Stereoselective Rh^{I}-Catalysed Tandem Conjugate Addition of Boronic Acids-Michael Cyclization

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Supplementary material

General procedures and copies of ^{1}H and ^{13}C-NMR spectra

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General Methods

All starting boronic acids were commercially available research-grade chemicals, and were used without further purification. The Rh^{I}-catalysts were commercially available. Research-grade dioxane was used without further purification. Deionized water was used as co-solvent. Silica gel 60 F254 was used for TLC, and the spots were detected with UV or vanillin solution. Flash column chromatography was carried out on silica gel 60. ^{1}H-NMR spectra were recorded at 200 MHz, 300 MHz or 500 MHz as indicated, in $CDCl_3$ solution. ^{13}C-NMR spectra were recorded at 50.5 MHz, 75.5 MHz or 125.75 MHz as indicated in $CDCl_3$ solution.

Synthesis of the starting materials 1a-d

(*E,E*)-4, 4'-(1, 2-Phenylen)dibut-3-en-2-one, **1a**

To a solution of phtaldialdehyde (1.0 g, 7.45 mmol) in THF (10 mL) was added (2-oxopropylene)triphenylphosphorane (5.4 g, 17.13 mmol). The mixture was heated at reflux 18 h. The solvent was removed in vacuo and the crude product was purified by column chromatography (hexane - AcOEt, 50:50). **1a** was isolated in 90% yield.

R_f (hexane - AcOEt, 50:50) = 0.4.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.3 (s, 6H, C**H**$_3$), 6.55 (d, ^{3}J= 16.0 Hz, 2H, CH=C**H**-C=O), 7.35-7.70 (m, 4H, **H**-Ar), 7.80 (d, ^{3}J= 16.0 Hz, 2H, C**H**=CH-C=O) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 27.9 (**C**H$_3$), 27.9 (**C**H$_3$), 127.6 (CH=**C**H-C=O), 127.6 (CH=**C**H-C=O),130.3 (**C**H-Ar), 130.3 (**C**H-Ar), 131.8 (**C**H-Ar), 131.8 (**C**H-Ar), 134.4 (**C**-Ar), 134.4 (**C**-Ar), 139.5 (**C**H=CH-C=O), 139.5 (**C**H=CH-C=O), 197.5 (**C**=O), 197.5 (**C**=O) ppm.

(*E,E*)-3, 3'-(1,2-Phenylen)bis(1-phenylprop-2-en-1-one), **1b**

To a solution of phtaldialdehyde (405 mg, 3.02 mmol) in dioxane (8 mL) was added (benzoylmethylene)triphenylphosphorane (2.87 g, 7.55 mmol). The mixture was stirred at reflux 18 h. The solvent was removed in vacuo and the crude product was purified by column chromatography (hexane - AcOEt, 7:3). **1b** was isolated in 82% yield.

R_f (hexane - AcOEt, 70:30) = 0.5.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 7.37 (d, ^{3}J= 15.6 Hz, 2H, CH=C**H**-C=O), 7.41-7.64 (m, 10H, **H**-Ar), 8.02 (d, ^{3}J= 8 Hz, 4H, **H**-Ar), 8.15 (d, ^{3}J= 15.6 Hz, 2H, C**H**=CH-C=O) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 126.2 (CH=**C**H-C=O), 126.2 (CH=**C**H-C=O),128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 128.8 (**C**H-Ar), 128.8 (**C**H-Ar), 128.8 (**C**H-Ar), 128.8 (**C**H-Ar), 130.2 (**C**H-Ar), 130.2 (**C**H-Ar), 133.0 (**C**H-Ar), 133.0 (**C**H-Ar), 136.6 (**C**-Ar), 136.6 (**C**-Ar), 137.4 (**C**-Ar), 137.4 (**C**-Ar), 141.8 (**C**H=CH-C=O), 141.8 (**C**H=CH-C=O), 189.5 (**C**=O), 189.5 (**C**=O) ppm.

(*E,E*)-4-[2-(3-Oxo-3-phenylprop-1-enyl)phenyl]but-3-en-2-one, **1c**

To a solution of phtaldialdehyde (1 g, 7.45 mmol) in THF (15 mL) at 60ºC was added dropwise over a period of 1h a solution of (benzoylmethylene)-triphenylphosphorane (2.83 g, 7.45 mmol) in THF (40 mL), and the mixture was then stirred 18 h. (2-Oxopropylene)triphenylphosphorane (4.74 g, 14.9 mmol) was added and the resulting mixture was stirred at reflux 18 h. The solvent was removed in vacuo to give an oil which was purified by column chromatography (Hexane - AcOEt, 70:30). **1c** was isolated in 63% yield.

R_f (hexane - AcOEt, 70:30) = 0.3.

^{1}H-RMN ($CDCl_3$, 300 MHz): δ 2.23 (s, 3H, C**H**$_3$), 6.47 (d, ^{3}J= 16.0 Hz, 1H, CH=C**H**-C=O-CH_3), 7.21-7.59 (m, 8H, **H**-Ar y CH=C**H**-C=O-Ph), 7.75 (d, ^{3}J= 15.8 Hz, 1H, C**H**=CH-C=O-CH_3), 7.87-8.06 (m, 3H, **H**-Ar y C**H**=CH-C=O-Ph) ppm.

^{13}C-RMN ($CDCl_3$, 75.5 MHz): δ 28.0 (**C**H_3) 125.7 (CH=**C**H-C=O-Ph), 128.0 (CH=**C**H-C=O-CH_3), 128.2 (**C**H-Ar), 128.8 (**C**H-Ar), 128.9 (**C**H-Ar), 128.9 (**C**H-Ar), 129.0 (**C**H-Ar), 129.0 (**C**H-Ar), 130.6 (**C**H-Ar), 130.6 (**C**H-Ar), 133.3 (**C**H-Ar), 135.0 (**C**-Ar), 135.2 (**C**-Ar), 138.1 (**C**-Ar), 140.1 (**C**H=CH-C=O-Ph), 141.2 (**C**H=CH-C=O-CH_3), 189.8 (Ph-**C**=O), 198.0 (CH_3-**C**=O) ppm.

(*E,E*)-Dimethyl 3, 3'-(1,2-phenylene)diacrylate, **1d**

To a solution of phtaldialdehyde (1.0 g, 7.45 mmol) in THF (10 mL) was added (methoxycarbonylmethylene)triphenylphosphorane (5.7 g, 17.13 mmol). The mixture was heated at reflux 18 h. The solvent was removed in vacuo and the crude product was purified by column chromatography (hexane - AcOEt, 60:40). **1d** was isolated in 92% yield.

R_f (hexane - AcOEt, 60:40) = 0.7.

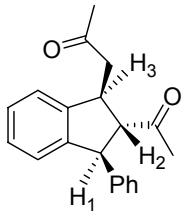
^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.75 (s, 6H, OC**H**$_3$), 6.29 (d, ^3J= 15.8 Hz, 2H, CH=C**H**-C=O), 7.29-7.40 (m, 2H, **H**-Ar), 7.47-7.57 (m, 2H, **H**-Ar), 7.97 (d, 2H, ^3J= 15.8 Hz, C**H**=CH-C=O) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 51.8 (O**C**H$_3$), 51.8 (O**C**H$_3$), 121.5 (CH=**C**H-C=O), 121.5 (CH=**C**H-C=O), 127.6 (**C**H-Ar), 127.6 (**C**H-Ar), 130.1 (**C**H-Ar), 130.1 (**C**H-Ar), 134.3 (**C**-Ar), 134.3 (**C**-Ar), 141.5 (**C**H=CH-C=O), 141.5 (**C**H=CH-C=O), 166.8 (**C**=O), 166.8 (**C**=O) ppm.

Rhodium-catalyzed conjugate addition reactions, General Procedure.

To a mixture of $RB(OH)_2$ (0.30 mmol) and $[Rh(cod)]BF_4$ (5 mg, 0.01 mmol Rh^I) under Ar was added a solution of the starting material **1a** – **d** (0.20 mmol) in dioxane-H_2O (10:1, 0.5 mL) followed by the base (0.20 mmol).The reaction mixture was stirred at 25ºC for 18 h and filtered over a Celite pad covered with $MgSO_4$. The Celite pad was rinsed with Et_2O. Evaporation under vacuum afforded the crude reaction products, which were purified by column chromatography (hexane - AcOEt).

(1S, 2S*, 3S*)*-2-acetyl-1-acetylmethyl-3-phenylindane**, 2aa**



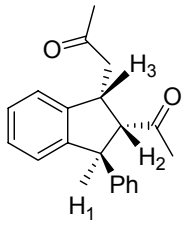
2aa

R_f (hexane - AcOEt, 70:30) = 0.4.

^{1}H-RMN ($CDCl_3$, 500 MHz): δ 2.08 (s, 3H, C**H**$_3$), 2.24 (s, 3H, C**H**$_3$), 2.72 (dd, ^2J= 16.6 Hz, ^3J= 8.2 Hz, 1H, **H**$_{4'}$), 3.16 (dd, ^2J= 16.6 Hz, ^3J= 5.2Hz, 1H, **H**$_4$), 3.26 (t, ^3J= 9.1 Hz, 1H, **H**$_2$), 4.04-4.11 (m, 1H, **H**$_3$), 4.41 (d, .^3J= 9.4 Hz, 1H, **H**$_1$), 6.83 (d, ^3J= 8.1Hz, 1H, **H**-Ar), 7.17-7.43 (m, 8H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.3 (**C**H$_3$), 30.6 (**C**H$_3$), 41.9 (**C**-H$_3$), 48.6 (**C**H$_2$), 55.2 (**C**-H$_1$), 69.0 (**C**-H$_2$), 123.1 (**C**H-Ar), 125.1 (**C**H-Ar), 127.2 (**C**H-Ar), 127.5 (**C**H-Ar), 127.5 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 143.2 (**C**-Ar), 144.0 (**C**-Ar), 144.3 (**C**-Ar), 207.6 (**C**=O), 209.2 (**C**=O) ppm.

(1R, 2S*, 3S*)*-2-Acetyl-1-acetylmethyl-3-phenylindane, **3aa**



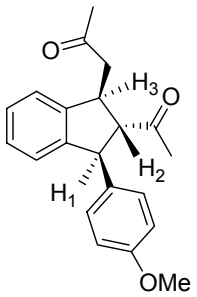
3aa

R_f (hexane - AcOEt, 70:30) = 0.5.

^{1}H-RMN ($CDCl_3$, 500 MHz): δ 2.08 (s, 3H, C**H**$_3$), 2.10 (s, 3H, C**H**$_3$), 2.52 (dd, ^2J= 18.3 Hz, ^3J= 5.2 Hz, 1H, **H**$_{4'}$), 2.97 (dd, ^2J= 18.3 Hz, ^3J= 8.7 Hz, 1H, **H**$_4$), 3.71 (dd, ^3J= 7.8, 10.4 Hz, 1H, **H**$_2$), 4.12-4.22 (m, 1H, **H**$_3$), 4.74 (d, ^3J= 10.4 Hz, 1H, **H**$_1$), 6.87 (d, ^3J= 7.0 Hz, 1H, **H**-Ar), 7.17-7.25 (m, 8H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.5 (**C**H$_3$), 32.4 (**C**H$_3$), 41.4 (**C**-H$_3$), 45.7 (**C**H$_2$), 52.0 (**C**-H$_1$), 64.8 (**C**-H$_2$), 123.8 (**C**H-Ar), 125.2 (**C**H-Ar), 126.9 (**C**H-Ar), 127.4 (**C**H-Ar), 127.5 (**C**H-Ar), 128.4 (**C**H-Ar), 128.4 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 142.5 (**C**-Ar), 144.6 (**C**-Ar), 144.9 (**C**-Ar), 207.4 (**C**=O), 209.9 (**C**=O) ppm.

(1S, 2S*, 3S*)*-2-Acetyl-1-acetylmethyl-3-(4-methoxyphenyl)indane**, 2ab**



2ab

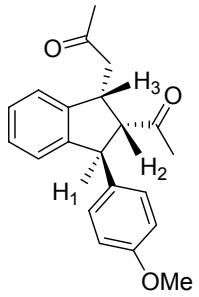
R_f (hexane - AcOEt, 70:30) = 0.3.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.05 (s, 3H, C**H**$_3$), 2.22 (s, 3H, C**H**$_3$), 2.67 (dd, ^2J= 16.5 Hz ^3J=8.1 Hz, 1H, **H**$_{4'}$), 3.12 (dd, ^2J= 16.5 Hz, ^3J= 5.3 Hz, 1H, **H**$_4$), 3.19 (t, ^3J= 9.5 Hz, 1H, **H**$_2$), 3.81 (s, 3H, OC**H**$_3$), 3.95-4.11 (m, 1H, **H**$_3$), 4.32 (d, ^3J= 9.6 Hz, 1H, **H**$_1$), 6.77-6.92 (m, 3H, **H**-Ar), 7.07-7.29 (m, 5H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.3 (**C**H$_3$), 30.9 (**C**H$_3$), 41.7 (**C**-H$_3$), 48.6 (**C**H$_2$), 54.5 (**C**-H$_1$), 55.3 (**C**-H$_2$), 69.3 (O**C**H$_3$), 114.2 (**C**H-Ar), 114.2 (**C**H-Ar), 123.0 (**C**H-Ar),

124.9 (**C**H-Ar), 127.4 (**C**H-Ar), 127.5 (**C**H-Ar), 129.4 (**C**H-Ar), 129.4 (**C**H-Ar), 135.1 (**C**-Ar), 143.9 (**C**-Ar), 144.6 (**C**-Ar), 158.7 (**C**-Ar), 207.7 (**C**=O), 209.4 (**C**=O) ppm.

(1R, 2S*, 3S*)*-2-Acetyl-1-acetylmethyl-3-(4-methoxyphenyl)indane, **3ab.**



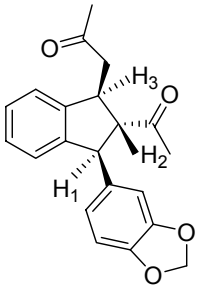
3ab

R_f (hexane - AcOEt, 70:30) = 0.4.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.07 (s, 3H, C**H**$_3$), 2.09 (s, 3H, C**H**$_3$), 2.49 (dd, ^2J= 18.3 Hz ^3J= 5.2 Hz, 1H, **H**$_{4'}$), 2.95 (dd, ^2J= 18.2 Hz, ^3J= 8.6 Hz, 1H, **H**$_4$), 3.65 (dd, ^3J= 7.7, 10.4 Hz, 1H, **H**$_2$), 3.79 (s, 3H, OC**H**$_3$), 4.07-4.20 (m, 1H, **H**$_3$), 4.68 (d, ^3J= 10.3 Hz, 1H, **H**$_1$), 6.79-6.90 (m, 3H, **H**-Ar), 7.05-7.28 (m, 5H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.5 (**C**H$_3$), 32.5 (**C**H$_3$), 41.4 (**C**-H$_3$), 45.7 (**C**H$_2$), 51.3 (**C**-H$_1$), 55.3 (**C**-H$_2$), 65.0 (O**C**H$_3$), 114.1 (**C**H-Ar), 114.1 (**C**H-Ar), 123.9 (**C**H-Ar), 125.2 (**C**H-Ar), 127.4 (**C**H-Ar), 127.5 (**C**H-Ar), 129.4 (**C**H-Ar), 129.4 (**C**H-Ar), 134.5 (**C**-Ar), 144.8 (**C**-Ar), 144.8 (**C**-Ar),158.6 (**C**-Ar), 207.5 (**C**=O), 210.1 (**C**=O) ppm.

(1S, 2S*, 3S*)*-2-Acetyl-1-acetylmetyl-3-(3, 4-methylenedioxyphenyl)indane**, 2ac**



2ac

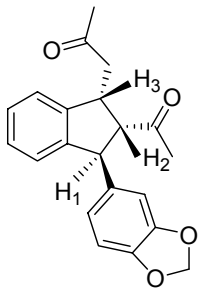
R_f (hexane - AcOEt, 70:30) = 0.4.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.08 (s, 3H, C**H**$_3$), 2.22 (s, 3H, C**H**$_3$), 2.67 (dd, ^2J= 16.7 Hz, ^3J= 8.2 Hz, 1H, **H**$_{4'}$), 3.13 (dd, ^2J= 16.6 Hz, ^3J= 5.2 Hz, 1H, **H**$_4$), 3.16 (t, ^3J= 9.4

Hz, 1H, **H**$_2$), 3.93-4.07 (m, 1H, **H**$_3$), 4.30 (d, ^3J= 9.6 Hz, 1H, **H**$_1$), 5.96 (s, 2H, O-C**H**$_2$-O), 6.60-6.88 (m, 4H, **H**-Ar), 7.09-7.29 (m, 3H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.3 (**C**H$_3$), 30.6 (**C**H$_3$), 41.7 (**C**-H$_3$), 48.6 (**C**H$_2$), 55.0 (**C**-H$_1$), 69.2 (**C**-H$_2$), 101.1 (O-**C**H$_2$-O), 108.3 (**C**H-Ar), 108.3 (**C**H-Ar), 121.9 (**C**H-Ar), 123.1 (**C**H-Ar), 124.9 (**C**H-Ar), 127.5 (**C**H-Ar), 127.5 (**C**H-Ar), 137.0 (**C**-Ar), 143.9 (**C**-Ar), 144.3 (**C**-Ar), 146.7 (**C**-Ar), 148.2 (**C**-Ar), 207.6 (**C**=O), 209.2 (**C**=O) ppm.

(1R, 2S*, 3S*)*-2-Acetyl-1-acetylmethyl-3-(3, 4-methylenedioxyphenyl)indane**, 3ac**



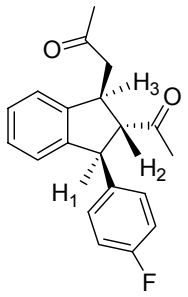
3ac

R$_f$ (hexane - AcOEt, 70:30) = 0.5.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.08 (s, 3H, C**H**$_3$), 2.09 (s, 3H, C**H**$_3$), 2.48 (dd, ^2J= 18.4 Hz, ^3J= 5.1 Hz, 1H, **H**$_{4'}$), 2.94 (dd, ^2J= 18.2 Hz, ^3J= 8.8 Hz, 1H, **H**$_4$), 3.63 (dd, ^3J= 10.4, 7.8 Hz, 1H, **H**$_2$), 4.06-4.20 (m, 1H, **H**$_3$), 4.66 (d, ^3J= 10.6 Hz, 1H, **H**$_1$), 5.94 (s, 2H, O-**C**H$_2$-O), 6.59-6.93 (m, 4H, **H**-Ar), 7.13-7.28 (m, 3H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 125.75 MHz): δ 30.1 (**C**H$_3$), 32.9 (**C**H$_3$), 41.7 (**C**-H$_3$), 46.1 (**C**H$_2$), 55.2 (**C**-H$_1$), 65.3 (**C**-H$_2$), 101.36 (O-**C**H$_2$-O), 108.7 (**C**H-Ar), 108.8 (**C**H-Ar), 122.2 (**C**H-Ar), 124.2 (**C**H-Ar), 125.6 (**C**H-Ar), 127.9 (**C**H-Ar), 128.0 (**C**H-Ar), 136.7 (**C**-Ar), 144.9 (**C**-Ar), 145.1 (**C**-Ar), 146.9 (**C**-Ar), 148.3 (**C**-Ar), 207.3 (**C**=O), 210.4 (**C**=O) ppm.

(1S, 2S*, 3S*)*-2-Acetyl-1-acetylmethyl-3-(4-fluorophenyl)indane, **2ad.**



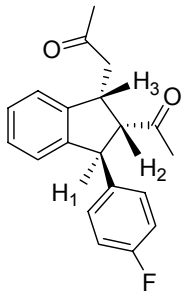
2ad

R_f (hexane - AcOEt, 70:30) = 0.4.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.06 (s, 3H, C**H**$_3$), 2.22 (s, 3H, C**H**$_3$), 2.69 (dd, ^2J= 16.8 Hz, ^3J= 8.3 Hz, 1H, **H**$_{4'}$), 3.13 (dd, ^2J= 16.8 Hz, ^3J= 5.2 Hz, 1H, **H**$_4$), 3.18 (t, ^3J= 9.2 Hz, 1H, **H**$_2$), 3.94-4.09 (m, 1H, **H**$_3$), 4.30 (d, ^3J= 9.5 Hz, 1H, **H**$_1$), 6.79 (d, ^3J= 7.6 Hz, 1H, **H**-Ar), 6.97-7.29 (m, 7H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 75.5 MHz): δ 31.1 (**C**H$_3$), 31.4 (**C**H$_3$), 42.2 (**C**-H$_3$), 48.8 (**C**H$_2$), 54.8 (**C**-H$_1$), 69.6 (**C**-H$_2$), 116.0 (**C**H-Ar), 116.3 (**C**H-Ar), 123.5 (**C**H-Ar), 125.2 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 130.3 (**C**H-Ar), 130.4 (**C**H-Ar), 139.3 (**C**-Ar), 144.3 (**C**-Ar), 144.5 (**C**-Ar), 160.7 (**C**-F Ar), 164.1 (**C**-F Ar), 208.1 (**C**=O), 209.5 (**C**=O) ppm.

(1R, 2S*, 3S*)*-2-Acetyl-1-acetylmethyl-3-(4-fluorophenyl)indane, **3ad**



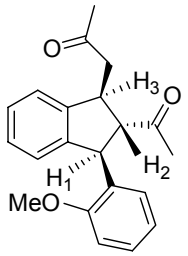
3ad

R_f (hexane - AcOEt, 70:30) = 0.5.

^{1}H-RMN ($CDCl_3$, 500 MHz): δ 2.10 (s, 3H, C**H**$_3$), 2.11 (s, 3H, C**H**$_3$), 2.53 (dd, ^2J= 18.3 Hz, ^3J= 5.2 Hz, 1H, **H**$_{4'}$), 2.94 (dd, ^2J= 18.3 Hz, ^3J= 8.6 Hz, 1H, **H**$_4$), 3.66 (dd, ^3J= 7.8, 10.5 Hz, 1H, **H**$_2$), 4.15-4.21 (m, 1H, **H**$_2$), 4.75 (d, ^3J= 10.4 Hz, 1H, **H**$_1$), 6.87 (d, ^3J= 7.4 Hz, 1H, **H**-Ar), 6.99-7.30 (m, 7H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 125.75 MHz): δ 31.3 (**C**H_3), 32.7 (**C**H_3), 41.8 (**C**-H_3), 46.0 (**C**H_2), 51.5 (**C**-H_1), 65.5 (**C**-H_2), 115.8 (**C**H-Ar), 116.0 (**C**H-Ar), 124.3 (**C**H-Ar), 125.5 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 130.3 (**C**H-Ar), 130.3 (**C**H-Ar), 138.6 (**C**-Ar), 144.7 (**C**-Ar), 145.2 (**C**-Ar), 161.4 (**C**-F Ar), 163.3 (**C**-F Ar), 207.7 (**C**=O), 210.1 (**C**=O) ppm.

(1S, 2S*, 3R*)*-2-Acetyl-1-acetylmethyl-3-(2-methoxyphenyl)indane, **2ae**



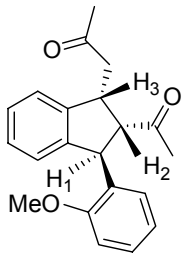
2ae

R_f (hexane - AcOEt, 70:30) = 0.3

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.17 (s, 3H, C**H**$_3$), 2.18 (s, 3H, C**H**$_3$), 2.65 (dd, ^2J= 16.9 Hz, ^3J= 8.4 Hz, 1H, **H**$_{4'}$), 3.05 (dd, ^2J= 16.2 Hz, ^3J= 5.2 Hz, 1H, **H**$_4$), 3.08 (t, ^3J= 8.2 Hz, 1H, **H**$_2$), 3.70 (s, 3H, OC**H**$_3$), 3.95-4.01 (m, 1H, **H**$_3$), 4.90 (d, ^3J= 8.4 Hz, 1H, **H**$_1$), 6.84-7.05 (m, 4H, **H**-Ar), 7.12-7.30 (m, 4H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 29.2 (**C**H_3), 30.2 (**C**H_3), 42.1 (**C**-H_3), 47.8 (**C**-H_1), 49.3 (**C**H_2), 55.2 (**C**-H_2), 67.6 (O**C**H_3), 110.6 (**C**H-Ar), 120.9 (**C**H-Ar), 123.3 (**C**H-Ar), 125.0 (**C**H-Ar), 127.1 (**C**H-Ar), 127.3 (**C**H-Ar), 128.1 (**C**H-Ar), 128.7 (**C**H-Ar), 131.9 (**C**-Ar), 144.0 (**C**-Ar), 144.5 (**C**-Ar), 157.3 (**C**-Ar), 207.6 (**C**=O), 209.6 (**C**=O) ppm.

(1R, 2S*, 3R*)*-2-Acetyl-1-acetylmethyl-3-(2-methoxyphenyl)indane**, 3ae**



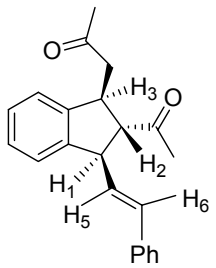
3ae

R_f (hexane - AcOEt, 70:30) = 0.4.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.12 (s, 3H, C**H**$_3$), 2.13 (s, 3H, C**H**$_3$), 2.68 (dd, ^2J= 18.3 Hz, ^3J= 5.2 Hz, 1H, **H**$_{4'}$), 3.07 (dd, ^2J= 18.3 Hz, ^3J= 9.0 Hz, 1H, **H**$_4$), 3.80 (s, 3H, OC**H**$_3$), 3.82 (dd, ^3J= 8.2, 7.2 Hz, 1H, **H**$_2$), 3.99-4.13 (m, 1H, **H**$_3$), 5.01 (d, ^3J= 8.0 Hz, 1H, **H**$_1$), 6.80-6.96 (m, 4H, **H**-Ar), 7.11-7.29 (m, 4H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.4 (**C**H$_3$), 31.9 (**C**H$_3$), 41.1 (**C**-H$_3$), 45.4 (**C**H$_2$), 46.7 (**C**-H$_1$), 55.4 (**C**-H$_2$), 61.4 (O**C**H$_3$), 110.8 (**C**H-Ar), 120.7 (**C**H-Ar), 123.3 (**C**H-Ar), 124.9 (**C**H-Ar), 127.1 (**C**H-Ar), 127.2 (**C**H-Ar), 127.9 (**C**H-Ar), 128.6 (**C**H-Ar), 131.0 (**C**-Ar), 144.3 (**C**-Ar), 145.0 (**C**-Ar), 157.5 (**C**-Ar), 207.9 (**C**=O), 210.4 (**C**=O) ppm.

(1S, 2S*, 3R*)*-2-Acetyl-1-acetylmethyl-3-(styryl)indane, **2af**



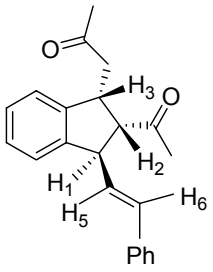
2af

R_f (hexane - AcOEt, 70:30) = 0.3.

^{1}H-RMN ($CDCl_3$, 300 MHz): δ 2.25 (s, 3H, C**H**$_3$), 2.30 (s, 3H, C**H**$_3$), 2.68 (dd, ^2J= 16.6 Hz, ^3J= 8.3 Hz, 1H, **H**$_{4'}$), 3.06 (t, ^3J= 8.8 Hz, 1H, **H**$_2$), 3.11 (dd, ^2J= 16.5 Hz, ^3J= 5.4 Hz, 1H, **H**$_4$), 4.01 (t, ^3J= 9.2 Hz, 1H, **H**$_1$), 4.03-4.09 (m, 1H, **H**$_3$), 6.26 (dd, ^3J= 9.0, 15.7 Hz, 1H, **H**$_5$), 6.62 (d, ^3J= 15.6 Hz, 1H, **H**$_6$), 7.12-7.47 (m, 9H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.1 (**C**H$_3$), 30.7 (**C**H$_3$), 41.5 (**C**-H$_3$), 48.5 (**C**H$_2$), 52.6 (**C**-H$_1$), 65.9 (**C**-H$_2$), 123.2 (**C**H-Ar), 124.4 (**C**H-Ar), 126.2 (**C**H-Ar), 126.2 (**C**H-Ar), 127.2 (**C**H-Ar), 127.5 (**C**H-Ar), 127.5 (**C**H-Ar), 128.4 (**C**H-Ar), 128.4 (**C**H-Ar), 130.7 (**C**H=CH), 132.6 (CH=**C**H), 140.0 (**C**-Ar), 142.0 (**C**-Ar), 143.5 (**C**-Ar), 207.0 (**C**=O), 209.1 (**C**=O) ppm.

(1R, 2S*, 3R*)*-2-Acetyl-1-acetylmethyl-3-(styryl)indane, **3af**



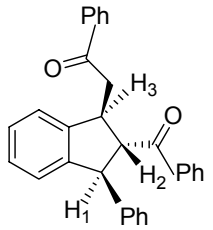
3af

R_f (hexane - AcOEt, 70:30) = 0.4

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.08 (s, 3H, C**H**$_3$), 2.22 (s, 3H, C**H**$_3$), 2.48 (dd, ^2J= 18.1 Hz, ^3J= 4.9 Hz, 1H, **H**$_{4'}$), 2.92 (dd, ^2J= 18.2 Hz, ^3J= 8.9 Hz, 1H, **H**$_4$), 3.54 (dd, ^3J= 9.9, 8.0 Hz, 1H, **H**$_2$), 4.03-4.17 (m, 1H, **H**$_3$), 4.32 (t, ^3J=9.4 Hz, 1H, **H**$_1$), 6.11 (dd, ^3J= 8.4, 15.7 Hz, 1H, **H**$_5$), 6.60 (d, ^3J= 15.7 Hz, 1H, **H**$_6$), 7.09-7.43 (m, 9H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 125.5 MHz): δ 30.9 (**C**H$_3$), 32.9 (**C**H$_3$), 41.8 (**C**-H$_3$), 46.1 (**C**H$_2$), 50.2 (**C**-H$_1$), 62.1 (**C**-H$_2$), 124.4 (**C**H-Ar), 125.1 (**C**H-Ar), 126.7 (**C**H-Ar), 126.7 (**C**H-Ar), 127.9 (**C**H-Ar), 128.0 (**C**H-Ar), 128.9 (**C**H-Ar), 129.0 (**C**H-Ar), 130.0 (**C**H-Ar), 130.2 (**C**H=CH), 133.4 (CH=**C**H), 137.3 (**C**-Ar), 144.0 (**C**-Ar), 144.9 (**C**-Ar), 207.8 (**C**=O), 210.3 (**C**=O) ppm.

(1S, 2S*, 3S*)*-2-Benzoyl-1-benzoylmethyl-3-phenylindane, **2ba**



2ba

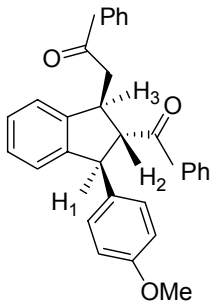
R_f (hexane - AcOEt, 90:10) = 0.2.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.31 (dd, ^2J = 17.1 Hz, ^3J = 7.6 Hz, 1H, **H**$_{4'}$), 3.66 (dd, ^2J = 17.1 Hz, ^3J = 5.5 Hz, 1H, **H**$_4$), 4.23 (t, ^3J = 8.5 Hz, 1H, **H**$_2$), 4.39-4.53 (m, 1H, **H**$_3$), 4.64 (d, ^3J = 8.6 Hz, 1H, **H**$_1$), 6.93 (d, ^3J = 6.9 Hz, 1H, **H**-Ar), 7.10-7.32 (m, 10H, **H**-

Ar), 7.35-7.56 (m, 4H, **H**-Ar), 7.60 (d, ^3J = 7.2 Hz, 2H, **H**-Ar), 7.86 (d, ^3J = 7.1 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 43.6 (**C**H_2), 44.0 (**C**-H_3), 56.4 (**C**-H_1), 63.3 (**C**-H_2), 123.3 (**C**H-Ar), 125.1 (**C**H-Ar), 126.9 (**C**H-Ar), 127.5 (**C**H-Ar), 127.5 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 128.2 (**C**H-Ar), 128.2 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 132.8 (**C**H-Ar), 133.1 (**C**H-Ar), 136.9 (**C**-Ar), 137.7 (**C**-Ar), 143.5 (**C**-Ar), 144.4 (**C**-Ar), 144.7 (**C**-Ar), 198.4 (**C**=O), 201.6 (**C**=O) ppm.

