

Supporting Information

Rhodium-Catalyzed Tandem Conjugate Addition-Mannich Cyclization Reaction: Straightforward Access to Fully Substituted Tetrahydroquinolines

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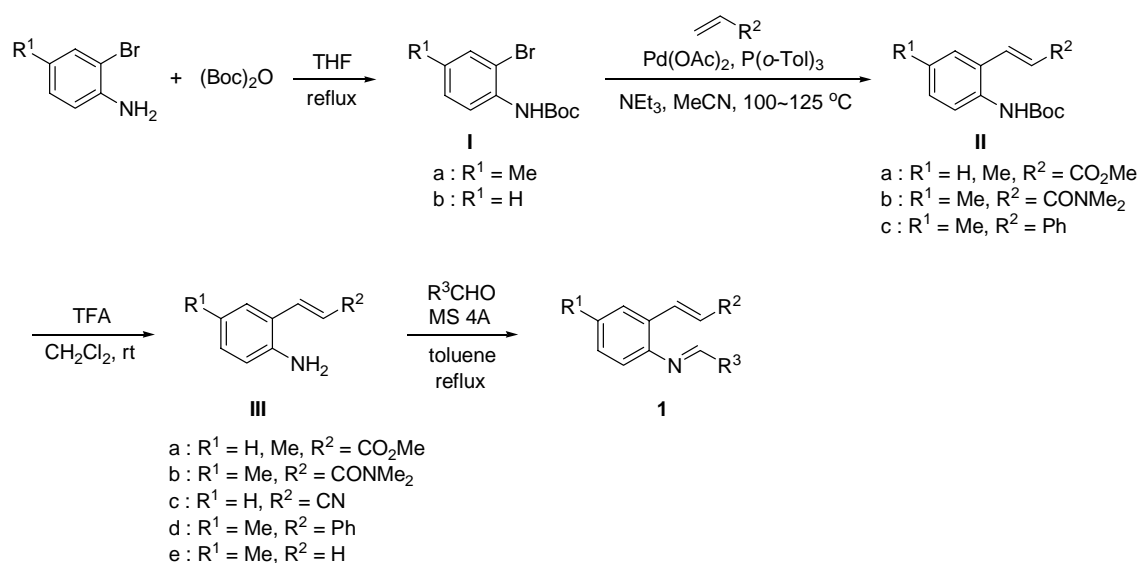
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General Information

Nuclear Magnetic Resonance spectra were recorded on 400 MHz instrument. Spectra were recorded in CDCl₃ solutions referenced to TMS or solvent residual peak. High Resolution Mass Spectra were measured using EI at 70 eV. IR spectra were taken as neat for liquids on NaCl plates using FT-IR Spectrophotometer. Flash chromatography was performed on silica gel 230-400 mesh. All catalysts were purchased in the higher quality and used as received. Unless otherwise noted, all commercially obtained reagents were used as received. 1,4-Dioxane and THF were all distilled from sodium benzophenone ketyl immediately prior to use. Toluene was distilled from CaH₂ immediately prior to use. Thin layer chromatograms (TLC) was visualized via UV and Cerium Molybdate (Hanessian's Stain).



General procedure for the preparation of N-Boc aniline I

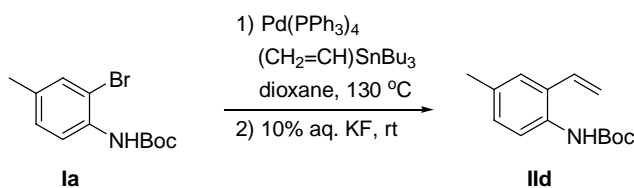
To a solution of 2-bromo-4-methylaniline or 2-bromoaniline in THF (0.4 M) was added (Boc)₂O (1 equiv). The reaction mixture was stirred at reflux for 24 hours, and then the solvent was evaporated. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1 : 50) to give the corresponding product. (**Ia** : 92%, **Ib** : 93%)

General procedure for Heck reaction for the synthesis of **IIa-c**¹

To a solution of **I** in MeCN (0.4 M) in a pressure tube were added Pd(OAc)₂ (**a-b**: 10 mol %, **c** : 1 mol %), P(*o*-Tol)₃ (**a-b**: 20 mol %, **c** : 8 mol %), NEt₃ (**a-b**: 5 equiv, **c** : 0.5 mL/1 mmol), and the corresponding olefin (**a-b**: 3 equiv, **c** : 1.25 equiv). The pressure tube was tightly capped, heated at 100 °C (**c**) or 125 °C (**a-b**) for 12 hours. After the reaction was completed, the reaction mixture was filtered through Celite, quenched with distilled water, extracted with CH₂Cl₂ (three times), washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc:*n*-Hexane = 1:10~1:20) to give the corresponding product. (**IIa** : 63~65%, **IIb** : 49%, **IIc** : 78%)

¹ Ziegler, Jr. C. B.; Heck, R. F. *J. Org. Chem.* **1978**, *43*, 2941.

Synthesis of *N*-Boc-4-methyl-2-vinylaniline (**II**d)²

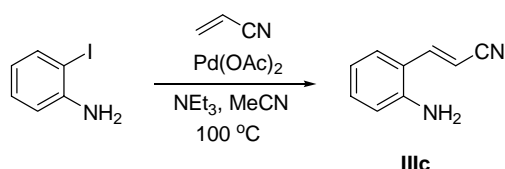


To a solution of **Ia** and tetrakis(triphenylphosphine)palladium (2 mol %) in dioxane (7.5 mL/1 mmol) in a pressure tube was added tributyl(vinyl)tin (1.2 equiv). The pressure tube was tightly capped, heated at 130 °C for 5 hours, and then cooled to rt. After 10% aqueous KF solution (12.5 mL/1 mmol) was added to the mixture, the reaction mixture was allowed to stand for 2 hours and then filtered through Celite, washed with water and EtOAc. The filtrate was transferred to separatory funnel and extracted with EtOAc (three times), washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1 : 20) to give the **II d** (48%) as a colorless oil.

General procedure for the *N*-Boc deprotection

To a solution of **II** in CH₂Cl₂ (0.3 M) was added TFA (CH₂Cl₂/TFA = 5/1). The reaction mixture was stirred at rt for 0.5-2 hours. After the reaction was completed, the residue was diluted with CH₂Cl₂, basified with sat. NaHCO₃ solution, extracted with CH₂Cl₂ (three times), washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1 : 10 ~ EtOAc only) to give the corresponding product. (**IIIa** : 90~92%, **IIIb** : 88%, **III d** : 91%, **IIIe** : 89%)

Synthesis of 3-(2-aminophenyl)acrylonitrile (**IIIc**)¹



To a solution of 2-iodoaniline in MeCN (0.5 M) in a pressure tube were added Pd(OAc)₂ (1 mol %), NEt₃ (1 mL/1 mmol), and acrylonitrile (1.25 equiv). The pressure tube was tightly capped, heated at 100 °C for 40 hours. After the reaction was completed, the reaction mixture was filtered through Celite, quenched with distilled water, extracted with CH₂Cl₂ (three times), washed with brine, dried over MgSO₄, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1 : 5) to give the **IIIc** (54%) as a yellow solid.

General procedure for the preparation of imine substrates 1

To a solution of amine in toluene (0.2 M) was added aldehyde (1.05 equiv). The reaction mixture was stirred over molecular sieves 4 Å (480 mg/1.00 mmol substrate) for 18 hours at 100 °C, after

² Lee, B. S.; Lee, J. H.; Chi, D. Y. *J. Org. Chem.* **2002**, *67*, 7884.

which it was filtered through Celite and concentrated *in vacuo*. The resulting imines were clean by ^1H NMR and were used in the cyclization reactions without purification.

3-[2-(Benzylideneamino)-5-methylphenyl]acrylic acid methyl ester (1a)

δ_{H} (CDCl_3 , 400 MHz) 2.38 (s, 3H), 3.78 (s, 3H), 6.47 (d, $J = 16.1$ Hz, 1H), 6.94 (d, $J = 7.8$ Hz, 1H), 7.21 (dd, $J = 1.4, 8.2$ Hz, 1H), 7.44 (s, 1H), 7.49 (d, $J = 2.0$ Hz, 1H), 7.50 (d, $J = 2.0$ Hz, 2H), 7.93 (d, $J = 3.1$ Hz, 1H), 7.95 (t, $J = 2.7$ Hz, 1H), 8.22 (d, $J = 16.4$ Hz, 1H), 8.39 (s, 1H). δ_{C} (CDCl_3 , 100 MHz) 20.9, 51.5, 118.4, 127.8, 128.1, 128.7, 128.9, 131.4, 131.9, 135.6, 136.0, 141.6, 148.8, 160.0, 167.5.

3-[2-(Benzylideneamino)phenyl]acrylic acid methyl ester (1b)

δ_{H} (CDCl_3 , 400 MHz) 3.78 (s, 3H), 6.49 (d, $J = 16.1$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 7.24 (t, $J = 7.2$ Hz, 1H), 7.39 (ddd, $J = 1.4, 7.5, 15.0$ Hz, 1H), 7.46-7.51 (m, 3H), 7.62 (dd, $J = 0.7, 7.8$ Hz, 1H), 7.94-7.96 (m, 2H), 8.23 (d, $J = 16.1$ Hz, 1H), 8.37 (s, 1H). δ_{C} (CDCl_3 , 100 MHz) 51.4, 118.7, 125.9, 127.3, 128.2, 128.7, 128.9, 131.1, 131.6, 135.9, 141.5, 151.2, 160.7, 167.5.

3-[2-(4-Methoxybenzylideneamino)-5-methylphenyl]acrylic acid methyl ester (1c)

δ_{H} (CDCl_3 , 400 MHz) 2.37 (s, 3H), 3.78 (s, 3H), 3.88 (s, 3H), 6.46 (d, $J = 16.4$ Hz, 1H), 6.92 (d, $J = 8.2$ Hz, 1H), 6.99 (d, $J = 8.6$ Hz, 2H), 7.20 (d, $J = 7.8$ Hz, 1H), 7.42 (s, 1H), 7.88 (d, $J = 8.9$ Hz, 2H), 8.20 (d, $J = 16.4$ Hz, 1H), 8.31 (s, 1H). δ_{C} (CDCl_3 , 100 MHz) 20.9, 51.5, 55.4, 114.1, 118.3, 118.6, 127.8, 128.0, 129.1, 130.6, 131.9, 135.2, 141.8, 149.2, 159.3, 162.3, 167.6.

3-[5-Methyl-2-(4-nitrobenzylideneamino)phenyl]acrylic acid methyl ester (1d)

δ_{H} (CDCl_3 , 400 MHz) 2.40 (s, 3H), 3.79 (s, 3H), 6.46 (d, $J = 16.4$ Hz, 1H), 6.99 (d, $J = 8.2$ Hz, 1H), 7.23-7.26 (m, 1H), 7.47 (s, 1H), 8.11 (d, $J = 8.9$ Hz, 2H), 8.23 (d, $J = 16.1$ Hz, 1H), 8.34 (d, $J = 8.6$ Hz, 2H), 8.50 (s, 1H). δ_{C} (CDCl_3 , 100 MHz) 21.0, 51.6, 117.9, 118.9, 124.0, 127.9, 128.8, 129.5, 131.9, 137.1, 141.1, 141.3, 147.5, 149.3, 157.1, 167.4.

3-[2-(2-Bromobenzylideneamino)-5-methylphenyl]acrylic acid methyl ester (1e)

δ_{H} (CDCl_3 , 400 MHz) 2.39 (s, 3H), 3.79 (s, 3H), 6.46 (d, $J = 16.1$ Hz, 1H), 6.98 (d, $J = 7.9$ Hz, 1H), 7.23 (dd, $J = 1.4, 7.8$ Hz, 1H), 7.33 (ddd, $J = 1.7, 7.9, 15.4$ Hz, 1H), 7.42 (d, $J = 7.8$ Hz, 1H), 7.45 (s, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 8.23 (d, $J = 16.4$ Hz, 1H), 8.30 (dd, $J = 1.7, 7.8$ Hz, 1H), 8.79 (s, 1H). δ_{C} (CDCl_3 , 100 MHz) 20.9, 51.5, 118.5, 118.6, 126.1, 127.7, 127.7, 128.5, 129.2, 131.9, 132.5, 133.1, 134.3, 136.2, 141.5, 148.4, 158.9, 167.5.

3-[5-Methyl-2-(6-methylpyridin-2-ylmethyleneamino)phenyl]acrylic acid methyl ester (1f)

δ_{H} (CDCl_3 , 400 MHz) 2.37 (s, 3H), 2.62 (s, 3H), 3.78 (s, 3H), 6.45 (d, $J = 16.4$ Hz, 1H), 7.03 (d, $J = 7.9$ Hz, 1H), 7.21 (dd, $J = 1.4, 8.2$ Hz, 1H), 7.24 (d, $J = 8.2$ Hz, 1H), 7.44 (s, 1H), 7.71 (t, $J = 7.7$ Hz, 1H), 8.11 (d, $J = 7.8$ Hz, 1H), 8.26 (d, $J = 16.1$ Hz, 1H), 8.52 (s, 1H). δ_{C} (CDCl_3 , 100 MHz) 20.9, 24.2, 51.5, 118.2, 118.5, 118.9, 124.9, 127.7, 128.6, 131.9, 136.4, 136.8, 141.5, 147.7, 153.8, 158.2, 160.7, 167.5.

3-[5-Methyl-2-(5-methylfuran-2-ylmethyleneamino)phenyl]acrylic acid methyl ester (1g)

δ_{H} (CDCl_3 , 400 MHz) 2.36 (s, 3H), 2.44 (s, 3H), 3.77 (s, 3H), 6.17 (dd, $J = 0.7, 3.4$ Hz, 1H), 6.45 (d, $J = 16.1$ Hz, 1H), 6.87-6.89 (m, 2H), 7.17 (dd, $J = 1.7, 7.9$ Hz, 1H), 7.41 (s, 1H), 8.05 (s, 1H), 8.17 (d, $J = 16.0$ Hz, 1H). δ_{C} (CDCl_3 , 100 MHz) 13.9, 20.8, 51.4, 108.7, 118.3, 118.5, 118.7, 127.7, 127.9, 131.8, 135.3, 141.7, 147.8, 149.2, 150.7, 156.8, 167.5.

3-[5-Methyl-2-(3-phenylallylideneamino)phenyl]acrylic acid methyl ester (1h)

δ_{H} (CDCl₃, 400 MHz) 2.37 (s, 3H), 3.79 (s, 3H), 6.45 (d, $J = 16.1$ Hz, 1H), 6.88 (d, $J = 7.9$ Hz, 1H), 7.15-8.19 (m, 11H). δ_{C} (CDCl₃, 100 MHz) 20.8, 51.4, 118.3, 118.4, 127.4, 127.6, 128.1, 128.6, 128.8, 129.5, 131.8, 135.4, 135.8, 141.5, 144.1, 148.8, 161.6, 167.4.

3-[2-(Ethoxycarbonylmethyleneamino)-5-methylphenyl]acrylic acid methyl ester (1i)

δ_{H} (CDCl₃, 400 MHz) 1.42 (t, $J = 7.2$ Hz, 3H), 2.38 (s, 3H), 3.78 (s, 3H), 4.42 (q, $J = 7.2$ Hz, 2H), 6.46 (d, $J = 16.1$ Hz, 1H), 6.89 (d, $J = 8.2$ Hz, 1H), 7.20 (d, $J = 8.2$ Hz, 1H), 7.44 (s, 1H), 7.81 (s, 1H), 8.07 (d, $J = 16.1$ Hz, 1H). δ_{C} (CDCl₃, 100 MHz) 14.1, 21.0, 51.6, 62.0, 118.0, 119.8, 128.2, 128.9, 131.7, 138.4, 140.5, 145.9, 151.3, 162.9, 167.2.

3-[2-(4-Methoxybenzylideneamino)-5-methylphenyl]-*N,N*-dimethylacrylamide (1j)

δ_{H} (CDCl₃, 400 MHz) 2.36 (s, 3H), 3.02 (s, 3H), 3.09 (s, 3H), 3.85 (s, 3H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.94-6.99 (m, 3H), 7.14 (dd, $J = 1.5, 7.8$ Hz, 1H), 7.36 (d, $J = 1.4$ Hz, 1H), 7.87 (d, $J = 8.9$ Hz, 2H), 8.02 (d, $J = 15.7$ Hz, 1H), 8.28 (s, 1H). δ_{C} (CDCl₃, 100 MHz) 20.8, 35.7, 37.3, 55.3, 114.0, 118.6, 119.3, 128.7, 128.9, 129.2, 130.5, 130.8, 135.0, 139.5, 149.1, 158.9, 162.2, 167.1.

3-[2-(4-Methoxybenzylideneamino)phenyl]acrylonitrile (1k)

δ_{H} (CDCl₃, 400 MHz) 3.90 (s, 3H), 6.00 (d, $J = 16.8$ Hz, 1H), 7.01-7.03 (m, 3H), 7.23 (t, $J = 8.6$ Hz, 1H), 7.43 (ddd, $J = 1.2, 7.8, 15.2$ Hz, 1H), 7.49 (d, $J = 7.0$ Hz, 1H), 7.86-7.92 (m, 3H), 8.31 (s, 1H). δ_{C} (CDCl₃, 100 MHz) 55.4, 97.0, 114.3, 118.8, 118.9, 125.7, 127.1, 127.3, 128.6, 130.8, 131.9, 147.8, 151.2, 160.3, 162.7.

***N*-(4-Methoxybenzylidene)-(4-methyl-2-styrylphenyl)amine (1l)**

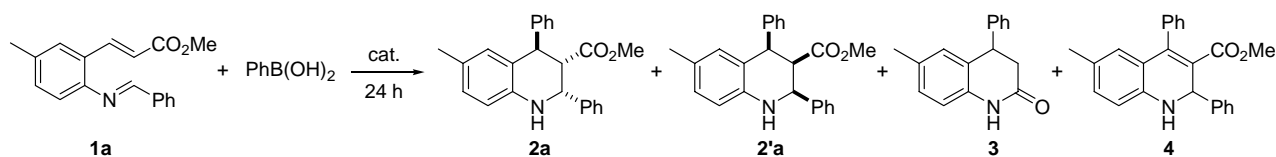
δ_{H} (CDCl₃, 400 MHz) 2.43 (s, 3H), 3.89 (s, 3H), 6.94 (d, $J = 7.8$ Hz, 1H), 7.03 (d, $J = 8.6$ Hz, 2H), 7.11-7.17 (m, 2H), 7.26-7.28 (m, 1H), 7.35-7.39 (m, 2H), 7.54-7.56 (m, 3H), 7.69 (dd, $J = 3.1, 16.4$ Hz, 1H), 7.92-7.94 (m, 2H), 8.36 (s, 1H). δ_{C} (CDCl₃, 100 MHz) 21.0, 55.3, 114.1, 118.3, 125.4, 126.1, 127.2, 128.5, 129.0, 129.2, 129.5, 130.4, 130.8, 135.1, 137.9, 147.8, 158.6, 162.1.

***N*-Benzylidene-(4-methyl-2-vinylphenyl)amine (1m)**

δ_{H} (CDCl₃, 400 MHz) 2.39 (s, 3H), 5.29 (dd, $J = 1.4, 11.0$ Hz, 1H), 5.76 (dd, $J = 1.4, 17.8$ Hz, 1H), 6.91 (d, $J = 8.2$ Hz, 1H), 7.12 (dd, $J = 1.7, 7.8$ Hz, 1H), 7.26 (dd, $J = 10.9, 17.8$ Hz, 1H), 7.42 (d, $J = 0.7$ Hz, 1H), 7.48-7.50 (m, 3H), 7.93-7.95 (m, 2H), 8.39 (s, 1H). δ_{C} (CDCl₃, 100 MHz) 21.0, 114.4, 118.1, 126.1, 128.7, 128.8, 129.3, 131.1, 133.3, 135.4, 136.4, 147.3, 159.4.

Systematic screen

Reactions were conducted at 0.1 M concentration in sealed vials under argon. To a solution of **1a** in solvent were added catalyst (5 mol %, 10 mol % Rh), base (2 equiv), additive, and phenylboronic acid (2.5 equiv). The resulting mixture was heated with stirring for 24 hours at the reported temperature. After the reaction was completed (by TLC), the mixture was cooled, quenched with distilled water, extracted with CH₂Cl₂ (three times), dried over MgSO₄, and concentrated *in vacuo*. Yields and the ratio of two isomers were determined by ¹H NMR using trichloroethylene as an internal standard. Trace amount of compound **4** was observed in most of the reactions.



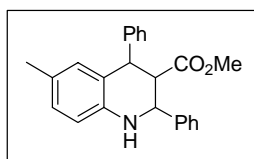
Entry	Catalyst	Base	Additive	Solvent	<i>T</i> (°C)	1a (%)	2a+2'a (%)	2a:2'a	3 (%)
1	[Rh(OH)(cod)] ₂	-	-	dioxane	60	46	35	50:50	10
2	[Rh(OH)(cod)] ₂	KOH ^a	-	dioxane	60	74	15	50:50	-
3	[Rh(OH)(cod)] ₂	-	MS 4Å ^b	dioxane	60	32	51	50:50	10
4	[Rh(OH)(cod)] ₂	KOH ^a	MS 4Å ^b	dioxane	60	85	13	48:52	-
5	[Rh(OH)(cod)] ₂	NEt ₃	-	dioxane	60	10	90	67:33	-
6	[Ir(cod)Cl] ₂	NEt ₃	-	toluene	60	100	-	-	-
7	[Rh(OH)(cod)] ₂	NEt ₃	-	dioxane	80	-	100	71:29	-
8	[Rh(OH)(cod)] ₂	NEt ₃	-	toluene	80	33	66	75:25	-
9	[Rh(OH)(cod)] ₂	NEt ₃	-	THF	80	4	95	33:67	-
10	[Rh(OH)(cod)] ₂	NEt ₃	-	acetone	80	29	71	29:71	-
11	[Rh(OH)(cod)] ₂	KOH ^a	-	dioxane	80	-	79	78:22	17
12	[Rh(OH)(cod)] ₂	KOH	-	dioxane	80	6	75	67:33	15
13	[Rh(OH)(cod)] ₂	NaOH ^a	-	dioxane	80	9	65	71:29	13
14	[Rh(OH)(cod)] ₂	NaOH	-	dioxane	80	-	87	70:30	13
15	[Rh(OH)(cod)] ₂	Na ₂ CO ₃	-	dioxane	80	8	66	62:38	13
16	[Rh(OH)(cod)] ₂	K ₂ CO ₃	-	dioxane	80	-	81	70:30	16
17	[Rh(OH)(cod)] ₂	Cs ₂ CO ₃	-	dioxane	80	-	100	42:58	-
18	[Rh(OH)(cod)] ₂	K ₃ PO ₄	-	dioxane	80	-	100	72:28	-
19	[Rh(OH)(cod)] ₂	-	-	dioxane	80	7	70	67:33	16
20	[Rh(OH)(cod)] ₂	-	H ₃ BO ₃ ^c	dioxane	80	-	52	75:25	32
21	[Rh(OH)(cod)] ₂	K ₃ PO ₄	H ₂ O ^d	dioxane	80	-	40	72:28	-
22	[Rh(OH)(cod)] ₂	K ₃ PO ₄	MS 4Å ^b	dioxane	80	-	100	75:25	-
23	[Rh(OH)(cod)] ₂	K ₃ PO ₄	-	dioxane	60	-	100	71:29	-
24	[Rh(OH)(cod)] ₂	K ₃ PO ₄	-	dioxane	40	60	40	71:29	-
25	[Rh(OH)(cod)] ₂	K ₃ PO ₄	-	dioxane	RT	100	-	-	-
26 ^e	[Rh(OH)(cod)] ₂	K ₃ PO ₄	-	dioxane	60	-	100	75:25	-
27 ^f	[Rh(OH)(cod)] ₂	K ₃ PO ₄	-	dioxane	60	4	93	71:29	3

a. Performed with 0.3 equiv of base. b. Performed with Molecular Sieves 4Å (480 mg/1 mmol substrate). c. Performed with 1.2 equiv of H₃BO₃. d. Performed in dioxane/H₂O (10/1). e. Performed with 2 mol % [Rh(OH)(cod)]₂ (4 mol % Rh). f. Performed with 1 mol % [Rh(OH)(cod)]₂ (2 mol % Rh).

General procedure for rhodium(I)-catalyzed tandem conjugate addition-Mannich cyclization reaction of imine-substituted electron-deficient alkenes **1** with arylboronic acids

To a solution of the substrate **1** (0.15 mmol) in 1,4-dioxane (0.1 M) were added [Rh(OH)(cod)]₂, K₃PO₄ (2 equiv, 0.3 mmol), and boronic acid (2.5 equiv, 0.375 mmol). The resulting mixture was stirred at the reported temperature for 1-48 hours. After the reaction was completed, the reaction mixture was quenched with distilled water, extracted with CH₂Cl₂ (three times), washed with brine, dried over MgSO₄, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc : *n*-Hexane = 1:2~1:10) to give the corresponding product **2**.

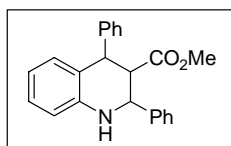
6-Methyl-2,4-diphenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (**2a**)



2 mol % [Rh(OH)(cod)]₂ at 80 °C for 1 h
a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 77:23 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl₃, 400 MHz) 2.14 (s, 3H), 3.35 (dd, $J = 4.1, 7.2$ Hz, 1H), 3.42 (s, 3H), 4.30 (d, $J = 7.2$ Hz, 1H), 4.71 (d, $J = 4.1$ Hz, 1H), 6.55 (s, 1H), 6.60 (d, $J = 7.9$ Hz, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 7.16-7.42 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.5, 42.6, 51.2, 52.0, 54.6, 114.1, 121.8, 126.3, 126.5, 126.6, 126.9, 127.7, 127.9, 128.2, 128.3, 128.6, 129.3, 130.8, 141.4, 141.7, 144.9, 171.7. Representative signals corresponding to the minor isomer: δ_{H} (CDCl₃, 400 MHz) 2.14 (s, 3H), 3.13 (s, 3H), 3.24 (dd, $J = 3.2, 6.0$ Hz, 1H), 4.66 (d, $J = 5.8$ Hz, 1H), 4.87 (d, $J = 3.1$ Hz, 1H), 6.63 (d, $J = 8.2$ Hz, 1H), 6.66 (s, 1H), 6.90 (d, $J = 7.8$ Hz, 1H), 7.16-7.42 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.5, 47.4, 50.6, 53.0, 58.6, 114.5, 114.8, 121.8, 125.2, 126.1, 127.0, 127.1, 128.1, 128.4, 128.5, 128.9, 129.5, 129.8, 140.8, 141.2, 142.5, 169.8. ν_{max} (NaCl)/cm⁻¹ 3384, 3025, 2921, 2852, 2351, 1735, 1617, 1508, 1454, 1360, 1264, 1219, 1165, 1088, 1029, 811, 752, 701. HREIMS m/z 357.1728 (M)⁺, calcd for C₂₄H₂₃NO₂ 357.1729.

2,4-Diphenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (**2b**)

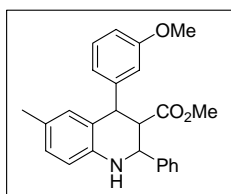


2 mol % [Rh(OH)(cod)]₂ at 60 °C for 12 h
a yellow oil (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 63:37 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl₃, 400 MHz) 3.41 (dd, $J = 4.4, 7.9$ Hz, 1H), 3.43 (s, 3H), 4.32 (d, $J = 7.9$ Hz, 1H), 4.76 (d, $J = 4.4$ Hz, 1H), 6.62-7.44 (m, 14H). δ_{C} (CDCl₃, 100 MHz) 42.2, 51.2, 51.7, 54.7, 113.8, 117.7, 122.0, 126.3, 126.6, 127.4, 127.8, 128.3, 128.6, 129.3, 130.5, 141.5, 143.6, 144.5, 171.5.

Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 3.14 (s, 3H), 3.26 (dd, $J = 3.3, 5.9 \text{ Hz}$, 1H), 4.69 (d, $J = 6.1 \text{ Hz}$, 1H), 4.92 (d, $J = 3.5 \text{ Hz}$, 1H), 6.62-7.44 (m, 14H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 47.3, 50.6, 52.8, 58.4, 114.5, 117.6, 121.6, 126.4, 126.5, 127.0, 127.2, 128.1, 128.4, 128.9, 129.5, 140.6, 141.0, 144.9, 169.8. $\nu_{\text{max}} (\text{NaCl})/\text{cm}^{-1}$ 3392, 3028, 2951, 2855, 2356, 1735, 1605, 1490, 1454, 1434, 1366, 1267, 1162, 1117, 1077, 1029, 802, 750, 701. HREIMS m/z 343.1570 (M^+), calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2$ 343.1572.

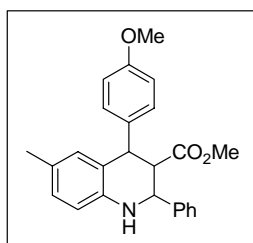
4-(3-Methoxyphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2c)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 77:23 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.34 (dd, $J = 4.1, 6.8 \text{ Hz}$, 1H), 3.42 (s, 3H), 3.77 (s, 3H), 4.27 (d, $J = 6.8 \text{ Hz}$, 1H), 4.71 (d, $J = 4.1 \text{ Hz}$, 1H), 6.58-7.41 (m, 12H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 42.7, 51.2, 51.9, 54.6, 55.1, 114.1, 121.6, 121.7, 126.3, 126.6, 127.0, 127.7, 127.9, 128.2, 128.3, 128.6, 129.2, 130.7, 141.3, 141.6, 146.6, 159.4, 171.6. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.16 (s, 3H), 3.23 (dd, $J = 3.3, 6.0 \text{ Hz}$, 1H), 3.75 (s, 3H), 4.62 (d, $J = 5.8 \text{ Hz}$, 1H), 4.86 (d, $J = 3.1 \text{ Hz}$, 1H), 6.58-7.41 (m, 12H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 47.5, 50.6, 52.9, 55.0, 58.6, 111.0, 112.7, 113.3, 114.5, 114.7, 119.6, 121.9, 128.1, 128.9, 129.3, 129.3, 129.7, 140.8, 142.4, 142.8, 159.4, 169.8. $\nu_{\text{max}} (\text{NaCl})/\text{cm}^{-1}$ 3382, 3031, 2922, 2855, 2362, 1734, 1599, 1508, 1489, 1455, 1436, 1357, 1264, 1216, 1158, 1048, 811, 738, 701. HREIMS m/z 387.1832 (M^+), calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_3$ 387.1834.

4-(4-Methoxyphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2d)

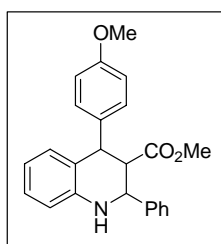


2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a white solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 71:29 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.30 (dd, $J = 4.1, 7.2 \text{ Hz}$, 1H), 3.42 (s, 3H), 3.79 (s, 3H), 4.24 (d, $J = 7.2 \text{ Hz}$, 1H), 4.69 (d, $J = 4.1 \text{ Hz}$, 1H), 6.55 (s, 1H), 6.58 (d, $J = 8.2 \text{ Hz}$, 1H), 6.81-7.41 (m, 10H).

$\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 41.7, 51.2, 52.1, 54.7, 55.1, 113.6, 114.1, 122.2, 126.3, 126.6, 127.7, 128.1, 128.2, 128.6, 130.2, 130.7, 136.9, 141.3, 141.7, 158.1, 171.7. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.15 (s, 3H), 3.20 (dd, $J = 3.4, 5.8 \text{ Hz}$, 1H), 3.80 (s, 3H), 4.60 (d, $J = 5.8 \text{ Hz}$, 1H), 4.86 (d, $J = 3.1 \text{ Hz}$, 1H), 6.61 (d, $J = 8.2 \text{ Hz}$, 1H), 6.65 (s, 1H), 6.81-7.41 (m, 10H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.6, 46.5, 50.6, 53.1, 55.1, 58.6, 114.8, 126.9, 127.8, 128.0, 129.2, 130.5, 133.1, 140.8, 141.7, 158.5, 169.9 (8 carbons are missing due to overlapping). $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3393, 3025, 2920, 2849, 2362, 1735, 1615, 1508, 1456, 1363, 1249, 1175, 1105, 1032, 812, 743, 701. HREIMS m/z 387.1833 (M^+), calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_3$ 387.1834.

