Ni-Catalyzed Enantioselective Intermolecular Hydroamination of Branched 1,3-Dienes Using Primary Aliphatic Amines

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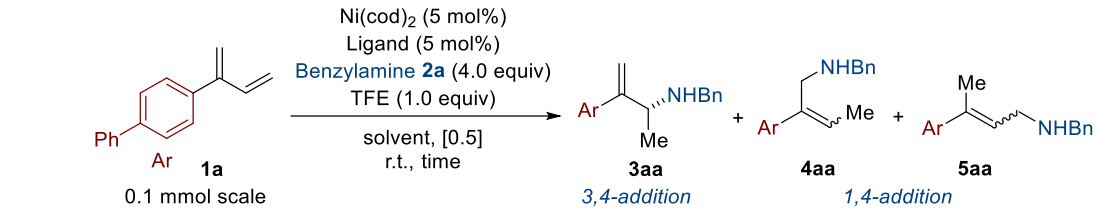
1. General Information

Unless otherwise noted, all reactions were carried out under air. All liquid amines were distilled and degassed by thr*ee* successive "freeze-pump-thaw" cycles, followed by drying over activated 4Å MS. THF, Et_2O CH_2Cl_2, toluene, and pentane were degassed by N_2 bubbling and dried over activated alumina columns. Mesitylene was dried and distilled over CaH_2 and degassed by thr*ee* successive "freeze-pump-thaw" cycles. $Ni(cod)_2$ was dissolved in toluene (*ca*. 1g/20mL), filtered over Celite, and recrystallized at −78 °C. Unless otherwise specified, all the dienes were prepared according to reported literature procedures.[1] All other reagents were purchased from Aldrich, Fluka, Acros or Strem and used without purification. NMR spectra were recorded on AMX−400 and AMX−500 Bruker Avance spectrometers at 298 K. ^1H and $^{13}C\{^1H\}$ NMR chemical shifts are given in ppm relative to $SiMe_4$, with the solvent resonance used as internal reference. ^1H NMR spectra were referenced to $CHCl_3$ (δ = 7.26 ppm), methanol (δ = 3.31 ppm) and toluene (δ = 6.98 ppm) and $^{13}C\{^1H\}$ NMR spectra were referenced to $CDCl_3$ (δ = 77.16 ppm), methanol-*d*$_4$ (δ = 49.00 ppm) and toluene-*d*$_8$ (δ = 20.40 ppm). $^{31}P\{^1H\}$ NMR chemical shifts are reported in ppm relative to H_3PO_4. $^{19}F\{^1H\}$ NMR chemical shifts are reported in ppm relative to $CFCl_3$. Infrared spectra were obtained on a Perkin−Elmer 1650 FT-IR spectrometer using neat samples on a diamond ATR Golden Gate sampler. HRMS were obtained on a Xevo G2 Tof spectrometer (Ionization mode: ESI positive polarity; Mobile phase: MeOH 100 µl/min). Mass spectrum is calibrated by the use of the MS lockspray system (LeuEnk calibration solution). The enantiomeric excesses (*ee*'s) were determined by HPLC, SFC and GC analyses. HPLC analyses were performed on a Shimadzu CTO-20AA with column DAICEL OD-H, OJ-H, AD-H and IC. SFC analyses were performed on a Waters Acquity UPC2 with columns OD-3, OJ-3, OZ-3, OB-H, AZ-3, AD, AS-3, AY-H. Retention times (t_R) are given in minutes. GC analyses were performed on HP−6890, column HYDRODEX γ-DiMOM, HYDRODEX β-3P and HYDRODEX TBDM, 50 m. Optical rotations were recorded using an OMNI Lab JASCO P-1030 polarimeter using 589 nm emission band of a sodium lamp. Thin layer chromatography (TLC) was performed on plates of silica precoated with 0.25 mm Kieselgel 60 F_{254} from *Merck*. Flash chromatography was performed using silica gel SiliaFlash® P60 (230-400 mesh) from *Silicycle*.

2. Reaction optimization



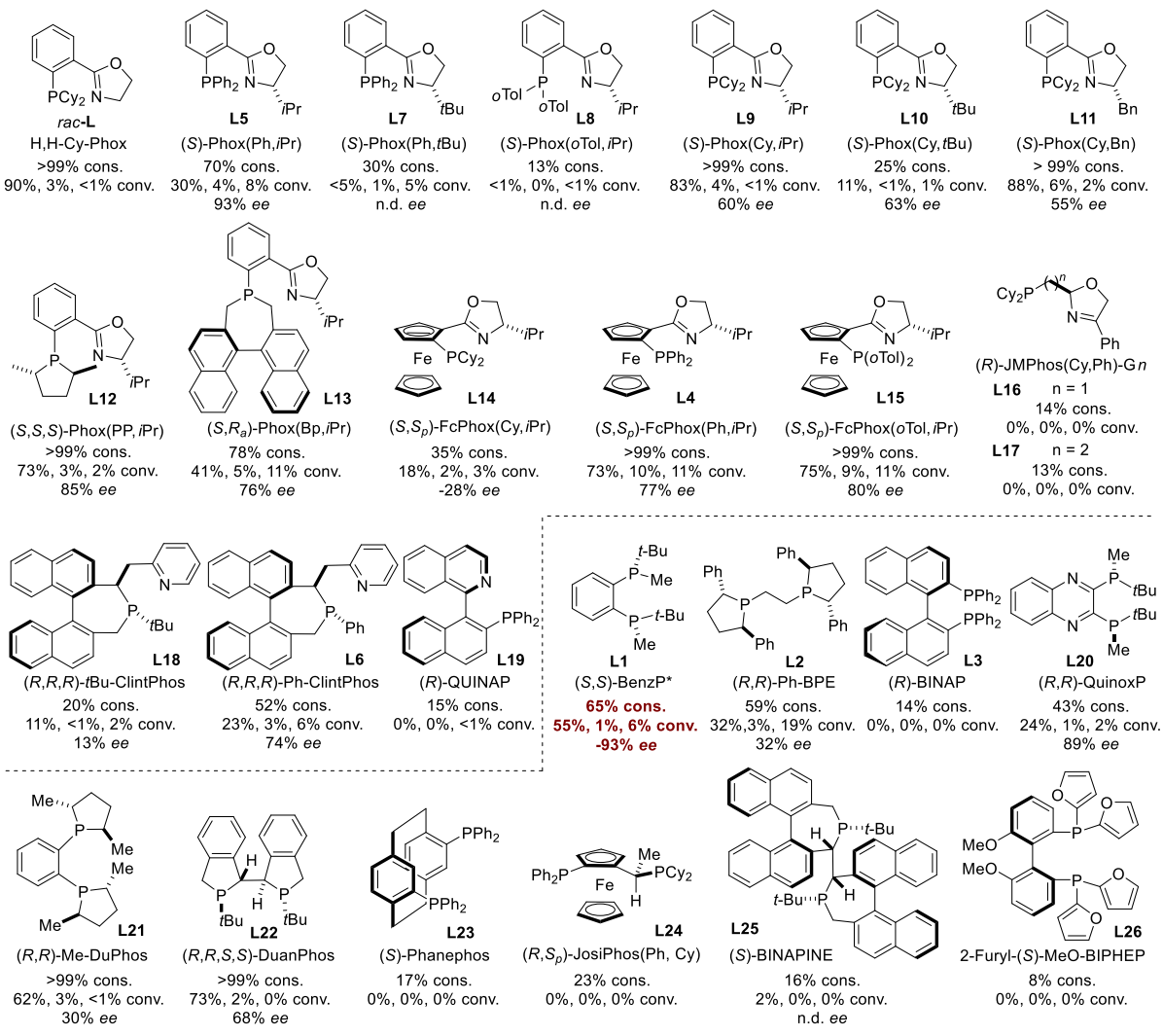
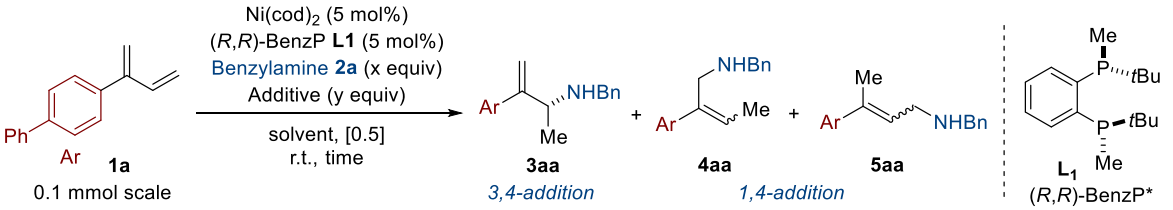


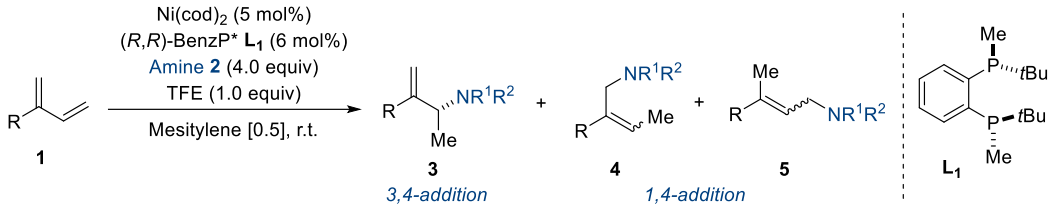
Table S1: **Ligand screening.** [a] Reaction conditions: all reactions were performed with diene **1a** (0.10 mmol, 1.0 equiv), benzylamine **2a** (0.40 mmol, 4.0 equiv), $Ni(cod)_2$ (0.005 mmol, 5 mol%), ligand (0.005 mmol, 5 mol%), 2,2,2-trifluoroethanol (0.10 mmol, 1.0 equiv) in mesitylene (0.20 mL, 0.5 M) at room temperature. Consumption of **1a**, conversions of **3aa**, **4aa** and **5aa** were assessed by ^1H NMR of the crude reaction mixture using an internal standard. n.d. = not determined.



Entry	Solvent	Additive	Time (h)	x	y	**1a** Cons. (%)	**3aa** (%)	**4aa** (%)	**5aa** (%)	*ee* **3aa** (%)
1[b]	Mes.	TFE	24	4	1	65	55	1	6	-93
2[b]	Mes.	TFE	48	4	1	>99	72	2	8	-93
3	PhMe	TFE	24	4	1	60	52	<1	8	91
4	**Mes.**	**TFE**	**48**	**4**	**1**	**>99**	**79**	**3**	**11**	**93**
5	THF	TFE	48	4	1	57	43	2	4	95
6	Et_2O	TFE	48	4	1	46	36	1	3	95
7	Et_2O	TFE	48	4	1	>99	74	2	8	93
8	CH_2Cl_2	TFE	48	4	1	8	0	0	0	--
9	Mes.	TFE	48	2	1	30	17	<1	2	86
10[c]	Mes.	TFE	24	4	1	>99	70	3	11	87
11	Mes	EtOH	24	4	1	4	0	0	0	--
12	Mes.	$Ph_2P(O)OH$	24	4	1	>99	88	3	4	90
13	Et_2O	$Ph_2P(O)OH$	24	4	1	80	72	2	2	83
14	Mes.	$Ph_2P(O)OH$	48	2	1	>99	84	3	3	88
15	Mes.	$Ph_2P(O)OH$	48	4	0.2	>99	92	3	4	91
16	Mes.	$Ph_2P(O)OH$	48	2	0.2	>99	90	3	2	91

Table S2: **Other condition optimization.** [a] Reaction conditions: all reactions were performed with diene **1a** (0.10 mmol, 1.0 equiv), benzylamine **2a** (0.40 mmol, 4.0 equiv or 0.20 mmol, 2.0 equiv), $Ni(cod)_2$ (0.005 mmol, 5 mol%), (*R*,*R*)-BenzP* **L1** (0.005 mmol, 5 mol%), 2,2,2-trifluoroethanol (0.10 mmol, 1.0 equiv) or diphenylphosphonic acid (0.10 mmol, 1.0 equiv or 0.020 mmol, 0.20 equiv) in solvent (0.20 mL, 0.5 M) at room temperature. Consumption of **1a** and conversions were assessed by ^{1}H NMR of the crude reaction mixture using an internal standard. [b] Using (*S*,*S*)-BenzP* as ligand. [c] At 40 °C. Mes. = mesitylene, THF = tetrahydrofuran, TFE = 2,2,2-trifluoroethanol.

3. General procedure for the amination reaction

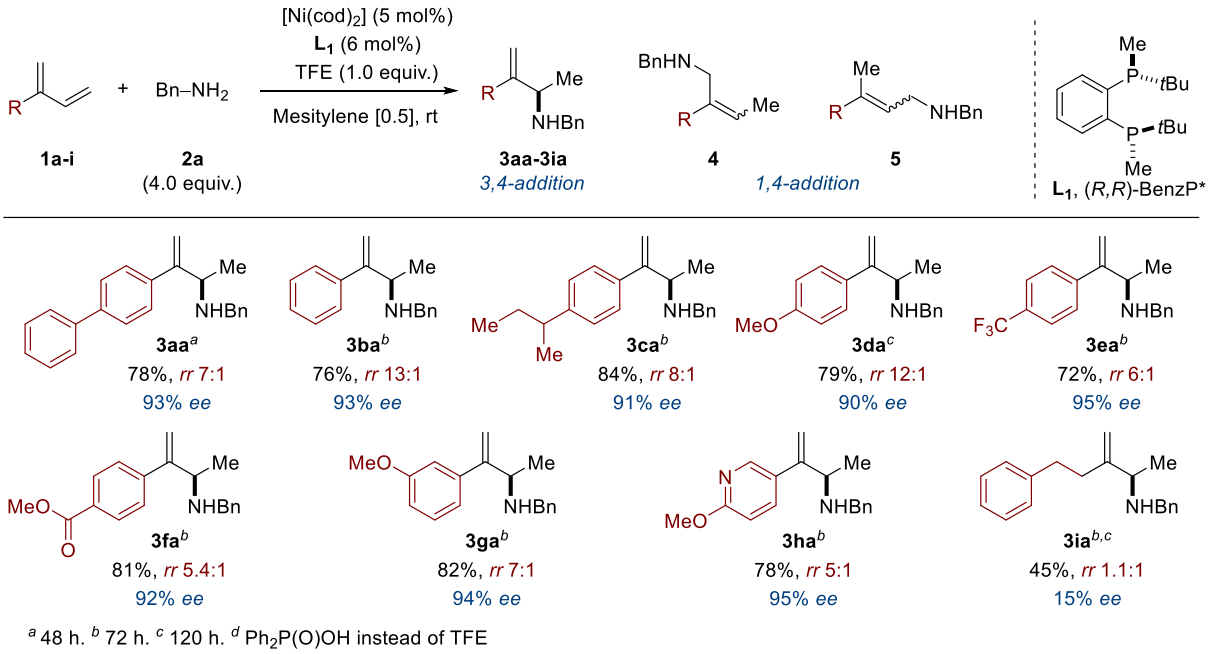


In a N_2-filled glovebox, $Ni(cod)_2$ (0.0125 mmol, 3.4 mg, 5 mol%) and (*R*,*R*)-BenzP* **L_1** (0.015 mmol, 4.2 mg, 6 mol%) were charged in a 5 mL Schlenk tube and dissolved in anhydrous mesitylene (0.50 mL, 0.50 M). After stirring at room temperature for 10 min, the appropriate diene **1** (0.25 mmol, 1.0 equiv), the appropriate amine **2** (1.00 mmol, 4.0 equiv) and TFE (0.25 mmol, 19 µL, 1.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and the reaction mixture was stirred at room temperature. After complete consumption of diene **1** (determined by TLC), the reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (10 mL) and concentrated under vacuum to afford the crude mixture. The conversion and isomeric ratio were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. The residue was purified by silica gel column chromatography to afford the analytically pure hydroamination product **3**.

*Note: All racemates were prepared according to a similar procedure using H,H-Cy-Phox rac-**L** as ligand (mesitylene [0.5], room temperature, 24 h).*

4. Substrate scope

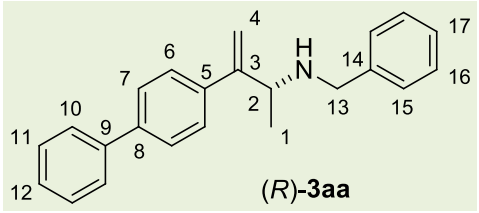
4.1 Scope in diene



[a] 48 h. [b] 72 h. [c] 120 h. [d] $Ph_2P(O)OH$ instead of TFE

Figure S1. Scope of the Ni-catalyzed hydroamination of 2-substituted 1,3-dienes - Variation of the diene component. 0.25-0.40 mmol scale. Yields of 3,4-addition product after purification. Regioselectivity expressed as the ratio between 3,4- and 1,4-addition products as determined by ^{1}H NMR using an internal standard (**3**:[**4**+**5**]). Enantiomeric excess determined by GC or HPLC equipped with chiral columns. [a] 48 h. [b] 72 h. [c] 120 h.

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-benzylbut-3-en-2-amine 3aa



Synthesized at room temperature for 48 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), benzylamine **2a** (109 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3aa**: 79%, *r.r.* = 7:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 5:1) led to the desired product as a yellow solid (61.1 mg, 78% yield, 93% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.63 (d, $^3J_{HH}$ = 7.4 Hz, 2H, *H*-10), 7.58 (d, $^3J_{HH}$ = 8.2 Hz, 2H, *H*-7), 7.52 – 7.43 (m, 4H, *H*-6+*H*-11), 7.40 – 7.25 (m, 6H, *H*-12+*H*-15+*H*-16+*H*-17), 5.40 (s, 1H, *H*-4), 5.38 (s, 1H, *H*-4), 3.91 (d, $^2J_{HH}$ = 13.1 Hz, 1H, *H*-13), 3.86 – 3.73 (m, 2H, *H*-13'+*H*-2), 1.65 (s, 1H, N*H*), 1.29 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.5 (*C*-3), 140.9 (*C*-9), 140.7 (*C*-14), 140.3 (*C*-8), 140.2 (*C*-5), 128.9 (*C*H-11), 128.5 (*C*H-16), 128.4 (*C*H-15), 127.5 (*C*H-6), 127.4 (*C*-12), 127.14 (*C*H-10), 127.06 (*C*H-7+*C*H-17), 113.0 (CH_2-4), 56.7 (*C*H-2), 51.5 (CH_2-13), 21.8 (CH_3-1).

m.p. = 44.2 – 46.0 °C.

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{23}H_{24}N^+$: 314.1904; found: 314.1939.

IR (neat) ν (cm^{-1}): 3025, 2924, 2853, 1623, 1487, 1452, 1369, 1152, 1120, 1077, 1004, 916, 841, 771, 740, 694.

HPLC: 93% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 7.2 min, t_R (minor) = 15.7 min.

[α]$^{20}_D$ = +7.0 (*c* 1.0, $CHCl_3$).

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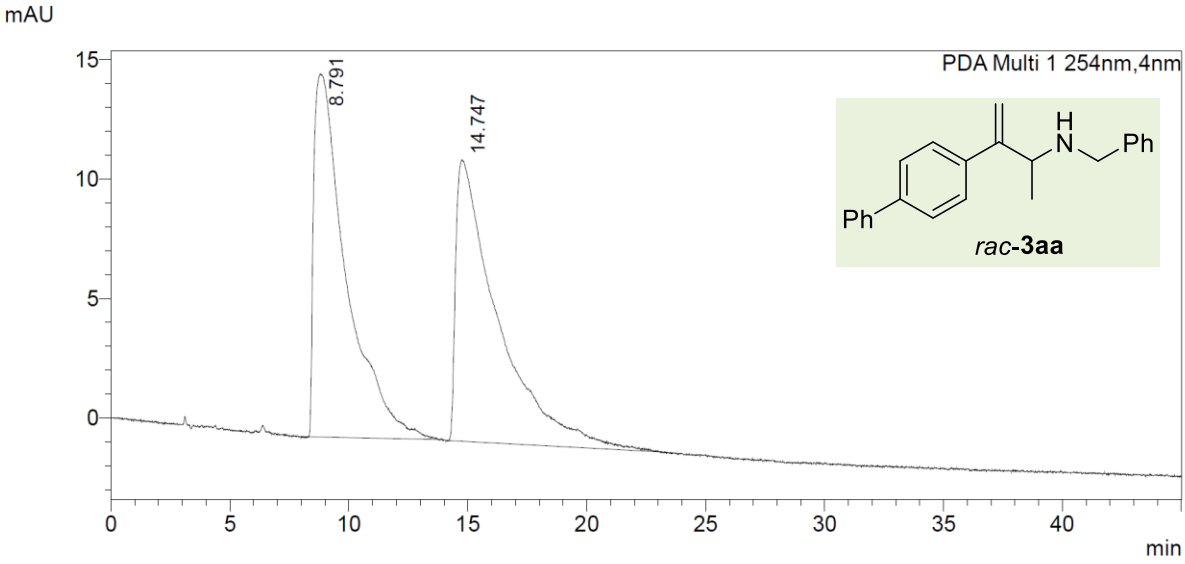

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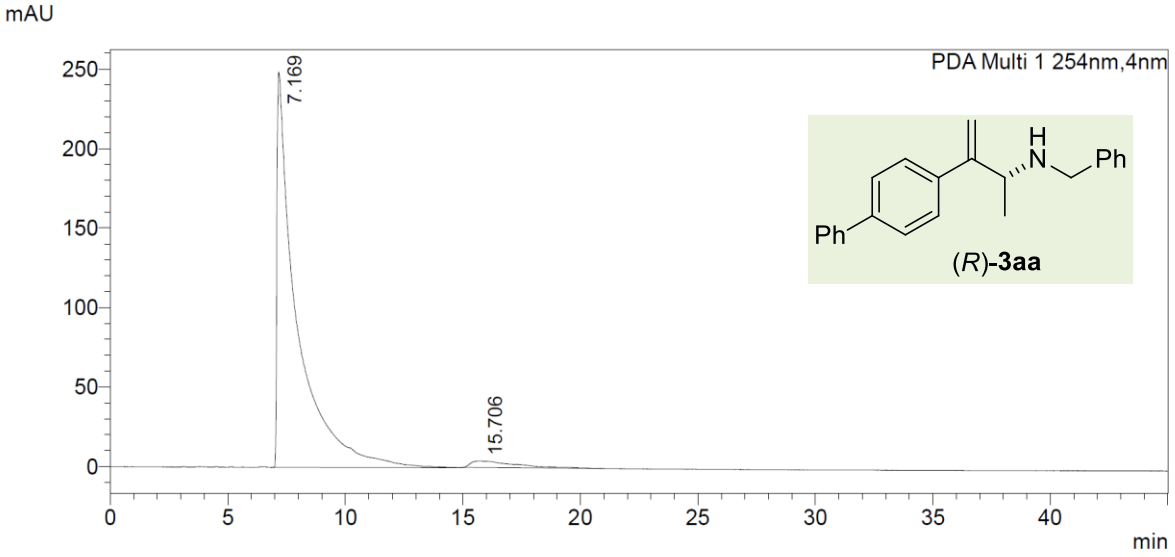

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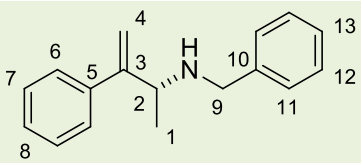
(*R*)-*N*-Benzyl-3-phenylbut-3-en-2-amine 3ba



(*R*)-**3ba**

Synthesized at room temperature for 72 h following the general procedure using buta-1,3-dien-2-ylbenzene **1b** (33.0 mg, 0.25 mmol, 1.0 equiv), benzylamine **2a** (109 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1b**: >95%, conversion of **3ba**: 76%, *r.r.* = 13:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product as a pale yellow oil (45.0 mg, 76% yield, 93% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.41 – 7.36 (m, 2H, H-*Ar*), 7.35 – 7.22 (m, 8H, H-*Ar*), 5.35 – 5.29 (m, 2H, H-*4*), 3.87 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*9*), 3.81 – 3.72 (m, 2H, H-*9* + H-*2*), 1.51 (s, 1H, N*H*), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

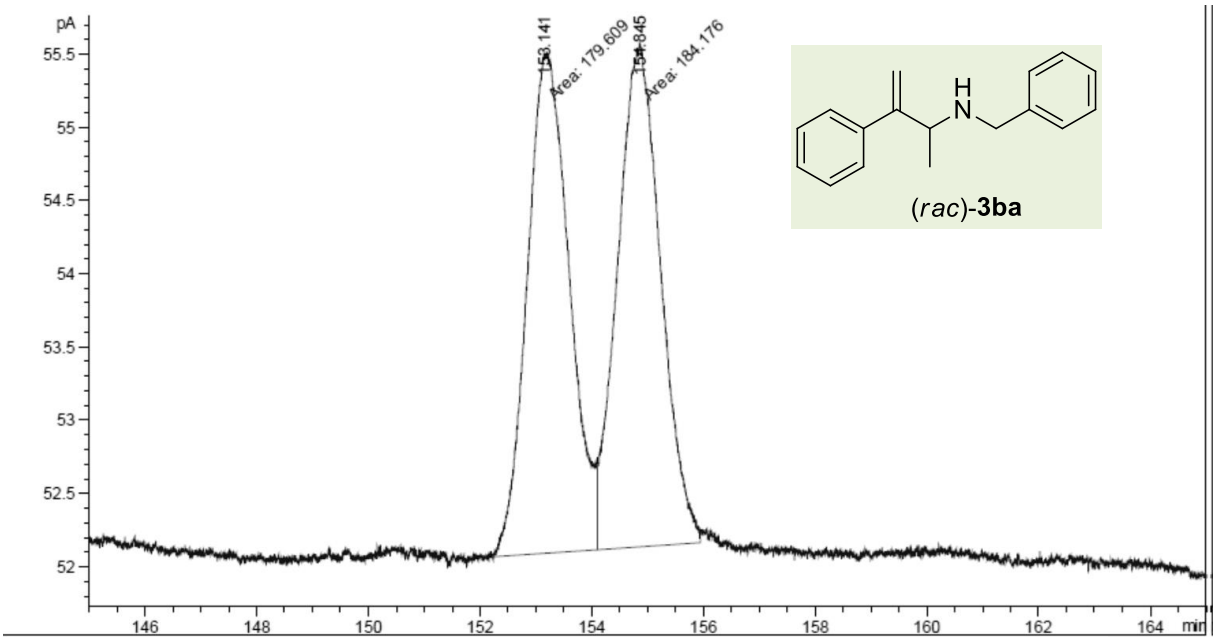
^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 152.0 (*C*-3), 141.4 (*C*-5), 140.8 (*C*-10), 128.5 (*C*H-Ar), 128.3 (*2xC*H-Ar), 127.5 (*C*H-8), 127.2 (*C*H-12), 127.0 (*C*H-13), 112.9 (CH_2-4), 56.8 (*C*H-2), 51.5 (CH_2-9), 21.8 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{17}H_{20}N^+$: 238.1591; found: 238.1590.

IR (neat) ν (cm^{-1}): 3027, 2967, 2929, 1627, 1600, 1493, 1452, 1369, 1315, 1150, 1072, 1027, 906, 778, 734, 695.

Chiral GC: 93% *ee*, chiral stationary column: Hydrodex γ–DiMOM, mobile phase: H_2 (45 cm/s), temperature gradient: 145 °C isothermal, t_R (minor) = 153.5 min, t_R (major) = 155.1 min.

[α]$^{20}_D$ = +3.1 (*c* 0.47, CH_2Cl_2).



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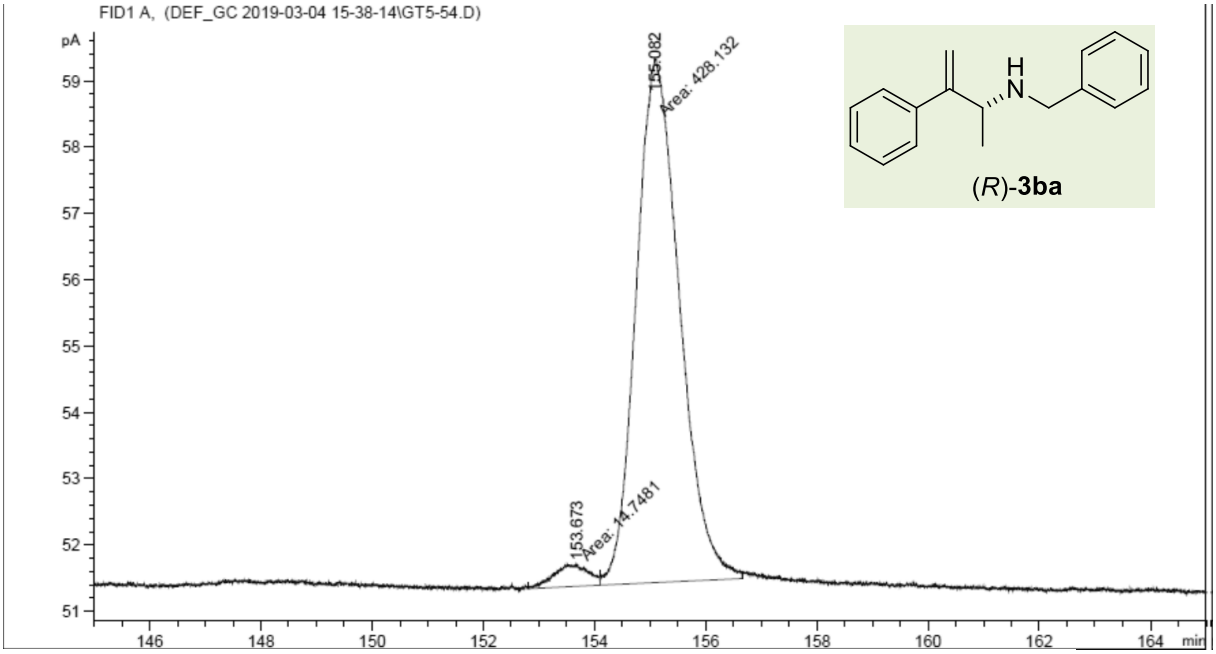

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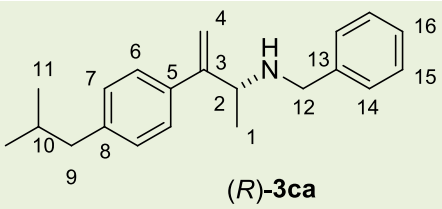
(*R*)-*N*-Benzyl-3-(4-isobutylphenyl)but-3-en-2-amine 3ca



(*R*)-**3ca**

Synthesized at room temperature for 48 h following the general procedure using 1-(buta-1,3-dien-2-yl)-4-isobutylbenzene **1c** (75.0 mg, 0.40 mmol, 1.0 equiv), benzylamine **2a** (175 µL, 1.60 mmol, 4.0 equiv), $Ni(cod)_2$ (5.5 mg, 0.020 mmol, 5 mol%), (*R,R*)-BenzP* (6.8 mg, 0.024 mmol, 6 mol%), 2,2,2-trifluoroethanol (29 µL, 0.40 mmol, 1.0 equiv) and mesitylene (0.80 mL, 0.5 M). Consumption of **1c**: >95%, conversion of **3ca**: 84%, *r.r.* = 8:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product as a pale yellow oil (99.0 mg, 84% yield, 91% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.34 – 7.27 (m, 6H, H-*15* + H-*14* + H-*6*), 7.26 – 7.22 (m, 1H, H-*16*), 7.10 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-*7*), 5.33 – 5.28 (m, 2H, H-*4*), 3.85 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*12*), 3.79 – 3.71 (m, 2H, H-*2* + H-*12*), 2.47 (d, $^3J_{HH}$ = 7.2 Hz, 3H, H-*9*), 1.87 ($hept_{app}$, $^3J_{HH}$ = 6.6 Hz, 1H, H-*10*), 1.52 (s, 1H, N-*H*), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*), 0.92 (d, $^3J_{HH}$ = 6.6 Hz, 6H, H-*11*)

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 151.9 (*C-3*), 141.1 (*C-8*), 140.9 (*C-13*), 129.1 (*C-5*), 128.5 (*C*H-*Ar*), 128.4 (CH-*Ar*), 1267.0 (*C*H-*16*), 126.8 (*C*H-*Ar*), 112.2 (CH_2-*4*), 56.7 (*C*H-*2*), 51.5 (CH_2-*12*), 45.2 (CH_2-*9*), 30.4 (*C*H-*10*), 22.6 (CH_3-*11*), 21.8 (CH_3-*1*).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{21}H_{28}N^+$: 294.2217; found: 294.2247.

IR (neat) ν (cm^{-1}): 3026, 2955, 1625, 1510, 1495, 1454, 1367, 1151, 1120, 906, 847, 801, 731, 697.

HPLC: 91% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 5.3 min, t_R (major) = 5.9 min.

[α]$^{20}_D$ = +2.8 (*c* 0.74, $CHCl_3$).

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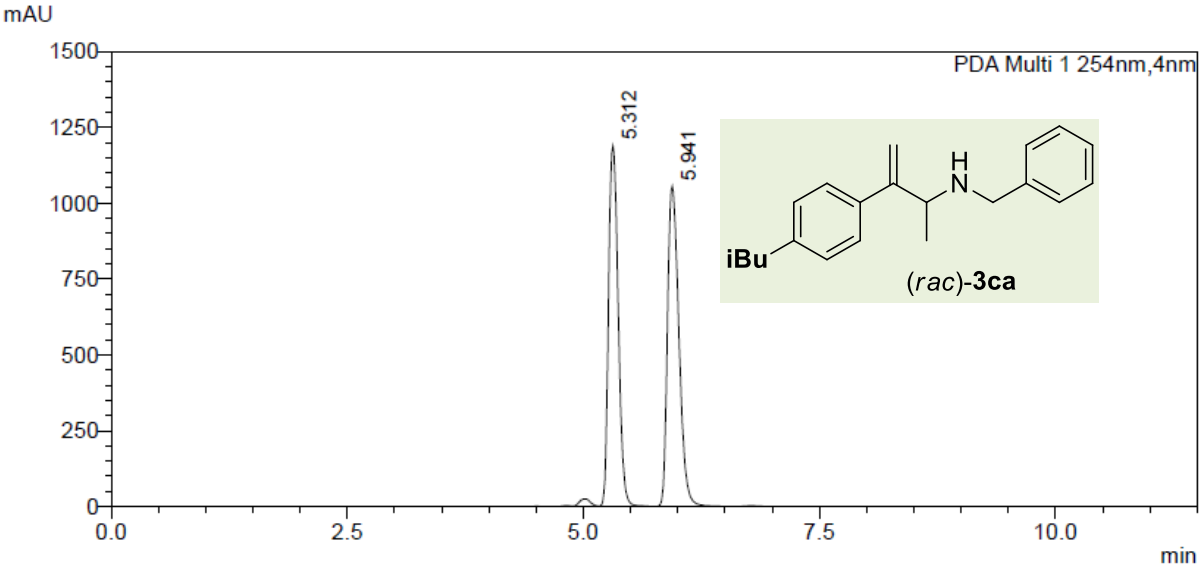

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Total		100.000

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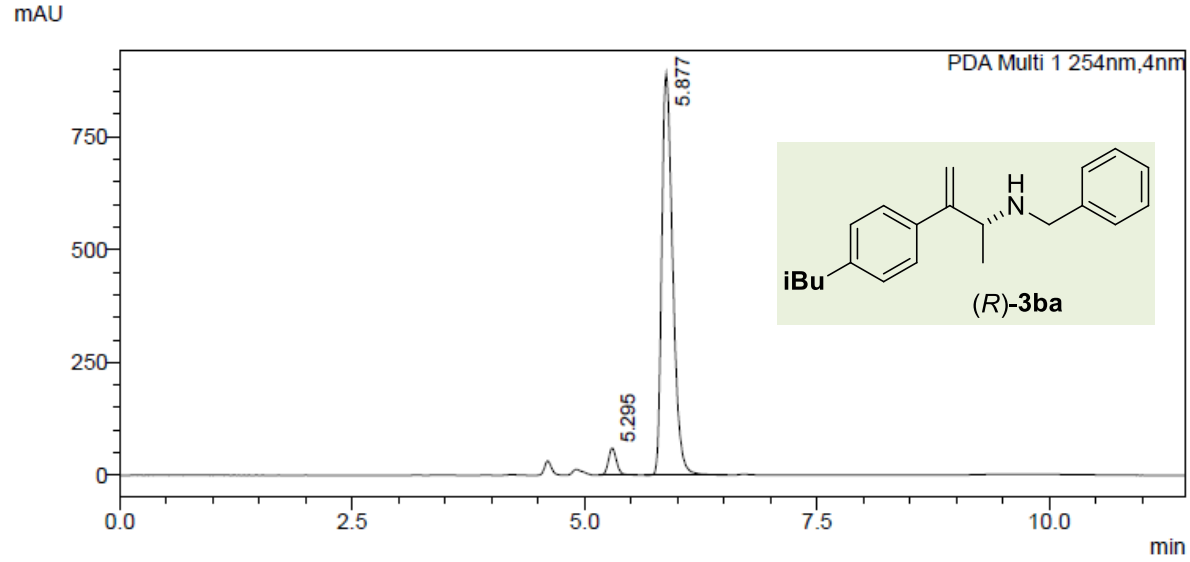

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PDA Ch1 254nm

Peak#	Ret. Time	Area%
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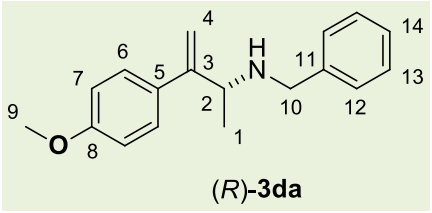
Total		100.000

(*R*)-*N*-Benzyl-3-(4-methoxyphenyl)but-3-en-2-amine 3da



(*R*)-**3da**

Synthesized at room temperature for 120 h following the general procedure using 1-(buta-1,3-dien-2-yl)-4-methoxybenzene **1d** (40.0 mg, 0.25 mmol, 1.0 equiv), benzylamine **2a** (110 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1d**: 91%, conversion of **3da**: 81%, *r.r.* = 12:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 3:2) led to the desired product as a pale yellow oil (52.0 mg, 79% yield, 90% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.37 – 7.29 (m, 6H, H-*6* + H-*12* + H-*13*), 7.26 – 7.22 (m, 1H, H-*14*), 6.88 – 6.83 (m, 2H, H-*7*), 5.26 – 5.24 (m, 2H, H-*4*), 3.85 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*10*), 3.82 (s, 3H, H-*9*), 3.76 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*10*), 3.72 (q, $^3J_{HH}$ = 6.6 Hz, 1H, H-*2*), 1.53 (s, 1H, N-*H*), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 159.2 (*C-8*), 151.3 (*C-3*), 140.9 (*C-11*), 133.7 (*C-5*), 128.5 (*C*H-*Ar*), 128.3 (*C*H-*Ar*), 128.2 (*C*H-*Ar*), 127.0 (*C*H-*14*), 113.7 (CH_2-*7*), 111.7 (*C*H-*4*), 56.8 (*C*H-*2*), 55.4 (CH_3-*9*), 51.5 (CH_2-*10*), 21.7 (CH_3-*1*).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{18}H_{22}NO^+$: 268.1696; found: 268.1731.

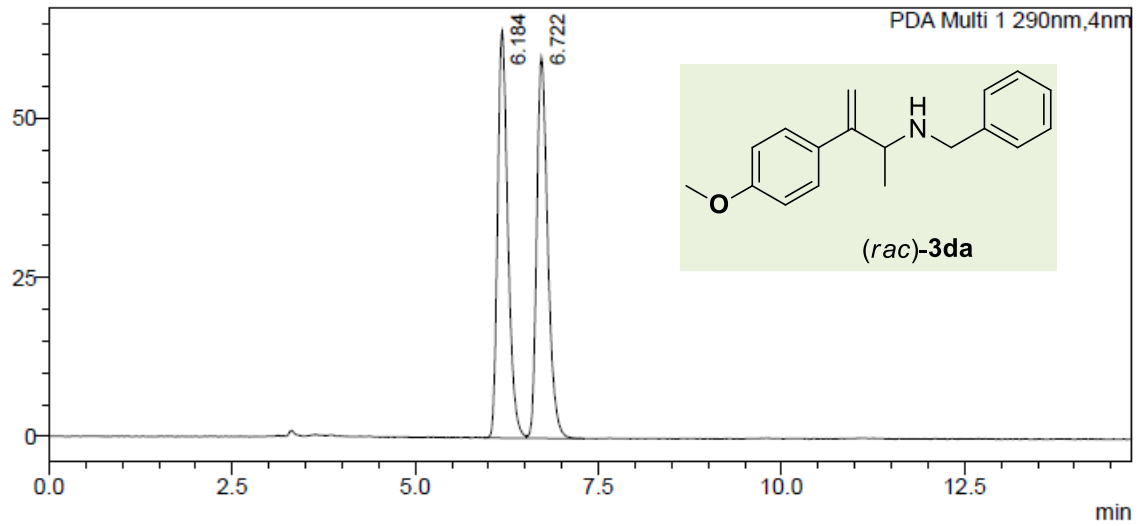
IR (neat) ν (cm^{-1}): 3029, 2928, 1607, 1509, 1454, 1369, 1292, 1243, 1179, 1150, 1113, 1032, 903, 834, 733, 697.

HPLC: 90% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 98/2, 1.0 mL/min, 290 nm, 30 °C, t_R (minor) = 6.0 min, t_R (major) = 6.6 min.

$[\alpha]^{20}_D$ = +4.2 (*c* 1.0, CH_2Cl_2).

<Chromatogram>

mAU



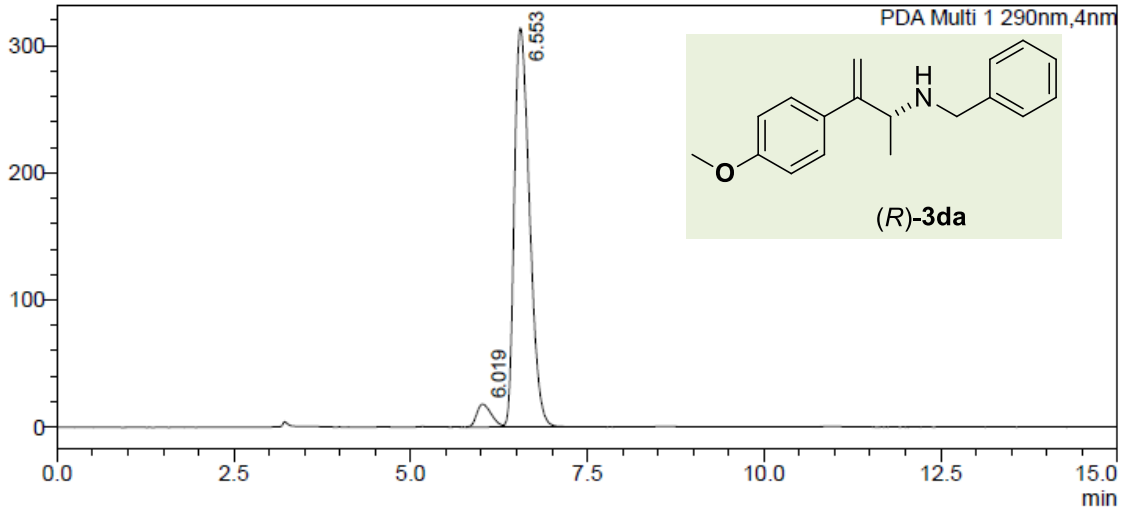
<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area%
1	6.184	49.908
2	6.722	50.092
Total		100.000

<Chromatogram>

mAU

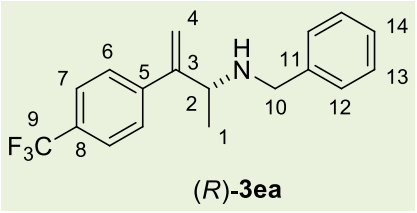


<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area%
1	6.019	5.266
2	6.553	94.734
Total		100.000

(*R*)-*N*-Benzyl-3-(4-(trifluoromethyl)phenyl)but-3-en-2-amine 3ea



(*R*)-**3ea**

Synthesized at room temperature for 72 h following the general procedure using 1-(buta-1,3-dien-2-yl)-4-(trifluoromethyl)benzene **1e** (50.0 mg, 0.25 mmol, 1.0 equiv), benzylamine **2a** (110 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1e**: >95%, conversion of **3ea**: 83%, *r.r.* = 6:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product as a pale yellow oil (59.0 mg, 77% yield, 95% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.57 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-*7*), 7.51 (d, $^3J_{HH}$ = 8.2 Hz, 2H, H-*6*), 7.35 – 7.28 (m, 4H, H-*12* + H-*13*), 7.27 – 7.22 (m, 1H, H-*14*), 5.41 (t, $^2J_{HH}$ = 1.1 Hz, 2H, H-*4*), 5.35 (d, $^2J_{HH}$ = 1.1 Hz, 1H, H-*4*), 3.87 (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-*10*), 3.81 – 3.70 (m, 2H, H-*10* + H-*2*), 1.44 (s, 1H, N-*H*), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 151.3 (*C-3*), 145.1 (*C-5*), 140.8 (*C-11*), 129.7 ($^2J_{CF}$, q, *J* = 32 Hz, *C-8*), 128.6 (*C*H-*Ar*), 128.3 (*C*H-*Ar*), 127.7 (*C* H-*6*), 127.1 (*C*H-*14*), 125.2 ($^3J_{CF}$, *J* = 4 Hz, *C*H-*7*), 124.5 (q, $^1J_{CF}$ = 272 Hz, *C-9*), 57.2 (*C*H-*2*), 51.6 (*C*H_2-*10*), 21.7 (*C*H_3-*1*).

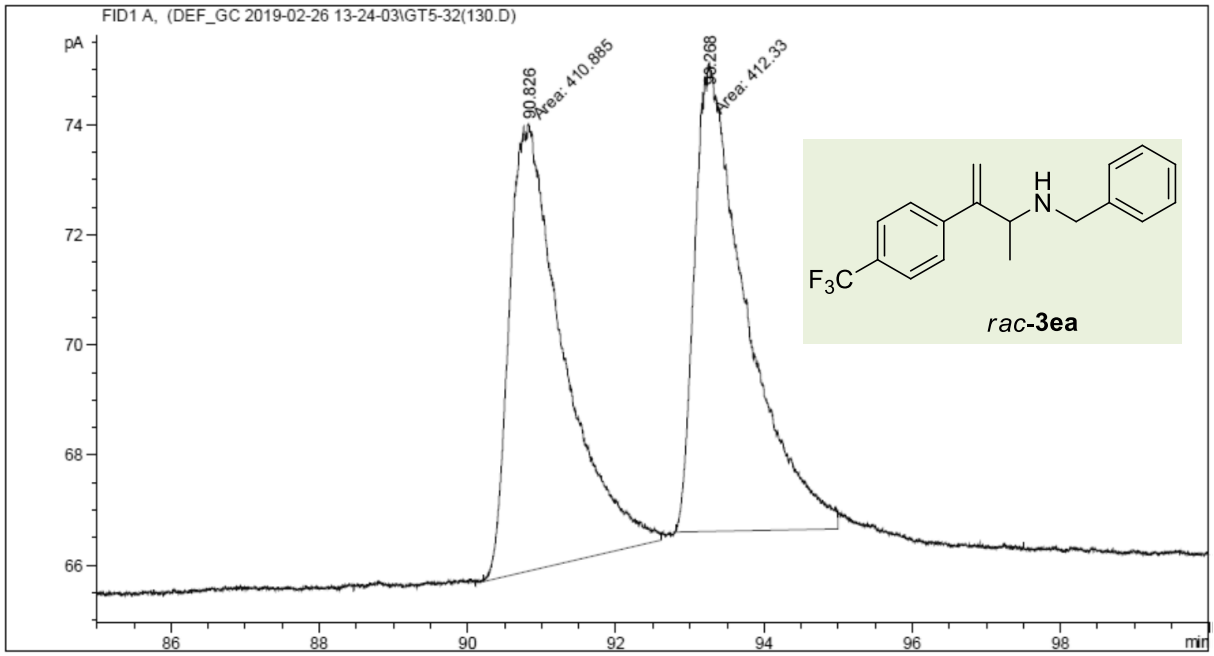
^{19}F{^{1}H} NMR (280 MHz, $CDCl_3$) δ (ppm) = -62.49.

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{18}H_{19}F_3N^+$: 306.1465; found: 306.1461.

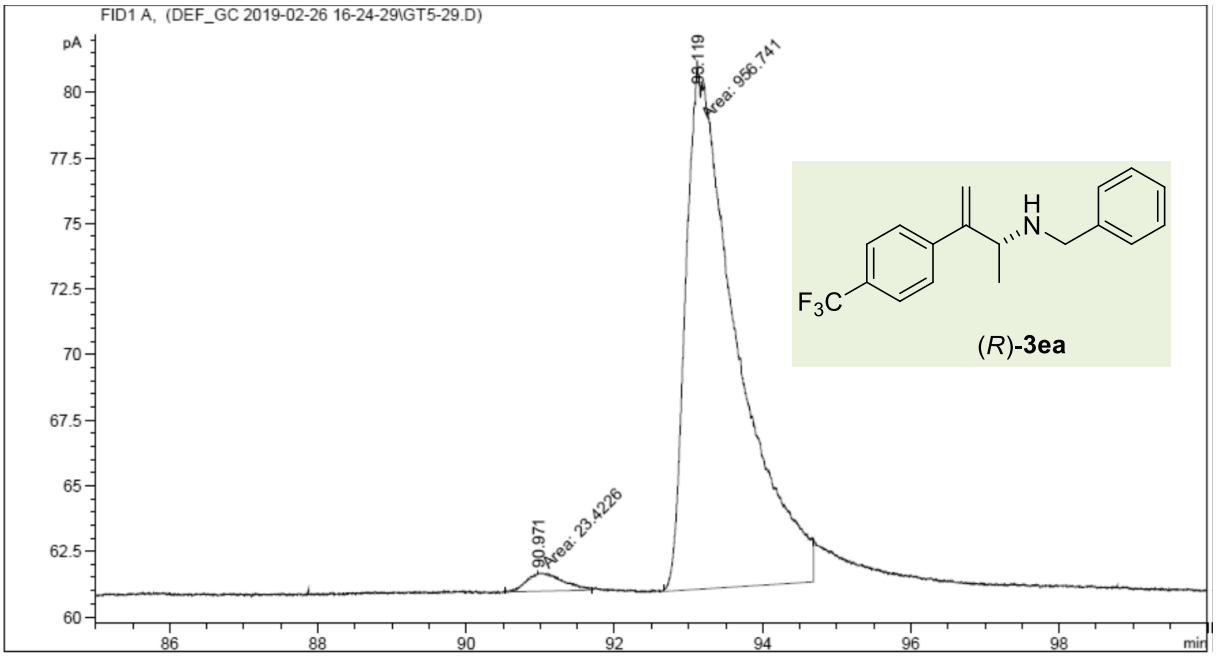
IR (neat) ν (cm^{-1}): 3030, 2970, 1616, 1495, 1453, 1404, 1372, 1322, 1163, 1118, 1065, 1015, 915, 846, 735, 698.

Chiral GC: 95% *ee*, chiral stationary column: Hydrodex β–3P, mobile phase: H_2 (45 cm/s), temperature gradient: 130 °C isothermal, t_R (minor) = 90.9 min, t_R (major) = 93.1 min.

[α]$^{20}_D$ = +6.6 (*c* 1.34, CH_2Cl_2).

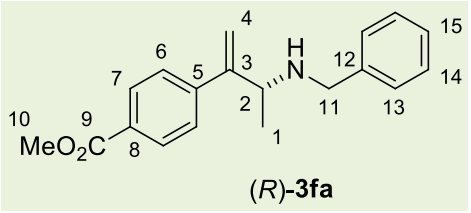


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	90.826	MM	0.8414	410.88467	8.13883	49.91219
2	93.268	MM	0.8040	412.33047	8.54738	50.08781



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	90.971	MM	0.5384	23.42261	7.25067e-1	2.38966
2	93.119	MM	0.7920	956.74139	20.13446	97.61034

(*R*)-*N*-Benzyl-3-(3-methoxyphenyl)but-3-en-2-amine 3fa



(*R*)-**3fa**

Synthesized at room temperature for 72 h following the general procedure using methyl 4-(buta-1,3-dien-2-yl)benzoate **1f** (47.0 mg, 0.25 mmol, 1.0 equiv), benzylamine **2a** (110 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1f**: >95%, conversion of **3fa**: 85%, *r.r.* = 5.4:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product as a pale yellow oil (60.0 mg, 81% yield, 92% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.01 – 7.95 (m, 2H, H-*7*), 7.46 (d, $^3J_{HH}$ = 8.4 Hz, 2H, H-*6*), 7.36 – 7.29 (m, 4H, H-*13* + H-*14*), 7.28 – 7.22 (m, 1H, H-*15*), 5.42 (s, 1H, H-*4*), 5.39 (s, 1H, H-*4*), 3.92 (s, 3H, H-*10*), 3.87 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*11*), 3.79 – 3.69 (m, 2H, H-*2*+H-*11*), 1.51 (s, 1H, N-*H*), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 167.1 (*C-9*), 151.2 (*C-3*), 146.0 (*C-5*), 140.6 (*C-12*), 129.7 (*C*H-*7*), 129.2 (C-*8*), 128.6 (*C*H-*Ar*), 128.3 (*C*H-*Ar*), 127.17 (*C*H-*Ar*), 127.15 (*C*H-*Ar*), 114.6 (CH_2-*4*), 56.7 (CH-*2*), 52.2 (CH_2-*11*), 51.4 (CH_3-*10*), 21.7 (CH_3-*1*).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{19}H_{21}NO_2^+$: 296.1645; found: 296.1646.

IR (neat) ν (cm^{-1}): 3028, 2953, 1718, 1601, 1435, 1274, 1183, 1107, 1017, 967, 912, 862, 782, 697.

HPLC: 92% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 95/5, 1.0 mL/min, 290 nm, 30 °C, t_R (major) = 7.8 min, t_R (minor) = 9.9 min.

$[\alpha]^{20}_D$ = +3.5 (*c* 0.96, CH_2Cl_2).

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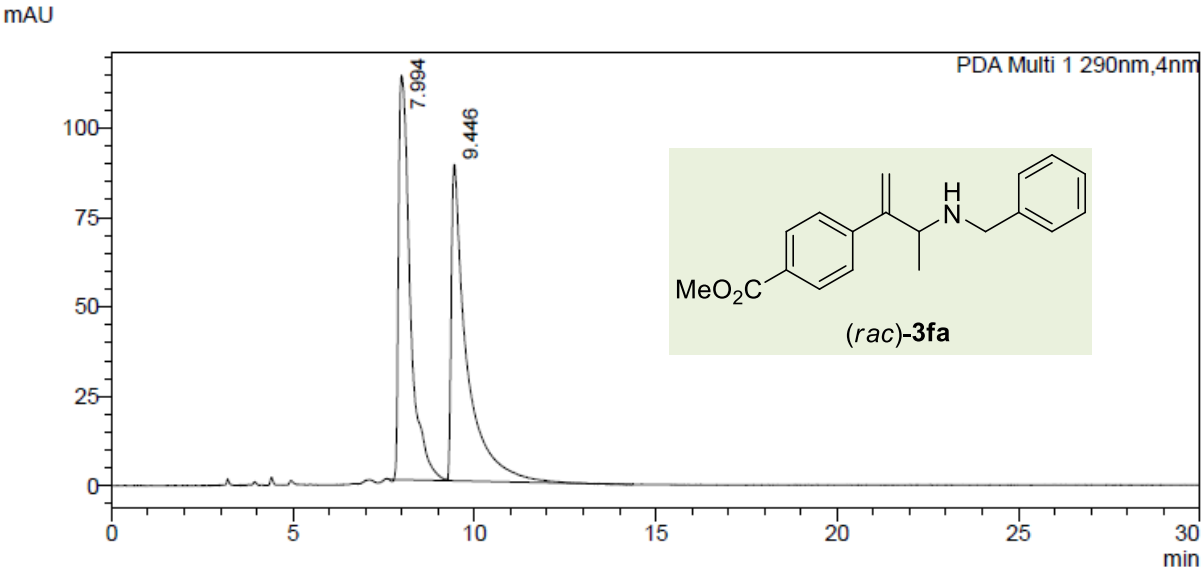

<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area%
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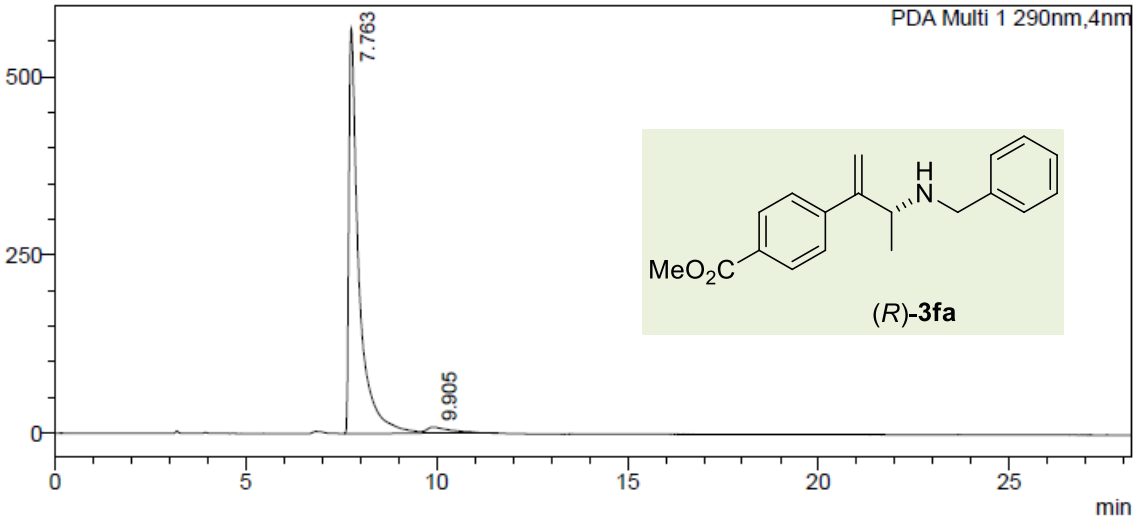
2	9.446	50.729
Total		100.000

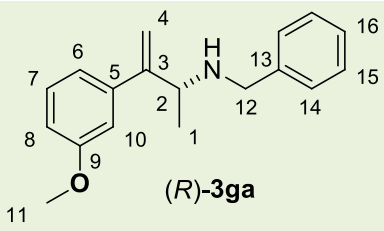


<Peak Table>

PDA Ch1 290nm

Peak#	Ret. Time	Area%
1	7.763	96.180
2	9.905	3.820
Total		100.000

(*R*)-*N*-Benzyl-3-(3-methoxyphenyl)but-3-en-2-amine 3ga



(*R*)-**3ga**

Synthesized at room temperature for 72 h following the general procedure using 1-(buta-1,3-dien-2-yl)-3-methoxybenzene **1g** (64.0 mg, 0.40 mmol, 1.0 equiv), benzylamine **2a** (175 µL, 1.60 mmol, 4.0 equiv), $Ni(cod)_2$ (5.5 mg, 0.020 mmol, 5 mol%), (*R,R*)-BenzP* (6.8 mg, 0.024 mmol, 6 mol%), 2,2,2-trifluoroethanol (29 µL, 0.40 mmol, 1.0 equiv) and mesitylene (0.80 mL, 0.5 M). Consumption of **1g** >95%, conversion of **3ga**: 88%, *r.r.* = 7:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 3:2) led to the desired product as a pale yellow oil (88.0 mg, 82% yield, 94% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.34 – 7.30 (m, 4H, H-*14* + H-*15*), 7.26 – 7.21 (m, 2H, H-7 + H-*16*), 6.98 – 6.95 (m, 1H, H-*6*), 6.95 – 6.93 (m, 1H, H-*10*), 6.84 (ddd, $^3J_{HH}$ = 8.1, $^4J_{HH}$ = 2.5, 0.8 Hz, 1H, H-*8*), 5.32 (s, 2H, H-*4*), 3.87 (d, $^2J_{HH}$ = 13.0 Hz, 1H, H-*12*), 3.80 (s, 3H, H-*11*), 3.76 (d, $^2J_{HH}$ = 13.0 Hz, 1H, H-*12*), 3.72 (q, $^3J_{HH}$ = 6.6 Hz, 1H, H-*2*), 1.54 (s, 1H, N-*H*), 1.23 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 159.6 (*C-9*), 151.9 (*C-3*), 142.9 (*C-5*), 140.8 (*C-13*), 129.3 (*C*H-*7*), 128.5 (*C*H-*Ar*), 128.3 (*C*H-*Ar*), 127.0 (*C*H-*16*), 119.7 (CH_2-*4*), 113.04 (*C*H-*Ar*), 112.97 (*C*H-*Ar*), 112.8 (*C*H-*Ar*), 56.8 (*C*H-*2*), 55.4 (CH_3-*11*), 51.4 (CH_2-*12*), 21.7 (CH_3-*1*).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{18}H_{22}NO^+$: 268.1696; found: 268.1731.

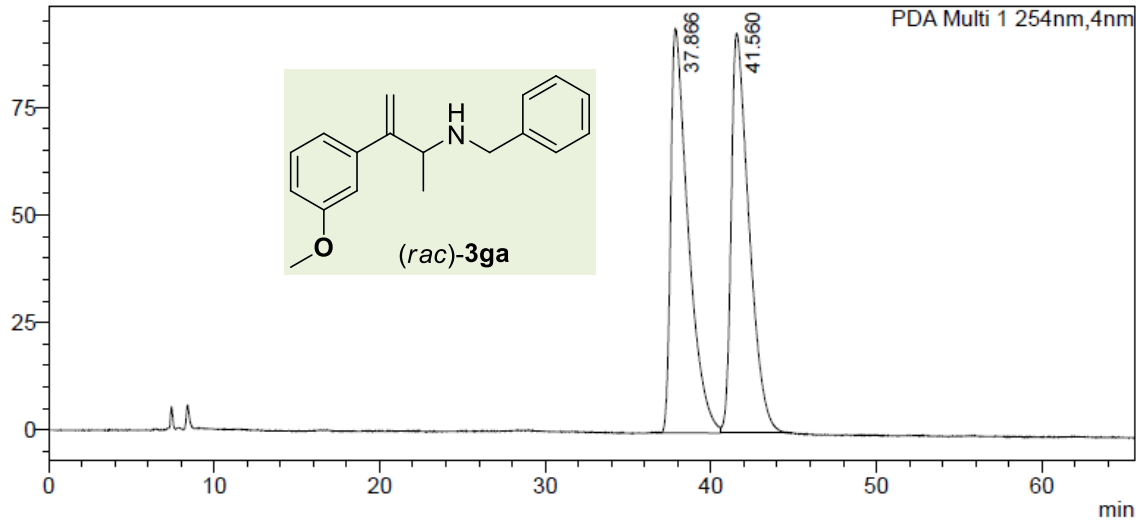
IR (neat) ν (cm^{-1}):3064, 2962, 2833, 1597, 1575, 1487, 1453, 1428, 1369, 1315, 1285, 1221, 1145, 1045, 907, 784, 730, 696.

HPLC: 94% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 99.5/0.05, 0.50 mL/min, 254 nm, 30 °C, t_R (major) = 37.0 min, t_R (minor) = 42.1 min.

[α]$^{20}_D$ = +2.1 (*c* 0.84, $CHCl_3$).

<Chromatogram>

mAU

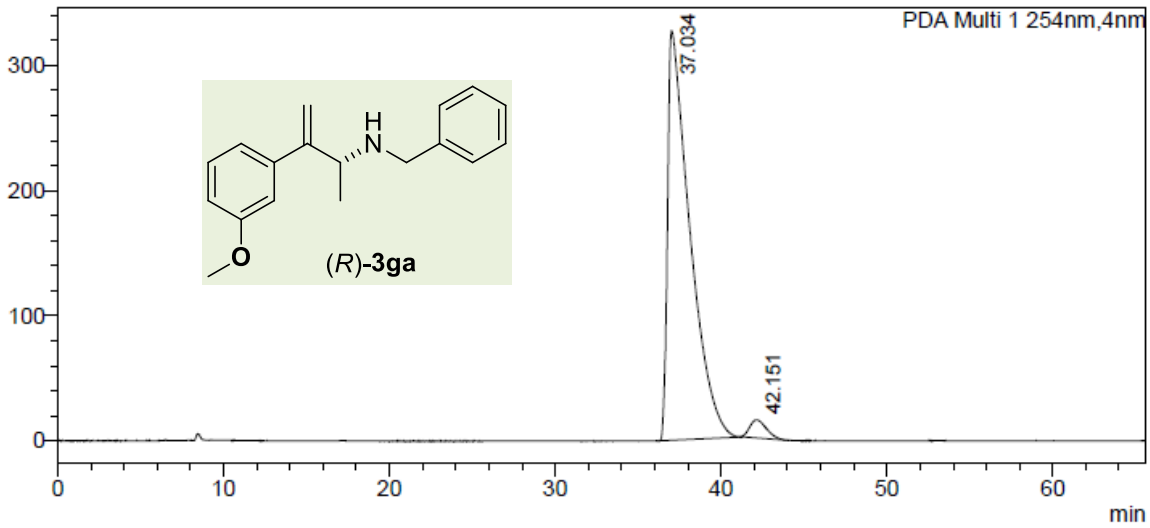


PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	37.866	49.795
2	41.560	50.205
Total		100.000

<Chromatogram>

mAU

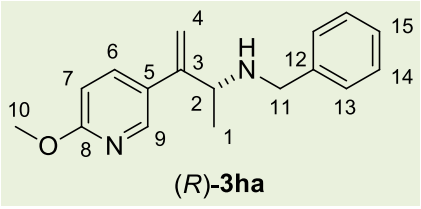


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	37.034	96.797
2	42.151	3.203
Total		100.000

(*R*)-*N*-Benzyl-3-(6-methoxypyridin-3-yl)but-3-en-2-amine 3ha



(*R*)-**3ha**

Synthesized at room temperature for 72 h following the general procedure using 5-(buta-1,3-dien-2-yl)-2-methoxypyridine **1h** (65.0 mg, 0.40 mmol, 1.0 equiv), benzylamine **2a** (175 µL, 1.60 mmol, 4.0 equiv), $Ni(cod)_2$ (5.5 mg, 0.020 mmol, 5 mol%), (*R,R*)-BenzP* (6.8 mg, 0.024 mmol, 6 mol%), 2,2,2-trifluoroethanol (29 µL, 0.40 mmol, 1.0 equiv) and mesitylene (0.80 mL, 0.5 M). Consumption of **1h**: >95%, conversion of **3ha**: 80%, *r.r.* = 5:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 3:2) led to the desired product as a clear colorless oil (84.0 mg, 78% yield, 95% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 8.22 (d, $^4J_{HH}$ = 2.1 Hz, 1H, H-*9*), 7.65 (dd, $^3J_{HH}$ = 8.7, $^4J_{HH}$ = 2.5 Hz, 1H, H-*6*), 7.36 – 7.28 (m, 4H, H-*13* + H-*14*), 7.29 – 7.22 (m, 1H, H-*15*), 6.70 (dd, $^3J_{HH}$ = 8.7, $^5J_{HH}$ = 0.6 Hz, 1H, H-*7*), 5.30 (s, 1H, H-*4*), 5.26 (d, $^2J_{HH}$ = 1.2 Hz, 1H, H-*4*), 3.94 (s, 3H, H-*10*), 3.86 (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-*11*), 3.74 (d, $^2J_{HH}$ = 13.2 Hz, 1H, H-*11*), 3.67 (q, $^3J_{HH}$ = 6.3 Hz, 1H, H-*2*), 1.48 (s, 1H, N-*H*), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 163.7 (*C-8*), 148.5 (*C-3*), 145.2 (*C*H-*9*), 140.7 (*C-12*), 137.7 (*C*H-*6*), 129.8 (*C-5*), 128.6 (*C*H-*Ar*), 128.3 (*C*H-*Ar*), 127.1 (*C*H-*15*), 113.4 (CH_2-*4*), 110.3 (*C*H-*7*), 57.2 (*C*H-*2*), 53.6 (CH_3-*10*), 51.5 (CH_2-*11*), 21.6 (CH_3-*1*).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{17}H_{20}N_2O^+$: 269.1649; found: 269.1689.

IR (neat) ν (cm^{-1}): 3027, 2971, 624, 1599, 1490, 1455, 1366, 1282, 1248, 1126, 1024, 907, 832, 734, 697.

HPLC: 95% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 99.5/0.05, 0.50 mL/min, 254 nm, 30 °C, t_R (major) = 40.8 min, t_R (minor) = 44.8 min.

[α]$^{20}_D$ = +16.7 (*c* 1.01, $CHCl_3$).

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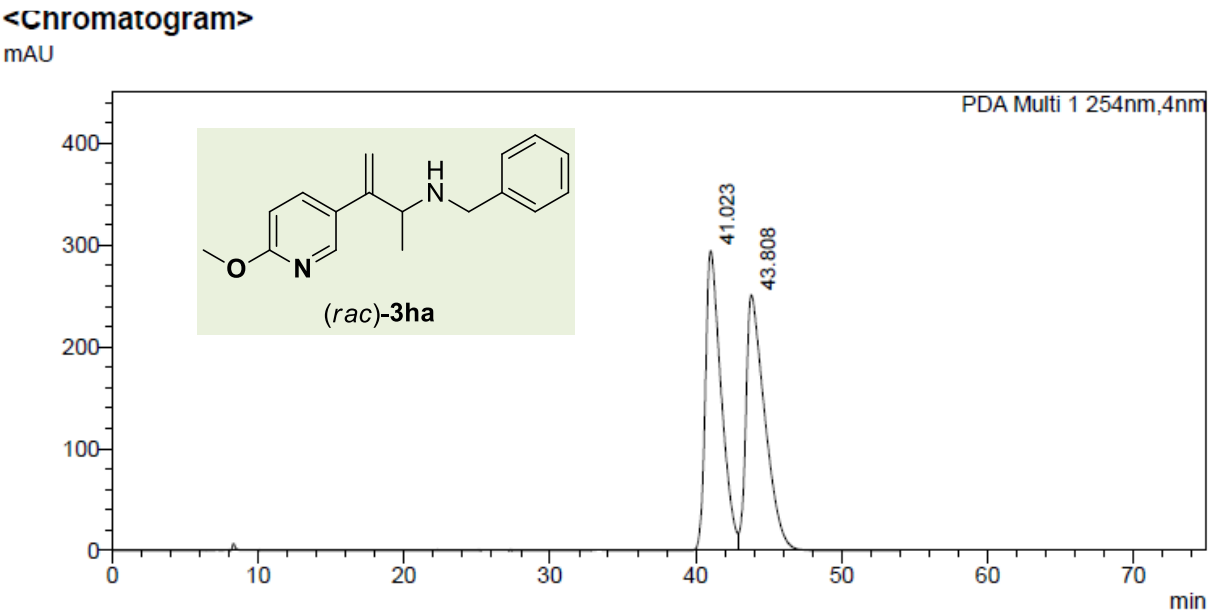

<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	41.023	49.349
2	43.808	50.651
Total		100.000

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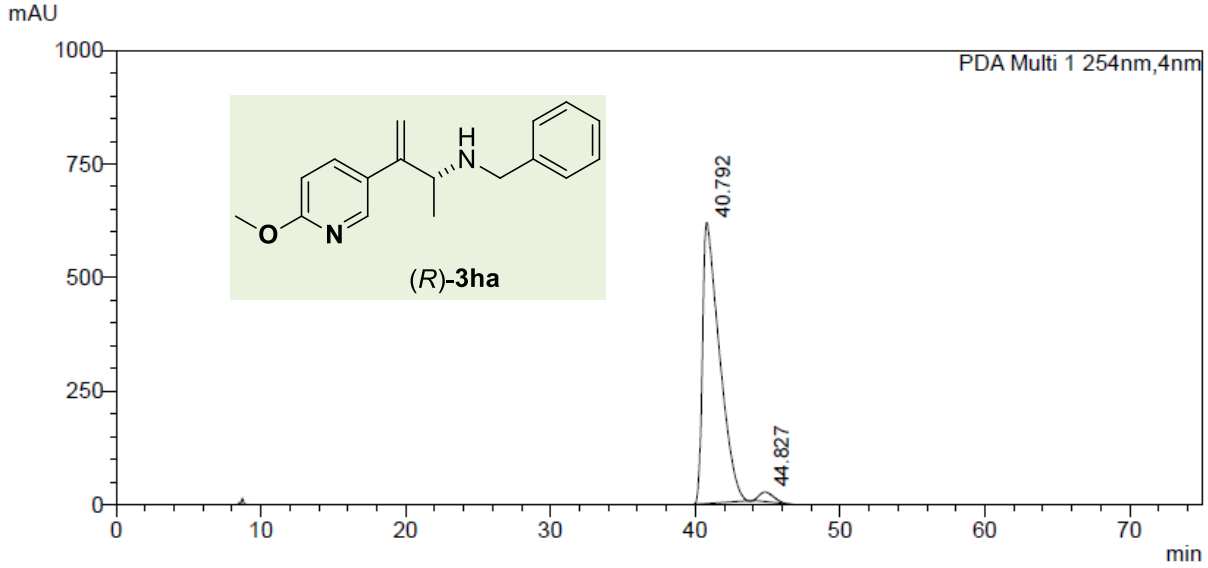
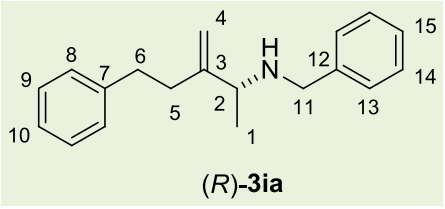


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	40.792	97.244
2	44.827	2.756
Total		100.000

(*R*)-*N*-Benzyl-3-methylene-5-phenylpentan-2-amine 3ia



(*R*)-**3ia**

Synthesized at room temperature for 72 h following the general procedure using (3-methylenepent-4-en-1-yl)benzene **1i** (40.0 mg, 0.25 mmol, 1.0 equiv), benzylamine **2a** (110 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), $Ph_2P(O)OH$ (55.0 mg, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1i**: 93%, conversion of **3ia**: 48%, *r.r.* = 1.1:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product as a pale yellow oil (30.0 mg, 45% yield, 15% *ee*).

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.29 – 7.13 (m, 10H, H-*Ar*), 5.01 (s, 1H, H-*4*), 4.90 (q, $^2J_{HH}$ = 1.4 Hz, 1H, H-*4*), 3.67 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*11*), 3.56 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*11*), 3.23 (q, $^3J_{HH}$ = 6.6 Hz, 1H, H-*2*), 2.85 – 2.67 (m, 2H, H-*5*), 2.43 – 2.21 (m, 2H, H-*6*), 1.26 (s, 1H, N-*H*), 1.14 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ (ppm) = 151.7 (*C-3*), 142.5 (*C-7*), 141.0 (*C-12*), 128.52 (*C*H-*Ar*), 128.48 (*C*H-*Ar*), 128.46 (*C*H-*Ar*), 128.3 (*C*H-*Ar*), 126.9 (*C*H-*10* or *C*H-*15*), 125.9 (*C*H-*10* or *C*H-*15*), 110.0 (CH_2-*4*), 58.8 (*C*H-*2*), 51.6 (CH_2-*11*), 34.7 (CH_2-*6*), 33.0 (CH_2-*5*), 21.4 (CH_3-*1*).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{19}H_{24}N^+$: 266.1914; found: 266.1937.

IR (neat) ν (cm^{-1}): 3027, 2925, 1643, 1604, 1495, 1453, 1369, 1317, 1202, 1120, 1029, 897, 738, 695.

HPLC: 15% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 13.2 min, t_R (minor) = 14.7 min.

[α]$^{20}_D$ = +1.8 (*c* 0.355, CH_2Cl_2).

