Supporting Information

Regioselective [2+1] Photocycloaddition of 2-Pyridones and Diazo Compounds

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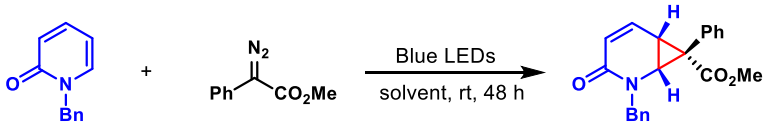
1. General information

All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under argon atmosphere or in the argon-filled glove box. Unless otherwise noted, all solvents were dried by JC Meyer Solvent Drying System. Most reagents were purchased from commercial sources and used without further purification, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on 0.2 mm commercial silica gel plates, using UV light as the visualizing agent or basic solution of $KMnO_4$ or acidic solution of *p*-anisaldehyde and heat as a developing agent. All NMR spectra were recorded on a Bruker spectrometer at 400 MHz (^{1}H NMR), 500 MHz (^{1}H NMR), 600 MHz (^{1}H NMR), 100 MHz (^{13}C NMR), 125 MHz (^{13}C NMR), 150 MHz (^{13}C NMR), 375 MHz (^{19}F NMR), 470 MHz (^{19}F NMR), 565 MHz (^{19}F NMR), 243 MHz (^{31}P NMR) and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$, 7.26 ppm ^{1}H NMR, 77.16 ppm ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, br = broad. High resolution mass spectra (HRMS) were recorded on DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer.

2. Optimization of the reaction conditions

2.1 Optimization of conditions for 2-pyridone and diazocompounds

Table S1. Screening of solvents

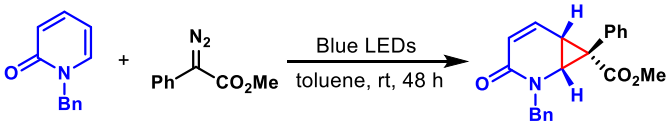


1a **2a** **3**

Entry[a]	solvent	**3a**/[%][b]
1	DMF	0
2	DMSO	0
3	MeCN	0
4	THF	0
5	DME	41
6	DCM	25
7	DCE	41
8	dioxane	trace
9	PhCl	34
10	toluene	42
11	xylene	5
12	$PhCF_3$	45
13	Heptane	trace

[a] Conditions: **1a** (0.1 mmol), **2a** (1.0 equiv) were dissolved in 0.5 mL of solvent indicated and were irradiated at room temperature with blue LEDs (5 W, 465 nm) for 48 h. [b] Isolated yield.

Table S2. Screening the ratio of 1a and 2a

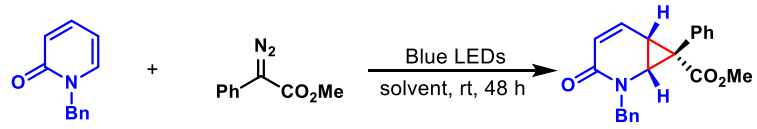


1a **2a** **3**

Entry[a]	X[b]	**3a**/[%][c]
1	1.0	42
2	1.2	44
3	1.5	56
4	2.0	60

[a] Conditions: **1a** (0.1 mmol), **2a** (x equiv), were dissolved in 0.5 mL of solvent indicated and were irradiated at room temperature with blue LEDs (5 W, 465 nm) for 48 h. [b] equivment [c] Isolated yield

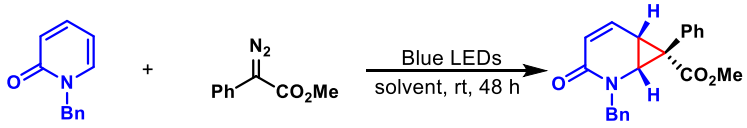
Table S3. Screening the ratio of toluene and DCE



Entry[a]	solvent[b]	**3**/[%][c]
1	1:1	63
2	4:1	72
3	9:1	70
4	20:1	75
5	30:1	74

[a] Conditions: **1a** (0.1 mmol), **2a** (2.0 equiv) were dissolved in 0.25 mL of solvent indicated and were irradiated at room temperature with blue LEDs (5 W, 465 nm) for 48 h. [b] The ratio of toluene:DCE. [c] Isolated yield.

Table S4. Screening of solvent mix ratios



Entry[a]	solvent[b]	**3a**/[%][c]
1	toluene:DCE (20:1)	75
2	toluene:DCM(20:1)	68
3	toluene:DME(20:1)	67
4	$PhCF_3$:DCE(20:1)	71
5	$PhCF_3$:DCM(20:1)	66
6	$PhCF_3$:DME(20:1)	55
7	PhCl:DCE(20:1)	81
8	PhCl:DCM(20:1)	70
9	PhCl:DME(20:1)	59

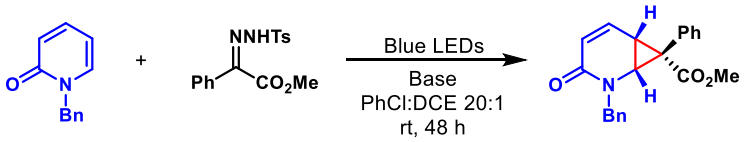
[a] Conditions: **1a** (0.1 mmol), **2a** (2.0 equiv) were dissolved in 0.25 mL of solvent indicated and were irradiated at room temperature with blue LEDs (5 W, 465 nm) for 48 h. [b] system concentration with 0.4 mol/L. [c] Isolated yield.

