Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

An Acid Promoted *Pseudocine* Substitution Manifold of γ-Aminocyclopentenone Enables Divergent Access to Polycyclic Indole Derivatives

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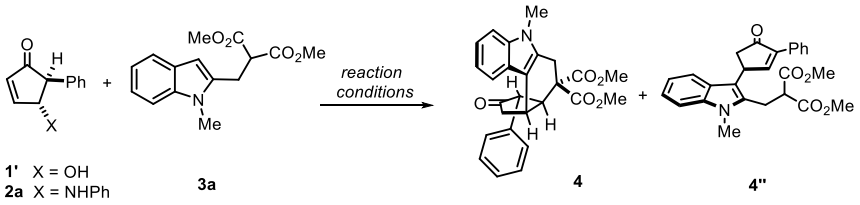
1. General Experimental:

Unless otherwise noted, all new reactions reported herein were performedusing oven-dried or flame-dried glassware under argon atmosphere and stirred magnetically. Solvents received from commercial sources were dried using standard protocols before using in this study and for THF, it was used as freshly distilled. Unless noted, all the reagents and catalysts were used as it was received from commercial sources and no further purification was made on those. Reaction monitoring was performed via TLC, using Merck silica gel 60 F 254 plates. TLC plates were visualized either under UV light (254 nm) or by using 10% ethanolic phosphomolybdic acid (PMA) or 1% aqueous $KMnO_4$ or iodine. Silica gel of 230-400 mesh size was used for the flash column chromatography. 1H, 13C NMR spectra were recorded on Avance III, Bruker at 400 MHz, 100 MHz and 376 MHz spectrometers respectively using $CDCl_3$. In the experimental section, the ^1H NMR chemicals shift are expressed in the form of ppm (δ) relative to δ = 7.26 for $CDCl_3$ whereas ^{13}C NMR chemical shift are expressed relative to δ = 77.16. The following abbreviations were used to refer to multiplicities: s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet. HRMS and Electron Spray Ionization (ESI) (m/z) spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS.

2. Detailed Optimization of the Reaction Conditions

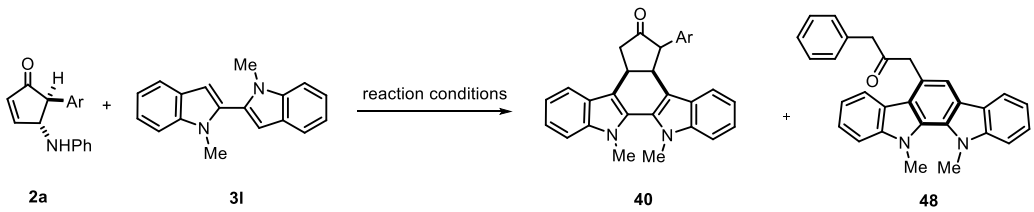
(a)



entry	*substrates*	*promoter*	*equiv.*	*solvent*	*time (h)*	*temp(°C)*	*additive*	*product*	*yield[%][b]*
1	**2a**	*p*-TsOH	2	CH_2Cl_2	12	*rt*	-	**4/4″**	NR
2	**2a**	*p*-TsOH	2	CH_2Cl_2	12	50	-	**4/4″**	0/61
3	**2a**	TfOH	2	CH_2Cl_2	6	*rt*	-	**4/4″**	NR
4	**2a**	BCl_3	2	CH_2Cl_2	6	*rt*	-	**-**	c.m[c]
5	**2a**	$SnCl_4$	2	CH_2Cl_2	12	50	-	**4/4″**	35/0
6	**2a**	$AlCl_3$	2	CH_2Cl_2	12	50	**-**	**4/4″**	92/0
7	**2a**	$AlCl_3$	1.5	CH_2Cl_2	12	50	**-**	**4/4″**	15/74
8	**2a**	$AlCl_3$	1	CH_2Cl_2	12	50	-	**4/4″**	30/55
9	**2a**	$AlCl_3$	0.5	CH_2Cl_2	12	50	-	**4/4″**	15/40
10	**2a**	$AlCl_3$	2	CH_3CN	12	50	-	**4/4″**	26/43
11	**2a**	$AlCl_3$	2	THF	12	50	-	**4/4″**	0/0
12	**2a**	$Sc(OTf)_3$	1	CH_2Cl_2	12	50	-	**4/4″**	81/0
13	**2a**	$Sc(OTf)_3$	0.5	CH_2Cl_2	12	50	-	**4/4″**	62/20
14	**2a**	$Sc(OTf)_3$	0.2	CH_2Cl_2	12	50	-	**4/4″**	25/10
15	**2a**	$BF_3.Et_2O$	2	CH_2Cl_2	2	rt	-	**4/4″**	0/90
16	**2a**	$BF_3.Et_2O$	2	CH_2Cl_2	2	rt	$Cu(OAc)_2,H_2O$	**4/4″**	5/74
17	**2a**	$BF_3.Et_2O$	2	CH_2Cl_2	12	50	$Cu(OAc)_2,H_2O$	**4/4″**	58/35
18	**2a**	$BF_3.Et_2O$	2	toluene	2	80	-	**4/4″**	0/63
19	**1'**	$AlCl_3$	2	CH_2Cl_2	2	50	-	**4/4″**	55/0

Table S1. [a]General reaction conditions: cyclopentenone Compound (1.0 equiv), indole derivativewere taken in solvent (0.1 M) and Lewis/Bronsted acid was added to the reaction mixture. The reaction was run for specific time and temperature. [b]Yields of the isolated product. [c]Complex mixture.

(b)*Optimization condition using 2, 2'-bisindole*[a]



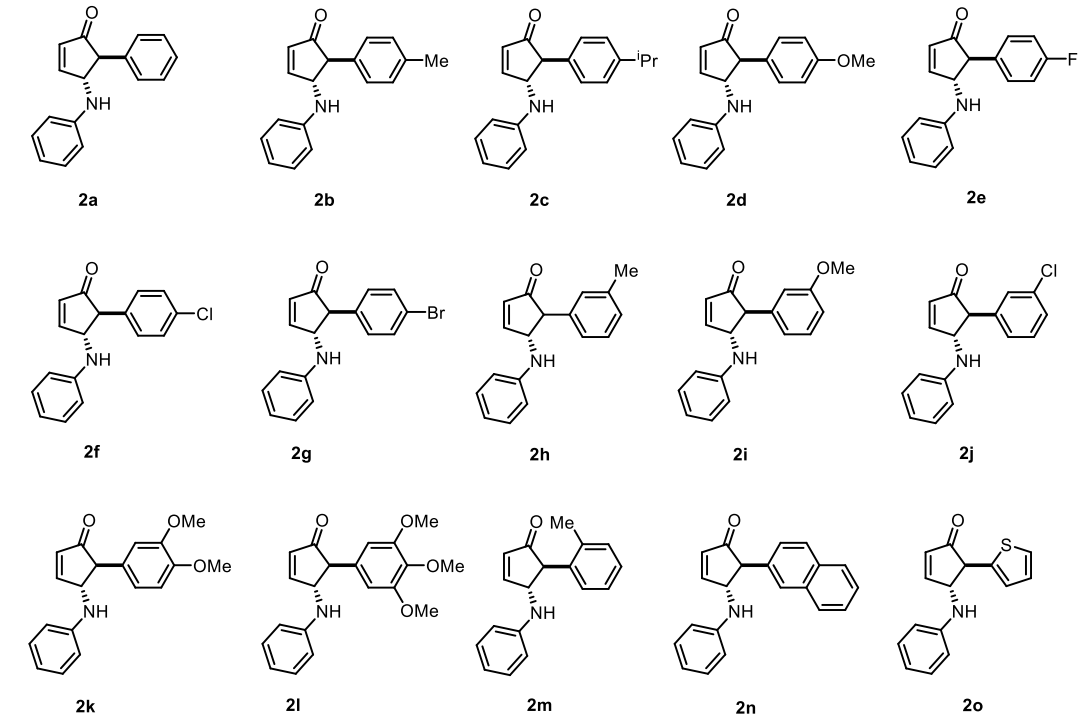
2a **3l** **40** **48**

entry	*Promoter*	*Time(h)*	*Solvent*	*Temp(°C)*	**40/48***yield[%]*[b]
1	*p*-TsOH	14	CH_2Cl_2	50	84/0
2	$BF_3.Et_2O$	14	CH_2Cl_2	50	40/25
3	$AlCl_3$	24	CH_2Cl_2	50	10/53

Table S2. [a]General reaction conditions: cyclopentenone Compound (1.0 equiv), 2,2'-bisindole(1.0 equiv) were taken in solvent (0.1 M) and Lewis/Bronsted acid was added to the reaction mixture. The reaction was run for specific time and temperature. [b]Yields of the isolated product.

3. Preparation of the starting materials:

3.1. *Preparation of 4-aminocyclopentenones*: Following 4-aminocyclopentenone derivatives were used in the study and prepared following the literature procedures.[1]



regioisomeric starting materials:

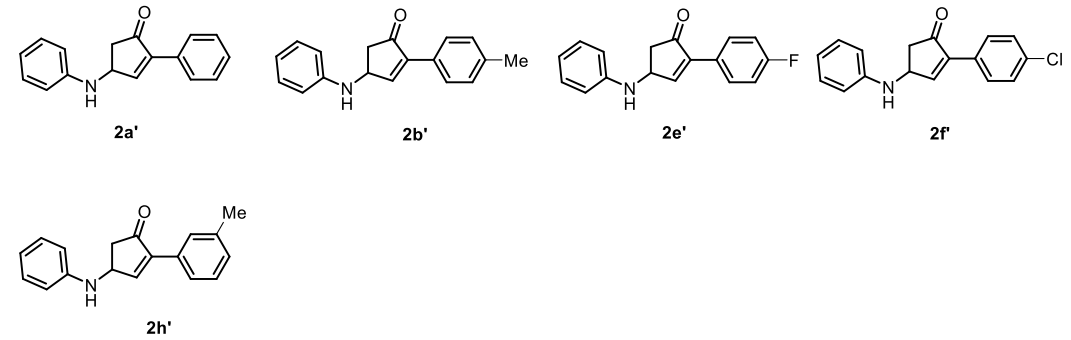


Figure S1. List of the amino-cyclopentenones used in the study

3.2 Synthesis of Indole derivatives:

Among the indole derivatives used in the study, compounds **3a**-**3l** were prepared following the reported procedure.[2-4]

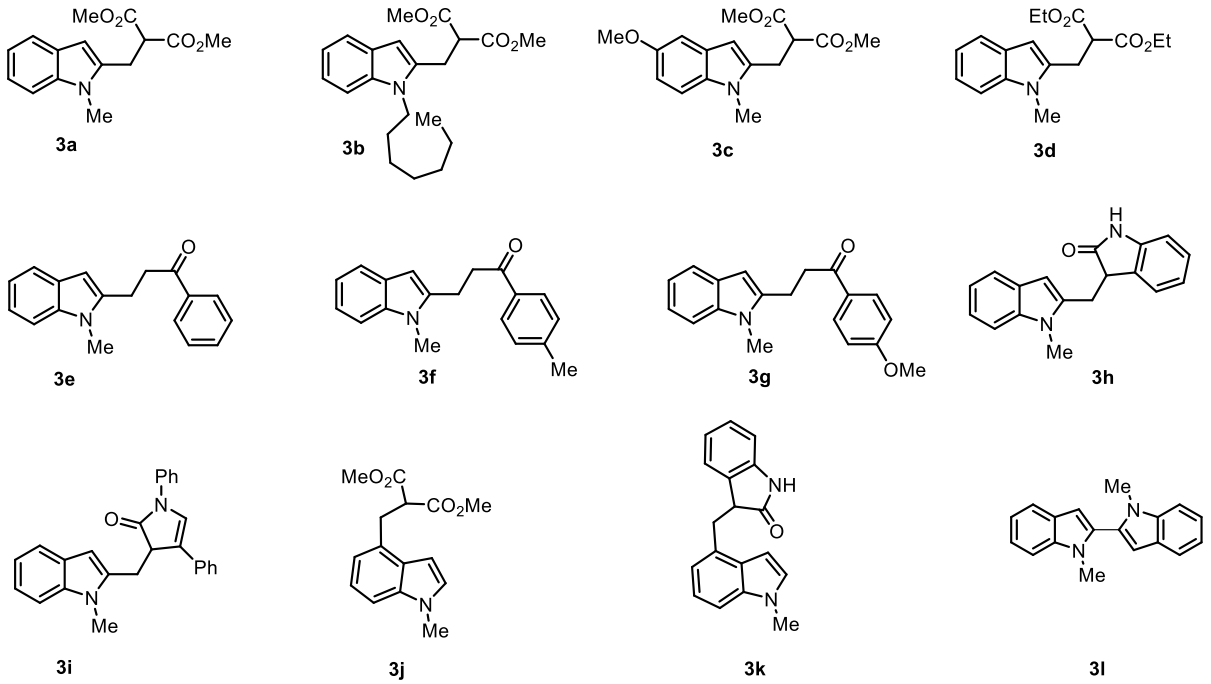
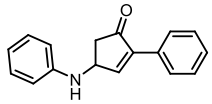


Figure S2. List of the indole derivatives used in the study

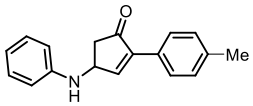
3.3. Characterization of newly synthesized starting material: ***amino-cyclopentenones***

2-phenyl-4-(phenylamino)cyclopent-2-en-1-one(2a')



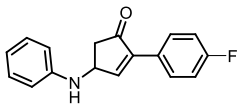
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 – 7.82 (m, 3H), 7.51 – 7.49 (m, 3H), 7.35 (t, *J* = 7.4 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 2H), 4.86 (d, *J* = 2.5 Hz, 1H), 3.68 (brs, 1H), 3.22 (dd, *J* = 18.6, 6.1 Hz, 1H), 2.53 (d, *J* = 18.7 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 204.7, 155.8, 146.6, 144.3, 130.7, 129.6, 129.2, 128.7, 127.5, 118.8, 113.7, 51.20, 44.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+C_{17}H_{16}NO^+$ Calcd.250.1226, Found 250.1228.

4-(phenylamino)-2-(p-tolyl)cyclopent-2-en-1-one(2b')



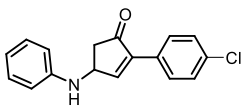
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.81 (s, 1H), 7.74 (d, *J* = 5.9 Hz, 2H), 7.34 – 7.32 (m, 4H), 6.92 (brs, 1H), 6.81 (d, *J* = 6.3 Hz, 2H), 4.87 (brs, 1H), 3.90 (brs, 1H), 3.22 (dd, *J* = 18.2, 4.9 Hz, 1H), 2.56 – 2.48 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 204.9, 155.0, 146.6, 144.0, 139.2, 129.6, 129.3, 127.8, 127.4, 118.7, 113.7, 51.1, 44.6, 21.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+C_{18}H_{18}NO^+$Calcd. 264.1383, Found 264.1378.

2-(4-fluorophenyl)-4-(phenylamino)cyclopent-2-en-1-one(2e')



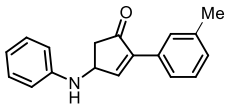
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69-7.67 (m, 3H), 7.22-7.18 (m, 2H), 7.05 –7.01 (apt, 2H), 6.77 (t, *J* = 6.4 Hz, 1H), 6.66 (d, *J* = 7.2 Hz, 2H), 4.71 (brs, 1H), 3.30 (brs, 1H), 3.07 (dd, *J* = 18.5, 5.2 Hz, 1H), 2.38 (d, *J* = 18.5 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 204.6, 163.3(d, *J* = 247.8 Hz), 155.5, 146.5, 143.1, 129.7, 129.4 (d, *J* = 8.1 Hz), 126.80 (d, *J* = 3.1 Hz), 118.9, 115.7 (d, *J* = 3.1 Hz), 113.7, 51.1, 44.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{17}H_{15}FNO^+$Calcd. 268.1132, Found 268.1153.

2-(4-chlorophenyl)-4-(phenylamino)cyclopent-2-en-1-one(2f')



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.83 (brs, 1H), 7.77 (d, *J* = 7.7 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.34 – 7.31 (m, 2H), 6.91 (t, *J* = 6.8 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 4.85 (brs, 1H), 3.61 (brs, 1H), 3.21 (d, *J* = 17.3 Hz, 1H), 2.52 (d, *J* = 18.8 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 204.4, 156.0, 146.5, 143.1, 135.2, 129.9,128.9, 128.8, 118.9, 115.2, 113.8, 51.2, 44.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{17}H_{15}ClNO^+$ Calcd. 284.0837, Found 284.0838.

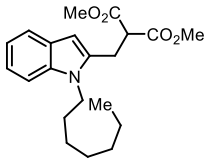
4-(phenylamino)-2-(m-tolyl)cyclopent-2-en-1-one(2h')



^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (d, *J* = 2.3 Hz, 1H), 7.49 (d, *J* = 10.7 Hz, 2H), 7.24 – 7.11 (m, 4H), 6.78 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.2 Hz, 2H), 4.71 – 4.70 (m, 1H), 3.57 (brs, 1H), 3.07 (dd, *J* = 18.6, 6.2 Hz, 1H), 2.41 – 2.33 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 204.7, 155.8, 146.6, 144.4, 138.3, 130.6, 123.0 129.7, 128.6, 128.1, 124.6, 118.7, 113.7, 51.2, 44.6, 21.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{18}H_{18}NO^+$Calcd. 264.1383, Found 264.1379.

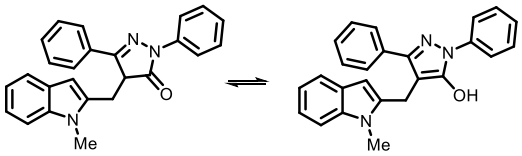
3.4. Characterization of newly synthesized staring material: ***indole derivatives***

Dimethyl 2-((1-heptyl-1H-indol-2-yl)methyl)malonate(3b)



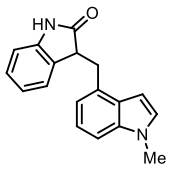
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.08 (t, *J* = 7.3 Hz, 1H), 6.27 (s, 1H), 4.11 (t, *J* = 7.6 Hz, 2H), 3.94 (t, *J* = 7.6 Hz, 1H), 3.78 (s, 6H), 3.41 (d, *J* = 7.7 Hz, 2H), 1.79-1.74 (m, 2H), 1.37 – 1.27 (m, 8H), 0.91 (t, *J* = 6.5 Hz, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 169.2, 136.8, 136.3, 127.9, 121.1, 120.2, 119.4, 109.3, 99.4, 53.0, 51.0, 43.4, 31.8, 30.3, 29.1, 27.1, 26.0, 22.7, 14.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{21}H_{30}NO_4^+$Calcd. 360.2169, Found 360.2169.

4-((1-methyl-1H-indol-2-yl)methyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one(3i)



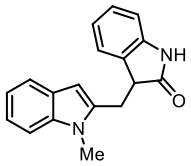
^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.43 (m, 5H), 7.41-7.37 (m, 4H), 7.35 – 7.30 (m, 5H), 7.24 – 7.16 (m, 3H), 7.14-7.11 (d, *J* = 3.4 Hz, 3H), 7.06 – 7.03 (m, 2H), 6.12 (brs, 2H), 4.09 (t, *J* = 5.4 Hz, 1H), 3.71 (s, 2H), 3.53 (d, *J* = 5.4 Hz, 2H), 3.46 (s, 2H), 3.40 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz)δ 172.8, 158.4, 150.5, 138.8, 137.9,137.8, 137.3, 134.7, 130.7 (2), 130.2, 129.0 (2), 128.9, 128.8,128.5, 127.8(2), 127.7, 126.8, 125.8, 125.6, 121.3, 120.9, 120.3, 120.1, 119.6, 119.4(2), 109.3, 109.0, 101.1, 100.0, 50.1, 29.6, 29.5, 26.0, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{25}H_{22}N_3O^+$Calcd.380.1757, Found 380.1747.

3-((1-methyl-1H-indol-4-yl)methyl)indolin-2-one(3k)



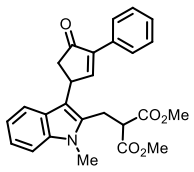
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.15 (s, 1H), 7.3**4** (d, *J* = 7.9 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.13 (s, 1H), 7.01 (d, *J* = 6.6 Hz, 1H), 6.95 (d, *J* = 7.4 Hz, 1H), 6.85 (t, *J* = 7.1 Hz, 1H), 6.70 (s, 1H), 6.55 (d, *J* = 7.0 Hz, 1H), 4.02 (d, *J* = 10.3 Hz, 1H), 3.94 (d, *J* = 14.1 Hz, 1H), 3.87 (s, 3H), 3.09 (t, *J* = 12.0 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 180.5, 141.5, 136.9, 130.7, 129.8, 128.8, 128.0, 127.8, 125.4, 122.0, 121.5, 120.4, 109.7, 108.2, 99.4, 46.6, 35.0, 33.1; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{18}H_{16}N_2NaO^+$Calcd. 299.1155, Found 299.1157.

3-((1-methyl-1H-indol-2-yl)methyl)indolin-2-one(3h)



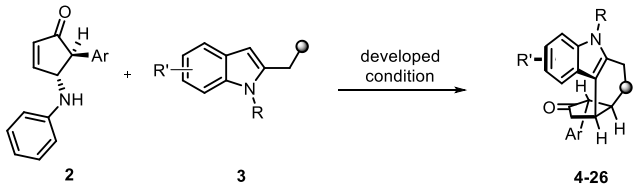
^{1}H NMR ($CDCl_3$, 400 MHz) δ 9.06 (s, 1H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.96-6.90 (m, 3H), 6.33 (s, 1H), 3.82 (dd, *J* = 10.1, 3.5 Hz, 1H), 3.69 (s, 3H), 3.63 (d, *J* = 3.5 Hz, 1H), 3.10 (dd, *J* = 15.3, 10.2 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 179.6, 141.6, 137.6, 137.0, 129.1, 128.4, 127.7, 125.0, 122.5, 121.2, 120.2, 119.6, 110.0, 109.2, 101.0, 45.7, 29.9, 28.0; **HRMS (ESI-TOF)** m/z: $[M+Na]^+$ $C_{18}H_{16}N_2NaO^+$Calcd. 299.1155, Found 299.1154.

4 Dimethyl 2-((1-methyl-3-(4-oxo-3-phenylcyclopent-2-en-1-yl)-1H-indol-2-yl)methyl)malonate (4'')



In a mixture of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in DCM was added $BF_3.OEt_2$(0.025 mL, 0.2 mmol). The reaction was stirred at room temperature and solvent was evaporated. Crude residue was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white foam in 90% (0.078 g) yield. R_f 0.25 (EtOAc: Hexane 3:7);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 3H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.1 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.19 (t, *J* = 7.6 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 4.50 – 4.49 (m, 1H), 3.74 (s, 6H), 3.73 (s, 3H), 3.69 (d, *J* = 7.4 Hz, 1H), 3.53 (d, *J* = 7.5 Hz, 2H), 3.13 (dd, *J* = 19.0, 6.9 Hz, 1H), 2.81 (dd, *J* = 19.1, 2.2 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 207.6, 168.8, 162.9, 142.8, 137.7, 132.6, 131.7, 128.7, 127.4, 125.9, 122.0, 119.7, 119.1, 112.0, 109.5, 53.1, 52.1, 44.5, 36.0, 30.0, 24.0;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{26}H_{26}NO_5^+$ Calcd. 432.1805, Found 432.1808.

5. General Procedure for [4+2]-annulation products (4-26)

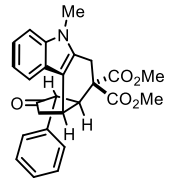


2 **3** **4-26**

In a 10 mL sealed tube, 4-aminocyclopentenone (**2**, 1.0 equiv) and indole-derived bis-nucleophiles (**3**, 1.0 equiv) were taken in anhydrous CH_2Cl_2 (0.1 M) under N_2 atmosphere. To this solution were added $AlCl_3$ (2.0 equiv) and the reaction mixture was stirred at 50˚C temperature until completion of the reaction as determined by TLC analysis (typical reaction time, 8-14h). It was then quenched with water (5-10 mL) and extracted in CH_2Cl_2 (3 × 10mL). The combined organic layer was washed with Brine, dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the desired products (**4-26**).

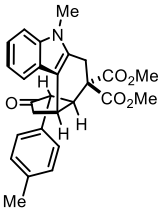
6. Preparation and characterization data of annulation product(4-26)

***Dimethyl (3S,3aS,10cR)-6-methyl-2-oxo-3-phenyl-2,3,3a,5,6,10c hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(4)**



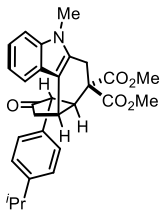
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 1.0 g, 4.0 mmol, 1.0 equiv) and indole derivative (**3a**, 1.1 g, 4.0 mmol, 1.0 equiv) in presence of $AlCl_3$ (1.1 g, 8.0 mmol) delivered compound **4**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as brown solid in 81% (1.39 g) yield.**mp**: 220-223^oC R_f0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.35-7.30 (m, 3H), 7.22 (app t, , *J* =7.6 Hz, 2H), 7.14-7.06 (m, 3H), 4.30 (t, *J* = 7.3 Hz, 1H), 3.84 (dd, *J* = 11.9, 6.4 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.60 – 3.51 (m, 2H), 3.12 (app t, *J* = 15.3 Hz, 2H), 2.97 (dd, *J* = 18.6, 8.4 Hz, 1H), 2.89 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.3, 170.1, 169.2, 138.2, 138.0, 131.3, 129.5, 128.7, 127.4, 126.1, 121.8, 119.4, 118.5, 109.3, 109.0, 56.2, 55.3, 53.4, 52.4, 47.1, 43.5, 31.1, 29.5, 23.6;**HRMS (ESI-TOF)**m/z: $[M+H]^+C_{26}H_{26}NO_5^+$Calcd. 432.1805, Found 432.1802.

Dimethyl (3S,3aS,10cR)-6-methyl-2-oxo-3-(p-tolyl)-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate(5)



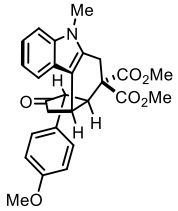
Following the general procedure, reaction of 4-aminocyclopentenone (**2b**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053g, 0.4 mmol) delivered compound **5**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as brown solid in 90% (0.08 g) yield. R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz)δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.16-7.08 (m, 3H), 7.01 (d, *J* = 7.8 Hz, 2H), 4.28 (t, *J* = 7.4 Hz, 1H), 3.81 (dd, *J* = 12.3, 6.3 Hz, 1H), 3.71 (s, 3H), 3.64 (s, 3H), 3.59 – 3.49 (m, 2H), 3.10 (dd, *J* = 15.2, 8.7 Hz, 2H), 2.98 – 2.92 (m, 4H), 2.30 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz)δ 216.6, 170.1, 169.2, 138.1, 137.1, 134.8, 131.3, 129.3(2), 126.1, 121.7, 119.4, 118.5, 109.2, 109.1, 56.2, 54.9, 53.3, 52.4, 47.0, 43.4, 31.1, 29.5, 23.6, 21.2;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{27}H_{28}NO_5^+$ Calcd.446.1962, Found 446.1958.

Dimethyl (3S,3aS,10cR)-3-(4-isopropylphenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate(6)



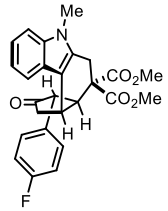
Following the general procedure, reaction of 4-aminocyclopentenone (**2c**, 0.058 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **6**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 86% (0.081 g) yield. R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ7.49 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24-7.17 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.9 Hz, 2H), 4.28 (t, *J* = 7.2 Hz, 1H), 3.81 (dd, *J* = 12.0, 6.5 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.60-3.48 (m, 2H), 3.13 – 3.08 (m, 2H), 2.97 (dd, *J* = 18.6, 8.4 Hz, 1H), 2.91 – 2.84 (m, 4H), 1.21 (d, *J* = 6.9 Hz, 6H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.8, 170.1, 169.2, 148.0, 138.1, 135.2, 131.3, 129.4, 126.7, 126.1, 121.7, 119.4, 118.5, 109.2, 109.0, 56.1, 54.9, 53.3, 52.2, 47.2, 43.5, 33.9, 31.1, 29.5, 24.1, 24.0, 23.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{32}NO_5^+$ Calcd. 474.2275, Found 474.2275.

***Dimethyl (3S,3aS,10cR)-3-(4-methoxyphenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(7)**



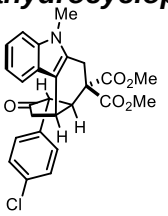
Following the general procedure, reaction of 4-aminocyclopentenone (**2d**, 0.056 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **7**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as brown solid in 79% (0.073 g) yield.**mp**: 214-217ºC; R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 4.28 (t, *J* = 7.2 Hz, 1H), 3.80 – 3.76 (m, 4H), 3.72(s,3H), 3.65 (s, 3H), 3.59 – 3.50 (m, 2H), 3.11- 3.07 (m, 2H), 2.98 – 2.92 (m, 4H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.9, 170.1, 169.3, 158.8, 138.1, 131.3, 130.5, 129.8, 126.0, 121.7, 119.4, 118.5, 114.1, 109.2, 109.0, 56.1, 55.4, 54.4, 53.4, 52.6, 47.0, 43.3, 31.0, 29.5, 23.5;HRMS (ESI-TOF) m/z: $[M+H]^+$ $C_{27}H_{28}NO_6^+$ Calcd. 462.1911, Found 462.1908.

***Dimethyl (3S,3aS,10cR)-3-(4-fluorophenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(8)**



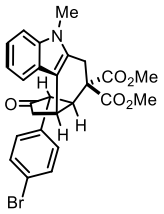
Following the general procedure, reaction of 4-aminocyclopentenone (**2e**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **8**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 70% (0.063 g) yield. R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 7.0 Hz, 3H), 7.03 (t, *J* = 8.4 Hz, 2H), 4.30 (t, *J* = 7.2 Hz, 1H), 3.78 (dd, *J* = 12.0, 6.4 Hz, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 3.60 – 3.49 (m, 2H), 3.13 (dd, *J* = 21.3, 15.5 Hz, 2H), 3.00 – 2.92 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.1, 170.0, 169.2, 162.1(d, *J* = 245.1 Hz), 138.2, 133.7 (d, *J* = 3.2 Hz), 131.1(d, *J* = 8 Hz), 129.4, 126.0, 121.8, 119.5, 118.5, 115.5(d, *J* = 21.3 Hz), 109.3, 108.9, 56.1, 54.5, 53.4, 52.5, 47.0, 43.3, 31.1, 29.5, 23.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{25}FNO_5^+$ Calcd. 450.1711, Found 450.1709.

***Dimethyl (3S,3aS,10cR)-3-(4-chlorophenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(9)**



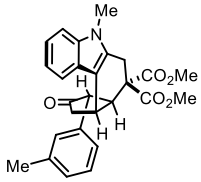
Following the general procedure, reaction of 4-aminocyclopentenone (**2f**, 0.057 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **9**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as brown solid in 63% (0.059 g) yield.mp: 239-242^{o}C; R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.3 Hz, 3H), 7.23 (t, *J* = 7.6 Hz, 1H), 7.13-7.07 (m, 3H), 4.30 (t, *J* = 7.1 Hz, 1H), 3.78 (dd, *J* = 12.1, 6.6 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 3H), 3.60 – 3.48 (m, 2H), 3.16 – 3.08 (m, 2H), 3.02 – 2.92 (m, 4H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 215.7, 169.9, 169.2, 138.1, 136.4, 133.4, 131.2, 130.8, 128.8, 126.0, 121.8, 119.5, 118.5, 109.3, 108.9, 56.1, 54.7, 53.4, 52.5, 46.9, 43.4, 31.1, 29.5, 23.5;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{26}H_{25}ClNO_5^+$Calcd.466.1416, Found 466.1411.

***Dimethyl (3S,3aS,10cR)-3-(4-bromophenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(10)**



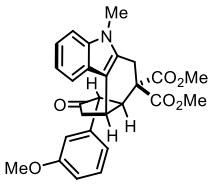
Following the general procedure, reaction of 4-aminocyclopentenone (**2g**, 0.065 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **10**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 66% (0.078 g) yield.**mp**: 230-233^oC; R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.52 – 7.49 (m, 3H), 7.34 (d, *J* = 8.2 Hz, 1H), 7.27 (dd, *J* = 14.0, 6.5 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.05 (d, *J* = 8.3 Hz, 2H), 4.33 (t, *J* = 7.2 Hz, 1H), 3.81 (dd, *J* = 12.1, 6.5 Hz, 1H), 3.75 (s, 3H), 3.68 (s, 3H), 3.63 – 3.51 (m, 2H), 3.18 – 3.11 (m, 2H), 3.03 (s, 3H), 2.98 (dd, *J* = 18.9, 8.5 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 215.6, 169.9, 169.2, 138.1, 136.9, 131.7, 131.2, 131.1, 126.0, 121.8, 121.4, 119.5, 118.5, 109.3, 108.9, 56.1, 54.8, 53.4, 52.5, 46.9, 43.4, 31.1, 29.5, 23.5;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{26}H_{25}BrNO_5^+$Calcd.510.0911, Found 510.0909.

***Dimethyl (3S,3aS,10cR)-6-methyl-2-oxo-3-(m-tolyl)-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(11)**



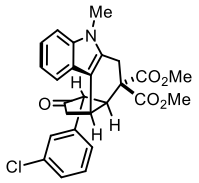
Following the general procedure, reaction of 4-aminocyclopentenone (**2h**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **11**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 76% (0.068 g) yield.**mp**: 180-183^oC; R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.49 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24-7.19 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.3 Hz, 2H), 4.29 (t, *J* = 7.3 Hz, 1H), 3.83 (dd, *J* = 11.8, 6.5 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.60-3.49 (dd, *J*= 28.9, 11.4 Hz, 2H), 3.10 (d, *J* = 15.3 Hz, 2H), 2.97 (dd, *J* = 18.8, 8.4 Hz, 1H), 2.91 (s, 3H), 2.34 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.5, 170.1, 169.2, 138.1, 137.8, 131.3, 130.1, 128.5, 128.2, 126.6, 126.1, 121.7, 119.4, 118.5, 109.2, 109.1, 56.2, 55.2, 53.3, 52.3, 47.0, 43.6, 31.1, 29.5, 23.5, 21.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+ C_{27}H_{28}NO_5^+$ Calcd. 446.1962, Found 446.1964.

***Dimethyl (3S,3aS,10cR)-3-(3-methoxyphenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(12)**



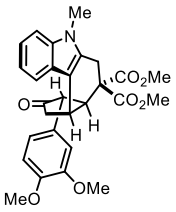
Following the general procedure, reaction of 4-aminocyclopentenone (**2i**, 0.056 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **12**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as yellow solid in 85% (0.078 g) yield. R_f 0.30 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.23 (dd, *J* = 16.5, 8.2 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 8.2 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 6.67 (s, 1H), 4.29 (t, *J* = 7.1 Hz, 1H), 3.86 – 3.83 (m, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.64 (s, 3H), 3.60 – 3.49 (m, 2H), 3.11 (dd, *J* = 15.2, 8.5 Hz, 2H), 3.00 – 2.93 (m, 4H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.0, 170.1, 169.2, 159.7, 139.4, 138.1, 131.3, 129.6, 126.0, 121.7(2), 119.4, 118.5, 115.2, 112.9, 109.2, 109.0, 56.2, 55.4, 55.2, 53.3, 52.3, 46.9, 43.5, 31.1, 29.4, 23.5;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{27}H_{28}NO_6^+$ Calcd. 462.1911, Found 462.1908.

Dimethyl (3S,3aS,10cR)-3-(3-chlorophenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate(13)



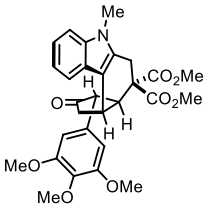
Following the general procedure, reaction of 4-aminocyclopentenone (**2j**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **13**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 85% (0.079 g) yield.**mp**:190-195^{o}C; R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.24 – 7.20 (m, 3H), 7.13 (s, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.1 Hz, 1H), 4.29 (t, *J* = 7.2 Hz, 1H), 3.80 (dd, *J* = 12.0, 6.5 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 3.59 - 3.46 (m, 2H), 3.11 (app t, *J* = 15.2 Hz, 2H), 3.01 (s, 3H), 2.95 (dd, *J* = 18.7, 8.4 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 215.3, 169.9, 169.1, 139.8, 138.1, 134.4, 131.1, 129.9, 129.2, 128.1, 127.6, 126.0, 121.8, 119.5, 118.5, 109.3, 108.8, 56.1, 54.9, 53.4, 52.4, 46.7, 43.4, 31.1, 29.5, 23.5;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{25}ClNO_5^+$ Calcd. 466.1416, Found 466.1413.

***Dimethyl (3S,3aS,10cR)-3-(3,4-dimethoxyphenyl)-6-methyl-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(14)**



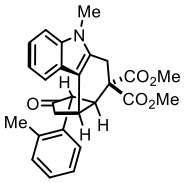
Following the general procedure, reaction of 4-aminocyclopentenone (**2k**, 0.062 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **14**, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound as white solid in 63% (0.062 g) yield. R_f 0.30 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.62 (s, 1H), 4.29 (t, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.81 – 3.78 (m, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 3.60-3.51 (m, 2H), 3.12 – 3.07 (m, 2H), 3.00 (s, 3H), 3.00 – 2.93 (m, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.6, 170.1, 169.3, 148.9, 148.4, 138.1, 131.2, 130.3, 126.0, 121.9, 121.7, 119.4, 118.5, 112.4, 111.3, 109.2, 109.0, 56.2, 56.1, 56.0, 54.8, 53.3, 52.6, 47.0, 43.0, 31.0, 29.5, 23.5; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{28}H_{30}NO_7^+$ Calcd. 492.2017, Found 492.2016.

***Dimethyl (3S,3aS,10cR)-6-methyl-2-oxo-3-(3,4,5-trimethoxyphenyl)-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(15)**



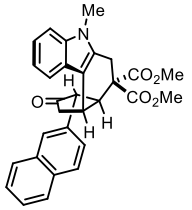
Following the general procedure, reaction of 4-aminocyclopentenone (**2l**, 0.068 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **15**, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound as white solid in 76% (0.079 g) yield. R_f 0.30 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.48 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.31 (s, 2H), 4.30 (t, *J* = 7.3 Hz, 1H), 3.87 (s, 6H), 3.80 (s, 3H), 3.75 (t, *J* =3.6, 1H), 3.72 (s, 3H), 3.64 (s, 3H), 3.60 – 3.50 (m, 2H), 3.10 (app t, *J* = 14.9 Hz, 2H), 3.04 (s, 3H), 2.97 (dd, *J* = 18.7, 8.5 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.3, 170.1, 169.3, 153.2, 138.2, 137.3, 133.5, 131.2, 126.0, 121.8, 119.5, 118.5, 109.3, 109.0, 106.6, 60.9, 56.3, 56.2, 55.5, 53.4, 52.5, 47.2, 43.5, 31.1, 29.5, 23.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{29}H_{32}NO_8^+$Calcd. 522.2122, Found 522.2122.

***Dimethyl (3S,3aS,10cR)-6-methyl-2-oxo-3-(o-tolyl)-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(16)**



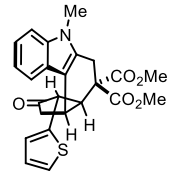
Following the general procedure, reaction of 4-aminocyclopentenone (**2m**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **16**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 61% (0.054 g) yield.**mp**: 224-227ºC R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.23 – 7.14 (m, 5H), 4.38 (t, *J* = 7.2 Hz, 1H), 4.04 - 4.00 (m, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.66 – 3.44 (m, 3H), 3.14 (d, *J* = 18.6 Hz, 1H), 3.03 (dd, *J* = 18.7, 8.3 Hz, 1H),, 2.91 (s, 3H), 2.37 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.2, 170.1, 169.4, 138.1, 131.2, 130.8, 127.2, 126.2, 126.1, 121.8, 121.3, 120.2, 119.6, 119.4, 118.5, 109.3, 109.1, 56.2, 53.3, 52.4, 50.2, 47.0, 43.3, 31.2, 29.5, 23.7, 20.5;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{27}H_{28}NO_5^+$ Calcd.446.1962, Found 446.1963.

***Dimethyl (3S,3aS,10cR)-6-methyl-3-(naphthalen-2-yl)-2-oxo-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(17)**



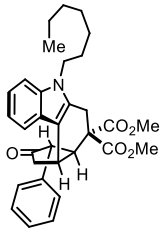
Following the general procedure, reaction of 4-aminocyclopentenone (**2n**, 0.06 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **17**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 73% (0.07 g) yield. R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.84-7.80 (m, 3H), 7.60 (s, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.49-7.44 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.28 – 7.22 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.36 (t, *J* = 7.0 Hz, 1H), 3.99 (dd, *J* = 12.0, 6.5 Hz, 1H), 3.74 (s, 3H), 3.69 – 3.58 (m, 5H), 3.35 (d, *J* = 12.0 Hz, 1H), 3.16 (d, *J* = 18.6 Hz, 1H), 3.05 (dd, *J* = 18.6, 8.3 Hz, 1H), 2.62 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.2, 170.1, 169.2, 138.2, 135.2, 133.3, 132.7, 131.4, 129.0, 128.4, 127.9, 127.6, 126.7, 126.4, 126.1(2), 121.8, 119.5, 118.5, 109.3, 109.1, 56.2, 55.4, 53.4, 52.3, 46.9, 43.6, 31.2, 29.5, 23.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{28}NO_5^+$ Calcd. 482.1962, Found 482.1967.

***Dimethyl (3R,3aS,10cR)-6-methyl-2-oxo-3-(thiophen-2-yl)-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(18)**



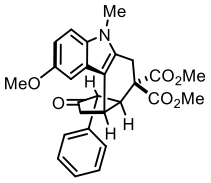
Following the general procedure, reaction of 4-aminocyclopentenone (**2o**, 0.051 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053g, 0.4 mmol) delivered compound **18**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 51% (0.045 g) yield.**mp**: 130-133^oC; R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.07 (t, *J* = 7.4 Hz, 1H), 6.92 (t, *J* = 4.0 Hz, 1H), 6.84 (d, *J* = 3.2 Hz, 1H), 4.25 (t, *J* = 6.9 Hz, 1H), 3.76 (dd, *J* = 11.6, 6.4 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.61 - 3.43 (m, 3H), 3.14 (s, 3H), 3.07 – 2.92 (m, 2H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 214.1, 170.0, 169.4, 140.1, 138.1, 131.2, 127.3, 126.8, 126.0, 125.3, 121.8, 119.4, 118.5, 109.3, 108.6, 56.2, 53.4, 52.7, 49.9, 48.0, 42.6, 31.1, 29.5, 23.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{24}H_{24}NO_5S^+$Calcd. 438.1370, Found 438.1368.

***Dimethyl (3S,3aS,10cR)-6-heptyl-2-oxo-3-phenyl-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(19)**



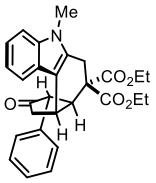
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3b**, 0.072 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **19**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 72% (0.074 g) yield.mp: 235-238^oC; R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.37-7.33 (m, 3H), 7.28 – 7.21 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 4.32 (t, *J* = 7.2 Hz, 1H), 4.17 - 4.08 (m, 2H), 3.87 (dd, *J* = 11.9, 6.5 Hz, 1H), 3.70 – 3.63 (m, 4H), 3.52 (d, *J* = 17.3 Hz, 1H), 3.15 (dd, *J* = 20.1, 15.5 Hz, 2H), 3.00 (dd, *J* = 18.6, 8.5 Hz, 1H), 2.92 (s, 3H), 1.80 - 1.75 (m, 2H), 1.38 – 1.32 (m, 8H), 0.92 (t, *J* = 6.4 Hz, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.4, 169.9, 169.2, 137.9, 137.4, 130.8, 129.5, 128.6, 127.4, 126.2, 121.6, 119.3, 118.5, 109.5, 109.0, 56.2, 55.4, 53.2, 52.3, 47.0, 43.4(2), 31.8, 31.1, 30.4, 29.2, 27.1, 23.5, 22.7, 14.2;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{32}H_{38}NO_5^+$Calcd.516.2744, Found516.2744.

***Dimethyl (3S,3aS,10cR)-9-methoxy-6-methyl-2-oxo-3-phenyl-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(20)**



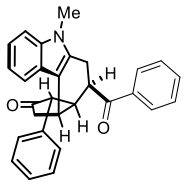
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.050 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3c**, 0.061 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **20**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 91% (0.084 g) yield. R_f 0.30 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.37 (t, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 8.8 Hz, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 6.97 (brs, 1H), 6.93 – 6.90 (m, 1H), 4.31 (t, *J* = 7.2 Hz, 1H), 3.89 – 3.86 (m, 4H), 3.72 (s, 3H), 3.69 (s, 3H), 3.59 (q, *J* = 17.7 Hz, 2H), 3.17 (dd, *J* = 23.2, 15.3 Hz, 2H), 3.00 (dd, *J* = 18.5, 8.4 Hz, 1H), 2.93 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.4, 170.1, 169.1, 154.0, 137.9, 133.4, 131.9, 129.5, 128.6, 127.4, 126.3, 111.3, 109.9, 108.5, 101.0, 56.2, 56.1, 55.2, 53.3, 52.3, 47.0, 43.3, 31.0, 29.6, 23.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{27}H_{28}NO_6^+$ Calcd. 462.1911, Found 462.1907.

***Diethyl (3S,3aS,10cR)-6-methyl-2-oxo-3-phenyl-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(21)**



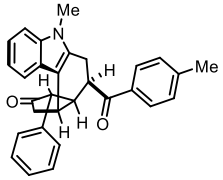
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3d**, 0.061 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **21**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as brown solid in 85% (0.078 g) yield.**mp**: 194-197^{o}C; R_f0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.34-7.30 (m, 3H), 7.26 – 7.20 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 4.34 (t, *J* = 7.2 Hz, 1H), 4.20 – 4.12 (m, 1H), 4.09 – 4.01 (m, 1H), 3.85 (dd, *J* = 11.8, 6.5 Hz, 1H), 3.72 (s, 3H), 3.63 – 3.51 (m, 3H), 3.14 (dd, *J* = 21.3, 15.3 Hz, 2H), 3.01 – 2.89 (m, 2H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.90 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.6, 169.6, 168.9, 138.2, 138.1, 131.4, 129.5, 128.6, 127.4, 126.1, 121.6, 119.3, 118.5, 109.2, 109.1, 62.0, 61.7, 56.3, 55.2, 47.0, 43.6, 31.2, 29.4, 23.5, 14.0, 13.5;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{28}H_{30}NO_5^+$ Calcd. 460.2118, Found 460.2118.