(1S, 2S*, 3S*)*-2-Benzoyl-1-benzoylmethyl-3-(4-methoxyphenyl)indane, **2bb**



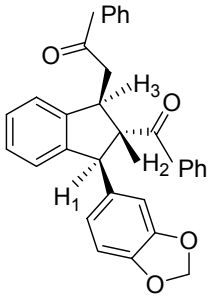
2bb

R_f (hexane - AcOEt, 85:15) = 0.2.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.29 (dd, ^2J = 17.1 Hz, ^3J = 7.5 Hz, 1H, $\mathbf{H}_{4'}$), 3.63 (dd, ^2J = 17.1 Hz, ^3J = 5.5 Hz, 1H, $\mathbf{H}_4$), 3.77 (s, 3H, -OC$\mathbf{H}_3$), 4.17 (t, ^3J = 8.5 Hz, 1H, $\mathbf{H}_2$), 4.35-4.49 (m, 1H, $\mathbf{H}_3$), 4.58 (d, ^3J = 8.7 Hz, 1H, $\mathbf{H}_1$), 6.78 (d, ^3J = 8.7 Hz, 2H, **H**-Ar), 6.91 (d, ^3J = 6.6 Hz, 1H, **H**-Ar), 7.05 (d, ^3J = 8.7 Hz, 2H, **H**-Ar), 7.16-7.64 (m, 11H, **H**-Ar), 7.85 (d, ^3J = 8.6 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 43.6 (**C**H_2), 43.9 (**C**-H_3), 55.2 (O**C**H_3), 55.7 (**C**-H_1), 63.5 (**C**-H_2) 114.0 (**C**H-Ar), 123.2 (**C**H-Ar), 125.1 (**C**H-Ar), 127.3 (**C**H-Ar), 127.4 (**C**H-Ar), 127.4 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 128.2 (**C**H-Ar), 128.2 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 129.5 (**C**H-Ar), 129.5 (**C**H-Ar), 132.7 (**C**H-Ar), 133.1 (**C**H-Ar), 135.5 (**C**-Ar), 137.0 (**C**-Ar), 137.7 (**C**-Ar), 144.5 (**C**-Ar), 144.7 (**C**-Ar), 158.5 (**C**-Ar), 198.6 (**C**=O), 201.9 (**C**=O) ppm.

(1S,2S*,3S*)*-2-Benzoyl-1-benzoylmethyl-3-(3,4-methylenedioxyphenyl)indane, **2bc**



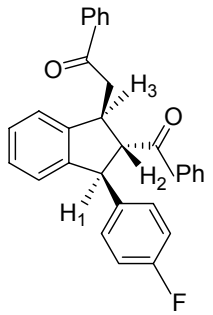
2bc

R_f (hexane - AcOEt, 85:15) = 0.4.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.29 (dd, ^2J = 17.2 Hz, ^3J = 7.5 Hz, 1H, $\mathbf{H}_{4'}$), 3.63 (dd, ^2J = 17.1 Hz, ^3J = 5.4 Hz, 1H, $\mathbf{H}_4$), 4.17 (t, ^3J = 8.5 Hz, 1H, $\mathbf{H}_2$), 4.32-4.47 (m, 1H, $\mathbf{H}_3$), 4.57 (d, ^3J = 8.7 Hz, 1H, $\mathbf{H}_1$), 5.91 (s, 2H, O-C$\mathbf{H}_2$-O), 6.53-6.69 (m, 2H, **H**-Ar), 6.93 (d, ^3J = 7.88 Hz, 1H, **H**-Ar), 7.15-7.58 (m, 10H, **H**-Ar), 7.65 (d, ^3J = 8.7 Hz, 2H, **H**-Ar), 7.84 (d, ^3J = 8.7 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 43.5 (**C**H_2), 43.9 (**C**-H_3), 56.1 (**C**-H_1), 63.3 (**C**-H_2), 100.9 (O-**C**H_2-O), 108.2 (**C**H-Ar), 108.5 (**C**H-Ar), 122.0 (**C**H-Ar), 123.2 (**C**H-Ar), 125.1 (**C**H-Ar), 127.5 (**C**H-Ar), 127.5 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.4 (**C**H-Ar), 128.4 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 132.0 (**C**H-Ar), 133.1 (**C**H-Ar), 136.8 (**C**-Ar), 137.4 (**C**-Ar), 137.7 (**C**-Ar), 144.4 (**C**-Ar), 144.5 (**C**-Ar), 146.5 (**C**-Ar), 147.9 (**C**-Ar), 198.4 (**C**=O), 201.7 (**C**=O) ppm.

(1S, 2S*, 3S*)*-2-Benzoyl-1-benzoylmethyl-3-(4-fluorophenyl)indane, **2bd**



2bd

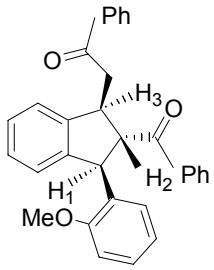
R_f (hexane - AcOEt, 85:15) = 0.2.

^{1}H-RMN ($CDCl_3$, 500 MHz): δ 3.34 (dd, ^2J = 17.2 Hz, ^3J = 7.9 Hz, 1H, $\mathbf{H}_{4'}$), 3.65 (dd, ^2J = 17.1 Hz, ^3J = 5.7 Hz, 1H, $\mathbf{H}_4$), 4.23 (t, ^3J = 8.0 Hz, 1H, $\mathbf{H}_2$), 4.42-4.48 (m, 1H, $\mathbf{H}_3$),

4.65 (d, ^3J = 8.0 Hz, 1H, $\mathbf{H}_1$), 6.90-6.98 (m, 2H, $\mathbf{H}_{Forto}$-Ar), 7.11-7.15 (m, 2H, H_{Fmeta}-Ar), 7.22-7.31 (m, 6H, **H**-Ar), 7.41-7.48 (m, 3H, **H**-Ar), 7.53-7.58 (m, 1H, **H**-Ar), 7.62 (d, ^3J = 8.2 Hz, 2H, **H**-Ar), 7.87 (d, ^3J = 8.2 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 43.2 (**C**H_2), 43.9 (**C**-H_3), 55.6 (**C**-H_1), 63.4 (**C**-H_2) 115.3 (**C**H-Ar), 115.7 (**C**H-Ar), 123.3 (**C**H-Ar), 124.9 (**C**H-Ar), 127.6 (**C**H-Ar), 127.6 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.4 (**C**H-Ar), 128.4 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 129.9 (**C**H-Ar), 130.1 (**C**H-Ar), 132.9 (**C**H-Ar), 133.2 (CH-Ar), 136.8 (**C**-Ar), 137.6 (**C**-Ar), 139.2 (**C**-Ar), 144.2 (**C**-Ar), 144.5 (**C**-Ar), 159.5 (**C**-F Ar), 164.4 (**C**-F Ar), 198.4 (**C**=O), 201.5 (**C**=O) ppm.

(1S, 2S*, 3R*)*-2-benzoyl-1-benzoylmethyl-3-(2-methoxiphenyl)indane, **2be**



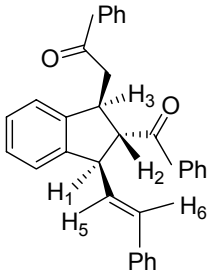
2be

R_f (hexane - AcOEt, 85:15) = 0.2.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.23 (dd, ^2J = 16.7 Hz, ^3J = 7.8 Hz, 1H, $\mathbf{H}_{4'}$), 3.27 (s, 3H, OC$\mathbf{H}_3$) 3.60 (dd, ^2J = 16.7 Hz, ^3J = 5.7 Hz, 1H, $\mathbf{H}_4$), 4.05 (t, ^3J = 7.7 Hz, 1H, $\mathbf{H}_2$), 4.37-4.51 (m, 1H, $\mathbf{H}_3$), 4.99 (d, ^3J = 7.9 Hz, 1H, $\mathbf{H}_1$), 6.65 (d, ^3J = 7.6 Hz, 1H, **H**-Ar), 6.85-7.65 (m, 15H, **H**-Ar), 7.84 (d, ^3J = 7.0 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 44.1 (**C**-H_3), 44.4 (**C**H_2), 49.5 (O**C**H_3), 54.6 (**C**-H_1), 61.5 (**C**-H_2) 110.3 (**C**H-Ar), 120.7 (**C**H-Ar), 123.6 (**C**H-Ar), 125.2 (**C**H-Ar), 127.1 (**C**H-Ar), 127.3 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 128.1 (**C**H-Ar), 128.1 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 132.2 (**C**-Ar), 132.4 (**C**H-Ar), 133.0 (**C**H-Ar), 136.9 (**C**-Ar), 137.6 (**C**-Ar), 143.8 (**C**-Ar), 145.2 (**C**-Ar), 157.3 (**C**-Ar), 198.7 (**C**=O), 201.6 (**C**=O) ppm.

(1S, 2S*, 3R*)*-2-Benzoyl-1-benzoylmethyl-3-(styryl)indane, **2bf**



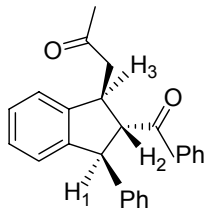
2bf

R_f (hexane - AcOEt, 90:10) = 0.5.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.31 (dd, ^2J = 17.1 Hz, ^3J = 7.9 Hz, 1H, $\mathbf{H}_{4'}$), 3.63 (dd, ^2J = 17.1 Hz, ^3J = 5.6 Hz, 1H, $\mathbf{H}_4$), 4.04-4.28 (m, 2H, $\mathbf{H}_1$ y $\mathbf{H}_2$), 4.37-4.52 (m, 1H, $\mathbf{H}_3$), 6.31 (dd, ^3J = 7.7, 15.7 Hz, 1H, $\mathbf{H}_5$), 6.43 (d, ^3J = 15.6 Hz, 1H, $\mathbf{H}_6$), 7.12-7.61 (m, 15H, **H**-Ar), 7.83-8.03 (m, 4H, **H**-Ar), ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 43.7 (**C**-H_3), 44.0 (**C**H_2), 53.8 (**C**-H_1), 59.8 (**C**-H_2), 123.7 (**C**H-Ar), 124.8 (**C**H-Ar), 126.3 (**C**H-Ar), 126.3 (**C**H-Ar), 127.4 (**C**H-Ar), 127.5 (**C**H-Ar), 127.7 (**C**H-Ar), 128.1 (**C**H-Ar), 128.1 (**C**H-Ar), 128.4 (**C**H-Ar), 128.4 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H=CH), 128.6 (CH=**C**H), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 131.1 (**C**H-Ar), 132.4 (**C**H-Ar), 133.0 (**C**H-Ar), 133.2 (**C**H-Ar), 136.9 (**C**-Ar), 137.5 (**C**-Ar), 137.5 (**C**-Ar), 143.3 (**C**-Ar), 144.4 (**C**-Ar), 198.4 (**C**=O), 201.1 (**C**=O) ppm.

(1S, 2S*, 3S*)*-1-Acetylmethyl-2-benzoyl-3-phenylindane, **2ca**



2ca

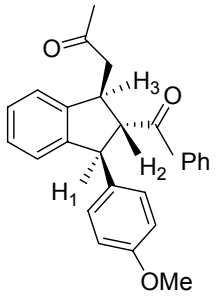
R_f (hexane - AcOEt, 80:20) = 0.3.

^{1}H-RMN ($CDCl_3$, 300 MHz): δ 2.12 (s, 3H, C$\mathbf{H}_3$), 2.77 (dd, ^2J = 17.0 Hz, ^3J = 7.5 Hz, 1H, $\mathbf{H}_{4'}$), 3.09 (dd, ^2J = 17.0 Hz, ^3J = 5.4 Hz, 1H, $\mathbf{H}_4$), 4.14 (t, ^3J = 8.6 Hz, 1H, $\mathbf{H}_2$),

4.22-4.33 (m, 1H, **H**$_3$), 4.58 (d, ^3J = 8.5 Hz, 1H, **H**$_1$), 6.93 (d, ^3J = 7.8 Hz, 1H, **H**-Ar), 7.09-7.33 (m, 10H, **H**-Ar), 7.46 (t, ^3J = 7.10 Hz, 1H, H-Ar), 7.60 (d, ^3J = 7.9 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 30.1 (**C**H$_3$) 43.5 (**C**-H$_3$), 48.29 (**C**H$_2$), 56.4 (**C**-H$_1$), 63.2 (**C**-H$_2$), 123.0 (**C**H-Ar), 125.1 (**C**H-Ar), 127.0 (**C**H-Ar), 127.4 (**C**H-Ar), 127.5 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.5 (**C**H-Ar), 128.5 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 132.9 (**C**H-Ar), 137.6 (**C**-Ar), 143.2 (**C**-Ar), 144.3 (**C**-Ar), 144.3 (**C**-Ar), 201.7 (Ph-**C**=O), 207.2 (CH$_3$-**C**=O) ppm.

(1S, 2S*, 3S*)*-1-Acetylmethyl-2-benzoyl-3-(4-methoxyphenyl)indane, **2cb**



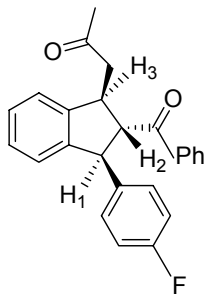
2cb

R$_f$ (hexane - AcOEt, 70:30) = 0.4.

^{1}H-RMN ($CDCl_3$, 300 MHz): δ 2.12 (s, 3H, C**H**$_3$), 2.75 (dd, ^2J = 17.0 Hz, ^3J = 7.5 Hz, 1H, **H**$_{4'}$), 3.08 (dd, ^2J = 17.0 Hz, ^3J = 5.4 Hz, 1H, **H**$_4$), 3.78 (s, 3H, -OC**H**$_3$), 4.11 (t, ^3J = 8.8 Hz, 1H, **H**$_2$), 4.19-4.30 (m, 1H, **H**$_3$), 4.54 (d, ^3J = 9.0 Hz, 1H, **H**$_1$), 6.79 (d, ^3J = 8.7 Hz, 2H, **H**-Ar), 6.85-7.34 (m, 8H, H-Ar), 7.47 (t, ^3J = 7.4 Hz, 1H, **H**-Ar), 7.62 (d, ^3J = 8.2 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 75.5 MHz): δ 30.6 (CH$_3$), 43.9 (**C**-H$_3$), 48.7 (**C**H$_2$), 55.7 (**C**-H$_1$), 56.1 (O**C**H$_3$), 63.8 (**C**-H$_2$) 114.4 (**C**H-Ar), 114.4 (**C**H-Ar), 123.4 (**C**H-Ar), 125.5 (**C**H-Ar), 127.8 (**C**H-Ar), 127.9 (**C**H-Ar), 128.5 (**C**H-Ar), 128.7 (**C**H-Ar), 128.9 (**C**H-Ar), 129.1 (**C**H-Ar), 129.8 (**C**H-Ar), 129.9 (**C**H-Ar), 133.3 (**C**H-Ar), 135.7 (**C**-Ar), 138.1 (**C**-Ar), 144.6 (**C**-Ar), 145.1 (**C**-Ar), 158.9 (**C**-Ar), 198.6 (Ph-**C**=O), 201.9 (CH$_3$-**C**=O) ppm.

(1S, 2S*, 3S*)*-1-Acetylmethyl-2-benzoyl-3-(4-fluorophenyl)indane, **2cc**



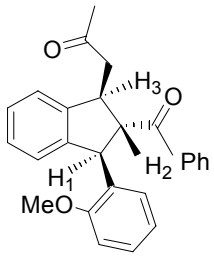
2cc

R_f (hexane - AcOEt, 70:30) = 0.3.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.12 (s, 3H, C**H**$_3$) 2.75 (dd, ^2J = 16.8 Hz, ^3J = 7.2 Hz, 1H, **H**$_{4'}$), 3.07 (dd, ^2J = 16.8 Hz, ^3J = 5.3 Hz, 1H, **H**$_4$), 4.11 (t, ^3J = 9.1 Hz, 1H, **H**$_2$), 4.15-4.31 (m, 1H, **H**$_3$), 4.56 (d, ^3J = 9.1 Hz, 1H, **H**$_1$), 6.81-7.35 (m, 10H, **H**-Ar), 7.47 (t, ^3J = 7.4 Hz, 1H, **H**-Ar), 7.60 (d, ^3J = 7.3 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 75.5 MHz): δ 30.7 (**C**H$_3$), 43.8 (**C**-H$_3$), 48.3 (**C**H$_2$), 56.0 (**C**-H$_1$), 63.7 (**C**-H$_2$) 115.7 (**C**H-Ar), 116.0 (**C**H-Ar), 123.4 (**C**H-Ar), 125.4 (**C**H-Ar), 128.0 (**C**H-Ar), 128.0 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 128.3 (**C**H-Ar), 130.4 (**C**H-Ar), 130.5 (**C**H-Ar), 133.5 (**C**H-Ar), 138.0 (**C**-Ar), 139.3 (**C**-Ar), 144.6 (**C**-Ar), 144.6 (**C**-Ar), 160.6 (**C**-F Ar), 163.9 (**C**-F Ar), 202.0 (Ph-**C**=O), 207.6 (CH$_3$-**C**=O) ppm.

(1S, 2S*, 3R*)*-1-Acetylmethyl-2-benzoyl-3-(2-methoxyphenyl)indane, **2cd**



2cd

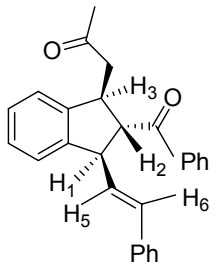
R_f (hexane - AcOEt, 80:20) = 0.2.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.12 (s, 3H, C**H**$_3$), 2.68 (dd, ^2J = 16.4 Hz, ^3J = 7.8 Hz, 1H, **H**$_{4'}$), 3.06 (dd, ^2J = 16.4 Hz, ^3J = 5.7 Hz, 1H, **H**$_4$), 3.26 (s, 3H, OC**H**$_3$), 3.98 (t, ^3J =

8.1 Hz, 1H, **H**$_2$), 4.22-4.36 (m, 1H, **H**$_3$), 4.95 (d, ^3J = 8.5 Hz, 1H, **H**$_1$), 6.63 (d, ^3J = 8.3 Hz, 1H, **H**-Ar), 6.84-7.32 (m, 9H, **H**-Ar), 7.45 (t, ^3J = 7.3 Hz, 1H, **H**-Ar), 7.61 (d, ^3J = 7.3 Hz, 2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 75.5 MHz): δ 30.6 (**C**H$_3$), 43.9 (**C**-H$_3$), 49.5 (**C**-H$_1$), 49.9 (**C**H$_2$), 55.0 (O**C**H$_3$), 62.0 (**C**-H$_2$), 110.6 (**C**H-Ar), 121.1 (**C**H-Ar), 123.7 (**C**H-Ar), 125.5 (**C**H-Ar), 127.5 (**C**H-Ar), 127.7 (**C**H-Ar), 128.4 (**C**H-Ar), 128.5 (**C**H-Ar), 128.6 (**C**H-Ar), 128.7 (**C**H-Ar), 128.9 (**C**H-Ar), 129.0 (**C**H-Ar), 132.2 (**C**H-Ar), 132.9 (**C**-Ar), 137.9 (**C**-Ar), 144.2 (**C**-Ar), 145.3 (**C**-Ar), 157.7 (**C**-Ar), 202.0 (Ph-**C**=O), 208.0 (CH$_3$-**C**=O) ppm.

(1S, 2S*, 3R*)*-1-Acetylmethyl 2-benzoyl-3-(styryl)indane, **2ce**



2ce

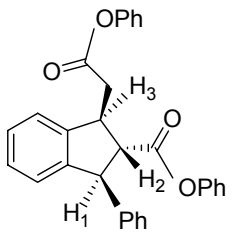
R$_f$ (hexane - AcOEt, 80:20) = 0.3.

^{1}H-RMN ($CDCl_3$, 200 MHz): δ 2.13 (s, 3H, C**H**$_3$), 2.74 (dd, ^2J = 16.8 Hz, ^3J = 7.8 Hz, 1H, **H**$_{4'}$), 3.06 (dd, ^2J = 16.8 Hz, ^3J = 5.8 Hz, 1H, **H**$_4$), 3.99 (t, ^3J = 7.9 Hz, 1H, **H**$_2$), 4.14 (t, ^3J = 7.9 Hz, 1H, **H**$_1$), 4.15-4.31 (m, 1H, **H**$_3$), 6.25 (dd, ^3J = 8.1, 15.6 Hz, 1H, **H**$_5$), 6.36 (t, ^3J = 15.6 Hz, 1H, **H**$_6$), 7.10-7.59 (m, 12H, **H**-Ar), 7.96 (d, ^3J = 8.6 Hz ,2H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 75.5 MHz): δ 30.6 (**C**H$_3$), 43.6 (**C**-H$_3$), 49.2 (**C**H$_2$), 54.1 (**C**-H$_1$), 60.1 (**C**-H$_2$), 123.8 (**C**H-Ar), 125.2 (**C**H-Ar), 126.7 (**C**H-Ar), 127.9 (**C**H-Ar), 127.9 (**C**H-Ar), 128.1 (**C**H-Ar), 128.4 (**C**H-Ar), 128.5 (**C**H-Ar), 128.6 (**C**H-Ar), 128.8 (**C**H-Ar), 128.9 (**C**H-Ar), 129.0 (**C**H-Ar), 129.1 (**C**H-Ar), 131.2 (**C**H-Ar), 133.0 (**C**H=CH), 133.5 (CH=**C**H), 137.2 (**C**-Ar), 137.9 (**C**-Ar), 143.6 (**C**-Ar), 144.4 (**C**-Ar), 201.6 (Ph-**C**=O), 207.6 (CH$_3$-**C**=O) ppm.

(1S,2S*,3R*)*-3-Phenyl-2-phenyloxycarbonyl-3-phenyloxycarbonylmethyl-2-benzoyl-3-phenyl)indane, **2ea**

A mixture of **2ba** (42 mg, 0.1 mmol), mCPBA (70%, 348.3 mg, 2.02 mmol), and p-TsOH.H_2O (69.14 mg, 0.36 mmol) in CH_2Cl_2 (1mL) was stirred at rt for 40 h. The mixture was diluted with CH_2Cl_2 and washed with saturated Na_2SO_3 aqueous solution, saturated $NaHCO_3$ aqueous solution, and brine. The organic phase was dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography (Hexane-AcOEt, 85:15) to afford **2ea**.(85%)



2ea

R_f (hexane - AcOEt, 80:20) = 0.5.

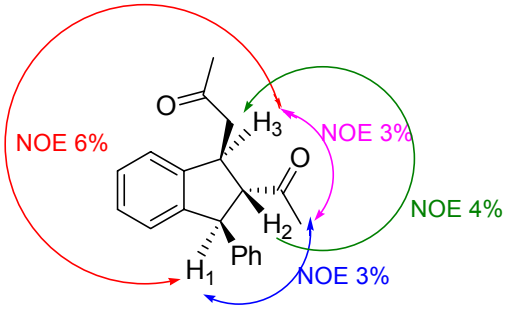
^{1}H-RMN ($CDCl_3$, 200 MHz): δ 3.11 (dd, ^2J = 16.0 Hz, ^3J = 7.9 Hz, 1H, $\mathbf{H}_{4'}$), 3.37 (dd, ^2J = 16.1 Hz, ^3J = 5.1 Hz, 1H, $\mathbf{H}_4$), 3.47 (t, ^3J = 9.7 Hz, 1H, $\mathbf{H}_2$), 4.17-4.33 (m, 1H, $\mathbf{H}_3$), 4.80 (d, ^3J = 10.0 Hz, 1H, $\mathbf{H}_1$), 6.91-7.45 (m, 19H, **H**-Ar) ppm.

^{13}C-RMN ($CDCl_3$, 50.5 MHz): δ 38.7 (**C**H_2), 44.1 (**C**-H_3), 54.8 (**C**-H_1), 61.2 (**C**-H_2), 121.6 (**C**H-Ar), 121.6 (**C**H-Ar), 123.0 (**C**H-Ar), 125.1 (**C**H-Ar), 125.8 (**C**H-Ar), 125.9 (**C**H-Ar), 127.3 (**C**H-Ar), 127.6 (**C**H-Ar), 127.9 (**C**H-Ar), 128.3 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 128.6 (**C**H-Ar), 128.7 (**C**H-Ar), 128.7 (**C**H-Ar), 129.3 (**C**H-Ar), 129.3 (**C**H-Ar), 129.4 (**C**H-Ar), 129.7 (**C**H-Ar), 133.1 (**C**-Ar), 142.4 (**C**-Ar), 142.8 (**C**-Ar), 144.3 (**C**-Ar), 150.7 (**C**-Ar), 170.4 (Ph-**C**=O), 172.4 (CH_3-**C**=O) ppm.

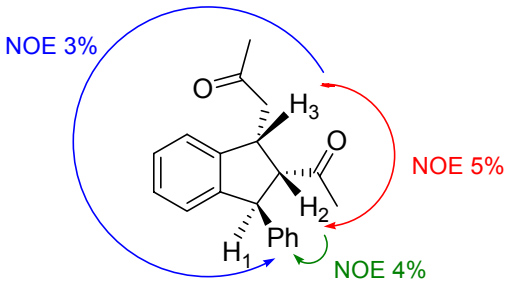
Stereochemical assignment of the reaction products.

The stereochemistry of the reaction products **2** and **3** was assigned by the coupling constants in the corresponding ^{1}H-NMR spectra and by NOE meassurements. NOE data of **2aa**, **3aa**, **2bd** and **2ca** are shown, together with the corresponding NOE spectra.

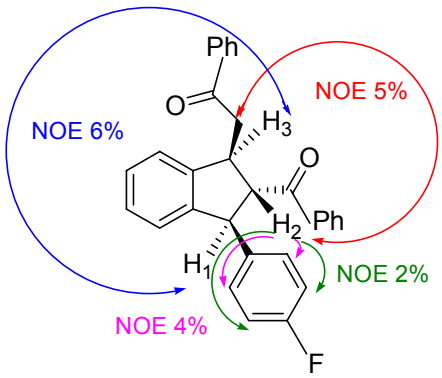
The assignment (regiochemistry) of compounds **2c** was based on their HMBC spectra, as shown for **2ca**.



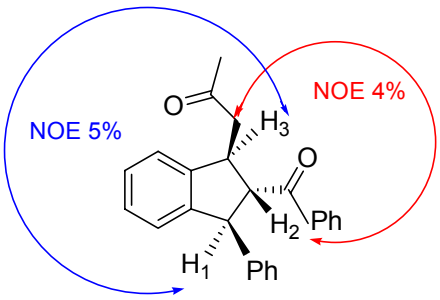
2aa



3aa



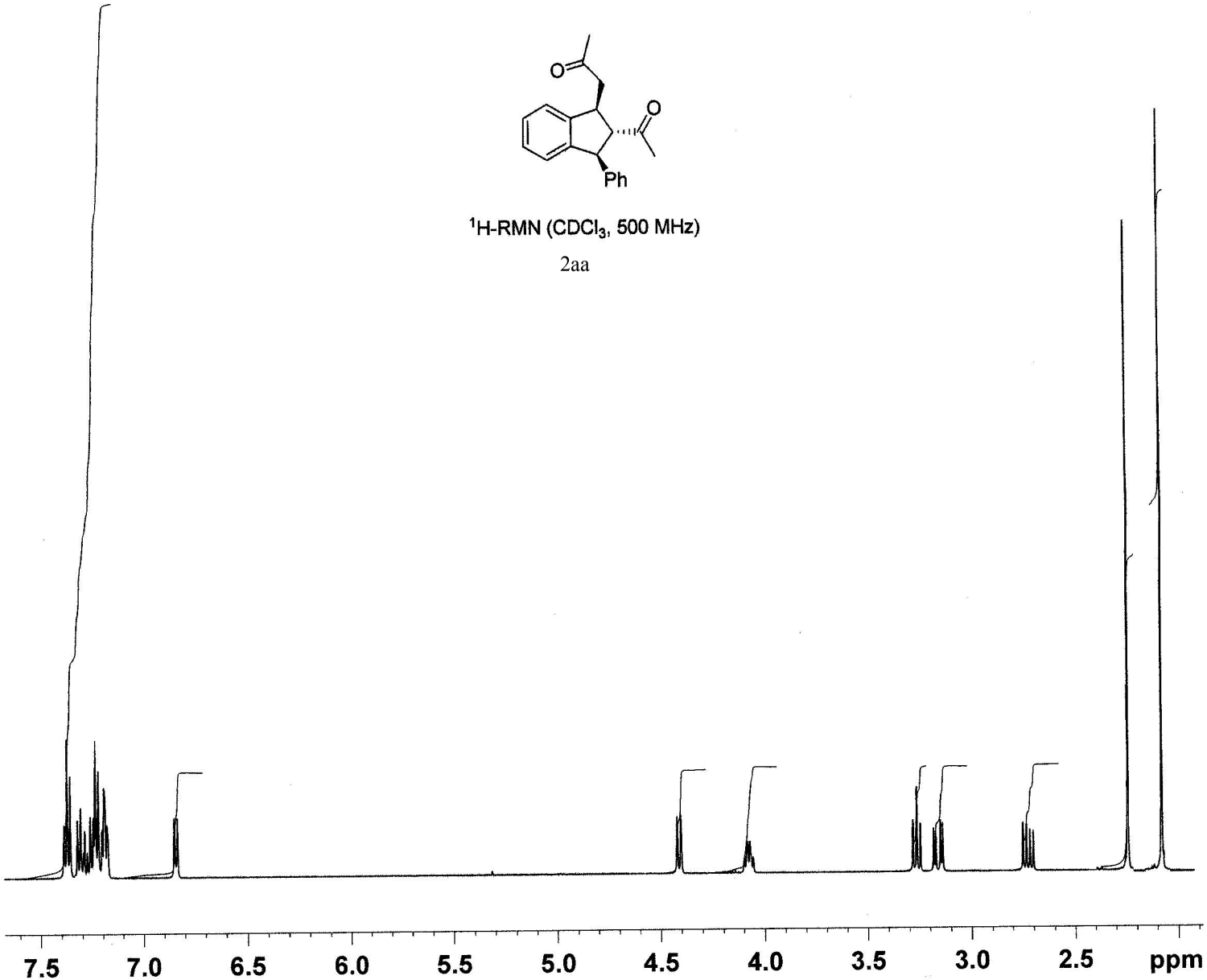
2bd

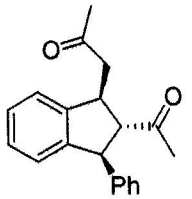


2ca

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

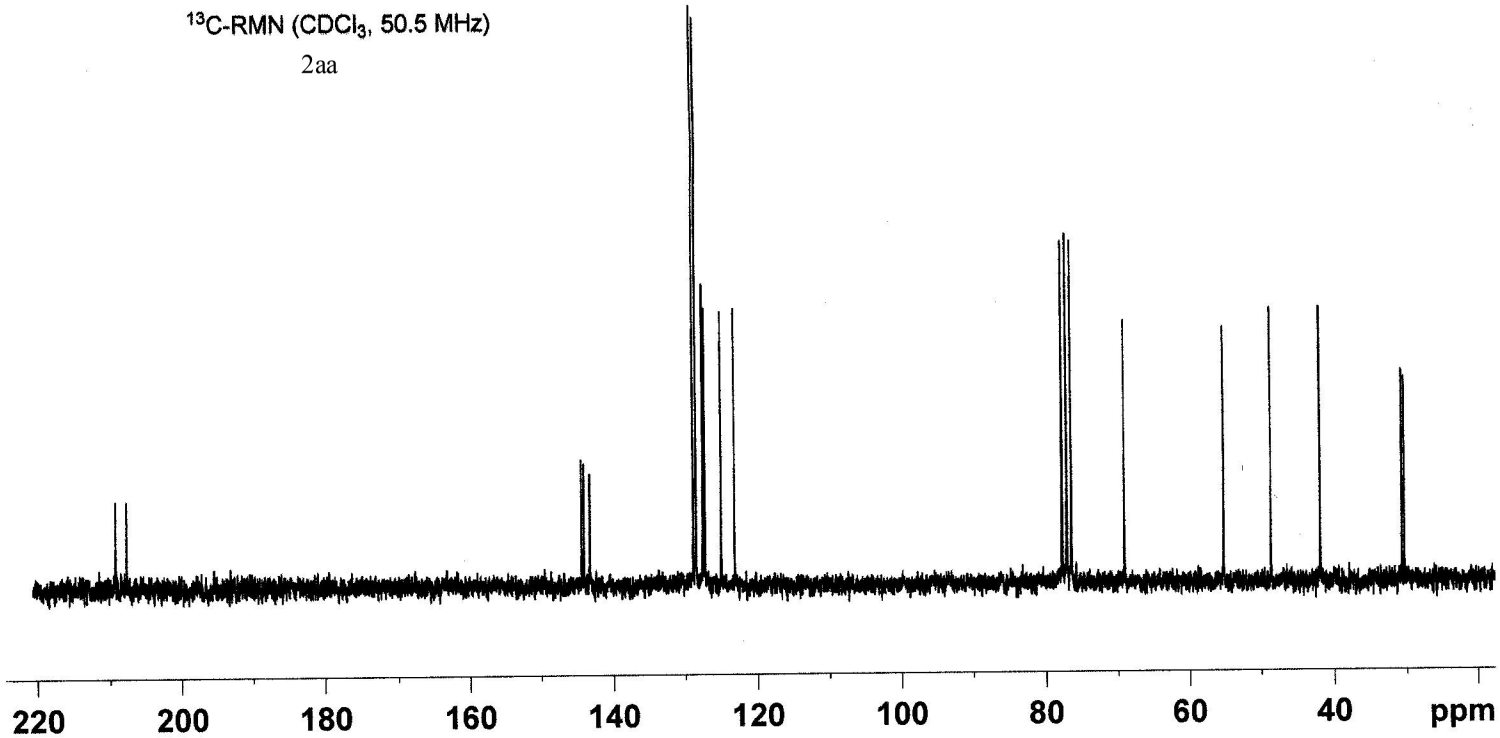
2aa

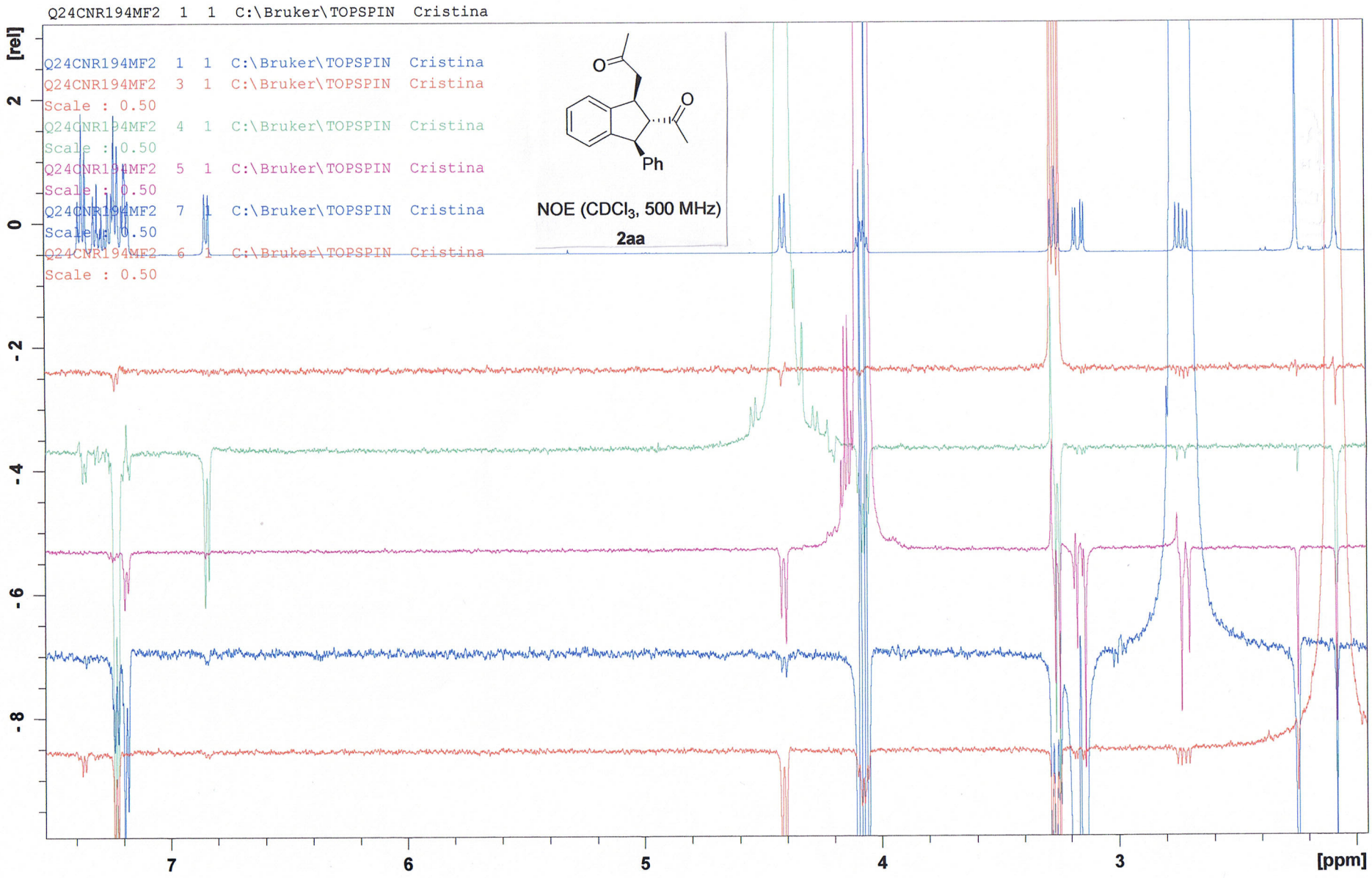




^{13}C-RMN ($CDCl_3$, 50.5 MHz)

