. for $C_{16}H_{24}O_2N_2$ $[M+Na]^+$ 299.1730, found: 299.1732.

3.2.5.19. (2*R*,5*S*)-2-(*tert*-butyl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one (1c)



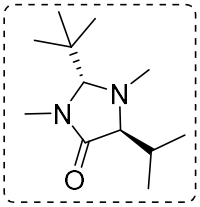
To solution of (2R,5S)-2-(tert-butyl)-5-(4-hydroxybenzyl)-3-methylimidazolidin-4-one hydrochloride (**1´b**) (600 mg, 2.0 mmol, 1.0 eq.) and NaOH (3.5 eq.) in anhydrous DMSO (2 mL, 1 M) at 0 °C was added methyl iodide (374 μL, 6 mmol, 3.0 eq.). The mixture was heated at 50 °C for 24 hours. After the reaction time, the mixture diluted with water and extracted with ethyl acetate (×3). The combined organic layers were dried over $MgSO_4$, concentrated and separated with the column chromatography (pet. ether/EtOAc 4:1) to give desired product (296 mg, 51%) as a white solid. R_f = 0.32 (pet. ether/EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.30 – 7.18 (m, 2H, 2×ArH), 6.85 (d, J = 8.7 Hz, 2H, 2×ArH), 4.00 (dd, J = 11.2, 3.4 Hz, 1H, $CHC(CH_3)_3$), 3.79 (s, 3H, OCH_3), 3.50 (s, 1H, $CHCH_2$), 3.26 (dd, J = 16.8, 3.4 Hz, 1H, CH_2Ar), 3.01 (s, 3H, NMe), 2.86 (dd, J = 16.8, 11.2 Hz, 1H, CH_2Ar), 2.36 (s, 3H, NMe), 1.00 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 175.2 (C=O), 158.1 (ArC), 131.1 (ArC), 129.1 (ArC), 114.0 (ArC), 93.0 ($CC(CH_3)_3$), 62.6 (CCH_2), 55.3 (OMe), 40.2 (NMe), 39.1(NMe), 32.2, 31.0, 26.4; **HRMS** (ESI^+): m/z calcd. for $C_{17}H_{26}O_2N_2$ $[M+H]^+$ 291.2067, found: 291.2072.

3.2.5.20. (2*R*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (1d)



Following **procedure C**, Methyl iodide (522μL, 8.4 mmol) was added to solution of K_2CO_3 (1.55 g, 11.2 mmol) and related imidazolidinone hydrochloride (**1´c**) (1.3 g, 5.6 mmol) to give title compound (772 mg, 56%) as a colorless oil. R_f = 0.24 (pet. ether/EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.34 (qd, *J* = 7.7, 6.7, 3.6 Hz, 3H, PhH), 7.19 (d, *J* = 7.2 Hz, 2H, PhH), 4.77 (s, 1H, CHPh), 3.80 (s, 1H, $CHC(CH_3)_3$), 3.10 (s, 3H, NMe), 2.10 (s, 3H, NMe), 1.05 (s, 9H, $C(CH_3)_3$). **^{13}C NMR** (126 MHz, $CDCl_3$) δ_C = 174.0 (C=O), 135.1 (PhC), 130.3 (PhC), 128.4 (PhC), 128.1 (PhC), 91.5 ($C(CH_3)_3$), 68.7 (CPh), 40.8 (NMe), 39.5 (NMe), 32.1 $C(CH_3)_3$, 26.2 (CH3); **HRMS** (ESI^+): m/z calcd. for $C_{15}H_{22}ON_2$ $[M+H]^+$ 247.1805, found: 247.1805.

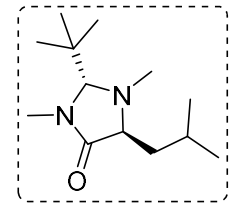
3.2.5.21. (2*R*,5*S*)-2-(*tert*-butyl)-5-isopropyl-1,3-dimethylimidazolidin-4-one (1e)



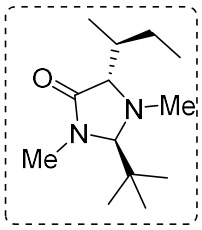
Following **procedure C**, Methyl iodide (562μL, 9.1mmol) was added to solution of K_2CO_3 (1.68 g, 12.2 mmol) and related imidazolidinone hydrochloride (**1´d**) (1.2 g, 6.1mmol) to give title compound (845mg, 65%) as a pale yellow oil. R_f = 0.30 (pet. ether/EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 3.59 (d, *J* = 1.6 Hz, 1H, $CHC(CH_3)_3$), 3.36 – 3.28 (m, 1H, $CHCH(CH_3)_2$)), 2.88 (s, 3H, NMe), 2.42 (s, 3H, NMe), 2.15 – 2.01 (m, 1H, $CH(CH_3)_2$), 1.07 (d, *J* = 6.9 Hz, 3H, CH_3CH), 0.92 (d, *J* = 6.7 Hz, 3H, CH_3CH), 0.90 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 174.4 (C=O), 90.8 ($C(CH_3)_3$), 67.1 ($CCH(CH_3)_2$), 39.3 (NMe), 38.3 (NMe), 31.5, 26.9, 26.5, 20.4, 18.0; **HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}ON_2$ $[M+H]^+$213.1961, found: 213.1961.

3.2.5.22. (2*R*,5*S*)-2-(*tert*-butyl)-5-isobutyl-1,3-dimethylimidazolidin-4-one (1f)

Following **procedure C**, Methyl iodide (332μL, 5.35 mmol) was added to solution of K_2CO_3 (993 mg, 7.2 mmol) and related imidazolidinone hydrochloride (**1´e**) (900 mg, 3.57mmol) to give title compound (507 mg, 62%) as a pale yellow oil. R_f = 0.29 (pet. ether/EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 3.57 (dd, J = 10.0, 4.8 Hz, 1H, $CHCH_2$), 3.41 (s, 1H, $CHC(CH_3)_3$), 2.95 (s, 3H, NMe), 2.30 (s, 3H, NMe), 1.87 (dt, J = 15.1, 6.3 Hz, 1H, CCH_2C), 1.63 – 1.42 (m, 2H, CCH_2CH), 0.96 (s, 9H, $C(CH_3)_3$), 0.94 (d, J = 3.5 Hz, 3H, CCH_3), 0.93 (d, J = 3.3 Hz, 3H, CCH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_c = 176.2 (C=O), 93.3 ($CC(CH_3)_3$), 60.5 ($CHCH_2$), 40.6 (NMe), 38.8 (NMe), 34.8, 32.2, 26.5, 25.5, 23.2, 21.8; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{26}ON_2$ $[M+H]^+$ 227.2118, found: 227.2119.



3.2.5.23. (2*R*,5*S*)-5-((*S*)-*sec*-butyl)-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one (1g)

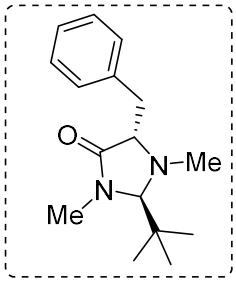


Following **procedure C**, Methyl iodide (332μL, 5.35 mmol) was added to solution of K_2CO_3 (993mg, 7.2 mmol) and related imidazolidinone hydrochloride (**1´f**) (900 mg, 3.6 mmol) to give title compound (441 mg, 54%) as a colorless oil. R_f = 0.28 (pet. ether/EtOAc 4:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.65 (d, *J* = 1.8 Hz, 1H, $CHC(CH_3)_3$), 3.50 – 3.44 (m, 1H, $CHCH(CH_3)CH_2$), 2.91 (s, 3H, NMe), 2.46 (s, 3H, NMe), 1.85 (dddd, *J* = 13.4, 8.7, 4.3, 2.0 Hz, 1H), 1.62 (dtd, *J* = 14.9, 7.5, 4.7 Hz, 1H), 1.54 – 1.39 (m, 1H), 0.94 (s, 9H, $C(CH_3)_3$), 0.92 – 0.87

(m, 6H, 2×CH_3); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.5 (C=O), 90.8 ($C(CH_3)_3$), 65.8 ($CCH(CH_3)CH_2$),39.5 (NMe), 38.3 (NMe), 33.9, 31.6, 26.8, 26.5, 15.0, 12.1; **HRMS** (ESI^+): m/z calcd. for $C_{13}H_{26}ON_2$ $[M+H]^+$ 227.2118, found: 227.2118.

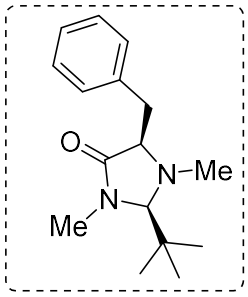
3.2.5.24. (2*R*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one (1h)

Following **procedure C**, Methyl iodide (0.45 mL, 7.28 mmol) was added to solution of K_2CO_3 (1.34 g, 9.7 mmol) and related imidazolidinone (**2h**) (1.193 g, 4.85 mmol) to give title compound (870 mg, 69%) as a pale yellow oil. R_f = 0.35 (pet. ether/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.40 – 7.27 (m, 4H, 4×ArH), 7.21 (t, J = 7.2 Hz, 1H, ArH), 4.06 (dd, J = 11.3, 3.3 Hz, 1H, $CHCH_2$), 3.52 (s, 1H, $CHC(CH_3)_3$), 3.34 (dd, J = 17.0, 3.3 Hz, 1H, CH_2Ph), 3.02 (s, 3H, NMe), 2.93 (dd, J = 17.0, 11.3 Hz, 1H, 1H, CH_2Ph), 2.36 (s, 3H, NMe), 1.01 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C =179.6 (C=O), 139.1 (ArC), 128.5(ArC), 128.2 (ArC), 126.2 (ArC), 93.0 ($CC(CH_3)_3$), 62.4 (CCH_2),40.3(NCH_3), 39.1(NCH_3), 32.3, 31.9, 26.4; **HRMS** (ESI^+): m/z calcd. for $C_{16}H_{24}ON_2$ $[M+H]^+$261.1961, found: 261.1964.

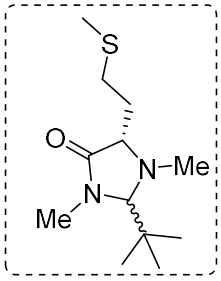


3.2.5.25. (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one (1i)

Following **procedure C**, Methyl iodide (90 μL, 1.45 mmol) was added to solution of K_2CO_3 (1.34 g, 9.7 mmol) and related imidazolidinone (**1´g**) (238mg, 0.97 mmol) to give title compound (196 mg, 78%) as a pale yellow oil. R_f = 0.27 (pet. ether/EtOAc 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.30 – 7.26 (m, 4H, 4×ArH), 7.24 – 7.18 (m, 1H, ArH), 3.55 (s, 1H, $CHC(CH_3)_3$), 3.23 – 3.15 (m, 2H, $CHCH_2$ and CH_2Ph), 2.95 (d, J = 0.5 Hz, 3H, NMe), 2.77 – 2.62 (m, 1H, CH_2Ph), 2.06 (s, 3H, NMe), 0.95 (s, 9H, $C(CH_3)_3$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 173.4 (C=O), 139.0 (ArC), 129.7 (ArC), 128.3 (ArC), 126.3 (ArC), 91.5 ($CC(CH_3)_3$),70.3 (CCH_2), 46.6 (NMe), 40.0 (NMe), 37.4, 31.4, 26.1; **HRMS** (ESI^+): m/z calcd. for $C_{16}H_{24}ON_2$ $[M+H]^+$ 261.1961, found: 261.1962.



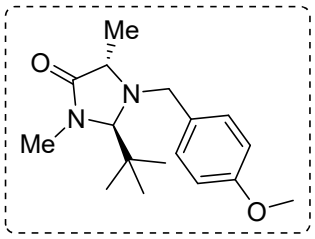
3.2.5.26. (5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-(2-(methylthio)ethyl)imidazolidin-4-one (1j)



Following **procedure C**, Methyl iodide (1.3*m*L, 20.0 mmol) was added to solution of K_2CO_3 (1.38 g, 20.0 mmol) and related imidazolidinone hydrochloride (**1´i**) (2.66 g, 10.0 mmol) to give title compound (1.71 g, 70%, 93:7 trans:cis) as a pale yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 3.70 – 3.61 (m, 1H, $CHCH_{2\ (maj)}$), 3.55 (s, 0.06H, $CHC(CH_3)_{3\ (min)}$), 3.46 (s, 1H, $CHC(CH_3)_{3\ (maj)}$), 3.42 – 3.35 (m, 0.04H, $CHCH_{2\ (min)}$), 2.94 (s, 3H, $NMe_{(maj)}$), 2.89 (s, 0.17H, $NMe_{(min)}$), 2.73 – 2.60 (m, 2H, $SCH_{2\ (maj)}$), 2.49 (s, 0.19H, $NMe_{(min)}$), 2.34 (d, *J* = 0.9 Hz, 3H, $NMe_{(maj)}$), 2.33 – 2.30 (s, 0.23H, $SMe_{(min)}$), 2.10 (d, *J* = 1.1 Hz, 3H, $SMe_{(maj)}$), 2.05 – 1.99 (m, 1H, $CH_2CH_{(maj)}$), 1.85 (dtd, *J* = 14.0, 8.3, 5.6 Hz, 1H, $CH_2CH_{(maj)}$), 0.94 (d, *J* = 1.1 Hz, 9H, $C(CH_3)_{3\ (maj)}$), 0.91 (d, *J* = 1.0 Hz, 0.66H, $C(CH_3)_{3\ (min)}$); **^{13}C NMR** (126 MHz, CDCl3) δ_c= 175.3 ($C{=}O_{(maj)}$), 174.0 ($C{=}O_{(min)}$), 93.0 ($CC(CH_3)_{3\ (maj)}$), 91.7 ($CC(CH_3)_{3\ (min)}$), 66.4 ($CHCH_{2\ (min)}$), 61.2 ($CHCH_{2\ (maj)}$), 46.9 ($NMe_{(min)}$), 40.2 ($NMe_{(maj)}$), 38.9 ($NMe_{(maj)}$), 37.2 ($NMe_{(min)}$), $33.2_{(min)}$, $32.1_{(maj)}$, $31.4_{(maj)}$, $31.3_{(min)}$, $30.5_{(min)}$, $26.5_{(maj)}$, $26.4_{(maj)}$, $26.3_{(min)}$, $26.0_{(min)}$, $15.4_{(maj)}$, $15.3_{(min)}$; **HRMS** (ESI^+): m/z calcd. for $C_{12}H_{24}N_2OS$ $[M+H]^+$ 245.1682, found: 245.1682.

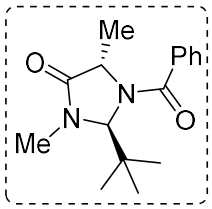
3.2.5.27. (2*R*,5*S*)-2-(*tert*-butyl)-1-(4-methoxybenzyl)-3,5-dimethylimidazolidin-4-one (1k)

Following general **procedure C**, 4-Methoxybenzyl chloride (2.240mL, 16 mmol) was added to



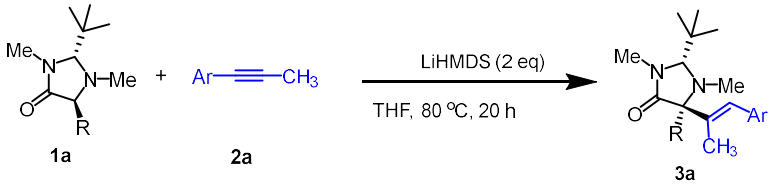
solution of K_2CO_3 (2.65 g, 19.2 mmol) and related imidazolidinone hydrochloride (**1´j**) (1.65 g, 8.0 mmol) to give title compound (976 mg, 42%) as a pale-yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ_H = 7.30 – 7.16 (m, 2H, Ph), 6.86 (d, *J* = 8.6 Hz, 2H, Ph), 4.07 (d, *J* = 14.2 Hz, 1H, NCH_2Ph), 3.83 (q, J = 7.3 Hz, 1H, $CHCH_3$), 3.80 (s, 3H, NMe), 3.78 (d, J = 1.2 Hz, 1H, $CHC(CH_3)_3$), 3.49 (d, *J* = 14.2 Hz, 1H, NCH_2Ph), 2.99 (s, 3H, OMe), 1.21 (d, *J* = 7.4 Hz, 3H, CH_3CH), 0.86 (s, 9H, $C(CH_3)_3$).**^{13}C NMR** (126 MHz, $CDCl_3$) δ_C = 176.3 (C=O), 158.7 (PhC), 132.0 (PhC), 129.3 (PhC), 113.8 (PhC), 89.2 ($CC(CH_3)_3$), 58.2 (CCH_3), 55.3(NCH_2), 54.7 (OMe), 39.1 (NMe), 32.2, 26.4 (($CH_3)_3C$), 13.4; **HRMS** (ESI^+): m/z calcd. for $C_{17}H_{26}O_2N_2$ $[M+H]^+$ 291.2067, found: 291.2069.

3.2.5.28. (2*S*,5*S*)-1-benzoyl-2-(*tert*-butyl)-3,5-dimethylimidazolidin-4-one (1l)[1]



To solution of (2*R*,5*S*)-2-*tert*-butyl-3,5-dimethylimidazolidin-4-one (**1´a**) (2 g, 9.7 mmol, 1.0 eq.) and Et_3N (2.7ml) in anhydrous CH_2Cl_2 (10 mL, 1 M) at 0 °C was added benzoyl chloride (1.13mL, 9.7 mmol, 1.0 eq.). The mixture was left to stir at room temperature for 12 h. The mixture diluted with 10 mL Et_2O and washed with Na_2CO_3 (2N, ×2) and water. The organic layers were dried over $MgSO_4$, concentrated and recrystallized in Et_2O/pentan to give titled product (1.91 g, 72%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ_H = 7.64 – 7.57 (m, 2H, Ph), 7.53 – 7.39 (m, 3H, Ph), 5.67 (s, 1H, $CHC(CH_3)_3$), 4.26 (q, *J* = 6.6 Hz, 1H, $CHCH_3$), 3.07 (s, 3H, NMe), 1.07 (s, 9H, $C(CH_3)_3$), 0.98 (d, *J* = 6.6 Hz, 3H, CH_3CH); **^{13}C NMR** (101 MHz, $CDCl_3$) δ_C = 172.4 (C=O), 171.2 (C=O), 137.1 (PhC), 134.6 (PhC), 131.6 (PhC), 130.6 (PhC), 129.0 (PhC), 127.7 (PhC), 80.0 ($CC(CH_3)_3$), 57.5 (CCH_3), 40.8 (NMe), 32.2, 26.4($(CH_3)_3$C), 19.5; **HRMS** (ESI^+): m/z calcd. for $C_{16}H_{22}O_2N_2$ $[M+H]^+$ 275.1754, found: 275.1758.Data in agreement with reported values.[1]

4. General procedure for the hydroalkylation of alkynes/alleneswith imidazolidinone derivatives



4.1. Alkynes (D): A flame-dried sealed Schlenk tube was charged with imidazolidinone derivative (**1a-l**) (0.2 mmol, 1.0 eq) and alkyne (0.2 mmol,1.0 eq.; if it is solid) and it was evacuated and backfilled with argon. Then 1.0 mL of THF, alkyne (0.2 mmol,1.0 eq; if it is liquid) and LiHMDS (0.4 mL, 1.0 M in THF, 2.0 eq) were addedwhile maintaining an argon counterflow. The tube was sealed with a screw-cap and theresulting mixture was stirred at 80 °C for 20h. After completion of thereaction the mixture was allowed to cooldown to r.t. Then, it was quenched byadding aq. sat. NH_4Cl (5 mL) and extracted with ethyl acetate (3x 10 mL). The combined organic layers weredried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flashcolumn chromatography using hexanes/ethyl acetate eluents to afford the pure desire compound.

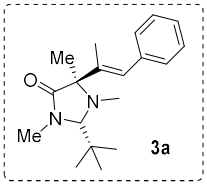
4.2. Allenes (E): A flame-dried sealed Schlenk tube was charged with imidazolidinone derivative(**1a-l**) (0.2 mmol, 1.0 eq) and alkyne (0.2 mmol,1.0 eq.; if it is solid) and it was evacuated and backfilled with argon. Then 1.0 mL of THF, alkyne (0.2 mmol,1.0 eq; if it is liquid) and LiHMDS (0.4 mL, 1.0 M in THF, 2.0 eq) were addedwhile maintaining an argon counterflow. The tube was sealed with a screw-cap and theresulting mixture was stirred at 80 °C for 20h. The workup procedure is same to the previous one.

4.3. Large scale procedure

A flame-dried sealed Schlenk tube was charged with (2R,5S)-2-(tert-butyl)-1,3,5-trimethylimidazolidin-4-one (**1a**) (1.0 g, 5.5 mmol) and it was evacuated and backfilled with argon. Then 4.0 mL of THF, and 1-phenyl-1-propyne (0.64g, 5.5 mmol) and LiHMDS (11 mL, 1.0 M in THF, 11 mmol) were addedwhile maintaining an argon counterflow. The tube was sealed with a screw-cap and theresulting mixture was stirred at 80 °C for 24 h. After completion of the reaction the mixture was allowed to cool down to r.t. Then, it was quenched byadding aq. sat. NH_4Cl (50 mL) and extracted with ethyl acetate (3x 50mL). The combined organic layers weredried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flashcolumn chromatography using hexanes/ethyl acetate eluents (5:1) to afford the pure product (74%, 1.22 g).

4.4. Spectral data for the alkenylated imidazolidinone compounds

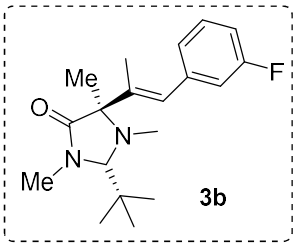
4.4.1. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3a)



Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-Phenyl-1-propyne (24 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (50 mg, 83%). TLC (SiO_2): R_f = 0.19 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 10.4, 4.7 Hz, 2H, Ph), 7.27 – 7.18 (m, 3H, Ph), 6.60 (s, 1H, CH=C), 3.86 (s, 1H, $CHC(CH_3)_3$), 3.01 (s, 3H, NMe), 2.43 (s, 3H, NMe), 1.55 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.51 (s, 3H, CH_3C), 1.01 (s, 9H, $(CH_3)_3C$);**^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.6 (C=O), 137.8, 137.7, 129.3, 129.3, 128.1, 128.1, 126.6, 90.2($CC(CH_3)_3$), 70.2 (CCH_3), 38.5 (NMe), 37.0 (NMe), 31.6, 26.7 ($(CH_3)_3$)C), 22.9, 15.7(CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{19}H_{28}N_2O$ $[M+H]^+$ 300.2202, found: 300.2274;

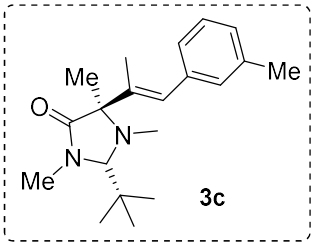
4.4.2. (2*R*,5*R*)-2-(*tert*-butyl)-5-((*E*)-1-(3-fluorophenyl)prop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3b)

Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-fluoro-3-(prop-1-yn-1-yl)benzene (27 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (54 mg, 85%).TLC (SiO_2):R_f = 0.26 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 1H, Ph), 7.02 (d, *J* = 7.8 Hz, 1H, Ph), 6.99 – 6.88 (m, 2H, Ph), 6.55 (s, 1H, CH=C), 3.87 (s, 1H, $CHC(CH_3)_3$), 3.01 (s, 3H, NMe), 2.44 (s, 3H, NMe), 1.55 (d, *J* = 1.0 Hz, 3H, CH_3C=CH), 1.52 (s, 3H, CH_3C), 1.01 (s, 9H, $(CH_3)_3$)C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.3 (C=O), 162.7 (d, *J* = 245.3 Hz), 139.9 (d, *J* = 7.7 Hz), 129.5 (d, *J* = 8.4 Hz), 128.4, 125.1 (d, *J* = 2.9 Hz), 116.0(d, *J* = 21.5 Hz), 113.5 (d, *J* = 21.1 Hz), 90.2 ($CC(CH_3)_3$), 70.2 (CCH_3), 38.54 (NMe), 37.1(NMe), 31.6, 26.7 ($(CH_3)_3$)C), 22.8, 15.7 (CH_3C=CH); **^{19}F NMR** (282 MHz, $CDCl_3$) δ -113.77; **HRMS** (ESI^+): m/z calcd. for $C_{19}H_{27}FN_2O$ $[M+H]^+$ 318.2107, found: 318.2178.

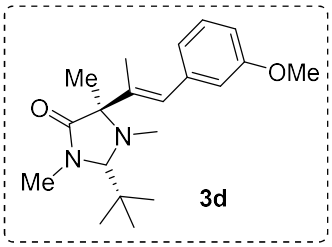


4.4.3. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(m-tolyl)prop-1-en-2-yl)imidazolidin-4-one (3c)

Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-methyl-3-(prop-1-yn-1-yl)benzene (26 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (50 mg, 80%); TLC (SiO_2):R_f = 0.3 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.7 Hz, 1H, Ph), 7.08 – 7.02 (m, 3H, Ph), 6.58 (s, 1H, CH=C), 3.87 (s, 1H, $CHC(CH_3)_3$), 3.01 (s, 3H, NMe), 2.46 (s, 3H, NMe), 2.34 (s, 3H, MeAr), 1.56 (d, *J* = 0.7 Hz, 3H, CH_3C=CH), 1.54 (s, 3H, CH_3C), 1.03 (s, 9H, $(CH_3)_3$)C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.7, 130.0, 128.0, 127.5, 126.3, 90.4 ($CC(CH_3)_3$), 38.5 (NMe), 31.7, 26.7 ($(CH_3)_3$)C), 22.8, 21.5, 15.8 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{20}H_{30}N_2O$ $[M+H]^+$ 314.2358, found: 314.2431.

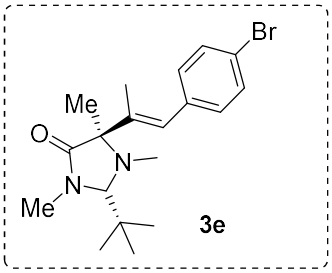


4.4.4. (2*R*,5*R*)-2-(*tert*-butyl)-5-((*E*)-1-(3-methoxyphenyl)prop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3d)



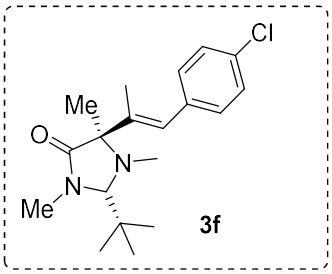
Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-methoxy-3-(prop-1-yn-1-yl)benzene(30 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (51 mg, 77%).TLC (SiO_2):R_f = 0.2 (hexanes:ethylacetate = 5:1); **^{1}H NMR** (400 MHz, $CDCl_3$)δ 7.22 (d, *J* = 7.8 Hz, 1H, Ph), 6.84 (d, *J* = 7.7 Hz, 1H, Ph), 6.78 (dt, *J* = 8.1, 2.4 Hz, 2H, Ph), 6.57 (s, 1H, CH=C), 3.86 (s, 1H, $CHC(CH_3)_3$), 3.80 (s, 3H, OMe), 3.01 (s, 3H, NMe), 2.44 (s, 3H, NMe), 1.55 (d, *J* = 1.1 Hz, 3H, CH_3C=CH), 1.51 (s, 3H, CH_3C), 1.01 (s, 9H, $((CH_3)_3)C$); **^{13}C NMR** (101 MHz, $CDCl_3$)δ 175.6 (C=O), 159.4, 139.2, 138.0, 129.3, 129.1, 121.8, 114.8, 112.4, 90.2 ($CC(CH_3)_3$), 70.2 (CCH_3), 55.3 (OMe), 38.5 (NMe), 37.1 (NMe), 31.6, 26.7 ($((CH_3)_3)C$), 22.8, 15.7 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{20}H_{30}N_2O_2$ $[M+H]^+$ 330.2307, found: 330.2382.

4.4.5. (2*R*,5*R*)-5-((*E*)-1-(4-bromophenyl)prop-1-en-2-yl)-2-(*tert*-butyl)-1,3,5-trimethylimidazolidin-4-one (3e)



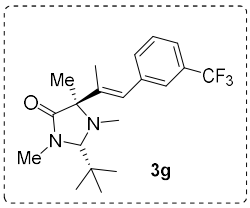
Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-bromo-4-(prop-1-yn-1-yl)benzene(40 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (65 mg, 85%).TLC (SiO_2):R_f = 0.2 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$)δ 7.46 – 7.41 (m, 2H, Ph), 7.14 – 7.09 (m, 2H, Ph), 6.51 (s, 1H, CH=C), 3.86 (s, 1H, $CHC(CH_3)_3$), 3.00 (s, 3H, NMe), 2.43 (s, 3H, NMe), 1.52 (d, J = 1.0 Hz, 3H, CH_3C=CH), 1.51 (s, 3H, CH_3C), 1.01 (s, 9H, $((CH_3)_3)C$); **^{13}C NMR** (101 MHz, $CDCl_3$)δ 175.3 (C=O), 138.7, 136.6, 131.3, 130.9, 128.3, 120.6, 90.2 ($CC(CH_3)_3$), 70.3 (CCH_3), 38.5 (NMe), 37.1 (NMe), 31.6, 26.7($(CH_3)_3)C$), 22.8, 15.7 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{19}H_{27}BrN_2O$ $[M+H]^+$ 378.1307, found: 378.1227.

4.4.6. (2*R*,5*R*)-2-(*tert*-butyl)-5-((*E*)-1-(4-chlorophenyl)prop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3f)



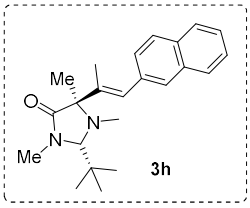
Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-chloro-4-(prop-1-yn-1-yl)benzene(30 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (57 mg, 85%).TLC (SiO_2):R_f = 0.23 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H, Ph), 7.20 – 7.15 (m, 2H, Ph), 6.53 (s, 1H, CH=C), 3.86 (s, 1H, $CHC(CH_3)_3$), 3.00 (s, 3H, NMe), 2.42 (s, 3H, NMe), 1.52 (d, *J* = 0.9 Hz, 3H, CH_3C=CH), 1.50 (s, 3H, CH_3C), 1.00 (s, 9H, $((CH_3)_3)C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.4 (C=O), 138.6, 136.1, 132.4, 130.6, 130.6, 130.5, 128.29, 128.3, 128.3, 128.2, 90.2 ($CC(CH_3)_3$), 70.2 (CCH_3), 38.5 (NMe), 37.1 (NMe), 31.6, 26.7 ($(CH_3)_3)C$), 22.8, 15.6 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{19}H_{27}ClN_2O$ $[M+H]^+$ 334.1812, found: 334.1767.

4.4.7. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(3-(trifluoromethyl)phenyl)prop-1-en-2-yl)imidazolidin-4-one (3g)



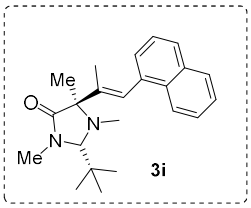
Following the general **procedure D**, **1a** (37 mg, 0.2 mmol), 1-(prop-1-yn-1-yl)-3-(trifluoromethyl)benzene (37 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (62 mg, 84%). TLC (SiO_2):R_f = 0.24 (hexanes:ethylacetate = 5:1); **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53 – 7.37 (m, 4H, Ph), 6.61 (s, 1H, CH=C), 3.88 (s, 1H,$CHC(CH_3)_3$), 3.01 (s, 3H, NMe), 2.44 (s, 3H, NMe), 1.55 (d, *J* = 1.2 Hz, 3H,CH_3C=CH), 1.52 (s, 3H,CH_3C), 1.01 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.3 (C=O), 139.8, 138.4, 132.5, 130.6 (q, *J* = 31.9 Hz), 128.6, 128.6, 128.1, 126.0 (q, *J* = 4.0 Hz), 125.3, 123.4 (q, *J* = 3.6 Hz), 123.2, 90.2 (CC(CH3)3)), 70.2 (CCH3), 38.6 (NMe), 37.1 (NMe), 31.7, 29.8, 26.7 ($(CH_3)_3)C$), 22.8, 15.6 (CH3C=CH); **^{19}F NMR (470 MHz, $CDCl_3$)** δ -62.68; **HRMS** (ESI^+): m/z calcd. for $C_{20}H_{27}F_3N_2O[M+H]^+$ 368.2075, found: 369.2147.

4.4.8. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(naphthalen-2-yl)prop-1-en-2-yl)imidazolidin-4-one (3h)



Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),2-(prop-1-yn-1-yl)naphthalene(34 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (63 mg, 90%).TLC (SiO_2): R_f = 0.24 (hexanes:ethylacetate = 5:1); **^{1}H NMR (**400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 3H, Ar), 7.71 (s, 1H, Ar), 7.49 – 7.41 (m, 2H, Ar), 7.39 (dd, *J* = 8.5, 1.7 Hz, 1H, Ar), 6.76 (s, 1H,CH=C), 3.89 (s, 1H,CHC$(CH_3)_3$), 3.03 (s, 3H, NMe), 2.49 (s, 3H, NMe), 1.63 (d, *J* = 0.9 Hz, 3H,CH_3C=CH), 1.59 (s, 3H,CH_3C), 1.03 (s, 9H, $(CH_3)_3$C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5 (C=O), 138.1, 135.2, 133.3, 132.3, 129.6, 128.0, 128.0, 127.7, 127.6, 127.6, 126.1, 125.8, 90.3 (CC$(CH_3)_3$)), 70.4 (CCH3), 38.5 (NMe), 37.3 (NMe), 31.7, 26.7 ($(CH_3)_3$)C), 22.9, 15.8 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{23}H_{30}N_2O$ $[M+H]^+$ 350.2358, found: 350.2306.

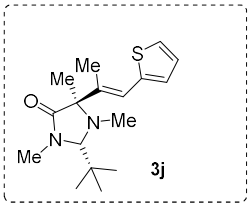
4.4.9. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(naphthalen-1-yl)prop-1-en-2-yl)imidazolidin-4-one (3i)



Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-(prop-1-yn-1-yl)naphthalene(34 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (60 mg, 85%).TLC (SiO_2):R_f = 0.23 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 8.6, 4.4 Hz, 1H, Ar), 7.88 – 7.82 (m, 1H, Ar), 7.76 (d, *J* = 8.2 Hz, 1H, Ar), 7.51 – 7.46 (m, 2H, Ar), 7.46 – 7.42 (m, 1H, Ar), 7.32 (d, *J* = 7.0 Hz, 1H, Ar), 6.99 (s, 1H,CH=C), 3.88 (s, 1H,CHC$(CH_3)_3$), 3.02 (s, 3H, NMe), 2.56 (s, 3H, NMe), 1.64 (s, 3H,CH_3C), 1.40 (d, *J* = 1.0 Hz, 3H,CH_3C=CH), 1.03 (s, 9H, $(CH_3)_3$C); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.5, 139.7, 135.2, 133.6, 132.0, 128.4, 127.6, 127.3, 126.8, 126.0, 125.8, 125.4, 125.3, 90.0 (CC$(CH_3)_3$)), 70.0 (CCH_3), 38.6 (NMe), 37.2 (NMe), 31.6, 26.7 ($(CH_3)_3$)C), 22.8, 15.8 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{23}H_{30}N_2O$ $[M+H]^+$ 350.2358, found: 350.2431.

4.4.10. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(thiophen-2-yl)prop-1-en-2-yl)imidazolidin-4-one (3j)

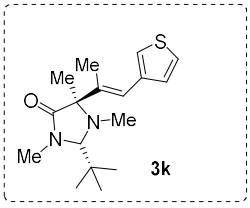
Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),2-(prop-1-yn-1-yl)thiophene (25 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (48 mg, 78%). TLC (SiO_2): R_f = 0.24 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 4.3, 2.0 Hz, 1H, Ar), 7.03 (dd, *J* = 5.1, 2.8 Hz, 2H, Ar), 6.73 (s, 1H,CH=C), 3.89 (s, 1H,CHC$(CH_3)_3$), 3.03 (s, 3H, NMe), 2.42 (s, 3H, NMe), 1.72 (s, 3H,CH_3C=CH), 1.55 (s, 3H,CH_3C), 1.03 (s, 9H, $(CH_3)_3$C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 128.0, 126.9, 125.5, 124.2, 124.0, 122.8, 122.7, 116.7, 90.5 (CC$(CH_3)_3$)), 77.3 (CCH_3), 38.5 (NMe), 31.7 (NMe), 26.7 (($(CH_3)_3$)C), 25.8, 23.1, 16.6 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{17}H_{26}N_2OS$; $[M+H]^+$ 306.1766, found: 306.1838.



3j

4.4.11. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(thiophen-3-yl)prop-1-en-2-yl)imidazolidin-4-one (3k)

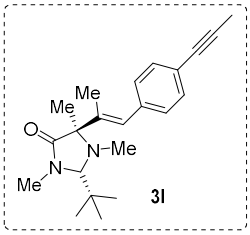
Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),2-(prop-1-yn-1-yl)thiophene(25 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (50 mg, 82%).TLC (SiO_2):R_f = 0.21 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 5.2, 2.7 Hz, 1H, Ar), 7.16 (d, *J* = 2.9 Hz, 1H, Ar), 7.08 (dd, *J* = 5.0, 1.1 Hz, 1H, Ph), 6.53 (s, 1H,CH=C), 3.86 (s, 1H,CHC$(CH_3)_3$), 3.01 (s, 3H, NMe), 2.40 (s, 3H, NMe), 1.62 (d, *J* = 0.8 Hz, 3H,CH_3C=CH), 1.49 (s, 3H,CH_3C), 1.00 (s, 9H, $(CH_3)_3$C); **^{13}C NMR (**126 MHz, $CDCl_3$) δ 175.6 (C=O), 138.5, 137.1, 129.2, 124.7, 123.5, 123.2, 90.3 (CC$(CH_3)_3$)), 70.5 (CCH3), 38.5 (NMe), 37.3 (NMe), 31.6, 26.7(($(CH_3)_3$)C),23.0, 16.3 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{17}H_{26}N_2OS[M+H]^+$ 306.1766, found: 306.1840.



3k

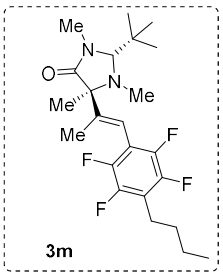
4.4.12. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(4-(prop-1-yn-1-yl)phenyl)prop-1-en-2-yl)imidazolidin-4-one (3l)

Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1,4-di(prop-1-yn-1-yl)benzene(30 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (53 mg, 78%).TLC (SiO_2):R_f = 0.2 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.2 Hz, 2H, Ph), 7.17 (d, *J* = 8.2 Hz, 2H, Ph), 6.55 (s, 1H,CH=C), 3.87 (s, 1H,CHC$(CH_3)_3$), 3.01 (s, 3H, NMe), 2.44 (s, 3H, NMe), 2.05 (s, 3H, CH_3CC), 1.56 (s, 3H), 1.53 (s, 3H), 1.02 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 175.3 (C=O), 137.9, 136.8, 131.2, 129.2, 122.3, 90.3 (CC$(CH_3)_3$)), 86.2 (C_{SP}), 79.8 (C_{SP}), 70.5 (CCH3), 38.5 (NMe), 31.7, 26.7 (($CH_3)_3$)C), 22.9, 15.8 (CH_3C=CH), 4.5 (CH_3CC); **HRMS** (ESI^+): m/z calcd. for $C_{22}H_{30}N_2O$ $[M+H]^+$ 338.2358, found: 338.2433.



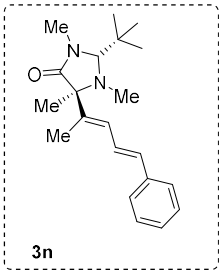
4.4.13. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(4-(prop-1-yn-1-yl)phenyl)prop-1-en-2-yl)imidazolidin-4-one (3m)

Following the general **procedure D**, **1a** (37 mg, 0.2 mmol),1-butyl-2,3,5,6-tetrafluoro-4-(prop-1-yn-1-yl)benzene(50 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (65 mg, 76%).TLC (SiO_2):R_f = 0.33 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.21 (s, 1H,CH=C), 3.86 (s, 1H,CHC$(CH_3)_3$), 3.01 (s, 3H, NMe), 2.72 (t, *J* = 7.6 Hz, 2H, CH_2Ar), 2.46 (s, 3H, NMe), 1.63 – 1.56 (m, 2H, $CH_2CH_2CH_3$), 1.55 (s, 3H, CH_3C=CH), 1.41 (s, 3H, CH_3C), 1.37 (dt, *J* = 14.7, 7.4 Hz, 2H, CH_2CH_3), 1.02 (s, 9H, $(CH_3)_3C$), 0.94 (t, *J* = 7.3 Hz, 3HCH_3CH_2); **^{13}C NMR** (126 MHz, $CDCl_3$)δ 174.5 (C=O), 146.0 – 145.8 (m), 144.9 (dd, *J* = 4.8, 2.2 Hz), 144.1 – 143.8 (m), 142.6 – 142.4 (m), 119.9 – 119.5 (m), 115.0 – 114.9 (m), 114.2 (t, *J* = 18.3 Hz), 90.0(CC$(CH_3)_3$)), 70.1 (CCH3), 38.8 (NMe), 37.2 (NMe), 31.7, 31.5, 31.0, 31.0, 31.0, 29.8, 26.7(($CH_3)_3$)C), 22.7, 22.60, 22.4, 16.6, 16.5, 16.5, 13.8, 1.1; **^{19}F NMR** (471 MHz, $CDCl_3$)δ -140.36 (dd, *J* = 22.6, 12.4 Hz), -145.89 (dd, *J* = 22.6, 12.5 Hz); **HRMS** (ESI^+): m/z calcd. for $C_{23}H_{32}F_4N_2O[M+H]^+$428.2451, found: 428.2525.



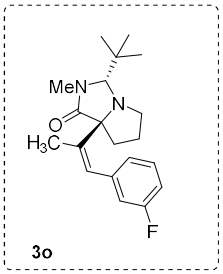
4.4.14. (2*S*,5*S*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((2*E*,4*E*)-5-phenylpenta-2,4-dien-2-yl)imidazolidin-4-one (3n)

Following the general **procedure D**, **1a** (37 mg, 0.2 mmol), (E)-pent-1-en-3-yn-1-ylbenzene(29 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (54 mg, 82%).TLC (SiO_2):R_f = 0.2 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 2H, Ph), 7.34 – 7.28 (m, 2H, Ph), 7.24 – 7.19 (m, 1H,Ph), 6.99 (dd, *J* = 15.5, 10.8 Hz, 1H,CH=C), 6.59 (d, *J* = 15.5 Hz, 1H,CH=C), 6.30 (d, *J* = 10.8 Hz, 1H,CH=C), 3.85 (s, 1H,CHC$(CH_3)_3$), 3.00 (s, 3H, NMe), 2.38 (s, 3H, NMe), 1.59 (d, *J* = 0.7 Hz, 3H,CH_3C=CH), 1.47 (s, 3H,CH_3C), 1.00 (s, 9H, $(CH_3)_3$C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.5 (C=O), 137.8, 137.6, 133.3, 129.0, 128.7, 127.6, 126.5, 124.9, 90.2 (CC$(CH_3)_3$)), 70.2 (CCH3), 38.5 (NMe), 37.3 (NMe), 31.6, 27.2, 26.7 ($(CH_3)_3$)C), 22.7, 14.8 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{21}H_{30}N_2O$ $[M+H]^+$ 326.2358, found: 326.2431.

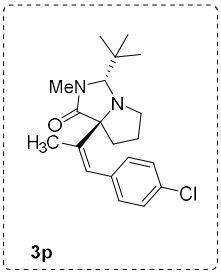


4.4.15. (3*R*,7a*S*)-3-(*tert*-butyl)-7a-((*Z*)-1-(3-fluorophenyl)prop-1-en-2-yl)-2-methylhexahydro-1H-pyrrolo[1,2-c]imidazol-1-one (3o)

Following the general **procedure D**, **1m** (40 mg, 0.2 mmol), 1-fluoro-3-(prop-1-yn-1-yl)benzene (27 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (43 mg, 65%).TLC (SiO_2):R_f = 0.23 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1H, Ph), 6.99 (d, *J* = 7.7 Hz, 1H, Ph), 6.94 – 6.85 (m, 3H, Ph andCH=C), 3.59 (s, 1H,CHC$(CH_3)_3$), 3.27 (ddd, *J* = 10.9, 7.4, 5.9 Hz, 1H, CH_2N), 2.96 (s, 3H, NMe), 2.87 – 2.81 (m, 1H, CH_2N), 2.15 (dt, *J* = 13.1, 6.7 Hz, 1H), 2.03 (d, *J* = 1.3 Hz, 3H,CH_3C=CH), 2.00 – 1.93 (m, 1H), 1.82 – 1.74 (m, 1H), 1.66 – 1.57 (m, 1H), 0.97 (s, 9H, $(CH_3)_3$C); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.5 (C=O), 161.8, 140.8, 129.42(d, *J* = 8.6 Hz), 124.9 (d, *J* = 3.0 Hz), 115.8 (d, *J* = 21.1 Hz), 112.9 (d, *J* = 21.2 Hz), 92.4 (CC$(CH_3)_3$)), 59.9 (NC (CO)), 37.5 (NMe), 36.9 (NCH_2), 31.4, 29.8, 26.4, 25.2, 14.5, 14.2, 1.1; **^{19}F NMR (470 MHz, $CDCl_3$)** δ -114.13 (dd, *J* = 17.4, 8.6 Hz).



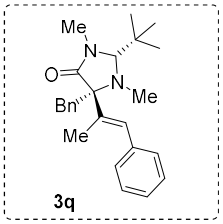
4.4.16. (3*R*,7a*S*)-3-(*tert*-butyl)-7a-((*Z*)-1-(4-chlorophenyl)prop-1-en-2-yl)-2-methylhexahydro-1H-pyrrolo[1,2-c]imidazol-1-one (3p)



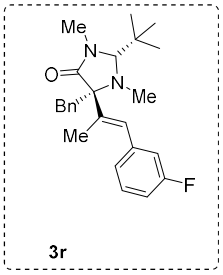
Following the general **procedure D**, **1m** (40 mg, 0.2 mmol), 1-chloro-4-(prop-1-yn-1-yl)benzene (30 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (47 mg, 68%).TLC (SiO_2):R_f = 0.22 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 1H, Ph), 7.25 (d, *J* = 2.5 Hz, 1H, Ph), 7.17 – 7.12 (m, 2H, Ph), 6.87 (s, 1H, CH=C), 3.59 (s, 1H, $CHC(CH_3)_3$), 3.33 – 3.24 (m, 1H, CH_2N), 2.96 (s, 3H, NMe), 2.87 – 2.80 (m, 1H, CH_2N), 2.16 (dt, *J* = 13.1, 6.7 Hz, 1H), 2.00 (d, *J* = 1.3 Hz, 3H, CH_3C=CH), 1.95 (dd, *J* = 13.0, 7.0 Hz, 1H), 1.78 (dt, *J* = 12.4, 6.2 Hz, 1H), 1.62 (dd, *J* = 13.5, 6.1 Hz, 1H), 0.97 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.6 (C=O), 140.3, 137.0, 131.8, 130.4, 128.2, 123.9, 92.5 (CC(CH3)3)), 60.0 (NC (CO)), 37.6 (NMe), 36.9 (NCH_2), 31.4, 29.8, 26.4, 25.2, 14.5 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{20}H_{27}ClN_2O$ $[M+H]^+$ 346.1812, found: 347.1882.

4.4.17. (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethyl-5-((*E*)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3q)

Following the general **procedure D**, **(**2*R*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one (52 mg, 0.2 mmol),1-Phenyl-1-propyne (24 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (64 mg, 84%).TLC (SiO_2):R_f = 0.33 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 10.5, 4.7 Hz, 1H, Ph), 7.27 (s, 5H, Ph), 7.26 – 7.20 (m, 4H, Ph), 6.76 (s, 1H,CH=C), 3.78 (s, 1H,$CHC(CH_3)_3$), 3.44 (d,*J* =13.1 Hz, 1H, CH_2Ph) 3.05 (d, *J* = 13.1 Hz, 1H, CH_2Ph), 2.91 (s, 3H, NMe), 2.52 (s, 3H, NMe), 1.58 (d, *J* = 0.7 Hz, 3H, CH_3C=CH), 0.49 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6 (C=O), 138.3, 137.8, 131.7, 129.5, 129.4, 128.2, 128.1, 128.1, 128.0, 126.7, 126.3, 90.0 ($CC(CH_3)_3$)), 74.9 (CCH_3), 39.1 (NMe), 37.6 (NMe), 37.0, 31.1, 31.0, 26.4 (($CH_3)_3$)C), 15.9 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{25}H_{32}N_2O$ $[M+Na]^+$ 376.2515, found: 376.2402.

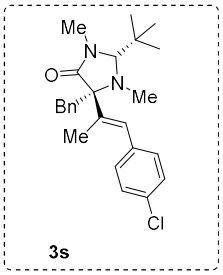


4.4.18. (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-5-((*E*)-1-(3-fluorophenyl)prop-1-en-2-yl)-1,3-dimethylimidazolidin-4-one (3r)



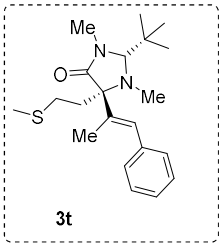
Following the general **procedure D**, **(**2R,5S)-5-benzyl-2-(tert-butyl)-1,3-dimethylimidazolidin-4-one (52 mg, 0.2 mmol),1-fluoro-3-(prop-1-yn-1-yl)benzene (27 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (68 mg, 87%).TLC (SiO_2): R_f = 0.3 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 2H, Ph), 7.25 – 7.20 (m, 3H, Ph), 7.18 – 7.13 (m, 1H, Ph), 7.03 (d, *J* = 7.7 Hz, 1H, Ph), 6.99 – 6.90 (m, 2H, Ph), 6.71 (s, 1H,CH=C), 3.78 (s, 3H,CHC$(CH_3)_3$), 3.41 (d, *J* = 13.1 Hz, 1H, CH_2Ph), 3.02 (d, *J* = 13.1 Hz, 1H, CH_2Ph), 2.91 (s, 3H, NMe), 2.51 (s, 3H, NMe), 1.57 (d, *J* = 0.7 Hz, 3H, (CH_3C=CH)), 0.49 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4 (C=O), 163.6, 161.7, 140.4, 140.0 (d, *J* = 7.8 Hz), 138.1, 131.7, 129.6 (d, *J* = 8.4 Hz), 128.4 (d, *J* = 2.1 Hz), 128.0, 126.4, 125.1 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 21.4 Hz), 113.6 (d, *J* = 21.0 Hz), 89.9 ($CC(CH_3)_3$), 74.8 (CCH_3), 39.1 (NMe), 37.6 (NMe), 36.9, 31.1, 26.4($(CH_3)_3C$), 15.9 (CH_3C=CH); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.67 (m); **HRMS** (ESI^+): m/z calcd. for$C_{25}H_{31}FN_2O[M+H]^+$ 394.2420, found: 394.2496.

4.4.19. (2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-5-((*E*)-1-(4-chlorophenyl)prop-1-en-2-yl)-1,3-dimethylimidazolidin-4-one (3s)



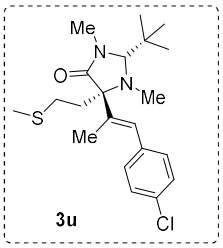
Following the general **procedure D**, **(**2*R*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one (52 mg, 0.2 mmol),1-chloro-4-(prop-1-yn-1-yl)benzene (30 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (73 mg, 90%). TLC (SiO_2): R_f = 0.35 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H, Ph), 7.24 – 7.21 (m, 4H, Ph), 7.20 – 7.12 (m, 3H, Ph), 6.69 (s, 1H,CH=C), 3.77 (s, 1H,CHC$(CH_3)_3$), 3.41 (d, *J* = 13.1 Hz, 1H, CH_2Ph), 3.02 (d, *J* = 13.2 Hz, 1H, CH_2Ph), 2.90 (s, 3H, NMe), 2.50 (s, 3H, NMe), 1.55 (d, *J* = 0.9 Hz, 3H, CH_3C=CH), 0.48 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.4 (C=O), 140.0, 138.1, 136.1, 132.5, 131.7, 130.6, 128.3, 128.3, 128.0, 126.4, 89.9 ($CC(CH_3)_3$), 74.8 (CCH_3), 39.1 (NMe), 37.6 (NMe), 36.9, 31.1, 26.4 ($(CH_3)_3C$), 15.8 CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for $C_{25}H_{31}FN_2O$ $[M+H]^+$ 410.2125, found: 410.2204.

4.4.20. (2*R*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-(2-(methylthio)ethyl)-5-((*E*)-1-phenylprop-1-en-2-yl)imidazolidin-4-one(3t)



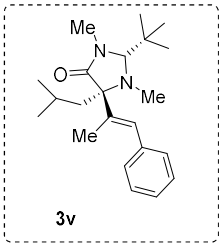
Following the general **procedure D**, (2R,5S)-2-(tert-butyl)-1,3-dimethyl-5-(2-(methylthio)ethyl)imidazolidin-4-one(52 mg, 0.2 mmol),1-Phenyl-1-propyne (24 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (63 mg, 87%).TLC (SiO_2):R_f = 0.2 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 2H, Ph), 7.25 – 7.20 (m, 3H, Ph), 6.60 (s, 1H,CH=C), 3.86 (s, 1H,CHC$(CH_3)_3$), 3.01 (s, 3H, NMe), 2.88 (td, *J* = 12.3, 4.9 Hz, 1H, CH_2CH_2S), 2.54 (td, *J* = 12.4, 4.5 Hz, 1H, CH_2CH_2S), 2.45 (s, 3H, NMe), 2.32 – 2.18 (m, 2H, CH_2S), 2.15 (s, 3H, SMe), 1.56 (d, *J* = 0.8 Hz, 3H, CH_3C=CH), 1.05 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.4 (C=O), 137.5, 137.0, 130.1, 129.3, 128.2, 126.8, 90.4 ($CC(CH_3)_3$), 73.1 (CCH_3), 38.4 (NMe), 37.7 (NMe), 35.3, 31.4, 30.2, 27.3 $(CH_3)_3C$), 16.0, 15.6 ;**HRMS** (ESI^+): m/z calcd. for $C_{21}H_{32}N_2OS$ $[M+H]^+$360.2235, found: 360.2309.

4.4.21. (2*S*,5*S*)-2-(*tert*-butyl)-5-((*E*)-1-(4-chlorophenyl)prop-1-en-2-yl)-1,3-dimethyl-5-(2-(methylthio)ethyl)imidazolidin-4-one (3u)



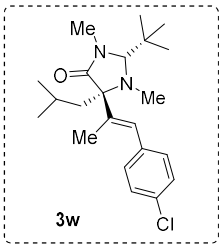
Following the general **procedure D**, (2*R*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-(2-(methylthio)ethyl)imidazolidin-4-one (52 mg, 0.2 mmol),1-chloro-4-(prop-1-yn-1-yl)benzene (49 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (70 mg, 88%).TLC (SiO_2):R_f = 0.3 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 2H, Ph), 7.22 – 7.10 (m, 2H, Ph), 6.53 (s, 1H,CH=C), 3.85 (s, 1H,CHC$(CH_3)_3$), 3.01 (s, 3H, NMe), 2.86 (td, *J* = 12.4, 4.8 Hz, 1H,CH_2CH_2S), 2.54 – 2.47 (m, 1H, CH_2CH_2S), 2.43 (s, 3H, NMe), 2.24 (ddd, *J* = 21.1, 15.1, 4.6 Hz, 2H, CH_2S), 2.14 (s, 3H, SMe), 1.53 (d, *J* = 0.8 Hz, 3H, CH_3C=CH), 1.04 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.1 (C=O), 137.9, 135.8, 132.6, 130.5, 128.8, 128.4, 90.3 ($CC(CH_3)_3$), 73.1(CCH_3), 38.3 (NMe), 37.7 (NMe), 35.2, 31.4, 30.2, 27.3 (($CH_3)_3C$), 16.0, 15.6 (CH3C=CH);**HRMS** (ESI^+): m/z calcd. for $C_{21}H_{31}ClN_2OS$ $[M+H]^+$ 394.1846, found: 394.1919.

4.4.22. (2*S*,5*S*)-2-(*tert*-butyl)-5-isobutyl-1,3-dimethyl-5-((*E*)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3v)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-5-isobutyl-1,3-dimethylimidazolidin-4-one(46 mg, 0.2 mmol),1-Phenyl-1-propyne (24 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (50 mg, 73%).TLC (SiO_2):R_f = 0.33 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H, Ph), 7.24 – 7.17 (m, 3H, Ph), 6.57 (s, 1H,CH=C), 3.88 (s, 1H,CHC$(CH_3)_3$), 3.02 (s, 3H, NMe), 2.46 (s, 3H, NMe), 1.97 – 1.88 (m, 1H, C$H(CH_3)_2$), 1.84 (d, *J* = 5.0 Hz, 2H, $CH_2CH(CH_3)_2$), 1.53 (s, 3H, CH_3C=CH), 1.06 (s, 9H, $(CH_3)_3$C), 1.05 – 0.99 (m, 6H, $(CH_3)_2CH_2$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.2 (C=O), 138.5, 138.0, 129.7, 129.3, 128.1, 126.6, 90.6 (C$C(CH_3)_3$), 73.8 (CCH_3), 42.6 (NMe), 38.4 (NMe), 37.7, 31.4, 29.8, 27.3, 25.6, 24.8, 24.3, 16.0 (CH_3C=CH), 1.08; **HRMS** (ESI^+): m/z calcd. for$C_{22}H_{34}N_2O$ $[M+H]^+$ 342.2671, found: 342.2634.

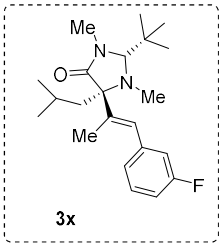
4.4.23. (2*S*,5*S*)-2-(*tert*-butyl)-5-((*E*)-1-(4-chlorophenyl)prop-1-en-2-yl)-5-isobutyl-1,3-dimethylimidazolidin-4-one(3w)



Following the general **procedure D**, (2S,5S)-2-(tert-butyl)-5-isobutyl-1,3-dimethylimidazolidin-4-one(46 mg, 0.2 mmol),1-chloro-4-(prop-1-yn-1-yl)benzene (49 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (58 mg, 76%).TLC (SiO_2):R_f = 0.28 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30 – 7.26 (m, 2H, Ph), 7.16 – 7.11 (m, 2H, Ph), 6.51 (s, 1H,CH=C), 3.88 (s, 1H,CHC$(CH_3)_3$), 3.02 (s, 3H, NMe), 2.45 (s, 3H, NMe), 1.96 – 1.86 (m, 1H, C$H(CH_3)_2$), 1.85 – 1.81 (m, 2H,$CH_2CH(CH_3)_2$), 1.51 (s, 3H, CH_3C=CH), 1.06 (s, 9H, $(CH_3)_3$C), 1.02 (dd, *J* = 18.4, 6.6 Hz, 6H, $(CH_3)_2$CH); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.0 (C=O), 139.4, 136.3, 132.4, 130.6, 128.5, 128.3, 90.6 (C$C(CH_3)_3$), 73.8 (CCH_3), 42.5 (NMe), 38.4 (NMe), 37.7, 31.4, 27.3 ($(CH_3)_3$C), 25.5, 24.7, 24.3, 15.9 (CH_3C=CH), 1.1; **HRMS** (ESI^+): m/z calcd. for$C_{22}H_{33}ClN_2O$ $[M+H]^+$ 376.2281, found: 342.2634.

4.4.24. (2*S*,5*S*)-2-(*tert*-butyl)-5-((*E*)-1-(3-fluorophenyl)prop-1-en-2-yl)-5-isobutyl-1,3-dimethylimidazolidin-4-one (3x)

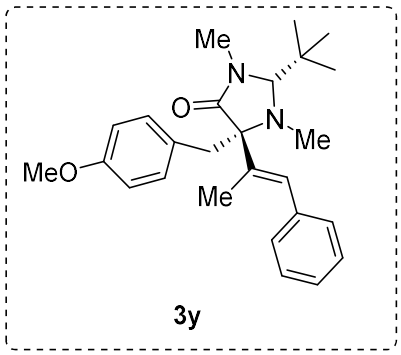
Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-5-isobutyl-1,3-dimethylimidazolidin-4-one (46 mg, 0.2 mmol), 1-fluoro-3-(prop-1-yn-1-yl)benzene (27 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (56 mg, 78%).TLC (SiO_2):R_f = 0.3 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H, Ph), 6.98 (d, *J* = 7.7 Hz, 1H, Ph), 6.94 – 6.88 (m, 2H, Ph), 6.53 (s, 1H,CH=C), 3.88 (s, 1H,CHC$(CH_3)_3$), 3.02 (s, 3H, NMe), 2.45 (s, 3H, NMe), 1.96 – 1.86 (m, 1H, CH$(CH_3)_2$), 1.83 (d, *J* = 5.2 Hz, 2H, CH_2CH$(CH_3)_2$), 1.53 (s, 3H, CH_3C=CH), 1.06 (s, 9H, $(CH_3)_3$C), 1.02 (dd, *J* = 23.0, 6.6 Hz, 6H, $(CH_3)_2$CH). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.6 (C=O), 161.7, 129.5 (d, *J* = 8.5 Hz),125.1 (d, *J* = 2.7 Hz),116.0 (d, *J* = 21.4 Hz),113.5 (d, *J* = 21.1 Hz), 90.6 (CC$(CH_3)_3$), 42.4 (NMe), 38.4 (NMe), 31.4, 27.3, 25.5, 24.7, 24.3, 16.0 (CH_3C=CH), 1.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.97 – -115.34 (m); **HRMS** (ESI^+): m/z calcd. for$C_{22}H_{33}FN_2O$ $[M+H]^+$ 360.2577, found: 360.2651.



3x

4.4.25. (2*S*,5*S*)-2-(*tert*-butyl)-5-(4-methoxybenzyl)-1,3-dimethyl-5-((*E*)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3y)

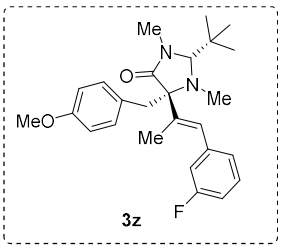
Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one (60 mg, 0.2 mmol), 1-Phenyl-1-propyne (24 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (62 mg, 76%).TLC (SiO_2): R_f = 0.23 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.6 Hz, 2H, Ph), 7.26 – 7.21 (m, 3H, Ph), 7.17 – 7.13 (m, 2H, Ph), 6.80 – 6.77 (m, 2H, Ph), 6.75 (s, 1H, CH=C), 3.78 (s, 1H,CHC$(CH_3)_3$), 3.76 (s, 3H, OMe), 3.36 (d, *J* = 13.3 Hz, 1H, CH_2Ar), 2.99 (d, *J* = 13.3 Hz, 1H, CH_2Ar), 2.91 (s, 3H,NMe), 2.50 (s, 3H, NMe), 1.57 (d, *J* = 0.7 Hz, 3H, CH_3C=CH), 0.53 (s, 9H, $(CH_3)_3$C); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.7 (C=O), 158.4, 139.0, 137.8, 132.6, 130.4, 129.4, 129.3, 128.1, 128.1, 126.7, 113.5, 89.9 (CC$(CH_3)_3$), 74.8 (CCH_3), 55.4 (OMe), 38.2 (NMe), 37.6 (NMe), 36.9, 31.1, 26.5



3y

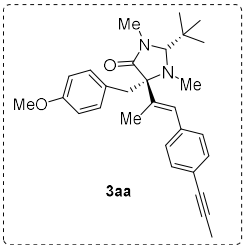
($(CH_3)_3C$), 15.9 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{26}H_{34}N_2O_2$ $[M+H]^+$406.2620, found: 406.2692.

4.4.26. (2*S*,5*S*)-2-(*tert*-butyl)-5-((*E*)-1-(3-fluorophenyl)prop-1-en-2-yl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one(3z)



Following the general **procedure D**, (2S,5S)-2-(tert-butyl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one (60 mg, 0.2 mmol),1-fluoro-3-(prop-1-yn-1-yl)benzene (27 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (65 mg, 78%).TLC (SiO_2):R_f= 0.2 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H, Ph), 7.16 – 7.12 (m, 2H, Ph), 7.02 (d, *J* = 7.7 Hz, 1H, Ph), 6.98 – 6.90 (m, 2H, Ph), 6.80 – 6.76 (m, 2H, Ph), 6.70 (s, 1H,CH=C), 3.78 (s, 1H,$CHC(CH_3)_3$), 3.76 (s, 3H, OMe), 3.34 (d, *J* = 13.3 Hz, 1H, CH_2Ar), 2.96 (d, *J* = 13.4 Hz, 1H, CH_2Ar), 2.90 (s, 3H, NMe), 2.49 (s, 3H, NMe), 1.56 (d, *J* = 0.8 Hz, 3H, CH_3C=CH), 0.53 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.5 (C=O), 162.6 (d, *J* = 245.3 Hz), 158.5, 140.4, 140.0 (d, *J* = 7.7 Hz), 132.5, 130.2, 129.6 (d, *J* = 8.4 Hz), 128.3 (d, *J* = 2.1 Hz), 125.1 (d, *J* = 2.8 Hz), 116.1, 116.0, 113.6, 113.6, 113.5, 89.9 ($CC(CH_3)_3$), 74.8 (CCH_3), 55.4 (OMe), 38.2 (NMe), 37.6 (NMe), 36.9, 31.1, 26.4 ($(CH_3)_3C$), 15.9 (CH_3C=CH); **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.69 (dd, *J* = 9.0, 6.2 Hz); **HRMS** (ESI^+): m/z calcd. for$C_{26}H_{33}FN_2O_2$ $[M+H]^+$ 424.2526, found: 424.2597.

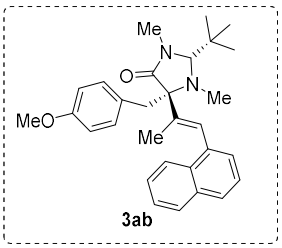
4.4.27. (2*S*,5*S*)-2-(*tert*-butyl)-5-(4-methoxybenzyl)-1,3-dimethyl-5-((*E*)-1-(4-(prop-1-yn-1-yl)phenyl)prop-1-en-2-yl)imidazolidin-4-one (3aa)



Following the general **procedure D**, (2S,5S)-2-(tert-butyl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one (60 mg, 0.2 mmol), 1,4-di(prop-1-yn-1-yl)benzene (31 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (65 mg, 74%). TLC (SiO_2): R_f = 0.18 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 8.2 Hz, 2H, Ph), 7.18 (s, 1H, Ph), 7.14 (dt, *J* = 4.9, 3.9 Hz, 3H, Ph), 6.80 – 6.75 (m, 2H, Ph), 6.69 (s, 1H,CH=C), 3.77 (s, 1H,$CHC(CH_3)_3$), 3.76 (s, 3H, OMe), 3.34 (d, *J* = 13.3 Hz, 1H, CH_2Ar), 2.90 (s, 3H, NMe), 2.98 (d, *J* = 13.3 Hz, 1H, CH_2Ar), 2.90 (s, 3H, NMe), 2.06 (d, *J* = 5.0 Hz, 3H, CH_3CC), 1.57 (t, *J* = 2.4 Hz, 3H, CH_3C=CH), 0.53 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7 (C=O), 158.5, 139.7, 137.0, 132.6, 131.3, 130.4, 129.2, 129.0, 122.3,

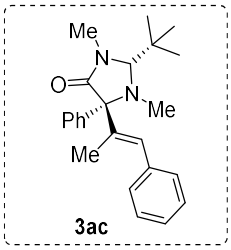
113.6, 90.0 ($CC(CH_3)_3$), 86.1 (C_{SP}), 79.8 (C_{SP}), 74.9 (CCH_3), 55.5 (OMe), 38.3 (NMe), 37.6 (NMe), 37.0, 31.1, 29.8, 26.5 ($(CH_3)_3C$), 16.0 (CH_3C=CH), 4.4 (MeCC); **HRMS** (ESI^+): m/z calcd. for$C_{29}H_{36}N_2O_2[M+H]^+$ 444.2777, found: 444.2853.

4.4.28. (2*S*,5*S*)-2-(*tert*-butyl)-5-(4-methoxybenzyl)-1,3-dimethyl-5-((*E*)-1-(naphthalen-1-yl)prop-1-en-2-yl)imidazolidin-4-one (3ab)



Following the general **procedure D**, (2S,5S)-2-(tert-butyl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one (60 mg, 0.2 mmol),1-(prop-1-yn-1-yl)naphthalene (33 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (69 mg, 75%).TLC (SiO_2):R_f= 0.25 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 6.5, 3.0 Hz, 1H, Ar), 7.89 – 7.83 (m, 1H, Ar), 7.77 (d, *J* = 8.2 Hz, 1H, Ar), 7.54 – 7.48 (m, 1H, Ar), 7.47 – 7.43 (m, 1H, Ar), 7.33 (d, *J* = 7.0 Hz, 1H, Ar), 7.24 – 7.19 (m, 1H, Ar), 7.10 (s, 1H,CH=C), 6.84 – 6.79 (m, 1H, Ar), 3.80 (s, 1H,$CHC(CH_3)_3$), 3.78 (s, 3H, OMe), 3.50 (d, *J* = 13.4 Hz, 1H, CH_2Ar), 3.14 (d, *J* = 13.4 Hz, 1H, CH_2Ar), 2.92 (s, 3H, NMe), 2.63 (s, 3H, NMe), 1.43 (d, *J* = 0.8 Hz, 3H, CH_3C=CH), 0.56 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7 (C=O), 158.5, 140.9, 135.4, 133.7, 132.6, 132.0, 130.5, 128.4, 127.8, 127.3, 126.8, 126.1, 125.9, 125.4, 125.4, 113.6, 89.9 ($CC(CH_3)_3$), 74.8 (CCH_3), 55.5 (OMe), 38.3 (NMe), 37.7 (NMe), 37.2, 31.1, 29.8, 26.5($(CH_3)_3C$), 16.1 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{30}H_{36}N_2O_2$ $[M+H]^+$456.2777, found: 456.2849.

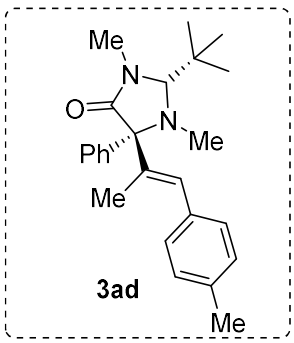
4.4.29. (2*S*,5*R*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenyl-5-((*E*)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3ac)



Following the general **procedure D**, (2S,5S)-2-(tert-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol),1-Phenyl-1-propyne (24 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (61 mg, 85%).TLC (SiO_2): R_f = 0.33 (hexanes:ethylacetate = 5:1).n**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 5.5 Hz, 2H, Ph), 7.34 (t, *J* = 7.9 Hz, 2H, Ph), 7.29 – 7.23 (m, 3H, Ph), 7.17 (t, *J* = 7.4 Hz, 1H, Ph), 7.13 (d, *J* = 7.3 Hz, 2H, Ph), 5.92 (s, 1H,CH=C), 3.96 (s, 1H,$CHC(CH_3)_3$), 3.04 (s, 3H, NMe), 2.67 (s, 3H, NMe), 1.73 (d, *J* = 1.1 Hz, 3H, CH_3C=CH), 0.95 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6 (C=O), 141.2, 139.6, 137.6, 133.6, 129.0, 129.0, 128.4, 128.0, 128.0, 127.5, 127.0, 126.6, 90.4

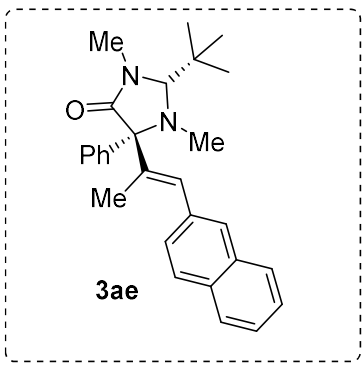
(CC(CH_3)$_3$), 39.2 (NMe), 39.1 (NMe), 31.6, 26.7 ((CH_3)$_3$C), 16.5(CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{24}H_{30}N_2O$ $[M+H]^+$ 362.2358, found: 362.2394.

4.4.30. (2*S*,5*R*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenyl-5-((E)-1-(p-tolyl)prop-1-en-2-yl)imidazolidin-4-one (3ad)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol),1-methyl-4-(prop-1-yn-1-yl)benzene (26 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (61 mg, 80%). TLC (SiO_2): R_f = 0.37 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.3 Hz, 1H, Ph), 7.33 (t, *J* = 7.9 Hz, 1H, Ph), 7.26 – 7.21 (m, 1H, Ph), 7.05 (dd, *J* = 20.6, 8.1 Hz, 1H, Ph), 5.87 (s, 1H,CH=C), 3.95 (s, 1H,CHC(CH_3)$_3$), 3.03 (s, 3H, NMe), 2.66 (s, 3H, NMe), 2.30 (s, 3H, MeAr), 1.72 (d, J = 1.1 Hz, 3H, , CH_3C=CH), 0.95 (s, 9H, (CH_3)$_3$C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.7 (C=O), 141.3, 138.9, 136.4, 134.7, 133.5, 129.0, 128.8, 127.5, 126.9, 90.4 (CC(CH_3)$_3$), 39.2 (NMe), 39.1 (NMe), 31.6, 26.8 ((CH_3)$_3$C), 21.2, 16.5 (CH_3C=CH), 3.1, 1.1; **HRMS** (ESI^+): m/z calcd. for$C_{25}H_{32}N_2O$ $[M+H]^+$ 376.2515, found: 376.2589.

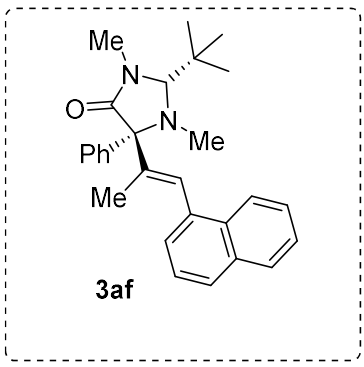
4.4.31. (2*S*,5*R*)-2-(*tert*-butyl)-1,3-dimethyl-5-((*E*)-1-(naphthalen-2-yl)prop-1-en-2-yl)-5-phenylimidazolidin-4-one(3ae)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol),2-(prop-1-yn-1-yl)naphthalene (35 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol)to give title compound (72 mg, 88%). TLC (SiO_2): R_f= 0.24 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H, Ar), 7.79 – 7.70 (m, 3H, Ar), 7.60 (s, 1H, Ar), 7.46 – 7.34 (m, 4H, Ar), 7.31 – 7.24 (m, 2H, Ar), 6.08 (s, 1H,CH=C), 3.98 (s, 1H,CHC(CH_3)$_3$), 3.06 (s, 3H, NMe), 2.72 (s, 3H, NMe), 1.80 (d, *J* = 1.2 Hz, 3H, CH_3C=CH), 0.97 (s, 9H, (CH_3)$_3$C); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.6 (C=O), 141.2, 140.1, 135.2, 133.7, 133.3, 132.2, 128.5, 127.9, 127.7, 127.6, 127.5, 127.5, 127.4, 127.0, 126.1, 125.8, 90.4 (CC(CH_3)$_3$),

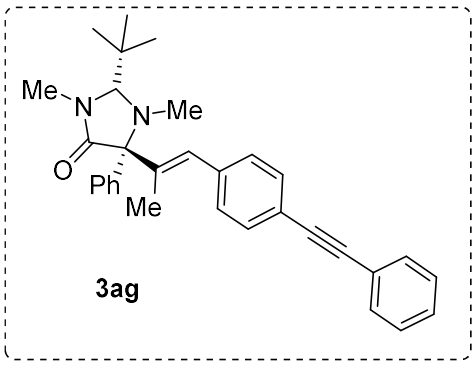
39.3 (NMe), 39.1 (NMe), 31.7, 26.8 ($(CH_3)_3C$), 16.6 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{28}H_{32}N_2O$ $[M+H]^+$ 412.2515, found: 412.2587.

4.4.32. (2*S*,5*R*)-2-(*tert*-butyl)-1,3-dimethyl-5-((*E*)-1-(naphthalen-1-yl)prop-1-en-2-yl)-5-phenylimidazolidin-4-one(3af)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol),1-(prop-1-yn-1-yl)naphthalene (35 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (64 mg, 78%). TLC (SiO_2): R_f= 0.34 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.3 Hz, 2H, Ar), 7.83 – 7.77 (m, 1H, Ar), 7.73 – 7.67 (m, 2H, Ar), 7.48 – 7.35 (m, 5H, Ar), 7.29 – 7.23 (m, 3H, Ar), 6.33 (s, 1H,CH=C), 3.99 (s, 1H, $CHC(CH_3)_3$), 3.05 (s, 3H, NMe), 2.82 (s, 3H, NMe), 1.59 (d, *J* = 1.1 Hz, 3H, CH_3C=CH), 0.99 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5 (C=O), 141.3, 141.3, 135.3, 133.6, 132.3, 131.9, 128.4, 128.3, 127.6, 127.2, 127.1, 126.3, 126.0, 125.8, 125.3, 125.2, 90.3 ($CC(CH_3)_3$), 39.4 (NMe), 39.1 (NMe), 31.7, 29.8, 26.8 ($(CH_3)_3C$), 16.5 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{28}H_{32}N_2O$ $[M+H]^+$ 412.2515, found: 412.2593.

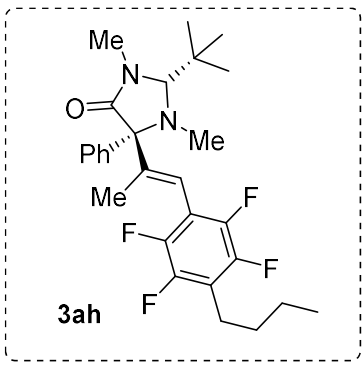
4.4.33. (2*S*,5*R*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenyl-5-((*E*)-1-(4-(phenylethynyl)phenyl)prop-1-en-2-yl)imidazolidin-4-one(3ag)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol),1-(phenylethynyl)-4-(prop-1-yn-1-yl)benzene(45 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (71 mg, 77%). TLC (SiO_2): R_f = 0.24 (hexanes:ethylacetate = 5:1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H, Ph), 7.54 – 7.48 (m, 2H, Ph), 7.46 – 7.40 (m, 2H, Ph), 7.38 – 7.23 (m, 6H, Ph), 7.12 (d, *J* = 8.2 Hz, 2H, Ph), 5.91 (s, 1H,CH=C), 3.97 (s, 1H,$CHC(CH_3)_3$), 3.04 (s, 3H, NMe), 2.68 (s, 3H, NMe), 1.74 (d, *J* = 1.1 Hz, 3H, CH_3C=CH), 0.95 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.5 (C=O), 141.1, 140.6, 137.7, 133.1,

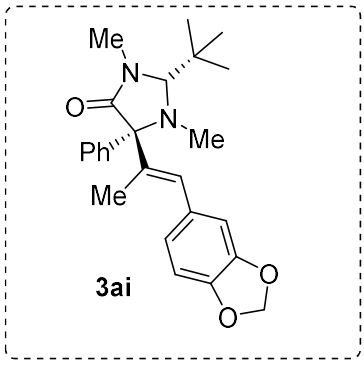
131.7, 131.3, 129.0, 128.4, 128.4, 128.3, 127.6, 127.1, 123.4, 121.5, 90.4 ($CC(CH_3)_3$), 89.8 (C_{SP}), 89.5 (C_{SP}), 39.3 (NMe), 39.1 (NMe), 31.6, 29.8, 26.7 ($(CH_3)_3C$), 16.6 ($CH_3C{=}CH$); **HRMS** (ESI^+): m/z calcd. for$C_{32}H_{34}N_2O$ $[M+H]^+$ 462.2671, found: 462.2647.

4.4.34.(2*S*,5*R*)-2-(*tert*-butyl)-5-((*E*)-1-(4-butyl-2,3,5,6-tetrafluorophenyl)prop-1-en-2-yl)-1,3-dimethyl-5-phenylimidazolidin-4-one(3ah)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol), 1-butyl-2,3,5,6-tetrafluoro-4-(prop-1-yn-1-yl)benzene (50 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (80 mg, 82%). TLC (SiO_2): R_f = 0.24 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.3 Hz, 2H, Ph), 7.35 (t, *J* = 7.9 Hz, 2H, Ph), 7.26 (d, *J* = 14.6 Hz, 1H , Ph), 5.57 (s, 1H, CH=C), 3.96 (s, 1H, $CHC(CH_3)_3$), 3.03 (s, 3H, NMe), 2.68 (s, 5H, NMe and CH_2Ar), 2.71 – 2.65 (m, 2H, $CH_2CH_2CH_3$), 1.56 (d, *J* = 1.3 Hz, 3H, $CH_3C{=}CH$), 1.34 (dq, *J* = 14.7, 7.3 Hz, 2H, CH_2CH_3), 0.97 (s, 9H, $(CH_3)_3C$), 0.92 (t, *J* = 7.3 Hz, 3H CH_3CH_2); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.9 (C=O), 146.7, 140.4, 128.4 (d, *J*= 2.6 Hz), 127.6, 127.3, 119.1 (d, *J* = 2.2 Hz), 90.0 ($CHC(CH_3)_3$), 39.1 (NMe), 38.9 (NMe), 31.7, 31.4, 26.8 ($(CH_3)_3C$), 22.6, 22.4, 17.1 ($(CH_3)_3C$), 13.8, 1.1; **^{19}F NMR** (471 MHz, $CDCl_3$) δ -140.57 (dd, *J* = 22.7, 12.5 Hz), -145.98 (dd, *J* = 22.7, 12.6 Hz); **HRMS** (ESI^+): m/z calcd. for$C_{28}H_{34}F_4N_2O$ $[M+H]^+$490.2607, found: 490.2683.

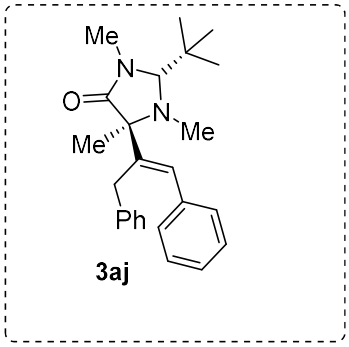
4.4.35. (2*S*,5*R*)-5-((*E*)-1-(benzo[d][1,3]dioxol-5-yl)prop-1-en-2-yl)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one(3ai)



Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol),5-(prop-1-yn-1-yl)benzo[d][1,3]dioxole (33 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (66 mg, 80%). TLC (SiO_2): R_f = 0.2 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (s, 2H, Ph), 7.35 (t, *J* = 7.9 Hz, 2H, Ph), 7.29 – 7.25 (m, 1H, Ph),

6.74 (d, J = 8.0 Hz, 1H, Ph), 6.68 (d, J = 1.5 Hz, 1H), Ph, 6.60 (dd, J = 8.1, 1.4 Hz, 1H, Ph), 5.93 (s, 2H, OCH_2O), 5.83 (s, 1H, CH=C), 3.97 (s, 1H,$CHC(CH_3)_3$), 3.05 (s, 3H, NMe), 2.68 (s, 3H, NMe), 1.73 (d, J = 1.0 Hz, 3H, CH_3C=CH), 0.97 (s, 9H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 173.6 (C=O), 147.4, 146.2, 141.21, 138.6, 133.2, 131.6, 128.4, 127.5, 127.0, 122.8, 109.3, 108.0, 101.0, 90.4 ($CH(CH_3)_3$), 39.2 (NMe), 39.1 (NMe), 31.6, 26.7 (($CH_3)_3C$), 16.6 (CH_3C=CH); **HRMS** (ESI^+): m/z calcd. for$C_{25}H_{30}N_2O_3$ $[M+H]^+$ 406.2256, found: 406.2329.

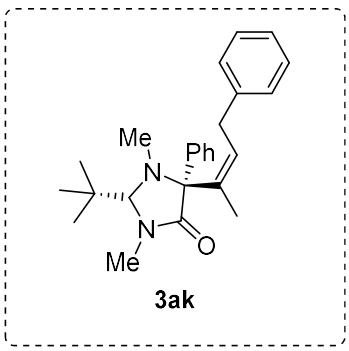
4.4.36. (2S,5S)-2-(tert-butyl)-5-((E)-1,3-diphenylprop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3aj)



3aj

Following the general **procedure D**, (2S,5S)-2-(tert-butyl)-1,3,5-trimethylimidazolidin-4-one (37 mg, 0.2 mmol), 1,3-diphenylpropa-1,2-diene (39 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (56 mg, 74%). TLC (SiO_2): R_f = 0.25 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.21 (m, 6H, Ph), 7.20 – 7.10 (m, 4H, Ph), 6.81 (s, 1H, CH=C), 3.88 (s, 1H, $CHC(CH_3)_3$), 3.84 (d, J = 16.3 Hz, 1H, CH_2Ph), 3.09 (d, J = 16.3 Hz, 1H, CH_2Ph), 2.51 (s, 3H, MeN-CO), 2.46 (s, 3H, Me-N), 1.52 (s, 3H, MeC=CH), 0.96 (s, 1H, $(CH_3)_3C$); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.2 (C=O), 139.5 (Ph), 138.2 (Ph), 137.1 (Ph), 132.8 (Ph), 128.6 (Ph, 2C), 128.3 (Ph), 128.0 (Ph), 127.1 (Ph), 126.0 (Ph), 89.6 (($CH_3)_3C$), 70.0 (MeCNMe(CO)), 38.7 (NMe), 36.8 (NMe), 35.5, 31.4, 29.8 ($PhCH_2$), 26.7 (($CH_3)_3C$), 23.4.

4.4.37. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-phenyl-5-((Z)-4-phenylbut-2-en-2-yl)imidazolidin-4-one (3ak)

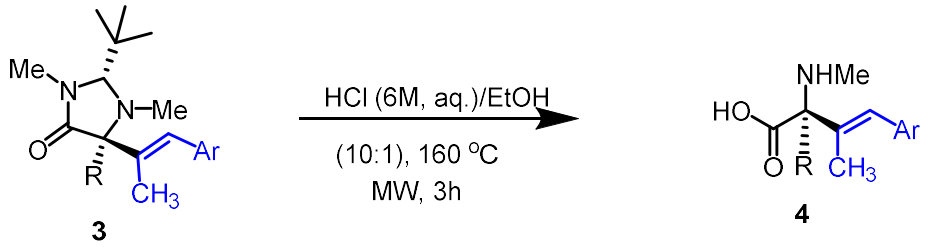


3ak

Following the general **procedure D**, (2*S*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one (50 mg, 0.2 mmol), buta-1,2-dien-1-ylbenzene (26 mg, 0.2 mmol) and LiHMDS (0.4 mL, 1.0 M in THF, 0.4 mmol) to give title compound (56 mg, 71%). TLC (SiO_2): R_f= 0.28 (hexanes:ethylacetate = 5:1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 (d, J = 7.5 Hz, 2H, Ph), 7.39 – 7.09 (m, 8H, Ph), 5.22 (qd, J = 6.9, 1.2 Hz, 1H, C=CH), 3.81 (s, 1H, $CHC(CH_3)_3$), 3.43 (d, J = 16.3 Hz, 1H, $PhCH_2$), 3.12 (d, J = 16.3 Hz, 1H, $PhCH_2$), 2.84 (s, 3H, CH_3N-CO), 2.59 (s, 3H,

$\underline{CH_3}$-N), 1.48 (dd, J = 6.9, 0.5 Hz, 3H, $\underline{CH_3}$C=CH), 0.89 (s, 5H).; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.0 (C=O), 142.1 (Ph), 139.7 (C=CH), 139.1 (Ph), 131.4 (Ph), 128.7 (Ph), 128.5 (Ph), 128.1 (Ph), 127.3 (Ph), 126.7 (Ph), 125.8 (Ph), 90.0 ($(CH_3)_3C$), 76.7 (MeCNMe(CO)), 39.8 (NMe), 39.1 (NMe), 35.6, 31.6, 26.8 ($(CH_3)_3C$), 14.8 ($C=C\underline{CH_3}$).

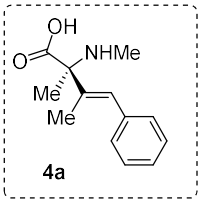
5. General procedure for the hydrolysis of imidazolidinone derivatives to synthesis amino acids



3 **4**

Procedure F: Based on a known and available procedure in the literature[2], a sealed microwave tube was charged with synthesized alpha-alkenylated imidazolidinone derivative (**3**) (1.0 eq), HCl (6.0 M, aq.)/EtOH (10:1, 0.2 M) and heated in a microwave reactor at 160 °C for 3 h. The cooled reaction mixture was diluted with water and washed with dichlorometane (3 times) and then concentrated under vacuum. Furthre hydrolyze did under basic conditions using NaOH (10% w/w, aq.)/DMSO (5:1) at 100 °C for 6h. After acidifying and extraction with dichlorometane a crude product was obtained. To purified the resulting crude product an ion-exchange chromatography (Dowex®50W8-200, 100 –200 mesh) was used, and cholumn was washed with deionised water and the product was eluted with NH_3 (3.5% w/w, aq.). The aqueous fractions which are ninhydrin-positive were combined and concentrated under vacuum. The obtained solid was dissolved in methanol, filtered and concentrated in vacuo. More drying under high vacuum afforded the pure amino acid derivative.

5.1. (S,E)-2,3-dimethyl-2-(methylamino)-4-phenylbut-3-enoic acid (4a)

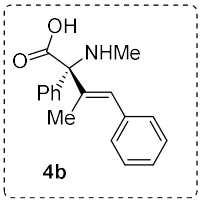


4a

Following the general **procedure F**, 0.2 mmol of imidazolidinone was used. (32 mg, 74%). **^{1}H NMR** (400 MHz, MeOD) δ 7.37-7.19 (m, 5H, ArH), 6.62 (s, 1H, C$\underline{H}$=C), 2.44 (s, 3H, NMe), 1.73 (d, J = 3.0 Hz, 3H CH=C$\underline{Me}$), 1.59 (s, 3H, CMe); **^{13}C NMR** (126 MHz, MeOD) δ 171.9 (C=O), 137.2 (Ar), 135.7 (Ar), 130.3 (Ar), 130.1 (Ar), 129.5 (Ar), 129.0 (Ar), 70.7 ($\underline{C}$-C=C), 27.0

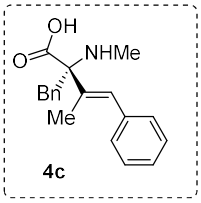
(NMe), 18.4 (C=C<u>Me</u>), 14.48 (Me).; **HRMS** (ESI$^+$): m/z calcd. For $C_{13}H_{17}NO_2$ $[M+H]^+$ 220.1259, found: 220.1295.

5.2. (R,E)-3-methyl-2-(methylamino)-2,4-diphenylbut-3-enoic acid (4b)



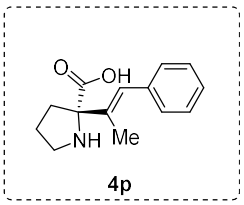
Following the general **procedure F**, 0.2 mmol of imidazolidinone was used. (43 mg, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84-7.71 (m, 4H, ArH), 7.46-7.34 (m, 6H, ArH), 6.63 (s, 1H, C<u>H</u>=C), 2.84 (s, 3H, NMe), 1.74 (d, *J* = 1.5 Hz, 3H, <u>CH_3</u>C=C); **HRMS** (ESI$^+$): m/z calcd. for$C_{15}H_{20}N_2O_2$ $[M+H]^+$260.1525, found: 260.1541.

5.3. (S,E)-2-benzyl-3-methyl-2-(methylamino)-4-phenylbut-3-enoic acid (4c)



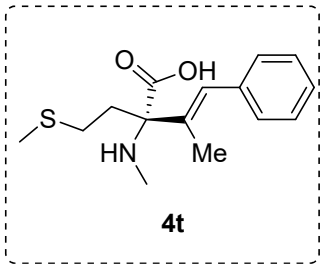
Following the general **procedure F**, 0.2 mmol of imidazolidinone was used. (42 mg, 72%). **^{1}H NMR** (400 MHz, MeOD) δ 7.49 – 7.03 (m, 10H, ArH), 6.64 (s, 1H, C=C<u>H</u>), 3.34 (d, J = 14.0 Hz, 1H, C<u>H_2</u>Ph), 3.23 (d, J = 13.2 Hz, 1H, C<u>H_2</u>Ph), 2.33 (s, 3H, NMe), 1.28 (s, 3H, C=CC<u>H_3</u>); **HRMS** (ESI$^+$): m/z calcd. For $C_{19}H_{21}NO_2$ $[M+H]^+$ 296.1572, found: 296.1601.

5.4. (S,E)-2-(1-phenylprop-1-en-2-yl)pyrrolidine-2-carboxylic acid (4d)



Following the general **procedure F**, 0.2 mmol of imidazolidinone was used. (35 mg, 75%). **^{1}H NMR** (400 MHz, MeOD) δ 7.34-7.23 (m, 5H, ArH), 6.62 (s, 1H, C<u>H</u>=C), 3.48-3.46 (m, 1H, <u>CH_2</u>N), 3.13-3.11 (m, 1H, <u>CH_2</u>N), 2.20-2.17 (m, 2H, C<u>CH_2</u>CH_2CH_2N), 1.89 (d, *J* = 4.0 Hz, 3H, <u>CH_3</u>C=C), 0.90-0.82 (m, 2H, CCH_2<u>CH_2</u>CH_2N); **HRMS** (ESI$^+$): m/z calcd. For $C_{14}H_{18}NO_2$ $[M+H]^+$ 232.1259, found: 232.1332.

5.5. (S,E)-3-methyl-2-(methylamino)-2-(2-(methylthio)ethyl)-4-phenylbut-3-enoic acid (4t)

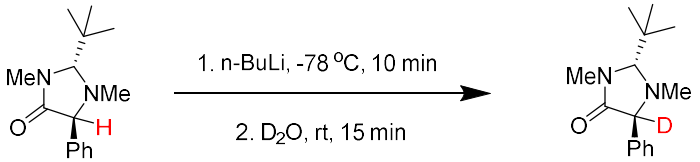


Following the general **procedure F**, 0.2 mmol of imidazolidinone was used. (35 mg, 63%). **^{1}H NMR** (400 MHz, MeOD) δ 7.36 – 7.29 (m, 2H, Ph), 7.29 – 7.19 (m, 3H, Ph), 6.63 (s, 1H, C<u>H</u>=C), 4.39 (ddd, *J* = 9.0, 8.2, 3.3 Hz, 1H, MeS-C<u>H_2</u>), 4.23 (td, *J* = 9.1, 6.5 Hz, 1H, MeS-C<u>H_2</u>), 2.56 (ddd, *J* = 13.3, 6.5, 3.3 Hz, 1H, MeS-CH_2-C<u>H_2</u>), 2.39 – 2.31 (m, 1H, MeS-CH_2-C<u>H_2</u>), 2.37 (s, 3H, N<u>CH_3</u>), 1.90 (d, *J* = 1.3 Hz, 3H, S<u>CH_3</u>), 1.39

– 1.21 (m, 3H, C=C$\underline{CH_3}$); **HRMS** (ESI^+): m/z calcd. For $C_{15}H_{21}NO_2S$ $[M+H]^+$ 280.1293, found: 280.1312.

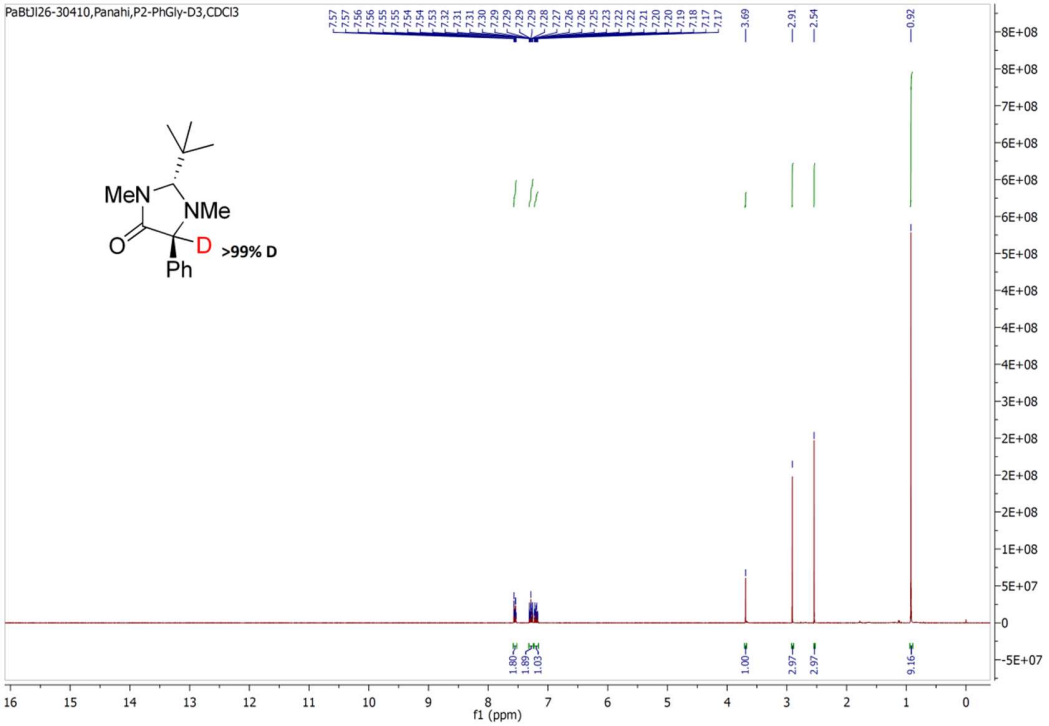
6. Deuterium labeling experiments

6.1. Synthesis of 2-(tert-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one-5-d (1d-d_1)

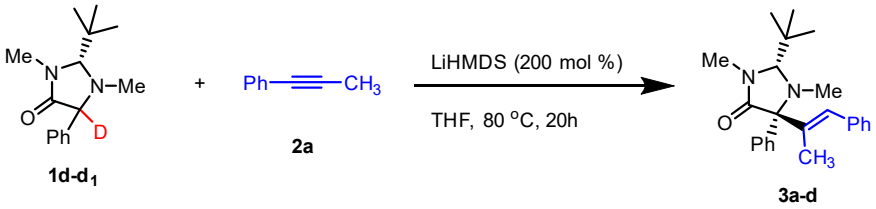


1d **1d-d_1**

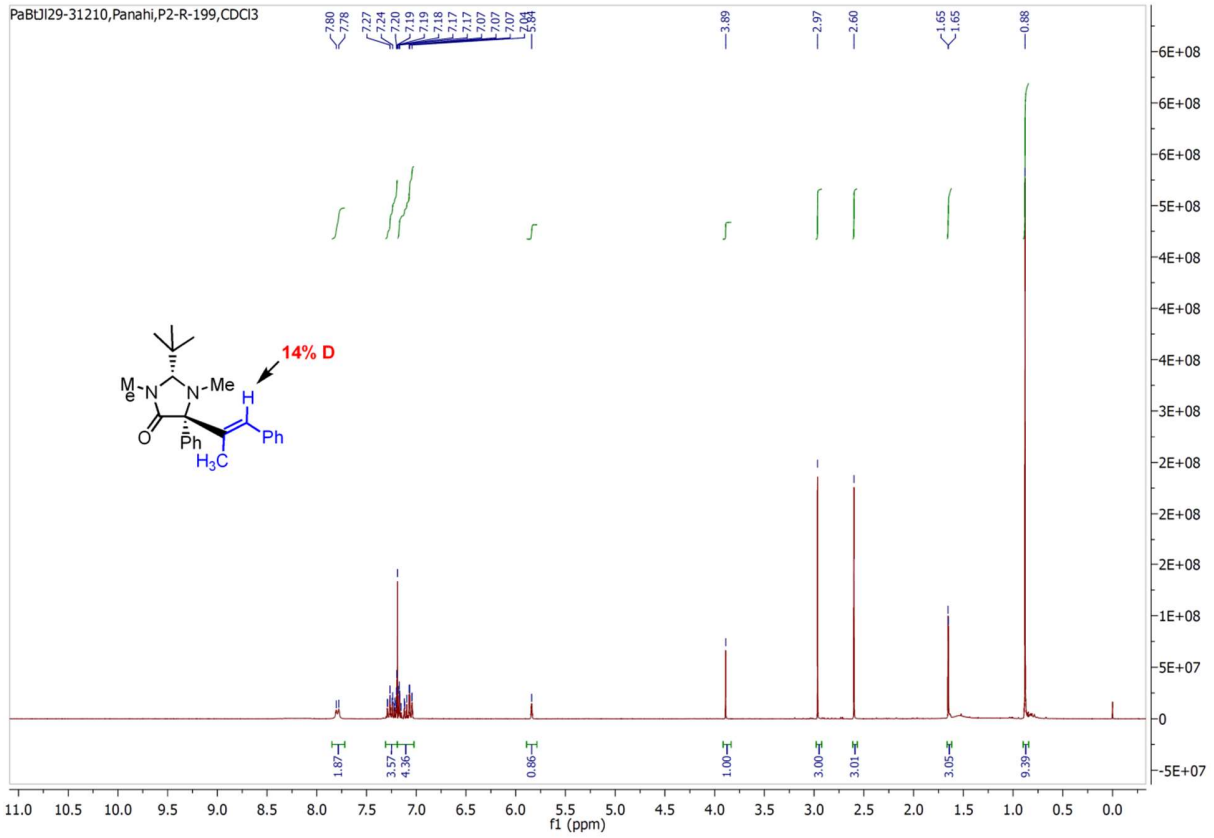
In order to synthesize **1d-d1**, a sealed Schlenk tube was charged with **1d** (0.5 mmol, 123 mg) and dry THF (1.0 mL). The reaction mixture was cold down to -78 °C using a mixture of acetone and dry ice. Then n-BuLi (2.5 M in hexanes, 0.2 mL), was added to the reaction mixture via syringe under Ar flow. The tube was sealed with a screw-cap and the resulting mixture was stirred at -78 °C for 10 min. Then D_2O (0.25 mL, excess) was added to the reaction mixture and cooling bath removed to increase the temperature to room temperature, under this conditions reaction mixture was stirred for 15 minutes. Afterward, the mixture was diluted dry THF (5 mL) and organic layer was separated, dried over Na_2SO_4 and concentrated under reduced pressure. The resulting product is containing **1D-d_1** with >99% deuterium labeling.



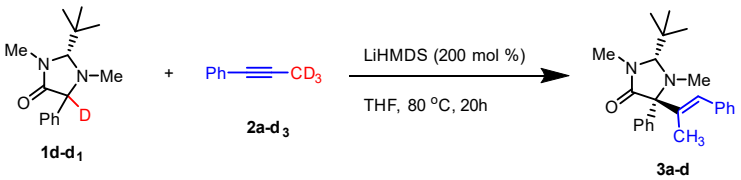
6.2. Reaction of 2-(tert-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one-5-d (1d-d$_1$) with 1-phenyl-1-propyneunder optimized conditions



Same to general **procedure D**: A flame-dried sealed Schlenk tube was charged with imidazolidinone derivative (**1d-d$_1$**) (0.2 mmol, 50 mg) and it was evacuated and backfilled with argon. Then 1.0 mL of THF, 1-phenyl-1-propyne**2a** (0.2 mmol, 27 µL) and LiHMDS (0.4 mL, 1.0 M in THF) were added while maintaining an argon counter flow. The tube was sealed with a screw-cap and the resulting mixture was stirred at 80 °C for 20h. After completion of the reaction the mixture was allowed to cool down to r.t. Then, it was quenched by adding aq. sat. NH_4Cl (5 mL) and extracted with ethyl acetate (3x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash column chromatography using hexanes/ethyl acetate eluents to afford the pure **3a-d**.

