Kinetic resolution of primary allylic amines via palladium-catalyzed asymmetric allylic alkylation of malononitriles

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Supporting information

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General information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-400 FT (400 MHz and 100 MHz, respectively) using tetramethylsilane as an internal reference. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad signal. Chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz, respectively. Electron spray ionization (ESI) mass spectrometry data were acquired using a Thermo LTQ Orbitrap XL instrument equipped with an ESI source and controlled by Xcalibur software. High pressure liquid chromatography (HPLC) analyses were performed on a Hewlett-Packard 1200 Series instrument equipped with an isostatic pump using a Daicel Chiralpak column (AS, AD, OD, 250 x 4.6 mm) with isopropanol/hexane as mobile phase, and the UV detection was monitored at 254 nm or 220 nm. The chiral HPLC methods were calibrated with the corresponding racemic mixtures. Optical rotations were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp at λ = 589 nm and reported as $[\alpha]_D^{T\,^\circ C}$ (c = g/100 mL, solvent). Melting points are uncorrected.

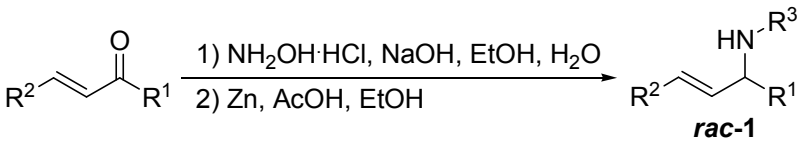
The preparation of racemic allylic amines is shown below. The highly enantioenriched allylic amines shown in Scheme 3, **1a** and ***ent*-1a**, were prepared according to our general procedure for the kinetic resolution at 56% conversion using (*S*)-BINAP and (*R*)-BINAP as the ligand, respectively. Malononitriles **2a-d**[1] and sulfonyl hydrazides **3a**, **3c**, and **3d**[2] were prepared according to literature procedures. The rest of chemicals were purchased from the Sinopharm Chemical Reagent Co., Sinocompound, Meryer, Acros, Alfa Aesar, and TCI, and used as received.

Abbreviations: Ac = acetyl. BINAP = 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl. Bn = benzyl. dba = dibenzylideneacetone. DIOP = ((2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(methylene))bis-(diphenylphosphine). dppb = 1,4-bis(diphenylphosphino)butane. MOP = (2'-methoxy-[1,1'-binaphthalen]-2-yl)diphenylphosphine. ms = molecular sieves. SynPhos = 6,6'-bis(diphenylphosphino)-2,2',3,3'-tetrahydro-5,5'-bibenzo[*b*][1,4]dioxine. THF = tetrahydrofuran, TMS = trimethylsilyl.

Preparation of racemic allylic amines

Racemic allylic amines ***rac*-1f** (R^1 = $CH_2CH{=}CH_2$, R^2 = Ph)[3] and ***rac*-1p** (R^1 = Ph, R^2 = H)[4] were prepared according to literature procedures. Shown below are the methods for the preparation of the rest of racemic allylic amines.

(1) Method A[5]



***rac*-1**

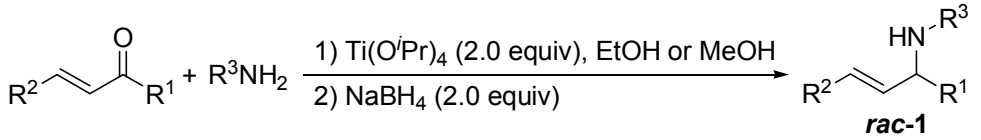
Entry	R^1	R^2	***rac*-1**	Yield (%)
1	$(CH_2)_3Me$	Ph	***rac*-1c**	64
2	$(CH_2)_7Me$	Ph	***rac*-1d**	58
3	$(CH_2)_2Ph$	Ph	***rac*-1e**	61
4	Me	cyclohexyl	***rac*-1o**	56

To a mixture of hydroxylamine hydrochloride (2.08 g, 30 mmol) and an α,β-unsaturated ketone

(25 mmol) in 80% ethanol (vol% aqueous, 20 mL) at room temperature was added sodium hydroxide (2.00 g, 50 mmol) portionwise. The mixture was heated under reflux for 10 min and then poured into ice-cooled aqueous HCl (1.7 M, 30 mL). The white solid was filtered, and washed with water to give the corresponding oxime.

To a solution of the oxime in ethanol (30 mL) and acetic acid (30 mL) was added zinc dust (3.25 g, 50 mmol) in portions and then the solution was refluxed for 1.0 h. The precipitate was filtered and washed with ethanol (2 x 50 mL). The filtrate was concentrated and the residue was dissolved in aqueous HCl (6 M, 25 mL), and extracted with dichloromethane (2 x 50 mL). The aqueous acidic layer was treated with solid sodium hydroxide (6.25 g, 156 mmol) and extracted with ether (2 x 50 mL). The combined organic extracts were dried (BaO) and concentrated to give amine ***rac*-1**.

(2) Method B[6]

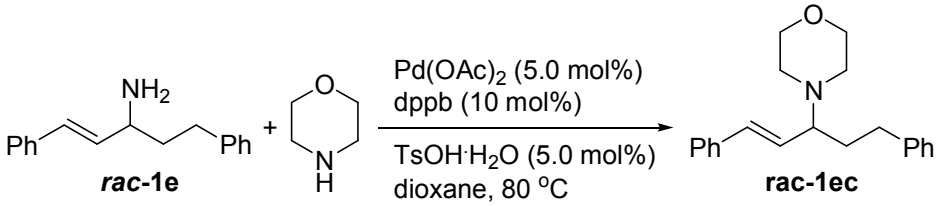


Entry	R^1	R^2	R^3	***rac*-1**	Yield (%)
1	Et	Ph	H	***rac*-1a**	62
2	Me	Ph	H	***rac*-1b**	68
3	Ph	Ph	H	***rac*-1g**	76
4	Et	4-$MeOC_6H_4$	H	***rac*-1h**	64
5	Et	4-FC_6H_4	H	***rac*-1i**	78
6	Et	4-ClC_6H_4	H	***rac*-1j**	61
7	Et	4-NCC_6H_4	H	***rac*-1k**	62
8	Me	2-naphthyl	H	***rac*-1l**	74
9	Et	benzo[*b*]thien-2-yl	H	***rac*-1m**	45
10	Me	(*E*)-PhCH=CH	H	***rac*-1n**	38
11	$(CH_2)_2Ph$	Ph	Me	***rac*-1ea**	32
12	$(CH_2)_2Ph$	Ph	Bn	***rac*-1eb**	28

A mixture of an α,β-unsaturated ketone (3.0 mmol), titanium(IV) isopropoxide (1.82 mL, 1.71 g, 6.0 mmol), and ammonia in ethanol (2.0 M, 7.50 mL, 15 mmol) [For entry 11, methylamine in methanol (2.0 M, 7.50 mL, 15 mmol); For entry 12, benzylamine (1.64 mL, 1.61 g, 15 mmol) in methanol (7.50 mL)] was stirred under nitrogen at room temperature for 12 h. Sodium borohydride (170 mg, 4.5 mmol) was then added and the resulting mixture was stirred at room temperature for an additional 12 h. A second batch of sodium borohydride (56.7 mg, 1.5 mmol) was added and stirred for an additional 12 h. The reaction was quenched with ammonium hydroxide (2.0 M, 10 mL). The resulting precipitate (composed of inorganic byproducts) was filtered through celite and washed with ethyl acetate. The aqueous solution was acidified with aqueous 1 M HCl (PH < 4). The resulting solution was extracted with ethyl acetate (3 x 20 mL) and the organic layers were discarded. The

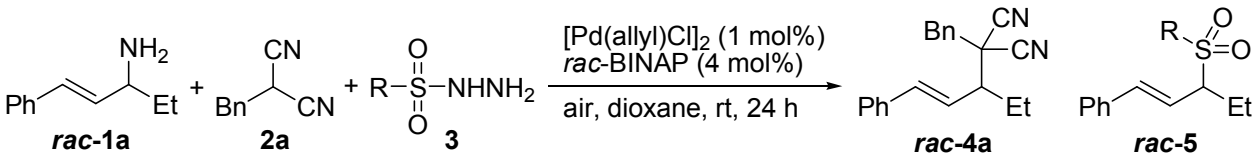
aqueous layer was then treated with aqueous 10% sodium hydroxide (PH = 10-12) and extracted with ethyl acetate (5 x 50 mL). The combined organic layers were washed with brine, and then dried with anhydrous sodium sulfate. The organic layer was concentrated under reduced pressure and the residue was purified by flash chromatography (99:1 ethyl acetate/triethylamine to 90:10:1 ethyl acetate/methanol/triethylamine) to give amine ***rac*-1**.

(3) Method C[7]

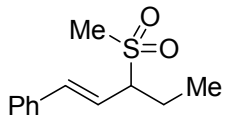


A mixture of amine ***rac*-1e** (237 mg, 1.0 mmol), morpholine (0.107 mL, 105 mg, 1.2 mmol), $TsOH{\cdot}H_2O$ (9.51 mg, 5 mol%), dppb (42.6 mg, 10 mol%), and $Pd(OAc)_2$ (11.2 mg, 5 mol%) in dioxane (1.0 mL) was heated under nitrogen at 80 °C for 4 h. The mixture was cooled to room temperature and purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:20~1:2), to give amine ***rac*-1ec** (264 mg, 86%) as a colorless oil.

Survey of sulfonyl hydrazides (Scheme 2)

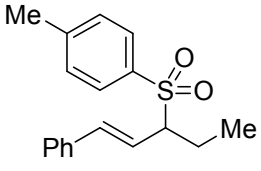


The reaction was performed following the general procedure shown below but without 5 Å molecular sieves and using racemic BINAP instead of (*S*)-BINAP as the ligand. The analytic data for the minor products, ***rac*-5**, were shown below.



***rac*-5a**

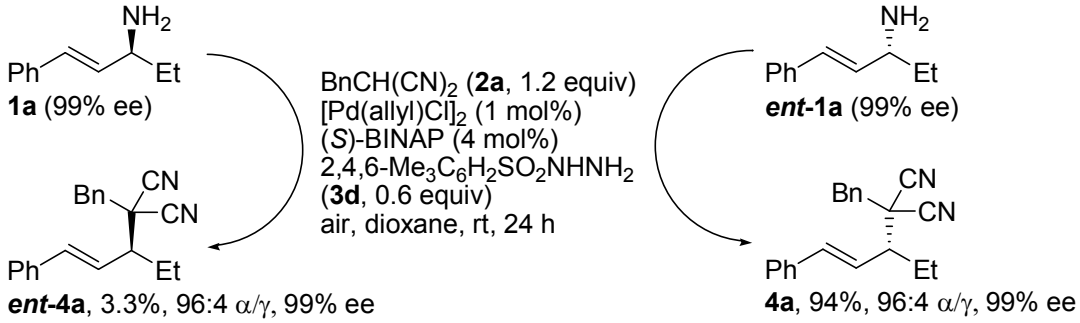
Sulfone ***rac*-5a**, light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.41 (m, 2H), 7.39-7.29 (m, 3H), 6.70 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 16.0, 9.6 Hz, 1H), 3.56-3.49 (m, 1H), 2.86 (s, 3H), 2.34-2.23 (m, 1H), 1.88-1.76 (m, 1H), 1.05 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 135.4, 128.8, 126.7, 121.8, 70.0, 38.4, 19.7, 11.3; HRMS (ESI) calcd for $C_{12}H_{16}O_2Na^+$ $(M+Na)^+$ 247.07632, found 247.07597.



***rac*-5b**

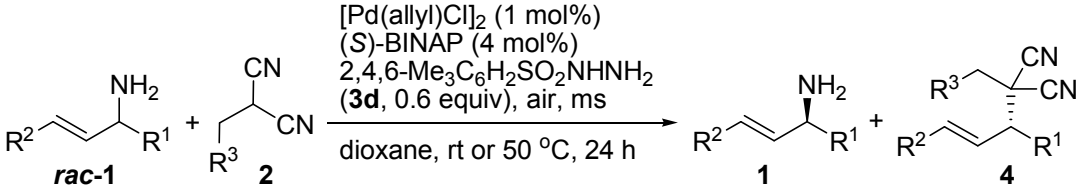
Sulfone ***rac*-5b**,[5] white solid; m.p. 66-67 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 8.4 Hz, 2H), 7.34-7.27 (m, 7H), 6.31 (d, J = 16.0 Hz, 1H), 5.90 (dd, J = 16.0, 9.6 Hz, 1H), 3.57-3.51 (m, 1H), 2.42 (s, 3H), 2.30-2.20 (m, 1H), 1.80-1.70 (m, 1H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 138.1, 136.0, 134.7, 129.5, 129.2, 128.6, 126.6, 121.2, 71.1, 21.6, 21.0, 11.4.

Allylic alkylation with enantioenriched primary allylic amines (Scheme 3)



The reaction was performed following the general procedure shown below but without 5 Å molecular sieves.

General procedure for the kinetic resolution of primary allylic amines (Table 2)



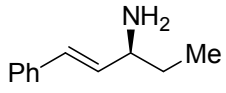
A mixture of racemic primary allylic amine ***rac*-1** (0.30 mmol), malononitrile **2** (0.18 mmol), mesitylsulfonyl hydrazide (**3d**) (12.9 mg, 0.060 mmol), 5 Å molecular sieves (30 mg), (*S*)-BINAP (7.5 mg, 4 mol%), and $[Pd(allyl)Cl]_2$ (1.1 mg, 1 mol%) in dioxane (1.8 mL) was stirred under air at room temperature or at 50 °C for 4 h. A second batch of mesitylsulfonyl hydrazide (**3d**) (12.9 mg, 0.060 mmol) was added, and 4 h later a third batch of mesitylsulfonyl hydrazide (**3d**) (12.9 mg, 0.060 mmol) was added. The resulting mixture was stirred for 12 h, and quenched with aqueous HCl (2.0 M, 5.0 mL) solution. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 x 5.0 mL). The organic layers were combined, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:20~1:40), to give malononitrile **4**. The α/γ selectivity for the formation of malononitrile **4** was determined by integrating the allylic proton signals in the ^{1}H NMR spectra of the crude product, and in each case the α-product **4** was separated from the γ-product by silica gel chromatography.

The aqueous layer was basified with 15% aqueous NaOH (pH = 10) and extraction with diethyl ether (5 x 10 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was purified by silica gel chromatography, eluting with ethyl acetate/triethylamine (100:1), to give chiral amine **1**.

The absolute configuration of compounds **1b**, **1g**, **1p**, **4b**, and **4o** was assigned by comparison of the optical rotation (or the chiral HPLC trace) with that reported in the literature (see below) and that of compounds **1a**, **1b**, **1e**, **1f**, **1g**, **1l**, **1n**, **1o**, and **1p** was assigned by benzoylation. The absolute

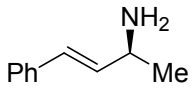
configuration of the rest of new products shown in Table 2 was assigned by analogy.

Analytical data for the products shown in Table 2



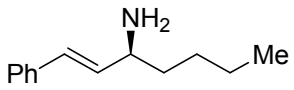
1a

Amine **1a**,[6] light yellow oil; $[\alpha]_D^{20}$ = -18.4 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.33-7.27 (m, 2H), 7.24-7.18 (m, 1H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.43-3.35 (m, 1H), 1.59-1.50 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 134.1, 129.5, 128.5, 127.3, 126.3, 55.6, 30.5 10.5. The ee was determined to be 95% by converting it to compound **1Bz-a** (see below).



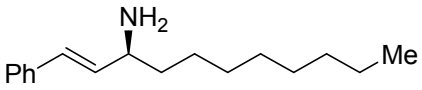
1b

Amine **1b**,[8] light yellow oil; $[\alpha]_D^{20}$ = -19.6 (*c* = 1.01, $CHCl_3$); Lit.[8]: $[\alpha]_D^{20}$ = 25.8 (*c* = 1.16, $CHCl_3$, *R*-enantiomer, >99% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.38-7.34 (m, 2H), 7.33-7.27 (m, 2H), 7.24-7.18 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 6.8 Hz, 1H), 3.70-3.62 (m, 1H), 1.25 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.2, 128.5, 127.8, 127.3, 126.2, 49.3, 23.9. The ee was determined to be 97% by converting it to compound **1Bz-b** (see below).



1c

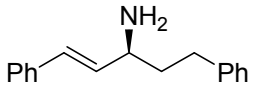
Amine **1c**, light yellow oil; $[\alpha]_D^{20}$ = -28.7 (*c* = 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.33-7.27 (m, 2H), 7.24-7.19 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 7.6 Hz, 1H), 3.49-3.42 (m, 1H), 1.53-1.46 (m, 2H), 1.39-1.28 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.1, 128.9, 128.5, 127.3, 126.2, 54.2, 37.6, 28.4, 22.7, 14.1; HRMS (ESI) calcd for $C_{13}H_{20}N^+$ $(M+H)^+$ 190.15903, found 190.15872. The ee was determined to be 90% by converting it to compound **1Bz-c** (see below).



1d

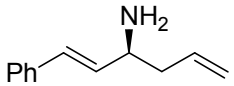
Amine **1d**, light yellow oil; $[\alpha]_D^{20}$ = -21.5 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.34-7.27 (m, 2H), 7.24-7.19 (m, 1H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.49-3.42 (m, 1H), 1.55-1.46 (m, 2H), 1.38-1.19 (m, 12H), 0.87 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.1, 128.9, 128.5, 127.3, 126.2, 54.2, 37.9, 31.9, 29.7, 29.6, 29.3, 26.2, 22.7, 14.1; HRMS (ESI) calcd for $C_{17}H_{27}NNa^+$ $(M+Na)^+$ 268.20357, found 268.20374.

The ee was determined to be 96% by converting it to compound **1Bz-d** (see below).



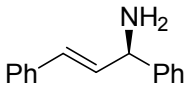
1e

Amine **1e**, light yellow oil; $[\alpha]_D^{20}$ = -18.9 (*c* = 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.36 (m, 2H), 7.34-7.26 (m, 4H), 7.25-7.16 (m, 4H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.17 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.53-3.47 (m, 1H), 2.75-2.65 (m, 2H), 1.90-1.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 137.1, 134.7, 129.4, 128.6, 128.4, 127.4, 126.3, 125.8, 53.7, 39.4, 32.5; HRMS (ESI) calcd for $C_{17}H_{20}N^+$ $(M+H)^+$ 238.15903, found 238.15904. The ee was determined to be 94% by converting it to compound **1Bz-e** (see below).



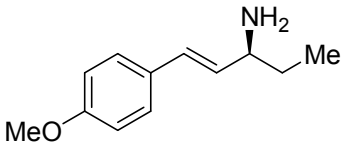
1f

Amine **1f**,[3] light yellow oil; $[\alpha]_D^{20}$ = -21.3 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.33-7.27 (m, 2H), 7.25-7.19 (m, 1H), 6.51 (d, *J* = 16.0 Hz, 1H), 6.20 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.88-5.76 (m, 1H), 5.19-5.06 (m, 2H), 3.62-3.53 (m, 1H), 2.40-2.31 (m, 1H), 2.28-2.19 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.1, 135.0, 134.2, 129.0, 128.6, 127.3, 126.3, 117.8, 53.2, 42.5. The ee was determined to be 60% by converting it to compound **1Bz-f** (see below).



1g

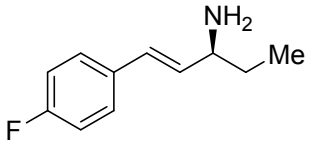
Amine **1g**,[9] yellow oil; $[\alpha]_D^{20}$ = 15.4 (*c* = 1.03, $CHCl_3$); $[\alpha]_D^{20}$ = 28.6 (*c* = 1.00, CH_2Cl_2); Lit.[9]: $[\alpha]_D^{20}$ = 44.8 (*c* = 0.9, CH_2Cl_2, *R*-enantiomer, >99% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 6H), 7.31-7.24 (m, 3H), 7.24-7.17 (m, 1H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.36 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.69 (d, *J* = 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.5, 136.9, 133.8, 129.1, 128.6, 128.5, 127.4, 127.2, 126.7, 126.4, 58.0. The ee was determined to be 70% by converting it to compound **1Bz-g** (see below).



1h

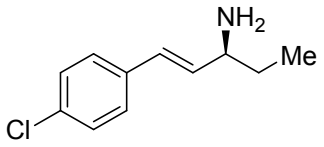
Amine **1h**, light yellow oil; $[\alpha]_D^{20}$ = -32.4 (*c* = 1.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 (d, *J* = 16.0 Hz, 1H), 5.99 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.79 (s, 3H), 3.39-3.32 m, 1H), 1.58-1.46 (m, 2H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 132.5, 130.0, 128.6, 127.4, 114.0, 55.7, 55.3, 30.8, 10.6; HRMS (ESI) calcd for $C_{12}H_{17}ONNa^+$ $(M+Na)^+$ 214.12024, found 214.12022. The ee was determined to be 85% by

converting it to compound **1Bz-h** (see below).



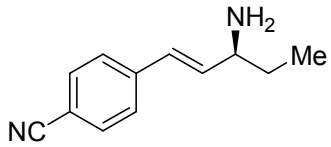
1i

Amine **1i**, light yellow oil; $[\alpha]_D^{20}$ = -21.4 (*c* = 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 2H), 7.02-6.95 (m, 2H), 6.47 (d, *J* = 16.0 Hz, 1H), 6.05 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.47-3.40 (m, 1H), 2.58 (s, br, 2H), 1.67-1.51 (m, 2H), 0.93 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3 (d, $^1J_{C\text{-}F}$ = 245.1 Hz), 133.1 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 132.6, 129.2, 127.9 (d, $^3J_{C\text{-}F}$ = 7.9 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.5 Hz), 55.6, 30.0, 10.4; HRMS (ESI) calcd for $C_{11}H_{15}NF^+$ $(M+H)^+$ 180.11830, found 180.11775. The ee was determined to be 93% by converting it to compound **1Bz-i** (see below).



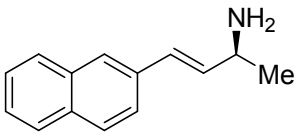
1j

Amine **1j**, light yellow oil; $[\alpha]_D^{20}$ = -17.5 (*c* = 1.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.23 (m, 4H), 6.43 (d, *J* = 16.0 Hz, 1H), 6.12 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.42-3.35 (m, 1H), 1.56-1.50 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 135.3, 132.8, 128.7, 128.0, 127.5, 55.6, 30.7, 10.5; HRMS (ESI) calcd for $C_{11}H_{15}NCl^+$ $(M+H)^+$ 196.08875, found 196.08872. The ee was determined to be 94% by converting it to compound **1Bz-j** (see below).



1k

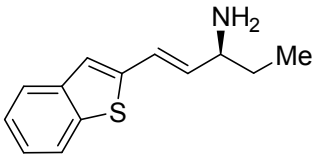
Amine **1k**, light yellow oil; $[\alpha]_D^{20}$ = -38.6 (*c* = 1.09, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.61-7.56 (m, 2H), 7.46-7.42 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.29 (dd, *J* = 16.0, 7.2 Hz, 1H), 3.50-3.42 (m, 1H), 2.02 (s, br, 2H), 1.63-1.51 (m, 2H), 0.95 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.7, 138.2, 132.4, 128.0, 126.8, 119.0, 110.5, 55.4, 30.4, 10.4; HRMS (ESI) calcd for $C_{12}H_{15}N_2^+$ $(M+H)^+$ 187.12298, found 187.12291. The ee was determined to be 91% by converting it to compound **1Bz-k** (see below).



1l

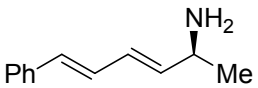
Amine **1l**,[6] colorless oil; $[\alpha]_D^{20}$ = -19.8 (*c* = 1.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (m, 3H), 7.71 (s, 1H), 7.61-7.57 (m, 1H), 7.47-7.39 (m, 2H), 6.63 (d, *J* = 16.0 Hz, 1H),

6.34 (dd, J = 16.0, 6.8 Hz, 1H), 3.76-3.69 (m, 1H), 1.29 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 134.6, 133.6, 132.8, 128.2, 128.0, 127.9, 127.6, 126.2, 126.0, 125.7, 123.6, 49.4, 23.9. The ee was determined to be 99% by converting it to compound **1Bz-l** (see below).



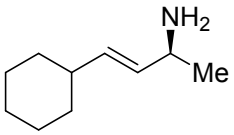
1m

Amine **1m**, yellow oil; $[\alpha]_D^{20}$ = -60.5 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.71 (m, 1H), 7.67-7.63 (m, 1H), 7.32-7.22 (m, 2H), 7.10 (s, 1H), 6.70 (d, J = 15.6 Hz, 1H), 6.08 (dd, J = 15.6, 7.2 Hz, 1H), 3.43-3.36 (m, 1H), 1.60-1.51 (m, 2H), 0.96 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 140.1, 138.7, 137.3, 124.5, 124.3, 123.3, 123.0, 122.2, 55.4, 30.6, 10.5; HRMS (ESI) calcd for $C_{13}H_{15}NSNa^+$ $(M+Na)^+$ 240.08174, found 240.08110 The ee was determined to be 91% by converting it to compound **1Bz-m** (see below).



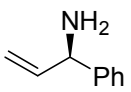
1n

Amine **1n**,[6] yellow oil; $[\alpha]_D^{20}$ = -34.5 (c = 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.34 (m, 2H), 7.32-7.27 (m, 2H), 7.23-7.18 (m, 1H), 6.74 (dd, J = 15.6, 10.4, 1H), 6.50 (d, J = 15.6 Hz, 1H), 6.27 (dd, J = 15.2, 10.4 Hz, 1H), 5.80 (dd, J = 15.2, 6.6 Hz, 1H), 3.63-3.54 (m, 1H), 2.49 (s, br, 2H), 1.21 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5, 137.4, 131.6, 128.7, 128.6, 128.4, 127.4, 126.2, 49.0, 23.8. The ee was determined to be 80% by converting it to compound **1Bz-n** (see below).



1o

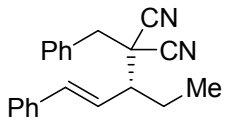
Amine **1o**,[5] yellow oil; $[\alpha]_D^{20}$ = -8.4 (c = 1.06, $CHCl_3$); Lit.[5]: $[\alpha]_D^{20}$ = -15.5 (c = 1.1, $CHCl_3$, *S*-enantiomer, 99% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (dd, J = 15.6, 6.4 Hz, 1H), 5.37 (dd, J = 15.6, 6.4 Hz, 1H), 3.46-3.39 (m, 1H), 1.92-1.84 (m, 1H), 1.75-1.60 (m, 3H), 1.29-0.99 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.6, 133.9, 49.1, 40.3, 33.1, 26.2, 26.1, 24.2. The ee was determined to be 70% by converting it to compound **1Bz-o** (see below).



1p

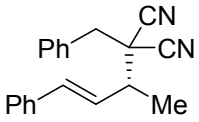
Amine **1p**,[4] yellow oil; $[\alpha]_D^{20}$ = 8.6 (c = 1.03, $CHCl_3$); Lit.[4]: $[\alpha]_D^{25}$ = -10.2 (c = 4, $CHCl_3$, *S*-enantiomer, >99.6% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.30 (m, 4H), 7.28-7.22 (m, 1H),

6.02 (ddd, J = 17.2, 10.4, 6.4 Hz, 1H), 5.27-5.20 (m, 1H), 5.13-5.09 (m, 1H), 4.54-4.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4, 142.2, 128.5, 127.1, 126.6, 113.7, 58.4. The ee was determined to be 89% by converting it to compound **1Bz-p** (see below).



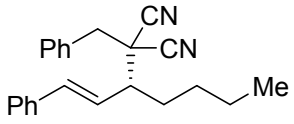
4a

Malononitrile **4a**, light yellow oil; $[\alpha]_D^{20}$ = 35.5 (c = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.42-7.35 (m, 7H), 7.34-7.30 (m, 1H), 6.63 (d, J = 15.6 Hz, 1H), 6.02 (dd, J = 15.6, 9.6 Hz, 1H), 3.27 (d, J = 13.6 Hz, 1H), 3.09 (d, J = 13.6 Hz, 1H), 2.61-2.53 (m, 1H), 2.18-2.08 (m, 1H), 1.82-1.71 (m, 1H), 1.01 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 135.6, 132.4, 130.2, 128.9, 128.8, 128.7, 128.6, 126.7, 123.9, 115.1, 114.4, 52.1, 44.6, 42.1, 24.7, 11.8; HRMS (ESI) calcd for $C_{21}H_{20}N_2Na^+$ $(M+Na)^+$ 323.15187, found 323.15183. The ee was determined to be 86% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 99:1, flow rate = 1.0 mL/min): t_R (minor) = 13.3 min, t_R (major) = 11.6 min.



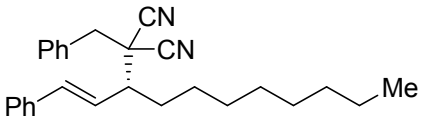
4b

Malononitrile **4b**,[1] white solid; m.p. 112.1-113.0 °C; $[\alpha]_D^{20}$ = 24.6 (c = 1.04, $CHCl_3$); Lit.[1]: $[\alpha]_D^{25}$ = -32.3 (c = 1.0, $CHCl_3$, *S*-enantiomer, 95% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.28 (m, 10H), 6.65 (d, J = 15.6 Hz, 1H), 6.17 (dd, J = 15.6, 9.2 Hz, 1H), 3.23 (d, J = 14.0 Hz, 1H), 3.10 (d, J = 14.0 Hz, 1H), 2.94-2.85(m, 1H), 1.54 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6, 132.4, 130.2, 128.9, 128.8, 128.7, 128.5, 126.7, 125.5, 114.9, 114.3, 45.1, 44.8, 41.7, 17.7. The ee was determined to be 79% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 97:3, flow rate = 1.0 mL/min): t_R (minor) = 15.5 min, t_R (major) = 14.7 min.



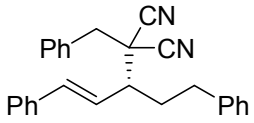
4c

Malononitrile **4c**, light yellow oil; $[\alpha]_D^{20}$ = 34.1 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.42-7.29 (m, 8H), 6.62 (d, J = 15.6 Hz, 1H), 6.04 (dd, J = 15.6, 9.6 Hz, 1H), 3.26 (d, J = 14.0 Hz, 1H), 3.08 (d, J = 14.0 Hz, 1H), 2.70-2.61 (m, 1H), 2.09-1.99 (m, 1H), 1.84-1.69 (m, 1H), 1.47-1.24 (m, 4H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.6, 132.4, 130.2, 128.9, 128.8, 128.7, 128.6, 126.7, 124.3, 115.1, 114.4, 50.6, 44.7, 42.1, 31.3 29.3, 22.3, 13.9; HRMS (ESI) calcd for $C_{23}H_{24}N_2Na^+$ $(M+Na)^+$ 351.18317, found 351.18295. The ee was determined to be 94% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 6.8 min, t_R (major) = 8.1 min.



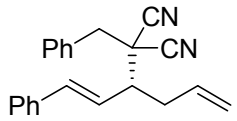
4d

Malononitrile **4d**, light yellow oil; $[\alpha]_D^{20}$ = 48.6 (*c* = 1.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.47-7.43 (m, 2H), 7.41-7.36 (m, 7H), 7.34-7.30 (m, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.03 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.08 (d, *J* = 13.6 Hz, 1H), 2.69-2.61 (m, 1H), 2.05-1.98 (m, 1H), 1.81-1.72 (m, 1H), 1.60-1.20 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 135.6, 132.4, 130.2, 128.9 128.8, 128.7, 128.6, 126.7, 124.3, 115.1, 114.4, 50.6, 44.7, 42.0, 31.8, 31.5, 29.3, 29.2, 27.1, 22.6, 14.1; HRMS (ESI) calcd for $C_{27}H_{32}N_2Na^+$ $(M+Na)^+$ 407.24577, found 407.24542. The ee was determined to be 94% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 6.3 min, t_R (major) = 8.5 min.



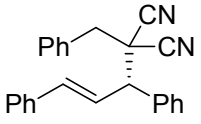
4e

Malononitrile **4e**, light yellow oil; $[\alpha]_D^{20}$ = 35.7 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.49-7.45 (m, 2H), 7.42-7.27 (m, 10H), 7.25-7.17 (m, 3H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.09 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.22 (d, *J* = 14.0 Hz, 1H), 3.04 (d, *J* = 14.0 Hz, 1H), 2.91-2.83 (m, 1H), 2.72-2.55 (m, 2H), 2.46-2.36 (m, 1H), 2.16-2.07 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 137.9, 135.5, 132.3, 130.2, 128.9, 128.7, 128.6, 128.4, 126.7, 126.4, 123.8, 114.9, 114.3, 49.7, 44.6, 41.9, 32.9, 32.8; HRMS (ESI) calcd for $C_{27}H_{24}N_2Na^+$ $(M+Na)^+$ 399.18317, found 399.18292. The ee was determined to be 93% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 9.7 min, t_R (major) = 12.1 min.



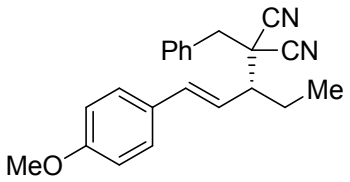
4f

Malononitrile **4f**, white solid; m.p. 68.3-69.1 °C; $[\alpha]_D^{20}$ = 48.0 (*c* = 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46-7.29 (m, 10H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.06 (dd, *J* = 16.0, 9.6 Hz, 1H), 5.79-5.68 (m, 1H), 5.21-5.10 (m, 2H), 3.28 (d, *J* = 13.6 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 1H), 2.86-2.72 (m, 2H), 2.60-2.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.6, 135.6, 133.4, 132.3, 130.3, 129.0, 128.9, 128.8, 128.7, 126.8, 123.6, 118.7, 114.9, 114.2, 50.2, 44.2, 42.0, 36.2; HRMS (ESI) calcd for $C_{22}H_{20}N_2Na^+$ $(M+Na)^+$ 335.15187, found 335.15189. The ee was determined to be 94% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 11.5 min, t_R (major) = 13.8 min.



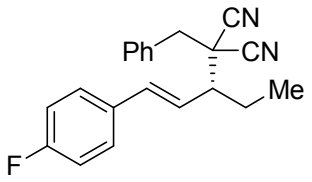
4g

Malononitrile **4g**, white solid; m.p. 153.0-154.0 °C; $[\alpha]_D^{20}$ = -16.8 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.48-7.27 (m, 13H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.66 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.90 (d, *J* = 8.8 Hz, 1H), 3.23 (d, *J* = 13.6 Hz, 1H), 3.03 (d, *J* = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.3, 135.6, 132.2, 130.3, 129.3, 129.0, 128.9, 128.8, 128.7, 128.6, 126.8, 123.6, 114.8, 114.4, 55.9, 45.8, 42.5. HRMS (ESI) calcd for $C_{25}H_{20}N_2Na^+$ $(M+Na)^+$ 371.15187, found 371.15088. The ee was determined to be 60% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 15.5 min, t_R (major) = 13.1 min.



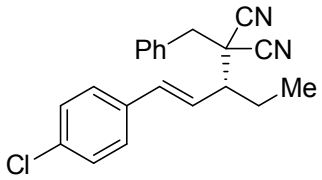
4h

Malononitrile **4h**, light yellow oil; $[\alpha]_D^{20}$ = 41.4 (*c* = 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.36 (m, 7H), 6.93-6.87 (m, 2H), 6.56 (d, *J* = 15.6 Hz, 1H), 5.87 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.83 (s, 3H), 3.27 (d, *J* = 13.6 Hz, 1H), 3.07 (d, *J* = 13.6 Hz, 1H), 2.57-2.49 (m, 1H), 2.16-2.05 (m, 1H), 1.80-1.68 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 136.9, 132.5, 130.2, 128.9, 128.6, 128.4, 127.9, 121.5, 115.2, 114.5, 114.2, 55.4, 52.3, 44.7, 42.1, 24.8, 11.8; HRMS (ESI) calcd for $C_{22}H_{22}ON_2Na^+$ $(M+Na)^+$ 353.16243, found 353.16232. The ee was determined to be 96% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 70:30, flow rate = 1.0 mL/min): t_R (minor) = 6.7 min, t_R (major) = 16.4 min.



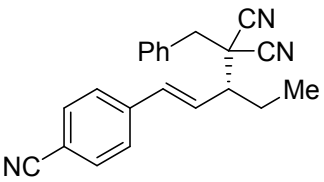
4i

Malononitrile **4i**, light yellow oil; $[\alpha]_D^{20}$ = 38.6 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.36 (m, 7H), 7.09-7.02 (m, 2H), 6.59 (d, *J* = 15.6 Hz, 1H), 5.94 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.25 (d, *J* = 13.6 Hz, 1H), 3.09 (d, *J* = 13.6 Hz, 1H), 2.59-2.51 (m, 1H), 2.16-2.08 (m, 1H), 1.80-1.70 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.9 (d, $^1J_{C\text{-}F}$ = 246.9 Hz), 136.3, 132.4, 131.8 (d, $^4J_{C\text{-}F}$ = 3.3 Hz), 130.2, 128.9, 128.7, 128.3 (d, $^3J_{C\text{-}F}$ = 8.1 Hz), 123.7 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 115.8 (d, $^2J_{C\text{-}F}$ = 21.6 Hz), 115.1, 114.4, 52.1, 44.6, 42.0, 24.7, 11.8; HRMS (ESI) calcd for $C_{21}H_{19}N_2FNa^+$ $(M+Na)^+$ 341.14245, found 341.14233. The ee was determined to be 88% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 6.2 min, t_R (major) = 10.5 min.



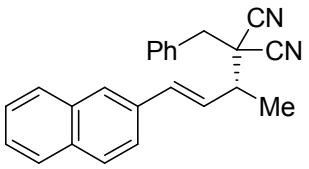
4j

Malononitrile **4j**, light yellow oil; $[\alpha]_D^{20}$ = 35.4 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.32 (m, 9H), 6.58 (d, *J* = 15.6 Hz, 1H), 6.00 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.24 (d, *J* = 13.6 Hz, 1H), 3.09 (d, *J* = 13.6 Hz, 1H), 2.60-2.50 (m, 1H), 2.17-2.08 (m, 1H), 1.81-1.69 (m, 1H), 1.00 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 134.3, 134.1, 132.3, 130.2, 129.0, 128.9, 128.8, 127.9, 124.6, 115.0, 114.4, 52.1, 44.6, 42.0, 24.6, 11.8; HRMS (ESI) calcd for $C_{21}H_{19}N_2ClNa^+$ $(M+Na)^+$ 357.11290, found 357.11270. The ee was determined to be 84% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 6.7 min, t_R (major) = 9.9 min.



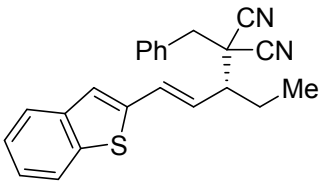
4k

Malononitrile **4k**, light yellow oil; $[\alpha]_D^{20}$ = 32.0 (*c* = 1.07, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 6.8, 1.6 Hz, 2H), 7.53 (d, *J* = 6.0 Hz, 2H), 7.42-7.35 (m, 5H), 6.65 (d, *J* = 15.6 Hz, 1H), 6.17 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.23 (d, *J* = 13.6 Hz, 1H), 3.12 (d, *J* = 13.6 Hz, 1H), 2.64-2.56 (m, 1H), 2.18-2.11 (m, 1H), 1.82-1.73 (m, 1H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 135.8, 132.7, 132.1, 130.2, 129.0, 128.9, 128.1, 127.2, 118.6, 114.7, 114.3, 111.9, 51.9, 44.4, 42.0, 24.4, 11.8; HRMS (ESI) calcd for $C_{22}H_{19}N_3Na^+$ $(M+Na)^+$ 348.14712, found 348.14700. The ee was determined to be 90% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 70:30, flow rate = 1.0 mL/min): t_R (minor) = 11.4 min, t_R (major) = 20.3 min.



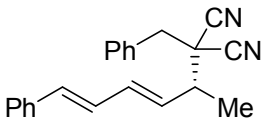
4l

Malononitrile **4l**, light yellow oil; $[\alpha]_D^{20}$ = 33.6 (*c* = 1.08, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.85-7.78 (m, 4H), 7.65-7.62 (m, 1H), 7.51-7.47 (m, 2H), 7.43-7.35 (m, 5H), 6.81 (d, *J* = 15.6 Hz, 1H), 6.30 (dd, *J* = 15.6, 8.8 Hz, 1H), 3.27 (d, *J* = 13.6 Hz, 1H), 3.14 (d, *J* = 13.6 Hz, 1H), 2.99-2.92 (m, 1H), 1.59 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.7, 133.4, 133.0, 132.4, 130.2, 128.9, 128.7, 128.5, 128.1, 127.7, 127.0, 126.6, 126.4, 125.8, 123.4, 114.9, 114.3, 45.1, 45.0, 41.8, 17.8; HRMS (ESI) calcd for $C_{24}H_{20}N_2Na^+$ $(M+Na)^+$ 359.15187, found 359.15161. The ee was determined to be 73% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 21.1 min, t_R (major) = 19.3 min.



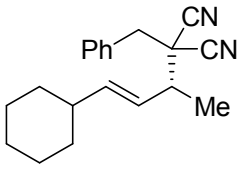
4m

Malononitrile **4m**, white solid; m.p. 161-162 °C; $[\alpha]_D^{20}$ = 26.8 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.75 (m, 1H), 7.74-7.68 (m, 1H), 7.41-7.30 (m, 7H), 7.25-7.23 (m, 1H), 6.85 (d, *J* = 15.6 Hz, 1H), 5.92 (dd, *J* = 15.6, 10.0 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 3.10 (d, *J* = 13.6 Hz, 1H), 2.62-2.51 (m, 1H), 2.17-2.10 (m, 1H), 1.83-1.74 (m, 1H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4, 139.7, 139.0, 132.3, 131.1, 130.2, 128.9, 128.7, 125.8, 125.3, 124.7, 124.2, 123.8, 122.3, 115.0, 114.2, 52.0, 44.5, 42.0, 24.7, 11.8; HRMS (ESI) calcd for $C_{23}H_{20}N_2NaS^+$ $(M+Na)^+$ 379.12394, found 379.12396. The ee was determined to be 95% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 9.8 min, t_R (major) = 28.7 min.



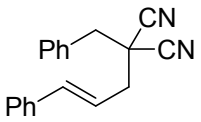
4n

Malononitrile **4n**, light yellow oil; $[\alpha]_D^{20}$ = 14.2 (*c* = 1.06, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.31 (m, 9H), 7.28-7.24 (m, 1H), 6.82 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.62 (d, *J* = 15.6 Hz, 1H), 6.45 (dd, *J* = 14.8, 10.4 Hz, 1H), 5.79 (dd, *J* = 14.8, 8.8 Hz, 1H), 3.21 (d, *J* = 13.7 Hz, 1H), 3.08 (d, *J* = 13.7 Hz, 1H), 2.83 (dq, *J* = 13.6, 6.8 Hz, 1H), 1.50 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 135.8, 134.5, 132.4, 130.2, 129.1, 128.9, 128.7, 128.1, 127.3, 126.6, 114.9, 114.3, 45.1, 44.6, 41.6 17.6; HRMS (ESI) calcd for $C_{22}H_{20}N_2Na^+$ $(M+Na)^+$ 335.15187, found 335.15179. The ee was determined to be 69% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 70:30, flow rate = 1.0 mL/min): t_R (minor) = 11.5 min, t_R (major) = 22.1 min.



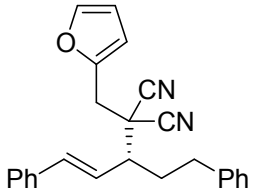
4o

Malononitrile **4o**,[1] light yellow oil; $[\alpha]_D^{20}$ = 4.3 (*c* = 1.04, $CHCl_3$); Lit.[1]: $[\alpha]_D^{20}$ = -9.8 (*c* = 1.0, $CHCl_3$, *S*-enantiomer, 98% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.43-7.32 (m, 5H), 5.70 (dd, *J* = 15.6, 7.2 Hz, 1H), 5.40 (ddd, *J* = 15.6, 8.8, 1.2 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 3.02 (d, *J* = 13.6 Hz, 1H), 2.67-2.59 (m, 1H), 2.10-2.00 (m, 1H), 1.79-1.71 (m, 4H), 1.41 (d, *J* = 6.8 Hz, 3H), 1.35-1.10 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 132.6, 130.2, 128.8, 128.6, 124.0, 115.0, 114.4, 45.1, 44.2, 41.4, 40.7, 32.8, 32.7, 26.0, 25.8, 17.6. The ee was determined to be 46% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 14.8 min, t_R (major) = 16.6 min.



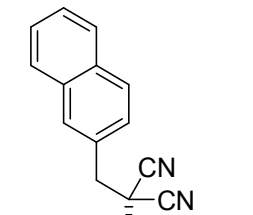
4p

Malononitrile **4p**,[10] light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.27 (m, 10H), 6.71 (d, J = 15.6 Hz, 1H), 6.27 (dt, J = 15.6, 7.6 Hz 1H), 3.25 (s, 2H), 2.88 (dd, J = 7.6, 0.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 135.7, 131.9, 130.2, 129.0, 128.9, 128.7, 128.5, 126.7, 119.1, 115.0, 42.7, 40.9, 39.6.



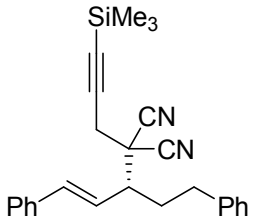
4q

Malononitrile **4q**, light yellow oil; $[\alpha]_D^{20}$ = 36.8 (c = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.40-7.35 (m, 3H), 7.34-7.26 (m, 3H), 7.23-7.15 (m, 3H), 6.62 (d, J = 16.0 Hz, 1H), 6.39-6.34 (m, 2H), 6.03 (dd, J = 16.0, 10.0 Hz, 1H), 3.33 (d, J = 14.8 Hz, 1H), 3.22 (d, J = 14.8 Hz, 1H), 2.87-2.79 (m, 1H), 2.66-2.52 (m, 2H), 2.41-2.31 (m, 1H), 2.11-2.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.3, 143.4, 140.1, 138.2, 135.4, 128.8, 128.7, 128.6, 128.4, 126.7, 126.3, 123.4, 114.6, 114.1, 110.8, 110.6, 48.6, 42.5, 34.6, 32.8, 32.5; HRMS (ESI) calcd for $C_{25}H_{22}ON_2Na^+$ $(M+Na)^+$ 389.16243, found 389.16208. The ee was determined to be 93% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 70:30, flow rate = 1.0 mL/min): t_R (minor) = 8.7 min, t_R (major) = 9.6 min.



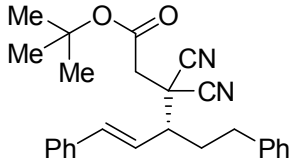
4r

Malononitrile **4r**, light yellow oil; $[\alpha]_D^{20}$ = 43.0 (c = 1.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.81 (m, 4H), 7.52-7.28 (m, 10H), 7.24-7.17 (m, 3H), 6.64 (d, J = 16.0 Hz, 1H), 6.13 (dd, J = 16.0, 10.0 Hz, 1H), 3.40 (d, J = 14.0 Hz, 1H), 3.22 (d, J = 14.0 Hz, 1H), 2.92-2.83 (m, 1H), 2.75-2.68 (m, 1H), 2.64-2.55 (m, 1H), 2.47-2.38 (m, 1H), 2.18-2.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 138.0, 135.5, 133.2, 133.1, 129.8, 129.7, 128.9, 128.8, 128.7, 128.5, 128.0, 127.7, 127.5, 126.8, 126.6, 126.5, 126.4, 123.8, 115.0, 114.3, 49.8, 44.6, 42.1, 32.9, 32.8; HRMS (ESI) calcd for $C_{31}H_{26}N_2Na^+$ $(M+Na)^+$ 449.19882, found 449.19806. The ee was determined to be 99% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 70:30, flow rate = 1.0 mL/min): t_R (minor) = 23.2 min, t_R (major) = 33.3 min.



4s

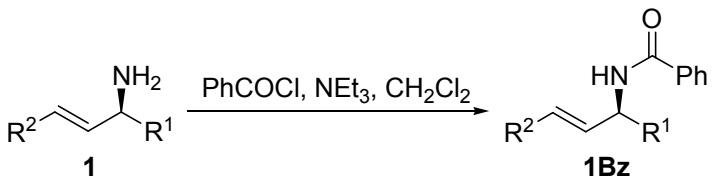
Malononitrile **4s**, light yellow oil; $[\alpha]_D^{20}$ = 47.2 (*c* = 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.11 (m, 10H), 6.59 (d, *J* = 15.6 Hz, 1H), 5.90 (dd, *J* = 15.6, 10.0 Hz, 1H), 2.95 (d, *J* = 16.8 Hz, 1H), 2.88-2.76 (m, 3H), 2.61-2.52 (m, 1H), 2.38-2.29 (m, 1H), 2.10-2.00 (m, 1H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.9, 138.3, 135.4, 128.9, 128.8, 128.7 128.4, 126.7, 126.5, 122.7, 114.3, 113.8, 96.0, 92.9, 47.8, 41.5, 32.8, 32.4, 28.5, -0.33; HRMS (ESI) calcd for $C_{26}H_{28}N_2NaSi^+$ $(M+Na)^+$ 419.19140, found 419.19070. The ee was determined to be 94% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 4.8 min, t_R (major) = 5.7 min.



4t

Malononitrile **4t**, light yellow oil; $[\alpha]_D^{20}$ = 40.2 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.15 (m, 10H), 6.55 (d, *J* = 15.6 Hz, 1H), 5.97 (dd, *J* = 15.6, 10.0 Hz, 1H), 2.94 (d, *J* = 16.8 Hz, 1H), 2.88-2.82 (m, 1H), 2.79-2.72 (m, 2H), 2.63-2.57 (m, 1H), 2.43-2.35 (m, 1H), 2.13-2.05 (m, 1H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 140.0, 138.2, 135.3, 132.1, 128.9, 128.7, 128.5, 126.8, 126.4, 123.2, 114.8, 114.0, 84.0, 49.0, 41.1, 38.6, 32.8, 32.5, 27.9; HRMS (ESI) calcd for $C_{26}H_{28}O_2N_2Na$ $(M+Na)^+$ 423.20430, found 423.20410. The ee was determined to be 87% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 6.5 min, t_R (major) = 8.3 min.

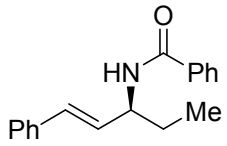
Benzoylation of chiral amines for ee determination



1 **1Bz**

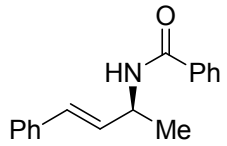
To a solution of chiral amine **1** (0.10 mmol) and triethylamine (0.021 mL, 15.2 mg, 0.15 mmol) in dichloromethane (0.40 mL) at 0 °C was added dropwise a solution of benzoyl chloride (16.9 mg, 0.014 mL, 0.12 mmol) in dichloromethane (0.10 mL). The mixture was allowed to warm to room temperature and stirred overnight. The mixture was quenched with water (0.50 mL) and extracted with dichloromethane (2.5 mL), and the aqueous layer was washed with dichloromethane (1.5 mL). The organic layers were combined, dried over sodium sulfate, and concentrated. The residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether (1:5~1:10), to give

amide **1Bz**.



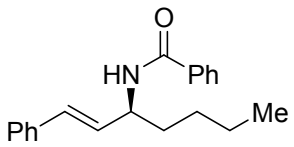
1Bz-a

Amide **1Bz-a**,[6] prepared from chiral amine **1a** in 99% yield. White solid; m.p. 125.6-126.8 °C; $[\alpha]_D^{20}$ = -31.2 (*c* = 1.00, $CHCl_3$); Lit.[6]: $[\alpha]_D^{20}$ = 17.2 (*c* = 1.0, $CHCl_3$, *R*-enantiomer, 68.6% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.75 (m, 2H), 7.56-7.14 (m, 8H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.19 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.82-4.74 (m, 1H), 1.85-1.63 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 136.7, 134.8, 131.5, 130.9, 129.6, 128.6, 128.5, 127.6, 126.9, 126.4, 52.9, 28.3, 10.4. The ee was determined to be 95% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 9.6 min, t_R (major) = 11.6 min.



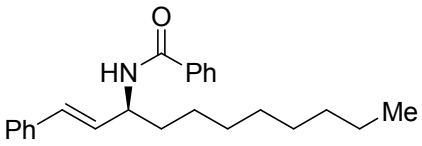
1Bz-b

Amide **1Bz-b**,[6] prepared from chiral amine **1b** in 99% yield. White solid; m.p. 118.0-119.0 °C; $[\alpha]_D^{20}$ = -26.4 (*c* = 1.02, $CHCl_3$); Lit.[6]: $[\alpha]_D^{20}$ = 13.2 (*c* = 1.0, $CHCl_3$, *R*-enantiomer, 68.2% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 2H), 7.51-7.46 (m, 1H), 7.44-7.39 (m, 2H), 7.37-7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.26-7.20 (m, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 6.30-6.22 (m, 2H), 5.01-4.91 (m, 1H), 1.44 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 136.6, 134.6, 131.4, 130.8, 130.0, 128.6, 127.6, 126.9, 126.4, 46.9, 20.7. The ee was determined to be 97% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 70:30, flow rate = 1.0 mL/min): t_R (minor) = 6.4 min, t_R (major) = 10.6 min.



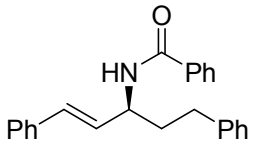
1Bz-c

Amide **1Bz-c**, prepared from chiral amine **1c** in 99% yield. White solid; m.p. 117.8-118.6 °C; $[\alpha]_D^{20}$ = -33.6 (*c* = 1.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.76 (m, 2H), 7.50-7.15 (m, 8H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.43 (d, *J* = 6.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 5.6 Hz, 1H), 4.88-4.76 (m, 1H), 1.76-1.65 (m, 2H), 1.46-1.25 (m, 4H), 0.94-0.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 136.7, 134.7, 131.4, 130.6, 130.0, 128.5, 127.5, 127.0, 126.4, 51.6, 35.0, 28.1, 22.5, 14.0; HRMS (ESI) calcd for $C_{20}H_{23}ONNa^+$ $(M+Na)^+$ 316.16719, found 316.16718. The ee was determined to be 90% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 20.9 min, t_R (major) = 17.3 min.



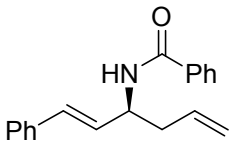
1Bz-d

Amide **1Bz-d**, prepared from chiral amine **1d** in 99% yield. White solid; m.p. 99.8-101.0 °C; $[\alpha]_D^{20}$ = -42.3 (*c* = 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.2 Hz, 2H), 7.52-7.41 (m, 3H), 7.38-7.20 (m, 5H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.23-6.13 (m, 2H), 4.88-4.78 (m, 1H), 1.78-1.67 (m, 2H), 1.49-1.25 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 136.7, 134.8, 131.4, 130.7, 129.9, 128.6, 128.5, 127.6, 126.9, 126.4, 51.5, 35.4, 31.8, 29.5 29.2, 26.0, 22.7, 14.1; HRMS (ESI) calcd for $C_{24}H_{31}ONNa^+$ $(M+Na)^+$ 372.22979, found 372.22974. The ee was determined to be 96% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 17.8 min, t_R (major) = 13.5 min.



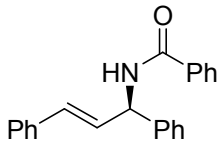
1Bz-e

Amide **1Bz-e**,[11] prepared from chiral amine **1e** in 99% yield. White solid; m.p. 163-164 °C; $[\alpha]_D^{20}$ = -15.6 (*c* = 1.01, $CHCl_3$); Lit.[11]: $[\alpha]_D^{20}$ = -8.4 (*c* = 1.0, $CHCl_3$, *S*-enantiomer, 52% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.73-7.69 (m, 2H), 7.53-7.48 (m, 1H), 7.46-7.40 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.17 (m, 8H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.4 Hz, 1H), 6.08 (d, *J* = 8.0 Hz, 1H), 4.98-4.87 (m, 1H), 2.82-2.77 (m, 2H), 2.14-2.08 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 141.5, 139.7, 136.6, 136.0, 134.5, 131.5, 131.2, 129.4, 128.6, 128.4, 127.7, 126.9, 126.5, 126.1, 51.4, 36.8, 32.3. The ee was determined to be 94% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 19.8 min, t_R (major) = 24.4 min.



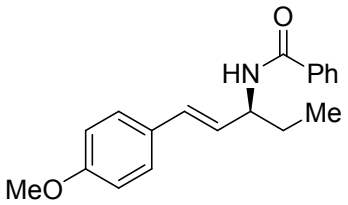
1Bz-f

Amide **1Bz-f**,[11] prepared from chiral amine **1f** in 99% yield. White solid; m.p. 99.0-100.1 °C; $[\alpha]_D^{20}$ = -20.2 (*c* = 1.05, $CHCl_3$); Lit.[11]: $[\alpha]_D^{20}$ = -23.6 (*c* = 1.0, $CHCl_3$, *S*-enantiomer, 76% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.2 Hz, 2H), 7.51-7.46 (m, 1H), 7.44-7.38 (m, 2H), 7.36-7.19 (m, 5H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.40 (d, *J* = 7.2 Hz, 1H), 6.22 (dd, *J* = 16.0, 6.0 Hz, 1H), 5.94-5.78 (m, 1H), 5.21-5.12 (m, 2H), 5.00-4.89 (m, 1H), 2.55-2.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 136.6, 134.6, 133.9, 131.5, 130.7, 129.1, 128.6, 128.5, 127.6, 126.9, 126.4, 118.6, 50.4, 39.5. The ee was determined to be 60% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 19.9 min, t_R (major) = 24.2 min.



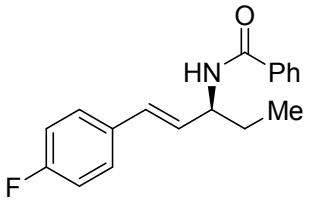
1Bz-g

Amide **1Bz-g**,[12] prepared from chiral amine **1g** in 99% yield. White solid; m.p. 163.1-164.2 °C; $[\alpha]_D^{20}$ = 12.4 (*c* = 1.05, $CHCl_3$); Lit.[12]: $[\alpha]_D^{23}$ = 20.4 (*c* = 1.0, $CHCl_3$, *R*-enantiomer, 95% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 7.53-7.47 (m, 1H), 7.46-7.35 (m, 8H), 7.34-7.26 (m, 3H), 7.25-7.20 (m, 1H), 6.66-6.61 (m, 2H), 6.43 (dd, *J* = 16.0, 6.0 Hz, 1H), 6.05-5.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5 140.8, 136.4, 134.3, 131.7, 128.9, 128.7, 128.6, 127.8, 127.2, 127.0, 126.6, 55.2. The ee was determined to be 70% by HPLC analysis (Chiralpak AS, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 23.9 min, t_R (major) = 10.3 min.



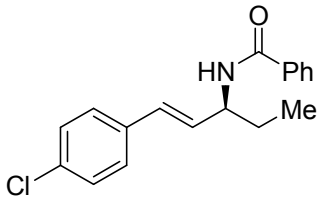
1Bz-h

Amide **1Bz-h**, prepared from chiral amine **1h** in 99% yield. White solid; m.p. 131.2-132.1 °C; $[\alpha]_D^{20}$ = -33.2 (*c* = 1.08, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.52-7.46 (m, 1H), 7.45-7.39 (m, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.10-6.02 (m, 2H), 4.78-4.69 (m, 1H), 3.80 (s, 3H), 1.80-1.70 (m, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.8, 159.2, 134.8, 131.4, 130.4, 129.4, 128.5, 127.5, 127.3, 126.9, 113.9, 55.3, 52.9, 28.3, 10.4; HRMS (ESI) calcd for $C_{19}H_{21}O_2NNa^+$ $(M+Na)^+$ 318.14645, found 318.14645. The ee was determined to be 85% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 13.2 min, t_R (major) = 9.0 min.



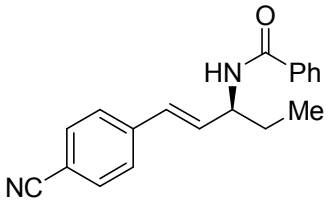
1Bz-i

Amide **1Bz-i**, prepared from chiral amine **1i** in 99% yield. Colorless oil; $[\alpha]_D^{20}$ = -45.1 (*c* = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.54-7.42 (m, 3H), 7.35-7.30 (m, 2H), 7.01-6.96 (m, 2H), 6.56(d, *J* = 16.0 Hz, 1H), 6.17-6.07 (m, 2H), 4.80-4.71 (m, 1H), 1.81-1.72 (m, 2H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 162.3 (d, $^1J_{C\text{-}F}$ = = 245.4 Hz), 134.7, 133.5, 132.9 (d, $^4J_{C\text{-}F}$ = 3.1 Hz), 131.6, 129.8, 128.6, 127.9 (d, $^3J_{C\text{-}F}$ = 7.8 Hz), 126.9, 115.5 ($^2J_{C\text{-}F}$, *J* = 21.6 Hz), 52.9, 28.3, 10.4; HRMS (ESI) calcd for $C_{18}H_{18}ONFNa^+$ $(M+Na)^+$ 306.12646, found 306.12646. The ee was determined to be 93% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 7.9 min, t_R (major) = 6.4 min.



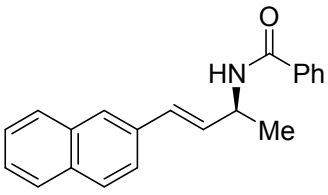
1Bz-j

Amide **1Bz-j**, prepared from chiral amine **1j** in 99% yield. White solid; m.p. 129.6-130.1 °C; $[\alpha]_D^{20}$ = -12.8 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.50-7.45 (m, 1H), 7.42-7.36 (m, 2H), 7.24-7.20 (m, 4H), 6.54 (s, br, 1H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.13 (dd, *J* = 16.0, 6.4 Hz, 1H), 4.78-4.66 (m, 1H), 1.80-1.68 (m, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 135.2, 134.6, 133.1, 131.4, 130.4, 129.5, 128.6, 128.5, 127.5 126.9., 52.9, 28.1, 10.4; HRMS (ESI) calcd for $C_{18}H_{18}ONClNa^+$ $(M+Na)^+$ 322.09691, found 322.09692. The ee was determined to be 94% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 9.3 min, t_R (major) = 6.7 min.



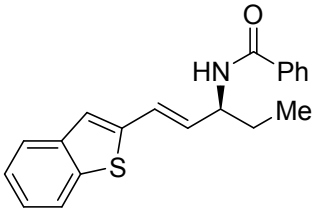
1Bz-k

Amide **1Bz-k**, prepared from chiral amine **1k** in 99% yield. White solid; m.p. 86.1-87.3 °C; $[\alpha]_D^{20}$ = -41.6 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.80 (m, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.54-7.49 (m, 1H), 7.47-7.40 (m, 4H), 6.59 (d, *J* = 16.0 Hz, 1H), 6.32 (dd, *J* = 16.0, 6.4 Hz, 1H), 6.27 (s, br, 1H), 4.82-4.74 (m, 1H), 1.84-1.73 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 141.3, 134.4, 133.9, 132.4, 131.7, 129.2, 128.7, 127.0, 126.9, 118.9, 110.7, 52.9, 28.1, 10.5; HRMS (ESI) calcd for $C_{19}H_{18}ON_2Na^+$ $(M+Na)^+$ 313.13113, found 313.13119. The ee was determined to be 91% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 24.9 min, t_R (major) = 12.0 min.



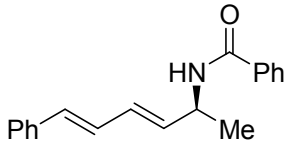
1Bz-l

Amide **1Bz-l**,[6] prepared from chiral amine **1l** in 98% yield. White solid; m.p. 126.0-127.3 °C; $[\alpha]_D^{20}$ = -21.5 (*c* = 1.03, $CHCl_3$); Lit.[6]: $[\alpha]_D^{20}$ = 12.7 (*c* = 1.0, $CHCl_3$, *R*-enantiomer, 62.4% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.74 (m, 5H), 7.72-7.70 (m, 1H), 7.58-7.55 (m, 1H), 7.52-7.40 (m, 5H), 6.73 (d, *J* = 16.0 Hz, 1H), 6.39 (dd, *J* = 16.0, 5.6 Hz, 1H), 6.28 (d, *J* = 8.0 Hz, 1H), 5.08-4.97 (m, 1H), 1.48 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 134.6, 134.1, 133.5, 133.0, 131.5, 131.2, 130.1, 128.6, 128.2, 128.0, 127.6, 127.0, 126.4, 126.3, 125.9, 123.5, 47.0, 20.7. The ee was determined to be 99% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 19.0 min, t_R (major) = 16.9 min.



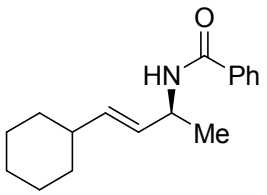
1Bz-m

Amide **1Bz-m**, prepared from chiral amine **1m** in 99% yield. White solid; m.p. 116.0-117.0 °C; $[\alpha]_D^{20}$ = -21.6 (*c* = 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.2 Hz, 2H), 7.75-7.72 (m, 1H), 7.68-7.64 (m, 1H), 7.54-7.49 (m, 1H), 7.48-7.42 (m, 2H), 7.33-7.26 (m, 2H), 7.12 (s, 1H), 6.82 (d, *J* = 15.6 Hz, 1H), 6.16 (d, *J* = 8.0 Hz, 1H), 6.10 (dd, *J* = 15.6, 6.4 Hz, 1H), 4.84-4.75 (m, 1H), 1.84-1.73 (m, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 141.8, 140.0, 138.8, 134.6, 131.9, 131.6, 128.6, 126.9, 124.9, 124.7, 124.4, 123.5, 123.1, 122.2, 52.6, 28.2, 10.4; HRMS (ESI) calcd for $C_{20}H_{19}ONNaS^+$ $(M+Na)^+$ 344.10796, found 344.10797. The ee was determined to be 91% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 12.7 min, t_R (major) = 8.8 min.



1Bz-n

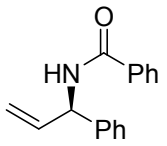
Amide **1Bz-n**,[6] prepared from chiral amine **1n** in 99% yield. White solid; m.p. 143.1-143.8.0 °C; $[\alpha]_D^{20}$ = -21.4 (*c* = 1.05, $CHCl_3$); Lit.[6]: $[\alpha]_D^{20}$ = 16.5 (*c* = 1.0, $CHCl_3$, *R*-enantiomer, 65.8% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.83-7.77 (m, 2H), 7.53-7.47 (m, 1H), 7.46-7.41 (m, 2H), 7.39-7.36 (m, 2H), 7.33-7.28 (m, 2H), 7.24-7.19 (m, 1H), 6.75 (dd, *J* = 15.6, 10.4 Hz, 1H), 6.54 (d, *J* = 15.6 Hz, 1H), 6.39 (dd, *J* = 15.2, 10.4 Hz, 1H), 6.17 (d, *J* = 8.0 Hz, 1H), 5.87 (dd, *J* = 15.2, 5.6 Hz, 1H), 4.95-4.85 (m, 1H), 1.40 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 137.1, 134.9, 134.6, 132.8, 131.5, 130.4, 128.6, 128.1, 127.6, 126.9, 126.4, 46.7, 20.6. The ee was determined to be 80% by HPLC analysis (Chiralpak OD, λ = 280 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 20.5 min, t_R (major) = 16.9 min.



1Bz-o

Amide **1Bz-o**,[5] prepared from chiral amine **1o** in 99% yield. White solid; m.p. 76.5-77.1 °C; $[\alpha]_D^{20}$ = -10.8 (*c* = 1.04, $CHCl_3$); Lit.[5]: $[\alpha]_D^{20}$ = -21.1 (*c* = 0.52, $CHCl_3$, *S*-enantiomer, 99% ee); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2H), 7.51-7.46 (m, 1H), 7.45-7.39 (m, 2H), 6.01 (d, *J* = 7.2 Hz, 1H), 5.61 (ddd, *J* = 15.6, 6.4, 1.2 Hz, 1H), 5.47 (ddd, *J* = 15.6, 6.4, 1.2 Hz, 1H), 4.79-4.67 (m, 1H), 1.98-1.90 (m, 1H), 1.76-1.60 (m, 4H), 1.31 (d, *J* = 8.4 Hz, 3H), 1.30-0.99 (m, 6H); ^{13}C NMR

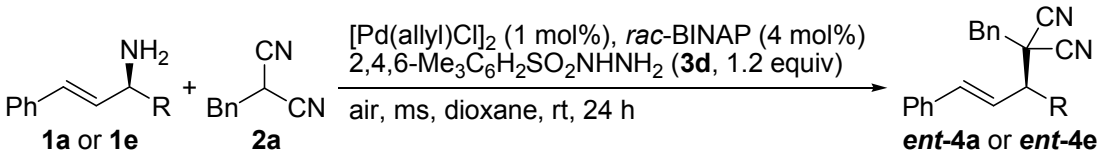
(100 MHz, $CDCl_3$) δ 166.5, 137.0, 134.9, 131.3, 128.5, 126.9, 46.7, 40.3, 32.9, 32.8, 26.1, 26.0, 20.9. The ee was determined to be 70% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 6.7 min, t_R (major) = 8.3 min.



1Bz-p

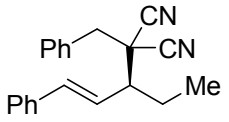
Amide **1Bz-p**,[13] prepared from chiral amine **1p** in 99% yield. White solid; m.p. 97.0-98.1 °C; $[\alpha]_D^{20}$ = 25.4 (*c* = 1.08, $CHCl_3$); Lit.[13]: $[\alpha]_D^{22}$ = -52.4 (*c* = 1, $CHCl_3$, *S*-enantiomer, 90% ee); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.77 (m, 2H), 7.53-7.47 (m, 1H), 7.45-7.27 (m, 7H), 6.43 (d, *J* = 7.2 Hz, 1H), 6.11 (ddd, *J* = 17.2, 10.0, 5.2 Hz, 1H), 5.88-5.83 (m, 1H), 5.33-5.27 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 140.5, 137.1, 134.3, 131.6, 128.8, 128.6, 127.8, 127.3, 127.0, 116.2, 55.5. The ee was determined to be 89% by HPLC analysis (Chiralpak AD, λ = 220 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 22.1 min, t_R (major) = 13.5 min.

Enantiospecific allylic alkylation (Scheme 4)



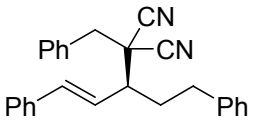
1a or **1e** **2a** ***ent*-4a** or ***ent*-4e**

The reaction was performed following the general procedure shown above but using racemic BINAP instead of (*S*)-BINAP.



***ent*-4a**

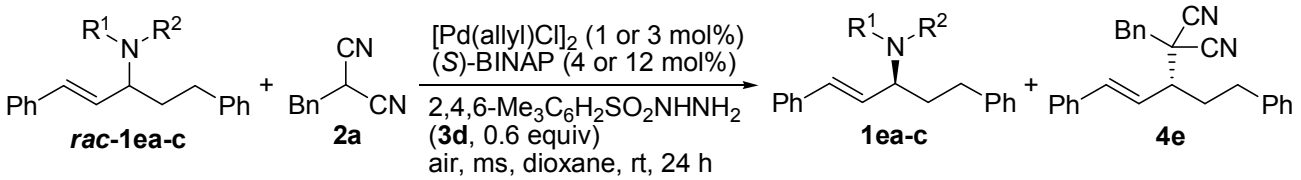
Malononitrile ***ent*-4a**, light yellow oil; 95% ee as determined by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 99:1, flow rate = 1.0 mL/min): t_R (minor) = 11.1 min, t_R (major) = 12.6 min; $[\alpha]_D^{20}$ = -41.2 (*c* = 1.00, $CHCl_3$).



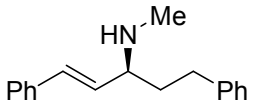
***ent*-4e**

Malononitrile ***ent*-4e**, light yellow oil; 94% ee as determined by HPLC analysis Chiralpak OD, λ = 254 nm, hexane/isopropanol = 80:20, flow rate = 1.0 mL/min): t_R (minor) = 12.7 min, t_R (major) = 10.0 min; $[\alpha]_D^{20}$ = -36.4 (*c* = 1.04, $CHCl_3$).

Kinetic resolution of secondary and tertiary allylic amines (Scheme 5)

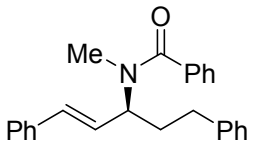


The reaction was performed following the general procedure shown above. Analytical data for the products are shown below.



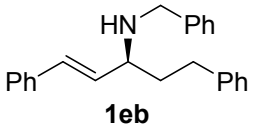
1ea

Amine **1ea**, light yellow oil; $[\alpha]_D^{20}$ = -42.8 (*c* = 1.04, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.35-7.25 (m, 5H), 7.20-7.16 (m, 3H), 6.50 (d, *J* = 16.0 Hz, 1H), 6.03 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.16-3.08 (m, 1H), 2.75-2.62 (m, 2H), 2.41 (s, 3H), 2.01-1.93 (m, 1H), 1.90-1.82 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.9, 136.8, 132.6, 131.3, 128.6, 128.4, 127.6, 126.4, 125.9, 62.7, 37.0, 33.7, 32.2; HRMS (ESI) calcd for $C_{18}H_{22}N^+$ $(M+H)^+$ 252.17468, found 252.17435. The ee was determined to be 91% by converting it to compound **1Bz-ea** (see below).



1Bz-ea

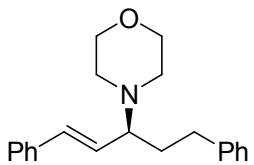
Amide **1Bz-ea** was prepared from chiral amine **1ea** in 99% yield according to the above procedure (Benzoylation of chiral amines for ee determination). Yellowish oil; $[\alpha]_D^{20}$ = -24.5 (*c* = 1.02, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$, mixture of rotamers) δ 7.48-7.09 (m, 15H), 6.65-6.40 (m 1H), 6.30-6.10 (m, 1H), 4.50-4.40 (m, 1H), 3.05 (s, 3H), 2.65-2.45 (m, 1H), 2.15-1.95 (m, 2H), 1.75-1.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, mixture of rotamers) δ 172.7, 171.8, 140.7, 136.6, 136.3, 132.6, 131.7, 129.5, 128.7, 128.5, 128.2, 128.0, 127.5, 126.9, 126.5, 126.4, 126.2, 100.0, 59.8, 54.4, 34.2, 32.9, 32.4, 27.7; HRMS (ESI) calcd for $C_{25}H_{26}NO^+$ $(M+H)^+$ 356.20089, found 356.20012. The ee was determined to be 91% by HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 12.1 min, t_R (major) = 15.4 min.



1eb

Amine **1eb**, light yellow oil; $[\alpha]_D^{20}$ = -28.6 (*c* = 1.03, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.39 (m, 2H), 7.36-7.29 (m, 6H), 7.27-7.23 (m, 4H), 7.19-7.14 (m, 3H), 6.49 (d, *J* = 16.0 Hz, 1H), 6.08 (dd, *J* = 16.0, 8.4 Hz, 1H), 3.86 (d, *J* = 13.2 Hz, 1H), 3.69 (d, *J* = 13.2 Hz, 1H), 3.29-3.22 (m, 1H), 2.75-2.61 (m, 2H), 1.99-1.83 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 140.2, 137.0, 132.4, 132.0, 128.6, 128.4, 128.3, 127.5, 127.0, 126.4, 125.8, 60.2, 51.3, 37.5, 32.3; HRMS (ESI) calcd for $C_{24}H_{26}N^+$ $(M+H)^+$ 328.20598, found 328.20548. The ee was determined to be 70% by

HPLC analysis (Chiralpak OD, λ = 254 nm, hexane/isopropanol = 90:10, flow rate = 1.0 mL/min): t_R (minor) = 23.9 min, t_R (major) = 10.3 min.



1ec

Amine **1ec**, light yellow oil; $[\alpha]_D^{20}$ = -18.5 (*c* = 1.05, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.14 (m, 10H), 6.46 (d, *J* = 16.0 Hz, 1H), 6.15 (dd, *J* = 16.0, 8.8 Hz, 1H), 3.76-3.64 (m, 4H), 2.95-2.88 (m, 1H), 2.76-2.68 (m, 1H), 2.66-2.58 (m, 3H), 2.54-2.47 (m, 2H), 2.12-2.02 (m, 1H), 1.87-1.77 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.1, 136.7, 133.3, 129.0, 128.6, 128.4, 128.3, 127.5, 126.3, 125.7, 67.4, 67.2, 50.3, 33.5, 32.4; HRMS (ESI) calcd for $C_{21}H_{26}ON^+$ $(M+H)^+$ 308.20089, found 308.20041. The ee was determined to be 43% by HPLC analysis (Chiralpak AD, λ = 254 nm, hexane/isopropanol = 95:5, flow rate = 1.0 mL/min): t_R (minor) = 11.1 min, t_R (major) = 8.3 min.