(*3S,3aR,4S,10cR)-4-benzoyl-6-methyl-3-phenyl-3,3a,4,5,6,10c hexahydrocyclopenta[c]carbazol-2(1H)-one*(22)



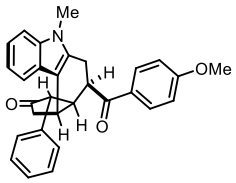
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3e**, 0.053 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **22**, which was purified by brown gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as white solid in 52% (0.044 g) yield. R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.69 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.48 – 7.37 (m, 6H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25-7.29 (m, 3H), 7.09 (t, *J* = 7.4 Hz, 1H), 3.99-3.97 (m, 1H), 3.80-3.77 (m, 1H), 3.71 (s, 3H), 3.39 (d, *J* = 11.3 Hz, 1H), 3.32-3.25 (m, 2H), 3.09 (dd, *J* = 17.7, 7.3 Hz, 2H), 2.89 (dd, *J* = 19.1, 8.5 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.7, 200.9, 137.7, 137.5, 135.8, 133.4, 132.6, 129.2, 128.9, 128.5, 127.8, 126.4, 121.3, 119.2, 118.3, 109.2, 108.6, 57.6, 46.3, 44.0, 41.1, 29.6, 29.5, 20.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{26}NO_2^+$ Calcd. 420.1958, Found 420.1957.

***(3S,3aR,4S,10cR)-6-methyl-4-(4-methylbenzoyl)-3-phenyl-3,3a,4,5,6,10c-hexahydrocyclopenta[c]carbazol-2(1H)-one*(23)**



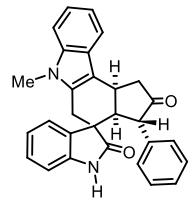
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**5f**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **23**, which was purified by silica gel column chromatography (Hexane/EtOAc 9:1) to furnish the title compound as brown solid in 51% (0.044 g) yield. R_f 0.30 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.60 (d, *J* = 7.9 Hz, 2H), 7.48-7.44 (m, 3H), 7.38 (t, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.26-7.19(m, 5H), 7.10 (t, *J* = 7.4 Hz, 1H), 3.97 – 3.96 (m, 1H), 3.80-3.76 (m, 1H), 3.71 (s, 3H), 3.39 (d, *J* = 11.2 Hz, 1H), 3.31-3.27 (m, 2H), 3.10 – 3.05 (m, 2H), 2.89 (dd, *J* = 19.0, 8.4 Hz, 1H), 2.42 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.8, 200.4, 144.3, 137.6(2), 133.2, 132.8, 129.6, 129.2, 128.9, 128.6, 127.7, 126.4, 121.2, 119.2, 118.3, 109.1, 108.6, 57.7, 46.5, 44.0, 41.0, 29.6, 29.4, 21.8, 20.3;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{28}NO_2^+$Calcd. 434.2115, Found 434.2113.

***(3S,3aR,4S,10cR)-4-(4-methoxybenzoyl)-6-methyl-3-phenyl-3,3a,4,5,6,10c-hexahydrocyclopenta[c]carbazol-2(1H)-one*(24)**



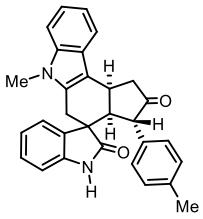
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3g**, 0.059 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **24**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as brown solid in 47% (0.042 g) yield. R_f 0.30 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.70 (d, *J* = 8.7 Hz, 2H), 7.46 (dd, *J* = 14.7, 7.6 Hz, 3H), 7.38 (d, *J* = 7.1 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 5.9 Hz, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.10 (t, *J* = 7.4 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 3.96 – 3.93 (m, 1H), 3.87 (s, 3H), 3.80 (d, *J* = 7.2 Hz, 1H), 3.70 (s, 3H), 3.39 (d, *J* = 10.7 Hz, 1H), 3.30 – 3.24 (m, 2H), 3.10 – 3.03 (m, 2H), 2.91 (dd, *J* = 19.1, 8.4 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 217.0, 199.3, 163.7, 137.7, 137.6, 132.9, 130.8, 129.2, 128.9, 128.6, 127.7, 126.5, 121.2, 119.2, 118.3, 114.1, 109.1, 108.6, 57.8, 55.7, 46.7, 44.1, 40.7, 29.7, 29.5, 20.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{28}NO_3^+$ Calcd. 450.2064, Found 450.2063.

3-((1S,5S)-5-(2-ethyl-1-methyl-1H-indol-3-yl)-3-oxo-2-phenylcyclopentyl)indolin-2-one(25)



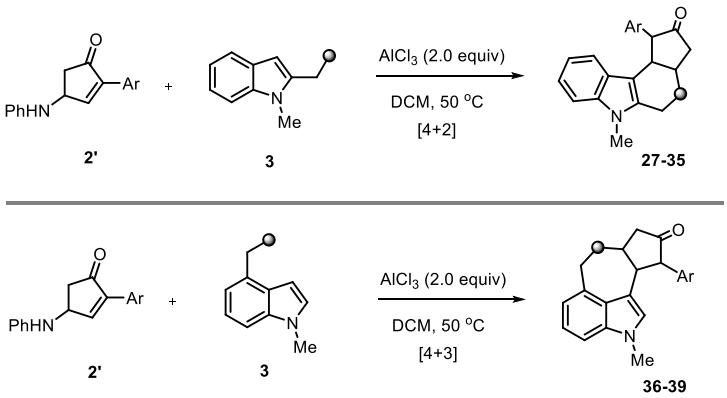
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.025 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3h**, 0.028 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **25** as yellowish brown solid in 69% (0.03 g) yield as mixture of diastereomers (*dr* 1:1). R_f 0.2 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.73 (s, 1H), 8.30 (s, 0.75H), 7.54 (d, *J* = 7.8 Hz, 0.88H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.23 – 7.15 (m, 8H), 7.13-7.11 (m, 5H), 7.09 – 7.03 (m, 4H), 6.86-6.81 (m, 2H), 6.76 (d, *J* = 7.6 Hz, 1H), 6.70 - 6.63 (m, 2H), 4.15 (q, *J* = 9.9 Hz, 1H), 4.04 (t, *J* = 7.0 Hz, 0.85H), 3.58 (s, 2H), 3.55 (s, 3H), 3.46 (d, *J* = 8.7 Hz, 1.65H), 3.27 (d, *J* = 15.8 Hz, 1H), 3.13 (d, *J* = 17.4 Hz, 0.79H), 3.10 – 2.94 (m, 2H), 2.92 (brs, 1H), 2.84 – 2.76 (m, 3H), 2.67 (dd, *J* = 18.9, 11.1 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.7, 216.1, 181.0, 179.9, 140.9, 140.0, 139.9, 139.0, 138.3, 138.0, 133.6, 132.7, 132.4, 130.6, 129.2, 129.0, 128.6(2), 128.2, 127.7, 127.2, 126.9, 126.4, 126.0, 125.5, 124.4, 122.8, 122.7,121.8, 121.7, 119.7, 119.6, 118.7(2), 110.6, 110.3, 110.2, 109.4(2), 109.0, 56.3, 54.0, 51.9, 50.3, 48.9, 48.0, 43.7, 43.4, 31.6, 31.2, 29.9, 29.5(2), 25.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{25}N_2O_2^+$Calcd.433.1911, Found 433.1913.

***3-((1S,5S)-5-(2-ethyl-1-methyl-1H-indol-3-yl)-3-oxo-2-(p-tolyl)cyclopentyl)indolin-2-one*(26)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2b**, 0.026 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3h**, 0.028 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **26** as white solid in 65% (0.029 g) yield as mixture of diastereomers (*dr*3:1).R_f 0.2 (EtOAc: Hexane 3:7); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.85 (s, 1H), 8.42 (s, 0.37H), 7.61 (d, *J* = 7.9 Hz, 0.39H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz,1.4H), 7.29 (t, *J* = 7.4 Hz, 1.37H), 7.19 (t, *J* = 7.6 Hz, 3H), 7.14 – 7.02 (m, 5H), 6.94 (d, *J* = 7.4 Hz, 0.42H),), 6.90 (d, *J* = 7.8 Hz, 1H), 6.87-6.81 (m, 1H), 6.79-6.72 (m, 2H), 4.23 (dd, *J* = 19.4, 9.8 Hz, 1H), 4.11 (t, *J* = 7.5 Hz, 0.39H), 3.66 (s, 1H), 3.64 (s, 3H), 3.55-3.52 (m, 1.5H), 3.36 (d, *J* = 15.9 Hz, 1H), 3.20 (d, *J* = 17.3 Hz, 0.36H), 3.12 (dd, *J* = 18.9, 10.1 Hz, 1H), 3.03 (dd, *J* = 9.6, 6.6 Hz, 0.36H), 2.96 (brs, 1H), 2.90 (d, *J* = 15.8 Hz, 1H), 2.84 (t, *J* = 8.7 Hz, 0.44H), 2.73 (dd, *J* = 18.6, 11.2 Hz, 1H), 2.26 (s, 3H), 2.16 (s, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.9, 181.1, 140.9, 138.0, 136.9, 135.9, 132.7, 130.7, 129.7, 129.2, 127.5, 126.4, 125.4, 122.8, 121.7, 119.7, 118.7, 110.5, 110.4, 109.4, 55.9, 51.9, 50.3, 43.4, 31.7, 30.0, 29.5, 21.1; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{27}N_2O_2^+$Calcd. 447.2067, Found 447.2068.

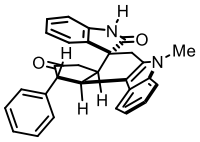
7. General procedure for compounds27-39 via formal [4+2]/[4+3]-annulation



In a 10 mL sealed tube, 4-Aminocyclopentenone (**2′**, 1.0 equiv) and indole-derived bis-nucleophiles (**3**, 1.0 equiv) were taken in anhydrous CH_2Cl_2 (0.1 M) under N_2 atmosphere. To this solution were added $AlCl_3$ (2.0 equiv) and the reaction mixture was stirred at 50°C temperature until completion of the reaction as determined by TLC analysis (typical reaction time, 6-8 h). It was then quenched with water (5-10 mL) and extracted in CH_2Cl_2 (3×10 mL). The combined organic layer was washed with Brine, dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the desired products (**27-39**).

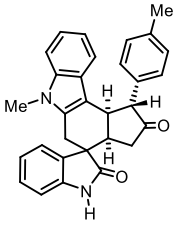
8. Preparation and characterization data of compounds(27-39)

3-((1R,2R)-2-(2-ethyl-1-methyl-1H-indol-3-yl)-4-oxo-3-phenylcyclopentyl)indolin-2-one(27)



Following the general procedure, reaction of 4-aminocyclopentenone (**2a'**, 0.025 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3h**, 0.028 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **27** in 84% (0.036 g) yield as mixture of diastereomers (*dr* 6:1).R_f 0.2 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.09 (s, 1H), 7.33 (dd, *J* = 13.6, 7.1 Hz, 4H), 7.25 – 7.19 (m, 5H), 7.12 (dd, *J* = 12.0, 7.7 Hz, 3H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.84 – 6.79 (m, 3H), 6.45 (d, *J* = 7.9 Hz, 1H), 4.26 (t, *J* = 8.3 Hz, 1H), 3.86 (d, *J* = 9.2 Hz, 1H), 3.57(s, 3H), 3.30 – 3.25 (m, 2H), 2.93 (d, *J* = 16.3 Hz, 1H), 2.65 (dd, *J* = 18.9, 9.4 Hz, 1H), 2.18 (dd, *J* = 18.8, 2.2 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.1, 181.4, 141.1, 139.9, 137.9, 132.6, 130.9, 129.2(2), 128.8, 127.5, 126.5, 125.5, 122.7, 121.4, 120.0, 119.3, 110.7, 109.7, 109.0, 60.2, 51.0, 42.7, 40.3, 29.8, 29.5, 29.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{25}N_2O_2^+$Calcd. 433.1911, Found 433.1913.

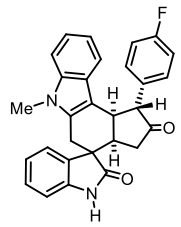
*3-((1R,2R)-2-(2-ethyl-1-methyl-1H-indol-3-yl)-4-oxo-3-(p-tolyl)cyclopentyl)indolin-2-one(*28)



Following the general procedure, reaction of 4-aminocyclopentenone (**2b'**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3h**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **28** in 80% (0.071 g) yieldas mixture of diastereomers (*dr*1:1) R_f 0.2 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.14 (s, 1H), 9.07 (s, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 2H), 7.24 – 7.16 (m, 12H), 7.11 (d, *J* = 7.5 Hz, 1H), 6.95 – 6.87 (m, 5H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 7.9 Hz, 1H), 4.33 (t, *J* = 8.2 Hz, 1H), 4.21 (s, 1H), 4.11 (d, *J* = 5.7 Hz, 1H), 3.89 (d, *J* = 8.9 Hz, 1H), 3.66 (s, 3H), 3.64 (s, 3H), 3.50 (d, *J* = 16.6 Hz, 1H), 3.36 – 3.32 (m, 2H), 3.01 (d, *J* = 16.3 Hz, 1H), 2.92- 2.79 (m, 4H), 2.75 – 2.68 (m, 1H), 2.41 (s, 3H), 2.34 (s, 3H), 2.25 (dd, *J* = 18.9, 2.5 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 217.8, 216.4, 181.5, 181.1, 141.1, 140.0, 138.2, 137.9, 137.1, 136.9(2), 136.2, 133.3, 132.5, 131.9, 130.9, 129.9, 129.8, 129.2, 128.6 (2), 127.8, 126.5, 126.0, 125.5, 124.4, 123.0, 122.7, 121.8, 121.4, 120.1, 119.6, 119.2, 118.8, 110.7, 110.3, 109.9, 109.4, 109.3, 108.9, 59.8, 59.4, 51.0,

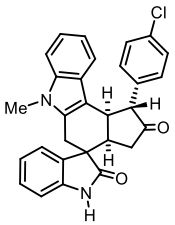
49.0, 42.5, 41.5, 40.3(2), 40.2, 39.0, 29.8, 29.5, 29.0, 25.5, 21.3, 21.2; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{27}N_2O_2^+$Calcd.447.2067, Found 447.2068.

***3-((1R,2R)-2-(2-ethyl-1-methyl-1H-indol-3-yl)-3-(4-fluorophenyl)-4-oxocyclopentyl)indolin-2-one*(29)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2e'**, 0.027 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3h**, 0.028 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **29** in 58% (0.026 g) yield as mixture of diastereomers (*dr* 2:1) R_f 0.2 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.71 (s, 1H), 8.63 (s, 0.53H), 7.46 (d, *J* = 7.9 Hz, 0.6H), 7.37 (d, *J* = 8.2 Hz, 0.62H), 7.31-7.28 (m, 2H), 7.25 – 7.21 (m, 6H), 7.18 – 7.14 (m, 2H), 7.12 – 7.08 (t, *J* = 7.0 Hz, 3H), 7.03 (t, *J* = 8.6 Hz, 1H), 6.93 (t, *J* = 7.7 Hz, 2H), 6.88 -6.81 (m, 3H), 6.45 (d, *J* = 7.9 Hz, 1H), 4.25 (t, *J* = 8.5 Hz, 1H), 4.18 (s, 0.6H), 4.07 (d, *J* = 5.6 Hz, 0.6H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.65 (s, 1.68H), 3.63 (s, 3H), 3.47 (d, *J* = 16.8 Hz, 0.72H), 3.36- 3.31 (m, 2H), 2.99 (d, *J* = 16.3 Hz, 1H), 2.87 – 2.77 (m, 2.47H), 2.69 (dd, *J* = 18.9, 9.3 Hz, 1H), 2.22 (d, *J* = 20.3 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 217.1, 215.9, 181.2, 180.9, 162.3(d, *J* = 244.6 Hz), 162.0 (d, *J* = 244.6 Hz), 141.0, 140.0, 138.3, 138.0, 135.6 (d, *J* = 3.2 Hz), 134.8 (d, *J* = 3.2 Hz), 133.2, 132.7, 132.0, 130.84, 130.4 (d, *J* = 8.0 Hz), 129.5(d, *J* = 8.0 Hz), 128.8, 126.4, 125.93, 125.6, 124.4, 123.1, 122.8, 121.9, 121.5, 119.8, 119.7, 119.4, 118.7, 116.1 (d, *J* = 21.3 Hz), 116.0 (d, *J* = 21.3 Hz), 110.7, 110.2, 109.5 (d, *J* = 3.8 Hz), 109.0 (d, *J* = 5.9 Hz), 59.5, 58.9, 51.1, 49.0, 42.8, 41.4, 40.3, 40.2(2), 39.0, 29.5(2), 29.2, 25.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{24}FN_2O_2^+$Calcd. 451.1816, Found 451.1820.

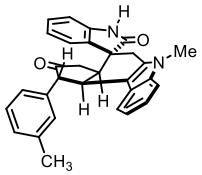
***3-((1R,2R)-3-(4-chlorophenyl)-2-(2-ethyl-1-methyl-1H-indol-3-yl)-4-oxocyclopentyl)indolin-2-one(*30)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2f'**, 0.027 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3h**, 0.028 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **30** in 65% (0.03 g) yield as mixture of diastereomers (*dr* 1:1). R_f 0.2 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.94 (s, 1H), 8.87 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 3H), 7.33 – 7.30 (m, 4H), 7.24 – 7.21 (m, 6H), 7.19 -7.15 (m, 2H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.96 – 6.92 (m, 2H),

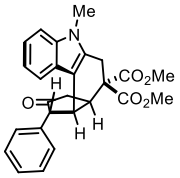
6.90 – 6.83 (m, 4H), 6.52 (d, *J* = 7.9 Hz, 1H), 4.28 (t, *J* = 8.3 Hz, 1H), 4.19 (s, 1H), 4.08 (d, *J* = 5.1 Hz, 1H), 3.88 (d, *J* = 9.3 Hz, 1H), 3.65 (s, 3H), 3.64 (s, 3H), 3.48 (d, *J* = 16.8 Hz, 1H), 3.36-3.32 (m, 2H), 3.00 (d, *J* = 16.3 Hz, 1H), 2.88 – 2.79 (m, 4H), 2.73 – 2.65 (m, 1H), 2.24 (d, *J* = 19.1 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.8, 215.5, 181.2, 180.8, 141.0, 140.0, 138.4, 138.3, 138.0, 137.5, 133.4, 133.(2), 132.7, 132.0, 130.8, 130.2, 129.3 (2), 128.8, 126.4, 125.9, 125.5, 124.3, 123.1, 122.8, 121.9, 121.6, 119.7 (2), 119.4, 118.6, 110.7, 110.3, 109.5 (2), 109.1, 108.9, 59.6, 59.1, 51.0, 49.0, 42.6, 41.3, 40.3(2), 40.2, 39.0, 29.5 (2), 29.1, 25.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{24}ClN_2O_2^+$ Calcd.467.1521, Found 467.1503.

***3-((1R,2R)-2-(2-ethyl-1-methyl-1H-indol-3-yl)-4-oxo-3-(m-tolyl)cyclopentyl)indolin-2-one*(31)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2h'**, 0.026 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3h**, 0.028 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **31** in 77% (0.034 g) yield as mixture of diastereomers (*dr* 4:1). R_f 0.2 (EtOAc: Hexane 4:6); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.97 (s, 1H), 7.30 (t, *J* = 7.9 Hz, 2H), 7.22 – 7.16(m, 4H), 7.13 – 7.09 (m, 4H), 6.94 – 6.85 (m, 4H), 4.32 (t, *J* = 8.3 Hz, 1H), 3.88 (d, *J* = 9.1 Hz, 1H), 3.64 (s, 3H), 3.37 – 3.33 (m, 2H), 3.01 (d, *J* = 16.3 Hz, 1H), 2.73 (dd, *J* = 18.9, 9.4 Hz, 1H), 2.38 (s, 3H), 2.25 (dd, *J* = 18.8, 2.2 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz)δ 216.4, 181.4, 141.0, 139.8, 138.8, 137.9, 132.5, 130.9, 129.7, 129.2, 129.0, 128.3, 126.5, 125.8, 125.6, 122.8, 121.4, 120.1, 119.2, 110.7, 109.9, 108.9, 60.2, 51.0, 49.0, 42.8, 40.4(2), 29.5, 21.6; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{27}N_2O_2^+$Calcd.447.2067, Found 447.2067.

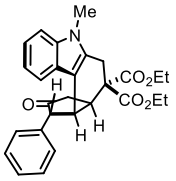
***Dimethyl (3aR,10cS)-6-methyl-2-oxo-1-phenyl-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate*(32)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2a'**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3a**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound **32** as white solid in 72% (0.062 g) yield. R_f 0.30 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.47 – 7.42 (m, 4H), 7.35 (d, *J* = 6.6 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.05 (t, *J* = 7.4 Hz, 1H), 4.29 (d, *J* = 6.6 Hz, 1H), 3.96 (s, 1H), 3.87-3.80 (m, 4H),3.71 (s, 3H), 3.70 (s, 3H), 3.61 (d, *J* = 17.2 Hz, 1H), 3.36 (d, *J* = 17.0 Hz, 1H), 2.50 (dd, *J* = 18.5, 8.6 Hz, 1H),

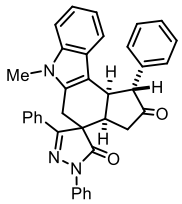
2.33 (dd, *J* = 18.6, 11.9 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 215.8, 170.6, 170.1, 138.6, 138.2, 131.2, 129.2, 128.0, 127.3, 126.1, 121.8, 119.4, 118.7, 109.3, 108.9, 59.7, 56.5, 53.5, 53.4, 40.4, 38.8, 38.5, 29.5, 23.7; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{26}NO_5^+$ Calcd. 432.1805, Found 432.1809.

Diethyl (3aR,10cS)-6-methyl-2-oxo-1-phenyl-2,3,3a,5,6,10c-hexahydrocyclopenta[c]carbazole-4,4(1H)-dicarboxylate(33)



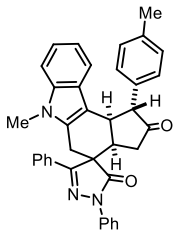
Following the general procedure, reaction of 4-aminocyclopentenone (**2a'**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3d**, 0.061 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound **33** as white solid in 70% (0.064 g) yield.**mp**:174-177^{o}C; R_f 0.30 (EtOAc: Hexane 3:7); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.49-7.43 (m, 4H), 7.36 (d, *J* = 7.0 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.5 Hz, 1H), 4.33 – 4.27 (m, 3H), 4.24 – 4.17 (m, 1H), 4.16 – 4.07 (m, 1H), 3.98 (s, 1H), 3.87-3.80 (m, 1H), 3.72 (s, 3H), 3.61 (d, *J* = 17.1 Hz, 1H), 3.35 (d, *J* = 17.0 Hz, 1H), 2.53 (dd, *J* = 18.5, 8.6 Hz, 1H), 2.36 (dd, *J* = 18.5, 11.9 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.1 Hz, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 215.9, 170.2, 169.6, 138.6, 138.1, 131.4, 129.2, 128.0, 127.3, 126.1, 121.7, 119.4, 118.7, 109.2, 108.9, 62.4, 62.1, 59.9, 56.7, 40.4, 38.8, 38.4, 29.4, 23.7, 14.2, 14.0; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{28}H_{30}NO_5^+$Calcd. 460.2118, Found 460.2114.

(1R,3aR,4S,10cR)-6-methyl-1,1',3'-triphenyl-1,3,3a,5,6,10c-hexahydro-2H-spiro[cyclopenta[c]carbazole-4,4'-pyrazole]-2,5'(1'H)-dione(34)



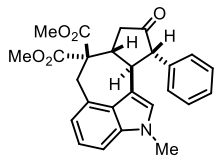
Following the general procedure, reaction of 4-aminocyclopentenone (**2a'**, 0.025 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3i**, 0.038 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound **34** as white solid in 53% (0.029 g) yield as mixture of diastereomers (*dr* 5:1).**mp**: 246-245^{o}C; R_f 0.40 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.05 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.9 Hz, 2H), 7.42 – 7.35 (m, 2H), 7.32 – 7.27 (m, 5H), 7.21 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 4.6 Hz, 2H), 6.70 (s, 1H), 5.97 (d, *J* = 7.9 Hz, 1H), 4.06 (dd, *J* = 10.7, 7.4 Hz, 1H), 3.79 (s, 3H), 3.56 (s, 2H), 3.31 – 3.24 (m, 1H), 2.63 – 2.50 (m, 2H), 2.18 (d, *J* = 19.6 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.3, 175.4, 161.6, 139.0, 137.9, 137.7, 132.9, 130.9, 130.6, 129.2, 129.1, 129.0(2), 128.0, 127.5, 127.1, 126.4, 126.0, 121.7, 120.1, 119.3, 109.8, 108.8, 60.4, 57.3, 43.2, 40.6, 40.3, 29.7, 27.0;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{36}H_{30}N_3O_2^+$Calcd.536.2333, Found 536.2329.

(1R,3aR,4S,10cR)-6-methyl-1',3'-diphenyl-1-(p-tolyl)-1,3,3a,5,6,10c-hexahydro-2H-spiro[cyclopenta[c]carbazole-4,4'-pyrazole]-2,5'(1'H)-dione(35)



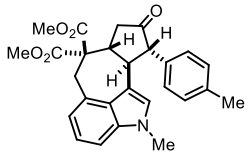
Following the general procedure, reaction of 4-aminocyclopentenone (**2b'**, 0.026 g, 0.1 mmol, 1.0 equiv) and indole derivative (**3i**, 0.038 g, 0.1 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.027 g, 0.2 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound **35** as white solid in 56% (0.031 g) yield as mixture of diastereomers (*dr* 2:1). R_f 0.40 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ7.96 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 7.40 – 7.28 (m, 5H), 7.24 – 7.17 (m, 7H), 7.15 – 7.12 (m, 2H), 7.10-7.04 (m, 4H), 7.04 – 6.98 (m, 3H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.64 (t, *J* = 7.4 Hz, 0.67H), 6.57 (d, *J* = 7.6 Hz, 1H), 6.41 (d, *J* = 7.9 Hz, 1H), 6.02 (d, *J* = 7.9 Hz, 0.58H), 4.12 (d, *J* = 8.0 Hz, 1H), 3.98 (dd, *J* = 10.0, 7.5 Hz, 0.62H), 3.84 (t, *J* = 7.6 Hz, 1H), 3.69 (s, 1.82H), 3.61 (s, 3H), 3.48 (d, *J* = 17.6 Hz, 2H), 3.37 – 3.26 (m, 2H), 3.21 – 3.17 (m, 0.62H), 2.62 (dd, *J* = 19.4, 9.2 Hz, 1H), 2.51 – 2.41 (m,1.27H), 2.36 (dd, *J* = 19.6, 5.0 Hz, 1H), 2.29 (s, 3H), 2.25 (s, 1.71H), 2.08 (d, *J* = 19.2 Hz, 0.64H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ216.5, 216.4, 175.3, 174.8, 161.60, 160.7, 137.9,137.8, 137.7, 136.6, 135.9, 132.9, 130.8, 130.7,130.6(2), 129.8, 129.7(2), 129.2, 129.1,129.0, 128.9(2) 128.7, 128.1,127.1, 126.4, 126.3, 126.0, 121.7, 120.1, 119.7, 119.4, 119.2, 110.1, 110.0, 108.8 (2), 60.0 (2), 57.3, 55.40, 42.9, 42.7, 40.6, 40.3, 39.9, 37.8, 29.7, 29.6, 26.9, 25.8, 21.3;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{37}H_{32}N_3O_2^+$Calcd.550.2489, Found 550.2481.

***Dimethyl (3S,3aS,10aR)-5-methyl-2-oxo-3-phenyl-2,3,3a,5,9,10a-hexahydroazuleno[4,5,6-cd]indole-10,10(1H)-dicarboxylate*(36)**



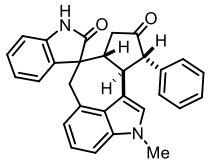
Following the general procedure, reaction of 4-aminocyclopentenone (**2a'**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3j**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound **36** as white solid in 63% (0.054 g) yield. R_f 0.35 (EtOAc: Hexane 3:7); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.44– 7.32 (m, 5H), 7.12 (d, *J* = 3.8 Hz, 2H), 6.90 (t, *J* = 3.6 Hz, 1H), 6.45 (s, 1H), 4.37 (t, *J* = 11.5 Hz, 1H), 4.03 (d, *J* = 15.1 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.73 – 3.70 (m, 1H), 3.60 (s, 3H), 3.57 (d, *J* = 15.1 Hz, 1H), 3.21-3.14 (m, 1H), 2.84 (dd, *J* = 18.6, 8.3 Hz, 1H), 2.57 (dd, *J* = 18.7, 11.7 Hz, 1H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 214.1, 172.0, 171.3, 137.4, 136.5, 130.0, 129.1, 128.7, 127.6, 127.0, 124.7, 122.3, 119.7, 117.3, 108.0, 62.6, 61.7, 53.0, 52.7, 45.6, 43.2, 42.2, 40.1, 32.9; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{26}H_{26}NO_5^+$ Calcd. 432.1805, Found 432.1812.

***dimethyl (3S,3aS,10aR)-5-methyl-2-oxo-3-(p-tolyl)-2,3,3a,5,9,10a-hexahydroazuleno[4,5,6-cd]indole-10,10(1H)-dicarboxylate*(37)**



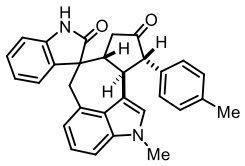
Following the general procedure, reaction of 4-aminocyclopentenone (**2b'**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3j**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound **37** as white solid in 67% (0.060 g) yield. R_f 0.35 (EtOAc: Hexane 3:7);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.27 – 7.22 (m, 4H), 7.11 (d, *J* = 4.0 Hz, 2H), 6.90 (t, *J* = 3.9 Hz, 1H), 6.48 (s, 1H), 4.33 (t, *J* = 11.5 Hz, 1H), 4.03 (d, *J* = 15.1 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.72-3.69 (m, 1H), 3.61 (s, 3H), 3.56 (d, *J* = 8.0 Hz, 1H), 3.20-3.13 (m, 1H), 2.83 (dd, *J* = 18.6, 8.3 Hz, 1H), 2.55 (dd, *J* = 18.7, 11.7 Hz, 1H), 2.38 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 214.4, 172.0, 171.3, 137.2, 136.4, 134.3, 130.0, 129.8, 128.5, 127.1, 124.7, 122.2, 119.7, 117.3, 108.0, 62.3, 61.7, 52.9, 52.6, 45.5, 43.1, 42.2, 40.0, 32.9, 21.3;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{27}H_{28}NO_5^+$Calcd.432.1962, Found 432.1963.

***(3S,3aS,10aR)-5-methyl-3-phenyl-1,3,3a,5,9,10a-hexahydro-2H-spiro[azuleno[4,5,6-cd]indole-10,3'-indoline]-2,2'-dione*(38)**



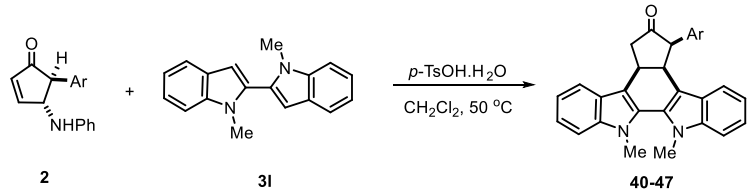
Following the general procedure, reaction of 4-aminocyclopentenone (**2a'**, 0.05 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3k**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **38** as white solid in 61% (0.053 g) yield. R_f 0.3 (EtOAc: Hexane 4:6); **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.20 (s, 1H), 7.49 (d, *J* = 7.4 Hz, 2H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 8.1 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 6.9 Hz, 1H), 6.63 (s, 1H), 4.86 (t, *J* = 10.9 Hz, 1H), 4.24 (d, *J* = 14.4 Hz, 1H), 3.70 (s, 3H), 3.57 (d, *J* = 11.4 Hz, 1H), 2.98 (dd, *J* = 20.4, 10.4 Hz, 1H), 2.76 (d, *J* = 14.5 Hz, 1H), 2.39-2.22 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 214.1, 180.8, 139.4, 137.4, 136.6, 135.0, 130.5, 129.1, 128.8, 128.4, 128.2, 127.5, 124.2, 123.6, 122.9, 122.4, 120.7, 119.8, 109.9, 108.4, 62.6, 55.4, 48.0, 40.9, 40.8, 40.5, 32.9; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{25}N_2O_2^+$Calcd. 433.1911, Found 433.1912.

***(3S,3aS,10aR)-5-methyl-3-(p-tolyl)-1,3,3a,5,9,10a-hexahydro-2H-spiro[azuleno[4,5,6-cd]indole-10,3'-indoline]-2,2'-dione*(39)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2b'**, 0.053 g, 0.2 mmol, 1.0 equiv) and indole derivative (**3k**, 0.055 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound, which was purified by silica gel column chromatography (Hexane/EtOAc 7:3) to furnish the title compound **39** as white solid in 62% (0.054 g) yield. R_f 0.3 (EtOAc: Hexane 4:6);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.25 - 7.18 (m, 4H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.92 (t, *J* = 7.3 Hz, 2H), 6.84 (d, *J* = 7.5 Hz, 1H), 6.70 (d, *J* = 6.9 Hz, 1H), 6.64 (s, 1H), 4.82 (t, *J* = 11.0 Hz, 1H), 4.24 (d, *J* = 14.3 Hz, 1H), 3.69 (s, 3H), 3.52 (d, *J* = 11.4 Hz, 1H), 2.96 (dd, *J* = 20.4, 10.4 Hz, 1H), 2.75 (d, *J* = 14.5 Hz, 1H), 2.38 (s, 3H), 2.34-2.21 (m, 2H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 214.4, 180.7, 139.3, 137.2, 136.6, 135.0, 134.3, 130.5, 129.8, 128.6, 128.5, 128.2, 124.2, 123.6, 122.9, 122.4, 120.8, 119.7, 109.9, 108.4, 62.4, 55.4, 48.0, 40.9(2) , 40.4, 32.9, 21.3; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{27}N_2O_2^+$ Calcd. 447.2067, Found 447.2064.

9. General procedure for the preparation of compounds 40-47

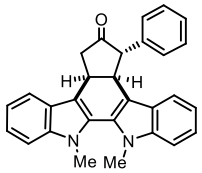


2 **3l** **40-47**

In a 10 mL sealed tube, 4-Aminocyclopentenone (**2**, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 1.0 equiv) were taken in anhydrous CH_2Cl_2 (0.1 M) under N_2 atmosphere. To this solution were added *p*-TsOH.H_2O (2.0 equiv) and the reaction mixture was stirred at 50^{o}C temperature until completion of the reaction as determined by TLC analysis (typical reaction time, 12-14 h). It was then quenched with water (5-10 mL) and extracted in CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with Brine, dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the desired products **(40-47).**

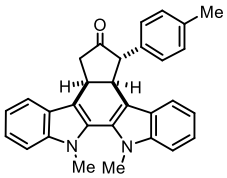
10. Preparation and characterization of compounds 40-47

***(4cS,5S,7aS)-12,13-dimethyl-5-phenyl-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(40)**



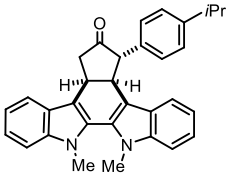
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **40**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 84% (0.07 g) yield.**mp**: 210-213^oC; R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.24- 7.18 (m, 5H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.6 Hz, 1H), 7.02 – 7.00 (m, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.11 (t, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 3.93 – 3.91 (m, 1H), 3.88 (s, 3H), 3.54 (t, *J* = 14.6 Hz, 2H), 3.06 (dd, *J* = 18.8, 8.6 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.9, 140.7, 140.2, 138.6, 130.9, 129.7, 129.2, 128.8, 127.7, 127.5, 127.2, 122.2, 121.1, 120.9, 120.6, 119.0, 118.8, 114.8, 113.3, 110.6, 110.1, 59.2, 46.1, 43.7, 34.8, 34.5, 34.3;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{29}H_{25}N_2O^+$Calcd.417.1961, Found 417.1954.

(*4cS,5S,7aS)-12,13-dimethyl-5-(p-tolyl)-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(41)



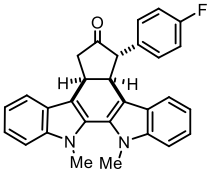
Following the general procedure, reaction of 4-aminocyclopentenone (**2b**, 0.053 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **41**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 86% (0.074 g) yield.**mp**: 206-209^oC; R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 4.20 (t, *J* = 8.0 Hz, 1H), 4.04 – 4.00 (m, 4H), 3.97 (s, 3H), 3.63 (dd, *J* = 15.0, 9.7 Hz, 2H), 3.14 (dd, *J* = 18.8, 8.6 Hz, 1H), 2.37 (s, 3H);**^{13}C{^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 217.0, 140.6, 140.2, 136.6, 135.4, 130.9, 129.7, 129.5, 128.9, 127.6, 127.5, 122.1, 122.0, 120.8, 120.5, 118.9, 118.8, 114.9, 113.3, 110.5, 110.0, 58.8, 45.8, 43.5, 34.8, 34.5, 34.3, 21.2;**HRMS (ESI-TOF)** m/z: $[M+H]^+ C_{30}H_{27}N_2O^+$Calcd.431.2118, Found 431.2117.

***(4cS,5S,7aS)-5-(4-isopropylphenyl)-12,13-dimethyl-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(42)**



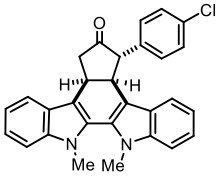
Following the general procedure, reaction of 4-aminocyclopentenone (**2c**, 0.058 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of*p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **42**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as gummy solid in 89% (0.082 g) yield.**mp**: 232-235^{o}C; R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.70 (d, *J* = 7.9 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.36-7.29 (m, 2H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.18 – 7.16 (m, 3H), 7.03 (d, *J* = 7.9 Hz, 2H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 4.20 (t, *J* = 7.9 Hz, 1H), 4.04 (s, 3H), 4.00 – 3.95 (m, 4H), 3.66 – 3.61 (m, 2H), 3.14 (dd, *J* = 18.8, 8.7 Hz, 1H), 2.95-2.88 (m, 1H), 1.28 (d, *J* = 6.9 Hz, 6H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 217.1, 147.8, 140.6, 140.2, 135.8, 130.9, 129.7, 129.0, 127.7, 127.5, 126.8, 122.1, 122.0, 120.8, 120.4, 119.0, 118.9, 114.9, 113.3, 110.54, 110.0, 58.8, 46.2, 43.5, 34.8, 34.5, 34.1, 33.9, 24.2, 24.1;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{32}H_{31}N_2O^+$Calcd. 459.2431, Found 459.2426.

***(4cS,5S,7aS)-5-(4-fluorophenyl)-12,13-dimethyl-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(43)**



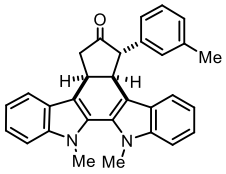
Following the general procedure, reaction of 4-aminocyclopentenone (**2e**, 0.053 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **43**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 76% (0.066 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.05-7.03 (m, 2H), 7.00 – 6.92 (m, 3H), 6.62 (d, *J* = 7.9 Hz, 1H), 4.18 (t, *J* = 8.7 Hz, 1H), 4.04 (s, 3H), 3.97 (s, 3H), 3.92 (dd, *J* = 11.9, 7.7 Hz, 1H), 3.63 (dd, *J* = 21.8, 15.5 Hz, 2H), 3.13 (dd, *J* = 18.9, 8.6 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.5, 162.1 (d, *J* = 243.8 Hz), 140.7, 140.2, 134.3 (d, *J* = 3.2 Hz), 130.9, 130.7(d, *J* =8 Hz), 129.7, 127.6, 127.5, 122.2 (d, *J* = 6.9 Hz), 120.9, 120.7, 119.0, 118.5, 115.8, 115.6, 114.5, 113.2, 110.6, 110.1, 58.4, 46.1, 43.5, 34.8, 34.5, 34.3;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{24}FN_2O^+$Calcd. 435.1867, Found 435.1863.

***(4cS,5S,7aS)-5-(4-chlorophenyl)-12,13-dimethyl-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(44)**



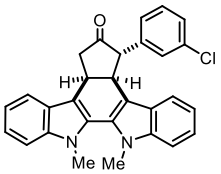
Following the general procedure, reaction of 4-aminocyclopentenone (**2f**, 0.057 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **44**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 82% (0.074 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.72 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.40-7.35 (m, 2H), 7.33-7.28 (m, 3H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 7.9 Hz, 1H), 4.23 (t, *J* = 8.1 Hz, 1H), 4.08 (s, 3H), 4.01 (s, 3H), 3.99 – 3.96 (m, 1H), 3.67 (dd, *J* = 25.3, 15.5 Hz, 2H), 3.17 (dd, *J* = 18.9, 8.6 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.4, 140.6, 140.1, 137.0, 133.1, 130.8, 130.5, 129.7, 128.9, 127.5, 127.4, 122.3, 122.2, 120.9, 120.8, 119.0, 118.5, 114.3, 113.1, 110.6, 110.1, 58.5, 45.9, 43.5, 34.9, 34.6, 34.3;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{24}ClN_2O^+$ Calcd. 451.1572, Found 451.1566.

***(4cS,5S,7aS)-12,13-dimethyl-5-(m-tolyl)-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(45)**



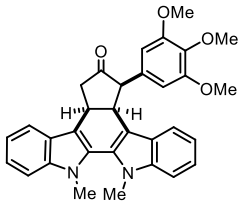
Following the general procedure, reaction of 4-aminocyclopentenone (**2h**, 0.05 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **45**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 80% (0.069 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 6.92 -6.88 (m, 3H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.17 (t, *J* = 7.6 Hz, 1H), 4.02 (s, 3H), 4.00 – 3.97 (m, 1H), 3.96 (s, 3H), 3.58 (dd, *J* = 20.9, 15.2 Hz, 2H), 3.12 (dd, *J* = 18.7, 8.5 Hz, 1H), 2.27 (s, 3H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 217.0, 140.7, 140.3, 138.5, 138.3, 131.0, 129.9, 129.8, 128.7, 128.0, 127.7, 127.6, 126.1, 122.2, 122.1, 120.9, 120.6, 119.0, 118.9, 115.1, 113.4, 110.6, 110.0, 59.1, 46.0, 43.8, 34.8, 34.6, 34.4, 21.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{27}N_2O^+$ Calcd. 431.2118, Found 431.2114.

***(4cS,5S,7aS)-5-(3-chlorophenyl)-12,13-dimethyl-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(46)**



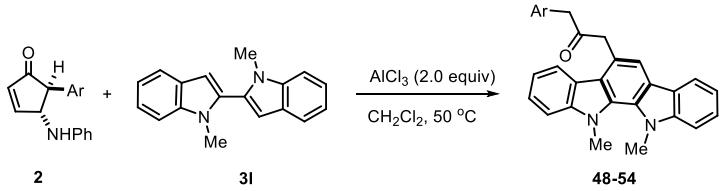
Following the general procedure, reaction of 4-aminocyclopentenone (**2j**, 0.057 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **46**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 71% (0.064 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* =7.2 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.11 (s, 1H), 6.95 (dd, *J* = 13.3, 6.7 Hz, 2H), 6.66 (d, *J* = 7.9 Hz, 1H), 4.18 (t, *J* = 8.0 Hz, 1H), 4.04 (s, 3H), 4.01 – 3.93 (m, 4H), 3.62 (dd, *J* = 27.7, 15.4 Hz, 2H), 3.14 (dd, *J* = 18.9, 8.6 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.0, 140.5 (2), 140.1, 134.5, 130.8, 130.0, 129.7, 129.2, 127.5, 127.4 (3), 122.3, 122.2, 120.9, 120.8, 119.0, 118.5, 114.2, 113.0, 110.6, 110.1, 58.7, 45.9, 43.5, 34.9, 34.5, 34.4;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{29}H_{24}ClN_2O^+$ Calcd.451.1572, Found 451.1572.

***(4cS,5R,7aS)-12,13-dimethyl-5-(3,4,5-trimethoxyphenyl)-4c,5,7,7a,12,13-hexahydro-6H-cyclopenta[c]indolo[2,3-a]carbazol-6-one*(47)**



Following the general procedure, reaction of 4-aminocyclopentenone (**2l**, 0.068 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of *p*-TsOH.H_2O (0.069 g, 0.4 mmol) delivered compound **47**, which was purified by silica gel column chromatography (Hexane/EtOAc 3:7) to furnish the title compound as white solid in 69% (0.071 g) yield. R_f 0.30 (EtOAc: Hexane 4:6);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.26 (s, 2H), 4.18 (t, *J* = 7.9 Hz, 1H), 4.04 (s, 3H), 3.97 – 3.93 (m, 4H), 3.83 (s, 3H), 3.68 (s, 6H), 3.62 – 3.47 (m, 2H), 3.14 (dd, *J* = 18.8, 8.6 Hz, 1H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 216.7, 153.4, 140.7, 140.3, 137.4, 134.1, 130.9, 129.7, 127.7, 127.5, 122.3 (2), 120.9, 120.7, 119.0, 118.9, 114.9, 113.2, 110.6, 110.1, 106.4, 61.0, 59.1, 56.2, 46.0, 43.7, 34.9, 34.6, 34.2;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{32}H_{31}N_2O_4^+$ Calcd. 507.2278, Found 507.2285.

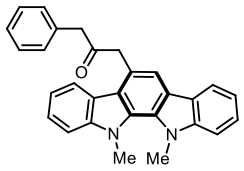
11. General procedure for compounds(48-54)



In a 10 mL sealed tube, 4-Aminocyclopentenone (**2**, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 1.0 equiv) were taken in anhydrous CH_2Cl_2 (0.1 M) under N_2 atmosphere. To this solution were added $AlCl_3$ (2.0 equiv) and the reaction mixture was stirred at 50^oC temperature until completion of the reaction as determined by TLC analysis (typical reaction time, 16-24 h). It was then quenched with water (5-10 mL) and extracted in CH_2Cl_2 (3 × 10 mL). The combined organic layer was washed with Brine, dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The crude product was purified by silica gel column chromatography to afford the desired products **(48-54).**

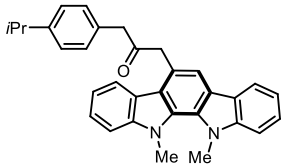
12. Preparation and characterization data for compounds(48-54)

1-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)-3-phenylpropan-2-one(48)



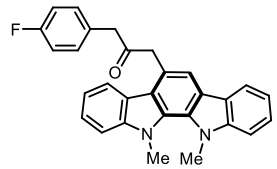
Following the general procedure, reaction of 4-aminocyclopentenone (**2a**, 0.05 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **48**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 53% (0.044 g) yield.**mp**: 167-170; R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.71 (s, 1H), 7.53 – 7.50 (m, 4H), 7.35 (t, *J* = 6.8 Hz, 1H), 7.30- 7.24 (m, 4H), 7.11 (d, *J* = 7.4 Hz, 2H), 4.46 (s, 2H), 4.18 (s, 3H), 4.16 (s, 3H), 3.76 (s, 2H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 207.3, 144.3, 143.8, 134.3, 130.3, 129.8, 129.2, 128.6, 127.0, 125.7, 125.2, 124.8, 124.5, 123.5, 122.1, 121.9, 121.7, 120.3, 120.2, 119.9, 115.5, 110.4, 110.1, 49.0, 48.8, 36.8, 36.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{25}N_2O^+$Calcd. 417.1961, Found 417.1951.

