Supporting Information

Siteselective Functionalization of 7-Azaindoles via Carbene Transfer and Isolation of N-Aromatic Zwitterions

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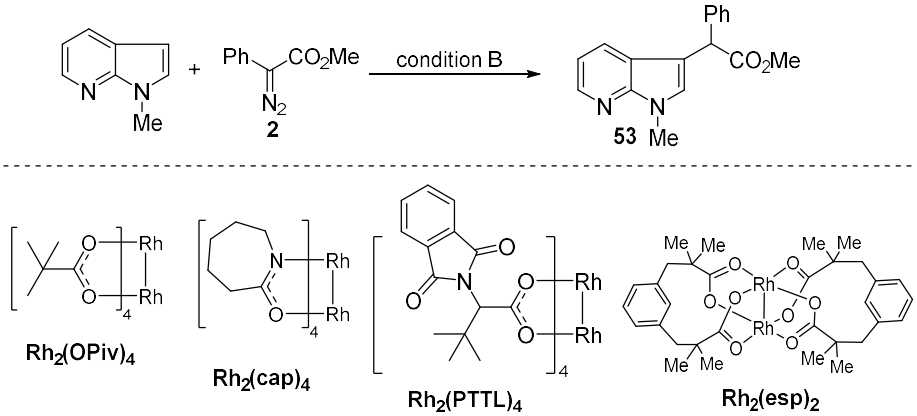
General information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. Commercially obtained reagents were used as received. Analytical thin layer chromatography (TLC) was carried out using pre-coated (0.20 mm thickness) silica gel plates with F_{254} indicator. For column chromatography, 200-300 mesh silica gel was used. ^{1}H NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer in $CDCl_3$ or DMSO-d_6. ^{13}C NMR were recorded on Bruker 75 MHz, 100 MHz spectrometer in $CDCl_3$ or DMSO-d_6. ^{19}F NMR were recorded on Bruker 282 MHz spectrometer in $CDCl_3$. Data for ^{1}H NMR spectra were reported relative to tetramethylsilane (TMS) as an internal standard (0 ppm) or relative to DMSO-d_6 as an internal standard (2.50 ppm), and were reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, and m = multiplet. Data for ^{13}C NMR spectra were reported relative to $CDCl_3$ as an internal standard (77.16 ppm) or relative to DMSO-d_6 as an internal standard (39.52 ppm), and were reported in terms of chemical shift (δ ppm). High resolution mass spectra (HRMS) were performed on Agilent 6540 Q-TOF or Agilent 6230A TOF mass spectrometer (ESI).

[Ru(*p*-cymene)I_2]$_2$ was purchased from Engry Chemical. $AgNTf_2$,[1] $Rh_2(PTTL)_4$,[2] diazo compounds[3] and 7-Azaindole[4] derivatives were known compounds and prepared according to the literature procedures.

Optimization of the reaction conditions for Scheme 3[a]

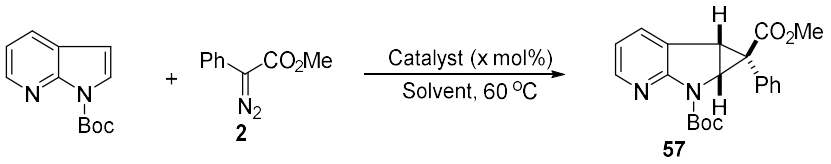


Entry	Catalyst (x mol%)	Solvent	time (h)	Yield (%)[b]
1	$Ru(PPh_3)_3Cl_2$ (2)	DCM	1	-
2	$CpRu(PPh_3)_2Cl$ (2)	DCM	1	-
3	[Ru(*p*-cymene)$_2Cl_2$] (2)	DCM	1	-
4	[Ru(*p*-cymene)$_2I_2$] (2)	DCM	1	-
5	AgOTf (2)	DCM	1	10
6	$AgNTf_2$ (2)	DCM	1	13
7	$Cu(OTf)_2$ (2)	DCM	1	15
8	$Cu(MeCN)_4BF_4$ (2)	DCM	1	trace
9	$Rh_2(TFA)_4$ (2)	DCM	0.5	48
10	$Rh_2(cap)_4$ (2)	DCM	0.5	trace

11	$Rh_2(esp)_2$ (2)	DCM	0.5	27
12	$Rh_2(OAc)_4$ (2)	DCM	0.5	18
13	$Rh_2(PTTL)_4$ (2)	DCM	0.5	62
14	$Rh_2(Opiv)_4$ (2)	DCM	0.5	22
15	$Rh_2(PTTL)_4$ (2)	$CHCl_3$	0.5	18
16	$Rh_2(PTTL)_4$ (2)	DCE	0.5	15
17	$Rh_2(PTTL)_4$ (2)	toluene	0.5	18
19	$Rh_2(PTTL)_4$ (2)	dioxane	0.5	10
20	$Rh_2(PTTL)_4$ (2)	*c*-hexane	0.5	52
21	$Rh_2(PTTL)_4$ (2)	MeCN	0.5	12
22	$Rh_2(PTTL)_4$ (2)	THF	0.5	8
23	$Rh_2(PTTL)_4$ (1)	DCM	0.5	47
24 [c]	$Rh_2(PTTL)_4$ (2)	DCM	0.5	74

[a] Reaction condition: 7-azaindole (0.2 mmol), **2** (0.24 mmol), Catalyst (x mol%) in solvent (4 mL), rt. [b] Isolated yield. [c] **2** (0.3 mmol).

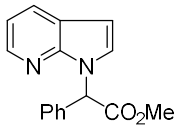
Optimization of the reaction conditions for Scheme 4[a]



Entry	Catalyst (x mol%)	Solvent	time (h)	Yield (%)[b]
1	$Ru(PPh_3)_3Cl_2$ (2)	DCM	4	12
2	$CpRu(PPh_3)_2Cl$ (2)	DCM	4	18
3	[Ru(*p*-cymene)$_2Cl_2$] (2)	DCM	4	-
4	[Ru(*p*-cymene)$_2I_2$] (2)	DCM	4	-
5	$Rh_2(esp)_2$ (2)	DCM	4	<10
6	$Rh_2(PTTL)_4$ (2)	DCM	4	19
7	$Rh_2(Opiv)_4$ (2)	DCM	4	-
8	$Cu(OTf)_2$ (2)	DCM	4	-
9	$Cu(MeCN)_4BF_4$ (2)	DCM	4	-
10	$Cu(MeCN)_4PF_6$ (2)	DCM	4	-
11	AgOTf (2)	DCM	4	23
12	$AgNTf_2$ (2)	DCM	4	28
13	$AgBF_4$ (2)	DCM	4	10
14	$AgPF_6$ (2)	DCM	4	20
15	CH_3CO_2Ag (2)	DCM	4	15
16	AgF (2)	DCM	4	23
17	$AgNTf_2$ (2)	DMF	4	-
18	$AgNTf_2$ (2)	DCE	4	-
19	$AgNTf_2$ (2)	toluene	4	-
20	$AgNTf_2$ (2)	dioxane	4	-
21	$AgNTf_2$ (2)	*c*-hexane	4	-

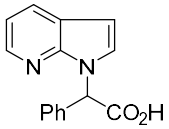
22	$AgNTf_2$ (2)	THF	4	-
23	$AgNTf_2$ (2)	MeCN	4	40
24	$AgNTf_2$ (4)	MeCN	4	43
25	$AgNTf_2$ (5)	MeCN	4	48
26 [c]	$AgNTf_2$ (5)	MeCN	6	63

[a] Reaction condition: 7-azaindole (0.2 mmol), **2** (0.24 mmol), Catalyst (x mol%) in solvent (4 mL), 60 °C. [b] Isolated yield. [c] **2** (0.4 mmol) was used.



methyl 2-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)acetate (3)

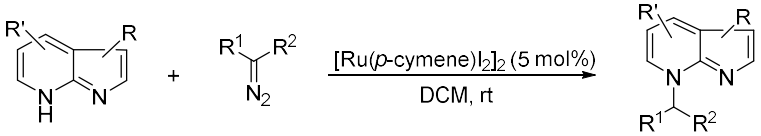
Obtained in 10% yield as colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (dd, J = 4.8, 1.5 Hz, 1H), 7.89 (dd, J = 7.8, 1.5 Hz, 1H), 7.42-7.35 (m, 5H), 7.26 (d, J = 3.7 Hz, 1H), 7.08 (dd, J = 7.8, 4.8 Hz, 1H), 6.92 (s, 1H), 6.46 (d, J = 3.7 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 147.7, 142.9, 135.1, 129.2, 129.0, 128.9, 128.4, 126.9, 120.7, 116.5, 100.6, 59.3, 52.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1128; Found 267.1124.



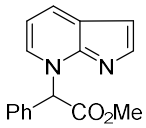
2-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-1-yl)acetic acid (6)

Obtained from **3** in 92% yield as a white solid, mp: 144-146 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.36 (s, 1H), 8.31 (s, 1H), 7.93 (s, 1H), 7.45 (s, 2H), 7.37-7.36 (m, 4H), 7.06 (s, 1H), 6.87 (s, 1H), 6.46 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 145.6, 140.4, 135.1, 131.3, 129.1, 129.0, 128.9, 128.5, 122.6, 116.2, 100.9, 61.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O_2$ 253.0972; Found 253.0973.

General procedure for Scheme 2

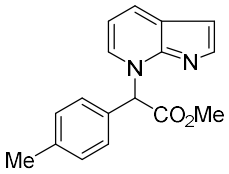


Under argon atmosphere, to a dry tube was added 7-azaindole (0.2 mmol, 1 equiv), [Ru(*p*-cymene)I_2]$_2$ (0.01 mmol, 5 mol%) and DCM (1 mL). Then diazo compound (0.4 mmol, 2 equiv) in DCM (1 mL) was added via a syringe pump over 2 h at room temperature. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether) to give desired product. [Note: for **27**-**31**, diazo compound (0.3 mmol, 1.5 equiv) in DCM (1 mL) was added in one portion, then stirred at 60 °C for 5 h.]



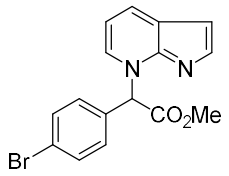
methyl 2-phenyl-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (5)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (43.4 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 2.6 Hz, 1H), 7.62 (s, 1H), 7.51 (d, *J* = 6.5 Hz, 1H), 7.46 (s, 5H), 6.80 (t, *J* = 6.5 Hz, 1H), 6.71 (d, *J* = 2.6 Hz,1H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 149.0, 145.0, 132.6, 131.1, 130.2, 129.9, 129.6, 129.4, 127.9, 108.9, 102.0, 64.7, 53.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1128; Found 267.1128.



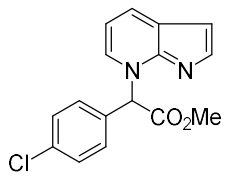
methyl 2-(7H-pyrrolo[2,3-b]pyridin-7-yl)-2-(p-tolyl)acetate (7)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (49.2 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 2.6 Hz, 1H), 7.55 (s, 1H), 7.50 (d, *J* = 6.4 Hz, 1H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.79 (t, *J* = 6.9 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 3H), 2.39 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 149.0, 145.0, 140.1, 131.0 , 130.3, 130.2, 129.4, 129.3, 127.8, 108.8, 101.9, 64.6, 53.2, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2$ 281.1285; Found 281.1286.



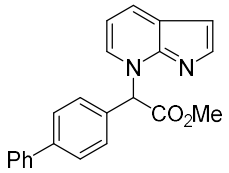
methyl 2-(4-bromophenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (8)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (55.7 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14-8.07 (m, 1H), 7.89 (d, *J* = 2.6 Hz, 1H), 7.64-7.55 (m, 3H), 7.51 (d, *J* = 6.4 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.82 (t, *J* = 6.4 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 148.8, 145.1, 132.8, 131.8, 131.2, 130.9, 130.3, 127.6, 124.4, 109.0, 102.2, 63.9, 53.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2$ 345.0233; Found 345.0230.



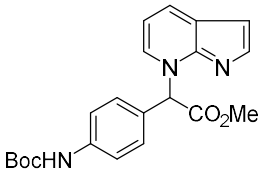
methyl 2-(4-chlorophenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (9)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (46.8 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 2.6 Hz, 1H), 7.61 (s, 1H), 7.50 (d, *J* = 6.5 Hz, 1H), 7.44-7.37 (m, 4H), 6.81 (t, *J* = 6.5 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 148.9, 145.2, 136.2, 131.2, 131.1, 130.6, 130.3, 129.8, 127.6, 109.0, 102.2, 63.8, 53.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}ClN_2O_2$ 301.0738; Found 301.0737.



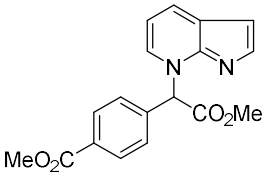
methyl 2-([1,1'-biphenyl]-4-yl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (10)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (51.9 mg, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.92 (d, *J* = 2.6 Hz, 1H), 7.71-7.35 (m, 11H), 6.87-6.79 (m, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 149.0, 145.2, 142.9, 139.9, 131.4, 131.1, 130.3, 129.8, 129.0, 128.2, 128.0, 127.8, 127.2, 108.9, 102.0, 64.4, 53.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2O_2$ 343.1441; Found 343.1445.



methyl 2-(4-((tert-butoxycarbonyl)amino)phenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (11)

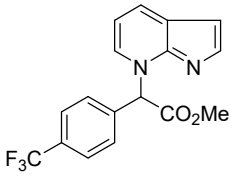
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:2, yellow oil (60.1 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 2.4 Hz, 1H), 7.51-7.44 (m, 4H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.04 (s, 1H), 6.78 (t, *J* = 6.9 Hz, 1H), 6.70 (d, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 1.50 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 152.6, 148.9, 145.0, 140.2, 131.1, 130.3, 130.2, 127.8, 126.3, 119.2, 108.9, 102.0, 81.1, 64.5, 53.2, 28.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{24}N_3O_4$ 382.1761; Found 382.1761.



methyl 4-(2-methoxy-2-oxo-1-(7H-pyrrolo[2,3-b]pyridin-7-yl)ethyl)benzoate (12)

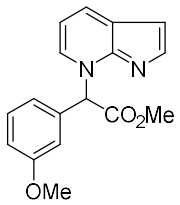
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (44 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (t, *J* = 6.8 Hz, 3H), 7.91 (d, *J* = 2.4 Hz, 1H), 7.72 (s, 1H), 7.56-7.48 (m, 3H), 6.81 (t, *J* = 6.8

Hz, 1H), 6.72 (d, J = 2.4 Hz, 1H), 3.93 (s, 3H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 166.1, 149.0, 145.3, 137.5, 131.5, 131.1, 130.7, 130.4, 129.2, 127.7, 109.0, 102.2, 63.9, 53.4, 52.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_4$ 325.1183; Found 325.1181.



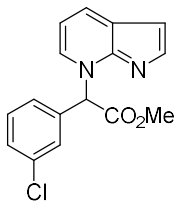
methyl 2-(7H-pyrrolo[2,3-b]pyridin-7-yl)-2-(4-(trifluoromethyl)phenyl)acetate (13)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, yellow oil (47.4 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 7.3 Hz, 1H), 7.91 (d, J = 2.2 Hz, 1H), 7.78-7.70 (m, 3H), 7.59 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 6.9 Hz, 1H), 6.84 (t, J = 6.9 Hz, 1H), 6.73 (d, J = 2.5 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.5, 148.9, 145.3, 136.9, 132.0 (q, C-F, $^2J_{C\text{-}F}$ = 32.9 Hz), 131.2, 130.4, 129.6, 127.6, 126.5 (q, C-F, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.6 (q, C-F, $^1J_{C\text{-}F}$ = 270.8 Hz), 109.1, 102.3, 63.7, 53.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}F_3N_2O_2$ 335.1002; Found 335.1006.



methyl 2-(3-methoxyphenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (14)

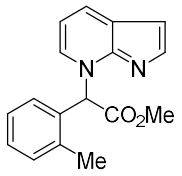
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (49.1 mg, 83% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (dd, J = 7.3, 1.0 Hz, 1H), 7.89 (d, J = 2.6 Hz, 1H), 7.61-7.50 (m, 2H), 7.41-7.30 (m, 1H), 7.05-6.95 (m, 3H), 6.77 (dd, J = 7.3, 6.6 Hz, 1H), 6.70 (d, J = 2.6 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 160.4, 148.9, 145.0, 133.8, 131.1, 130.6, 130.2, 127.9, 121.4, 115.4, 115.2, 108.9, 102.0, 64.7, 55.4, 53.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_3$ 297.1234; Found 297.1231.



methyl 2-(3-chlorophenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (15)

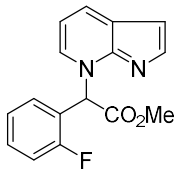
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (44.4 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.4, 0.9 Hz, 1H), 7.90 (d, J = 2.6 Hz, 1H), 7.63 (s, 1H), 7.54 (d, J = 6.4 Hz, 1H), 7.48-7.31 (m, 4H), 6.82 (t, J=6.4, 1H), 6.72 (d, J = 2.6 Hz, 1H), 3.86 (s, 3H). ^{13}C NMR (75 MHz,

$CDCl_3$) δ 168.6, 148.9, 145.2, 135.5, 134.7, 131.1, 130.8, 130.4, 130.2, 129.3, 127.6, 127.4, 109.0, 102.2, 63.8, 53.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}ClN_2O_2$ 301.0738; Found 301.0734.



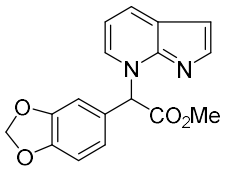
methyl 2-(7H-pyrrolo[2,3-b]pyridin-7-yl)-2-(o-tolyl)acetate (16)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (28 mg, 50% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.3, 1.1 Hz, 1H), 7.91 (d, J = 2.6 Hz, 1H), 7.65 (s, 1H), 7.45-7.28 (m, 5H), 6.78 (dd, J = 7.3, 6.4 Hz, 1H), 6.71 (d, J = 2.6 Hz, 1H), 3.86 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 148.8, 145.2, 139.0, 131.8, 131.1, 130.7, 130.2, 130.1, 129.0, 127.4, 126.7, 108.9, 101.8, 63.0, 53.2, 19.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2$ 281.1285; Found 281.1285.



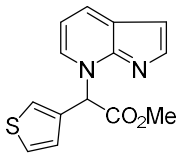
methyl 2-(2-fluorophenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (17)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (45.4 mg, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 7.3 Hz, 1H), 7.91 (d, J = 2.4 Hz, 1H), 7.77 (s, 1H), 7.58-7.49 (m, 2H), 7.47-7.40 (m, 1H), 7.24-7.13 (m, 2H), 6.79 (t, J = 6.9 Hz, 1H), 6.70 (d, J = 2.4 Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 160.9 (d, C-F, $^1J_{C\text{-}F}$ = 250.3 Hz), 148.9, 145.25, 132.2 (d, C-F, $^3J_{C\text{-}F}$ = 8.5 Hz), 131.4, 131.09, 130.42, 127.5 (d, C-F, $^4J_{C\text{-}F}$ = 2.6 Hz), 125.1 (d, C-F, $^3J_{C\text{-}F}$ = 3.6 Hz), 120.8 (d, C-F, $^2J_{C\text{-}F}$ = 14.0 Hz), 116.6 (d, C-F, $^2J_{C\text{-}F}$ = 21.4 Hz), 109.0, 102.1, 59.8, 53.5. ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}FN_2O_2$ 285.1034; Found 285.1030.



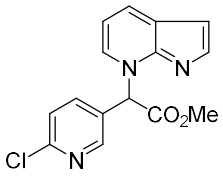
methyl 2-(benzo[d][1,3]dioxol-5-yl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (18)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (44 mg, 71% yield). ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, J = 7.3, 0.9 Hz, 1H), 7.89 (d, J = 2.6 Hz, 1H), 7.55 (d, J = 6.0 Hz, 1H), 7.47 (s, 1H), 7.00-6.78 (m, 4H), 6.70 (d, J = 2.6 Hz, 1H), 6.03-5.98 (m, 2H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 149.0, 148.9, 148.7, 145.1, 131.0, 130.2, 127.5, 125.7, 123.5, 109.6, 109.1, 108.8, 102.0, 101.8, 64.5, 53.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N_2O_4$ 311.1026; Found 311.1026.



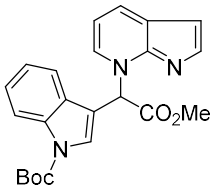
methyl 2-(7H-pyrrolo[2,3-b]pyridin-7-yl)-2-(thiophen-3-yl)acetate (19)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (34.2 mg, 63% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.3 Hz, 1H), 7.89 (d, *J* = 2.6 Hz, 1H), 7.60 (s, 1H), 7.57-7.48 (m, 2H), 7.46-7.39 (m, 1H), 7.11 (d, *J* = 4.3 Hz, 1H), 6.82 (t, *J* = 6.9 Hz, 1H), 6.71 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.1, 148.8, 145.1, 132.5, 131.2, 130.3, 127.9, 127.7, 127.6, 127.0, 108.9, 102.0, 60.3, 53.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{13}N_2O_2S$ 273.0692; Found 273.0690.



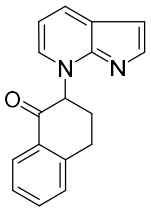
methyl 2-(6-chloropyridin-3-yl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (20)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:2, yellow oil (26.4 mg, 44% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 2.6 Hz, 1H), 8.12 (dd, *J* = 7.3, 0.8 Hz, 1H), 7.89 (d, *J* = 2.6 Hz, 1H), 7.79 (dd, *J* = 8.3, 2.6 Hz, 1H), 7.69 (s, 1H), 7.58 (d, *J* = 6.2 Hz, 1H), 7.40 (d, *J* = 8.3 Hz, 1H), 6.90-6.84 (m, 1H), 6.73 (d, *J* = 2.6 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.9, 153.0, 149.8, 148.8, 145.5, 139.4, 131.3, 130.6, 128.4, 127.2, 125.0, 109.3, 102.5, 61.4, 53.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}ClN_3O_2$ 302.0691; Found 302.0695.



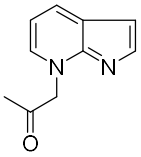
tert-butyl 3-(2-methoxy-2-oxo-1-(7H-pyrrolo[2,3-b]pyridin-7-yl)ethyl)-1H-indole-1-carboxylate (21)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, yellow oil (65.6 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.2 Hz, 1H), 7.96 (d, *J* = 2.3 Hz, 1H), 7.90 (s, 1H), 7.82 (s, 1H), 7.69 (d, *J* = 6.4 Hz, 1H), 7.36-7.30 (m, 2H), 7.13 (t, *J* = 7.2 Hz, 1H), 6.78-6.71 (m, 2H), 3.85 (s, 3H), 1.70 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 149.2, 148.8, 145.3, 135.6, 131.2, 130.2, 128.4, 127.5, 127.0, 125.7, 123.7, 119.1, 115.6, 112.6, 108.9, 102.0, 84.9, 57.7, 53.5, 28.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}N_3O_4$ 406.1761; Found 406.1766.



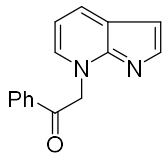
2-(7H-pyrrolo[2,3-b]pyridin-7-yl)-3,4-dihydronaphthalen-1(2H)-one (22)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow solid (38.3 mg, 73% yield), mp: 201-203 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18-8.04 (m, 2H), 7.83 (d, *J* = 2.6 Hz, 1H), 7.62-7.50 (m, 2H), 7.36 (dd, *J* = 13.0, 7.7 Hz, 2H), 6.92 (dd, *J* = 7.3, 6.5 Hz, 1H), 6.79-6.67 (m, 2H), 3.62-3.44 (m, 1H), 3.28-3.16 (m, 1H), 2.91-2.61 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 149.0, 144.7, 143.2, 134.5, 131.8, 130.8, 130.4, 129.0, 128.2, 127.5, 127.2, 109.2, 101.9, 65.2, 30.6, 29.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{15}N_2O$ 263.1179; Found 263.1179.



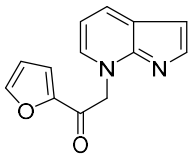
1-(7H-pyrrolo[2,3-b]pyridin-7-yl)propan-2-one (23)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with MeOH/DCM = 1:40-1:10, yellow solid (23.3 mg, 67% yield), mp: 95-97 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (dd, *J* = 7.4, 0.9 Hz, 1H), 7.83 (d, *J* = 2.6 Hz, 1H), 7.45 (d, *J* = 5.8 Hz, 1H), 6.89 (dd, *J* = 7.4, 5.8 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 5.48 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 148.6, 145.3, 131.3, 130.6, 129.9, 109.0, 101.9, 60.4, 27.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{10}H_{11}N_2O$ 175.0866; Found 175.0865.



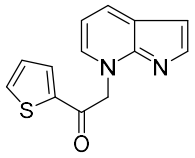
1-phenyl-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)ethan-1-one (24)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with MeOH/DCM = 1:40-1:10, yellow solid (38.2 mg, 81% yield), mp: 189-190 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.07-8.00 (m, 2H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.66-7.59 (m, 1H), 7.53-7.45 (m, 3H), 6.86 (dd, *J* = 7.4, 6.4 Hz, 1H), 6.68 (d, *J* = 2.6 Hz, 1H), 6.09 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.0, 149.0, 145.2, 134.4, 134.3, 131.1, 130.5, 130.4, 129.0, 128.3, 108.9, 101.9, 57.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{15}H_{12}N_2NaO$ 259.0842; Found 259.0840.



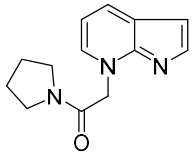
1-(furan-2-yl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)ethan-1-one (25)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with MeOH/DCM = 1:40-1:10, yellow solid (37 mg, 82% yield), mp: 147-149 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.67-7.61 (m, 1H), 7.57-7.49 (m, 1H), 7.41-7.35 (m, 1H), 6.91-6.81 (m, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.62-6.53 (m, 1H), 5.94 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.0, 150.6, 148.8, 147.5, 145.2, 131.2, 130.5, 130.4, 119.0, 112.9, 108.9, 101.8, 56.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2O_2$ 227.0815; Found 227.0811.



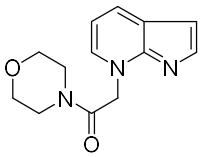
2-(7H-pyrrolo[2,3-b]pyridin-7-yl)-1-(thiophen-2-yl)ethan-1-one (26)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with MeOH/DCM = 1:40-1:10, yellow solid (41.6 mg, 86% yield), mp: 170-172 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 7.4, 0.8 Hz, 1H), 7.97 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.82 (d, *J* = 2.6 Hz, 1H), 7.71 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.55 (d, *J* = 6.0 Hz, 1H), 7.15 (dd, *J* = 6.0, 4.0 Hz, 1H), 6.86 (dd, *J* = 7.4, 6.4 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 6.00 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 184.0, 148.8, 145.1, 140.7, 135.4, 133.4, 131.3, 130.6, 130.4, 128.6, 109.0, 102.0, 56.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2OS$ 243.0587; Found 243.0583.



1-(pyrrolidin-1-yl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)ethan-1-one (27)

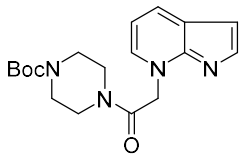
The title compound was prepared via general procedure, purified by flash chromatography on silica gel, eluted with MeOH/DCM = 1:40-1:10, yellow solid (28.3 mg, 62% yield), mp: 116-118 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.78 (d, *J* = 2.7 Hz, 1H), 7.74 (d, *J* = 5.7 Hz, 1H), 6.95 (dd, *J* = 7.5, 5.7 Hz, 1H), 6.66 (d, *J* = 2.7 Hz, 1H), 5.51 (s, 2H), 3.67 (t, *J* = 6.8 Hz, 2H), 3.47 (t, *J* = 6.8 Hz, 2H), 2.04-1.98 (m, 2H), 1.92-1.83 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 147.4, 142.4, 132.0, 131.8, 129.9, 109.9, 102.0, 53.8, 46.4, 46.1, 26.1, 24.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3O$ 230.1288; Found 230.1285.



1-morpholino-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)ethan-1-one (28)

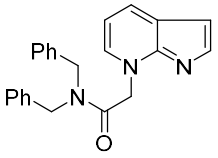
The title compound was prepared via general procedure, purified by flash chromatography on silica gel, eluted with MeOH/DCM = 1:40-1:10, yellow solid (32.8 mg, 67% yield), mp: 183-186 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.4 Hz, 1H), 7.81 (d, *J* = 2.6 Hz, 1H), 7.66 (d, *J* = 6.9 Hz, 1H), 6.89 (t, *J* = 6.9 Hz, 1H), 6.67 (d, *J* = 2.6 Hz, 1H), 5.49 (s, 2H), 3.71-3.58 (m, 8H). ^{13}C NMR

(75 MHz, $CDCl_3$) δ 164.3, 148.5, 144.6, 131.3, 130.5, 130.3, 109.1, 101.9, 66.6, 66.5, 52.0, 45.8, 42.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{16}N_3O_2$ 246.1237; Found 246.1240.



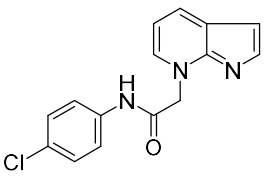
tert-butyl 4-(2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetyl)piperazine-1-carboxylate (29)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel, eluted with MeOH/DCM = 1:40-1:10, yellow solid (52.2 mg, 76% yield), mp: 134-136 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.4 Hz, 1H), 7.79 (d, *J* = 2.6 Hz, 1H), 7.64 (d, *J* = 6.2 Hz, 1H), 6.92-6.80 (m, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 5.47 (s, 2H), 3.64-3.53 (m, 4H), 3.49-3.39 (m, 4H), 1.47 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.4, 154.4, 148.4, 144.5, 131.3, 130.6, 130.3, 109.1, 101.9, 80.5, 52.2, 45.2, 42.2, 28.4. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{24}N_4NaO_3$ 367.1741; Found 367.1736.



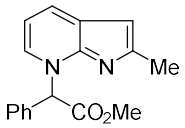
N,N-dibenzyl-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetamide (30)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel, eluted with MeOH/DCM = 1:40-1:10, yellow solid (55.3 mg, 78% yield), mp: 104-106 °C. ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.4, 1.0 Hz, 1H), 7.84 (d, *J* = 2.6 Hz, 1H), 7.62 (dd, *J* = 6.3, 1.0 Hz, 1H), 7.42-7.20 (m, 10H), 6.85 (dd, *J* = 7.4, 6.3 Hz, 1H), 6.66 (d, *J* = 2.6 Hz, 1H), 5.49 (s, 2H), 4.74 (s, 2H), 4.66 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 148.8, 145.1, 136.3, 135.9, 131.1, 130.6, 130.4, 129.2, 128.8, 128.4, 128.0, 127.7, 126.6, 108.8, 101.8, 52.4, 50.2, 49.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{22}N_3O$ 356.1757; Found 356.1759.



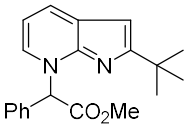
N-(4-chlorophenyl)-2-(7H-pyrrolo[2,3-b]pyridin-7-yl)acetamide (31)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel, eluted with MeOH/DCM = 1:40-1:10, yellow solid (40.4 mg, 71% yield), mp: 183-186 °C. ^1H NMR (300 MHz, DMSO) δ 10.84 (s, 1H), 8.27 (dd, *J* = 7.4, 0.9 Hz, 1H), 8.12 (d, *J* = 5.7 Hz, 1H), 7.66-7.59 (m, 3H), 7.38 (d, *J* = 9.0 Hz, 1H), 7.04 (dd, *J* = 7.4, 5.7 Hz, 1H), 6.61 (d, *J* = 2.6 Hz, 1H), 5.59 (s, 2H). ^{13}C NMR (75 MHz, DMSO) δ 165.3, 148.0, 143.7, 138.1, 133.2, 132.1, 129.6, 129.3, 127.6, 121.0, 109.4, 101.6, 55.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}ClN_3O$ 286.0742; Found 286.0741.



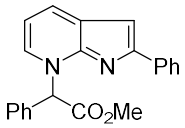
methyl 2-(2-methyl-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (32)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (48.7 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.2 Hz, 1H), 7.63 (s, 1H), 7.48-7.40 (m, 5H), 7.38 (d, *J* = 6.5 Hz, 1H), 6.69 (t, *J* = 6.5 Hz, 1H), 6.40 (s, 1H), 3.83 (s, 3H), 2.62 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 156.6, 149.6, 133.2, 131.7, 129.7, 129.5, 129.2, 127.9, 126.3, 108.7, 99.7, 64.2, 53.1, 18.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2$ 281.1285; Found 281.1285.



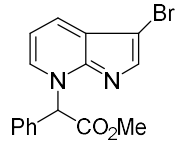
methyl 2-(2-(tert-butyl)-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (33)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (49.5 mg, 77% yield). ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 7.95 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.67-7.61 (m, 3H), 7.49-7.43 (m, 3H), 7.23 (s, 1H), 6.81 (t, *J* = 7.3 Hz, 1H), 6.33 (s, 1H), 3.74 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (75 MHz, DMSO-*d*$_6$) δ 169.1, 168.8, 148.4, 133.6, 131.1, 130.2, 130.0, 129.6, 129.1, 127.5, 108.9, 95.1, 65.8, 53.3, 34.3, 30.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{23}N_2O_2$ 323.1754; Found 323.1754.



methyl 2-phenyl-2-(2-phenyl-7H-pyrrolo[2,3-b]pyridin-7-yl)acetate (34)

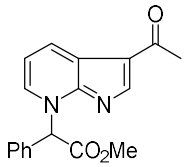
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (61.5 mg, 90% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.3 Hz, 2H), 7.94 (dd, *J* = 7.3, 1.1 Hz, 1H), 7.70 (s, 1H), 7.49-7.39 (m, 8H), 7.32-7.26 (m, 1H), 7.01 (s, 1H), 6.70 (t, *J* = 7.3, 1.1 Hz 1H), 3.84 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.3, 155.9, 150.0, 136.9, 133.0, 131.8, 129.8, 129.6, 129.4, 128.6, 127.8, 127.4, 126.8, 126.7, 109.2, 97.4, 64.5, 53.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{19}N_2O_2$ 343.1441; Found 343.1444.



methyl 2-(3-bromo-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (35)

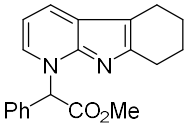
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (57.1 mg, 83% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.4 Hz, 1H), 7.81 (s, 1H), 7.58 (d, *J* = 6.4 Hz, 1H), 7.54 (s, 1H), 7.48-7.42 (m, 5H),

6.88 (t, *J* = 6.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 147.7, 143.8, 132.1, 130.8, 130.2, 129.7, 129.4, 129.2, 128.3, 109.5, 88.2, 64.3, 53.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2$ 345.0233; Found 345.0236.



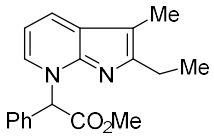
methyl 2-(3-acetyl-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (36)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (53.5 mg, 87% yield) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 7.4 Hz, 1H), 8.45 (s, 1H), 7.64 (d, *J* = 6.4 Hz, 1H), 7.58 (s, 1H), 7.51-7.42 (m, 5H), 7.07 (t, *J* = 6.4 Hz, 1H), 3.87 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.3, 168.6, 152.3, 151.2, 135.3, 131.8, 130.3, 129.9, 129.8, 129.4, 127.8, 118.7, 113.1, 65.2, 53.5, 27.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_3$ 309.1234; Found 309.1231.



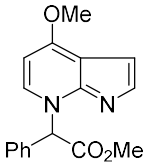
methyl 2-phenyl-2-(5,6,7,8-tetrahydro-1H-pyrido[2,3-b]indol-1-yl)acetate (37)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (53.1 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 1H), 7.63 (s, 1H), 7.42 (m, 5H), 7.37 (d, *J* = 4.0 Hz, 1H), 6.66 (t, *J* = 8.0 Hz, 1H), 3.82 (s, 3H), 2.99 (t, *J* = 4.0 Hz, 2H), 2.76 (t, *J* = 4.0 Hz, 2H), 2.00-1.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.3, 154.8, 149.1, 133.3, 130.1, 129.6 , 129.4 , 129.2 , 126.3 , 126.1 , 109.9 , 107.8 , 64.0 , 53.1 , 27.5 , 24.0 , 23.6 , 21.6. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{20}N_2NaO_2$ 343.1417; Found 343.1412.



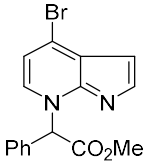
methyl 2-(2-ethyl-3-methyl-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (38)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (40 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 4.0 Hz, 1H), 7.60 (s, 1H), 7.43 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 1H), 6.73-6.61 (t, *J* = 8.0 Hz, 1H), 3.83 (d, *J* = 4.0 Hz, 3H), 2.89 (dd, *J* = 16.0, 8.0 Hz, 2H), 2.30 (s, 3H), 1.34 (dd, *J* = 16.0, 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 158.0, 148.3, 133.3, 131.7, 129.6, 129.4, 129.3, 126.4, 126.1, 107.6, 105.6, 63.9, 53.0, 23.1, 14.5, 8.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_2$ 309.1598; Found 309.1594.



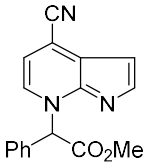
methyl 2-(4-methoxy-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (39)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (47.9 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 4.0 Hz, 1H), 7.49 (s, 1H), 7.46-7.42 (m, 5H), 7.40 (s, 1H), 6.77 (d, *J* = 4.0 Hz, 1H), 6.34 (d, *J* = 8.0 Hz, 1H), 4.12 (s, 3H), 3.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 161.4, 150.9, 140.6, 132.8, 130.6, 129.8, 129.6, 129.3, 114.8, 99.7, 96.5, 64.0, 56.9, 53.2. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{16}N_2NaO_3$ 319.1053; Found 319.1056.



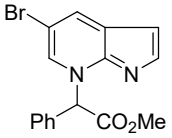
methyl 2-(4-bromo-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (40)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (58.4 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 2.4 Hz, 1H), 7.52 (s, 1H), 7.48-7.41 (m, 5H), 7.36 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 147.8, 145.6, 132.2, 130.9, 130.2, 129.7, 129.3, 127.9, 112.9, 103.0, 64.7, 53.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2$ 345.0233; Found 345.0230.



methyl 2-(4-cyano-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (41)

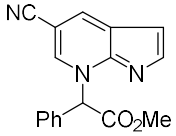
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (36.6 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 2.4 Hz, 1H), 7.65-7.59 (m, 2H), 7.52-7.43 (m, 5H), 7.03 (d, *J* = 6.7 Hz, 1H), 6.92 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 150.0, 149.3, 132.7, 131.6, 130.5, 129.9, 129.4, 127.3, 116.3, 111.5, 110.5, 102.0, 65.4, 53.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}N_3O_2$ 292.1081; Found 292.1079.



methyl 2-(5-bromo-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (42)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (51.6 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.92 (d, *J* = 2.4 Hz, 1H), 7.57 (d, *J* = 12.0 Hz, 2H), 7.51 - 7.43 (m, 5H), 6.66 (d, *J* =

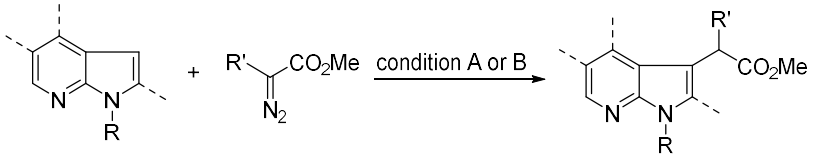
2.4 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 148.1, 147.3, 133.4, 131.9, 131.3, 130.3, 129.8, 129.4, 127.6, 102.1, 102.0, 65.0, 53.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2$ 345.0233; Found 345.0236.



methyl 2-(5-cyano-7H-pyrrolo[2,3-b]pyridin-7-yl)-2-phenylacetate (43)

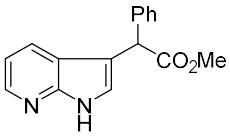
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:1, yellow oil (34.9 mg, 60% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, *J* = 1.4 Hz, 1H), 8.00 (d, *J* = 2.7 Hz, 1H), 7.84 (d, *J* = 1.4 Hz, 1H), 7.56-7.50 (m, 4H), 7.48-7.43 (m, 2H), 6.82 (d, *J* = 2.7 Hz, 1H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.3, 148.5, 148.2, 132.5, 131.4, 131.1, 130.8, 130.4, 130.1, 129.4, 117.4, 104.3, 94.1, 65.4, 53.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}N_3O_2$ 292.1081; Found 292.1079.

General procedure for Scheme 3



Condition A (R = H): Under argon atmosphere, to a dry tube was added 7-azaindole (0.2 mmol, 1 equiv), $AgNTf_2$ (0.01 mmol, 5 mol%) and MeCN (2 mL), then diazo compound (0.24 mmol, 1.2 equiv) in MeCN (2 mL) was added in a portion. The reaction was stirred at 80 °C in a heating block for 4 h, then another portion of diazo compound (0.16 mmol, 0.8 equiv) was added and stirred for further 3 h. The reaction mixture was cooled and concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether) to give desired product.

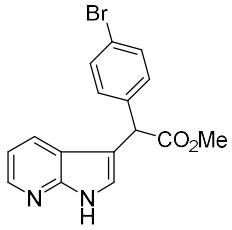
Condition B (R = Me): Under argon atmosphere, to a dry tube was added 7-azaindol (0.2 mmol, 1 equiv), $Rh_2(PTTL)_4$ (0.004 mmol, 2 mol%) and DCM (2 mL), then diazo compound (0.3 mmol, 1.5 equiv) in DCM (2 mL) was added in a portion. The reaction was stirred at rt for 0.5 h. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether) to give desired product.



methyl 2-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (4)

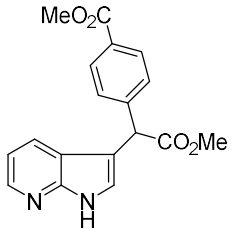
The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (23.9 mg, 45% yield), mp: 148-150 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 8.30 (d, *J* = 4.2 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.41 (s, 1H), 7.39-7.24 (m, 5H), 7.02 (m, 1H), 5.25 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 149.1, 142.6, 138.3, 128.7, 128.4, 128.0, 127.5, 124.4, 119.6, 115.6, 111.7,

52.4, 49.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1128; Found 267.1125.



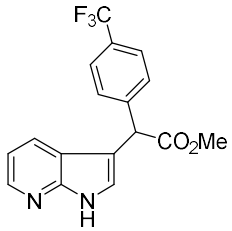
methyl 2-(4-bromophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (44)

The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (44.7 mg, 65% yield), mp: 145-147 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 11.51 (s, 1H), 8.32 (dd, *J* = 4.8, 1.1 Hz, 1H), 7.74 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.48-7.41 (m, 2H), 7.39 (s, 1H), 7.29-7.25 (m, 2H), 7.04 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.20 (s, 1H), 3.76 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 149.1, 142.8, 137.3, 131.8, 130.2, 127.9, 124.3, 121.5, 119.3, 115.8, 111.2, 52.5, 48.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}BrN_2O_2$ 345.0233; Found 345.0235.



methyl 4-(2-methoxy-2-oxo-1-(1H-pyrrolo[2,3-b]pyridin-3-yl)ethyl)benzoate (45)

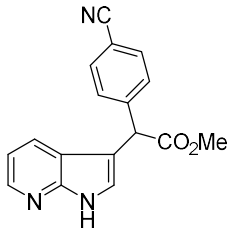
The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:3, white solid (36.9 mg, 57% yield), mp: 137-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.47 (s, 1H), 8.32 (d, *J* = 4.8 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 7.04 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.30 (s, 1H), 3.90 (s, 3H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 166.8, 149.1, 143.3, 142.9, 130.0, 129.4, 128.5, 127.9, 124.3, 119.3, 115.8, 111.0, 52.6, 52.2, 49.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_4$ 325.1183; Found 325.1183.



methyl 2-(1H-pyrrolo[2,3-b]pyridin-3-yl)-2-(4-(trifluoromethyl)phenyl)acetate (46)

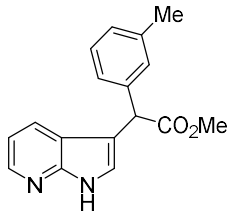
The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (33.4 mg, 50% yield), mp: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.23 (s, 1H), 8.33 (d, *J* = 4.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.41 (s, 1H), 7.09-7.02 (m, 1H), 5.30 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 149.0, 143.1, 142.2, 129.77 (q, C-F, $^2J_{C\text{-}F}$ =

32.4 Hz), 128.8, 127.8, 125.6 (q, C-F, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 124.2, 124.1 (q, C-F, $^{1}J_{C\text{-}F}$ = 270.0 Hz), 119.2, 115.9, 111.0, 52.6, 48.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.54. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}F_3N_2O_2$ 335.1002; Found 335.1003.



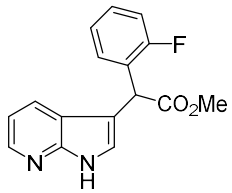
methyl 2-(4-cyanophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (47)

The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:6-1:3, white solid (32.5 mg, 56% yield), mp: 142-144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.33 (s, 1H), 8.34 (dd, *J* = 4.8, 1.4 Hz, 1H), 7.72 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.65-7.60 (m, 2H), 7.55-7.49 (m, 2H), 7.43 (s, 1H), 7.06 (dd, *J* = 7.9, 4.8 Hz, 1H), 5.29 (s, 1H), 3.78 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 149.0, 143.5, 143.1, 132.5, 129.3, 127.8, 124.3, 119.1, 118.6, 116.0, 111.5, 110.4, 52.7, 49.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{14}N_3O_2$ 292.1081; Found 292.1079.



methyl 2-(1H-pyrrolo[2,3-b]pyridin-3-yl)-2-(m-tolyl)acetate (48)

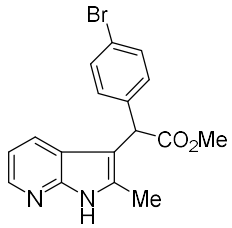
The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (23.5 mg, 42% yield), mp: 105-107 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.44 (s, 1H), 8.31 (d, *J* = 4.8 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.39 (s, 1H), 7.22-7.19 (m, 3H), 7.09 (m, 1H), 7.03 (dd, *J* = 8.0, 4.8 Hz, 1H), 5.20 (s, 1H), 3.76 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.2, 149.1, 142.7, 138.4, 138.1, 129.1, 128.5, 128.3, 127.9, 125.4, 124.2, 119.5, 115.7, 111.9, 52.4, 49.0, 21.5. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2$ 281.1285; Found 281.1288.



methyl 2-(2-fluorophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (49)

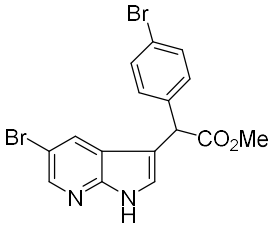
The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (23.8 mg, 42% yield), mp: 119-121 °C.^{1}H NMR (400 MHz, $CDCl_3$) δ 11.64 (s, 1H), 8.33 (d, *J* = 4.6 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.42 (s, 1H), 7.33-7.22 (m, 2H), 7.12-7.03 (m, 3H), 5.54 (s, 1H), 3.77 (s, 3H). ^{13}C NMR

(100 MHz, $CDCl_3$) δ 172.5, 160.4 (d, C-F, $^1J_{C\text{-}F}$ = 246.3 Hz), 149.0, 142.8, 130.0 (d, C-F, $^4J_{C\text{-}F}$ = 3.3 Hz), 129.1 (d, C-F, $^3J_{C\text{-}F}$ = 8.3 Hz), 128.0, 125.8 (d, C-F, $^3J_{C\text{-}F}$ = 14.6 Hz), 124.5, 124.3 (d, C-F, $^4J_{C\text{-}F}$ = 3.7 Hz), 119.4 (d, C-F, $^2J_{C\text{-}F}$ = 23.0 Hz), 115.9, 115.4 (d, C-F, $^2J_{C\text{-}F}$ = 22.0 Hz), 110.2, 52.6, 41.6. ^{19}F NMR (282 MHz, $CDCl_3$) δ -117.41. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{14}FN_2O_2$ 285.1034; Found 285.1038.



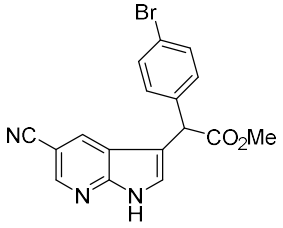
methyl 2-(4-bromophenyl)-2-(2-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (50)

The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (43.6 mg, 61% yield), mp: 143-145 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.39 (s, 1H), 8.22 (d, *J* = 3.6 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.43-7.38 (m, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.01 (m, 1H), 5.21 (s, 1H), 3.74 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.0, 148.4, 140.7, 137.5, 134.9, 131.5, 129.9, 128.0, 121.0, 120.6, 115.7, 106.0, 52.4, 47.4, 12.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}BrN_2O_2$ 359.0390; Found 359.0391.



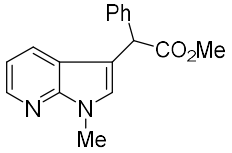
methyl 2-(5-bromo-1H-pyrrolo[2,3-b]pyridin-3-yl)-2-(4-bromophenyl)acetate (51)

The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (48.8 mg, 58% yield), mp: 154-156 °C.^{1}H NMR (300 MHz, $CDCl_3$) δ 11.22 (s, 1H), 8.34 (d, *J* = 2.2 Hz, 1H), 7.87 (d, *J* = 2.2 Hz, 1H), 7.48-7.45 (d, *J* = 9.0Hz, 2H), 7.38 (d, *J* = 2.2 Hz, 1H), 7.26-7.23 (d, *J* = 9.0Hz, 2H), 5.13 (s, 1H), 3.77 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 147.3, 143.5, 136.8, 131.9, 130.1, 130.0, 125.8, 121.7, 120.9, 111.6, 111.1, 52.7, 48.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{13}Br_2N_2O_2$ 422.9338; Found 422.9339.



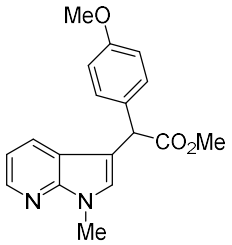
methyl 2-(4-bromophenyl)-2-(5-cyano-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (52)

The title compound was prepared via general procedure condition A, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:5-1:3, white solid (39.1 mg, 53% yield), mp: 169-172 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.97 (s, 1H), 8.58 (d, *J* = 2.0 Hz, 1H), 8.05 (d, *J* = 2.0 Hz, 1H), 7.53 (s, 1H), 7.49-7.46 (d, *J* = 9.0Hz, 2H), 7.26-7.23 (d, *J* = 9.0Hz, 2H), 5.17 (s, 1H), 3.79 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.0, 149.5, 145.8, 136.3, 132.3, 132.1, 129.9, 126.7, 122.1, 118.7, 118.3, 113.0, 101.4, 52.8, 48.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{13}BrN_3O_2$ 370.0186; Found 370.0183.



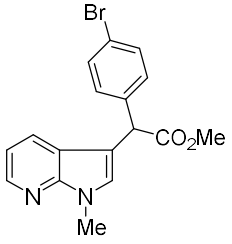
methyl 2-(1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-2-phenylacetate (53)

The title compound was prepared via general procedure condition B, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:10-1:4, yellow oil (41.4 mg, 74% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 4.6 Hz, 1.0 Hz, 1H), 7.71 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.43-7.27 (m, 5H), 7.17 (s, 1H), 6.98 (dd, *J* = 8.0, 4.6 Hz, 1H), 5.21 (s, 1H), 3.85 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.1, 148.0, 143.2, 138.2, 128.7, 128.4, 127.9, 127.5, 127.49, 119.4, 115.4, 110.6, 52.4, 48.9, 31.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{17}N_2O_2$ 281.1285; Found 281.1280.



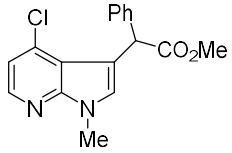
methyl 2-(4-methoxyphenyl)-2-(1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (54)

The title compound was prepared via general procedure condition B, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:10-1:4, yellow oil (32.2 mg, 52% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (dd, *J* = 4.7, 1.4 Hz, 1H), 7.70 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.33-7.28 (m, 2H), 7.15 (s, 1H), 6.99 (dd, *J* = 7.9, 4.7 Hz, 1H), 6.89-6.84 (m, 2H), 5.15 (s, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 158.9, 148.0, 143.1, 130.3, 129.4, 127.8, 127.5, 119.4, 115.4, 114.0, 110.9, 55.3, 52.4, 48.1, 31.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{19}N_2O_3$ 311.1390; Found 311.1390.



methyl 2-(4-bromophenyl)-2-(1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (55)

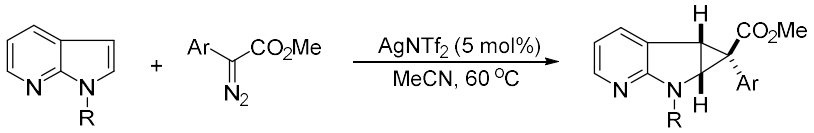
The title compound was prepared via general procedure, condition B, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:10-1:4, white solid (60.8 mg, 85% yield), mp: 88-90 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 4.6, 1.0 Hz, 1H), 7.68 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.17 (s, 1H), 6.99 (dd, *J* = 7.9, 4.6 Hz, 1H), 5.16 (s, 1H), 3.86 (s, 3H), 3.75 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.7, 148.0, 143.3, 137.3, 131.8, 130.1, 127.9, 127.4, 121.5, 119.2, 115.5, 109.9, 52.5, 48.4, 31.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}BrN_2O_2$ 359.0390; Found 359.0393.



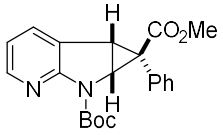
methyl 2-(4-chloro-1-methyl-1H-pyrrolo[2,3-b]pyridin-3-yl)-2-phenylacetate (56)

The title compound was prepared via general procedure condition B, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:10-1:4, white solid (51.4 mg, 82% yield), mp: 87-89 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (d, *J* = 5.2 Hz, 1H), 7.40-7.28 (m, 5H), 7.00 (d, *J* = 5.2 Hz, 1H), 6.97 (s, 1H), 5.70 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.6, 148.9, 143.3, 138.2, 135.8, 129.6, 128.8, 128.5, 127.5, 117.0, 116.6, 111.5, 52.5, 48.9, 31.6. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{16}ClN_2O_2$ 315.0895; Found 315.0895.

General procedure for scheme 4



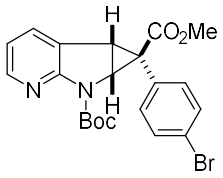
Under argon atmosphere, to a dry tube was added 7-azaindole (0.2 mmol, 1 equiv), $AgNTf_2$ (0.01 mmol, 5 mol%) and MeCN (2 mL), then diazo compound (0.2 mmol, 1 equiv) in MeCN (2 mL) was added in a portion. The reaction was stirred at 60 °C in a heating block for 4 h, then another portion of diazo compound (0.2 mmol, 1 equiv) was added and stirred at 60 °C for further 2 h. The reaction mixture was cooled and concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether) to give desired product.