References

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(2) (*a*) A. G. Myers, B. Zheng and M. Movassaghi, *J. Org. Chem.*, 1997, **62**, 7507; (*b*) F.-L. Yang, X.-T. Ma and S.-K. Tian, *Chem.-Eur. J.*, 2012, **18**, 1582.
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(4) M. Pallavicini, E. Valoti, L. Villa and O. Piccolo, *Tetrahedron: Asymmetry*, 2000, **11**, 4017.
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(8) A. R. Katritzky, D. Cheng and J. Li, *J. Org. Chem*., 1998, **63**, 3438.
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(10) K.-G. Shim, J. C. Park, C. S. Cho, S. C. Shim and Y. Yamamoto, *Chem. Commun.*, 2002, 852.
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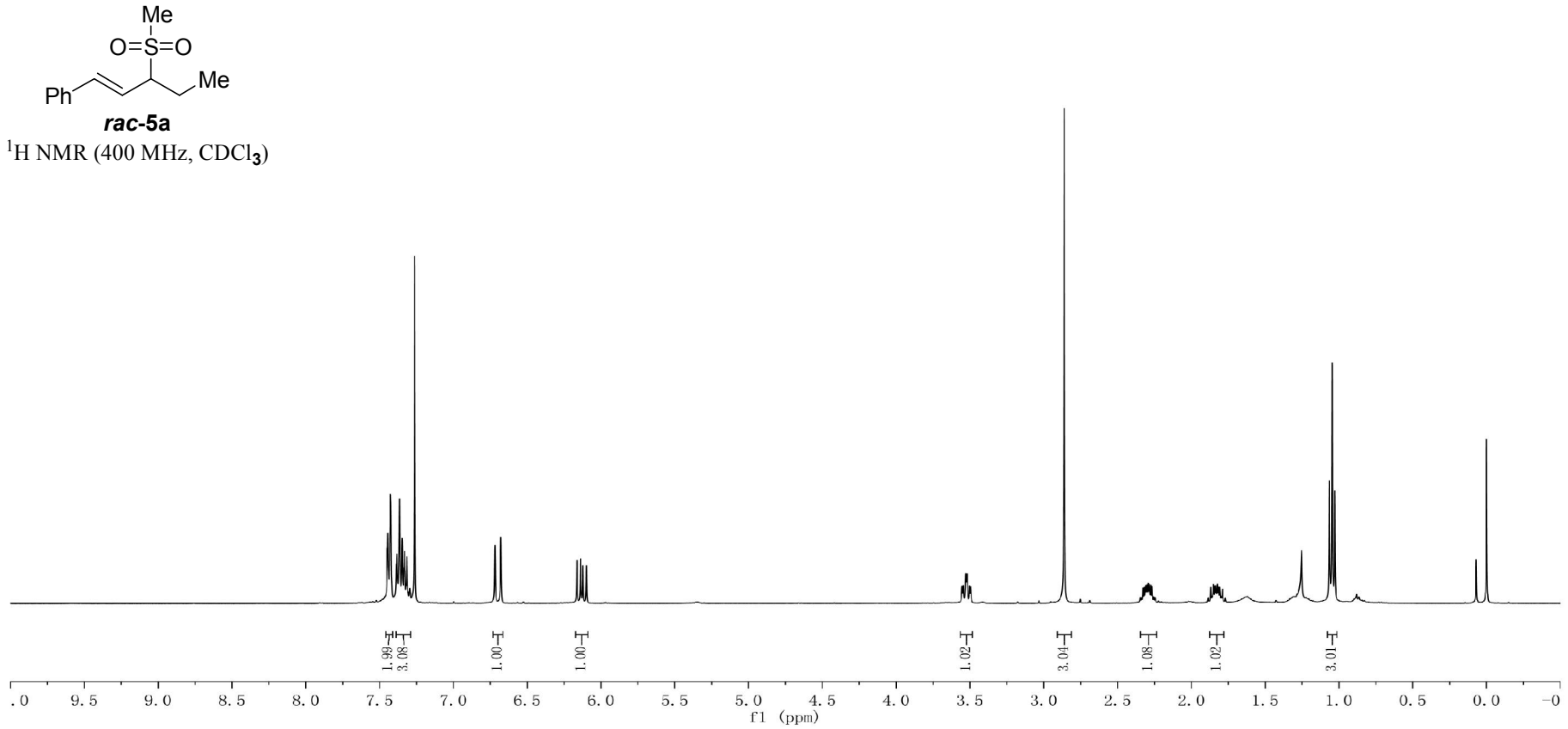
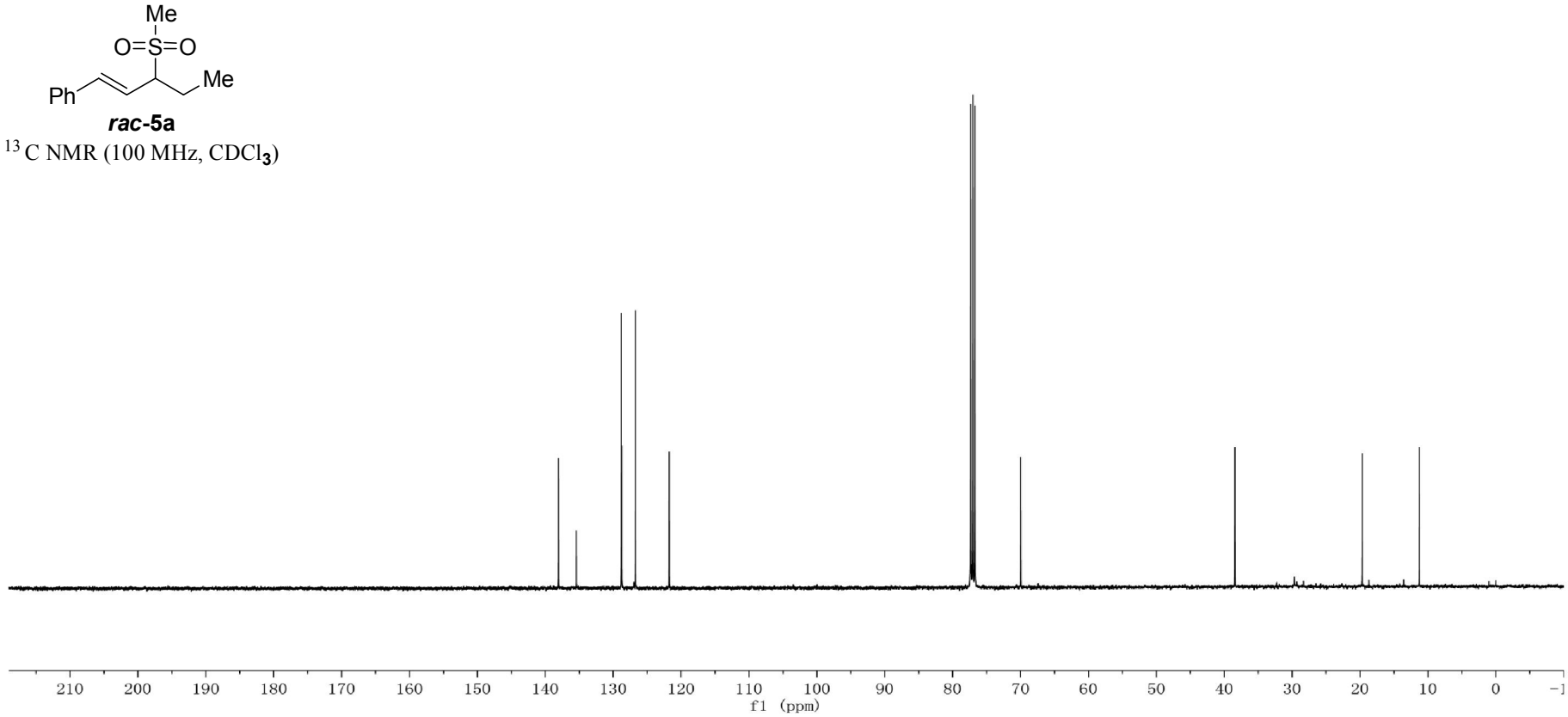
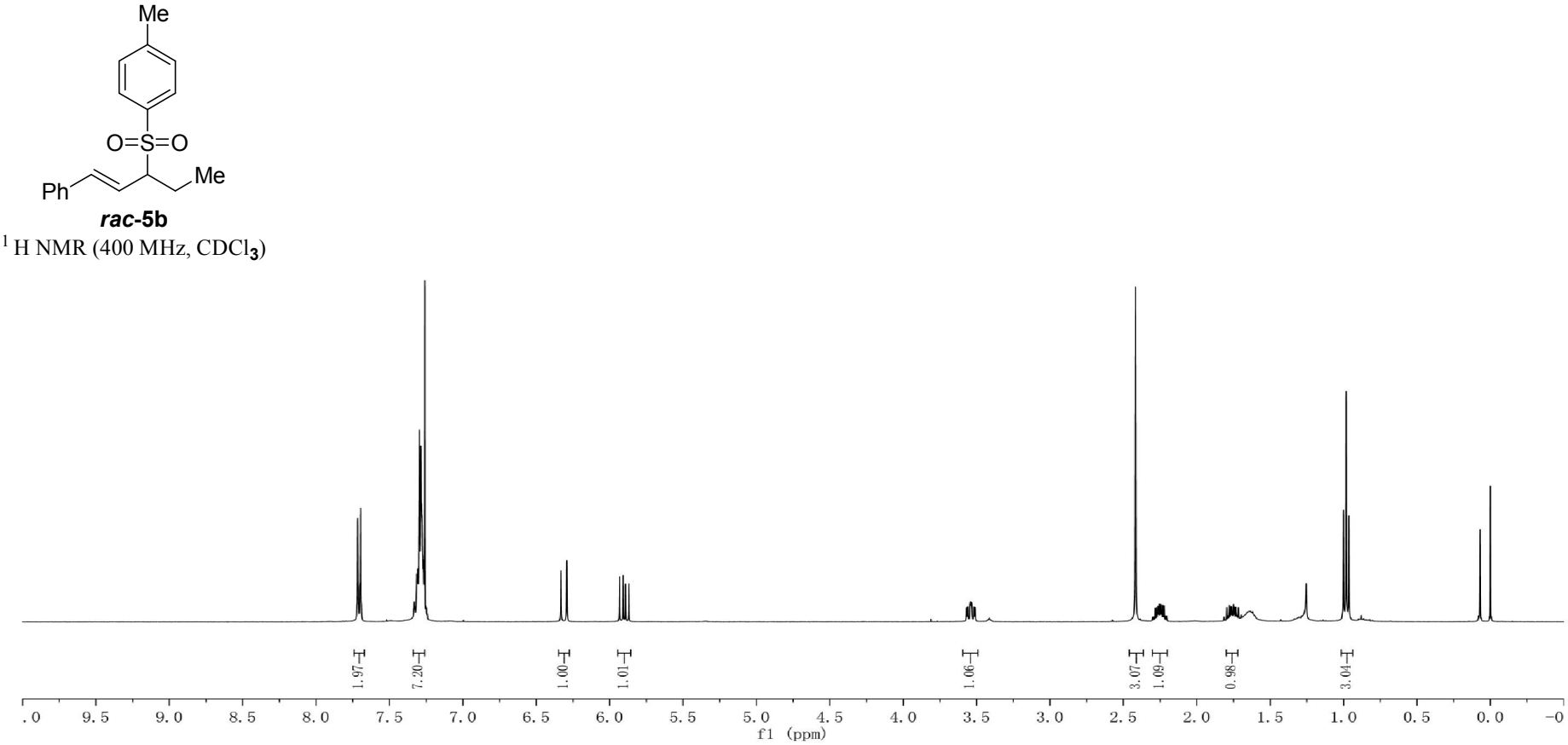

Me
O=S=O
Me
Ph
rac-5a
1H NMR (400 MHz, CDCl3)
7.447
7.444
7.427
7.386
7.383
7.366
7.347
7.335
7.331
7.321
7.314
7.262
6.718
6.679
6.163
6.138
6.123
6.099
3.554
3.545
3.528
3.520
3.503
3.494
2.862
2.319
2.308
2.300
2.293
2.284
2.271
2.266
1.868
1.850
1.841
1.834
1.823
1.816
1.807
1.789
1.065
1.046
1.028
0.000
1.99
3.08
1.00
1.00
1.02
3.04
1.08
1.02
3.01
f1 (ppm)



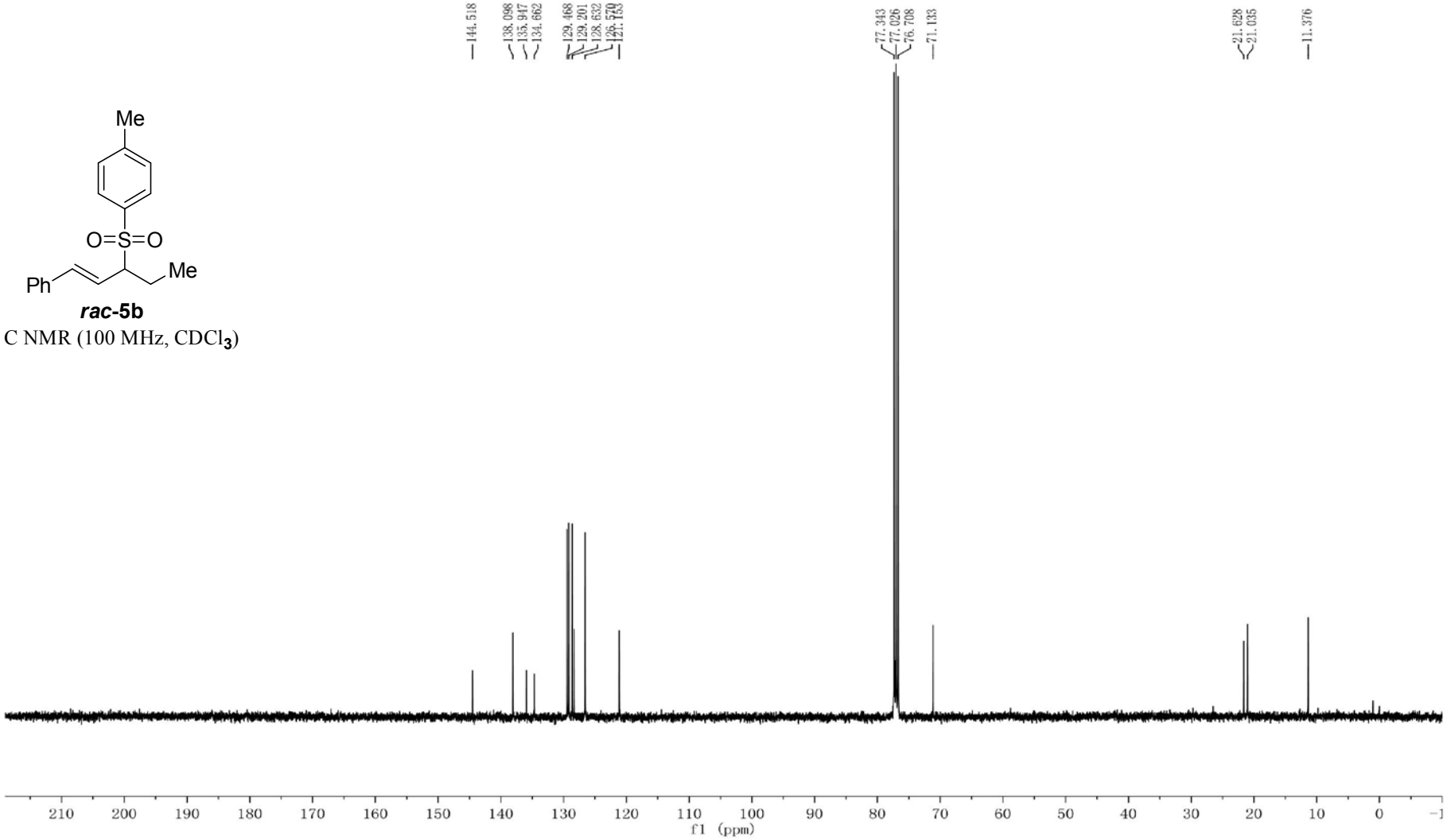
***rac*-5a**

^{13}C NMR (100 MHz, $CDCl_3$)



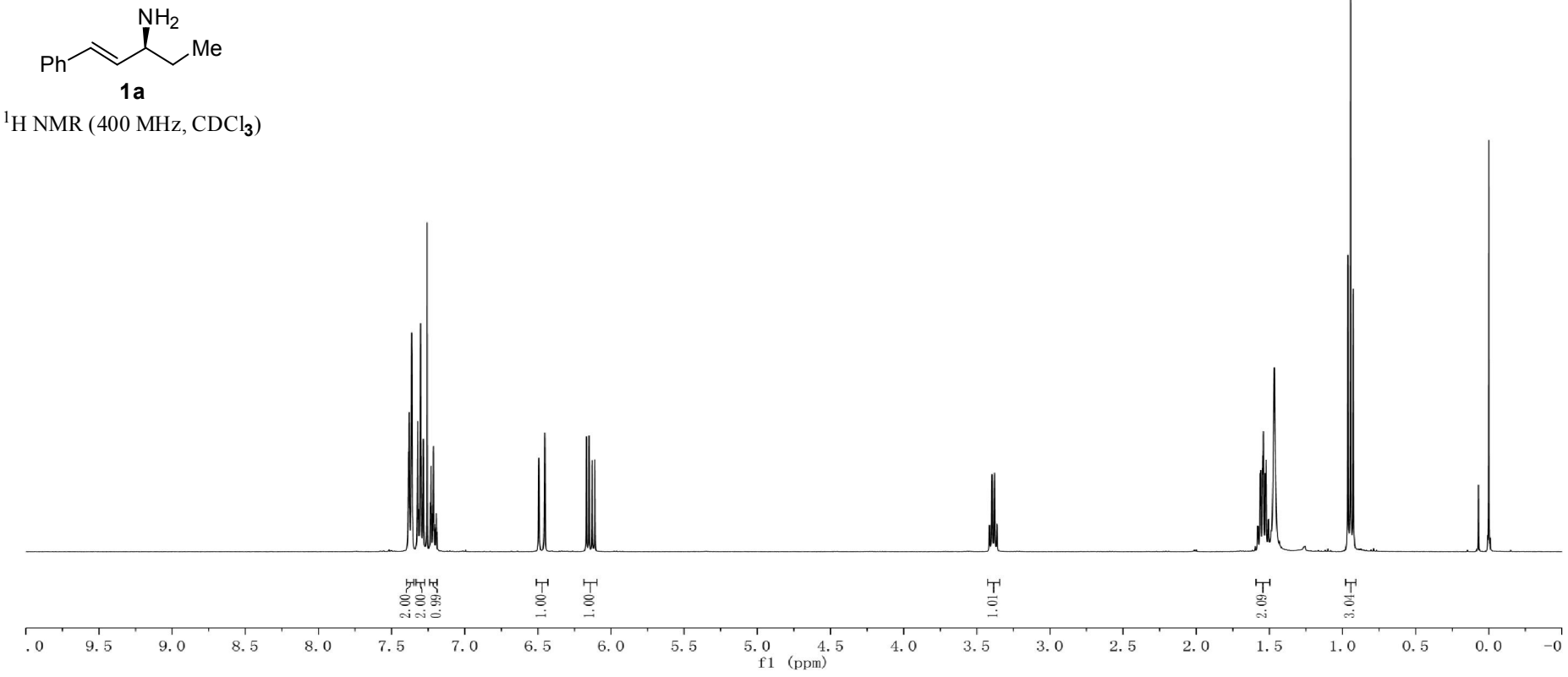
***rac*-5b**

^{1}H NMR (400 MHz, $CDCl_3$)

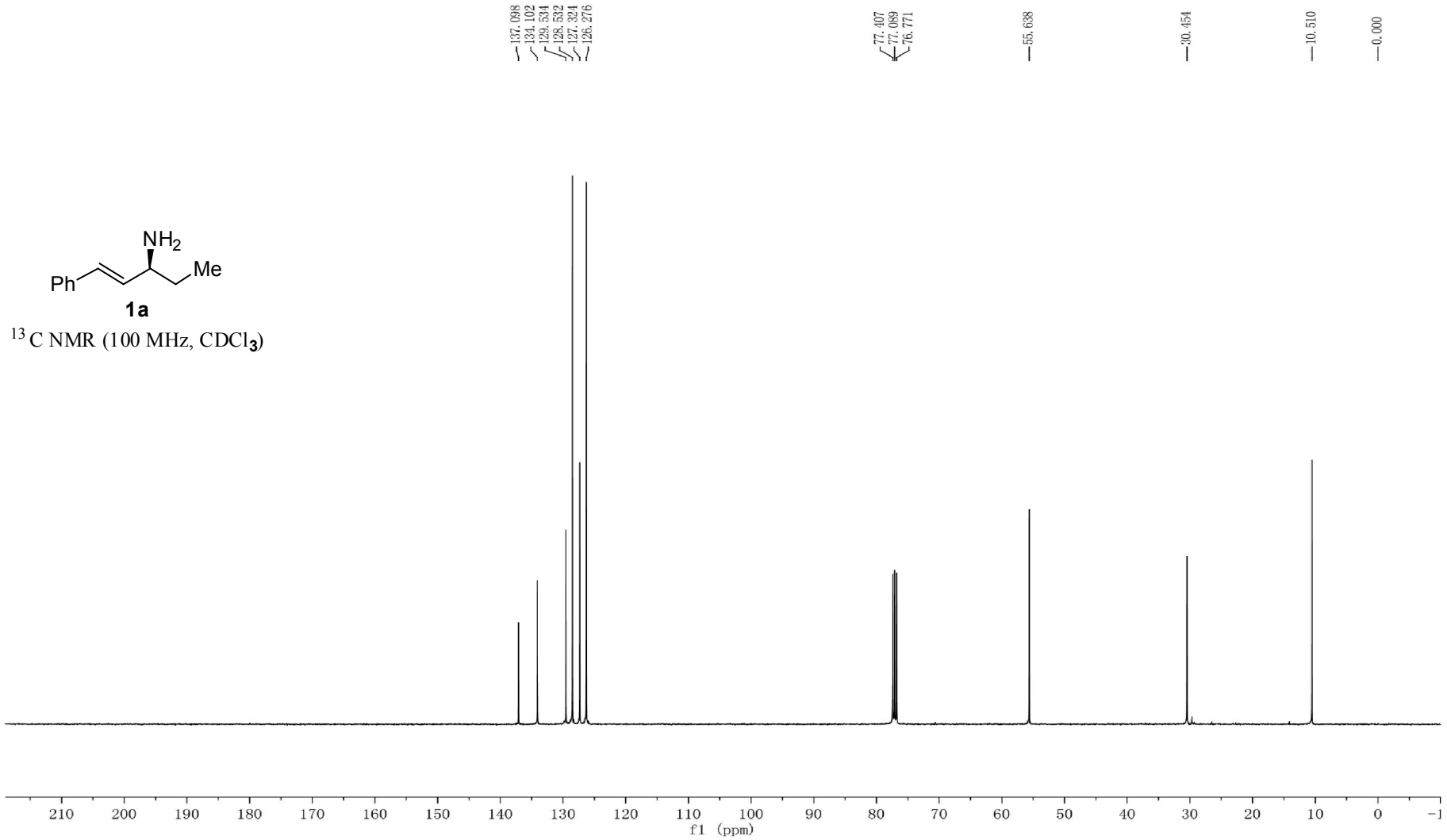


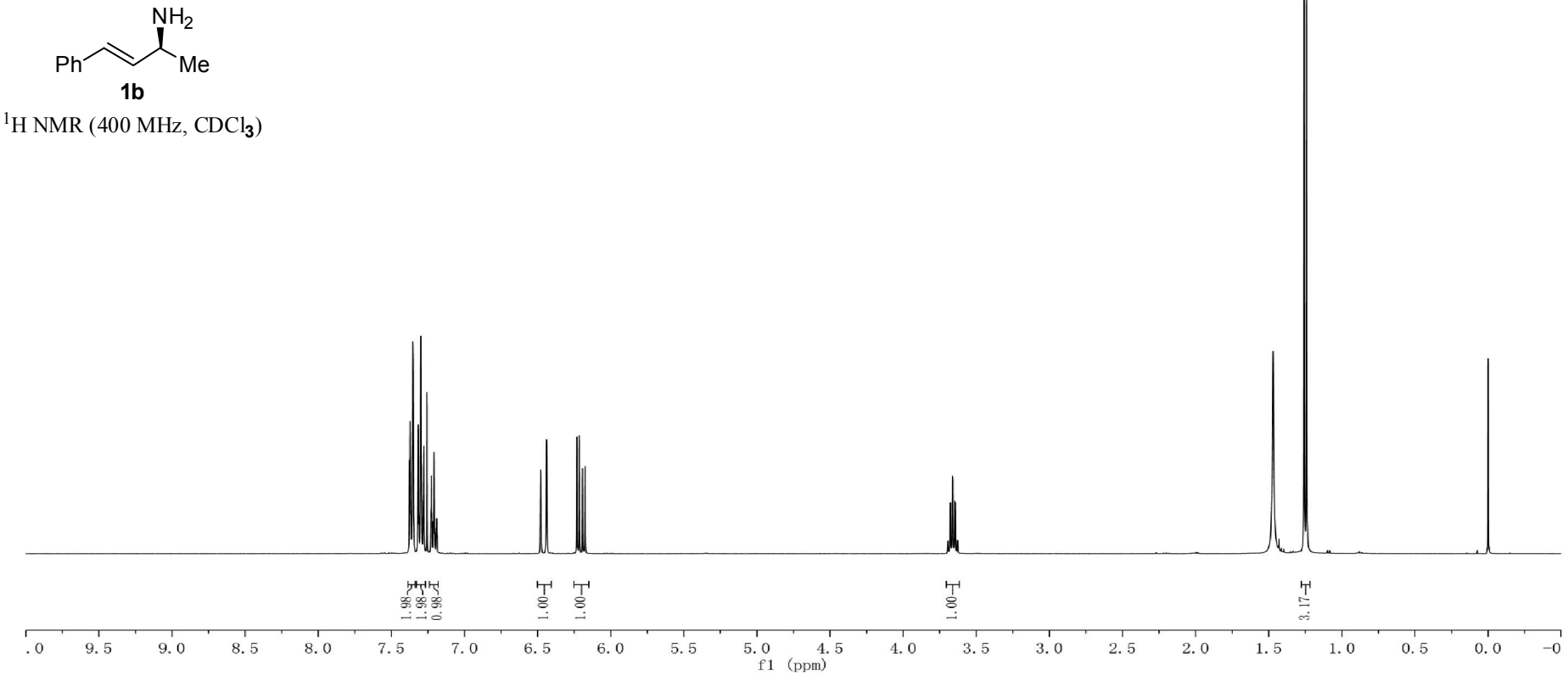
***rac*-5b**

^{13}C NMR (100 MHz, $CDCl_3$)

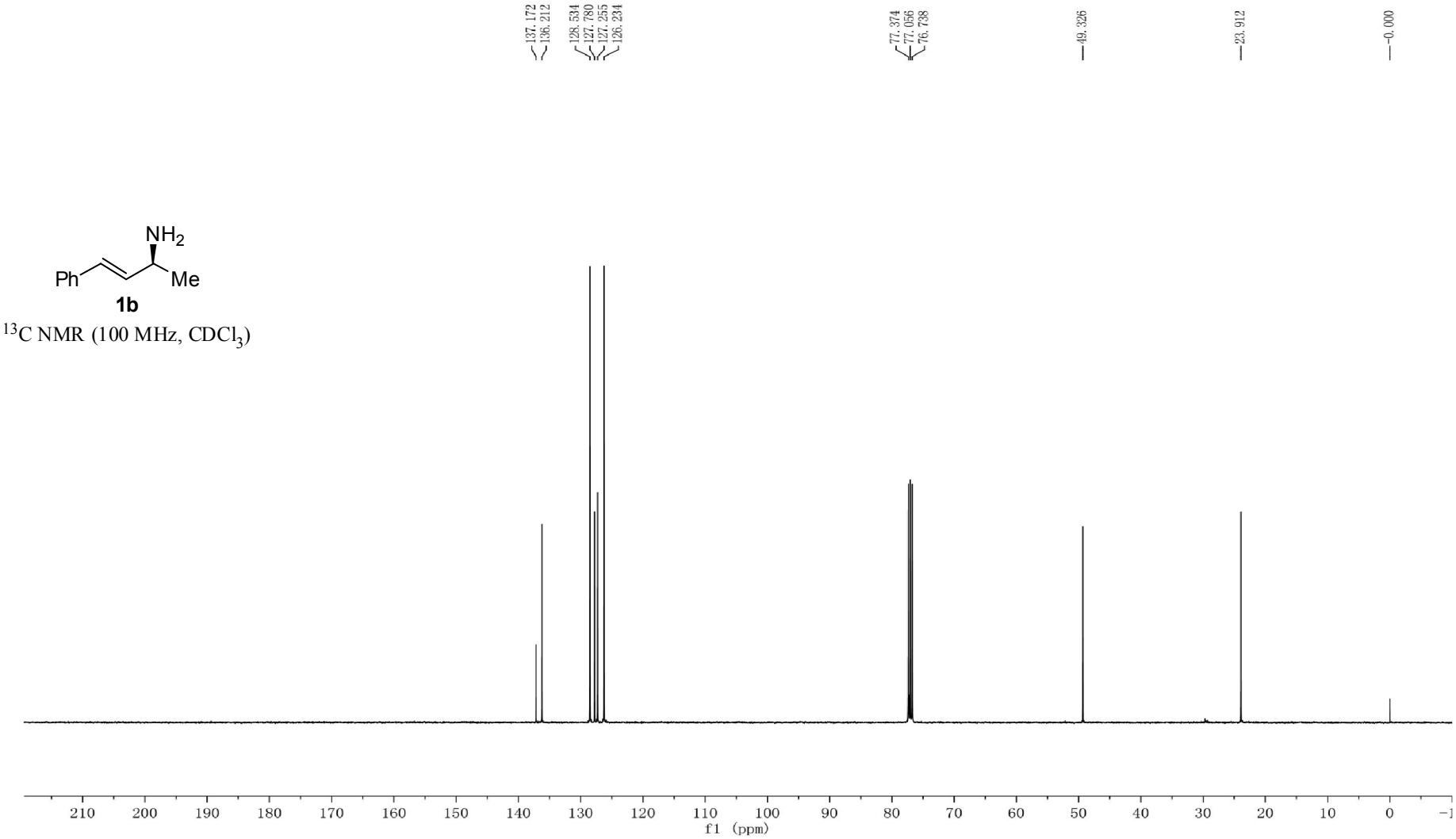


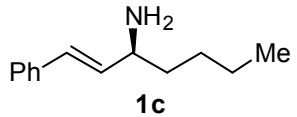
^{1}H NMR (400 MHz, $CDCl_3$)


137.098
134.102
129.534
128.532
127.324
126.276
77.407
77.089
76.771
55.638
30.454
10.510
0.000
NH2
Ph
Me
1a
13 C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



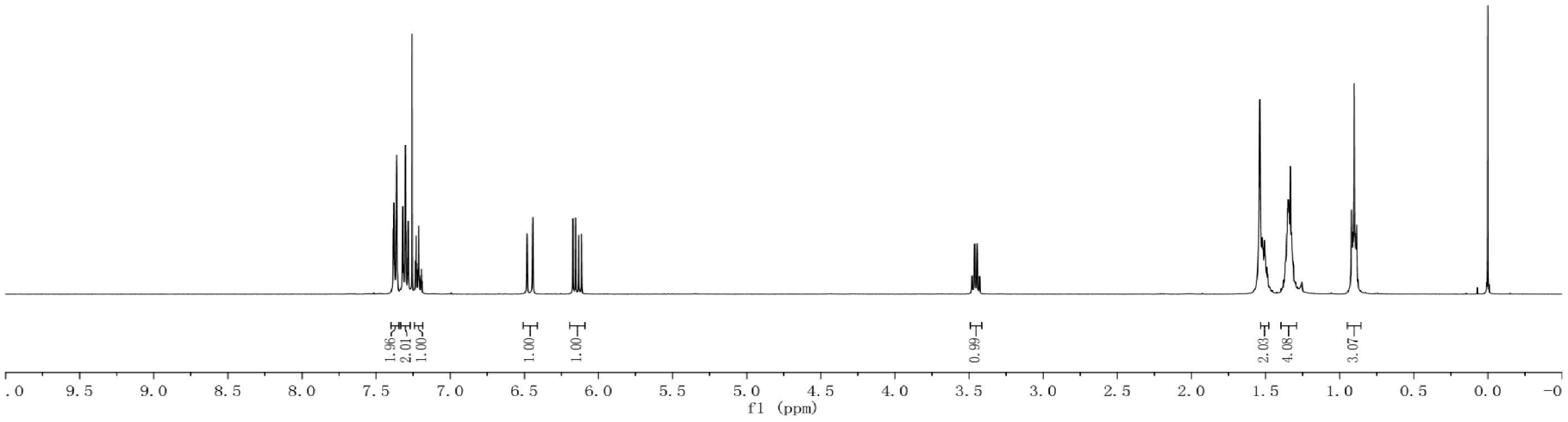
^{1}H NMR (400 MHz, $CDCl_3$)

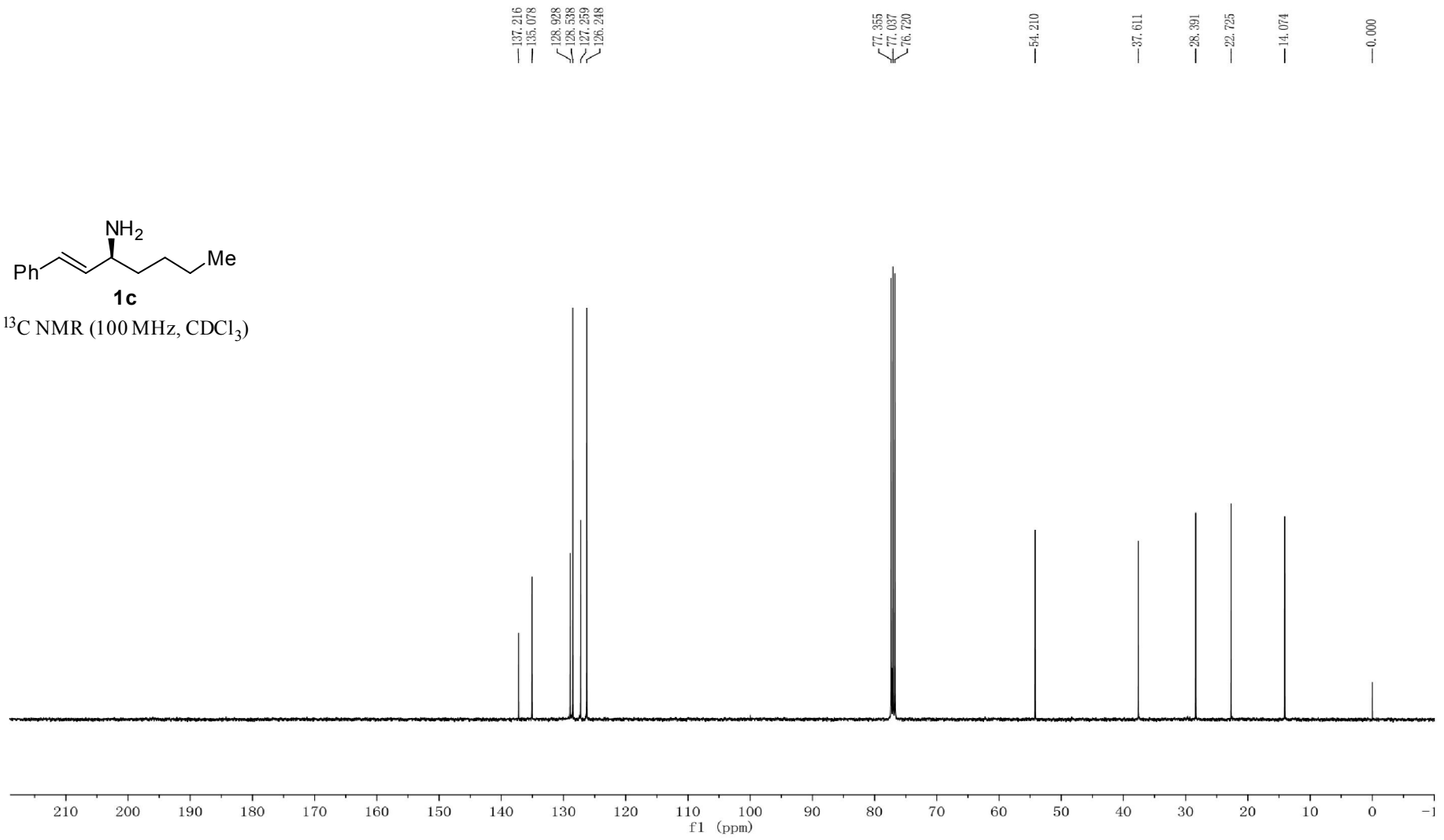

137.172
136.212
128.534
127.780
127.255
126.234
77.374
77.056
76.738
49.326
23.912
0.000
NH2
Ph
Me
1b
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

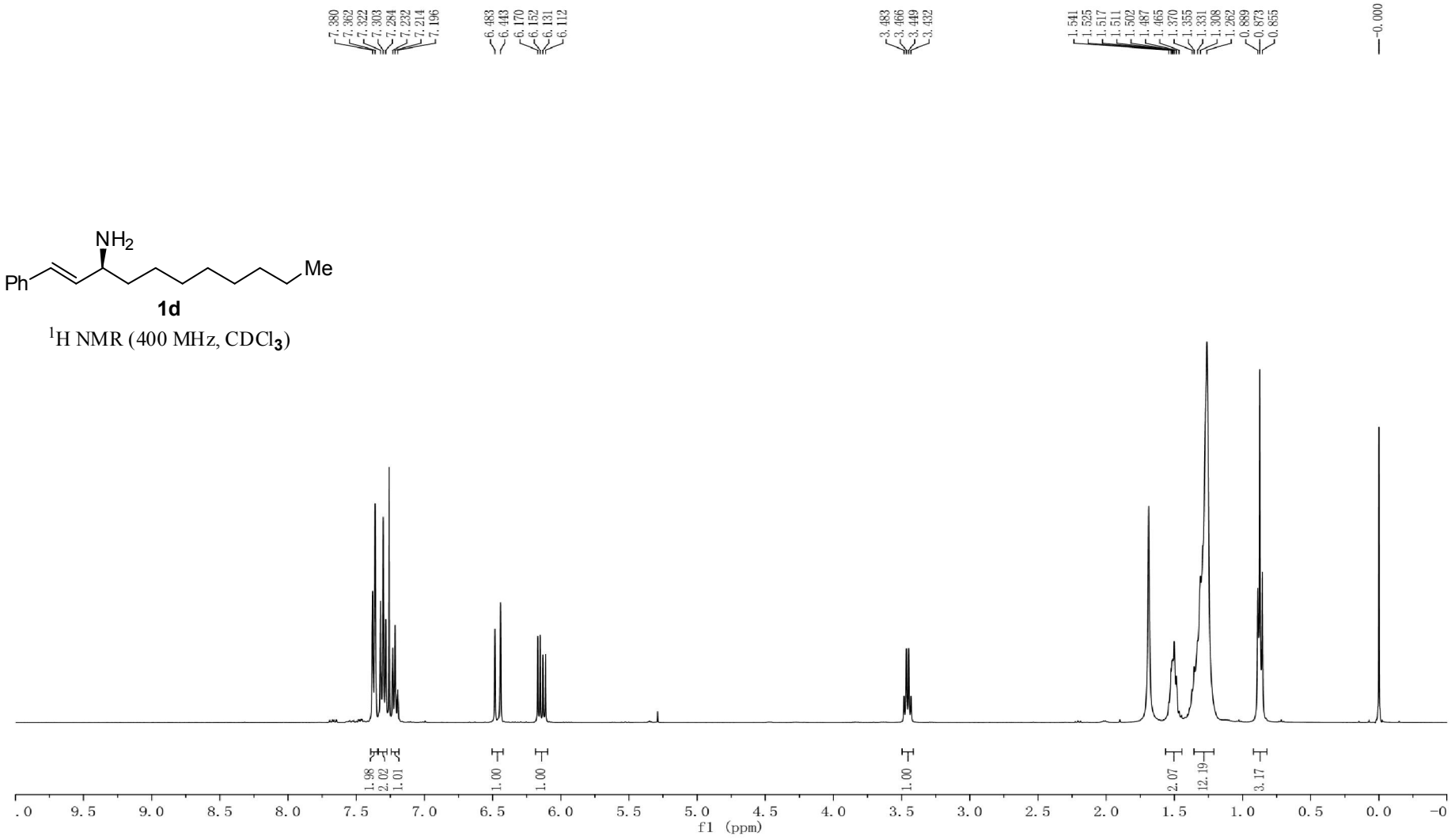


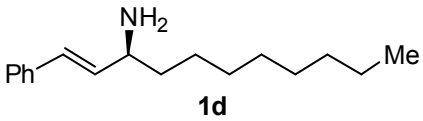
1c

^{1}H NMR (400 MHz, $CDCl_3$)



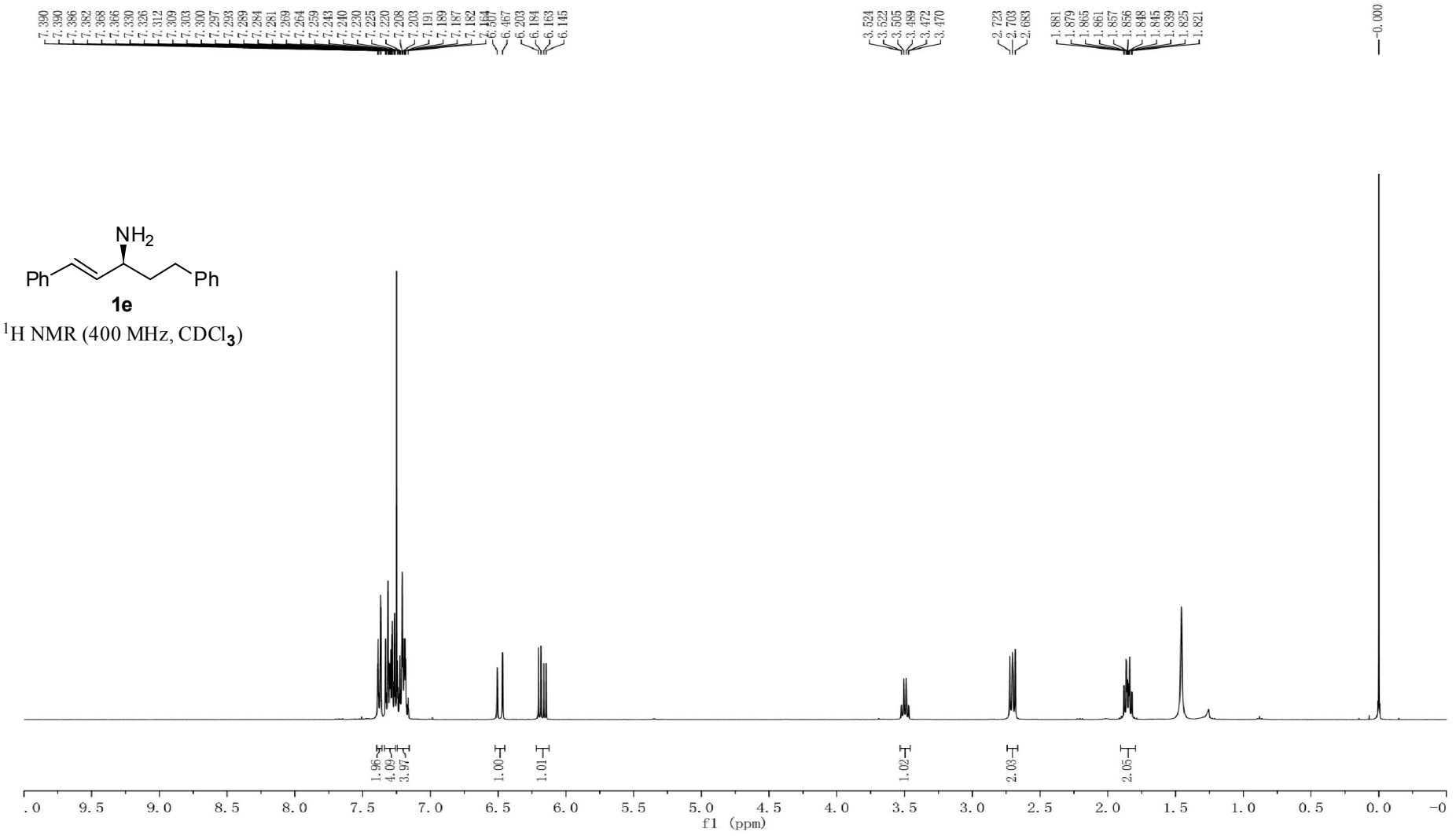

137.216
135.078
128.928
128.538
127.259
126.248
77.355
77.037
76.720
54.210
37.611
28.391
22.725
14.074
0.000
NH2
Ph
Me
1c
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

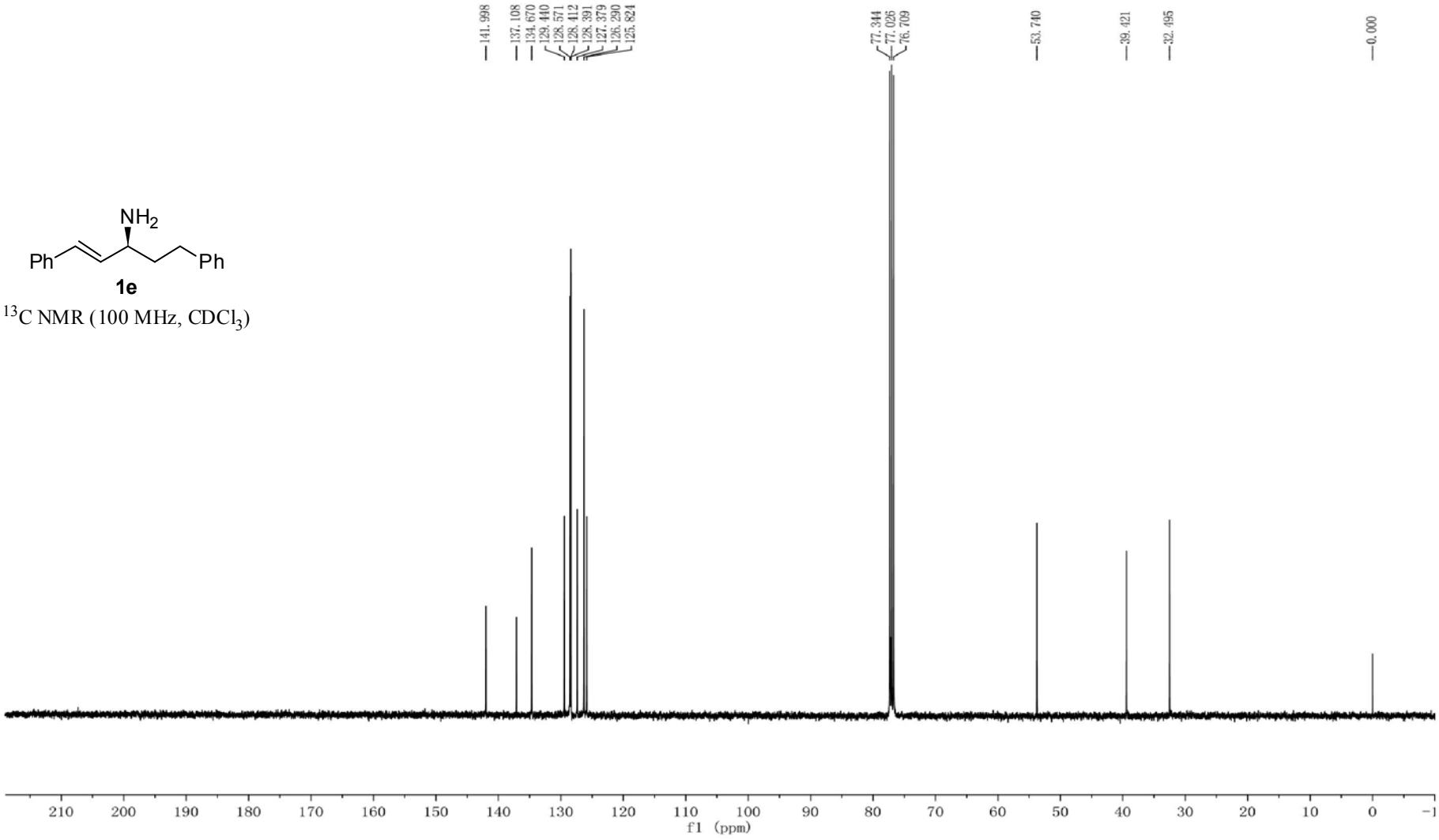

7.380
7.362
7.322
7.303
7.284
7.232
7.214
7.196
6.483
6.443
6.170
6.152
6.131
6.112
3.483
3.466
3.449
3.432
1.541
1.525
1.517
1.511
1.502
1.487
1.465
1.370
1.355
1.331
1.308
1.262
0.889
0.873
0.855
0.000
NH2
Ph
Me
1d
1H NMR (400 MHz, CDCl3)
1.98
2.02
1.01
1.00
1.00
1.00
2.07
12.19
3.17
f1 (ppm)



1d

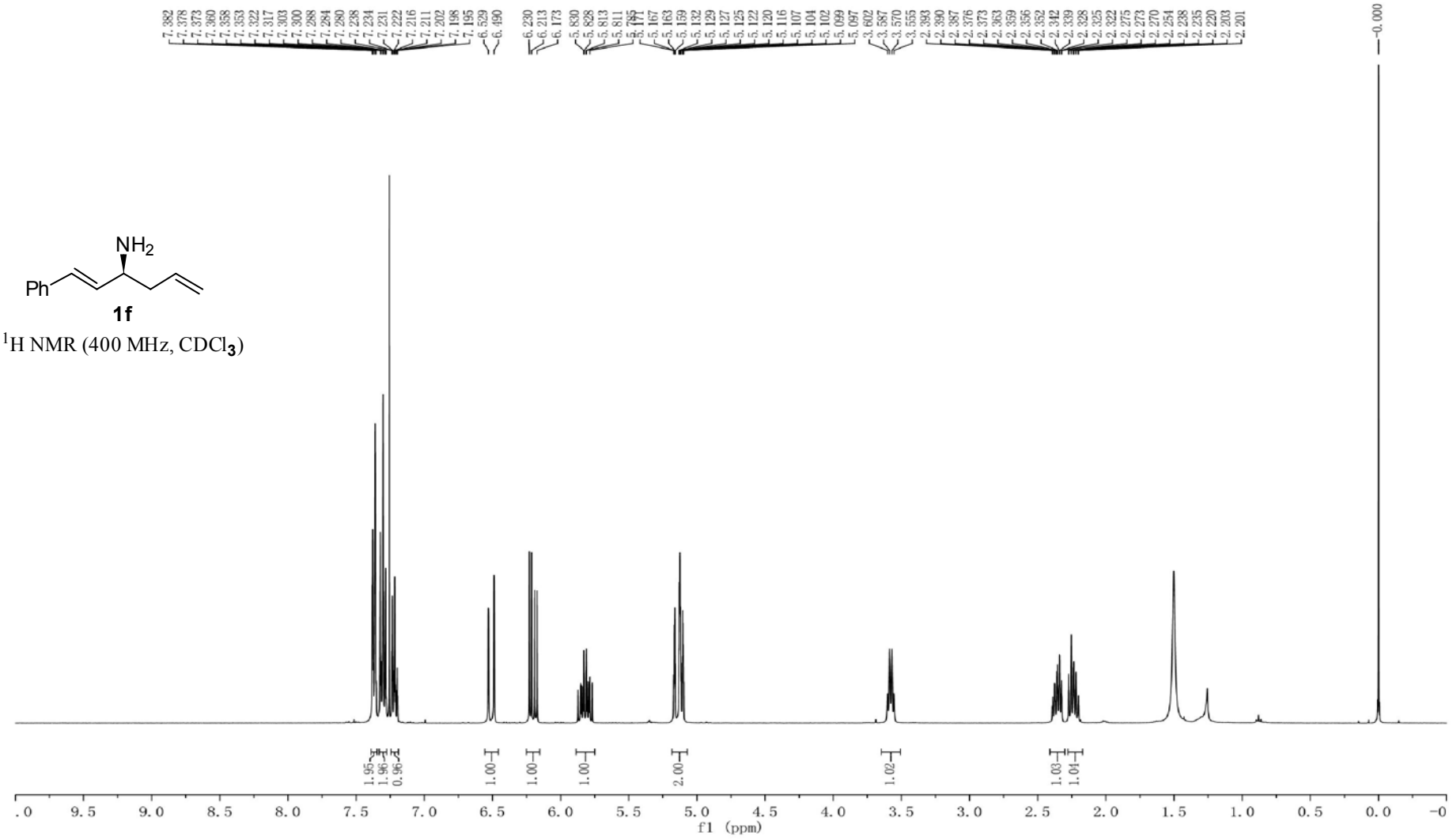
^{13}C NMR (100 MHz, $CDCl_3$)

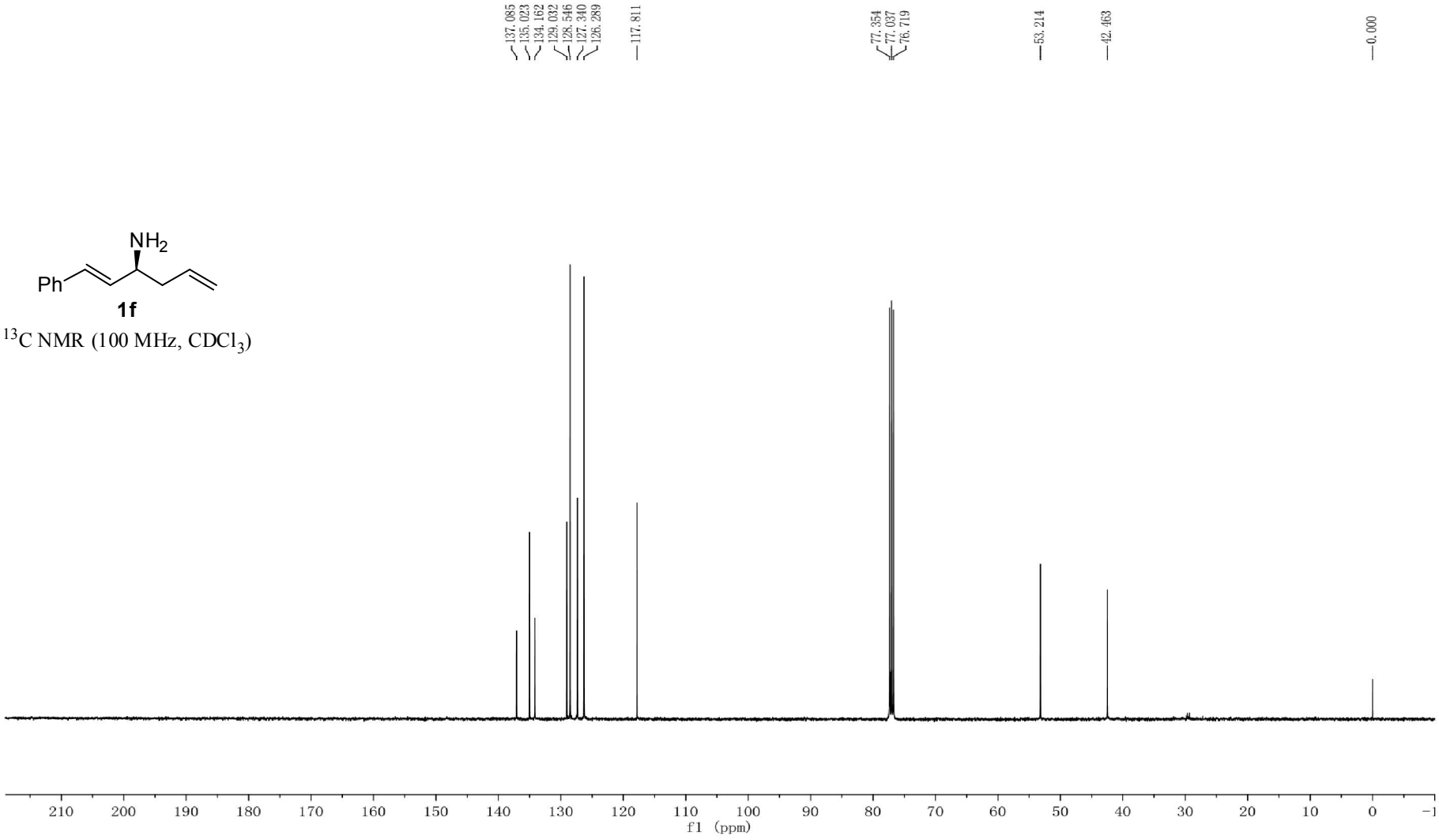

NH2
Ph
Ph
1e
1H NMR (400 MHz, CDCl3)
7.390
7.390
7.386
7.382
7.368
7.366
7.330
7.326
7.312
7.309
7.303
7.300
7.297
7.293
7.289
7.284
7.281
7.269
7.264
7.259
7.243
7.240
7.230
7.225
7.220
7.208
7.203
7.191
7.189
7.187
7.182
7.164
6.507
6.467
6.203
6.184
6.163
6.145
3.524
3.522
3.505
3.489
3.472
3.470
2.723
2.703
2.683
1.881
1.879
1.865
1.861
1.857
1.856
1.848
1.845
1.839
1.825
1.821
0.000
1.96
4.09
3.97
1.00
1.01
1.02
2.03
2.05
f1 (ppm)

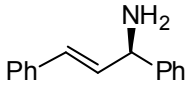


1e

^{13}C NMR (100 MHz, $CDCl_3$)

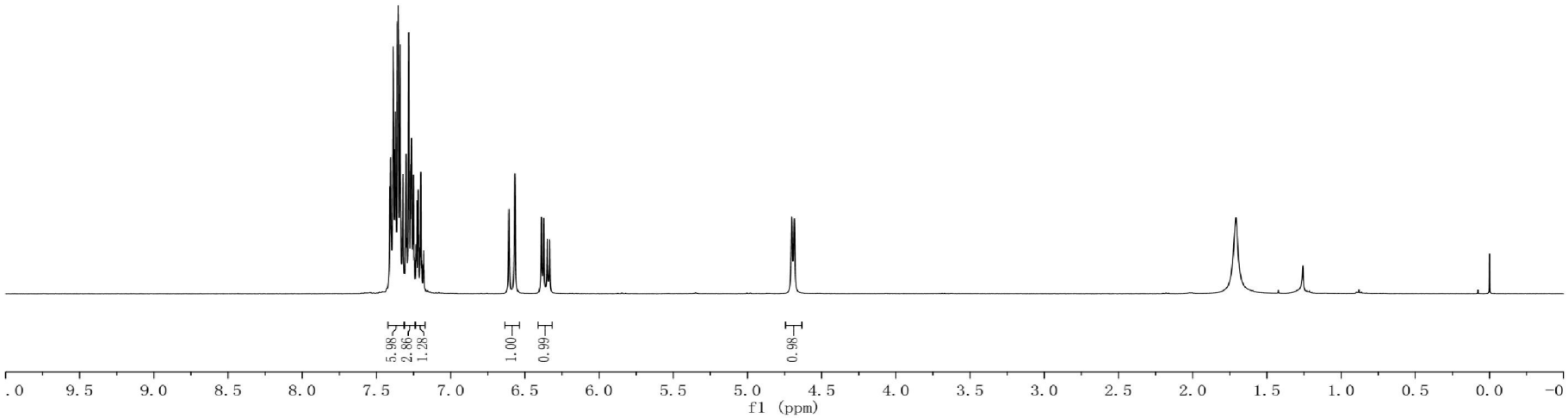

NH2
Ph
1f
1H NMR (400 MHz, CDCl3)
f1 (ppm)

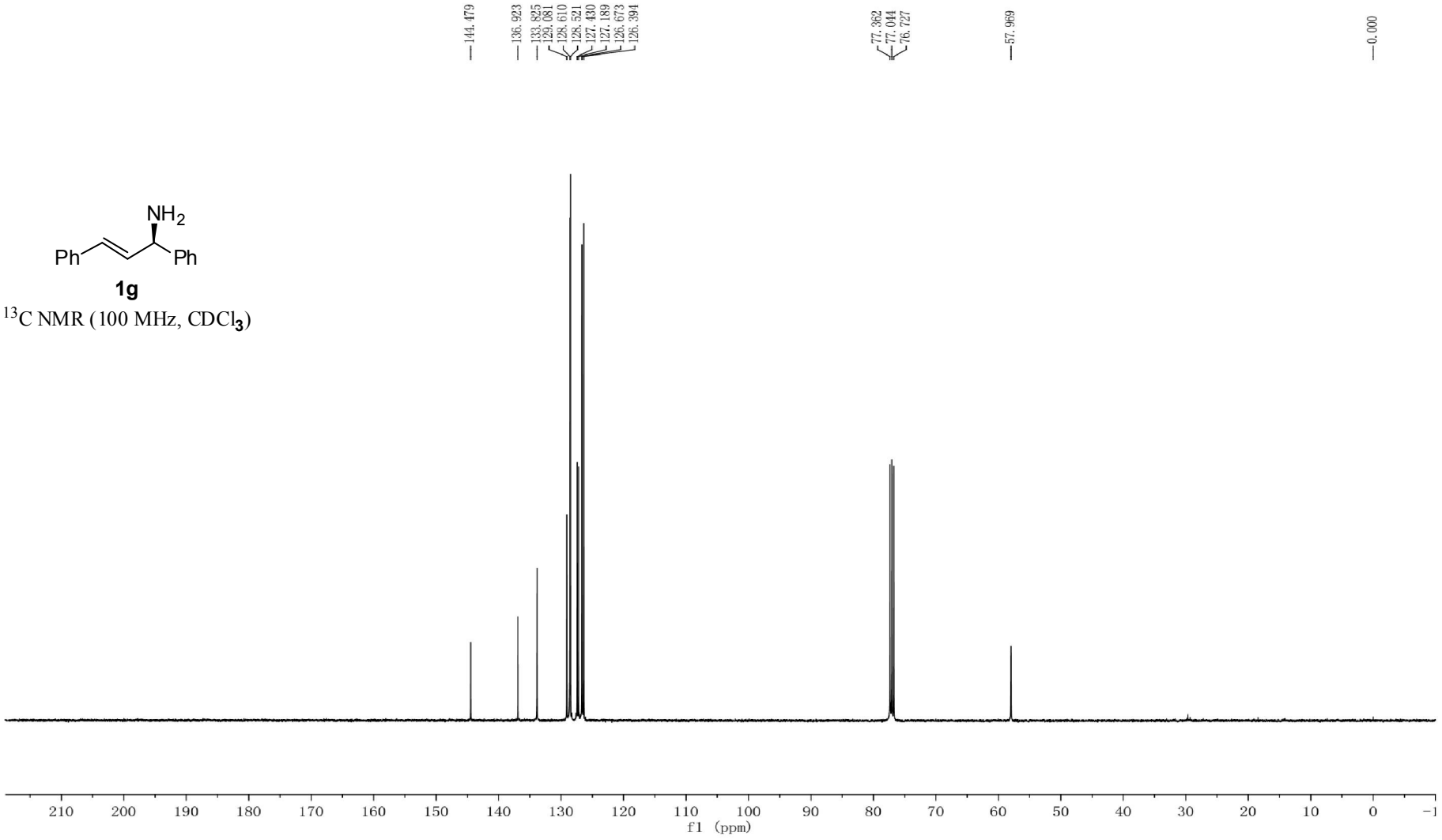

137.085
135.023
134.162
129.032
128.546
127.340
126.289
117.811
77.354
77.037
76.719
53.214
42.463
0.000
NH2
Ph
1f
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)

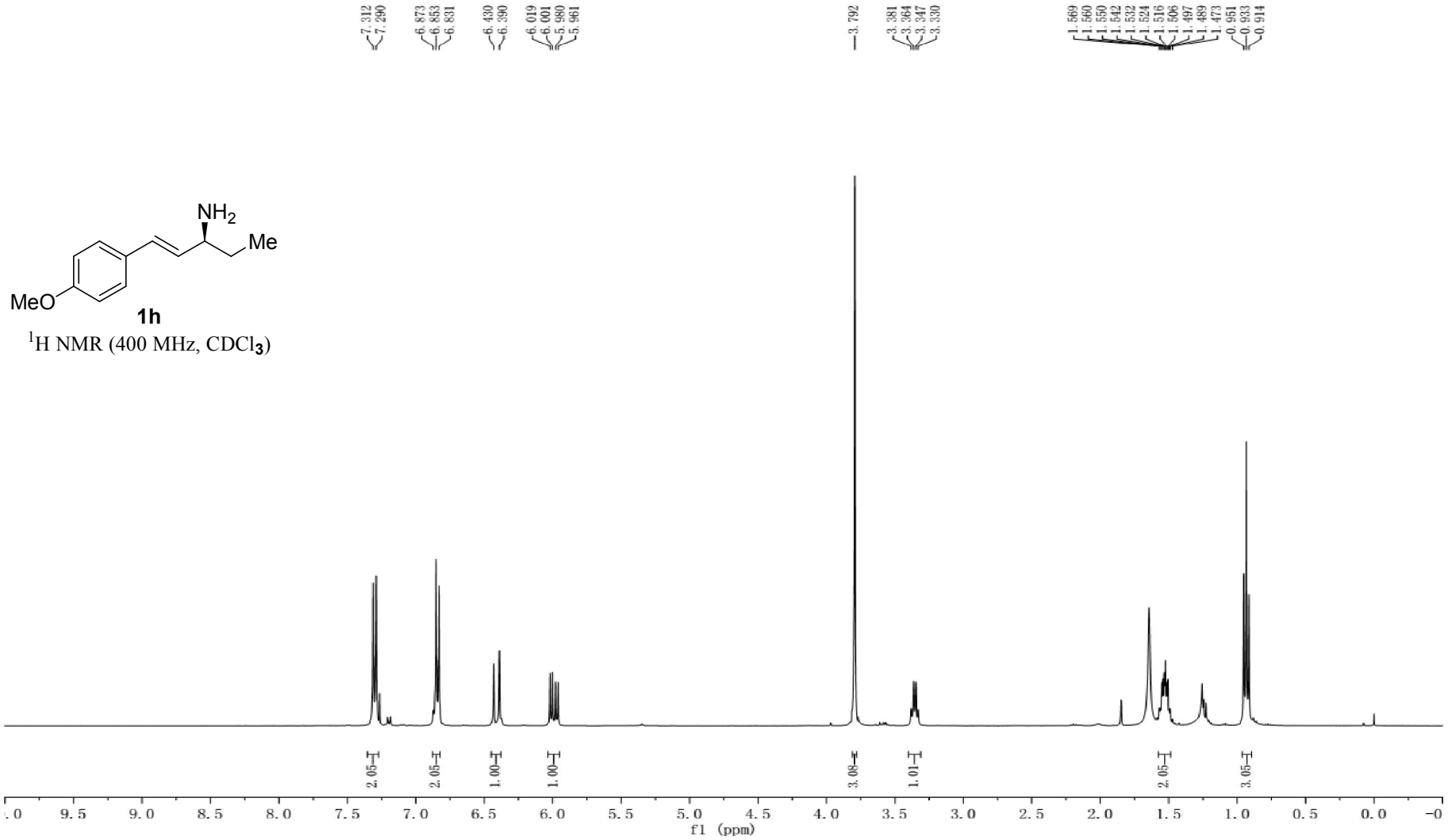


1g

^{1}H NMR (400 MHz, $CDCl_3$)

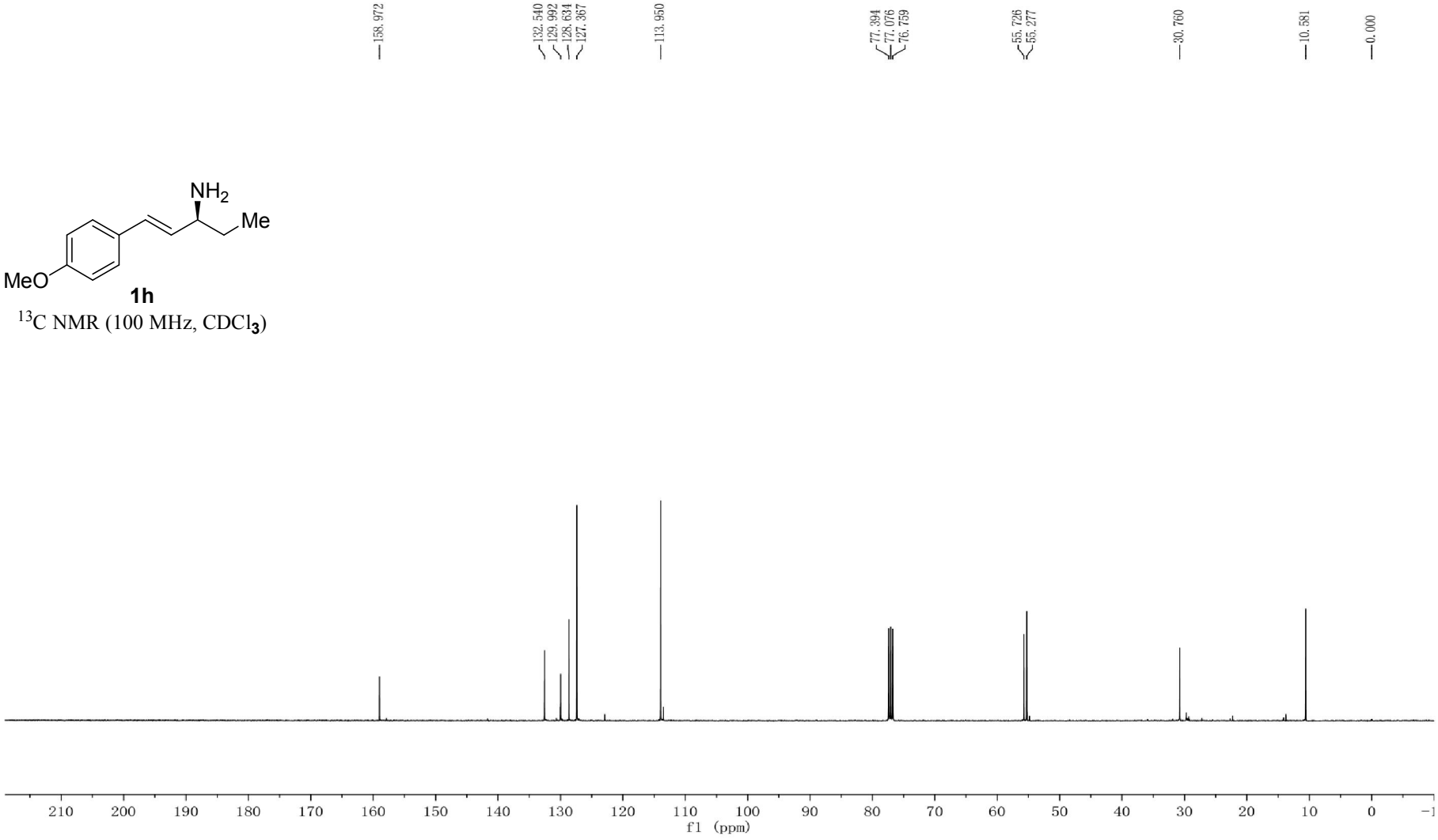



144.479
136.923
133.825
129.081
128.610
128.521
127.430
127.189
126.673
126.394
77.362
77.044
76.727
57.969
0.000
NH2
Ph
Ph
1g
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



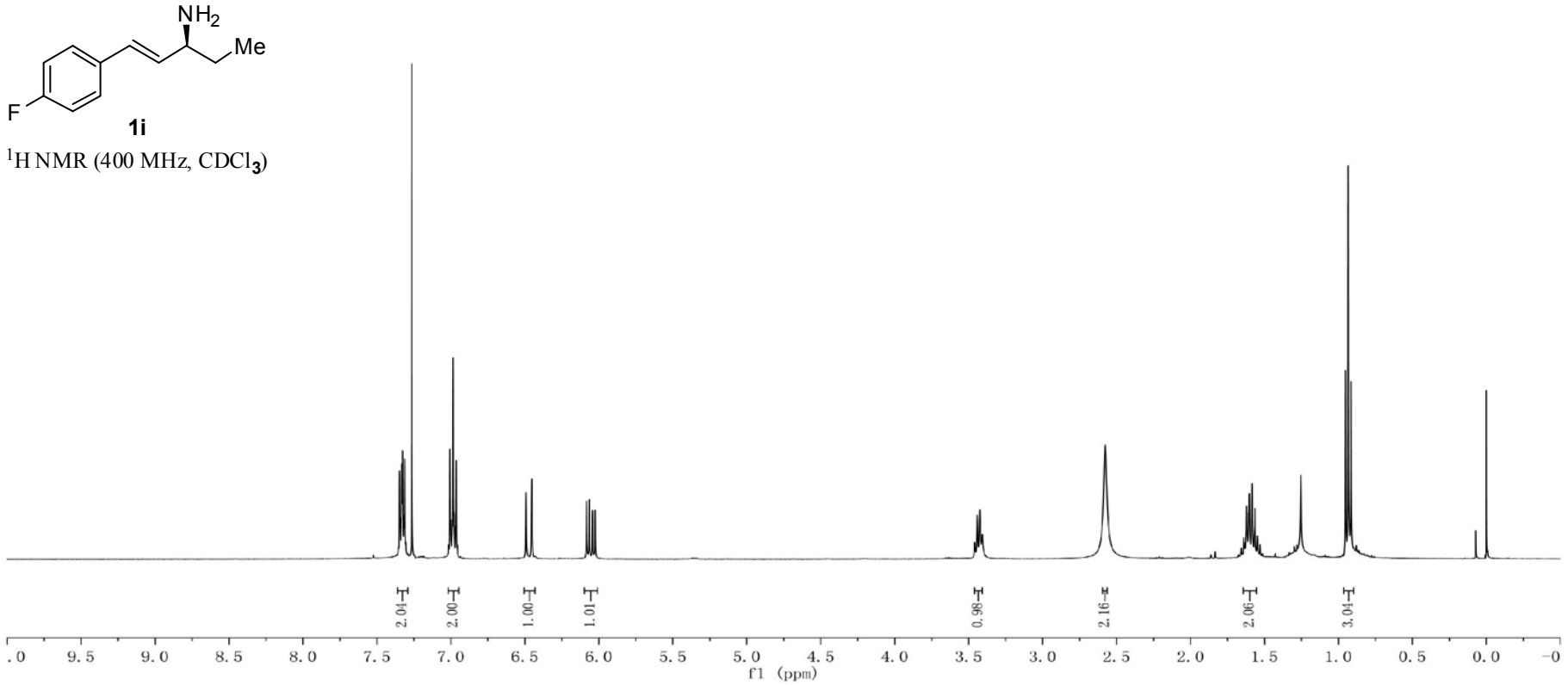
1h

^{1}H NMR (400 MHz, $CDCl_3$)



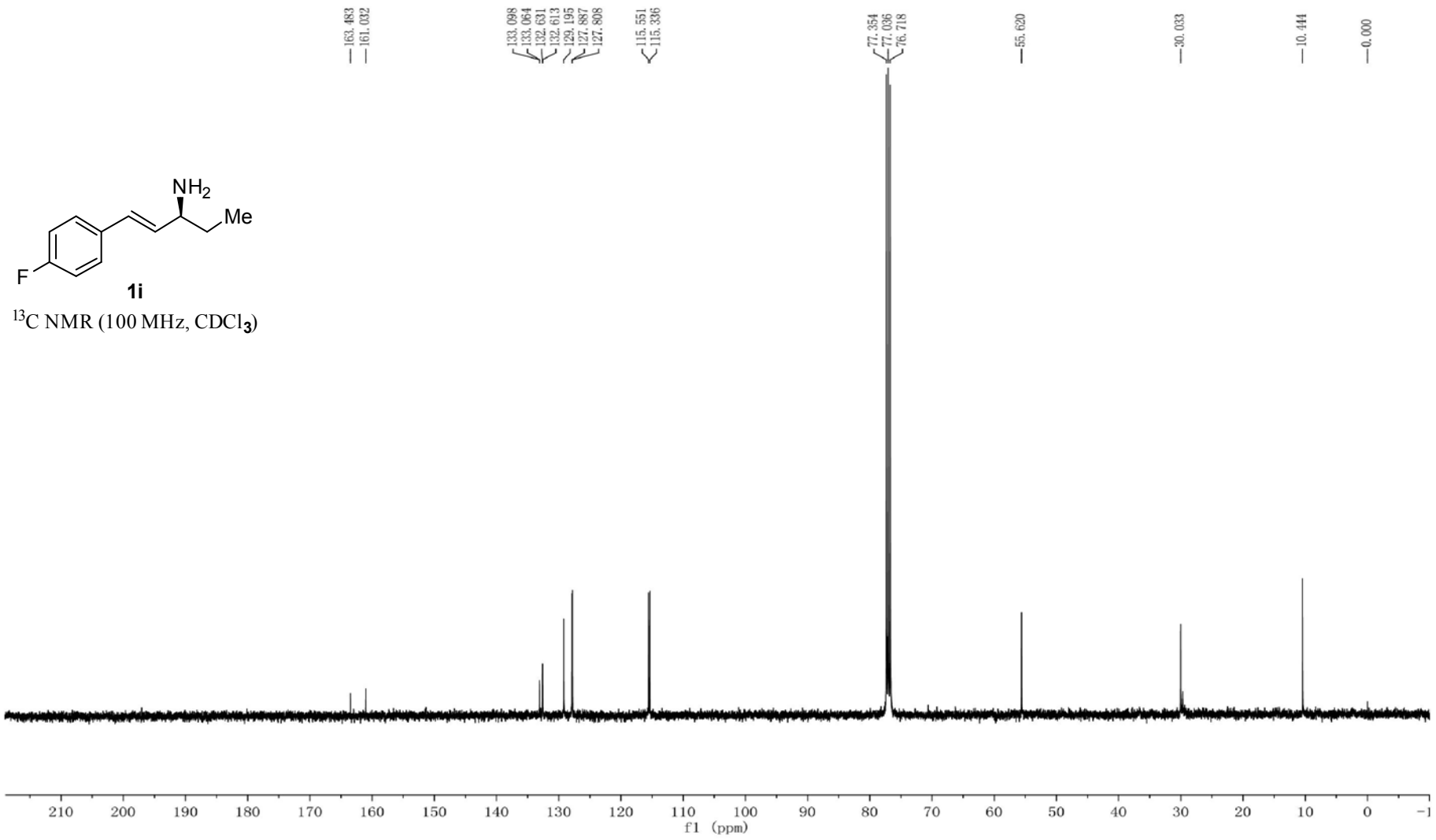
1h

^{13}C NMR (100 MHz, $CDCl_3$)



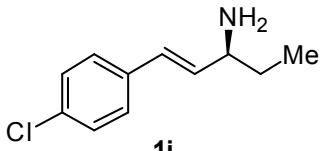
1i

^{1}H NMR (400 MHz, $CDCl_3$)