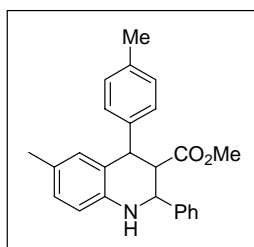
4-(4-Methoxyphenyl)-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2e)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a white solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 83:17 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 3.35 (dd, $J = 4.1, 7.9 \text{ Hz}$, 1H), 3.42 (s, 3H), 3.78 (s, 3H), 4.25 (d, $J = 7.8 \text{ Hz}$, 1H), 4.74 (d, $J = 4.4 \text{ Hz}$, 1H), 6.63-7.43 (m, 13H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 41.4, 51.2, 51.8, 54.8, 55.1, 113.6, 113.8, 117.7, 122.3, 126.6, 127.4, 127.8, 128.3, 130.2, 130.4, 136.6, 141.6, 143.6, 158.1, 171.6. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 3.15 (s, 3H), 3.22 (dd, $J = 3.3, 6.0 \text{ Hz}$, 1H), 3.79 (s, 3H), 4.62 (d, $J = 6.2 \text{ Hz}$, 1H), 4.90 (d, $J = 3.1 \text{ Hz}$, 1H), 6.61-7.43 (m, 13H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 46.5, 50.6, 53.0, 53.4, 58.4, 113.7, 114.4, 114.5, 122.1, 126.3, 126.9, 127.2, 127.9, 128.1, 128.1, 128.6, 128.9, 129.4, 130.5, 133.0, 140.7, 144.8, 158.5, 169.9. $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3382, 3018, 2922, 2852, 2360, 1736, 1650, 1606, 1541, 1509, 1456, 1366, 1249, 1163, 1111, 1032, 831, 751, 701. HREIMS m/z 373.1680 (M^+), calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3$ 373.1678.

6-Methyl-2-phenyl-4-*p*-tolyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2f)

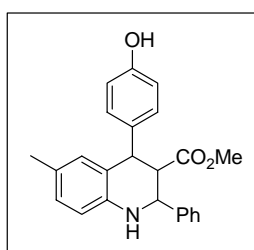


2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 71:29 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 2.33 (s, 3H), 3.32 (dd, $J = 4.1, 7.2 \text{ Hz}$, 1H), 3.42 (s, 3H), 4.27 (d, $J = 6.8 \text{ Hz}$, 1H), 4.70 (d, $J = 4.1 \text{ Hz}$, 1H), 6.57 (s, 1H), 6.60 (d, $J = 8.2 \text{ Hz}$, 1H), 6.89 (dd, $J = 1.9,$

7.7 Hz, 1H), 7.04-7.42 (m, 9H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 21.0, 42.2, 51.2, 52.1, 54.6, 114.1, 122.1, 126.3, 126.6, 127.7, 128.1, 128.2, 128.6, 129.0, 129.1, 130.8, 135.9, 141.7, 141.9, 171.7. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 2.34 (s, 3H), 3.16 (s, 3H), 3.22 (dd, $J = 3.2, 6.0 \text{ Hz}$, 1H), 4.62 (d, $J = 5.8 \text{ Hz}$, 1H), 4.87 (d, $J = 3.4 \text{ Hz}$, 1H), 6.64 (d, $J = 8.2 \text{ Hz}$, 1H), 6.66 (s, 1H), 6.89 (dd, $J = 1.9, 7.7 \text{ Hz}$, 1H), 7.04-7.42 (m, 9H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 21.1, 47.0, 50.6, 53.0, 58.6, 114.8, 122.1, 127.0, 127.8, 128.0, 129.3, 129.3, 136.5, 138.0, 140.8, 141.4, 142.3, 169.9 (2 carbons are missing due to overlapping). $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3376, 3019, 2921, 2849, 2362, 1734, 1615, 1508, 1451, 1431, 1363, 1267, 1218, 1165, 1085, 1026, 812, 743, 700. HREIMS m/z 371.1887 (M^+), calcd for $\text{C}_{25}\text{H}_{25}\text{NO}_2$ 371.1885.

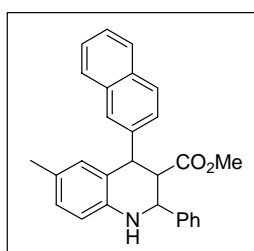
4-(4-Hydroxyphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2g)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a pale yellow solid (EtOAc : *n*-Hexane = 1 : 3)

The compound exists as a 77:23 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.32 (dd, $J = 4.3, 7.4 \text{ Hz}$, 1H), 3.43 (s, 3H), 4.22 (d, $J = 7.5 \text{ Hz}$, 1H), 4.70 (d, $J = 4.1 \text{ Hz}$, 1H), 5.45 (br s, 1H), 6.56 (s, 1H), 6.59 (d, $J = 8.2 \text{ Hz}$, 1H), 6.67-7.41 (m, 10H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 41.6, 51.3, 52.1, 54.8, 114.1, 115.2, 122.3, 126.3, 126.5, 127.7, 128.3, 128.6, 130.4, 130.7, 136.6, 141.2, 141.6, 154.2, 172.1. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.17 (s, 3H), 3.23 (dd, $J = 3.2, 6.0 \text{ Hz}$, 1H), 4.59 (d, $J = 5.8 \text{ Hz}$, 1H), 4.85 (d, $J = 3.1 \text{ Hz}$, 1H), 6.62-7.41 (m, 12H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 46.4, 50.9, 53.3, 58.5, 115.0, 115.2, 122.2, 127.0, 127.9, 128.1, 128.2, 128.9, 129.3, 130.6, 132.8, 140.6, 142.2, 154.7, 170.5. $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3365, 3025, 2923, 2849, 2362, 1733, 1717, 1651, 1615, 1508, 1456, 1436, 1363, 1261, 1218, 1168, 1097, 1026, 834, 808, 735, 701. HREIMS m/z 373.1680 (M^+), calcd for $\text{C}_{24}\text{H}_{23}\text{NO}_3$ 373.1678.

6-Methyl-4-naphthalen-2-yl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2h)

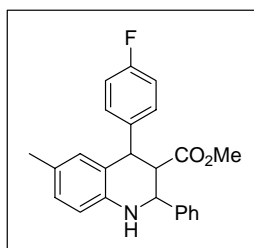


2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h

a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 83:17 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.10 (s, 3H), 3.41 (s, 3H), 3.49 (dd, $J = 4.1, 7.9 \text{ Hz}$, 1H), 4.45 (d, $J = 7.9 \text{ Hz}$, 1H), 4.77 (d, $J = 4.5 \text{ Hz}$, 1H), 6.55 (s, 1H), 6.63 (d, $J = 8.2 \text{ Hz}$, 1H), 6.90-7.83 (m, 13H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.4, 42.4, 51.2, 51.7, 55.0, 114.1, 121.8, 125.5, 125.9, 126.4, 126.6, 127.0, 127.2, 127.5, 127.8, 128.1, 128.3, 128.6, 129.4, 130.9, 132.3, 133.2, 141.4, 141.7, 142.0, 171.6. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.11 (s, 3H), 3.09 (s, 3H), 3.32 (dd, $J = 3.1, 6.1 \text{ Hz}$, 1H), 4.83 (d, $J = 5.8 \text{ Hz}$, 1H), 4.93 (d, $J = 3.1 \text{ Hz}$, 1H), 6.67 (d, $J = 7.8 \text{ Hz}$, 1H), 6.70 (s, 1H), 6.90-7.83 (m, 13H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 47.6, 50.6, 52.9, 58.7, 114.5, 114.8, 121.8, 125.2, 125.6, 125.7, 125.8, 126.2, 126.3, 127.4, 128.0, 128.1, 128.9, 129.9, 132.6, 133.4, 133.6, 138.8, 140.7, 142.5, 169.8. $\nu_{\text{max}} (\text{NaCl})/\text{cm}^{-1}$ 3376, 3031, 2921, 2855, 2362, 1734, 1717, 1649, 1620, 1508, 1456, 1357, 1261, 1216, 1165, 1026, 814, 748, 698. HREIMS m/z 407.1885 (M)⁺, calcd for C₂₈H₂₅NO₂ 407.1885.

4-(4-Fluorophenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2i)

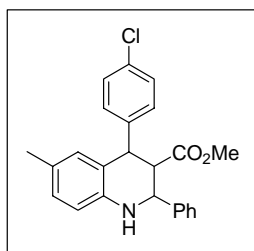


2 mol % [Rh(OH)(cod)]₂ at 60 °C for 24 h

a white solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 77:23 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.33 (dd, $J = 4.3, 8.0 \text{ Hz}$, 1H), 3.43 (s, 3H), 4.26 (d, $J = 8.2 \text{ Hz}$, 1H), 4.72 (d, $J = 4.1 \text{ Hz}$, 1H), 6.49 (s, 1H), 6.59 (d, $J = 8.2 \text{ Hz}$, 1H), 6.88-7.43 (m, 10H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.4, 41.4, 51.2, 52.0, 54.9, 114.0, 115.0, 115.2, 121.8, 126.5, 127.8, 128.4, 130.8, 140.3, 140.4, 141.2, 141.6, 160.2, 162.7, 171.5. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.15 (s, 3H), 3.14 (s, 3H), 3.21 (dd, $J = 3.3, 6.0 \text{ Hz}$, 1H), 4.65 (d, $J = 5.8 \text{ Hz}$, 1H), 4.86 (d, $J = 3.1 \text{ Hz}$, 1H), 6.62-7.41 (m, 12H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 46.5, 50.6, 53.1, 58.5, 114.6, 121.6, 126.3, 126.9, 127.9, 129.1, 131.1, 133.1, 136.9, 137.9, 140.6, 142.5, 160.7, 163.1, 169.7. $\nu_{\text{max}} (\text{NaCl})/\text{cm}^{-1}$ 3383, 3028, 2917, 2850, 1738, 1603, 1507, 1454, 1220, 1158, 1094, 1015, 841, 812, 737, 701. HREIMS m/z 375.1634 (M)⁺, calcd for C₂₄H₂₂FNO₂ 375.1635.

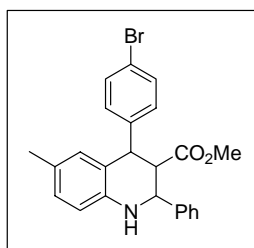
4-(4-Chlorophenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2j)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
 a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 91:9 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.13 (s, 3H), 3.33 (dd, $J = 4.3, 8.0 \text{ Hz}$, 1H), 3.44 (s, 3H), 4.24 (d, $J = 8.2 \text{ Hz}$, 1H), 4.72 (d, $J = 4.5 \text{ Hz}$, 1H), 6.47 (s, 1H), 6.58 (d, $J = 7.9 \text{ Hz}$, 1H), 6.88-7.43 (m, 10H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.4, 41.6, 51.3, 51.8, 55.0, 114.1, 121.5, 126.5, 127.0, 127.8, 128.3, 128.4, 130.6, 130.7, 132.2, 141.2, 141.5, 143.2, 171.4. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.15 (s, 3H), 3.20 (dd, $J = 3.4, 6.1 \text{ Hz}$, 1H), 4.63 (d, $J = 5.8 \text{ Hz}$, 1H), 4.85 (d, $J = 3.1 \text{ Hz}$, 1H), 6.61-7.43 (m, 12H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.8, 43.3, 50.6, 53.4, 55.0, 114.6, 124.7, 127.9, 128.2, 128.5, 128.6, 128.7, 129.0, 129.7, 133.3, 133.5, 137.9, 146.8, 148.8, 167.5. $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3365, 3021, 2922, 2849, 2356, 1735, 1615, 1508, 1489, 1455, 1241, 1218, 1165, 1089, 1014, 813, 740, 700. HREIMS m/z 391.1341 (M^+), calcd for $\text{C}_{24}\text{H}_{22}\text{ClNO}_2$ 391.1339.

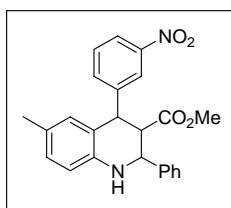
4-(4-Bromophenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2k)



5 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 48 h
 a white solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 63:37 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.13 (s, 3H), 3.33 (dd, $J = 4.3, 8.0 \text{ Hz}$, 1H), 3.44 (s, 3H), 4.23 (d, $J = 8.2 \text{ Hz}$, 1H), 4.32 (br s, 1H), 4.72 (d, $J = 4.1 \text{ Hz}$, 1H), 6.47 (s, 1H), 6.57-7.43 (m, 11H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.4, 41.6, 51.3, 51.8, 55.0, 114.1, 120.4, 121.4, 126.3, 126.5, 127.8, 128.3, 128.4, 128.6, 131.1, 131.4, 141.2, 141.5, 143.7, 171.4. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.14 (s, 3H), 3.15 (s, 3H), 3.20 (dd, $J = 3.2, 6.0 \text{ Hz}$, 1H), 4.06 (br s, 1H), 4.62 (d, $J = 6.2 \text{ Hz}$, 1H), 4.85 (d, $J = 3.1 \text{ Hz}$, 1H), 6.59-7.43 (m, 12H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 46.7, 50.7, 52.9, 58.6, 114.9, 120.9, 121.2, 127.0, 127.1, 128.1, 128.2, 128.3, 129.1, 130.6, 131.3, 140.3, 140.6, 142.5, 169.5. $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3382, 3019, 2922, 2849, 2351, 1734, 1717, 1615, 1508, 1487, 1456, 1363, 1258, 1216, 1167, 1068, 1012, 808, 743, 698. HREIMS m/z 435.0830 (M^+), calcd for $\text{C}_{24}\text{H}_{22}\text{BrNO}_2$ 435.0834.

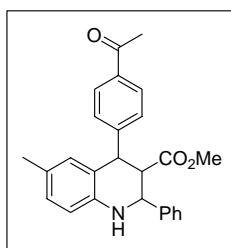
6-Methyl-4-(3-nitrophenyl)-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2l)



5 mol % [Rh(OH)(cod)]₂ at 80 °C for 48 h
a yellow solid (EtOAc : *n*-Hexane = 1 : 5)

The compound exists as a 83:17 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl₃, 400 MHz) 2.11 (s, 3H), 3.44 (dd, $J = 4.4, 9.2$ Hz, 1H), 3.46 (s, 3H), 4.37 (d, $J = 9.2$ Hz, 1H), 4.41 (br s, 1H), 4.80 (d, $J = 4.4$ Hz, 1H), 6.36 (s, 1H), 6.60 (d, $J = 8.1$ Hz, 1H), 6.90-8.18 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.4, 41.5, 51.5, 51.6, 55.3, 114.2, 120.7, 121.8, 124.3, 126.5, 127.1, 128.0, 128.4, 128.8, 129.2, 130.3, 135.8, 146.7, 148.3, 171.0 (2 carbons are missing due to overlapping). Representative signals corresponding to the minor isomer: δ_{H} (CDCl₃, 400 MHz) 2.14 (s, 3H), 3.15 (s, 3H), 3.27 (dd, $J = 3.3, 6.2$ Hz, 1H), 3.46 (s, 3H), 4.80 (m, 1H), 4.88 (d, $J = 3.0$ Hz, 1H), 6.52 (s, 1H), 6.65 (d, $J = 8.1$ Hz, 1H), 6.90-8.18 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.5, 46.8, 50.8, 53.0, 58.4, 115.1, 120.3, 122.3, 124.7, 126.3, 127.3, 128.3, 128.7, 135.7, 140.3, 142.6, 143.6, 144.9, 169.3 (3 carbons are missing due to overlapping). ν_{max} (NaCl)/cm⁻¹ 3393, 3019, 2922, 2853, 2362, 1737, 1617, 1527, 1508, 1451, 1349, 1266, 1167, 1117, 1080, 1023, 812, 736, 699. HREIMS m/z 402.1581 (M)⁺, calcd for C₂₄H₂₂N₂O₄ 402.1580.

4-(4-Acetylphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2m)

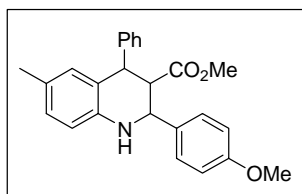


5 mol % [Rh(OH)(cod)]₂ at 80 °C for 48 h
a pale yellow solid (EtOAc : *n*-Hexane = 1 : 3)

The compound exists as a 67:33 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl₃, 400 MHz) 2.12 (s, 3H), 2.59 (s, 3H), 3.42 (dd, $J = 4.1, 8.6$ Hz, 1H), 3.44 (s, 3H), 4.33 (d, $J = 8.6$ Hz, 1H), 4.76 (d, $J = 4.1$ Hz, 1H), 6.43 (s, 1H), 6.60 (d, $J = 8.2$ Hz, 1H), 6.89-7.91 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.4, 26.5, 42.0, 51.3, 51.5, 55.1, 114.1, 121.2, 126.5, 127.0, 128.2, 128.3, 128.4, 129.7, 130.5, 135.6, 141.2, 141.5, 150.2, 171.3, 197.8 (1 carbon is missing due to overlapping). Representative signals corresponding to the minor isomer: δ_{H} (CDCl₃, 400 MHz) 2.14 (s, 3H), 2.60 (s, 3H), 3.13 (s, 3H), 3.24 (dd, $J = 3.2, 6.0$ Hz, 1H), 4.73 (d, $J = 5.8$ Hz, 1H), 4.87 (d, $J = 3.1$ Hz, 1H), 6.57 (s, 1H), 6.64 (d, $J = 8.2$ Hz, 1H), 6.89-7.91 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.5, 26.5, 47.2, 50.7, 52.8, 58.6, 115.0, 120.9, 126.3, 127.1, 127.9, 128.5, 128.6, 129.1, 129.8,

136.0, 140.5, 142.5, 147.1, 169.4, 199.6 (1 carbon is missing due to overlapping). ν_{\max} (NaCl)/ cm^{-1} 3375, 3025, 2920, 2849, 2356, 1734, 1683, 1605, 1508, 1456, 1435, 1417, 1361, 1268, 1168, 1119, 1016, 958, 842, 813, 736, 701. HREIMS m/z 399.1837 (M)⁺, calcd for $C_{26}H_{25}NO_3$ 399.1834.

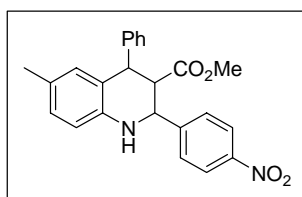
2-(4-Methoxyphenyl)-6-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2n)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80 °C for 1 h
a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 83:17 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl_3 , 400 MHz) 2.13 (s, 3H), 3.32 (dd, $J = 4.1, 7.2$ Hz, 1H), 3.44 (s, 3H), 3.78 (s, 3H), 4.28 (d, $J = 7.2$ Hz, 1H), 4.67 (d, $J = 4.1$ Hz, 1H), 6.54 (s, 1H), 6.59 (d, $J = 8.2$ Hz, 1H), 6.78-7.34 (m, 10H). δ_{C} (CDCl_3 , 100 MHz) 20.4, 42.5, 51.2, 52.0, 54.2, 55.1, 113.6, 114.1, 121.9, 126.4, 126.8, 127.7, 128.2, 128.3, 129.3, 130.7, 133.7, 141.4, 144.9, 159.0, 171.7. Representative signals corresponding to the minor isomer: δ_{H} (CDCl_3 , 400 MHz) 2.14 (s, 3H), 3.16 (s, 3H), 3.20 (dd, $J = 3.3, 6.0$ Hz, 1H), 3.80 (s, 3H), 4.64 (d, $J = 6.2$ Hz, 1H), 4.82 (d, $J = 3.4$ Hz, 1H), 6.65-7.34 (m, 12H). δ_{C} (CDCl_3 , 100 MHz) 20.5, 47.3, 50.6, 53.1, 55.2, 58.0, 113.8, 114.8, 121.8, 127.0, 127.5, 127.9, 129.5, 132.8, 141.2, 142.5, 159.2, 169.9 (3 carbons are missing due to overlapping). ν_{\max} (NaCl)/ cm^{-1} 3384, 3025, 2917, 2850, 2360, 1739, 1611, 1508, 1456, 1362, 1248, 1174, 1110, 1032, 833, 810, 737, 702. HREIMS m/z 387.1832 (M)⁺, calcd for $C_{25}H_{25}NO_3$ 387.1834.

6-Methyl-2-(4-nitrophenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2o)

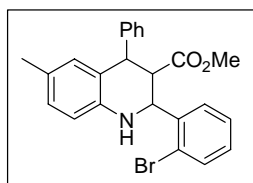


2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80 °C for 1 h
a yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 59:41 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl_3 , 400 MHz) 2.15 (s, 3H), 3.37 (dd, $J = 4.3, 7.0$ Hz, 1H), 3.43 (s, 3H), 4.29 (d, $J = 6.8$ Hz, 1H), 4.81 (d, $J = 4.1$ Hz, 1H), 6.58 (s, 1H), 6.64 (d, $J = 8.2$ Hz, 1H), 6.92 (dd, $J = 1.5, 8.0$ Hz, 1H), 7.14-7.36 (m, 7H), 8.13 (d, $J = 8.9$ Hz, 2H). δ_{C} (CDCl_3 , 100 MHz) 20.5, 42.6, 51.4, 51.9, 54.2, 114.4, 121.7, 123.5, 126.8, 127.6, 127.8, 128.4, 128.5, 129.2, 130.9, 140.5, 144.3, 147.4, 149.2, 171.1. Signals corresponding to the minor isomer: δ_{H} (CDCl_3 , 400 MHz) 2.15 (s, 3H), 3.12 (s, 3H), 3.27 (dd, $J = 3.1, 5.8$ Hz, 1H), 4.68 (d, $J = 5.8$ Hz, 1H), 4.99 (d, $J = 2.8$ Hz, 1H), 6.67-8.26 (m, 12H).

δ_{C} (CDCl₃, 100 MHz) 20.8, 43.6, 50.9, 114.7, 123.6, 124.9, 126.4, 127.2, 127.9, 128.5, 129.2, 129.9, 133.1, 133.8, 144.6, 146.3, 147.9, 167.0 (2 carbons are missing due to overlapping). ν_{max} (NaCl)/cm⁻¹ 3385, 3018, 2918, 2851, 2360, 1734, 1600, 1527, 1508, 1456, 1345, 1266, 1220, 1165, 1110, 1030, 856, 813, 739, 701. HREIMS m/z 402.1581 (M)⁺, calcd for C₂₄H₂₂N₂O₄ 402.1580.

2-(2-Bromophenyl)-6-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2p)



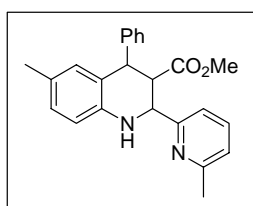
2 mol % [Rh(OH)(cod)]₂ at 80 °C for 1 h

a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 50:50 mixture of isomers.

δ_{H} (CDCl₃, 400 MHz) 2.15 (s, 3H), 2.18 (s, 3H), 3.09 (s, 3H), 3.35 (t, J = 3.4 Hz, 1H), 3.39 (s, 3H), 3.47 (dd, J = 3.3, 6.0 Hz, 1H), 4.45 (d, J = 3.4 Hz, 1H), 4.67 (d, J = 5.8 Hz, 1H), 4.93 (d, J = 3.4 Hz, 1H), 5.25 (d, J = 3.1 Hz, 1H), 6.65 (t, J = 7.4 Hz, 2H), 6.69 (s, 1H), 6.75 (s, 1H), 6.90-7.58 (m, 20H). δ_{C} (CDCl₃, 100 MHz) 20.5, 20.6, 44.3, 47.0, 49.5, 49.8, 50.5, 51.2, 52.3, 57.2, 114.8, 115.1, 121.5, 122.3, 122.9, 123.1, 126.1, 126.5, 127.0, 127.1, 127.2, 127.3, 127.5, 127.6, 127.8, 127.9, 128.0, 128.2, 128.4, 129.0, 129.2, 129.4, 129.7, 130.9, 132.8, 133.0, 139.2, 140.0, 141.0, 141.8, 142.3, 145.1, 169.5, 171.6. ν_{max} (NaCl)/cm⁻¹ 3364, 3019, 2918, 2849, 2362, 1735, 1617, 1508, 1470, 1435, 1265, 1170, 1024, 813, 736, 702. HREIMS m/z 435.0834 (M)⁺, calcd for C₂₄H₂₂BrNO₂ 435.0834.

6-Methyl-2-(6-methylpyridin-2-yl)-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2q)



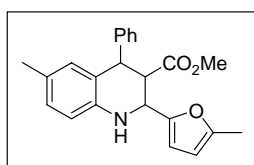
2 mol % [Rh(OH)(cod)]₂ at 80 °C for 1 h

a pale yellow solid (EtOAc : *n*-Hexane = 1 : 5)

The compound exists as a 59:41 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl₃, 400 MHz) 2.16 (s, 3H), 2.51 (s, 3H), 3.40 (s, 3H), 3.58 (dd, J = 5.5, 10.9 Hz, 1H), 4.18 (br s, 1H), 4.52 (d, J = 5.5 Hz, 1H), 4.69 (d, J = 10.9 Hz, 1H), 6.60 (d, J = 8.2 Hz, 1H), 6.77 (d, J = 1.4 Hz, 1H), 6.89 (dd, J = 1.7, 8.2 Hz, 1H), 7.03 (d, J = 7.5 Hz, 1H), 7.09-7.28 (m, 6H), 7.49 (t, J = 7.7 Hz, 1H). δ_{C} (CDCl₃, 100 MHz) 20.3, 24.4, 45.8, 48.3, 51.0, 53.7, 114.7, 119.7, 122.1, 122.3, 126.8, 128.1, 128.5, 129.1, 130.2, 136.7, 141.2, 142.6, 158.1, 159.7, 171.9 (1 carbon is missing due to overlapping). Signals corresponding to the minor isomer: δ_{H} (CDCl₃, 400 MHz) 2.14 (s, 3H), 2.51

(s, 3H), 3.40 (dd, $J = 3.9, 5.6$ Hz, 1H), 3.44 (s, 3H), 4.35 (d, $J = 5.5$ Hz, 1H), 4.71 (d, $J = 2.7$ Hz, 1H), 5.04 (br s, 1H), 6.62 (s, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 6.92 (d, $J = 7.7$ Hz, 1H), 7.00 (d, $J = 7.5$ Hz, 1H), 7.18-7.31 (m, 5H), 7.48 (t, $J = 7.7$ Hz, 1H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 24.2, 43.6, 50.0, 51.4, 54.2, 115.0, 117.8, 121.6, 126.4, 127.0, 128.3, 129.2, 130.8, 136.6, 141.1, 145.1, 157.1, 158.8, 171.6 (2 carbons are missing due to overlapping). $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3399, 3025, 2922, 2851, 2345, 1740, 1617, 1593, 1558, 1541, 1508, 1456, 1363, 1315, 1264, 1233, 1168, 1074, 1030, 806, 737, 702. HREIMS m/z 372.1836 (M^+), calcd for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_2$ 372.1838.

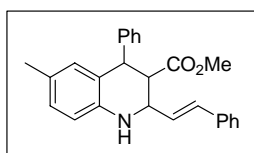
6-Methyl-2-(5-methylfuran-2-yl)-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2r)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a 83:17 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.10 (s, 3H), 2.21 (s, 3H), 3.39 (dd, $J = 3.8, 8.2$ Hz, 1H), 3.57 (s, 3H), 4.21 (br s, 1H), 4.37 (d, $J = 8.2$ Hz, 1H), 4.75 (d, $J = 4.1$ Hz, 1H), 5.84 (d, $J = 2.0$ Hz, 1H), 5.99 (d, $J = 2.8$ Hz, 1H), 6.50 (s, 1H), 6.58 (d, $J = 8.2$ Hz, 1H), 6.84 (d, $J = 7.9$ Hz, 1H), 7.19-7.31 (m, 5H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 13.4, 20.5, 42.5, 49.8, 49.9, 51.5, 106.1, 107.3, 114.8, 122.8, 126.4, 127.5, 128.0, 128.2, 129.4, 130.8, 140.6, 144.9, 151.1, 152.2, 171.6. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.13 (s, 3H), 2.26 (s, 3H), 3.28 (s, 3H), 3.36 (m, 1H), 4.57 (d, $J = 5.8$ Hz, 1H), 4.83 (d, $J = 2.7$ Hz, 1H), 5.89 (d, $J = 2.1$ Hz, 1H), 6.17 (d, $J = 3.1$ Hz, 1H), 6.65 (s, 1H), 6.68 (d, $J = 8.2$ Hz, 1H), 6.90 (d, $J = 8.2$ Hz, 1H), 7.19-7.31 (m, 5H). $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3385, 3019, 2923, 2849, 2356, 1740, 1617, 1559, 1508, 1454, 1435, 1373, 1265, 1220, 1168, 1121, 1025, 812, 789, 737, 702. HREIMS m/z 361.1679 (M^+), calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_3$ 361.1678.

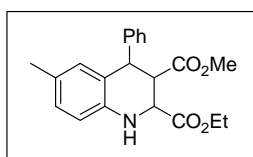
6-Methyl-4-phenyl-2-styryl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester (2s)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 1 h
a pale brown oil (EtOAc : *n*-Hexane = 1 : 10)

$\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.11 (s, 3H), 3.30 (dd, $J = 3.8, 8.5$ Hz, 1H), 3.58 (s, 3H), 4.13 (br s, 1H), 4.26 (dd, $J = 3.8, 7.2$ Hz, 1H), 4.45 (d, $J = 8.6$ Hz, 1H), 6.34-7.34 (m, 15H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.5, 42.6, 51.2, 51.6, 53.8, 114.8, 122.6, 126.5, 127.7, 127.8, 128.1, 128.3, 128.5, 129.3, 130.8, 132.0, 136.5, 140.3, 144.8, 172.0 (2 carbons are missing due to overlapping). $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3384, 3025, 2923, 2849, 2351, 1734, 1717, 1694, 1649, 1541, 1507, 1456, 1363, 1263, 1162, 1074, 1023, 967, 811, 746, 700. HREIMS m/z 383.1886 (M^+), calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_2$ 383.1885.

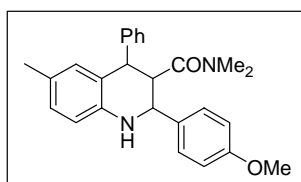
6-Methyl-4-phenyl-1,2,3,4-tetrahydroquinoline-2,3-dicarboxylic acid 2-ethyl ester 3-methyl ester (2t)



2 mol % [Rh(OH)(cod)]₂ at 80 °C for 1 h
a yellow solid (EtOAc : *n*-Hexane = 1 : 10)

The compound exists as a mixture of isomers and the ratio of isomers could not be determined. δ_{H} (CDCl₃, 400 MHz) 1.24 (t, $J = 7.2$ Hz, 3H), 2.18 (s, 3H), 3.28 (s, 3H), 3.93 (d, $J = 18.1$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 1H), 4.22 (d, $J = 18.4$ Hz, 1H), 4.76 (d, $J = 9.9$ Hz, 1H), 5.05 (d, $J = 9.9$ Hz, 1H), 6.43 (d, $J = 7.9$ Hz, 1H), 6.76 (s, 1H), 6.93 (d, $J = 7.9$ Hz, 1H), 7.08-7.23 (m, 5H). δ_{C} (CDCl₃, 100 MHz) 14.1, 14.2, 20.7, 21.3, 46.7, 47.5, 50.6, 51.4, 60.8, 61.4, 70.6, 106.8, 109.2, 121.1, 123.6, 125.4, 125.9, 126.9, 127.2, 127.7, 127.9, 128.1, 128.5, 128.7, 130.4, 130.7, 130.9, 134.4, 136.9, 140.0, 148.3, 163.0, 169.1, 170.1, 170.7 (3 carbons are missing due to overlapping). ν_{max} (NaCl)/cm⁻¹ 3210, 3025, 2950, 2849, 2351, 1748, 1701, 1617, 1497, 1456, 1373, 1279, 1199, 1165, 1104, 1026, 803, 737, 700. HREIMS m/z 353.1628 (M)⁺, calcd for C₂₁H₂₃NO₄ 353.1627.