1-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)-3-(4-isopropylphenyl)propan-2-one(49)



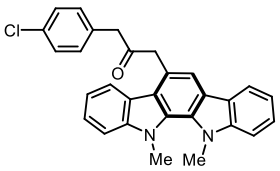
Following the general procedure, reaction of 4-aminocyclopentenone (**2c**, 0.058 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **49**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 46% (0.042 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.10 (d, *J* = 7.6 Hz, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.70 (s, 1H), 7.52-7.49 (m, 4H), 7.34- 7.31(m, 1H), 7.22 (t, *J* = 7.1 Hz, 1H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 7.9 Hz, 2H), 4.45 (s, 2H), 4.21 (s, 3H), 4.19 (s, 3H), 3.72 (s, 2H), 2.91-2.84 (m, 1H), 1.23 (d, *J* = 6.9 Hz, 6H);**^{13}C {^{1}H} NMR** (CDCl3, 100 MHz) δ 207.7, 147.5, 144.3, 143.8, 131.5, 130.3, 129.7, 129.2, 126.7, 125.7, 125.2, 124.8, 124.5, 123.5, 122.1, 121.9, 121.7, 120.3, 120.2, 120.0, 115.5, 110.4, 110.1, 48.9, 48.4, 36.8, 36.6, 33.8, 24.1;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{32}H_{31}N_2O^+$Calcd. 459.2431, Found 459.2426.

***1-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)-3-(4-fluorophenyl)propan-2-one*(50)**



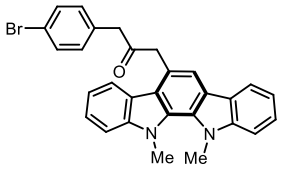
Following the general procedure, reaction of 4-aminocyclopentenone (**2e**, 0.053 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **50**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 57% (0.049 g) yield.**mp**: 175-178ºC; R_f0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.9 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.74 (s, 1H), 7.54 – 7.51 (m, 4H), 7.36 – 7.33 (m, 1H), 7.29 – 7.23 (m, 1H), 6.96 – 6.93 (m, 2H), 6.87 (t, *J* = 8.5 Hz, 2H), 4.45 (s, 2H), 4.21 (s, 3H), 4.19 (s, 3H), 3.69 (s, 2H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 207.3, 161.9(d, *J* = 243.5 Hz) 144.3, 143.8, 131.2(2), 130.4, 129.8 (d, *J* = 3.2 Hz), 129.3, 125.8, 125.3, 124.8, 124.5, 123.6, 122.2, 121.9, 121.6, 120.4 (d, *J* = 6.3 Hz), 120.0, 115.4 (d, *J* = 9.7 Hz), 115.2, 110.5, 110.2, 49.4, 47.6, 36.8, 36.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{29}H_{24}FN_2O^+$Calcd.435.1867, Found 435.1863.

***1-(4-chlorophenyl)-3-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)propan-2-one*(51)**



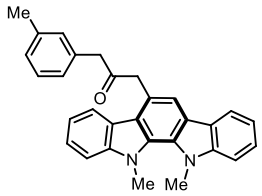
Following the general procedure, reaction of 4-aminocyclopentenone (**2f**, 0.057 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **51**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 54% (0.059 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H), 7.73 (s, 1H), 7.56 – 7.48 (m, 4H), 7.36 – 7.32 (m, 1H), 7.28-7.24 (m, 1H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.88 (d, *J* = 8.1 Hz, 2H), 4.44 (s, 2H), 4.20 (s, 3H), 4.18 (s, 3H), 3.68 (s, 2H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 207.0, 144.3, 143.8, 132.7, 132.5, 131.0, 130.3, 129.3, 128.5, 125.8, 125.3, 124.8, 124.4, 123.5, 122.2, 121.9, 121.5, 120.4, 120.3, 120.0, 115.5, 110.5, 110.2, 49.5, 47.7, 36.8, 36.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{29}H_{24}ClN_2O^+$ Calcd. 451.1572, Found 451.1565.

1-(4-bromophenyl)-3-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)propan-2-one(52)



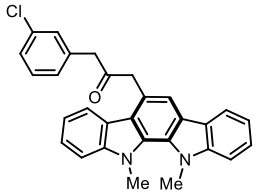
Following the general procedure, reaction of 4-aminocyclopentenone (**2g**, 0.065 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **52**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 53% (0.052 g) yield. **mp**: 177-180^oC; R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.73 (s, 1H), 7.54 – 7.51 (m, 4H), 7.36 – 7.32 (m, 1H), 7.28 – 7.23 (m, 3H), 6.81 (d, *J* = 8.1 Hz, 2H), 4.44 (s, 2H), 4.21 (s, 3H), 4.19 (s, 3H), 3.66 (s, 2H);**^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 206.9, 144.3, 143.7, 133.0, 131.4, 131.3, 130.3, 129.3, 125.8, 125.3, 124.7, 124.4, 123.5, 122.1, 121.8, 121.5, 120.8, 120.3, 120.2, 119.9, 115.5, 110.5, 110.2, 49.5, 47.8, 36.8, 36.6;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{29}H_{24}BrN_2O^+$Calcd.495.1067, Found 495.1066.

1-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)-3-(m-tolyl)propan-2-one(53)



Following the general procedure, reaction of 4-aminocyclopentenone (**2h**, 0.053 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **53**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 51% (0.044 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.12 (d, *J* = 7.8 Hz, 1H), 7.96 (d, *J* = 7.9 Hz, 1H), 7.71 (s, 1H), 7.55 – 7.48 (m, 4H), 7.36 – 7.32 (m, 1H), 7.27 – 7.20 (m, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 6.9 Hz, 2H), 4.45 (s, 2H), 4.19 (s, 3H), 4.17 (s, 3H), 3.72 (s, 2H), 2.25 (s, 3H); **^{13}C {^{1}H} NMR** ($CDCl_3$, 100 MHz) δ207.5, 144.2, 143.7, 138.3, 134.1, 130.5, 130.2, 129.2, 128.5, 127.7, 126.7, 125.7, 125.2, 124.7, 124.4, 123.4, 122.1, 121.9, 121.7, 120.3, 120.2, 119.9, 115.5, 110.4, 110.1, 48.9,48.8, 36.8, 36.6, 21.4; **HRMS (ESI-TOF)** m/z: $[M+H]^+$ $C_{30}H_{27}N_2O^+$ Calcd. 431.2118, Found 431.2117.

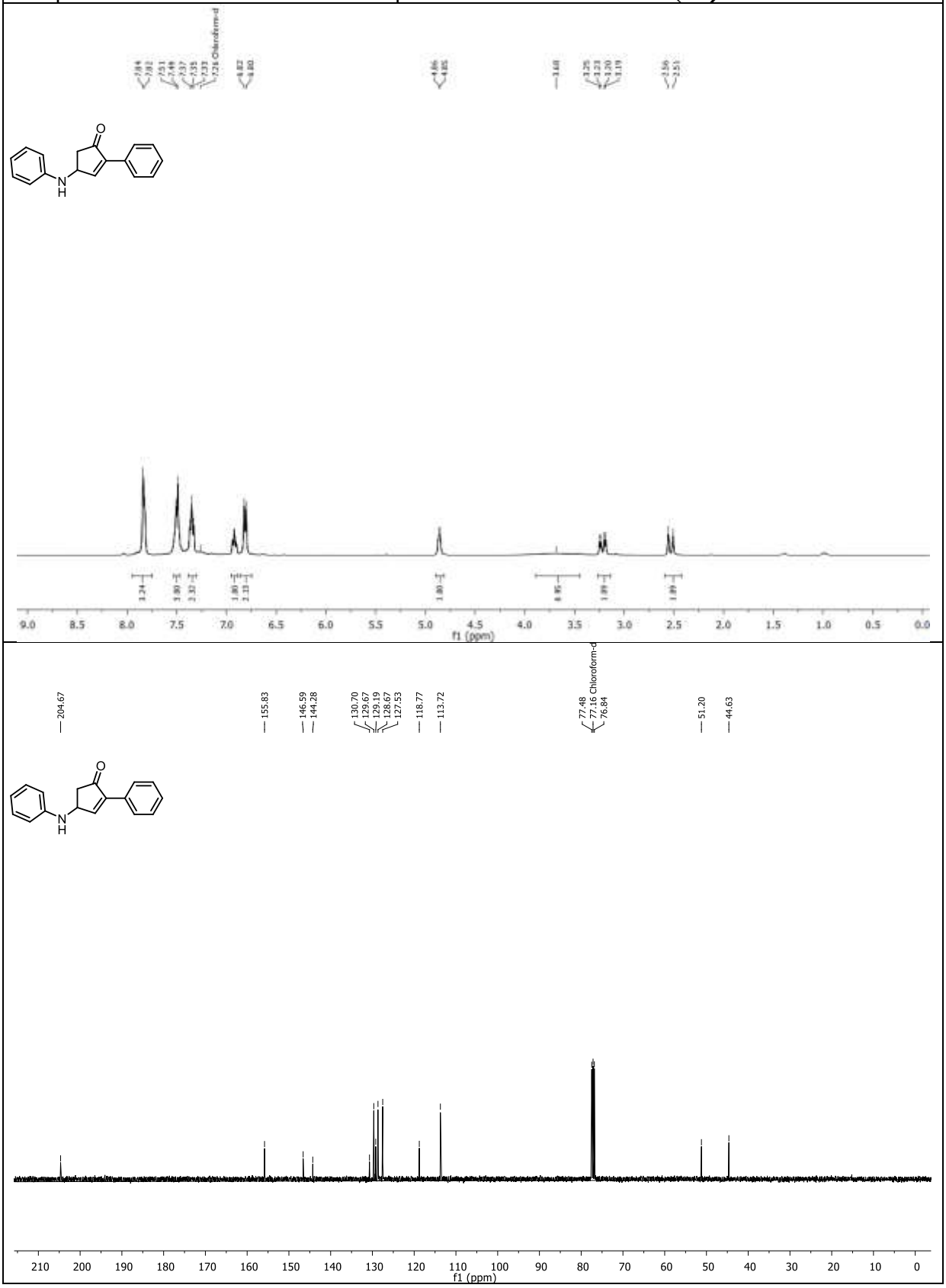
1-***(3-chlorophenyl)-3-(11,12-dimethyl-11,12-dihydroindolo[2,3-a]carbazol-5-yl)propan-2-one(54)***



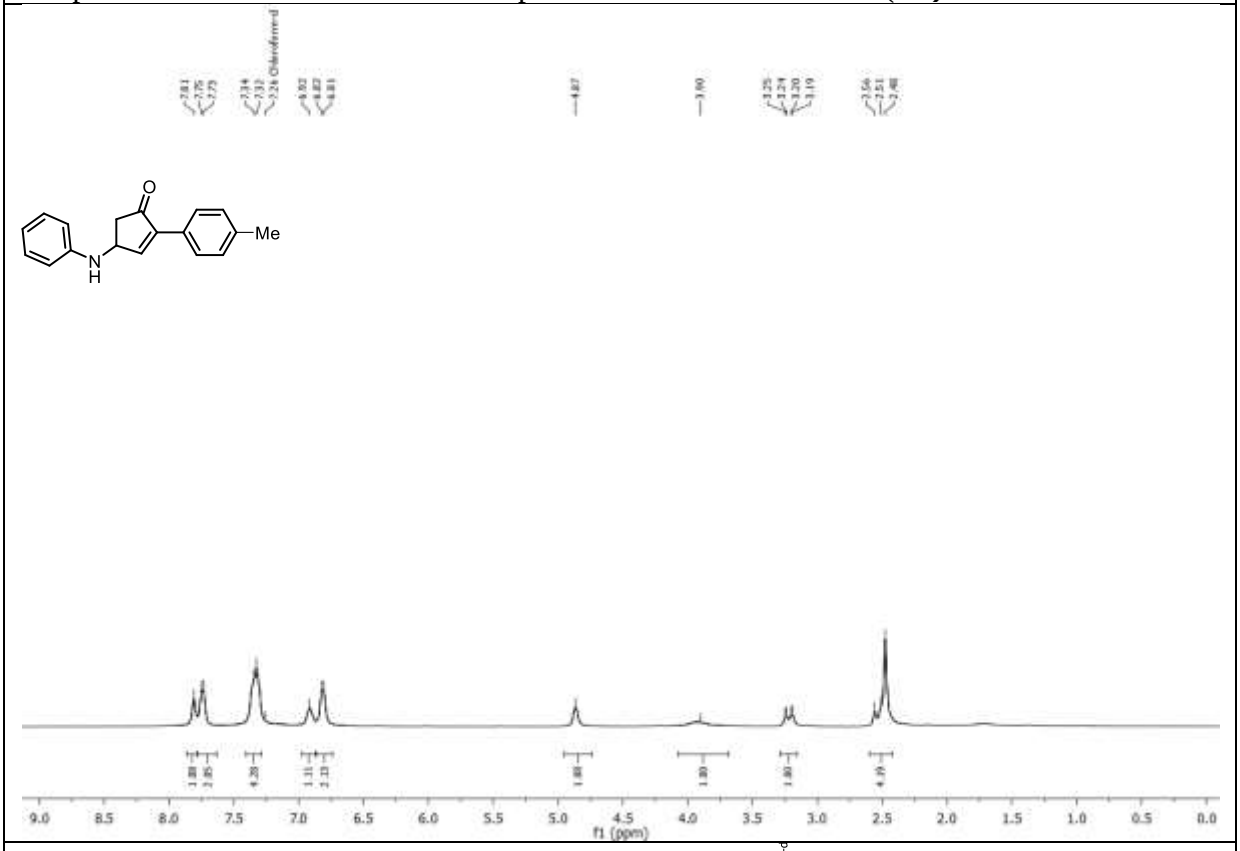
Following the general procedure, reaction of 4-aminocyclopentenone (**2j**, 0.057 g, 0.2 mmol, 1.0 equiv) and 1,1'-dimethyl-1H,1'H-2,2'-biindole (**3l**, 0.052 g, 0.2 mmol, 1.0 equiv) in presence of $AlCl_3$ (0.053 g, 0.4 mmol) delivered compound **54**, which was purified by silica gel column chromatography (Hexane/EtOAc 8:2) to furnish the title compound as white solid in 56% (0.050 g) yield. R_f 0.25 (EtOAc: Hexane 2:8);**^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.13 (d, *J* = 7.7 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.56-7.48 (m, 4H), 7.36 – 7.32 (m, 1H), 7.29 – 7.27 (m, 1H), 7.14-7.08 (m, 2H), 6.92 (s, 1H), 6.89 (d, *J* = 6.6 Hz, 1H), 4.45 (s, 2H), 4.21 (s, 3H), 4.19 (s, 3H), 3.68 (s, 2H);**{^{1}H} NMR** ($CDCl_3$, 100 MHz) δ 206.9, 144.2, 143.7, 136.0, 134.1, 130.2, 129.8, 129.6, 129.3, 127.9, 127.0, 125.8, 125.3, 124.7, 124.3, 123.5, 122.1, 121.8, 121.4, 120.4, 120.3, 120.0, 115.5, 110.4, 110.2, 49.5, 47.9, 36.9, 36.7;**HRMS (ESI-TOF)** m/z: $[M+H]^+C_{29}H_{24}ClN_2O^+$Calcd.451.1572, Found 451.1573.

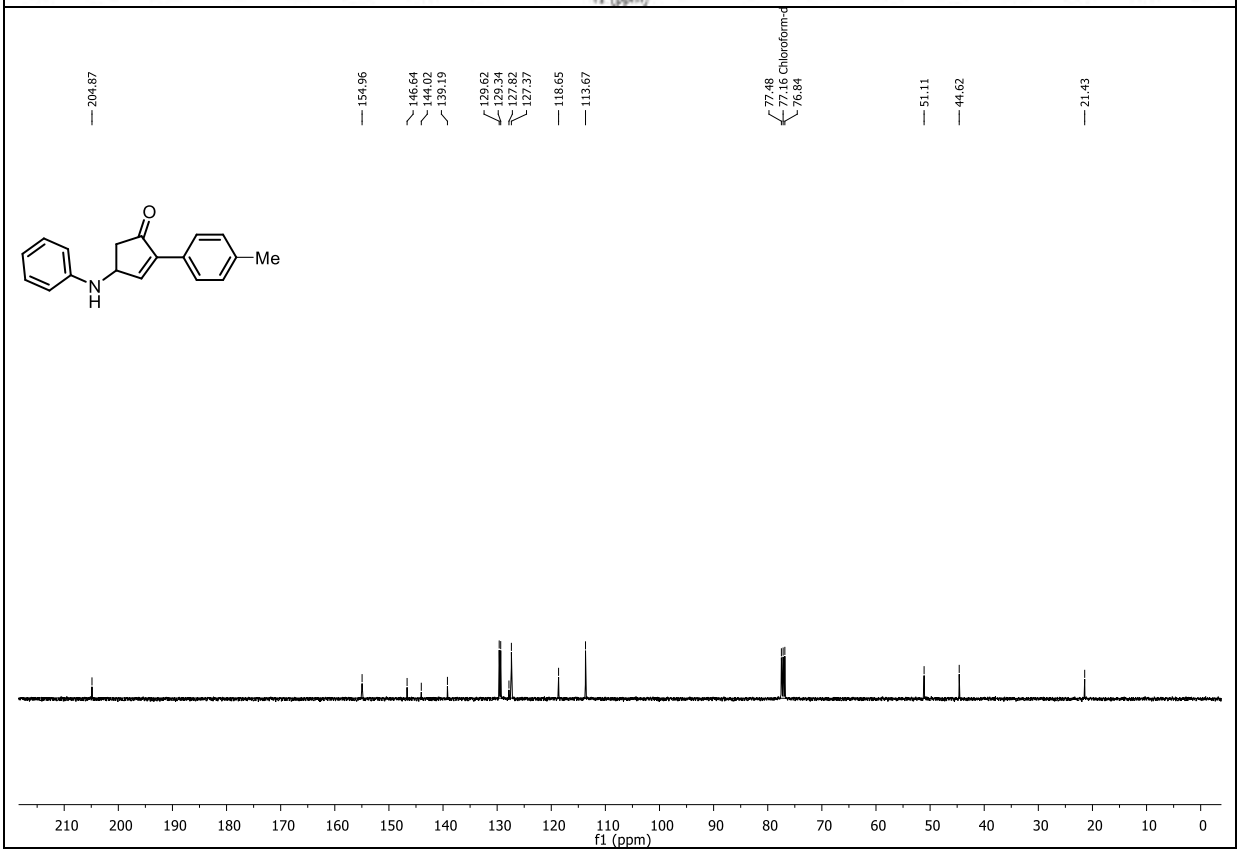
13. Spectral data for new compounds

^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***2a'***)

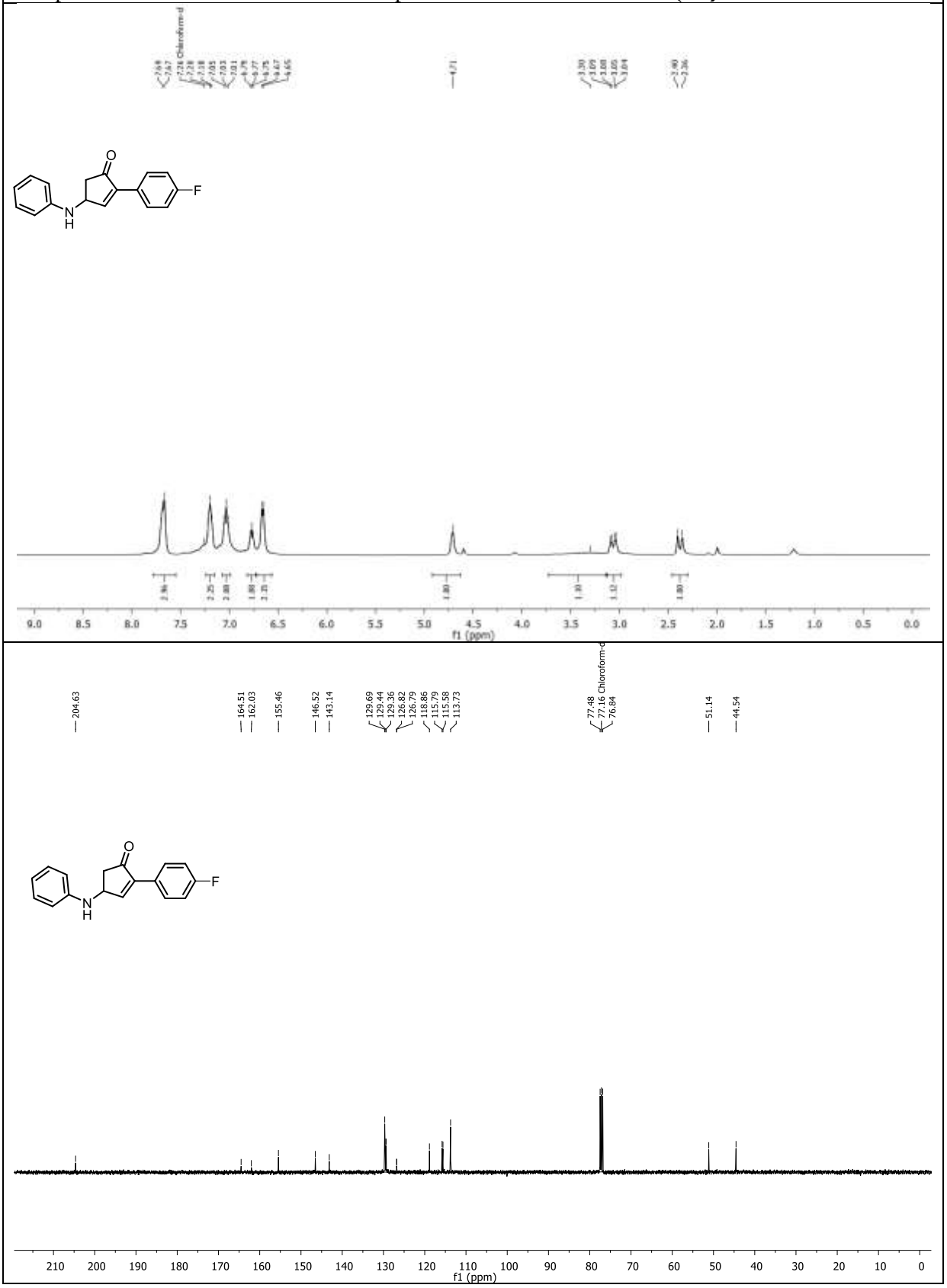


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***2b'***)

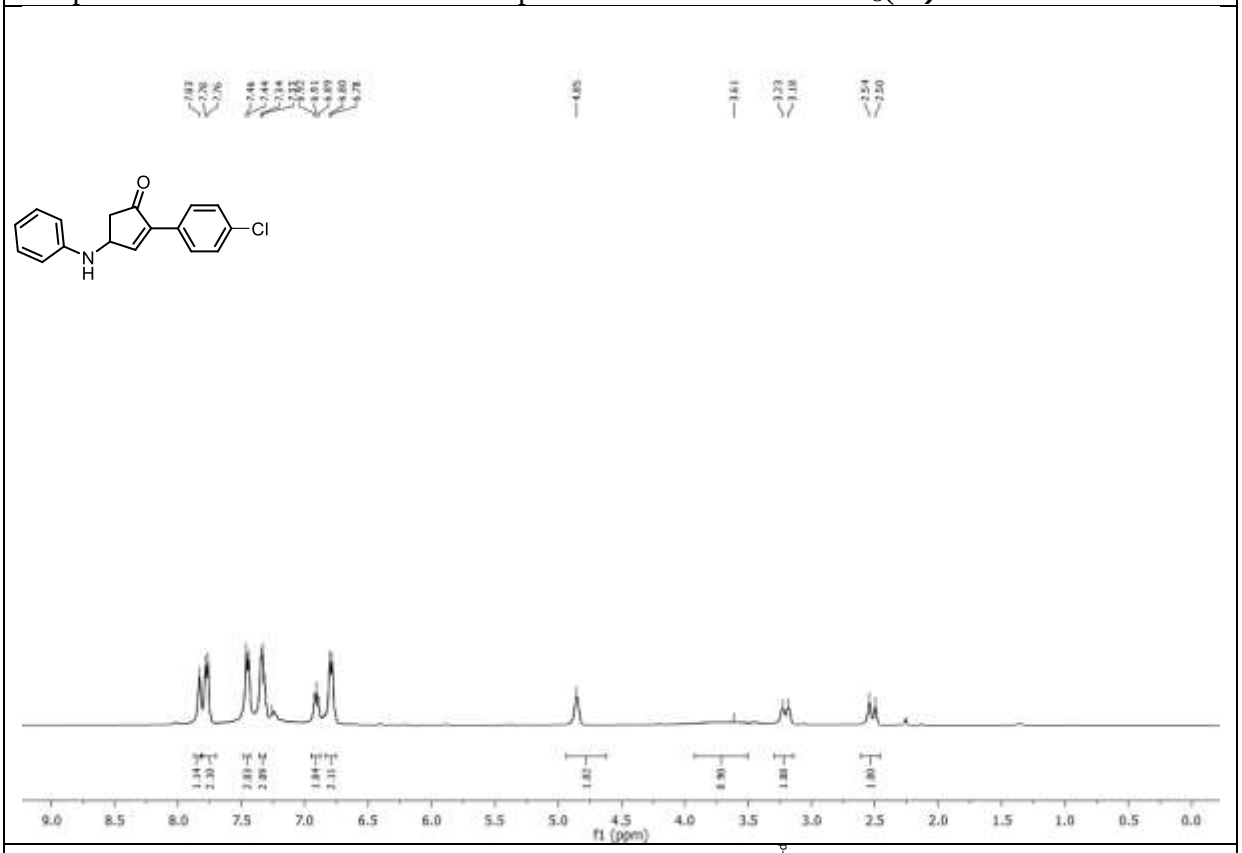


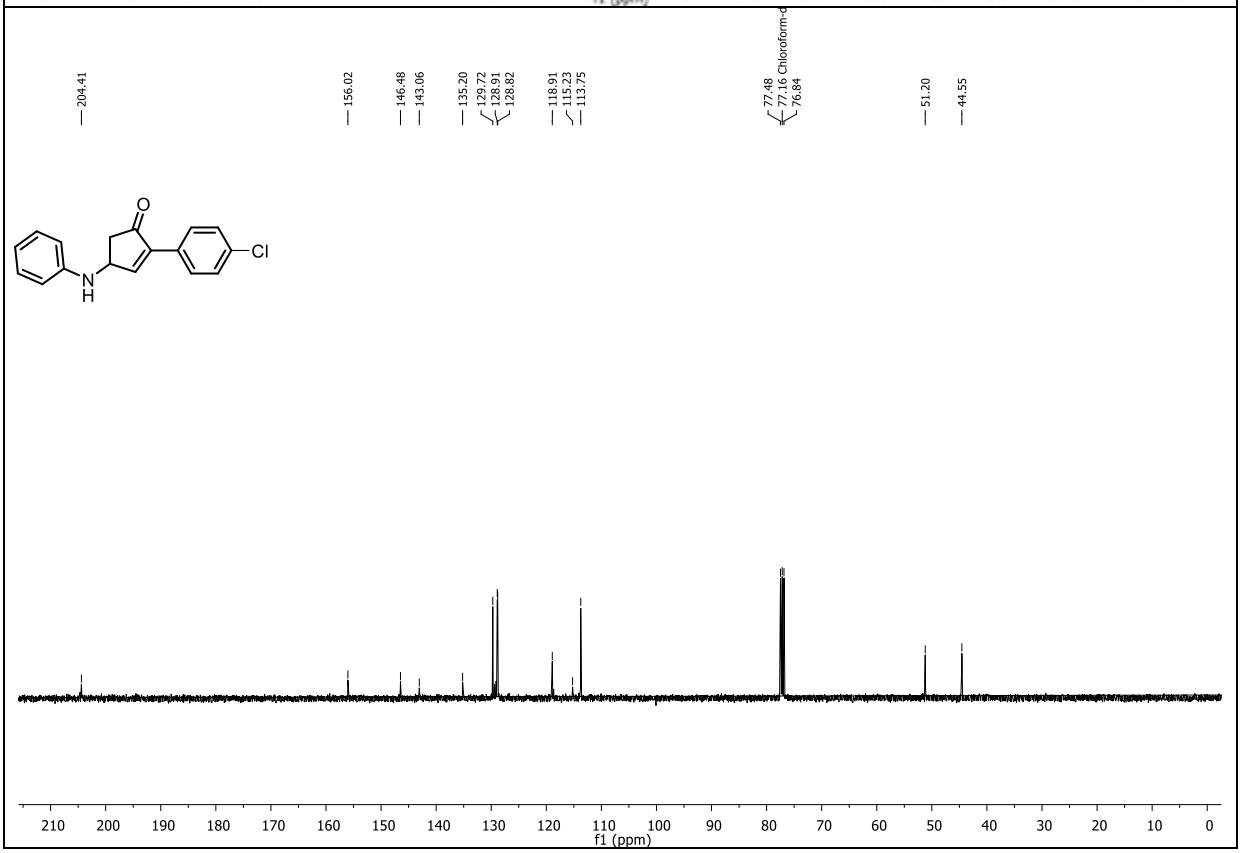


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***2e'***)

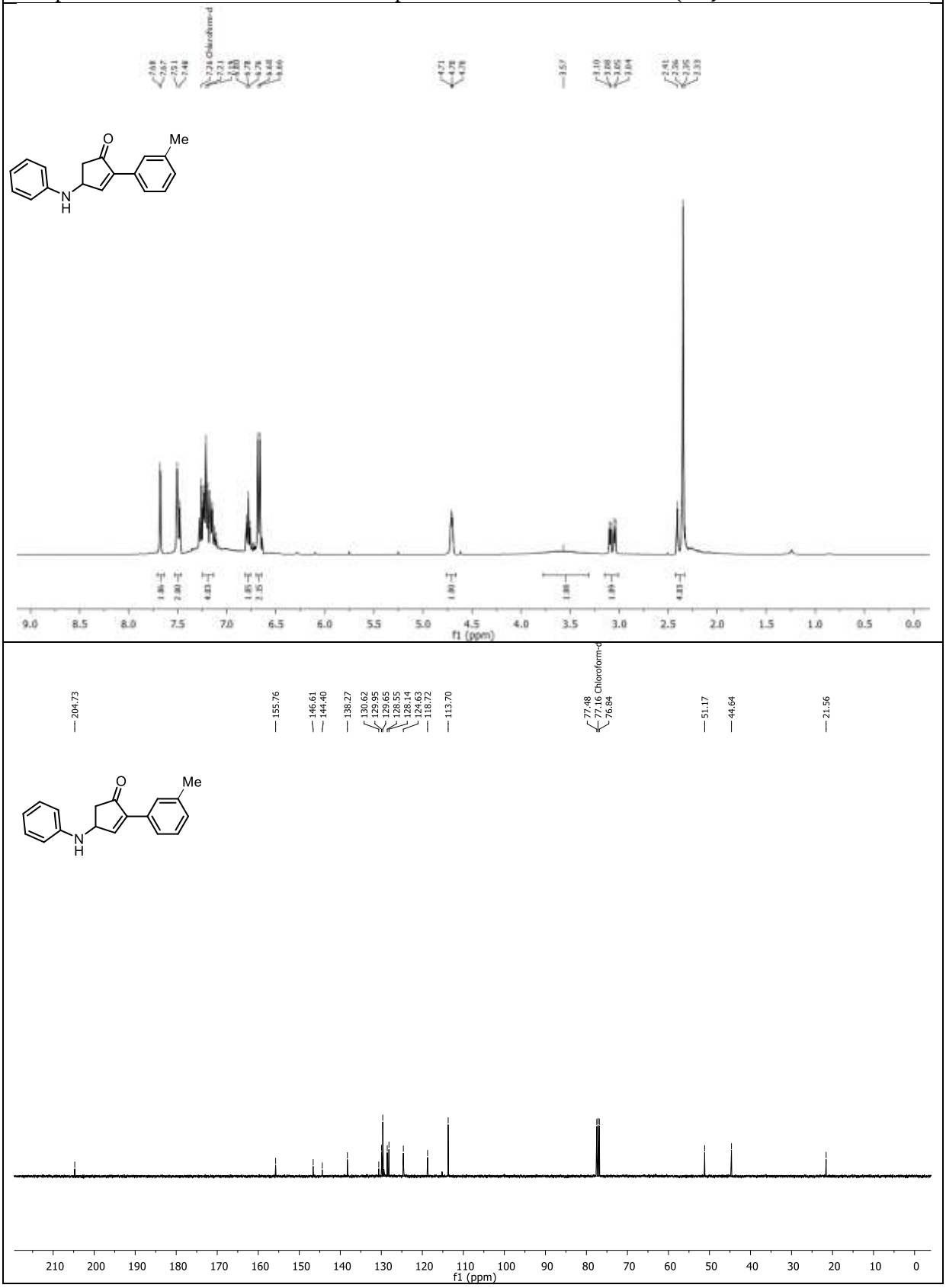


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***2f'***)



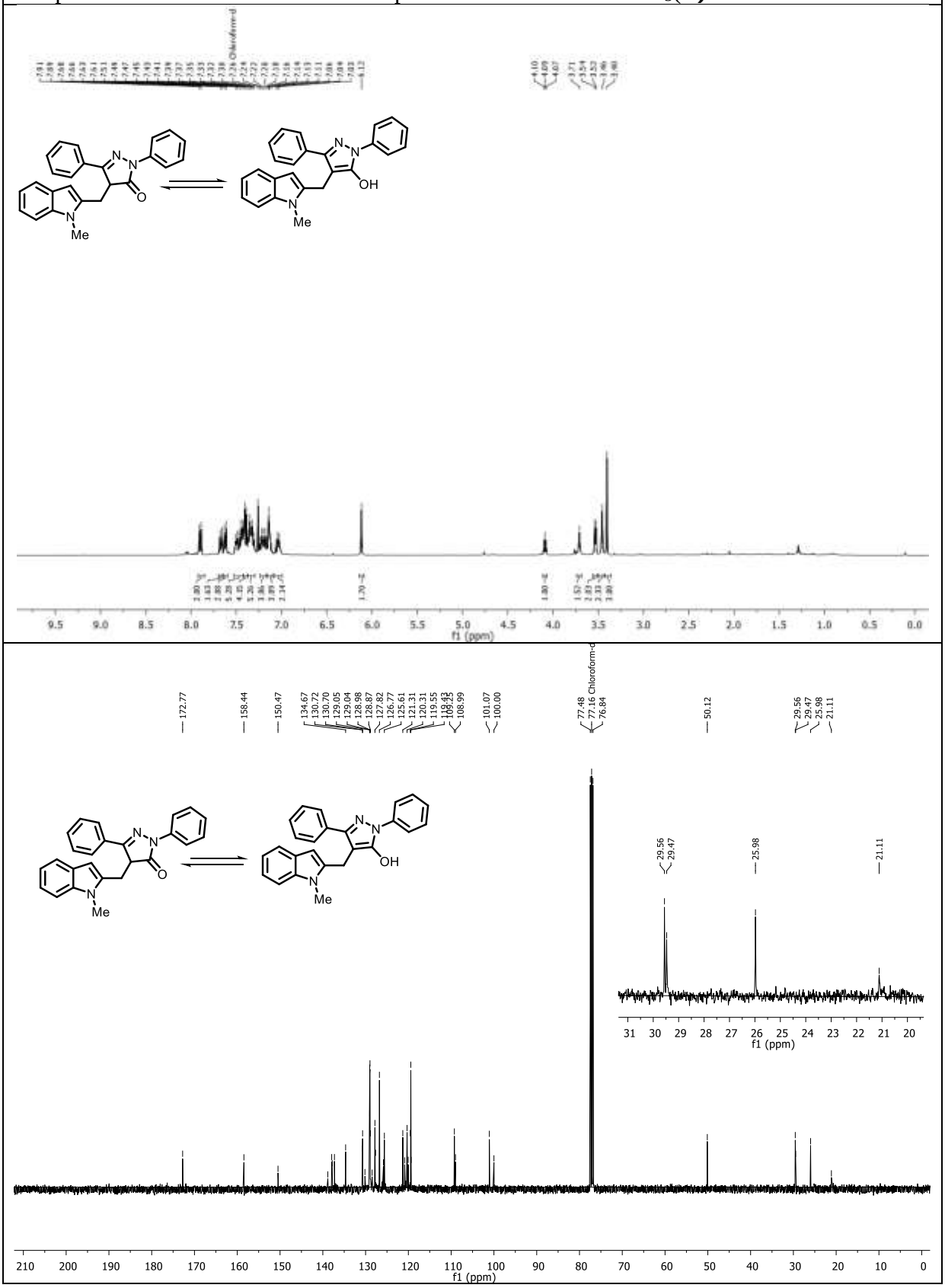


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***2h'***)

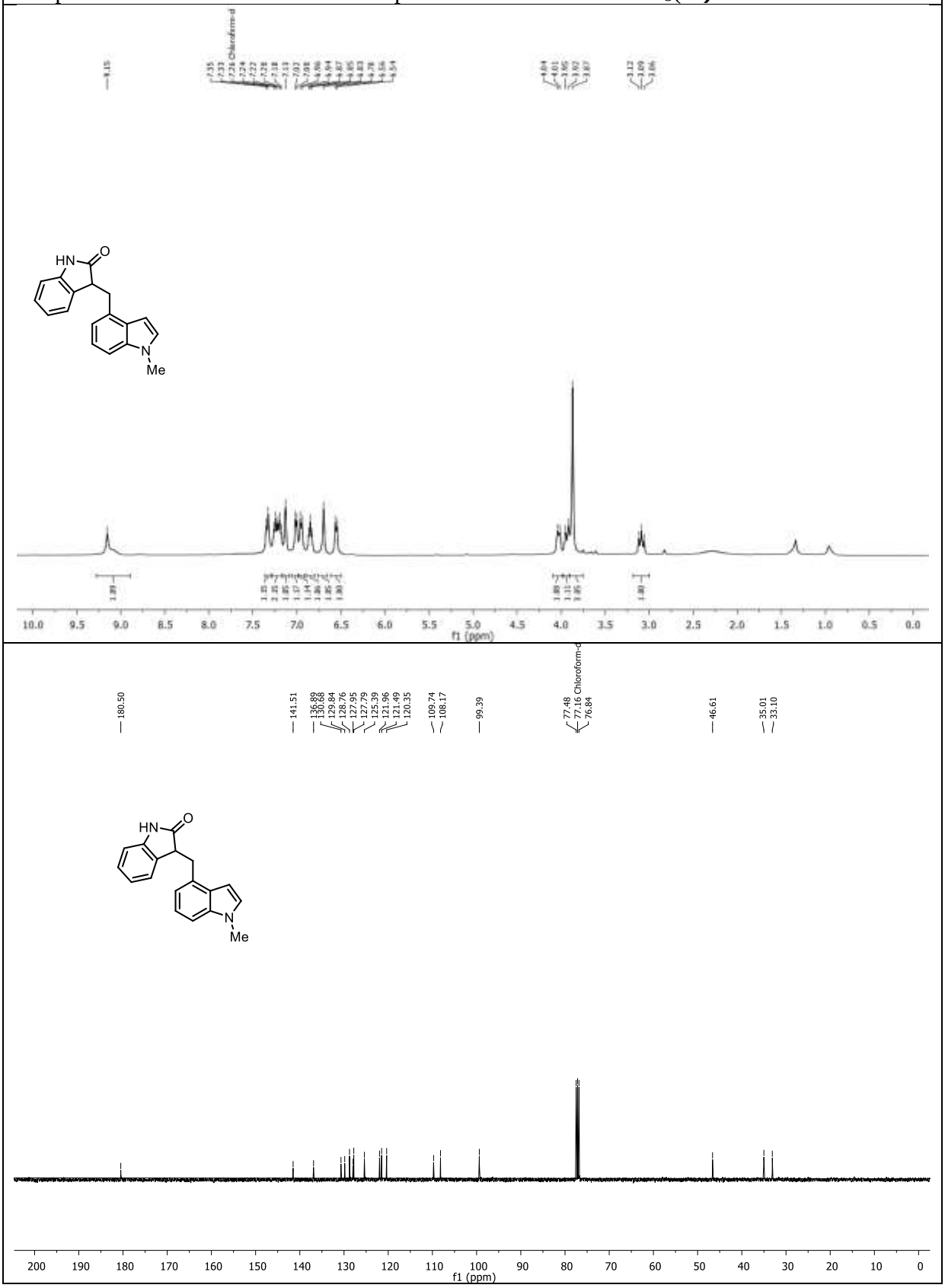


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***3b)***

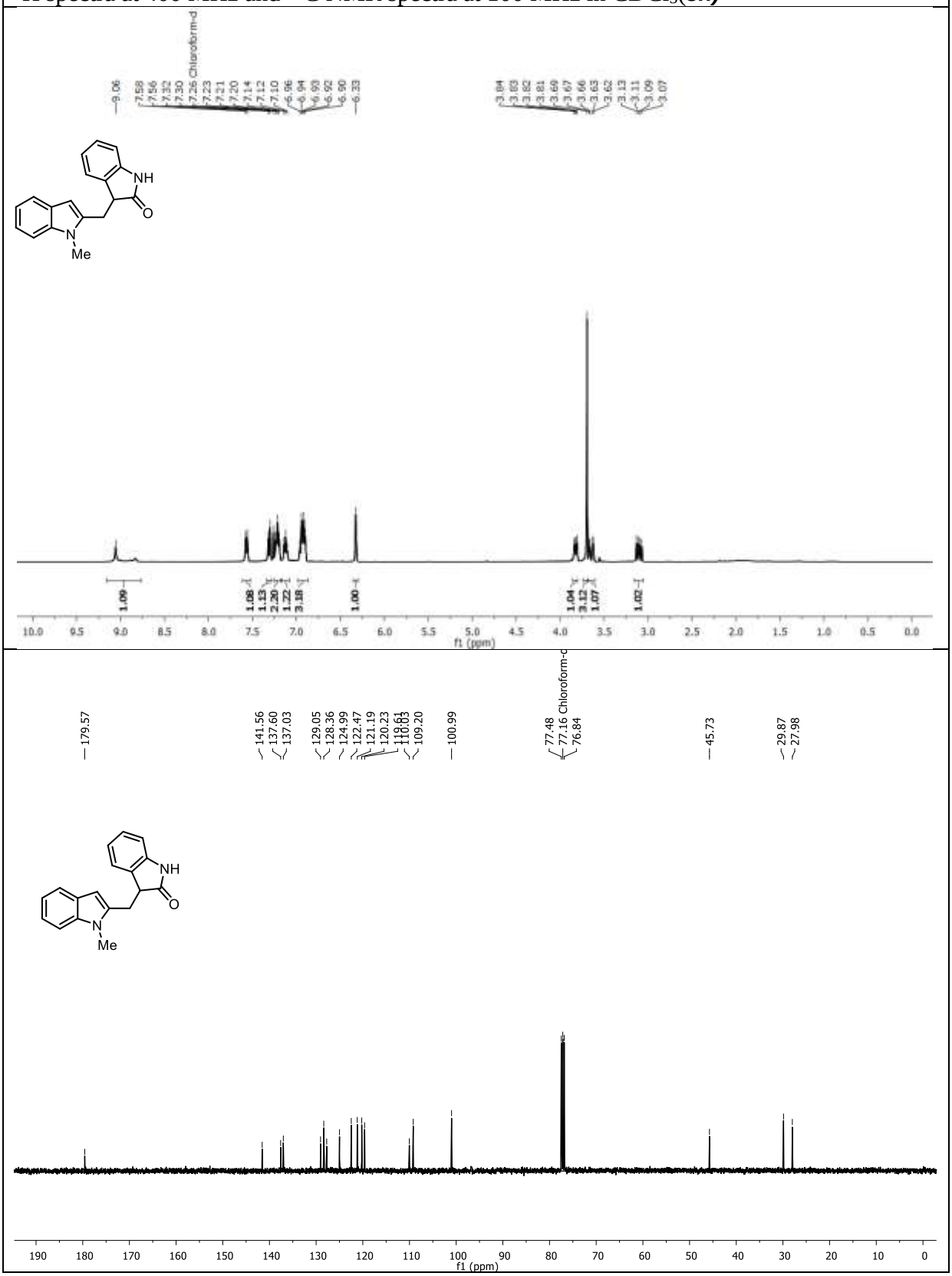
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***3i)***



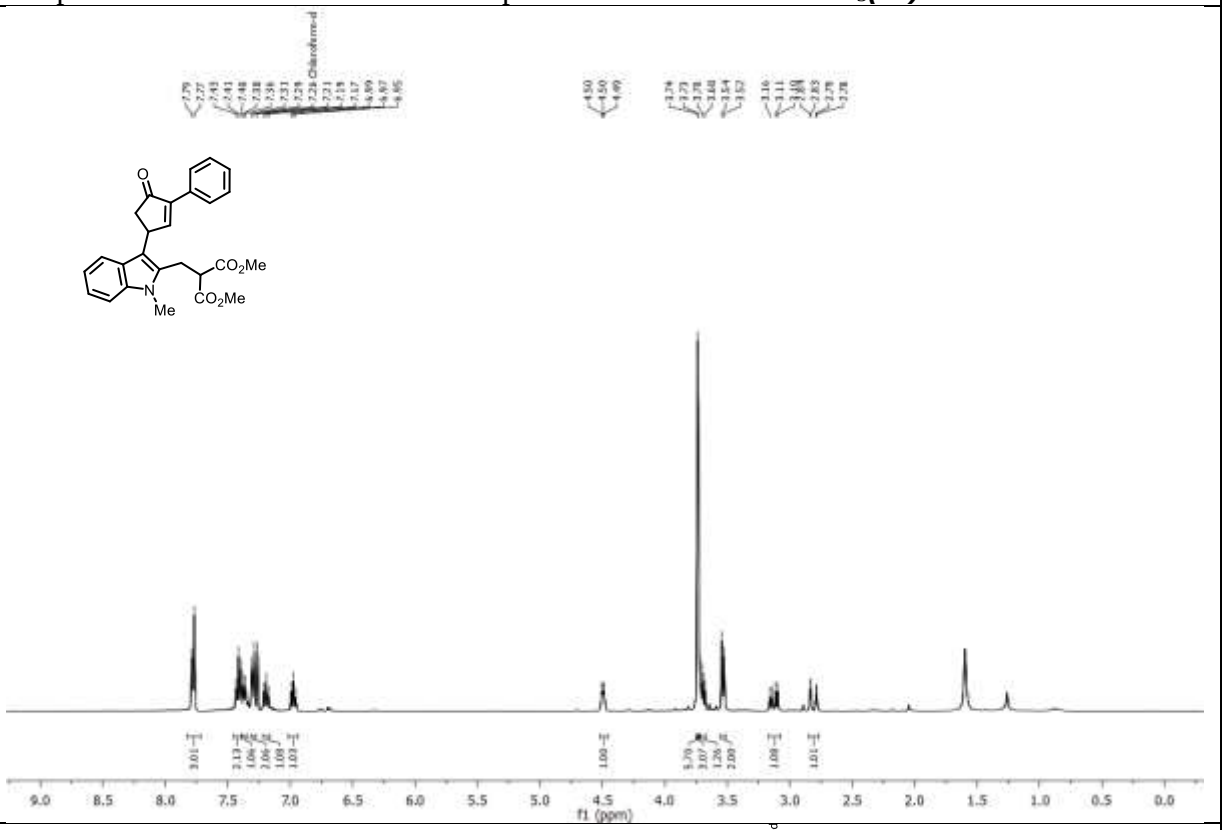
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***3k)***