Table S5. Screening of Conditions

Entry[a]	Change of conditions[b]	**3**/[%][c]
1	none	81
2	PhCl	59
3	DCE	58
4	dark	0

[a] Conditions: **1a** (0.1 mmol), **2a** (2.0 equiv) were dissolved in 0.25 mL of solvent indicated and were irradiated at room temperature with blue LEDs (5 W, 465 nm) for 48 h. [b] system concentration with 0.4 mol/L. [c] Isolated yield.

2.2 Optimization of conditions for 2-pyridone and hydrazones



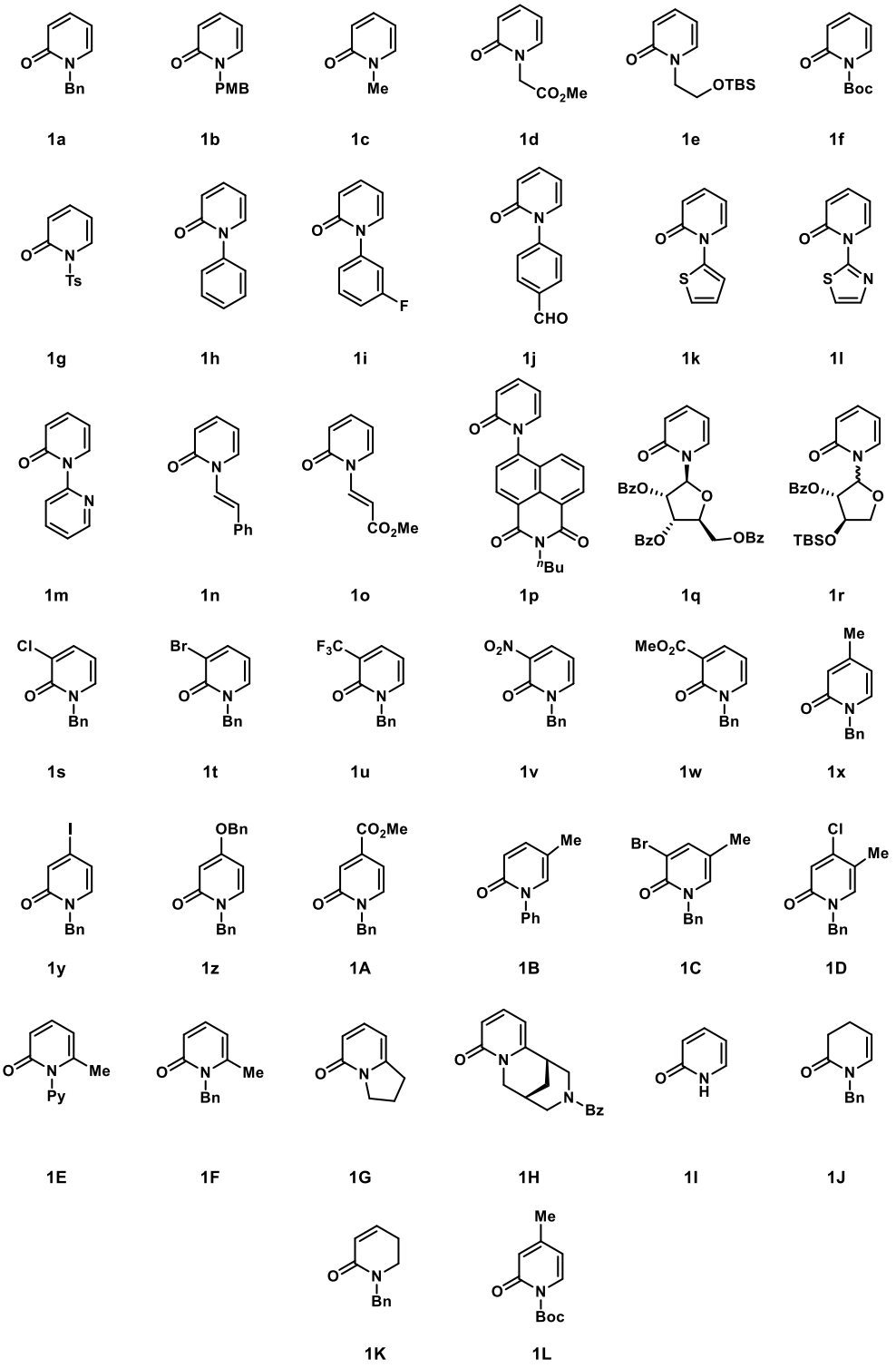