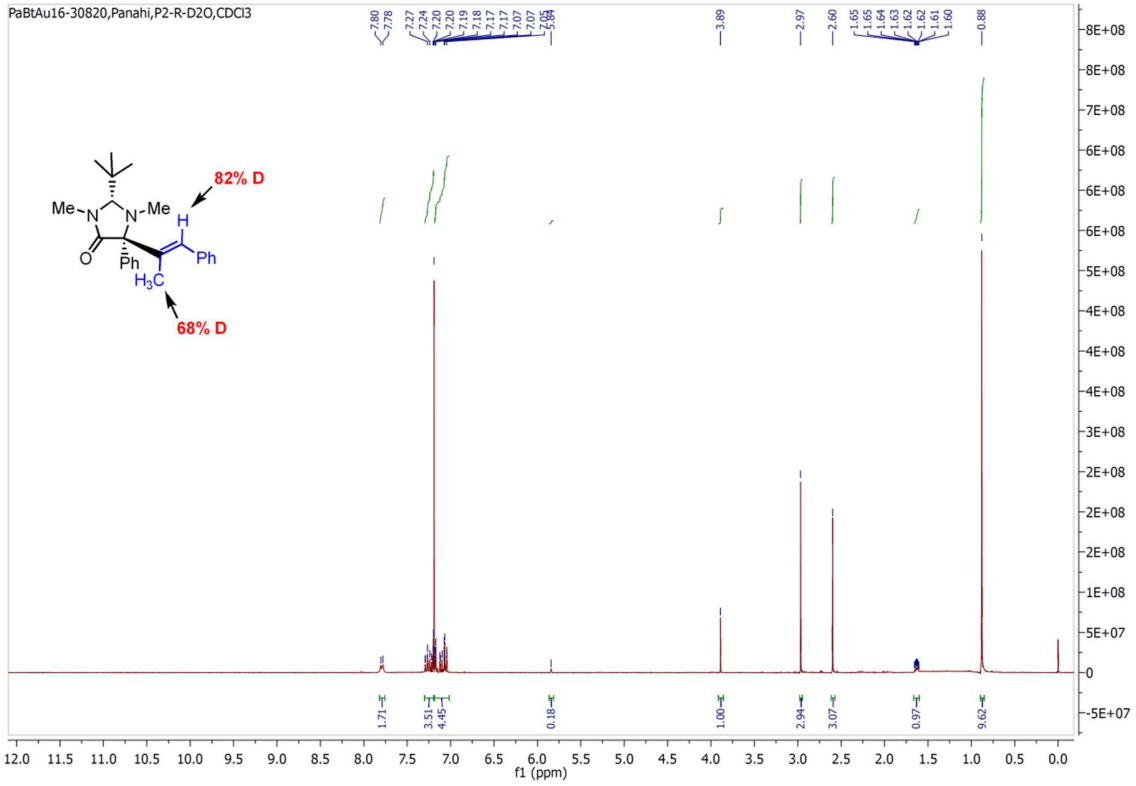


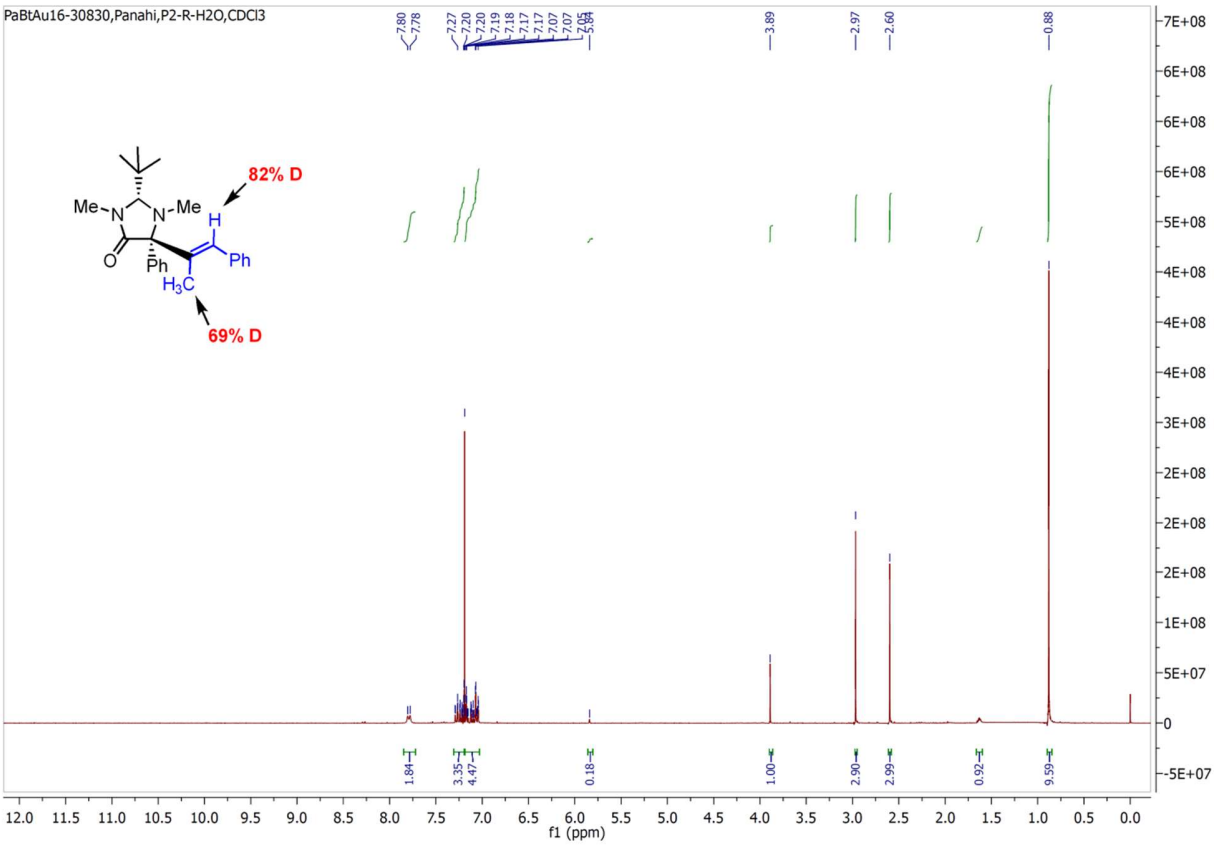
6.3. Reaction of 2-(tert-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one-5-d (1d-d$_1$) with (prop-1-yn-1-yl-d3)benzene under optimized conditions



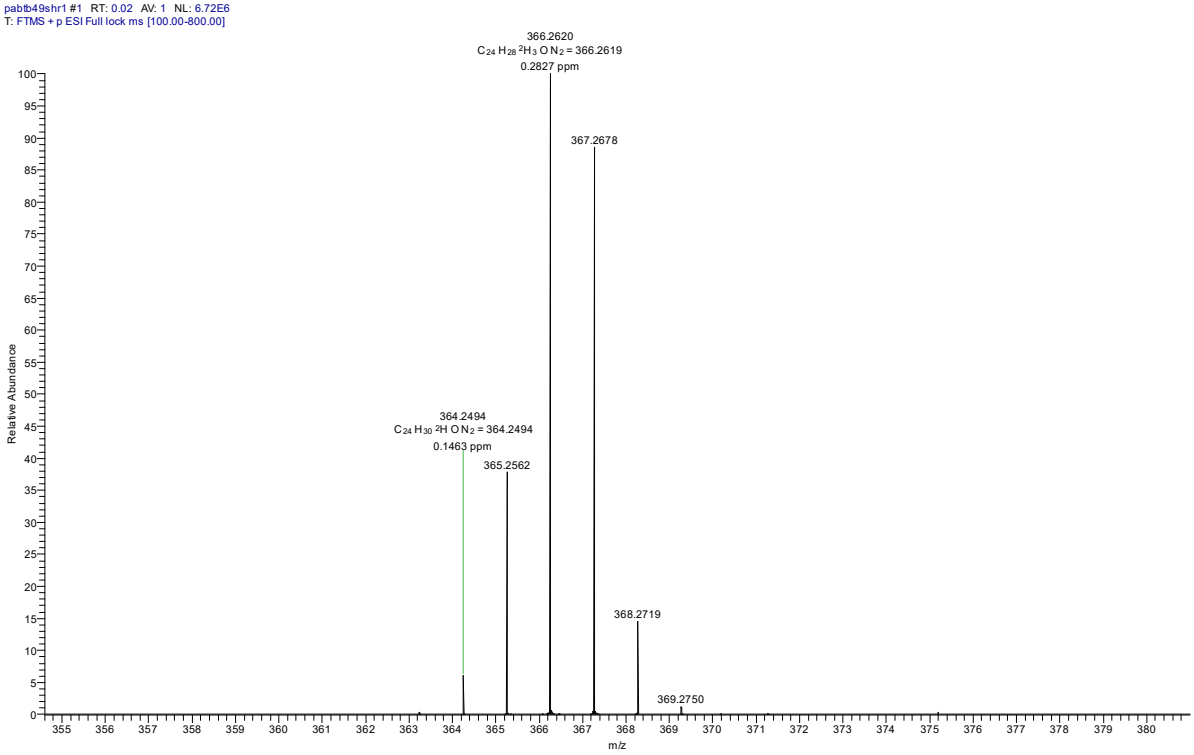
Same to the general **procedure D**: A flame-dried sealed Schlenk tube was charged with imidazolidinone derivative (**1d-d$_1$**) (0.2 mmol, 50 mg) and it was evacuated and backfilled with argon. Then 1.0 mL of THF, (prop-1-yn-1-yl-d3)benzene**2a-d$_3$** (0.2 mmol, 27 µL) and LiHMDS (0.4 mL, 1.0 M in THF) were added while maintaining an argon counter flow. The tube was sealed with a screw-cap and the resulting mixture was stirred at 80 °C for 20h. After completion of the reaction the mixture was allowed to cool down to r.t. In this step the quenching process was done using both D_2O and H_2O in order to find more information about the reaction mechanism. For each case, the product was extracted with ethyl acetate (3x 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure.

The crude product was purified by flash column chromatography using hexanes/ethyl acetate eluents to afford the pure **3a-d**.

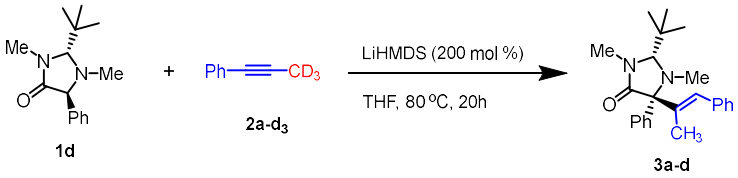




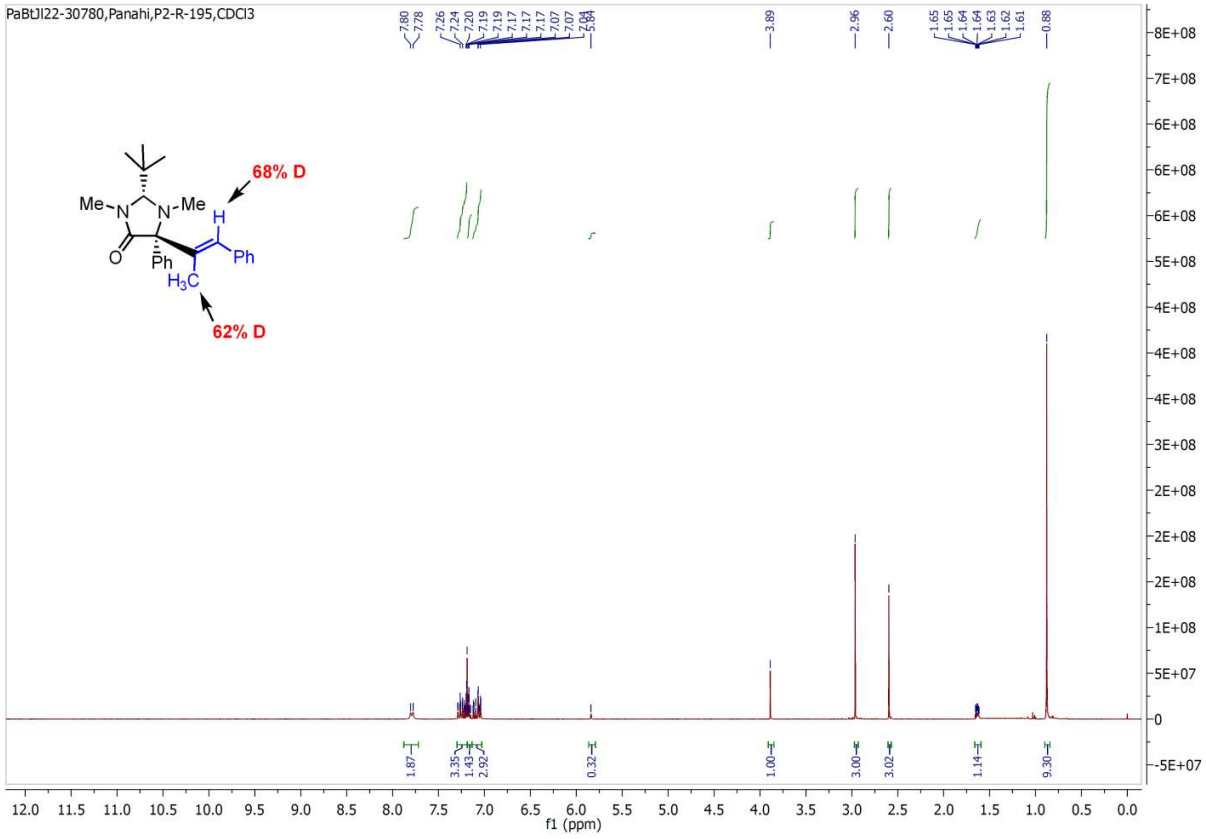
D:\data_2019\pabtb49shr1 9/10/2019 3:39:59 PM p2.r.d2o



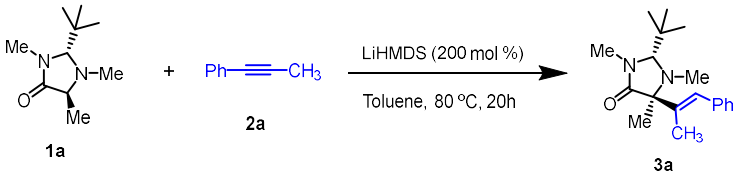
6.4. Reaction of 2-(tert-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one-5-d (1d-d_1) with (prop-1-yn-1-yl-d3)benzene under optimized conditions



Same to the general **procedure D**: A flame-dried sealed Schlenk tube was charged with imidazolidinone derivative (**1d**) (0.2 mmol, 50 mg) and it was evacuated and backfilled with argon. Then 1.0 mL of THF, 1-phenyl-1-propyne**2a** (0.2 mmol, 27 µL)and LiHMDS (0.4 mL, 1.0 M in THF) were added while maintaining an argon counter flow. The tube was sealed with a screw-cap and the resulting mixture was stirred at 80 °C for 20h. The workup procedure is according to general procedure **D**. The crude product was purified by flash column chromatography using hexanes/ethyl acetate eluents to afford the pure **3a-d**.



7. In situ IR (React IR) experiments



A three-neck Schlenk tube equipped with a stirrer bar, IR probe and argon inlet and a neck for the addition of reagents was used for React IR experiment.

1. First, 4.5 mL of anhydrous toluene was added to the IR reaction vessel and it was heated to 80 °C in order to have a background spectrum from tolueneat this temperature prior the in situ IR analysis.

2. Substrate**1a**(1.0 mmol) was added to the reaction tube and IR of starting material was recorded.

3. Then, LiHMDS solution in toluene (1M, 1.0 mmol, 1.0 mL) was added to the reaction mixture and it was stirred for 5 minutes to observe the peaks related to the enolate.

4. Afterward, a solution of **2a** (1.0 mmol) was injected to the reaction tube.

5. Another equivalent of LiHMDS solution in toluene (1M, 1.0 mmol, 1.0 mL) was added

6. Finally, the reaction was quenched after 8h using methanol.

8. Computational details

All the DFT calculations have been carried out with the Gaussian 09 package of program[6]and visualization of computed structures were generated usingCYLView.[7]Full geometryoptimization and Gibbs free energycorrection were performed with the B3LYP-D3(BJ)/6-31G(d) level[8,9,10]in the gas phase (T=298 K, P=1 bar).[8] The correctness of the optimized transition states (TS) and stable structures have been verified by intrinsic reaction coordinate (IRC) and the analytical frequency calculations respectively. Single point energies and solvation energy corrections were calculated with the M06-2X/6- 311+G(d,p) level[11] and using the SMD model[12](with THF as the solvent)based on the gas-phaseoptimized structuresrespectively.In this work, the free energy for each was calculated using the formula: G = E_{M06}^{SP} + $G_{B3LYP}^{Corre.}$+ $\Delta G^{1atm\rightarrow 1M}$; where $\Delta G^{1atm\rightarrow 1M}$ = 1.89 kcal/mol is the free-energy change for compression of 1 mol of an ideal gas from 1 atm to the 1 M solution-phase standard state. In the case of THF as a solvent and ligand, the free energy of the dimethyl ether (as a model of THF) is described as G = E_{M06}^{SP} + $G_{B3LYP}^{Corre.}$+ $\Delta G^{1atm\rightarrow 1M}$ + RT ln (12.2); where the last term corresponds to the free energy required to change the standard state of THF from 12.2 to 1 M.

Based on previous reports which revealed that LiHMDS exist as tri- and tetrasolvated monomer (LiHMDS .3THF) at high concentration of THF,LiHMDS .3DME was used as a modelof LiHMDS.[13]

---

[6]Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.

[7]CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (http://www.cylview.org)

[8]Becke, D. J. *Chem. Phys.***1993**, 98, 5648-5652.

[9]Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.***1988**, 37, 785-789.

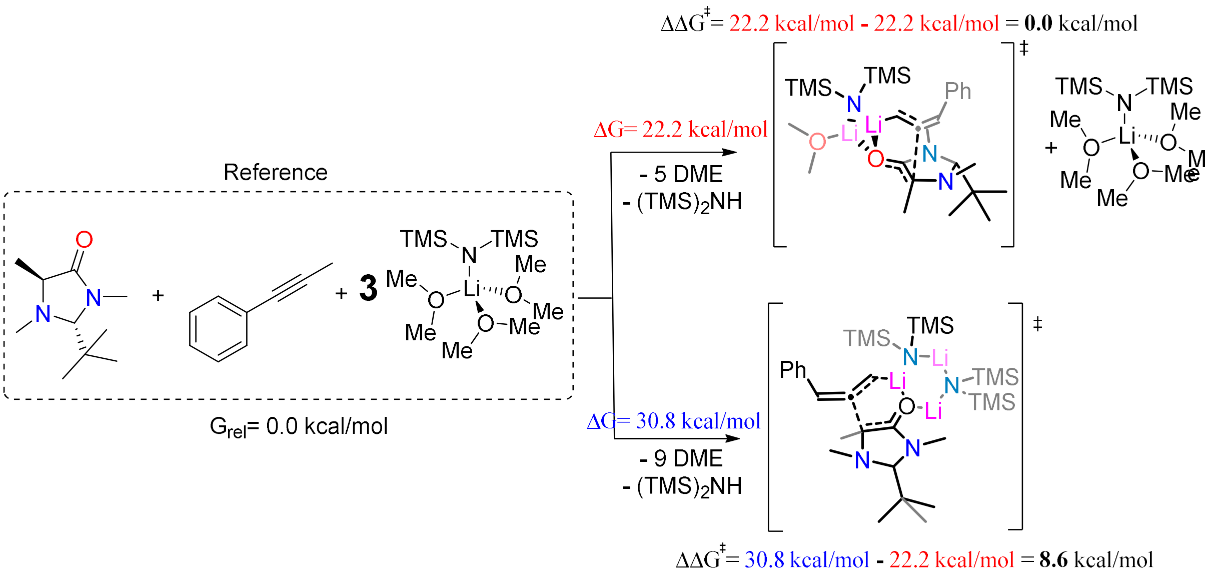
[10] Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.***2010**, 132, 154104-154119.

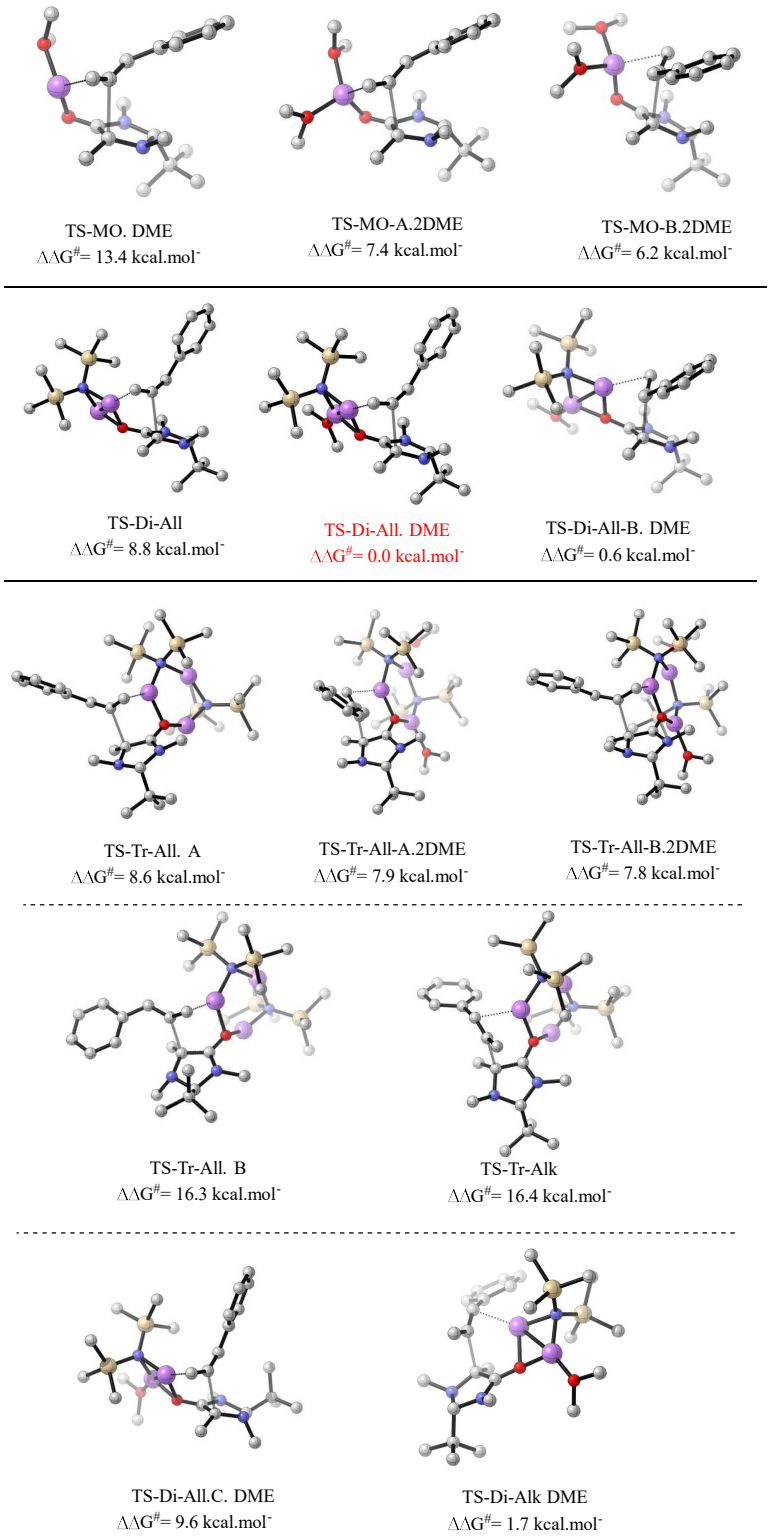
[11]Zhao, Y.; Truhlar, D. G. Theor. *Chem. Acc.***2008**, 120, 215-241.

[12]Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B***2009**, 113, 6378-6396.

[13]McNeil, A. J.;CollumD. B. *J. Am. Chem. Soc.***2005**, 127, 15, 5655–5661.

To compare the transition states, 4-Imidazolidinone X, 1-Phenyl-1-propyne, and 3×LiHMDS .3DME were selected as starting materialsand energy reference, for instance ΔΔG‡ for TS-Di-All. DME was obtainedfrom following equations:





Scheme S1. Relative Gibbs free energies (in kcal.mol^{-1}) and optimized structures of transition states of nucleophilic attack of 4-imidazolidinone to the alkyne.

9. HPLCdata

9.1. Starting materials

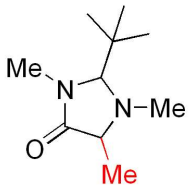
Sample ID: pa.Ala-Me-rac

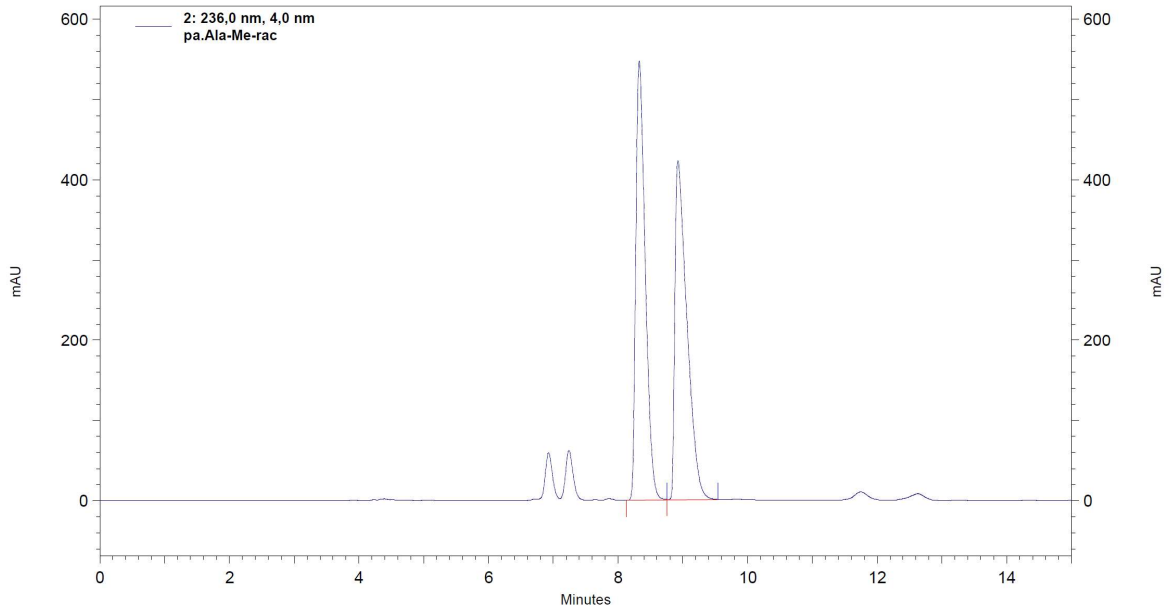
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Acquired: 18.03.2019 09:45:01 (GMT +01:00)

Vial: P1-E1

Injection Volume: 2µL





2: 236,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	8,328	50,289	741721063
2	8,925	49,711	733205326
Totals		100,000	1474926389

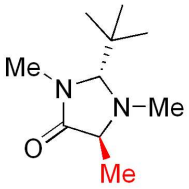
Sample ID: pa.Ala-Me-ee

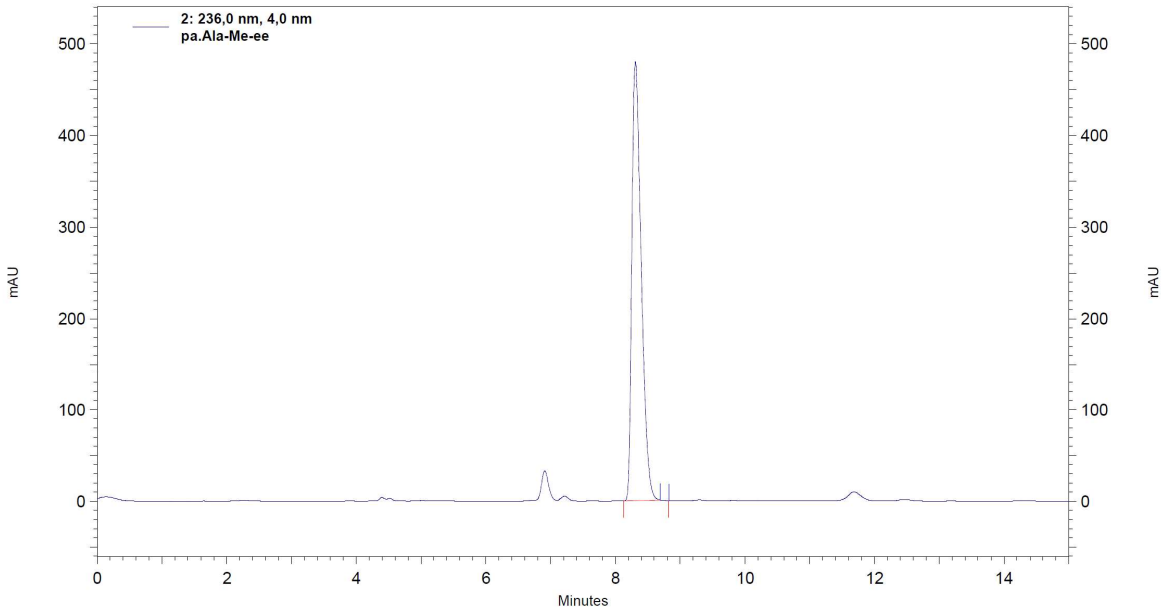
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Acquired: 18.03.2019 10:01:28 (GMT +01:00)

Vial: P1-E2

Injection Volume: 2µL





2: 236,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	8,308	100,000	646934360
2	8,825	0,000	6
3	8,825	0,000	6

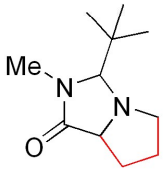
Totals			
		100,000	646934372

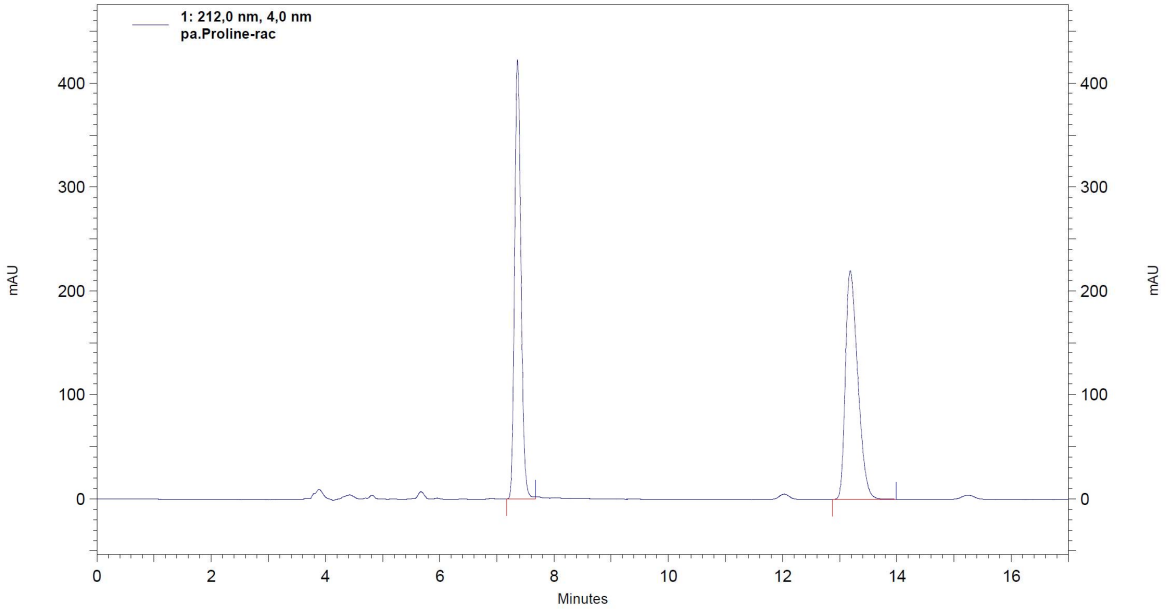
Sample ID: pa.Proline-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B3

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm

Results

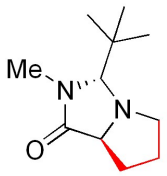
Peak Number	Retention Time	Area Percent	Area
1	7,362	49,767	437346431
2	13,182	50,233	441433240
Totals		100,000	878779671

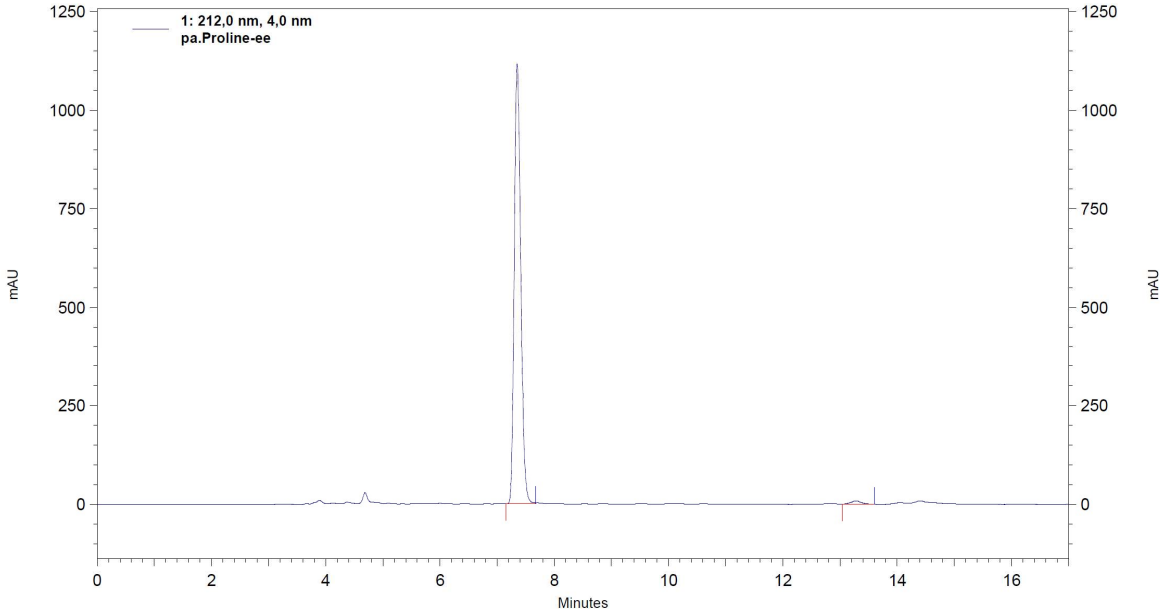
Sample ID: pa.Proline-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B7

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm

Results

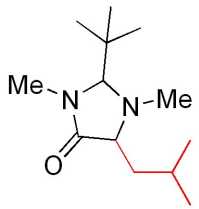
Peak Number	Retention Time	Area Percent	Area
1	7,350	98,824	1184281099
2	13,275	1,176	14096872
Totals		100,000	1198377971

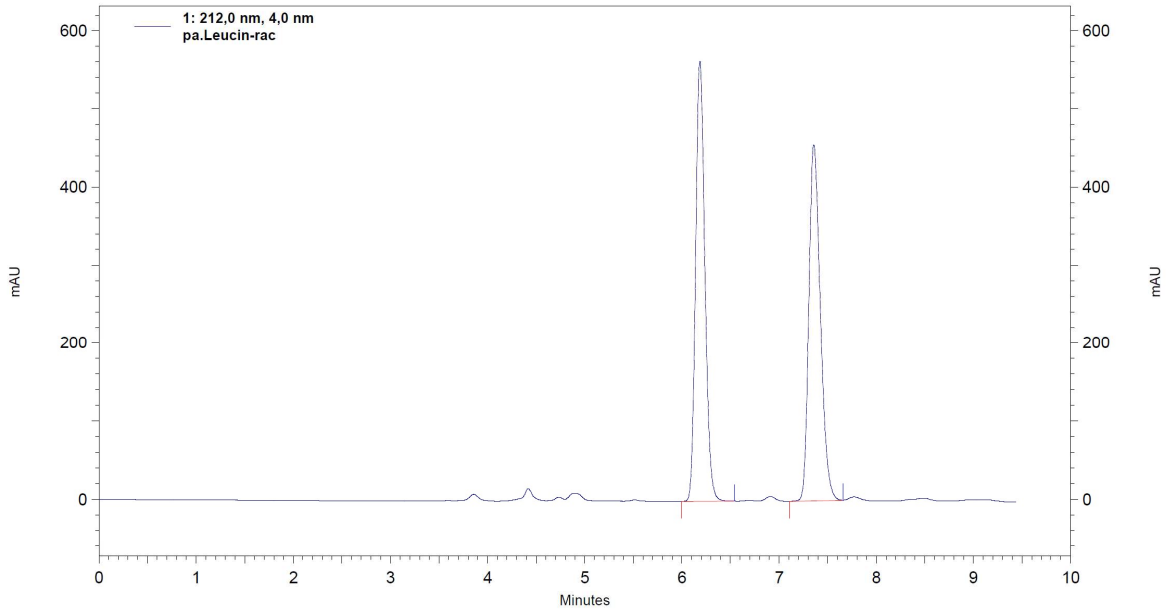
Sample ID: pa.Leucin-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_IPA 95_5, 0,5ml, 22°C.met

Vial: P1-B4

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm

Results

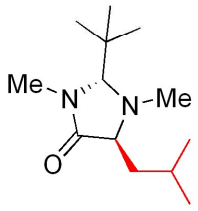
Peak Number	Retention Time	Area Percent	Area
1	6,185	49,862	501855085
2	7,358	50,138	504623217
Totals		100,000	1006478302

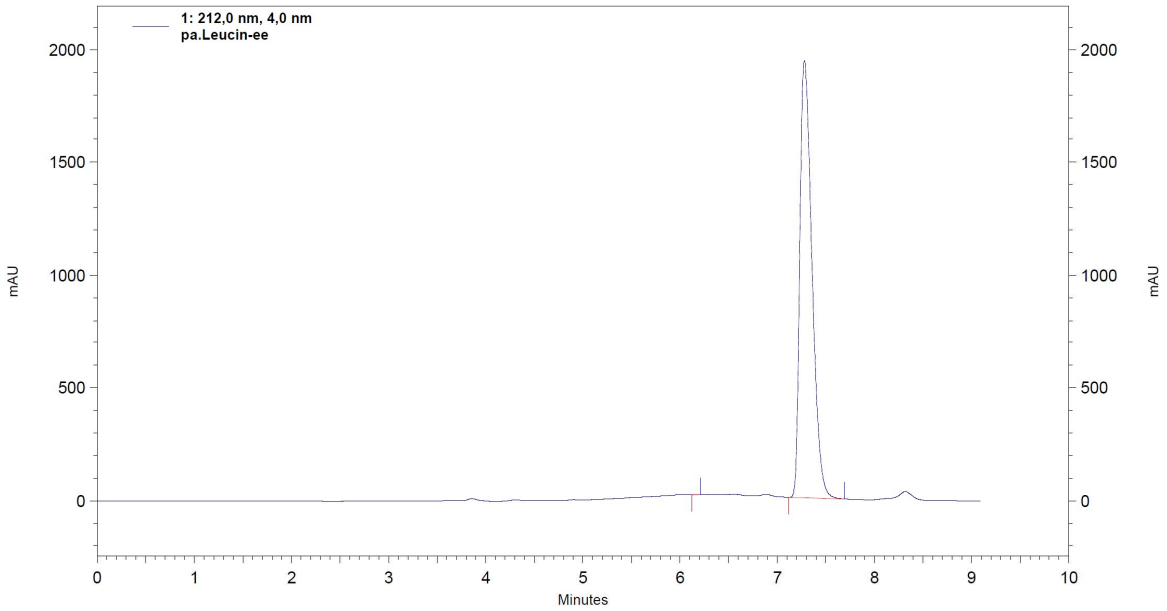
Sample ID: pa.Leucin-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_IPA 95_5, 0,5ml, 22°C.met

Vial: P1-B8

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm

Results

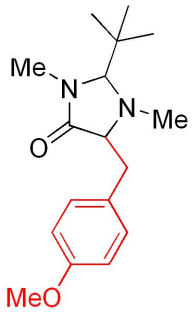
Peak Number	Retention Time	Area Percent	Area
1	6,203	0,002	43209
2	7,280	99,998	2251390383
Totals		100,000	2251433592

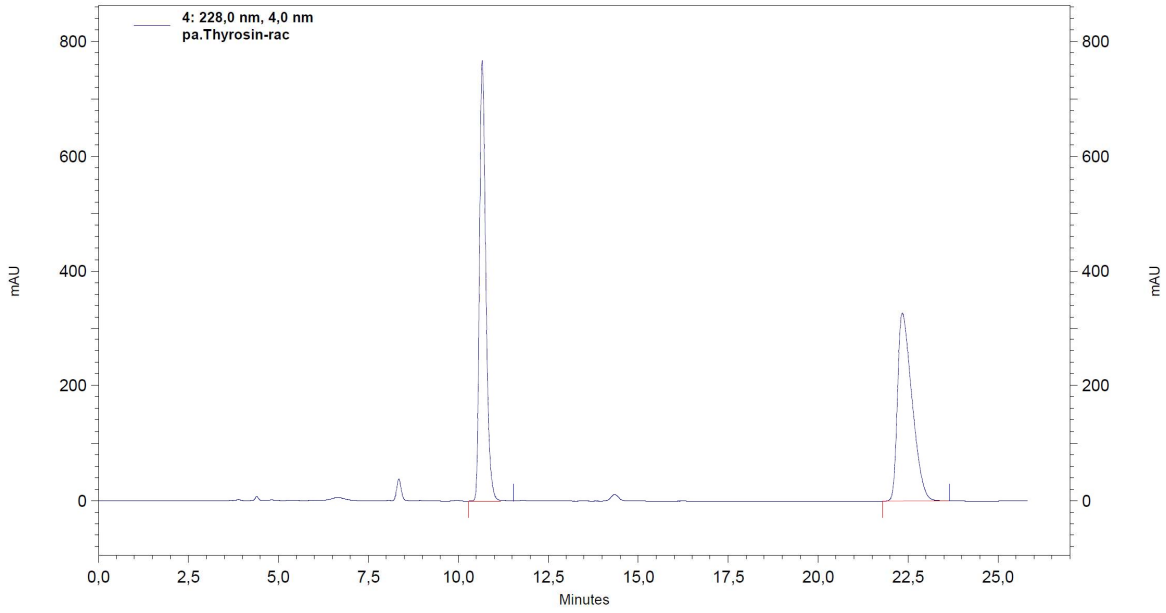
Sample ID: pa.Thyrosin-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B2

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

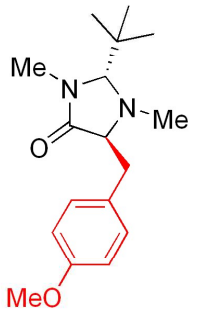
Peak Number	Retention Time	Area Percent	Area
1	10,665	50,584	1254515664
2	22,342	49,416	1225570791
Totals		100,000	2480086455

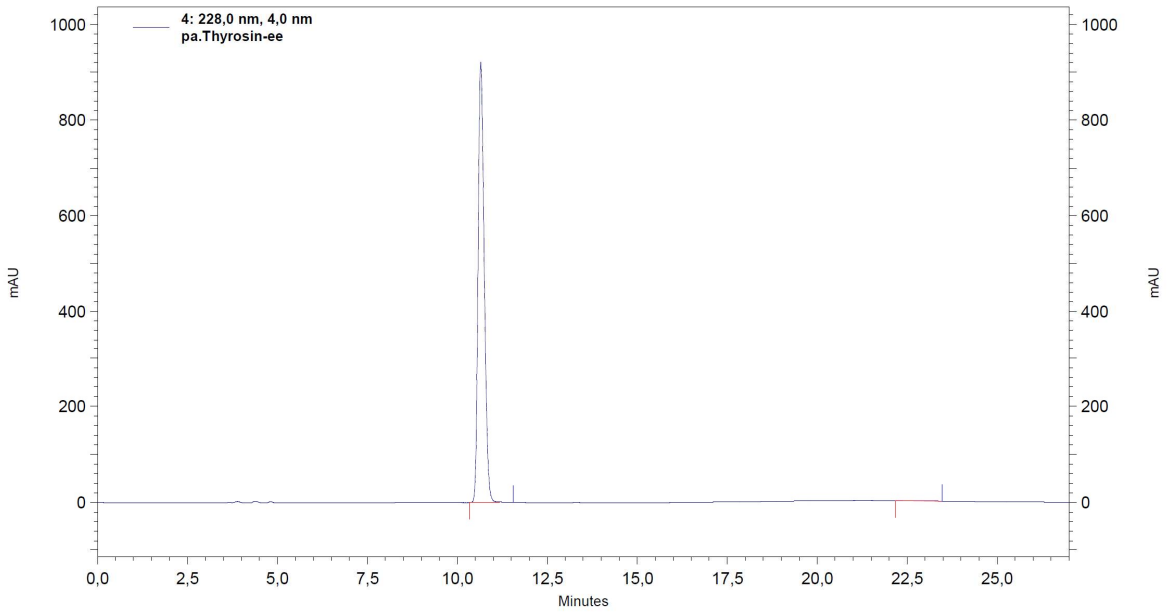
Sample ID: pa.Thyrosin-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B6

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

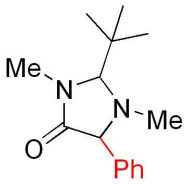
Peak Number	Retention Time	Area Percent	Area
1	10,650	99,879	1464923562
2	22,588	0,121	1777002
Totals		100,000	1466700564

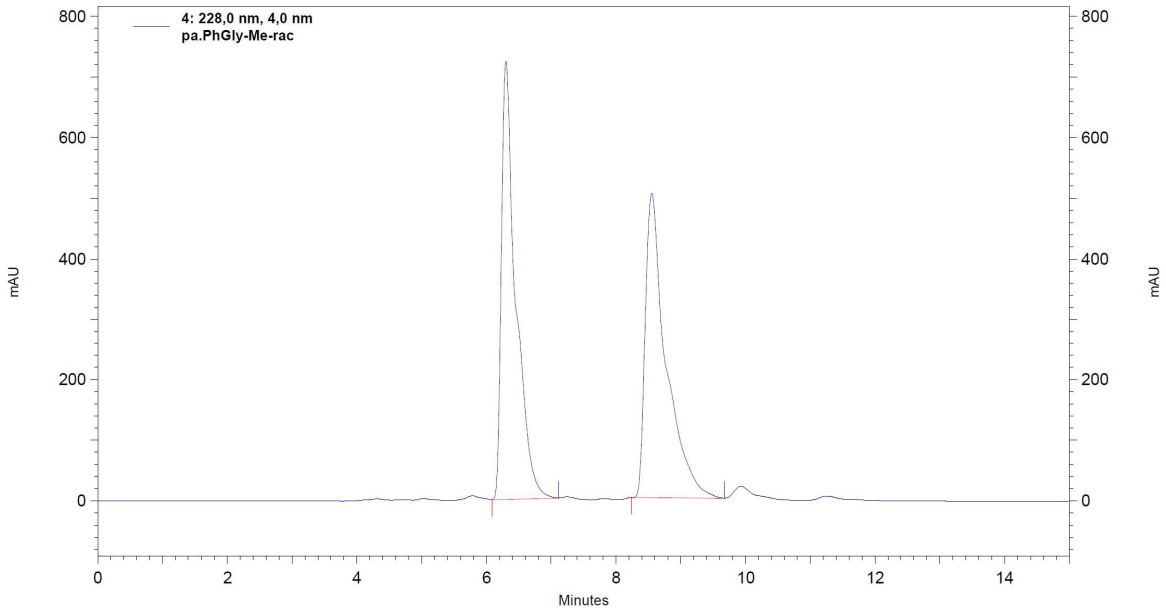
Sample ID: pa.PhGly-Me-rac

Method: C:\Enterprise\Methods\HPLC2\4_Chiralcel OD-3\System2, OD-3. Hep_EtOH 85_15, 0,5ml, 22°C.met

Vial: P1-A1

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

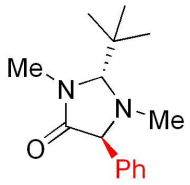
Peak Number	Retention Time	Area Percent	Area
1	6,307	49,767	1490724081
2	8,553	50,233	1504697018
Totals		100,000	2995421099

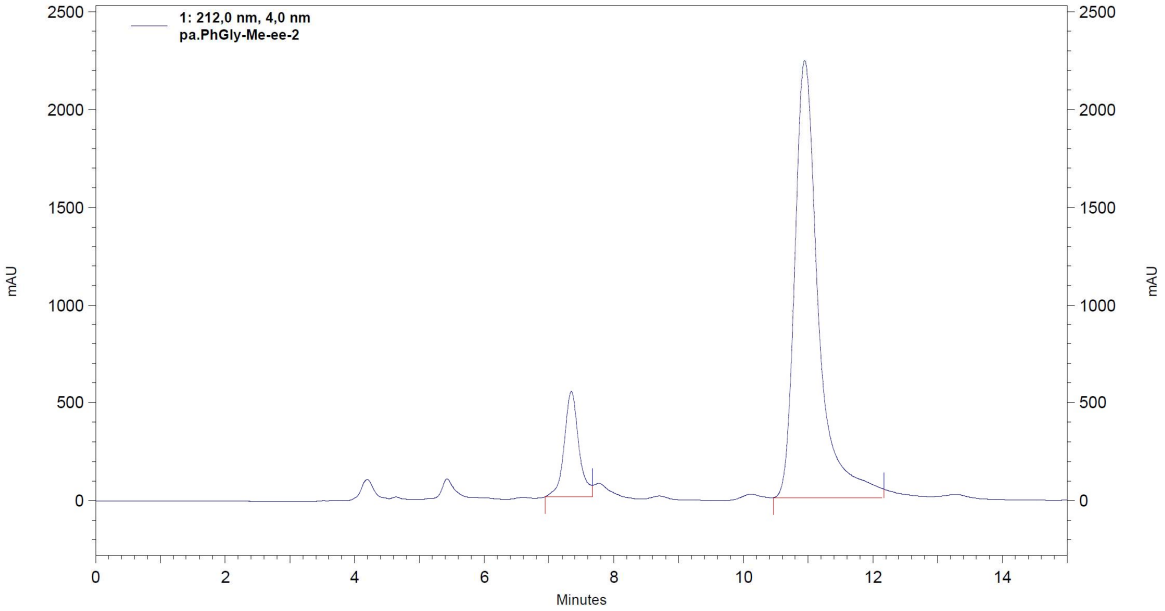
Sample ID: pa.PhGly-Me-ee-2

Method: C:\Enterprise\Methods\HPLC2\4_Chiralcel OD-3\System2, OD-3. Hep_EtOH 90_10, 0,5mL, 22°C.met

Vial: P1-C5

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm

Results

Peak Number	Retention Time	Area Percent	Area
1	7,345	12,884	1121684749
2	10,945	87,116	7584199480
Totals		100,000	8705884229

9.2. Products

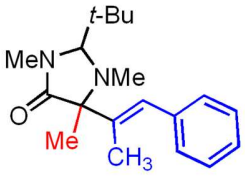
Sample ID: pa.P2-R3-rac

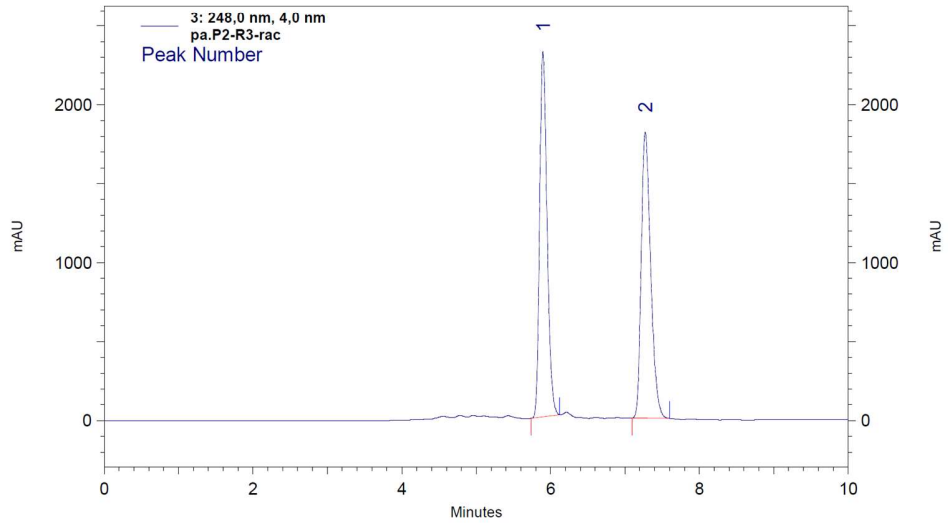
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Acquired: 12.03.2019 12:18:11 (GMT +01:00)

Vial: P1-B5

Injection Volume: 2 µL





3: 248,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	5,897	50,008	2146675913
2	7,272	49,992	2146018761
Totals		100,000	4292694674

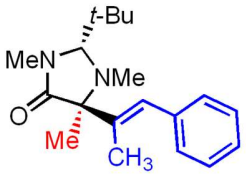
Sample ID: pa.P2-R33-ee

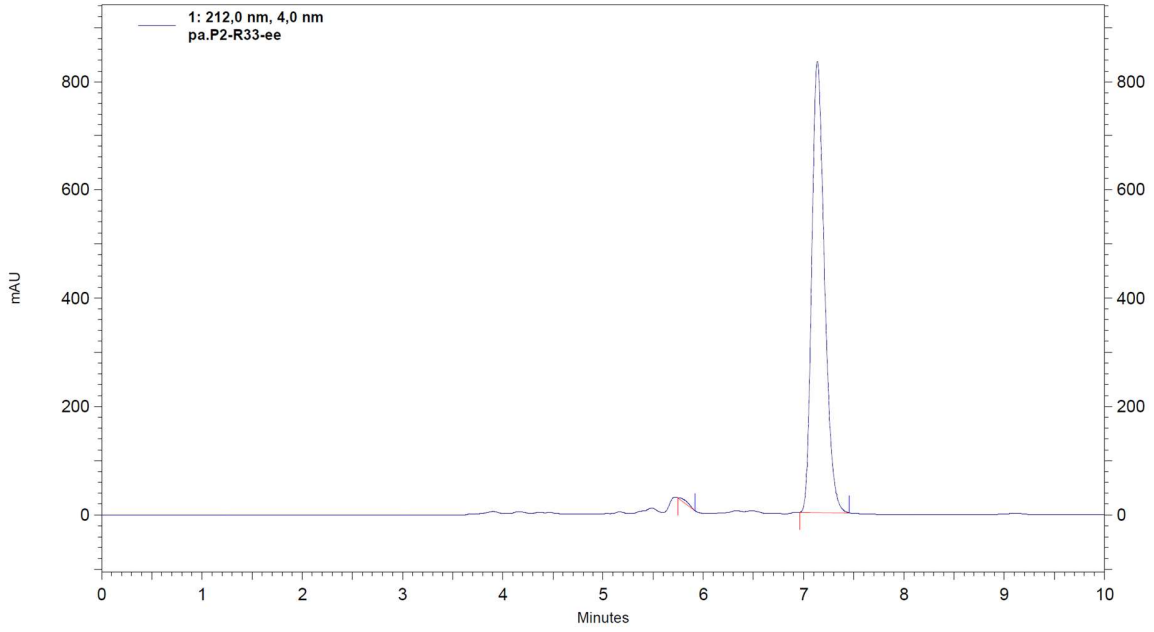
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Acquired: 22.03.2019 09:18:11 (GMT +01:00)

Vial: P1-F7

Injection Volume: 2µL





1: 212,0 nm, 4,0 nm
Results

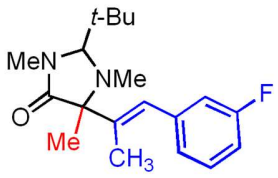
Peak Number	Retention Time	Area Percent	Area
1	5,745	0,441	4381376
2	7,137	99,559	989995740
Totals		100,000	994377116

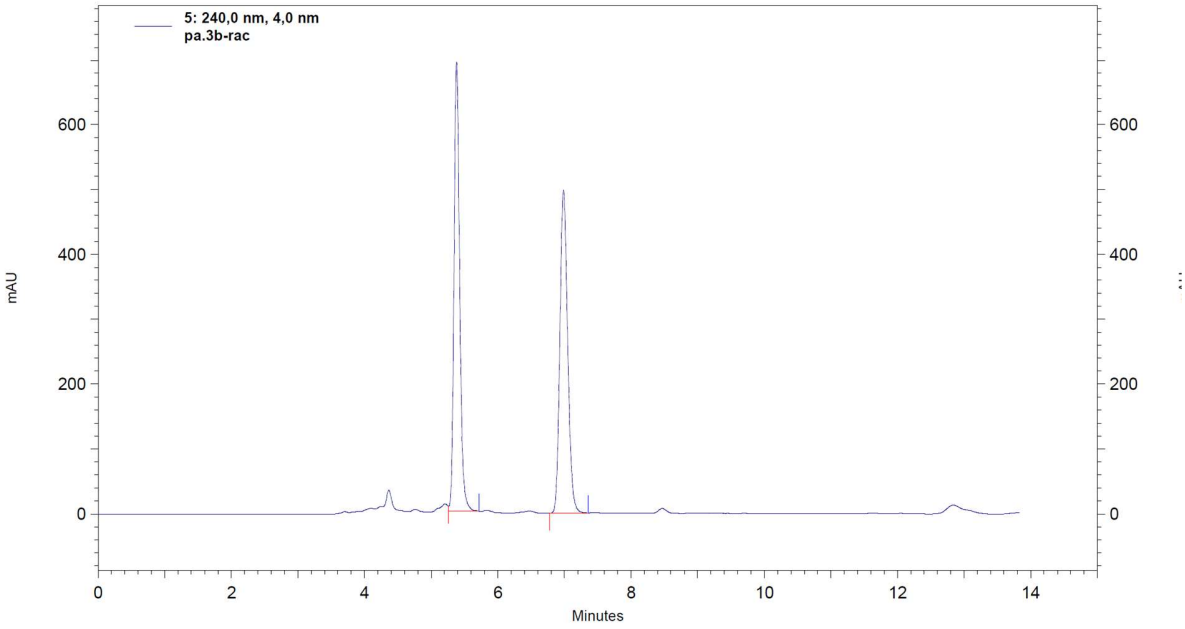
Sample ID: pa.3b-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C1

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

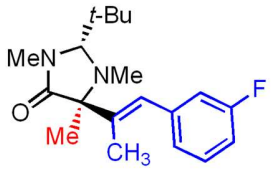
Peak Number	Retention Time	Area Percent	Area
1	5,382	50,312	549001478
2	6,987	49,688	542196330
Totals		100,000	1091197808

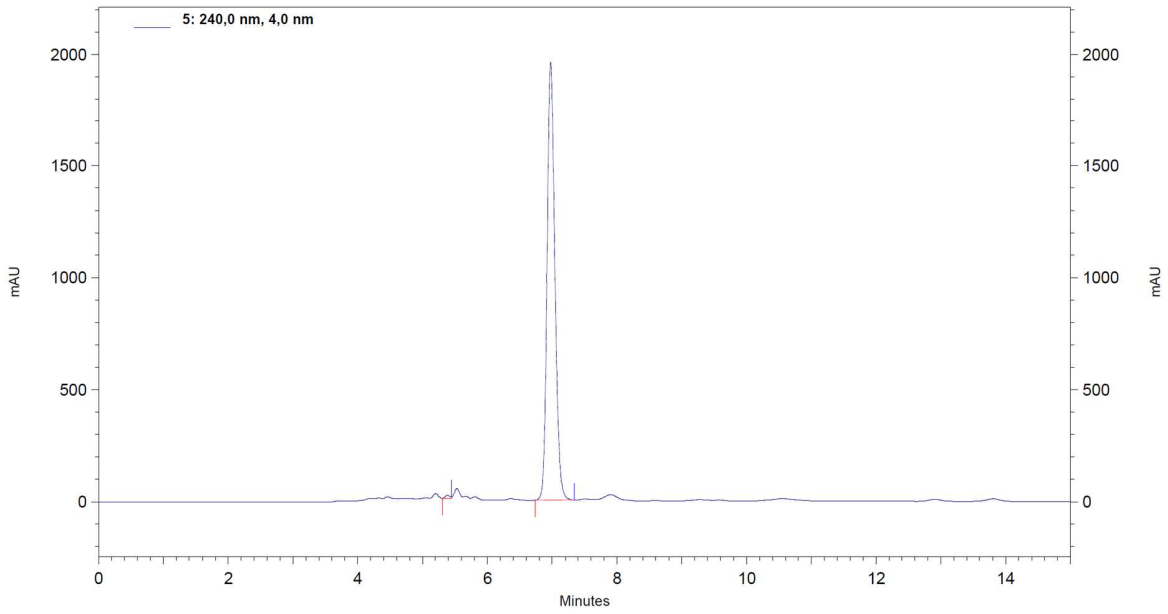
Sample ID: pa.3b-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C5

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

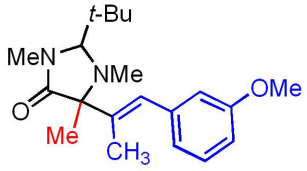
Peak Number	Retention Time	Area Percent	Area
1	5,383	0,409	8994012
2	6,977	99,591	2191676053
Totals		100,000	2200670065

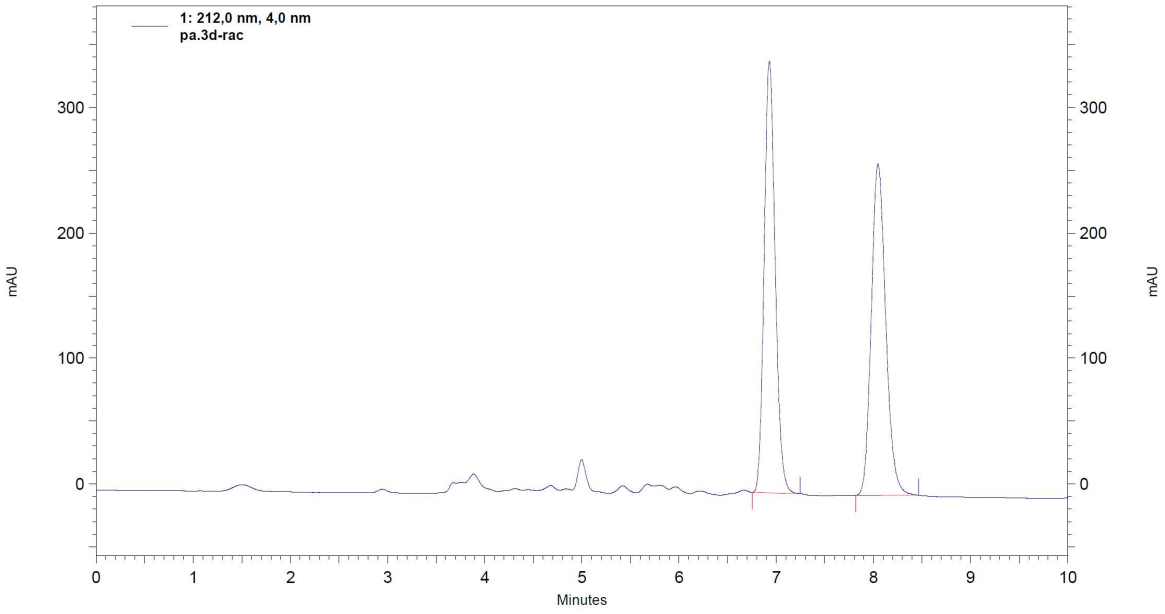
Sample ID: pa.3d-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C2

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm
Results

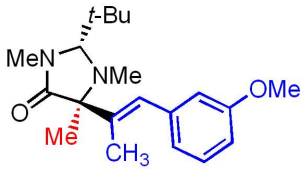
Peak Number	Retention Time	Area Percent	Area
1	6,930	49,827	364064189
2	8,048	50,173	366587256
Totals		100,000	730651445

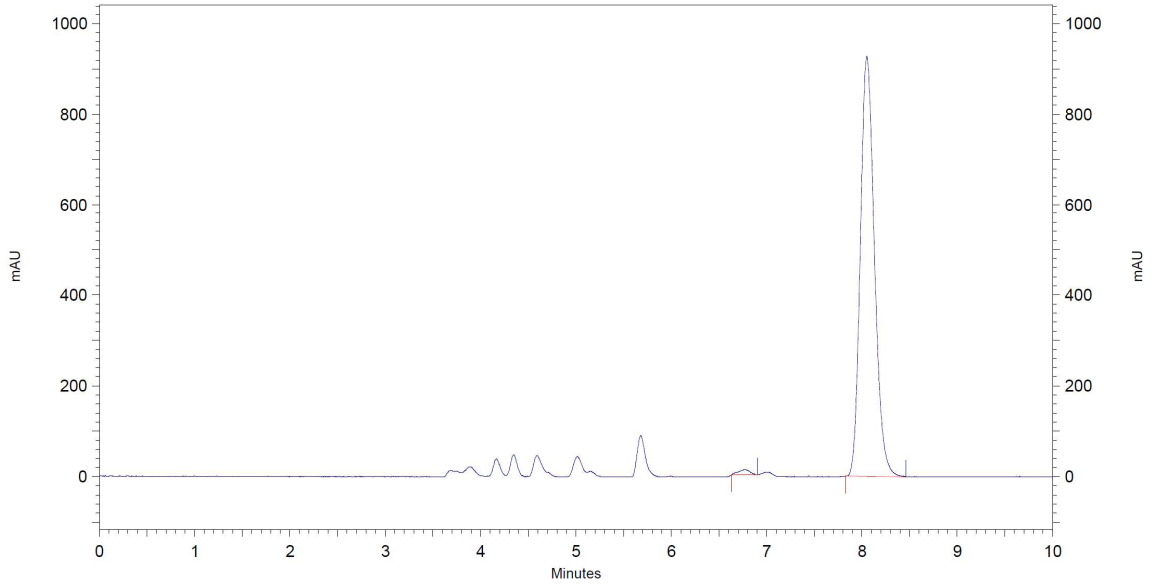
Sample ID: pa.3d-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-B2

Injection Volume: 5µL





Spectrum Max Plot
Results

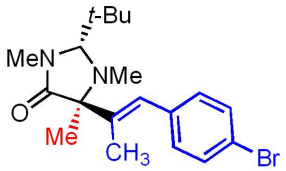
Peak Number	Retention Time	Area Percent	Area
1	6,770	0,940	12090422
2	8,052	99,060	1274226686
Totals		100,000	1286317108

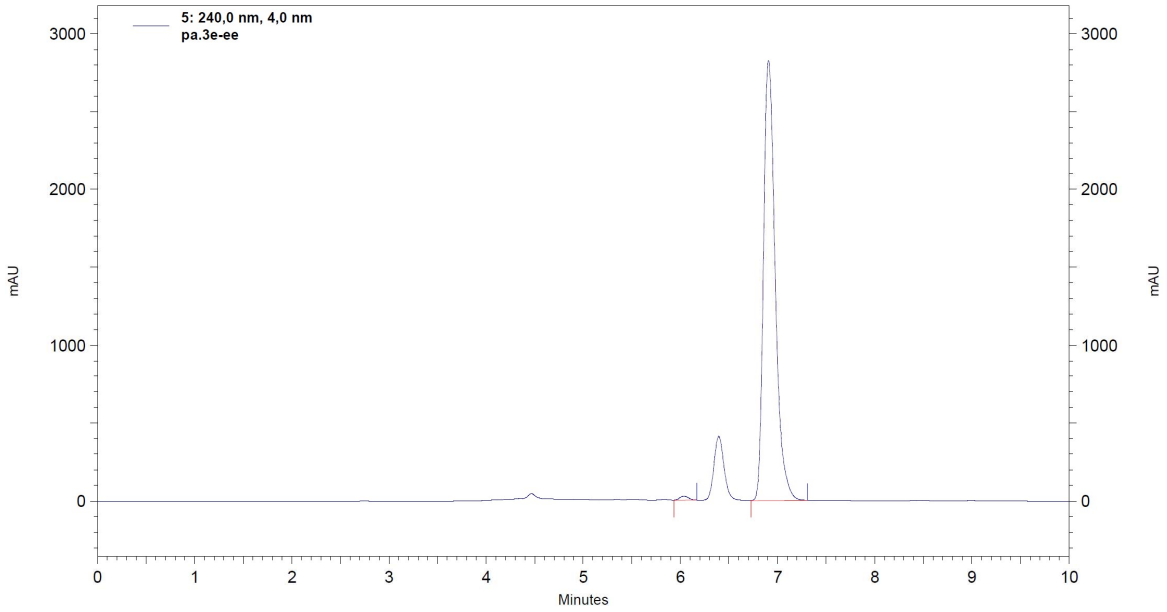
Sample ID: pa.3e-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C5

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

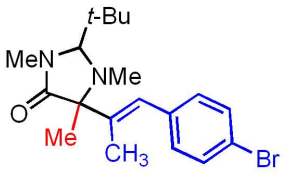
Peak Number	Retention Time	Area Percent	Area
1	6,037	0,676	21529135
2	6,907	99,324	3163140687
Totals		100,000	3184669822

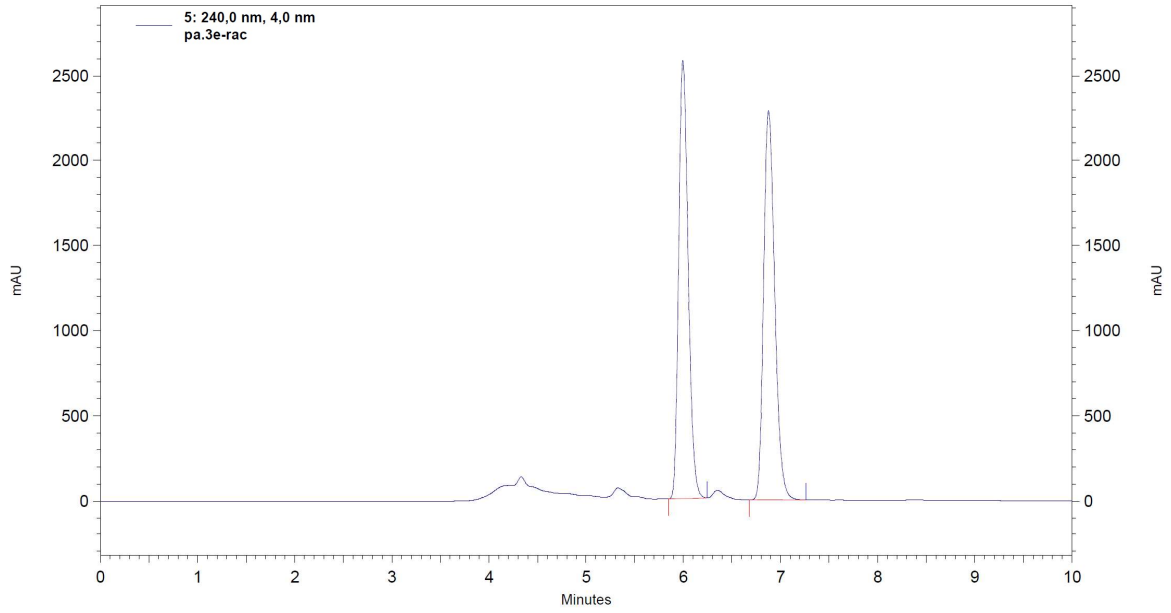
Sample ID: pa.3e-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C1

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

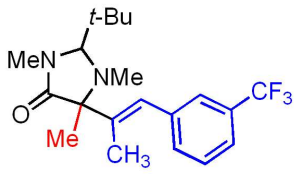
Peak Number	Retention Time	Area Percent	Area
1	5,995	49,081	2349734725
2	6,877	50,919	2437697857
Totals		100,000	4787432582

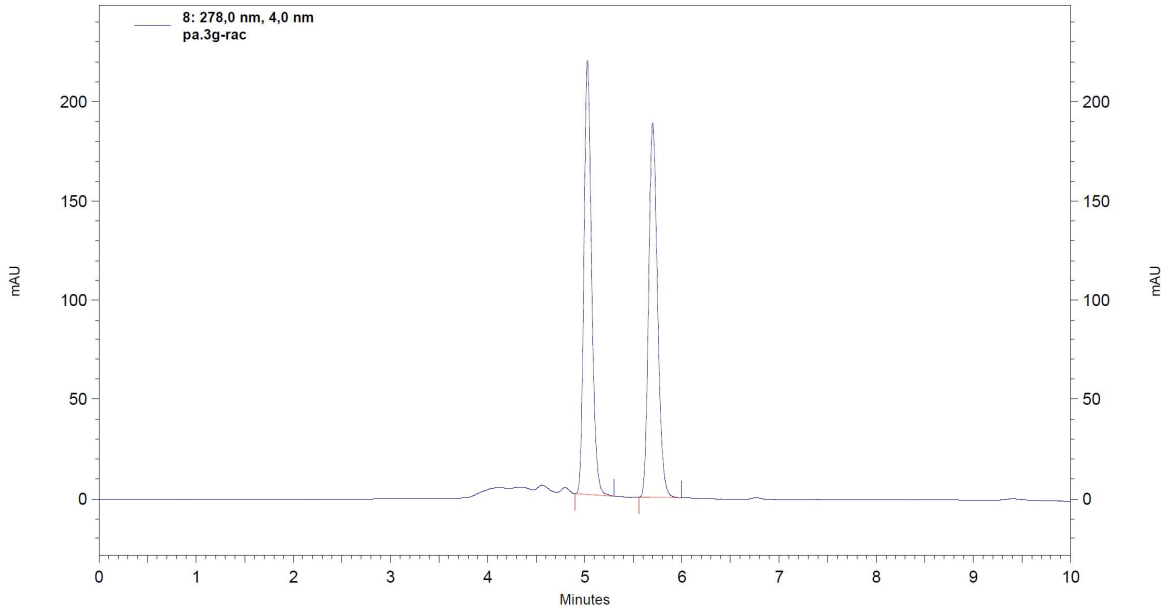
Sample ID: pa.3g-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B2

Injection Volume: 5µL





8: 278,0 nm, 4,0 nm
Results

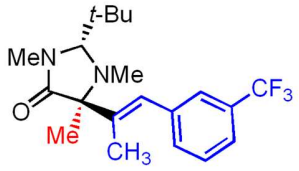
Peak Number	Retention Time	Area Percent	Area
1	5,028	50,081	161092245
2	5,700	49,919	160570386
Totals		100,000	321662631

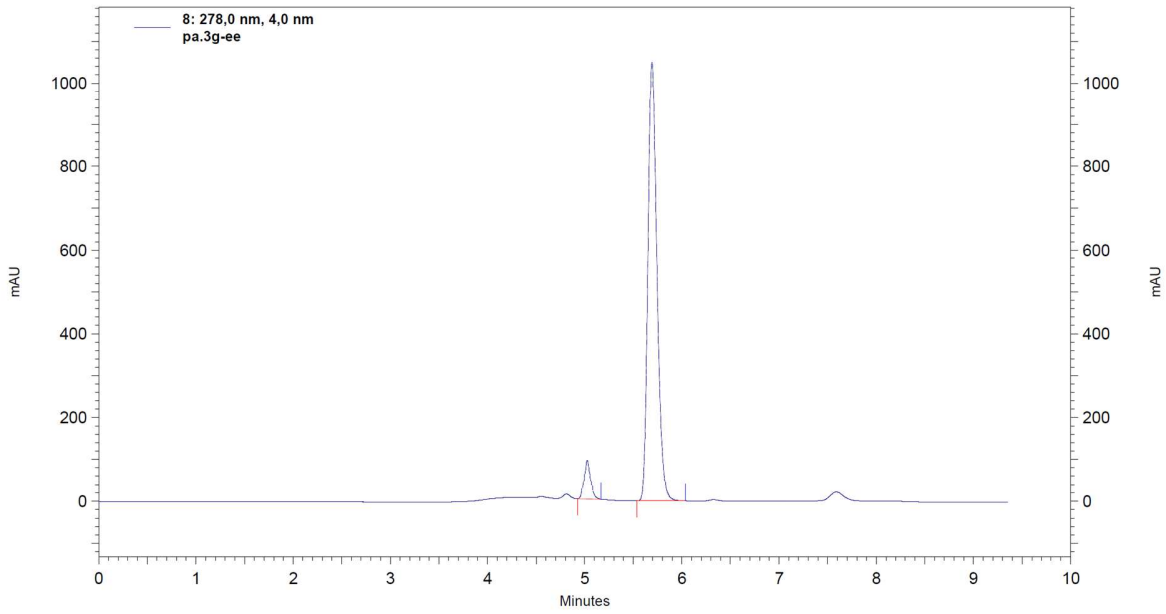
Sample ID: pa.3g-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-C2

Injection Volume: 5µL





8: 278,0 nm, 4,0 nm
Results

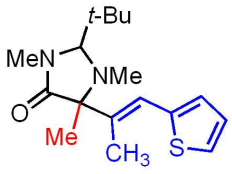
Peak Number	Retention Time	Area Percent	Area
1	5,027	3,972	41821594
2	5,692	96,028	1010897778
Totals		100,000	1052719372

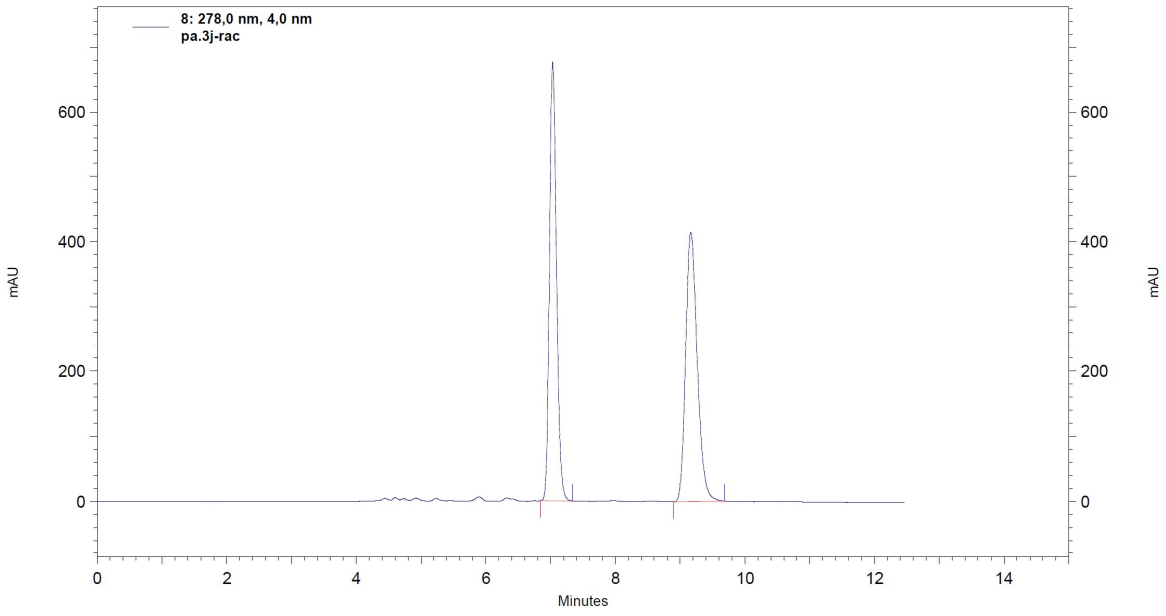
Sample ID: pa.3j-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C4

Injection Volume: 5µL





8: 278,0 nm, 4,0 nm
Results

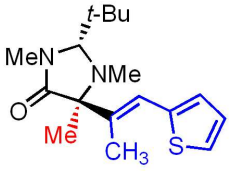
Peak Number	Retention Time	Area Percent	Area
1	7,032	49,826	686602720
2	9,165	50,174	691409361
Totals		100,000	1378012081

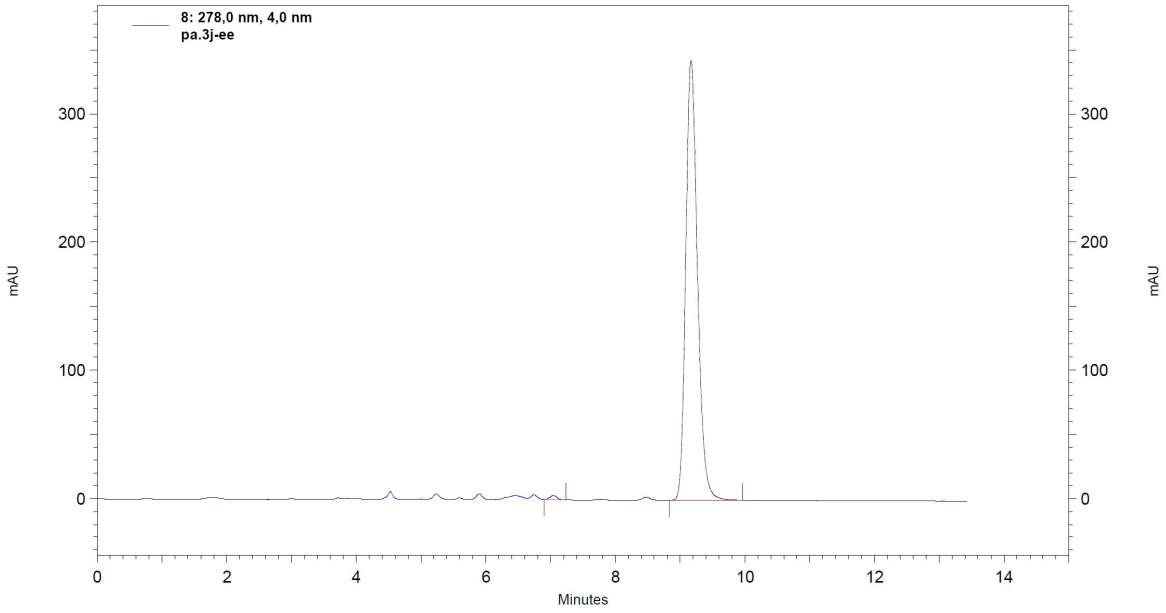
Sample ID: pa.3j-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-B4

Injection Volume: 5µL





8: 278,0 nm, 4,0 nm
Results

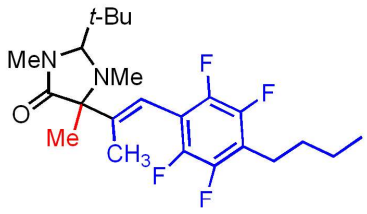
Peak Number	Retention Time	Area Percent	Area
1	7,040	0,533	3086642
2	9,168	99,467	576472721
Totals		100,000	579559363

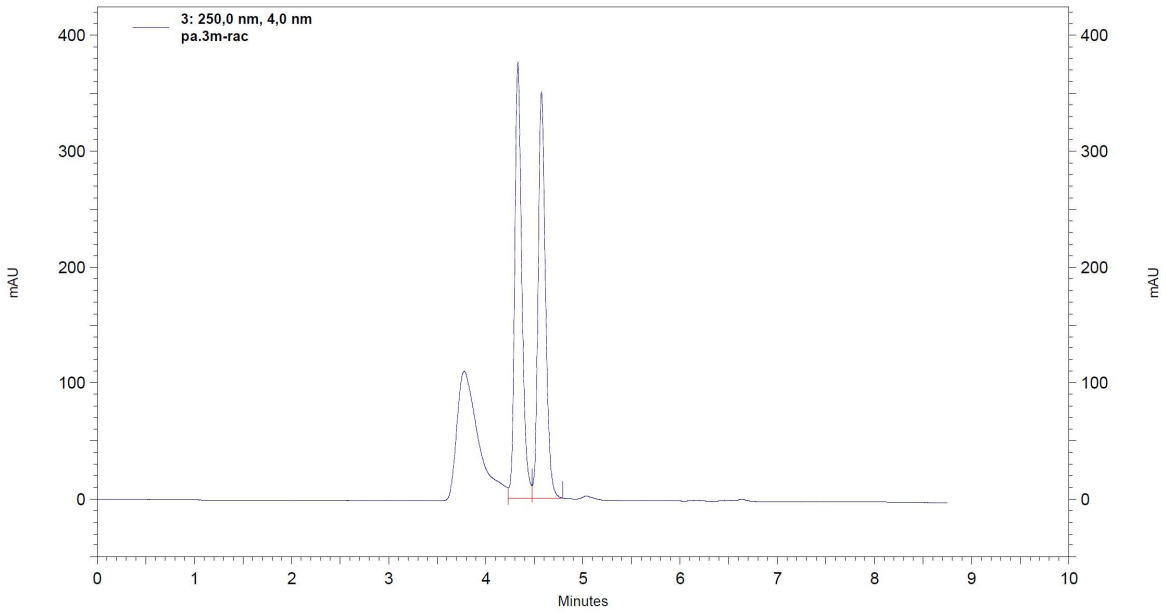
Sample ID: pa.3m-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C3

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

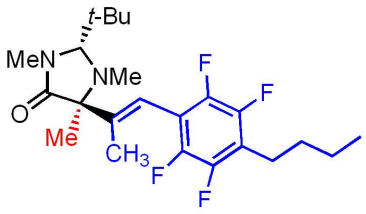
Peak Number	Retention Time	Area Percent	Area
1	4,330	50,794	256276087
2	4,573	49,206	248260007
Totals		100,000	504536094

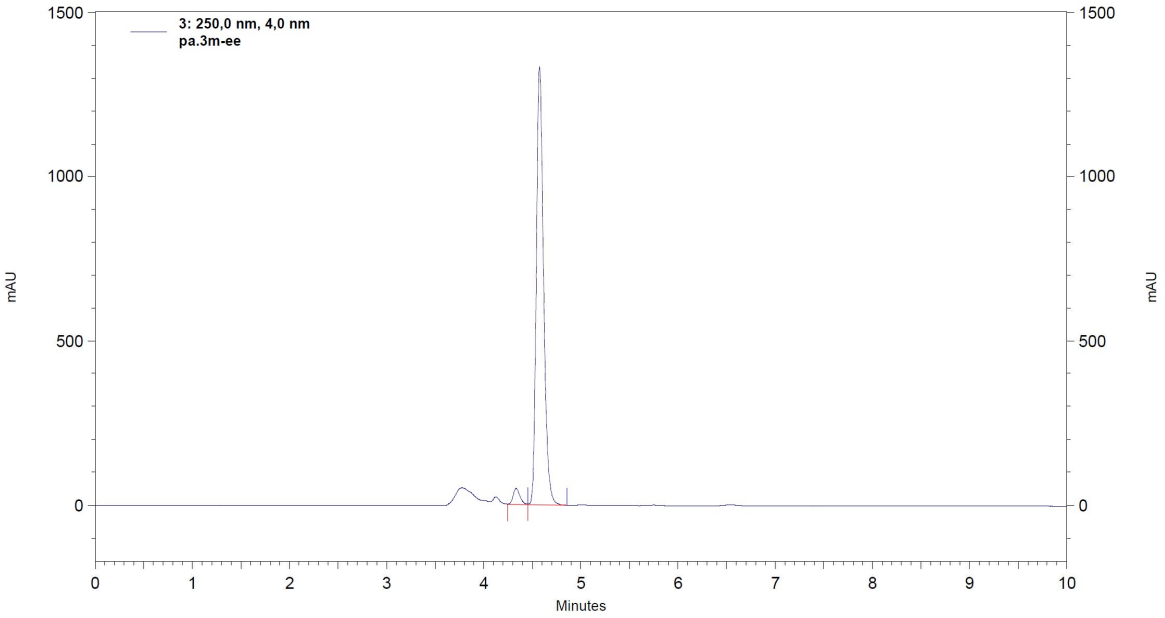
Sample ID: pa.3m-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-B3

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

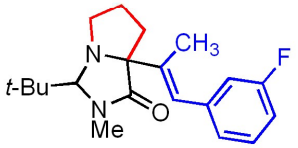
Peak Number	Retention Time	Area Percent	Area
1	4,333	3,286	31381691
2	4,575	96,714	923567485
Totals		100,000	954949176

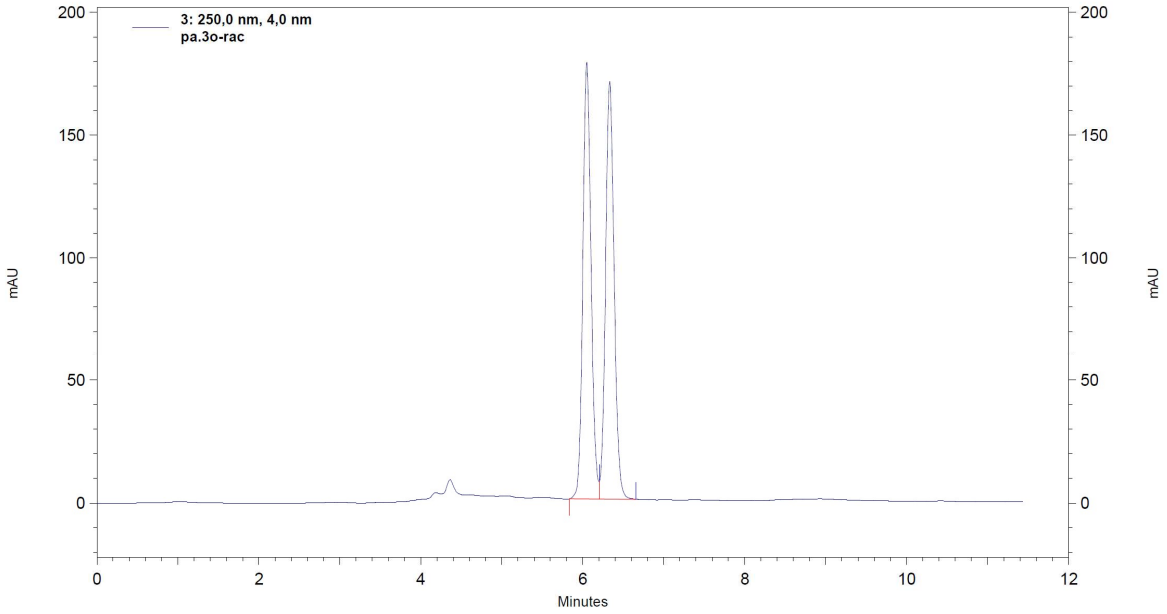
Sample ID: pa.3o-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_IPA, 90_10, 0.5ml, 22°C.met

Vial: P1-B3

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

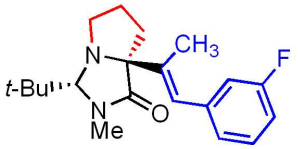
Peak Number	Retention Time	Area Percent	Area
1	6,047	50,003	167614270
2	6,333	49,997	167595499
Totals		100,000	335209769

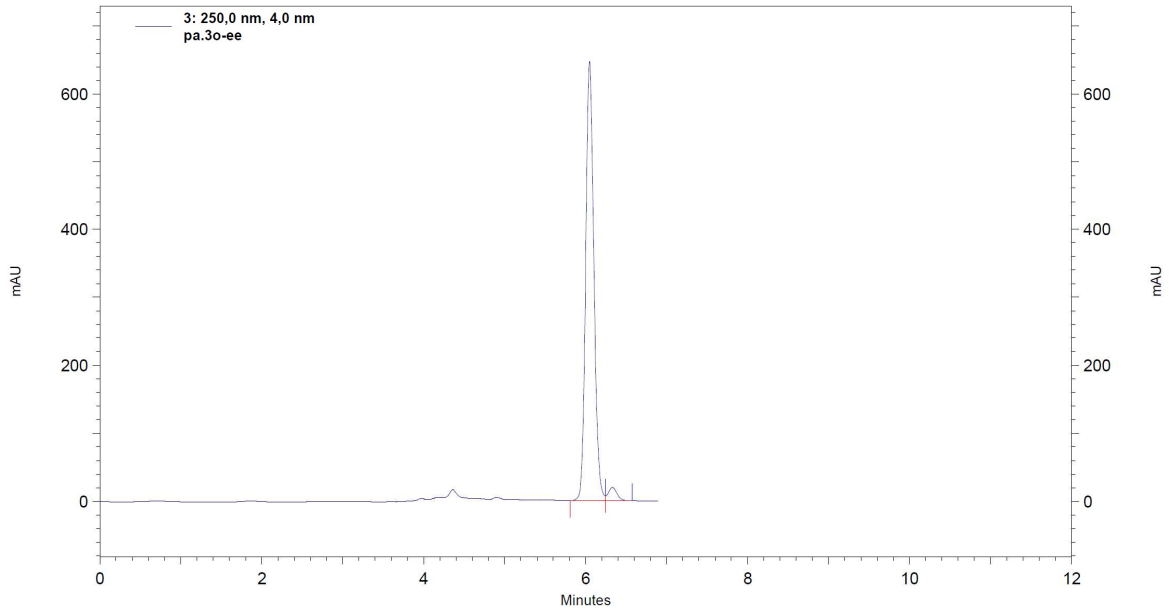
Sample ID: pa.3o-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_IPA, 90_10, 0.5ml, 22°C.met

Vial: P1-B7

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

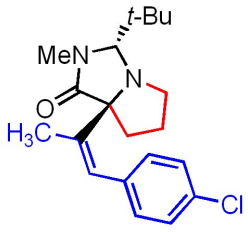
Peak Number	Retention Time	Area Percent	Area
1	6,047	96,913	607049340
2	6,333	3,087	19335381
Totals		100,000	626384721

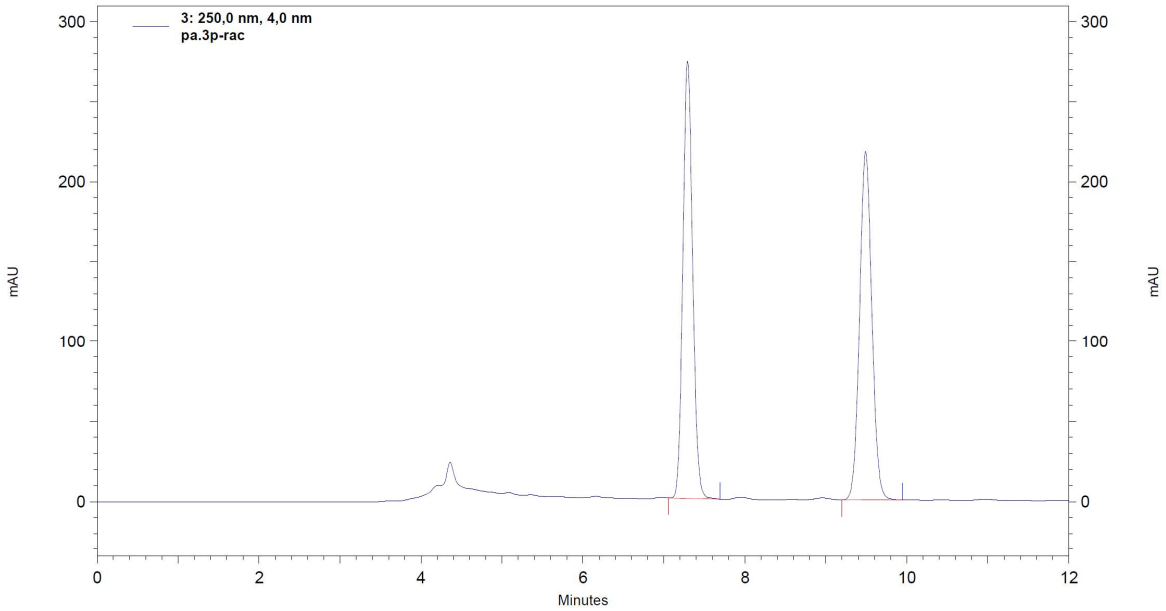
Sample ID: pa.3p-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_IPA, 90_10, 0.5ml, 22°C.met

Vial: P1-B5

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

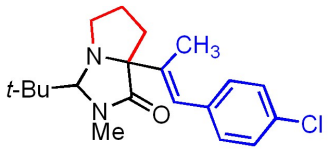
Peak Number	Retention Time	Area Percent	Area
1	7,293	49,922	305701803
2	9,493	50,078	306661972
Totals		100,000	612363775

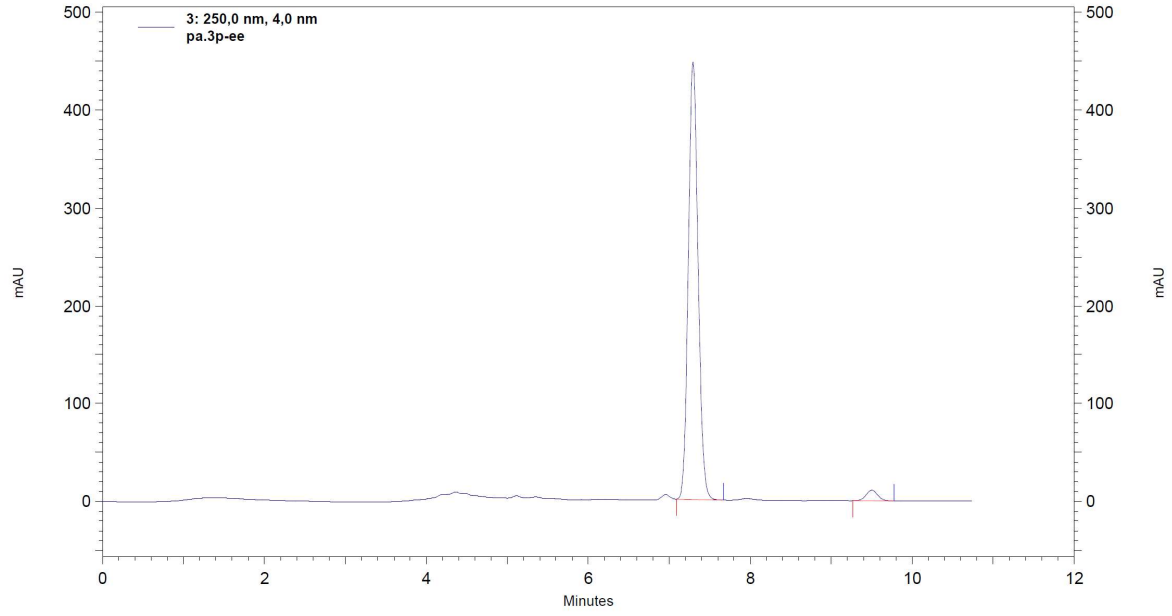
Sample ID: pa.3p-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_IPA, 90_10, 0.5ml, 22°C.met

Vial: P1-B6

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

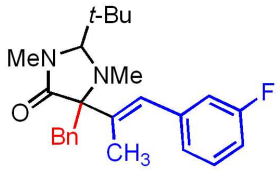
Peak Number	Retention Time	Area Percent	Area
1	7,293	97,190	501941867
2	9,500	2,810	14510036
Totals		100,000	516451903

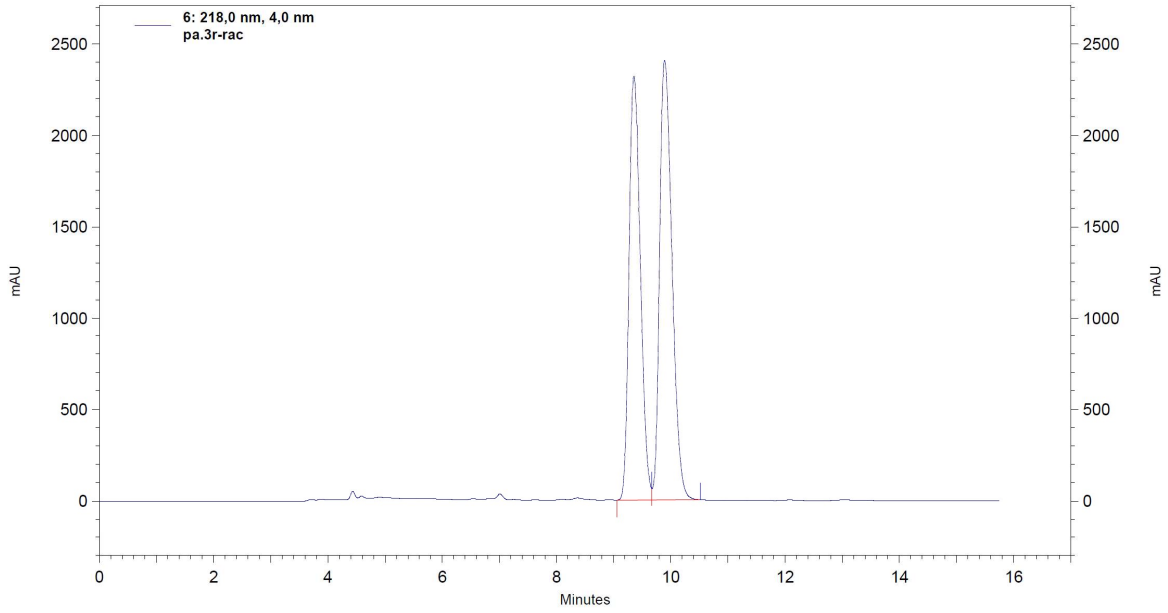
Sample ID: pa.3r-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C1

Injection Volume: 5µL





6: 218,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	9,357	46,923	4294004615
2	9,893	53,077	4857108158

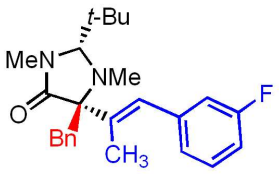
Totals			
		100,000	9151112773

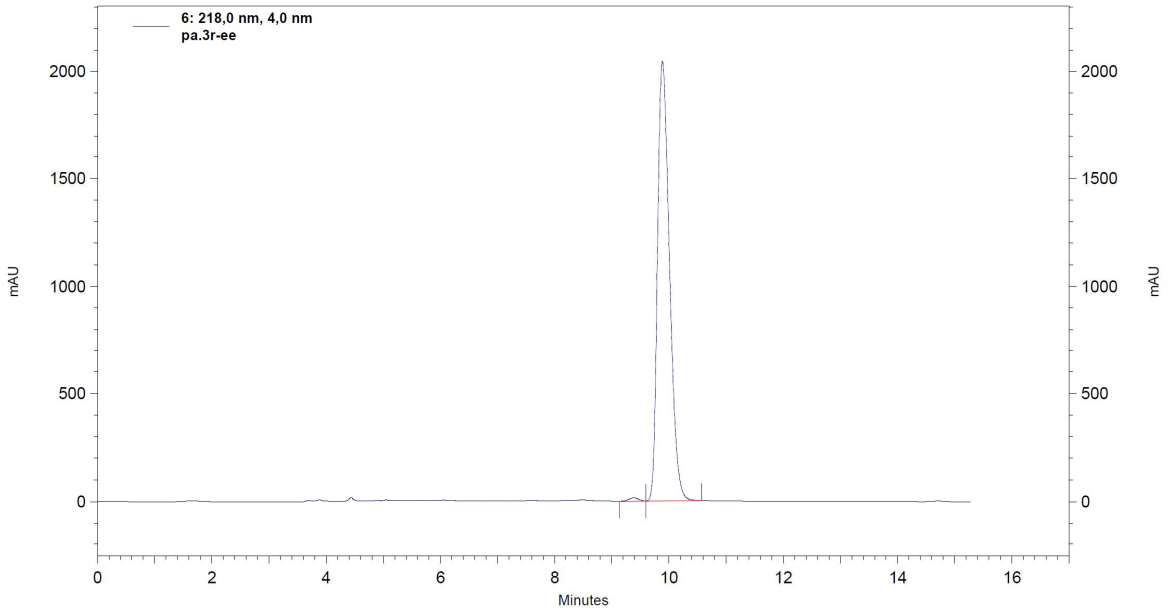
Sample ID: pa.3r-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C5

Injection Volume: 5µL





6: 218,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	9,382	0,625	25076355
2	9,885	99,375	3985323656
Totals		100,000	4010400011

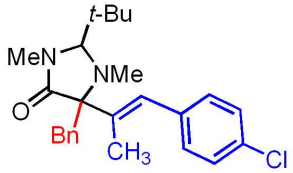
Sample ID: P2-89-99-rac

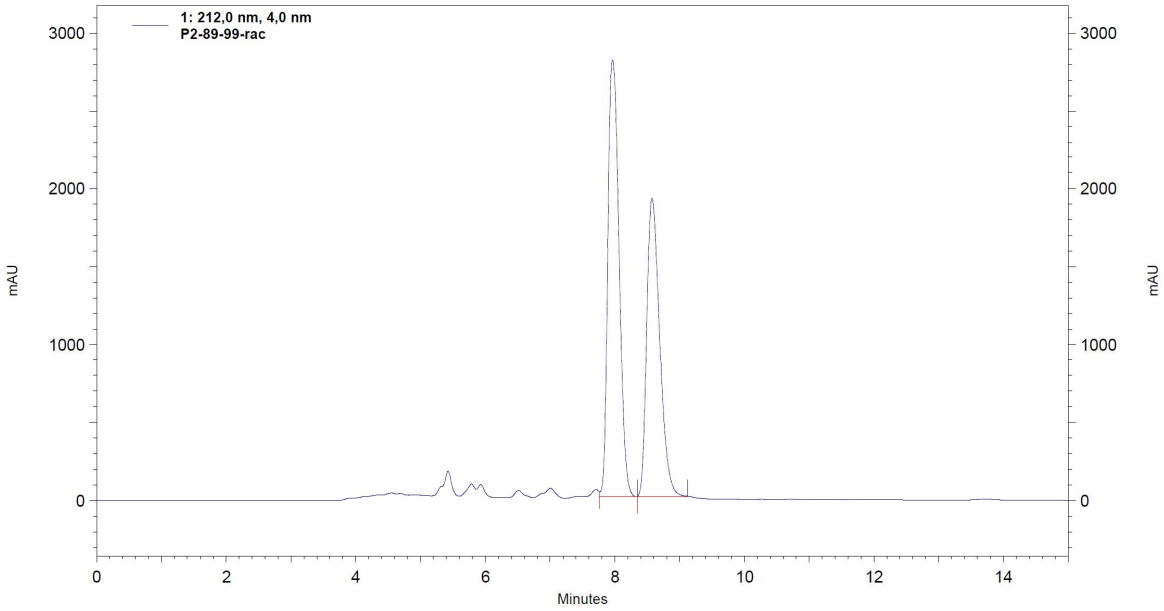
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Acquired: 02.07.2019 08:04:46 (GMT +02:00)

Vial: P1-E1

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm
Results

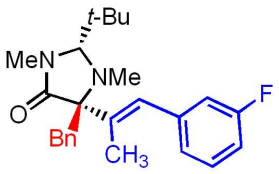
Peak Number	Retention Time	Area Percent	Area
1	7,965	55,660	4485511222
2	8,575	44,340	3573273203
Totals		100,000	8058784425

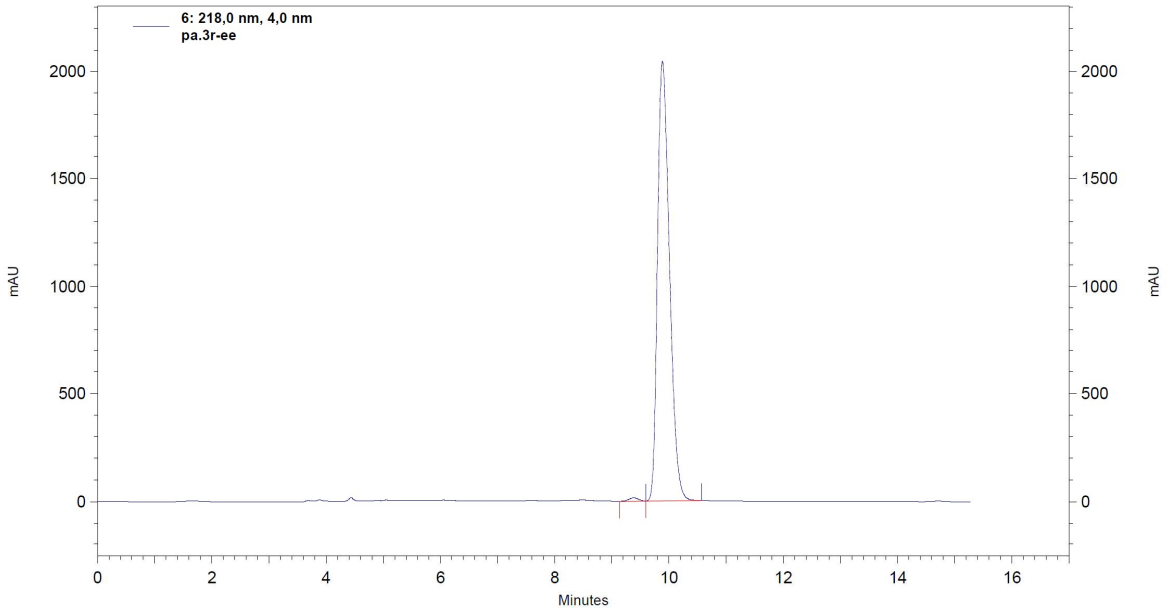
Sample ID: pa.3r-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C5

Injection Volume: 5µL





6: 218,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	9,382	0,625	25076355
2	9,885	99,375	3985323656
Totals		100,000	4010400011

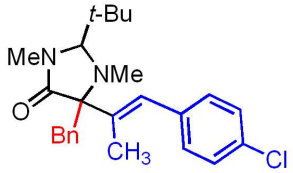
Sample ID: P2-89-99-rac

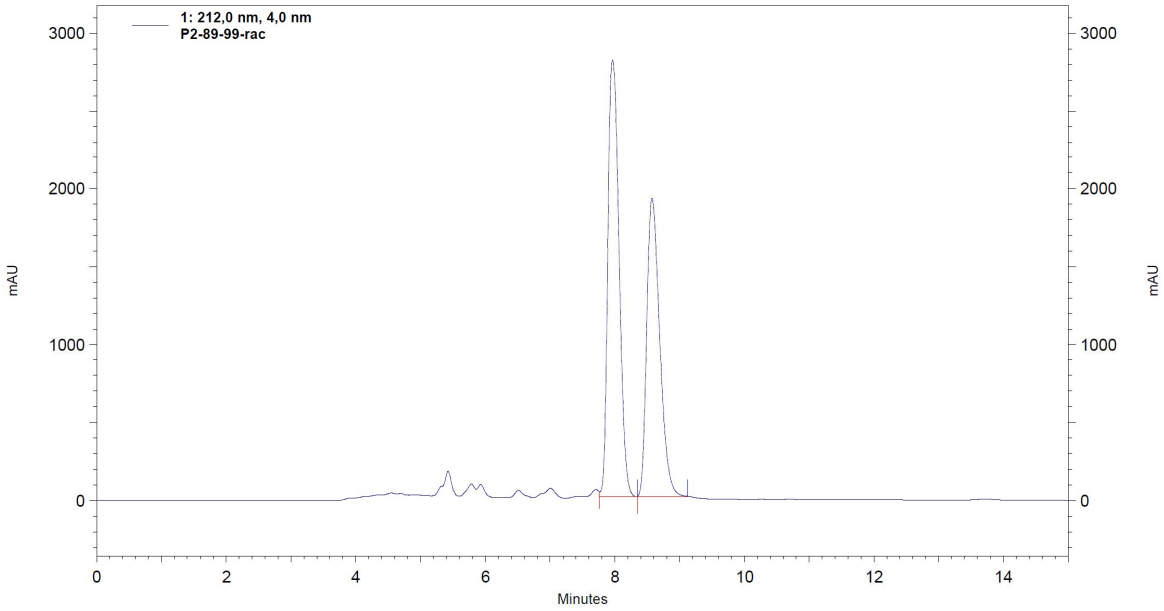
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Acquired: 02.07.2019 08:04:46 (GMT +02:00)