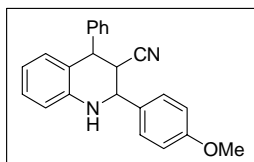
2-(4-Methoxyphenyl)-6-methyl-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid *N,N*-dimethylamide (2u)



2 mol % [Rh(OH)(cod)]₂ at 120 °C for 1 h
a white solid (EtOAc : *n*-Hexane = 1 : 2)

The compound exists as a 71:29 mixture of isomers. Signals corresponding to the major isomer: δ_{H} (CDCl₃, 400 MHz) 1.96 (s, 3H), 2.12 (s, 3H), 2.51 (s, 3H), 3.45 (dd, $J = 3.2, 5.6$ Hz, 1H), 3.79 (s, 3H), 4.61 (d, $J = 4.5$ Hz, 1H), 4.81 (d, $J = 2.7$ Hz, 1H), 6.59 (s, 1H), 6.64 (d, $J = 7.5$ Hz, 1H), 6.84-7.37 (m, 10H). δ_{C} (CDCl₃, 100 MHz) 20.6, 35.1, 36.7, 45.8, 48.2, 55.2, 59.0, 113.7, 115.8, 126.9, 127.1, 127.4, 127.6, 128.1, 128.7, 129.8, 134.1, 134.7, 135.5, 141.4, 159.3, 169.4. Signals corresponding to the minor isomer: δ_{H} (CDCl₃, 400 MHz) 2.14 (s, 3H), 2.47 (s, 3H), 2.77 (s, 3H), 3.67 (t, $J = 4.1$ Hz, 1H), 3.77 (s, 3H), 4.31 (d, $J = 4.4$ Hz, 1H), 4.52 (d, $J = 3.8$ Hz, 1H), 6.61-7.31 (m, 12H). δ_{C} (CDCl₃, 100 MHz) 20.5, 35.4, 36.8, 44.3, 47.8, 53.5, 55.2, 113.5, 114.4, 122.9, 126.2, 127.7, 128.3, 129.2, 130.8, 133.2, 141.8, 146.7, 159.2, 170.8 (2 carbons are missing due to overlapping). ν_{max} (NaCl)/cm⁻¹ 3218, 3059, 2923, 2849, 2362, 1733, 1714, 1636, 1603, 1555, 1542, 1508, 1457, 1397, 1340, 1252, 1178, 1094, 1031, 831, 754, 702. HREIMS m/z 400.2153 (M)⁺, calcd for C₂₆H₂₈N₂O₂ 400.2151.

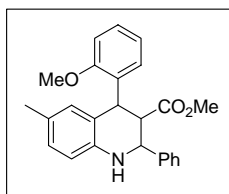
2-(4-Methoxyphenyl)-4-phenyl-1,2,3,4-tetrahydroquinoline-3-carbonitrile (2v)



2 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 80°C for 3 h
 a yellow solid (EtOAc : *n*-Hexane = 1 : 10)

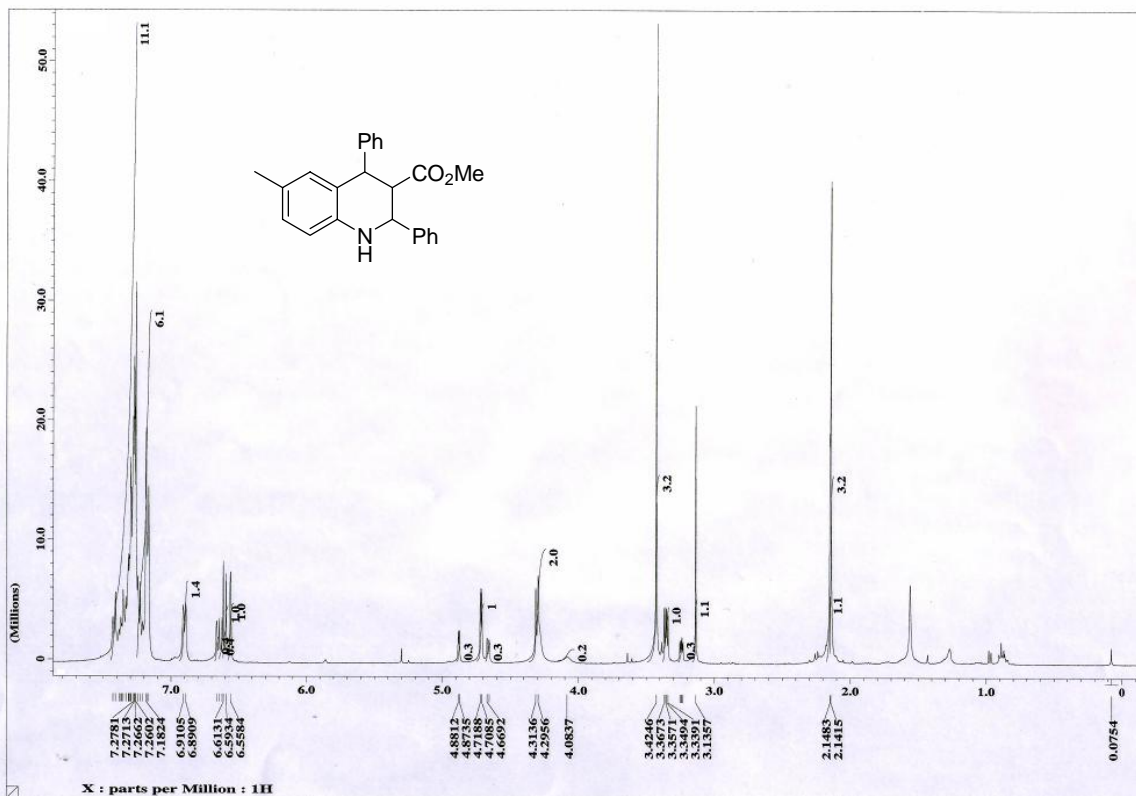
The compound exists as a 53:47 mixture of isomers. Signals corresponding to the major isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 3.17 (t, $J = 3.1 \text{ Hz}$, 1H), 3.80 (s, 3H), 4.22 (br s, 1H), 4.39 (d, $J = 2.7 \text{ Hz}$, 1H), 4.51 (d, $J = 3.1 \text{ Hz}$, 1H), 6.72-7.36 (m, 13H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 41.0, 45.9, 51.4, 55.3, 114.1, 114.2, 114.8, 117.8, 118.5, 127.3, 128.1, 128.4, 128.7, 128.8, 131.0, 131.1, 143.6, 143.7, 159.8. Representative signals corresponding to the minor isomer: $\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 3.25 (dd, $J = 2.2, 5.3 \text{ Hz}$, 1H), 3.82 (s, 3H), 4.13 (br s, 1H), 4.72 (d, $J = 5.5 \text{ Hz}$, 1H), 4.82 (d, $J = 2.4 \text{ Hz}$, 1H), 6.61-7.56 (m, 13H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 43.3, 47.7, 55.3, 57.9, 114.2, 115.1, 118.4, 118.5, 120.2, 127.9, 128.0, 128.1, 128.2, 128.6, 129.6, 131.0, 139.7, 144.4, 159.9. $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3384, 3008, 2922, 2852, 2362, 2237, 1734, 1606, 1511, 1486, 1453, 1340, 1298, 1250, 1180, 1110, 1027, 829, 751, 704. HREIMS m/z 340.1574 (M^+), calcd for $\text{C}_{23}\text{H}_{20}\text{N}_2\text{O}$ 340.1576.

4-(2-Methoxyphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester

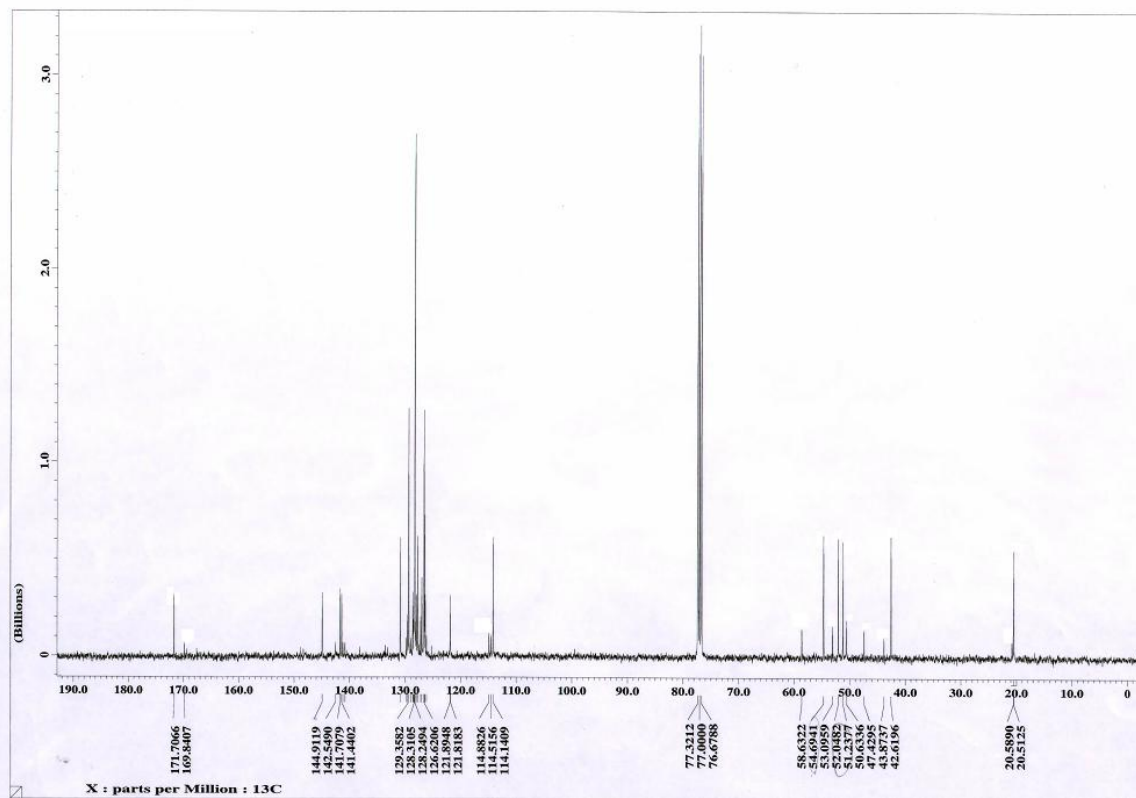


10 mol % $[\text{Rh}(\text{OH})(\text{cod})]_2$ at 120°C for 4 h
 a pale yellow solid (EtOAc : *n*-Hexane = 1 : 10)

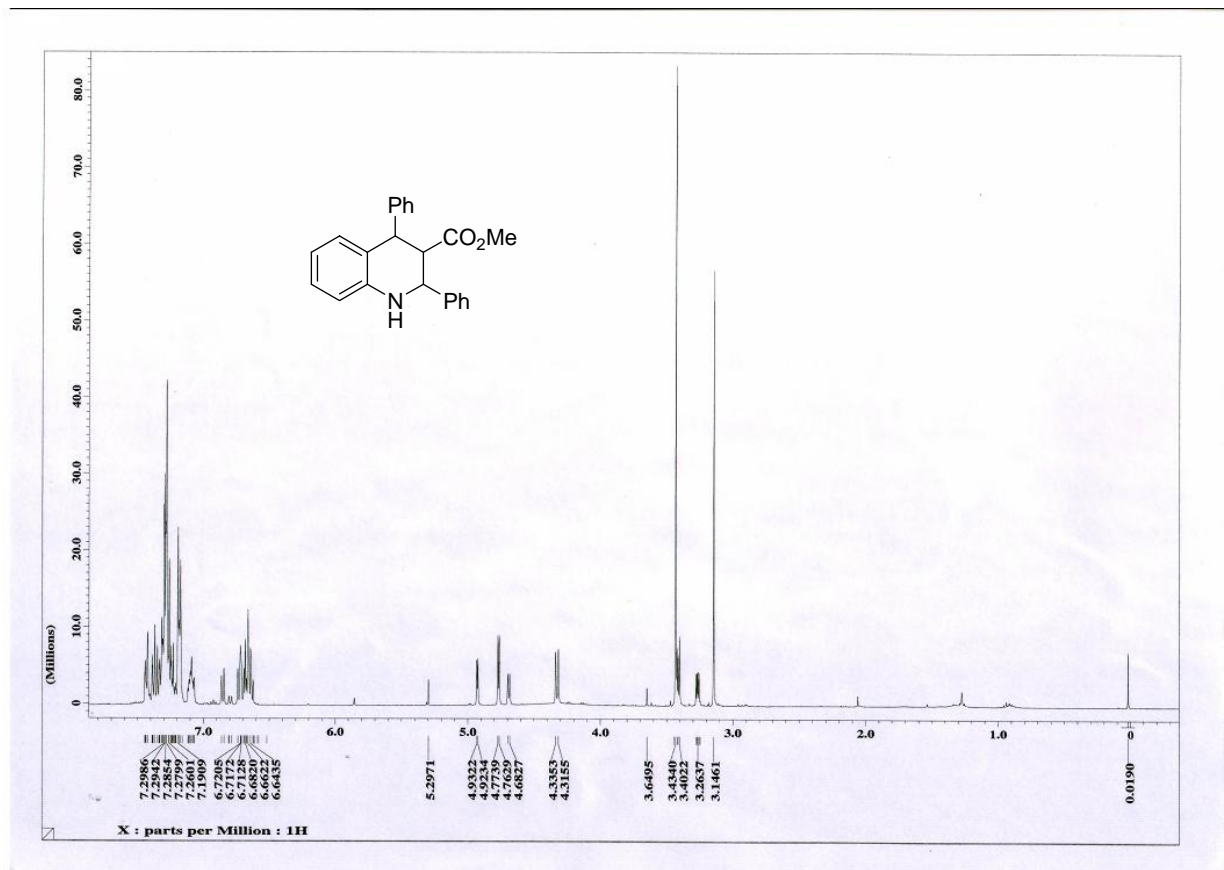
$\delta_{\text{H}}(\text{CDCl}_3, 400 \text{ MHz})$ 2.16 (s, 3H), 3.08 (s, 3H), 3.36 (dd, $J = 3.1, 6.2 \text{ Hz}$, 1H), 3.88 (s, 3H), 4.05 (br s, 1H), 4.83 (d, $J = 3.1 \text{ Hz}$, 1H), 5.18 (d, $J = 6.2 \text{ Hz}$, 1H), 6.64 (d, $J = 7.8 \text{ Hz}$, 1H), 6.73 (s, 1H), 6.84 (t, $J = 7.5 \text{ Hz}$, 1H), 6.89 (d, $J = 7.8 \text{ Hz}$, 2H), 7.12 (dd, $J = 1.4, 7.6 \text{ Hz}$, 1H), 7.20 (ddd, $J = 1.2, 8.6, 15.7 \text{ Hz}$, 1H), 7.29 (d, $J = 6.8 \text{ Hz}$, 1H), 7.34 (t, $J = 7.2 \text{ Hz}$, 2H), 7.43 (d, $J = 7.2 \text{ Hz}$, 2H). $\delta_{\text{C}}(\text{CDCl}_3, 100 \text{ MHz})$ 20.6, 38.3, 50.2, 50.5, 55.5, 58.3, 109.9, 115.2, 120.0, 122.1, 126.4, 126.9, 127.4, 127.7, 127.9, 128.5, 128.9, 129.4, 130.0, 141.1, 143.1, 157.8, 170.1. $\nu_{\text{max}}(\text{NaCl})/\text{cm}^{-1}$ 3374, 3026, 2917, 2856, 2368, 1733, 1616, 1508, 1493, 1454, 1435, 1349, 1266, 1218, 1171, 1089, 1030, 812, 753, 701.



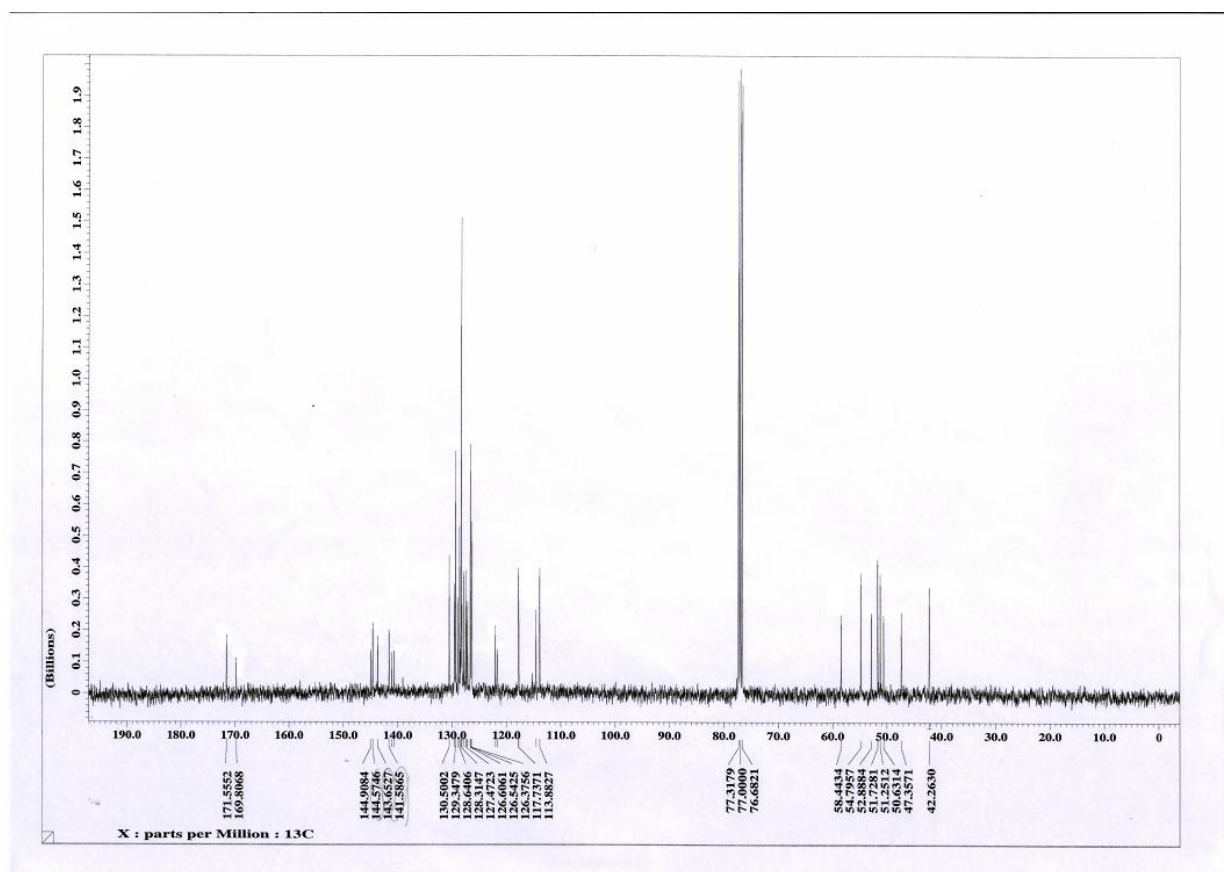
¹H NMR Spectrum of Compound 2a (CDCl₃, 400 MHz)



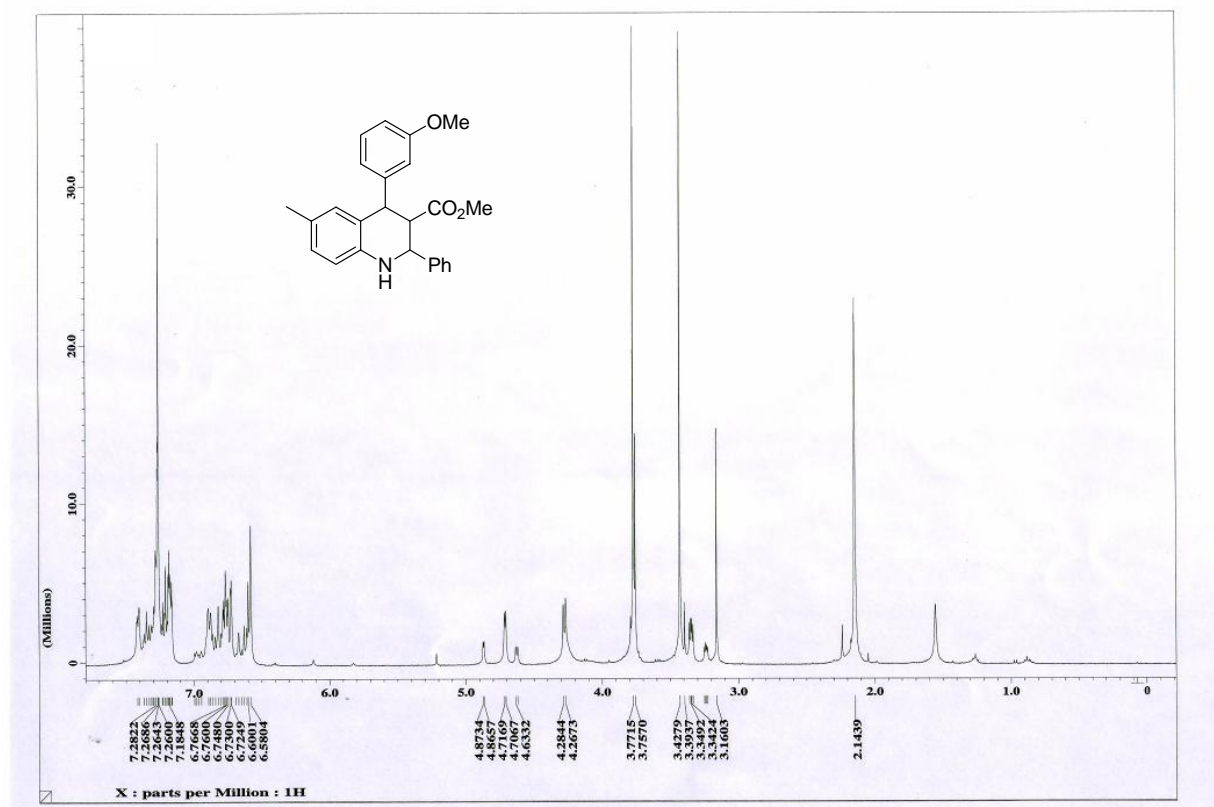
¹³C NMR Spectrum of Compound 2a (CDCl₃, 100 MHz)



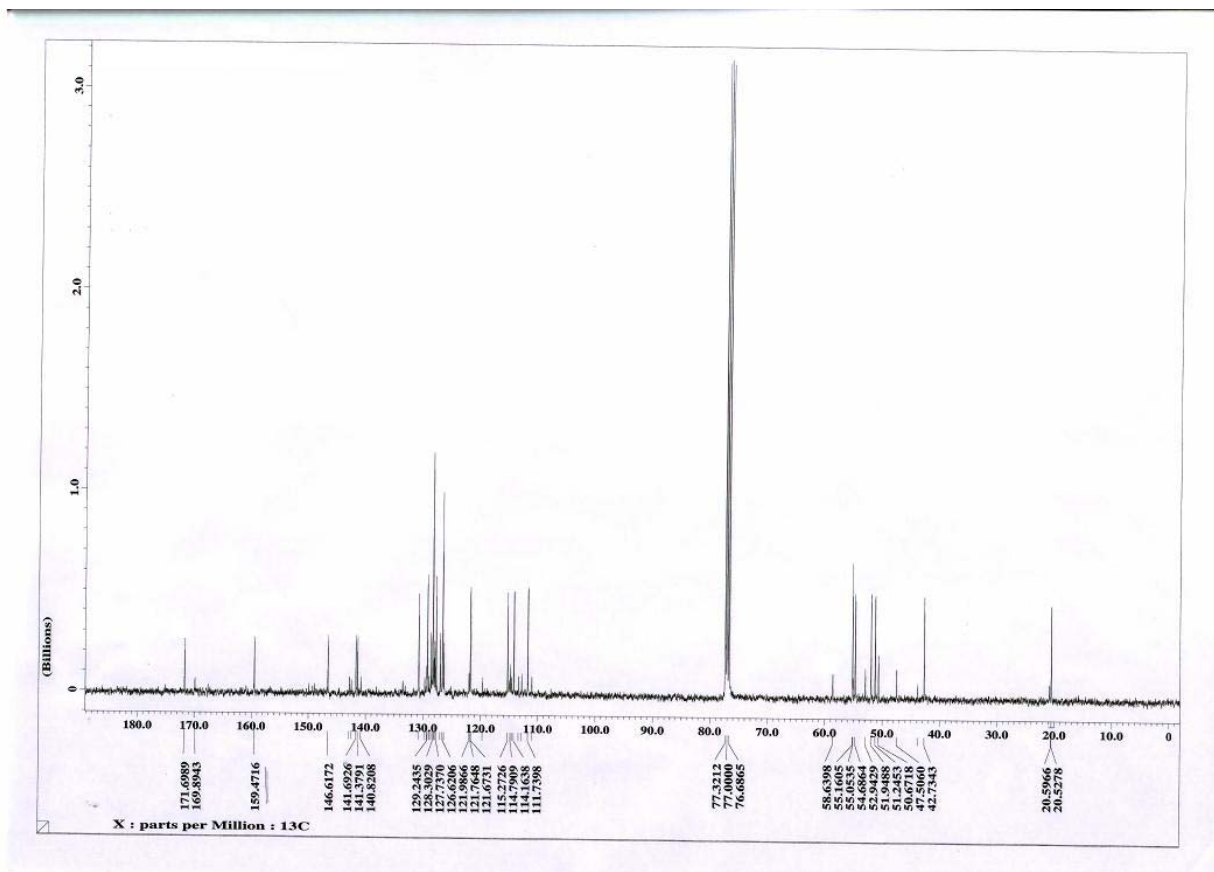
¹H NMR Spectrum of Compound **2b** (CDCl₃, 400 MHz)



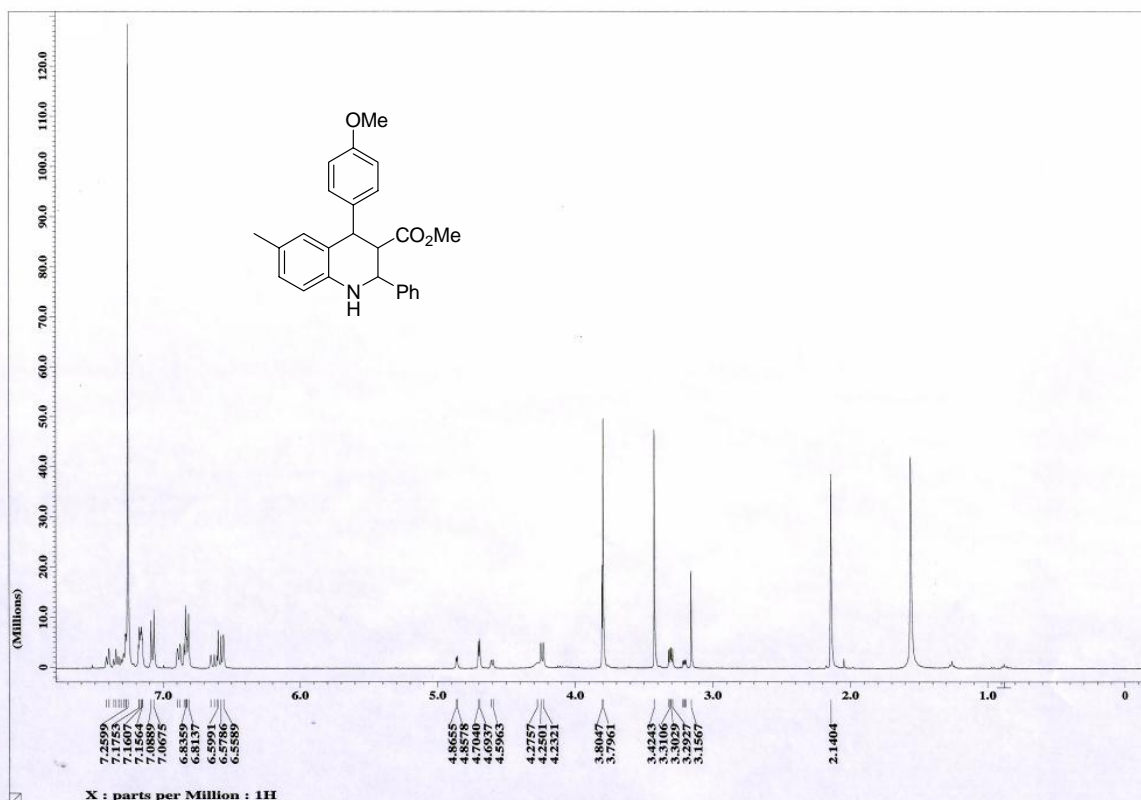
¹³C NMR Spectrum of Compound **2b** (CDCl₃, 100 MHz)



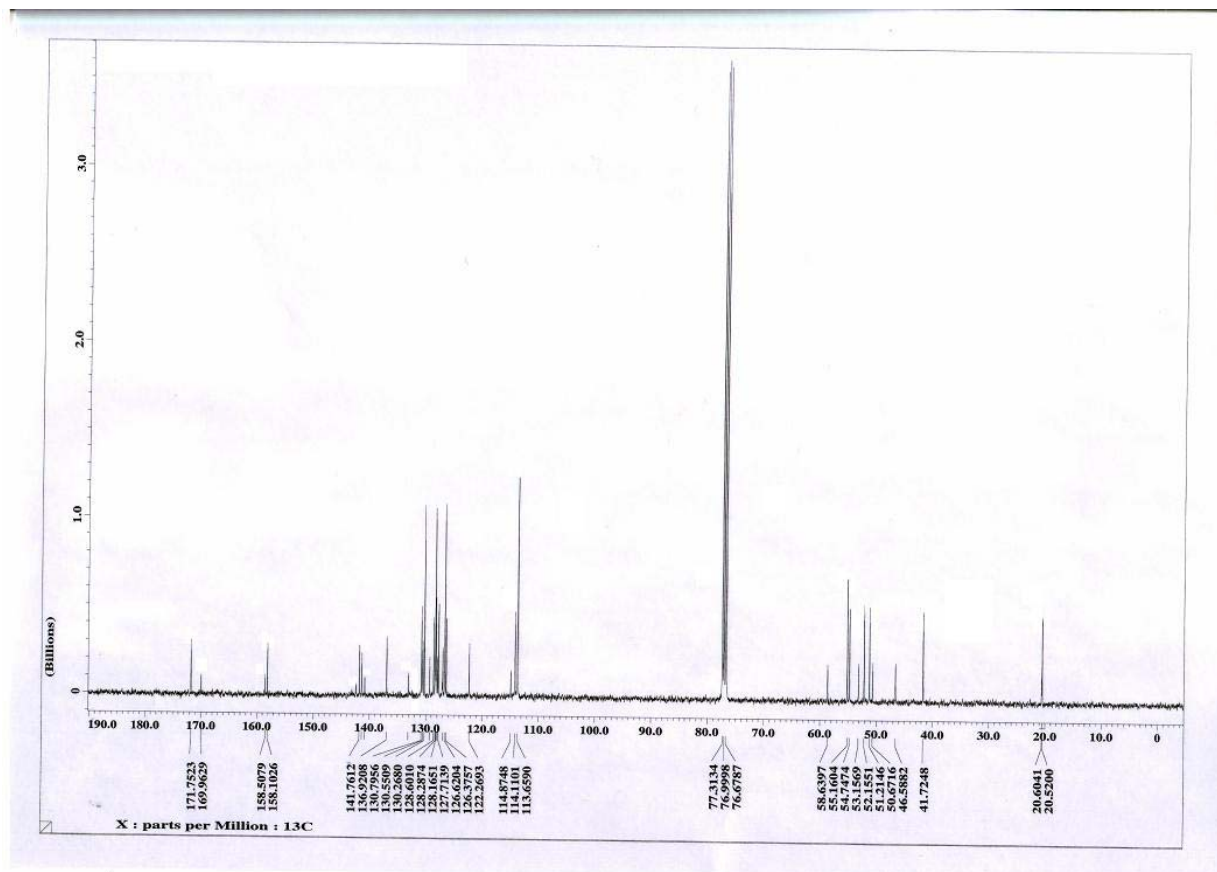
¹H NMR Spectrum of Compound 2c (CDCl₃, 400 MHz)