6-(tert-butyl) 5-methyl 5-phenyl-5,5a-dihydrocyclopropa[4,5]pyrrolo[2,3-b]pyridine-5,6(4bH)-dicarboxylate (57)

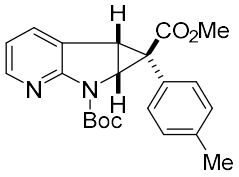
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, white solid (46 mg, 63% yield), mp: 150-152 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.66 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.10-7.05 (m, 3H), 7.03-6.95 (m, 2H), 6.79 (dd, *J* = 7.4, 5.1 Hz, 1H), 4.88 (d, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 3.65 (d, *J* = 7.1 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 155.6, 150.2, 147.5, 133.4,

132.1, 129.6, 128.1, 127.8, 122.7, 117.4, 82.6, 53.0, 49.0, 32.0, 31.6, 28.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{23}N_2O_4$ 367.1652; Found 367.1656.



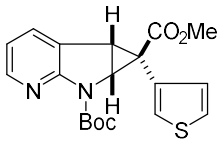
6-(tert-butyl) 5-methyl 5-(4-bromophenyl)-5,5a-dihydrocyclopropa[4,5]pyrrolo[2,3-b]pyridine-5,6(4bH)-dicarboxylate (58)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, white solid (63.8 mg, 72% yield), mp: 190-192 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (m, 1H), 7.66 (m, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 6.87 (s, 1H), 6.86-6.79 (m, 2H), 4.88 (d, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 3.65 (d, *J* = 7.1 Hz, 1H), 1.65 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 155.5, 150.1, 147.8, 133.7, 133.5, 131.4, 128.8, 122.3, 122.1, 117.6, 82.9, 53.0, 49.0, 32.0, 31.0, 28.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{22}BrN_2O_4$ 445.0757; Found 445.0757.



6-(tert-butyl) 5-methyl 5-(p-tolyl)-5,5a-dihydrocyclopropa[4,5]pyrrolo[2,3-b]pyridine-5,6(4bH)-dicarboxylate (59)

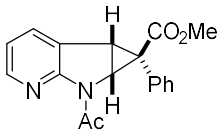
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, yellow oil (44 mg, 58% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 5.1, 1.6 Hz, 1H), 7.65 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.87 (s, 4H), 6.80 (dd, *J* = 7.4, 5.1 Hz, 1H), 4.85 (d, *J* = 7.1 Hz, 1H), 3.68 (s, 3H), 3.62 (d, *J* = 7.1 Hz, 1H), 2.16 (s, 3H), 1.65 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.4, 155.7, 150.2, 147.4, 137.4, 133.4, 131.9, 128.9, 126.4, 122.8, 117.4, 82.6, 52.9, 49.1, 32.0, 31.3, 28.3, 21.2. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}N_2O_4$ 381.1809; Found 381.1808.



6-(tert-butyl) 5-methyl 5-(thiophen-3-yl)-5,5a-dihydrocyclopropa[4,5]pyrrolo[2,3-b]pyridine-5,6(4bH)-dicarboxylate (60)

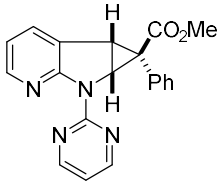
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, yellow oil (40.2 mg, 54% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.64 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.02 (m, 1H), 6.85-6.77(m, 2H), 6.71 (dd, *J* = 5.0, 1.6 Hz, 1H), 4.83 (d, *J* = 7.1 Hz, 1H), 3.70 (s, 3H), 3.63 (d, *J* = 7.1 Hz, 1H), 1.63 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 155.9, 150.2, 147.6, 133.1, 129.7, 129.5, 127.1, 124.8,

122.6, 117.5, 82.7, 52.95, 49.2, 32.3, 28.4, 26.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}N_2O_4S$ 373.1217; Found 373.1213.



methyl 6-acetyl-5-phenyl-4b,5,5a,6-tetrahydrocyclopropa[4,5]pyrrolo[2,3-b]pyridine-5-carboxylate (61)

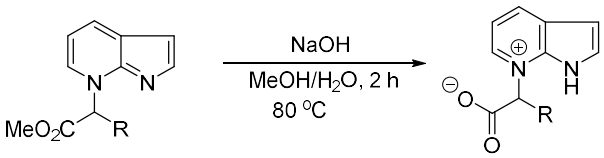
The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:8-1:2, white solid (43.6 mg, 71% yield), mp: 146-148 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.0, 1.6 Hz, 1H), 7.69 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.11-7.01 (m, 3H), 7.00-6.88 (m, 2H), 6.84 (dd, *J* = 7.4, 5.0 Hz, 1H), 5.13 (d, *J* = 6.9 Hz, 1H), 3.69 (d, *J* = 6.9 Hz, 1H), 3.66 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.8, 170.9, 154.6, 146.3, 133.9, 132.2, 129.7, 127.9, 127.6, 123.9, 118.0, 52.9, 47.9, 32.8, 31.1, 25.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{17}N_2O_3$ 309.1234;Found 309.1235. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{16}N_2NaO_3$ 331.1053; Found 331.1054.



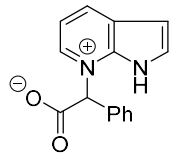
methyl 5-phenyl-6-(pyrimidin-2-yl)-4b,5,5a,6-tetrahydrocyclopropa[4,5]pyrrolo[2,3-b]pyridine-5-carboxylate (62)

The title compound was prepared via general procedure, purified by flash chromatography on silica gel eluting with EtOAc/PE = 1:6-1:1, white solid (43.2 mg, 63% yield), mp: 142-144 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (d, *J* = 6.0 Hz, 2H), 8.11 (dd, *J* = 6.0, 1.6 Hz, 1H), 7.71 (dd, *J* = 7.4, 1.6 Hz, 1H), 6.00-6.87 (m, 6H), 6.79 (dd, *J* = 7.4, 6.0 Hz, 1H), 5.35 (d, *J* = 7.1 Hz, 1H), 3.78 (d, *J* = 7.1 Hz, 1H), 3.70 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.7, 158.3, 158.2, 155.7, 147.3, 133.6, 132.2, 129.8, 127.9, 127.5, 123.8, 116.7, 114.7, 52.9, 50.5, 32.1, 31.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{17}N_4O_2$ 345.1346;Found 345.1349.

General procedure for scheme 5

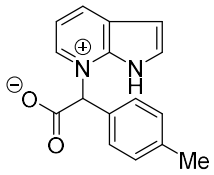


To a solution of NaOH (0.6 mmol, 3 equiv) in MeOH: H_2O (1:1, 3 ml) was added 7-alkylated azaindole (0.2 mmol, 1 equiv), the reaction solution was stirred at 80 °C in a heating block for 2 h under argon atmosphere. Then the reaction was cooled and concentrated under vacuum, the residue was acidified with HCl to adjust pH = 5~6 and extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum to give desired product.



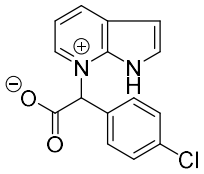
2-phenyl-2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)acetate (63)

The title compound was prepared via general procedure, pale yellow solid (47.8 mg, 95% yield), mp: 112-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.5 Hz, 1H), 7.99 (d, *J* = 6.2 Hz, 1H), 7.62 (m, 2H), 7.45-7.29 (m, 5H), 7.13 (m, 1H), 6.53 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.9, 140.2, 135.2, 134.4, 134.0, 130.8, 130.7, 129.5, 129.4, 127.0, 114.6, 102.7, 71.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{13}N_2O_2$ 253.0972; Found 253.0973



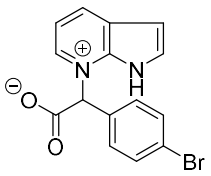
2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)-2-(p-tolyl)acetate (64)

The title compound was prepared via general procedure, pale yellow solid (51 mg, 96% yield), mp: 102-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 6.3 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.35 (s, 2H), 7.23-7.16 (m, 3H), 6.60 (d, *J* = 3.3 Hz, 1H), 2.37 (s, 3H).^{13}C NMR ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.8, 140.3, 139.5, 134.8, 134.0, 131.6, 130.9, 130.78, 130.0, 127.1, 114.4, 102.5, 71.9, 21.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1128; Found 267.1125



2-(4-chlorophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)acetate (65)

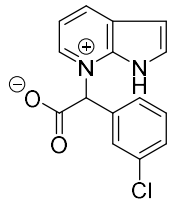
The title compound was prepared via general procedure, pale yellow solid (54.3 mg, 95% yield), mp: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 6.3 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 2.9 Hz, 1H), 7.36 (s, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.21 (m, 1H), 6.61 (d, *J* = 2.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 140.2, 135.6, 135.3, 134.1, 133.3, 132.0, 130.8, 129.5, 127.2, 114.7, 102.9, 70.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}ClN_2O_2$ 287.0582; Found 287.0583



2-(4-bromophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)acetate (66)

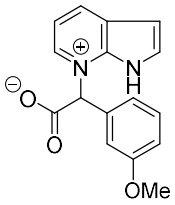
The title compound was prepared via general procedure, pale yellow solid (63.3 mg, 96% yield), mp: 111-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 6.3 Hz, 1H),

7.51 (s, 4H), 7.46 (d, J = 3.0 Hz, 1H), 7.37 (s, 1H), 7.26-7.21 (m, 1H), 6.66 (d, J = 3.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 140.3, 135.2, 134.0, 133.8, 132.5, 132.4, 130.9, 127.3, 124.0, 114.6, 102.9, 71.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}BrN_2O_2$ 331.0077; Found 331.0073.



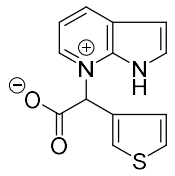
2-(3-chlorophenyl)-2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)acetate (67)

The title compound was prepared via general procedure, pale yellow solid (53.1 mg, 93% yield), mp: 114-116 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 7.7 Hz, 1H), 8.06 (d, J = 6.4 Hz, 1H), 7.63 (s, 1H), 7.53 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 3.3 Hz, 1H), 7.38 (s, 1H), 7.35-7.28 (m, 2H), 7.22 (t, J = 7.7 Hz, 1H), 6.62 (d, J = 3.3 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 140.2, 136.7, 135.4, 135.2, 134.2, 130.8, 130.6, 130.5, 129.7, 128.9, 127.2, 114.7, 103.0, 71.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}ClN_2O_2$ 287.0582; Found 287.0587.



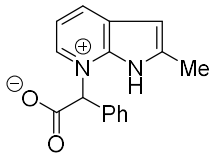
2-(3-methoxyphenyl)-2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)acetate (68)

The title compound was prepared via general procedure, pale yellow solid (53 mg, 94% yield), mp: 140-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 7.5 Hz, 1H), 8.10 (d, J = 6.0 Hz, 1H), 7.45 – 7.27 (m, 4H), 7.22 (t, J = 7.5 Hz, 1H), 7.16 (s, 1H), 6.94 (d, J = 7.5 Hz, 1H), 6.63 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 160.3, 140.3, 135.8, 134.9, 134.0, 131.0, 130.4, 127.1, 123.0, 116.0, 115.7, 114.5, 102.6, 72.0, 55.4. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_3$ 283.1077; Found 283.1079.



2-(1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)-2-(thiophen-3-yl)acetate (69)

The title compound was prepared via general procedure, pale yellow solid (47.4 mg, 92% yield), mp: 119-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 6.3 Hz, 1H), 7.76 (d, J = 1.7 Hz, 1H), 7.42 (d, J = 3.3 Hz, 1H), 7.40-7.33 (m, 2H), 7.27-7.21 (m 2H), 6.64 (d, J = 3.3 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.6, 140.1, 135.1, 134.7, 134.0, 130.8, 128.6, 128.5, 127.3, 127.1, 114.6, 102.7, 67.0. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{11}N_2O_2S$ 259.0536; Found 259.0534.

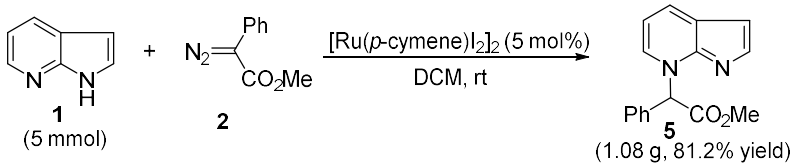


2-(2-methyl-1H-pyrrolo[2,3-b]pyridin-7-ium-7-yl)-2-phenylacetate (70)

The title compound was prepared via general procedure, pale yellow solid (51 mg, 96% yield), mp: 120-121 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.5 Hz, 1H), 7.87 (d, *J* = 6.3 Hz, 1H), 7.71-7.64 (m, 2H), 7.43-7.37 (m, 4H), 7.10 (dd, *J* = 7.5, 6.3 Hz, 1H), 6.30 (d, *J* = 0.9 Hz, 1H), 2.50 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 143.8, 140.6, 134.8, 132.5, 132.3, 130.7, 129.4, 129.3, 128.0, 114.3, 100.3, 71.8, 13.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{16}H_{15}N_2O_2$ 267.1128; Found 267.1127

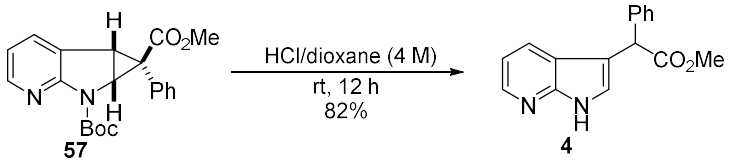
Further Elaboration for Scheme 6

1. Scheme 6-a



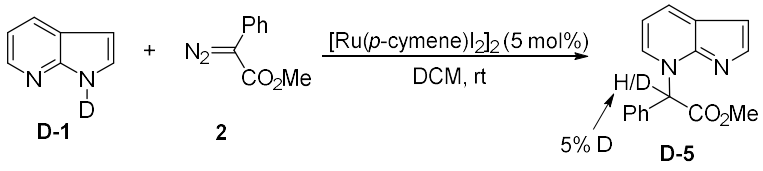
Under argon atmosphere, to a dry tube was added **1** (5 mmol, 1 equiv), [Ru(*p*-cymene) I_2]$_2$ (0.25 mmol, 5 mol%) and DCM (25 mL), then **2** (10 mmol, 2 equiv) in DCM (25 mL) was added via a syringe pump over 2 h at room temperature. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:5 to 1:1) to give **5** (1.08 g, 81.2% yield).

2. Scheme 6-b



To a solution of **57** (126 mg) in dioxane (2 mL) was added 4 M solution of HCl in dioxane (3 mL). The reaction solution was stirred at rt for 12 h. The reaction was basified with sat. $NaHCO_3$ and extracted with EtOAc, dried over Na_2SO_4, filtered and concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc/PE = 1:5-1:2) to give **4** as white solid (75 mg, 82% yield), mp: 147-149 °C.

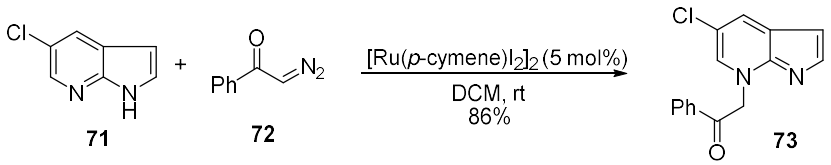
3. Scheme 6-c



The **D-1** was synthesized by dissolving 7-azaindole in CH_3OD, and then CH_3OD was gradually evaporated under vacuum. This procedure was repeated three times and give the product as white solid mp: 105-107 °C (98% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.09 (s, 1H), 8.36 (d, *J* = 4.0 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.41 (d, *J* = 4.0 Hz, 1H), 7.09 (dd, *J* = 8.0, 4.0 Hz, 1H), 6.51 (d, *J* = 4.0 Hz, 1H).

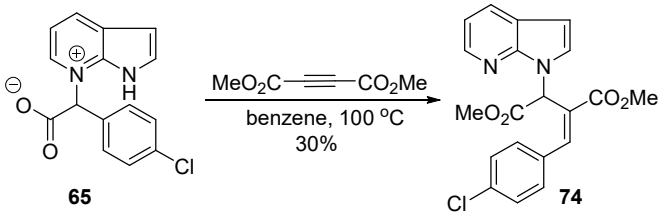
Under argon atmosphere, to a dry tube was added **D-1** (0.2 mmol, 1 equiv), [Ru(*p*-cymene)I_2]$_2$ (0.01 mmol, 5 mol%) and DCM (1 mL). Then **2** (0.4 mmol, 2 equiv) in DCM (1 mL) was added via a syringe pump over 2 h at room temperature. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether= 1:5-1:1) to give **D-5** as yellow oil (82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.3 Hz, 1H), 7.90 (d, *J* = 2.6 Hz, 1H), 7.62 (s, 1H), 7.51 (d, *J* = 6.5 Hz, 1H), 7.46 (s, 5H), 6.80 (t, *J* = 6.5 Hz, 1H), 6.71 (d, *J* = 2.6 Hz,1H), 3.85 (s, 3H).

4. Scheme 6-d



Under argon atmosphere, to a dry tube was added **71** (0.2 mmol, 1 equiv), [Ru(*p*-cymene)I_2]$_2$ (0.01 mmol, 5 mol%) and DCM (1 mL). Then **72** (0.4 mmol, 2 equiv) in DCM (1 mL) was added via a syringe pump over 2 h at room temperature. The reaction mixture was concentrated under vacuum, the residue was purified by column chromatography (silica gel, eluted with MeOH/DCM = 1:40-1:10) to give **73** yellow solid (46.4 mg, 86% yield), mp: 178-180 °C. ^{1}H NMR (300 MHz, CDCl3) δ 8.04 (d, J = 1.7 Hz, 1H), 8.02-7.97 (m, 2H), 7.83 (d, J = 2.6 Hz, 1H), 7.67-7.59 (m, 1H), 7.56 (d, J = 1.7 Hz, 1H), 7.52-7.45 (m, 2H), 6.61 (d, J = 2.6 Hz, 1H), 6.01 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.3, 148.0, 147.6, 134.6, 134.0, 131.0, 130.9, 129.1, 128.3, 128.2, 116.0, 102.0, 57.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{12}ClN_2O$ 271.0633; Found 271.0634

5. Scheme 6-e



Under argon atmosphere, to a dry tube was added **65** (0.2 mmol, 1 equiv), Dimethyl acetylenedicarboxylate (0.4 mmol, 2 equiv) and benzene (2 mL). Then the reaction mixture was stirred at 100 °C in a heating block for 10 h. The reaction mixture was cooled and concentrated under vacuum. The residue was purified by column chromatography (silica gel, eluted with EtOAc/PE = 1:10-1:3) to give **74** as a white solid (23 mg, 30% yield), mp: 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 4.7, 1.3 Hz, 1H), 8.06 (s, 1H), 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.52 (d, *J* = 3.7 Hz, 1H), 7.29-7.26 (m,2H), 7.22-7.19 (m, 2H), 7.08 (dd, *J* = 7.8, 4.7 Hz, 1H), 6.82 (s, 1H), 6.52 (d, *J* = 3.7 Hz, 1H), 3.92 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6,

167.3, 147.4, 145.1, 142.6, 136.0, 132.0, 130.9, 129.0, 128.95, 128.1, 127.5, 120.4, 116.5, 101.0, 53.0, 52.9, 52.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{18}ClN_2O_4$ 385.0950; Found 385.0951.

X-ray crystallographic data for 4, 6, 55, 58, 64,73, and 74.

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2034092 (**4**), 2035508 (**6**), 2034553 (**55**), 2034093 (**58**), 2034094 (**64**), 2040738 (**73**) and 2034095 (**74**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via the internet at https://www.ccdc.cam.ac.uk/structures/

The measurements were taken in a Bruker APEX-II CCD diffractometer. The data were integrated by Bruker APEX2 with multi-scan absorption corrections. The structure solution and refinement were processed by SHELXL (2018/3)

X-ray crystallographic data for 4

Method of crystallization: A solution of **4** in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 4

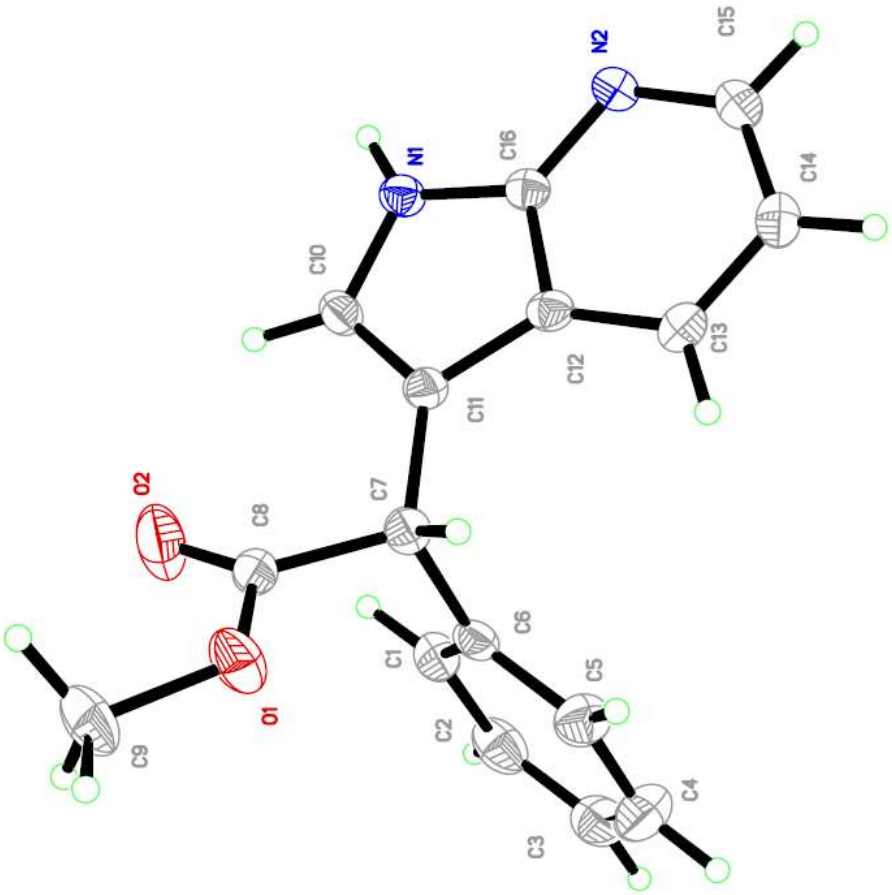


Figure S1. ORTEP diagram of compound **4**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{16}H_{14}N_2O_2$	
Formula weight	266.29	
Temperature	193 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 5.8443(2) Å	α = 90 °
	b = 31.3990(11) Å	β = 108.2680(10) °
	c = 7.7003(3) Å	γ = 90 °
Volume	1341.83(8) $Å^3$	
Z	4	
Density (calculated)	1.318 g/cm^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	560.0	
Crystal size	0.170 x 0.140 x 0.110 mm^3	
θ range for data collection	2.595 to 25.010 °	
Index ranges	$-6 \leq h \leq 6$, $-37 \leq k \leq 36$, $-9 \leq l \leq 8$	
Reflections collected	9943	
Independent reflections	2332 (R_{int} = 0.0287)	
Completeness to θ = 25.010 °	99.1 %	
Max. and min. transmission	0.990 and 0.985	
Data / restraints / parameters	2332 / 0 / 182	
Goodness-of-fit on F^2	1.055	
Final R indices [I > 2σ(I)]	R_1 = 0.0571, wR_2 = 0.1482	
R indices (all data)	R_1 = 0.0657, wR_2 = 0.1566	
Largest diff. peak and hole	0.570 and -0.238 $e.Å^{-3}$	

X-ray crystallographic data for 6

Method of crystallization: A solution of **6** in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 6

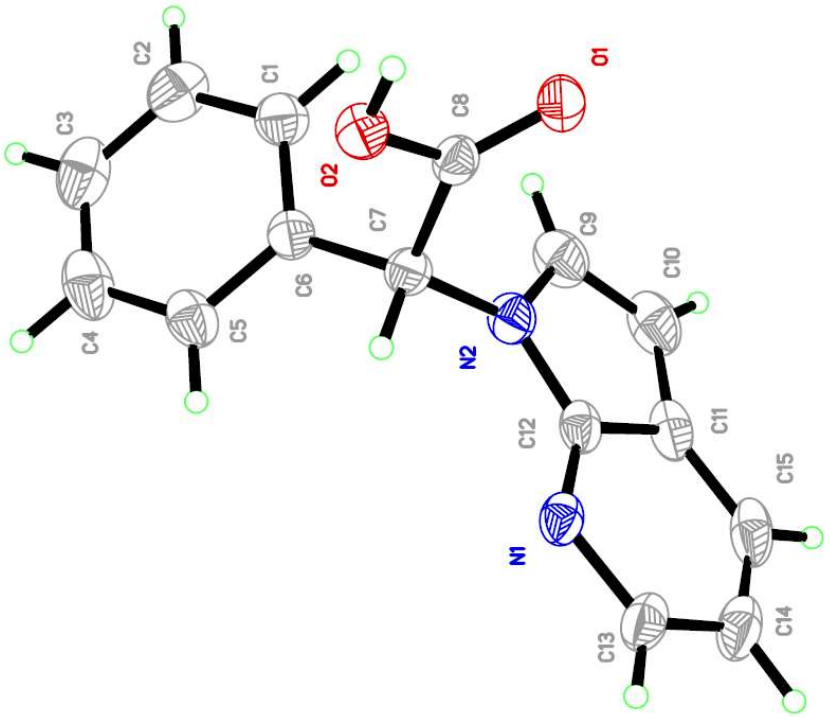


Figure S2. ORTEP diagram of compound **6**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{15}H_{12}N_2O_2$	
Formula weight	252.27	
Temperature	173 K	
Wavelength	1.34139 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.6611(9) Å	α = 90 °
	b = 13.3281(9) Å	β = 93.446(4) °
	c = 7.5812(6) Å	γ = 90 °
Volume	1277.00(16) $Å^3$	
Z	4	
Density (calculated)	1.312 g/cm^3	
Absorption coefficient	0.461 mm^{-1}	
F(000)	528.0	
Crystal size	0.120 x 0.110 x 0.080 mm^3	
θ range for data collection	3.042 to 52.999 °	
Index ranges	$-14 \leq h \leq 15$, $-15 \leq k \leq 15$, $-7 \leq l \leq 9$	
Reflections collected	8999	
Independent reflections	2228 (R_{int} = 0.0744)	
Completeness to θ = 52.999 °	99.5 %	
Max. and min. transmission	0.964 and 0.947	
Data / restraints / parameters	2228 / 0 / 174	
Goodness-of-fit on F^2	1.050	

Final R indices [I > 2σ(I)]	R_1 = 0.0528, wR_2 = 0.1360
R indices (all data)	R_1 = 0.0626, wR_2 = 0.1462
Largest diff. peak and hole	0.258 and -0.256 e.Å^{-3}

X-ray crystallographic data for 55

Method of crystallization: A solution of **55**in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 55

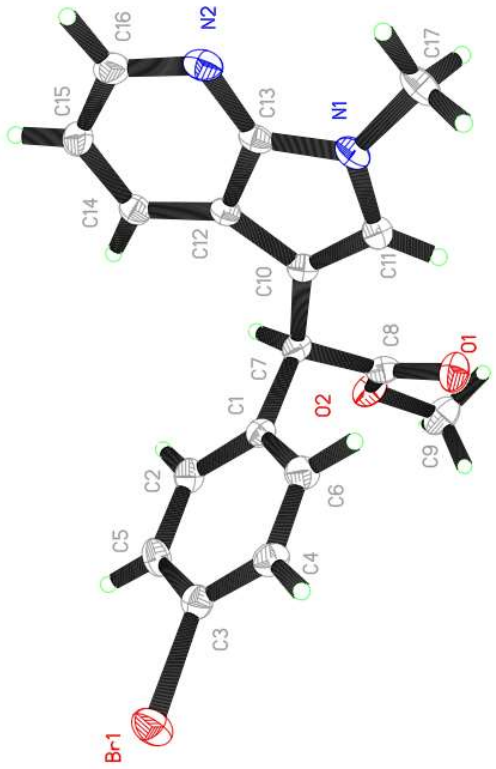


Figure S3. ORTEP diagram of compound **55**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{17}H_{15}BrN_2O_2$	
Formula weight	359.22	
Temperature	190 K	
Wavelength	1.34139 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 13.2878(5) Å	α = 90 °
	b = 11.0469(4) Å	β = 92.611(2) °
	c = 10.6436(4) Å	γ = 90 °
Volume	1560.74(10) Å^3	
Z	4	
Density (calculated)	1.529 g/cm^3	
Absorption coefficient	2.416 mm^{-1}	

F(000)	728.0
Crystal size	0.160 x 0.140 x 0.100 mm^3
θ range for data collection	2.896 to 53.877 °
Index ranges	$-16 \leq h \leq 15$, $-13 \leq k \leq 13$, $-12 \leq l \leq 12$
Reflections collected	14458
Independent reflections	2835 (R_{int} = 0.0431)
Completeness to θ = 53.594 °	99.5 %
Max. and min. transmission	0.794 and 0.699
Data / restraints / parameters	2835 / 0 / 201
Goodness-of-fit on F^2	0.857
Final R indices [I > 2σ(I)]	R_1 = 0.0341, wR_2 = 0.1107
R indices (all data)	R_1 = 0.0399, wR_2 = 0.1197
Largest diff. peak and hole	0.473 and - -0.461 e.$Å^{-3}$

X-ray crystallographic data for 58

Method of crystallization: A solution of **58** in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 58

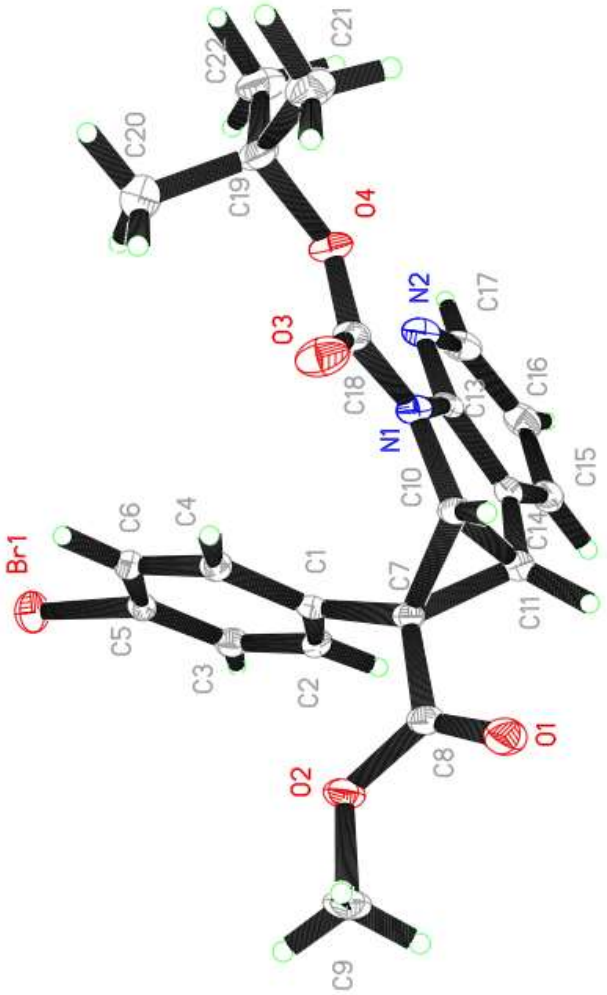


Figure S4. ORTEP diagram of compound **58**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{21}H_{21}BrN_2O_4$	
Formula weight	445.31	
Temperature	190 K	
Wavelength	1.34139 Å	
Crystal system	monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.9652(2) Å	α = 90 °
	b = 14.7093(4) Å	β = 97.0610(10) °
	c = 15.4216(4) Å	γ = 90 °
Volume	2018.25(9) $Å^3$	
Z	4	
Density (calculated)	1.466 g/cm^3	
Absorption coefficient	1.991 mm^{-1}	
F(000)	912.0	
Crystal size	0.220 x 0.200 x 0.160 mm^3	
θ range for data collection	3.626 to 53.897 °	
Index ranges	$-10 \leq h \leq 9$, $-16 \leq k \leq 17$, $-18 \leq l \leq 18$	

Reflections collected	14751
Independent reflections	3674 (R_{int} = 0.0355)
Completeness to θ = 53.594 °	99.5 %
Max. and min. transmission	0.741 and 0.669
Data / restraints / parameters	3674 / 0 / 257
Goodness-of-fit on F^2	0.847
Final R indices [I > 2σ(I)]	R_1 = 0.0346, wR_2 = 0.1118
R indices (all data)	R_1 = 0.0410, wR_2 = 0.1209
Largest diff. peak and hole	0.286 and -0.645 e.Å^{-3}

X-ray crystallographic data for 64

Method of crystallization: A solution of **64** in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 64

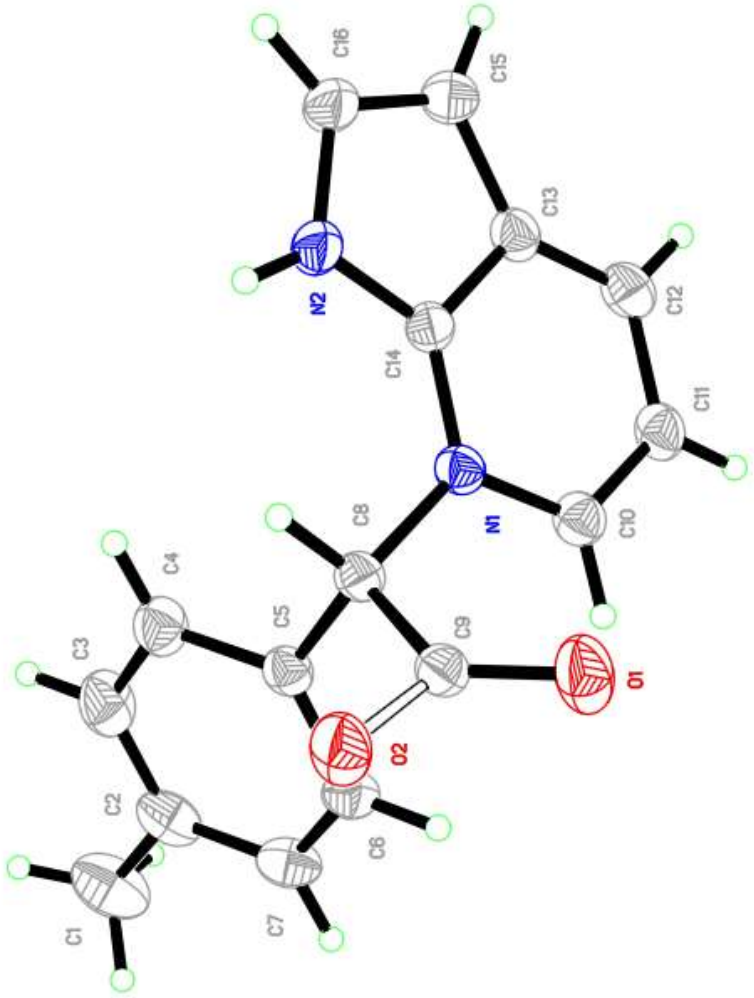


Figure S5. ORTEP diagram of compound **64**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{16}H_{14}N_2O_2$

Formula weight	272.48	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.5513(6) Å	α = 90 °
	b = 15.9964(8) Å	β = 95.314(2) °
	c = 21.2020(10) Å	γ = 90 °
Volume	3225.5(3) $Å^3$	
Z	8	
Density (calculated)	1.122 g/cm^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	1141	
Crystal size	0.180 x 0.130 x 0.110 mm^3	
θ range for data collection	2.312 to 25.009 °	
Index ranges	$-11 \leq h \leq 10$, $-19 \leq k \leq 19$, $-25 \leq l \leq 24$	
Reflections collected	24006.0	
Independent reflections	5660 (R_{int} = 0.0429)	
Completeness to θ = 25.009 °	99.5 %	
Max. and min. transmission	0.992 and 0.986	
Data / restraints / parameters	5660 / 12 / 391	
Goodness-of-fit on F^2	1.132	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0930, wR_2 = 0.2047	
R indices (all data)	R_1 = 0.1209, wR_2 = 0.2188	
Largest diff. peak and hole	0.796 and -0.652 $e.Å^{-3}$	

X-ray crystallographic data for 73

Method of crystallization: A solution of **73** in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 73

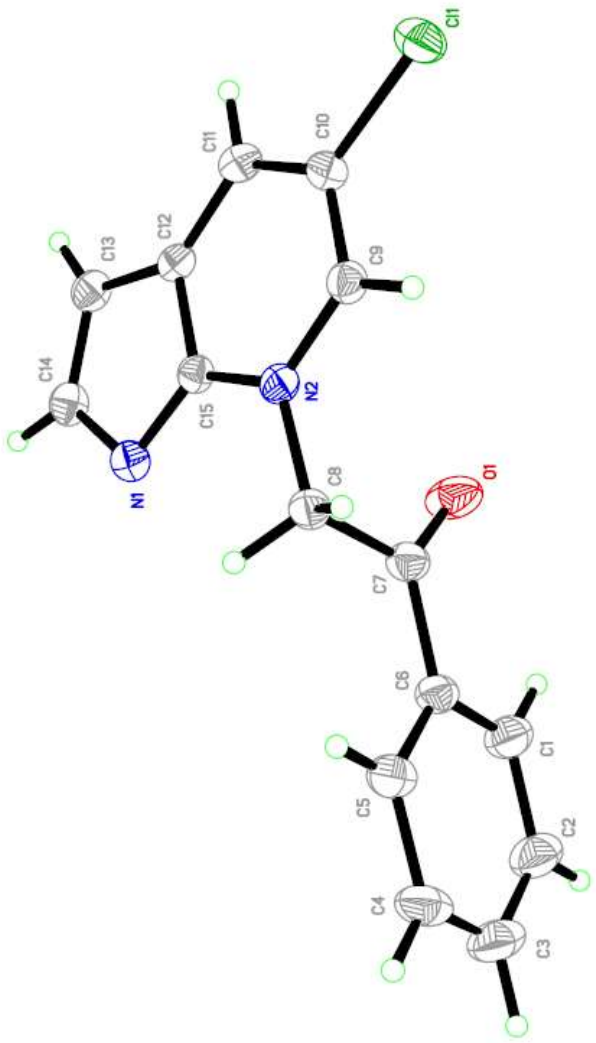


Figure S6. ORTEP diagram of compound **73**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{15}H_{11}ClN_2O$	
Formula weight	270.71	
Temperature	193 K	
Wavelength	1.34139 Å	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.9833(2) Å	α = 90 °
	b = 10.7873 (3) Å	β = 90 °
	c = 13.3896(4) Å	γ = 90 °
Volume	1297.53(6) $Å^3$	
Z	4	
Density (calculated)	1.386 g/cm^3	
Absorption coefficient	1.677 mm^{-1}	
F(000)	560	
Crystal size	0.120 x 0.110 x 0.090 mm^3	
θ range for data collection	4.579 to 62.054 °	
Index ranges	$-11 \leq h \leq 10$, $-13 \leq k \leq 13$, $-17 \leq l \leq 16$	

Reflections collected	12798
Independent reflections	3038 (R_{int} = 0.0680)
Completeness to θ = 53.594 °	98.9 %
Max. and min. transmission	0.864 and 0.824
Data / restraints / parameters	3038 / 0 / 172
Goodness-of-fit on F^2	1.022
Final R indices [I > 2σ(I)]	R_1 = 0.0339, wR_2 = 0.0816
R indices (all data)	R_1 = 0.0501, wR_2 = 0.0877
Largest diff. peak and hole	0.155 and -0.221 e.Å^{-3}

X-ray crystallographic data for 74

Method of crystallization: A solution of **74** in DCM/PE was added to a 5 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

Crystal data and structure for 74

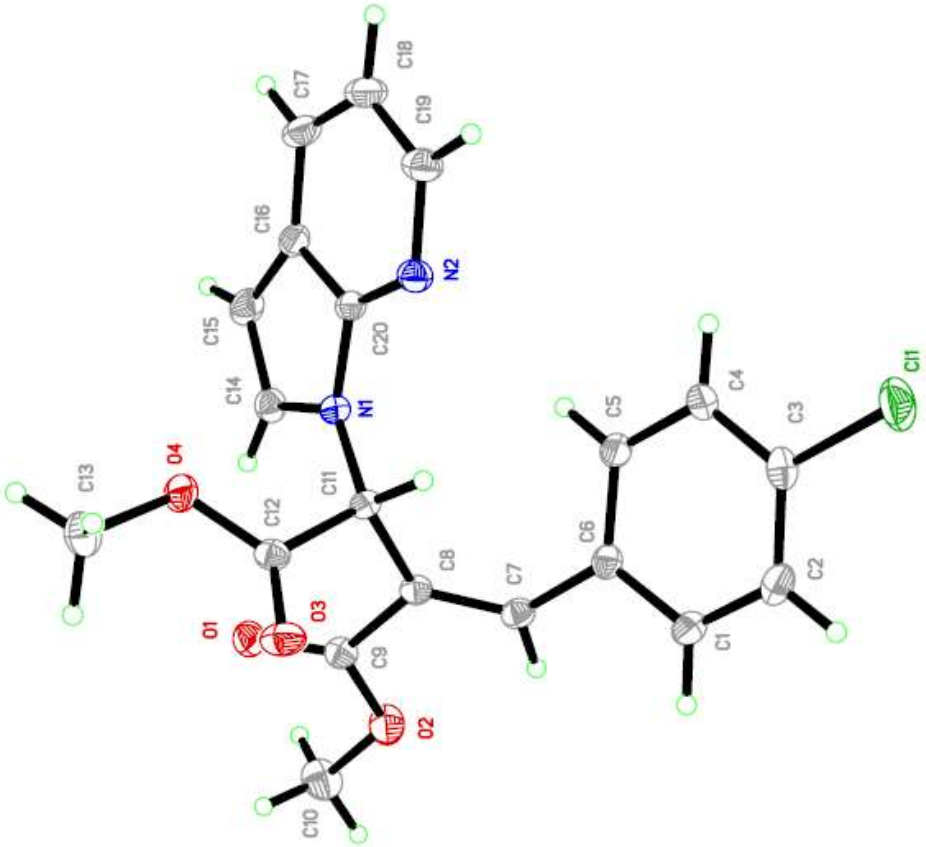


Figure S7. ORTEP diagram of compound **74**. Thermal ellipsoids are shown at the 50% level.

Empirical formula	$C_{20}H_{17}ClN_2O_4$
Formula weight	384.80
Temperature	193 K
Wavelength	1.34139 Å
Crystal system	monoclinic

Space group	C c	
Unit cell dimensions	a = 11.3217 (6) Å	α = 90 °
	b = 20.3289 (11) Å	β = 97.396 (2) °
	c = 7.8576 (4) Å	γ = 90 °
Volume	1793.44 (16) $Å^3$	
Z	4	
Density (calculated)	1.425 g/cm^3	
Absorption coefficient	1.407 mm^{-1}	
F(000)	800.0	
Crystal size	0.120 x 0.090 x 0.080 mm^3	
θ range for data collection	3.783 to 53.961 °	
Index ranges	$-13 \leq h \leq 13$, $-24 \leq k \leq 24$, $-9 \leq l \leq 9$	
Reflections collected	10076	
Independent reflections	3080 (R_{int} = 0.0496)	
Completeness to θ = 53.594 °	99.9 %	
Max. and min. transmission	0.896 and 0.849	
Data / restraints / parameters	3080 / 2 / 246	
Goodness-of-fit on F^2	1.034	
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0276, wR_2 = 0.0757	
R indices (all data)	R_1 = 0.0309, wR_2 = 0.0766	
Largest diff. peak and hole	0.147 and -0.208 $e.Å^{-3}$	

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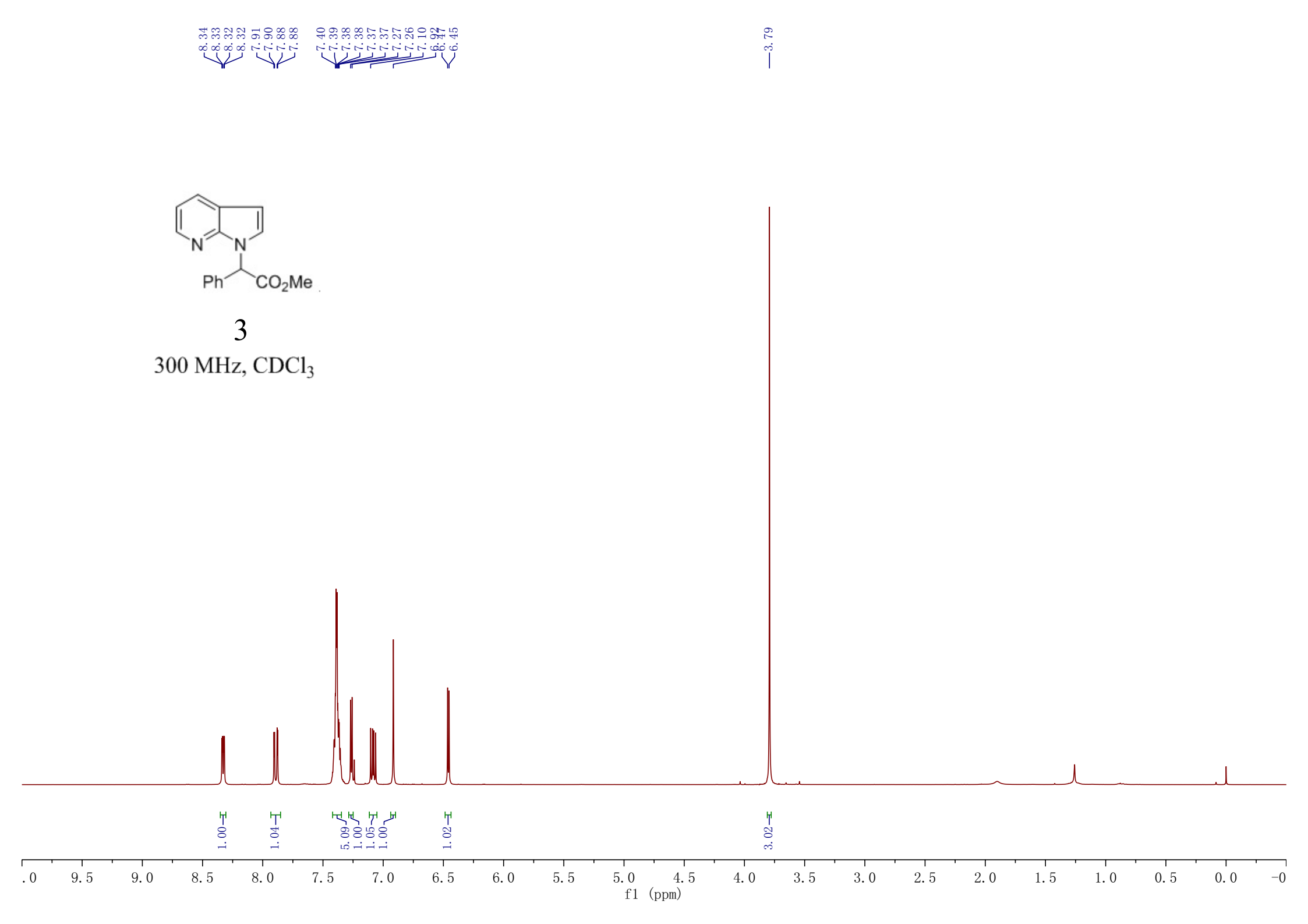
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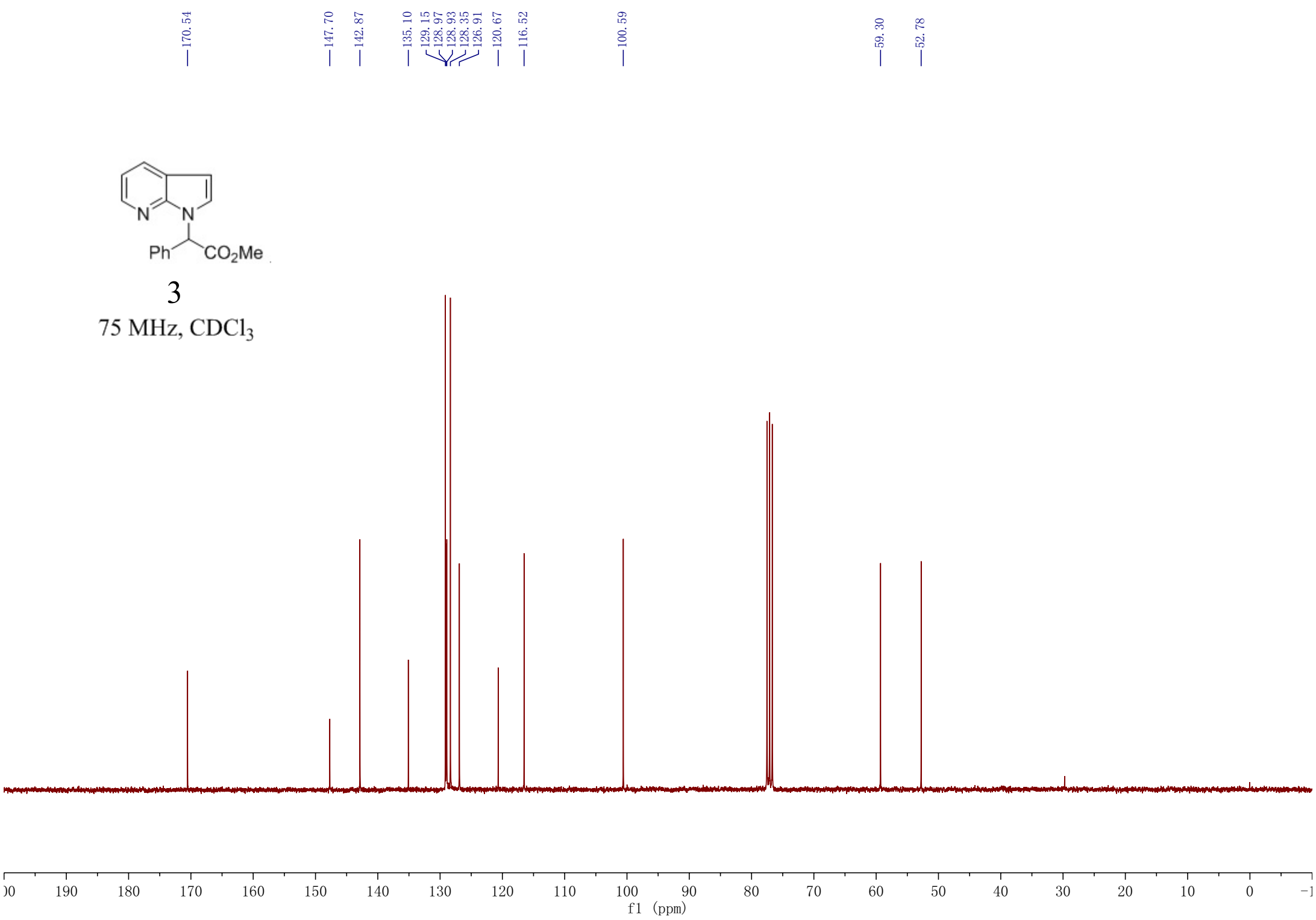
8.33
8.32
8.32
7.91
7.90
7.88
7.88
7.40
7.39
7.38
7.38
7.37
7.37
7.27
7.26
7.10
6.45
3.79
N
N
Ph
CO2Me
3
300 MHz, CDCl3
1.00
1.04
5.09
1.00
1.05
1.00
1.02
3.02
f1 (ppm)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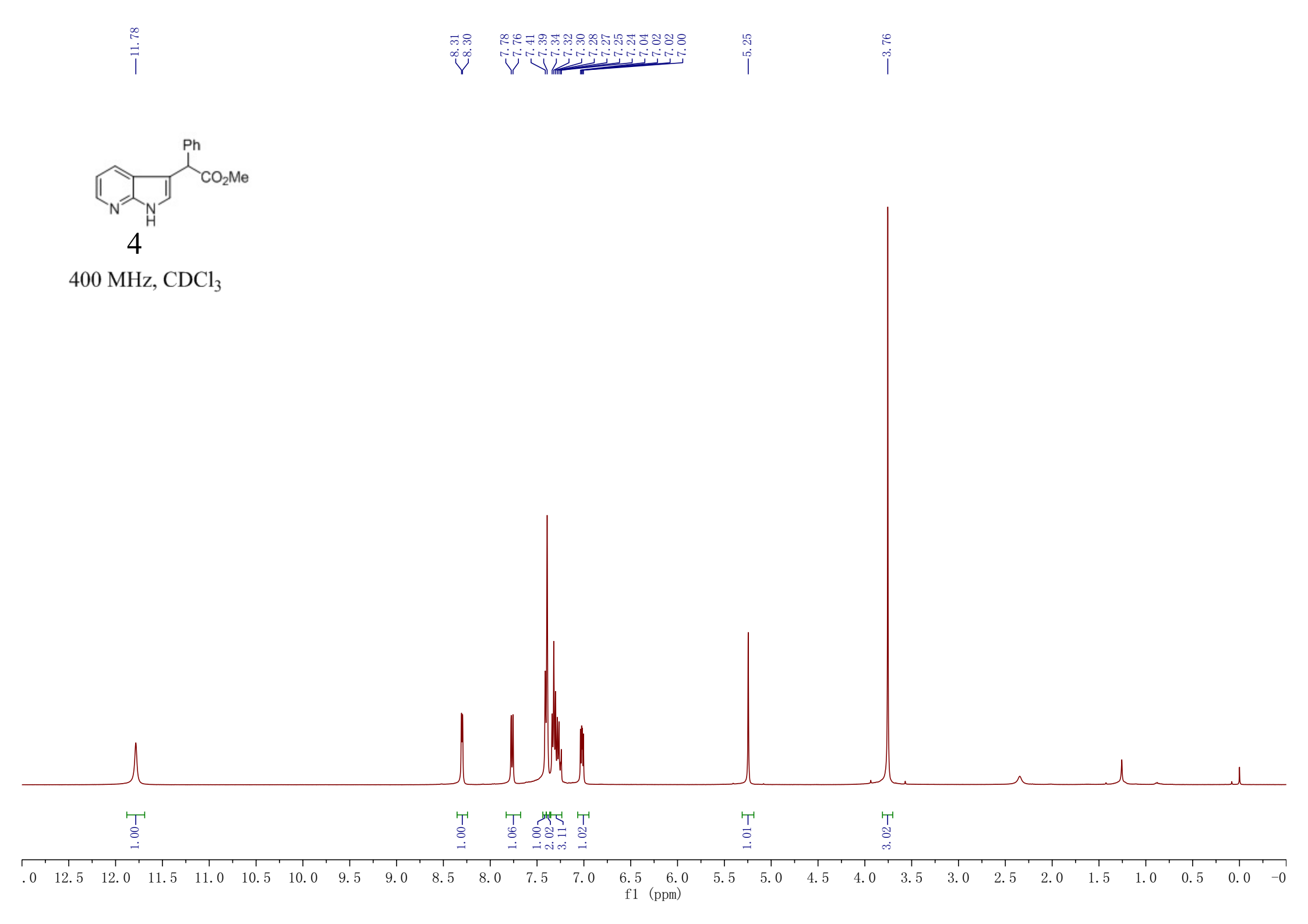
142.87
135.10
129.15
128.97
128.93
128.35
126.91
120.67
116.52
100.59
59.30
52.78
N
N
Ph
CO2Me
3
75 MHz, CDCl3
f1 (ppm)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8.31
8.30
7.78
7.76
7.41
7.39
7.34
7.32
7.30
7.28
7.27
7.25
7.24
7.04
7.02
7.02
7.00
5.25
3.76
Ph
CO2Me
N
N
H
4
400 MHz, CDCl3
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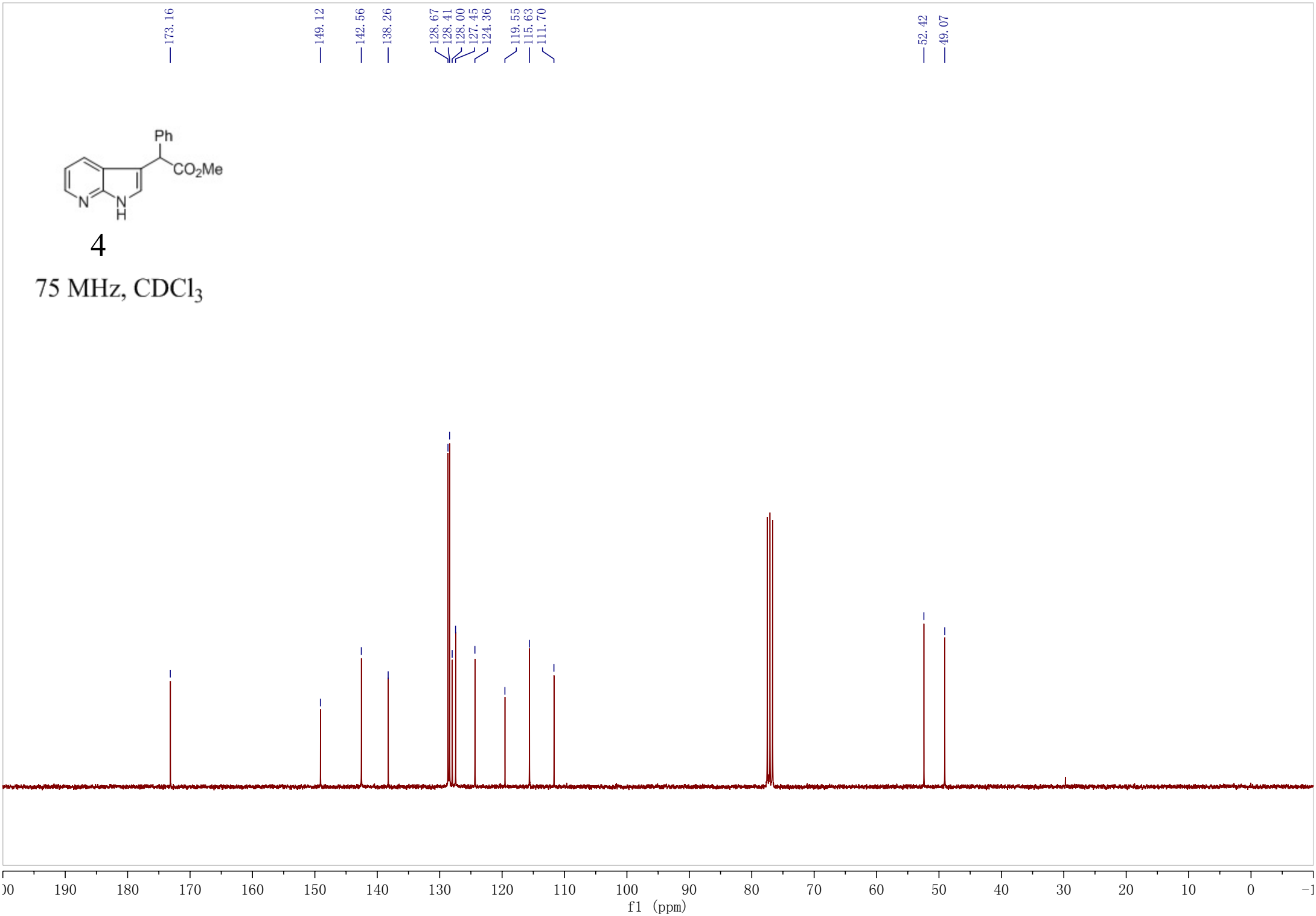
1.00
1.06
1.00
2.02
3.11
1.02
1.01
3.02
f1 (ppm)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128.67
128.41
128.00
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119.55
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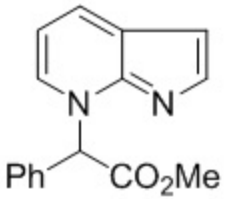
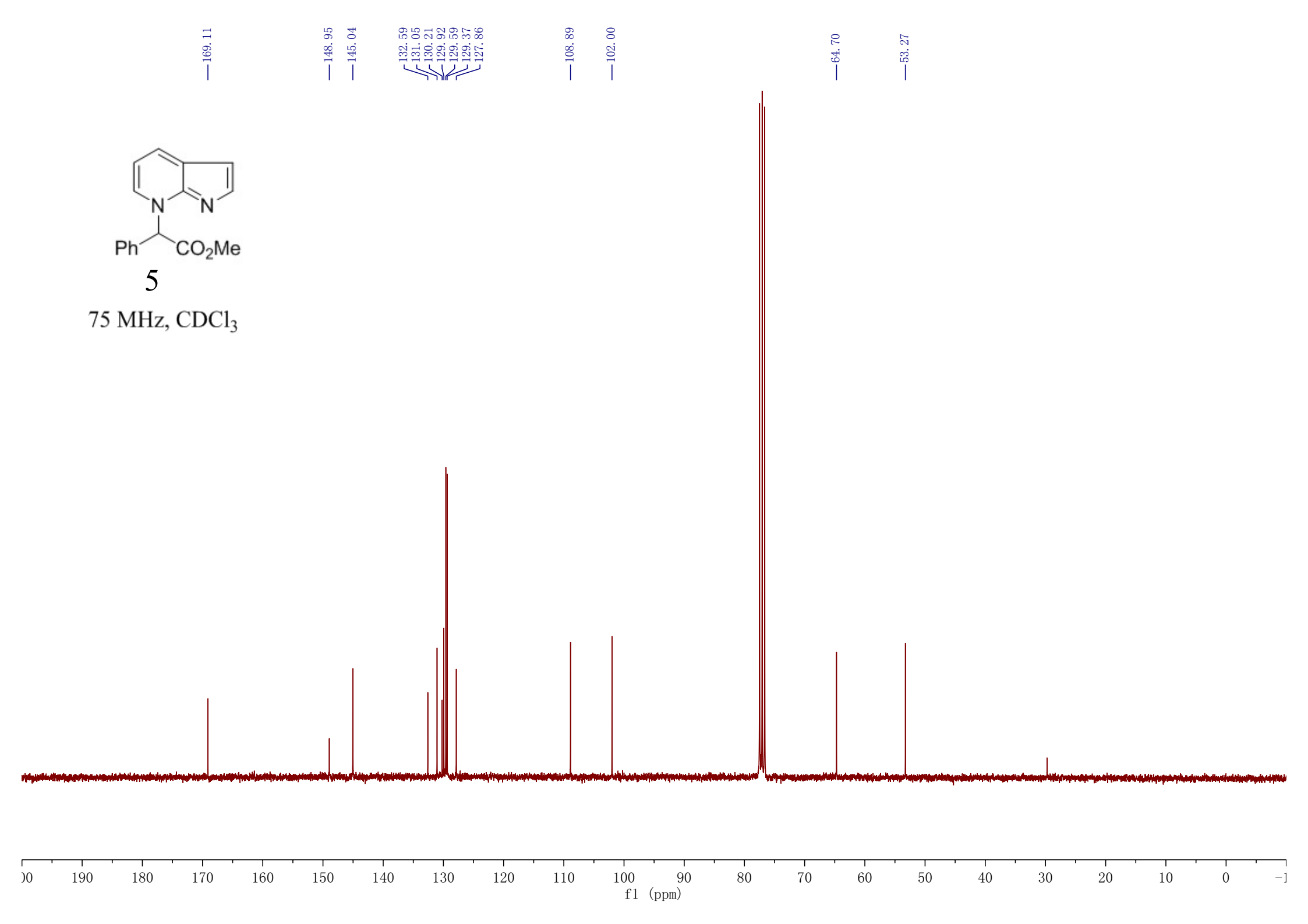
111.70
52.42
49.07
Ph
CO2Me
N
H
4
75 MHz, CDCl3
f1 (ppm)