Vial: P1-E1

Injection Volume: 5µL





1: 212,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	7,965	55,660	4485511222
2	8,575	44,340	3573273203
Totals		100,000	8058784425

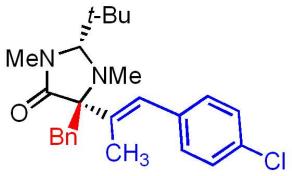
Sample ID: P2-R-99-ee

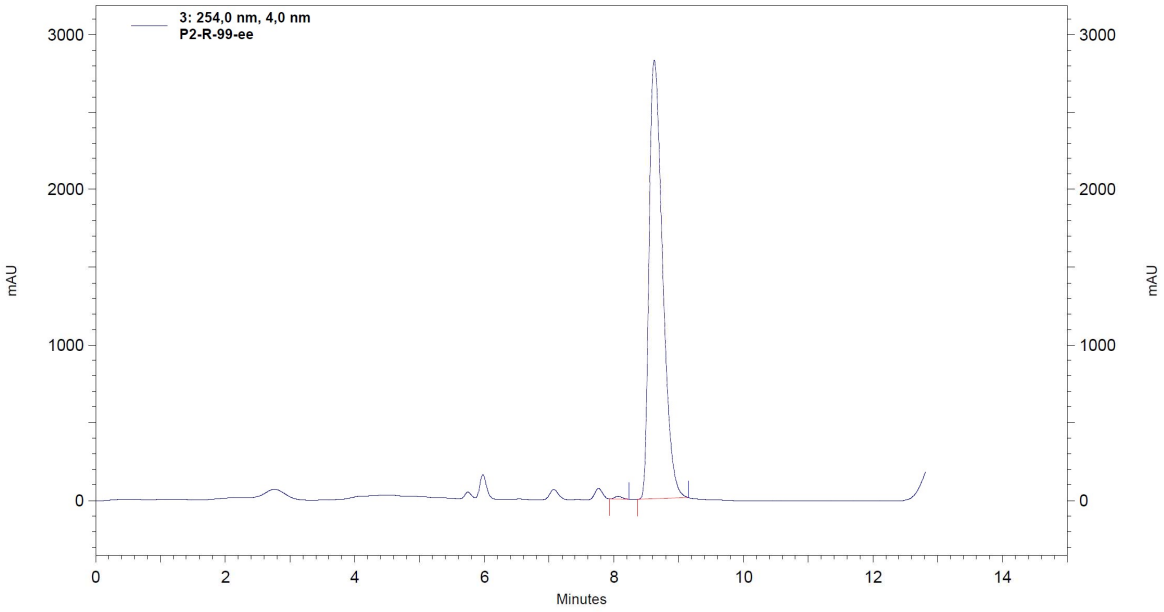
Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Acquired: 02.07.2019 08:38:47 (GMT +02:00)

Vial: P1-E1

Injection Volume: 5µL





3: 254,0 nm, 4,0 nm
Results

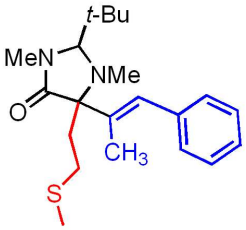
Peak Number	Retention Time	Area Percent	Area
1	8,068	0,344	18904356
2	8,623	99,656	5474498181
Totals		100,000	5493402537

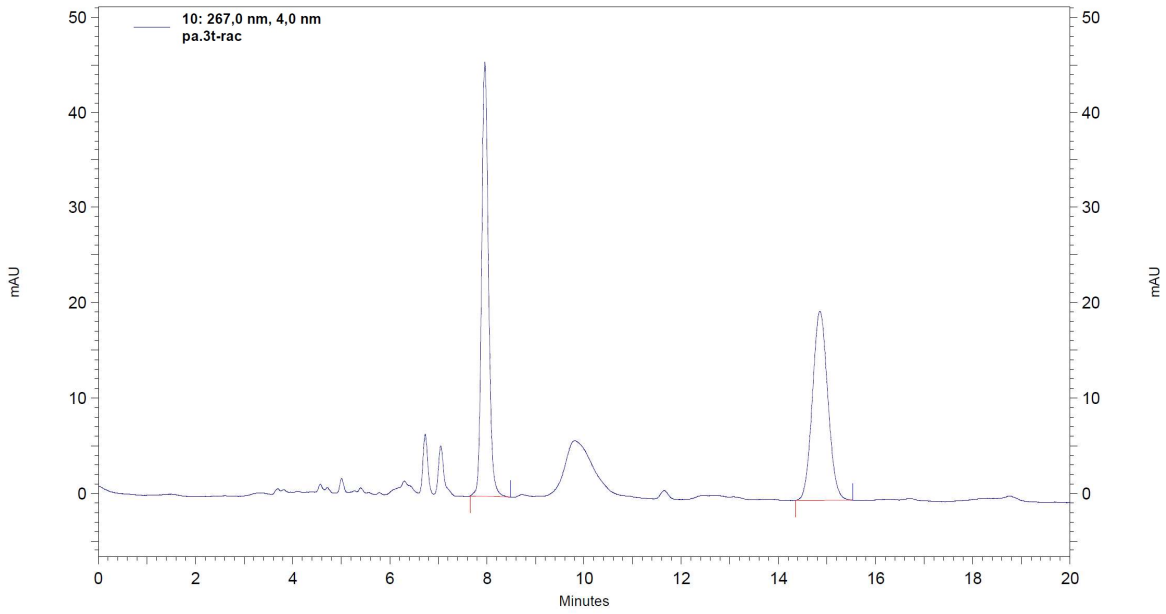
Sample ID: pa.3t-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B5

Injection Volume: 5µL





10: 267,0 nm, 4,0 nm
Results

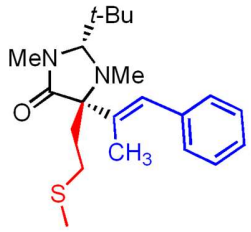
Peak Number	Retention Time	Area Percent	Area
1	7,957	50,548	59748079
2	14,855	49,452	58452878
Totals		100,000	118200957

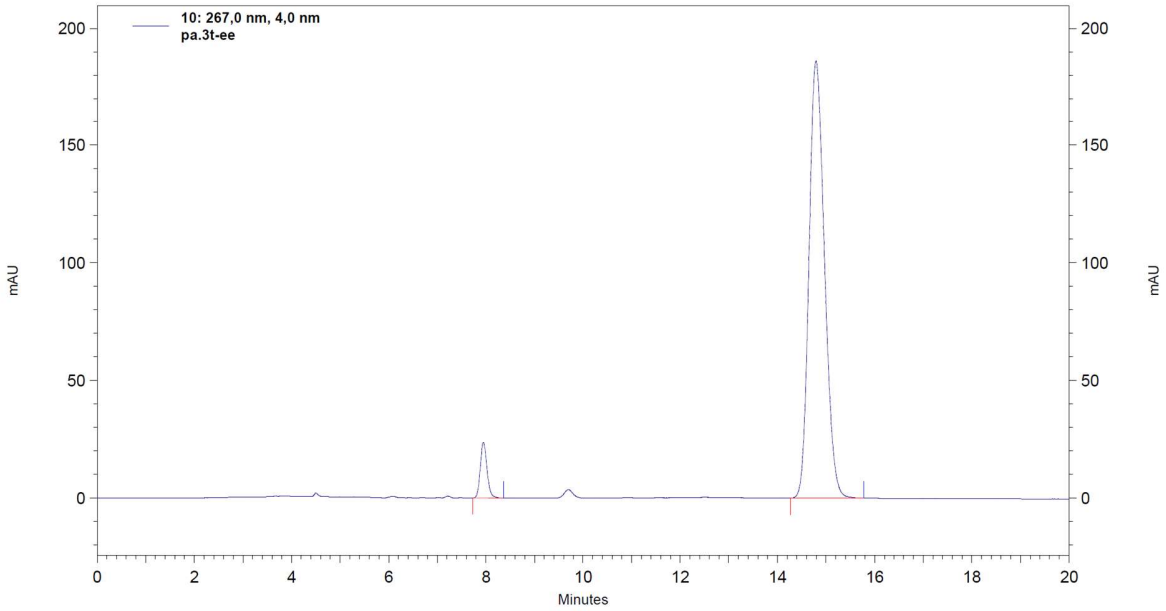
Sample ID: pa.3t-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B6

Injection Volume: 5µL





10: 267,0 nm, 4,0 nm
Results

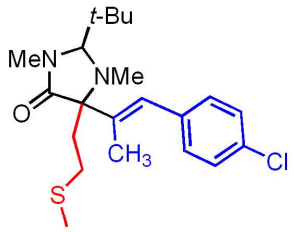
Peak Number	Retention Time	Area Percent	Area
1	7,950	5,223	30464885
2	14,793	94,777	552786889
Totals		100,000	583251774

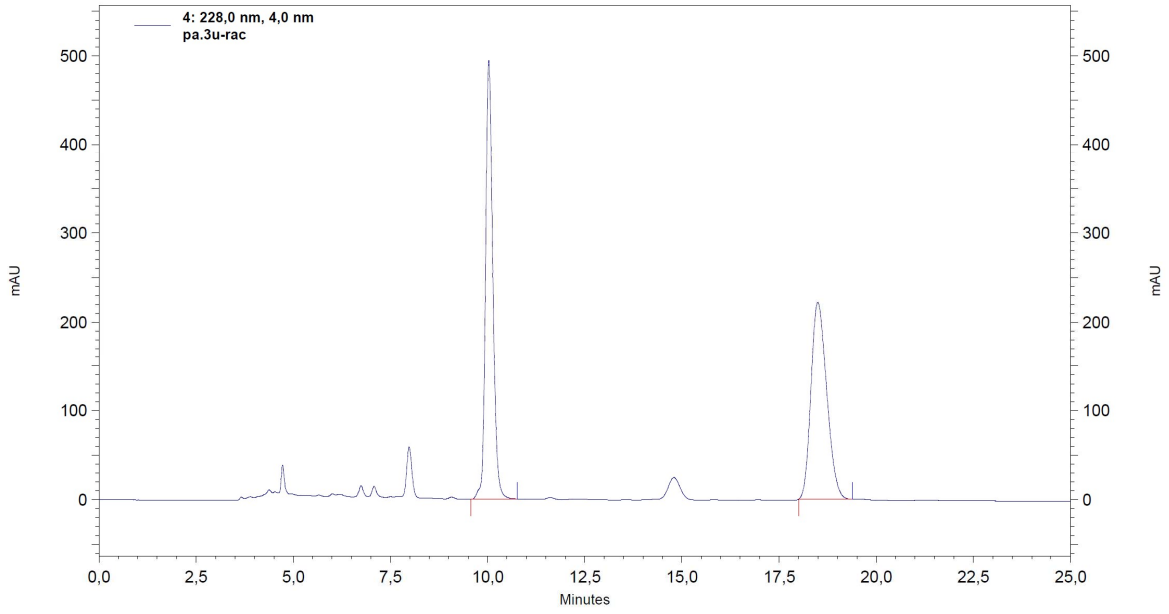
Sample ID: pa.3u-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B1

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

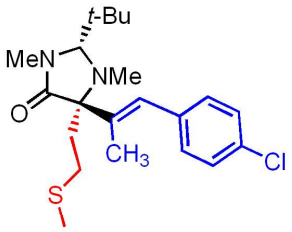
Peak Number	Retention Time	Area Percent	Area
1	10,033	50,841	862581093
2	18,498	49,159	834053077
Totals		100,000	1696634170

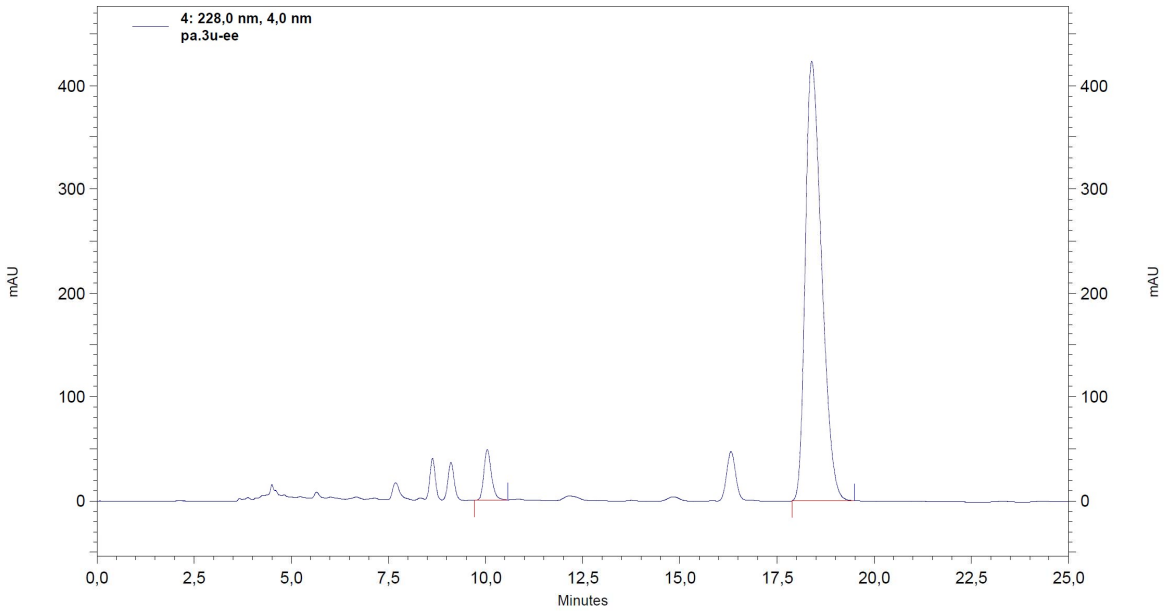
Sample ID: pa.3u-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B2

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

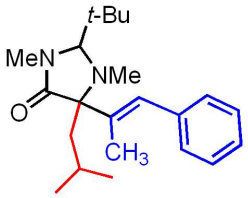
Peak Number	Retention Time	Area Percent	Area
1	10,045	5,172	90098669
2	18,395	94,828	1652027550
Totals		100,000	1742126219

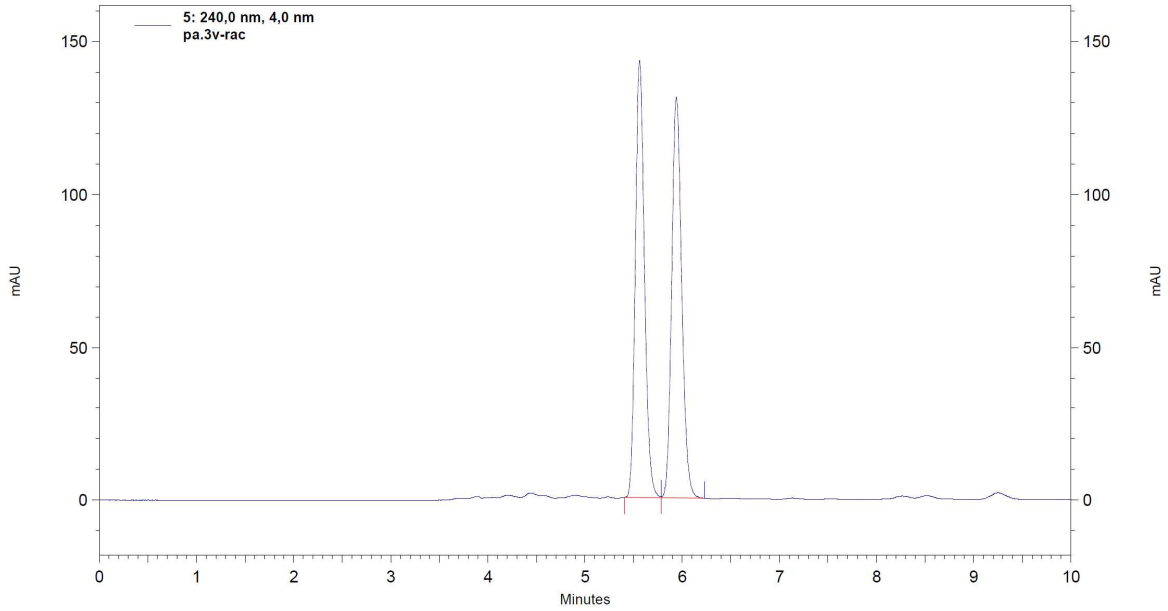
Sample ID: pa.3v-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C2

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

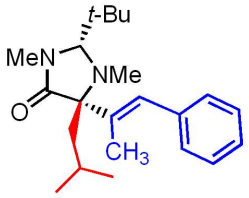
Peak Number	Retention Time	Area Percent	Area
1	5,562	49,850	125188286
2	5,940	50,150	125943746
Totals		100,000	251132032

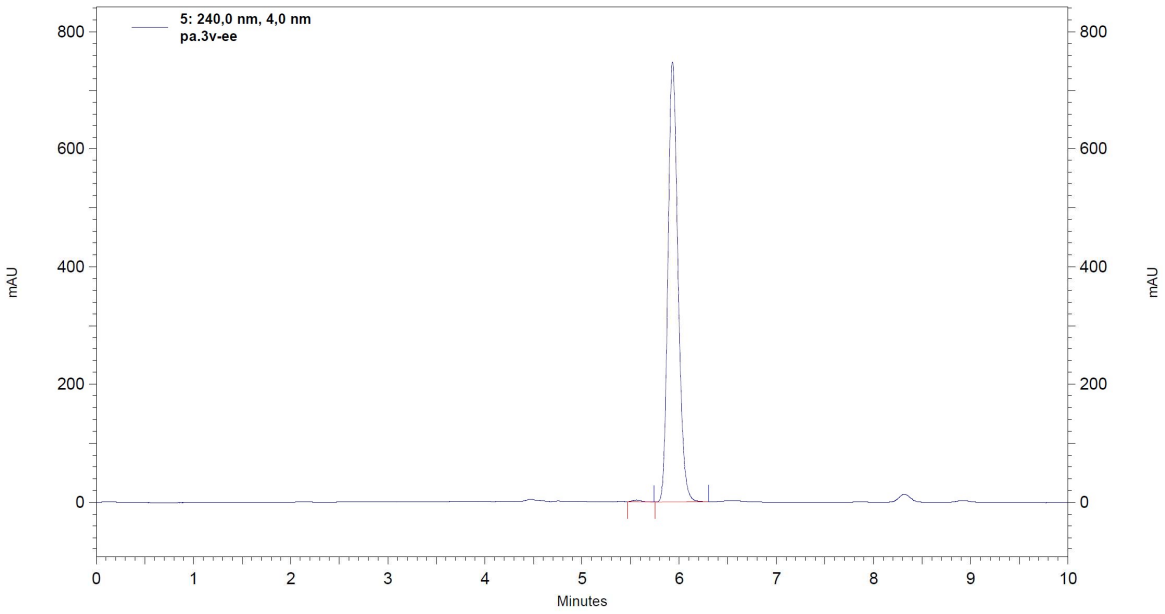
Sample ID: pa.3v-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C6

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

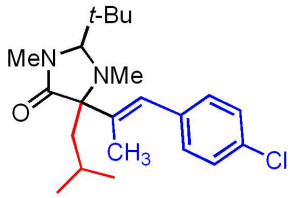
Peak Number	Retention Time	Area Percent	Area
1	5,558	0,377	2725237
2	5,932	99,623	719535563
Totals		100,000	722260800

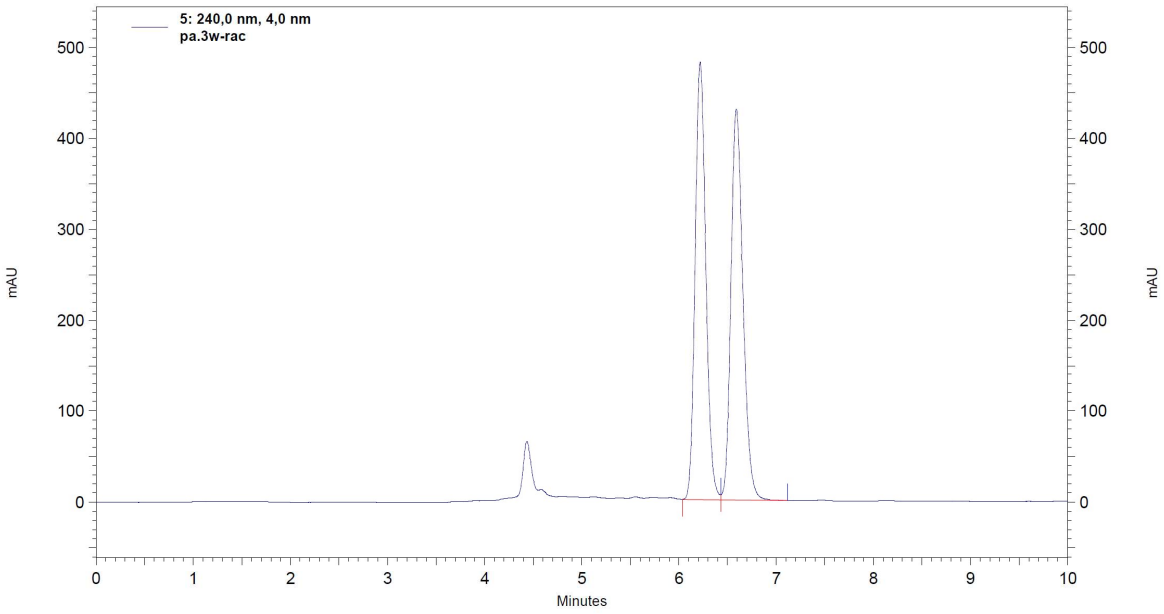
Sample ID: pa.3w-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C3

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

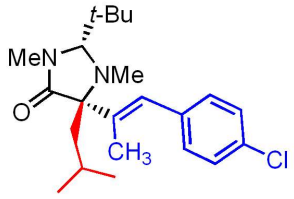
Peak Number	Retention Time	Area Percent	Area
1	6,218	49,814	493919674
2	6,590	50,186	497616987
Totals		100,000	991536661

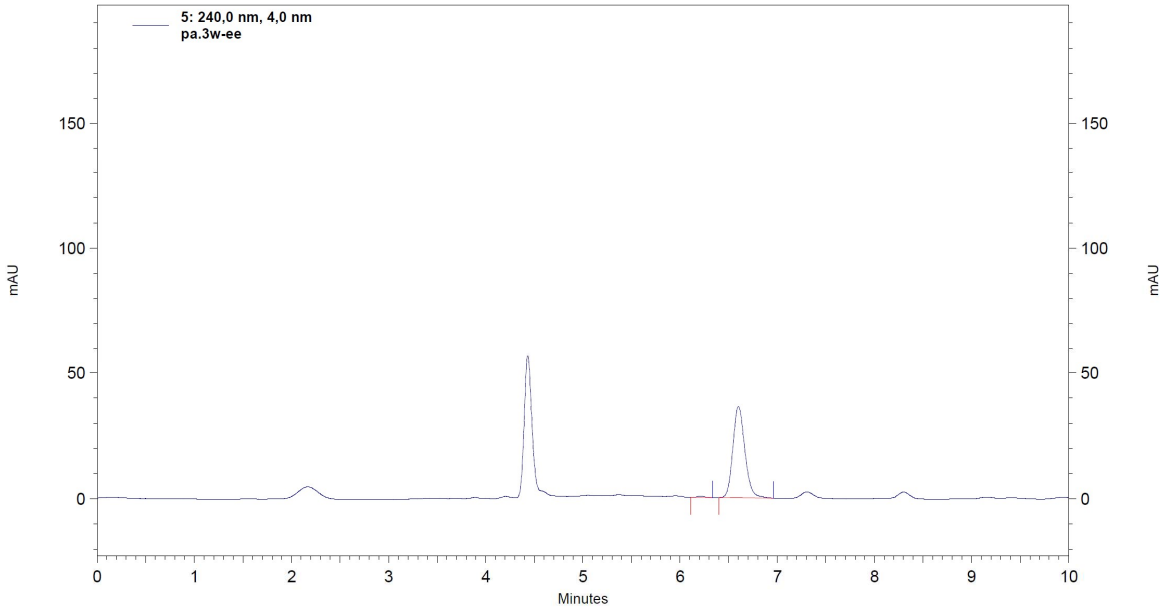
Sample ID: pa.3w-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 95_5,0,5ml, 22°C.met

Vial: P1-C7

Injection Volume: 5µL





5: 240,0 nm, 4,0 nm
Results

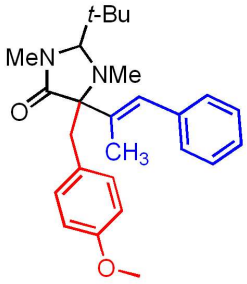
Peak Number	Retention Time	Area Percent	Area
1	6,212	0,956	402768
2	6,602	99,044	41730278
Totals		100,000	42133046

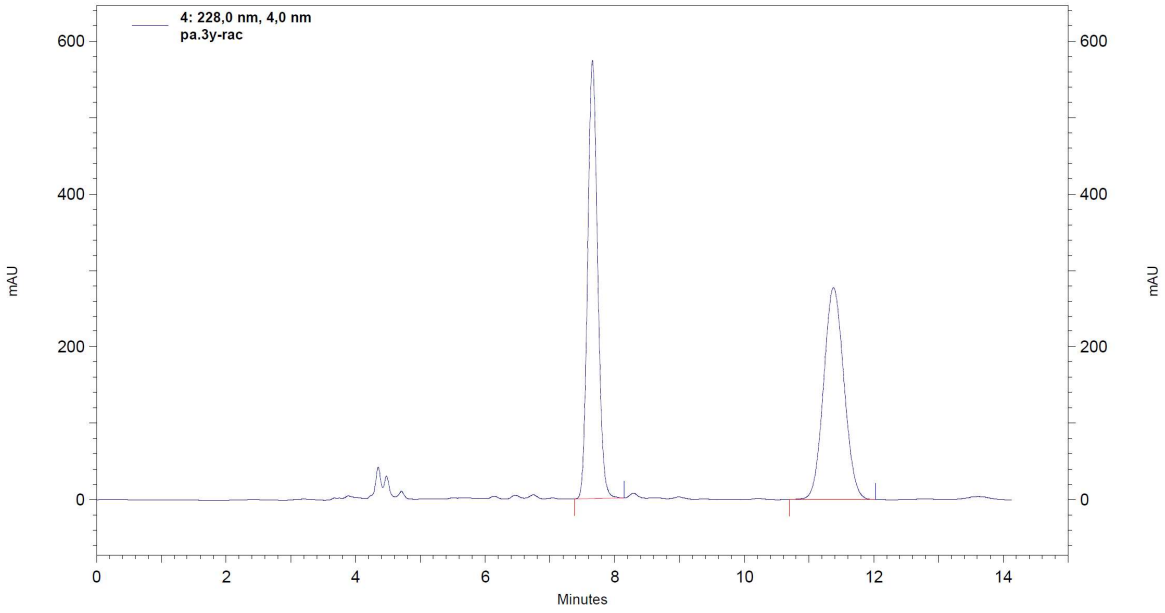
Sample ID: pa.3y-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C4

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

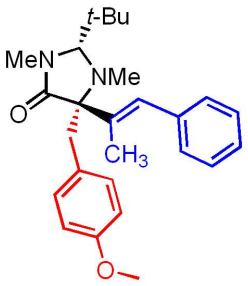
Peak Number	Retention Time	Area Percent	Area
1	7,657	50,328	826165711
2	11,378	49,672	815397788
Totals		100,000	1641563499

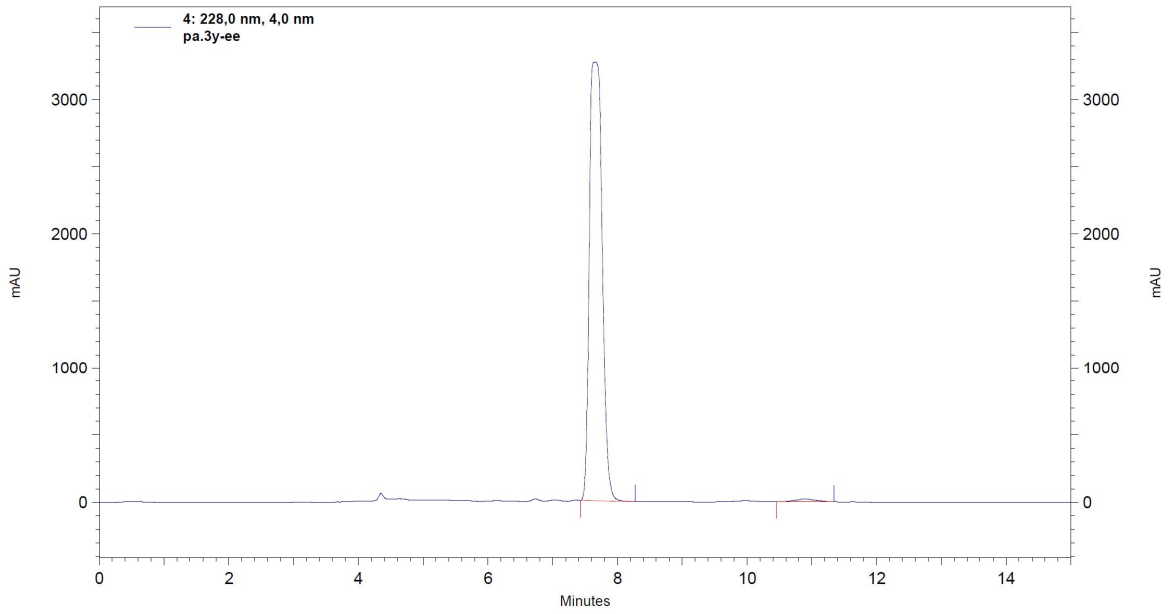
Sample ID: pa.3y-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C8

Injection Volume: 5µL





4: 228,0 nm, 4,0 nm
Results

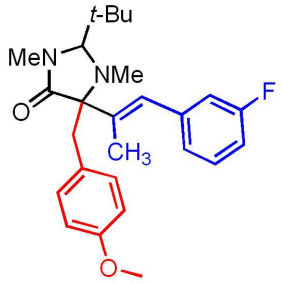
Peak Number	Retention Time	Area Percent	Area
1	7,667	98,931	6029611299
2	10,902	1,069	65147713
Totals		100,000	6094759012

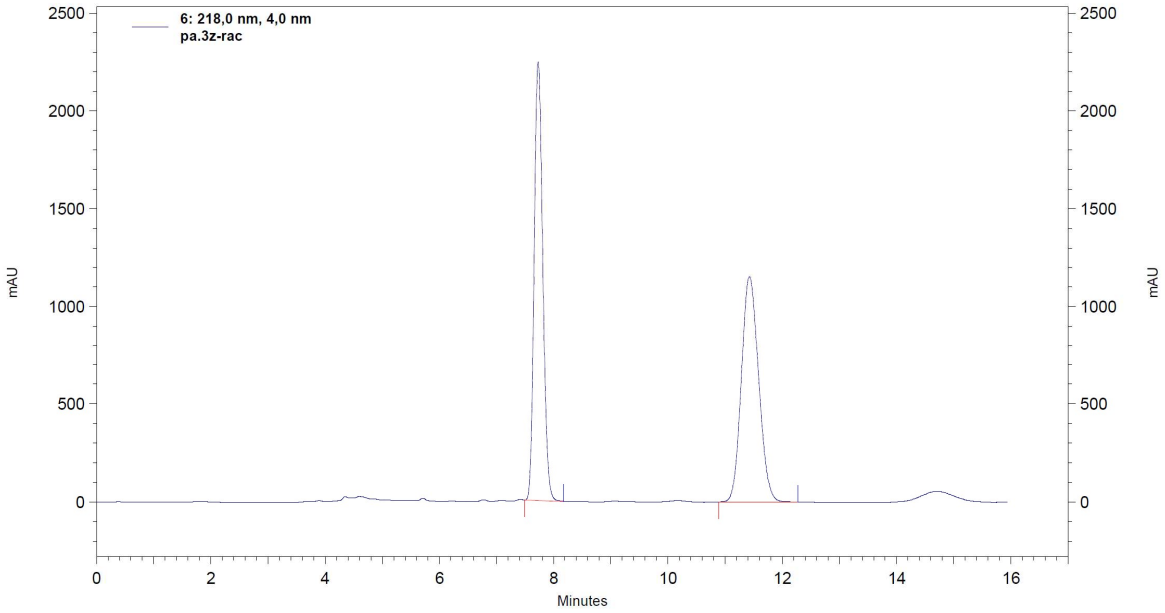
Sample ID: pa.3z-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C4

Injection Volume: 5µL





6: 218,0 nm, 4,0 nm
Results

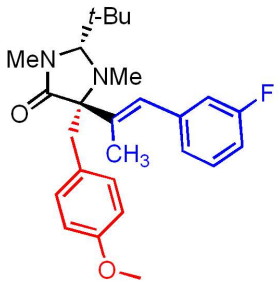
Peak Number	Retention Time	Area Percent	Area
1	7,728	49,280	3143849447
2	11,423	50,720	3235760276
Totals		100,000	6379609723

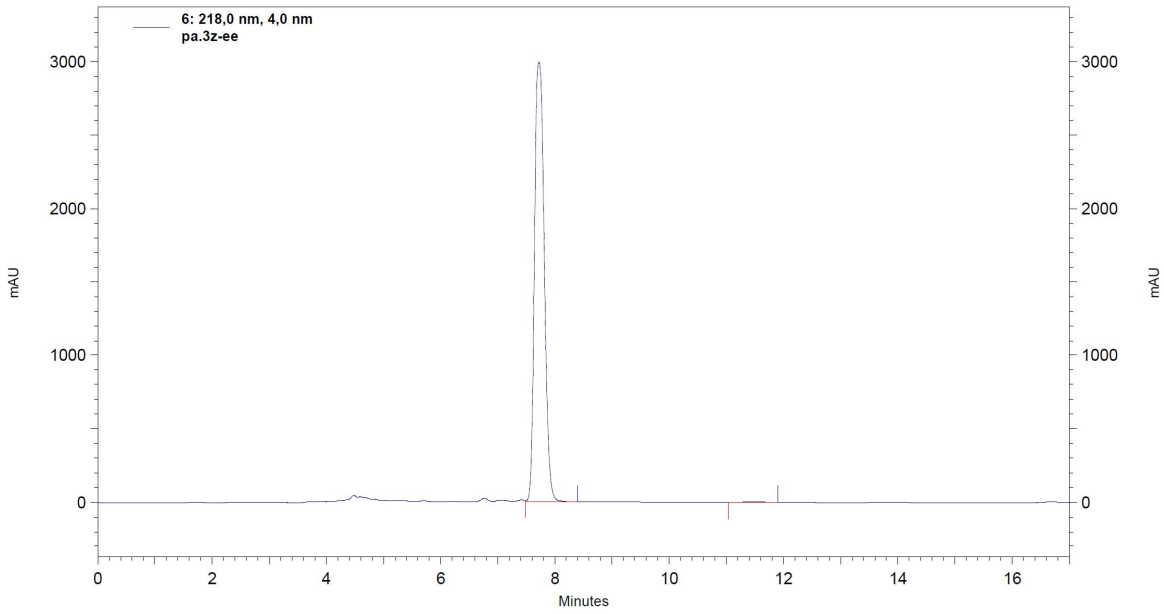
Sample ID: pa.3z-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C8

Injection Volume: 5µL





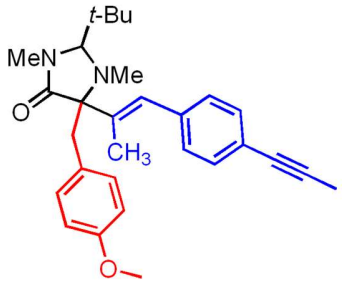
6: 218,0 nm, 4,0 nm
Results

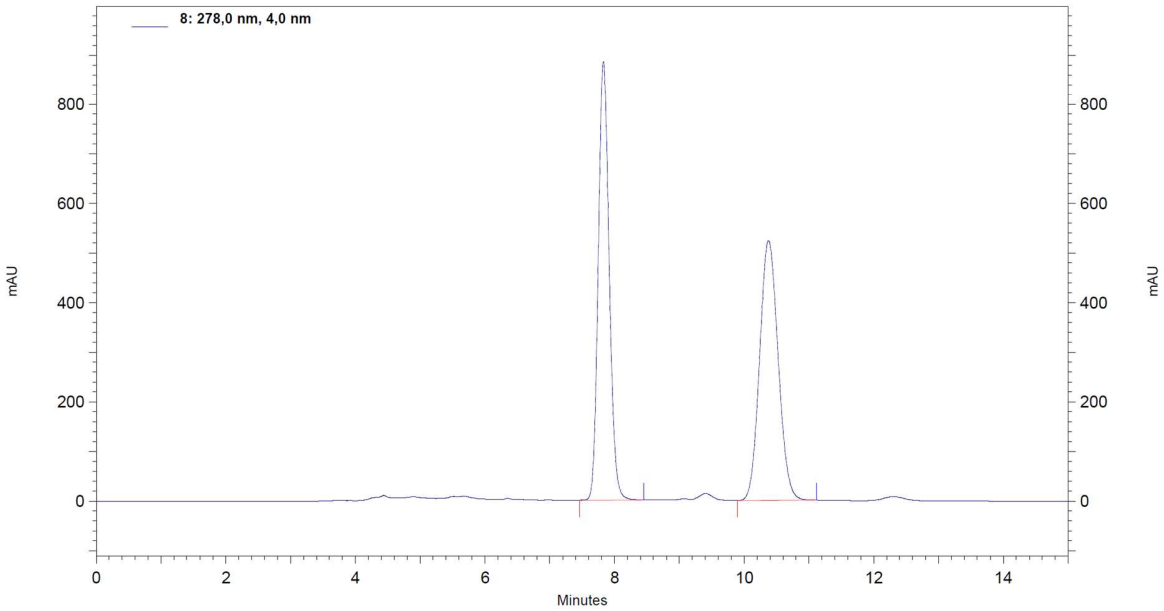
Peak Number	Retention Time	Area Percent	Area
1	7,722	99,787	4745665393
2	11,463	0,213	10117139
Totals		100,000	4755782532

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C3

Injection Volume: 5µL





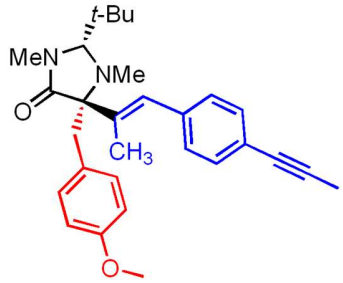
8: 278,0 nm, 4,0 nm
Results

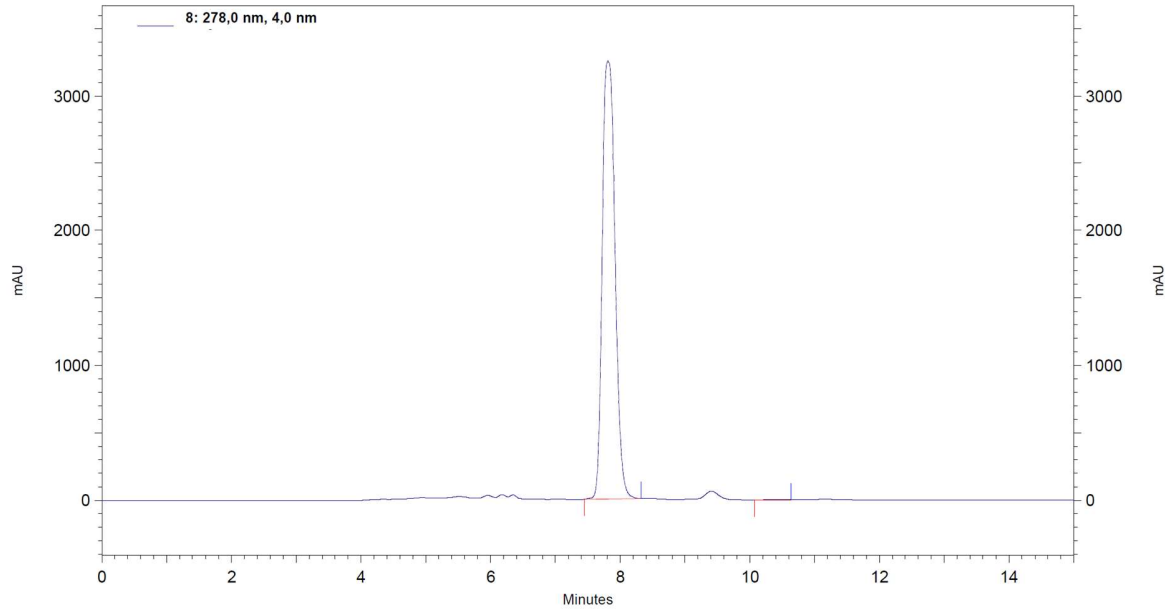
Peak Number	Retention Time	Area Percent	Area
1	7,828	49,936	1390894722
2	10,377	50,064	1394442401
Totals		100,000	2785337123

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C7

Injection Volume: 5µL





8: 278,0 nm, 4,0 nm
Results

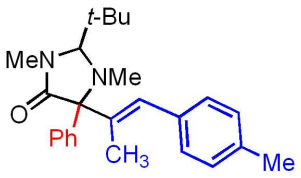
Peak Number	Retention Time	Area Percent	Area
1	7,810	99,910	5982455469
2	10,422	0,090	5416473
Totals		100,000	5987871942

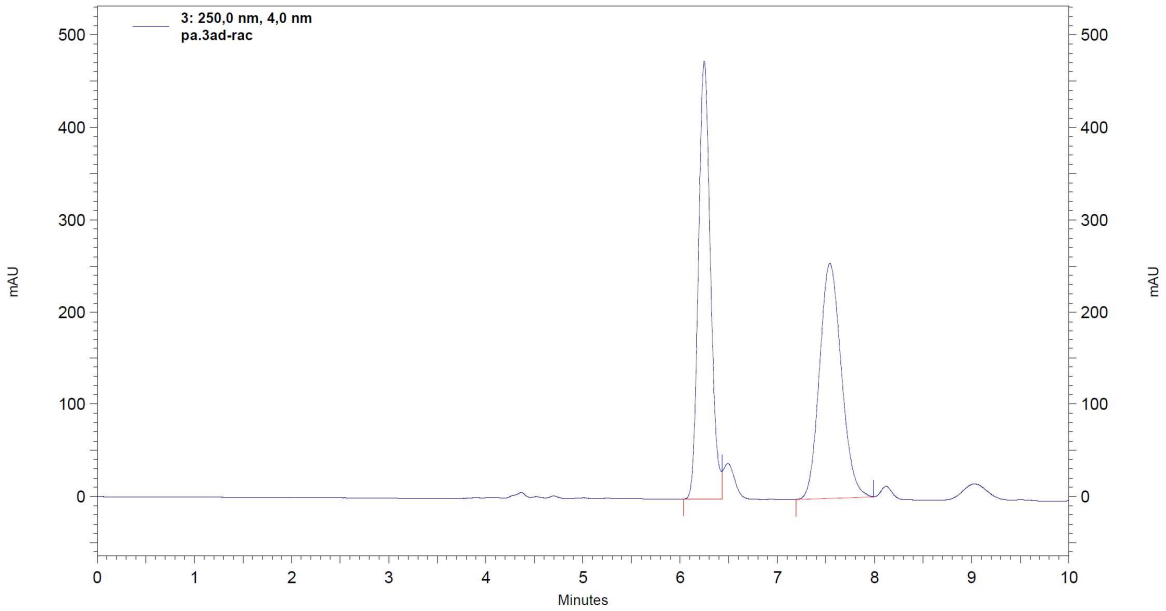
Sample ID: pa.3ad-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-C1

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

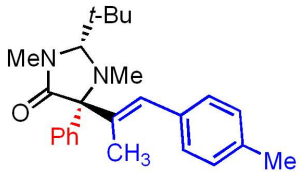
Peak Number	Retention Time	Area Percent	Area
1	6,247	50,659	547914460
2	7,542	49,341	533659026
Totals		100,000	1081573486

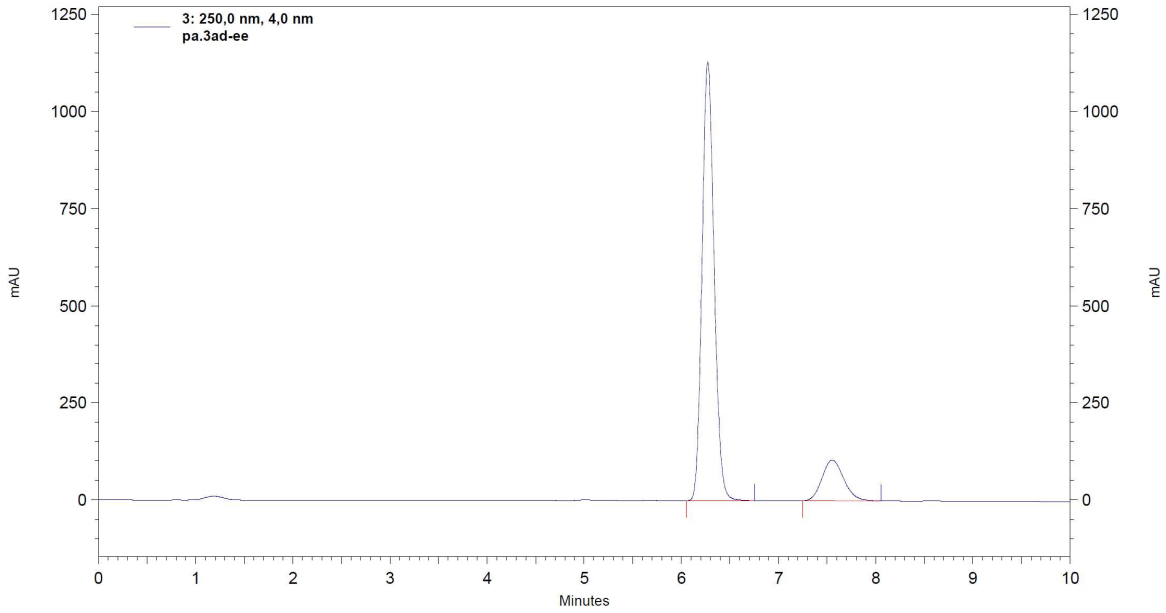
Sample ID: pa.3ad-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 85_15 0,5ml, 22°C.met

Vial: P1-B1

Injection Volume: 5µL





3: 250,0 nm, 4,0 nm
Results

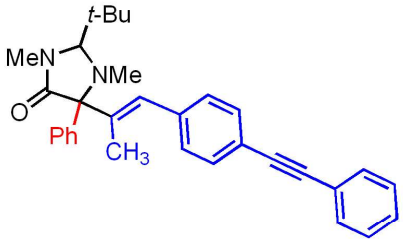
Peak Number	Retention Time	Area Percent	Area
1	6,272	85,601	1309898904
2	7,553	14,399	220343797
Totals		100,000	1530242701

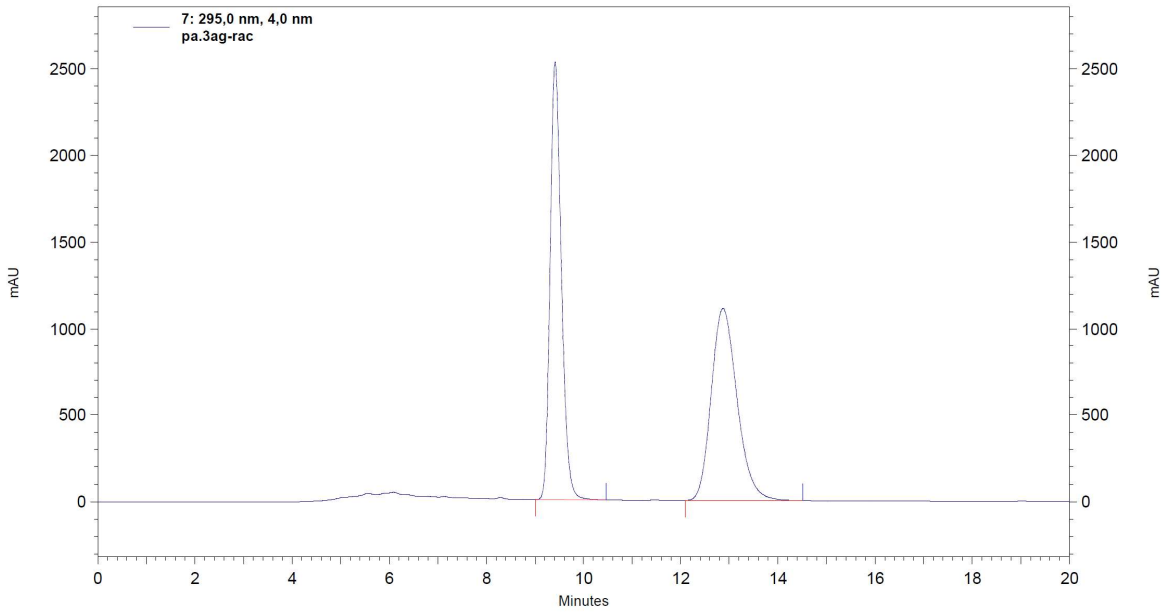
Sample ID: pa.3ag-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B1

Injection Volume: 5µL





7: 295,0 nm, 4,0 nm
Results

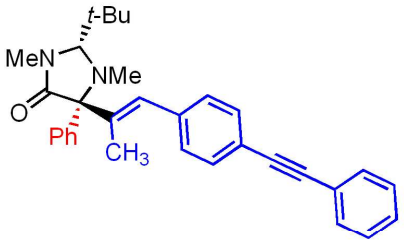
Peak Number	Retention Time	Area Percent	Area
1	9,413	49,667	5436747104
2	12,870	50,333	5509625233
Totals		100,000	10946372337

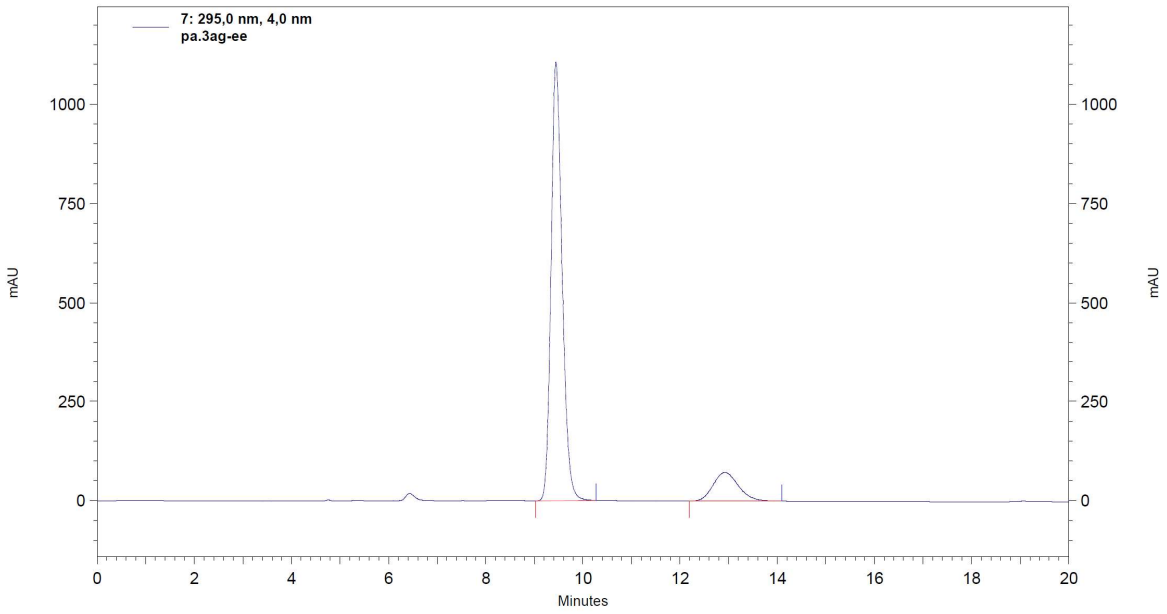
Sample ID: pa.3ag-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-C1

Injection Volume: 5µL





7: 295,0 nm, 4,0 nm

Results

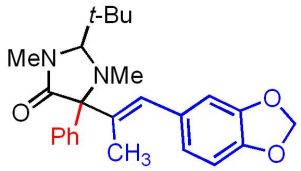
Peak Number	Retention Time	Area Percent	Area
1	9,445	86,796	2341348698
2	12,922	13,204	356184463
Totals		100,000	2697533161

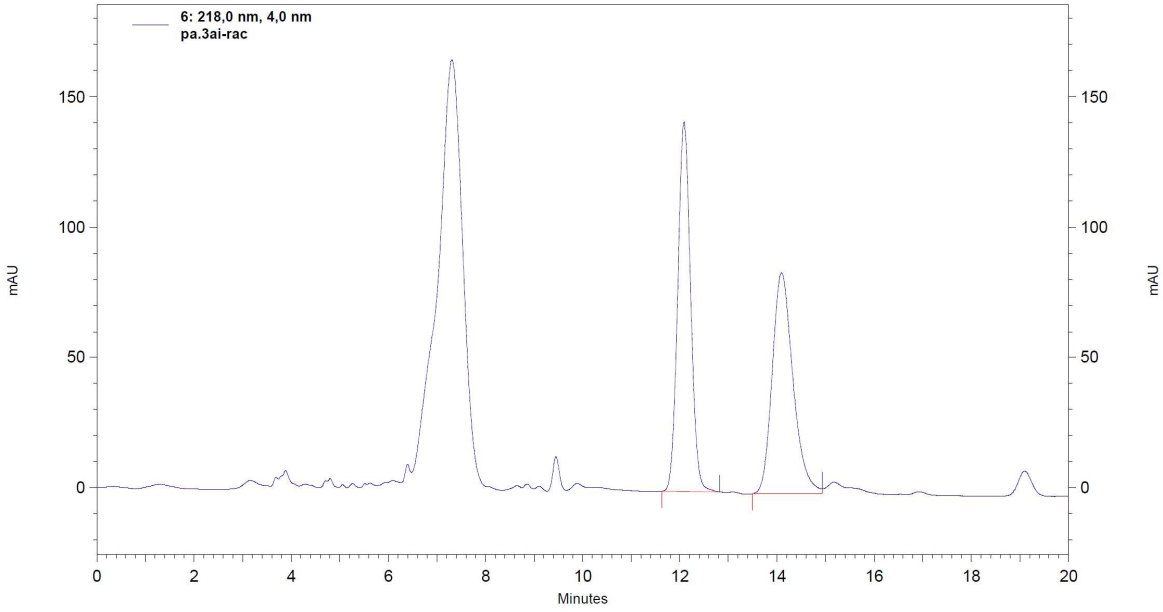
Sample ID: pa.3ai-rac

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-B2

Injection Volume: 5µL





6: 218,0 nm, 4,0 nm
Results

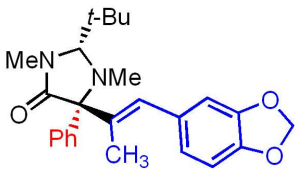
Peak Number	Retention Time	Area Percent	Area
1	12,087	50,894	350121922
2	14,095	49,106	337816582
Totals		100,000	687938504

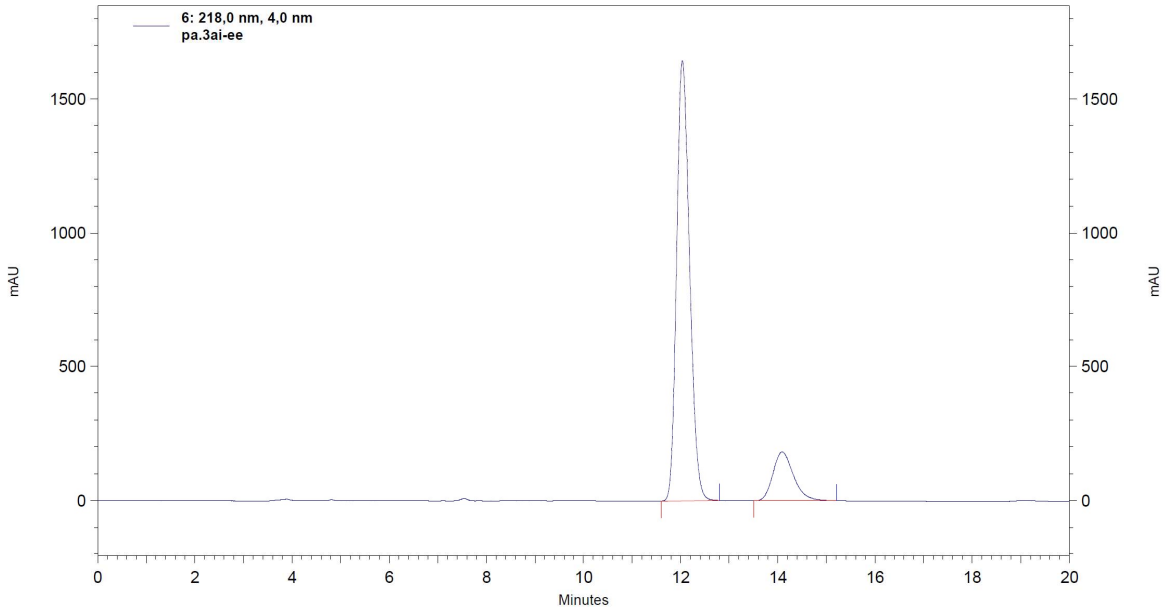
Sample ID: pa.3ai-ee

Method: C:\Enterprise\Methods\HPLC2\5_ChiralPAK AD-3\System2, AD-3, Hep_EtOH 90_10, 0,5ml, 22°C.met

Vial: P1-C2

Injection Volume: 5µL





6: 218,0 nm, 4,0 nm
Results

Peak Number	Retention Time	Area Percent	Area
1	12,035	85,023	4091120000
2	14,088	14,977	720648958
Totals		100,000	4811768958

10. X-ray crystallography of compound 3aa

X-ray and derived ORTEP structures provided by Dr. Daniel Kratzert, Krossing Group, Inorganic Chemistry Department, Albert-Ludwigs-University Freiburg.

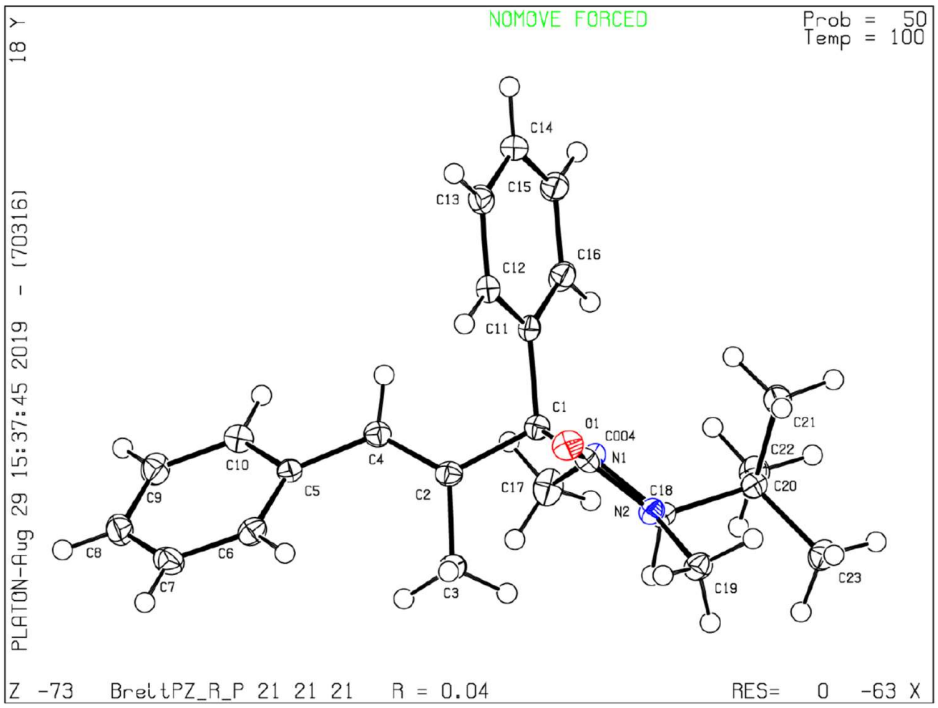


Table 1. Crystal data and structure refinement for BreitPZ_R_122_0m_a-finalcif.cif

CCDC number	1950247
Empirical formula	$C_{24}H_{30}N_2O$
Formula weight	362.50
Temperature [K]	100.0
Crystal system	orthorhombic
Space group (number)	$P2_12_12_1$ (19)
a [Å]	9.1380(11)
b [Å]	13.8136(18)
c [Å]	15.8299(19)

α [Å]	90
β [Å]	90
γ [Å]	90
Volume [Å^3]	1998.2(4)
Z	4
ρ_{calc} [g/cm^3]	1.205
μ [mm^{-1}]	0.073
F(000)	784
Crystal size [mm^3]	0.060×0.050×0.030
Crystal colour	colourless
Crystal shape	block
Radiation	MoK_α (λ=0.71073)
2Θ range [°]	3.91 to 53.61
Index ranges	-11 ≤ h ≤ 11 -17 ≤ k ≤ 17 -20 ≤ l ≤ 20
Reflections collected	53072
Independent reflections	4271 R_{int} = 0.1058 R_{sigma} = 0.0495
Completeness to θ = 25.242°	100.00
Data / Restraints / Parameters	4271/0/250
Goodness-of-fit on F^2	1.058
Final *R* indexes	R_1 = 0.0431

[$I \geq 2\sigma(I)$]	wR_2 = 0.0843
Final R indexes [all data]	R_1 = 0.0609 wR_2 = 0.0917
Largest peak/hole [eÅ^3]	0.17/-0.22
Flack X parameter	not applicable

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for BreitPZ_R_122_0m_a-finalcif.cif. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	***x***	***y***	***z***	U_{eq}
O1	0.5124(2)	0.85334(12)	0.41435(11)	0.0204(4)
N1	0.3887(2)	0.62361(15)	0.34405(12)	0.0162(5)
C1	0.4460(3)	0.71970(18)	0.31825(15)	0.0152(5)
N2	0.3975(2)	0.71742(15)	0.46348(12)	0.0162(5)
C2	0.3331(3)	0.77670(18)	0.26566(15)	0.0166(5)
C3	0.2042(3)	0.8138(2)	0.31513(16)	0.0220(6)
H3A	0.119768	0.820921	0.277448	0.033
H3B	0.228520	0.876858	0.339870	0.033
H3C	0.180320	0.767966	0.360292	0.033
C004	0.4600(3)	0.77257(18)	0.40347(16)	0.0166(6)
C4	0.3457(3)	0.78406(18)	0.18152(15)	0.0169(5)
H4	0.431934	0.757006	0.157766	0.020
C5	0.2426(3)	0.82885(18)	0.12077(15)	0.0157(5)
C9	0.1402(3)	0.82717(19)	-0.02071(16)	0.0231(6)
H9	0.132705	0.797399	-0.074633	0.028

C8	0.0583(3)	0.9090(2)	-0.00294(17)	0.0257(6)
H8	-0.004262	0.936103	-0.044605	0.031
C7	0.0688(3)	0.9508(2)	0.07631(17)	0.0241(6)
H7	0.012957	1.006941	0.088968	0.029
C6	0.1598(3)	0.91162(18)	0.13734(16)	0.0190(6)
H6	0.165938	0.941515	0.191271	0.023
C10	0.2332(3)	0.78838(19)	0.03975(15)	0.0200(6)
H10	0.291413	0.733596	0.026026	0.024
C11	0.5959(3)	0.71192(19)	0.27506(14)	0.0166(5)
C12	0.6731(3)	0.79632(19)	0.25633(14)	0.0177(5)
H12	0.631321	0.857496	0.269352	0.021
C13	0.8105(3)	0.7920(2)	0.21886(16)	0.0215(6)
H13	0.862702	0.850018	0.207405	0.026
C14	0.8717(3)	0.7030(2)	0.19809(15)	0.0238(6)
H14	0.965287	0.699770	0.172081	0.029
C15	0.7947(3)	0.6193(2)	0.21575(17)	0.0248(6)
H15	0.835875	0.558299	0.201539	0.030
C16	0.6578(3)	0.62321(19)	0.25407(15)	0.0208(6)
H16	0.606385	0.564995	0.265928	0.025
C17	0.2818(3)	0.5794(2)	0.28746(17)	0.0249(6)
H17A	0.257962	0.514201	0.307606	0.037
H17B	0.322752	0.575434	0.230364	0.037
H17C	0.192708	0.618937	0.286434	0.037

C18	0.3490(3)	0.62224(17)	0.43447(14)	0.0159(5)
H18	0.240195	0.617566	0.440090	0.019
C19	0.3658(3)	0.75702(19)	0.54704(15)	0.0204(6)
H19A	0.270980	0.732574	0.566643	0.031
H19B	0.362495	0.827836	0.543856	0.031
H19C	0.442492	0.737211	0.586681	0.031
C20	0.4217(3)	0.53753(18)	0.48371(15)	0.0181(6)
C21	0.5872(3)	0.55282(19)	0.48789(16)	0.0205(6)
H21A	0.633088	0.496952	0.515374	0.031
H21B	0.608511	0.611511	0.520440	0.031
H21C	0.626251	0.559816	0.430548	0.031
C22	0.3916(3)	0.44183(19)	0.43823(17)	0.0240(6)
H22A	0.436097	0.388519	0.469997	0.036
H22B	0.433792	0.444170	0.381339	0.036
H22C	0.285756	0.431522	0.434215	0.036
C23	0.3579(3)	0.5288(2)	0.57344(16)	0.0249(6)
H23A	0.387122	0.466641	0.598125	0.037
H23B	0.250889	0.532325	0.570731	0.037
H23C	0.395082	0.581753	0.608568	0.037

Table 3. Bond lengths and angles for BreitPZ_R_122_0m_a-finalcif.cif.

Atom - Atom	**Length [Å]**
O1 - C004	1.226(3)

N1 - C17	1.460(3)
N1 - C18	1.477(3)
N1 - C1	1.484(3)
C1 - C11	1.535(3)
C1 - C004	1.539(3)
C1 - C2	1.542(3)
N2 - C004	1.345(3)
N2 - C19	1.460(3)
N2 - C18	1.462(3)
C2 - C4	1.341(3)
C2 - C3	1.505(3)
C3 - H3A	0.9800
C3 - H3B	0.9800
C3 - H3C	0.9800
C4 - C5	1.481(3)
C4 - H4	0.9500
C5 - C6	1.396(3)
C5 - C10	1.402(3)
C9 - C8	1.384(4)
C9 - C10	1.388(4)
C9 - H9	0.9500
C8 - C7	1.384(4)
C8 - H8	0.9500

C7 - C6	1.385(4)
C7 - H7	0.9500
C6 - H6	0.9500
C10 - H10	0.9500
C11 - C16	1.390(4)
C11 - C12	1.395(4)
C12 - C13	1.390(3)
C12 - H12	0.9500
C13 - C14	1.390(4)
C13 - H13	0.9500
C14 - C15	1.382(4)
C14 - H14	0.9500
C15 - C16	1.392(4)
C15 - H15	0.9500
C16 - H16	0.9500
C17 - H17A	0.9800
C17 - H17B	0.9800
C17 - H17C	0.9800
C18 - C20	1.555(3)
C18 - H18	1.0000
C19 - H19A	0.9800
C19 - H19B	0.9800
C19 - H19C	0.9800

C20 - C21	1.529(3)
C20 - C22	1.530(4)
C20 - C23	1.540(3)
C21 - H21A	0.9800
C21 - H21B	0.9800
C21 - H21C	0.9800
C22 - H22A	0.9800
C22 - H22B	0.9800
C22 - H22C	0.9800
C23 - H23A	0.9800
C23 - H23B	0.9800
C23 - H23C	0.9800
Atom - Atom - Atom	**Angle [°]**
C17 - N1 - C18	115.1(2)
C17 - N1 - C1	116.18(19)
C18 - N1 - C1	111.40(19)
N1 - C1 - C11	112.0(2)
N1 - C1 - C004	102.27(18)
C11 - C1 - C004	110.42(19)
N1 - C1 - C2	111.70(19)
C11 - C1 - C2	113.11(19)
C004 - C1 - C2	106.67(19)

C004 - N2 - C19	120.8(2)
C004 - N2 - C18	114.61(19)
C19 - N2 - C18	124.1(2)
C4 - C2 - C3	124.0(2)
C4 - C2 - C1	121.2(2)
C3 - C2 - C1	114.6(2)
C2 - C3 - H3A	109.5
C2 - C3 - H3B	109.5
H3A - C3 - H3B	109.5
C2 - C3 - H3C	109.5
H3A - C3 - H3C	109.5
H3B - C3 - H3C	109.5
O1 - C004 - N2	125.6(2)
O1 - C004 - C1	126.0(2)
N2 - C004 - C1	108.3(2)
C2 - C4 - C5	128.5(2)
C2 - C4 - H4	115.8
C5 - C4 - H4	115.8
C6 - C5 - C10	117.7(2)
C6 - C5 - C4	124.4(2)
C10 - C5 - C4	117.8(2)
C8 - C9 - C10	120.4(3)
C8 - C9 - H9	119.8

C10 - C9 - H9	119.8
C9 - C8 - C7	119.2(3)
C9 - C8 - H8	120.4
C7 - C8 - H8	120.4
C8 - C7 - C6	120.7(3)
C8 - C7 - H7	119.6
C6 - C7 - H7	119.6
C7 - C6 - C5	121.0(2)
C7 - C6 - H6	119.5
C5 - C6 - H6	119.5
C9 - C10 - C5	121.0(2)
C9 - C10 - H10	119.5
C5 - C10 - H10	119.5
C16 - C11 - C12	118.7(2)
C16 - C11 - C1	122.1(2)
C12 - C11 - C1	119.2(2)
C13 - C12 - C11	120.8(2)
C13 - C12 - H12	119.6
C11 - C12 - H12	119.6
C12 - C13 - C14	120.2(2)
C12 - C13 - H13	119.9
C14 - C13 - H13	119.9
C15 - C14 - C13	119.2(2)

C15 - C14 - H14	120.4
C13 - C14 - H14	120.4
C14 - C15 - C16	120.9(3)
C14 - C15 - H15	119.5
C16 - C15 - H15	119.5
C11 - C16 - C15	120.3(2)
C11 - C16 - H16	119.9
C15 - C16 - H16	119.9
N1 - C17 - H17A	109.5
N1 - C17 - H17B	109.5
H17A - C17 - H17B	109.5
N1 - C17 - H17C	109.5
H17A - C17 - H17C	109.5
H17B - C17 - H17C	109.5
N2 - C18 - N1	102.60(18)
N2 - C18 - C20	112.94(19)
N1 - C18 - C20	113.0(2)
N2 - C18 - H18	109.4
N1 - C18 - H18	109.4
C20 - C18 - H18	109.4
N2 - C19 - H19A	109.5
N2 - C19 - H19B	109.5
H19A - C19 - H19B	109.5

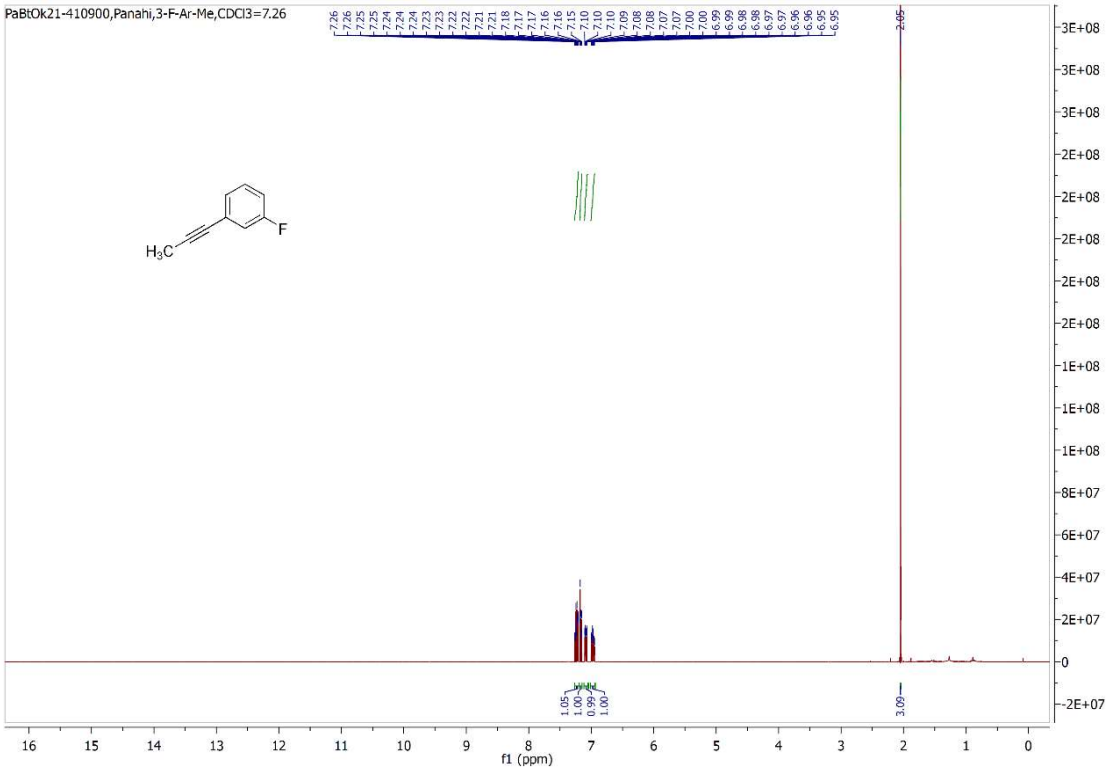
N2 - C19 - H19C	109.5
H19A - C19 - H19C	109.5
H19B - C19 - H19C	109.5
C21 - C20 - C22	108.5(2)
C21 - C20 - C23	110.2(2)
C22 - C20 - C23	107.3(2)
C21 - C20 - C18	109.9(2)
C22 - C20 - C18	109.7(2)
C23 - C20 - C18	111.1(2)
C20 - C21 - H21A	109.5
C20 - C21 - H21B	109.5
H21A - C21 - H21B	109.5
C20 - C21 - H21C	109.5
H21A - C21 - H21C	109.5
H21B - C21 - H21C	109.5
C20 - C22 - H22A	109.5
C20 - C22 - H22B	109.5
H22A - C22 - H22B	109.5
C20 - C22 - H22C	109.5
H22A - C22 - H22C	109.5
H22B - C22 - H22C	109.5
C20 - C23 - H23A	109.5
C20 - C23 - H23B	109.5

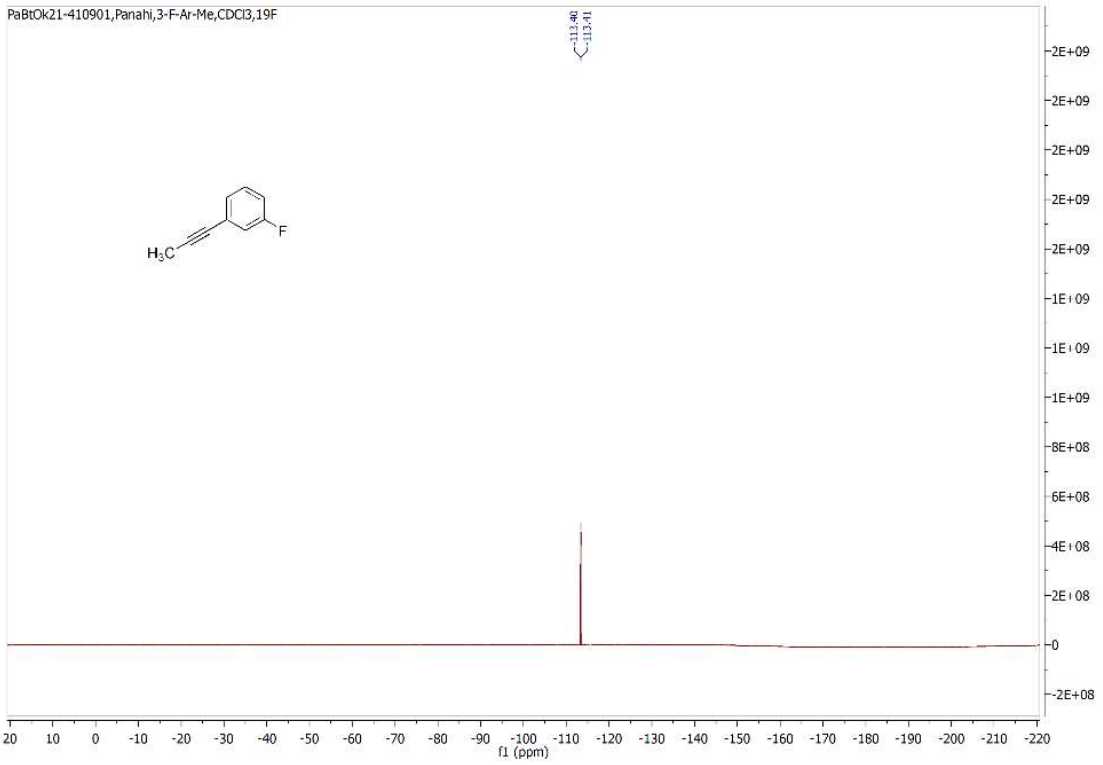
H23A - C23 - H23B	109.5
C20 - C23 - H23C	109.5
H23A - C23 - H23C	109.5
H23B - C23 - H23C	109.5

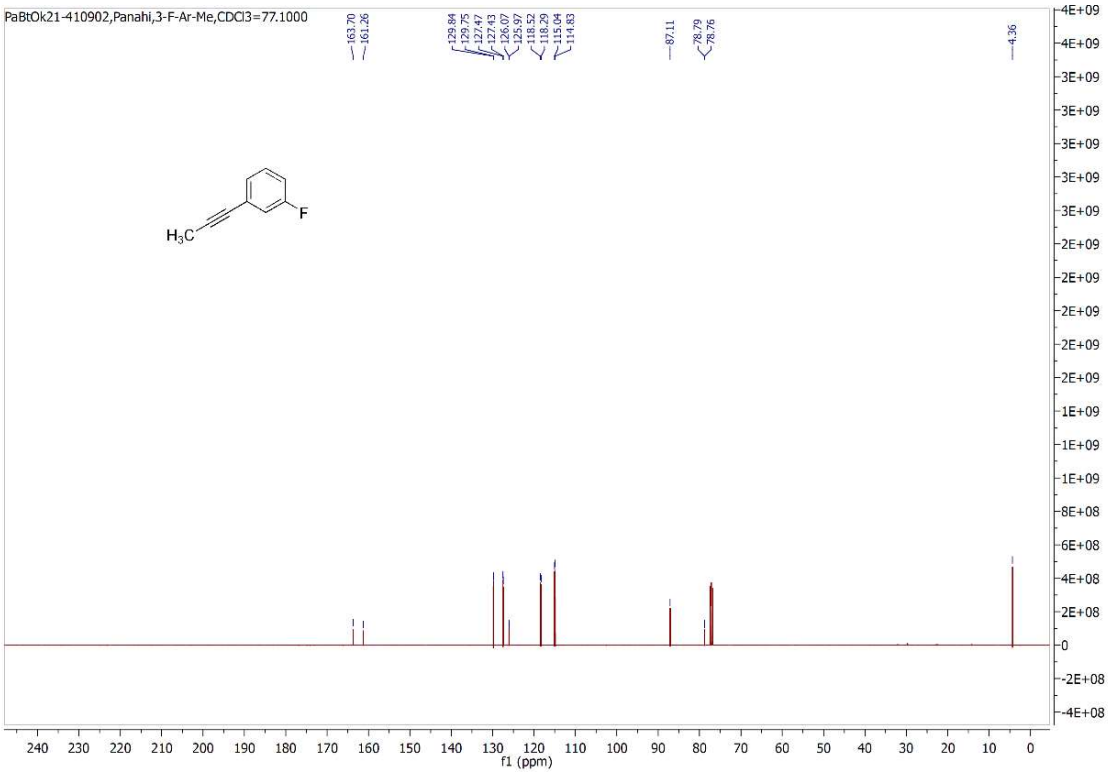
11. Copy of ^{1}HNMR and ^{13}CNMR of synthesized compounds

11.1.Aryl-methyl alkynes derivative

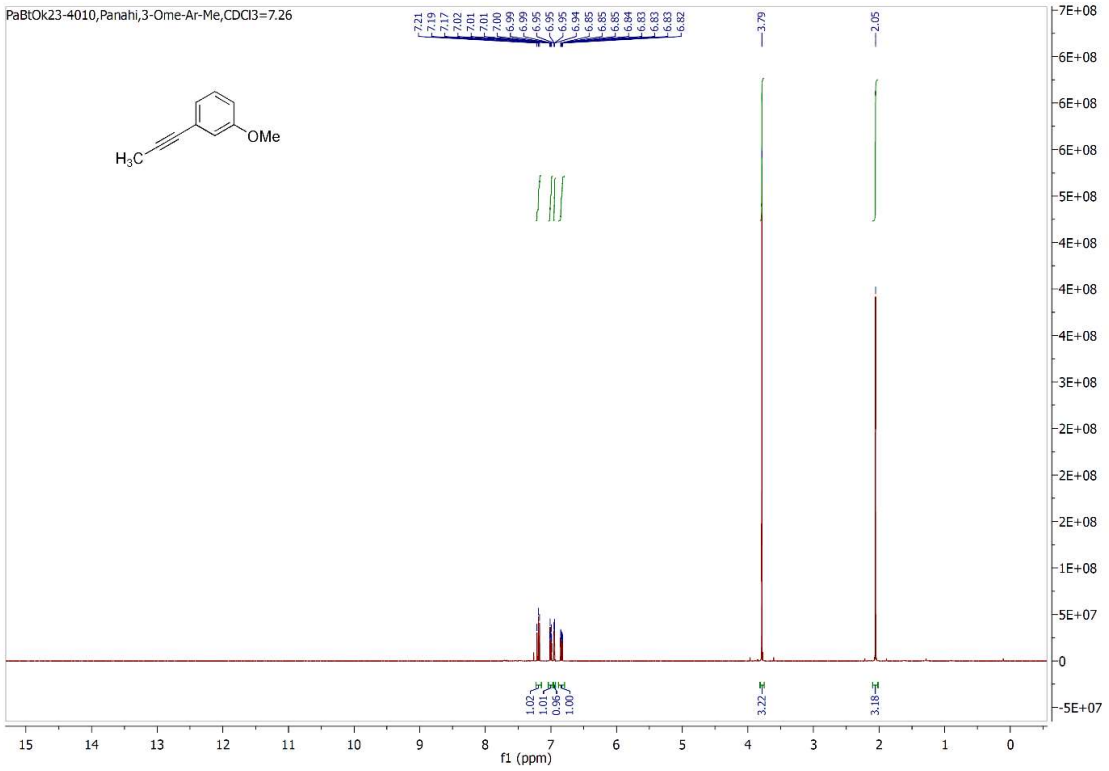
11.1.1. 1-Fluoro-3-(prop-1-yn-1-yl)benzene (2b)

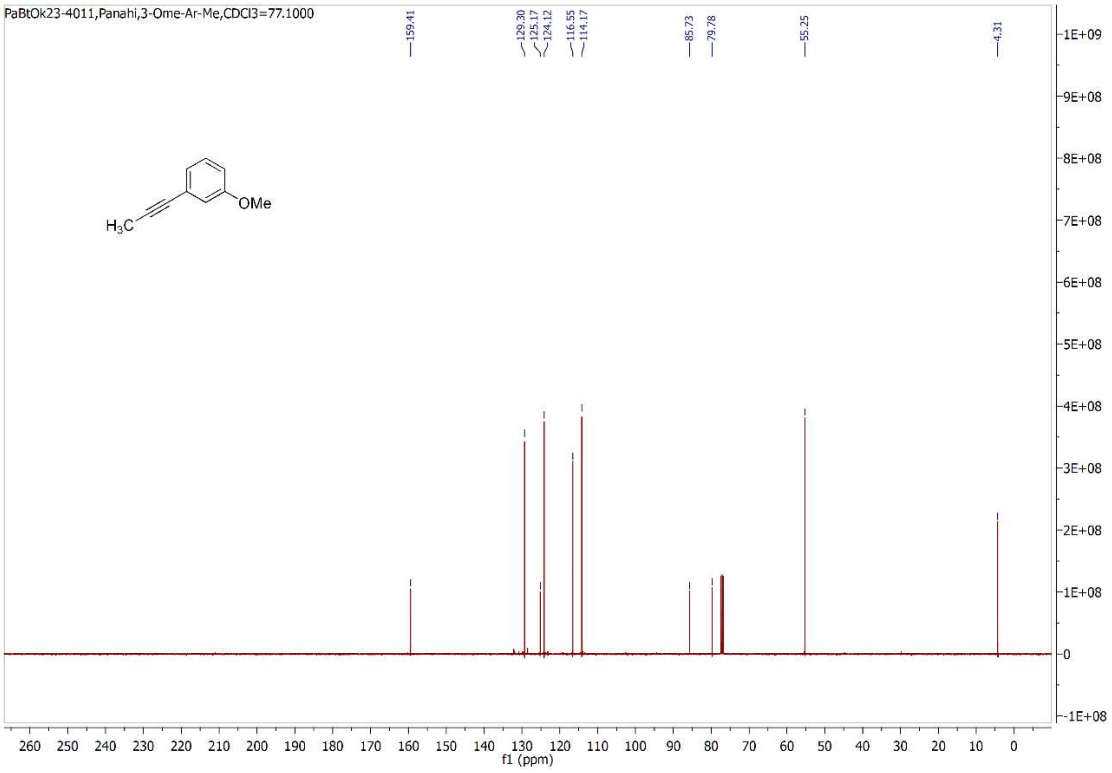



PaBtOk21-410901,Panahi,3-F-Ar-Me,CDCl3,19F
-113.40
-113.41
F
H3C
f1 (ppm)

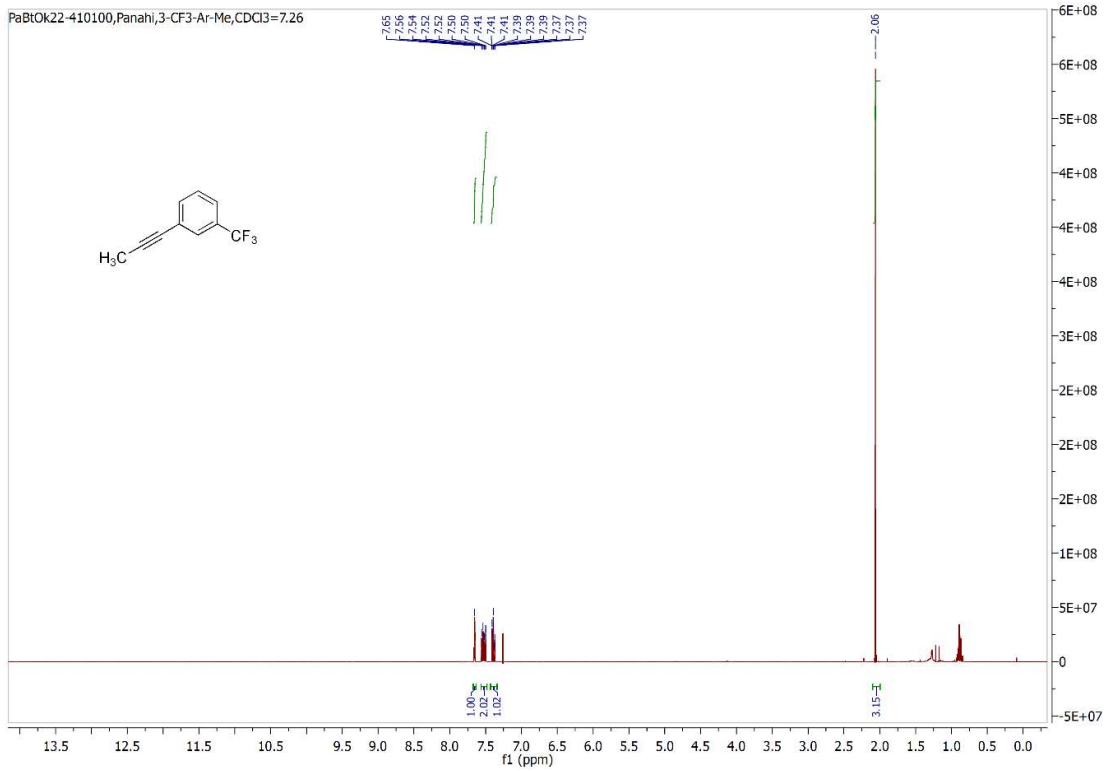

PaBtOk21-410902,Panahi,3-F-Ar-Me,CDCl3=77.1000
163.70
161.26
129.84
129.75
127.47
127.43
126.07
125.97
118.53
118.20
115.04
114.83
87.11
78.79
78.76
4.36
F
H3C
f1 (ppm)

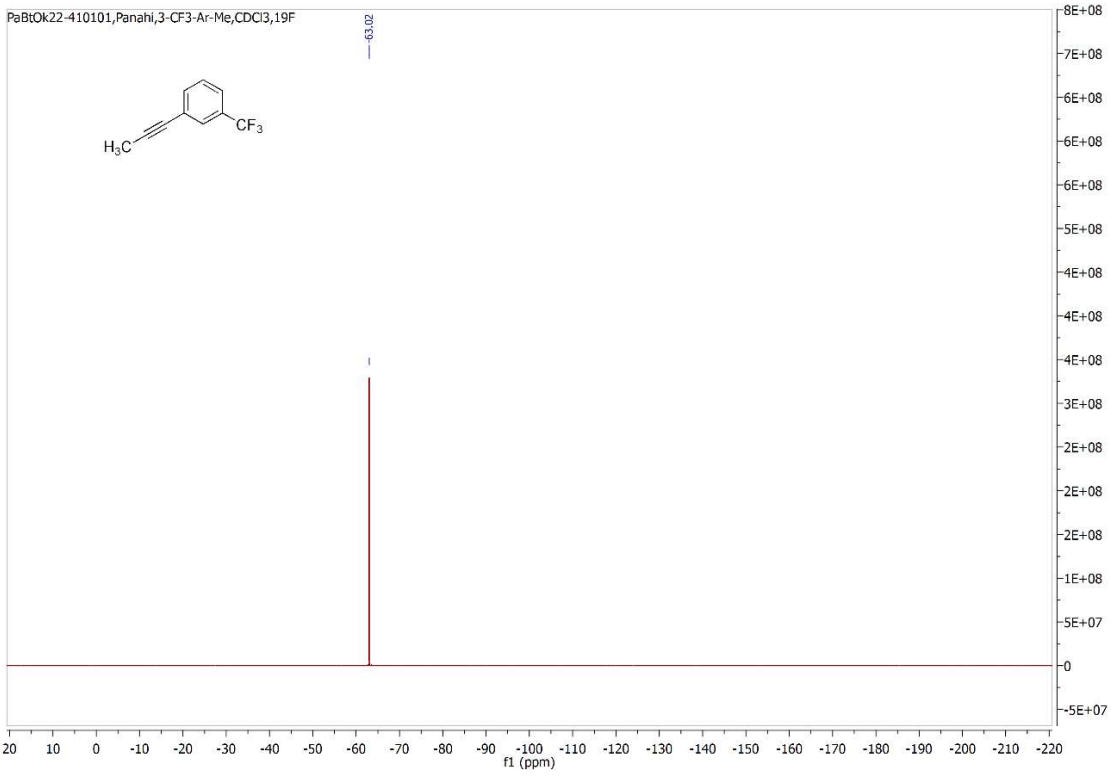
11.1.2. 1-Methoxy-3-(prop-1-yn-1-yl)benzene (2d)

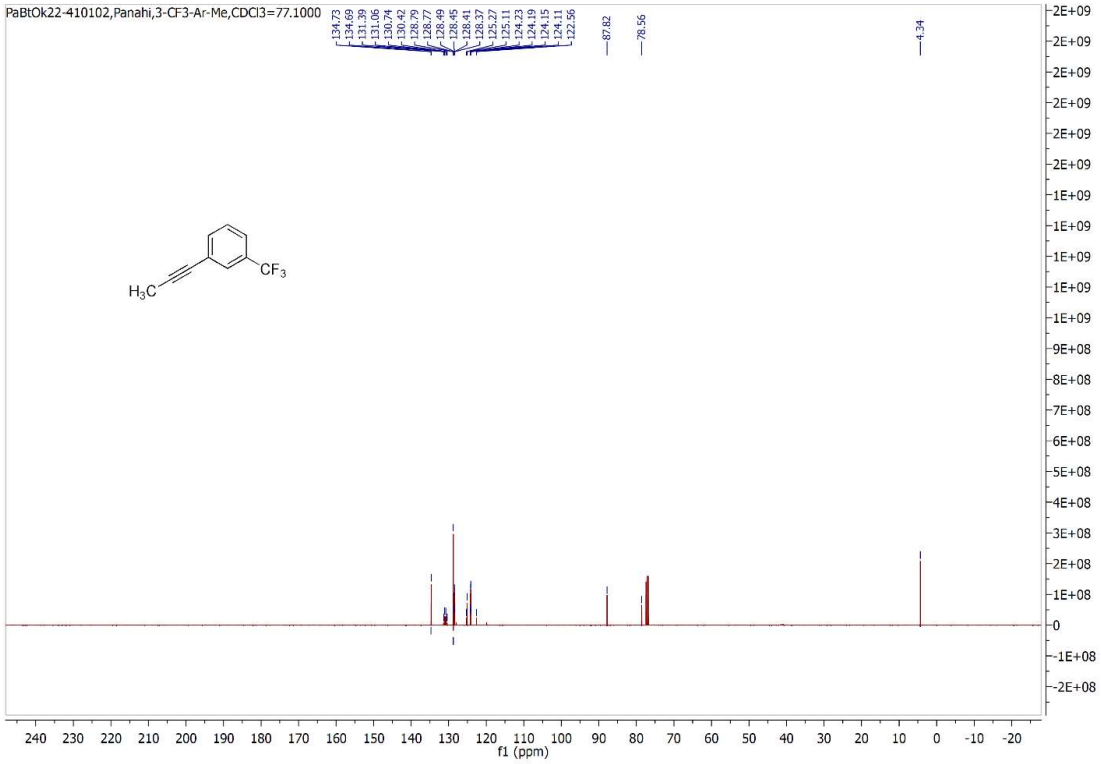




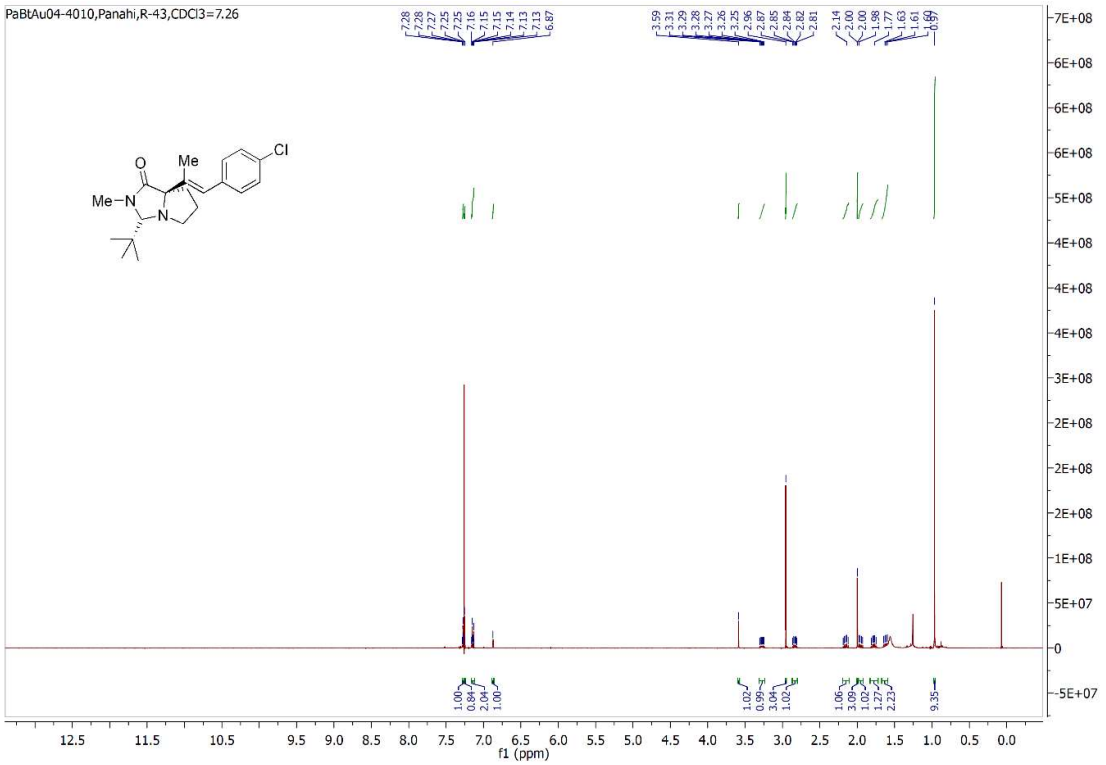
11.1.3.1-(Prop-1-yn-1-yl)-3-(trifluoromethyl)benzene (2e)

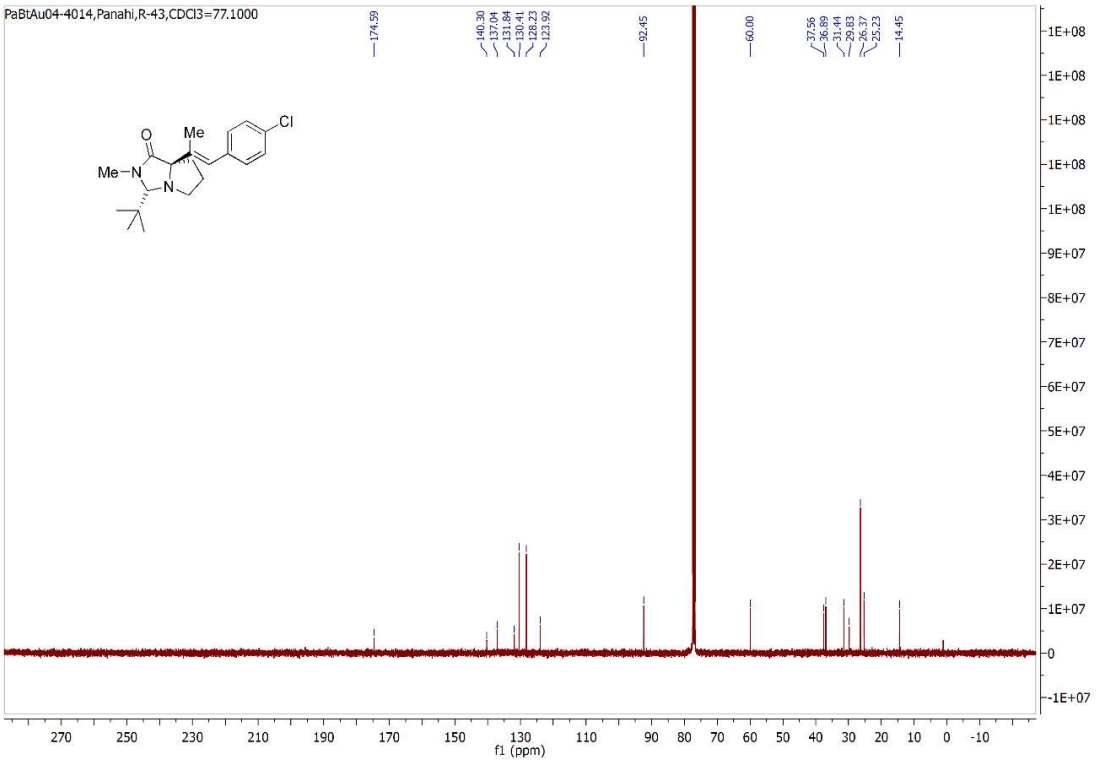




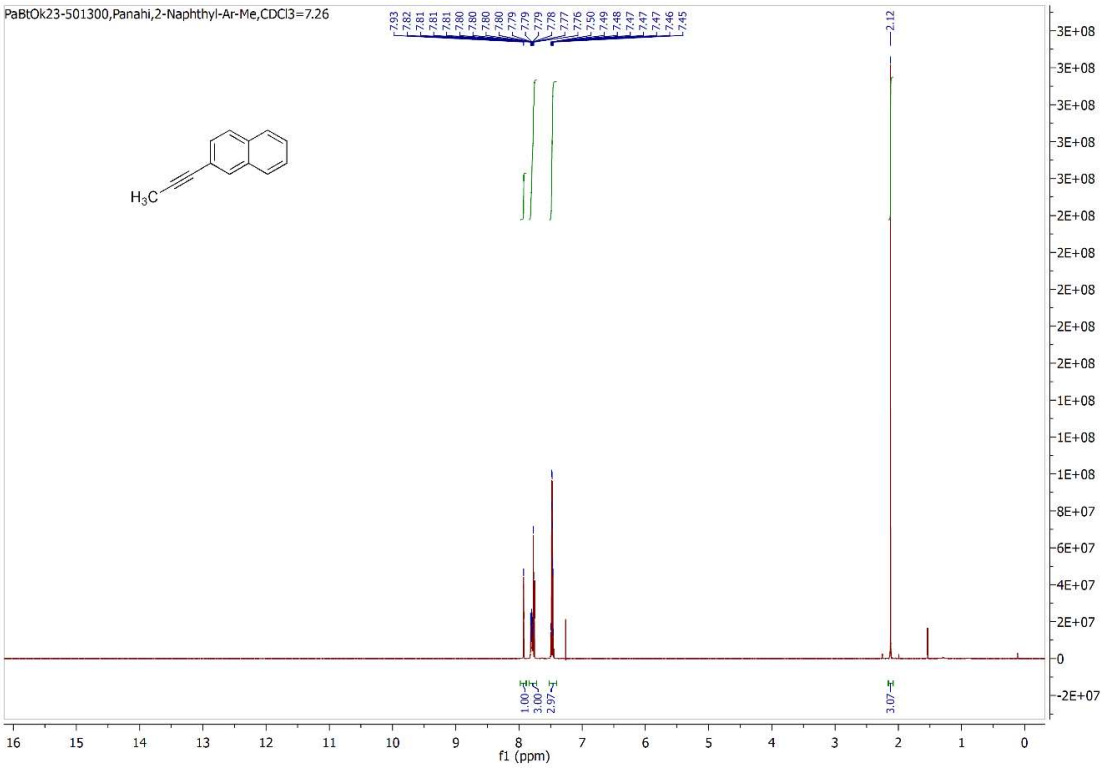


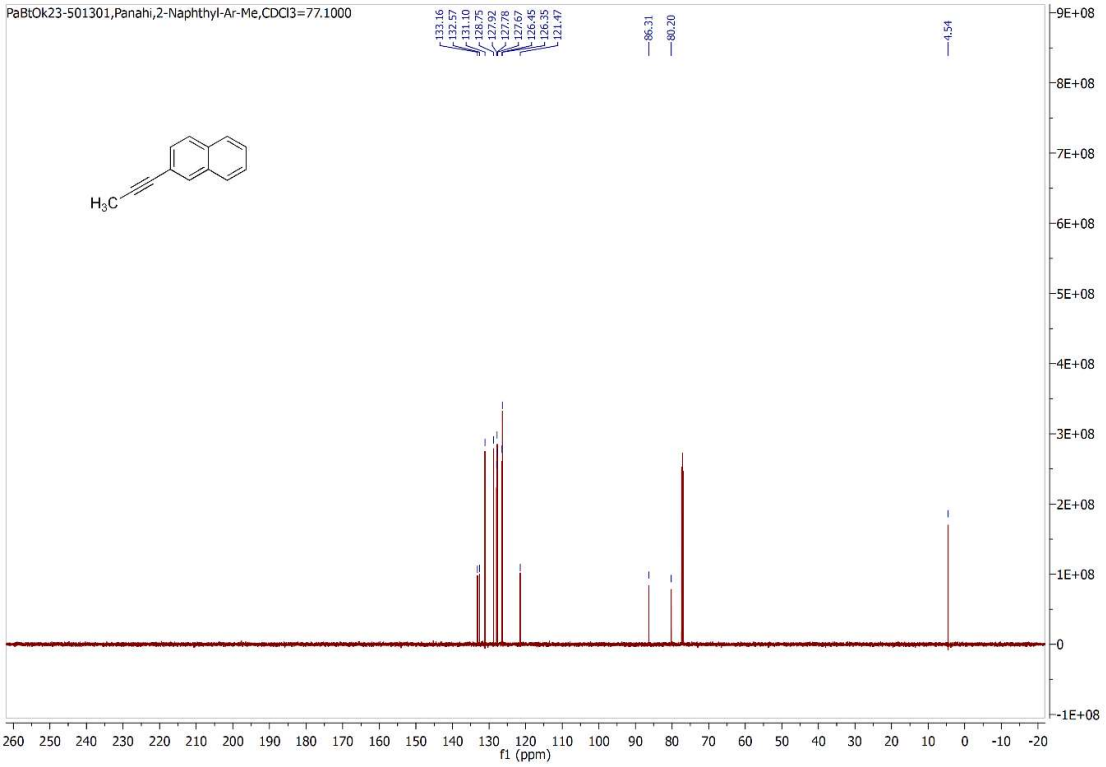
11.1.4. 1-Chloro-4-(prop-1-yn-1-yl)benzene (2g)