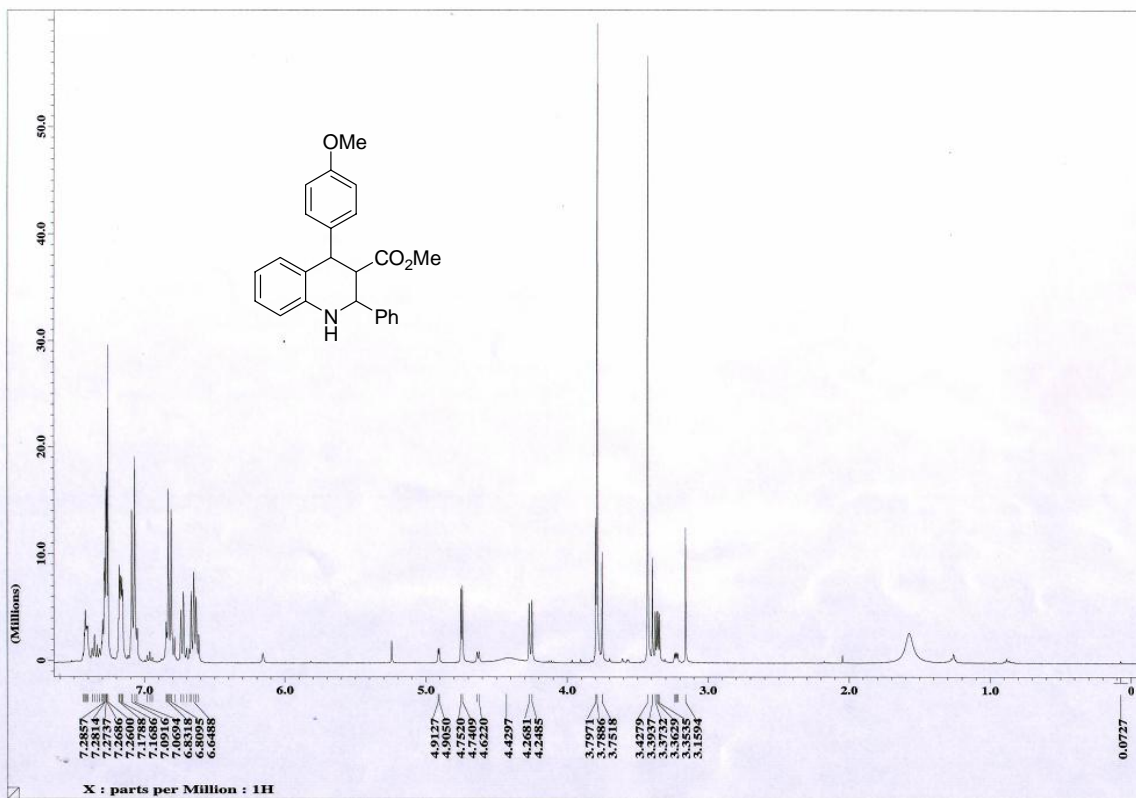
¹³C NMR Spectrum of Compound 2c (CDCl₃, 100 MHz)



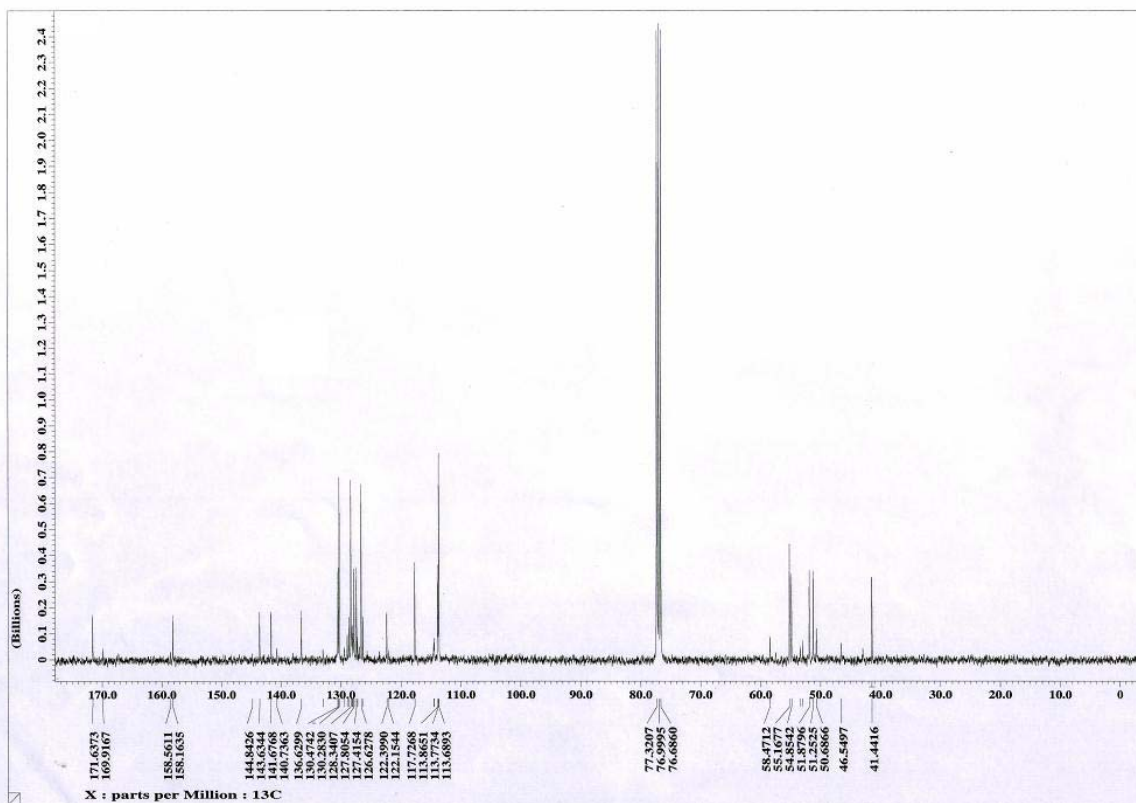
¹H NMR Spectrum of Compound 2d (CDCl₃, 400 MHz)



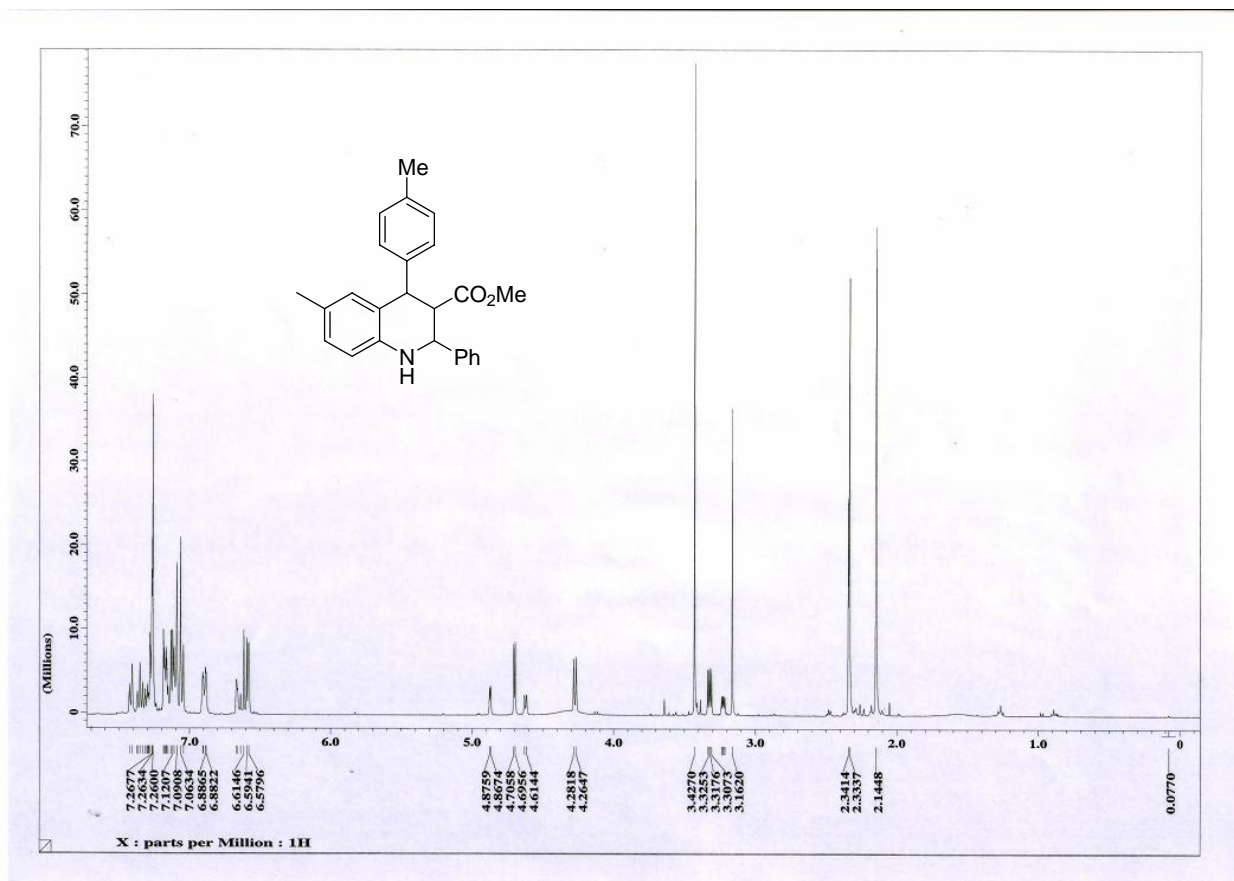
¹³C NMR Spectrum of Compound 2d (CDCl₃, 100 MHz)



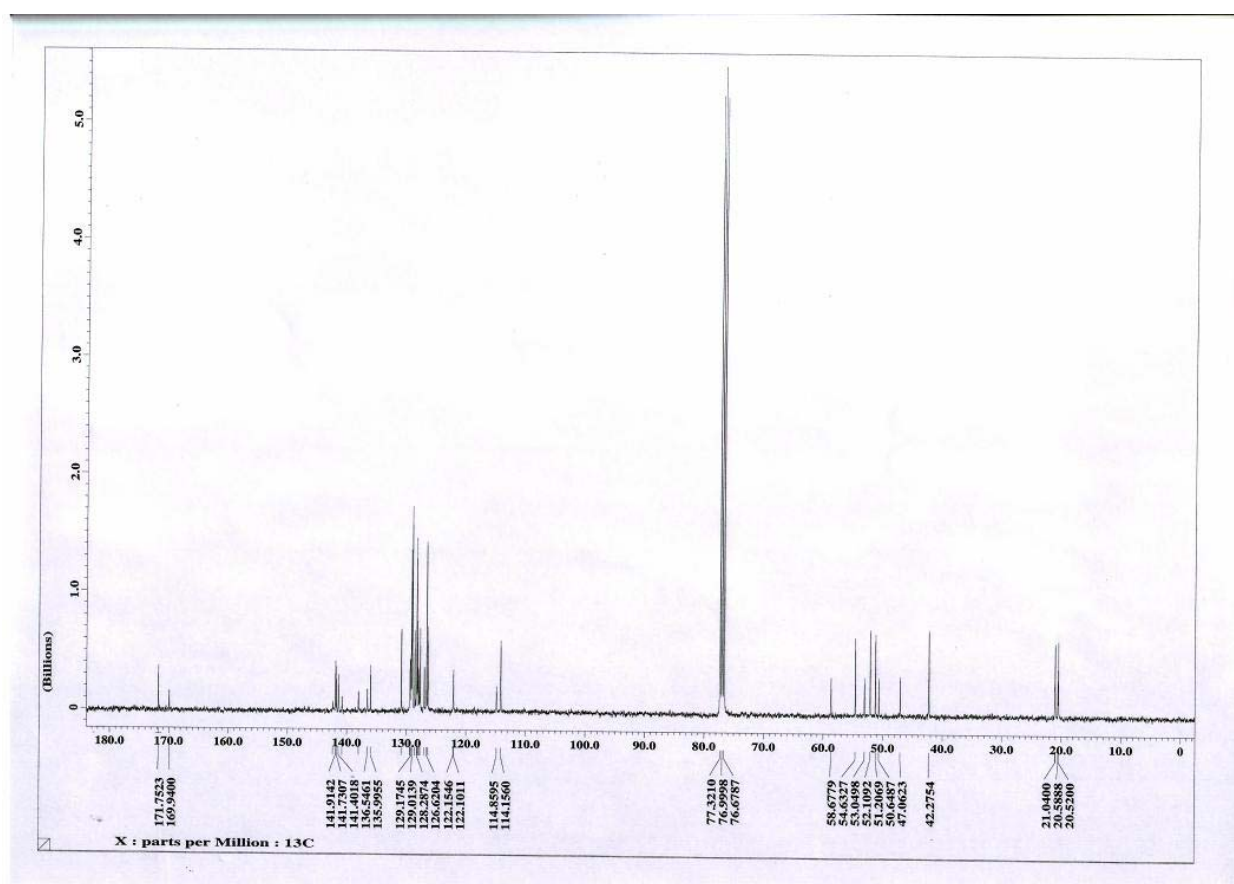
¹H NMR Spectrum of Compound 2e (CDCl₃, 400 MHz)



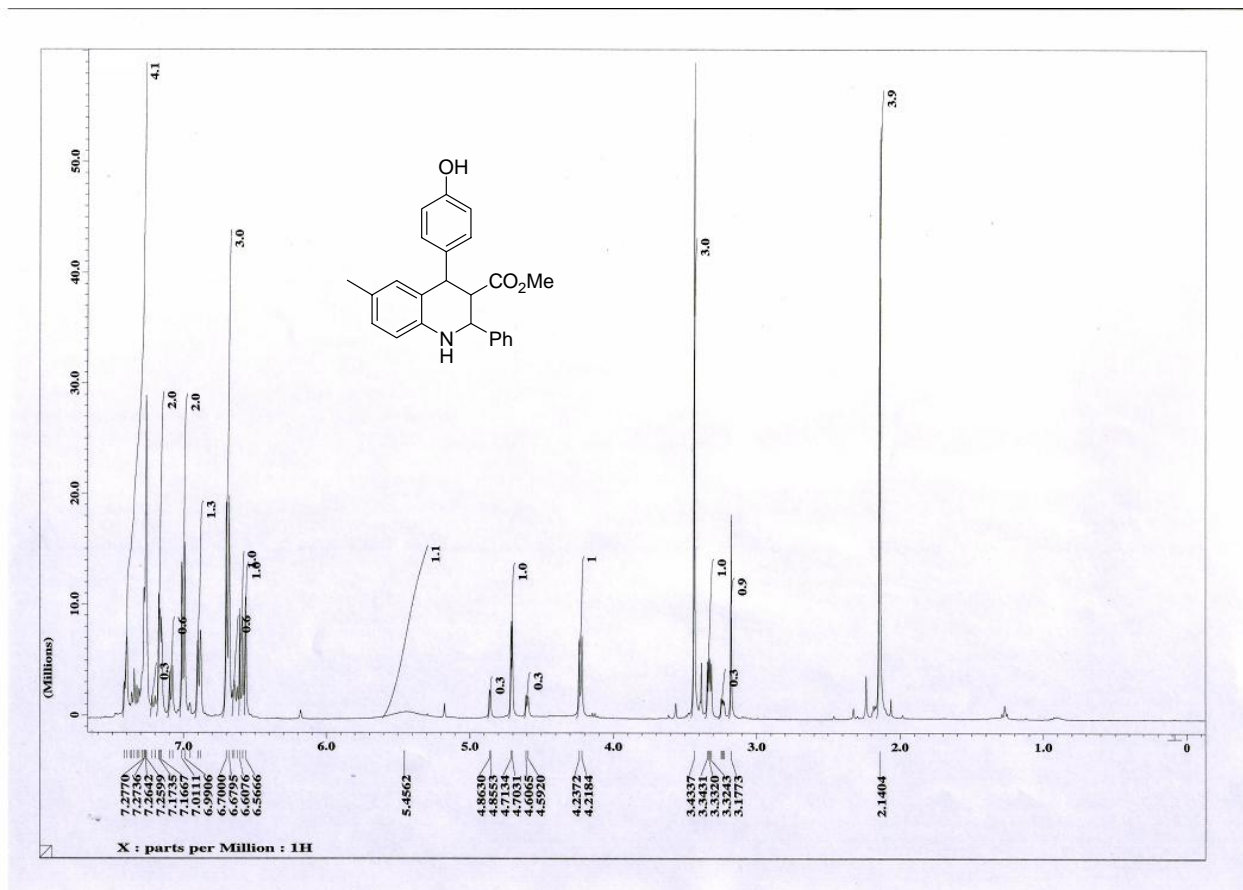
¹³C NMR Spectrum of Compound 2e (CDCl₃, 100 MHz)



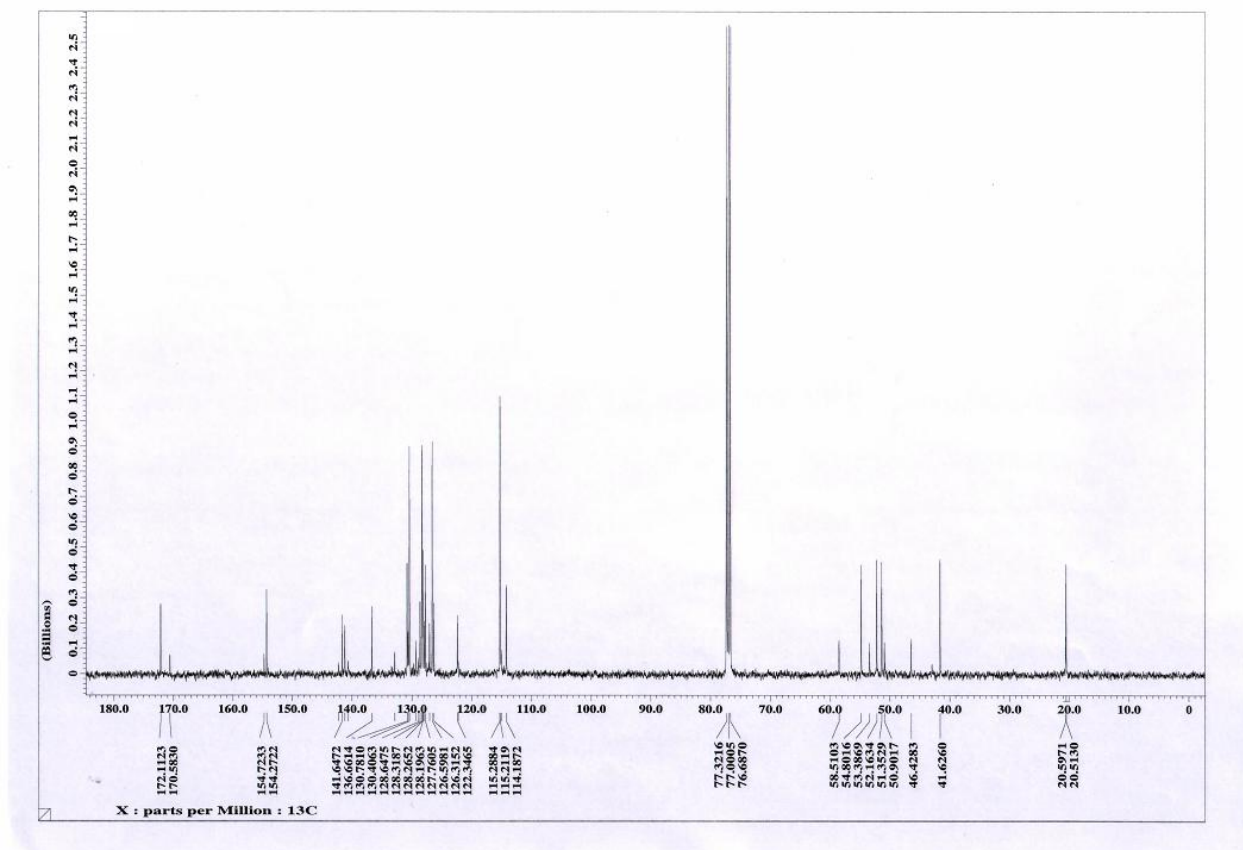
¹H NMR Spectrum of Compound **2f** (CDCl₃, 400 MHz)



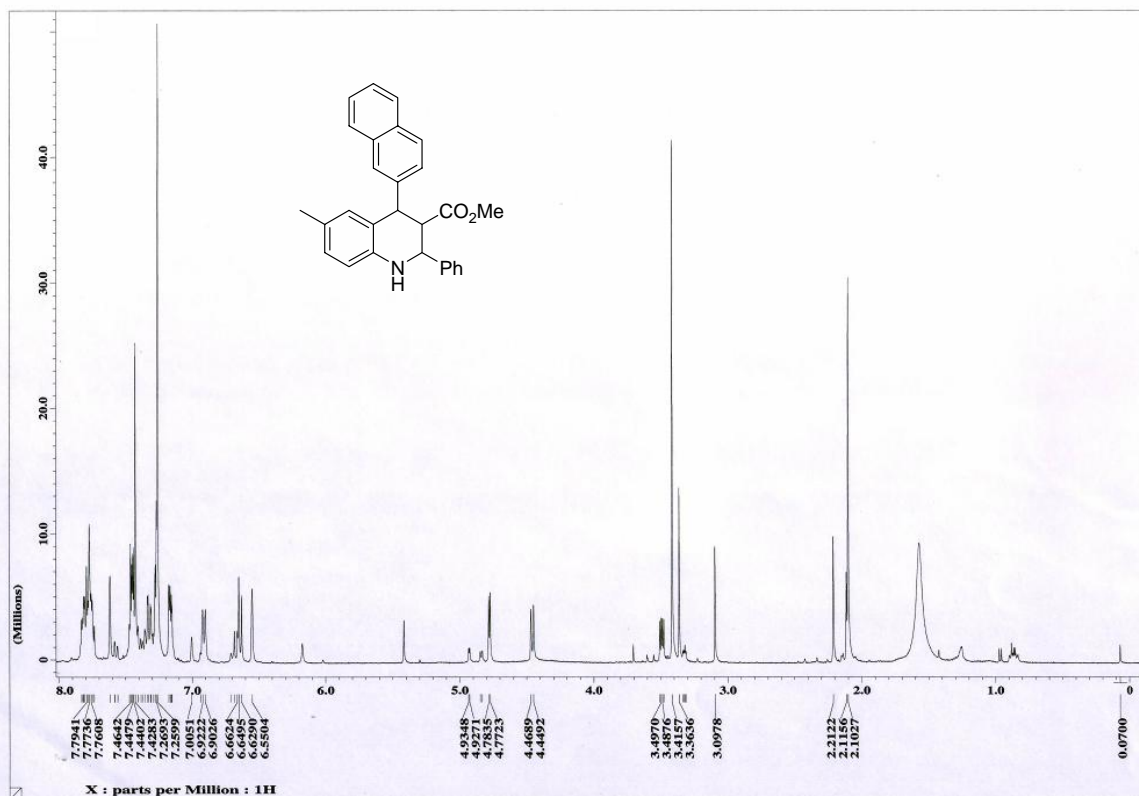
¹³C NMR Spectrum of Compound **2f** (CDCl₃, 100 MHz)



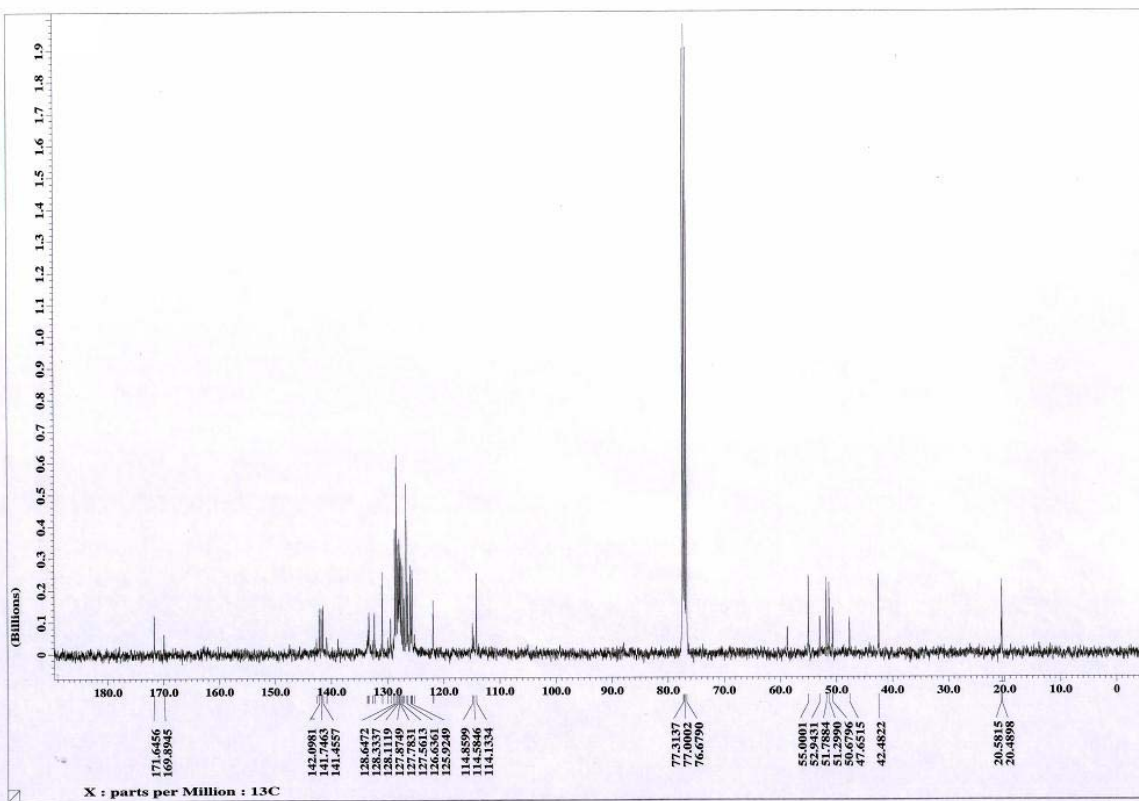
¹H NMR Spectrum of Compound **2g** (CDCl₃, 400 MHz)



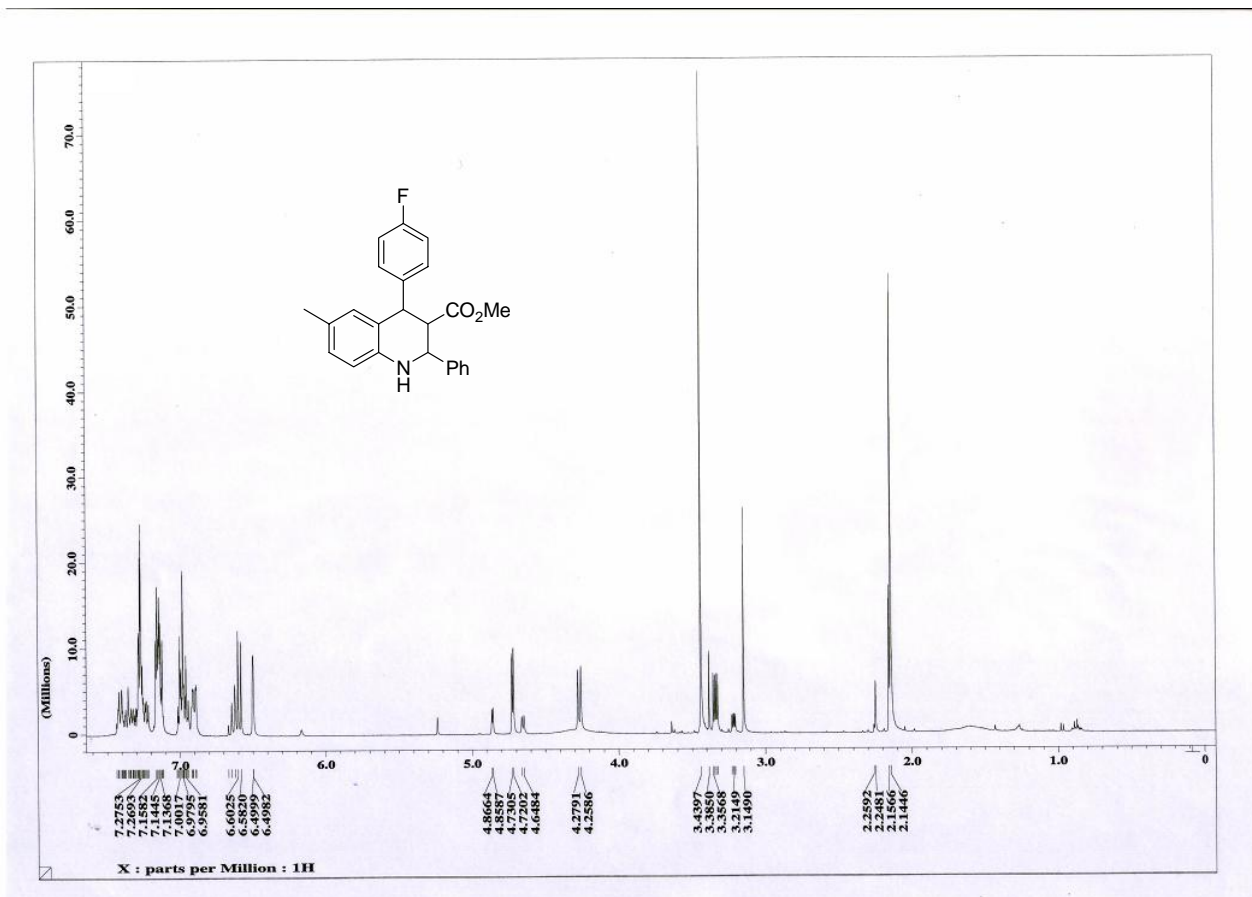
¹³C NMR Spectrum of Compound **2g** (CDCl₃, 100 MHz)



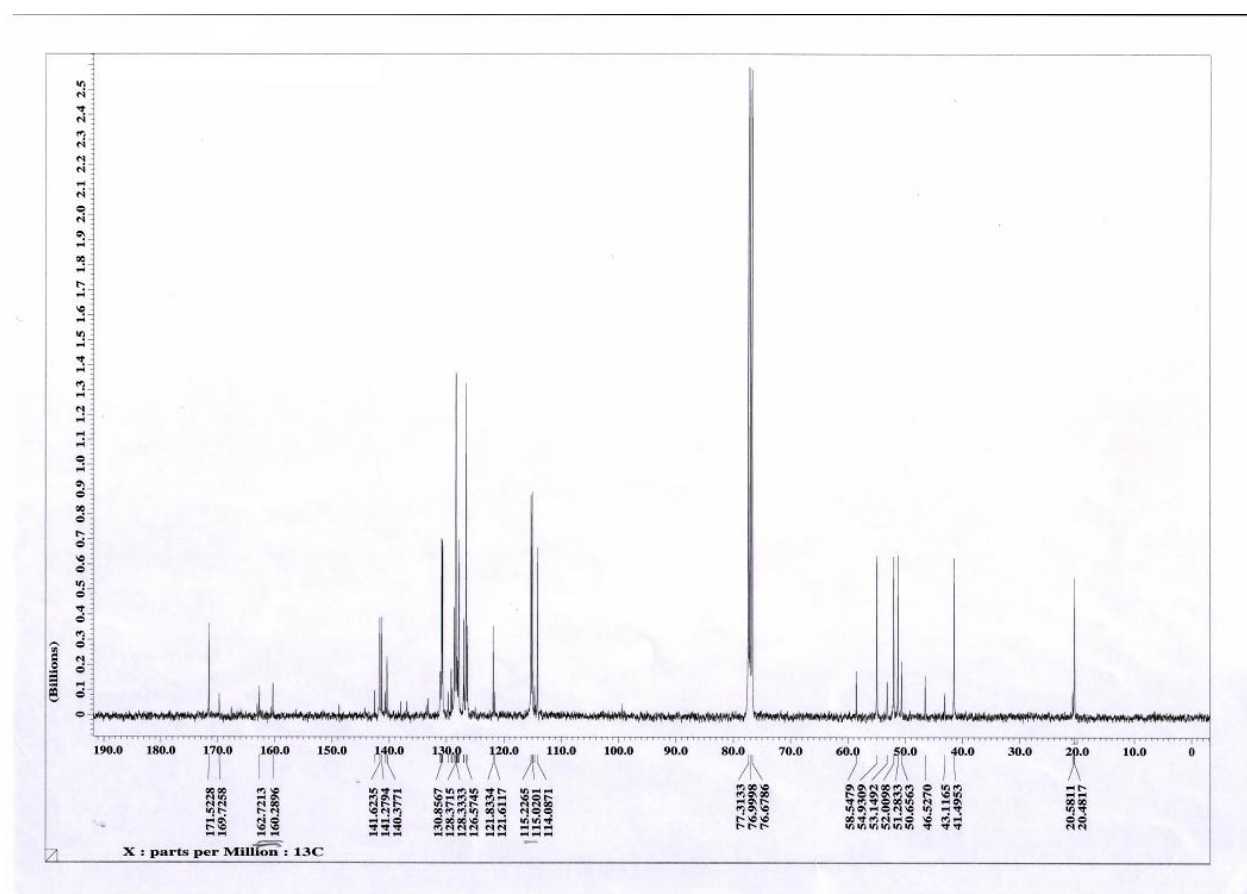
¹H NMR Spectrum of Compound **2h** (CDCl₃, 400 MHz)