5

400 MHz, $CDCl_3$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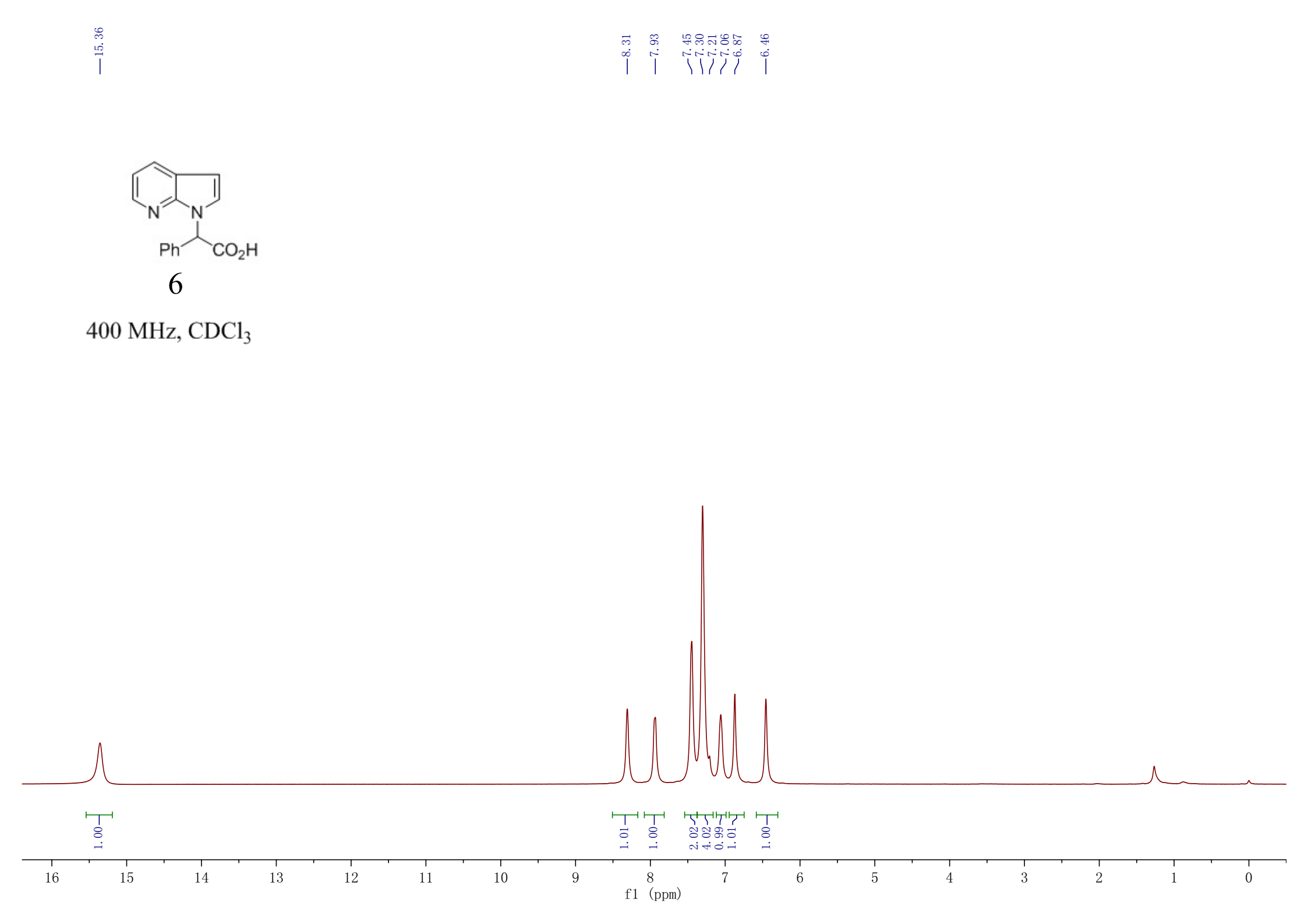
148.95
145.04
132.59
131.05
130.21
129.92
129.59
129.37
127.86
108.89
102.00
64.70
53.27
N
N
Ph
CO2Me
5
75 MHz, CDCl3
f1 (ppm)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7.93
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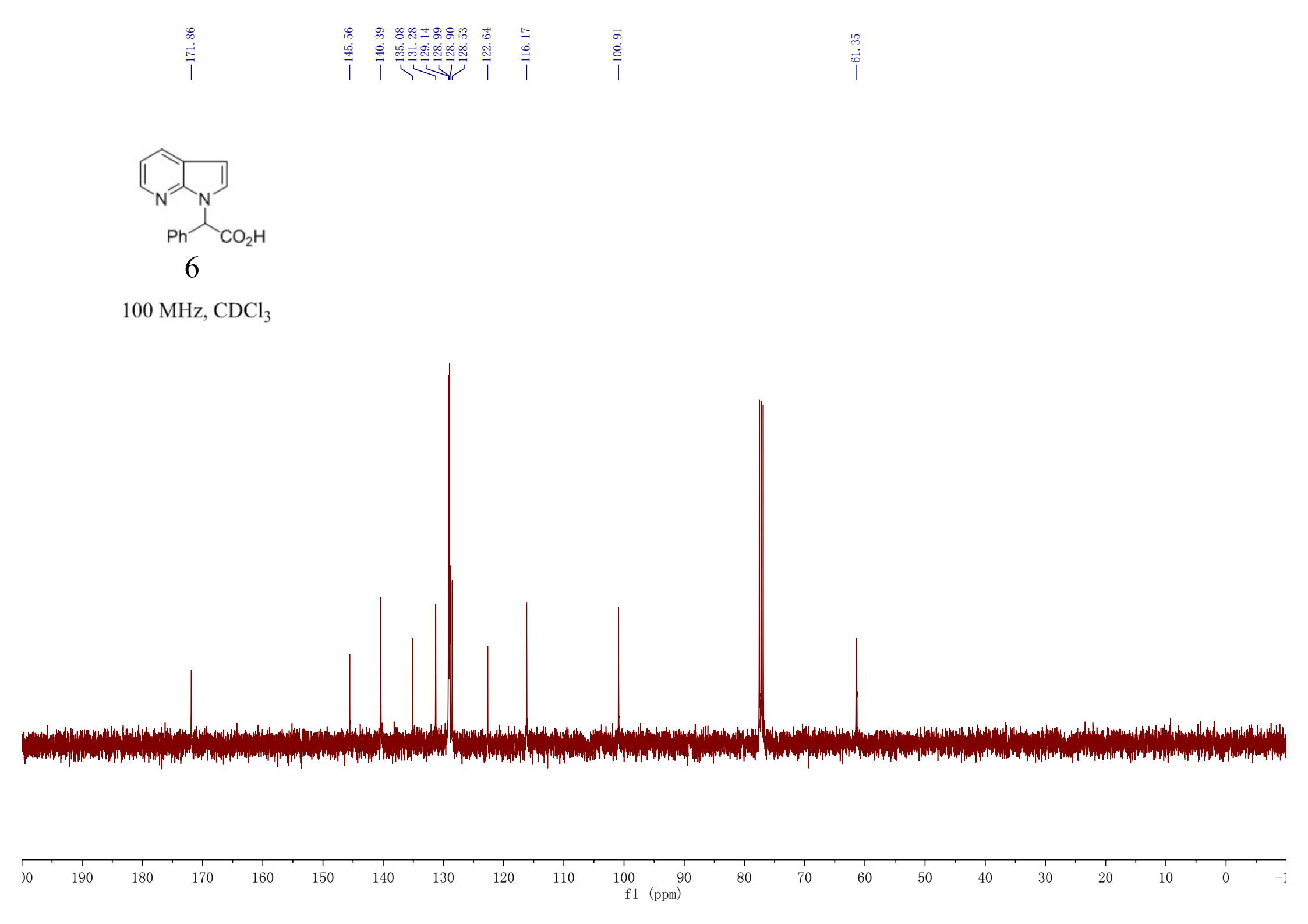
7.30
7.21
7.06
6.87
6.46
N
N
Ph
CO2H
6
400 MHz, CDCl3
1.00
1.01
1.00
2.02
4.02
0.99
1.01
1.00
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)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131.28
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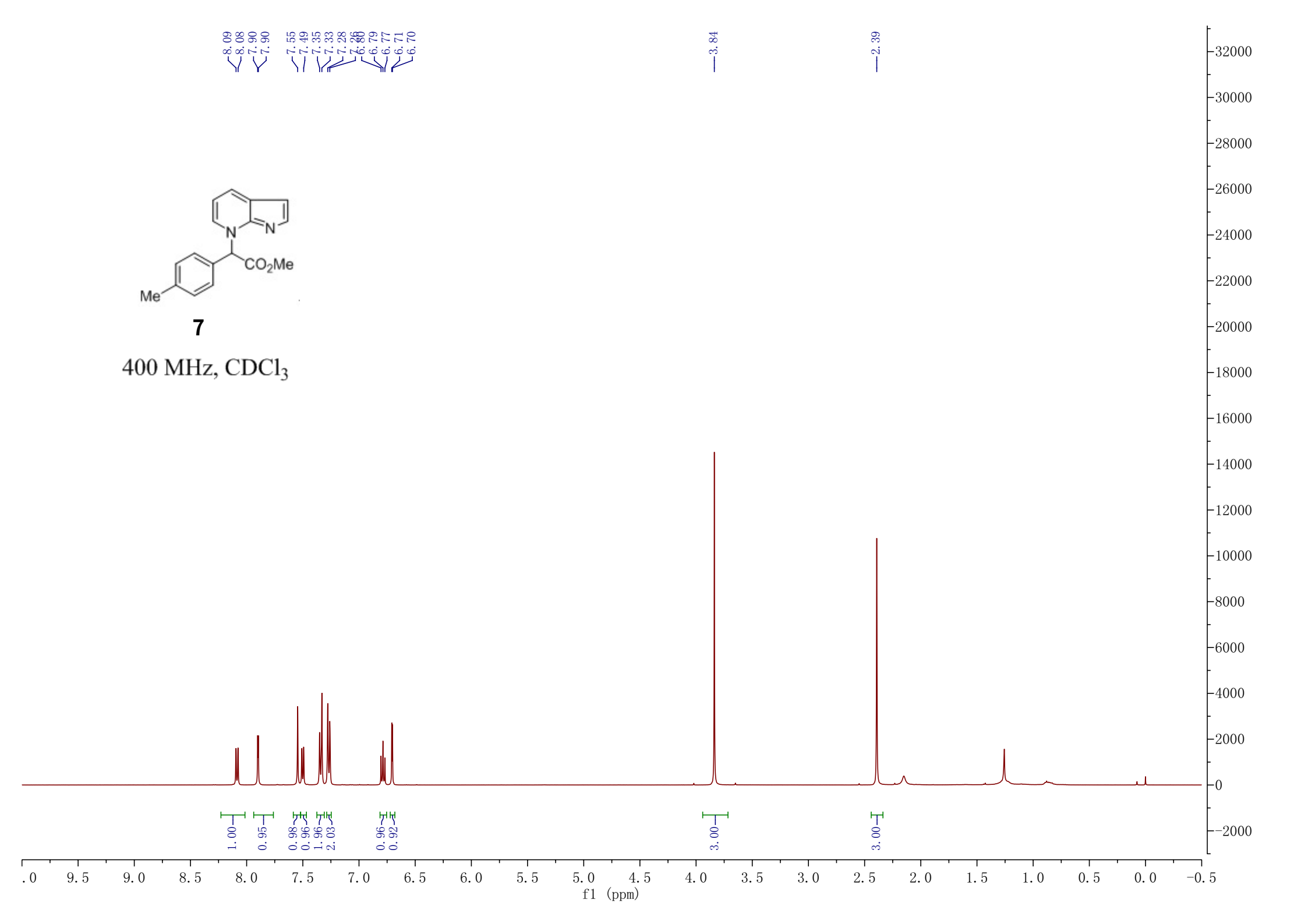
61.35
N
N
Ph
CO2H
6
100 MHz, CDCl3
f1 (ppm)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7.55
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7.28
6.79
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6.71
6.70
3.84
2.39
N
N
CO2Me
Me
7
400 MHz, CDCl3
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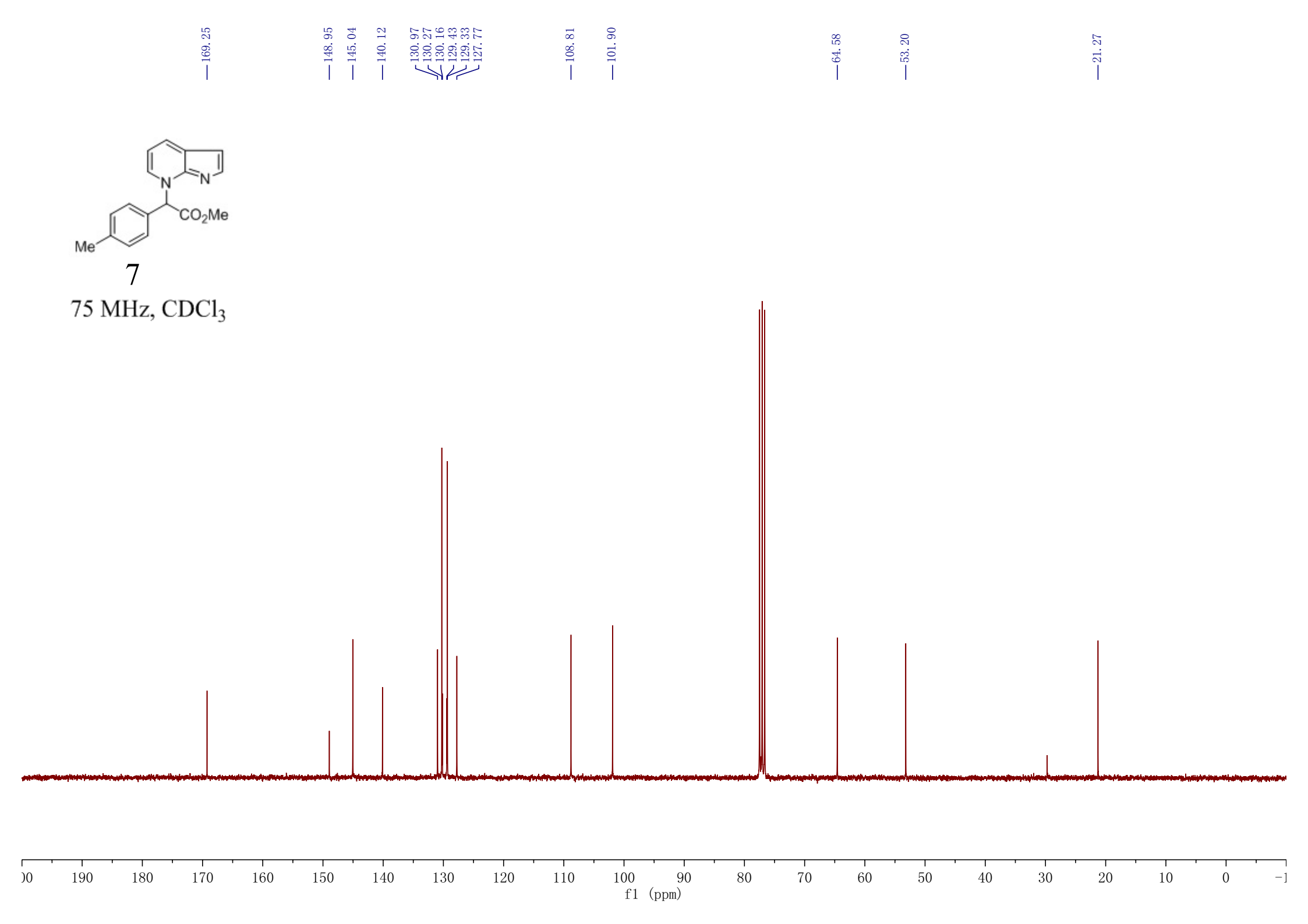
0.95
0.98
0.96
1.96
2.03
0.96
0.92
3.00
3.00
f1 (ppm)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148.95
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140.12
130.97
130.27
130.16
129.43
129.33
127.77
108.81
101.90
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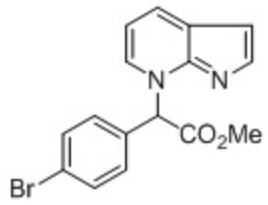
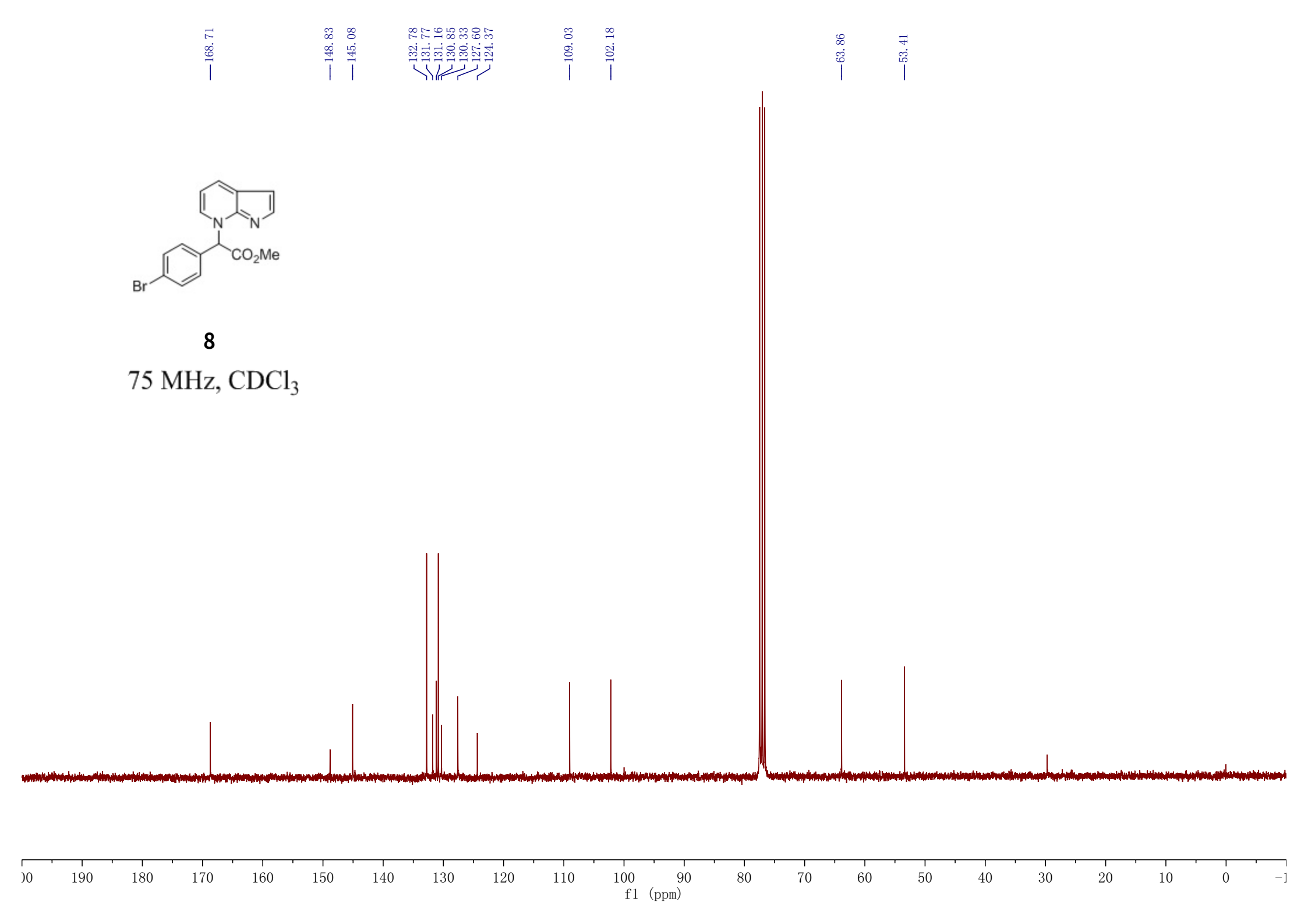
N
CO2Me
Me
7
75 MHz, CDCl3
f1 (ppm)



8

400 MHz, $CDCl_3$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131.77
131.16
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130.33
127.60
124.37
109.03
102.18
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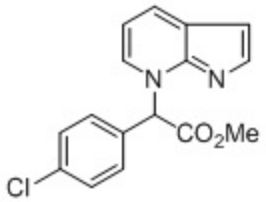
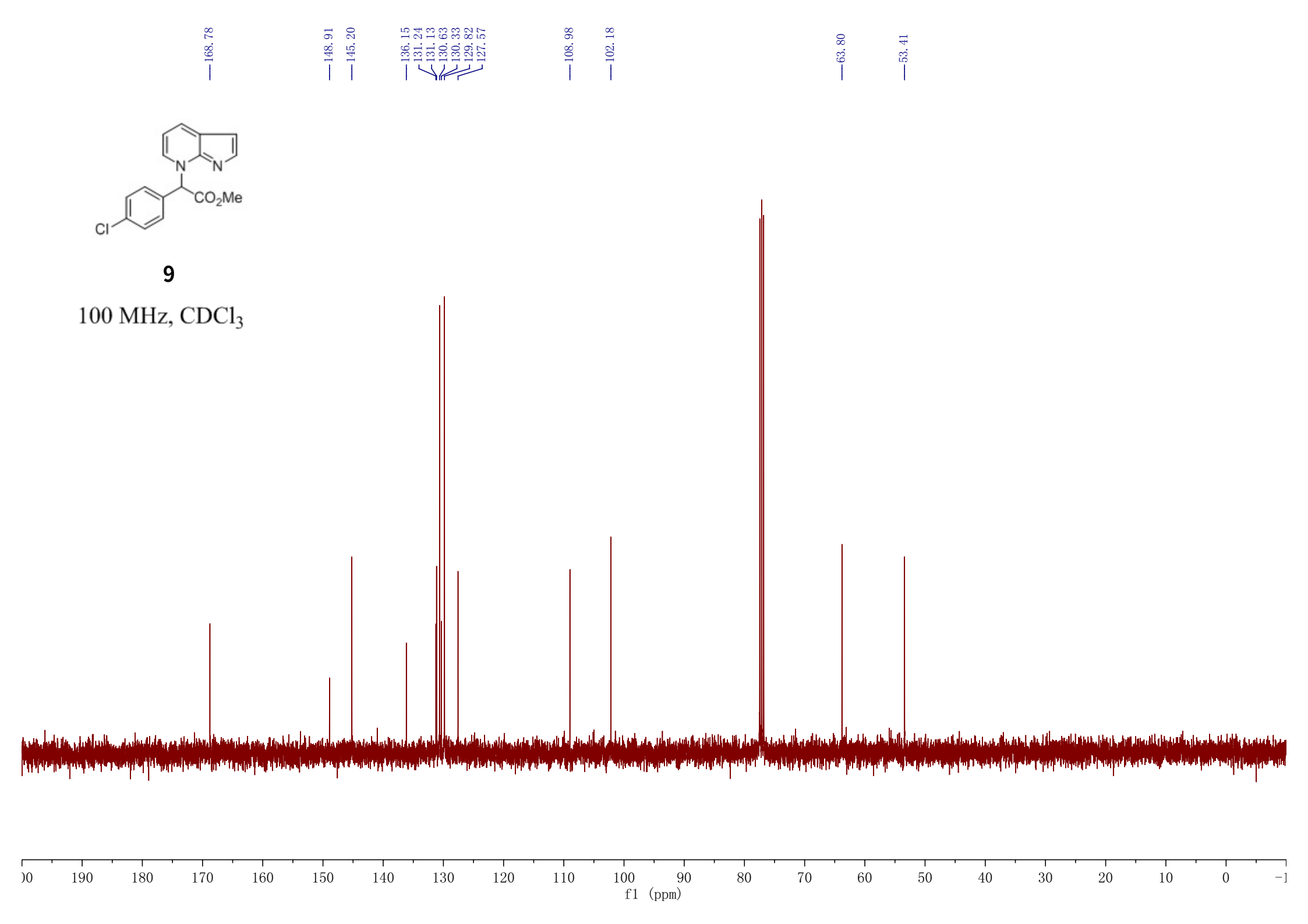
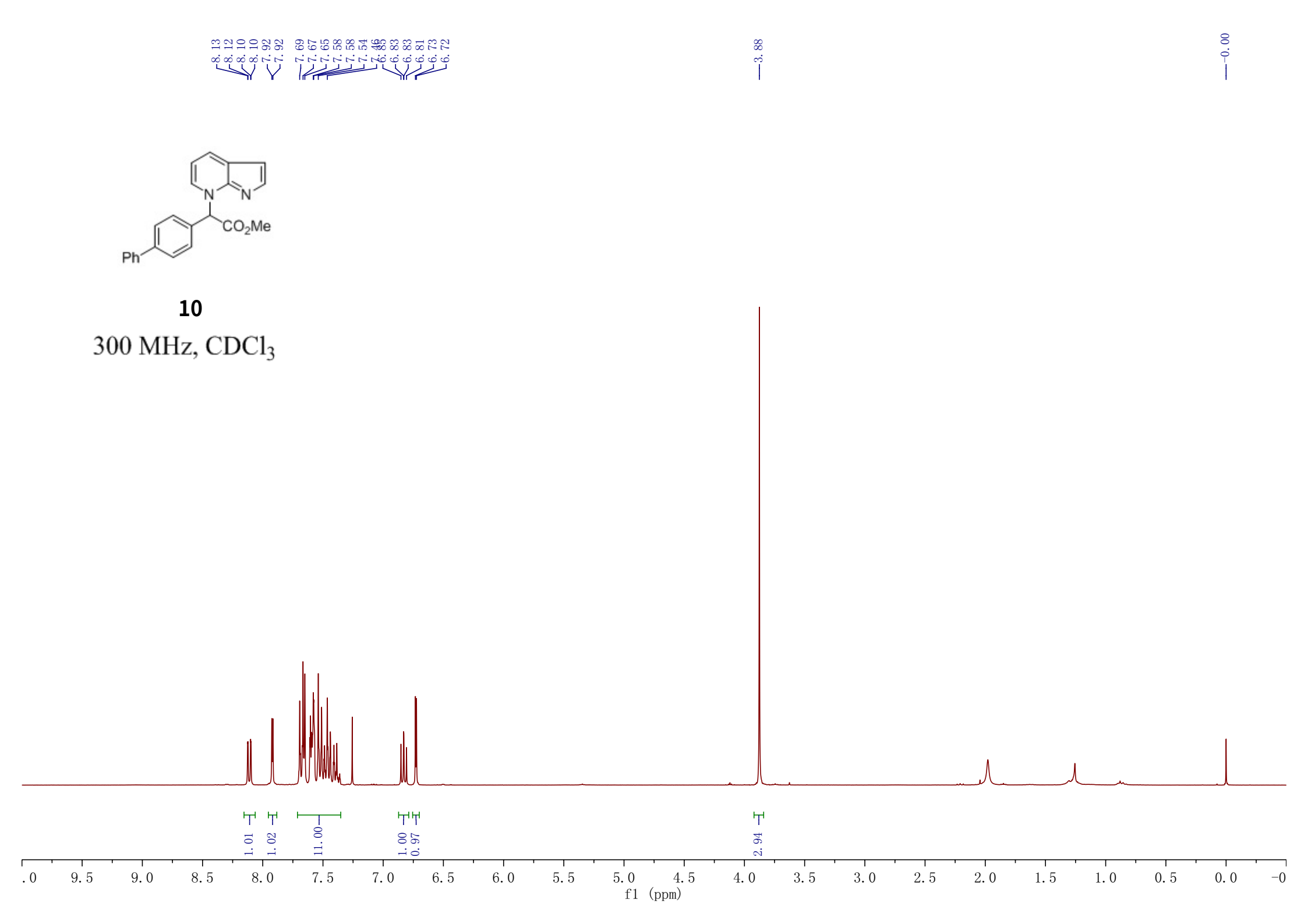
N
CO2Me
Br
8
75 MHz, CDCl3
f1 (ppm)

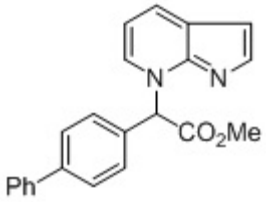


9

400 MHz, $CDCl_3$


168.78
148.91
145.20
136.15
131.24
131.13
130.63
130.33
129.82
127.57
108.98
102.18
63.80
53.41
N
N
CO2Me
Cl
9
100 MHz, CDCl3
f1 (ppm)


8.13
8.12
8.10
8.10
7.92
7.92
7.69
7.67
7.65
7.58
7.58
7.54
6.83
6.83
6.81
6.73
6.72
3.88
0.00
N
N
CO2Me
Ph
10
300 MHz, CDCl3
1.01
1.02
11.00
1.00
0.97
2.94
f1 (ppm)

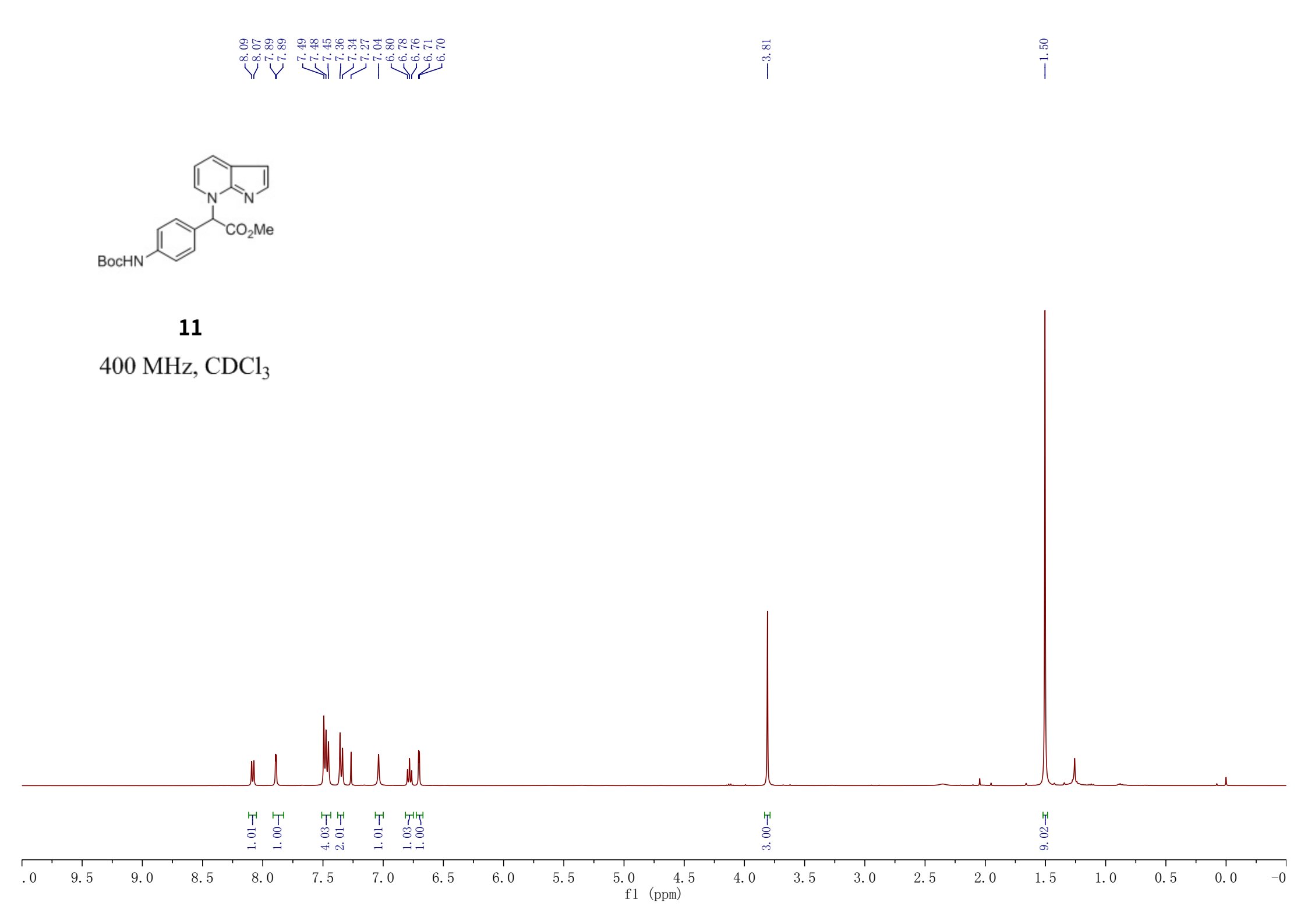


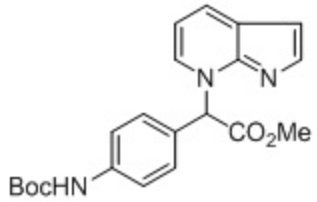
10

75 MHz, $CDCl_3$

169.14
149.01
145.16
142.89
139.85
131.41
131.06
130.26
129.81
128.99
128.24
128.01
127.83
127.18
108.91
102.03
64.42
53.32

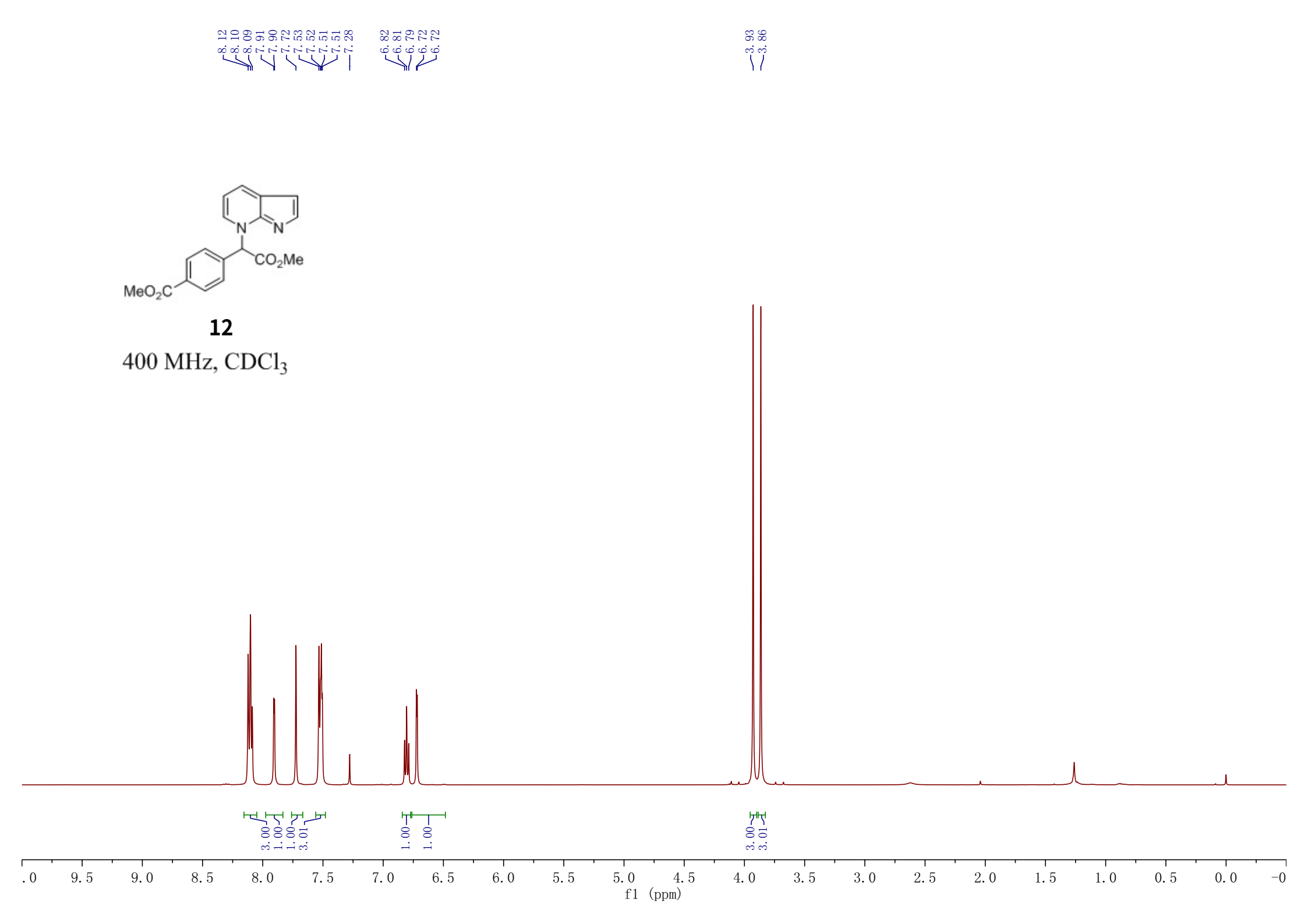
f1 (ppm)

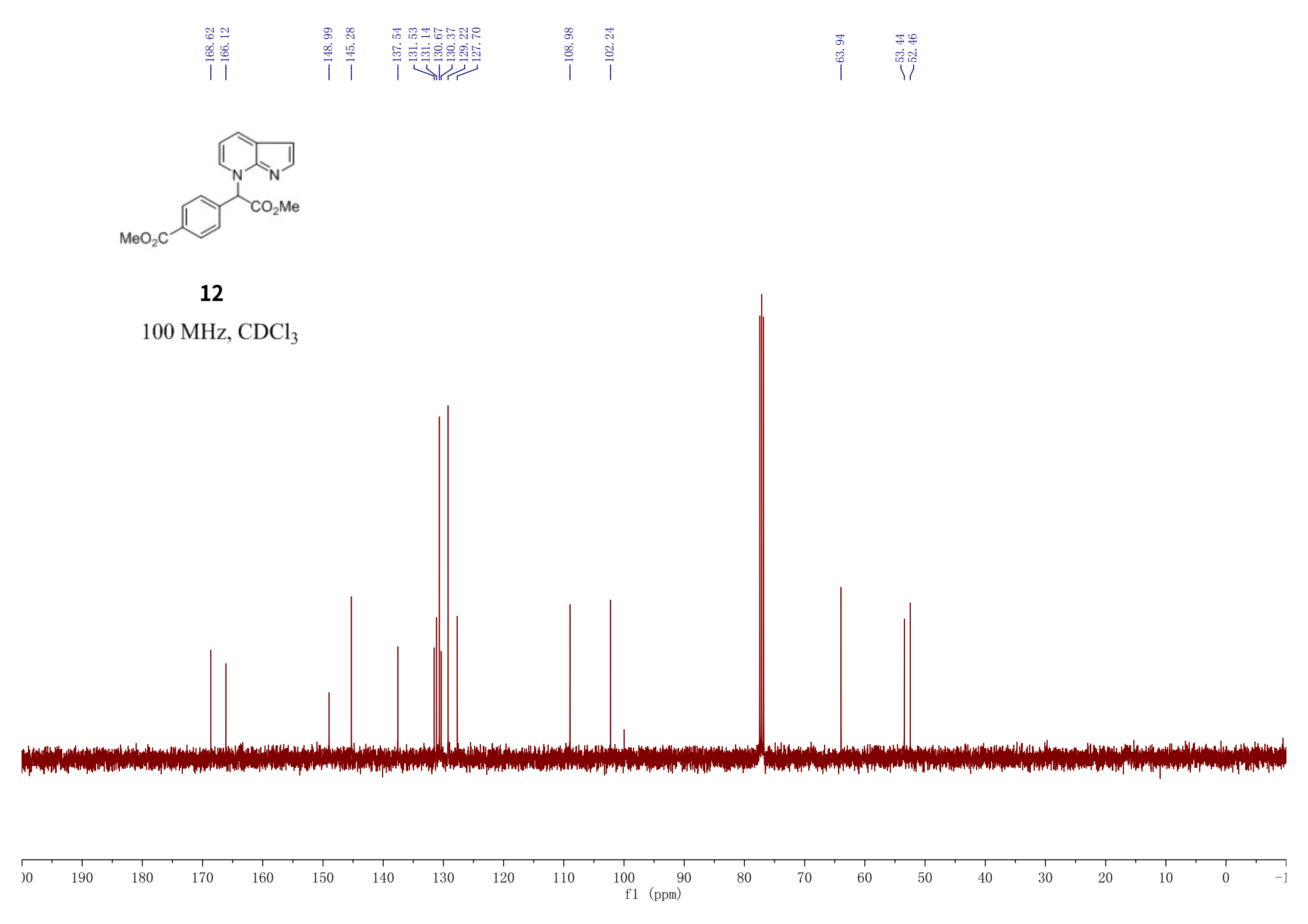

8.09
8.07
7.89
7.89
7.49
7.48
7.45
7.36
7.34
7.27
7.04
6.80
6.78
6.76
6.71
6.70
3.81
1.50
N
N
CO2Me
BocHN
11
400 MHz, CDCl3
1.01
1.00
4.03
2.01
1.01
1.03
1.00
3.00
9.02
f1 (ppm)

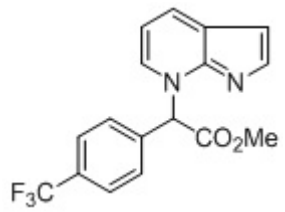


11

100 MHz, $CDCl_3$

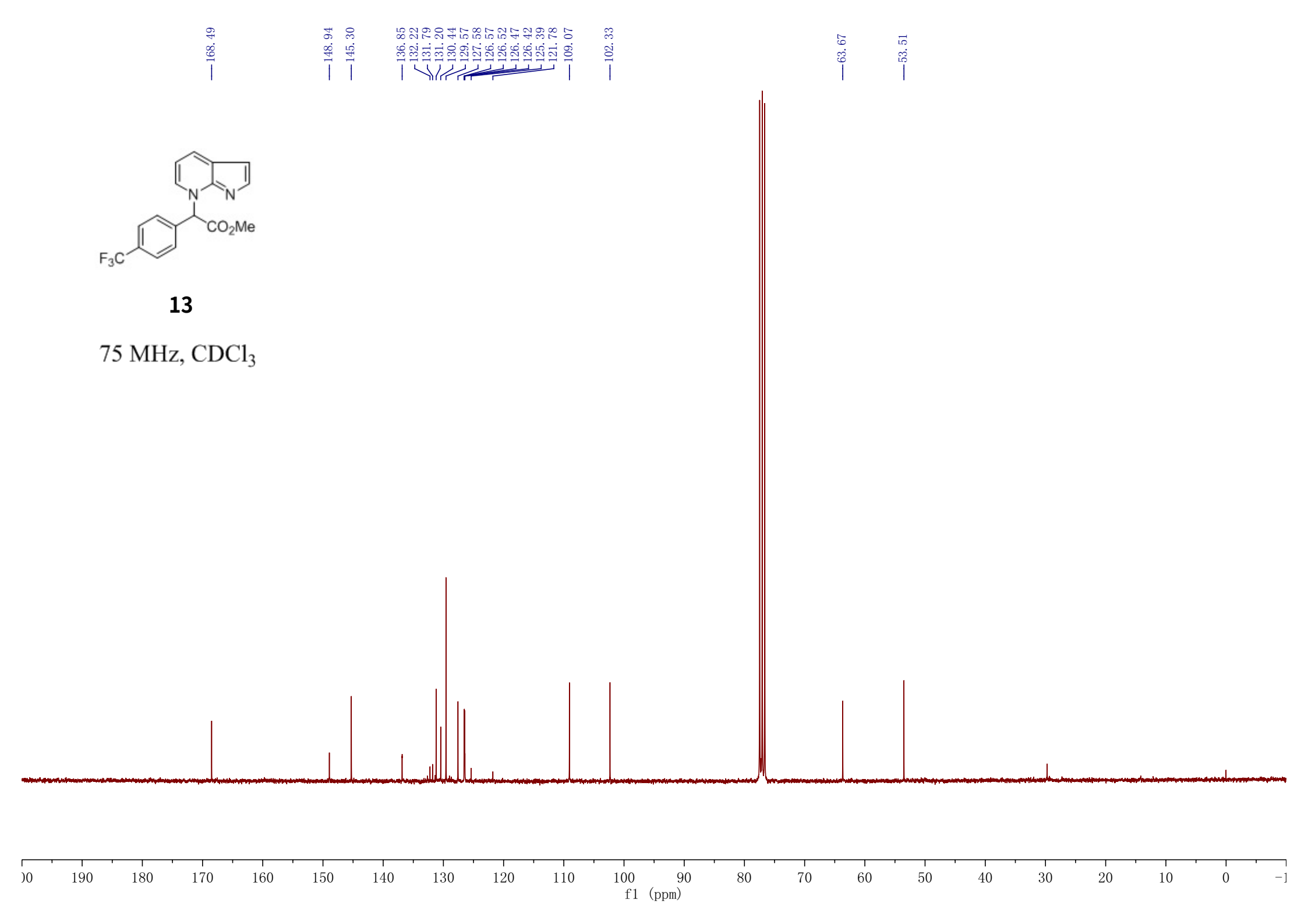

8.12
8.10
8.09
7.91
7.90
7.72
7.53
7.52
7.51
7.51
7.28
6.82
6.81
6.79
6.72
6.72
3.93
3.86
N
N
CO2Me
MeO2C
12
400 MHz, CDCl3
3.00
1.00
1.00
3.01
1.00
1.00
3.00
3.01
f1 (ppm)

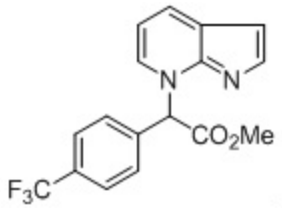

168.62
166.12
148.99
145.28
137.54
131.53
131.14
130.67
130.37
129.22
127.70
108.98
102.24
63.94
53.44
52.46
N
N
CO2Me
MeO2C
12
100 MHz, CDCl3
f1 (ppm)