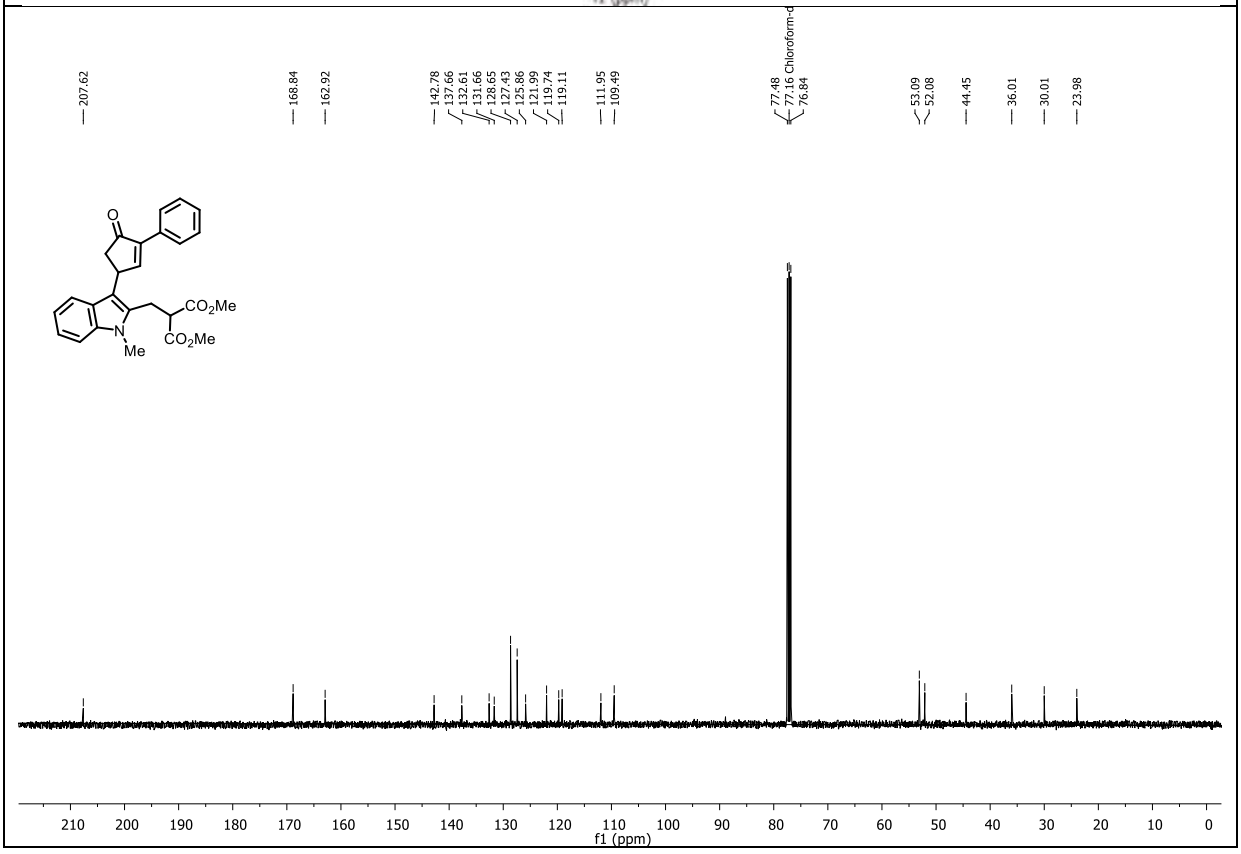


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$(***3h)***

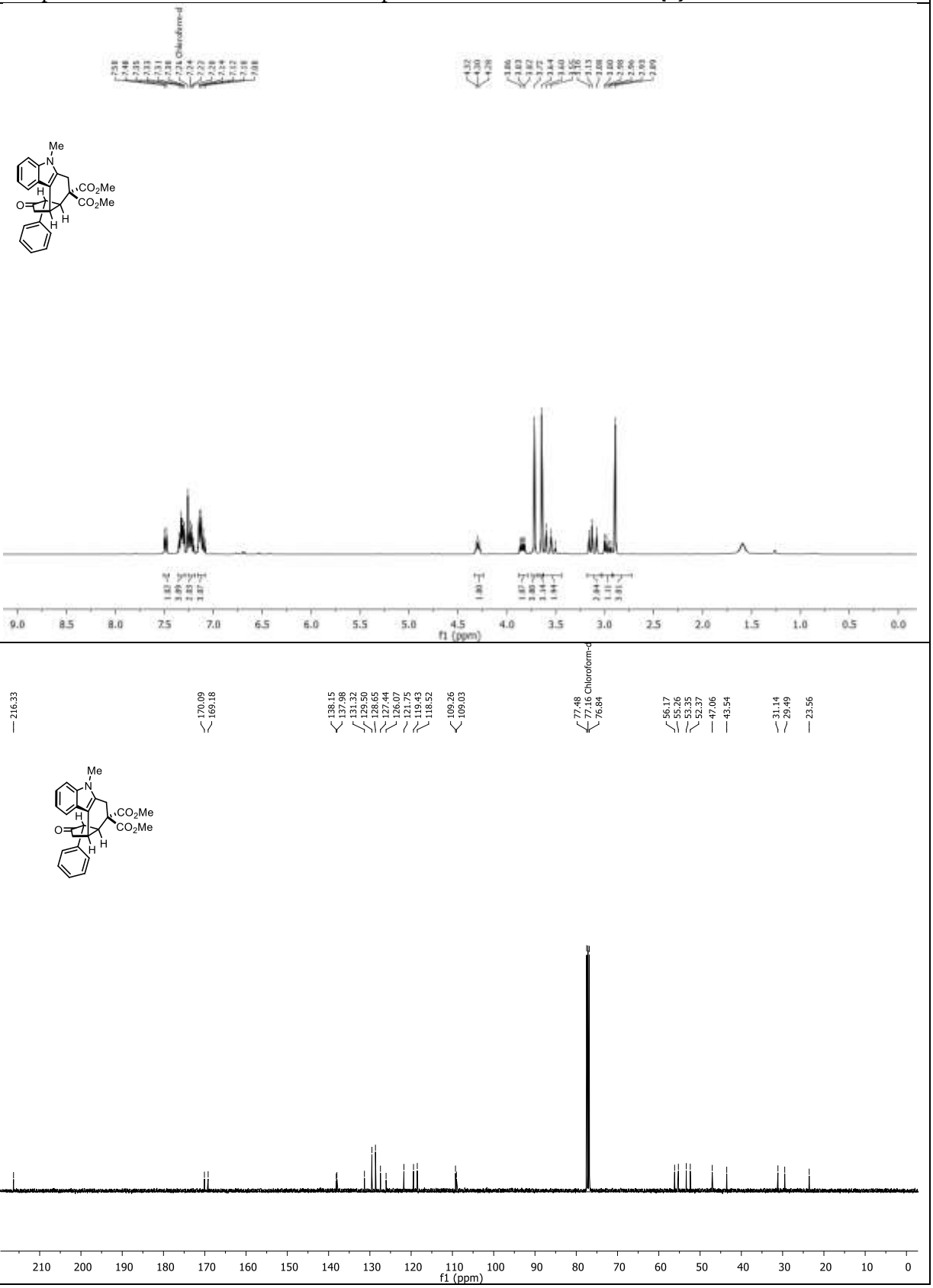


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(4'')***

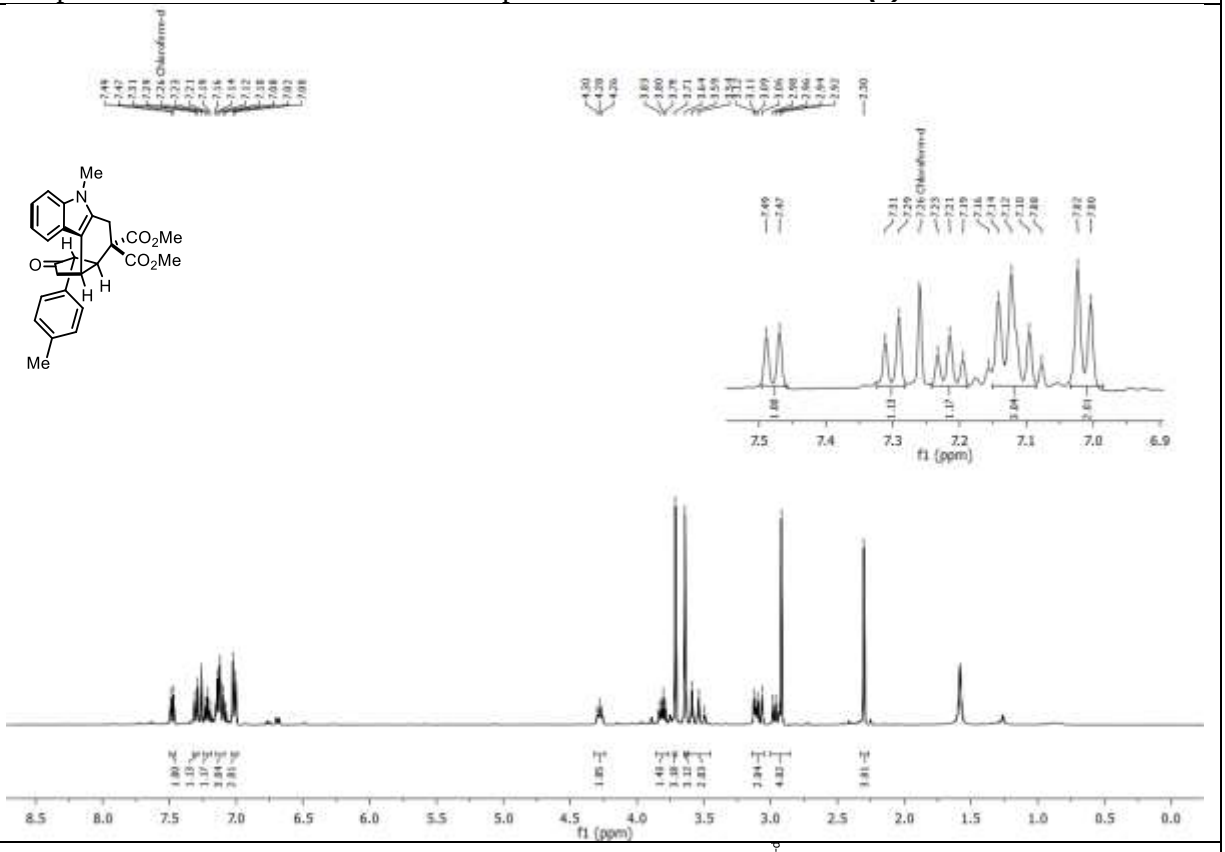


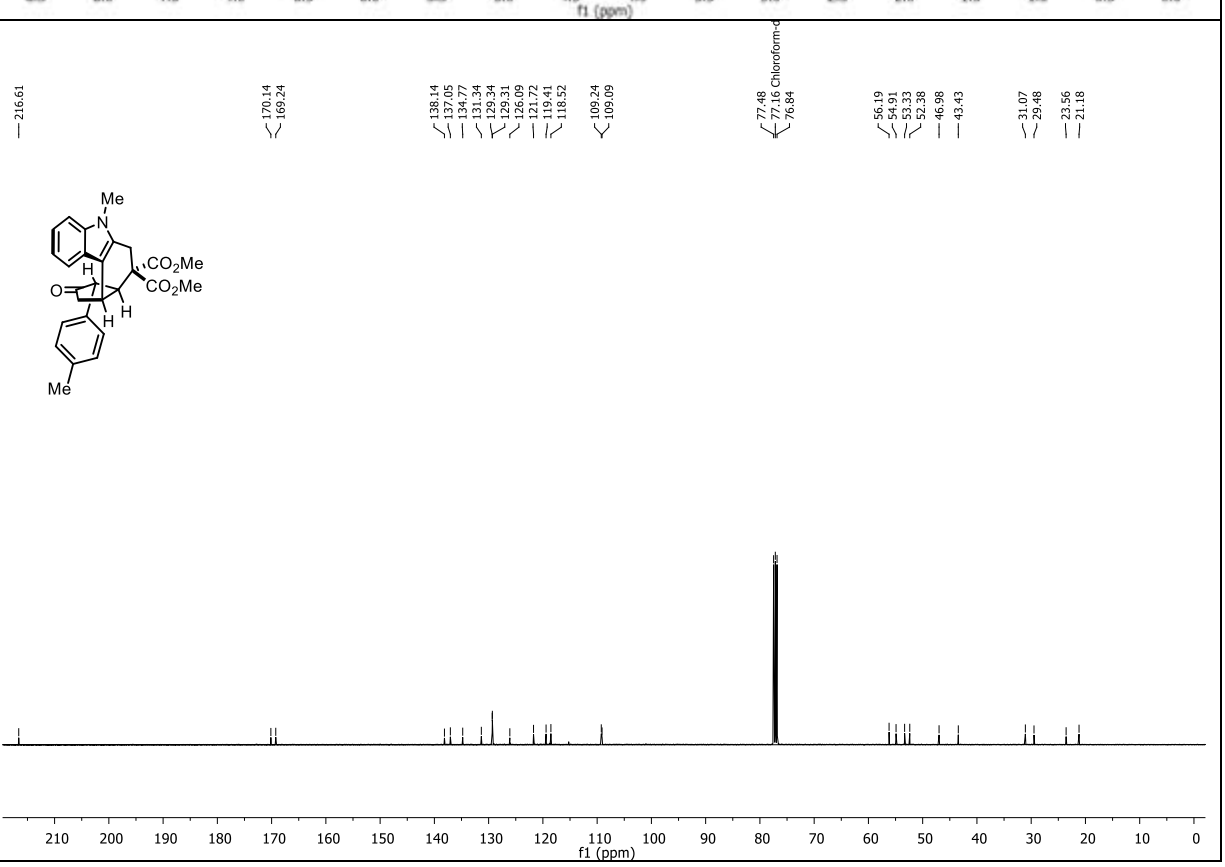


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(4)***

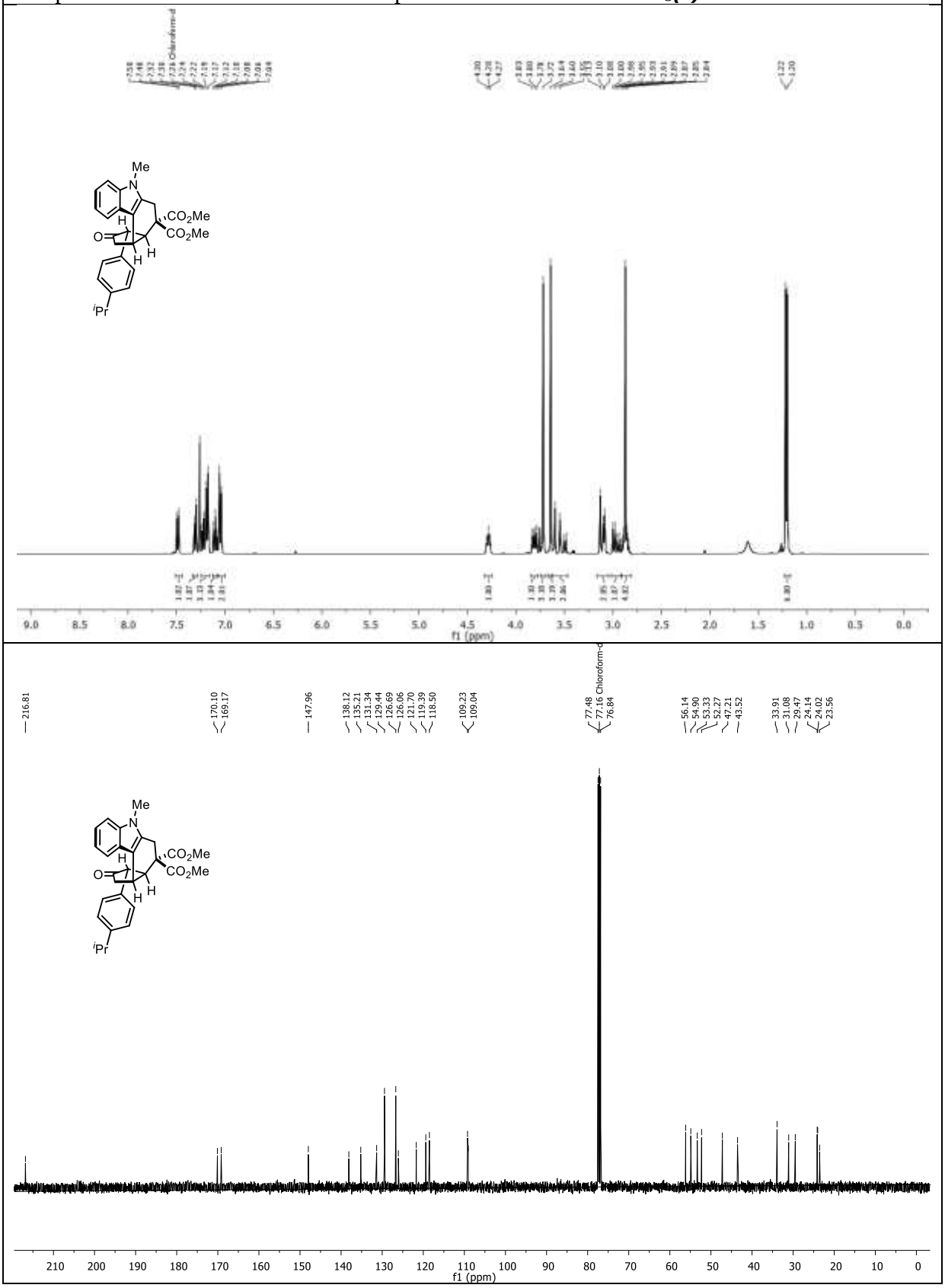


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(5)***

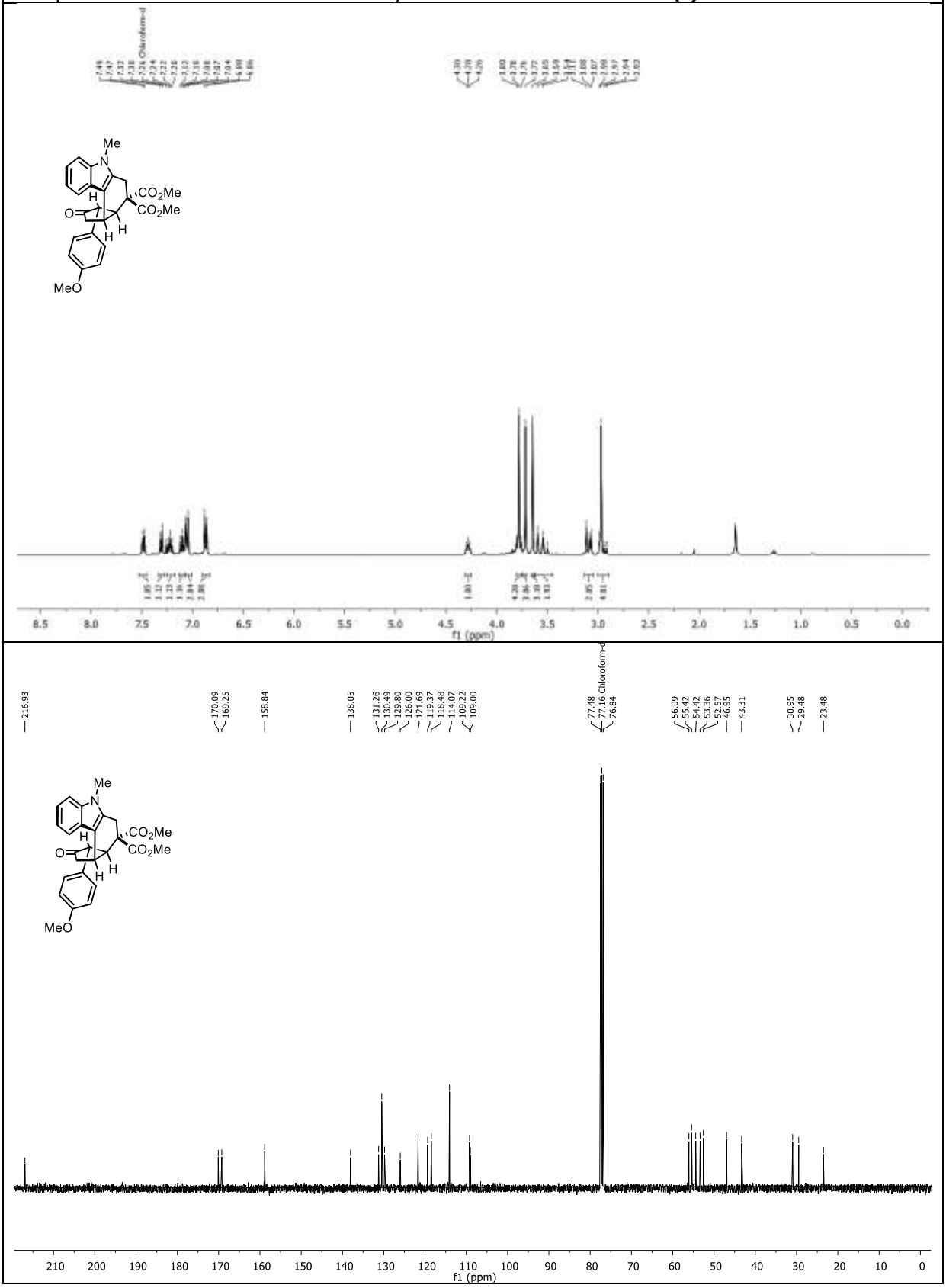




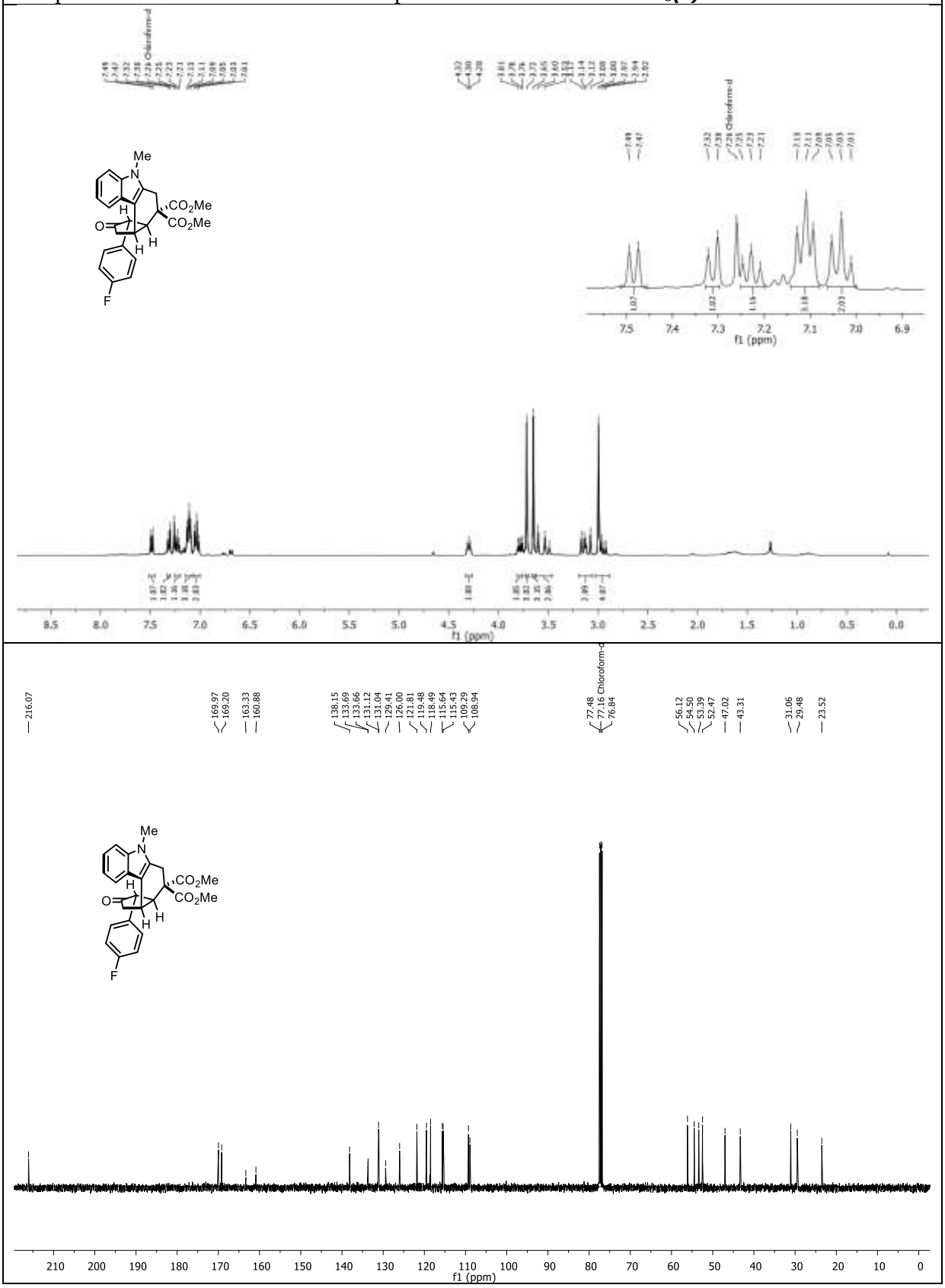
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(6)***



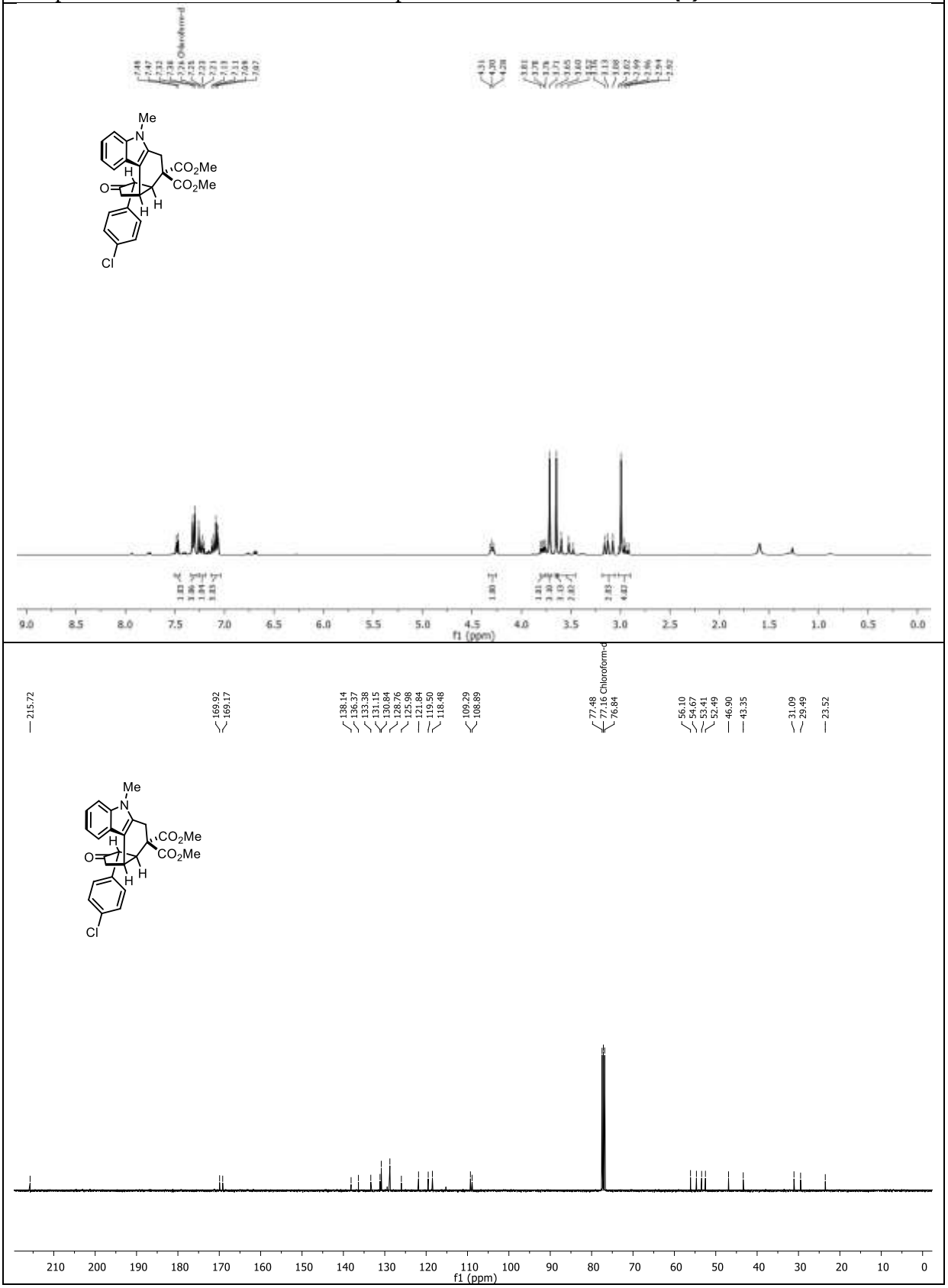
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(7)***



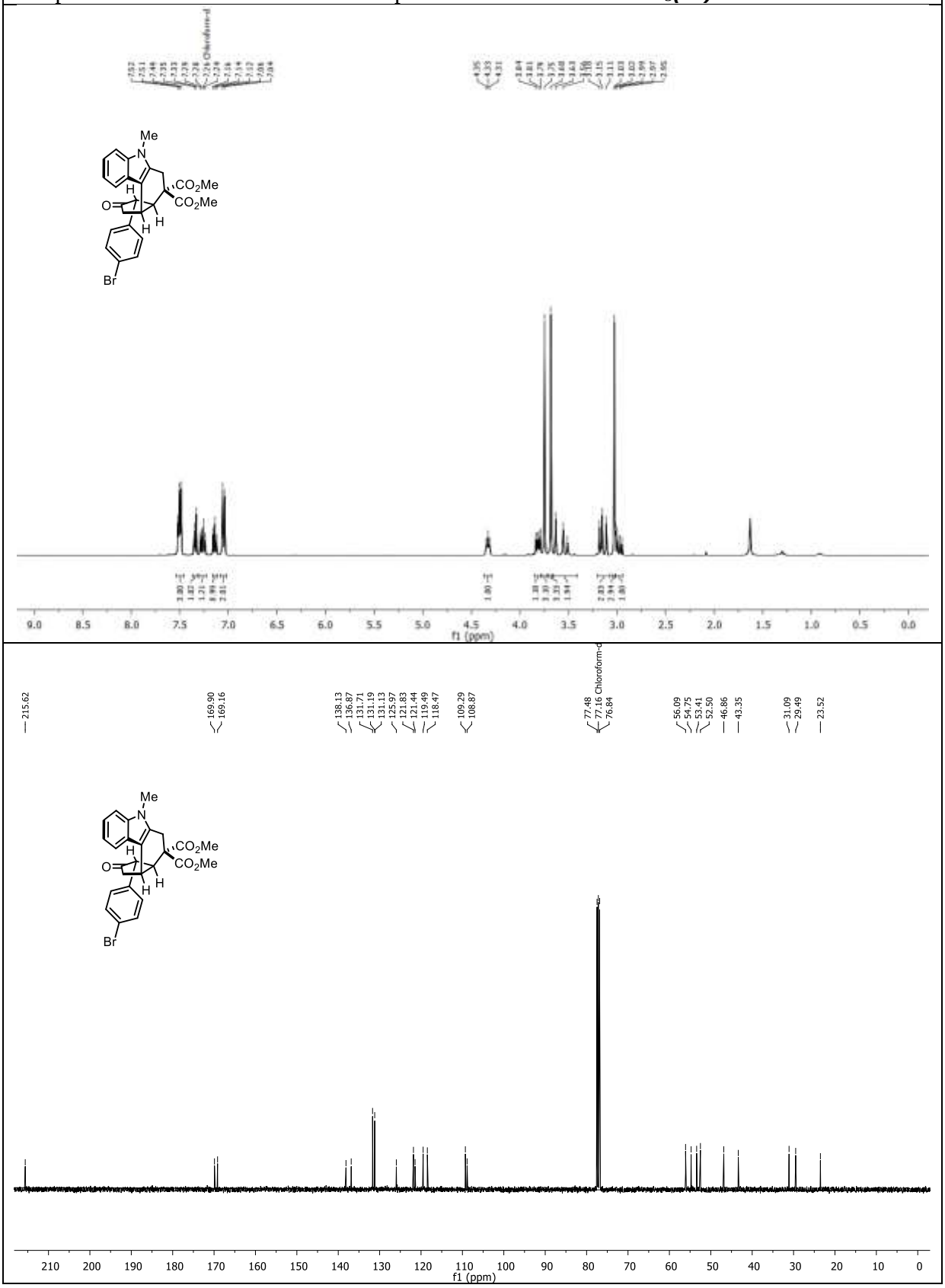
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(8)***



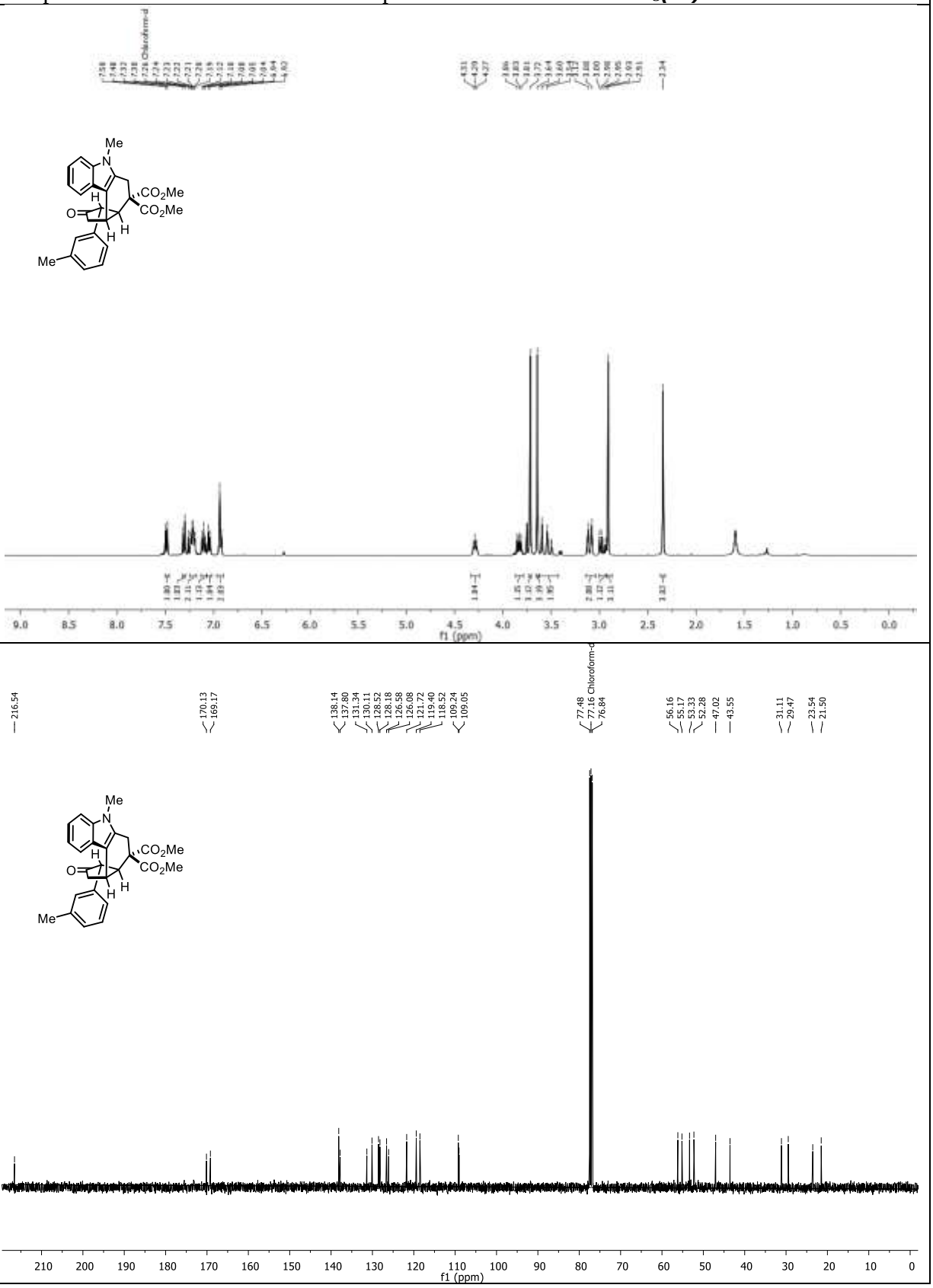
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(9)***



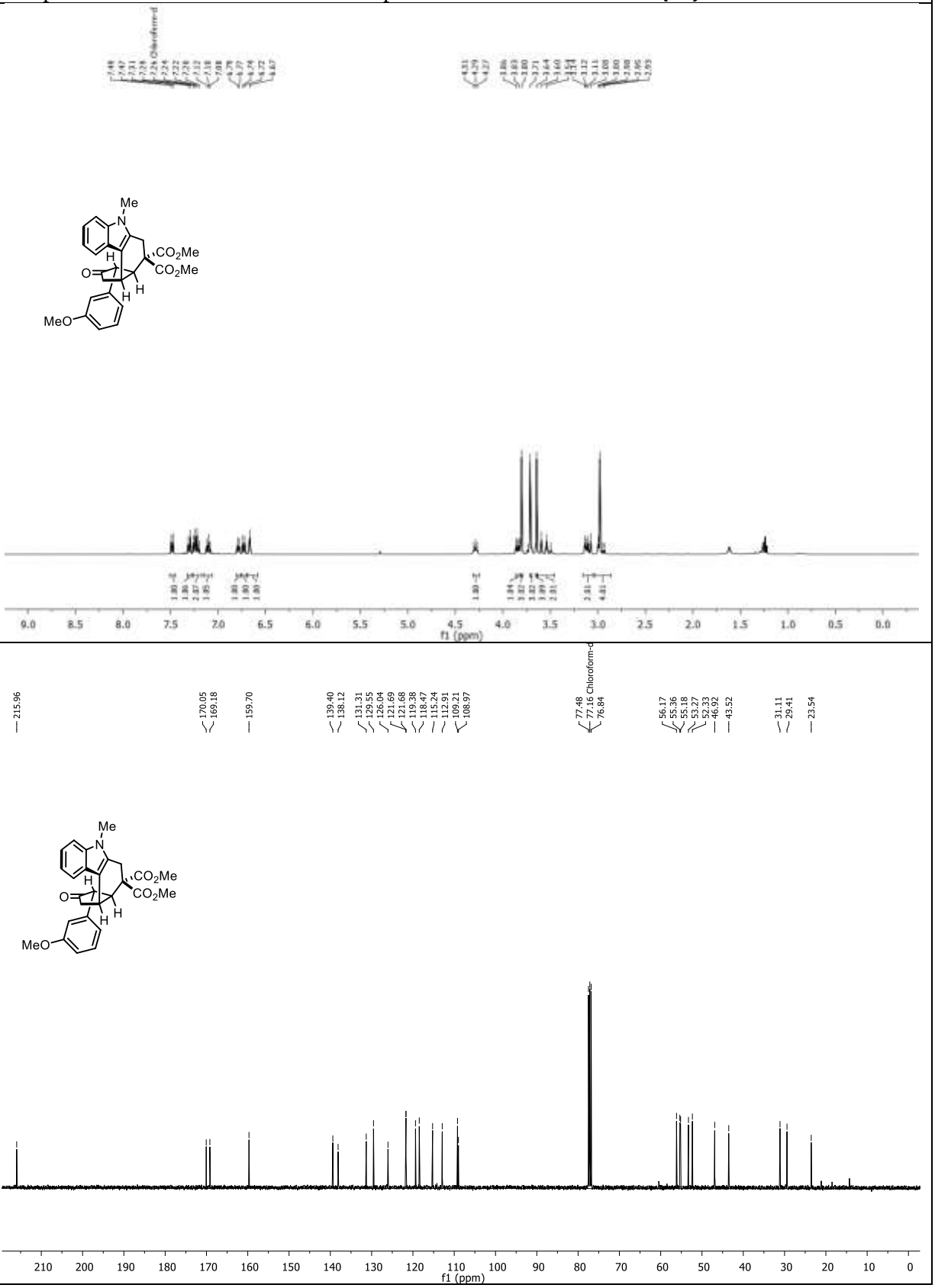
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(10)***



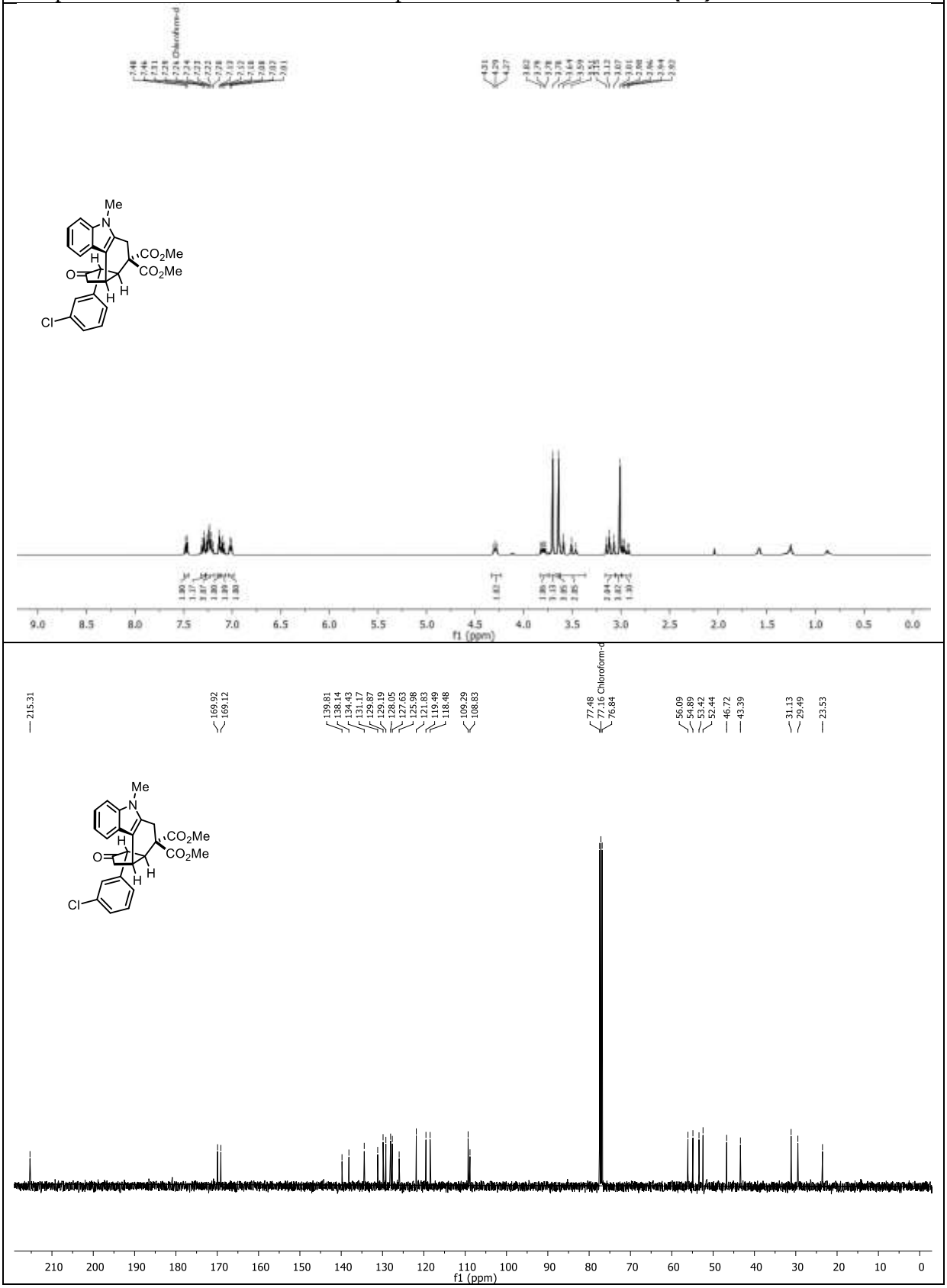
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(11)***



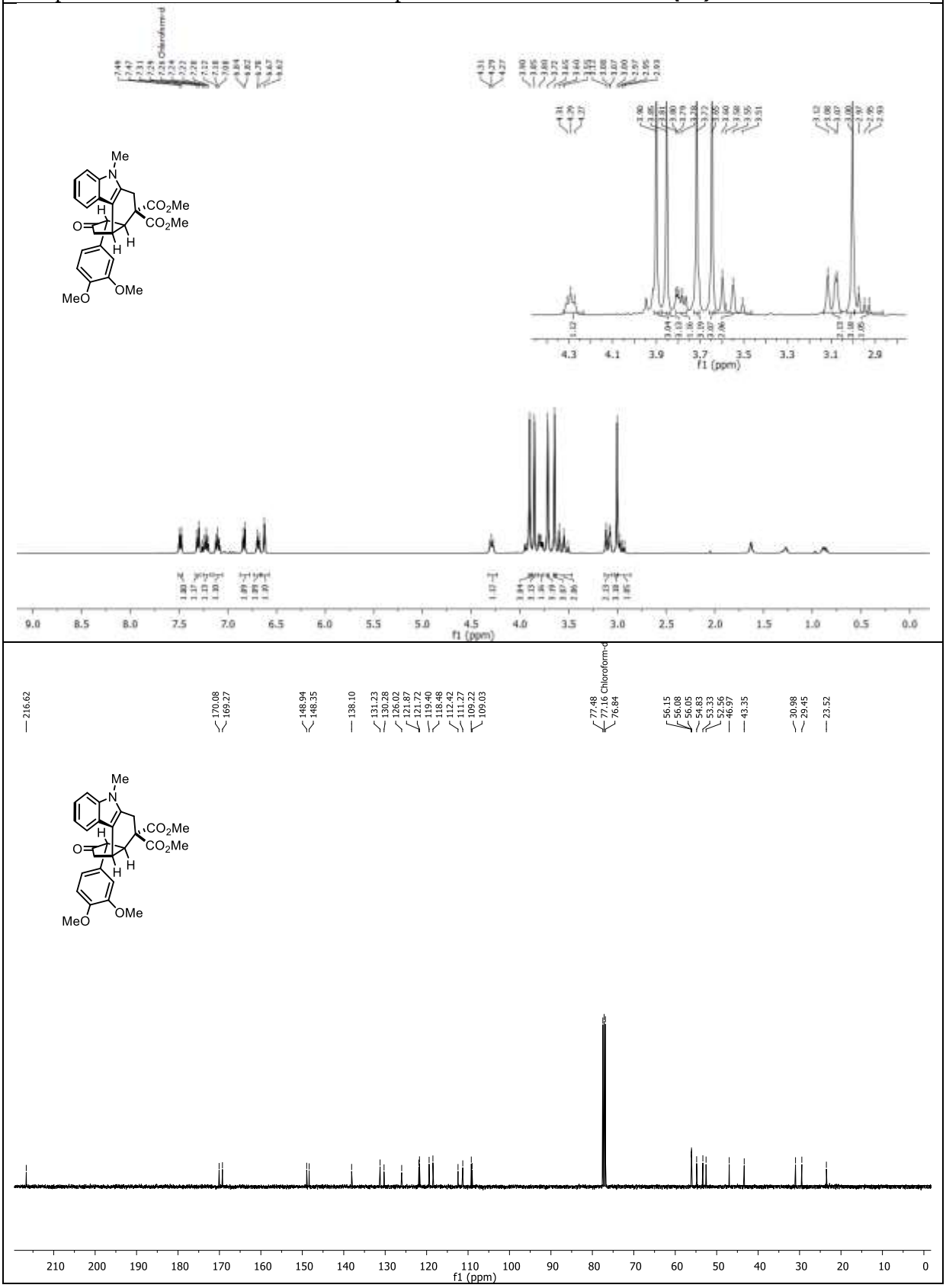
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(12)***