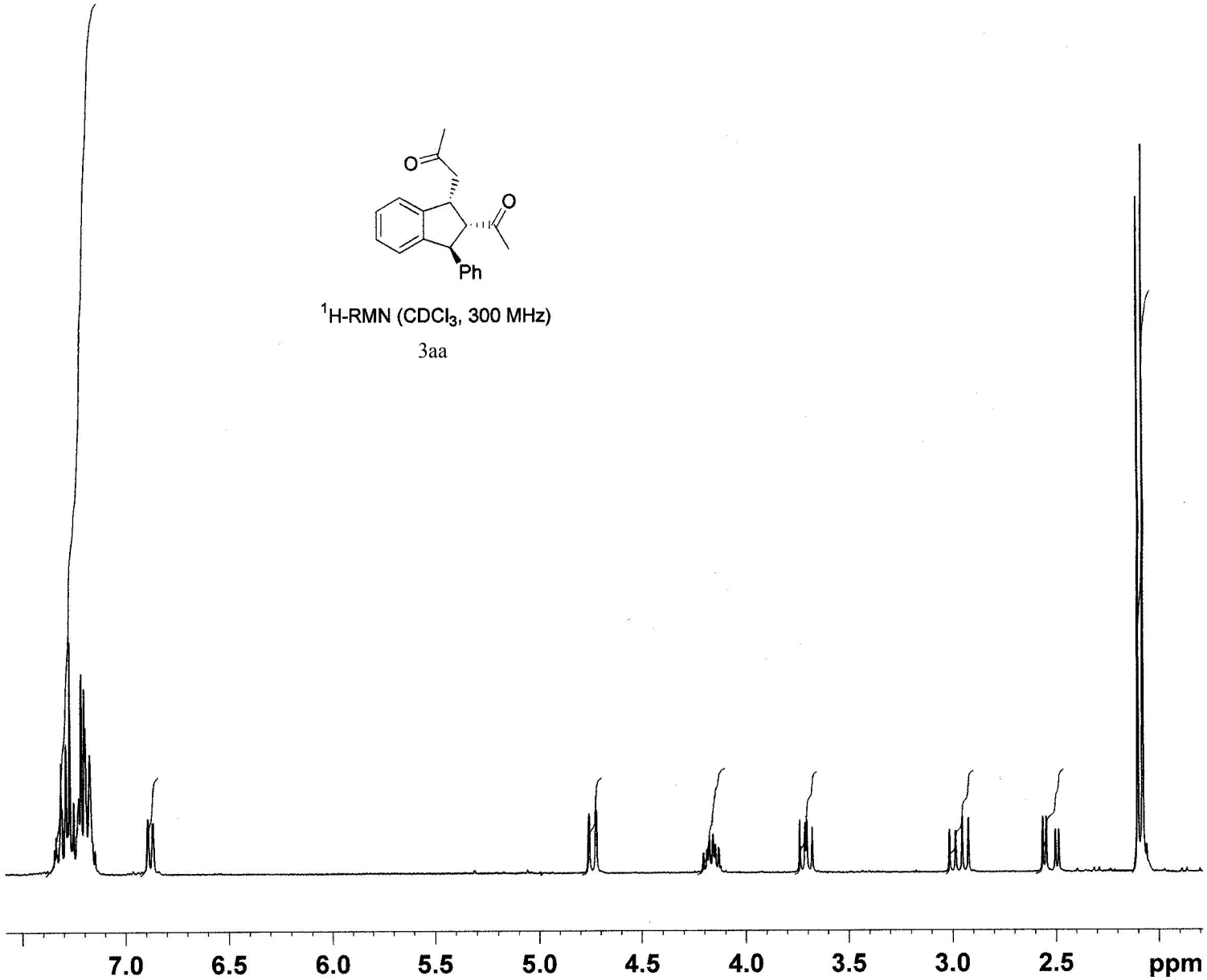
2aa

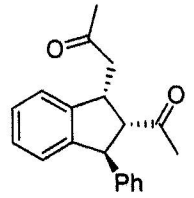



Q24CNR194MF2 1 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF2 1 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF2 3 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.50
Q24CNR194MF2 4 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.50
Q24CNR194MF2 5 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.50
Q24CNR194MF2 7 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.50
Q24CNR194MF2 6 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.50
O
O
Ph
NOE (CDCl3, 500 MHz)
2aa
[rel]
2
0
-2
-4
-6
-8
7
6
5
4
3
[ppm]

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

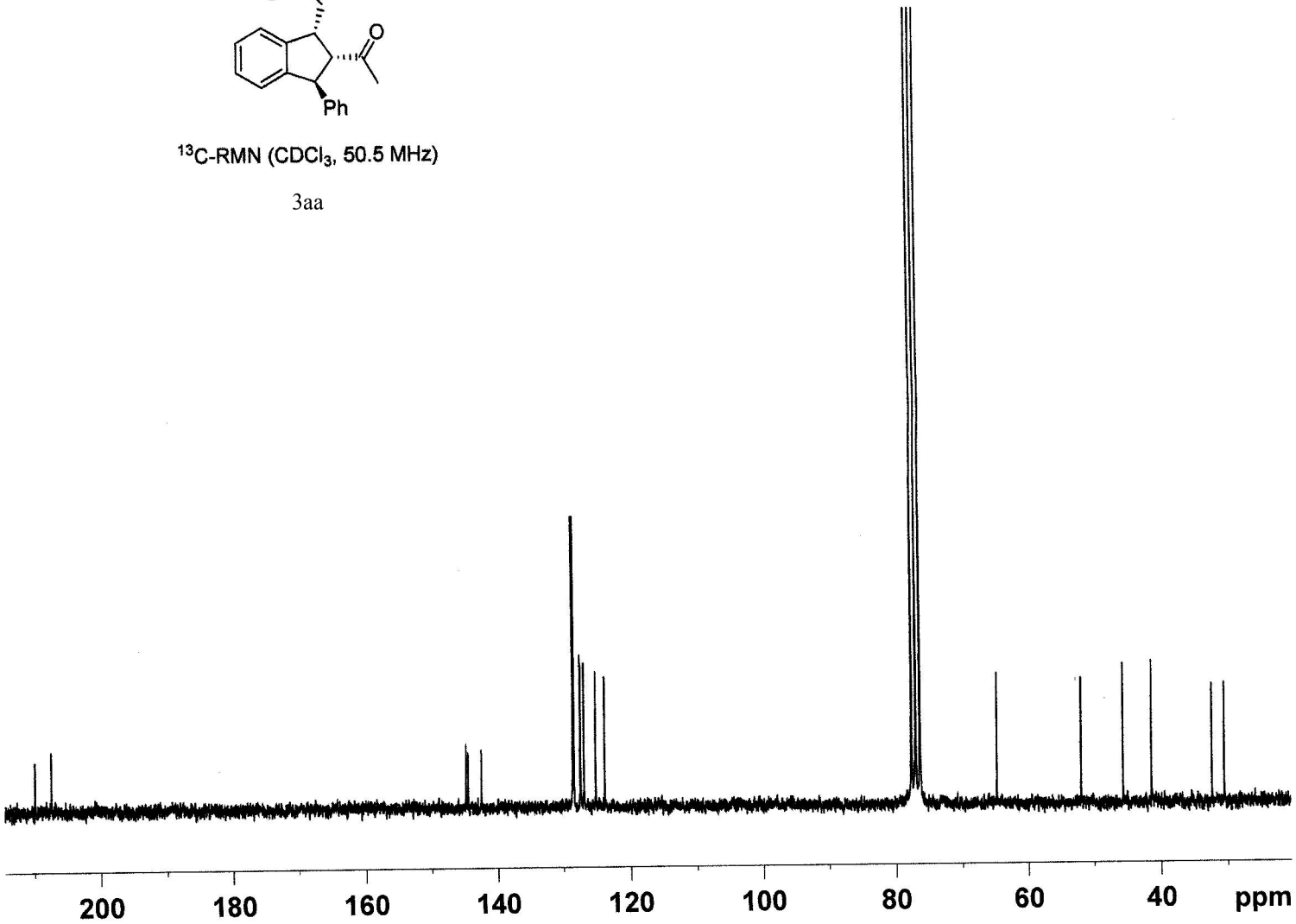
3aa

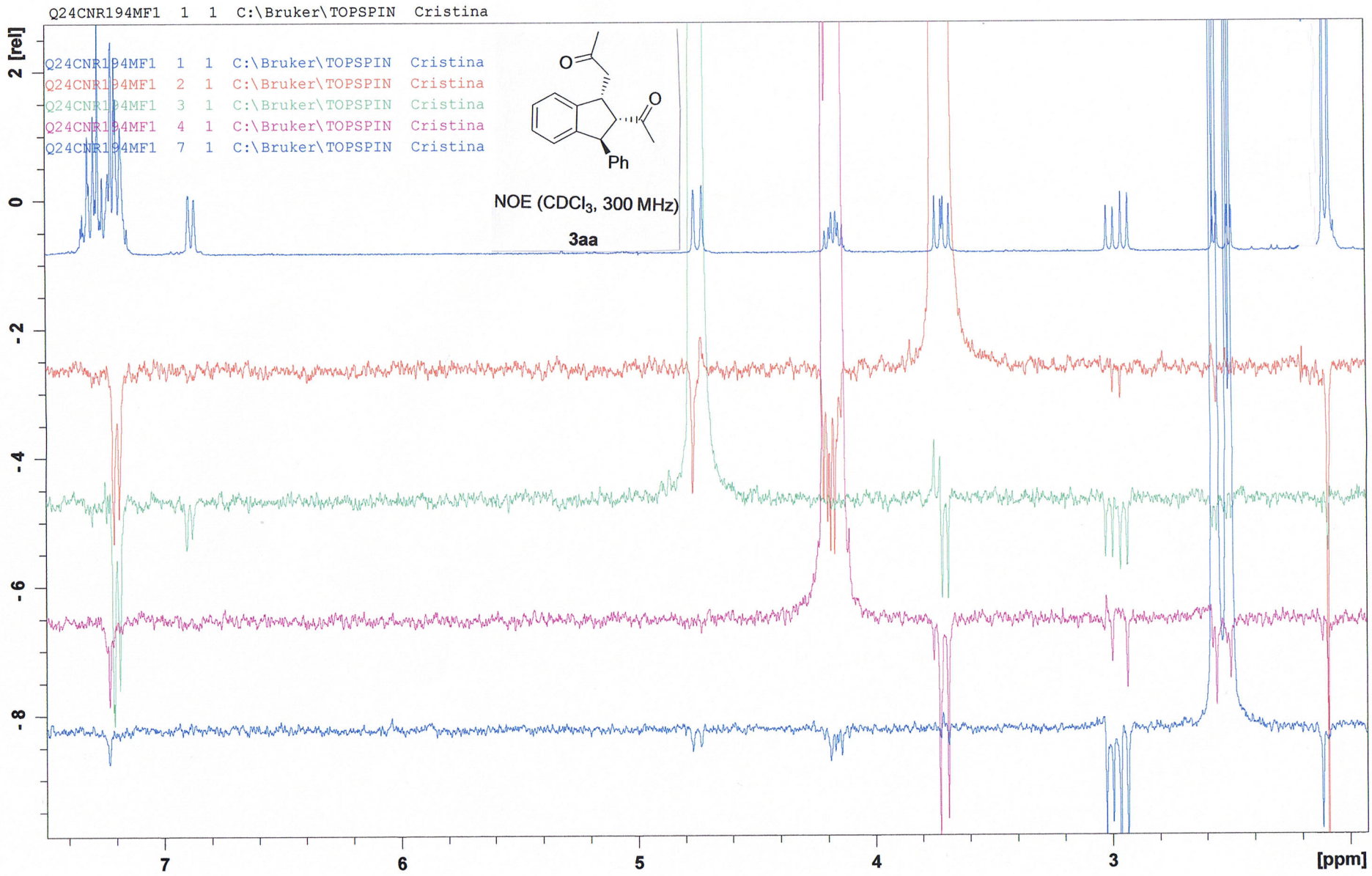


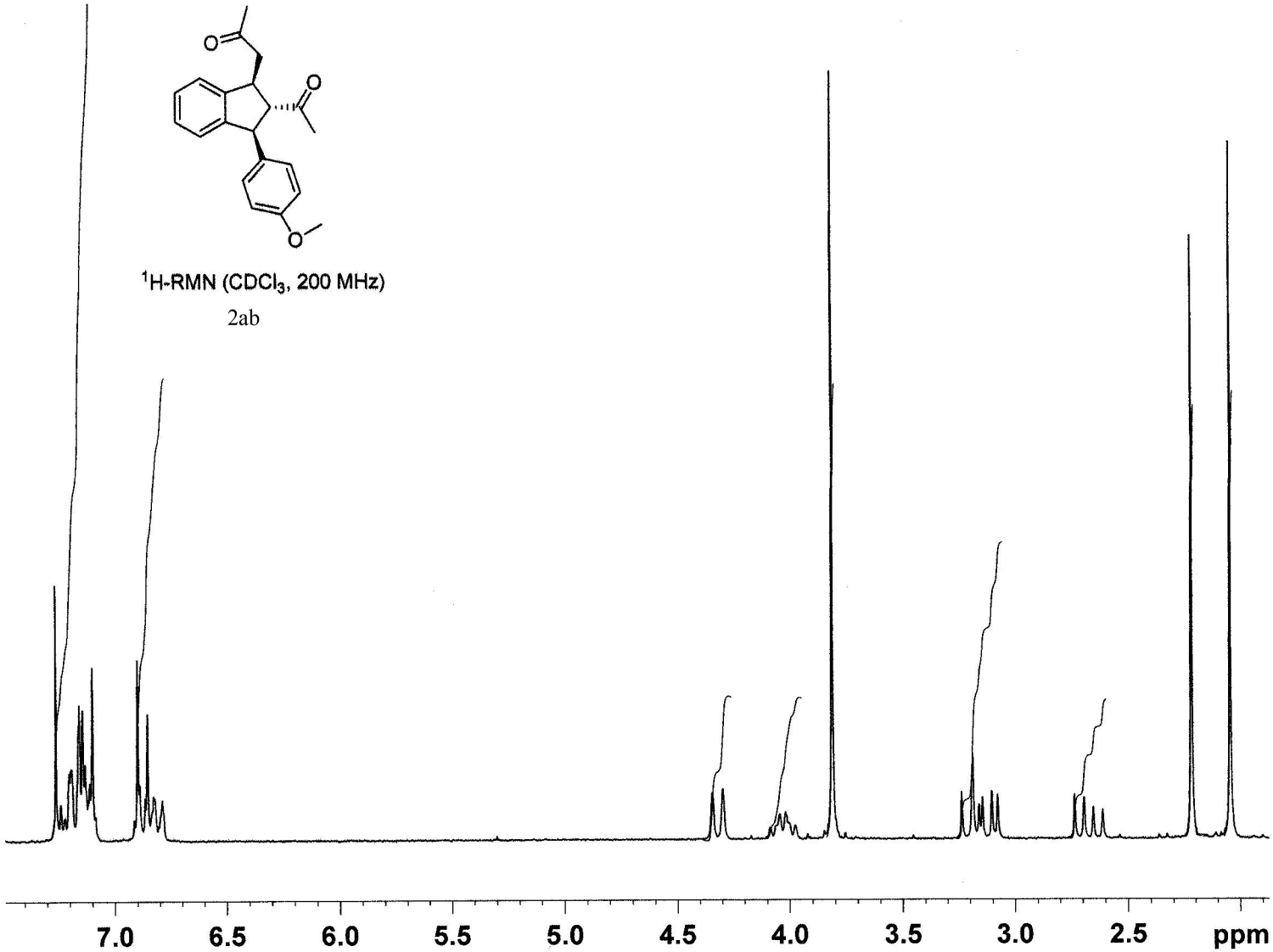


^{13}C-RMN ($CDCl_3$, 50.5 MHz)

3aa

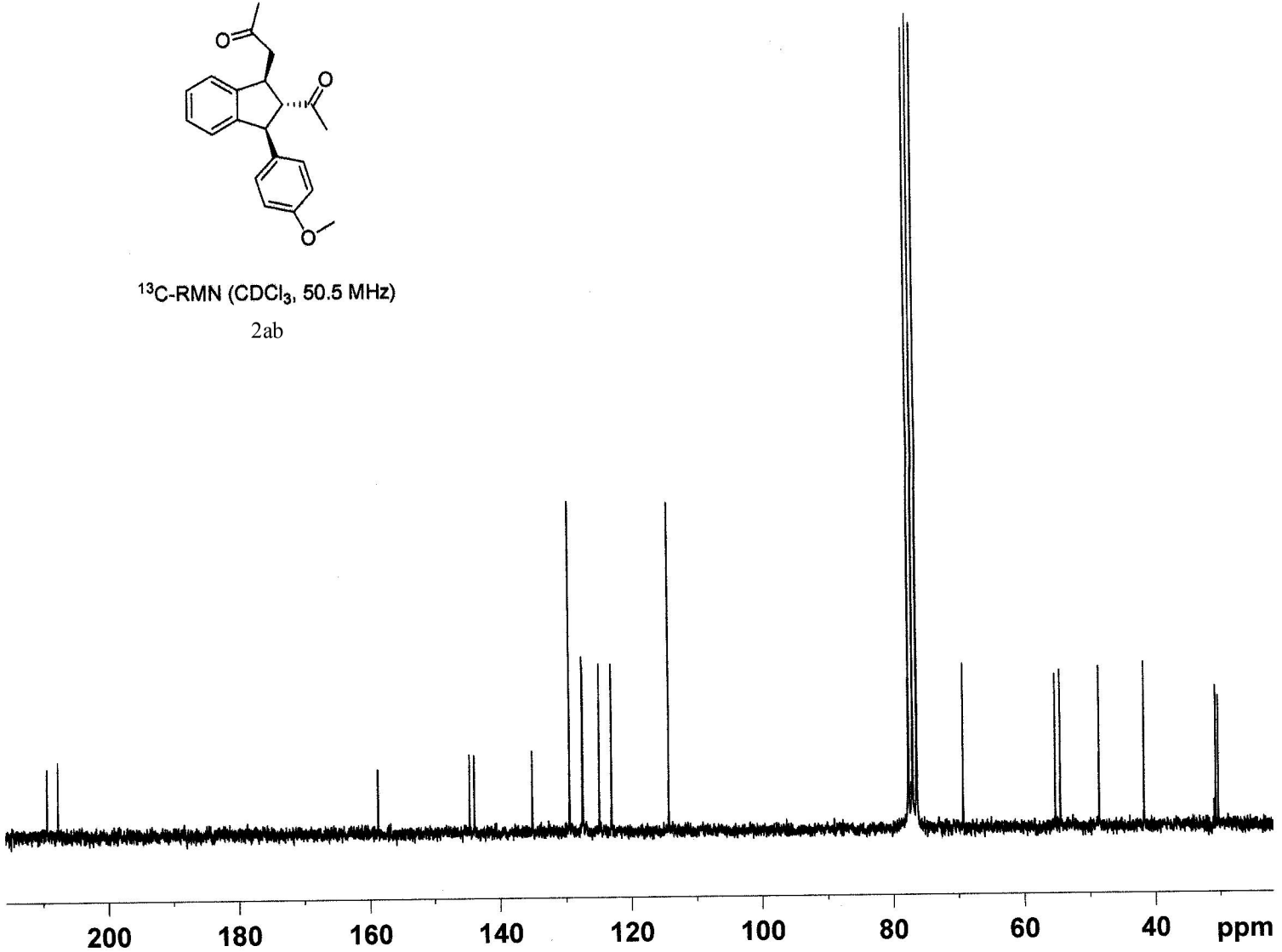


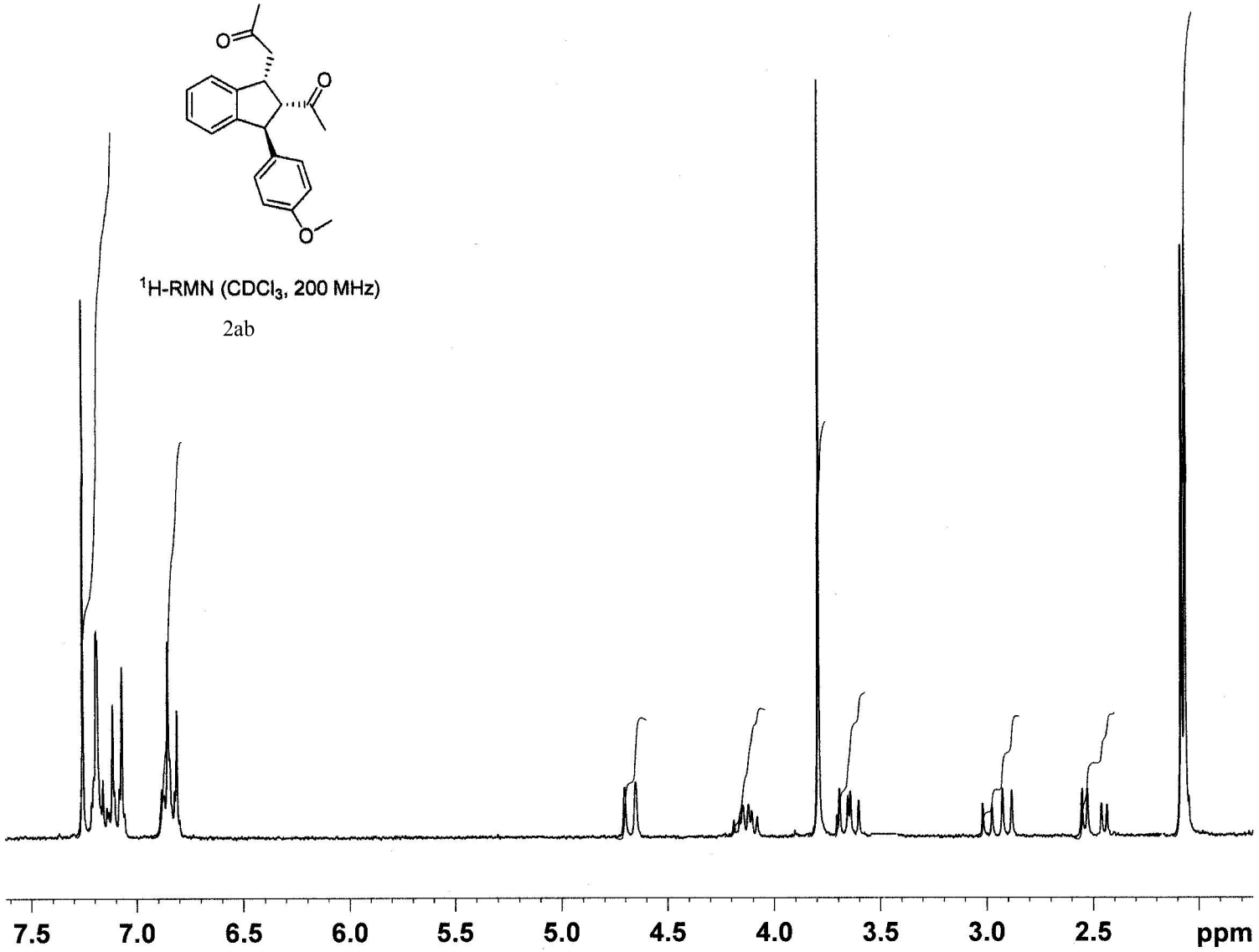

Q24CNR194MF1 1 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF1 1 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF1 2 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF1 3 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF1 4 1 C:\Bruker\TOPSPIN Cristina
Q24CNR194MF1 7 1 C:\Bruker\TOPSPIN Cristina
O
O
Ph
NOE (CDCl3, 300 MHz)
3aa
2 [rel]
0
-2
-4
-6
-8
7
6
5
4
3
[ppm]


^{1}H-RMN ($CDCl_3$, 200 MHz)
2ab
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

^{13}C-RMN ($CDCl_3$, 50.5 MHz)

2ab



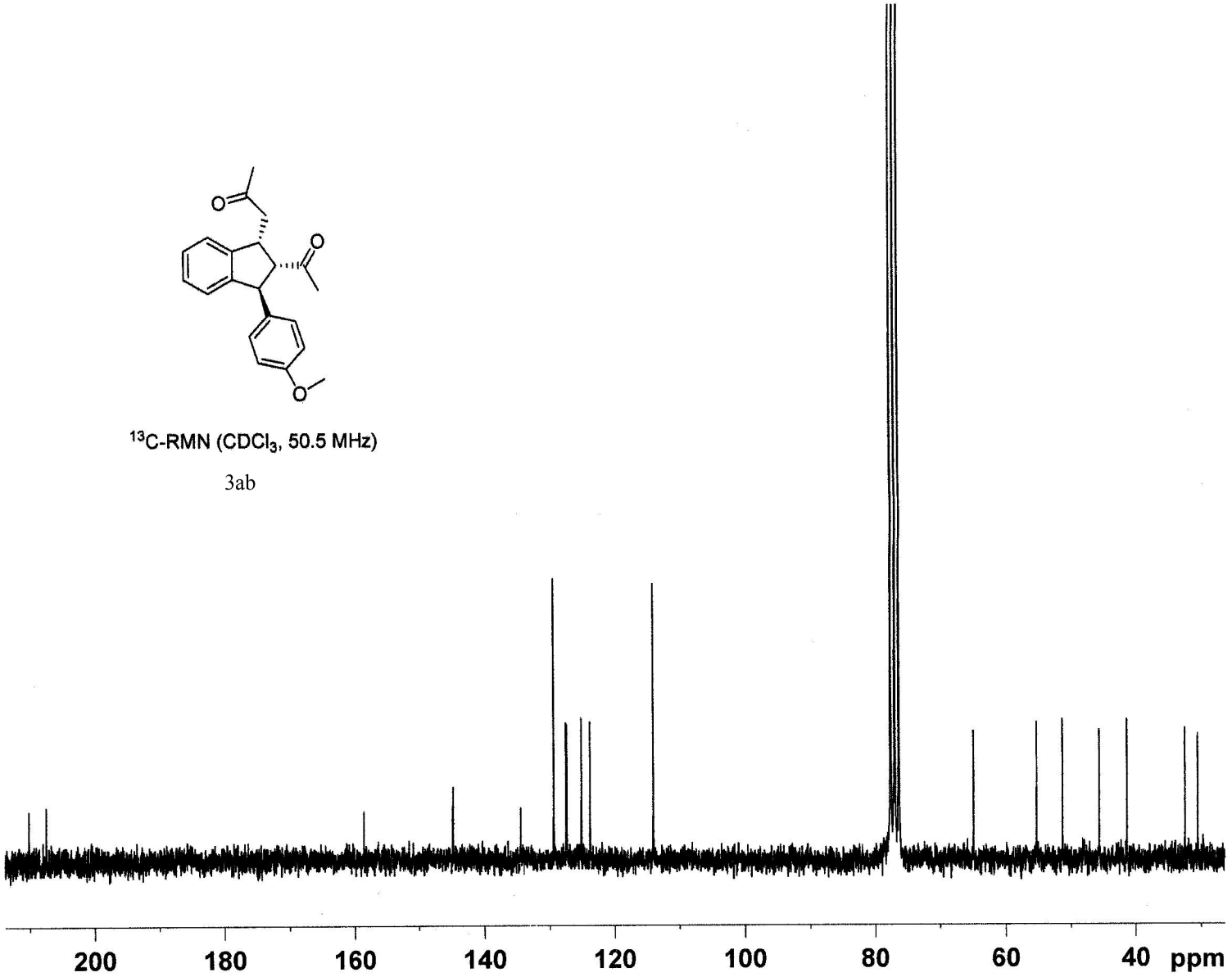


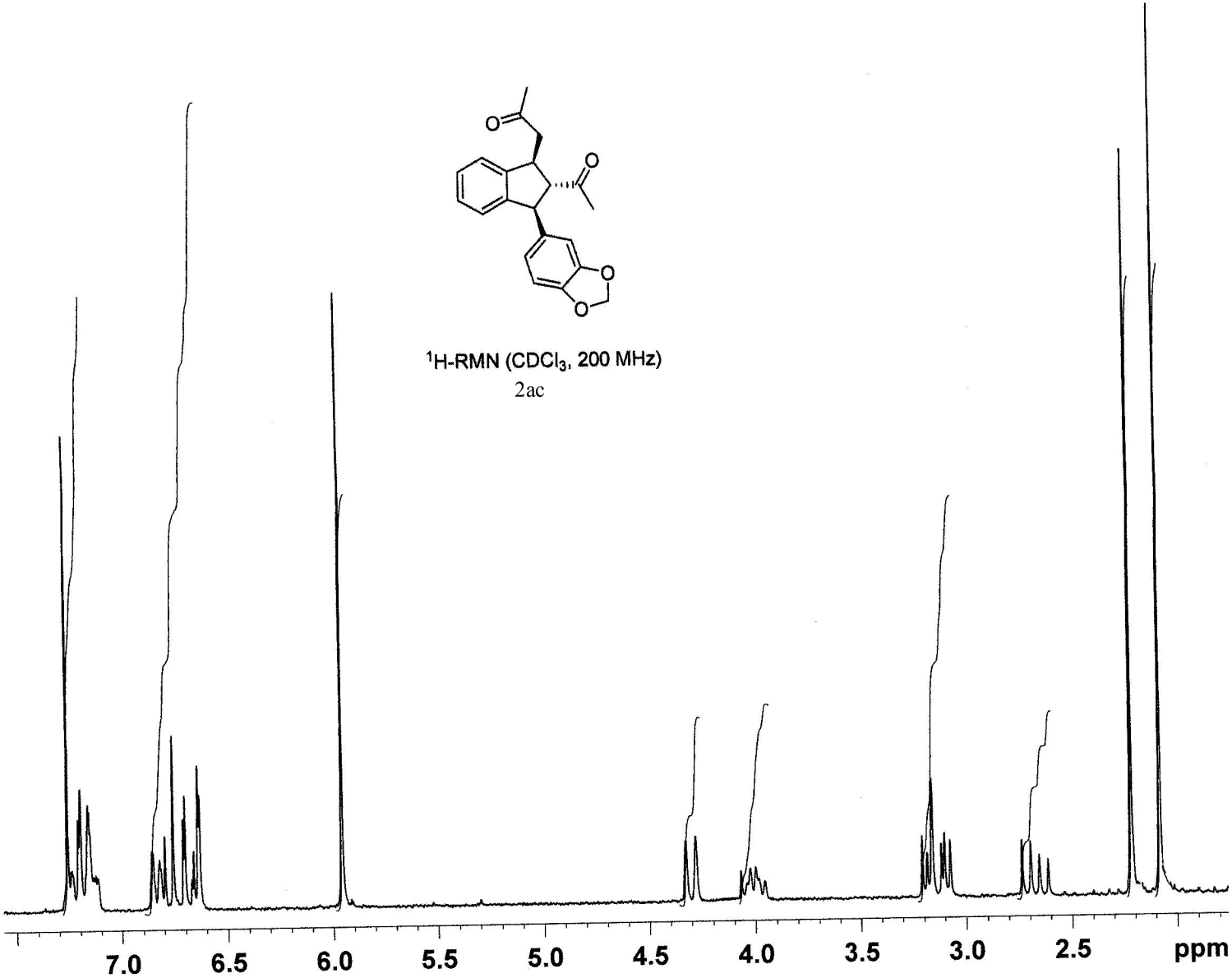
^{1}H-RMN ($CDCl_3$, 200 MHz)