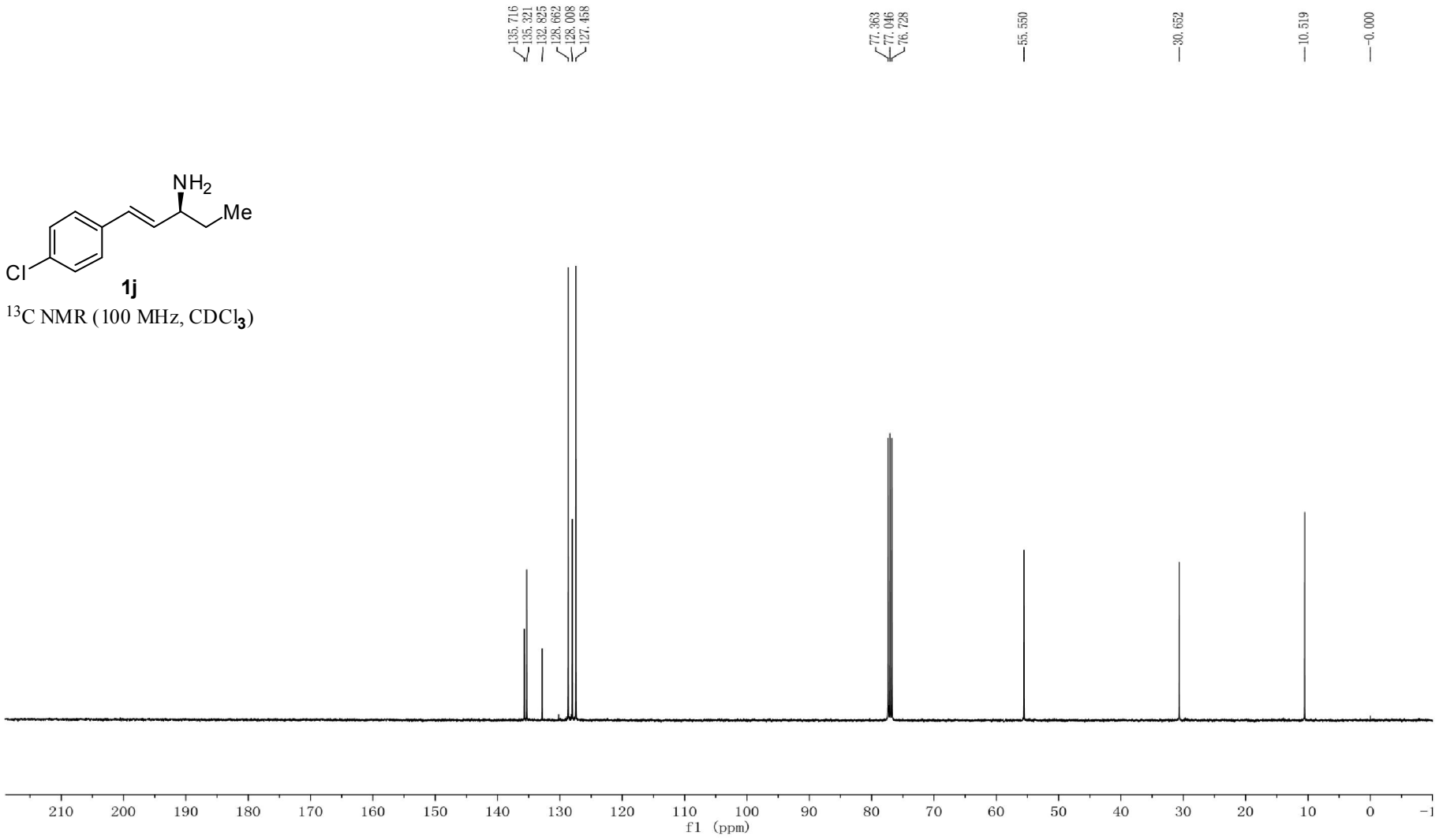
1i

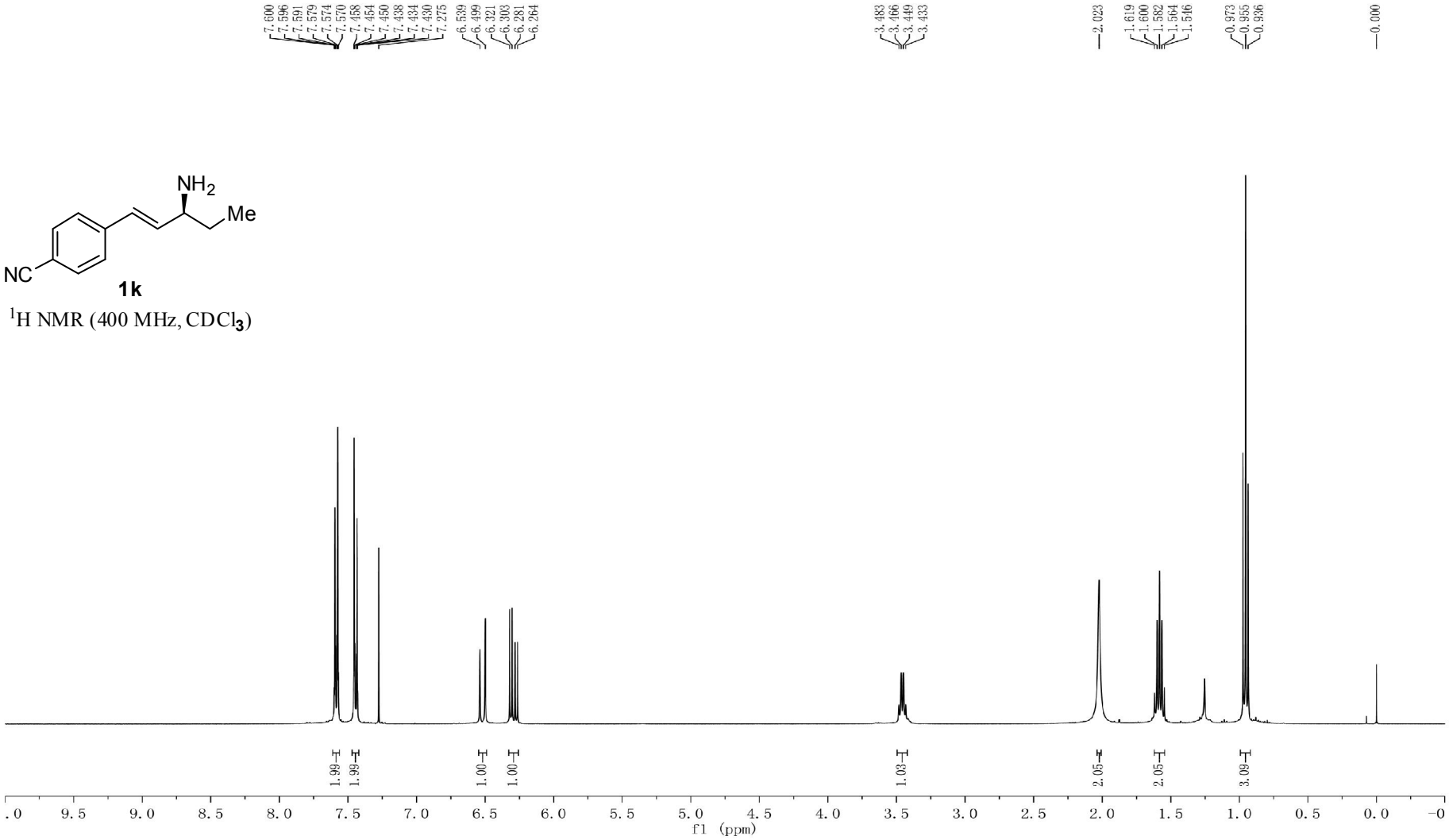
^{13}C NMR (100 MHz, $CDCl_3$)



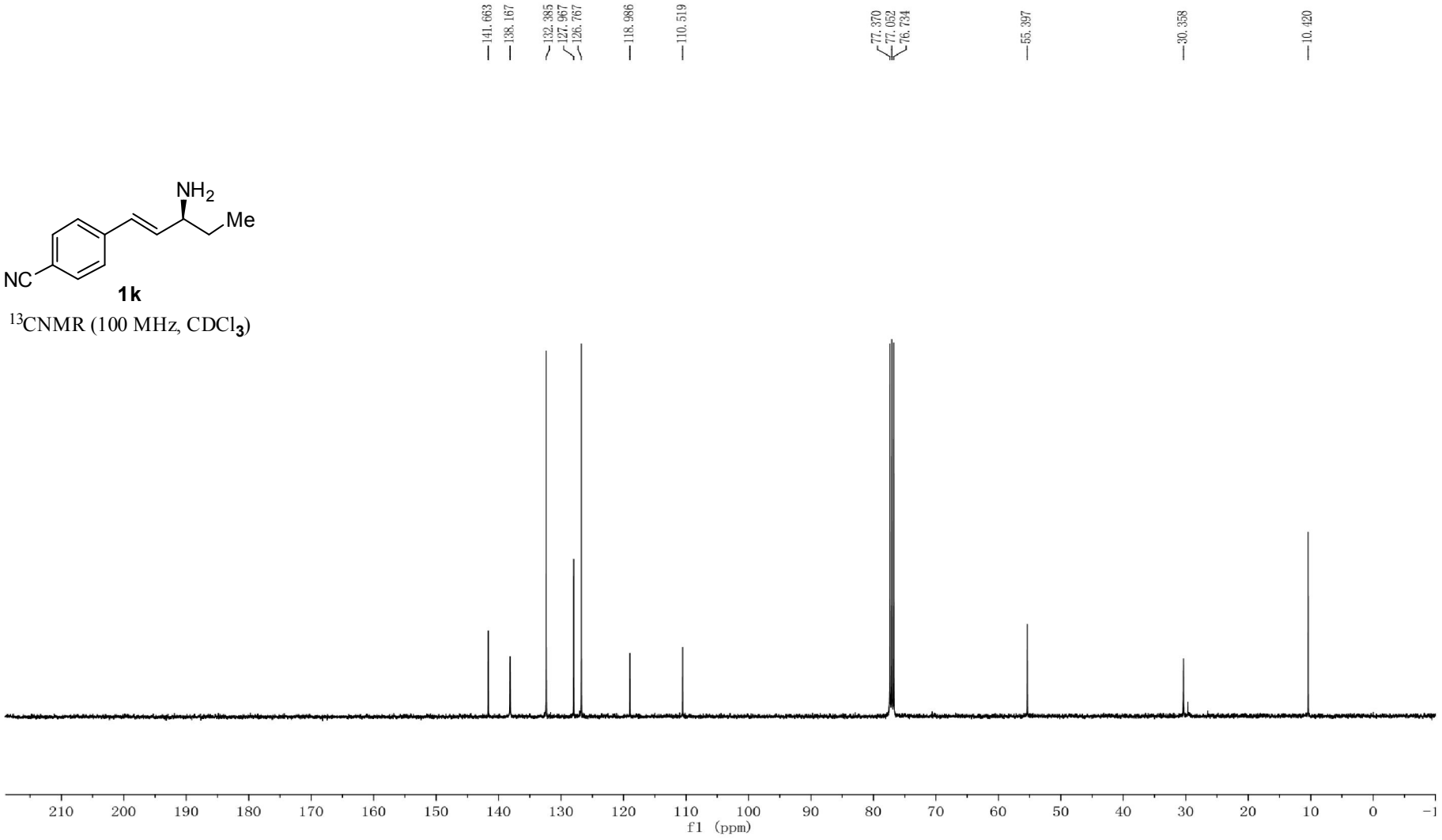
1j

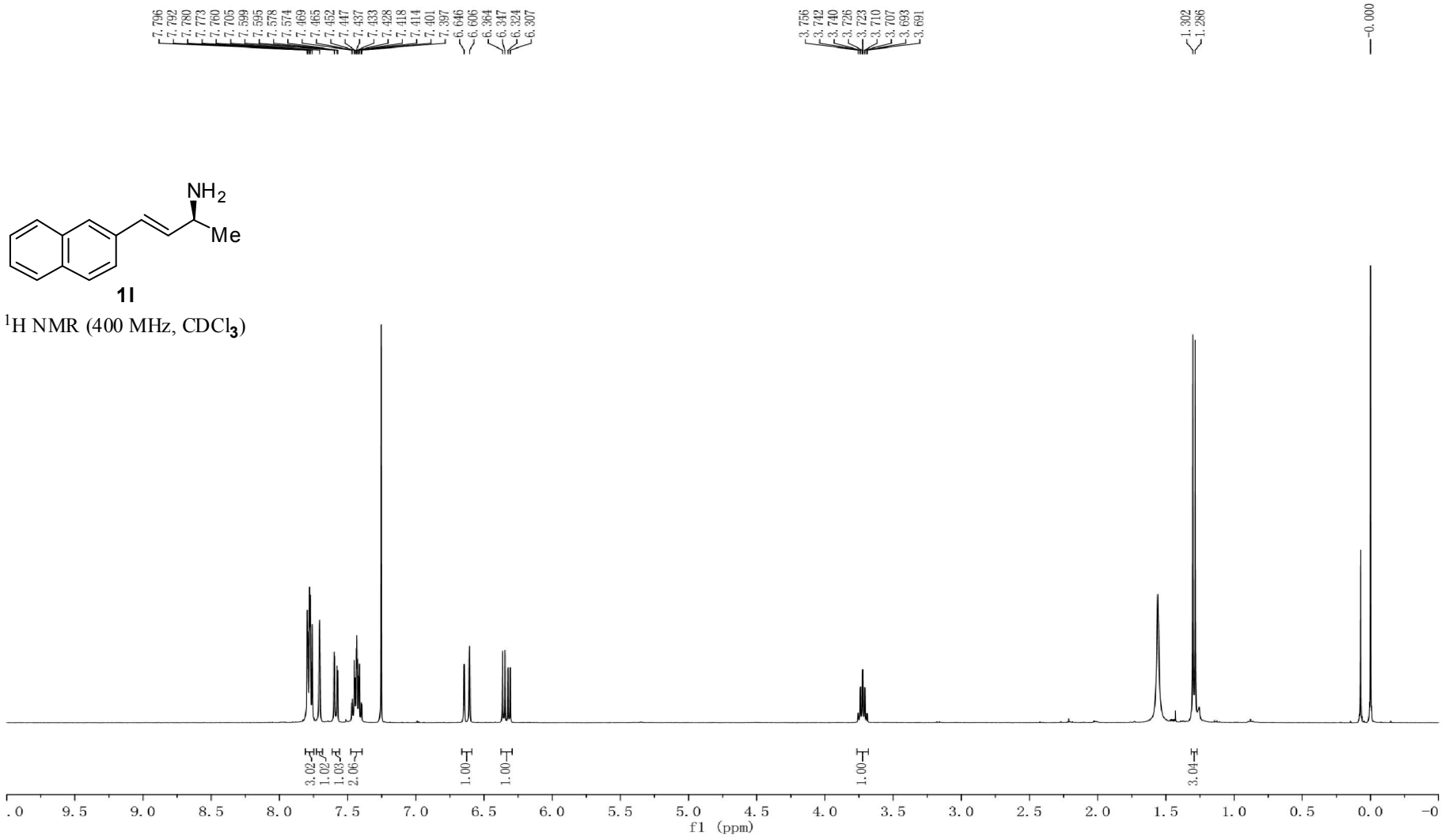
^{1}H NMR (400 MHz, $CDCl_3$)


135.716
135.321
132.825
128.662
128.008
127.458
77.363
77.046
76.728
55.550
30.652
10.519
-0.000
NH2
Me
Cl
1j
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



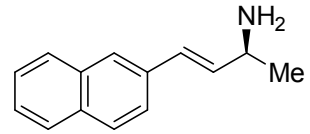
^{1}H NMR (400 MHz, $CDCl_3$)


141.663
138.167
132.385
127.967
126.767
118.986
110.519
77.370
77.052
76.734
55.397
30.358
10.420
NH2
Me
NC
1k
13CNMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −1
f1 (ppm)



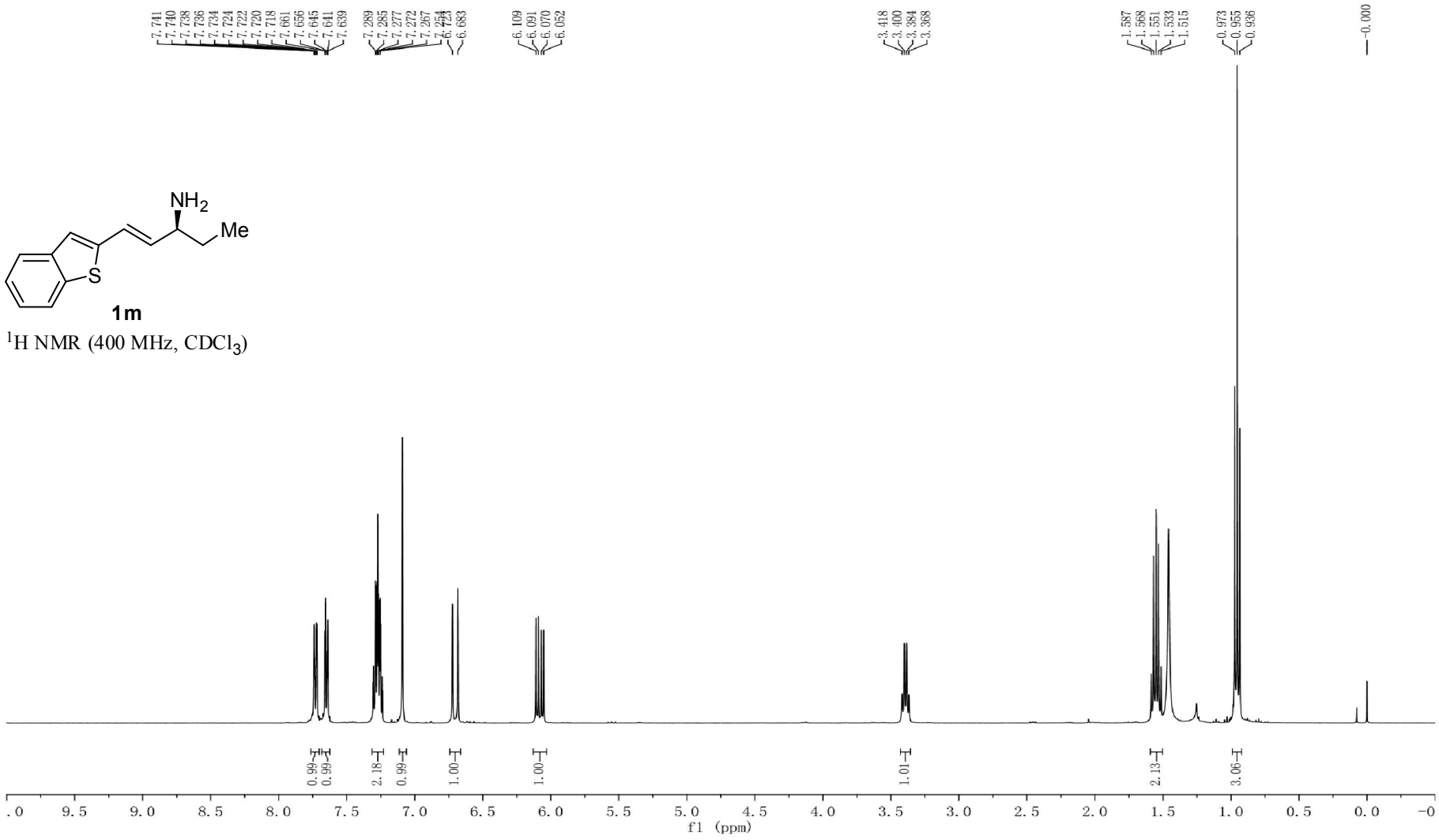
1l

^{1}H NMR (400 MHz, $CDCl_3$)



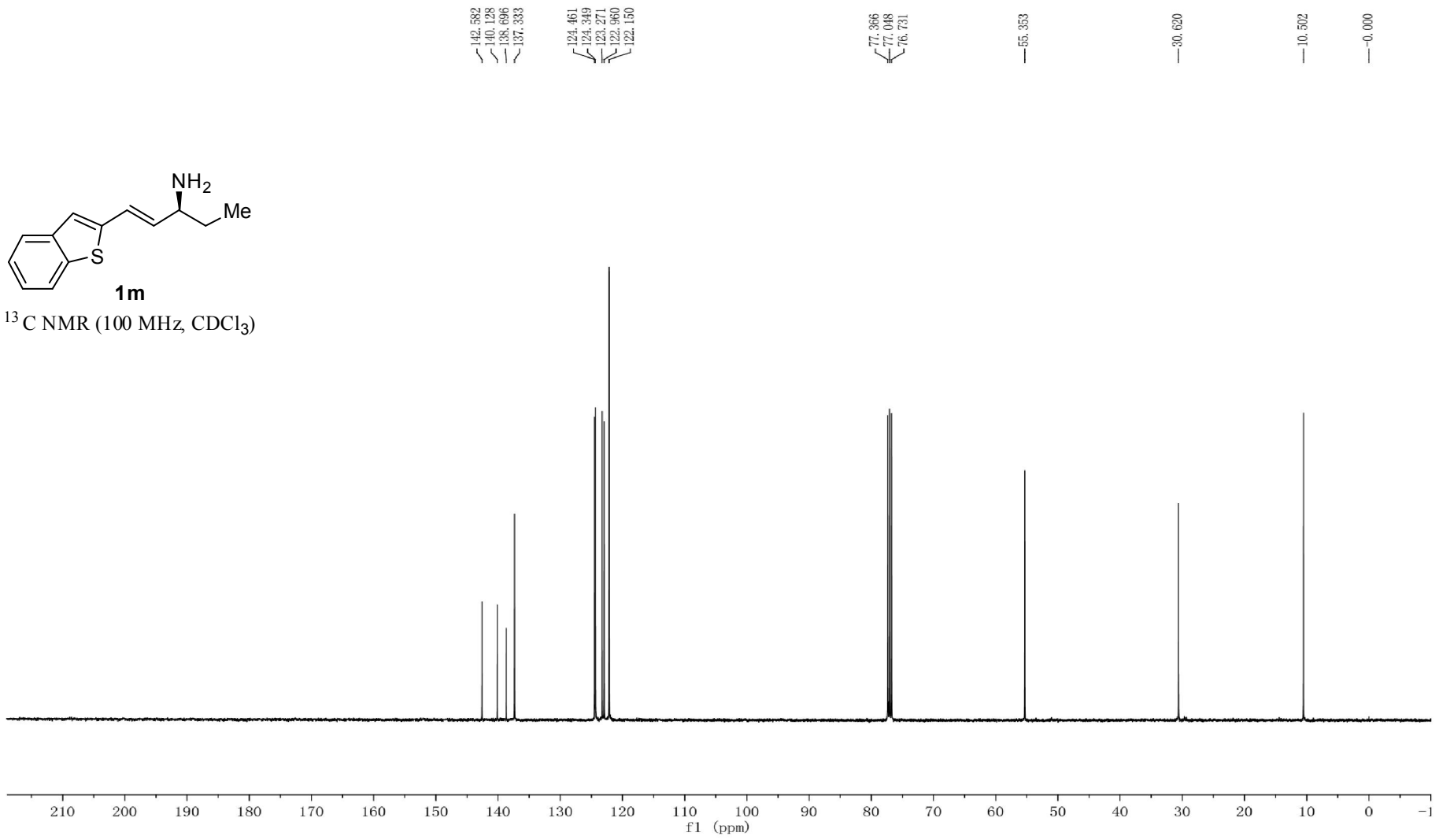
1l

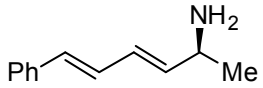
^{13}C NMR (100 MHz, $CDCl_3$)



1m

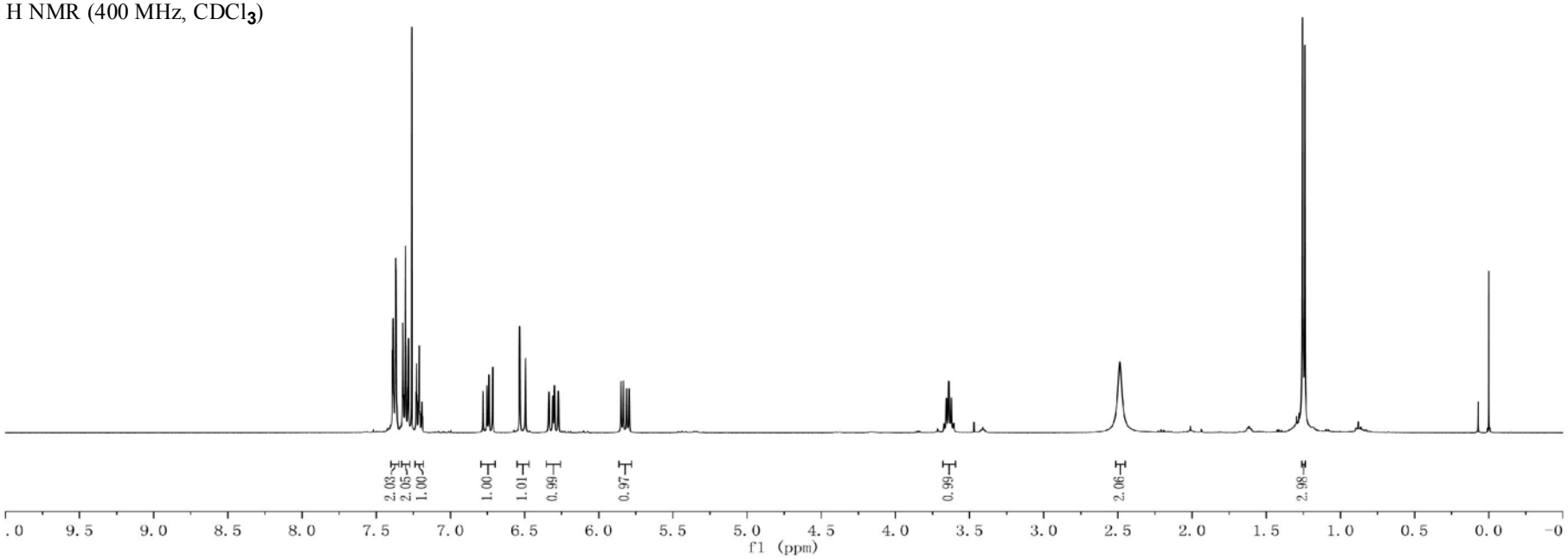
^{1}H NMR (400 MHz, $CDCl_3$)

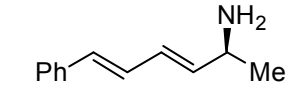

142.582
140.128
138.696
137.333
124.461
124.349
123.271
122.960
122.150
77.366
77.048
76.731
55.353
30.620
10.502
-0.000
NH2
Me
S
1m
13 C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



1n

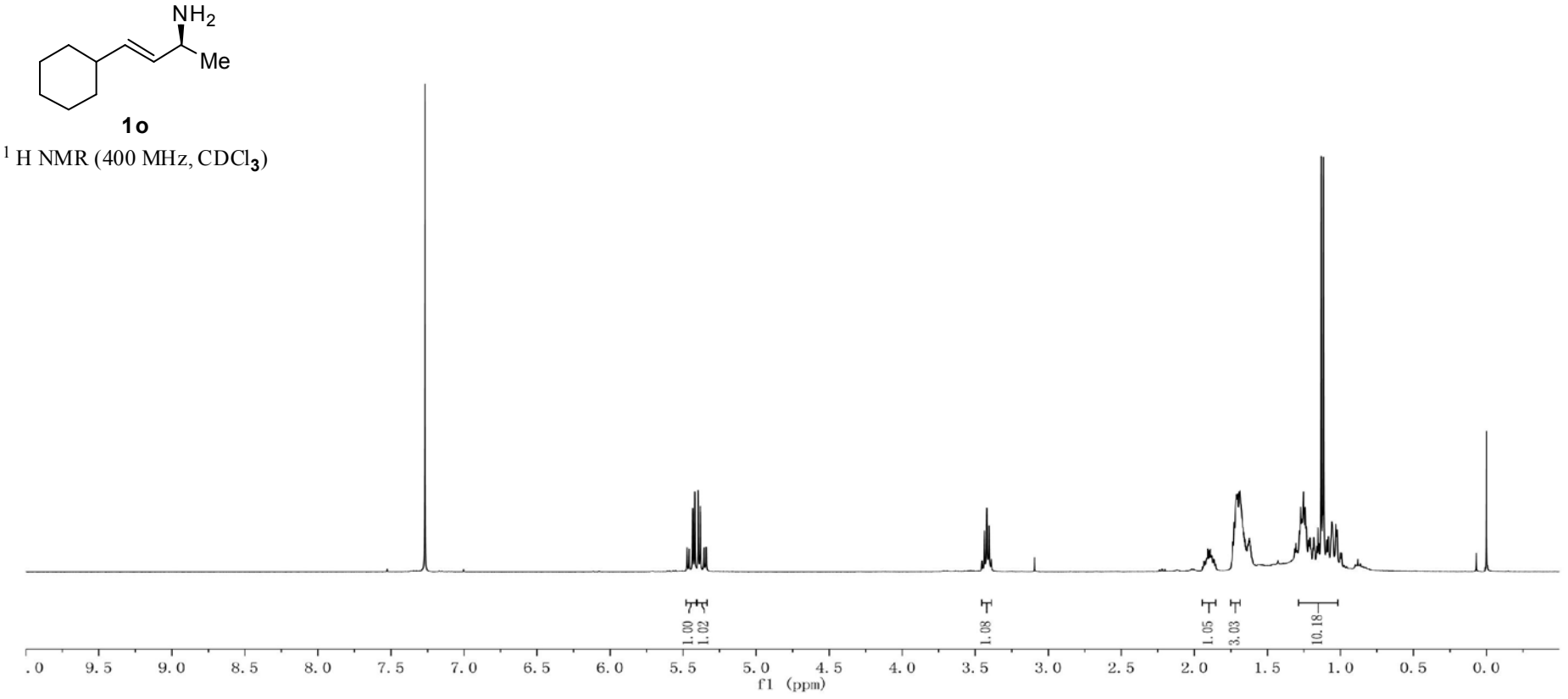
^{1}H NMR (400 MHz, $CDCl_3$)

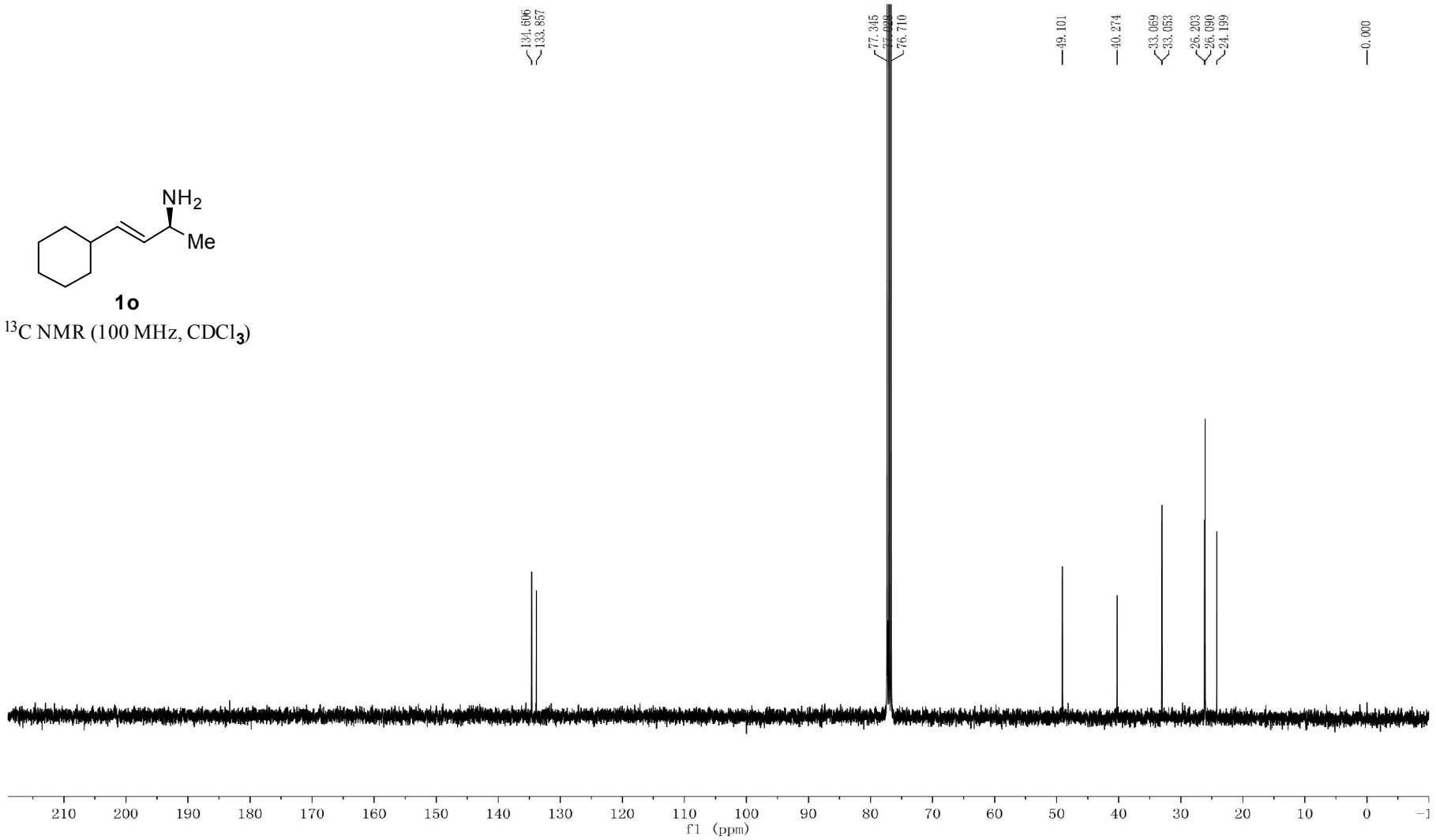




1n

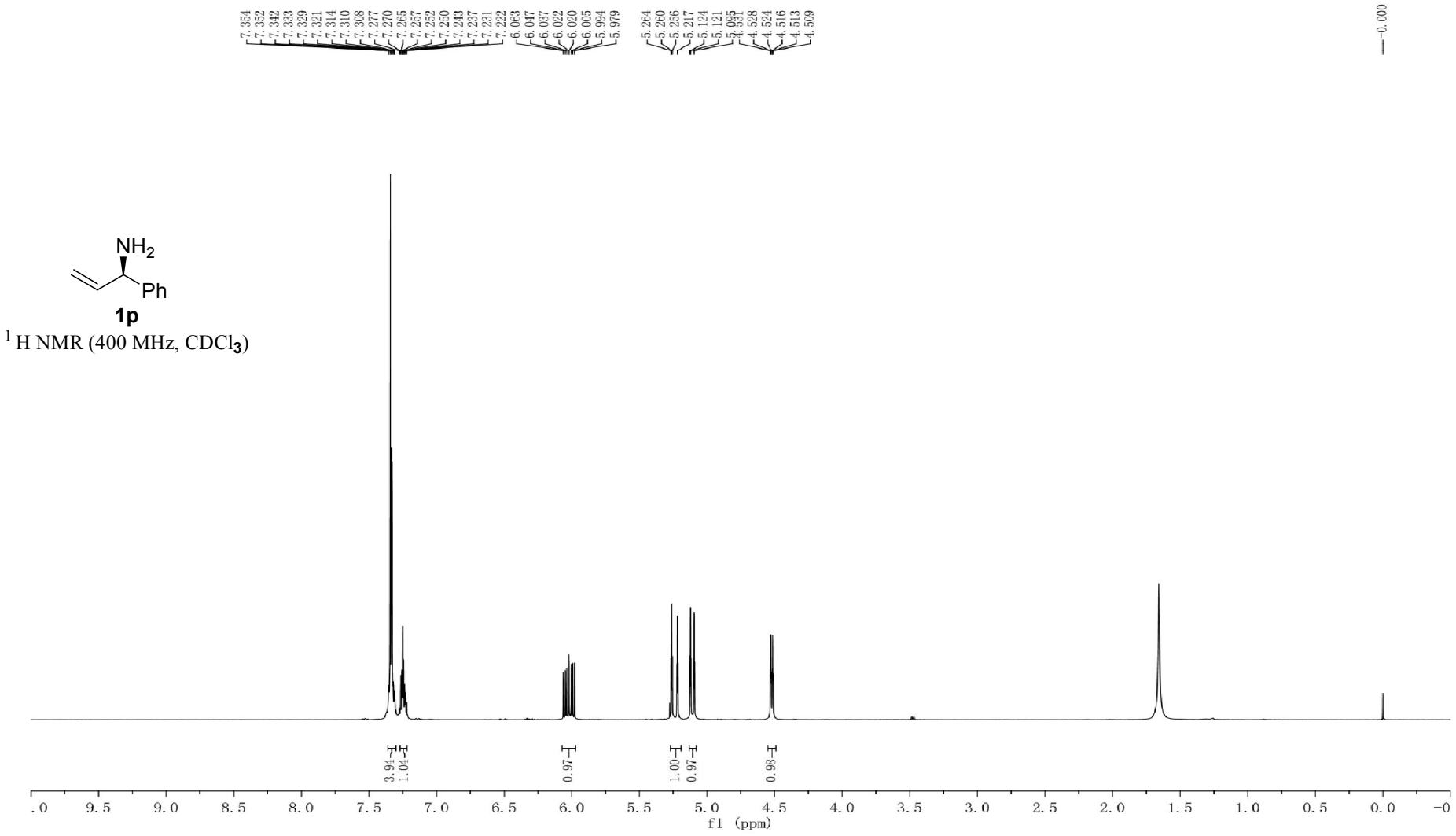
^{13}C NMR (100 MHz, $CDCl_3$)

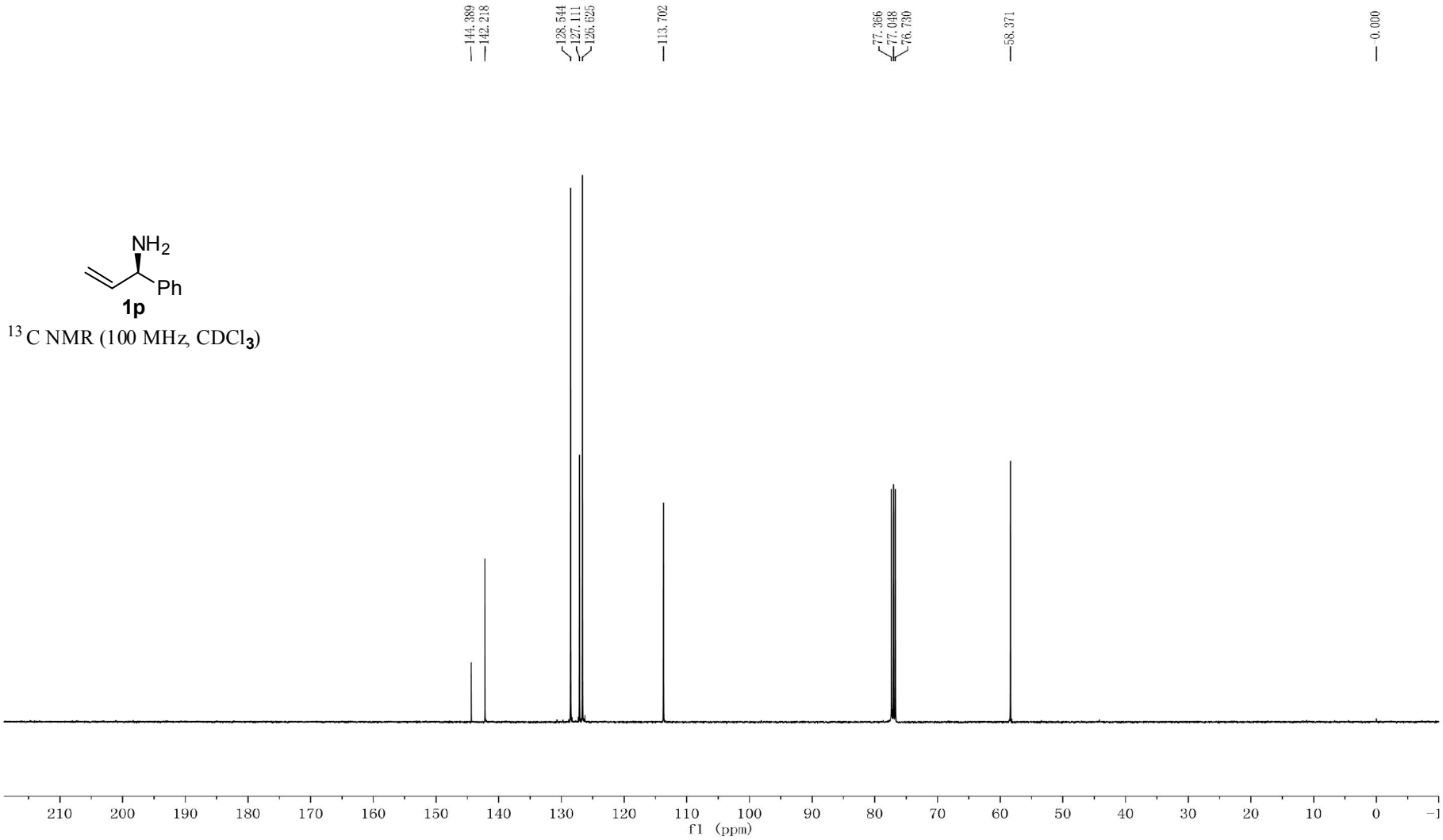

NH2
Me
1o
1H NMR (400 MHz, CDCl3)
7.267
5.473
5.458
5.434
5.419
5.397
5.382
5.380
5.357
5.343
5.341
3.453
3.437
3.421
3.405
3.389
1.907
1.899
1.892
1.883
1.736
1.727
1.711
1.703
1.695
1.688
1.661
1.654
1.650
1.632
1.624
1.619
1.273
1.264
1.253
1.241
1.234
1.153
1.132
1.122
1.116
1.059
1.055
1.031
0.000
1.00
1.02
1.08
1.05
3.03
10.18
f1 (ppm)



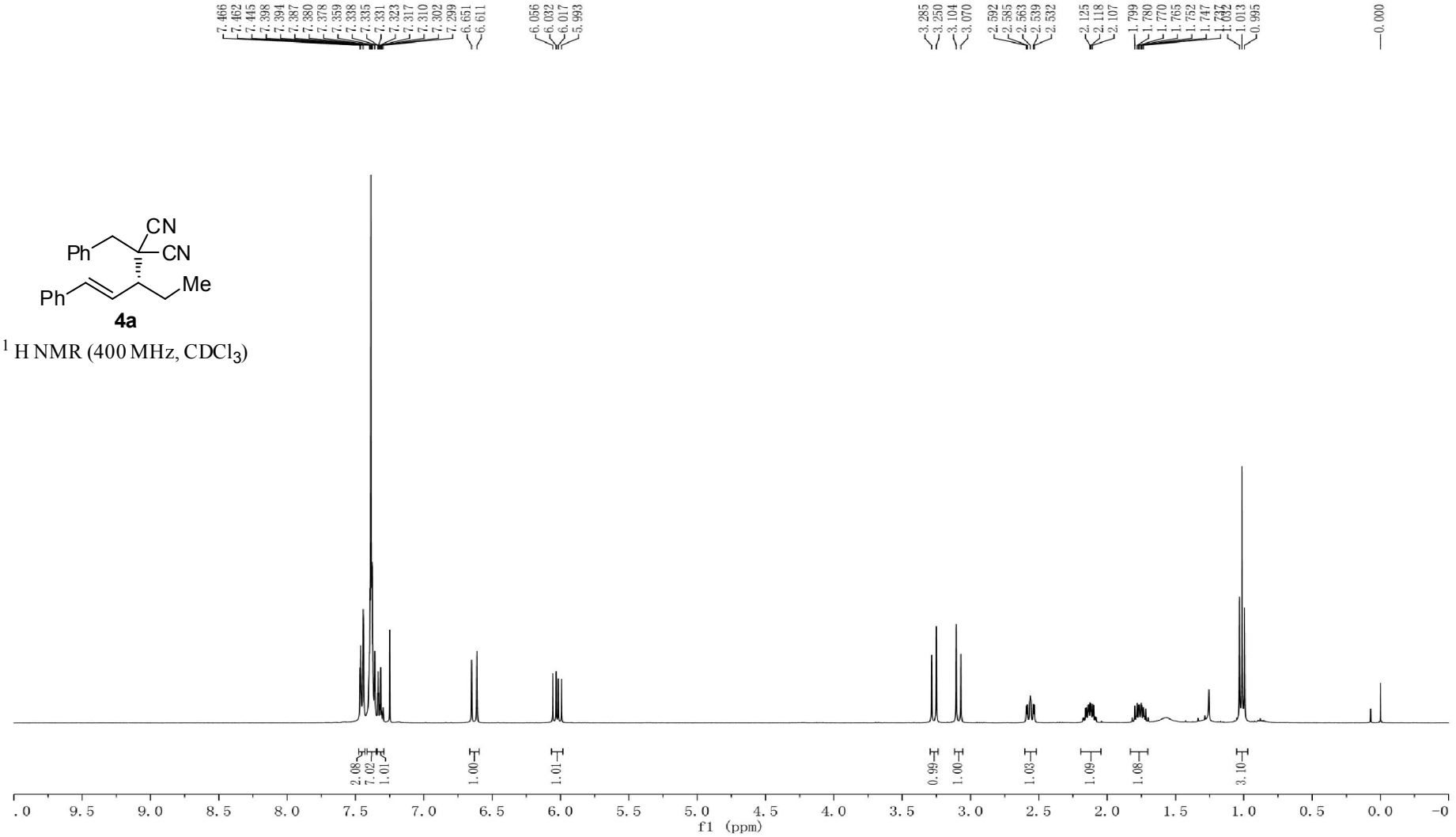
1o

^{13}C NMR (100 MHz, $CDCl_3$)

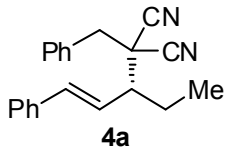

NH2
Ph
1p
1H NMR (400 MHz, CDCl3)
7.354
7.352
7.342
7.333
7.329
7.321
7.314
7.310
7.308
7.277
7.270
7.265
7.257
7.252
7.250
7.243
7.237
7.231
7.222
6.063
6.047
6.037
6.022
6.020
6.005
5.994
5.979
5.264
5.260
5.256
5.217
5.124
5.121
4.531
4.528
4.524
4.516
4.513
4.509
-0.000
3.94
1.04
0.97
1.00
0.97
0.98
f1 (ppm)



^{13}C NMR (100 MHz, $CDCl_3$)

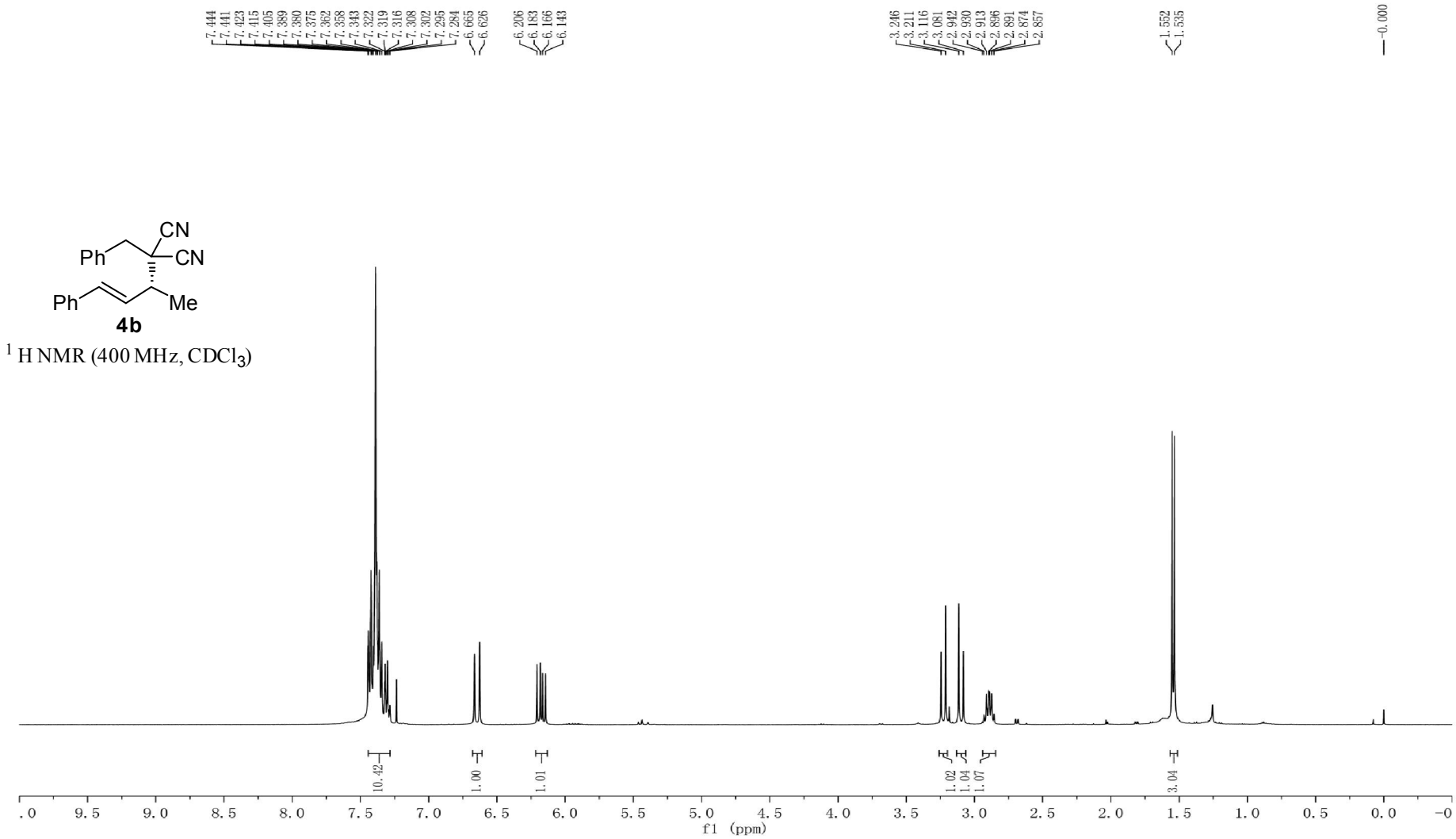


^{1}H NMR (400 MHz, $CDCl_3$)

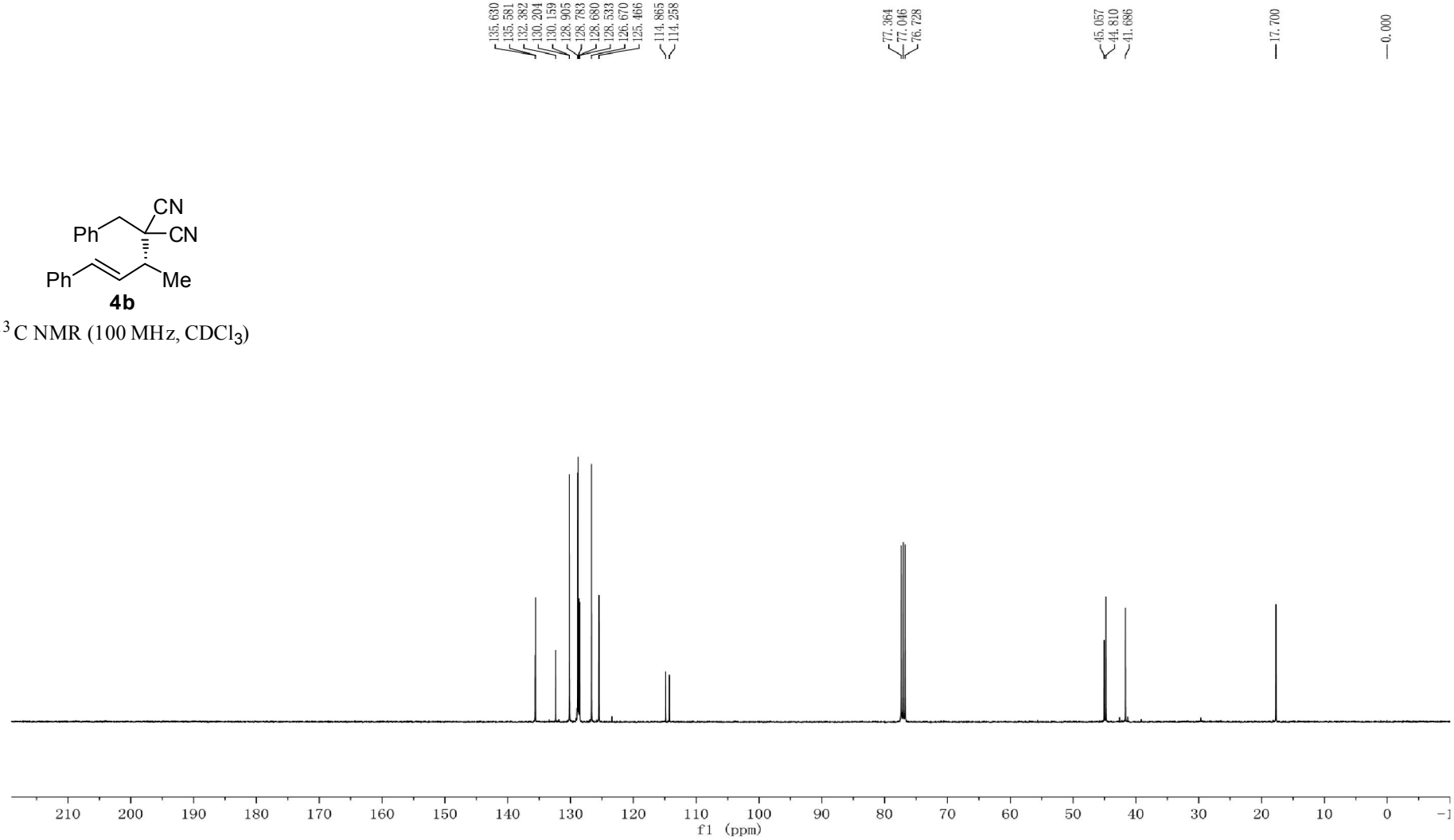


4a

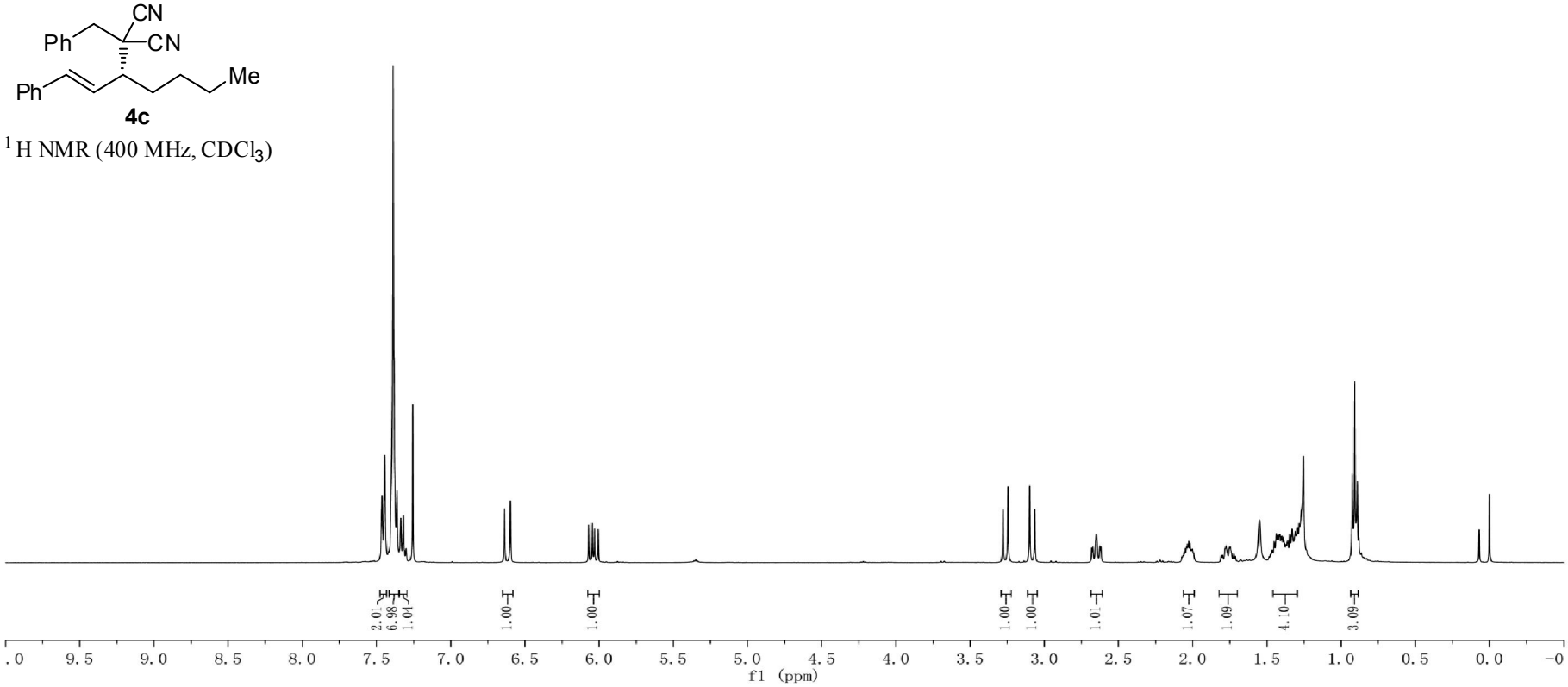
^{13}C NMR (100 MHz, $CDCl_3$)



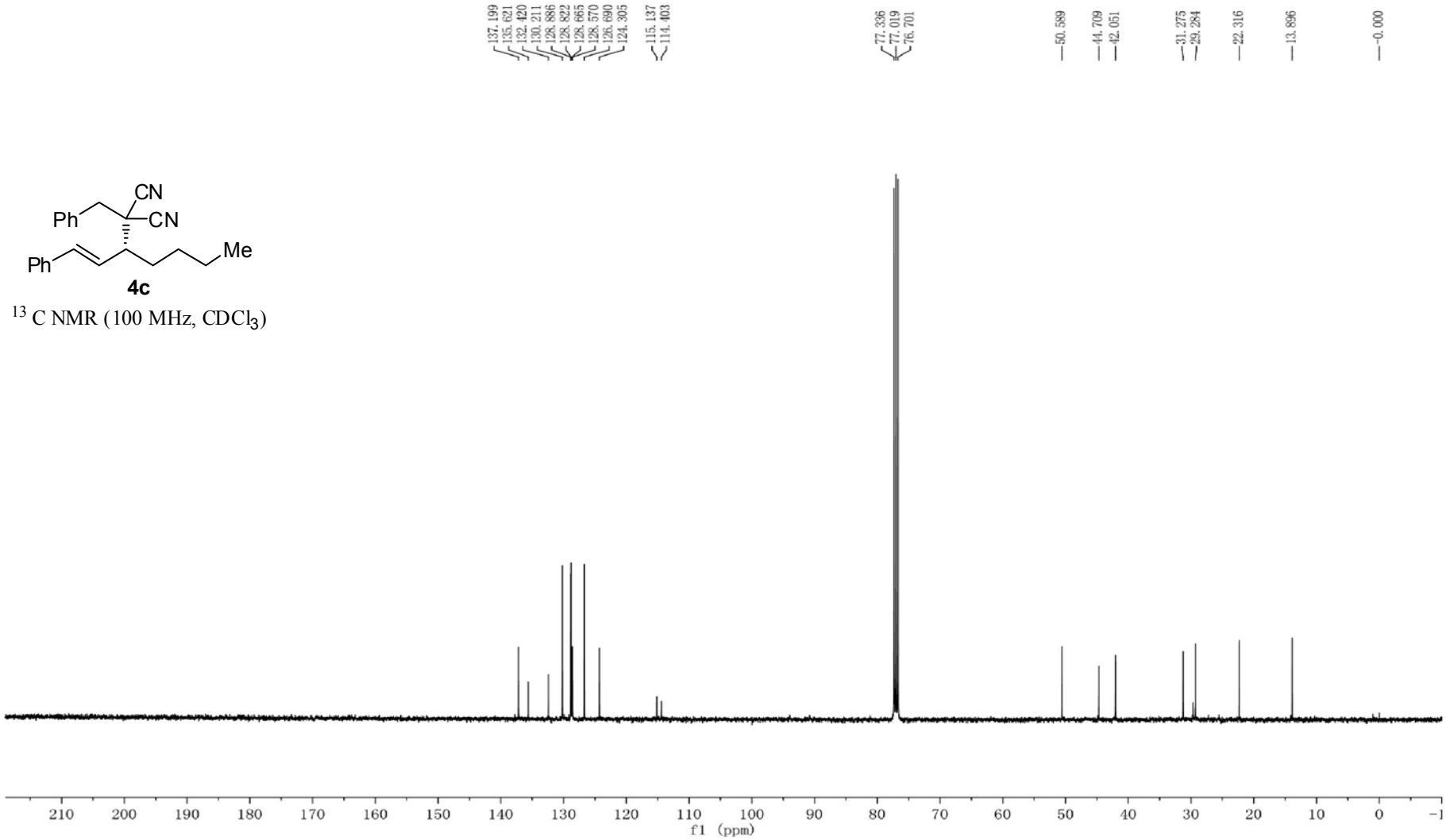
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (100 MHz, $CDCl_3$)

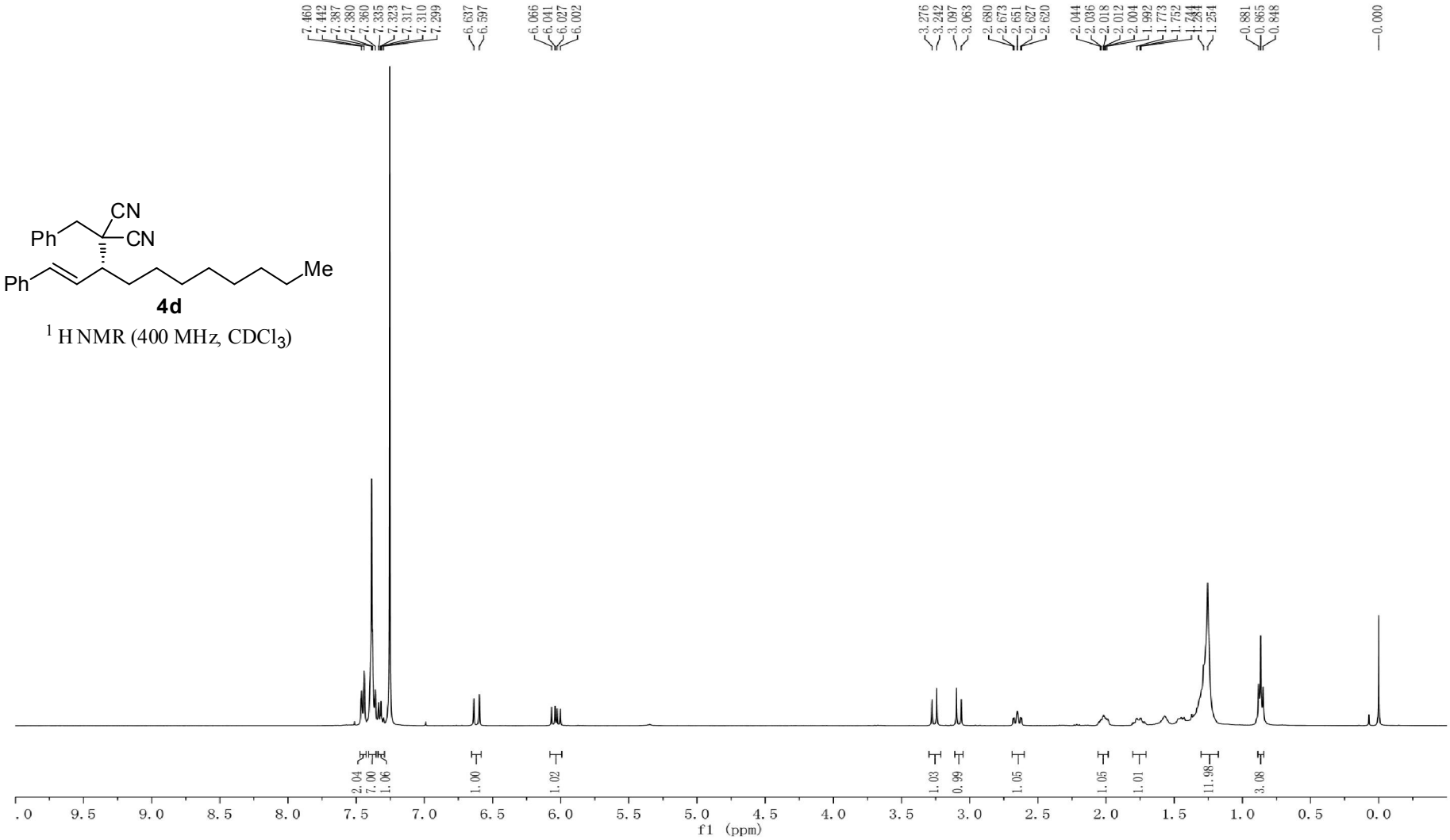


^{1}H NMR (400 MHz, $CDCl_3$)

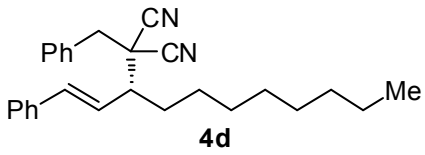


4c

^{13}C NMR (100 MHz, $CDCl_3$)

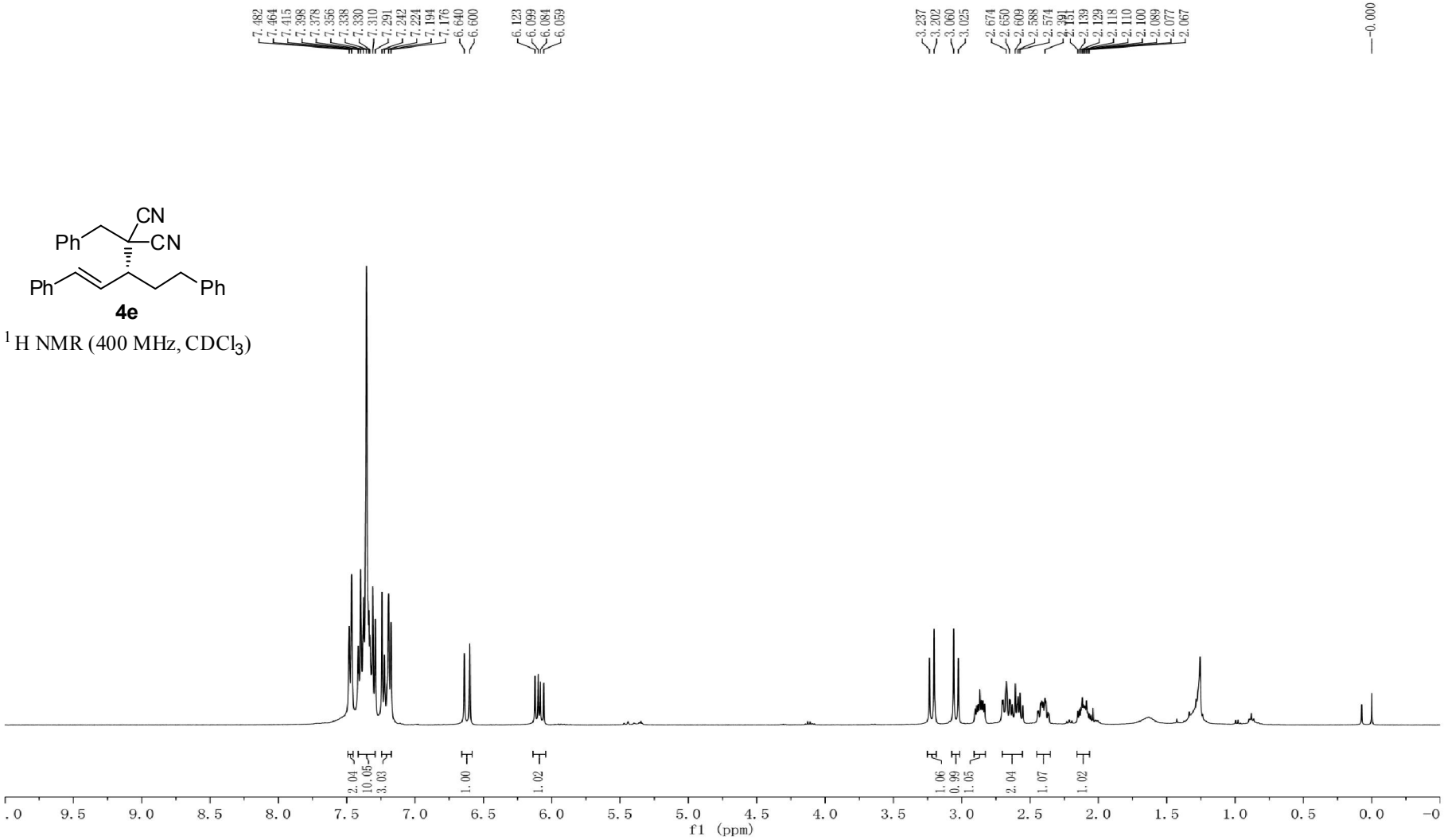


^{1}H NMR (400 MHz, $CDCl_3$)



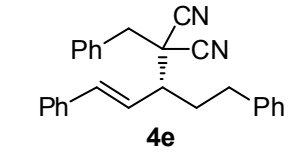
4d

^{13}C NMR (100 MHz, $CDCl_3$)



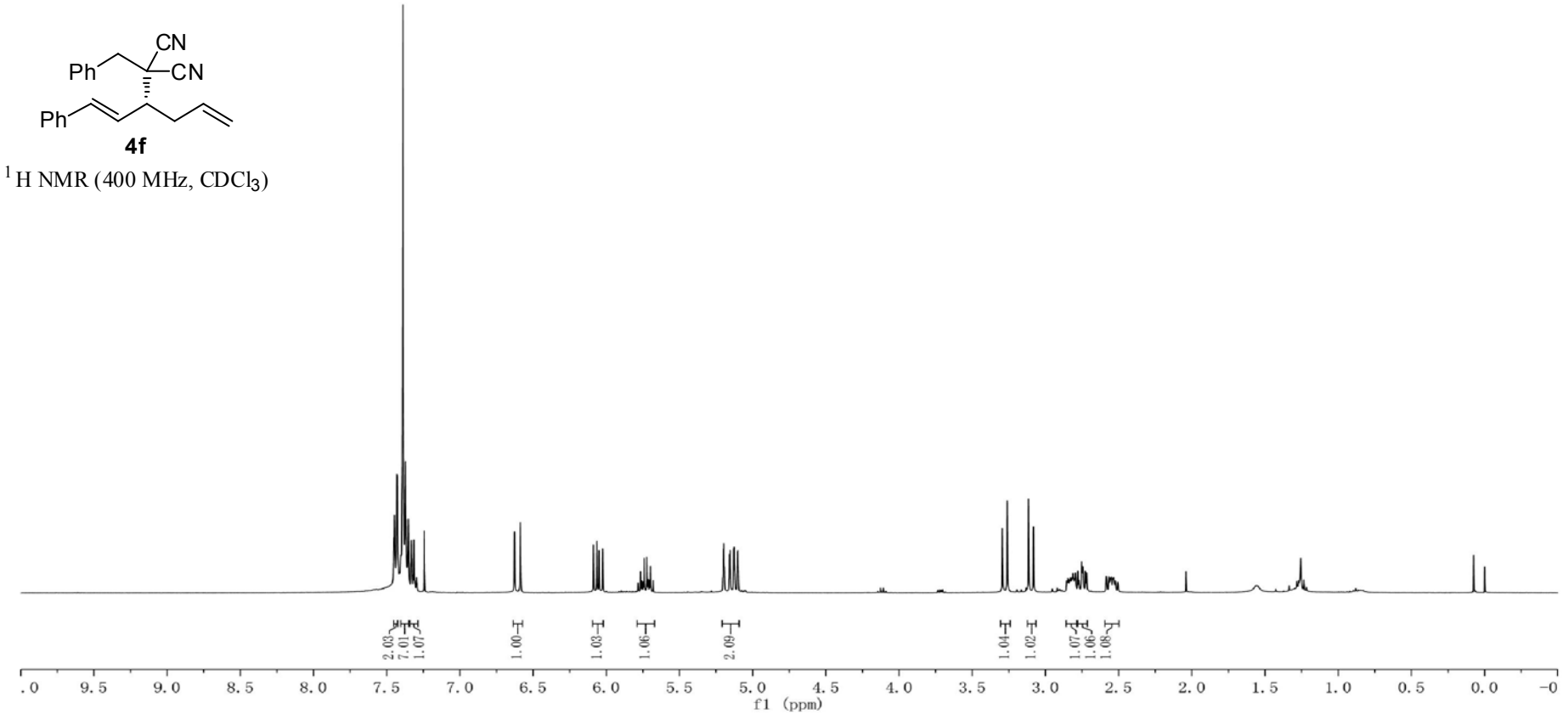
4e

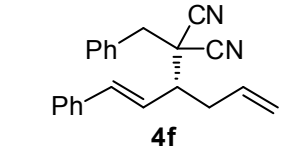
^{1}H NMR (400 MHz, $CDCl_3$)



4e

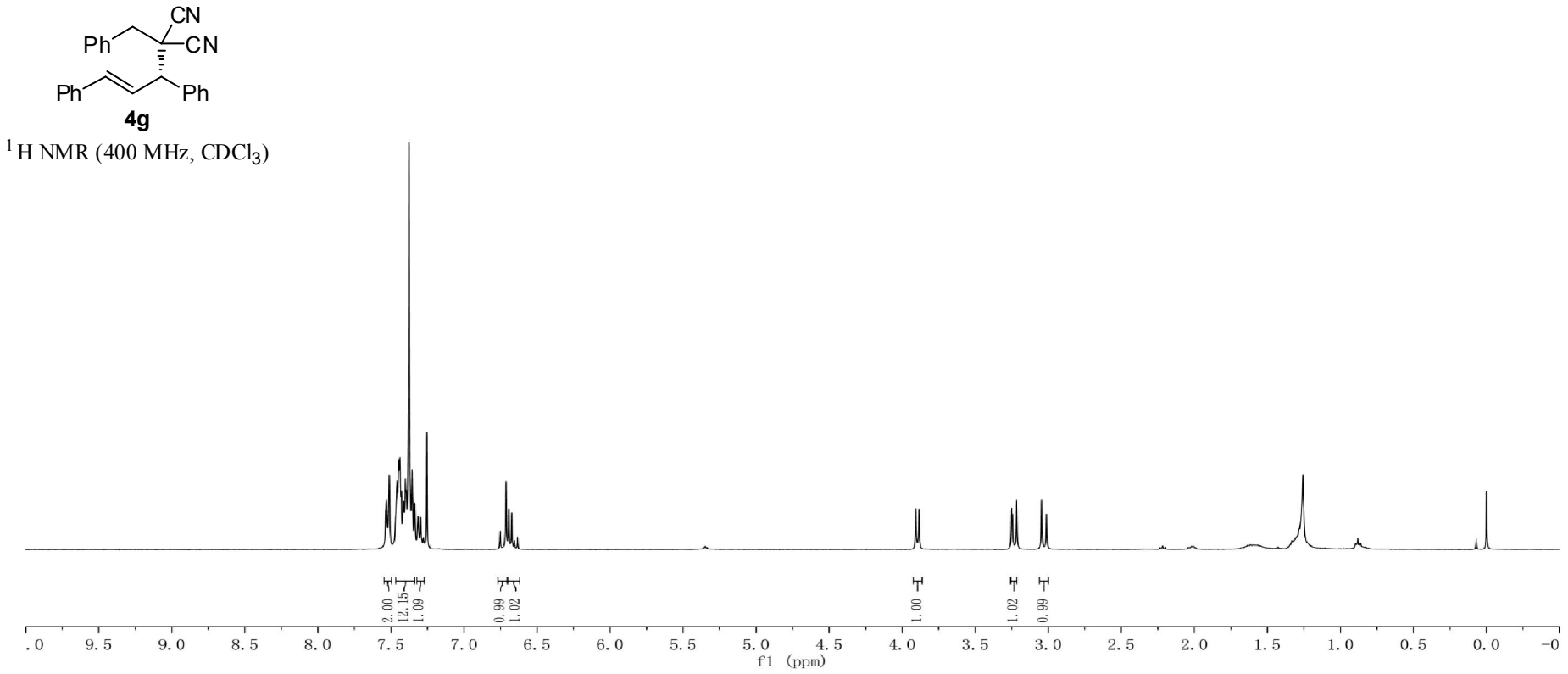
^{13}C NMR (100 MHz, $CDCl_3$)


CN
Ph
CN
Ph
4f
1H NMR (400 MHz, CDCl3)
f1 (ppm)

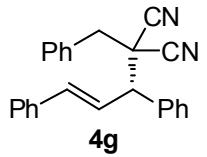


4f

^{13}C NMR (100 MHz, $CDCl_3$)