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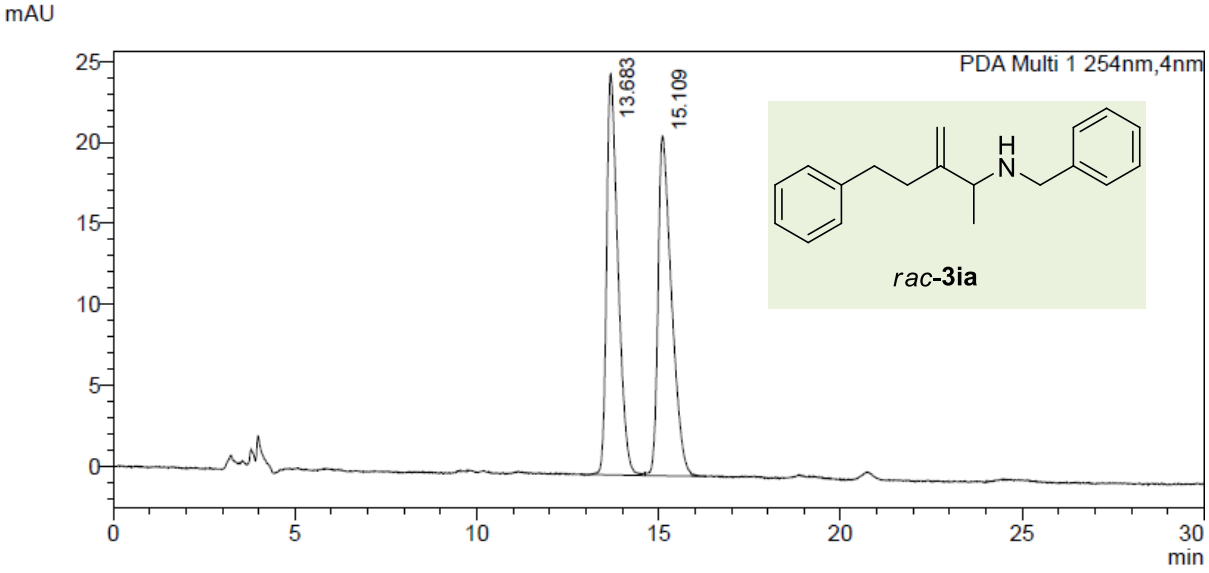
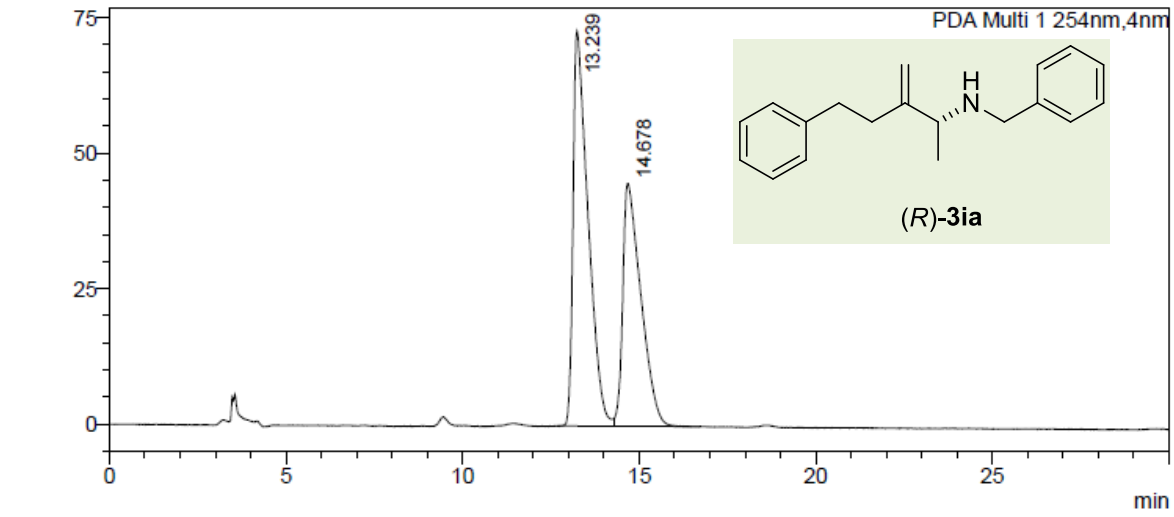


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	13.683	49.778
2	15.109	50.222
Total		100.000

<Chromatogram>



PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	13.239	57.325
2	14.678	42.675
Total		100.000

4.2 Scope in amines

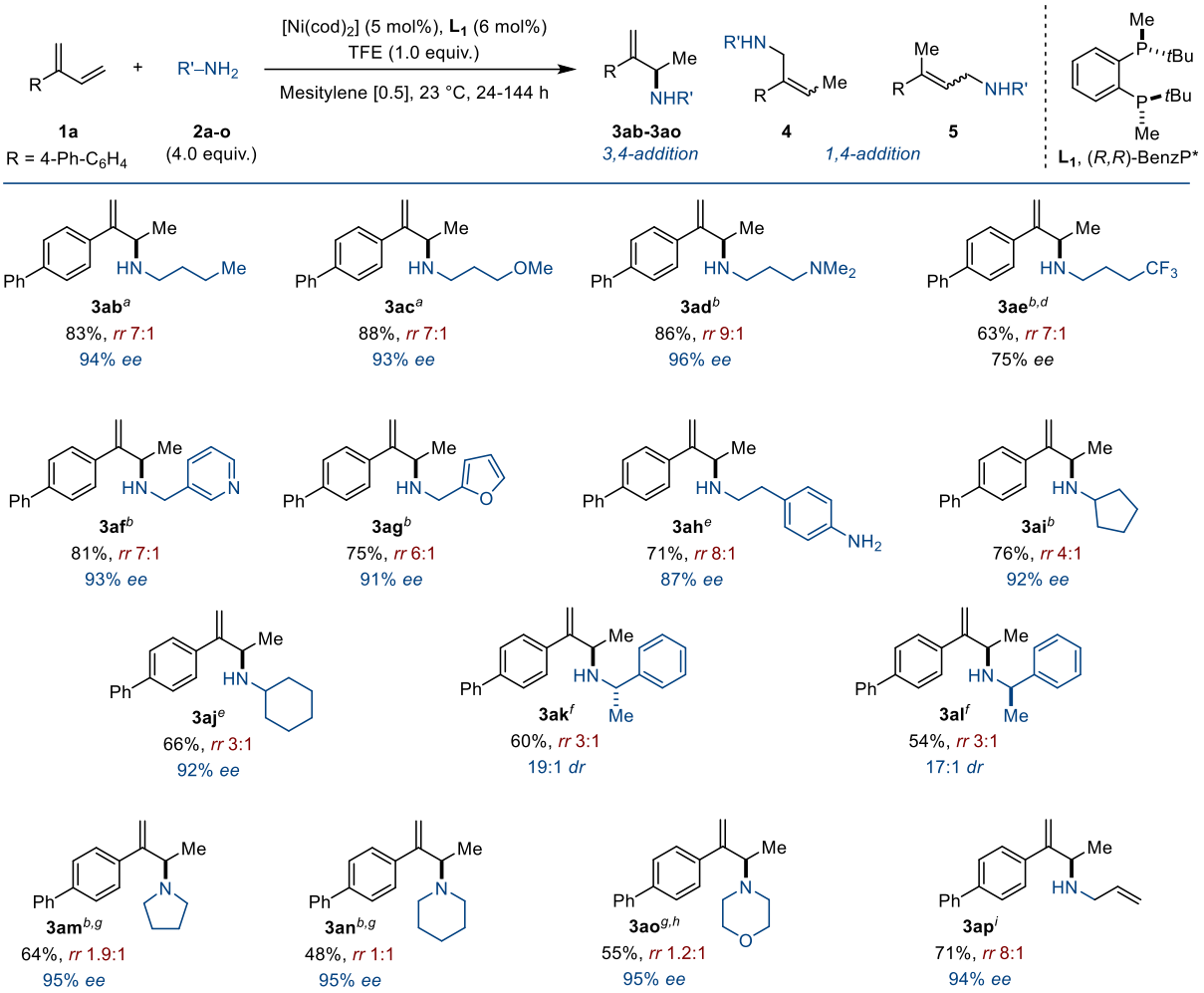
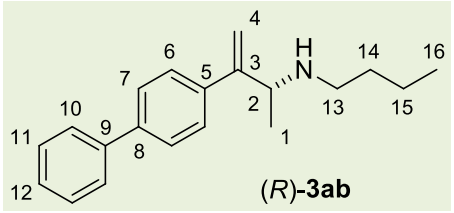


Figure S2. Scope of the Ni-catalyzed hydroamination of 2-substituted 1,3-dienes - Variation of the amine component. 0.25-0.40 mmol scale. Yields of 3,4-addition product after purification. Regioselectivity expressed as the ratio between 3,4- and 1,4-addition products as determined by ^{1}H NMR using an internal standard (**3**:[**4**+**5**]). Enantiomeric excess determined by GC or HPLC equipped with chiral columns. [a] 48 h. [b] 72 h. [c] 120 h. [d] 40 °C. [e] 96 h. [f] 144 h. [g] 0.2 equiv. $Ph_2P(O)OH$ instead of TFE. [h] 24 h. [i] 20 h

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-butylbut-3-en-2-amine 3ab



Synthesized at room temperature for 48 h in 0.40 mmol scale following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (82.5 mg, 0.40 mmol, 1.0 equiv), *n*-butylamine **2b** (158 µL, 1.60 mmol, 4.0 equiv), $Ni(cod)_2$ (5.5 mg, 0.020 mmol, 5 mol%), (*R,R*)-BenzP* (6.8 mg, 0.024 mmol, 6 mol%), 2,2,2-trifluoroethanol (30 µL, 0.40 mmol, 1.0 equiv) and mesitylene (0.80 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3ab**: 87%, *r.r.* = 7:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 3:1) led to the desired product as a colorless viscous oil (93.0 mg, 83% yield, 94% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.54 (m, 4H, *H*-10+*H*-7), 7.51 – 7.40 (m, 4H, *H*-6+*H*-11), 7.39 – 7.30 (m, 1H, *H*-12), 5.33 (s, 1H, *H*-4), 5.29 (s, 1H, *H*-4), 3.74 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 2.77 – 2.53 (m, 2H, *H*-13), 1.54 – 1.46 (m, 2H, *H*-14), 1.41 – 1.22 (m, 3H, *H*-15+N*H*), 1.25 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1), 0.91 (t, $^3J_{HH}$ = 7.3 Hz, 3H, *H*-16).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.9 (*C*-3), 140.9 (*C*-9), 140.4 (*C*-5), 140.3 (*C*-8), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.13 (*C*H-10), 127.05 (*C*H-7), 112.5 (CH_2-4), 57.5 (*C*H-2), 47.4 (CH_2-13), 32.6 (CH_2-14), 21.8 (CH_3-1), 20.7 (CH_2-15), 14.2 (CH_3-16).

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{20}H_{26}N^+$: 280.2060; found: 280.2067.

IR (neat) ν (cm^{-1}): 3030, 2958, 2926, 2870, 1625, 1601, 1486, 1448, 1370, 1137, 1077, 1007, 907, 842, 769, 739, 695.

HPLC: 94% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 6.2 min, t_R (major) = 7.5 min.

$[\alpha]^{20}_D$ = −3.8 (*c* 0.1, $CHCl_3$).

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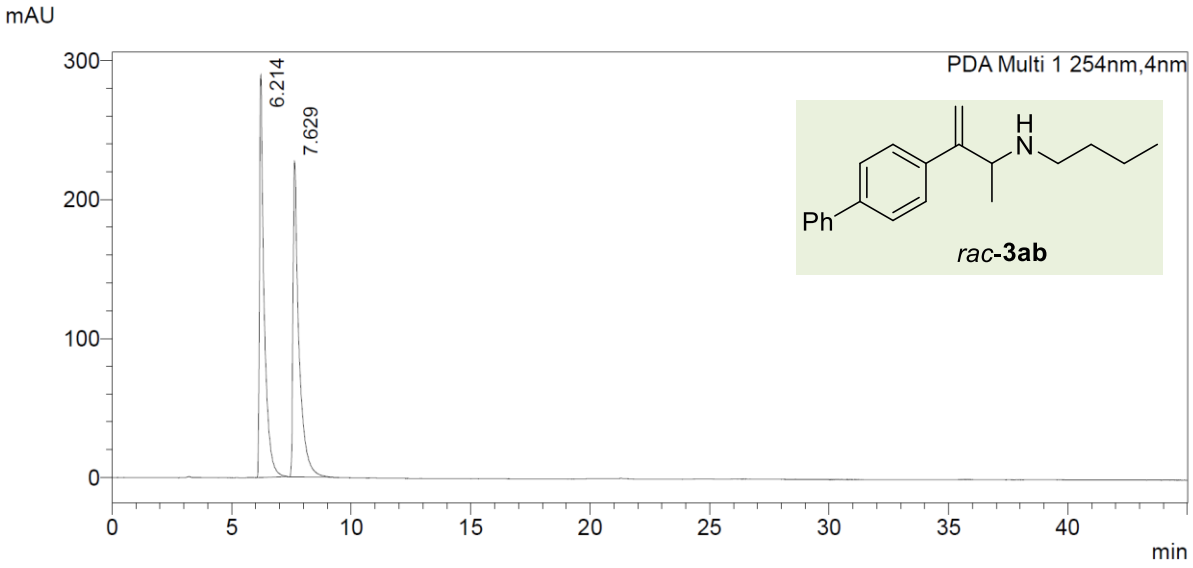

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Total		100.000

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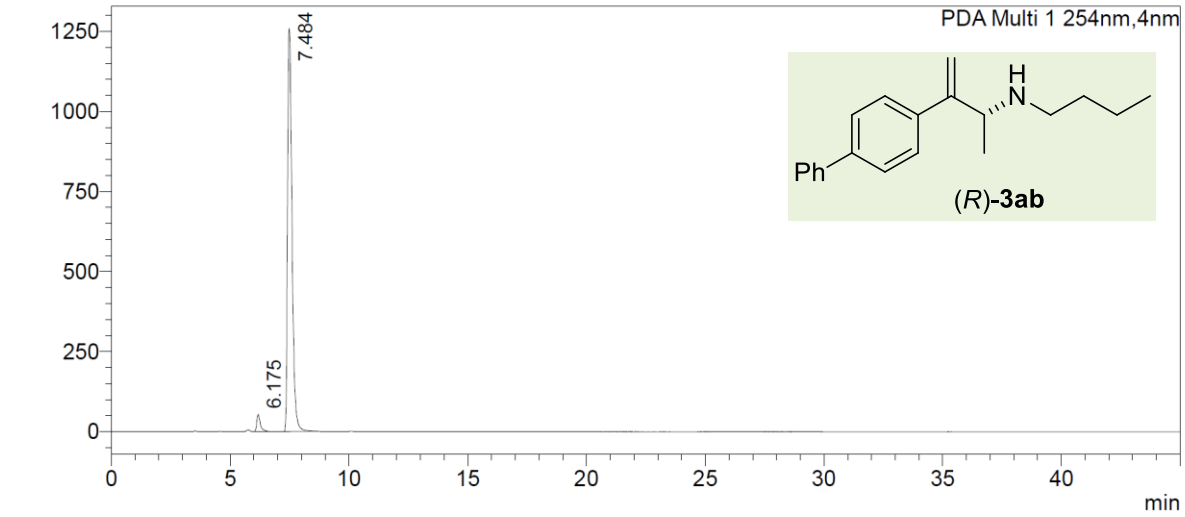
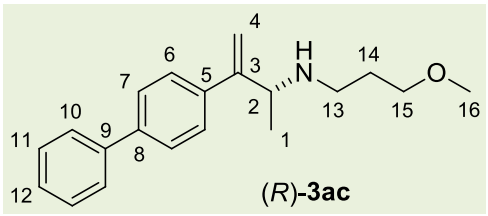


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.175	3.231
2	7.484	96.769
Total		100.000

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-(3-methoxypropyl)but-3-en-2-amine 3ac



(*R*)-**3ac**

Synthesized at room temperature for 72 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), 3-methoxypropylamine **2c** (102 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3ac**: 87%, *r.r.* = 7:1. Purification by flash chromatography over silica gel (CH_2Cl_2:MeOH = 20:1) led to the desired product as a yellow viscous oil (65.3 mg, 88% yield, 93% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.54 (m, 4H, *H*-7+*H*-10), 7.50 – 7.41 (m, 4H, *H*-6+*H*-11), 7.38 – 7.31 (m, 1H, *H*-12), 5.35 (d, $^2J_{HH}$ = 1.0 Hz, 1H, *H*-4), 5.30 (s, 1H, *H*-4), 3.78 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.45 (t, $^3J_{HH}$ = 6.2 Hz, 2H, *H*-15), 3.29 (s, 3H, *H*-16), 2.87 – 2.69 (m, 2H, *H*-13), 2.42 (br, 1H, N*H*), 1.81 (p, $^3J_{HH}$ = 6.5 Hz, 2H, *H*-14), 1.28 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.3 (*C*-3), 140.9 (*C*-8), 140.4 (*C*-9), 140.2 (*C*-5), 128.9 (*C*H-11), 127.5 (*C*H-7), 127.4 (*C*H-12), 127.12 (*C*H-6), 127.10 (*C*H-10), 113.0 (CH_2-4), 71.6 (CH_2-15), 58.8 (CH_3-16), 57.5 (*C*H-2), 44.9 (CH_2-13), 30.1 (CH_2-14), 21.4 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{20}H_{26}NO^+$: 296.2009; found: 296.2069.

IR (neat) ν (cm^{-1}): 3030, 2925, 2867, 1626, 1598, 1486, 1448, 1387, 1191, 1116, 1077, 1038, 1006, 907, 844, 771, 741, 697.

HPLC: 93% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 95/5, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 10.7 min, t_R (major) = 13.5 min.

[α]$^{20}_D$ = +9.4 (*c* 1.0, $CHCl_3$).

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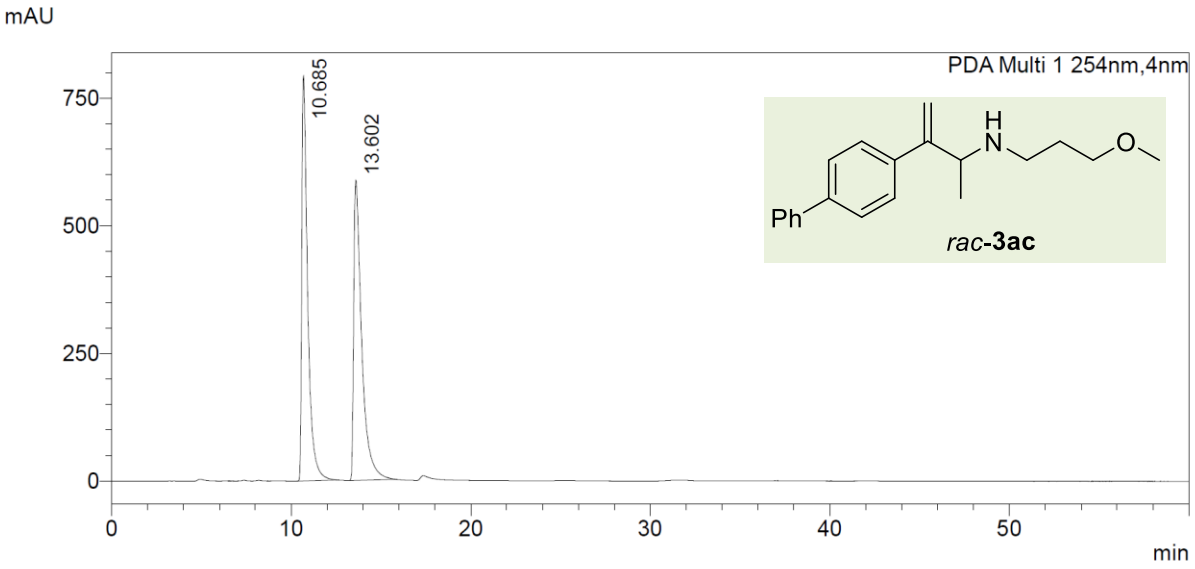

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Total		100.000

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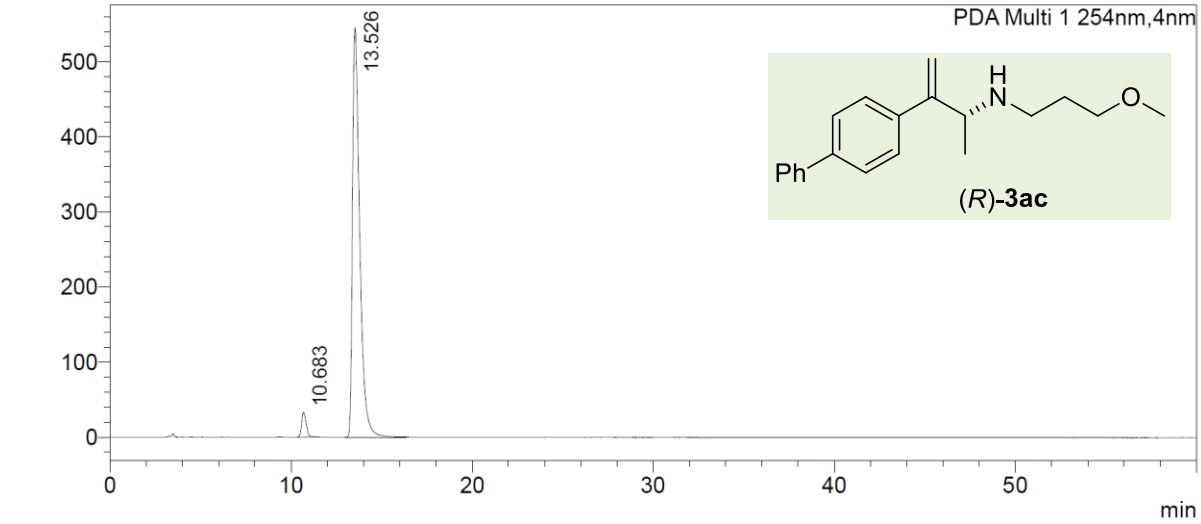
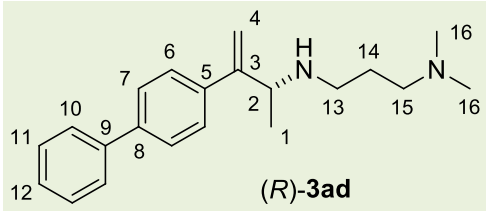


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	10.683	3.654
2	13.526	96.346
Total		100.000

(*R*)-*N*^{1}-(3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)-*N*^{3},*N*^{3}-dimethylpropane-1,3-diamine 3ad



(*R*)-**3ad**

Synthesized at room temperature for 72 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), 3-(dimethylamino)-1-propylamine **2d** (126 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3ad**: 88%, *r.r.* = 9:1. Purification by flash chromatography over silica gel (CH_2Cl_2:MeOH = 3:1, with 1% Et_3N) led to the desired product as a yellow viscous oil (66.2 mg, 86% yield, 96% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.63 – 7.54 (m, 4H, *H*-7+*H*-10), 7.50 – 7.41 (m, 4H, *H*-6+*H*-11), 7.37 – 7.31 (m, 1H, *H*-12), 5.32 (d, $^2J_{HH}$ = 1.1 Hz, 1H, *H*-4), 5.27 (s, 1H, *H*-4) 3.73 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 2.78 – 2.61 (m, 2H, *H*-13), 2.38 – 2.26 (m, 2H, *H*-15), 2.21 (s, 6H, *H*-16), 1.68 (p, $^3J_{HH}$ = 7.1 Hz, 2H, *H*-14), 1.26 (s, 1H, N*H*), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, 3H, H-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.7 (*C*-3), 140.9 (*C*-9), 140.34 (*C*-8), 140.30 (*C*-5), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.12 (*C*H-10), 127.05 (*C*H-7), 112.6 (CH_2-4), 58.3 (CH_2-15), 57.5 (*C*H-2), 46.1 (CH_2-13), 45.7 (CH_3-16), 28.4 (CH_2-14), 21.7 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{21}H_{29}N_2^+$: 309.2326; found: 296.2354.

IR (neat) ν (cm^{-1}): 3345, 3029, 2941, 2764, 1629, 1589, 1486, 1462, 1379, 1265, 1150, 1081, 1040, 1006, 909, 842, 769, 740, 697.

HPLC: 96% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, t_R (major) = 11.1 min, t_R (minor) = 14.7 min. (After protecting the secondary amine with Boc (*tert*-butyloxycarbonyl) group, the enantiomeric excess of protected product can be determined by chiral AD-H column)

[α]$^{20}_D$ = −2.7 (*c* 0.2, $CHCl_3$).

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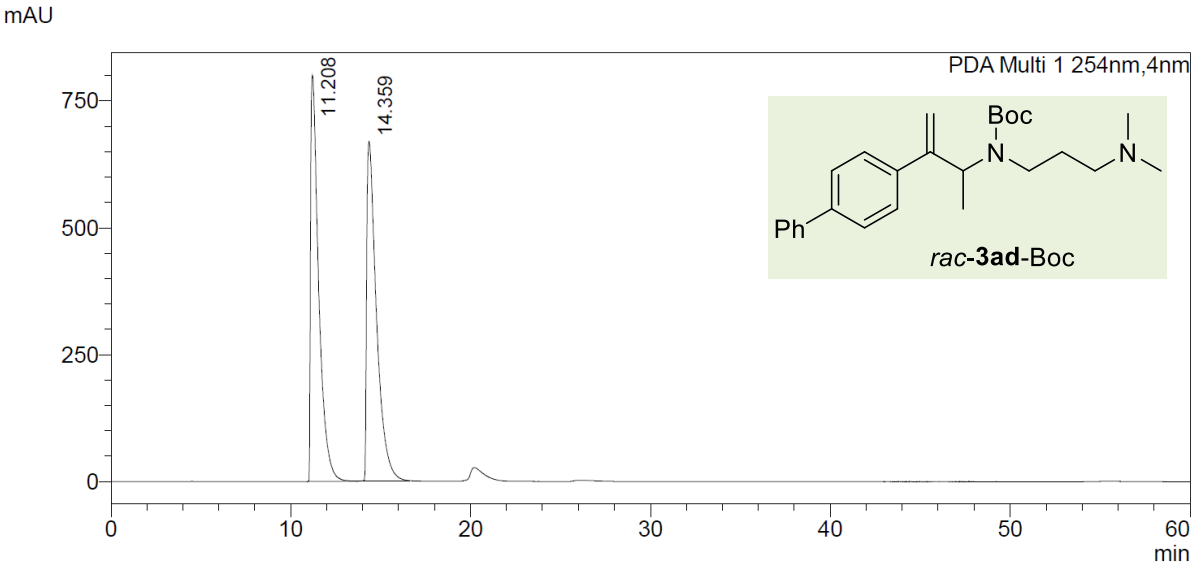

<Peak Table>

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Total		100.000

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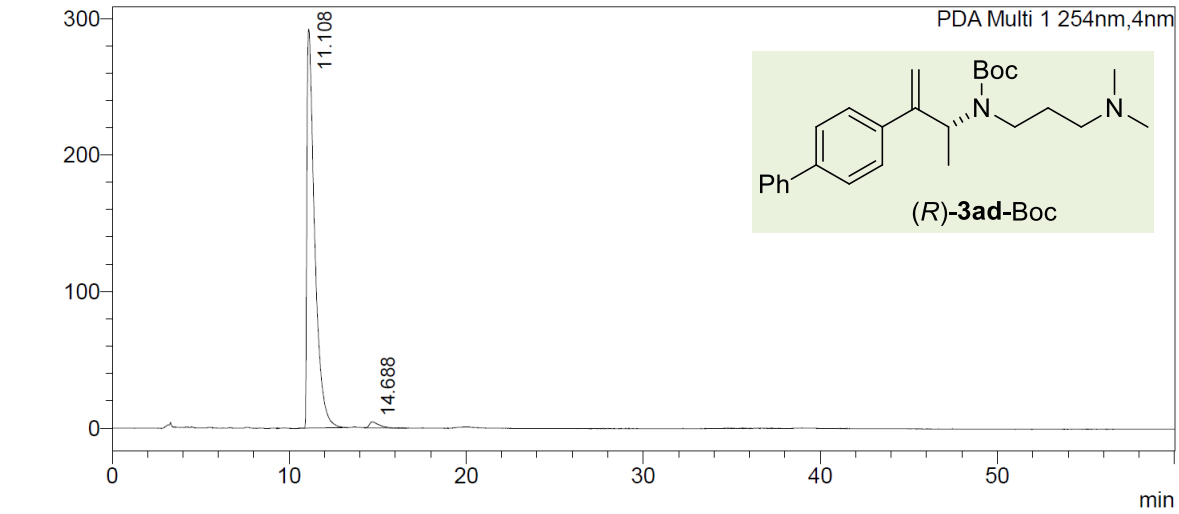
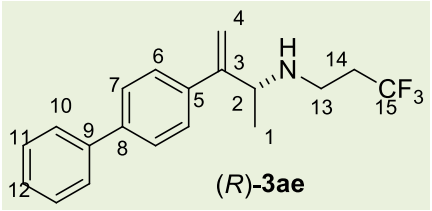


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	11.108	98.241
2	14.688	1.759
Total		100.000

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-(3,3,3-trifluoropropyl)but-3-en-2-amine 3ae



Synthesized at 40 °C for 72 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (52.0 mg, 0.25 mmol, 1.0 equiv), 3,3,3-trifluoropropan-1-amine **2e** (113.0 mg, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%),2,2,2-trifluoroethanol (18 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >95%, conversion of **3ae**: 65%, *r.r.* = 7:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 6:1) led to the desired product as a pale yellow oil (50.0 mg, 63% yield, 75% *ee*).

^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.58 (m, 2H, H-*10*), 7.61 – 7.54 (m, 2H, H-*7*), 7.50 – 7.41 (m, 4H, H-*6* + H-*11*), 7.35 (tt, $^3J_{HH}$ = 6.9, $^4J_{HH}$ = 1.4 Hz, 1H, H-*12*), 5.36 (s, 1H, H-*4*), 5.30 (s, 1H, H-*4*), 3.75 (q, $^3J_{HH}$ = 6.5 Hz, 1H, H-*2*), 2.97 (dt, $^2J_{HH}$ = 12.2, $^3J_{HH}$ = 7.4 Hz, 1H, H-*13*), 2.88 (dt, $^2J_{HH}$ = 12.2, $^3J_{HH}$ = 6.9 Hz, 1H, H-*13*), 2.34 (dtd_{app}, *J* = 14.3, 10.7, 5.4 Hz, 2H, H-*14*), 1.56 (s, 1H, N-*H*), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 3H, H-*1*).

^{13}C{^{1}H} NMR (130 MHz, $CDCl_3$) δ (ppm) = 151.0 (*C-3*), 140.8 (*C-9*), 140.5 (*C-8*), 139.9 (*C-5*), 128.9 (*C*H-*11*), 127.48 (*C*H-*12*), 127.44 (*C*H-*6*),127.1 (*C*H-*7* + *C*H-*10*), 126.8 (q, $^1J_{CF}$ = 277 Hz, *C-15*), 113.1 (CH_2-*4*), 57.5 (*C*H-*2*), 40.3 (q, $^3J_{CF}$ = 2 Hz, CH_2-*13*), 34.7 (q, $^2J_{CF}$ = 27 Hz, CH_2-*14*), 21.7 (CH_3-*1*).

^{19}F{^{1}H} NMR (280 MHz, Toluene-d_8) δ (ppm) = -65.00.

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{19}H_{20}NF_3^+$: 320.1621; found: 320.1646.

IR (neat) ν (cm^{-1}): 3030, 2967, 1625, 1601, 1487, 1444, 1373, 1340, 1252, 1113, 1004, 911, 844, 770, 740, 696.

HPLC: 75% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 99/1, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 29.5 min, t_R (major) = 39.1 min.

[α]$^{20}_D$ = -33.96 (*c 0.*25, CH_2Cl_2).

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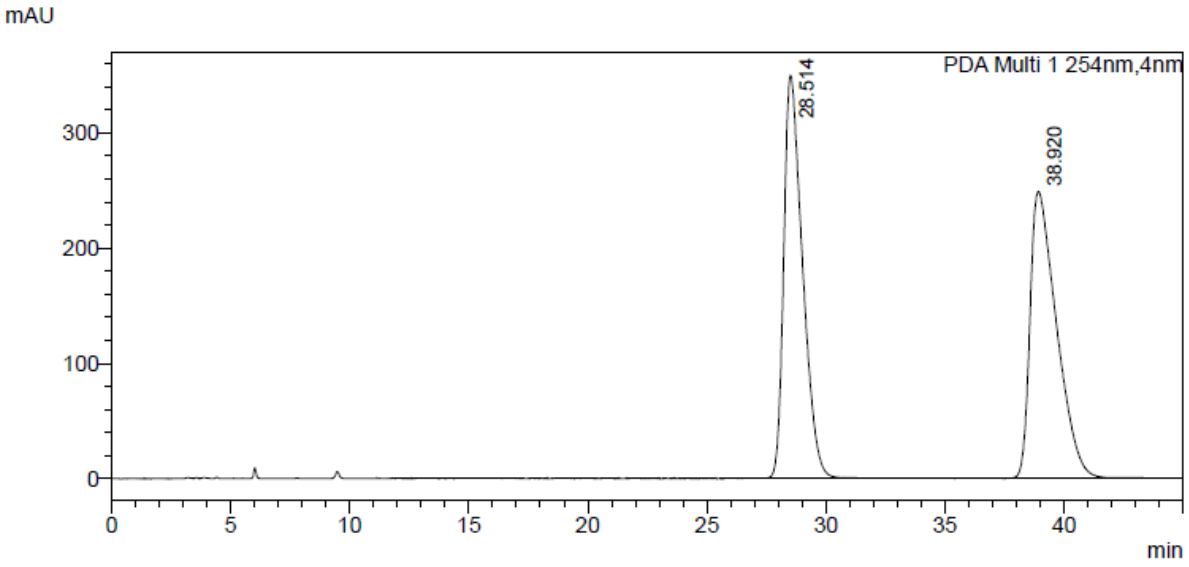

<Peak Table>

PDA Ch1 254nm

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2	38.920	50.116
Total		100.000

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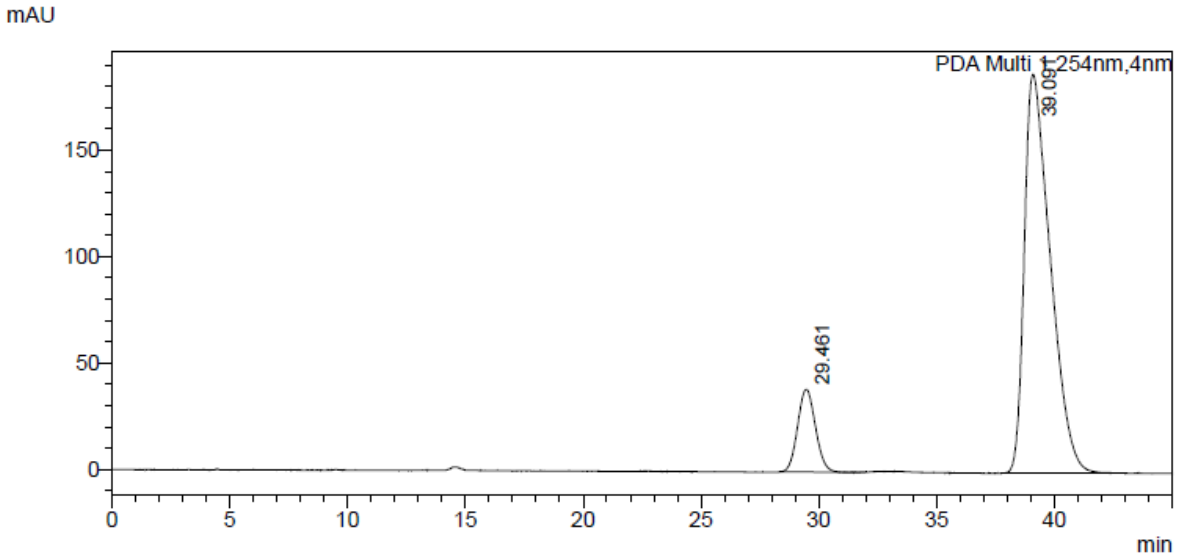
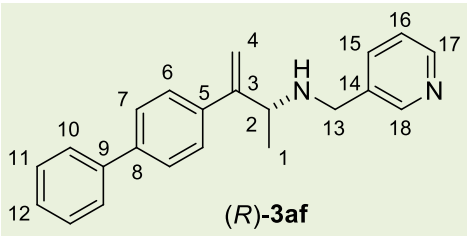


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	29.461	12.403
2	39.091	87.597
Total		100.000

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-(pyridin-3-ylmethyl)but-3-en-2-amine 3af



(*R*)-**3af**

Synthesized at room temperature for 72 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), 3-picolylamine **2f** (114 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 94%, conversion of **3af**: 68%, *r.r.* = 7:1. Purification by flash chromatography over silica gel (CH_2Cl_2:MeOH = 20:1) led to the desired product as a white solid (64.0 mg, 81% yield, 93% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.58 (d, $^4J_{HH}$ = 1.7 Hz, 1H, *H*-18), 8.51 (dd, $^3J_{HH}$ = 4.8, $^4J_{HH}$ = 1.6 Hz, 1H, *H*-17), 7.67 (dt, $^3J_{HH}$ = 7.8, $^4J_{HH}$ = 1.9 Hz, 1H, *H*-15), 7.64 – 7.53 (m, 4H, *H*-7+*H*-10), 7.51 – 7.41 (m, 4H, *H*-6+*H*-11), 7.39 – 7.31 (m, 1H, *H*-12), 7.25 (dd, 1H, $^3J_{HH}$ = 7.6, 4.8 Hz, 1H, *H*-16), 5.39 (d, $^2J_{HH}$ = 1.3 Hz, 1H, *H*-4), 5.35 (s, 1H, *H*-4), 3.90 (d, $^2J_{HH}$ = 13.4 Hz, 1H, *H*-13), 3.83 – 3.73 (m, 2H, *H*-2+*H*-13), 1.50 (s, 1H, N*H*), 1.29 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.3 (*C*-3), 149.9 (*C*H-18), 148.6 (*C*H-17), 140.8 (*C*-9), 140.5 (*C*-8), 140.0 (*C*-5), 136.1 (*C*-14), 136.0 (*C*H-15), 128.9 (*C*H-11), 127.49 (*C*H-6), 127.45 (*C*H-12), 127.13 (*C*H-10), 127.11 (*C*H-7), 123.5 (*C*H-16), 113.1 (CH_2-4), 57.0 (*C*H-2), 48.8 (CH_2-13), 21.8 (CH_3-1).

m.p. = 84.1 – 86.4 °C.

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{22}H_{23}N_2^+$: 315.1856; found: 315.1881.

IR (neat) ν (cm^{-1}): 3291, 3034, 2964, 2927, 2825, 1621, 1579, 1486, 1446, 1423, 1374, 1158, 1128, 1085, 1005, 903, 842, 770, 740, 711, 690.

HPLC: 93% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 85/15, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 25.6 min, t_R (major) = 27.8 min.

[α]$^{20}_D$ = +10.7 (*c* 1.0, $CHCl_3$).

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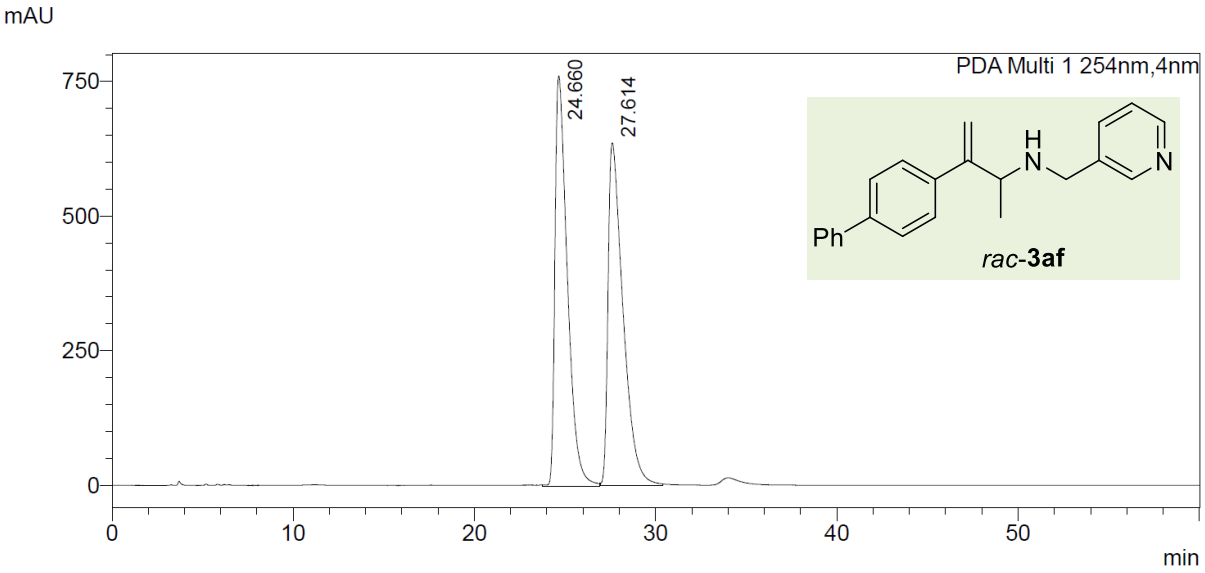

<Peak Table>

PDA Ch1 254nm

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Total		100.000

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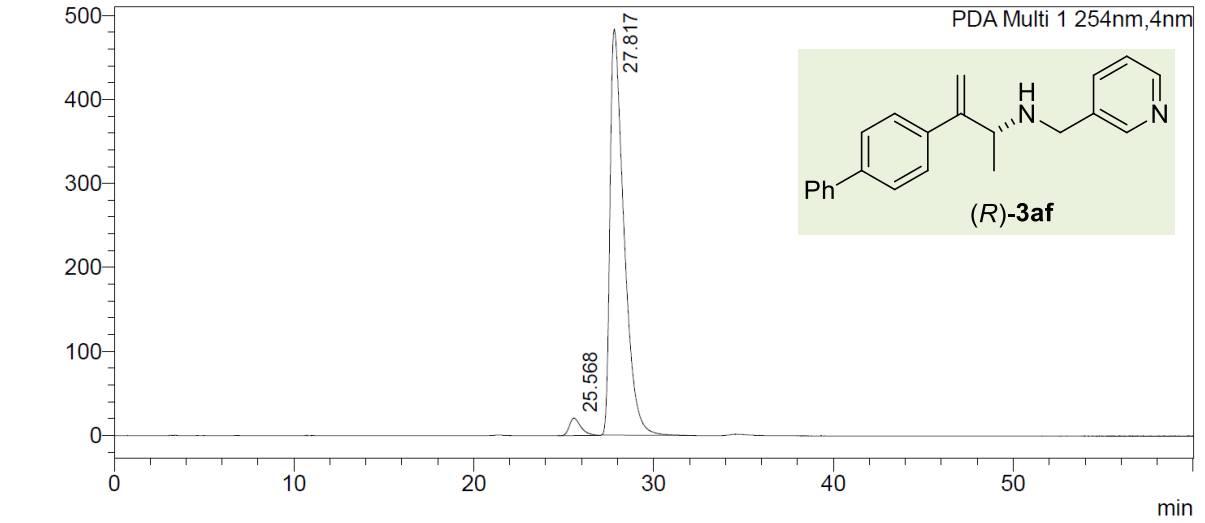
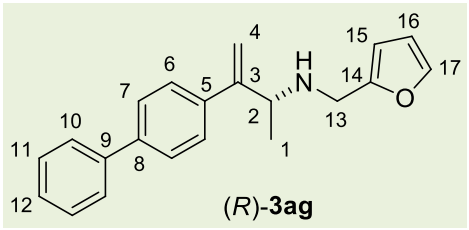


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	25.568	3.348
2	27.817	96.652
Total		100.000

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-(furan-2-ylmethyl)but-3-en-2-amine 3ag



(*R*)-**3ag**

Synthesized at room temperature for 72 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), furfurylamine **2g** (88 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 97%, conversion of **3ag**: 80%, *r.r.* = 6:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 4:1) led to the desired product as a colorless viscous oil (56.7 mg, 75% yield, 91% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.54 (m, 4H, *H*-7+*H*-10), 7.50 – 7.41 (m, 4H, *H*-6+*H*-11), 7.41 – 7.38 (m, 1H, *H*-17), 7.38 – 7.31 (m, 1H *H*-12), 6.37 – 6.31 (m, 1H, *H*-16), 6.19 (d, $^3J_{HH}$ = 3.1 Hz, 1H, *H*-15), 5.38 (s, 1H, *H*-4), 5.35 (s, 1H, *H*-4), 3.89 (d, $^2J_{HH}$ = 14.4 Hz, 1H, *H*-13), 3.85 – 3.73 (m, 2H, *H*-2+*H*-13), 1.65 (s, 1H, N*H*), 1.25 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 154.3 (*C*-14), 151.2 (*C*-3), 141.9 (*C*H-17), 140.9 (*C*-9), 140.4 (*C*-5), 140.2 (*C*-8), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.14 (*C*H-10), 127.07 (*C*H-7), 113.0 (CH_2-4), 110.3 (*C*H-16), 107.0 (*C*H-15), 56.2 (*C*H-2), 43.8 (CH_2-13), 21.7 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{21}H_{22}NO^+$: 304.1696; found: 304.1701.

IR (neat) ν (cm^{-1}): 3030, 2965, 2926, 2852, 1810, 1624, 1600, 1505, 1486, 1447, 1401, 1370, 1148, 1074, 1008, 912, 844, 770, 735, 695, 598.

HPLC: 91% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 90/10, 0.50 mL/min, 254 nm, 30 °C, t_R (minor) = 29.1 min, t_R (major) = 30.8 min.

[α]$^{20}_D$ = +11.8 (*c* 1.0, $CHCl_3$).

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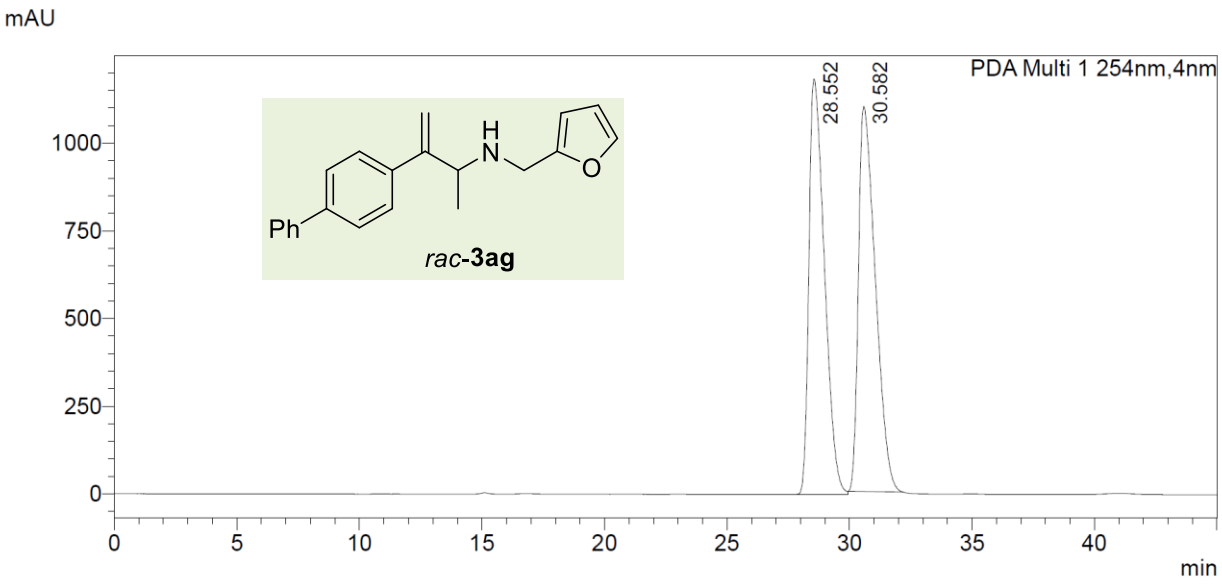

<Peak Table>

PDA Ch1 254nm

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2	30.582	50.211
Total		100.000

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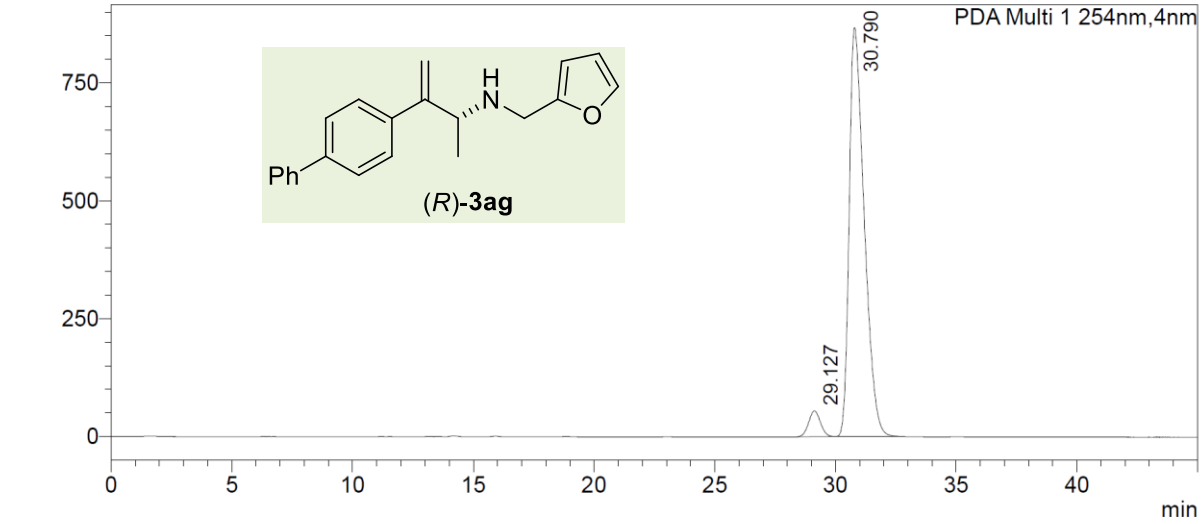
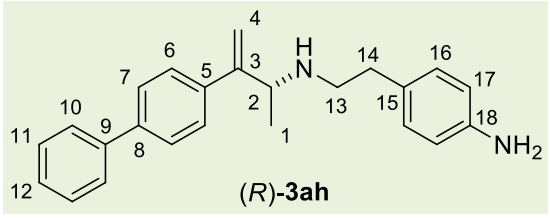


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	29.127	4.692
2	30.790	95.308
Total		100.000

(*R*)-4-(2-((3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)amino)ethyl)aniline 3ah



(*R*)-**3ah**

Synthesized at room temperature for 96 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), 4-(2-aminoethyl)aniline **2h** (136 mg, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 99%, conversion of **3ah**: 74%, *r.r.* = 8:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 1:2, with 0.2% Et_3N) led to the desired product as a yellow solid (60.6 mg, 71% yield, 87% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.59 (m, 2H, *H*-10), 7.56 – 7.51 (m, 2H, *H*-7), 7.48 – 7.42 (m, 2H, *H*-11), 7.42 – 7.38 (m, 2H, *H*-6), 7.38 – 7.33 (m, 1H, *H*-12), 6.99 (d, $^3J_{HH}$ = 8.3 Hz, 2H, *H*-16), 6.68 – 6.54 (m, 2H, *H*-17), 5.29 (d, $^2J_{HH}$ = 1.3 Hz, 1H, *H*-4), 5.20 (s, 1H, *H*-4), 3.72 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.53 (s, 2H, NH_2), 2.94 – 2.81 (m, 2H, *H*-13), 2.79 – 2.64 (m, 2H, *H*-14), 1.37 (s, 1H, N*H*), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.8 (*C*-3), 144.7 (*C*-18), 140.9 (*C*-9), 140.3 (*C*-5), 140.2 (*C*-8), 130.2 (*C*-15), 129.6 (*C*H-16), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.1 (*C*H-10), 127.0 (*C*H-7), 115.4 (*C*H-17), 112.6 (CH_2-4), 57.4 (*C*H-2), 49.0 (CH_2-13), 35.7 (CH_2-14), 21.6 (CH_3-1).

m.p. = 61.9 – 64.0 °C.

HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{24}H_{27}N_2^+$: 343.2169; found: 343.2211.

IR (neat) ν (cm^{-1}): 3452, 3358, 3204, 3028, 2966, 2924, 2845, 1620, 1515, 1486, 1445, 1369, 1272, 1179, 1149, 1122, 1086, 1007, 907, 843, 819, 770, 739, 695.

HPLC: 93% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 37.0 min, t_R (major) = 39.7 min.

[α]$^{20}_D$ = +0.2 (*c* 1.0, $CHCl_3$).

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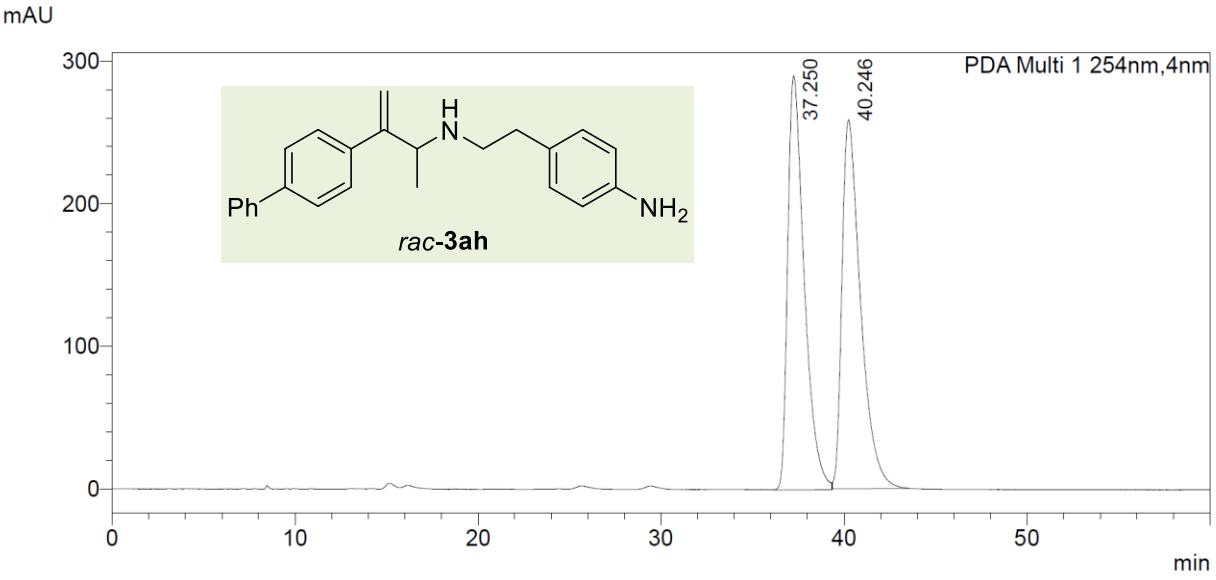

<Peak Table>

PDA Ch1 254nm

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2	40.246	50.064
Total		100.000

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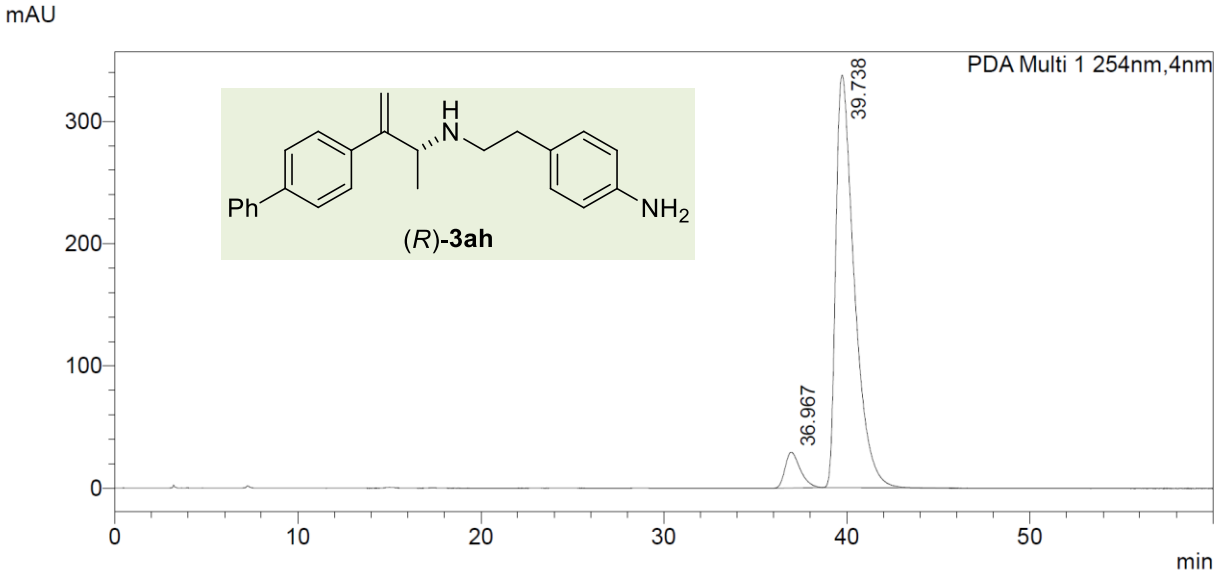
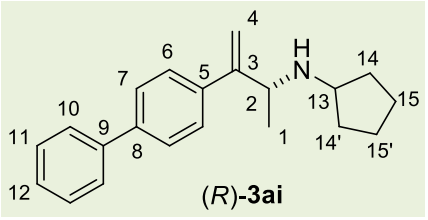


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	36.967	6.646
2	39.738	93.354
Total		100.000

(*R*)-*N*-(3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)cyclopentanamine 3ai



Synthesized at room temperature for 72 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), cyclopentylamine **2i** (99 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3ai**: 75%, *r.r.* = 4:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 1:1) led to the desired product as a yellow viscous oil (55.7 mg, 76% yield, 92% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.54 (m, 4H, *H*-7+*H*-10), 7.50 – 7.41 (m, 4H, *H*-6+*H*-11), 7.38 – 7.31 (m, 1H, *H*-12), 5.32 (s, 1H, *H*-4), 5.30 (s, 1H, *H*-4), 3.80 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.23 (p, $^3J_{HH}$ = 7.0 Hz, 1H, *H*-13), 1.95 – 1.83 (m, 2H, *H*-14), 1.76 – 1.64 (m, 2H, *H*-15), 1.58 – 1.47 (m, 2H, *H*-15), 1.41 – 1.25 (m, 3H, N*H*+*H*-14), 1.24 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 152.1 (*C*-3), 140.9 (*C*-9), 140.4 (*C*-5), 140.3 (*C*-8), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.1 (*C*H-10), 127.0 (*C*H-7), 112.6 (CH_2-4), 57.2 (*C*H-13), 55.9 (*C*H-2), 33.7 (CH_2-14), 33.4 (CH_2-14), 24.2 (CH_2-15), 24.0 (CH_2-15), 22.3 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{21}H_{26}N^+$: 292.2060; found: 296.2106.

IR (neat) ν (cm^{-1}): 3030, 2953, 2865, 1625, 1601, 1486, 1447, 1367, 1148, 1084, 1007, 906, 841, 769, 739, 695.

HPLC: 92% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 7.2 min, t_R (major) = 8.2 min.

[α]$^{20}_D$ = +1.0 (*c* 1.0, $CHCl_3$).

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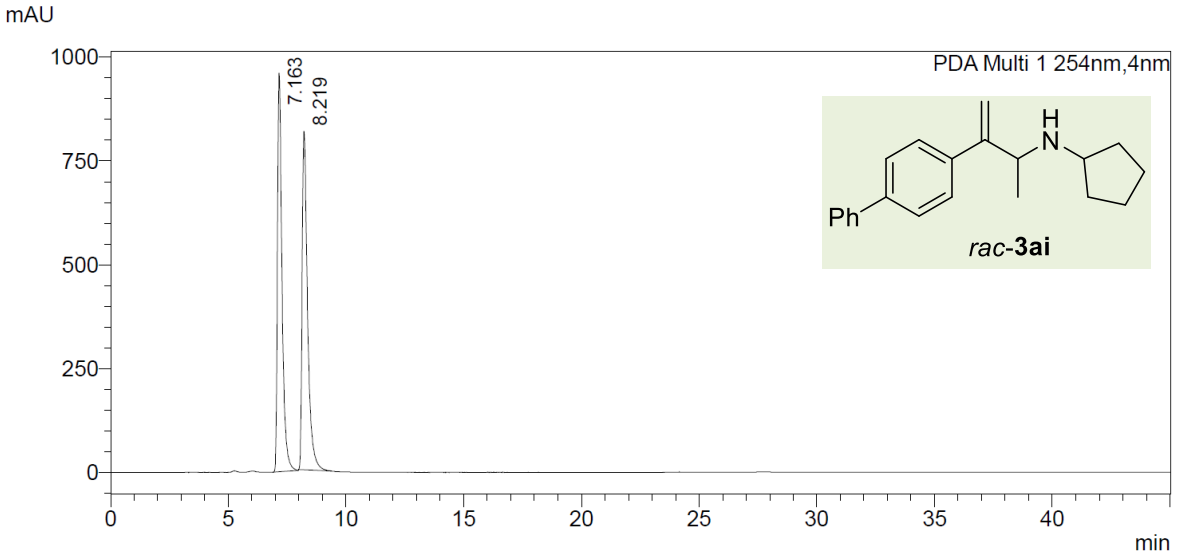

<Peak Table>

PDA Ch1 254nm

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2	8.219	50.094
Total		100.000

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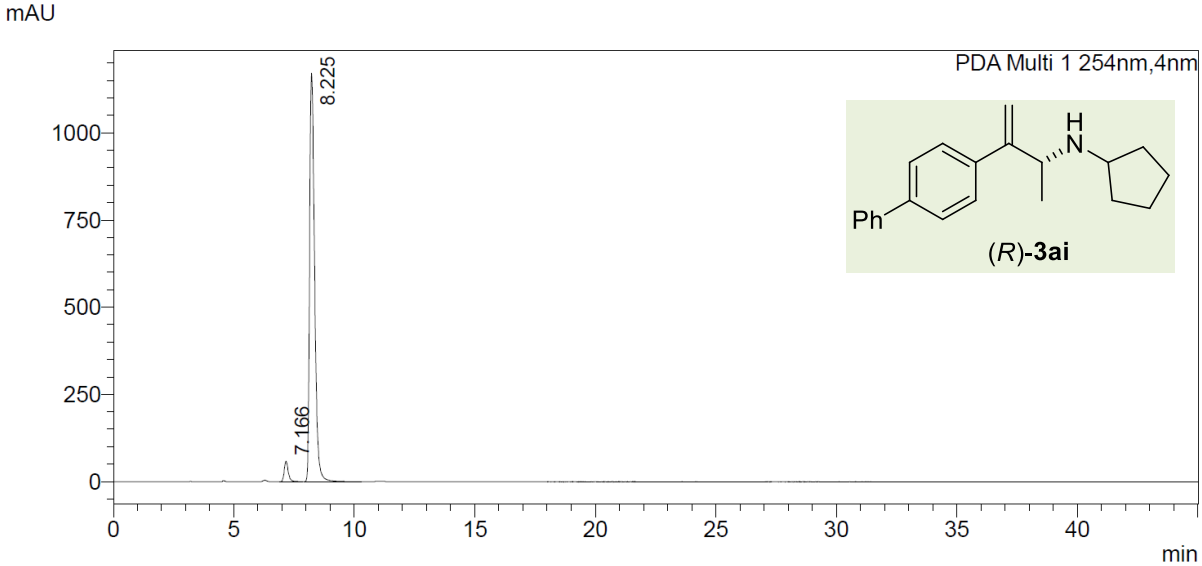
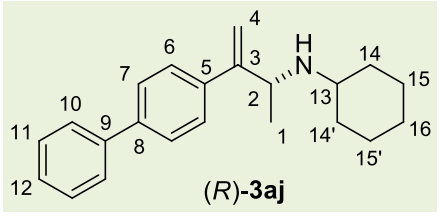


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	7.166	3.866
2	8.225	96.134
Total		100.000

(*R*)-*N*-(3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)cyclohexanamine 3aj



(*R*)-**3aj**

Synthesized at room temperature for 96 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), cyclohexylamine **2j** (114 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 94%, conversion of **3aj**: 68%, *r.r.* = 3:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 2:1) led to the desired product as a colorless viscous oil (50.2 mg, 66% yield, 92% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 – 7.54 (m, 4H, *H*-7+*H*-10), 7.50 – 7.40 (m, 4H, *H*-6+*H*-11), 7.39 – 7.30 (m, 1H, *H*-12), 5.31 (d, $^2J_{HH}$ = 0.8 Hz, 1H, *H*-4), 5.26 (s, 1H, *H*-4), 3.92 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 2.65 – 2.51 (m, 1H, *H*-13), 2.05 – 1.93 (m, 1H, *H*-14), 1.89 – 1.79 (m, 1H, *H*-14), 1.78 – 1.67 (m, 2H, *H*-15+*H*-15), 1.66 – 1.56 (m, 1H, *H*-16), 1.32 – 1.04 (m, 6H, N*H*+*H*-14+*H*-14'+*H*-15+*H*-15'+*H*-16), 1.22 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 152.2 (*C*-3), 140.9 (*C*-9), 140.4 (*C*-5), 140.2 (*C*-8), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.1 (*C*H-10), 127.0 (*C*H-7), 112.5 (CH_2-4), 53.81 (*C*H-2 or *C*H-13), 53.77 (*C*H-13 or *C*H-2), 34.4 (CH_2-14), 33.7 (CH_2-14), 26.3 (CH_2-16), 25.5 (CH_2-15), 25.2 (CH_2-15), 22.5 (CH_3-1).

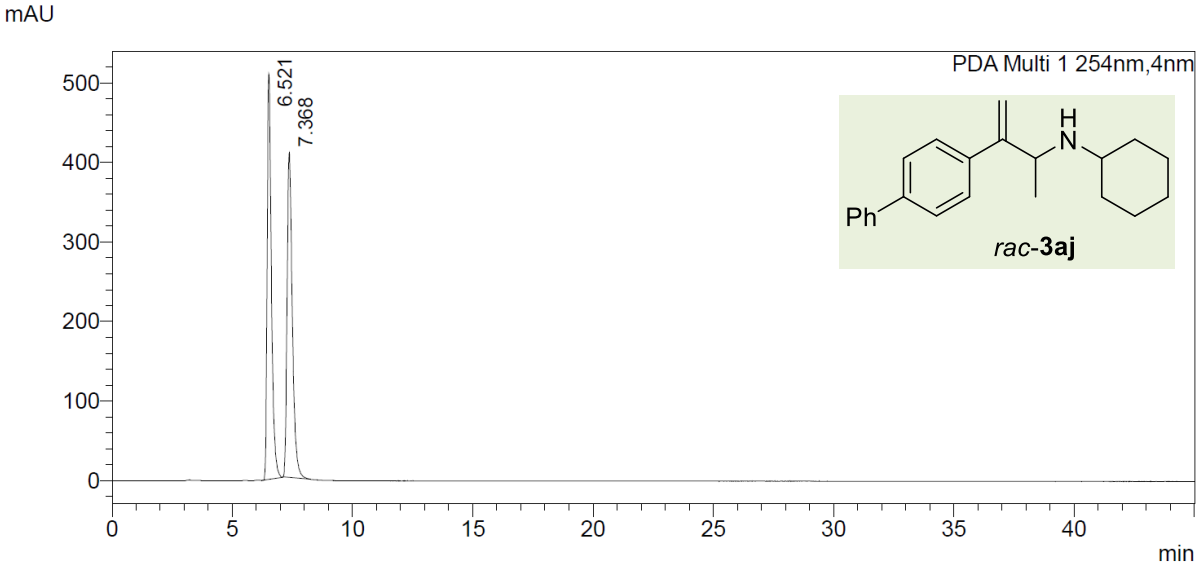
HRMS (ESI^+): calculated $[M+H]^+$ for $C_{22}H_{28}N^+$: 306.2217; found: 306.2249.

IR (neat) ν (cm^{-1}): 2924, 2851, 1601, 1486, 1447, 1368, 1276, 1261, 1132, 1084, 1007, 906, 842, 765, 749, 695.

HPLC: 92% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 6.4 min, t_R (major) = 7.7 min.

[α]$^{20}_D$ = −5.6 (*c* 1.0, $CHCl_3$).

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
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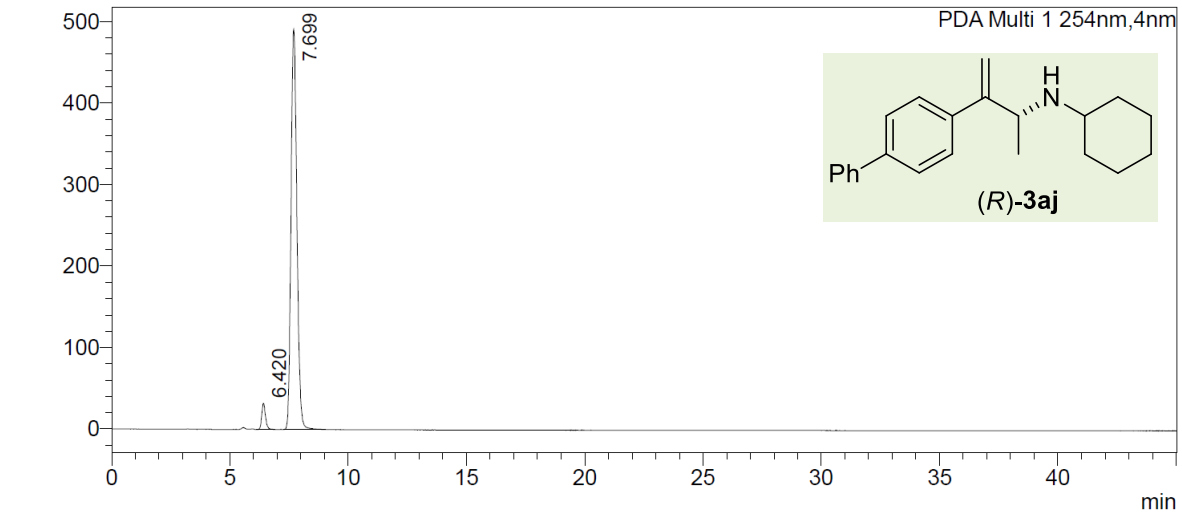
2	7.368	49.953
Total		100.000

<Chromatogram>

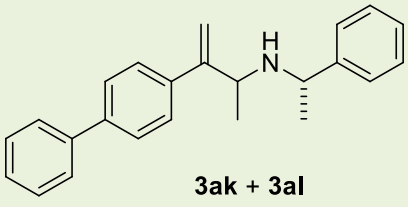


<Peak Table>

PDA Ch1 254nm

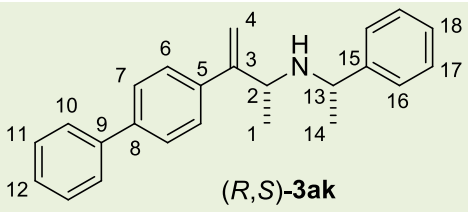
Peak#	Ret. Time	Area%
1	6.420	3.964
2	7.699	96.036
Total		100.000

3-([1,1'-Biphenyl]-4-yl)-*N*-((*S*)-1-phenylethyl)but-3-en-2-amine 3ak+3al



Synthesized at room temperature for 24 h following the general racemic procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (20.6 mg, 0.10 mmol, 1.0 equiv), (*S*)-1-phenylethylamine **2k** (52 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (1.4 mg, 0.005 mmol, 5 mol%), H,H-Cy-Phox (1.7 mg, 0.005 mmol, 5 mol%), 2,2,2-trifluoroethanol (7.5 µL, 0.10 mmol, 1.0 equiv) and mesitylene (0.2 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3ak**+**3al**: 86%, *r.r.* > 19:1, *d.r.* = 1.05:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 6:1) led to the desired product as a colorless viscous oil. *Diasteroisomeric ratio (d.r.) was calculated by integration of non isochronic signals of ^{1}H NMR of crude reaction mixture (δ = 3.60 ppm and 3.40 ppm).*

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-((*S*)-1-phenylethyl)but-3-en-2-amine 3ak



Synthesized at room temperature for 144 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), (*S*)-1-phenylethylamine **2k** (129 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 94%, conversion of **3ak**: 61%, *r.r.* = 3:1, *d.r.* = 19:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 6:1) led to the desired product as a colorless viscous oil (49.4 mg, 60% yield, 19:1 *d.r.*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56 – 7.49 (m, 2H, *H*-10), 7.47 – 7.41 (m, 2H, *H*-7), 7.40 – 7.33 (m, 2H, *H*-11), 7.30 – 7.16 (m, 8H, *H*-6+*H*-12+*H*-16+*H*-17+*H*-18), 5.24 (d, $^2J_{HH}$ = 1.0 Hz, 1H, *H*-4), 5.21 (d, $^2J_{HH}$ = 1.0 Hz, 1H, *H*-4), 3.88 (q, $^3J_{HH}$ = 6.6 Hz, 1H, *H*-13), 3.60 (q, $^3J_{HH}$ = 6.3 Hz, 1H, *H*-2), 1.41 (s, 1H, N*H*), 1.30 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-14), 1.18 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

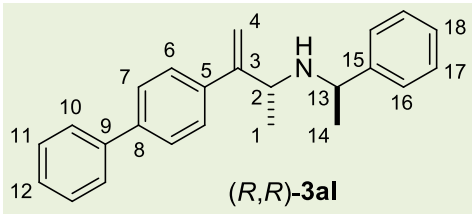
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 152.4 (*C*-3), 145.8 (*C*-15), 140.9 (*C*-9), 140.29 (*C*-5), 140.26 (*C*-8), 128.9 (*C*H-11), 128.6 (*C*H-17), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.1 (*C*H-10), 127.05 (*C*H-18), 126.99 (*C*H-7), 126.8 (*C*H-16), 112.5 (CH_2-4), 55.0 (*C*H-13), 53.5 (*C*H-2), 24.0 (CH_3-14), 20.7 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{24}H_{26}N^+$: 328.2060; found: 328.2081.

IR (neat) ν (cm^{-1}): 3060, 3028, 2966, 2926, 2864, 1624, 1601, 1487, 1449, 1369, 1130, 1076, 1007, 907, 843, 766, 740, 697.

[α]$^{20}_D$ = +23.5 (*c* 1.0, $CHCl_3$).

(*R*)-3-([1,1'-Biphenyl]-4-yl)-N-((*R*)-1-phenylethyl)but-3-en-2-amine 3al



(*R*,*R*)-**3al**

Synthesized at room temperature for 144 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), (*R*)-1-phenylethylamine **2l** (129 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 84%, conversion of **3al**: 56%, *r.r.* = 3:1, *d.r.* = 17:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 8:1) led to the desired product as a colorless viscous oil (44.2 mg, 54% yield, 17:1 *d.r.*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57 – 7.49 (m, 2H, *H*-10), 7.48 – 7.41 (m, 2H, *H*-7), 7.40 – 7.33 (m, 2H, *H*-11), 7.31 – 7.15 (m, 8H, *H*-6+*H*-12+*H*-16+*H*-17+*H*-18), 5.24 (d, $^2J_{HH}$ = 0.8 Hz, 1H, *H*-4), 5.13 (s, 1H, *H*-4), 3.86 (q, $^3J_{HH}$ = 6.6 Hz, 1H, *H*-13), 3.40 (q, $^3J_{HH}$ = 6.6 Hz, 1H, *H*-2), 1.44 (s, 1H, N*H*), 1.28 (d, $^3J_{HH}$ = 6.7 Hz, 3H, *H*-14), 1.04 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

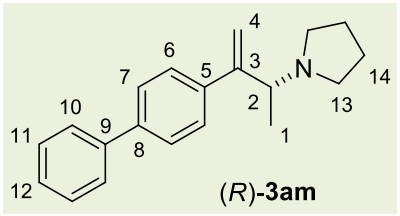
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.8 (*C*-3), 146.2 (*C*-15), 140.9 (*C*-9), 140.5 (*C*-5), 140.2 (*C*-8), 128.9 (*C*H-11), 128.6 (*C*H-17), 127.6 (*C*H-6), 127.4 (*C*H-12), 127.1 (*C*H-10), 127.05 (*C*H-18), 126.98 (*C*H-7), 126.9 (*C*H-16), 112.5 (CH_2-4), 55.2 (*C*H-13), 55.0 (*C*H-2), 25.1 (CH_3-14), 22.9 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{24}H_{26}N^+$: 328.2060; found: 328.2081.

IR (neat) ν (cm^{-1}): 3060, 3028, 2962, 2924, 2864, 1625, 1601, 1487, 1448, 1369, 1133, 1079, 1007, 908, 842, 764, 740, 697.

[α]$^{20}_D$ = +28.8 (*c* 1.0, $CHCl_3$).

(*R*)-1-(3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)pyrrolidine 3am



Synthesized at room temperature for 72 h using diphenylphosphinic acid as additive following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), pyrrolidine **2m** (84 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), diphenylphosphinic acid (10.9 mg, 0.05 mmol, 0.20 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3am**: 67%, *r.r.* = 1.9:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 2:1) led to the desired product as a colorless oil (44.5 mg, 64% yield, 95% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.59 (m, 4H, *H*-6+*H*-10), 7.58 – 7.53 (m, 2H, *H*-7), 7.48 – 7.39 (m, 2H, *H*-11), 7.34 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *H*-12), 5.34 (s, 2H, *H*-4), 3.19 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 2.70 – 2.54 (m, 4H, *H*-13), 1.86 – 1.75 (m, 4H, *H*-14), 1.27 (d, $^3J_{HH}$ = 6.5 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.8 (*C*-3), 141.1 (*C*-9), 140.4 (*C*-5), 140.2 (*C*-8), 128.9 (*C*H-11), 127.7 (*C*H-6), 127.3 (*C*H-12), 127.1 (*C*H-10), 126.9 (*C*H-7), 114.2 (CH_2-4), 65.9 (*C*H-2), 52.8 (CH_2-13), 23.7 (CH_2-14), 21.0 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{20}H_{24}N^+$: 278.1904; found: 278.2004.

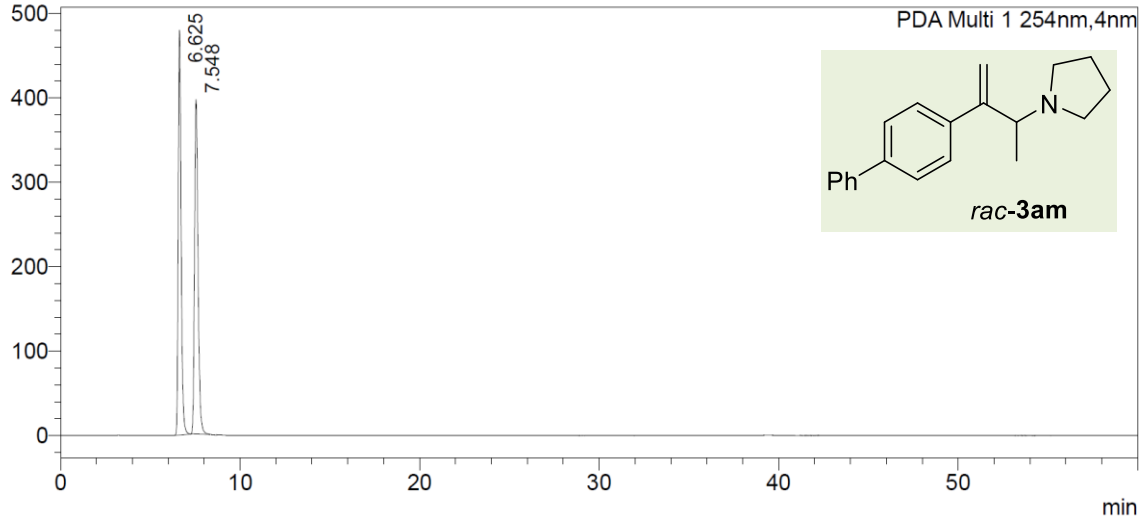
IR (neat) ν (cm^{-1}): 3029, 2967, 2927, 2873, 2782, 1678, 1624, 1601, 1486, 1449, 1370, 1314, 1196, 1142, 1076, 1007, 906, 843, 770, 741, 695.

HPLC: 95% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 98/2, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 6.7 min, t_R (major) = 7.5 min.