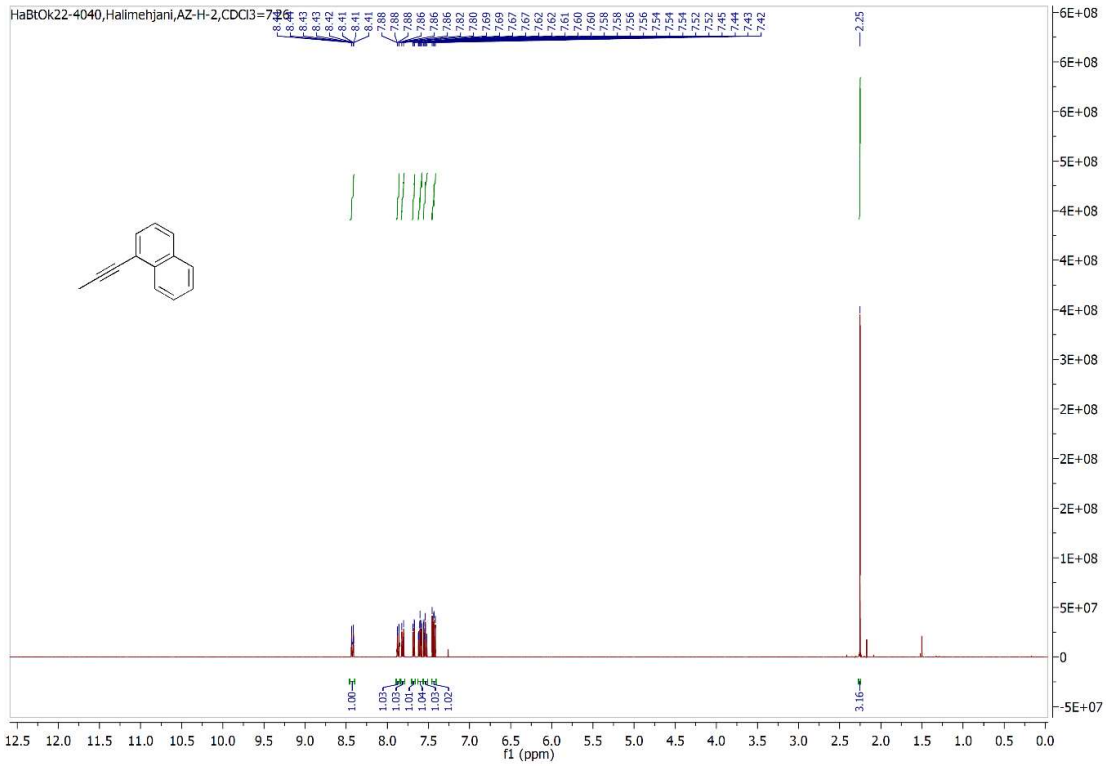


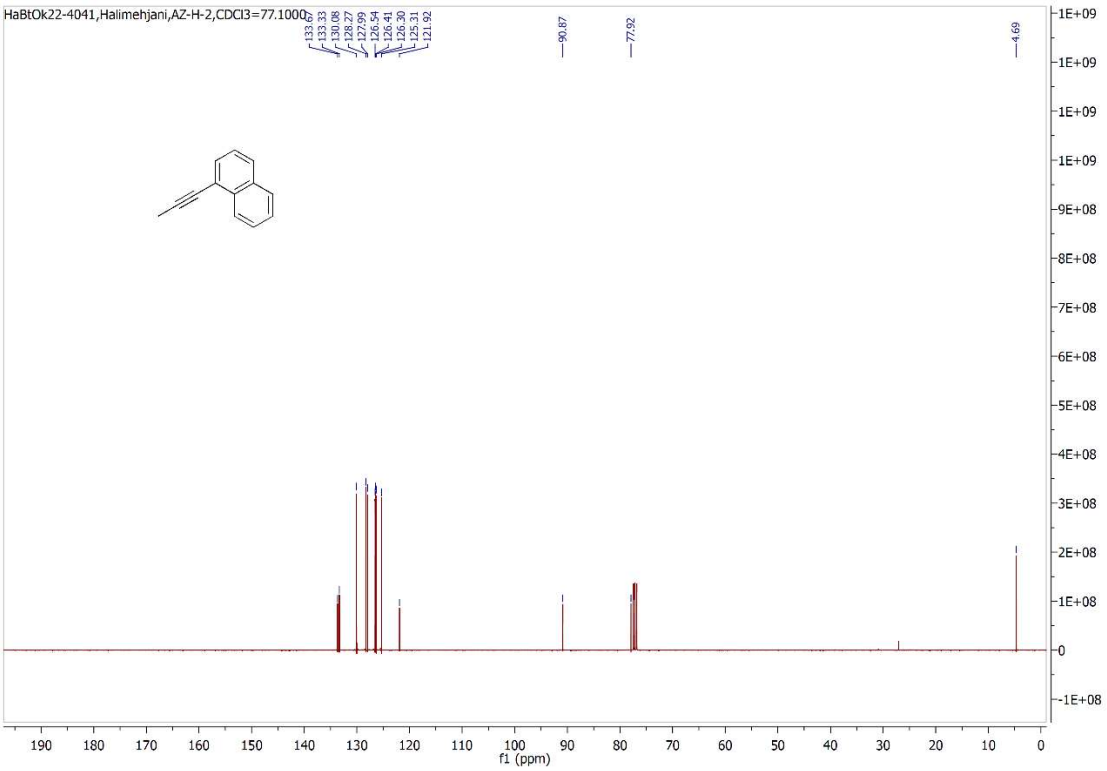
11.1.5.2-(Prop-1-yn-1-yl)naphthalene (2h)



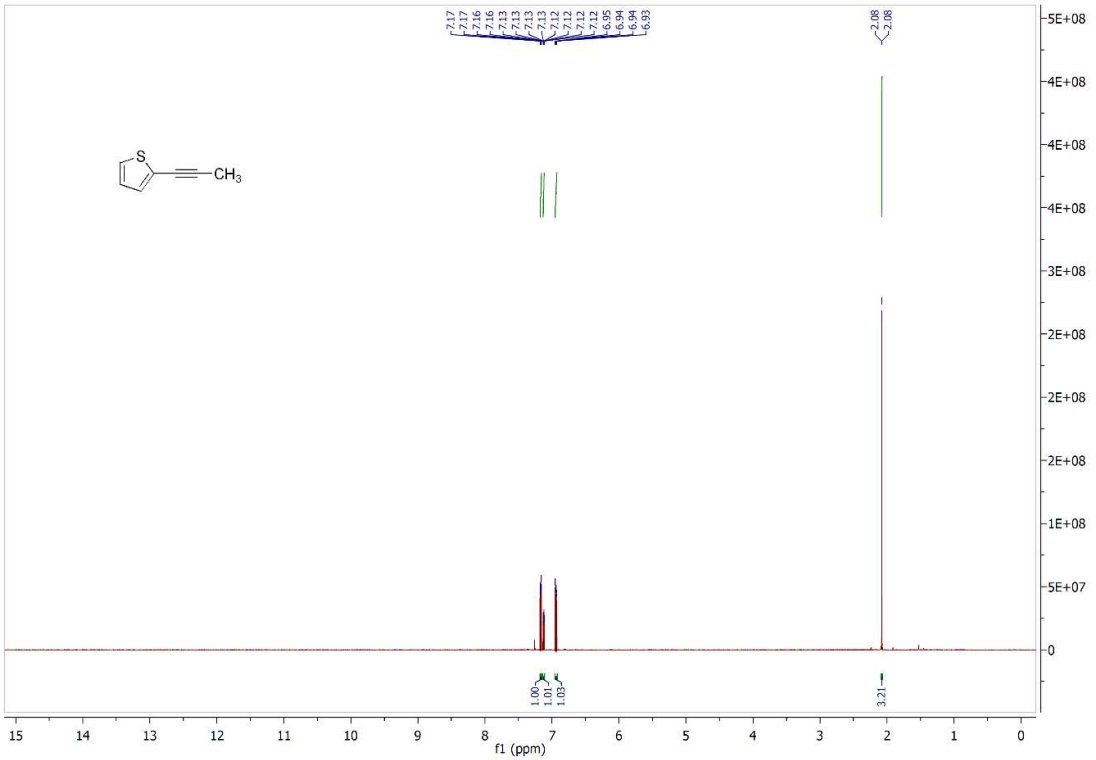


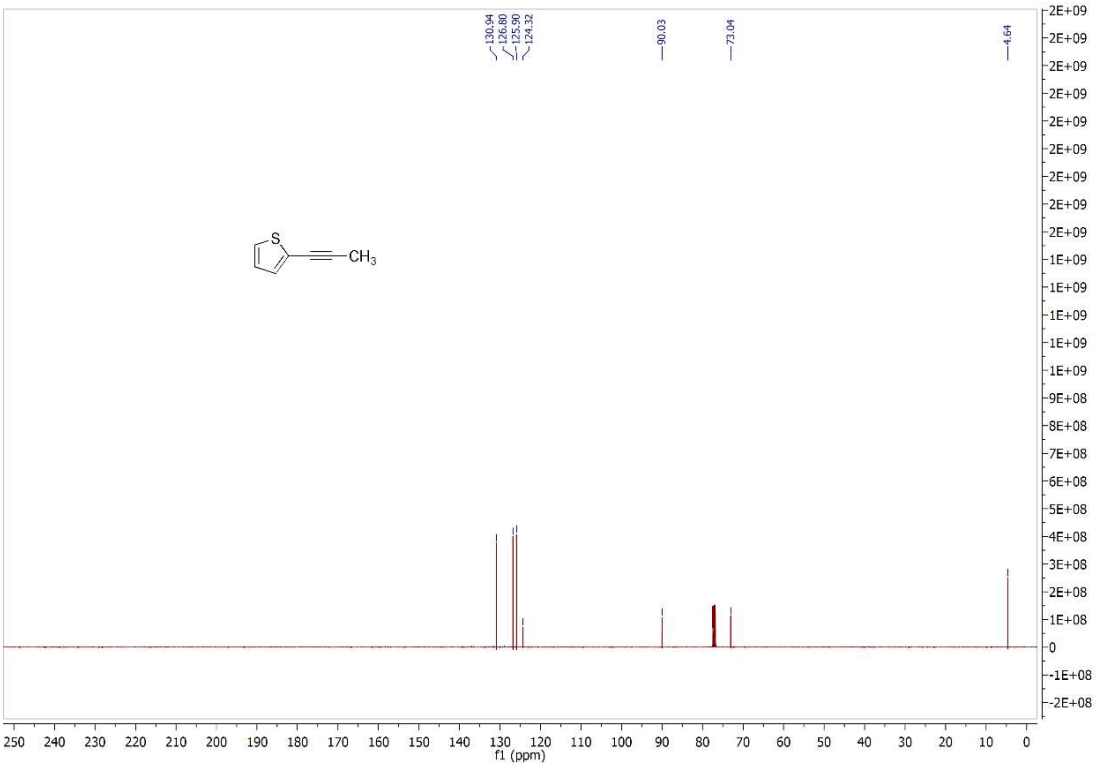
11.1.6.1-(Prop-1-yn-1-yl)naphthalene (2i)



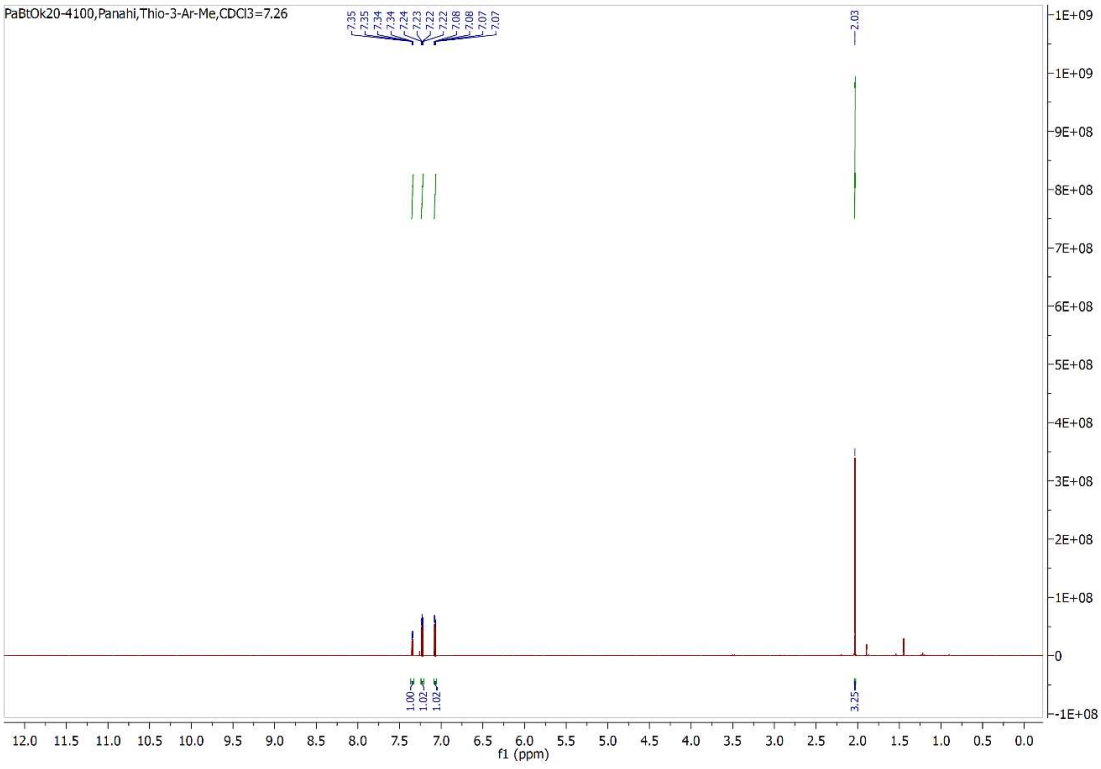


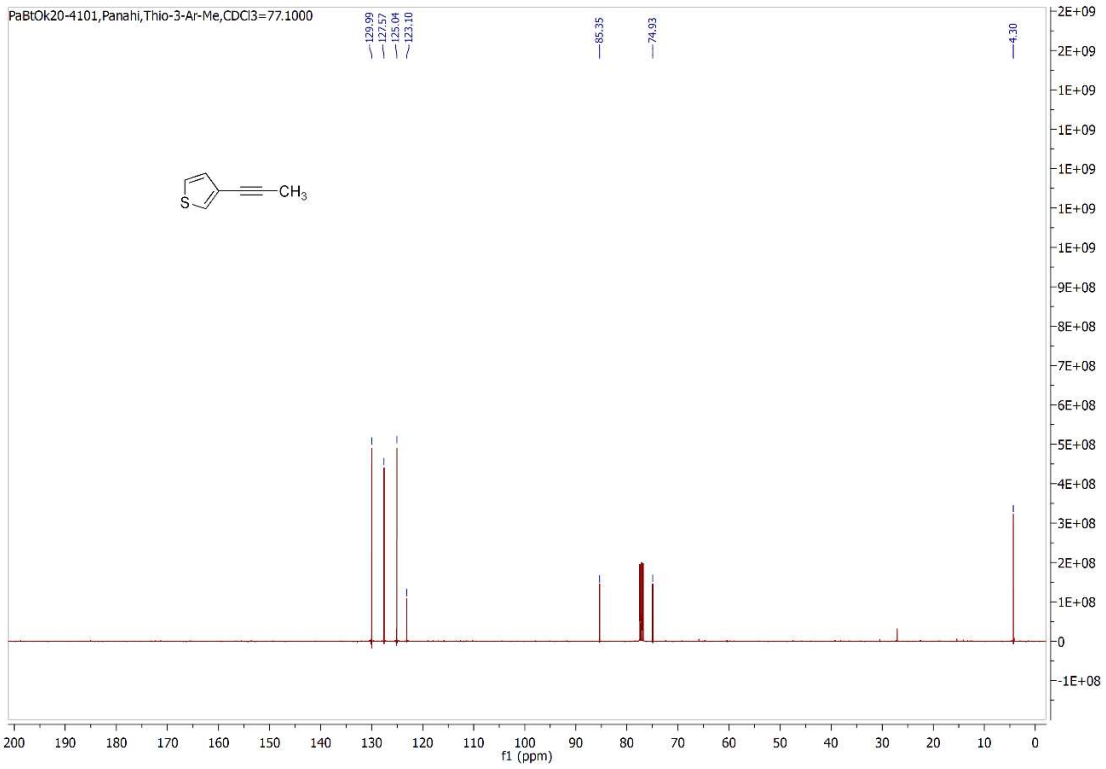
11.1.7. 2-(Prop-1-yn-1-yl)thiophene (2j)



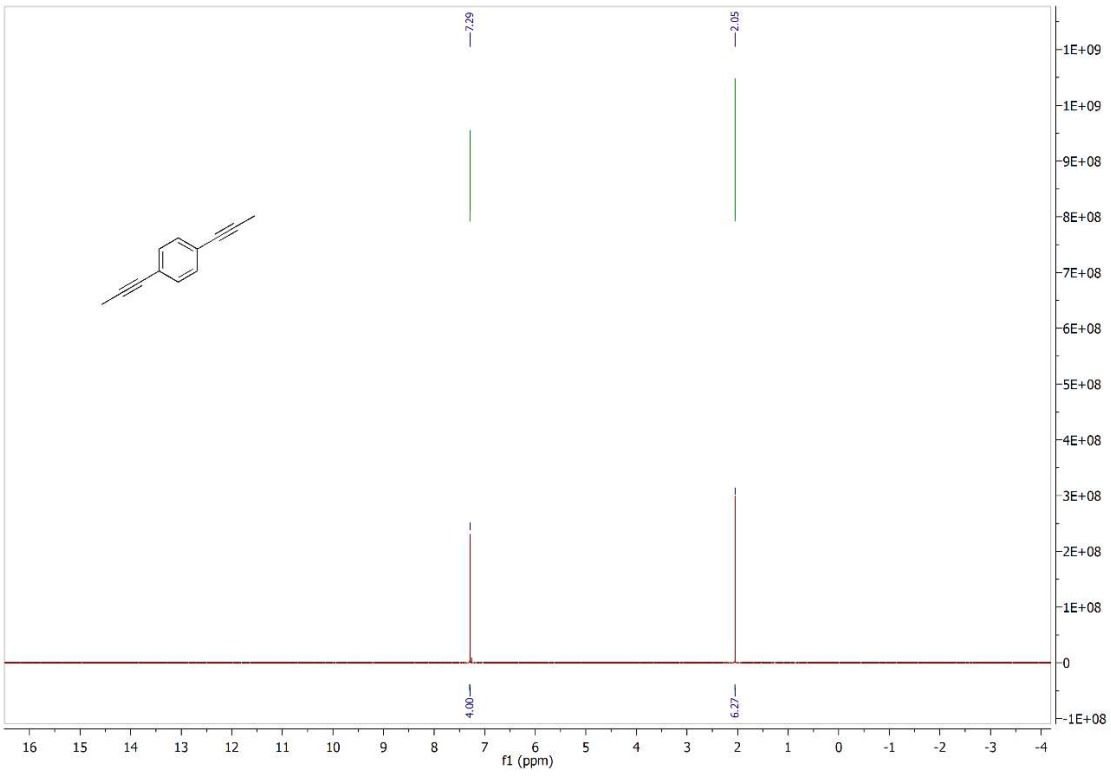


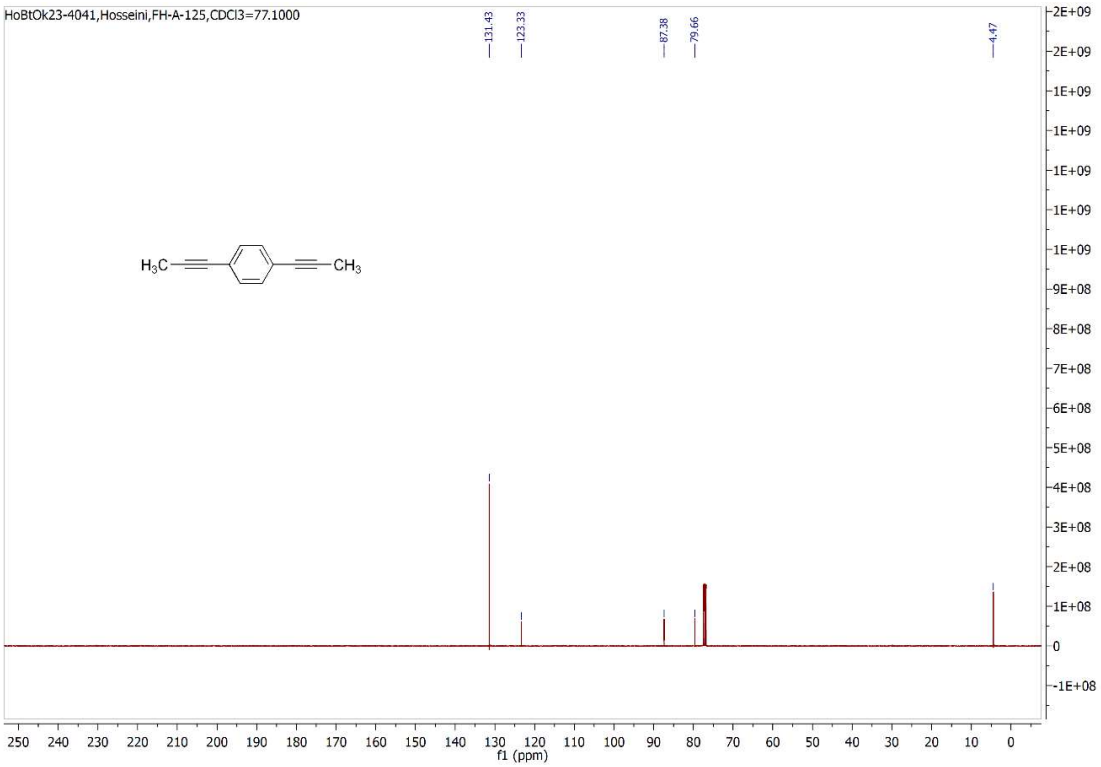
11.1.8. 3-(Prop-1-yn-1-yl)thiophene (2k)



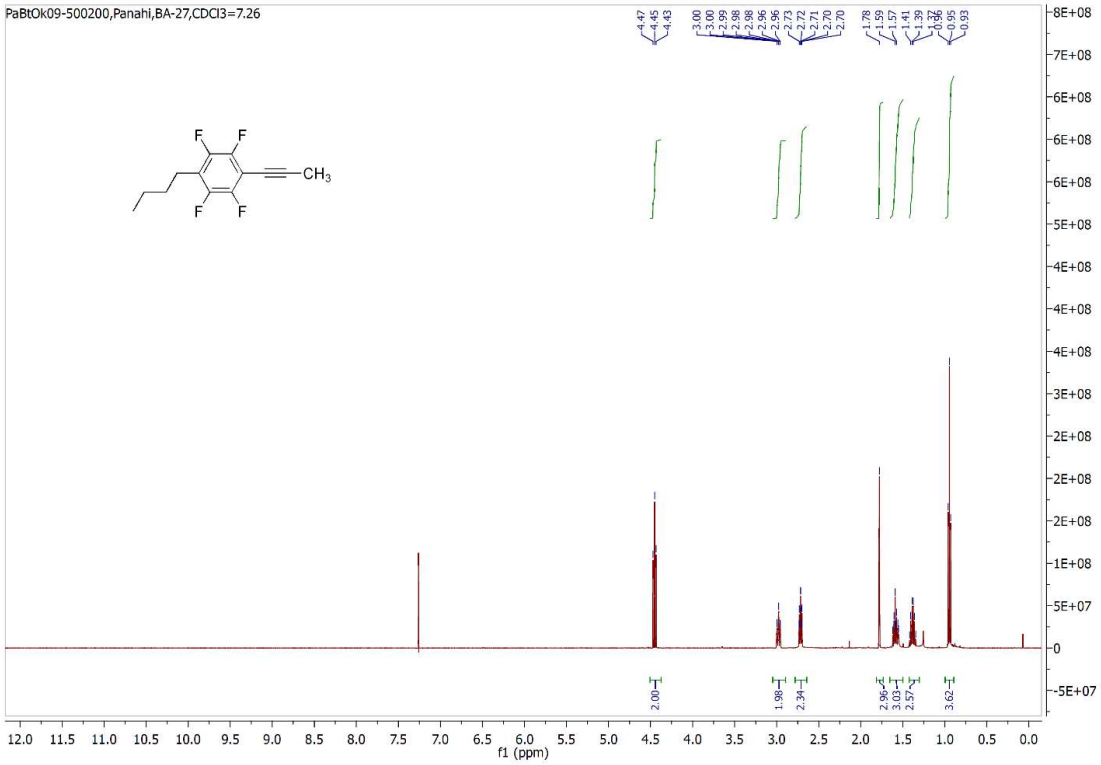


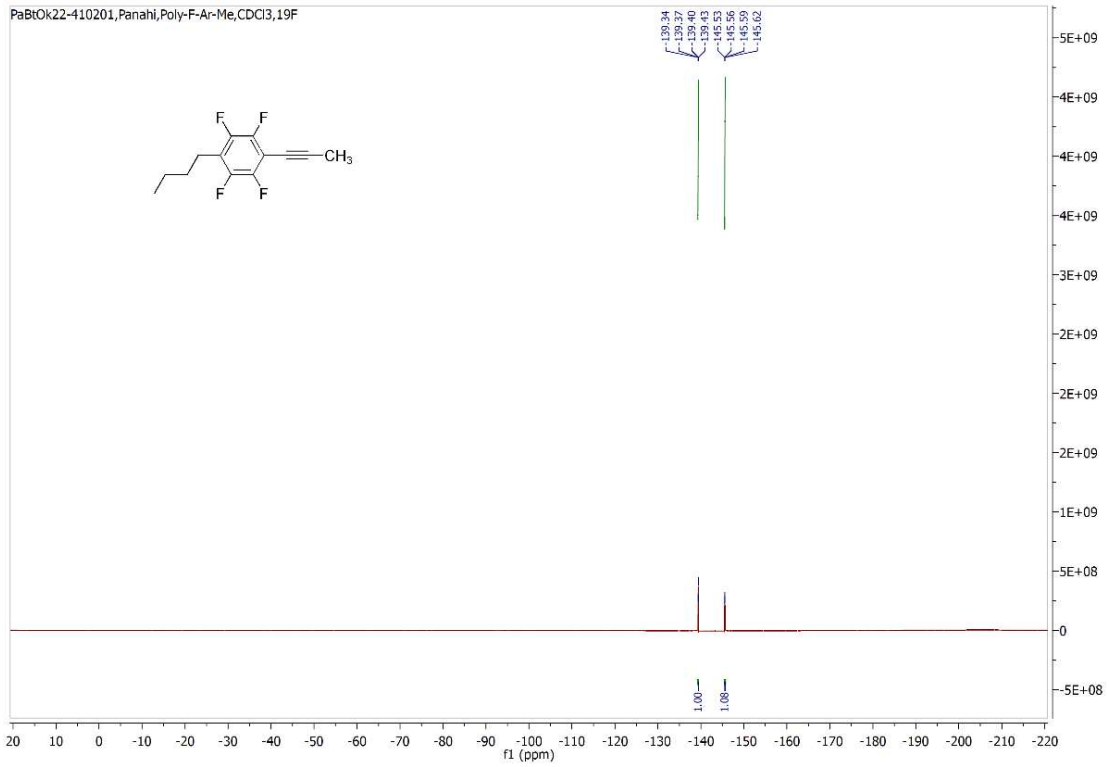
11.1.9. 1,4-Di(prop-1-yn-1-yl)benzene (2l)

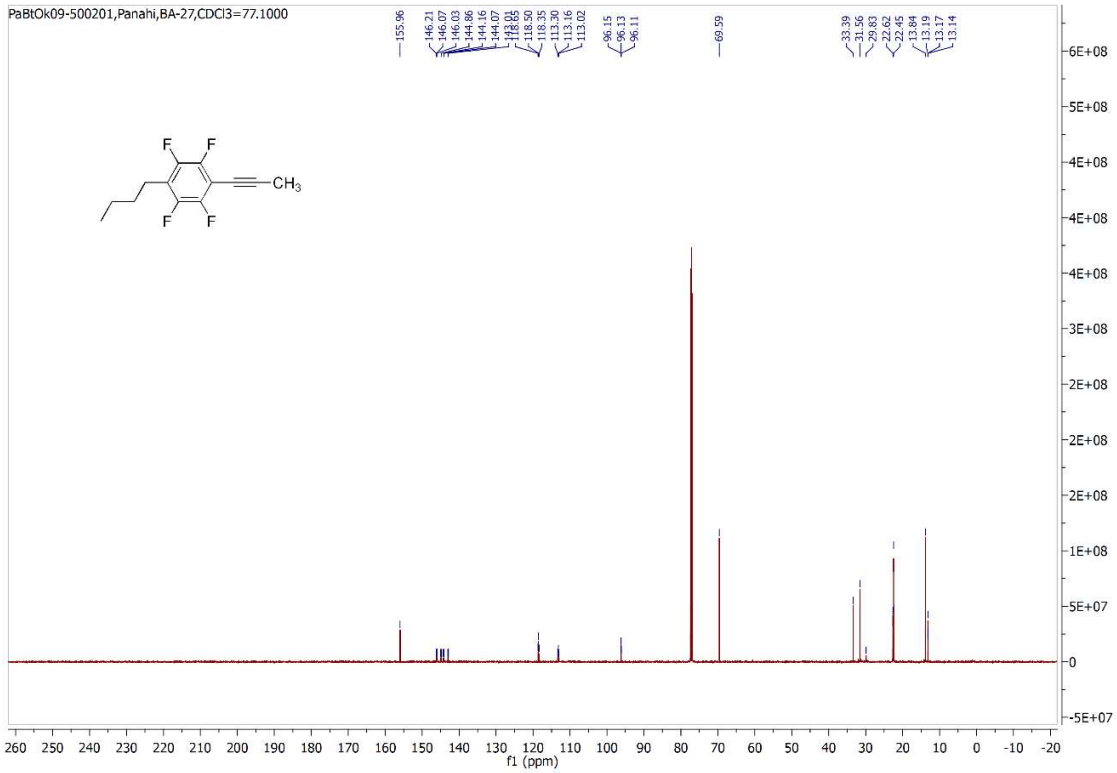




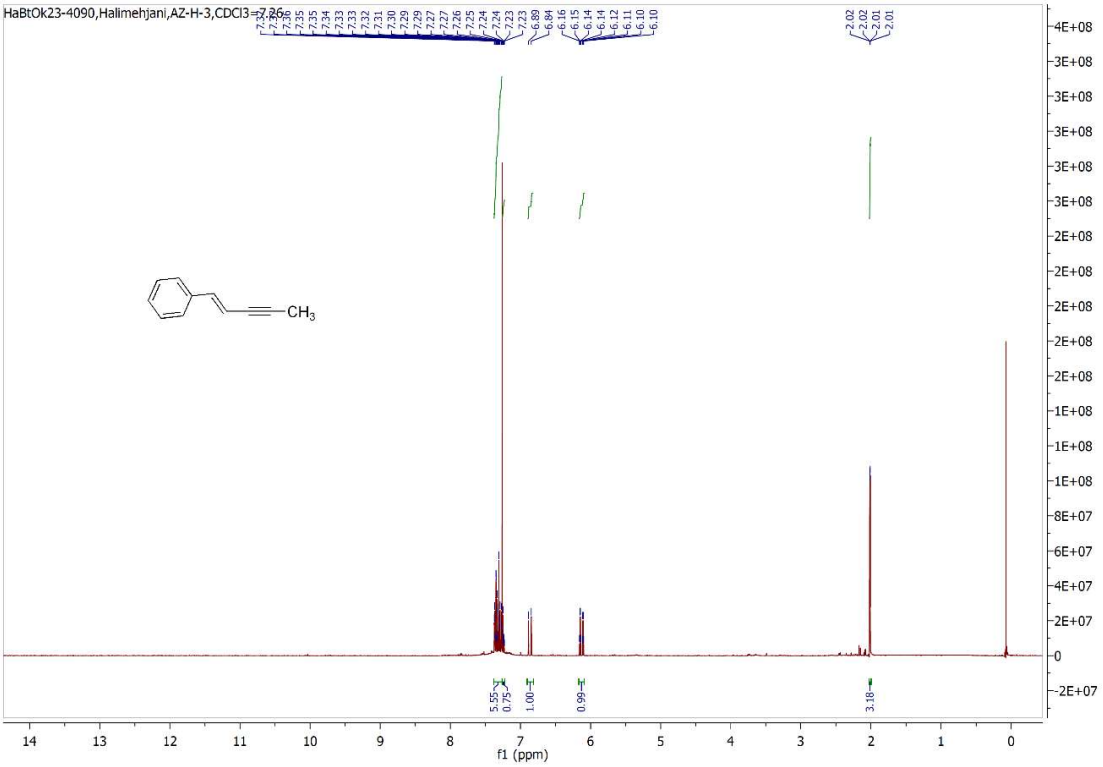
11.1.10. 1-Butyl-2,3,5,6-tetrafluoro-4-(prop-1-yn-1-yl)benzene (2m)

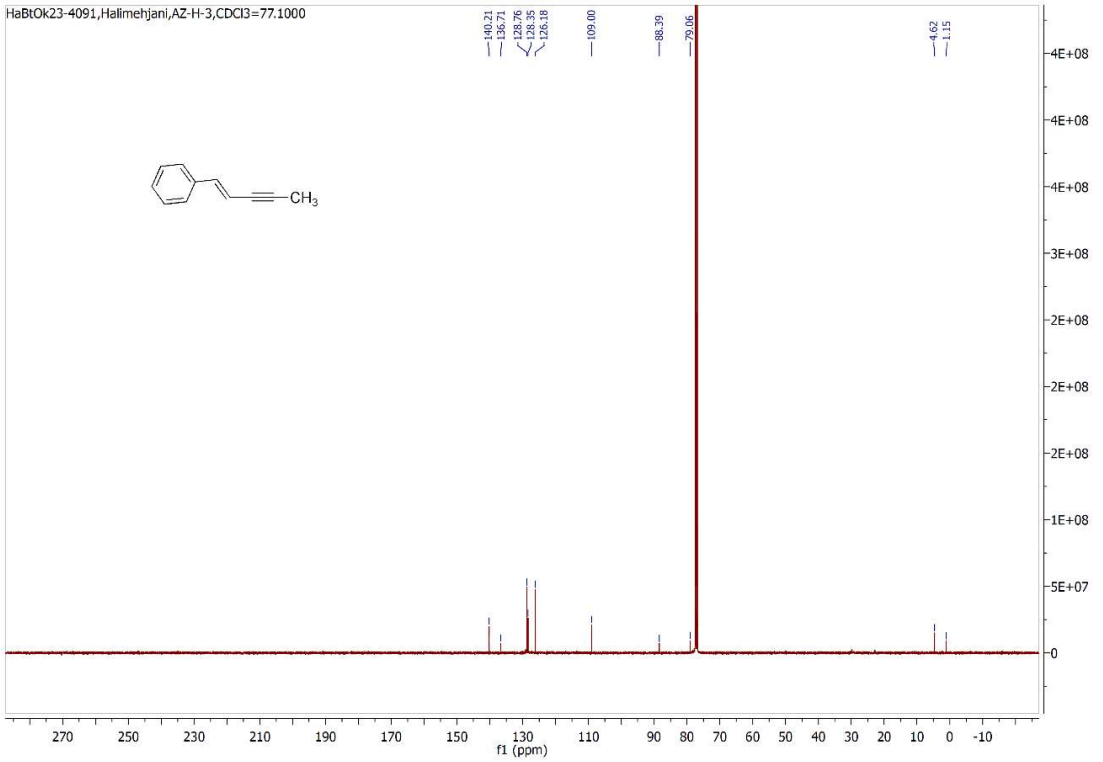



PaBtOk22-410201,Panahi,Poly-F-Ar-Me,CDCl3,19F
-139.34
-139.37
-139.40
-139.43
-145.53
-145.56
-145.59
-145.62
F
F
F
F
CH3
1.00
1.08
f1 (ppm)

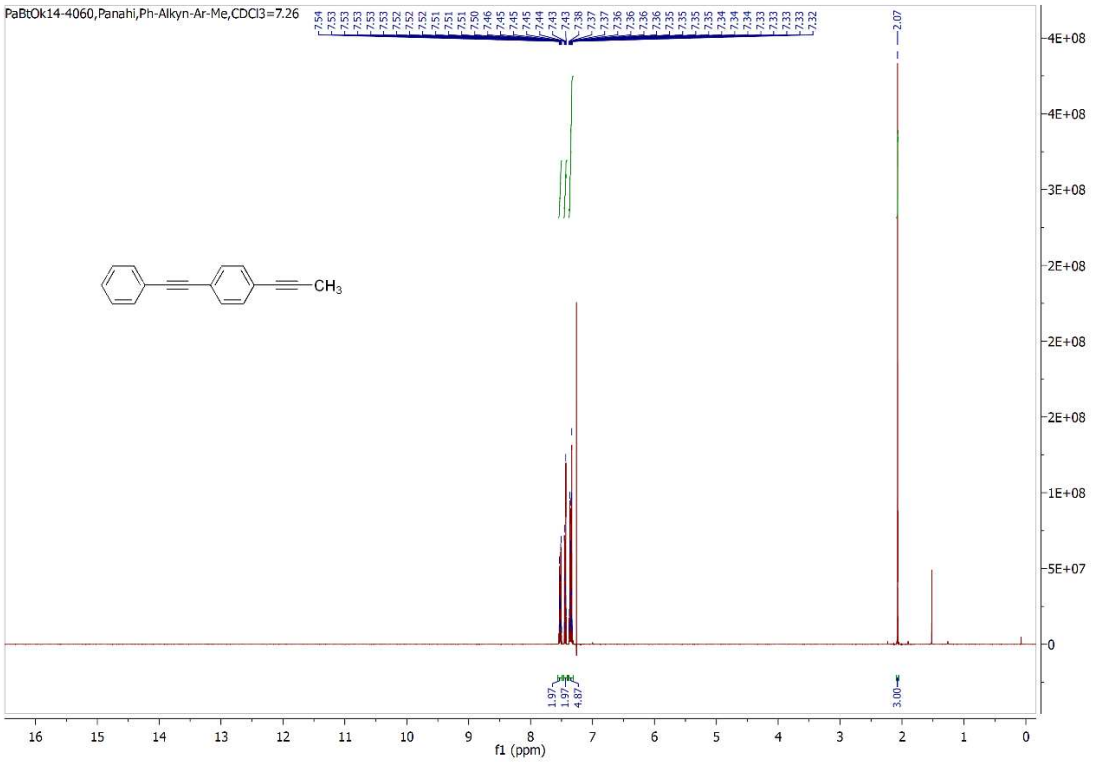

PaBtOk09-500201,Panahi,BA-27,CDCl3=77.1000
155.96
146.21
146.07
146.03
144.86
144.16
144.07
118.85
118.81
118.50
118.35
113.30
113.16
113.02
96.15
96.13
96.11
69.59
33.39
31.56
29.83
22.62
22.45
13.84
13.19
13.17
13.14
F
F
F
F
CH3
f1 (ppm)

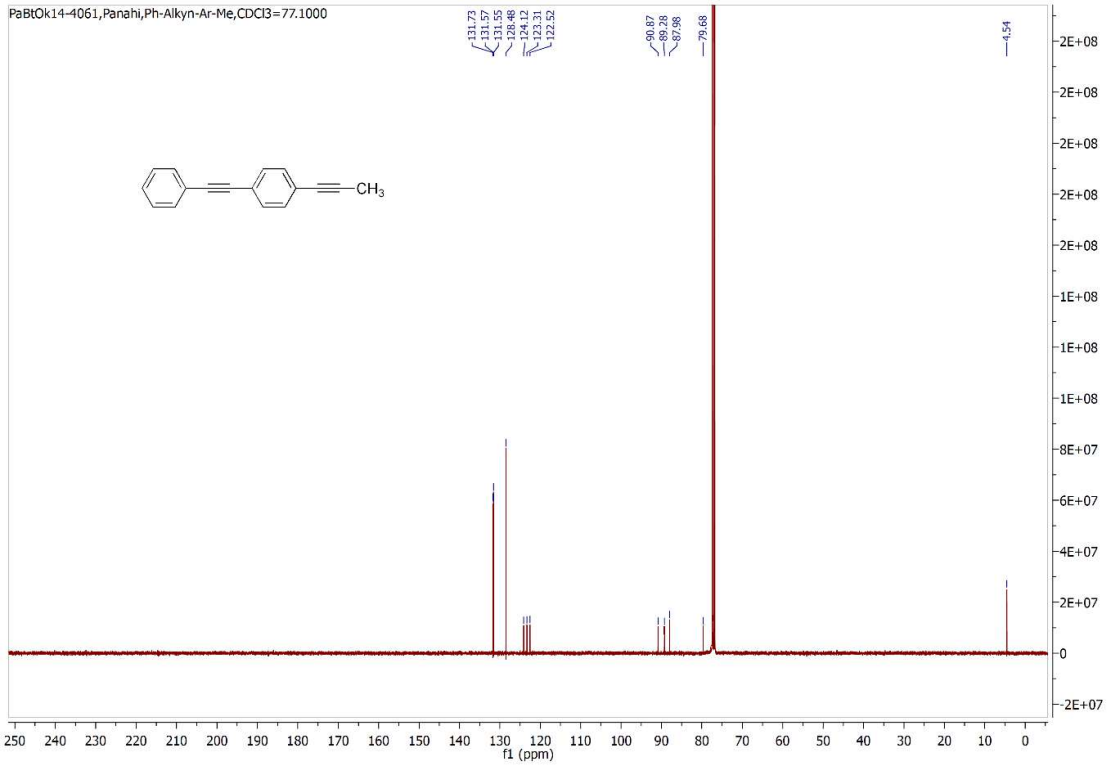
11.1.11. (E)-Pent-1-en-3-yn-1-ylbenzene (2n)



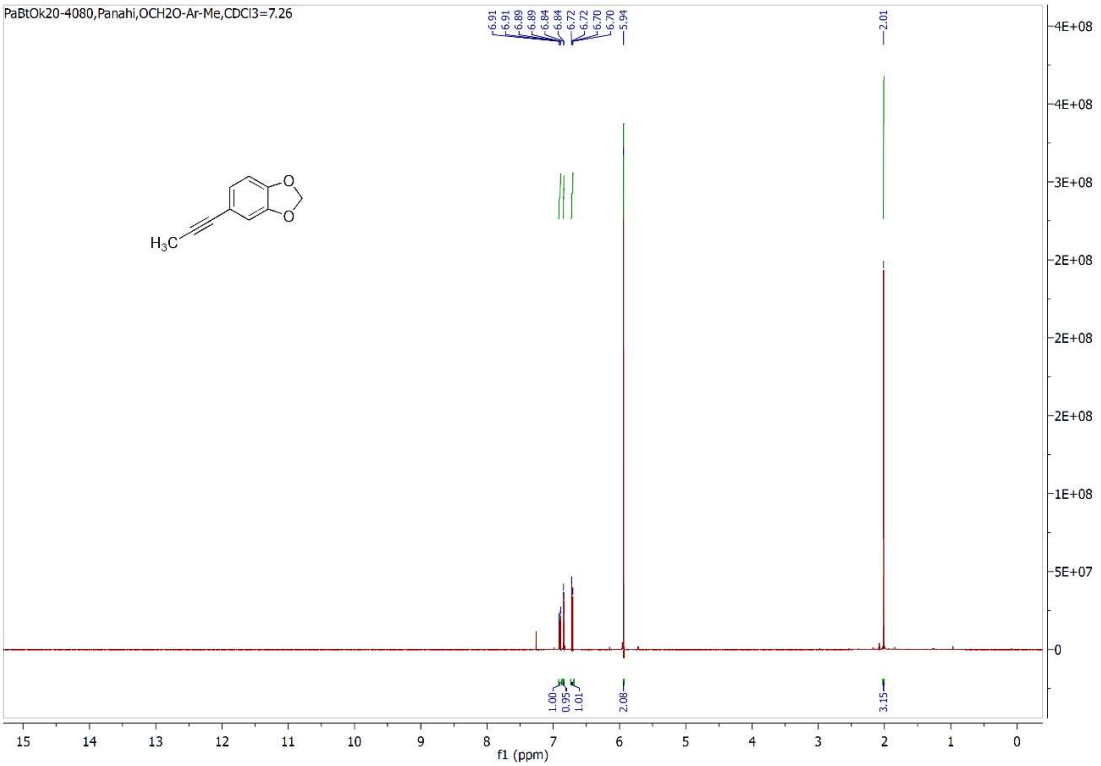


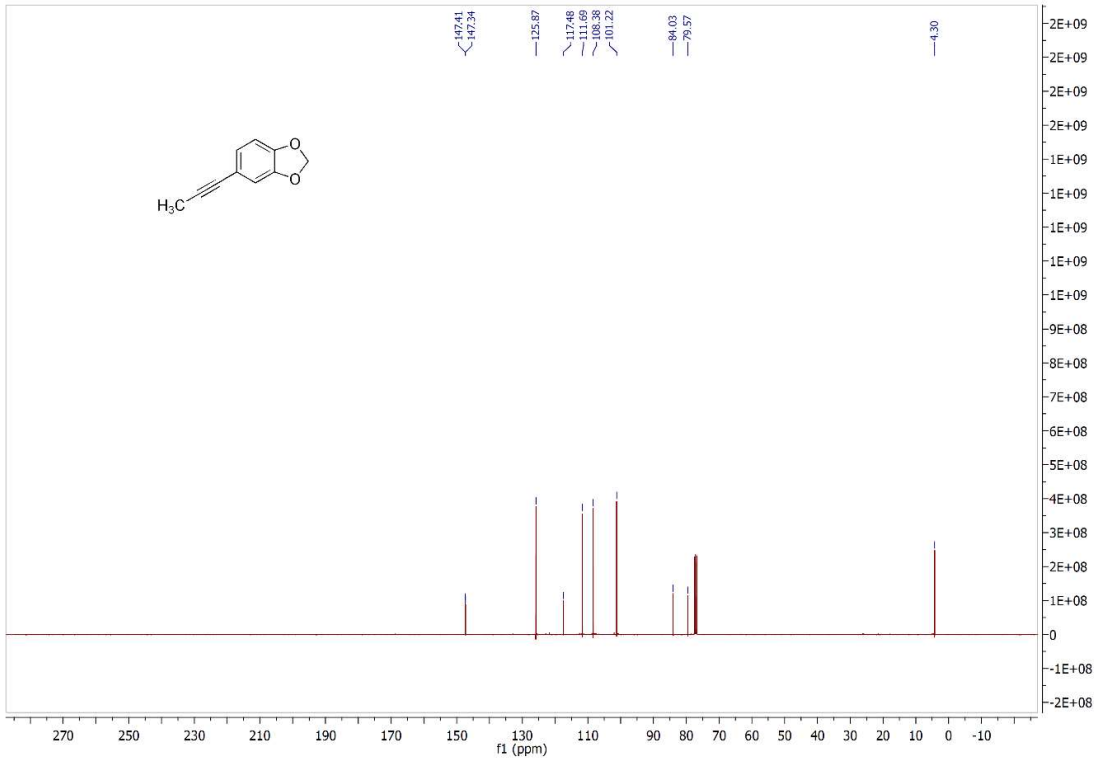
11.1.12. 1-(Phenylethynyl)-4-(prop-1-yn-1-yl)benzene (2o)





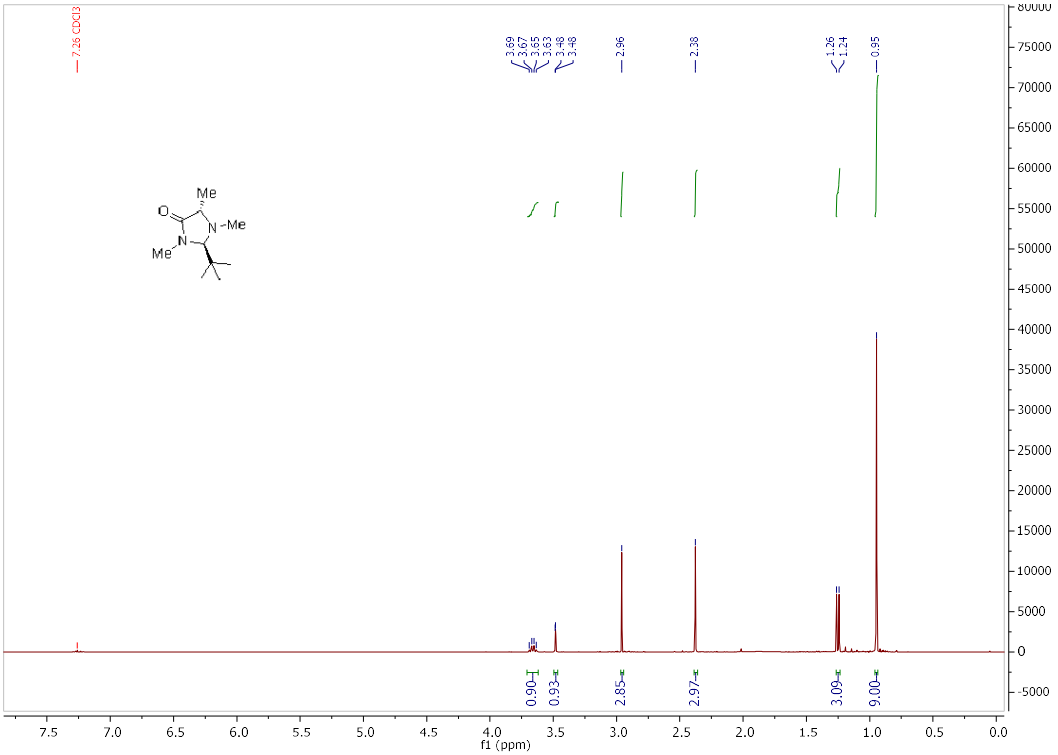
11.1.13. 5-(Prop-1-yn-1-yl)benzo[d][1,3]dioxole (2p)

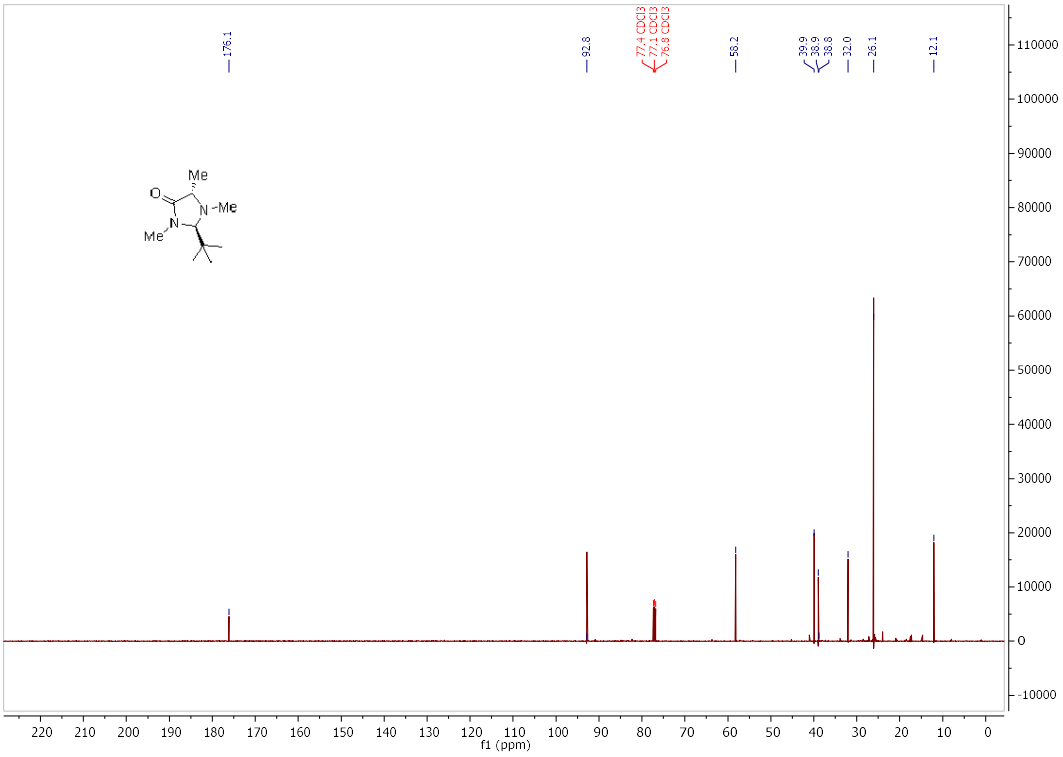




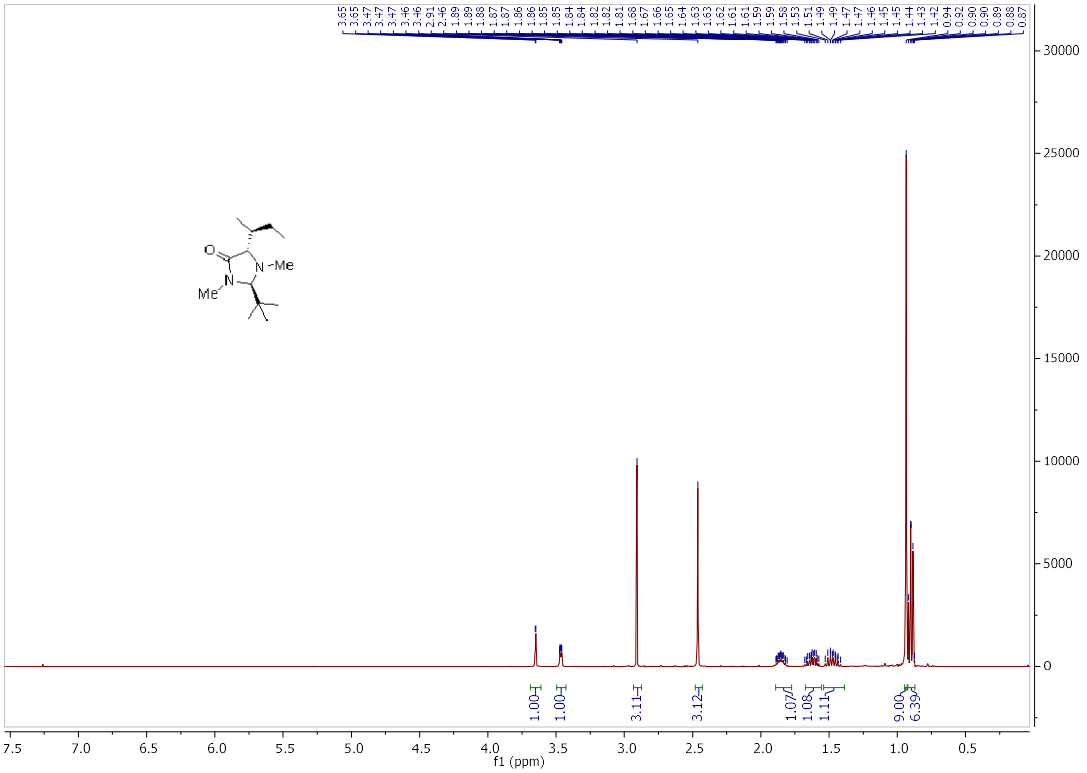
11.2. Iimidazolidinone derivatives

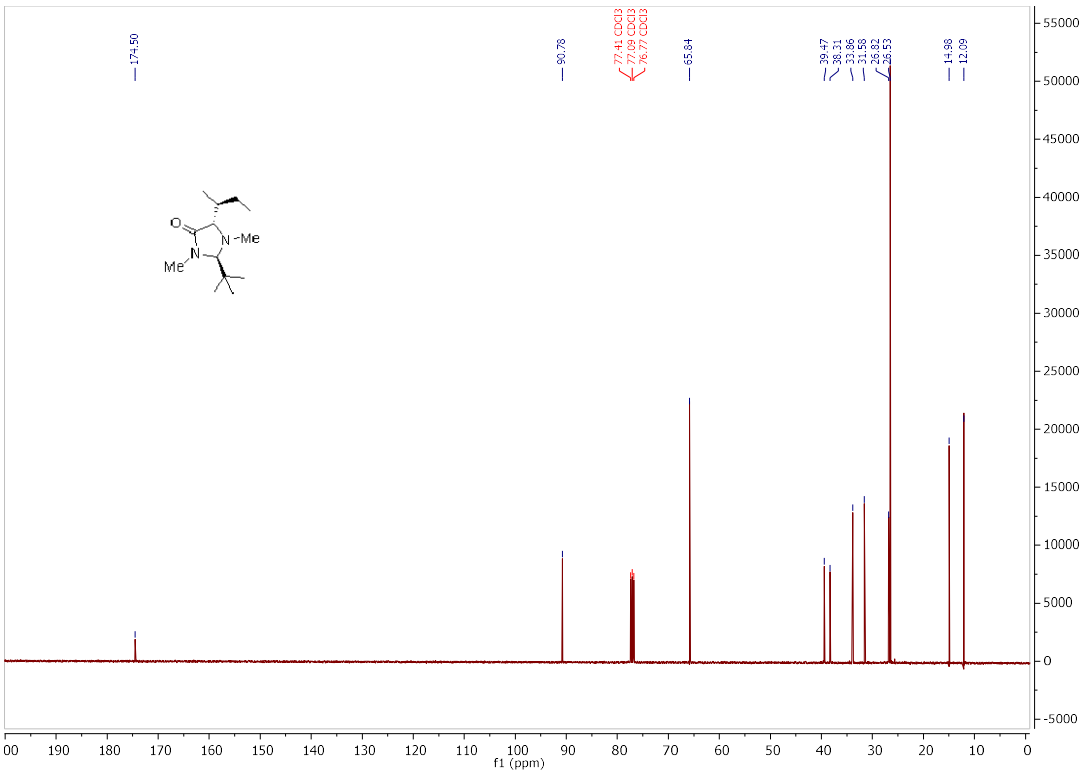
11.2.1 (2*R*,5*S*)-2-(*tert*-butyl)-1,3,5-trimethylimidazolidin-4-one



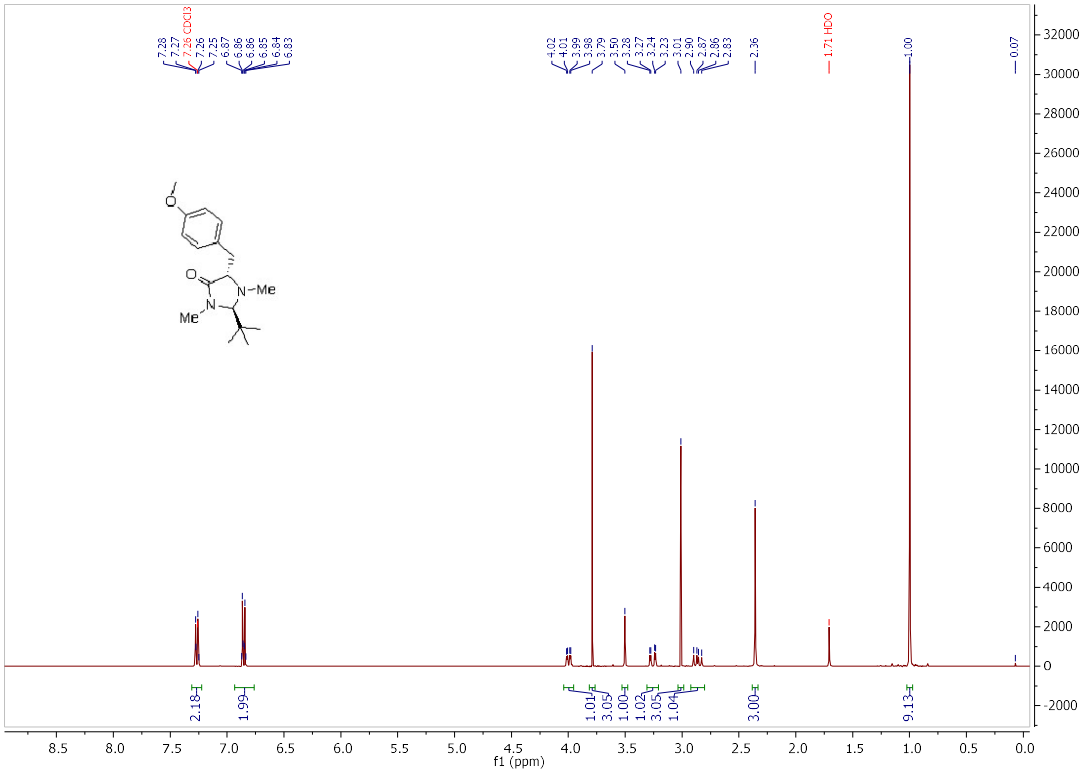


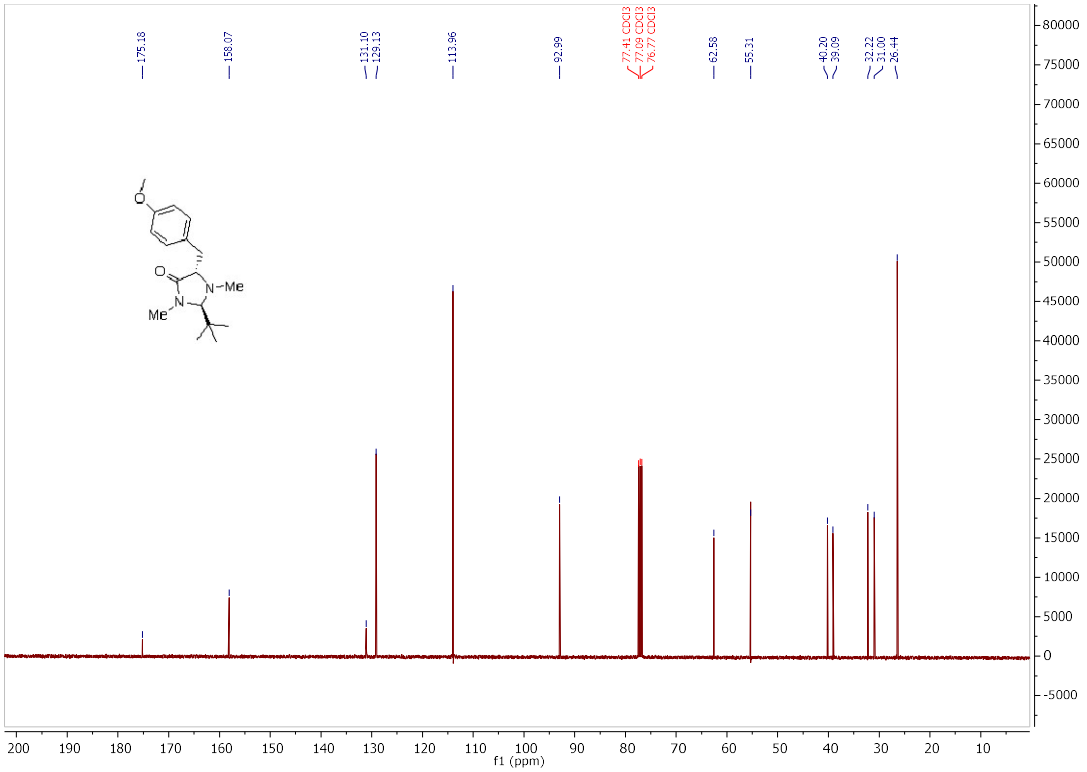
11.2.2. (2*R*,5*S*)-5-((*S*)-*sec*-butyl)-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one



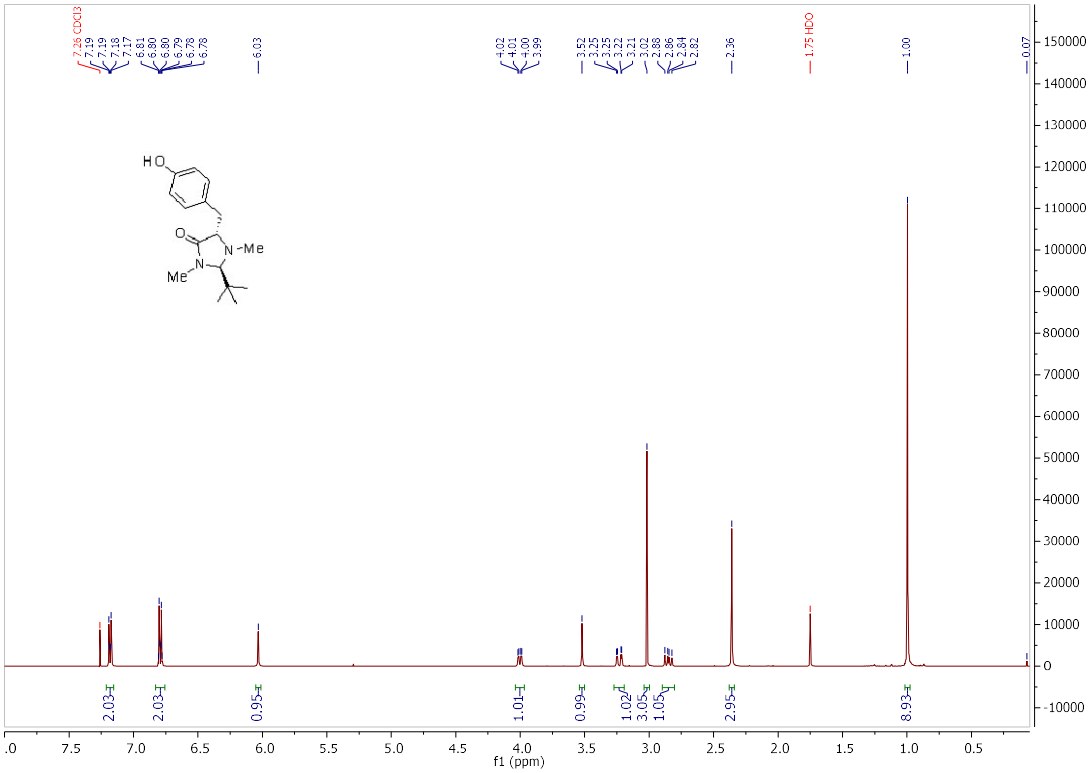


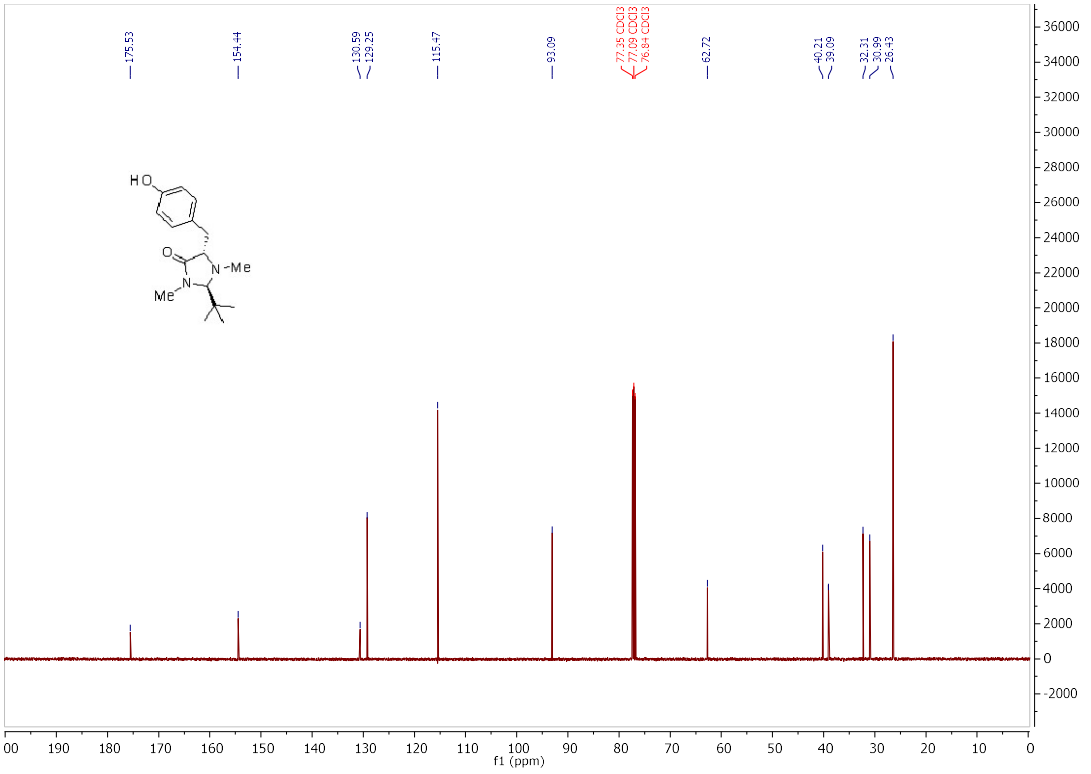
11.2.3. (2*R*,5*S*)-2-(*tert*-butyl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one



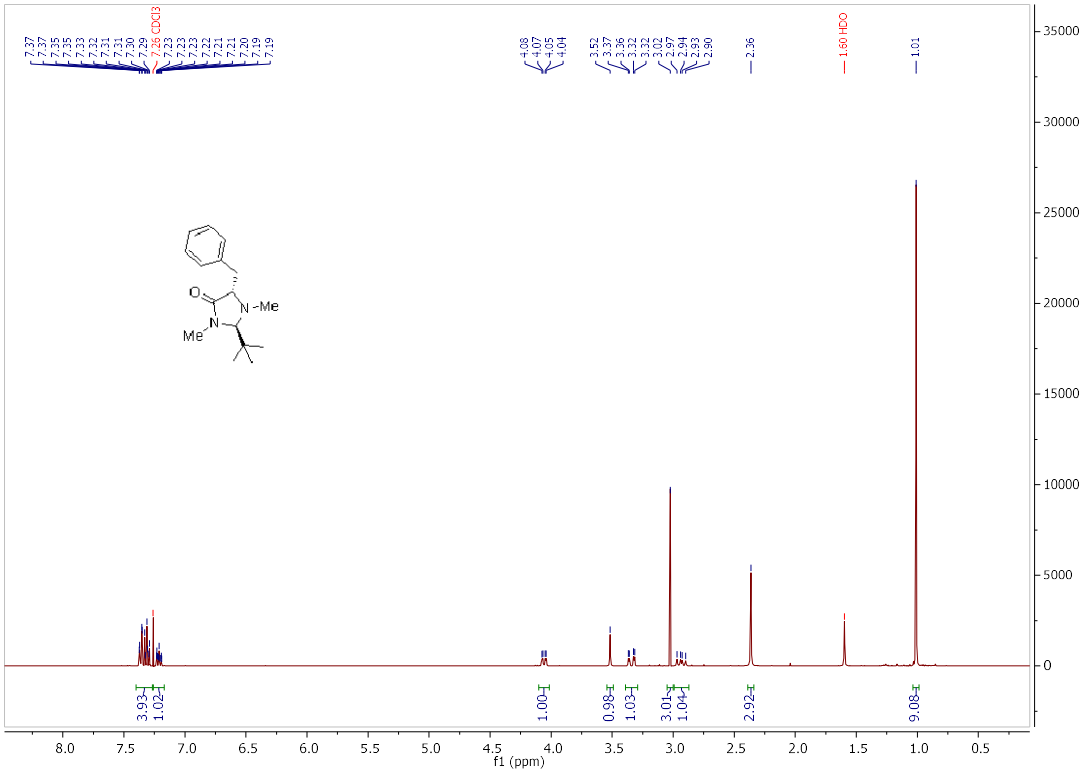


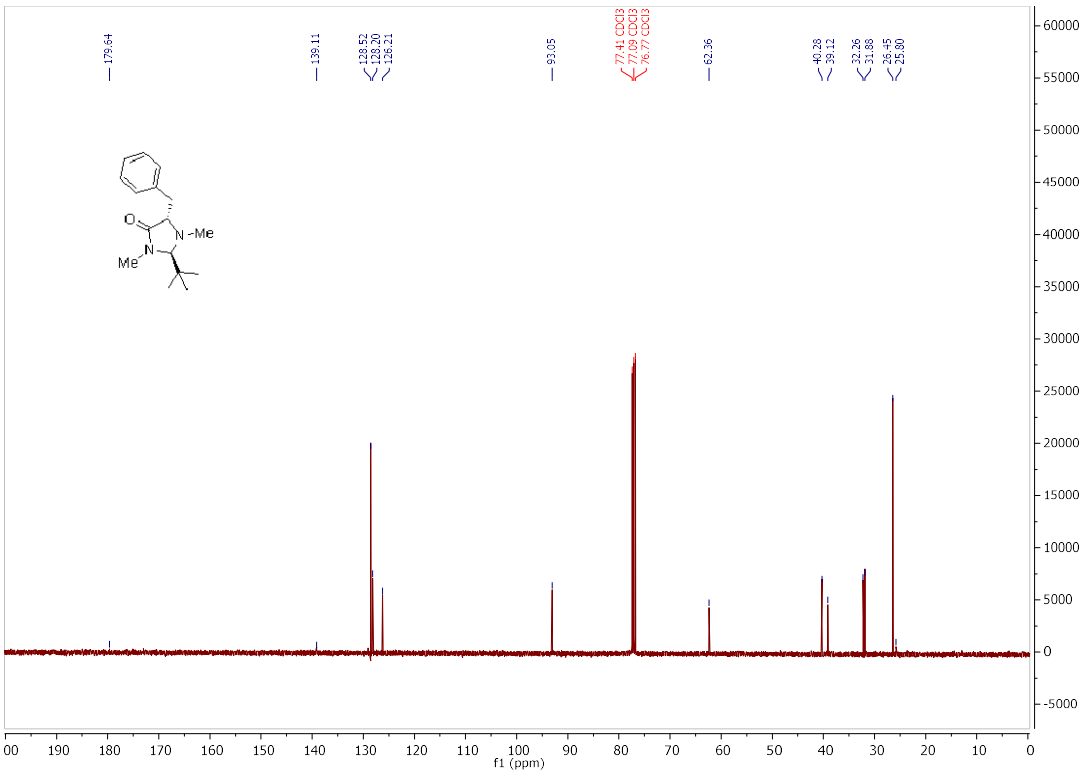
11.2.4. (2*R*,5*S*)-2-(*tert*-butyl)-5-(4-hydroxybenzyl)-1,3-dimethylimidazolidin-4-one



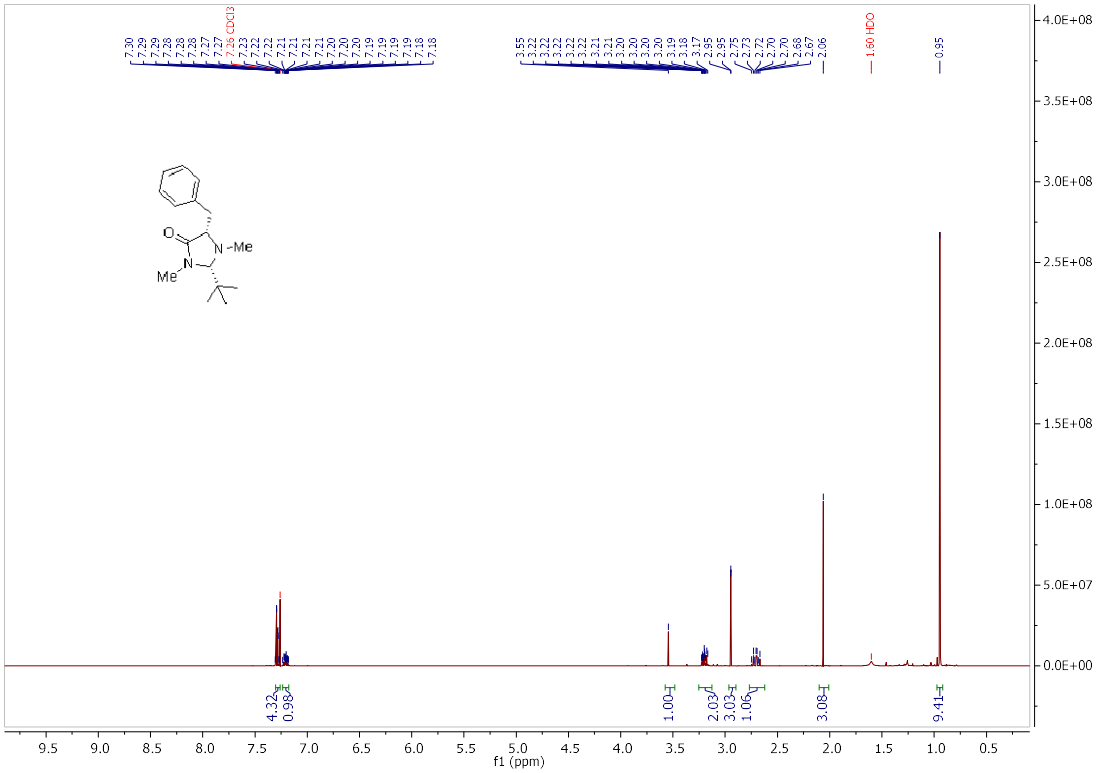


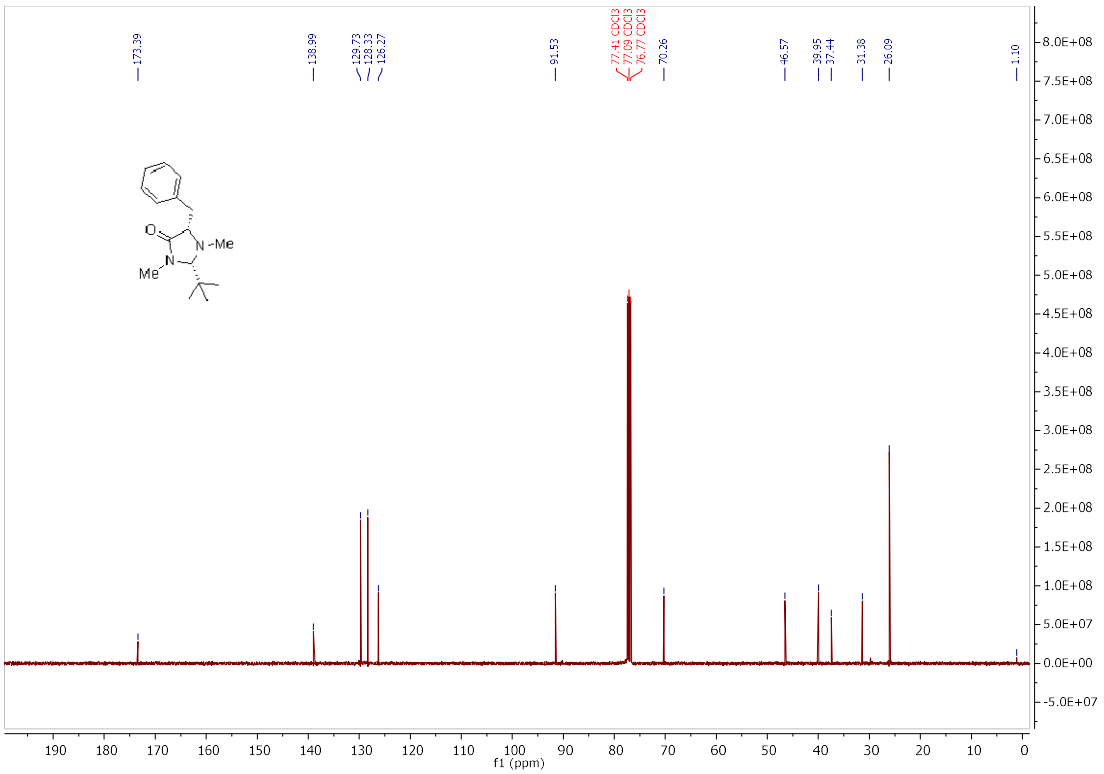
11.2.5. (2*R*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one



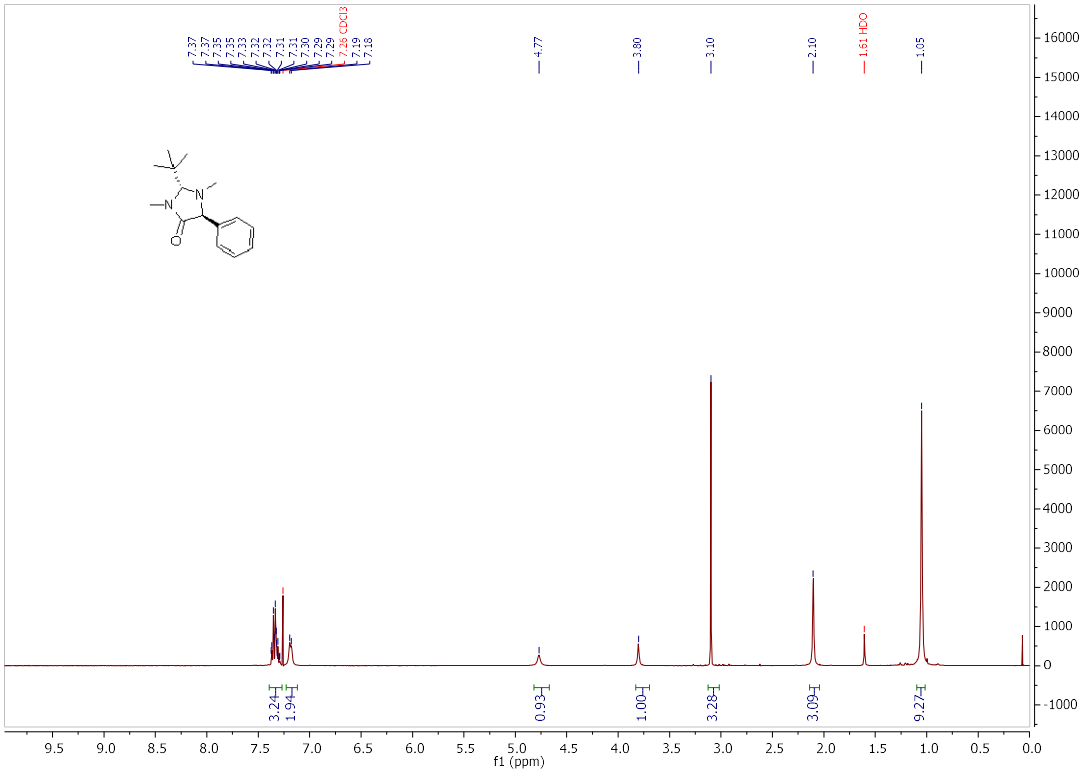


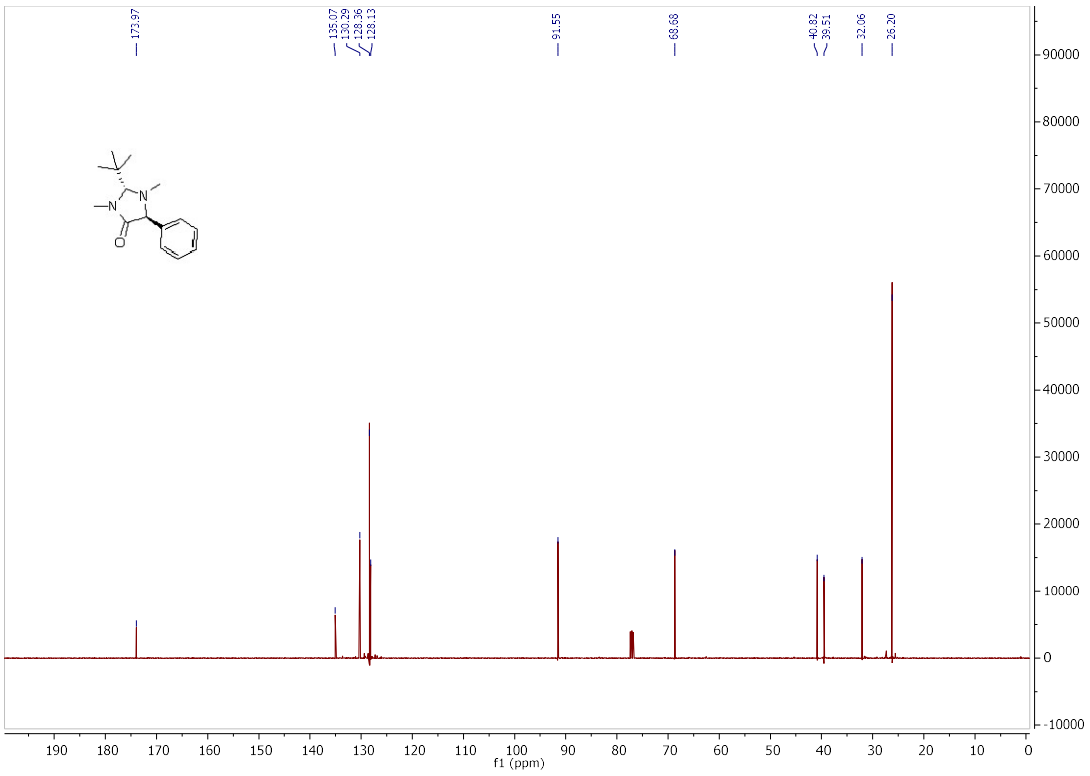
11.2.6.(2*S*,5*S*)-5-benzyl-2-(*tert*-butyl)-1,3-dimethylimidazolidin-4-one



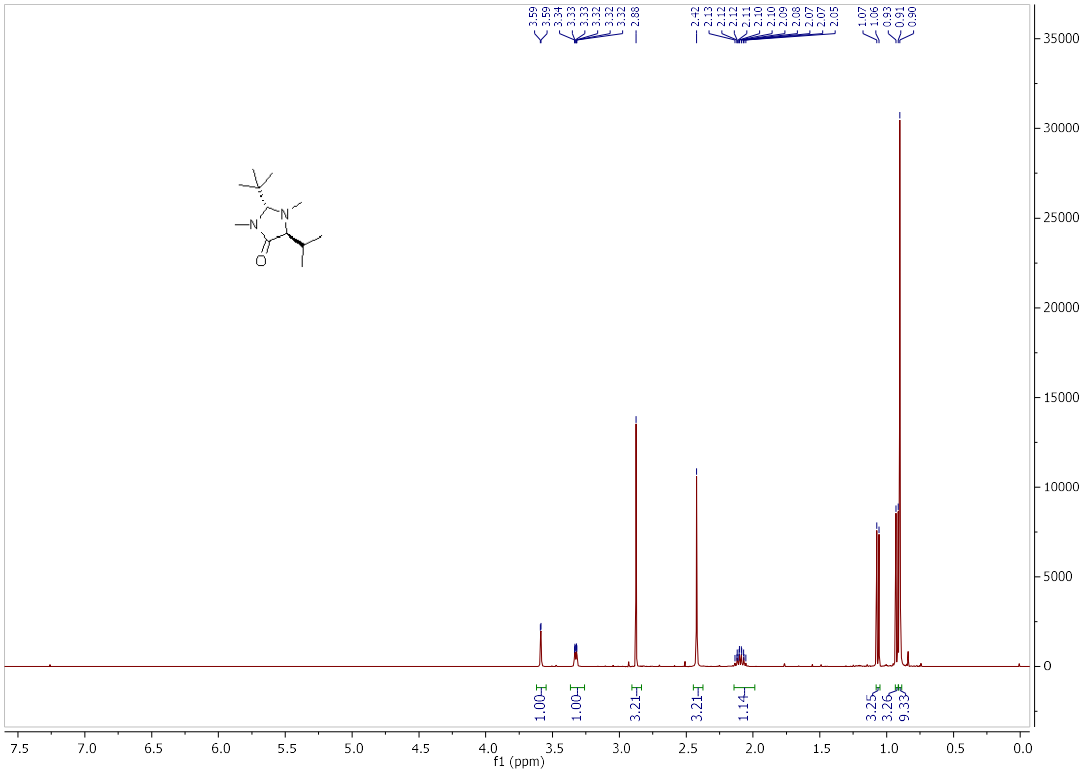


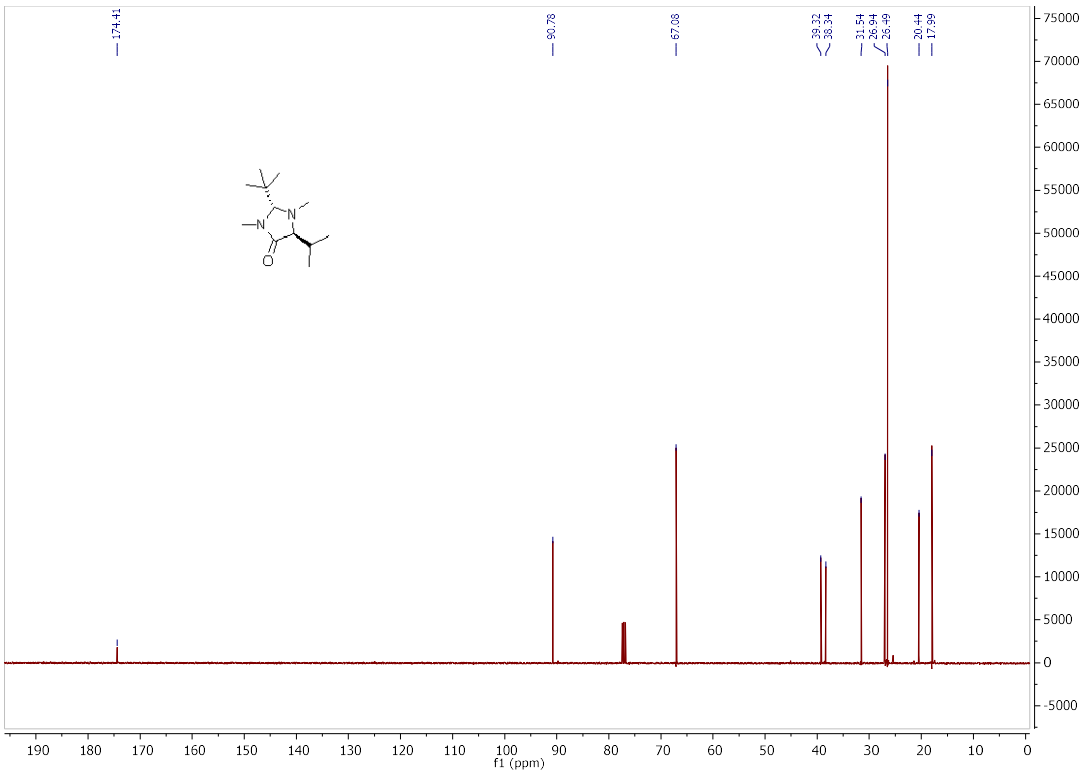
11.2.7. (2*R*,5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one



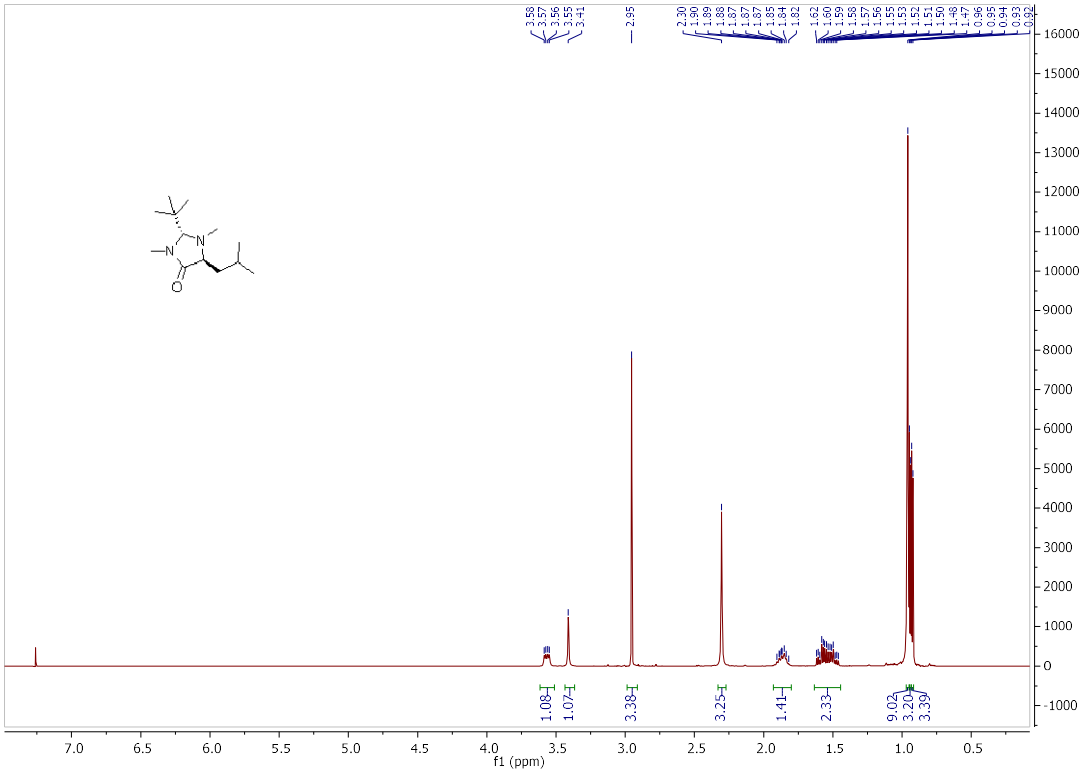


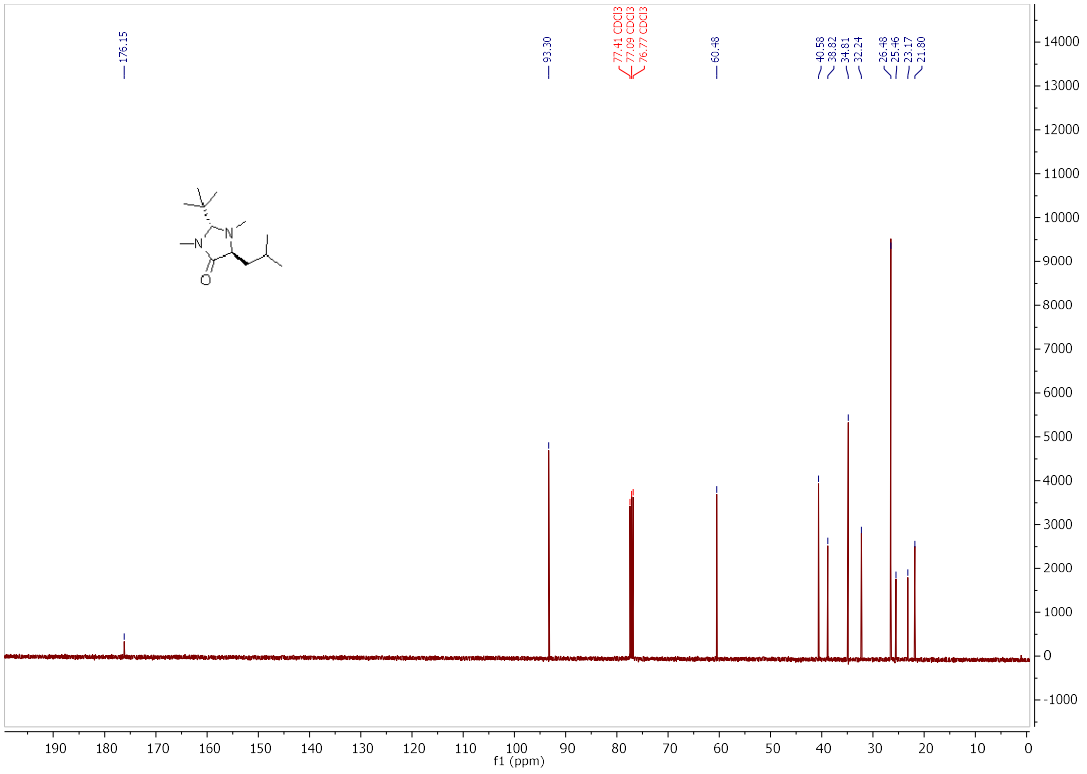
11.2.8. (2*R*,5*S*)-2-(*tert*-butyl)-5-isopropyl-1,3-dimethylimidazolidin-4-one



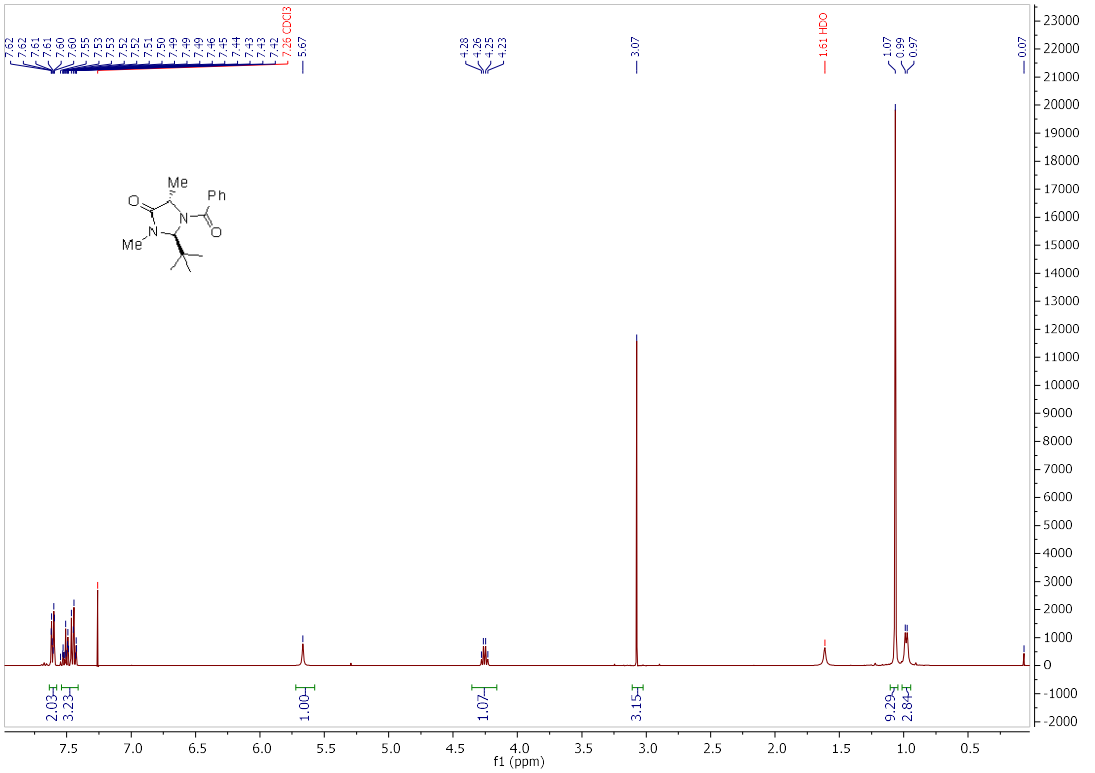


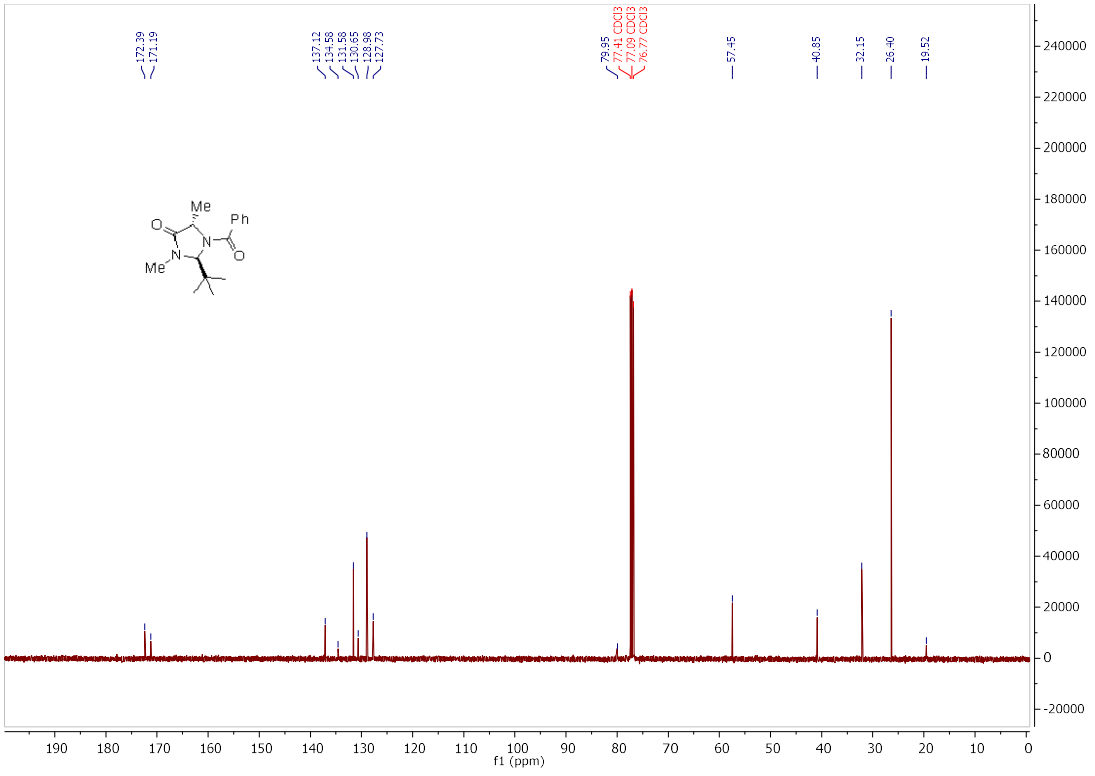
11.2.9. (2*R*,5*S*)-2-(*tert*-butyl)-5-isobutyl-1,3-dimethylimidazolidin-4-one



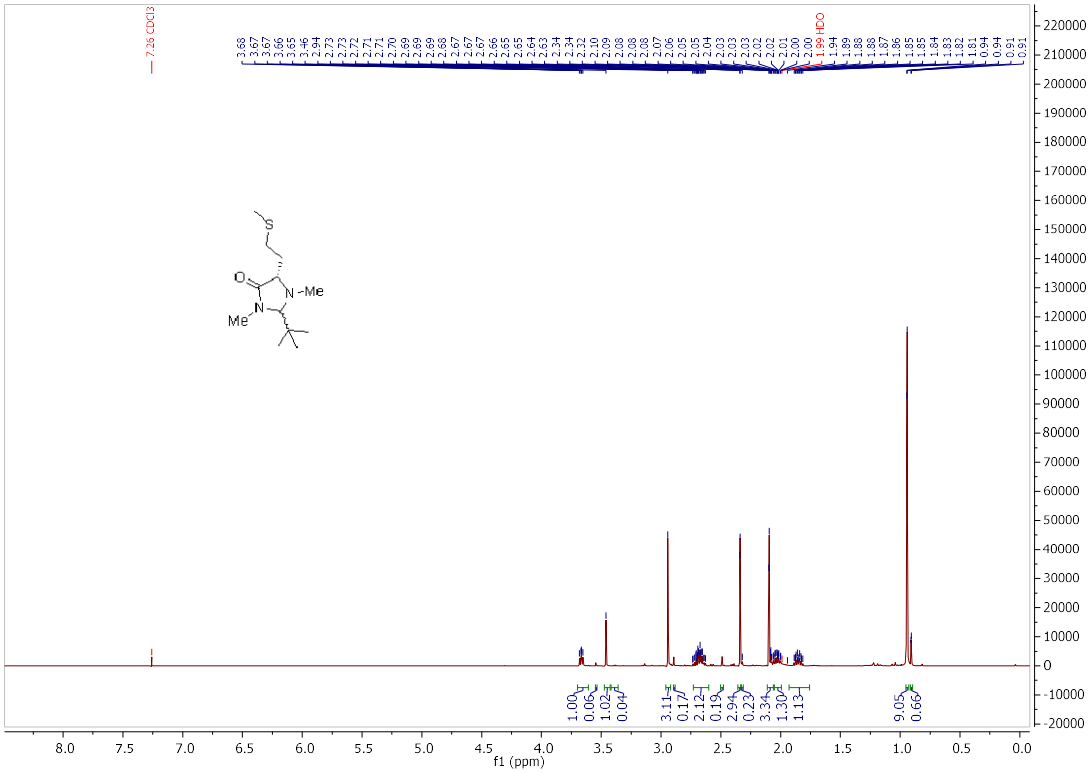


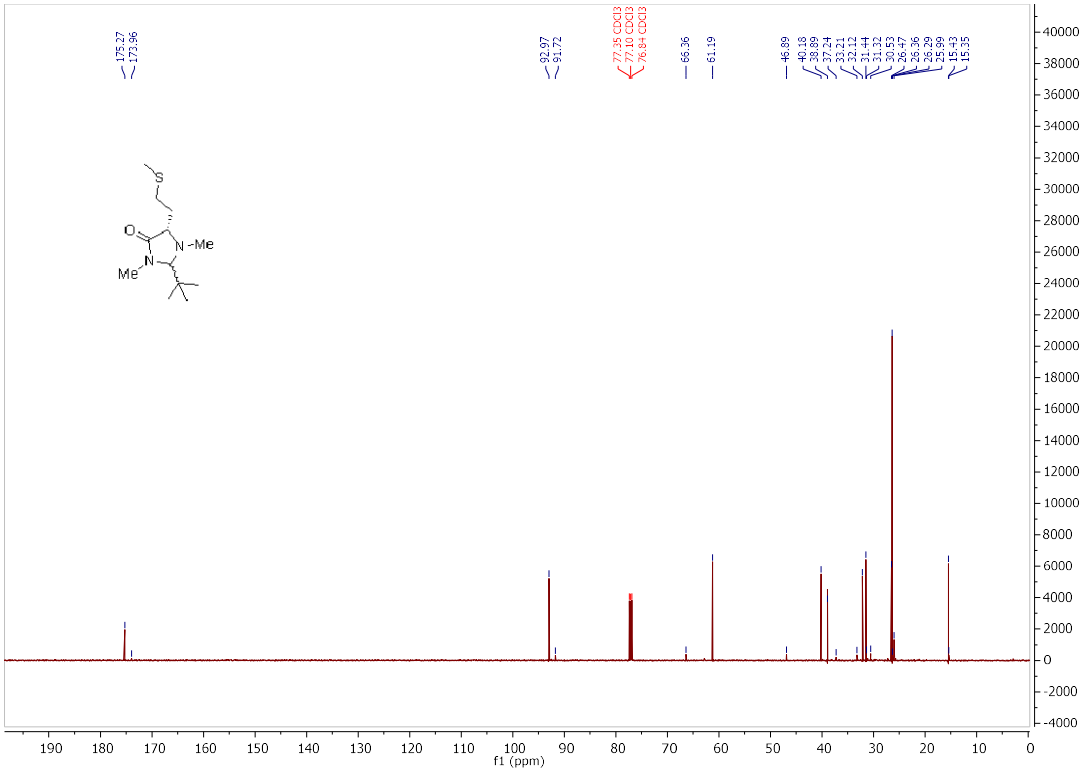
11.2.10. (2*S*,5*S*)-1-benzoyl-2-(*tert*-butyl)-3,5-dimethylimidazolidin-4-one