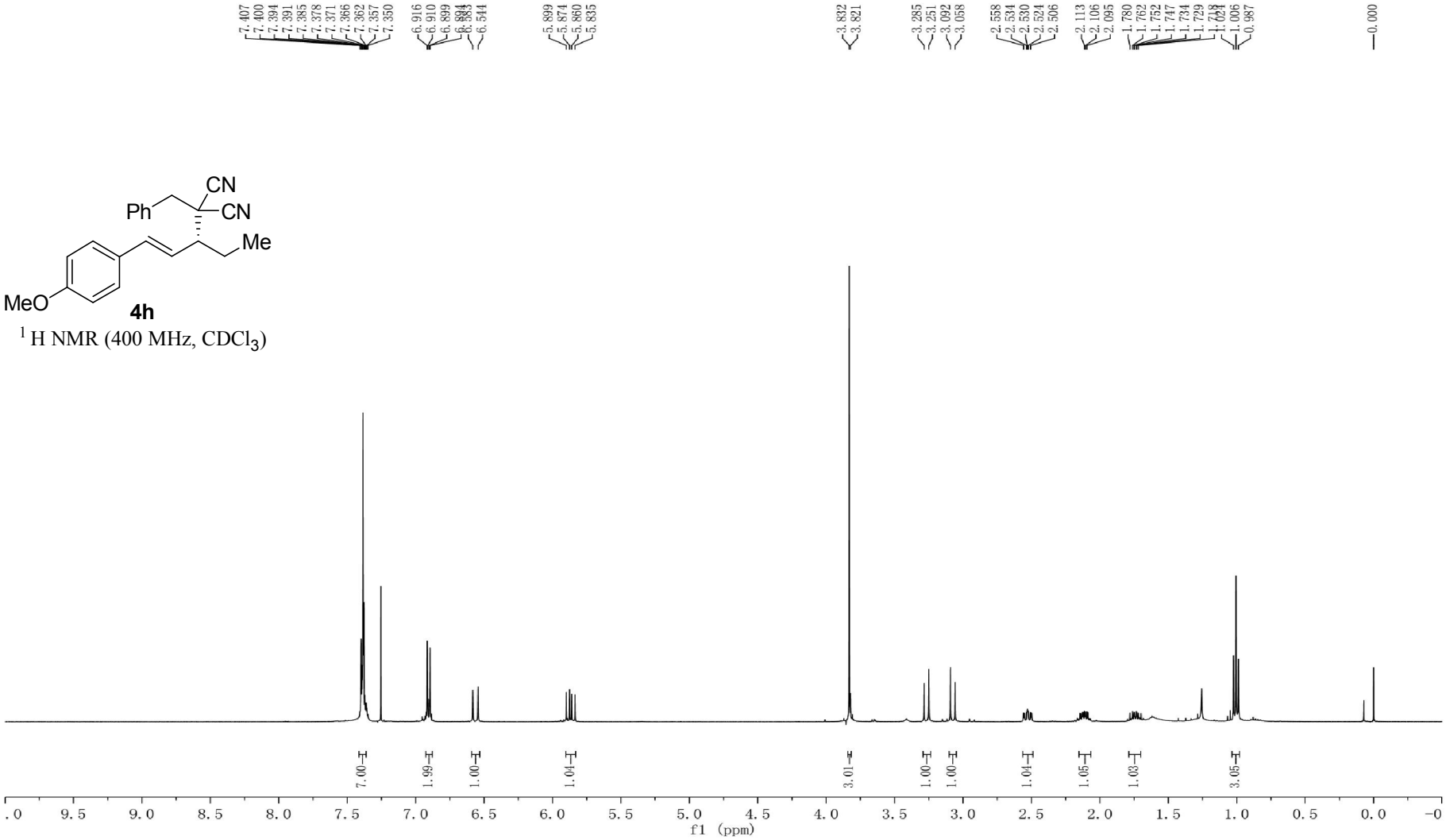


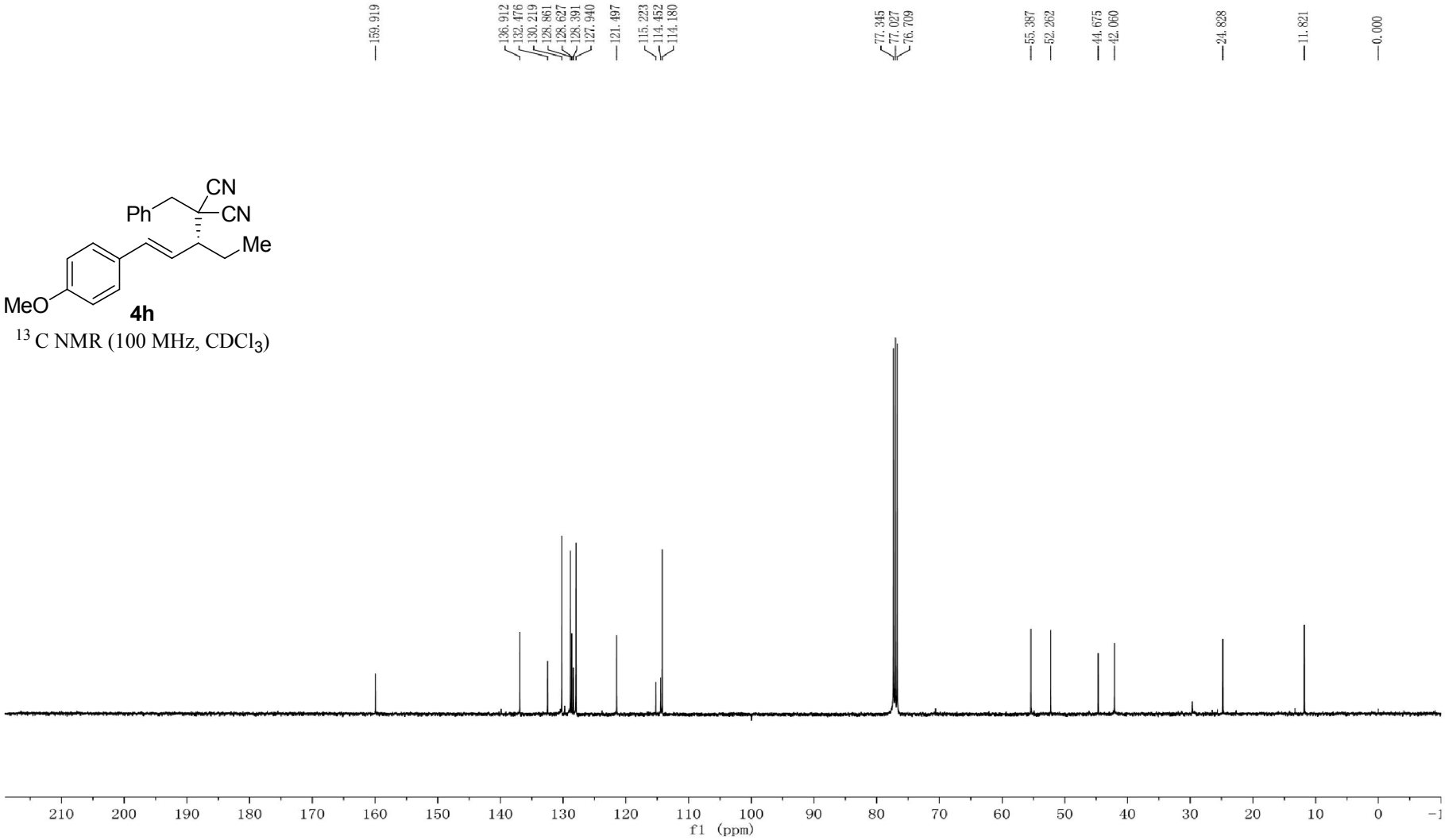
^{1}H NMR (400 MHz, $CDCl_3$)

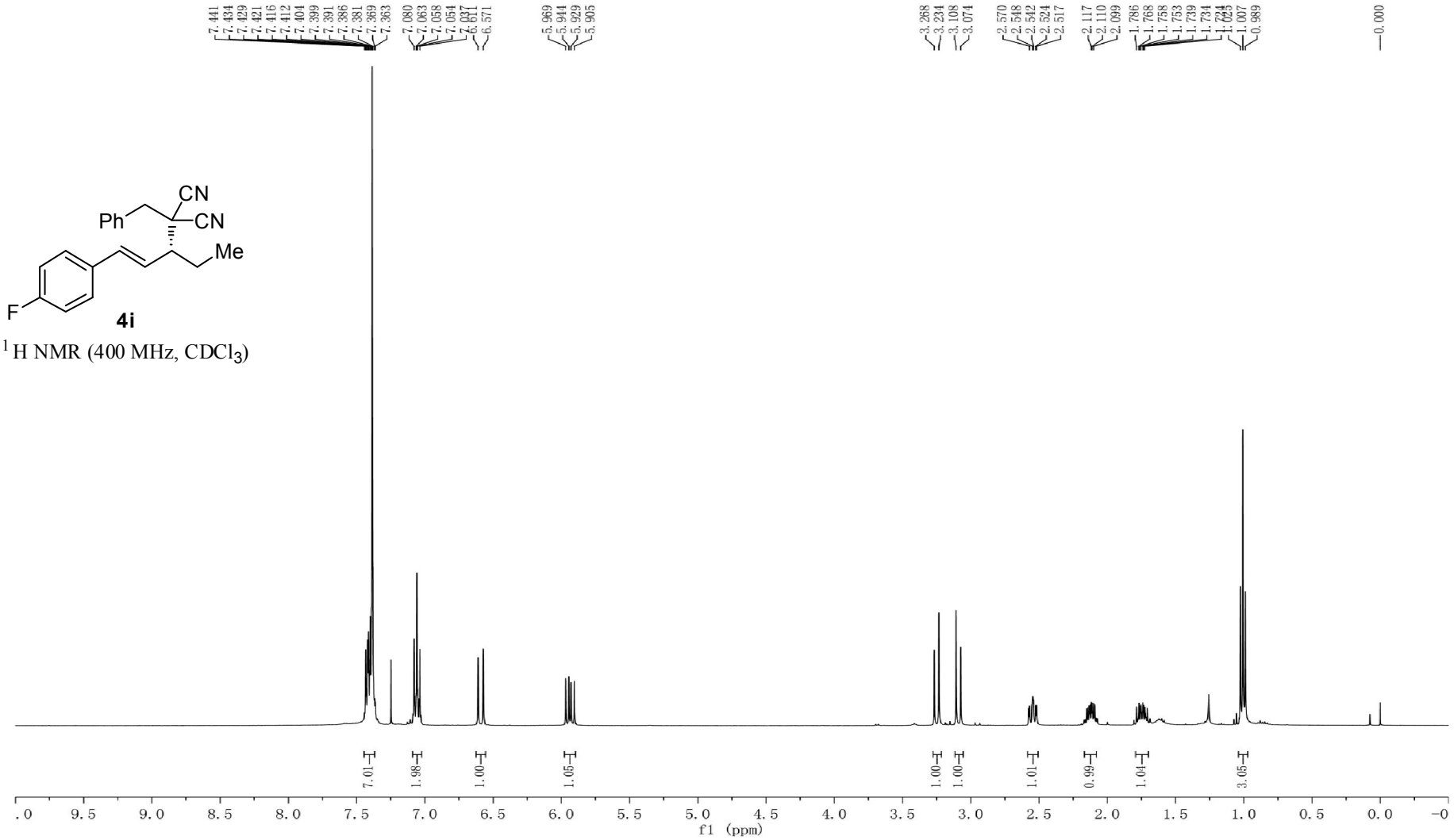


4g

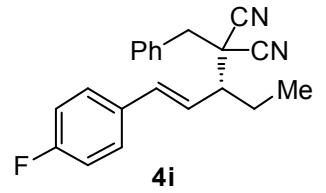
^{13}C NMR (100 MHz, $CDCl_3$)


CN
Ph
CN
Me
MeO
4h
1 H NMR (400 MHz, CDCl3)
7.407
7.400
7.394
7.391
7.385
7.378
7.371
7.366
7.362
7.357
7.350
6.916
6.910
6.899
6.544
5.899
5.874
5.860
5.835
3.832
3.821
3.285
3.251
3.092
3.058
2.558
2.534
2.530
2.524
2.506
2.113
2.106
2.095
1.780
1.762
1.752
1.747
1.734
1.729
1.006
0.987
0.000
7.00
1.99
1.00
1.04
3.01
1.00
1.00
1.04
1.05
1.03
3.05
f1 (ppm)


159.919
136.912
132.476
130.219
128.861
128.627
128.391
127.940
121.497
115.223
114.452
114.180
77.345
77.027
76.709
55.387
52.262
44.675
42.060
24.828
11.821
0.000
CN
Ph
CN
Me
MeO
4h
13 C NMR (100 MHz, 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)

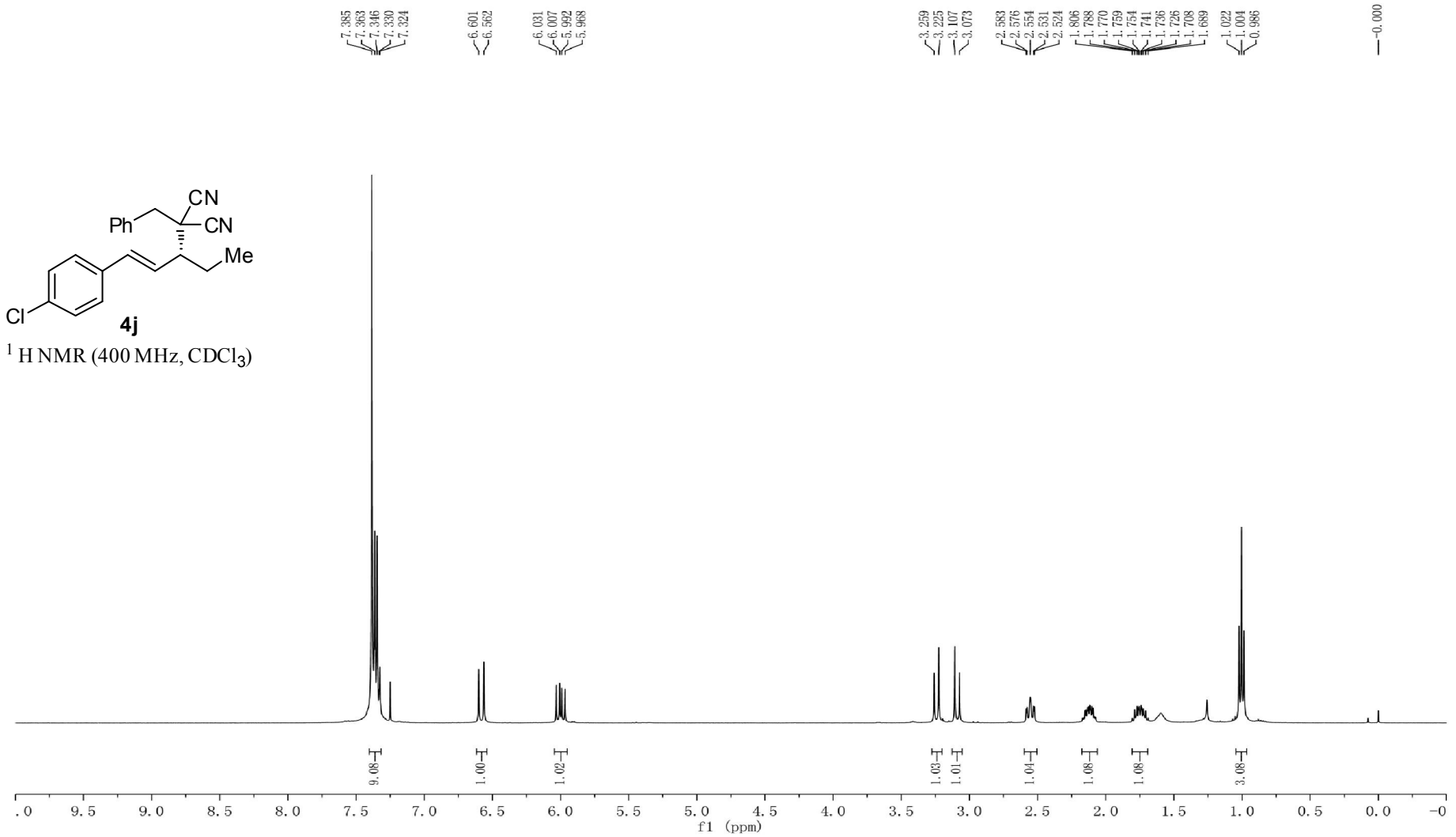


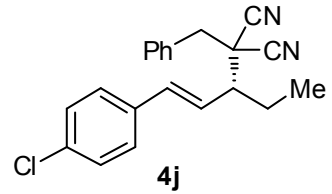
^{1}H NMR (400 MHz, $CDCl_3$)



4i

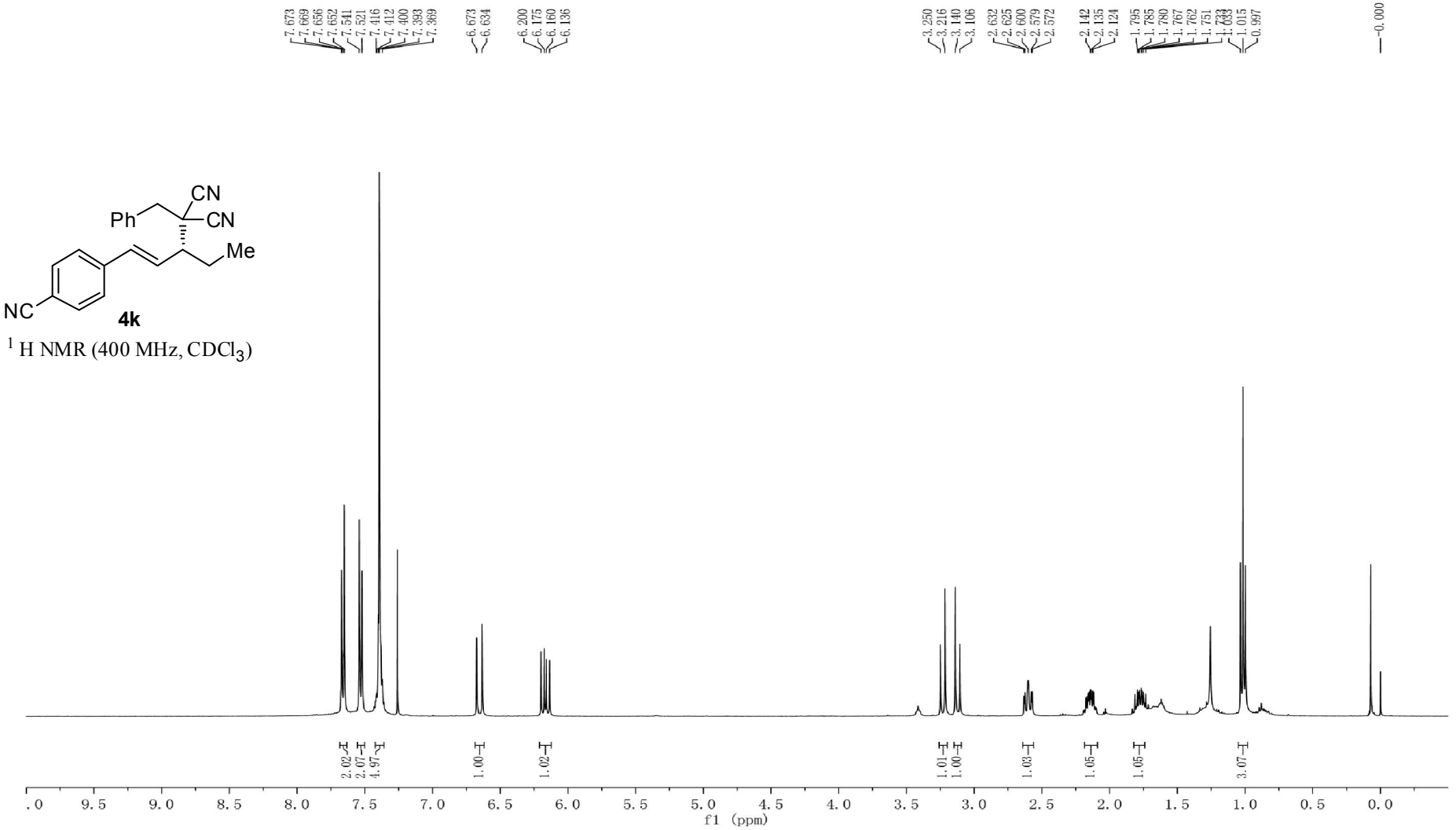
^{13}C NMR (100 MHz, $CDCl_3$)


7.385
7.363
7.346
7.330
7.324
6.601
6.562
6.031
6.007
5.992
5.968
3.259
3.225
3.107
3.073
2.583
2.576
2.554
2.531
2.524
1.806
1.788
1.770
1.759
1.754
1.741
1.736
1.726
1.708
1.689
1.022
1.004
0.986
0.000
CN
Ph
CN
Me
Cl
4j
1 H NMR (400 MHz, CDCl3)
9.08
1.00
1.02
1.03
1.01
1.04
1.08
1.08
3.08
f1 (ppm)

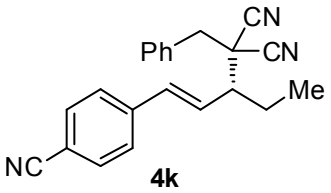


4j

^{13}C NMR (100 MHz, $CDCl_3$)

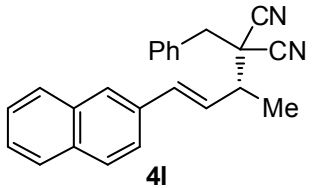


^{1}H NMR (400 MHz, $CDCl_3$)



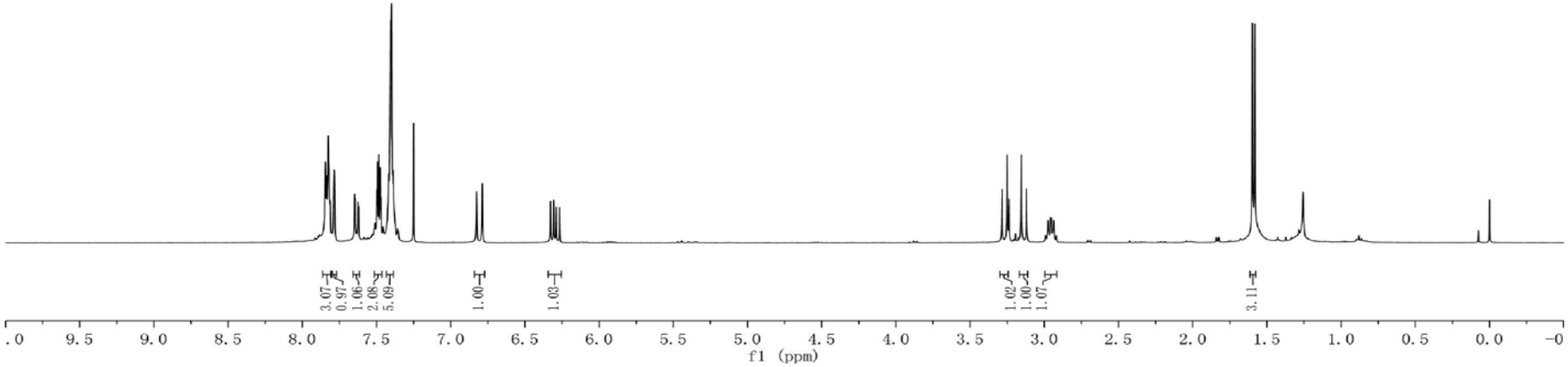
4k

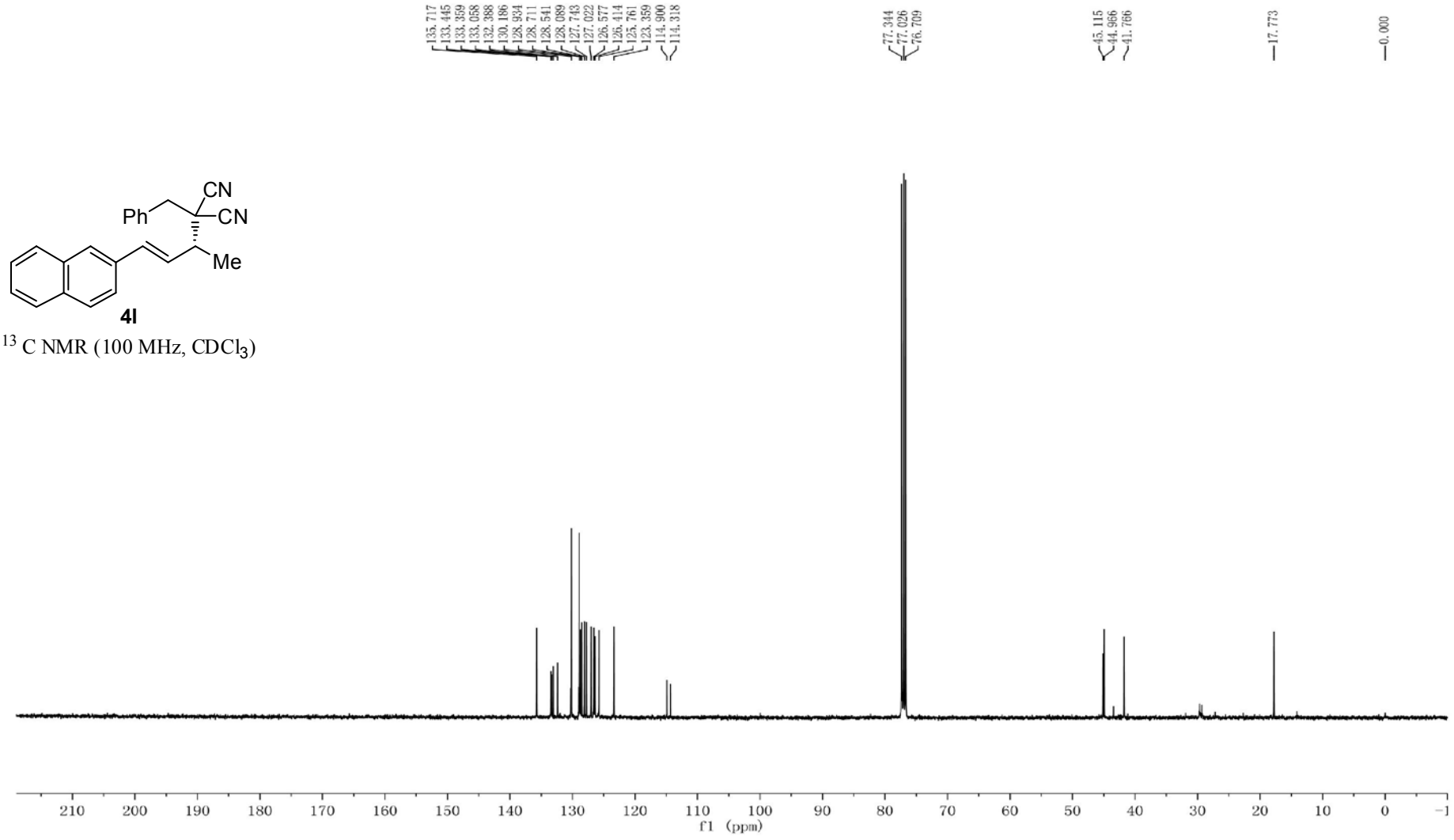
^{13}C NMR (100 MHz, $CDCl_3$)



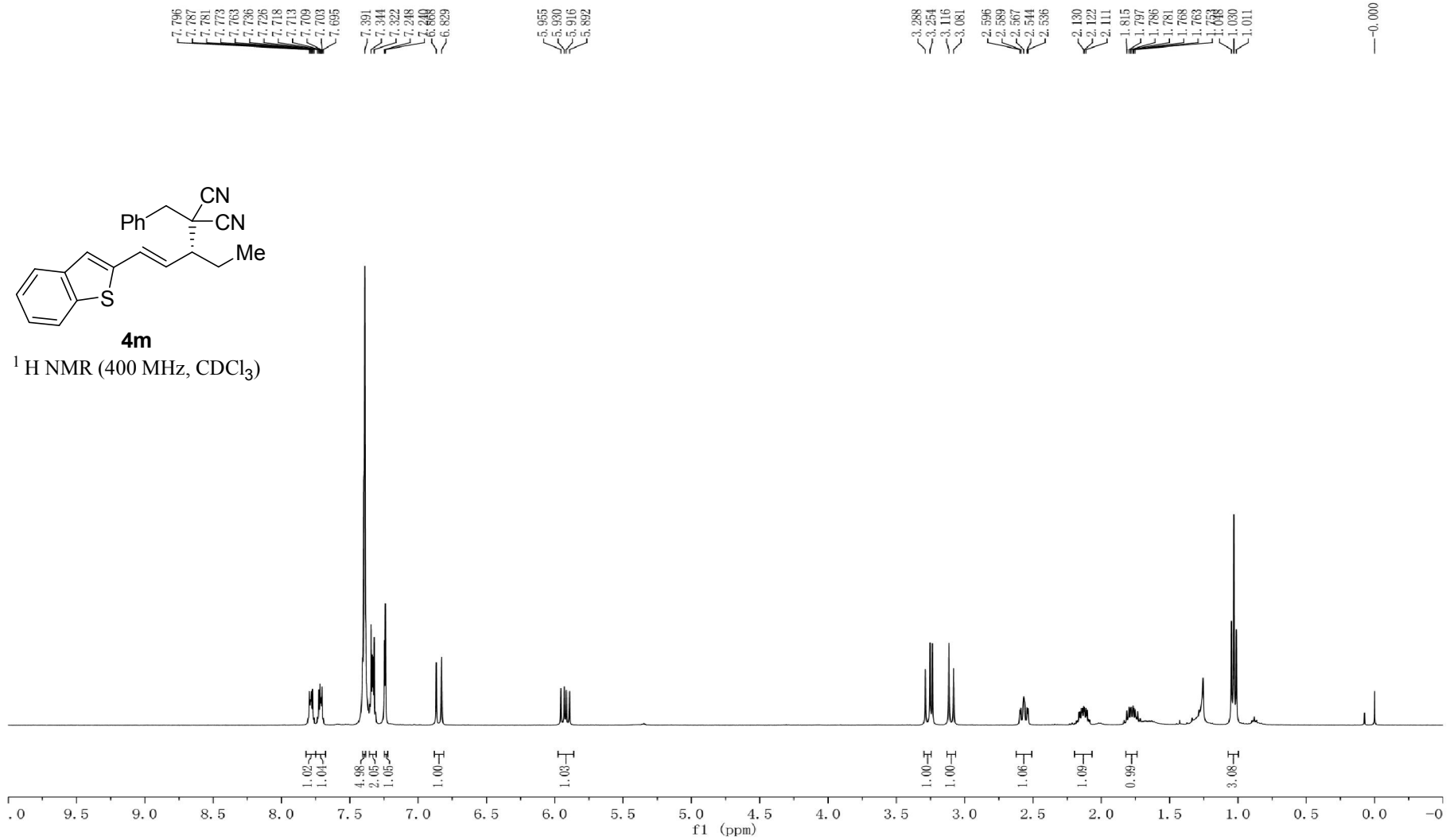
4l

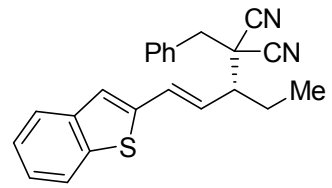
^{1}H NMR (400 MHz, $CDCl_3$)





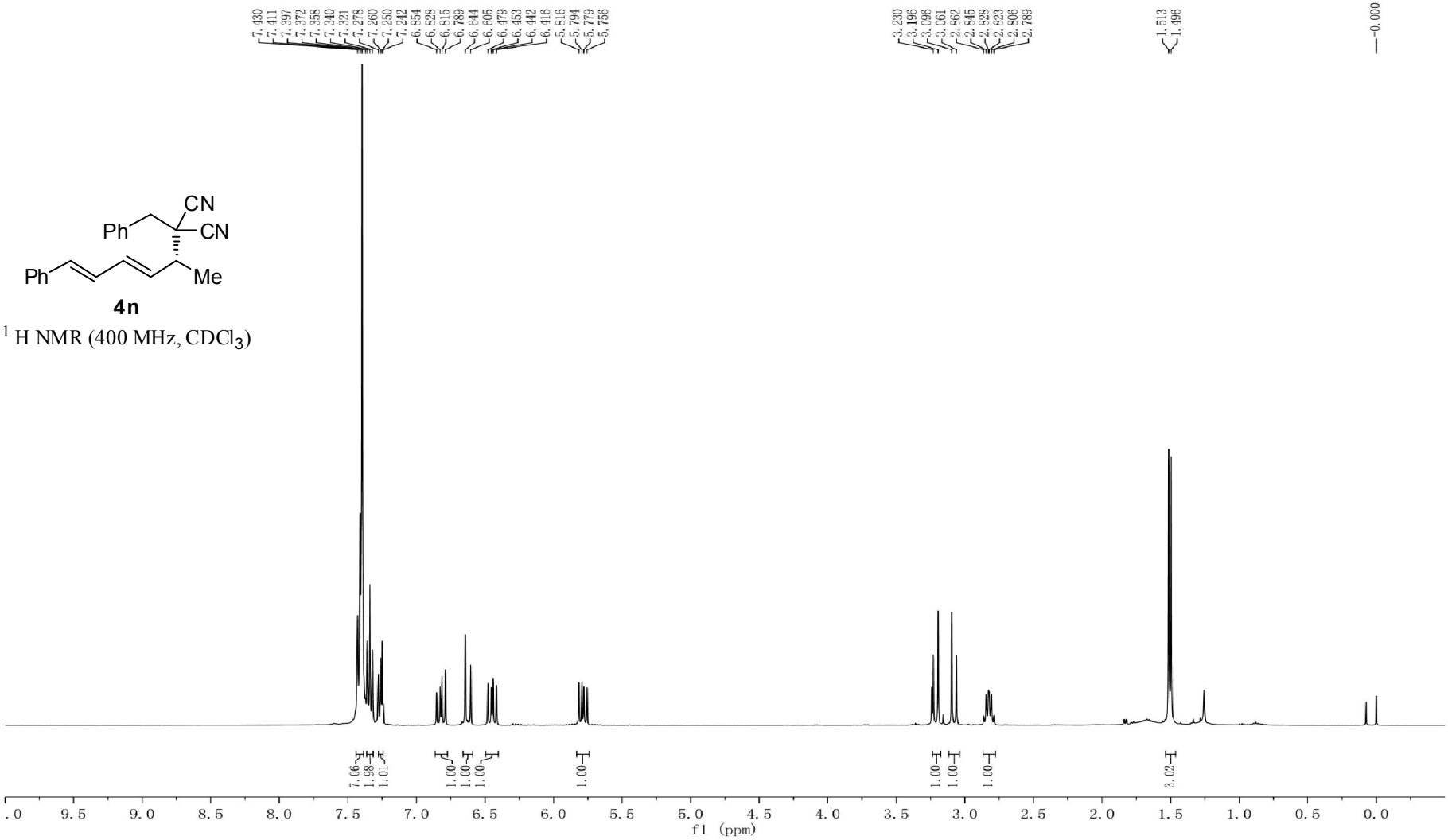
^{13}C NMR (100 MHz, $CDCl_3$)

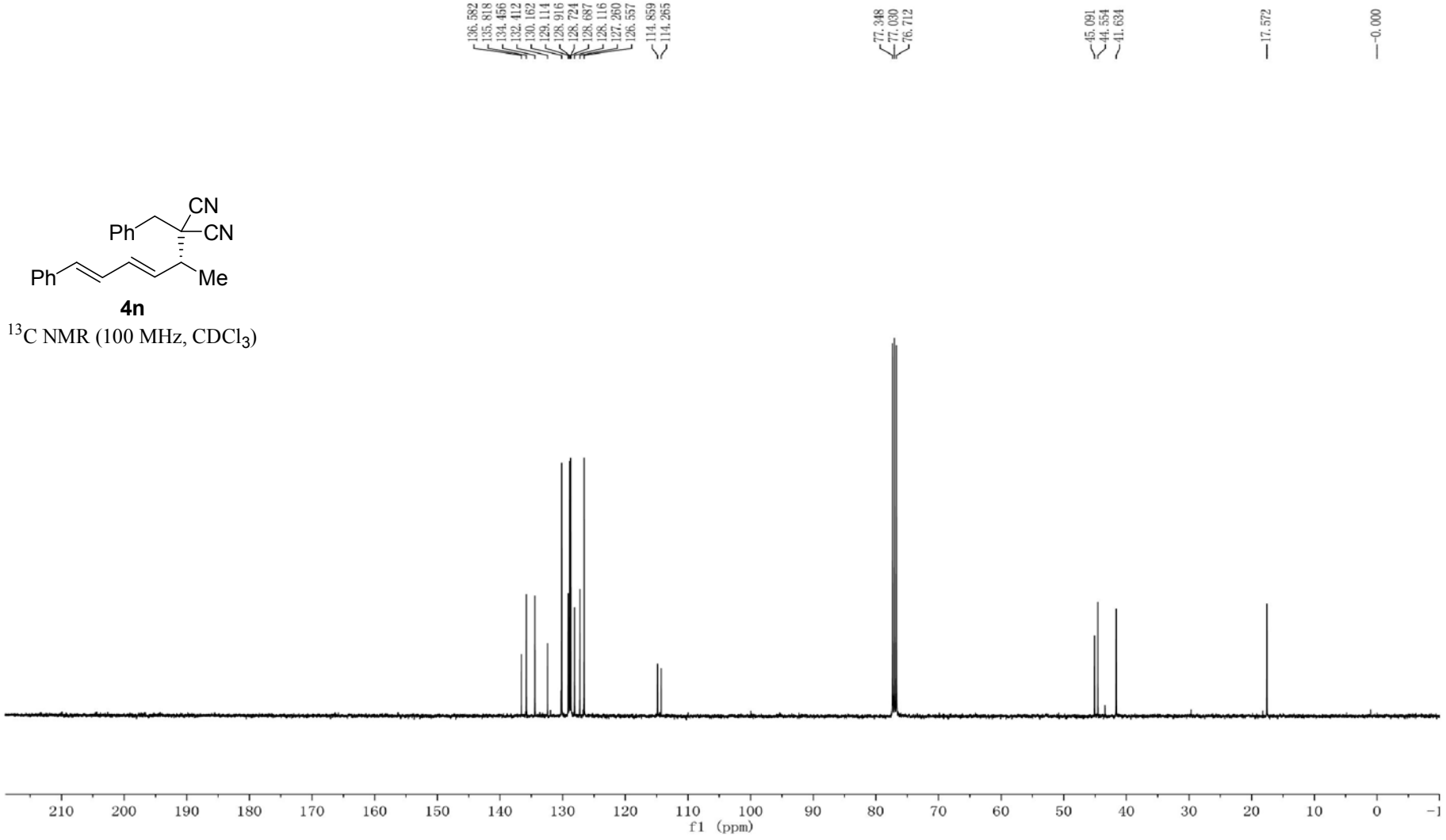

CN
Ph
CN
Me
S
4m
1 H NMR (400 MHz, CDCl3)
f1 (ppm)



4m

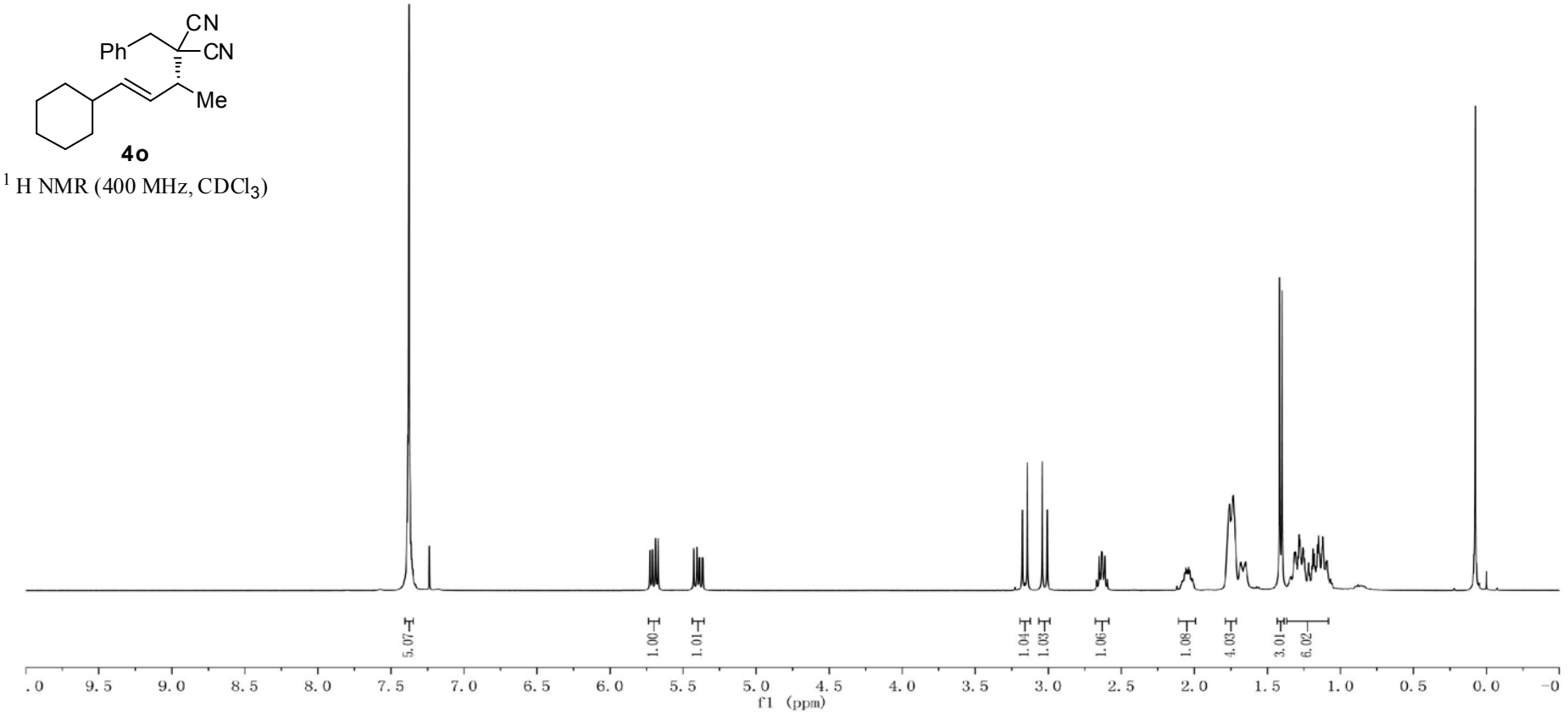
^{13}C NMR (100 MHz, $CDCl_3$)

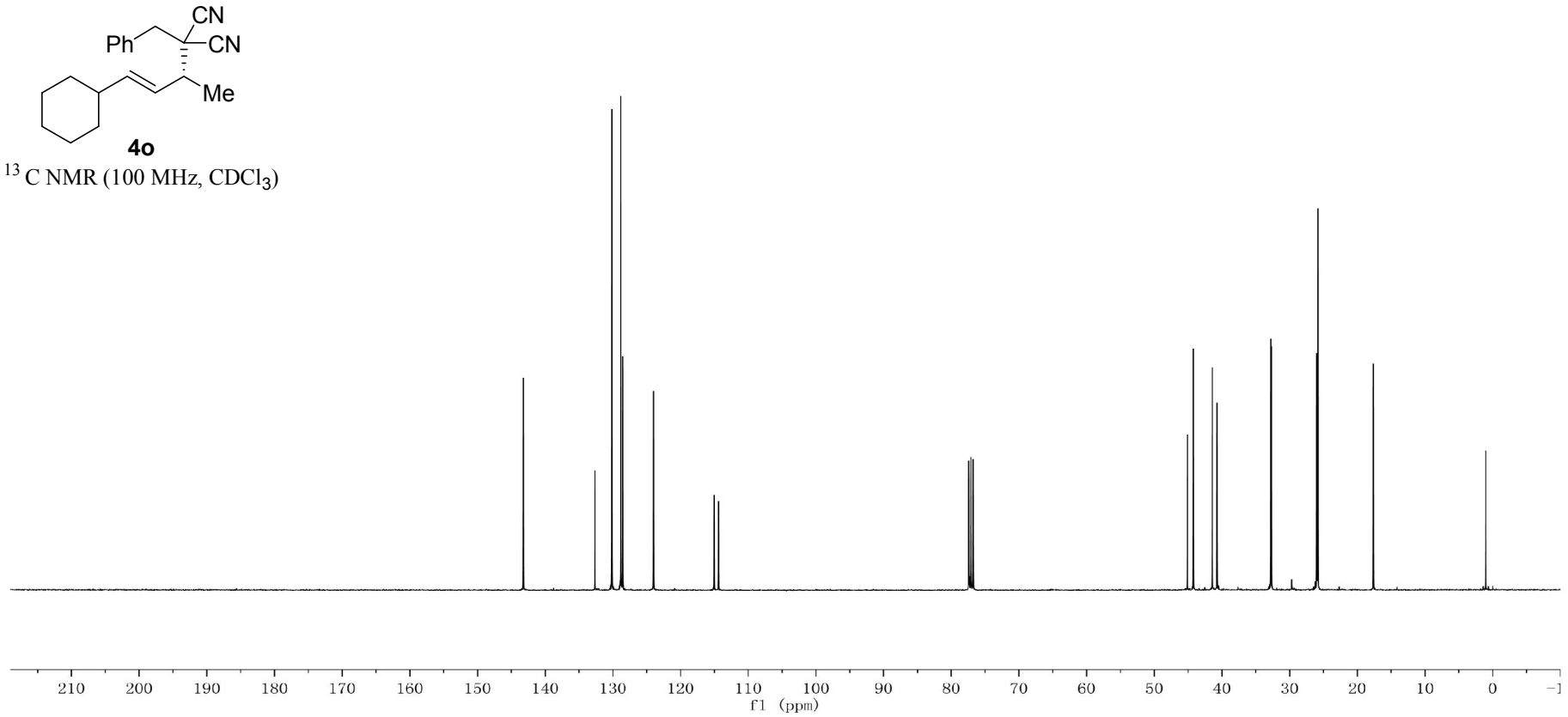

CN
Ph
CN
Ph
Me
4n
1 H NMR (400 MHz, CDCl3)
7.430
7.411
7.397
7.372
7.358
7.340
7.321
7.278
7.260
7.250
7.242
6.854
6.828
6.815
6.789
6.644
6.605
6.479
6.453
6.442
6.416
5.816
5.794
5.779
5.756
3.230
3.196
3.096
3.061
2.862
2.845
2.828
2.823
2.806
2.789
1.513
1.496
0.000
7.06
1.98
1.01
1.00
1.00
1.00
1.00
1.00
1.00
3.02
f1 (ppm)

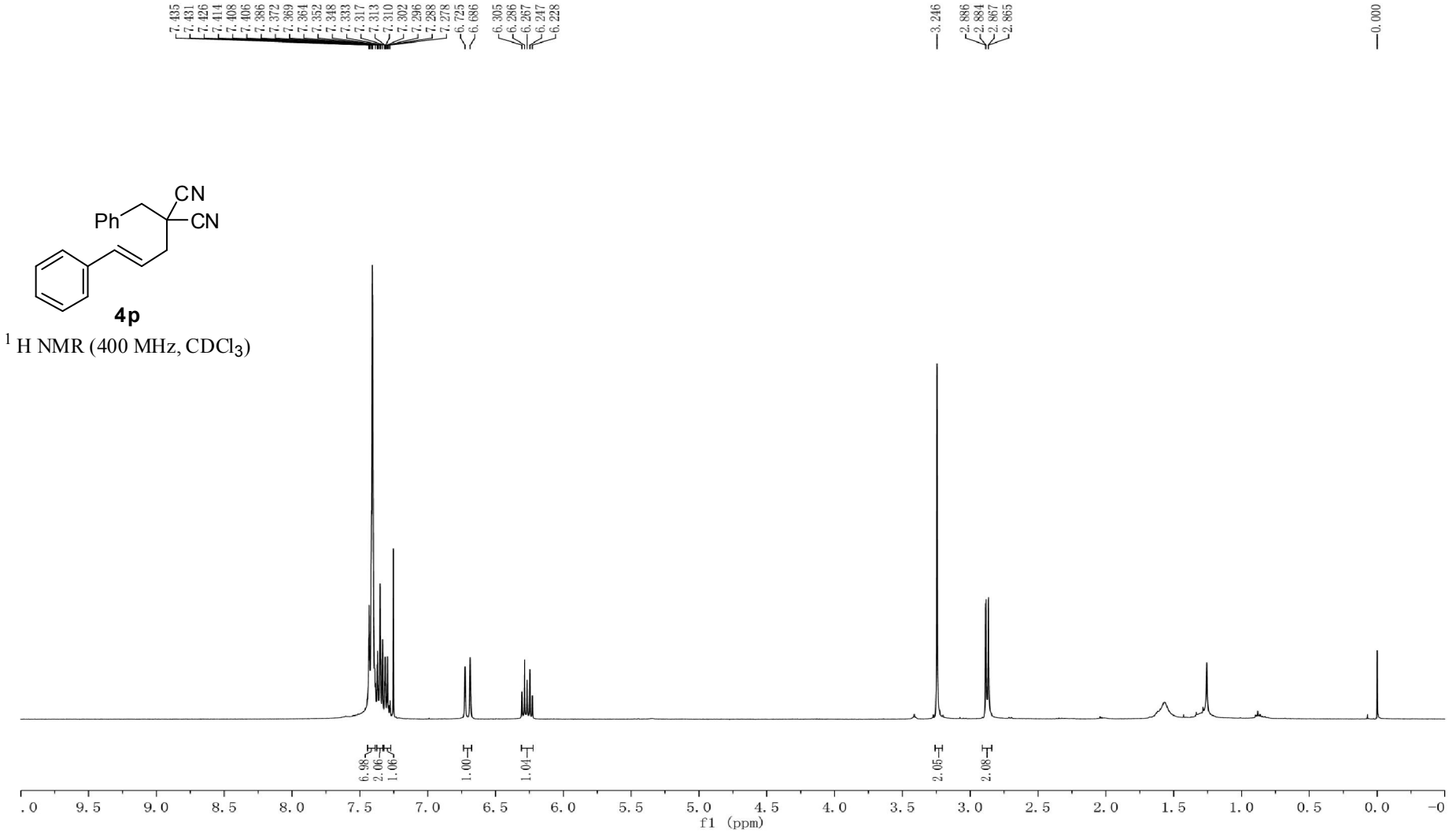


4n

^{13}C NMR (100 MHz, $CDCl_3$)

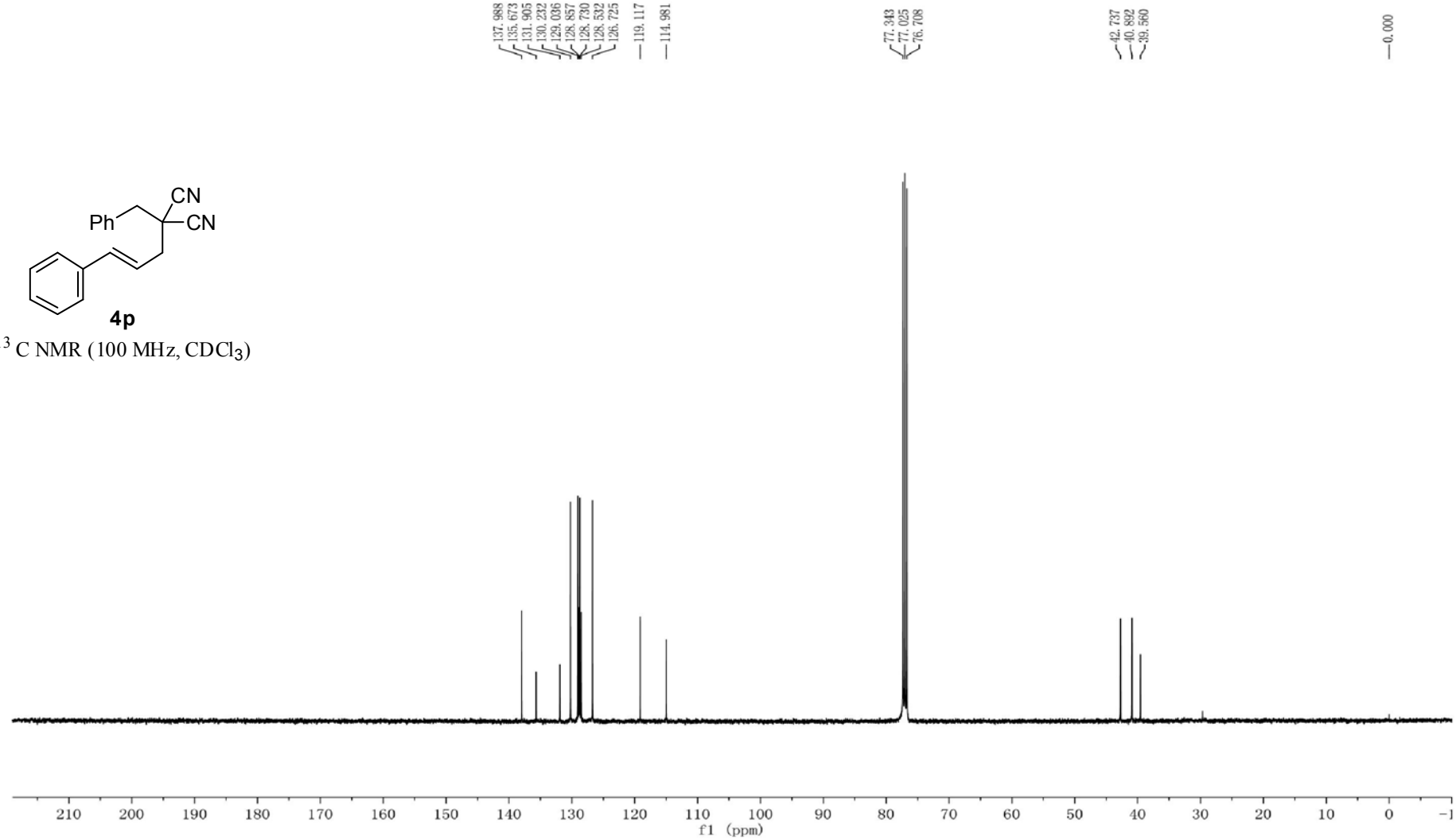

CN
Ph
CN
Me
4o
1 H NMR (400 MHz, CDCl3)
7.390
7.384
7.377
7.362
7.357
7.337
7.332
7.237
5.727
5.709
5.688
5.671
5.428
5.425
5.406
5.403
5.390
5.387
5.367
5.365
3.177
3.143
3.041
3.007
2.652
2.635
2.630
2.613
2.596
2.058
2.050
2.039
2.030
1.737
1.733
1.416
1.399
1.314
1.308
1.290
1.283
1.276
1.257
1.253
1.187
1.180
1.157
1.150
0.000
5.07
1.00
1.01
1.04
1.03
1.06
1.08
4.03
3.01
6.02
f1 (ppm)


143.243
132.642
130.159
128.841
128.567
123.984
115.029
114.399
77.407
77.089
76.771
45.106
44.237
41.427
40.717
32.772
32.705
25.997
25.830
17.621
0.000
CN
Ph
CN
Me
4o
13 C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)

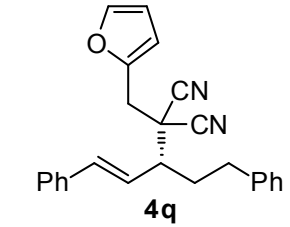


4p

^{1}H NMR (400 MHz, $CDCl_3$)

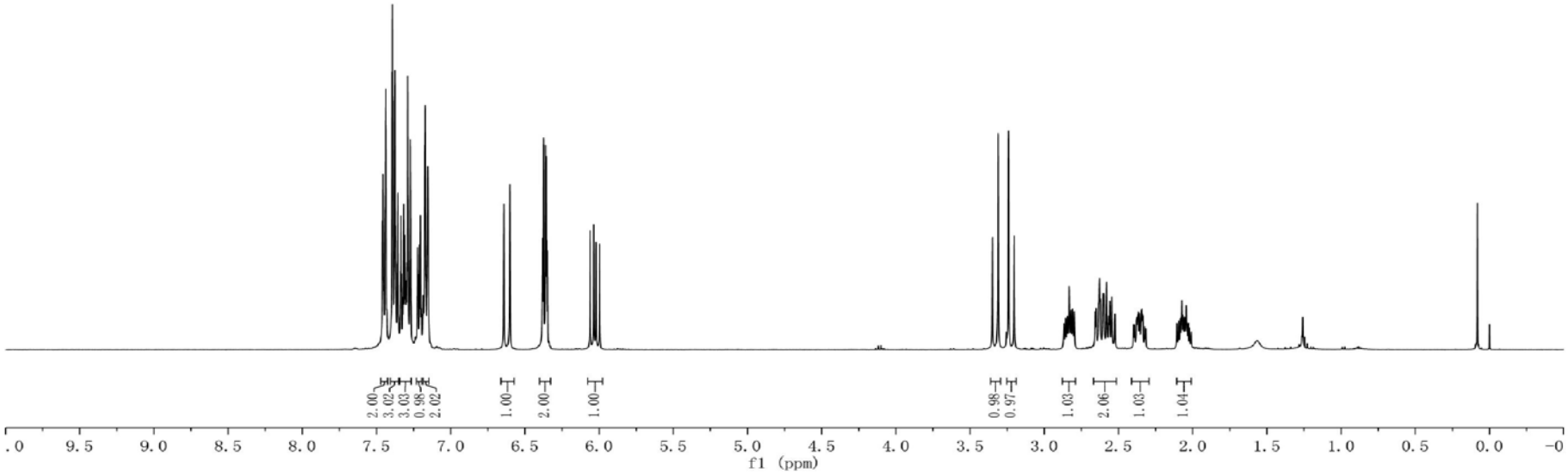


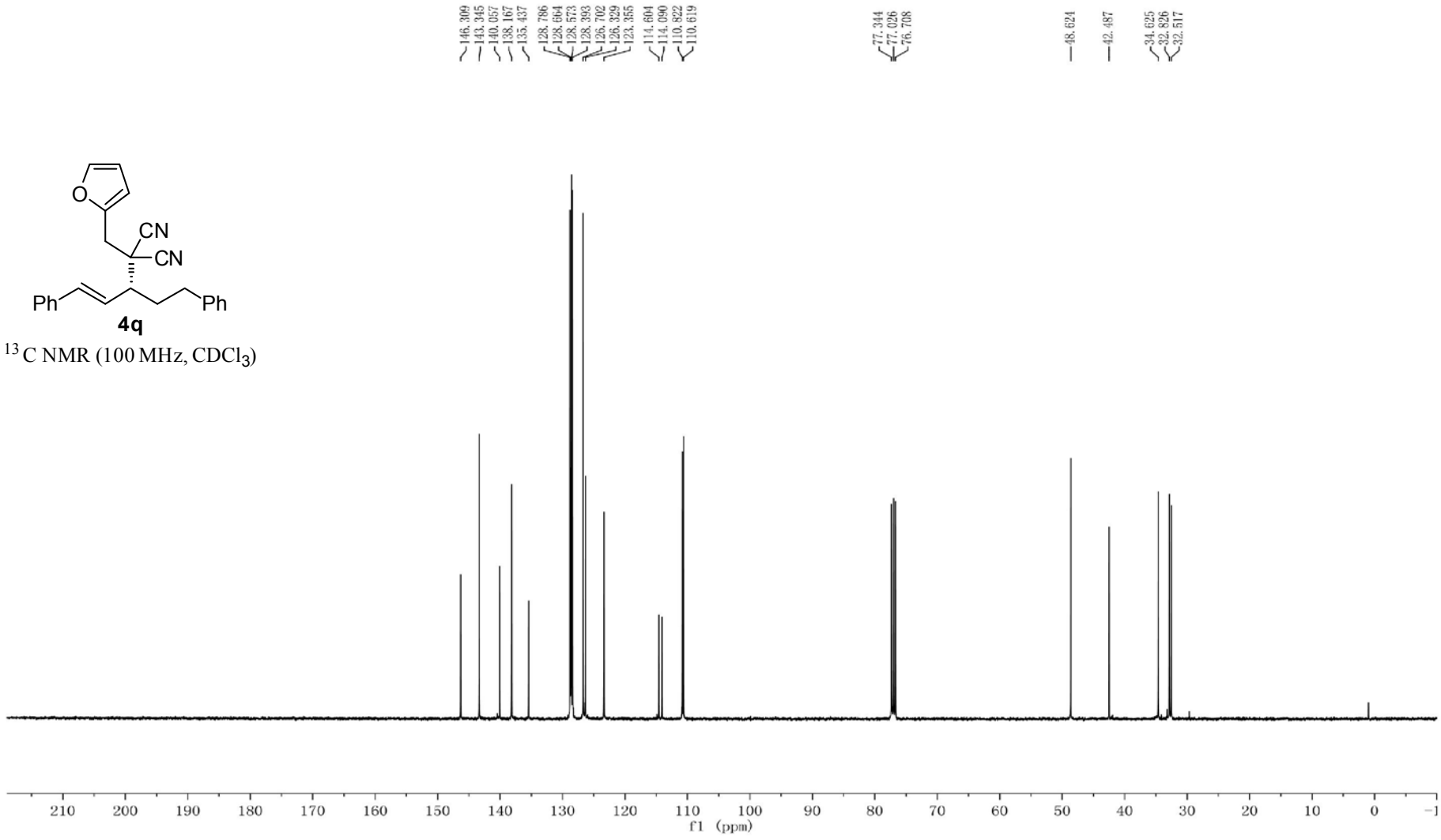
^{13}C NMR (100 MHz, $CDCl_3$)



4q

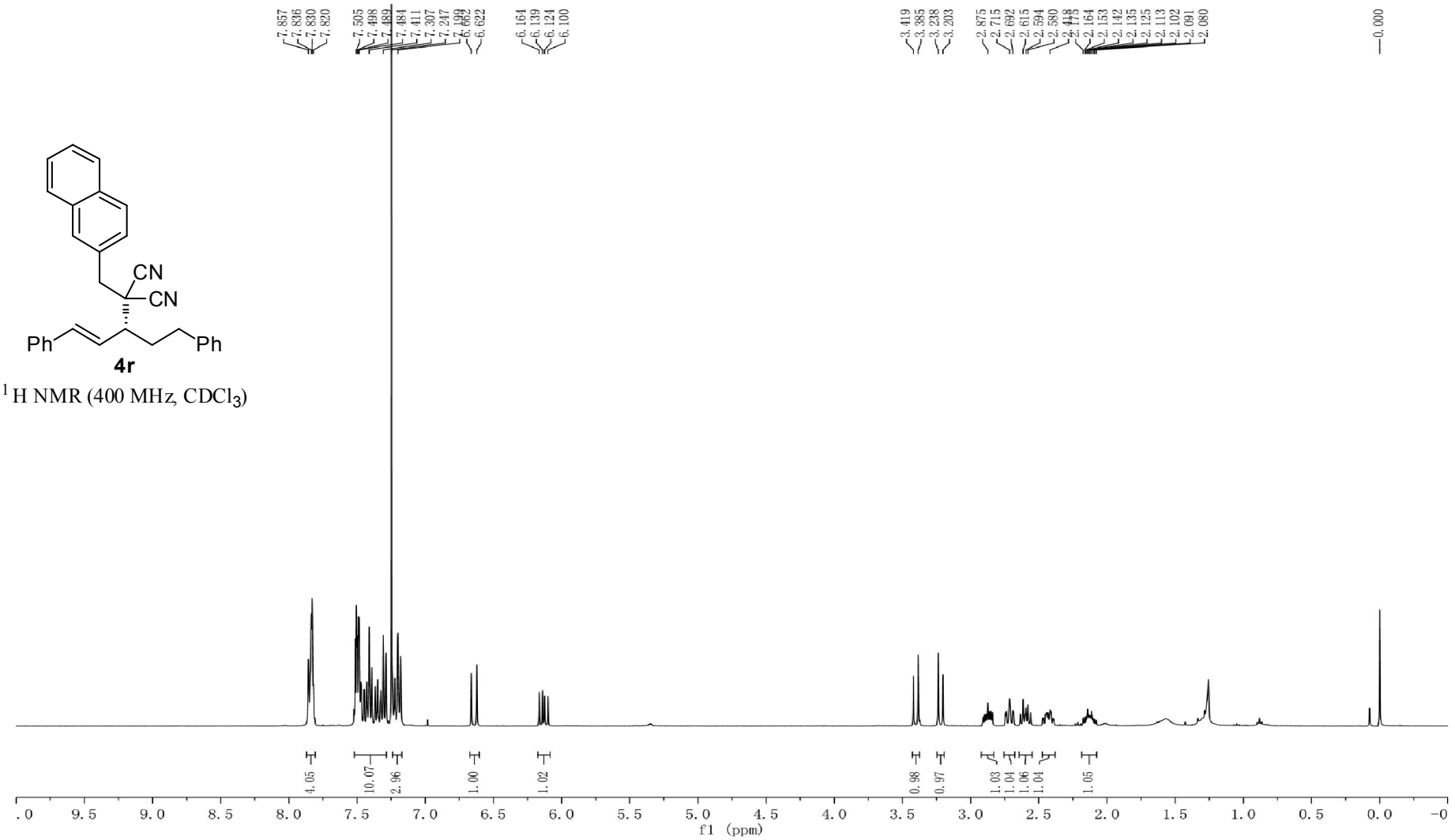
^{1}H NMR (400 MHz, $CDCl_3$)



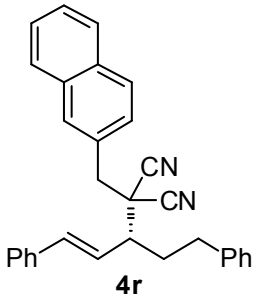


4q

^{13}C NMR (100 MHz, $CDCl_3$)

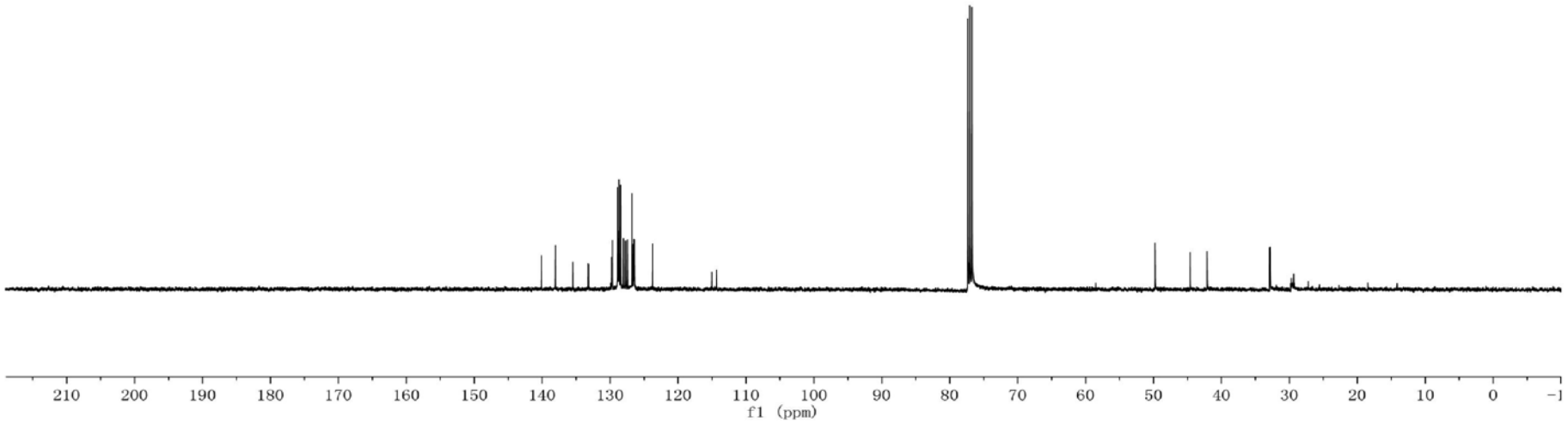


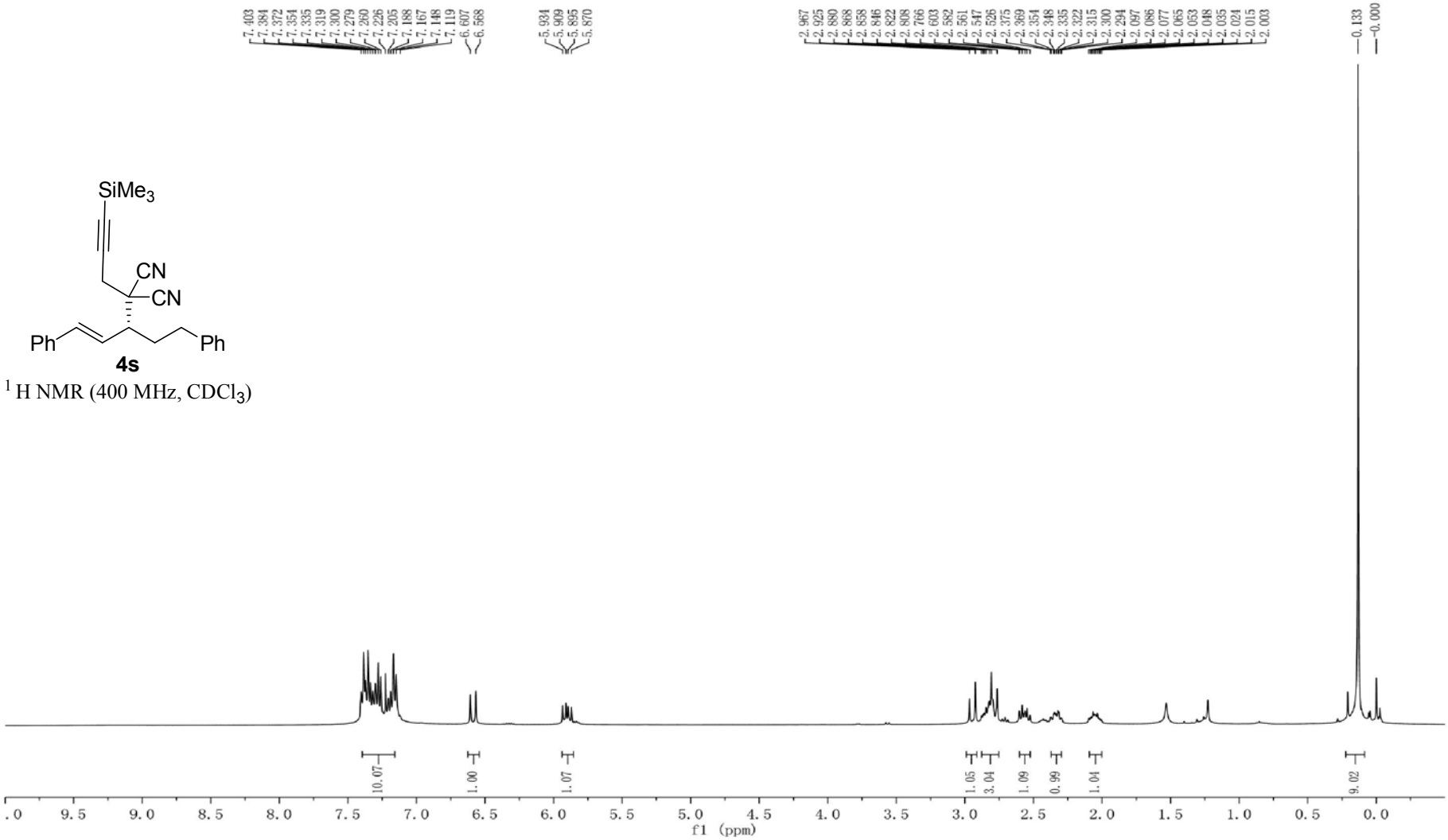
^{1}H NMR (400 MHz, $CDCl_3$)



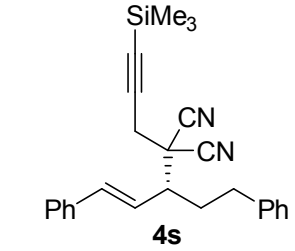
4r

^{13}C NMR (100 MHz, $CDCl_3$)



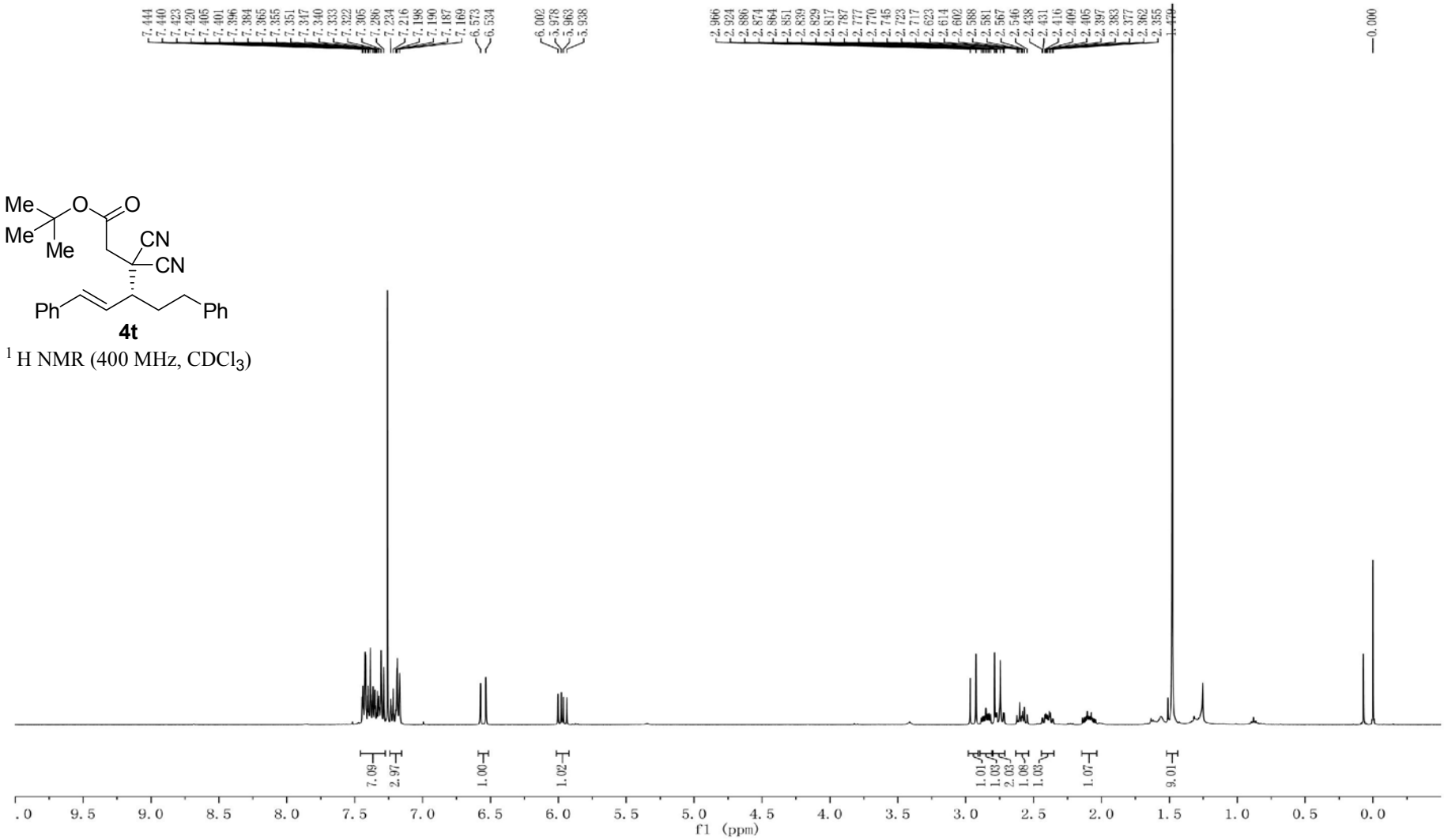


^{1}H NMR (400 MHz, $CDCl_3$)

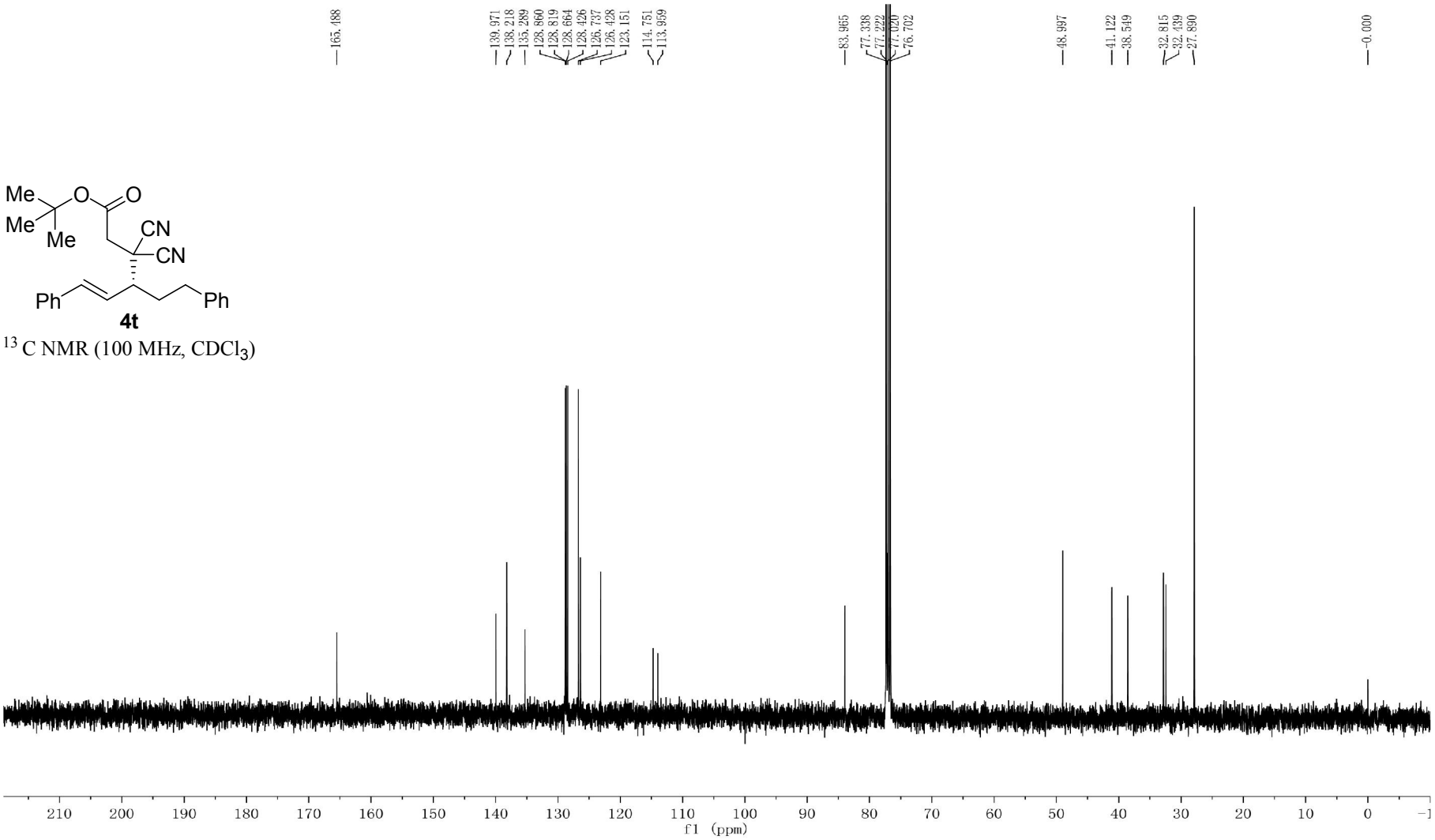


4s

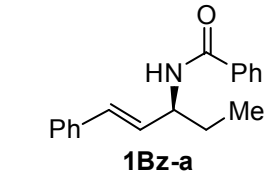
^{13}C NMR (100 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)