13

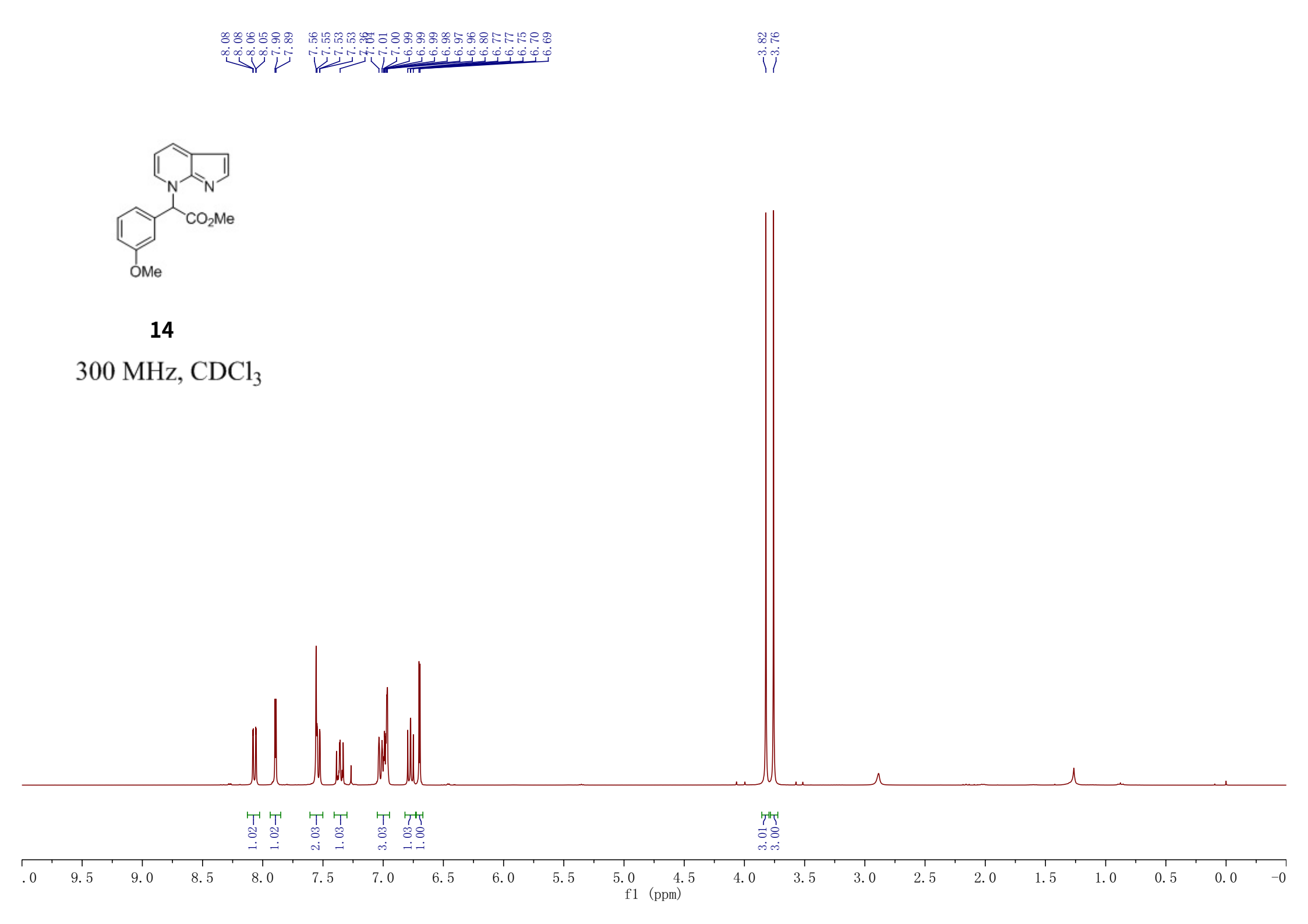
400 MHz, $CDCl_3$

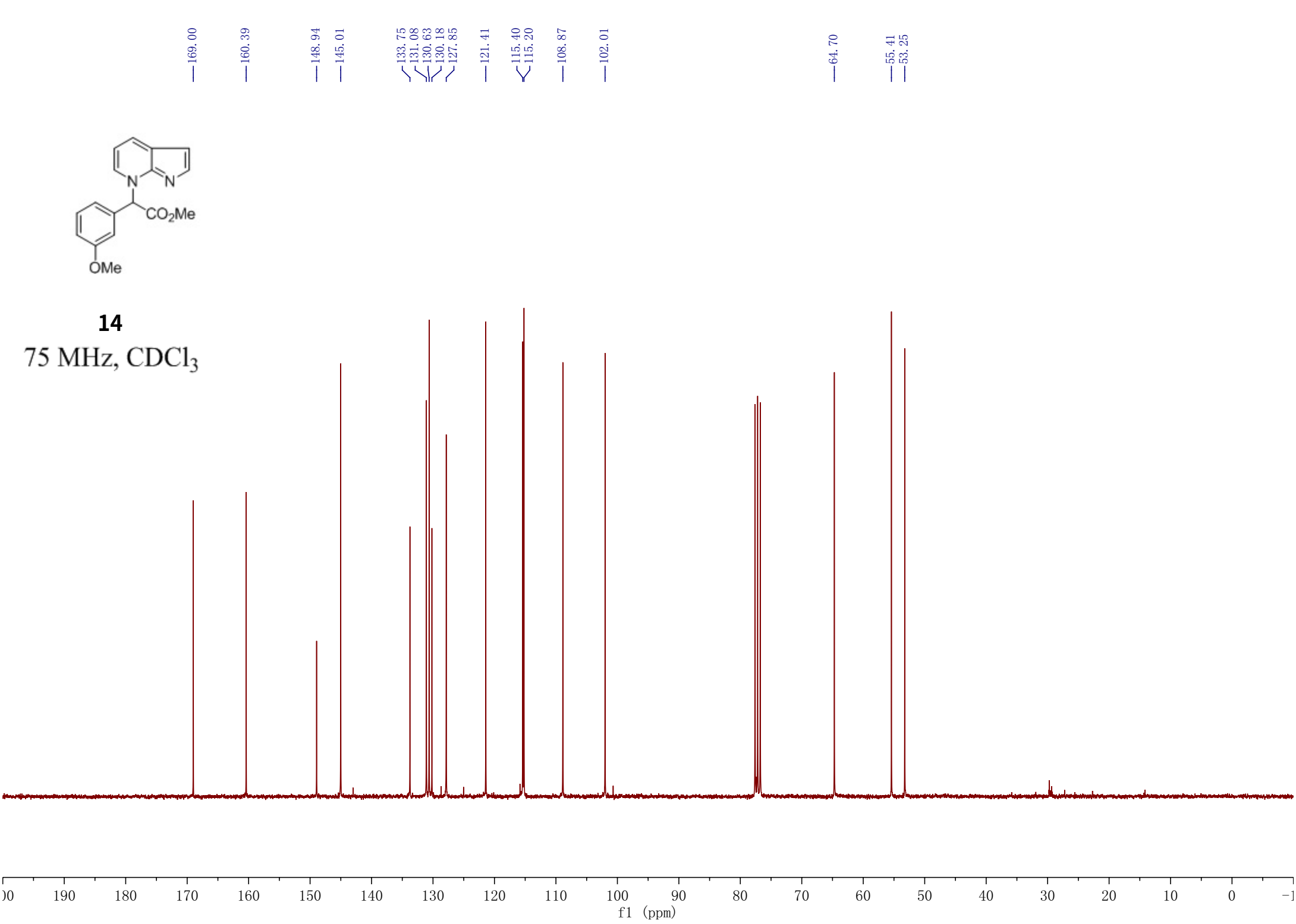

168.49
148.94
145.30
136.85
132.22
131.79
131.20
130.44
129.57
127.58
126.57
126.52
126.47
126.42
125.39
121.78
109.07
102.33
63.67
53.51
N
N
CO2Me
F3C
13
75 MHz, CDCl3
f1 (ppm)

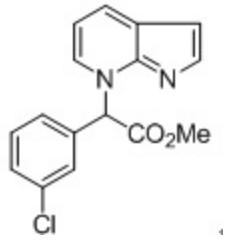


13

282 MHz, $CDCl_3$

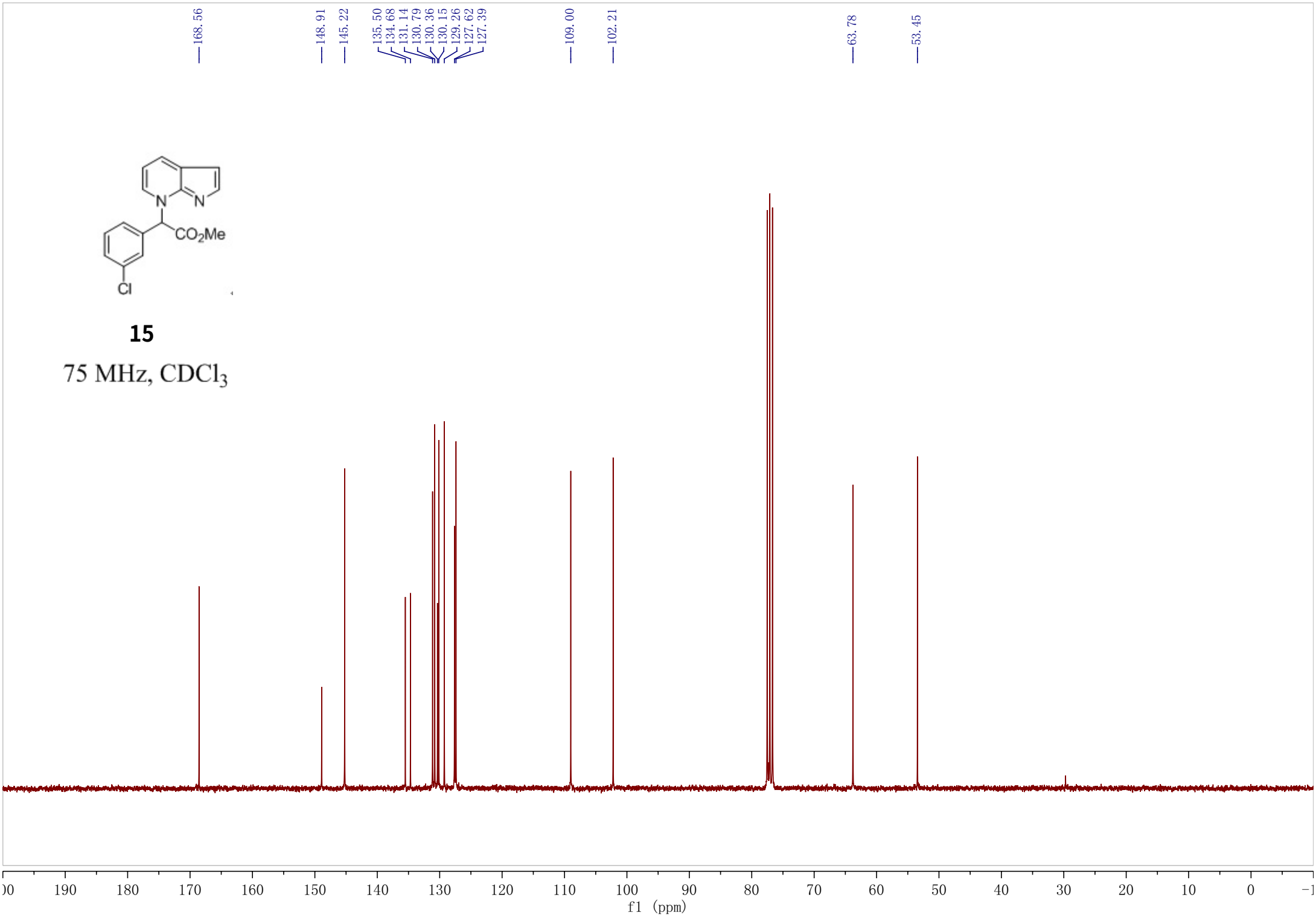

8.08
8.08
8.06
8.05
7.90
7.89
7.56
7.55
7.53
7.53
7.36
7.04
7.01
7.00
6.99
6.99
6.99
6.98
6.97
6.96
6.80
6.77
6.77
6.75
6.70
6.69
3.82
3.76
N
N
CO2Me
OMe
14
300 MHz, CDCl3
1.02
1.02
2.03
1.03
3.03
1.03
1.00
3.01
3.00
f1 (ppm)

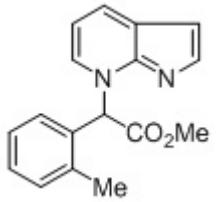

169.00
160.39
148.94
145.01
133.75
131.08
130.63
130.18
127.85
121.41
115.40
115.20
108.87
102.01
64.70
55.41
53.25
N
N
CO2Me
OMe
14
75 MHz, CDCl3
f1 (ppm)



15

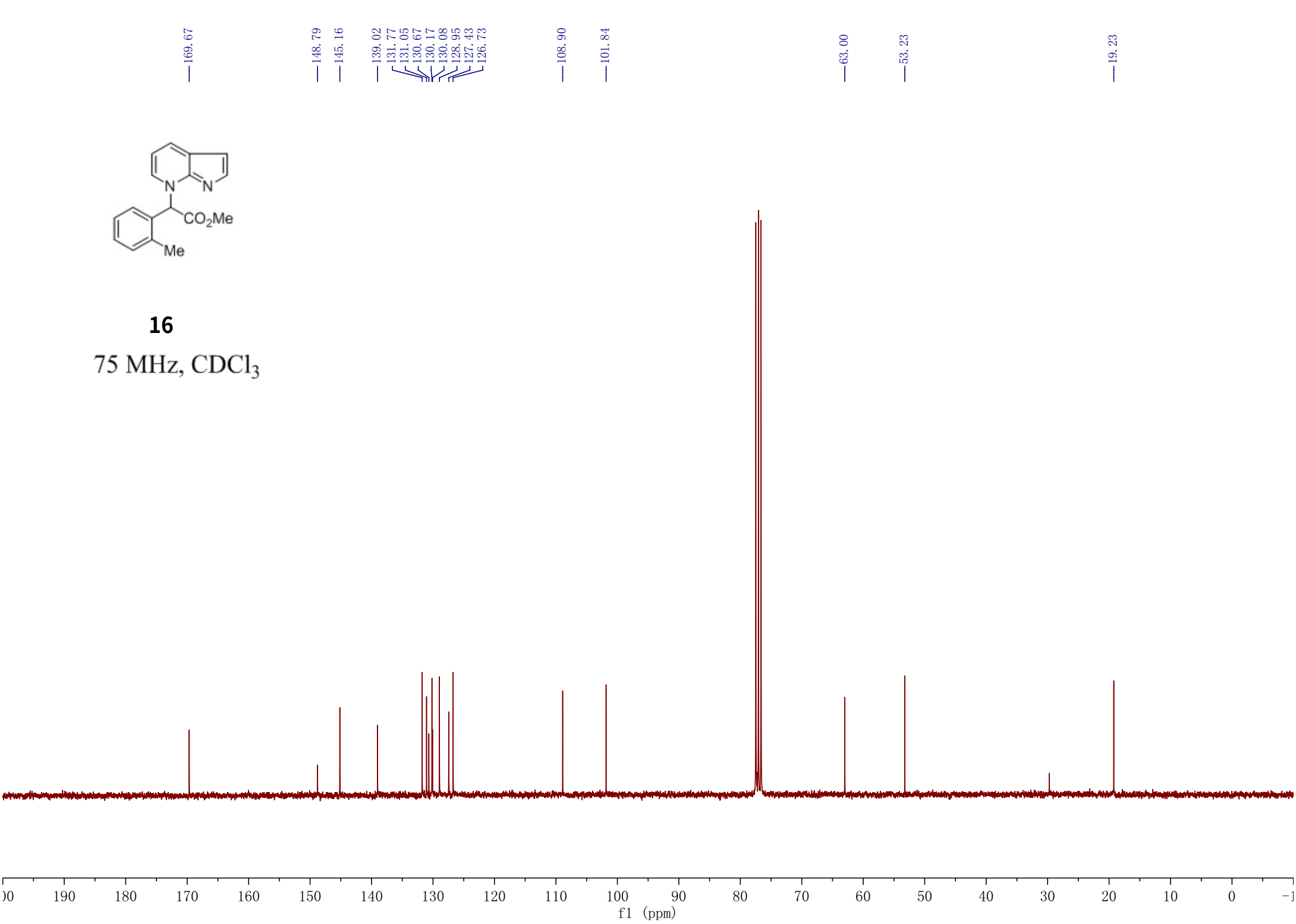
400 MHz, $CDCl_3$

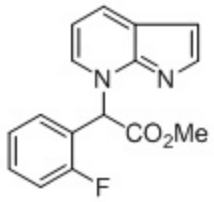

168.56
148.91
145.22
135.50
134.68
131.14
130.79
130.36
130.15
129.26
127.62
127.39
109.00
102.21
63.78
53.45
N
N
CO2Me
Cl
15
75 MHz, CDCl3
f1 (ppm)



16

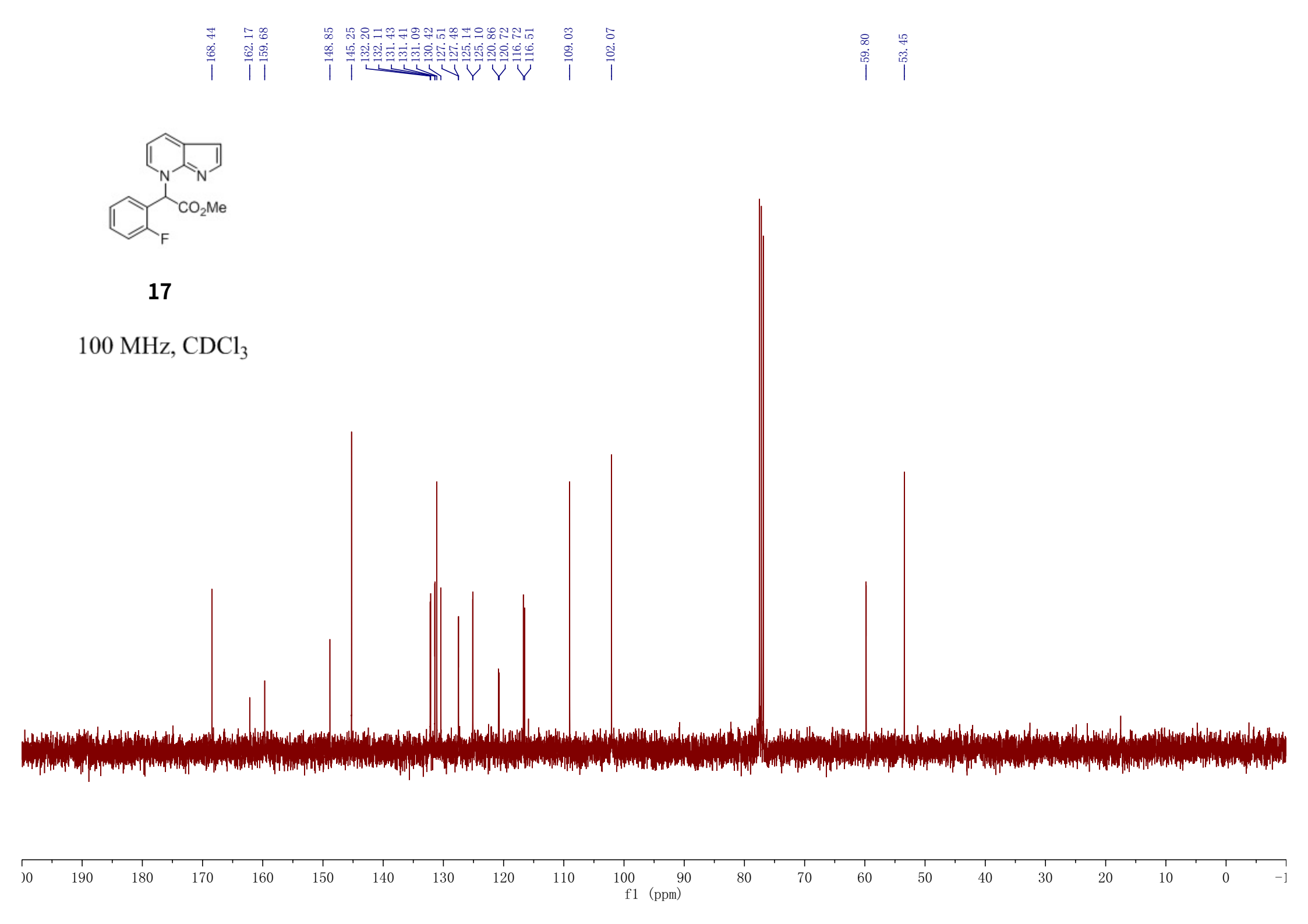
300 MHz, $CDCl_3$

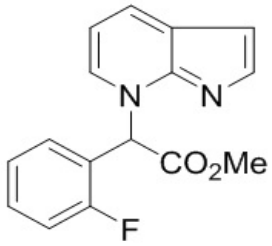

169.67
148.79
145.16
139.02
131.77
131.05
130.67
130.17
130.08
128.95
127.43
126.73
108.90
101.84
63.00
53.23
19.23
N
N
CO2Me
Me
16
75 MHz, CDCl3
f1 (ppm)



17

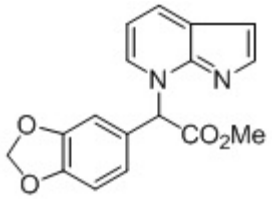
400 MHz, $CDCl_3$


168.44
162.17
159.68
148.85
145.25
132.20
132.11
131.43
131.41
131.09
130.42
127.51
127.48
125.14
125.10
120.86
120.72
116.72
116.51
109.03
102.07
59.80
53.45
N
N
CO2Me
F
17
100 MHz, CDCl3
f1 (ppm)



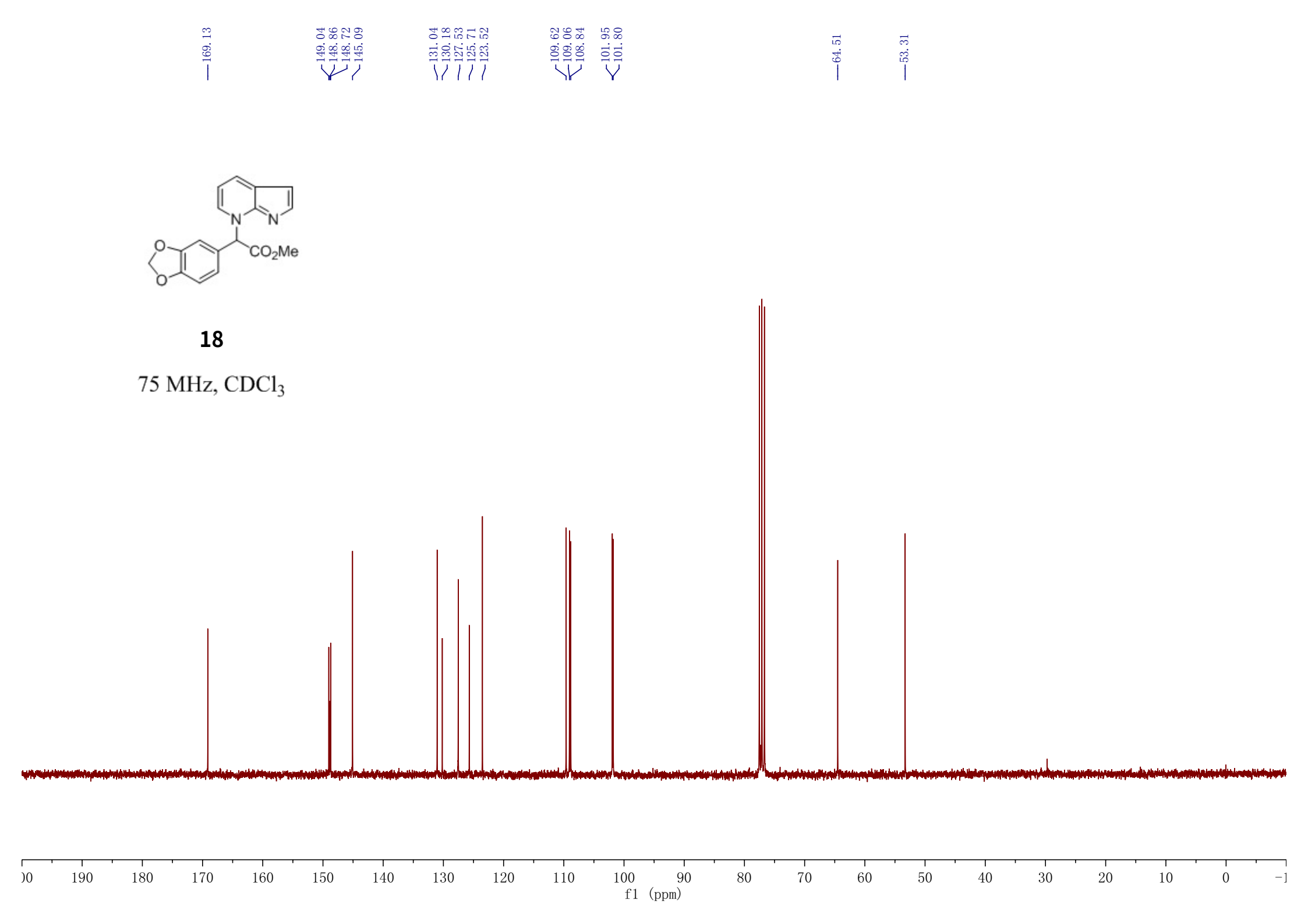
17

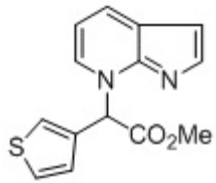
282 MHz, $CDCl_3$



18

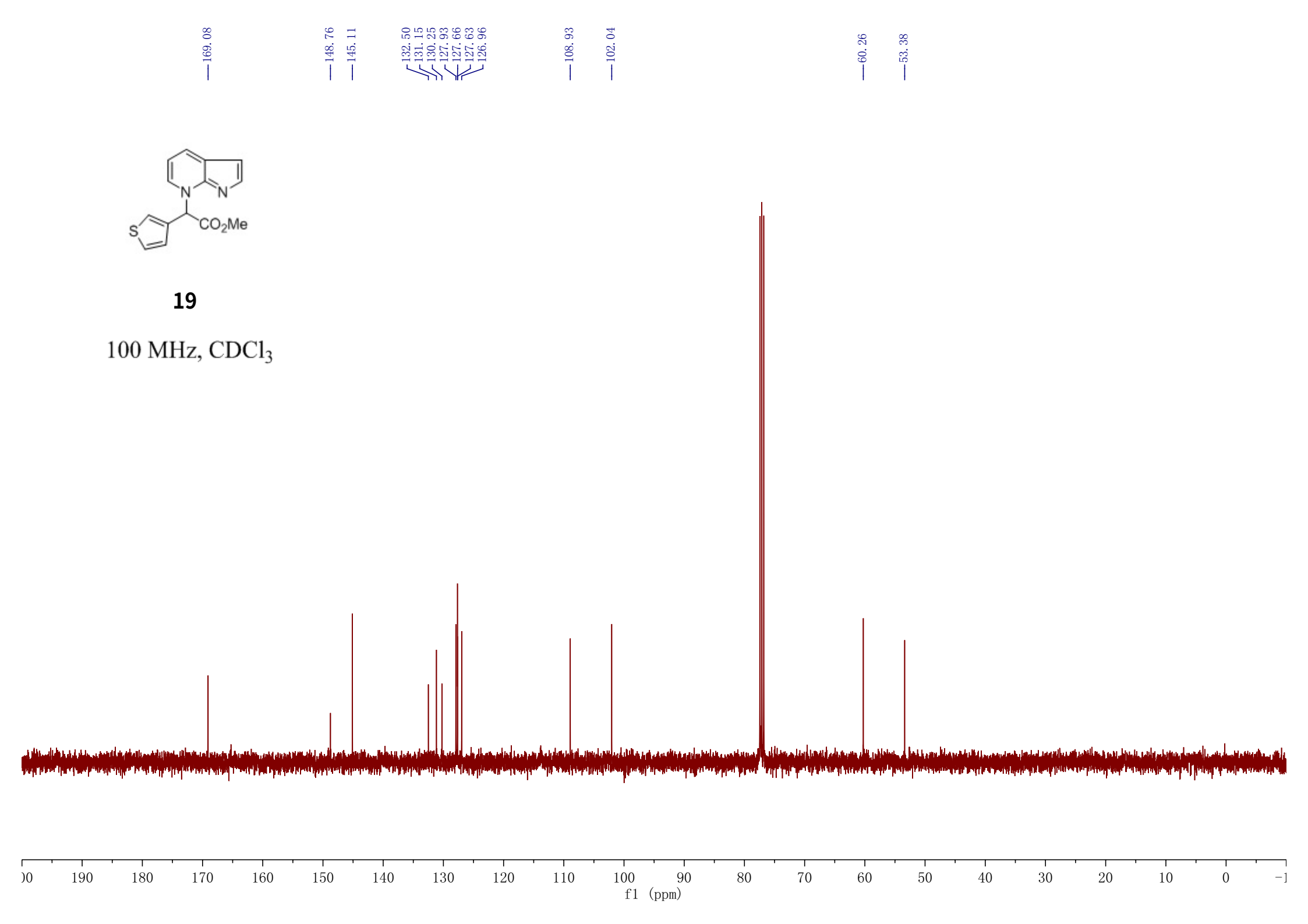
300 MHz, $CDCl_3$

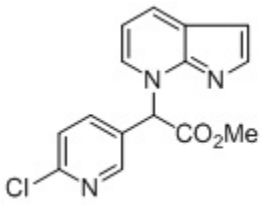

169.13
149.04
148.86
148.72
145.09
131.04
130.18
127.53
125.71
123.52
109.62
109.06
108.84
101.95
101.80
64.51
53.31
N
N
O
O
CO2Me
18
75 MHz, CDCl3
f1 (ppm)



19

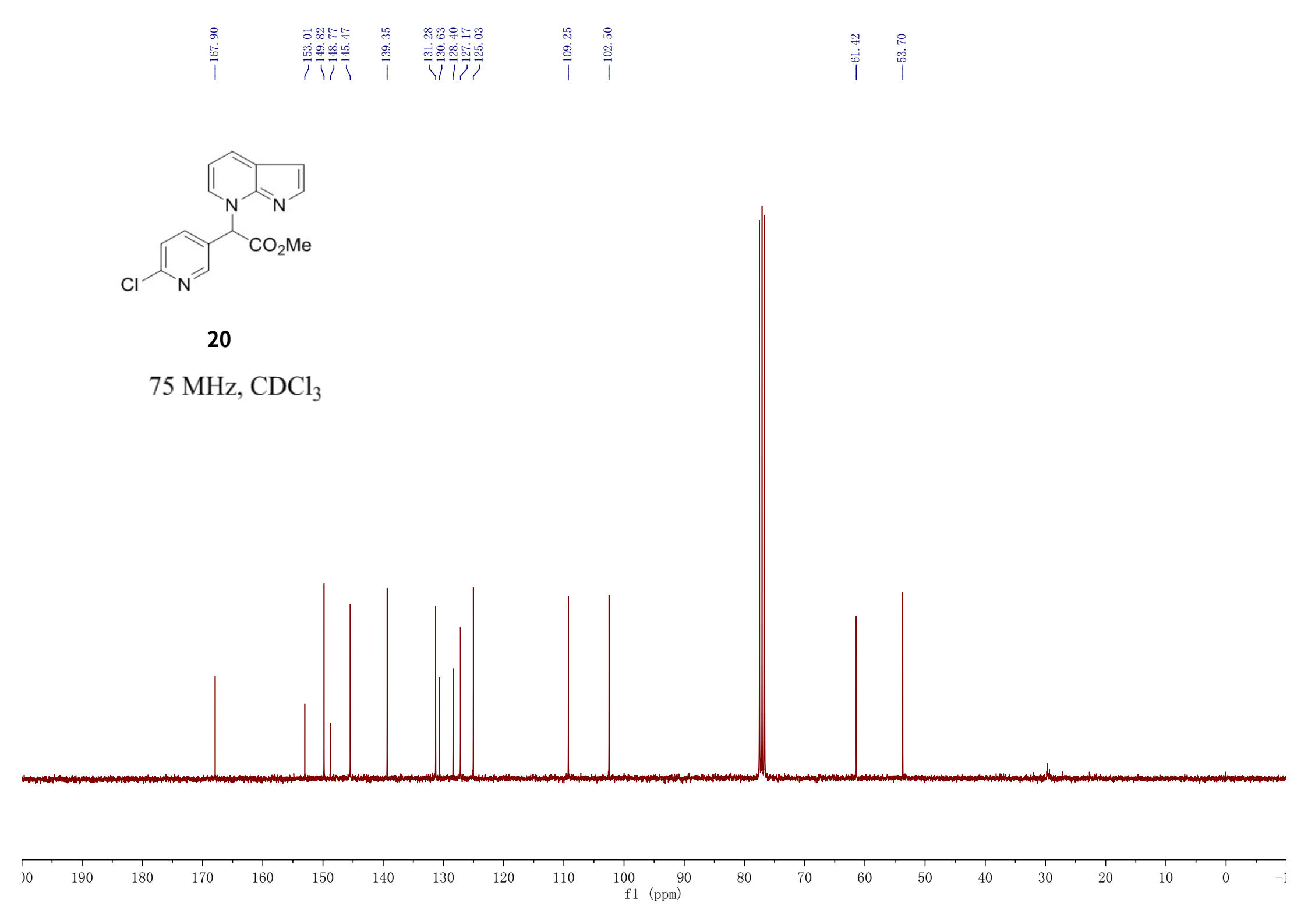
400 MHz, $CDCl_3$

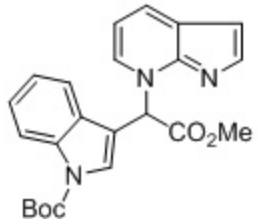

169.08
148.76
145.11
132.50
131.15
130.25
127.93
127.66
127.63
126.96
108.93
102.04
60.26
53.38
N
N
S
CO2Me
19
100 MHz, CDCl3
f1 (ppm)



20

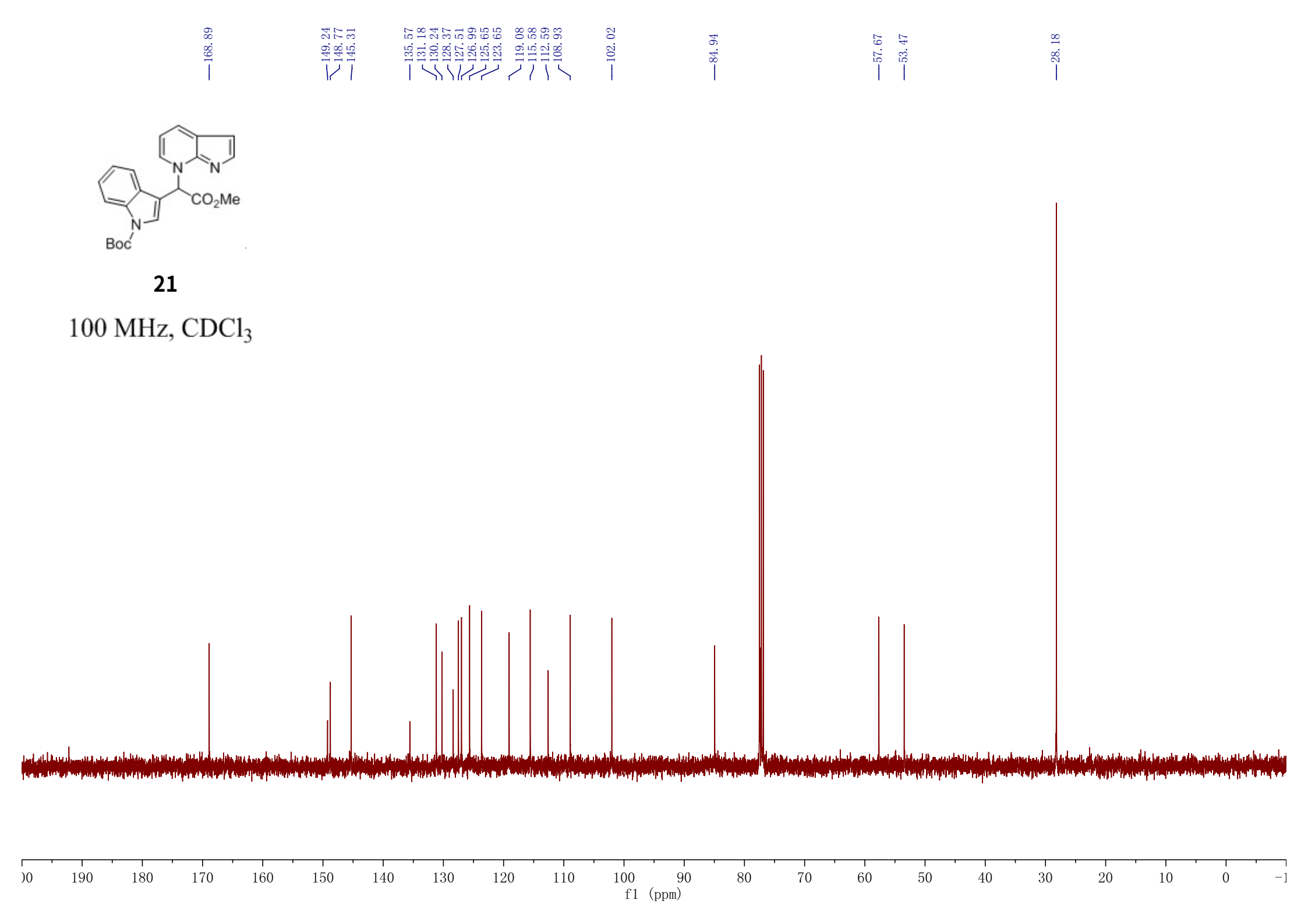
300 MHz, $CDCl_3$

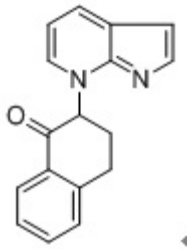

167.90
153.01
149.82
148.77
145.47
139.35
131.28
130.63
128.40
127.17
125.03
109.25
102.50
61.42
53.70
N
N
CO2Me
Cl
N
20
75 MHz, CDCl3
f1 (ppm)



21

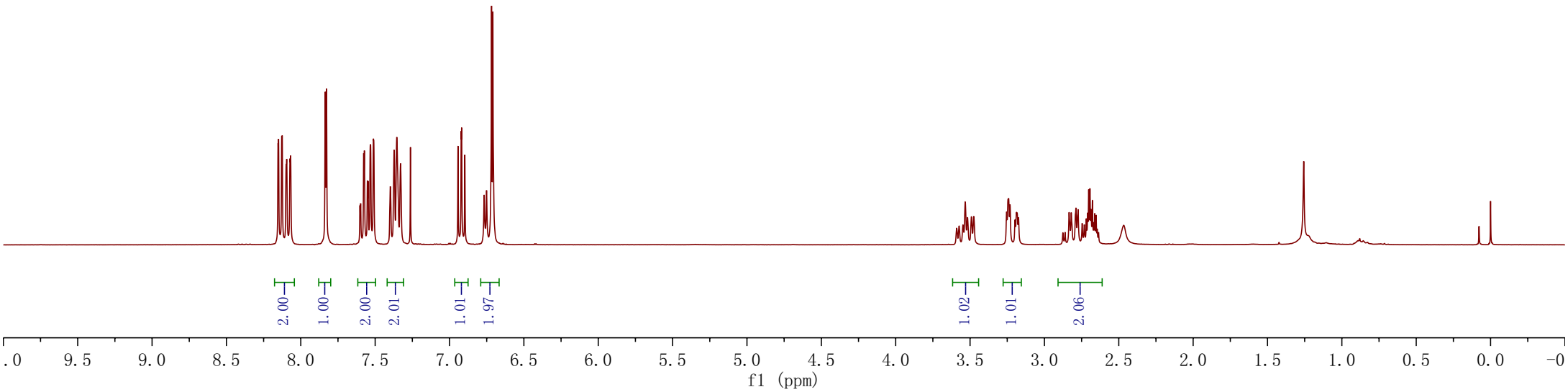
400 MHz, $CDCl_3$

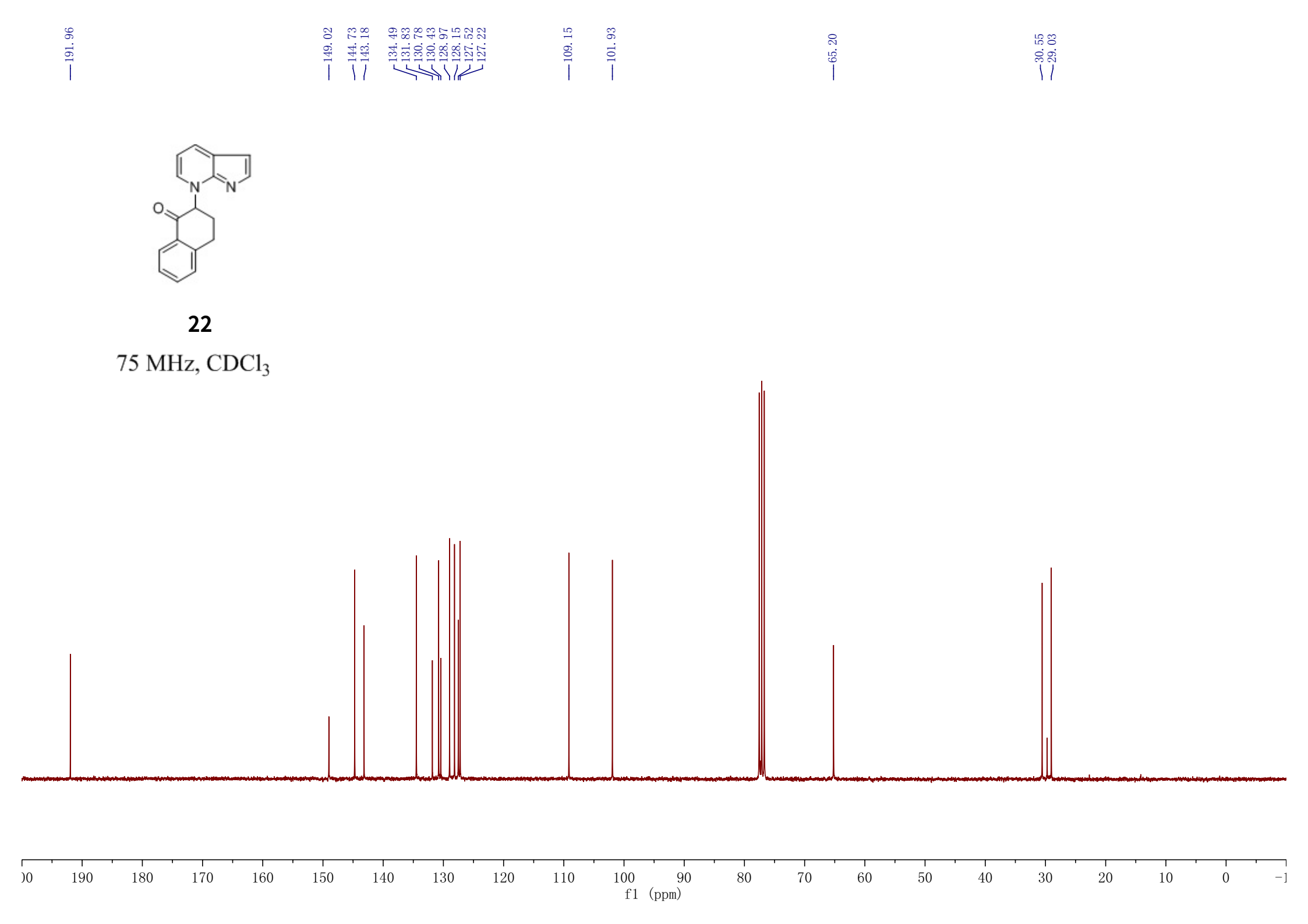

168.89
149.24
148.77
145.31
135.57
131.18
130.24
128.37
127.51
126.99
125.65
123.65
119.08
115.58
112.59
108.93
102.02
84.94
57.67
53.47
28.18
N
N
CO2Me
N
Boc
21
100 MHz, CDCl3
f1 (ppm)

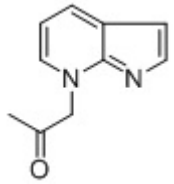


22

300 MHz, $CDCl_3$

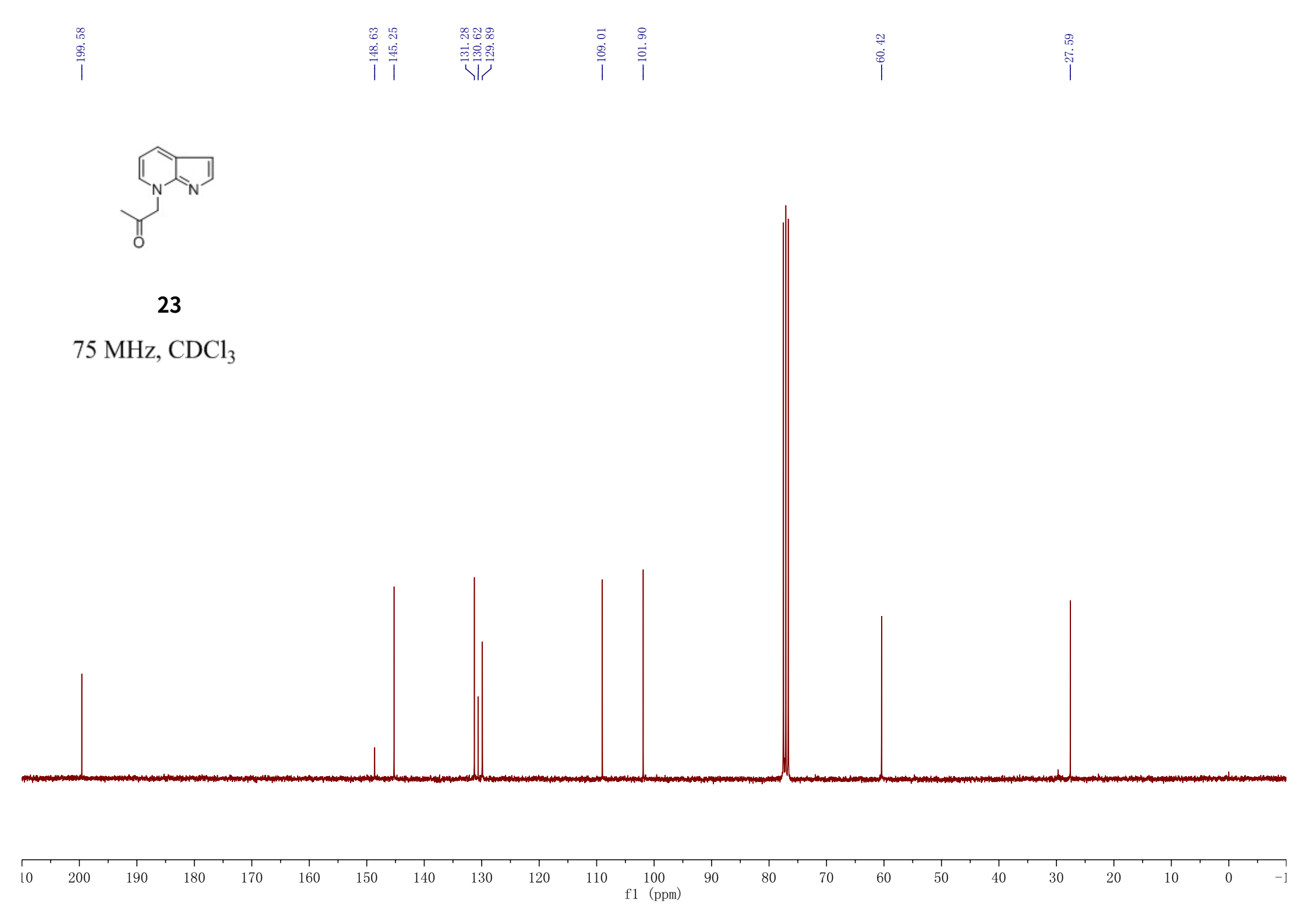


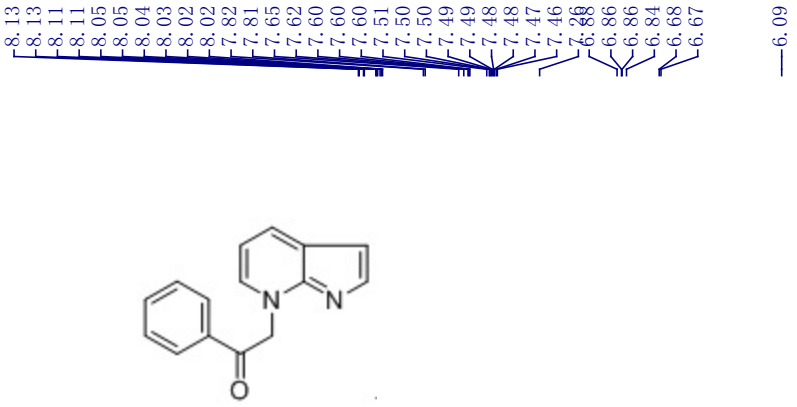

191.96
149.02
144.73
143.18
134.49
131.83
130.78
130.43
128.97
128.15
127.52
127.22
109.15
101.93
65.20
30.55
29.03
O
N
N
22
75 MHz, CDCl3
f1 (ppm)

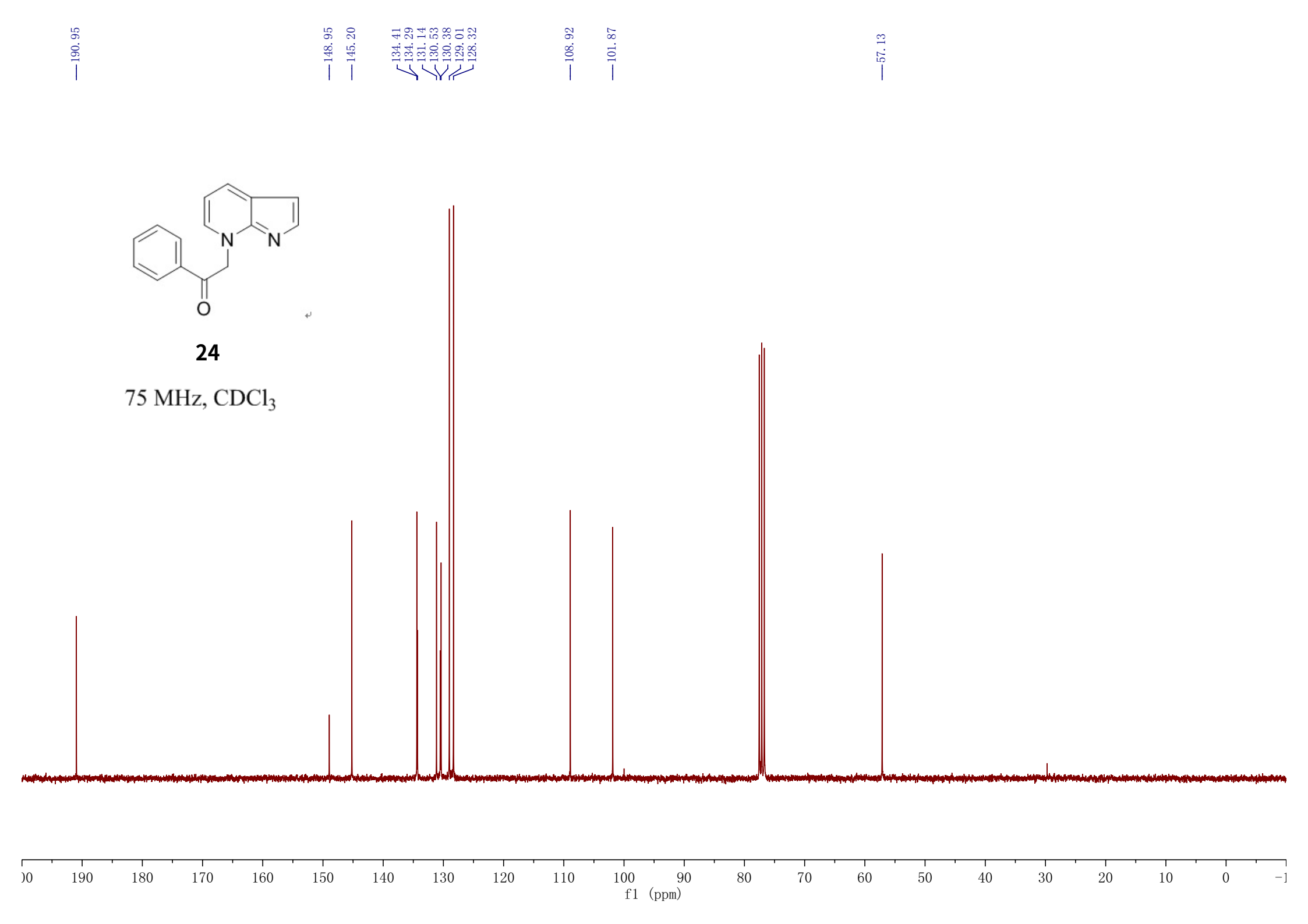


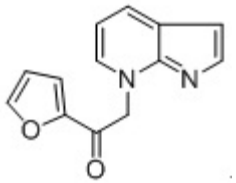
23

300 MHz, $CDCl_3$


199.58
148.63
145.25
131.28
130.62
129.89
109.01
101.90
60.42
27.59
N
N
O
23
75 MHz, CDCl3
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

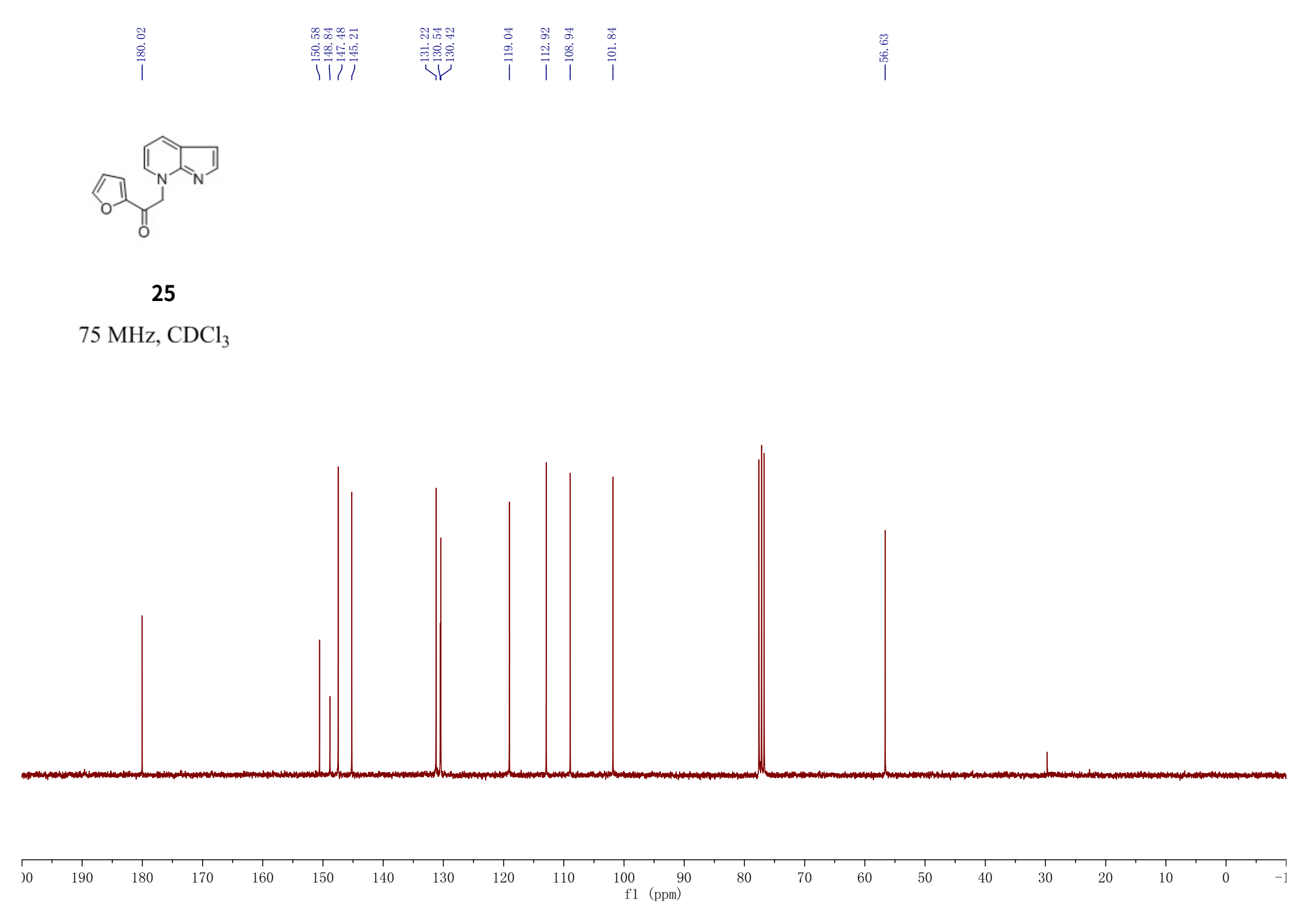

8.13
8.13
8.11
8.11
8.05
8.05
8.04
8.03
8.02
8.02
7.82
7.81
7.65
7.62
7.60
7.60
7.60
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.47
7.46
6.86
6.86
6.84
6.68
6.67
6.09
N
N
O
24
300 MHz, CDCl3
1.00
2.00
1.00
1.00
3.01
1.01
1.00
2.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

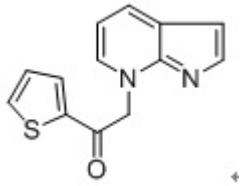

190.95
148.95
145.20
134.41
134.29
131.14
130.53
130.38
129.01
128.32
108.92
101.87
57.13
N
N
O
24
75 MHz, CDCl3
f1 (ppm)