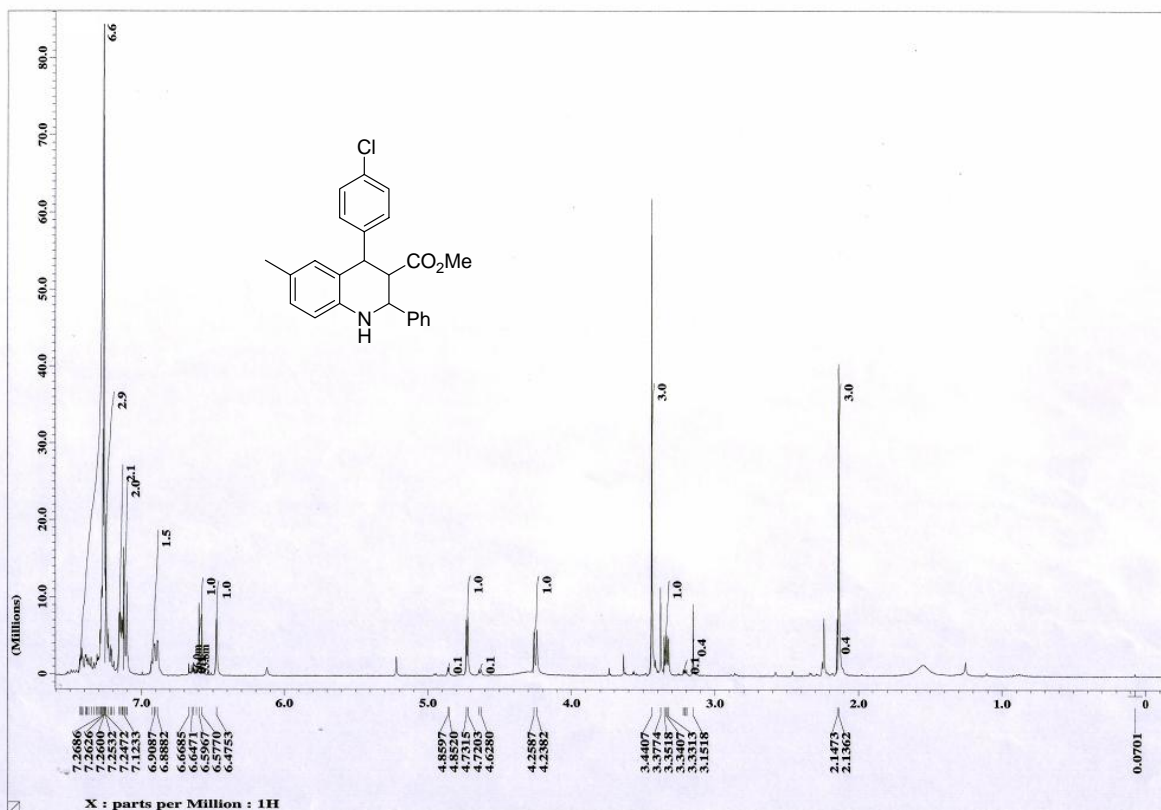
¹³C NMR Spectrum of Compound **2h** (CDCl₃, 100 MHz)



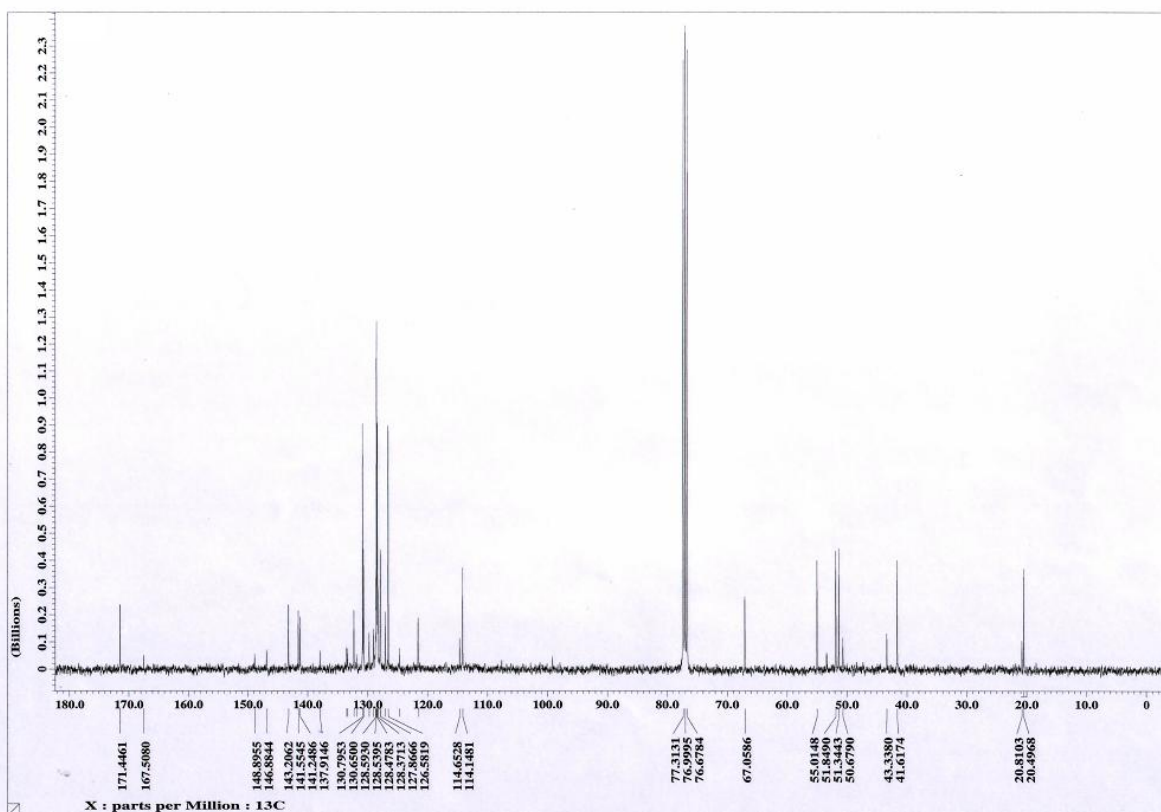
¹H NMR Spectrum of Compound 2i (CDCl₃, 400 MHz)



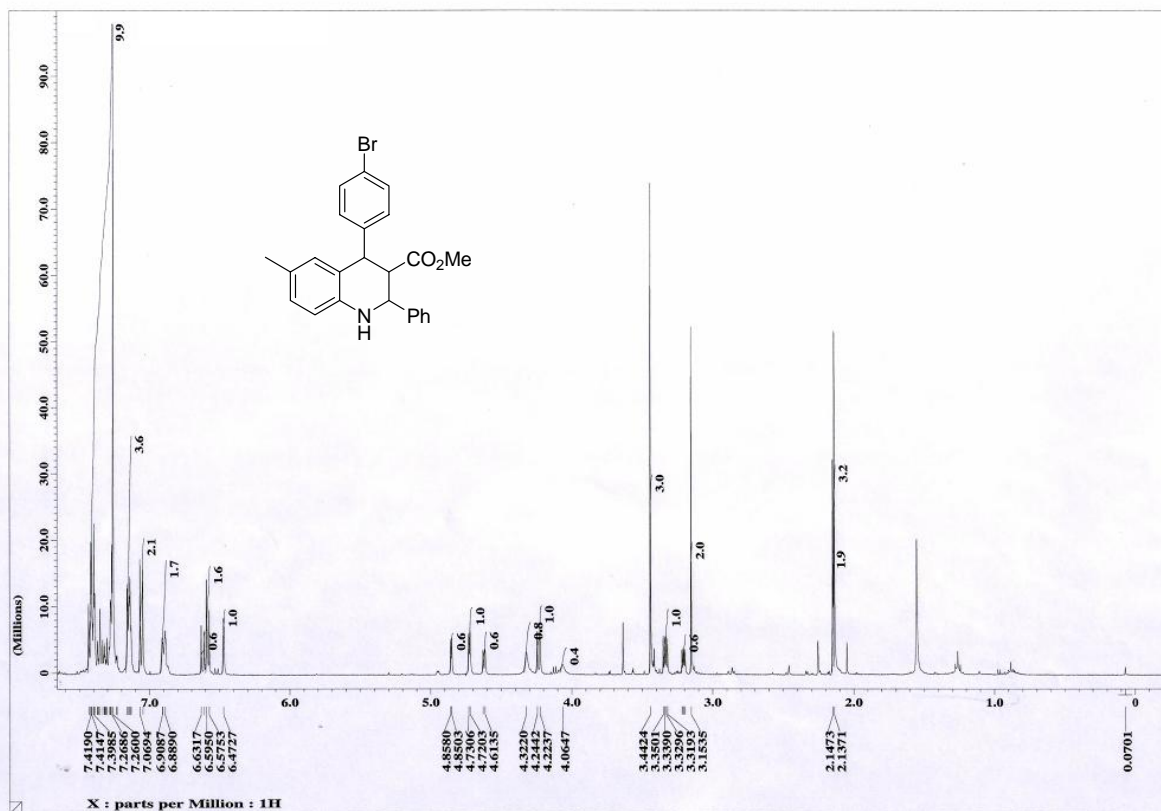
¹³C NMR Spectrum of Compound 2i (CDCl₃, 100 MHz)



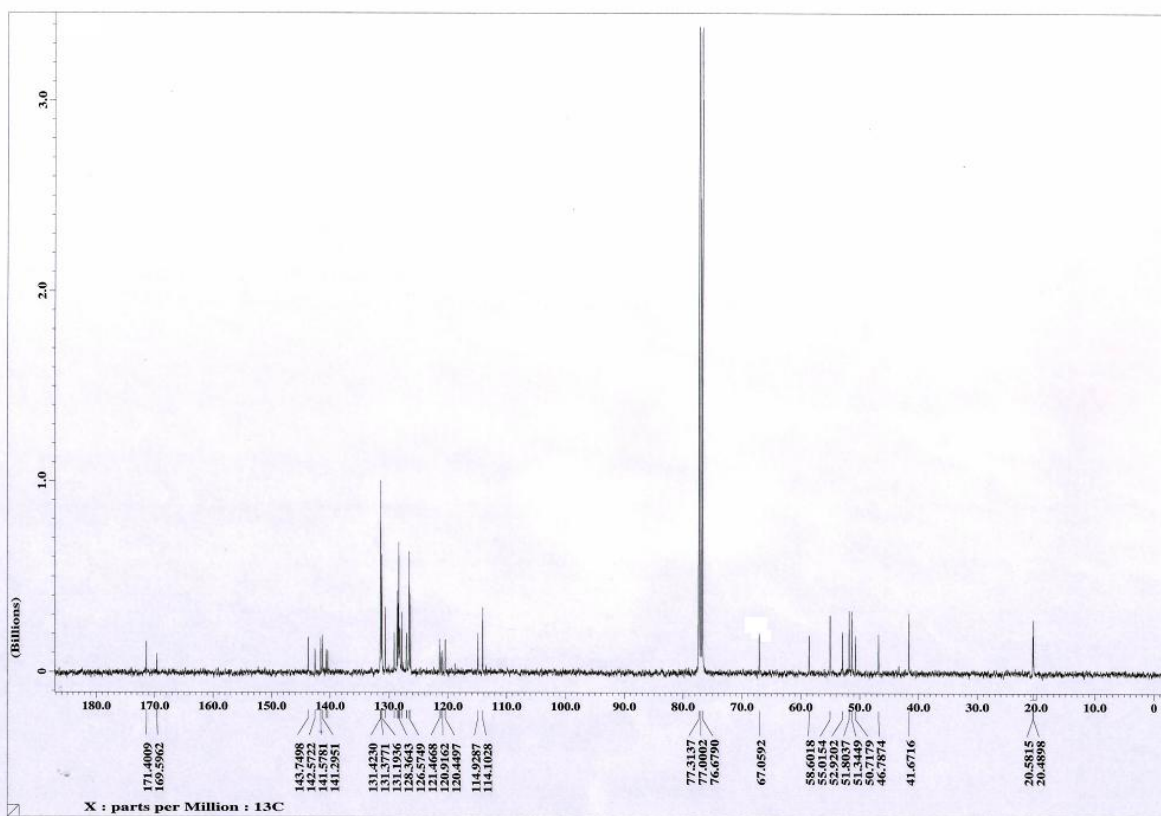
¹H NMR Spectrum of Compound **2j** (CDCl₃, 400 MHz)



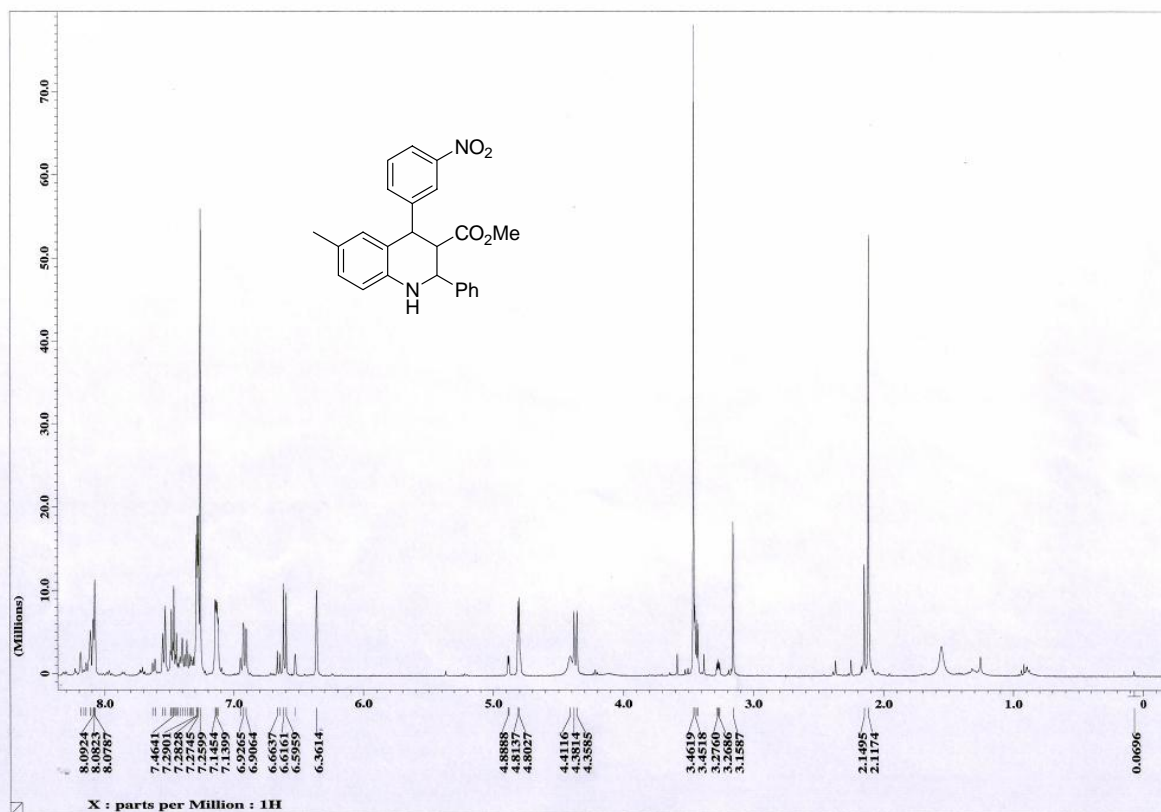
¹³C NMR Spectrum of Compound **2j** (CDCl₃, 100 MHz)



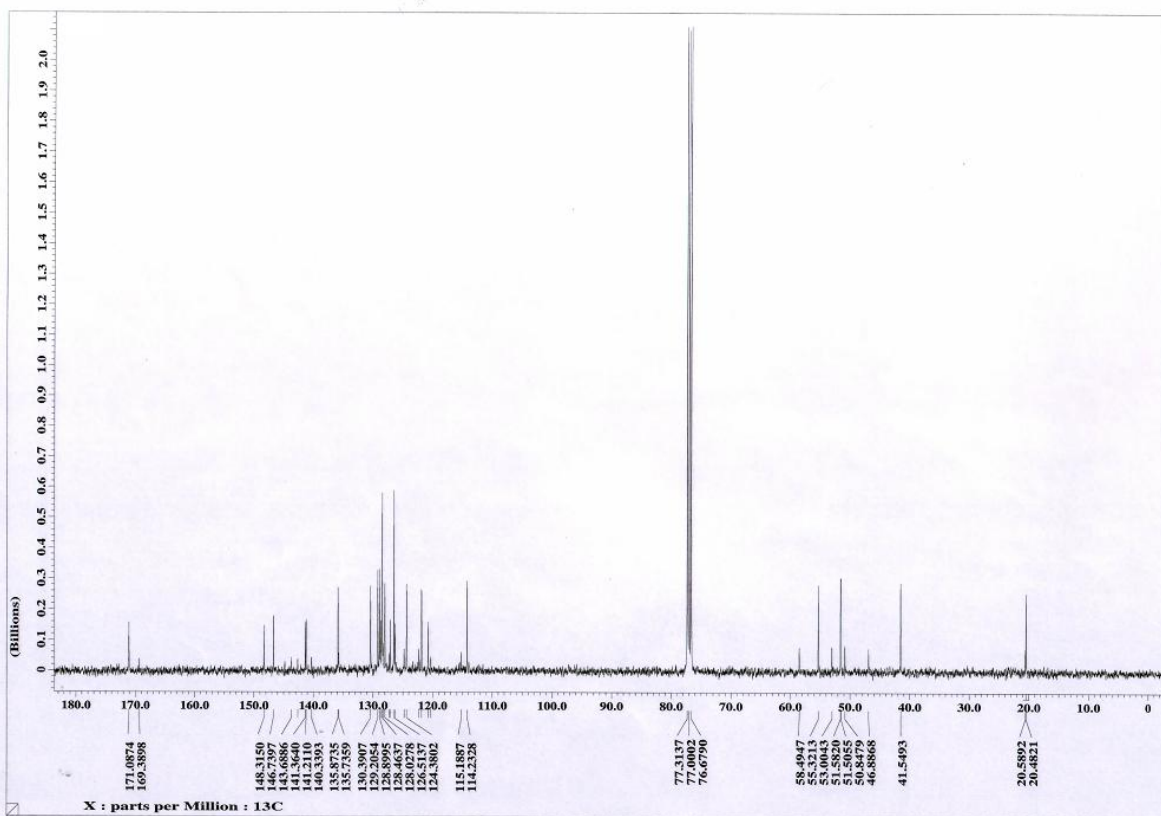
^1H NMR Spectrum of Compound **2k** (CDCl_3 , 400 MHz)



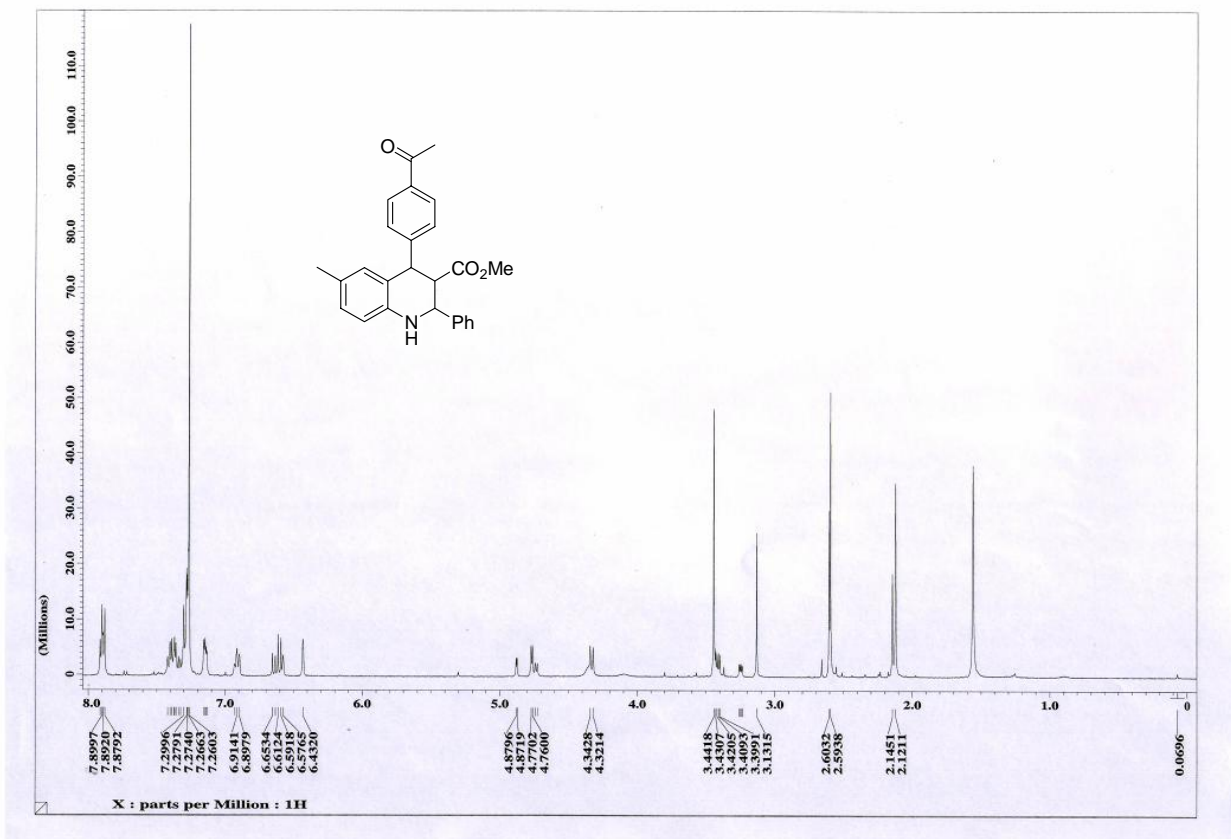
^{13}C NMR Spectrum of Compound **2k** (CDCl_3 , 100 MHz)



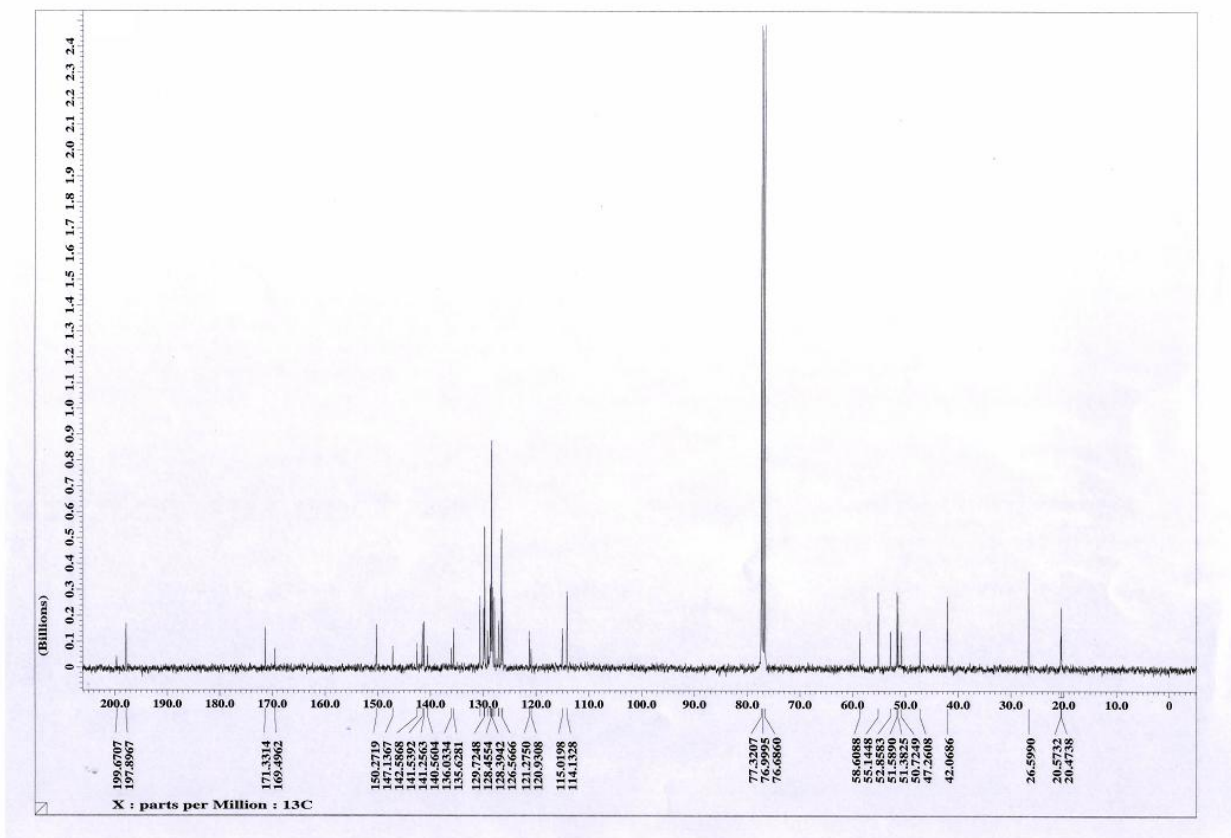
¹H NMR Spectrum of Compound **2I** (CDCl₃, 400 MHz)



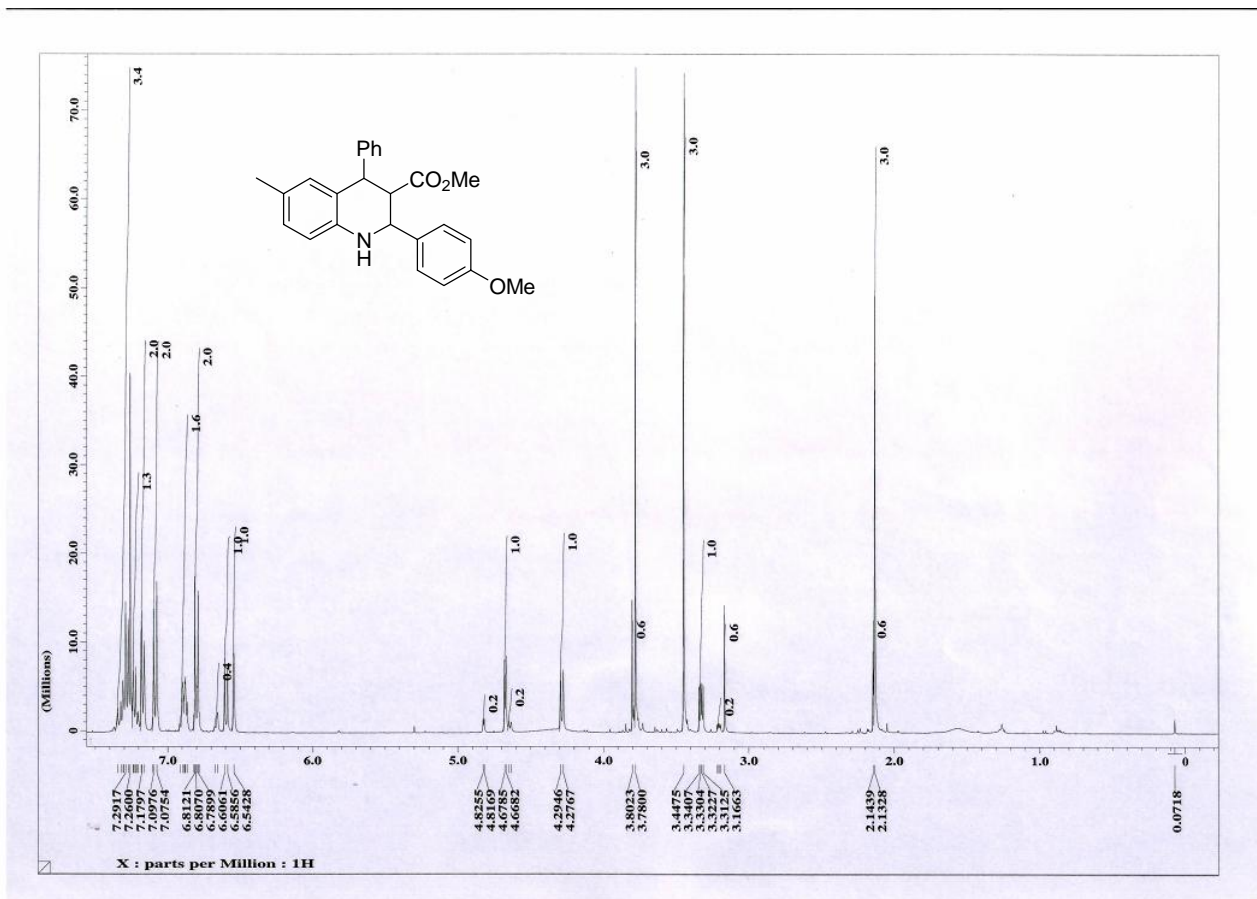
¹³C NMR Spectrum of Compound **2I** (CDCl₃, 100 MHz)



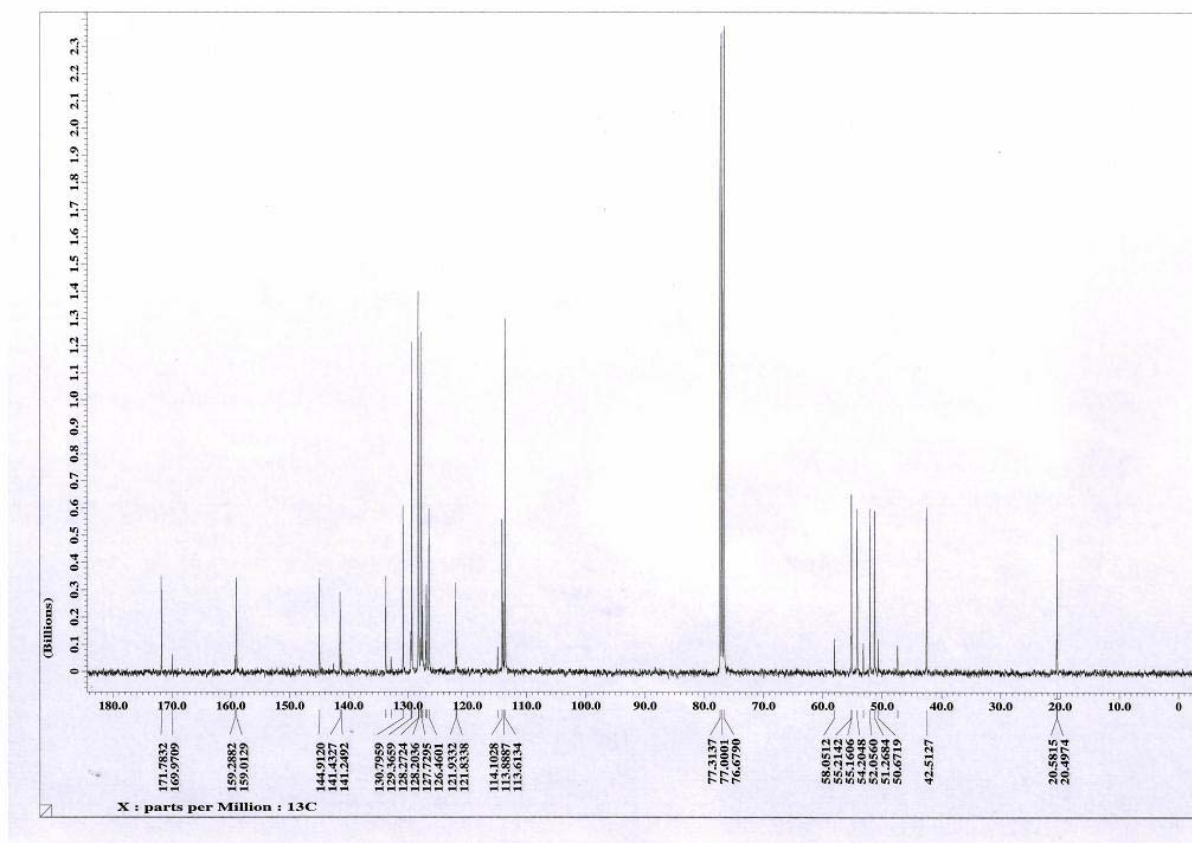
¹H NMR Spectrum of Compound **2m** (CDCl₃, 400 MHz)