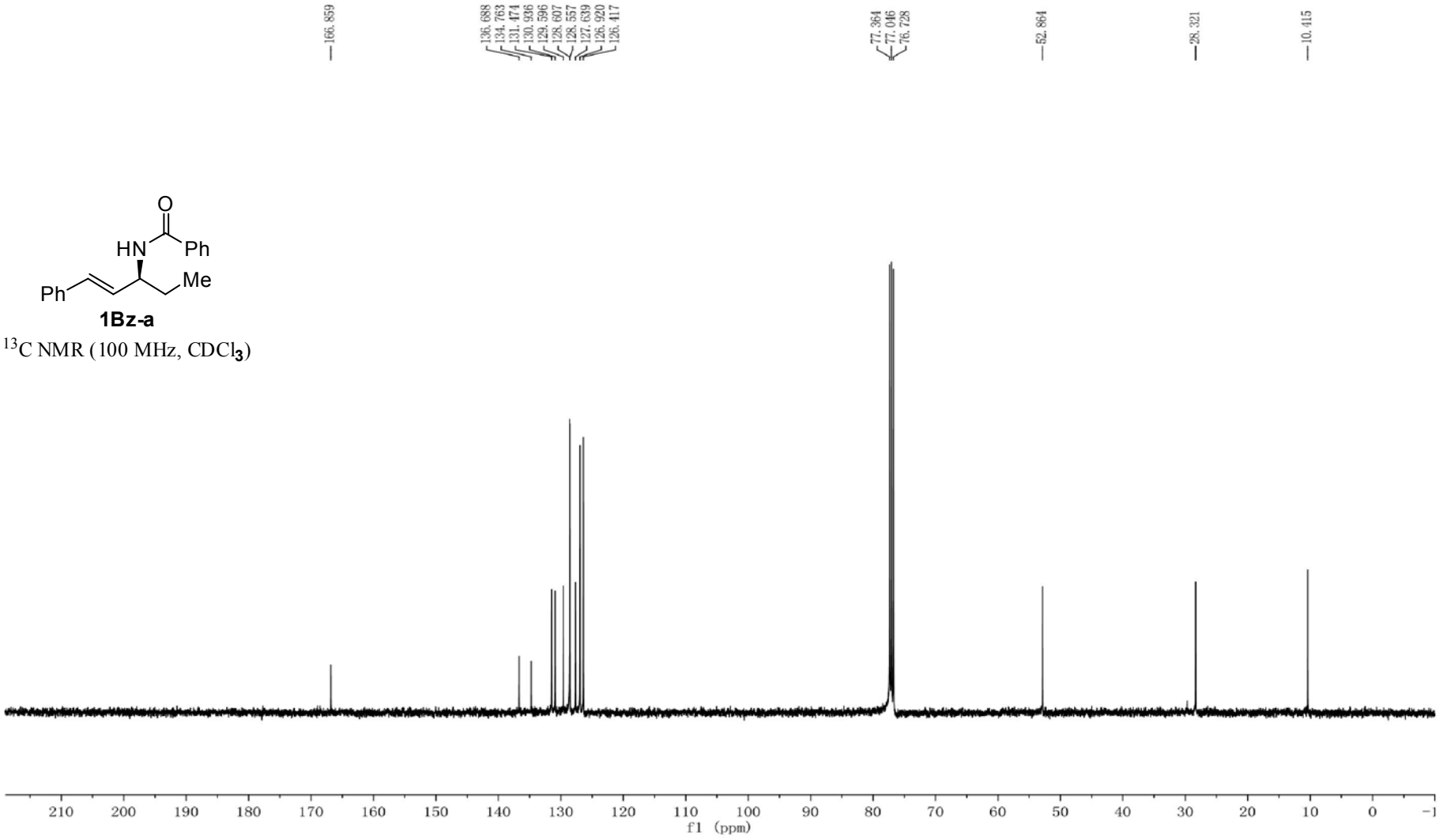


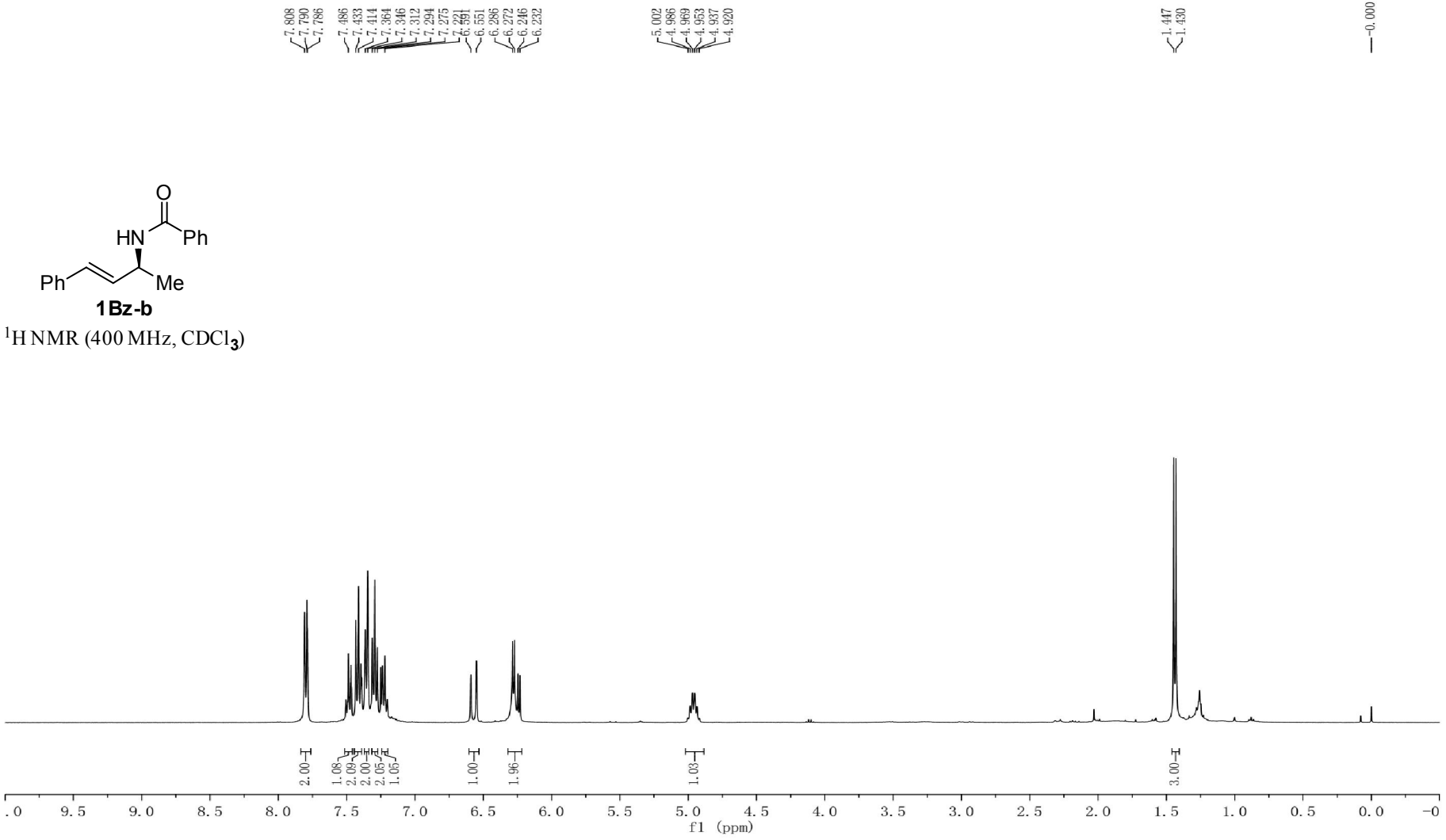
^{13}C NMR (100 MHz, $CDCl_3$)



1Bz-a

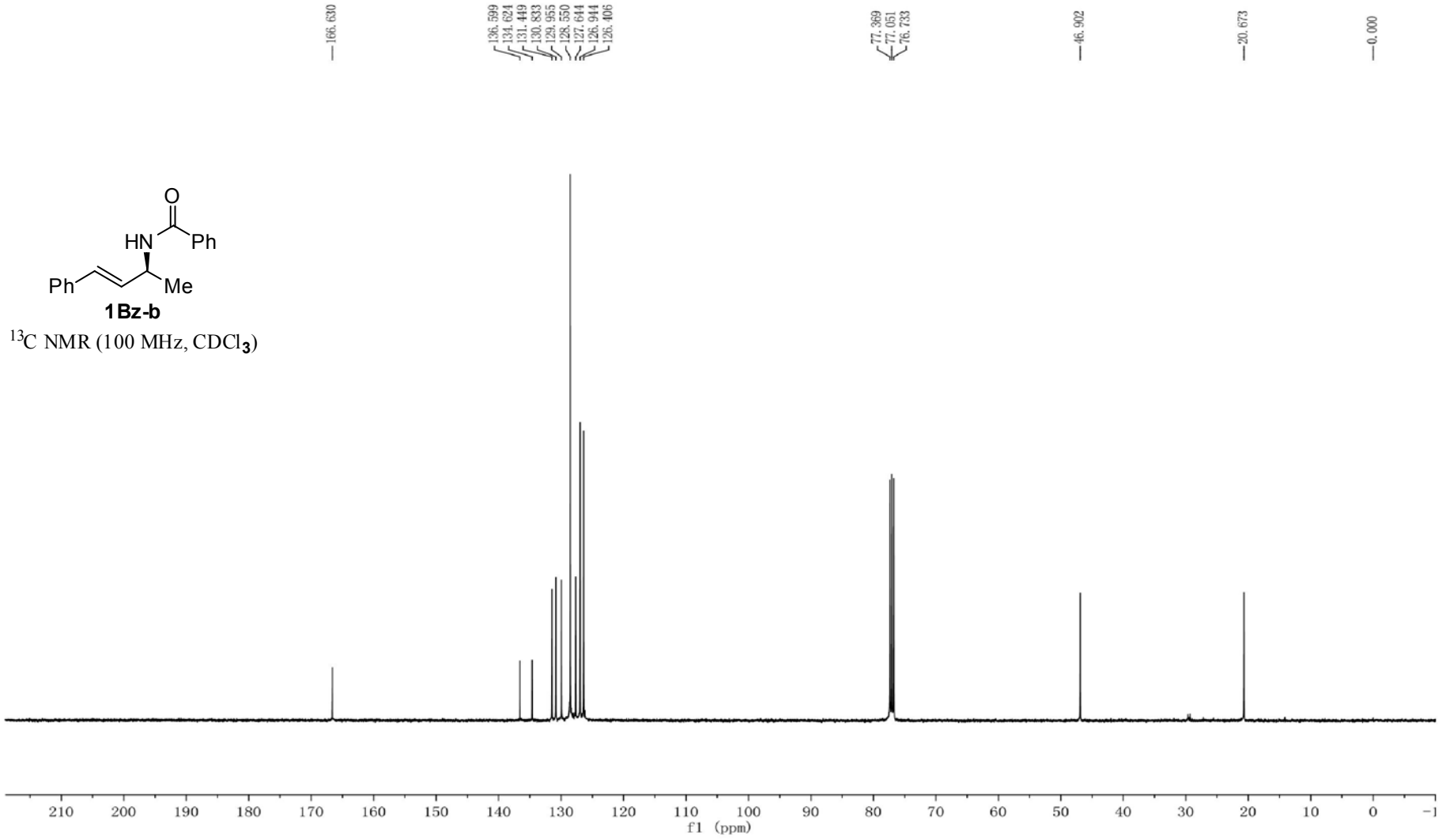
^{1}H NMR (400 MHz, $CDCl_3$)

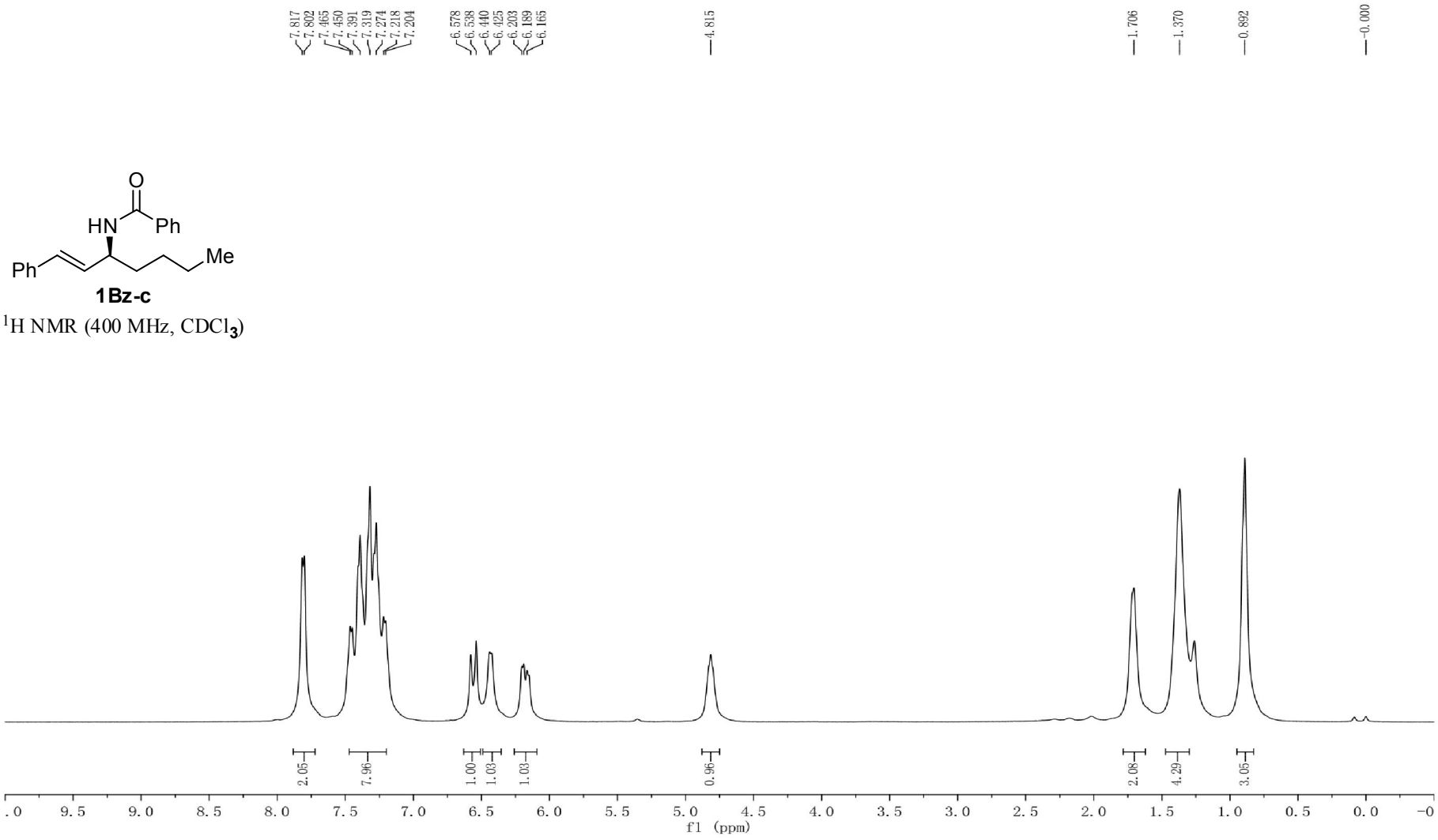

166.859
136.688
134.763
131.474
130.936
129.596
128.607
128.557
127.639
126.920
126.417
77.364
77.046
76.728
52.864
28.321
10.415
O
HN
Ph
Me
Ph
1Bz-a
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



1Bz-b

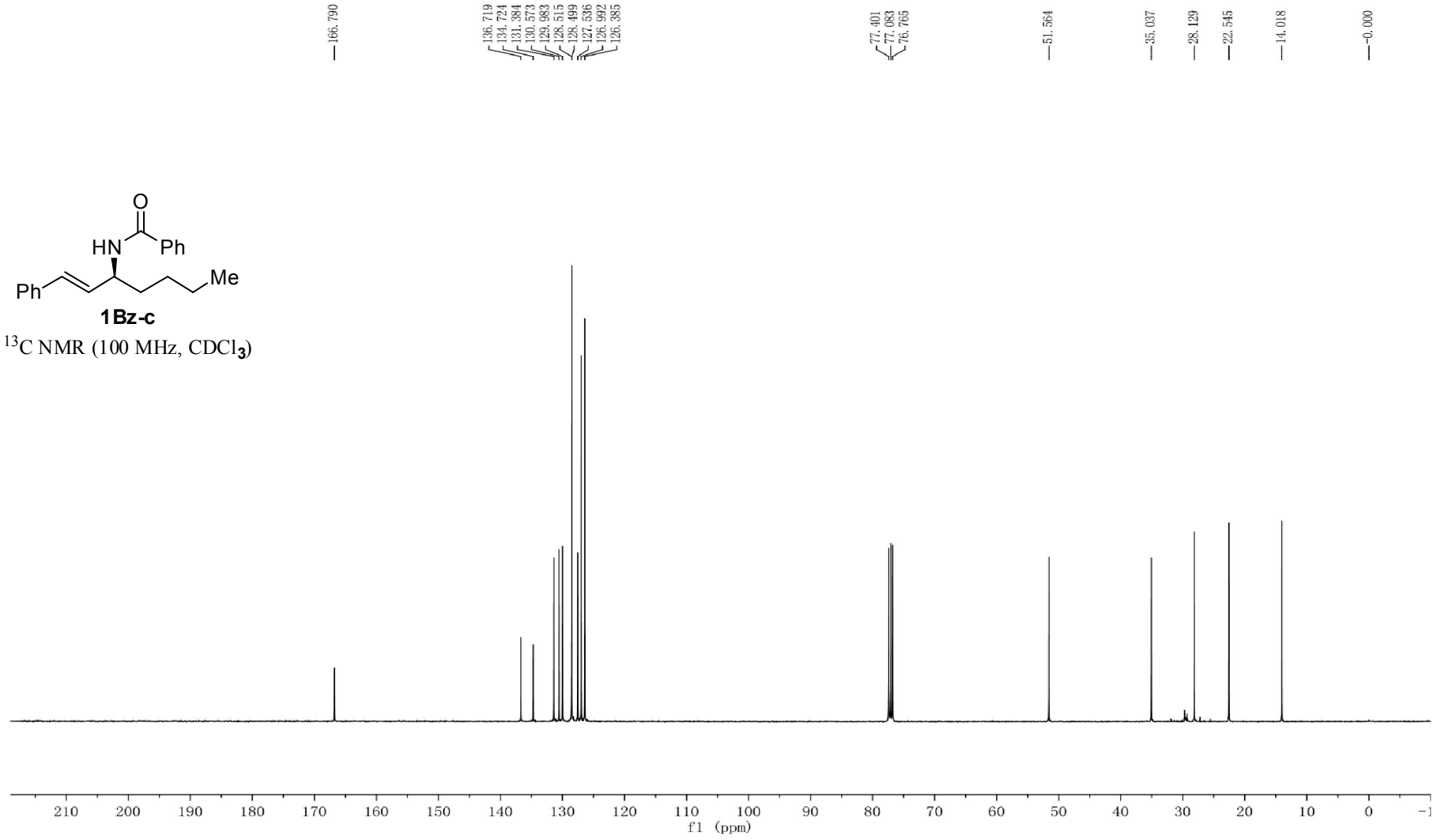
^{1}H NMR (400 MHz, $CDCl_3$)

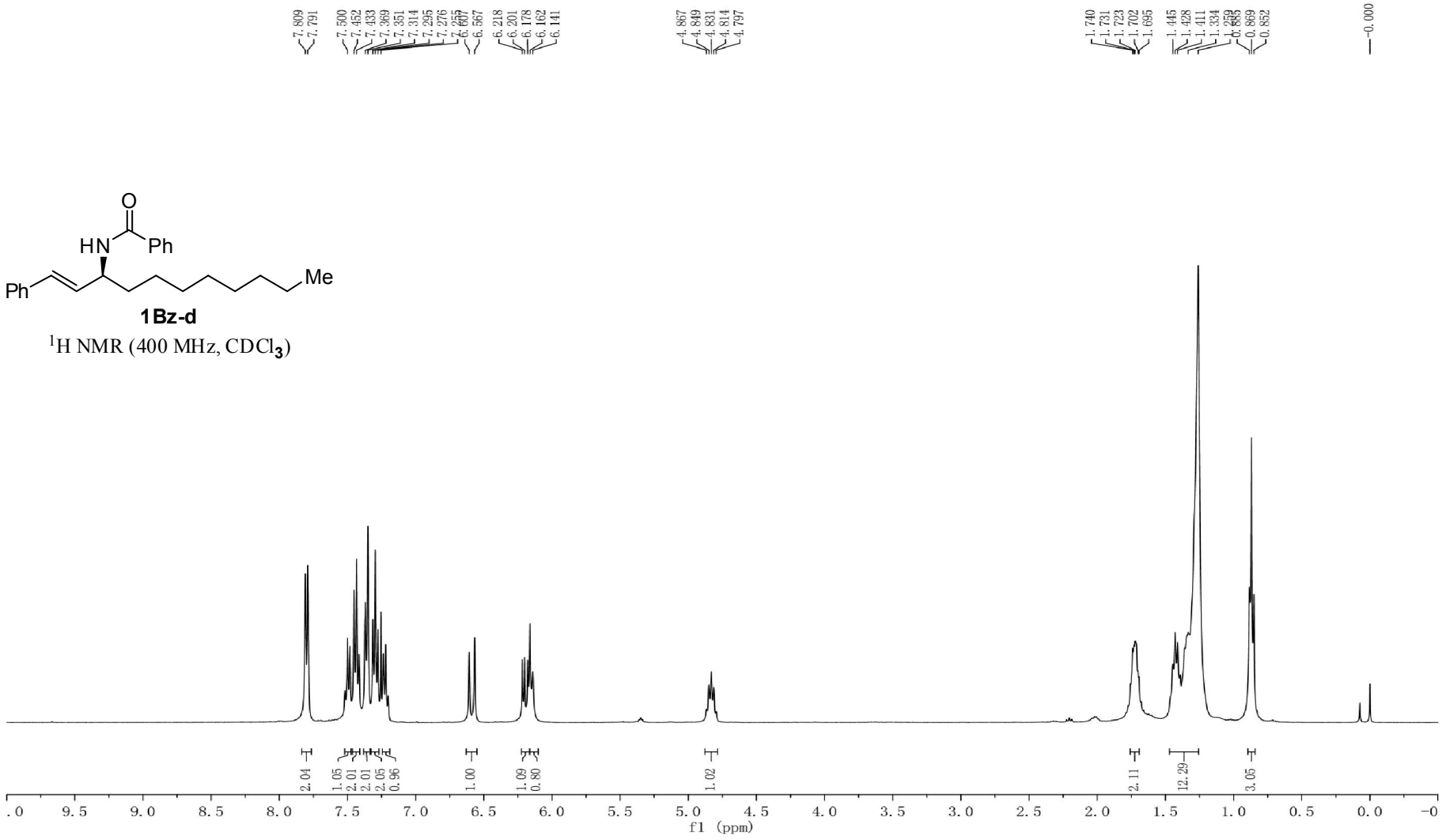

166.630
136.599
134.624
131.449
130.833
129.955
128.550
127.644
126.944
126.406
77.369
77.051
76.733
46.902
20.673
0.000
O
HN
Ph
Ph
Me
1Bz-b
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



1Bz-c

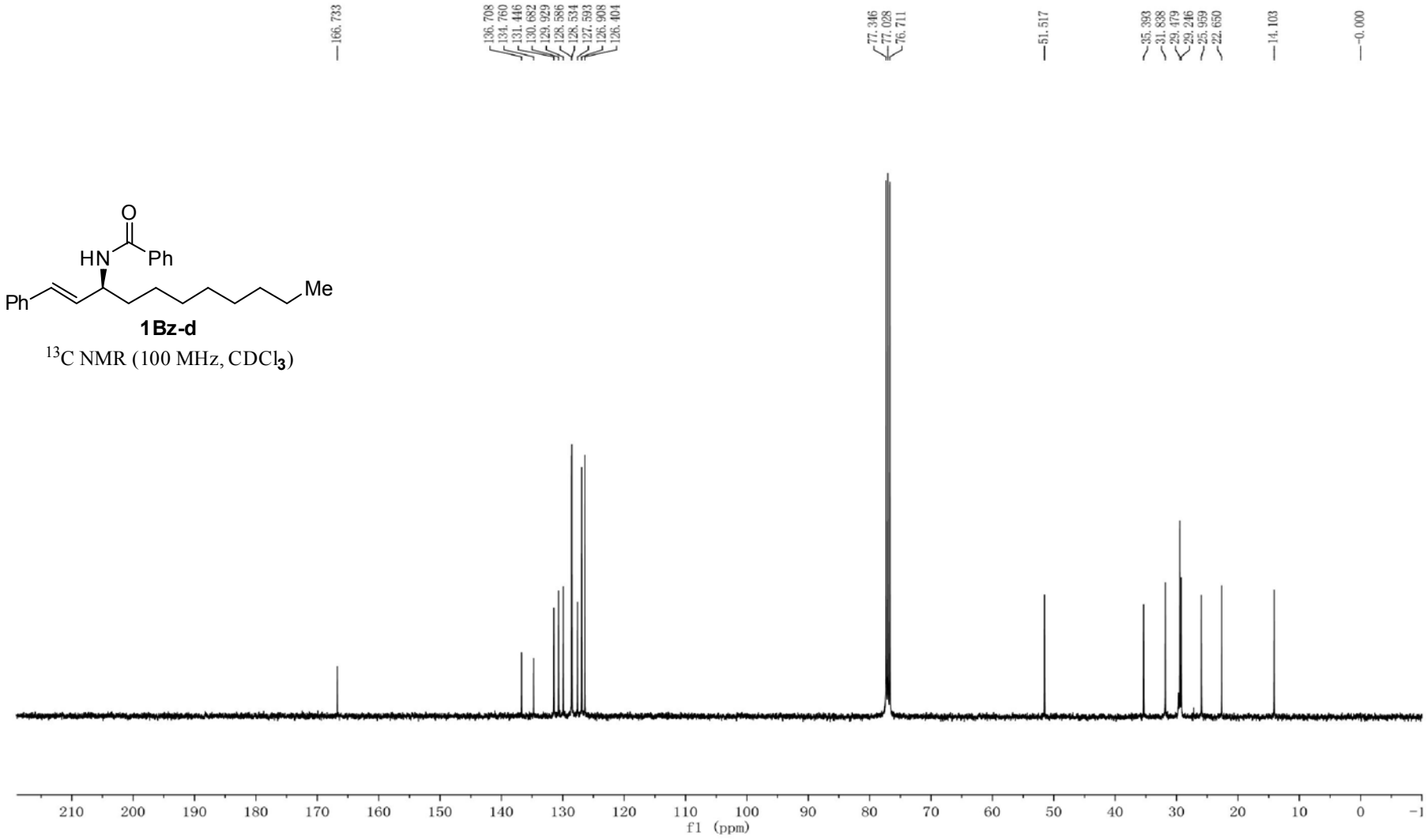
^{1}H NMR (400 MHz, $CDCl_3$)


166.790
136.719
134.724
131.384
130.573
129.983
128.515
128.499
127.536
126.992
126.385
77.401
77.083
76.765
51.564
35.037
28.129
22.545
14.018
0.000
O
HN
Ph
Ph
Me
1Bz-c
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



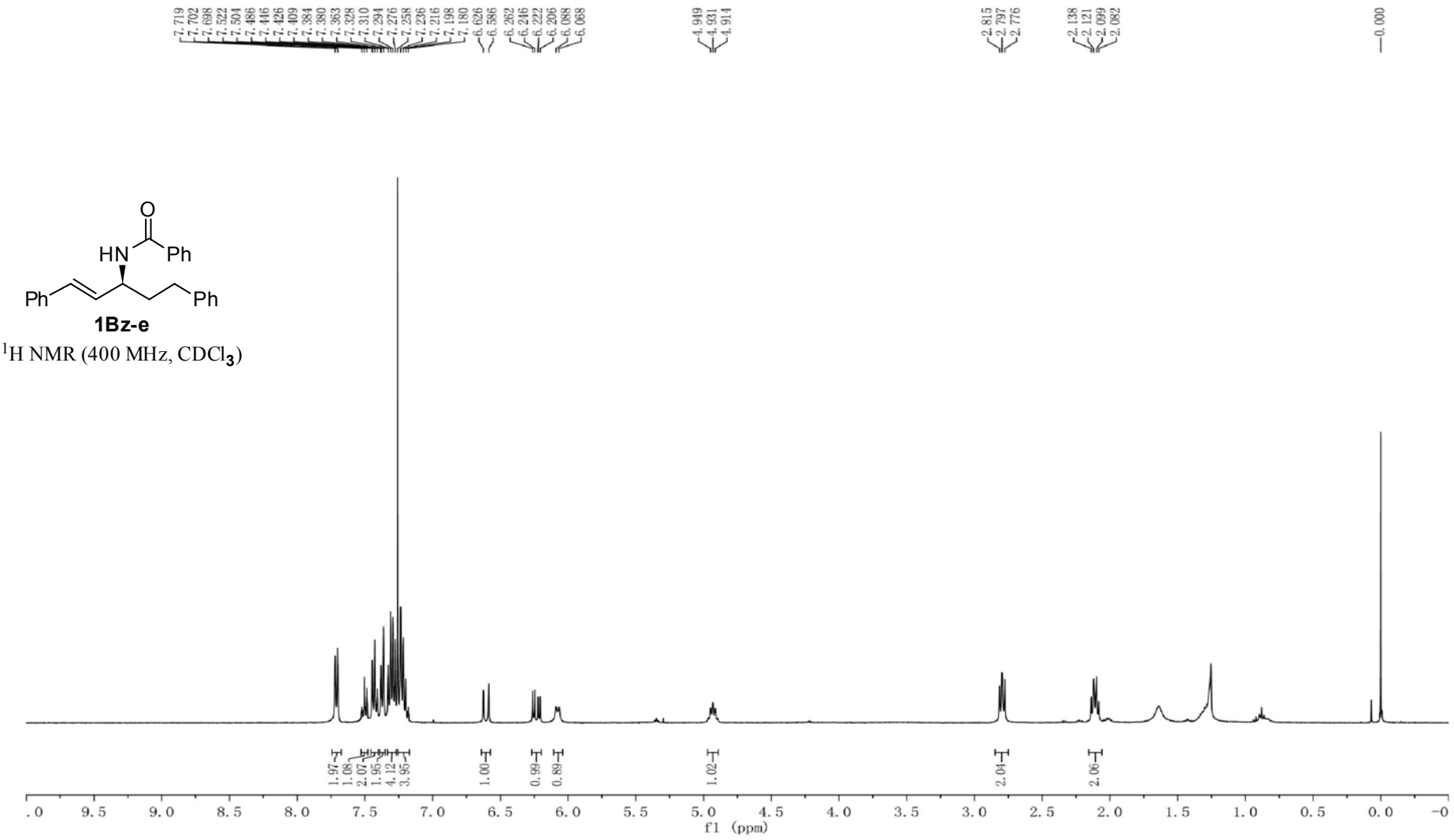
1Bz-d

^{1}H NMR (400 MHz, $CDCl_3$)



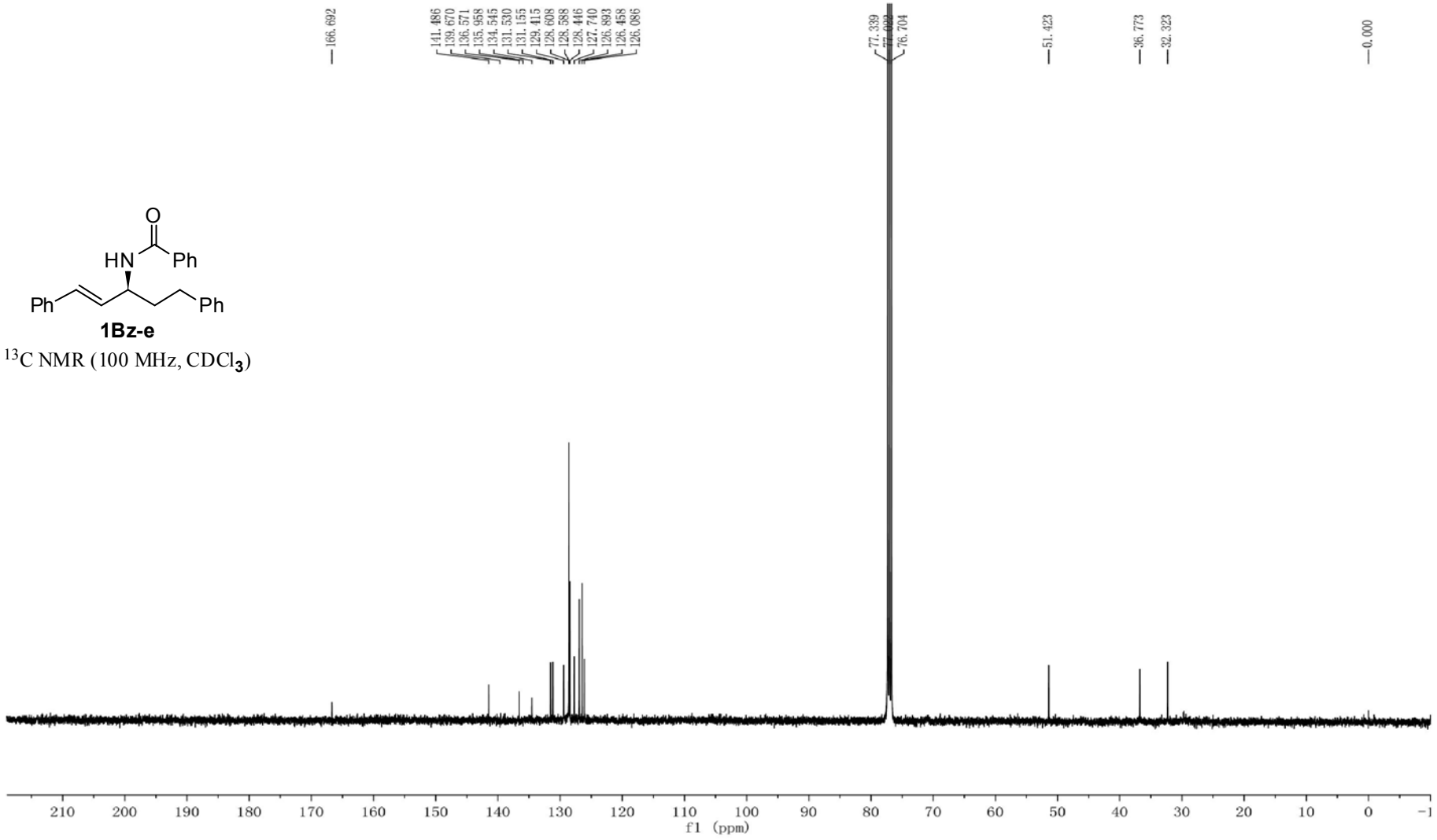
1Bz-d

^{13}C NMR (100 MHz, $CDCl_3$)



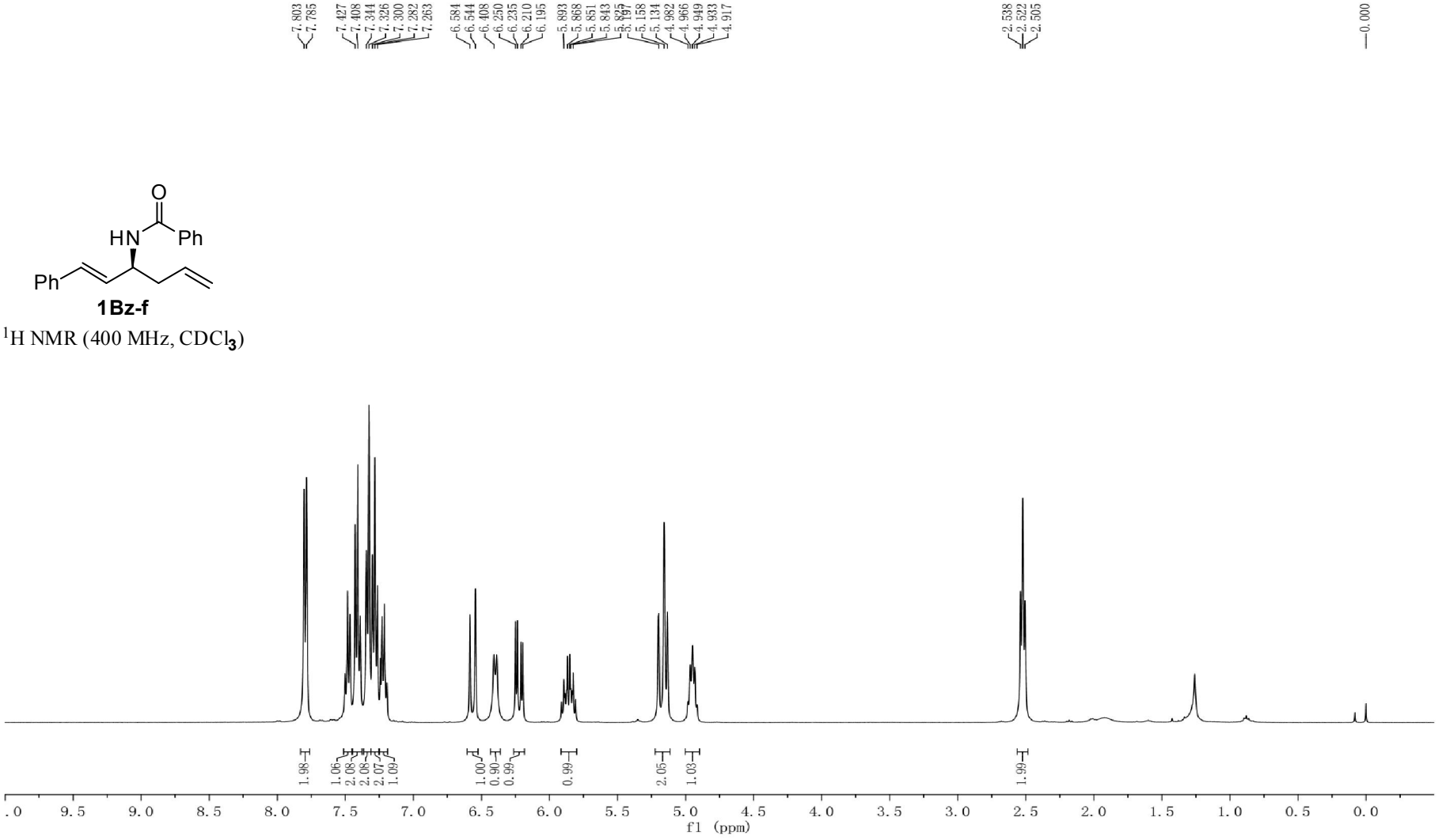
1Bz-e

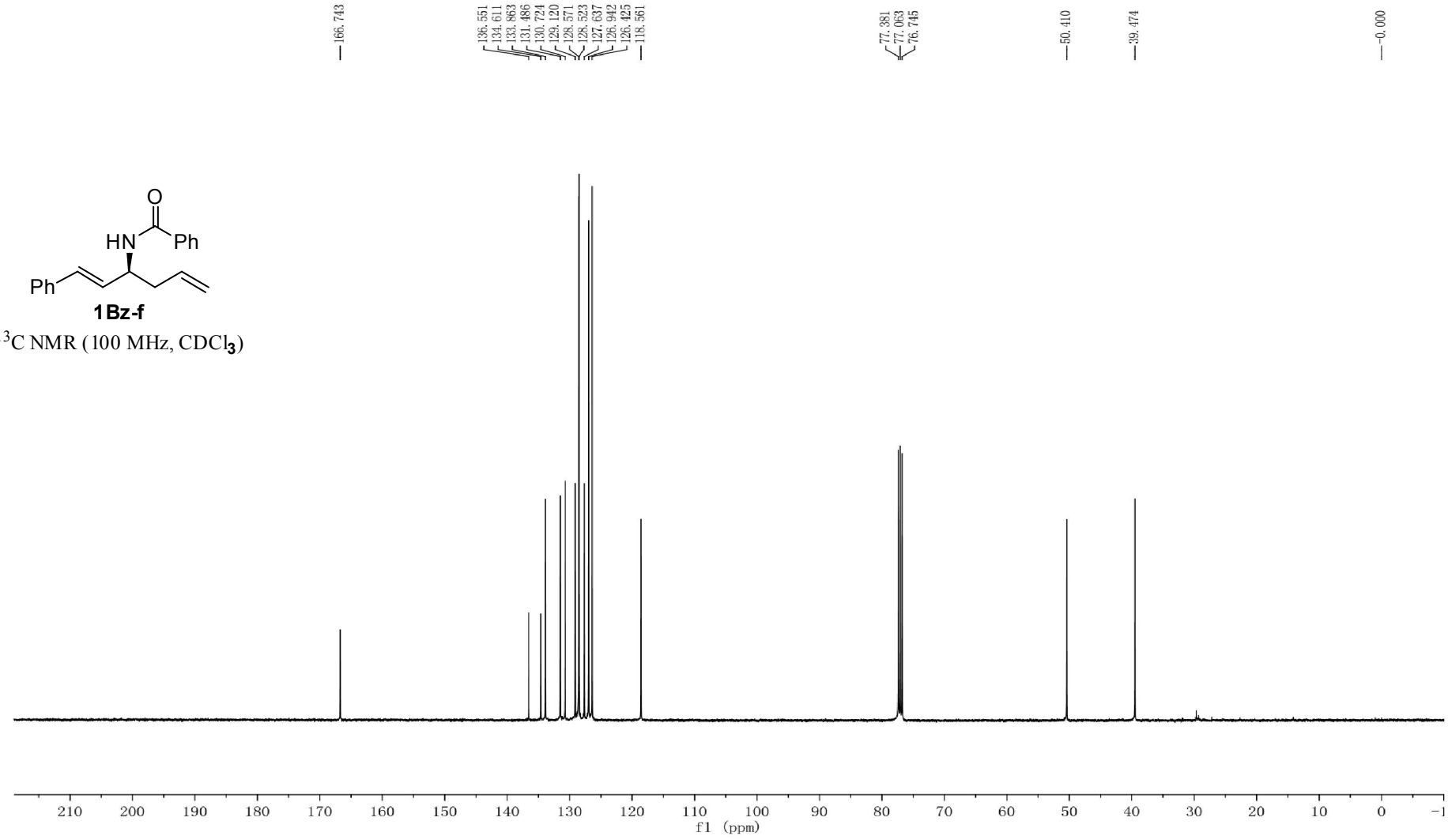
^{1}H NMR (400 MHz, $CDCl_3$)

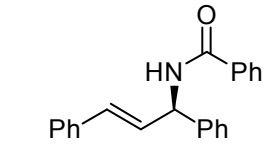


1Bz-e

^{13}C NMR (100 MHz, $CDCl_3$)

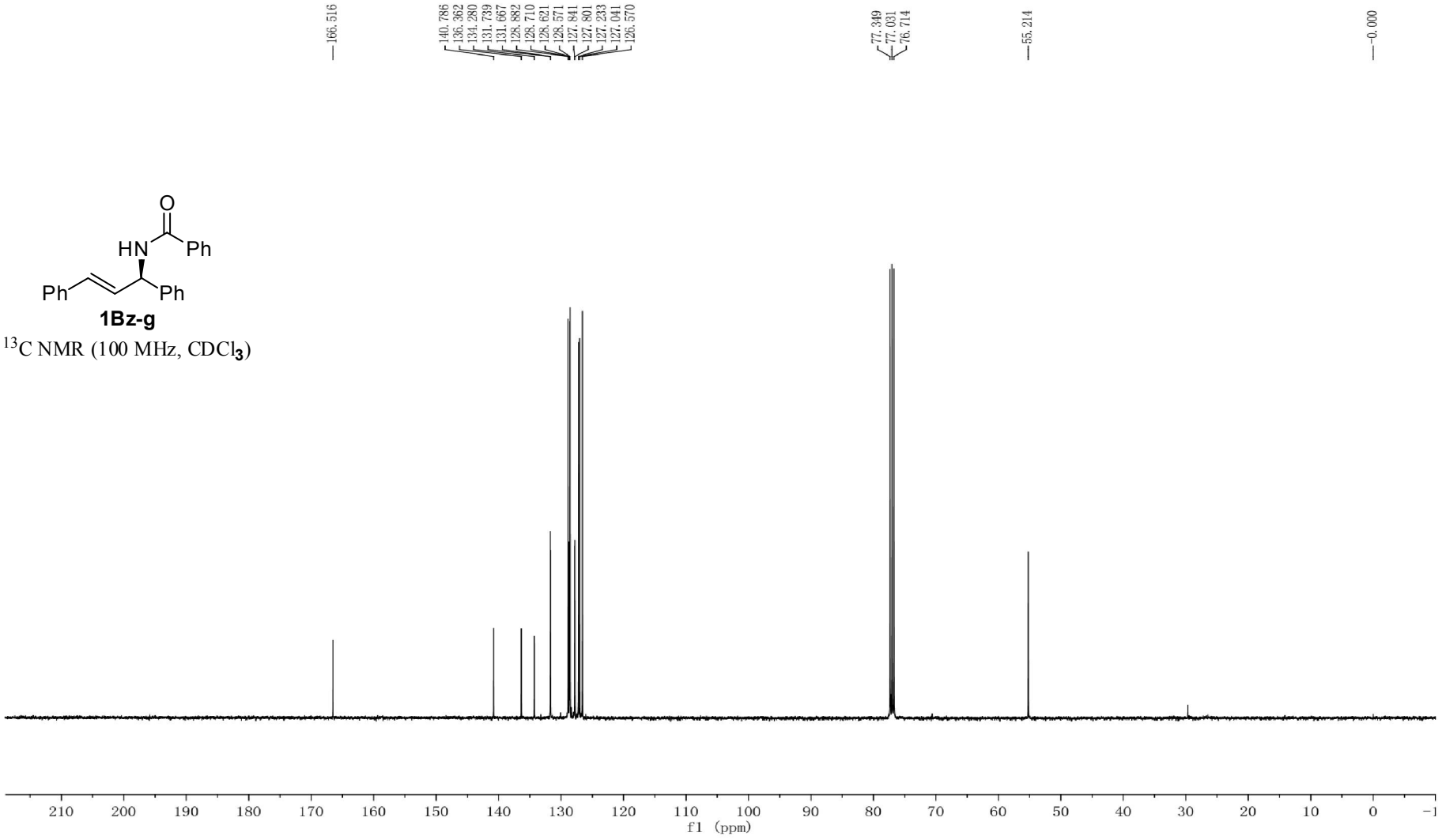

7.803
7.785
7.427
7.408
7.344
7.326
7.300
7.282
7.263
6.584
6.544
6.408
6.250
6.235
6.210
6.195
5.893
5.868
5.851
5.843
5.825
5.197
5.158
5.134
4.982
4.966
4.949
4.933
4.917
2.538
2.522
2.505
0.000
O
HN
Ph
Ph
1Bz-f
1H NMR (400 MHz, CDCl3)
1.98
1.06
2.08
2.08
2.07
1.09
1.00
0.90
0.99
0.99
2.05
1.03
1.99
f1 (ppm)

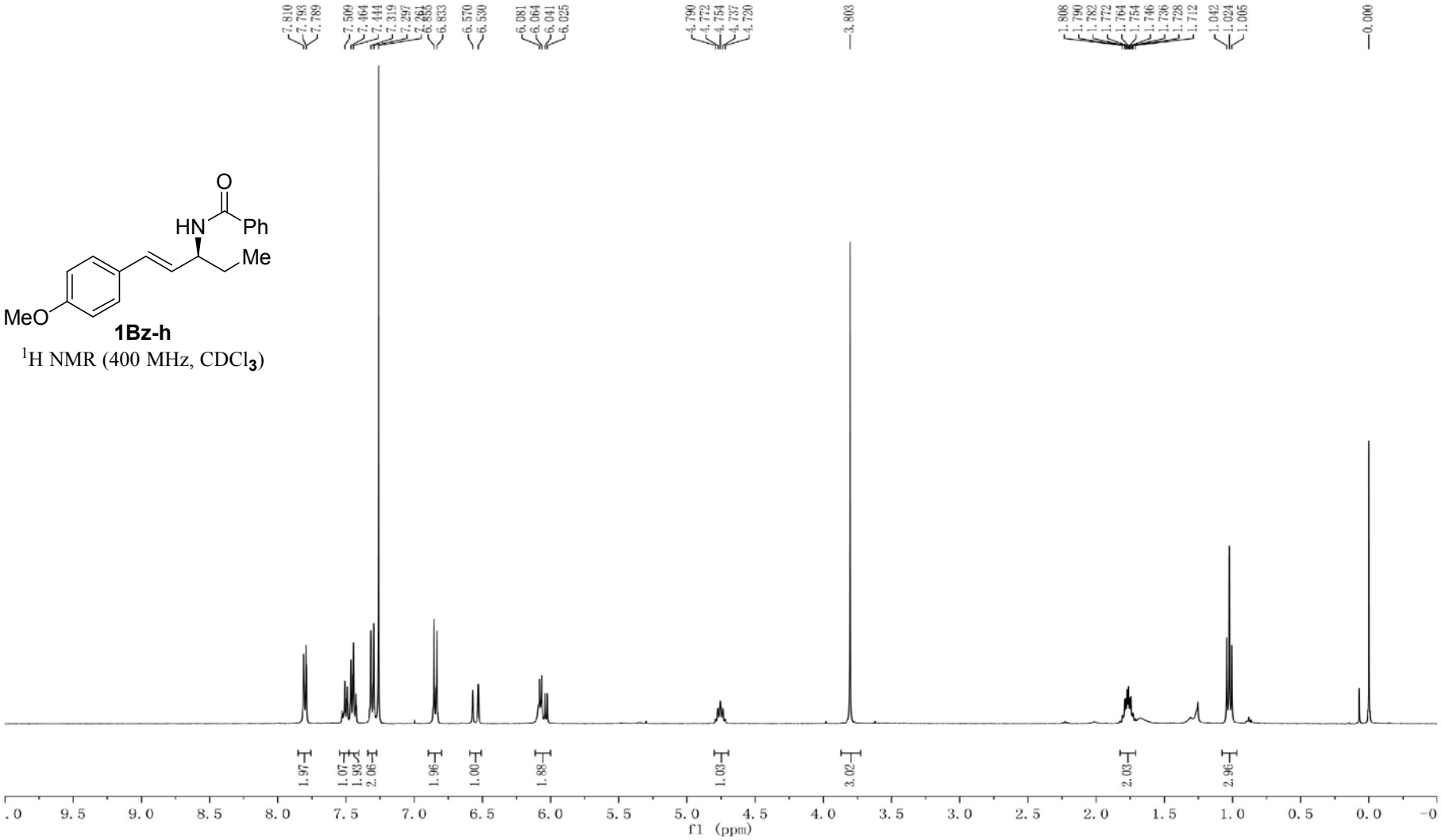

166.743
136.551
134.611
133.863
131.486
130.724
129.120
128.571
128.523
127.637
126.942
126.425
118.561
77.381
77.063
76.745
50.410
39.474
0.000
O
HN
Ph
Ph
1Bz-f
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



1Bz-g

^{1}H NMR (400 MHz, $CDCl_3$)

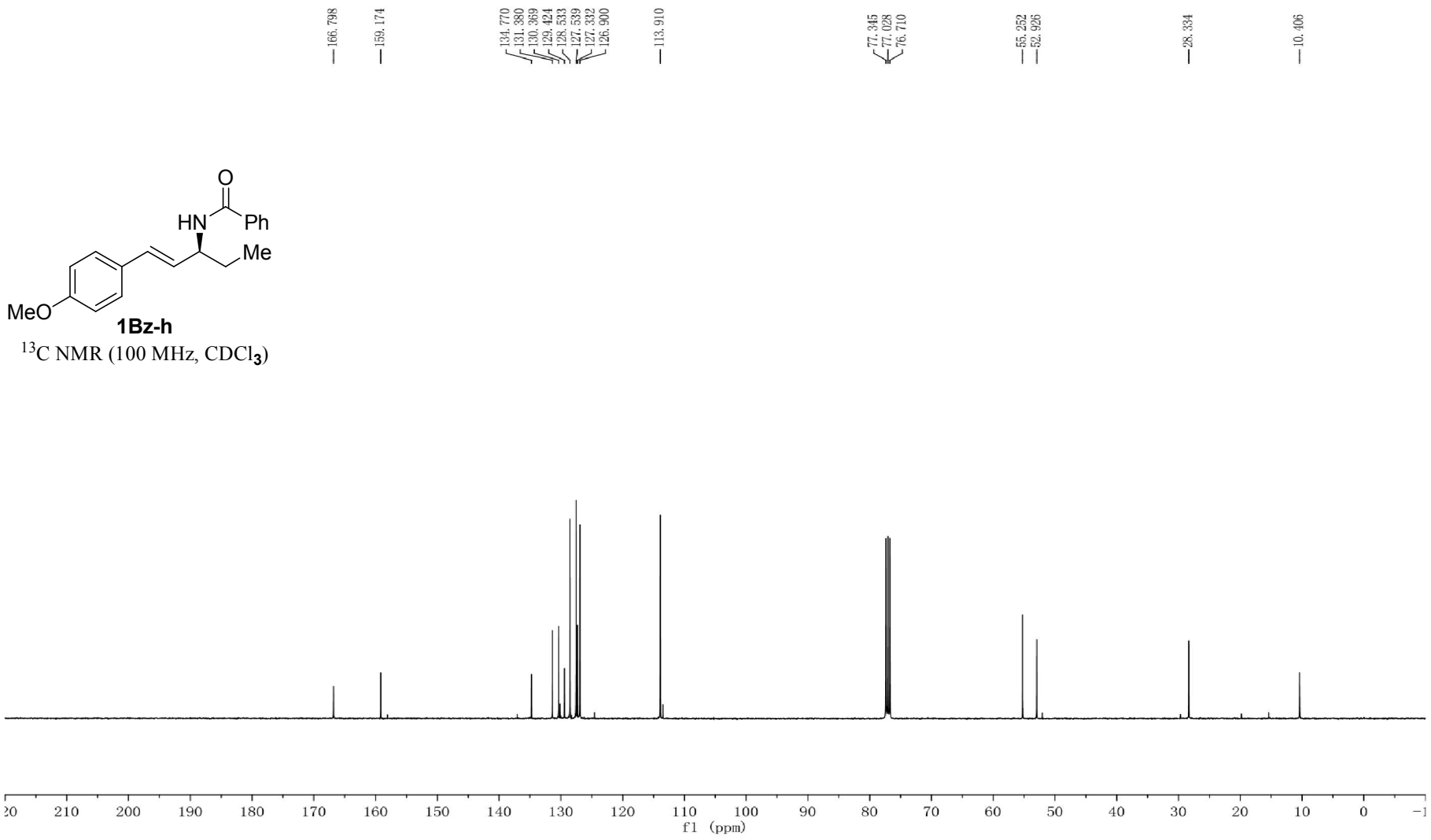

166.516
140.786
136.362
134.280
131.739
131.667
128.882
128.710
128.621
128.571
127.841
127.801
127.233
127.041
126.570
77.349
77.031
76.714
55.214
0.000
O
HN
Ph
Ph
Ph
1Bz-g
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



HN, O, Ph, Me, MeO

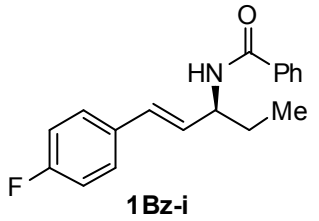
1Bz-h

^{1}H NMR (400 MHz, $CDCl_3$)



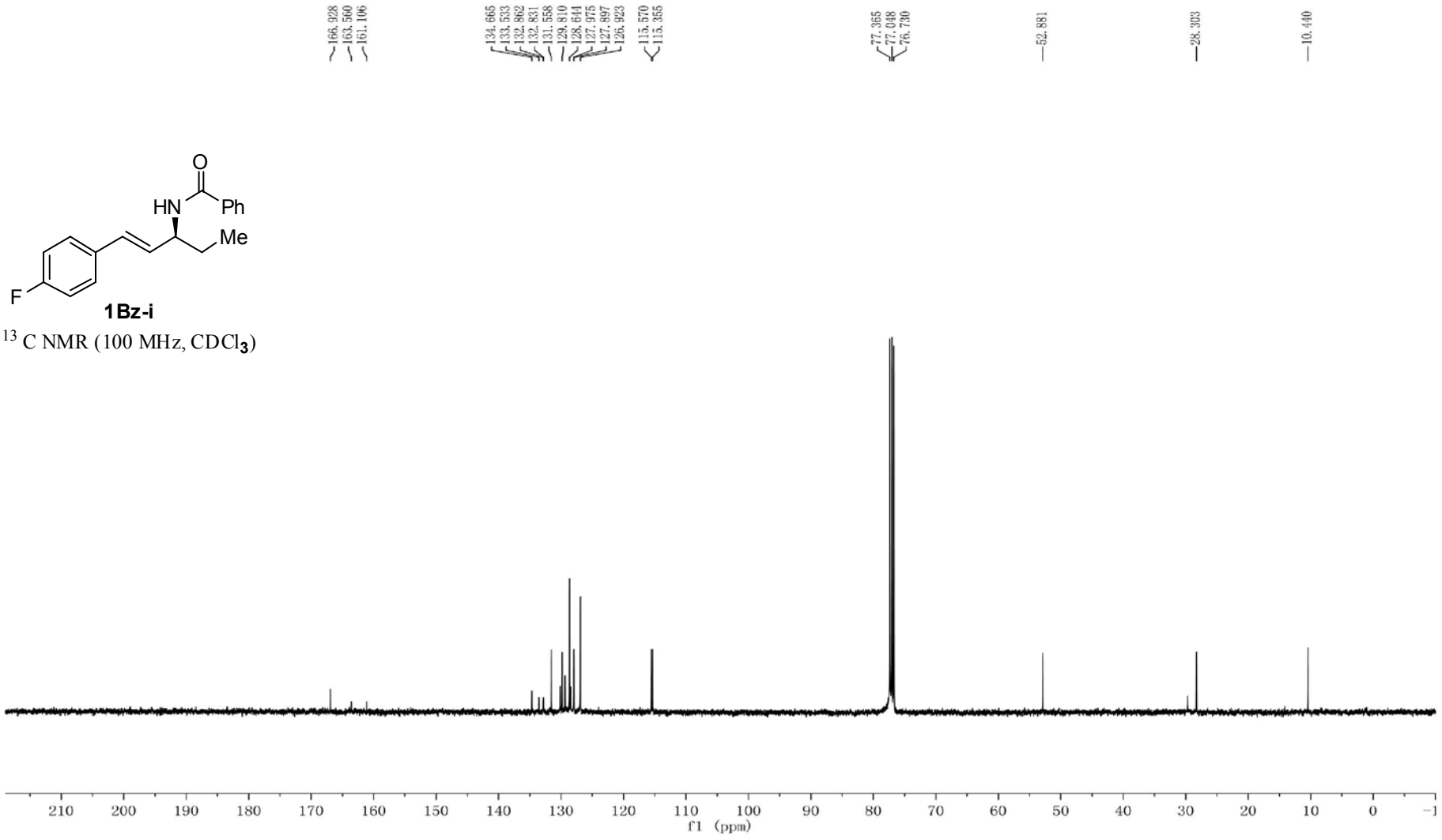
1Bz-h

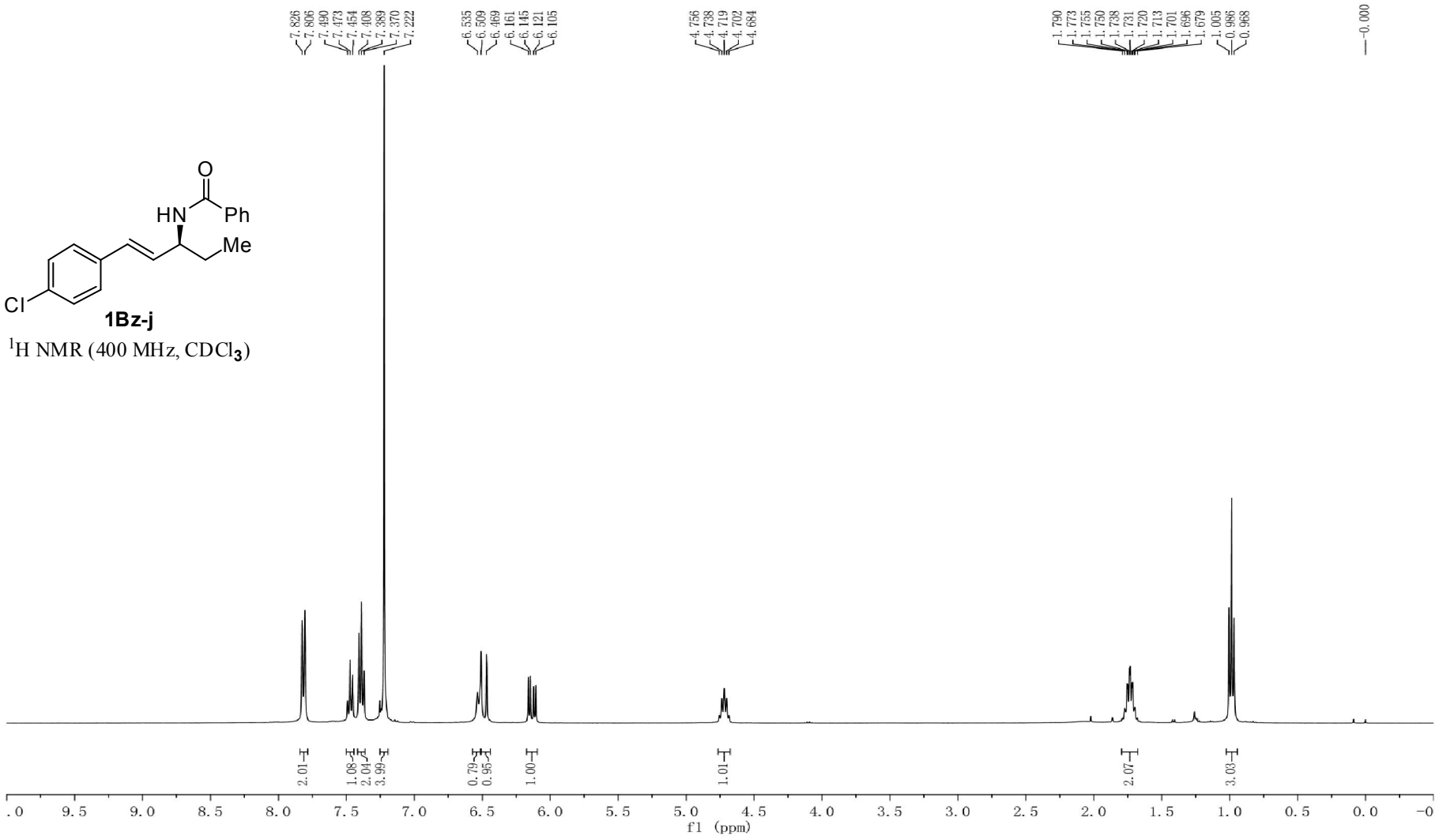
^{13}C NMR (100 MHz, $CDCl_3$)



1Bz-i

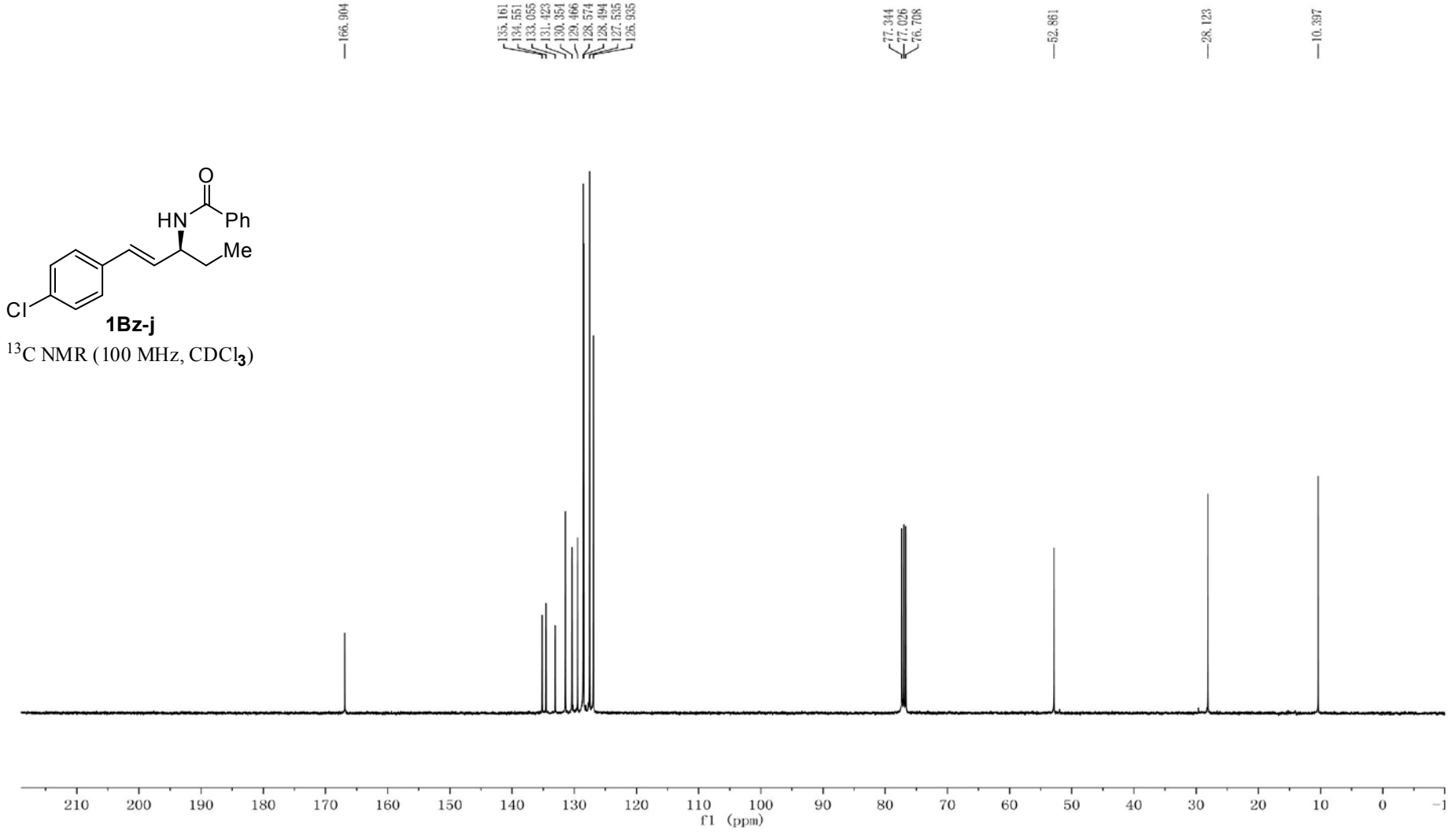
^{1}H NMR (400 MHz, $CDCl_3$)


166.928
163.560
161.106
134.665
133.533
132.862
132.831
131.558
129.810
128.644
127.975
127.897
126.923
115.570
115.355
77.365
77.048
76.730
52.881
28.303
10.440
O
HN
Ph
Me
F
1Bz-i
13 C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)



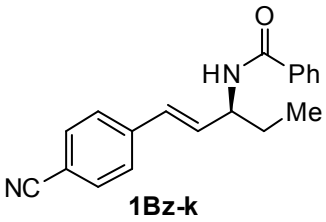
1Bz-j

^{1}H NMR (400 MHz, $CDCl_3$)



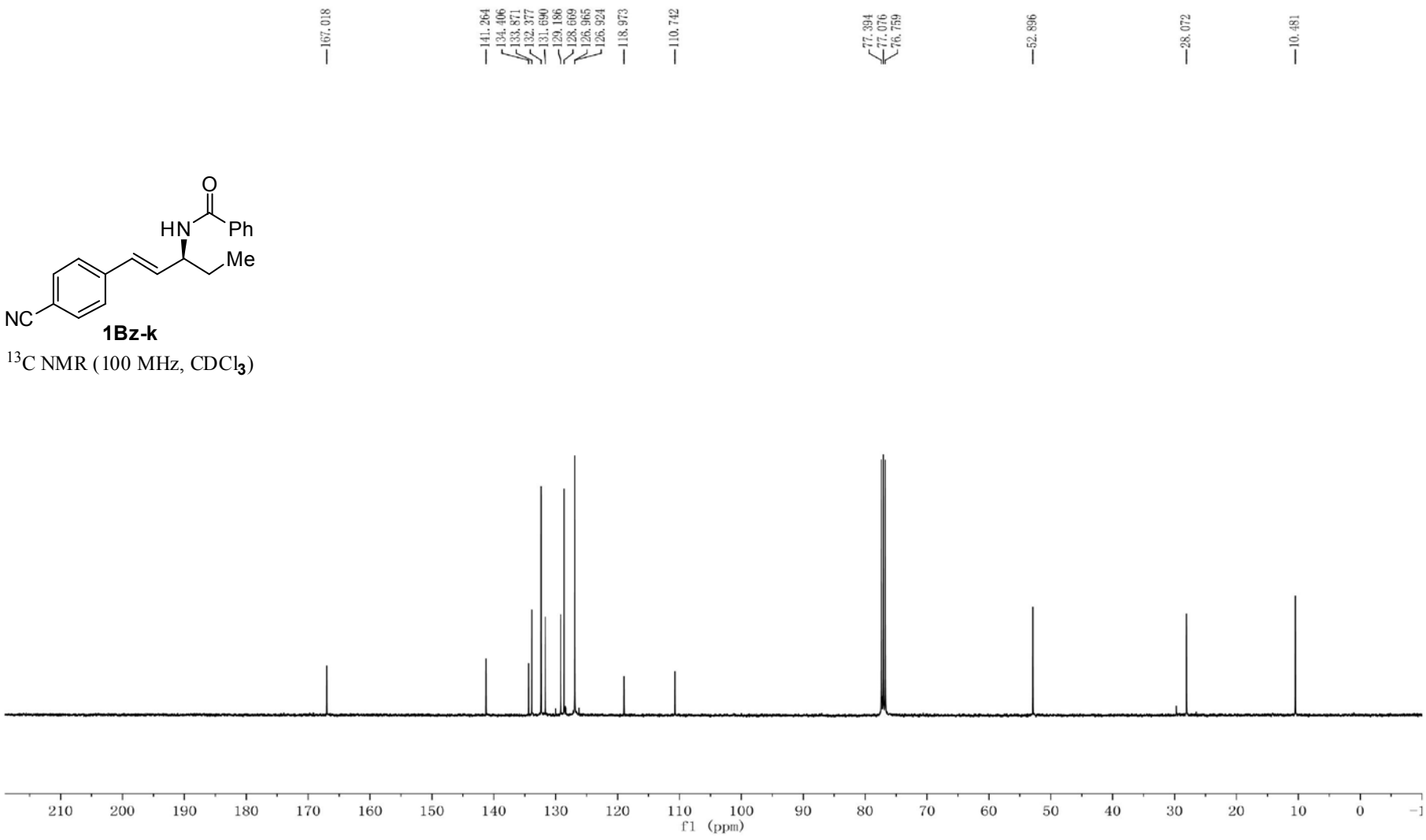
1Bz-j

^{13}C NMR (100 MHz, $CDCl_3$)

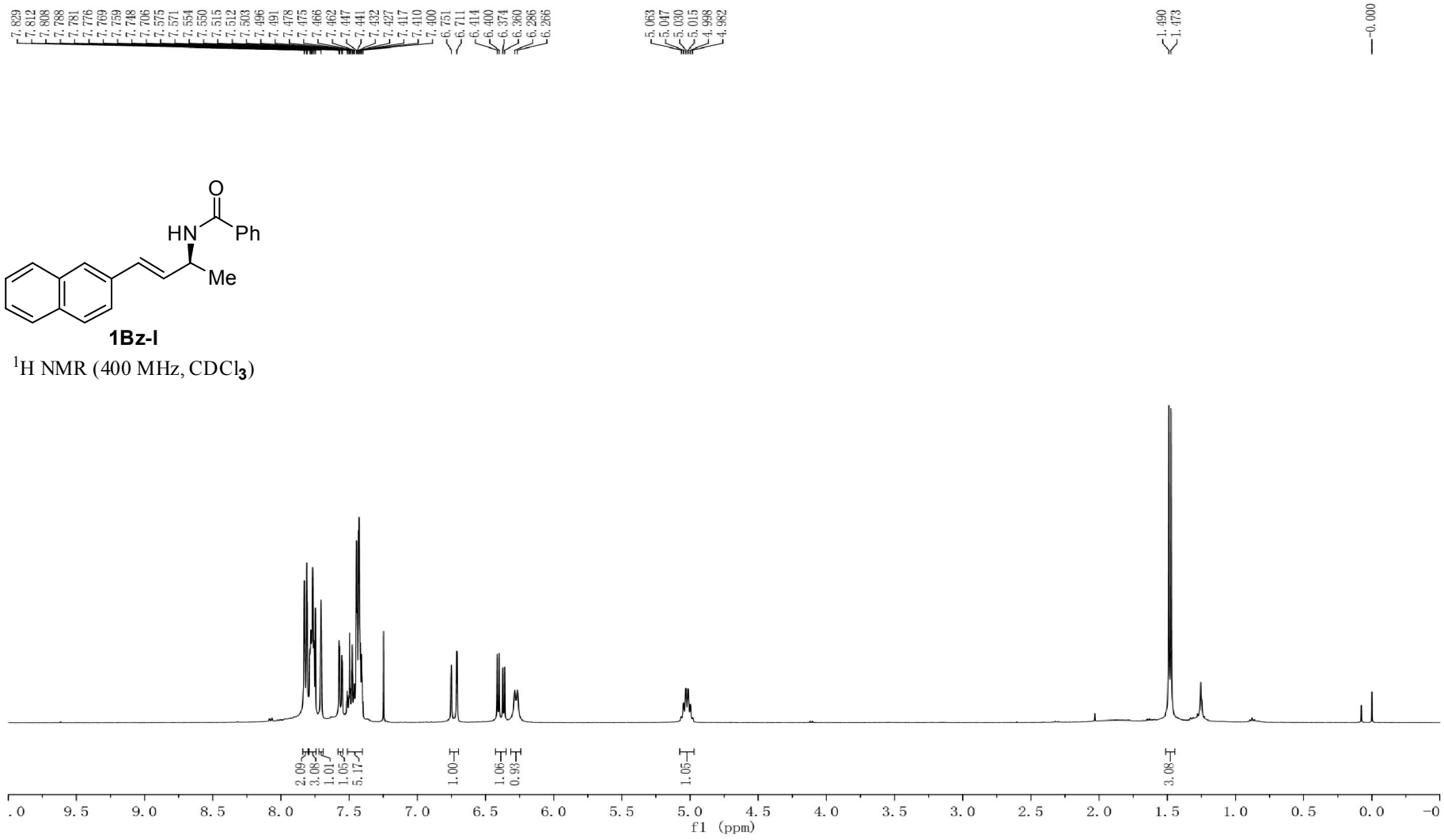


1Bz-k

^{1}H NMR (400 MHz, $CDCl_3$)

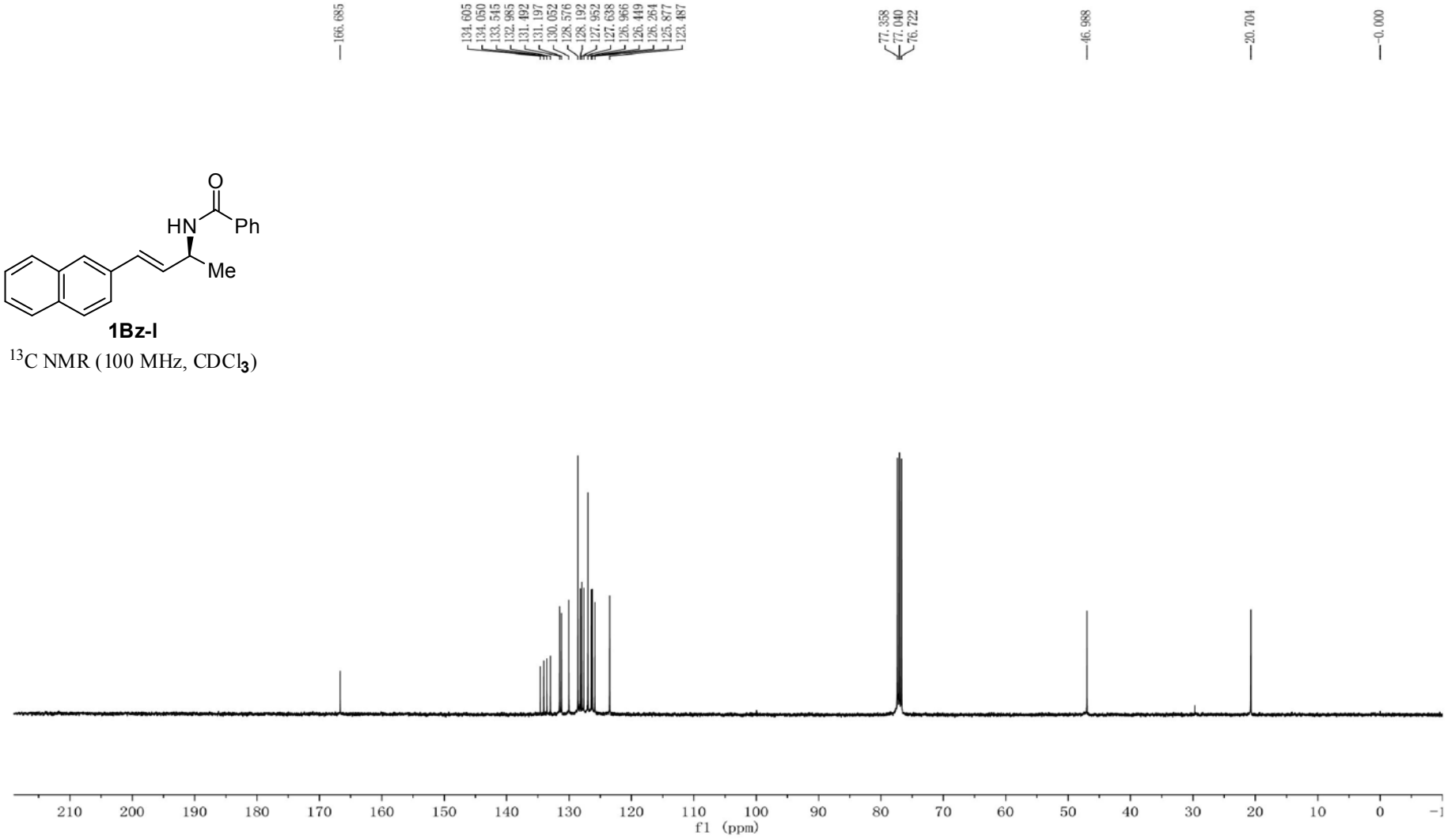


^{13}C NMR (100 MHz, $CDCl_3$)



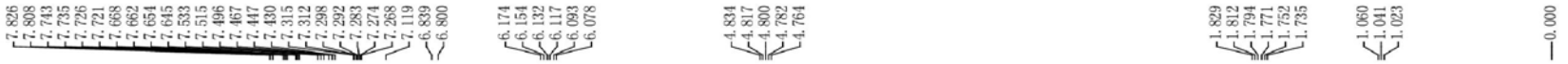
1Bz-I

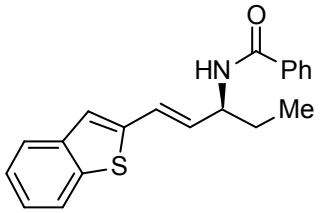
^{1}H NMR (400 MHz, $CDCl_3$)



1Bz-I

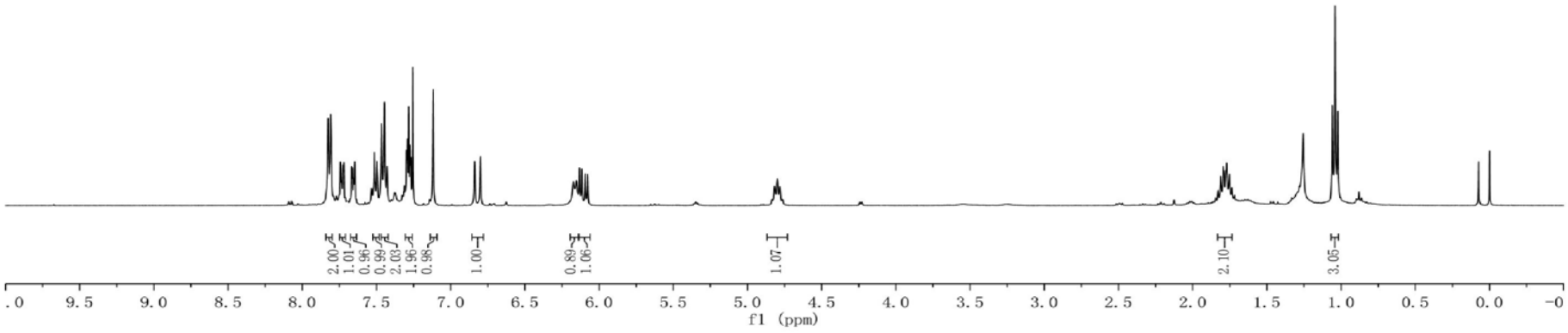
^{13}C NMR (100 MHz, $CDCl_3$)