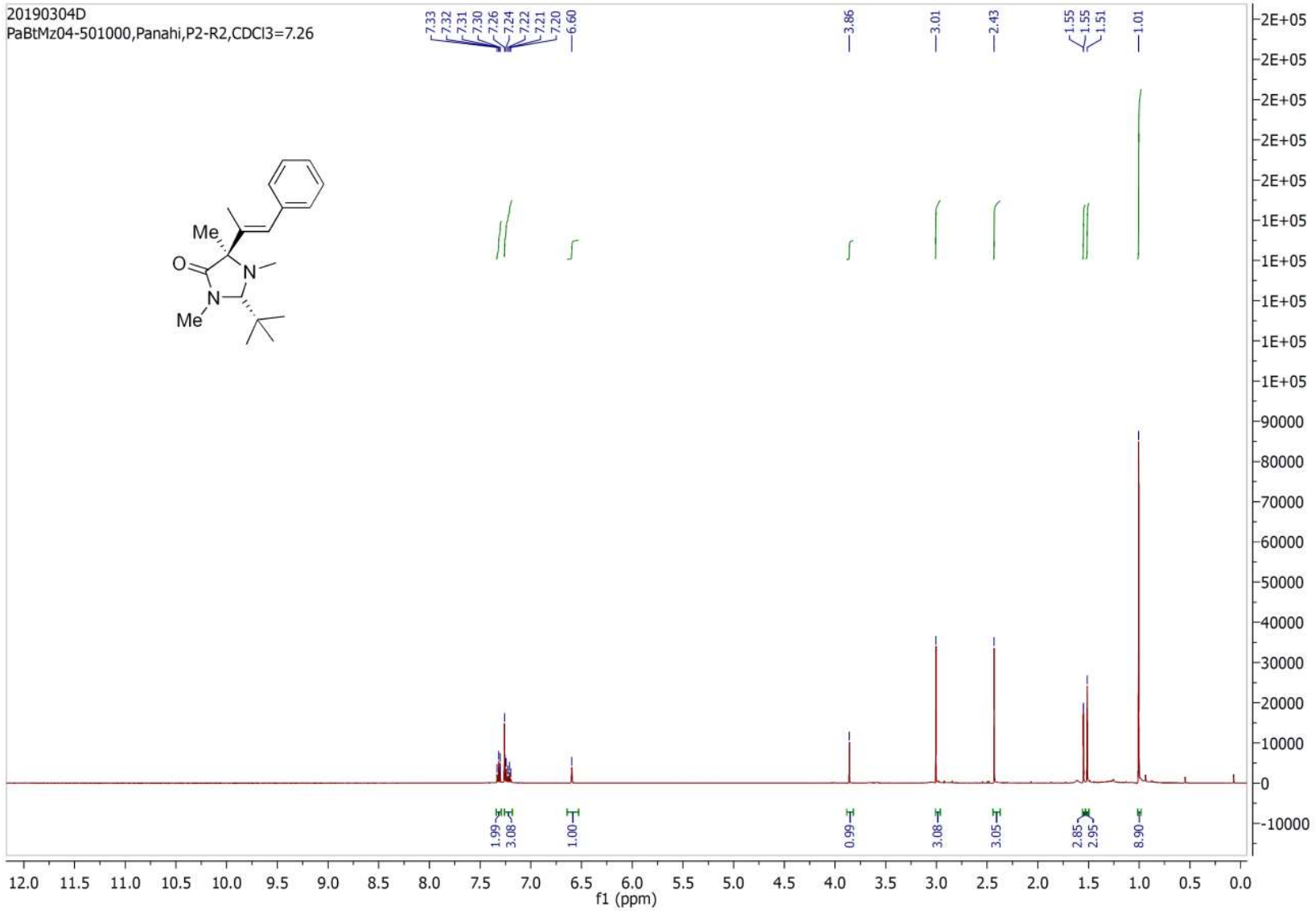
11.2.11. (5*S*)-2-(*tert*-butyl)-1,3-dimethyl-5-(2-(methylthio)ethyl)imidazolidin-4-one

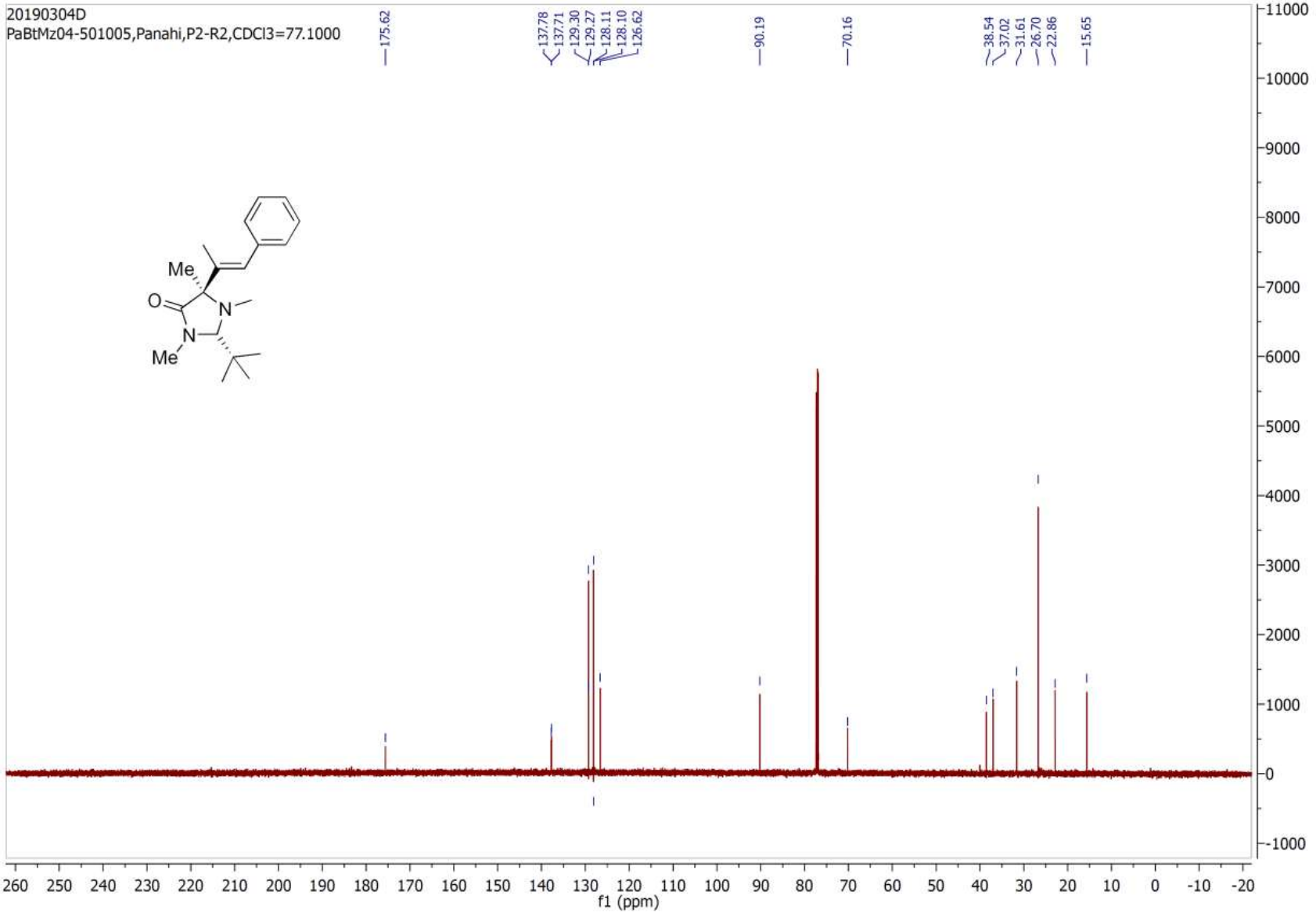




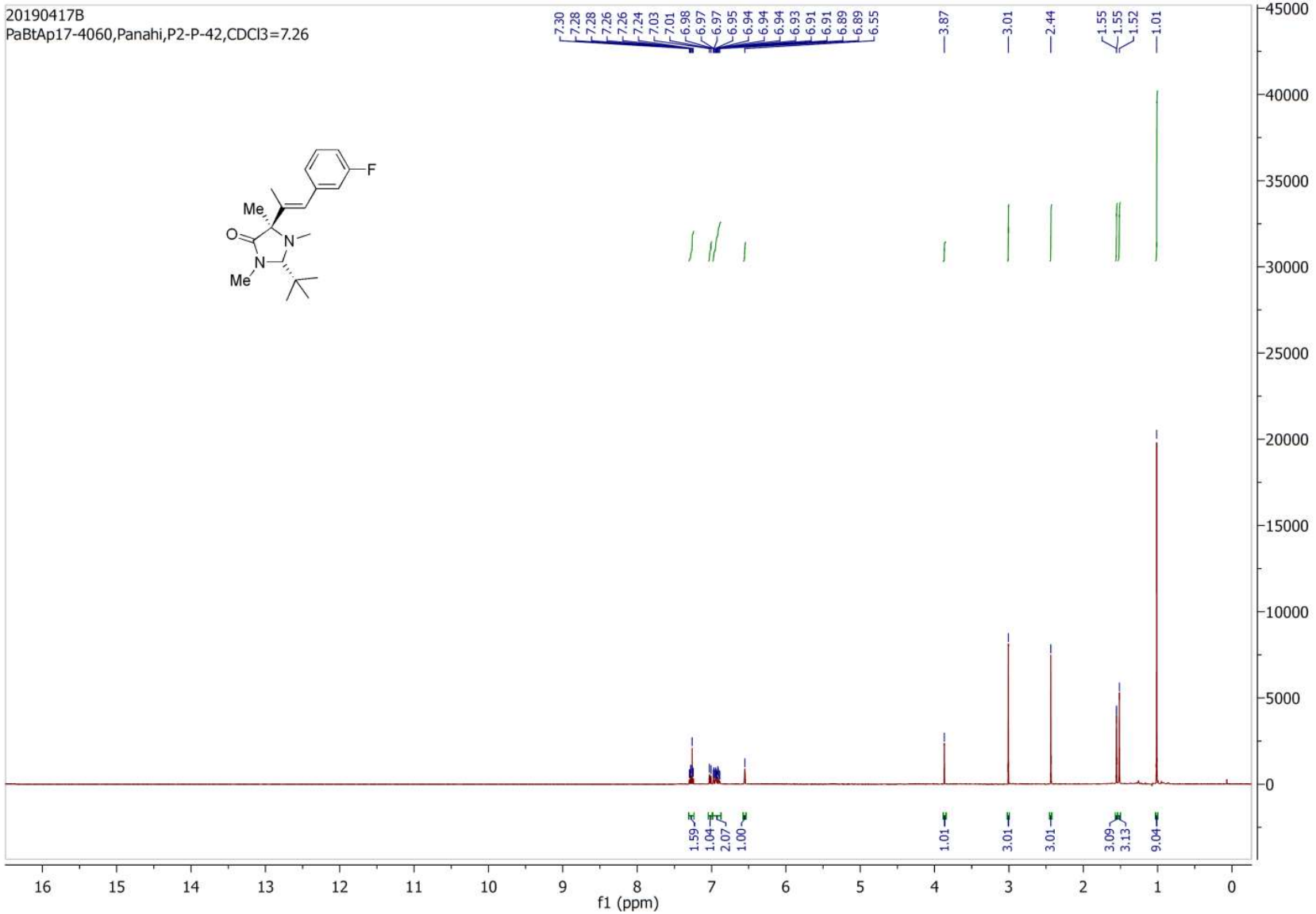
11.3. α-alkenylated imidazolidinones

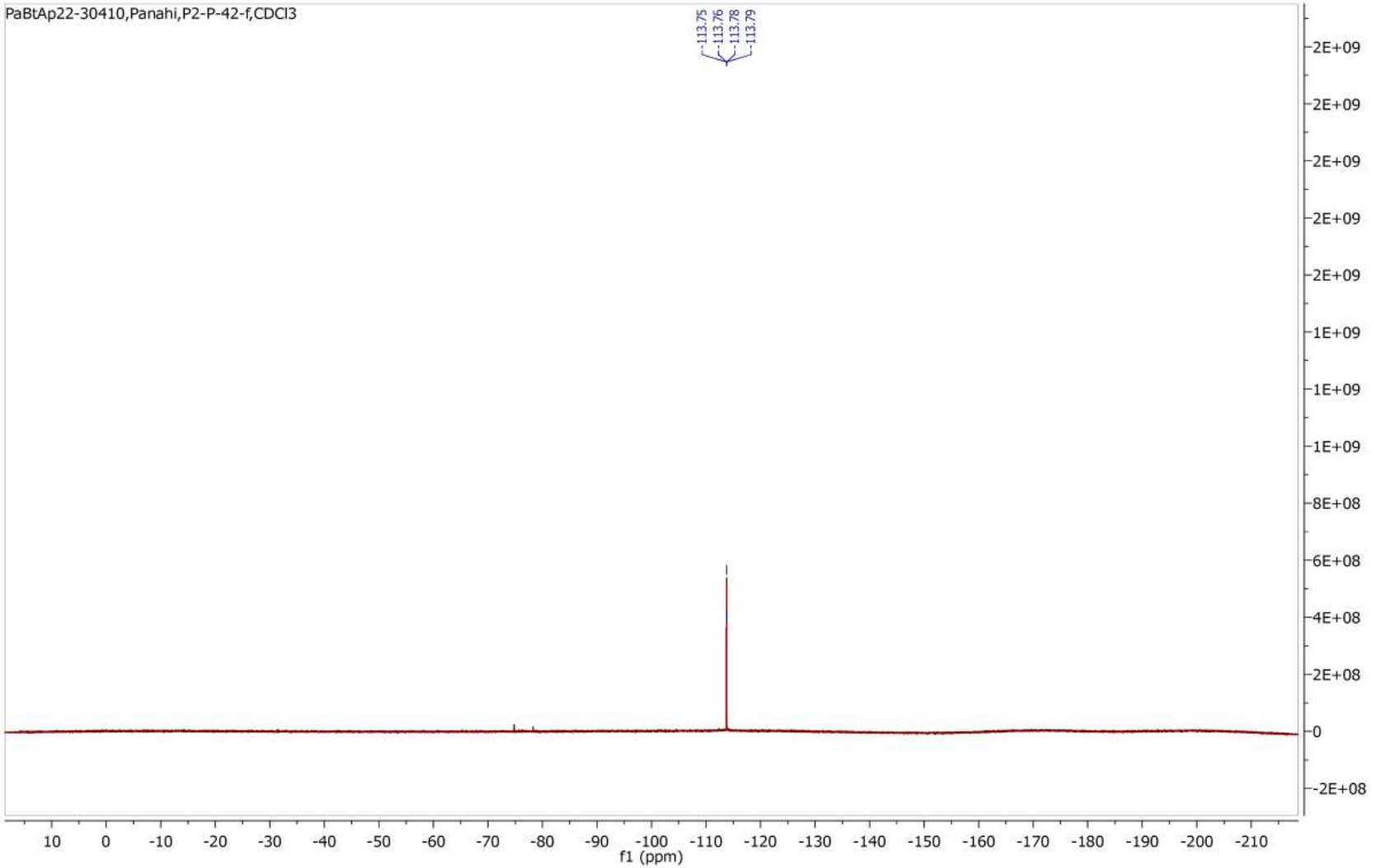
11.3.1. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3a)

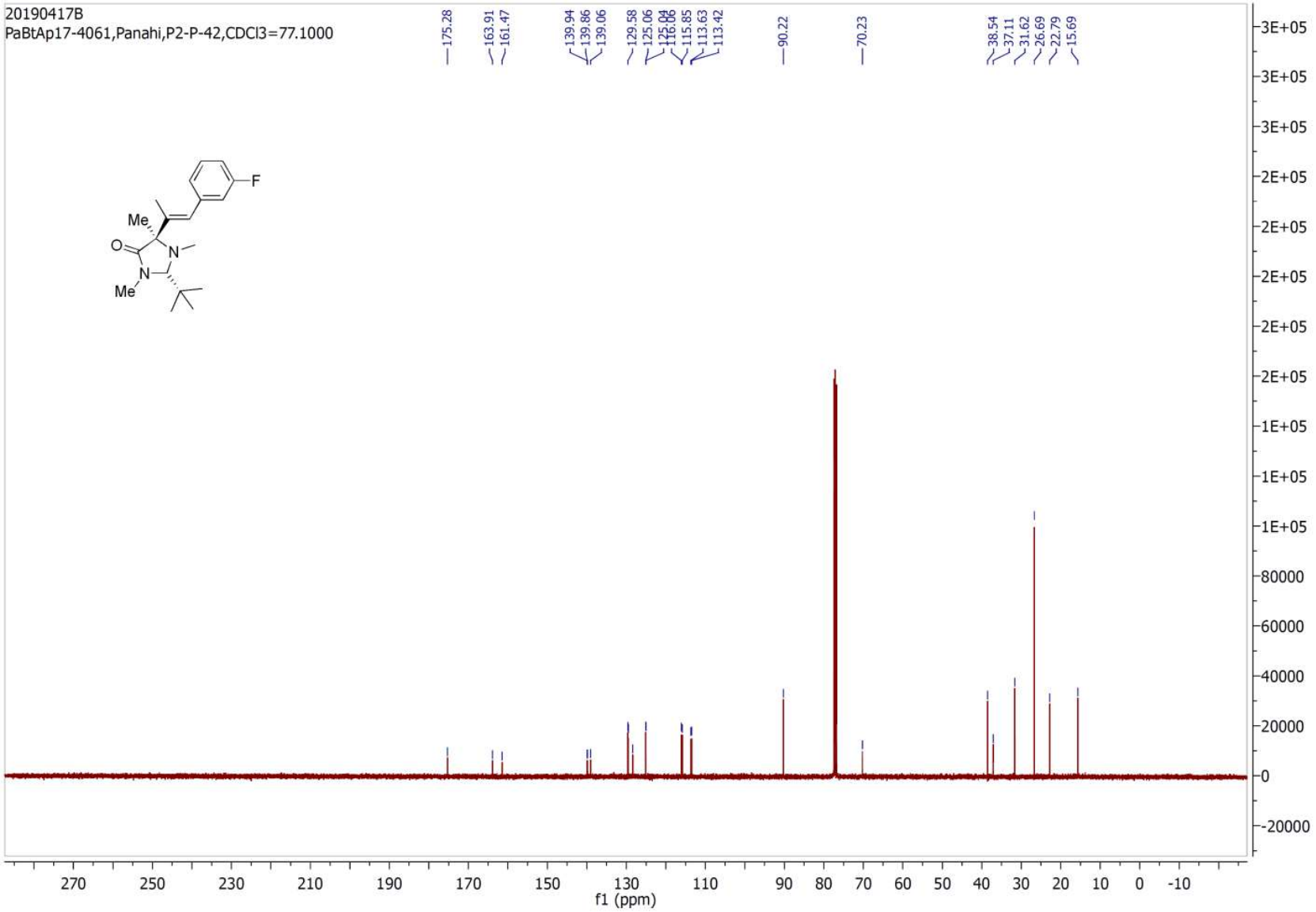



20190304D
PaBtMz04-501005,Panahi,P2-R2,CDCl3=77.1000
175.62
137.78
137.71
129.30
129.27
128.11
128.10
126.62
90.19
70.16
38.54
37.02
31.61
26.70
22.86
15.65
Me
O
N
N
Me
f1 (ppm)

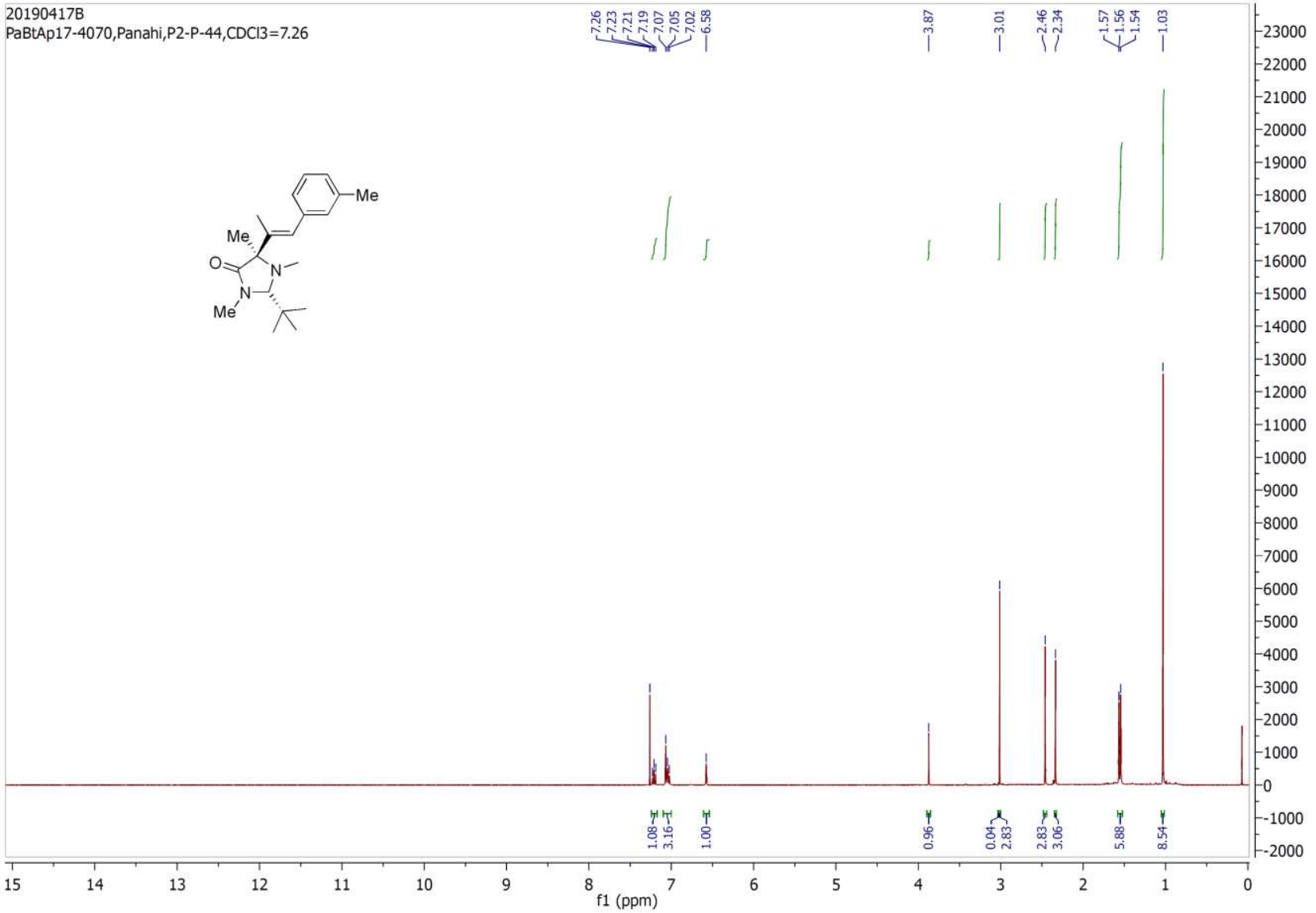
11.3.2. (2R,5R)-2-(tert-butyl)-5-((E)-1-(3-fluorophenyl)prop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3b)

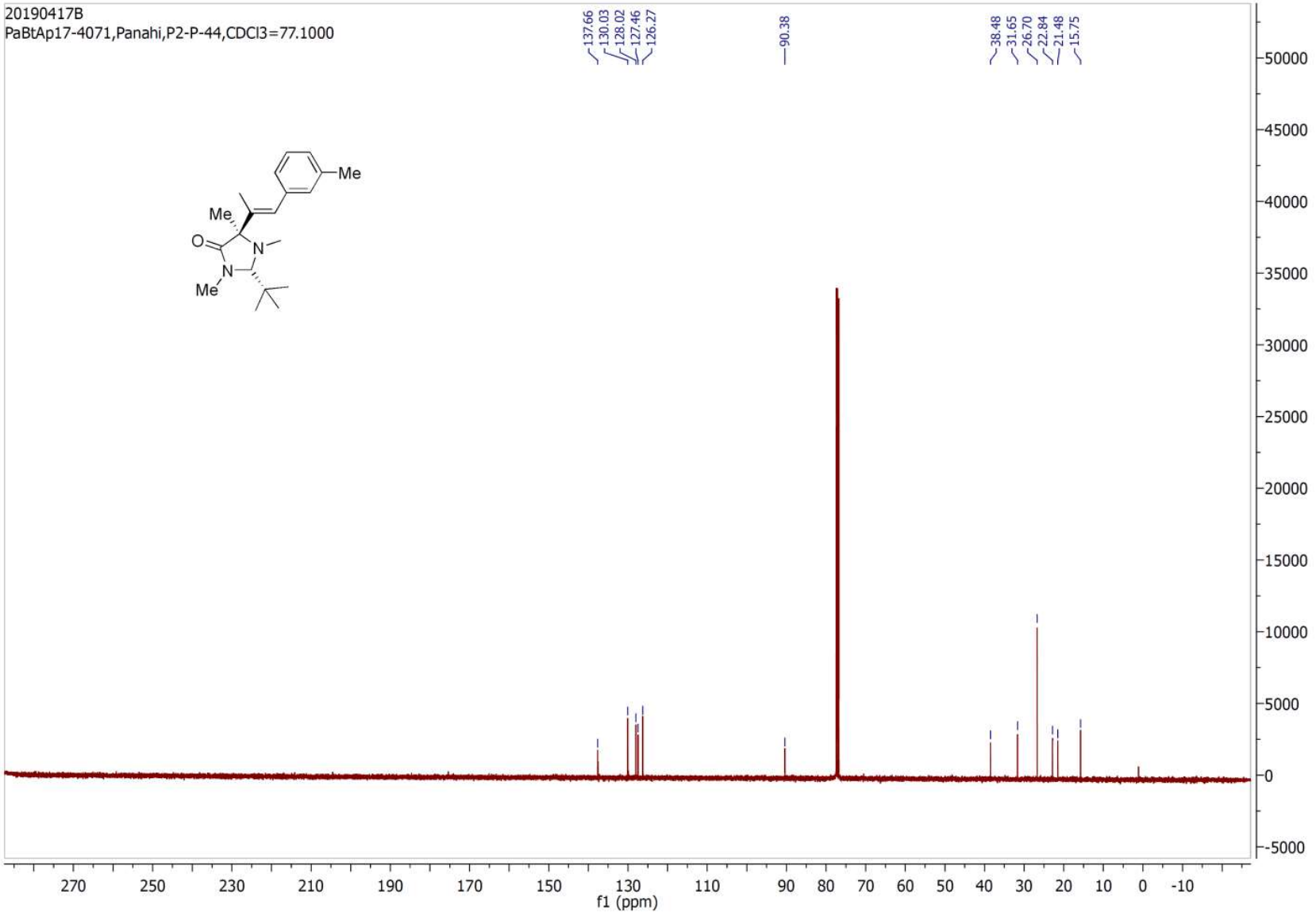



PaBtAp22-30410,Panahi,P2-P-42-f,CDCl3
-113.75
-113.76
-113.78
-113.79
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
8E+08
6E+08
4E+08
2E+08
0
-2E+08
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

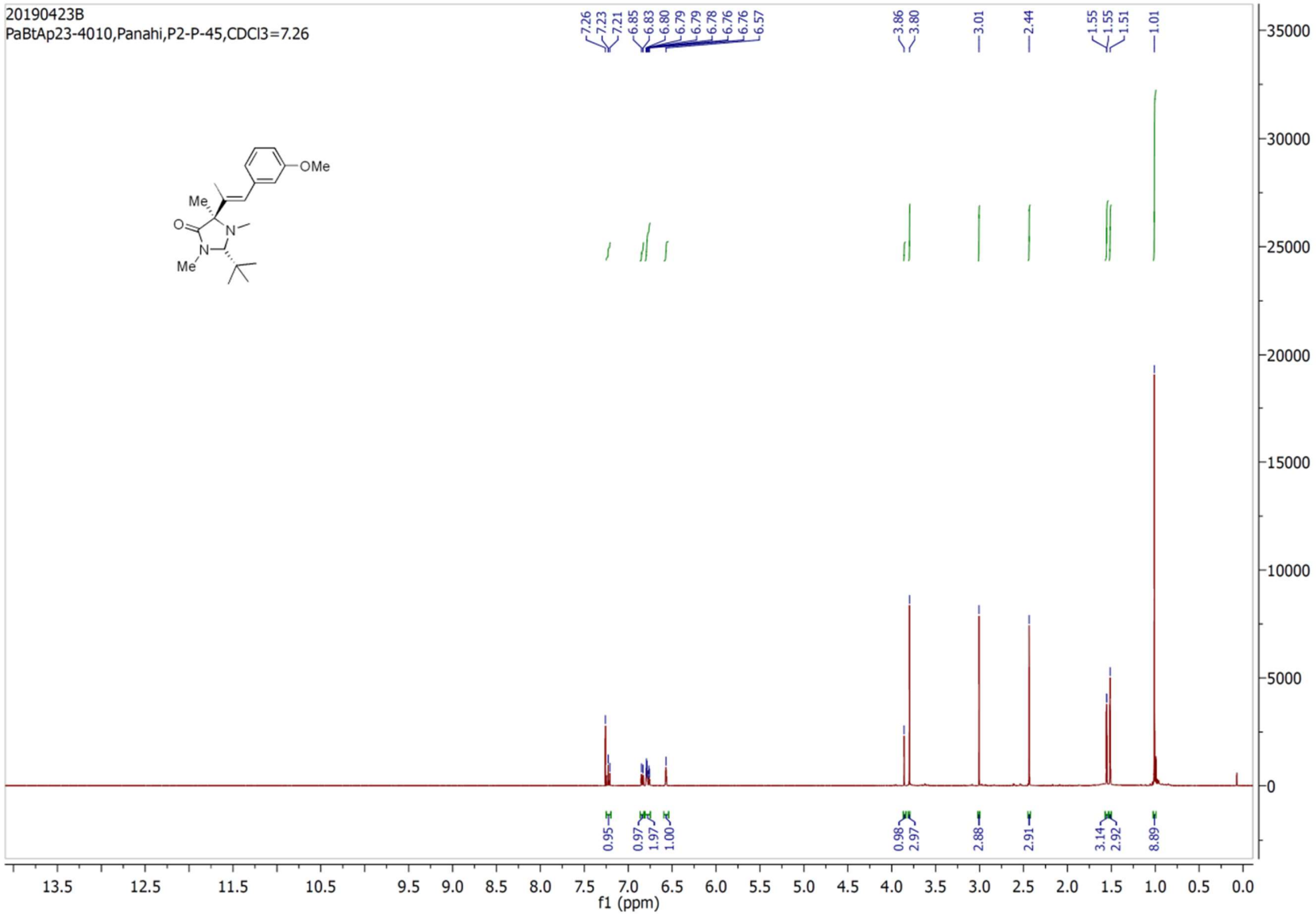

20190417B
PaBtAp17-4061,Panahi,P2-P-42,CDCl3=77.1000
175.28
163.91
161.47
139.94
139.86
139.06
129.58
125.06
125.04
116.06
115.85
113.63
113.42
90.22
70.23
38.54
37.11
31.62
26.69
22.79
15.69
F
Me
O
N
N
Me
3E+05
3E+05
3E+05
2E+05
2E+05
2E+05
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
80000
60000
40000
20000
0
-20000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

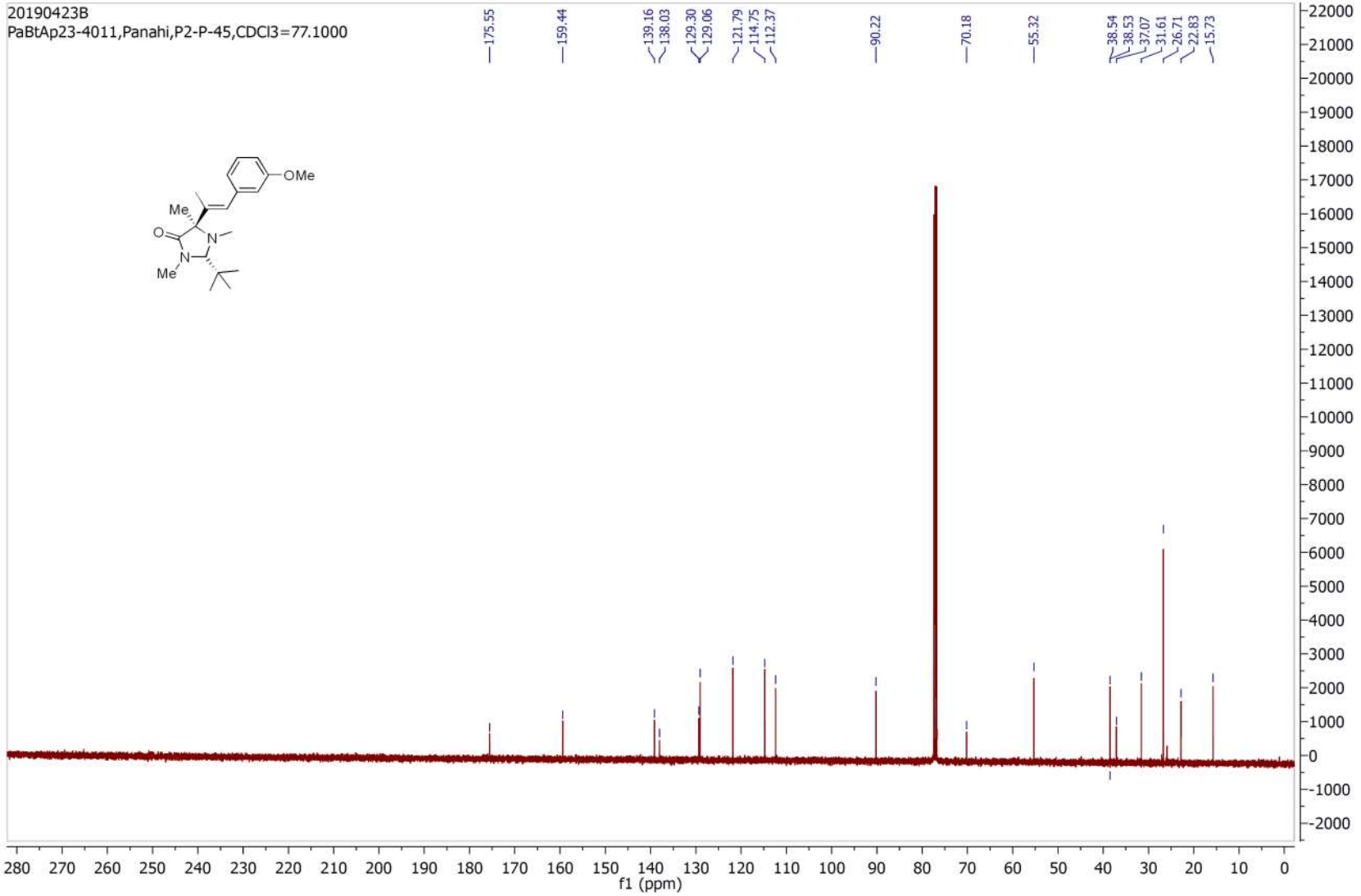
11.3.3. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(m-tolyl)prop-1-en-2-yl)imidazolidin-4-one (3c)



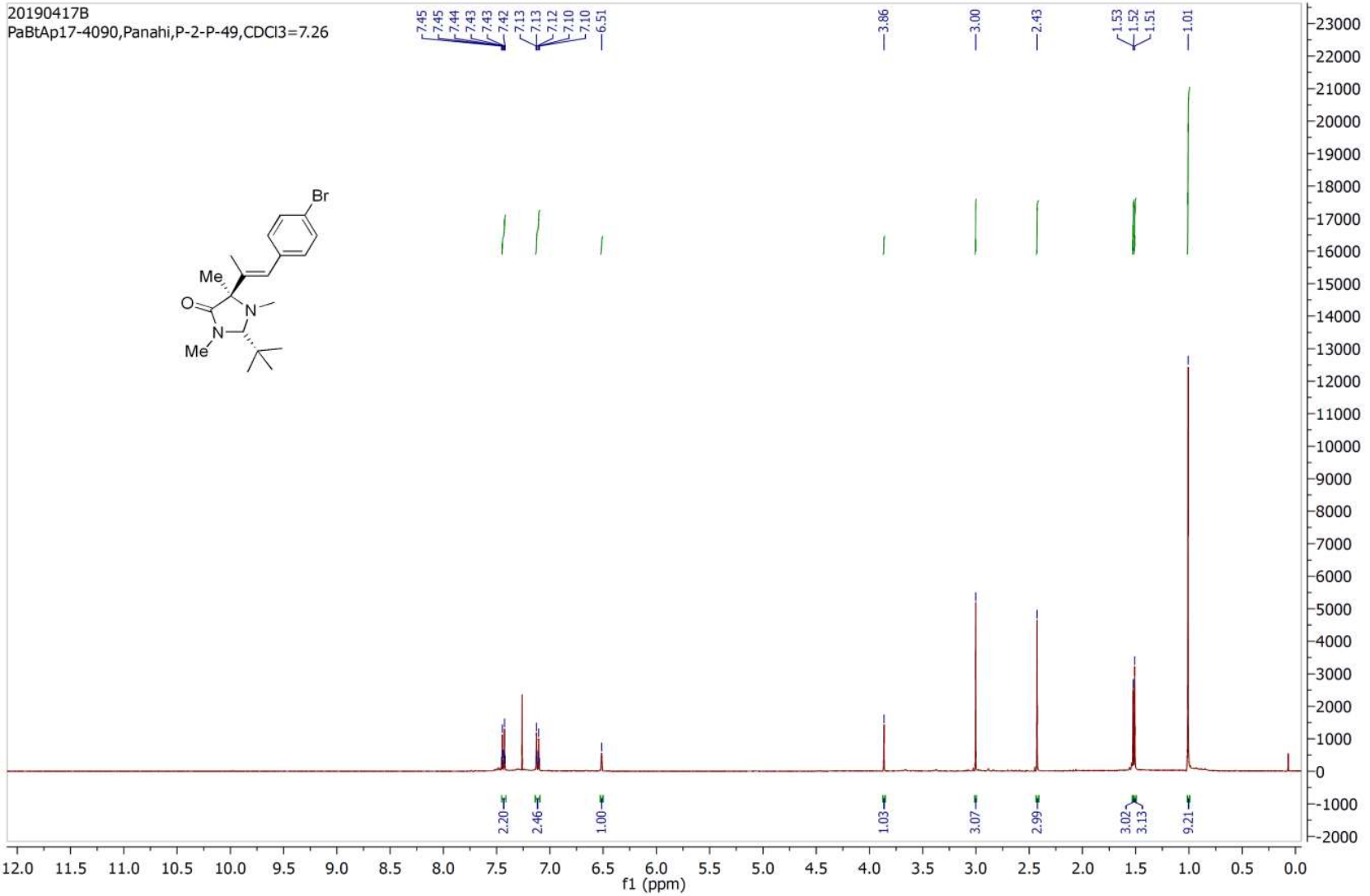

20190417B
PaBtAp17-4071,Panahi,P2-P-44,CDCl3=77.1000
137.66
130.03
128.02
127.46
126.27
90.38
38.48
31.65
26.70
22.84
21.48
15.75
Me
Me
O
N
N
Me
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

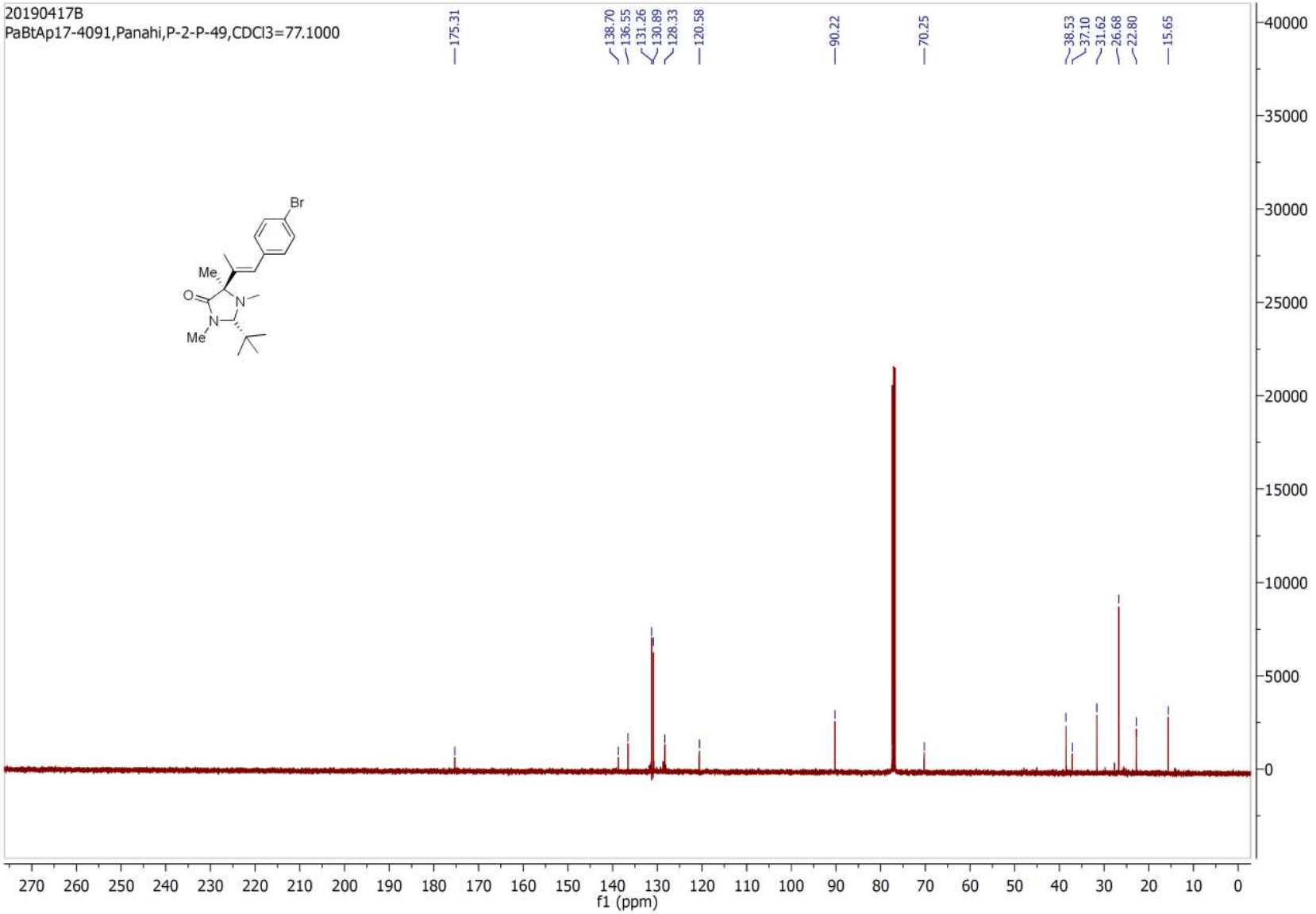
11.3.4. (2R,5R)-2-(tert-butyl)-5-((E)-1-(3-methoxyphenyl)prop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3d)



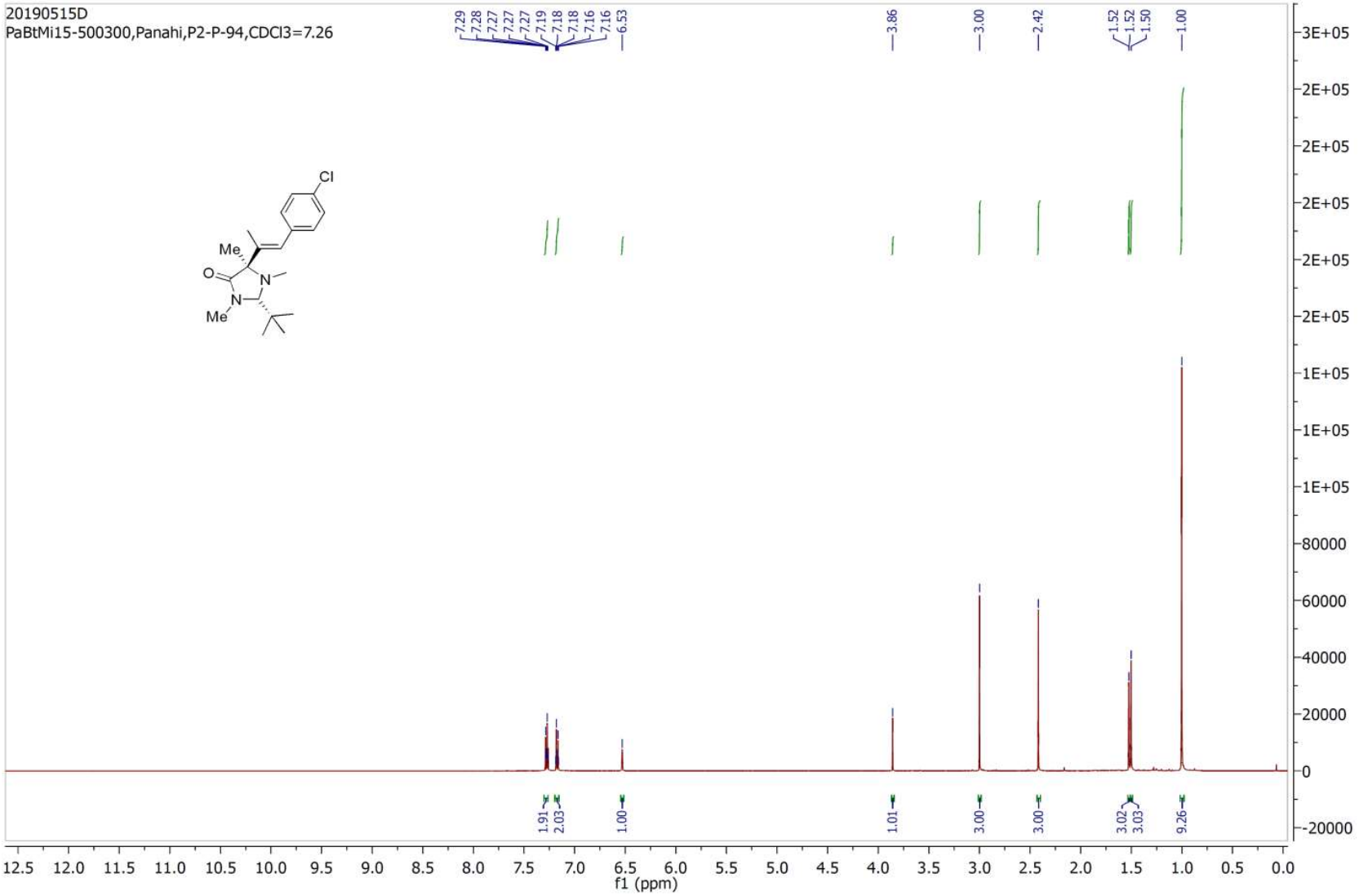

20190423B
PaBtAp23-4011,Panahi,P2-P-45,CDCl3=77.1000
175.55
159.44
139.16
138.03
129.30
129.06
121.79
114.75
112.37
90.22
70.18
55.32
38.54
38.53
37.07
31.61
26.71
22.83
15.73
OMe
Me
O
N
N
Me
f1 (ppm)

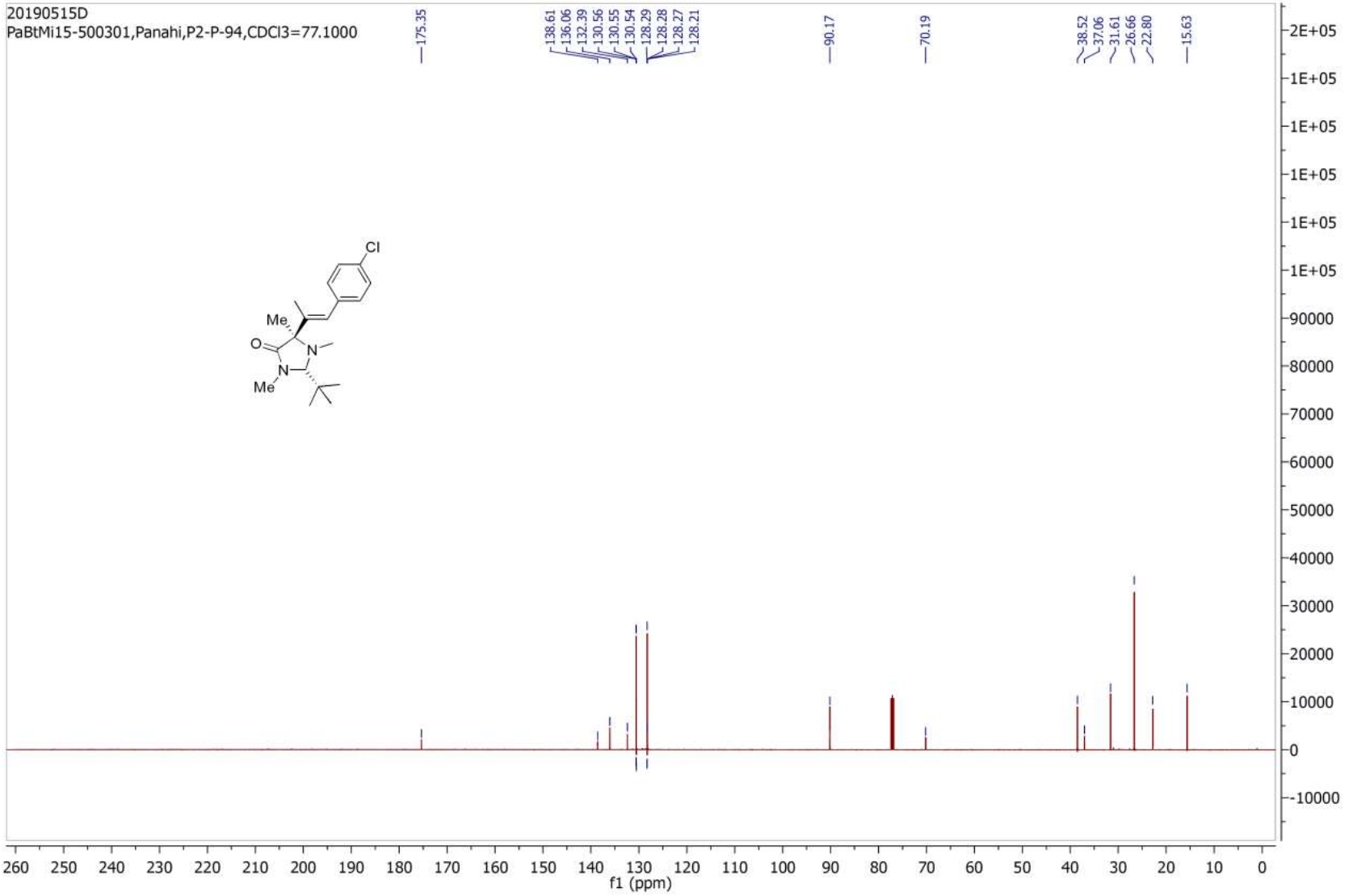
11.3.5. (2R,5R)-5-((E)-1-(4-bromophenyl)prop-1-en-2-yl)-2-(tert-butyl)-1,3,5-trimethylimidazolidin-4-one (3e)



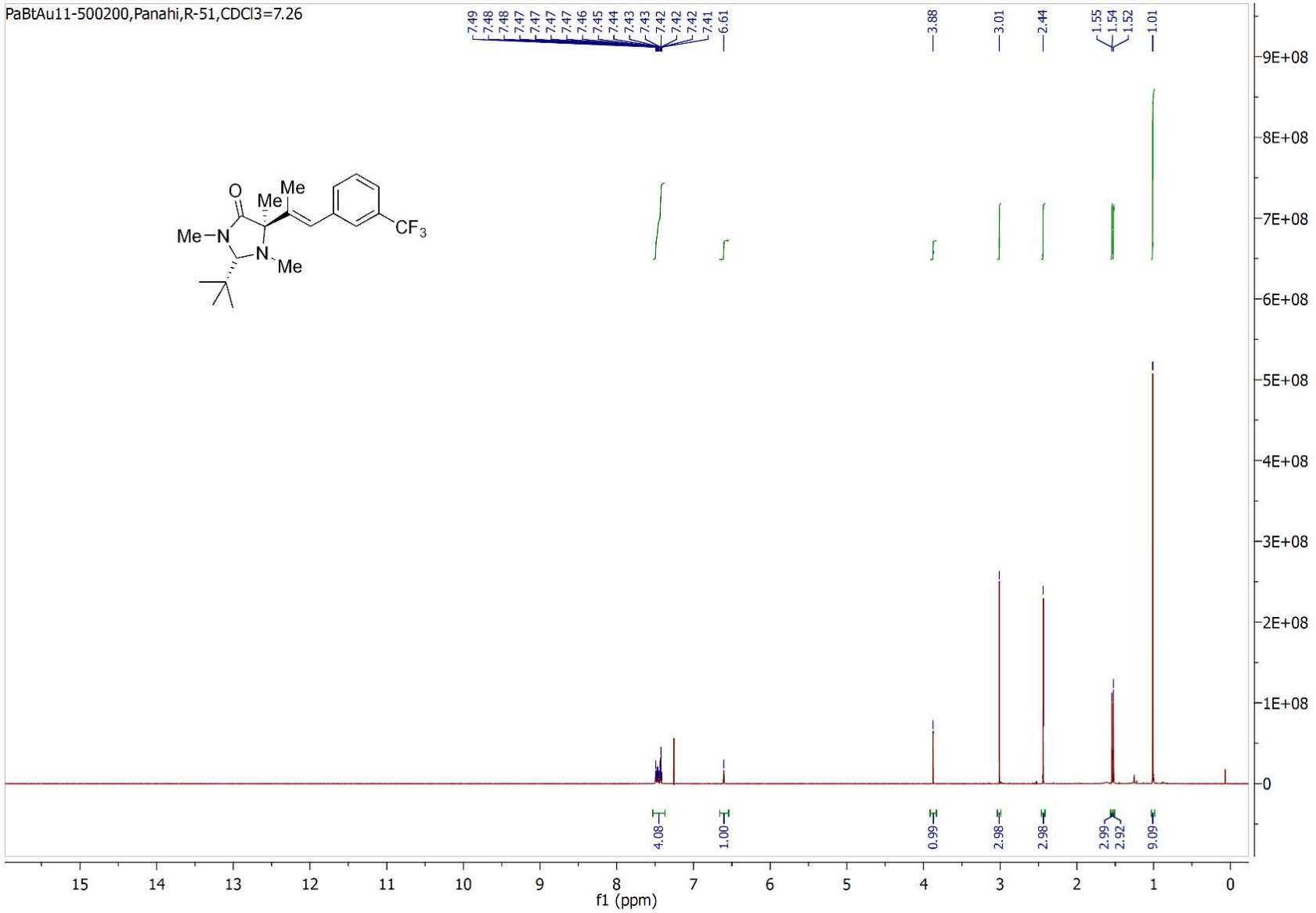

20190417B
PaBtAp17-4091,Panahi,P-2-P-49,CDCl3=77.1000
175.31
138.70
136.55
131.26
130.89
128.33
120.58
90.22
70.25
38.53
37.10
31.62
26.68
22.80
15.65
Br
Me
O
N
N
Me
40000
35000
30000
25000
20000
15000
10000
5000
0
270 260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

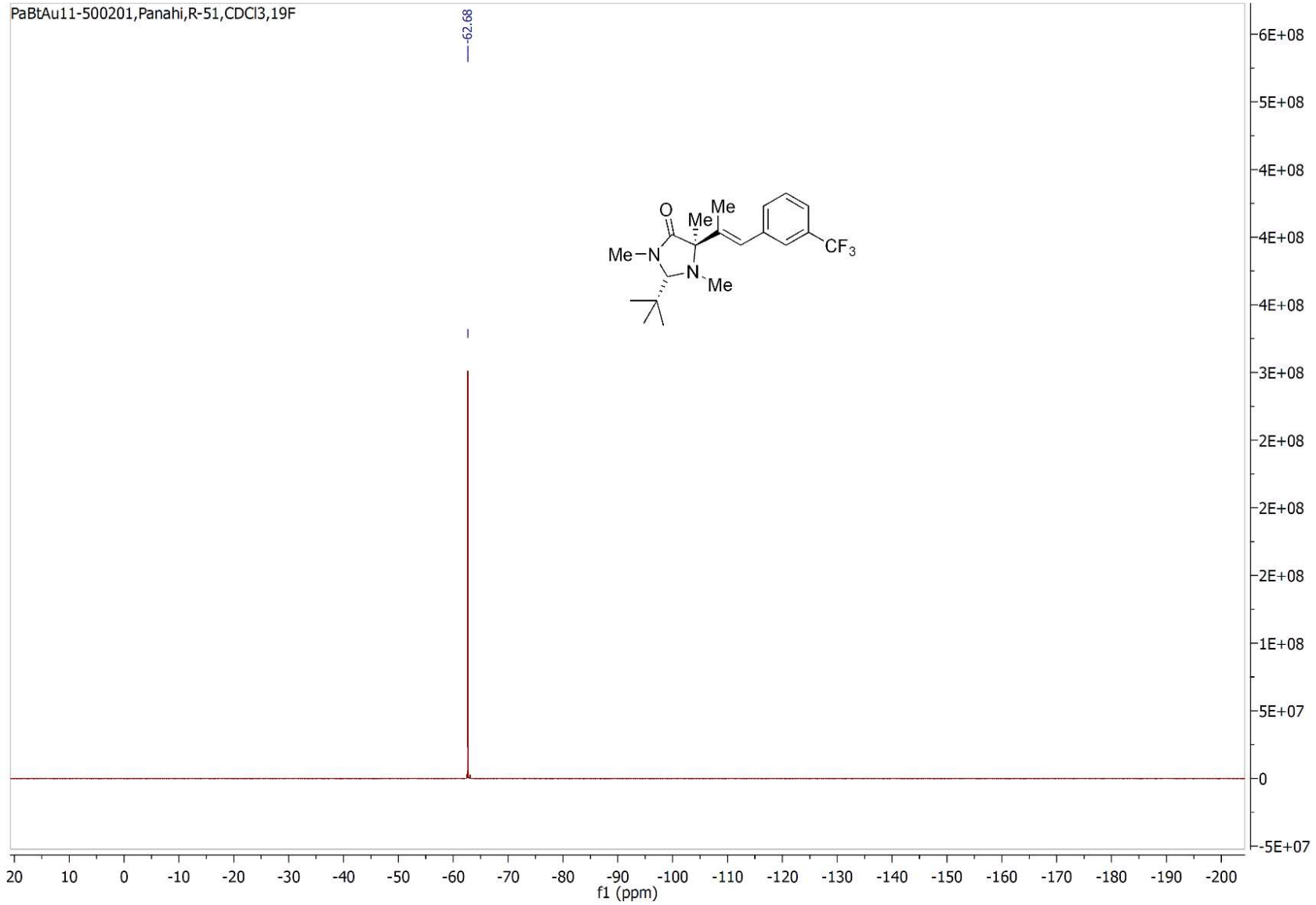
11.3.6. (2R,5R)-2-(tert-butyl)-5-((E)-1-(4-chlorophenyl)prop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3f)

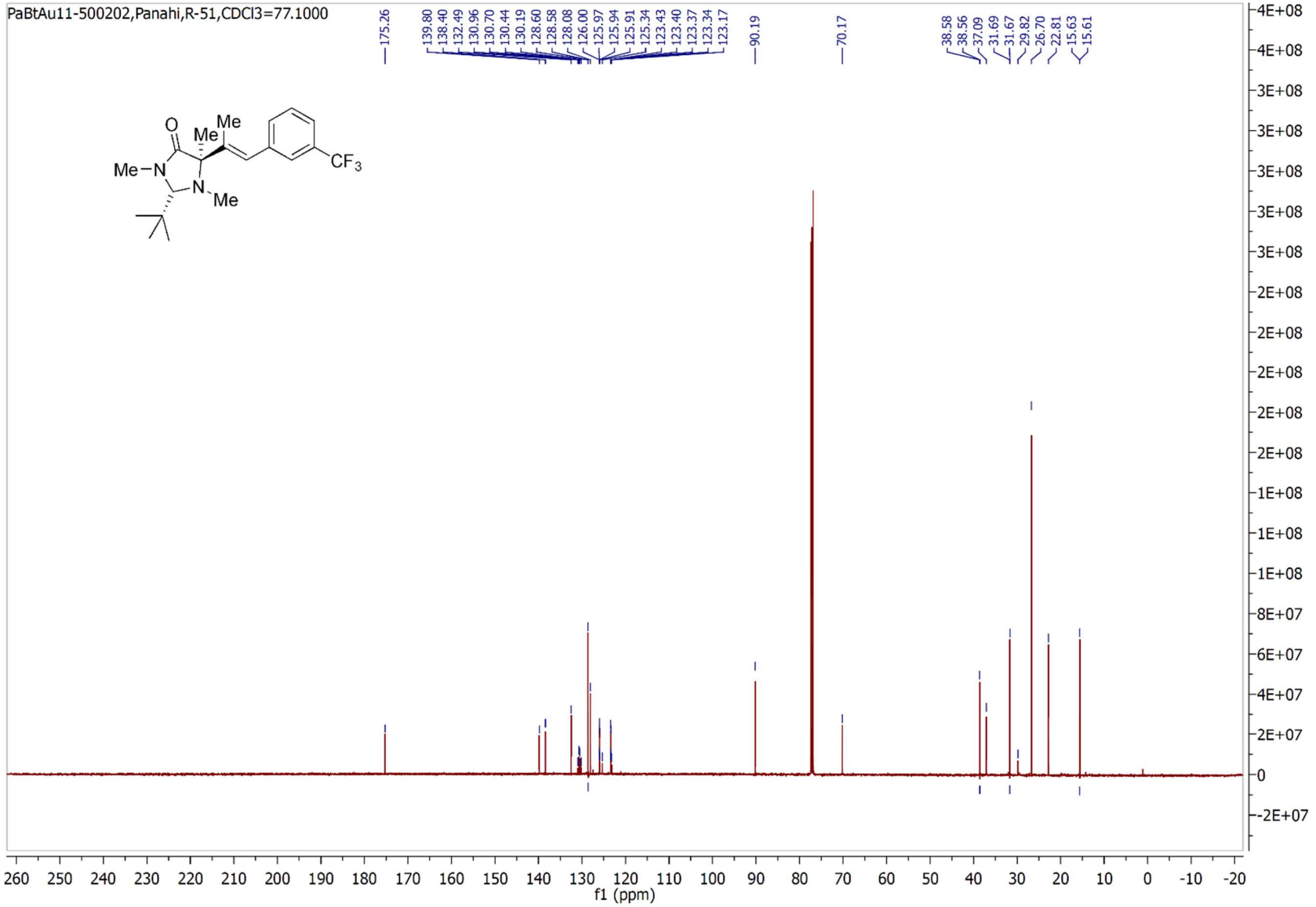



20190515D
PaBtMi15-500301,Panahi,P2-P-94,CDCl3=77.1000
175.35
138.61
136.06
132.39
130.56
130.55
130.54
128.29
128.28
128.27
128.21
90.17
70.19
38.52
37.06
31.61
26.66
22.80
15.63
Cl
Me
O
N
N
Me
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

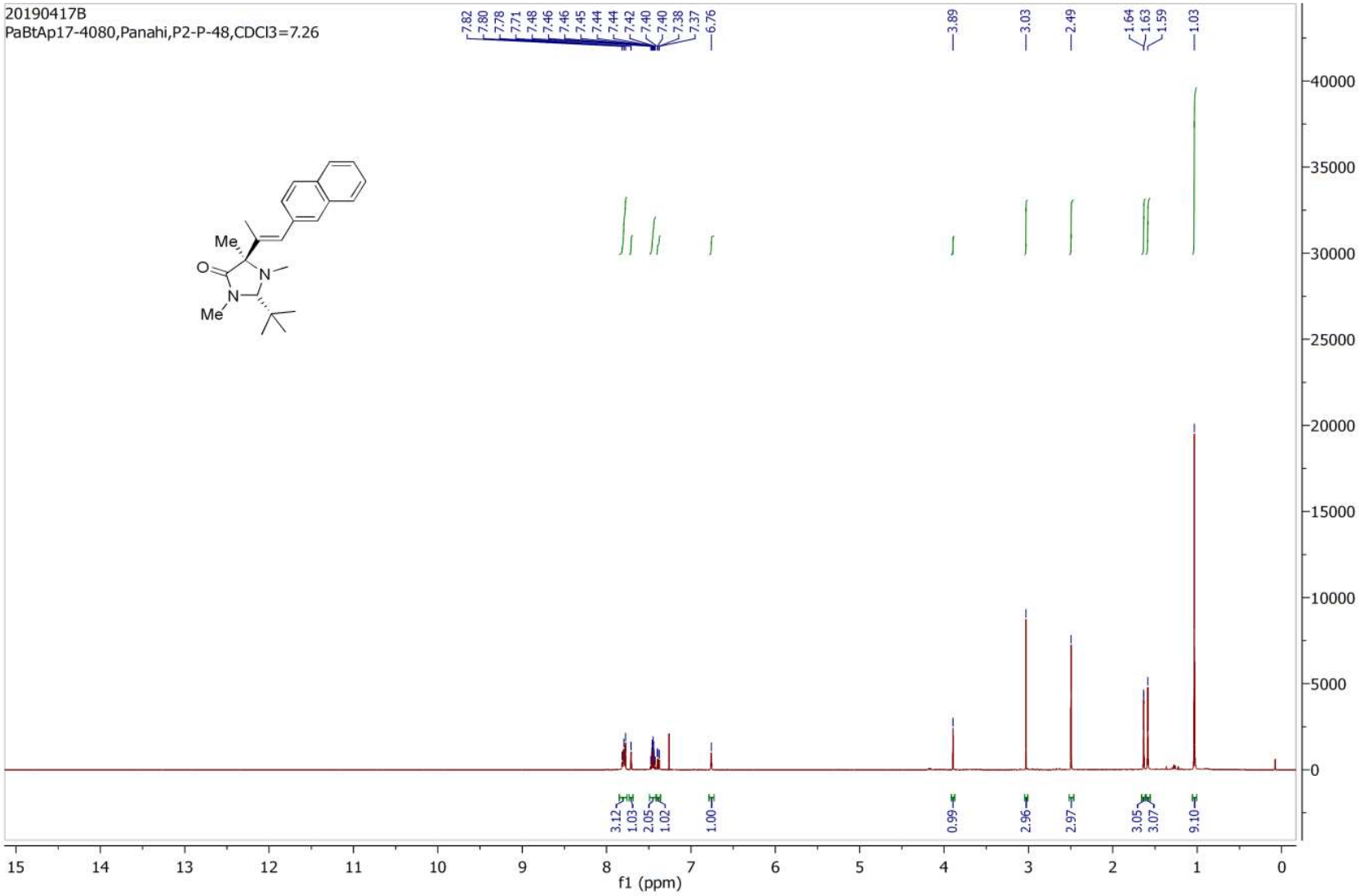
11.3.7. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(3-(trifluoromethyl)phenyl)prop-1-en-2-yl)imidazolidin-4-one (3g)

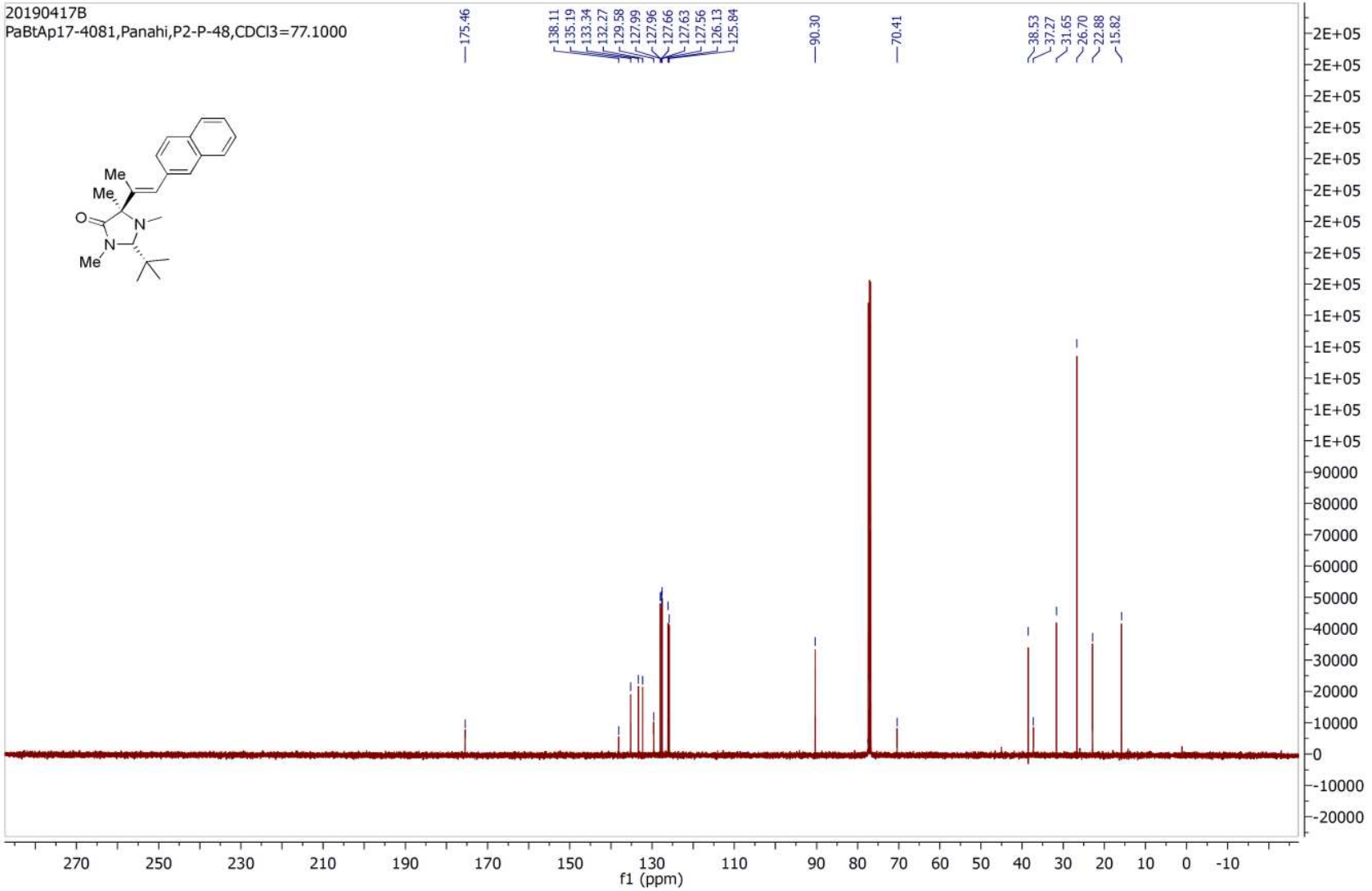



PaBtAu11-500201,Panahi,R-51,CDCl3,19F
-62.68
O
Me
Me
Me–N
N
Me
CF3
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200
f1 (ppm)

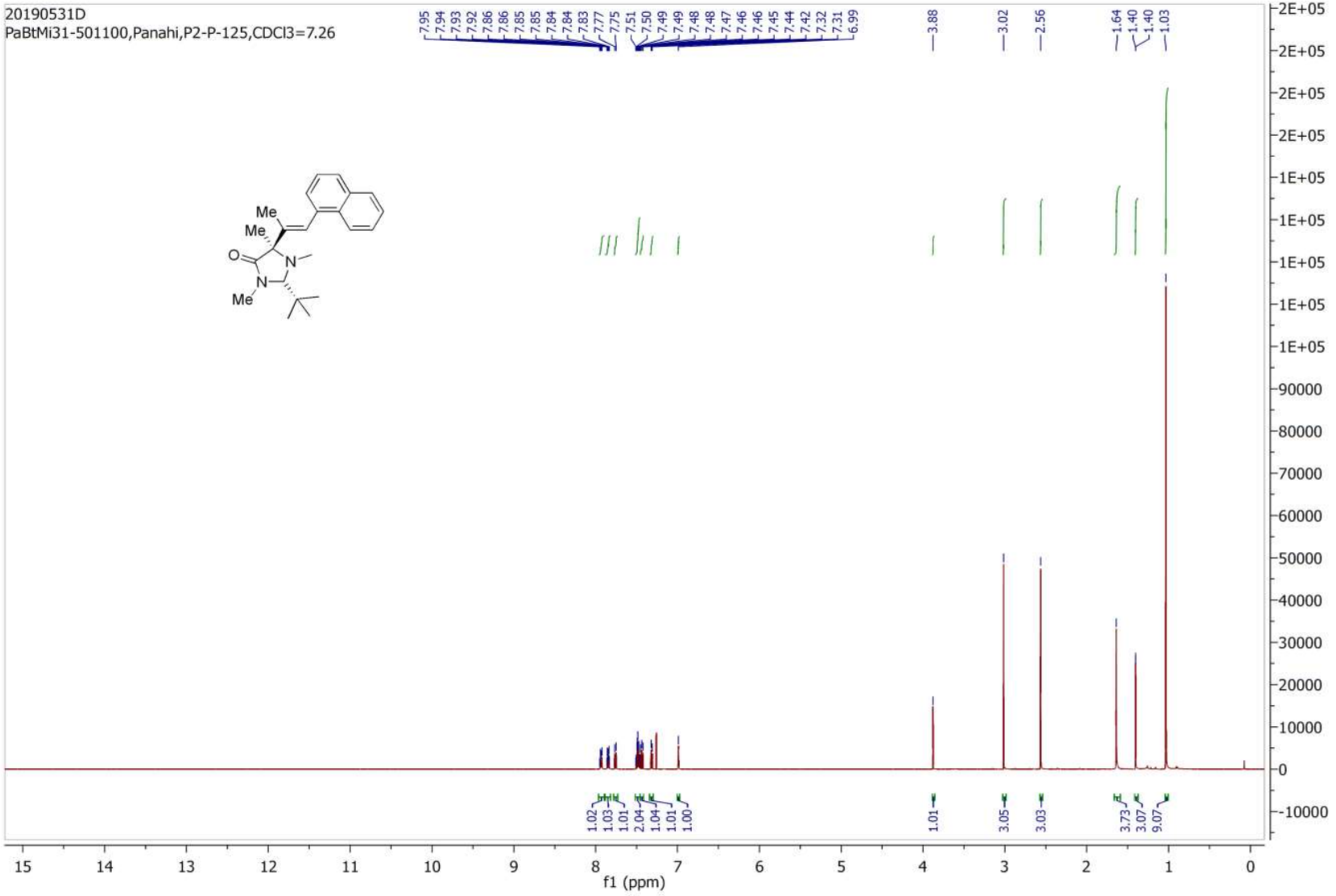

PaBtAu11-500202,Panahi,R-51,CDCl3=77.1000
175.26
139.80
138.40
132.49
130.96
130.70
130.44
130.19
128.60
128.58
128.08
126.00
125.97
125.94
125.91
125.34
123.43
123.40
123.37
123.34
123.17
90.19
70.17
38.58
38.56
37.09
31.69
31.67
29.82
26.70
22.81
15.63
15.61
O
Me
Me
Me–N
N
Me
CF3
f1 (ppm)

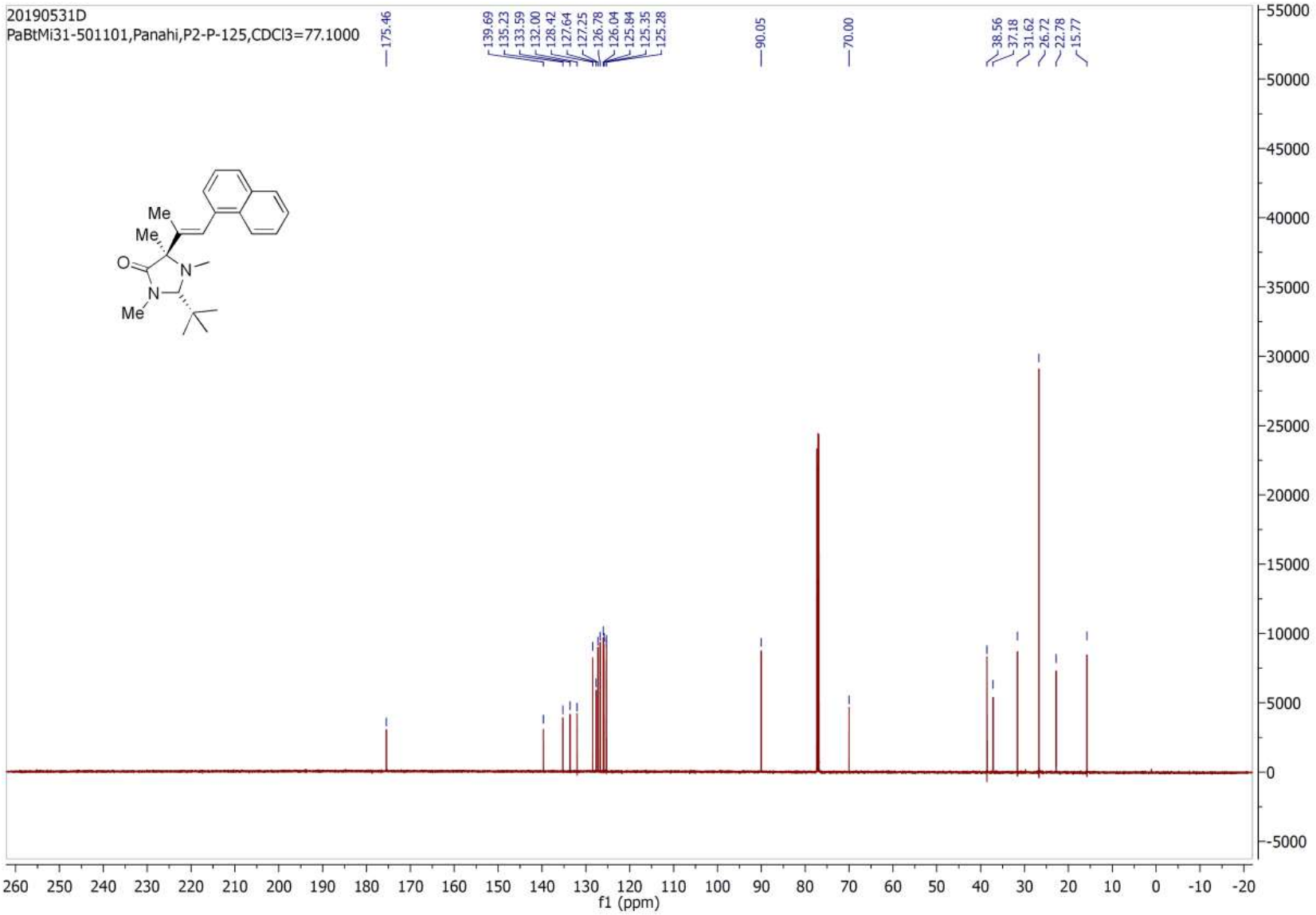
11.3.8. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(naphthalen-2-yl)prop-1-en-2-yl)imidazolidin-4-one (3h)



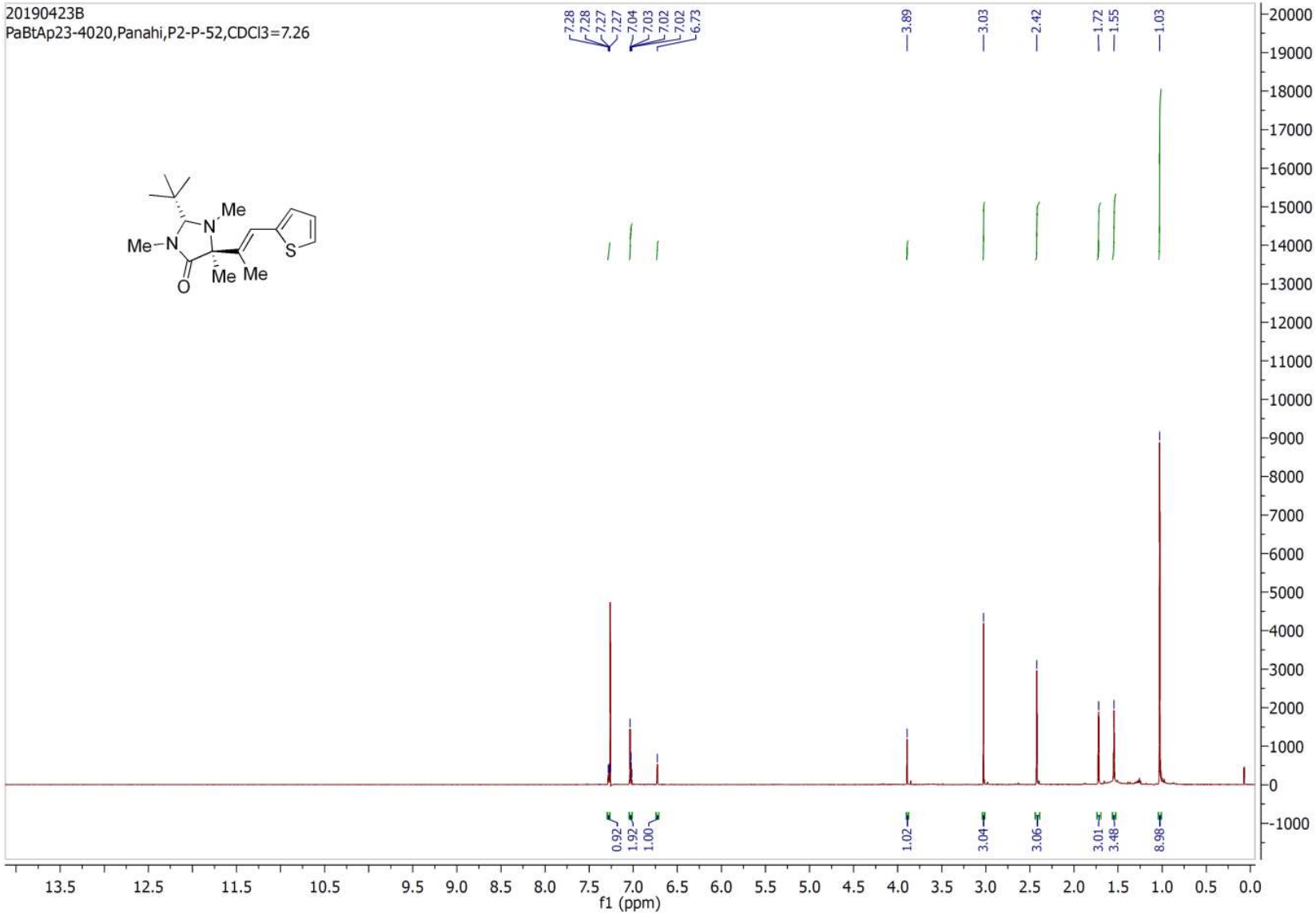

20190417B
PaBtAp17-4081,Panahi,P2-P-48,CDCl3=77.1000
175.46
138.11
135.19
133.34
132.27
129.58
127.99
127.96
127.66
127.63
127.56
126.13
125.84
90.30
70.41
38.53
37.27
31.65
26.70
22.88
15.82
Me
Me
O
N
N
Me
f1 (ppm)

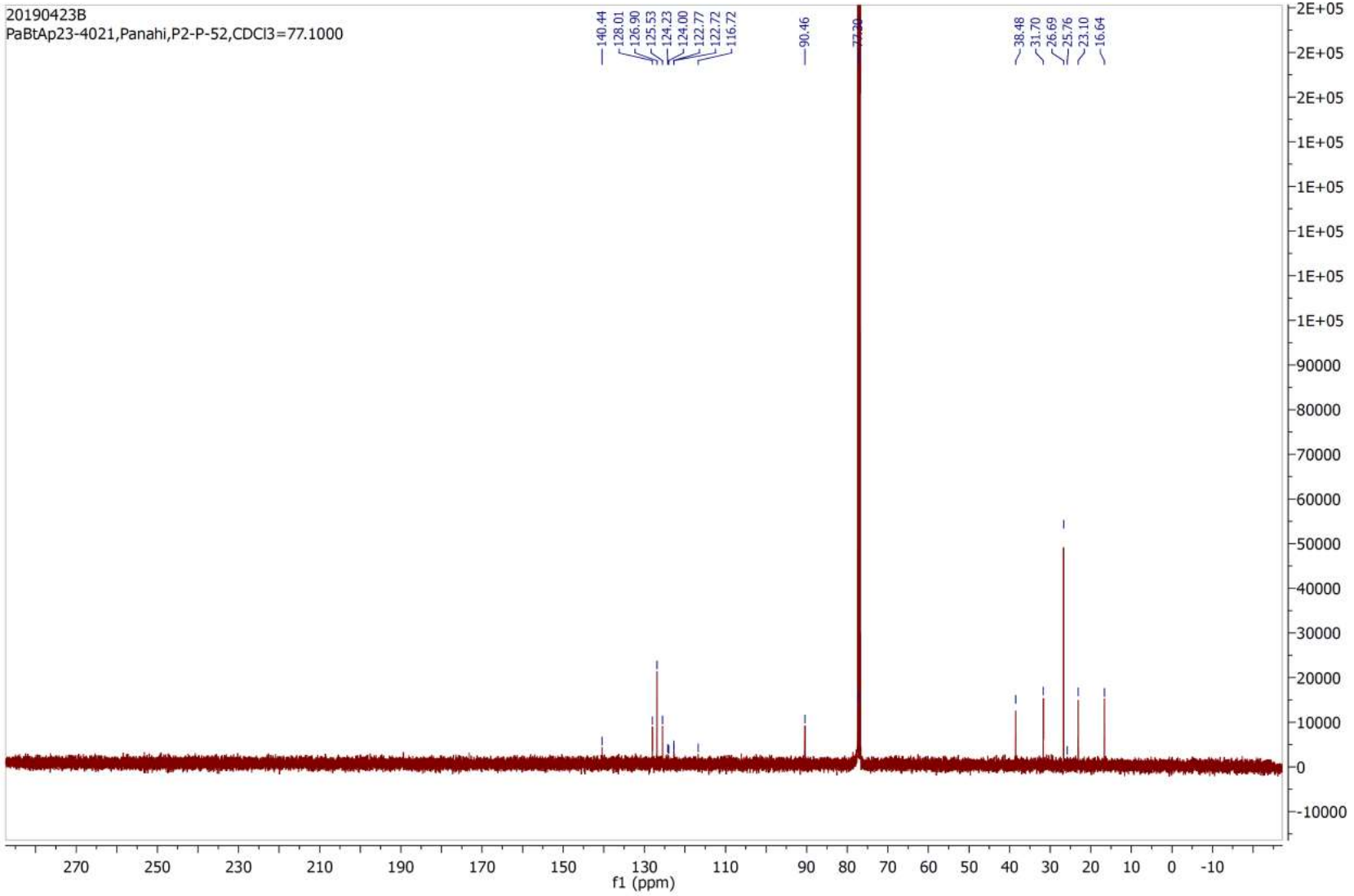
11.3.9. (2*R*,5*R*)-2-(*tert*-butyl)-1,3,5-trimethyl-5-((*E*)-1-(naphthalen-1-yl)prop-1-en-2-yl)imidazolidin-4-one (3i)



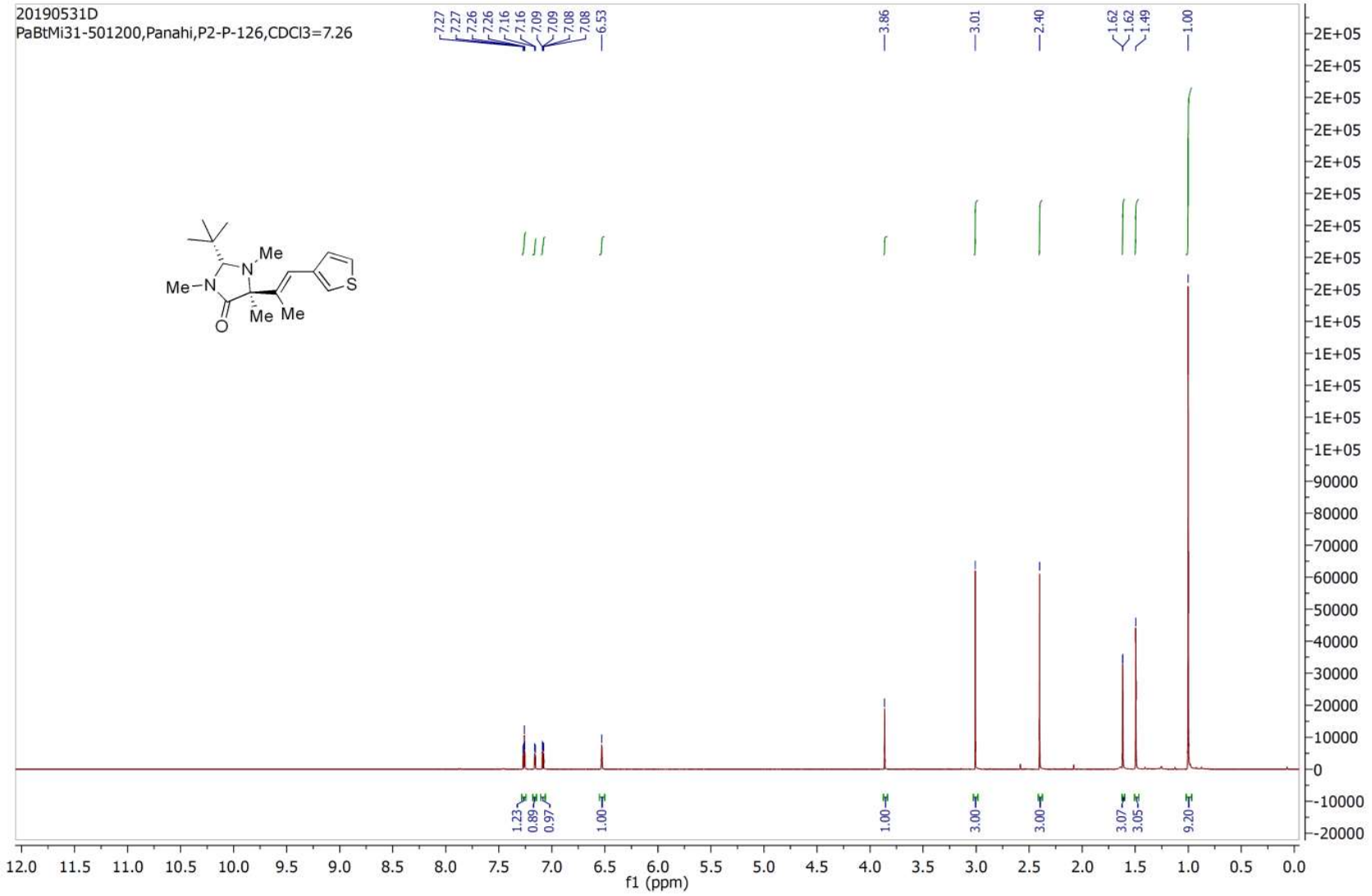

20190531D
PaBtMi31-501101,Panahi,P2-P-125,CDCl3=77.1000
175.46
139.69
135.23
133.59
132.00
128.42
127.64
127.25
126.78
126.04
125.84
125.35
125.28
90.05
70.00
38.56
37.18
31.62
26.72
22.78
15.77
Me
Me
O
N
N
Me
f1 (ppm)

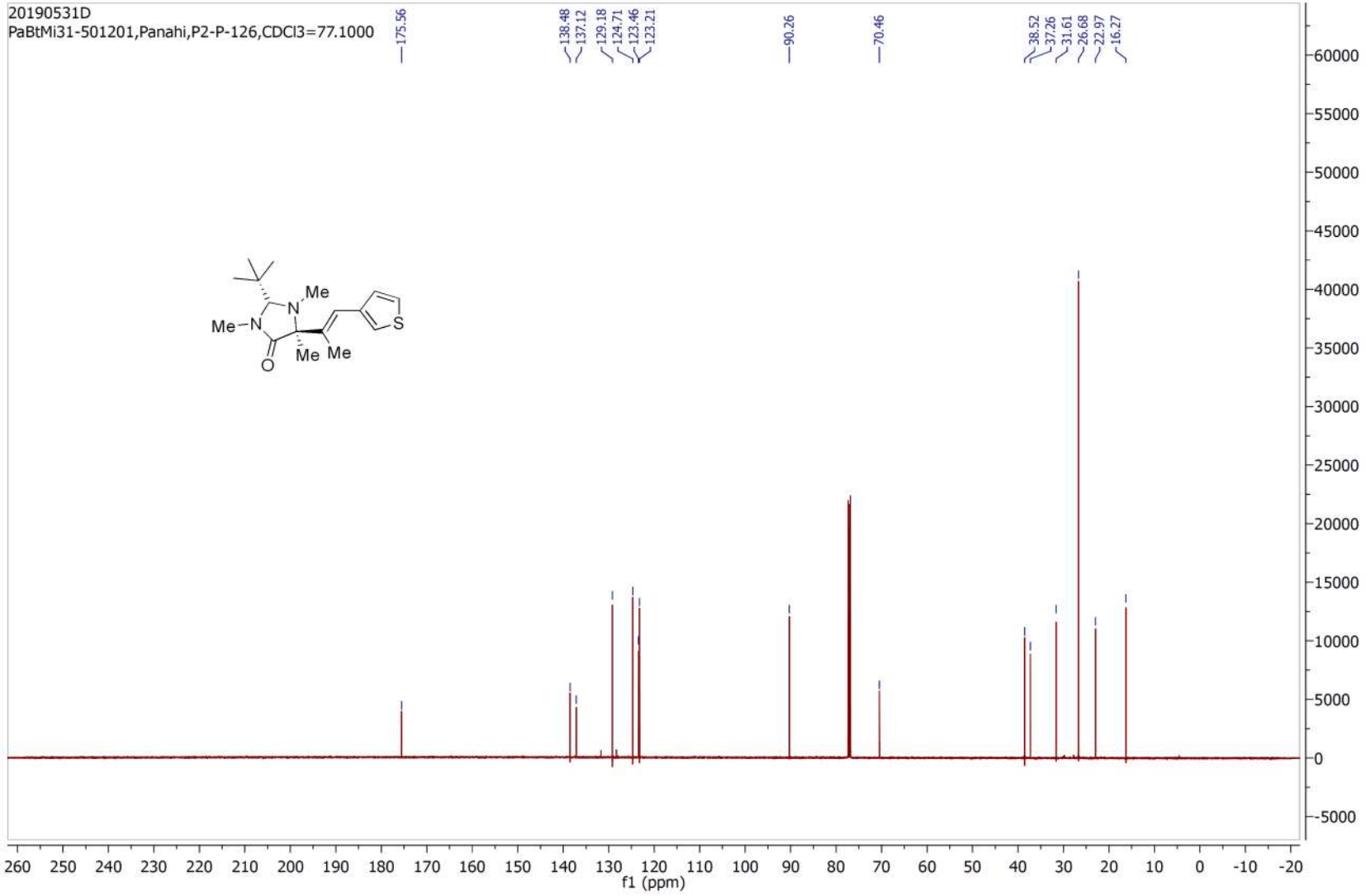
11.3.10. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(thiophen-2-yl)prop-1-en-2-yl)imidazolidin-4-one (3j)



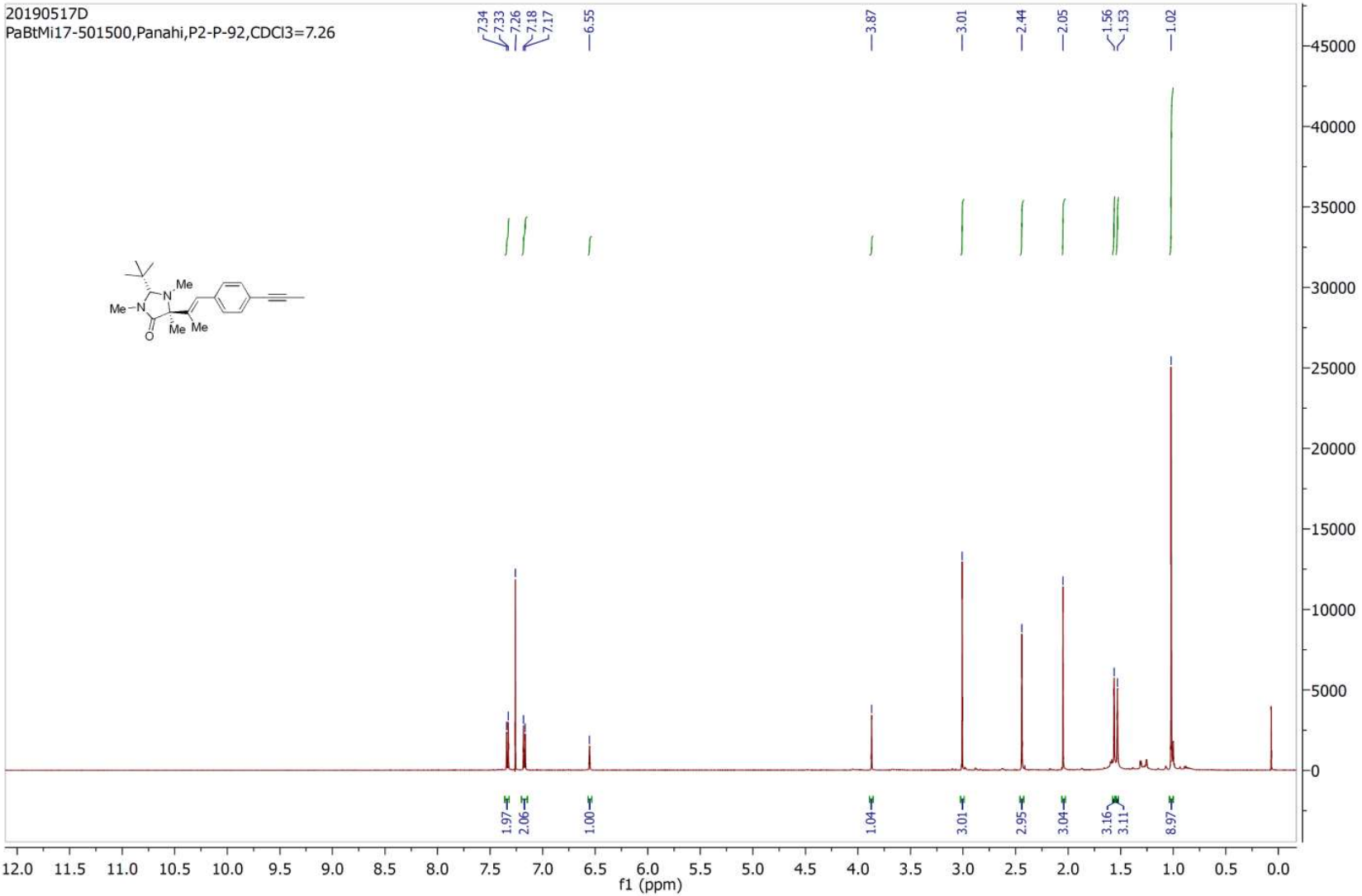

20190423B
PaBtAp23-4021,Panahi,P2-P-52,CDCl3=77.1000
140.44
128.01
126.90
125.53
124.23
124.00
122.77
122.72
116.72
90.46
77.20
38.48
31.70
26.69
25.76
23.10
16.64
2E+05
2E+05
2E+05
1E+05
1E+05
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

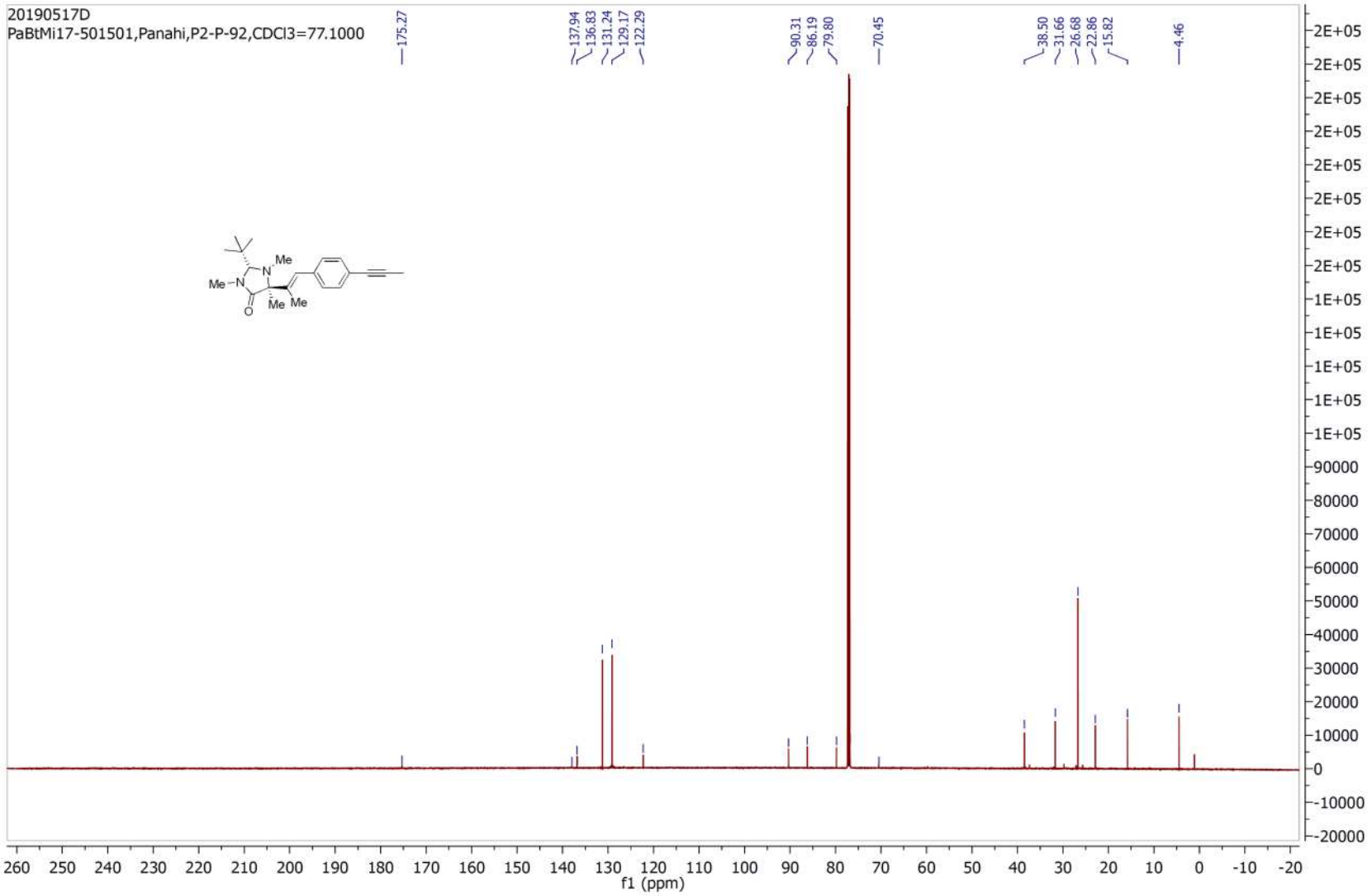
11.3.11. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(thiophen-3-yl)prop-1-en-2-yl)imidazolidin-4-one(3k)



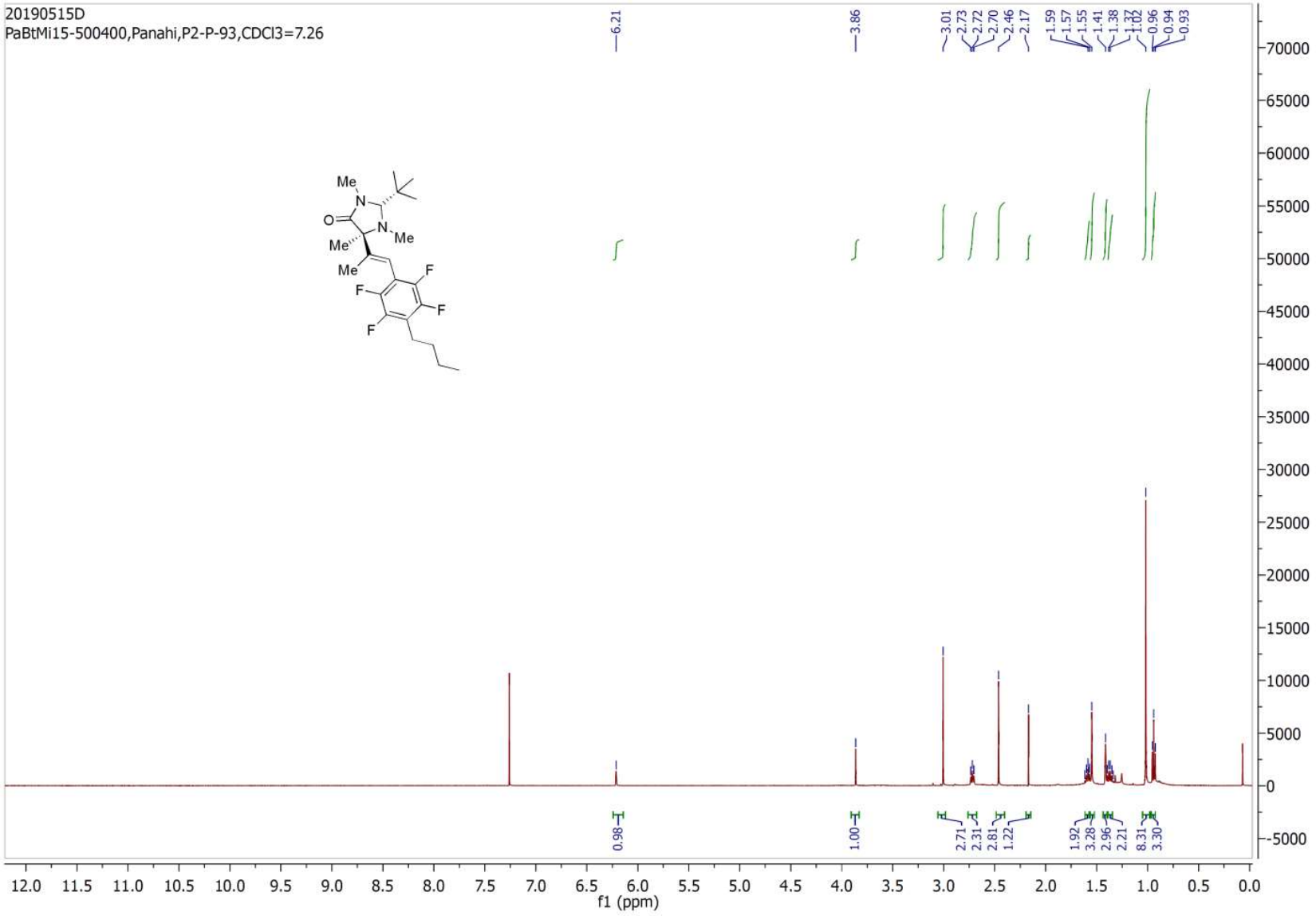

20190531D
PaBtMi31-501201,Panahi,P2-P-126,CDCl3=77.1000
175.56
138.48
137.12
129.18
124.71
123.46
123.21
90.26
70.46
38.52
37.26
31.61
26.68
22.97
16.27
Me
N
Me
N
S
Me
Me
O
f1 (ppm)