1a **2A** **3**

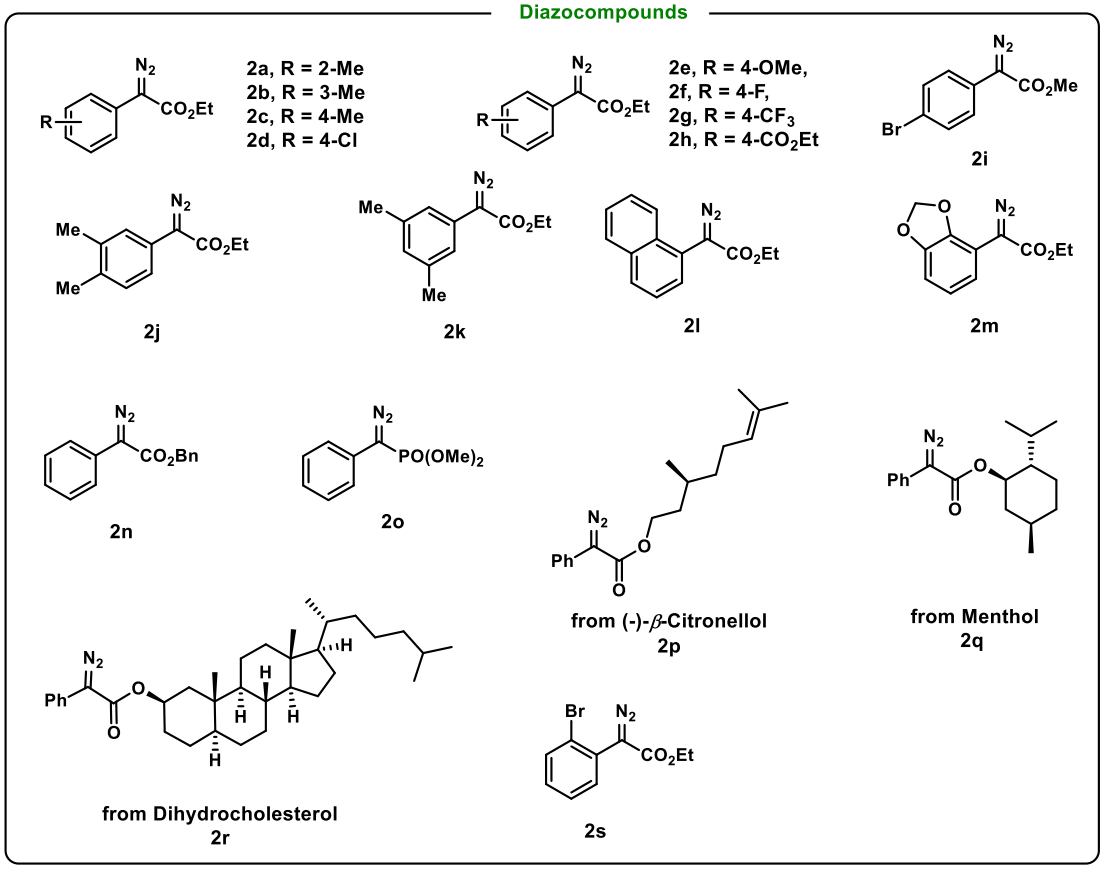
Entry[a]	Base	**3**/[%][b]
1	DIPEA	61
2	DABCO	65
3	Et_3N	64
4	DMAP	38
5	N,N,N'-Trimethylethylenediamine	40
6	DBU	44
7	Cs_2CO_3	68

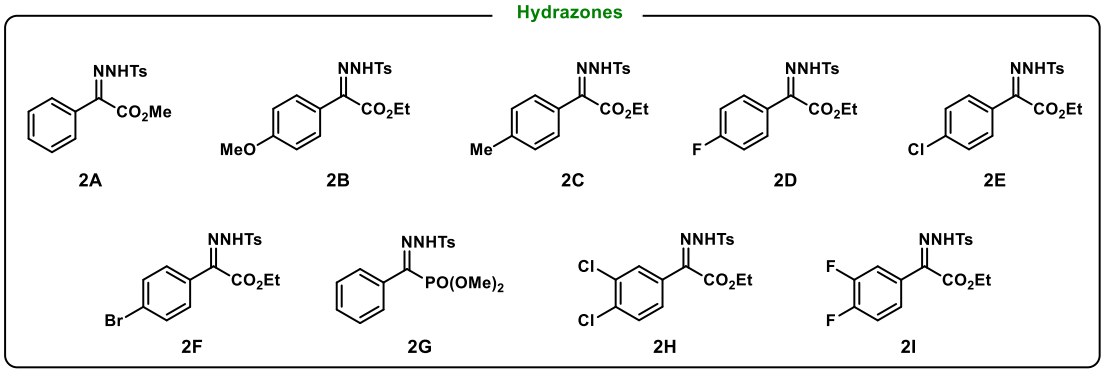
[a] Conditions: **1a** (0.1 mmol), **2A** (2.0 equiv) and base (4.0 equiv) were dissolved in 0.25 mL of solvent indicated and were irradiated at room temperature with blue LEDs (5 W, 465 nm) for 48 h. [b] Isolated yield.