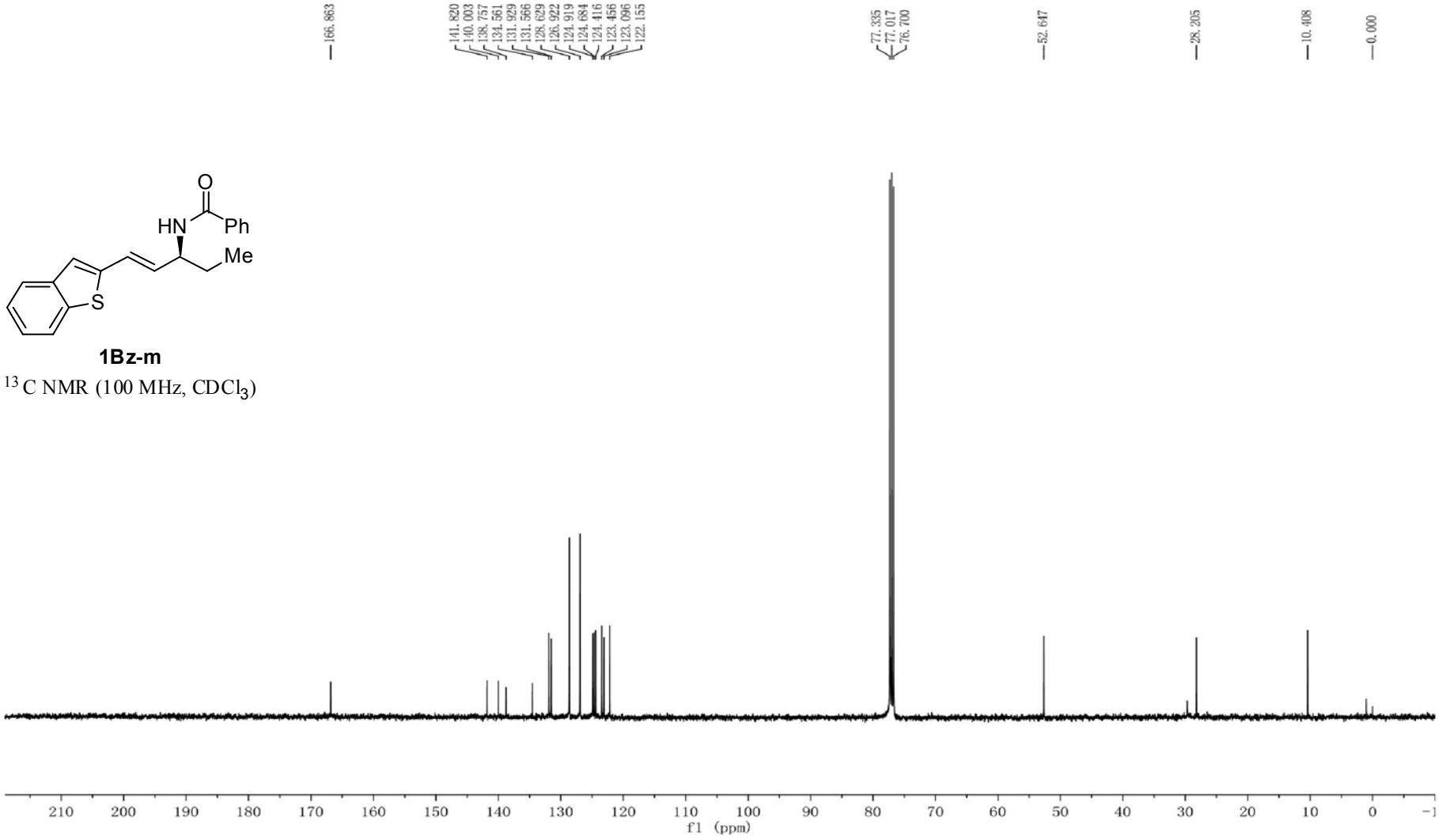




1Bz-m

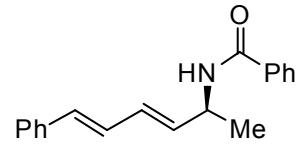
^{1}H NMR (400 MHz, $CDCl_3$)





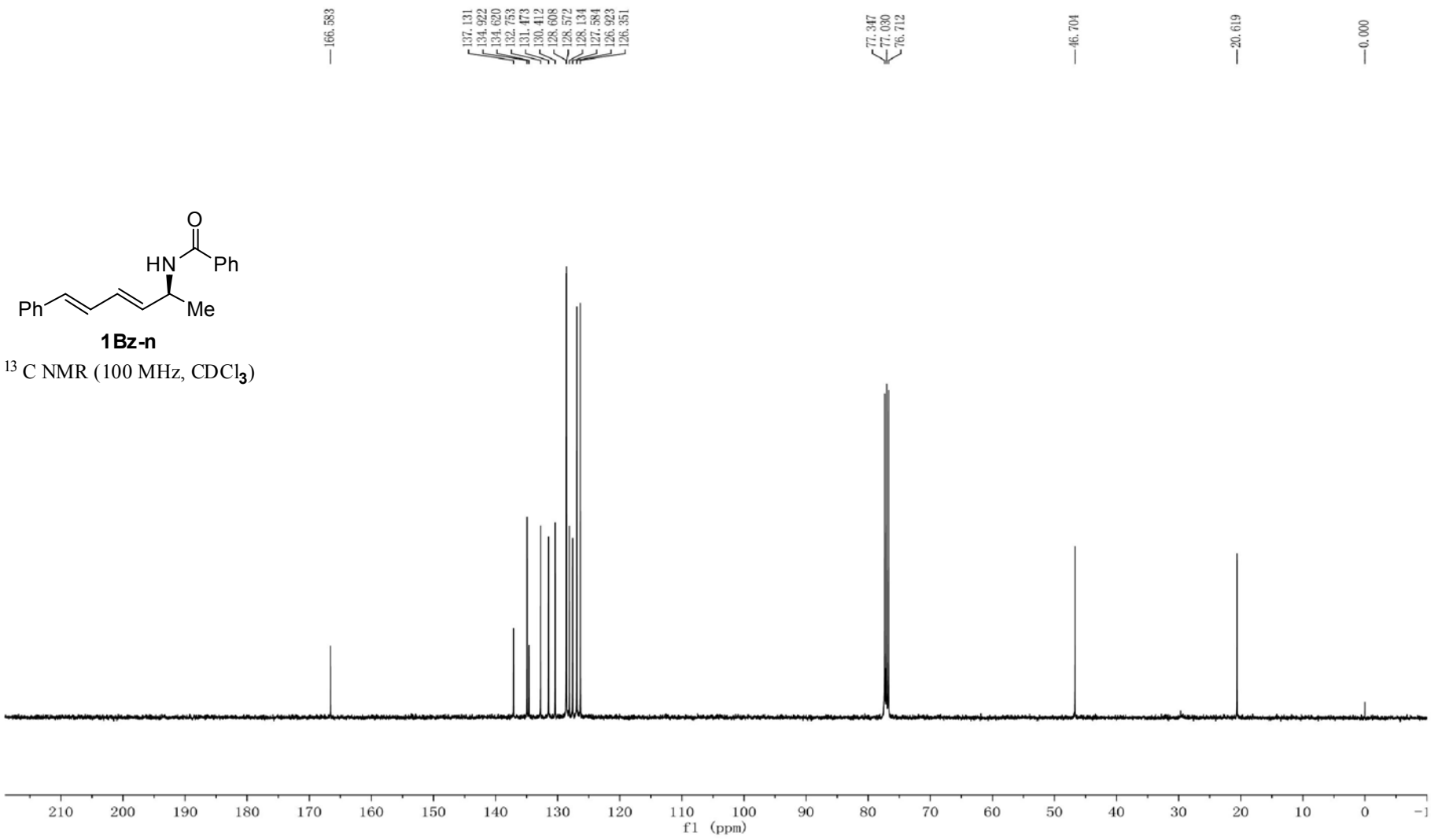
1Bz-m

^{13}C NMR (100 MHz, $CDCl_3$)



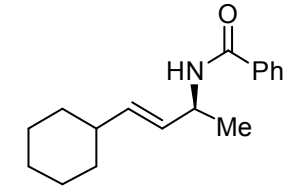
1Bz-n

^{1}H NMR (400 MHz, $CDCl_3$)



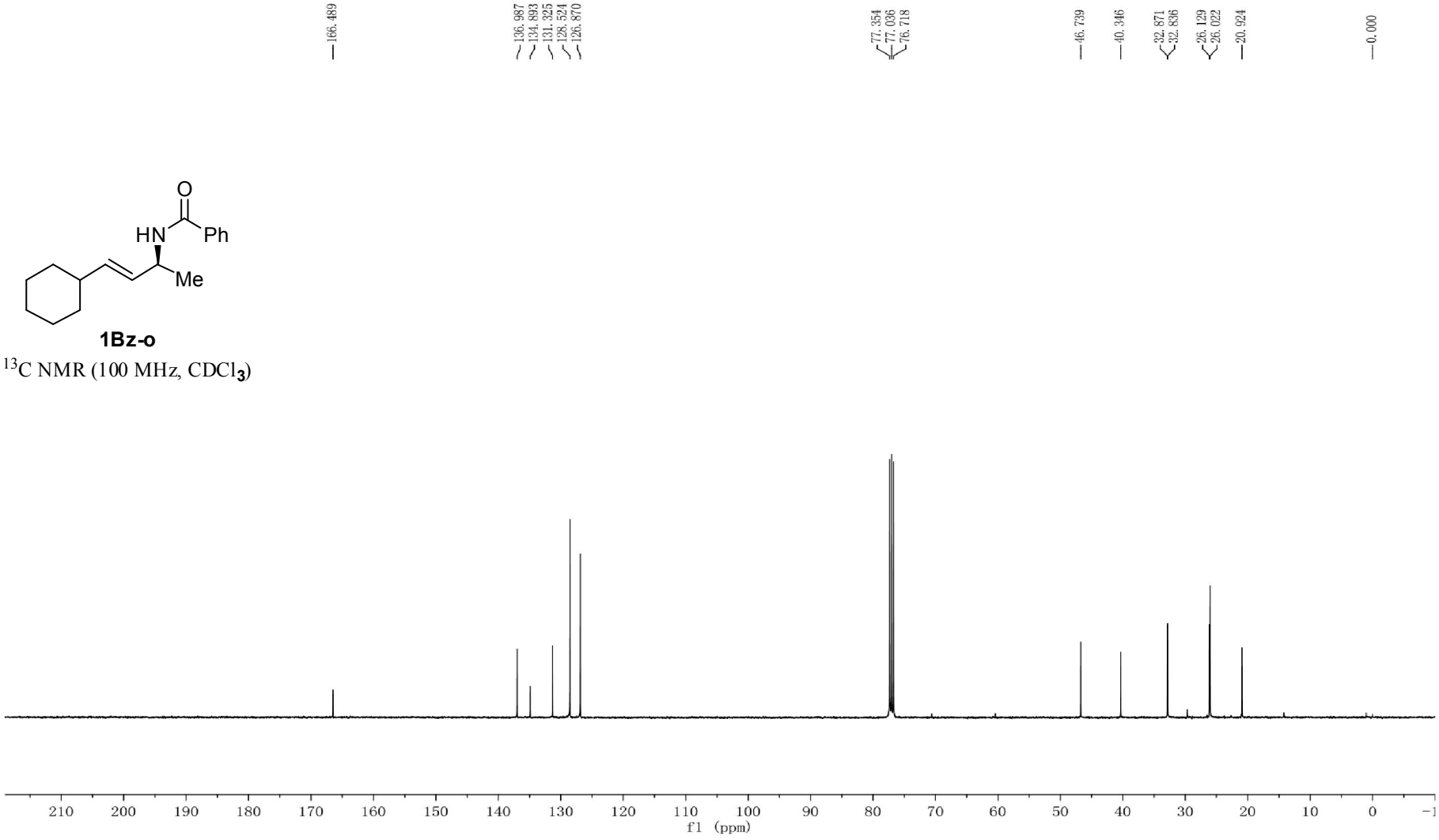
1Bz-n

^{13}C NMR (100 MHz, $CDCl_3$)



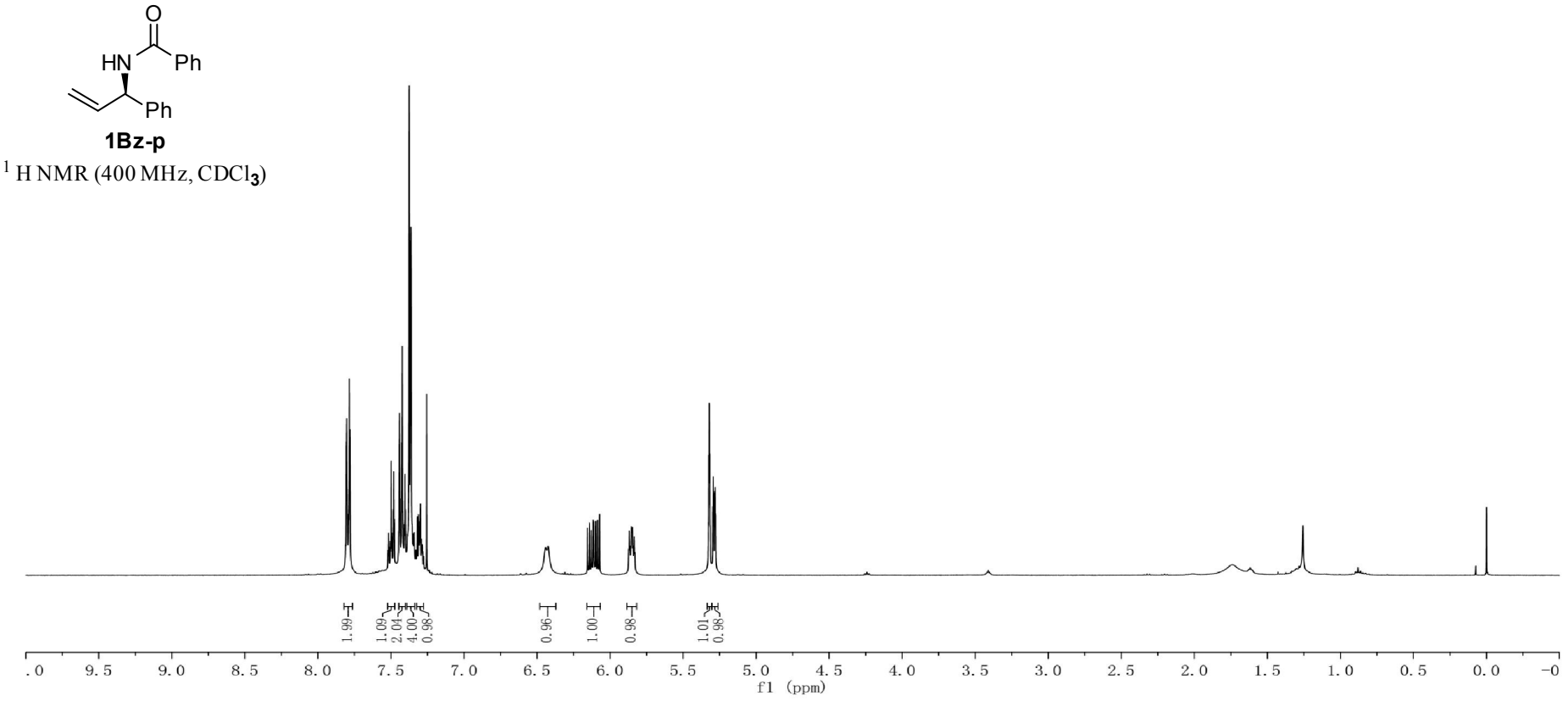
1Bz-o

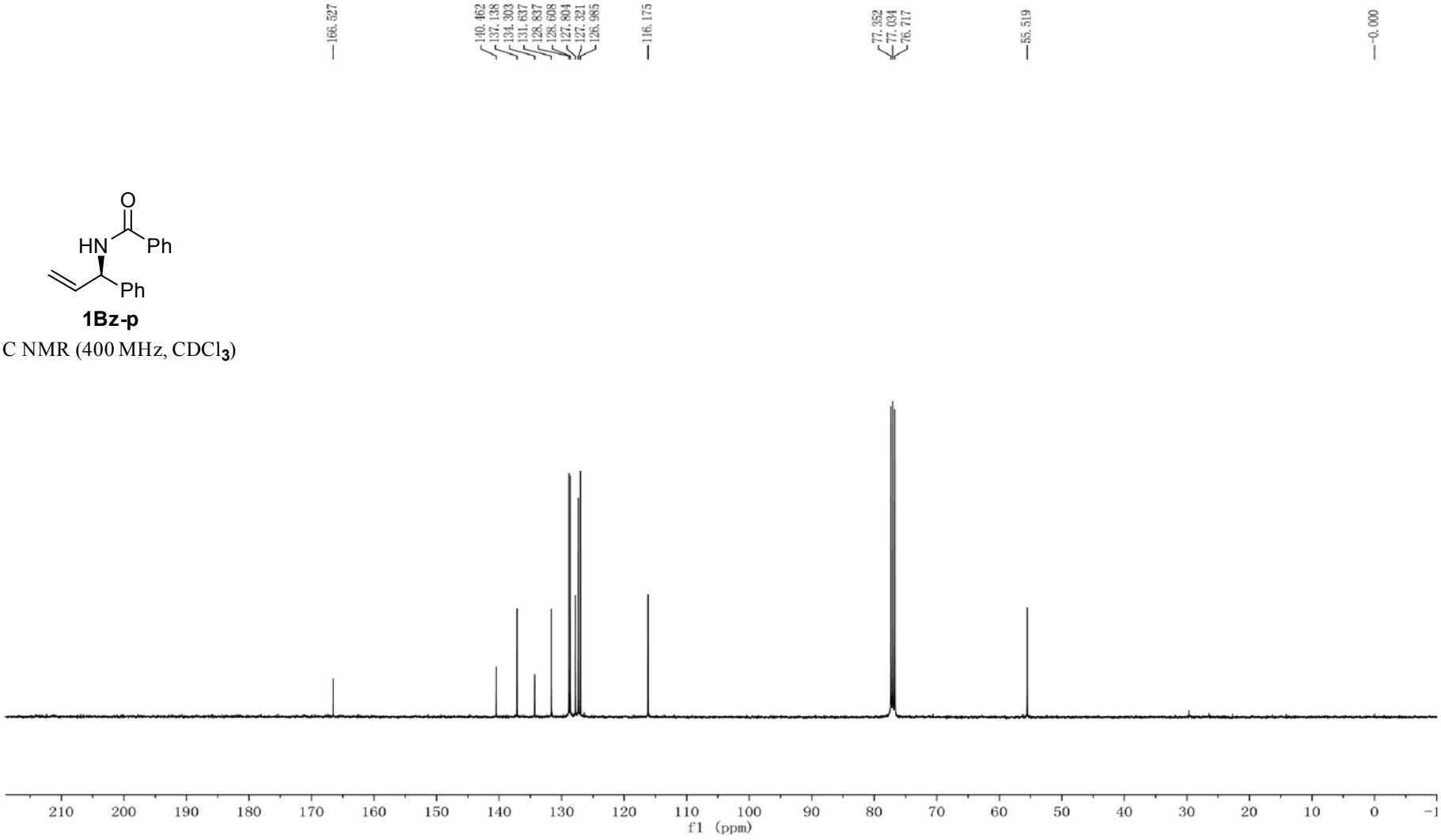
^{1}H NMR (400 MHz, $CDCl_3$)



1Bz-o

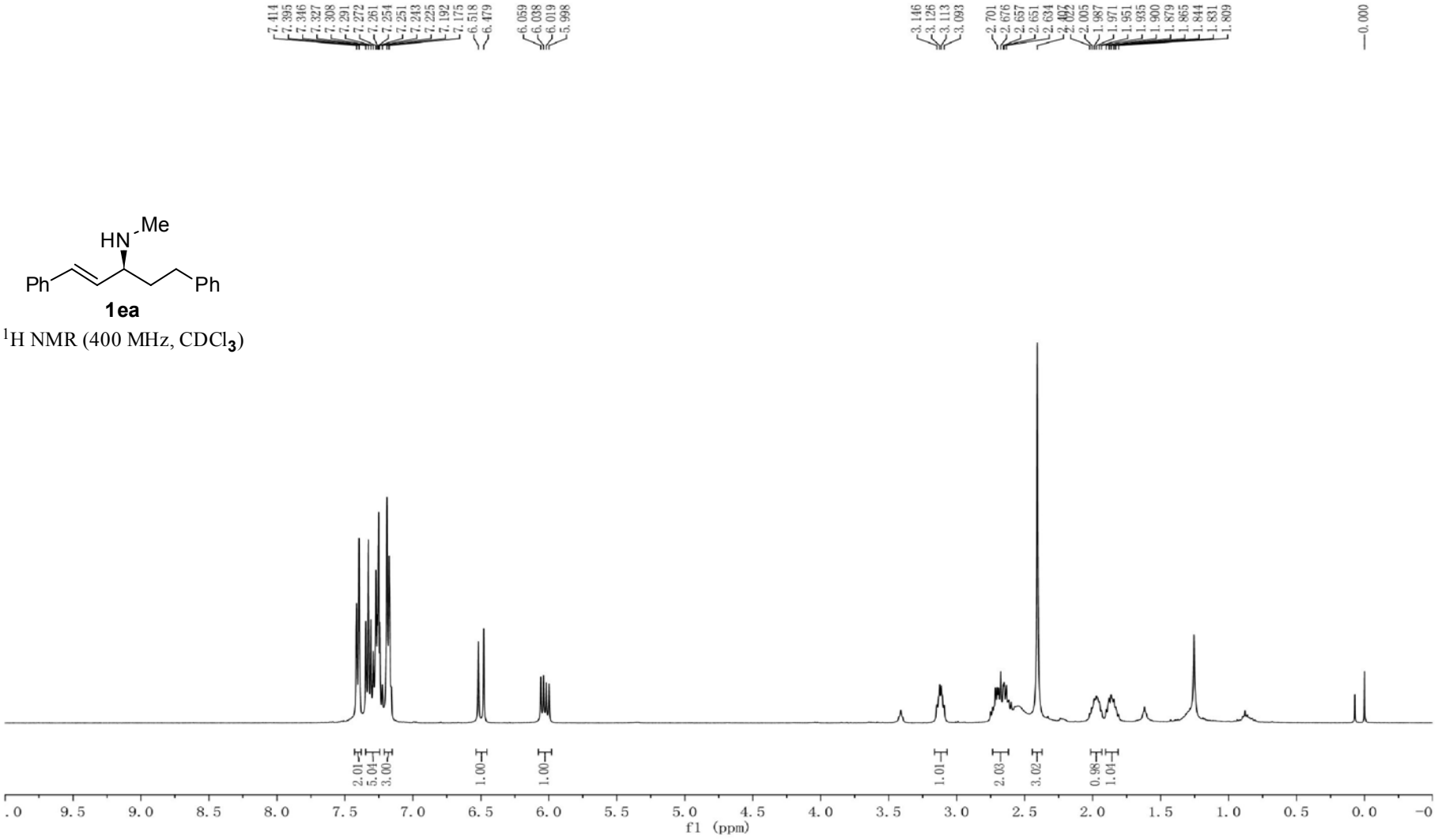
^{13}C NMR (100 MHz, $CDCl_3$)


O
HN
Ph
Ph
1Bz-p
1 H NMR (400 MHz, CDCl3)
7.811
7.805
7.803
7.799
7.790
7.785
7.781
7.499
7.490
7.441
7.438
7.426
7.422
7.405
7.375
7.366
6.424
6.141
6.116
6.111
6.098
6.086
6.072
5.325
5.321
5.318
5.315
5.296
5.294
5.290
5.284
5.282
5.280
5.277
0.000
1.99
1.09
2.04
4.00
0.98
0.96
1.00
0.98
1.01
0.98
f1 (ppm)



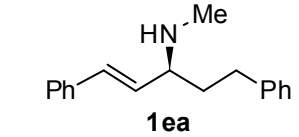
1Bz-p

^{13}C NMR (400 MHz, $CDCl_3$)



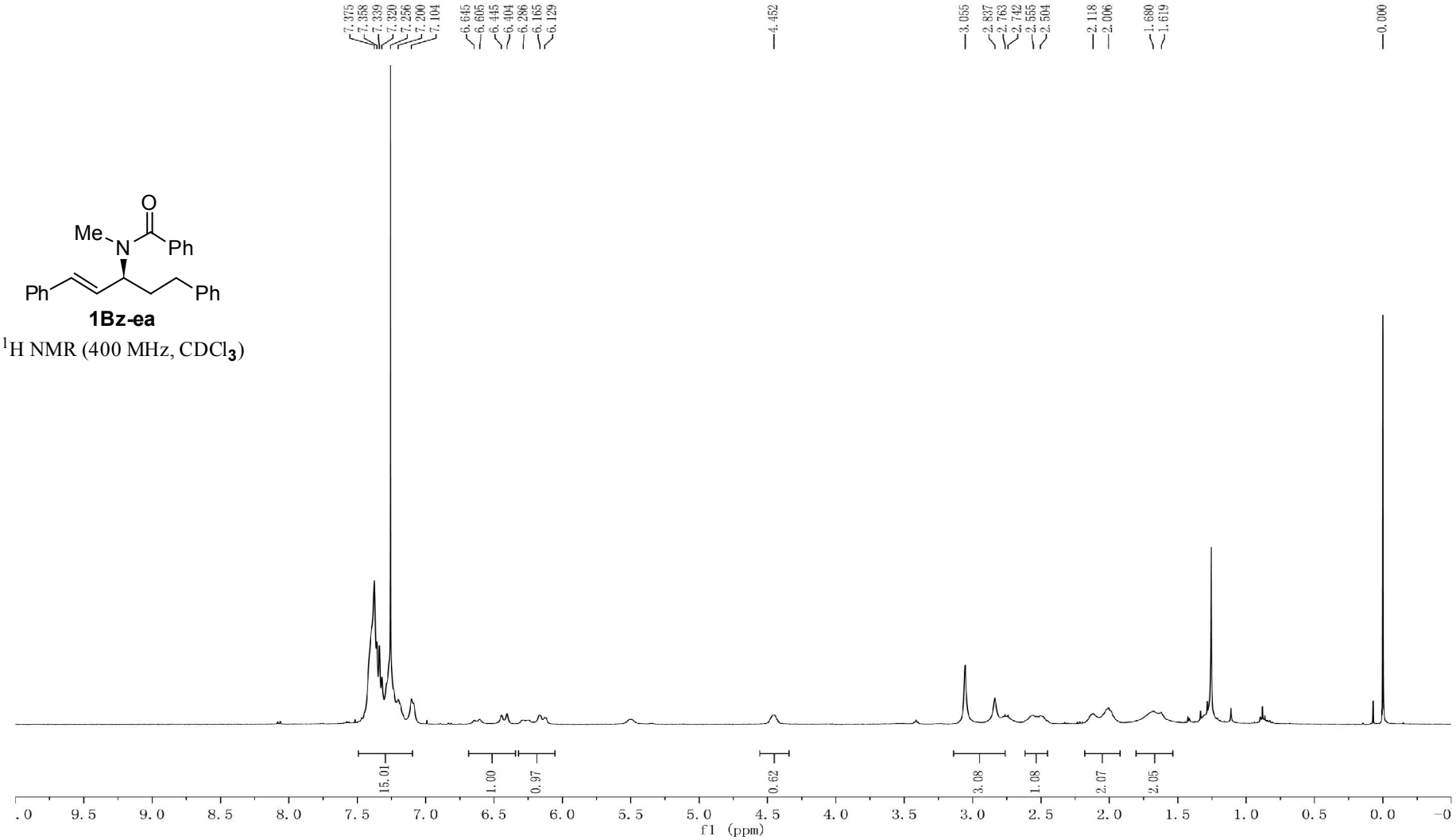
1ea

^{1}H NMR (400 MHz, $CDCl_3$)



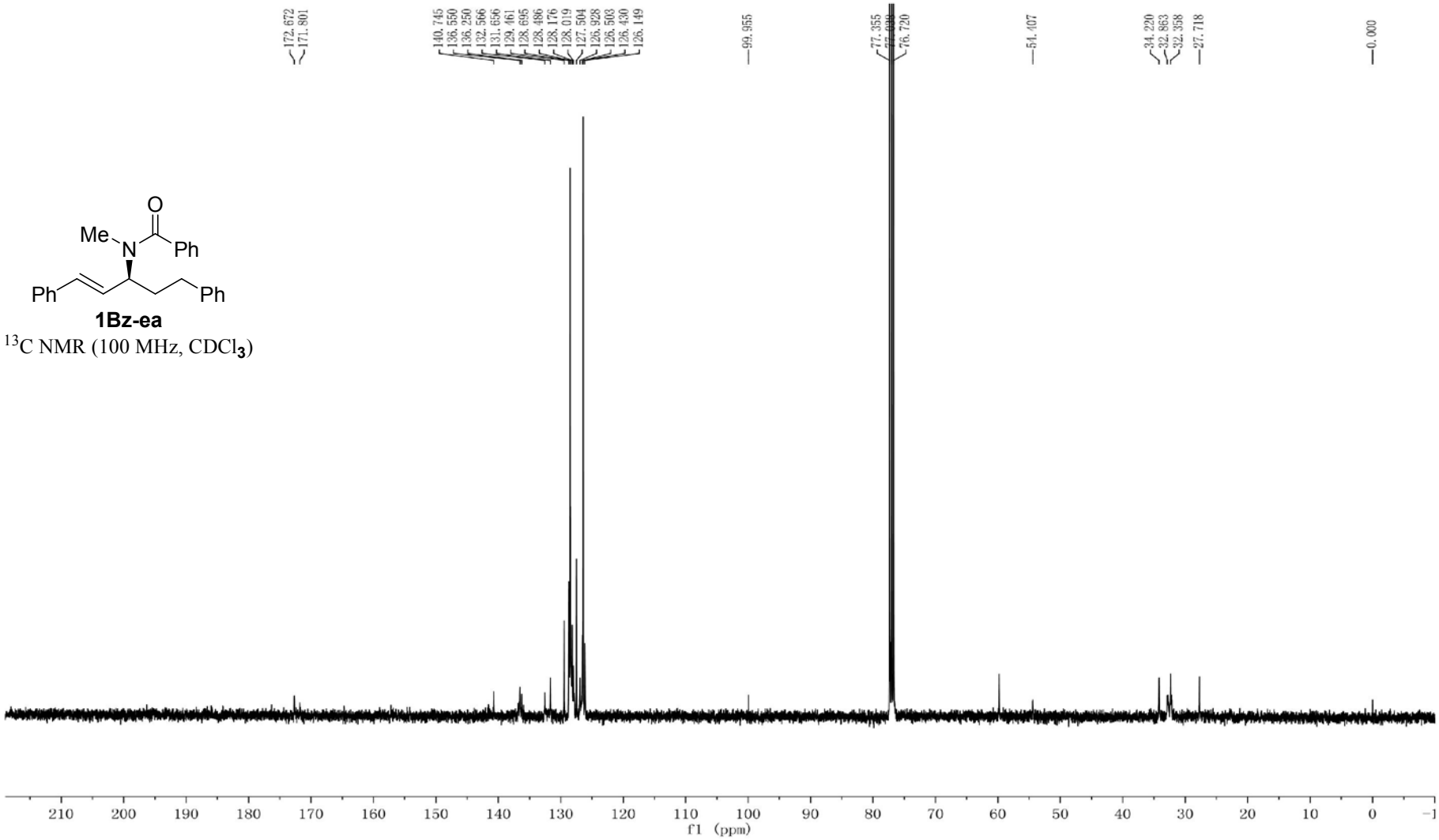
1ea

^{13}C NMR (100 MHz, $CDCl_3$)



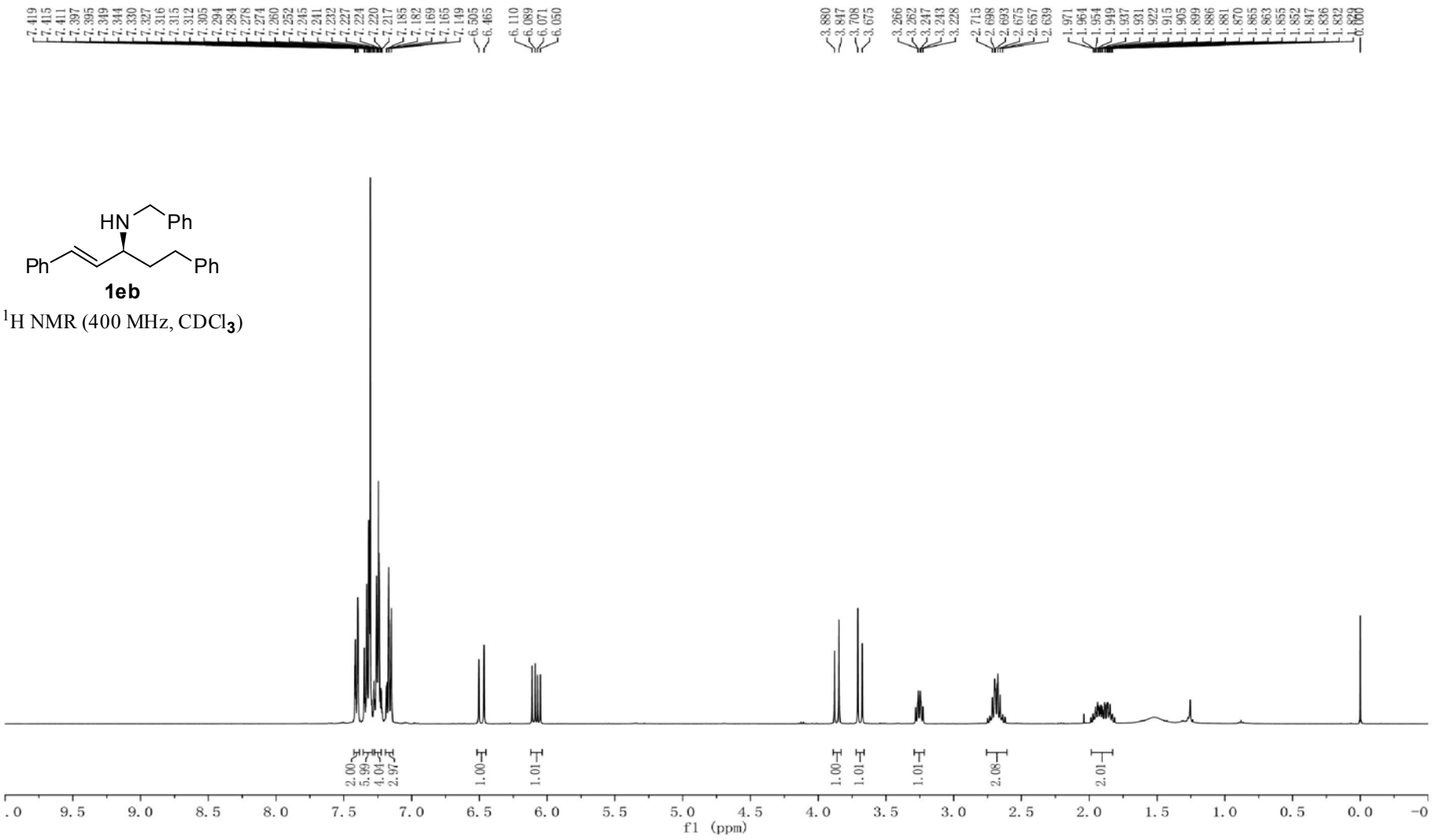
1Bz-ea

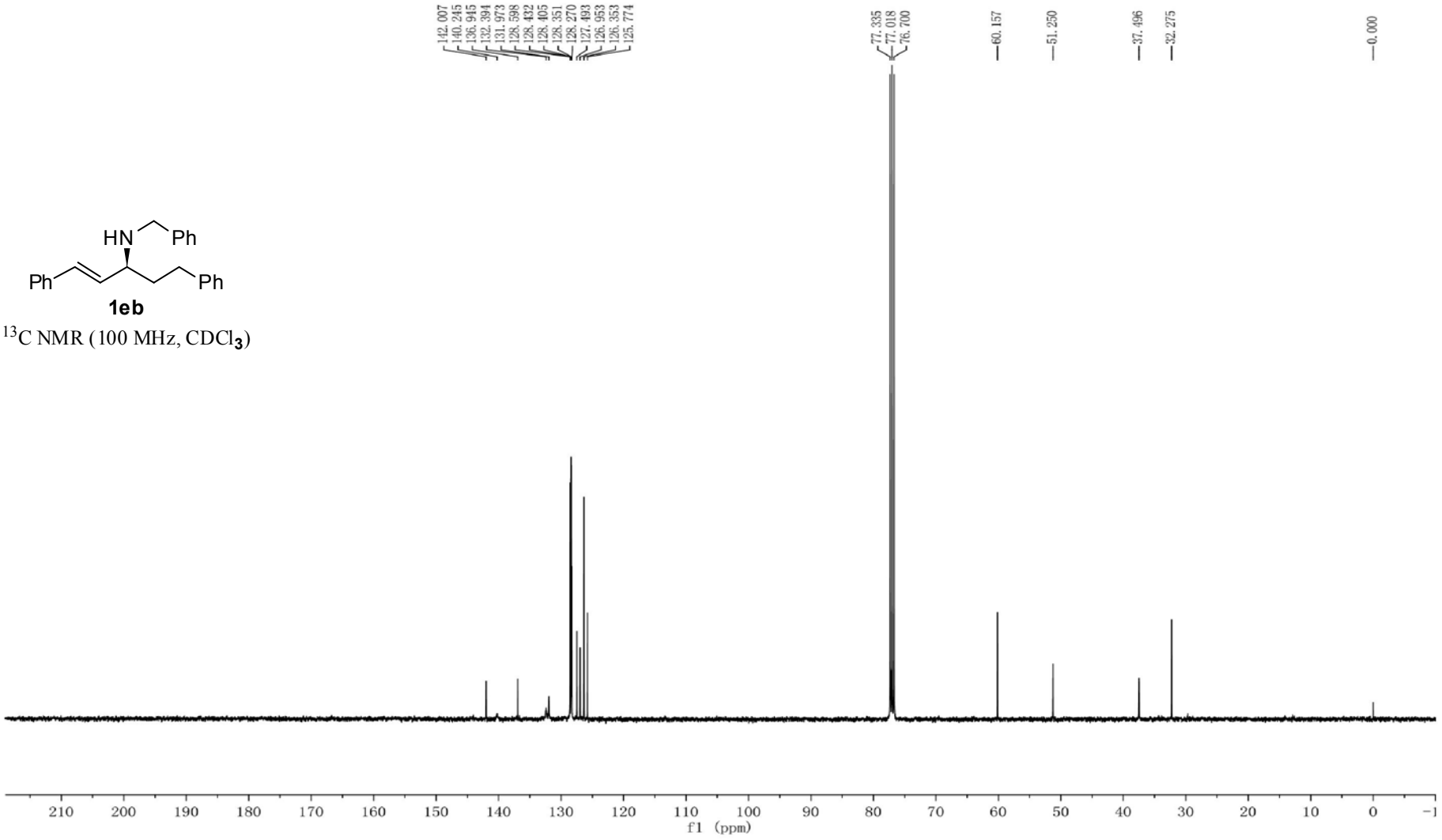
^{1}H NMR (400 MHz, $CDCl_3$)



1Bz-ea

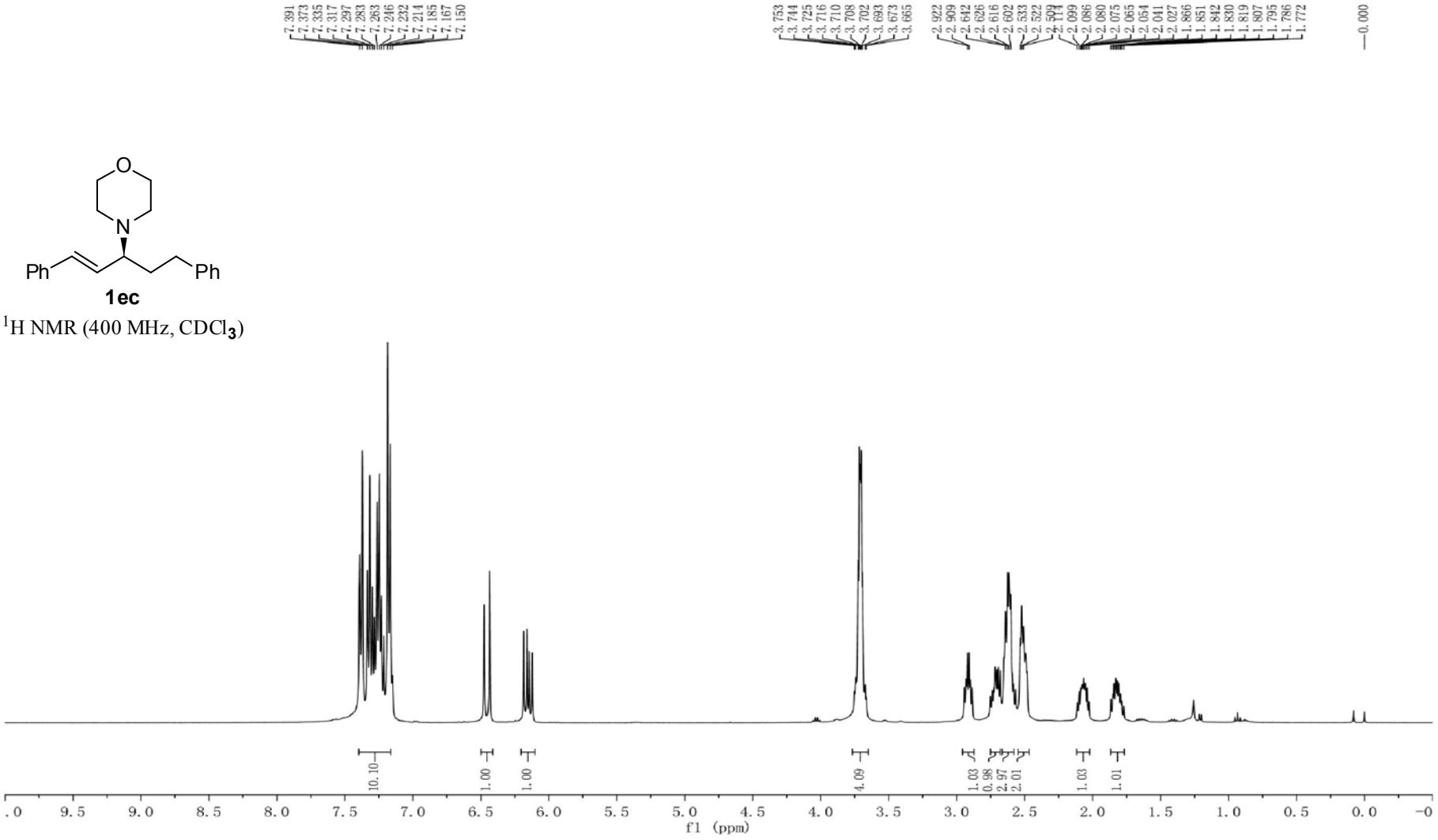
^{13}C NMR (100 MHz, $CDCl_3$)

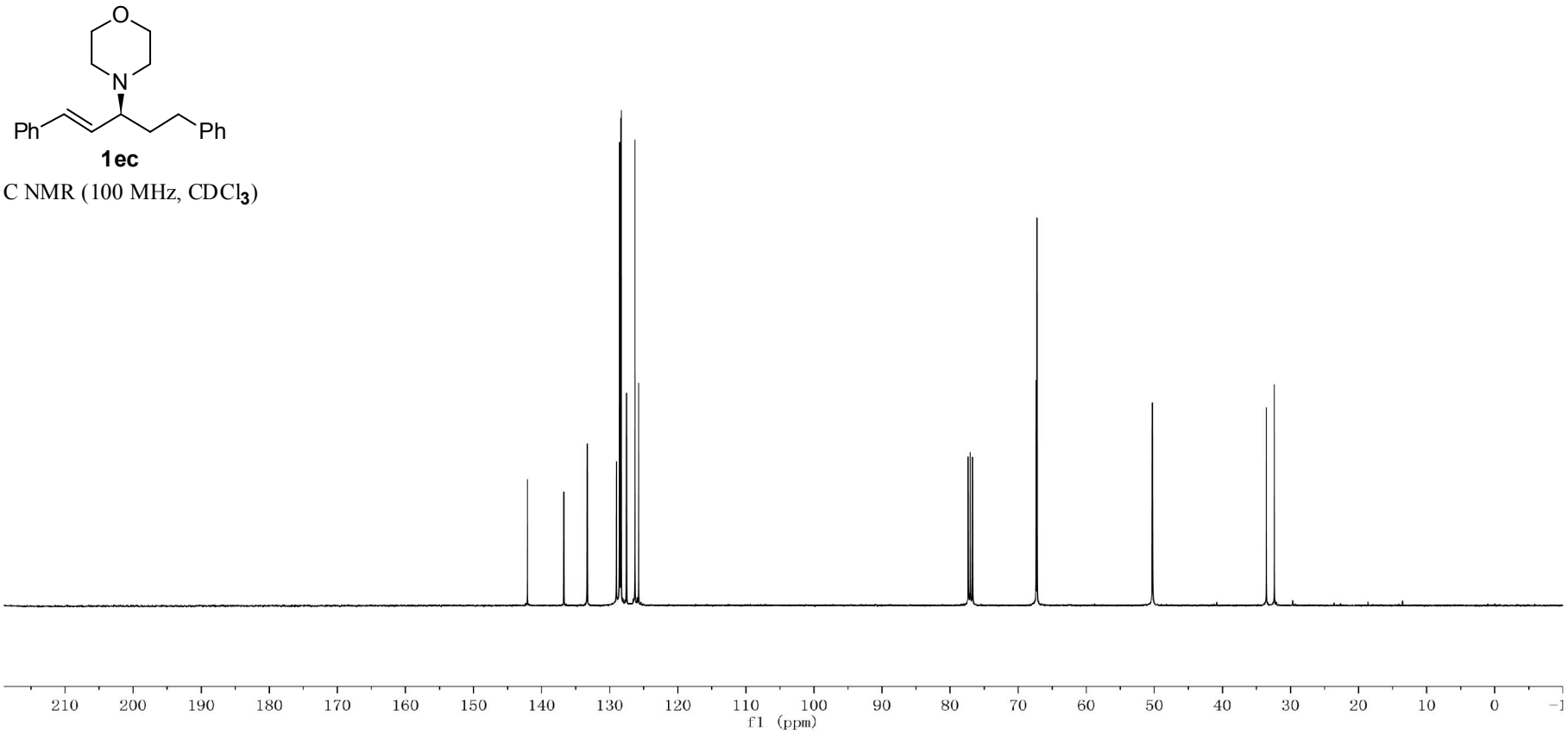

HN
Ph
Ph
Ph
1eb
^{1}H NMR (400 MHz, CDCl$_3$)
f1 (ppm)



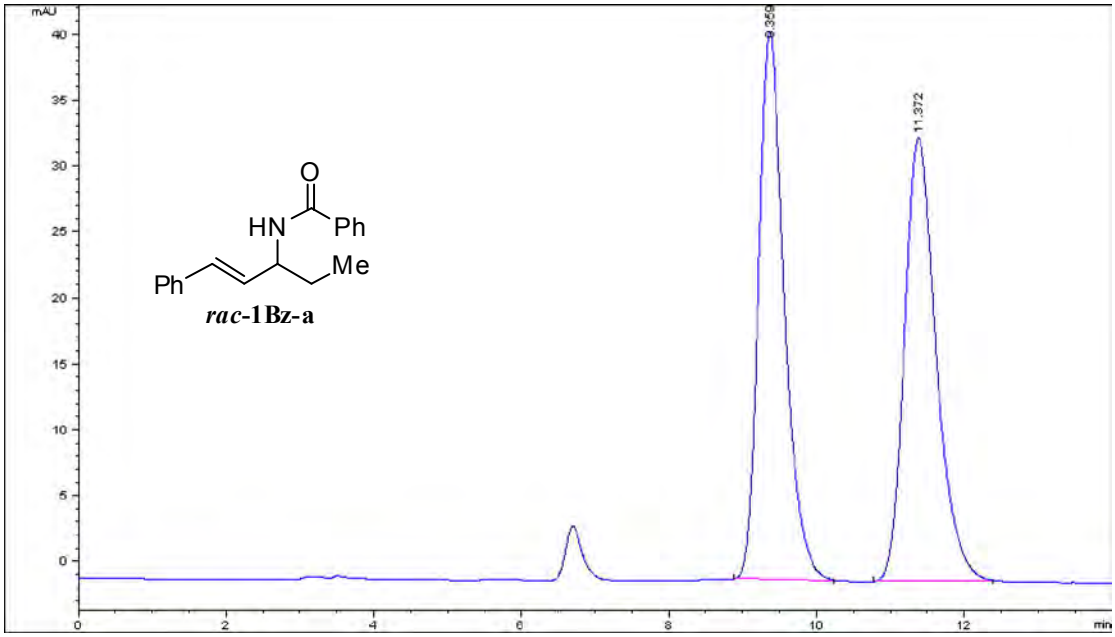
1eb

^{13}C NMR (100 MHz, $CDCl_3$)


7.391
7.373
7.335
7.317
7.297
7.283
7.263
7.246
7.232
7.214
7.185
7.167
7.150
3.753
3.744
3.725
3.716
3.710
3.708
3.702
3.693
3.673
3.665
2.922
2.909
2.642
2.626
2.616
2.602
2.533
2.522
2.509
2.114
2.099
2.086
2.080
2.075
2.065
2.054
2.041
2.027
1.866
1.851
1.842
1.830
1.819
1.807
1.795
1.786
1.772
0.000
O
N
Ph
Ph
1ec
[1]H NMR (400 MHz, CDCl3)
10.10
1.00
1.00
4.09
1.03
0.98
2.97
2.01
1.03
1.01
f1 (ppm)

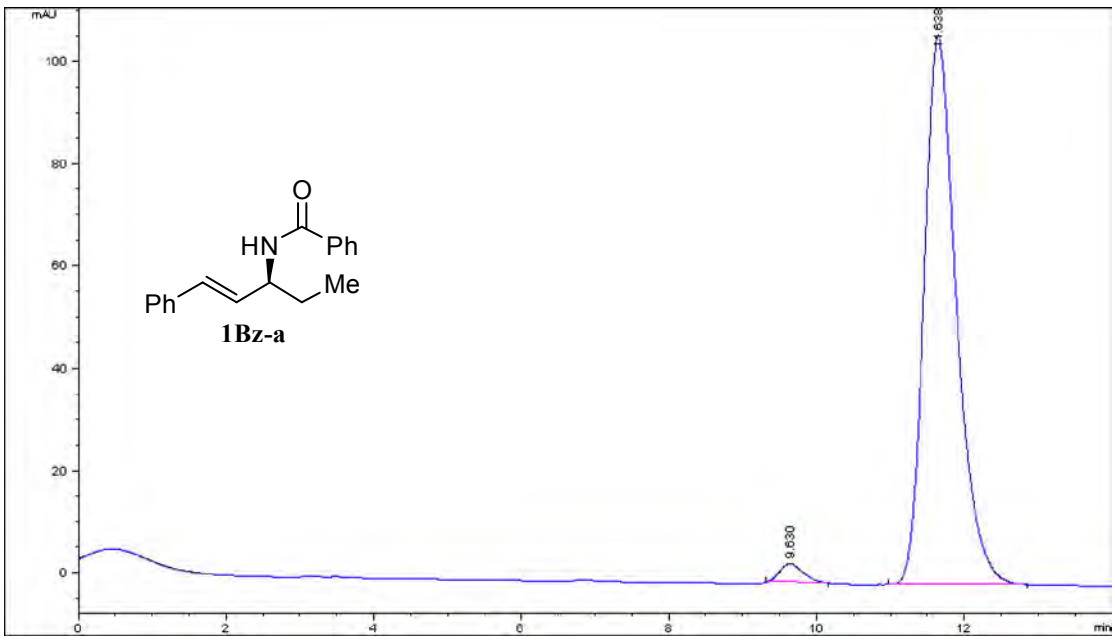


^{13}C NMR (100 MHz, $CDCl_3$)



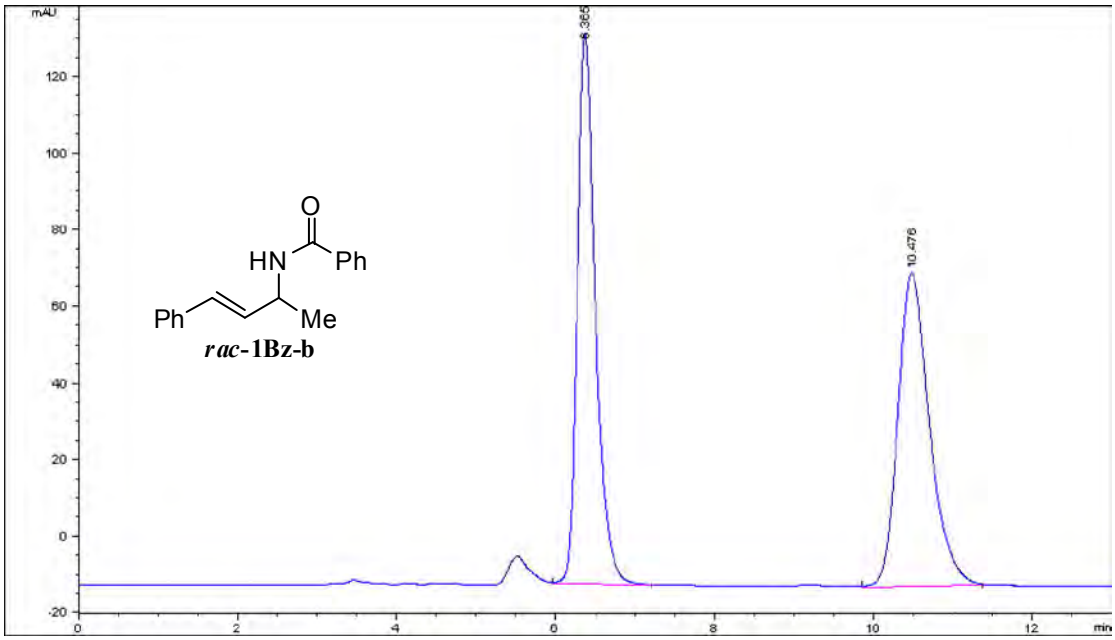
***rac*-1Bz-a**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.359	1006.6	41.5	0.3657	0.725	50.022
2	11.372	1005.7	33.7	0.4505	0.74	49.978

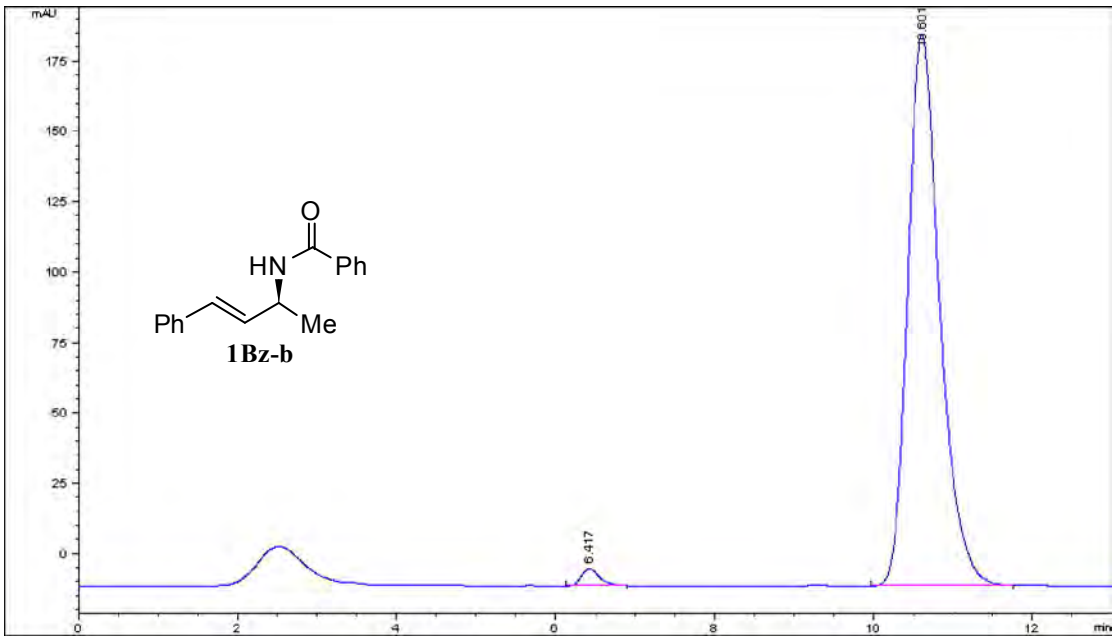


1Bz-a

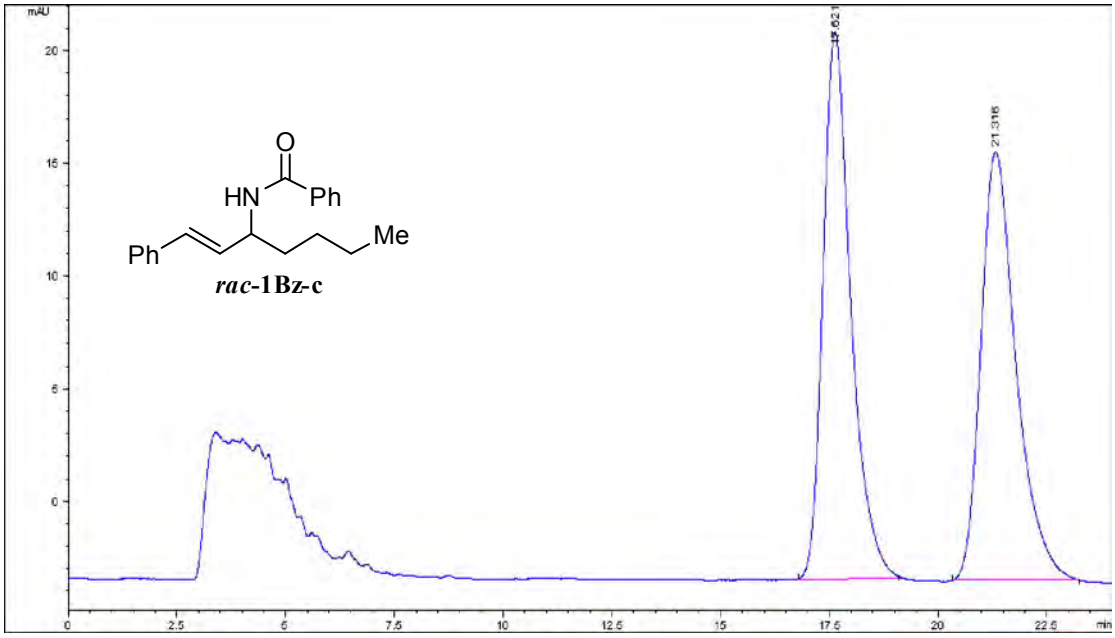
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.63	81.9	3.7	0.3719	0.783	2.459
2	11.638	3250.1	107.4	0.5043	0.737	97.541



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.365	2281.7	144	0.2387	0.688	50.261
2	10.476	2258	81.8	0.46	0.761	49.739

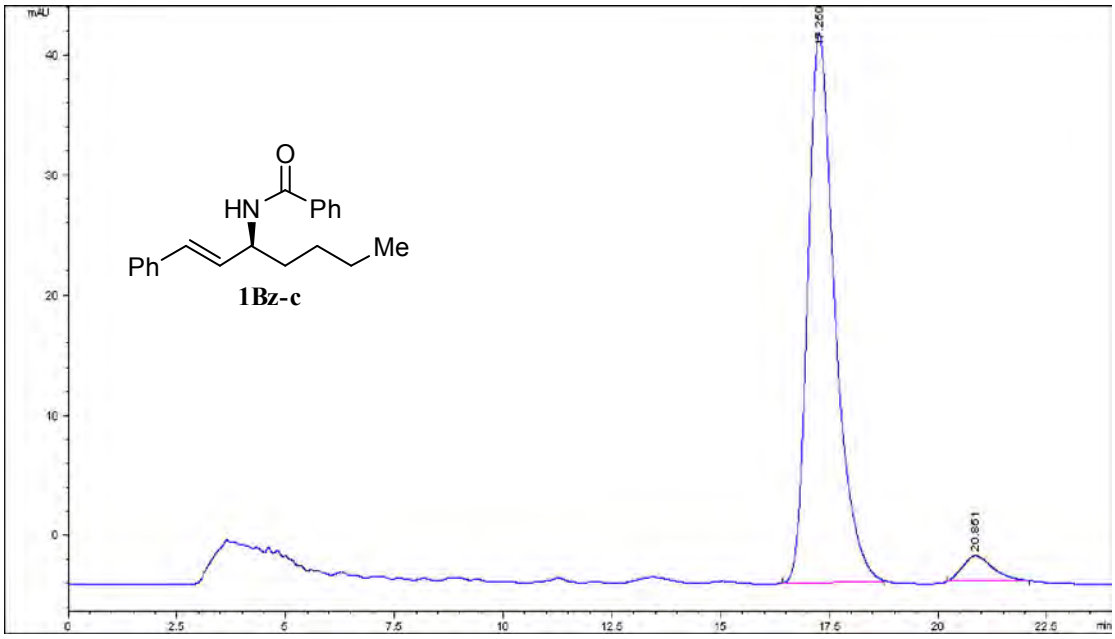


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.417	94.8	6	0.2372	0.701	1.705
2	10.601	5468.6	195.9	0.4261	0.731	98.295



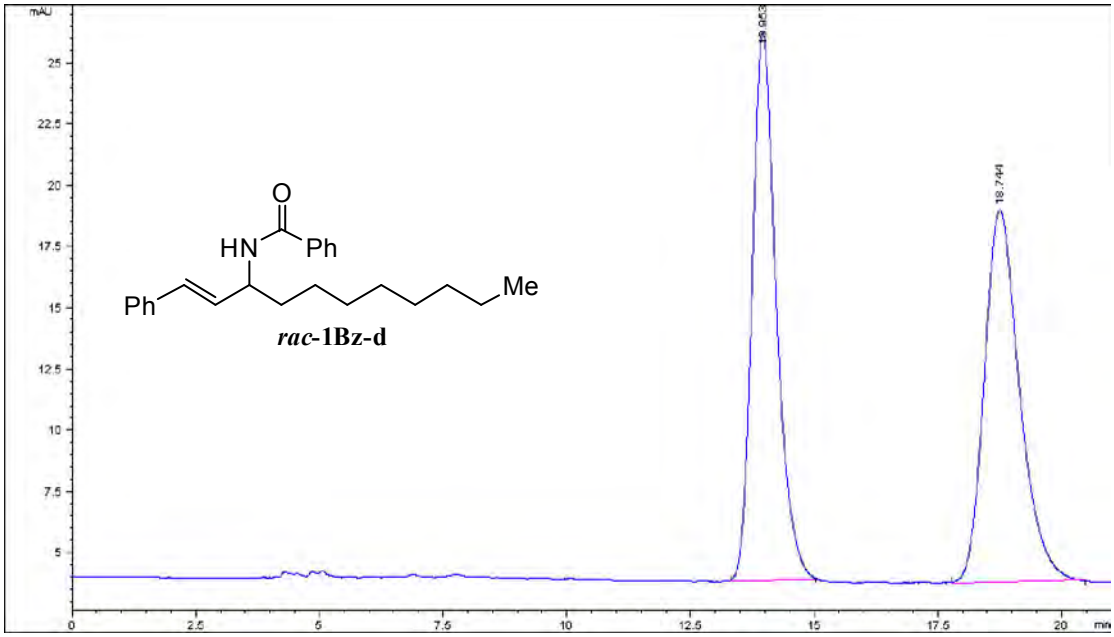
***rac*-1Bz-c**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.621	1083.2	24.3	0.6703	0.697	50.388
2	21.316	1066.5	19	0.936	0.691	49.612

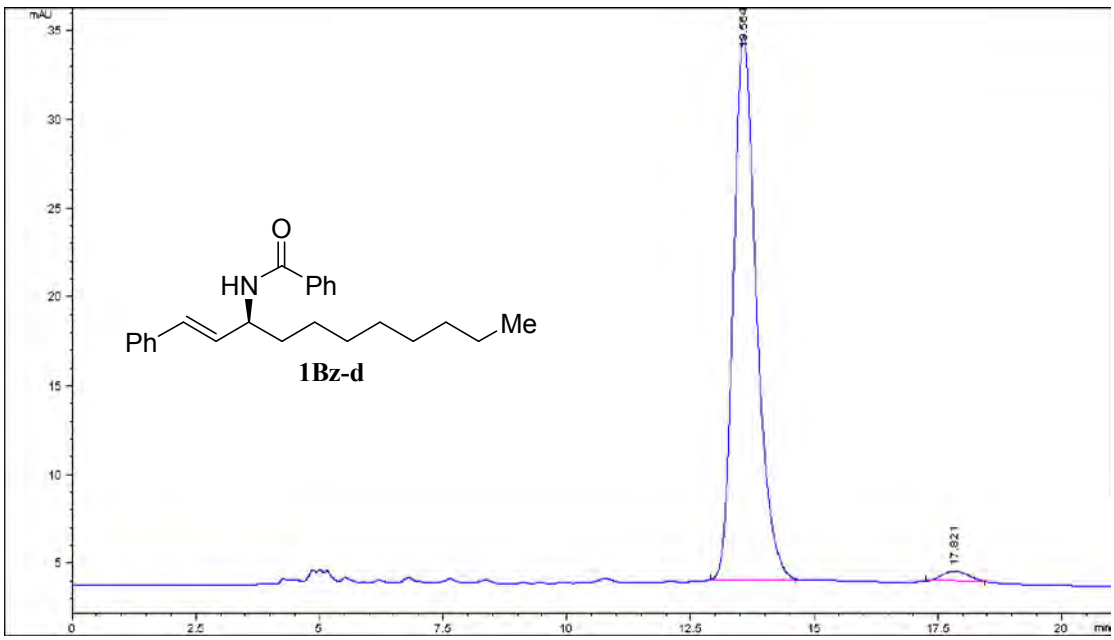


1Bz-c

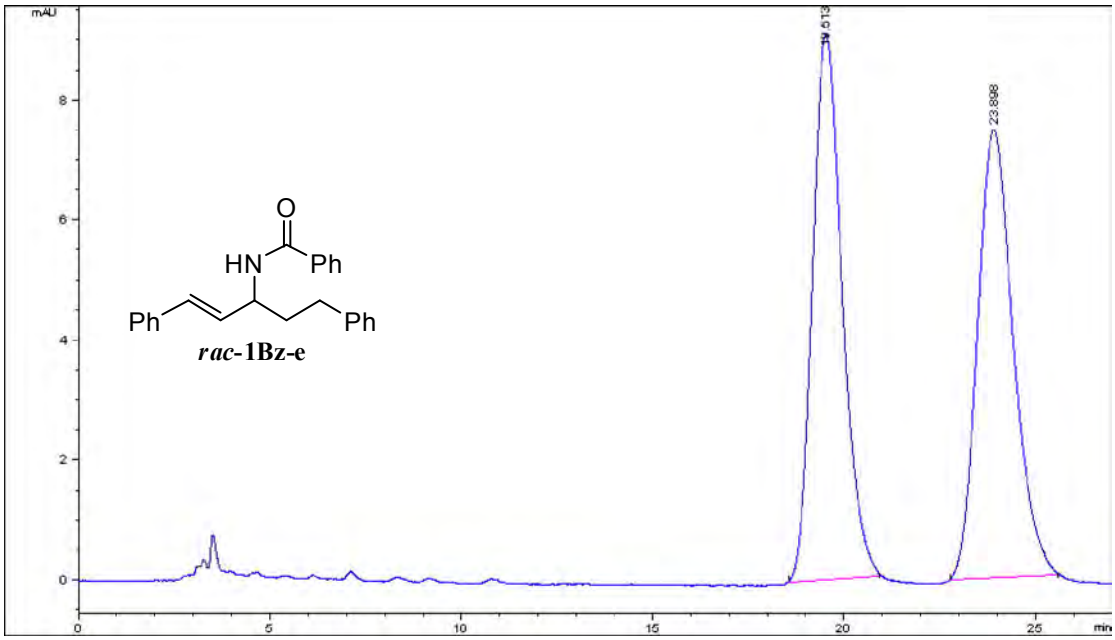
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	17.259	1982	45.8	0.6493	0.68	94.964
2	20.851	105.1	2.1	0.8188	0.779	5.036



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.953	760.1	22.4	0.5105	0.742	50.156
2	18.744	755.4	15.2	0.8275	0.765	49.844

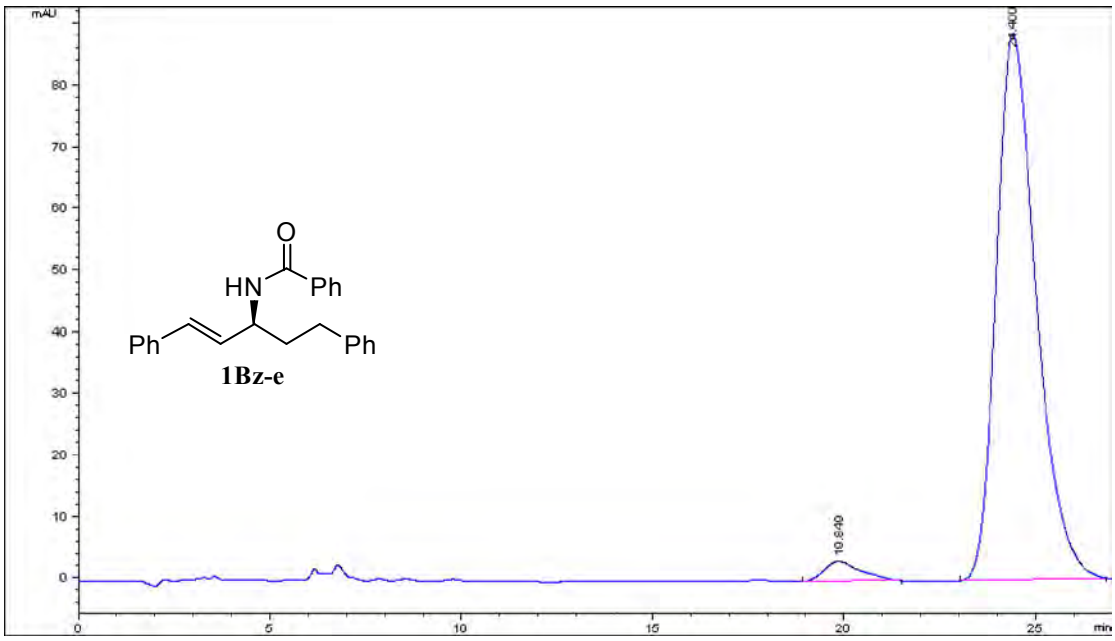


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.564	992.1	30.7	0.4888	0.741	97.902
2	17.821	21.3	5.8E-1	0.606	0.854	2.098



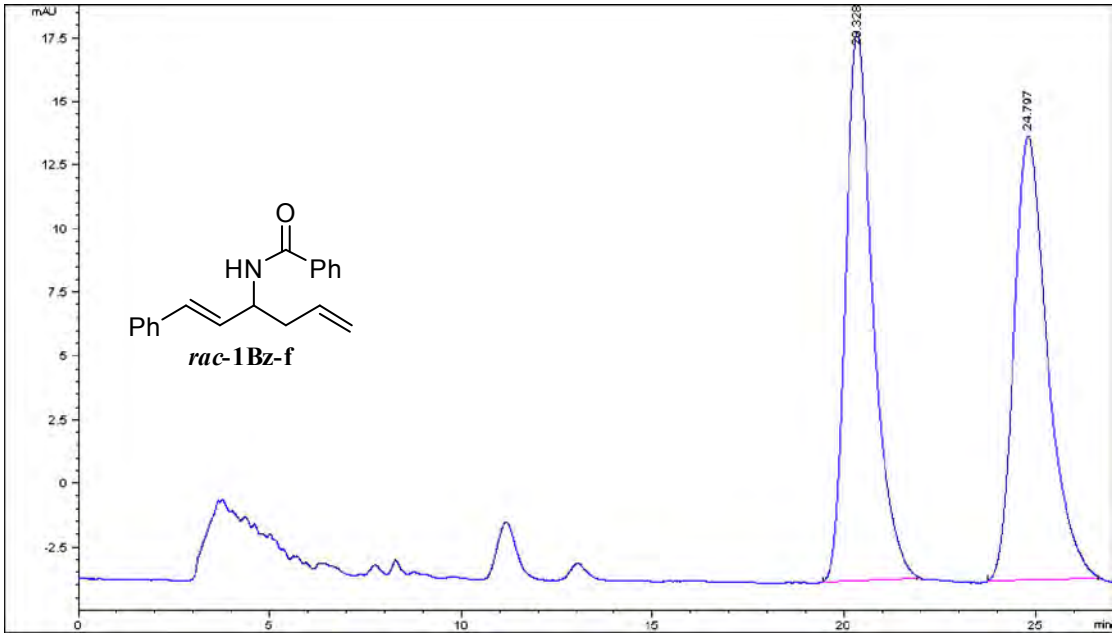
***rac*-1Bz-e**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.513	490.4	9.1	0.7966	0.778	50.170
2	23.898	487.1	7.5	0.9456	0.785	49.830

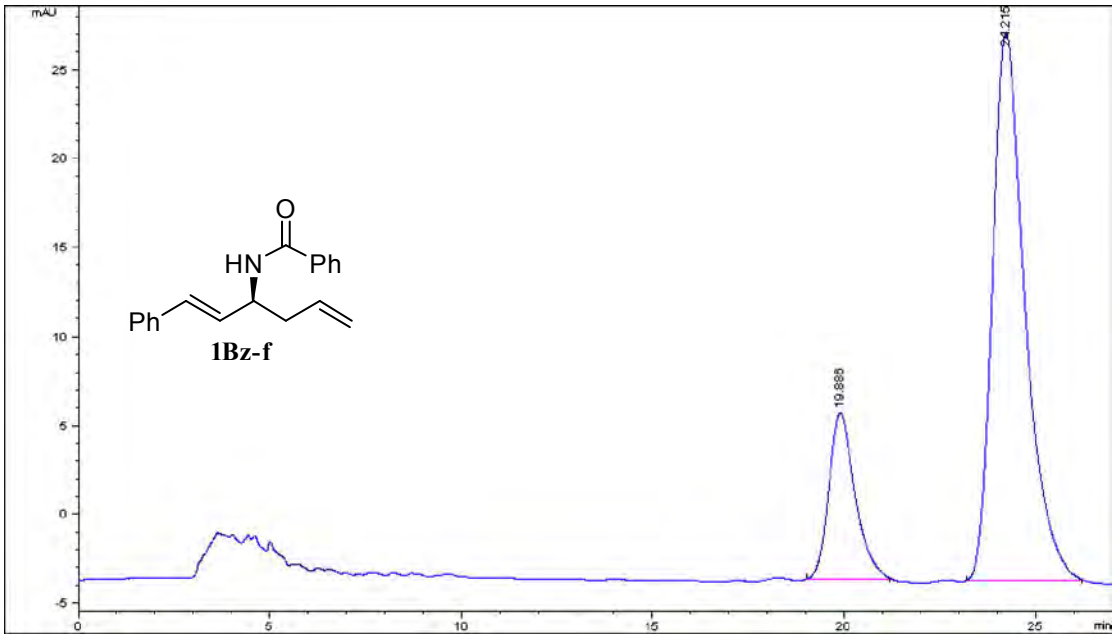


1Bz-e

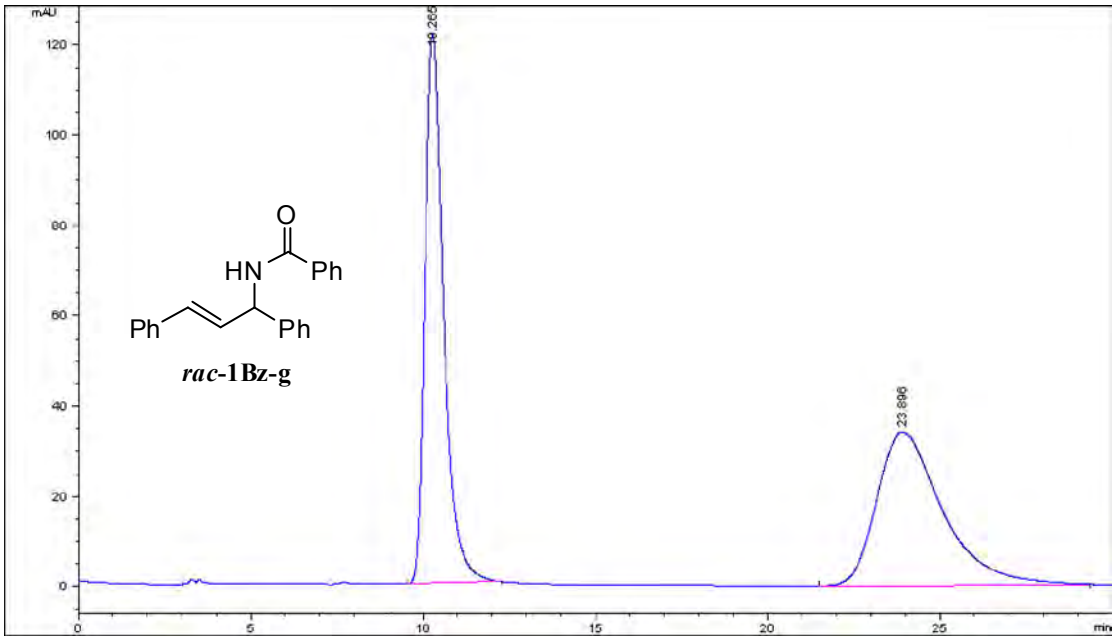
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.849	215.8	3.2	0.8761	0.603	3.243
2	24.4	6436.8	88.6	1.1027	0.678	96.757



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	20.328	1074.6	21.6	0.7446	0.675	50.189
2	24.797	1066.5	17.5	0.9094	0.685	49.811