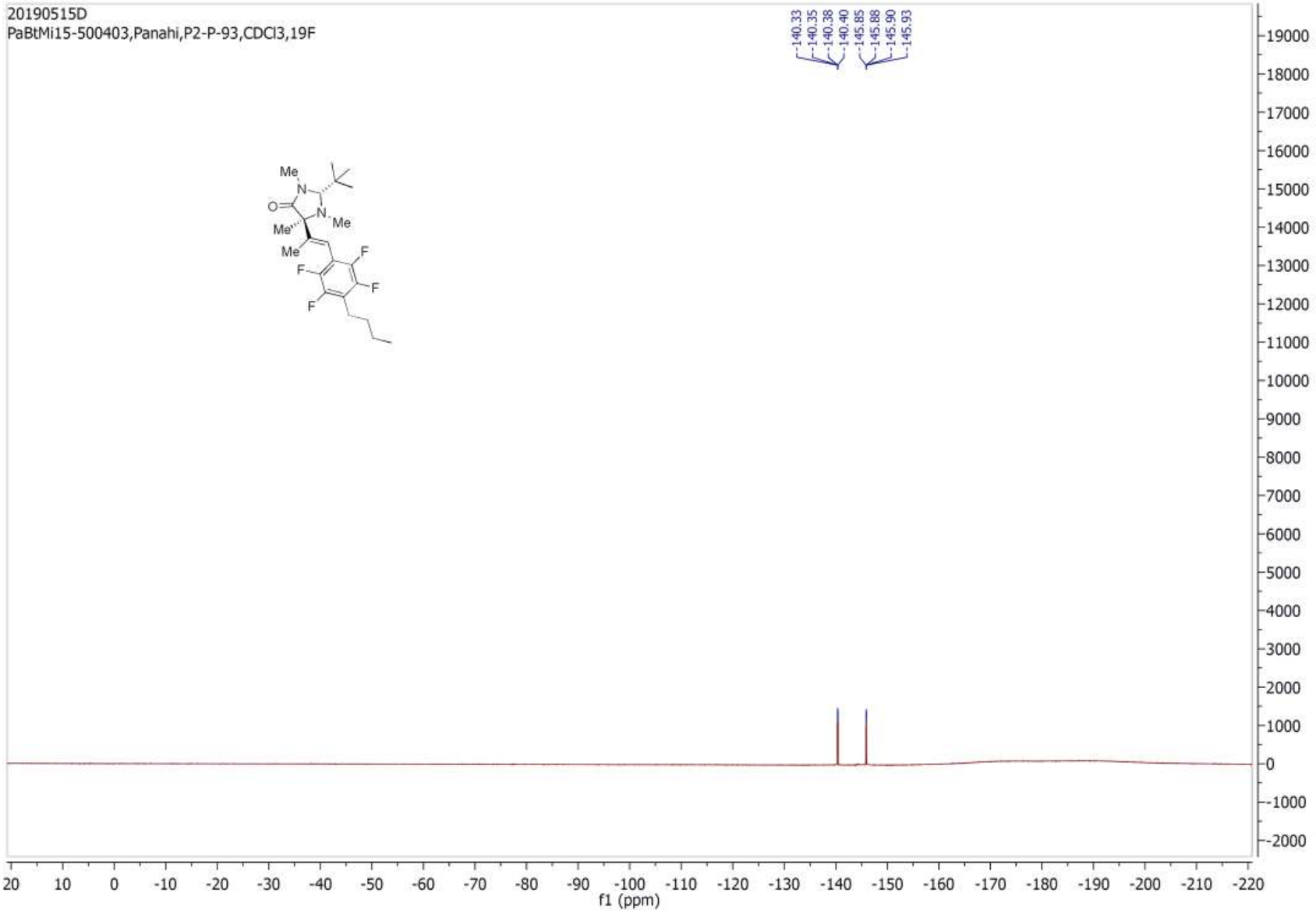
11.3.12. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(4-(prop-1-yn-1-yl)phenyl)prop-1-en-2-yl)imidazolidin-4-one(3l)

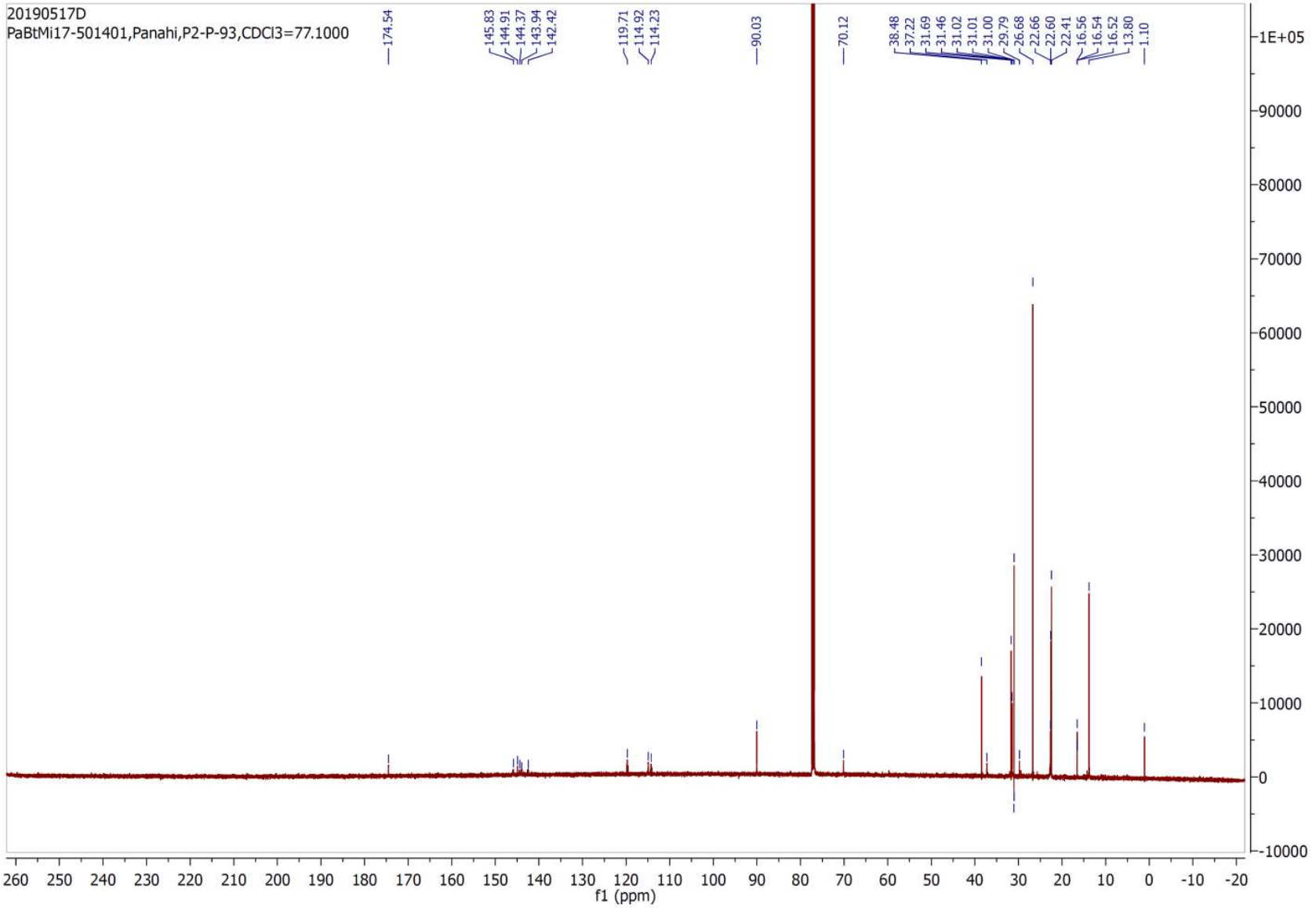


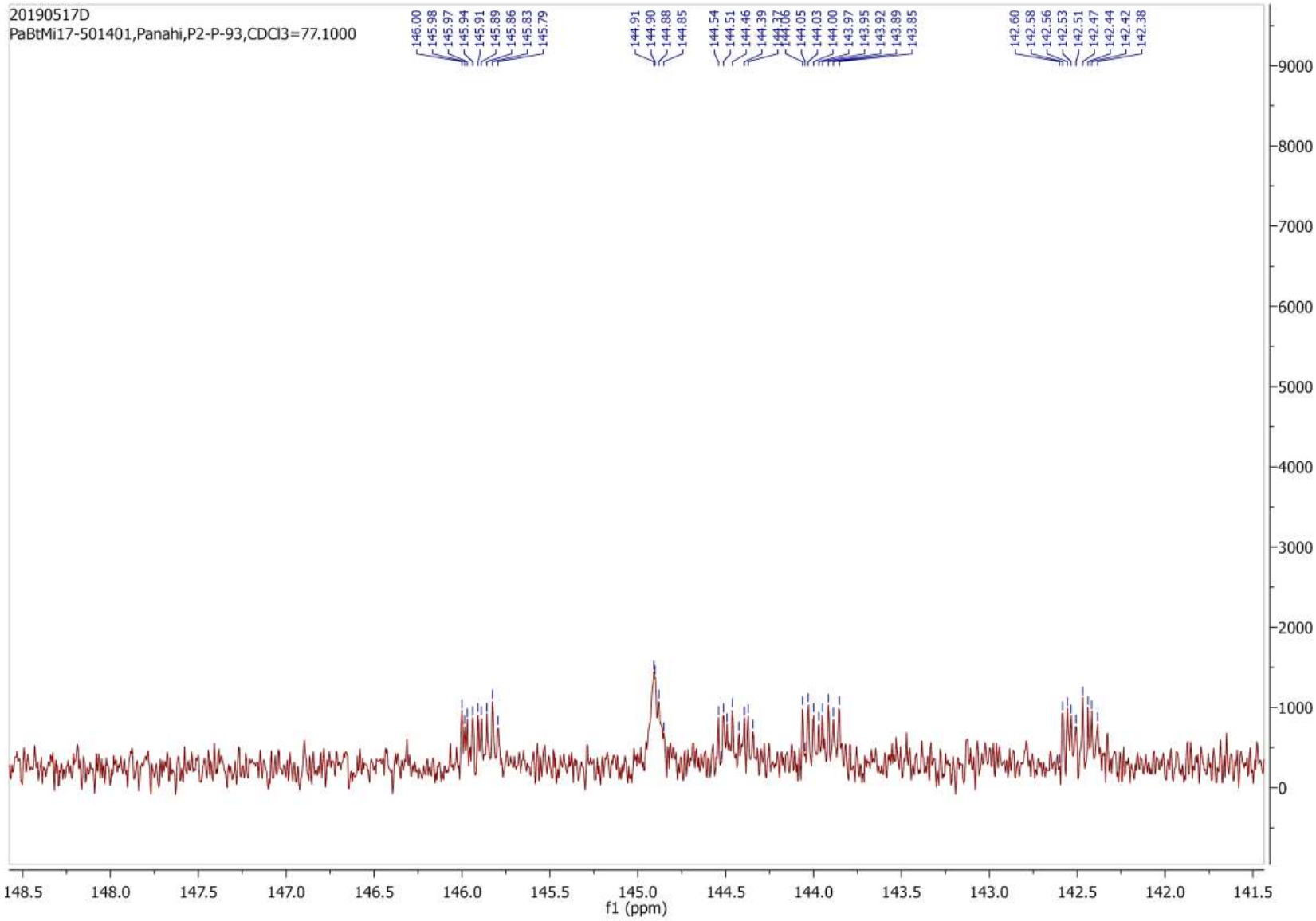

20190517D
PaBtMi17-501501,Panahi,P2-P-92,CDCl3=77.1000
175.27
137.94
136.83
131.24
129.17
122.29
90.31
86.19
79.80
70.45
38.50
31.66
26.68
22.86
15.82
4.46
Me
Me
Me
Me
O
f1 (ppm)

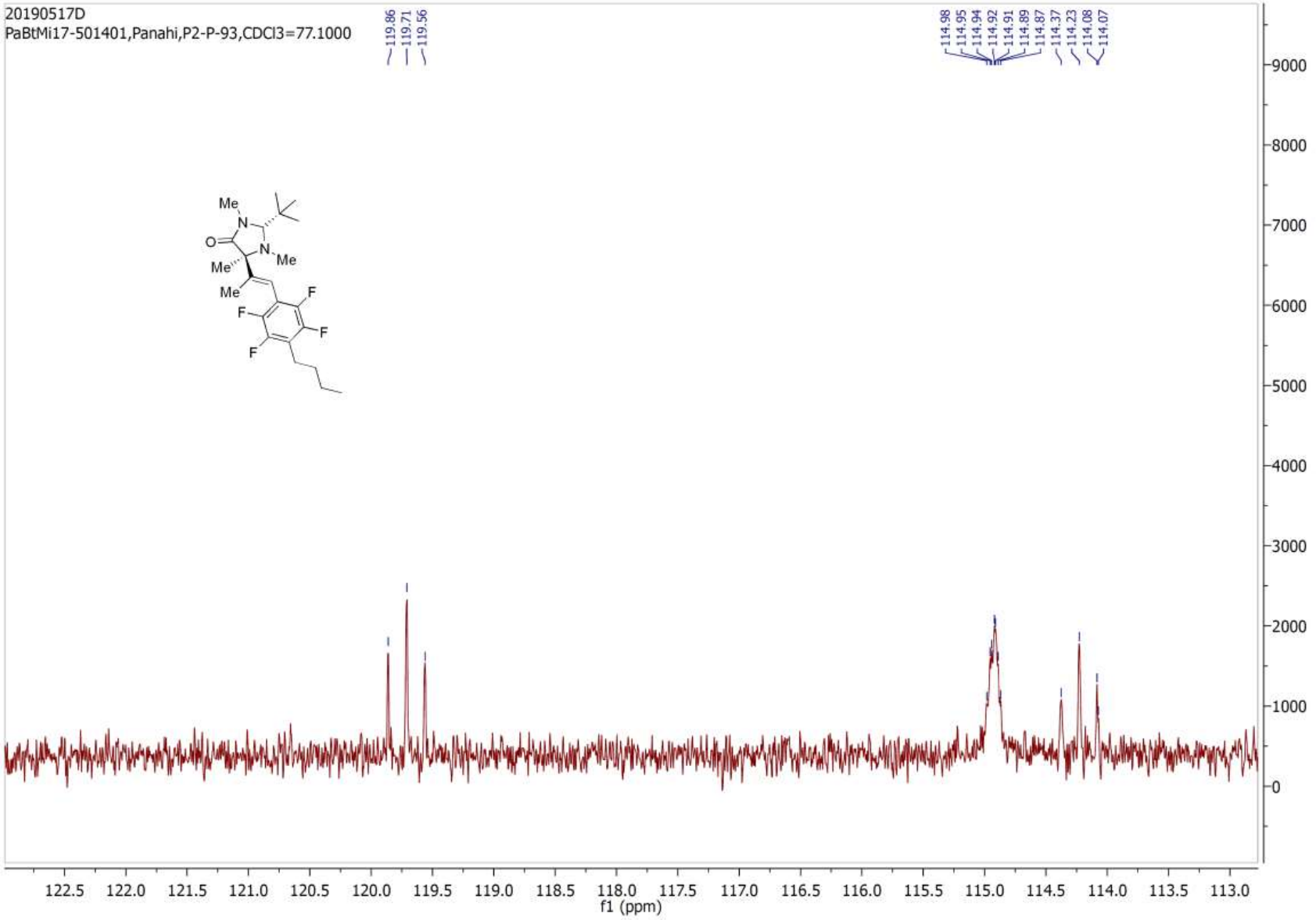
11.3.13. (2R,5R)-2-(tert-butyl)-1,3,5-trimethyl-5-((E)-1-(4-(prop-1-yn-1-yl)phenyl)prop-1-en-2-yl)imidazolidin-4-one(3m)



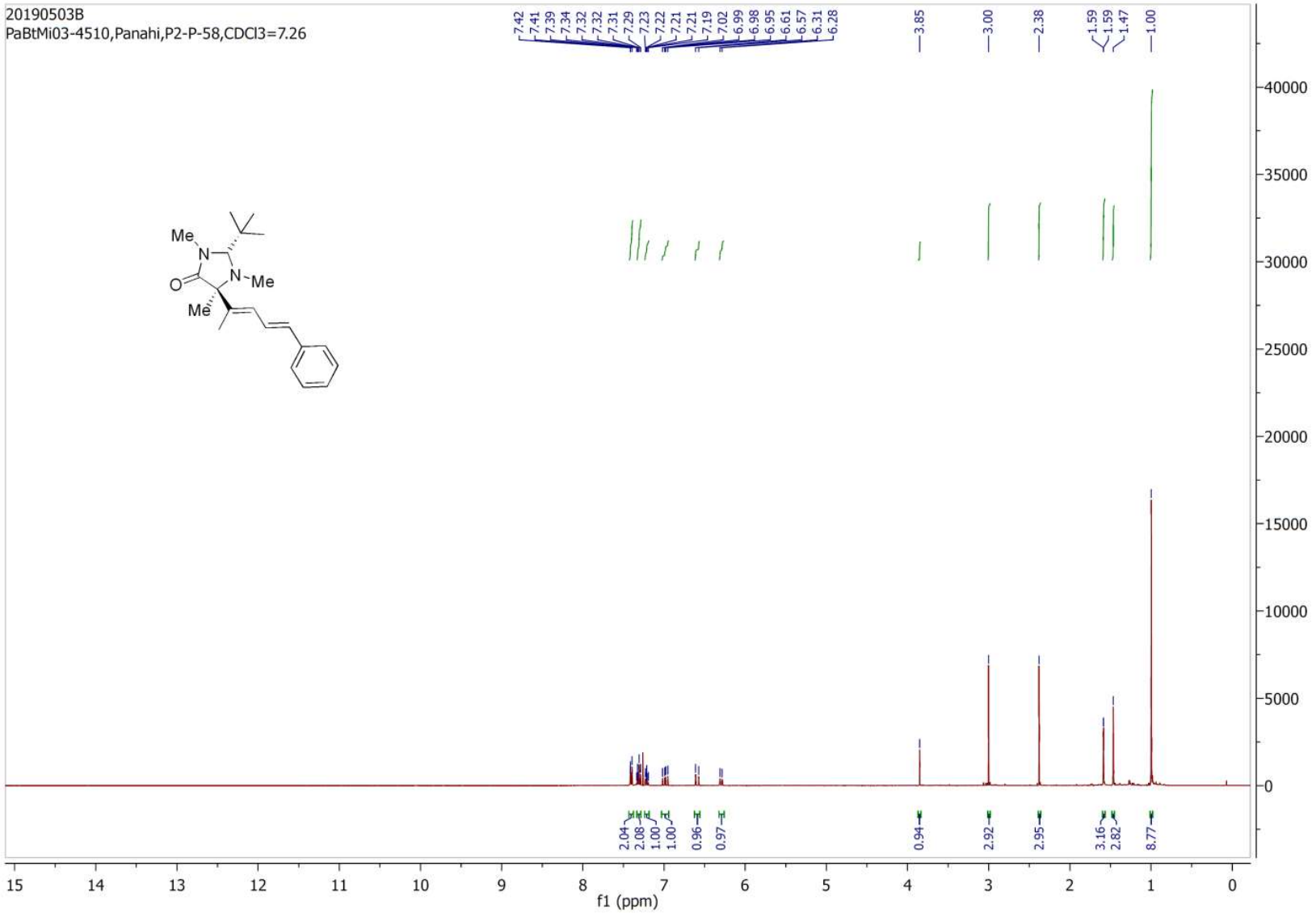

20190515D
PaBtMi15-500403,Panahi,P2-P-93,CDCl3,19F
140.33
140.35
140.38
140.40
145.85
145.88
145.90
145.93
Me
N
O
N
Me
Me
Me
F
F
F
F
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

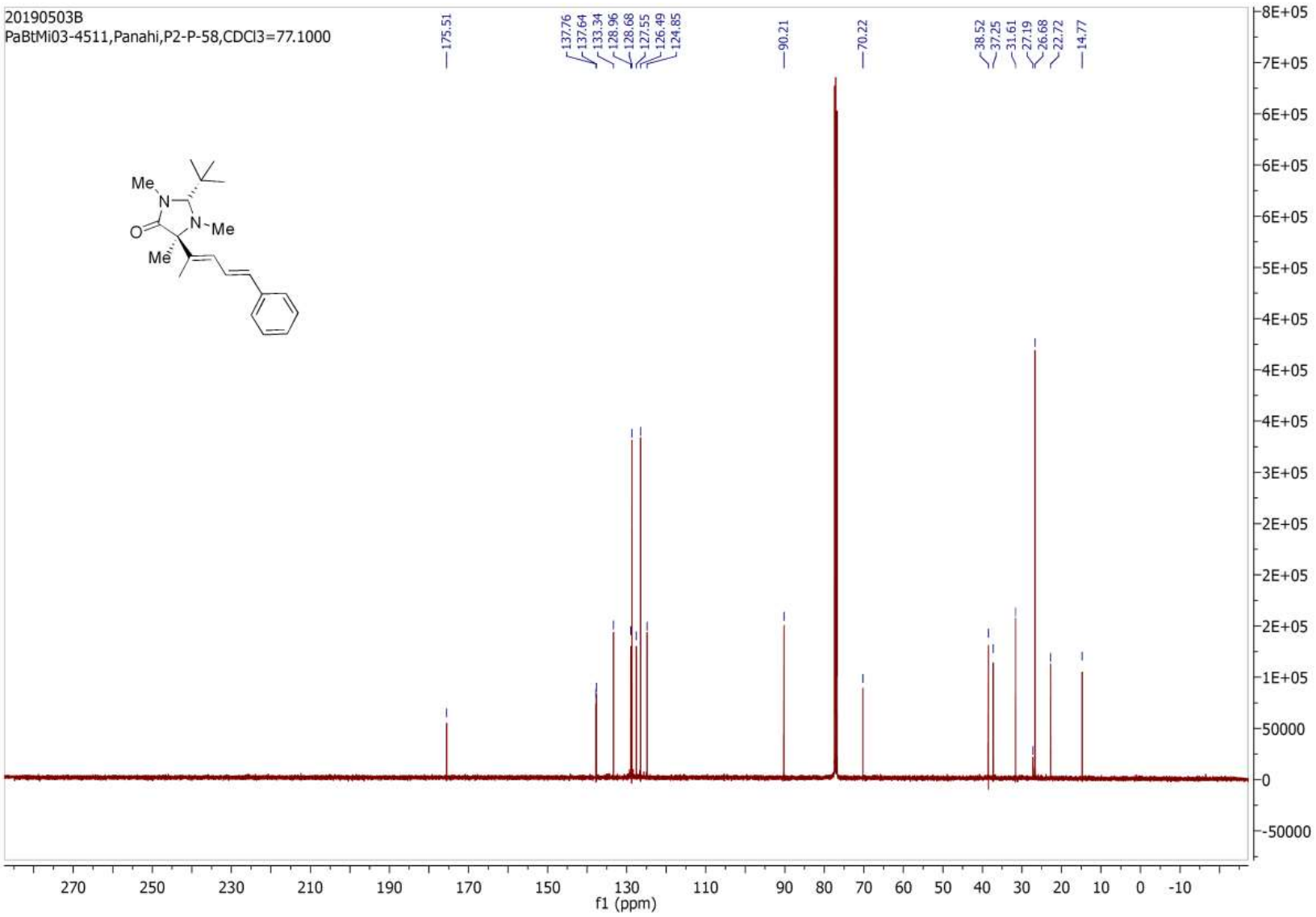

20190517D
PaBtMi17-501401,Panahi,P2-P-93,CDCl3=77.1000
174.54
145.83
144.91
144.37
143.94
142.42
119.71
114.92
114.23
90.03
70.12
38.48
37.22
31.69
31.46
31.02
31.01
31.00
29.79
26.68
22.66
22.60
22.41
16.56
16.54
16.52
13.80
1.10
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


20190517D
PaBtMi17-501401,Panahi,P2-P-93,CDCl3=77.1000
146.00
145.98
145.97
145.94
145.91
145.89
145.86
145.83
145.79
144.91
144.90
144.88
144.85
144.54
144.51
144.46
144.39
144.05
144.03
144.00
143.97
143.95
143.92
143.89
143.85
142.60
142.58
142.56
142.53
142.51
142.47
142.44
142.42
142.38
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
148.5
148.0
147.5
147.0
146.5
146.0
145.5
145.0
144.5
144.0
143.5
143.0
142.5
142.0
141.5
f1 (ppm)

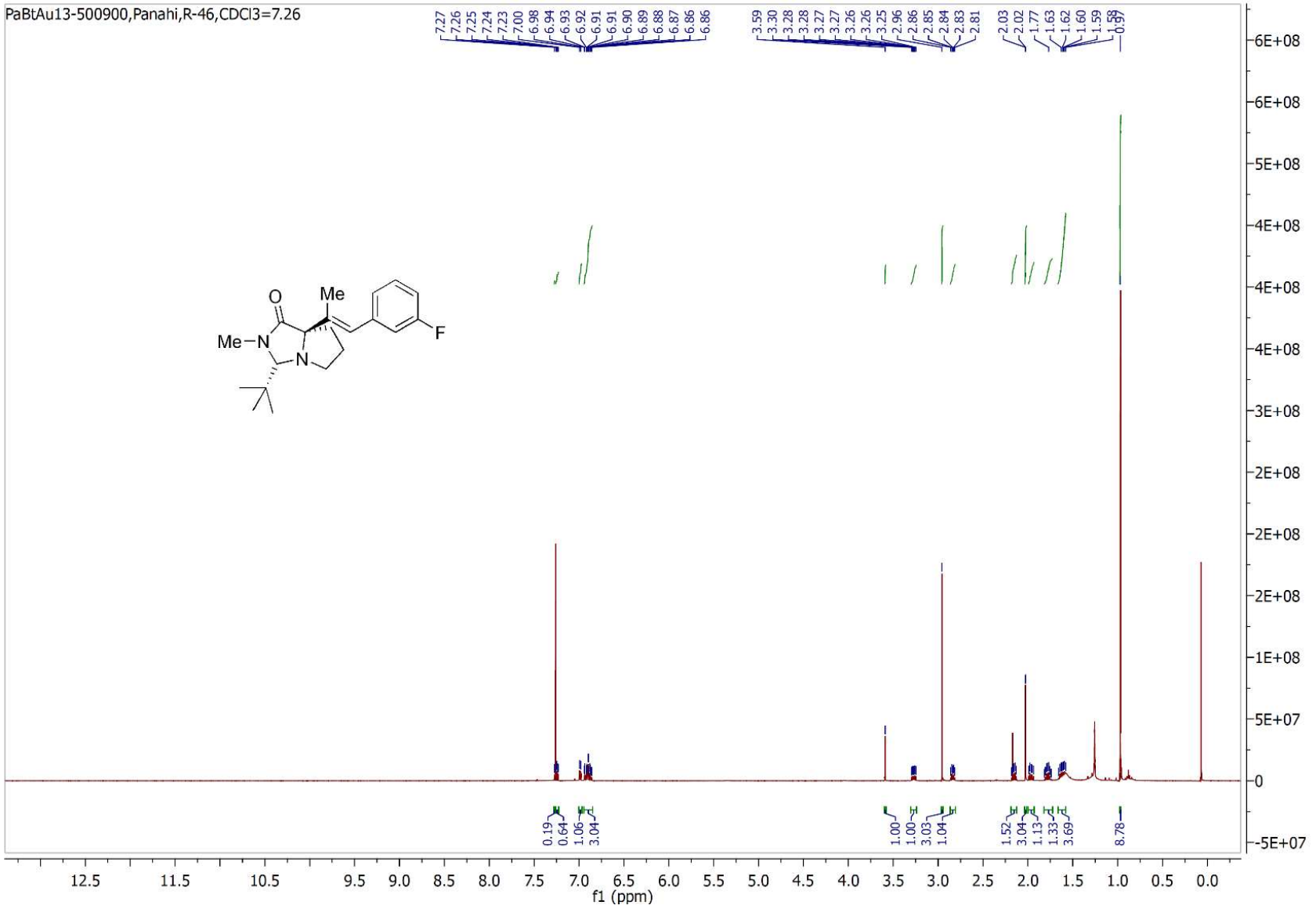

20190517D
PaBtMi17-501401,Panahi,P2-P-93,CDCl3=77.1000
119.86
119.71
119.56
114.98
114.95
114.94
114.92
114.91
114.89
114.87
114.37
114.23
114.08
114.07
Me
N
O
N
Me
Me
Me
F
F
F
F
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
122.5
122.0
121.5
121.0
120.5
120.0
119.5
119.0
118.5
118.0
117.5
117.0
116.5
116.0
115.5
115.0
114.5
114.0
113.5
113.0
f1 (ppm)

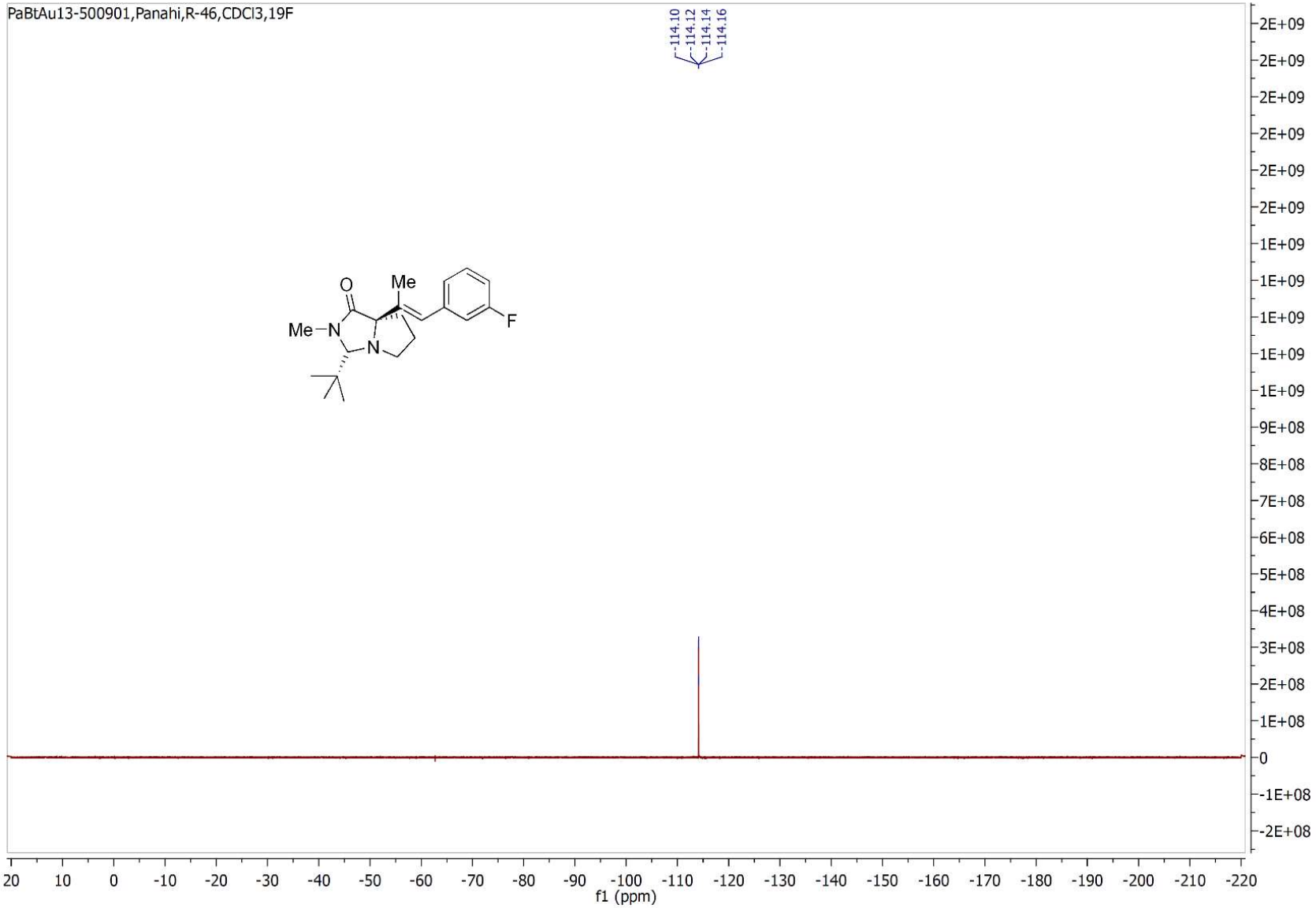
11.3.14. (2S,5S)-2-(tert-butyl)-1,3,5-trimethyl-5-((2E,4E)-5-phenylpenta-2,4-dien-2-yl)imidazolidin-4-one(3n)

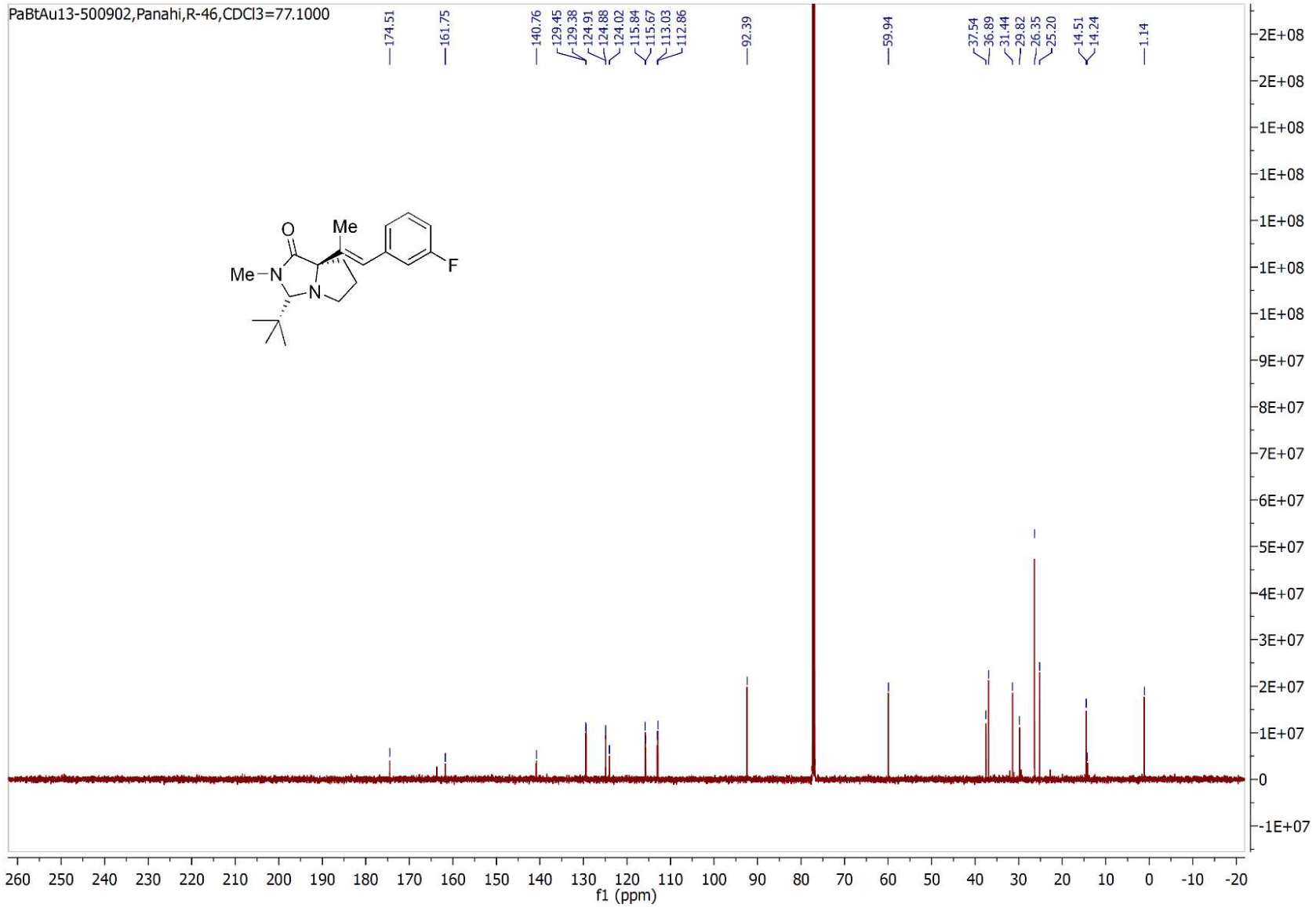



20190503B
PaBtMi03-4511,Panahi,P2-P-58,CDCl3=77.1000
175.51
137.76
137.64
133.34
128.96
128.68
127.55
126.49
124.85
90.21
70.22
38.52
37.25
31.61
27.19
26.68
22.72
14.77
Me
N
N
Me
O
Me
8E+05
7E+05
6E+05
6E+05
6E+05
5E+05
4E+05
4E+05
4E+05
3E+05
2E+05
2E+05
2E+05
1E+05
50000
0
-50000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

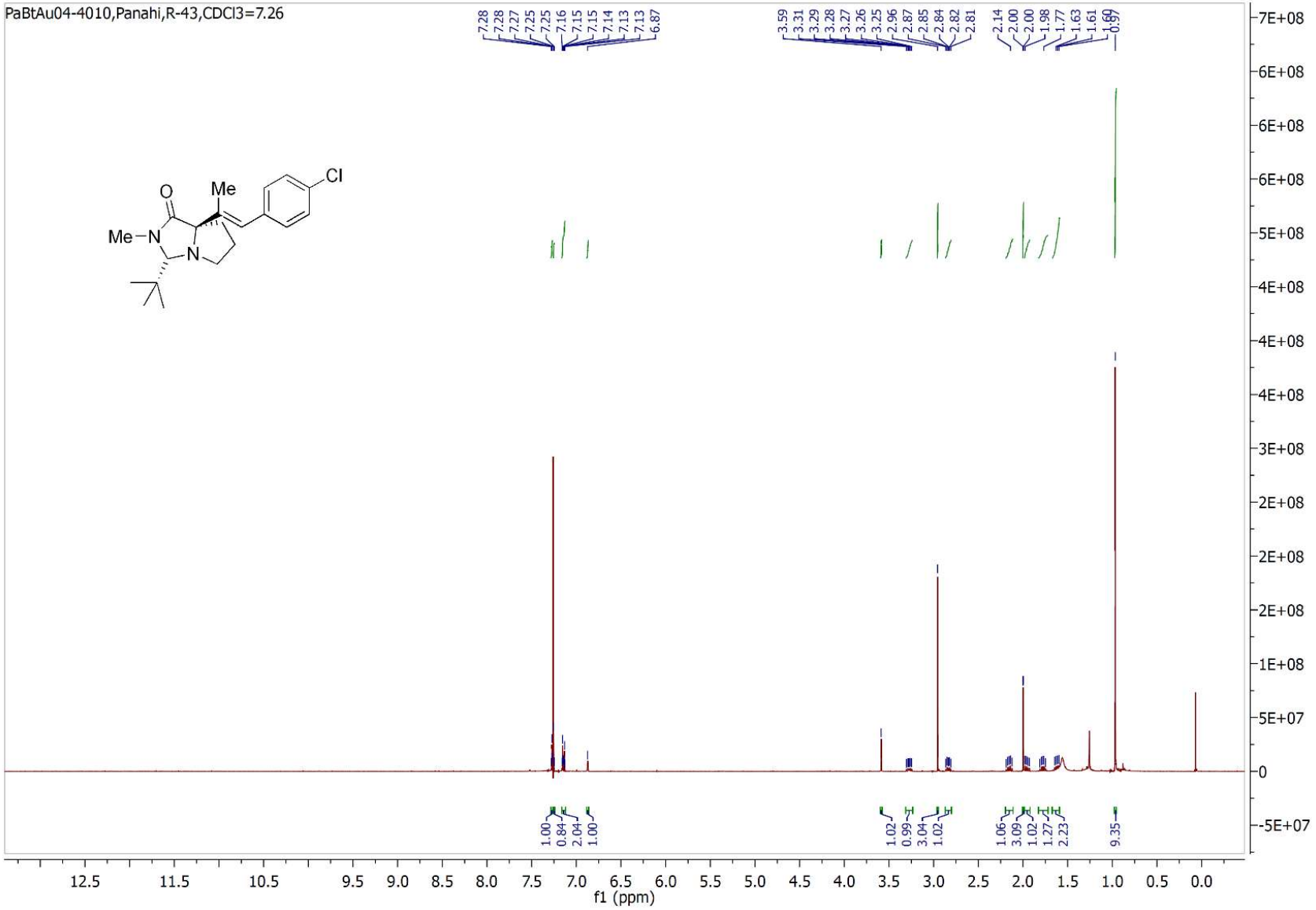
11.3.15. (3R,7aS)-3-(tert-butyl)-7a-((Z)-1-(3-fluorophenyl)prop-1-en-2-yl)-2-methylhexahydro-1H-pyrrolo[1,2-c]imidazol-1-one (3o)

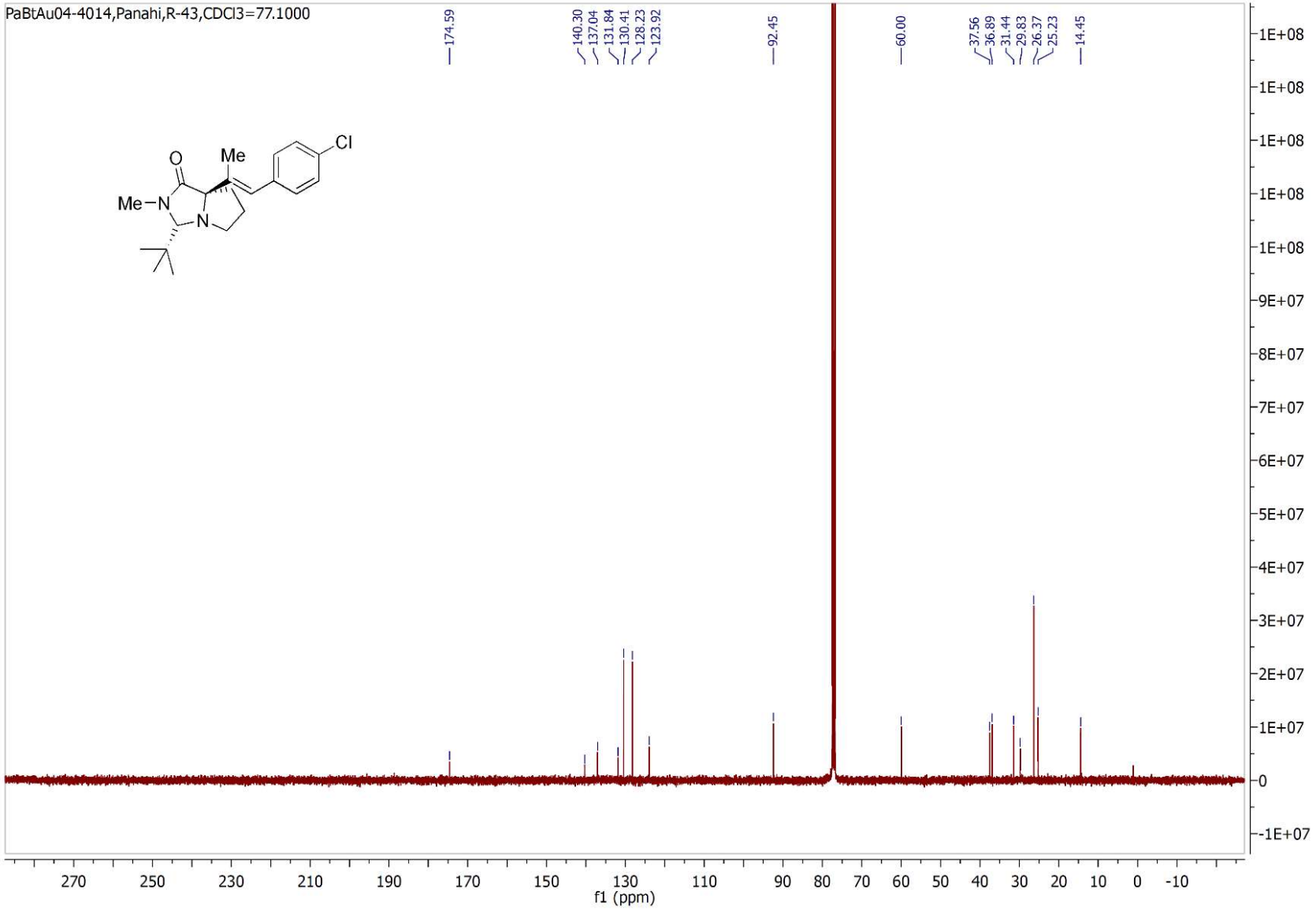



PaBtAu13-500901,Panahi,R-46,CDCl3,19F
-114.10
-114.12
-114.14
-114.16
O
Me
Me–N
N
F
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
2E+09
1E+09
1E+09
1E+09
1E+09
1E+09
1E+09
9E+08
8E+08
7E+08
6E+08
5E+08
4E+08
3E+08
2E+08
1E+08
0
-1E+08
-2E+08
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

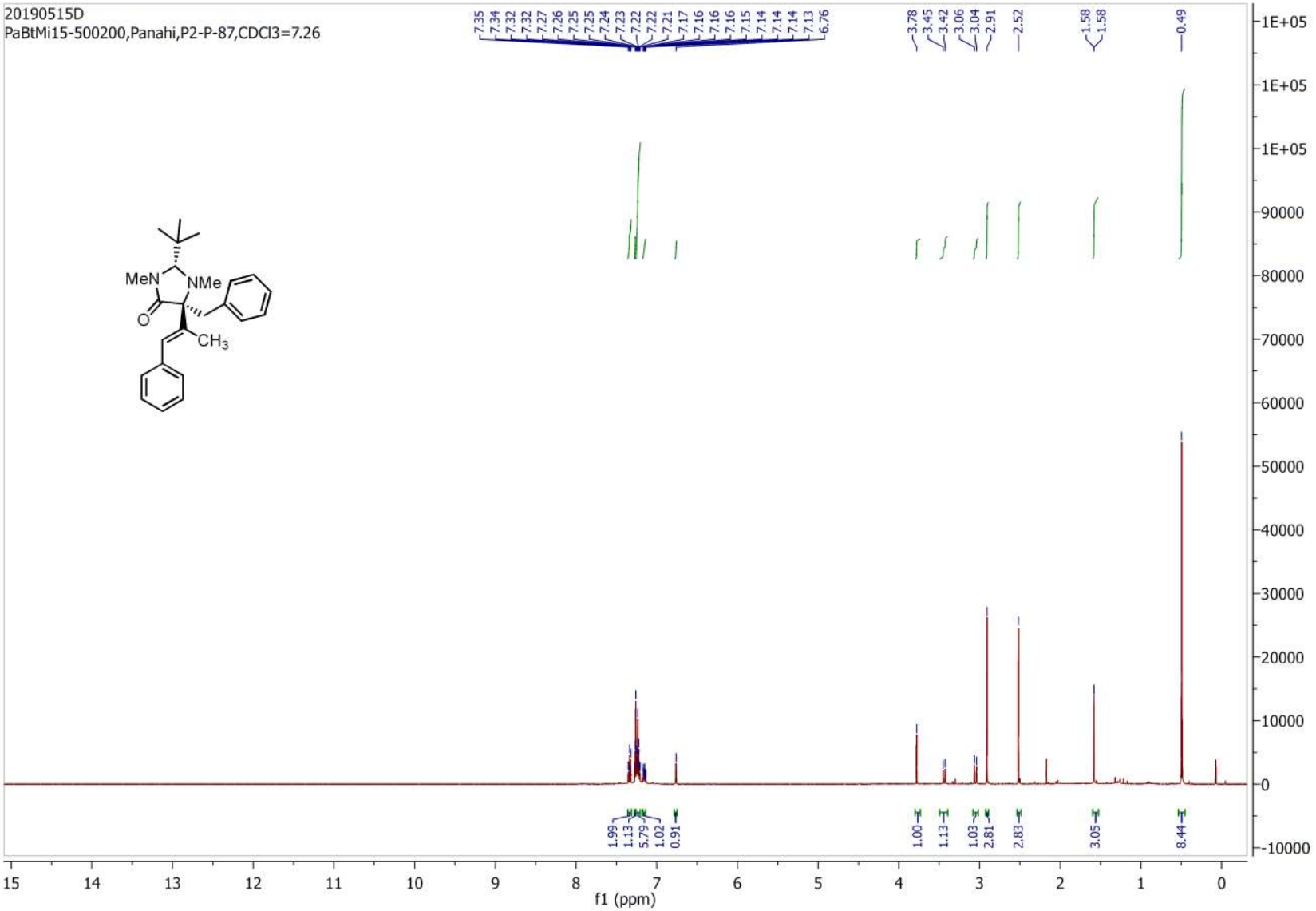

PaBtAu13-500902,Panahi,R-46,CDCl3=77.1000
174.51
161.75
140.76
129.45
129.38
124.91
124.88
124.02
115.84
115.67
113.03
112.86
92.39
59.94
37.54
36.89
31.44
29.82
26.35
25.20
14.51
14.24
1.14
O
Me
Me–N
N
F
f1 (ppm)

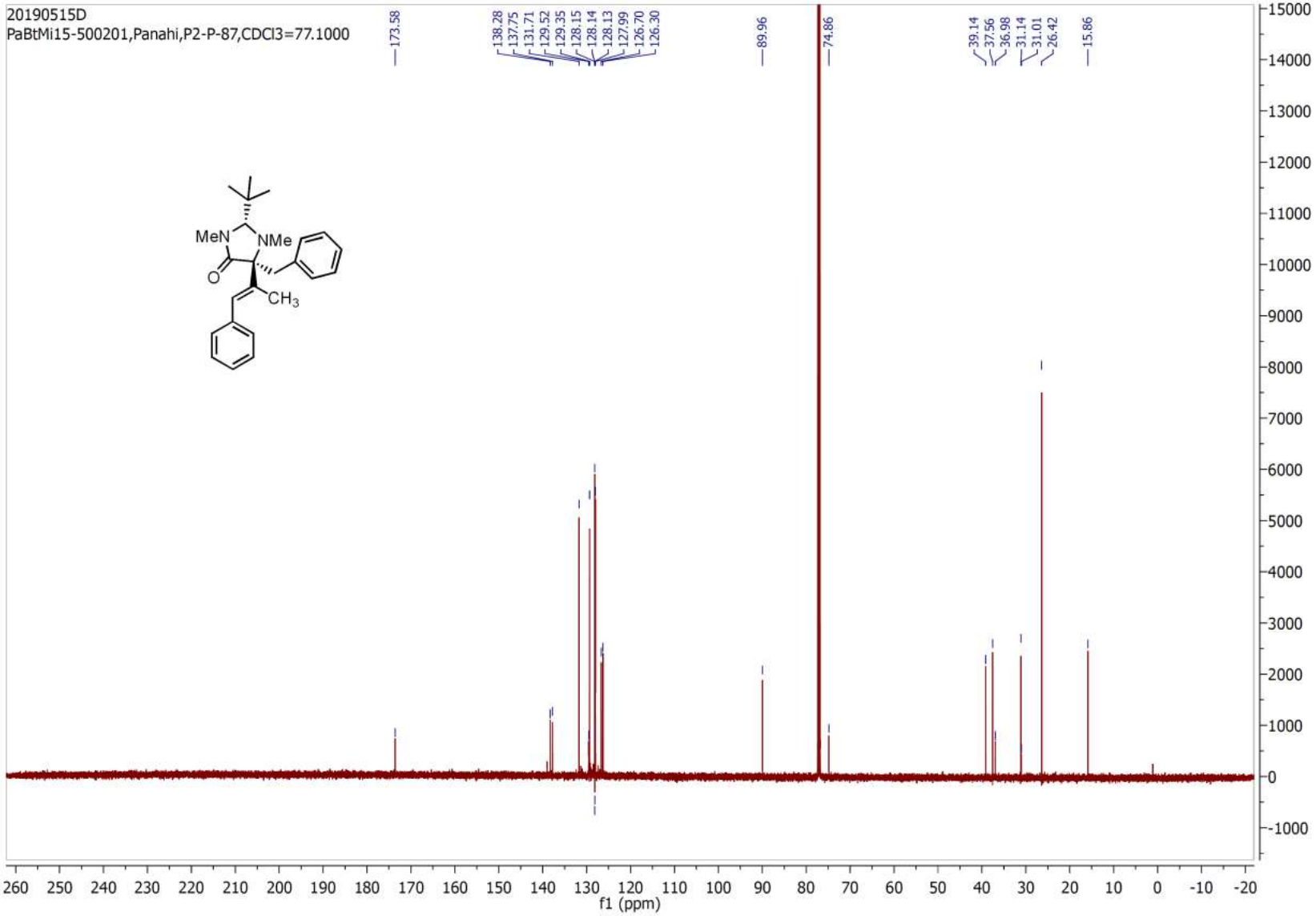
11.3.16. (3R,7aS)-3-(tert-butyl)-7a-((Z)-1-(4-chlorophenyl)prop-1-en-2-yl)-2-methylhexahydro-1H-pyrrolo[1,2-c]imidazol-1-one (3p)



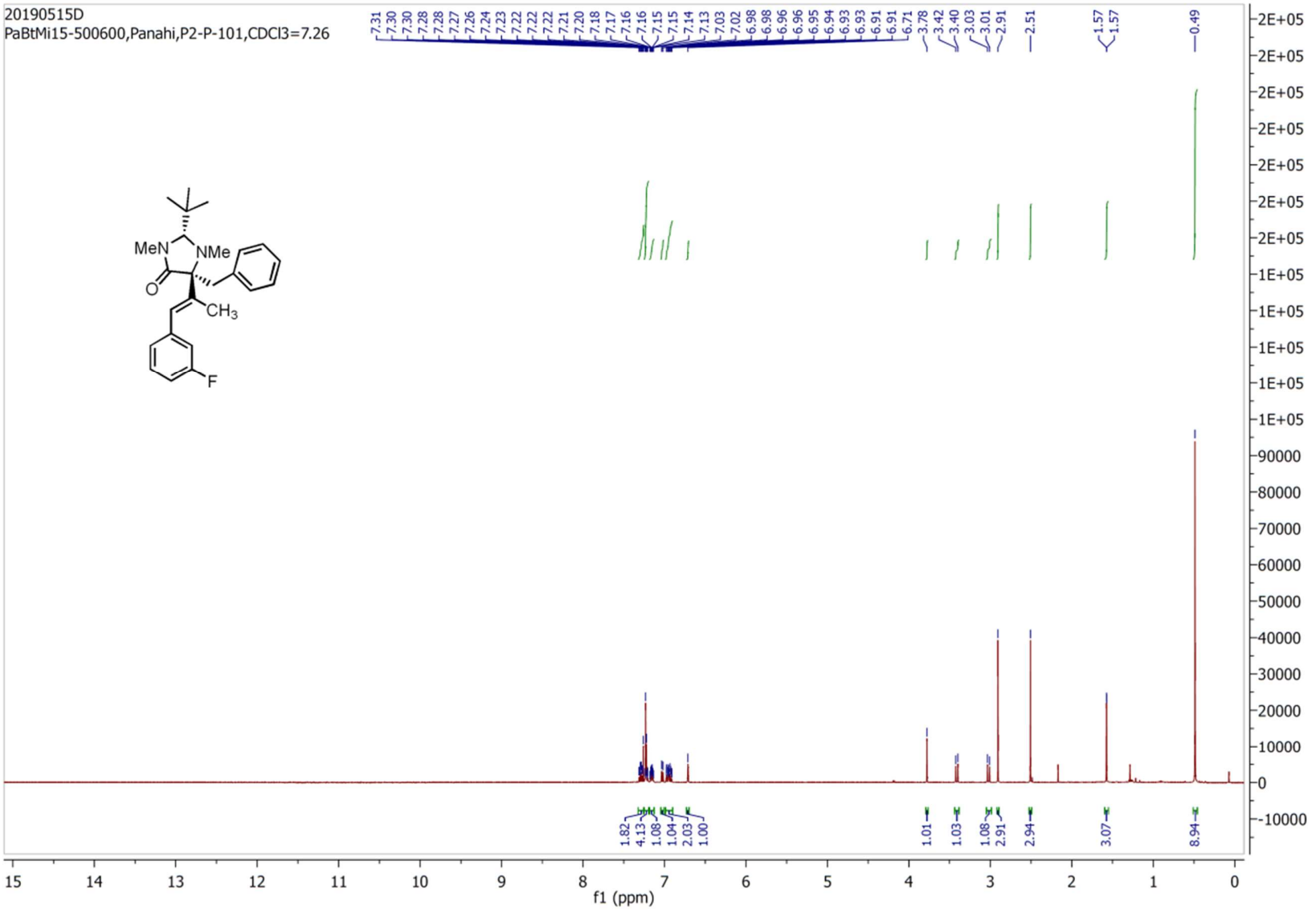

PaBtAu04-4014,Panahi,R-43,CDCl3=77.1000
174.59
140.30
137.04
131.84
130.41
128.23
123.92
92.45
60.00
37.56
36.89
31.44
29.83
26.37
25.23
14.45
O
Me
Me–N
N
Cl
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

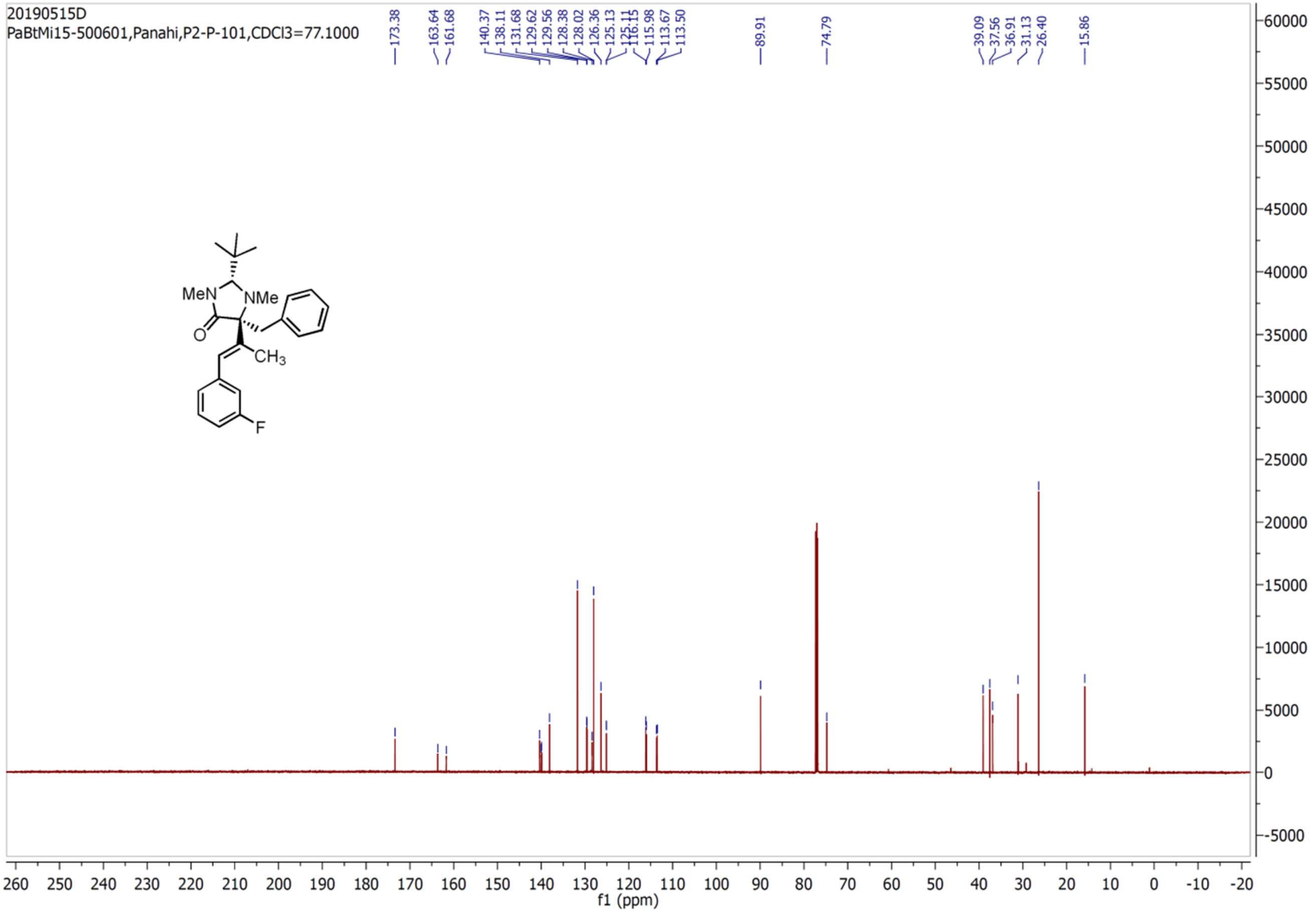
11.3.17. (2S,5S)-5-benzyl-2-(tert-butyl)-1,3-dimethyl-5-((E)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3q)

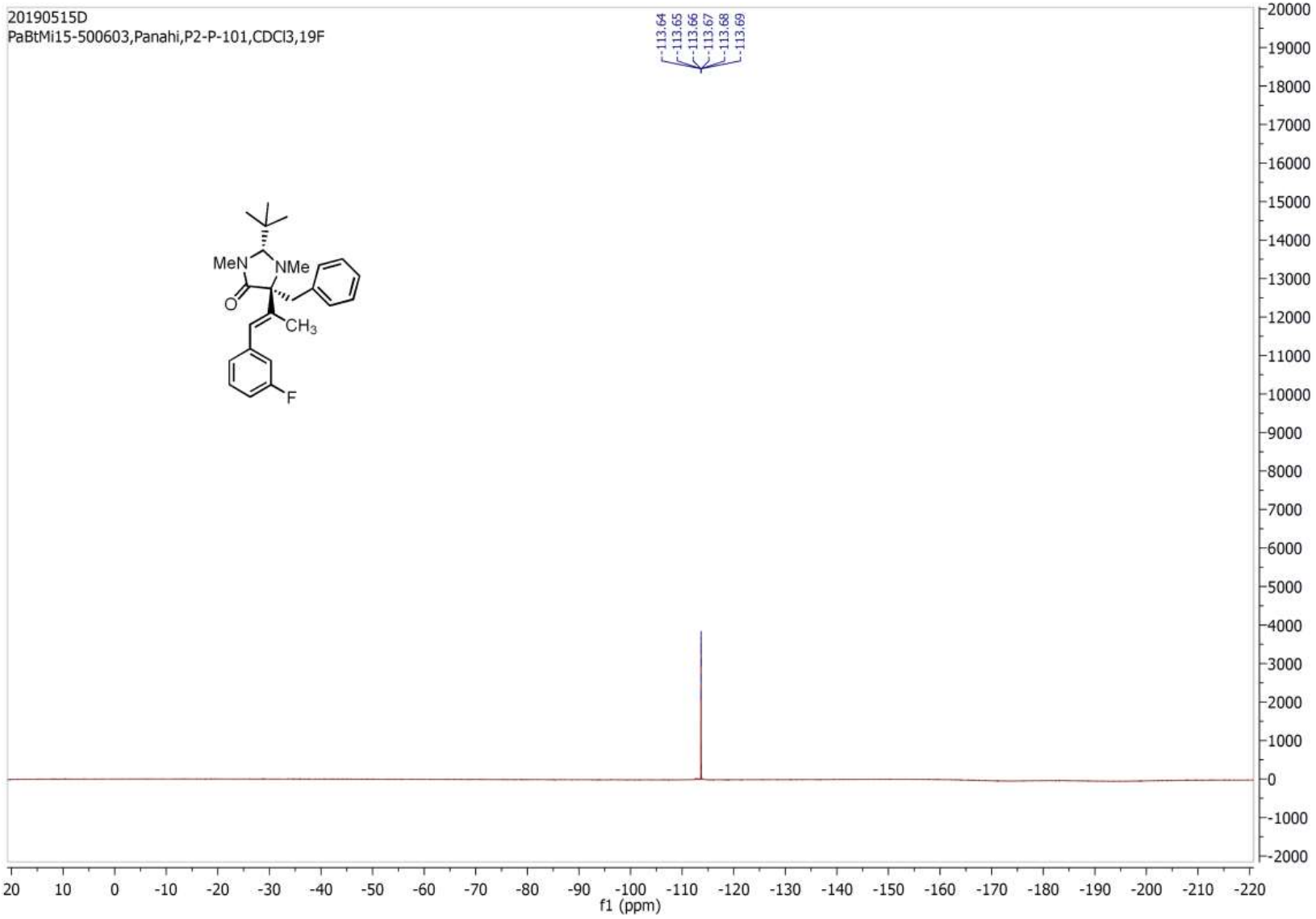



20190515D
PaBtMi15-500201,Panahi,P2-P-87,CDCl3=77.1000
173.58
138.28
137.75
131.71
129.52
129.35
128.15
128.14
128.13
127.99
126.70
126.30
89.96
74.86
39.14
37.56
36.98
31.14
31.01
26.42
15.86
MeN
NMe
O
CH3
f1 (ppm)

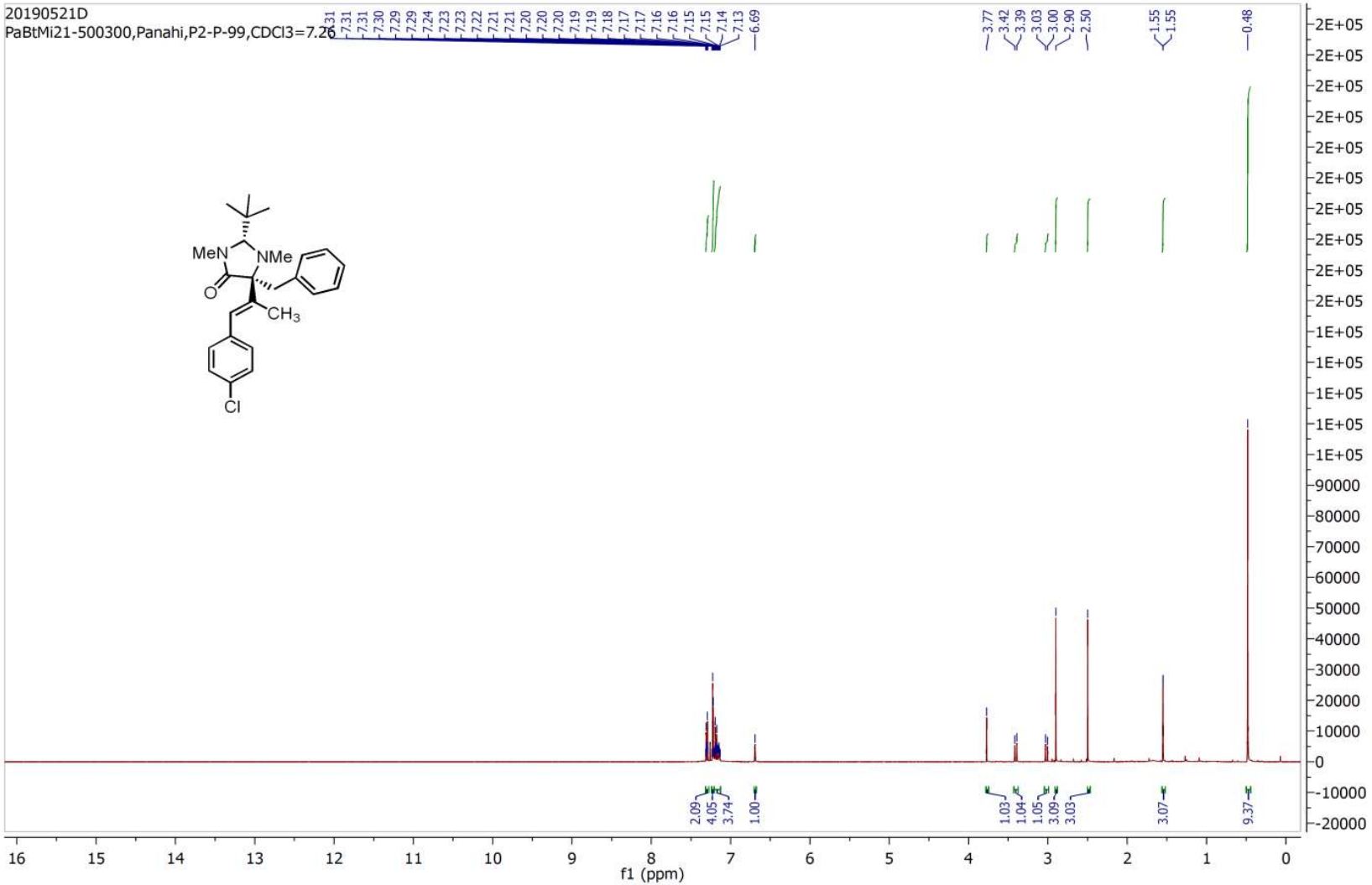
11.3.18. (2S,5S)-5-benzyl-2-(tert-butyl)-5-((E)-1-(3-fluorophenyl)prop-1-en-2-yl)-1,3-dimethylimidazolidin-4-one(3r)

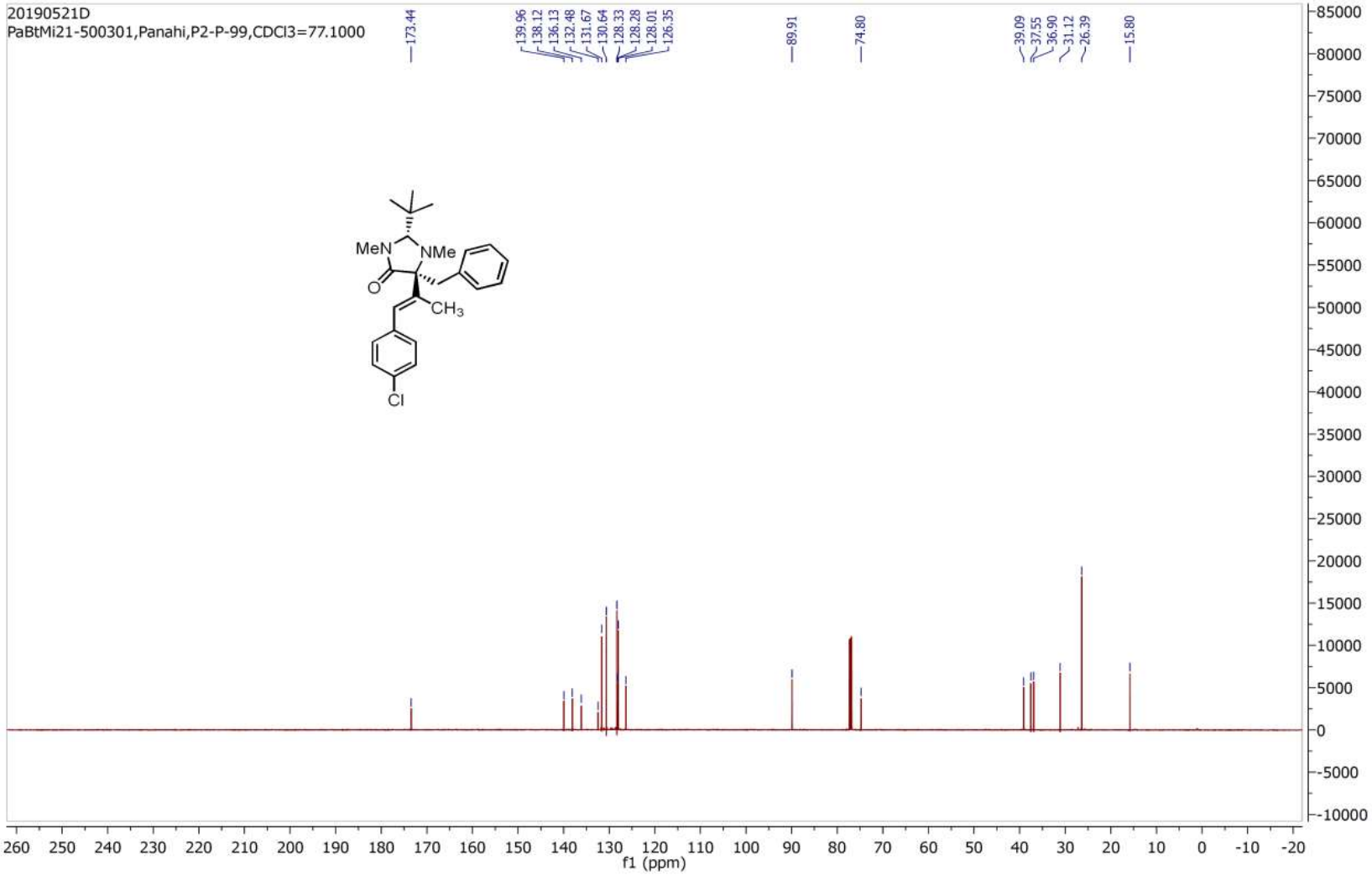



20190515D
PaBtMi15-500601,Panahi,P2-P-101,CDCl3=77.1000
173.38
163.64
161.68
140.37
138.11
131.68
129.62
129.56
128.38
128.02
126.36
125.13
125.11
116.15
115.98
113.67
113.50
89.91
74.79
39.09
37.56
36.91
31.13
26.40
15.86
MeN
NMe
O
CH3
F
f1 (ppm)

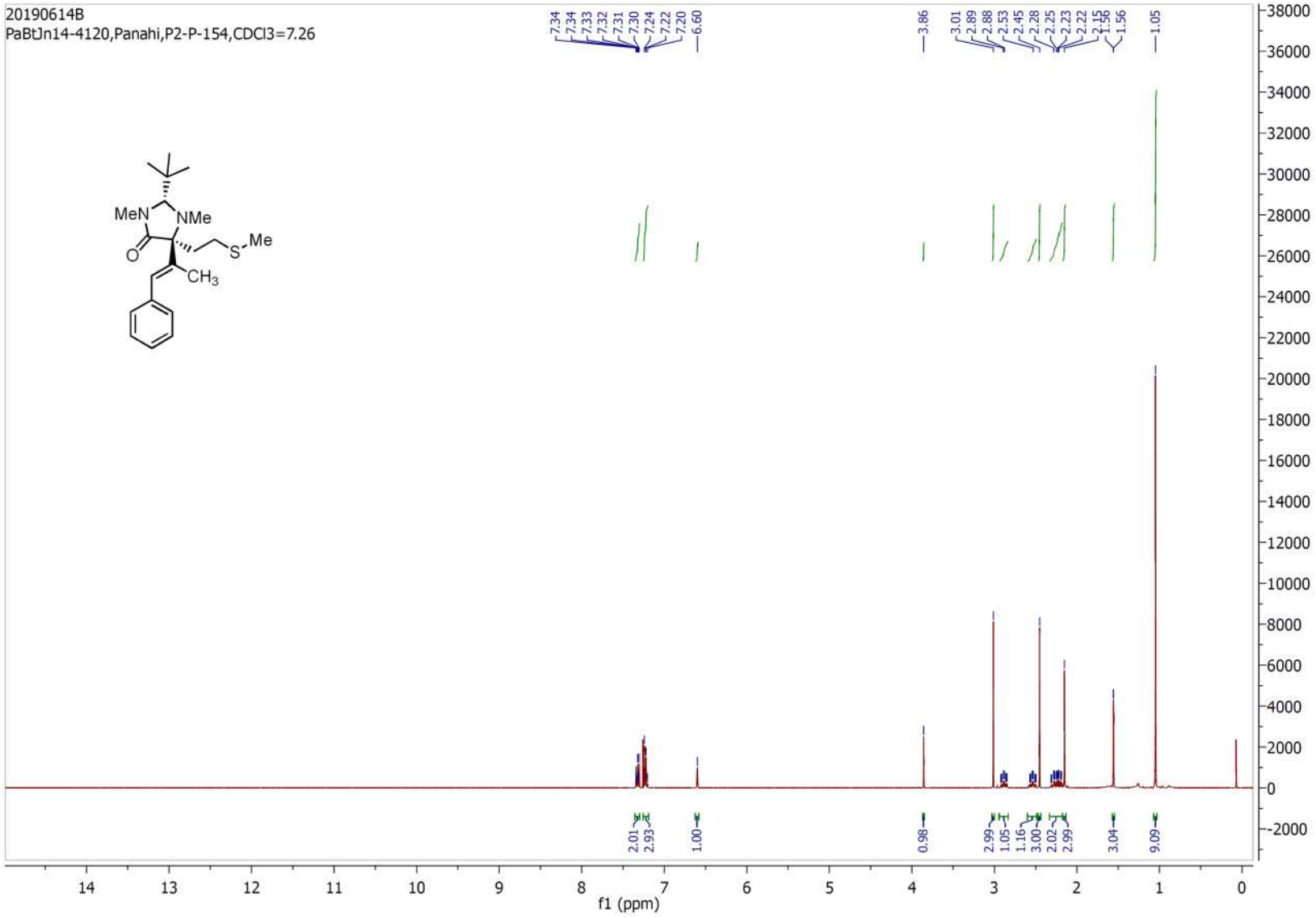

20190515D
PaBtMi15-500603,Panahi,P2-P-101,CDCl3,19F
-113.64
-113.65
-113.66
-113.67
-113.68
-113.69
MeN
NMe
O
CH3
F
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

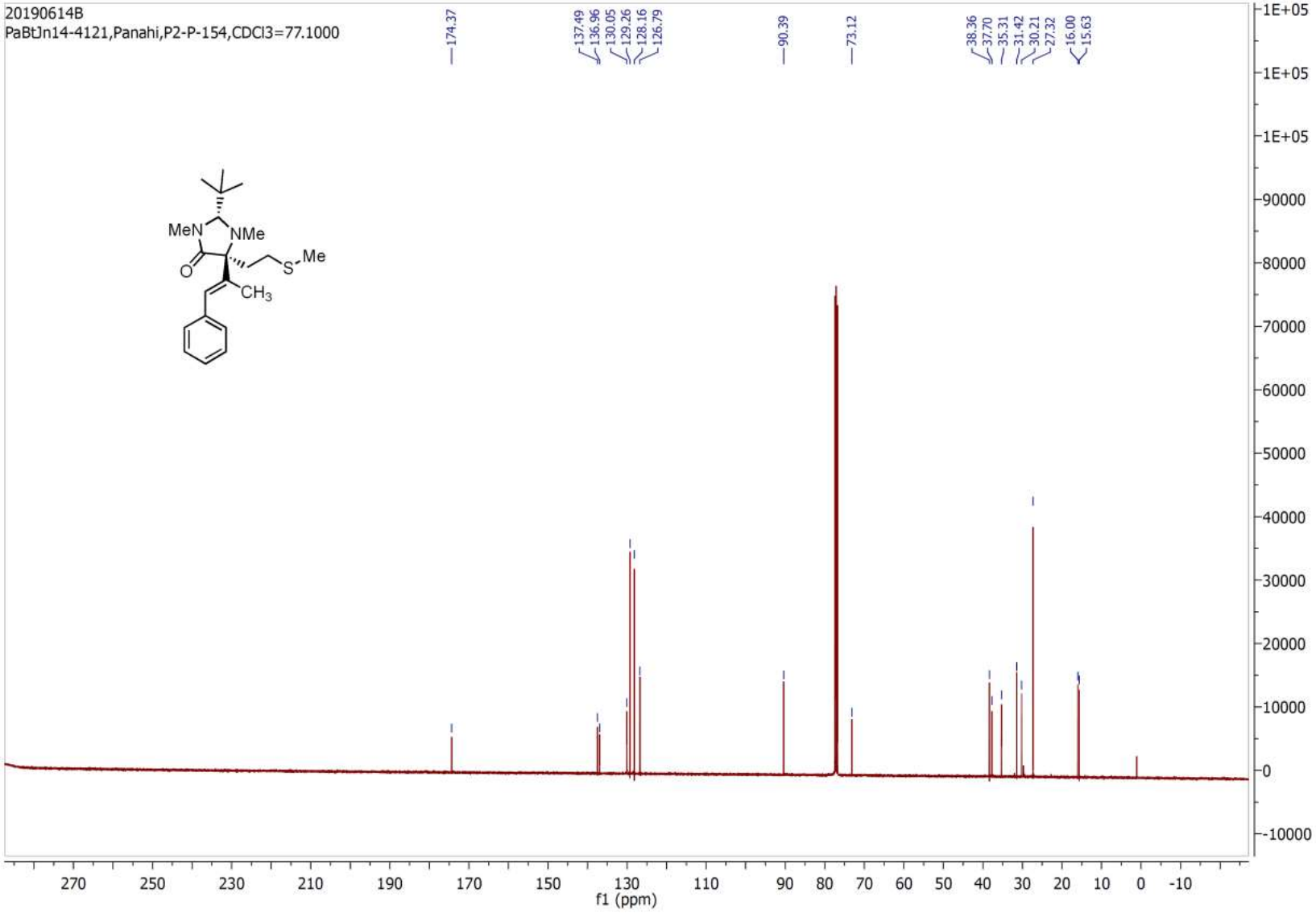
11.3.19. (2S,5S)-5-benzyl-2-(tert-butyl)-5-((E)-1-(4-chlorophenyl)prop-1-en-2-yl)-1,3-dimethylimidazolidin-4-one(3s)



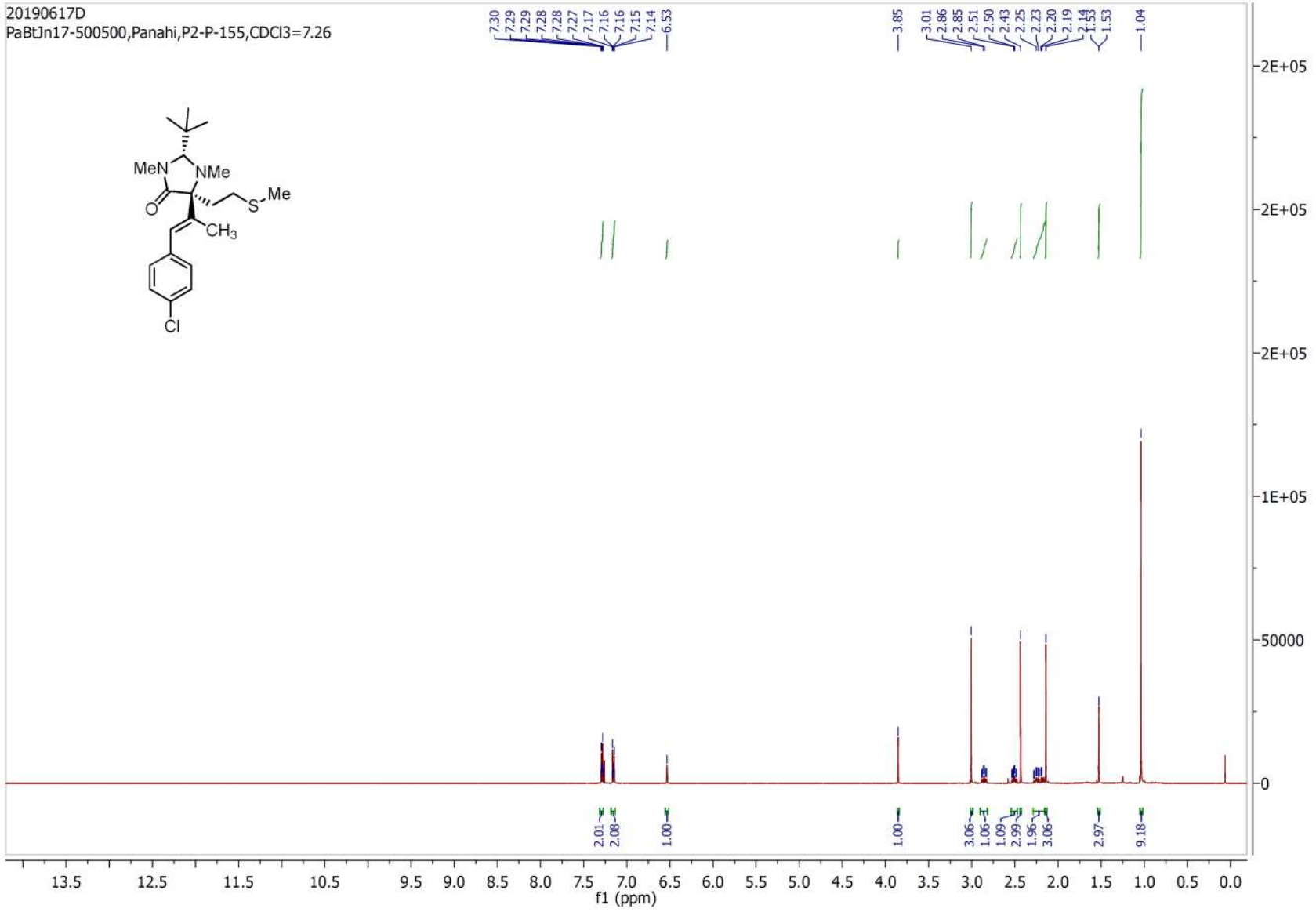

20190521D
PaBtMi21-500301,Panahi,P2-P-99,CDCl3=77.1000
173.44
139.96
138.12
136.13
132.48
131.67
130.64
128.33
128.28
128.01
126.35
89.91
74.80
39.09
37.55
36.90
31.12
26.39
15.80
MeN
NMe
O
CH3
Cl
f1 (ppm)

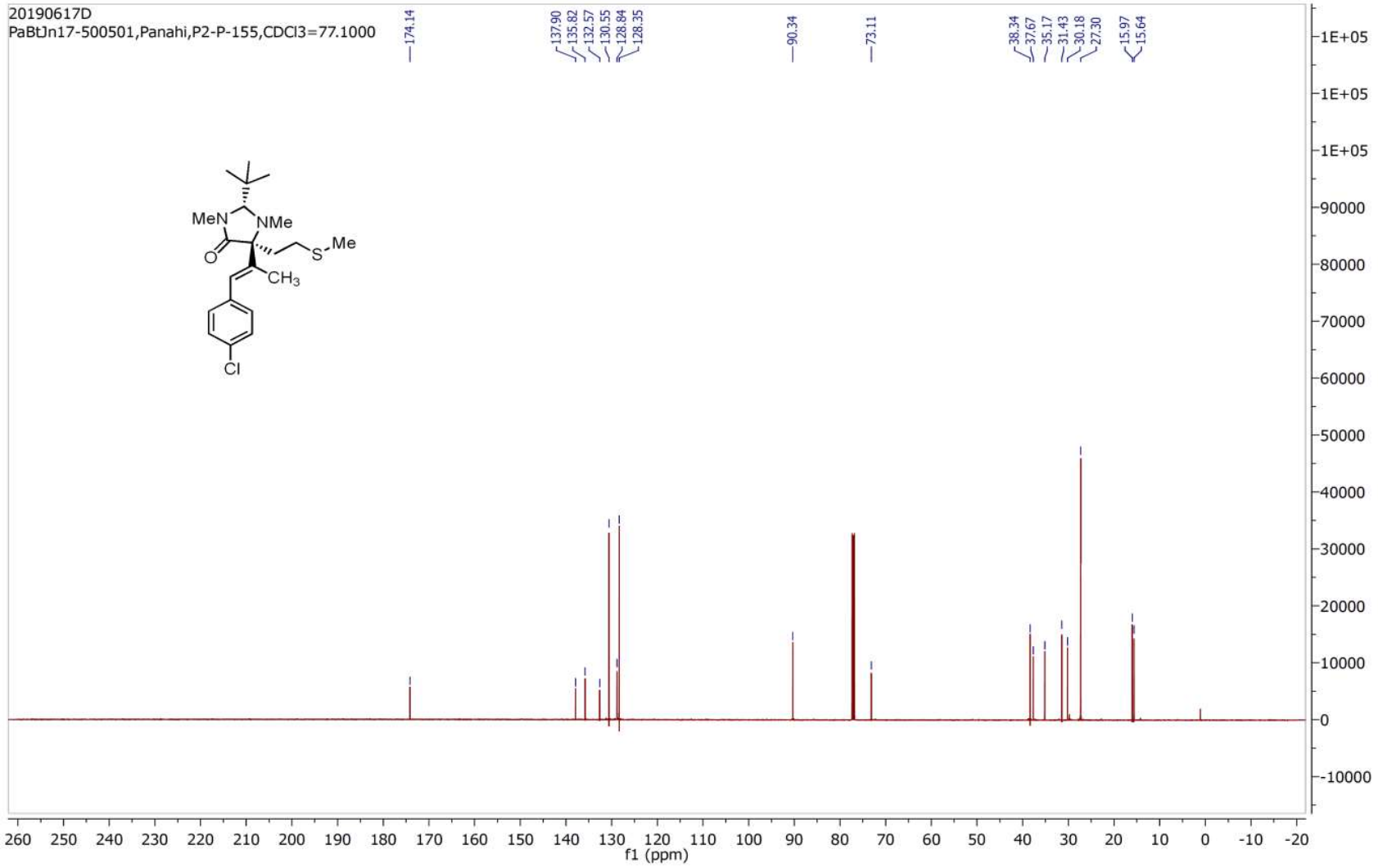
11.3.20. (2R,5S)-2-(tert-butyl)-1,3-dimethyl-5-(2-(methylthio)ethyl)-5-((E)-1-phenylprop-1-en-2-yl)imidazolidin-4-one(3t)



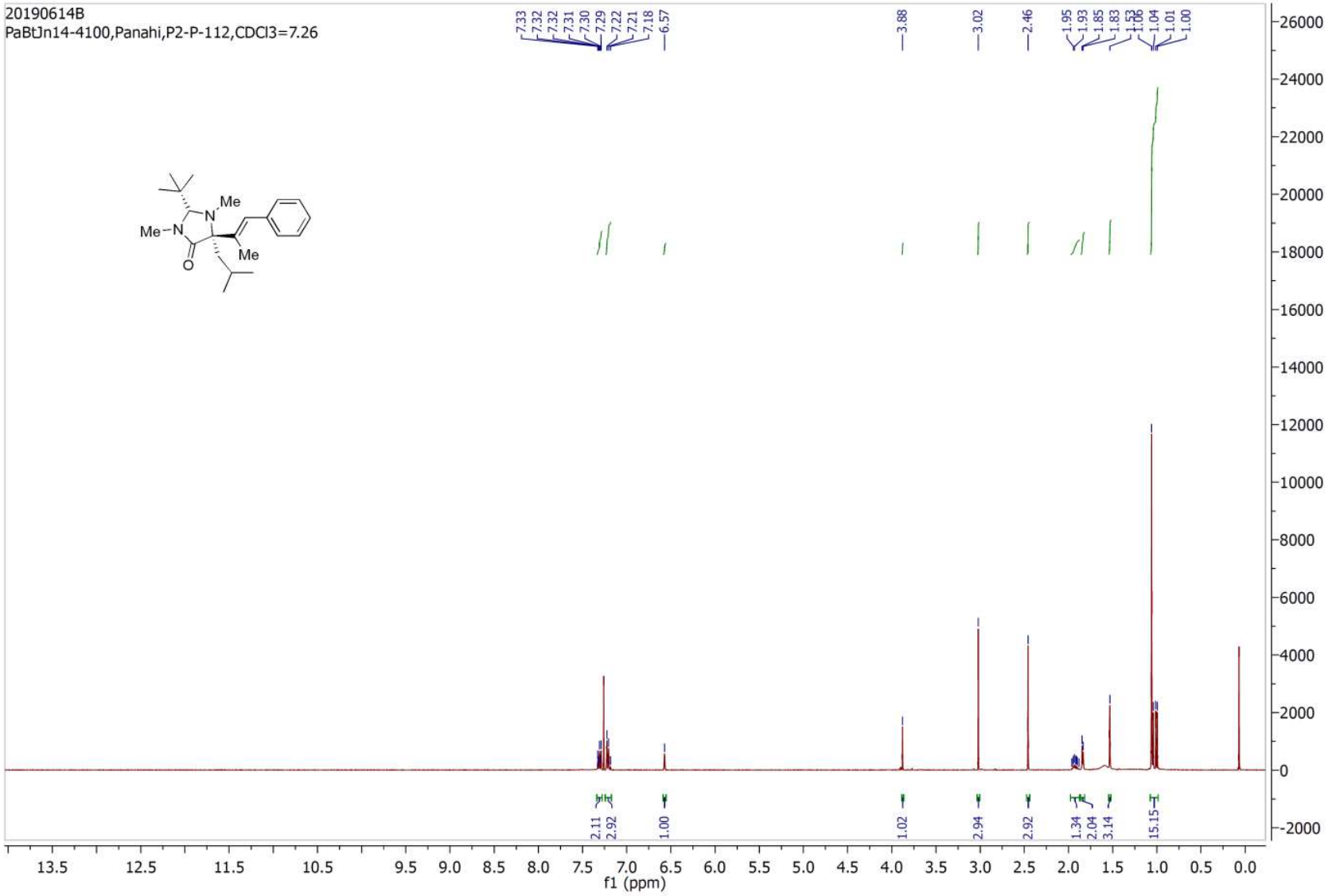

20190614B
PaBtJn14-4121,Panahi,P2-P-154,CDCl3=77.1000
174.37
137.49
136.96
130.05
129.26
128.16
126.79
90.39
73.12
38.36
37.70
35.31
31.42
30.21
27.32
16.00
15.63
MeN
NMe
O
S
Me
CH3
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

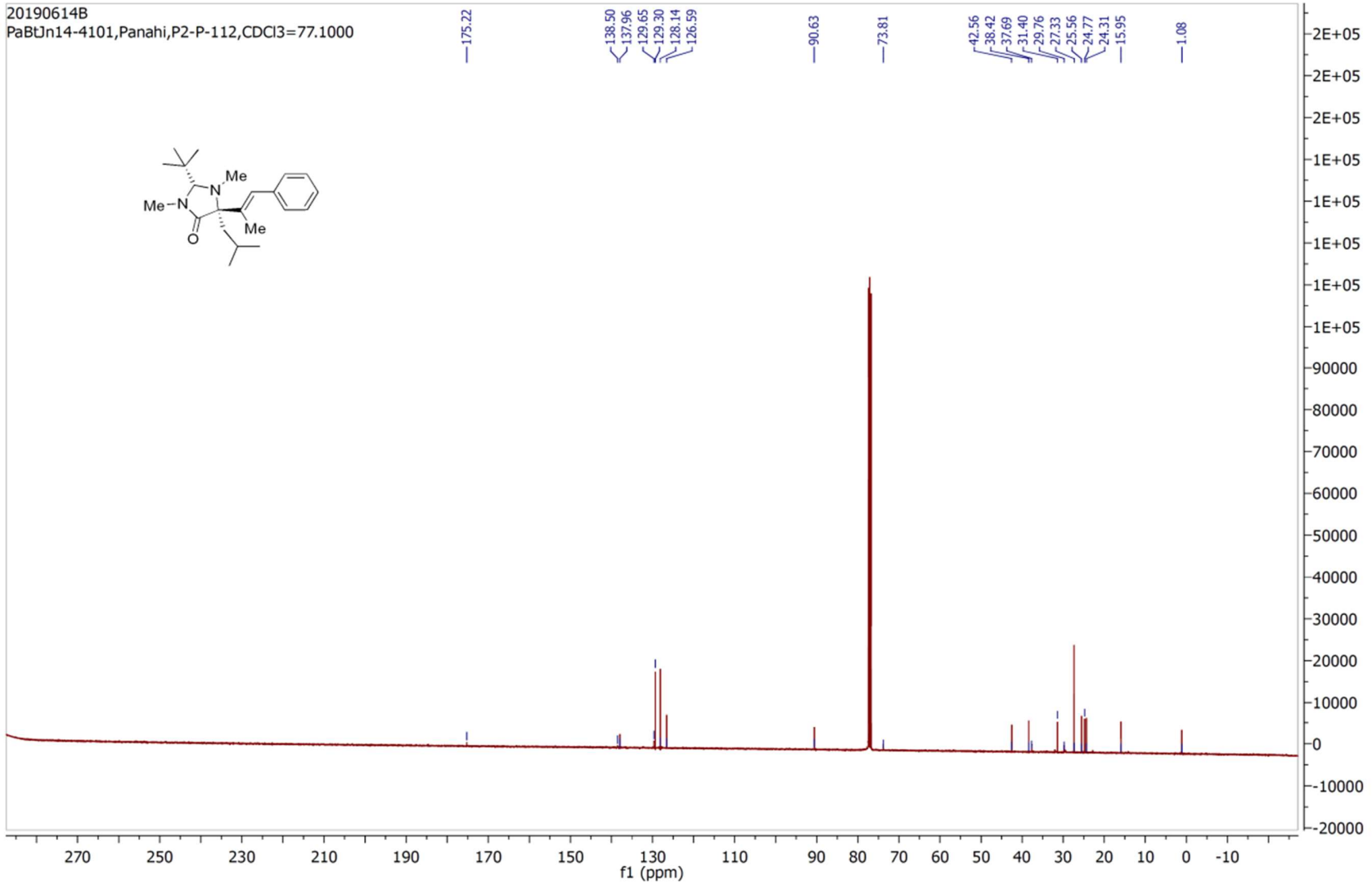
11.3.21. (2S,5S)-2-(tert-butyl)-5-((E)-1-(4-chlorophenyl)prop-1-en-2-yl)-1,3-dimethyl-5-(2-(methylthio)ethyl)imidazolidin-4-one(3u)



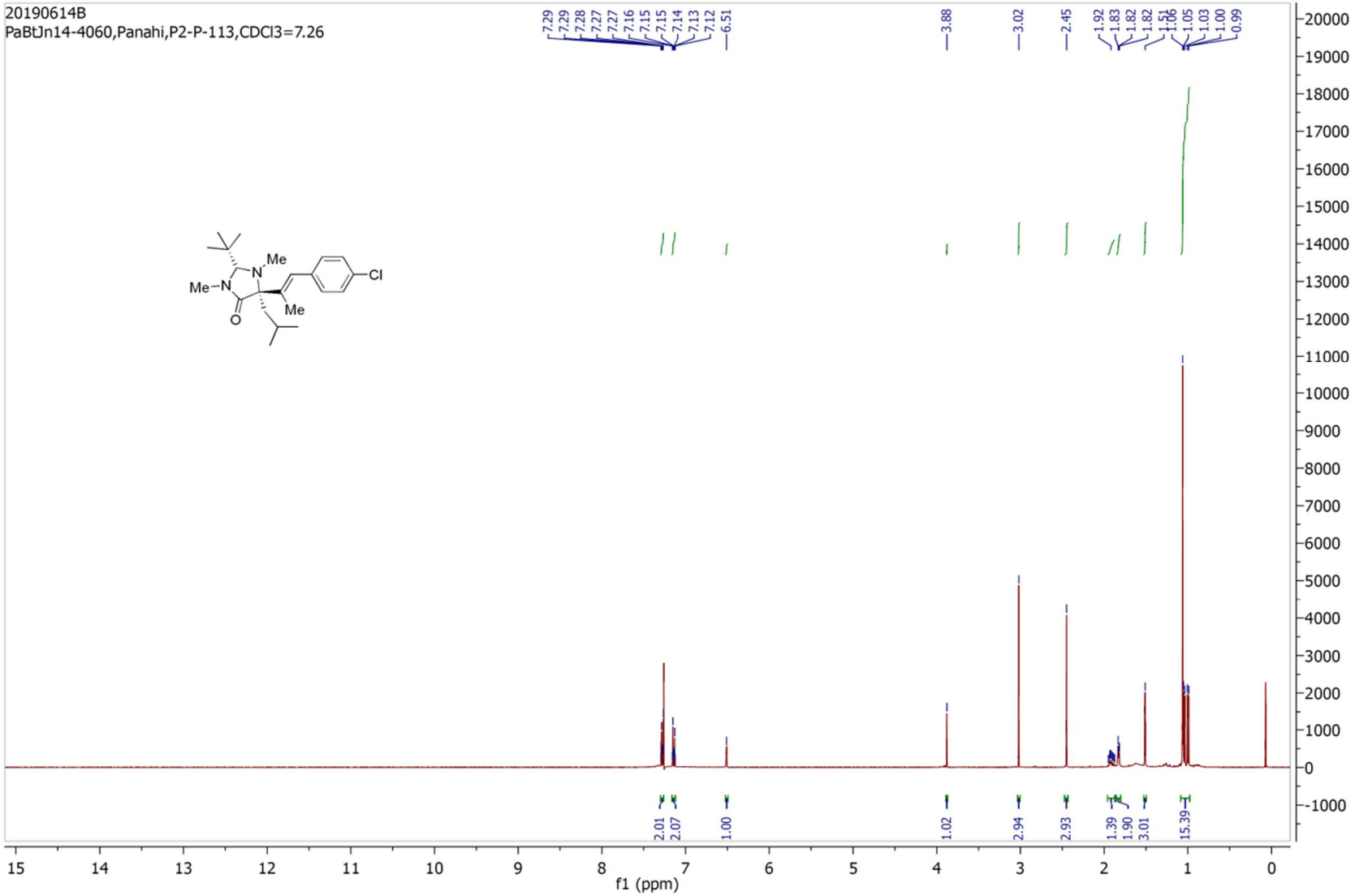

20190617D
PaBtJn17-500501,Panahi,P2-P-155,CDCl3=77.1000
174.14
137.90
135.82
132.57
130.55
128.84
128.35
90.34
73.11
38.34
37.67
35.17
31.43
30.18
27.30
15.97
15.64
MeN
NMe
O
S
Me
CH3
Cl
1E+05
1E+05
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

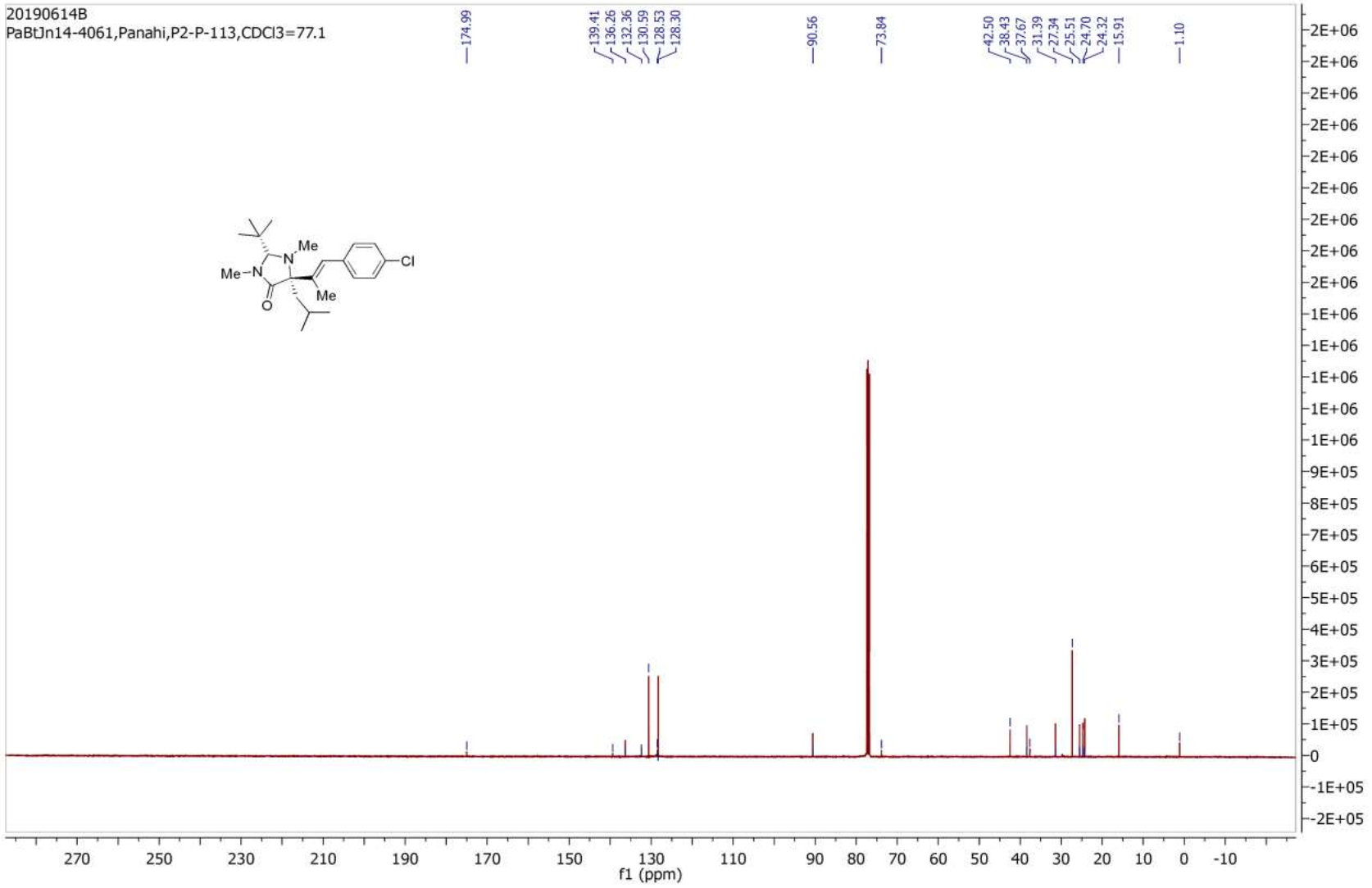
11.3.22. (2S,5S)-2-(tert-butyl)-5-isobutyl-1,3-dimethyl-5-((E)-1-phenylprop-1-en-2-yl)imidazolidin-4-one(3v)



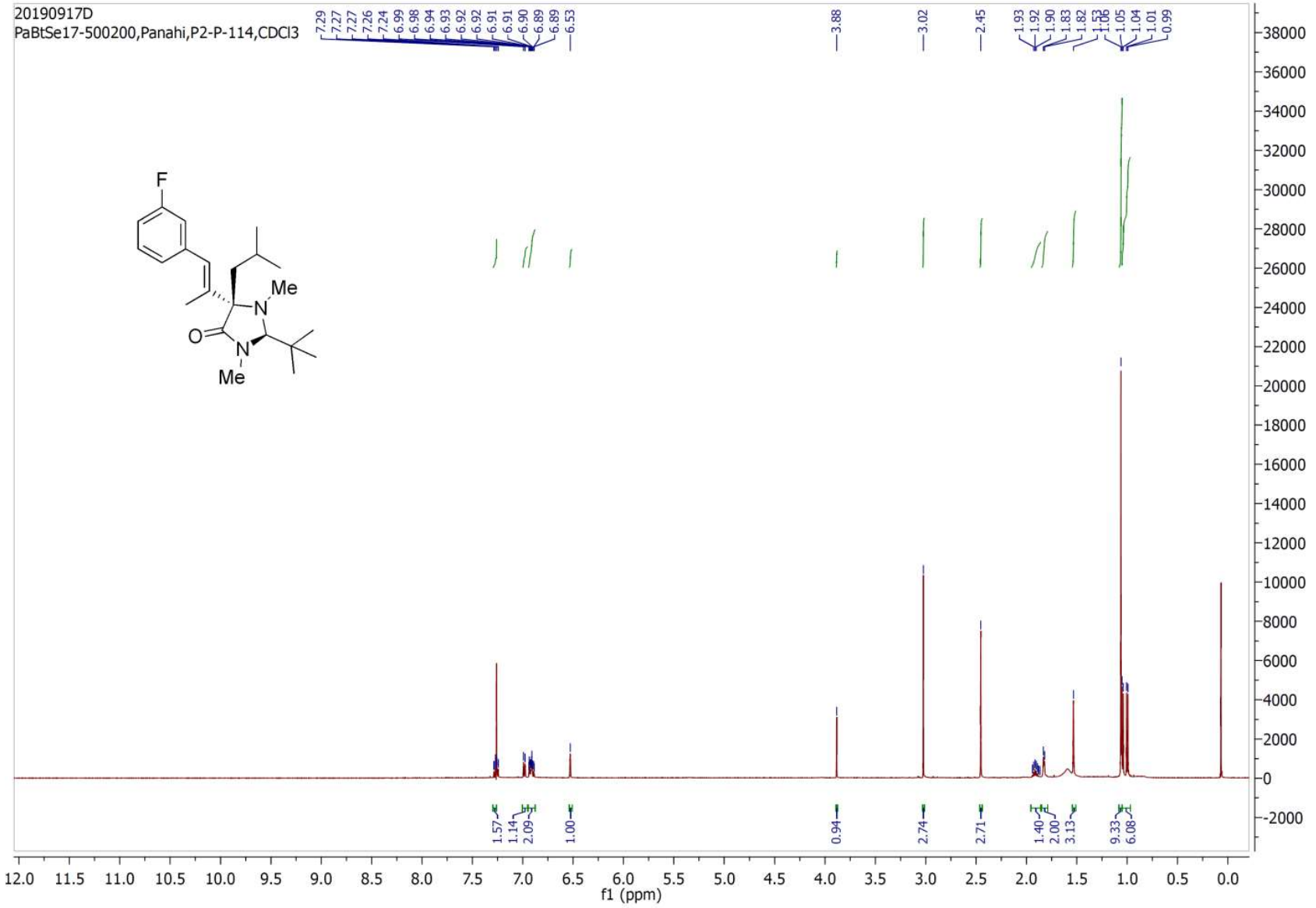

20190614B
PaBtJn14-4101,Panahi,P2-P-112,CDCl3=77.1000
175.22
138.50
137.96
129.65
129.30
128.14
126.59
90.63
73.81
42.56
38.42
37.69
31.40
29.76
27.33
25.56
24.77
24.31
15.95
1.08
Me
Me
Me
N
N
O
f1 (ppm)