3. Substrates involved in this work.

2-Pyridone reagents



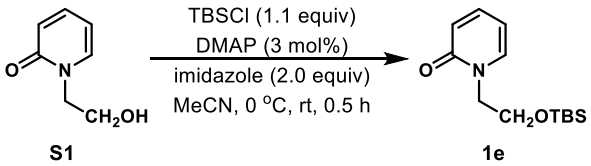




The 2-pyridones (**1o**)[1] (**1w**)[2] (**1z**)[3] (**1a, 1b, 1x**)[4] (**1d, 1F, 1B**)[5] (**1h**)[6] (**1m, 1E**)[7] (**1n**)[8] (**1G**)[9] (**1H**)[10] (**1k, 1l**)[11] (**1f, 1g, 1L**)[12] (**1v**)[13] (**1s, 1t, 1u**)[14] (**1i**)[15] (**1A**)[16] (**1J**)[17] were prepared according to the literature procedures. The **S5, 1c, 1I, 1K** obtained by commercial purchase. The diazocompounds (**2a, 2f, 2q, 2s**)[18] (**2b, 2c, 2e, 2g**)[19] (**2l**)[20] (**2p**)[21] (**2n, 2f, 2d, 2g, 2m**)[22] (**2k**)[23] (**2i**)[24] (**2h, 2j**)[25] (**2r**)[26] (**2n**)[27] (**2o**)[28] were known compounds and prepared according to literature procedures. The Hydrazone compounds (**2B**)[29] (**2A**)[30] (**2C, 2D**)[31] (**2E, 2F**)[32] (**2G**)[28] were known compounds and prepared according to literature procedures.

3.1 Procedure for synthesis of Substrate

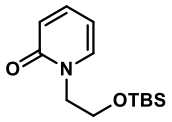
3.1.1 Procedure for synthesis of **1e**.[33]



S1 **1e**

In a round-bottom flask, **S1** (10 mmol), DMAP (3 mol%) and imidazole (2.0 equiv) was dissolved in MeCN (20 ml) at 0 ºC. Then TBSCl (1.1 equiv) were dropwise added. and the solution was stirred at room temperature for 30 min. The reaction mixture was poured into water and then the product was extracted with EtOAc (30 mL x 3), the combined layers were dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (eluent: Petroleum ether/EtOAc = 10:1–3:1) to give **1e**

1-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)pyridin-2(1*H*)-one (1e)



Physical state: brown solid;

Melting point: 32–35ºC;

Yield: 87%;

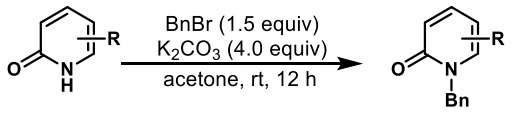
Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (m, *J* = 7.1, 5.0, 2.2 Hz, 2H), 6.54 (dd, *J* = 9.7, 1.4 Hz, 1H), 6.11 (td, *J* = 6.5, 1.3 Hz, 1H), 4.04 (t, *J* = 4.8 Hz, 2H), 3.92 – 3.83 (m, 2H), 0.82 (s, 9H), –0.09 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 162.74, 139.82, 139.71, 120.68, 105.09, 60.91, 52.46, 25.90, 18.26, –5.62.

HRMS (ESI–TOF): Calc'd. For: $C_{13}H_{24}NO_2Si^+$ [M+H$^+$] 254.1571, found: 254.1566

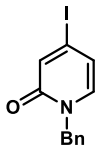
3.1.2 Procedure for synthesis of **1y**, **1D**.[4]



S2 **1y, 1D**

In a round-bottom flask, **S2** (10 mmol) and K_2CO_3 (4.0 equiv) was dissolved in acetone (15 ml). Then BnBr (1.5 equiv) were dropwised at room temperature, and the solution was stirred for 12 hours. The reaction mixture was poured into water and then the product was extracted with EtOAc (30 mL x 3), the combined layers were dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (eluent: Petroleum ether/EtOAc = 10:1–3:1) to give **1y, 1D.**

1-Benzyl-4-iodopyridin-2(1*H*)-one (1y)



Physical state: white solid;

Melting point: 95–96°C;

Yield: 78%;

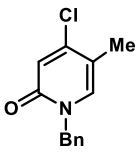
Rf = 0.4 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.26 (m, 5H), 7.13 (q, *J* = 1.7 Hz, 1H), 6.93 (d, *J* = 7.2 Hz, 1H), 6.45 (ddt, *J* = 7.1, 2.2, 1.2 Hz, 1H), 5.06 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.98, 136.64, 135.81, 130.44, 129.10, 128.37, 128.29, 115.61, 108.88, 51.87.

HRMS (ESI–TOF): Calc'd. For: $C_{12}H_{11}INO^+$ [M+H$^+$] 311.9880, found: 311.9874.

1-benzyl-4-chloro-5-methylpyridin-2(1*H*)-one (1D)



Physical state: white solid;

Melting point: 112–113°C;

Yield: 82%;

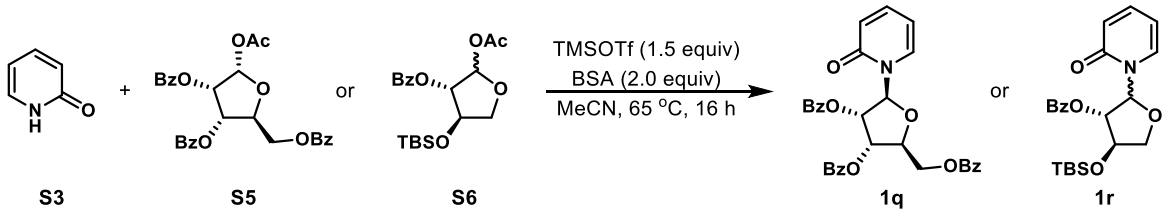
Rf = 0.2 (silica gel, PE: EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 – 7.41 (m, 6H), 6.89 (s, 1H), 5.27 (s, 2H), 2.23 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.36, 148.52, 136.22, 135.21, 129.06, 128.26, 128.18, 119.70, 115.08, 51.53, 16.22.