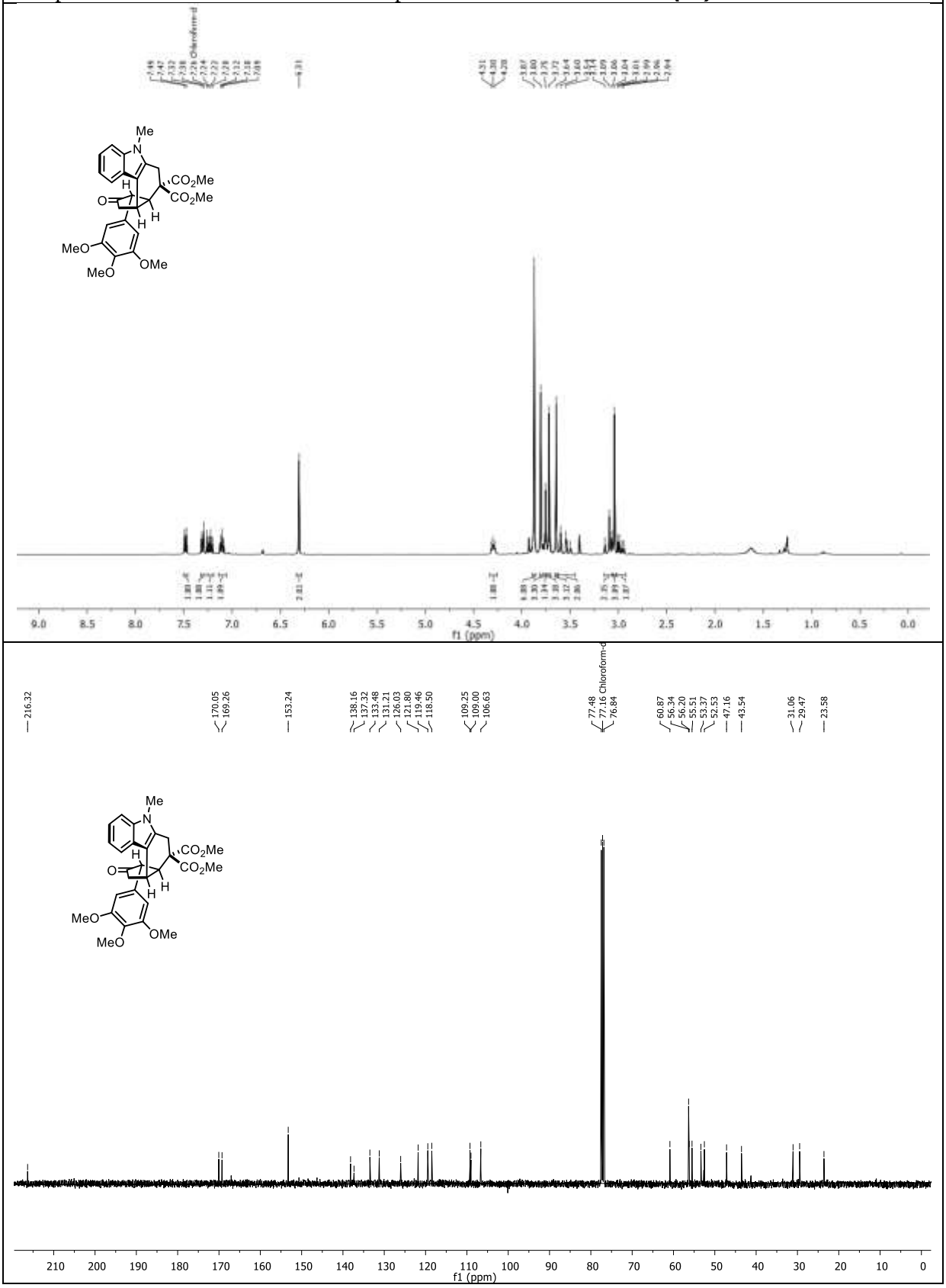
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(13)***



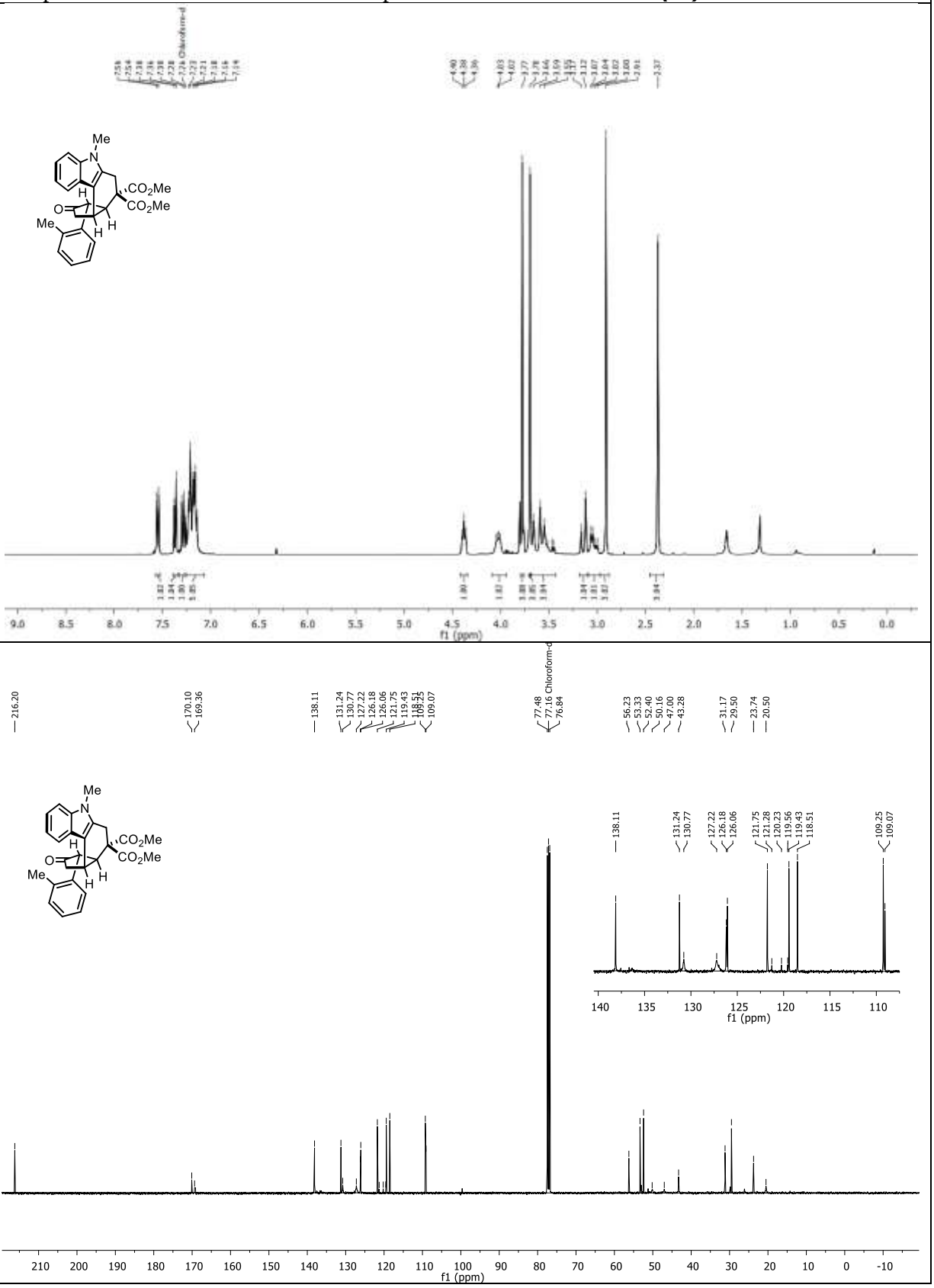
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(14)***



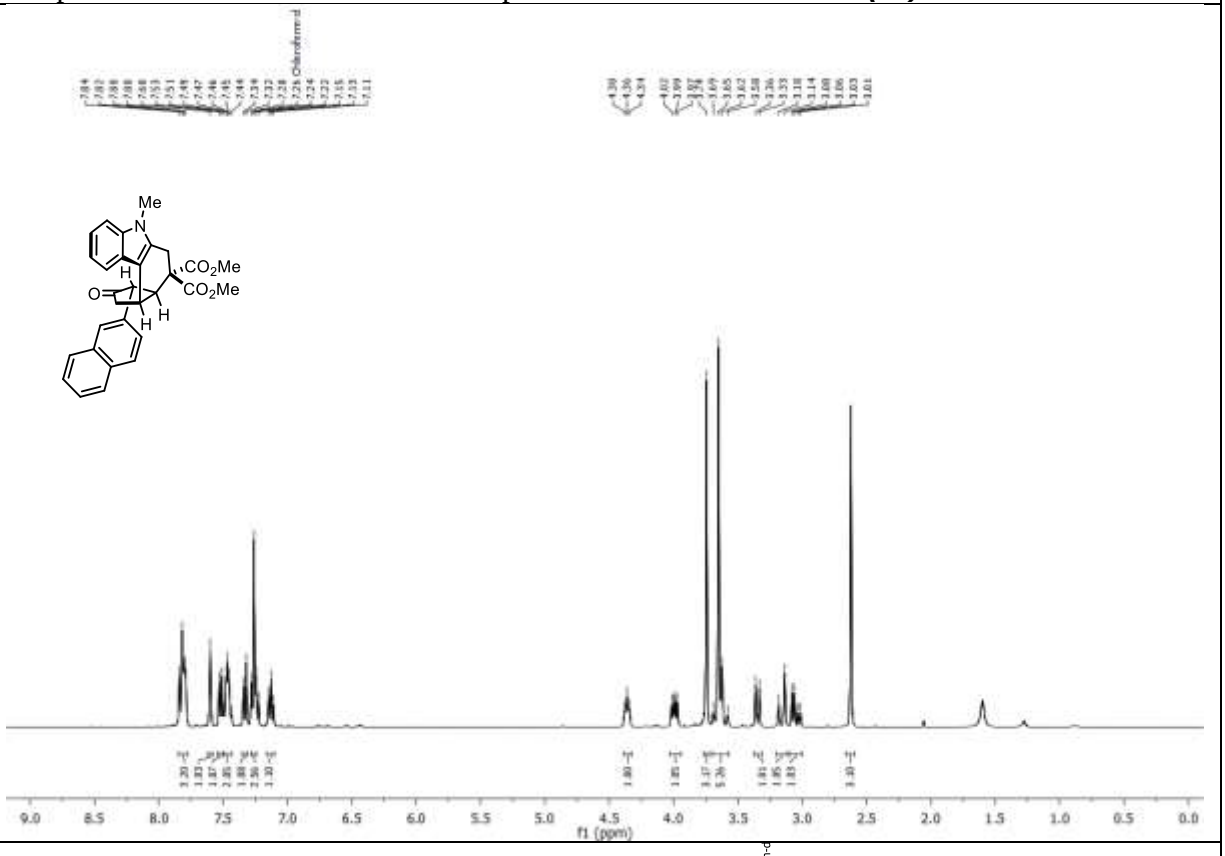
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(15)***

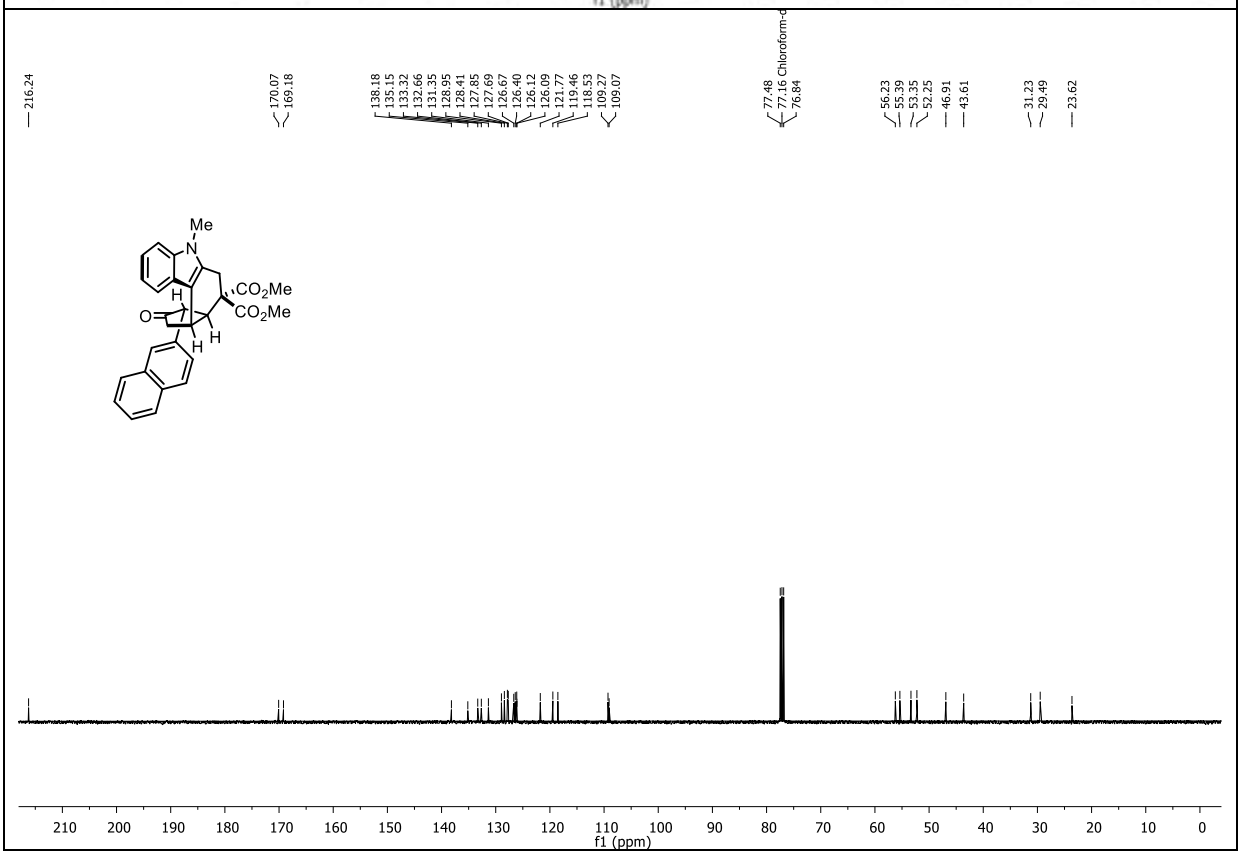


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(16)***

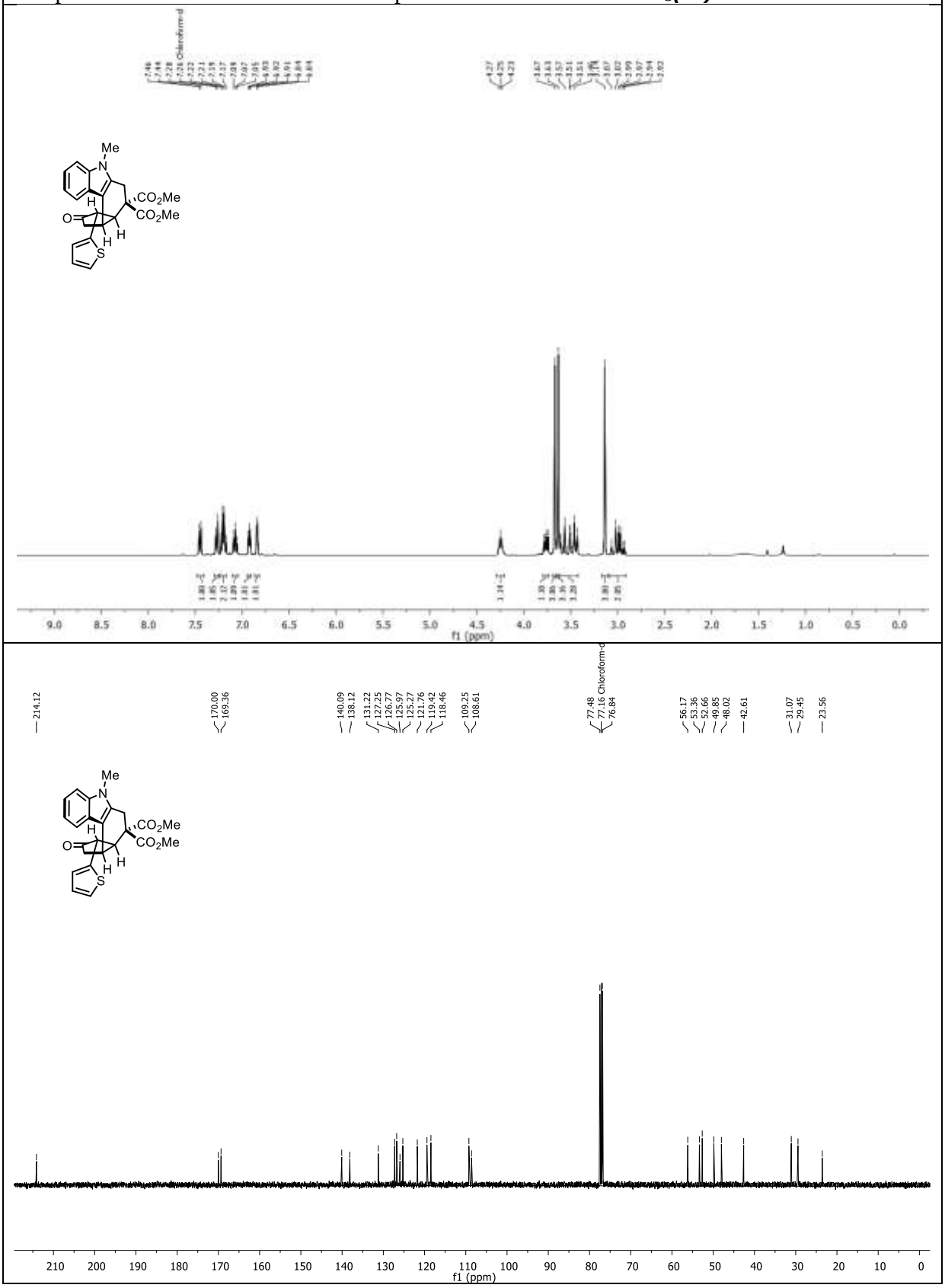


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(17)***

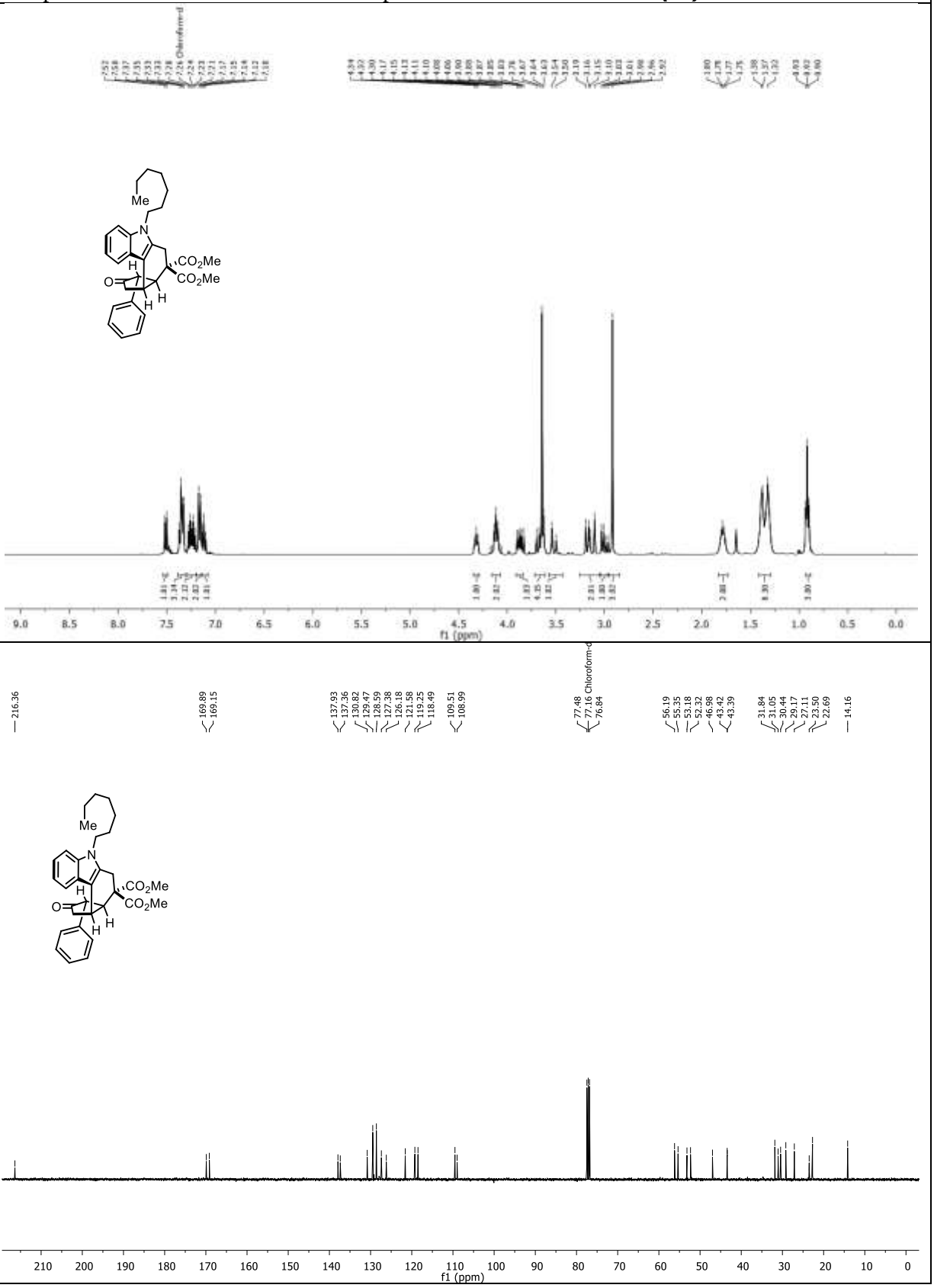




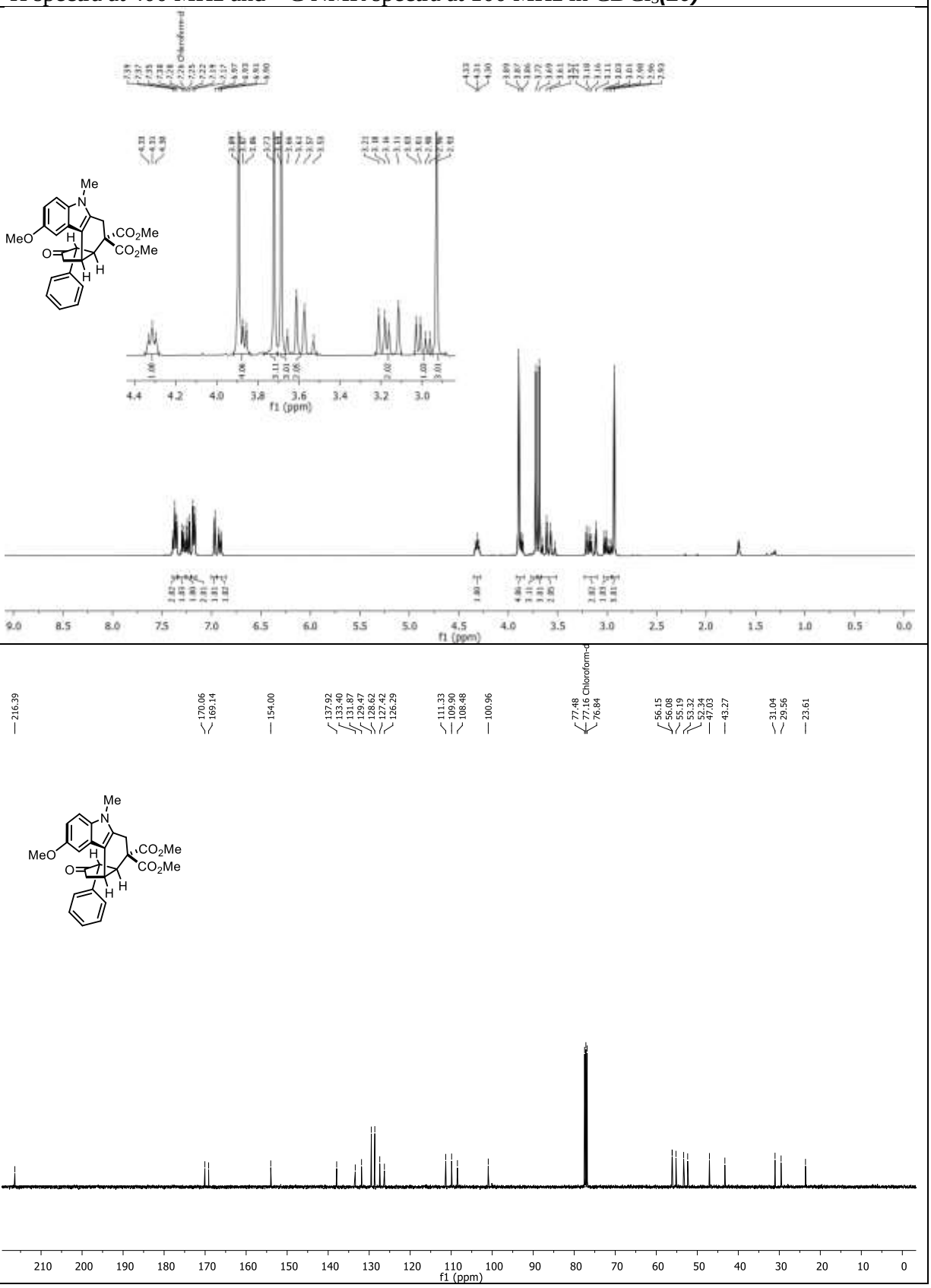
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(18)***



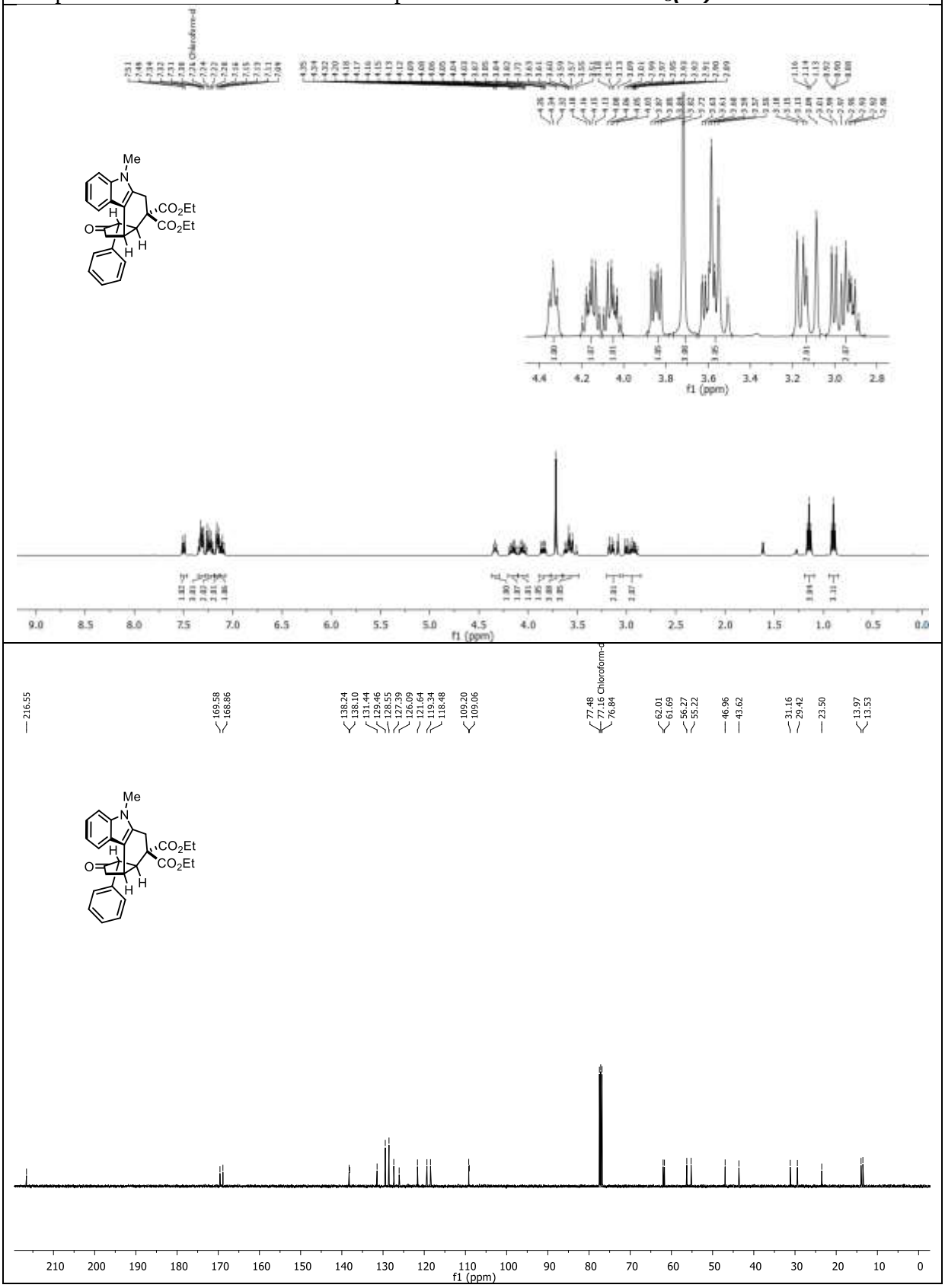
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(19)***



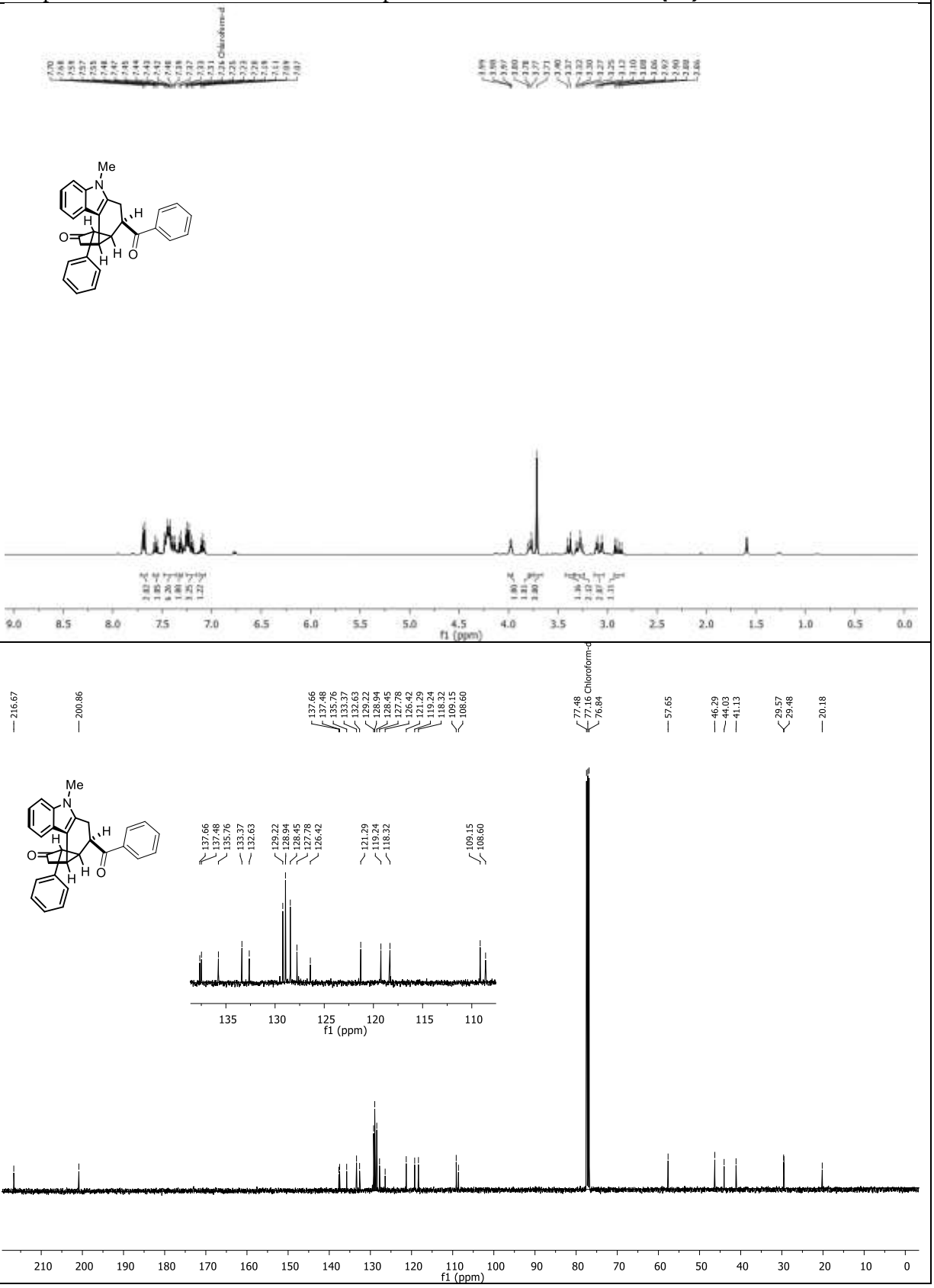
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(20)***



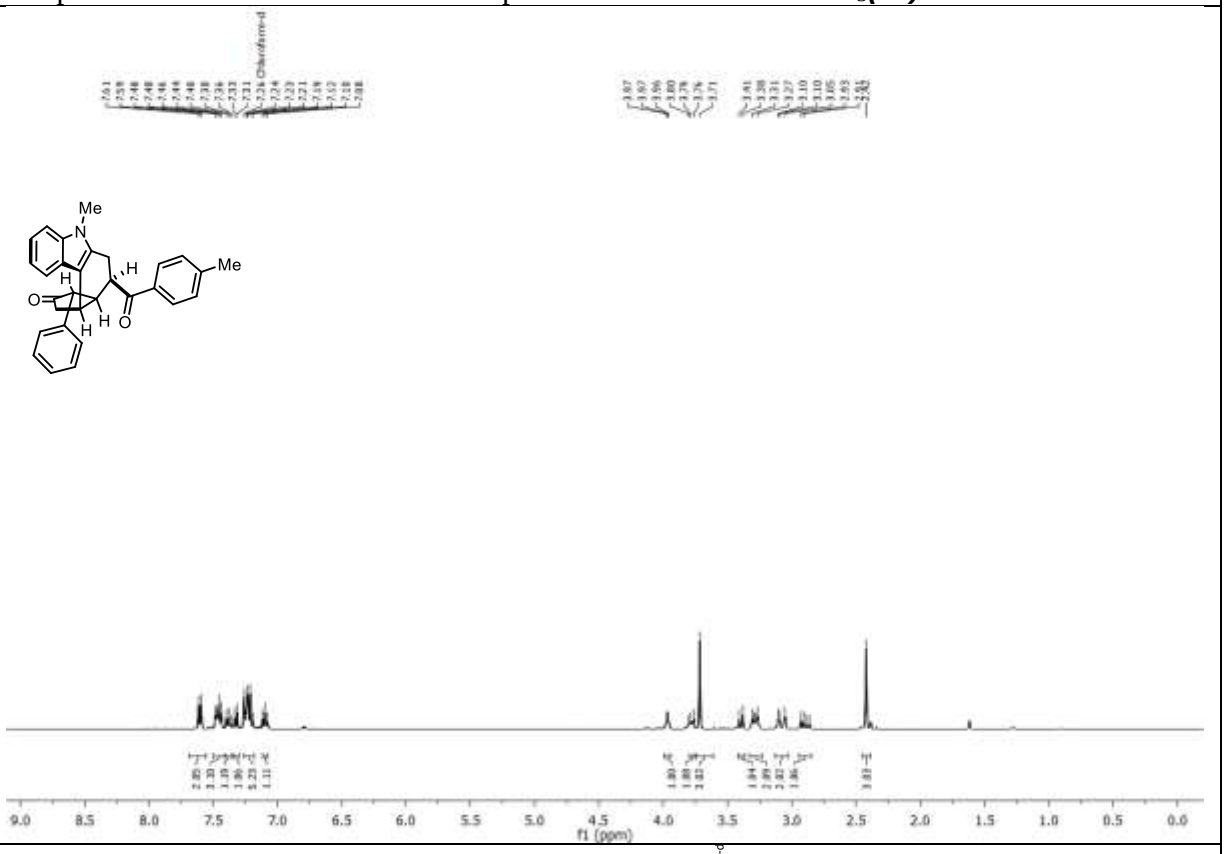
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(21)***

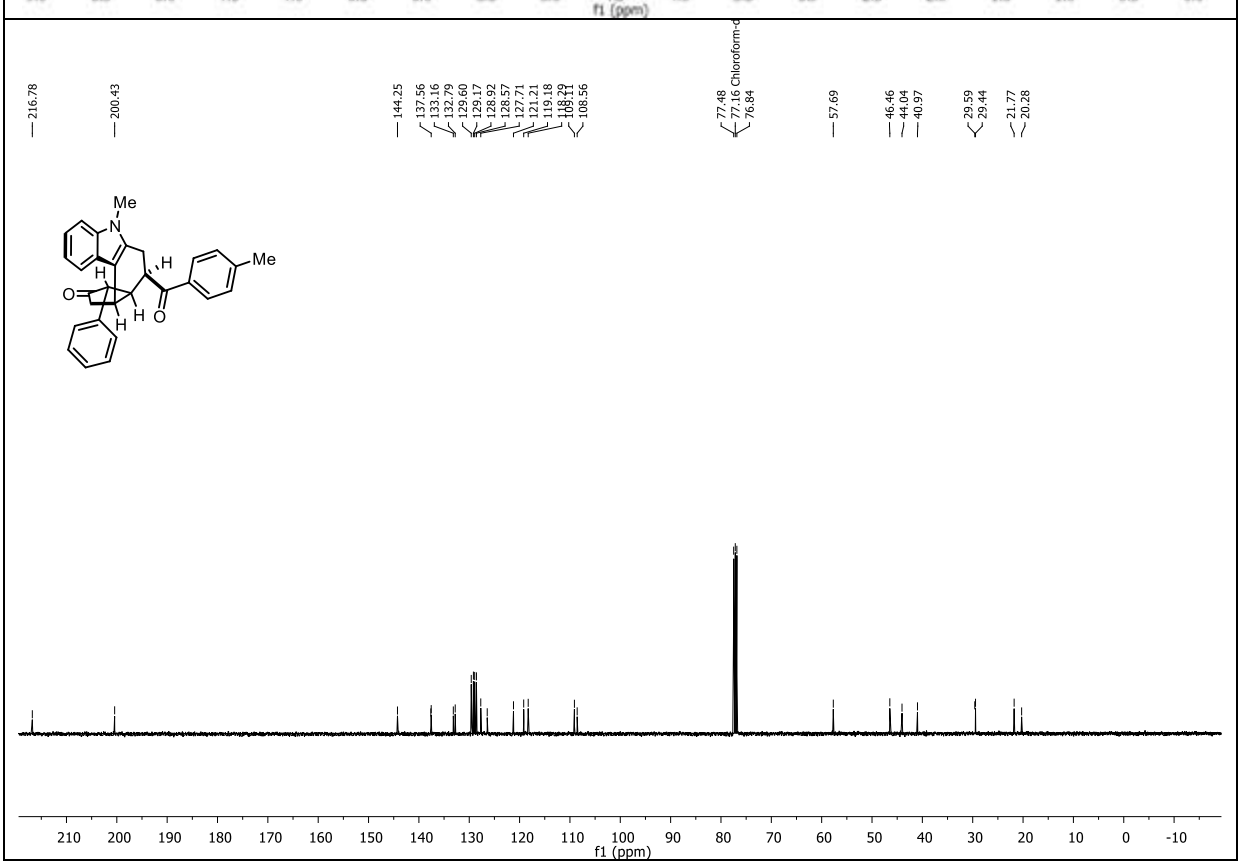


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(22)***

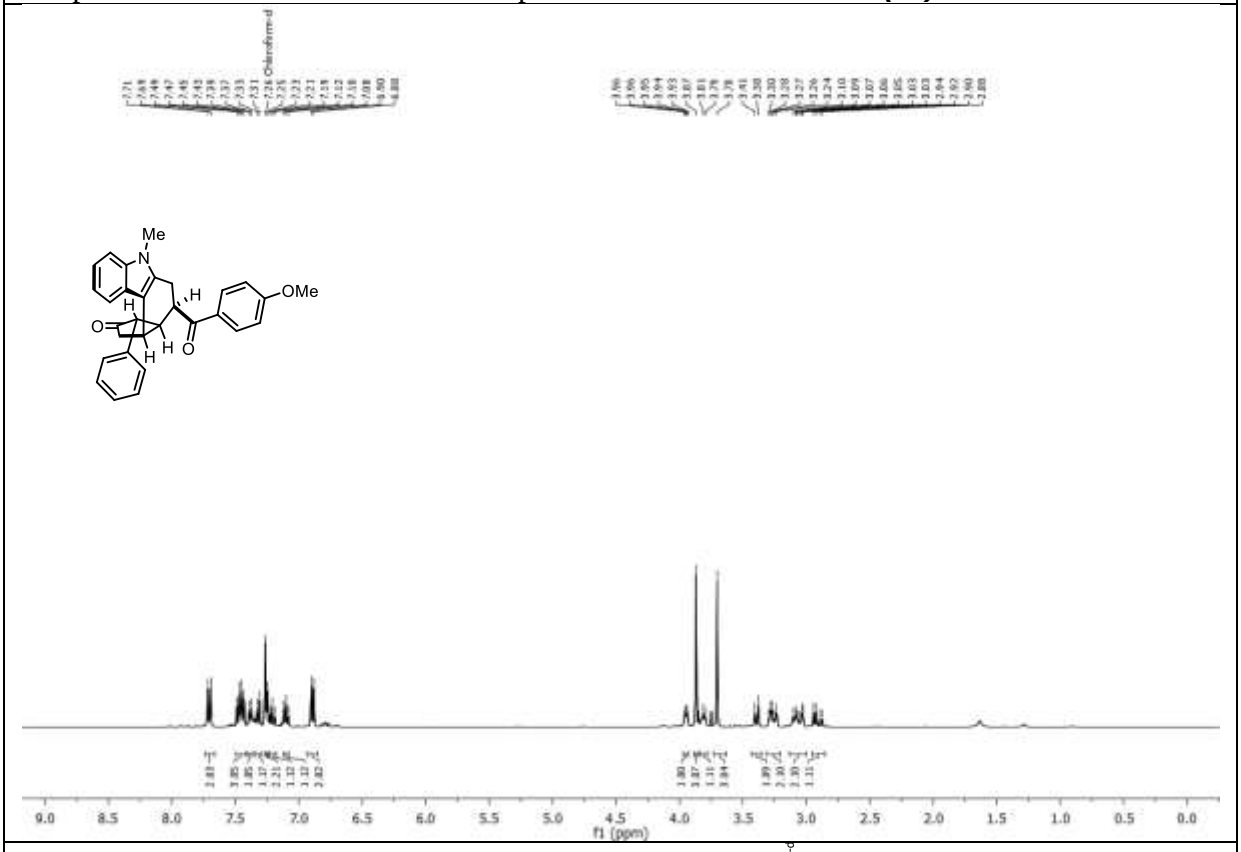


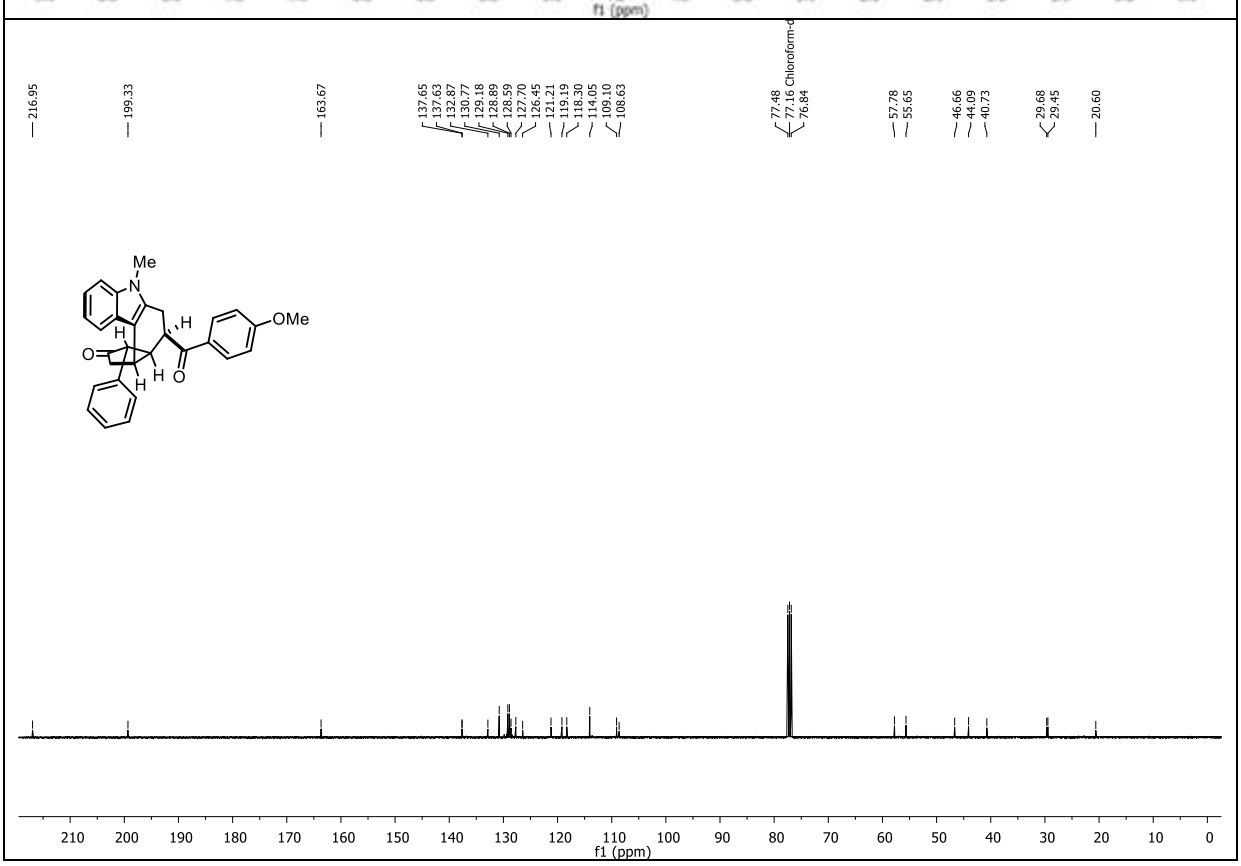
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(23)***