$[\alpha]^{20}_D$ = +49.7 (*c* 1.0, $CHCl_3$).

<Chromatogram>

mAU



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
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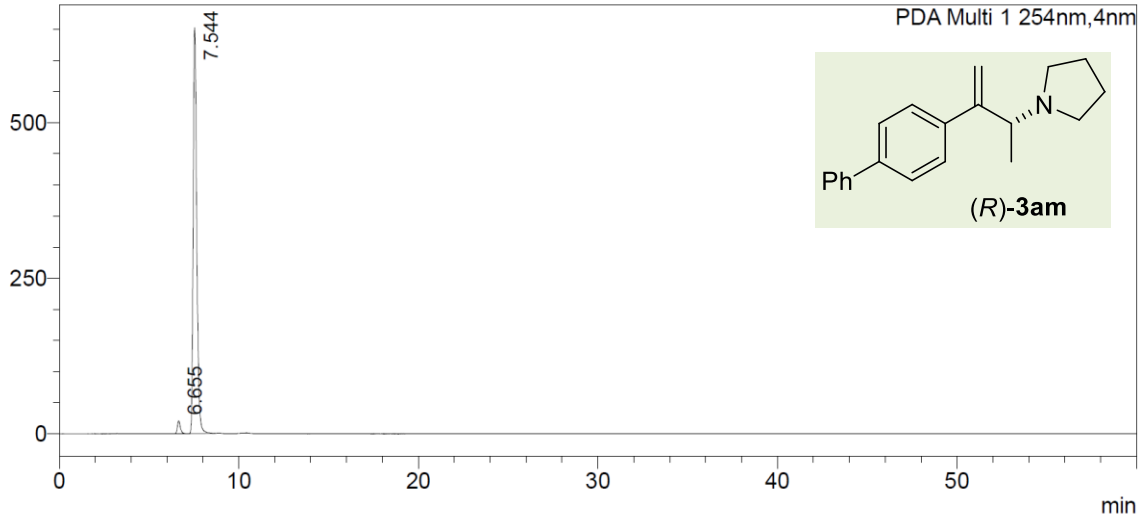
2	7.548	50.044
Total		100.000

<Chromatogram>

mAU

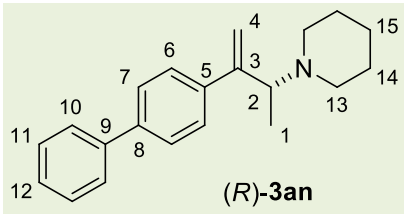


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	6.655	2.543
2	7.544	97.457
Total		100.000

(*R*)-1-(3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)piperidine 3an



Synthesized at room temperature for 72 h using diphenylphosphinic acid as additive following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), piperidine **2n** (99 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), diphenylphosphinic acid (10.9 mg, 0.05 mmol, 0.2 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3an**: 50%, *r.r.* = 1.0:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 6:1) led to the desired product as a colorless viscous oil (34.9 mg, 48% yield, >95% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.68 – 7.58 (m, 4H, *H*-6+*H*-10), 7.58 – 7.51 (m, 2H, *H*-7), 7.48 – 7.40 (m, 2H, *H*-11), 7.34 (t, $^3J_{HH}$ = 7.3 Hz, 1H, *H*-12), 5.39 (s, 1H, *H*-4), 5.25 (s, 1H, *H*-4), 3.39 (q, $^3J_{HH}$ = 6.6 Hz, 1H, *H*-2), 2.66 – 2.35 (m, 4H, *H*-13), 1.62 – 1.49 (m, 4H, *H*-14), 1.48 – 1.39 (m, 2H, *H*-15), 1.21 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

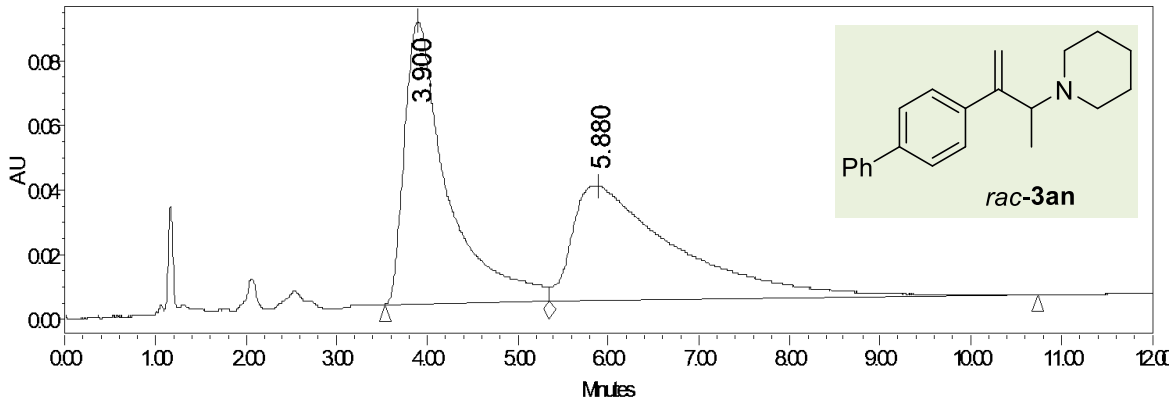
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 150.8 (*C*-3), 141.1 (*C*-5+*C*-9), 140.0 (*C*-8), 128.9 (*C*H-11), 127.7 (*C*H-6), 127.3 (*C*H-12), 127.1 (*C*H-10), 126.8 (*C*H-7), 114.0 (CH_2-4), 64.6 (*C*H-2), 51.3 (CH_2-13), 26.6 (CH_2-14), 25.0 (CH_2-15), 16.4 (CH_3-1).

HRMS (ESI^+): calculated $[M+H]^+$ for $C_{21}H_{26}N^+$: 292.2060; found: 292.2176.

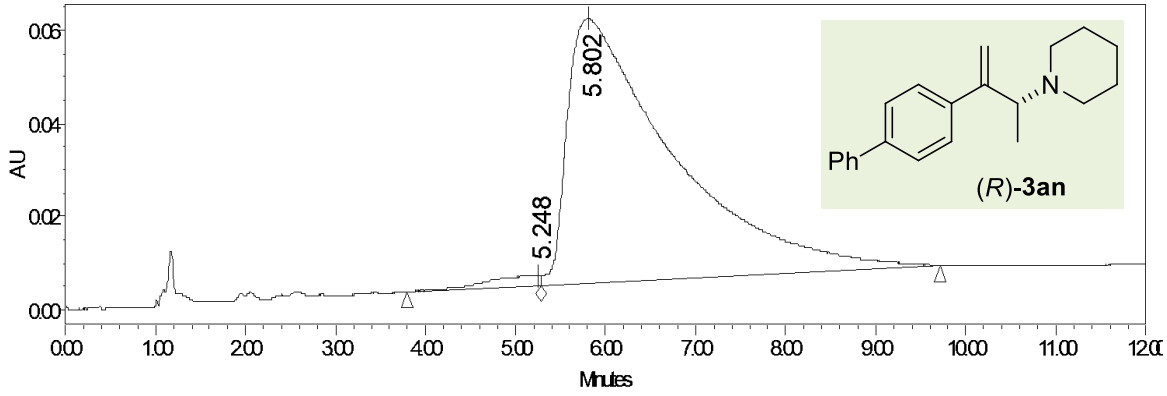
IR (neat) ν (cm^{-1}): 3032, 2929, 2852, 2795, 2751, 1622, 1601, 1486, 1445, 1373, 1321, 1153, 1116, 1036, 1007, 947, 905, 842, 768, 739, 695.

SFC: >95% *ee*, chiral stationary phase: AD column, gradient elution from 30% to 40% MeOH (12 min), 3 ml/min, 210 nm, t_R (minor) = 5.2 min, t_R (major) = 5.8 min.

[α]$^{20}_D$ = +38.6 (*c* 1.0, $CHCl_3$).

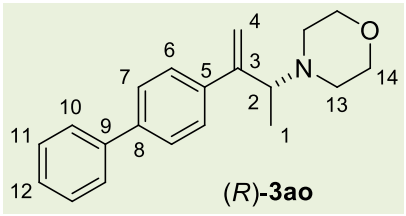


	Retention Time	Area	% Area
1	3.900	2873903	49.78
2	5.880	2899812	50.22



	Retention Time	Area	% Area
1	5.248	84592	1.79
2	5.802	4644243	98.21

(*R*)-4-(3-([1,1'-Biphenyl]-4-yl)but-3-en-2-yl)morpholine 3ao



Synthesized at room temperature for 24 h using diphenylphosphinic acid as additive following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), morpholine **2o** (88 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), diphenylphosphinic acid (10.9 mg, 0.05 mmol, 0.2 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: >99%, conversion of **3ao**: 56%, *r.r.* = 1.2:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 6:1) led to the desired product as a colorless viscous oil (40.2 mg, 55% yield, 95% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.70 – 7.62 (m, 4H, *H*-6+*H*-10), 7.62 – 7.56 (m, 2H, *H*-7), 7.51 – 7.43 (m, 2H, *H*-11), 7.41 – 7.34 (m, 1H, *H*-12), 5.45 (d, $^2J_{HH}$ = 1.2 Hz, 1H, *H*-4), 5.31 (s, 1H, *H*-4), 3.82 – 3.68 (m, 4H, *H*-14), 3.36 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 2.68 – 2.51 (m, 4H, *H*-13), 1.25 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 149.9 (*C*-3), 141.0 (*C*-9), 140.3 (*C*-5+*C*-8), 128.9 (*C*H-11), 127.6 (*C*H-6), 127.4 (*C*H-12), 127.1 (*C*H-10), 126.9 (*C*H-7), 114.9 (CH_2-4), 67.5 (CH_2-14), 65.1 (*C*H-2), 51.0 (CH_2-13), 16.8 (CH_3-1).

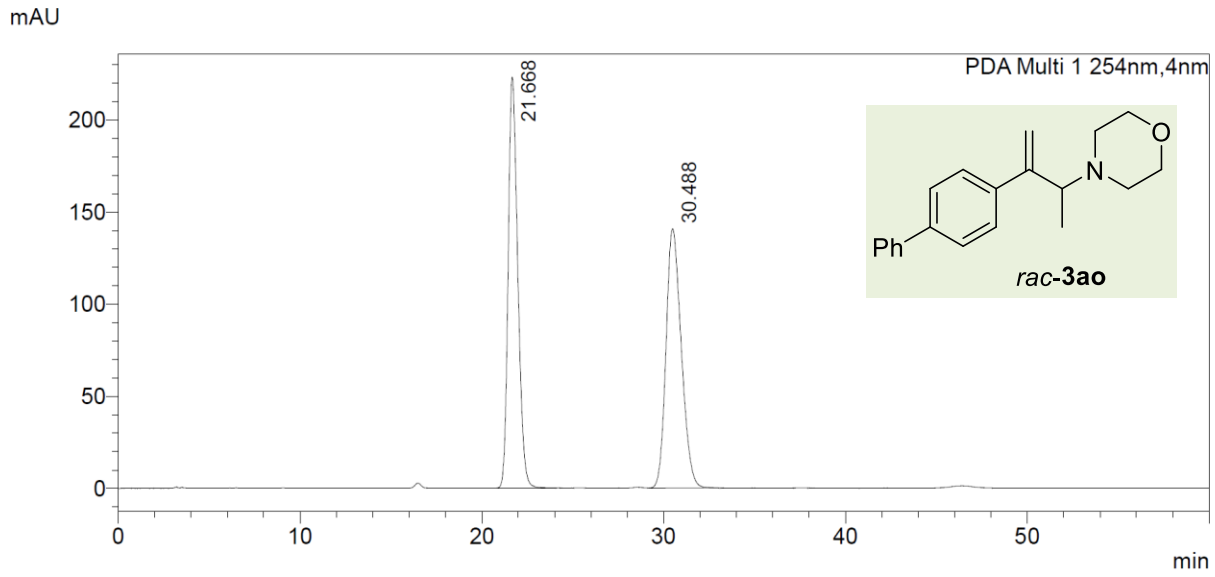
HRMS (ESI^+): calculated $[M+H]^+$ for $C_{20}H_{24}NO^+$: 294.1853; found: 294.1896.

IR (neat) ν (cm^{-1}): 3030, 2958, 2851, 2805, 1623, 1600, 1487, 1449, 1373, 1320, 1142, 1117, 1071, 1008, 955, 911, 845, 771, 741, 697.

HPLC: 95% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 95/5, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 21.6 min, t_R (major) = 30.9 min.

[α]$^{20}_D$ = +52.4 (*c* 1.0, $CHCl_3$).

<Chromatogram>

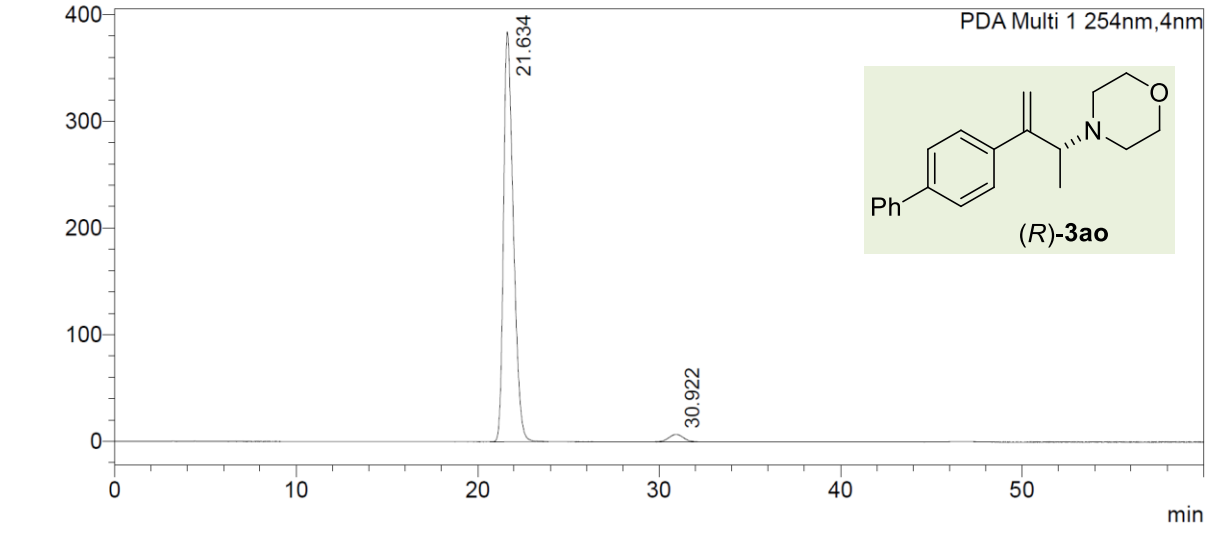


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	21.668	49.916
2	30.488	50.084
Total		100.000

<Chromatogram>

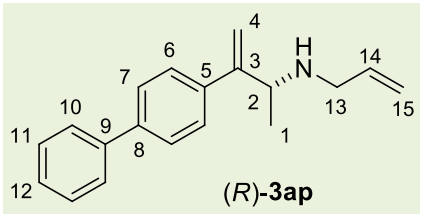


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	21.634	97.329
2	30.922	2.671
Total		100.000

(*R*)-3-([1,1'-Biphenyl]-4-yl)-*N*-allylbut-3-en-2-amine 3ap



Synthesized at room temperature for 24 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), allylamine **2p** (75 µL, 1.00 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 6 mol%), 2,2,2-trifluoroethanol (19 µL, 0.25 mmol, 1.0 equiv) and mesitylene (0.50 mL, 0.5 M). Consumption of **1a**: 99%, conversion of **3ap**: 71%, *r.r.* = 8:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 1:1) led to the desired product as a colorless viscous oil (46.1 mg, 70% yield, 94% *ee*).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.55 (m, 4H, *H*-7+*H*-10), 7.51 – 7.41 (m, 4H, *H*-6+*H*-11), 7.39 – 7.31 (m, 1H, *H*-12), 6.03 – 5.88 (m, 1H, *H*-14), 5.34 (d, $^2J_{HH}$ = 1.1 Hz, 1H, *H*-4), 5.29 (s, 1H, *H*-4), 5.21 (dd, $^3J_{HH}$ = 17.2, $^2J_{HH}$ = 1.6 Hz, 1H, *H*-15), 5.11 (dd, $^3J_{HH}$ = 10.4, $^2J_{HH}$ = 1.2 Hz, 1H, *H*-15), 3.78 (q, $^3J_{HH}$ = 6.5 Hz, 1H, *H*-2), 3.36 (dd, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 5.8 Hz, 1H, *H*-13), 3.28 (dd, $^2J_{HH}$ = 14.0, $^3J_{HH}$ = 6.2 Hz, 1H, *H*-13), 1.36 (s, 1H, N*H*), 1.25 (d, $^3J_{HH}$ = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 151.7 (*C*-3), 140.9 (*C*-9), 140.3 (*C*-5+*C*-8), 137.3 (*C*H-14), 128.9 (*C*H-11), 127.5 (*C*H-6), 127.4 (*C*H-12), 127.13 (*C*H-10), 127.07 (*C*H-7), 115.9 (CH_2-15), 112.7 (CH_2-4), 56.7 (*C*H-2), 50.1 (CH_2-13), 21.8 (CH_3-1).

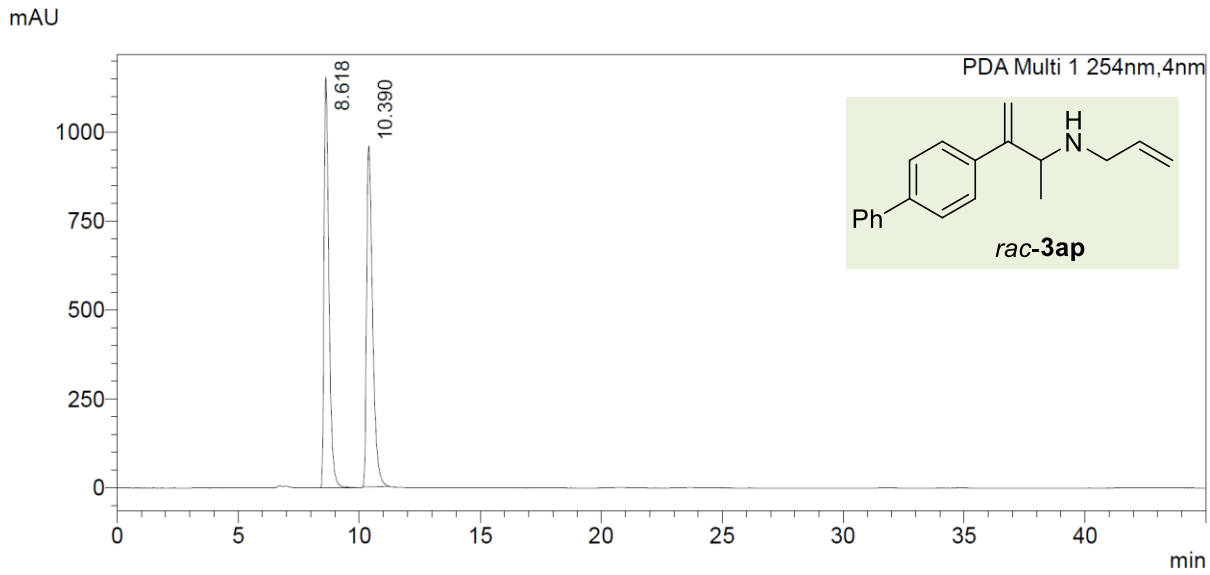
HRMS (ESI^+): calculated $[M+H]^+$ for $C_{19}H_{22}N^+$: 264.1747; found: 264.1752.

IR (neat) ν (cm^{-1}): 3077, 3030, 2970, 2925, 2868, 1642, 1601, 1486, 1447, 1370, 1120, 1078, 1006, 995, 910, 843, 769, 739, 695.

HPLC: 94% *ee*, chiral stationary column: OJ-H, mobile phase: hexane/*i*PrOH = 97/3, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 8.7 min, t_R (major) = 10.7 min.

[α]$^{20}_D$ = −12.6 (*c* 1.0, $CHCl_3$).

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
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2	10.390	50.292
Total		100.000

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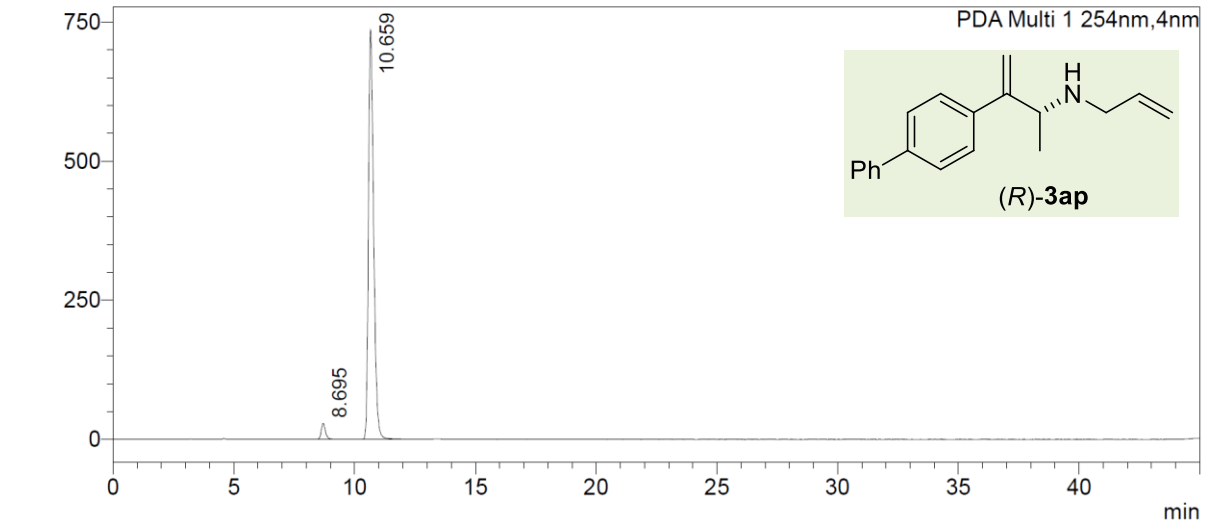
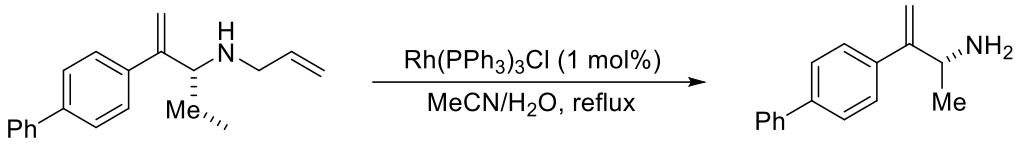


<Peak Table>

PDA Ch1 254nm

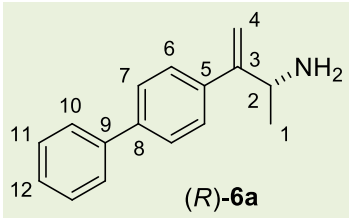
Peak#	Ret. Time	Area%
1	8.695	3.033
2	10.659	96.967
Total		100.000

5. Rh-catalyzed deallylation of 3ap



(*R*)-**3ap** (*R*)-**6a**

Modification of a reported method,[2] $Rh(PPh_3)_3Cl$ (1.8 mg, 0.002 mmol, 1% mol) was added to a solution of (*R*)-**3ap** (52.7 mg, 0.20 mmol, 94% *ee*, 1.0 equiv) in $MeCN/H_2O$ (degassed solvent, 2.0 mL, V/V = 85/15) under nitrogen atmosphere, and the mixture was heated at reflux (90 °C) for 7 h. The reaction mixture was cooled to room temperature, filtered over a short pad of silica gel (EtOAc and CH_2Cl_2 washing, with 5% MeOH) and concentrated *in vacuo* to afford the crude mixture. Consumption of **3ap**: 97%, conversion of **6a**: 81%. Then the residue was purified by silica gel column chromatography (CH_2Cl_2:MeOH = 10:1) afforded **6a** (36.3 mg, 81% yield, 94% *ee*) as a light yellow solid.



(*R*)-**6a**

^{1}H NMR (400 MHz, Methanol-d_4) δ (ppm) = 7.64 – 7.58 (m, 4H, *H*-7+*H*-10), 7.48 – 7.40 (m, 4H, *H*-6+*H*-11), 7.35 – 7.30 (m, 1H, *H*-12), 5.34 (s, 1H, *H*-4), 5.31 (s, 1H, *H*-4), 4.13 (q, *J* = 6.7 Hz, 1H, *H*-2), 1.27 (d, *J* = 6.6 Hz, 3H, *H*-1).

^{13}C{^{1}H} NMR (100 MHz, Methanol-d_4) δ (ppm) = 151.8 (*C*-3), 141.9 (*C*-8), 141.8 (*C*-9), 140.8 (*C*-5), 129.9 (*C*H-11), 128.5 (*C*H-12), 128.2 (*C*H-6), 128.1 (*C*H-7), 127.9 (*C*H-10), 111.6 (CH_2-4), 50.6 (*C*H-2), 22.3 (CH_3-1).

m.p. = 206.0 – 208.5 °C.

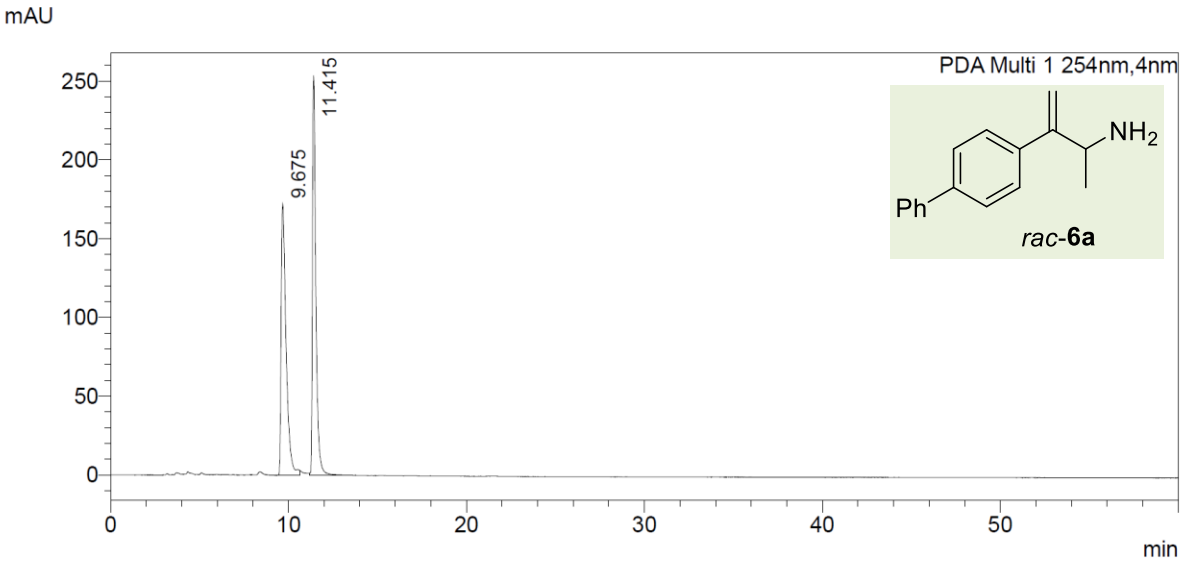
HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{16}H_{18}NO^+$: 224.1434; found: 224.1442.

IR (neat) ν (cm^{-1}): 3034, 2975, 2867, 2806, 2709, 2644, 2497, 1620, 1540, 1513, 1487, 1449, 1377, 1261, 1207, 1145, 1116, 1077, 1004, 909, 840, 769, 737, 694.

HPLC: 94% *ee*, chiral stationary column: AD-H, mobile phase: hexane/*i*PrOH = 95/5, 1.0 mL/min, 254 nm, 30 °C, t_R (minor) = 9.9 min, t_R (major) = 11.6 min.

[α]$^{20}_D$ = −60.6 (*c* 0.05, MeOH).

<Chromatogram>



<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
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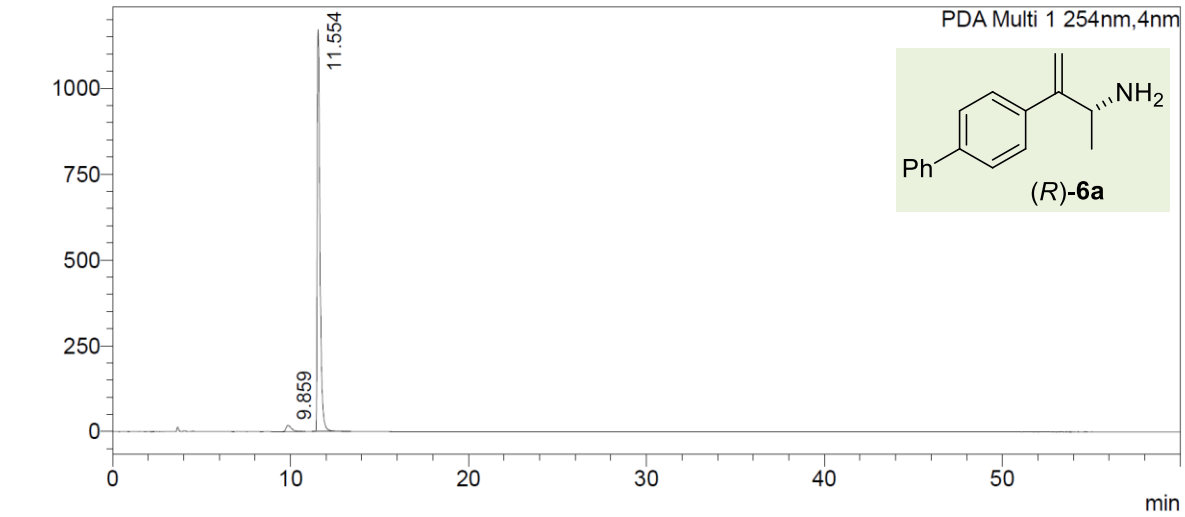
2	11.415	49.952
Total		100.000

<Chromatogram>



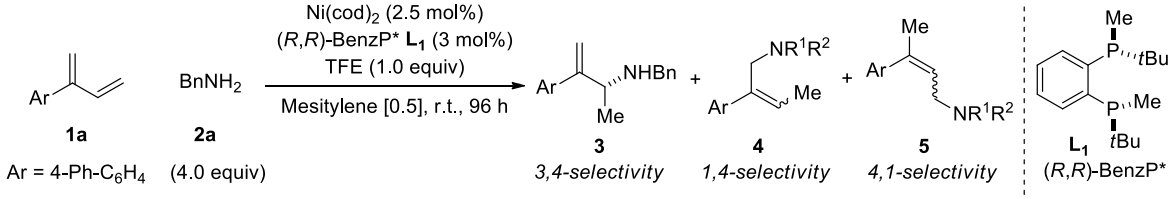
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area%
1	9.859	3.052
2	11.554	96.948
Total		100.000

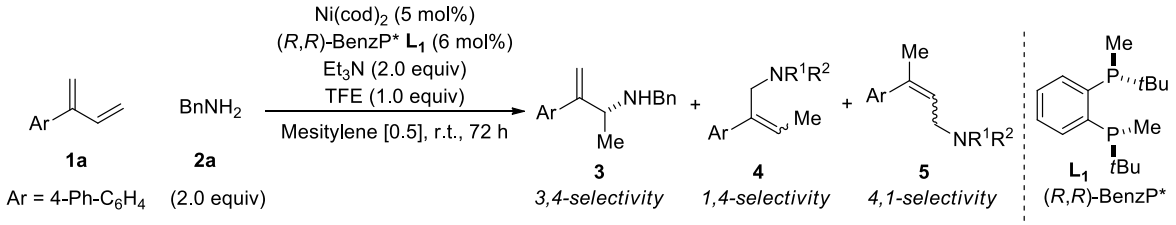
6. Improved sets of reaction conditions

6.1. Reduced Catalyst Loading



Performed at room temperature for 96 h following the general procedure using 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (103 mg, 0.50 mmol, 1.0 equiv), benzylamine **2a** (219 μL, 2.0 mmol, 4.0 equiv), $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 2.5 mol%), (*R,R*)-BenzP* (4.2 mg, 0.015 mmol, 3.0 mol%), 2,2,2-trifluoroethanol (38 μL, 0.50 mmol, 1.0 equiv) and mesitylene (1.0 mL, 0.50 M). Consumption of **1a**: >99%, conversion of **3aa**: 84%, *r.r.* = 6:1. Purification by flash chromatography over silica gel (pentane:EtOAc = 5:1) led to the desired product as a yellow solid (120.8 mg, 77% yield, 92% *ee*).

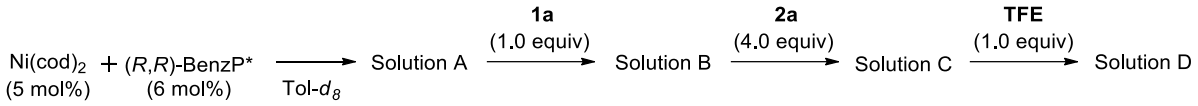
6.2. Reduced Amine Loading



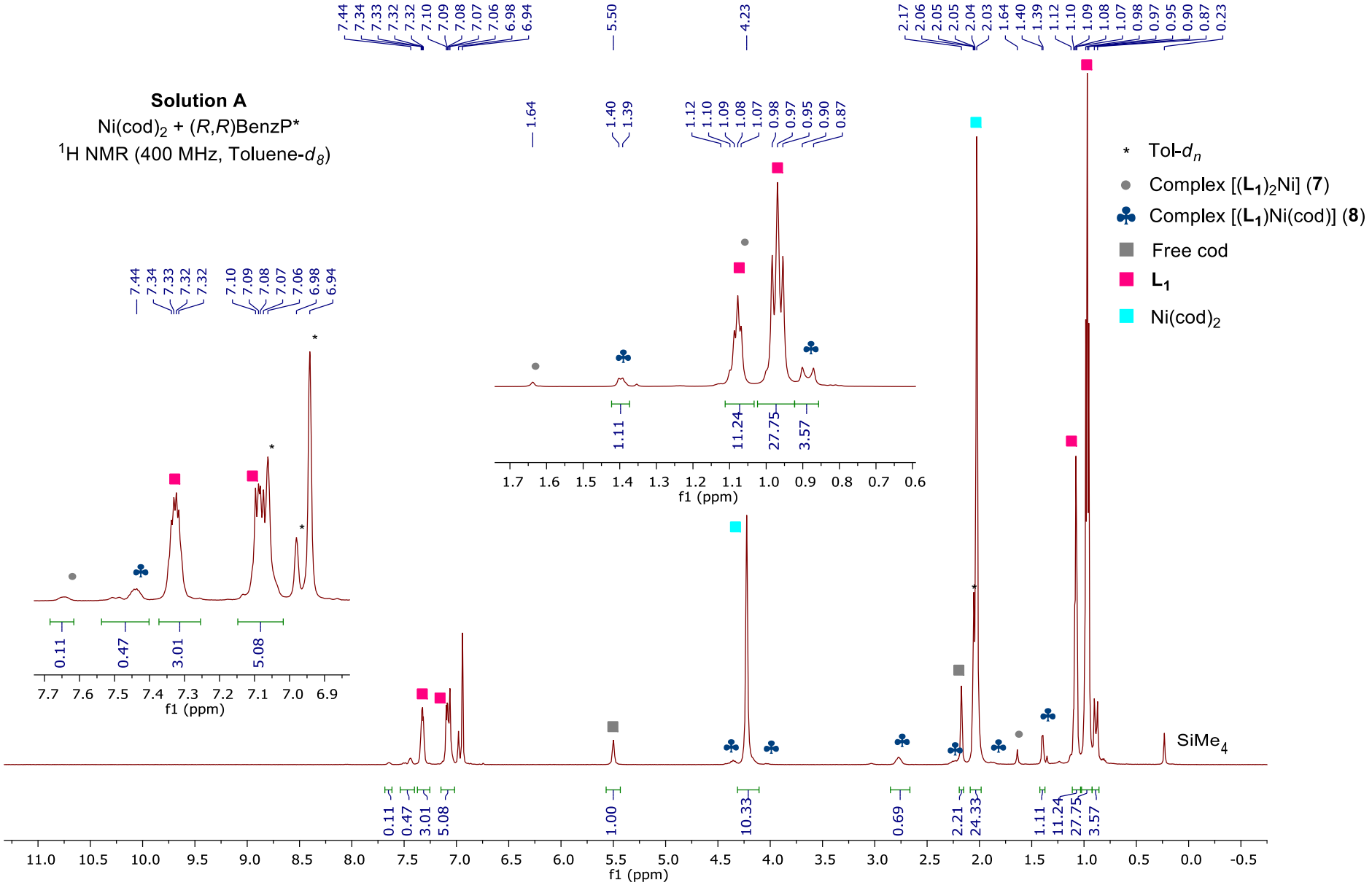
In a N_2-filled glovebox, $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%) and (*R*,*R*)-BenzP* **L_1** (4.2 mg, 0.015 mmol, 6 mol%) were charged in a 5 mL Schlenk tube and dissolved in anhydrous mesitylene (0.50 mL, 0.50 M). After stirring at room temperature for 10 min, the diene **1a** (51.6 mg, 0.25 mmol, 1.0 equiv), $BnNH_2$ **2a** (55 μL, 0.50 mmol, 4.0 equiv), Et_3N (28 μL, 0.50 mmol, 4.0 equiv) and TFE (19 μL, 0.25 mmol, 1.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and the reaction mixture was stirred at room temperature for 72 h. The reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (10 mL) and concentrated under vacuum to afford the crude mixture. The conversion and isomeric ratio were determined by ^1H NMR analysis of the crude reaction mixture using CH_2Br_2 as an internal standard. Consumption of **1a**: 85%, conversion of **3ap**: 75%, *r.r.* = 8:1. Purification by flash chromatography over silica gel (Pentane:EtOAc = 5:1) led to the desired product as a colorless oil (56.0 mg, 72% yield, 92% *ee*).

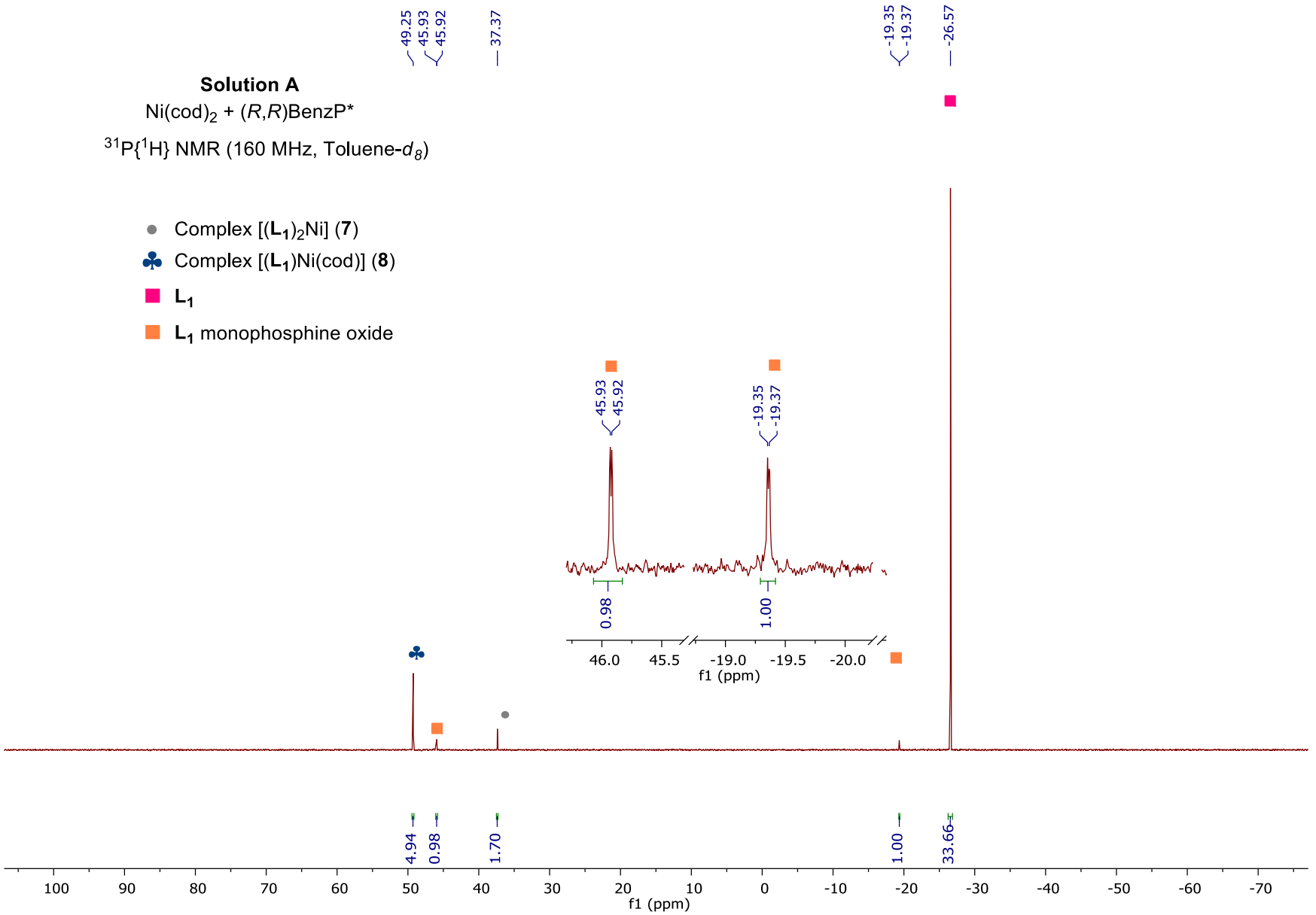
7. Supporting Organometallics

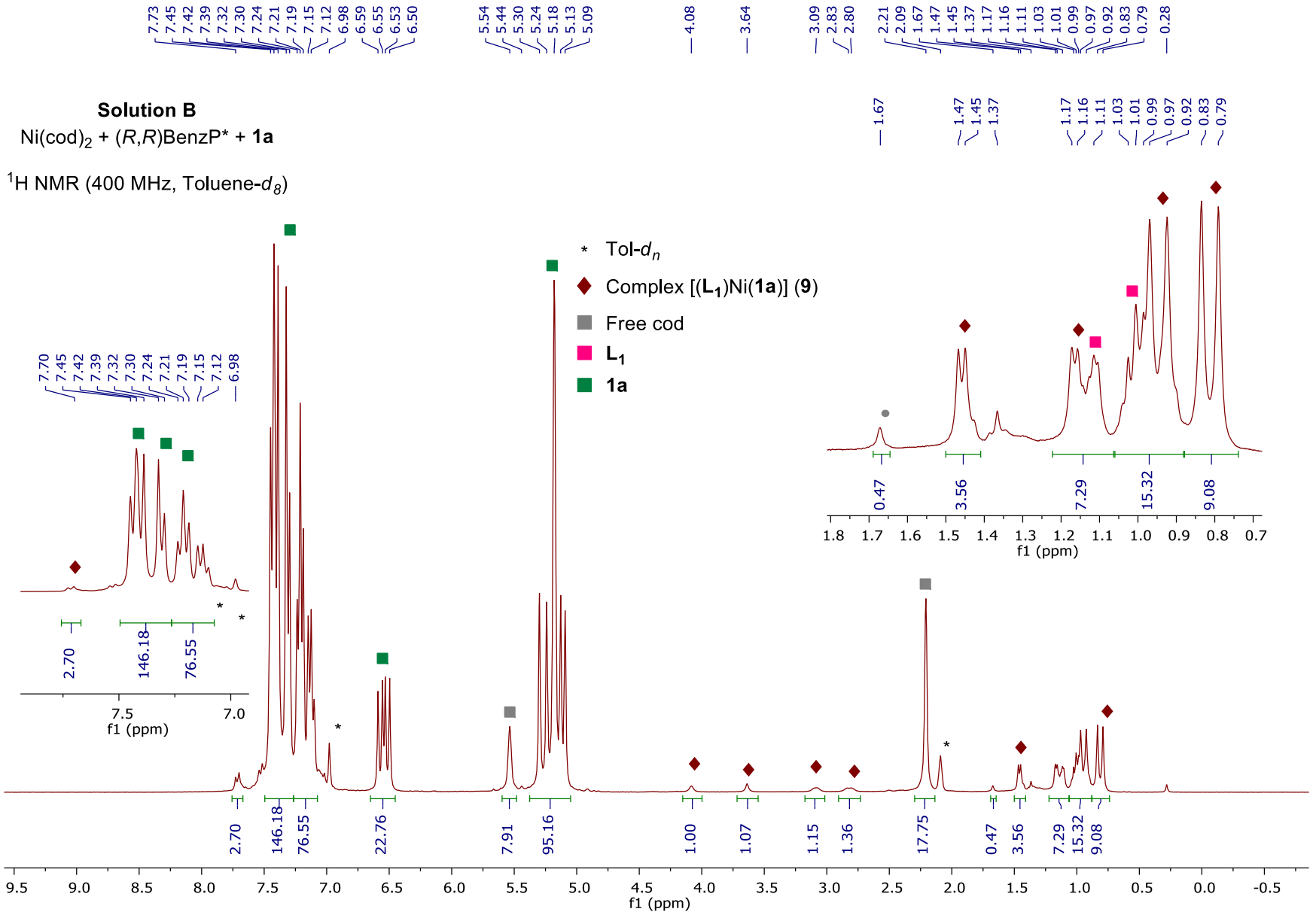
7.1. NMR Monitoring

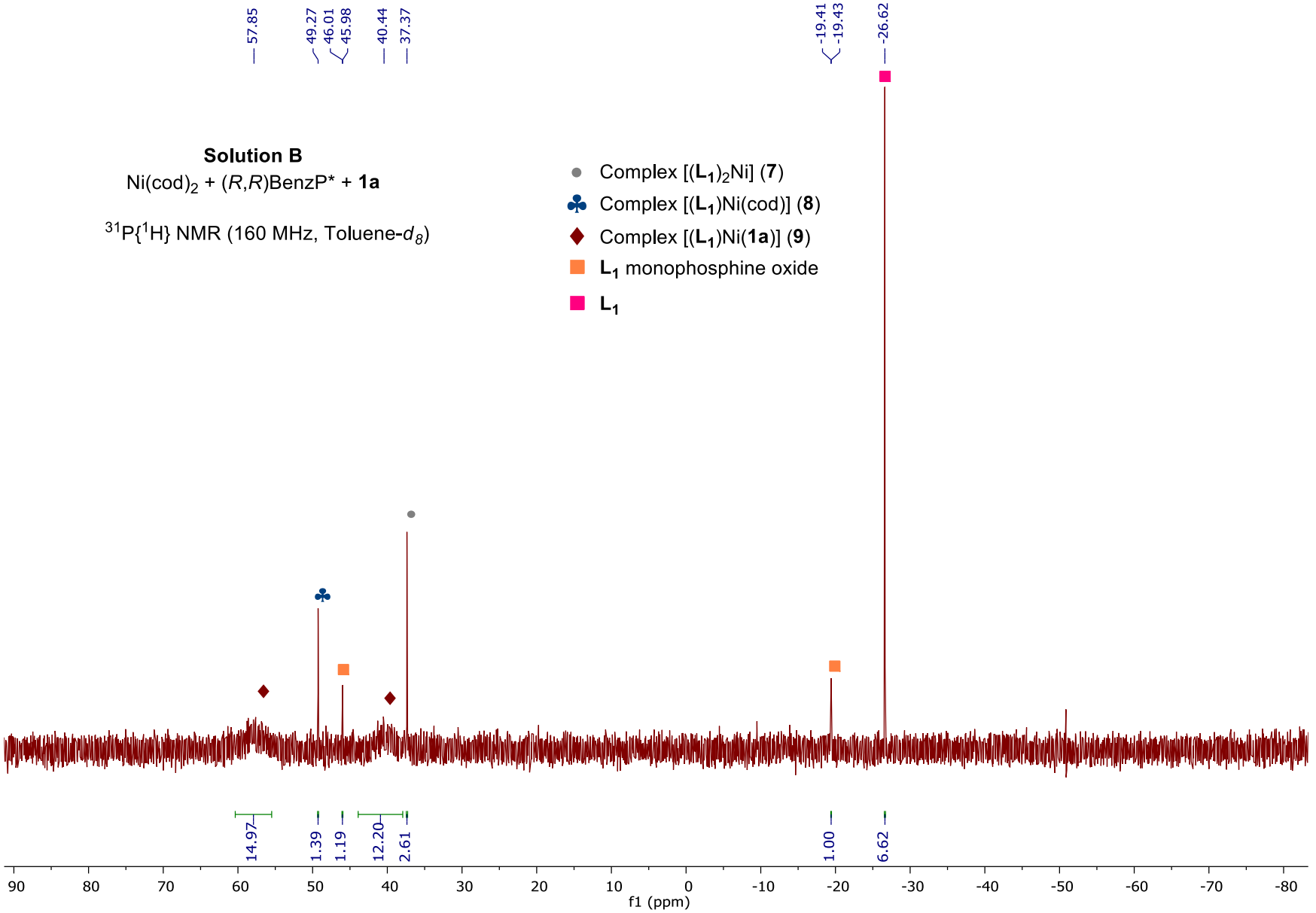


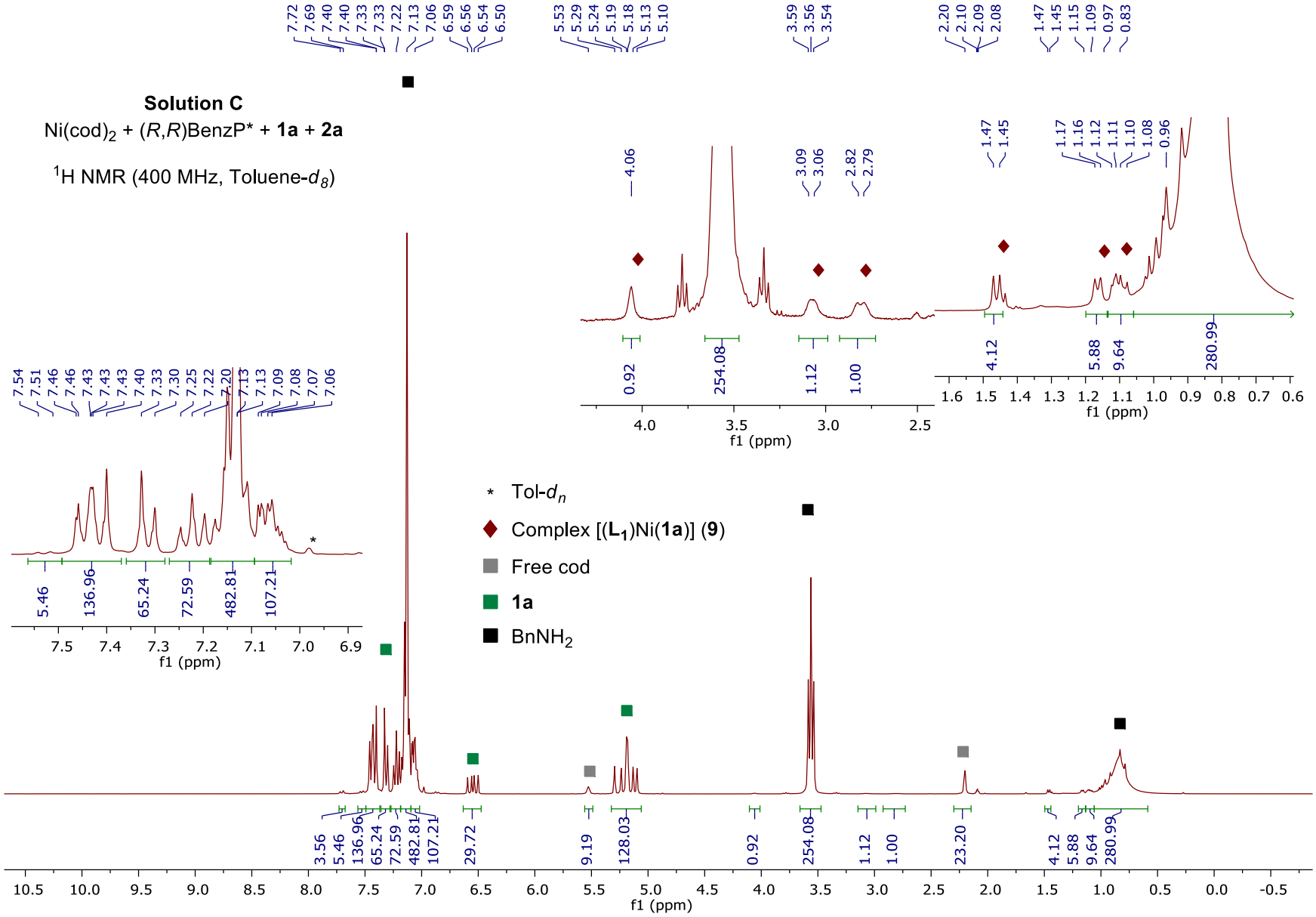
In a N_2-filled glovebox, a stock solution of $Ni(cod)_2$ (6.9 mg, 0.025 mmol) and (R,R)BenzP* (8.5 mg, 0.030 mmol) in toluene-d_8 (1.0 mL) was stirred for 5 min, and 0.40 mL of the resulting pale orange solution was introduced in a J-Young NMR tube (solution A). ^{1}H and $^{31}P\{^{1}H\}$ NMR of this solution were immediately recorded. In another J-Young tube was weighted 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (41.3 mg, 0.20 mmol, 1.0 equiv), to which was added 0.40 mL of the $Ni(cod)_2$/(R,R)BenzP* stock solution A, which resulted in an immediate change of color from pale orange to dark orange (solution B). ^{1}H and $^{31}P\{^{1}H\}$ NMR of this solution were immediately recorded. The J-Young tube containing solution B was brought back into the glovebox, and neat $BnNH_2$ **2a** (86.0 mg, 0.80 mmol, 4.0 equiv) was added to the tube (solution C). ^{1}H and $^{31}P\{^{1}H\}$ NMR of this solution were immediately recorded. The J-Young tube containing solution C was brought back into the glove-box, and neat 2,2,2-trifluoroethanol (20.0 mg, 0.20 mmol, 1.0 equiv) was added to the tube, which resulted in a slight change of color from dark orange to pale orange (solution D). ^{1}H, $^{19}F\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR of this solution were immediately recorded, and the evolution of the reaction mixture was monitored over 56 h.

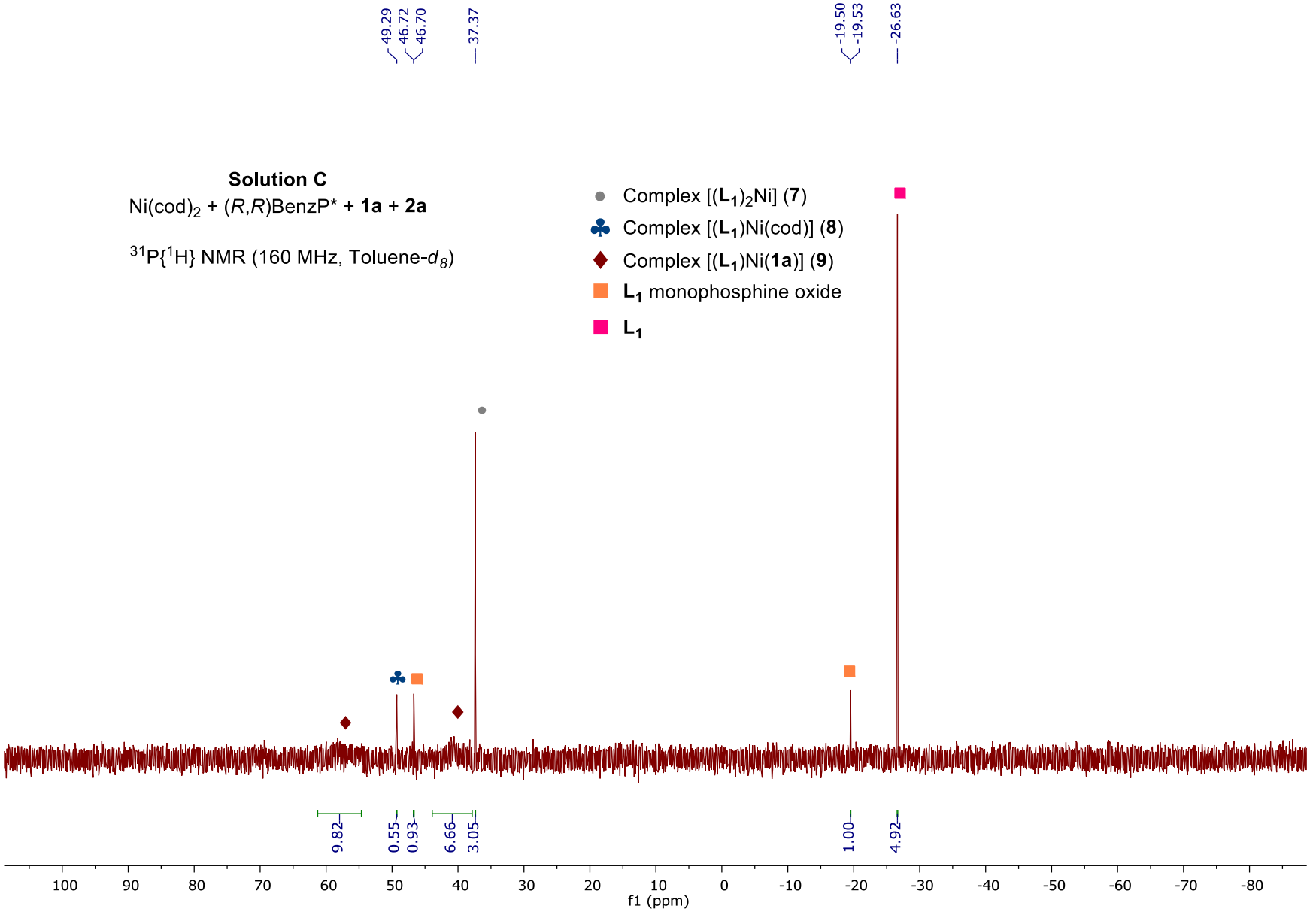

Solution A
Ni(cod)2 + (R,R)BenzP*
1H NMR (400 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Free cod
L1
Ni(cod)2
SiMe4
f1 (ppm)

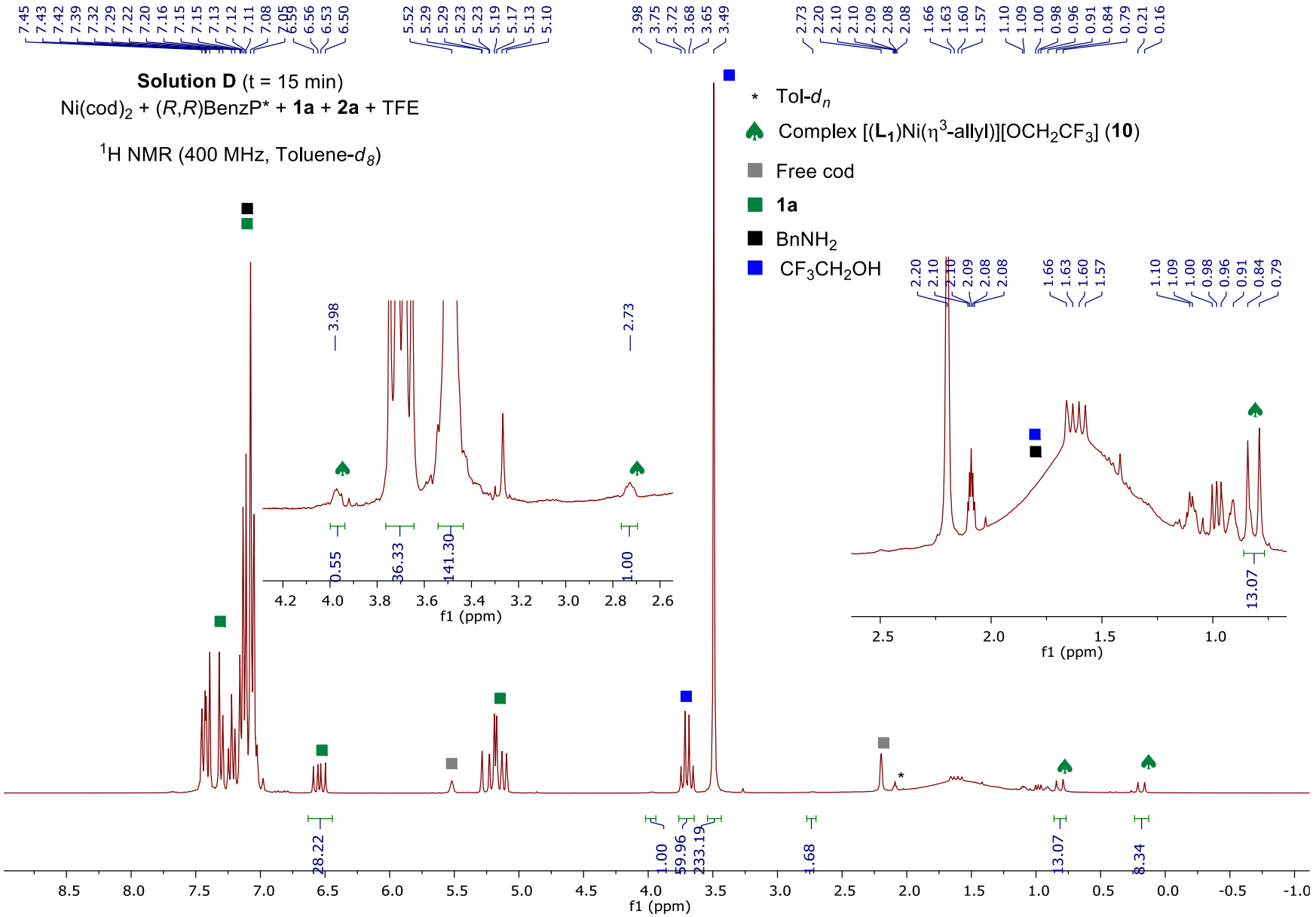

49.25
45.93
45.92
37.37
-19.35
-19.37
-26.57
Solution A
Ni(cod)2 + (R,R)BenzP*
31P{1H} NMR (160 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
L1
L1 monophosphine oxide
45.93
45.92
-19.35
-19.37
0.98
1.00
46.0
45.5
-19.0
-19.5
-20.0
f1 (ppm)
4.94
0.98
1.70
1.00
33.66
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
f1 (ppm)

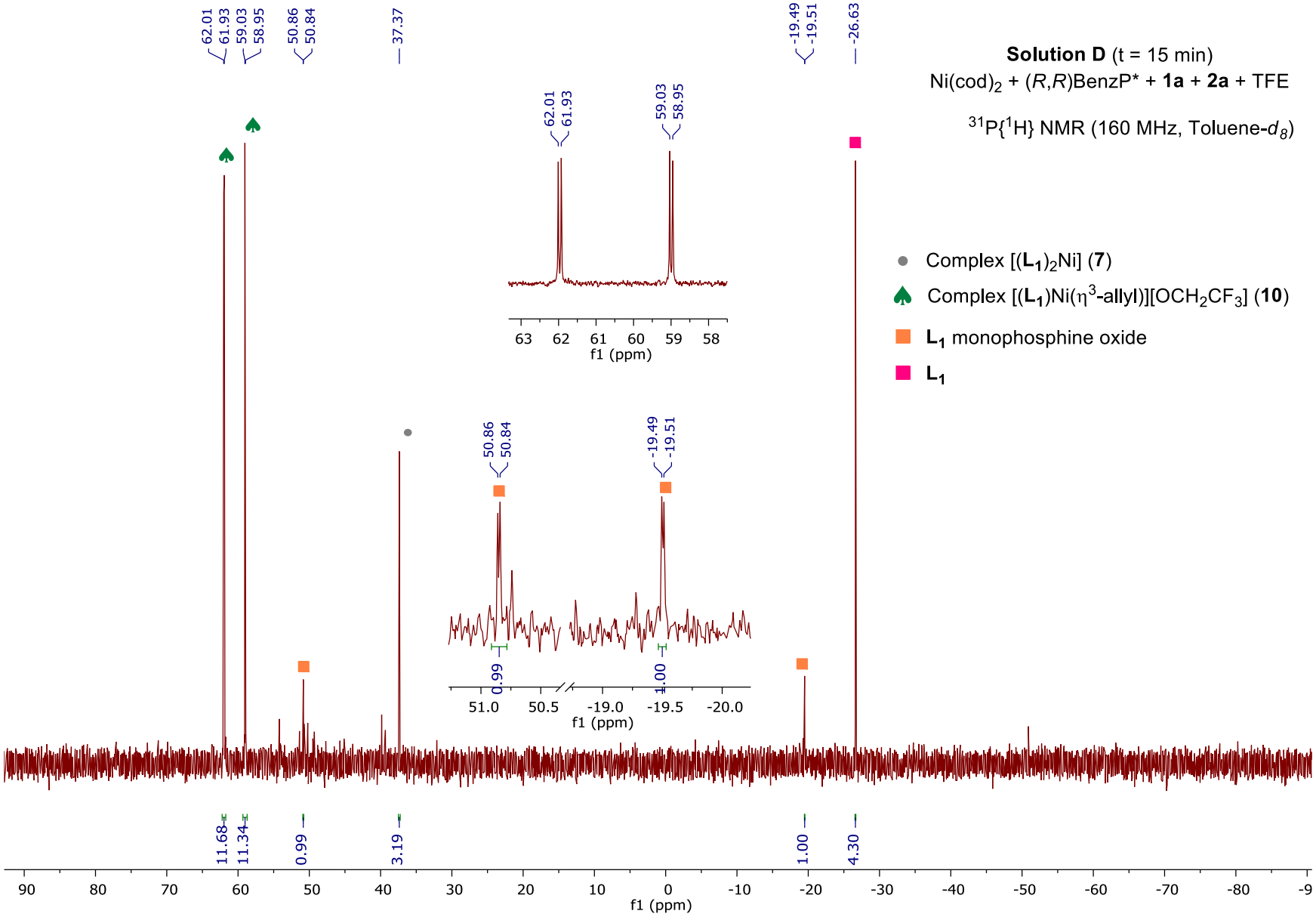

Solution B
Ni(cod)2 + (R,R)BenzP* + 1a
1H NMR (400 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)Ni(1a)] (9)
Free cod
L1
1a
f1 (ppm)


57.85
49.27
46.01
45.98
40.44
37.37
-19.41
-19.43
-26.62
Solution B
Ni(cod)2 + (R,R)BenzP* + 1a
31P{1H} NMR (160 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
L1 monophosphine oxide
L1
14.97
1.39
1.19
12.20
2.61
1.00
6.62
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)


Solution C
Ni(cod)2 + (R,R)BenzP* + 1a + 2a
1H NMR (400 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)Ni(1a)] (9)
Free cod
1a
BnNH2
f1 (ppm)


49.29
46.72
46.70
37.37
-19.50
-19.53
-26.63
Solution C
Ni(cod)2 + (R,R)BenzP* + 1a + 2a
31P{1H} NMR (160 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
L1 monophosphine oxide
L1
9.82
0.55
0.93
6.66
3.05
1.00
4.92
100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80
f1 (ppm)

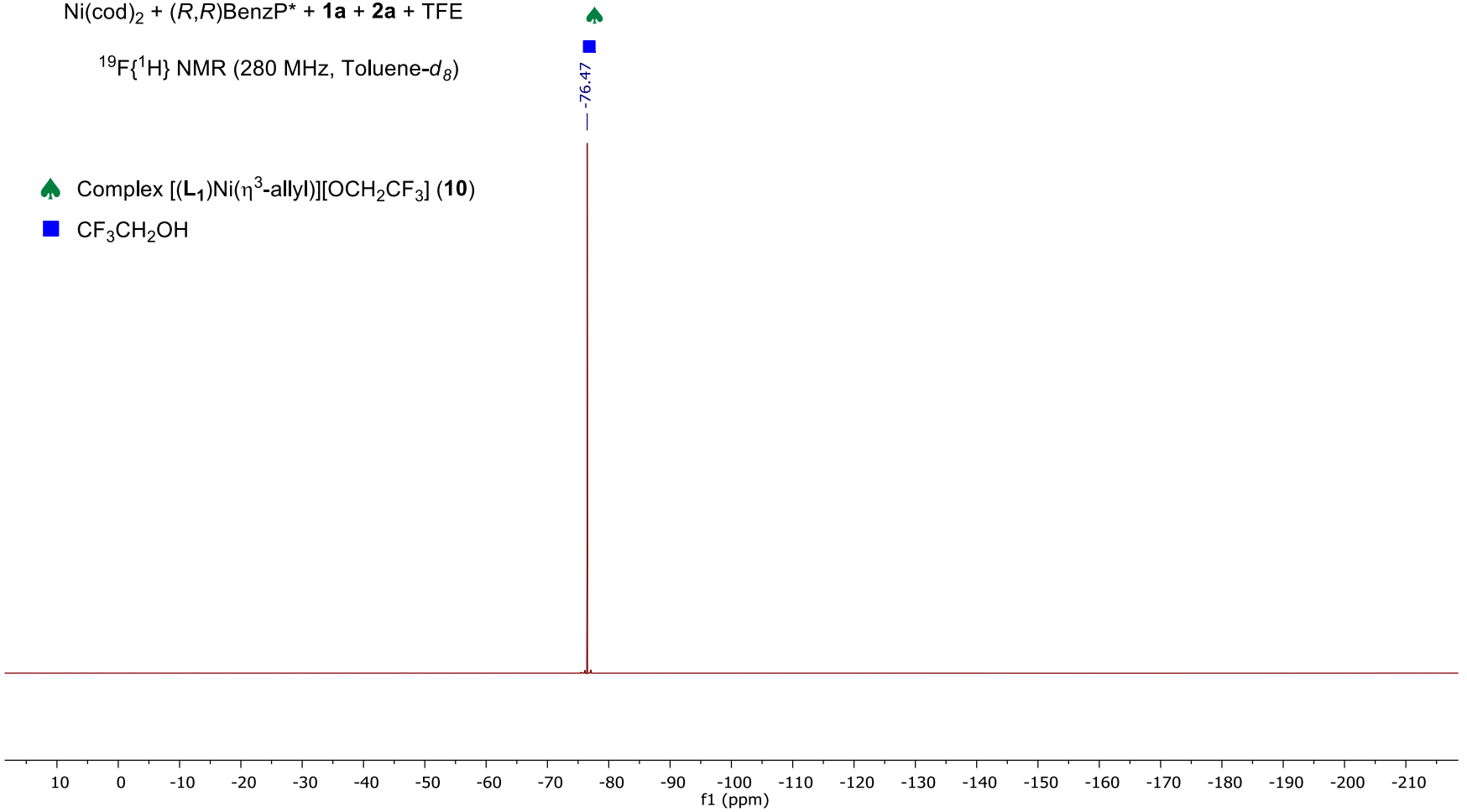

Solution D (t = 15 min)
Ni(cod)2 + (R,R)BenzP* + 1a + 2a + TFE
1H NMR (400 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
Free cod
1a
BnNH2
CF3CH2OH
f1 (ppm)

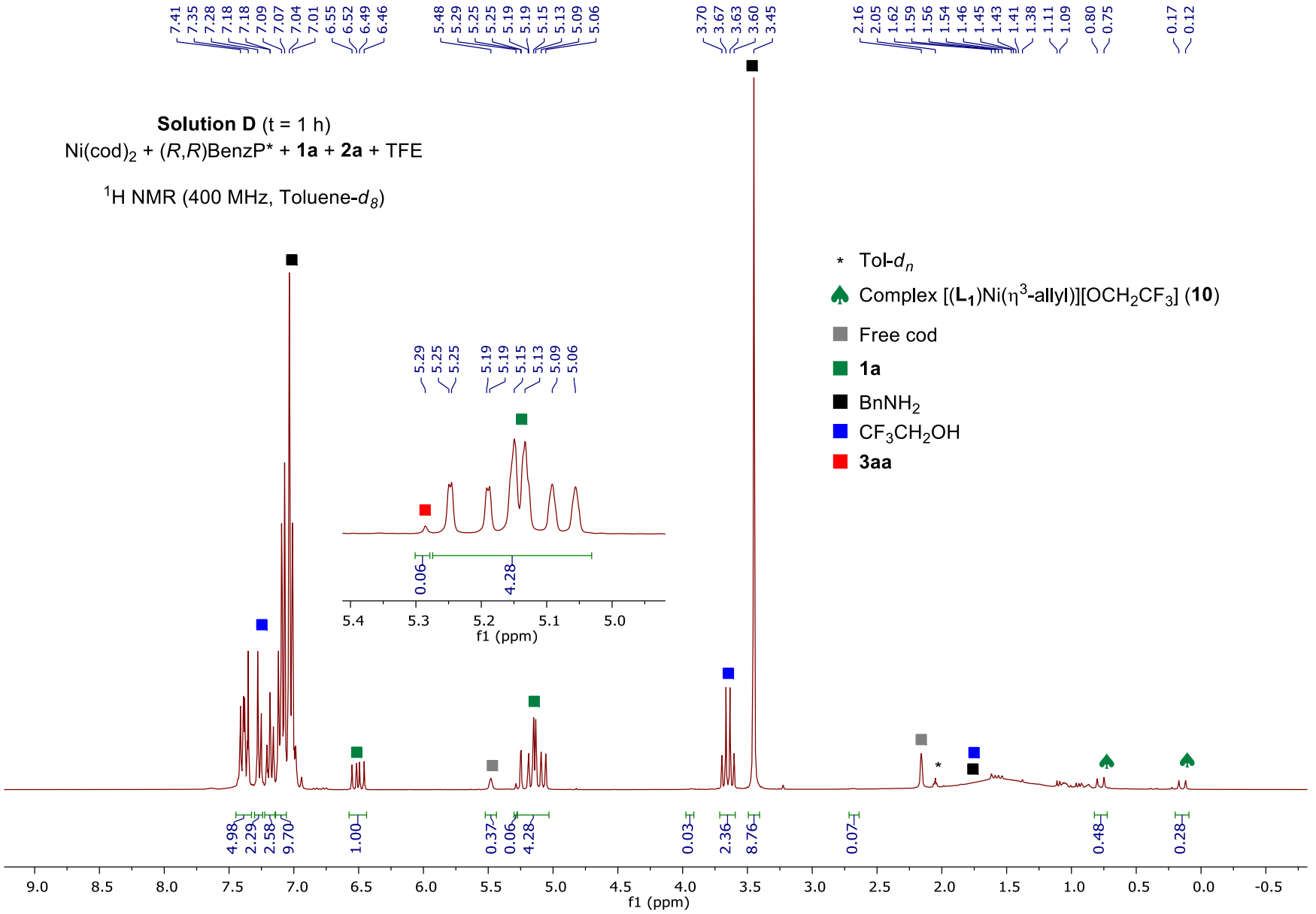

62.01
61.93
59.03
58.95
50.86
50.84
37.37
-19.49
-19.51
-26.63
Solution D (t = 15 min)
Ni(cod)2 + (R,R)BenzP* + 1a + 2a + TFE
31P{1H} NMR (160 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
L1 monophosphine oxide
L1
f1 (ppm)
0.99
1.00
11.68
11.34
0.99
3.19
1.00
4.30

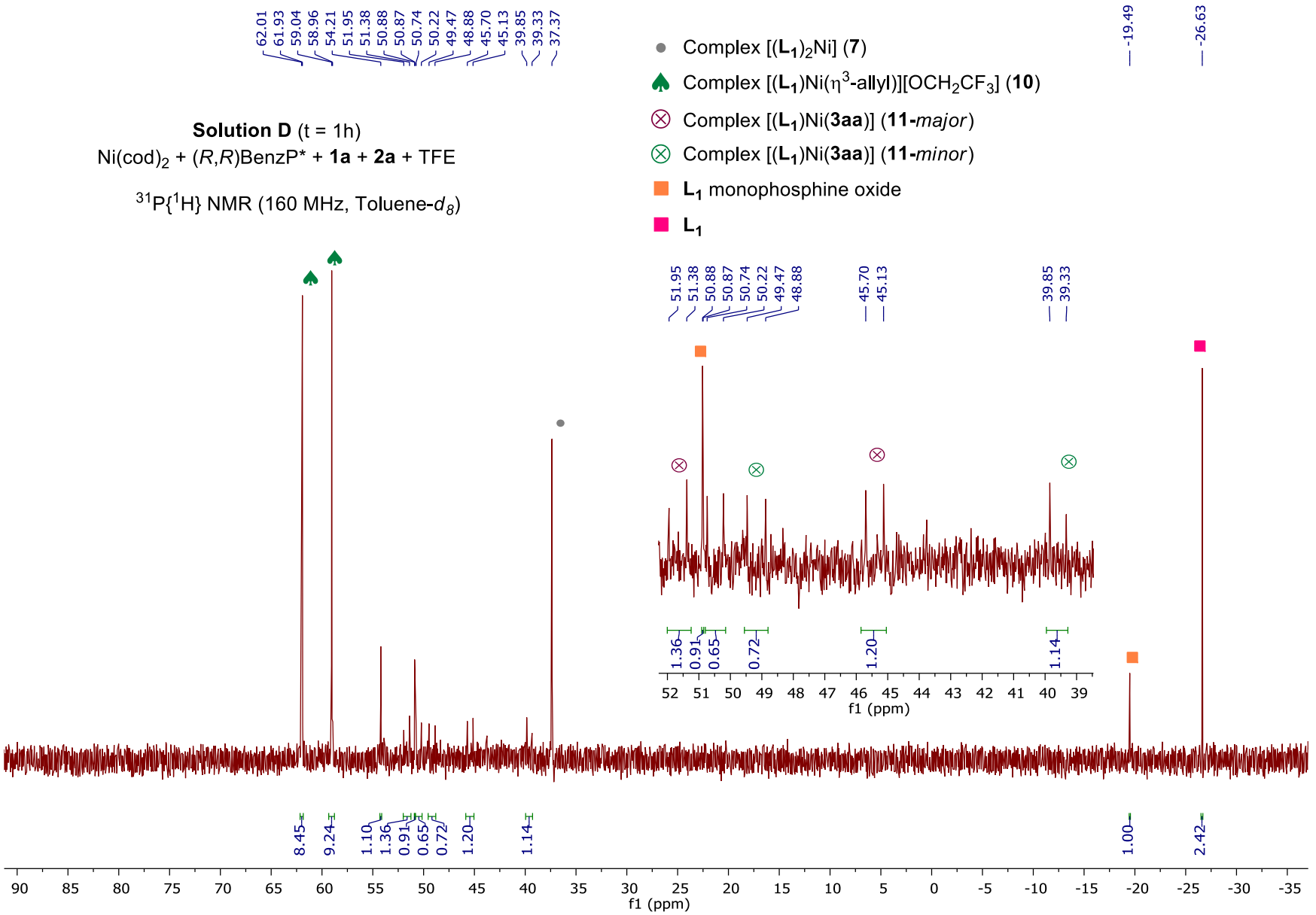
Solution D (t = 15 min)