HRMS (ESI–TOF): Calc'd. For: $C_{13}H_{13}ClNO^+$ [M+H$^+$] 234.0680, found: 234.0671

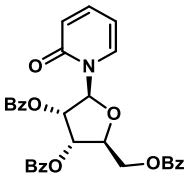
3.1.3 Procedure for synthesis of **1q-r**.[34]



S3 **S5** **S6** **1q** **1r**

In a round-bottom flask, **S3** (10 mmol) and **S5** or **S6**[35] (1.0 equiv) was dissolved in MeCN (15 mL). Then TMSOTf (1.5 equiv) and BSA (N,O-Bis(trimethylsilyl)acetamide) (2.0 equiv) were dropwised at 65^{o}C, and the solution was stirred for 16 hours. The reaction mixture was poured into water and then the product was extracted with EtOAc (30 mL x 3), the combined layers were dried over Na_2SO_4. And then concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1:3–1:1) to give **1q-1r.**

(*2S,3S,4S,5S*)-2-((Benzoyloxy)methyl)-5-(2-oxopyridin-1(2*H*)-yl)tetrahydrofuran-3,4-diyl dibenzoate (1q)



Physical state: white solid

Melting point: 86–89^{o}C

Yield: 83%

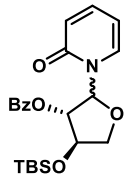
Rf = 0.4 (silica gel, PE: EtOAc = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.15 – 8.08 (m, 2H), 8.02 – 7.96 (m, 2H), 7.95 – 7.90 (m, 2H), 7.63 – 7.51 (m, 4H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.41 – 7.28 (m, 5H), 6.62 (d, *J* = 4.3 Hz, 1H), 6.54 (d, *J* = 9.2 Hz, 1H), 6.08 (td, *J* = 6.8, 1.3 Hz, 1H), 5.92 (t, *J* = 5.8 Hz, 1H), 5.81 (dd, *J* = 5.8, 4.3 Hz, 1H), 4.88 (dd, *J* = 12.2, 2.9 Hz, 1H), 4.78 (dt, *J* = 6.3, 3.3 Hz, 1H), 4.69 (dd, *J* = 12.3, 4.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.16, 162.42, 161.57, 151.33, 139.79, 133.68, 133.58, 130.51, 130.04, 129.39, 128.92, 128.57, 126.37, 125.71, 120.16, 105.24, 90.53, 82.59, 74.73, 67.89, 65.73, 25.83, 25.66, 18.29, 17.91, -4.65, -4.83, -4.85, -5.35.

HRMS (ESI–TOF): Calc'd. For: $C_{31}H_{26}NO_8^+$[M+H$^+$] 540.1653, found: 540.1655

(2*S*,3*S*,4*R*)-4-((*tert*-Butyldimethylsilyl)oxy)-2-(2-oxopyridin-1(2*H*)-yl)tetrahydrofuran-3-yl benzoate (1r)



Physical state: yellow solid;

Melting point: 112–115°C;

Yield: 62%;

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

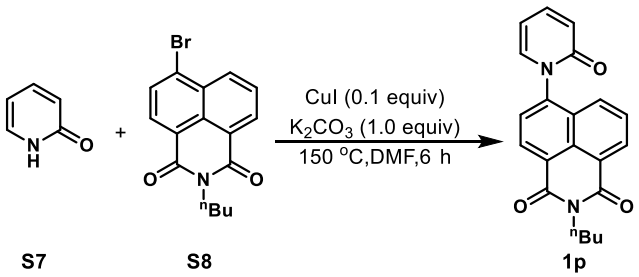
α: β = 3:1

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 – 7.85 (m, 2H), 7.85 – 7.79 (m, 1H), 7.56 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.44 – 7.35 (m, 1H), 7.28 (s, 1H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.14 (ddd, *J* = 9.0, 6.6, 2.1 Hz, 1H), 6.32 (dt, *J* = 9.1, 1.0 Hz, 1H), 6.17 (s, 1H), 6.00 (td, *J* = 6.8, 1.3 Hz, 1H), 4.20 – 4.15 (m, 1H), 4.14 – 4.06 (m, 2H), 3.66 (t, *J* = 5.8 Hz, 1H), 0.61 (s, 9H), –0.06 (d, *J* = 12.7 Hz, 3H), –0.16 (d, *J* = 12.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.16, 162.42, 139.79, 133.68, 133.58, 130.04, 128.57, 120.16, 105.24, 90.53, 82.59, 74.73, 67.89, 65.73, 25.83, 25.66, 18.29, 17.91, –4.65, –4.83, –4.85, –5.35.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{30}NO_5Si^+$ [M+H$^+$] 416.1888, found: 416.1891

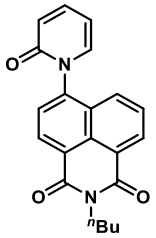
3.1.4 Procedure for synthesis of **1p**.[7]