25

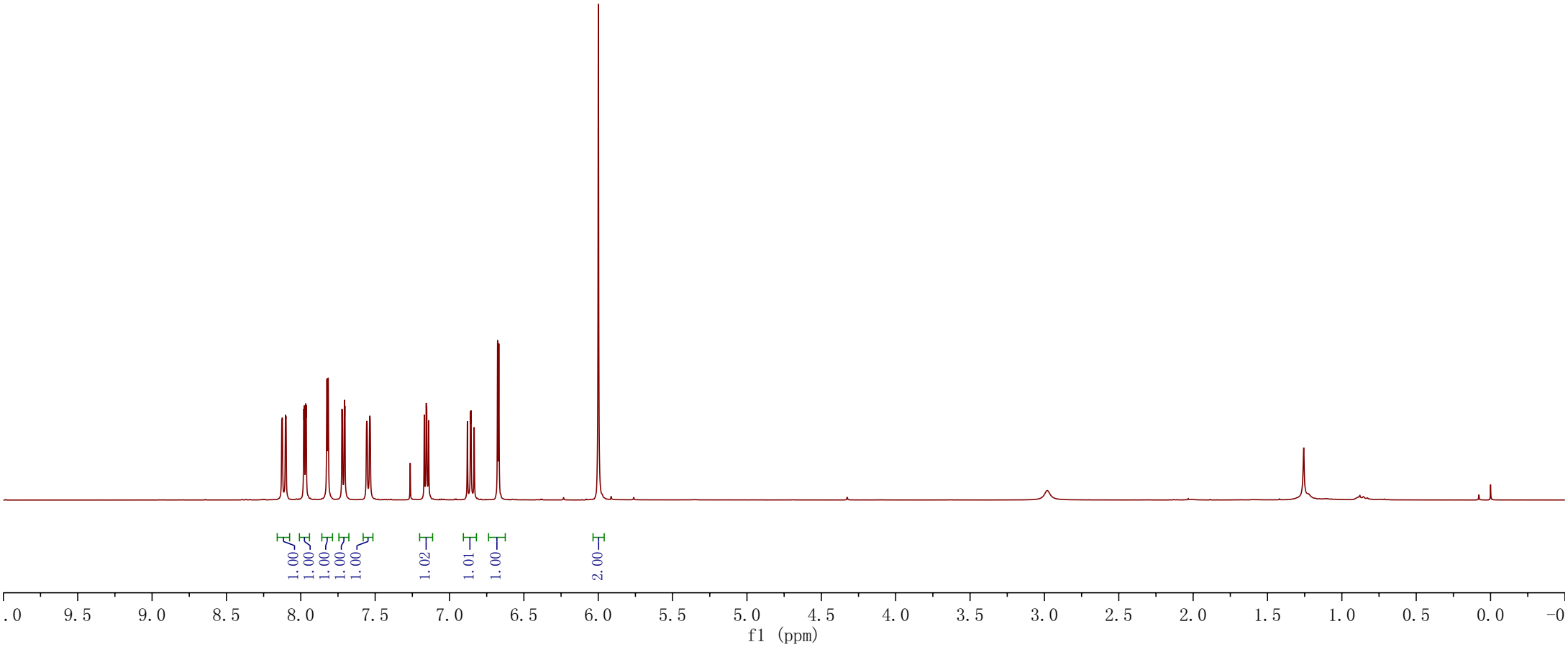
300 MHz, $CDCl_3$

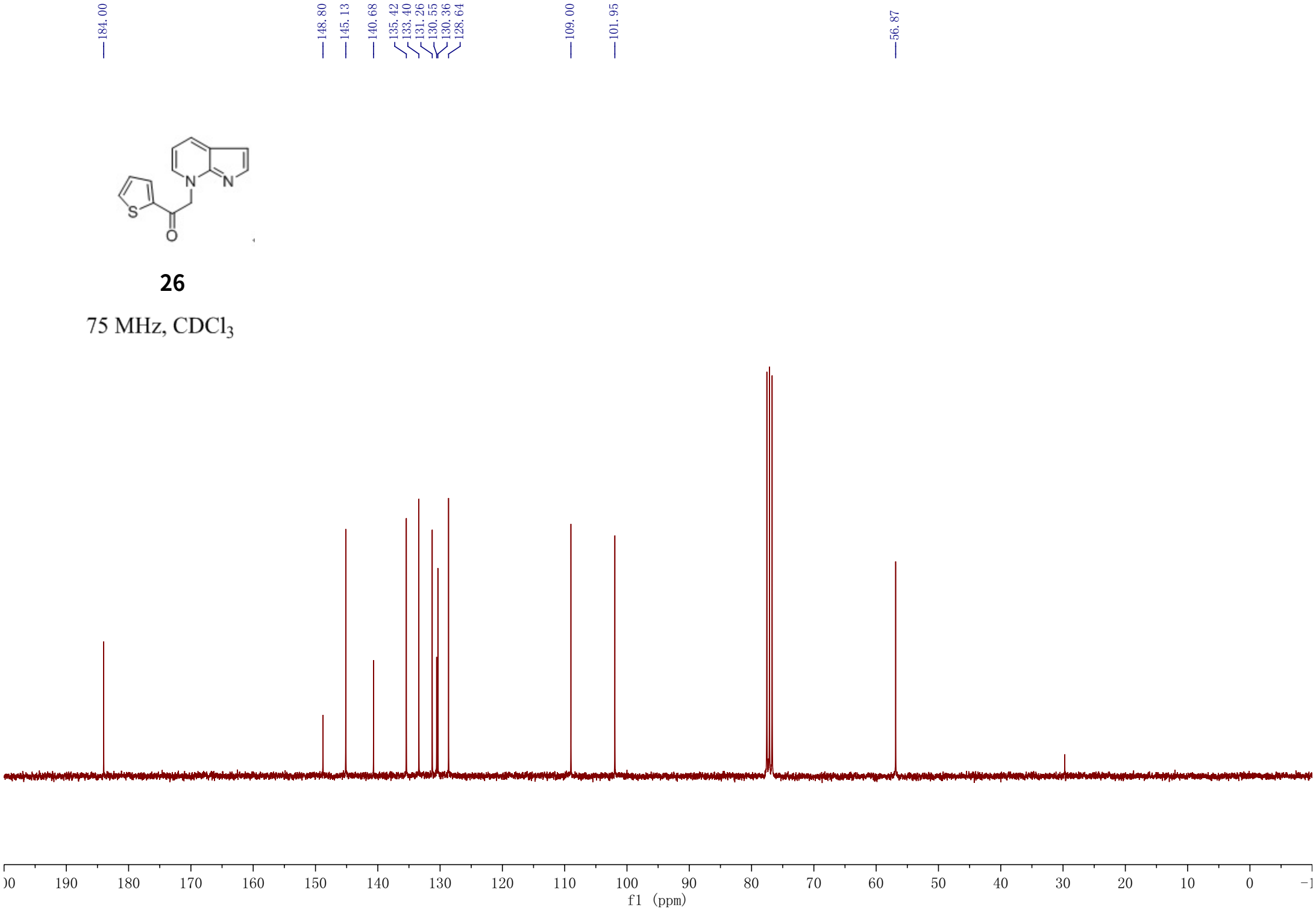

180.02
150.58
148.84
147.48
145.21
131.22
130.54
130.42
119.04
112.92
108.94
101.84
56.63
N
N
O
O
25
75 MHz, CDCl3
f1 (ppm)



26

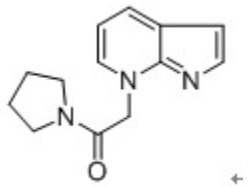
300 MHz, $CDCl_3$





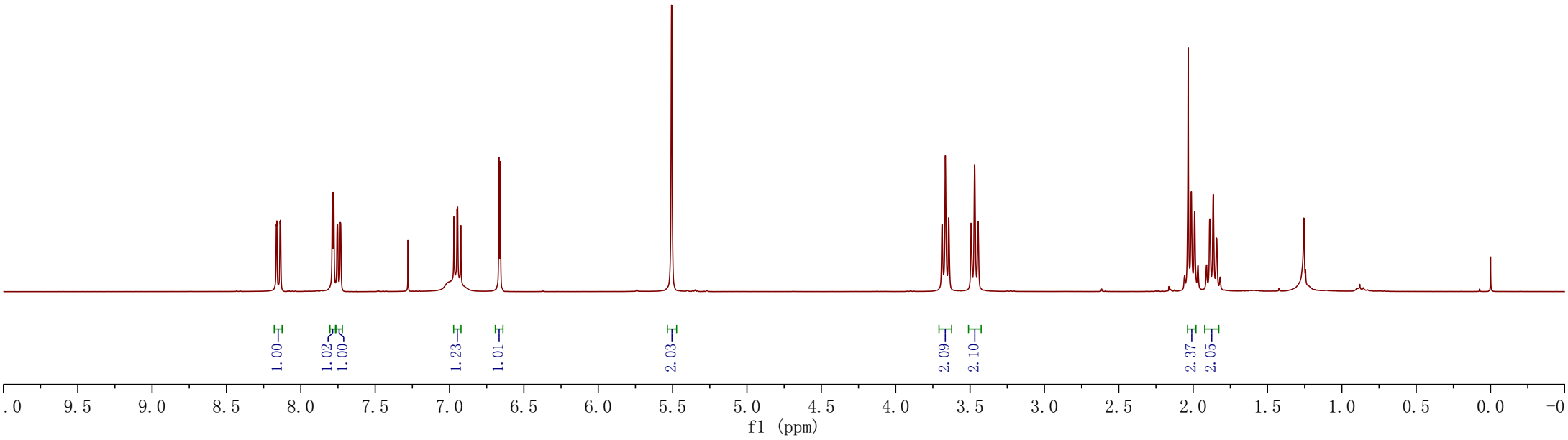
26

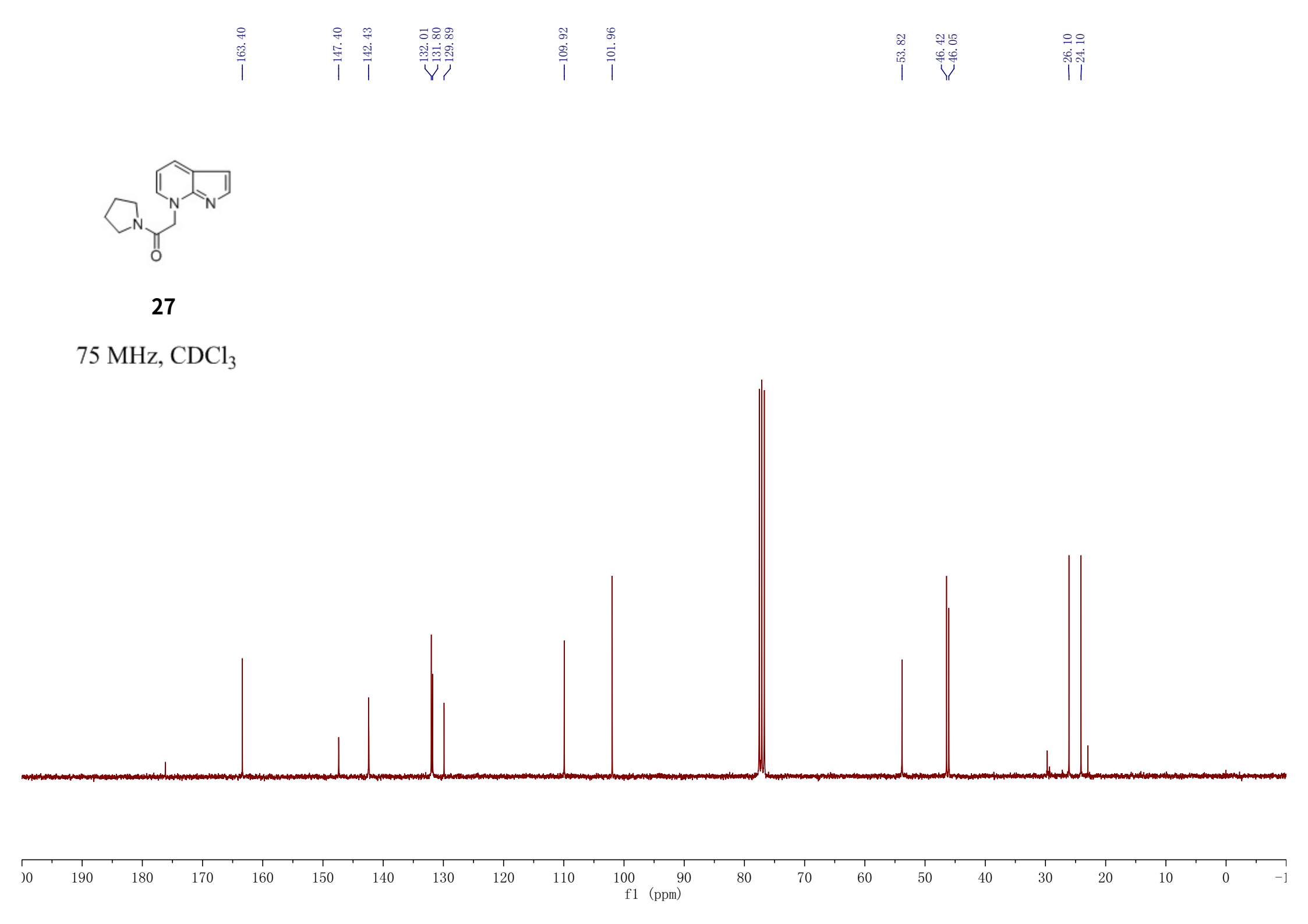
75 MHz, $CDCl_3$

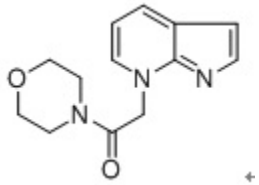


27

300 MHz, $CDCl_3$

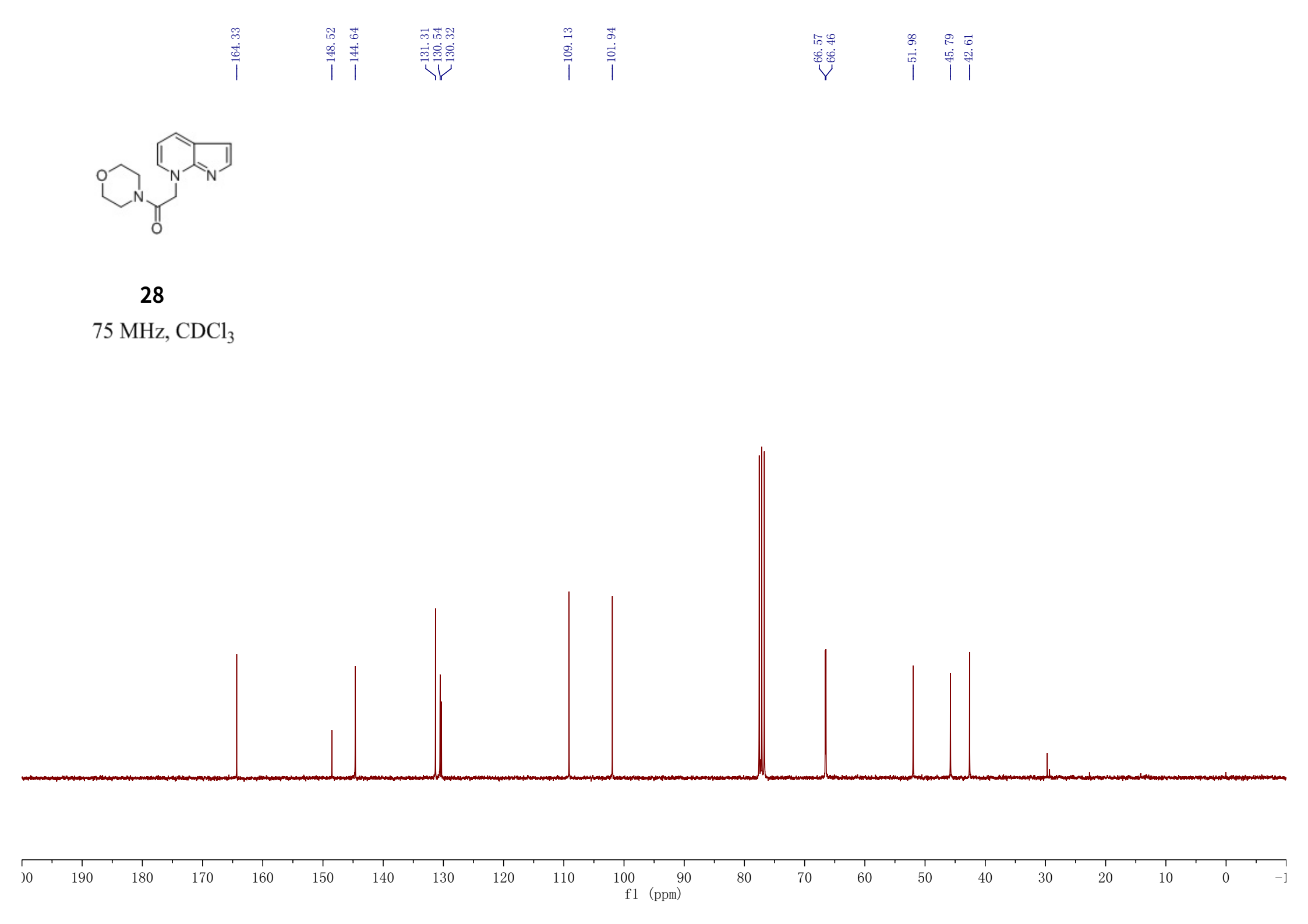


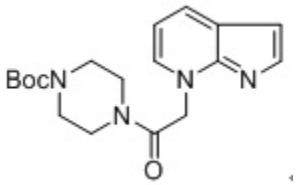

163.40
147.40
142.43
132.01
131.80
129.89
109.92
101.96
53.82
46.42
46.05
26.10
24.10
N
N
N
O
27
75 MHz, CDCl3
f1 (ppm)



28

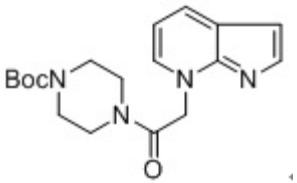
300 MHz, $CDCl_3$


164.33
148.52
144.64
131.31
130.54
130.32
109.13
101.94
66.57
66.46
51.98
45.79
42.61
O
N
N
N
O
28
75 MHz, CDCl3
f1 (ppm)



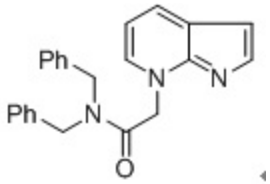
29

300 MHz, $CDCl_3$



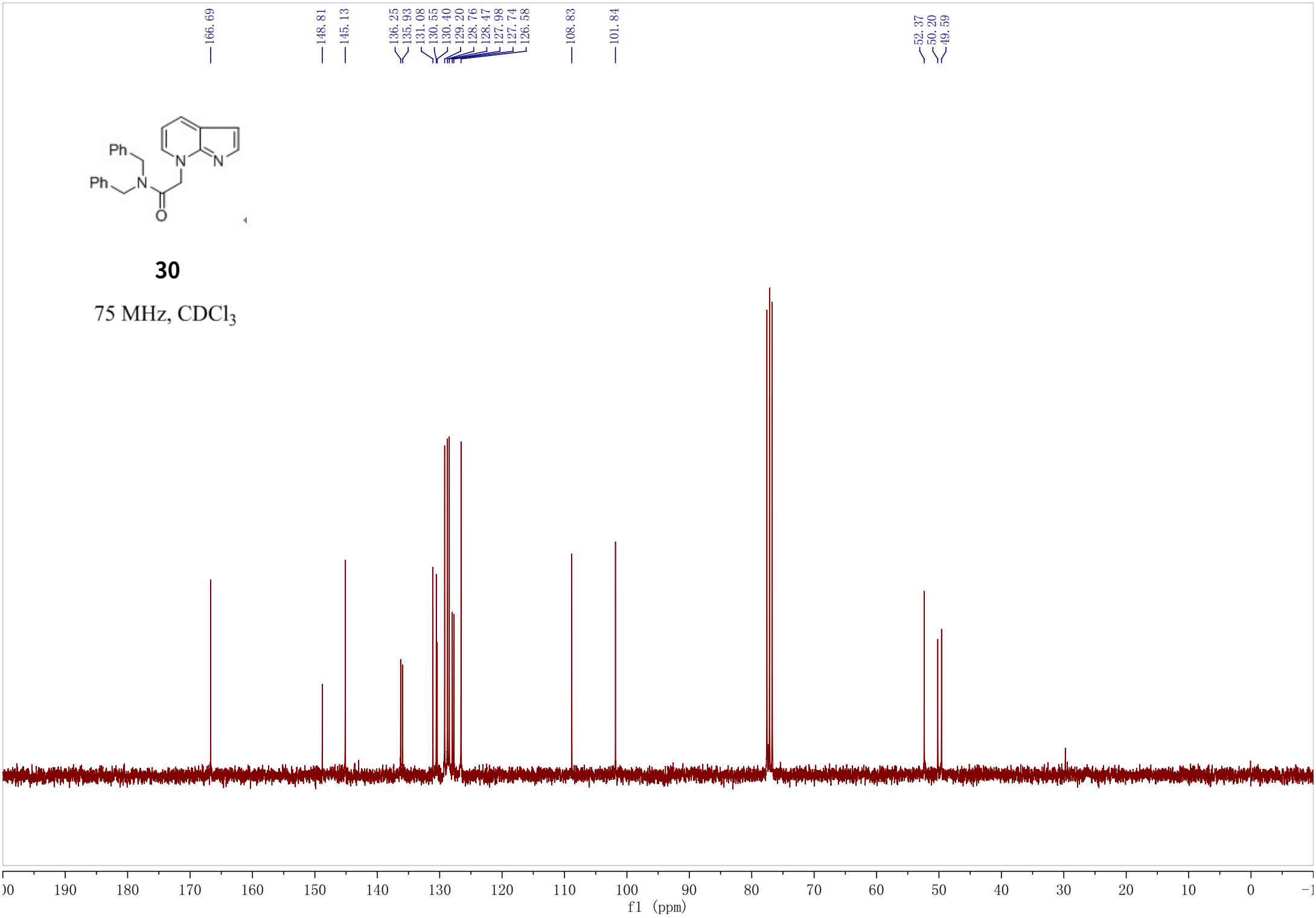
29

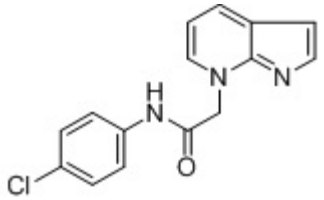
75 MHz, $CDCl_3$



30

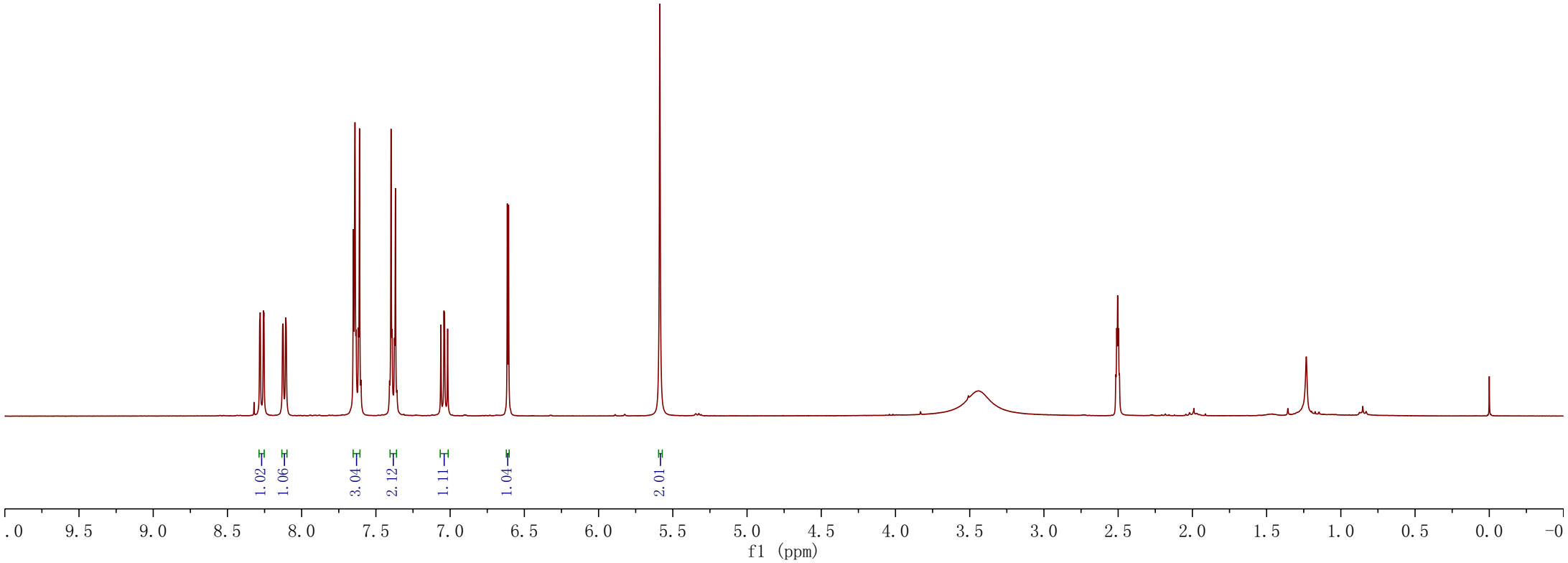
300 MHz, $CDCl_3$

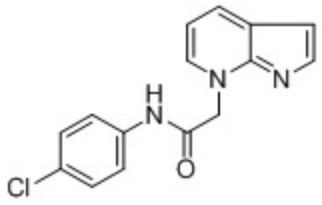

166.69
148.81
145.13
136.25
135.93
131.08
130.55
130.40
129.20
128.76
128.47
127.98
127.74
126.58
108.83
101.84
52.37
50.20
49.59
Ph
Ph
N
N
N
O
30
75 MHz, CDCl3
f1 (ppm)



31

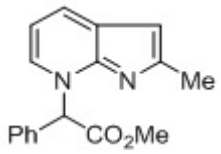
300 MHz, DMSO-d_6





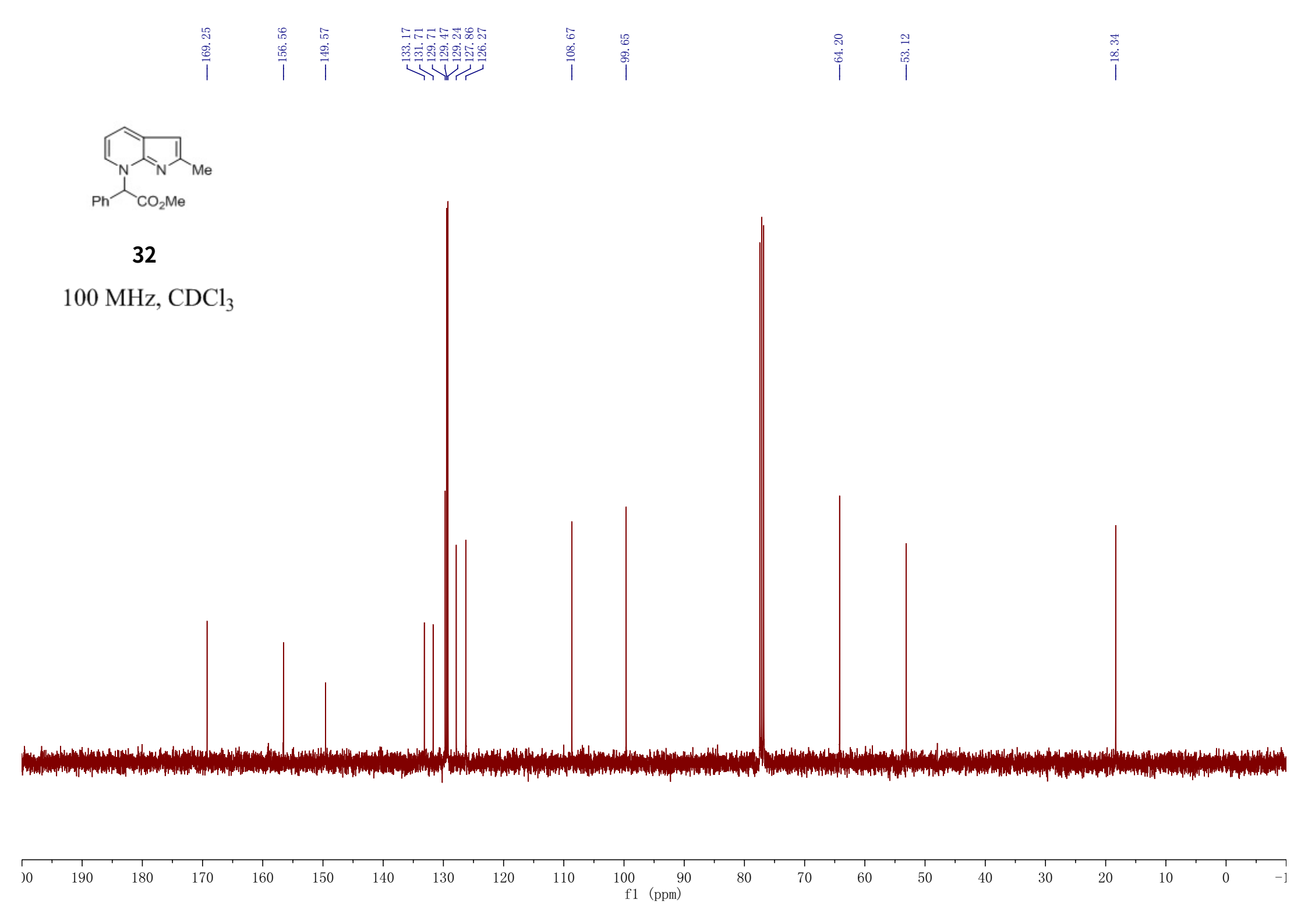
31

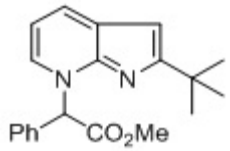
75 MHz, DMSO-d_6



32

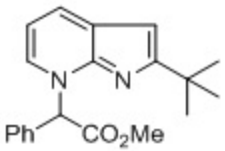
400 MHz, $CDCl_3$


169.25
156.56
149.57
133.17
131.71
129.71
129.47
129.24
127.86
126.27
108.67
99.65
64.20
53.12
18.34
N
N
Me
Ph
CO2Me
32
100 MHz, CDCl3
f1 (ppm)



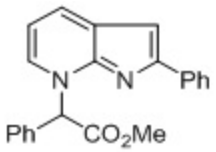
33

300 MHz, DMSO-d_6



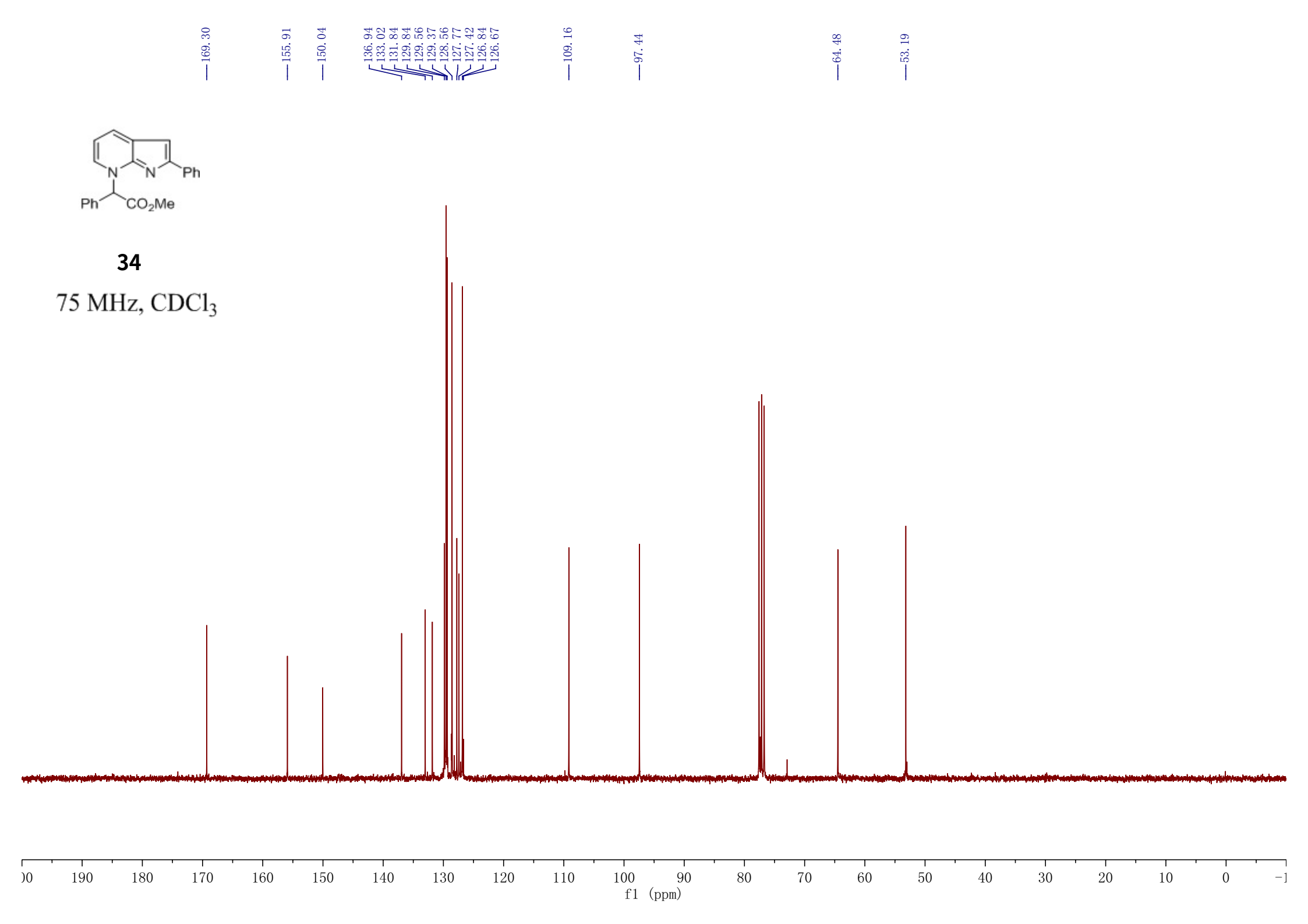
33

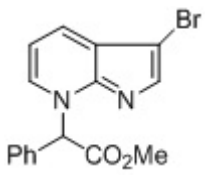
75 MHz, DMSO-d_6



34

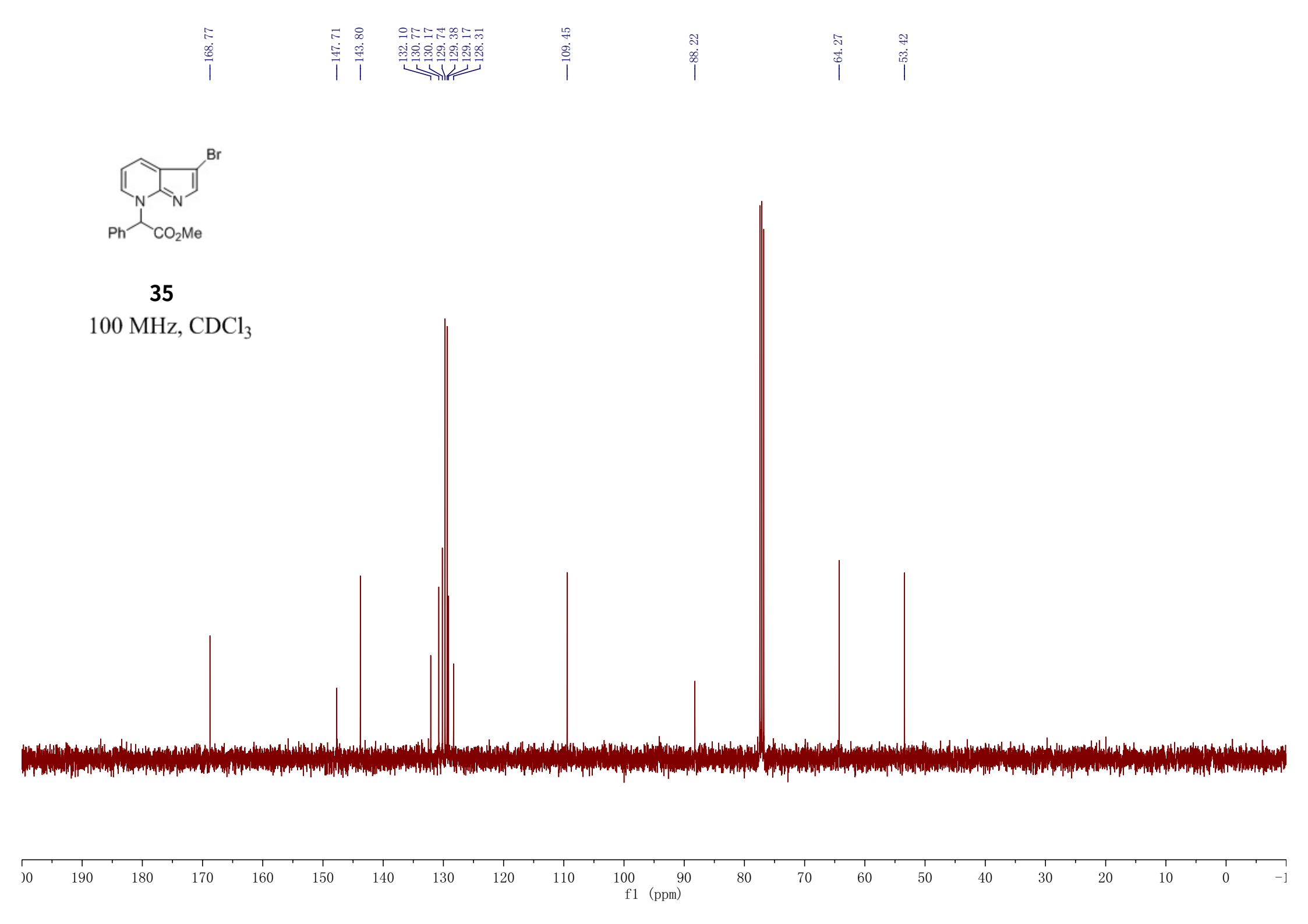
300 MHz, $CDCl_3$

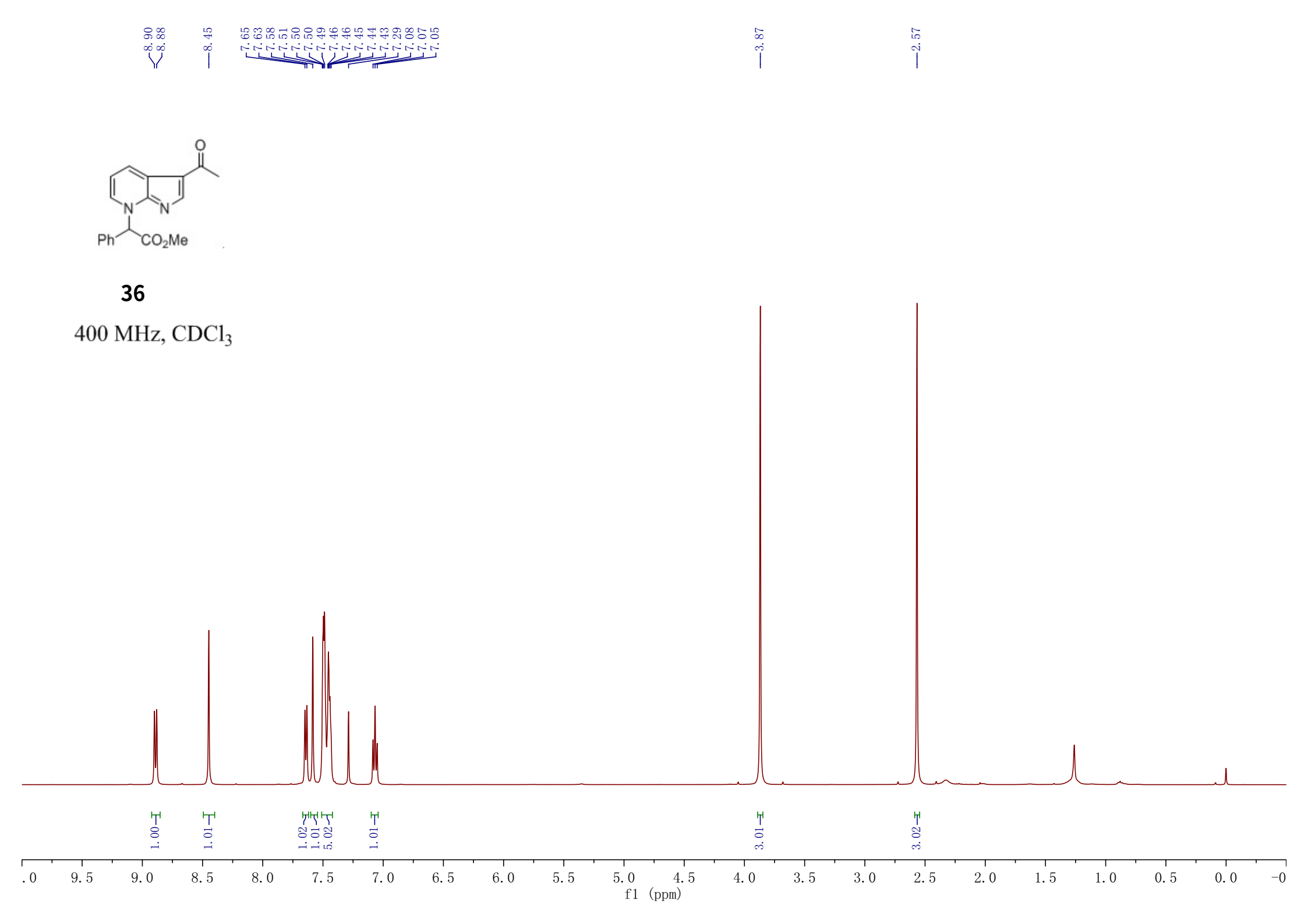

169.30
155.91
150.04
136.94
133.02
131.84
129.84
129.56
129.37
128.56
127.77
127.42
126.84
126.67
109.16
97.44
64.48
53.19
N
N
Ph
Ph
CO2Me
34
75 MHz, CDCl3
f1 (ppm)

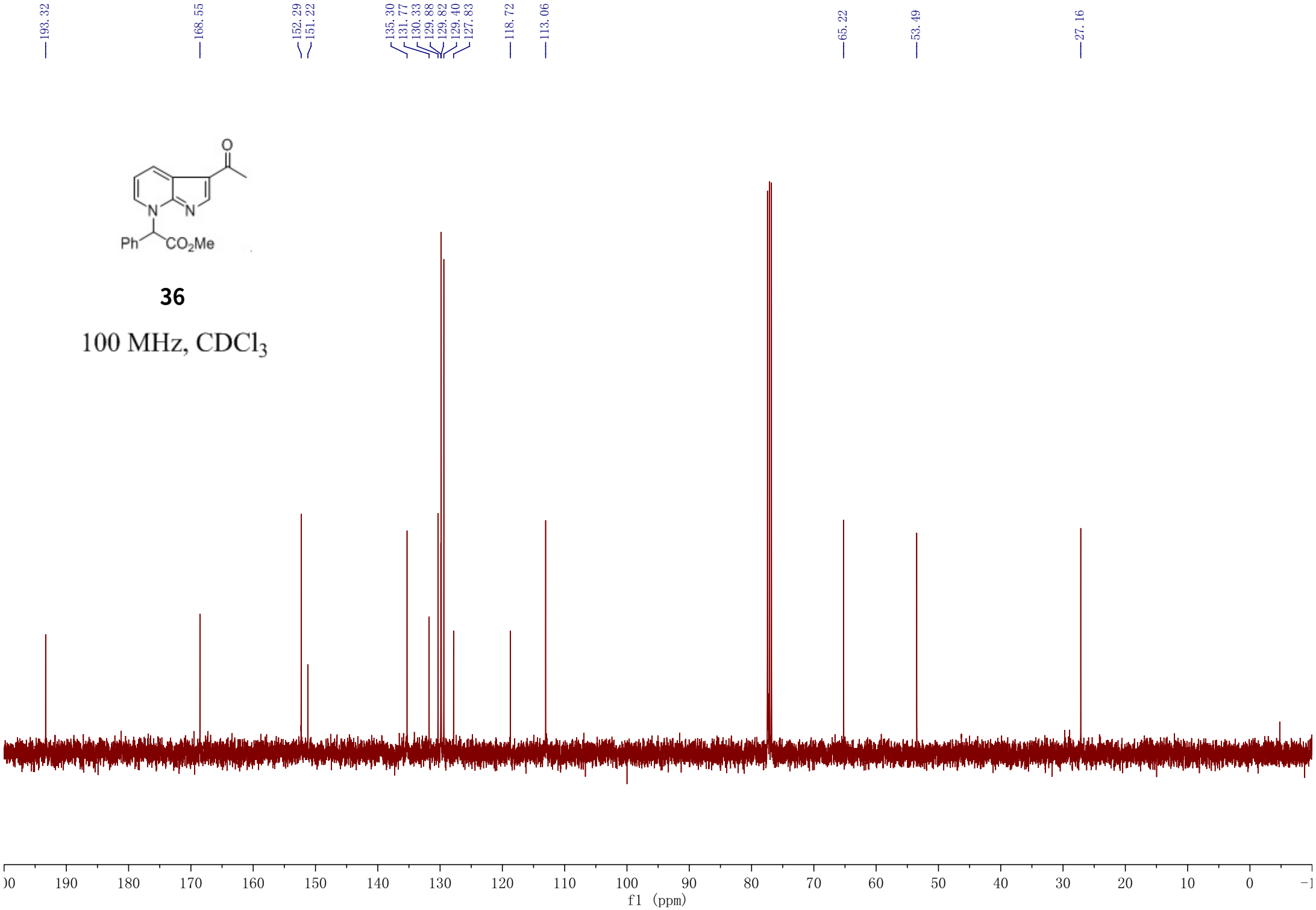


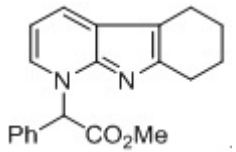
35

400 MHz, $CDCl_3$


168.77
147.71
143.80
132.10
130.77
130.17
129.74
129.38
129.17
128.31
109.45
88.22
64.27
53.42
Br
N
N
Ph
CO2Me
35
100 MHz, CDCl3
f1 (ppm)

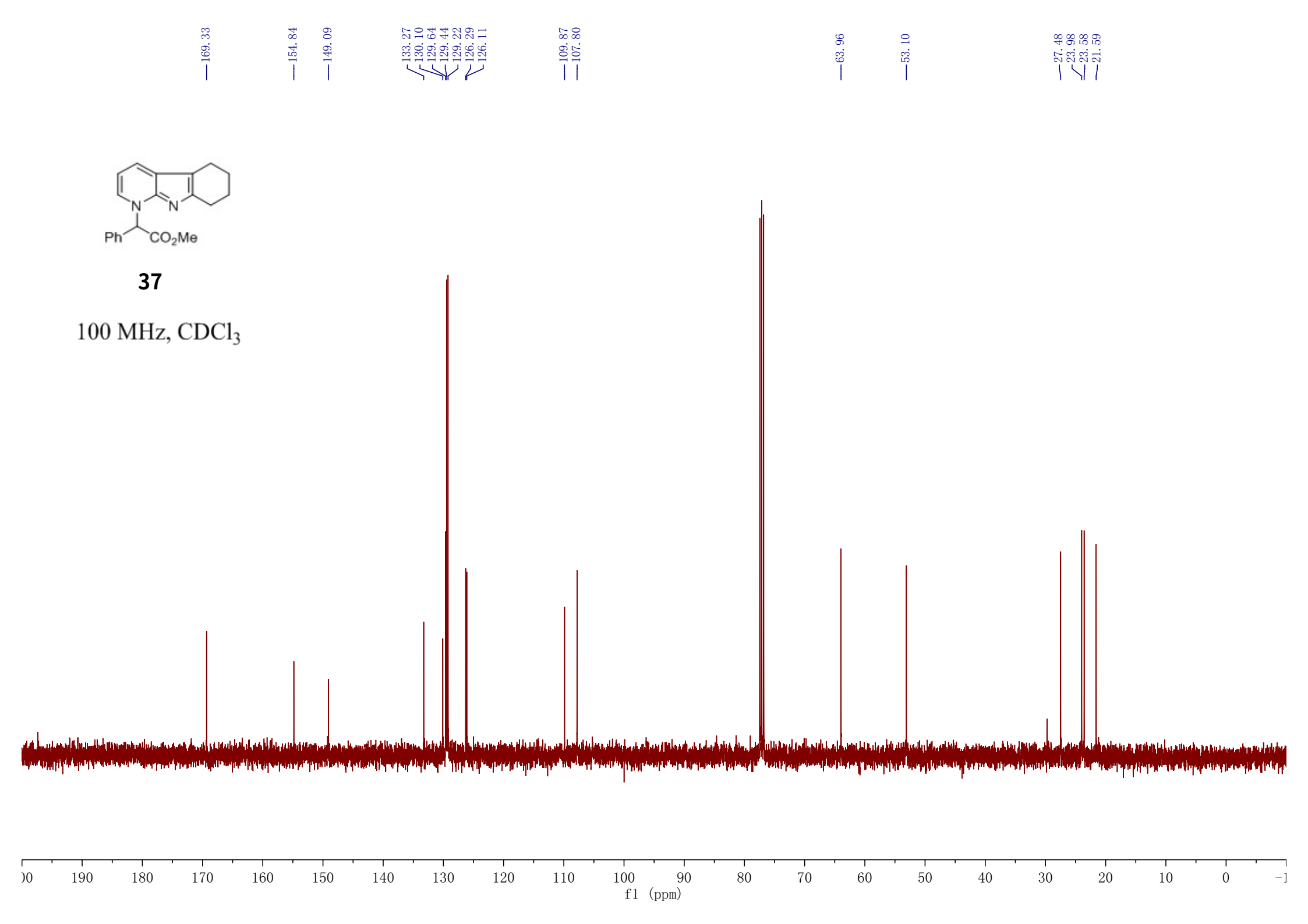

8.90
8.88
8.45
7.65
7.63
7.58
7.51
7.50
7.50
7.49
7.46
7.46
7.45
7.44
7.43
7.29
7.08
7.07
7.05
3.87
2.57
O
N
N
Ph
CO2Me
36
400 MHz, CDCl3
1.00
1.01
1.02
1.01
5.02
1.01
3.01
3.02
f1 (ppm)

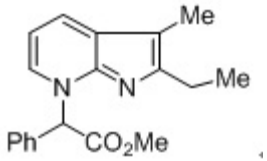

193.32
168.55
152.29
151.22
135.30
131.77
130.33
129.88
129.82
129.40
127.83
118.72
113.06
65.22
53.49
27.16
O
N
N
Ph
CO2Me
36
100 MHz, CDCl3
f1 (ppm)



37

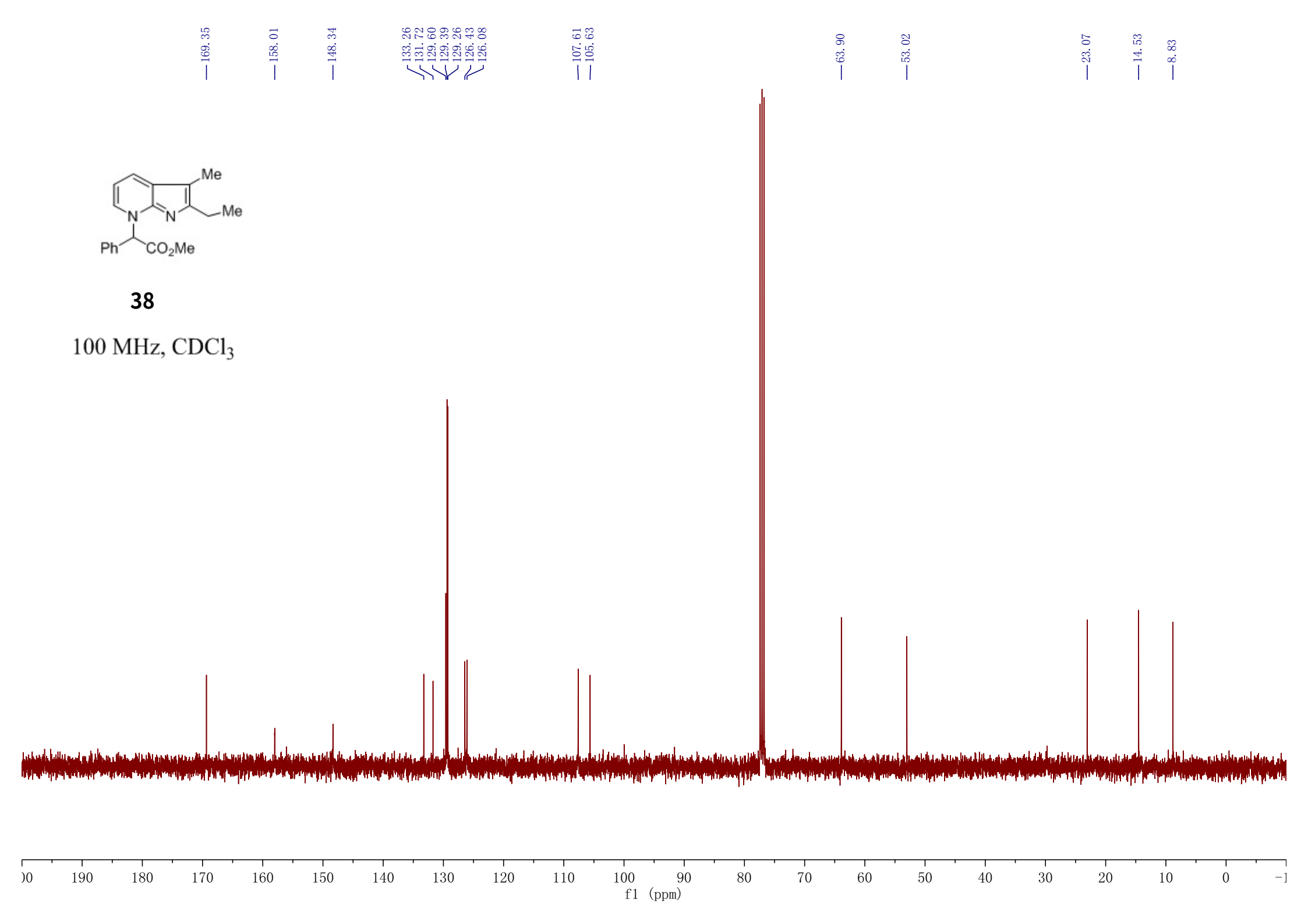
400 MHz, $CDCl_3$

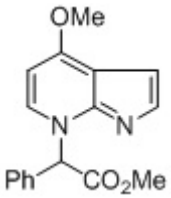

169.33
154.84
149.09
133.27
130.10
129.64
129.44
129.22
126.29
126.11
109.87
107.80
63.96
53.10
27.48
23.98
23.58
21.59
N
N
Ph
CO2Me
37
100 MHz, CDCl3
f1 (ppm)