$Ni(cod)_2$ + (*R*,*R*)BenzP* + **1a** + **2a** + TFE

$^{19}F\{^1H\}$ NMR (280 MHz, Toluene-d_8)




Solution D (t = 1 h)
Ni(cod)2 + (R,R)BenzP* + 1a + 2a + TFE
1H NMR (400 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
Free cod
1a
BnNH2
CF3CH2OH
3aa
f1 (ppm)


62.01
61.93
59.04
58.96
54.21
51.95
51.38
50.88
50.87
50.74
50.22
49.47
48.88
45.70
45.13
39.85
39.33
37.37
-19.49
-26.63
Solution D (t = 1h)
Ni(cod)2 + (R,R)BenzP* + 1a + 2a + TFE
31P{1H} NMR (160 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
Complex [(L1)Ni(3aa)] (11-major)
Complex [(L1)Ni(3aa)] (11-minor)
L1 monophosphine oxide
L1
8.45
9.24
1.10
1.36
0.91
0.65
0.72
1.20
1.14
1.00
2.42
f1 (ppm)

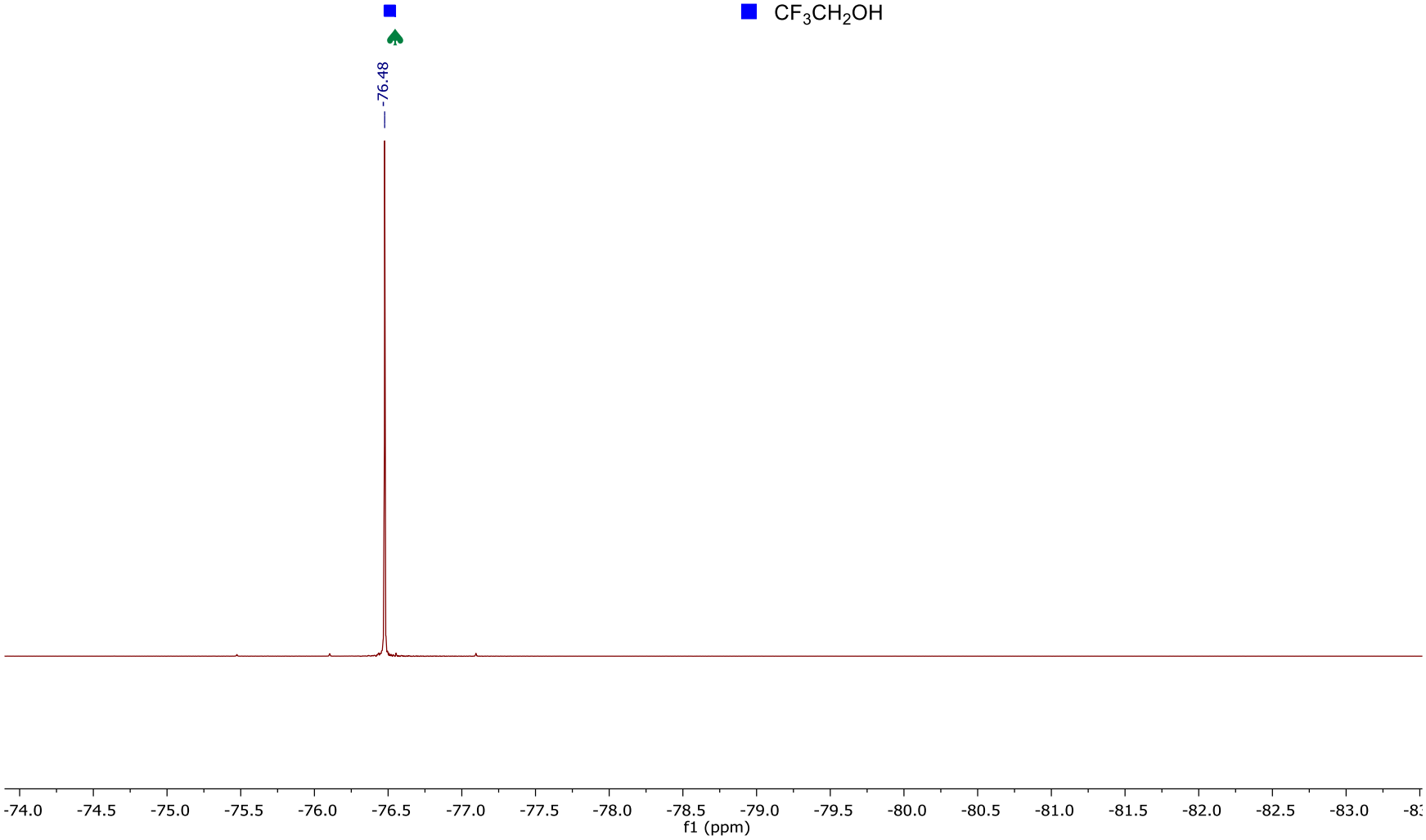
Solution D (t = 1 h)

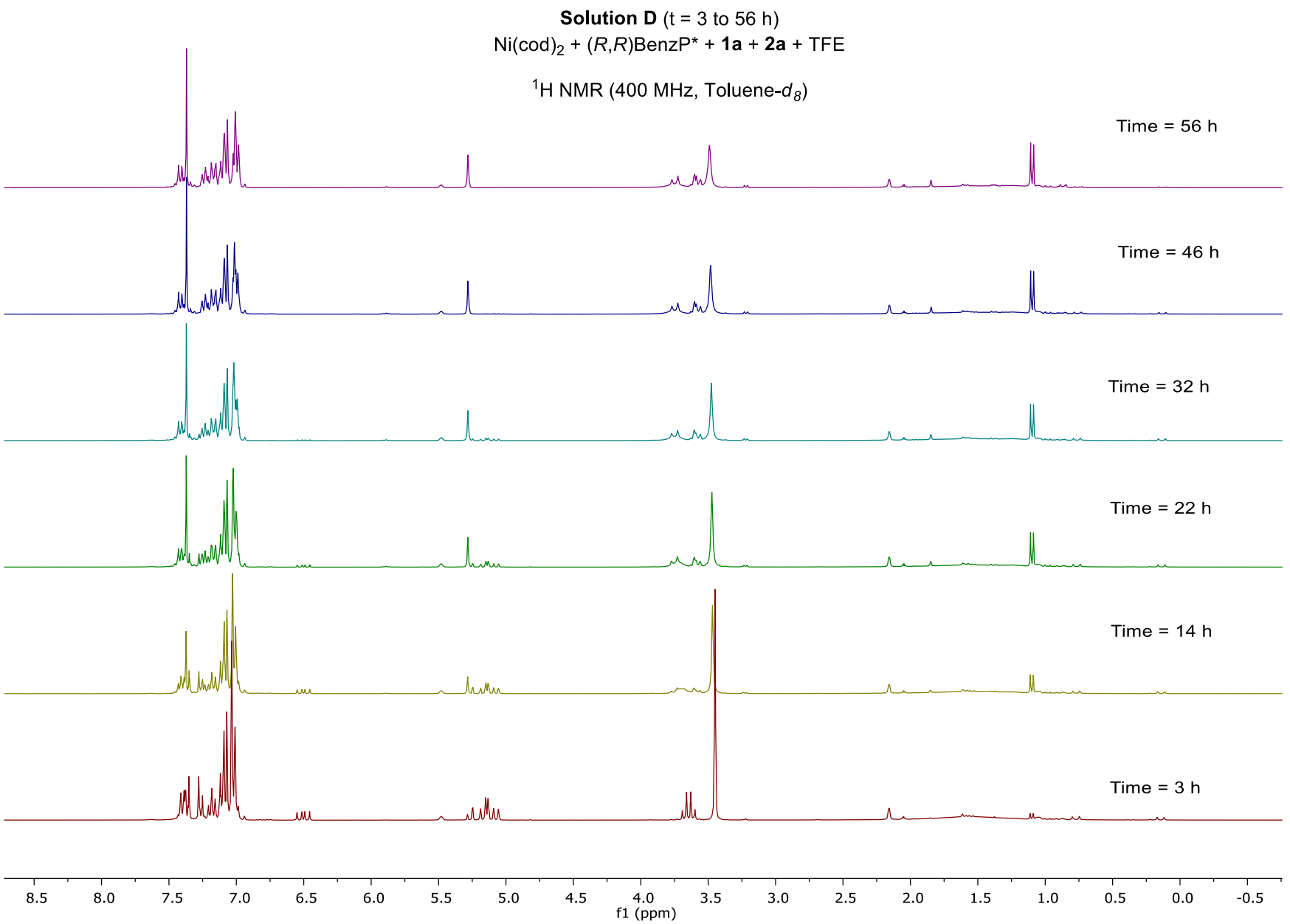
$Ni(cod)_2$ + (*R*,*R*)BenzP* + **1a** + **2a** + TFE

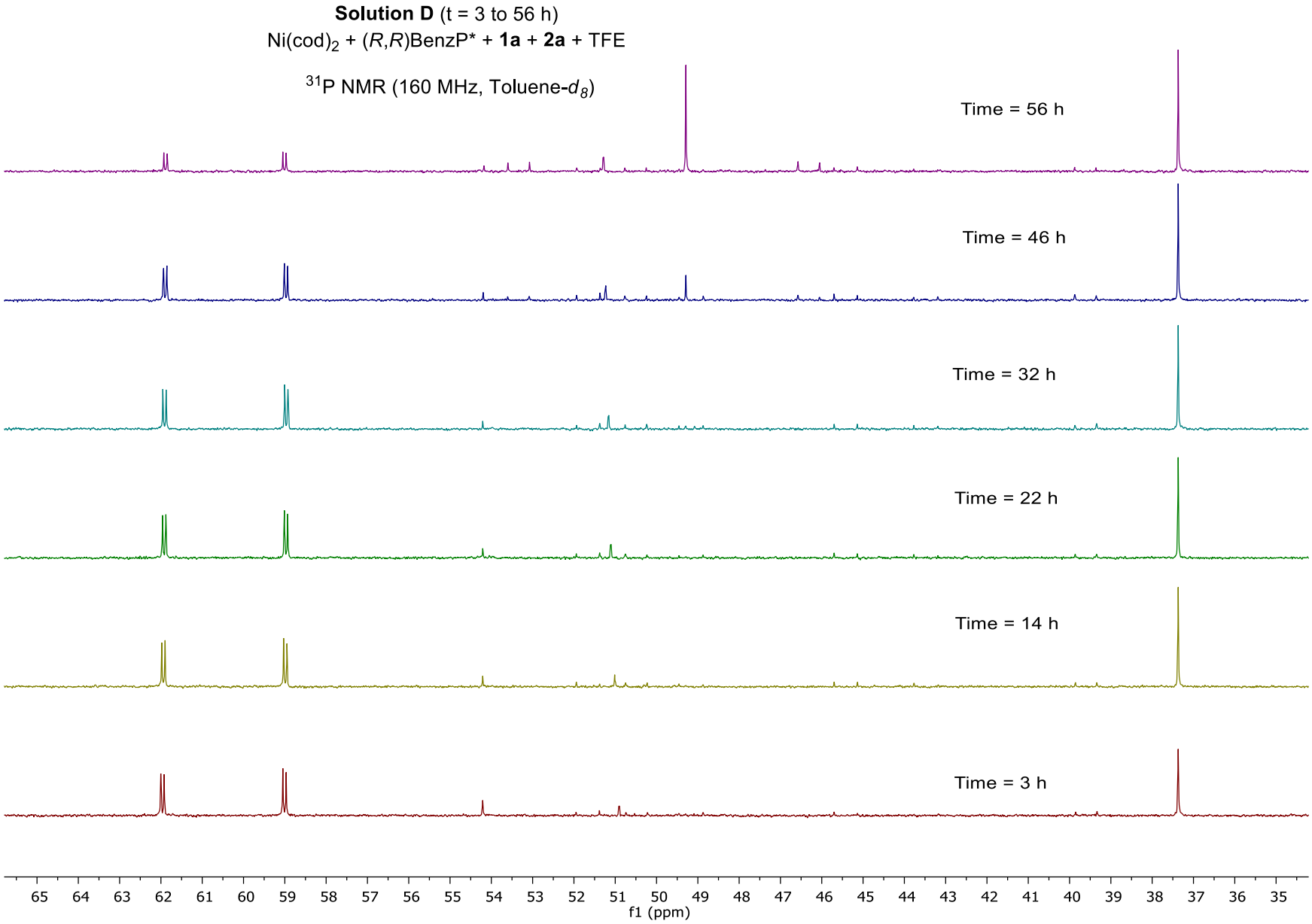
$^{19}F\{^1H\}$ NMR (280 MHz, Toluene-d_8)

♠ Complex [($\mathbf{L_1}$)Ni(η^3-allyl)][OCH_2CF_3] (**10**)

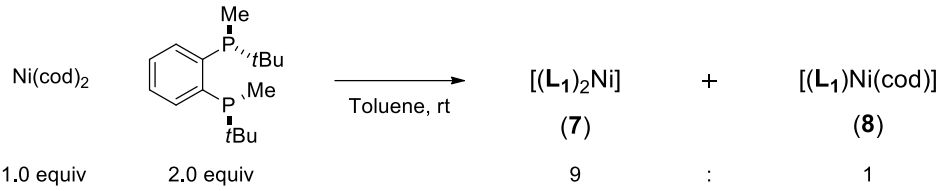
■ CF_3CH_2OH

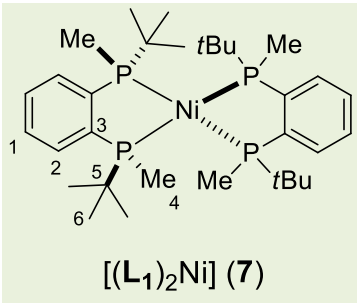



Solution D (t = 3 to 56 h)
Ni(cod)$_2$ + (*R*,*R*)BenzP* + **1a** + **2a** + TFE
^{1}H NMR (400 MHz, Toluene-d_8)
Time = 56 h
Time = 46 h
Time = 32 h
Time = 22 h
Time = 14 h
Time = 3 h
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Solution D (t = 3 to 56 h)
Ni(cod)$_2$ + (*R*,*R*)BenzP* + **1a** + **2a** + TFE
^{31}P NMR (160 MHz, Toluene-d_8)
Time = 56 h
Time = 46 h
Time = 32 h
Time = 22 h
Time = 14 h
Time = 3 h
65 64 63 62 61 60 59 58 57 56 55 54 53 52 51 50 49 48 47 46 45 44 43 42 41 40 39 38 37 36 35
f1 (ppm)

7.2. Synthesis of [(L$_1$)$_2$Ni] (7)





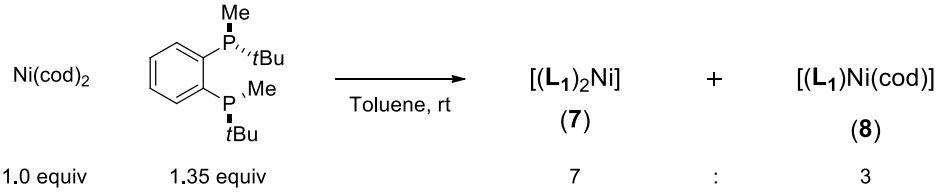
In a N_2-filled glovebox, a solution of Ni(cod)$_2$ (13.8 mg, 0.05 mmol, 1.0 equiv) and (R,R)BenzP* **L$_1$** (28.2 mg, 0.10 mmol, 2.0 equiv) in toluene (1.0 mL) was stirred for 2 h, then subjected to vacuum for 1 h. The resulting red-orange oil was dissolved in toluene (1.0 mL), and subjected to thr*ee* supplementary cycles of stirring (1 h)/vacuum (1 h)/dissolution (toluene, 1.0 mL), leading to a mixture of homoleptic complex [(**L$_1$**)$_2$Ni] (**7**) and [(**L$_1$**)Ni(cod)] (**8**) (red-orange oil, 33 mg, 9:1 ratio in favor of **7**).

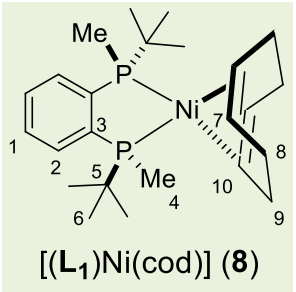
^{1}H NMR (500 MHz, Toluene-*d$_8$*) δ (ppm) = 7.71 – 7.64 (m, 2H, H-*1*), 7.12 – 7.07 (m, 2H, H-*2*), 1.68 (s, 6H, H-*4*), 1.14 – 1.09 (m, 9H, H-*6*).

^{13}C{^{1}H} NMR (130 MHz, Toluene-*d$_8$*) δ (ppm) = 149.9 – 148.9 (m, *C*-3), 129.3 (p_{app}, J_{PC} = 3 Hz, *C*H-2), 127.1 (*C*H-1), 32.2 (p_{app}, J_{PC} = 7 Hz, *C*-5), 28.9 (p_{app}, J_{PC} = 3 Hz, *C*H$_3$-6), 15.8 (p_{app}, J_{PC} = 8 Hz, *C*H$_3$-4).

^{31}P{^{1}H} NMR (160 MHz, Toluene-*d$_8$*) δ (ppm) = 37.37.

7.3. Synthesis of [(L$_1$)Ni(cod)] (8)





In a N_2-filled glovebox, a solution of Ni(cod)$_2$ (6.9 mg, 0.025 mmol, 1.0 equiv) and (*R*,*R*)BenzP* **L$_1$** (7.8 mg, 0.0275 mmol, 1.1 equiv) in toluene (1.0 mL) was stirred for 2 h, then subjected to vacuum for 1 h. The resulting red-orange oil was dissolved in toluene (1.0 mL), and subjected to thr*ee* supplementary cycles of stirring (1 h)/vacuum (1 h)/dissolution (toluene, 1.0 mL). Additional amounts of (*R*,*R*)BenzP* (1.5 mg, 0.0053 mmol, 0.25 equiv) were then added, followed by toluene (1.0 mL) and the reaction mixture was subjected to thr*ee* cycles of stirring (1 h)/vacuum

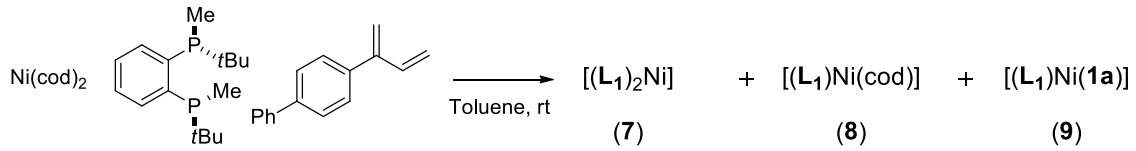
(1 h)/dissolution (toluene, 1.0 mL), leading to a mixture of [(**L₁**)₂Ni] (**7**) and [(**L₁**)Ni(cod)] (**8**) (red-orange oil, 13 mg, 7:3 ratio in favor of **8**).

^{1}H NMR (500 MHz, Toluene-*d₈*) δ (ppm) = 7.50 – 7.46 (m, 2H, H-*2*), 7.11 – 7.06 (m, 2H, H-*1*), 4.48 – 4.33 (m, 2H, H-*10*), 4.28 – 4.16 (m, 2H, H-*7*), 2.85 – 2.77 (m, 4H, H-*8* + H-*9*), 2.34 – 2.24 (m, 2H, H-*8* + H-*9*), 2.08 – 2.00 (m, 2H, H-*8* + H-*9*), 1.43 (d, $^{2}J_{PH}$ = 5.2 Hz, 6H, H-*4*), 0.92 (d, $^{3}J_{PH}$ = 12.7 Hz, 18H, H-*6*).

^{13}C{^{1}H} NMR (130 MHz, Toluene-*d₈*) δ (ppm) = 147.6 – 146.7 (m, *C-3*), 130.2 (t_{app}, J_{PC} = 7 Hz, *C*H-*2*), 127.8 (*C*H-*1*), 82.8 (CH-7), 81.9 (t_{app}, J_{PC} = 4 Hz, *C*H-*10*), 37.5 (t_{app}, J_{PC} = 6 Hz, *C*H_2-*8*), 32.31 – 31.95 (m, *C-5*), 28.1 (*C*H_2-*9*), 27.0 (t_{app}, J_{PC} = 4 Hz, *C*H_3-*6*), 8.28 (t_{app}, J_{PC} = 8.1 Hz, *C*H_3-*4*)

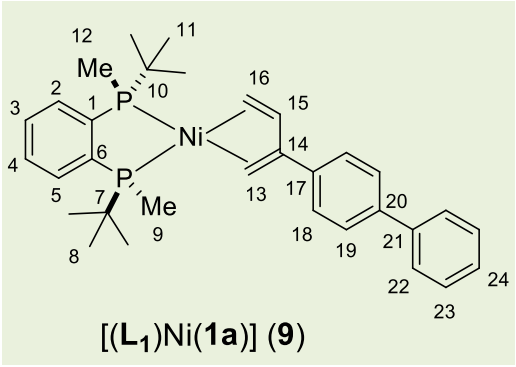
^{31}P{^{1}H} NMR (160 MHz, Toluene-*d₈*) δ (ppm) = 49.26.

7.4. Synthesis of [(L₁)Ni(1a)] (9)



In a N_2-filled glovebox, a solution of Ni(cod)₂ (27.5 mg, 0.10 mmol, 1.0 equiv) and (*R*,*R*)BenzP* **L₁** (28.2 mg, 0.10 mmol, 1.0 equiv) and 4-(buta-1,3-dien-2-yl)-1,1'-biphenyl **1a** (21.1 mg, 0.10 mmol, 1.0 equiv) in toluene (1.0 mL) was stirred for 0.5 h, then subjected to high vacuum for 1 h. The resulting red-orange oil was dissolved in toluene (1.0 mL), and subjected to ten supplementary cycles of stirring (1 h)/vacuum (1 h)/dissolution (toluene, 1.0 mL), leading to a mixture of [(**L₁**)Ni(cod)] (**8**) and [(**L₁**)Ni(**1a**)] (**9**) (red-orange oil, 56.0 mg, 94:6 ratio in favor of **9**). Residual peaks from diene **1a** and [(**L₁**)₂Ni] (**7**) were also present. *Due to the fluxional nature of the complex at rt, all 1D and 2D NMR spectra presented numerous weak and/or broad signals. Some carbons, such as olefinic carbons 13-16, were not even observed. Moreover, the presence of residual* [(**L₁**)Ni(cod)] (**8**) *further complicates the interpretation of the NMR spectra. Nevertheless, we propose a tentative assignment for some of the most well defined peaks, but urge the reader to take them with caution.*

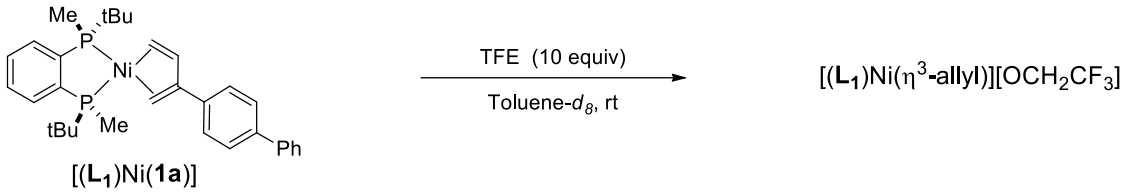
^{1}H NMR (500 MHz, Toluene-*d₈*) δ (ppm) = 7.71 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, H-*18*), 7.48 (m, H-*Ar*), 7.22 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, H-*Ar*), 5.22 (s, 1H, C=C-*H*), 4.09 (s, 1H, C=C-*H*), 3.66 (s, 1H, C=C-*H*), 3.09 (s, 1H, C=C-*H*), 2.83 (s, 1H, C=C-*H*), 1.46 (d, $^{2}J_{PH}$ = 5.4 Hz, 3H, H-*9* or H-*12*), 1.17 (d, $^{2}J_{PH}$ = 3.9 Hz, 3H, H-*9* or H-*12*), 0.95 (d, $^{3}J_{PH}$ = 13.4 Hz, 9H, H-*8* or H-*11*), 0.82 (d, $^{3}J_{PH}$ = 13.4 Hz, 9H, H-*8* or H-*11*).



$^{13}C\{^1H\}$ NMR (130 MHz, Toluene-d_8) δ (ppm) = 147.6 – 145.8 (*C-1* or *C-6*), 144.4 (C-*Ar*), 141.8 (*C-Ar*), 138.3 (*C-Ar*), 130.6 (d, $^1J_{PC}$ = 11 Hz, *CH-2* or CH-*5*), 130.1 (d, $^1J_{PC}$ = 11 Hz, *CH-2* or *CH-5*), 129.2 (*CH-Ar)*, 128.9 (*CH-Ar)*, 128.4 (*CH-Ar)*, 127.6– 127.1 (m, *CH-Ar*), 127.1 (*CH-Ar)*, 127.0 (*CH-Ar)*, 126.9 (*CH-Ar)*, 126.5 (*CH-Ar)*, 32.7 – 32.2 (m, *C-7* or *C-10*), 31.9 (dd, $^1J_{PC}$ = 16, $^4J_{PC}$ = 4 Hz, *C-7* or *C-10*), 27.4 (t_{app}, J_{PC} = 7 Hz, CH_3-*8* and CH_3-11), 9.9 (CH_3-*9* or CH_3-*12*), 7.1 (CH_3-*9* or CH_3-*12*).

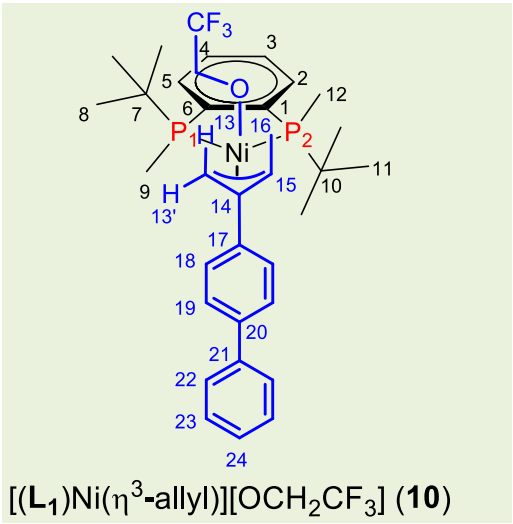
$^{31}P\{^1H\}$ NMR (160 MHz, Toluene-d_8) δ (ppm) = 57.91(broad), 40.44 (broad).

7.5. Synthesis of [(L₁)Ni(η³-allyl)][OCH₂CF₃] (10)



[(**L₁**)Ni(**1a**)] (**9**)

(**10**)



In a N_2-filled glovebox, a 2 mL vial was charged with complex [(**L₁**)Ni(**1a**)] (**9**) (5.5 mg, 0.010 mmol, 1.0 equiv), followed by toluene-d_8 (0.60 mL). To the resulting orange solution was added a 1.0 M solution of CF_3CH_2OH in toluene-d_8 (0.10 mL, 0.10 mmol, 10.0 equiv). The solution immediately changed color to pale orange/yellow. 0.40 mL of this solution was introduced in a J-Young tube and analyzed by NMR.

Due to the reversible nature of the reaction, the complex [(**L₁**)Ni(η³-allyl)][OCH_2CF_3] (**10**) *could only be observed in solution. Indeed, in vaccum concentration of this solution resulted in quantitative regeneration of the starting complex* [(**L₁**)Ni(**1a**)] (**9**).

^1H NMR (500 MHz, Toluene-d_8) δ (ppm) = 7.49 – 7.31 (m, 8H, H-*Ar*), 7.23 (t, $^3J_{HH}$ = 7.7 Hz, 2H, H-*Ar*), 7.16 – 7.12 (m, 1H, H-*24*), 7.11 – 7.09 (m, 2H, H-*18*), 5.43 – 5.20 (m, 1H, H-*15*), 3.90 – 3.86 (m, 1H, H-*13'*), 2.72 – 2.67 (m, 1H, H-*13*), 1.54 (d, $^2J_{PH}$ = 8.5 Hz, 3H, H-*9*), 1.50

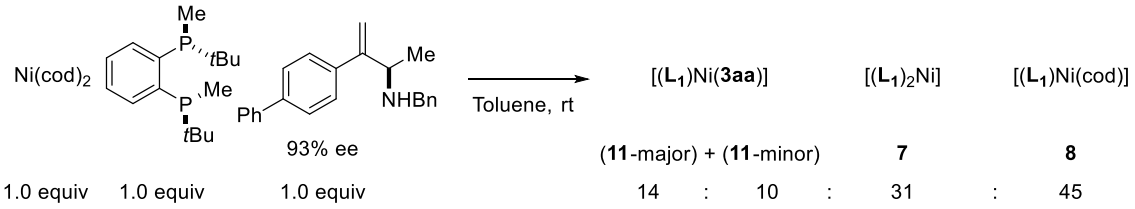
(d, $^2J_{PH}$ = 8.5 Hz, 3H, H-*12*), 0.90 – 0.86 (m, 3H, H-*16*), 0.80 (d, $^3J_{PH}$ = 15.6 Hz, 9H, H-*8*), 0.16 (d, $^3J_{PH}$ = 15.6 Hz, 9H, H-*11*).

^{13}C{^{1}H} NMR (130 MHz, Toluene-d_8) δ (ppm) = 143.3 (*C-20*), 139.8 (*C-21*), 139.5 – 138-5 (m, *C-1* and *C-6*), 137.1 (*C-17*), 132.3 – 131.9 (*CH-2* or *CH-5*), 131.8 (d, $^2J_{PP}$ = 14 Hz, *CH-2* or *CH-5*), 129.3 (*CH-22*), 128.4 (*CH-24*), 127.6 (*CH-3* or *CH-4*), 127.2 (*CH-3* or *CH-4*), 123.1 (*C-14*), 76.7 (d, $^2J_{PP}$ = 15 Hz, *CH-15*), 55.2 (dd, $^2J_{PP}$ = 19, 3 Hz, *CH$_2$-13*), 32.9 (d, $^2J_{PP}$ = 14 Hz, *C-7* or *C-10*), 32.7 (d, $^1J_{PP}$ = 13 Hz, *C-7* or *C-10*), 26.9 (d, $^2J_{PP}$ = 5 Hz, *CH$_3$-8*), 25.9 (d, $^2J_{PP}$ = 5 Hz, *CH$_3$-11*), 14.8 (*CH$_3$-16*), 7.7 (d, $^1J_{PP}$ = 25 Hz, *CH$_3$-9*), 5.3 (d, $^1J_{PP}$ = 24 Hz, *CH$_3$-12*).

^{31}P{^{1}H} NMR (160 MHz, Toluene-d_8) δ (ppm) = 61.51 (d, $^3J_{PP}$ = 9.7 Hz, P-*1*), 58.58 (d, $^3J_{PP}$ = 9.7 Hz, P-*2*).

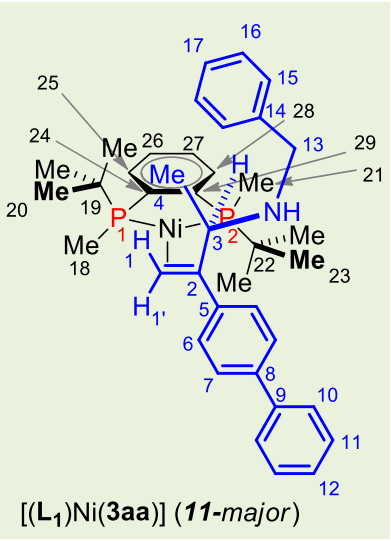
^{19}F{^{1}H} NMR (280 MHz, Toluene-d_8) δ (ppm) = -76.87.

7.6. Synthesis of [(L$_1$)Ni(3aa)] (11)



In a N_2-filled glovebox, to a solution of Ni(cod)$_2$ (8.8 mg, 0.032 mmol, 1.0 equiv) and (*R*,*R*)BenzP* **L$_1$** (9.0 mg, 0.032 mmol, 1.0 equiv) in toluene (0.50 mL) was added **3aa** (10.0 mg, 0.032 mmol, 1.0 equiv, 93% *ee*). The resulting solution was stirred for 1.0 h, then subjected to high vacuum for 1 h. The resulting red-orange oil was dissolved in toluene (1.0 mL), and subjected to ten supplementary cycles of stirring (1 h)/vacuum (1 h)/dissolution (toluene, 1.0 mL), leading to a mixture of two product-bound complexes [(**L$_1$**)Ni(**3aa**)] (**11**-*major*) and [(**L$_1$**)Ni(**3aa**)] (**11**-*minor*), along with [(**L$_1$**)$_2$Ni] (**7**) and [(**L$_1$**)Ni(cod)] (**8**) (red-orange oil, 18.0 mg, ratio **11**-*major*/**11**-*minor*/**7**/**8**=14:10:31:45).

Due to the complexity of mixture, it was not possible to fully attribute the ^{1}H and ^{13}C NMR peaks present in the spectrum. Nevertheless, we are confident that the observed peaks and correlations for **11**-*major are consistent with a* [(**L$_1$**)Ni(**3aa**)] *complex bound through the olefin π-system of* ***3aa****. Whether the nitrogen is bound or not is unclear. Only the peaks that could be attributed with confidence to this complex are reported. Due to numerous overlaps, we were not able to perform such an analysis for* **11**-*minor, and the corresponding peaks are not reported.*



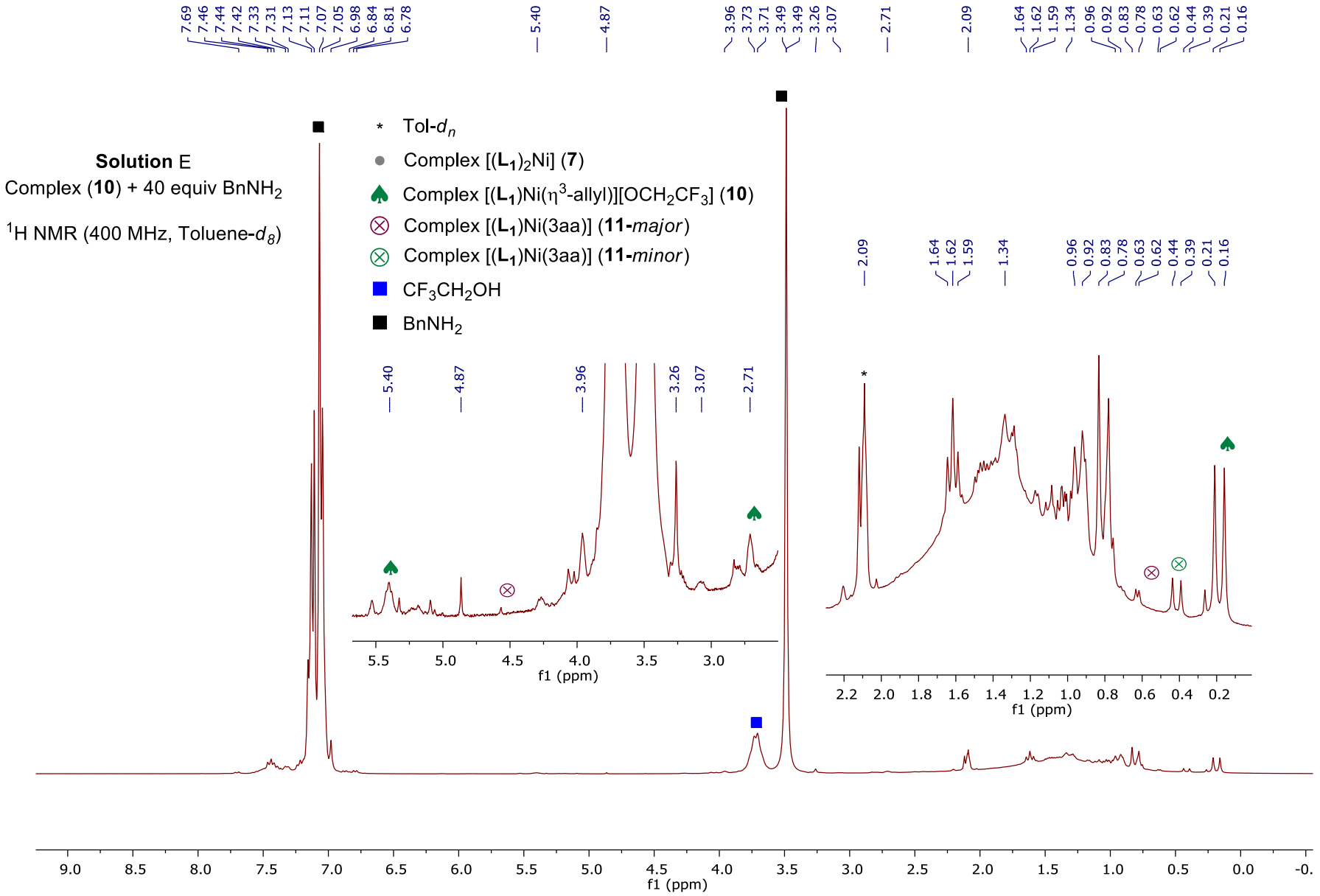
^{1}H NMR (500 MHz, Toluene-d_8) δ (ppm) = 4.31 – 4.25 (m, 1H, H-*3*), 4.07 – 4.02 (m, 1H, H-*13*), 3.89 – 3.84 (m, 1H, H-*13*), 3.25 (q_{app}, J = 4.5 Hz, 1H, H-*1'*), 2.53 (dt_{app}, J = 7.7, 4.1 Hz, 1H, H-*1'*), 1.65 (d, $^{3}J_{HH}$ = 5.8 Hz, 3H, H-*4*), 1.29 (d, $^{2}J_{PH}$ = 4.5 Hz, 3H, H-*18*), 1.01 (d, $^{3}J_{PH}$ = 13.2 Hz, 9H, H-*20*), 0.78 (d, $^{3}J_{PH}$ = 13.5 Hz, 9H, H-*23*), 0.63 (d, $^{2}J_{PH}$ = 5.2 Hz, 3H, H-*21*).

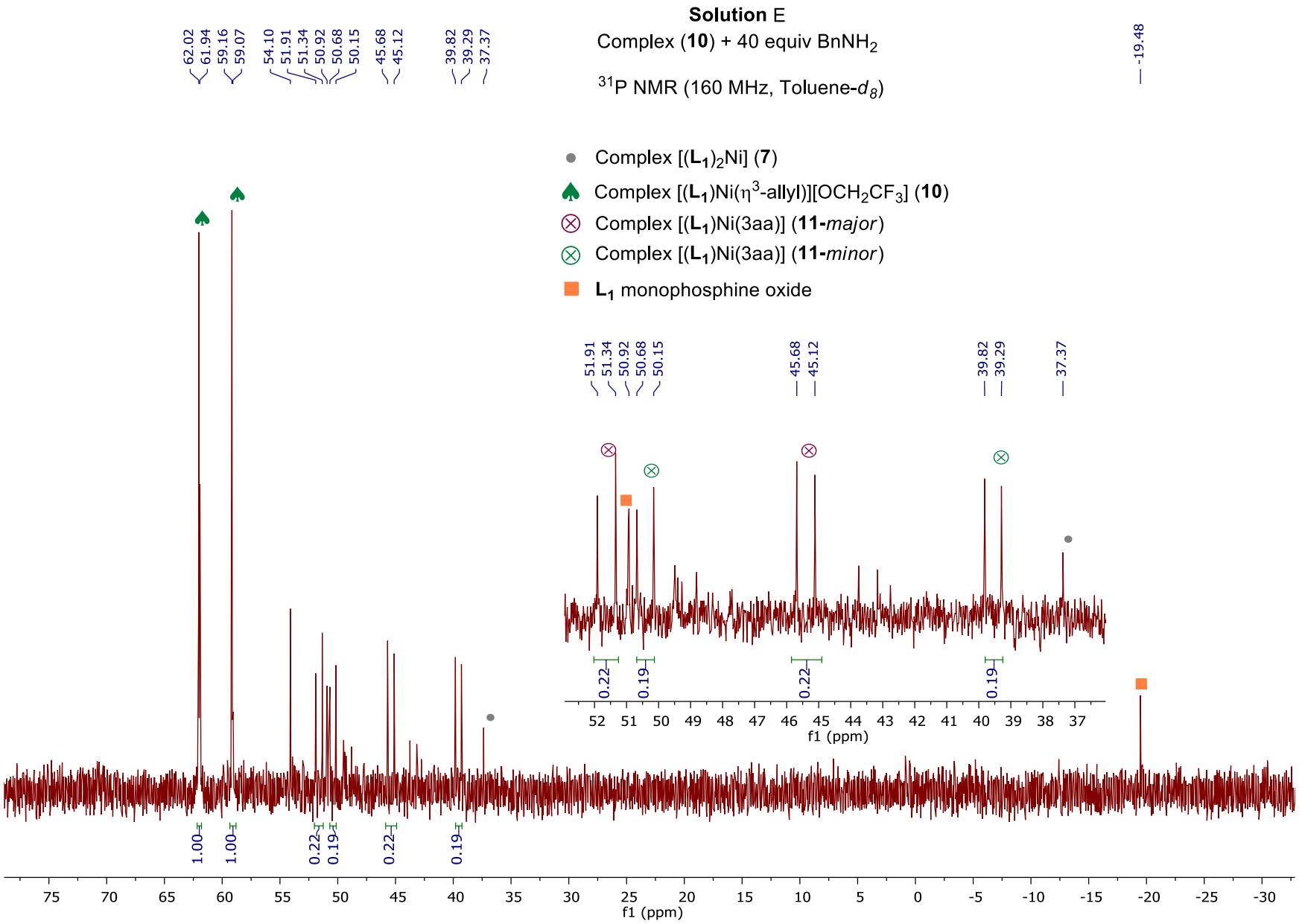
^{13}C{^{1}H} NMR (130 MHz, Toluene-d_8) δ (ppm) = 70.8 – 70.5 (m, *C-2*), 57.7 – 57.6 (m, *CH-3*), 49.1 (*CH_2-13*), 34.8 (dd, $^{2}J_{PP}$ = 22, 2 Hz, *CH_2-1*), 27.5 (dd, $^{2}J_{PP}$ = 8, $^{4}J_{PP}$ = 3 Hz, *CH_3-20*), 27.3 (d, $^{2}J_{PP}$ = 9 Hz, *CH_3-23*), 21.6 (*CH_3-4*), 7.9 (dd, $^{1}J_{PP}$ = 11, $^{4}J_{PP}$ = 8 Hz, *CH_3-18*), 4.7 (dd, $^{1}J_{PP}$ = 12, $^{4}J_{PP}$ = 5 Hz, *CH_3-21*).

^{31}P{^{1}H} NMR (160 MHz, Toluene-d_8) δ (ppm) = 51.58 (d, $^{3}J_{PP}$ = 69.4 Hz, P-*1*), 45.33 (d, $^{3}J_{PP}$ = 69.4 Hz, P-*2*).

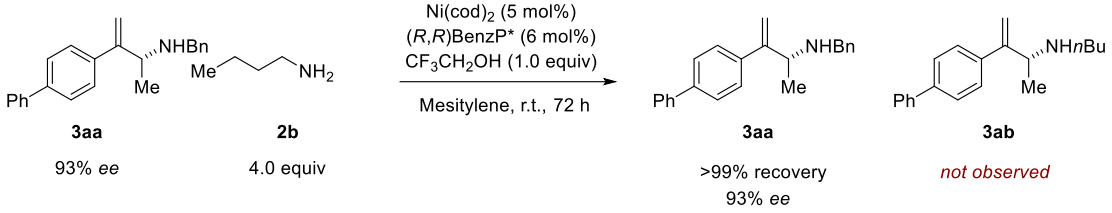
7.7. Reaction of [(L_1)Ni(η^3-allyl)][OCH_2CF_3] (10) with $BnNH_2$

In a N_2-filled glovebox, a 2 mL vial was charged with complex [(**L_1**)Ni(**1a**)] (**9**) (5.5 mg, 0.010 mmol, 1.0 equiv), followed by toluene-d_8 (0.60 mL). To the resulting orange solution was added a 1.0 M solution of CF_3CH_2OH in toluene-d_8 (0.10 mL, 0.10 mmol, 10.0 equiv). The solution immediately changed color to pale orange/yellow. $BnNH_2$ (43.0 mg, 0.40 mmol, 40.0 equiv) was then added, and the reaction mixture was stirred for 15 min (solution **E**). 0.40 mL of this solution was introduced in a J-Young tube and analyzed by ^1H and $^{31}P\{^1H\}$ NMR.


7.69
7.46
7.44
7.42
7.33
7.31
7.13
7.11
7.07
7.05
6.98
6.84
6.81
6.78
5.40
4.87
3.96
3.73
3.71
3.49
3.49
3.26
3.07
2.71
2.09
1.64
1.62
1.59
1.34
0.96
0.92
0.83
0.78
0.63
0.62
0.44
0.39
0.21
0.16
Solution E
Complex (10) + 40 equiv BnNH2
1H NMR (400 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
Complex [(L1)Ni(3aa)] (11-major)
Complex [(L1)Ni(3aa)] (11-minor)
CF3CH2OH
BnNH2
f1 (ppm)
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
-0.


Solution E
Complex (10) + 40 equiv BnNH2
31P NMR (160 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
Complex [(L1)Ni(3aa)] (11-major)
Complex [(L1)Ni(3aa)] (11-minor)
L1 monophosphine oxide
62.02
61.94
59.16
59.07
54.10
51.91
51.34
50.92
50.68
50.15
45.68
45.12
39.82
39.29
37.37
-19.48
1.00
1.00
0.22
0.19
0.22
0.19
f1 (ppm)
0.22
0.19
0.22
0.19
f1 (ppm)

8. Amine exchange experiment



3aa — 93% *ee*

2b — 4.0 equiv

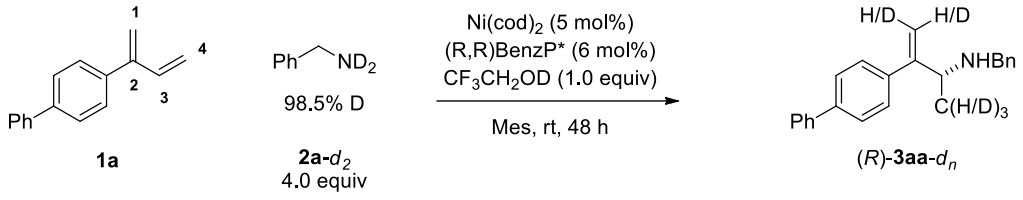
3aa — >99% recovery, 93% *ee*

3ab — *not observed*

In a N_2-filled glovebox, $Ni(cod)_2$ (1.4 mg, 0.005 mmol, , 5 mol%) and (*R*,*R*)-BenzP* **L_1** (1.7 mg, 0.006 mmol, 6 mol%) were weighted in a 5 mL Schlenk tube, and anhydrous mesitylene (0.20 mL, 0.5 M) was added. After stirring at room temperature for 10 min, allylic amine **3aa** (31.0 mg, 0.10 mmol, 1.0 equiv, 93% *ee*), *n*$BuNH_2$ **2b** (40 μL, 0.40 mmol, 4.0 equiv) and TFE (7 μL, 0.10 mmol, 1.0 equiv) were added sequentially. The tube was sealed, taken out of the glovebox and stirred at room temperature for 72 h. The reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (10 mL) and concentrated under vacuum to afford the crude mixture. Analysis by ^{1}H NMR showed >99% recovery of **3aa** and no traces of product **3ab**.

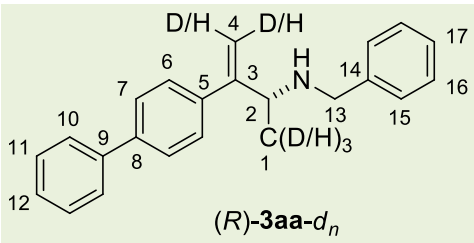
9. Deuterium labeling experiments

9.1. Model catalytic hydroamination using TFE-d_1 and $BnND_2$



Diene Cons.	Yield	ee	Deuterium Incorporation C1	C3	C4
>95%	76%	90%	57.5%	<2%	58%

In a N_2-filled glovebox, $Ni(cod)_2$ (3.4 mg, 0.0125 mmol, 5 mol%) and (*R*,*R*)-BenzP* **L_1** (4.2 mg, 0.015 mmol, 6 mol%) were weighted in a 5 mL Schlenk tube, and anhydrous mesitylene (0.50 mL, 0.5 M) was added. After stirring at room temperature for 10 min, diene **1a** (42.0 mg, 0.25 mmol, 1.0 equiv), TFE-d_1 (26.0 mg, 0.25 mmol, 1.0 equiv, 99.5% D) and Bn-ND_2 (110.0 mg, 1.00 mmol, 4.0 equiv, 98.5% D) were added sequentially. The tube was sealed, taken out of the glovebox and stirred at room temperature for 48 h. The reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (10 mL) and concentrated under vacuum to afford the crude mixture. Consumption of **1a**: >95%. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product **3aa**-d_n as a pale yellow oil (60.0 mg, 76% yield, 90% *ee*). ^{1}H NMR analysis showed 58% deuterium integration at C-*1* and 58% at C-*4*. No significant deuterium incorporation at any other position was observed.

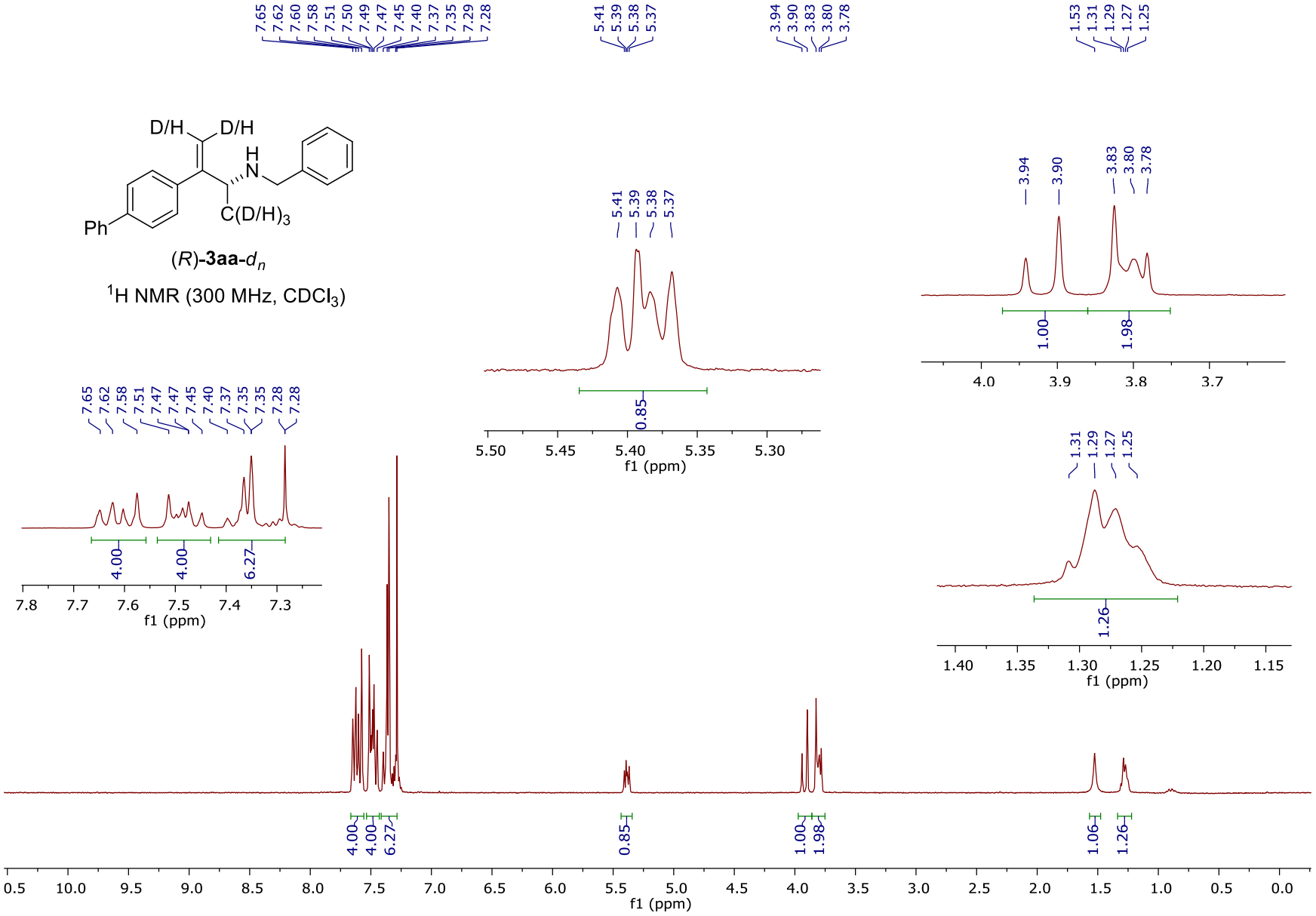


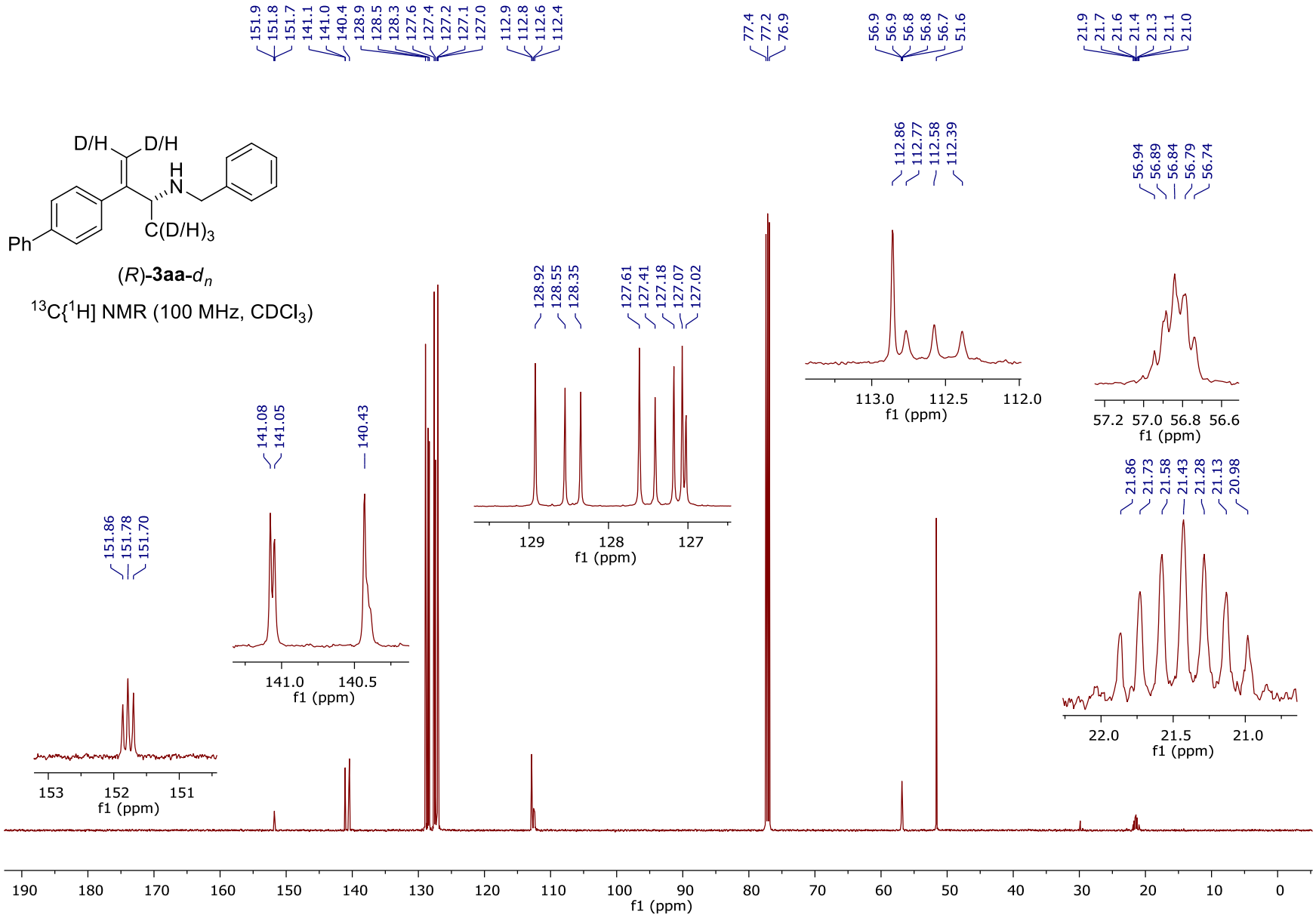
^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.56 (m, 4H, H-*Ar*), 7.53 – 7.43 (m, 4H, H-*Ar*), 7.42 – 7.29 (m, 6H, H-*Ar*), 5.42 – 5.34 (m, 0.85H, H-*4*), 3.92 (d, $^2J_{HH}$ = 13.1 Hz, 1H, H-*13*), 3.87 – 3.76 (m, 2H, H-*2* + H-*13*), 1.53 (s, 1H, N-H), 1.32 – 1.24 (m, 1.26H, H-*1*).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) = 152.3 – 150.9 (m, *C-3*), 141.08 (*C-Ar*), 141.05 (*C-Ar*), 140.4 (broad, *C-Ar*), 128.9 (*C*H-*Ar*), 128.6 (*C*H-*Ar*), 128.4 (*C*H-*Ar*), 127.6 (*C*H-*Ar*), 127.4 (*C*H-*Ar*), 127.2(*C*H-*Ar*), 127.1 (*C*H-*Ar*), 127.0 (*C*H-*Ar*), 113.20 – 112.02 (*C*(H/D)$_2$-*4*), 57.19 – 55.93 (*C*(H/D)$_1$-*2*), 51.6 (*C*H$_2$-*13*), 22.0 – 20.9 (m, *C*(H/D)$_3$-*1*).

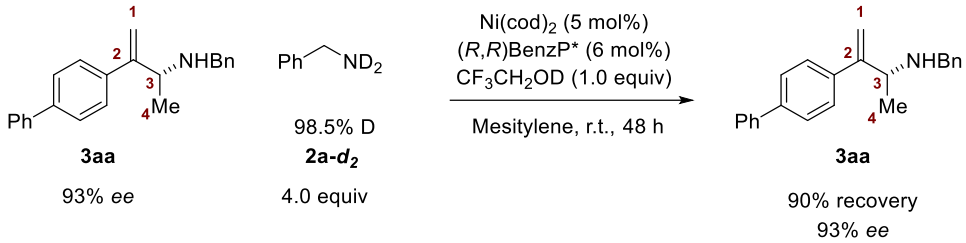
HRMS (ESI$^+$): calculated $[M+H]^+$ for $C_{17}H_{19}DN_2O^+$: 315.1942; found: 315.1969; 316.2030; 317.2091; 318.211 (major); 319.2205; 320.2244.

HPLC: 90% *ee*, chiral stationary column: OD-H, mobile phase: hexane/*i*PrOH = 99/1, 1mL/min, 254 nm, 30 °C, t_R (major) = 6.83 min, t_R (minor) = 15.14 min.


D/H
D/H
H
N
C(D/H)3
Ph
(R)-3aa-dn
1H NMR (300 MHz, CDCl3)
f1 (ppm)

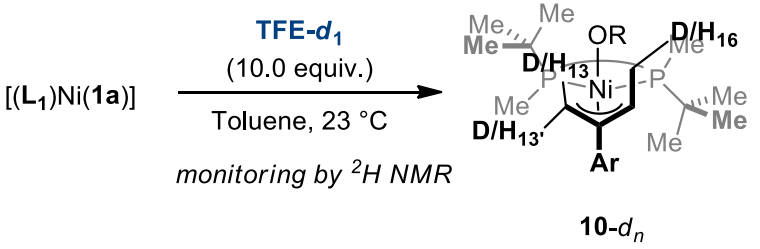

151.9
151.8
151.7
141.1
141.0
140.4
128.9
128.5
128.3
127.6
127.4
127.2
127.1
127.0
112.9
112.8
112.6
112.4
77.4
77.2
76.9
56.9
56.9
56.8
56.8
56.7
51.6
21.9
21.7
21.6
21.4
21.3
21.1
21.0
D/H
D/H
H
N
C(D/H)3
Ph
(R)-3aa-dn
13C{1H] NMR (100 MHz, CDCl3)
112.86
112.77
112.58
112.39
56.94
56.89
56.84
56.79
56.74
128.92
128.55
128.35
127.61
127.41
127.18
127.07
127.02
141.08
141.05
140.43
151.86
151.78
151.70
21.86
21.73
21.58
21.43
21.28
21.13
20.98
f1 (ppm)

9.2. Post-reaction deuterium incorporation experiment



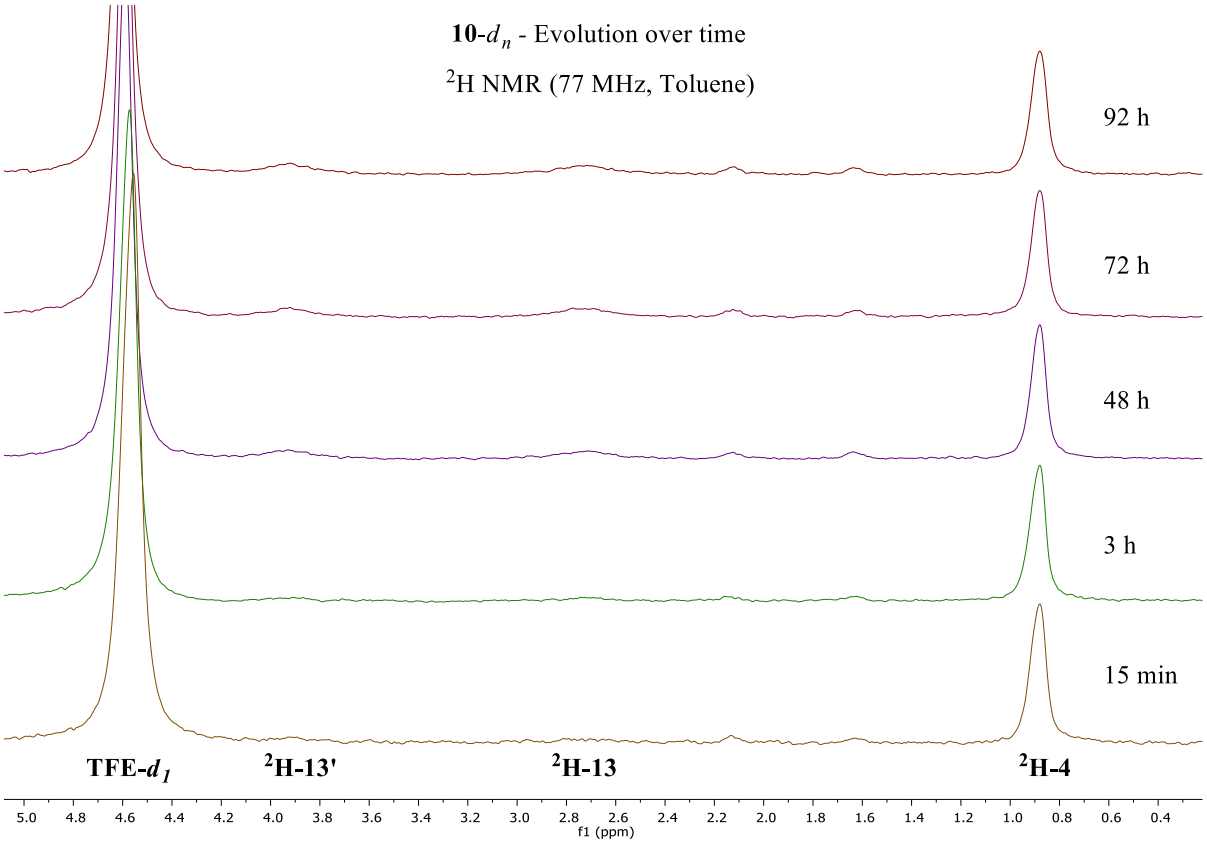
In a N_2-filled glovebox, $Ni(cod)_2$ (1.4 mg, 0.005 mmol, , 5 mol%) and (*R*,*R*)-BenzP* **L_1** (1.7 mg, 0.006 mmol, 6 mol%) were weighted in a 5 mL Schlenk tube, and anhydrous mesitylene (0.20 mL, 0.5 M) was added. After stirring at room temperature for 10 min, allylic amine **3aa** (31 mg, 0.10 mmol, 1.0 equiv, 93% *ee*), TFE-d_1 (10.0 mg, 0.10 mmol, 1.0 equiv, 99.5% D) and Bn-ND_2 (44.0 mg, 0.40 mmol, 4.0 equiv, 98.5% D) were added sequentially. The tube was sealed, taken out of the glovebox and stirred at room temperature for 48 h. The reaction mixture was filtered over a short pad of silica gel, washed with ethyl acetate (10 mL) and concentrated under vacuum to afford the crude mixture. Purification by flash chromatography over silica gel (pentane:EtOAc = 4:1) led to the desired product **3aa** as a pale yellow oil (28.0 mg, 90% recovery, 93% *ee*). ^1H NMR analysis did not show any trace of deuterium incorporation at any position.

9.3. Synthesis of 10-d_n using TFE-*d1* - ^{2}H NMR monitoring

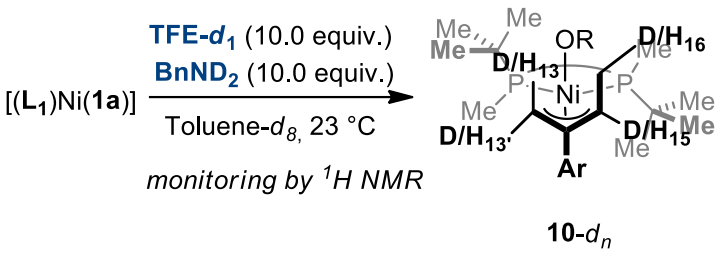


Time	^{2}H NMR integrals ^{2}*H-13*	^{2}*H-13'*	^{2}*H-16*
15 min	*<0.05*	*<0.05*	1.00
3 h	*<0.05*	*<0.05*	1.00
48 h	*0.13*	*0.16*	1.00
48 h	*0.14*	*0.16*	1.00
72 h	*0.20*	*0.24*	1.00

In a N_2-filled glovebox, a 2 mL vial was charged with complex [(**L$_1$**)Ni(**1a**)] (**9**) (5.5 mg, 0.010 mmol, 1.0 equiv), followed by toluene (0.60 mL). To the resulting orange solution was added a 1.0 M solution of CF_3CH_2OD in toluene (0.10 mL, 0.10 mmol, 10.0 equiv). The color of the solution changed immediately to pale orange/yellow. 0.40 mL of this solution was introduced in a J-Young tube. ^{2}H NMR monitoring showed very rapid and selective deuterium incorporation at C-*4* (D/H-16), and very slow deuterium incorporation at C-*1* (D/H-13 and D/H-13').



9.4. Synthesis of 10-d_n using TFE-d_1 and $BnND_2$- ^{1}H NMR monitoring



10-d_n

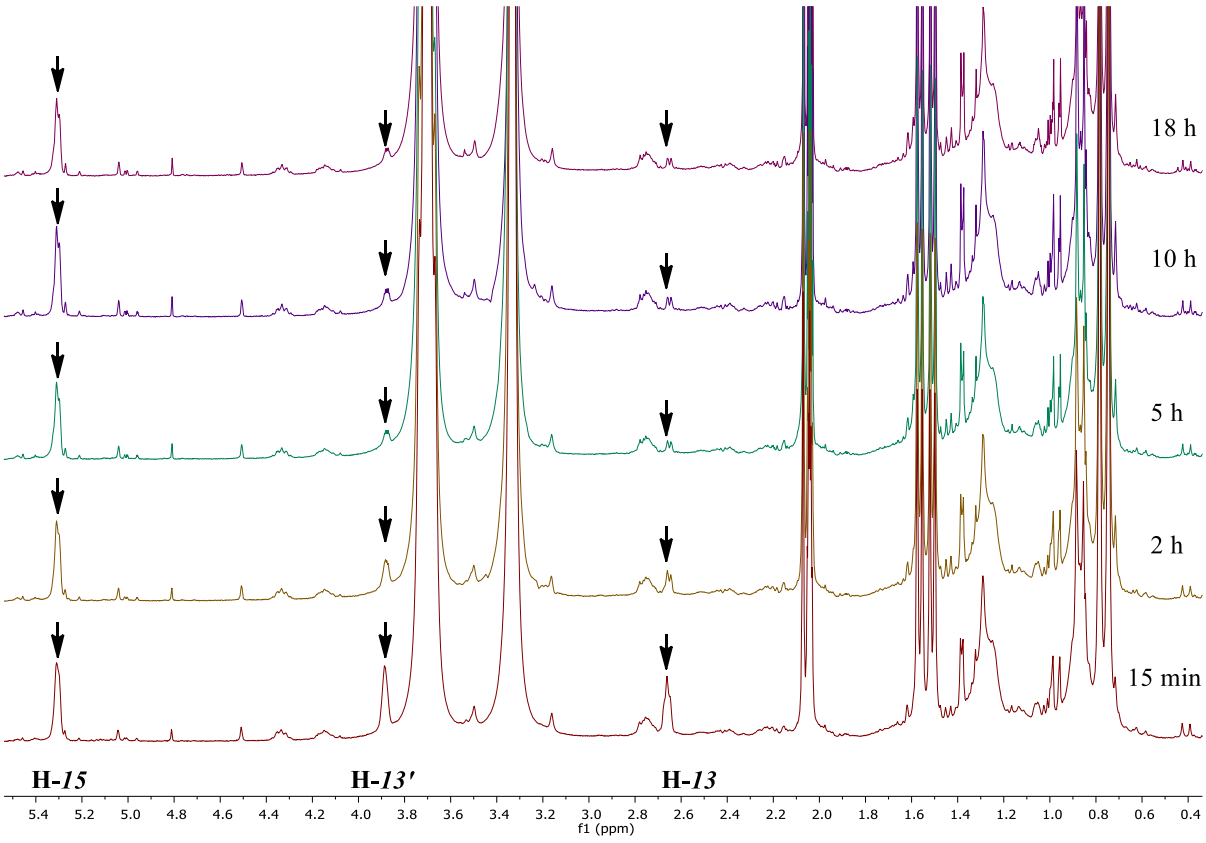
Time	^{1}H NMR integrals[a]		
	^{1}H-13'	*^{1}H-13*	*^{1}H-15*
20 min	1.03	0.84	1.00
2 h	0.65	0.45	1.00
5 h	0.36	0.24	0.95
10 h	0.35	0.22	1.02
18 h	0.38	0.24	1.01

a) ^{t}Bu signals from the ligand backbone were used as internal reference.

In a N_2-filled glovebox, a 2 mL vial was charged with complex [(**L$_1$**)Ni(**1a**)] (**9**) (16.6 mg, 0.030 mmol, 1.0 equiv), followed by toluene-d_8 (1.0 mL). To the resulting orange solution was added neat CF_3CH_2OD (31.0 mg, 0.303 mmol, 10.0 equiv). The color of the solution changed immediately to pale orange/yellow. 0.40 mL of this solution was introduced in a J-Young tube, followed by $BnND_2$ (13.0 mg, 0.120 mmol, 10.0 equiv). Deuterium integration at C-*1* (D/H-*13* and D/H-*13*') and C-*3* (D/H-*15*) was then monitored by ^{1}H NMR. Deuterium integration at C-*4* (D/H-*16*) could not be accomplished due to signals overlap.

10-d_n - Evolution over time

^{1}H NMR (400 MHz, Tol-d_8)



10. Kinetic studies

General:

In situ ^{1}H NMR monitoring was carried out in J-Young NMR tube using a AMX−500 Bruker Avance spectrometer. The reaction was monitored by following the consumption of substrate **1a** using the allylic proton at C-*3*. Spectra were collected at 298 K every 1 or 2 hours for the entirety of the experiment (5 scans, 10 seconds T1 relaxation delay). The data were treated using the methods for variable time normalization analysis.[3] Given the absence of by-products containing $BnNH_2$, the concentration of $BnNH_2$ [**2a**]$_t$ for each time *t* was calculated using the following formula: [**2a**]$_t$ = [**2a**]$_{t=0}$ - ([**1a**] $_{t=0}$ - [**1a**] $_t$).

Standard reaction procedure:

In an N_2-filled glove-box, a solution of Ni(cod)$_2$ (4.1 mg, 0.0150 mmol) and (R,R)BenzP* **L$_1$** (5.1 mg, 0.0181 mmol) in toluene-*d$_8$* (0.60 mL) was prepared in a 2 mL vial. After stirring for 5 min, substrate **1a** (61.9 mg, 0.300 mmol) was added, stirring for continued for 30 min, and $BnNH_2$ **2a** (128.6 mg, 131 μL, 1.200 mmol) was added. In a J-Young tube equipped with a sealed glass capillary containing an internal standard solution (*p*-methylanisole ~ 0.10 M; PPh_3 ~0.01 M; solvent: toluene-*d$_8$*) was introduced 0.49 mL of the resulting stock solution ([Ni(cod)$_2$] = 0.0205 M; [**L$_1$**] = 0.0248 M; [**1a**] = 0.410 M; [**2a**] = 1.641 M). ^{1}H NMR of this solution was acquired, allowing for calibration of the ^{1}H internal standard peaks (time = 0 s). The J-Young tube was then brought back into an N_2-filled glovebox, catalysis was initiated by addition of trifluoroethanol (20.0 mg, 0.200 mmol, 1.0 equiv, [TFE] = 0.410 M), and the reaction mixture was monitored over time by ^{1}H NMR.

Same excess

This reaction was carried out according to the standard reaction procedure, with the following concentrations: [Ni(cod)$_2$] = 0.0205 M; [**L$_1$**] = 0.0248 M; [**1a**] = 0.250 M; [**2a**] = 1.500 M; [TFE] = 0.410 M).

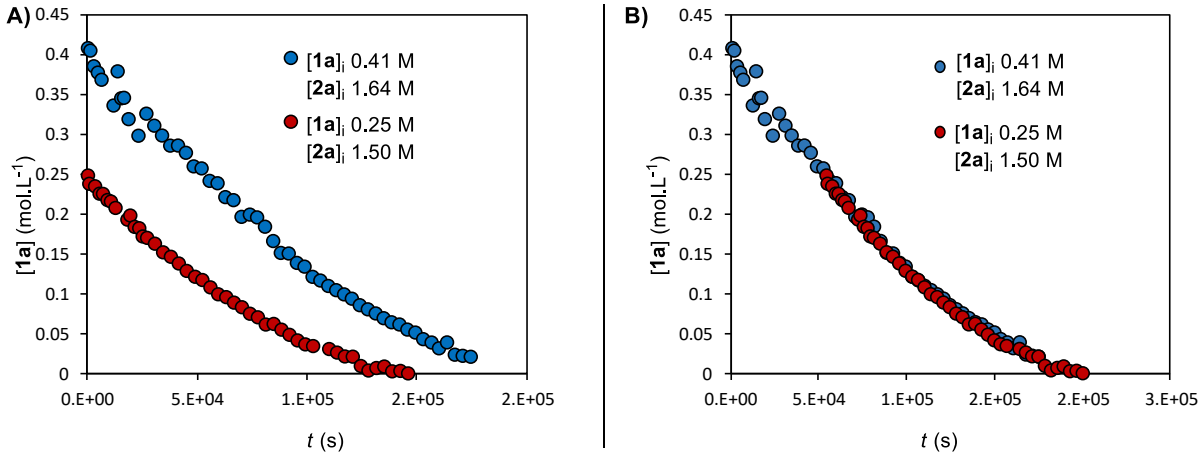


Figure S3. A) Reaction time course for "standard conditions" (blue points) and "same excess" experiment (red points). B) Reaction time course for standard and same excess experiments after time adjustment of the "same excess" experiment (red points; Δt = + 53550 s).

Order in catalyst

This reaction was carried out according to the standard reaction procedure, with the following concentrations: $[Ni(cod)_2]$ = 0.0410 M; [**L**$_1$] = 0.0496 M; [**1a**] = 0.410 M; [**2a**] = 1.641 M; [TFE] = 0.410 M).

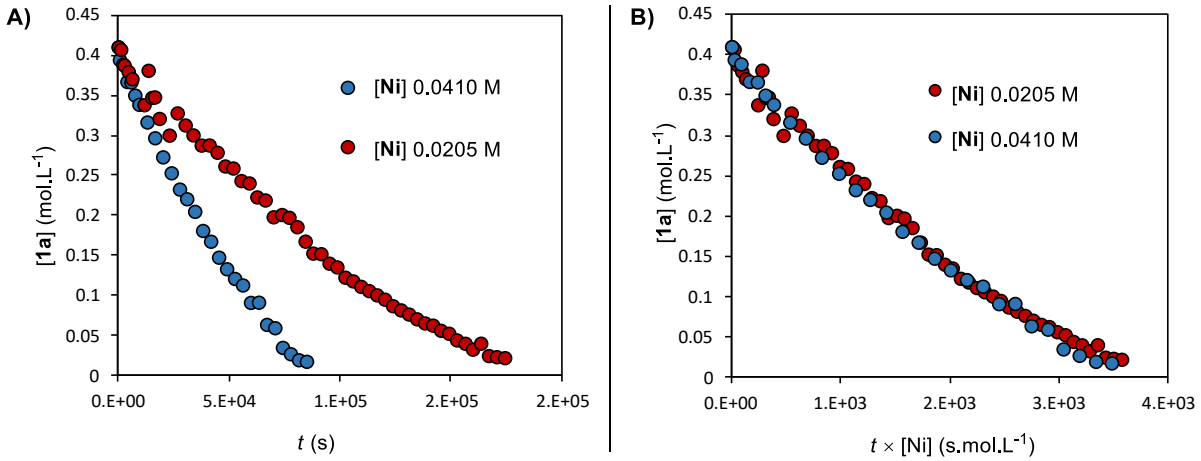


Figure S-4. A) Reaction time course for "standard conditions" (red points) and "Order in catalyst" experiment (blue points). B) Reaction time course for standard and "Order in catalyst" experiments after multiplication of the original time axis by the catalyst initial concentration (time x $[Ni(cod)]_2$).