2ab

^{13}C-RMN ($CDCl_3$, 50.5 MHz)

3ab



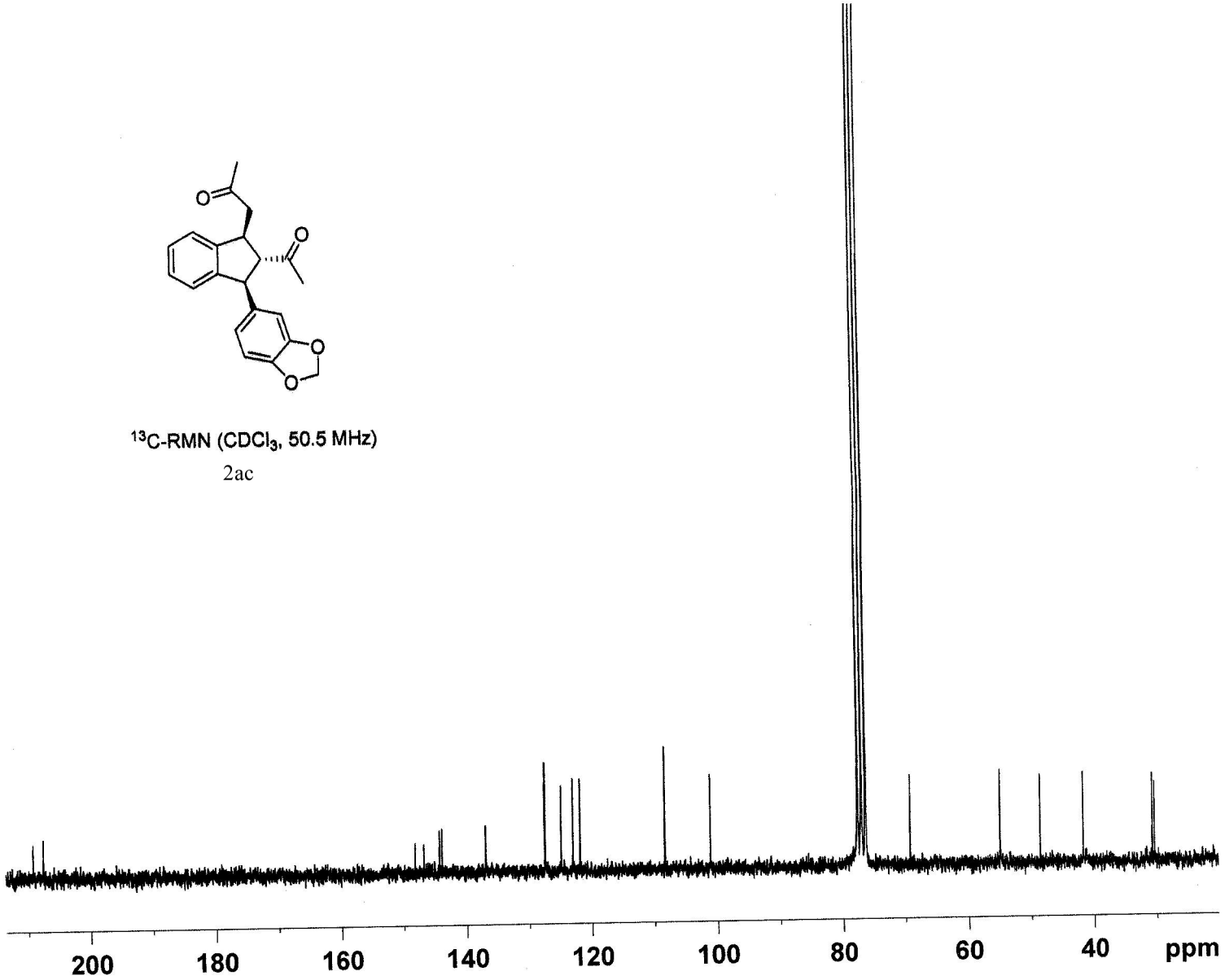


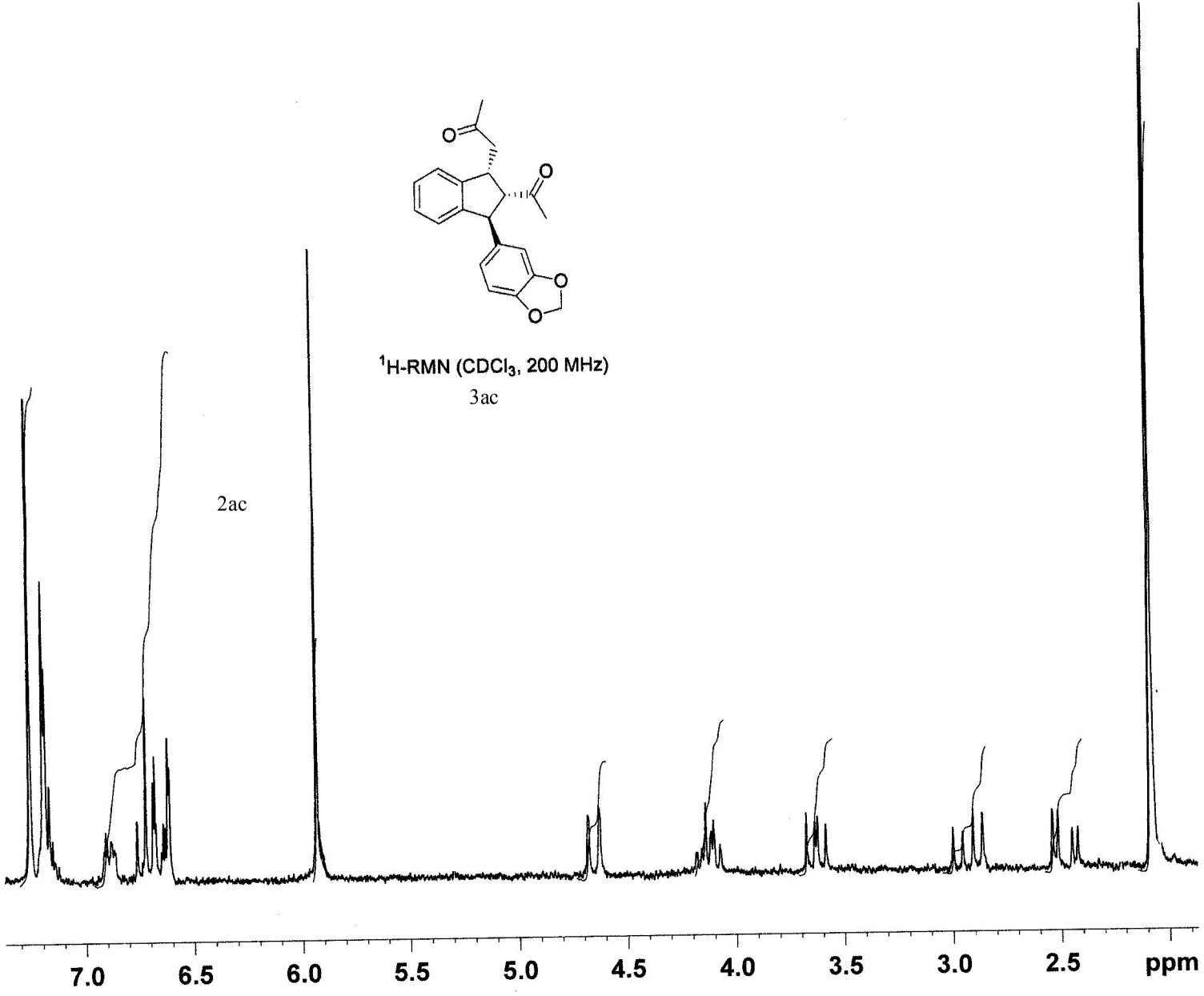
^{1}H-RMN ($CDCl_3$, 200 MHz)

2ac

^{13}C-RMN ($CDCl_3$, 50.5 MHz)

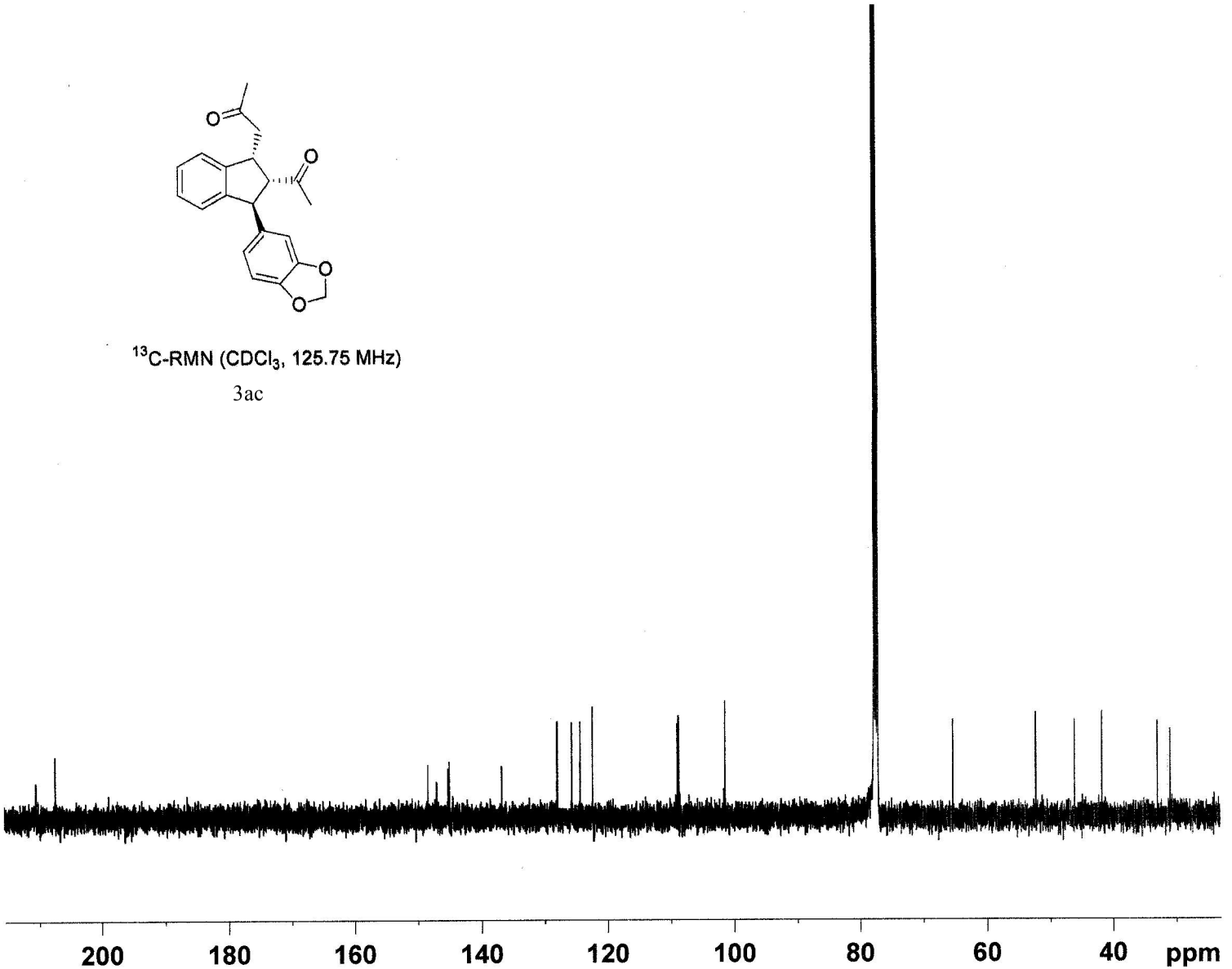
2ac




^{1}H-RMN ($CDCl_3$, 200 MHz)
3ac
2ac
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm

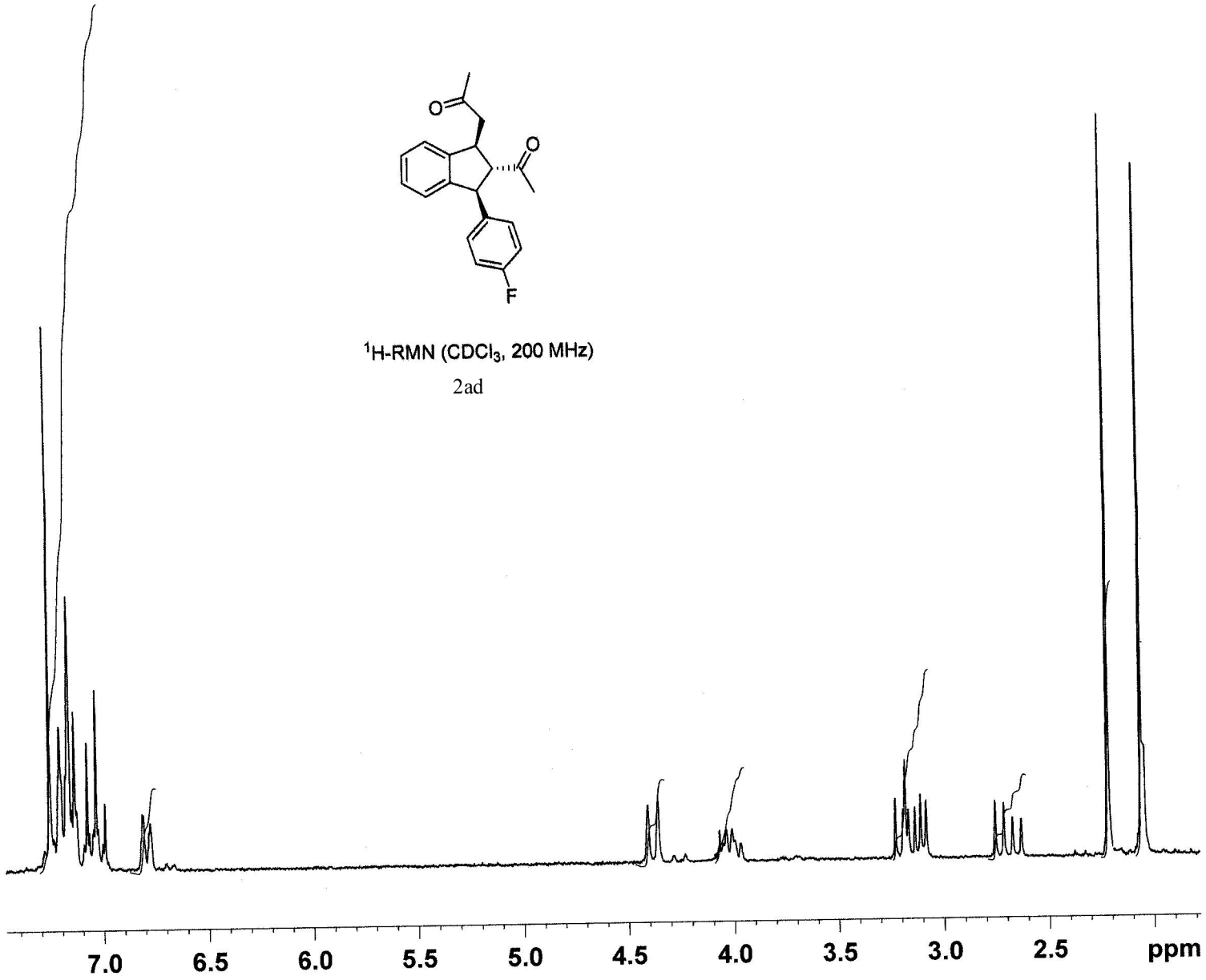
^{13}C-RMN ($CDCl_3$, 125.75 MHz)

3ac



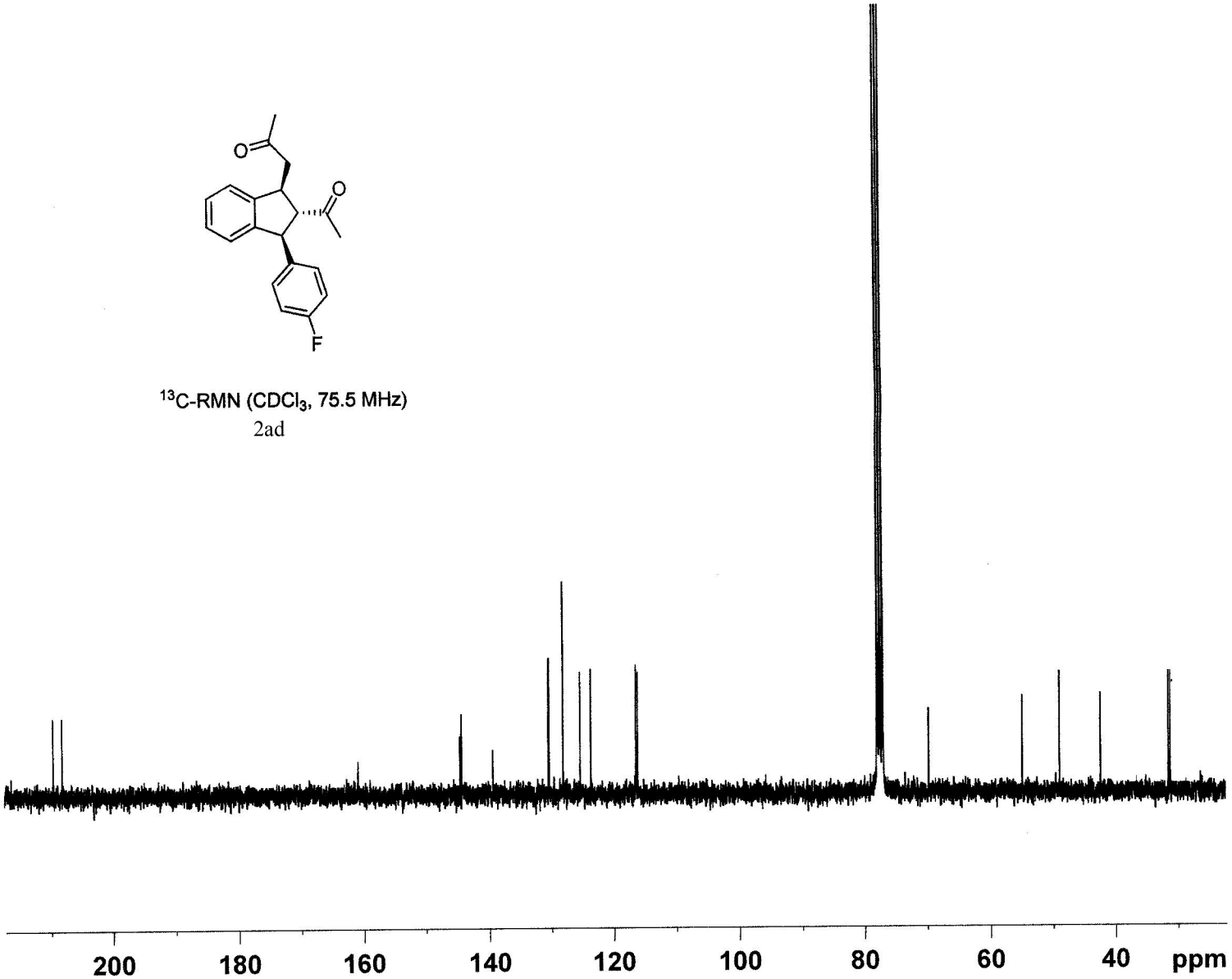
^{1}H-RMN ($CDCl_3$, 200 MHz)

2ad



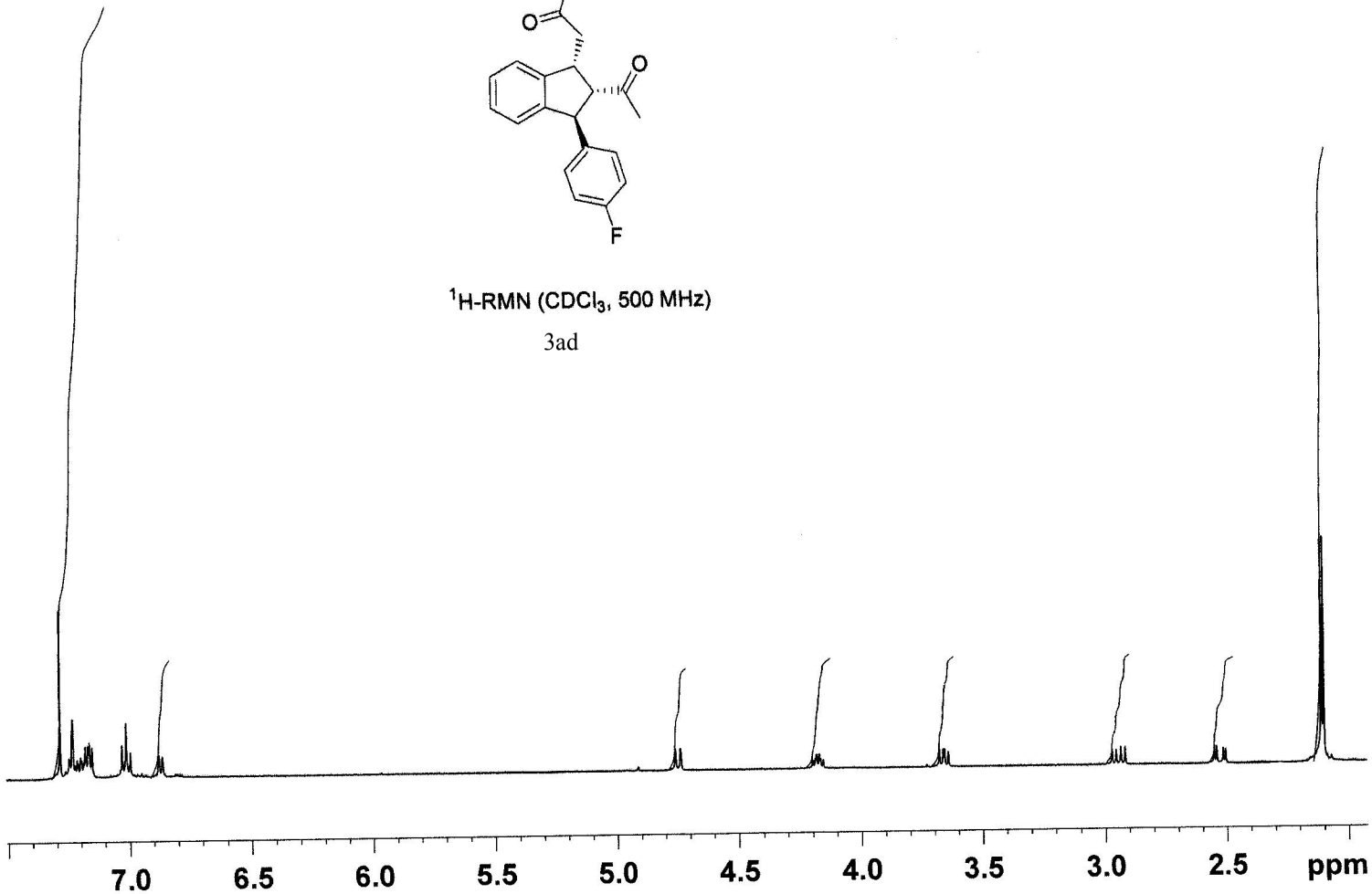
^{13}C-RMN ($CDCl_3$, 75.5 MHz)

2ad



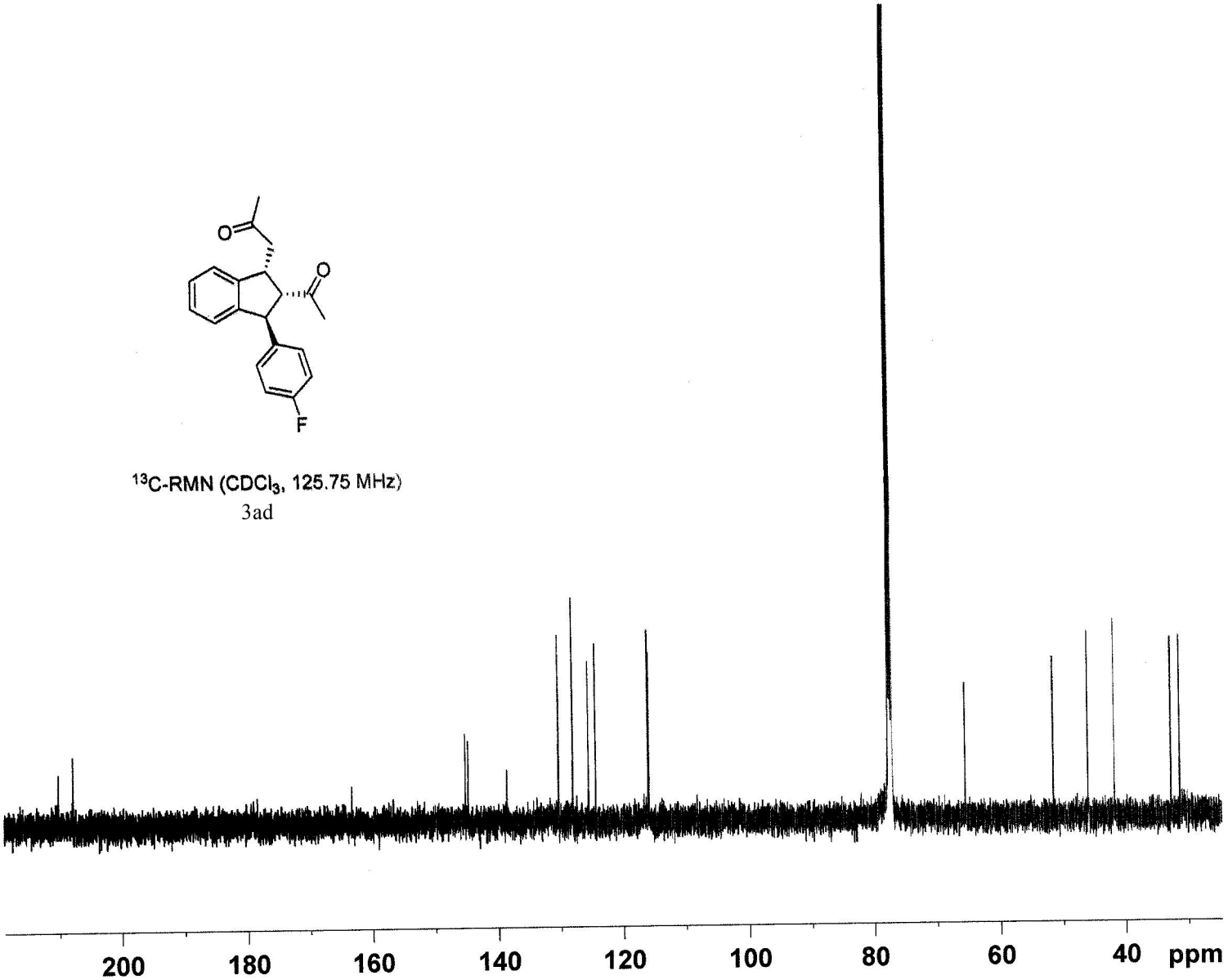
^{1}H-RMN ($CDCl_3$, 500 MHz)

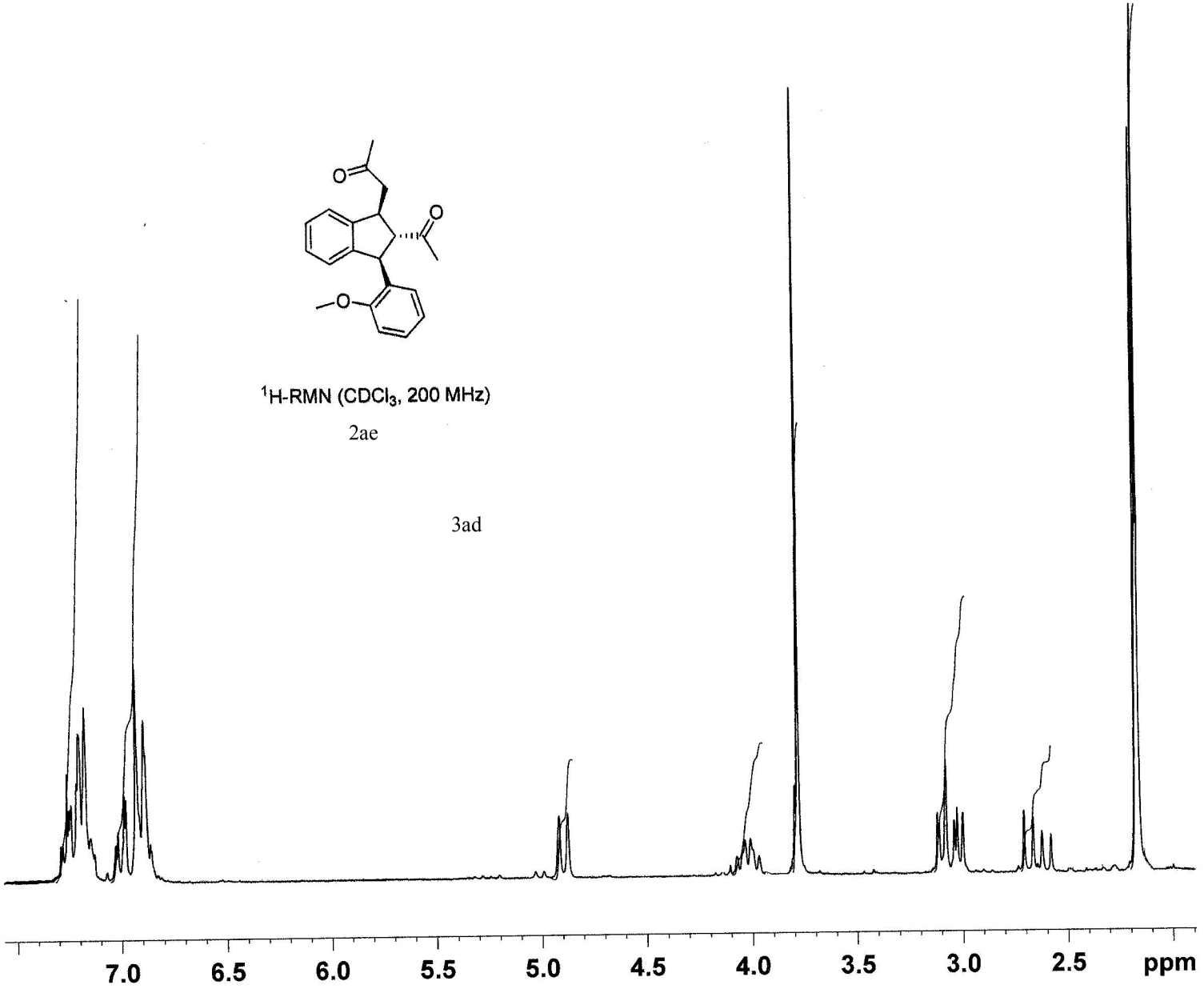
3ad

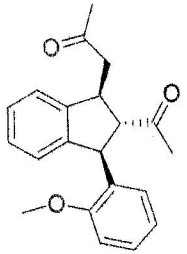


^{13}C-RMN ($CDCl_3$, 125.75 MHz)