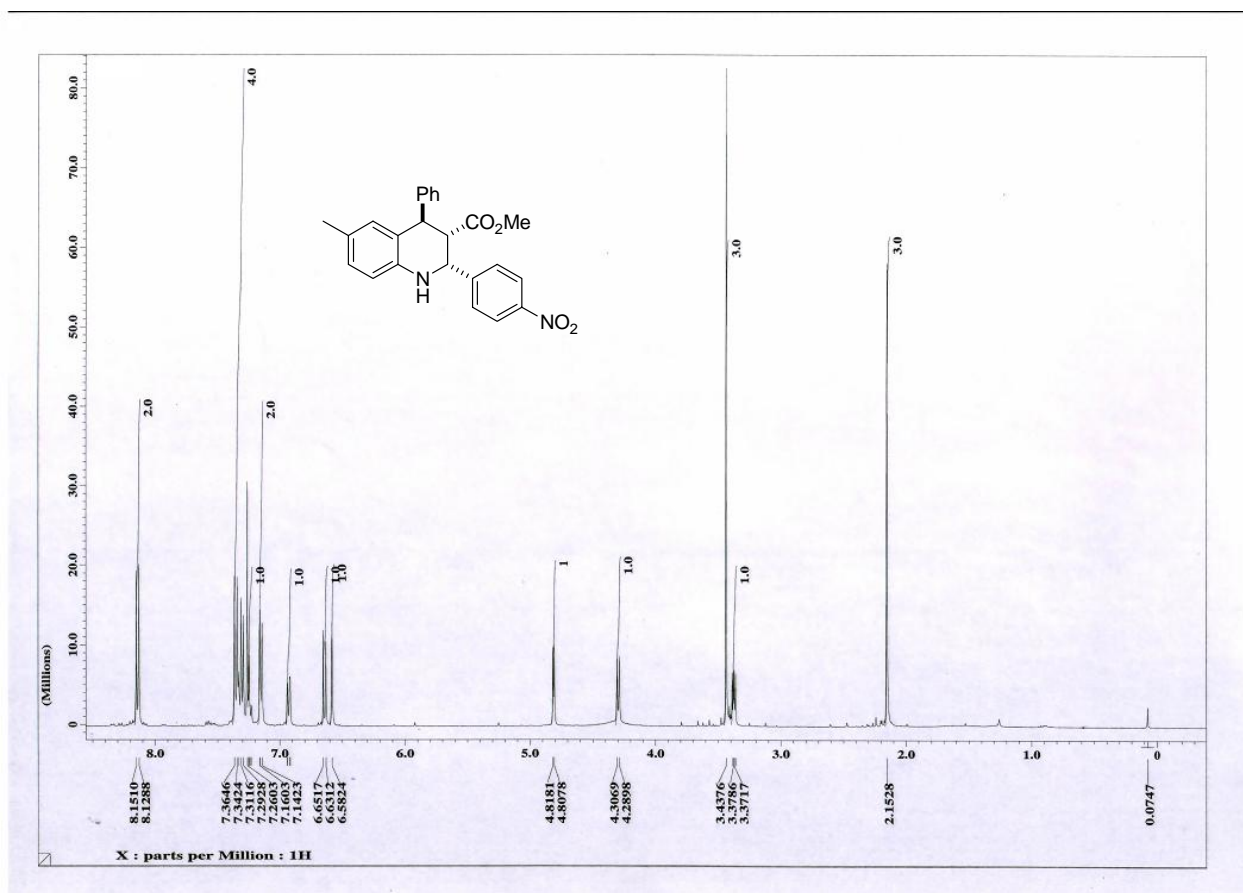
¹³C NMR Spectrum of Compound **2m** (CDCl₃, 100 MHz)



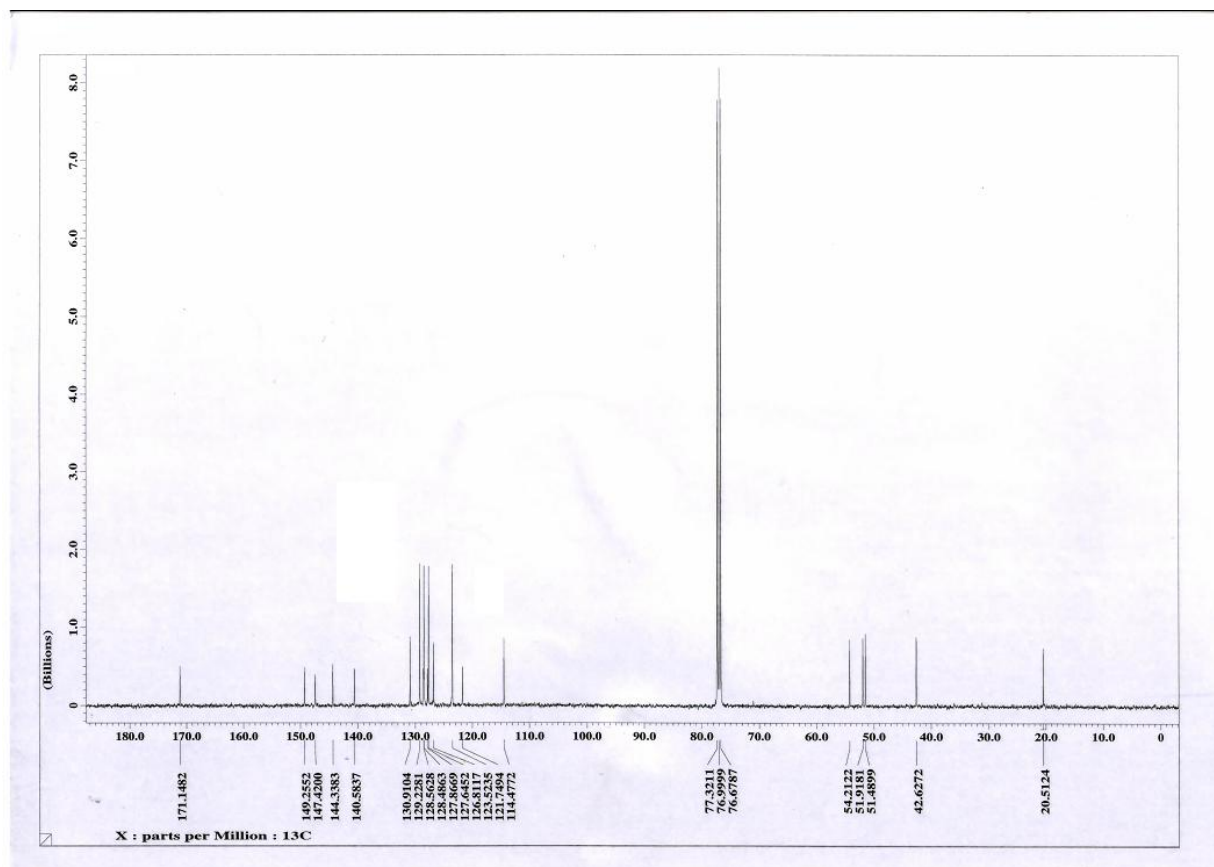
¹H NMR Spectrum of Compound **2n** (CDCl₃, 400 MHz)



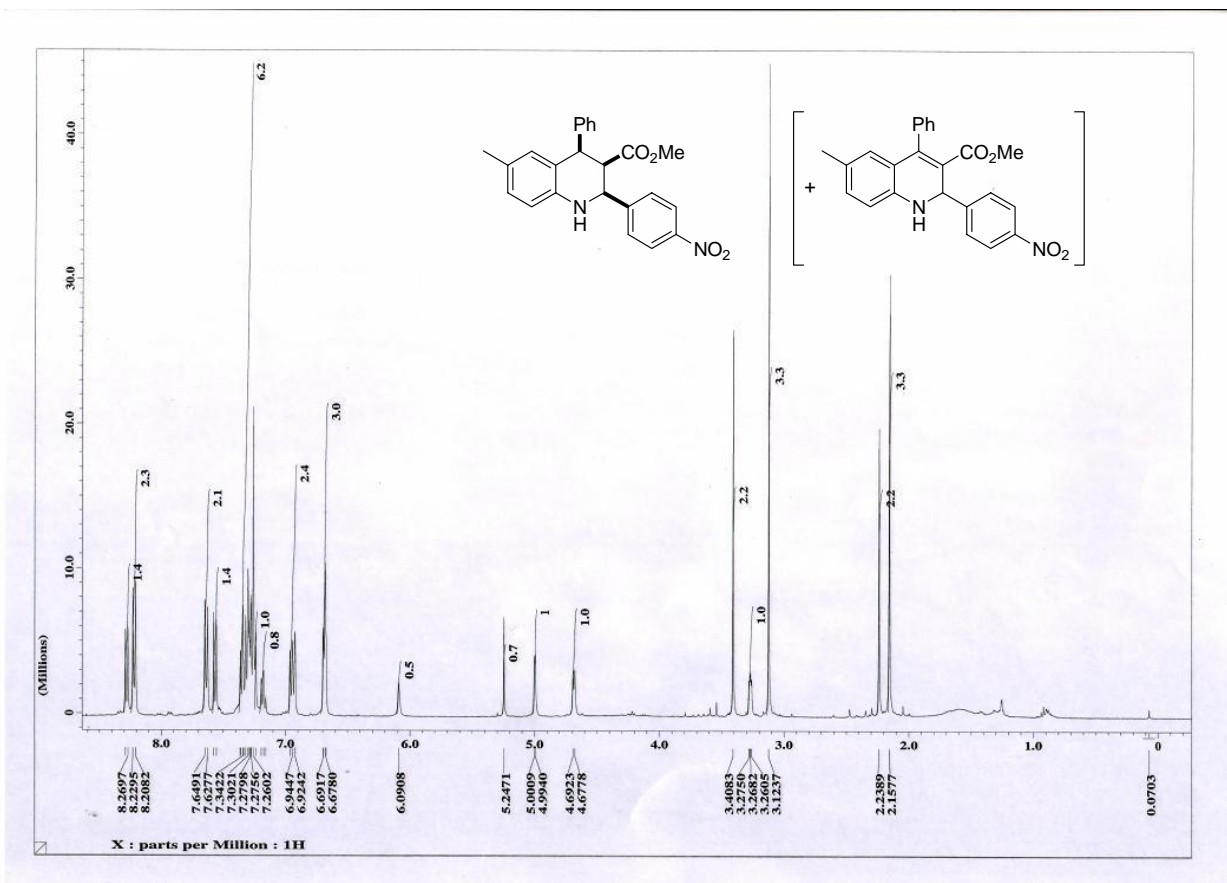
¹³C NMR Spectrum of Compound **2n** (CDCl₃, 100 MHz)



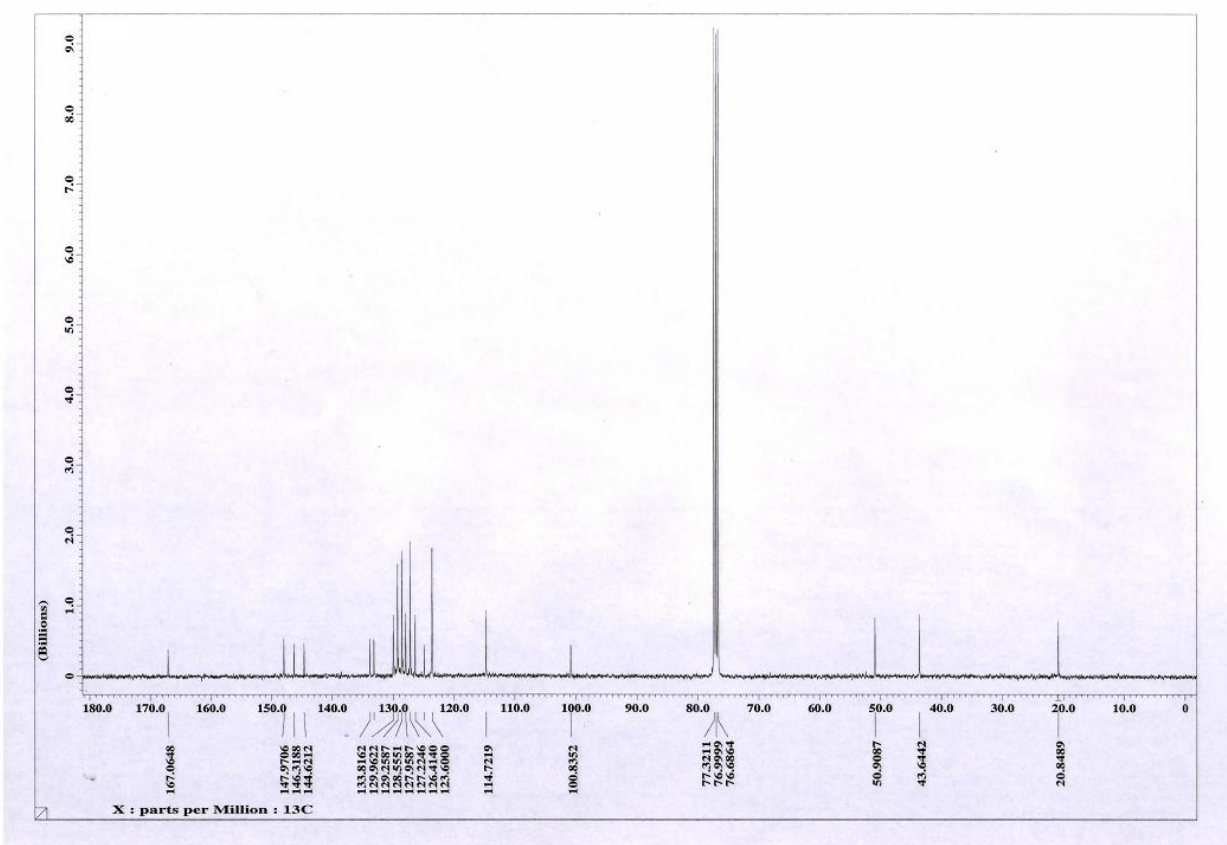
¹H NMR Spectrum of Compound **2o** (CDCl₃, 400 MHz)



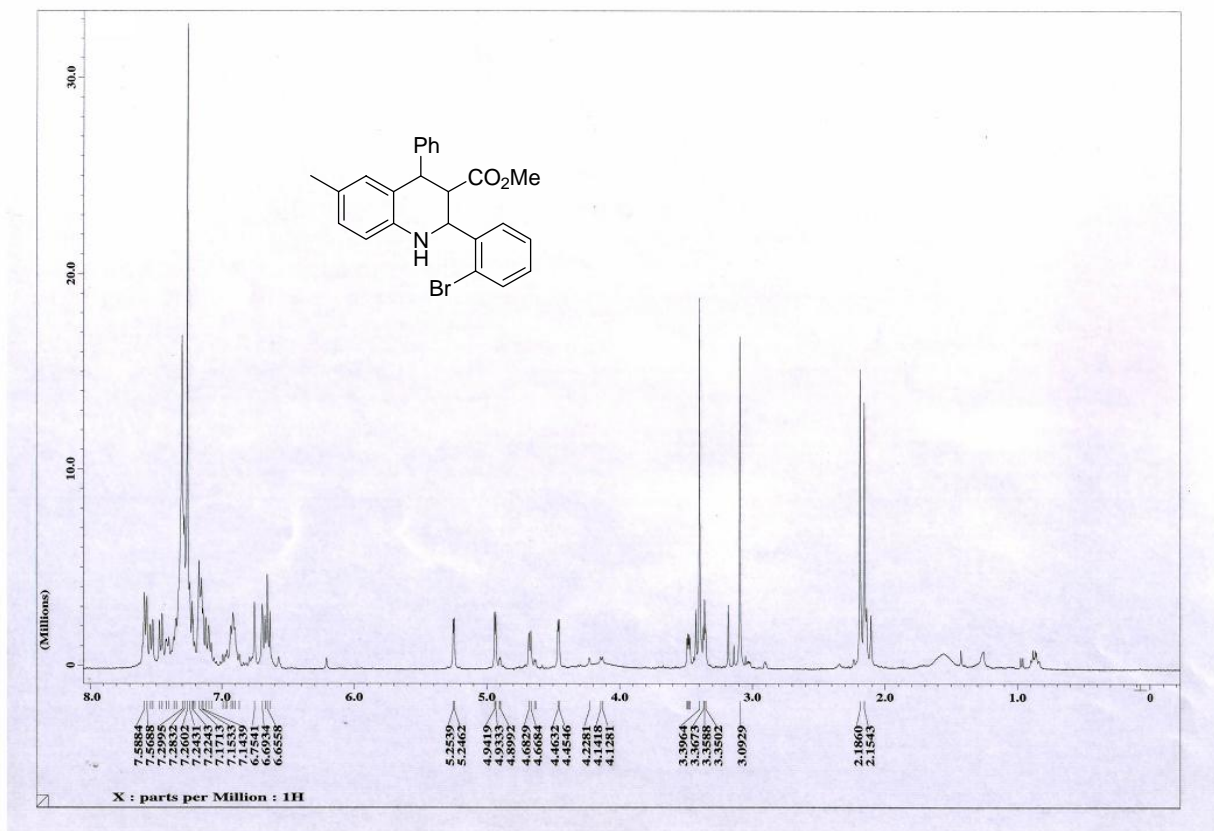
¹³C NMR Spectrum of Compound **2o** (CDCl₃, 100 MHz)



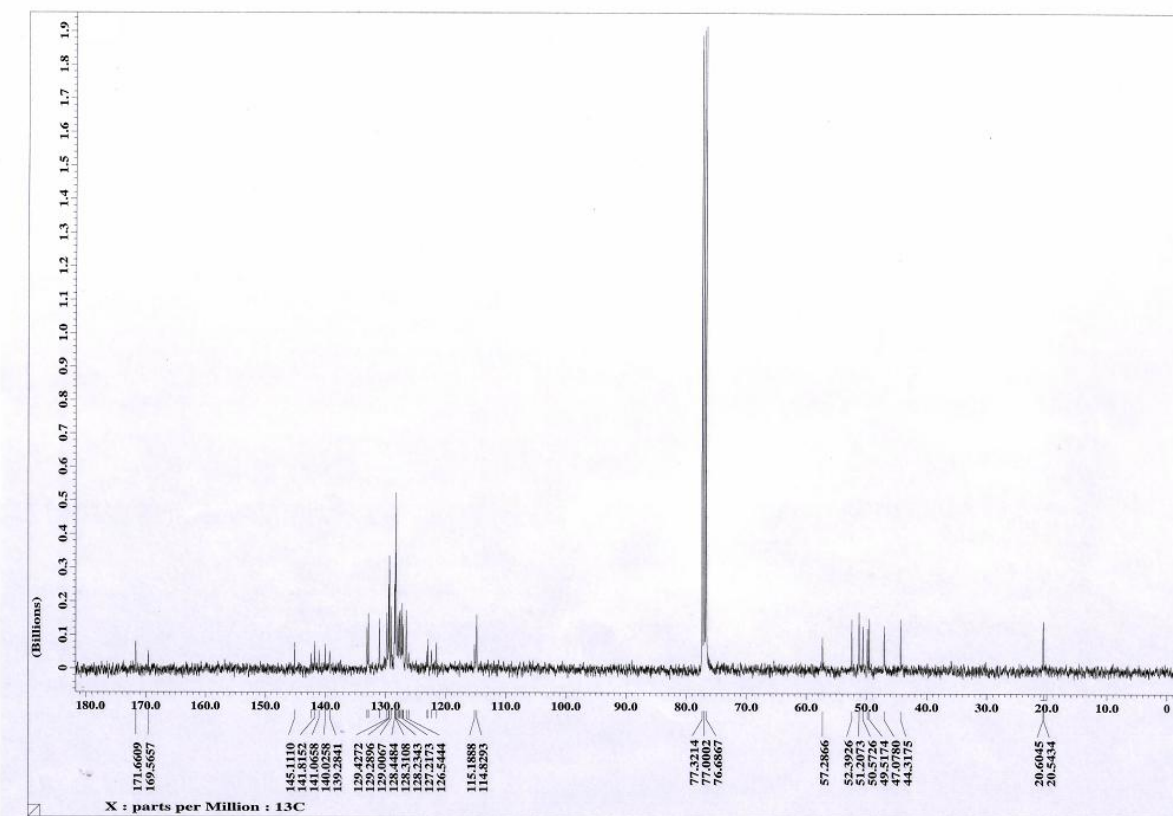
¹H NMR Spectrum of Compound 2'o (CDCl₃, 400 MHz)



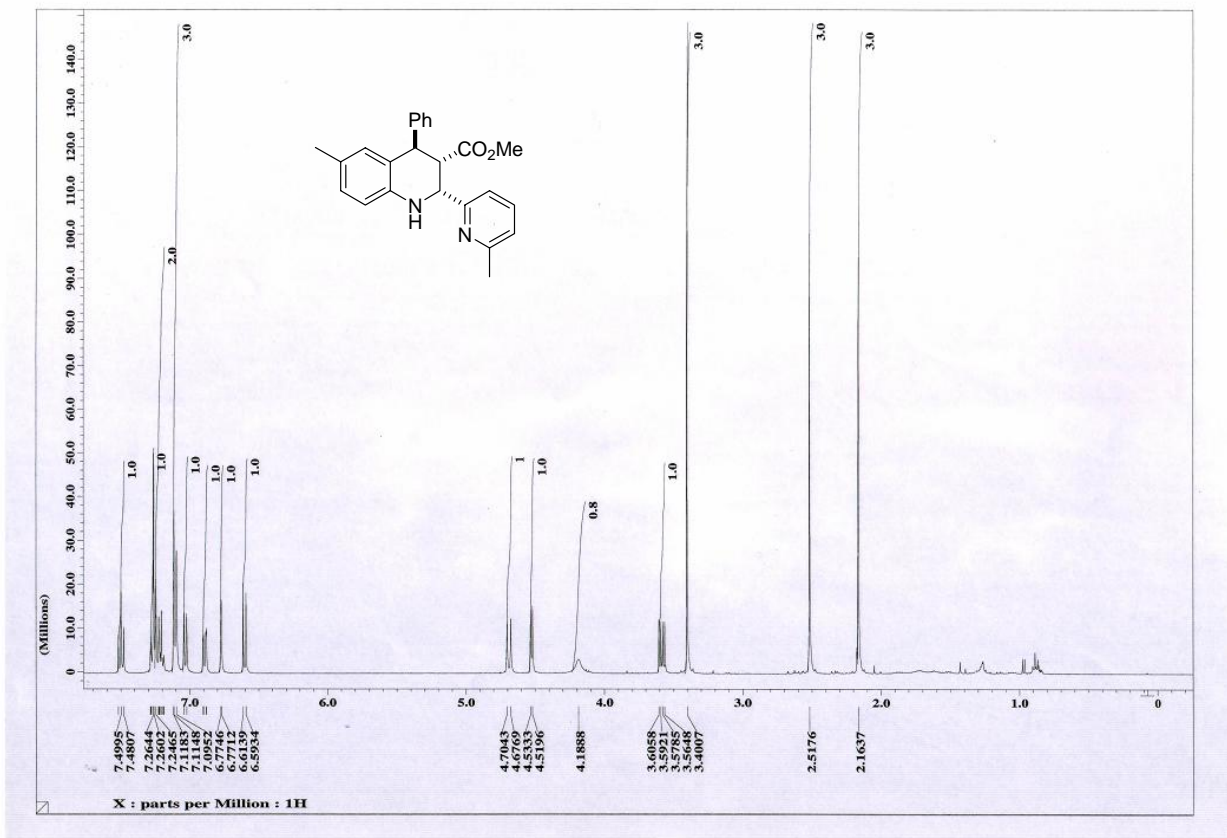
¹³C NMR Spectrum of Compound 2'o (CDCl₃, 100 MHz)



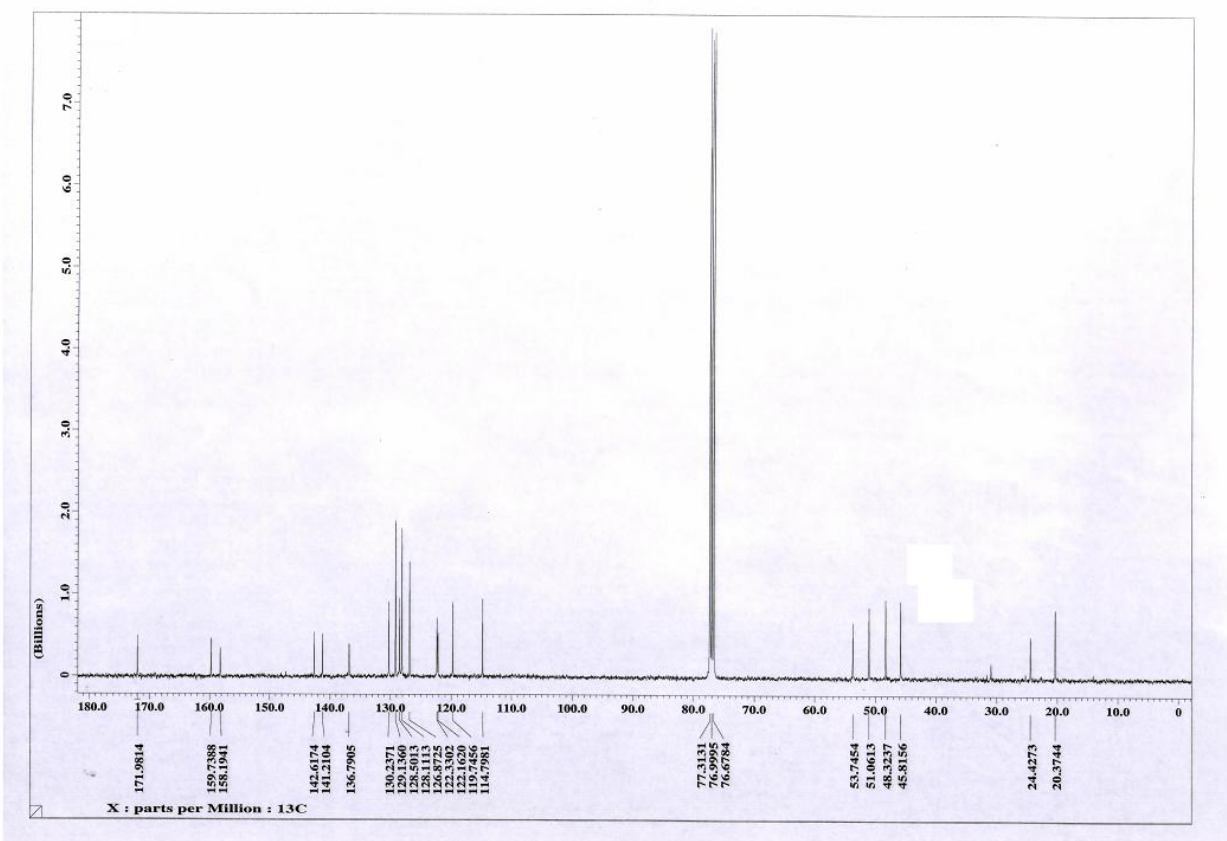
¹H NMR Spectrum of Compound **2p** (CDCl₃, 400 MHz)



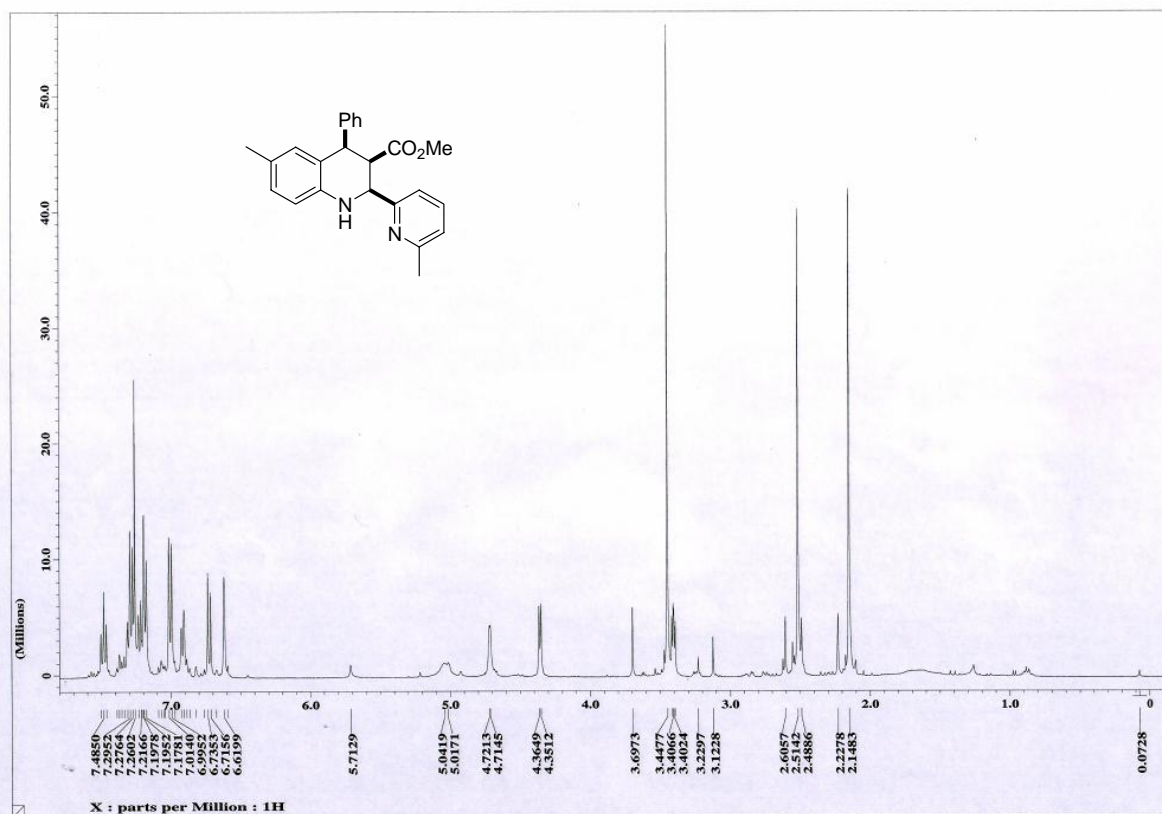
¹³C NMR Spectrum of Compound **2p** (CDCl₃, 100 MHz)