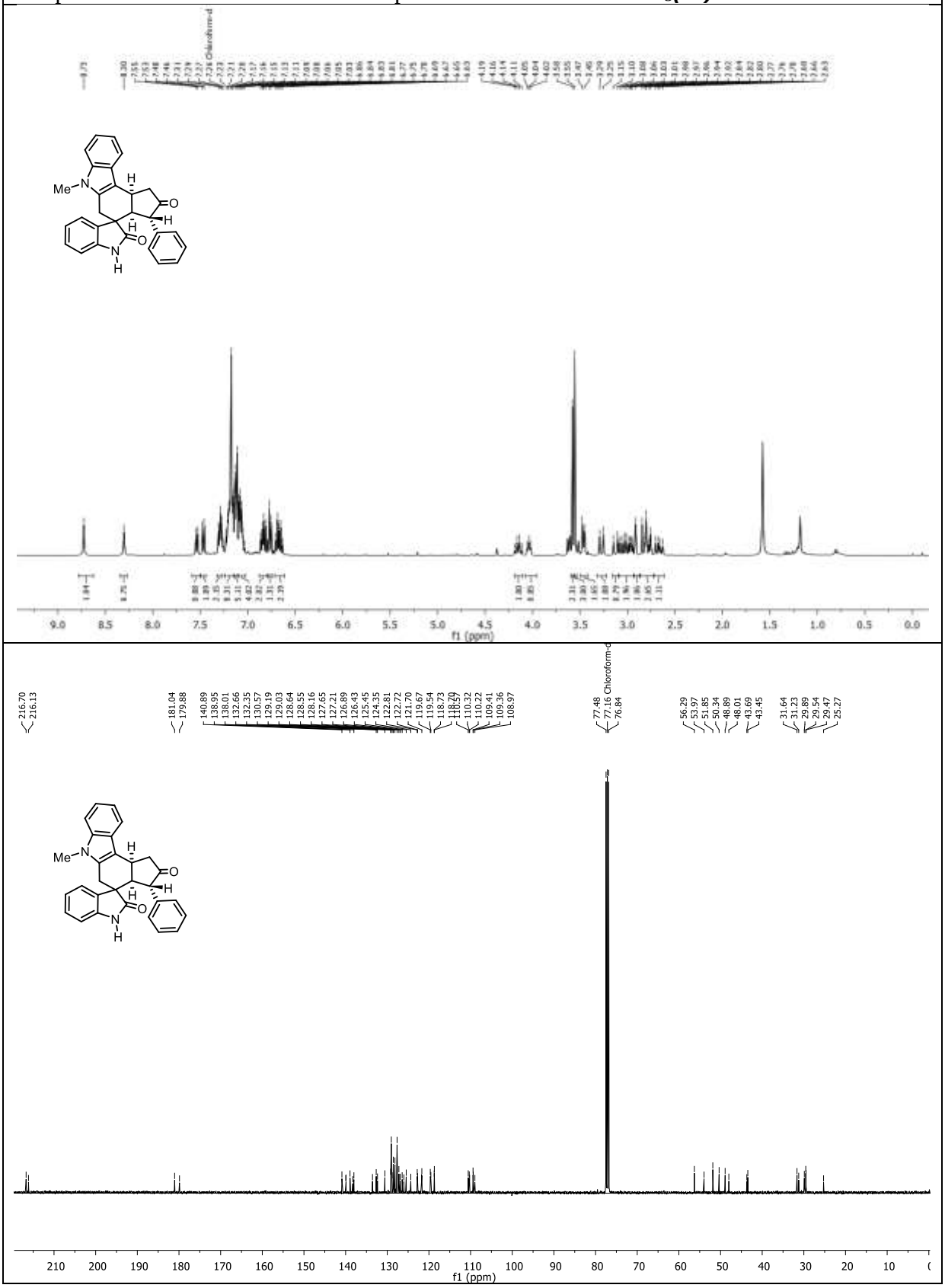


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(24)***

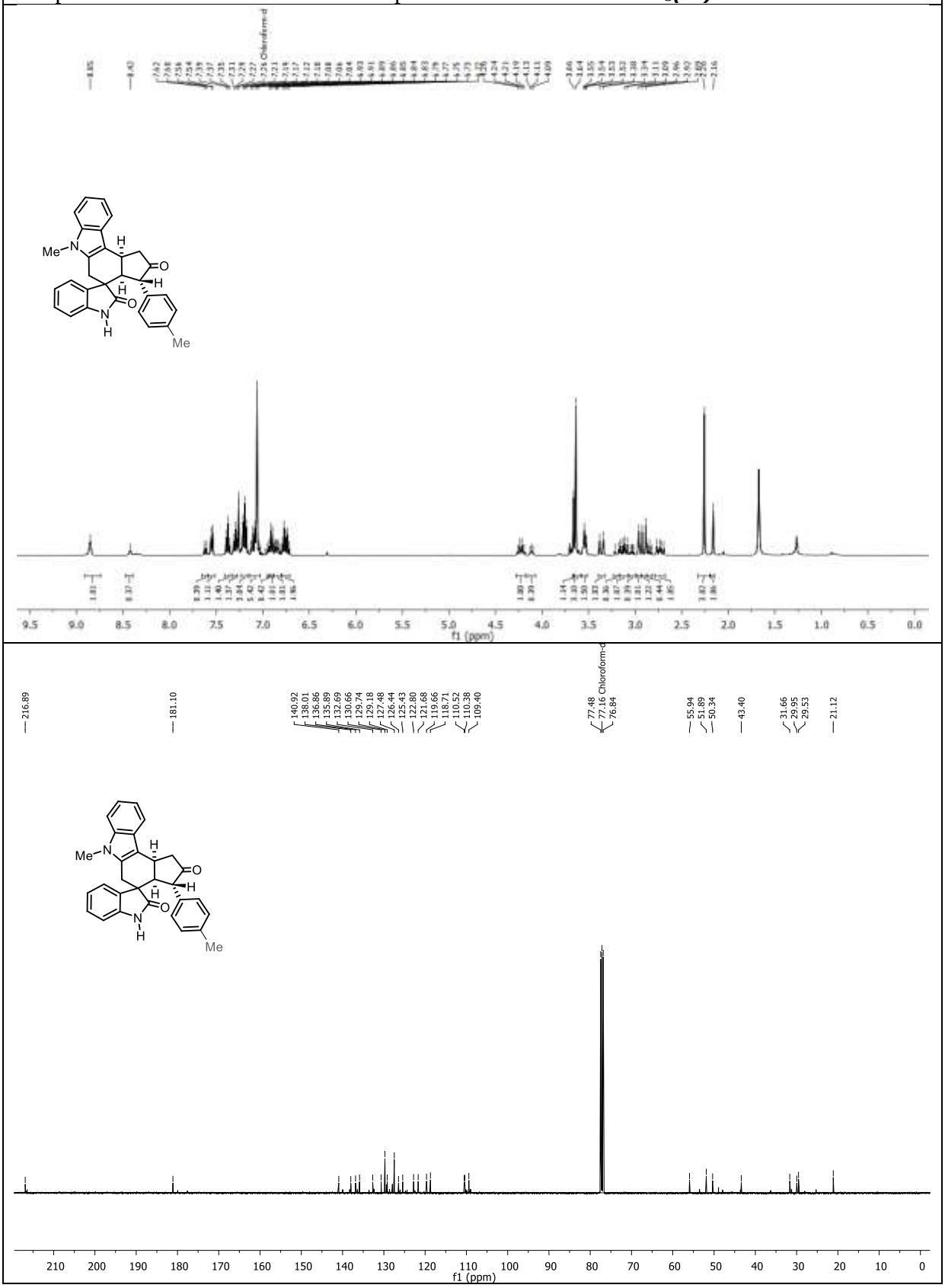




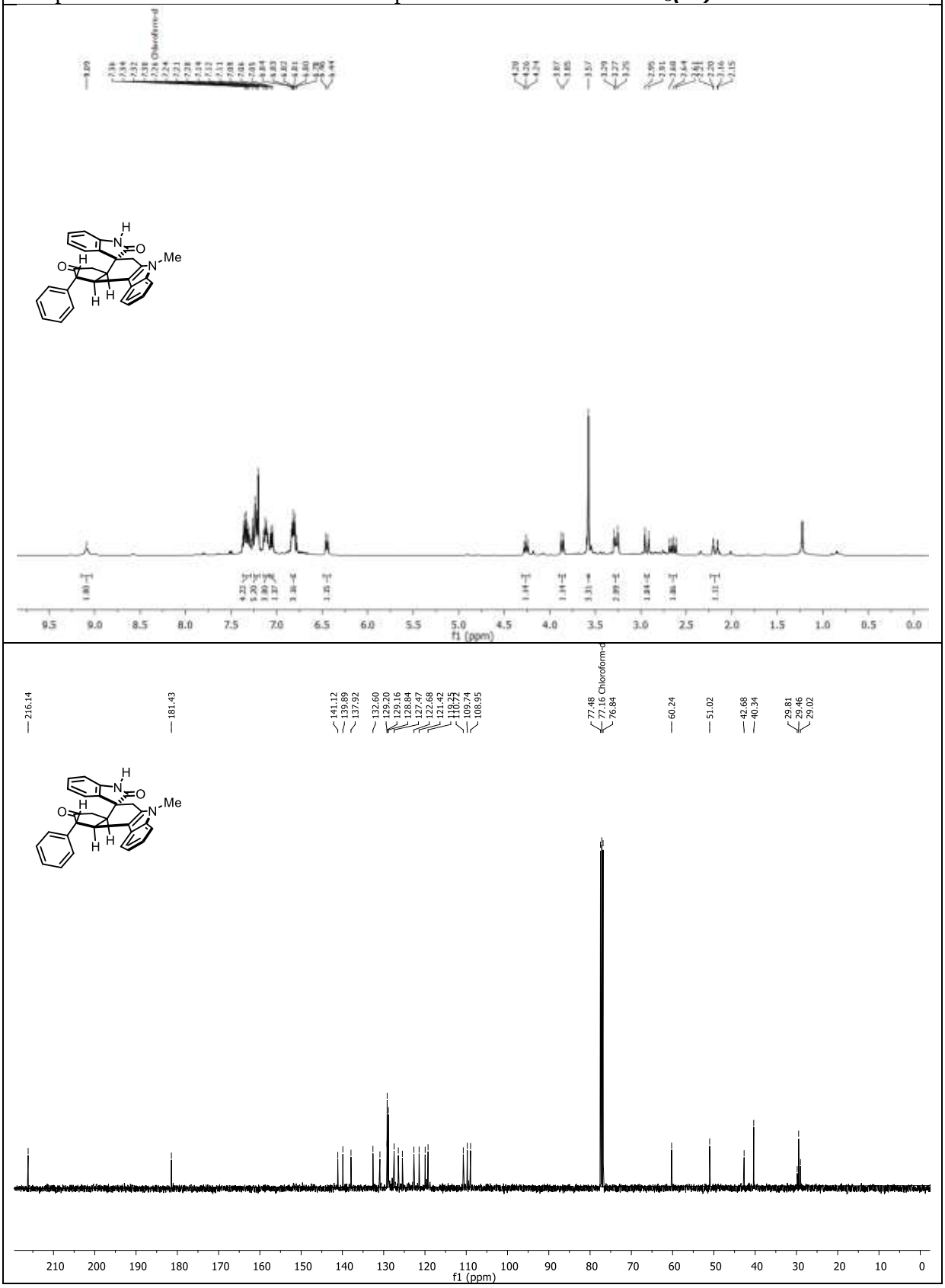
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(25)***



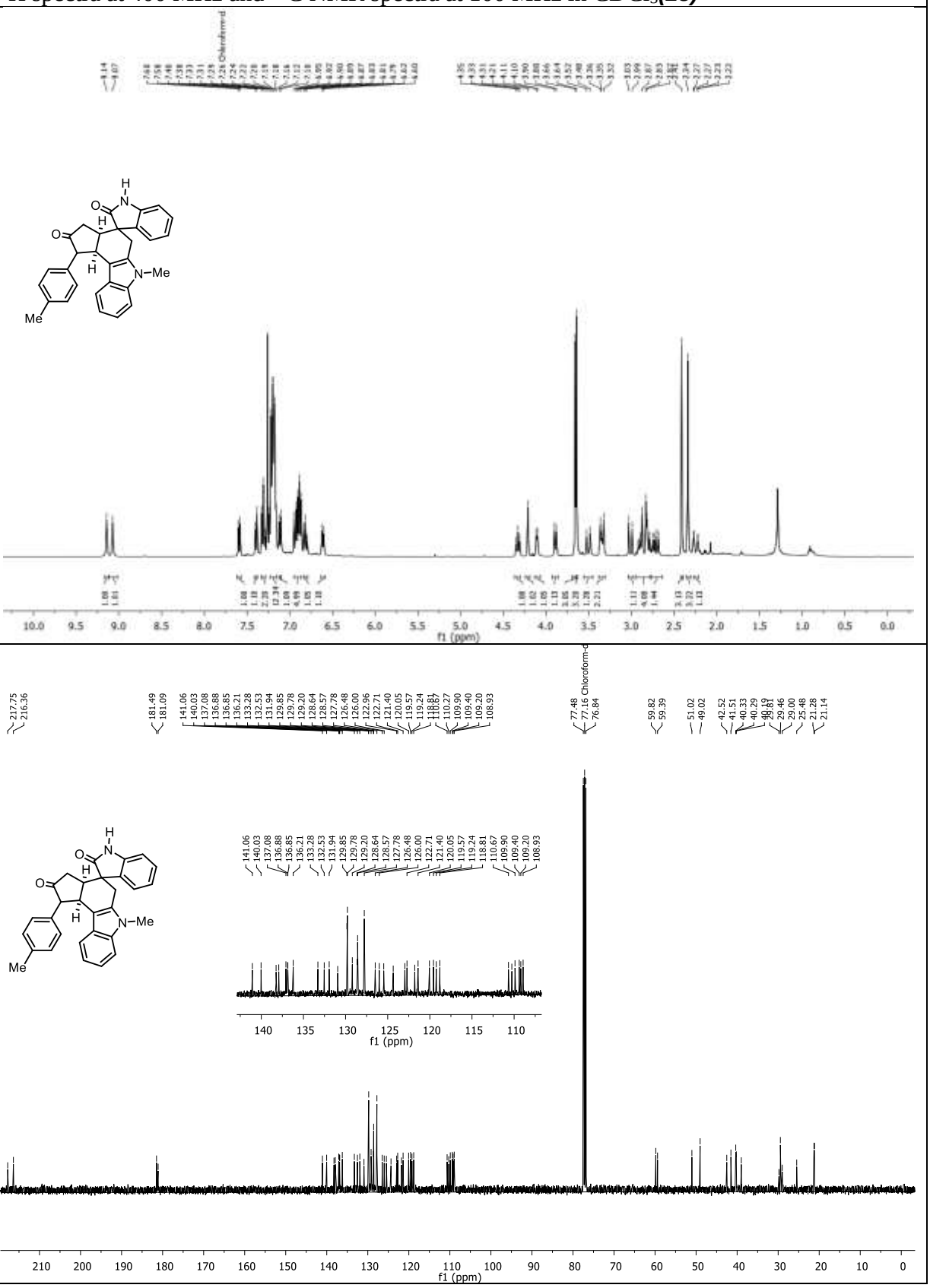
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(26)***



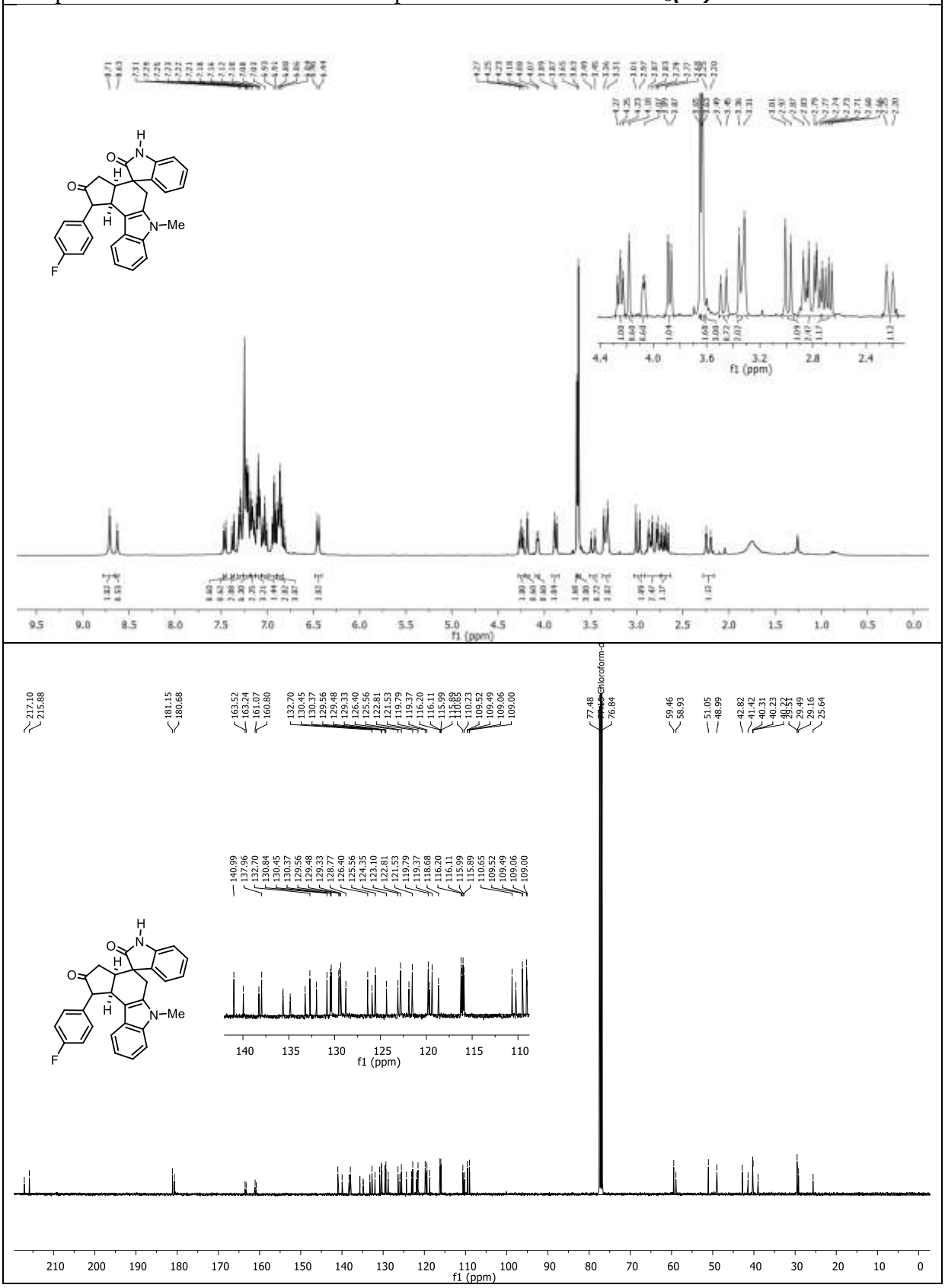
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(27)***



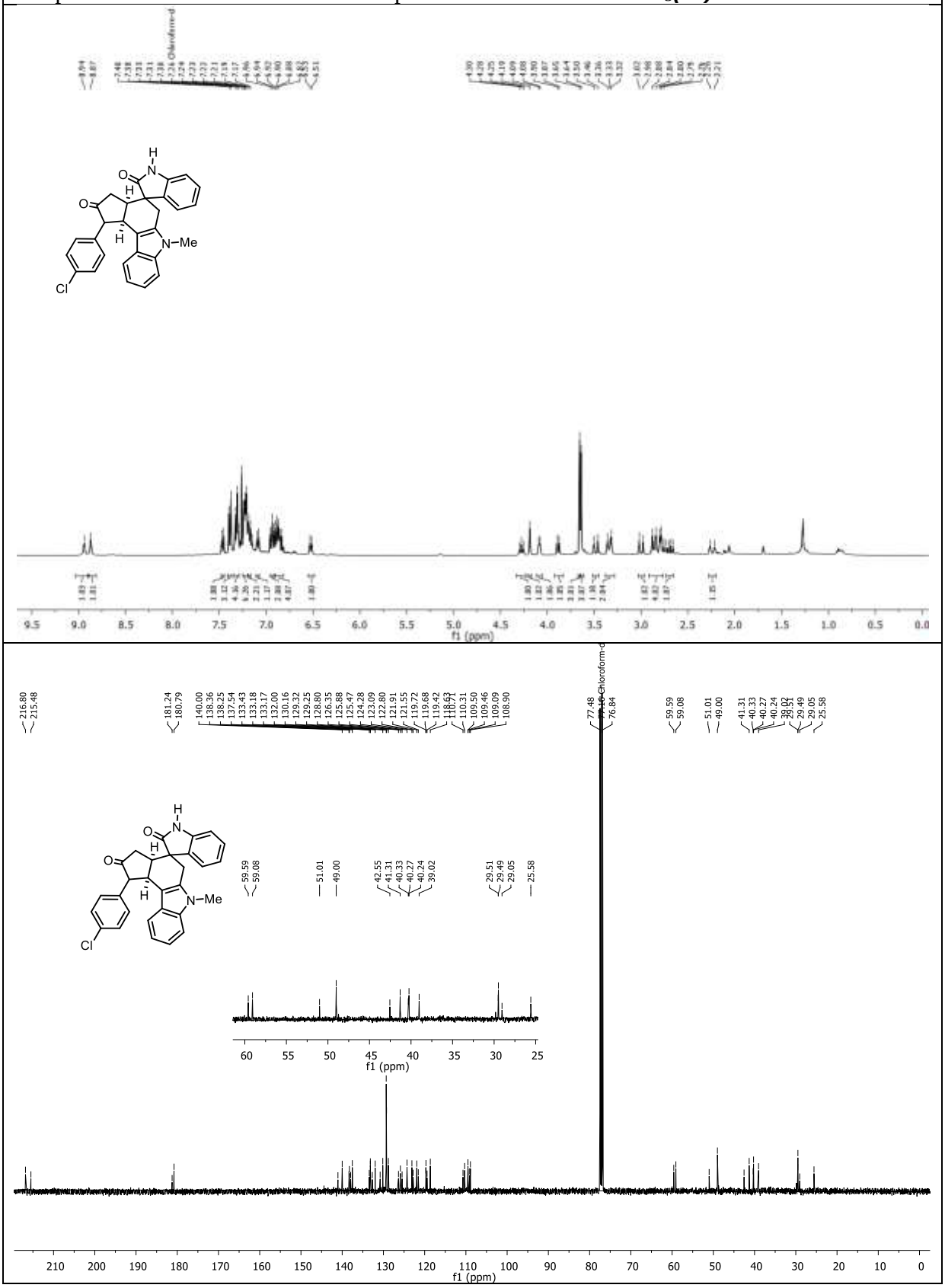
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(28)***



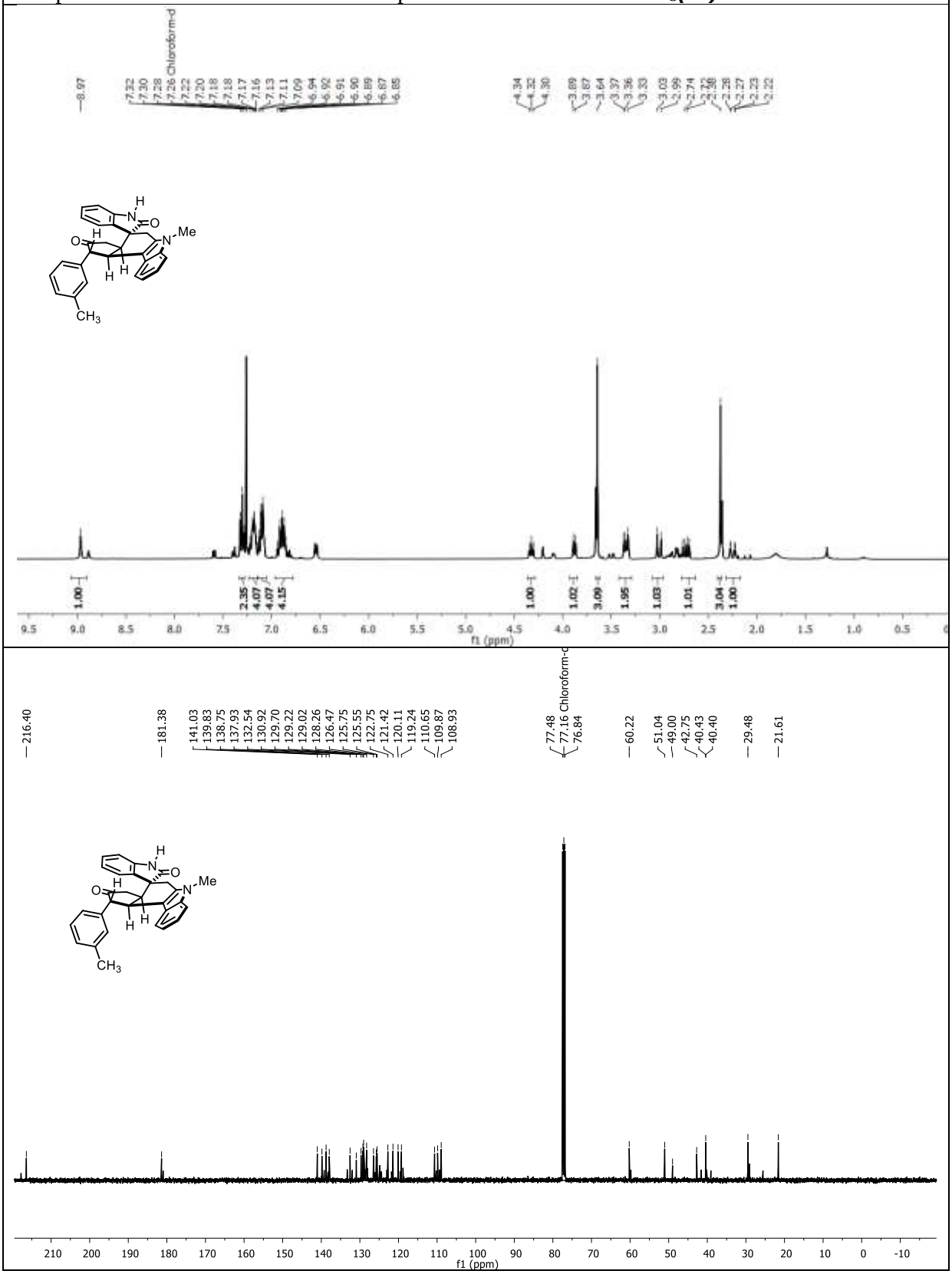
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(29)***



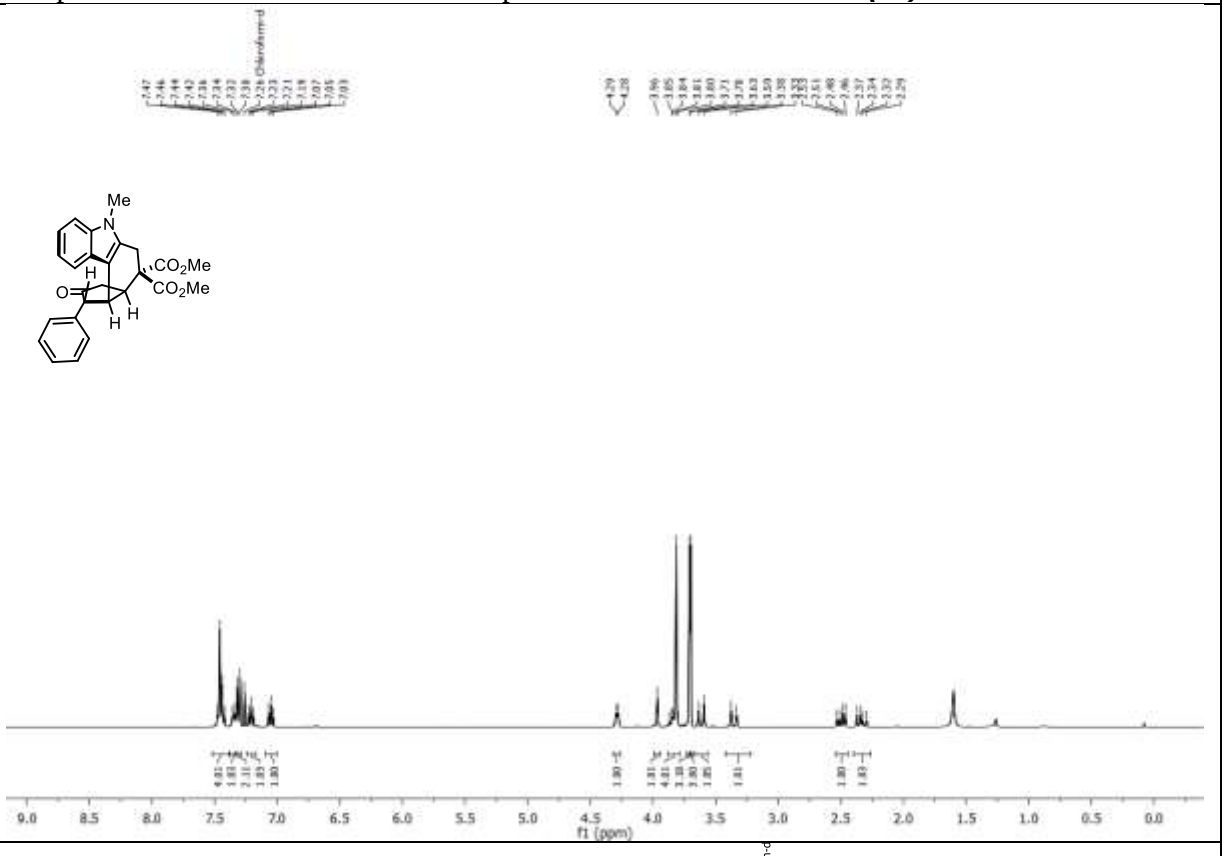
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(30)***

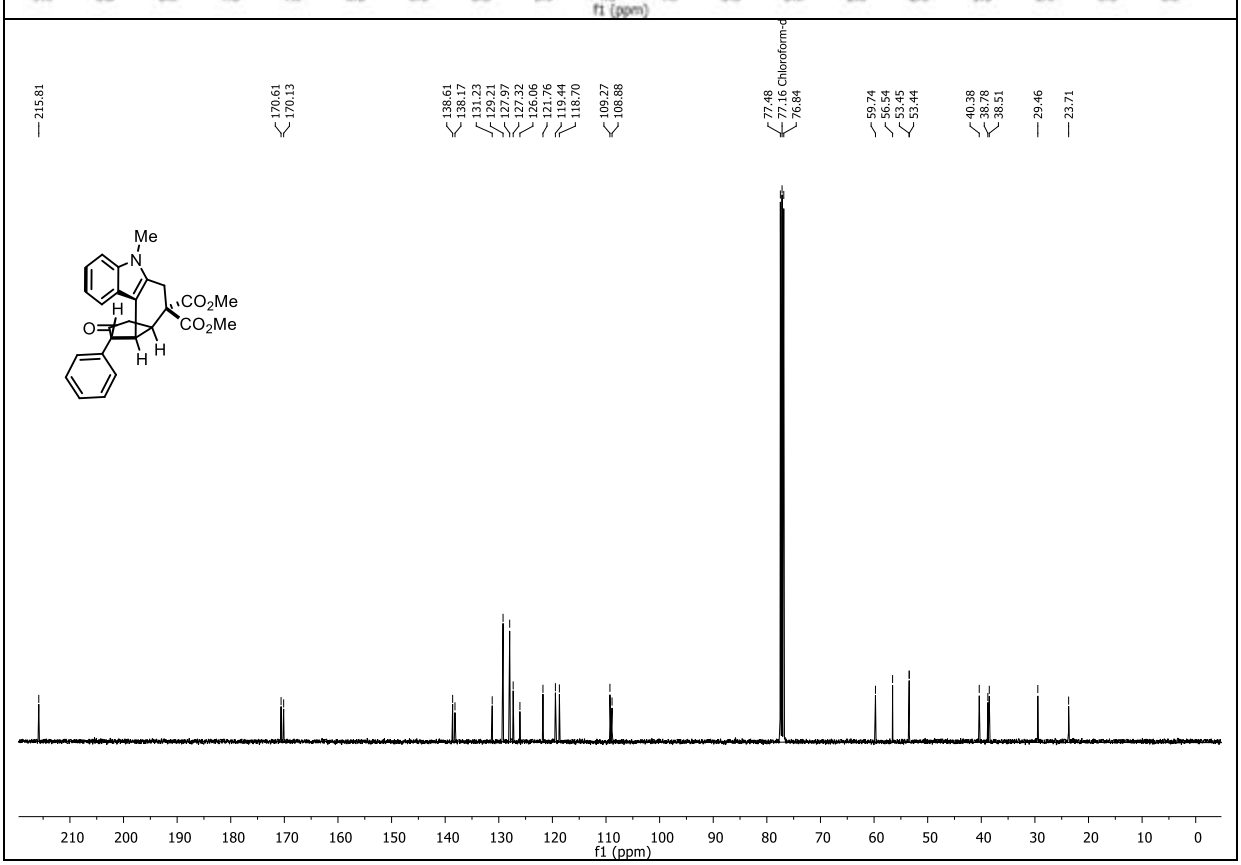


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(31)***

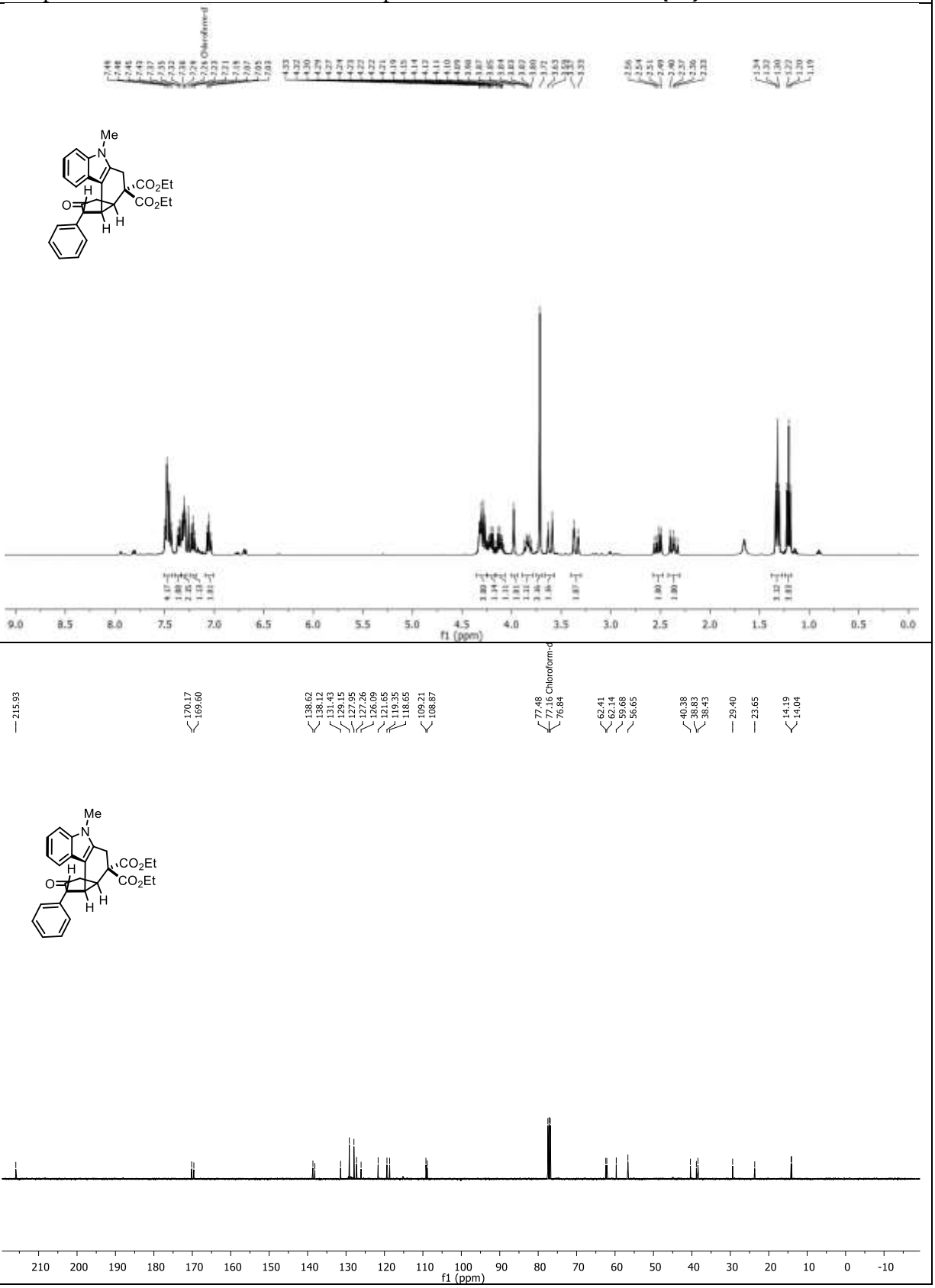


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(32)***

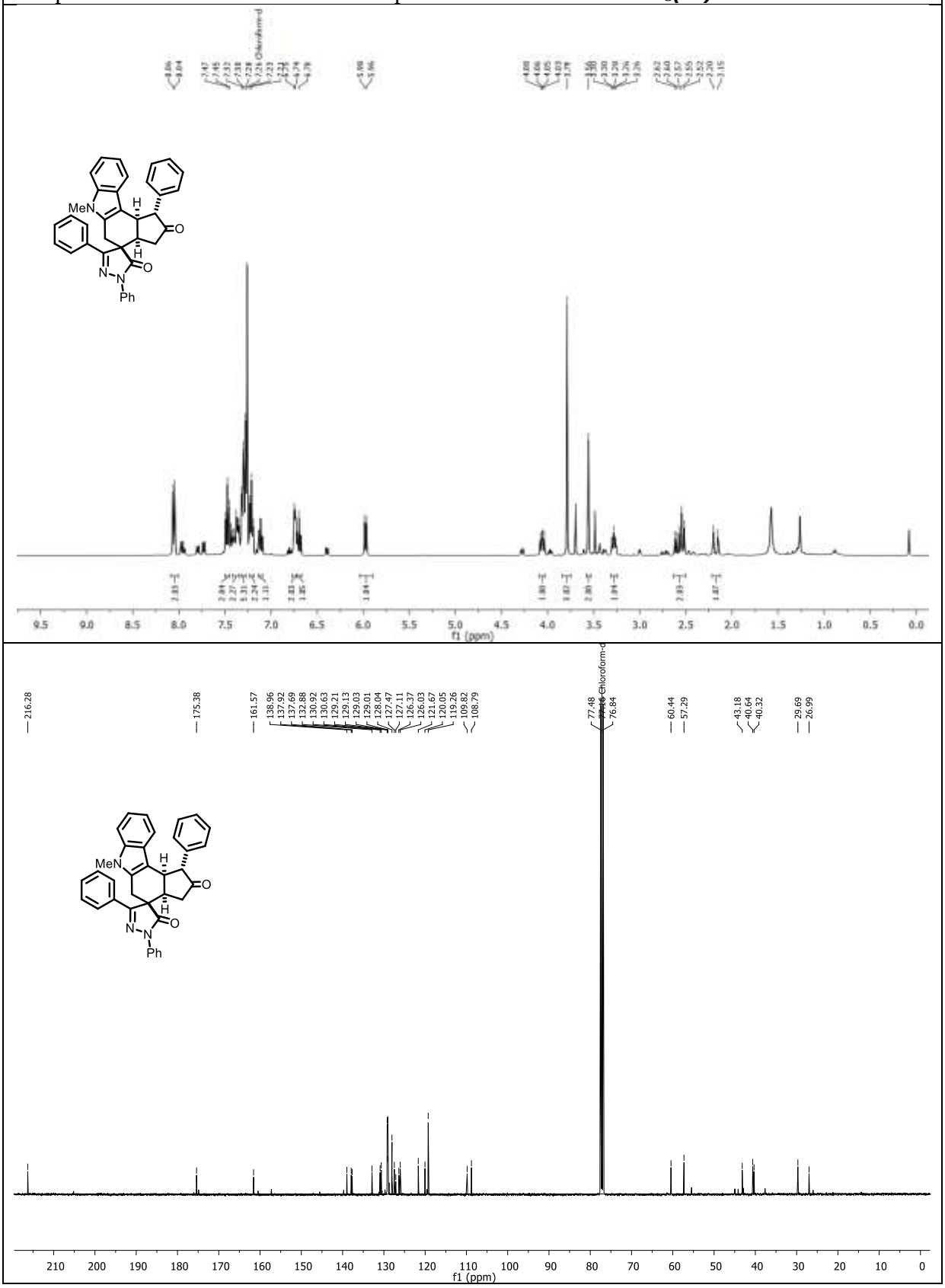




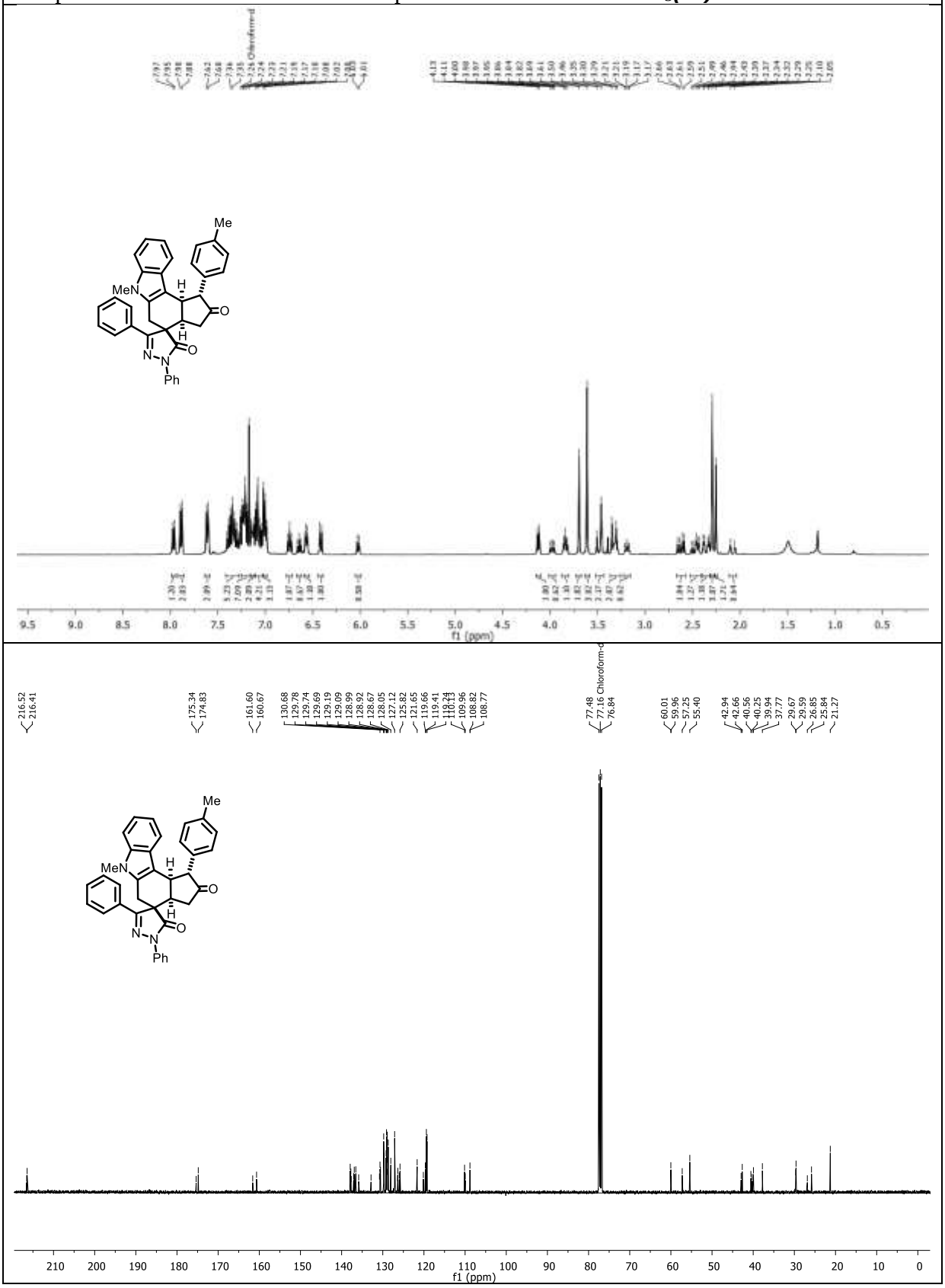
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(33)***



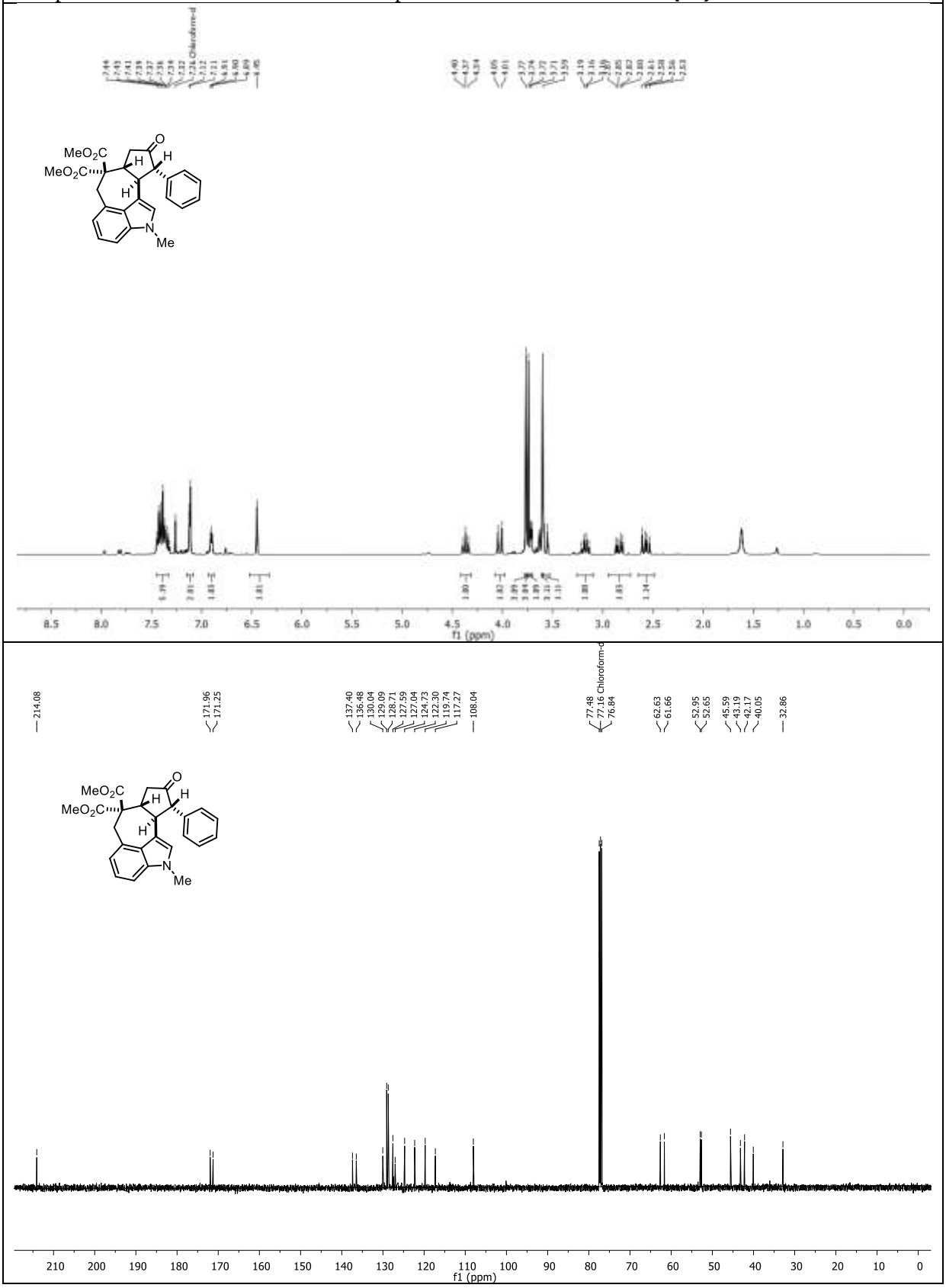
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(34)***