Order in diene 1a

This reaction was carried out according to the standard reaction procedure, with the following concentrations: [Ni(cod)$_2$] = 0.0205 M; [**L$_1$**] = 0.0248 M; [**1a**] = 0.615 M; [**2a**] = 1.641 M; [TFE] = 0.410 M).

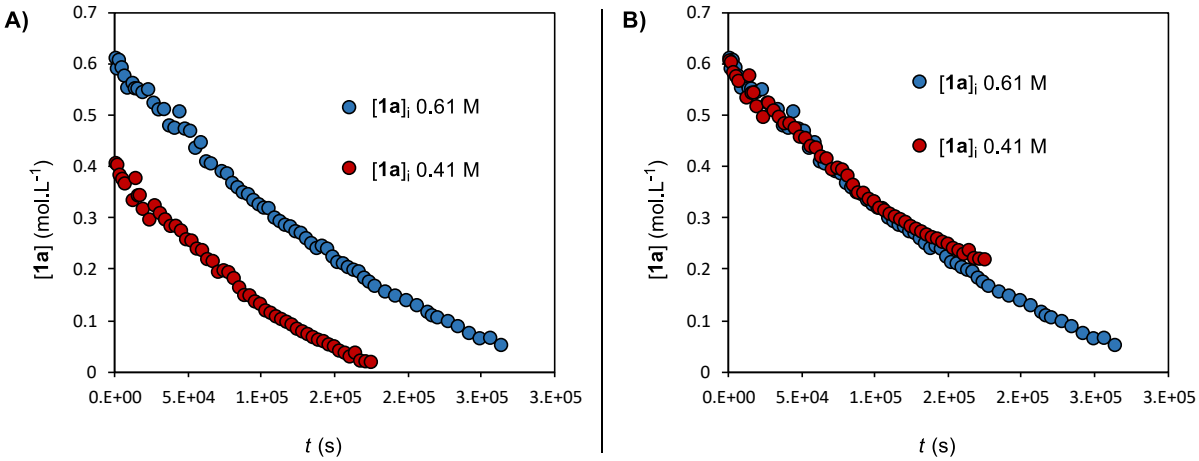


Figure S-5. A) Reaction time course for "standard conditions" (red points) and "Order in diene" experiment (blue points). B) Reaction time course for standard and "Order in diene" experiments after upward concentration shift of the "standard conditions" points (red points: [**1a**] + 0.205 M).

Order in TFE

These reactions were carried out according to the standard reaction procedure, with the following concentrations:

- Red points: [Ni(cod)$_2$] = 0.0205 M; [**L$_1$**] = 0.0248 M; [**1a**] = 0.410 M; [**2a**] = 1.641 M; [TFE] = 0.290 M).
- Yellow points: [Ni(cod)$_2$] = 0.0205 M; [**L$_1$**] = 0.0248 M; [**1a**] = 0.410 M; [**2a**] = 1.641 M; [TFE] = 0.530 M).

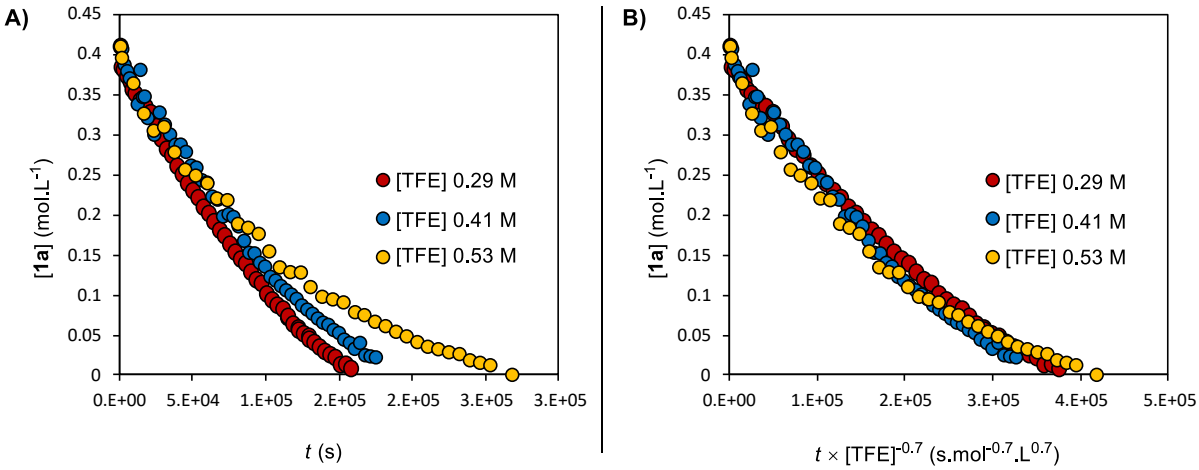


Figure S-6. A) Reaction time course for "standard conditions" (red points) and "Order in TFE" experiments (blue and yellow points). B) Reaction time course for standard and " Order in TFE " experiments after multiplication of the original time axis by $[TFE]^{-0.7}$ (time x $[TFE]^{-0.7}$).

Order in $BnNH_2$ 2a

These reactions were carried out according to the standard reaction procedure, with the following concentrations:

- Red points: $[Ni(cod)_2]$ = 0. 0205 M; [**L**$_1$] = 0.0248 M; [**1a**] = 0.410 M; [**2a**] = 1.290 M; [TFE] = 0.410 M).
- Yellow points: $[Ni(cod)_2]$ = 0. 0205 M; [**L**$_1$] = 0.0248 M; [**1a**] = 0.410 M; [**2a**] = 1.961 M; [TFE] 0.410 M).

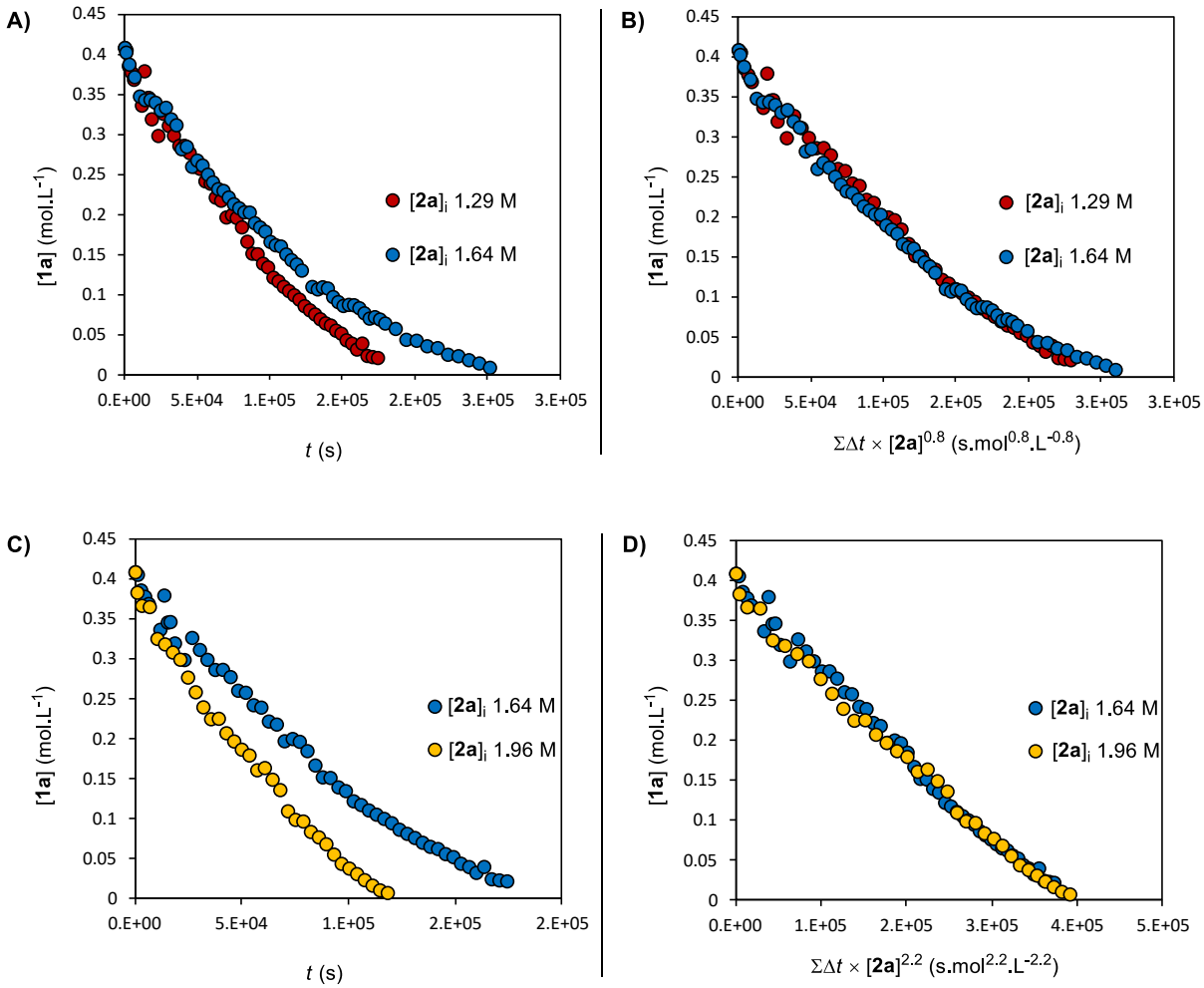


Figure S-7. A) and C) Reaction time course for standard conditions (blue points) and "Order in $BnNH_2$ **2a**" experiments (red and yellow points). B) Reaction time course for standard and "Order in $BnNH_2$ (1.29 M)" experiments after variable time normalization of the original time axis using $t_n=\sum_{i=1}^{n}(t_i - t_{i-1})(\frac{[2a]_i+[2a]_{i-1}}{2})^{0.8}$. D) Reaction time course for standard and "Order in $BnNH_2$ **2a** (1.96 M)" experiments after variable time normalization of the original time axis using $t_n=\sum_{i=1}^{n}(t_i - t_{i-1})(\frac{[2a]_i+[2a]_{i-1}}{2})^{2.2}$.

11. $BnNH_2$ NMR titration by TFE

In an N_2-filled glove-box, $BnNH_2$ (86 mg, 88 μL, 0.80 mmol) and toluene-d_8 (0.40 mL) were charged in a J-Young NMR tube equipped with a sealed glass capillary containing an internal standard solution (*p*-methylanisole ~ 0.010 M; solvent: toluene-d_8). ^1H NMR of this solution was recorded, the J-Young tube was brought back into the glovebox. Increasing amounts of trifluoroethanol were then added sequentially, and ^1H NMR spectra were recorded between each point (Figure S-8).

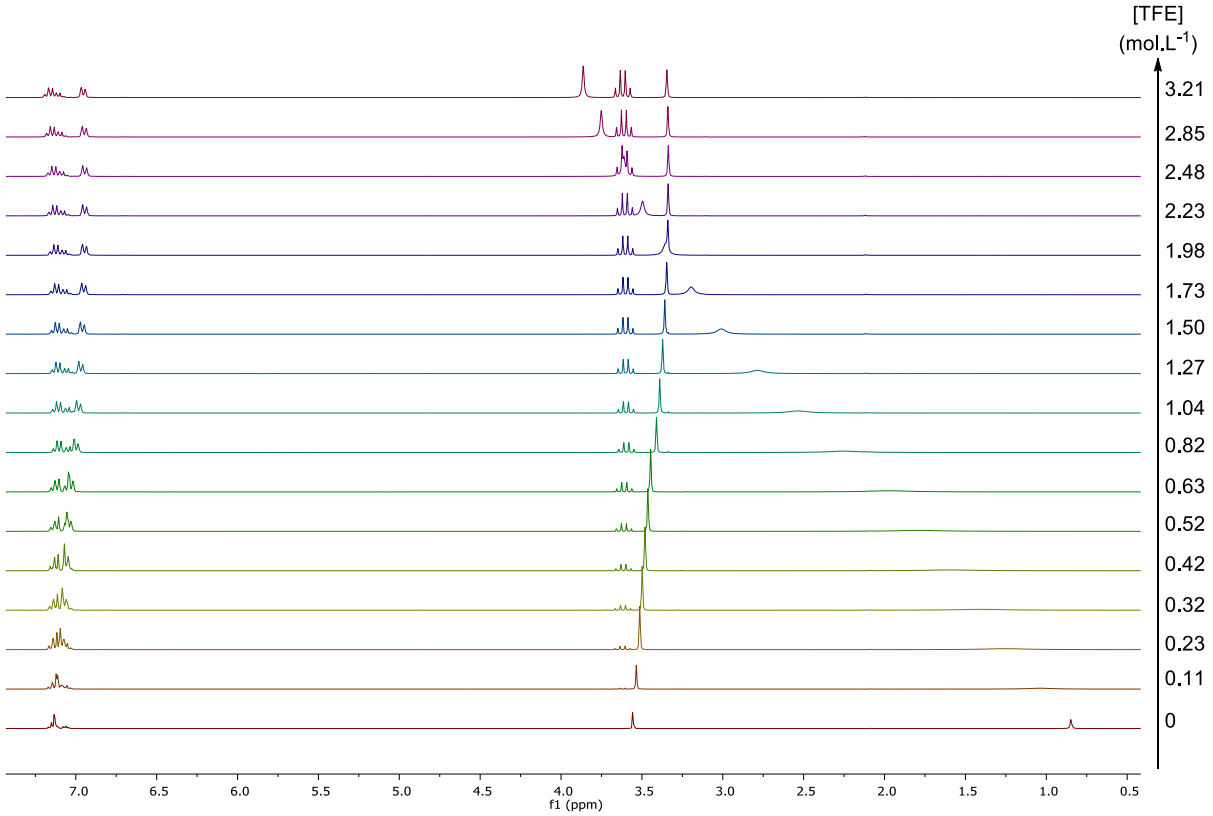


Figure S-8. ^1H NMR of [$BnNH_2$:TFE] solutions in toluene-d_8.

The $\Delta\delta$ ^1H NMR shift of the $BnNH_2$ benzylic protons for each point compared to the initial 1.64 M $BnNH_2$ solution was then plotted against the TFE concentration (Figure S-9).

These data were fitted to the 1:1, 2:1 or 1:2 binding models proposed by Thodarson *et al.*.[4] Good Root Means Square errors were obtained for the 1:2 and 2:1 $BnNH_2$:TFE models (RMS = 0.0028 and 0.0024 respectively). Although it is not possible to unequivocally determine which one of these fits is better, a 1:2 fit - where a $BnNH_2$:TFE dimer would form first prior to binding of a second equivalent of TFE to the lone pair of the oxygen of the first molecule of alcohol - seems more likely. Indeed, the signal of the benzylic hydrogens are no longer significantly shifting once the concentration in TFE and $BnNH_2$ are equals.

Subsequently, the signal of the exchangeable protons of benzylamine sharpen until a 1:2 stoichiometry is reached.

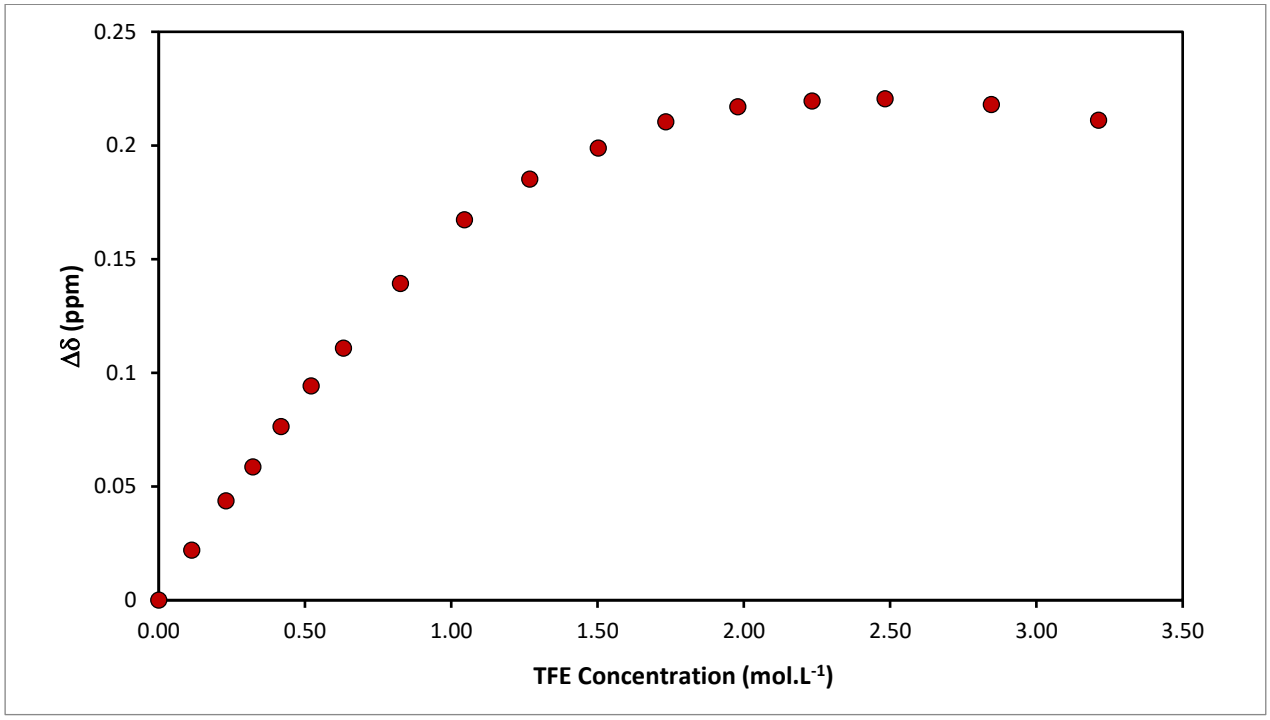
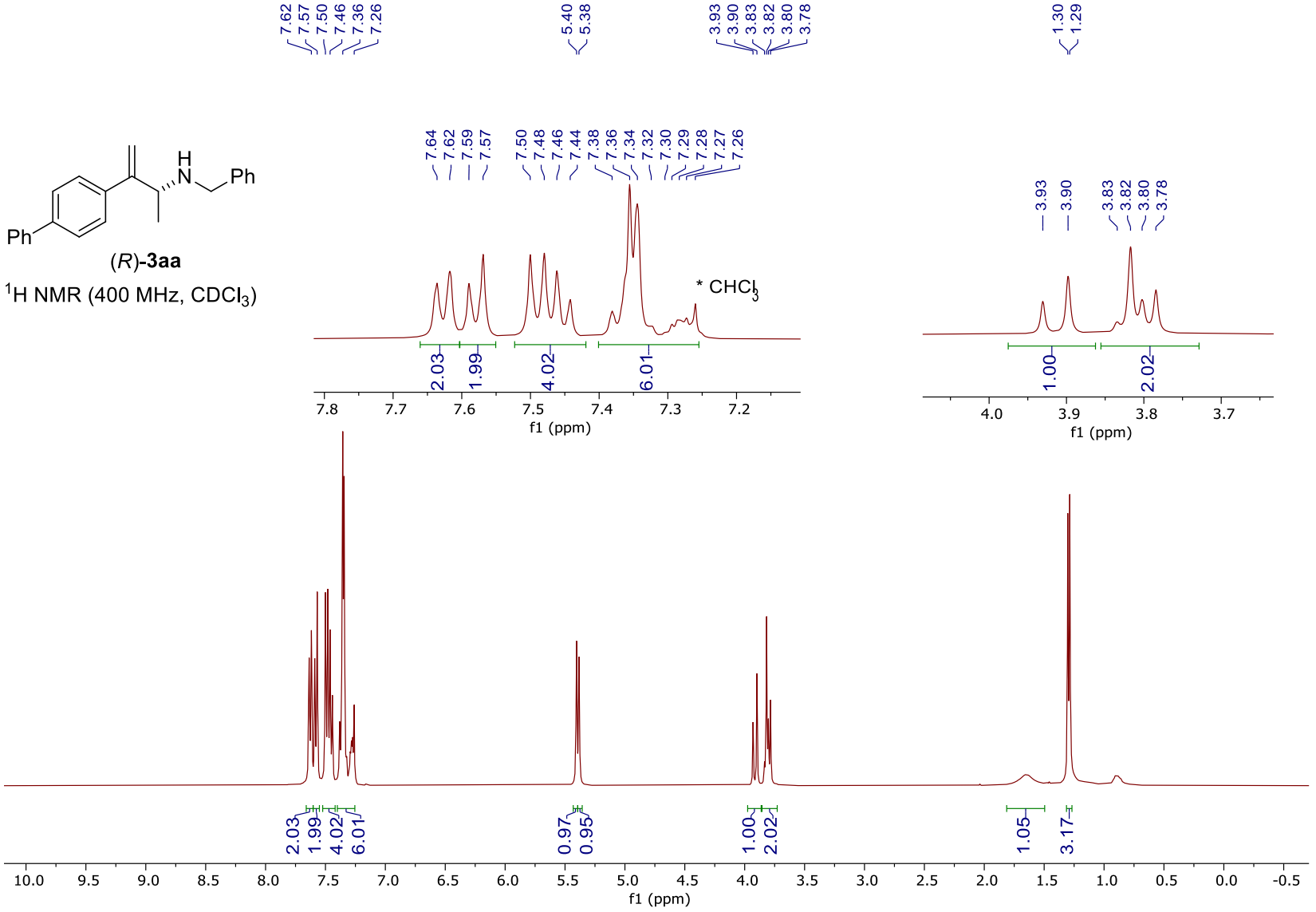
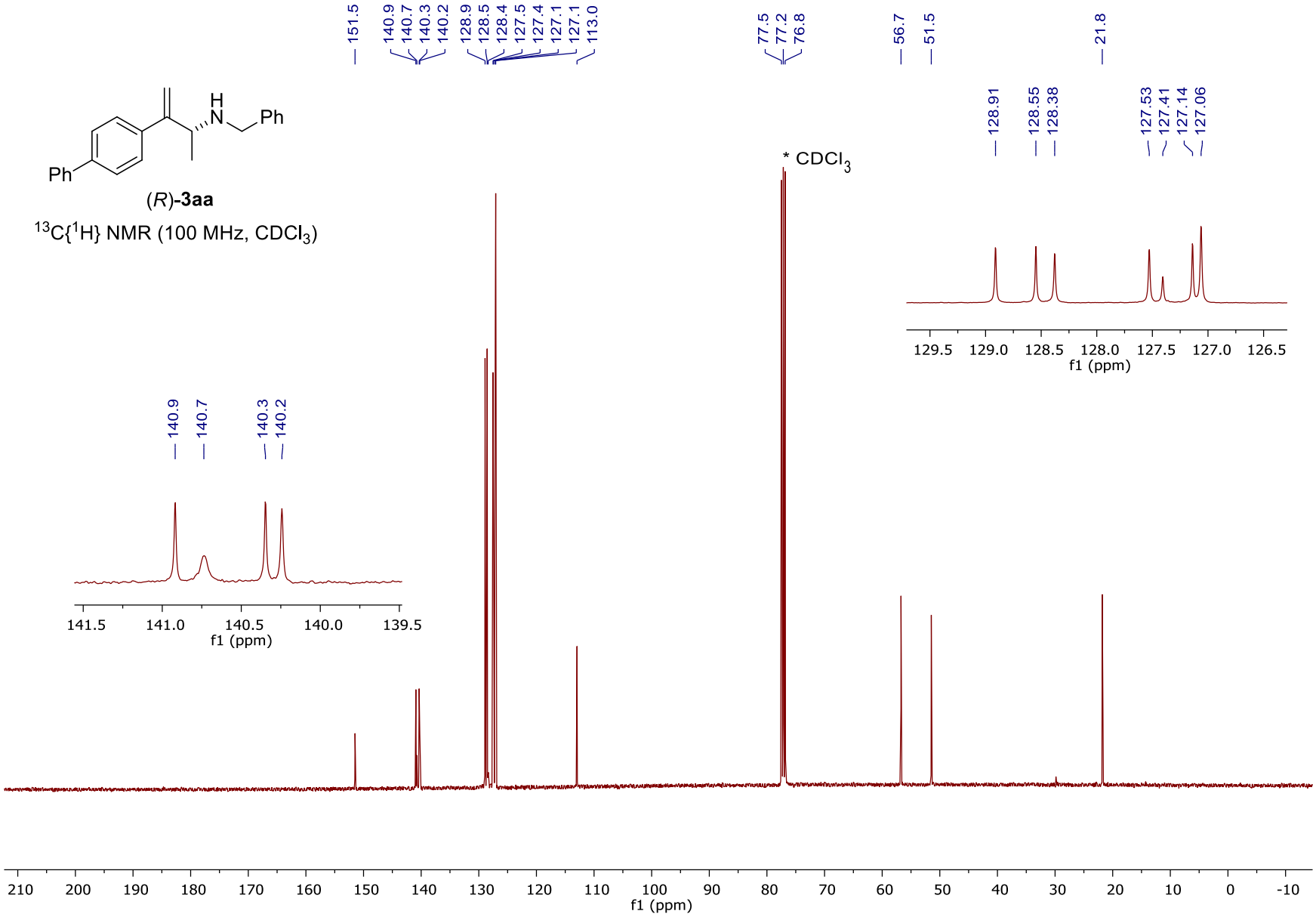
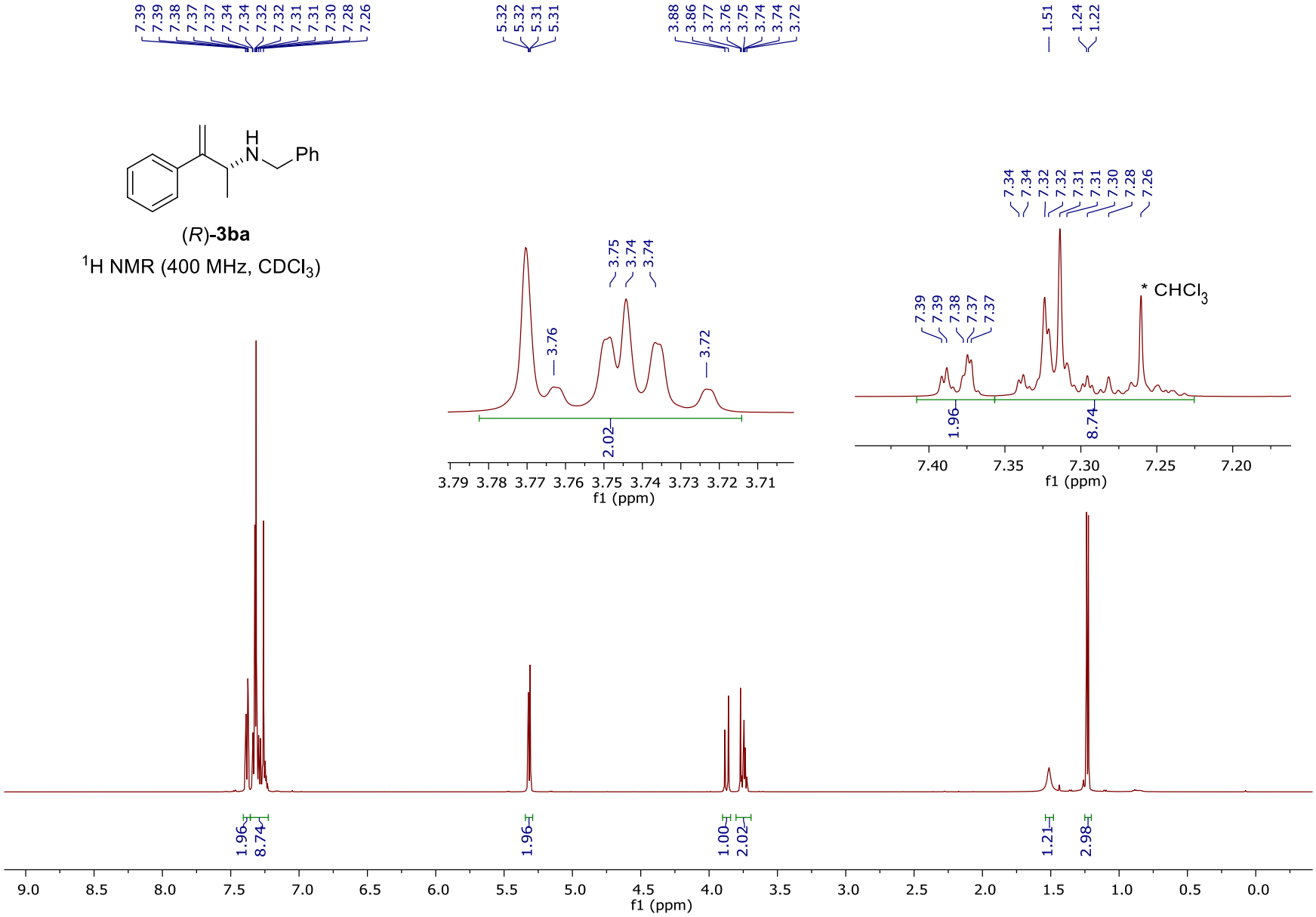


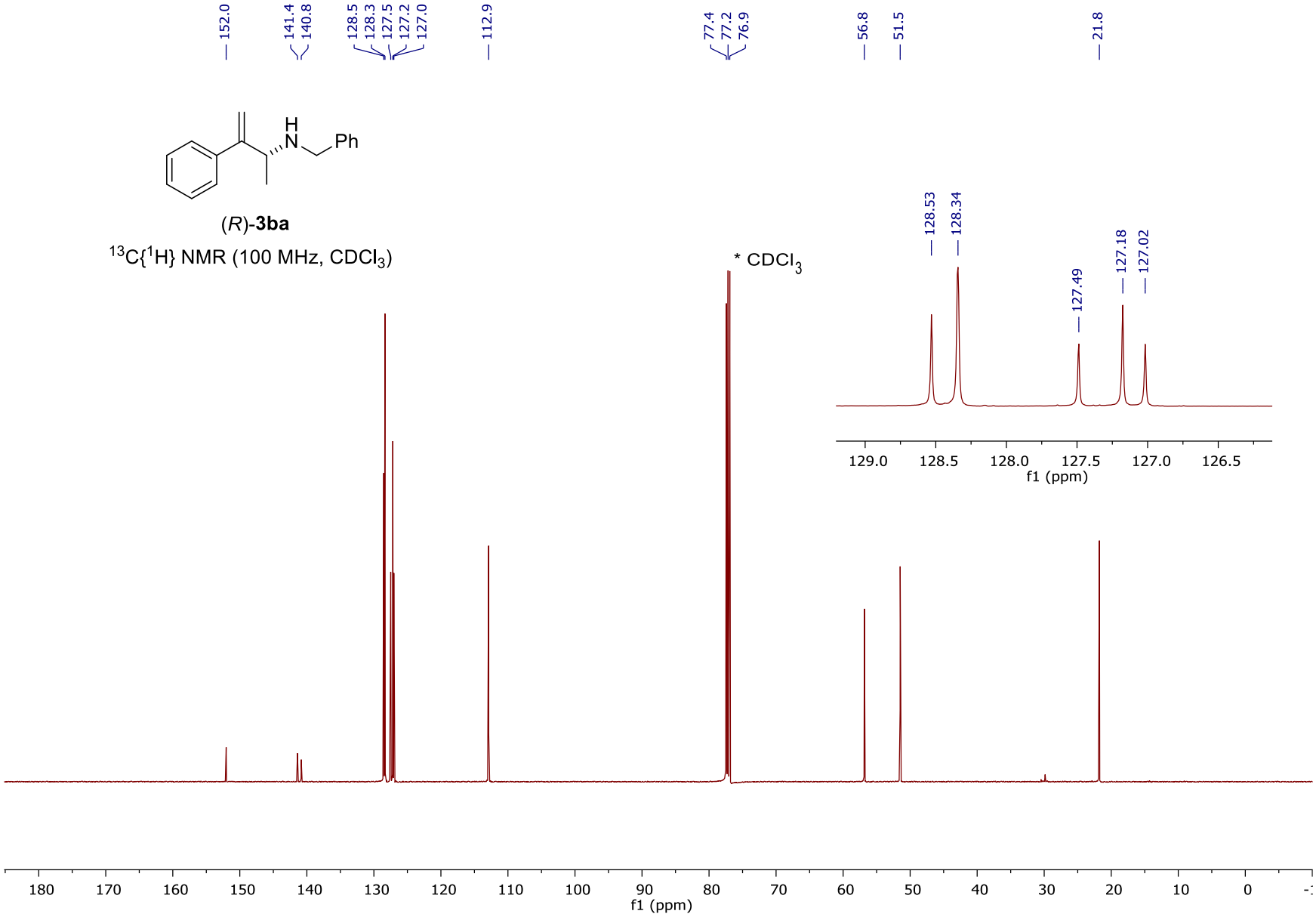
Figure S-9. ^{1}H NMR titration of Benzylic amine by CF_3CH_2OH.

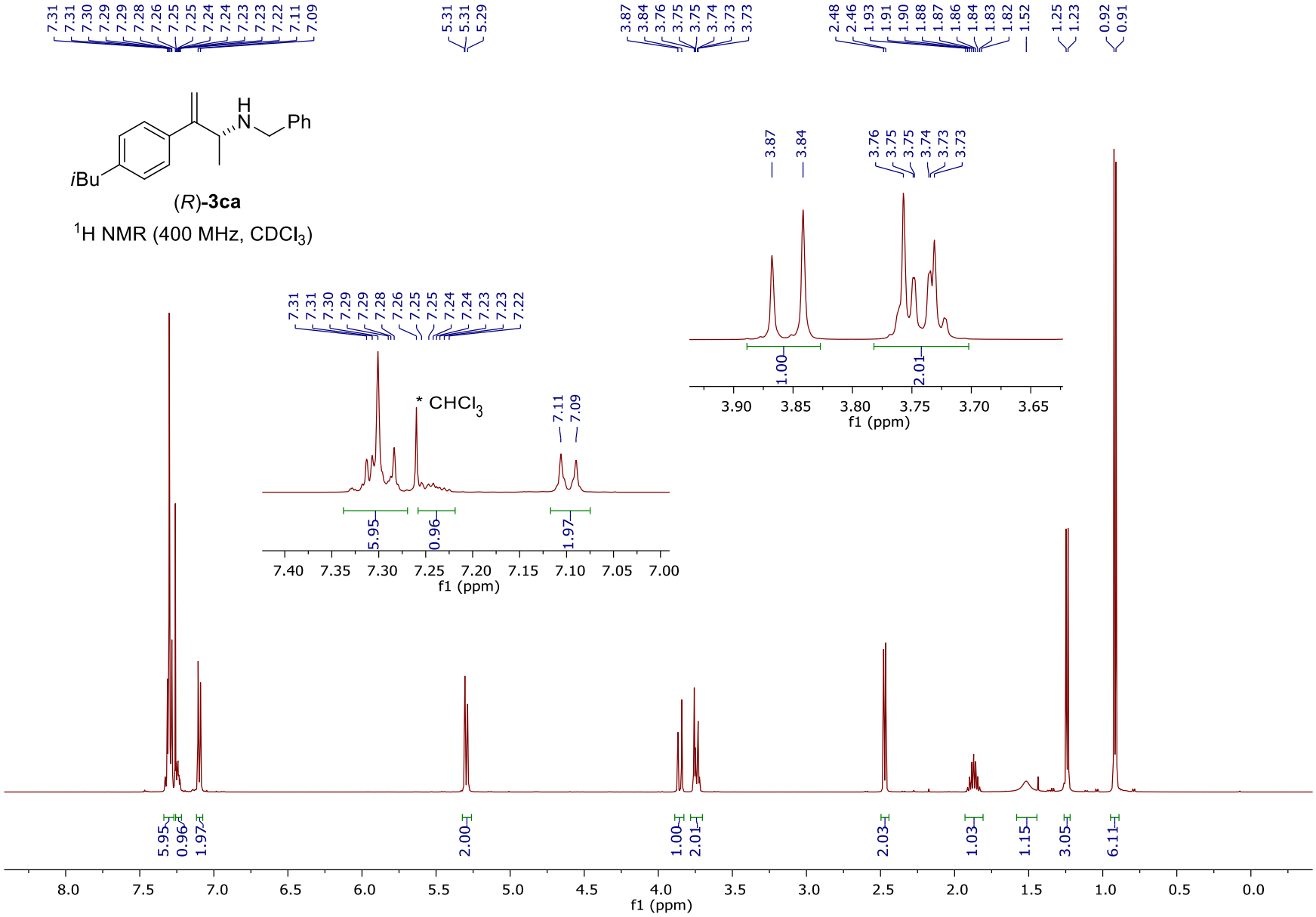
12. NMR Spectra of organic compounds

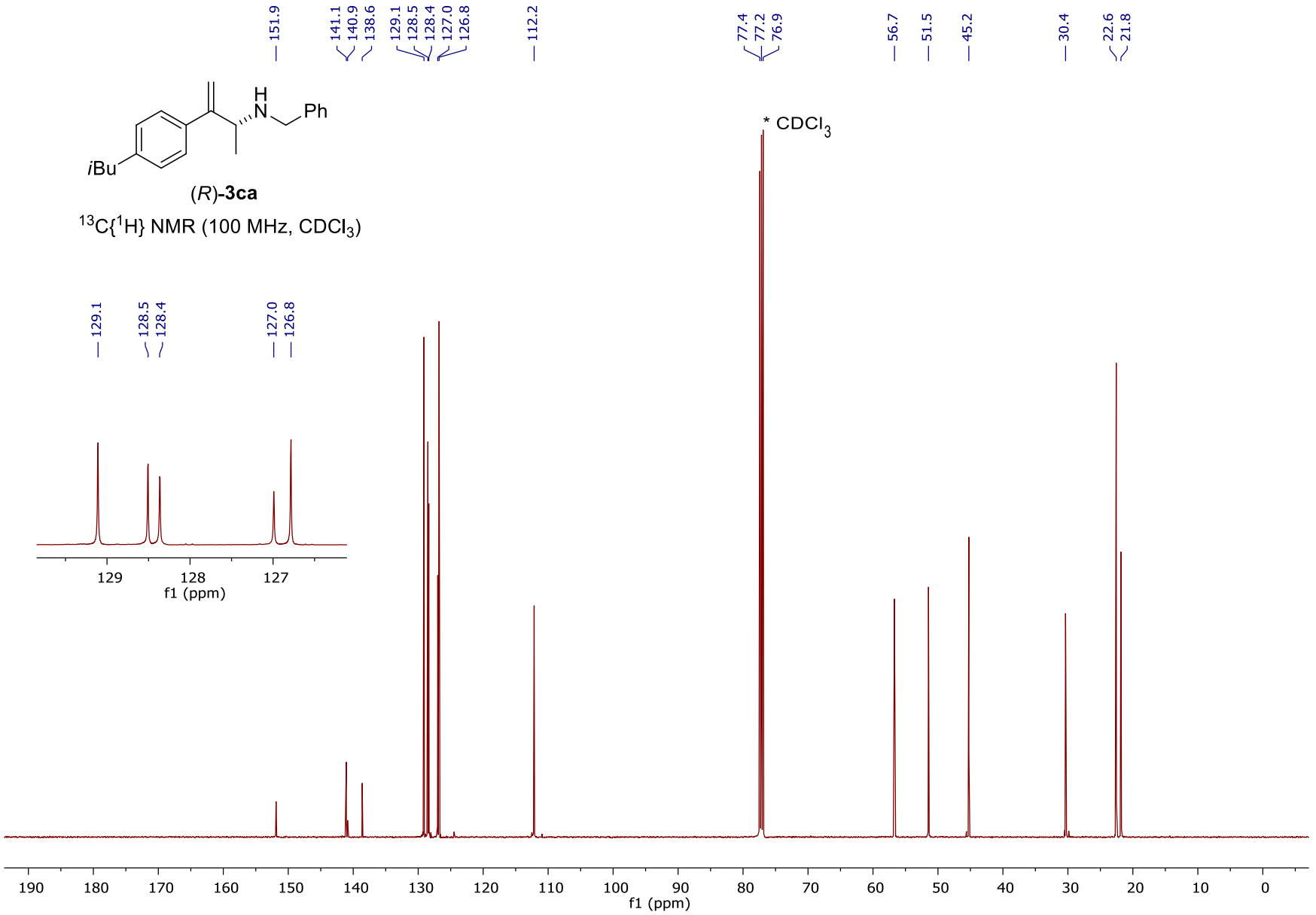

(R)-3aa
1H NMR (400 MHz, CDCl3)
* CHCl3
f1 (ppm)

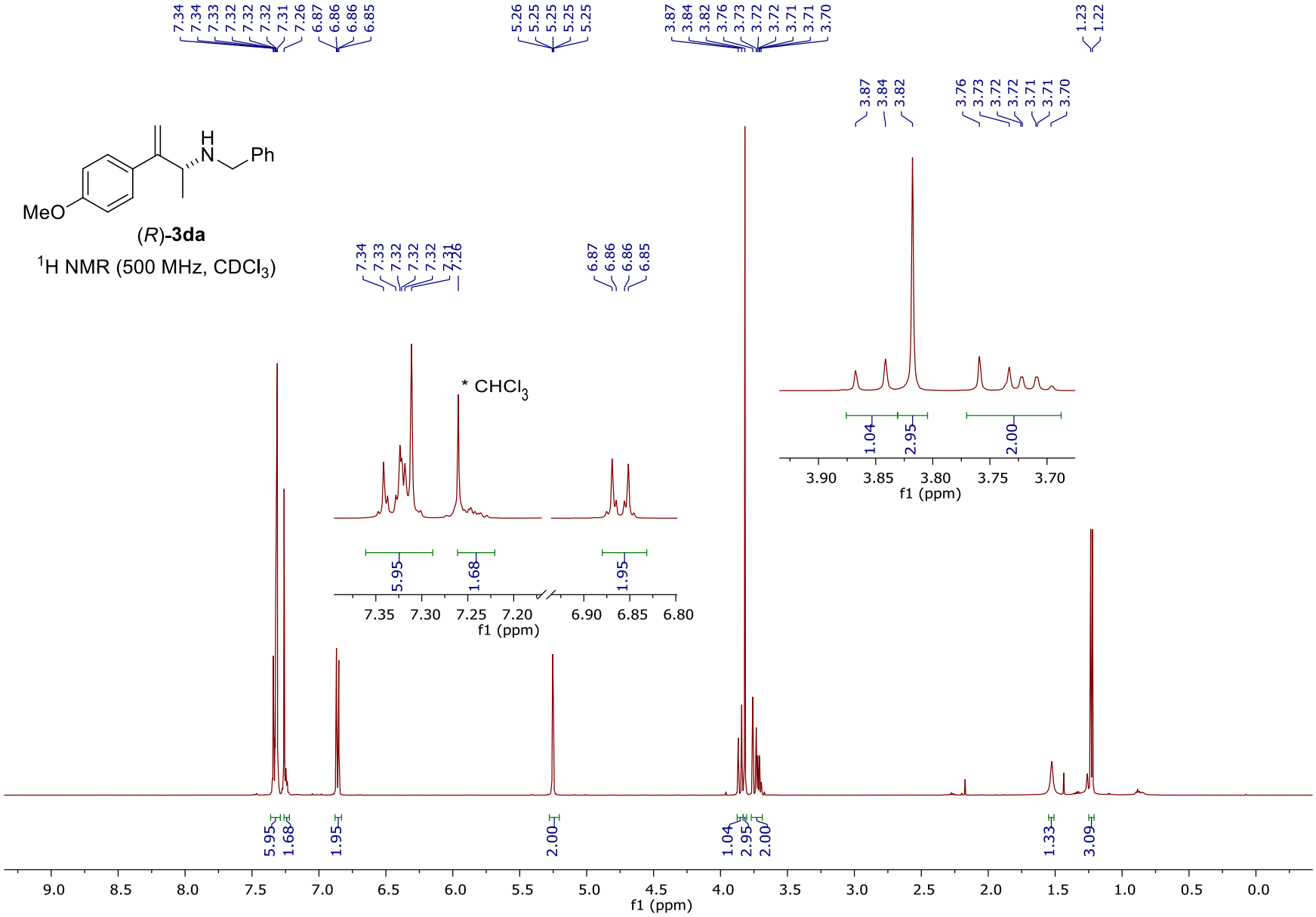

151.5
140.9
140.7
140.3
140.2
128.9
128.5
128.4
127.5
127.4
127.1
127.1
113.0
77.5
77.2
76.8
56.7
51.5
21.8
128.91
128.55
128.38
127.53
127.41
127.14
127.06
* CDCl3
H
N
Ph
Ph
(R)-3aa
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)
f1 (ppm)
f1 (ppm)

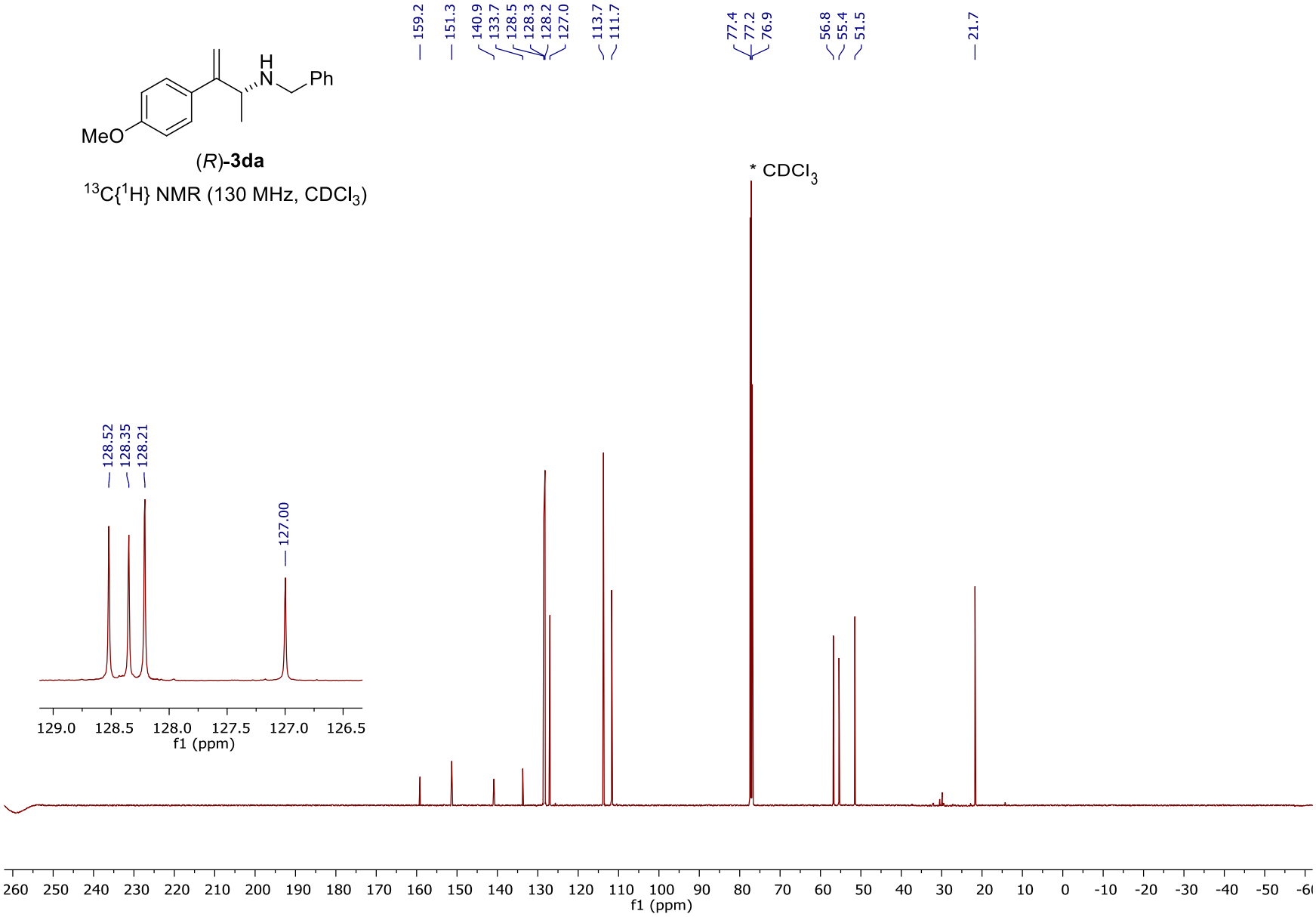

7.39 7.39 7.38 7.37 7.37 7.34 7.34 7.32 7.32 7.31 7.31 7.30 7.28 7.26
5.32 5.32 5.31 5.31
3.88 3.86 3.77 3.76 3.75 3.74 3.74 3.72
1.51
1.24 1.22
H
N
Ph
(R)-3ba
1H NMR (400 MHz, CDCl3)
3.75 3.74 3.74
3.76
3.72
2.02
3.79 3.78 3.77 3.76 3.75 3.74 3.73 3.72 3.71
f1 (ppm)
7.34 7.34 7.32 7.32 7.31 7.31 7.30 7.28 7.26
* CHCl3
7.39 7.39 7.38 7.37 7.37
1.96
8.74
7.40 7.35 7.30 7.25 7.20
f1 (ppm)
1.96 8.74 1.96 1.00 2.02 1.21 2.98
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)

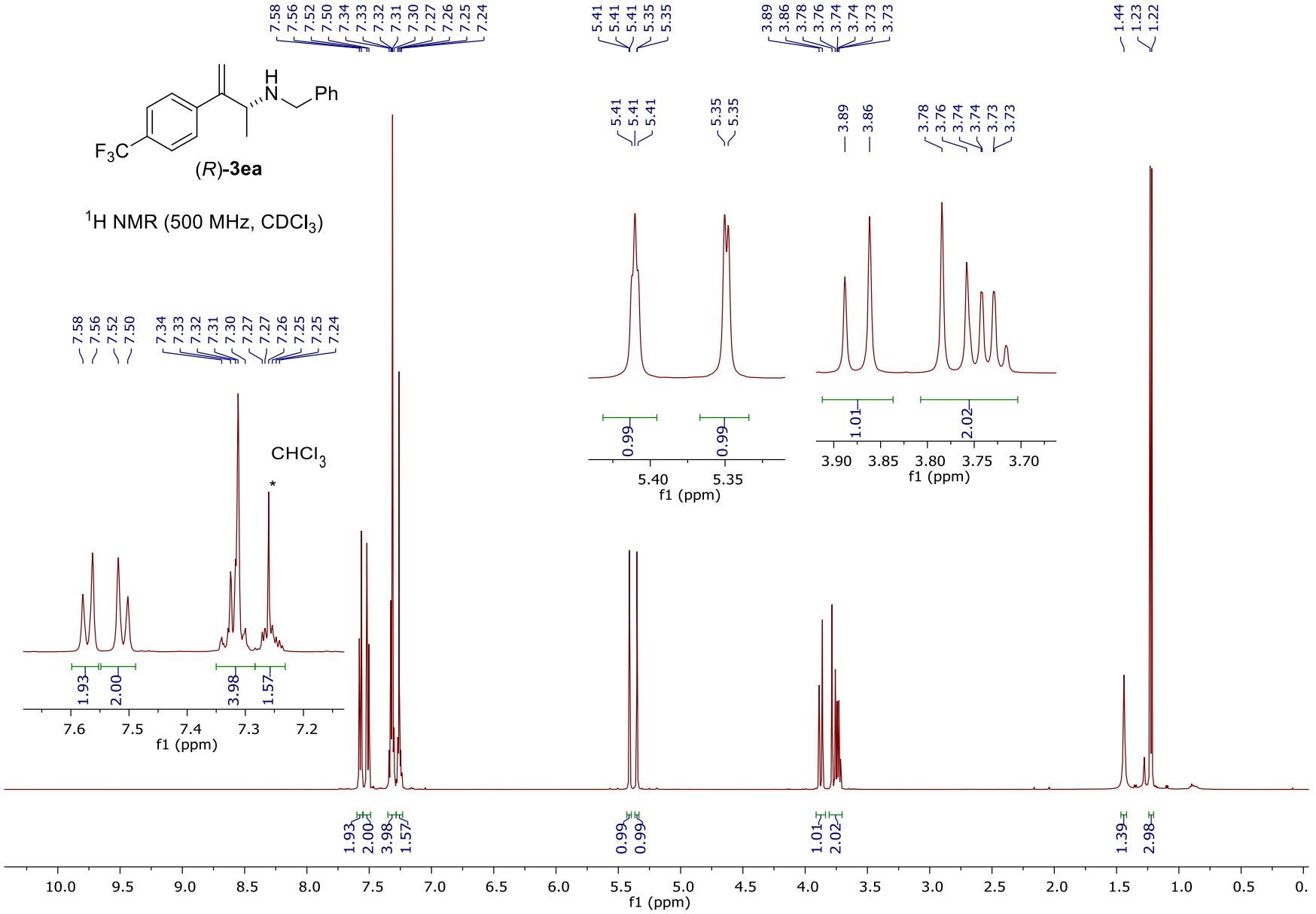

152.0
141.4
140.8
128.5
128.3
127.5
127.2
127.0
112.9
77.4
77.2
76.9
56.8
51.5
21.8
H
N
Ph
(R)-3ba
13C{1H} NMR (100 MHz, CDCl3)
* CDCl3
128.53
128.34
127.49
127.18
127.02
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

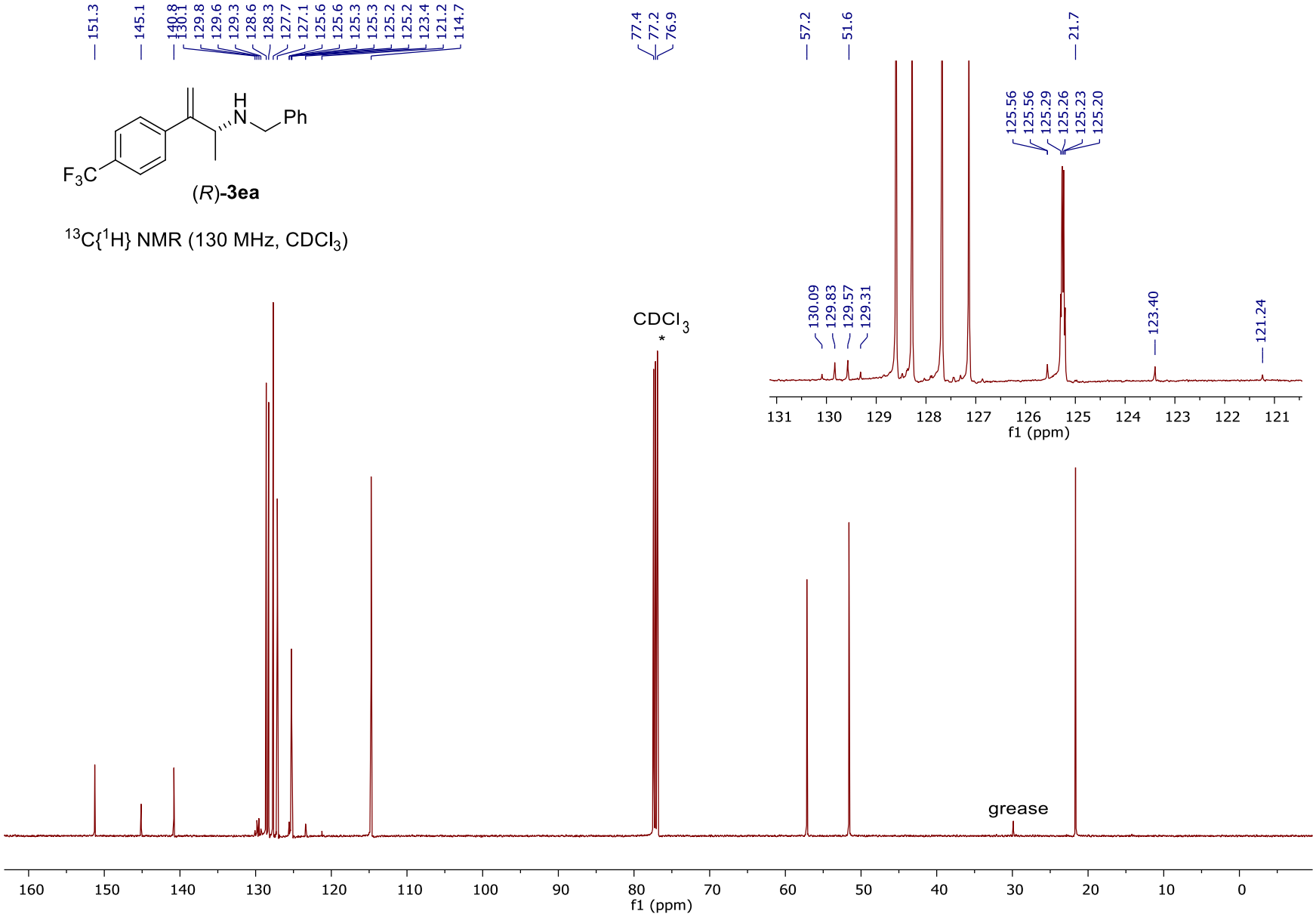

7.31 7.31 7.30 7.29 7.29 7.28 7.26 7.25 7.25 7.24 7.24 7.23 7.23 7.22 7.11 7.09
5.31 5.31 5.29
3.87 3.84 3.76 3.75 3.75 3.74 3.73 3.73
2.48 2.46 1.93 1.91 1.90 1.88 1.87 1.86 1.84 1.83 1.82 1.52
1.25 1.23
0.92 0.91
H
N
Ph
iBu
(R)-3ca
1H NMR (400 MHz, CDCl3)
* CHCl3
5.95
0.96
1.97
2.00
1.00
2.01
2.03
1.03
1.15
3.05
6.11
f1 (ppm)


151.9
141.1
140.9
138.6
129.1
128.5
128.4
127.0
126.8
112.2
77.4
77.2
76.9
56.7
51.5
45.2
30.4
22.6
21.8
* CDCl3
H
N
Ph
iBu
(R)-3ca
13C{1H} NMR (100 MHz, CDCl3)
f1 (ppm)


MeO
H
N
Ph
(R)-3da
1H NMR (500 MHz, CDCl3)
* CHCl3
f1 (ppm)


159.2
151.3
140.9
133.7
128.5
128.3
128.2
127.0
113.7
111.7
77.4
77.2
76.9
56.8
55.4
51.5
21.7
* CDCl3
MeO
H
N
Ph
(R)-3da
13C{1H} NMR (130 MHz, CDCl3)
128.52
128.35
128.21
127.00
129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
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 -30 -40 -50
f1 (ppm)


(R)-3ea
1H NMR (500 MHz, CDCl3)
CHCl3
f1 (ppm)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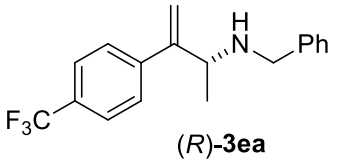
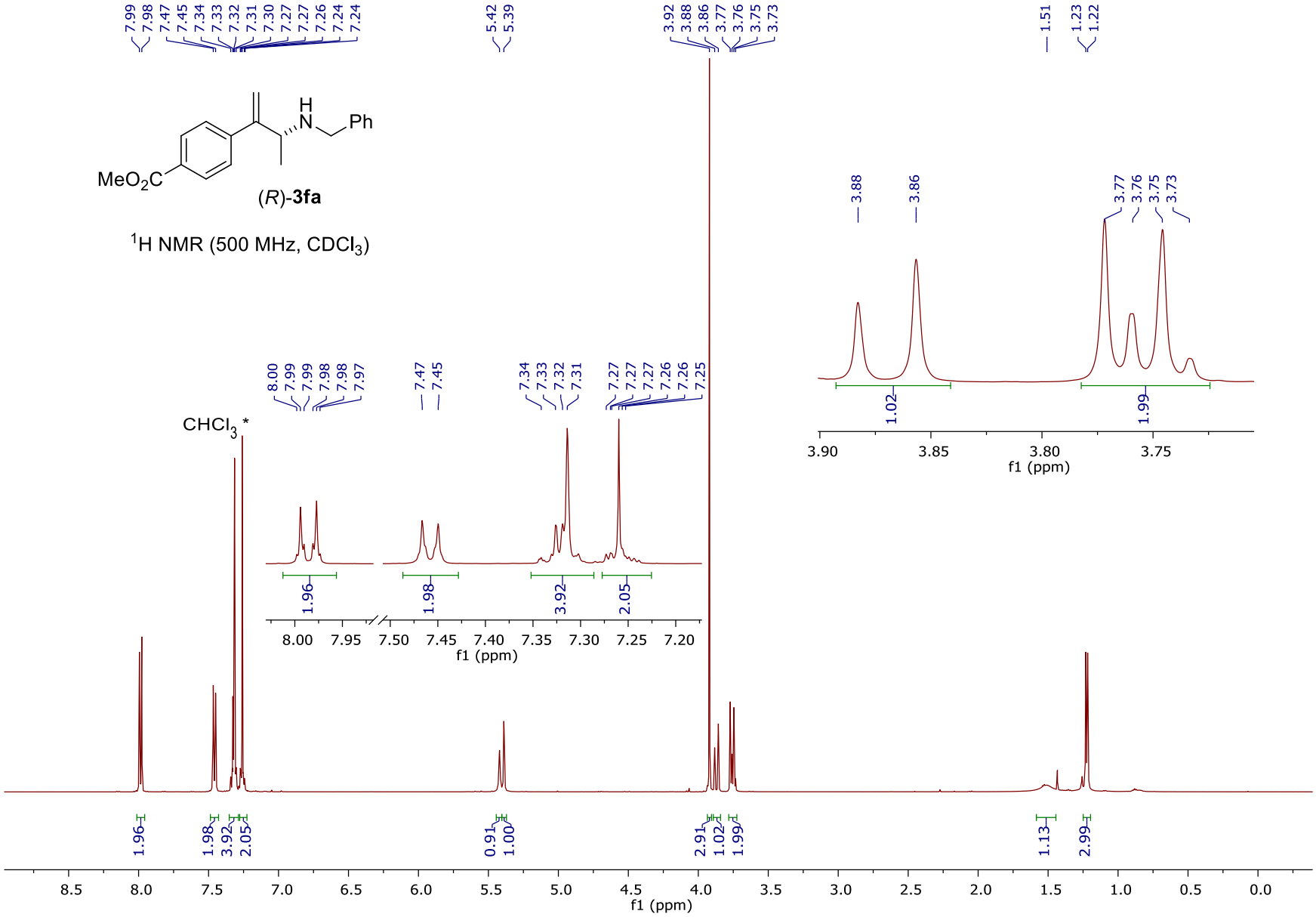
145.1
140.8
130.1
129.8
129.6
129.3
128.6
128.3
127.7
127.1
125.6
125.6
125.3
125.3
125.2
125.2
123.4
121.2
114.7
77.4
77.2
76.9
57.2
51.6
21.7
125.56
125.56
125.29
125.26
125.23
125.20
130.09
129.83
129.57
129.31
123.40
121.24
H
N
Ph
F3C
(R)-3ea
13C{1H} NMR (130 MHz, CDCl3)
CDCl3
*
grease
f1 (ppm)



(*R*)-**3ea**

$^{19}F\{^{1}H\}$ NMR (280 MHz, $CDCl_3$)


7.99
7.98
7.47
7.45
7.34
7.33
7.32
7.31
7.30
7.27
7.27
7.26
7.24
7.24
5.42
5.39
3.92
3.88
3.86
3.77
3.76
3.75
3.73
1.51
1.23
1.22
H
N
Ph
MeO2C
(R)-3fa
1H NMR (500 MHz, CDCl3)
CHCl3 *
3.88
3.86
3.77
3.76
3.75
3.73
1.02
1.99
3.90
3.85
3.80
3.75
f1 (ppm)
8.00
7.99
7.99
7.98
7.98
7.97
7.47
7.45
7.34
7.33
7.32
7.31
7.27
7.27
7.27
7.26
7.26
7.25
1.96
1.98
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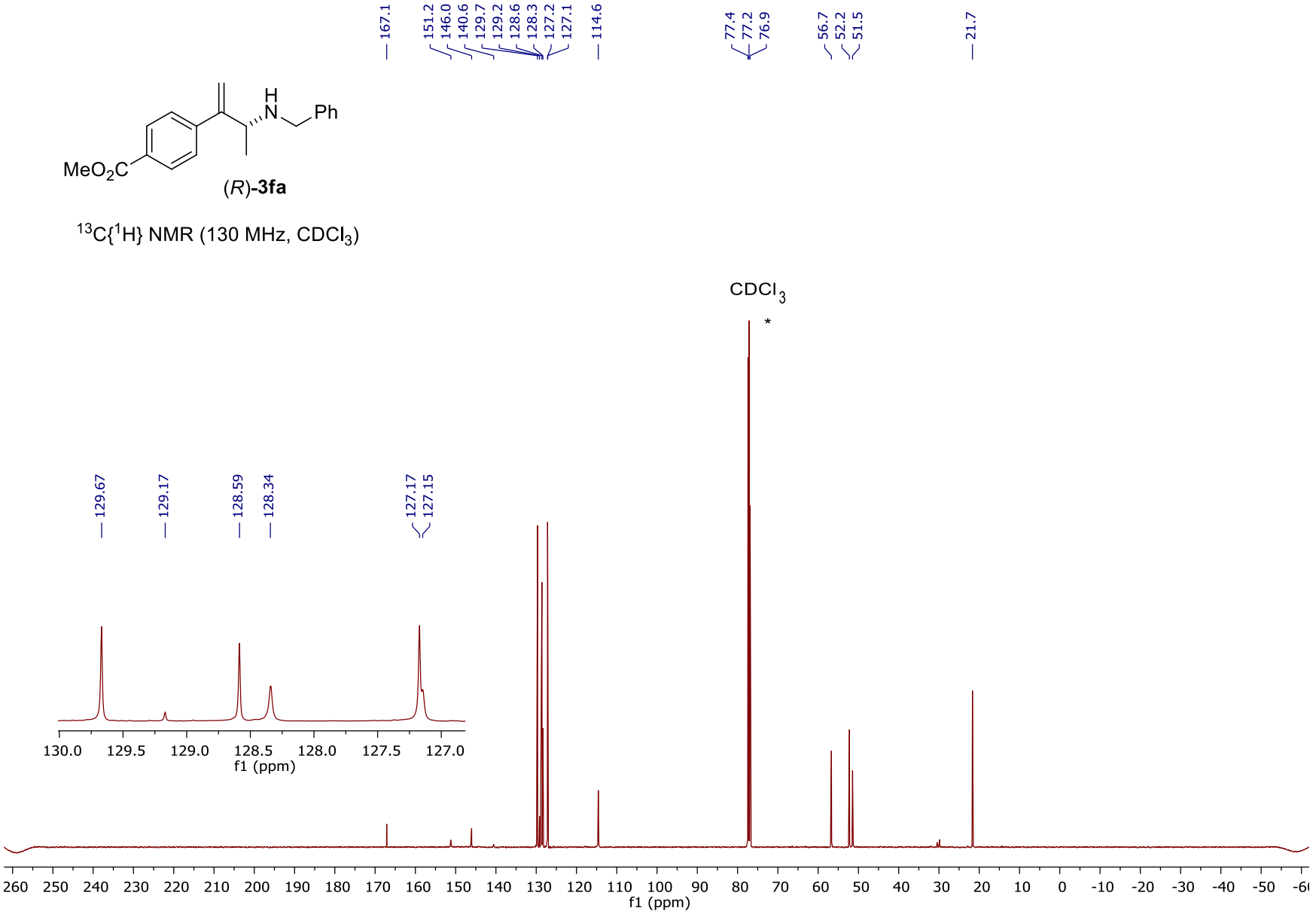
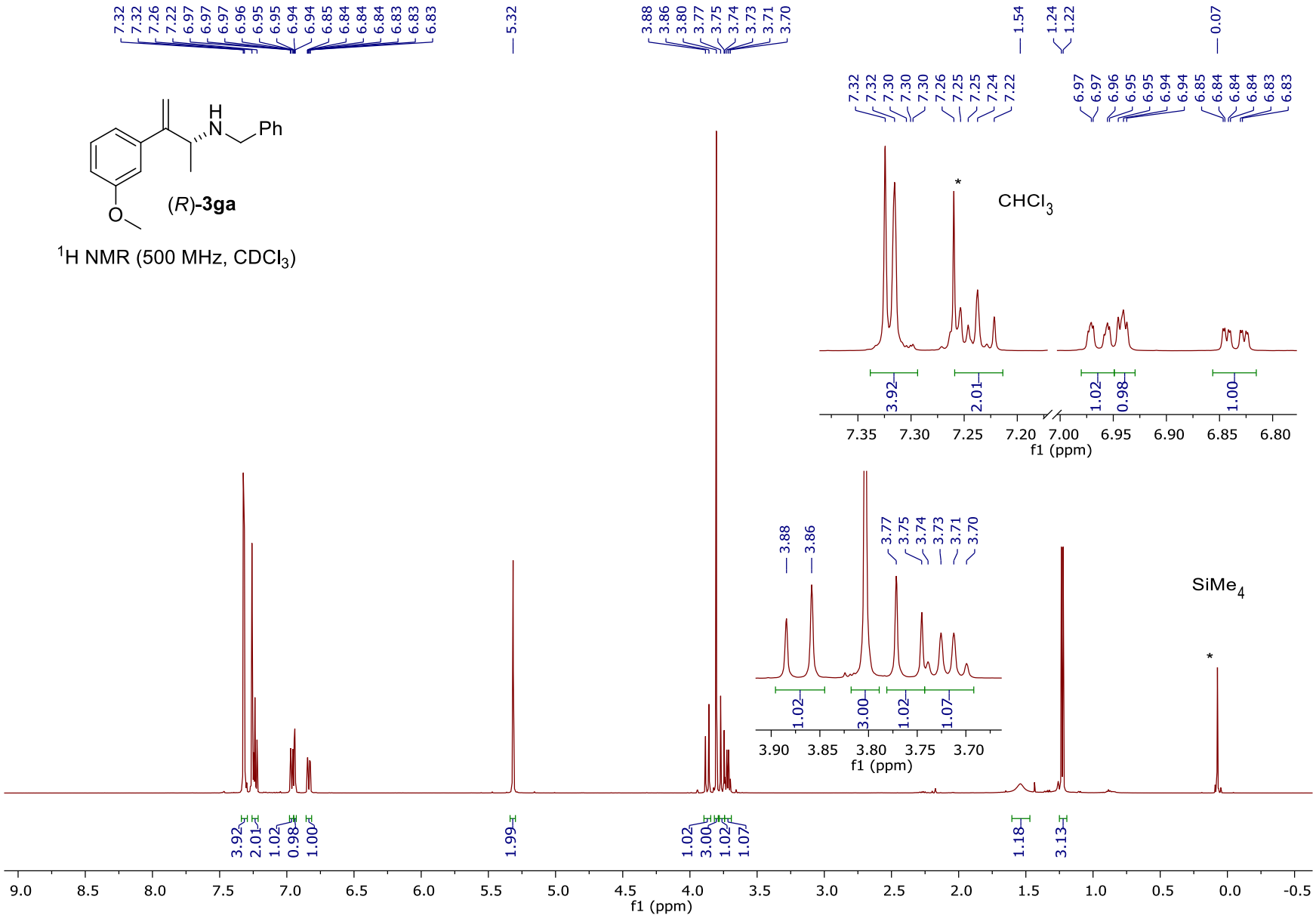
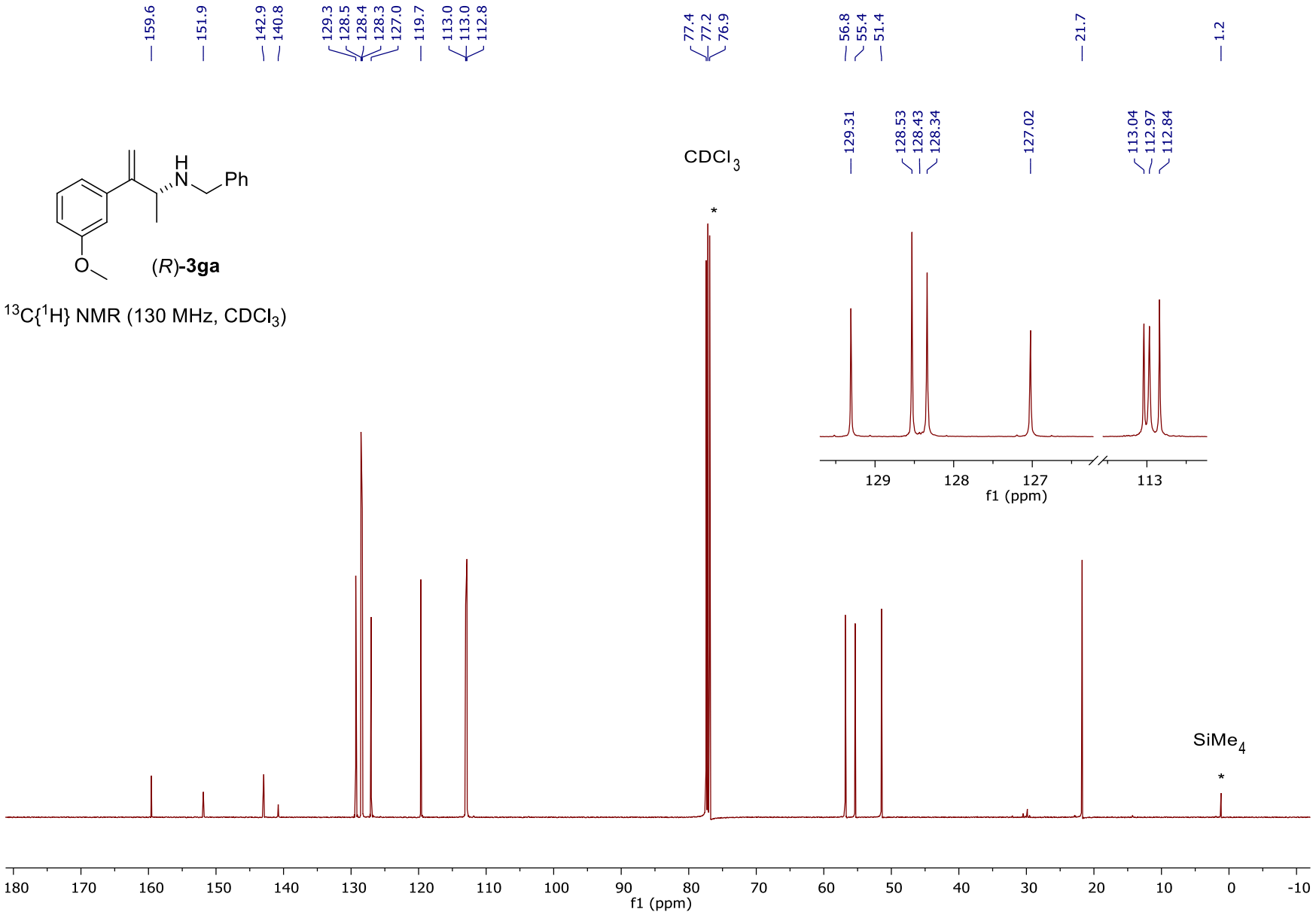
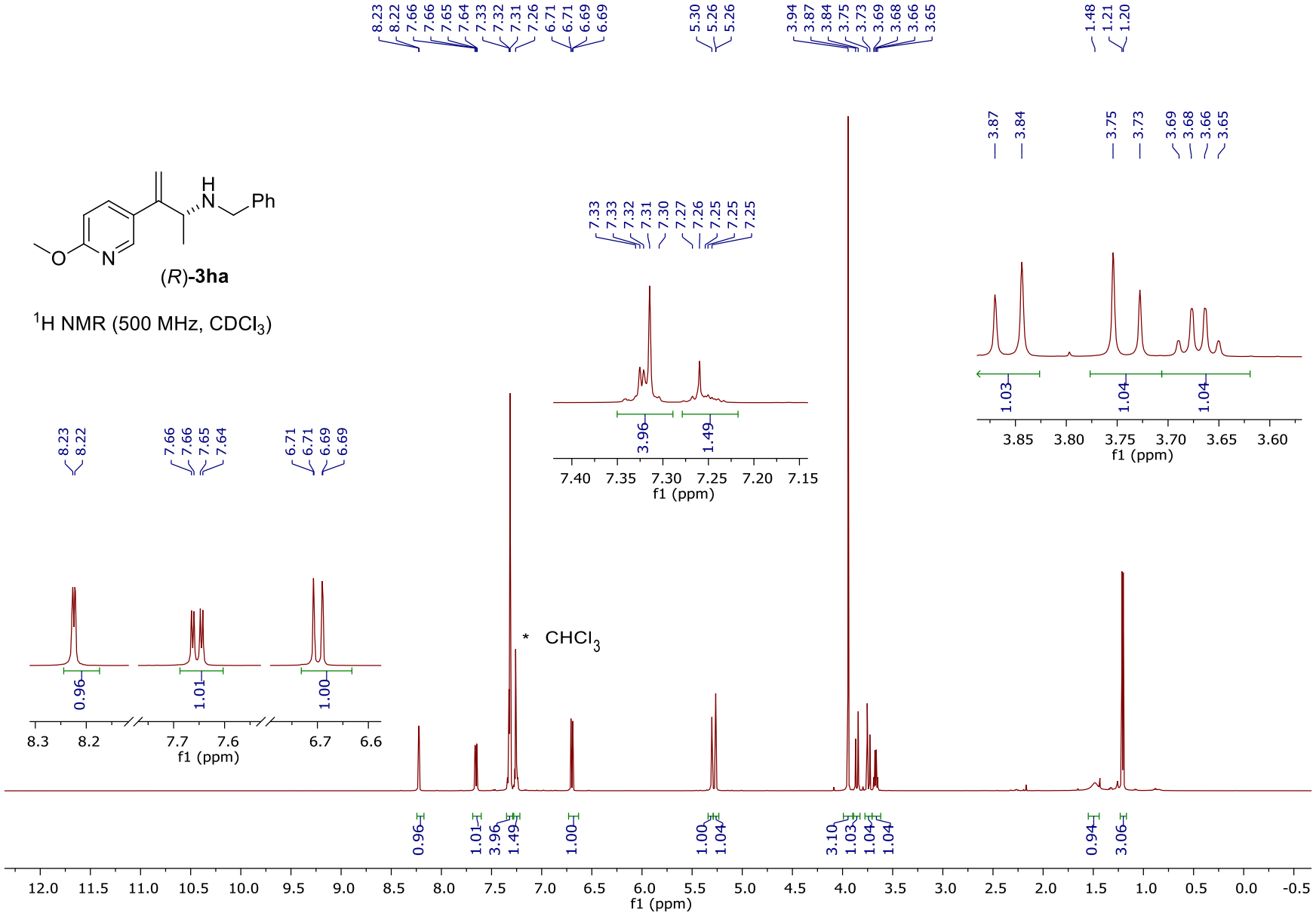
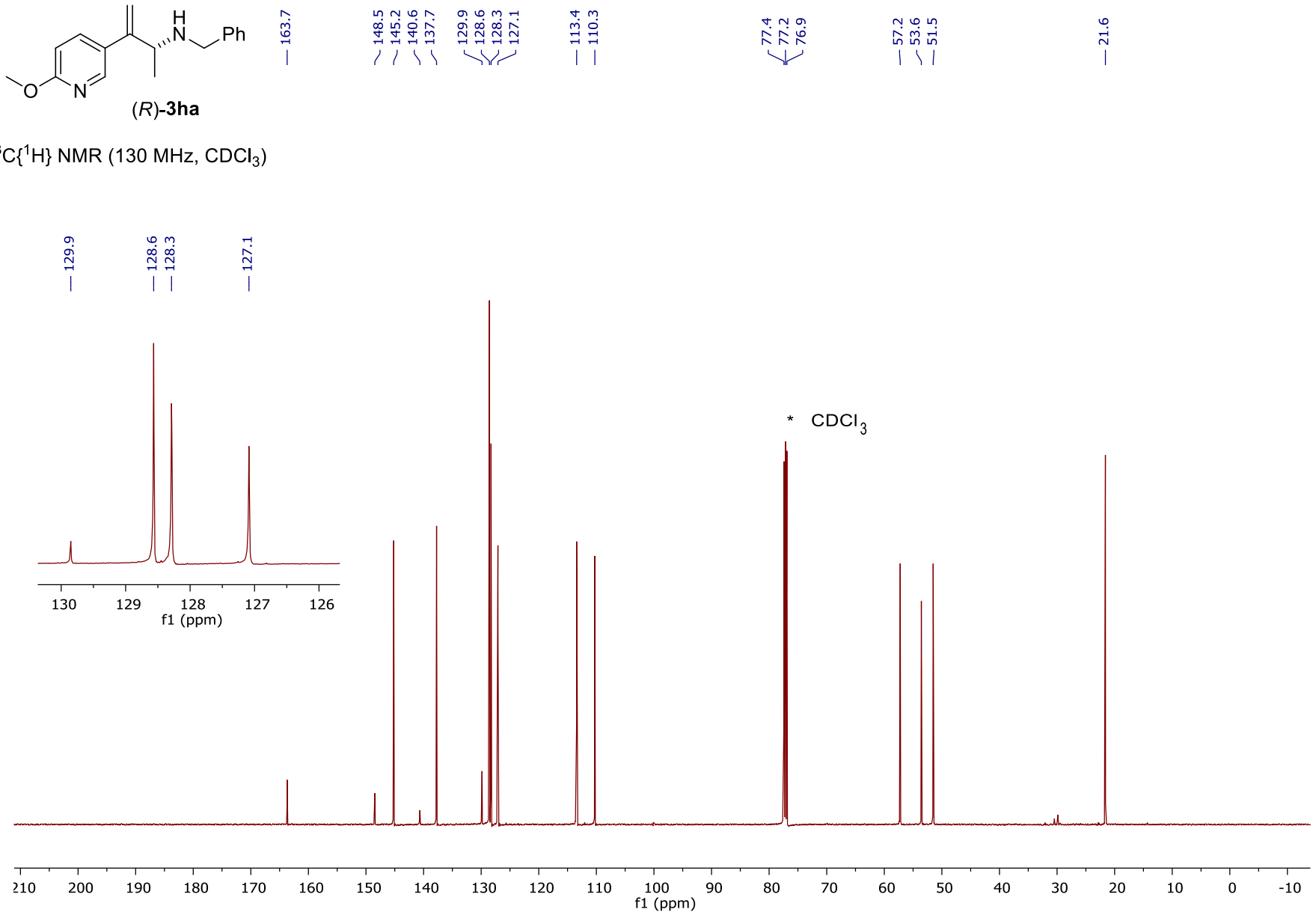
2.05
8.00
7.95
7.50
7.45
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
1.96
1.98
3.92
2.05
0.91
1.00
2.91
1.02
1.99
1.13
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