3ad

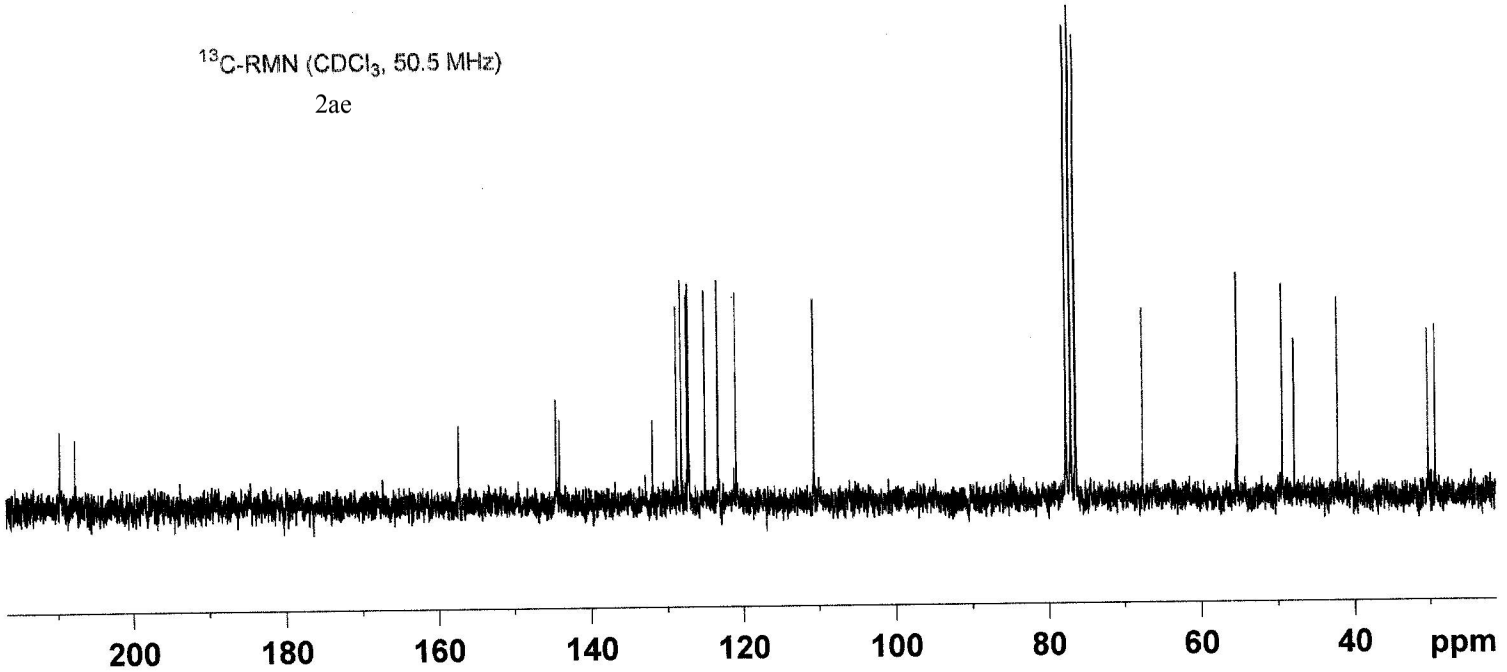



^{1}H-RMN ($CDCl_3$, 200 MHz)
2ae
3ad
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
ppm



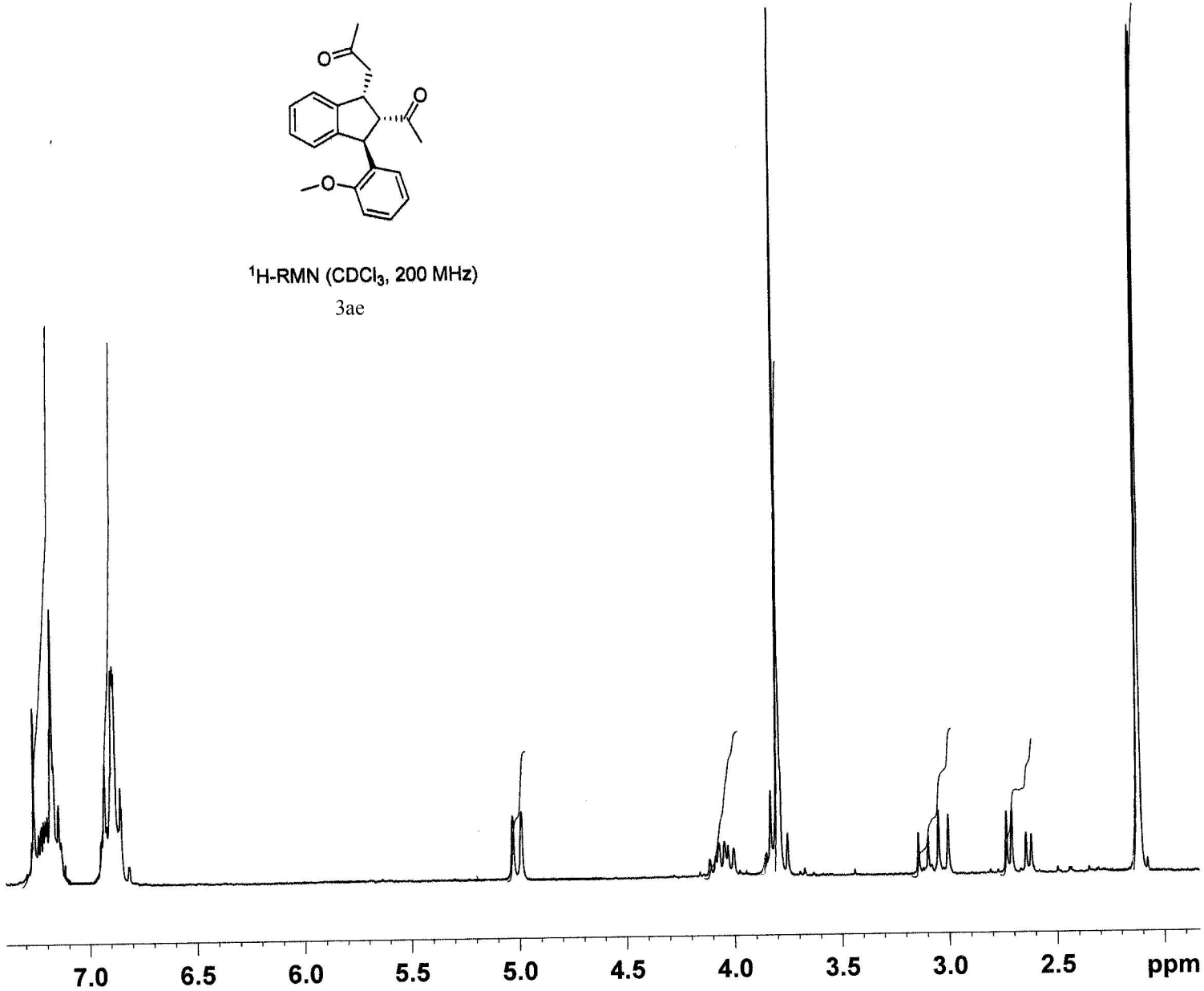
^{13}C-RMN ($CDCl_3$, 50.5 MHz)

2ae



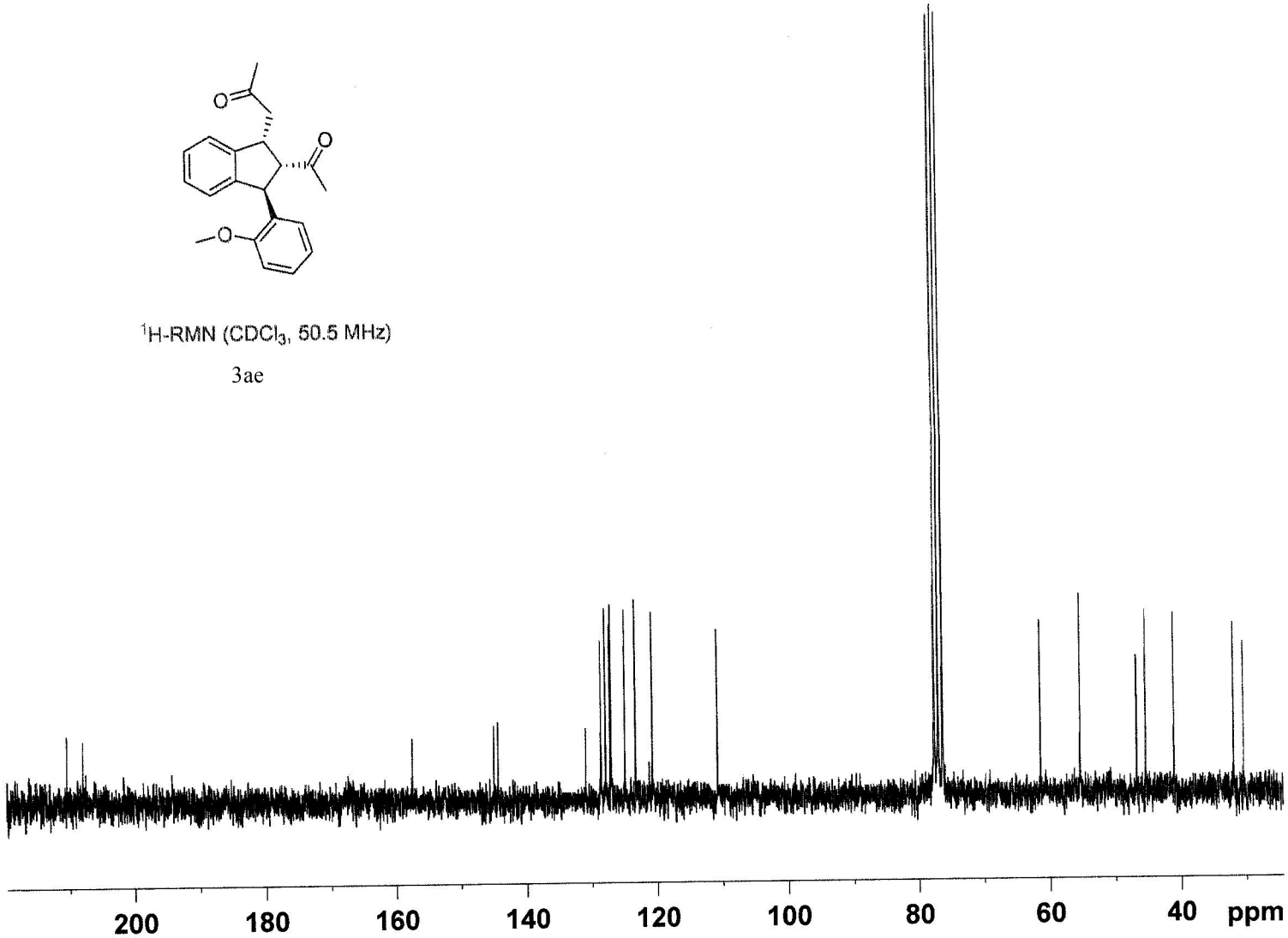
^{1}H-RMN ($CDCl_3$, 200 MHz)

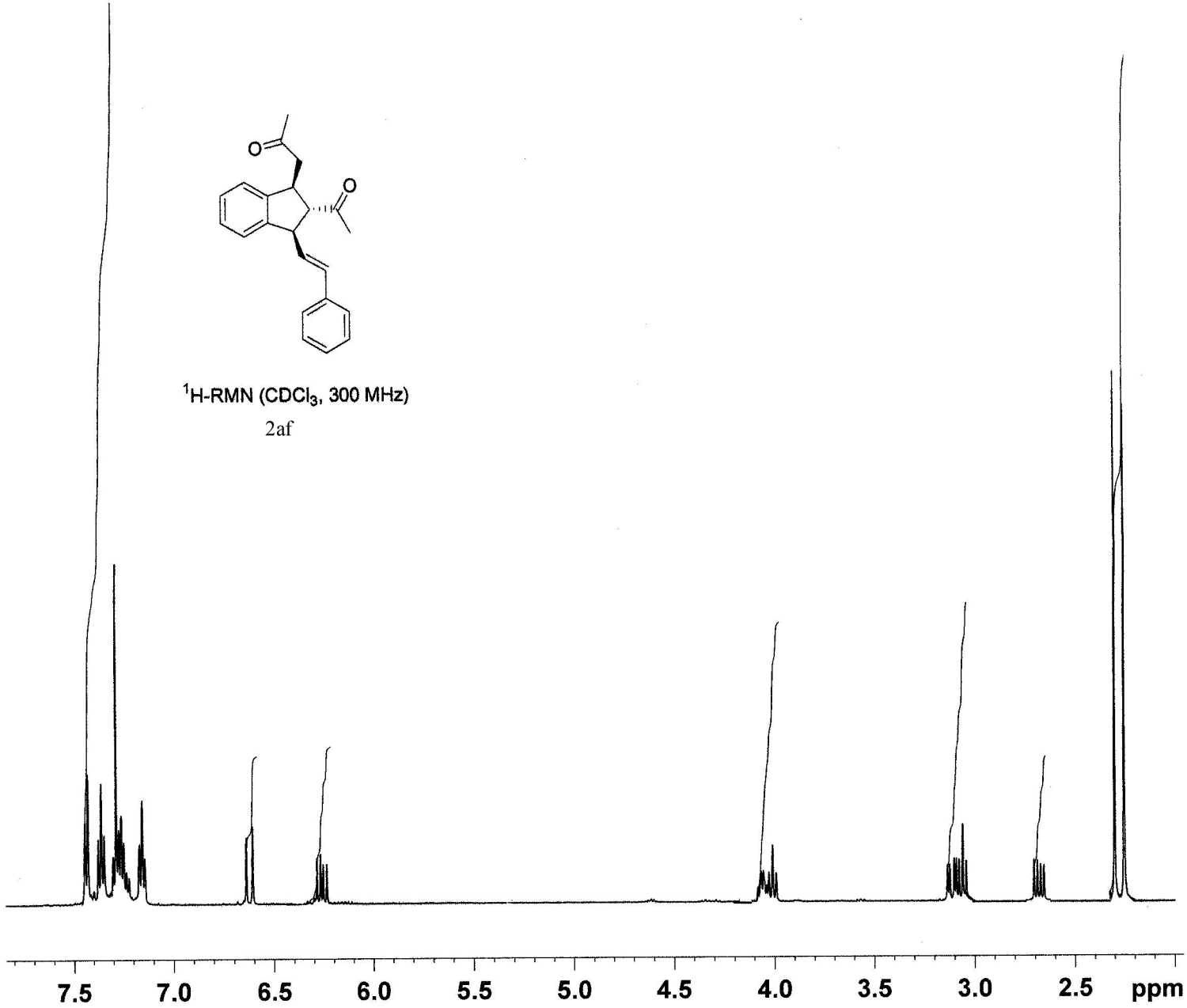
3ae



^{1}H-RMN ($CDCl_3$, 50.5 MHz)

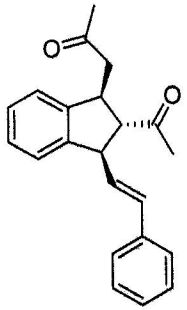
3ae





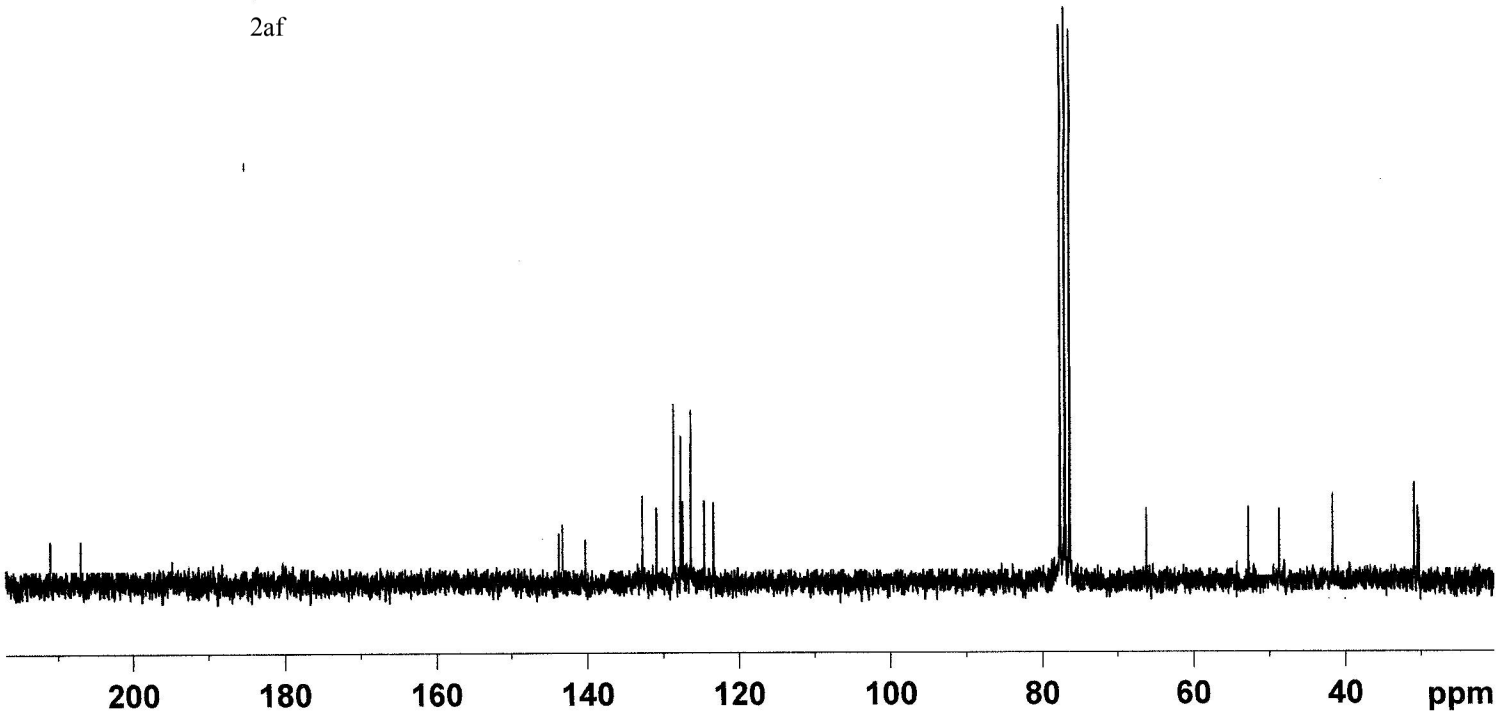
^{1}H-RMN ($CDCl_3$, 300 MHz)

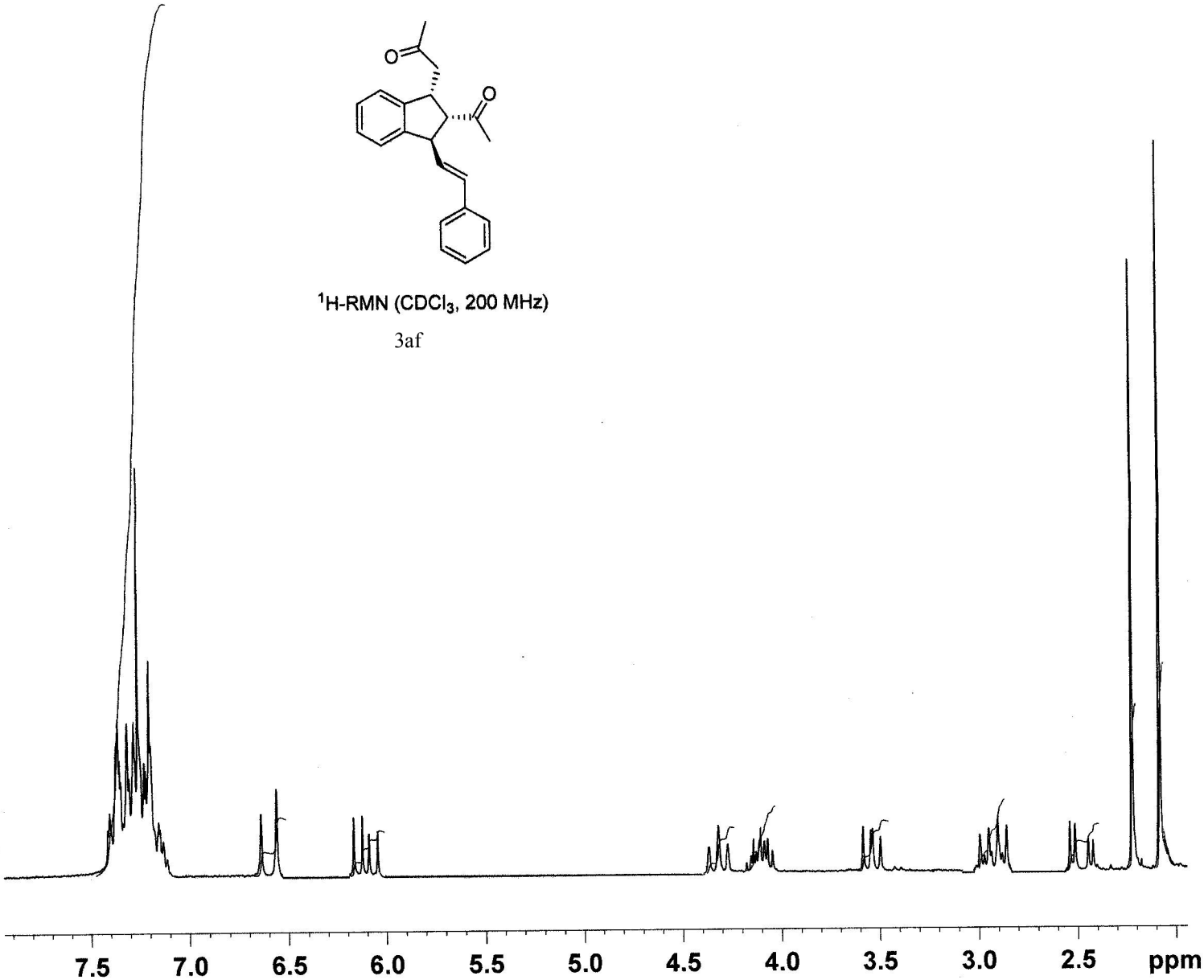
2af



^{13}C-RMN ($CDCl_3$, 50.5 MHz)

2af



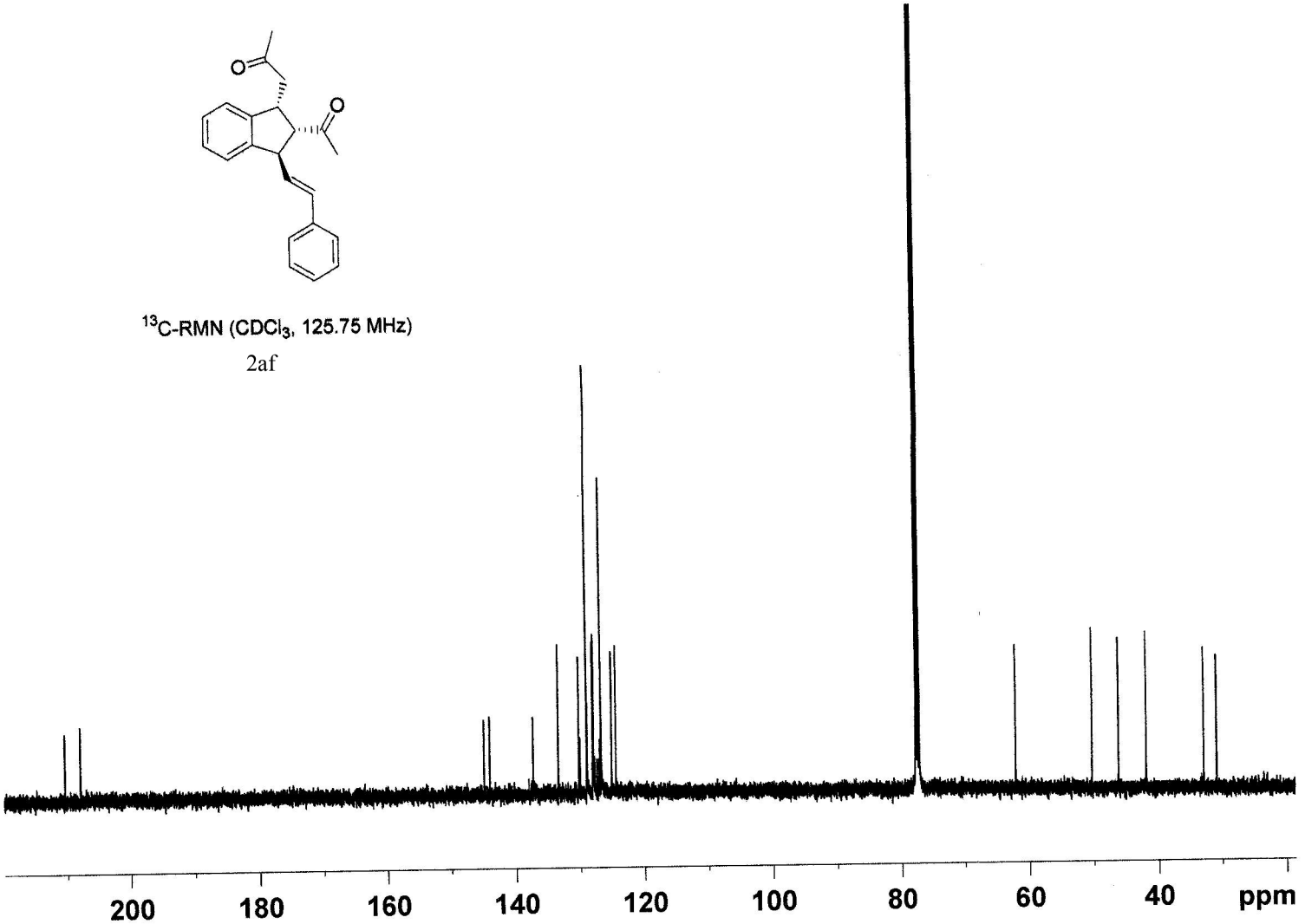


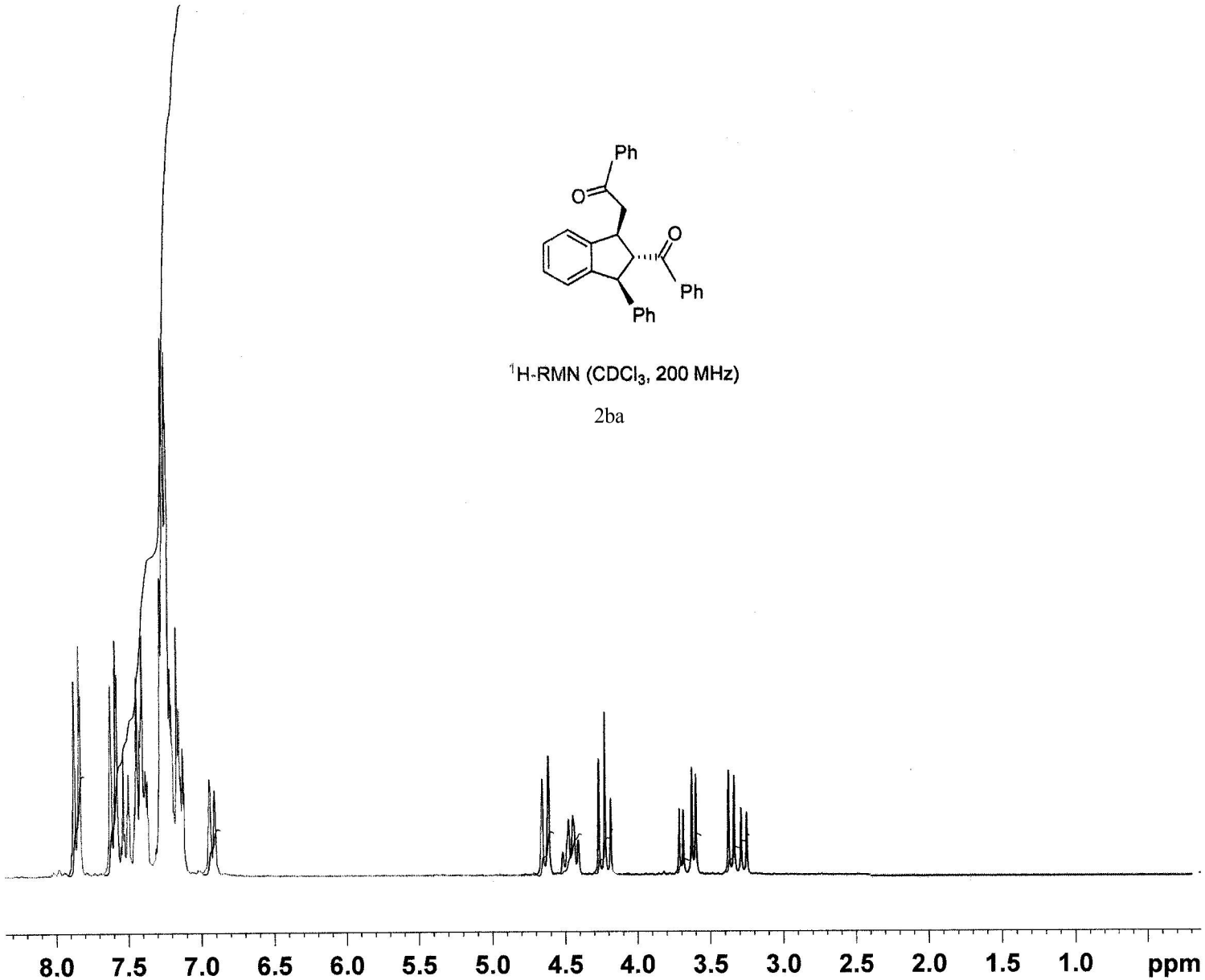
^{1}H-RMN ($CDCl_3$, 200 MHz)

3af

^{13}C-RMN ($CDCl_3$, 125.75 MHz)