S7 **S8** **1p**

In a round–bottom flask, **S7** (10 mmol) and **S8** (1.0 equiv), CuI (0.1 equiv) and K_2CO_3 (1.0 equiv) was dissolved in DMF (15 ml) at 150ºC. Then the reaction mixture was stirred for 6 hours, the reaction mixture was poured into water and then the product was extracted with EtOAc (30 mL x 3), the combined layers were dried over Na_2SO_4, and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (eluent: EtOAc/Petroleum ether = 1:3–1:1) to give **1p**

2-Butyl-6-(2-Oxopyridin-1(2*H*)-yl)-1*H*-benzo[de]isoquinoline-1,3(2*H*)-dione (1p)



Physical state: yellow solid

Melting point: 203–205ºC

Yield: 68%

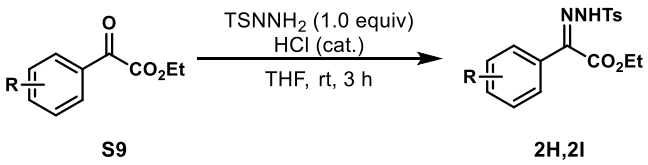
Rf = 0.3 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, *J* = 7.7 Hz, 1H), 8.65 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.88 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.78 (dd, *J* = 8.5, 7.2 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.57 (ddd, *J* = 9.1, 6.6, 2.1 Hz, 1H), 7.32 (dd, *J* = 6.9, 2.1 Hz, 1H), 6.77 (dt, *J* = 9.3, 1.1 Hz, 1H), 6.39 (td, *J* = 6.7, 1.2 Hz, 1H), 4.25 – 4.17 (m, 2H), 1.72 (tt, *J* = 9.2, 3.6 Hz, 2H), 1.45 (h, *J* = 7.4 Hz, 2H), 0.99 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 163.94, 163.49, 162.50, 143.05, 140.94, 137.98, 132.02, 131.27, 129.21, 129.07, 128.35, 128.12, 126.44, 123.92, 123.46, 122.34, 106.62, 40.54, 30.31, 20.49, 13.97.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{19}N_2O_3^+$ [M+H$^+$] 347.1390, found: 347.1382

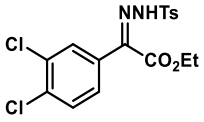
3.1.5 Procedure for synthesis of **2H**, **2I**.[32]



S9 **2H,2I**

In a round–bottom flask, **S9** (10 mmol) and $TSNNH_2$ (1.0 equiv) was dissolved in THF (15 ml) at room temperature. Then HCl (cat.) was dropwised. Then the reaction mixture was stirred for 3 hours, the hydrazones precipitate as needle–like crystals. Filtration of the crude mixture gives the pure product.

Ethyl (*E*)-2-(3,4-dichlorophenyl)-2-(2-tosylhydrazono)acetate (2H)



Physical state: yellow solid

Melting point: 93–95^{o}C

Yield: 48%

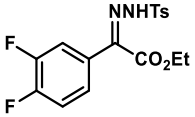
Rf = 0.3 (silica gel, PE: EtOAc = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.79 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 2.0 Hz, 1H), 7.44 – 7.30 (m, 4H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.34 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.59, 144.87, 135.26, 135.18, 134.08, 133.66, 132.40, 130.63, 130.14, 129.96, 128.11, 127.97, 62.86, 21.78, 14.08.

HRMS (ESI–TOF): Calc'd. For: $C_{17}H_{17}Cl_2N_2O_4S^+$ [M+H$^+$] 415.0281, found: 415.0279

Ethyl (*E*)-2-(3,4-difluorophenyl)-2-(2-tosylhydrazono)acetate (2I)



Physical state: yellow solid

Melting point: 40–42^{o}C

Yield: 86%

Rf = 0.3 (silica gel, PE: EtOAc = 4:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.73 (s, 1H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.26 (m, 4H), 7.12 (dt, *J* = 9.7, 8.3 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H).

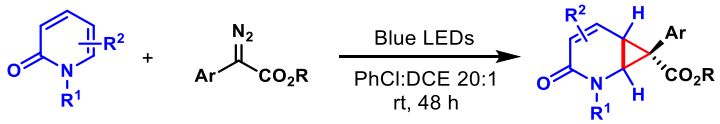
^{13}C NMR (100 MHz, $CDCl_3$): δ 161.65, 152.43, 152.30, 151.19, 151.06, 149.93, 149.80, 148.72, 148.60, 144.83, 144.82, 135.52, 135.32, 129.94, 128.05, 125.18, 125.12, 118.01, 117.81, 117.12, 116.94, 62.84, 21.74, 14.05.

^{19}F NMR (375 MHz, $CDCl_3$): δ –136.07, –137.53.

HRMS (ESI–TOF): Calc'd. For: $C_{17}H_{17}F_2N_2O_4S^+$ [M+H$^+$] 383.0872, found: 383.0368

4 General procedures for the synthesis of Products

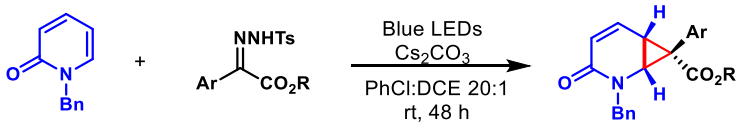
4.1 Reaction of 2-pyridones with aryl diazocompounds



1 **2** **3-54**

A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.1 mmol), **2** (2.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. and the mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 hours. After completion of the reaction (monitored by TLC), filtered through a thin pad of celite, eluting with EtOAc (30 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to give the desired product.