167.1
151.2
146.0
140.6
129.7
129.2
128.6
128.3
127.2
127.1
114.6
77.4
77.2
76.9
56.7
52.2
51.5
21.7
H
N
Ph
MeO2C
(R)-3fa
13C{1H} NMR (130 MHz, CDCl3)
CDCl3
*
129.67
129.17
128.59
128.34
127.17
127.15
130.0
129.5
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
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
-30
-40
-50
f1 (ppm)

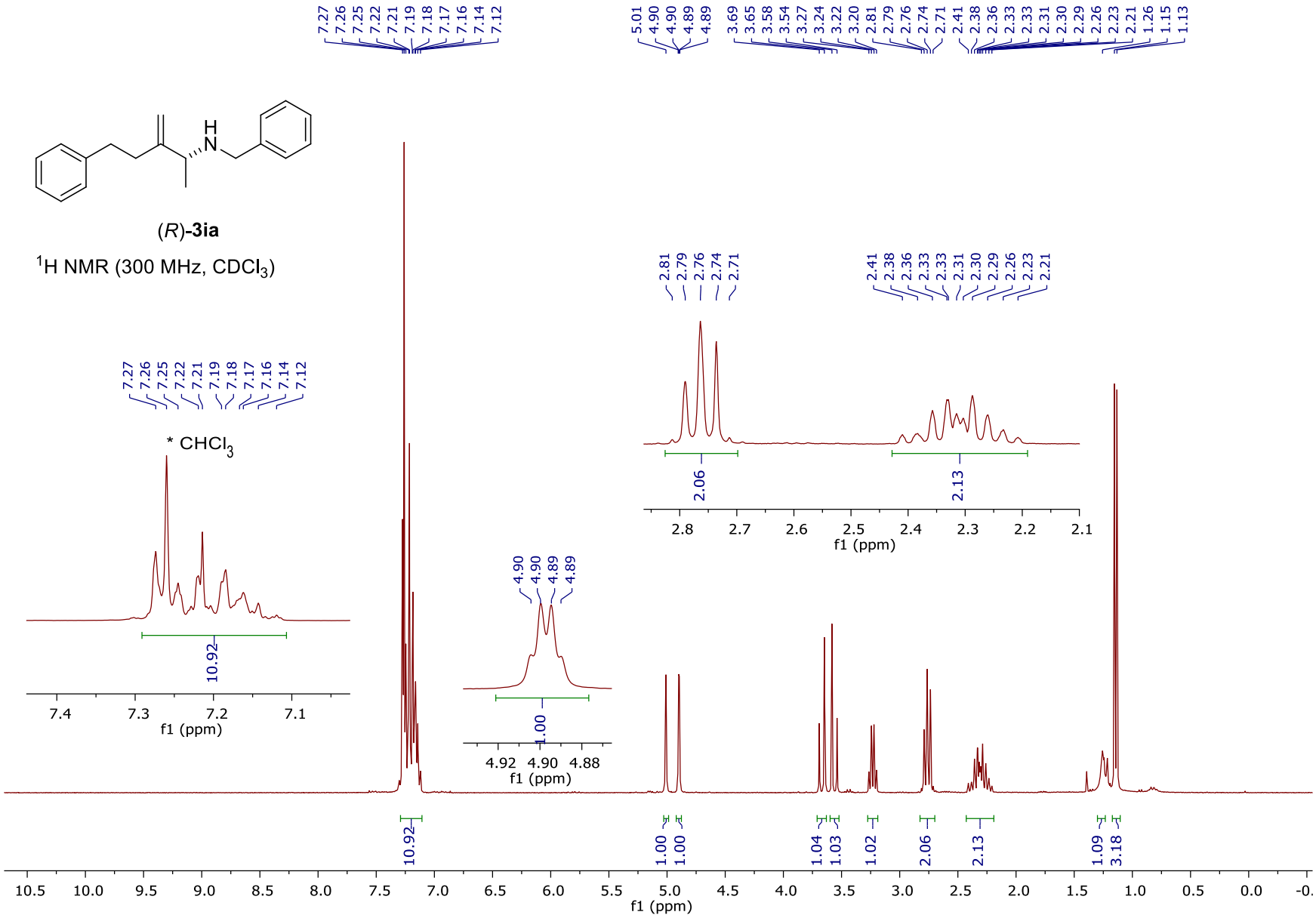

(R)-3ga
1H NMR (500 MHz, CDCl3)
CHCl3
SiMe4
f1 (ppm)

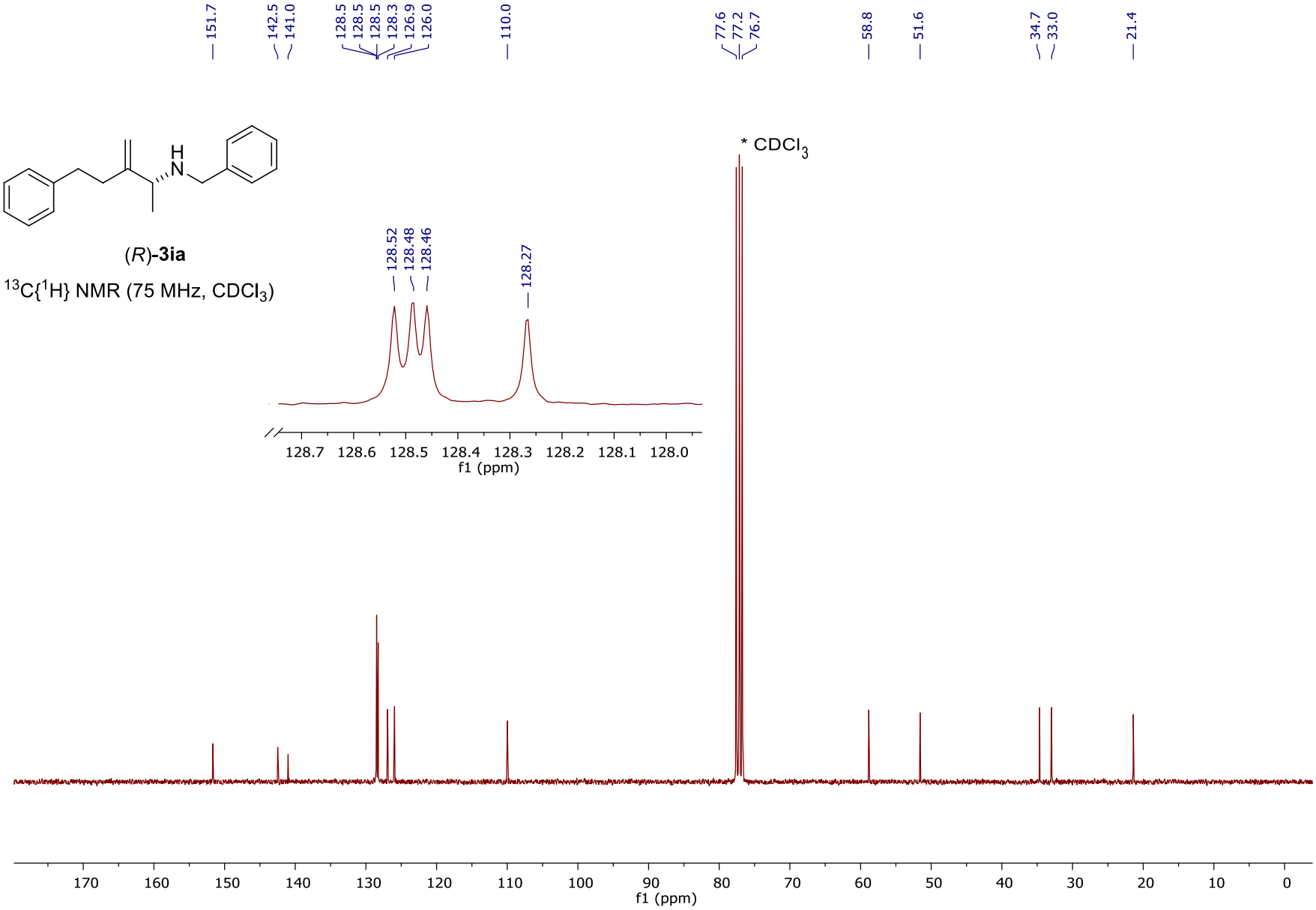

159.6
151.9
142.9
140.8
129.3
128.5
128.4
128.3
127.0
119.7
113.0
113.0
112.8
77.4
77.2
76.9
56.8
55.4
51.4
21.7
1.2
129.31
128.53
128.43
128.34
127.02
113.04
112.97
112.84
CDCl3
*
H
N
Ph
O
(R)-3ga
13C{1H} NMR (130 MHz, CDCl3)
129
128
127
113
f1 (ppm)
SiMe4
*
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


(R)-3ha
1H NMR (500 MHz, CDCl3)
* CHCl3
f1 (ppm)



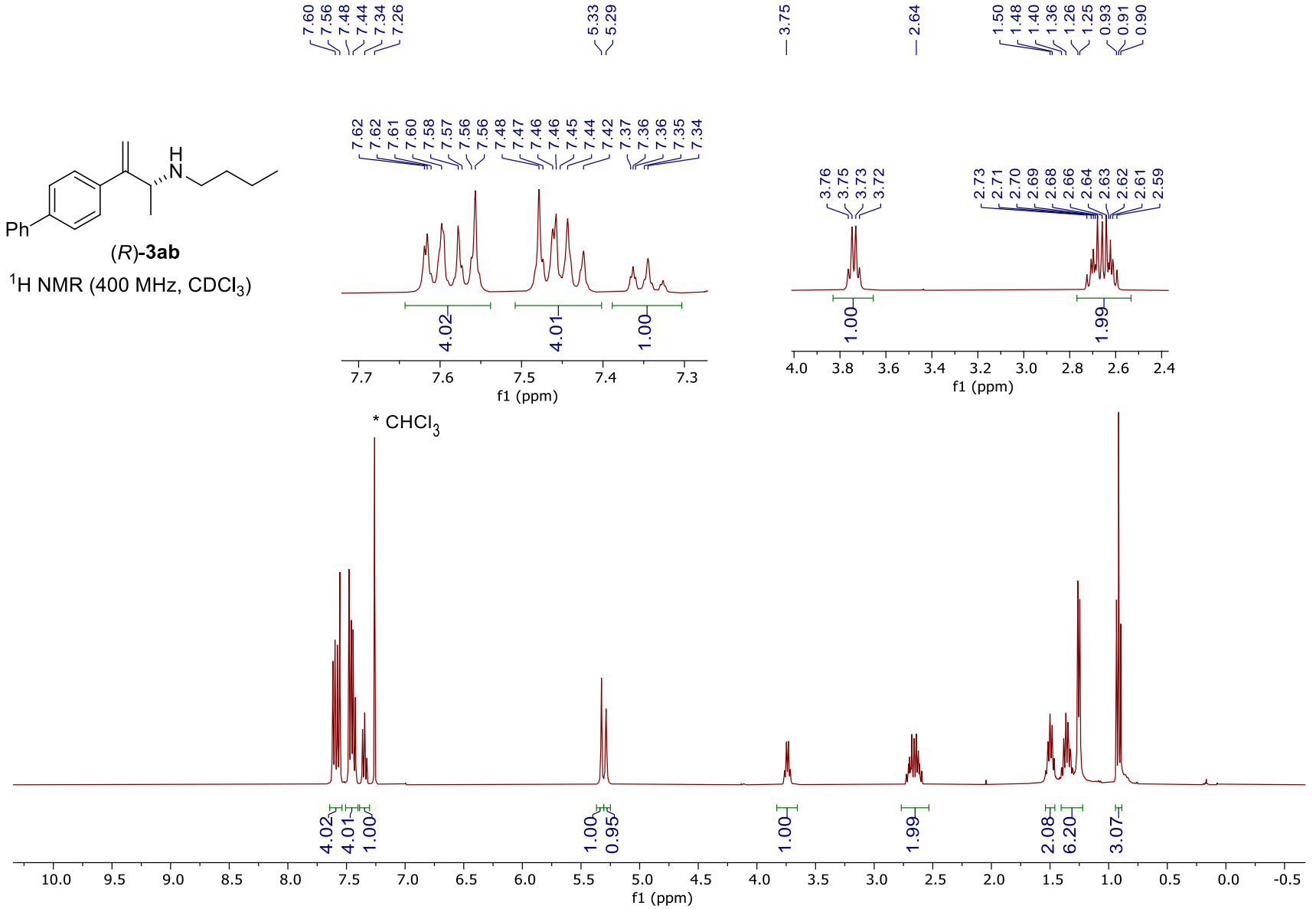
$^{13}C\{^{1}H\}$ NMR (130 MHz, $CDCl_3$)

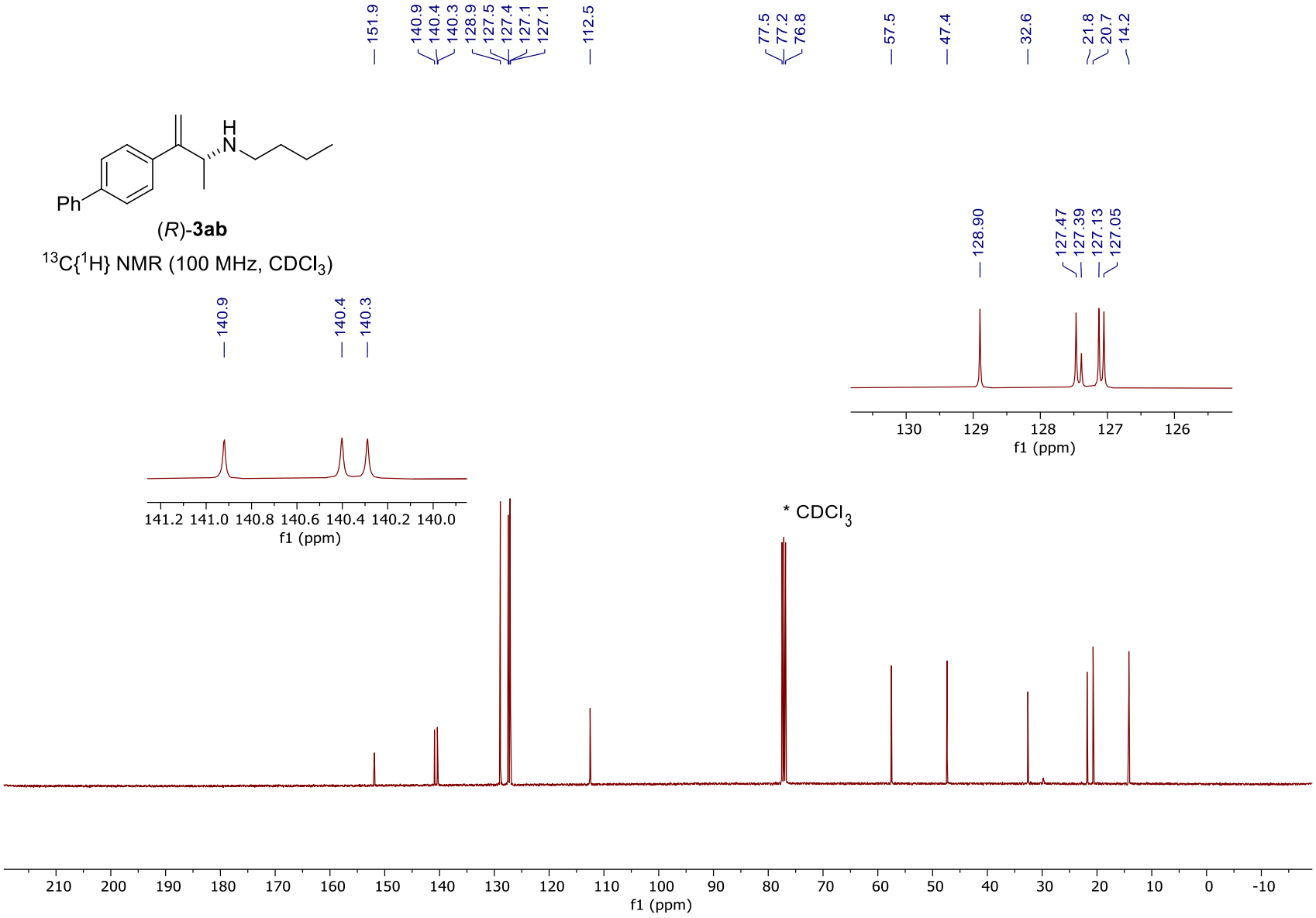

(R)-3ia
1H NMR (300 MHz, CDCl3)
* CHCl3
f1 (ppm)

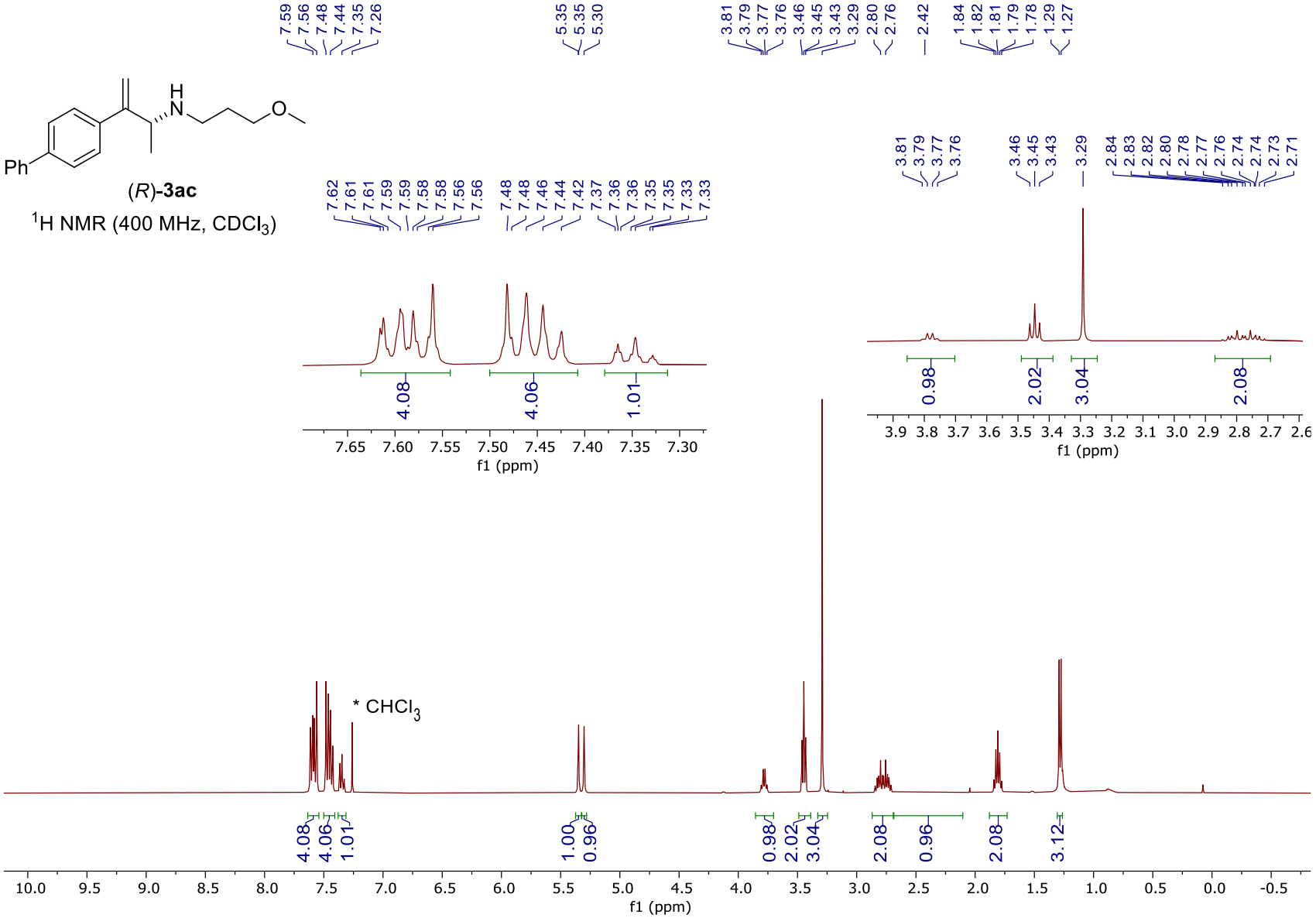


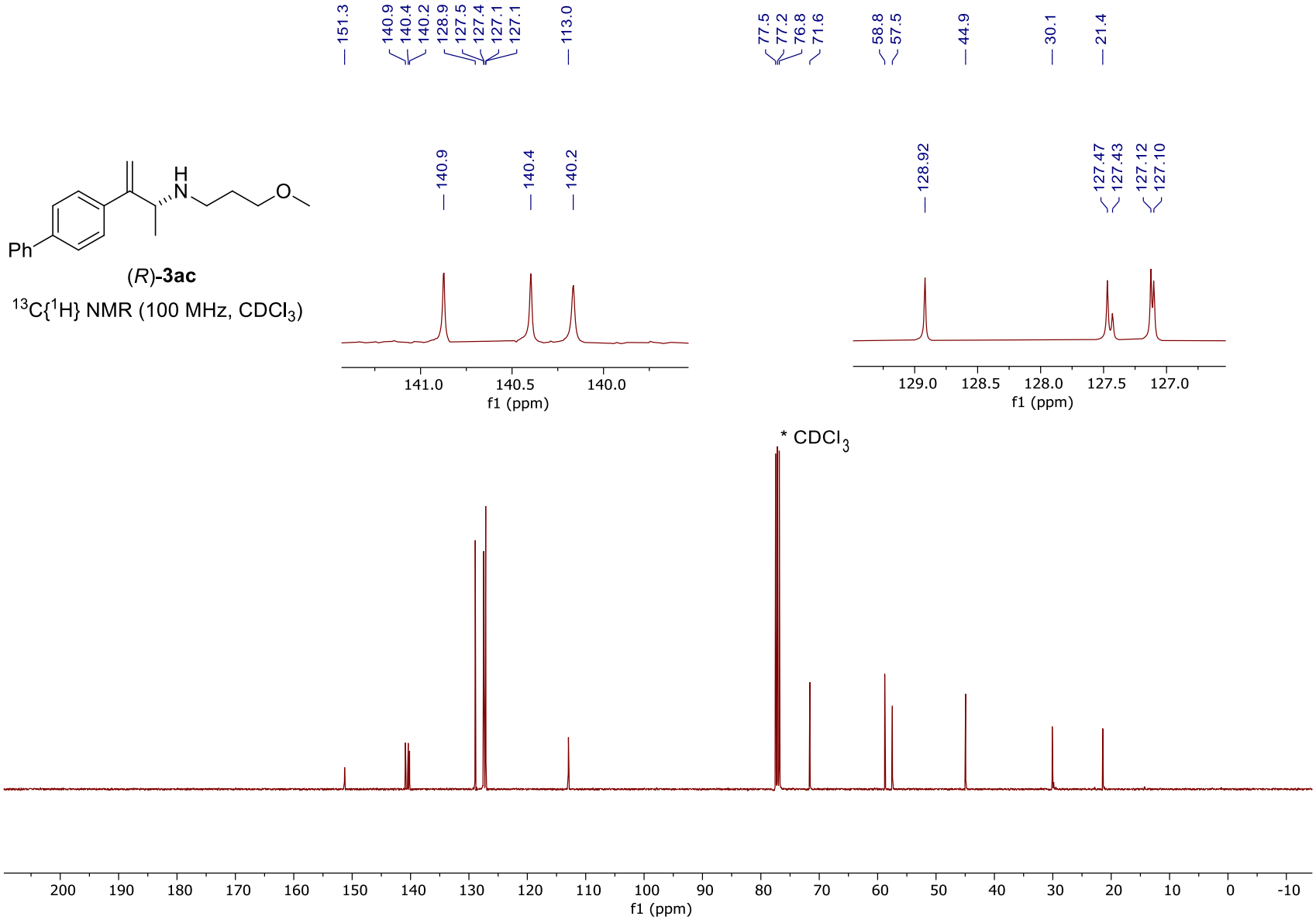
(*R*)-**3ia**

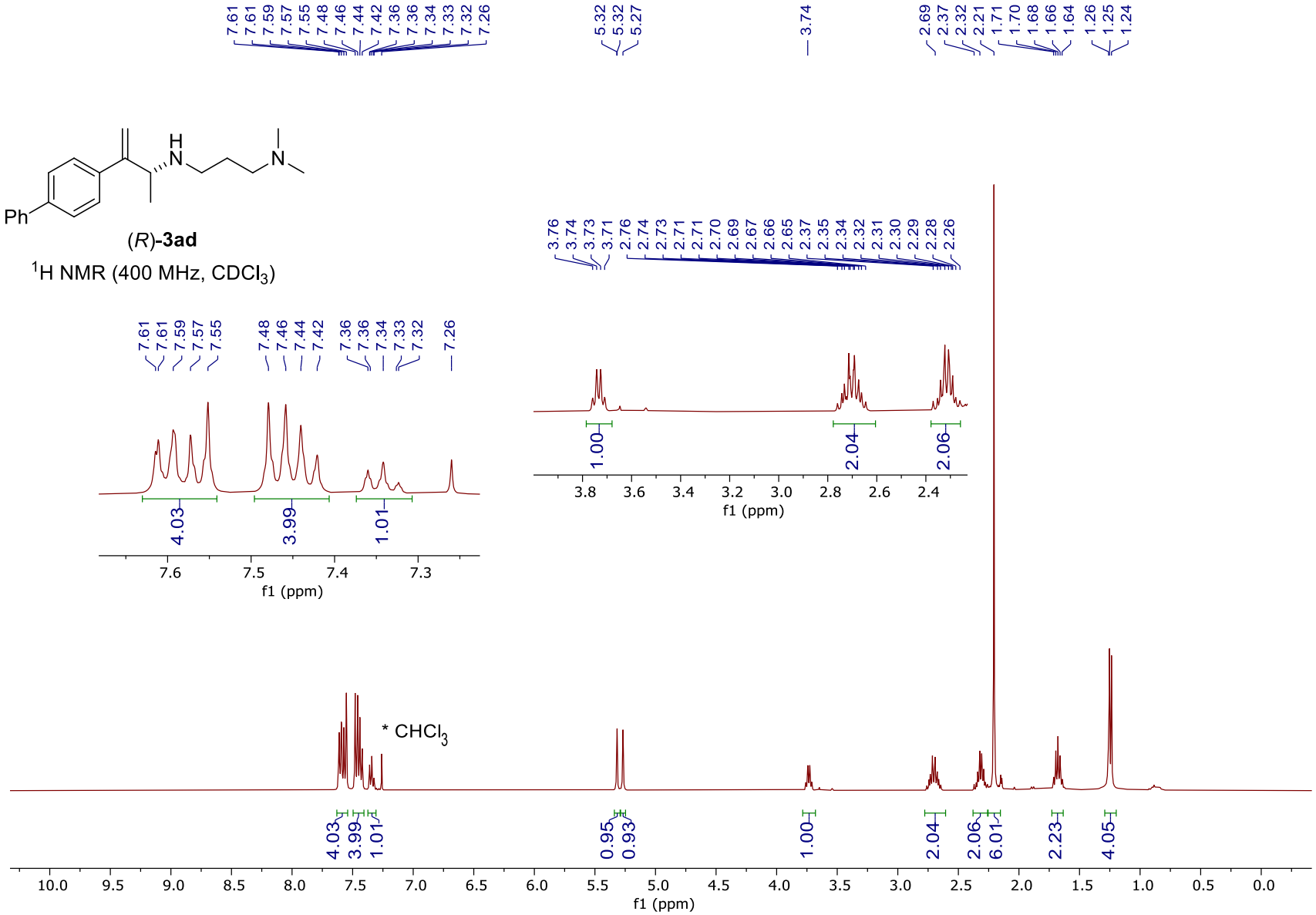
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$)

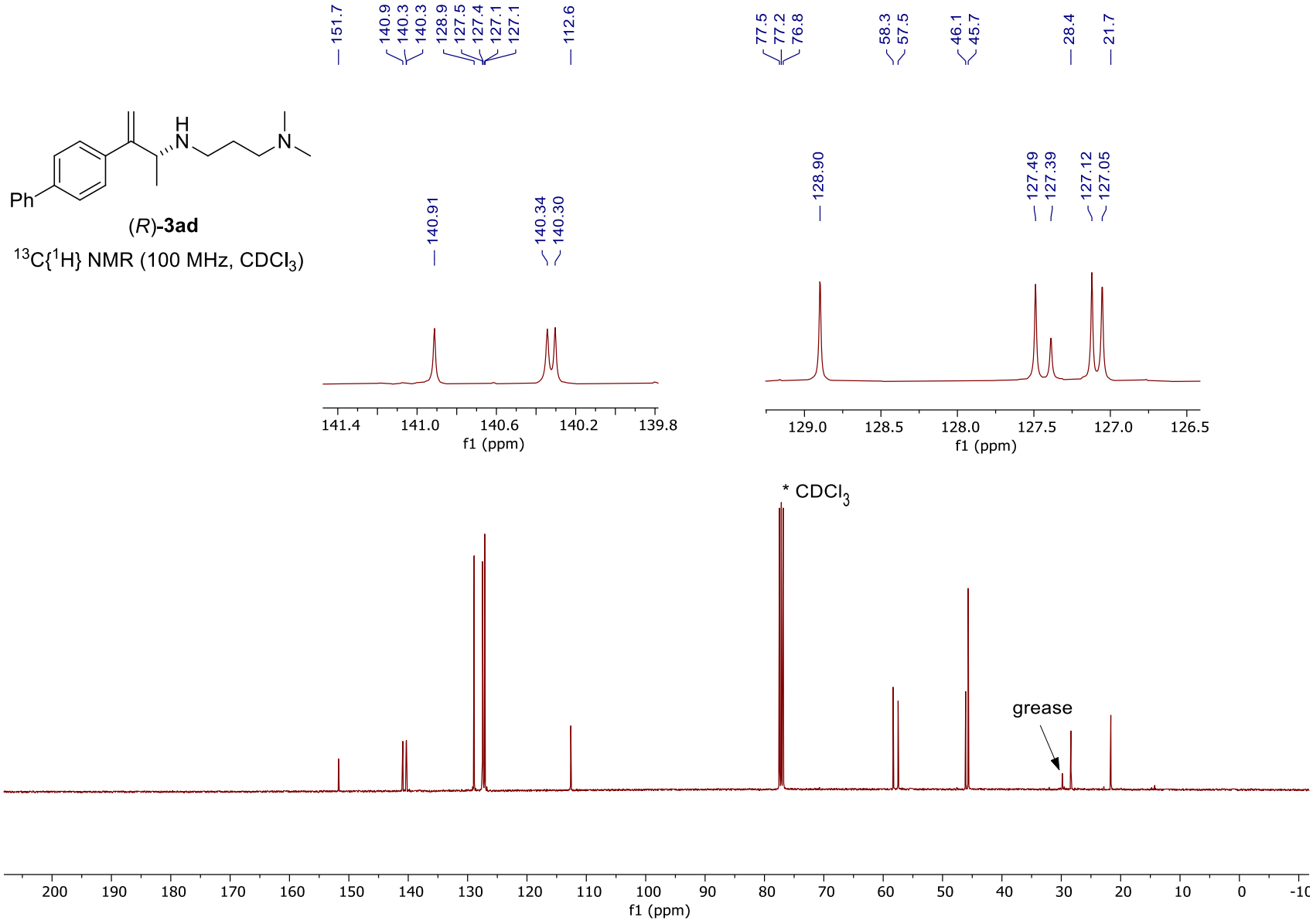

7.60
7.56
7.48
7.44
7.34
7.26
5.33
5.29
3.75
2.64
1.50
1.48
1.40
1.36
1.26
1.25
0.93
0.91
0.90
Ph
H
N
(R)-3ab
1H NMR (400 MHz, CDCl3)
4.02
4.01
1.00
1.00
1.99
f1 (ppm)
* CHCl3
4.02
4.01
1.00
1.00
0.95
1.00
1.99
2.08
6.20
3.07
f1 (ppm)

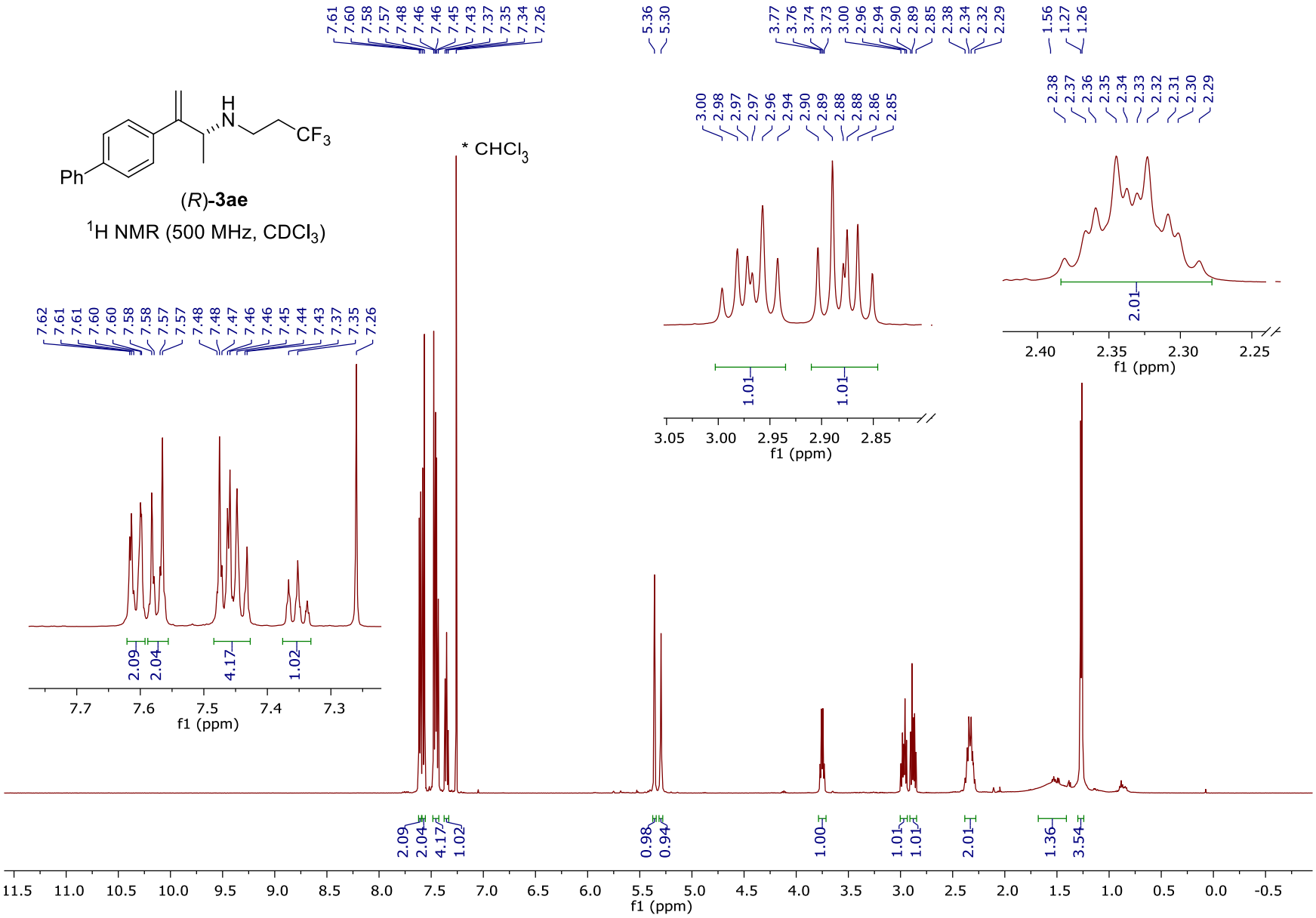

151.9
140.9
140.4
140.3
128.9
127.5
127.4
127.1
127.1
112.5
77.5
77.2
76.8
57.5
47.4
32.6
21.8
20.7
14.2
H
N
Ph
(R)-3ab
13C{1H} NMR (100 MHz, CDCl3)
128.90
127.47
127.39
127.13
127.05
130
129
128
127
126
f1 (ppm)
140.9
140.4
140.3
141.2 141.0 140.8 140.6 140.4 140.2 140.0
f1 (ppm)
* CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

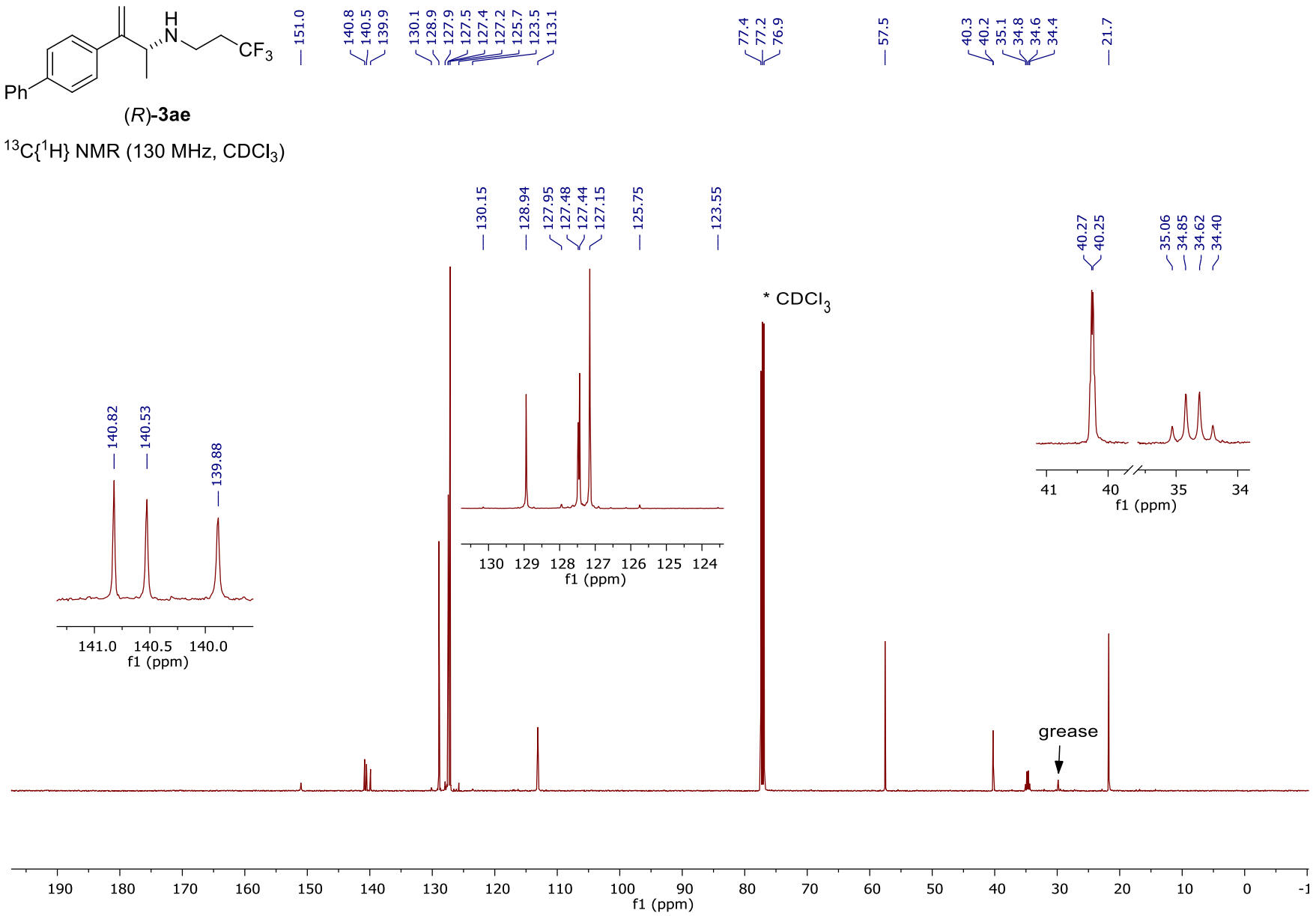

(R)-3ac
1H NMR (400 MHz, CDCl3)
* CHCl3
f1 (ppm)

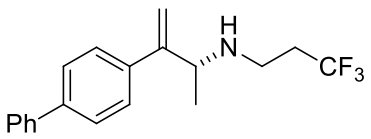

151.3
140.9
140.4
140.2
128.9
127.5
127.4
127.1
127.1
113.0
77.5
77.2
76.8
71.6
58.8
57.5
44.9
30.1
21.4
Ph
H
N
O
(R)-3ac
13C{1H} NMR (100 MHz, CDCl3)
140.9
140.4
140.2
141.0
140.5
140.0
f1 (ppm)
128.92
127.47
127.43
127.12
127.10
129.0
128.5
128.0
127.5
127.0
f1 (ppm)
* CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.61 7.61 7.59 7.57 7.55 7.48 7.46 7.44 7.42 7.36 7.36 7.34 7.33 7.32 7.26
5.32 5.32 5.27
3.74
2.69 2.37 2.32 2.21 1.71 1.70 1.68 1.66 1.64 1.26 1.25 1.24
Ph
H
N
N
(R)-3ad
1H NMR (400 MHz, CDCl3)
3.76 3.74 3.73 3.71 2.76 2.74 2.73 2.71 2.71 2.70 2.69 2.67 2.66 2.65 2.37 2.35 2.34 2.32 2.31 2.30 2.29 2.28 2.26
1.00
2.04
2.06
3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4
f1 (ppm)
7.61 7.61 7.59 7.57 7.55 7.48 7.46 7.44 7.42 7.36 7.36 7.34 7.33 7.32 7.26
4.03
3.99
1.01
7.6 7.5 7.4 7.3
f1 (ppm)
* CHCl3
4.03 3.99 1.01 0.95 0.93 1.00 2.04 2.06 6.01 2.23 4.05
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)


151.7
140.9
140.3
140.3
128.9
127.5
127.4
127.1
127.1
112.6
77.5
77.2
76.8
58.3
57.5
46.1
45.7
28.4
21.7
Ph
H
N
N
(R)-3ad
13C{1H} NMR (100 MHz, CDCl3)
140.91
140.34
140.30
141.4
141.0
140.6
140.2
139.8
f1 (ppm)
128.90
127.49
127.39
127.12
127.05
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
* CDCl3
grease
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

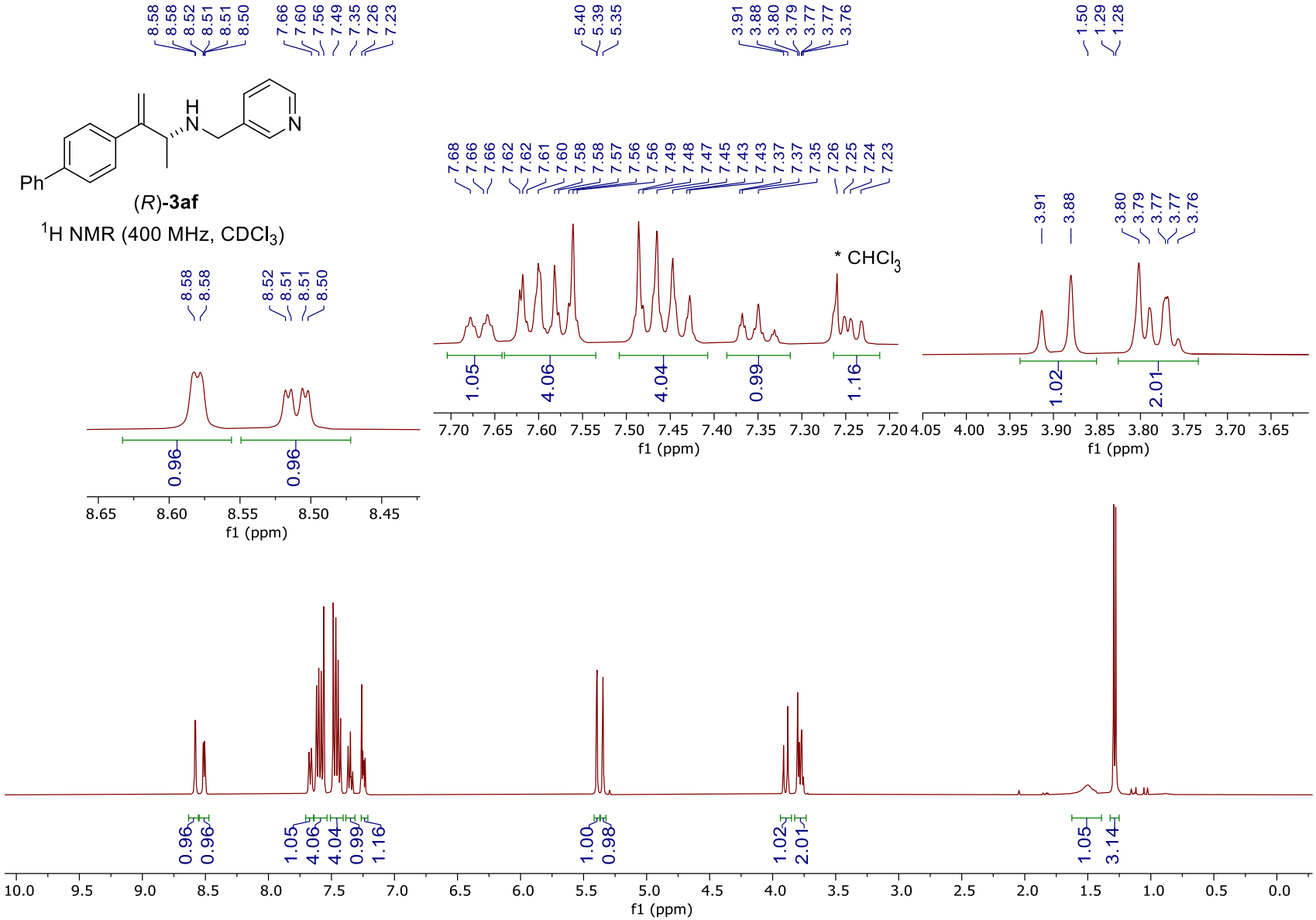

(R)-3ae
1H NMR (500 MHz, CDCl3)
* CHCl3
f1 (ppm)

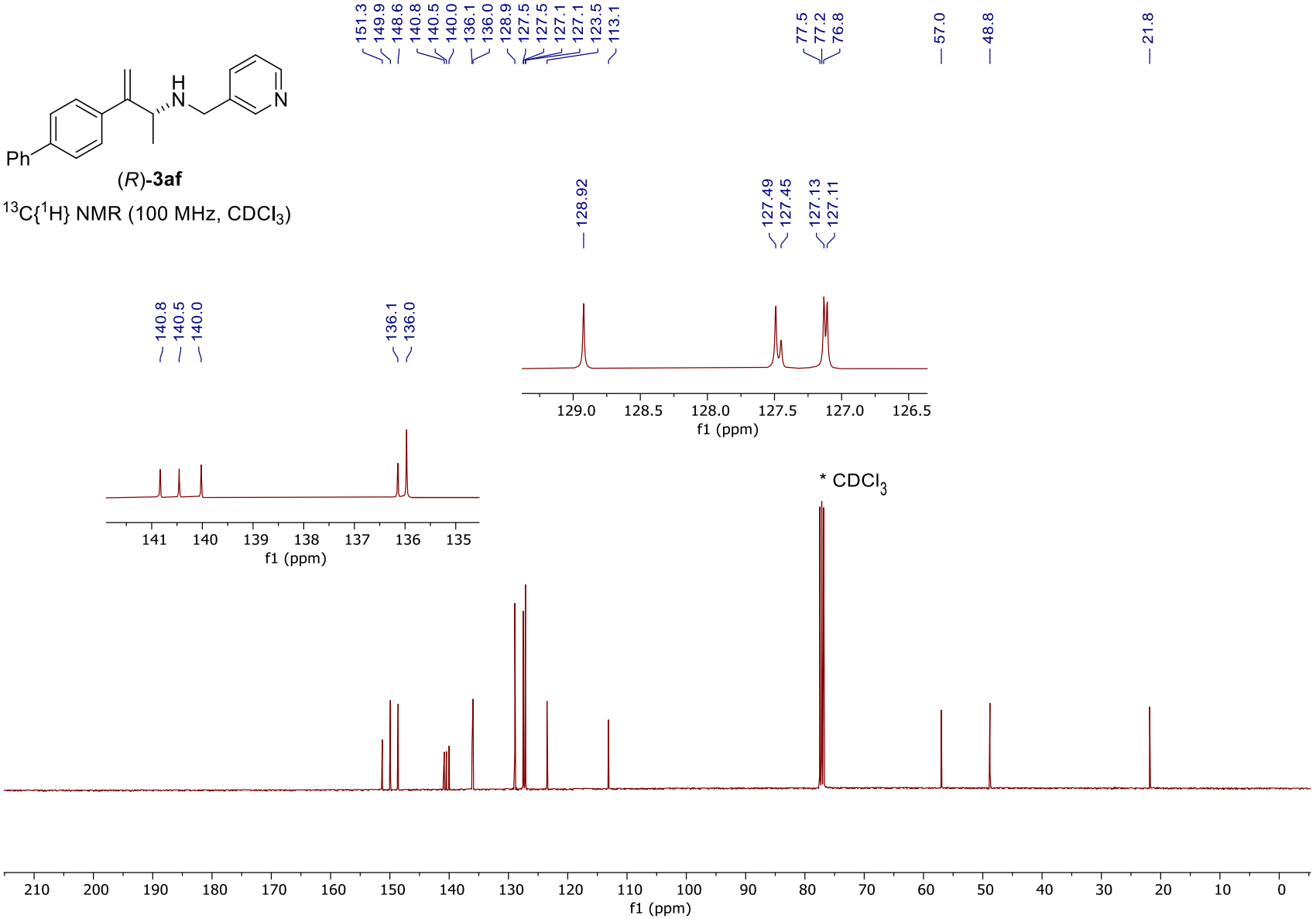

Ph
H
N
CF3
(R)-3ae
13C{1H} NMR (130 MHz, CDCl3)
151.0
140.8
140.5
139.9
130.1
128.9
127.9
127.5
127.4
127.2
125.7
123.5
113.1
77.4
77.2
76.9
57.5
40.3
40.2
35.1
34.8
34.6
34.4
21.7
* CDCl3
grease
f1 (ppm)
140.82
140.53
139.88
141.0 140.5 140.0
f1 (ppm)
130.15
128.94
127.95
127.48
127.44
127.15
125.75
123.55
130 129 128 127 126 125 124
f1 (ppm)
40.27
40.25
35.06
34.85
34.62
34.40
41 40 35 34
f1 (ppm)

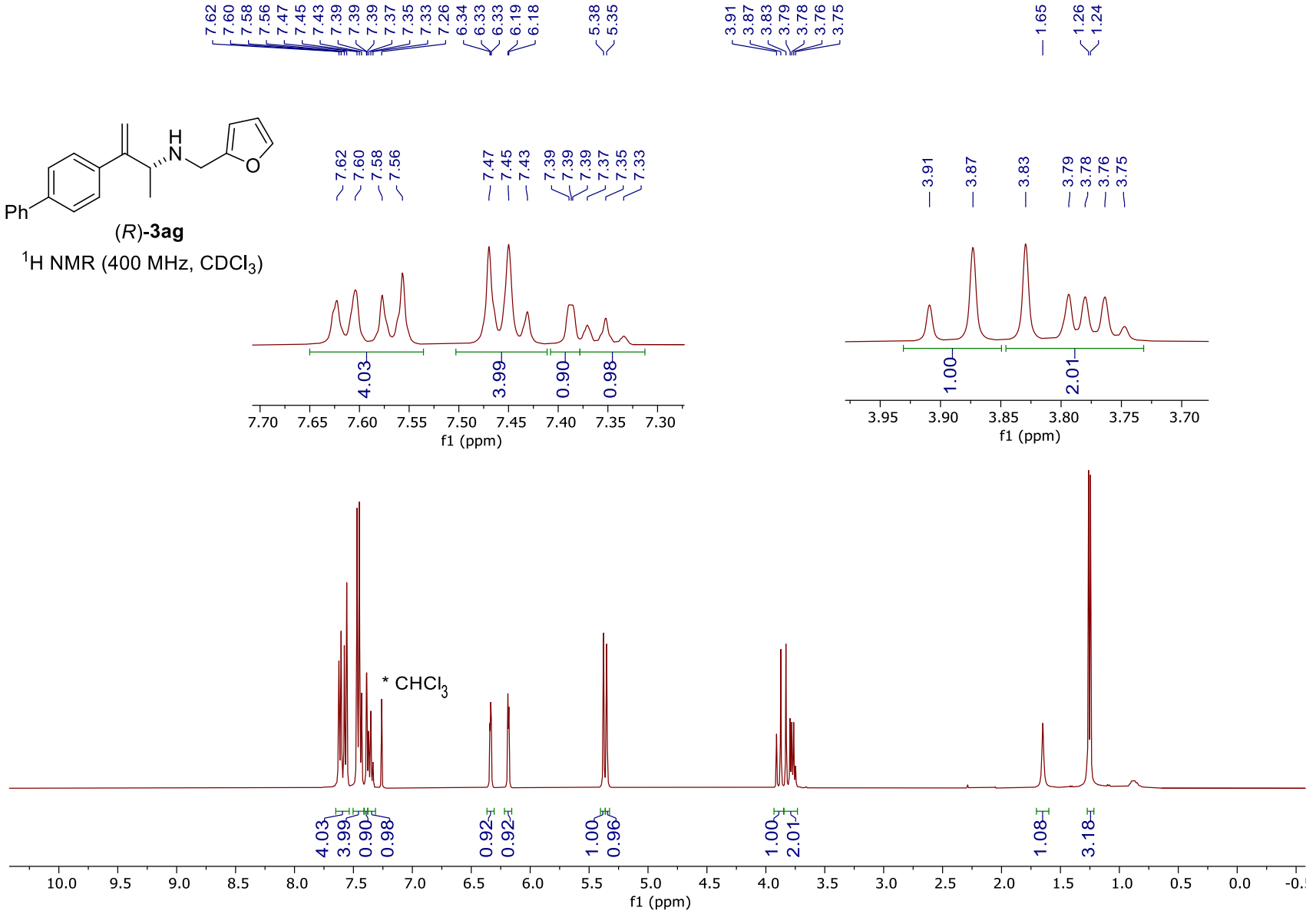


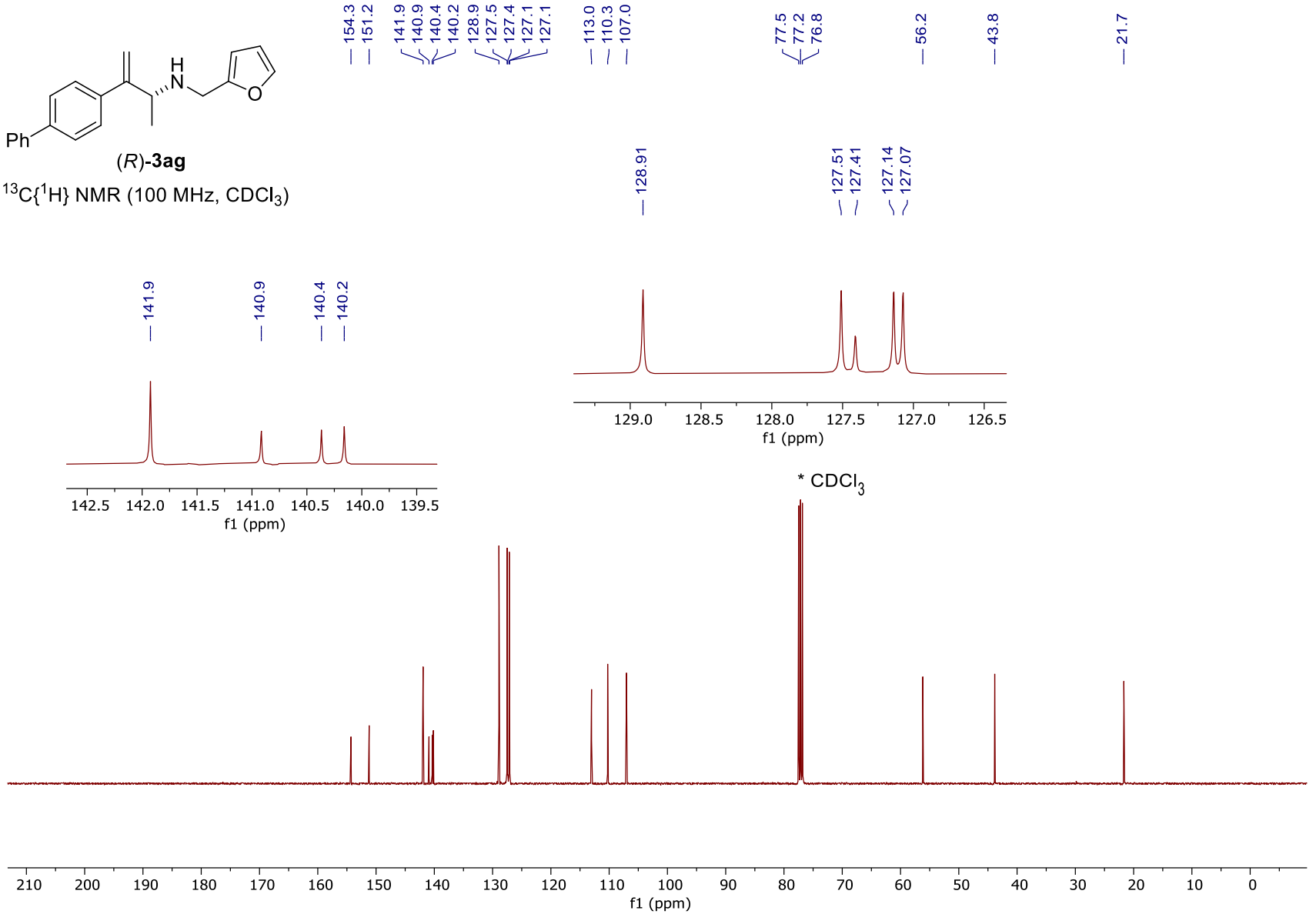
(*R*)-**3ae**

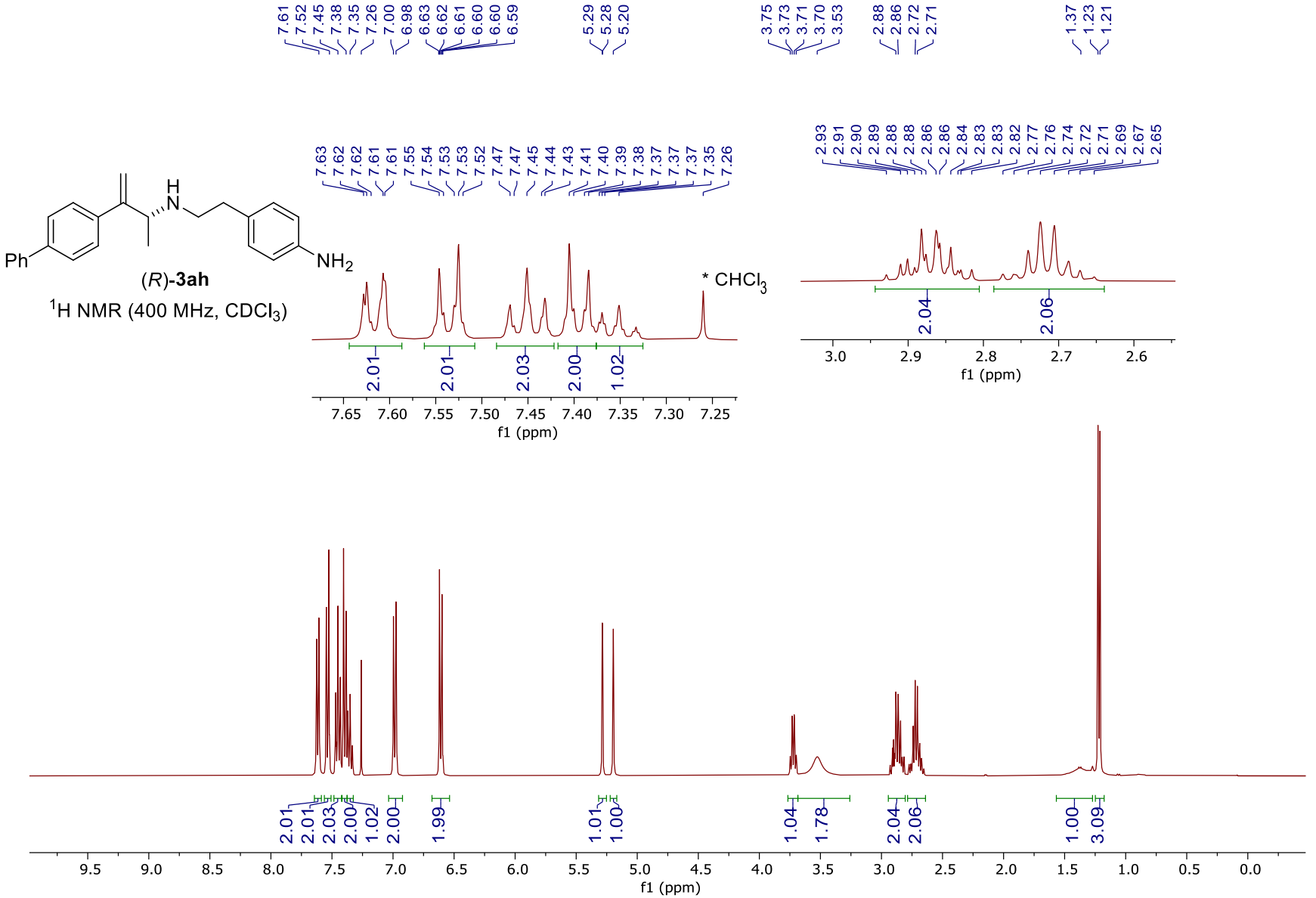
$^{19}F\{^{1}H\}$ NMR (280 MHz, $CDCl_3$)

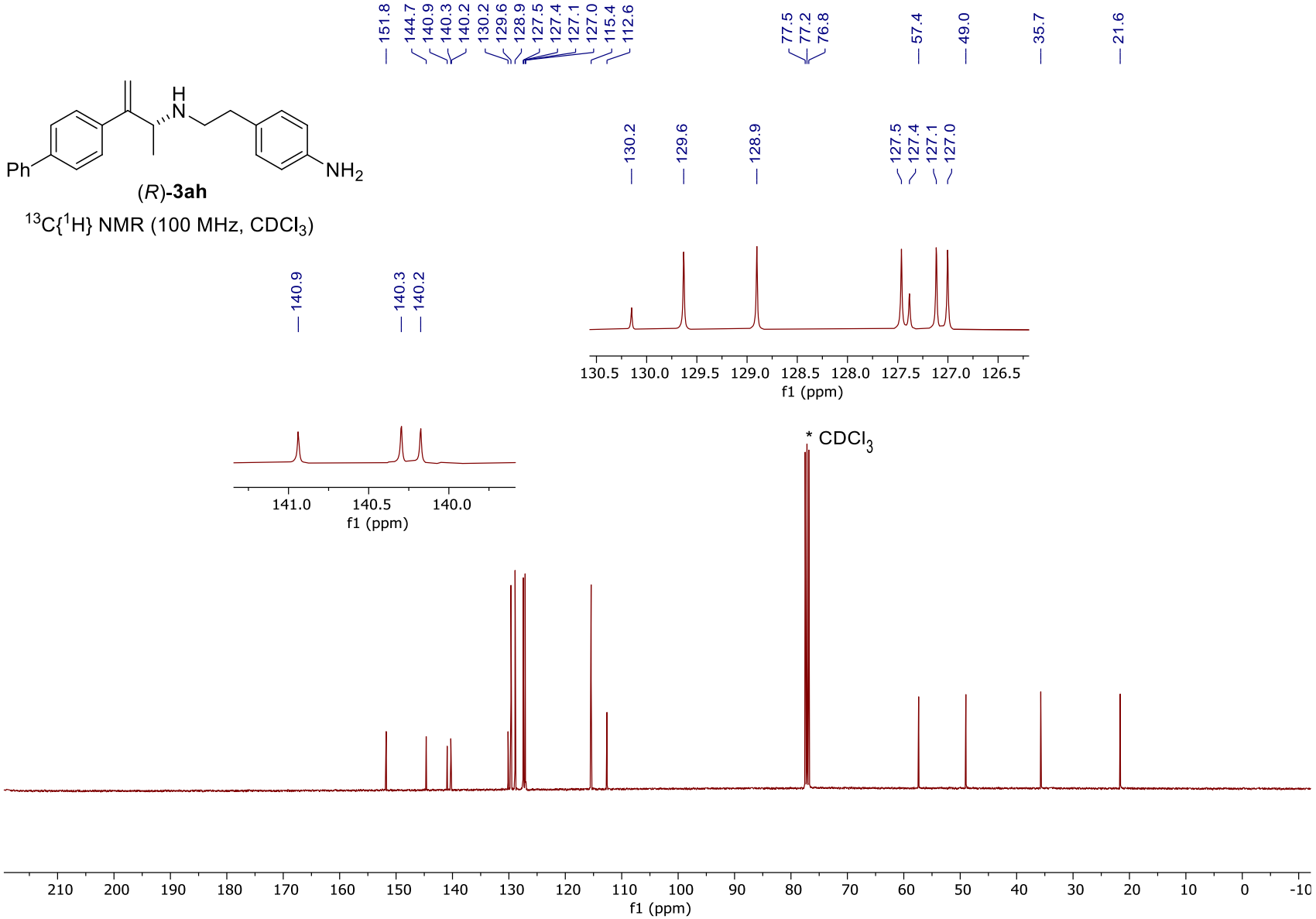

8.58 8.58 8.52 8.51 8.51 8.50 7.66 7.60 7.56 7.49 7.35 7.26 7.23
5.40 5.39 5.35
3.91 3.88 3.80 3.79 3.77 3.77 3.76
1.50 1.29 1.28
H
N
N
Ph
(R)-3af
1H NMR (400 MHz, CDCl3)
* CHCl3
0.96 0.96
1.05 4.06 4.04 0.99 1.16
1.02 2.01
1.00 0.98
1.02 2.01
1.05 3.14
f1 (ppm)

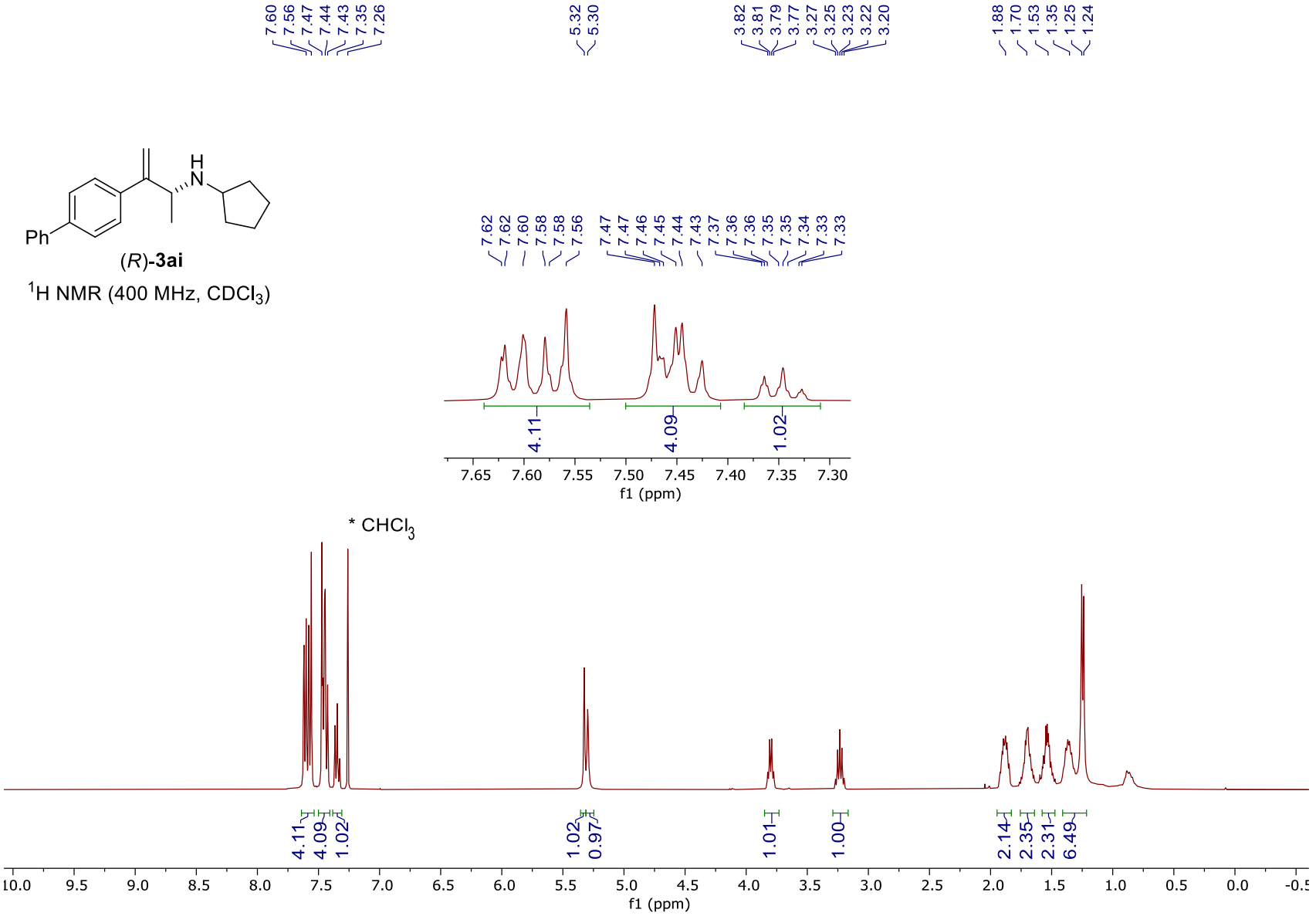

151.3
149.9
148.6
140.8
140.5
140.0
136.1
136.0
128.9
127.5
127.5
127.1
127.1
123.5
113.1
77.5
77.2
76.8
57.0
48.8
21.8
H
N
N
Ph
(R)-3af
13C{1H} NMR (100 MHz, CDCl3)
128.92
127.49
127.45
127.13
127.11
140.8
140.5
140.0
136.1
136.0
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
141
140
139
138
137
136
135
f1 (ppm)
* CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

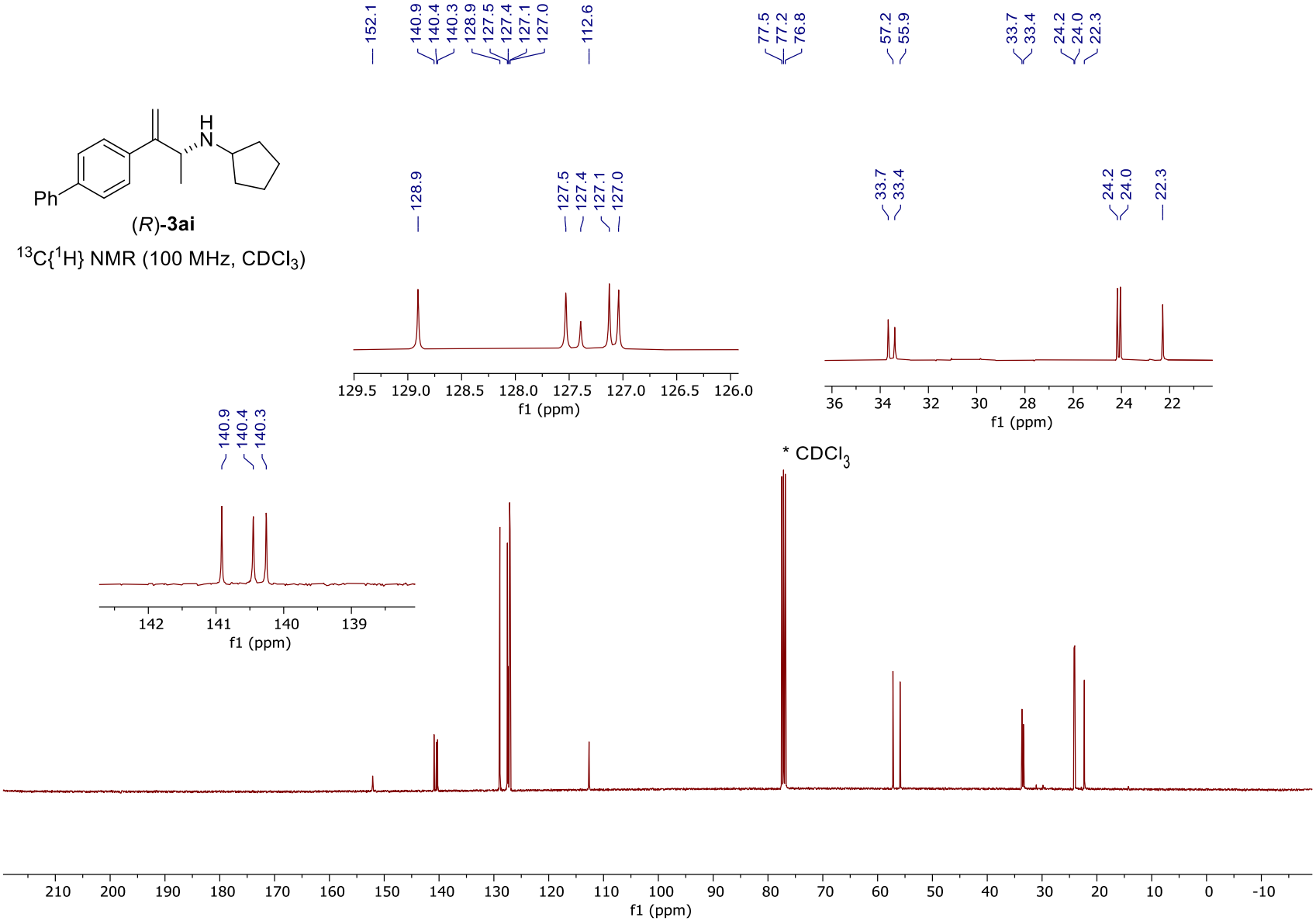

7.62
7.60
7.58
7.56
7.47
7.45
7.43
7.39
7.39
7.39
7.37
7.35
7.33
7.26
6.34
6.33
6.33
6.19
6.18
5.38
5.35
3.91
3.87
3.83
3.79
3.78
3.76
3.75
1.65
1.26
1.24
Ph
H
N
O
(R)-3ag
1H NMR (400 MHz, CDCl3)
4.03
3.99
0.90
0.98
1.00
2.01
f1 (ppm)
* CHCl3
4.03
3.99
0.90
0.98
0.92
0.92
1.00
0.96
1.00
2.01
1.08
3.18
f1 (ppm)