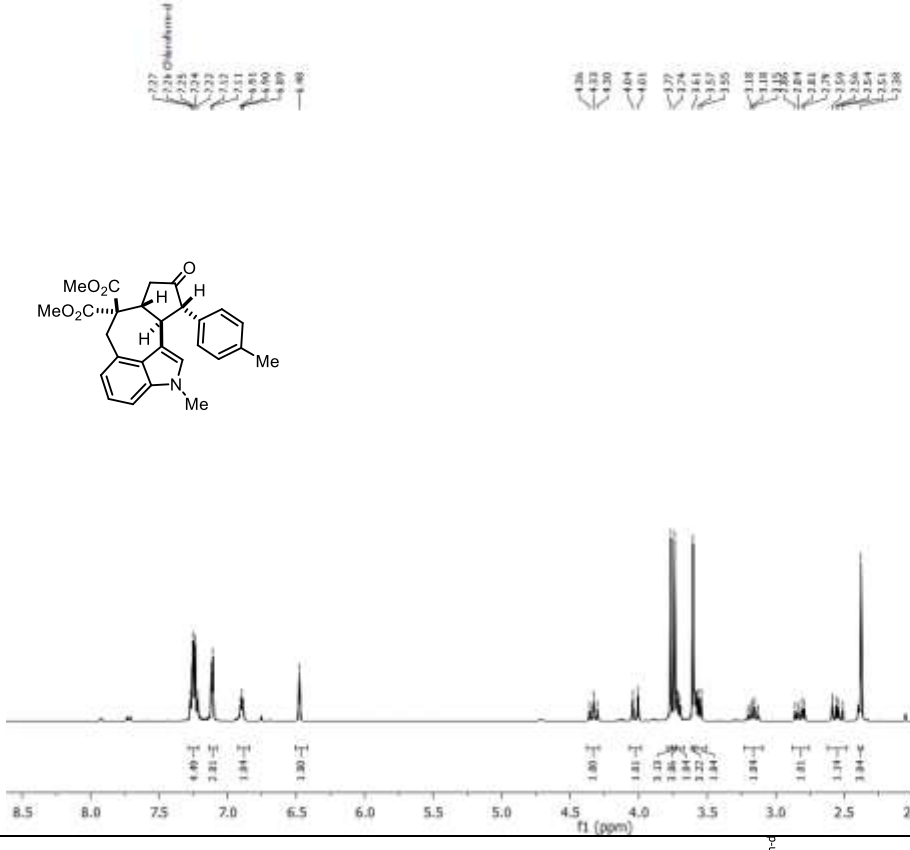
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(35)***

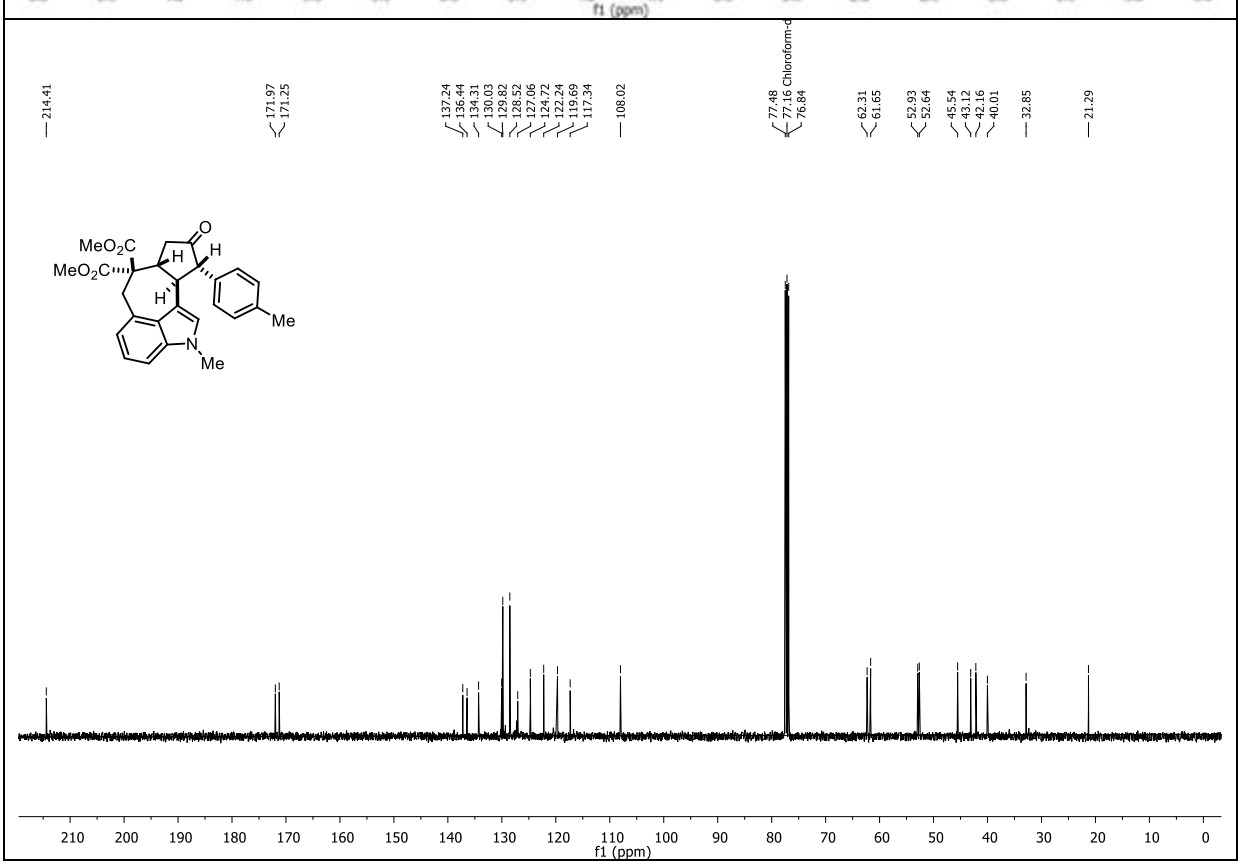


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(36)***

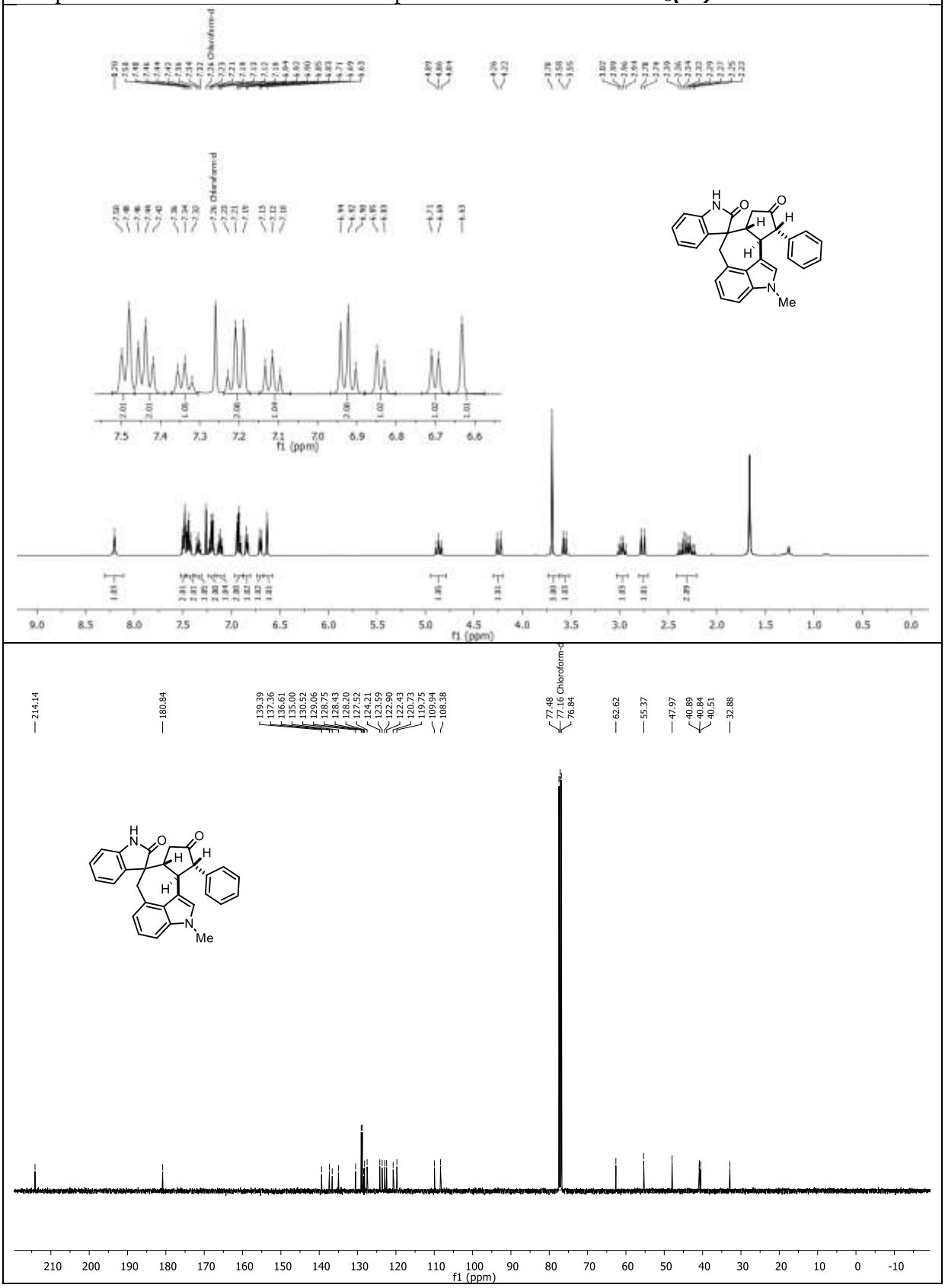


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(37)***

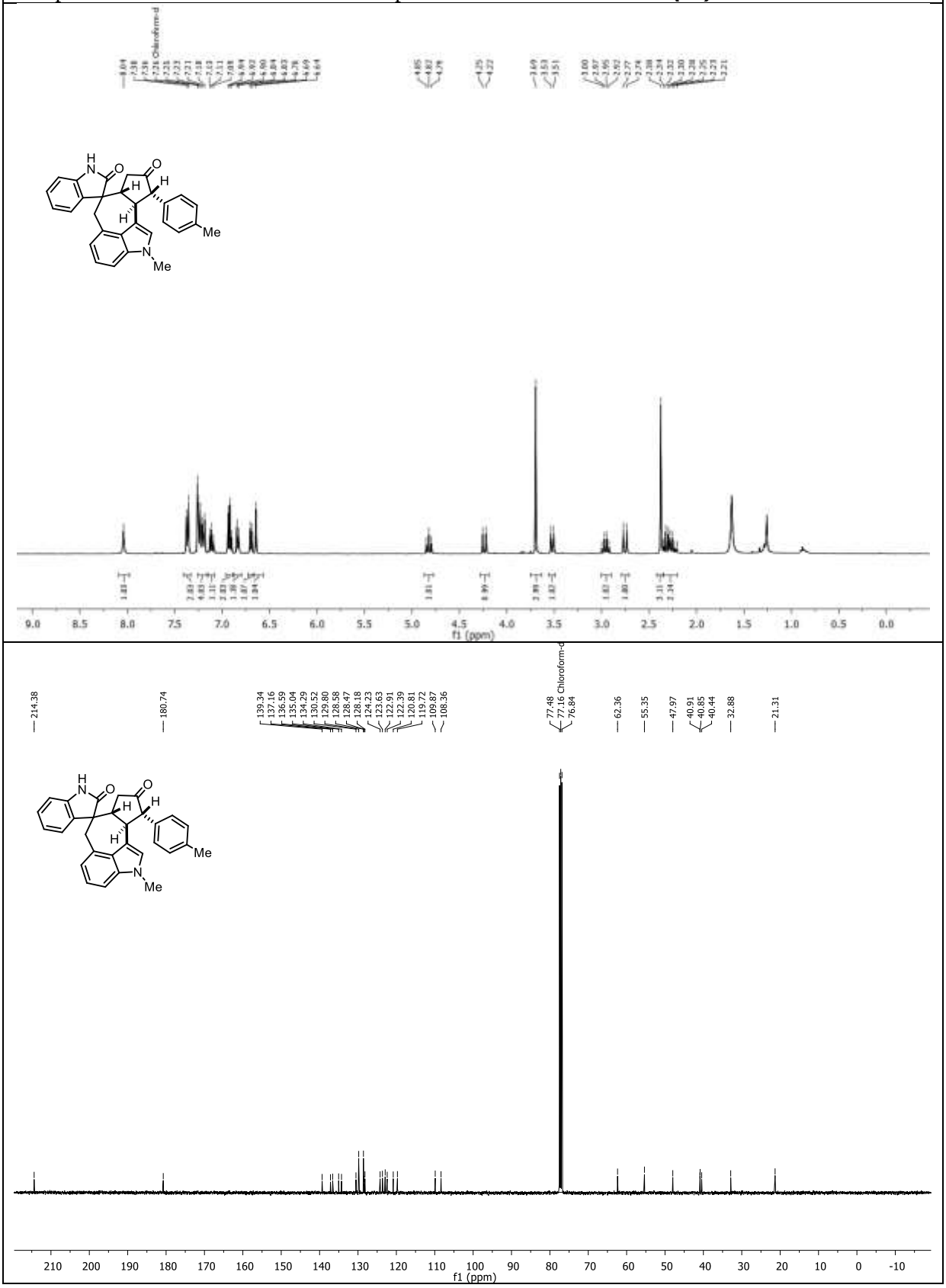


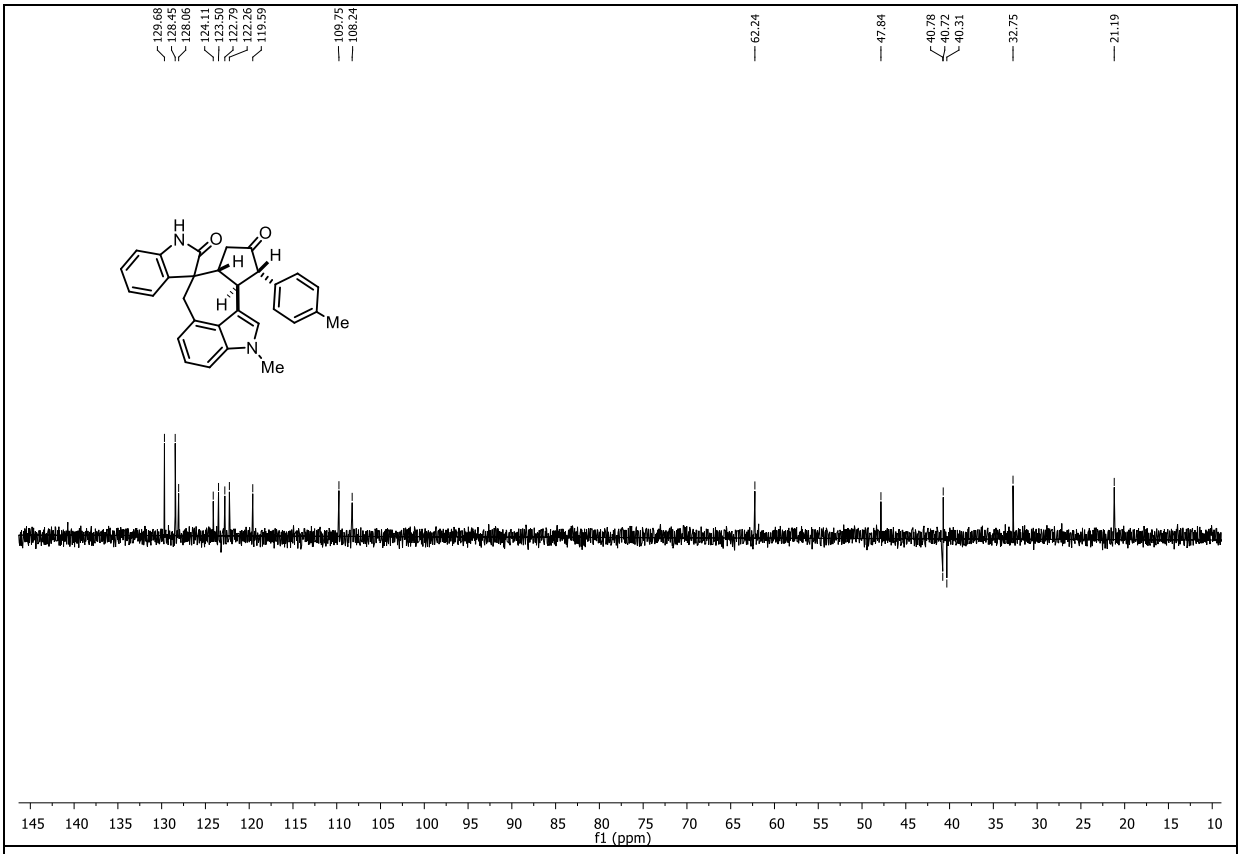


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(38)***

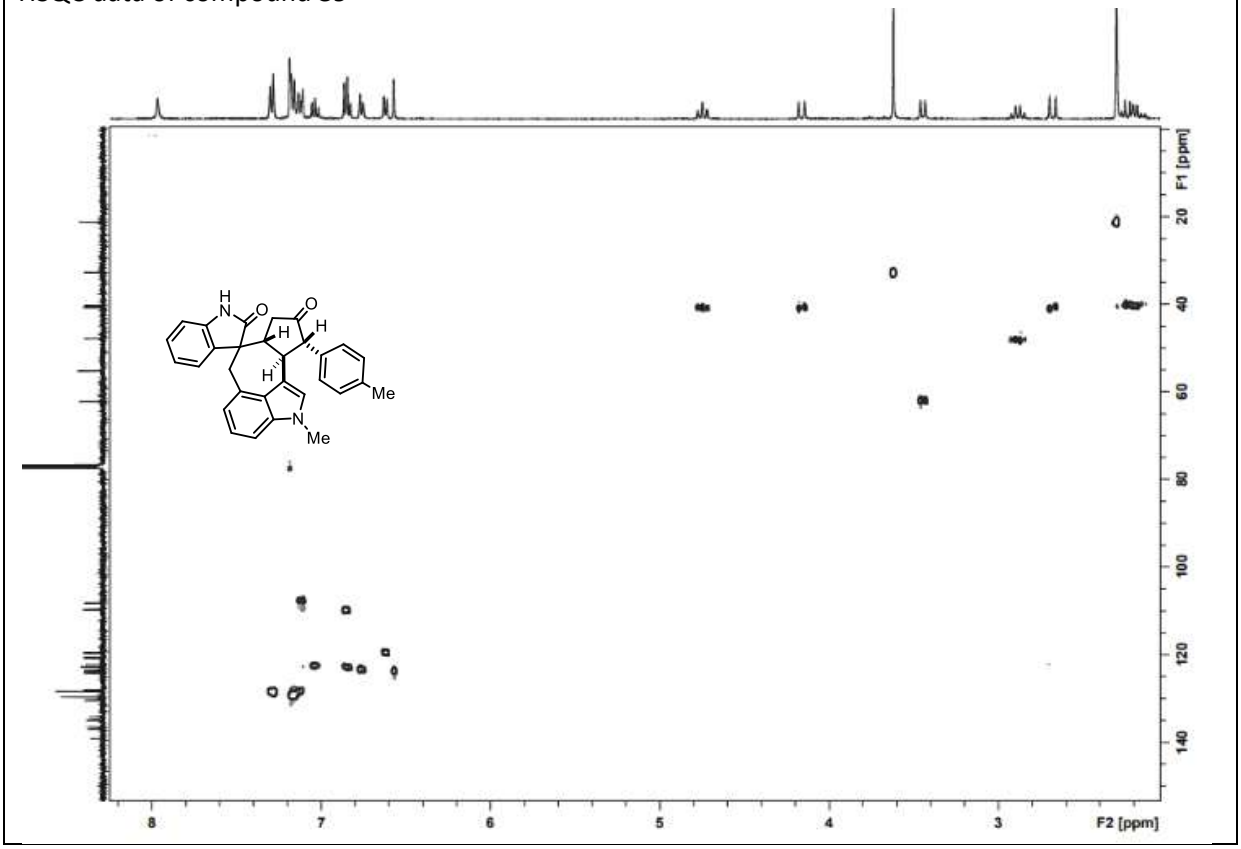


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(39)***

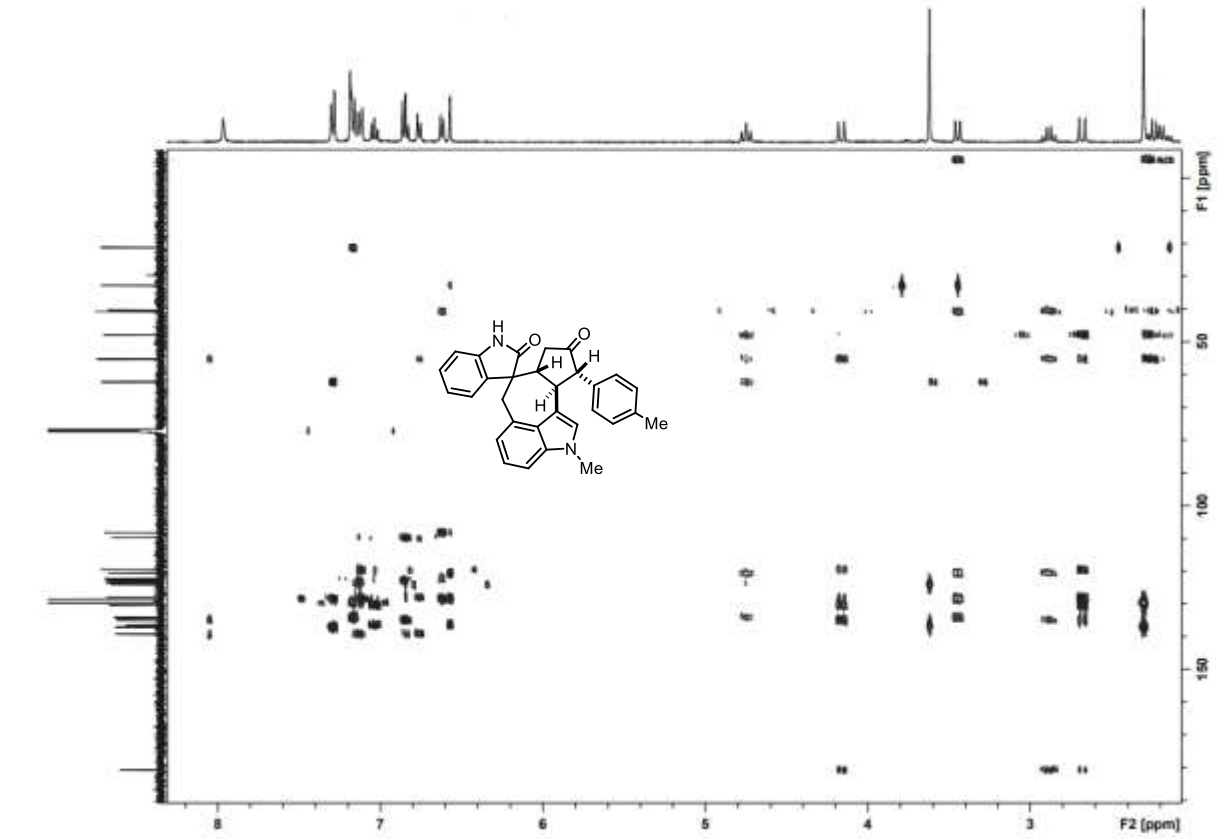




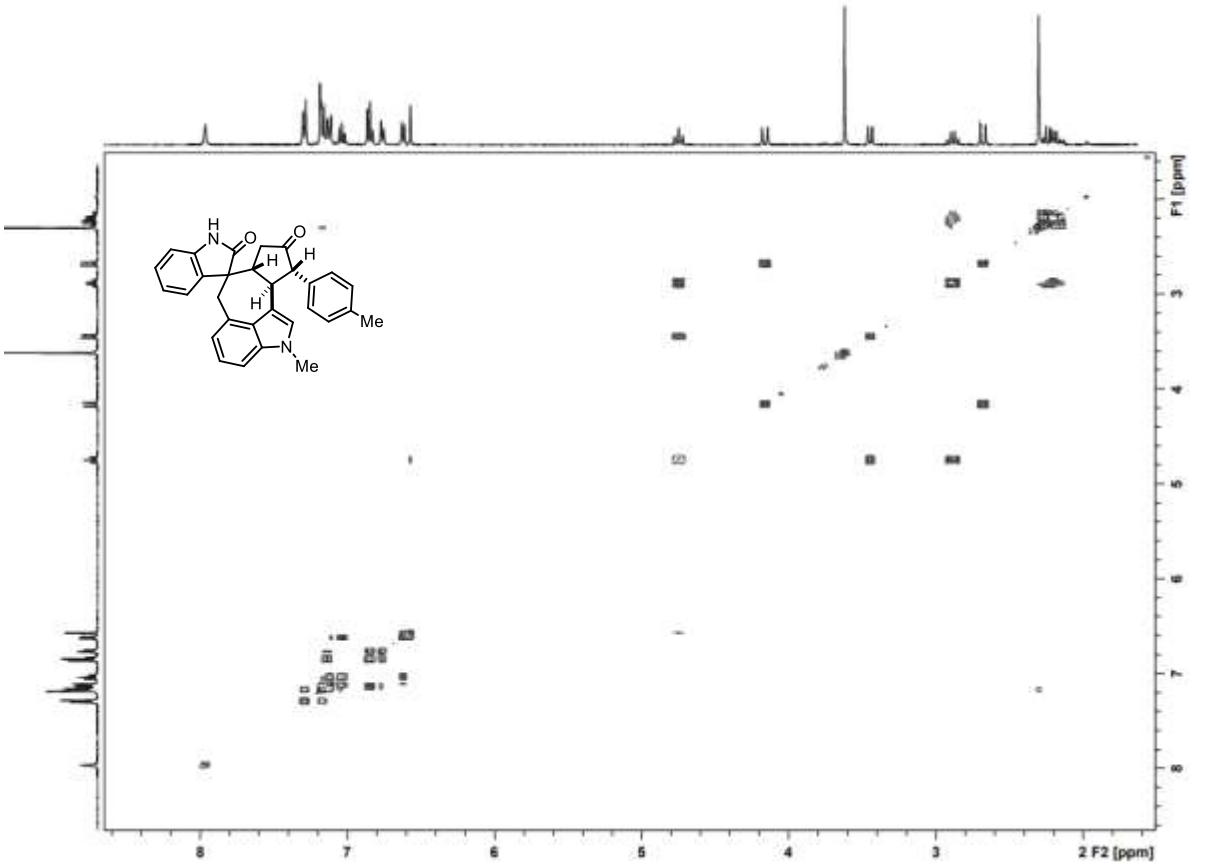
HSQC data of compound **39**



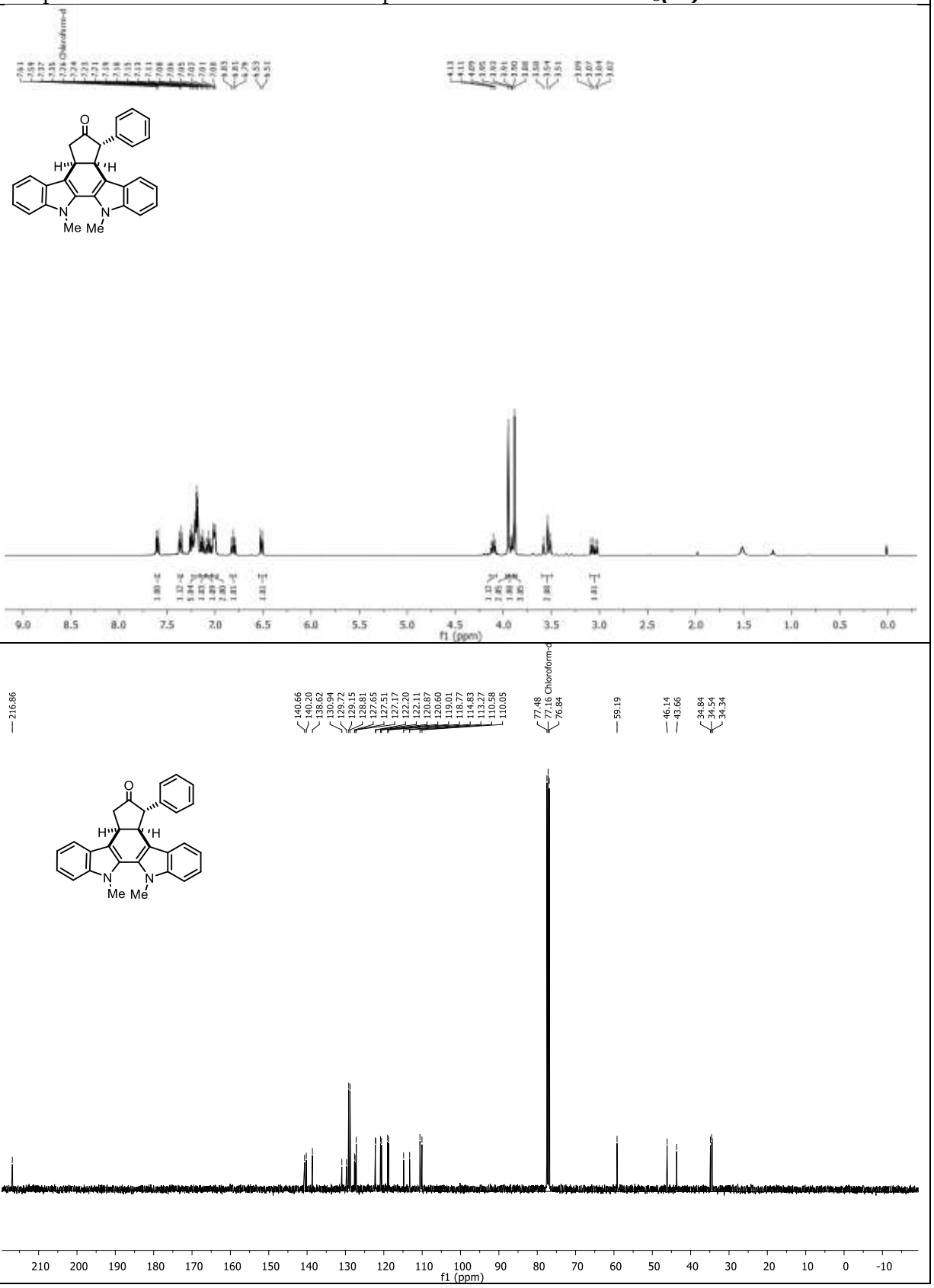
HMBC data of compound **39**



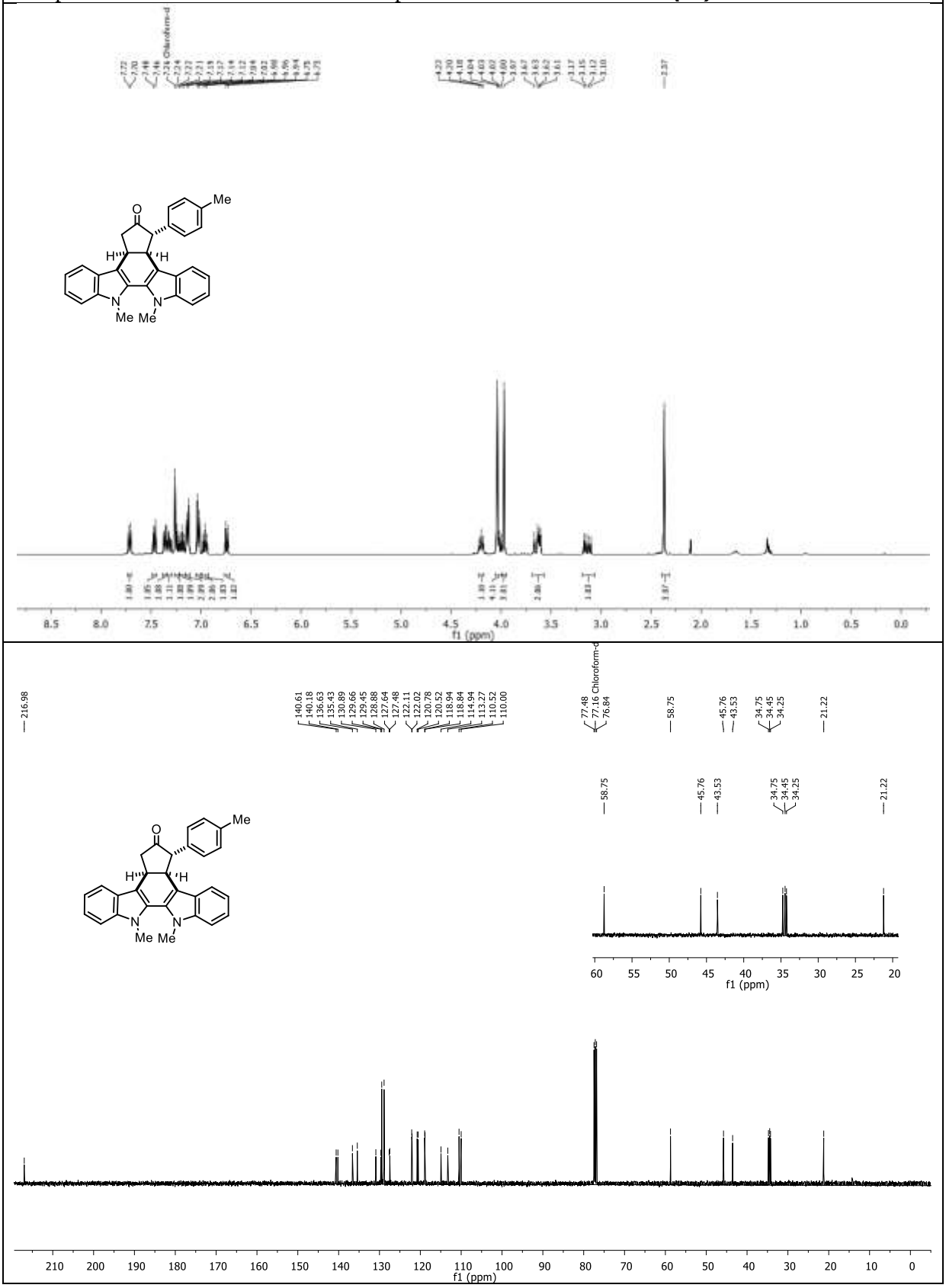
COSY data of compound **39**



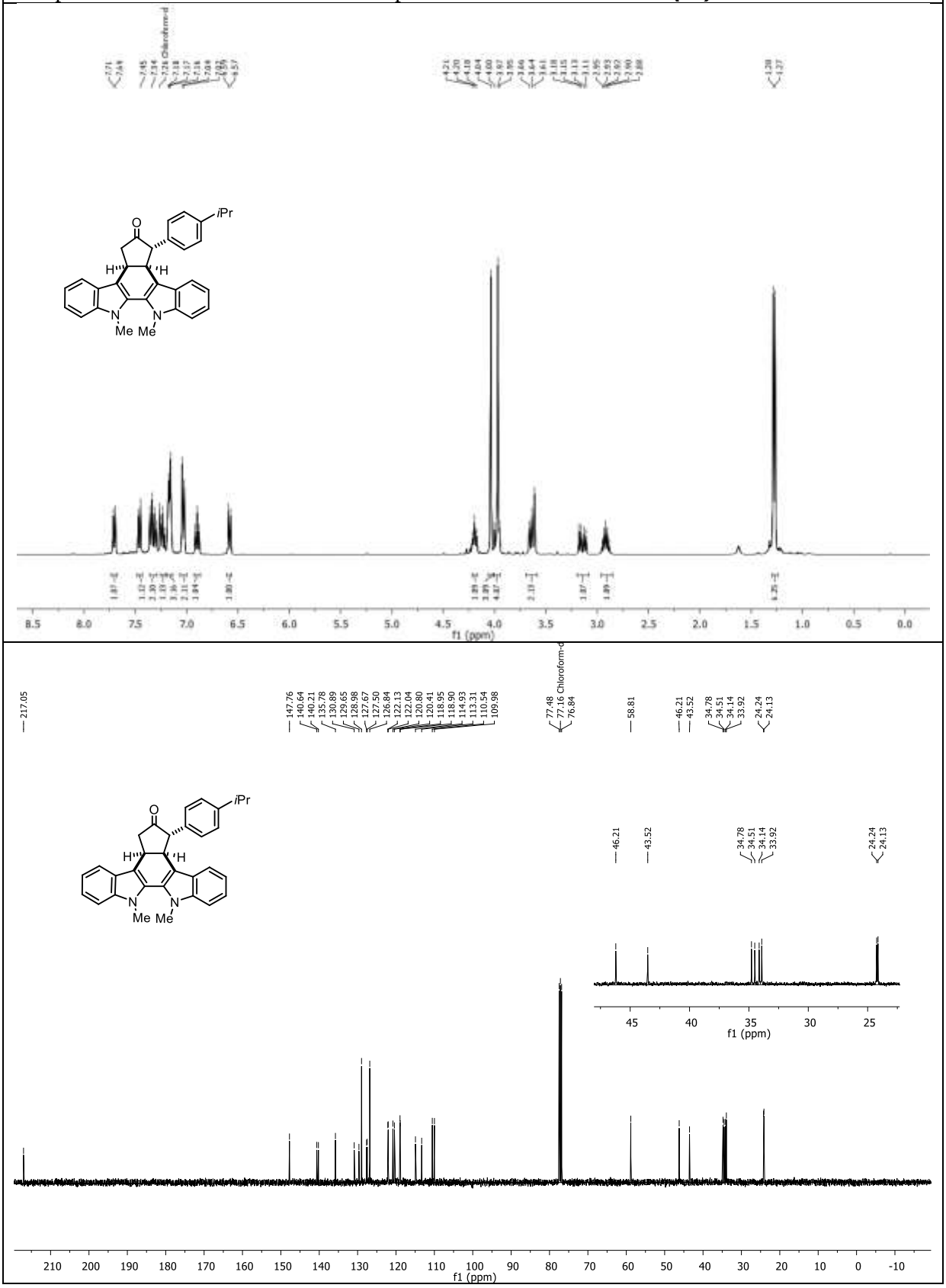
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(40)***