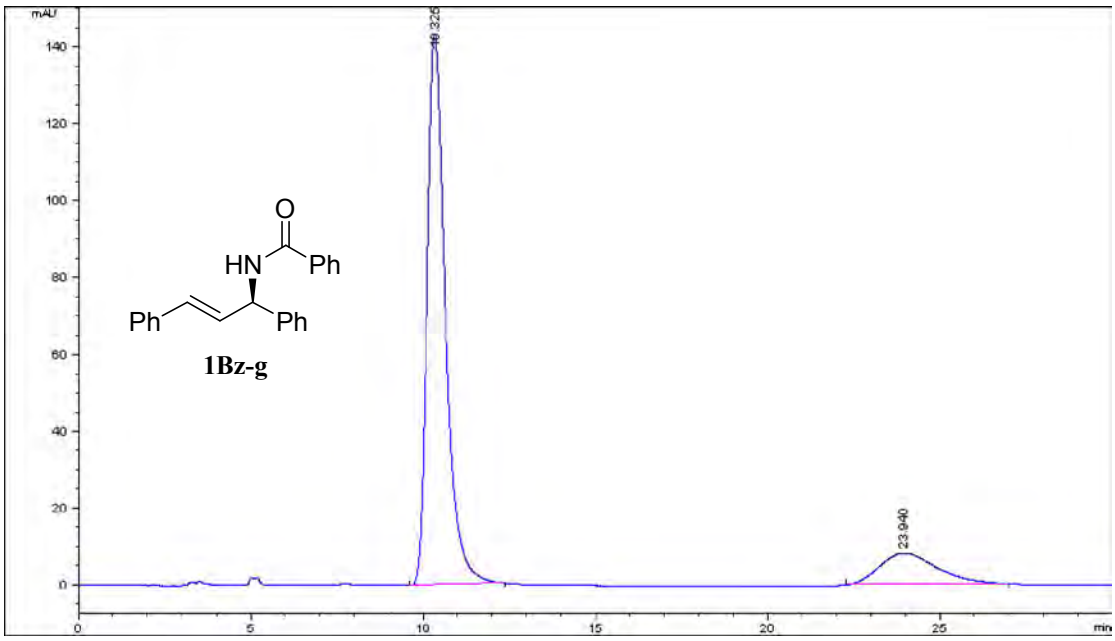


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.886	452.4	9.4	0.7015	0.724	19.829
2	24.215	1829.1	30.8	0.8901	0.656	80.171



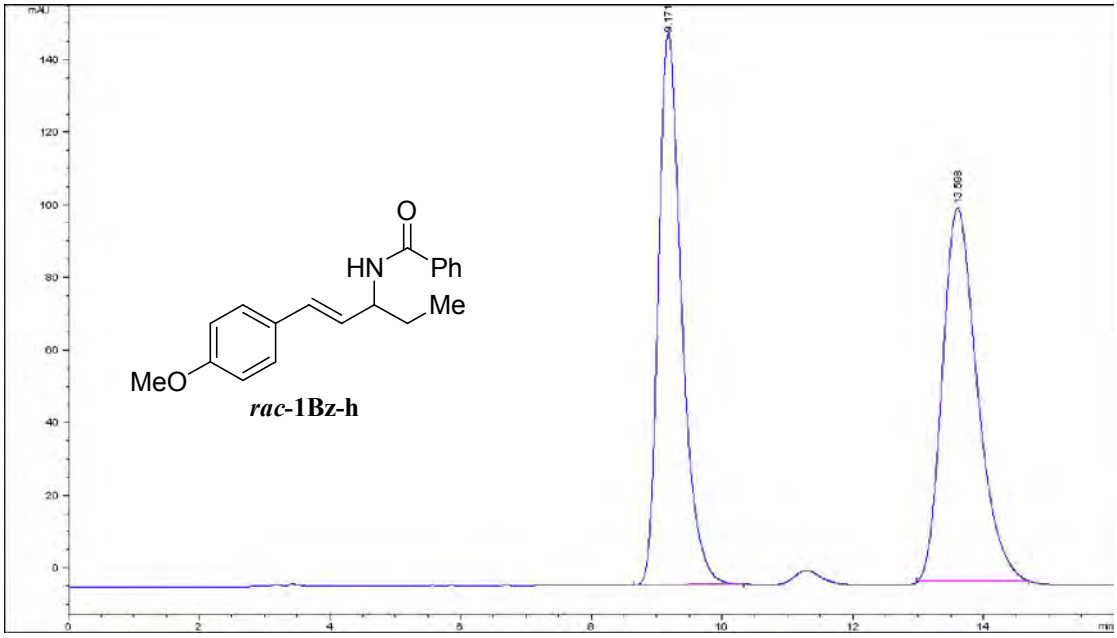
***rac*-1Bz-g**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.265	4585.9	121.8	0.5687	0.629	50.190
2	23.896	4551.1	34.2	2.2187	0.609	49.810



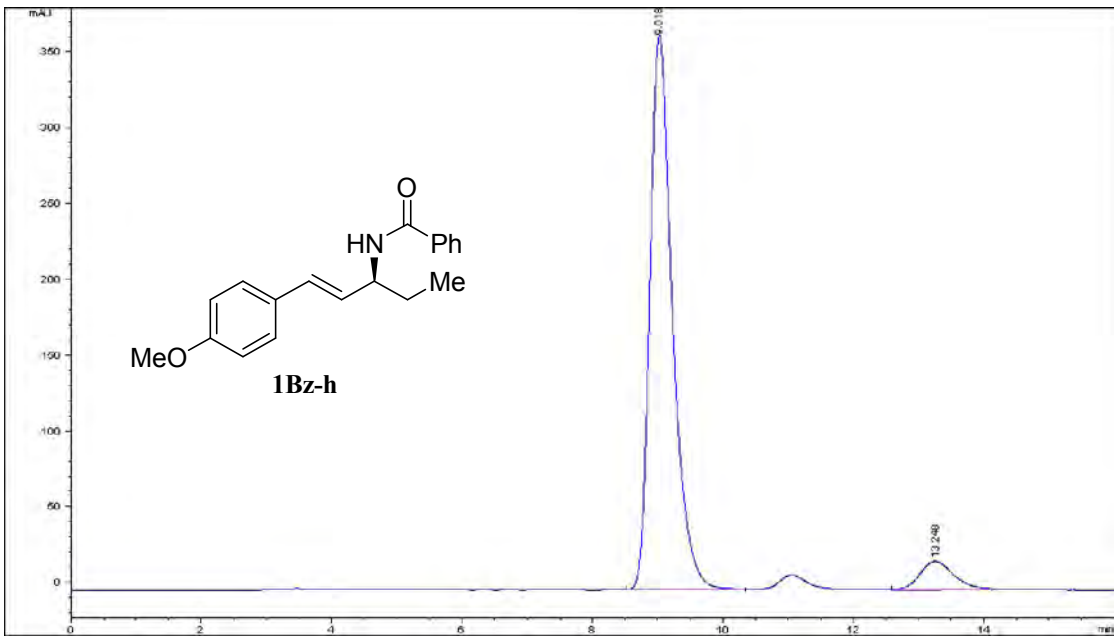
1Bz-g

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.325	5266.5	143.3	0.554	0.635	84.784
2	23.94	945.1	8.1	1.946	0.695	15.216



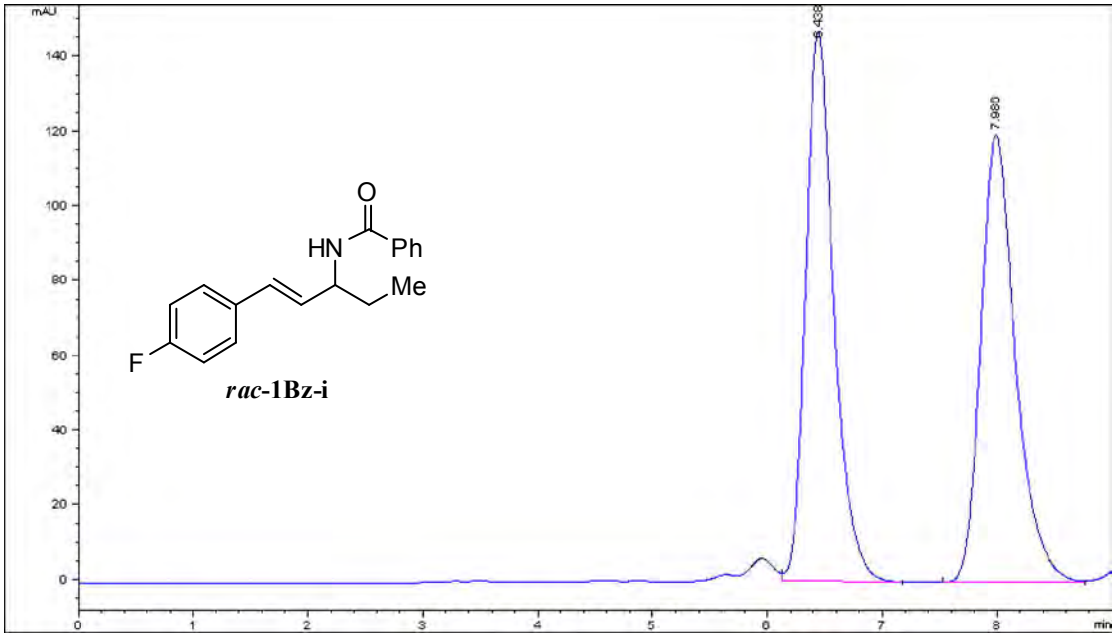
***rac*-1Bz-h**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.171	3761.9	152.3	0.3755	0.682	49.636
2	13.598	3817	102.8	0.6187	0.738	50.364



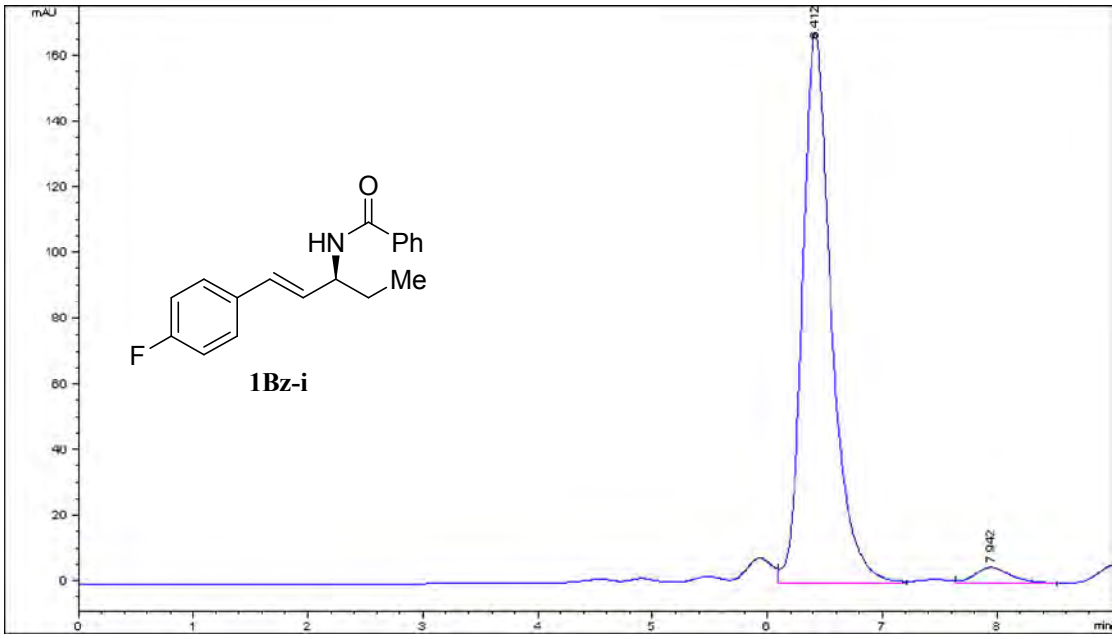
1Bz-h

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.018	8753.5	365.5	0.3624	0.666	92.599
2	13.248	699.6	19.1	0.6106	0.819	7.401



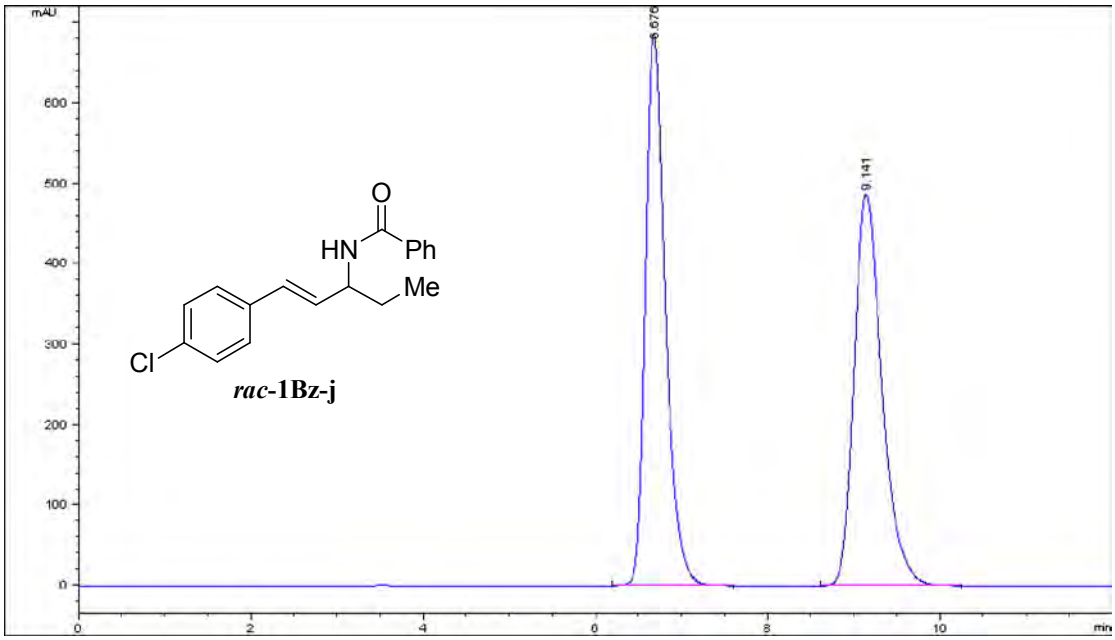
***rac*-1Bz-i**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.438	2519.5	147.1	0.2609	0.752	50.070
2	7.986	2512.5	119.8	0.3175	0.724	49.930



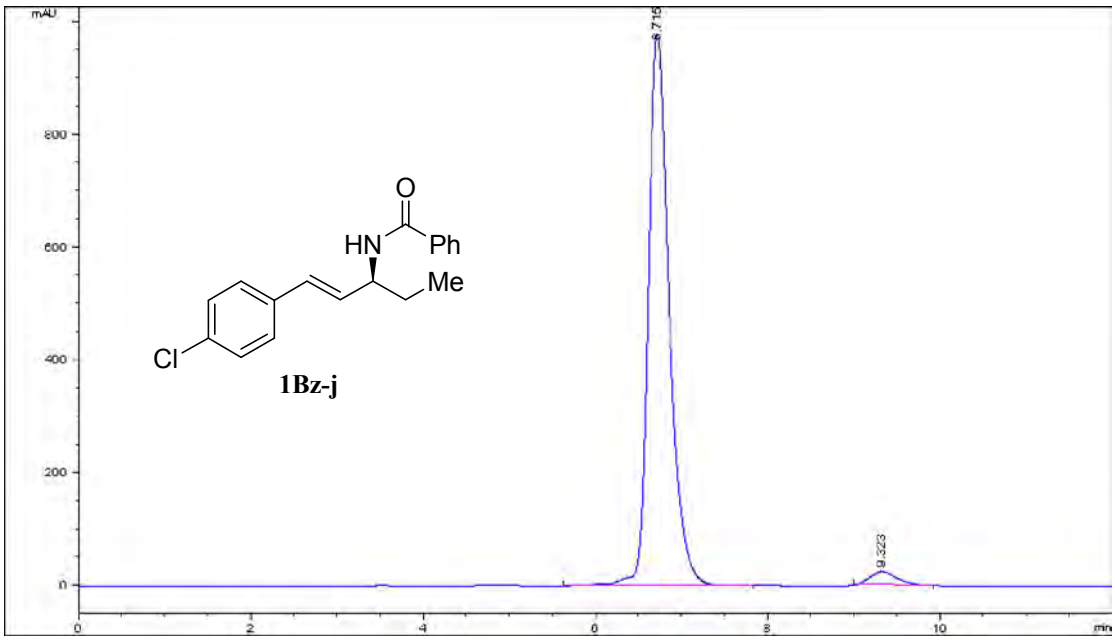
1Bz-i

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.412	2936.3	167.5	0.2642	0.73	96.457
2	7.942	107.8	4.9	0.3265	0.775	3.543



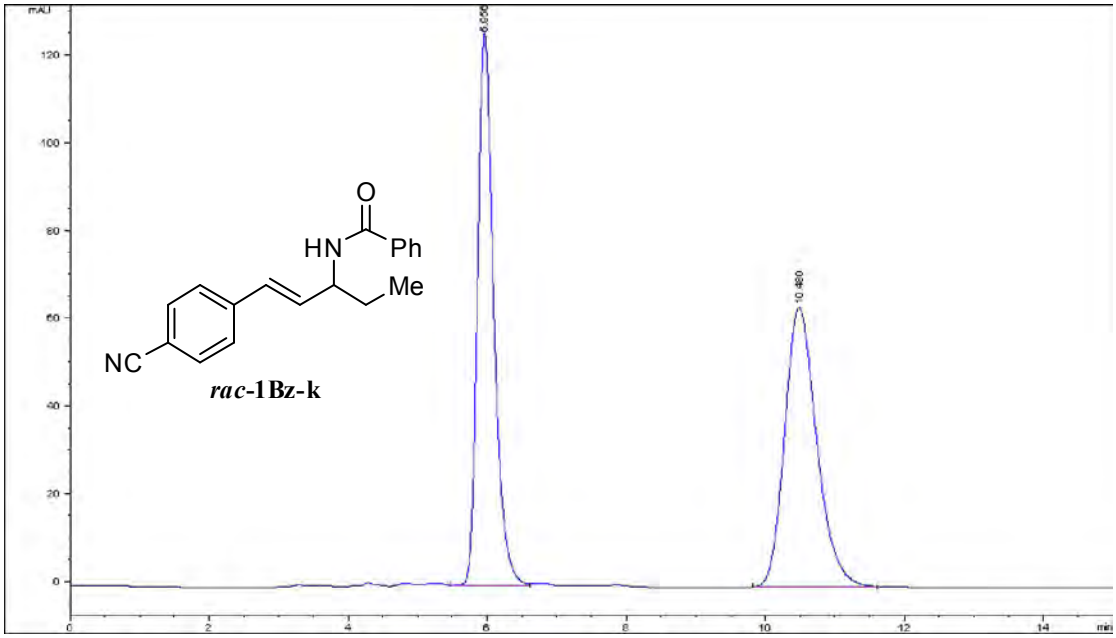
***rac*-1Bz-j**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.676	10992	687.2	0.2419	0.699	50.115
2	9.141	10941.7	486.1	0.3427	0.724	49.885



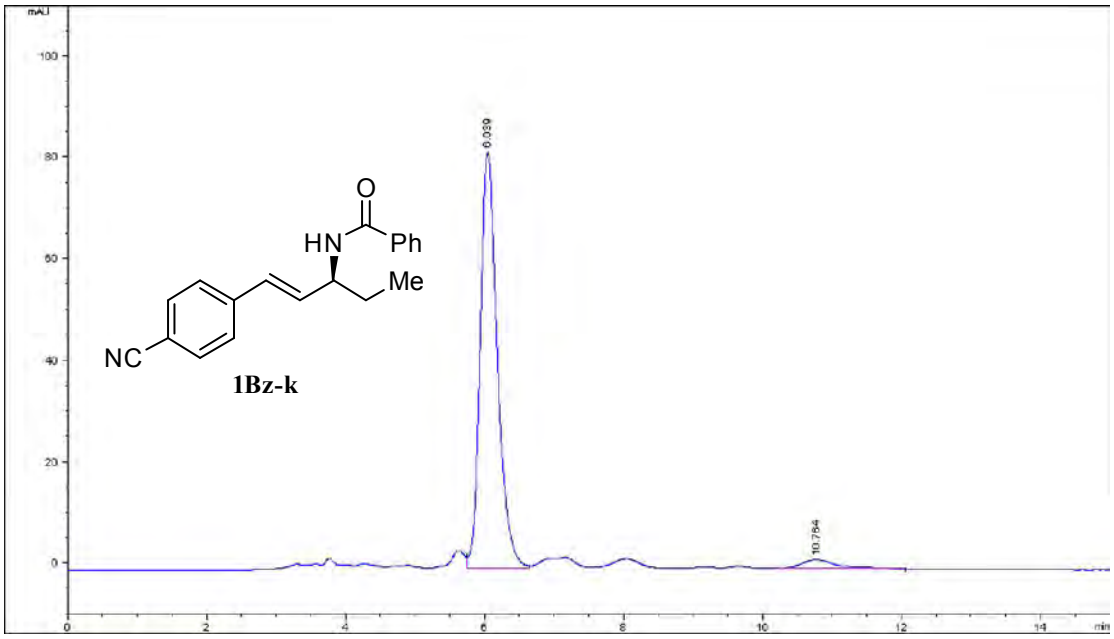
1Bz-j

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.715	16399.7	978.3	0.2794	0.731	96.931
2	9.323	519.2	23.5	0.3686	0.766	3.069



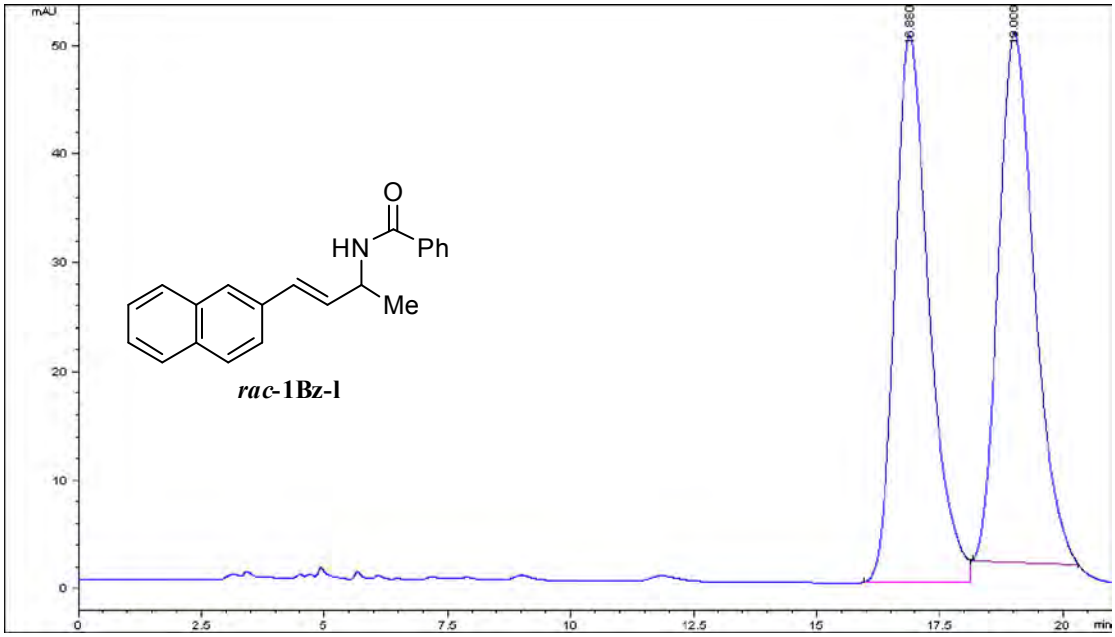
***rac*-1Bz-k**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.956	2056.9	126.2	0.247	0.712	50.183
2	10.48	2041.9	63.7	0.4919	0.774	49.817



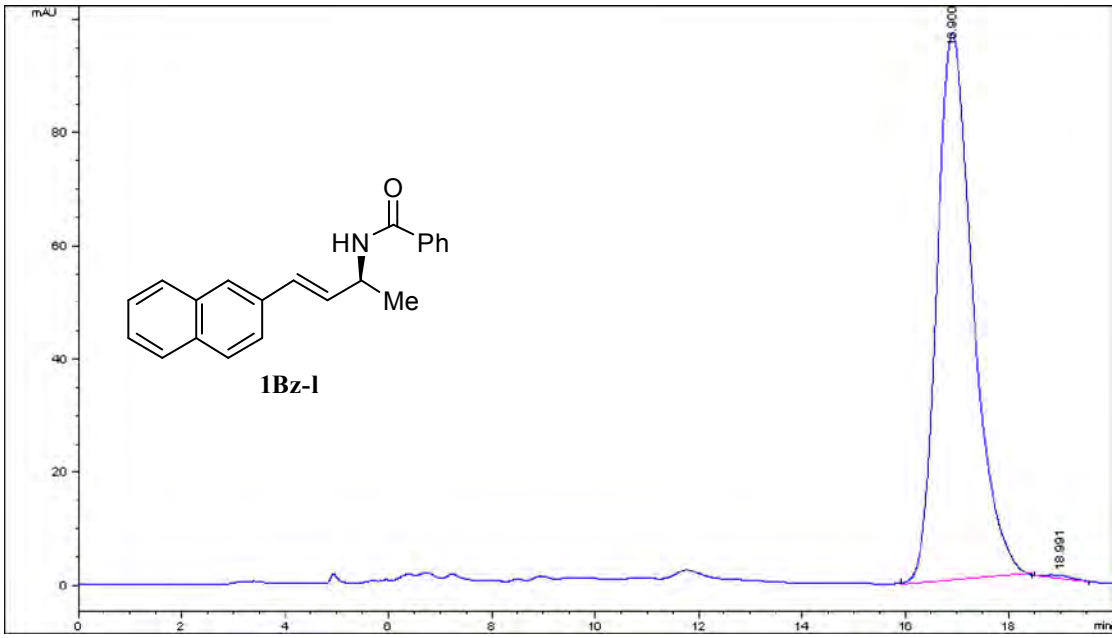
1Bz-k

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.039	1404.9	82.2	0.2592	0.727	95.382
2	10.764	68	1.8	0.5495	0.597	4.618



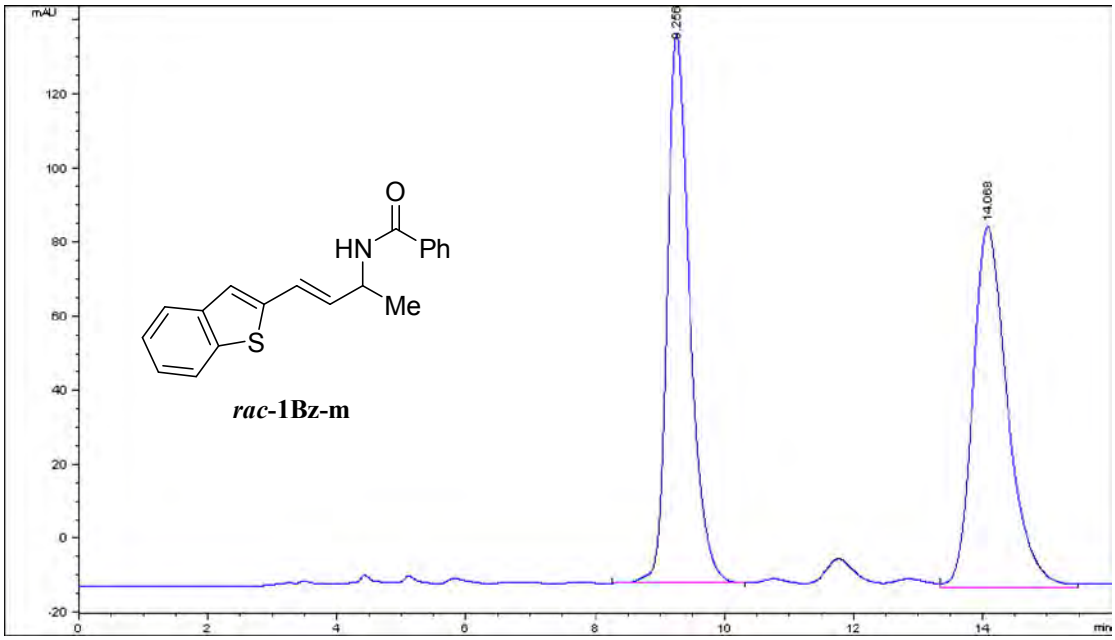
***rac*-1Bz-l**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.88	2435.9	50.3	0.7276	0.712	49.544
2	19.006	2480.7	48.8	0.8468	0.766	50.456



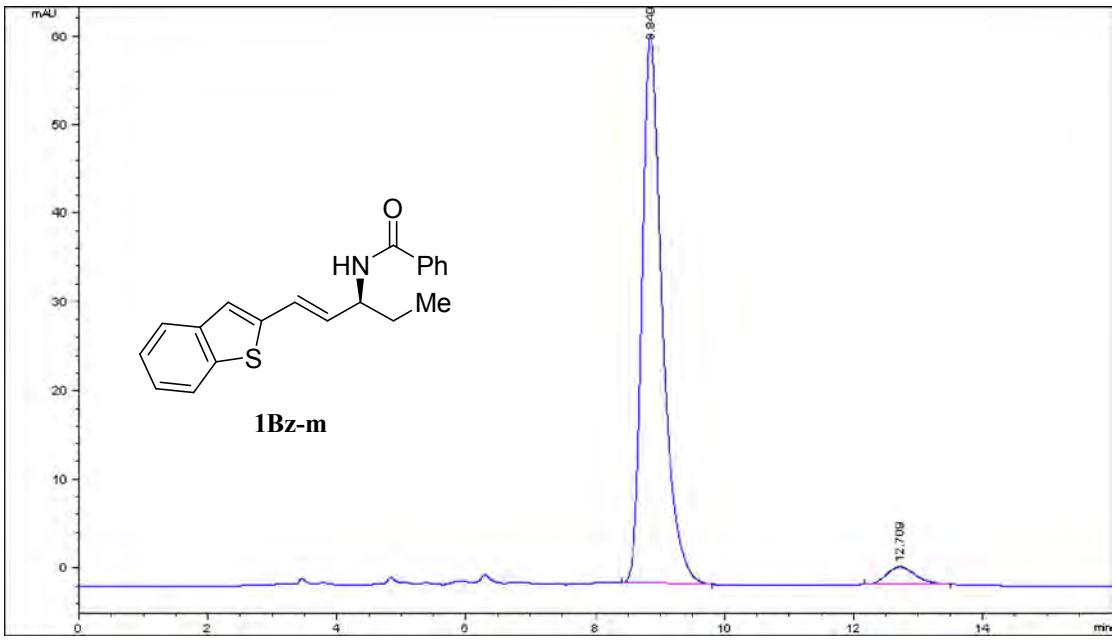
1Bz-l

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.9	4698	96.7	0.8094	0.722	99.488
2	18.991	24.2	6.2E-1	0.6502	0.243	0.512



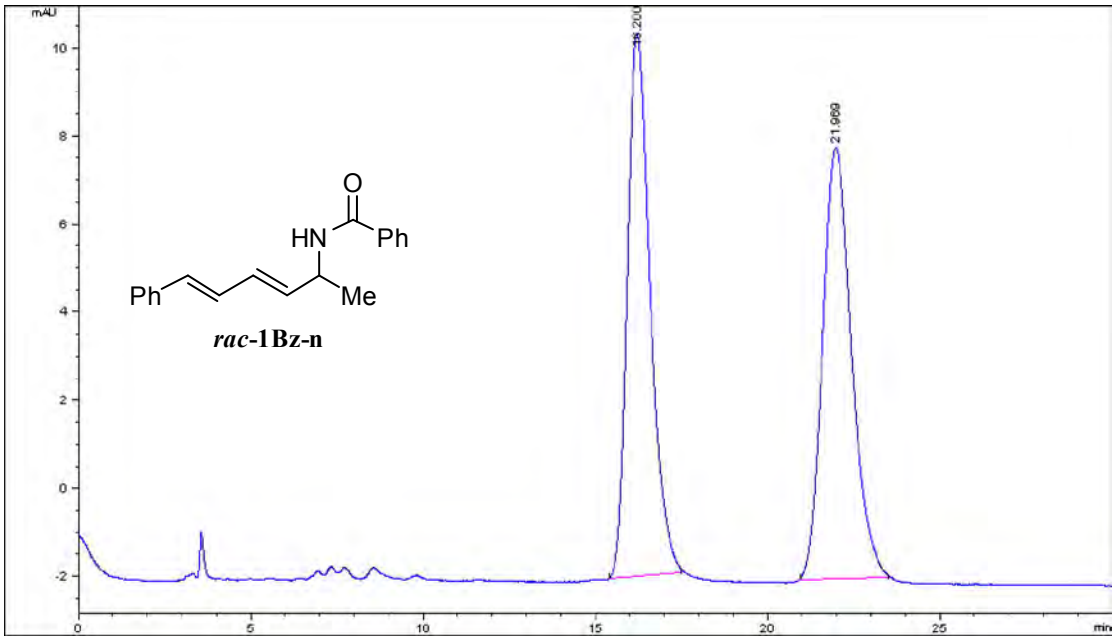
***rac*-1Bz-m**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.256	3613.1	148.5	0.3682	0.706	49.716
2	14.068	3654.4	97.5	0.6245	0.72	50.284



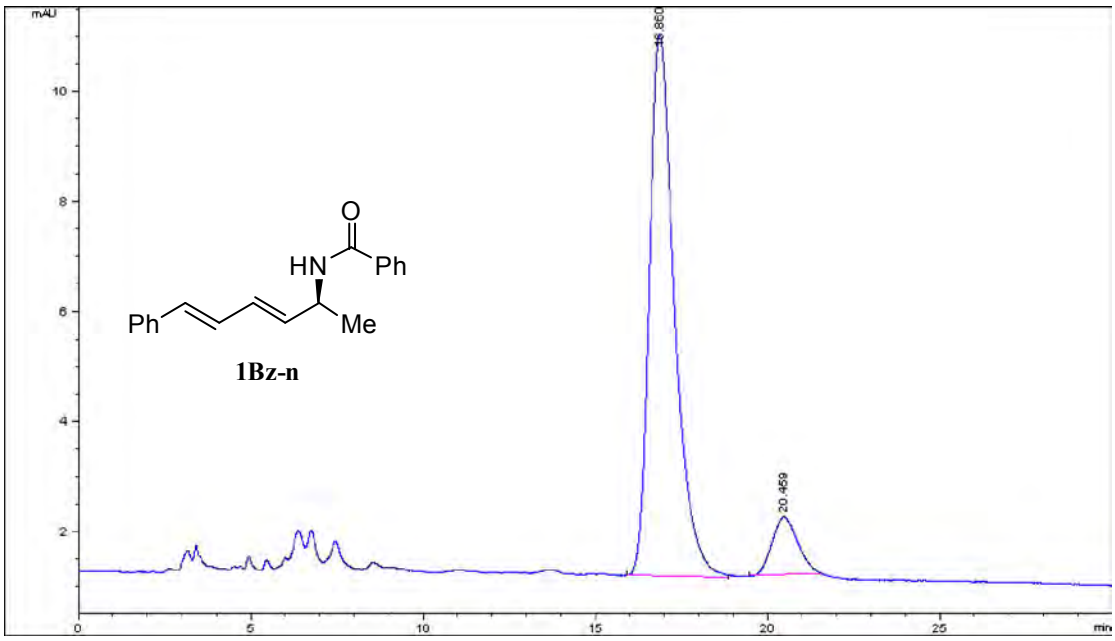
1Bz-m

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.849	1347.6	62	0.3266	0.668	95.657
2	12.709	61.2	2	0.4374	0.808	4.343



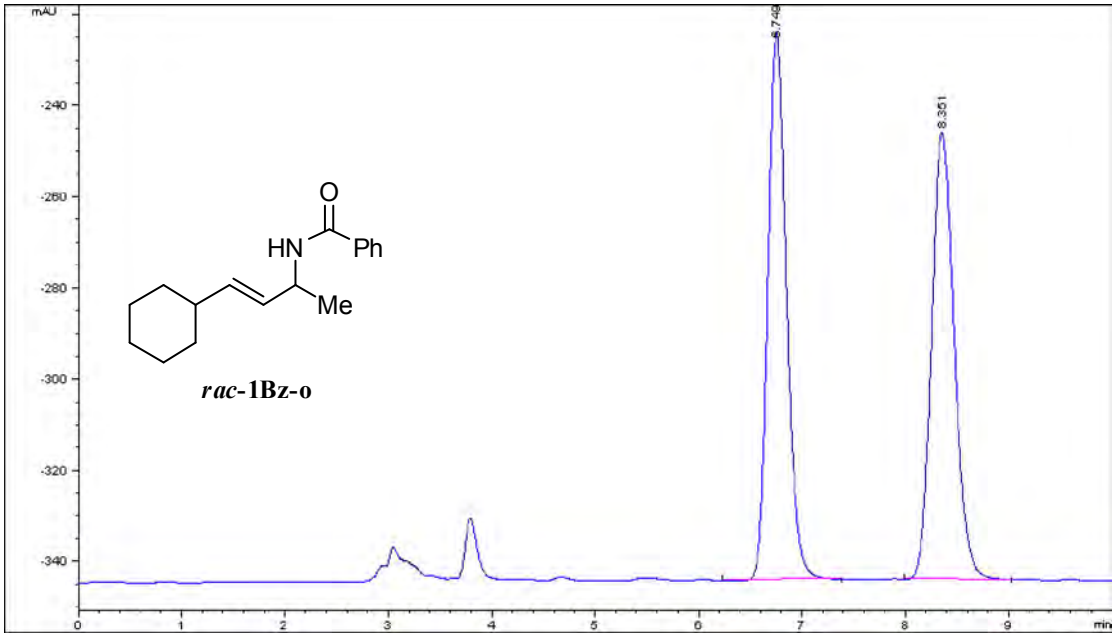
***rac*-1Bz-n**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.2	568.8	12.3	0.6982	0.696	49.784
2	21.969	573.8	9.8	0.8517	0.793	50.216



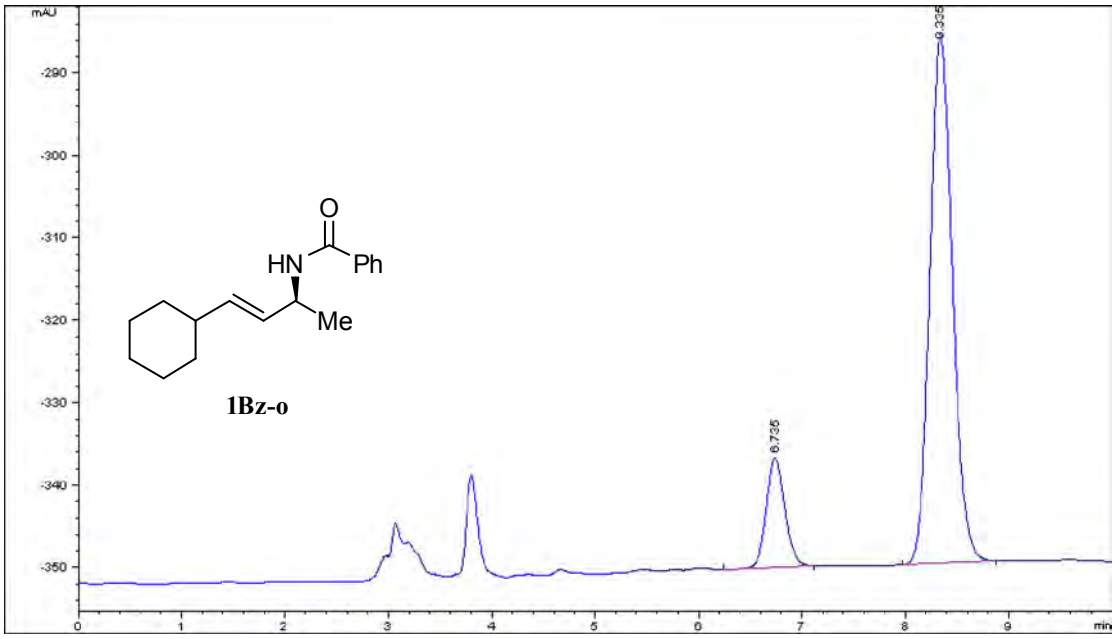
1Bz-n

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	16.86	499.6	9.9	0.8453	0.674	89.908
2	20.459	56.1	1.1	0.8821	0.81	10.032



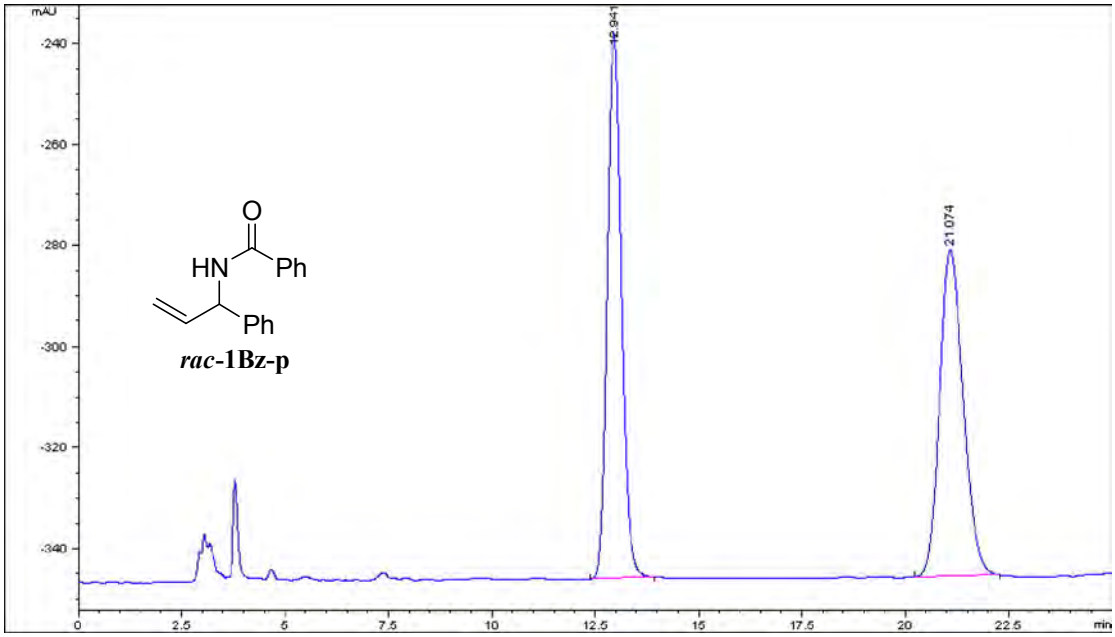
***rac*-1Bz-o**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.749	1507.8	120.3	0.1928	0.804	50.250
2	8.351	1492.9	98.1	0.2357	0.827	49.750



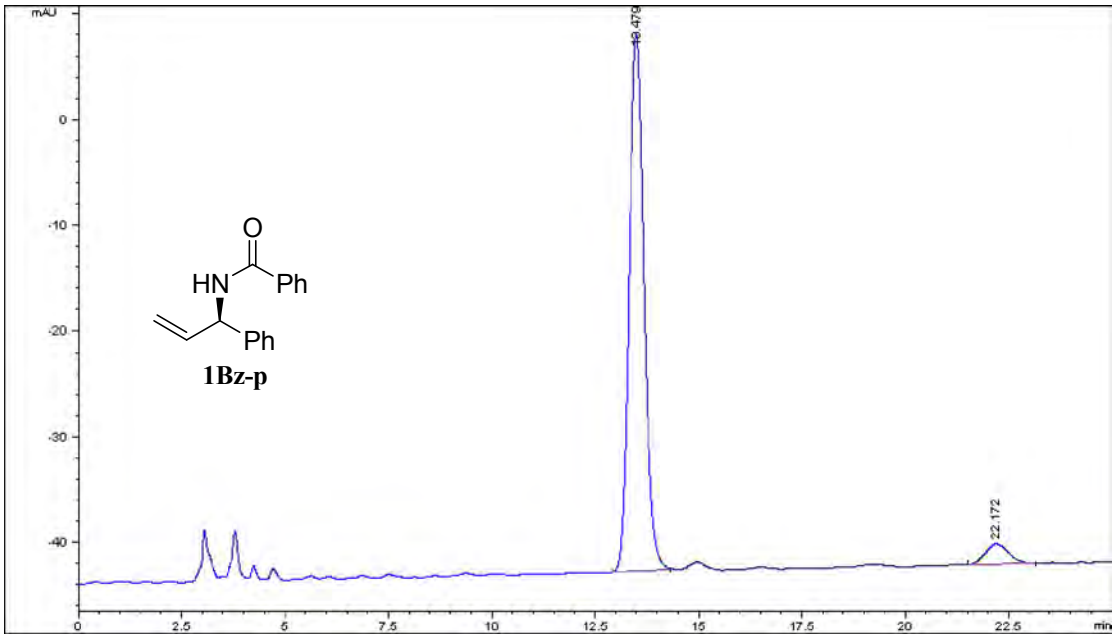
1Bz-o

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.735	169.3	13.4	0.1941	0.868	14.792
2	8.335	975.2	64.4	0.235	0.842	85.208



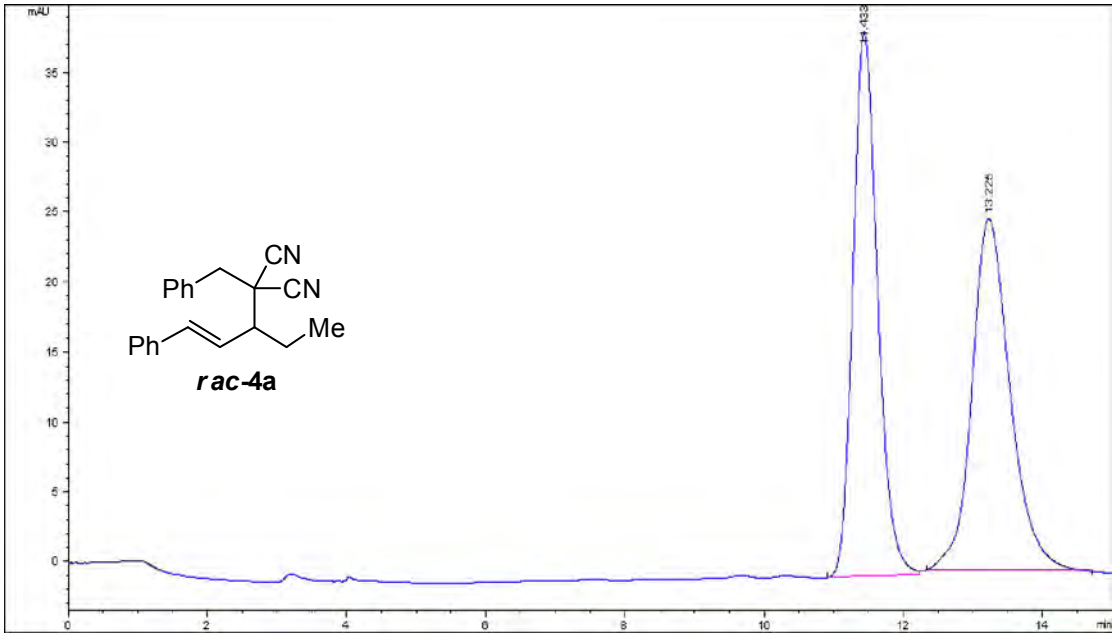
***rac*-1Bz-p**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.941	2573.1	108.1	0.3693	0.832	50.025
2	21.074	2570.5	64.6	0.6145	0.779	49.975

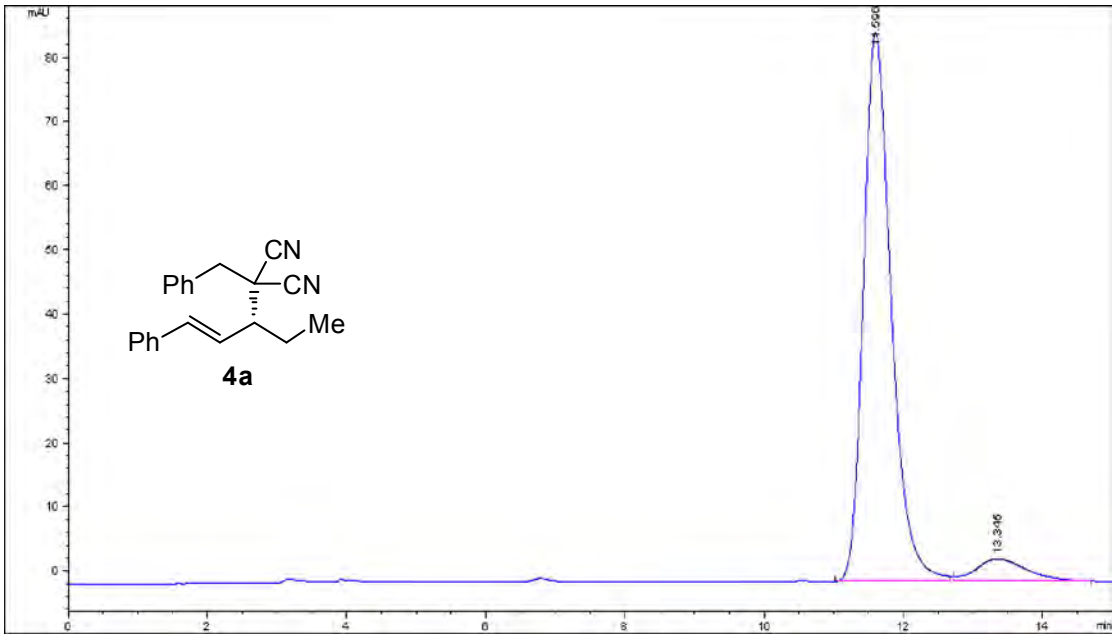


1Bz-p

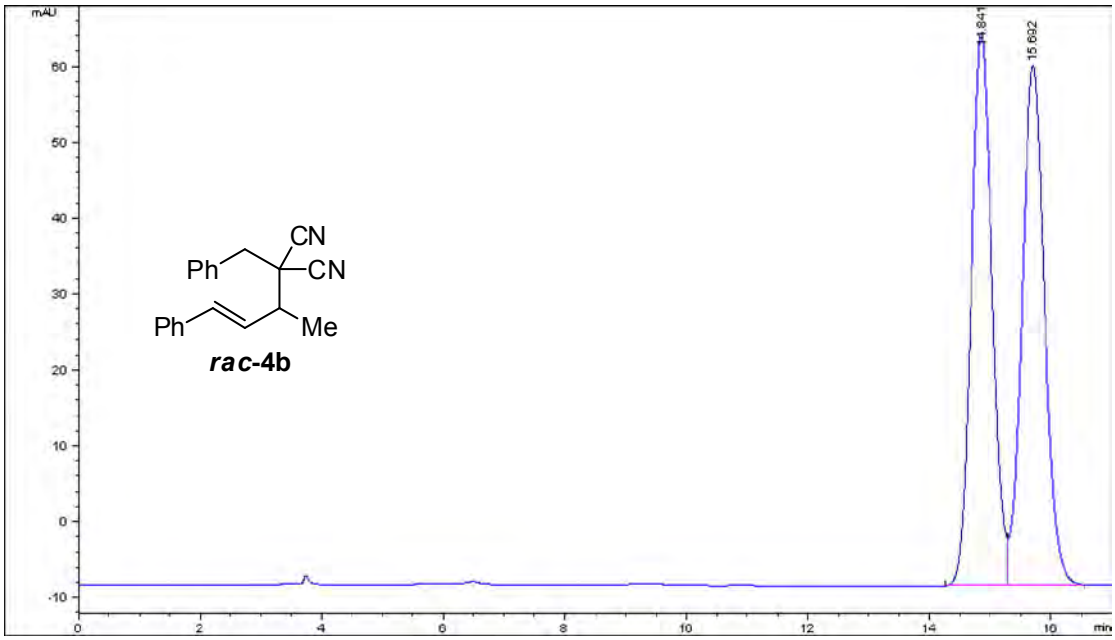
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.479	1265.6	50.9	0.3864	0.845	94.479
2	22.172	74	1.9	0.5517	0.783	5.521



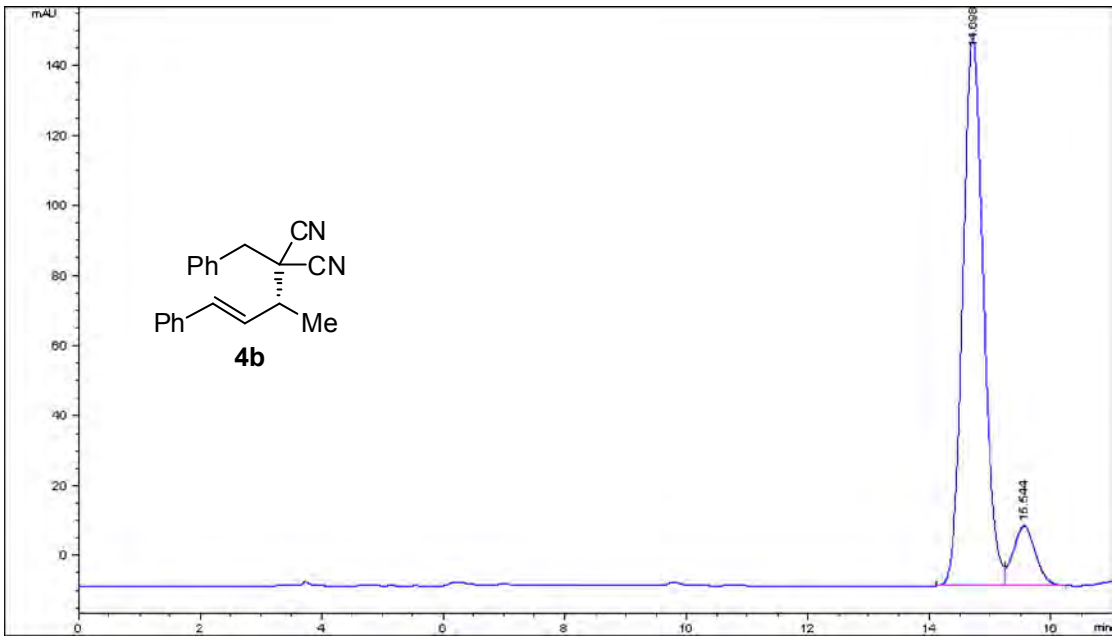
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.433	958.8	39	0.3788	0.789	49.970
2	13.225	959.9	25.1	0.6362	0.778	50.030



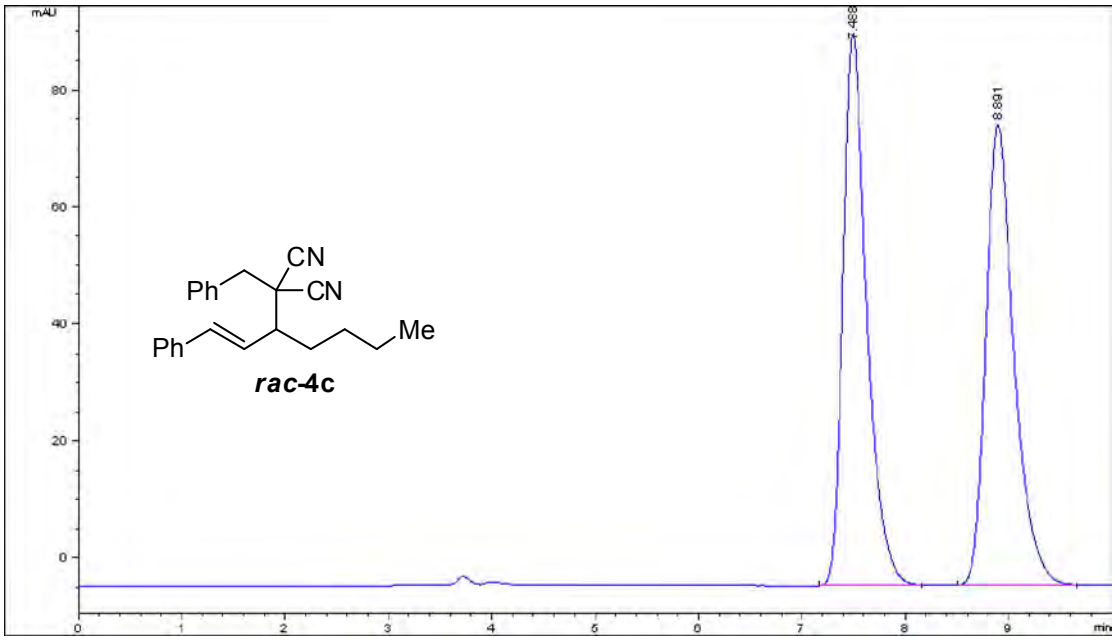
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.596	2364.2	85.4	0.4221	0.722	92.961
2	13.345	179	3.5	0.7241	0.709	7.039



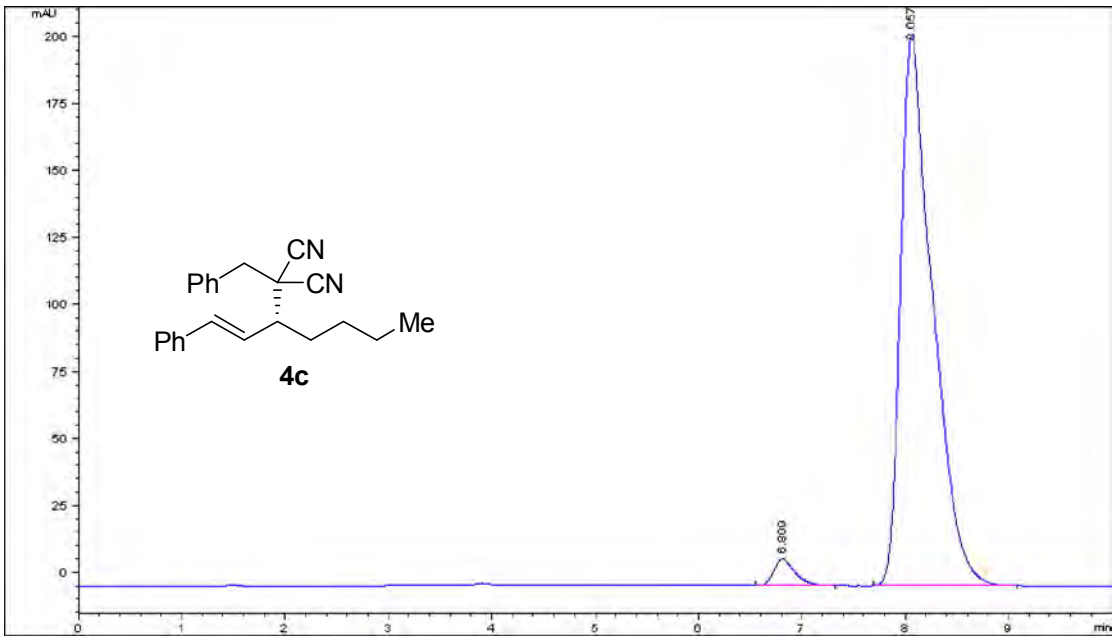
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.841	1730.5	72.8	0.3692	0.896	49.597
2	15.692	1758.6	68.5	0.3971	0.905	50.403



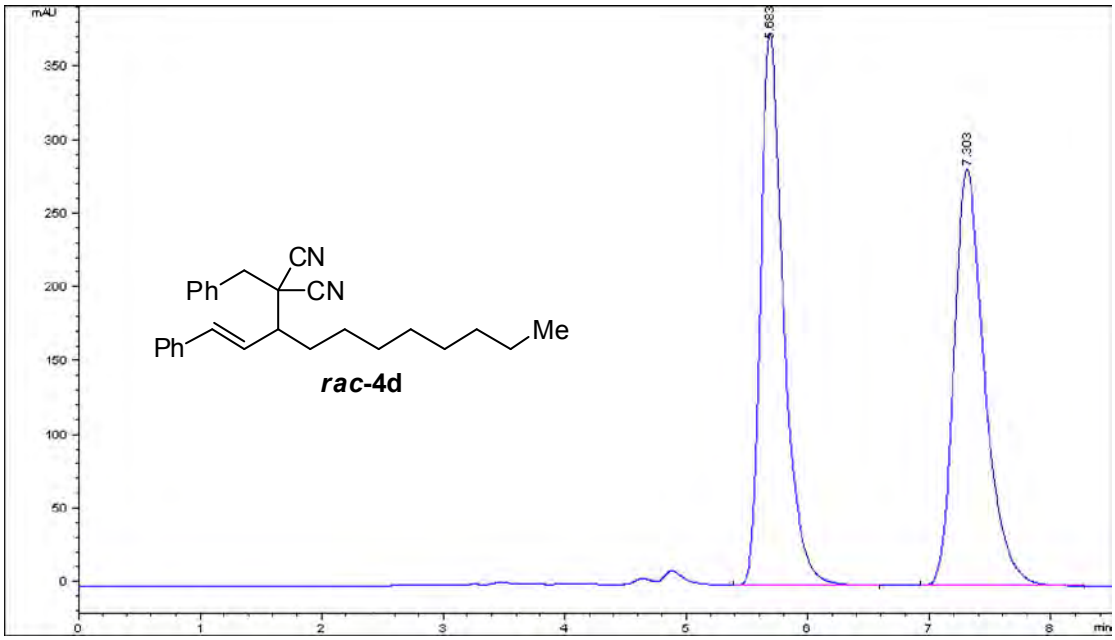
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.698	3717.9	157.5	0.3643	0.875	89.569
2	15.544	433	17.1	0.3891	0.896	10.431



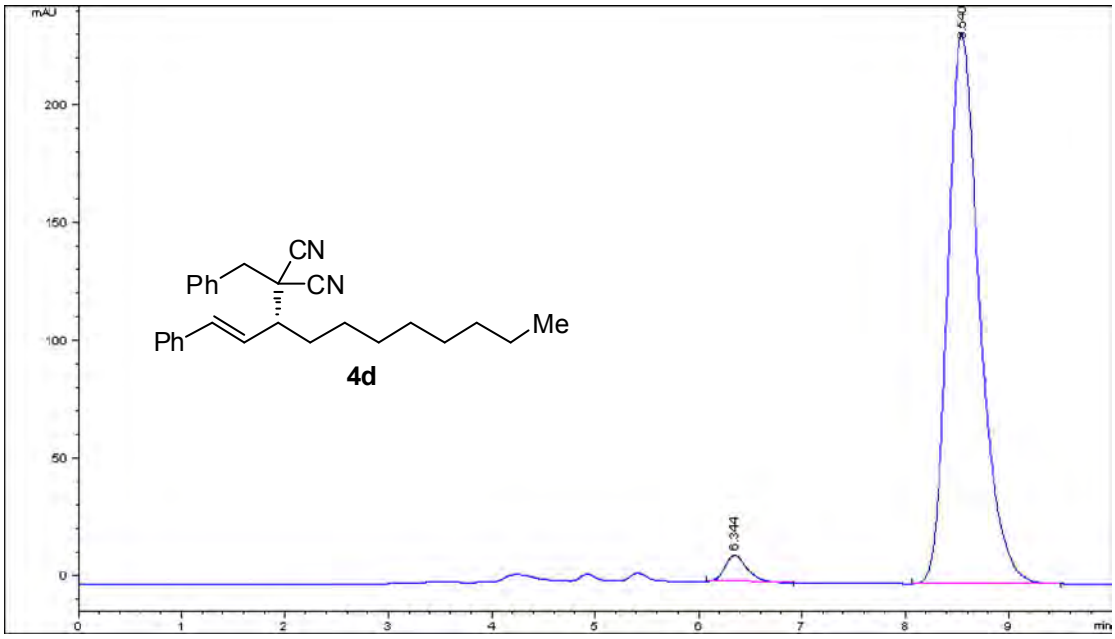
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.488	1499.8	94.3	0.2394	0.659	50.209
2	8.891	1487.3	78.6	0.2849	0.697	49.791



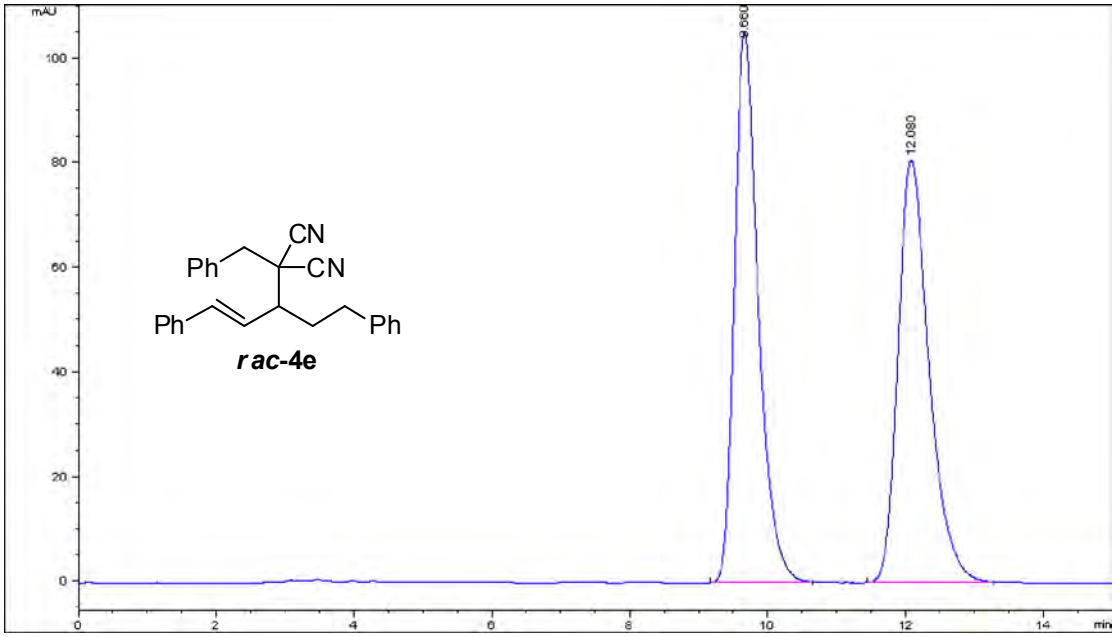
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.809	140.1	10	0.2106	0.672	3.082
2	8.057	4405	205.8	0.3036	0.49	96.918



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.683	4938.3	374.8	0.1974	0.638	50.107
2	7.303	4917.3	282	0.2631	0.693	49.893

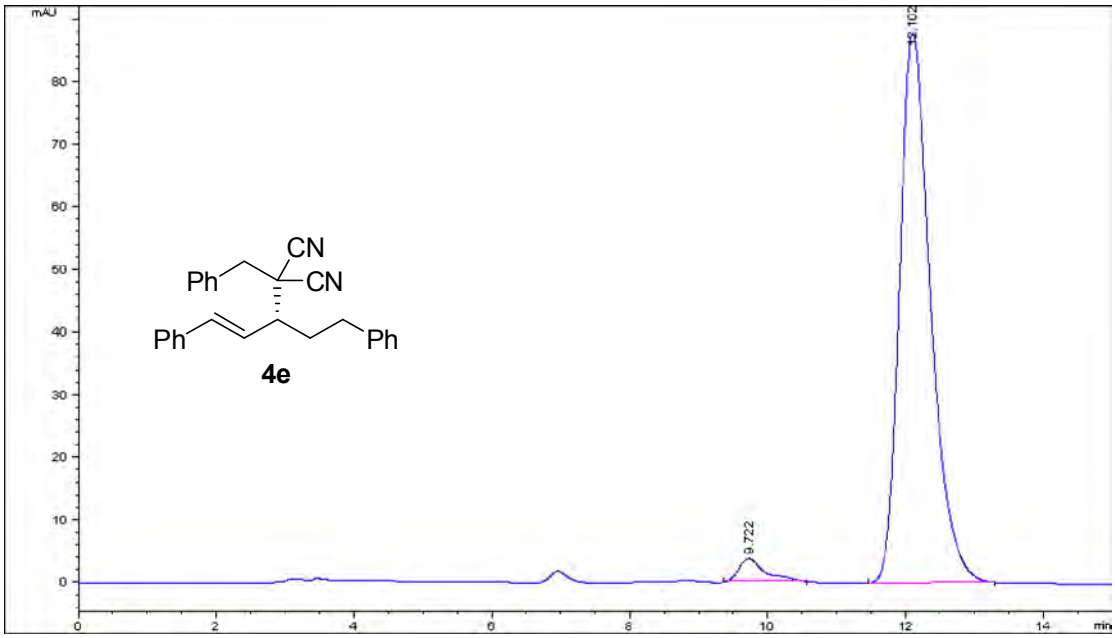


	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.344	167.7	11.2	0.2291	0.718	3.229
2	8.54	5024.3	234.2	0.3275	0.723	96.771



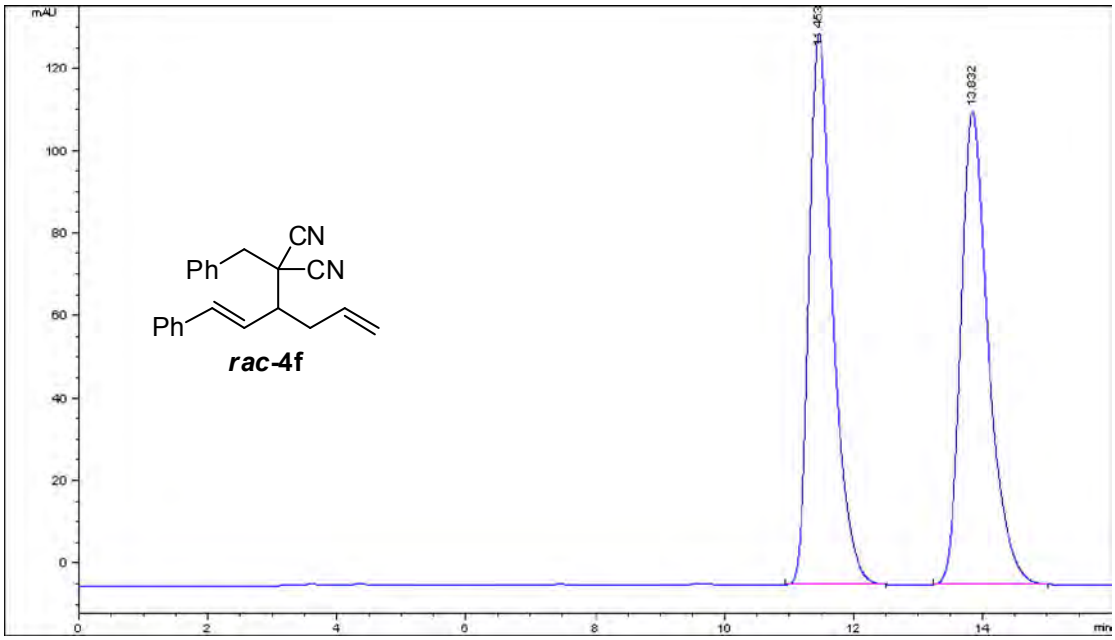
***rac*-4e**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.66	2529.1	105.2	0.3649	0.677	50.049
2	12.08	2524.1	80.7	0.4785	0.693	49.951

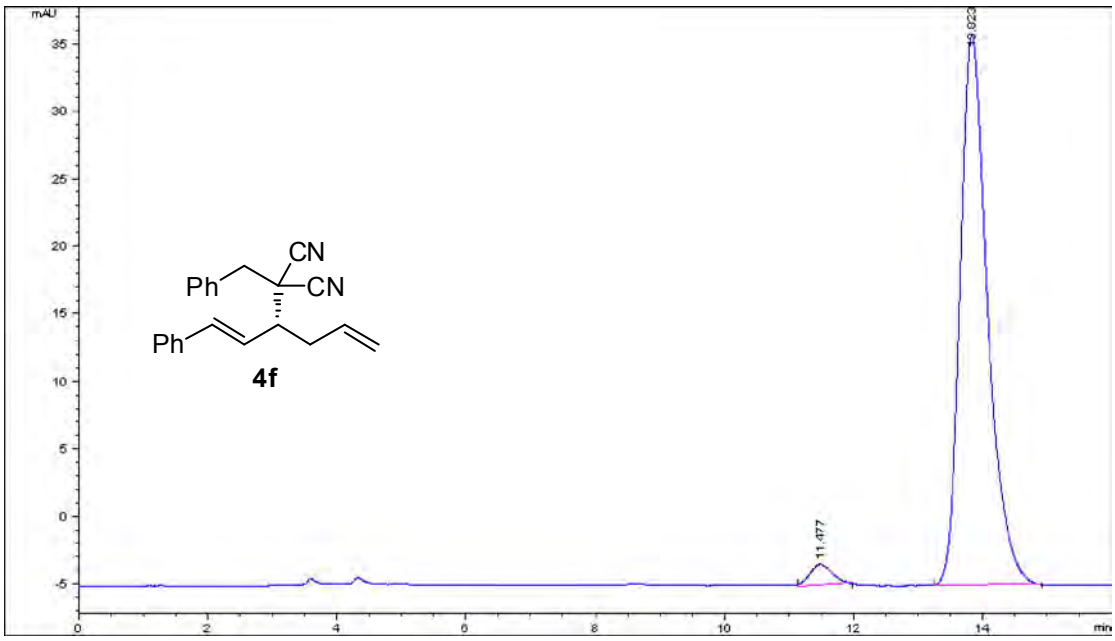


4e

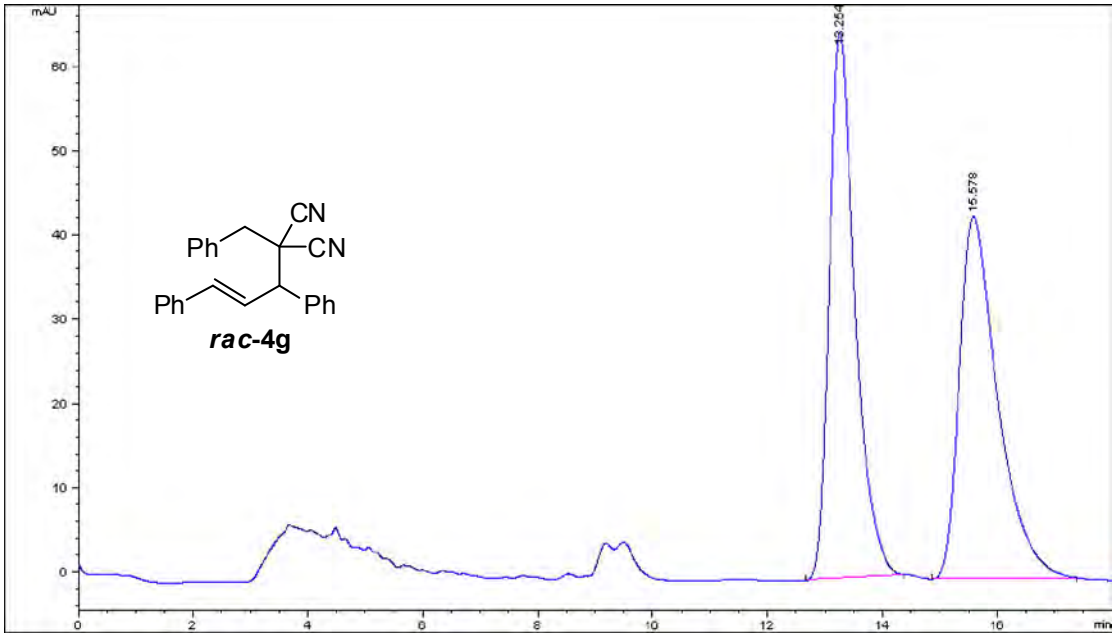
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.722	99.7	3.7	0.4523	0.567	3.500
2	12.102	2749.3	87.8	0.4789	0.694	96.500



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.453	3043.1	133.7	0.3829	0.646	50.028
2	13.832	3399.3	114.7	0.4461	0.682	49.972

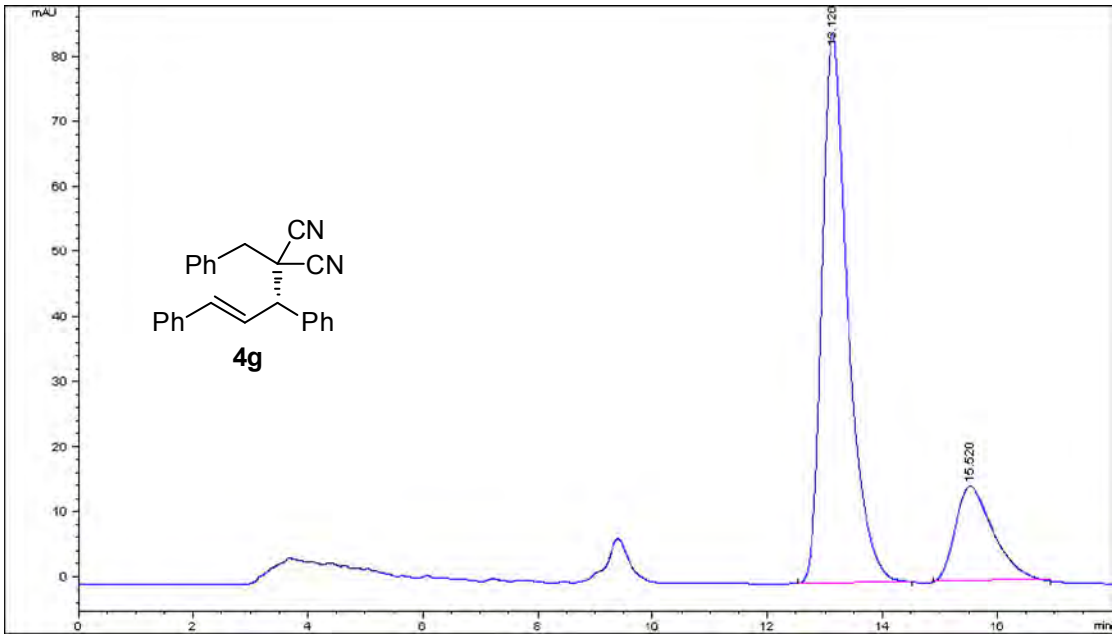


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.477	36.4	1.5	0.3923	0.877	2.937
2	13.823	1204.1	40.8	0.4477	0.701	97.063



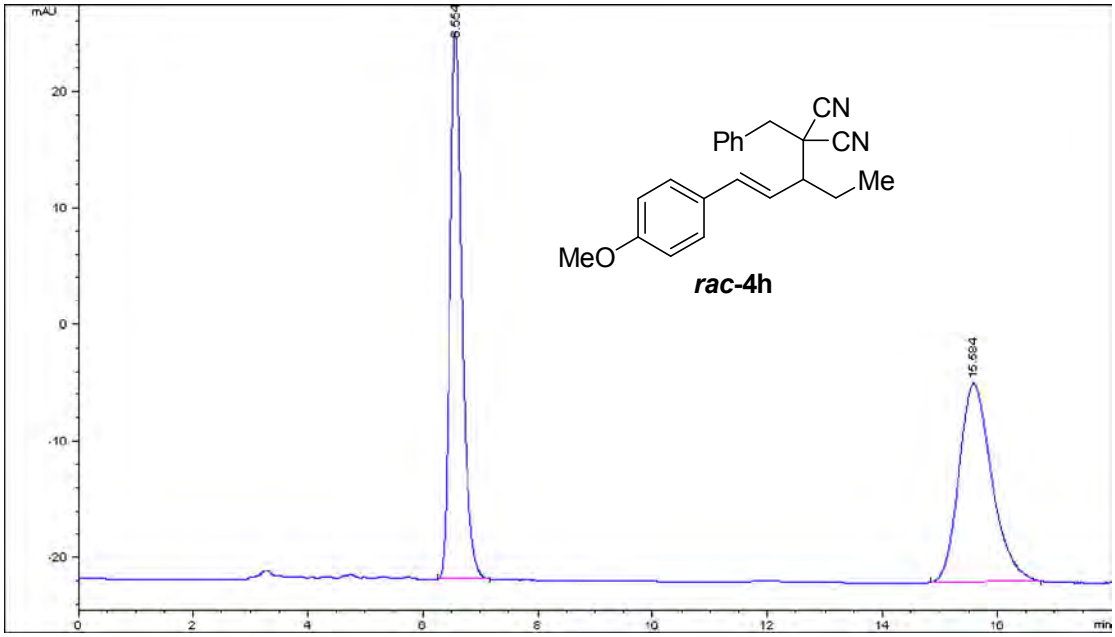
***rac*-4g**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.254	2026.7	64.8	0.4682	0.654	50.330
2	15.578	2000.1	42.9	0.6904	0.539	49.670