4.2 Reaction of 2-pyridones with hydrazones



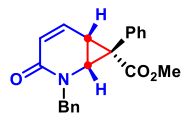
1 **2A-2l** **3, 38, 40-42, 55-58**

A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1** (0.1 mmol), **2** (2.0 equiv), Cs_2CO_3 (4.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. and the mixture was irradiation with a blue LED under nitrogen atmosphere at

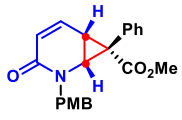
room temperature for 48 hours. After completion of the reaction (monitored by TLC), filtered through a thin pad of celite, eluting with EtOAc (30 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to give the desired product.

5 Analytical date

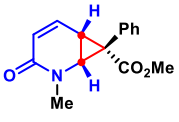
Reaction scope of 2-pyridones



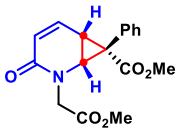
3: 81%



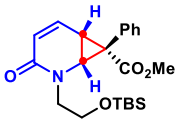
4: 81%,



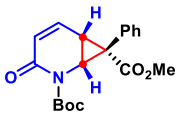
5: 84%



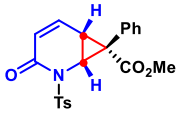
6: 51%



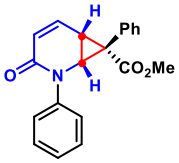
7: 82%



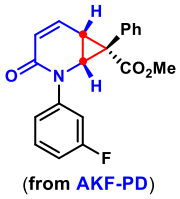
8: 71%



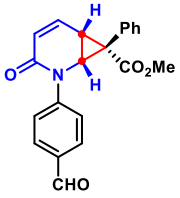
9: 75%



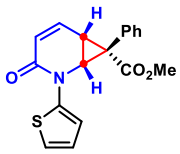
10: 79%



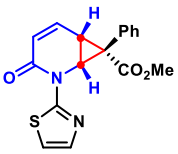
(from AKF-PD)
11: 52%



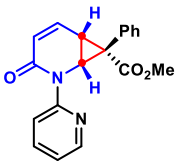
12: 87%



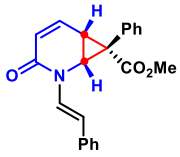
13: 62%



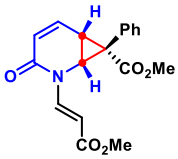
14: 66%



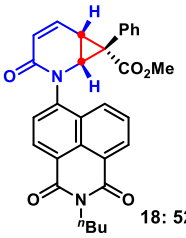
15: 86%



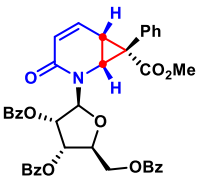
16: 70%



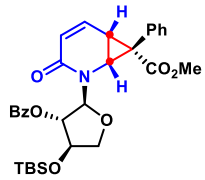
17: 85%



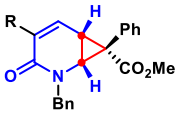
18: 52%



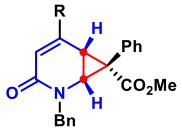
19: 62%, (*dr* = 3:2)



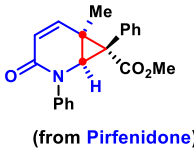
20: 87%, (*dr* = 1:1)



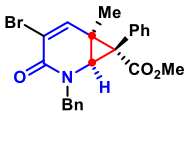
21: R = Cl, 55%
22: R = Br, 98%
23: R = CF_3, 86%
24: R = NO_2, 54%
25: R = CO_2Me, 52%



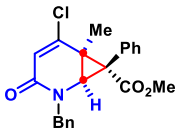
26: R = Me, 58%
27: R = I, 60%
28: R = OBn, 54%
29: R = CO_2Me, 84%