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(41)***

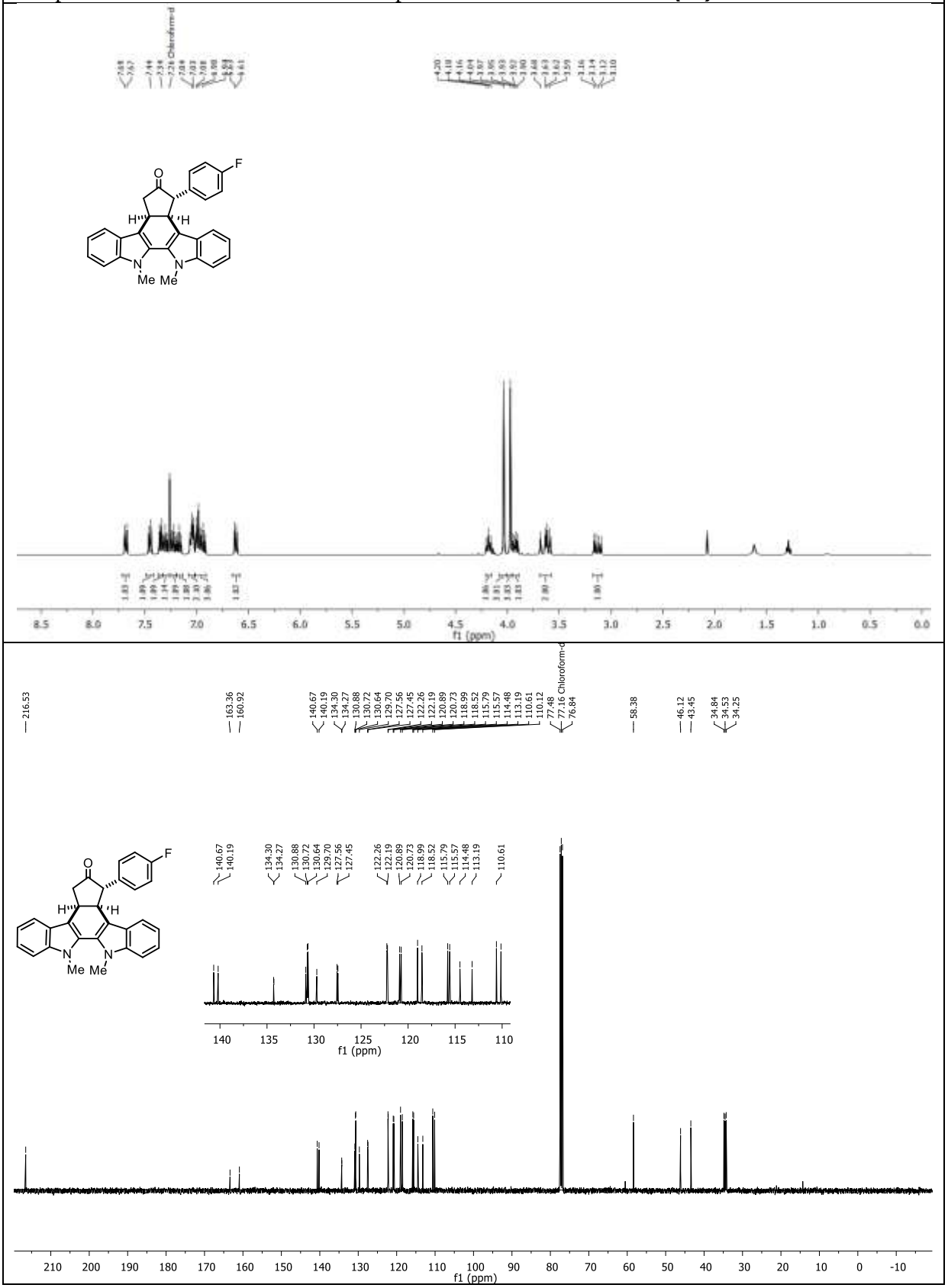


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(42)***

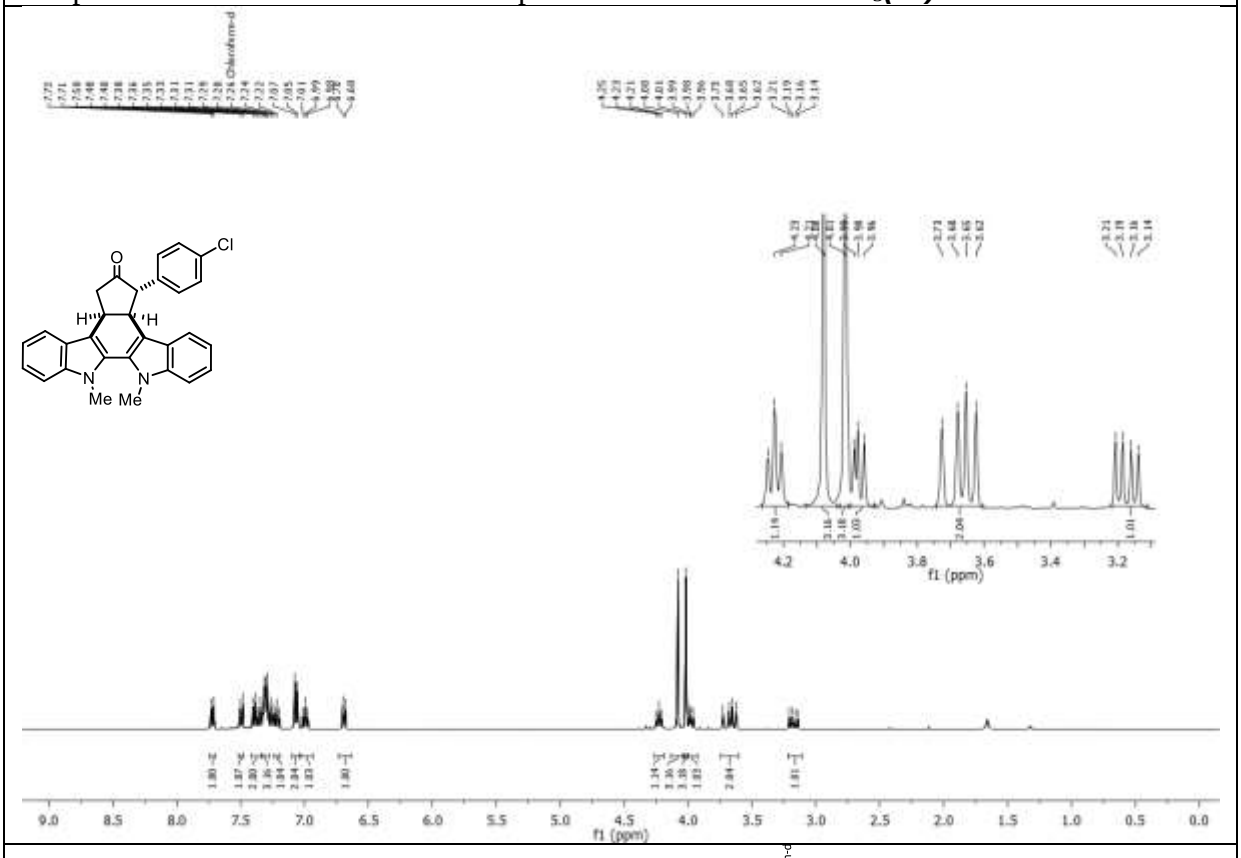


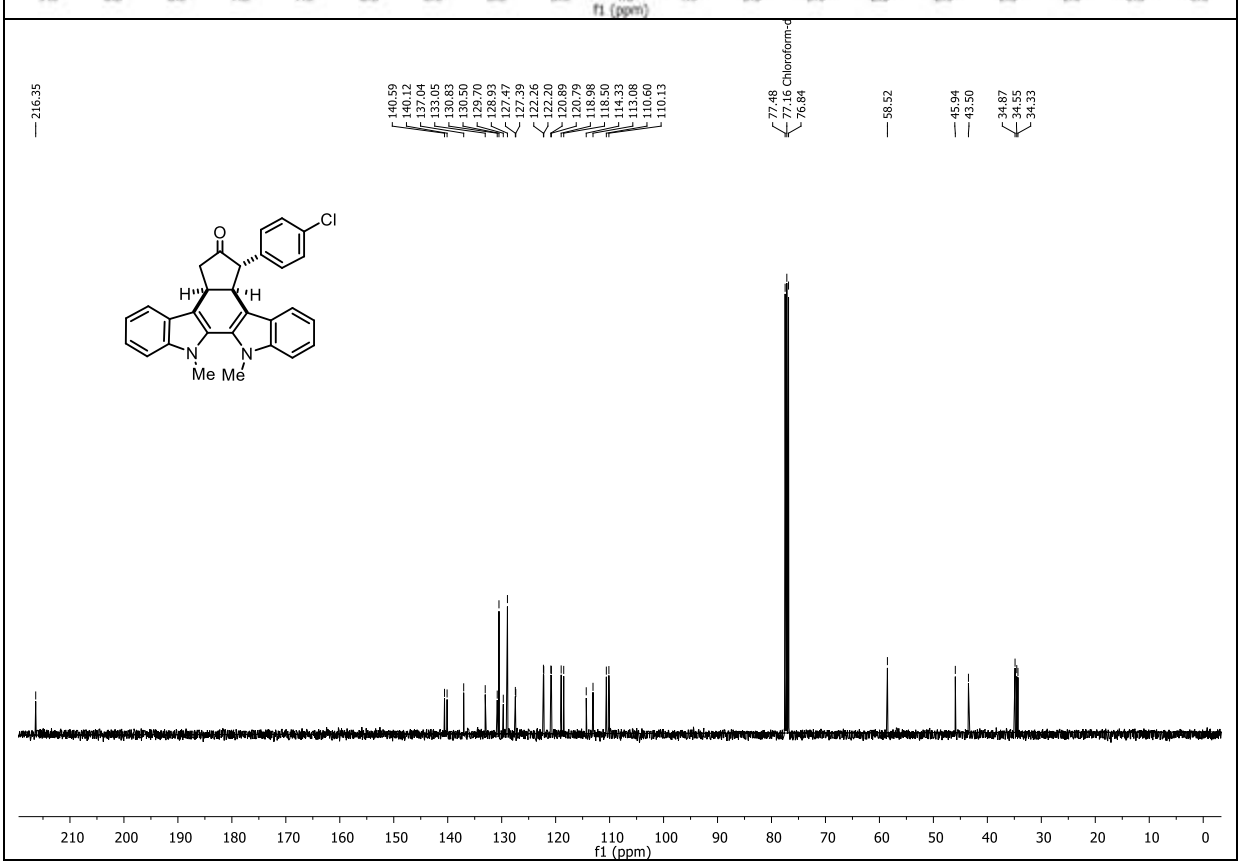
C

^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(43)***

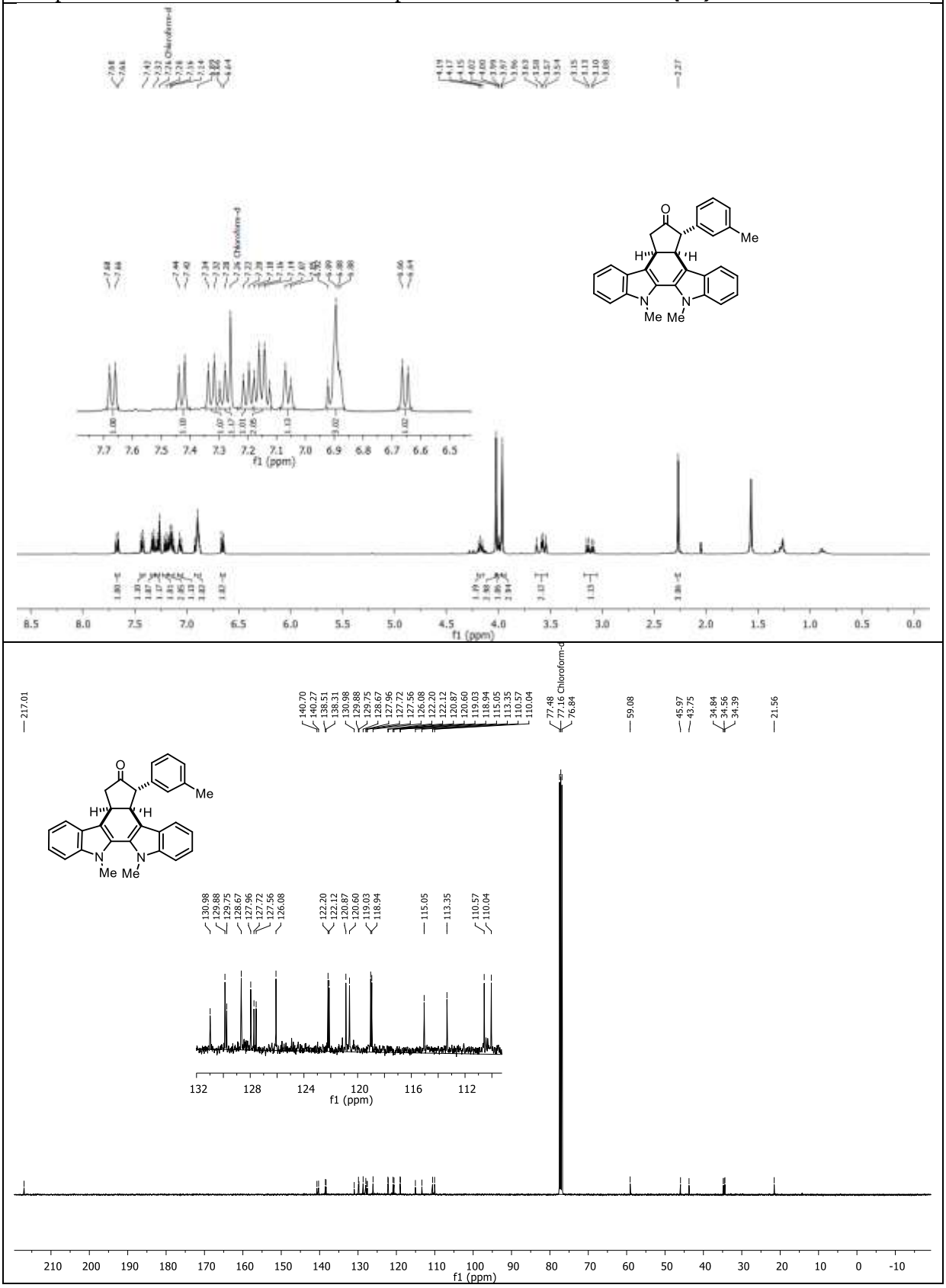


^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(44)***

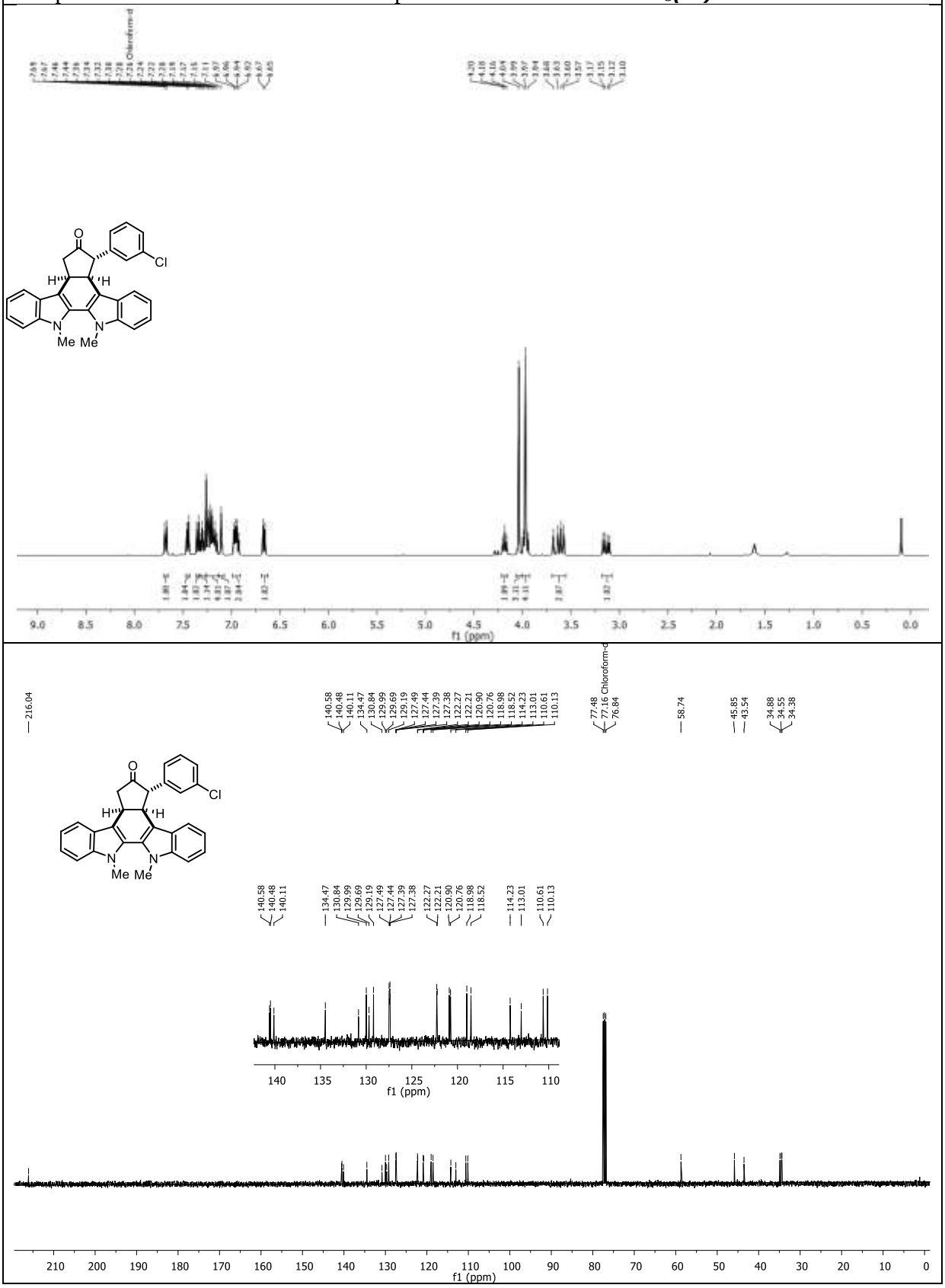




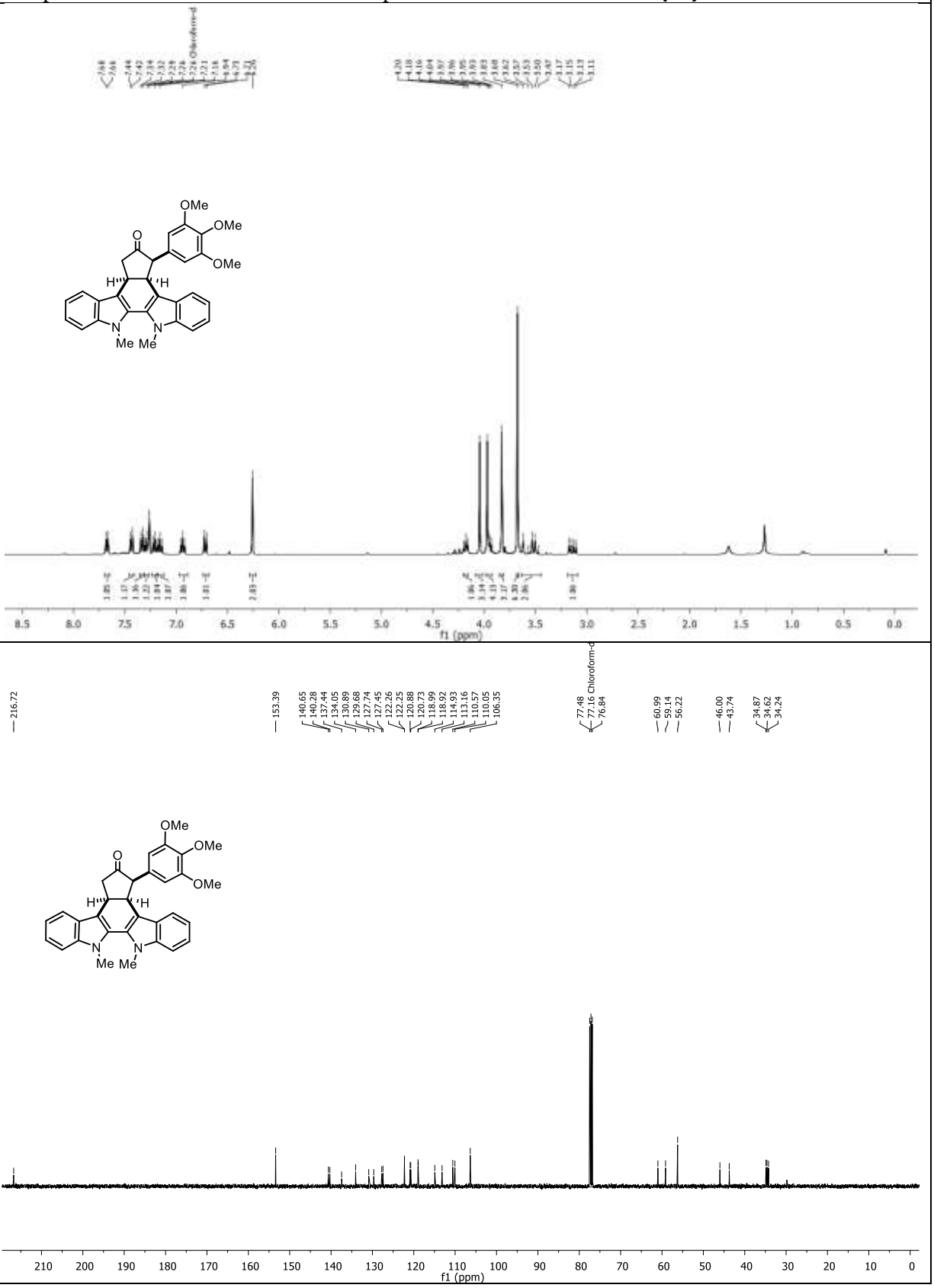
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(45)***



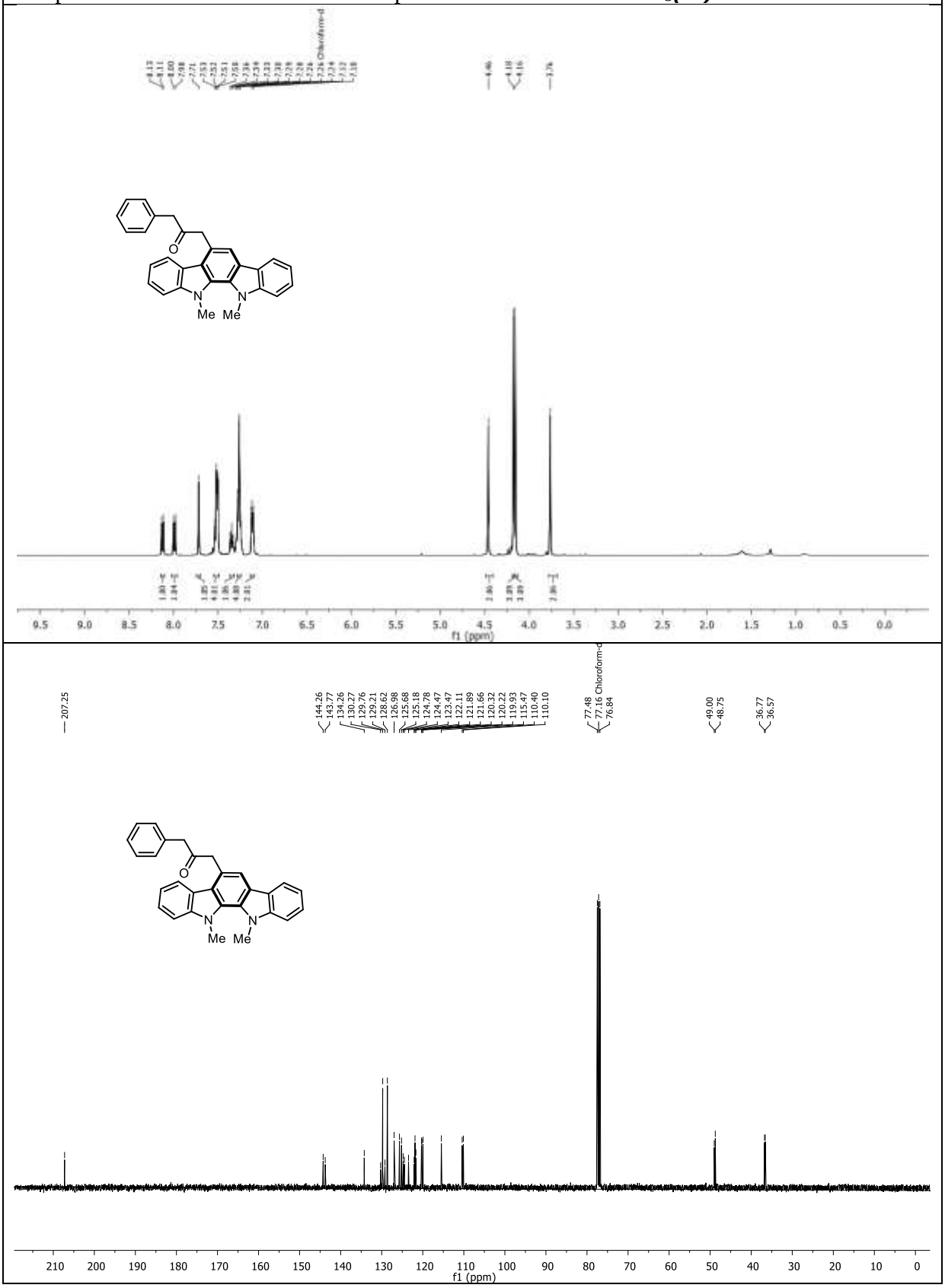
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(46)***



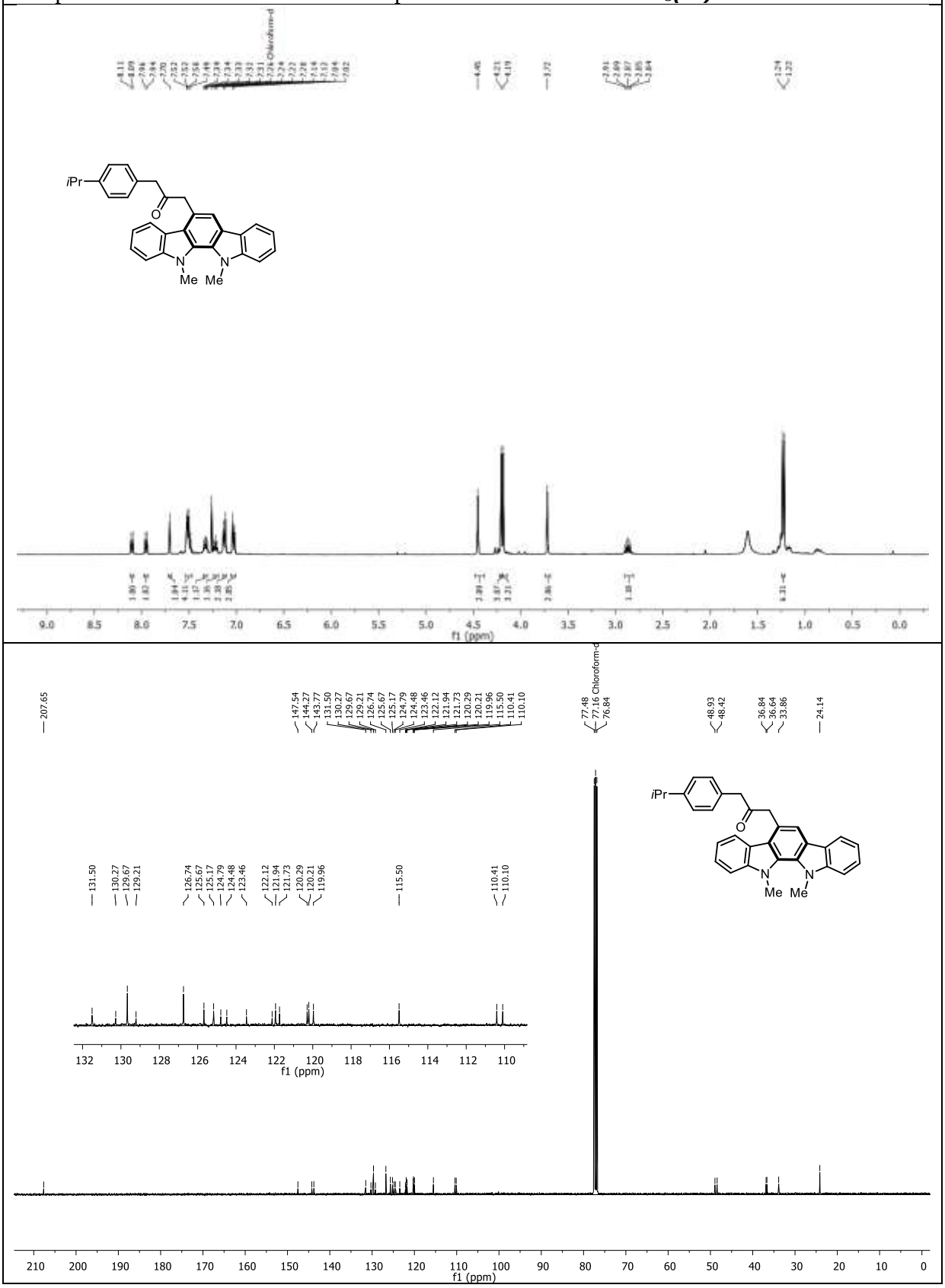
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(47)***



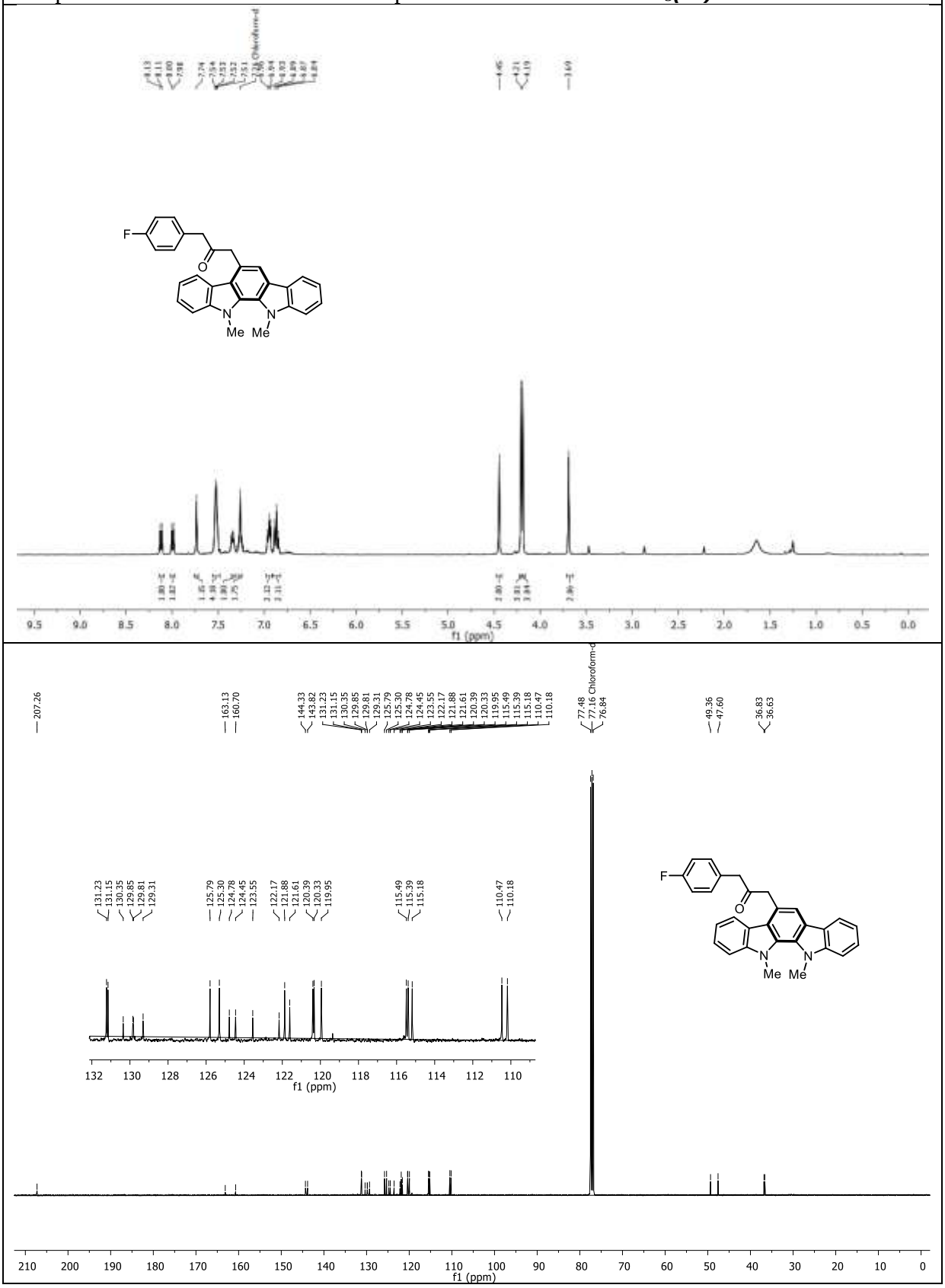
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(48)***



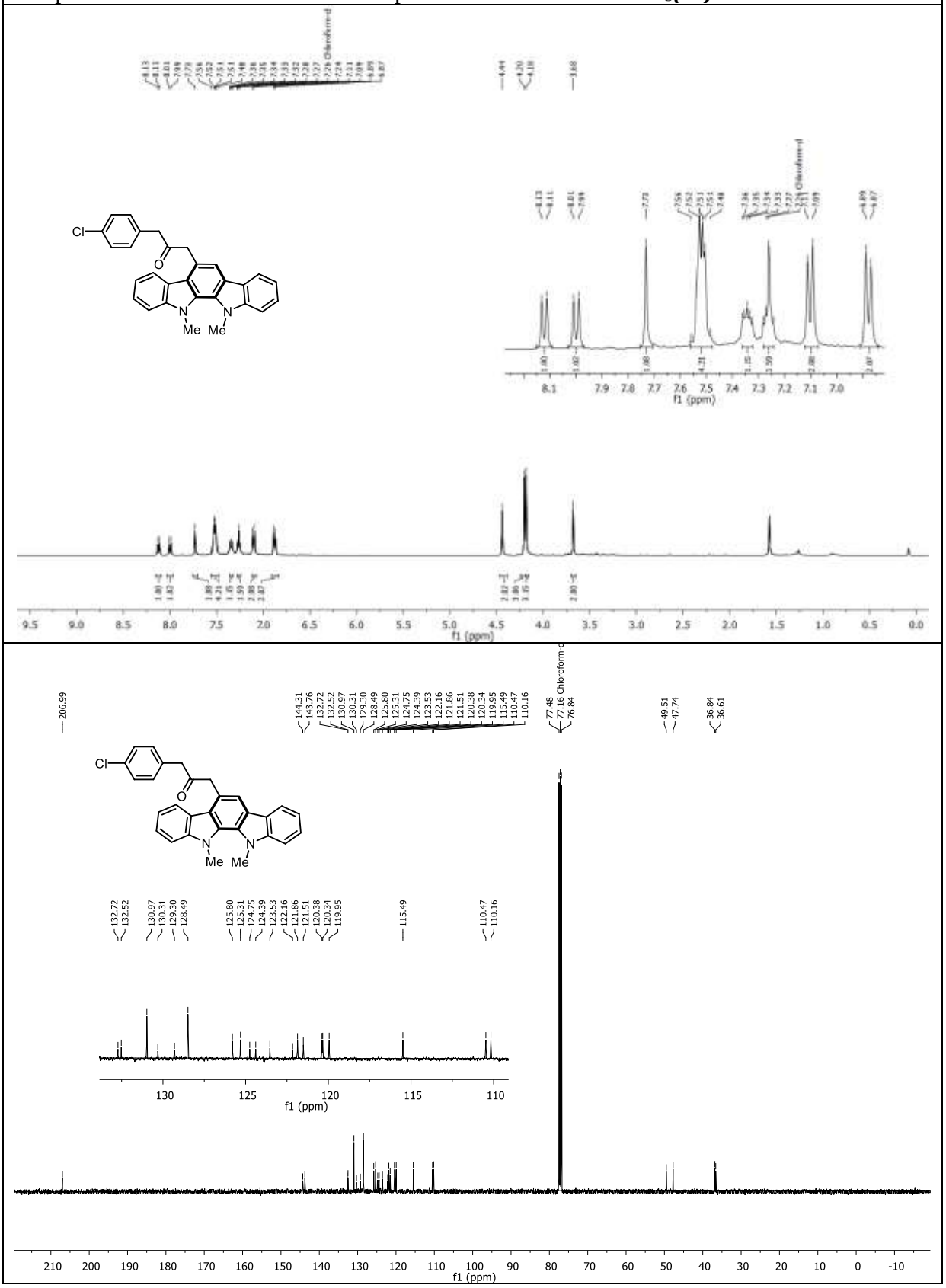
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(49)***



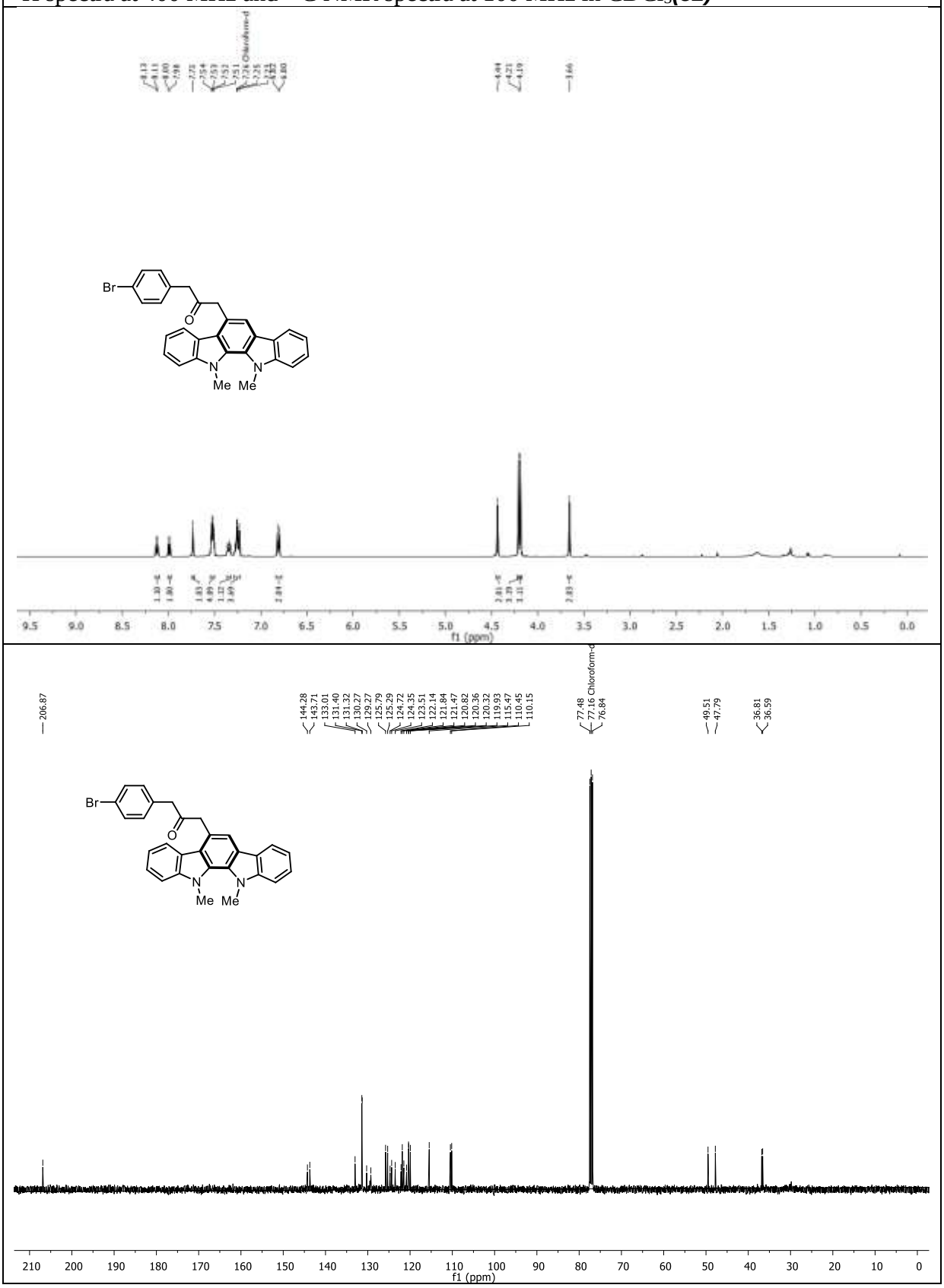
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(50)***



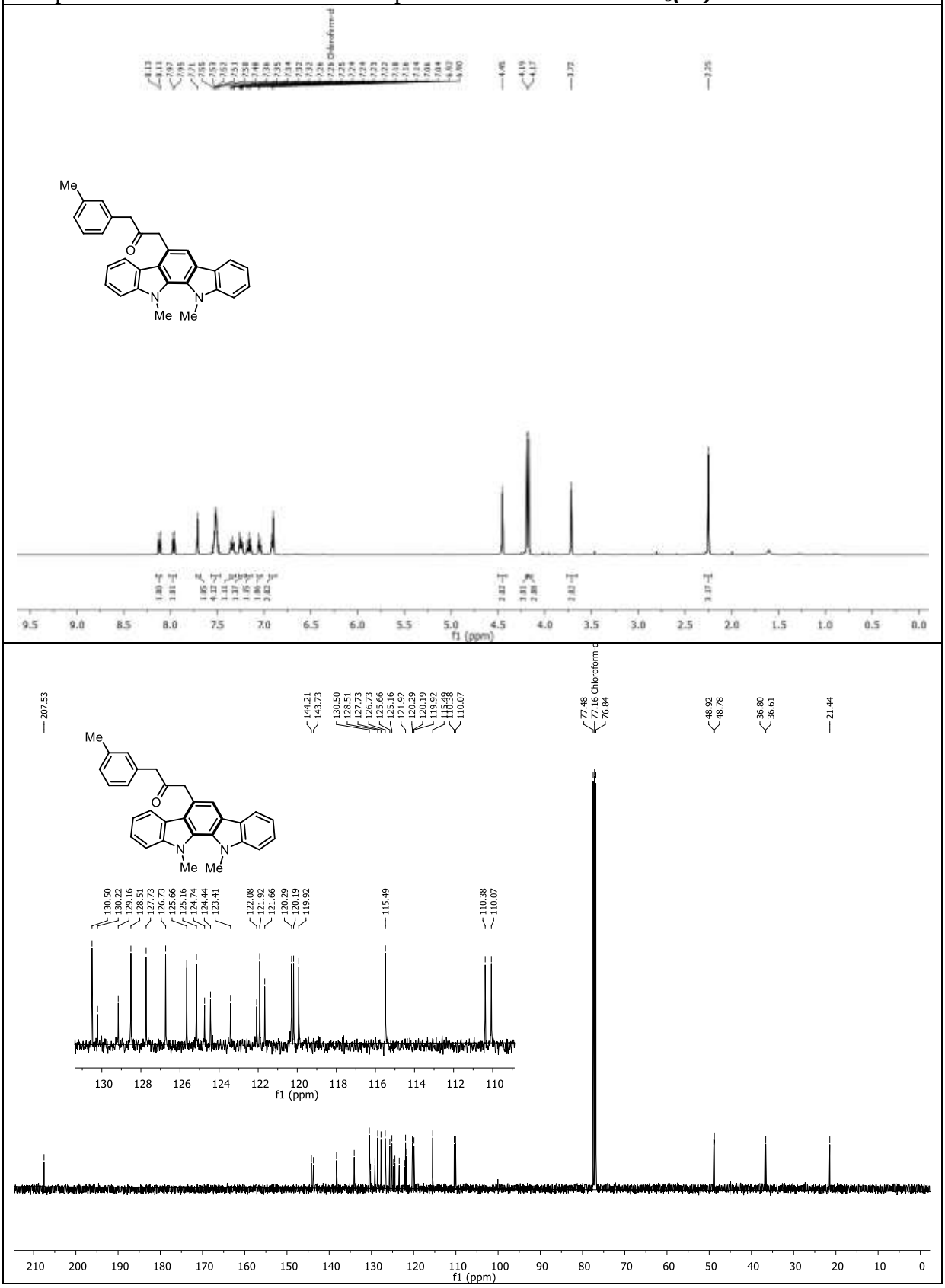
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(51)***



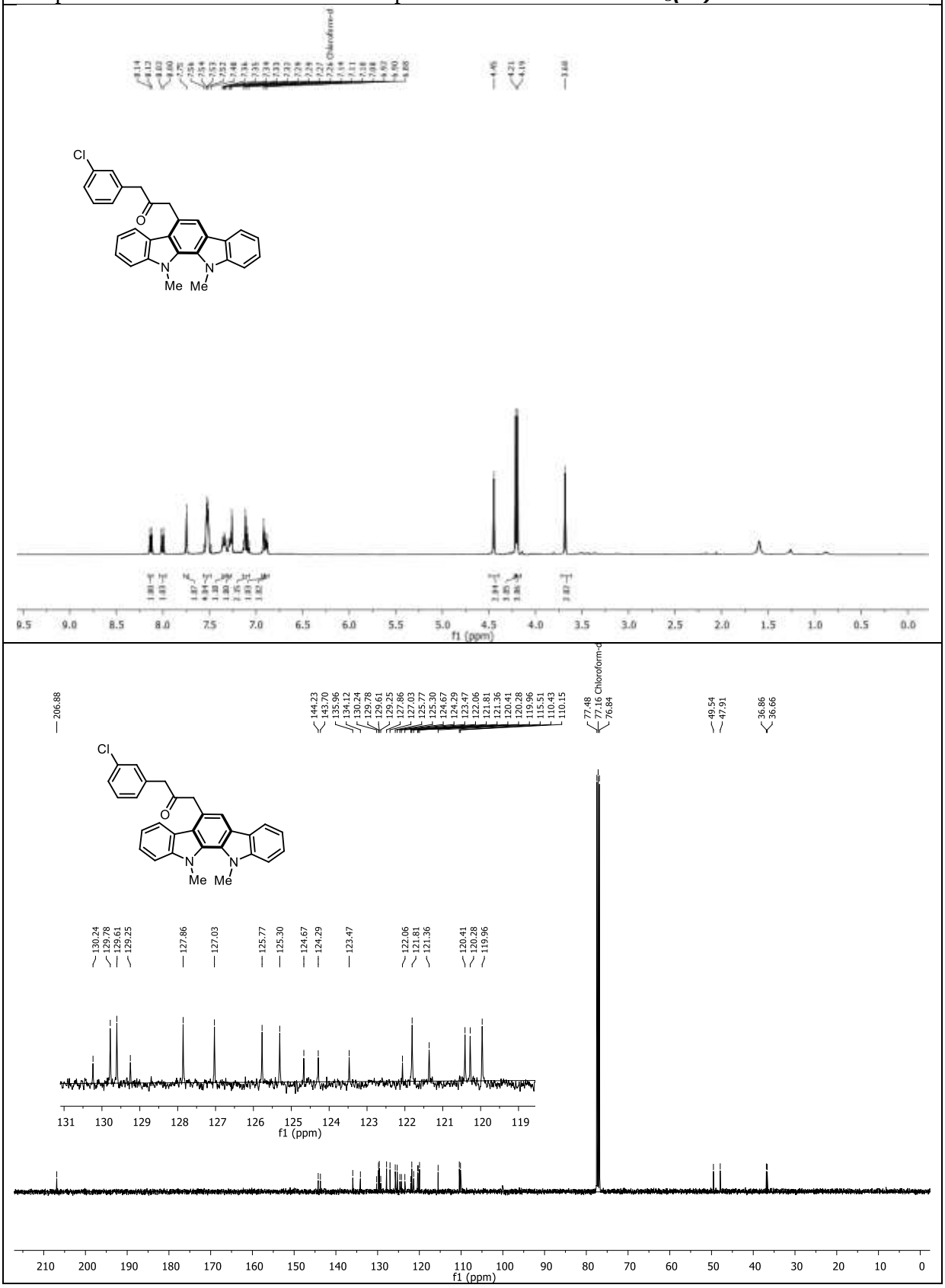
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(52)***



^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(53)***



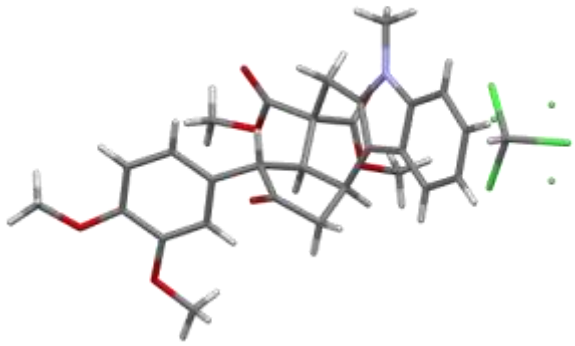
^{1}H spectra at 400 MHz and ^{13}C NMR spectra at 100 MHz in $CDCl_3$ ***(54)***



16. Crystallographic Data

Compound 14:

Crystal structures of **14** was obtained using a Bruker D8 Quest equipped with a micro-focus source for generating Mo Kα radiation (λ = 0.71073 Å) and a PHOTON II CMOS detector. Data were recorded at 298K. Integration and scaling of the recorded data were performed by SAINT[5] and SADABS program[6]respectively. Molecular structures were solved by direct methods using SHELXT-2018 and refined by full-matrix least-squares on F^2 using SHELXL-2018/3 version.[7] All non-hydrogen atoms in the compounds were refined anisotropically and hydrogen atoms were placed at calculated positions using riding models.



ORTEP diagram of 14 (CCDC No 2119664): Atoms are shown with 30% probability of thermal ellipsoids

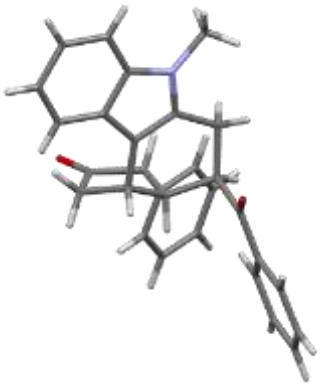
Table S3. Crystal data and refinement parameters

Empirical formula	$C_{28}H_{29}N_1O_7$, $CHCl_3$
Formula weight	610.89
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal size ($mm^{3)}$	0.48 × 0.23 × 0.12
a/Å	13.518(2)
b/Å	8.3005(13)
c/Å	25.702(4)
α/(°)	90
β/(°)	93.195(5)
γ/(°)	90

V/Å^3	2879.4(8)
Z	4
D_{cal}/g cm^{-3}	1.409
T/K	298(2)
μ/mm^{-1}	0.366
F_{000}	1272
Theta ranges for data collection	2.1° to 28.4°
Index ranges	-18 =< h =< 18, -11 =< k =< 11, -34 =< l =< 32
Reflections measured	68765
Unique reflections	7206
Observed reflections	5484
Parameters	394
Data completeness	99.5%
R_{int}	0.052
final R (I >2σ(I))	0.0670
final R (all data)	0.0889
final wR_2 (I >2σ(I))	0.1542
final wR_2 (all data)	0.1665
GOF on F^2	1.051
Highest peak and deepest hole	0.40 and -0.45 e/Å^3
CCDC No	**2119664**

Compound 26:

Crystal structures of **22** was determined using similar method as was used for compound **14**, described above.



ORTEP diagram of 22 (CCDC No 2119665): Atoms are shown with 30% probability of thermal ellipsoids

Table S4. Crystal data and refinement parameters

Empirical formula	$C_{29}H_{25}N_1O_2$
Formula weight	419.50
Wavelength/ Å	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Crystal size ($mm^{3)}$	0.21 × 0.16 × 0.08
a/Å	11.9836(17)
b/Å	8.6160(12)
c/Å	21.720(3)
α/(°)	90
β/(°)	98.210(4)
γ/(°)	90
V/$Å^3$	2219.6(5)
Z	4
D_{cal}/g cm^{-3}	1.255
T/K	298(2)
μ/mm^{-1}	0.078
F_{000}	888
Theta ranges for data collection	2.9° to 28.3°
Index ranges	-16 =< h =< 16, -11 =< k =< 11, -28 =< l =< 27
Reflections measured	66706
Unique reflections	5501
Observed reflections	4459
Parameters	291
Data completeness	99.5%
R_{int}	0.048
final *R* (I >2σ(I))	0.0507
final *R* (all data)	0.0635
final wR_2 (I >2σ(I))	0.1331
final wR_2 (all data)	0.1425
GOF on F^2	1.057
Highest peak and deepest hole	0.30 and -0.23 e/$Å^3$
CCDC No	**2119665**

ORTEP diagram of 27 (CCDC No 2119666): Atoms are shown with 30% probability of thermal ellipsoids

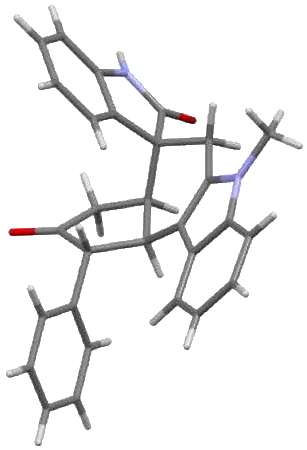


Table S5. Crystal data and refinement parameters

Empirical formula	$C_{29}H_{24}N_2O_2$
Formula weight	432.50
Wavelength/ Å	0.71073
Crystal system	Triclinic
Space group	*P*-1
Crystal size ($mm^{3)}$	0.36 × 0.19× 0.06
a/Å	10.0315(17) 13.014(2)
b/Å	10.8177(17)
c/Å	13.014(2)
α/(°)	97.315(5)
β/(°)	97.743(6)
γ/(°)	111.251(5)
V/$Å^3$	1280.3(4)
Z	2
D_{cal}/g cm^{-3}	1.122
T/K	298(2)
μ/mm^{-1}	0.071
F_{000}	456
Theta ranges for data collection	2.3° to 28.4°
Index ranges	-13 =< h =< 13, -14 =< k =< 14, -17 =< l =< 17

Reflections measured	57585
Unique reflections	6377
Observed reflections	4877
Parameters	304
Data completeness	99.2%
R_{int}	0.045
final R (I >2σ(I))	0.0661
final R (all data)	0.0819
final wR_2 (I >2σ(I))	0.2069
final wR_2 (all data)	0.2241
GOF on F^2	1.045
Highest peak and deepest hole	0.27 and -0.27 e/Å^3
CCDC No	**2119666**

17. References

1. (a)*see reference 7b-c from the main text*; (b) A. B. Gade and N. T. Patil, *Synlett.* **2017**, *28*, 1096–1100;

2. *see reference 11 from the main text*

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4. Fortes, M. P.; Bassaco, M. M.; Kaufman, T. S., Silveira, C.C. A convenient eco-friendly system for the synthesis of 5-sulfenyl tetrazole derivatives of indoles and pyrroles employing $CeCl_3$, 7H2O in PEG-400. *RSC Adv.***2014**, 4, 34519-34530.

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6. SADABS, Version 2.05; Bruker AXS Inc.: Madison, WI, 2002.

7. G. M. Sheldrick, *Acta Cryst. Sect. A.* **2015**, *71*, 3-8.