38

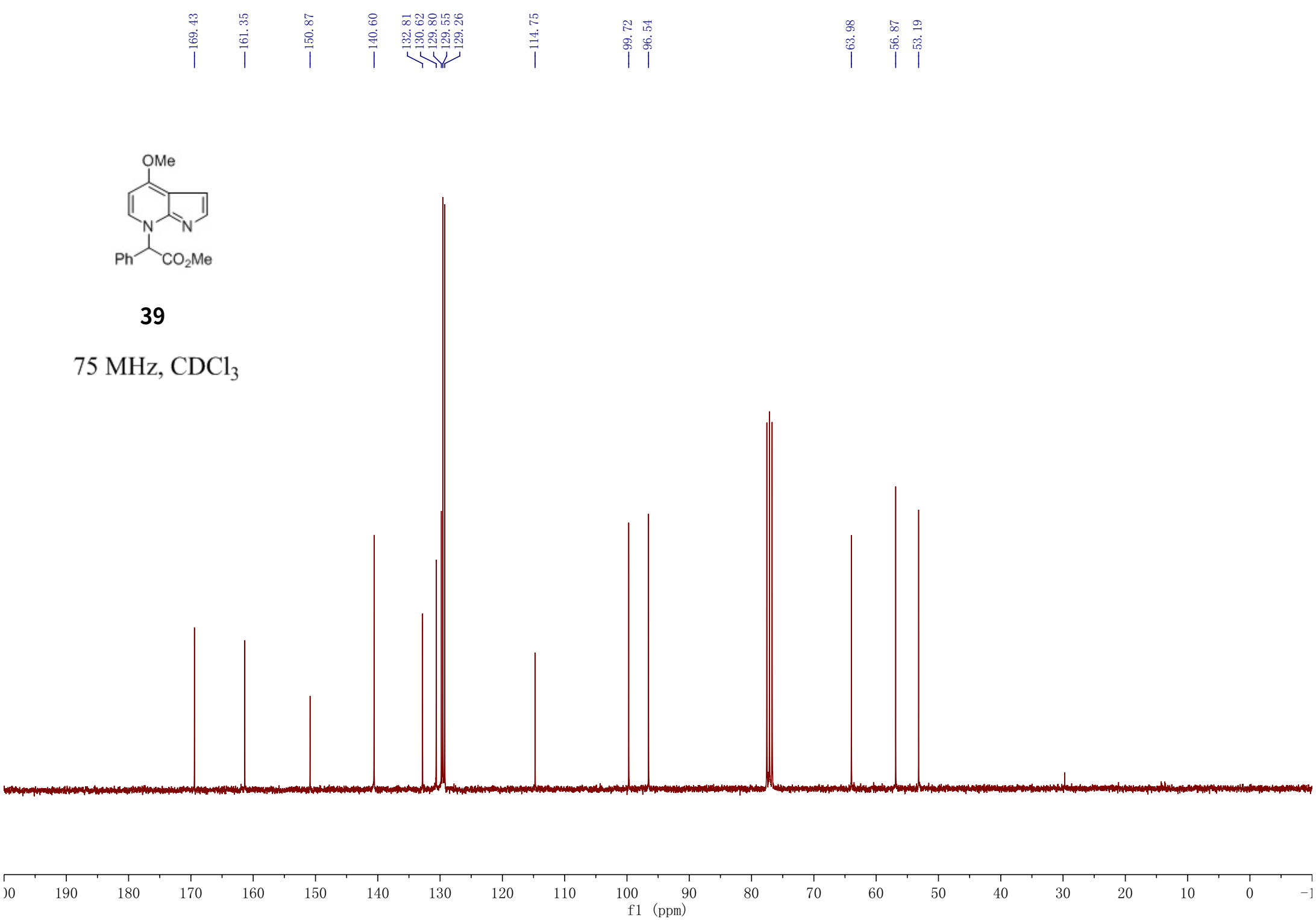
400 MHz, $CDCl_3$

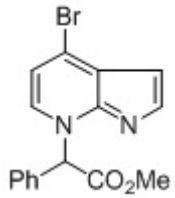

169.35
158.01
148.34
133.26
131.72
129.60
129.39
129.26
126.43
126.08
107.61
105.63
63.90
53.02
23.07
14.53
8.83
Me
Me
N
N
Ph
CO2Me
38
100 MHz, CDCl3
f1 (ppm)



39

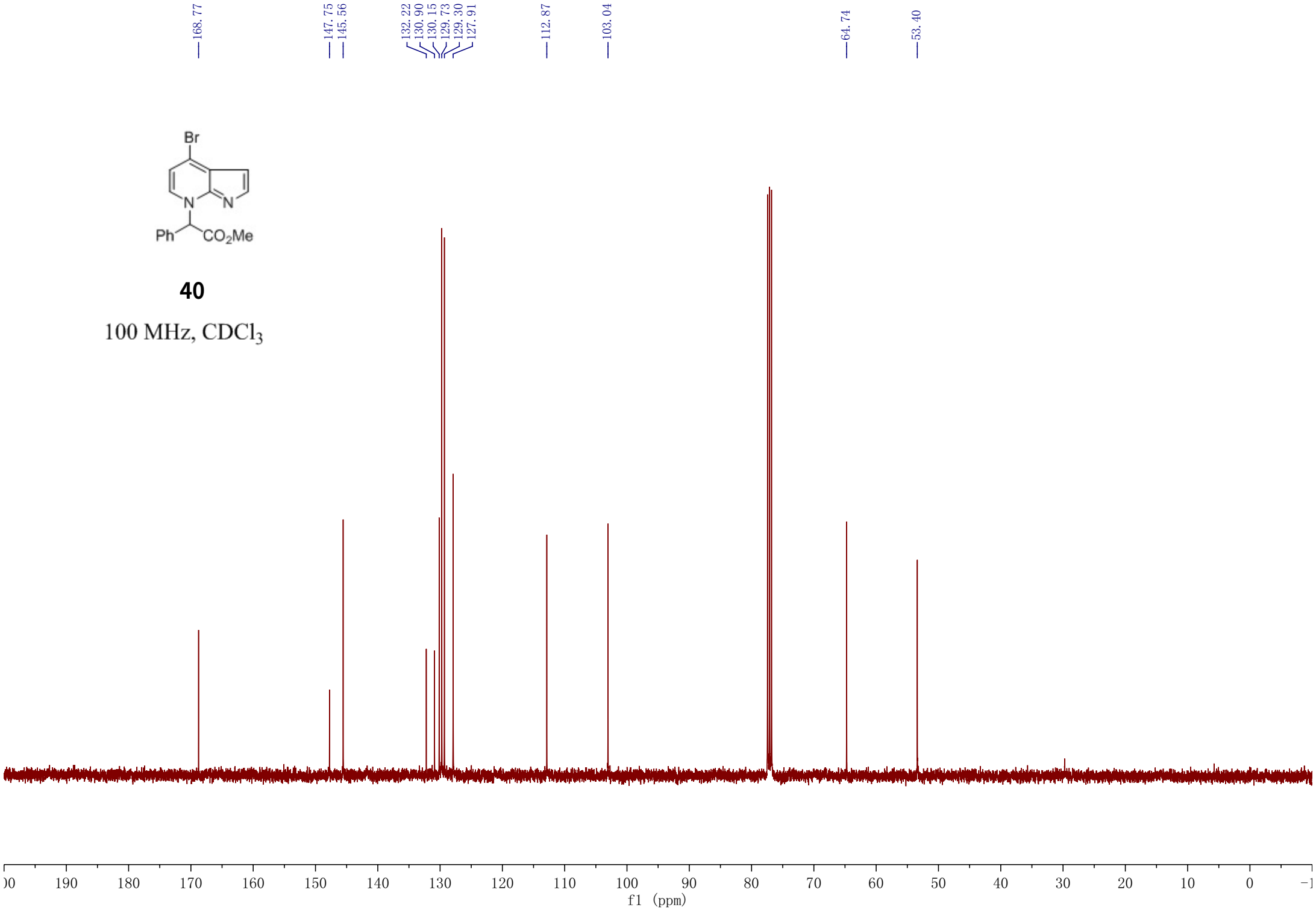
300 MHz, $CDCl_3$

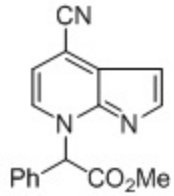

169.43
161.35
150.87
140.60
132.81
130.62
129.80
129.55
129.26
114.75
99.72
96.54
63.98
56.87
53.19
OMe
N
N
Ph
CO2Me
39
75 MHz, CDCl3
f1 (ppm)



40

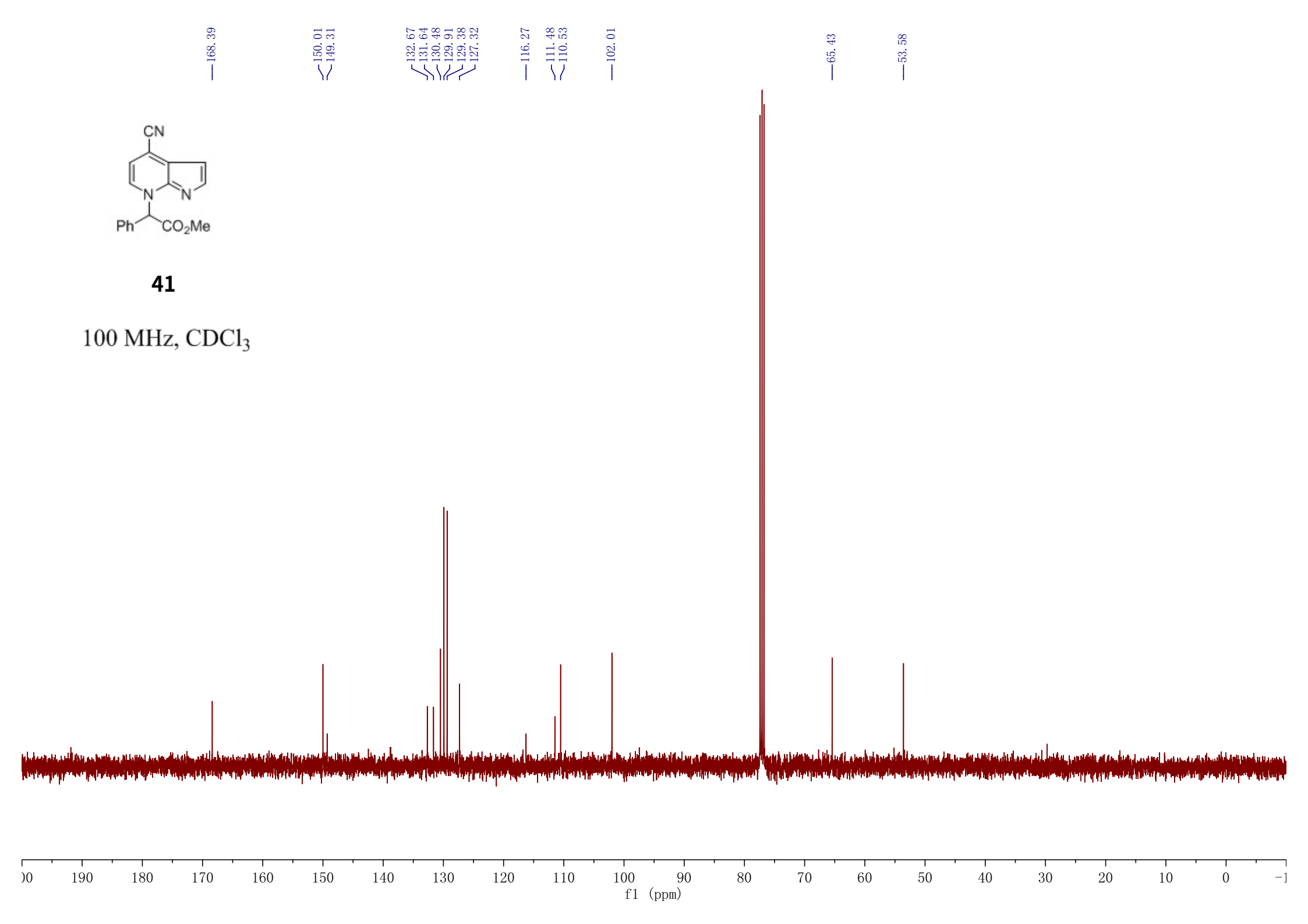
400 MHz, $CDCl_3$

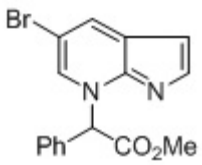

168.77
147.75
145.56
132.22
130.90
130.15
129.73
129.30
127.91
112.87
103.04
64.74
53.40
Br
N
N
Ph
CO2Me
40
100 MHz, CDCl3
f1 (ppm)



41

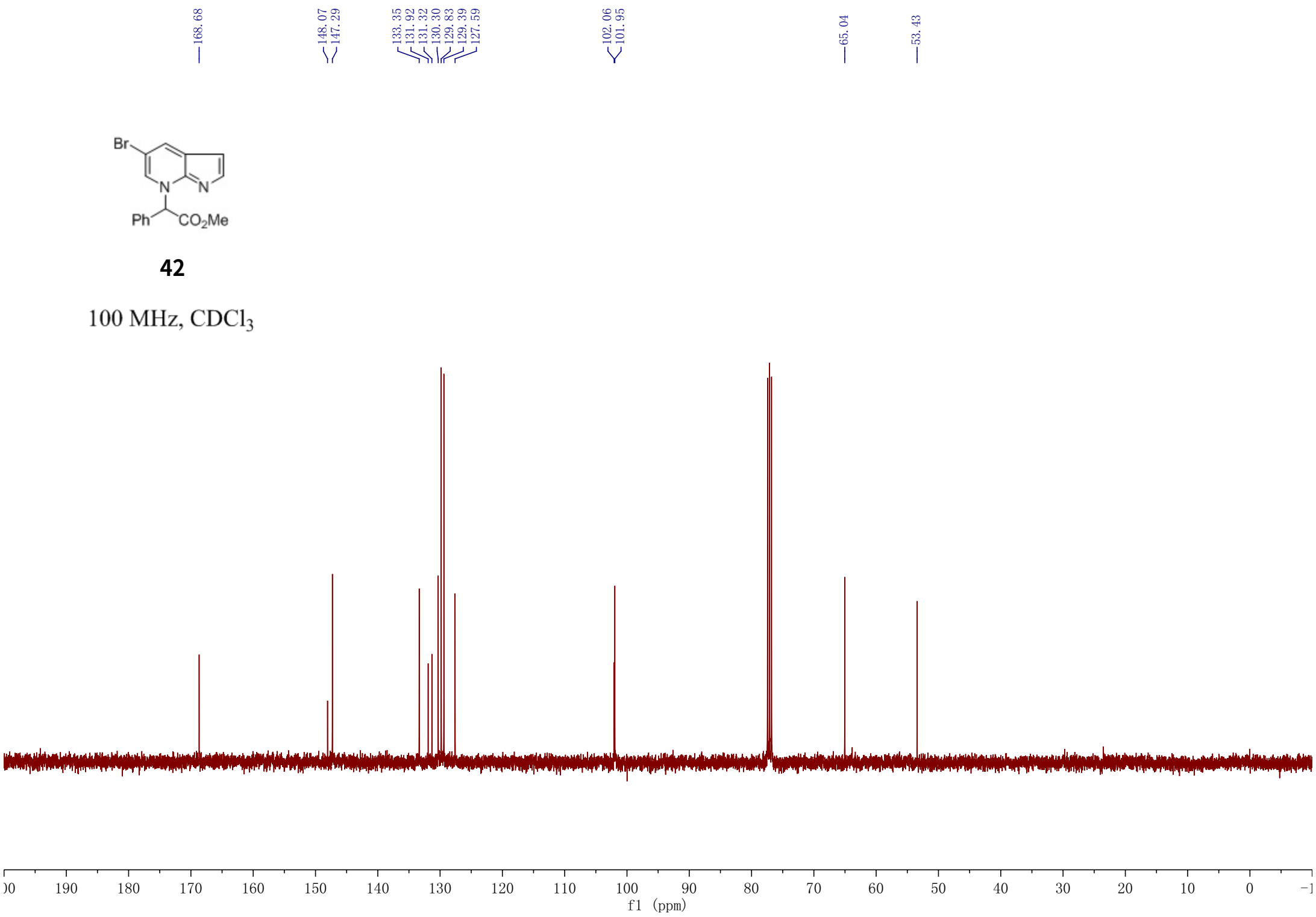
400 MHz, $CDCl_3$

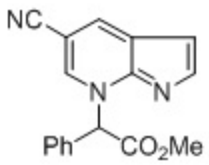

168.39
150.01
149.31
132.67
131.64
130.48
129.91
129.38
127.32
116.27
111.48
110.53
102.01
65.43
53.58
CN
N
N
Ph
CO2Me
41
100 MHz, CDCl3
f1 (ppm)



42

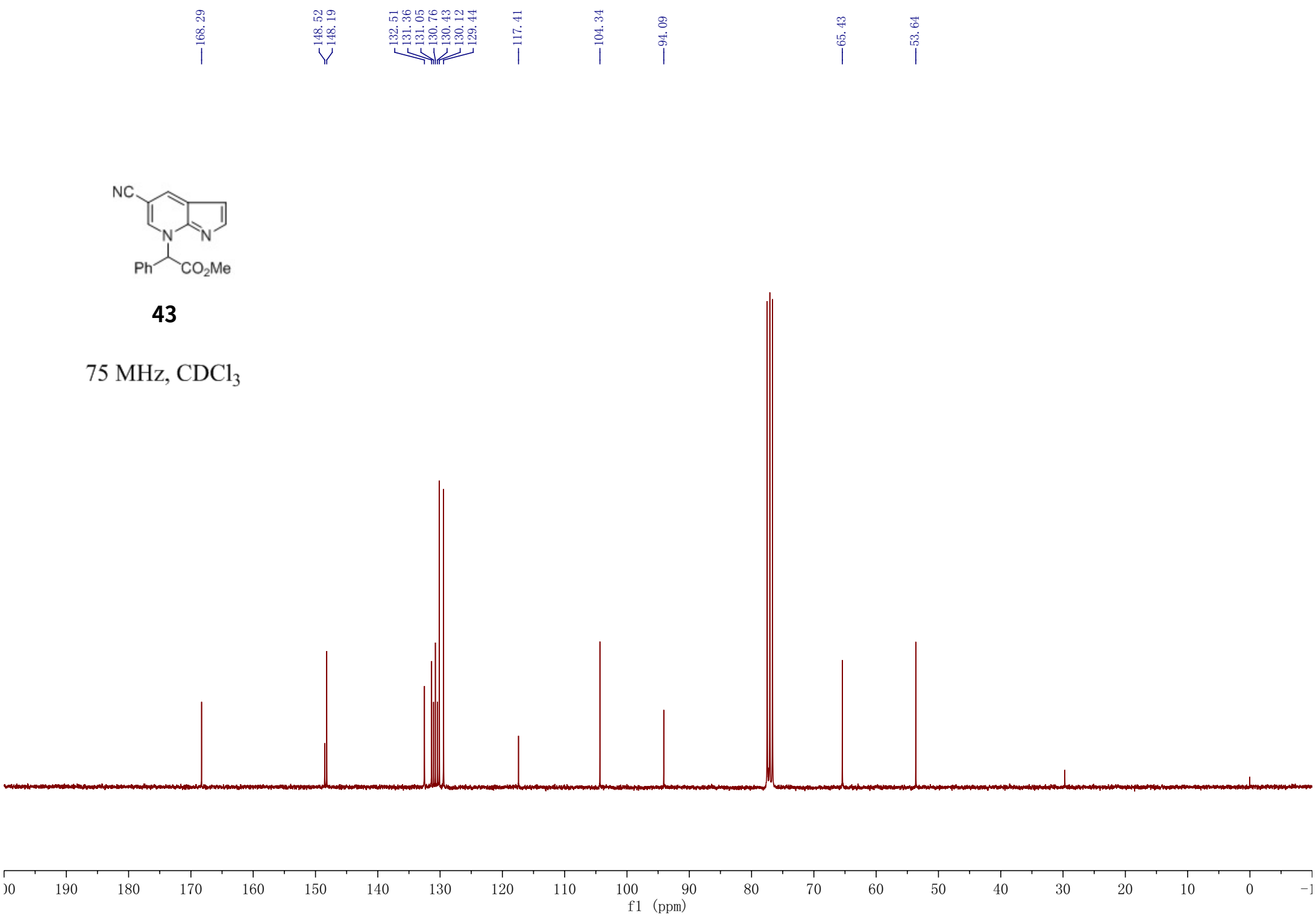
400 MHz, $CDCl_3$

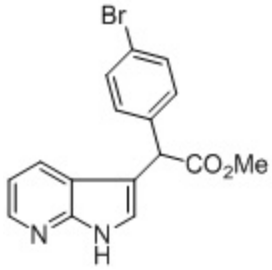

168.68
148.07
147.29
133.35
131.92
131.32
130.30
129.83
129.39
127.59
102.06
101.95
65.04
53.43
Br
N
N
Ph
CO2Me
42
100 MHz, CDCl3
f1 (ppm)



43

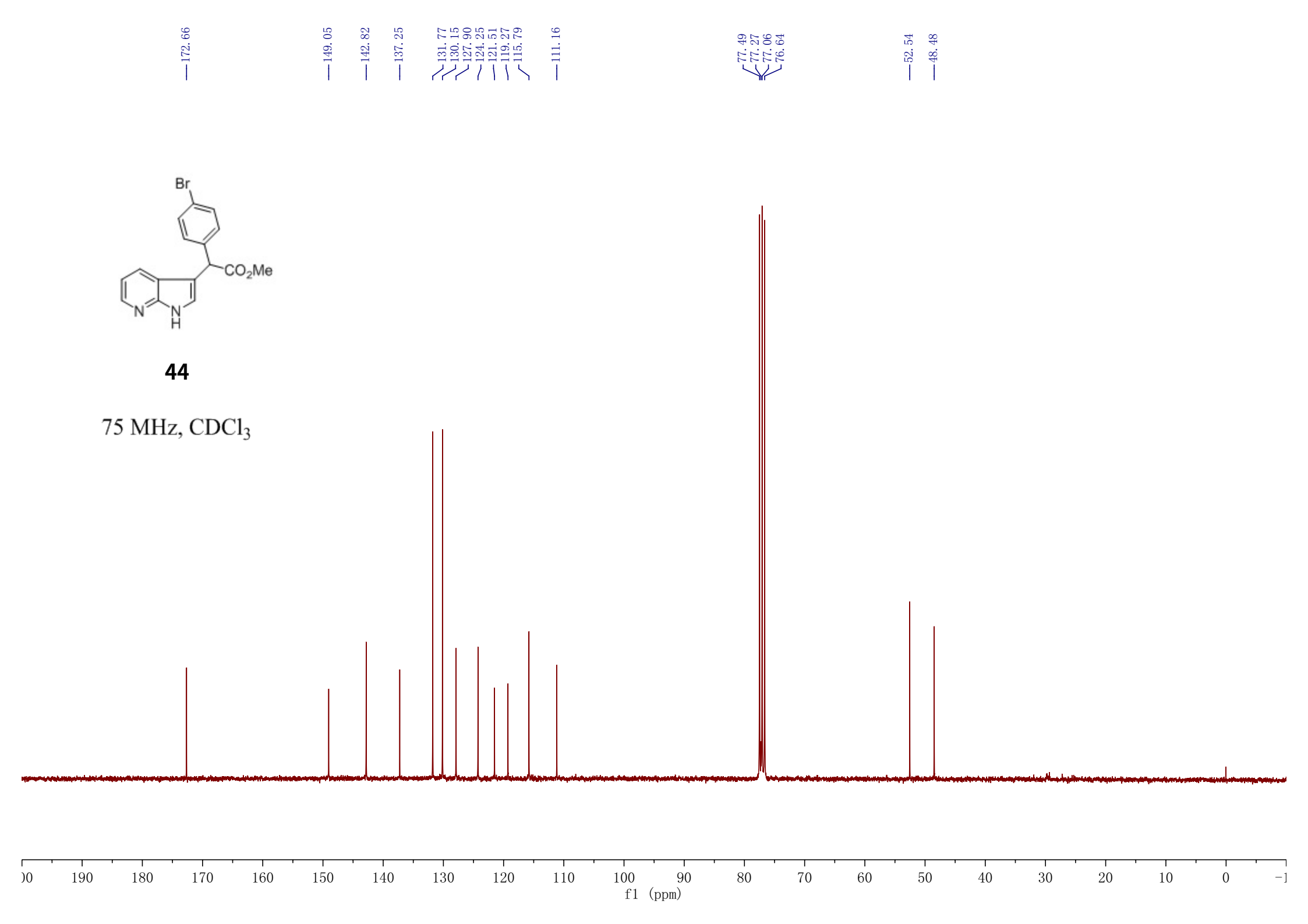
300 MHz, $CDCl_3$

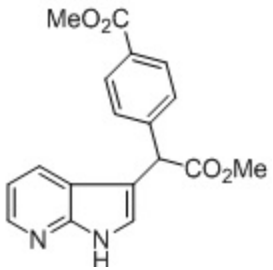

168.29
148.52
148.19
132.51
131.36
131.05
130.76
130.43
130.12
129.44
117.41
104.34
94.09
65.43
53.64
NC
N
N
Ph
CO2Me
43
75 MHz, CDCl3
f1 (ppm)



44

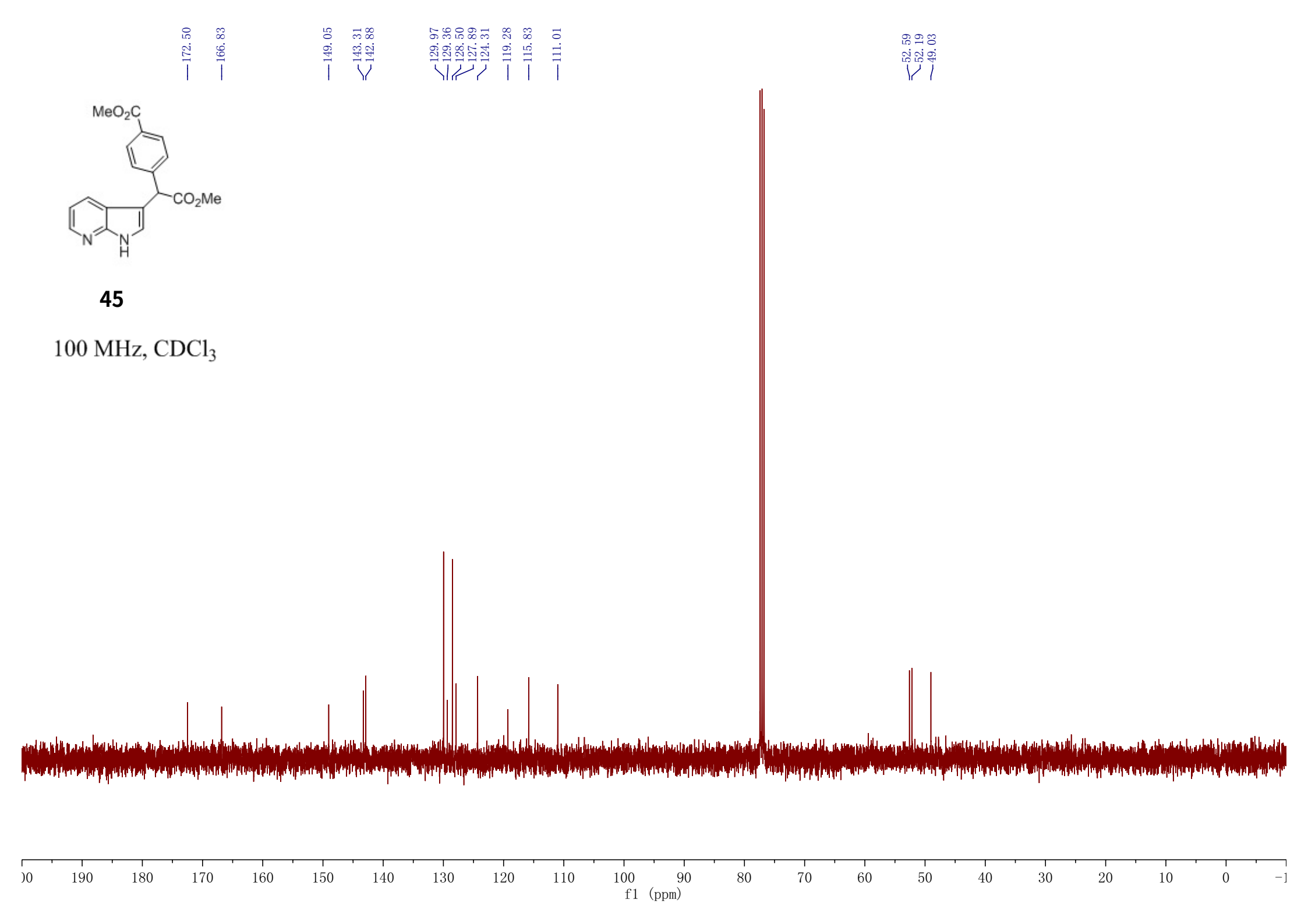
400 MHz, $CDCl_3$

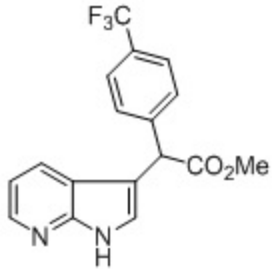

172.66
149.05
142.82
137.25
131.77
130.15
127.90
124.25
121.51
119.27
115.79
111.16
77.49
77.27
77.06
76.64
52.54
48.48
Br
CO2Me
N
H
44
75 MHz, CDCl3
f1 (ppm)



45

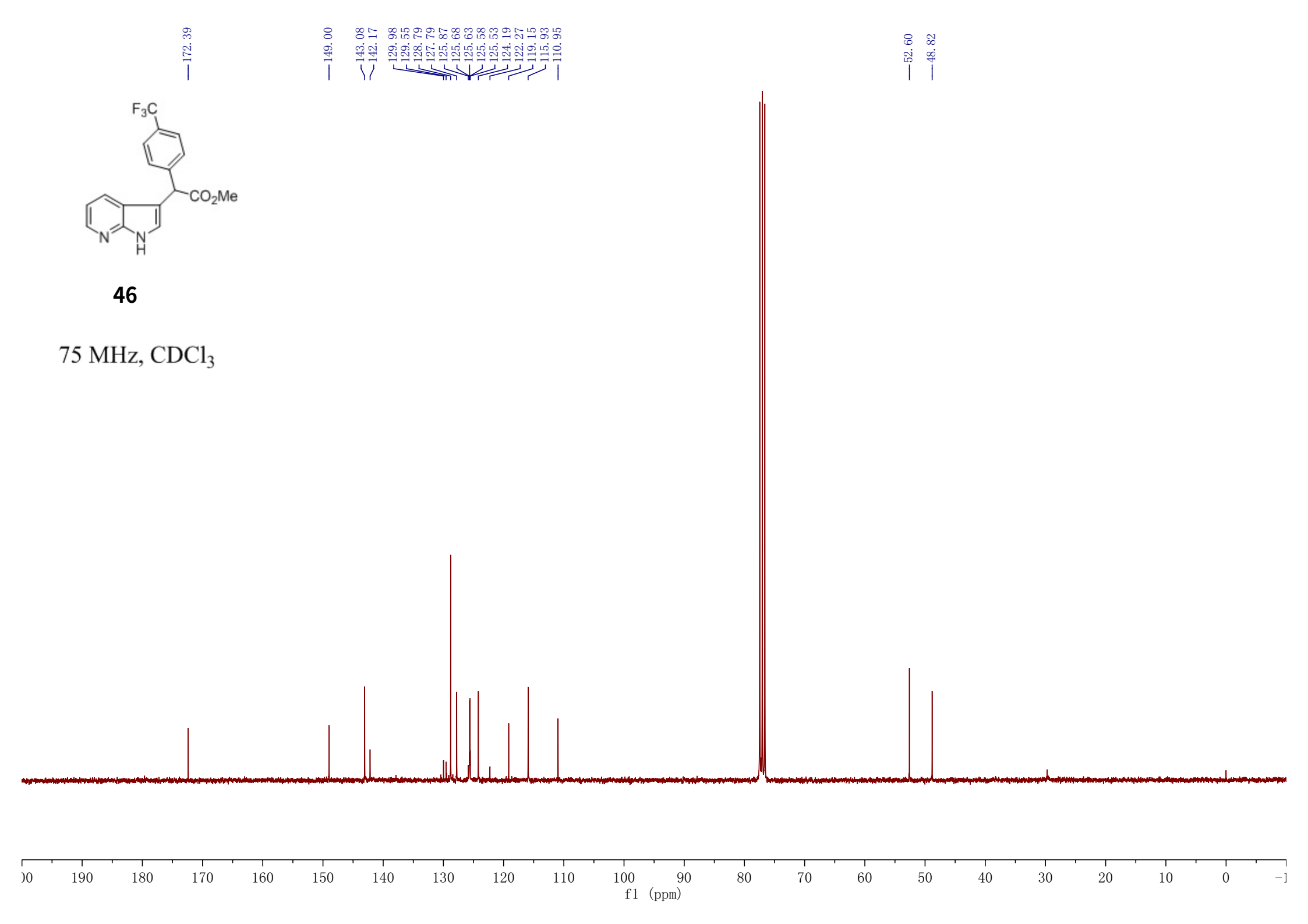
400 MHz, $CDCl_3$

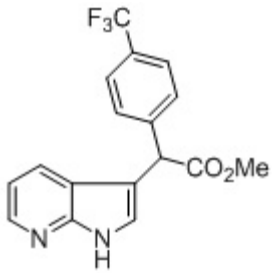

172.50
166.83
149.05
143.31
142.88
129.97
129.36
128.50
127.89
124.31
119.28
115.83
111.01
52.59
52.19
49.03
MeO2C
CO2Me
N
H
45
100 MHz, CDCl3
f1 (ppm)



46

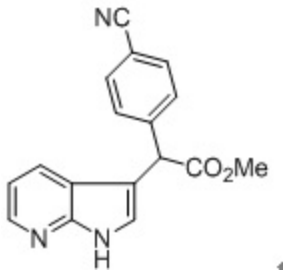
400 MHz, $CDCl_3$


172.39
149.00
143.08
142.17
129.98
129.55
128.79
127.79
125.87
125.68
125.63
125.58
125.53
124.19
122.27
119.15
115.93
110.95
52.60
48.82
F3C
CO2Me
N
H
46
75 MHz, CDCl3
f1 (ppm)



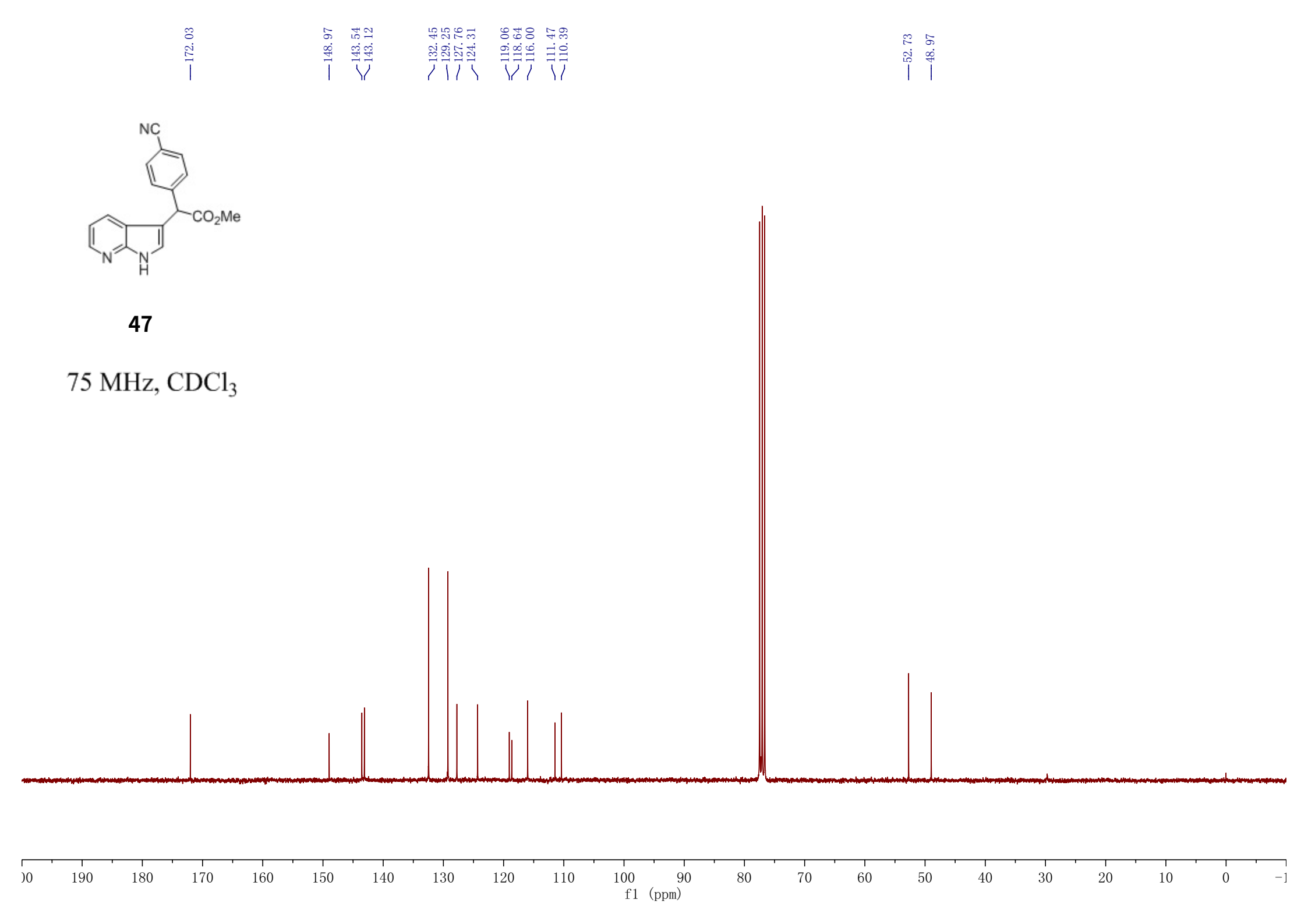
46

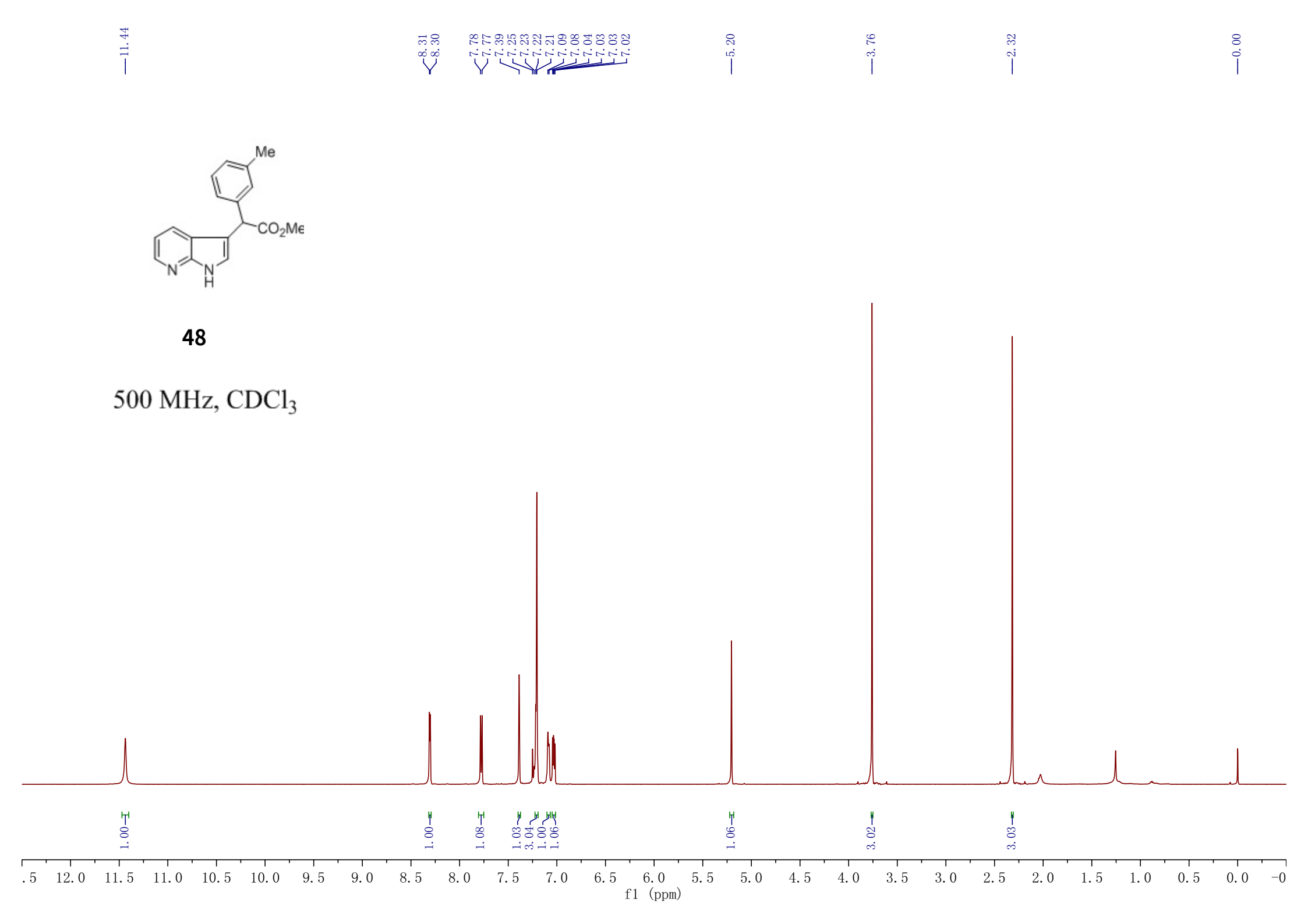
282 MHz, $CDCl_3$

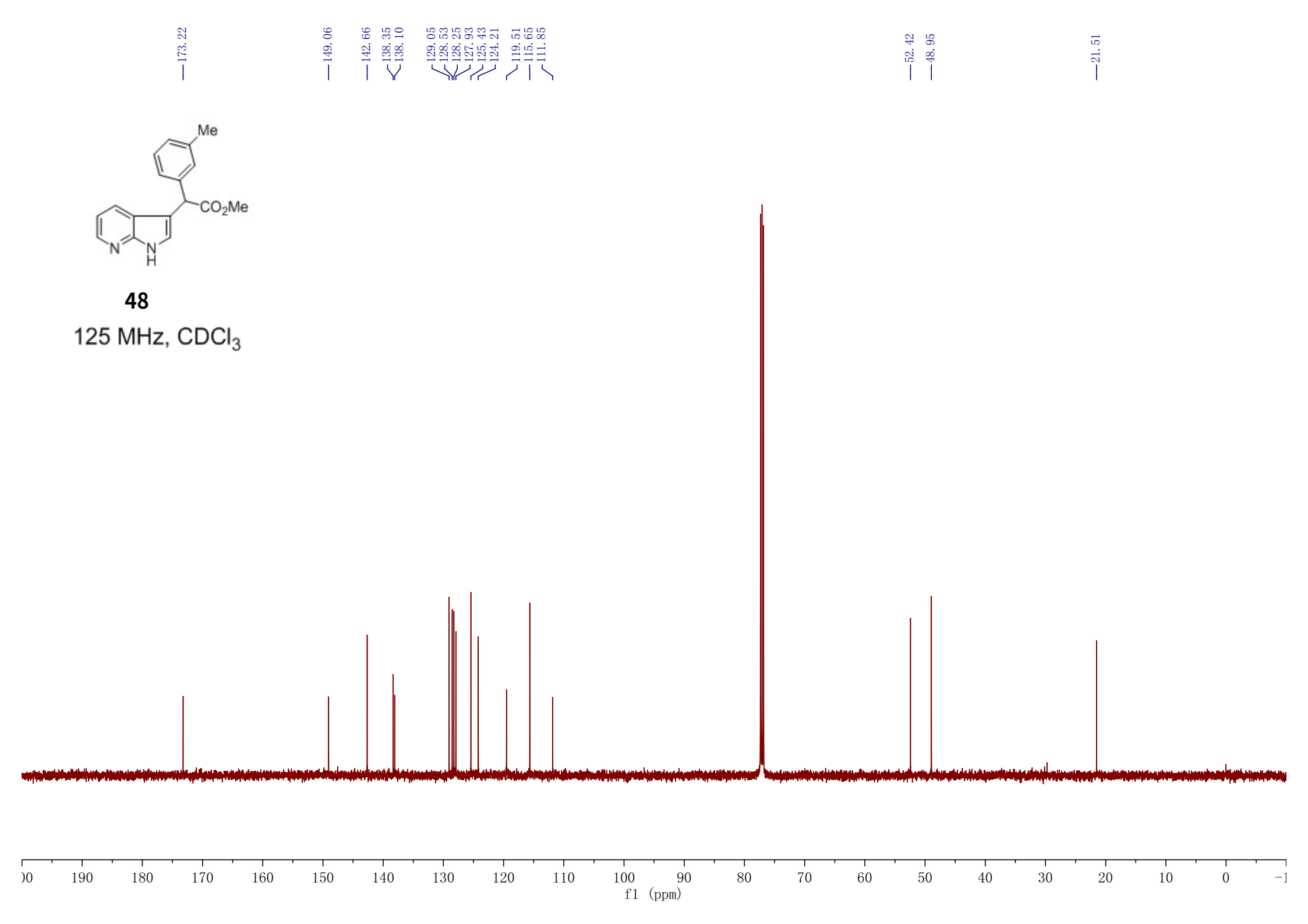


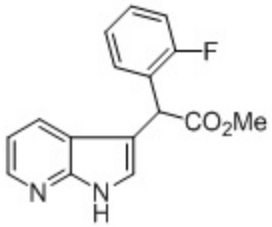
47

300 MHz, $CDCl_3$


172.03
148.97
143.54
143.12
132.45
129.25
127.76
124.31
119.06
118.64
116.00
111.47
110.39
52.73
48.97
NC
CO2Me
N
N
H
47
75 MHz, CDCl3
f1 (ppm)

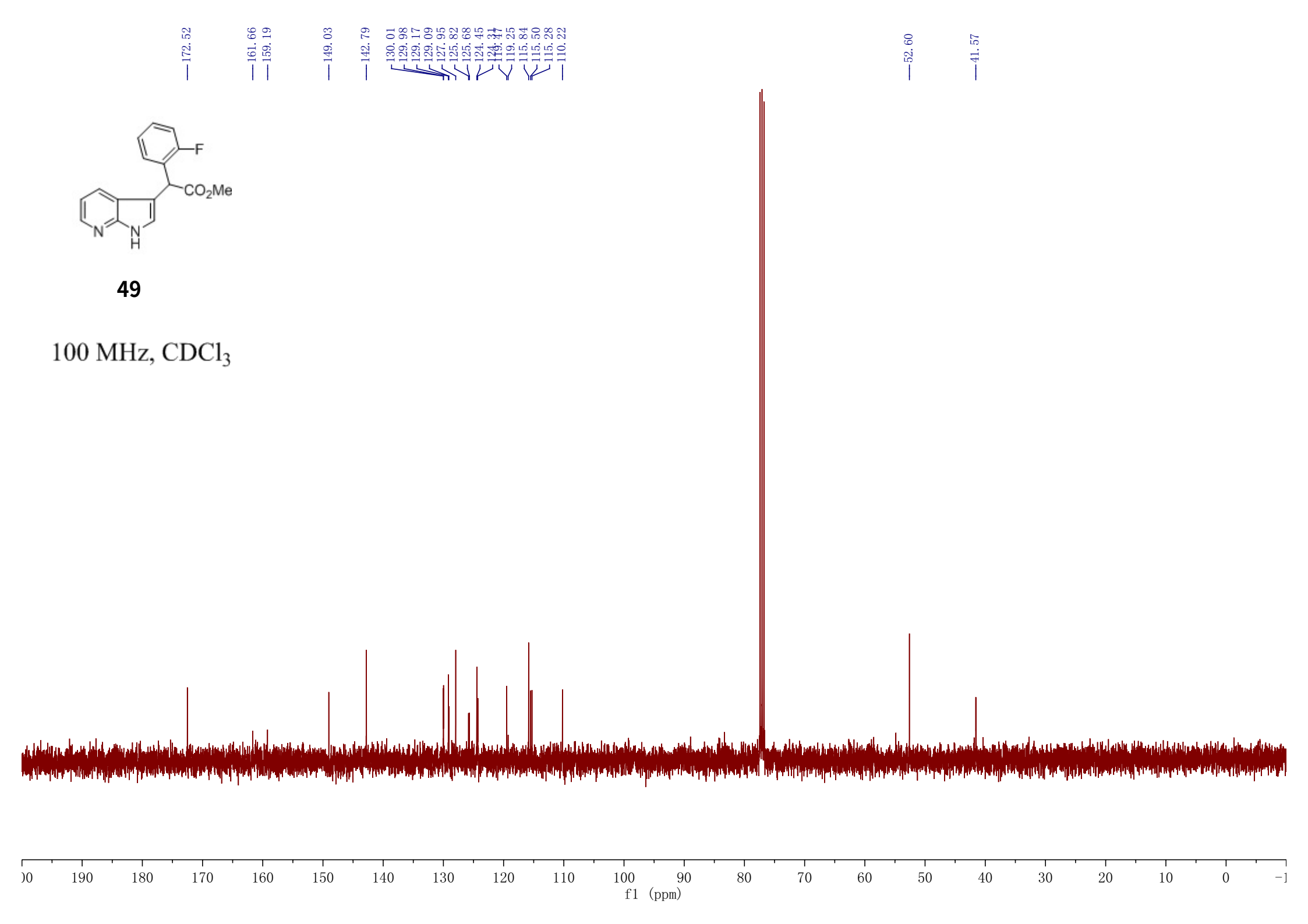

11.44
8.31
8.30
7.78
7.77
7.39
7.25
7.23
7.22
7.21
7.09
7.08
7.04
7.03
7.03
7.02
5.20
3.76
2.32
0.00
Me
CO2Me
N
N
H
48
500 MHz, CDCl3
1.00
1.00
1.08
1.03
3.04
1.00
1.06
1.06
3.02
3.03
f1 (ppm)

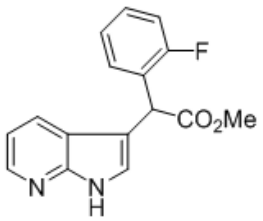

173.22
149.06
142.66
138.35
138.10
129.05
128.53
128.25
127.93
125.43
124.21
119.51
115.65
111.85
52.42
48.95
21.51
Me
CO2Me
N
H
48
125 MHz, CDCl3
f1 (ppm)



49

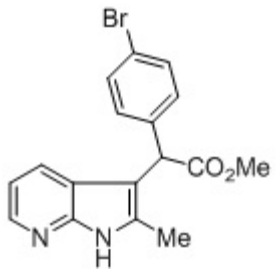
400 MHz, $CDCl_3$


172.52
161.66
159.19
149.03
142.79
130.01
129.98
129.17
129.09
127.95
125.82
125.68
124.45
119.47
119.25
115.84
115.50
115.28
110.22
52.60
41.57
F
CO2Me
N
H
49
100 MHz, CDCl3
f1 (ppm)



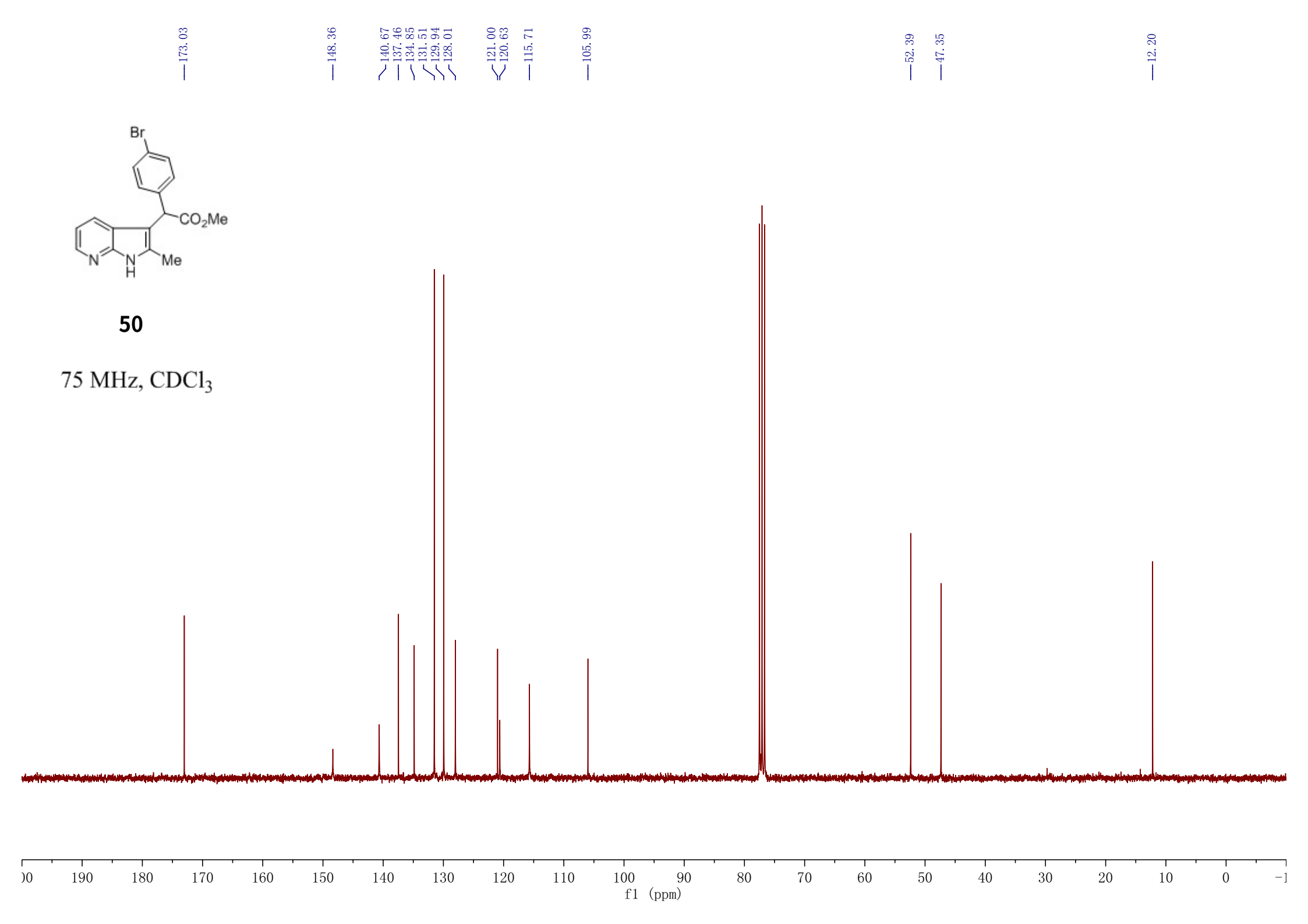
49

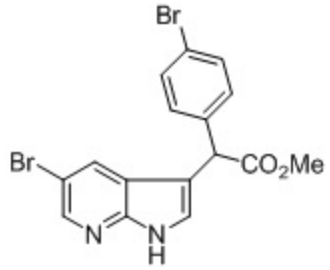
282 MHz, $CDCl_3$



50

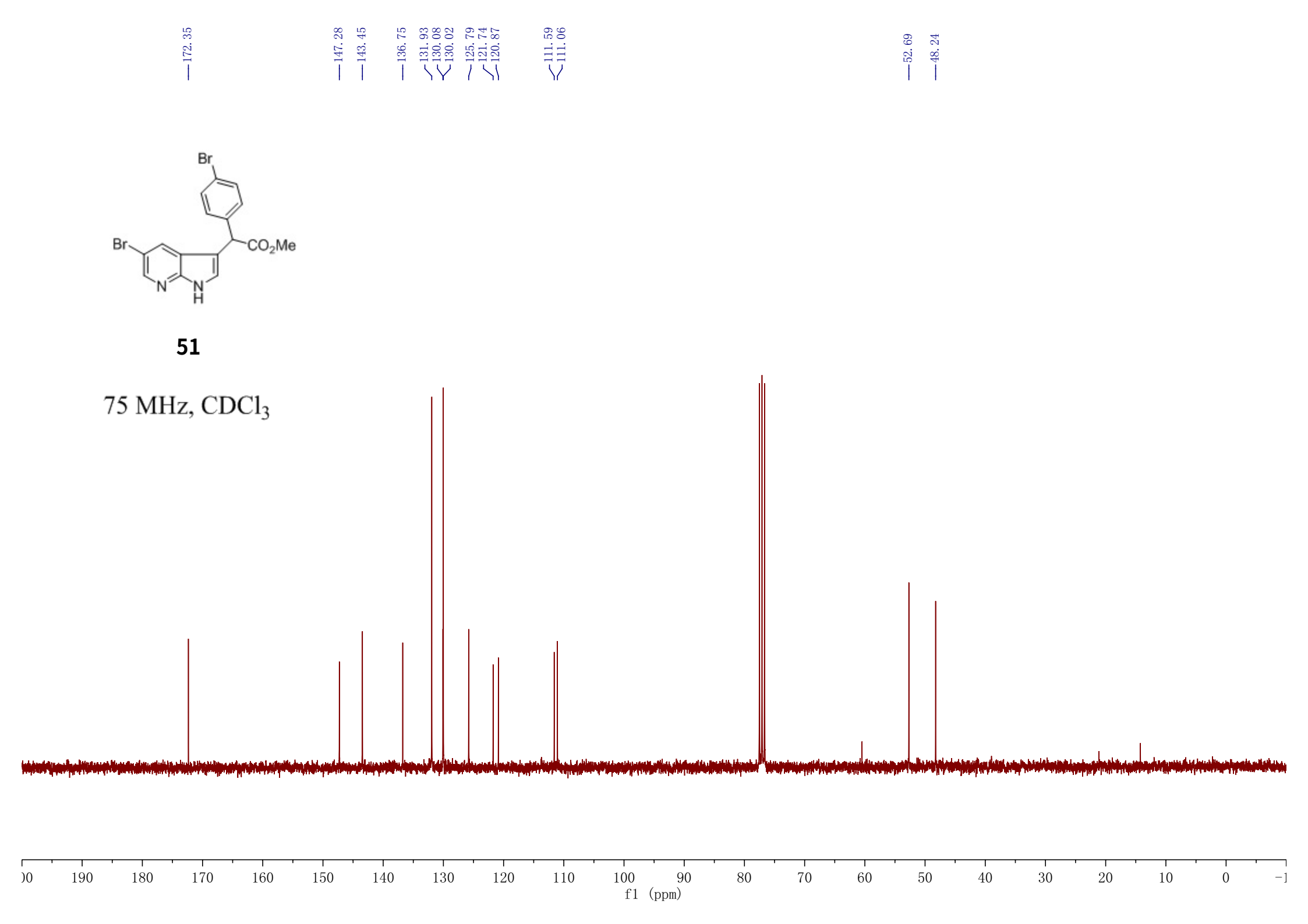
300 MHz, $CDCl_3$

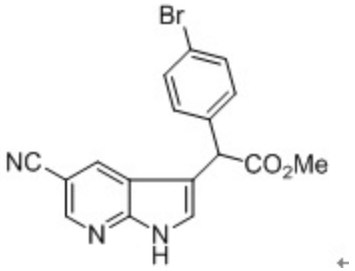

173.03
148.36
140.67
137.46
134.85
131.51
129.94
128.01
121.00
120.63
115.71
105.99
52.39
47.35
12.20
Br
CO2Me
N
H
N
Me
50
75 MHz, CDCl3
f1 (ppm)