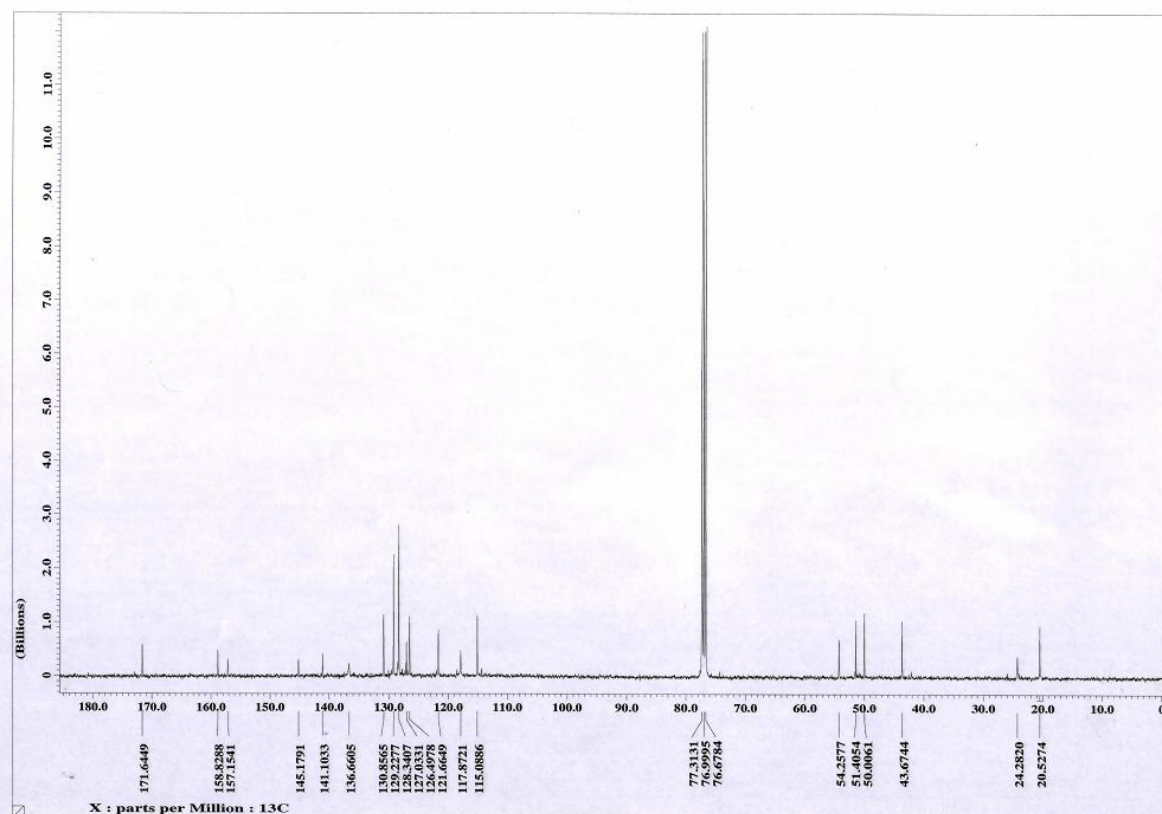
¹H NMR Spectrum of Compound 2q (CDCl₃, 400 MHz)



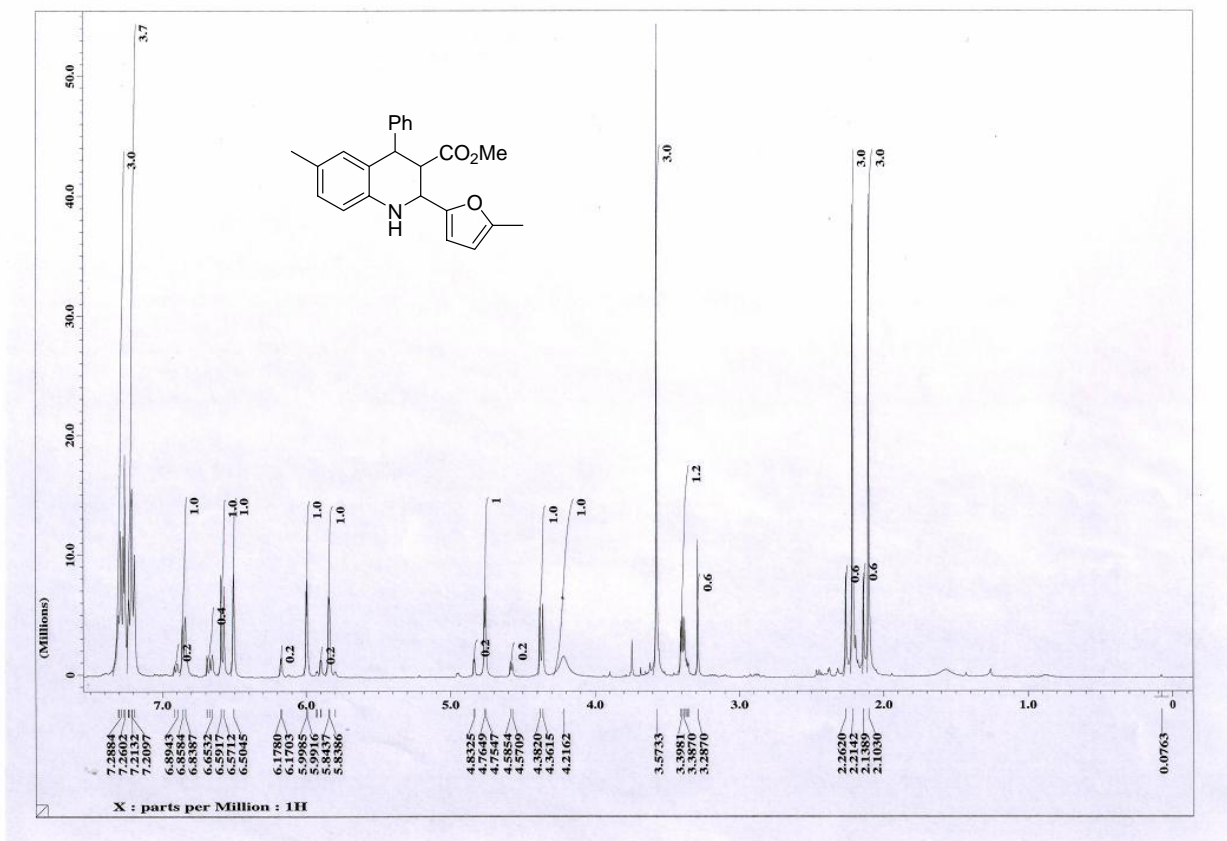
¹³C NMR Spectrum of Compound 2q (CDCl₃, 100 MHz)



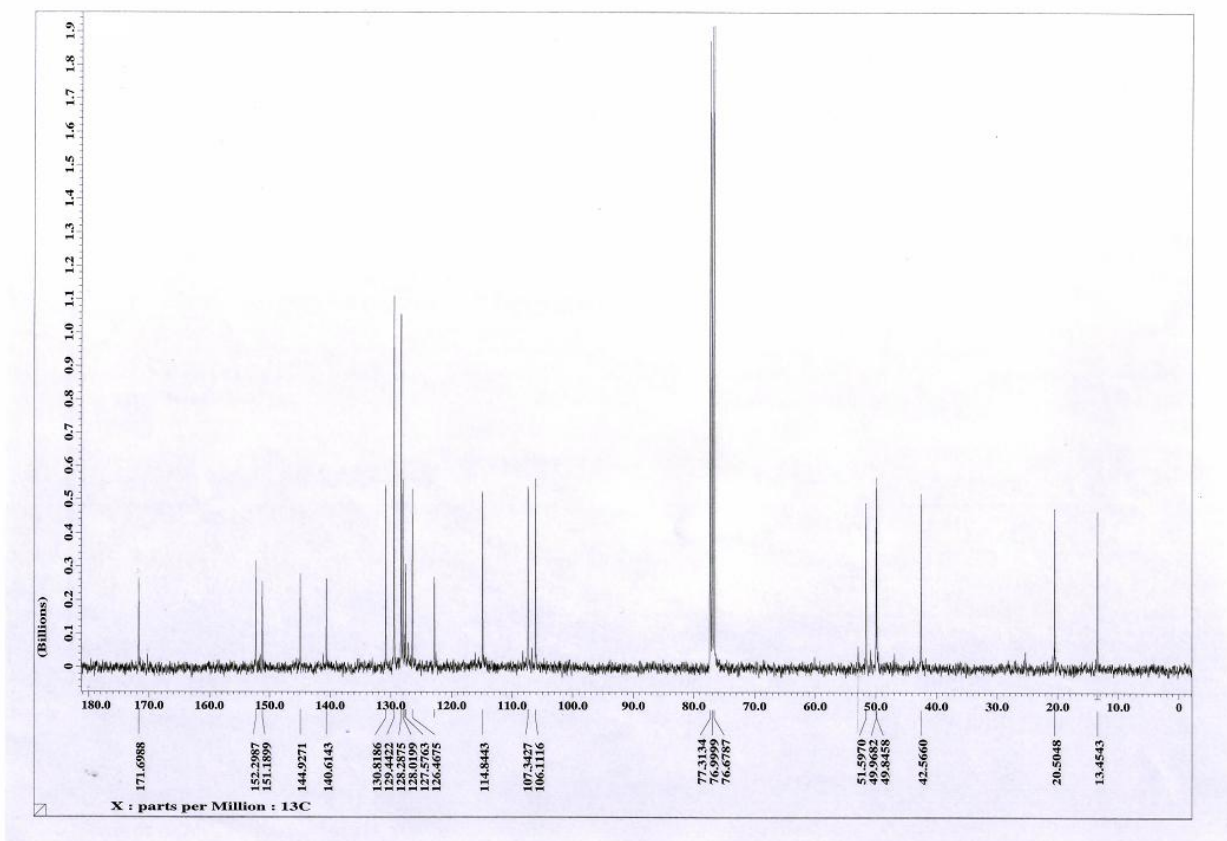
¹H NMR Spectrum of Compound 2'q (CDCl₃, 400 MHz)



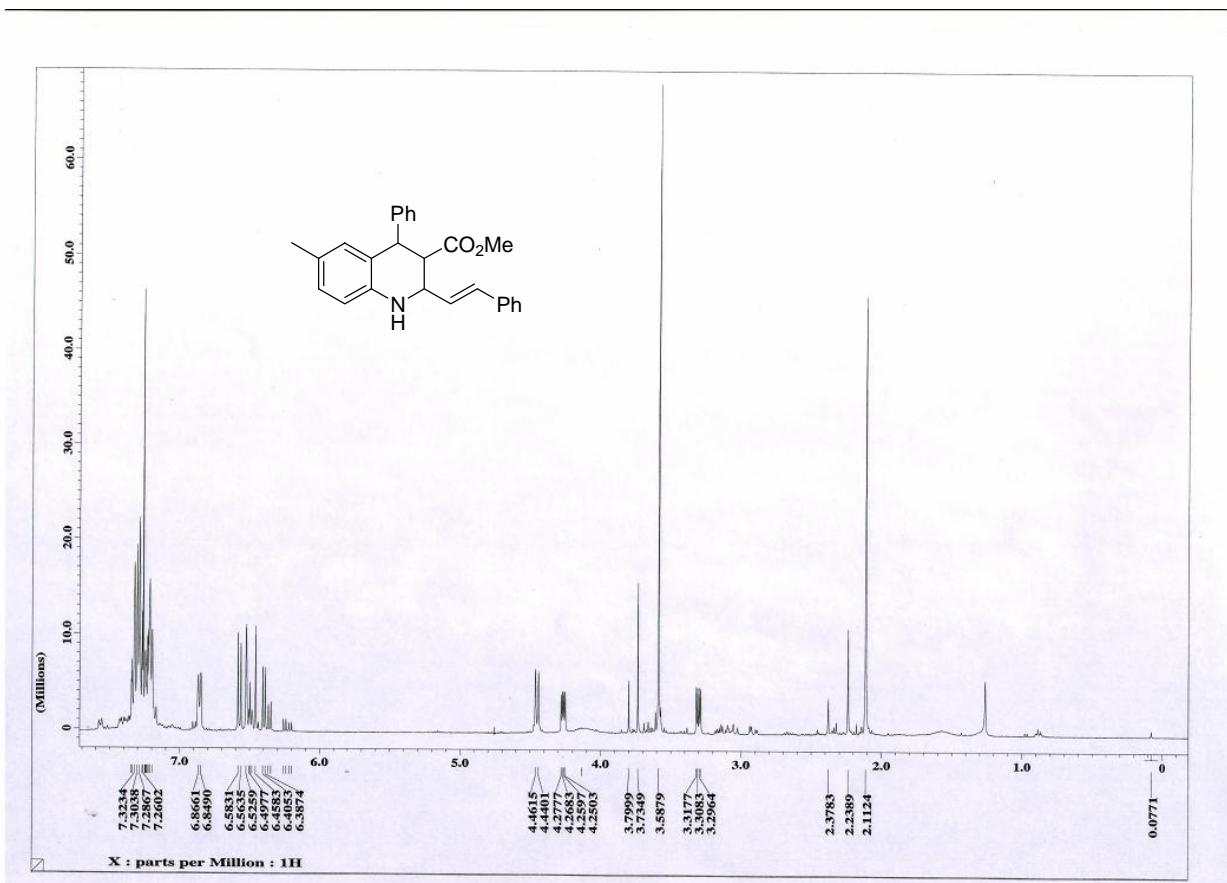
¹³C NMR Spectrum of Compound 2'q (CDCl₃, 100 MHz)



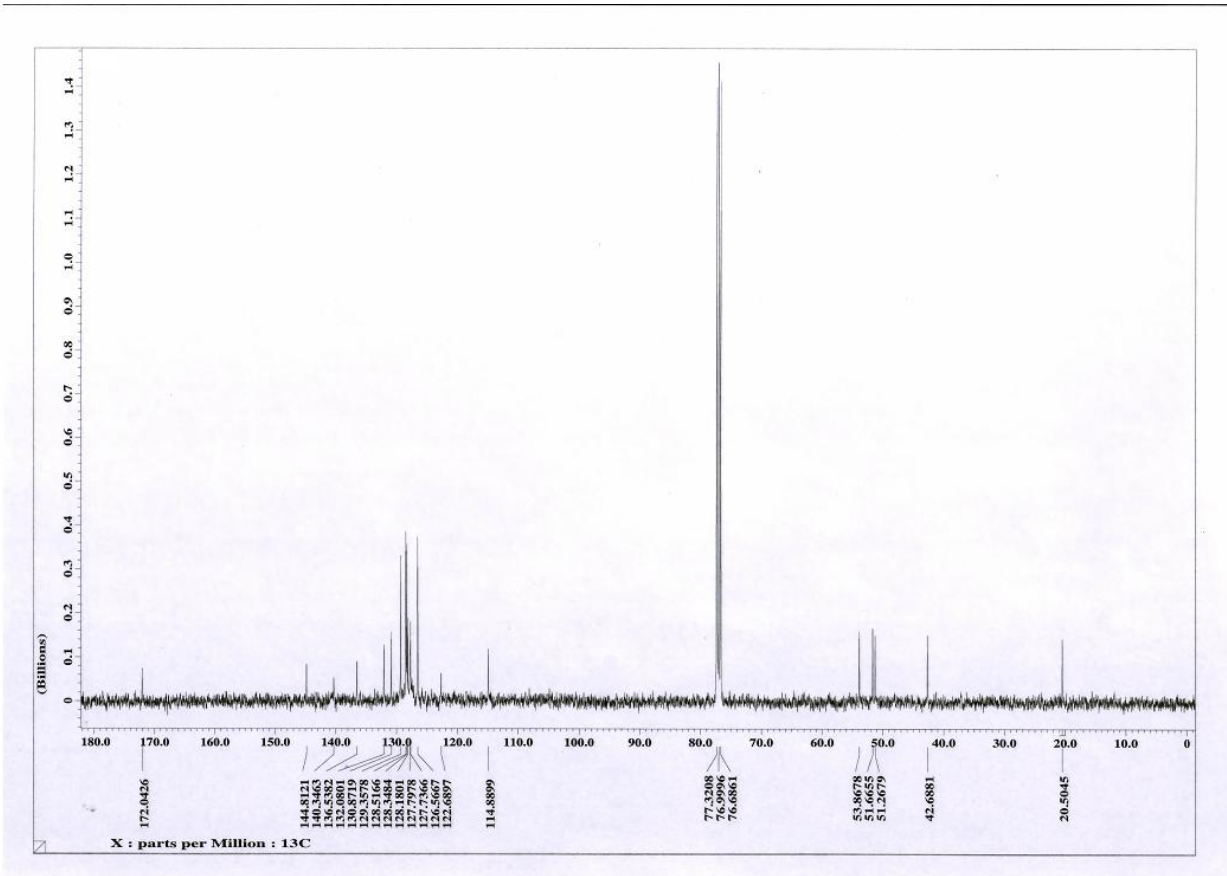
¹H NMR Spectrum of Compound **2r** (CDCl₃, 400 MHz)



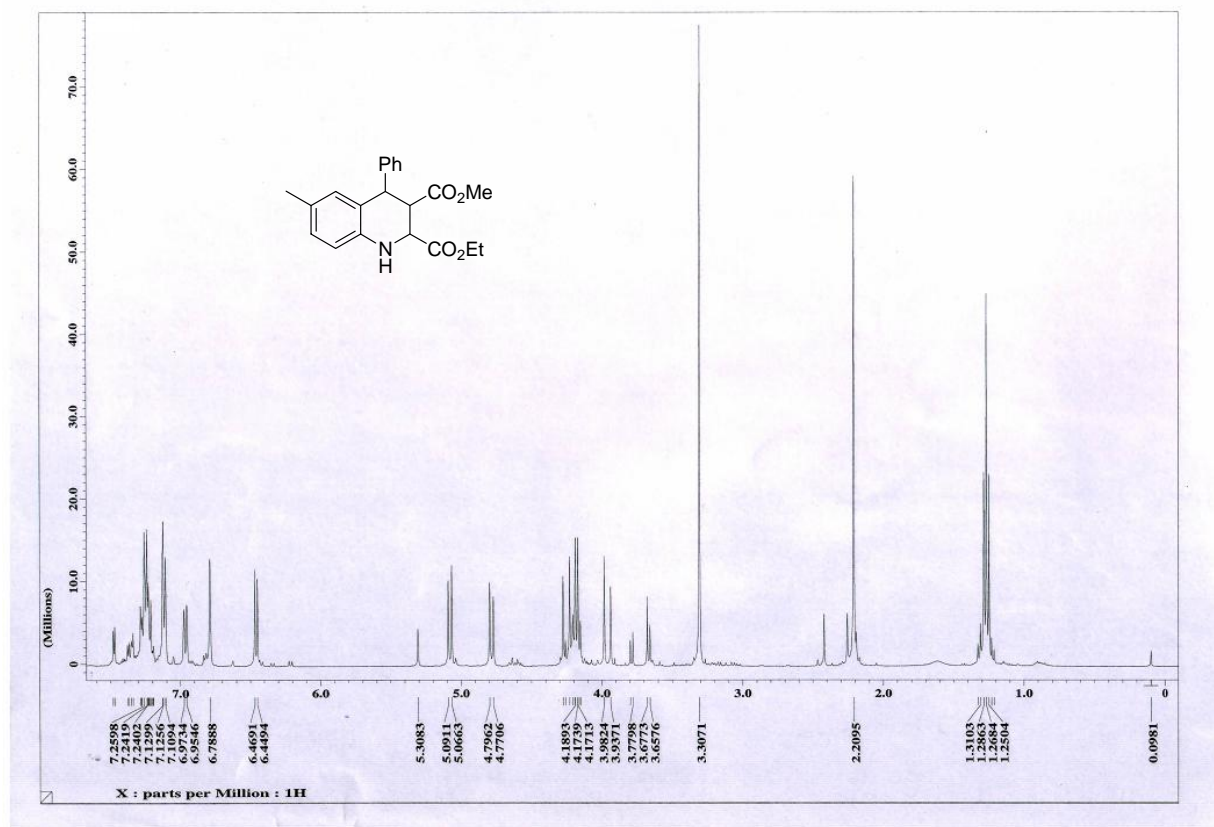
¹³C NMR Spectrum of Compound **2r** (CDCl₃, 100 MHz)



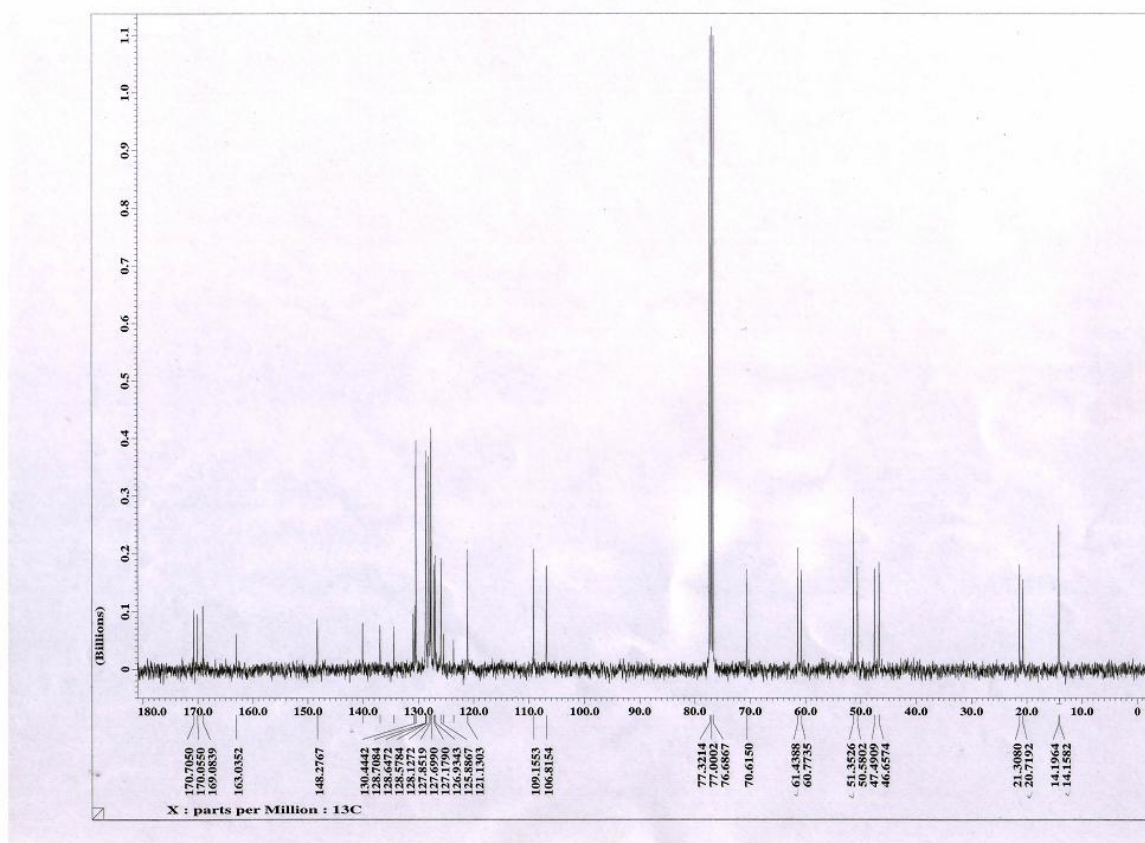
¹H NMR Spectrum of Compound 2s (CDCl₃, 400 MHz)



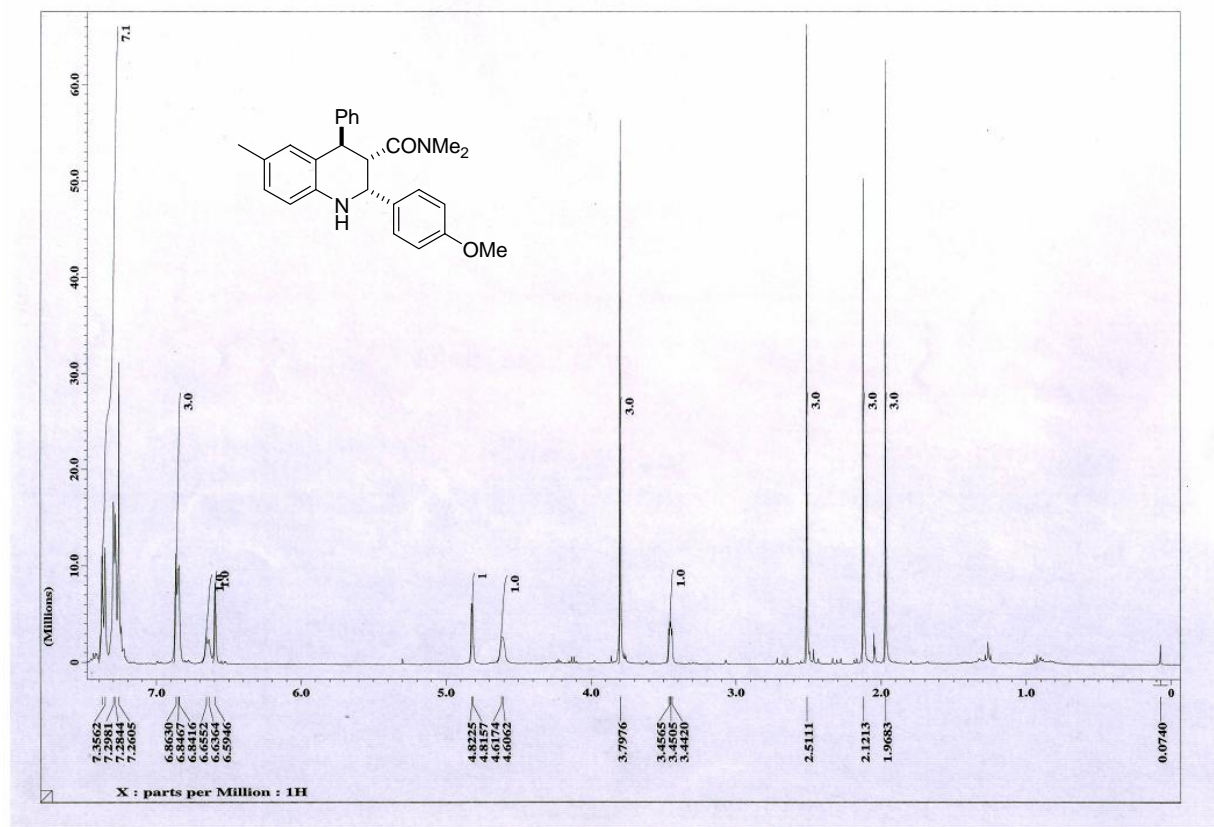
¹³C NMR Spectrum of Compound 2s (CDCl₃, 100 MHz)



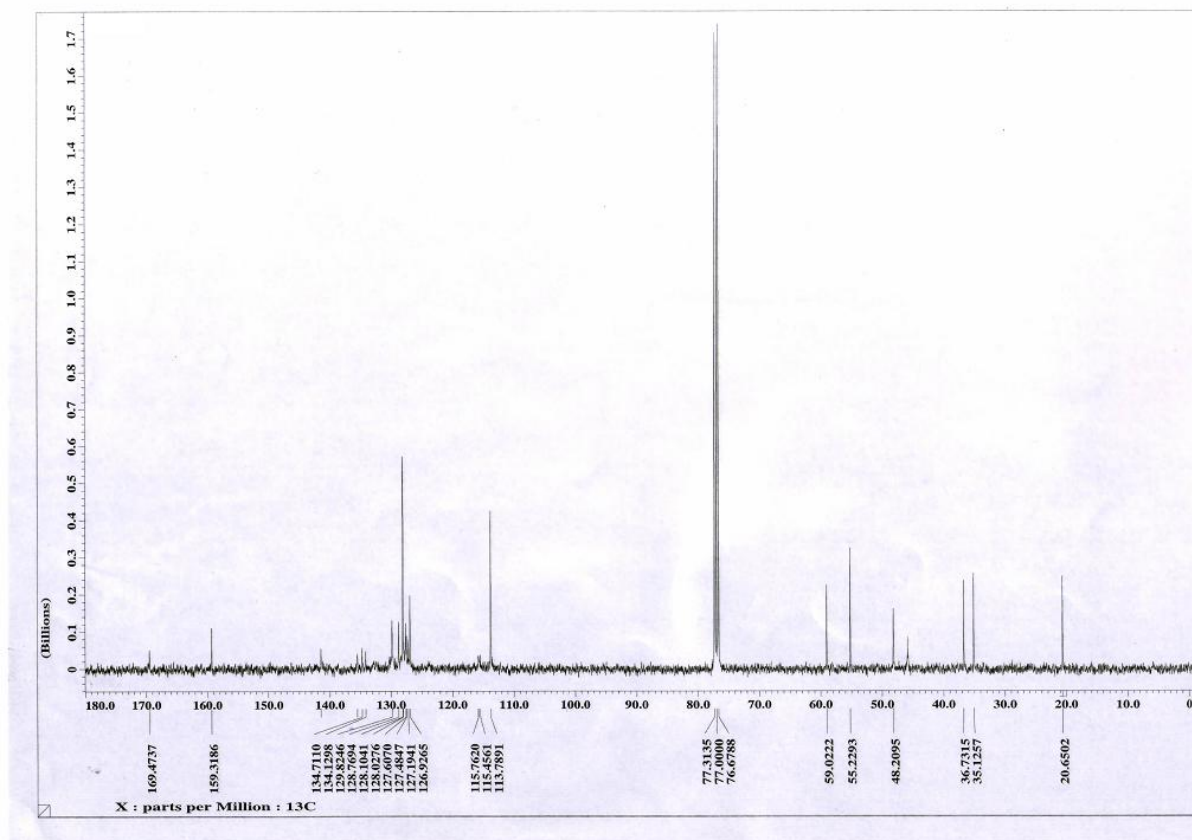
¹H NMR Spectrum of Compound **2t** (CDCl₃, 400 MHz)



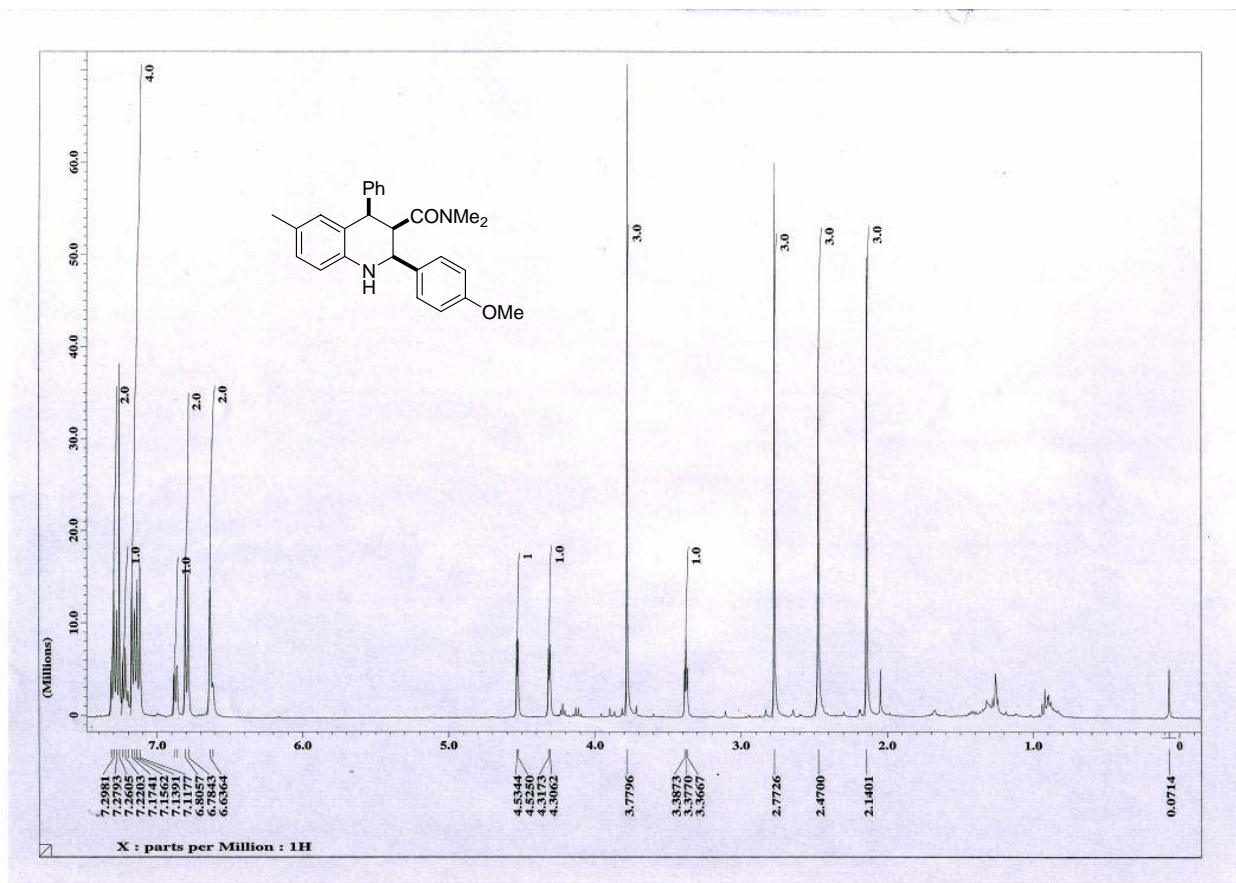
¹³C NMR Spectrum of Compound **2t** (CDCl₃, 100 MHz)