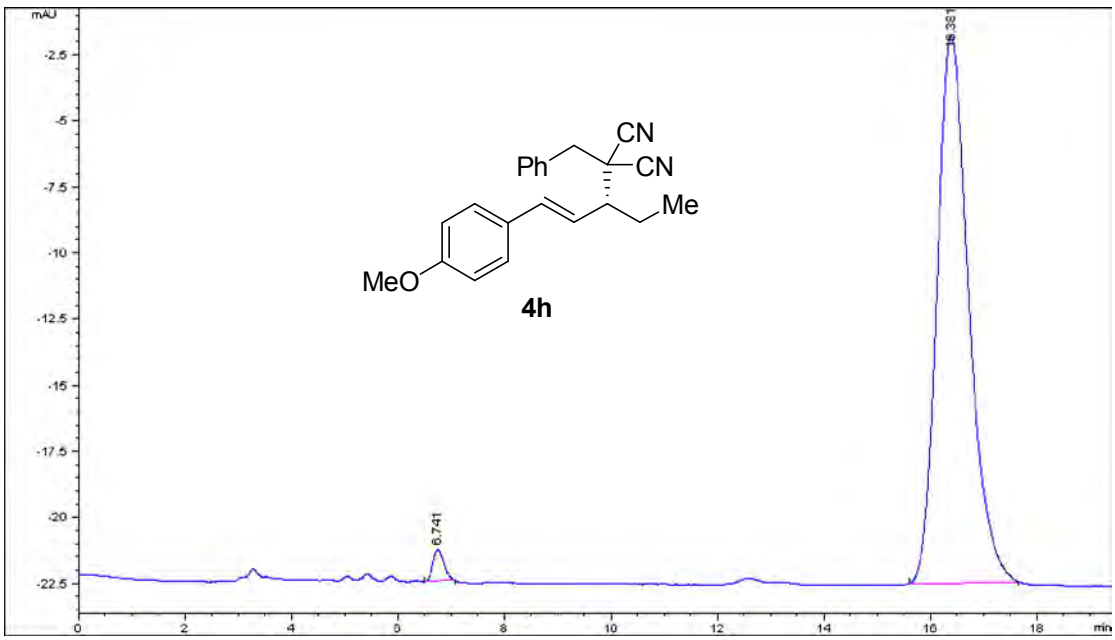
4g

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	13.126	2662.4	84.6	0.4718	0.639	80.000
2	15.52	665.6	14.6	0.7623	0.619	20.000



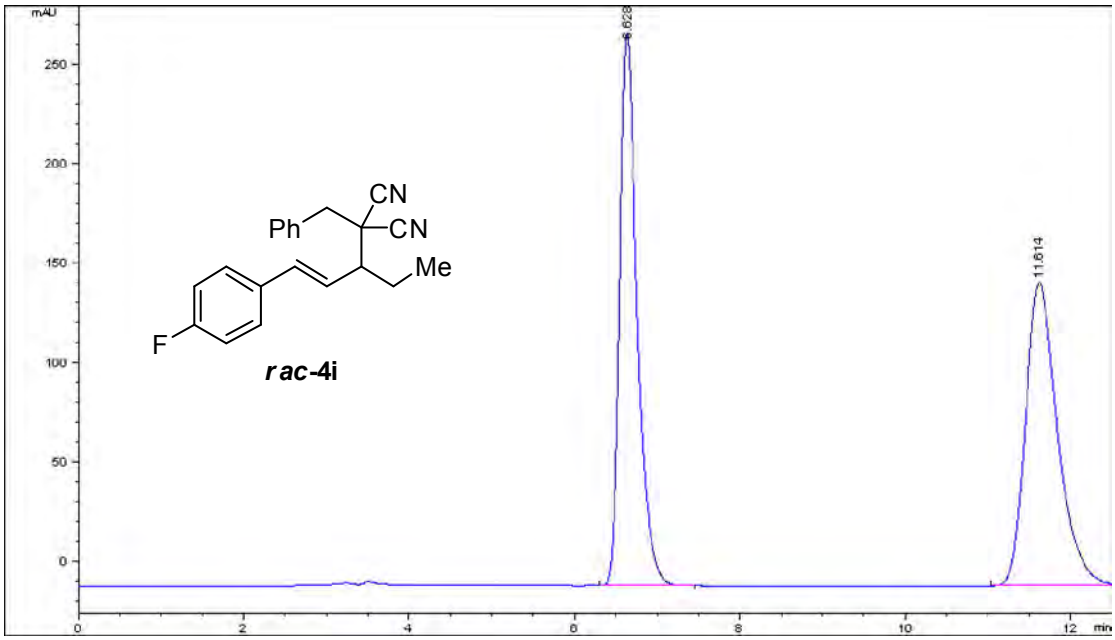
***rac*-4h**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.554	684.2	47	0.221	0.716	50.094
2	15.584	681.6	17.1	0.6091	0.767	49.906



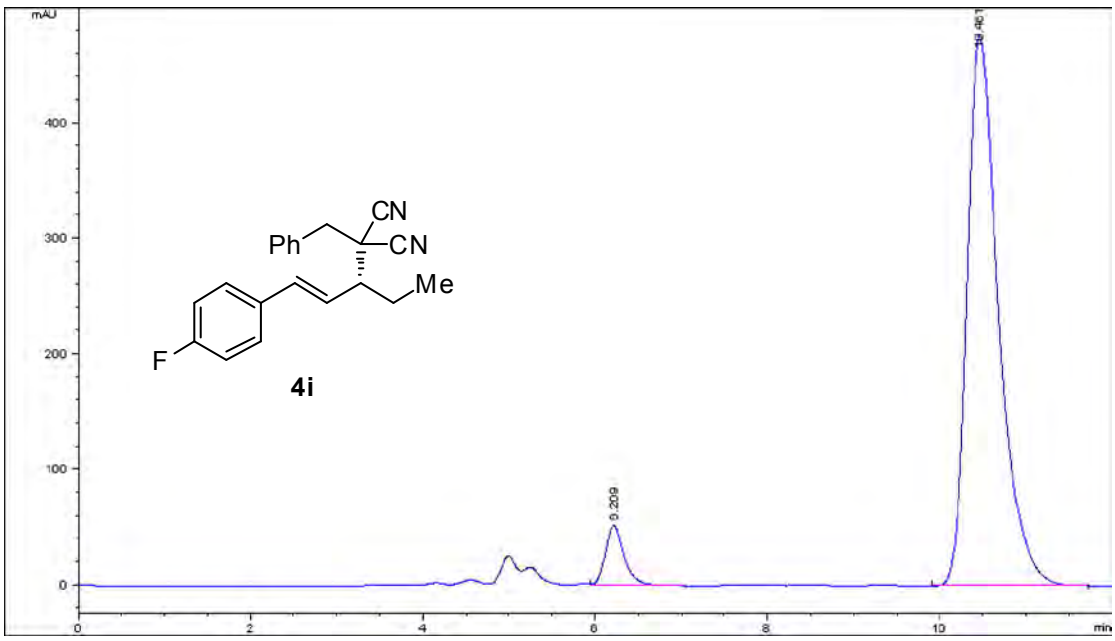
4h

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.741	17.5	1.2	0.241	0.791	1.989
2	16.381	862.1	20.8	0.6326	0.752	98.011



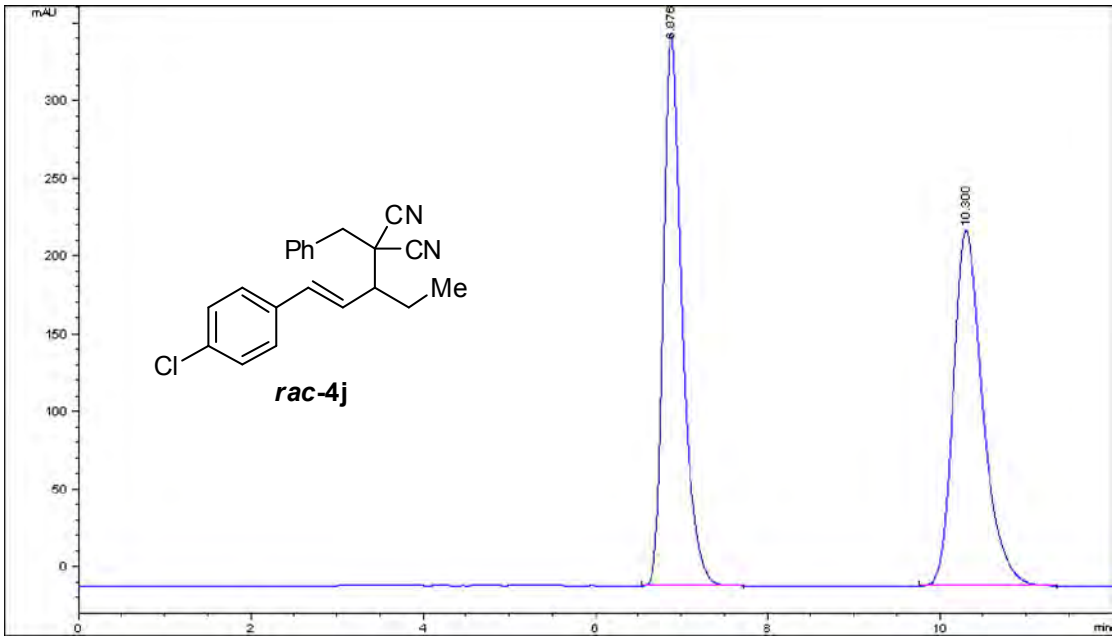
***rac*-4i**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.628	4070.1	277.5	0.2206	0.663	49.768
2	11.614	4108	152.1	0.4083	0.698	50.232



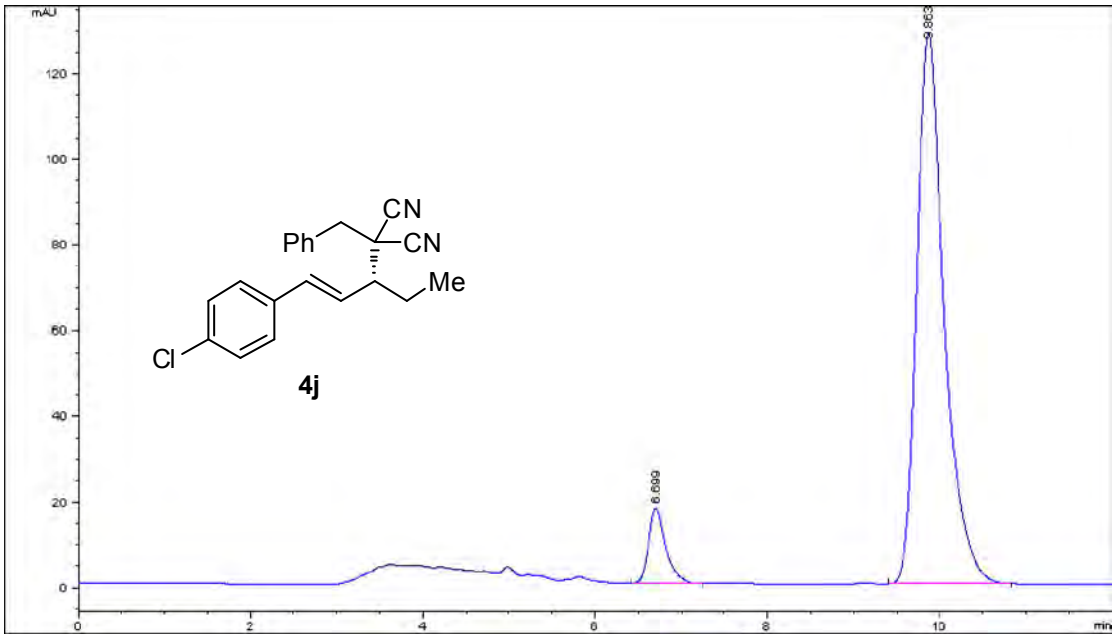
4i

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.209	803.9	52.6	0.2291	0.731	6.239
2	10.461	12082.5	476.8	0.3816	0.641	93.761



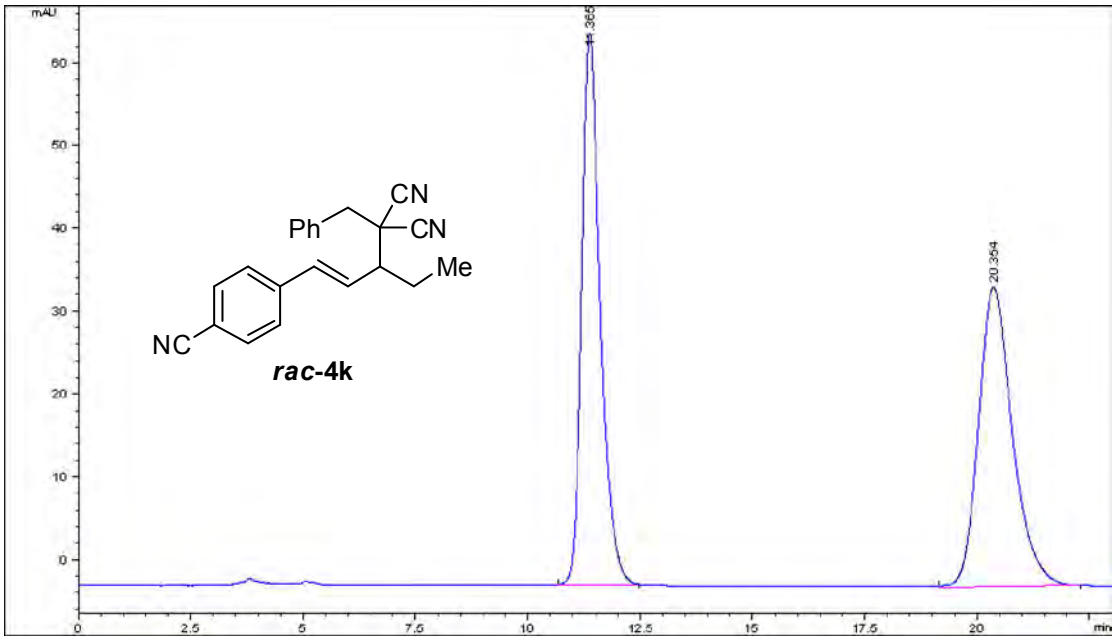
***rac*-4j**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.876	5425.5	355.6	0.2304	0.677	49.978
2	10.3	5430.2	228.5	0.3602	0.716	50.022

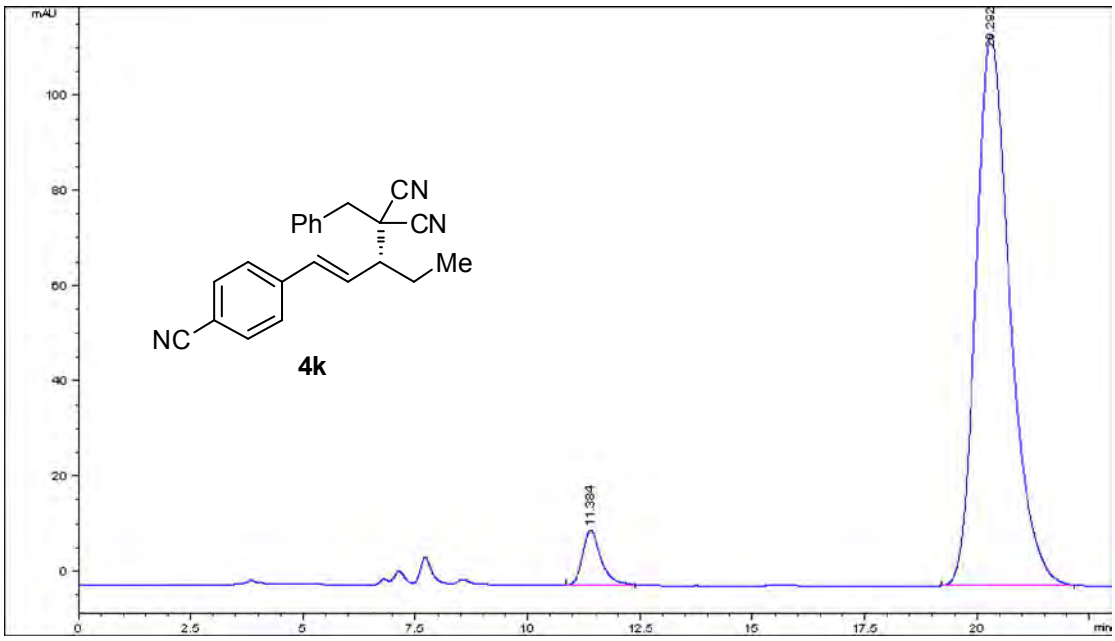


4j

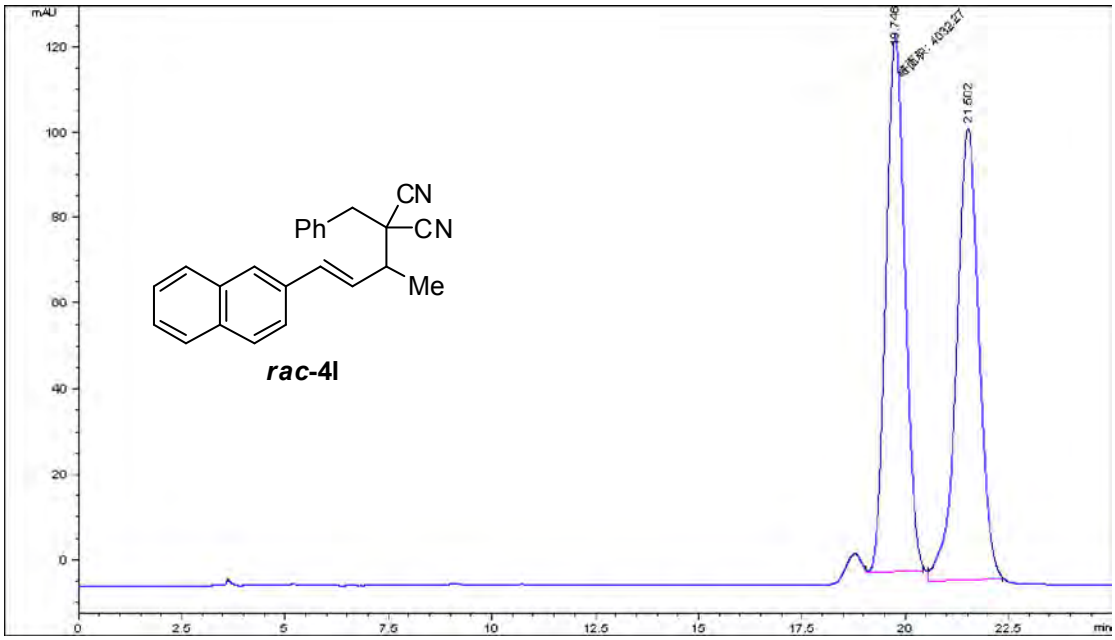
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.699	246.1	17.6	0.2065	0.692	7.957
2	9.863	2847.2	128.6	0.3226	0.681	92.043



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.365	1917.2	66.6	0.4346	0.695	50.138
2	20.354	1906.6	36.2	0.8788	0.77	49.862

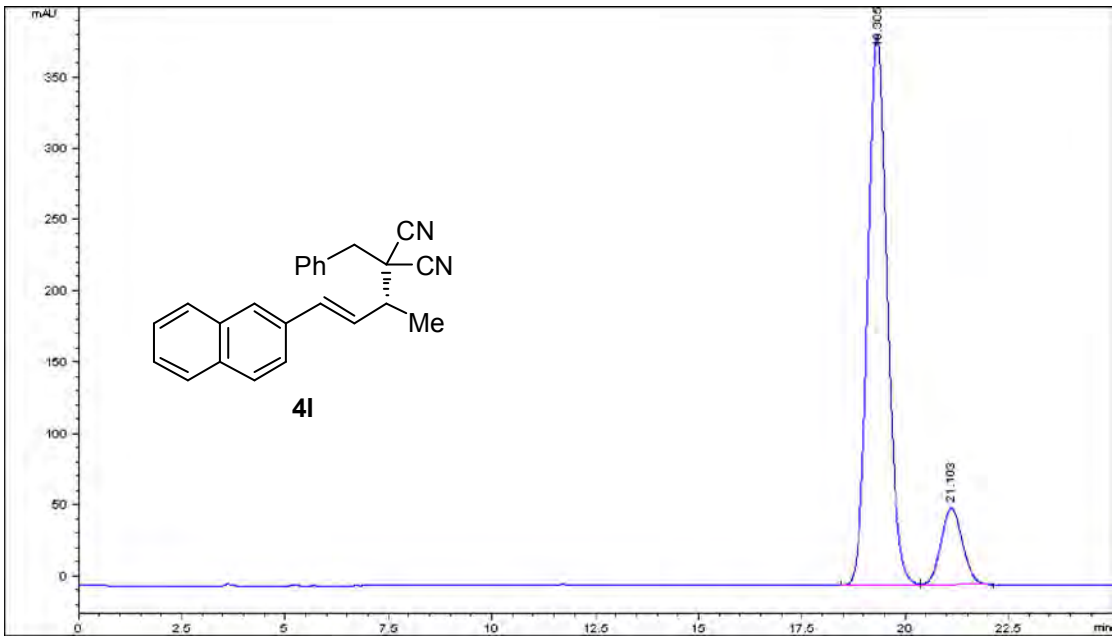


Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.384	328	11.5	0.4341	0.701	5.112
2	20.292	6088.3	115.8	0.7996	0.729	94.888



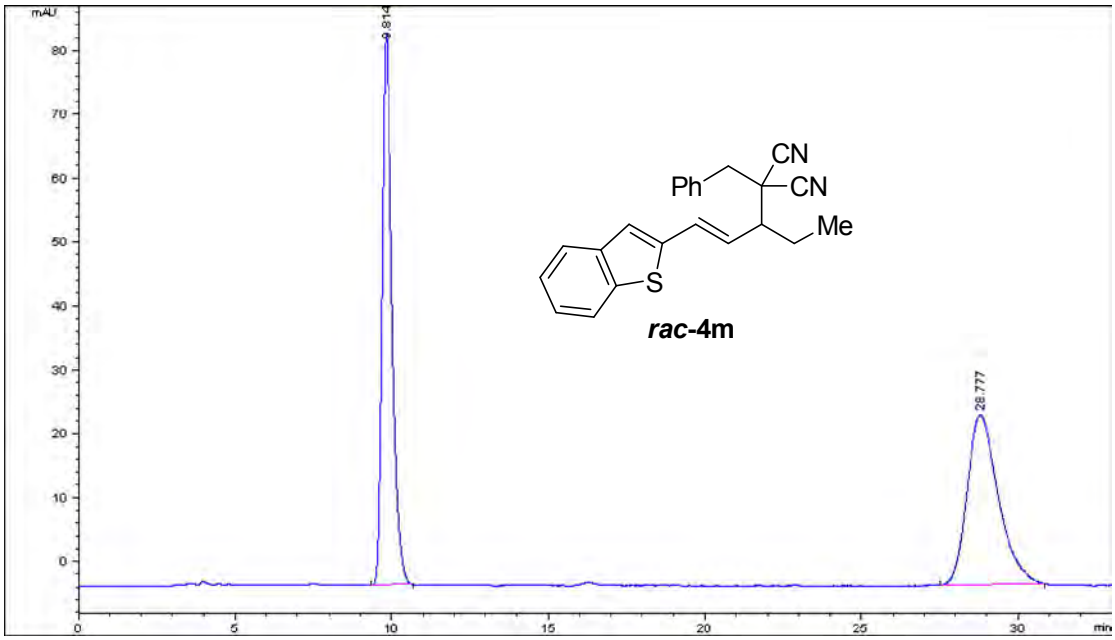
***rac*-4l**

Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.746	4032.3	126.1	0.5327	0.923	50.300
2	21.502	3984.2	105.6	0.6288	1.02	49.700

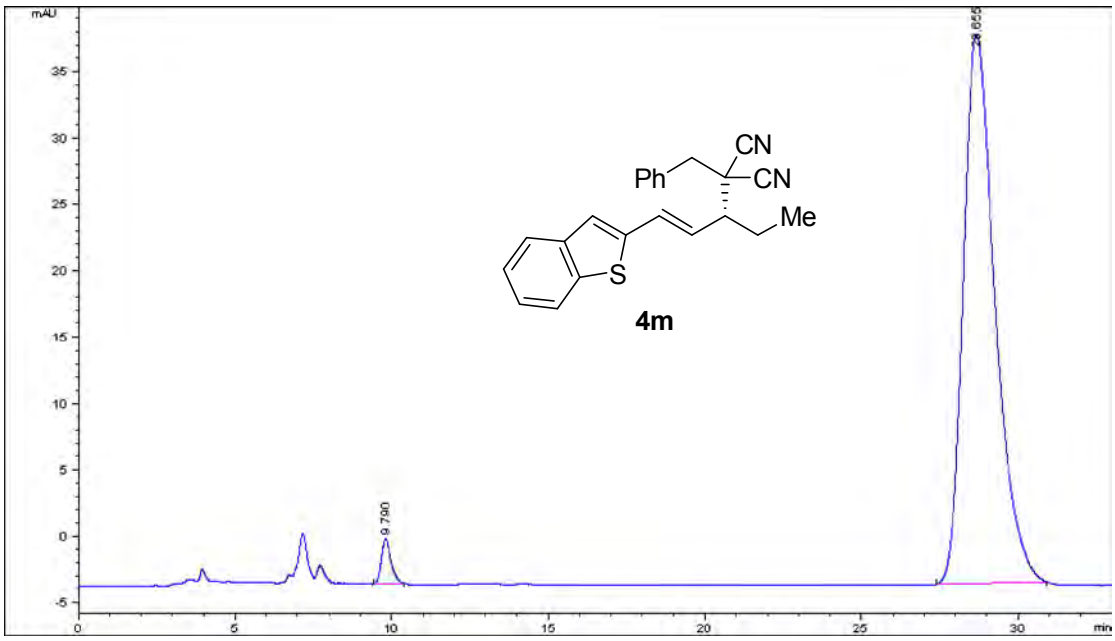


4l

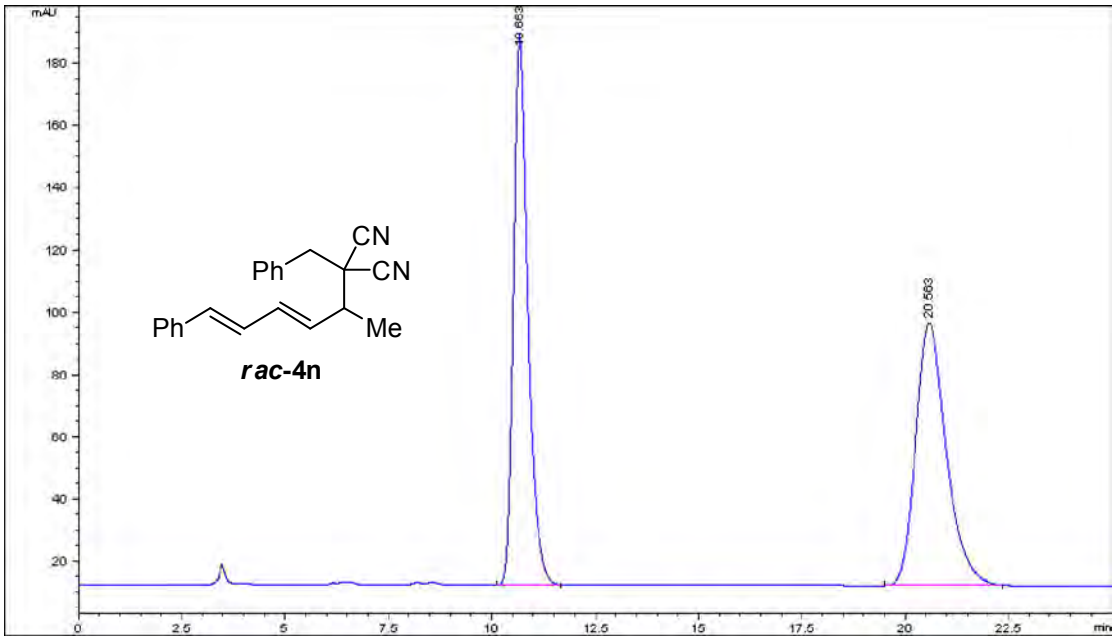
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	19.305	12671	386.3	0.5079	0.881	86.836
2	21.103	1954.5	54.1	0.5597	0.909	13.364



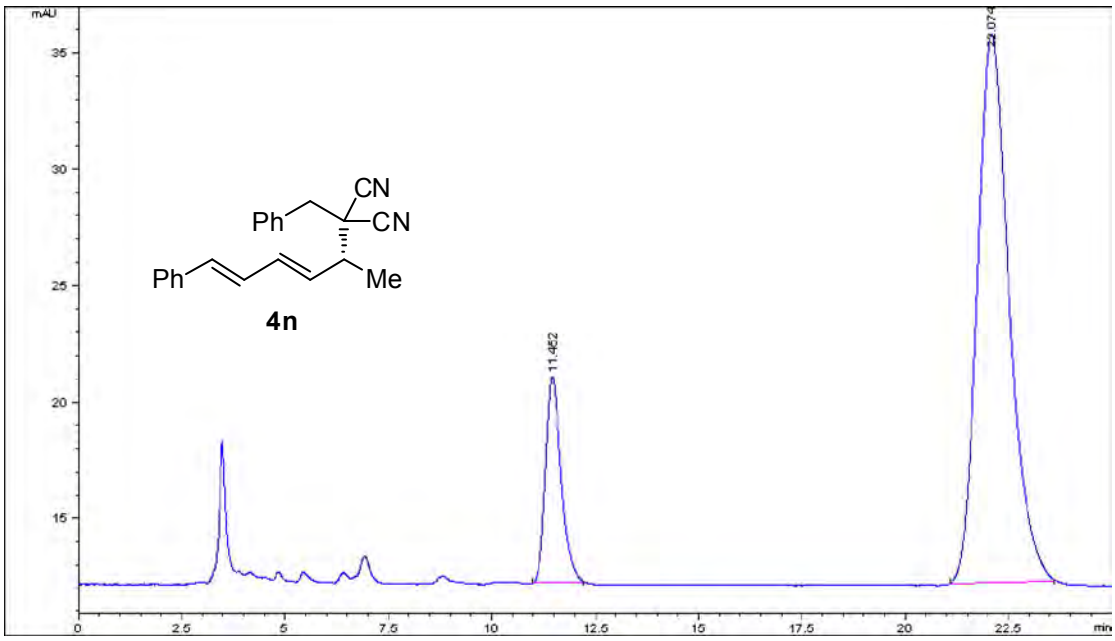
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.814	1876.8	86.4	0.3227	0.687	50.386
2	28.777	1848.1	26.6	1.0474	0.692	49.614



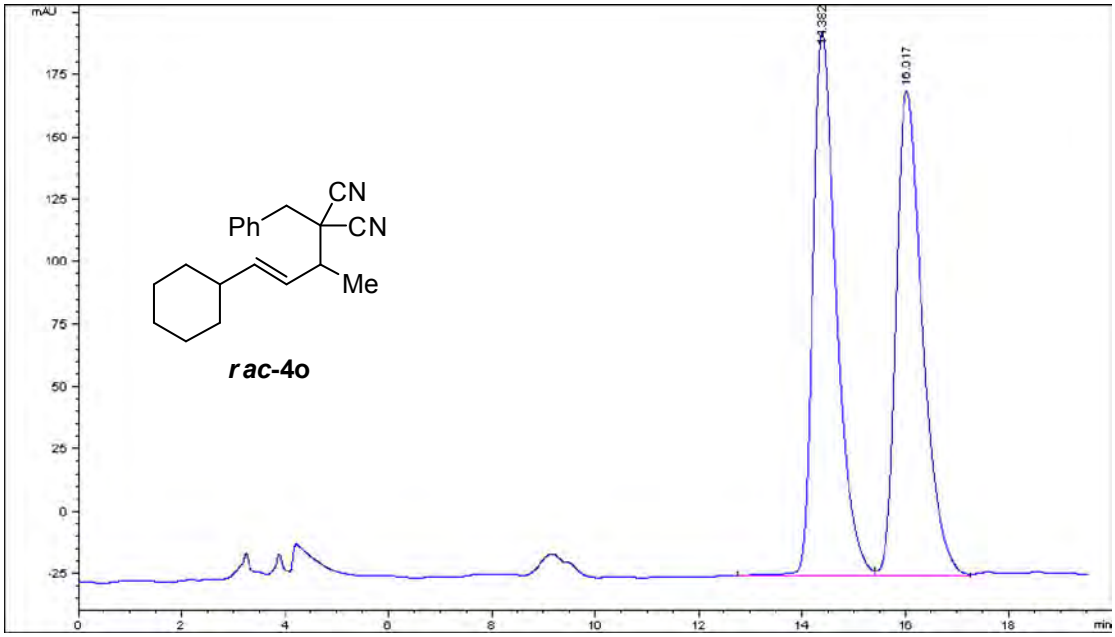
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.79	72.8	3.4	0.3201	0.706	2.433
2	28.655	2917.9	41.4	1.0738	0.663	97.567



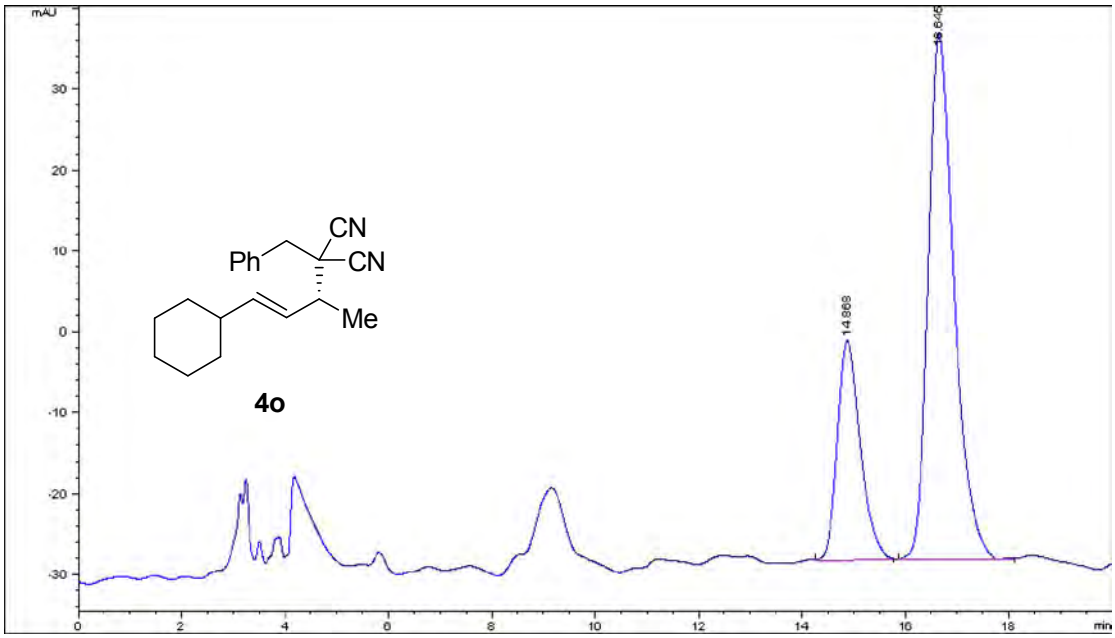
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.663	4322.9	177.4	0.3688	0.713	49.952
2	20.563	4331.2	84.3	0.7845	0.733	50.048



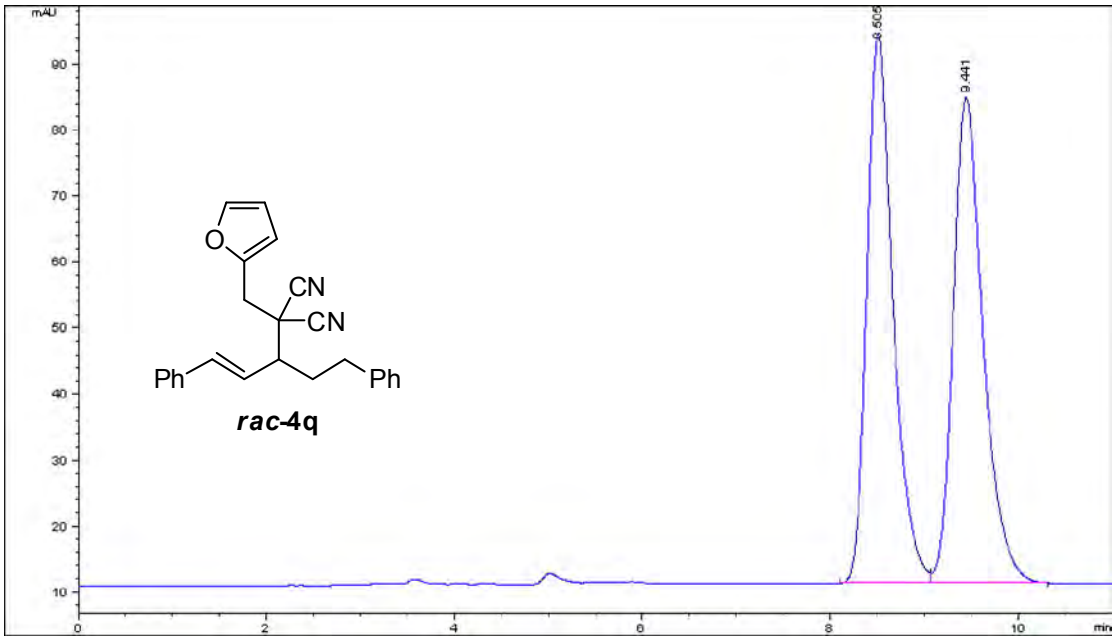
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.452	234.5	8.9	0.4	0.732	15.657
2	22.074	1263.2	23.6	0.8067	0.76	84.343



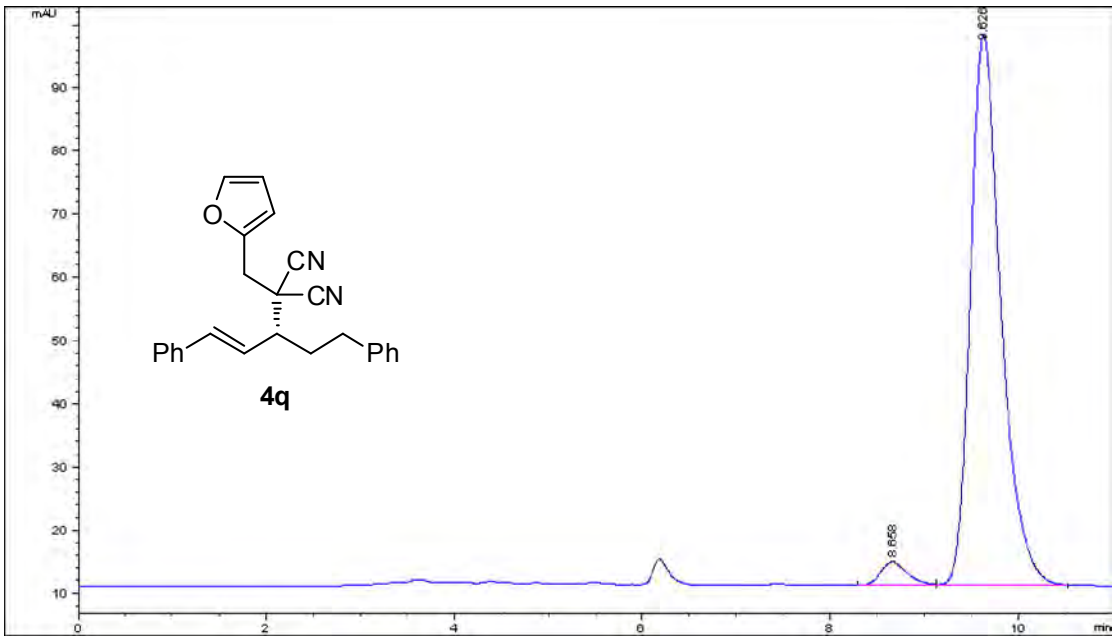
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.382	6898.4	218.2	0.4767	0.616	49.847
2	16.017	6940.8	194.6	0.5427	0.625	50.153



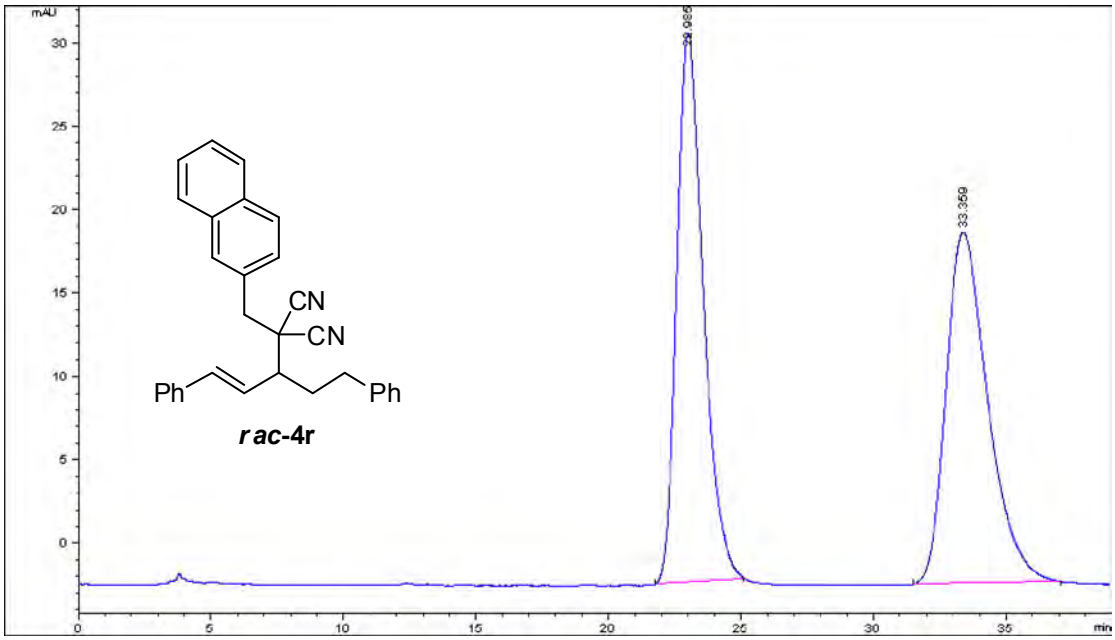
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	14.868	847.3	27.2	0.519	0.735	27.101
2	16.645	2279.1	65.1	0.5831	0.706	72.899



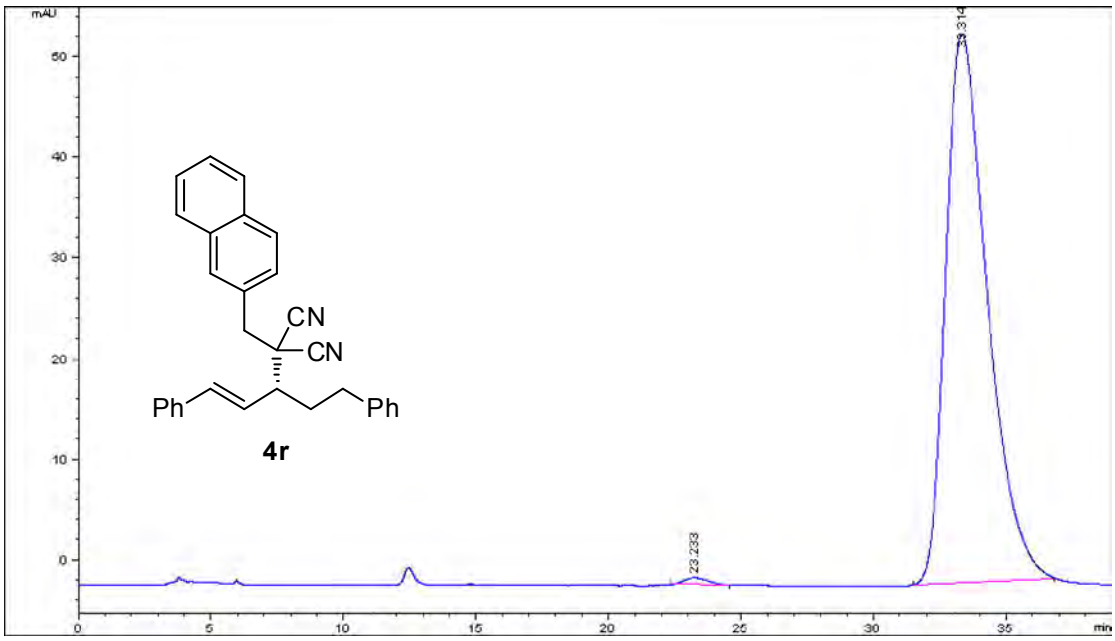
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.505	1616.8	83.3	0.2933	0.7	49.785
2	9.441	1630.7	73.6	0.3343	0.704	50.215



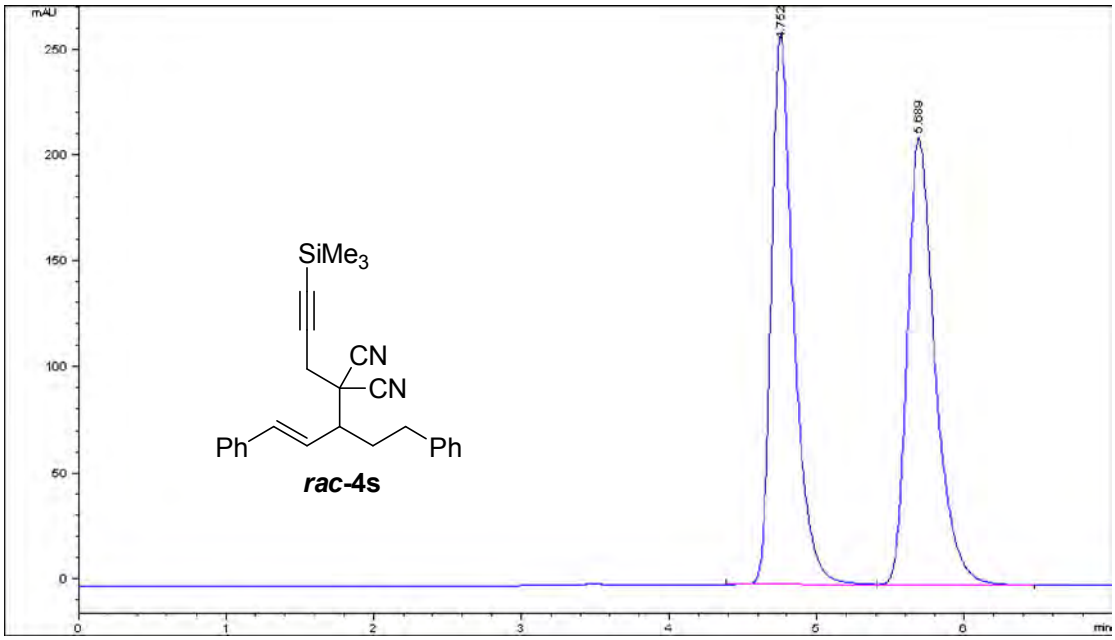
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.658	73.4	3.7	0.2992	0.733	3.581
2	9.626	1976.8	87.3	0.3429	0.698	96.419



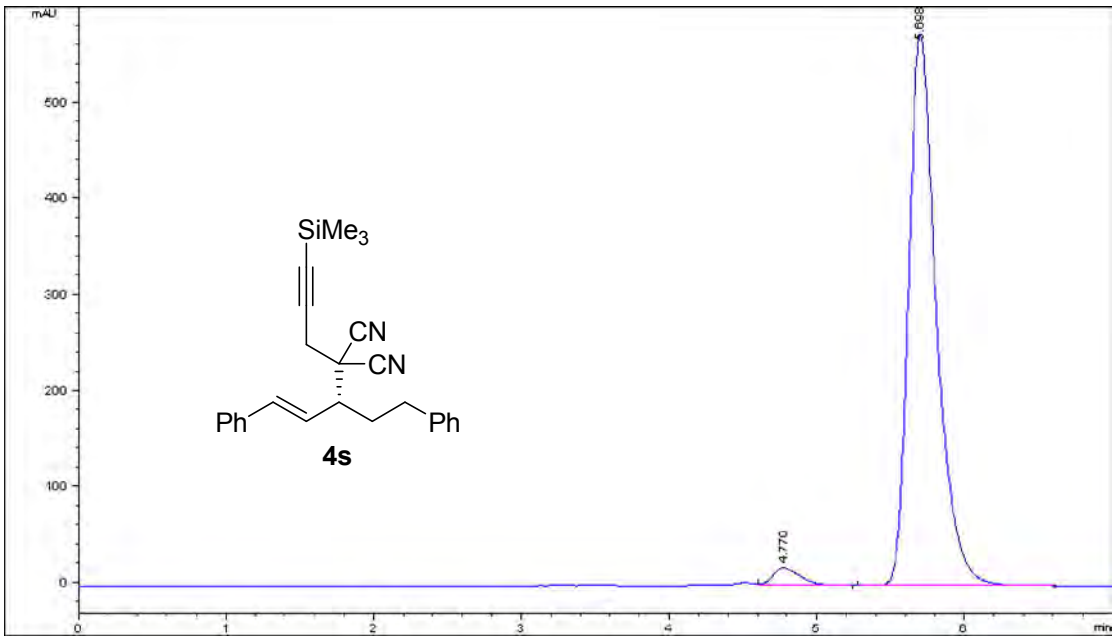
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	22.985	2304.8	33	1.0545	0.69	49.938
2	33.359	2310.5	21.1	1.8287	0.665	50.062



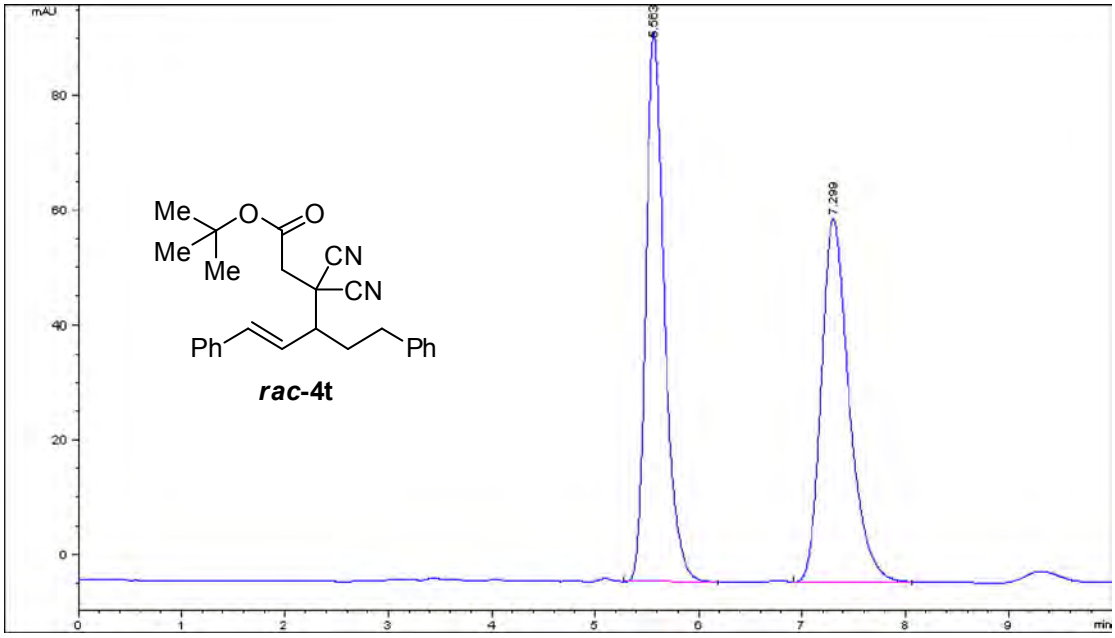
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	23.233	44.6	7E-1	1.0614	0.822	0.740
2	33.314	5981.5	54.6	1.6235	0.602	99.260



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	4.752	2743.4	260.4	0.1579	0.643	49.853
2	5.689	2759.6	211.1	0.1962	0.669	50.147



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	4.77	244.5	18.9	0.2021	0.582	3.156
2	5.698	7502.5	574.3	0.1961	0.669	96.844



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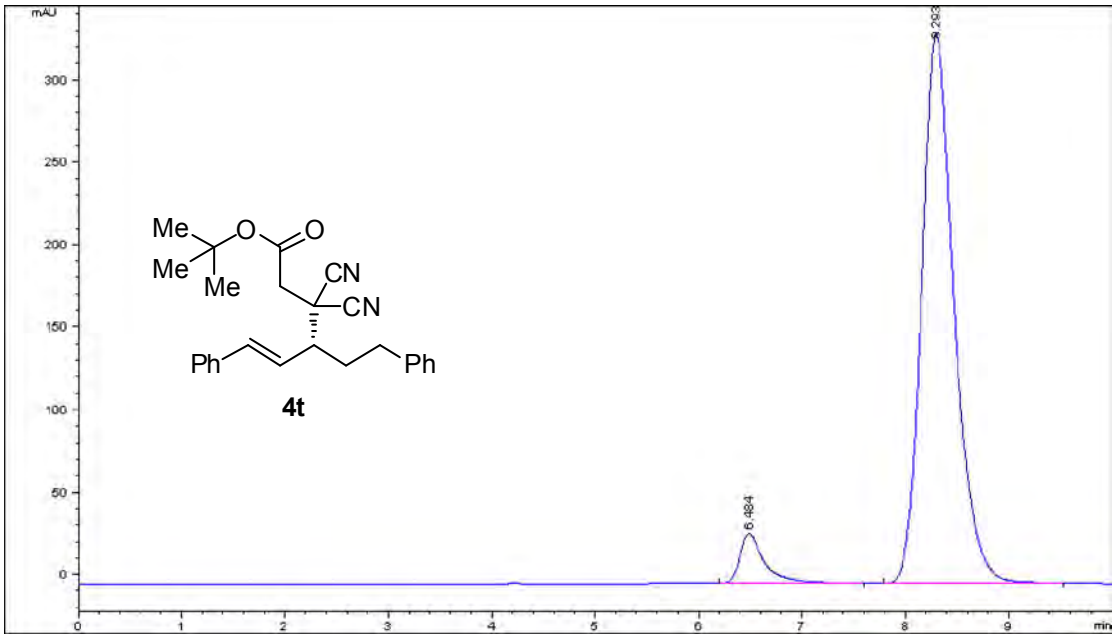
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	5.563	1197	95.8	0.188	0.717	50.175
2	7.299	1188.6	63.3	0.283	0.717	49.825



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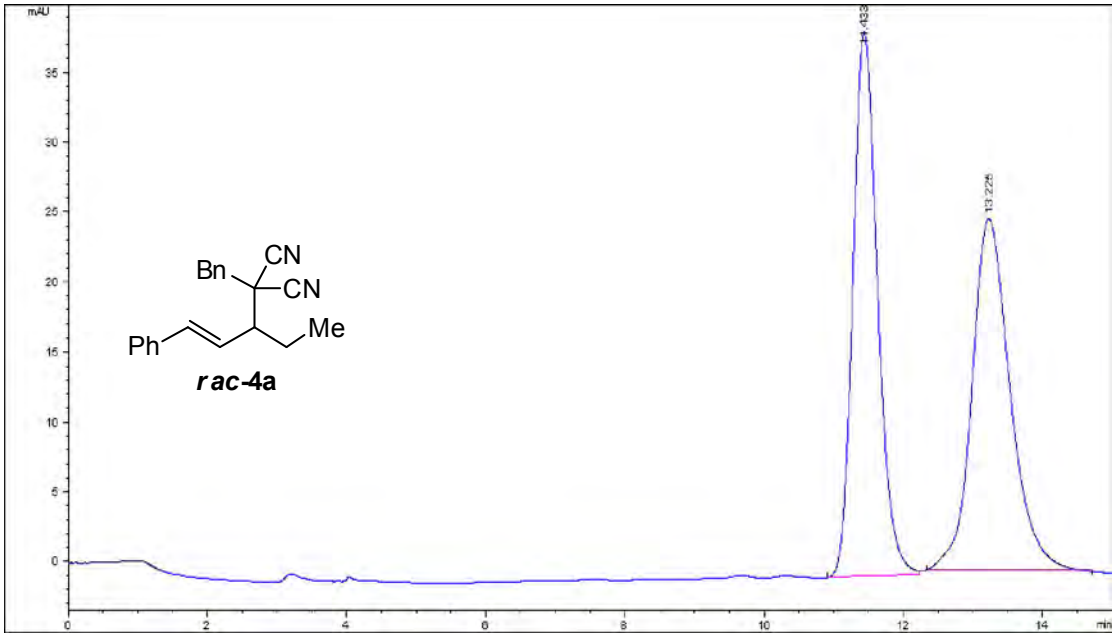
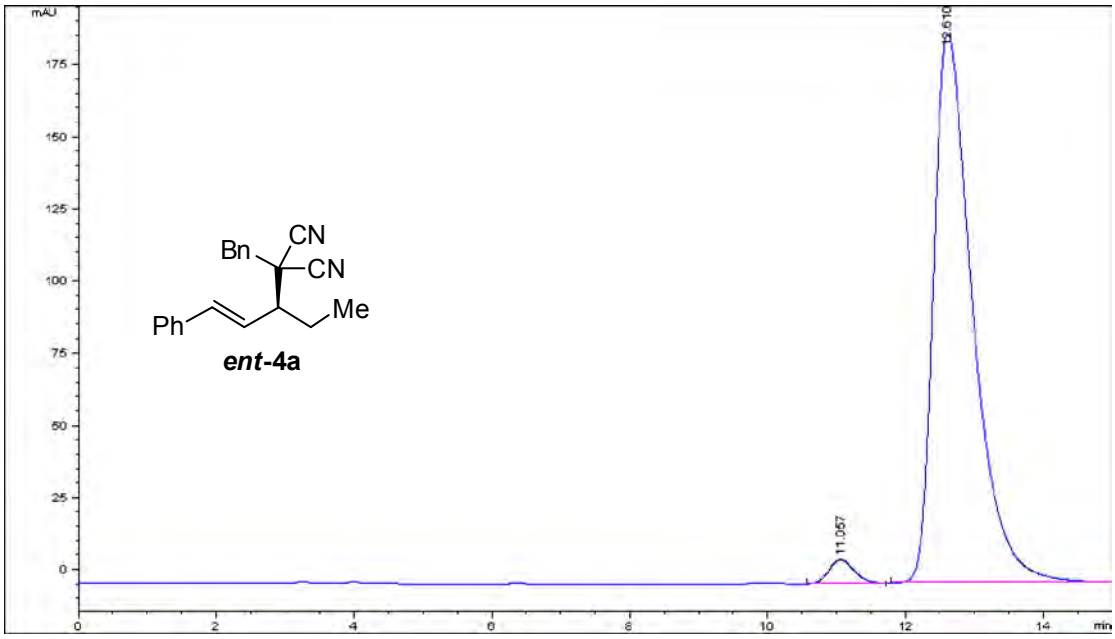
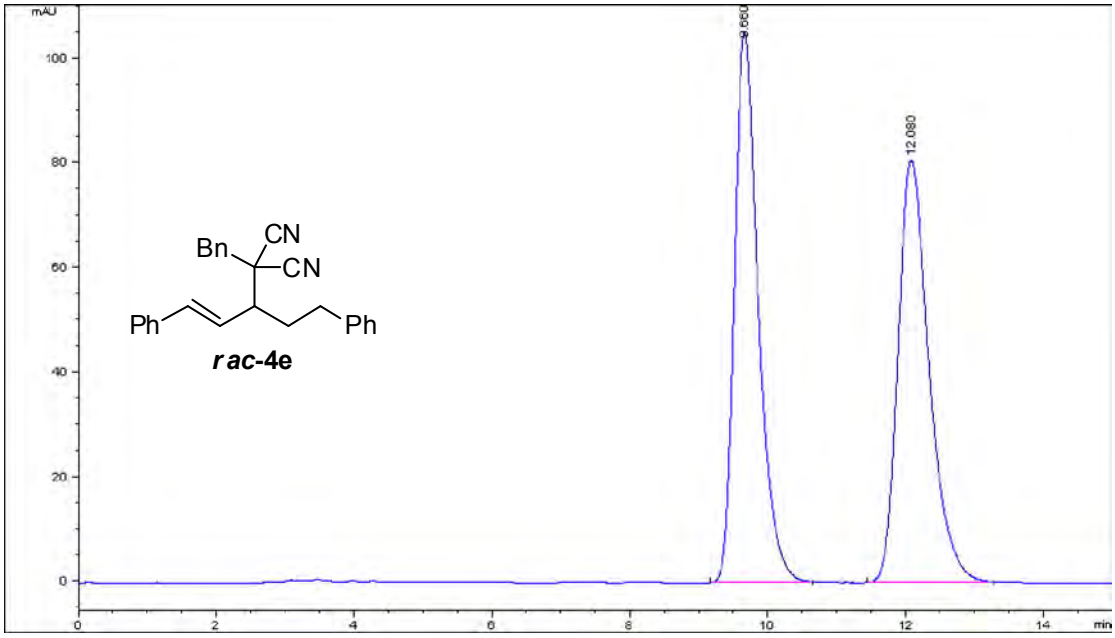
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	6.484	514.3	30.4	0.2456	0.528	6.631
2	8.293	7241.2	333.6	0.326	0.75	93.369



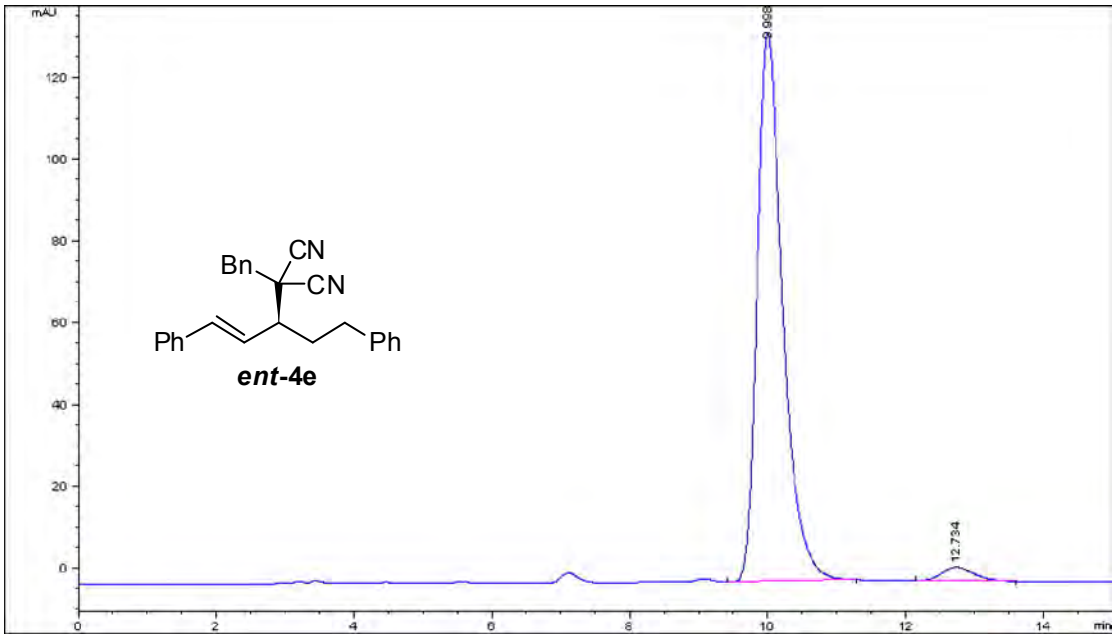
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.433	958.8	39	0.3788	0.789	49.970
2	13.225	959.9	25.1	0.6362	0.778	50.030



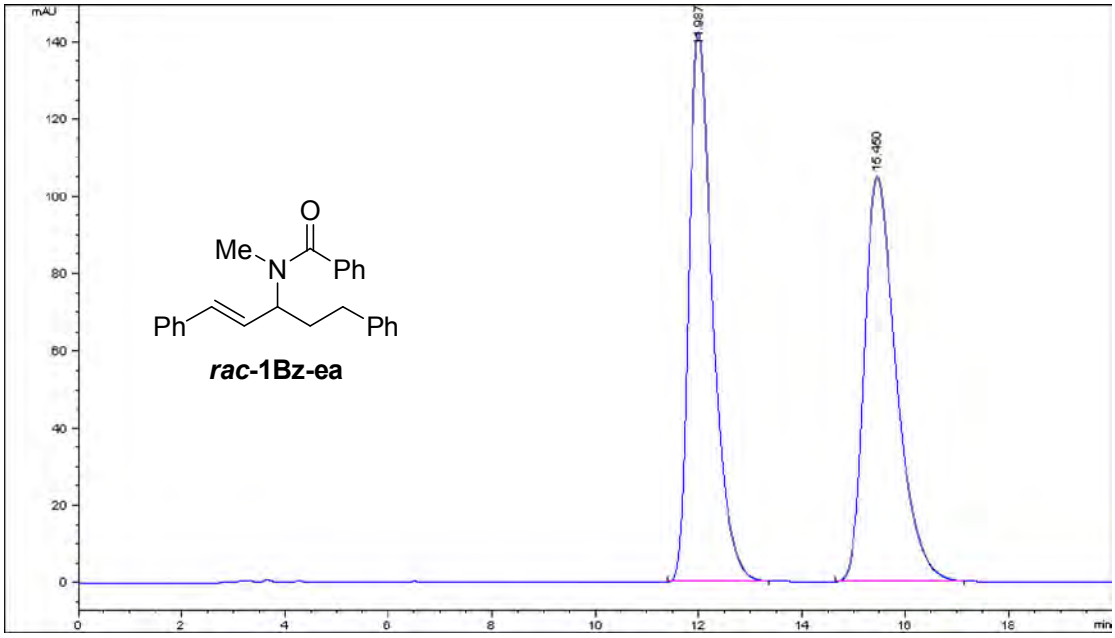
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.057	208.5	8.3	0.3934	0.83	2.700
2	12.61	7514.1	190.5	0.6576	0.549	97.300



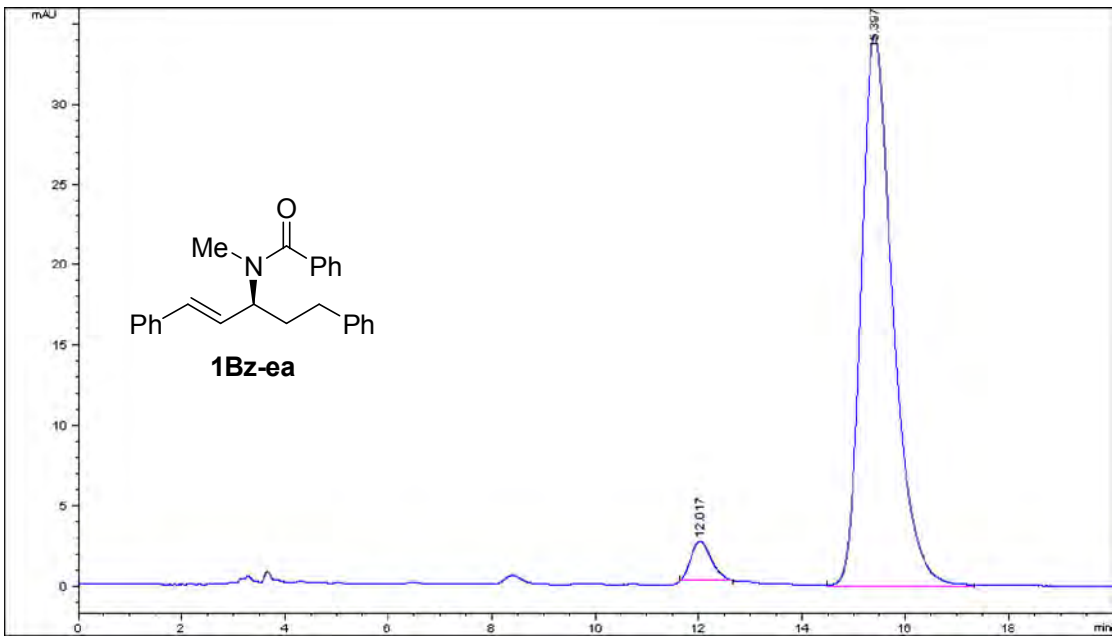
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.66	2529.1	105.2	0.3649	0.677	50.049
2	12.08	2524.1	80.7	0.4785	0.693	49.951



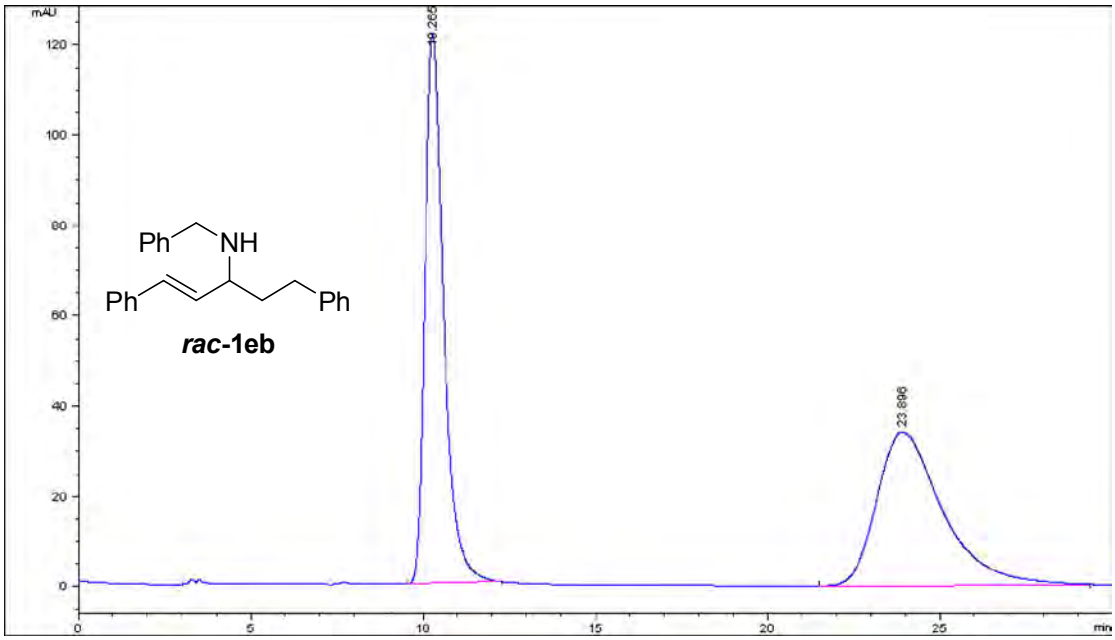
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	9.998	3452.7	134	0.3894	0.653	96.817
2	12.734	113.5	3.4	0.4906	0.782	3.183



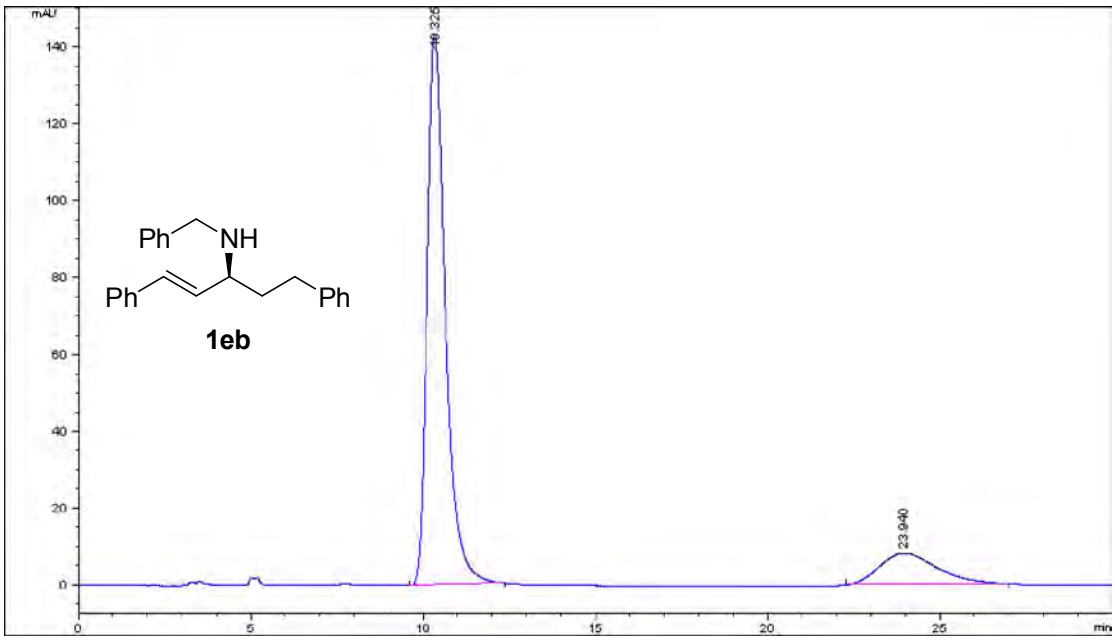
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	11.987	4525.8	142.2	0.4834	0.613	50.064
2	15.45	4514.2	104.8	0.6541	0.637	49.936



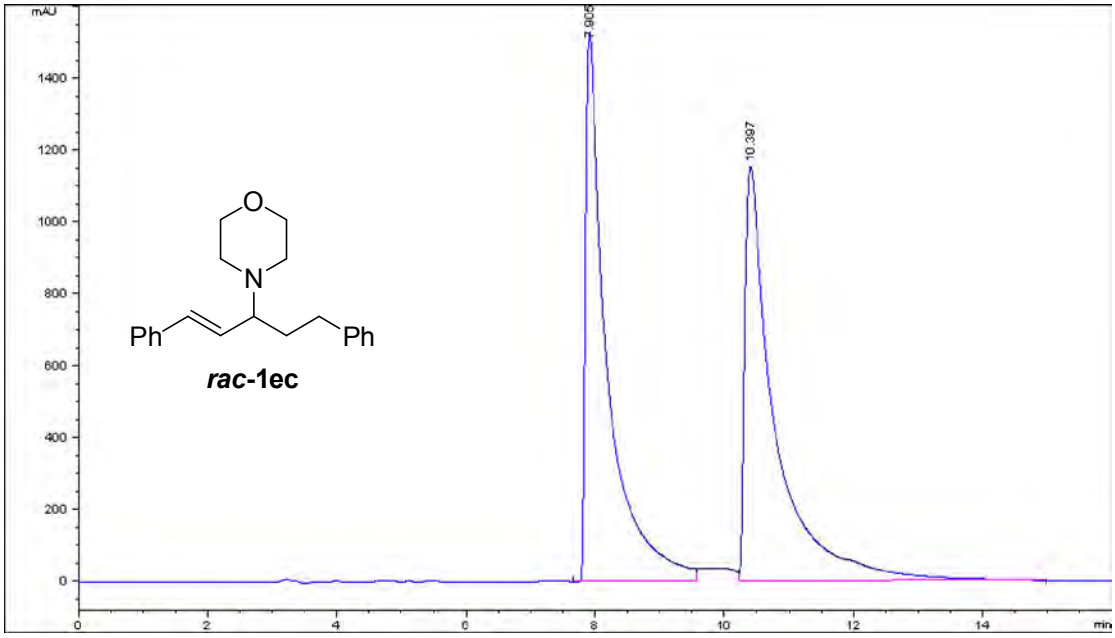
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	12.107	66.2	2.4	0.4593	0.754	4.313
2	15.397	1469.8	34.3	0.7132	0.7	95.687



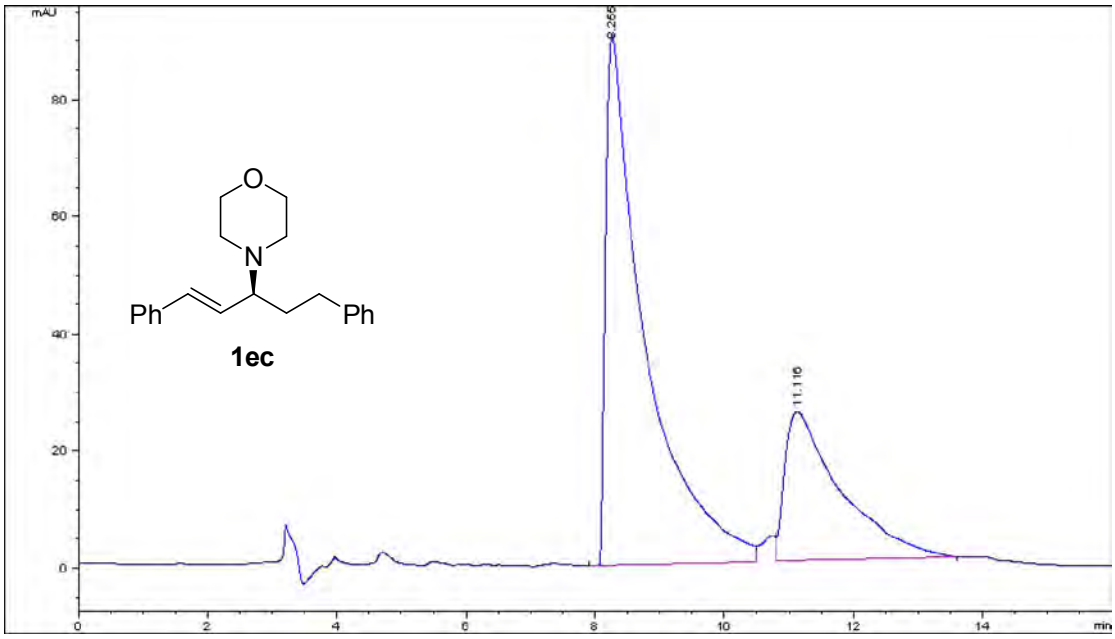
Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.265	4585.9	121.8	0.5687	0.629	50.190
2	23.896	455.1	34.2	2.2187	0.609	49.810



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	10.325	5266.5	143.3	0.554	0.635	84.784
2	23.94	945.1	8.1	1.946	0.695	15.216



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	7.905	35901.3	1528.6	0.3206	0.204	49.056
2	10.397	37282.6	1154.3	0.4394	0.195	50.944



Number	Time (min)	Area (mAU·s)	Height (mAU)	Width (min)	Symmetry factor	Area (%)
1	8.255	3833.8	90.9	0.5634	0.179	71.410
2	11.116	1534.9	25.5	0.8432	0.254	28.590