51

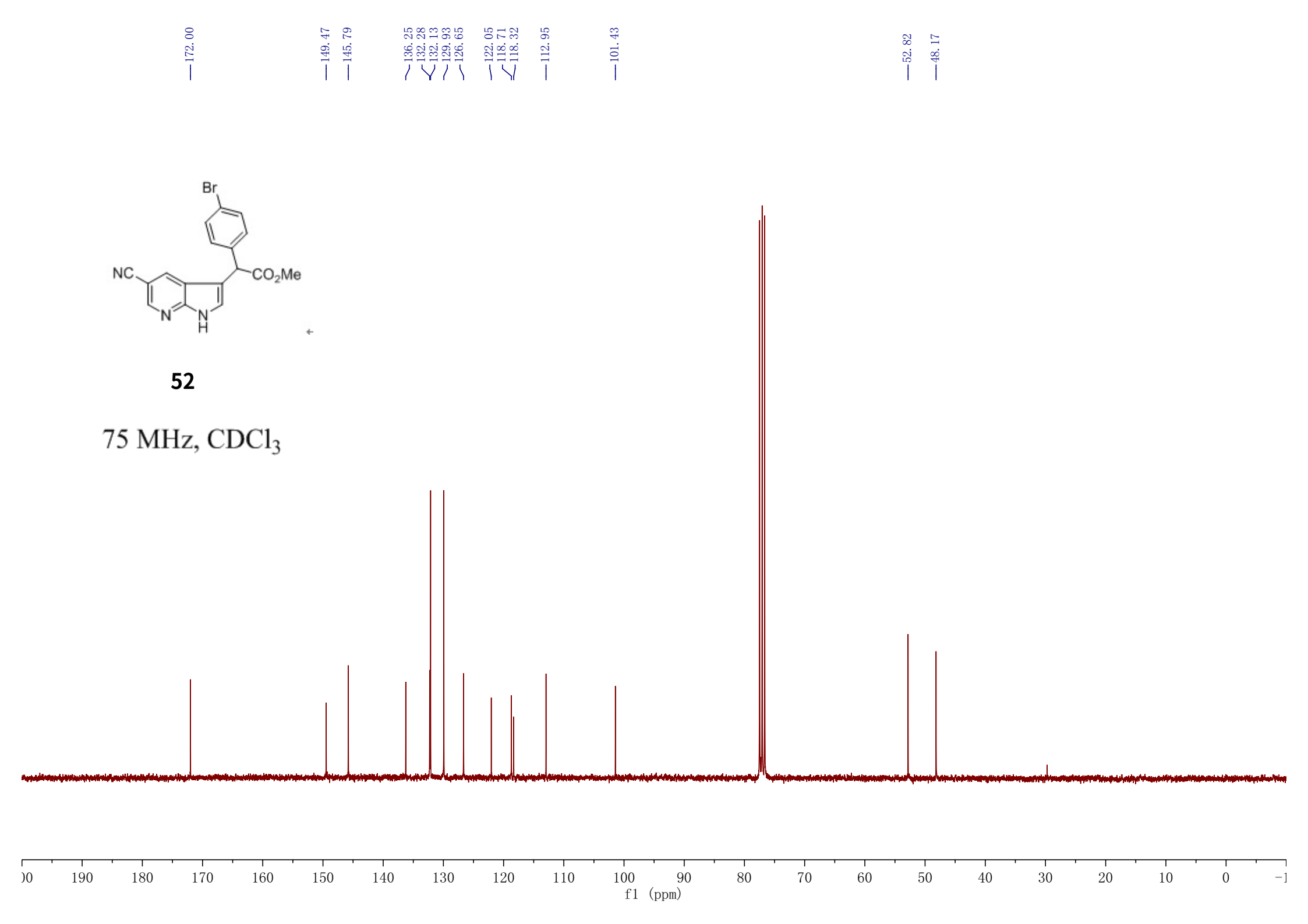
300 MHz, $CDCl_3$

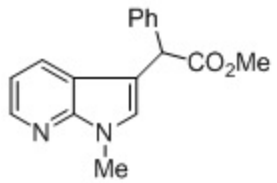

172.35
147.28
143.45
136.75
131.93
130.08
130.02
125.79
121.74
120.87
111.59
111.06
52.69
48.24
Br
Br
CO2Me
N
N
H
51
75 MHz, CDCl3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



52

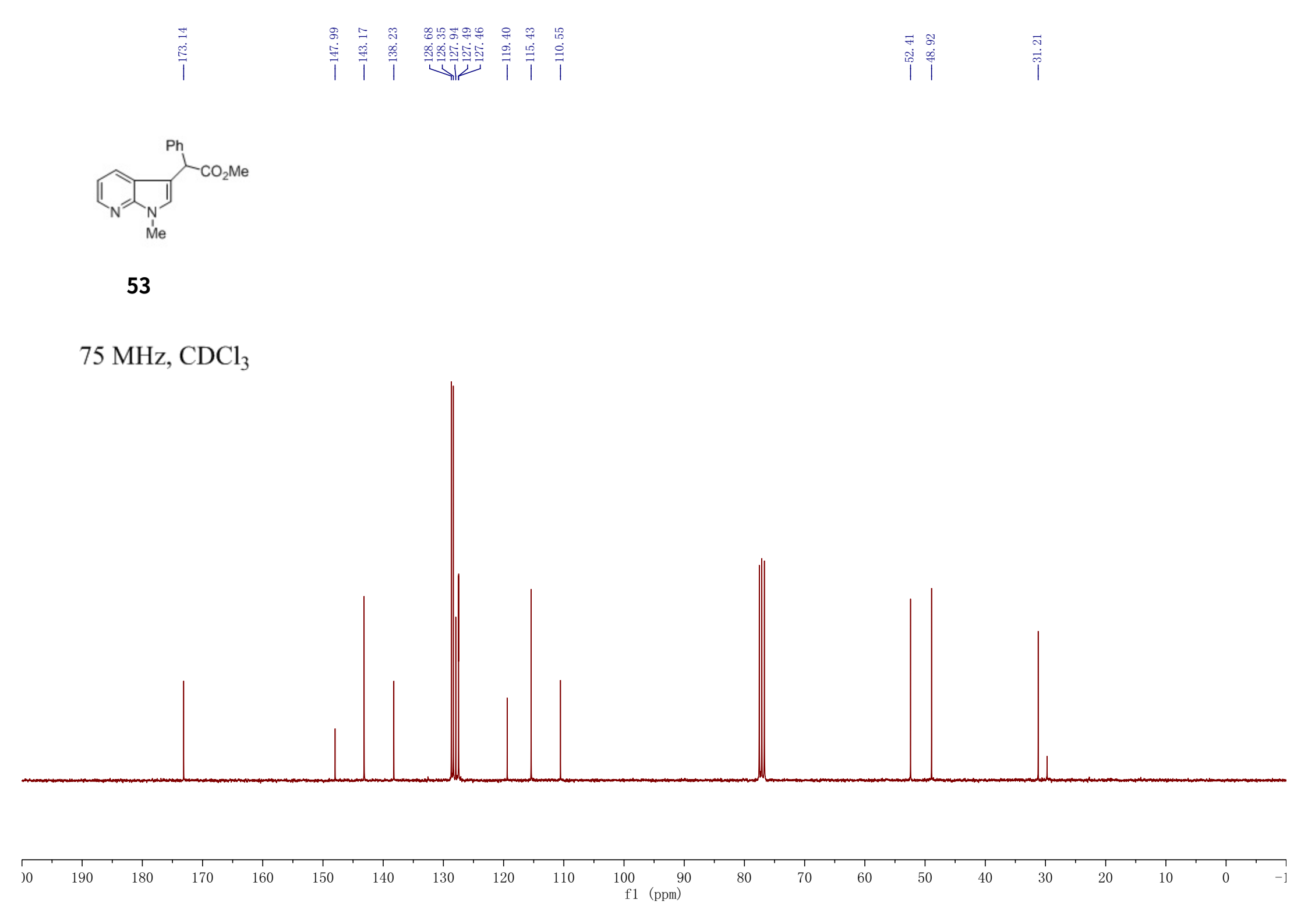
300 MHz, $CDCl_3$

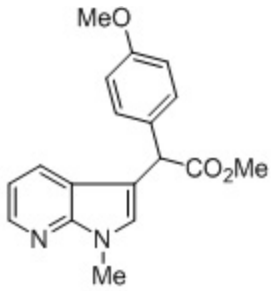

172.00
149.47
145.79
136.25
132.28
132.13
129.93
126.65
122.05
118.71
118.32
112.95
101.43
52.82
48.17
Br
NC
CO2Me
N
N
H
52
75 MHz, CDCl3
f1 (ppm)



53

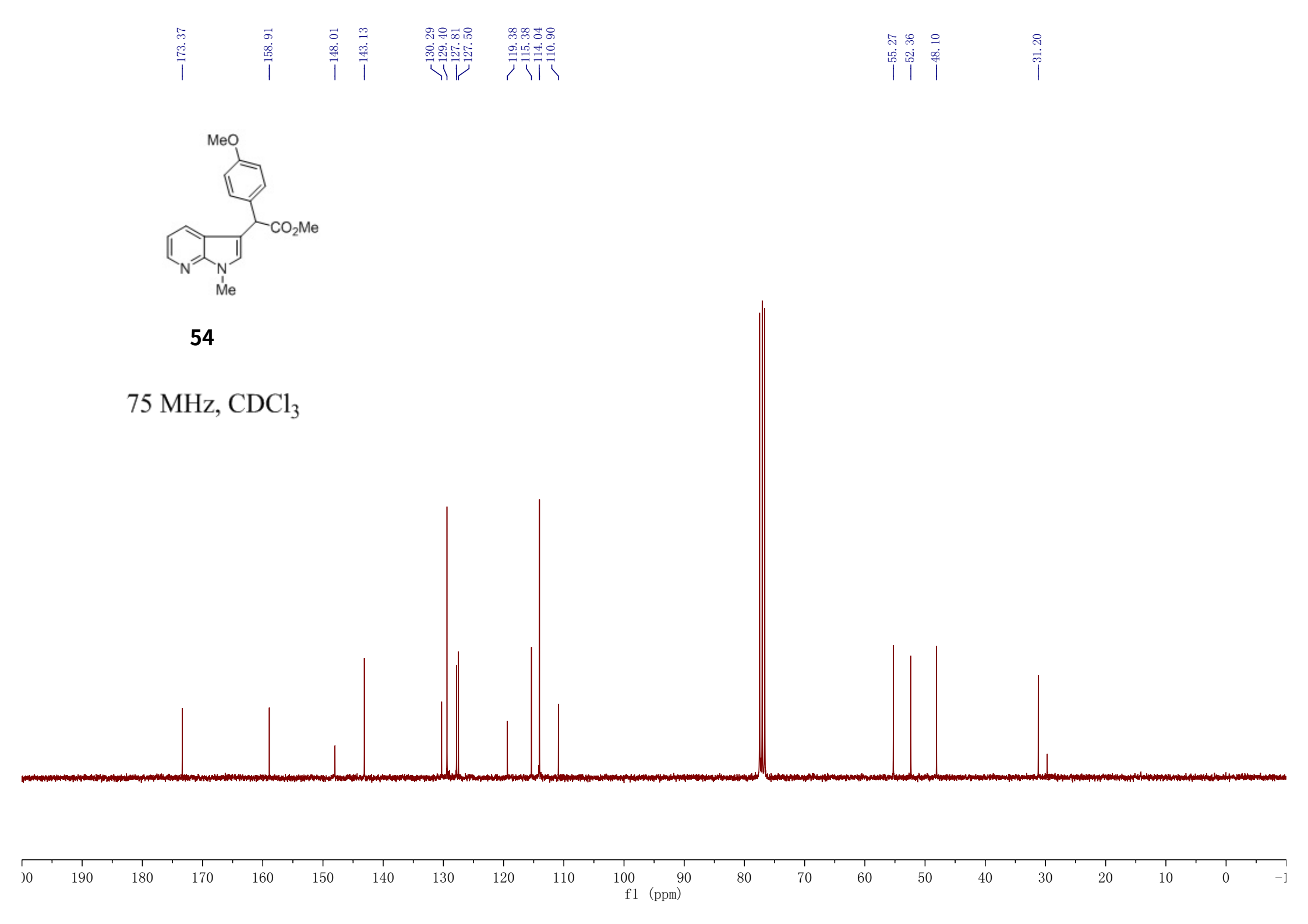
300 MHz, $CDCl_3$

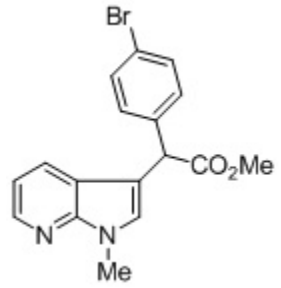

173.14
147.99
143.17
138.23
128.68
128.35
127.94
127.49
127.46
119.40
115.43
110.55
52.41
48.92
31.21
Ph
CO2Me
N
N
Me
53
75 MHz, CDCl3
f1 (ppm)



54

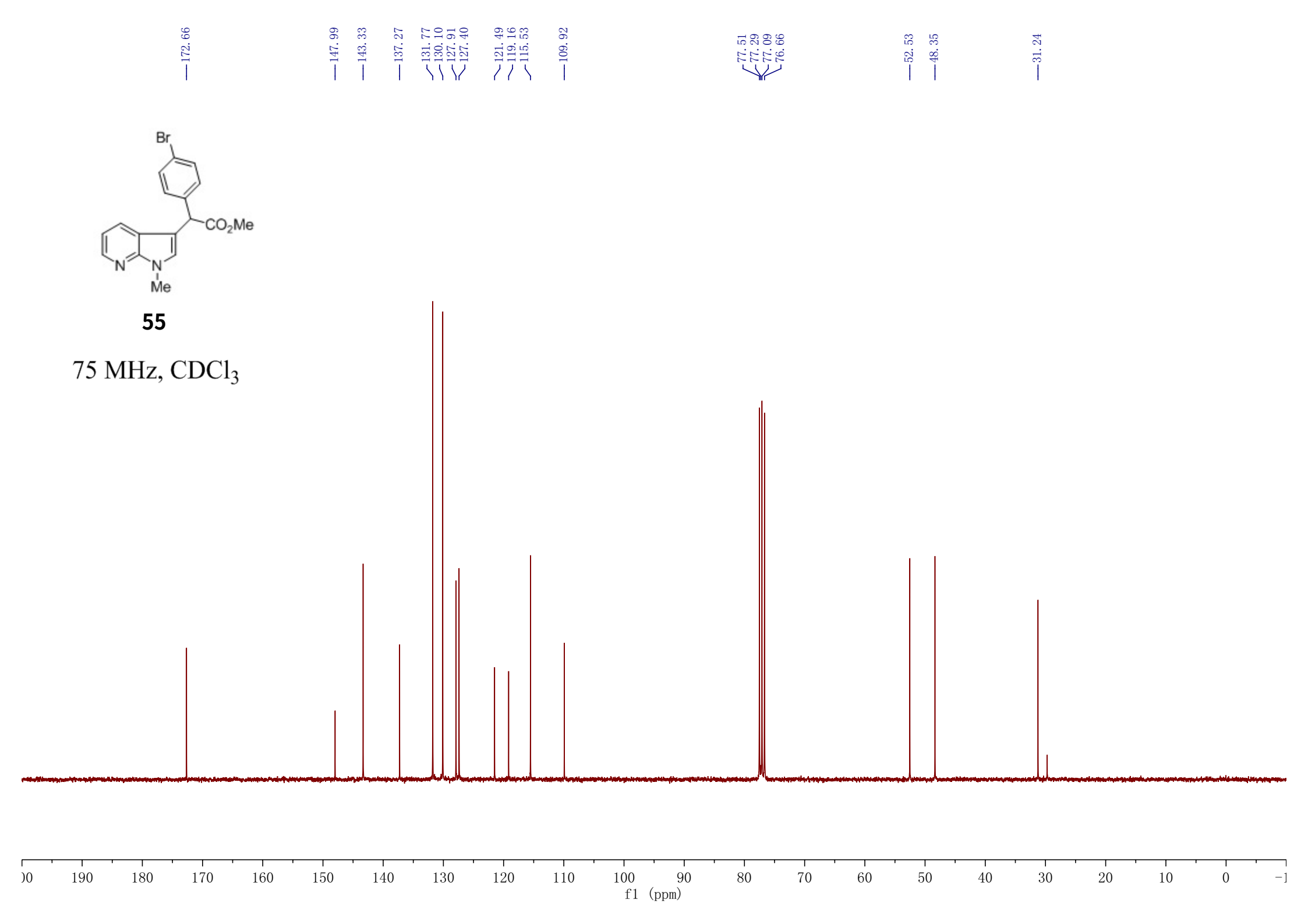
300 MHz, $CDCl_3$

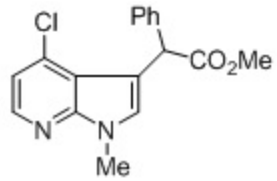

173.37
158.91
148.01
143.13
130.29
129.40
127.81
127.50
119.38
115.38
114.04
110.90
55.27
52.36
48.10
31.20
MeO
CO2Me
N
N
Me
54
75 MHz, CDCl3
f1 (ppm)



55

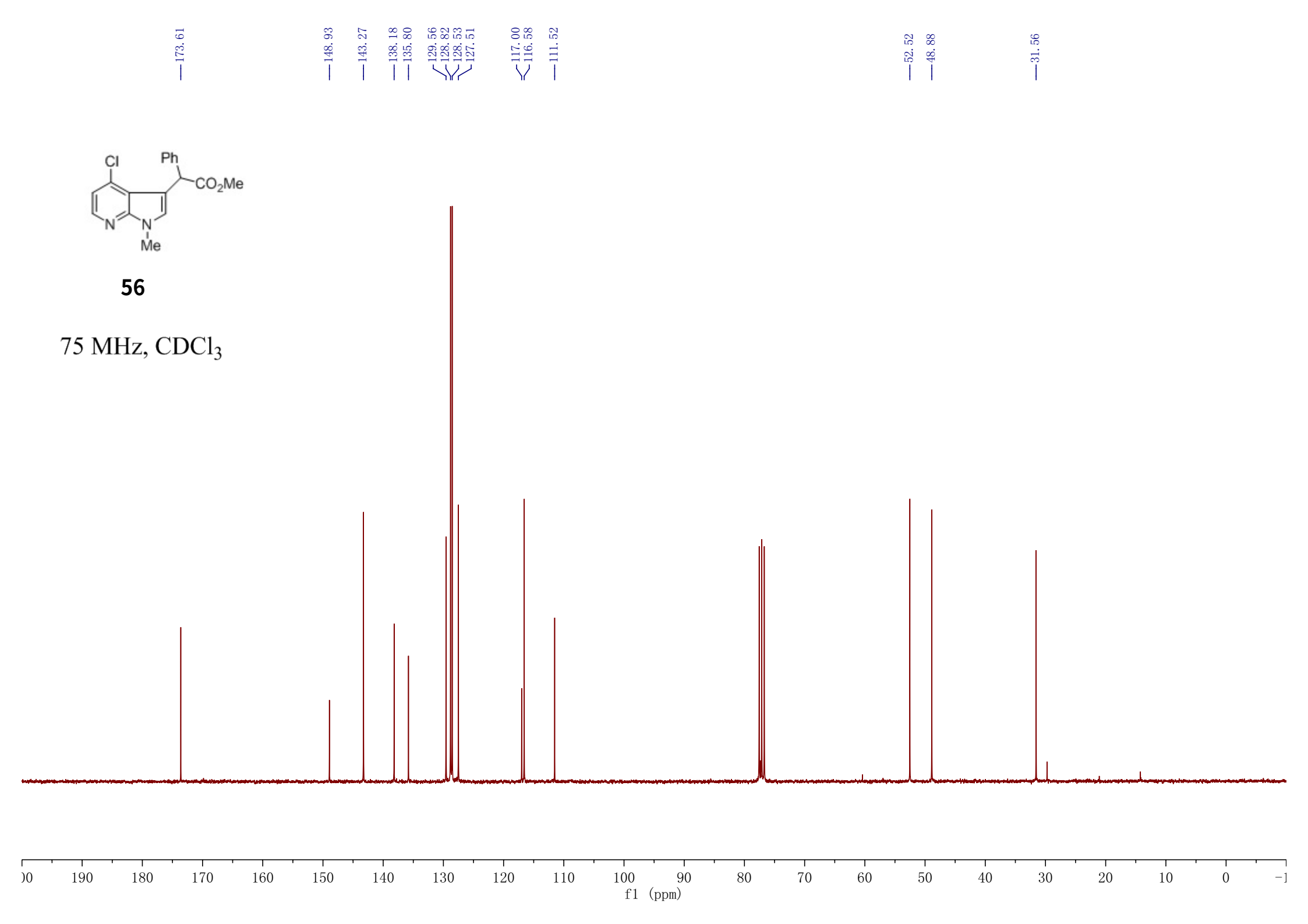
500 MHz, $CDCl_3$

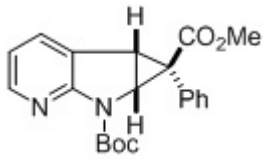

172.66
147.99
143.33
137.27
131.77
130.10
127.91
127.40
121.49
119.16
115.53
109.92
77.51
77.29
77.09
76.66
52.53
48.35
31.24
Br
CO2Me
N
N
Me
55
75 MHz, CDCl3
f1 (ppm)



56

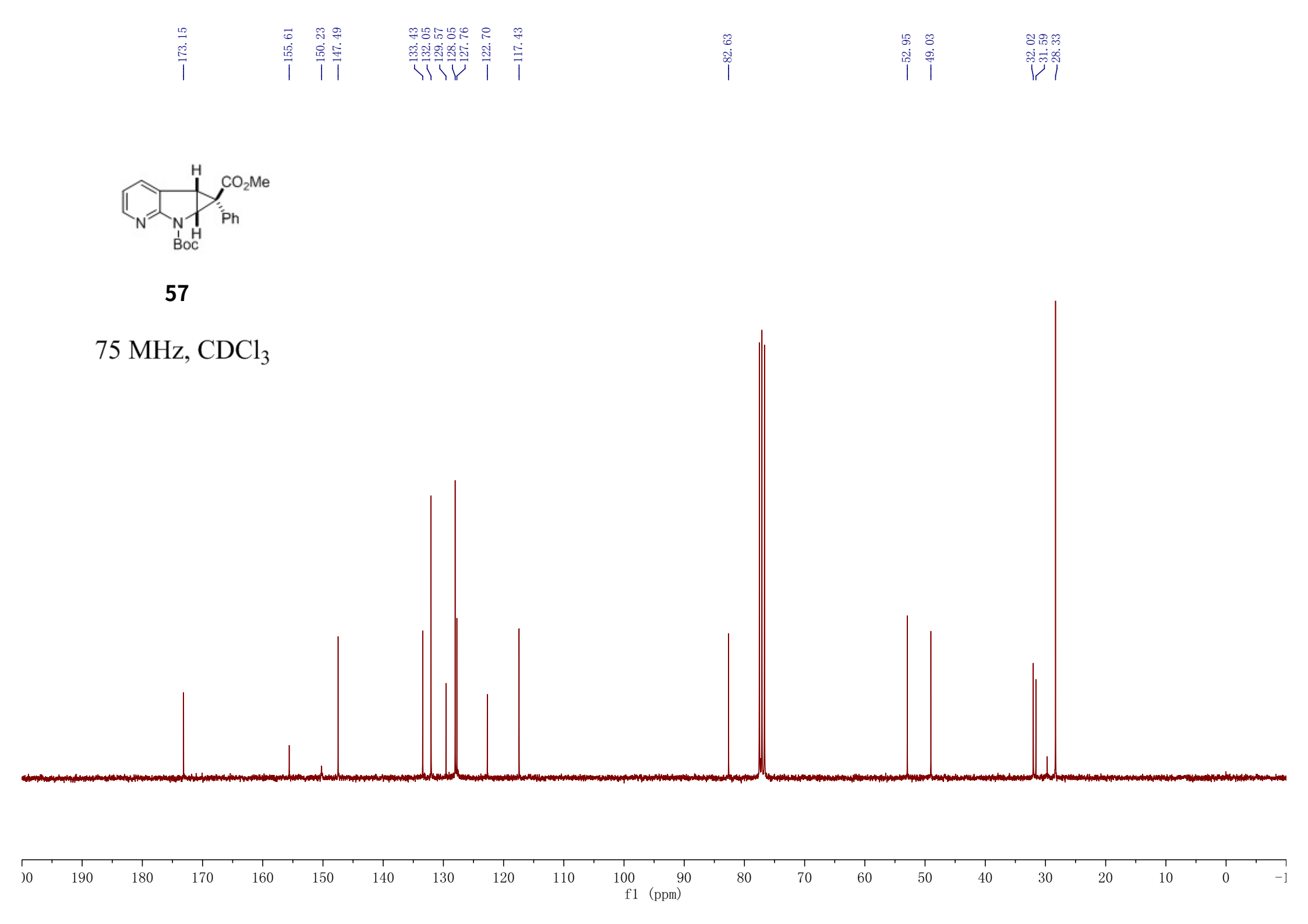
300 MHz, $CDCl_3$

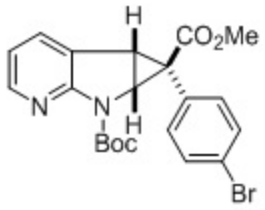

173.61
148.93
143.27
138.18
135.80
129.56
128.82
128.53
127.51
117.00
116.58
111.52
52.52
48.88
31.56
Cl
Ph
CO2Me
N
N
Me
56
75 MHz, CDCl3
f1 (ppm)



57

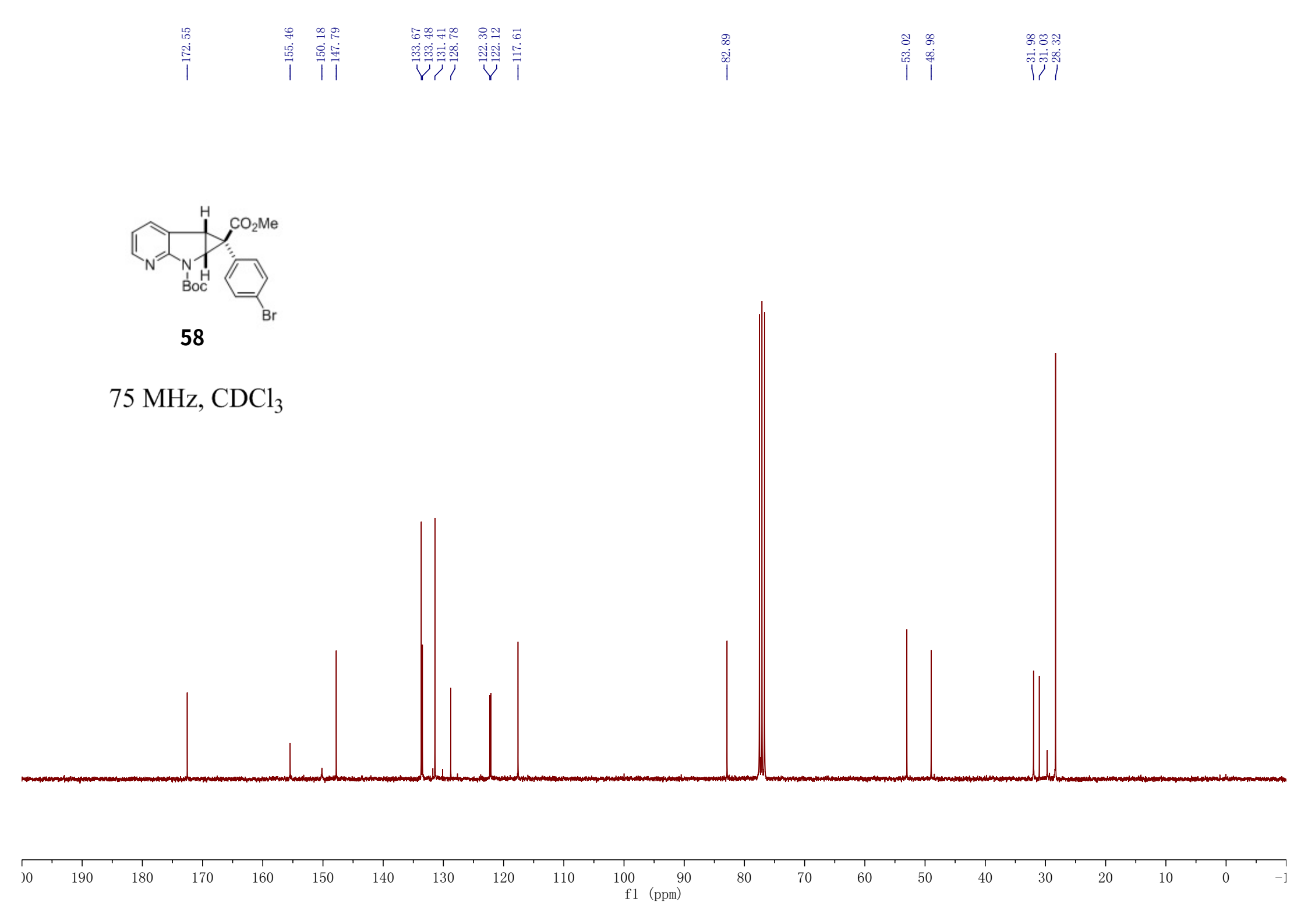
300 MHz, $CDCl_3$

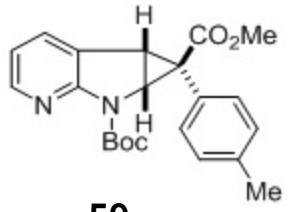

173.15
155.61
150.23
147.49
133.43
132.05
129.57
128.05
127.76
122.70
117.43
82.63
52.95
49.03
32.02
31.59
28.33
H
CO2Me
Ph
N
N
H
Boc
57
75 MHz, CDCl3
f1 (ppm)



58

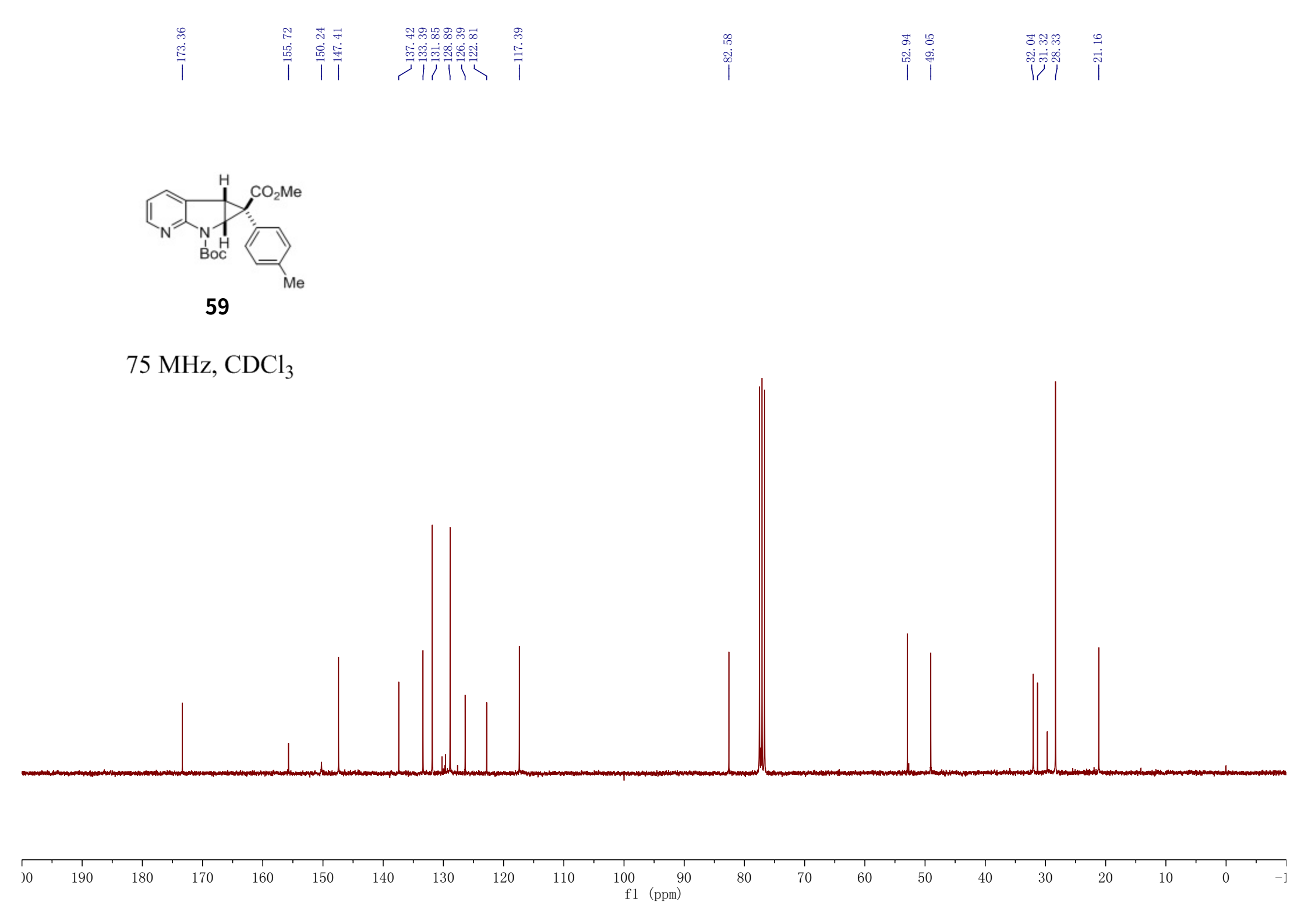
400 MHz, $CDCl_3$

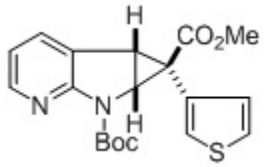

172.55
155.46
150.18
147.79
133.67
133.48
131.41
128.78
122.30
122.12
117.61
82.89
53.02
48.98
31.98
31.03
28.32
H
CO2Me
N
N
H
Boc
Br
58
75 MHz, CDCl3
f1 (ppm)



59

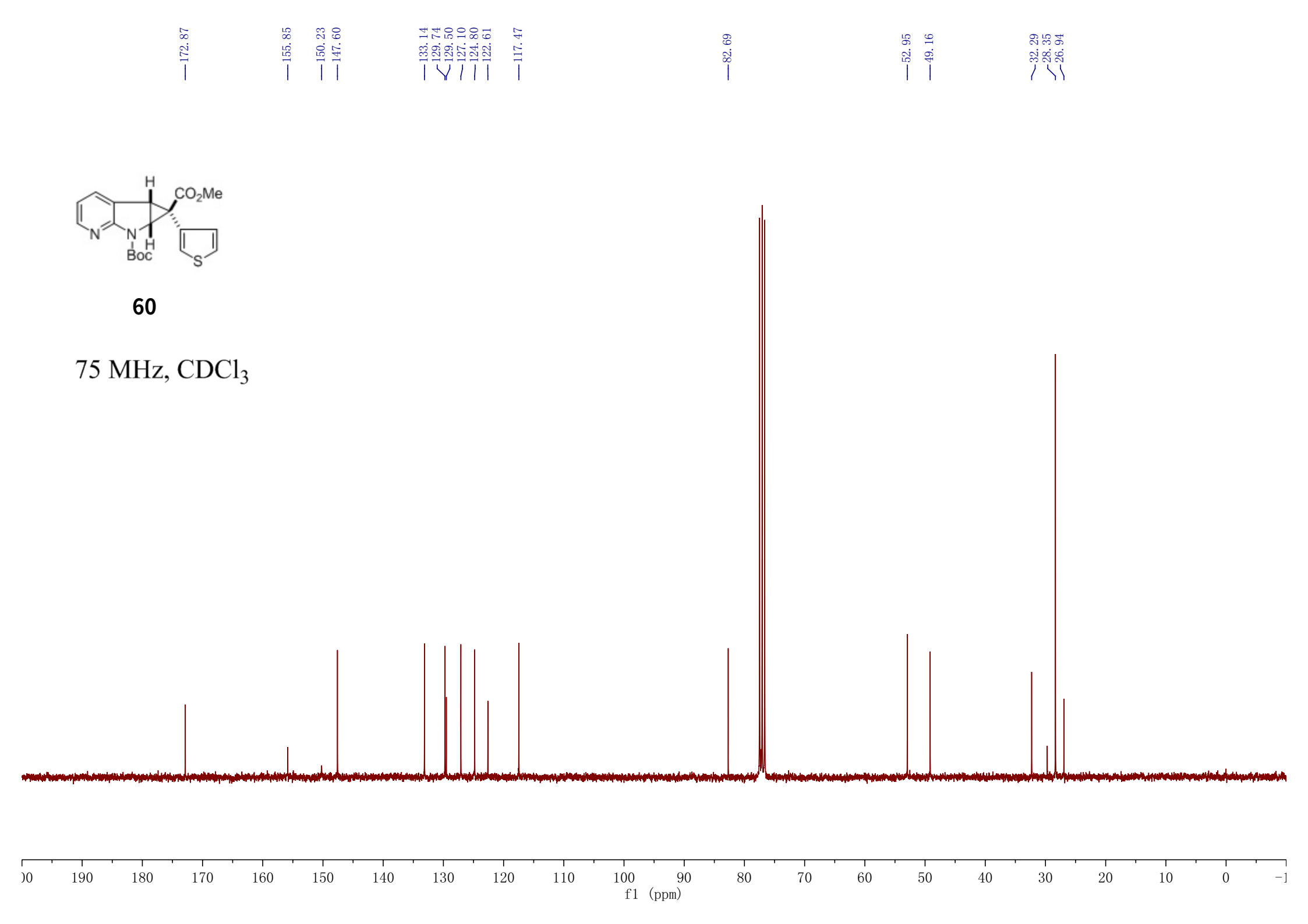
300 MHz, $CDCl_3$

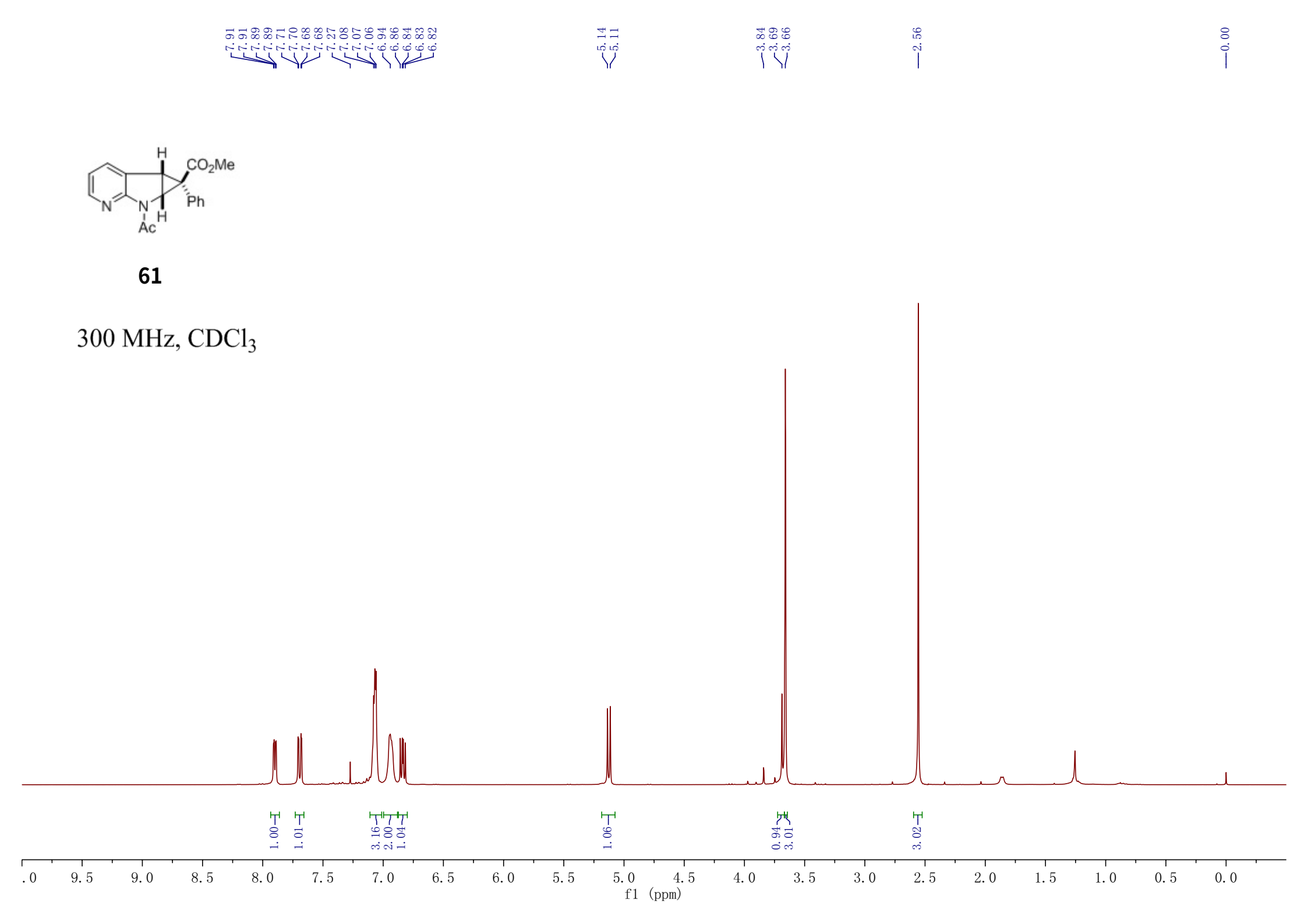

173.36
155.72
150.24
147.41
137.42
133.39
131.85
128.89
126.39
122.81
117.39
82.58
52.94
49.05
32.04
31.32
28.33
21.16
H
CO2Me
N
N
H
Boc
Me
59
75 MHz, CDCl3
f1 (ppm)

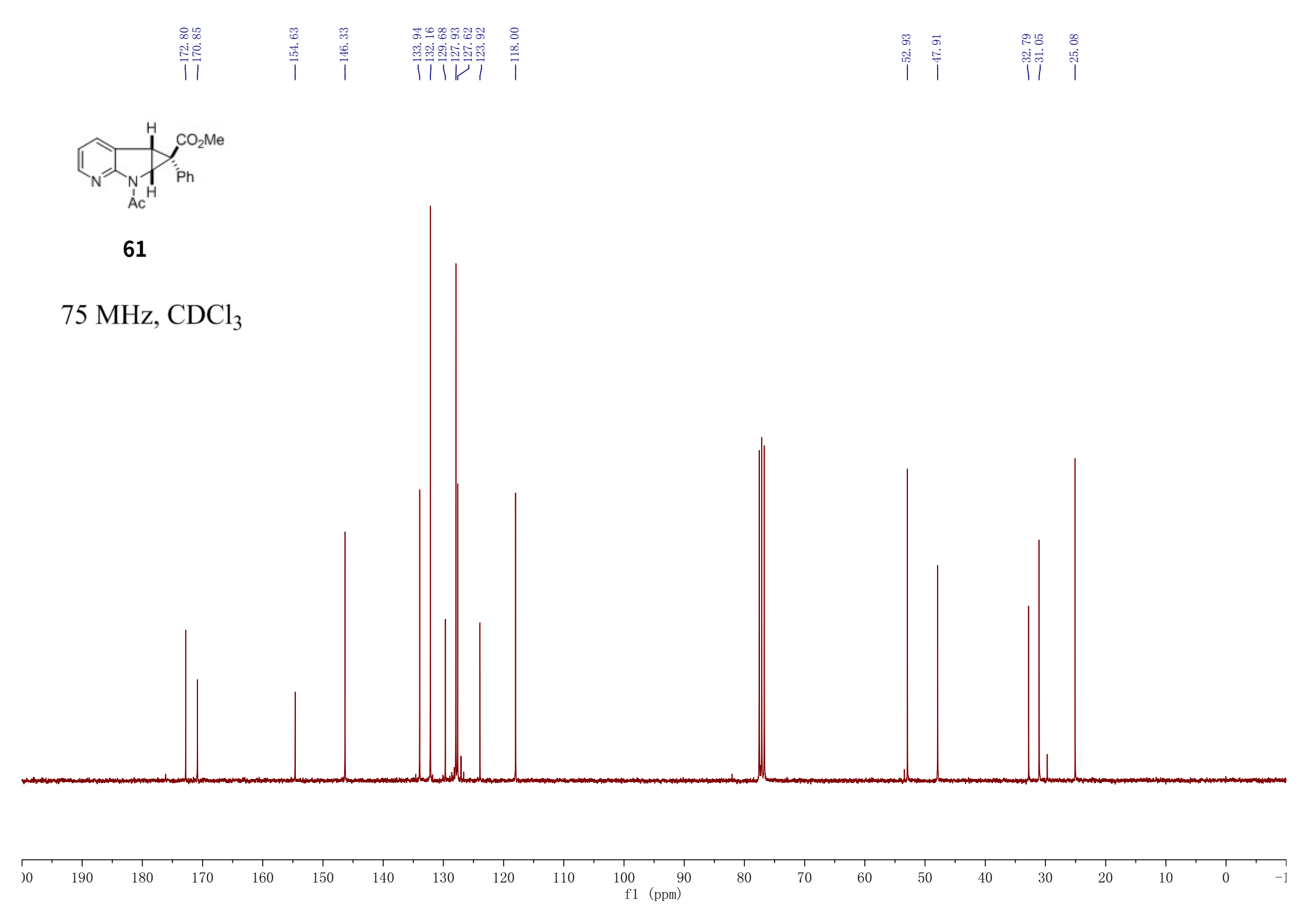


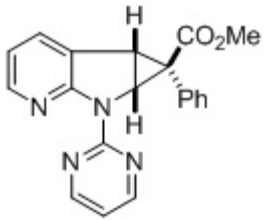
60

300 MHz, $CDCl_3$


172.87
155.85
150.23
147.60
133.14
129.74
129.50
127.10
124.80
122.61
117.47
82.69
52.95
49.16
32.29
28.35
26.94
H
CO2Me
N
N
H
Boc
S
60
75 MHz, CDCl3
f1 (ppm)


7.91
7.91
7.89
7.89
7.71
7.70
7.68
7.68
7.27
7.08
7.07
7.06
6.94
6.86
6.84
6.83
6.82
5.14
5.11
3.84
3.69
3.66
2.56
0.00
H
CO2Me
Ph
N
N
H
Ac
61
300 MHz, CDCl3
1.00
1.01
3.16
2.00
1.04
1.06
0.94
3.01
3.02
.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

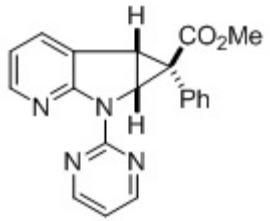

172.80
170.85
154.63
146.33
133.94
132.16
129.68
127.93
127.62
123.92
118.00
52.93
47.91
32.79
31.05
25.08
H
CO2Me
Ph
N
N
H
Ac
61
75 MHz, CDCl3
f1 (ppm)



62

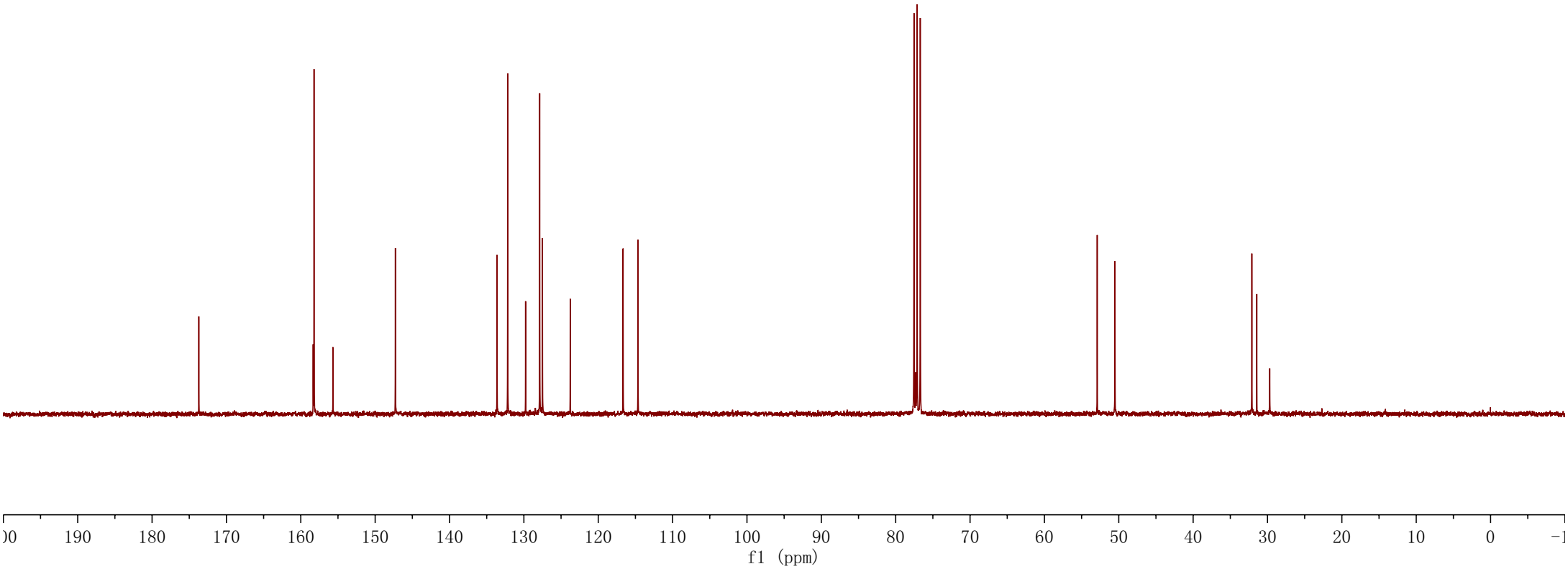
300 MHz, $CDCl_3$

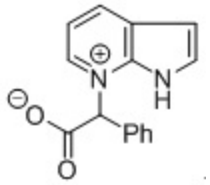
173.71
158.33
158.22
155.68
147.28
133.61
132.18
129.77
127.88
127.50
123.77
116.66
114.66
52.90
50.51
32.10
31.44