2af



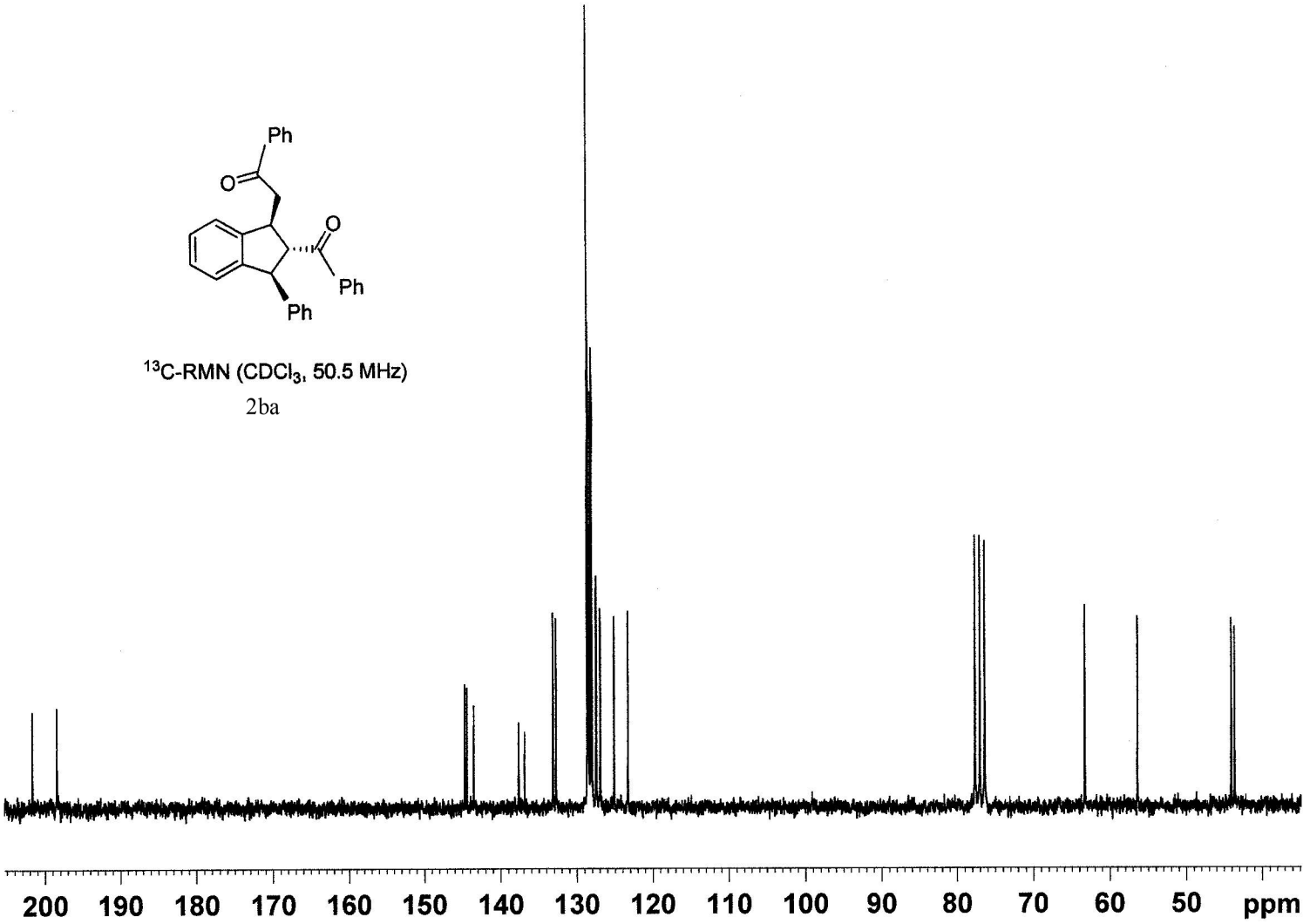


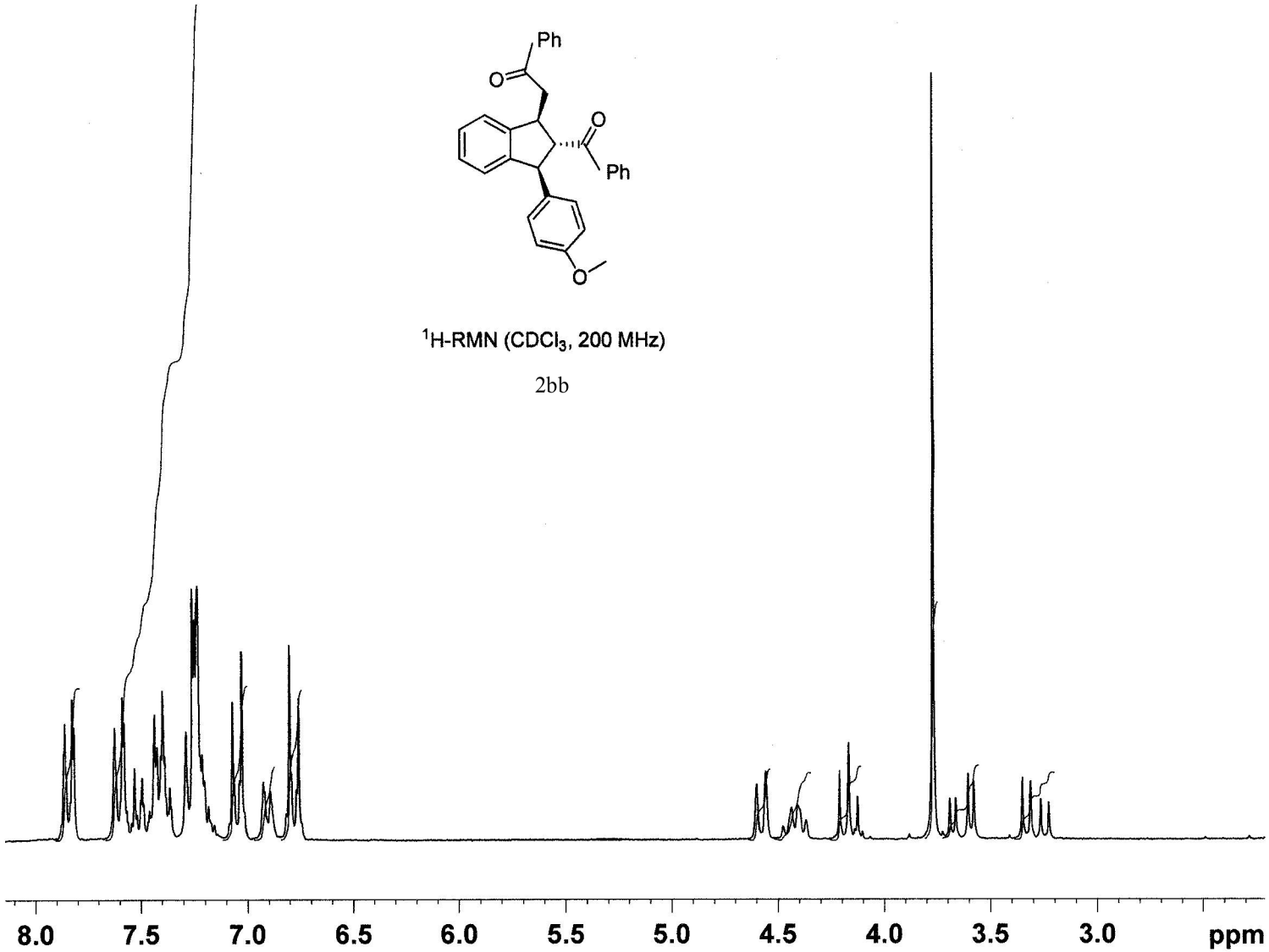
^{1}H-RMN ($CDCl_3$, 200 MHz)

2ba

^{13}C-RMN ($CDCl_3$, 50.5 MHz)

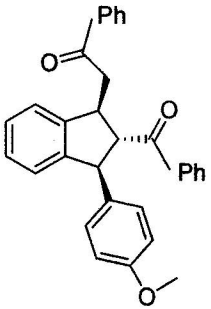
2ba





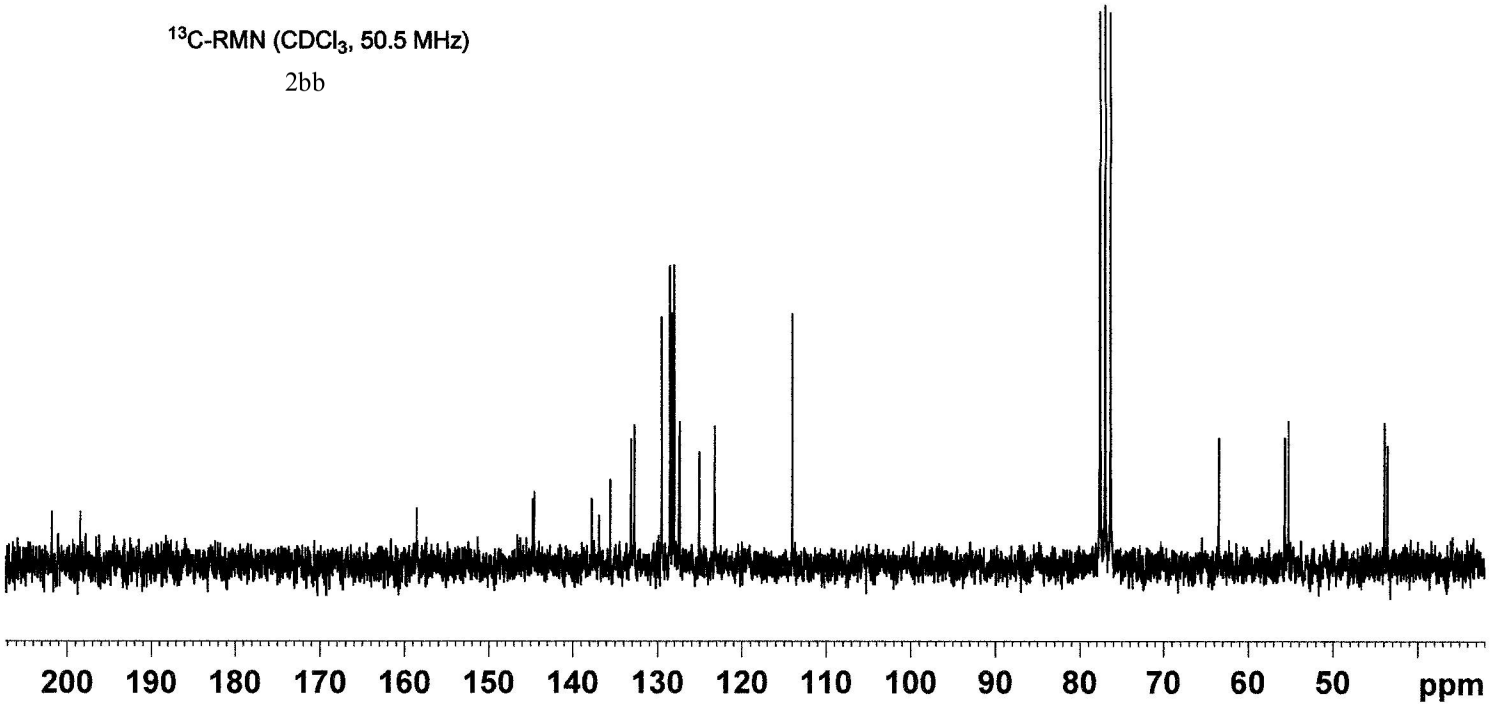
^{1}H-RMN ($CDCl_3$, 200 MHz)

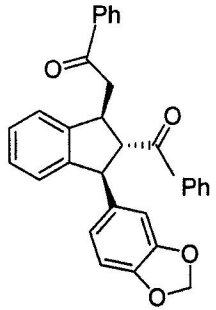
2bb



^{13}C-RMN ($CDCl_3$, 50.5 MHz)

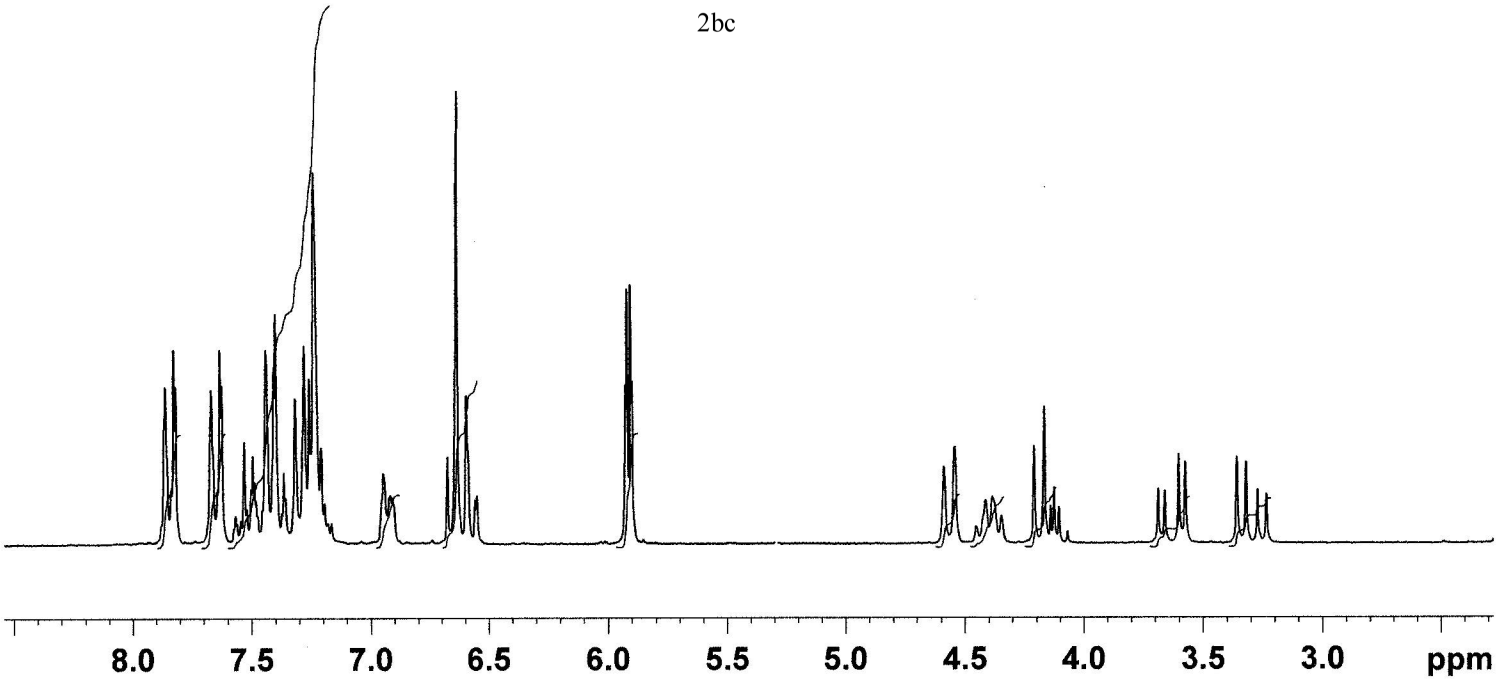
2bb

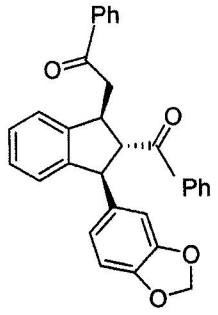




^{1}H-RMN ($CDCl_3$, 200 MHz)

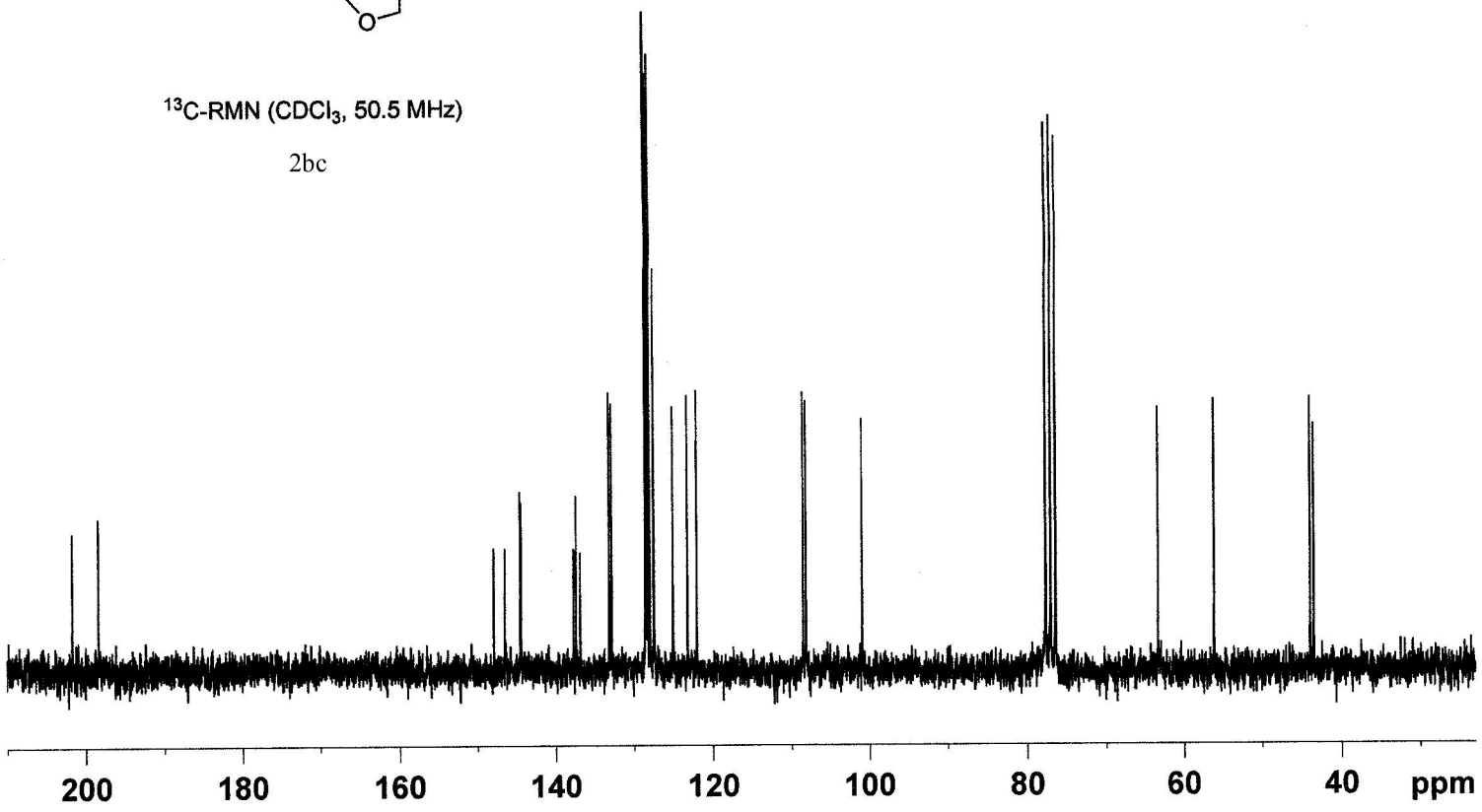
2bc

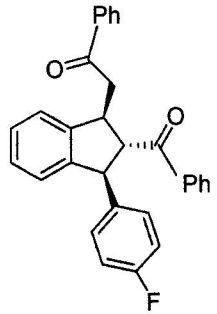




^{13}C-RMN ($CDCl_3$, 50.5 MHz)

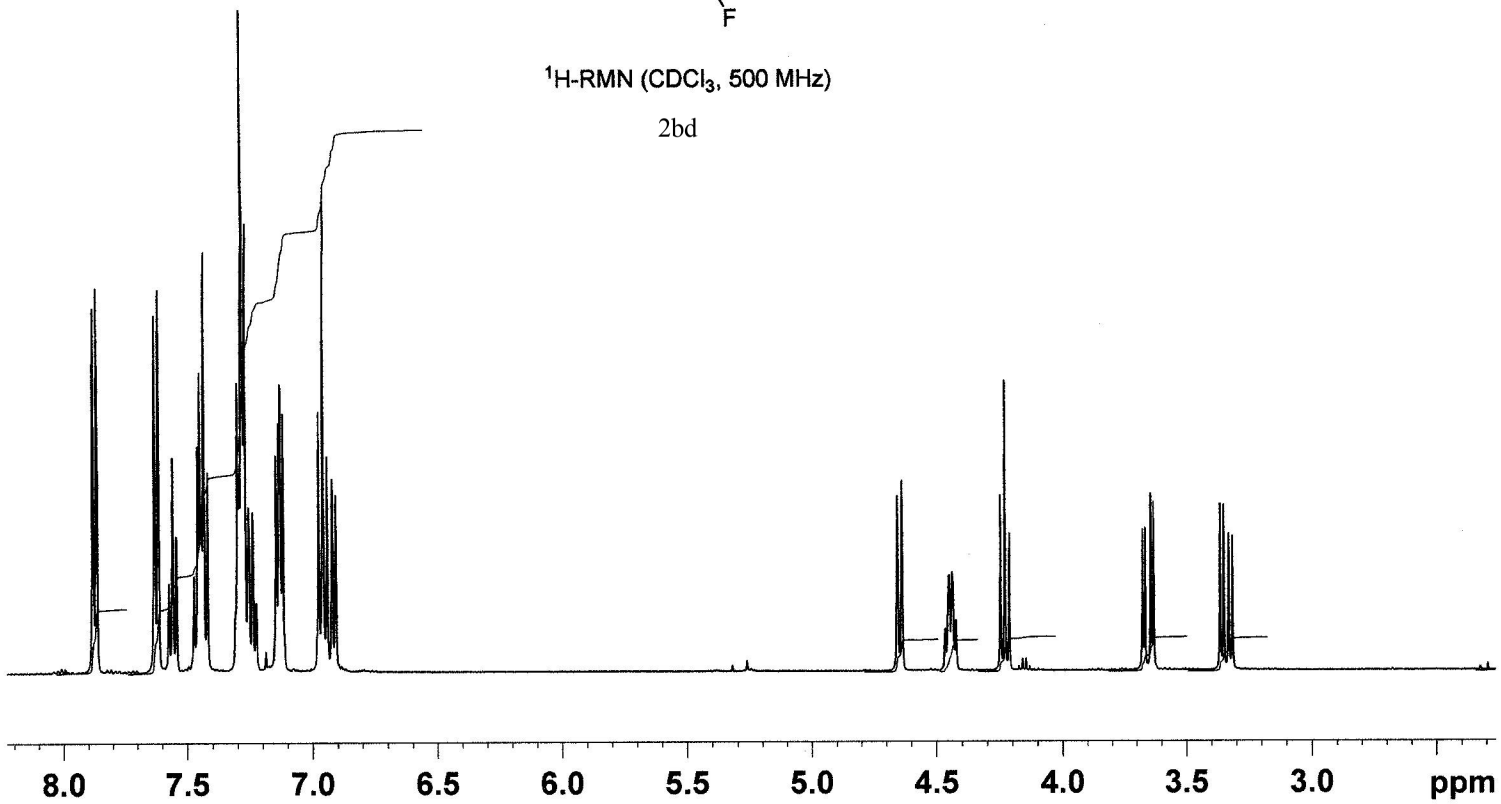
2bc

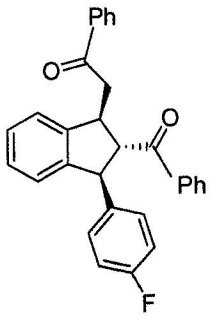




^{1}H-RMN ($CDCl_3$, 500 MHz)

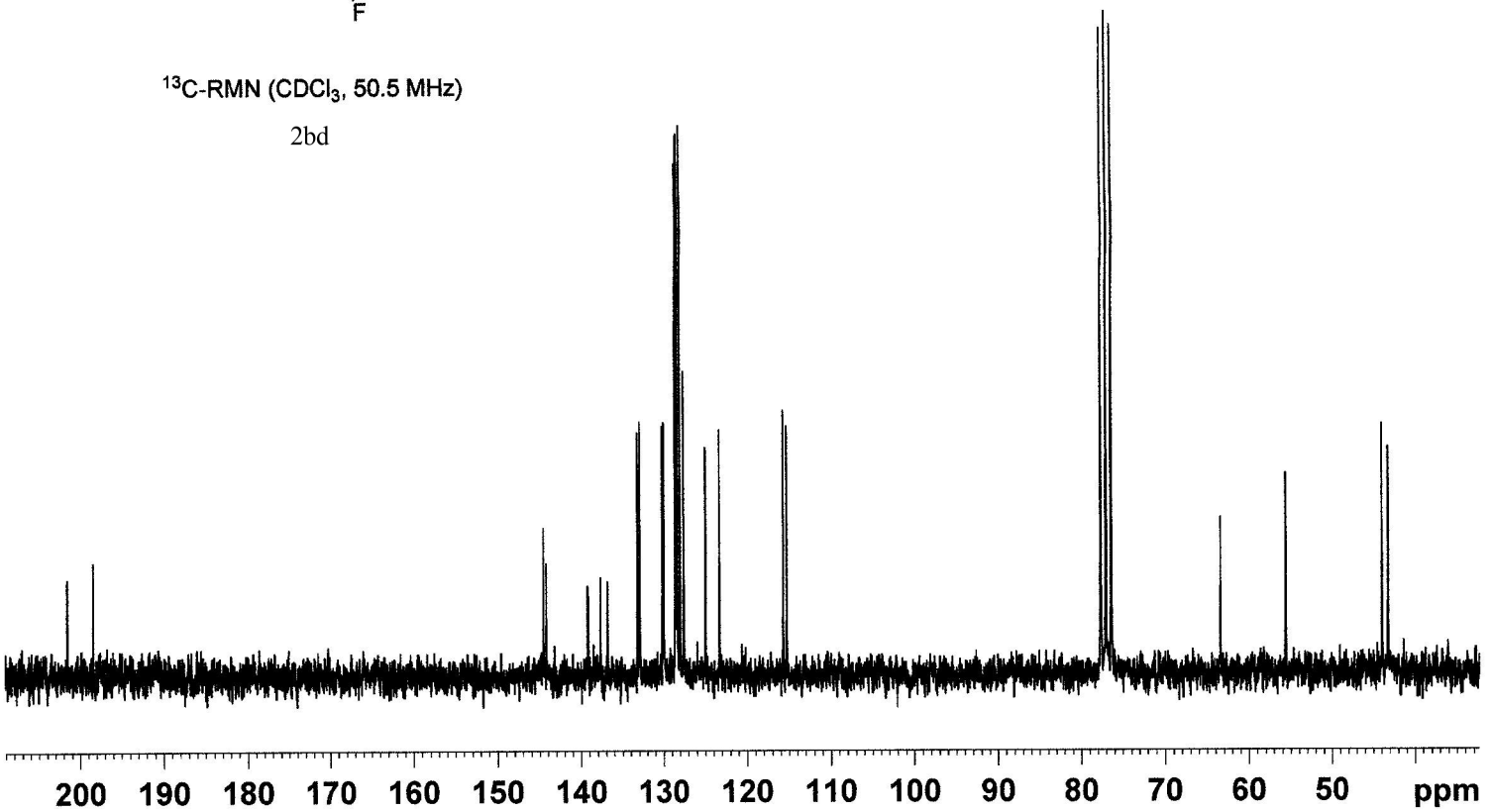
2bd

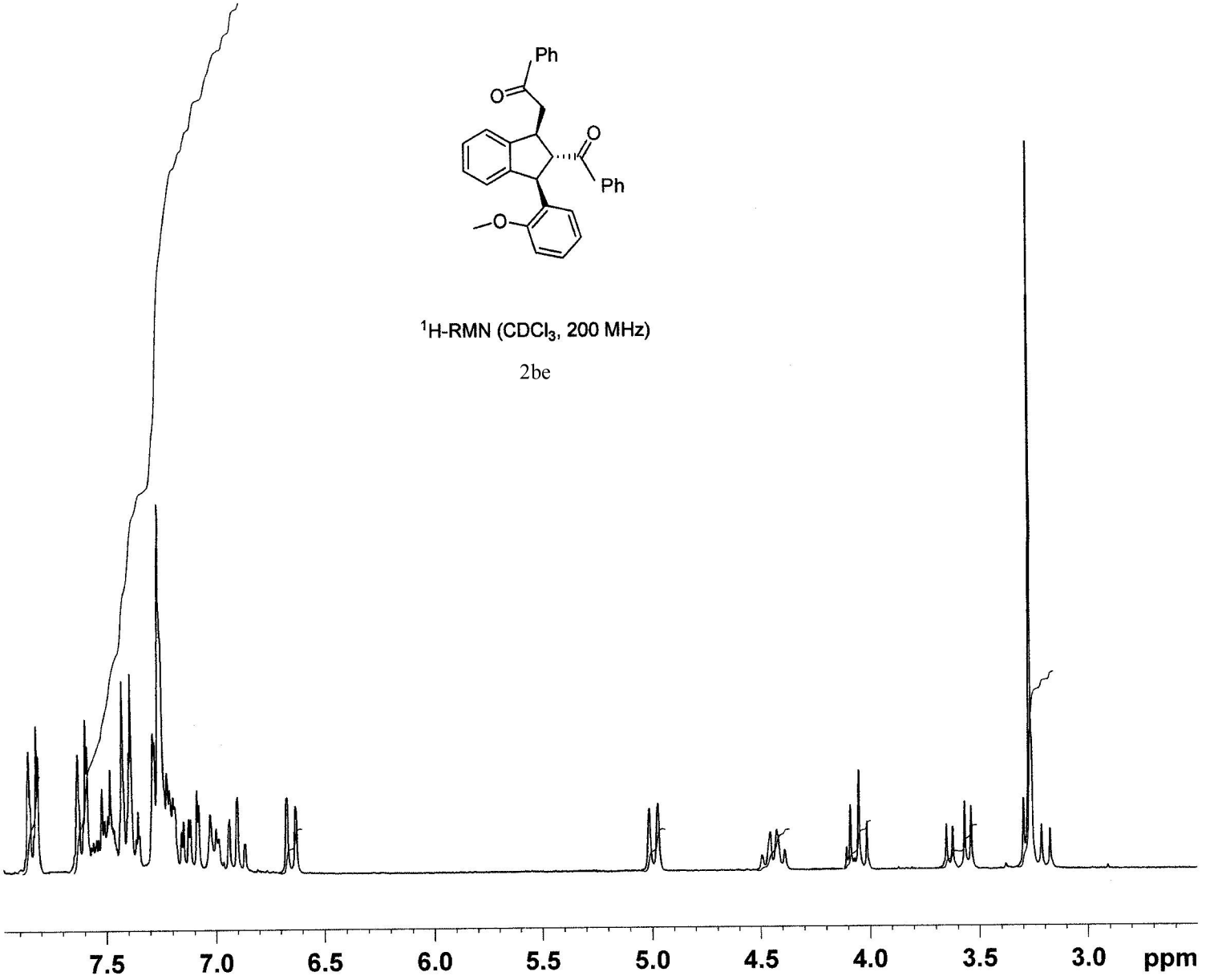




^{13}C-RMN ($CDCl_3$, 50.5 MHz)

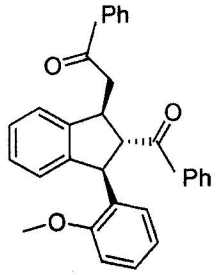
2bd





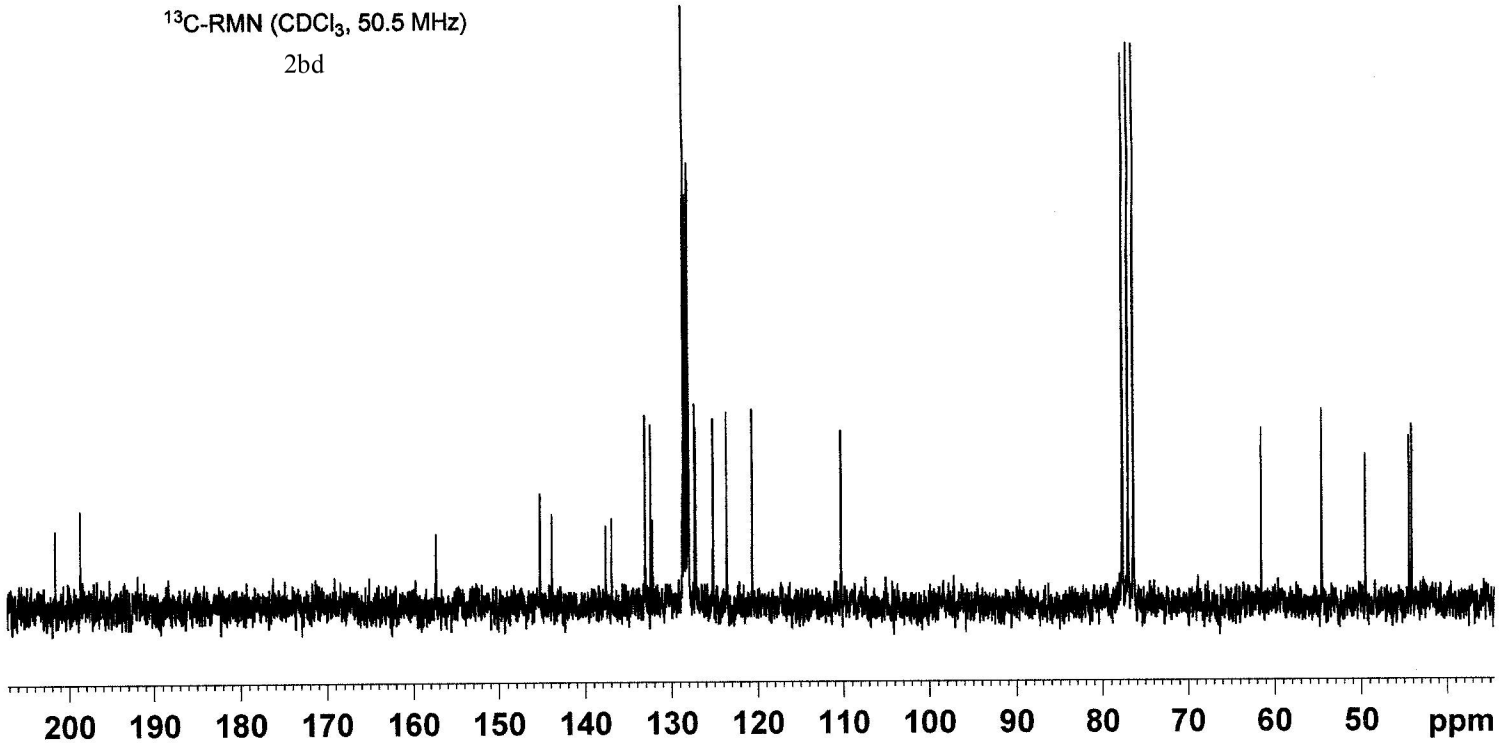
^{1}H-RMN ($CDCl_3$, 200 MHz)