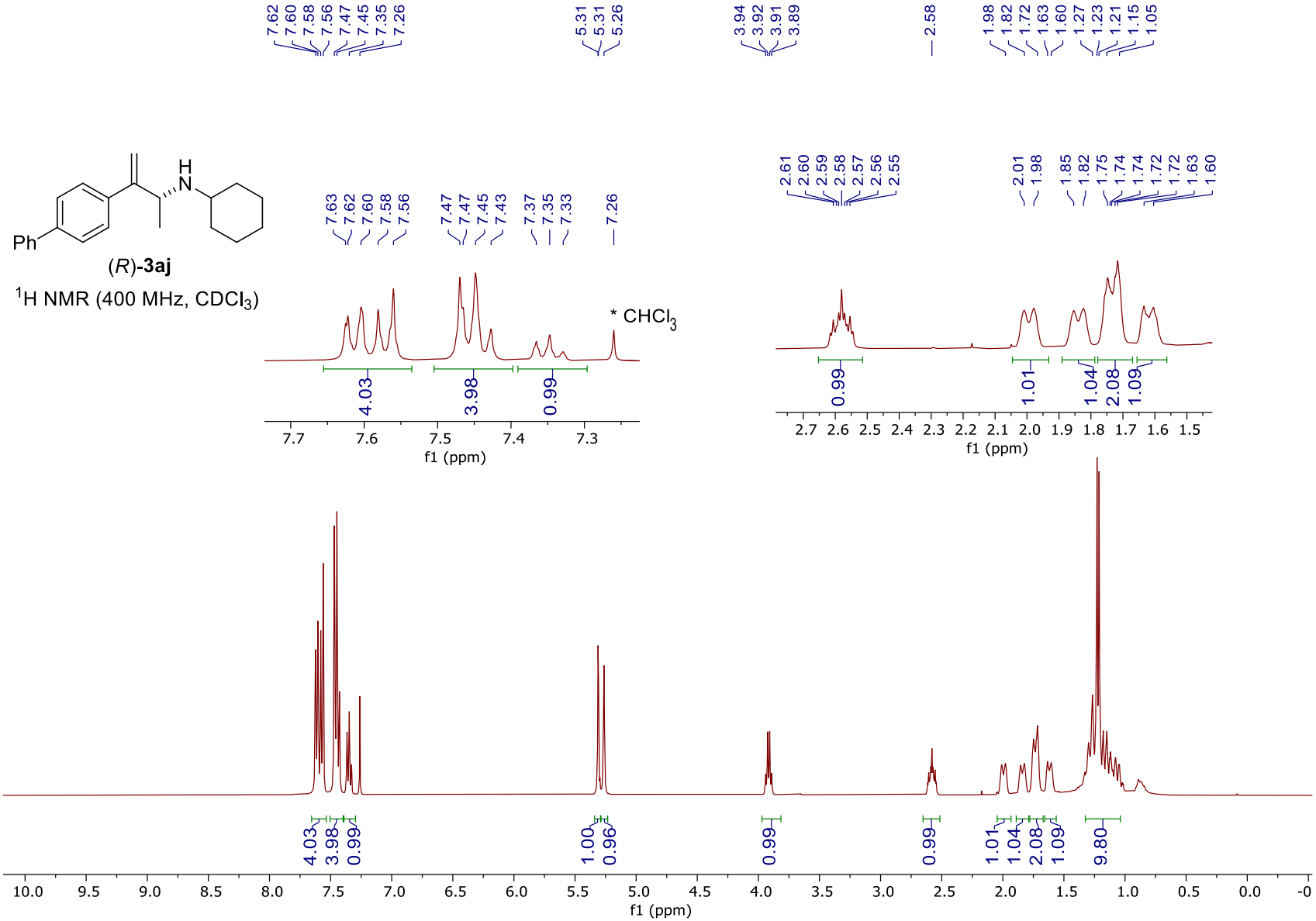

154.3
151.2
141.9
140.9
140.4
140.2
128.9
127.5
127.4
127.1
127.1
113.0
110.3
107.0
77.5
77.2
76.8
56.2
43.8
21.7
Ph
H
N
O
(R)-3ag
13C{1H} NMR (100 MHz, CDCl3)
128.91
127.51
127.41
127.14
127.07
141.9
140.9
140.4
140.2
142.5 142.0 141.5 141.0 140.5 140.0 139.5
f1 (ppm)
129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
* CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

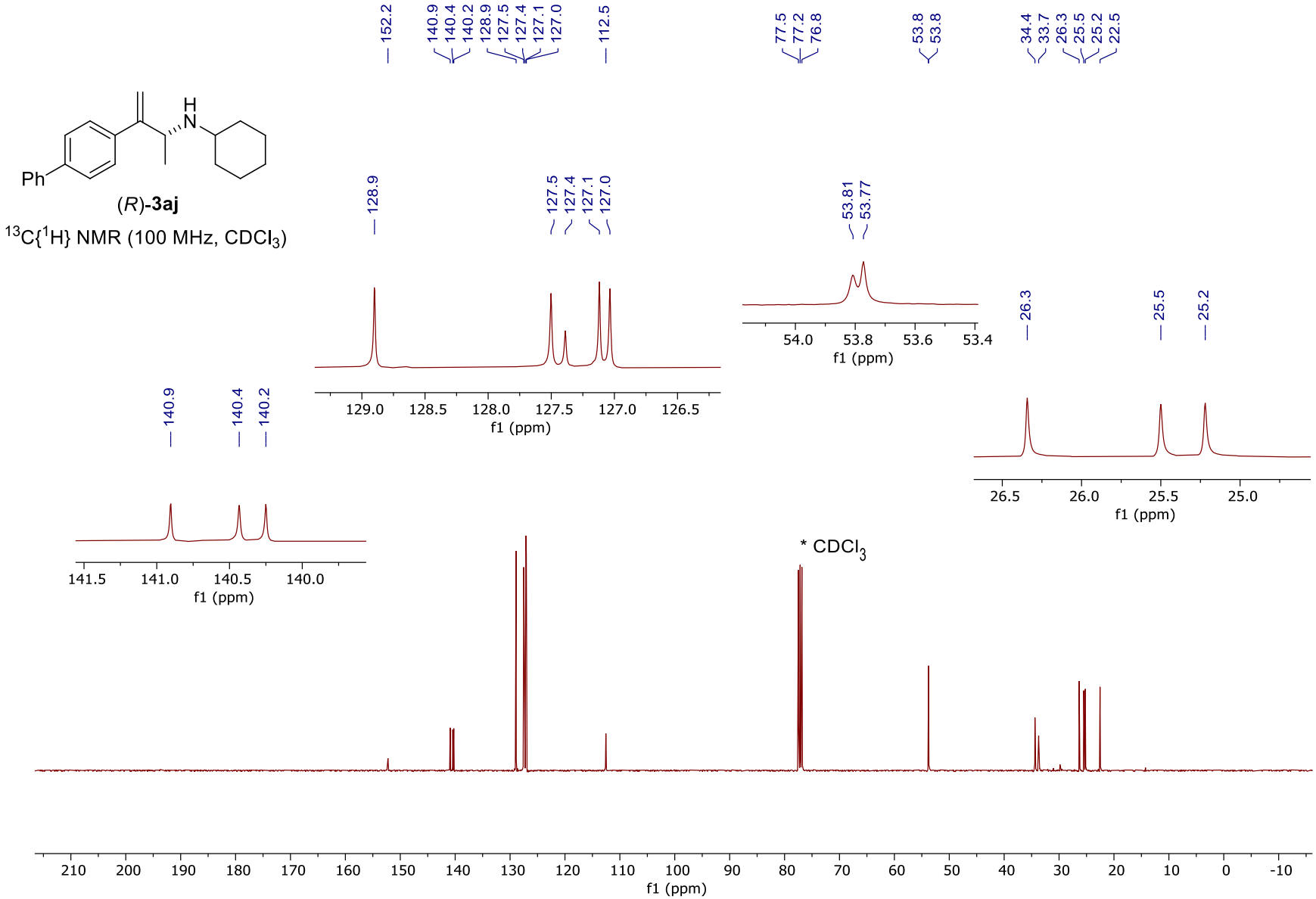

7.61 7.52 7.45 7.38 7.35 7.26 7.00 6.98 6.63 6.62 6.61 6.60 6.60 6.59
5.29 5.28 5.20
3.75 3.73 3.71 3.70 3.53
2.88 2.86 2.72 2.71
1.37 1.23 1.21
7.63 7.62 7.62 7.61 7.61 7.55 7.54 7.53 7.53 7.52 7.47 7.47 7.45 7.44 7.43 7.41 7.40 7.39 7.38 7.37 7.37 7.35 7.26
2.93 2.91 2.90 2.89 2.88 2.88 2.86 2.86 2.84 2.83 2.83 2.82 2.77 2.76 2.74 2.72 2.71 2.69 2.67 2.65
Ph
NH2
H
N
(R)-3ah
1H NMR (400 MHz, CDCl3)
* CHCl3
2.01 2.01 2.03 2.00 1.02
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30 7.25
f1 (ppm)
2.04 2.06
3.0 2.9 2.8 2.7 2.6
f1 (ppm)
2.01 2.01 2.03 2.00 1.02 2.00 1.99 1.01 1.00 1.04 1.78 2.04 2.06 1.00 3.09
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)

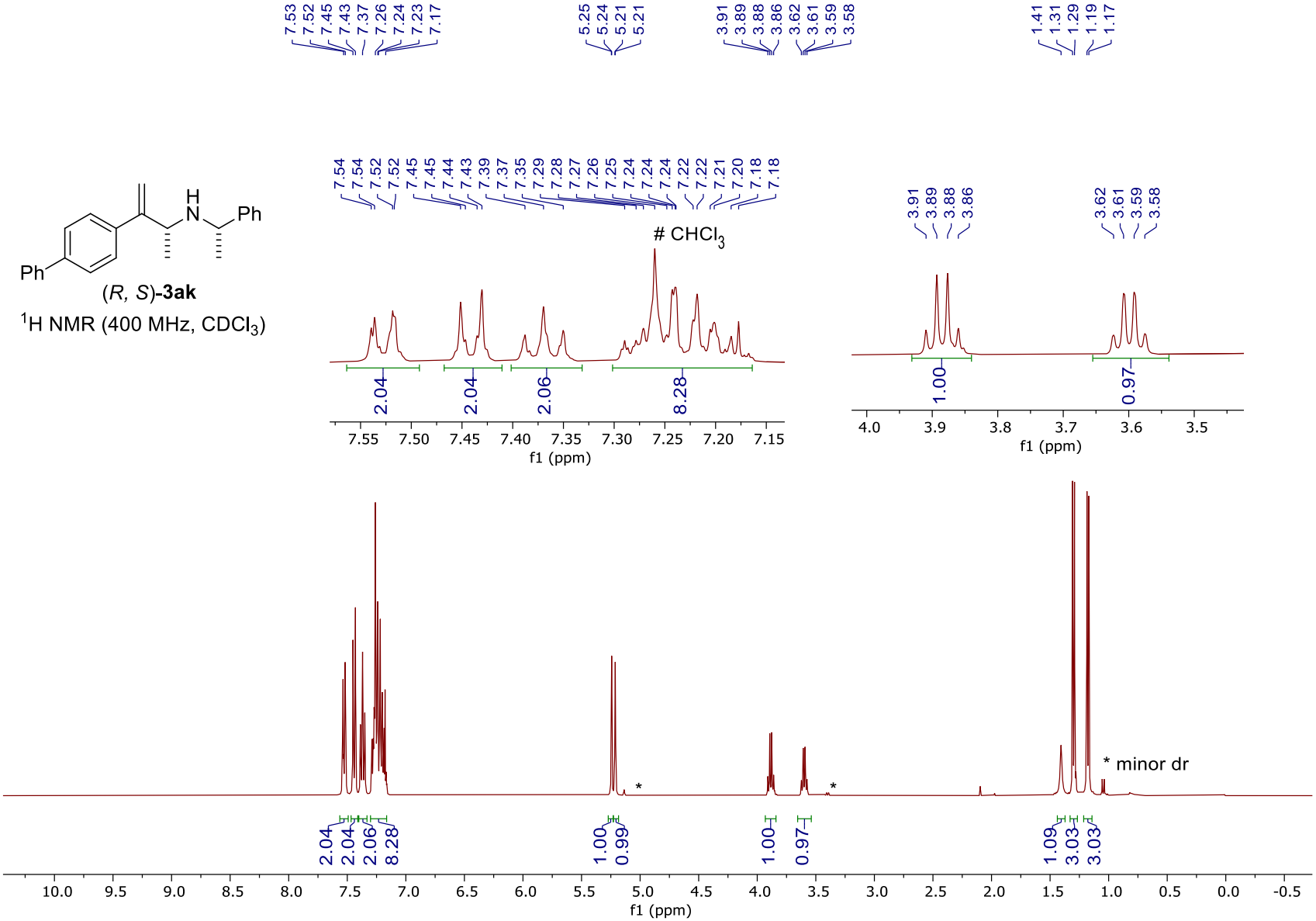

151.8
144.7
140.9
140.3
140.2
130.2
129.6
128.9
127.5
127.4
127.1
127.0
115.4
112.6
77.5
77.2
76.8
57.4
49.0
35.7
21.6
H
N
Ph
NH2
(R)-3ah
13C{1H} NMR (100 MHz, CDCl3)
130.2
129.6
128.9
127.5
127.4
127.1
127.0
130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
140.9
140.3
140.2
141.0 140.5 140.0
f1 (ppm)
* CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

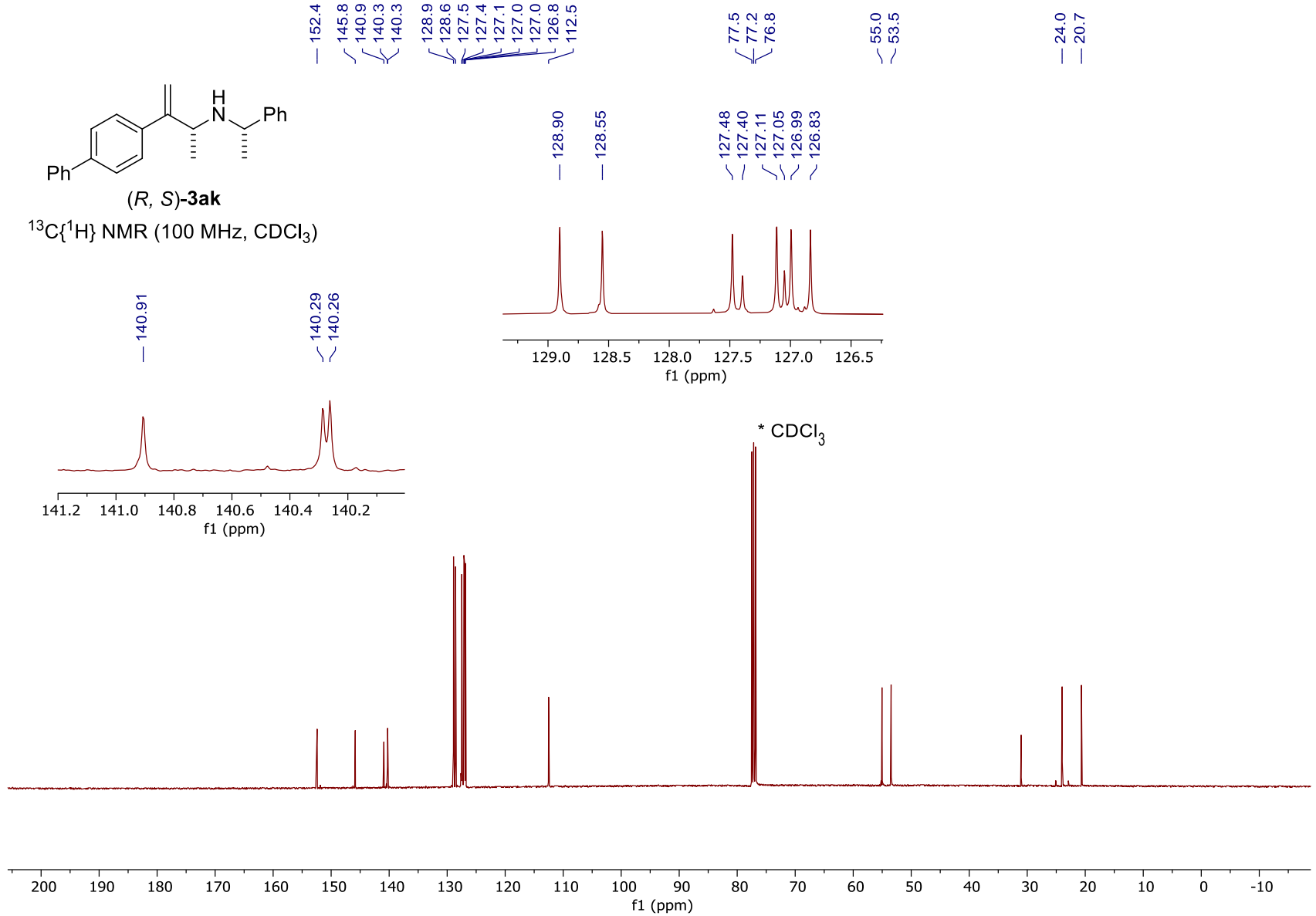

7.60
7.56
7.47
7.44
7.43
7.35
7.26
5.32
5.30
3.82
3.81
3.79
3.77
3.27
3.25
3.23
3.22
3.20
1.88
1.70
1.53
1.35
1.25
1.24
H
N
Ph
(R)-3ai
1H NMR (400 MHz, CDCl3)
7.62
7.62
7.60
7.58
7.58
7.56
7.47
7.47
7.46
7.45
7.44
7.43
7.37
7.36
7.36
7.35
7.35
7.34
7.33
7.33
4.11
4.09
1.02
7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
* CHCl3
4.11
4.09
1.02
1.02
0.97
1.01
1.00
2.14
2.35
2.31
6.49
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 -0.5
f1 (ppm)

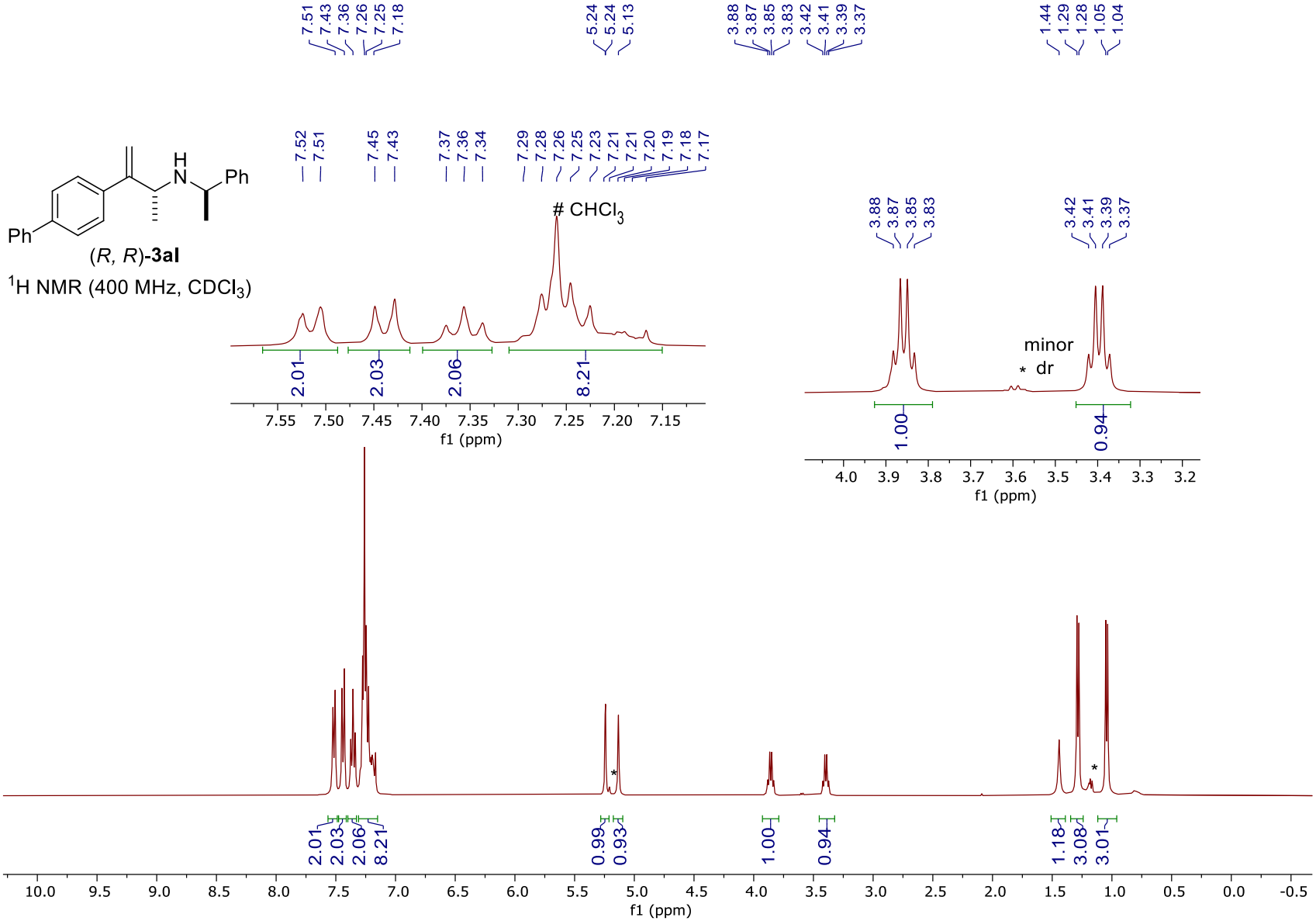

152.1
140.9
140.4
140.3
128.9
127.5
127.4
127.1
127.0
112.6
77.5
77.2
76.8
57.2
55.9
33.7
33.4
24.2
24.0
22.3
Ph
H
N
(R)-3ai
13C{1H} NMR (100 MHz, CDCl3)
* CDCl3
f1 (ppm)

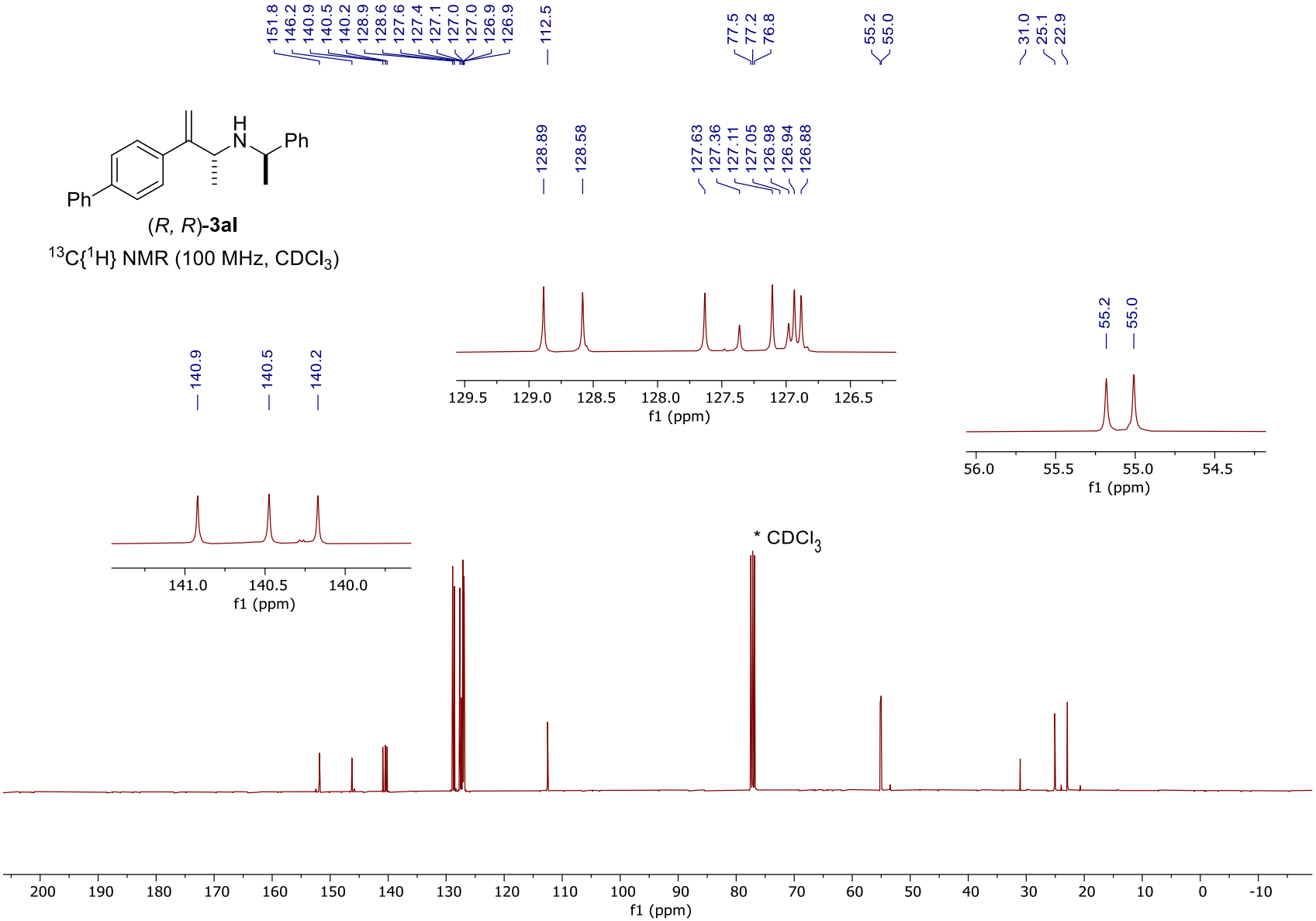

(R)-3aj
1H NMR (400 MHz, CDCl3)
* CHCl3
f1 (ppm)

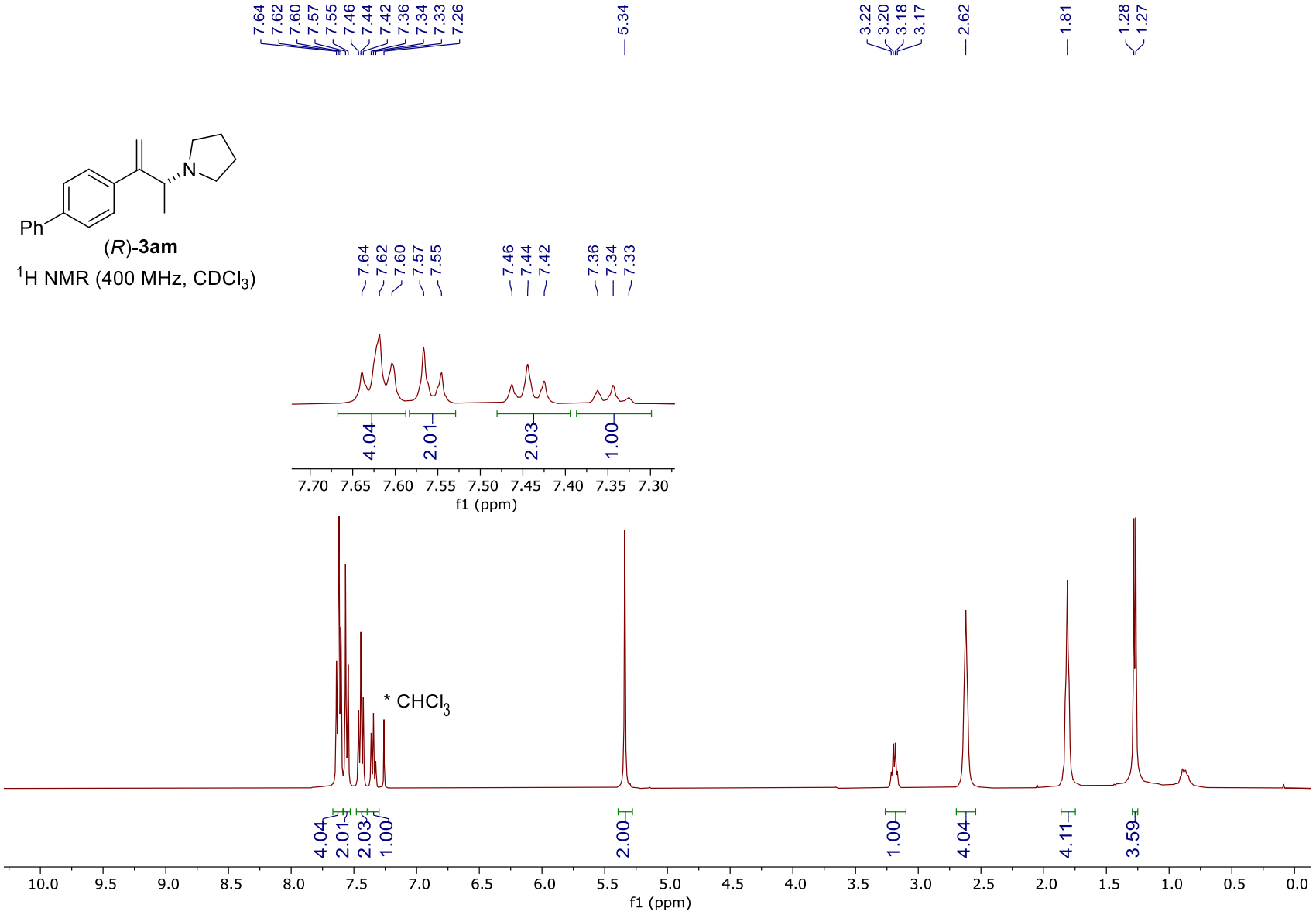

Ph
H
N
(R)-3aj
13C{1H} NMR (100 MHz, CDCl3)
152.2
140.9
140.4
140.2
128.9
127.5
127.4
127.1
127.0
112.5
77.5
77.2
76.8
53.8
53.8
34.4
33.7
26.3
25.5
25.2
22.5
* CDCl3
f1 (ppm)

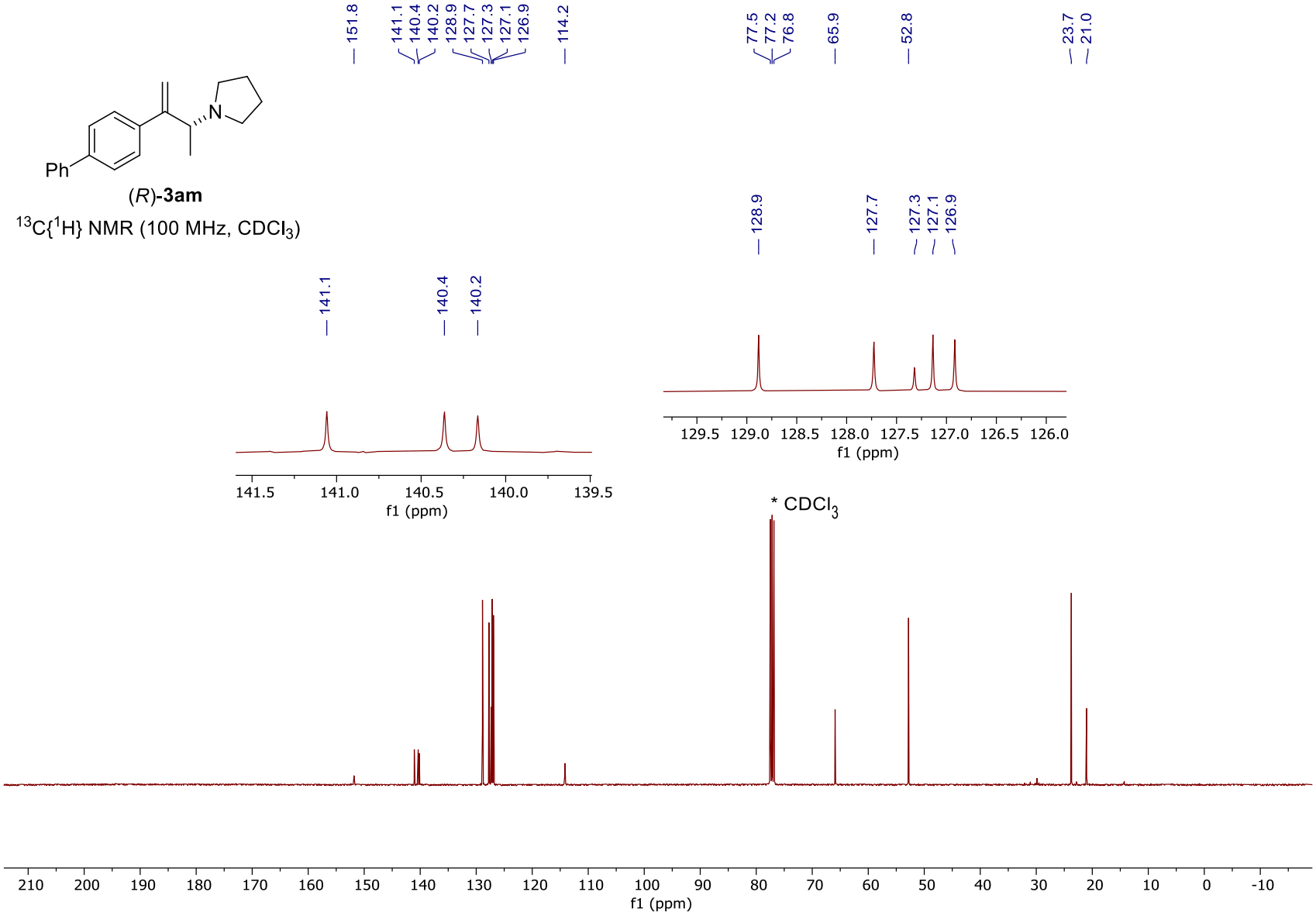

7.53
7.52
7.45
7.43
7.37
7.26
7.24
7.23
7.17
5.25
5.24
5.21
5.21
3.91
3.89
3.88
3.86
3.62
3.61
3.59
3.58
1.41
1.31
1.29
1.19
1.17
Ph
H
N
Ph
Ph
(R, S)-3ak
1H NMR (400 MHz, CDCl3)
CHCl3
2.04
2.04
2.06
8.28
1.00
0.97
f1 (ppm)
* minor dr
2.04
2.04
2.06
8.28
1.00
0.99
1.00
0.97
1.09
3.03
3.03

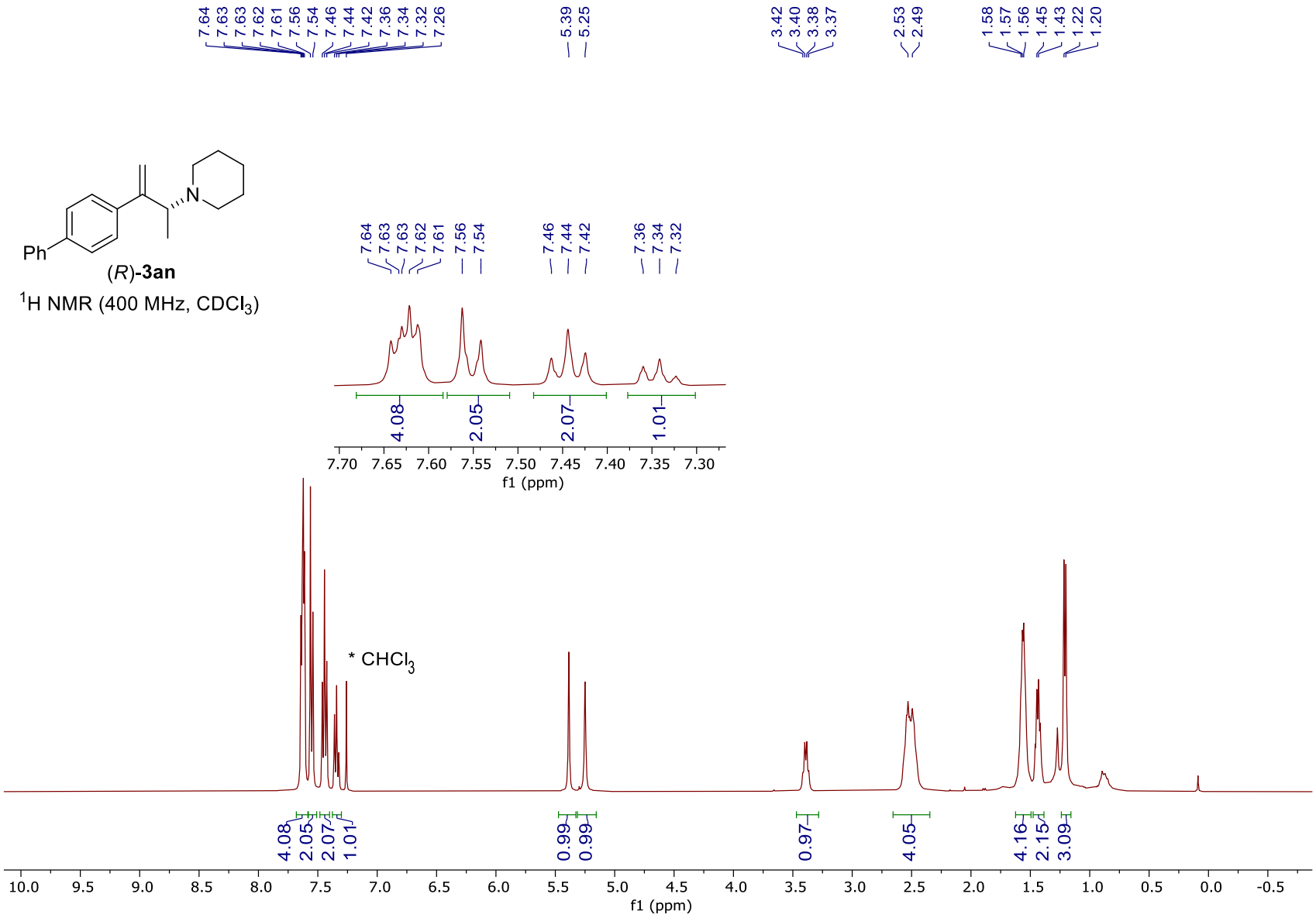

152.4
145.8
140.9
140.3
140.3
128.9
128.6
127.5
127.4
127.1
127.0
127.0
126.8
112.5
77.5
77.2
76.8
55.0
53.5
24.0
20.7
H
N
Ph
Ph
(R, S)-3ak
13C{1H} NMR (100 MHz, CDCl3)
128.90
128.55
127.48
127.40
127.11
127.05
126.99
126.83
129.0
128.5
128.0
127.5
127.0
126.5
f1 (ppm)
140.91
140.29
140.26
141.2
141.0
140.8
140.6
140.4
140.2
f1 (ppm)
* CDCl3
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

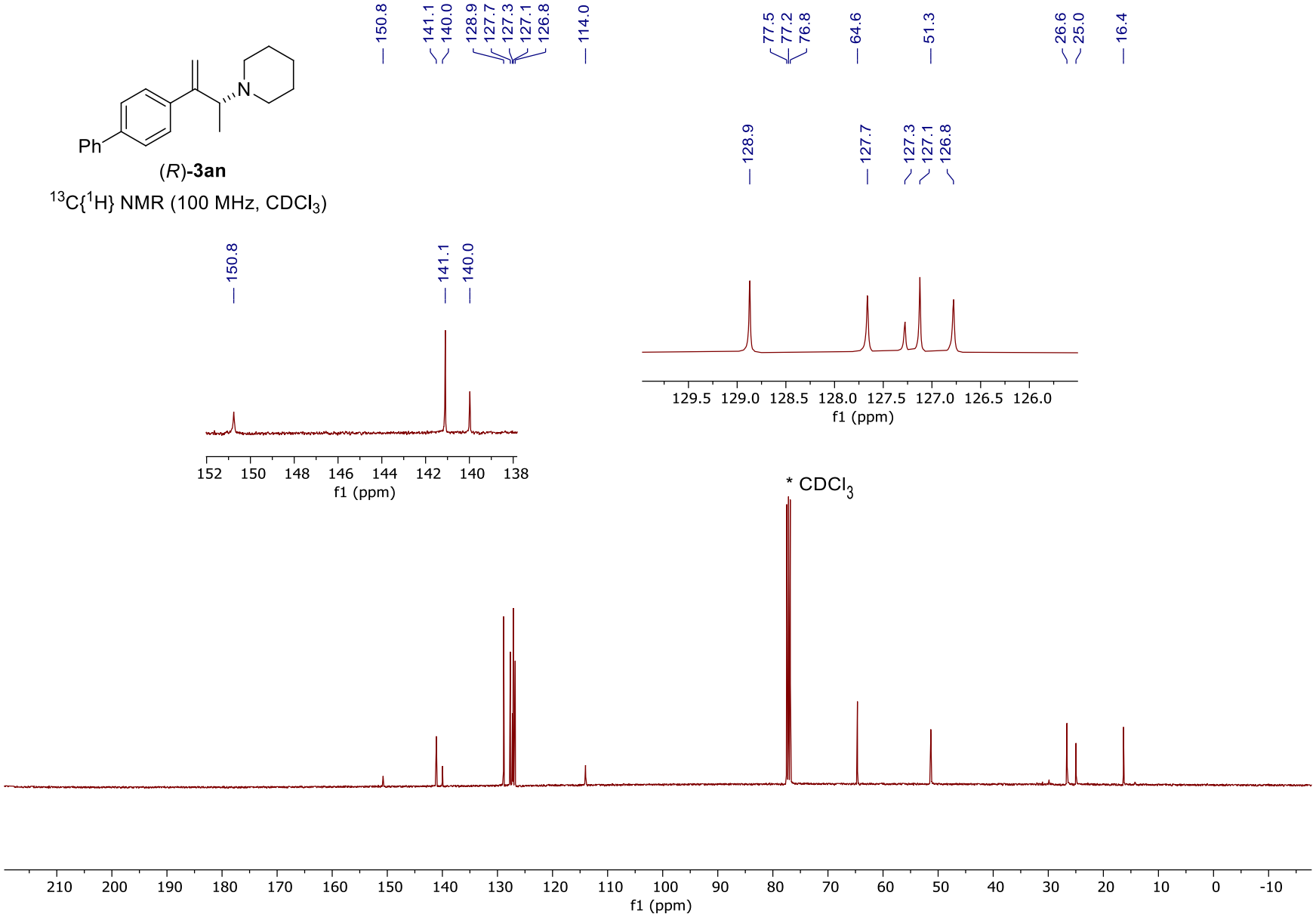

(R, R)-3al
1H NMR (400 MHz, CDCl3)
CHCl3
minor
* dr
f1 (ppm)

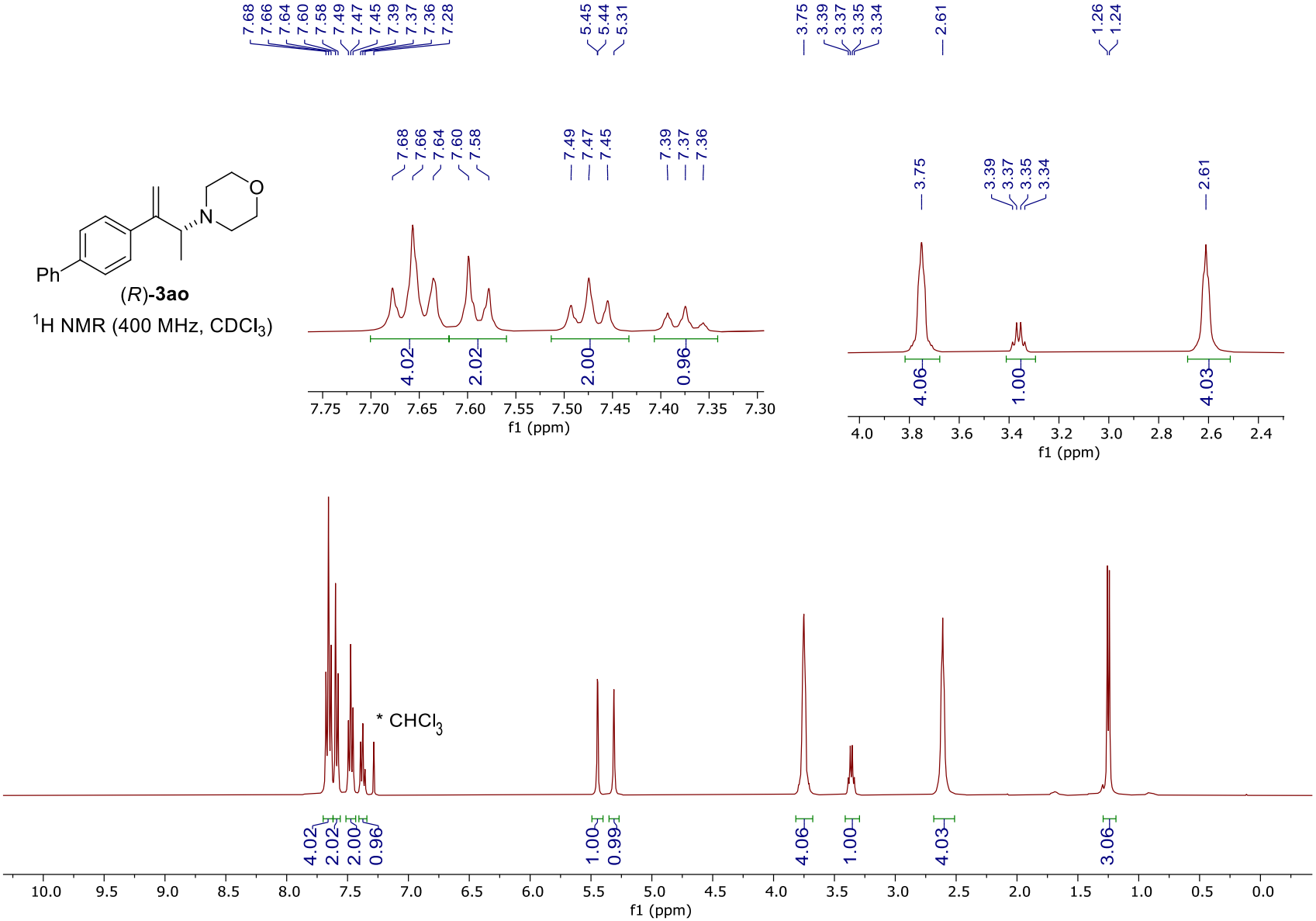

151.8
146.2
140.9
140.5
140.2
128.9
128.6
127.6
127.4
127.1
127.0
127.0
126.9
126.9
112.5
77.5
77.2
76.8
55.2
55.0
31.0
25.1
22.9
H
N
Ph
Ph
(R, R)-3al
13C{1H} NMR (100 MHz, CDCl3)
128.89
128.58
127.63
127.36
127.11
127.05
126.98
126.94
126.88
140.9
140.5
140.2
55.2
55.0
129.5 129.0 128.5 128.0 127.5 127.0 126.5
f1 (ppm)
56.0 55.5 55.0 54.5
f1 (ppm)
141.0 140.5 140.0
f1 (ppm)
* CDCl3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

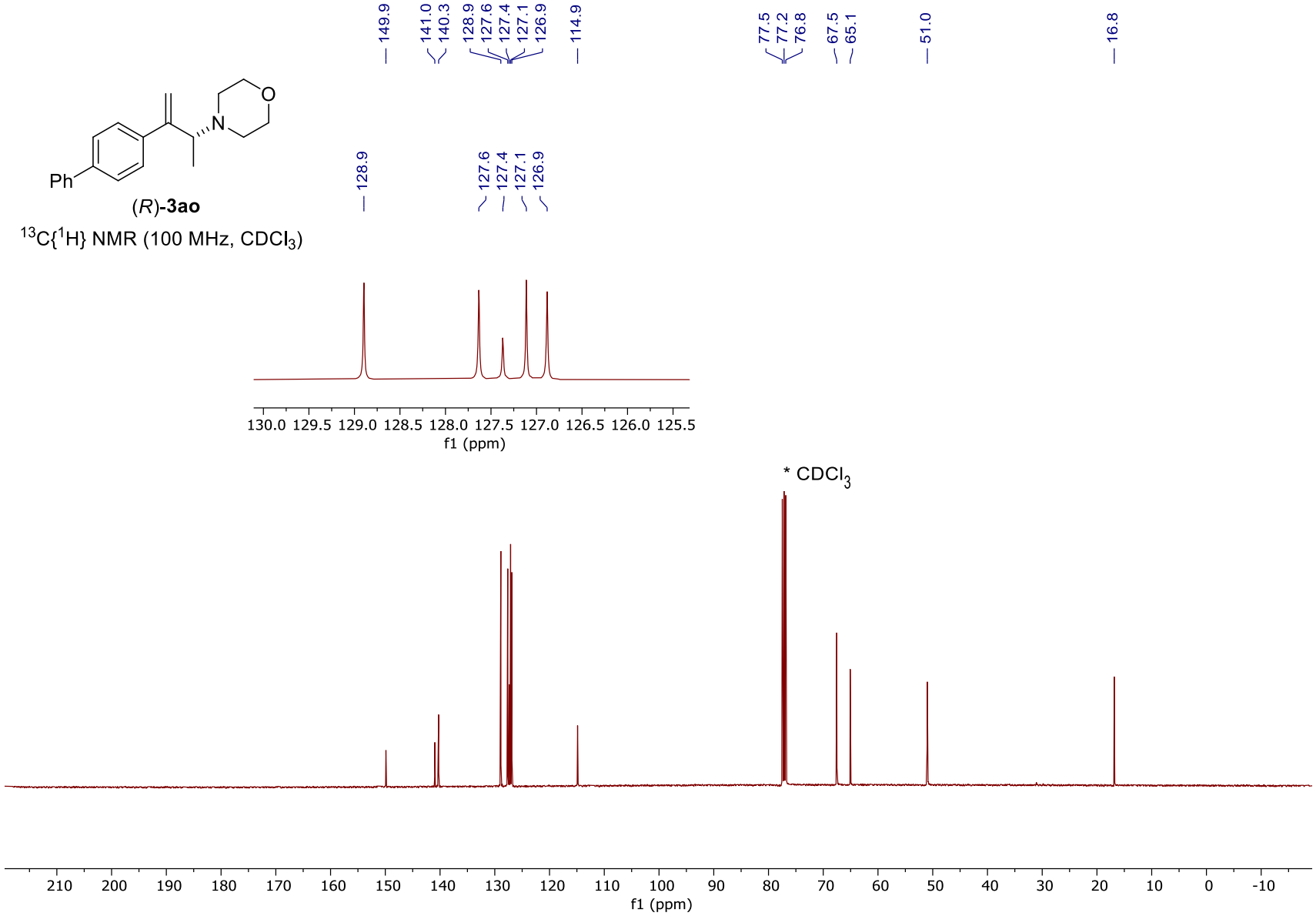

7.64
7.62
7.60
7.57
7.55
7.46
7.44
7.42
7.36
7.34
7.33
7.26
5.34
3.22
3.20
3.18
3.17
2.62
1.81
1.28
1.27
Ph
N
(R)-3am
1H NMR (400 MHz, CDCl3)
4.04
2.01
2.03
1.00
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
* CHCl3
4.04
2.01
2.03
1.00
2.00
1.00
4.04
4.11
3.59
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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)

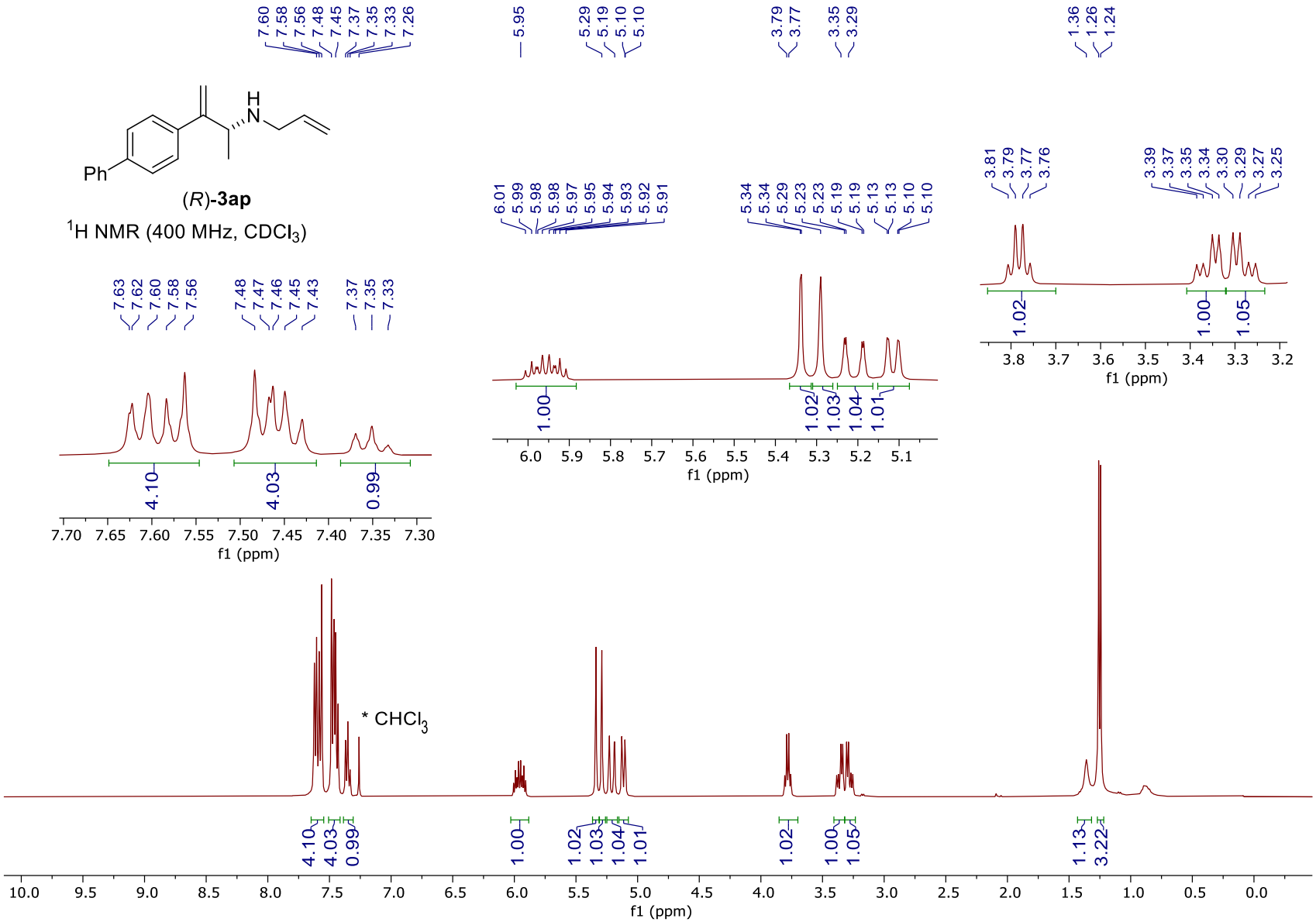

151.8
141.1
140.4
140.2
128.9
127.7
127.3
127.1
126.9
114.2
77.5
77.2
76.8
65.9
52.8
23.7
21.0
Ph
N
(R)-3am
13C{1H} NMR (100 MHz, CDCl3)
141.1
140.4
140.2
141.5
141.0
140.5
140.0
139.5
f1 (ppm)
128.9
127.7
127.3
127.1
126.9
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
f1 (ppm)
* CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

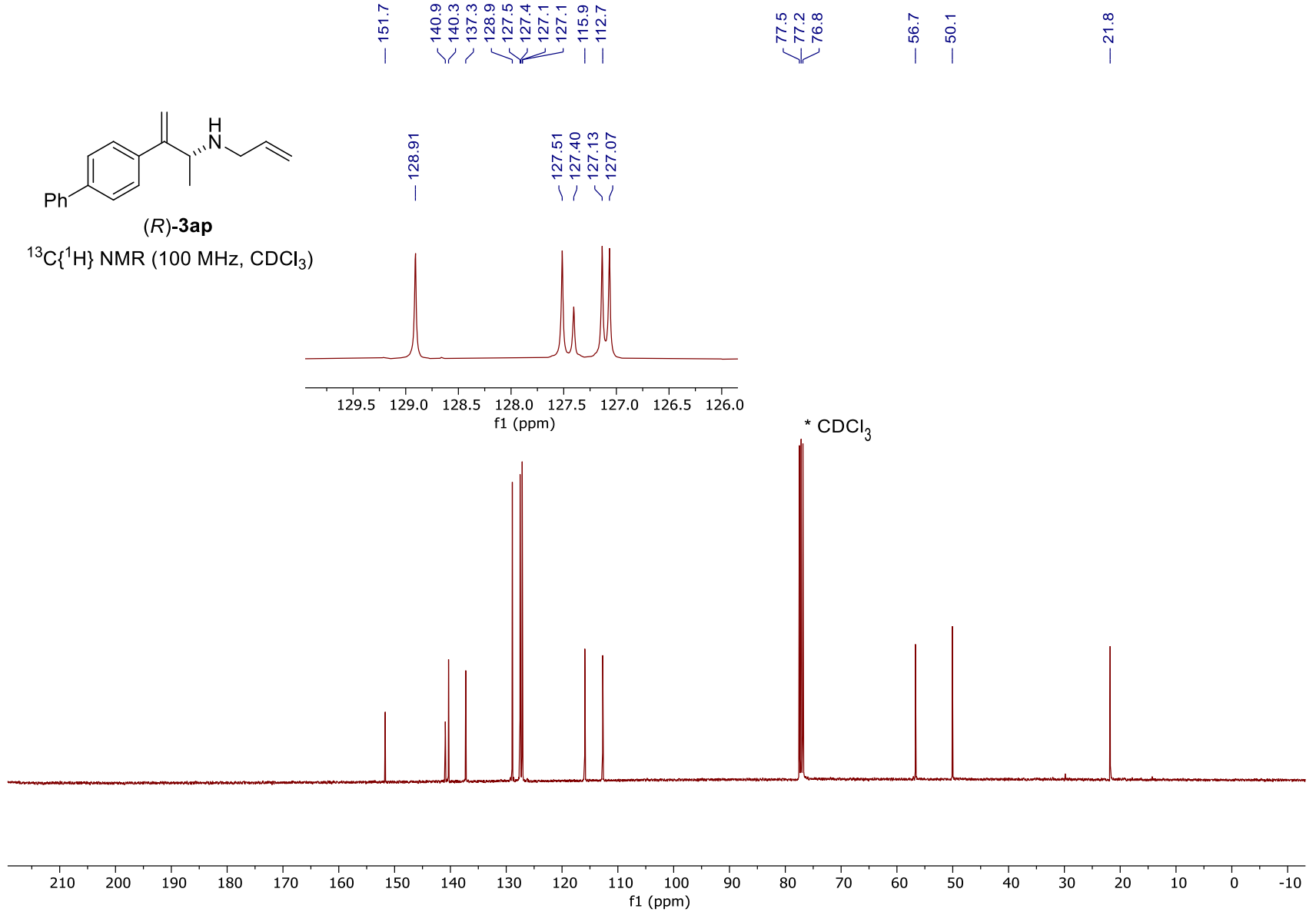

7.64
7.63
7.63
7.62
7.61
7.56
7.54
7.46
7.44
7.42
7.36
7.34
7.32
7.26
5.39
5.25
3.42
3.40
3.38
3.37
2.53
2.49
1.58
1.57
1.56
1.45
1.43
1.22
1.20
Ph
N
(R)-3an
1H NMR (400 MHz, CDCl3)
4.08
2.05
2.07
1.01
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35 7.30
f1 (ppm)
* CHCl3
0.99
0.99
0.97
4.05
4.16
2.15
3.09
10.0 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 -0.5
f1 (ppm)

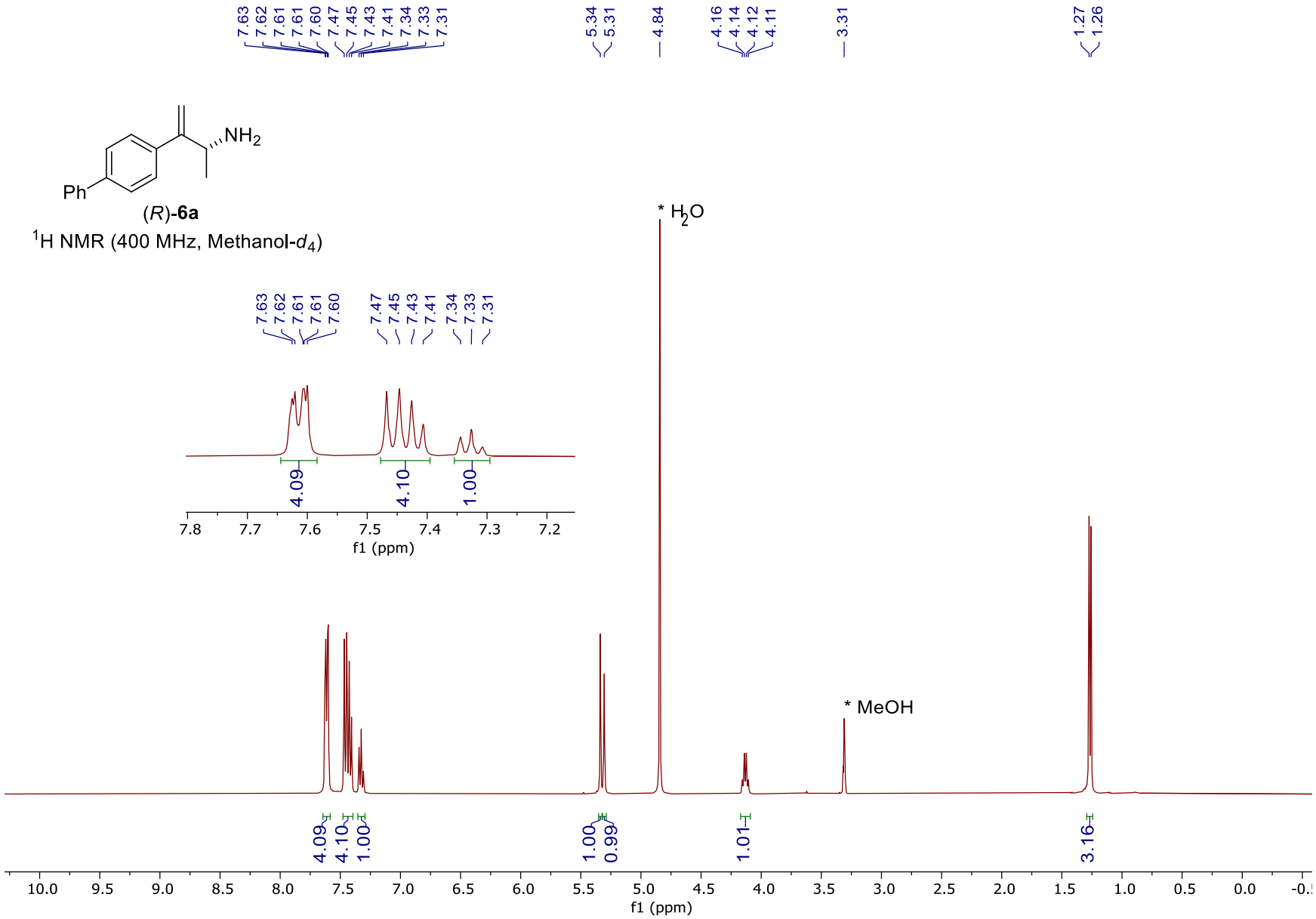

Ph
N
(R)-3an
13C{1H} NMR (100 MHz, CDCl3)
150.8
141.1
140.0
128.9
127.7
127.3
127.1
126.8
114.0
77.5
77.2
76.8
64.6
51.3
26.6
25.0
16.4
* CDCl3
f1 (ppm)

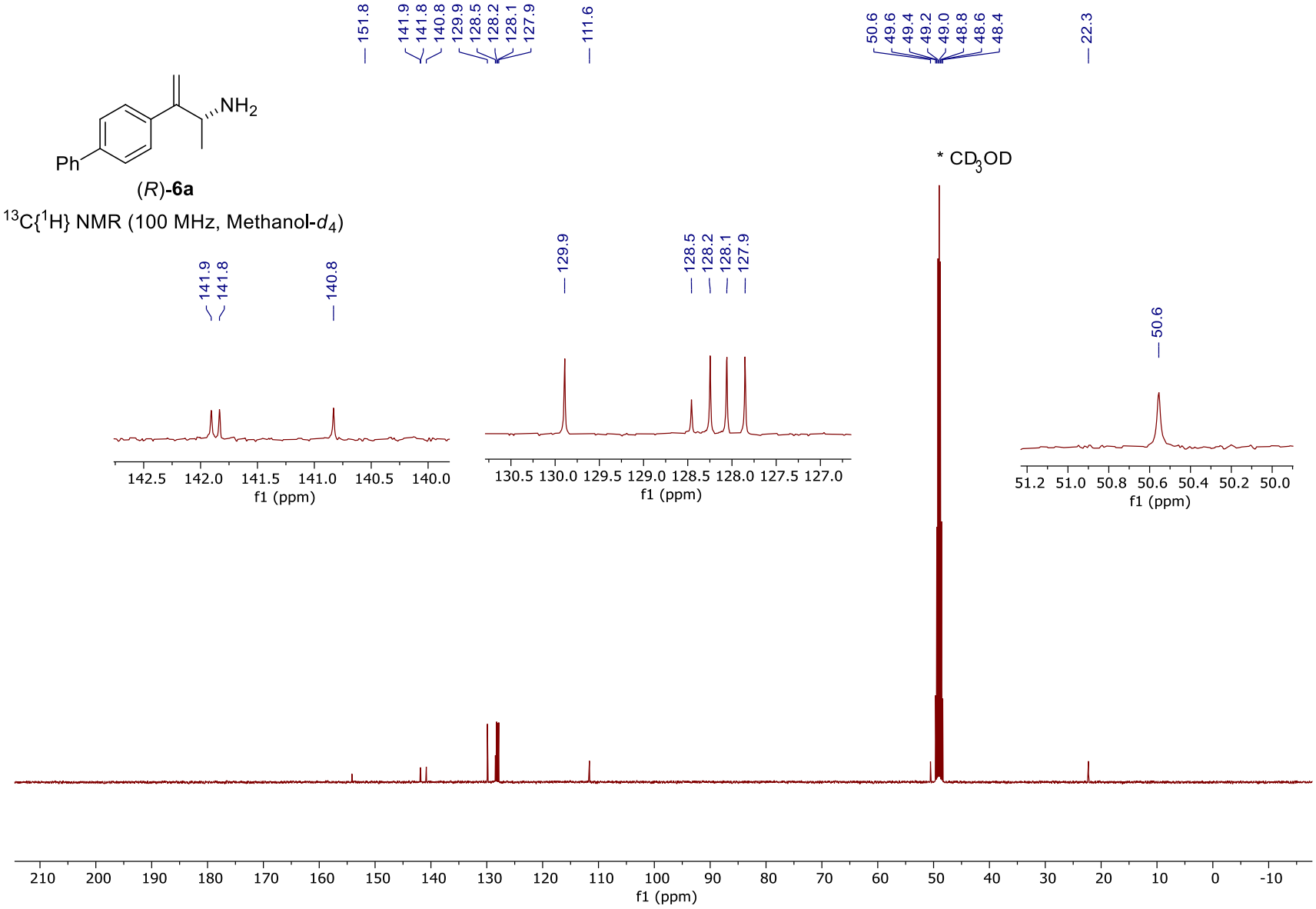

7.68
7.66
7.64
7.60
7.58
7.49
7.47
7.45
7.39
7.37
7.36
7.28
5.45
5.44
5.31
3.75
3.39
3.37
3.35
3.34
2.61
1.26
1.24
O
N
Ph
(R)-3ao
1H NMR (400 MHz, CDCl3)
4.02
2.02
2.00
0.96
f1 (ppm)
4.06
1.00
4.03
f1 (ppm)
* CHCl3
4.02
2.02
2.00
0.96
1.00
0.99
4.06
1.00
4.03
3.06
f1 (ppm)


149.9
141.0
140.3
128.9
127.6
127.4
127.1
126.9
114.9
77.5
77.2
76.8
67.5
65.1
51.0
16.8
O
N
Ph
(R)-3ao
13C{1H} NMR (100 MHz, CDCl3)
130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5
f1 (ppm)
* CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

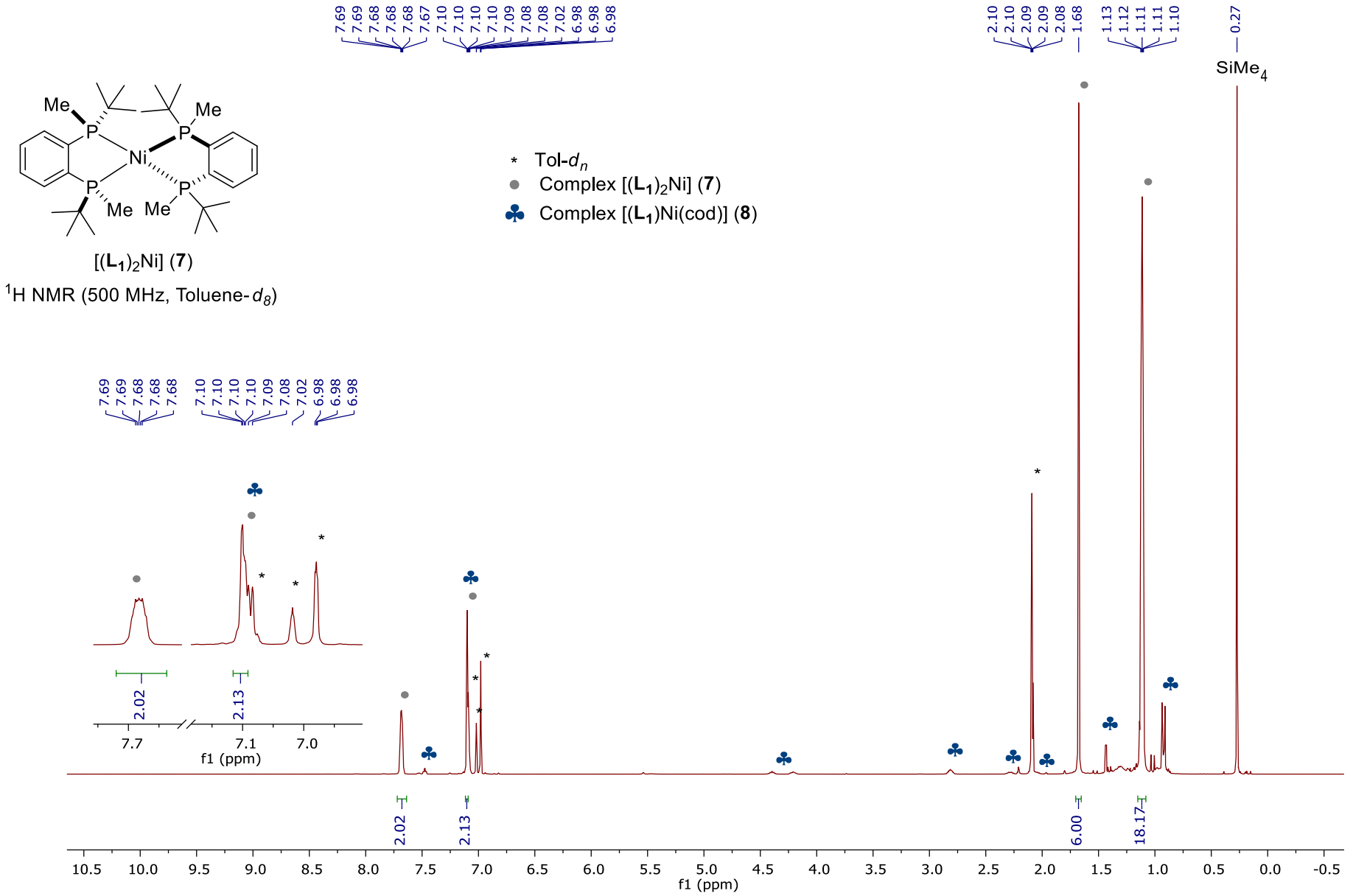

(R)-3ap
1H NMR (400 MHz, CDCl3)
* CHCl3
f1 (ppm)

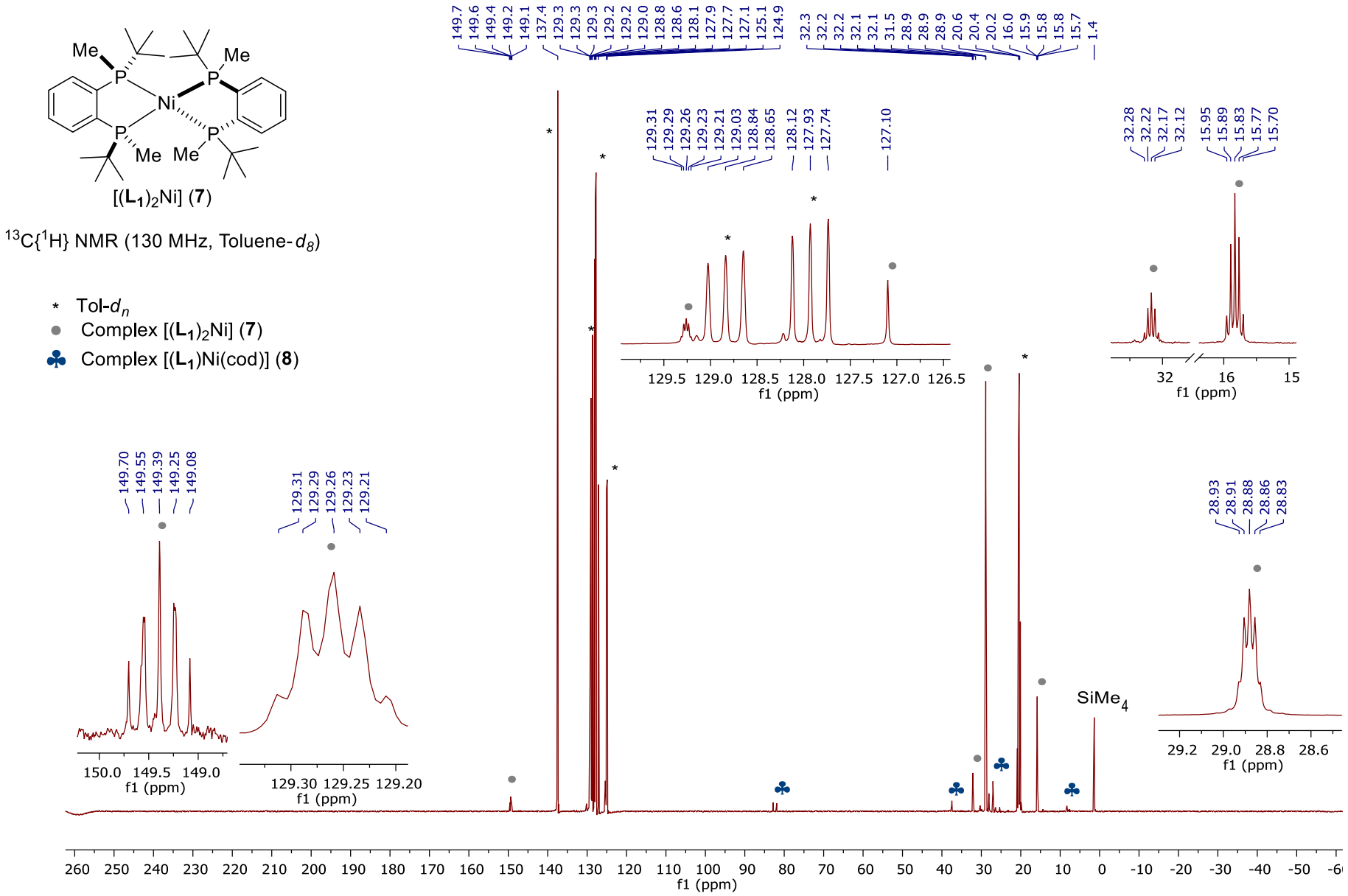

151.7
140.9
140.3
137.3
128.9
127.5
127.4
127.1
127.1
115.9
112.7
77.5
77.2
76.8
56.7
50.1
21.8
H
N
Ph
(R)-3ap
13C{1H} NMR (100 MHz, CDCl3)
128.91
127.51
127.40
127.13
127.07
129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0
f1 (ppm)
* CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