62

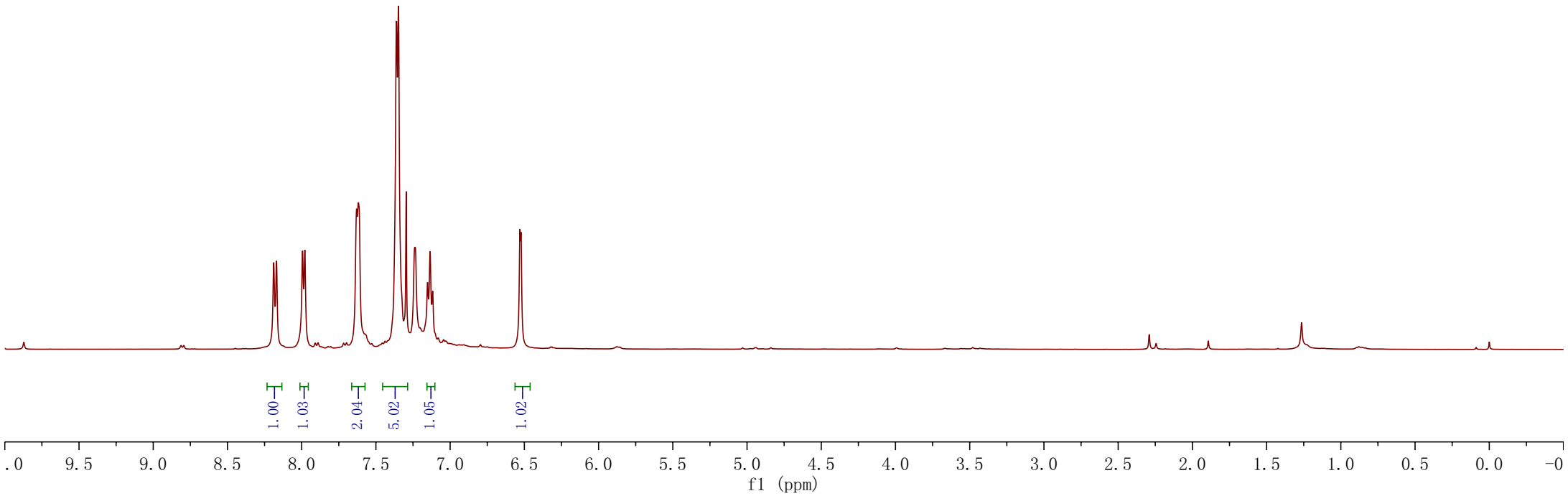
75 MHz, $CDCl_3$

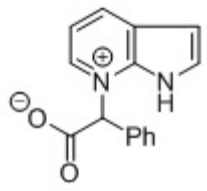




63

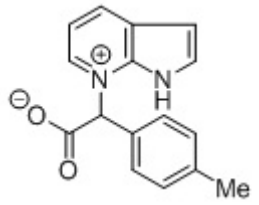
400 MHz, $CDCl_3$





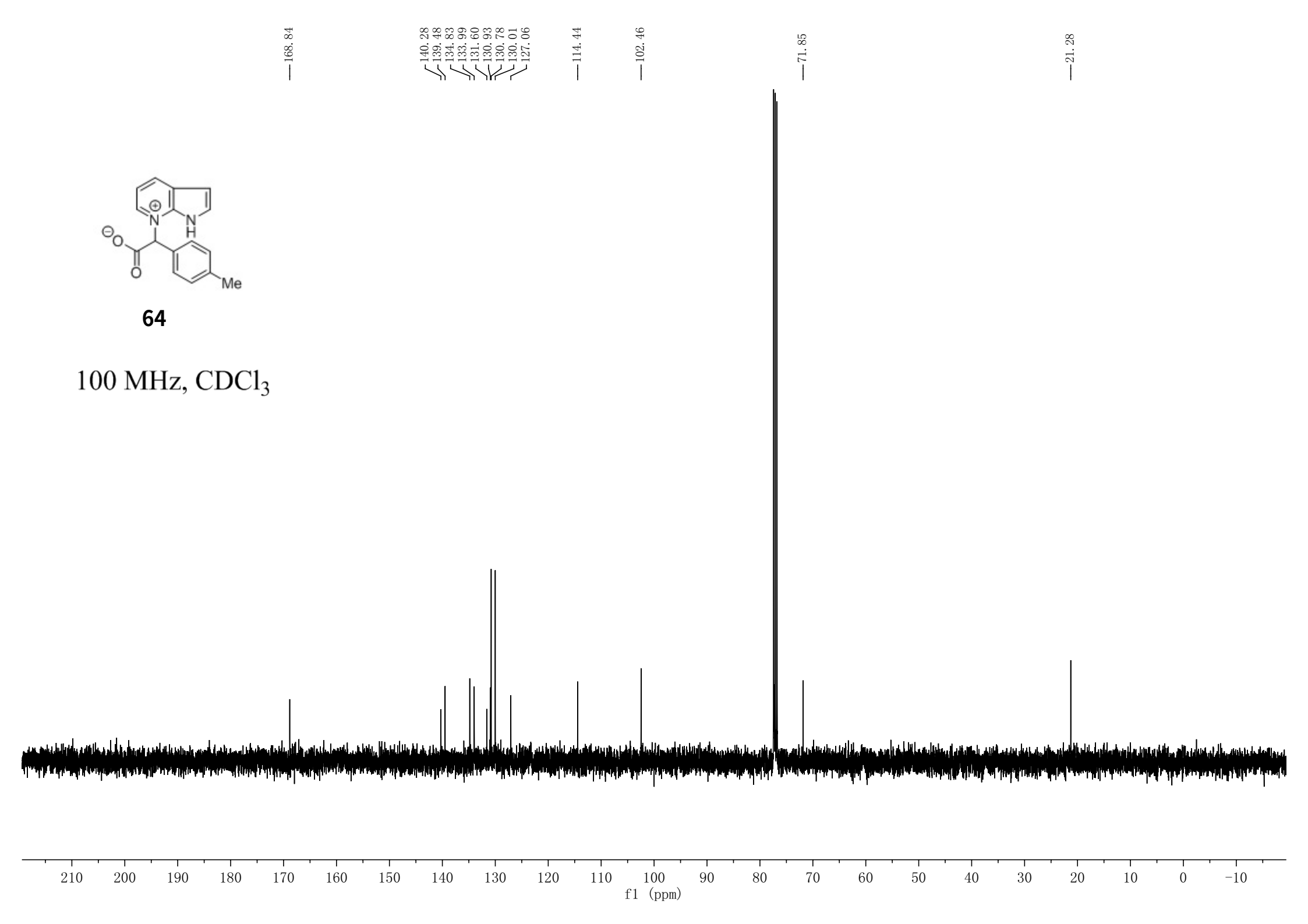
63

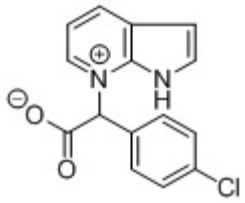
75 MHz, $CDCl_3$



64

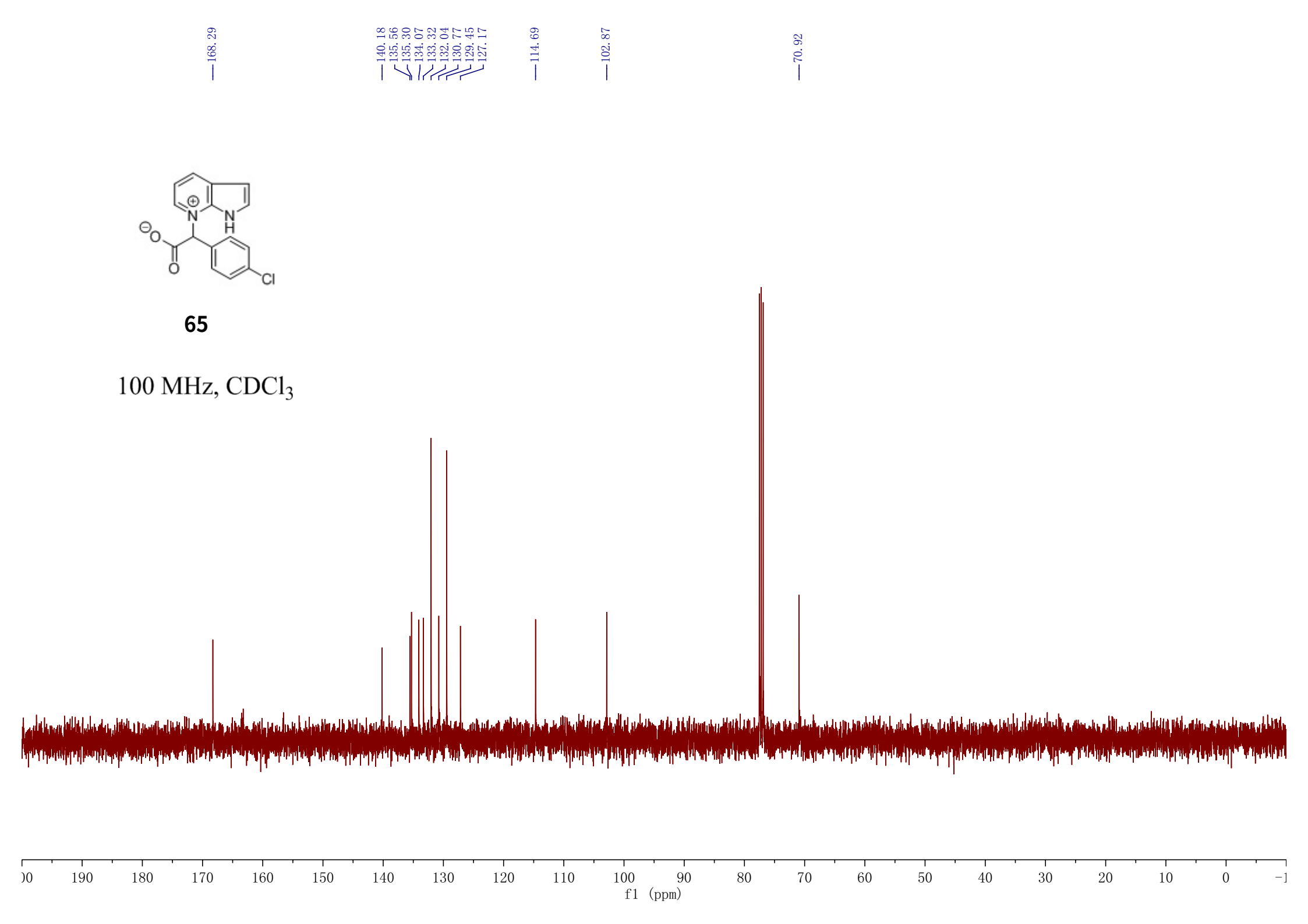
400 MHz, $CDCl_3$

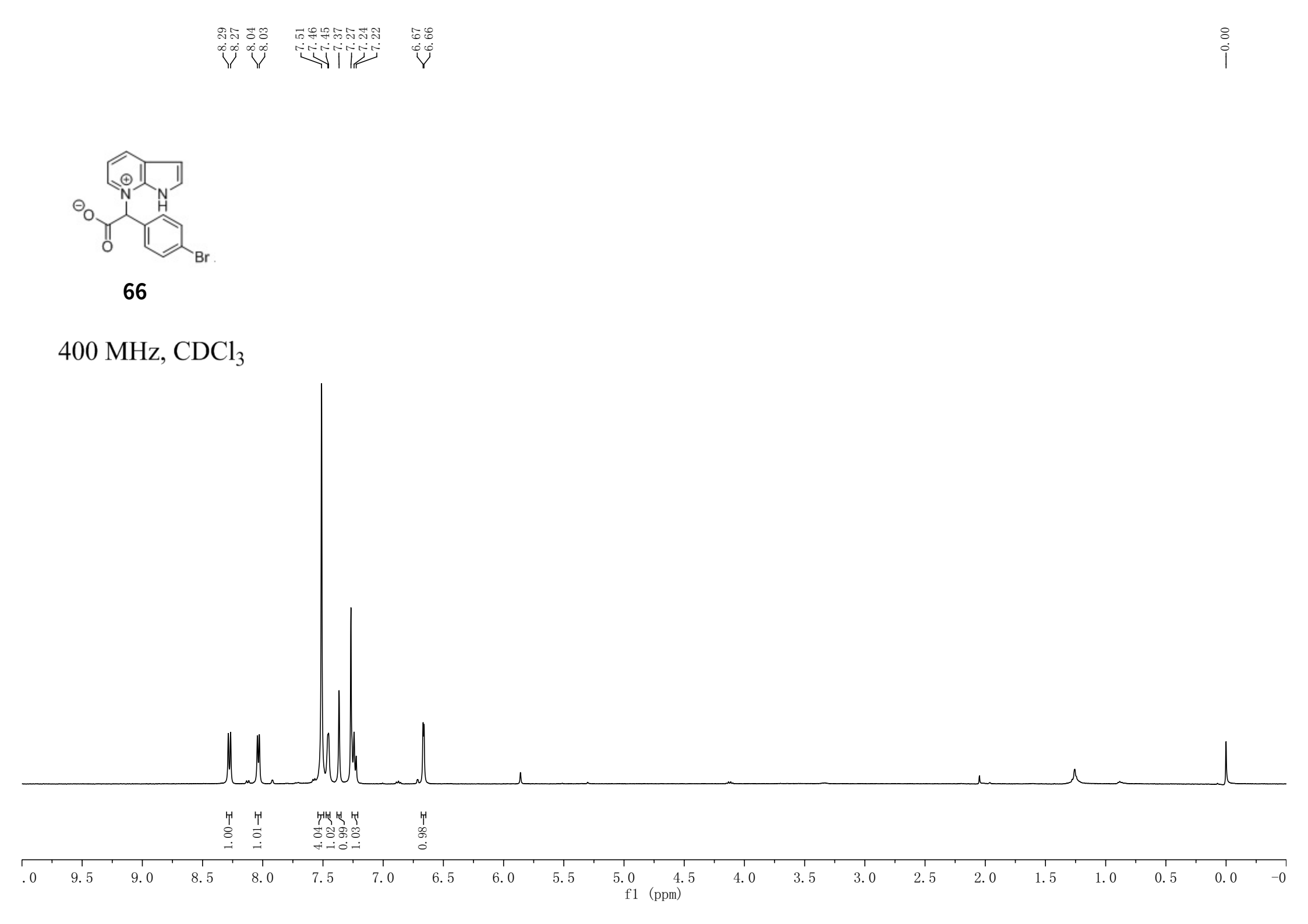

168.84
140.28
139.48
134.83
133.99
131.60
130.93
130.78
130.01
127.06
114.44
102.46
71.85
21.28
N
H
O
O
Me
64
100 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

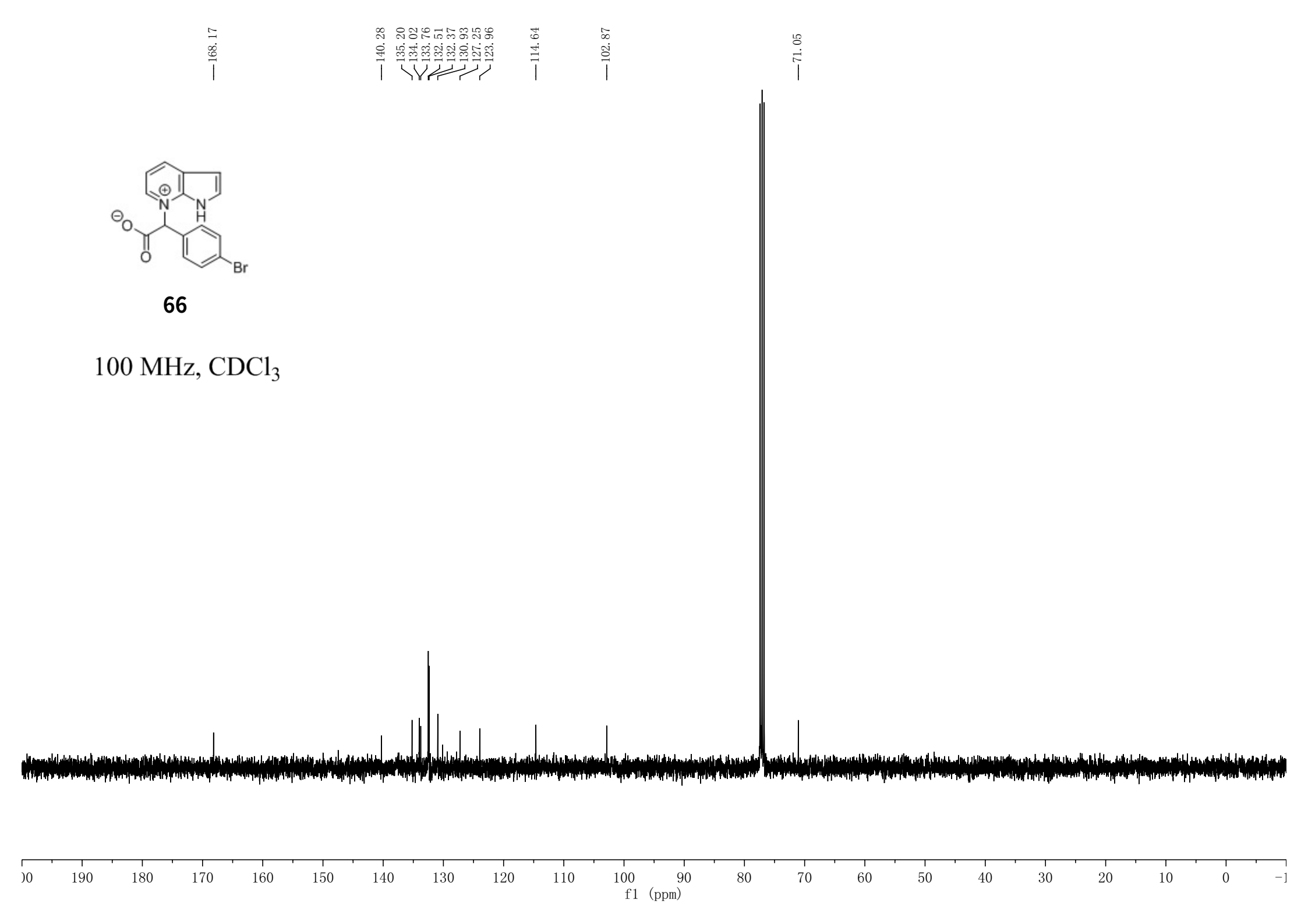


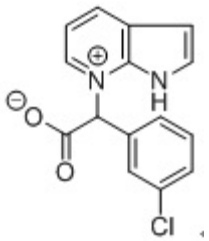
65

400 MHz, $CDCl_3$


168.29
140.18
135.56
135.30
134.07
133.32
132.04
130.77
129.45
127.17
114.69
102.87
70.92
N
H
O
O
Cl
65
100 MHz, CDCl3
f1 (ppm)


8.29
8.27
8.04
8.03
7.51
7.46
7.45
7.37
7.27
7.24
7.22
6.67
6.66
0.00
Br
66
400 MHz, CDCl3
1.00
1.01
4.04
1.02
0.99
1.03
0.98
f1 (ppm)

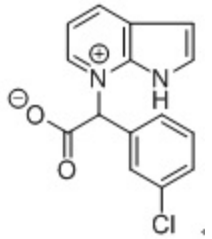

168.17
140.28
135.20
134.02
133.76
132.51
132.37
130.93
127.25
123.96
114.64
102.87
71.05
N
H
O
O
Br
66
100 MHz, CDCl3
f1 (ppm)



67

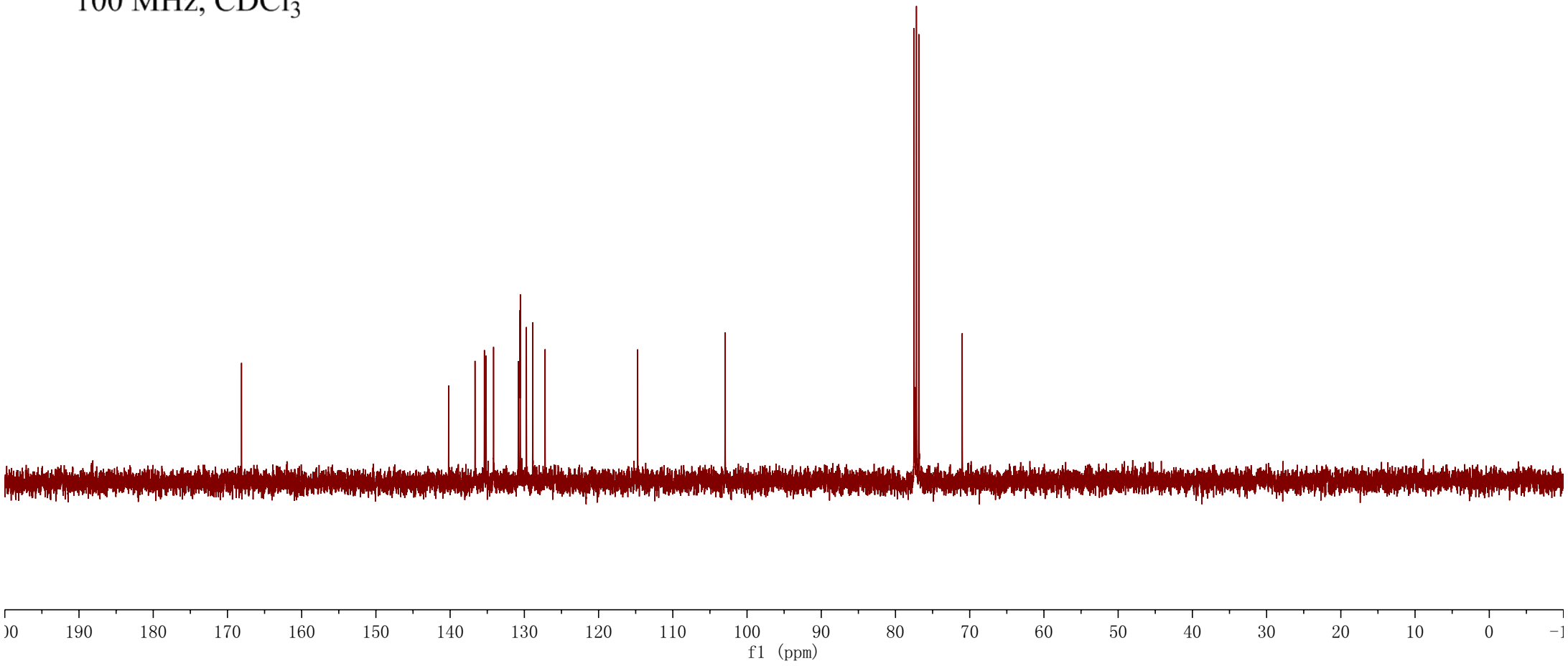
400 MHz, $CDCl_3$

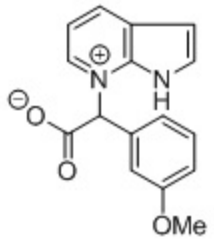
168.11
140.20
136.65
135.38
135.15
134.15
130.81
130.58
130.54
129.72
128.87
127.20
114.74
102.96
71.02



67

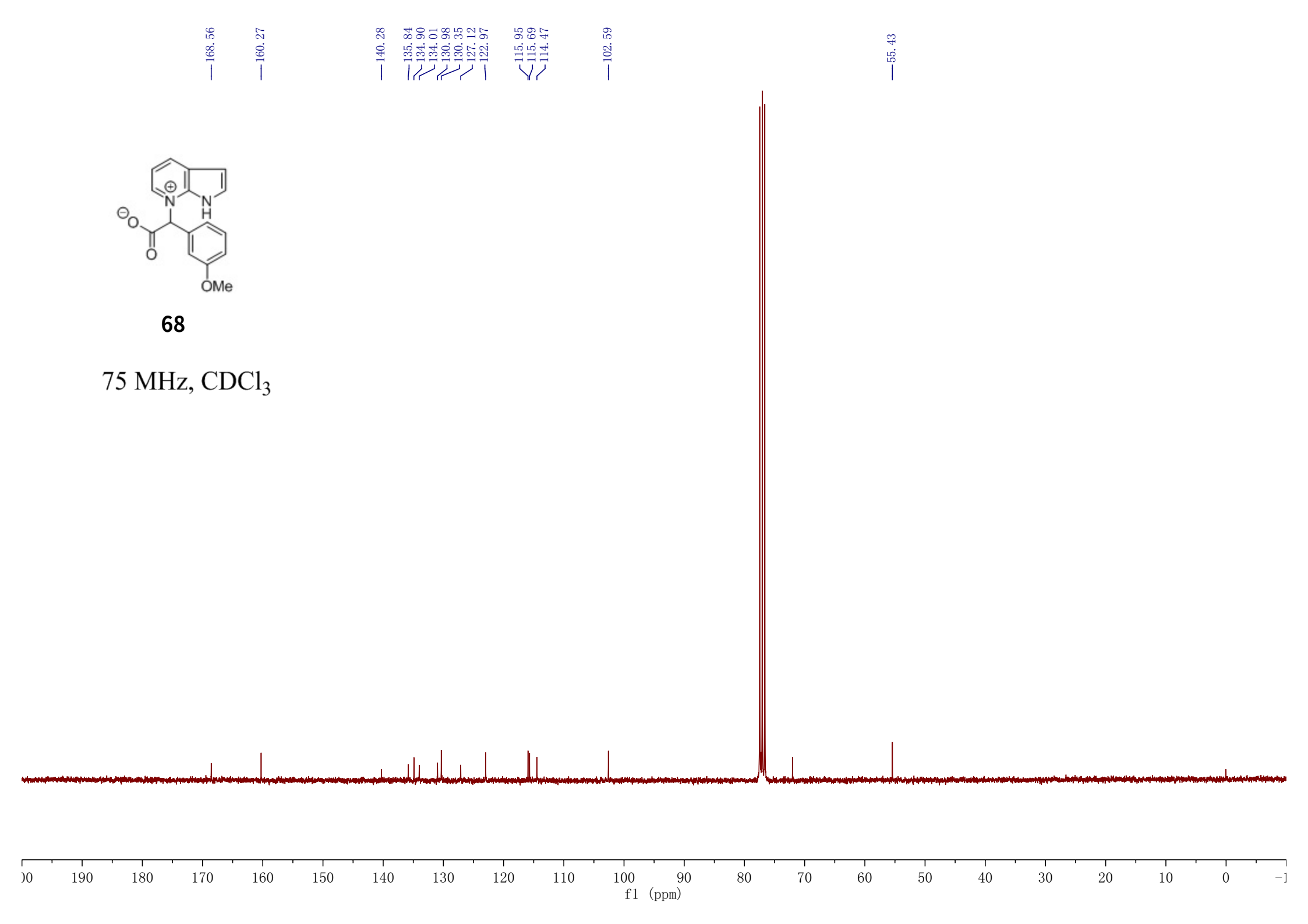
100 MHz, $CDCl_3$

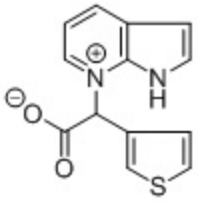




68

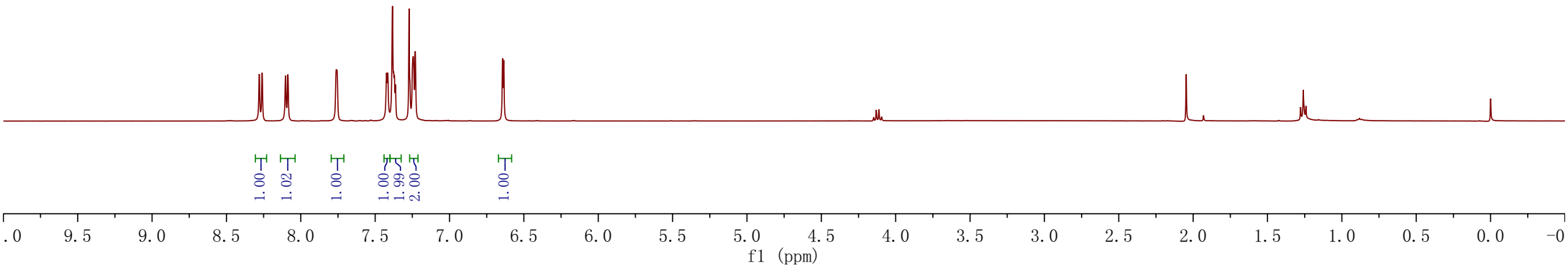
400 MHz, $CDCl_3$

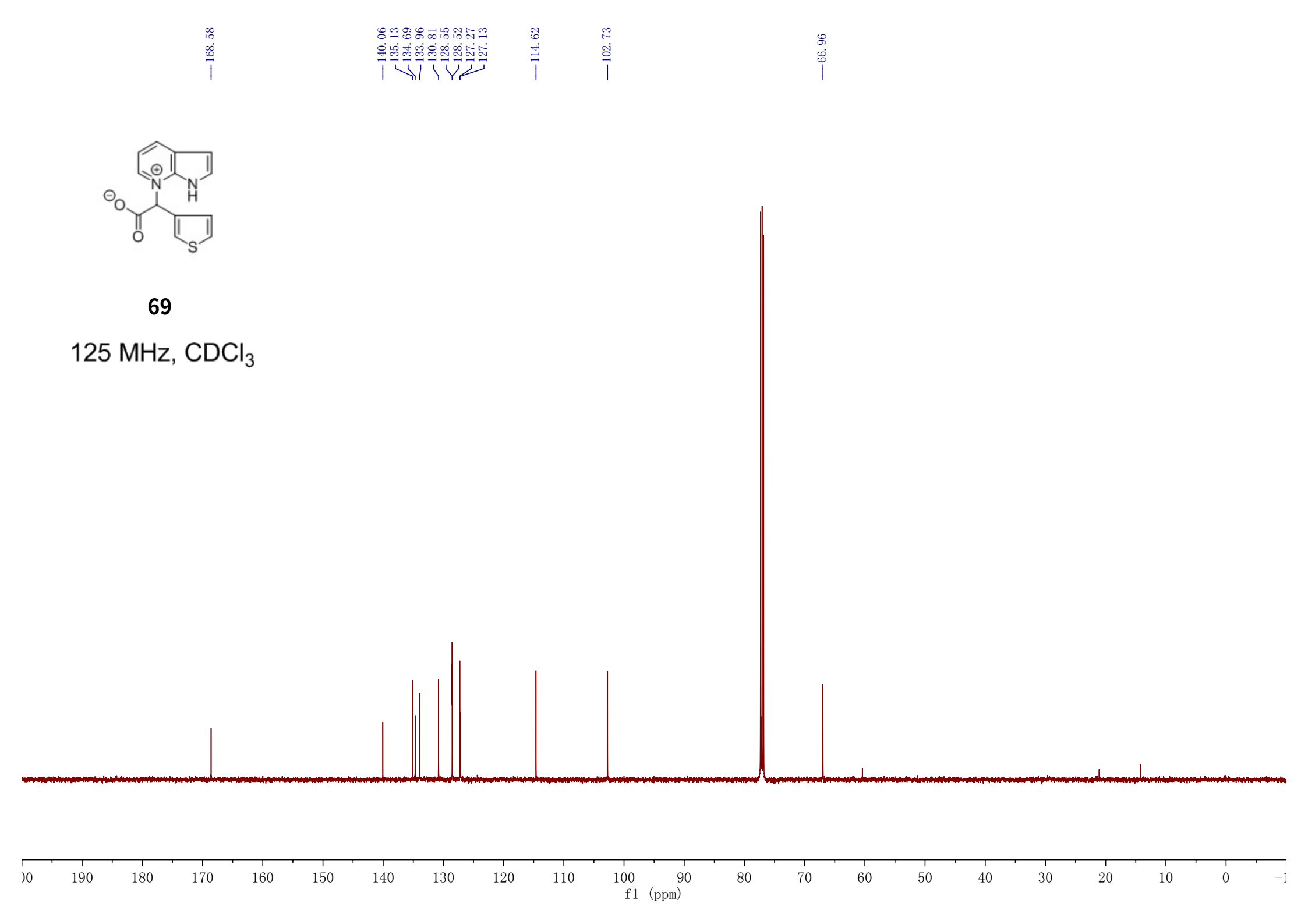

168.56
160.27
140.28
135.84
134.90
134.01
130.98
130.35
127.12
122.97
115.95
115.69
114.47
102.59
55.43
OMe
68
75 MHz, CDCl3
f1 (ppm)

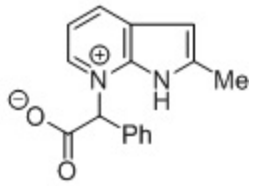


69

400 MHz, $CDCl_3$

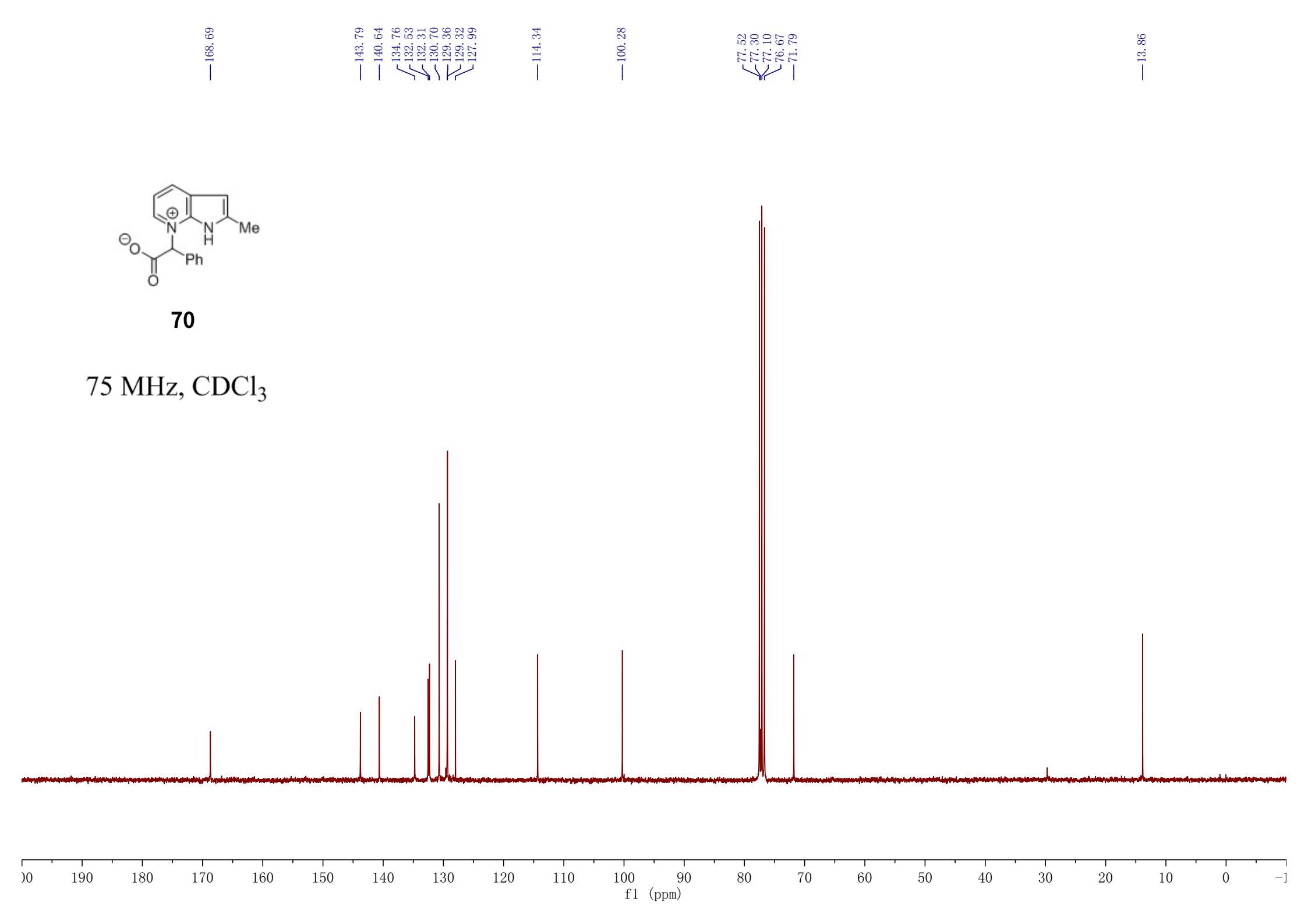


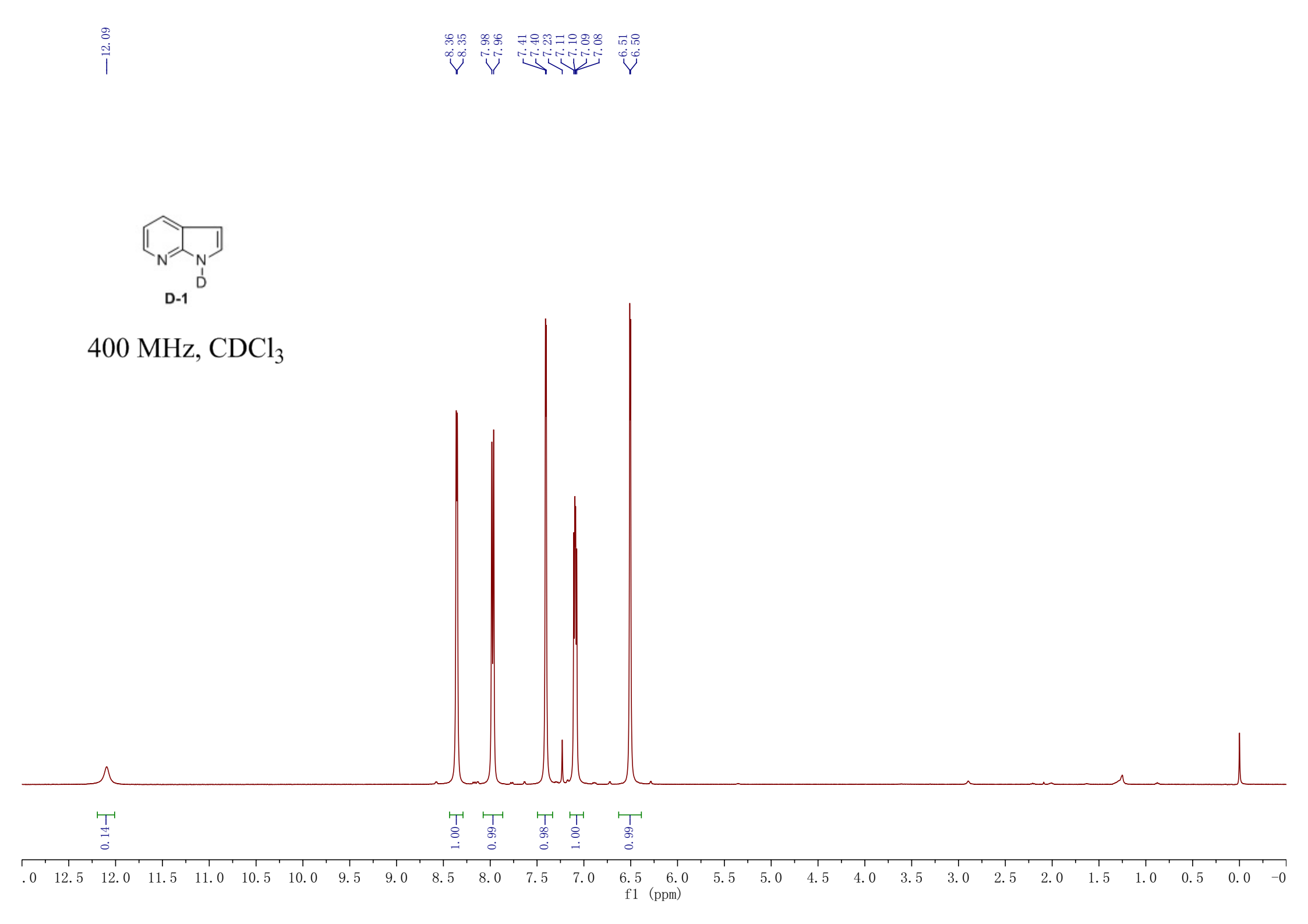

168.58
140.06
135.13
134.69
133.96
130.81
128.55
128.52
127.27
127.13
114.62
102.73
66.96
69
125 MHz, CDCl3
f1 (ppm)

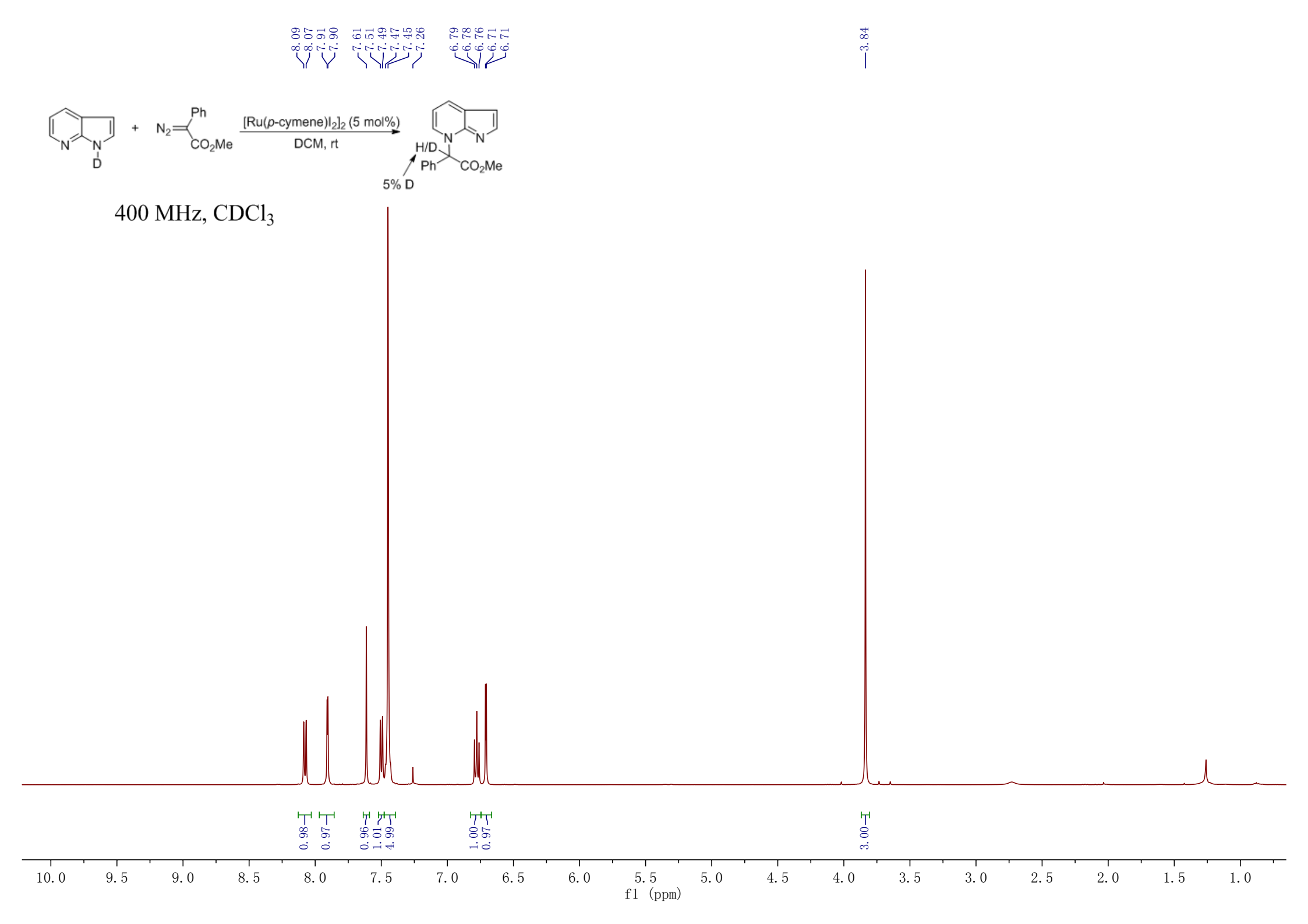


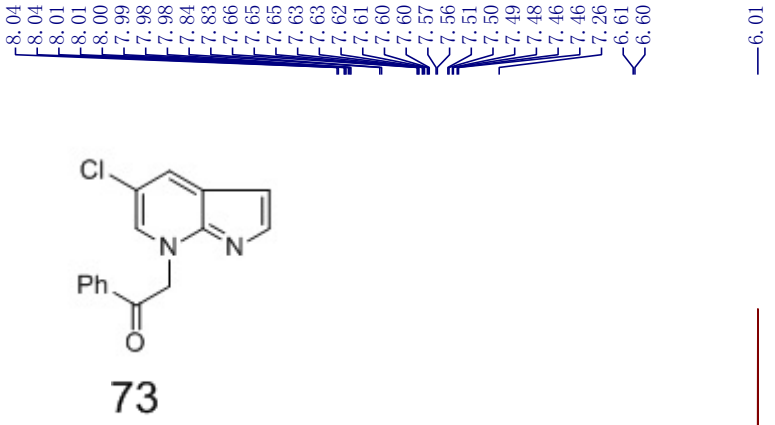
70

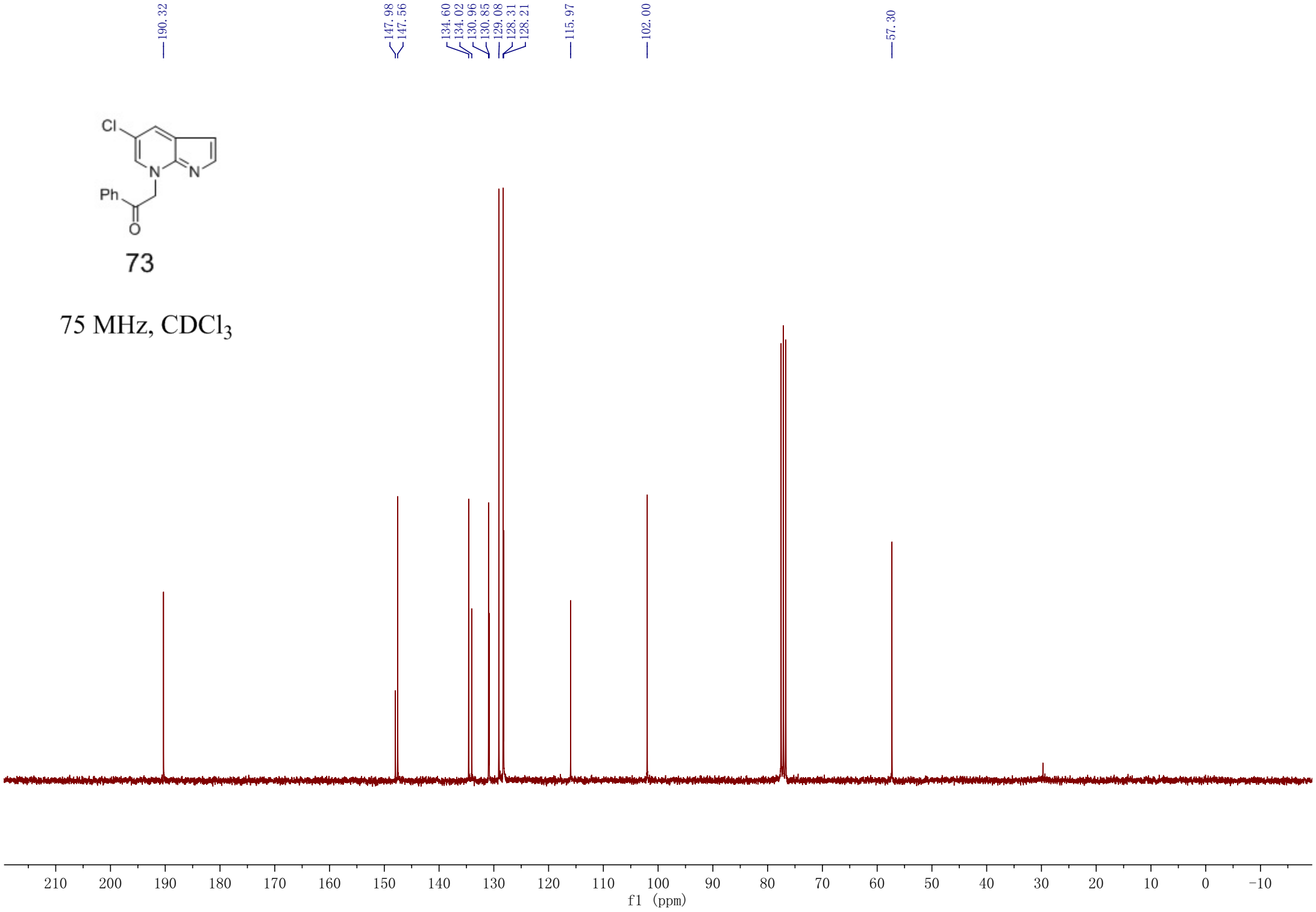
300 MHz, $CDCl_3$

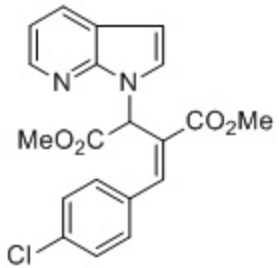

168.69
143.79
140.64
134.76
132.53
132.31
130.70
129.36
129.32
127.99
114.34
100.28
77.52
77.30
77.10
76.67
71.79
13.86
Me
N
H
Ph
O
O
70
75 MHz, CDCl3
f1 (ppm)


12.09
8.36
8.35
7.98
7.96
7.41
7.40
7.23
7.11
7.10
7.09
7.08
6.51
6.50
D-1
400 MHz, CDCl3
0.14
1.00
0.99
0.98
1.00
0.99
f1 (ppm)


8.09
8.07
7.91
7.90
7.61
7.51
7.49
7.47
7.45
7.26
6.79
6.78
6.76
6.71
6.71
3.84
Ph
N2
CO2Me
[Ru(p-cymene)I2]2 (5 mol%)
DCM, rt
N
N
D
H/D
Ph
CO2Me
5% D
400 MHz, CDCl3
0.98
0.97
0.96
1.01
4.99
1.00
0.97
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

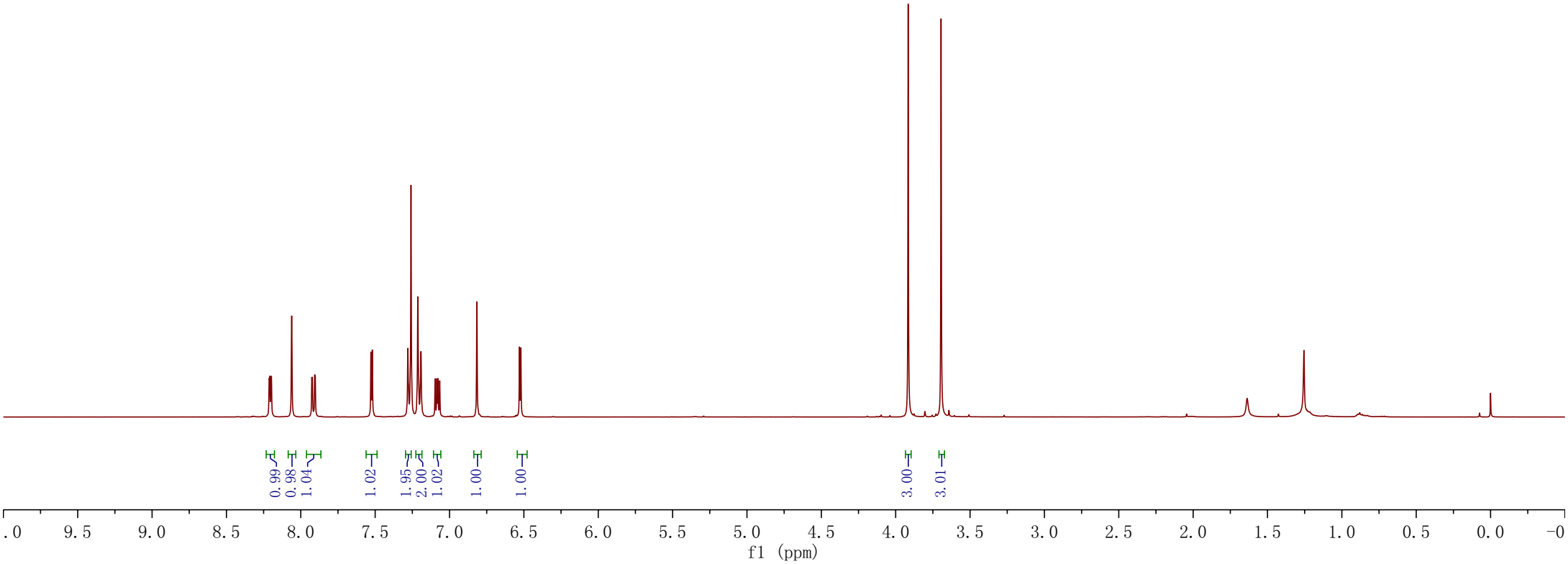

8.04
8.04
8.01
8.01
8.00
7.99
7.98
7.98
7.84
7.83
7.66
7.65
7.65
7.63
7.63
7.62
7.61
7.60
7.60
7.57
7.56
7.51
7.50
7.49
7.48
7.46
7.46
7.26
6.61
6.60
6.01
Cl
N
N
Ph
O
73
300 MHz, CDCl3
1.00
2.05
1.01
1.06
1.01
2.06
1.02
2.06
f1 (ppm)

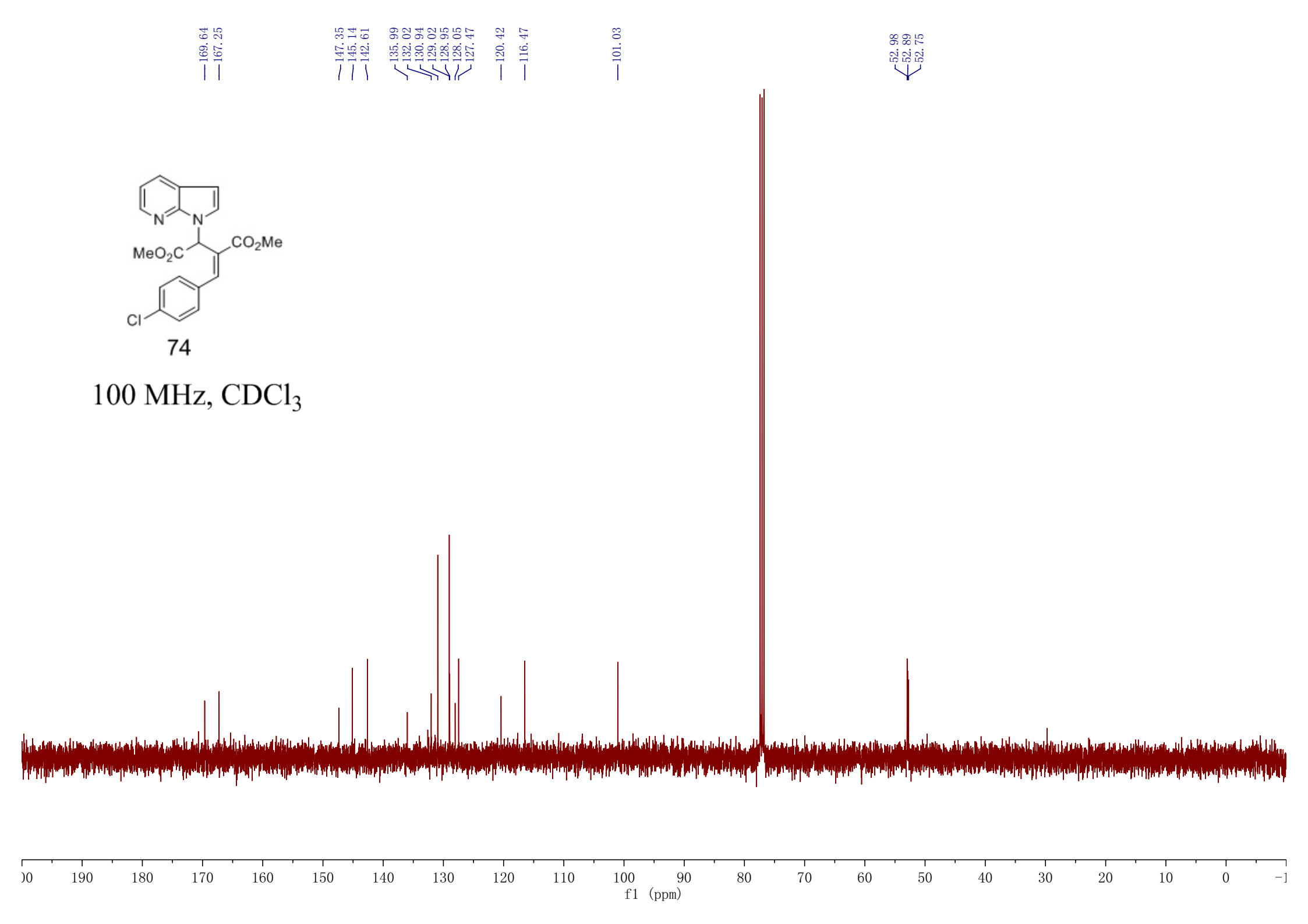

190.32
147.98
147.56
134.60
134.02
130.96
130.85
129.08
128.31
128.21
115.97
102.00
57.30
Cl
N
N
Ph
O
73
75 MHz, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



74

400 MHz, $CDCl_3$




169.64
167.25
147.35
145.14
142.61
135.99
132.02
130.94
129.02
128.95
128.05
127.47
120.42
116.47
101.03
52.98
52.89
52.75
N
N
MeO2C
CO2Me
Cl
74
100 MHz, CDCl3
f1 (ppm)