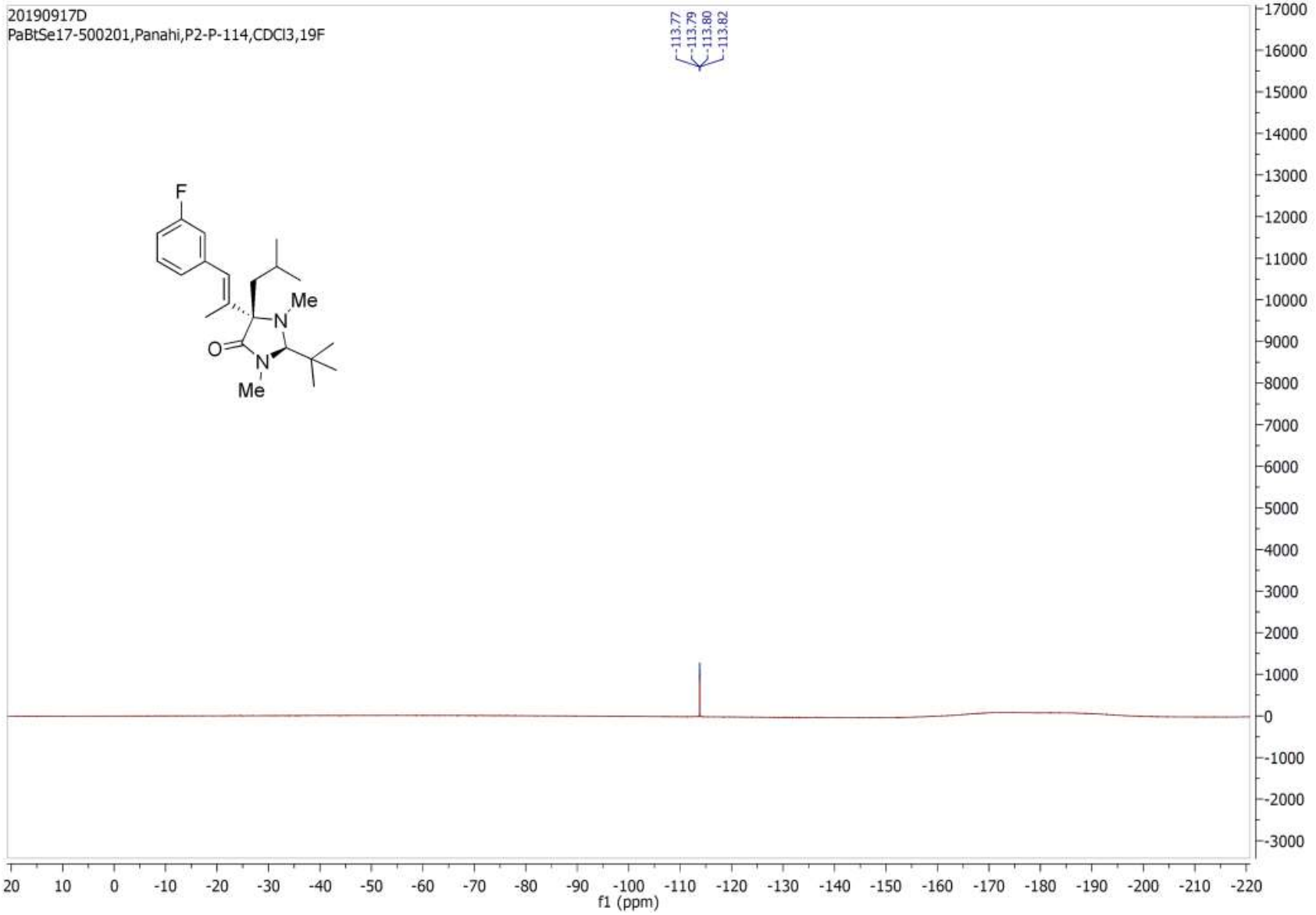
11.3.23. (2S,5S)-2-(tert-butyl)-5-((E)-1-(4-chlorophenyl)prop-1-en-2-yl)-5-isobutyl-1,3-dimethylimidazolidin-4-one(3w)

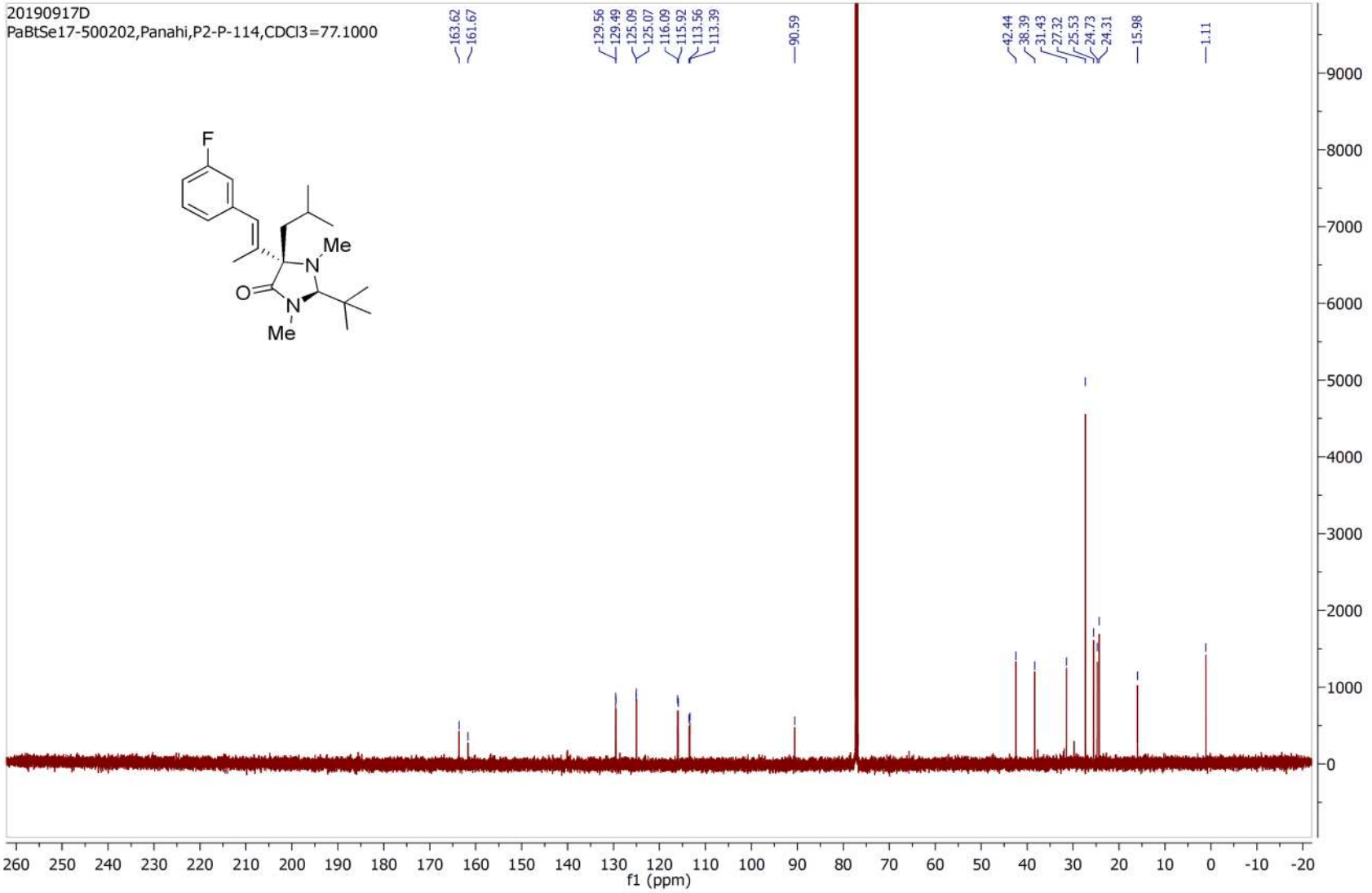



20190614B
PaBtJn14-4061,Panahi,P2-P-113,CDCl3=77.1
174.99
139.41
136.26
132.36
130.59
128.53
128.30
90.56
73.84
42.50
38.43
37.67
31.39
27.34
25.51
24.70
24.32
15.91
1.10
Me
N
Me
N
Me
O
Cl
2E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
-2E+05
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

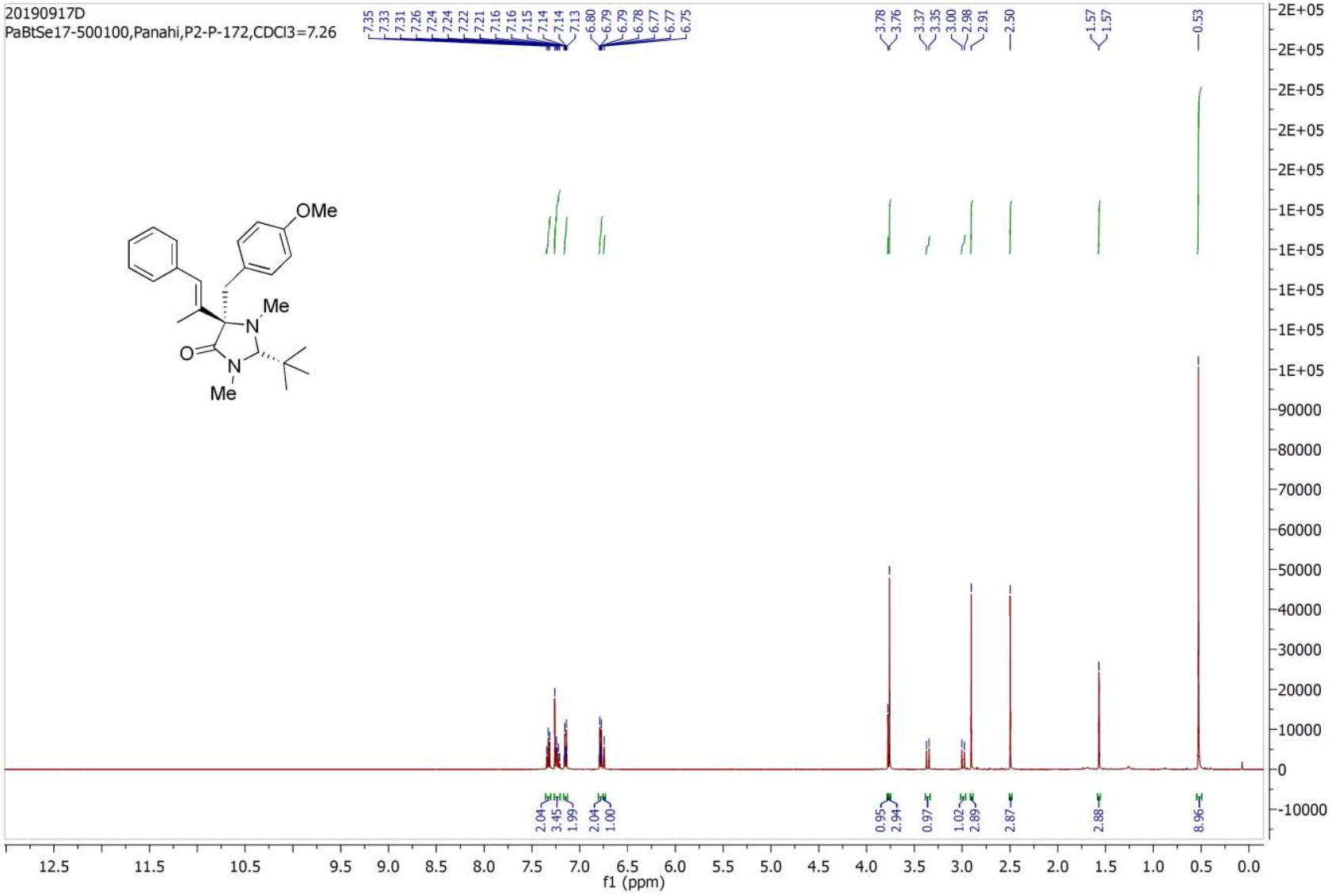
11.3.24. (2S,5S)-2-(tert-butyl)-5-((E)-1-(3-fluorophenyl)prop-1-en-2-yl)-5-isobutyl-1,3-dimethylimidazolidin-4-one (3x)

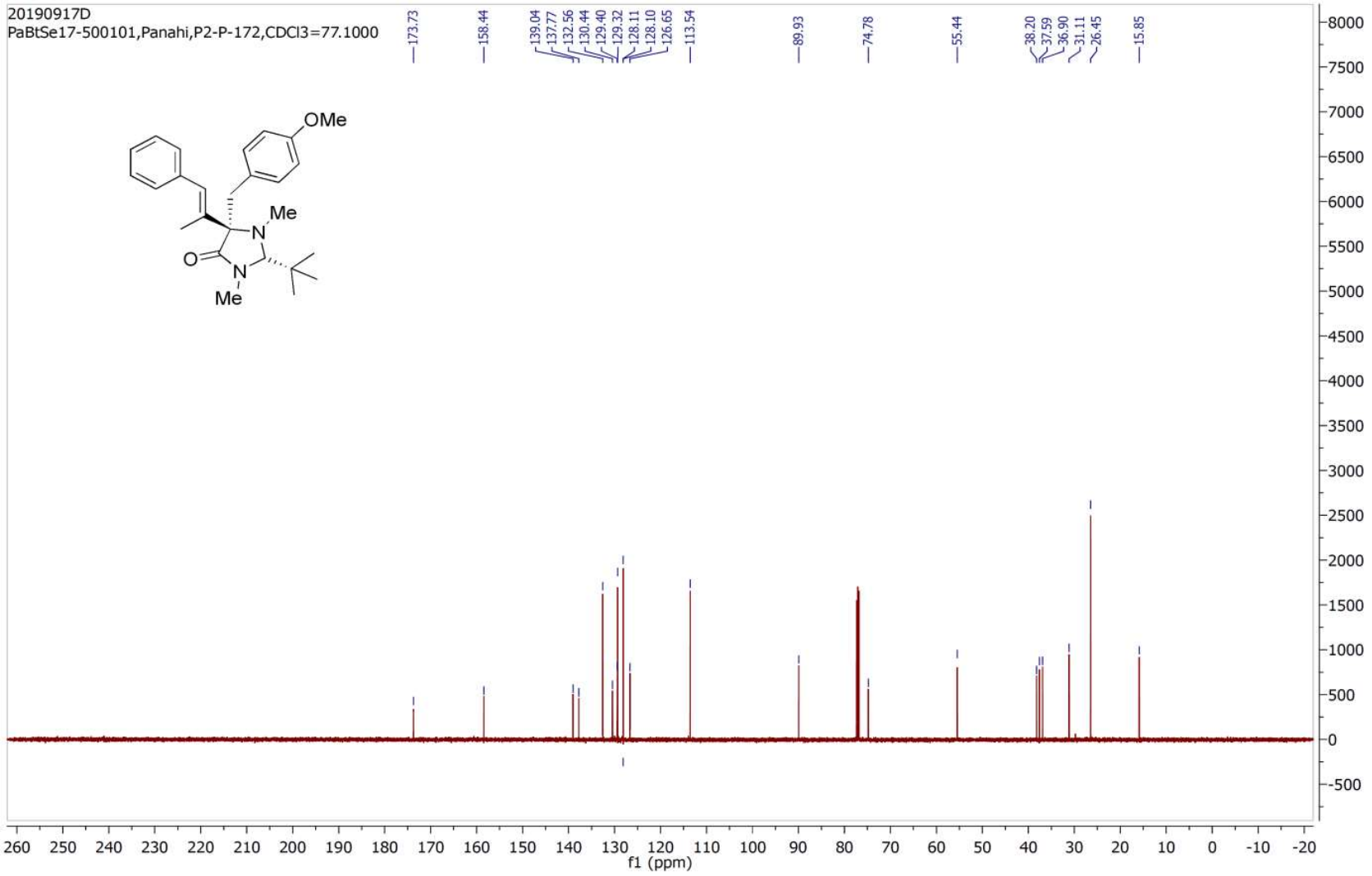



20190917D
PaBtSe17-500201,Panahi,P2-P-114,CDCl3,19F
-113.77
-113.79
-113.80
-113.82
F
Me
N
O
N
Me
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

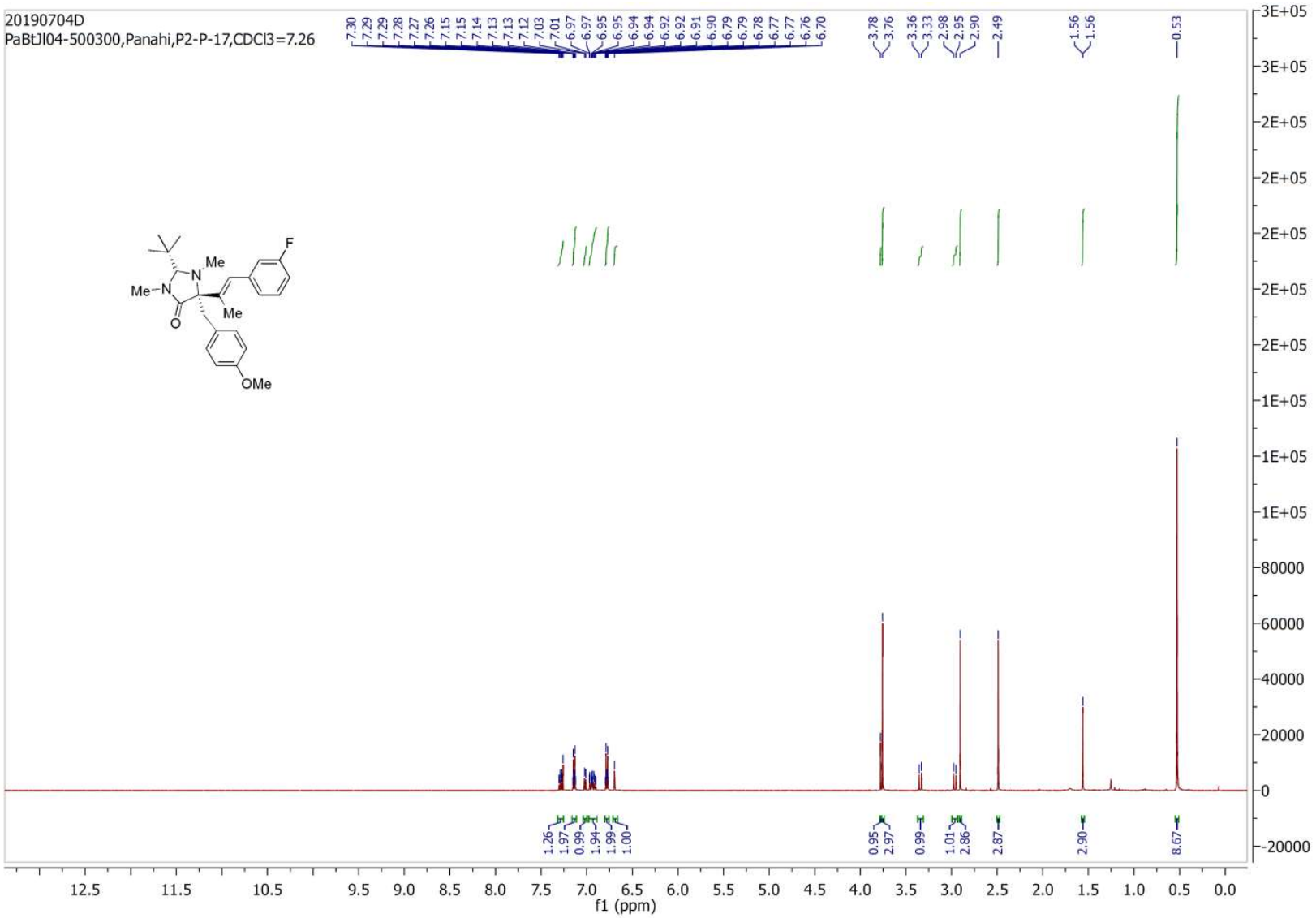

20190917D
PaBtSe17-500202,Panahi,P2-P-114,CDCl3=77.1000
163.62
161.67
129.56
129.49
125.09
125.07
116.09
115.92
113.56
113.39
90.59
42.44
38.39
31.43
27.32
25.53
24.73
24.31
15.98
1.11
F
Me
N
O
N
Me
f1 (ppm)

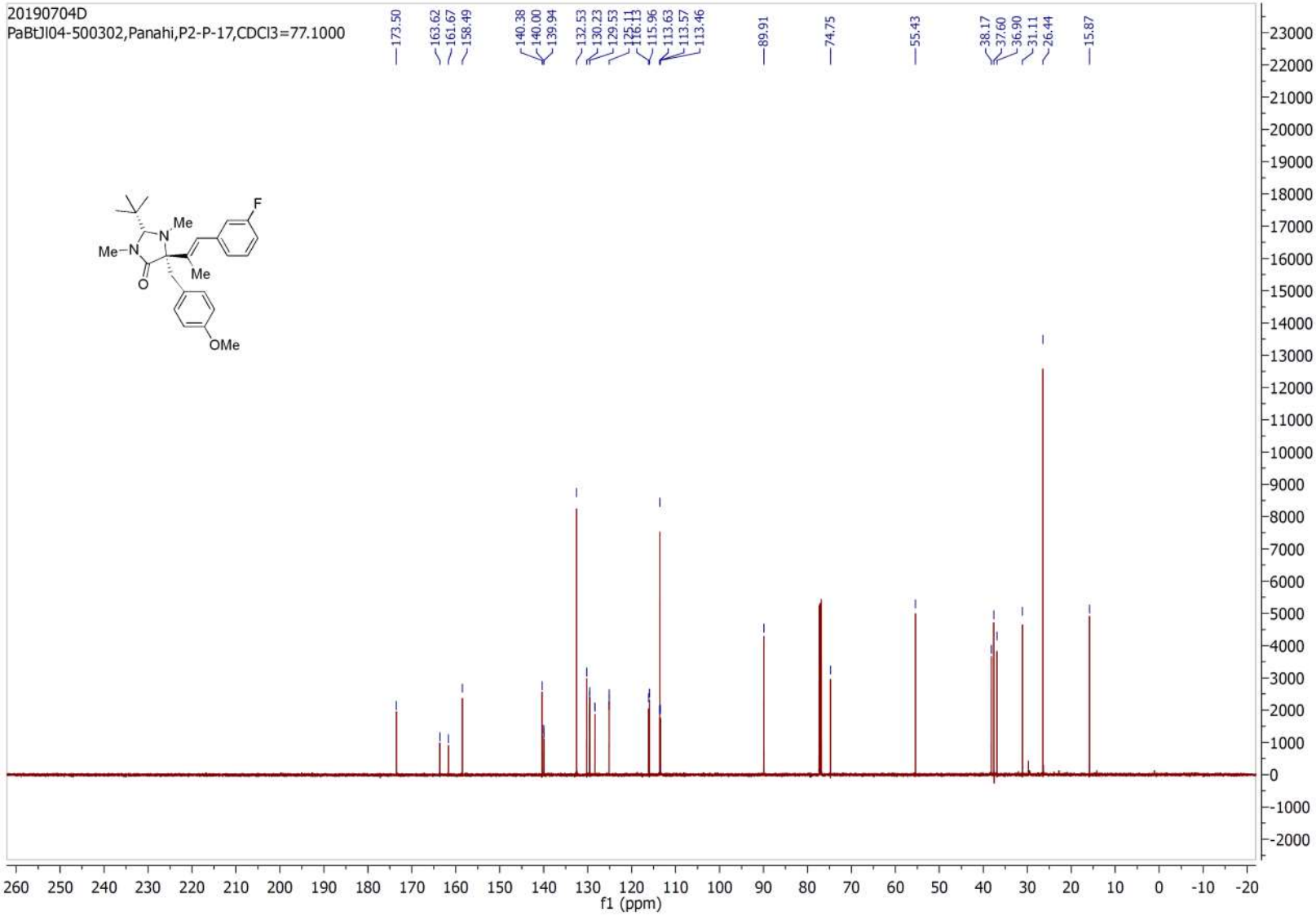
11.3.25. (2S,5S)-2-(tert-butyl)-5-(4-methoxybenzyl)-1,3-dimethyl-5-((E)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3y)

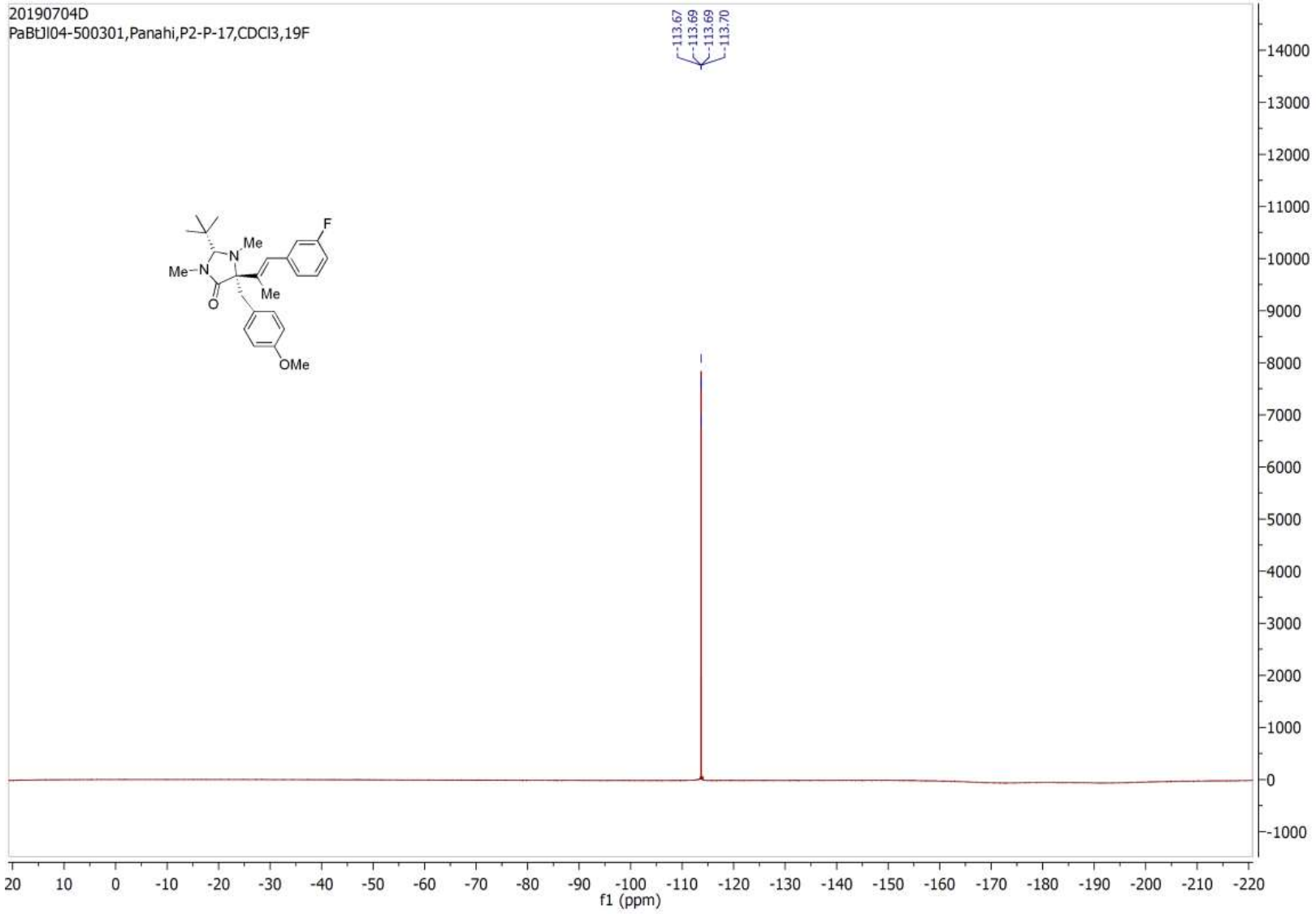



20190917D
PaBtSe17-500101,Panahi,P2-P-172,CDCl3=77.1000
173.73
158.44
139.04
137.77
132.56
130.44
129.40
129.32
128.11
128.10
126.65
113.54
89.93
74.78
55.44
38.20
37.59
36.90
31.11
26.45
15.85
OMe
Me
N
O
N
Me
f1 (ppm)

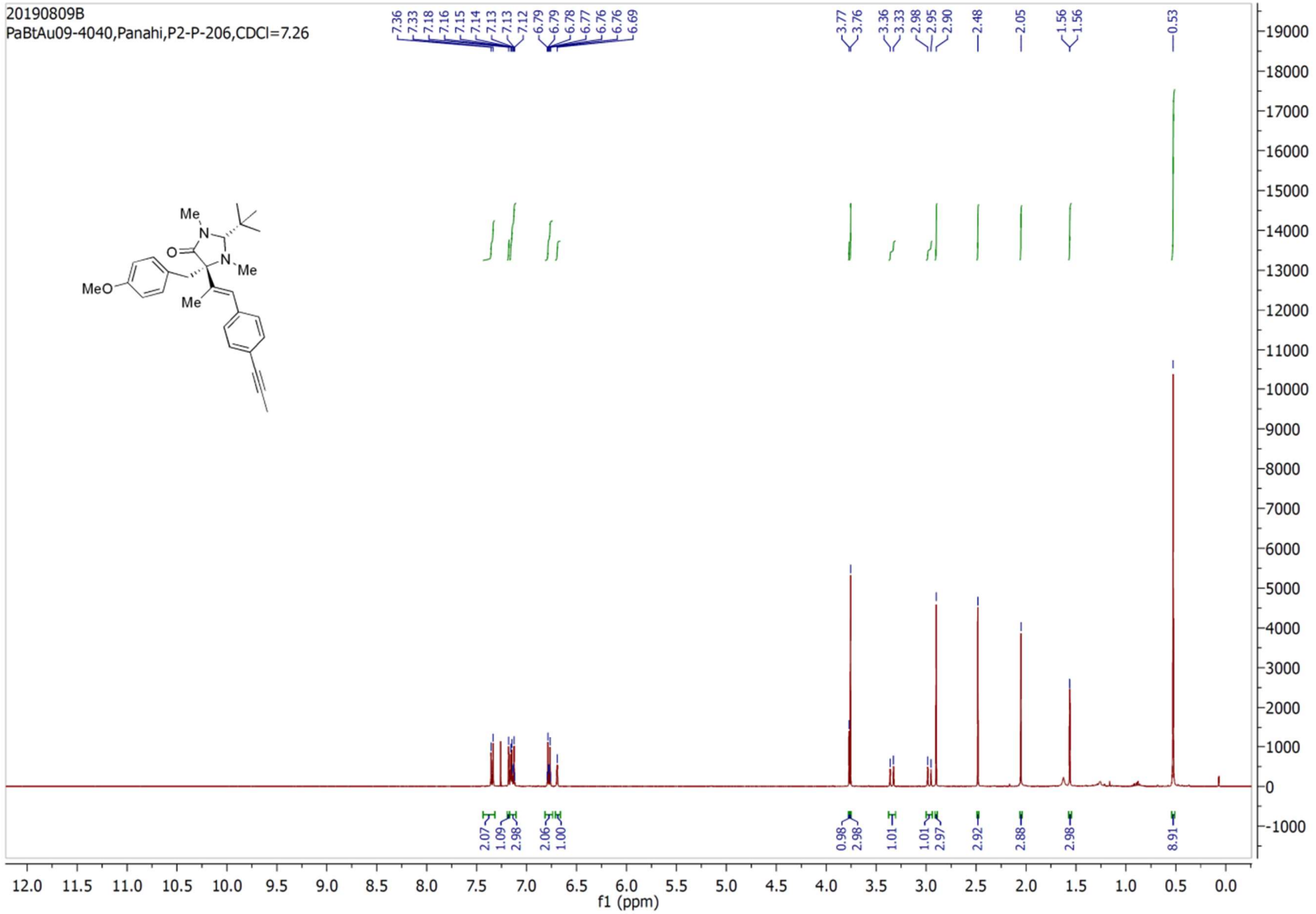
11.3.26. (2S,5S)-2-(tert-butyl)-5-((E)-1-(3-fluorophenyl)prop-1-en-2-yl)-5-(4-methoxybenzyl)-1,3-dimethylimidazolidin-4-one(3z)

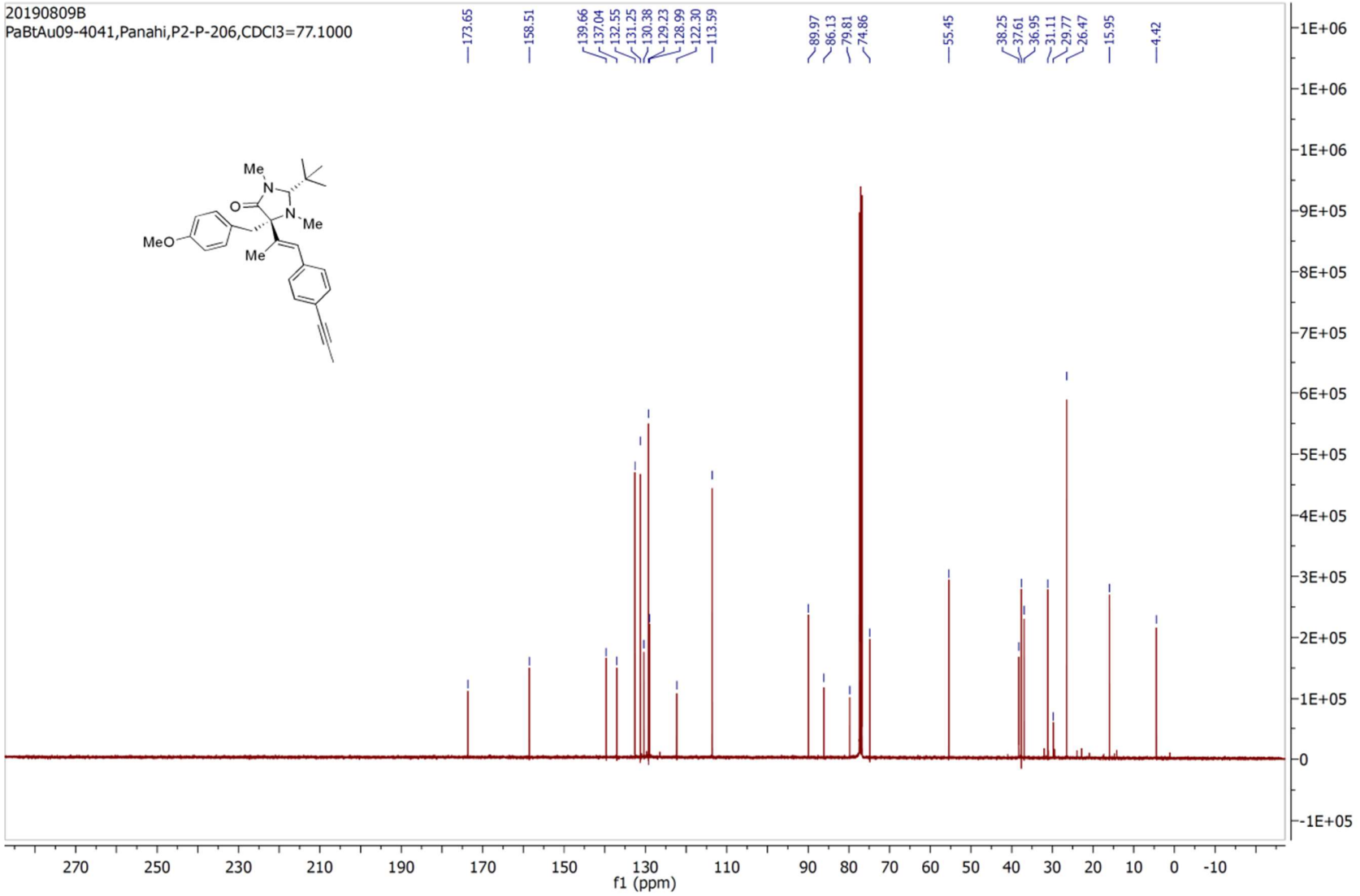



20190704D
PaBtJl04-500302,Panahi,P2-P-17,CDCl3=77.1000
173.50
163.62
161.67
158.49
140.38
140.00
139.94
132.53
130.23
129.53
125.11
116.13
115.96
113.63
113.57
113.46
89.91
74.75
55.43
38.17
37.60
36.90
31.11
26.44
15.87
Me
N
Me
N
O
Me
F
OMe
f1 (ppm)

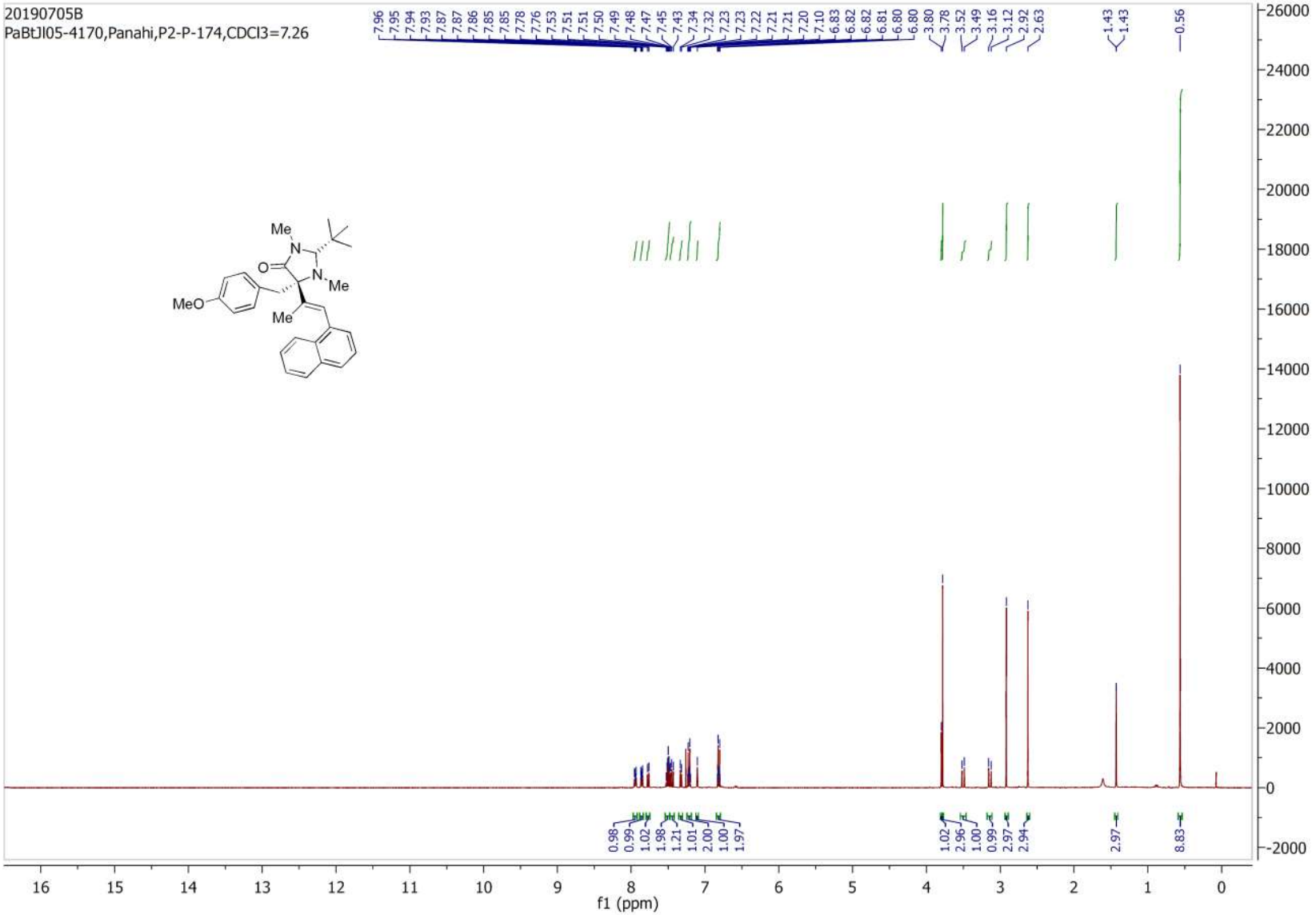

20190704D
PaBtJl04-500301,Panahi,P2-P-17,CDCl3,19F
-113.67
-113.69
-113.69
-113.70
F
Me
N
Me
N
Me
O
OMe
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -220
f1 (ppm)

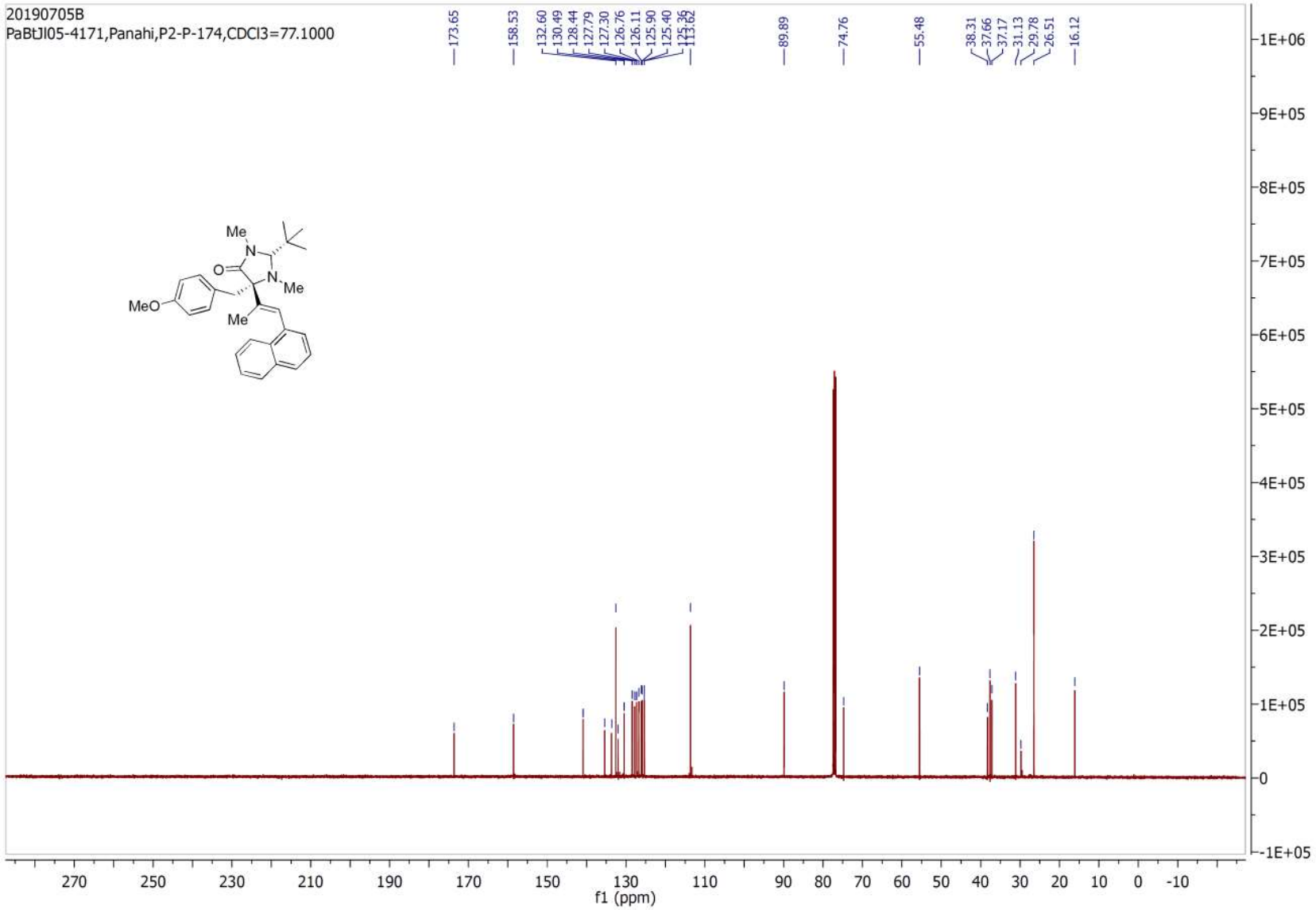
11.3.27. (2S,5S)-2-(tert-butyl)-5-(4-methoxybenzyl)-1,3-dimethyl-5-((E)-1-(4-(prop-1-yn-1-yl)phenyl)prop-1-en-2-yl)imidazolidin-4-one (3aa)



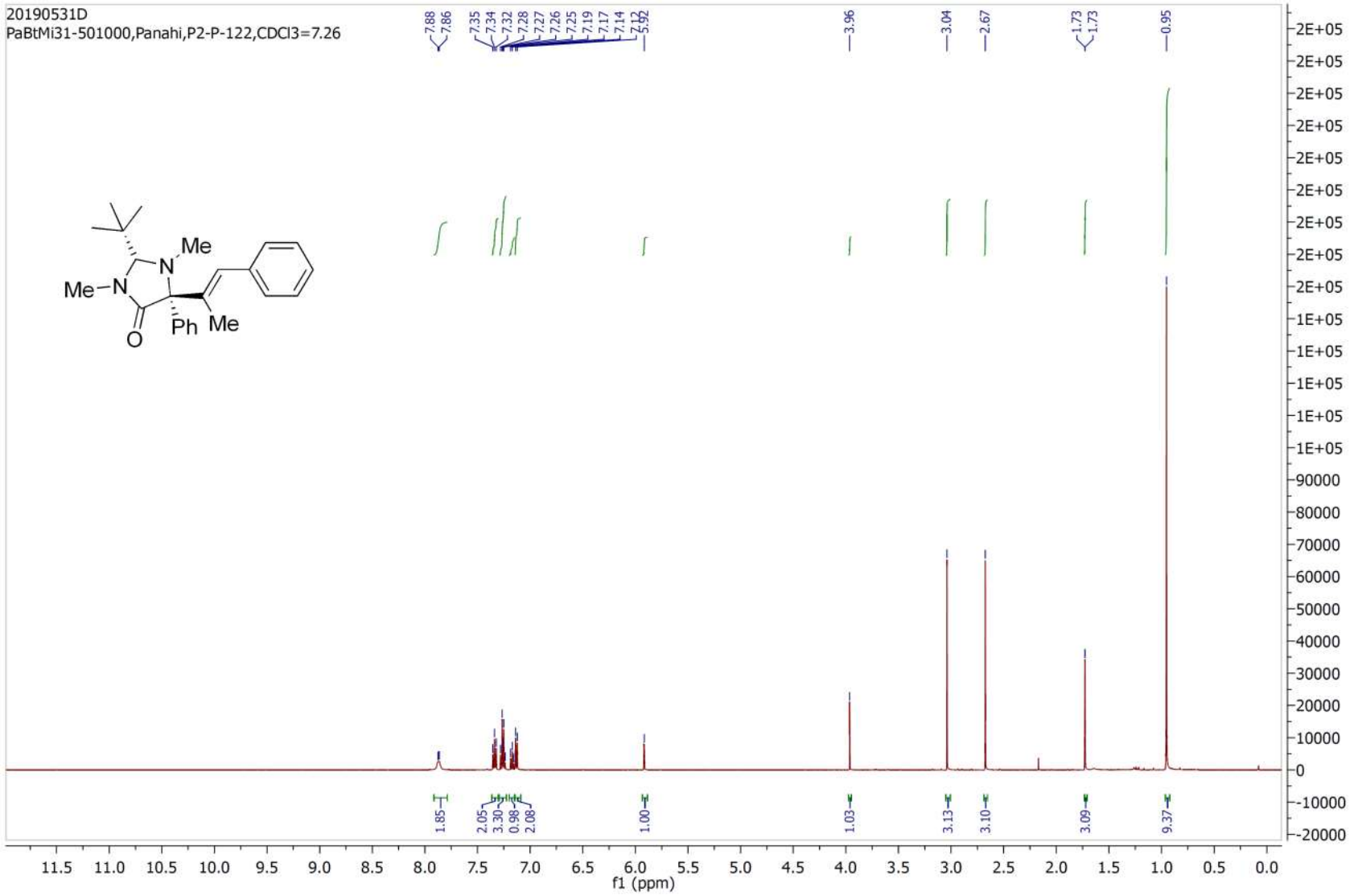

20190809B
PaBtAu09-4041,Panahi,P2-P-206,CDCl3=77.1000
173.65
158.51
139.66
137.04
132.55
131.25
130.38
129.23
128.99
122.30
113.59
89.97
86.13
79.81
74.86
55.45
38.25
37.61
36.95
31.11
29.77
26.47
15.95
4.42
Me
N
O
N
Me
MeO
Me
1E+06
1E+06
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

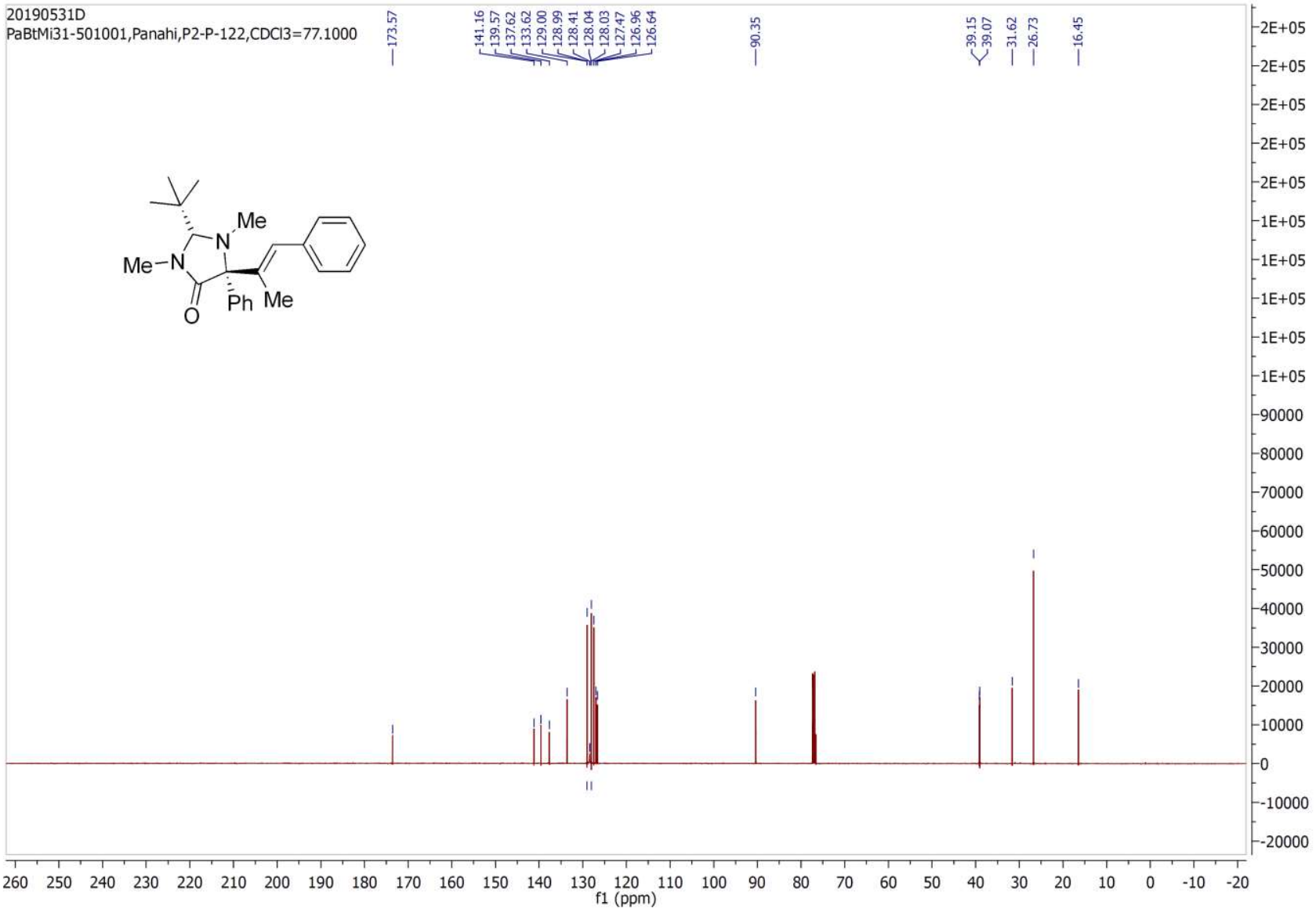
11.3.28. (2S,5S)-2-(tert-butyl)-5-(4-methoxybenzyl)-1,3-dimethyl-5-((E)-1-(naphthalen-1-yl)prop-1-en-2-yl)imidazolidin-4-one(3ab)



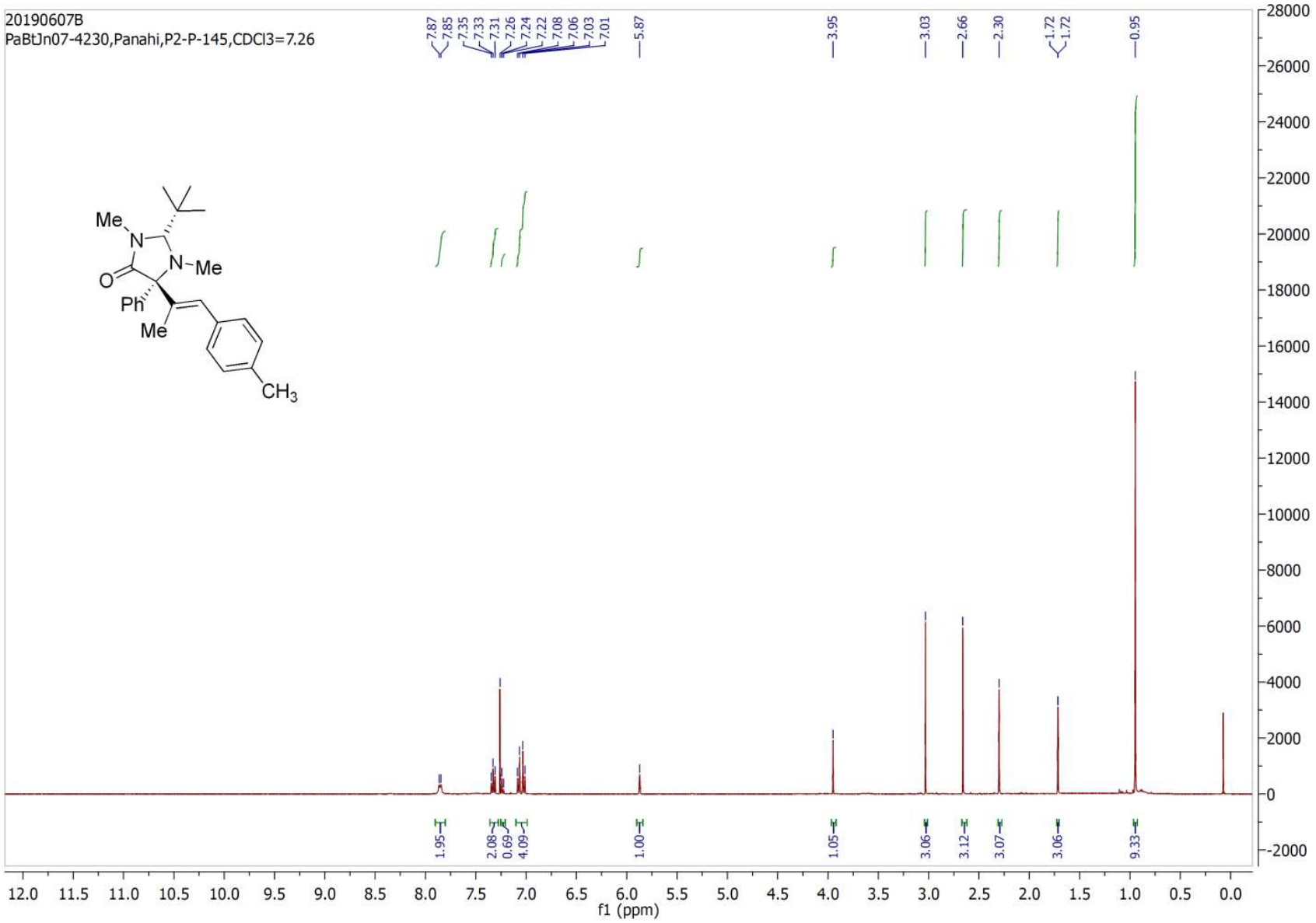

20190705B
PaBtJl05-4171,Panahi,P2-P-174,CDCl3=77.1000
173.65
158.53
132.60
130.49
128.44
127.79
127.30
126.76
126.11
125.90
125.40
113.62
89.89
74.76
55.48
38.31
37.66
37.17
31.13
29.78
26.51
16.12
Me
N
O
N
Me
MeO
Me
1E+06
9E+05
8E+05
7E+05
6E+05
5E+05
4E+05
3E+05
2E+05
1E+05
0
-1E+05
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

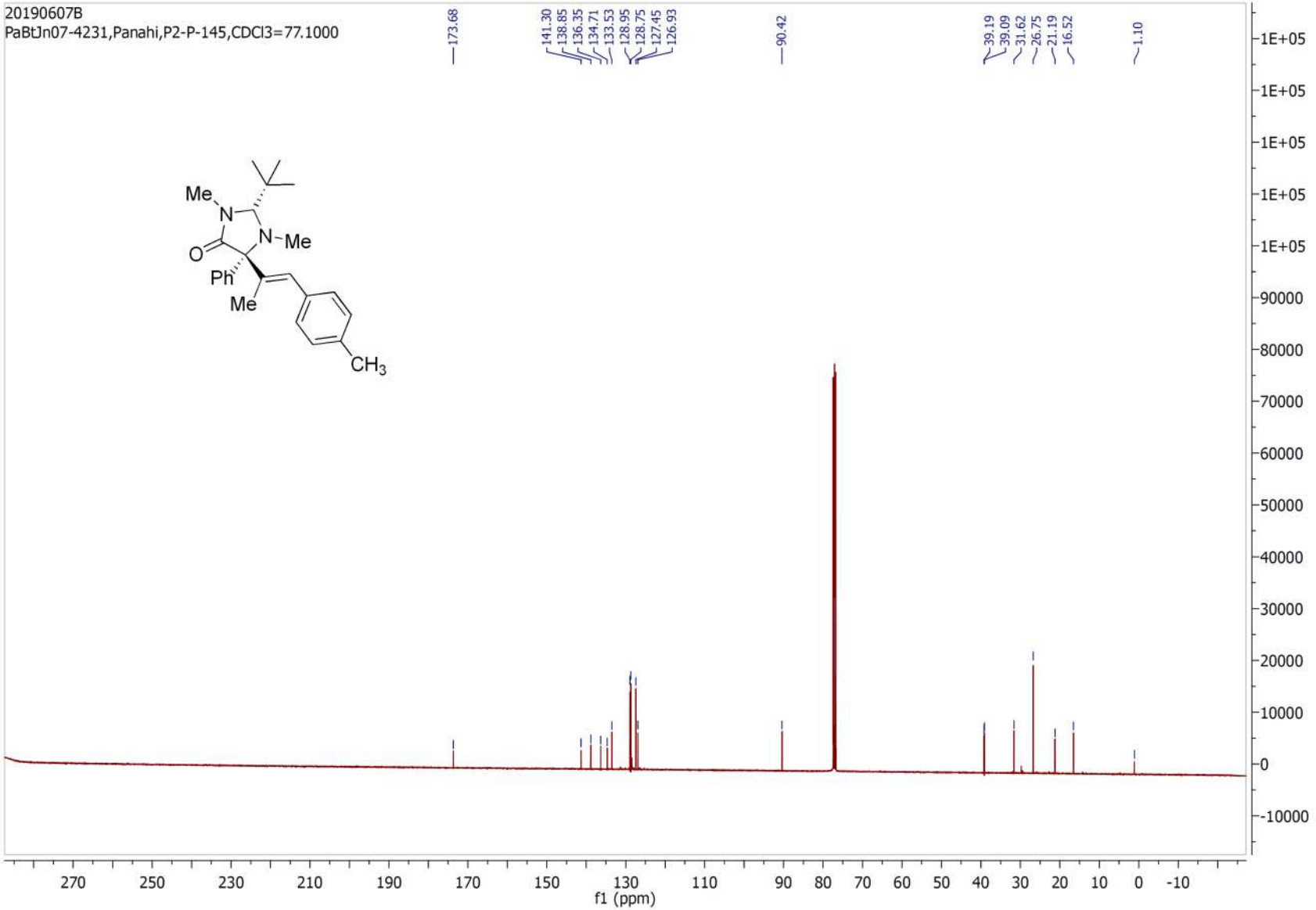
11.3.29. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-phenyl-5-((E)-1-phenylprop-1-en-2-yl)imidazolidin-4-one (3ac)



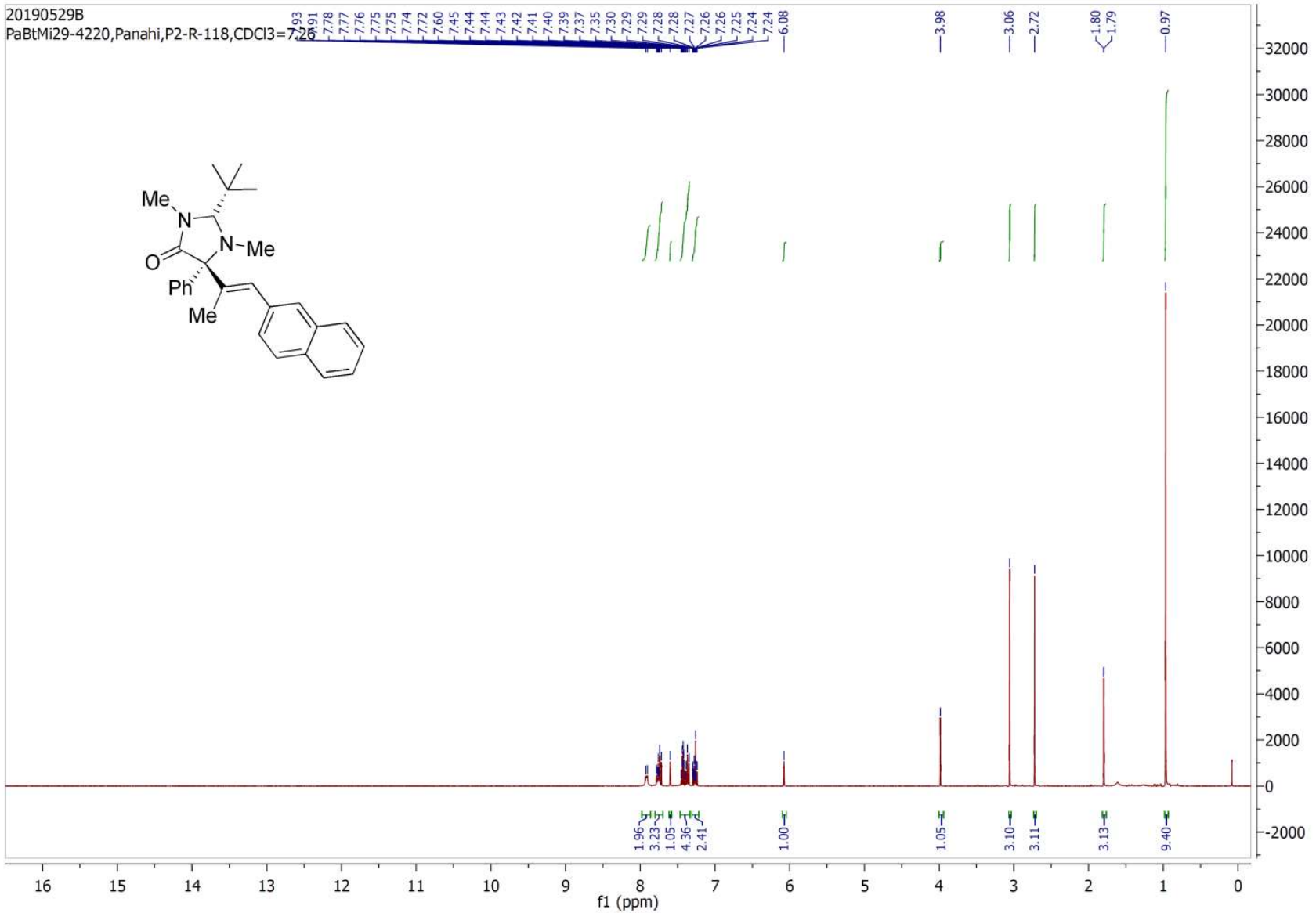

20190531D
PaBtMi31-501001,Panahi,P2-P-122,CDCl3=77.1000
173.57
141.16
139.57
137.62
133.62
129.00
128.99
128.41
128.04
128.03
127.47
126.96
126.64
90.35
39.15
39.07
31.62
26.73
16.45
Me
N
Me
N
Ph
Me
O
f1 (ppm)

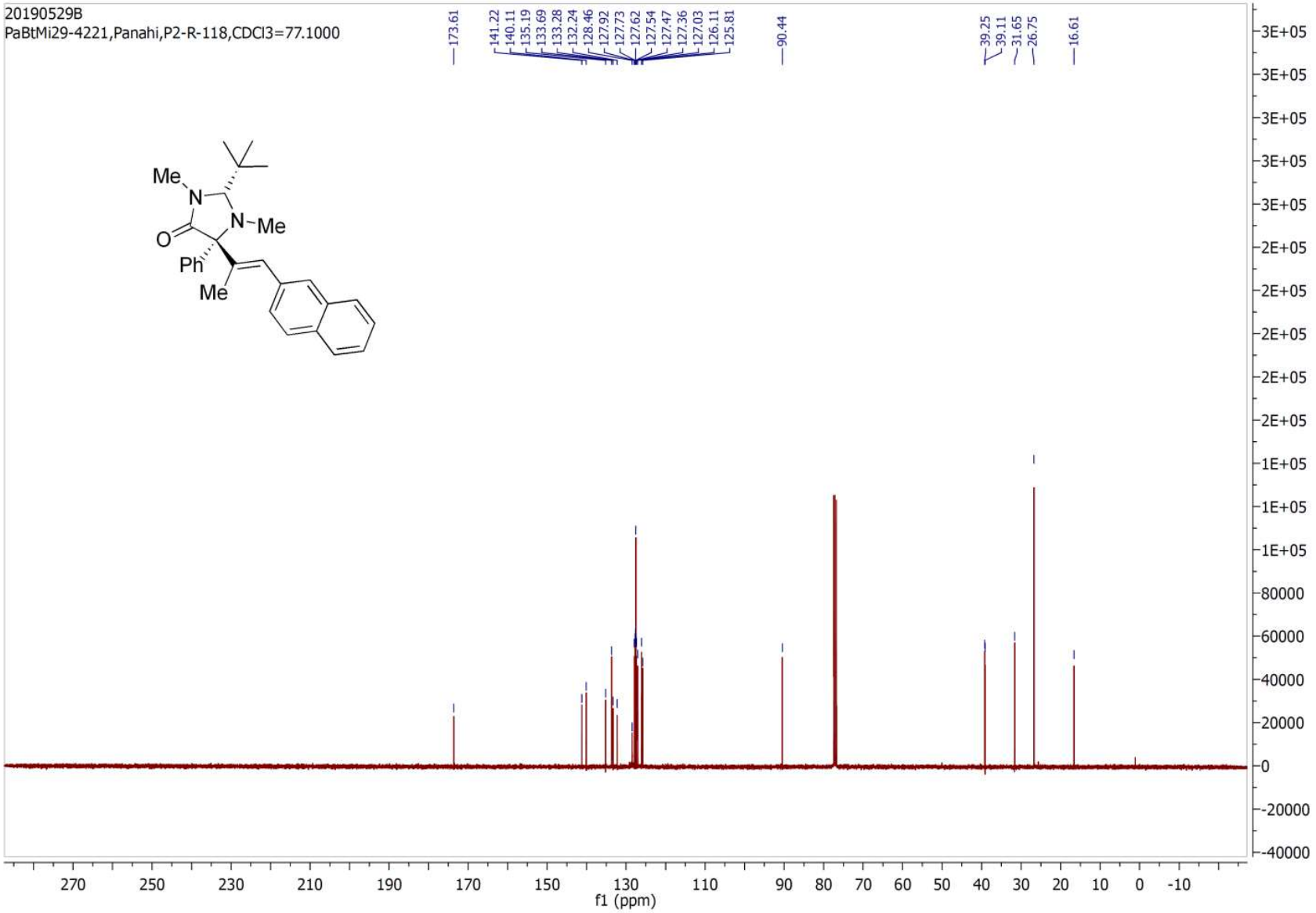
11.3.30. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-phenyl-5-((E)-1-(p-tolyl)prop-1-en-2-yl)imidazolidin-4-one (3ad)



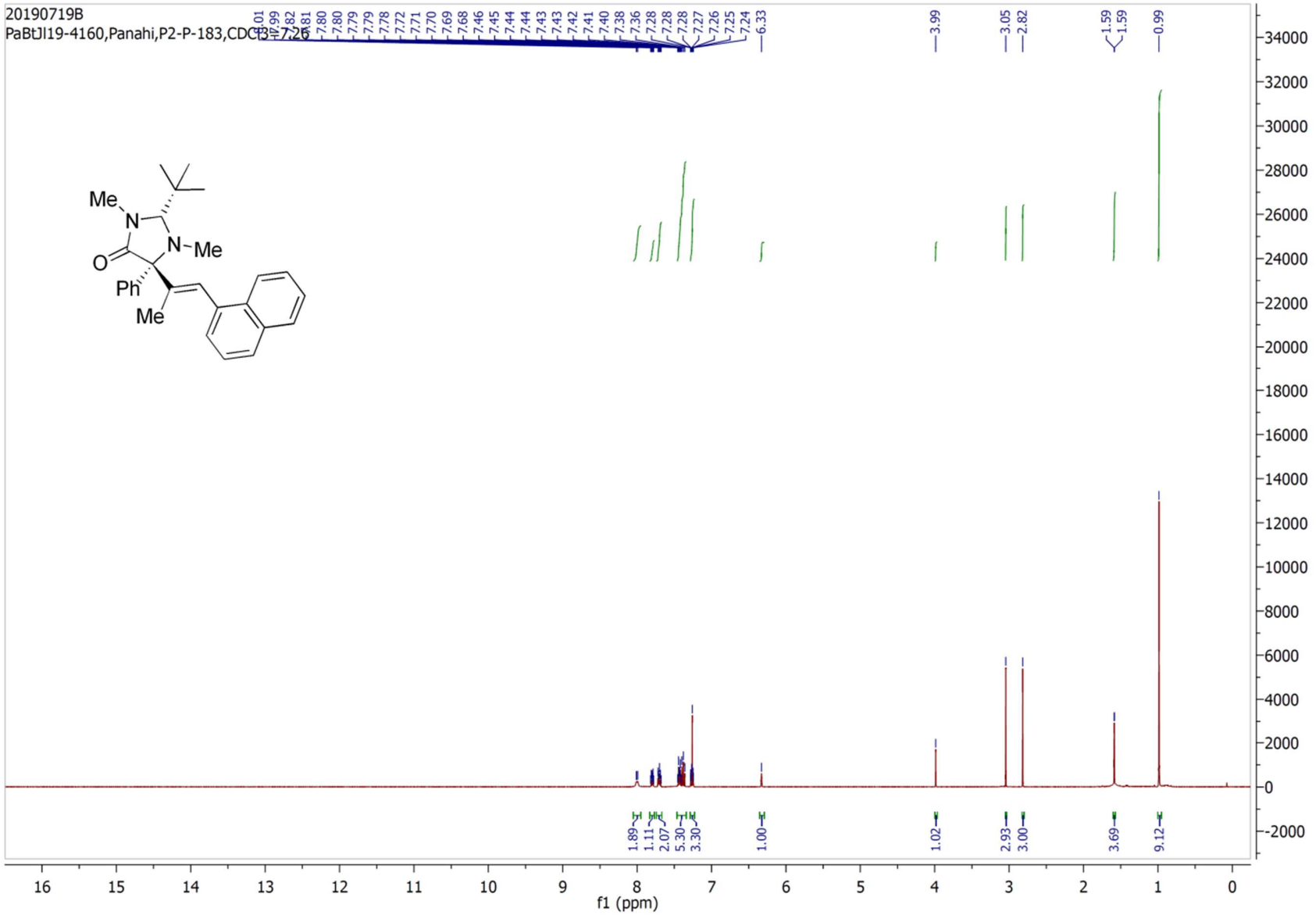

20190607B
PaBtJn07-4231,Panahi,P2-P-145,CDCl3=77.1000
173.68
141.30
138.85
136.35
134.71
133.53
128.95
128.75
127.45
126.93
90.42
39.19
39.09
31.62
26.75
21.19
16.52
1.10
Me
N
N
Me
O
Ph
Me
CH3
1E+05
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

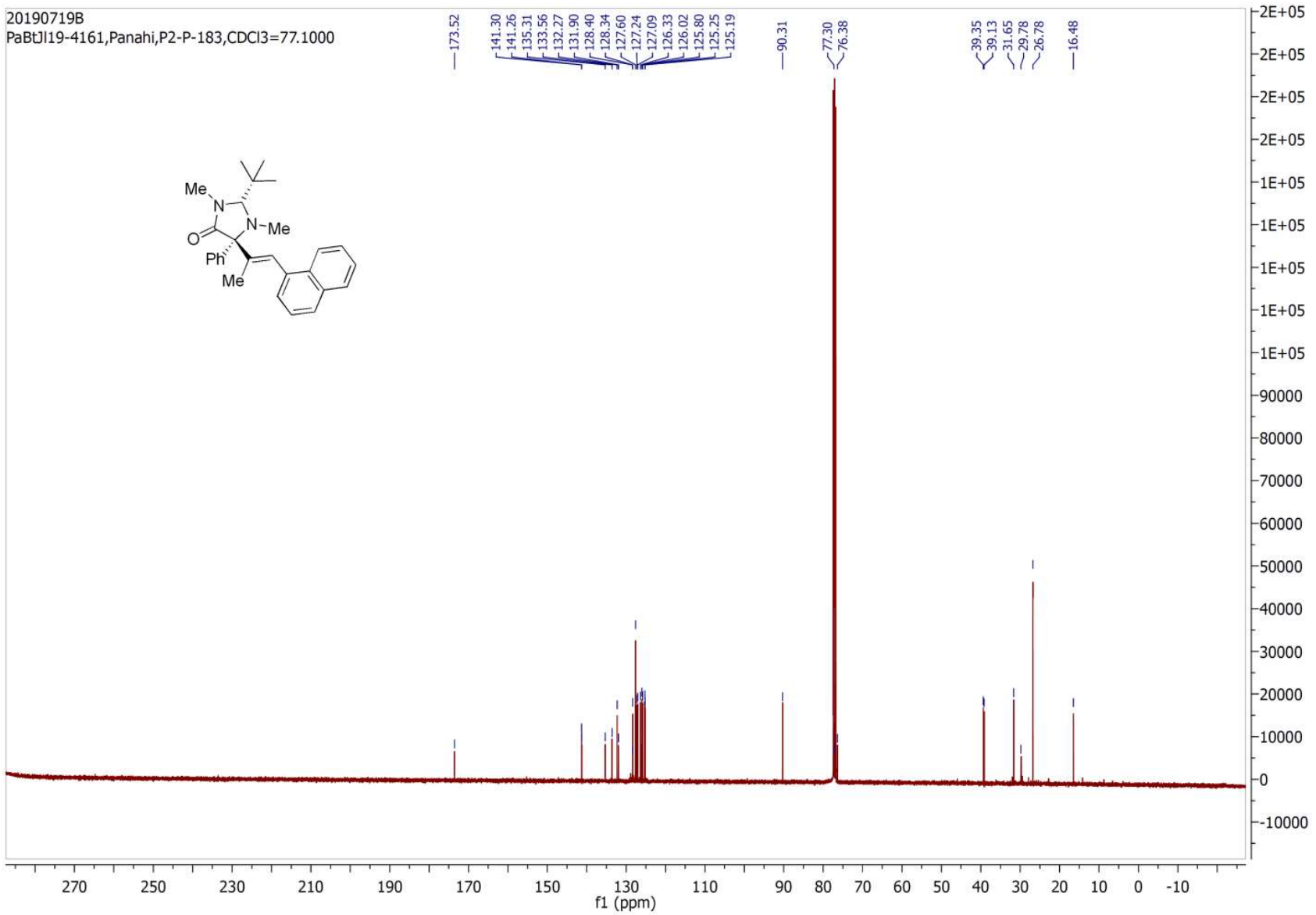
11.3.31. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-((E)-1-(naphthalen-2-yl)prop-1-en-2-yl)-5-phenylimidazolidin-4-one (3ae)



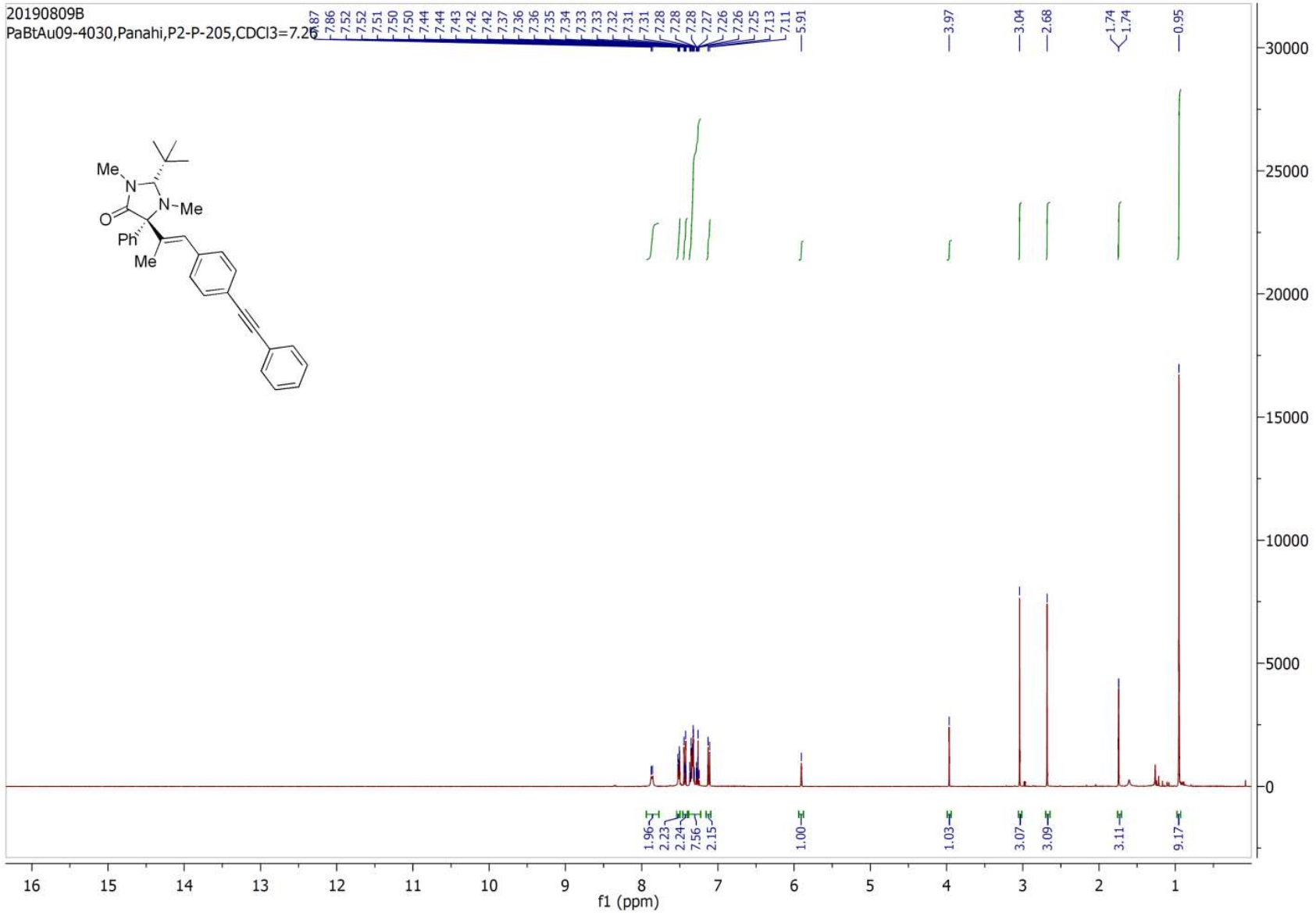

20190529B
PaBtMi29-4221,Panahi,P2-R-118,CDCl3=77.1000
173.61
141.22
140.11
135.19
133.69
133.28
132.24
128.46
127.92
127.73
127.62
127.54
127.47
127.36
127.03
126.11
125.81
90.44
39.25
39.11
31.65
26.75
16.61
Me
N
N
Me
O
Ph
Me
3E+05
2E+05
1E+05
80000
60000
40000
20000
0
-20000
-40000
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

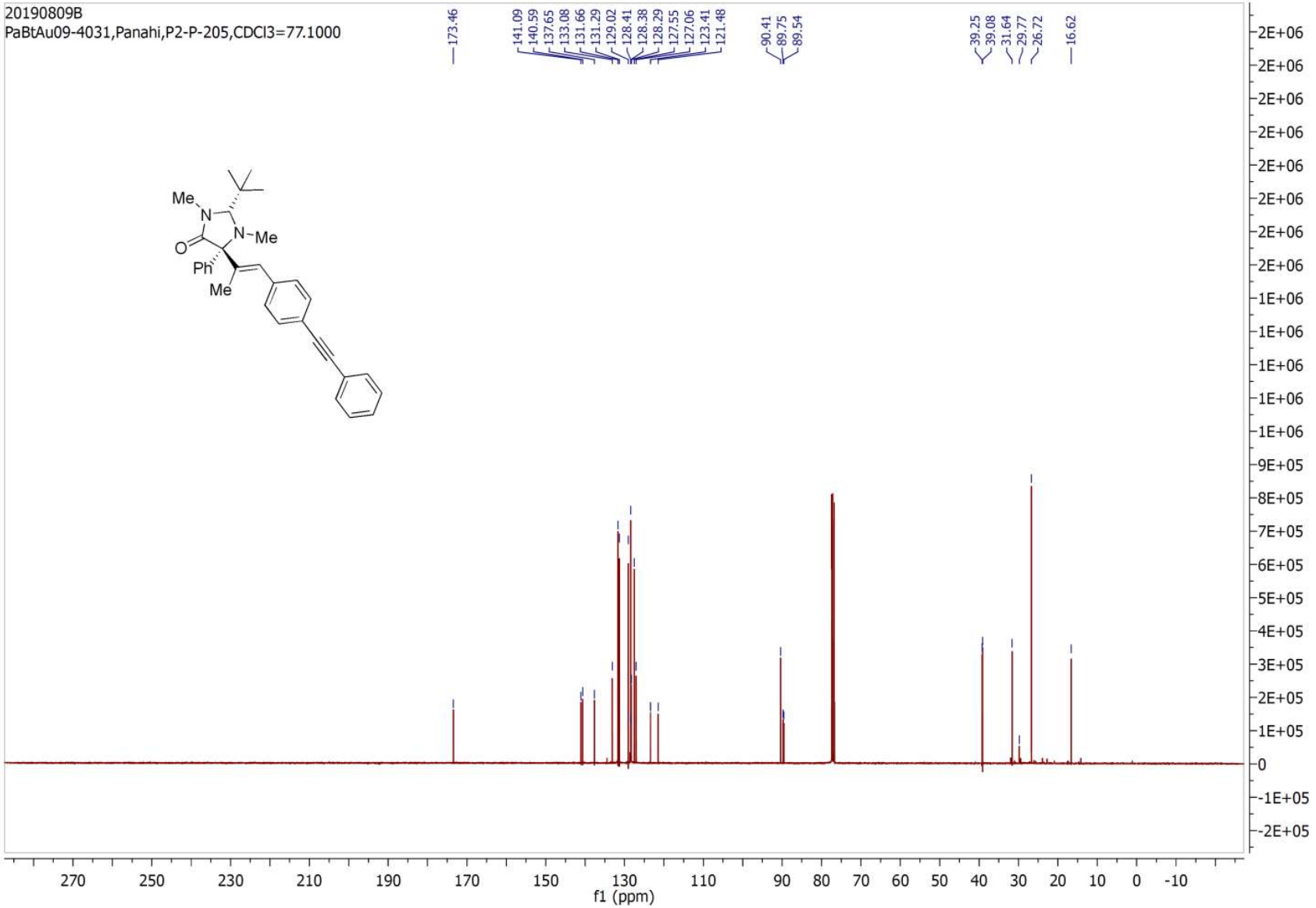
11.3.32. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-((E)-1-(naphthalen-1-yl)prop-1-en-2-yl)-5-phenylimidazolidin-4-one (3af)



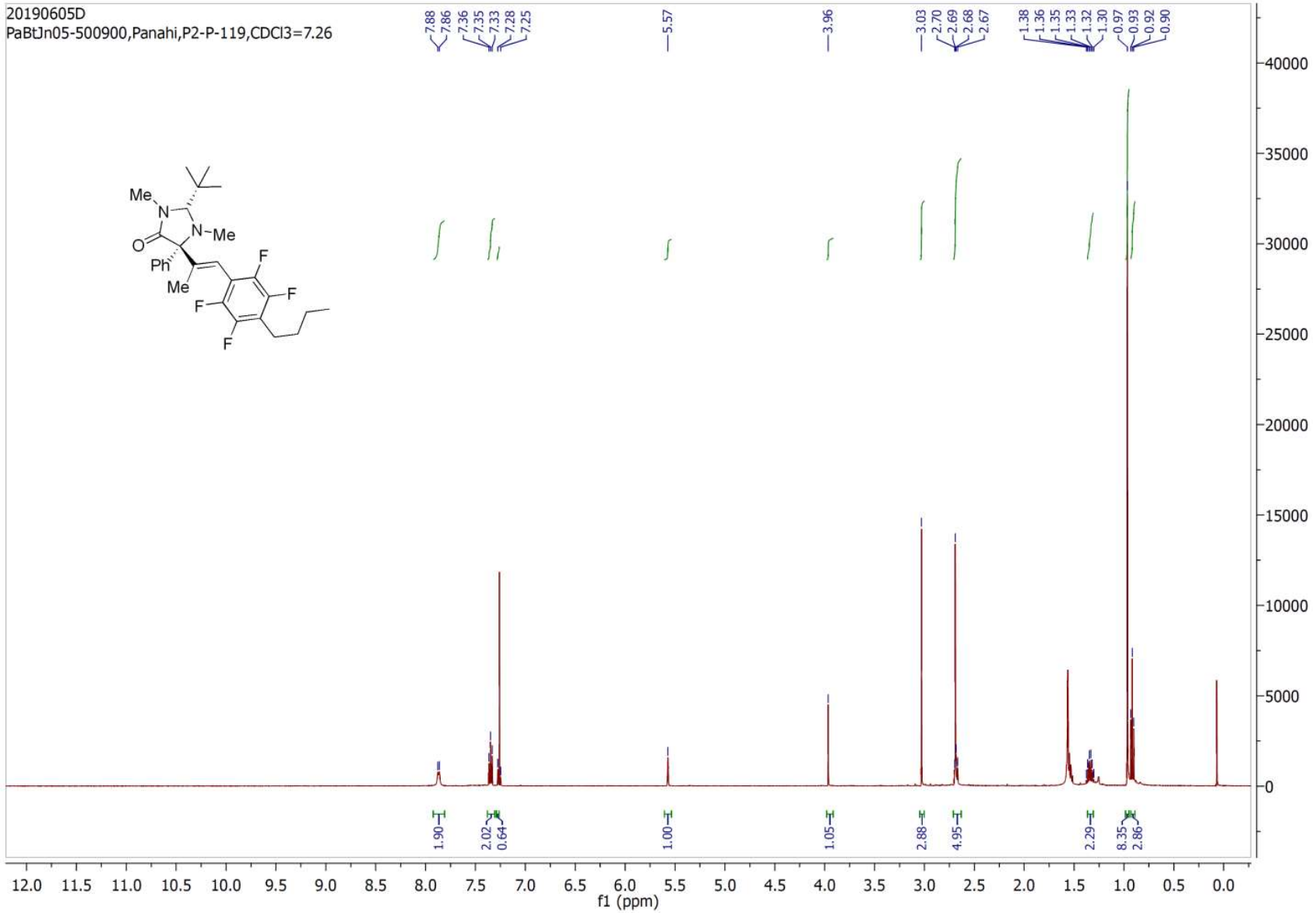

20190719B
PaBtJl19-4161,Panahi,P2-P-183,CDCl3=77.1000
173.52
141.30
141.26
135.31
133.56
132.27
131.90
128.40
128.34
127.60
127.24
127.09
126.33
126.02
125.80
125.25
125.19
90.31
77.30
76.38
39.35
39.13
31.65
29.78
26.78
16.48
Me
N
N
Me
O
Ph
Me
f1 (ppm)

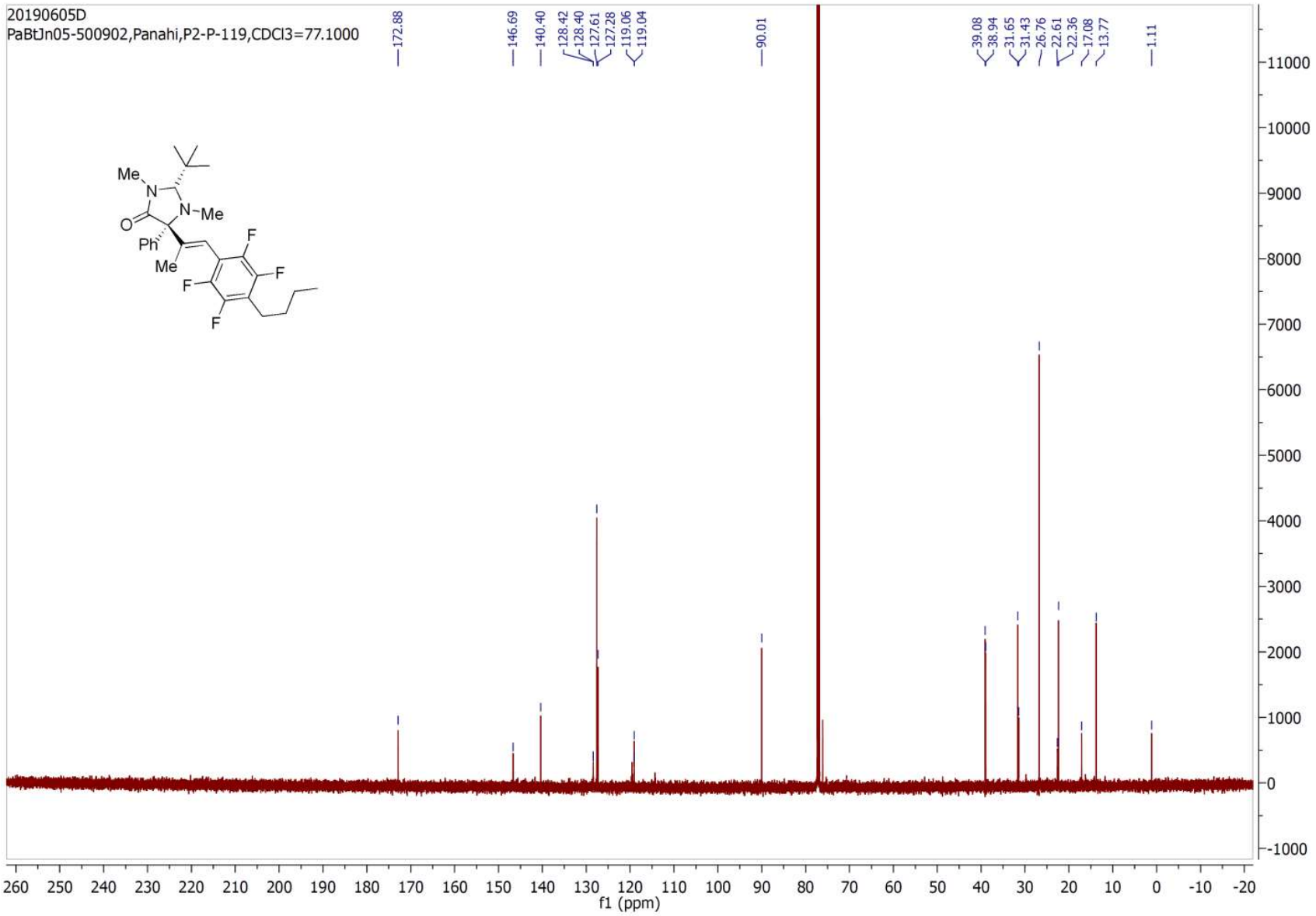
11.3.33. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-phenyl-5-((E)-1-(4-(phenylethynyl)phenyl)prop-1-en-2-yl)imidazolidin-4-one(3ag)

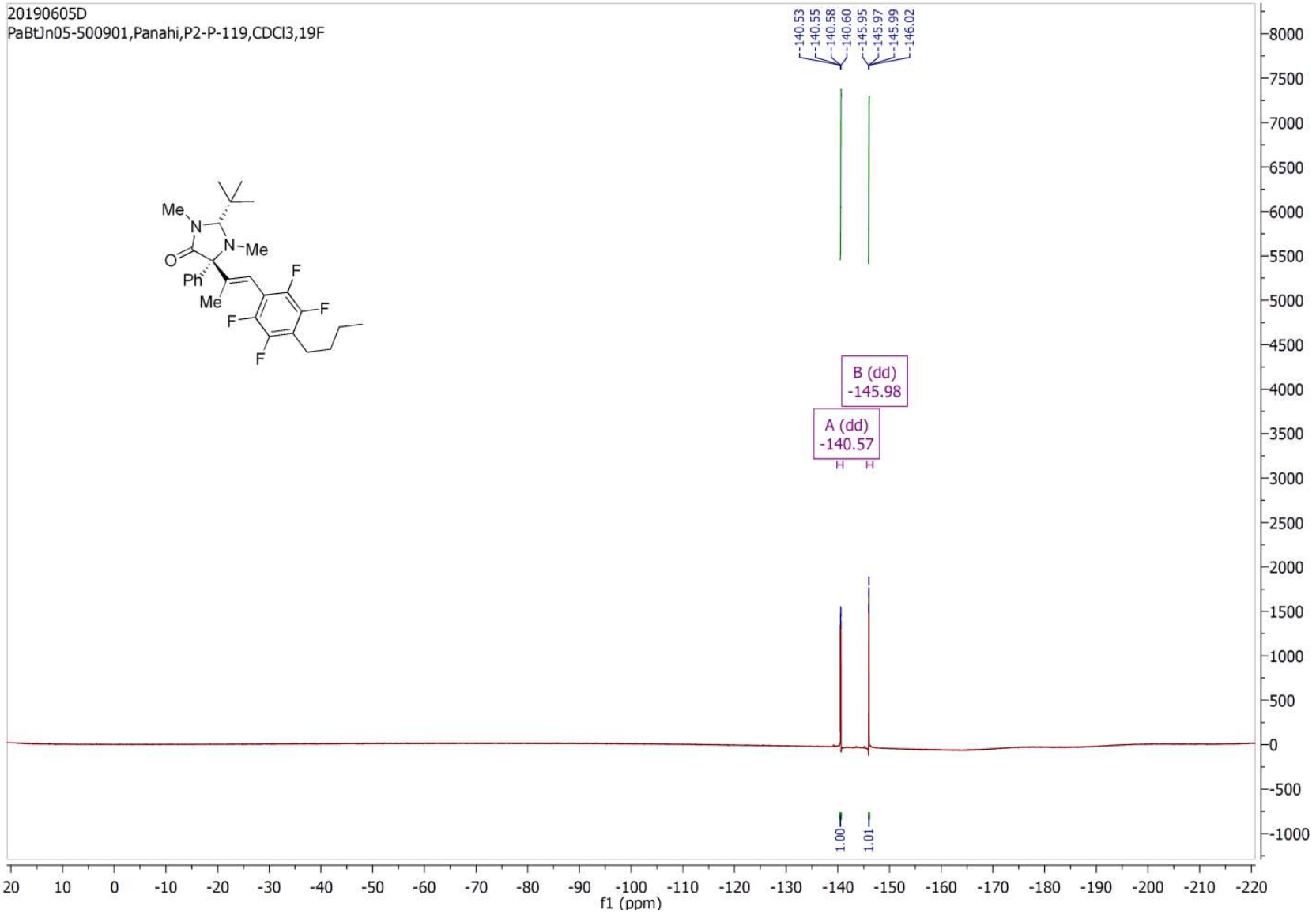



20190809B
PaBtAu09-4031,Panahi,P2-P-205,CDCl3=77.1000
173.46
141.09
140.59
137.65
133.08
131.66
131.29
129.02
128.41
128.38
128.29
127.55
127.06
123.41
121.48
90.41
89.75
89.54
39.25
39.08
31.64
29.77
26.72
16.62
Me
N
N
Me
O
Ph
Me
f1 (ppm)

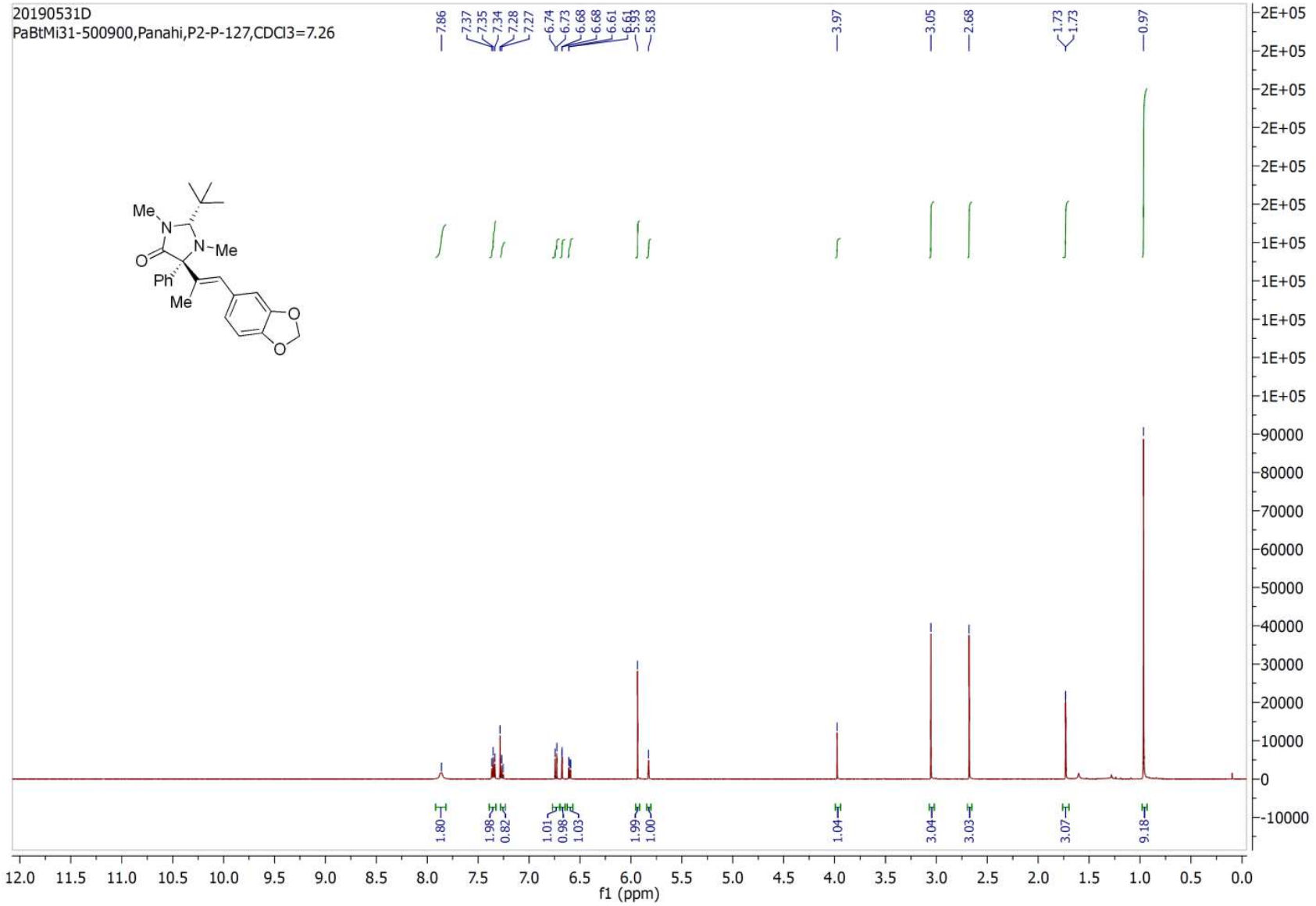
11.3.34.(2S,5R)-2-(tert-butyl)-5-((E)-1-(4-butyl-2,3,5,6-tetrafluorophenyl)prop-1-en-2-yl)-1,3-dimethyl-5-phenylimidazolidin-4-one(3ah)

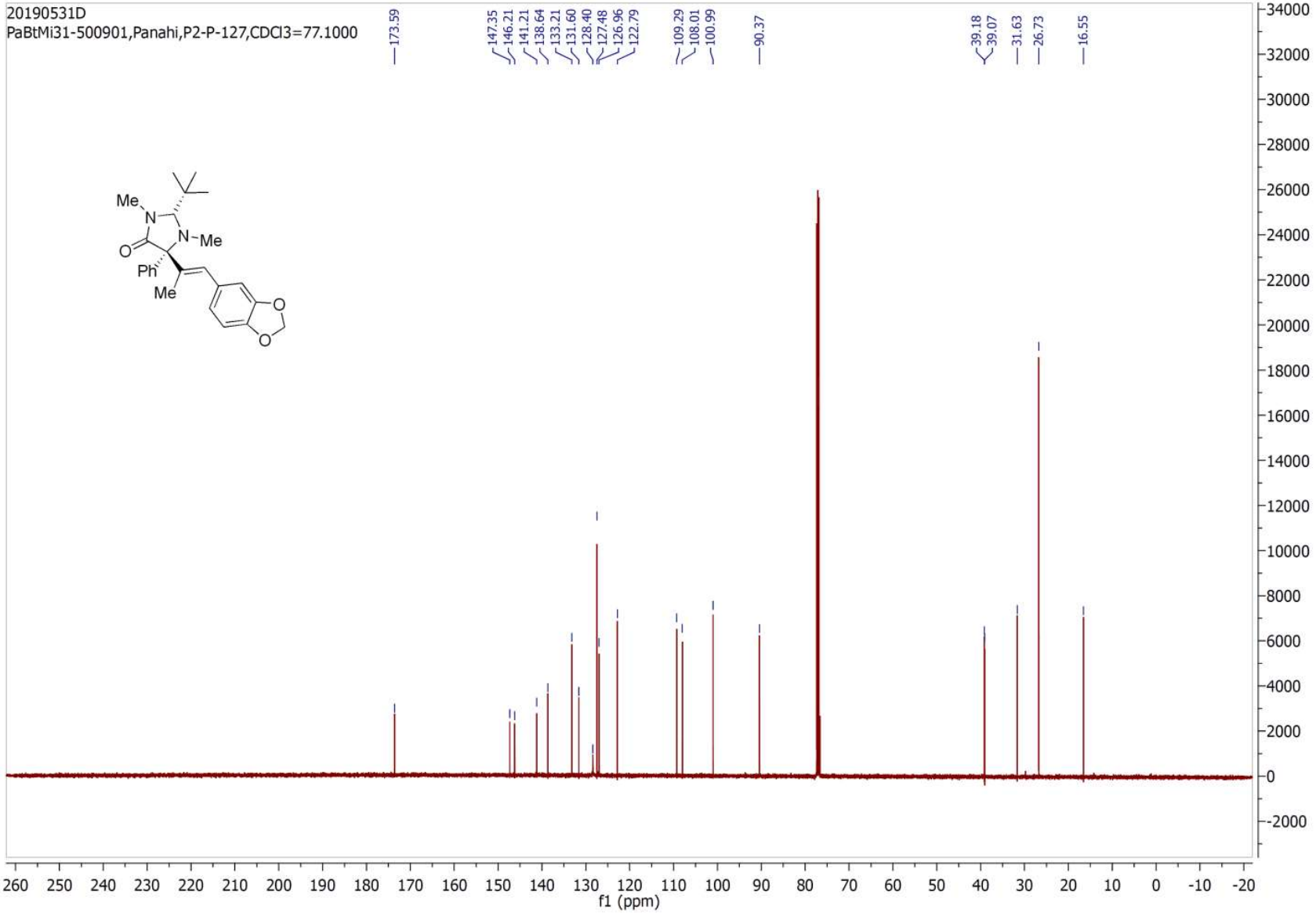



20190605D
PaBtJn05-500902,Panahi,P2-P-119,CDCl3=77.1000
172.88
146.69
140.40
128.42
128.40
127.61
127.28
119.06
119.04
90.01
39.08
38.94
31.65
31.43
26.76
22.61
22.36
17.08
13.77
1.11
Me
N
N
Me
O
Ph
Me
F
F
F
F
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
260 250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

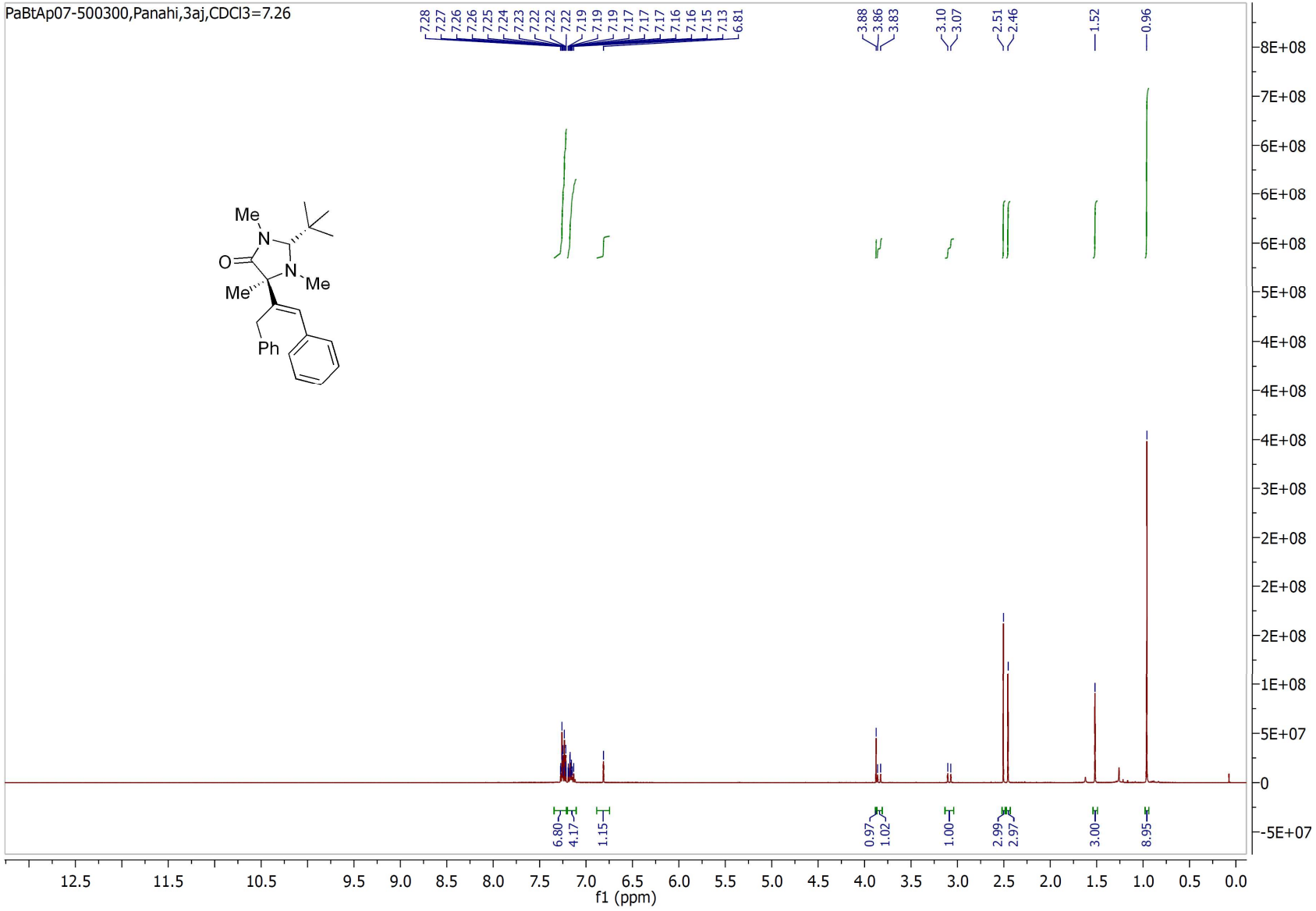

20190605D
PaBtJn05-500901,Panahi,P2-P-119,CDCl3,19F
-140.53
-140.55
-140.58
-140.60
-145.95
-145.97
-145.99
-146.02
B (dd)
-145.98
A (dd)
-140.57
H H
1.00
1.01
f1 (ppm)