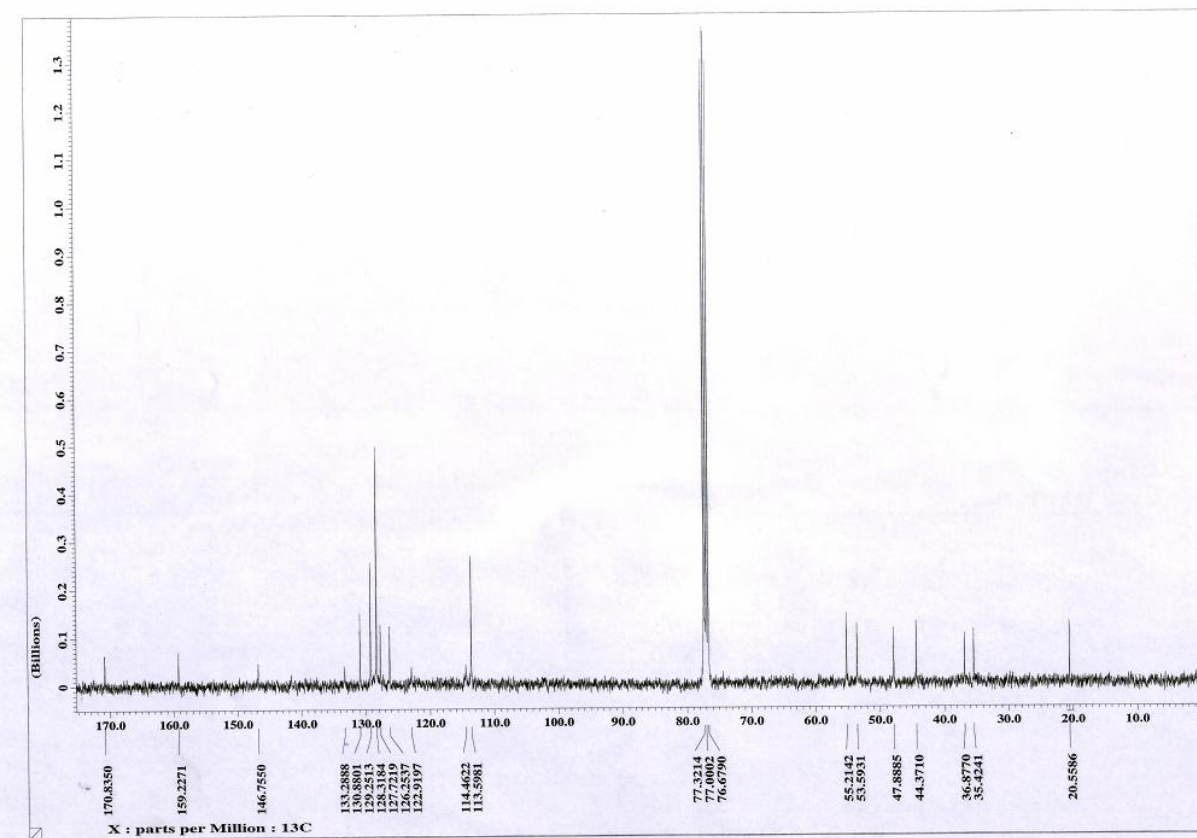
¹H NMR Spectrum of Compound **2u** (CDCl₃, 400 MHz)



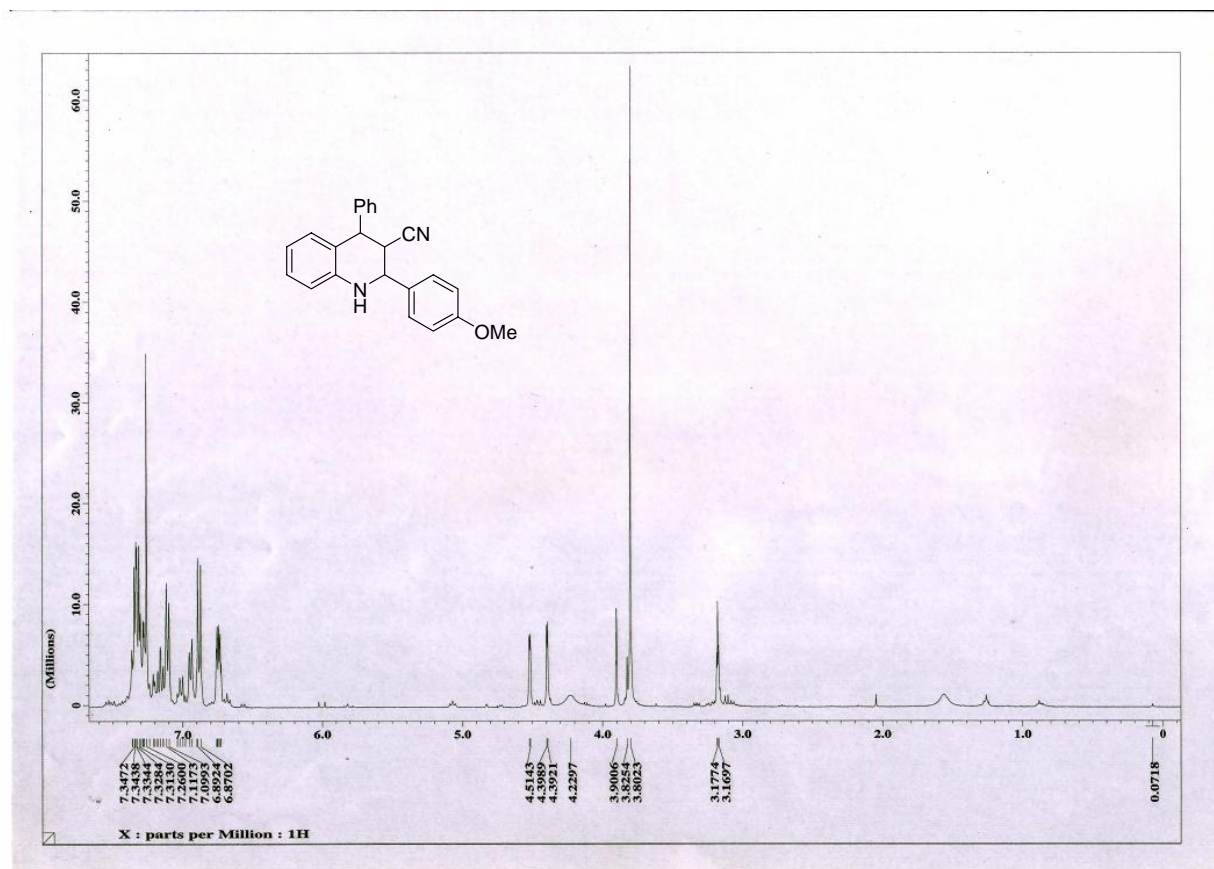
¹³C NMR Spectrum of Compound **2u** (CDCl₃, 100 MHz)



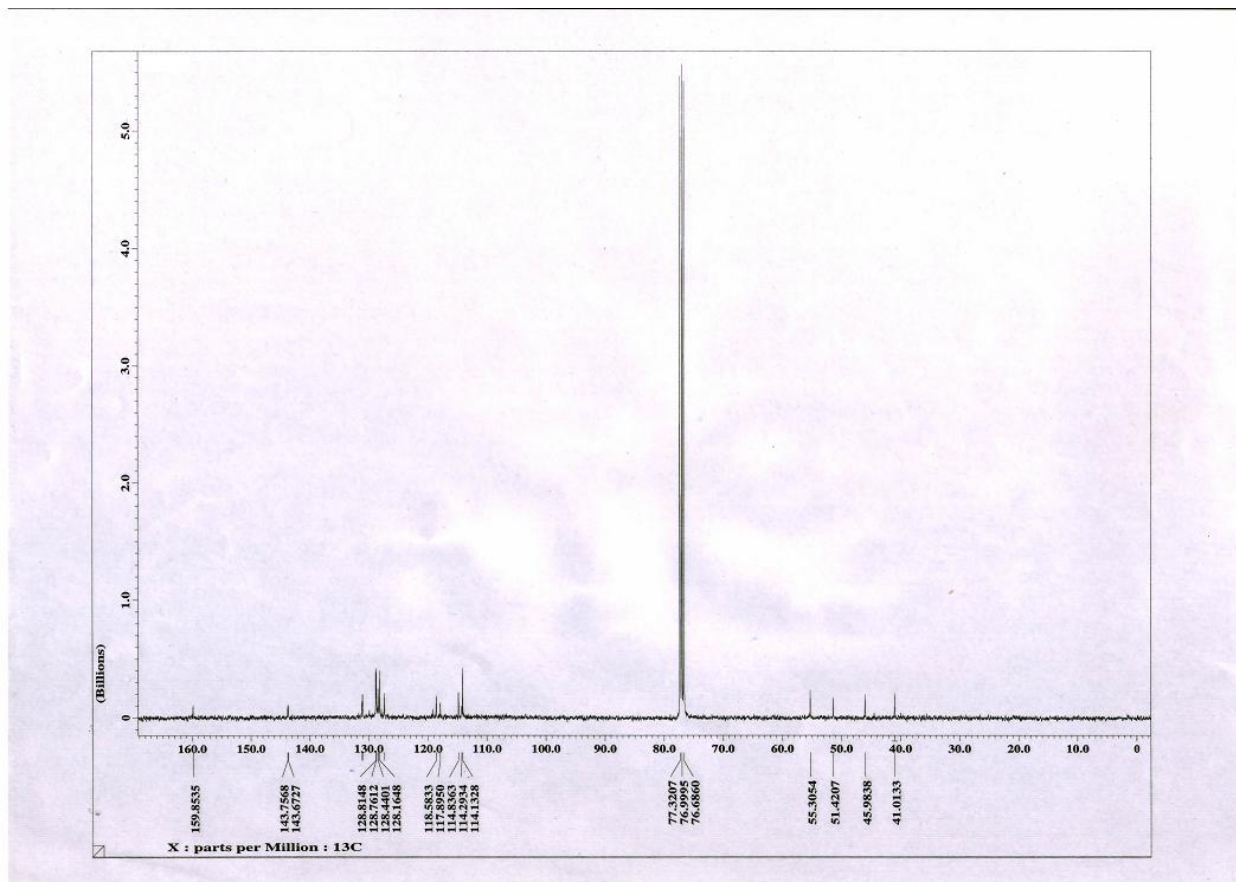
¹H NMR Spectrum of Compound 2'u (CDCl₃, 400 MHz)



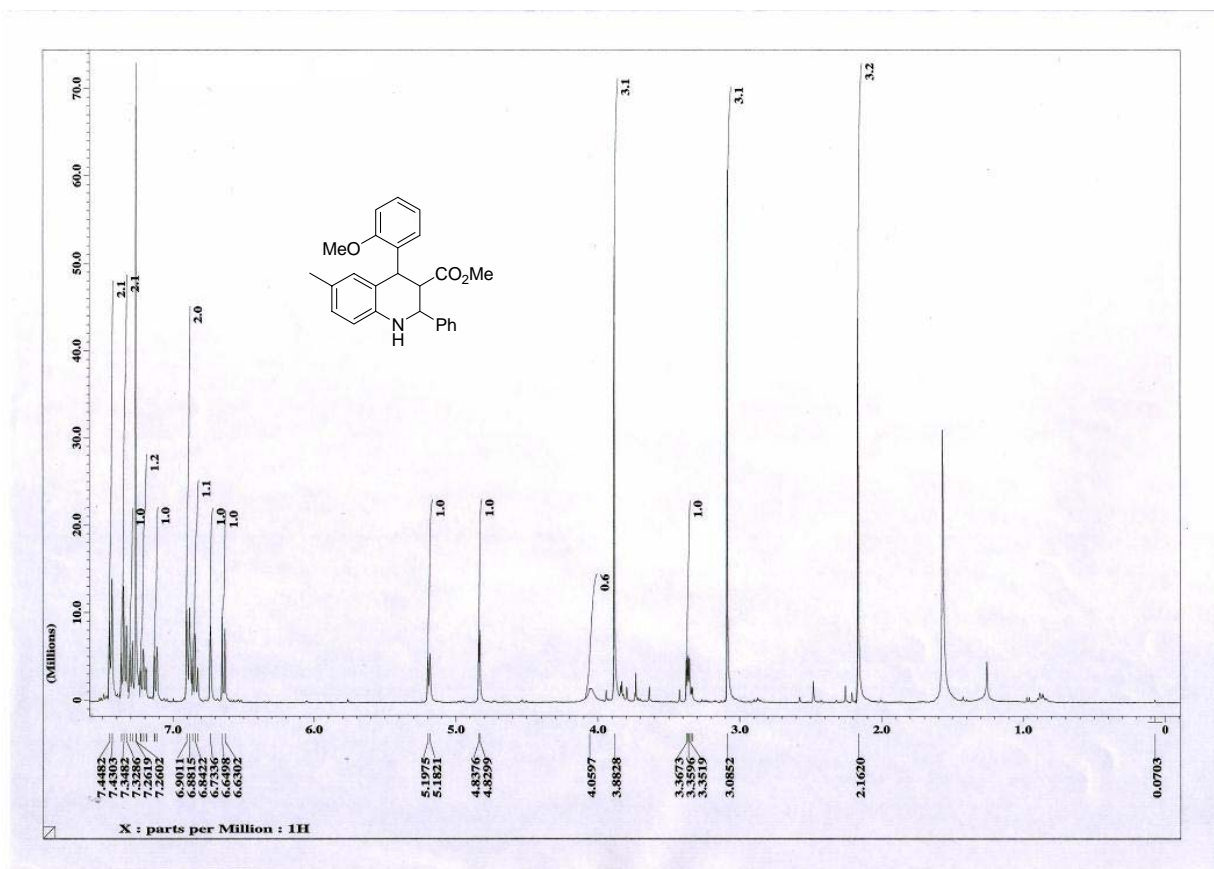
¹³C NMR Spectrum of Compound 2'u (CDCl₃, 100 MHz)



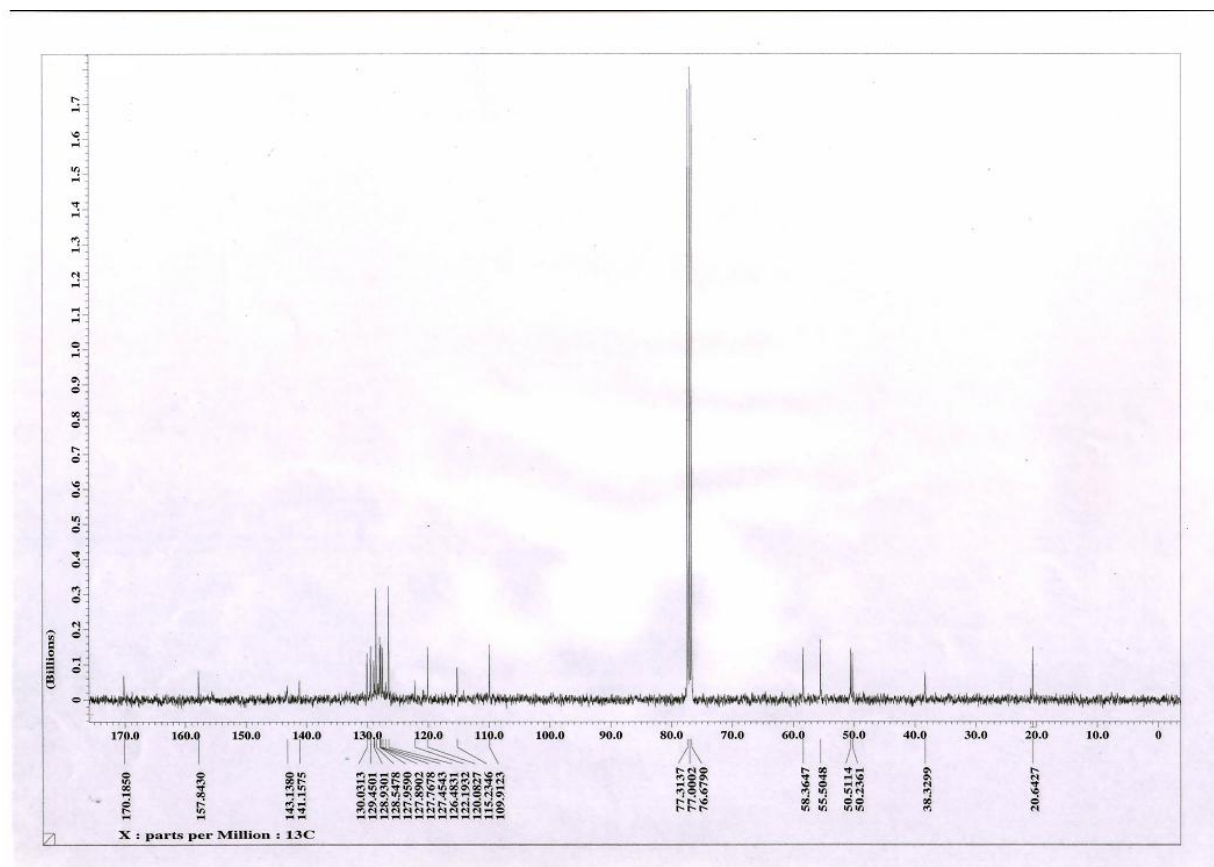
¹H NMR Spectrum of Compound 2v (CDCl₃, 400 MHz)



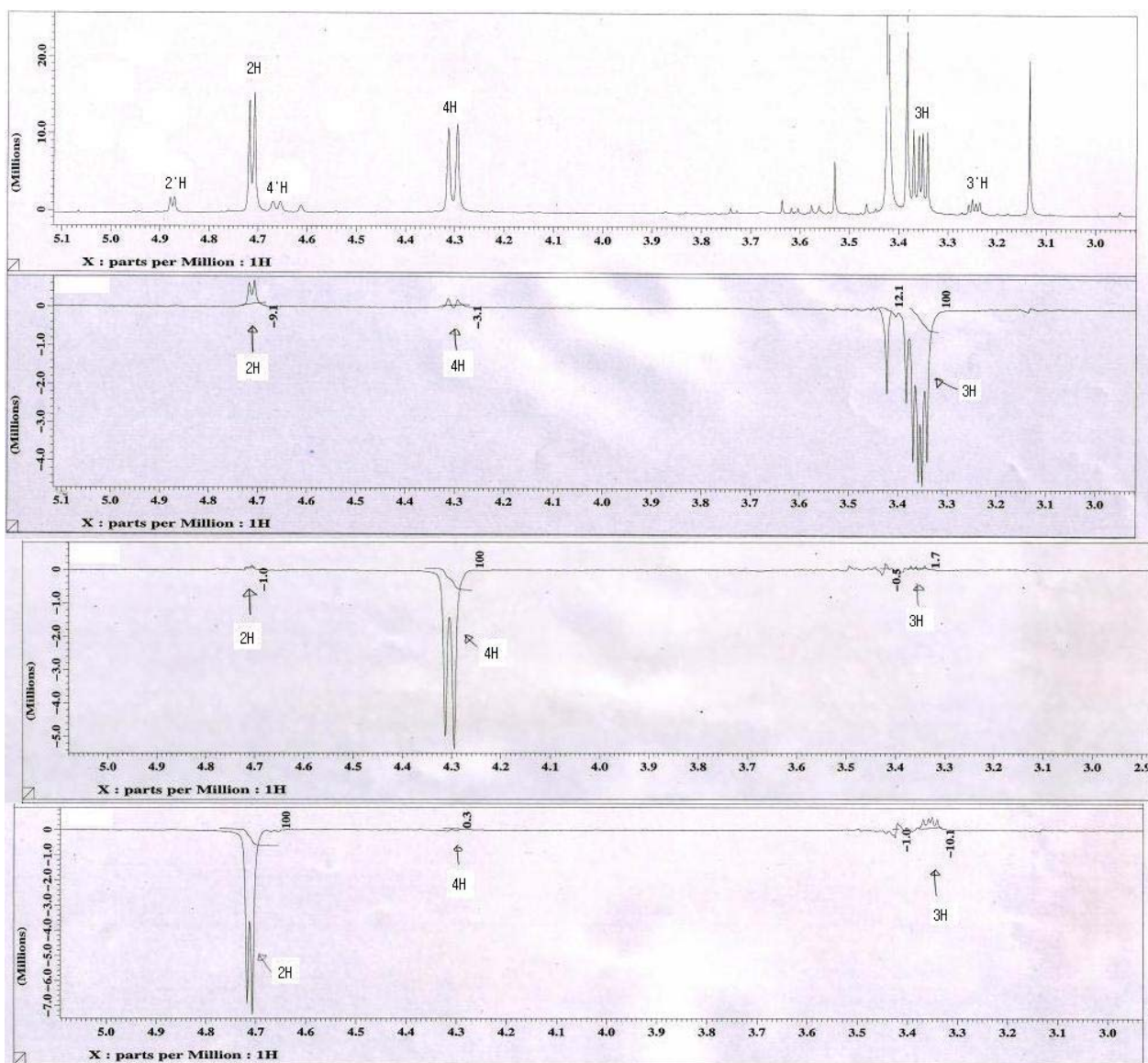
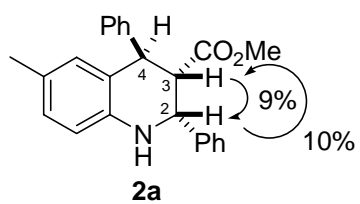
¹³C NMR Spectrum of Compound 2v (CDCl₃, 100 MHz)



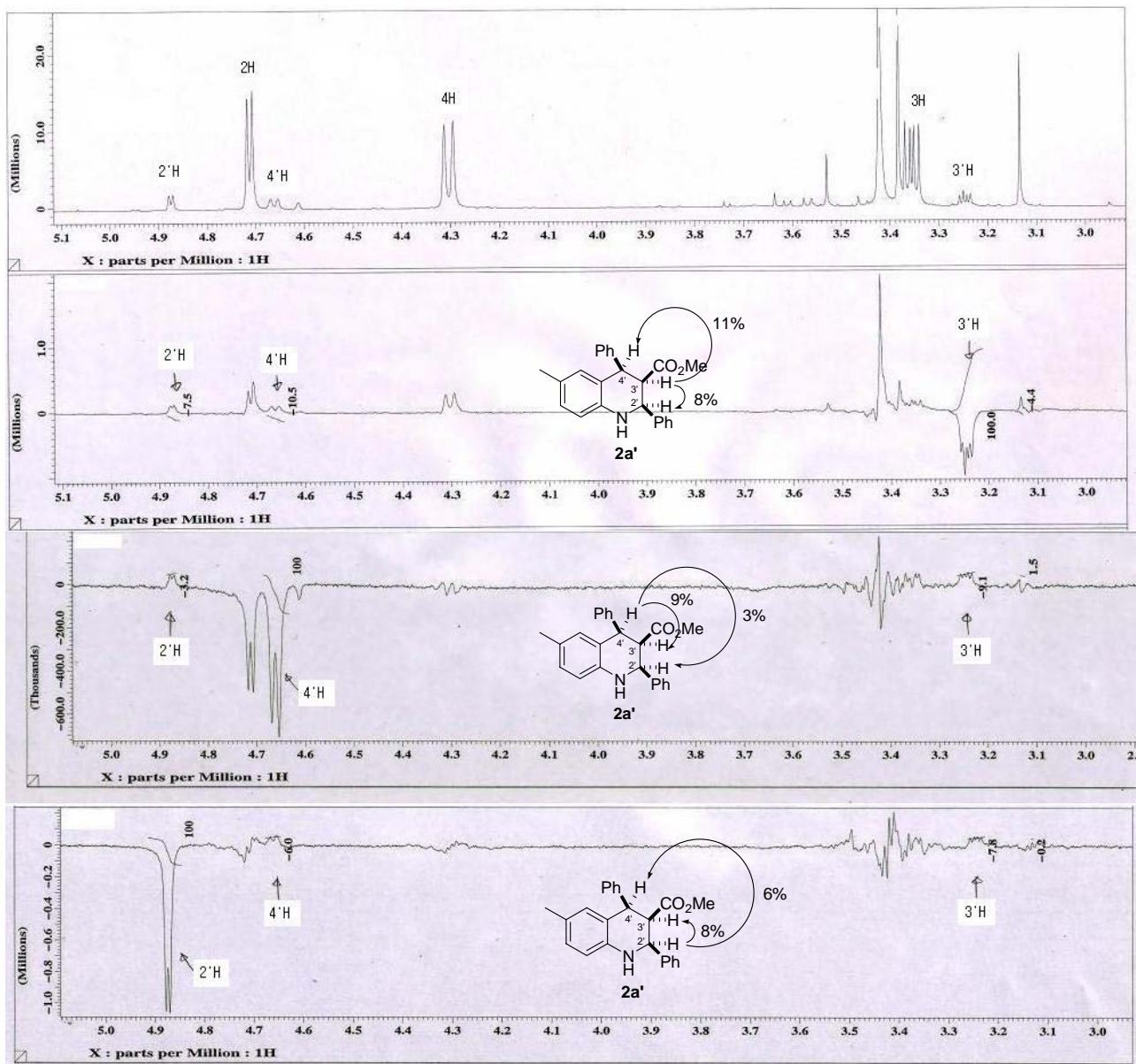
¹H NMR Spectrum of 4-(2-Methoxyphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester



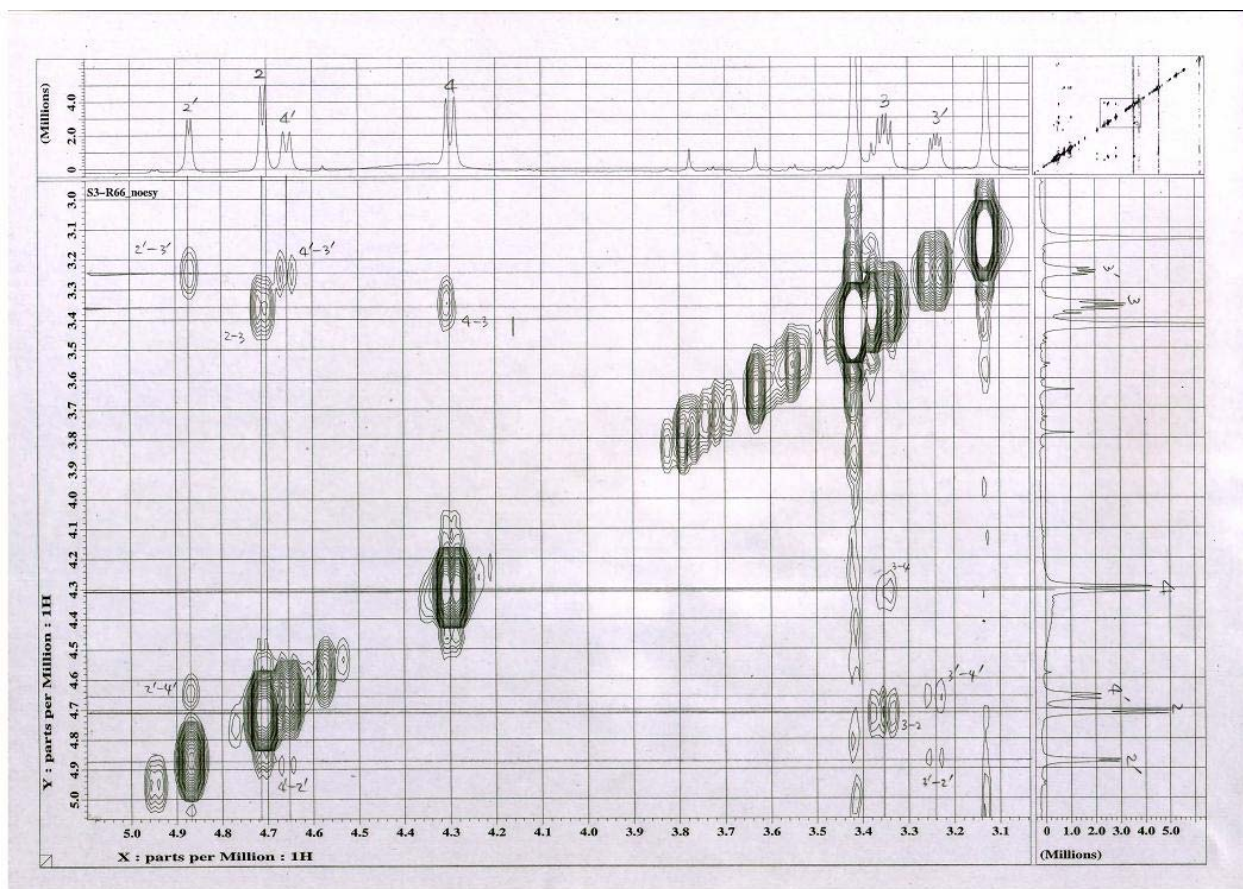
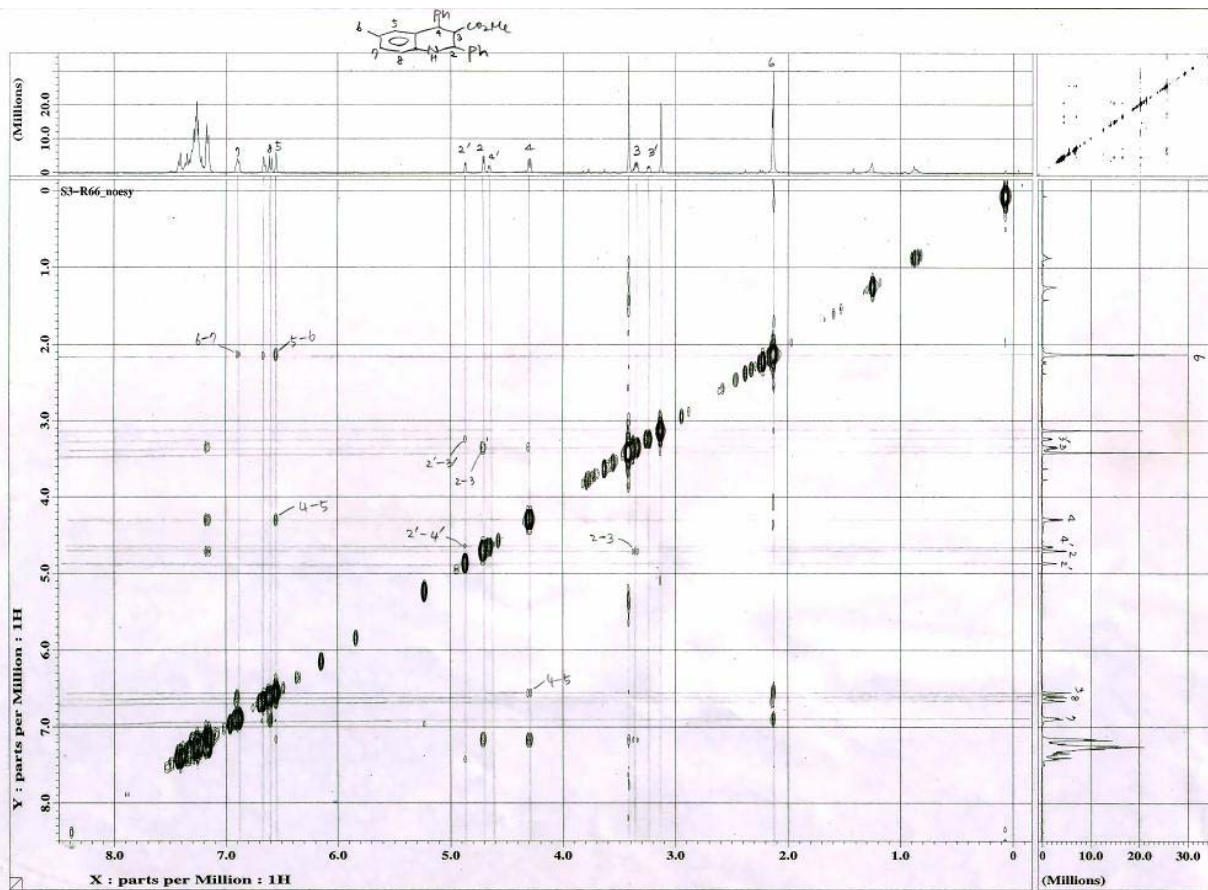
¹³C NMR Spectrum of 4-(2-Methoxyphenyl)-6-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline-3-carboxylic acid methyl ester



NOE Spectrum of Compound **2a**



NOE Spectrum of Compound **2'a**



NOESY Spectrum of Compound 2a