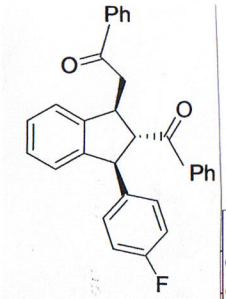
2be



^{13}C-RMN ($CDCl_3$, 50.5 MHz)

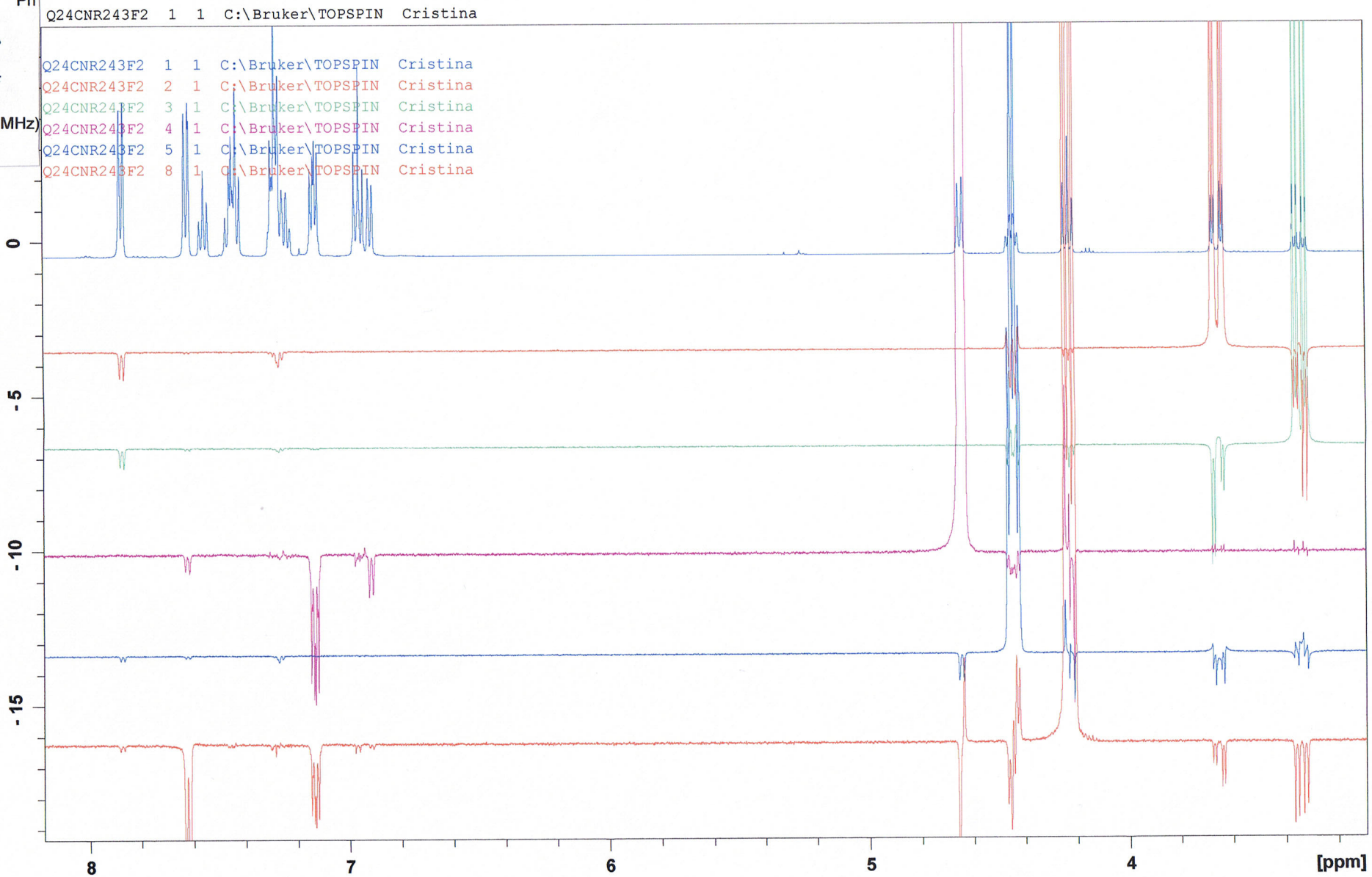
2bd

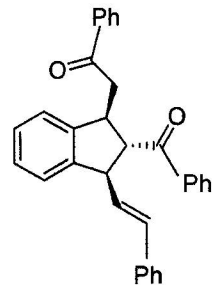




OE ($CDCl_3$, 500 MHz)

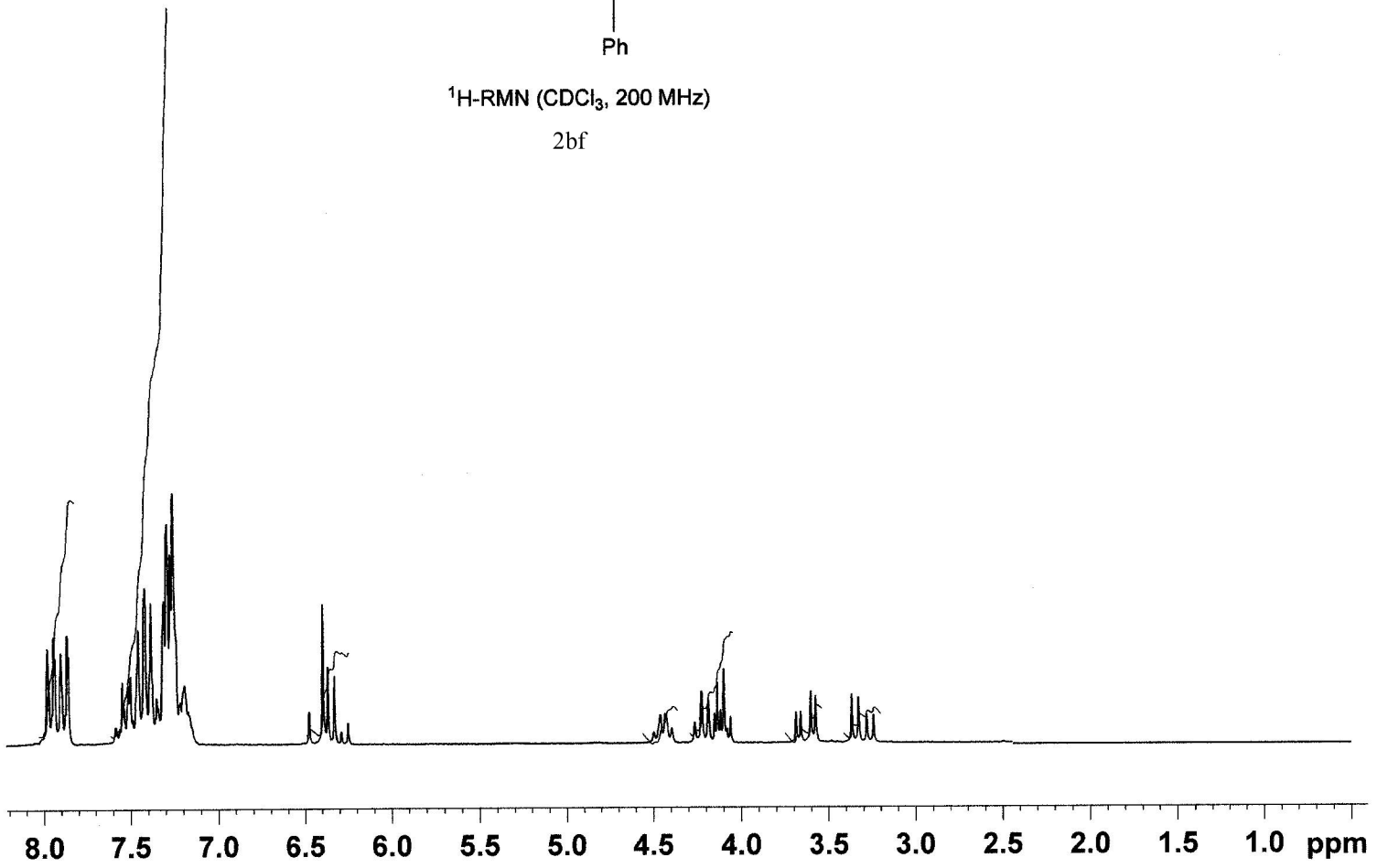
2bd

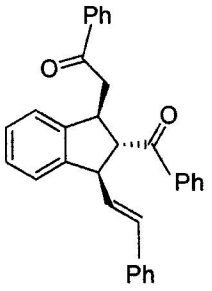




^{1}H-RMN ($CDCl_3$, 200 MHz)

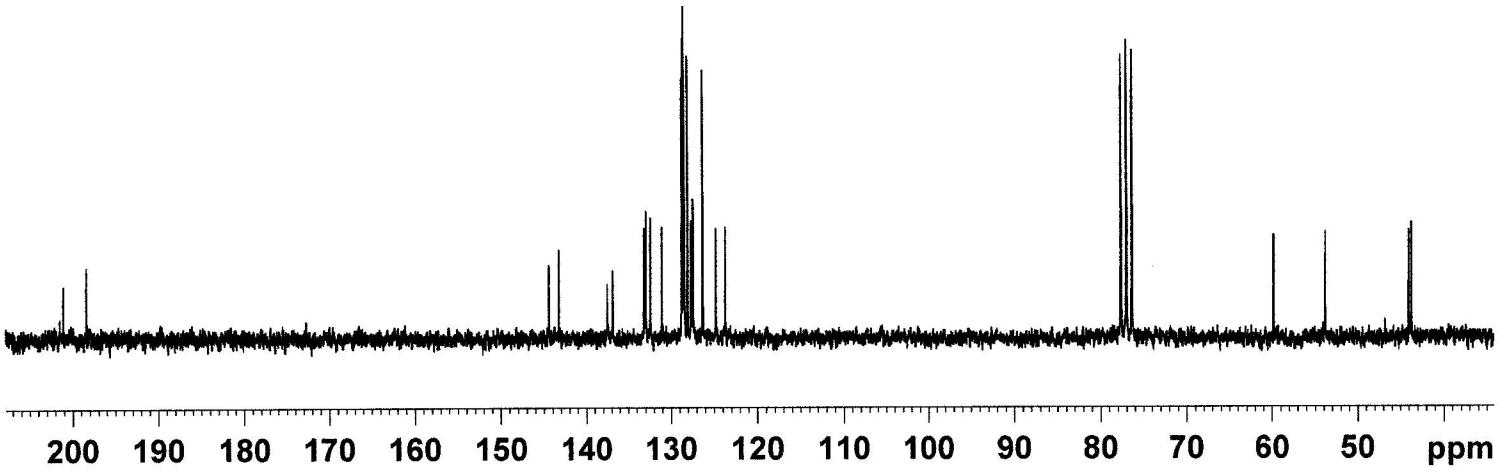
2bf

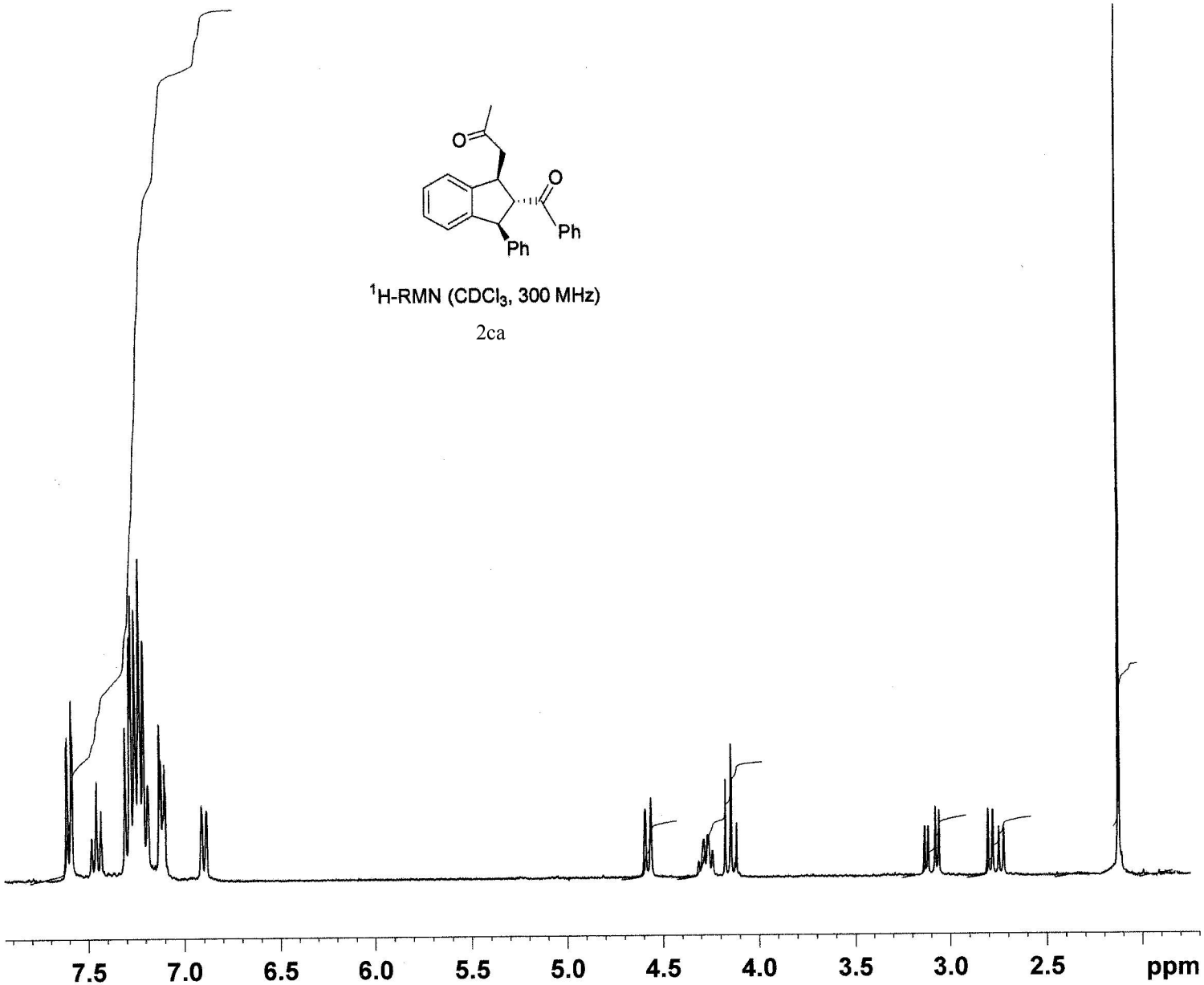




^{13}C-RMN ($CDCl_3$, 50.5 MHz)

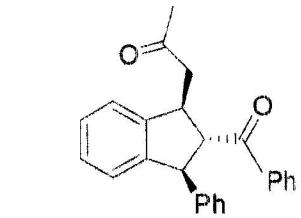
2bf





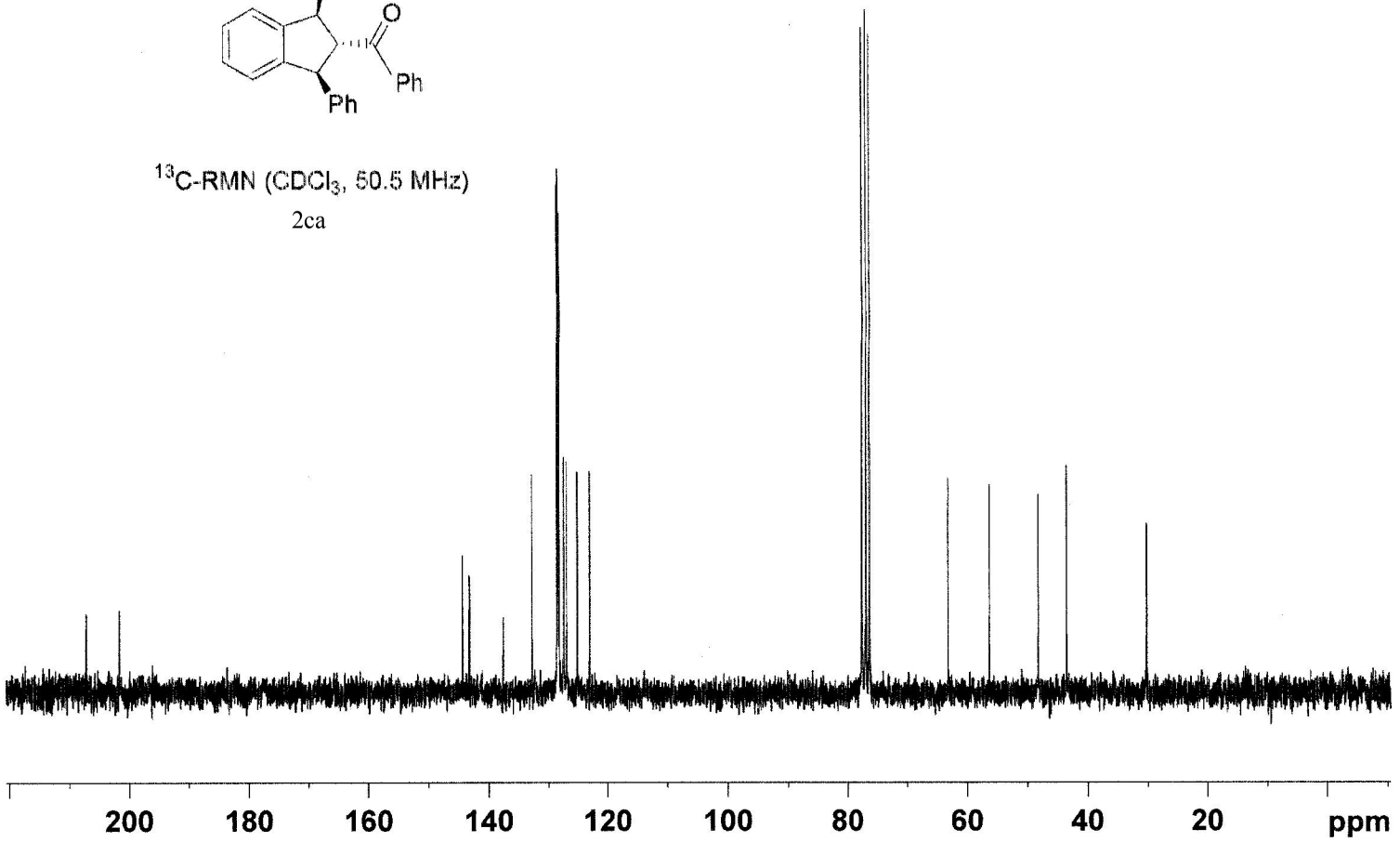
^{1}H-RMN ($CDCl_3$, 300 MHz)

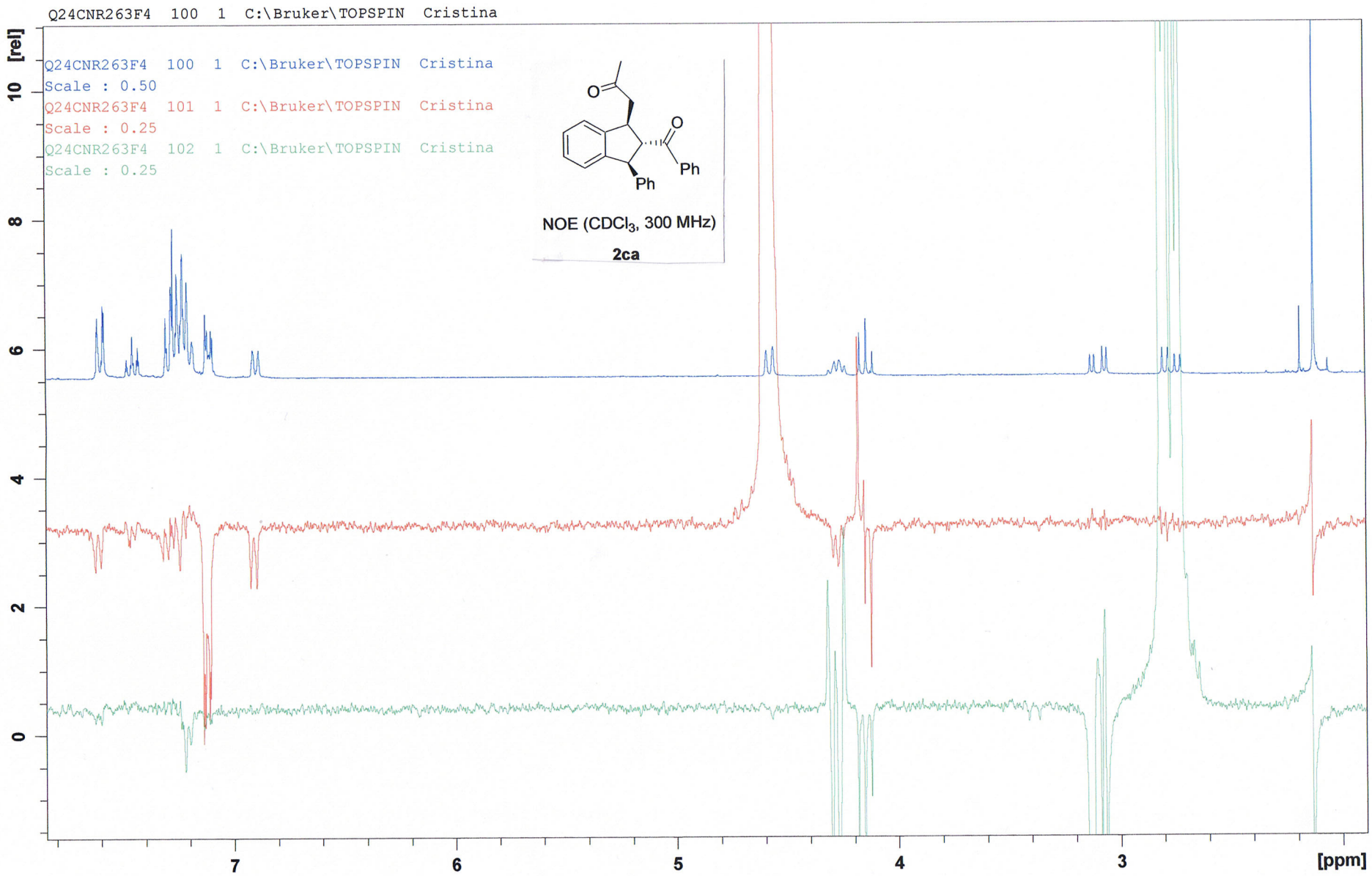
2ca

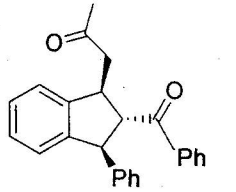


^{13}C-RMN ($CDCl_3$, 50.5 MHz)

2ca

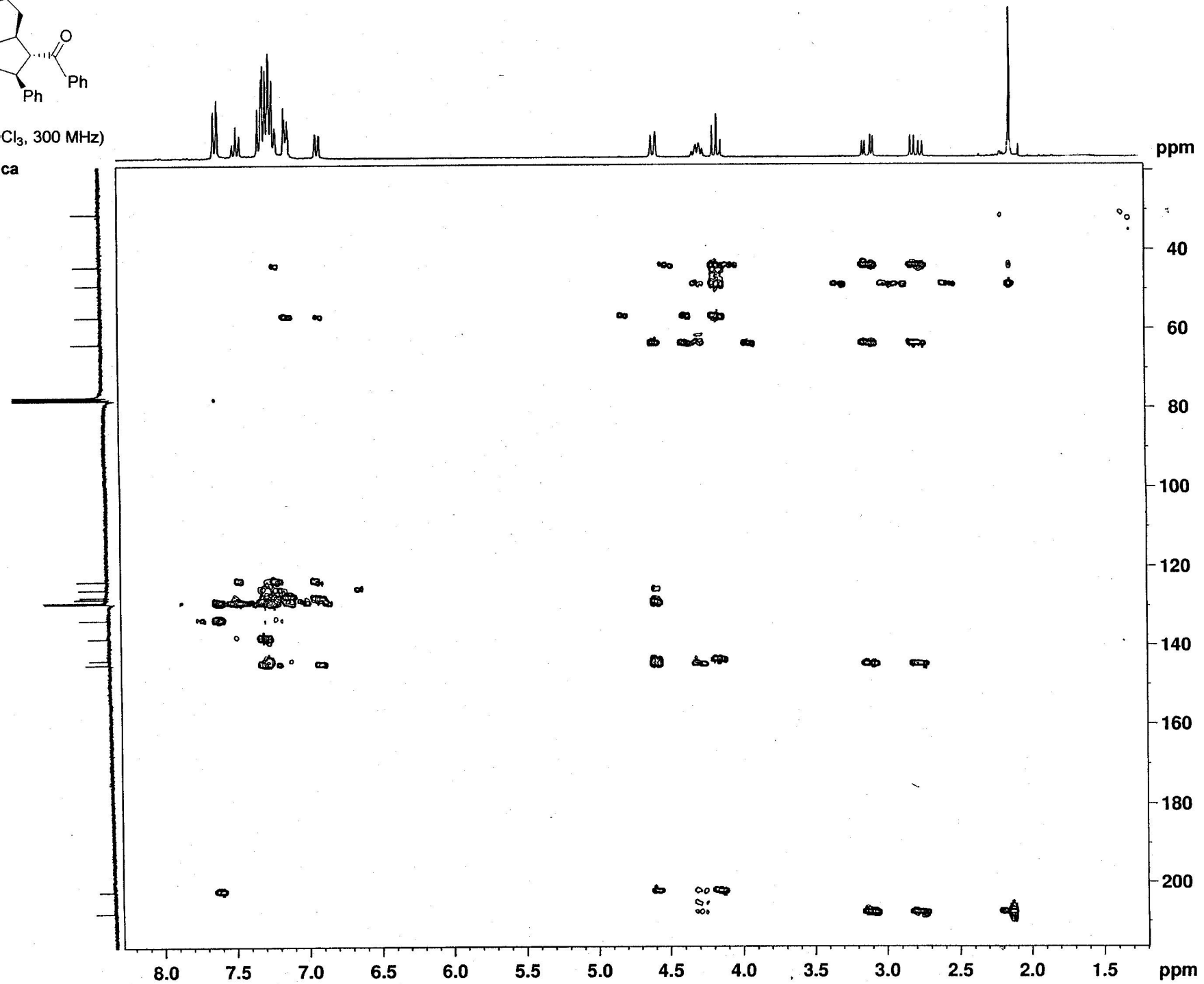


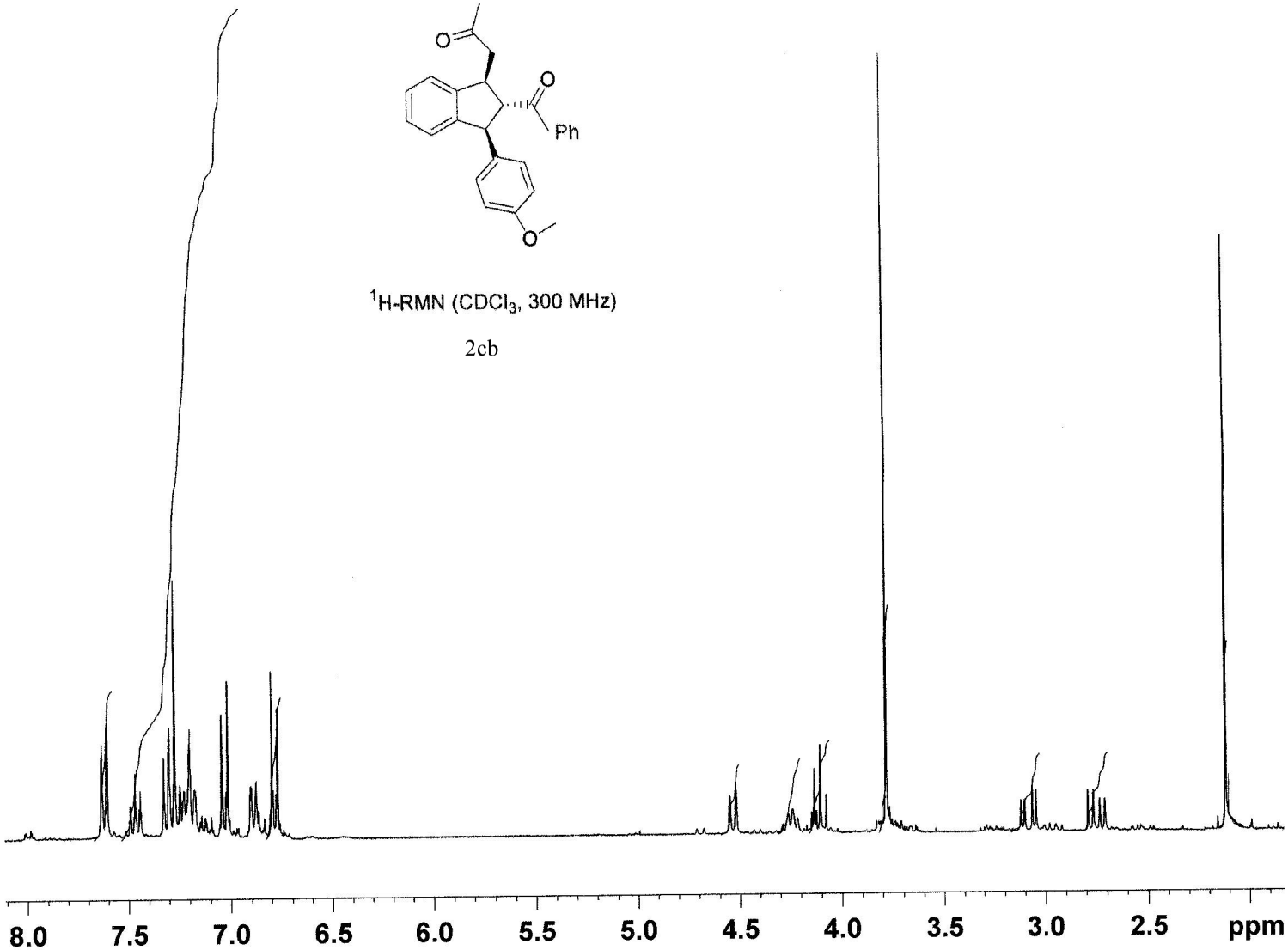

Q24CNR263F4 100 1 C:\Bruker\TOPSPIN Cristina
Q24CNR263F4 100 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.50
Q24CNR263F4 101 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.25
Q24CNR263F4 102 1 C:\Bruker\TOPSPIN Cristina
Scale : 0.25
O
O
Ph
Ph
NOE (CDCl3, 300 MHz)
2ca
10 [rel]
8
6
4
2
0
7
6
5
4
3
[ppm]



HMBC ($CDCl_3$, 300 MHz)