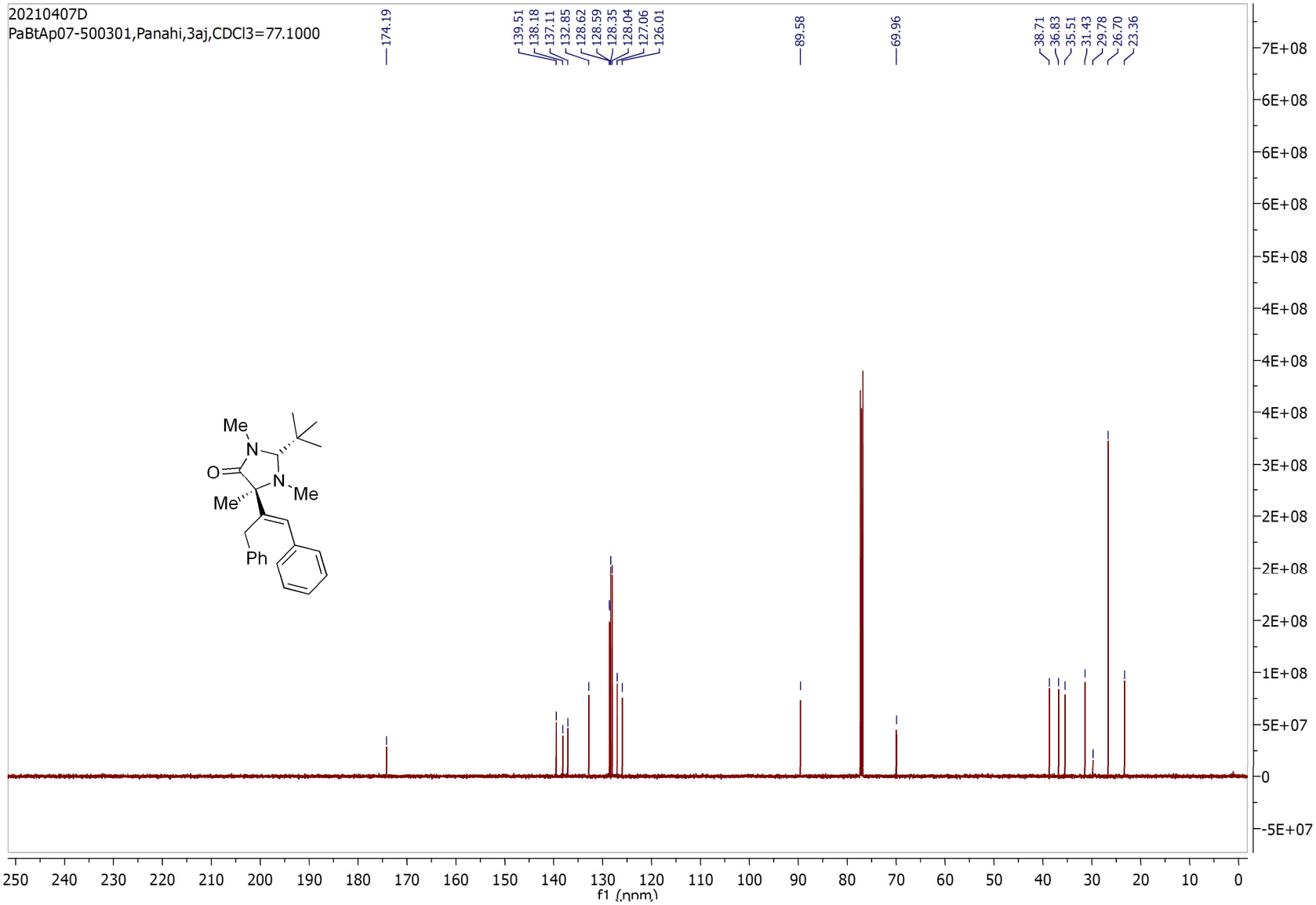
11.3.35. (2S,5R)-5-((E)-1-(benzo[d][1,3]dioxol-5-yl)prop-1-en-2-yl)-2-(tert-butyl)-1,3-dimethyl-5-phenylimidazolidin-4-one(3ai)



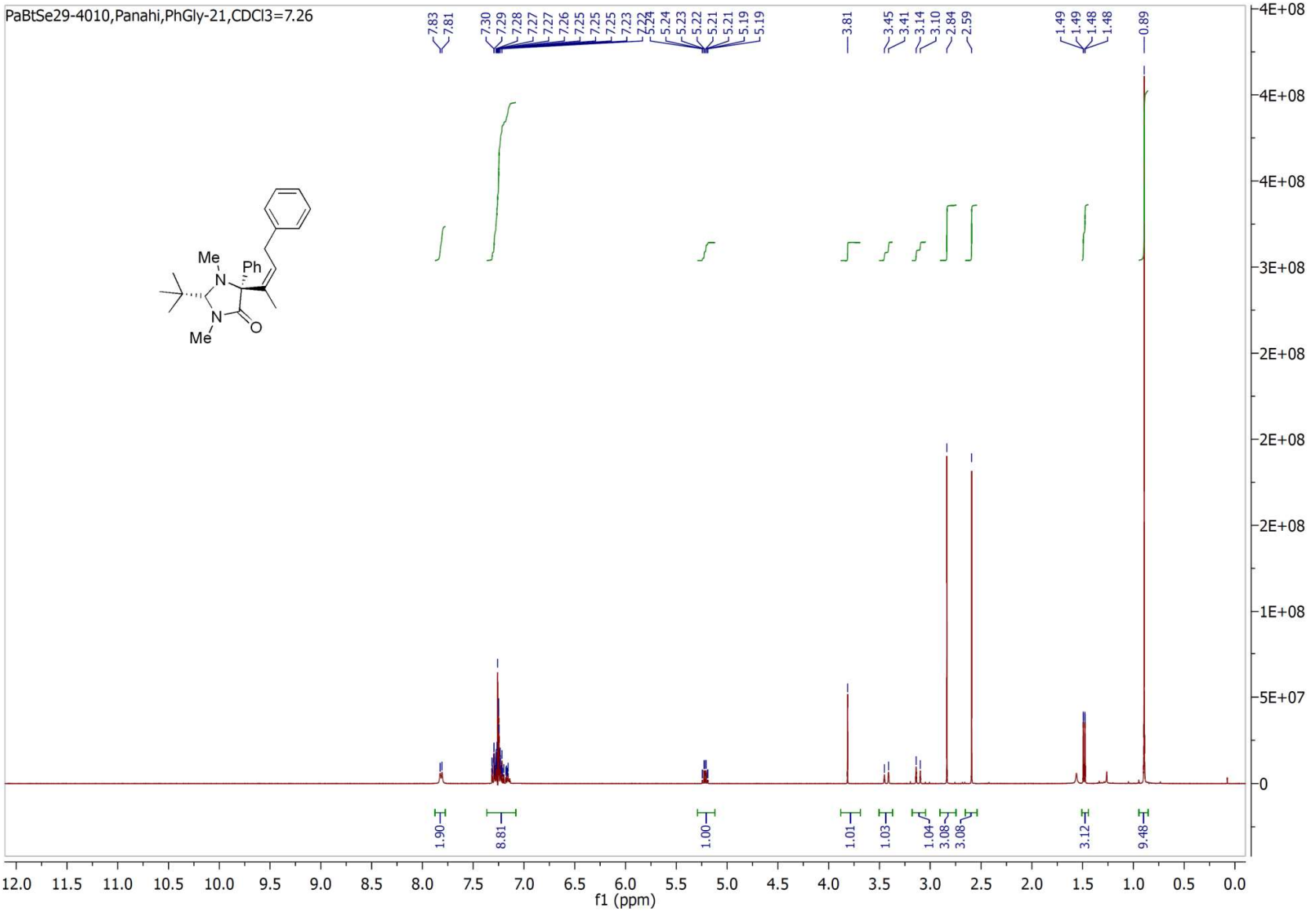

20190531D
PaBtMi31-500901,Panahi,P2-P-127,CDCl3=77.1000
173.59
147.35
146.21
141.21
138.64
133.21
131.60
128.40
127.48
126.96
122.79
109.29
108.01
100.99
90.37
39.18
39.07
31.63
26.73
16.55
Me
N
N
Me
O
Ph
Me
O
O
f1 (ppm)

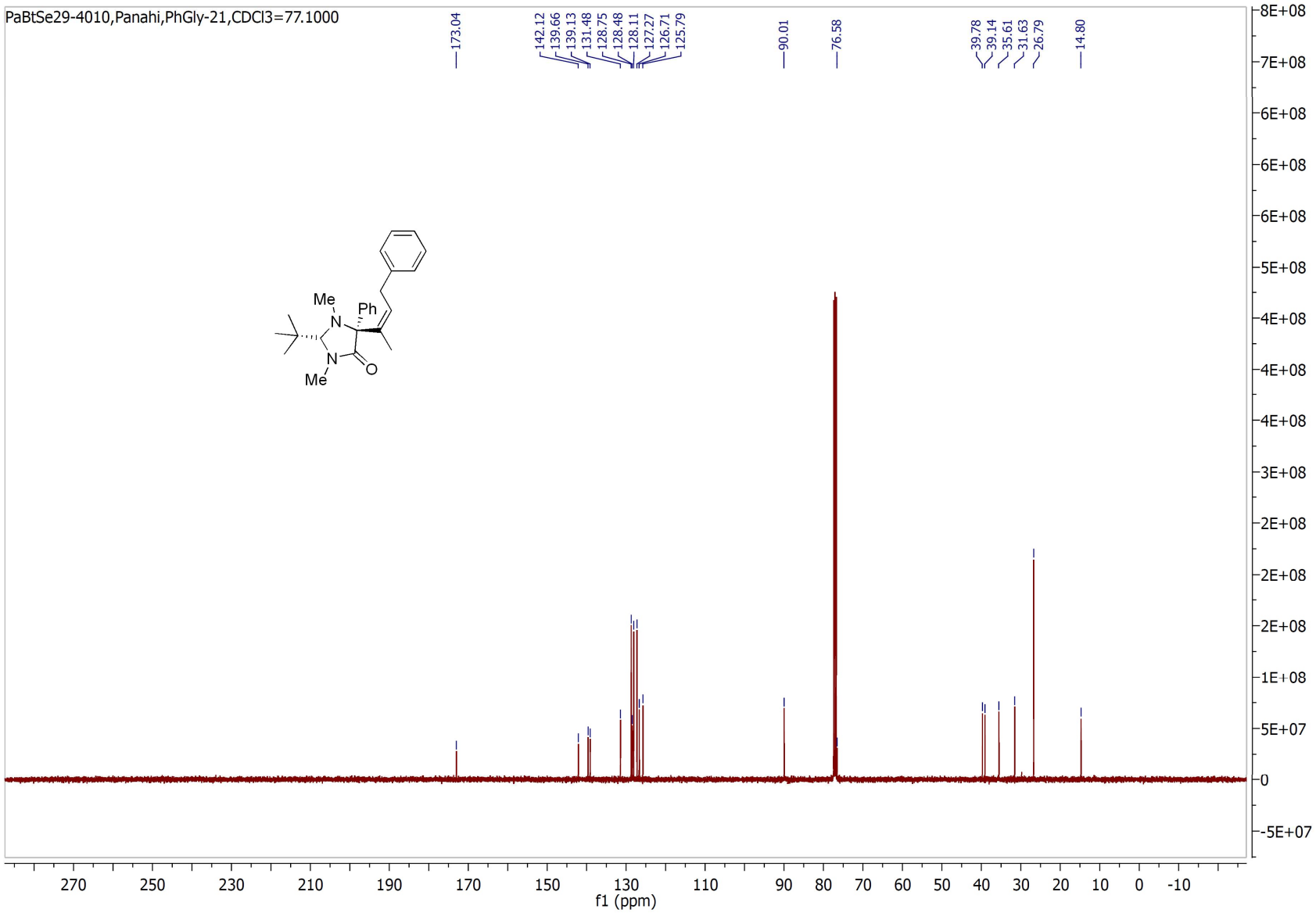
4.4.36. (2S,5S)-2-(tert-butyl)-5-((E)-1,3-diphenylprop-1-en-2-yl)-1,3,5-trimethylimidazolidin-4-one (3aj)

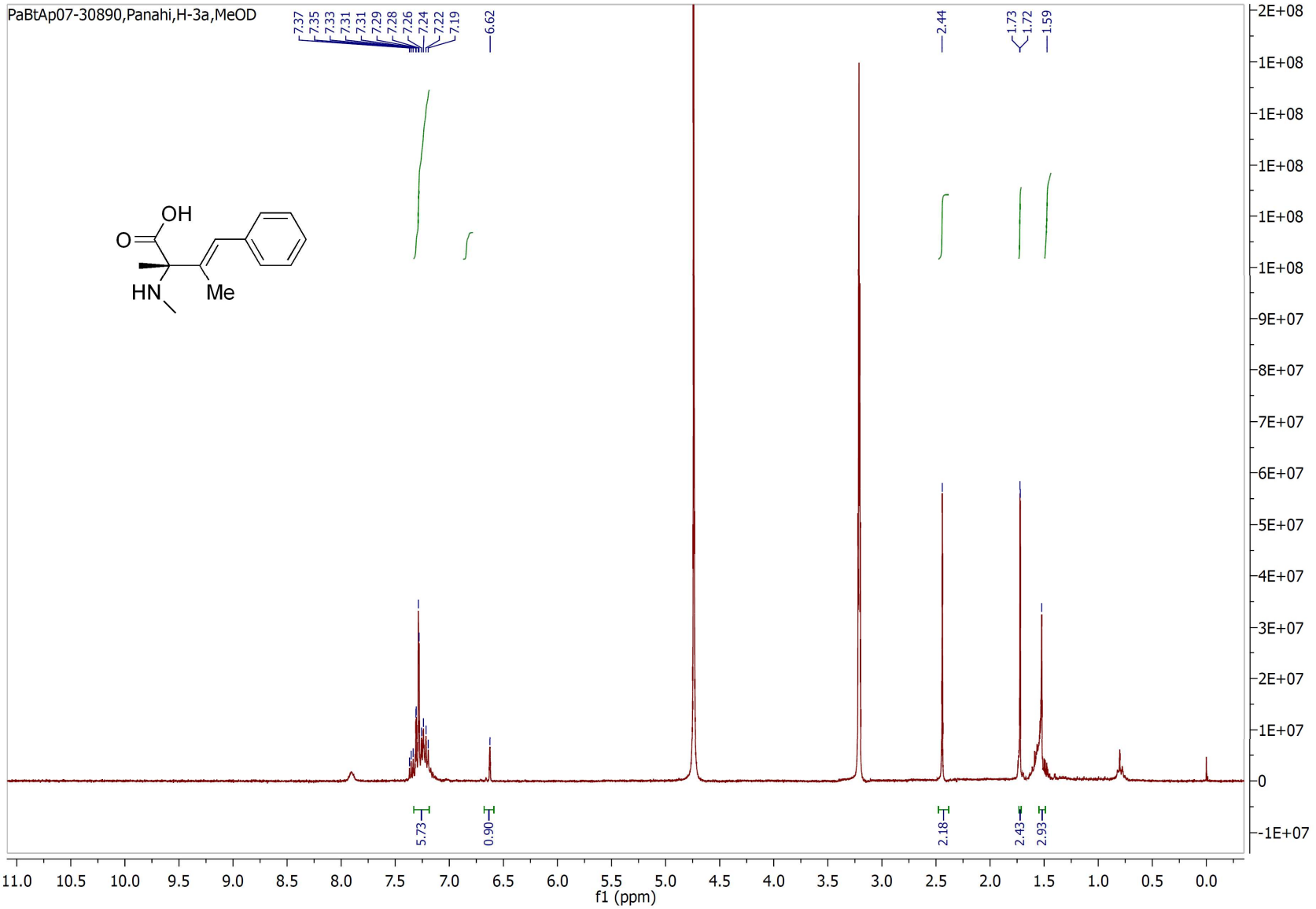


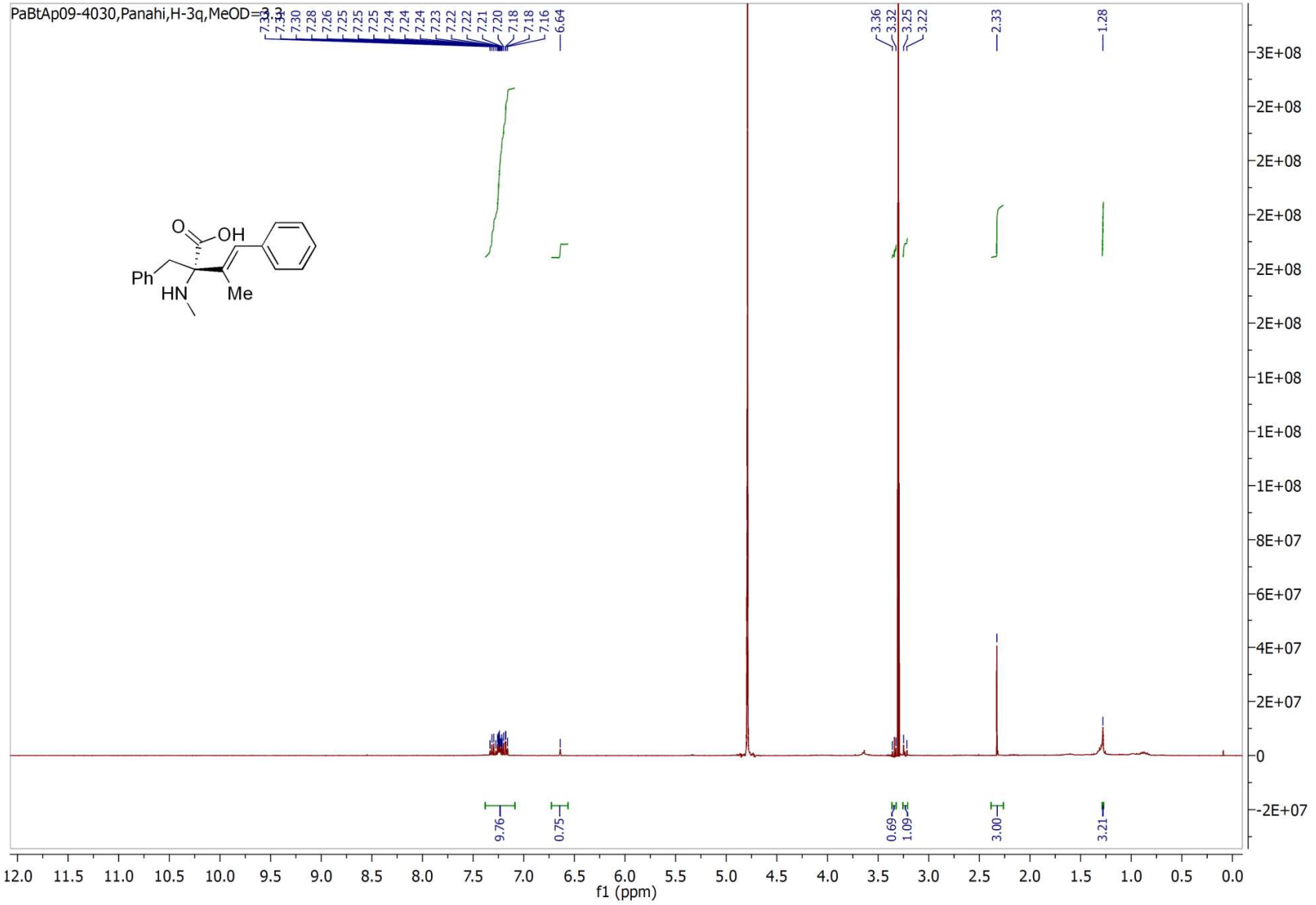

20210407D
PaBtAp07-500301,Panahi,3aj,CDCl3=77.1000
174.19
139.51
138.18
137.11
132.85
128.62
128.59
128.35
128.04
127.06
126.01
89.58
69.96
38.71
36.83
35.51
31.43
29.78
26.70
23.36
Me
N
O
N
Me
Me
Ph
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

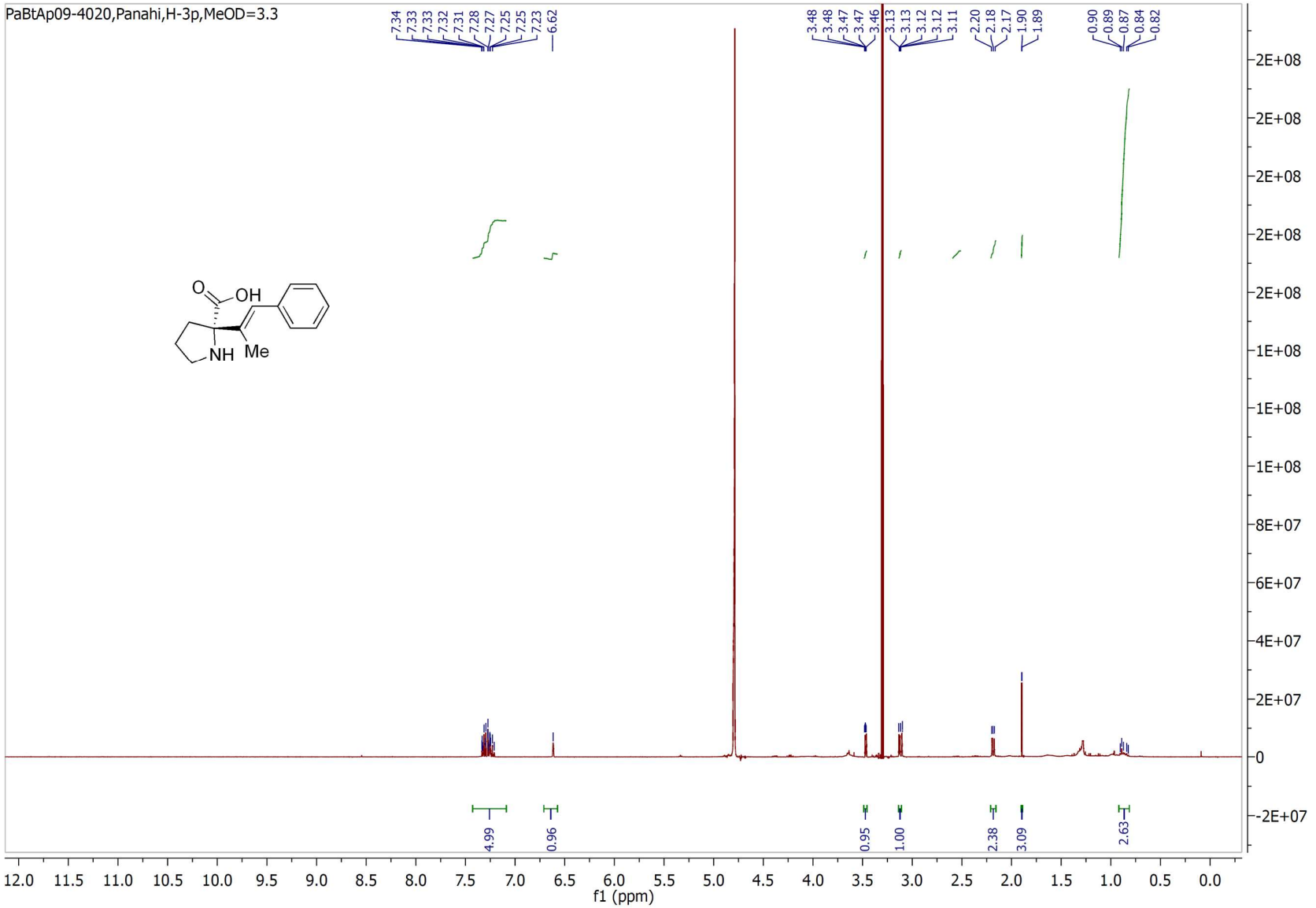
4.4.37. (2S,5R)-2-(tert-butyl)-1,3-dimethyl-5-phenyl-5-((Z)-4-phenylbut-2-en-2-yl)imidazolidin-4-one (3ak)

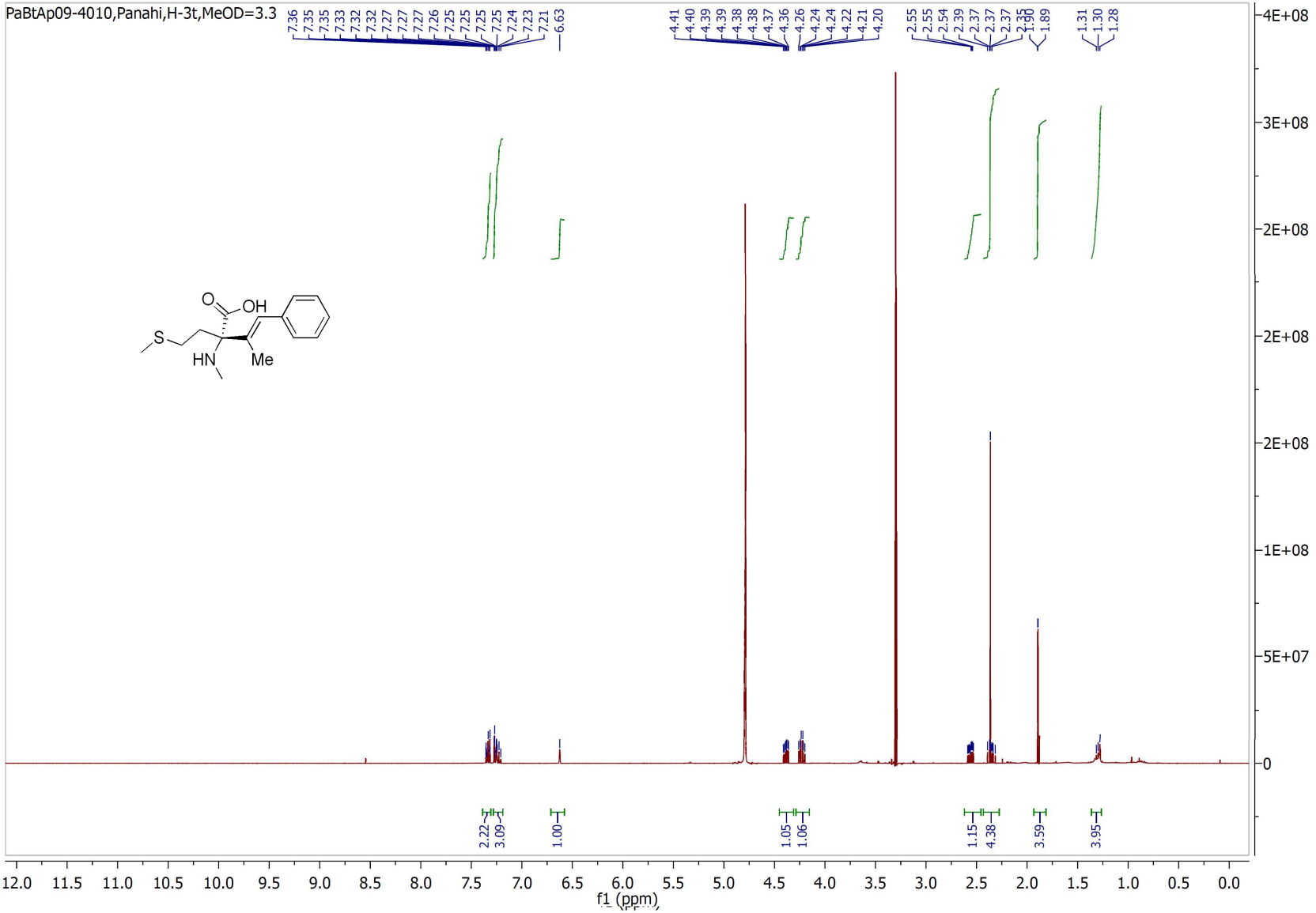


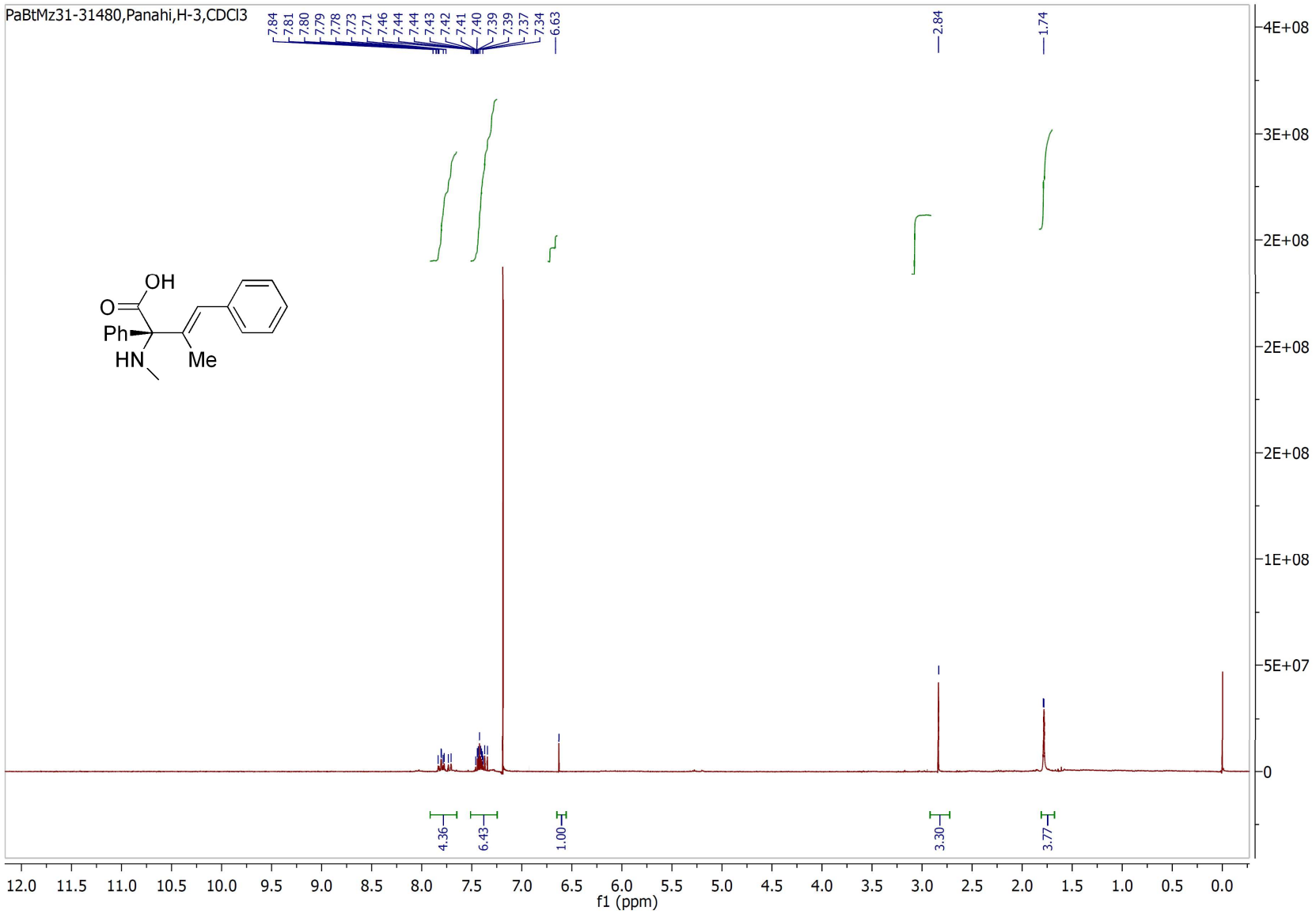

PaBtSe29-4010,Panahi,PhGly-21,CDCl3=77.1000
173.04
142.12
139.66
139.13
131.48
128.75
128.48
128.11
127.27
126.71
125.79
90.01
76.58
39.78
39.14
35.61
31.63
26.79
14.80
Me
Ph
N
N
Me
O
8E+08
7E+08
6E+08
6E+08
6E+08
5E+08
4E+08
4E+08
4E+08
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
-5E+07
270
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


PaBtAp07-30890,Panahi,H-3a,MeOD
7.37
7.35
7.33
7.31
7.31
7.29
7.28
7.26
7.24
7.22
7.19
6.62
2.44
1.73
1.72
1.59
OH
O
HN
Me
5.73
0.90
2.18
2.43
2.93
f1 (ppm)


PaBtAp09-4030,Panahi,H-3q,MeOD=3.3
7.34
7.33
7.30
7.28
7.26
7.25
7.25
7.25
7.24
7.24
7.24
7.23
7.22
7.22
7.21
7.20
7.18
7.18
7.16
6.64
3.36
3.32
3.25
3.22
2.33
1.28
O
OH
Ph
HN
Me
3E+08
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
9.76
0.75
0.69
1.09
3.00
3.21
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


PaBtAp09-4020,Panahi,H-3p,MeOD=3.3
7.34
7.33
7.33
7.32
7.31
7.28
7.27
7.25
7.25
7.23
6.62
3.48
3.48
3.47
3.47
3.46
3.13
3.13
3.12
3.12
3.11
2.20
2.18
2.17
1.90
1.89
0.90
0.89
0.87
0.84
0.82
O
OH
NH
Me
2E+08
2E+08
2E+08
2E+08
2E+08
1E+08
1E+08
1E+08
8E+07
6E+07
4E+07
2E+07
0
-2E+07
4.99
0.96
0.95
1.00
2.38
3.09
2.63
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


PaBtAp09-4010,Panahi,H-3t,MeOD=3.3
7.36 7.35 7.35 7.33 7.32 7.32 7.27 7.27 7.27 7.26 7.25 7.25 7.25 7.25 7.24 7.23 7.21 6.63
4.41 4.40 4.39 4.39 4.38 4.38 4.37 4.36 4.26 4.24 4.24 4.22 4.21 4.20
2.55 2.55 2.54 2.39 2.37 2.37 2.37 2.35 1.90 1.89
1.31 1.30 1.28
O
OH
S
HN
Me
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
2.22 3.09 1.00 1.05 1.06 1.15 4.38 3.59 3.95
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


PaBtMz31-31480,Panahi,H-3,CDCl3
7.84
7.81
7.80
7.79
7.78
7.73
7.71
7.46
7.44
7.44
7.43
7.42
7.41
7.40
7.39
7.39
7.37
7.34
6.63
2.84
1.74
OH
O
Ph
HN
Me
4E+08
3E+08
2E+08
2E+08
2E+08
1E+08
5E+07
0
4.36
6.43
1.00
3.30
3.77
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

12. Z-Matrix

TS-MO. DME

Li	1.83241100	-2.38744200	-0.49238800
O	3.40152300	-2.38061600	0.59066200
C	3.09999800	-2.52142100	1.98353300
C	4.46983600	-1.45995600	0.34444700
H	2.20778700	-3.14594500	2.05163000
H	3.94048600	-2.99379800	2.50801100
H	2.89373500	-1.53963200	2.43123400
H	4.66238400	-1.47409300	-0.72987500
H	5.37325500	-1.77412500	0.88269100
H	4.17491900	-0.44738500	0.64598200
C	-0.71575500	-1.35584000	-1.36521000
C	-0.47851700	-1.86461400	-0.07175700
N	-1.07834400	-1.02795600	0.83749000
C	-1.90192800	-0.01290000	0.17202700
N	-1.66126300	-0.28975800	-1.25928500
C	-0.70790900	-2.20354100	-2.59772600
C	-1.42519600	0.87284100	-2.11235500
O	0.26759900	-2.84920100	0.28536900
C	-3.42415300	-0.09198200	0.54582300
C	-4.22516700	0.82261200	-0.39954900
C	-3.92113700	-1.53708100	0.39262800

C	-3.65084900	0.40793200	1.98676500
C	-0.78310600	-1.06134800	2.24978000
H	-1.52937000	0.99089200	0.44264000
H	-1.70924100	-2.61156000	-2.80468900
H	-0.39611100	-1.65398600	-3.49536200
H	-0.02476500	-3.05147200	-2.47168400
H	-0.52012400	1.43473600	-1.84115100
H	-1.32348800	0.53279800	-3.14746400
H	-2.27915100	1.55196800	-2.07153400
H	-3.87518000	1.86161300	-0.34752500
H	-4.15038800	0.47968000	-1.43508600
H	-5.28436600	0.81679400	-0.11636000
H	-3.41139600	-2.21256200	1.08804900
H	-3.73509300	-1.89482400	-0.62573700
H	-4.99845500	-1.59683300	0.58831100
H	-3.23348000	-0.26679000	2.73797500
H	-3.20803300	1.40111600	2.13723200
H	-4.72494600	0.49136600	2.19052600
H	-0.68999100	-0.04131900	2.64065200
H	0.16011000	-1.59505100	2.38897500
H	-1.55198800	-1.58715400	2.83011500
C	2.10497700	-0.51099900	-2.31387700
H	1.60953800	-0.96176100	-3.17045200

C	1.47096800	-0.22039700	-1.17644700
C	1.52112900	0.47870900	-0.00971600
H	1.34876200	-0.06180500	0.91961900
H	3.15792900	-0.24840200	-2.44992000
C	1.43426000	1.92398400	0.09682700
C	1.10774100	2.51617700	1.33959200
C	1.61362100	2.79132100	-1.00662100
C	0.97817400	3.89526900	1.47436400
H	0.96018400	1.87308800	2.20549000
C	1.47543900	4.16895300	-0.86694300
H	1.86567500	2.36573200	-1.97395900
C	1.15958800	4.73629200	0.37206800
H	0.72939200	4.31755900	2.44544800
H	1.61916200	4.80910800	-1.73458100
H	1.05719100	5.81284500	0.47636200

TS-MO-A.2DME

Li	-2.64357300	0.05640100	-0.29380500
O	-3.03845800	1.51045000	-1.53211400
C	-2.54471400	1.31906600	-2.85758800
C	-3.02439000	2.87996300	-1.12820600
H	-2.49676800	0.24162400	-3.02280500

H	-3.21825800	1.78800300	-3.58803500
H	-1.53911000	1.74794500	-2.96306300
H	-3.48940200	2.92650100	-0.14125400
H	-3.60380100	3.49309200	-1.83186800
H	-1.99267700	3.24612100	-1.05835200
C	-0.31291900	-1.32284300	0.99360900
C	-0.55942900	-1.35723400	-0.39450300
N	0.65008800	-1.28848900	-1.04655300
C	1.77352400	-1.38986400	-0.11222000
N	1.09900600	-1.45369700	1.19955600
C	-1.23686300	-1.89769100	2.02123000
C	1.67430600	-0.62335400	2.25515200
O	-1.67738100	-1.33041500	-1.02574700
C	2.69492900	-2.63589800	-0.36885700
C	3.66237800	-2.80485000	0.81701500
C	1.83189600	-3.89981300	-0.49932100
C	3.54096200	-2.42563200	-1.64056500
C	0.77142500	-0.96588500	-2.44723200
H	2.39441200	-0.47974100	-0.18954900
H	-1.08196800	-2.98196600	2.14199500
H	-1.09039200	-1.44521400	3.01065400
H	-2.27934500	-1.73156100	1.73670600
H	1.60682300	0.45292000	2.04566600

H	1.14642900	-0.82681200	3.19220500
H	2.72444100	-0.88091100	2.40730600
H	4.28137600	-1.91023800	0.96253200
H	3.11581700	-3.00630400	1.74235700
H	4.33872400	-3.64766000	0.63093000
H	1.16487900	-3.84214500	-1.36623300
H	1.21448300	-4.02939700	0.39618900
H	2.46409200	-4.78865200	-0.61429000
H	2.93979800	-2.43295700	-2.55301700
H	4.08674100	-1.47393600	-1.60061700
H	4.28252400	-3.22788900	-1.73646100
H	1.60481200	-0.27067900	-2.60247600
H	-0.15991400	-0.49829000	-2.77370500
H	0.93769200	-1.85183000	-3.07408000
C	-1.57052800	1.34984500	1.81528900
H	-1.84250500	0.62237600	2.57569600
C	-0.69967100	1.09580000	0.84154300
C	0.08200100	1.63184900	-0.13674800
H	-0.04854900	1.25701000	-1.14939500
H	-2.02199300	2.34183500	1.91287400
C	1.29836700	2.38598200	0.09192500
C	2.23599300	2.54423800	-0.95701000
C	1.63333800	2.95136400	1.34613800

C	3.43257600	3.22840100	-0.76576200
H	2.00692800	2.12153800	-1.93377300
C	2.83433100	3.62884600	1.53244300
H	0.93180400	2.85187800	2.16993300
C	3.74631400	3.77694000	0.48190100
H	4.12870200	3.33127800	-1.59548300
H	3.06141700	4.05035000	2.50942200
H	4.68117700	4.30975500	0.63225200
O	-4.23022400	-0.62470400	0.57954100
C	-4.63410500	-1.95542700	0.25407800
C	-5.10543200	0.04120200	1.47757700
H	-3.84437700	-2.36641400	-0.37709300
H	-4.73194600	-2.55988600	1.16643600
H	-5.59331200	-1.94719200	-0.28167800
H	-4.67553000	1.02635800	1.67302300
H	-5.18606300	-0.51157700	2.42415300
H	-6.10733300	0.15609300	1.04051600

TS-MO-B.2DME

Li	0.18510100	2.31480400	-0.12476900
O	-1.47447000	1.83440400	0.49286700
C	-1.58435700	0.56343100	0.39730300

C	-0.74861800	-0.44534700	0.91218900
N	-1.27053200	-1.72483500	0.50658800
C	-2.46246500	-1.48567700	-0.32777600
N	-2.57708800	-0.02370900	-0.38480400
C	-0.05007500	-0.38205100	2.22812700
C	-3.73007700	-2.18500400	0.26403400
C	-4.95169700	-1.93049600	-0.63766400
C	-3.47001900	-3.70069100	0.33041300
C	-4.00791600	-1.65082200	1.67779900
C	-3.12318700	0.66505000	-1.53557600
C	-0.29363200	-2.65055000	-0.06081300
C	2.30639000	-0.18561500	0.17750500
C	1.17557500	0.10979500	-0.50623000
C	0.68293900	0.51229400	-1.68026300
H	-2.30421700	-1.87438400	-1.35196600
H	-0.66204600	-0.82955500	3.02465800
H	0.90733500	-0.92235800	2.20207400
H	0.16950400	0.65597200	2.49292100
H	-5.27956600	-0.88792400	-0.58793100
H	-4.73834800	-2.17528000	-1.68678200
H	-5.79597500	-2.55268800	-0.31744200
H	-4.35988000	-4.22209400	0.70280000
H	-3.23322100	-4.11285900	-0.65958800

H	-2.63964700	-3.92428300	1.00621600
H	-4.19995600	-0.57277300	1.65754300
H	-3.14837800	-1.83527500	2.32992500
H	-4.88512900	-2.14755500	2.11012700
H	-4.21266900	0.58970200	-1.58593600
H	-2.85417700	1.71922700	-1.44236300
H	-2.71397500	0.26564100	-2.47916600
H	0.56601100	-2.72585200	0.60984000
H	-0.73436500	-3.64567000	-0.16911300
H	0.08437400	-2.32092400	-1.04394800
H	2.46567500	0.28329500	1.14670200
H	1.33741400	0.96541700	-2.43033800
H	-0.35660200	0.36562700	-1.96206000
C	3.22340800	-1.26523100	-0.16508500
C	5.03388600	-3.37080900	-0.74601900
C	3.13692300	-1.99409000	-1.37307700
C	4.24522900	-1.62939700	0.74042800
C	5.13642500	-2.65860400	0.45283500
C	4.02476400	-3.02878000	-1.65186800
H	2.36340500	-1.73542200	-2.08995400
H	5.72704700	-4.17704300	-0.97004800
H	3.93051300	-3.57363600	-2.58870300
H	5.91326000	-2.91119600	1.17112700

H	4.32840800	-1.09175200	1.68332200
O	1.32690200	2.95620800	1.31122500
C	2.73505300	3.15666700	1.28534900
C	0.70153100	3.36318200	2.52619400
H	3.10231100	2.72054100	0.35438700
H	2.97915500	4.22814400	1.32446800
H	3.21443800	2.64630600	2.13159400
H	-0.35458100	3.10478900	2.42714500
H	0.81924100	4.44557700	2.68179700
H	1.13577500	2.82767200	3.38108300
O	0.12894600	3.88570100	-1.34788900
C	-0.67839200	3.73534600	-2.51431400
C	-0.11760800	5.11740100	-0.67320700
H	-0.43103500	2.76676200	-2.95100500
H	-1.74599700	3.75866600	-2.25674800
H	-0.45927600	4.53202100	-3.23847800
H	0.55828000	5.14921600	0.18249200
H	-1.15804500	5.16954200	-0.32230200
H	0.08748000	5.96929600	-1.33585600

TS-Di-All

Li	1.24924800	-0.80422800	-0.74394900

N	2.84822500	-0.91081300	0.39937400
Li	1.46736900	-1.78680000	1.40821500
Si	3.25207100	0.50669200	1.29265600
Si	3.91858600	-1.83626100	-0.58273200
C	1.87749400	0.78305200	2.59339400
C	3.27909200	2.07473200	0.22787000
C	4.89693800	0.37473000	2.23269800
C	4.81037300	-3.19326600	0.40144200
C	2.86905300	-2.70045800	-1.92554300
C	5.22768200	-0.80975000	-1.49753000
H	1.70383000	-0.08863400	3.24684100
H	0.93084600	1.04754600	2.10525500
H	2.13551100	1.61373600	3.26183100
H	2.28510600	2.27132100	-0.19370300
H	3.56743100	2.95985800	0.80901300
H	3.98744600	1.97594200	-0.60383600
H	4.90301000	-0.50018300	2.89563200
H	5.74649100	0.26972800	1.54687100
H	5.08002400	1.26366500	2.84948800
H	4.09090000	-3.89606800	0.84432800
H	5.39078500	-2.75428300	1.22259900
H	5.49925800	-3.77720400	-0.22202500
H	2.07101100	-3.32157900	-1.49561400

H	3.49108400	-3.35765000	-2.54580300
H	2.40254300	-1.97755200	-2.61274100
H	5.84316200	-1.44295100	-2.14899800
H	5.90334300	-0.29479000	-0.80422800
H	4.75671500	-0.04374900	-2.12667800
C	-1.69968300	-1.21020500	-1.23758500
C	-1.18082300	-1.42933500	0.03930500
N	-2.12461700	-1.09523200	0.98366500
C	-3.41822700	-0.83404400	0.33577800
N	-3.08616800	-0.85665600	-1.10078900
C	-1.26526500	-1.95123400	-2.46260400
C	-3.55634400	0.28756600	-1.88269200
O	0.01397300	-1.82393200	0.36860200
C	-4.52419700	-1.87957600	0.69990300
C	-5.77449100	-1.57611800	-0.14515900
C	-4.02513800	-3.29844100	0.38744200
C	-4.89740800	-1.76680300	2.18964600
C	-1.81156100	-0.80025600	2.36422900
H	-3.77980600	0.16480100	0.63549300
H	-1.46577100	-1.38563300	-3.38044000
H	-0.19171800	-2.16308200	-2.43573100
H	-1.79193100	-2.91291200	-2.54846200
H	-3.16574700	1.24999700	-1.52550100

H	-3.23698700	0.15680500	-2.92058700
H	-4.64945700	0.31957000	-1.87228900
H	-6.13884900	-0.55500600	0.02869000
H	-5.56085600	-1.69126100	-1.21152200
H	-6.58506700	-2.26619500	0.11628100
H	-3.14693100	-3.55329900	0.99133900
H	-3.75101400	-3.38221400	-0.66925100
H	-4.80828500	-4.03564900	0.60005400
H	-4.08155600	-2.08496900	2.84514800
H	-5.17231600	-0.73816900	2.45853200
H	-5.75950700	-2.40634300	2.41201300
H	-2.54004700	-0.08580900	2.75881100
H	-0.81745700	-0.34647100	2.43548200
H	-1.82988200	-1.69316100	3.00364400
C	0.56130900	0.66449200	-2.35929400
H	0.30601800	0.20209800	-3.30908700
C	-0.32490500	0.83048100	-1.36351700
C	-0.75080300	1.57799600	-0.33342500
H	-1.20063800	1.08687000	0.52450900
H	1.57354100	1.06639400	-2.26414500
C	-0.79631900	3.04208400	-0.30483000
C	-1.45312500	3.67966100	0.76711900
C	-0.21563000	3.85494300	-1.29924700

C	-1.52433100	5.06824700	0.84666200
H	-1.90866200	3.06969400	1.54505000
C	-0.29487400	5.24210200	-1.22068100
H	0.29592900	3.38519200	-2.13364500
C	-0.94606100	5.86001600	-0.14811900
H	-2.03370100	5.53367900	1.68698100
H	0.16093500	5.84802500	-1.99996100
H	-0.99817300	6.94362100	-0.08751700

TS-Di-All. DME

Li	-1.01645100	-0.08087300	1.19232000
N	-2.69172400	-0.26311300	0.21028700
Li	-1.52607200	-1.63324800	-0.55792100
Si	-3.04139400	0.95312600	-0.95566900
Si	-3.77920800	-0.88626600	1.38594500
C	-1.72258400	0.89756700	-2.33138800
C	-2.98243100	2.70541200	-0.23048000
C	-4.72754000	0.71788700	-1.81023500
C	-4.79514700	-2.34974000	0.71512900
C	-2.74927400	-1.54991900	2.85244400
C	-4.98993200	0.38759900	2.10531800
O	-1.75933000	-3.04428300	-1.78338200

C	-2.95699600	-3.28897200	-2.51846600
C	-0.78372600	-4.07942800	-1.89250800
H	-1.62735700	-0.09980300	-2.78639100
H	-0.74115200	1.19487900	-1.94204500
H	-1.97349200	1.59568500	-3.13978900
H	-1.97154700	2.93725700	0.12917600
H	-3.24470400	3.46864100	-0.97424700
H	-3.67445200	2.80795600	0.61447000
H	-4.77872000	-0.24763600	-2.33169800
H	-5.55589700	0.74245400	-1.09150700
H	-4.91273200	1.50346100	-2.55392500
H	-4.13414900	-3.16239500	0.38297500
H	-5.39504400	-2.03724000	-0.14901200
H	-5.47869000	-2.76542400	1.46627700
H	-2.02683900	-2.31678900	2.54081700
H	-3.39567100	-2.00104400	3.61579800
H	-2.18756700	-0.74597800	3.35249100
H	-5.62446500	-0.05788000	2.88199600
H	-5.65143600	0.80394600	1.33613100
H	-4.44665800	1.22609900	2.55933500
H	-3.62444000	-2.44768500	-2.32376000
H	-2.74260000	-3.35503300	-3.59344400
H	-3.43491900	-4.21787200	-2.18045900

H	0.05730900	-3.78312500	-1.26243400
H	-0.45171300	-4.18915100	-2.93378300
H	-1.19338100	-5.03498100	-1.53813300
C	1.94450900	-0.71654200	1.65381100
C	1.26064700	-1.18028000	0.52968500
N	2.11701900	-1.20300100	-0.55527500
C	3.48903700	-0.91012500	-0.11873200
N	3.33153300	-0.56492600	1.30656200
C	1.58787600	-1.07637100	3.06107500
C	3.98111400	0.67387400	1.73630500
O	0.01256100	-1.51621800	0.42268400
C	4.47379100	-2.10727100	-0.33012400
C	5.83648100	-1.73548600	0.28132600
C	3.92515700	-3.36178900	0.36562600
C	4.66456400	-2.37666100	-1.83395300
C	1.66327900	-1.12781700	-1.92801000
H	3.87589900	-0.04619500	-0.68803300
H	1.91299100	-0.31451800	3.78010700
H	0.50483700	-1.19071300	3.16797500
H	2.05721100	-2.02643500	3.35614600
H	3.61392800	1.56388700	1.20711200
H	3.79493000	0.81372600	2.80510500
H	5.06274300	0.59556500	1.59534000

H	6.24100300	-0.81739500	-0.16498400
H	5.75022100	-1.58632400	1.36138700
H	6.56324600	-2.53729400	0.10562600
H	2.96296400	-3.66243300	-0.06461300
H	3.77807100	-3.17103400	1.43361300
H	4.62410400	-4.19953100	0.25648400
H	3.75222400	-2.75621200	-2.30346600
H	4.97144900	-1.46823700	-2.36915500
H	5.44675300	-3.12924300	-1.98785600
H	2.34347800	-0.49595700	-2.50974500
H	0.66531100	-0.68228400	-1.96298800
H	1.61516300	-2.11004400	-2.41622000
C	-0.05551800	1.58794600	2.46087500
H	0.25816400	1.35826600	3.47550200
C	0.74239300	1.43361400	1.39240300
C	1.10620900	1.86750500	0.17556400
H	1.45237000	1.14825300	-0.56021700
H	-1.05609100	2.01283800	2.34063700
C	1.18413500	3.26944500	-0.24318800
C	1.71468500	3.56902200	-1.51416800
C	0.74482400	4.34285800	0.55780200
C	1.79797900	4.88250500	-1.96977800
H	2.05752200	2.75371700	-2.14846800

C	0.83686100	5.65470400	0.10291300
H	0.33162400	4.13434600	1.53984200
C	1.36029300	5.93559100	-1.16335500
H	2.20601400	5.08473000	-2.95713200
H	0.49082700	6.46597800	0.73874800
H	1.42160600	6.96103400	-1.51744000

TS-Di-All-B. DME

Li	-0.76305400	-0.68925600	0.06807500
N	-2.71248800	-0.86459400	-0.00258400
Li	-2.39474700	0.99468700	-0.53205600
Si	-3.43789300	-0.91342400	1.55737300
Si	-3.16827500	-1.87210000	-1.32467000
C	-2.95819300	0.67072600	2.50964400
C	-2.83760600	-2.37650100	2.60746300
C	-5.34008700	-0.97800000	1.52901500
C	-4.68064000	-1.17571900	-2.25120900
C	-1.73633500	-1.92135300	-2.57993300
C	-3.56315500	-3.66579800	-0.84418000
O	-3.48376600	2.54433500	-0.66482000
C	-4.90029100	2.50745900	-0.48780100
C	-2.89538900	3.80309500	-0.33499100

H	-3.21323800	1.58339800	1.95241500
H	-1.88053300	0.69640100	2.71666800
H	-3.47655400	0.72290300	3.47522600
H	-1.74506500	-2.35584600	2.71756400
H	-3.27381600	-2.36824600	3.61467700
H	-3.09994500	-3.33054000	2.13522600
H	-5.76702300	-0.11309000	1.00575500
H	-5.70489100	-1.87924900	1.02118300
H	-5.75108700	-0.98540400	2.54660400
H	-4.47727400	-0.16516800	-2.63378800
H	-5.55092500	-1.11061200	-1.58592400
H	-4.96348600	-1.79822500	-3.10961200
H	-1.48343300	-0.91828900	-2.94973400
H	-1.99700900	-2.53273100	-3.45292500
H	-0.82547400	-2.35633200	-2.14500100
H	-3.81340200	-4.26983600	-1.72548300
H	-4.41282900	-3.72355000	-0.15259400
H	-2.70417700	-4.13603200	-0.34945200
H	-5.23143600	1.51213100	-0.78842900
H	-5.16330000	2.68009100	0.56450800
H	-5.38492800	3.26441200	-1.11786600
H	-1.81985700	3.69651600	-0.48863800
H	-3.09487700	4.05954400	0.71482300

H	-3.28993200	4.59404500	-0.98583700
C	1.75772400	0.82707800	-0.95681300
C	0.65387500	1.48577000	-0.38703500
N	1.08232700	2.46692900	0.47512300
C	2.54780400	2.58634300	0.41164400
N	2.94637000	1.51997500	-0.52580100
C	1.76171400	0.27074300	-2.34489400
C	4.03876800	0.66446700	-0.06439300
O	-0.58787400	1.16994900	-0.48863600
C	3.03734800	3.99556200	-0.05536200
C	4.56919300	3.95926500	-0.20447600
C	2.40030100	4.34463200	-1.40896900
C	2.67170500	5.06333400	0.99238500
C	0.29631200	2.90453600	1.61301700
H	2.96083700	2.39430600	1.41950400
H	2.45934900	-0.57184300	-2.43367700
H	0.76640700	-0.09407600	-2.61767900
H	2.06977800	1.03671000	-3.06936900
H	3.81423900	0.16983000	0.89556900
H	4.21657700	-0.11968800	-0.80402000
H	4.95580500	1.24895400	0.04505200
H	5.05770400	3.66552200	0.73373600
H	4.86840000	3.25639000	-0.98674900

H	4.94563800	4.95177500	-0.47776600
H	1.30895600	4.40425800	-1.32872000
H	2.64840900	3.58191900	-2.15410100
H	2.76775300	5.31298100	-1.76866500
H	1.59311700	5.23738100	1.04379000
H	3.02128400	4.78167600	1.99426400
H	3.14162400	6.02002300	0.73603300
H	0.87119700	2.78871800	2.54134200
H	-0.60206800	2.28816000	1.67415100
H	-0.00975300	3.95348400	1.53330400
C	1.89601800	-2.16502300	-0.43374700
H	1.54031700	-2.25675000	-1.45809600
C	1.51334300	-1.09641600	0.30929600
C	1.07800000	-0.76512800	1.53886200
H	1.17457700	0.23704400	1.94922200
C	2.92376800	-3.12813400	-0.04250400
C	3.35459100	-4.09525500	-0.97685400
C	3.54130000	-3.13042500	1.22733600
C	4.34245400	-5.02226700	-0.65732400
H	2.90033800	-4.11116000	-1.96573700
C	4.53625400	-4.05241800	1.53886200
H	3.23068900	-2.39943300	1.96767400
C	4.94474600	-5.00841700	0.60369900

H	4.64684200	-5.75769600	-1.39850000
H	4.99505700	-4.02827600	2.52482700
H	5.71687200	-5.73071100	0.85428700
H	0.66281800	-1.52811100	2.20113200

TS-Tr-All. A

Li	-2.71057400	-1.15798400	0.13917500
Li	0.24130800	-0.59214100	0.53238600
Li	-1.82776200	1.32482200	-0.65807700
O	-0.17639900	1.19800200	-0.02567800
N	-3.53056100	0.46807700	-0.57821800
N	-1.06530200	-2.02687000	0.69918600
C	0.94245300	1.85629900	-0.06125300
C	2.06092500	1.60942000	-0.86896900
N	3.05560400	2.59824300	-0.53063200
C	2.55332600	3.39634600	0.60438100
N	1.22821400	2.81271500	0.86811500
C	1.96600400	1.19407600	-2.30282500
C	2.50913200	4.92642200	0.28330600
C	2.11260600	5.72804100	1.53744900
C	3.91347800	5.37691600	-0.15927400
C	1.50895800	5.18839900	-0.85346300

C	0.49376300	2.96335700	2.10963500
C	4.41947900	2.09317600	-0.37877000
Si	-3.86135000	0.10014100	-2.23886600
Si	-4.64581000	1.23562800	0.50569700
Si	-1.44011800	-2.25700300	2.37365900
Si	-0.61651600	-3.33556800	-0.35400200
C	-4.27210700	-1.74368900	-2.45602500
C	-5.27216300	1.06720100	-3.05423200
C	-2.28569200	0.50724100	-3.23973900
C	-6.21947000	0.20620700	0.76568900
C	-5.17094400	2.97219100	-0.06129500
C	-3.81525600	1.48434800	2.19734900
C	-0.91626600	-0.72365900	3.37150100
C	-3.33027600	-2.46714800	2.57998400
C	-0.64323300	-3.74893500	3.22852000
C	-1.95834800	-4.68434000	-0.42943500
C	1.01525200	-4.17663800	0.11112900
C	-0.39290700	-2.65829300	-2.11853100
C	3.05265300	-1.22826000	-0.74284700
C	2.59624600	-0.34450700	0.17776900
C	2.38715600	-0.22715100	1.50284700
H	3.18795100	3.24777100	1.49758400
H	1.92346600	2.07307300	-2.95980000

H	2.83380800	0.59308100	-2.60233200
H	1.07028600	0.58597200	-2.46974500
H	1.07558200	5.55065800	1.83493300
H	2.75957400	5.48409800	2.39007700
H	2.21396200	6.80210500	1.34402800
H	3.92077600	6.45735900	-0.34321100
H	4.66525800	5.16692300	0.61235900
H	4.21185000	4.87301500	-1.08249900
H	0.48805000	4.92421100	-0.55343400
H	1.77342200	4.59754400	-1.73685300
H	1.51401200	6.24822500	-1.13300200
H	-0.19425100	3.81679500	2.08787500
H	-0.08788000	2.05777300	2.29124100
H	1.19422500	3.10870400	2.93956700
H	4.66732700	1.47070900	-1.24173800
H	5.12722600	2.92494700	-0.34062800
H	4.54457400	1.47498400	0.52568600
H	-3.51034700	-2.41555900	-2.04072300
H	-5.22110800	-1.97256400	-1.95318200
H	-4.38423200	-2.01120800	-3.51430000
H	-6.22568900	0.92877800	-2.53129400
H	-5.41067800	0.72674800	-4.08821500
H	-5.06085300	2.14230000	-3.08393000

H	-1.38058900	0.03212600	-2.83865400
H	-2.11134900	1.59382100	-3.28209600
H	-2.37731800	0.16883600	-4.27919900
H	-6.77096000	0.08827200	-0.17562700
H	-6.89831500	0.67252200	1.49061200
H	-5.98240600	-0.80090800	1.13312300
H	-5.75180700	3.47515100	0.72238700
H	-5.78707500	2.94879300	-0.96611600
H	-4.29579500	3.60245900	-0.27354600
H	-4.46566700	2.07446800	2.85515600
H	-3.60425700	0.54062200	2.71103600
H	-2.86523500	2.02961000	2.10824000
H	-1.27457700	-0.78528200	4.40687200
H	0.17713700	-0.63223500	3.40698600
H	-1.31606900	0.20309800	2.94423200
H	-3.61551500	-2.51034300	3.63884900
H	-3.92611800	-1.65432800	2.13910300
H	-3.65659400	-3.40456300	2.11000800
H	-0.92689100	-4.69998600	2.76324900
H	0.45073300	-3.68068600	3.20484300
H	-0.95279200	-3.78964400	4.28072200
H	-2.09445000	-5.16091100	0.54972200
H	-1.69256400	-5.47299400	-1.14460400

H	-2.93334700	-4.28050100	-0.73311700
H	1.83042500	-3.44628500	0.17698900
H	1.29947100	-4.91287800	-0.65184700
H	0.95118800	-4.70199000	1.06972900
H	-1.33199200	-2.31424100	-2.56533400
H	0.31208600	-1.81733700	-2.14097200
H	0.01507500	-3.43617100	-2.77597000
H	2.51968000	-1.34720300	-1.68258600
H	2.32053100	-1.12271300	2.12381900
H	2.35222700	0.72976700	2.01754400
C	4.29474600	-1.99065000	-0.63294500
C	6.68898700	-3.50338500	-0.52857100
C	5.14562300	-1.93479600	0.49219200
C	4.68328400	-2.82645100	-1.70241100
C	5.85607700	-3.57403700	-1.64835800
C	6.32336300	-2.67487600	0.53693000
H	4.87137900	-1.30336600	1.33175600
H	7.60504400	-4.08612700	-0.48488500
H	6.96055200	-2.60951700	1.41603600
H	6.12286600	-4.21395100	-2.48626800
H	4.04558500	-2.88679900	-2.58211300

TS-Tr-All-A.2DME

Li	-2.86963600	0.87827600	-0.05038100
Li	0.11032800	1.03843200	0.33435600
Li	-1.10078900	-1.76234000	-0.06267400
O	0.46149000	-0.78708200	0.03607600
N	-3.01002300	-1.17670800	0.08463400
N	-1.36911000	2.26912500	-0.05313000
C	1.68697700	-1.18232700	0.24410000
C	2.45910600	-1.02827000	1.39335900
N	3.70965700	-1.68524900	1.19319500
C	3.72938100	-2.24812900	-0.16320200
N	2.42825100	-1.84316000	-0.73609700
C	1.89888900	-0.94002100	2.78020700
C	3.94586000	-3.79548600	-0.15867200
C	3.94297000	-4.33287700	-1.60072200
C	5.31679100	-4.10122700	0.47134900
C	2.83735500	-4.46795000	0.66373800
C	2.30878800	-1.47138900	-2.13674600
C	4.93178500	-1.06579500	1.70737500
Si	-3.46038300	-1.81538500	1.62842300
Si	-3.89731200	-1.59597300	-1.33882500
Si	-0.80593400	2.91800200	-1.55913700
Si	-1.85893700	3.32550100	1.22746300

C	-4.86379200	-0.89647500	2.52791100
C	-4.09843300	-3.61208400	1.59845300
C	-1.93771100	-1.75551900	2.77349400
C	-5.76739200	-1.26526200	-1.21965200
C	-3.81098700	-3.42086100	-1.87928400
C	-3.14316800	-0.62034400	-2.79448700
C	0.24707100	1.60503400	-2.44700100
C	-2.17439400	3.42556800	-2.78013100
C	0.31133200	4.44821800	-1.39411100
C	-3.14739200	4.61493700	0.67575000
C	-0.52411500	4.36369000	2.10402200
C	-2.56254800	2.24655600	2.63110800
O	-4.77762400	1.80214200	-0.29337400
O	-0.59577900	-3.63951700	-0.52341600
C	-0.88527500	-4.82447600	0.21582700
C	-0.12551300	-3.91886500	-1.83997100
C	-5.70027200	2.10634300	0.75137600
C	-5.27238300	2.23673400	-1.55889100
H	4.54614300	-1.80134200	-0.75941200
H	1.79744600	-1.94375900	3.21793000
H	2.53613600	-0.35291800	3.45113000
H	0.90629900	-0.48301900	2.76476600
H	2.95881500	-4.24193900	-2.06857200

H	4.66734000	-3.79916900	-2.22997000
H	4.21399500	-5.39507900	-1.61199500
H	5.53240000	-5.17442200	0.40912000
H	6.12513500	-3.56834500	-0.04631700
H	5.34071000	-3.81769600	1.52662200
H	1.85369400	-4.19583000	0.27220400
H	2.88477900	-4.13931200	1.70687400
H	2.93958100	-5.55981300	0.63778900
H	2.38448400	-2.34281700	-2.79170600
H	1.33554500	-1.00161200	-2.27971700
H	3.08046400	-0.74766700	-2.44006700
H	4.66813900	-0.23502100	2.36565400
H	5.53306200	-1.78177700	2.27983700
H	5.56062200	-0.65371400	0.90619800
H	-4.55203500	0.05931800	2.95983100
H	-5.70099000	-0.70813900	1.84575900
H	-5.24150000	-1.51462600	3.35277300
H	-5.10572900	-3.65392600	1.16495600
H	-4.17101300	-4.00258900	2.62190900
H	-3.47057700	-4.29479700	1.02010600
H	-1.58059300	-0.72418200	2.88623800
H	-1.08783200	-2.35222400	2.41279200
H	-2.18557100	-2.12877900	3.77518300

H	-6.23104100	-1.99266400	-0.54086800
H	-6.25883400	-1.37085200	-2.19537300
H	-5.98136400	-0.26881300	-0.82882900
H	-4.20816500	-3.52709200	-2.89743700
H	-4.40868300	-4.06287900	-1.22373500
H	-2.78791000	-3.80417600	-1.87624100
H	-3.78731100	-0.64416800	-3.68236700
H	-2.94088500	0.43193800	-2.56312600
H	-2.17866800	-1.06171100	-3.08188100
H	0.51555200	1.95676400	-3.45127600
H	1.18948400	1.39999400	-1.92136700
H	-0.29629600	0.65878700	-2.56021100
H	-1.74244100	3.99908300	-3.61041300
H	-2.68400800	2.56026600	-3.21898800
H	-2.92893700	4.05565900	-2.29647300
H	-0.21596800	5.30865800	-0.96466400
H	1.18837000	4.24604000	-0.76763800
H	0.67956500	4.74977200	-2.38309700
H	-2.67070300	5.38437100	0.05463400
H	-3.60411700	5.12570200	1.53312600
H	-3.94224700	4.15974900	0.08037500
H	0.14673100	3.75247000	2.71712100
H	-1.02300700	5.07188400	2.77980800

H	0.09060900	4.95114900	1.41422400
H	-3.21308300	1.43624500	2.28849200
H	-1.73565800	1.77193200	3.17586900
H	-3.13358100	2.83768400	3.35801300
H	-1.16322700	-4.51593500	1.22428100
H	-1.71880700	-5.37173600	-0.24340600
H	-0.00158400	-5.47274400	0.26468100
H	0.84139800	-4.43216400	-1.80034400
H	-0.00447500	-2.96288700	-2.34973000
H	-0.84699300	-4.53732000	-2.38991900
H	-5.92028000	3.18167600	0.77227200
H	-6.63495100	1.54541800	0.61439100
H	-5.24244100	1.81619700	1.69382200
H	-5.34087000	3.33195700	-1.59249200
H	-4.57487400	1.89761100	-2.32124200
H	-6.26176700	1.80329200	-1.75677900
C	1.90541500	1.97597200	1.48605400
H	1.60759400	1.76156200	2.50961300
C	2.75358400	1.20679700	0.78824500
C	3.72267400	1.18519500	-0.14467500
H	3.77957800	0.34298400	-0.82229600
H	1.56849600	2.92254500	1.06770100
C	4.84907300	2.11484300	-0.21807400

C	5.91293800	1.82661200	-1.09876400
C	4.94848800	3.28125500	0.56901700
C	7.02136600	2.66497800	-1.19446500
H	5.85743600	0.93238900	-1.71716600
C	6.06003100	4.11277300	0.47553500
H	4.14391600	3.52397600	1.25646300
C	7.10418300	3.81524600	-0.40697700
H	7.82383400	2.41809300	-1.88566400
H	6.11139400	5.00605400	1.09369500
H	7.96627000	4.47254300	-0.48137500

TS-Tr-All-B.2DME

Li	-2.66305000	-1.00231000	0.01362000
Li	0.34912500	-0.82229900	0.61190800
Li	-1.19818600	1.75336300	-0.22034200
O	0.39717000	1.04155700	0.37067300
N	-2.93038500	0.92044200	-0.70899500
N	-1.14434300	-2.04036500	0.90719800
C	1.60453900	1.49829000	0.29951800
C	2.60886400	1.13915300	-0.62137600
N	3.80618600	1.86634600	-0.26395700
C	3.51509500	2.66661300	0.93575700

N	2.12341300	2.31866300	1.27602600
C	2.36158800	0.97463500	-2.08917800
C	3.71752300	4.19308400	0.67096500
C	3.35984100	5.00769000	1.92678400
C	5.19705000	4.43836400	0.32483000
C	2.83707600	4.63493700	-0.50924300
C	1.66151700	2.27269700	2.65269200
C	5.03934200	1.08293700	-0.21046700
Si	-2.97905200	1.06367900	-2.43401000
Si	-4.23563300	1.55233300	0.23356300
Si	-1.22014100	-2.21690500	2.62851100
Si	-0.93950400	-3.43902200	-0.09924300
C	-3.96955600	-0.28765100	-3.33283800
C	-3.72855200	2.68914000	-3.09320700
C	-1.20839000	0.96727700	-3.11952300
C	-5.94720800	0.94856300	-0.33939800
C	-4.37271700	3.45182800	0.27079100
C	-3.96276900	1.06757500	2.05577000
C	-0.73889900	-0.57384400	3.46280300
C	-2.93051500	-2.70340700	3.30722400
C	-0.04112000	-3.52224600	3.35562300
C	-2.23309400	-4.79220400	0.24893600
C	0.74513700	-4.30303600	0.01292800

C	-1.06240600	-2.85991500	-1.91395200
O	-4.44692500	-2.16355800	-0.16758000
O	-0.86581200	3.71753700	-0.14861200
C	-1.03339600	4.64013000	-1.22322900
C	-0.76275600	4.36087800	1.11914400
C	-4.79699000	-2.97256900	-1.28995200
C	-5.41069600	-2.29143200	0.87663600
C	3.13794000	-1.75550600	-1.03732700
C	2.79625600	-0.97769500	0.02465600
C	2.58664100	-1.08408300	1.34905900
H	4.16652000	2.36943000	1.77647600
H	2.35104200	1.94940600	-2.59477200
H	3.15162200	0.36762600	-2.54669700
H	1.40933200	0.47263400	-2.27246800
H	2.28578700	4.98187500	2.13391900
H	3.88809800	4.63660400	2.81469200
H	3.64034800	6.05849000	1.79009800
H	5.37780500	5.50850900	0.16938900
H	5.86047300	4.10272500	1.13253400
H	5.47590800	3.91326100	-0.59302200
H	1.78469400	4.40359900	-0.31748400
H	3.13574400	4.11279200	-1.42308800
H	2.93201900	5.71443000	-0.67741700

H	1.51940600	3.27358000	3.06736400
H	0.71074000	1.74023100	2.67784800
H	2.38046100	1.73974900	3.29325100
H	5.14892700	0.51804500	-1.13911200
H	5.89919300	1.75095900	-0.11002200
H	5.05112100	0.35899800	0.62087100
H	-3.45933300	-1.25620700	-3.33094000
H	-4.95653700	-0.42244600	-2.87687200
H	-4.12122100	-0.00502100	-4.38254800
H	-4.80989200	2.73632800	-2.91599400
H	-3.57514500	2.75017200	-4.17860500
H	-3.28515600	3.58285600	-2.64264000
H	-0.73863800	0.01394700	-2.85046400
H	-0.55209500	1.76981900	-2.75646700
H	-1.21395600	1.03230800	-4.21479400
H	-6.24851100	1.47165000	-1.25589700
H	-6.72232800	1.13580000	0.41454300
H	-5.93347700	-0.12082700	-0.56533700
H	-5.11077500	3.76455600	1.02120700
H	-4.68817200	3.86083100	-0.69465900
H	-3.41587800	3.91483200	0.53176900
H	-4.85945800	1.25752900	2.65912900
H	-3.68533300	0.01790500	2.20183300

H	-3.14994200	1.66589400	2.48925100
H	-0.99610100	-0.58856400	4.52946800
H	0.34238000	-0.40142000	3.39146200
H	-1.25038300	0.28263600	3.00824800
H	-2.84966600	-2.95533000	4.37261600
H	-3.67071400	-1.90154600	3.22070800
H	-3.32223200	-3.58408500	2.78550300
H	-0.32544600	-4.54170100	3.06828900
H	0.99425800	-3.36570300	3.03316100
H	-0.06127200	-3.47378500	4.45229400
H	-1.96616400	-5.33576000	1.16409800
H	-2.29235200	-5.52822300	-0.56285300
H	-3.22589800	-4.36151400	0.40327800
H	1.57693500	-3.61203700	-0.16710100
H	0.80730700	-5.09052200	-0.75051700
H	0.90199800	-4.77742300	0.98724400
H	-1.89238700	-2.17134400	-2.11246200
H	-0.13998500	-2.33117200	-2.19090300
H	-1.16662400	-3.70583900	-2.60494800
H	-1.04563000	4.05940000	-2.14635200
H	-1.98071100	5.18576500	-1.12209200
H	-0.19751600	5.35082000	-1.25134800
H	0.12644600	5.00198400	1.15491200

H	-0.67058000	3.57639200	1.87084900
H	-1.65667300	4.96447600	1.32550700
H	-4.99765500	-4.00524000	-0.97702100
H	-5.68223300	-2.56425800	-1.79478000
H	-3.95306100	-2.97062300	-1.97692700
H	-5.35392200	-3.28784100	1.33293600
H	-5.18933400	-1.53506900	1.62763600
H	-6.42493000	-2.12230100	0.49108400
H	2.57355300	-1.67100000	-1.96333800
H	2.42935900	-2.06614100	1.79629800
H	2.65059000	-0.23949300	2.02995600
C	4.32131000	-2.60540900	-1.10185700
C	6.61793100	-4.25506700	-1.33991400
C	5.19452600	-2.80889100	-0.00971600
C	4.64024500	-3.25488500	-2.31559800
C	5.76325300	-4.06869000	-2.43006000
C	6.32242500	-3.61460500	-0.13240800
H	4.97397500	-2.32912600	0.93885200
H	7.49554300	-4.88963900	-1.42840700
H	6.97580100	-3.74982300	0.72679200
H	5.97518800	-4.55834000	-3.37794300
H	3.98792100	-3.11276000	-3.17511700

TS-Tr-All. B

Li	3.12601000	0.61254600	0.23727800
Li	0.12813800	0.47337700	0.92086100
Li	1.50819100	-1.09695400	-1.17837900
O	0.04343400	-1.11391700	-0.16088200
N	3.38722700	-0.75449300	-1.13163400
N	1.75058000	1.47507100	1.30288600
C	-1.20606800	-1.46199700	-0.23928400
C	-2.26829500	-0.69448400	-0.77964300
N	-3.45424600	-1.54377500	-0.70218900
C	-3.09203100	-2.81685400	-0.04255600
N	-1.68117600	-2.60174900	0.33300400
C	-1.98178500	0.10363300	-2.02688500
C	-4.04004400	-3.22459700	1.13777700
C	-5.50365900	-3.08842700	0.67256000
C	-3.81356000	-4.70346800	1.51998900
C	-3.82939000	-2.32310500	2.36089500
C	-0.81692300	-3.62847600	0.87414300
C	-4.17703900	-1.72631600	-1.95871100
Si	3.64035700	0.12168800	-2.60428600
Si	4.32210800	-2.11871100	-0.60831300
Si	2.29711800	0.95748000	2.86070900

Si	1.47417300	3.13582300	0.87603000
C	4.38654100	1.83574600	-2.25495800
C	4.74819800	-0.69760500	-3.90426200
C	1.93207700	0.36563900	-3.42472300
C	6.13164600	-1.66063900	-0.26350600
C	4.31050600	-3.55837800	-1.84908100
C	3.57304500	-2.82423900	0.98981600
C	1.43326300	-0.67371000	3.33101400
C	4.18325800	0.63773400	2.79395600
C	2.02572700	2.15126200	4.30616300
C	3.06275400	4.17666900	0.99730600
C	0.16127700	3.98949600	1.94821500
C	0.85361100	3.22092400	-0.91869700
C	-2.73996400	2.08685100	0.12786400
C	-2.33616900	0.88078000	0.64784700
C	-1.93710000	0.43790900	1.85559000
H	-3.12428700	-3.64751200	-0.77920700
H	-1.96251400	-0.52156700	-2.92837900
H	-2.70070300	0.91179700	-2.17153700
H	-1.00016200	0.57142700	-1.92139300
H	-5.73820900	-2.05469800	0.40489900
H	-5.71886100	-3.73541900	-0.18695700
H	-6.17532200	-3.38979600	1.48416800

H	-4.57586900	-5.01857200	2.24144500
H	-3.89736500	-5.36012500	0.64446000
H	-2.84127100	-4.88186900	1.98559100
H	-3.97210600	-1.27216700	2.09845800
H	-2.82116000	-2.42925600	2.77562900
H	-4.54347400	-2.58827300	3.14933100
H	-0.97634500	-4.57952300	0.35025400
H	0.21835700	-3.31064300	0.74043600
H	-0.99051800	-3.78500700	1.94331900
H	-4.47295800	-0.75145300	-2.35164000
H	-3.58535700	-2.25894200	-2.72555900
H	-5.08843100	-2.29799800	-1.78079300
H	3.80585300	2.42825700	-1.53660000
H	5.40320400	1.73009800	-1.85312700
H	4.45432000	2.43535700	-3.17145700
H	5.73966000	-0.94340900	-3.50601200
H	4.89315300	-0.01817700	-4.75365400
H	4.30464900	-1.62234100	-4.29036400
H	1.19466500	0.84005300	-2.76284700
H	1.51458800	-0.59185800	-3.77364200
H	2.00345500	1.01069300	-4.30908700
H	6.61221700	-1.26354000	-1.16649100
H	6.71684000	-2.52687000	0.06965500

H	6.21065400	-0.88957000	0.51395700
H	4.77372000	-4.45149200	-1.41071400
H	4.85467800	-3.32161400	-2.76912800
H	3.28378400	-3.82909700	-2.13321600
H	4.13608400	-3.70799800	1.31549300
H	3.57525400	-2.11177200	1.82079500
H	2.53284100	-3.14278500	0.83861900
H	1.95818000	-1.18090300	4.15020000
H	0.40774200	-0.48067500	3.67316500
H	1.37987900	-1.37922700	2.49235300
H	4.54255200	0.19035600	3.72944000
H	4.50991200	-0.04207800	1.99365200
H	4.71747800	1.58780000	2.65663800
H	2.51842900	3.11729400	4.14583000
H	0.95864100	2.34399200	4.46592800
H	2.43042000	1.72189600	5.23161800
H	3.44890500	4.17630700	2.02477500
H	2.88457900	5.22145000	0.71312700
H	3.86069100	3.79180800	0.34860700
H	-0.73659800	3.36766300	2.04951600
H	-0.14452100	4.94401300	1.50114500
H	0.53304000	4.20064300	2.95659000
H	1.58068600	2.82434300	-1.63613600

H	-0.08759100	2.67146200	-1.05229100
H	0.65494900	4.26226000	-1.20241500
H	-2.06182700	2.92851700	0.25779200
H	-2.15289300	1.01114200	2.75605300
H	-1.51007600	-0.54980400	2.02198100
C	-3.97346600	2.34800100	-0.58189700
C	-6.39114900	2.90834400	-1.96456900
C	-5.01394600	1.38986600	-0.66530300
C	-4.19738200	3.60092800	-1.19978400
C	-5.38239800	3.87361000	-1.87554600
C	-6.19371500	1.66738000	-1.34952200
H	-4.87826900	0.42518800	-0.18465800
H	-7.31396400	3.12140800	-2.49716900
H	-6.97326000	0.90929100	-1.39551400
H	-5.52043300	4.84692000	-2.34143500
H	-3.42040700	4.36088700	-1.14339000

TS-Tr-Alk

Li	2.44856300	-0.68414000	0.38728500
Li	0.11724400	1.10080000	0.65337000
Li	0.18109700	-1.58872800	-0.85523900
O	-0.89400500	-0.46368500	-0.00318800

N	1.99726300	-2.18264100	-0.80309100
N	1.97717600	0.93068000	1.36037600
C	-2.17675100	-0.30566500	0.09230700
C	-2.95066200	0.75046400	-0.45717300
N	-4.32228100	0.44494900	-0.09681900
C	-4.37072800	-0.75395100	0.74662800
N	-2.94925800	-1.12028800	0.85984300
C	-2.73972600	1.16286000	-1.89501300
C	-5.26661100	-1.89682600	0.15068000
C	-5.51089100	-3.00447700	1.19489400
C	-6.63308400	-1.29852000	-0.23183100
C	-4.60000200	-2.47475900	-1.10737600
C	-2.42229500	-2.13086300	1.75216400
C	-5.18773600	1.55777500	0.27156400
Si	2.16327700	-2.23134500	-2.52794100
Si	2.43179100	-3.50977300	0.21998800
Si	1.64271000	0.95659700	3.06600200
Si	3.21358800	1.98623200	0.73210000
C	3.88298000	-1.79212700	-3.17866900
C	1.65862800	-3.89979200	-3.28914000
C	0.91427500	-0.97251200	-3.24928800
C	3.94855100	-4.49273500	-0.35522300
C	0.97943500	-4.70918300	0.47325700

C	2.87940300	-2.82023800	1.93751800
C	0.10594400	-0.11082400	3.42717000
C	3.00194200	0.24782500	4.18757800
C	1.25896500	2.70855300	3.69542600
C	4.81420600	2.00363400	1.76179800
C	2.71273000	3.79834400	0.53132800
C	3.75660800	1.28567200	-0.96097500
H	-4.75820900	-0.50915200	1.75463600
H	-3.34202200	0.52210100	-2.55240200
H	-3.02772000	2.20331000	-2.06732300
H	-1.68922200	1.07458200	-2.18085400
H	-4.60506600	-3.55961700	1.44971300
H	-5.92671500	-2.58979100	2.12218900
H	-6.23408700	-3.73116300	0.80701500
H	-7.30534300	-2.09148400	-0.57863800
H	-7.11223400	-0.80931600	0.62564600
H	-6.52858600	-0.56605600	-1.03633000
H	-3.65716400	-2.98118600	-0.86931400
H	-4.38807800	-1.67662300	-1.82742300
H	-5.25869300	-3.20538700	-1.59041900
H	-2.51627800	-3.14059600	1.33432300
H	-1.36666000	-1.92430700	1.92516200
H	-2.95102500	-2.10000900	2.71086800

H	-4.79468600	2.46858500	-0.18712300
H	-6.21033000	1.41012300	-0.08923500
H	-5.23488800	1.71843700	1.36126000
H	4.16812700	-0.76938800	-2.91141000
H	4.63653500	-2.47058600	-2.76011500
H	3.92693700	-1.87997300	-4.27156000
H	2.33819900	-4.71345700	-3.01282100
H	1.64908800	-3.83855600	-4.38478100
H	0.65026100	-4.19325800	-2.96704900
H	1.08731600	0.05648200	-2.91433300
H	-0.14520400	-1.20634800	-3.04745300
H	0.99892100	-0.96881700	-4.34310500
H	3.78720200	-5.00722800	-1.30872900
H	4.21938900	-5.25362700	0.38757700
H	4.81388600	-3.82937900	-0.48055900
H	1.23979800	-5.53984100	1.14108900
H	0.65439100	-5.13881000	-0.48264400
H	0.11761900	-4.19040100	0.91730200
H	3.12784900	-3.64308100	2.61931400
H	3.76035200	-2.16181200	1.91597800
H	2.05649700	-2.26386200	2.40234300
H	-0.16979700	-0.01340300	4.48478600
H	-0.77698900	0.16711100	2.84223400

H	0.30692100	-1.17243300	3.23890400
H	2.63981500	0.19838800	5.22305000
H	3.28991900	-0.76642500	3.88977900
H	3.90550100	0.86529400	4.18384000
H	2.16612200	3.32445500	3.72830300
H	0.54548300	3.22070000	3.03719200
H	0.83849800	2.68828600	4.70899600
H	4.68210200	2.52545300	2.71695200
H	5.60662000	2.52757700	1.21166400
H	5.17360400	0.99088000	1.98414000
H	2.57734400	4.26530400	1.51378400
H	1.78168300	3.92490600	-0.02647500
H	3.49906100	4.35476300	0.00463600
H	4.28269100	0.32412600	-0.86228500
H	2.93342400	1.14426300	-1.67054500
H	4.46885700	1.97403400	-1.43239600
C	-1.19031100	3.01600700	0.01678100
C	-2.00093300	2.23737000	0.62761100
C	-2.52084200	2.13895100	2.03397200
H	-2.85417300	1.12825000	2.29040800
H	-1.75713900	2.44765000	2.75605800
H	-3.38046300	2.80625100	2.16506700
C	-0.61945800	3.40395900	-1.23106100

C	-1.04197600	4.59441100	-1.87554900
C	0.41342900	2.66835300	-1.86384300
C	-0.48105200	4.99772900	-3.08127400
H	-1.81841400	5.19222200	-1.40656500
C	0.98552500	3.08966800	-3.06086700
H	0.77984600	1.75461000	-1.40328300
C	0.54058500	4.25511500	-3.68729300
H	-0.83652200	5.91156600	-3.55183500
H	1.78222400	2.49853000	-3.50682700
H	0.98466100	4.58467500	-4.62197500

LiHMDS

N	0.01392800	0.68602100	-0.02632700
Li	-0.58734700	2.38091500	-0.01172200
Si	-1.52313200	-0.03479700	-0.00285200
Si	1.59592800	0.04037100	-0.00583000
C	2.01986000	-0.81227000	1.64002400
C	1.90053600	-1.22933500	-1.38774600
C	-2.76031300	1.46433500	0.06492900
C	-1.91256200	-1.10571100	1.51376300
C	-1.99714400	-1.02262600	-1.55113400
H	1.34992900	-1.66140900	1.82650900

H	3.04975400	-1.19228000	1.65306900
H	1.90693800	-0.11813100	2.48243700
H	1.68243900	-0.79829500	-2.37267400
H	2.93921400	-1.58441000	-1.39657900
H	1.25292000	-2.10726700	-1.26504900
H	-2.66834200	2.07203300	0.98293900
H	-3.79356600	1.09857600	0.06735700
H	-2.70104400	2.13179100	-0.81494400
H	-1.72124000	-0.55675900	2.44379400
H	-2.95513200	-1.44877200	1.52619500
H	-1.27097500	-1.99591200	1.52582200
H	-1.33926100	-1.89278500	-1.66749900
H	-3.03082900	-1.38960400	-1.50888400
H	-1.88854000	-0.41254800	-2.45636900
C	2.83927300	1.46244200	-0.24602000
H	3.87876600	1.11144600	-0.22792300
H	2.67929500	1.96565700	-1.20939900
H	2.73717000	2.21472600	0.54931200

LiHMDS.3DME

N	0.93683400	0.10766000	-0.11050600
Li	-0.96018700	-0.17573000	-0.00712600

Si	1.89705800	-1.26818200	0.16349900
Si	1.46016400	1.71343900	-0.28635100
C	1.22161400	2.72226800	1.31969300
C	3.28414900	1.94942200	-0.79290700
C	0.80104800	-2.80186800	0.49334900
C	3.05492600	-1.14088900	1.67854000
C	3.01562300	-1.75496900	-1.30389300
O	-1.52780100	-0.50314900	1.89704200
C	-0.57832200	-0.34144300	2.95092100
C	-2.78105400	-0.99926300	2.33452100
H	1.82818600	2.29860300	2.13101300
H	1.50615500	3.77679600	1.20660800
H	0.17371700	2.69464500	1.64874000
H	3.48616200	1.48817700	-1.76771300
H	3.53766100	3.01500700	-0.87095100
H	3.97409200	1.49889900	-0.06842000
H	0.09344100	-2.62394200	1.31300600
H	1.41421100	-3.67104300	0.76341200
H	0.21328600	-3.07337000	-0.39191300
H	2.48766400	-1.01574200	2.61018000
H	3.67833800	-2.03809800	1.79049100
H	3.72869500	-0.27909000	1.59093300
H	3.75316100	-0.97138000	-1.51582800

H	3.56516600	-2.68539700	-1.10727700
H	2.42618100	-1.90338200	-2.21821800
H	0.31609800	0.07625900	2.48939100
H	-0.34412500	-1.30854100	3.41625900
H	-0.97046600	0.34462000	3.71562200
H	-3.21956700	-0.34420600	3.10208700
H	-3.44076500	-1.01526300	1.46382000
H	-2.68521400	-2.01425700	2.74640600
C	0.44130000	2.61782000	-1.62469100
H	0.71855600	3.67608800	-1.71495000
H	0.58908800	2.14815200	-2.60628200
H	-0.63003700	2.57062500	-1.39751200
O	-1.56392100	-1.38344200	-1.49811600
O	-2.54812900	1.12304000	-0.24709900
C	-2.69497700	2.19970400	0.67352100
H	-2.22403600	3.11385200	0.28838900
H	-3.75810300	2.39535700	0.87578700
H	-2.19646200	1.89324400	1.59331500
C	-3.19440100	1.36874700	-1.49133600
H	-2.99851400	0.49932100	-2.11905500
H	-4.27796700	1.49034700	-1.34753300
H	-2.79198300	2.26909800	-1.97481700
C	-2.51213500	-2.43751800	-1.47931800

H	-3.11965900	-2.31218900	-0.57974100
H	-3.16393300	-2.40013500	-2.36484200
H	-2.01318300	-3.41595900	-1.44240100
C	-0.69381700	-1.42298000	-2.63128000
H	-1.26401700	-1.25340000	-3.55612300
H	0.04630000	-0.63732800	-2.47262800
H	-0.18141700	-2.39216600	-2.69173700

4-Imidazolidinone

C	1.51189900	-0.57302400	0.62785500
C	1.45981600	0.91603400	0.27319500
N	0.26677400	1.12813000	-0.35781500
C	-0.50415800	-0.10735100	-0.54239400
N	0.43520100	-1.19222700	-0.18197300
C	2.92225200	-1.13237500	0.47105400
C	0.86780800	-1.94774200	-1.35521000
O	2.31878900	1.75577200	0.50068300
C	-1.83616300	-0.19857100	0.26241600
C	-2.49672500	-1.54143700	-0.10221800
C	-1.57119600	-0.14577400	1.77494300
C	-2.78638600	0.94691700	-0.13406300
C	-0.02719900	2.39543400	-0.99914600

H	1.23575600	-0.65706900	1.68854800
H	-0.76604200	-0.18666700	-1.60865100
H	3.28190900	-1.06424300	-0.55970300
H	3.59002700	-0.52885900	1.09210000
H	2.97921000	-2.17502400	0.79889000
H	1.38956900	-1.34323100	-2.11986500
H	1.52970500	-2.76236900	-1.05177500
H	-0.01349200	-2.39918000	-1.82176700
H	-2.73854900	-1.58851700	-1.17239100
H	-1.83189400	-2.37606900	0.13877600
H	-3.43234900	-1.67030800	0.45410800
H	-1.02852900	0.76598000	2.05027400
H	-0.98767800	-1.01286700	2.09892900
H	-2.51847800	-0.15117300	2.32671000
H	-2.43918200	1.91423000	0.24013600
H	-2.90006200	1.02073600	-1.22332800
H	-3.78174400	0.77136600	0.29014500
H	-0.48939700	2.22047000	-1.97687700
H	0.91738100	2.93096200	-1.12596700
H	-0.69997500	3.02167500	-0.40382000

Alkyne

C	-2.14537600	1.20796400	0.00004700
C	-0.75263000	1.21241700	-0.00004300
C	-0.03537200	0.00027700	-0.00009000
C	-0.75204500	-1.21221400	-0.00004600
C	-2.14479700	-1.20842500	0.00004800
C	-2.84677300	-0.00039800	0.00009400
H	-2.68559300	2.15100700	0.00008300
H	-0.20486000	2.14998500	-0.00006600
H	-0.20374400	-2.14946800	-0.00006900
H	-2.68458100	-2.15171600	0.00008700
H	-3.93341100	-0.00065900	0.00017000
C	1.39355600	0.00052100	-0.00016700
C	2.60556700	0.00068600	-0.00021600
C	4.06490500	-0.00028000	0.00018300
H	4.46329500	-0.49124100	0.89717800
H	4.46368800	-0.53273900	-0.87260400
H	4.46300000	1.02154600	-0.02364000

DME

O	0.00000300	0.59018800	0.00001000
C	-1.17201800	-0.19528900	0.00000300
H	-1.23534800	-0.83961000	0.89356500

H	-2.02288000	0.49169300	-0.00106100
H	-1.23437100	-0.84109400	-0.89255800
C	1.17201300	-0.19529100	-0.00000500
H	1.23493300	-0.84018100	-0.89318200
H	2.02287000	0.49169900	0.00021700
H	1.23479600	-0.84052800	0.89294600

$(TMS)_2NH$

N	-0.00005000	0.03199200	-0.81647600
Si	-1.59218100	0.01161900	-0.08845800
Si	1.59199900	-0.00537300	-0.08846900
C	2.07537700	1.68060000	0.61895100
C	1.62118400	-1.26981600	1.31684400
C	-2.81839500	0.64216000	-1.38056700
C	-1.60690500	1.13379100	1.43286400
C	-2.09229900	-1.72981100	0.45447000
H	1.35487800	2.00727900	1.37829300
H	3.06655800	1.65138900	1.08931300
H	2.09753400	2.44683400	-0.16536700
H	1.37962400	-2.27333600	0.94802000
H	2.60964300	-1.31034400	1.79102100
H	0.89463700	-1.02040400	2.09997600

H	-2.59279400	1.67462700	-1.67242800
H	-3.84384200	0.62035300	-0.99206500
H	-2.80009200	0.02458100	-2.28756300
H	-1.35542600	2.16624000	1.16424600
H	-2.59502100	1.13707300	1.90939500
H	-0.88317500	0.80179000	2.18734000
H	-1.37583300	-2.13292000	1.18031100
H	-3.08406700	-1.73668100	0.92464300
H	-2.11993900	-2.41842000	-0.39868800
C	2.82127400	-0.49413000	-1.43798300
H	3.84584200	-0.51284300	-1.04711400
H	2.59880200	-1.48954300	-1.84026100
H	2.80344000	0.21806800	-2.27267700
H	0.00070700	0.05809000	-1.83156400

TS-Di-All.C.DME

Li	-1.00877500	0.00931500	1.23848500
N	-2.61503400	0.21392800	0.15062600
Li	-1.76429000	-1.35970600	-0.61278900
Si	-2.58160000	1.35748000	-1.13358400
Si	-3.91162400	-0.10613400	1.22893300
C	-1.23987200	0.79135300	-2.37565700
C	-2.14102700	3.10966800	-0.57032600
C	-4.21269800	1.44523900	-2.11264100

C	-5.15692800	-1.35149200	0.50304900
C	-3.19153400	-0.92153800	2.79844500
C	-4.87113200	1.43395700	1.78574900
O	-2.37524200	-2.83371100	-1.66396900
C	-3.45344400	-2.74187100	-2.59635300
C	-2.27601800	-4.11088000	-1.03013700
H	-1.44736600	-0.19864900	-2.81221400
H	-0.25158000	0.75138800	-1.90175800
H	-1.16606600	1.49271100	-3.21594200
H	-1.17004100	3.12633300	-0.06161500
H	-2.08279000	3.81343200	-1.41038800
H	-2.89553100	3.48729600	0.13149900
H	-4.51434000	0.45490800	-2.47887000
H	-5.03320200	1.82328700	-1.49040900
H	-4.12634600	2.11026000	-2.98140600
H	-4.64960700	-2.29559500	0.26075500
H	-5.59942200	-0.96492000	-0.42341500
H	-5.97533000	-1.58366600	1.19620700
H	-2.63695000	-1.84096600	2.56347000
H	-3.98737600	-1.19222500	3.50374800
H	-2.50705500	-0.24722800	3.33418900
H	-5.63975700	1.18747200	2.52926100
H	-5.37172900	1.92656600	0.94322300
H	-4.19119700	2.16782000	2.23669300
H	-3.43399800	-1.73088400	-3.00732300
H	-3.32164500	-3.47220600	-3.40538600
H	-4.41478100	-2.91091300	-2.09542600
H	-1.44680300	-4.04298600	-0.32291900

H	-2.07286800	-4.89305400	-1.77323500
H	-3.20365700	-4.34846900	-0.49199800
C	1.71460500	-1.35391500	1.73965400
C	0.95866300	-1.65577100	0.60070200
N	1.80751700	-1.79315100	-0.48781100
C	3.18998800	-1.96862500	-0.00665600
N	3.11642400	-1.45340000	1.38138200
C	1.23184600	-1.69733900	3.11682800
C	3.91922200	-2.22960100	2.32550700
O	-0.32853100	-1.69058700	0.48814900
C	4.29352900	-1.31807500	-0.91813100
C	4.53902600	-2.20684700	-2.15882600
C	3.90785100	0.09820800	-1.36294000
C	5.63014100	-1.22963600	-0.15534800
C	1.34844300	-2.39052900	-1.72418900
H	3.41119700	-3.06214400	0.02039600
H	1.69591500	-1.07851200	3.89267900
H	0.15224800	-1.53739800	3.17035300
H	1.41869200	-2.74867400	3.37476600
H	3.61802400	-3.29331900	2.37076700
H	4.97278800	-2.19089000	2.05608300
H	3.82481400	-1.80069300	3.32516300
H	4.75167900	-3.24473400	-1.87249200
H	3.69638900	-2.21351300	-2.85403600
H	5.40767900	-1.83287000	-2.71268300
H	3.75857400	0.75194300	-0.50098000
H	2.98548500	0.09961000	-1.95191800
H	4.70278500	0.52389700	-1.98677200

H	5.53936800	-0.58757500	0.72481700
H	5.99159200	-2.21759000	0.15505300
H	6.39389800	-0.79564500	-0.81074100
H	1.61337800	-1.78090300	-2.59298900
H	0.26114200	-2.47858300	-1.69067800
H	1.77705600	-3.39487700	-1.85847800
C	0.30906100	1.18832400	2.78385300
H	0.56571900	0.84906200	3.78242600
C	1.02383700	0.89473700	1.67964000
C	1.33623400	1.35425400	0.45158400
H	1.43442900	0.64267700	-0.36287500
H	-0.53045800	1.88622700	2.71312300
C	1.61627100	2.74780200	0.10037300
C	1.90057800	3.07001500	-1.24345500
C	1.59583400	3.80304400	1.03622500
C	2.14719700	4.38335200	-1.63549400
H	1.91497500	2.27565400	-1.98526500
C	1.85186000	5.11277200	0.64232800
H	1.37829900	3.58013200	2.07620900
C	2.12681400	5.41579700	-0.69527900
H	2.35631900	4.60126000	-2.68021300
H	1.83187500	5.90693800	1.38500000
H	2.31765300	6.44147000	-0.99926300

TS-Di-Alk.DME

Li	0.83649800	0.45047500	0.23275400
N	2.35120800	-0.79711100	0.11388100
Li	0.84482300	-1.97983500	-0.21348600

Si	3.01264300	-1.21452800	1.64526300
Si	3.24079300	-0.54615100	-1.34101100
C	1.64656400	-2.08531700	2.66169000
C	3.57155300	0.30067000	2.63693000
C	4.47067200	-2.43635900	1.56121900
C	3.68479500	-2.20151300	-2.17792900
C	2.16099800	0.41201200	-2.57987000
C	4.85623900	0.42602400	-1.10981900
O	0.52708500	-3.80233000	-0.65662200
C	1.50884000	-4.83580500	-0.56721300
C	-0.49067200	-4.06203400	-1.62430400
H	1.25240700	-2.98030900	2.15549800
H	0.80102700	-1.41363300	2.85958700
H	2.02919200	-2.41575700	3.63546500
H	2.74043000	1.00582700	2.76999100
H	3.94968500	0.03332900	3.63196600
H	4.37028400	0.83410500	2.10656300
H	4.19521500	-3.35746200	1.03051900
H	5.32952000	-2.00452200	1.03339300
H	4.80985600	-2.72111000	2.56537400
H	2.77428300	-2.76083200	-2.43658800
H	4.28224700	-2.83181600	-1.50773100
H	4.25544200	-2.05848800	-3.10437600
H	1.18143800	-0.06457100	-2.72434900
H	2.64664200	0.46649800	-3.56256800
H	1.98848700	1.44342600	-2.24654400
H	5.33660600	0.63729100	-2.07363700
H	5.57764400	-0.12620800	-0.49505800

H	4.67034100	1.38561600	-0.61294200
H	2.22335100	-4.53123700	0.19951800
H	1.03844000	-5.78460300	-0.27770600
H	2.03286800	-4.95775500	-1.52357200
H	-1.16349700	-3.20233100	-1.60952800
H	-1.04462100	-4.97387500	-1.36439800
H	-0.05328300	-4.17355900	-2.62585300
C	-2.03571000	1.06675800	-0.16946800
C	-1.72380400	-0.32137400	-0.12211500
N	-2.79214300	-1.03438400	0.33704200
C	-3.97849000	-0.16754800	0.45175300
N	-3.46499300	1.15541800	0.06438600
C	-1.51926900	1.90892900	-1.31098100
C	-3.92847000	2.30496600	0.83173900
O	-0.57278100	-0.83902300	-0.33695800
C	-5.16724300	-0.65121200	-0.44544900
C	-6.29649600	0.39365500	-0.39458700
C	-4.69130700	-0.81287400	-1.89724600
C	-5.72049500	-1.98829000	0.08366600
C	-2.64008300	-2.29777200	1.03367000
H	-4.32132500	-0.16961800	1.50494600
H	-1.57238200	2.97399500	-1.07944700
H	-0.47117000	1.68674300	-1.53143100
H	-2.10698600	1.71643700	-2.21778100
H	-3.78210400	2.20035100	1.91913300
H	-3.37008000	3.18527600	0.50501000
H	-4.98896000	2.49311100	0.64984300
H	-6.61198200	0.59870200	0.63662400

H	-5.98339700	1.33357400	-0.85673100
H	-7.17214500	0.02654000	-0.94211000
H	-3.92307200	-1.58989100	-1.98042100
H	-4.26827300	0.12757400	-2.26535300
H	-5.52889900	-1.09303400	-2.54653500
H	-5.01010700	-2.81031100	-0.04108400
H	-5.98384500	-1.92252200	1.14748600
H	-6.62949100	-2.26216000	-0.46409200
H	-3.28128300	-2.30985300	1.92152000
H	-1.59824100	-2.40877600	1.34741600
H	-2.90160600	-3.15841500	0.40747900
C	0.05757200	2.45224500	1.31058000
C	-0.88575400	1.59283500	1.43116300
C	-1.39361300	0.79268000	2.59990000
H	-1.14456400	-0.27180200	2.50214300
C	0.79404700	3.35433800	0.49816200
C	2.10876100	3.04169800	0.05862100
C	0.27941000	4.62851300	0.13581300
C	2.82816200	3.91891000	-0.74978200
H	2.57175700	2.11133000	0.38031700
C	1.01596000	5.50078000	-0.65462800
H	-0.71141900	4.90930700	0.48342000
C	2.29243600	5.15457100	-1.11893300
H	3.82432100	3.63548500	-1.08175300
H	0.58799100	6.46525100	-0.91978800
H	2.85978400	5.84134100	-1.74026700
H	-0.93759100	1.15790300	3.52475600
H	-2.48154800	0.84948100	2.70235200