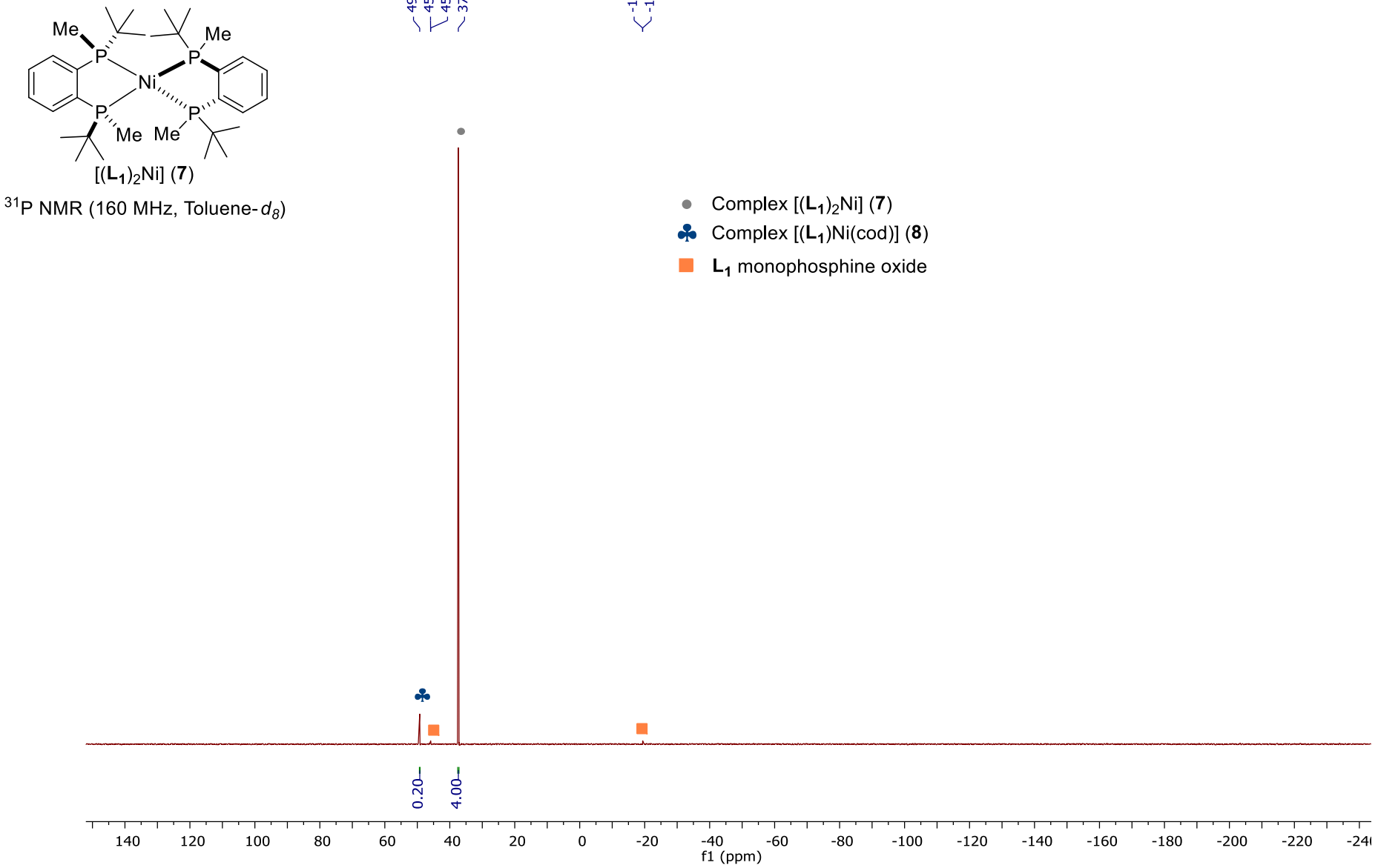

7.63
7.62
7.61
7.61
7.60
7.47
7.45
7.43
7.41
7.34
7.33
7.31
5.34
5.31
4.84
4.16
4.14
4.12
4.11
3.31
1.27
1.26
NH2
Ph
(R)-6a
1H NMR (400 MHz, Methanol-d4)
* H2O
* MeOH
4.09
4.10
1.00
1.00
0.99
1.01
3.16
f1 (ppm)

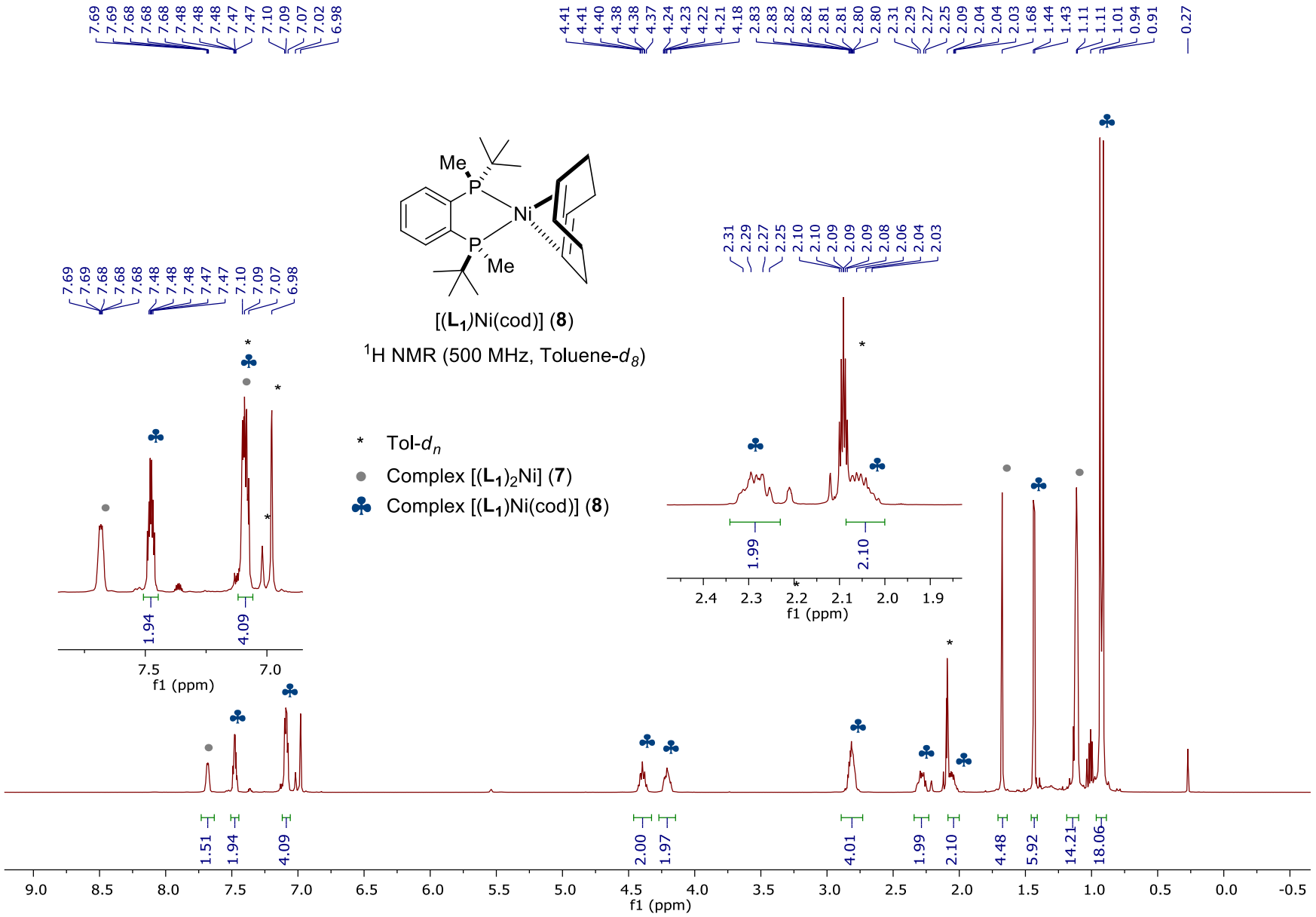

151.8
141.9
141.8
140.8
129.9
128.5
128.2
128.1
127.9
111.6
50.6
49.6
49.4
49.2
49.0
48.8
48.6
48.4
22.3
NH2
Ph
(R)-6a
13C{1H} NMR (100 MHz, Methanol-d4)
* CD3OD
141.9
141.8
140.8
129.9
128.5
128.2
128.1
127.9
50.6
142.5 142.0 141.5 141.0 140.5 140.0
f1 (ppm)
130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0
f1 (ppm)
51.2 51.0 50.8 50.6 50.4 50.2 50.0
f1 (ppm)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

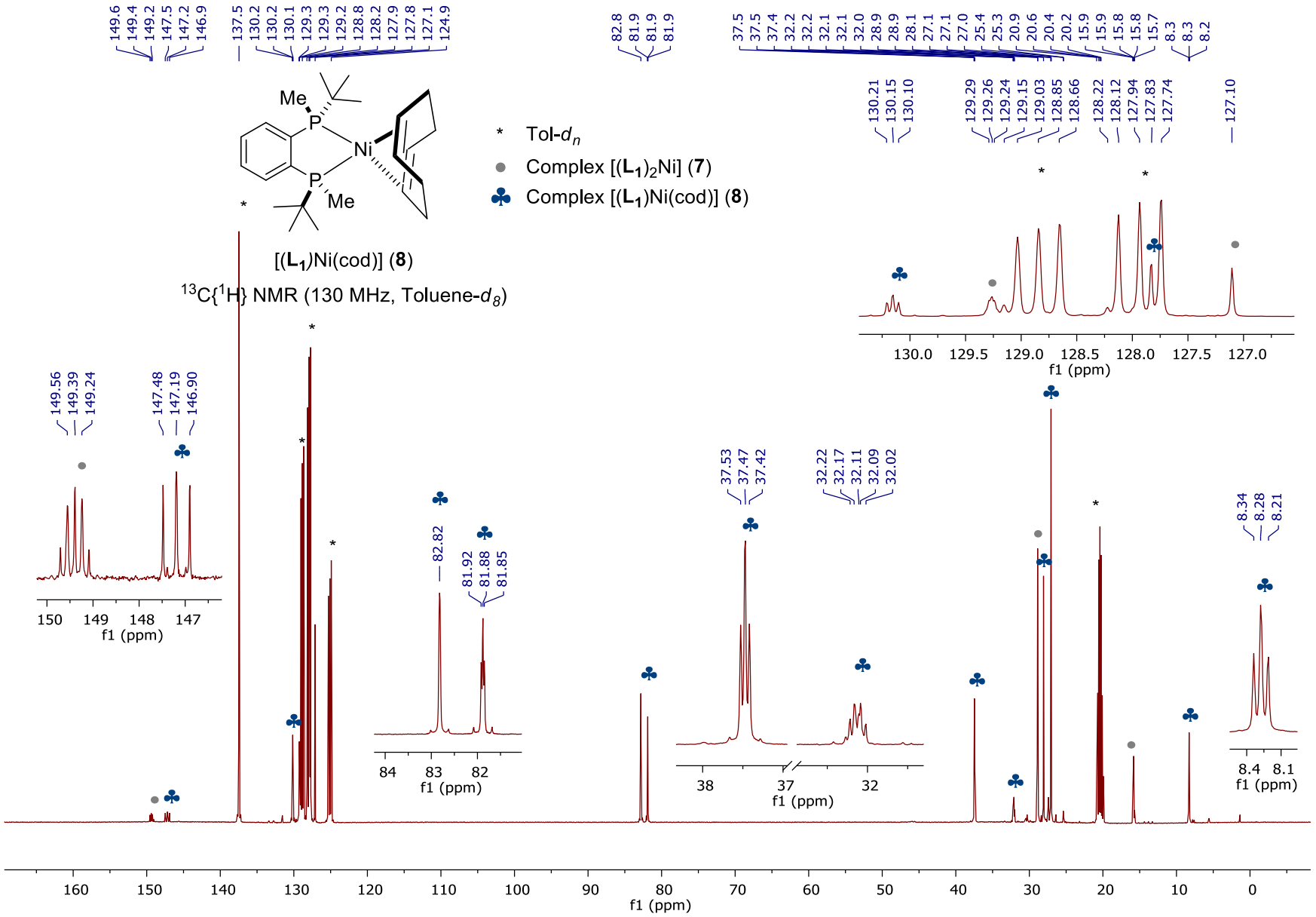
13. NMR Spectra of organometallic compounds

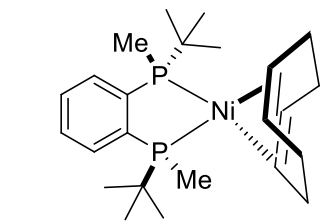

Me
Me
P
P
Ni
P
P
Me
Me
[(L1)2Ni] (7)
1H NMR (500 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
SiMe4
2.02
2.13
6.00
18.17
f1 (ppm)


Me
Me
P
P
Ni
P
P
Me
Me
[(L1)2Ni] (7)
13C{1H} NMR (130 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
SiMe4
f1 (ppm)


Me
Me
P
P
Ni
P
P
Me
Me
[(L1)2Ni] (7)
31P NMR (160 MHz, Toluene-d8)
49.26
45.91
45.90
37.37
-19.36
-19.37
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
L1 monophosphine oxide
0.20
4.00
140
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

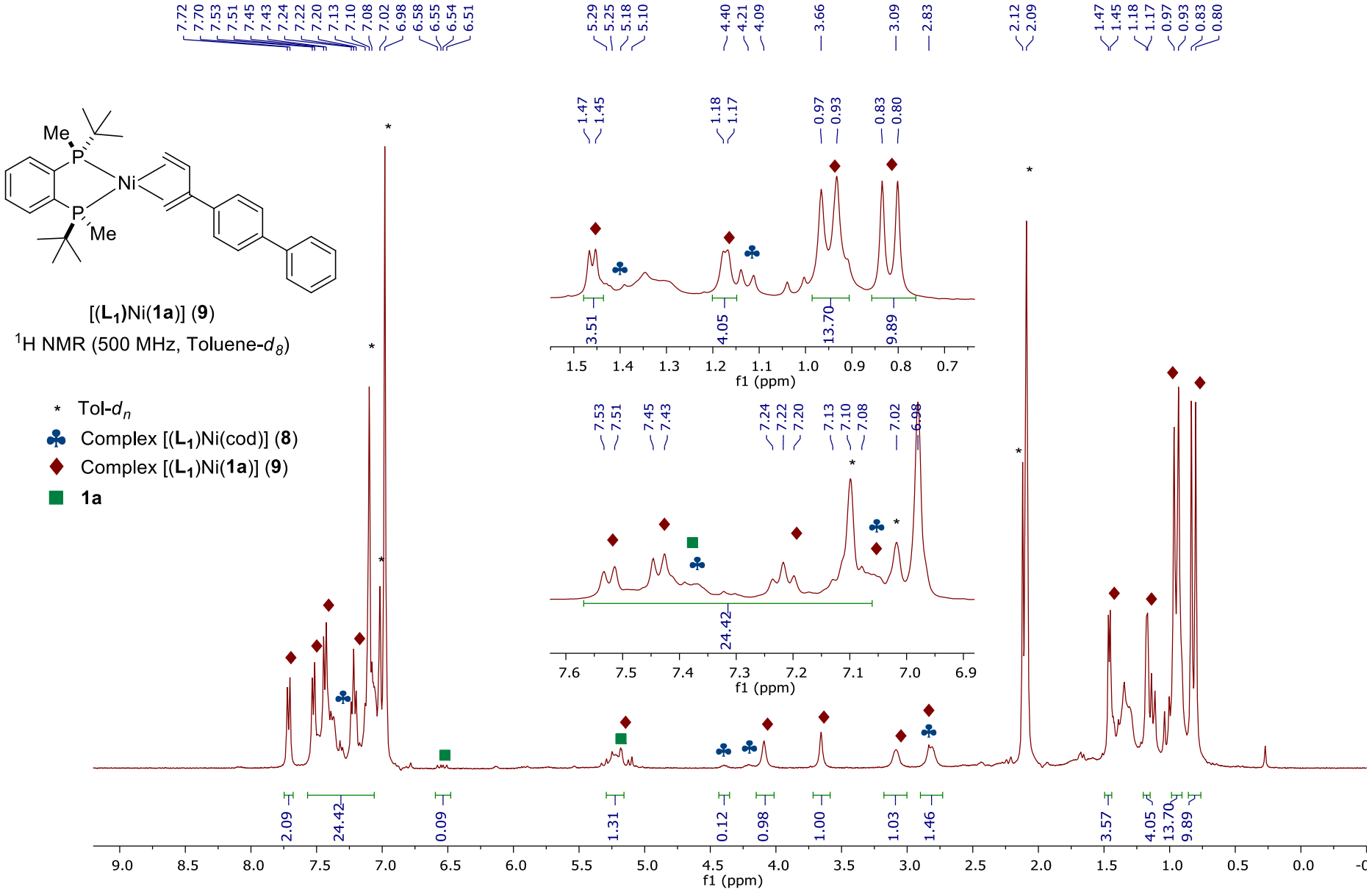

Me
P
Ni
P
Me
[(L1)Ni(cod)] (8)
1H NMR (500 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
f1 (ppm)

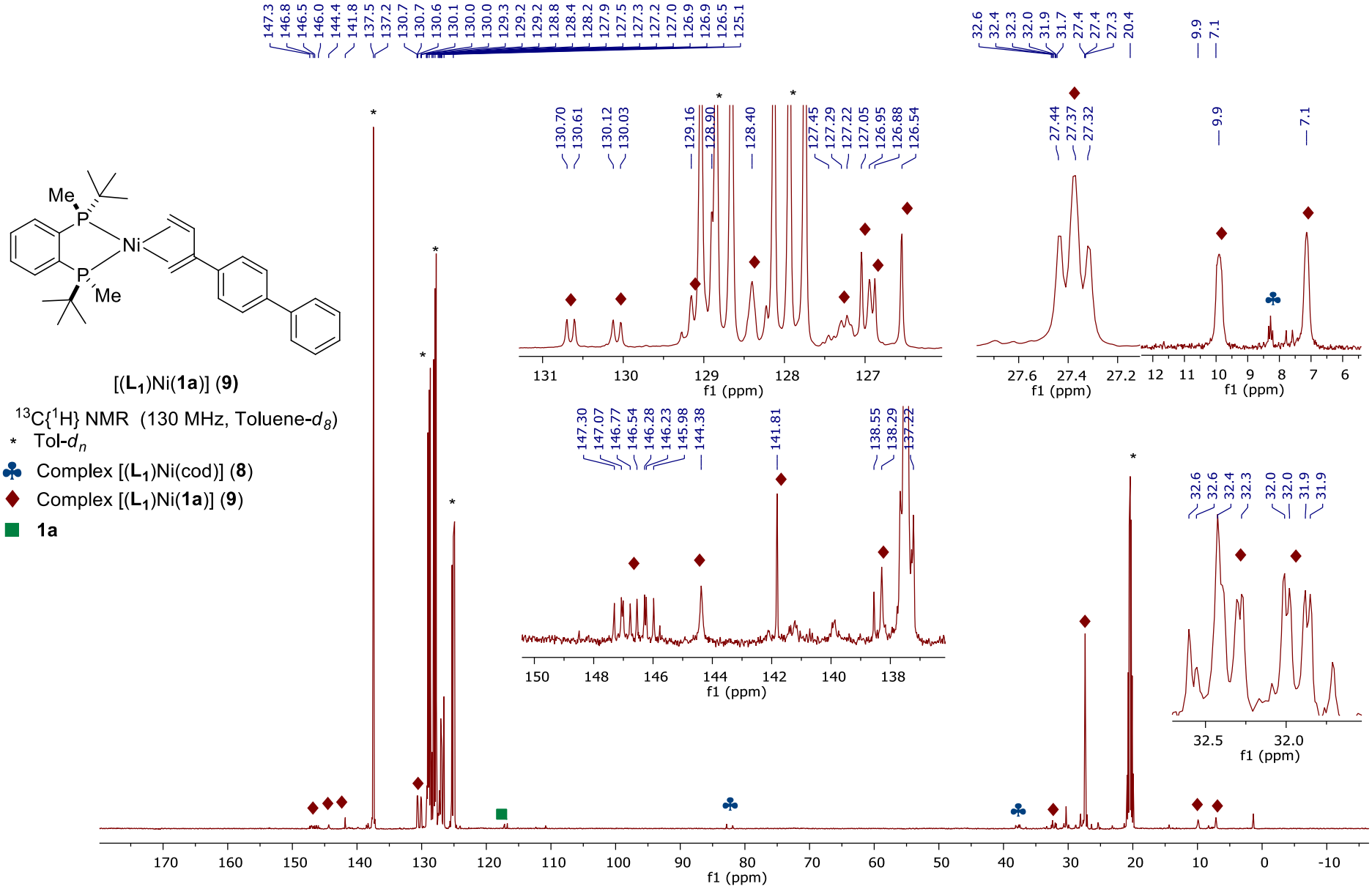

Me
P
Ni
P
Me
*
[(L1)Ni(cod)] (8)
13C{1H} NMR (130 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
f1 (ppm)

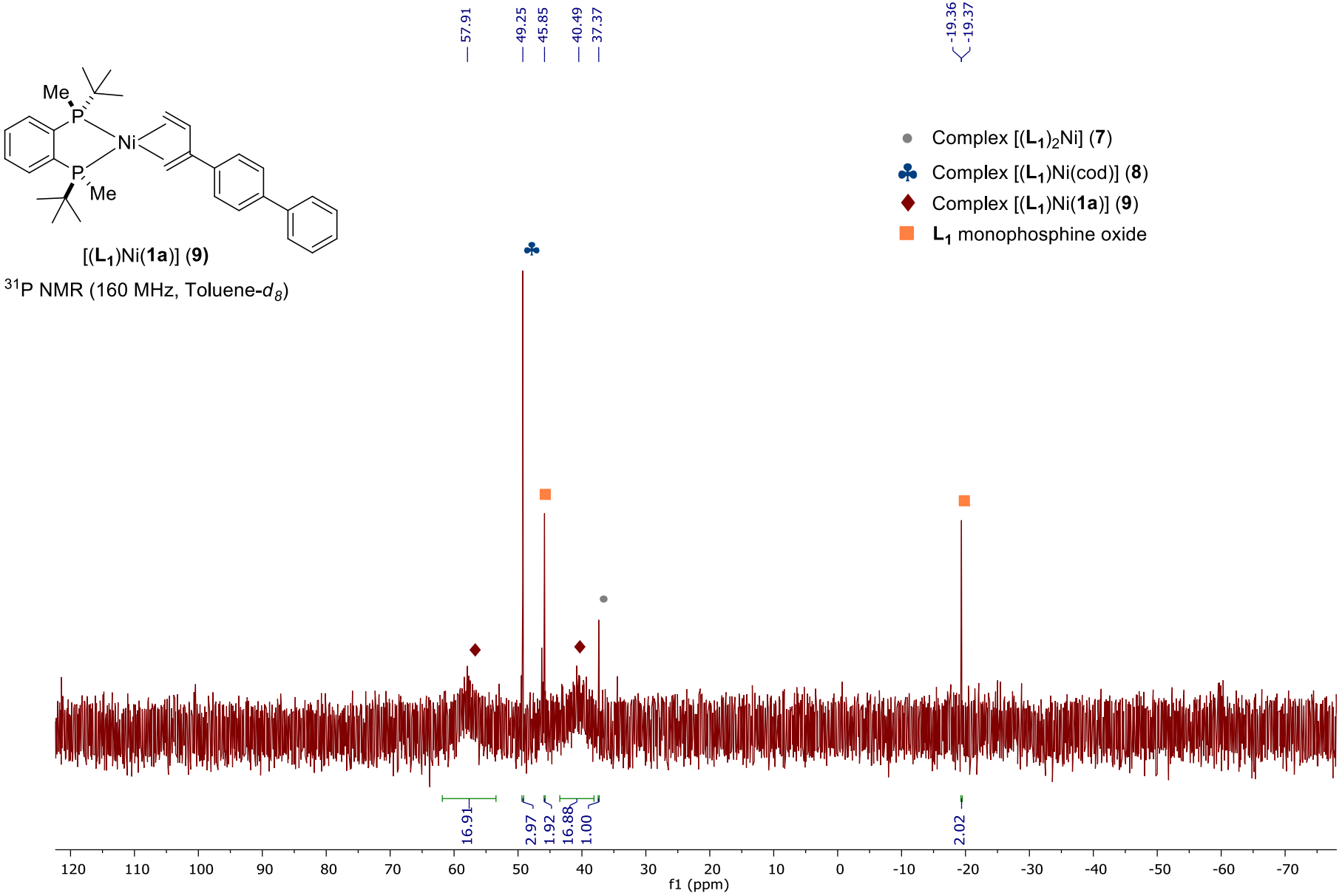


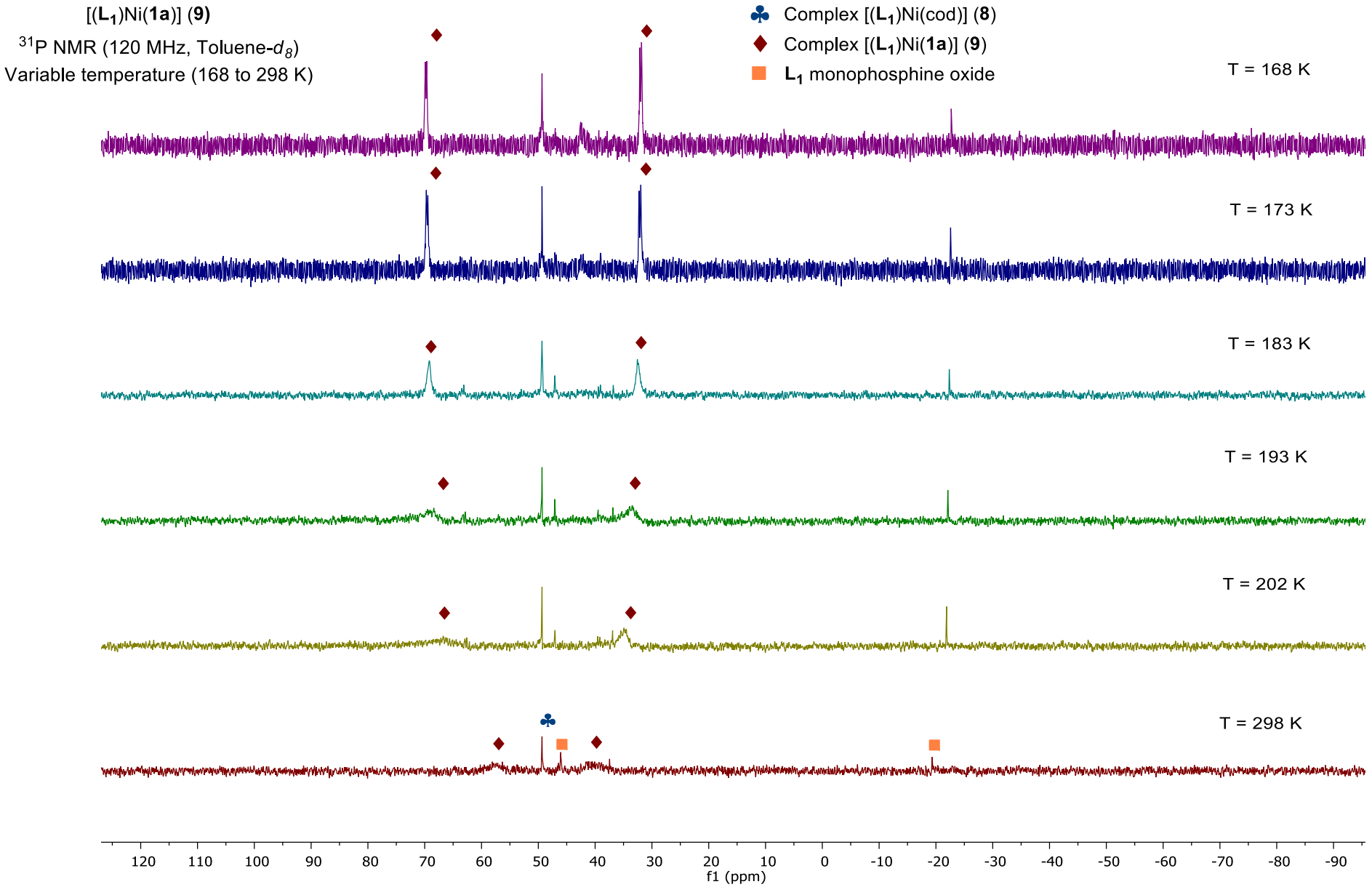
[(**L**$_1$)Ni(cod)] (**8**)

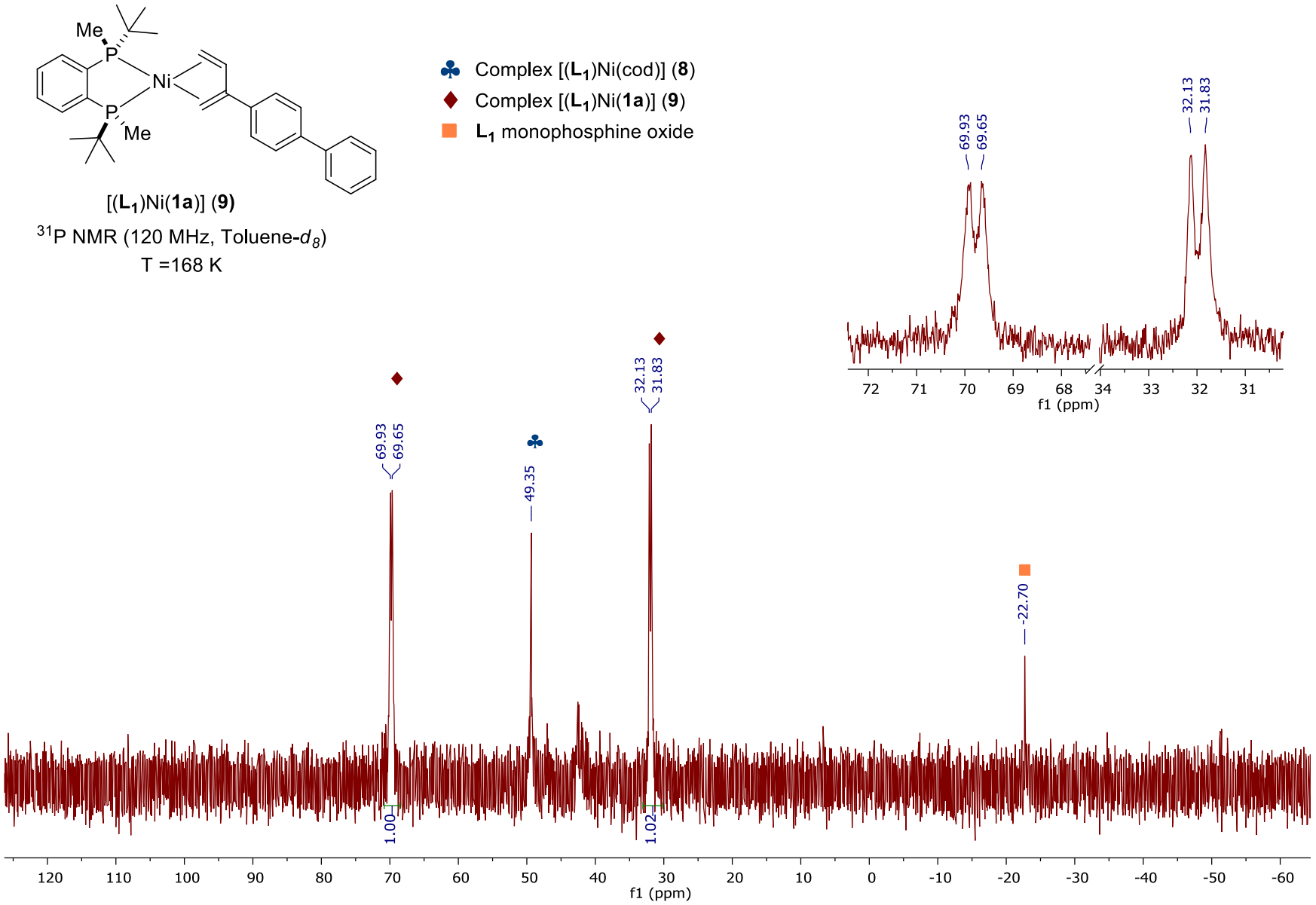
^{31}P NMR (160 MHz, Toluene-d_8)

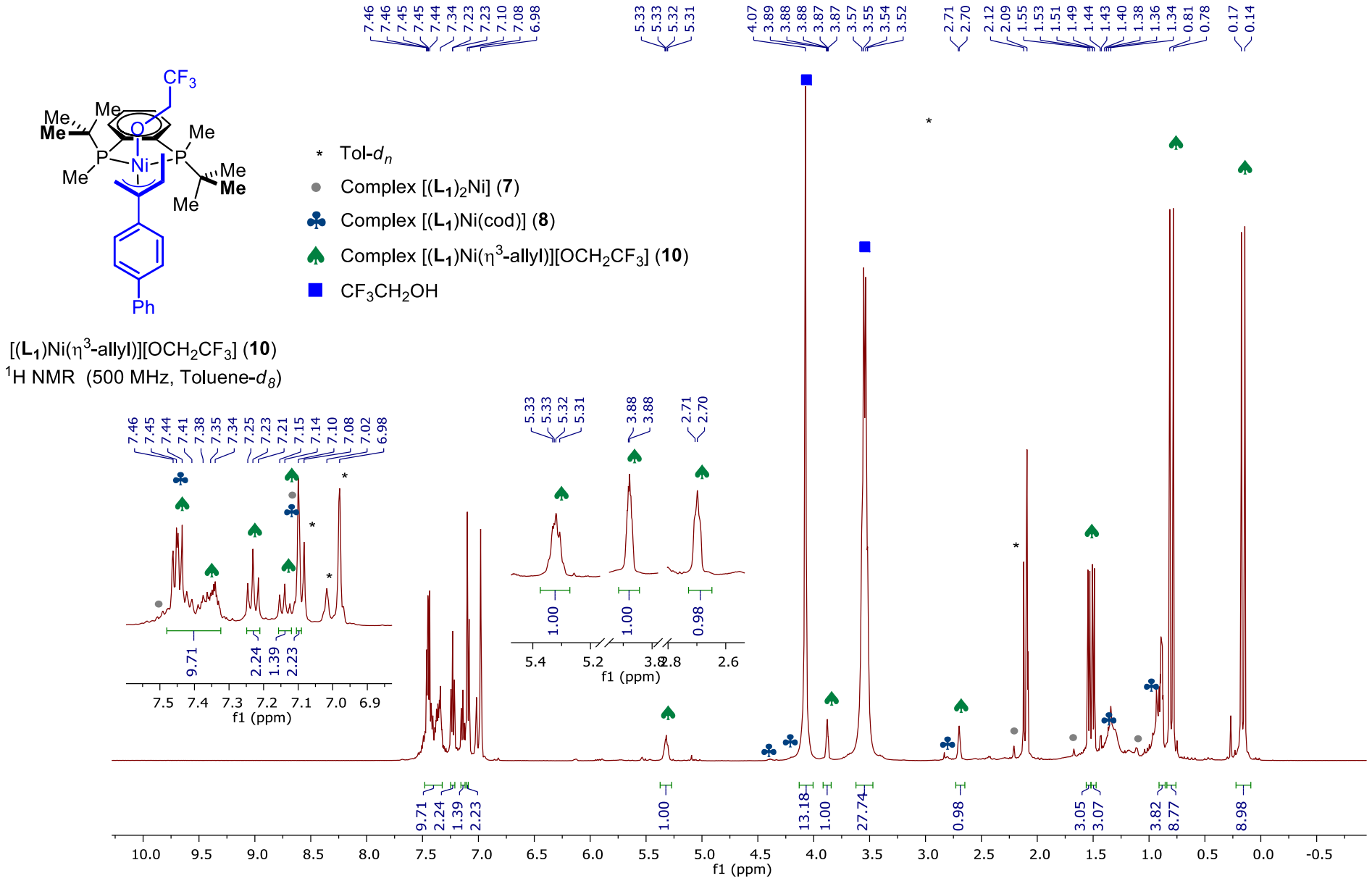

Me
P
Ni
P
Me
[(L1)Ni(1a)] (9)
1H NMR (500 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
1a
f1 (ppm)

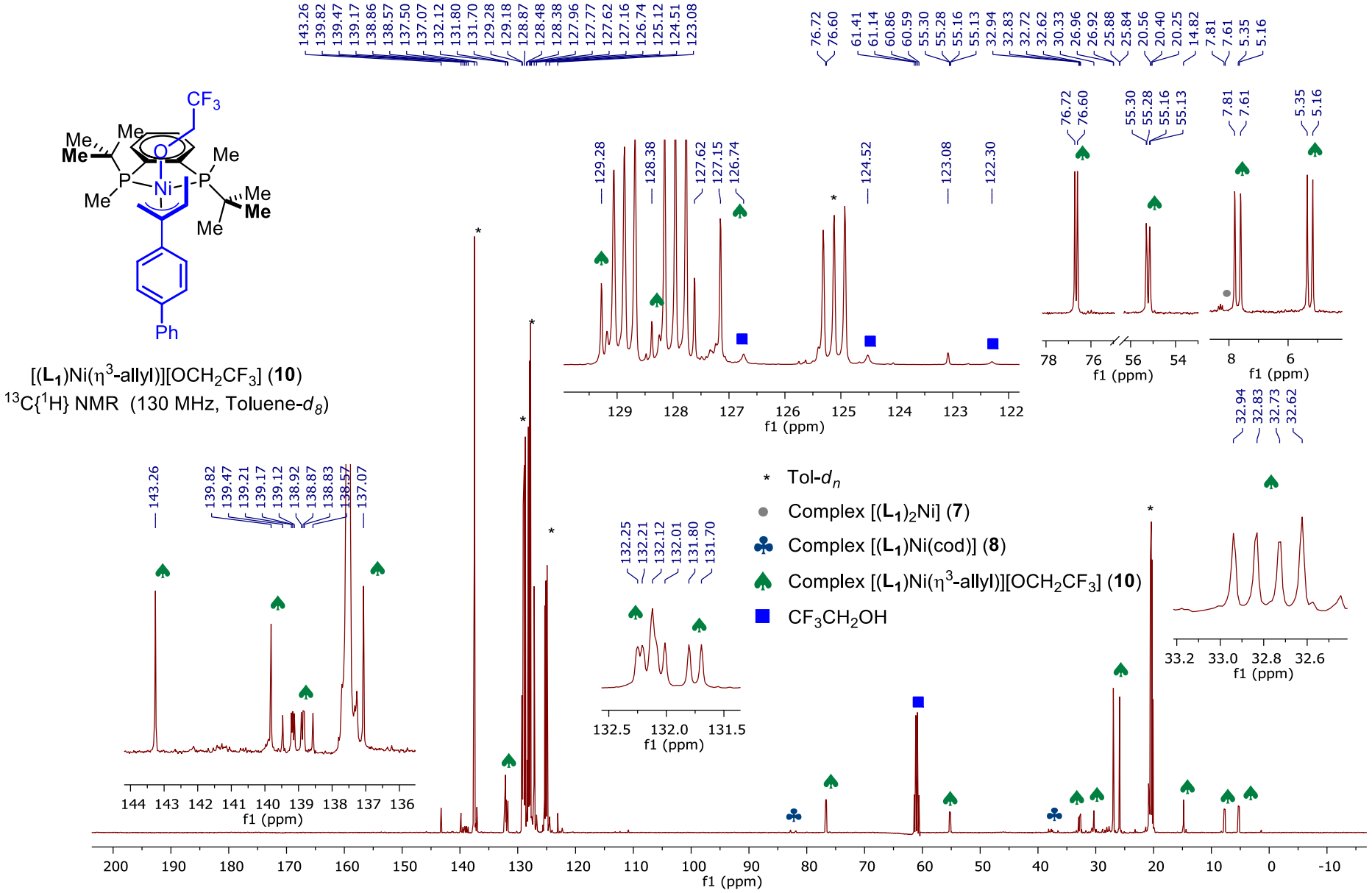

Me
P
Ni
P
Me
[(L1)Ni(1a)] (9)
13C{1H} NMR (130 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
1a
f1 (ppm)

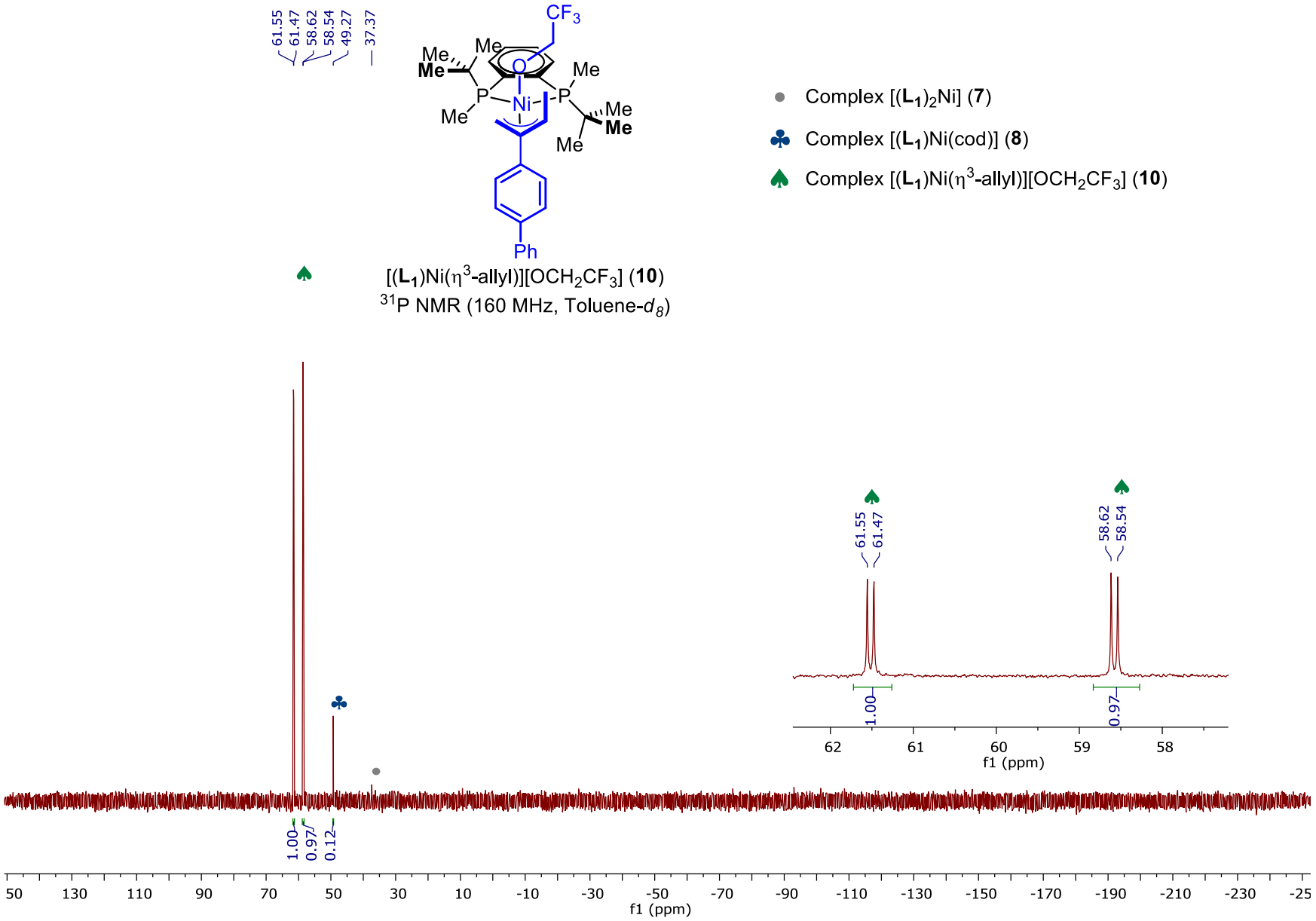

Me
P
Ni
P
Me
[(L1)Ni(1a)] (9)
31P NMR (160 MHz, Toluene-d8)
57.91
49.25
45.85
40.49
37.37
-19.36
-19.37
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
L1 monophosphine oxide
16.91
2.97
1.92
16.88
1.00
2.02
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70
f1 (ppm)

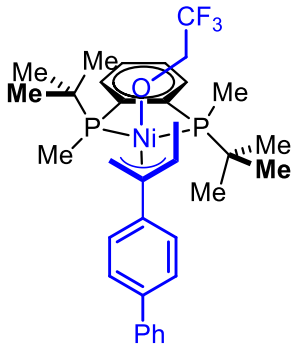

[(L1)Ni(1a)] (9)
31P NMR (120 MHz, Toluene-d8)
Variable temperature (168 to 298 K)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
L1 monophosphine oxide
T = 168 K
T = 173 K
T = 183 K
T = 193 K
T = 202 K
T = 298 K
120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


Me
P
Ni
P
Me
[(L1)Ni(1a)] (9)
31P NMR (120 MHz, Toluene-d8)
T =168 K
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(1a)] (9)
L1 monophosphine oxide
69.93
69.65
49.35
32.13
31.83
-22.70
1.00
1.02
f1 (ppm)


CF3
Me
Me
Me
Me
Me
Me
Me
Me
O
P
Ni
P
Ph
* Tol-d_n
Complex [($\mathbf{L_1}$)$_2$Ni] (**7**)
Complex [($\mathbf{L_1}$)Ni(cod)] (**8**)
Complex [($\mathbf{L_1}$)Ni(η^3-allyl)][OCH_2CF_3] (**10**)
CF_3CH_2OH
[($\mathbf{L_1}$)Ni(η^3-allyl)][OCH_2CF_3] (**10**)
^{1}H NMR (500 MHz, Toluene-d_8)
f1 (ppm)

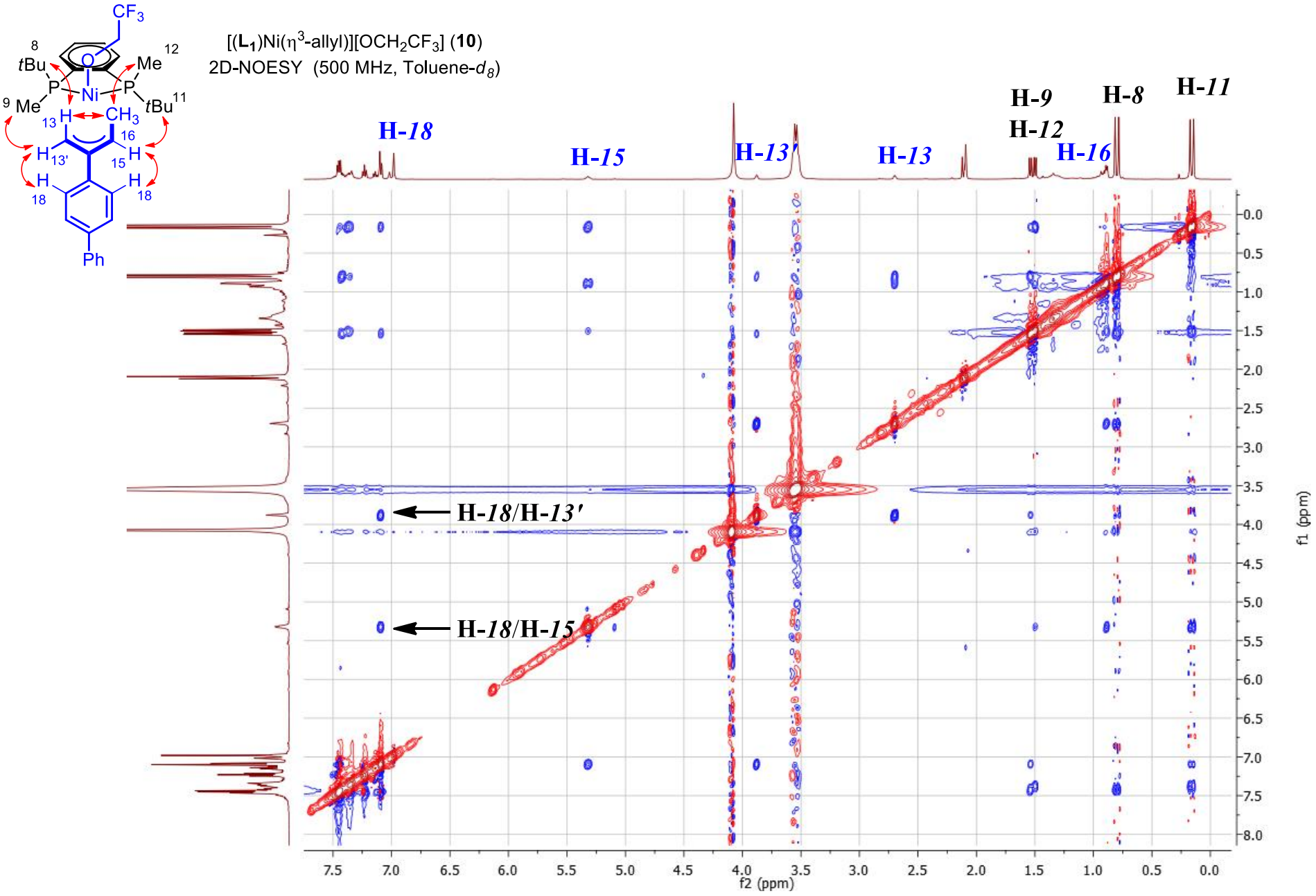

[(L1)Ni(η3-allyl)][OCH2CF3] (10)
13C{1H} NMR (130 MHz, Toluene-d8)
* Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
CF3CH2OH
f1 (ppm)

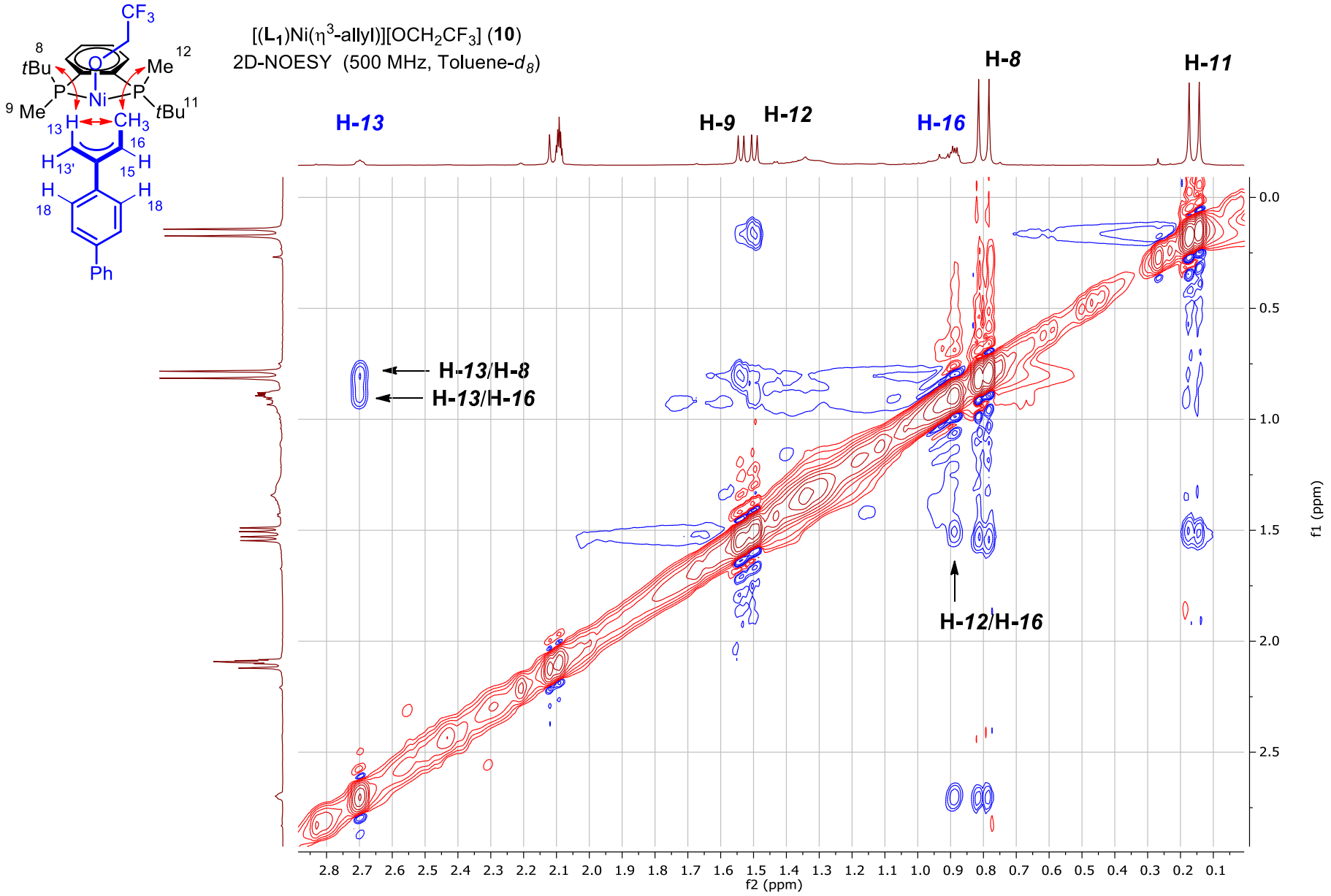

61.55
61.47
58.62
58.54
49.27
37.37
CF3
Me
Me
Me
O
Me
P
P
Ni
Me
Me
Me
Me
Ph
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(η3-allyl)][OCH2CF3] (10)
[(L1)Ni(η3-allyl)][OCH2CF3] (10)
31P NMR (160 MHz, Toluene-d8)
1.00
0.97
0.12
f1 (ppm)
1.00
0.97
f1 (ppm)

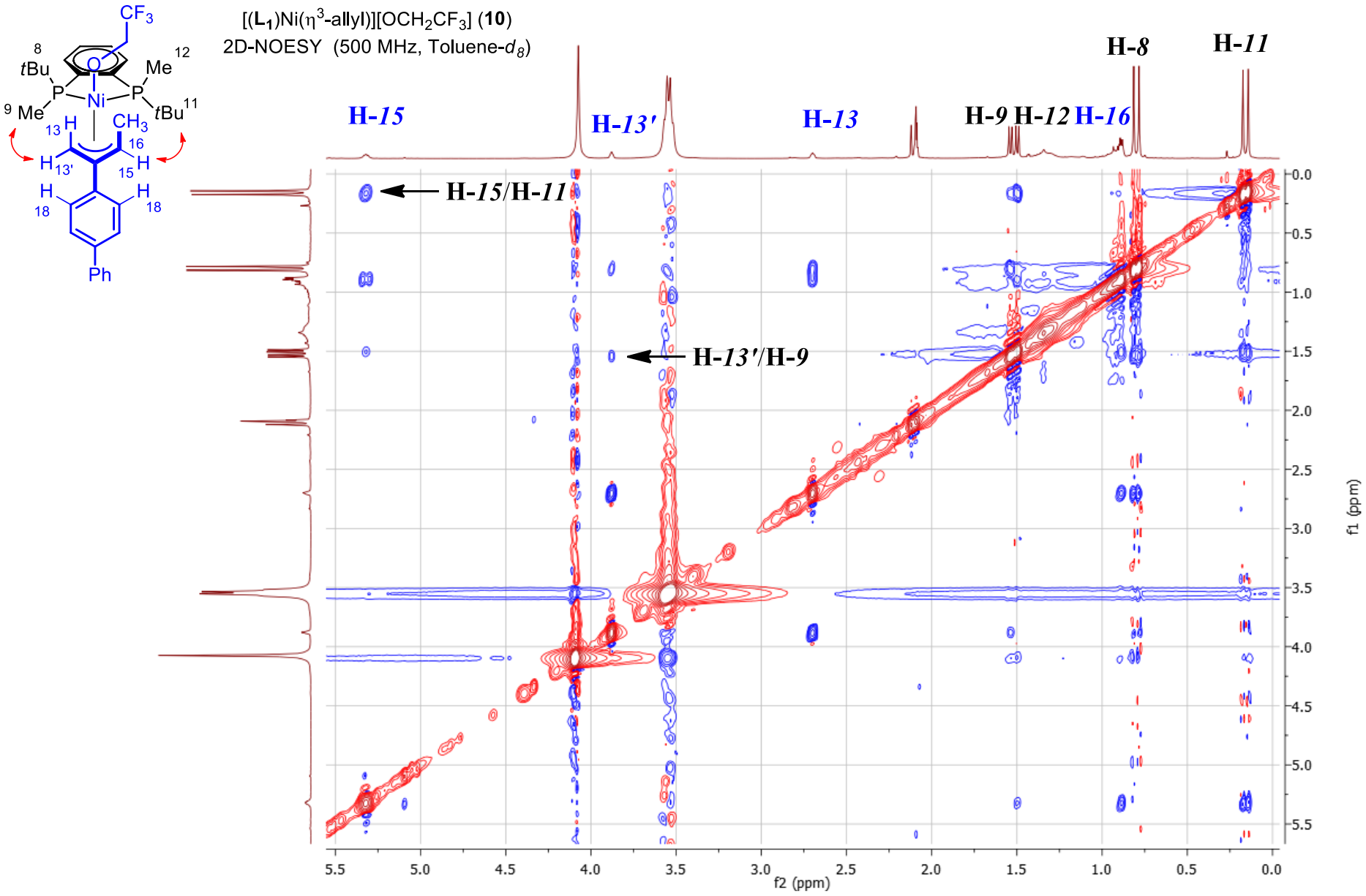


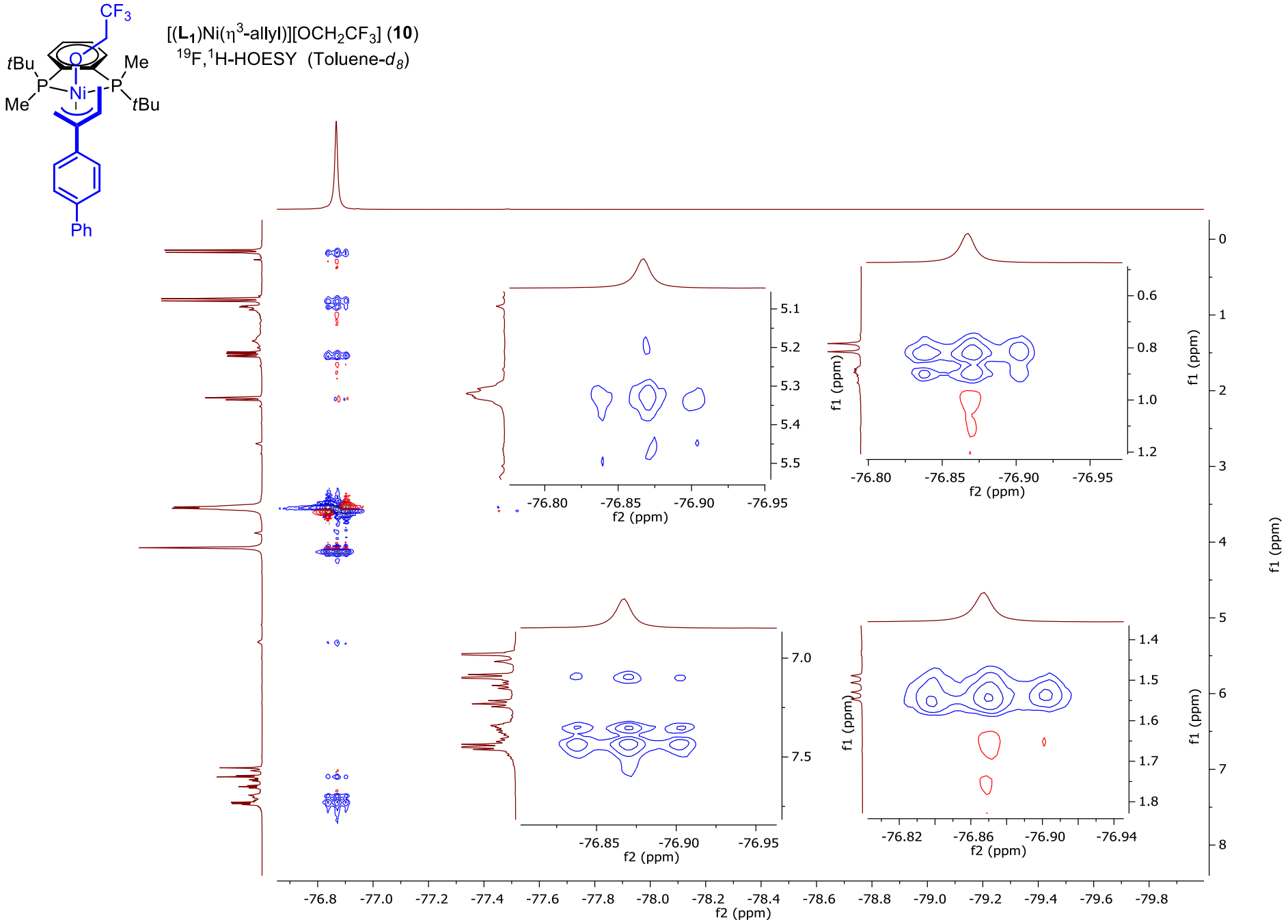
[(**L$_1$**)Ni(η^3-allyl)][OCH_2CF_3] (**10**)

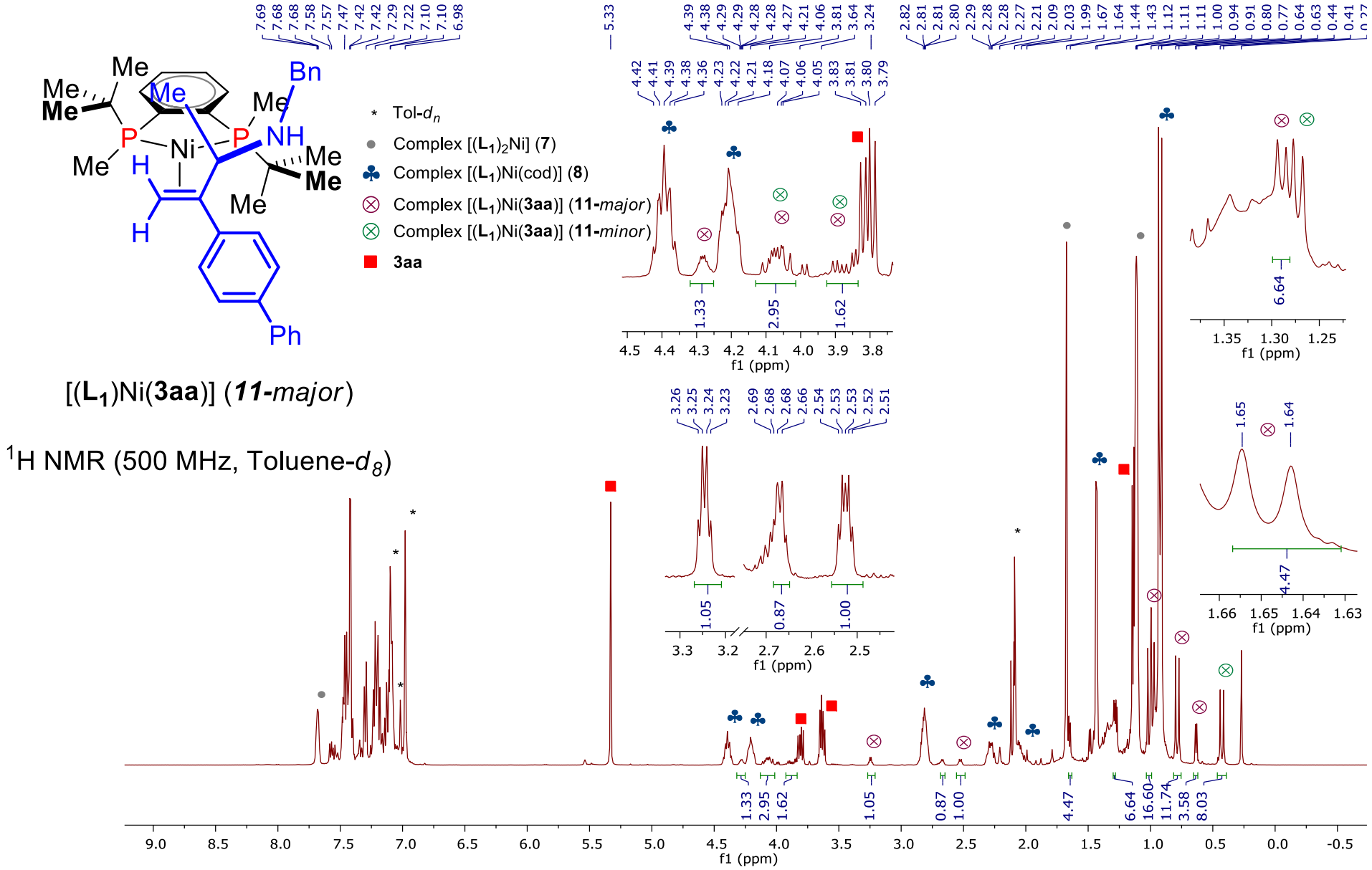
$^{19}F\{^1H\}$ NMR (280 MHz, Toluene-d_8)


[(L1)Ni(η3-allyl)][OCH2CF3] (10)
2D-NOESY (500 MHz, Toluene-d8)
CF3
8
tBu
12
Me
O
P
Ni
P
9 Me
tBu 11
13 H
CH3
16
H 13'
15 H
H 18
H 18
Ph
H-18
H-15
H-13'
H-13
H-9
H-12
H-8
H-16
H-11
H-18/H-13'
H-18/H-15
f2 (ppm)
f1 (ppm)


[(L1)Ni(η3-allyl)][OCH2CF3] (10)
2D-NOESY (500 MHz, Toluene-d8)
CF3
8
tBu
12
Me
O
P
Ni
P
9 Me
tBu11
13 H
CH3
16
H13'
15 H
H
18
H
18
Ph
H-13
H-9
H-12
H-16
H-8
H-11
H-13/H-8
H-13/H-16
H-12/H-16
f2 (ppm)
f1 (ppm)

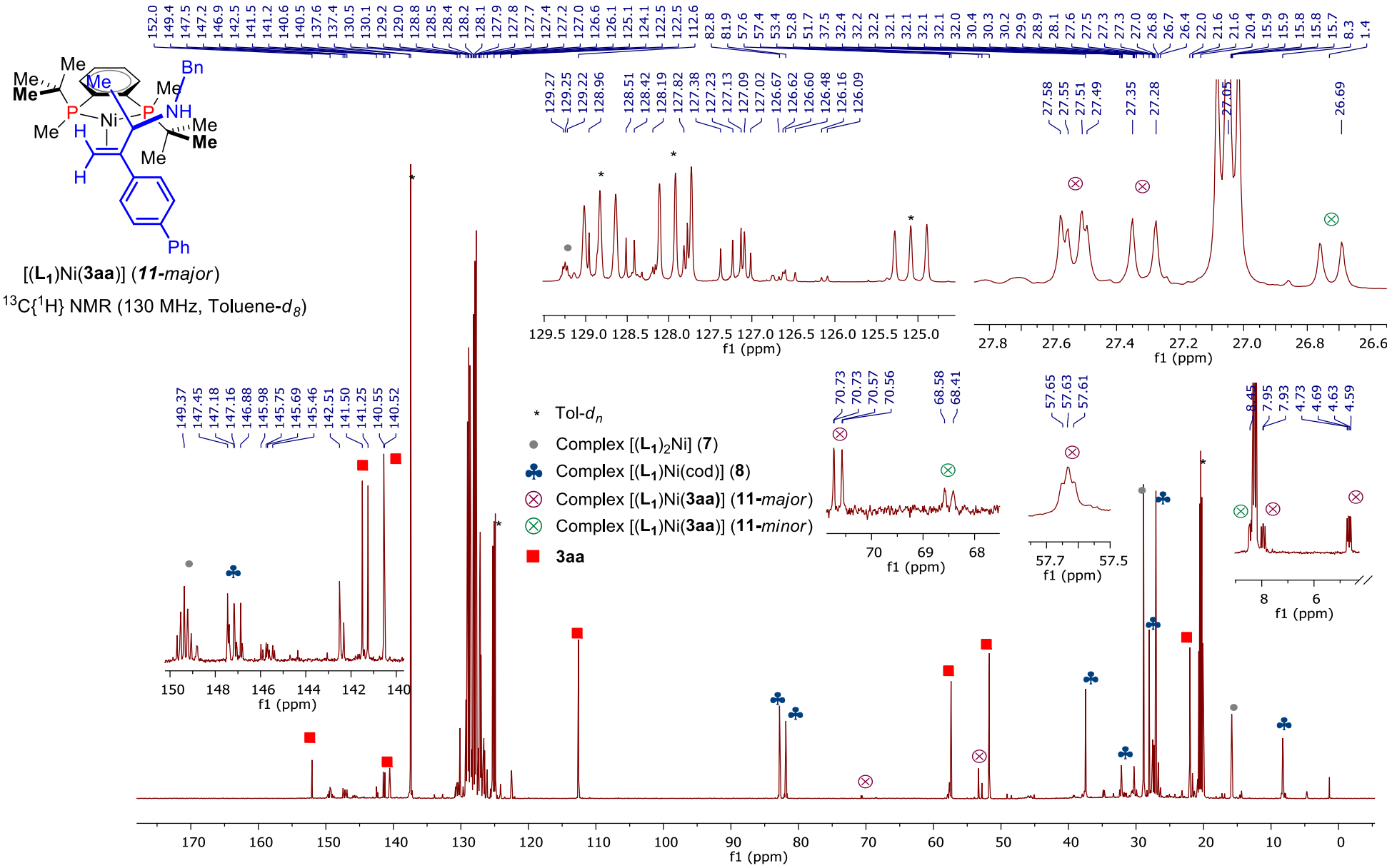

[(L1)Ni(η3-allyl)][OCH2CF3] (10)
2D-NOESY (500 MHz, Toluene-d8)
CF3
8
tBu
12
Me
O
P
Ni
P
9 Me
tBu 11
13 H
CH3
16
H13'
15 H
H
18
H
18
Ph
H-15
H-13'
H-13
H-9 H-12 H-16
H-8
H-11
H-15/H-11
H-13'/H-9
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f2 (ppm)
f1 (ppm)

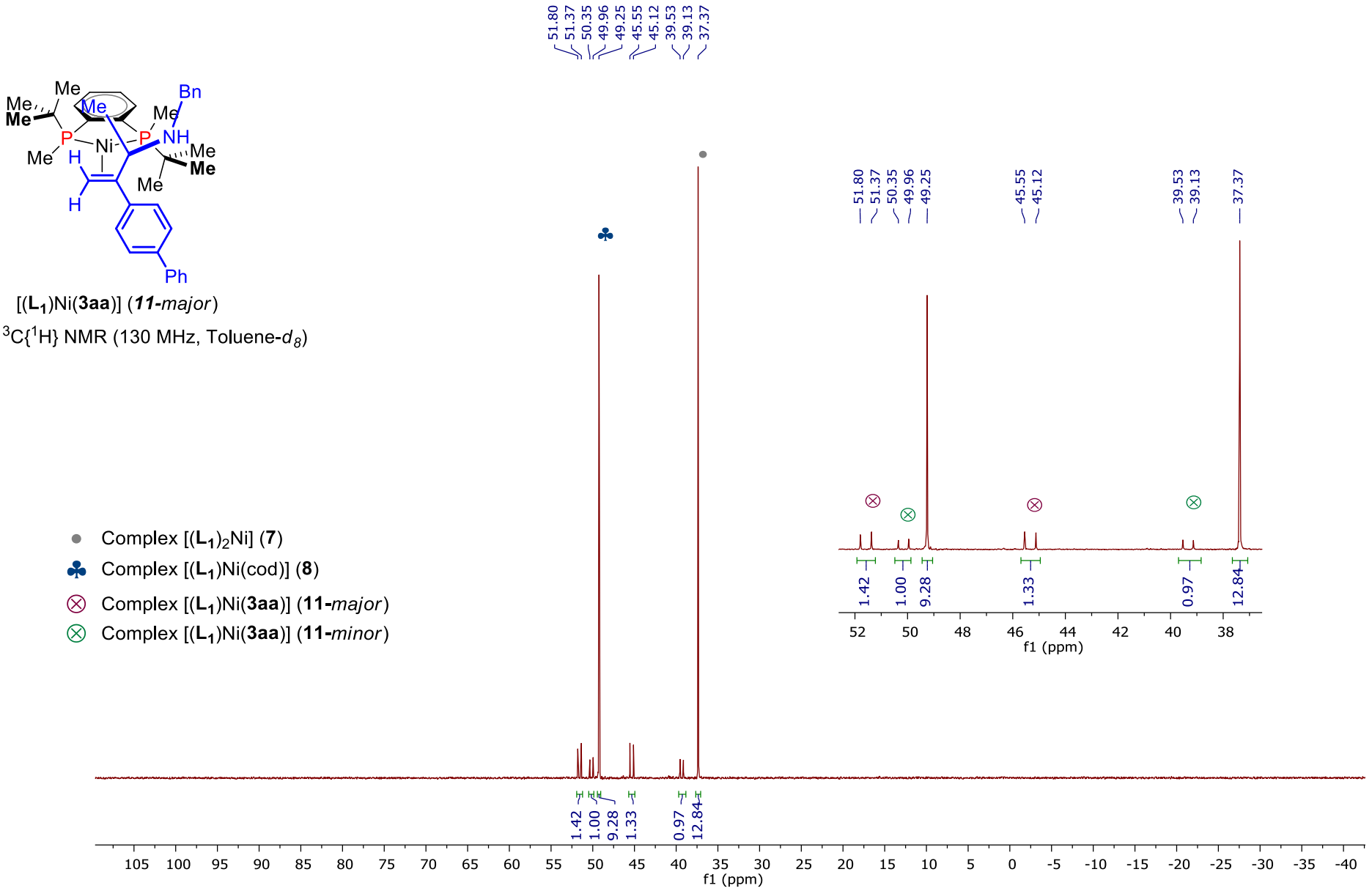

CF3
tBu
Me
P
Ni
P
Me
tBu
O
Ph
[(L1)Ni(η3-allyl)][OCH2CF3] (10)
19F,1H-HOESY (Toluene-d8)
f2 (ppm)
f1 (ppm)



[(L_1)Ni(**3aa**)] (***11*-*major***)

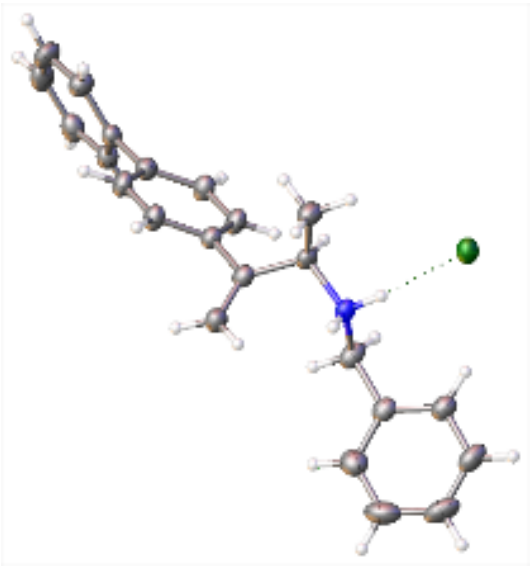
^{1}H NMR (500 MHz, Toluene-d_8)


[(L1)Ni(3aa)] (11-major)
13C{1H} NMR (130 MHz, Toluene-d8)
Tol-dn
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(3aa)] (11-major)
Complex [(L1)Ni(3aa)] (11-minor)
3aa
f1 (ppm)


[(L1)Ni(3aa)] (11-major)
13C{1H} NMR (130 MHz, Toluene-d8)
Complex [(L1)2Ni] (7)
Complex [(L1)Ni(cod)] (8)
Complex [(L1)Ni(3aa)] (11-major)
Complex [(L1)Ni(3aa)] (11-minor)
f1 (ppm)

14. X-Ray analysis

All data were collected on an Agilent Supernova diffractometer equipped with an ATLAS CCD detector using Cu radiation. The crystal was kept at 180.01(10) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimization.[5] Crystallographic data are found in **Table S3**.



Identification code	**3aa**
CCDC	1938704
Empirical formula	$C_{23}H_{24}ClN$
Formula weight	349.88
Temperature/K	180.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.48643(15)
b/Å	7.50634(11)
c/Å	12.56284(19)
α/°	90
β/°	91.0457(13)
γ/°	90
Volume/Å^3	988.72(2)
Z	2
ρ_{calc}g/cm^3	1.175
μ/mm^{-1}	1.719
F(000)	372.0
Crystal size/mm^3	0.957 × 0.155 × 0.076
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.038 to 141.102
Index ranges	-12 ≤ h ≤ 12, -9 ≤ k ≤ 9, -15 ≤ l ≤ 15
Reflections collected	15843
Independent reflections	3737 [R_{int} = 0.0315, R_{sigma} = 0.0208]
Data/restraints/parameters	3737/1/236
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0278, wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.0298, wR_2 = 0.0718
Largest diff. peak/hole / e Å^{-3}	0.13/-0.17
Flack parameter	-0.012(13)

Table S3. Crystal structure and data refinement for **3aa**-HCl salt (CCDC 1938704)

15. References

[1] Fiorito, D.; Folliet, S.; Liu, Y.; Mazet, C. A General Nickel-Catalyzed Kumada Vinylation for the Preparation of 2-Substituted 1,3-Dienes *ACS Catal.* **2018**, *8*, 1392.

[2] Doi, H. ; Sakai, T. ; Yamada, K.-I. ; Tomioka, K. *N*-Allyl-*N*-*tert*-butyldimethylsilylamine for chiral ligand-controlled asymmetric conjugate addition to *tert*-butyl alkenoates. *Chem. Commun.* **2004**, 1850.

[3] Burés, J. Variable Time Normalization Analysis: General Graphical Elucidation of Reaction Orders from Concentration Profiles. *Angew. Chem. Int. Ed.* **2016**, *55*, 16084-16087.

[4] (a) http://supramolecular.org (b) Thordarson, P. Determining Association Constants from Titration Experiments in Supramolecular Chemistry. *Chem. Soc. Rev.* **2011**, *40*, 1305. (c) Hibbert, D. B.; Thordarson, P. The Death of the Job Plot, Transparency, Open Science and Online Tools, Uncertainty Estimation Methods and Other Developments in Supramolecular Chemistry Data Analysis. *Chem. Commun.* **2016**, *52*, 12792. (d) Fit for 1:1 model: http://app.supramolecular.org/bindfit/view/4d262417-28b2-4c9b-8a4d-3a9f4f48be85. (e) Fit for 1:2 model: http://app.supramolecular.org/bindfit/view/65f19228-fb6e-48a1-9bd1-d8f2f5b5344f. (f) Fit for 2:1 model: http://app.supramolecular.org/bindfit/view/d1bb8d30-cf61-4fe6-afe9-b8adbe0af3e8.

[5] (a) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Cryst.* **2009**, *42*, 339. (b) Sheldrick, G. M. SHELXT - Integrated Space-Group and Crystal-Structure Determination. *Acta Cryst.* **2015**, *A71*, 3. (c) Sheldrick, G. M. Crystal Structure Refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3.