2ca



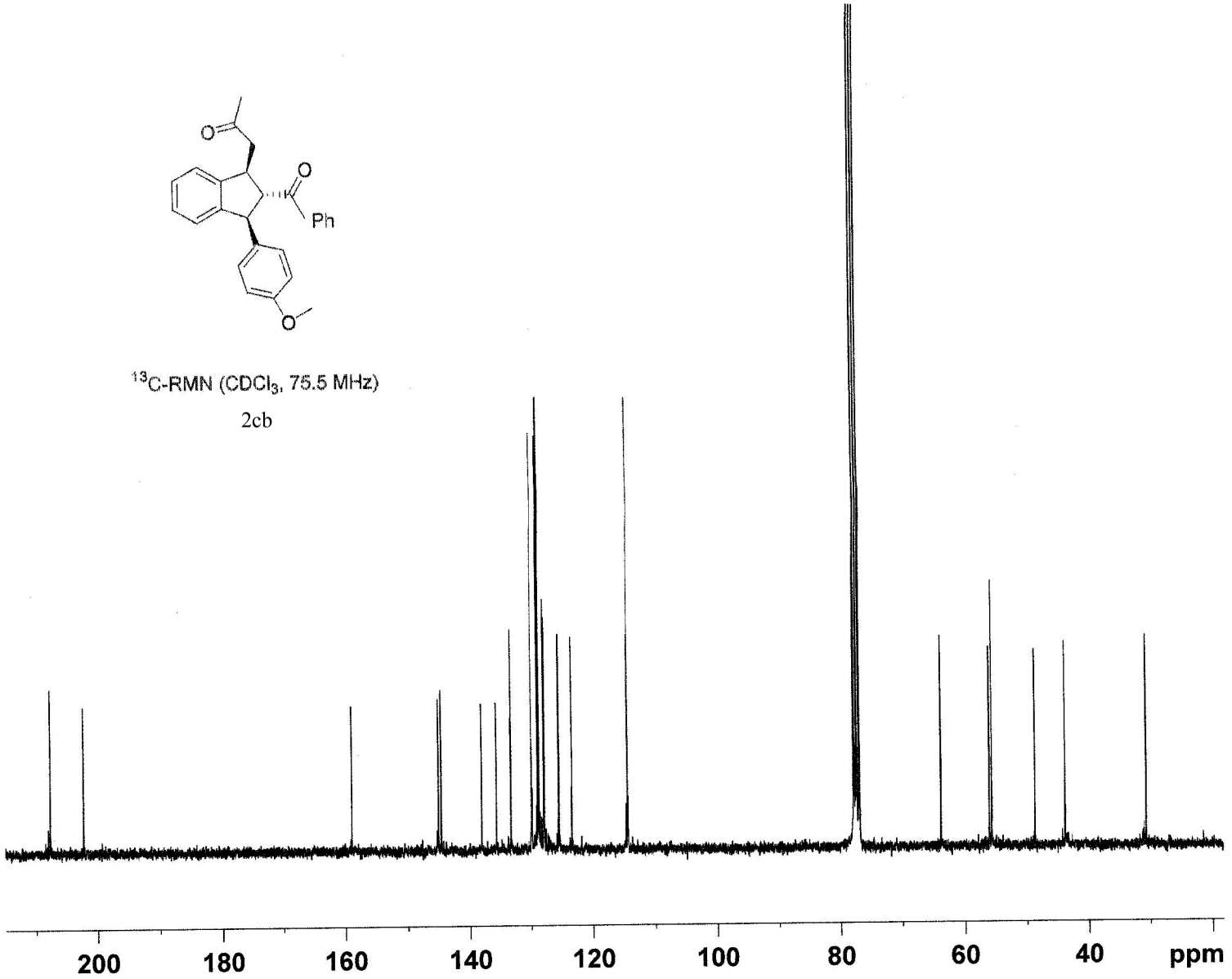


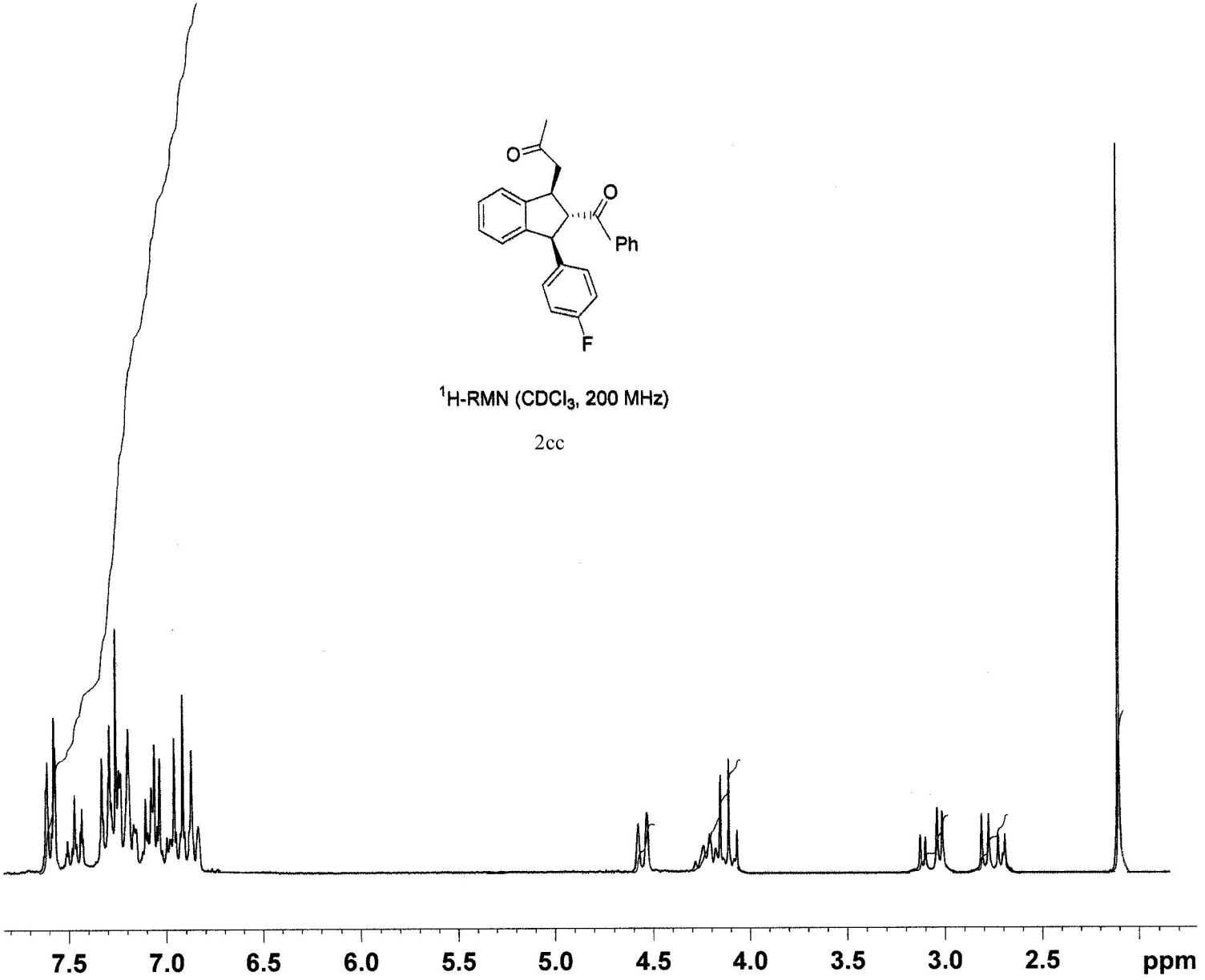
^{1}H-RMN ($CDCl_3$, 300 MHz)

2cb

^{13}C-RMN ($CDCl_3$, 75.5 MHz)

2cb



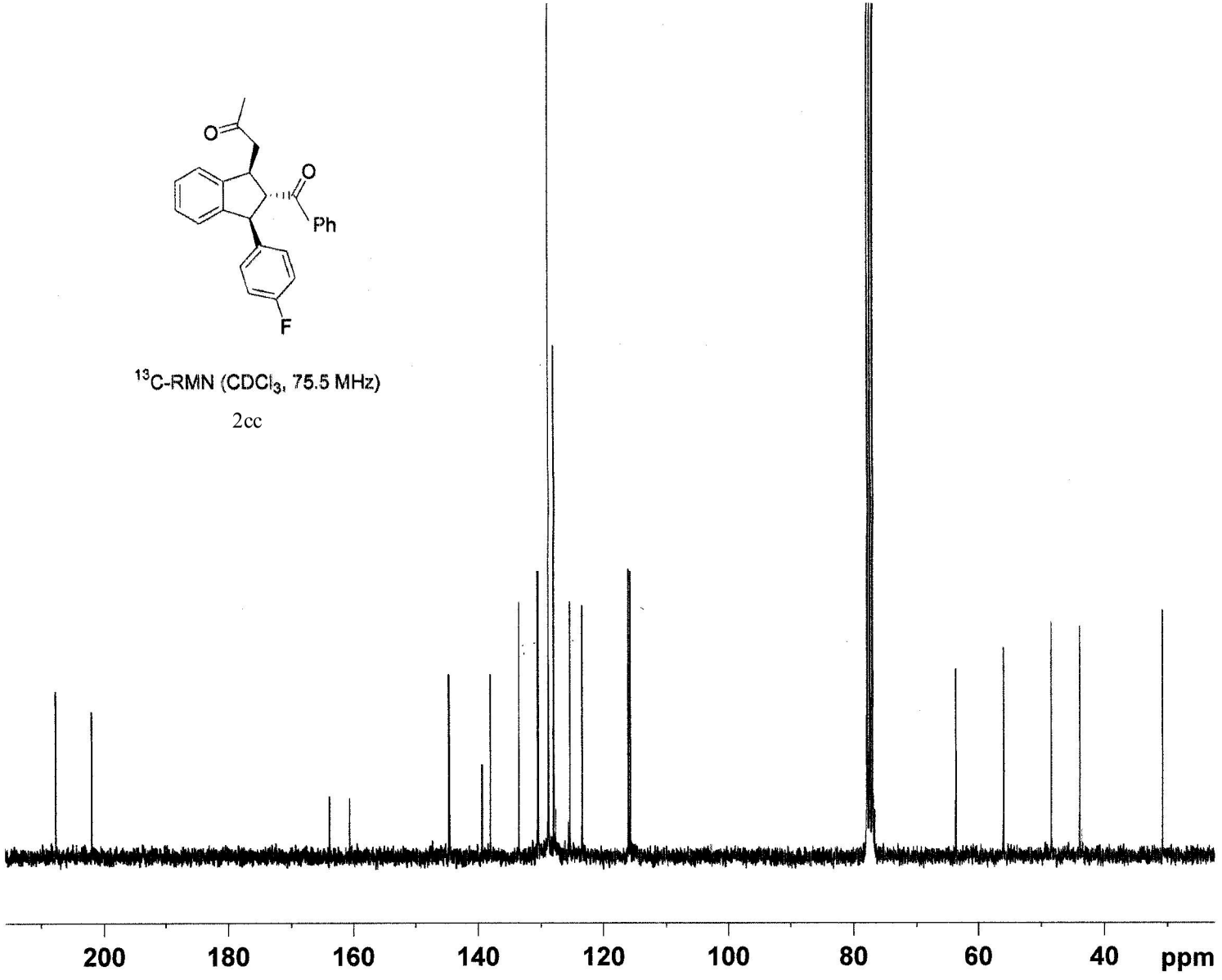


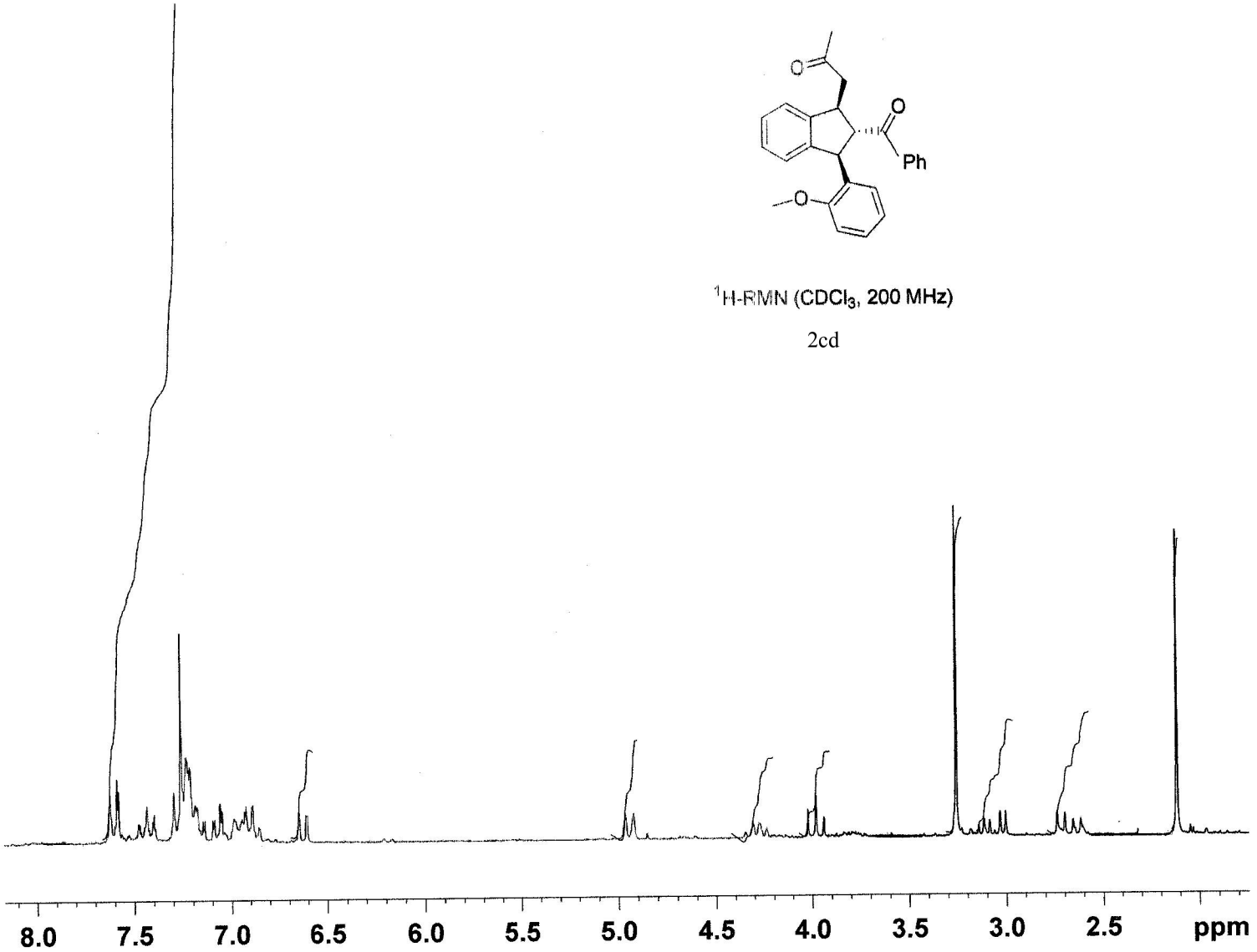
^{1}H-RMN ($CDCl_3$, 200 MHz)

2cc

^{13}C-RMN ($CDCl_3$, 75.5 MHz)

2cc



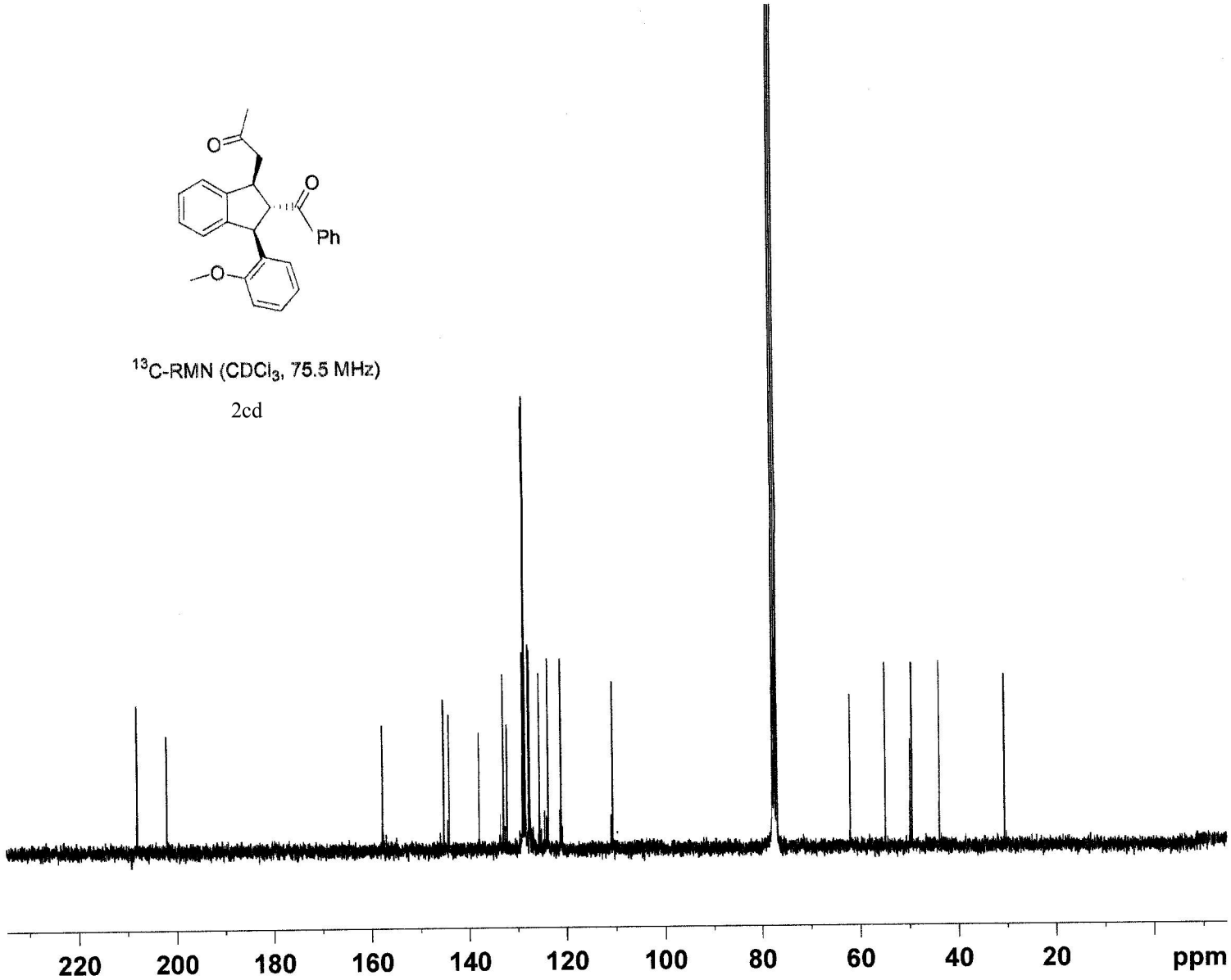


^{1}H-RMN ($CDCl_3$, 200 MHz)

2cd

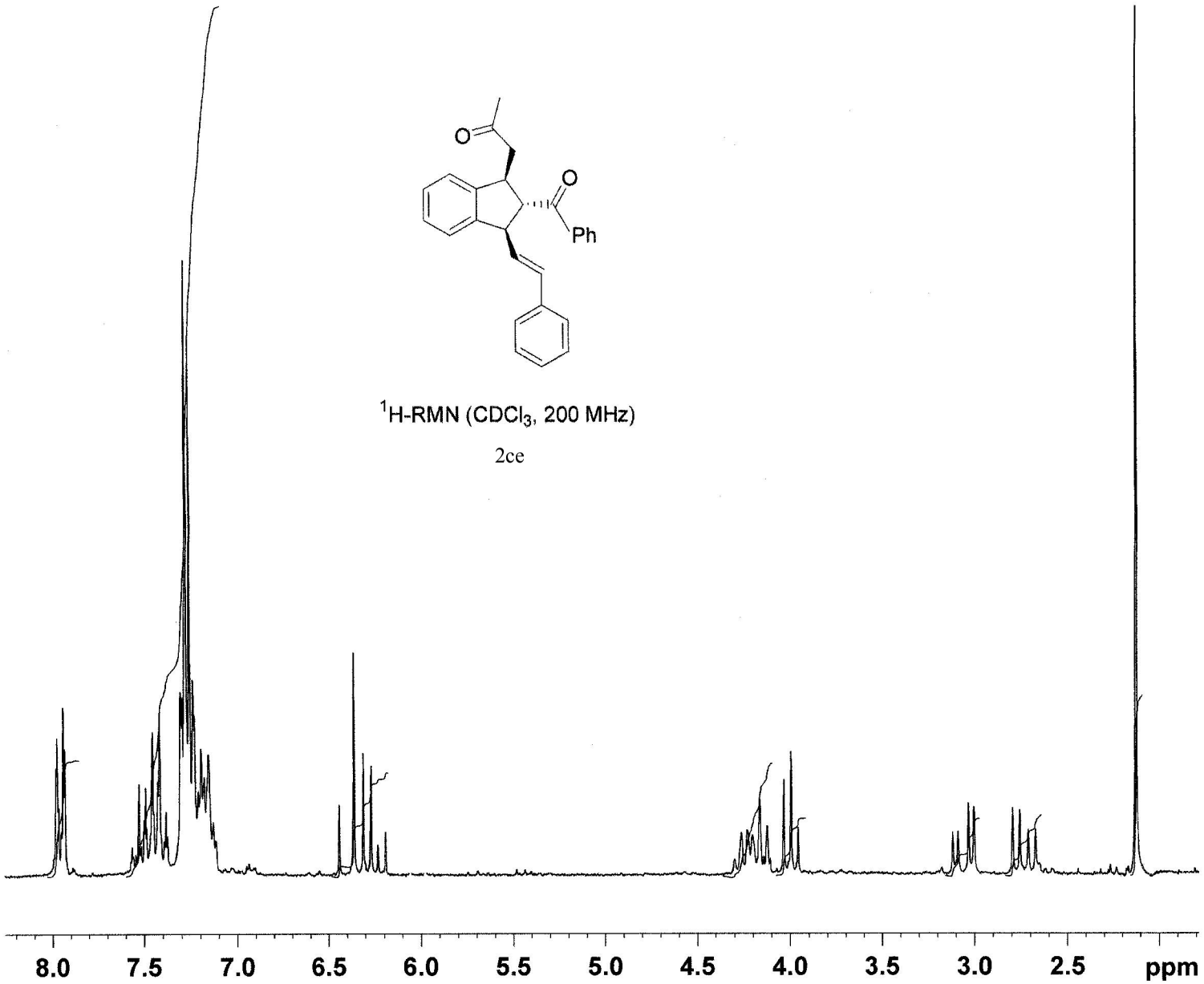
^{13}C-RMN ($CDCl_3$, 75.5 MHz)

2cd



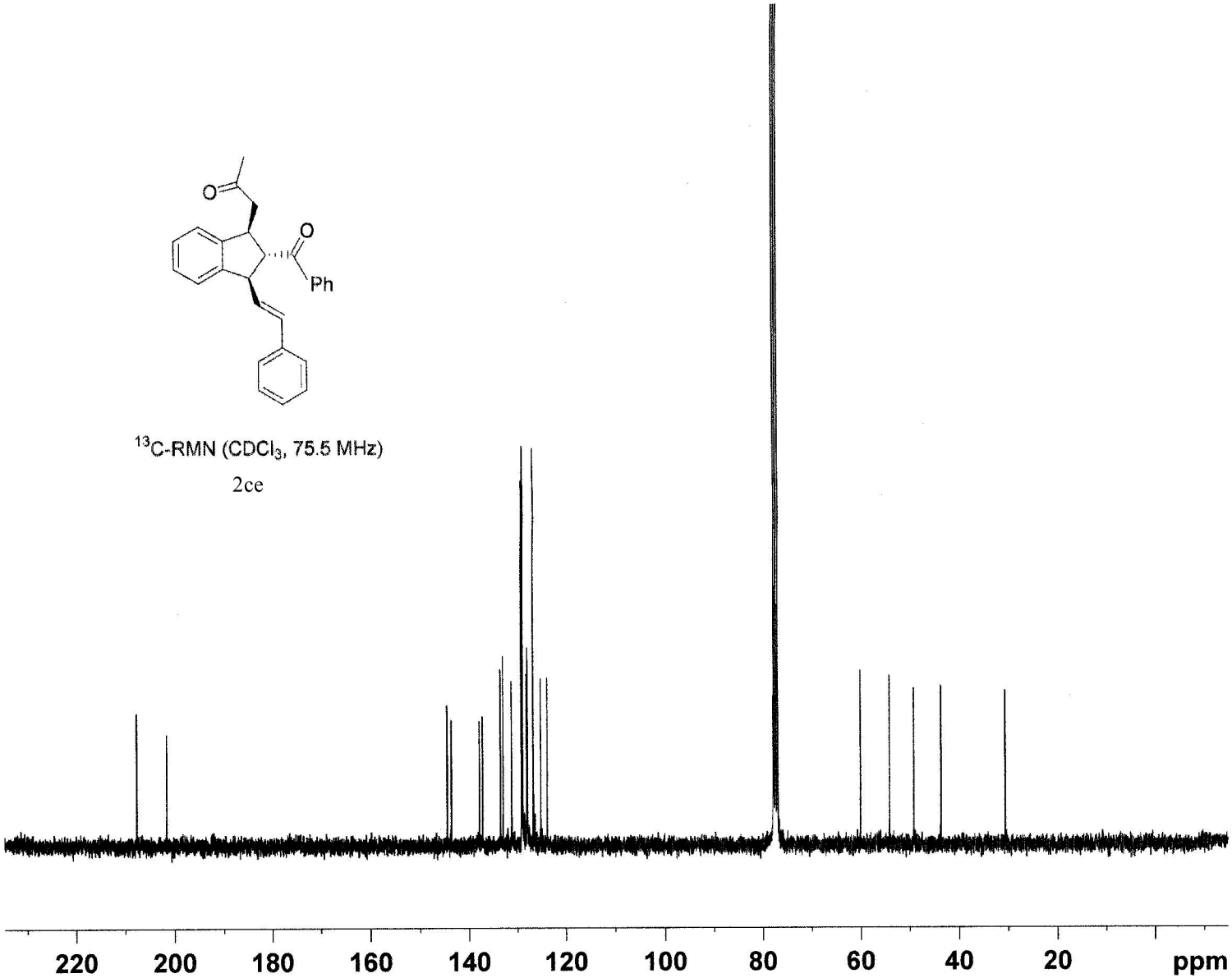
^{1}H-RMN ($CDCl_3$, 200 MHz)

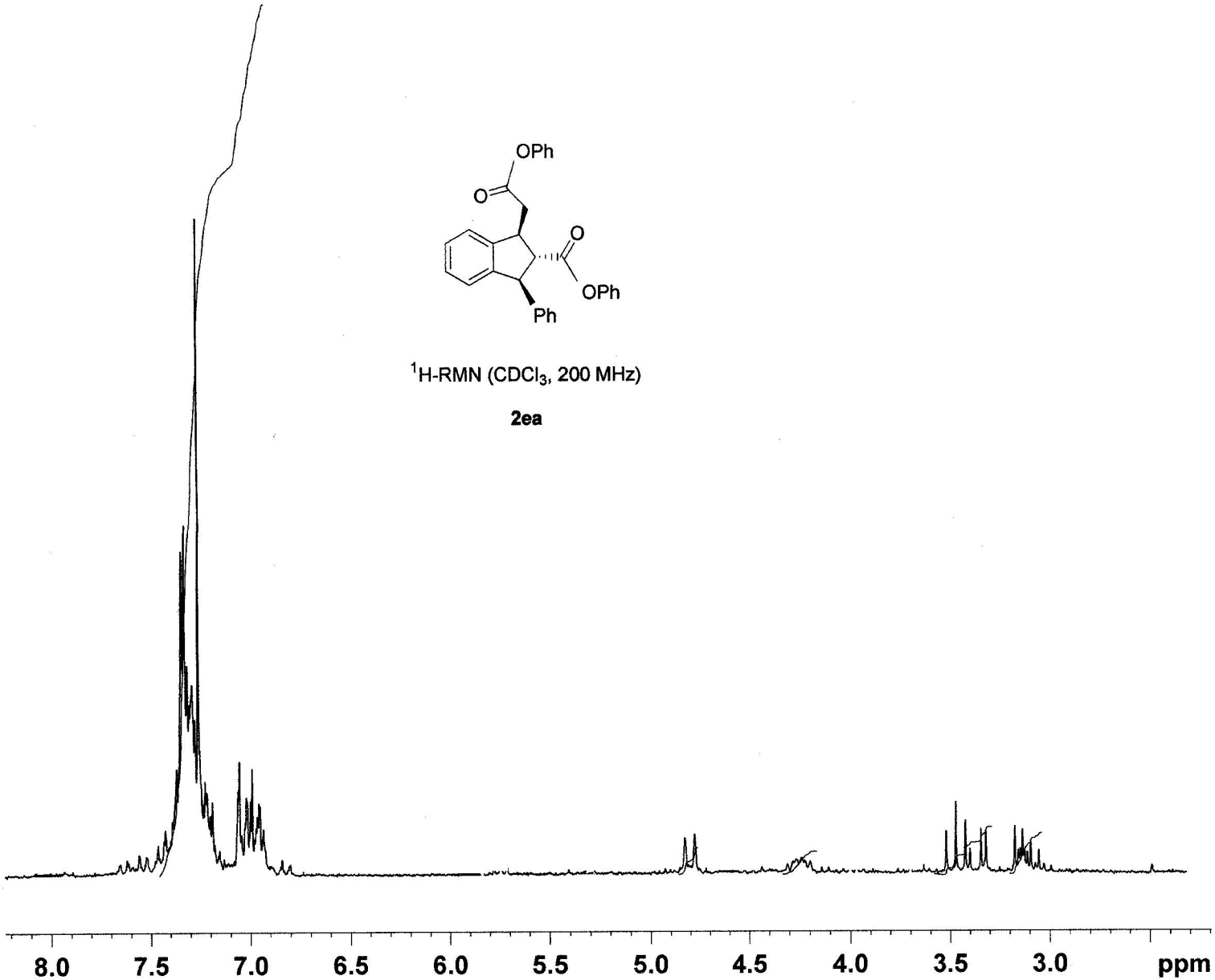
2ce



^{13}C-RMN ($CDCl_3$, 75.5 MHz)

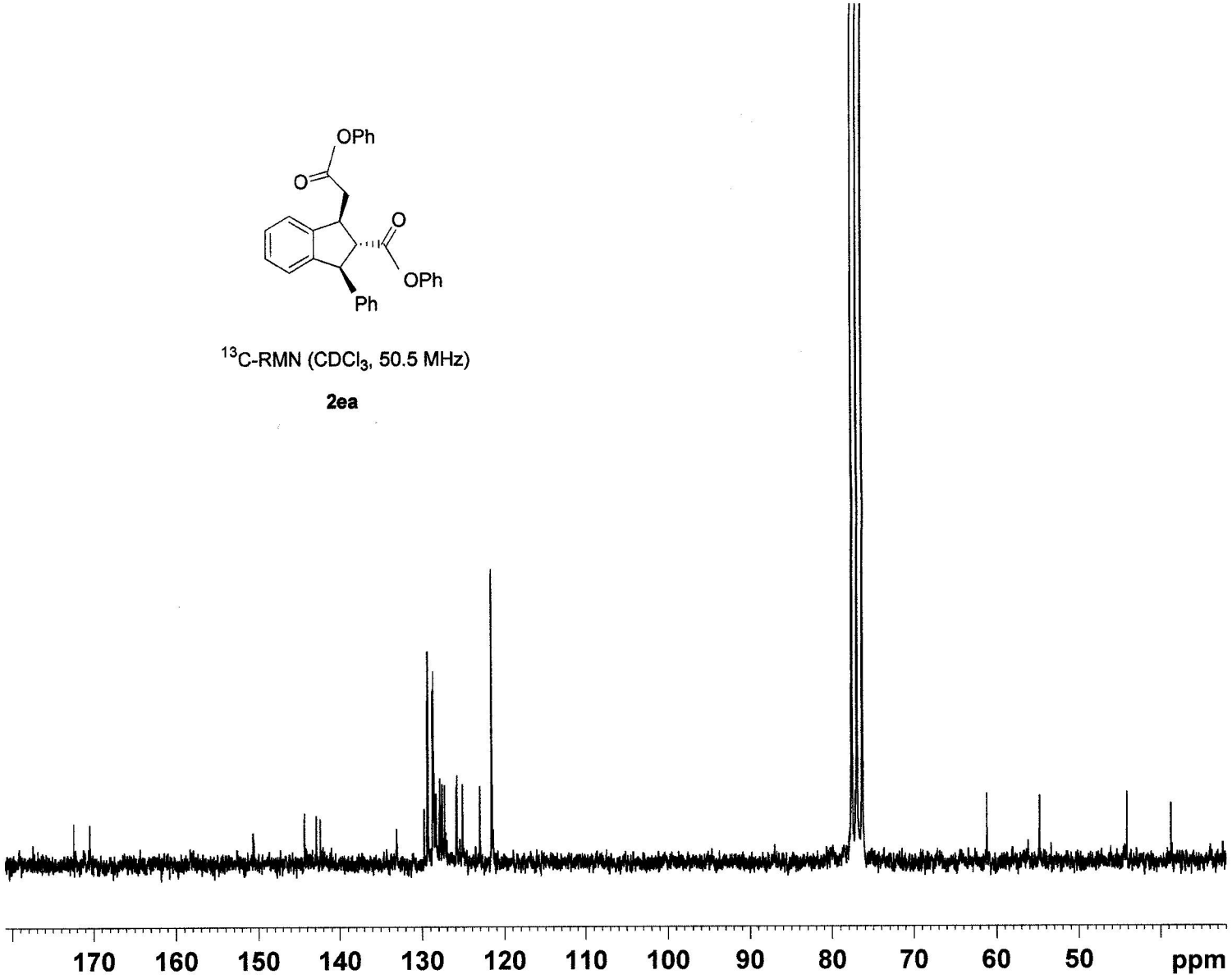
2ce





^{1}H-RMN ($CDCl_3$, 200 MHz)

2ea

^{13}C-RMN ($CDCl_3$, 50.5 MHz)

2ea