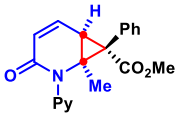
(from Pirfenidone)
30: 24%



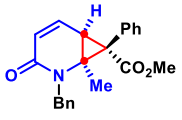
31: 57%



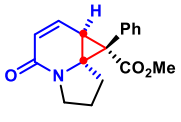
32: 64%



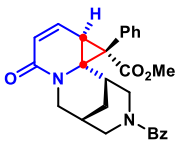
33: 51%



34: 30%

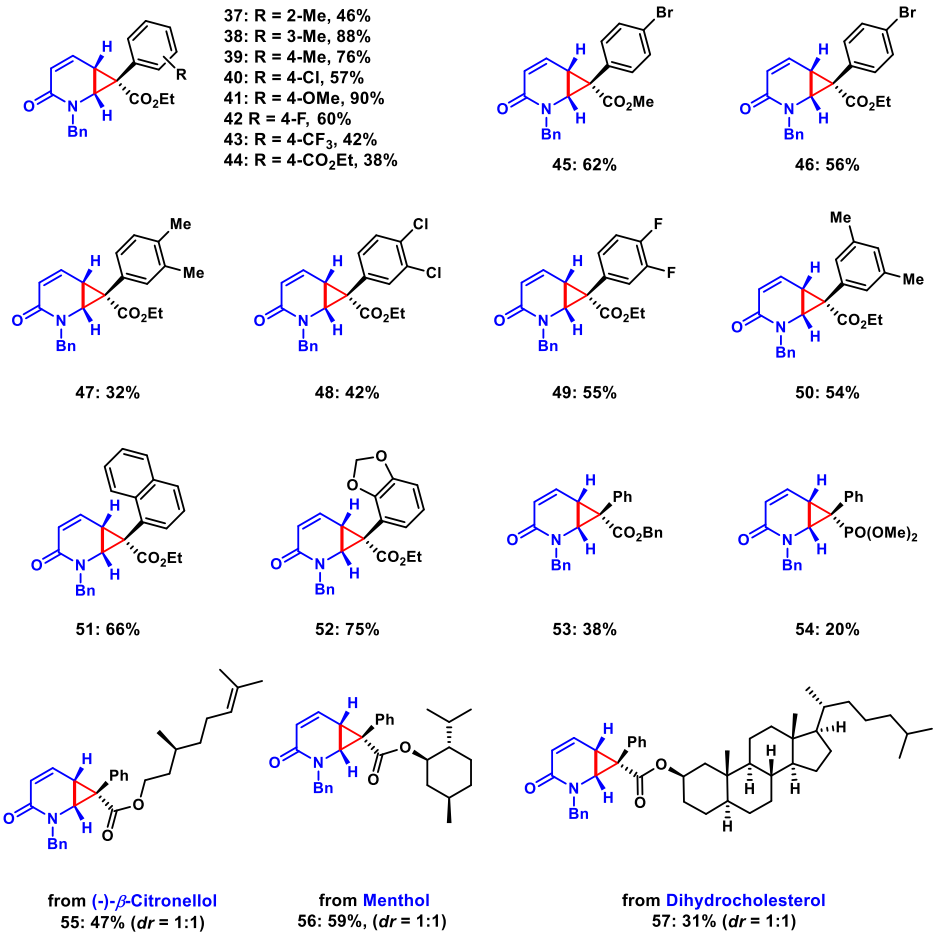


35: 38%



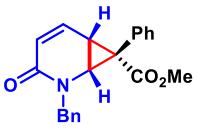
from (-)-Cytisine
36: 56%, (*dr* = 1:1)

Reaction scope of Diazocompounds and Hydrazones



6 Characterization data for the new compounds.

Methyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (3)



Physical state: yellow solid

Melting point: 161–164°C;

Yield: 81%;

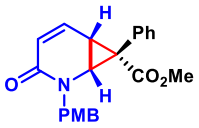
Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 3.8 Hz, 4H), 7.35 – 7.30 (m, 1H), 7.30 – 7.25 (m, 3H), 7.00 – 6.94 (m, 2H), 6.65 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.70 (d, *J* = 9.9 Hz, 1H), 5.52 (d, *J* = 14.7 Hz, 1H), 4.17 (d, *J* = 14.6 Hz, 1H), 3.89 (d, *J* = 8.9 Hz, 1H), 3.63 (s, 3H), 2.88 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.47, 161.43, 136.31, 136.18, 133.26, 129.50, 128.91, 128.50, 128.32, 128.14, 127.95, 126.47, 53.17, 50.55, 48.71, 33.85, 28.12.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{20}NO_3^+$[(M+H)$^+$] 334.1438, found: 334.1435

Methyl (1*R*,6*R*,7*R*)-2-(4-methoxybenzyl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (4)



Physical state: yellow solid;

Melting point: 113–114°C;

Yield: 81%;

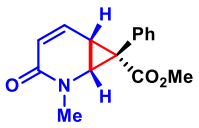
Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.26 (m, 4H), 7.25 (s, 1H), 6.98 – 6.93 (m, 2H), 6.92 – 6.87 (m, 2H), 6.63 (dd, *J* = 9.9, 5.2 Hz, 1H), 5.68 (d, *J* = 9.9 Hz, 1H), 5.43 (d, *J* = 14.4 Hz, 1H), 4.11 (d, *J* = 14.4 Hz, 1H), 3.88 (d, *J* = 8.9 Hz, 1H), 3.81 (s, 3H), 3.63 (s, 3H), 2.86 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.57, 161.37, 159.45, 136.16, 133.30, 129.89, 129.57, 128.51, 128.34, 128.15, 126.63, 114.30, 55.45, 53.20, 50.03, 48.58, 33.81, 28.19.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{22}NO_4^+$ [(M+H)$^+$] 364.1543, found: 364.1553

Methyl (1*R*,6*R*,7*R*)-2-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (5)



Physical state: white solid;

Melting point: 133–137°C;

Yield: 84%;

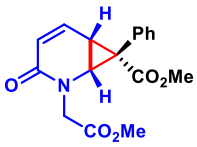
Rf = 0.3 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 – 7.26 (m, 2H), 7.26 – 7.22 (m, 1H), 7.02 – 6.97 (m, 2H), 6.63 (ddd, *J* = 9.8, 5.3, 0.7 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 3.84 (dd, *J* = 8.8, 0.7 Hz, 1H), 3.64 (s, 3H), 3.21 (s, 3H), 2.91 (dd, *J* = 8.8, 5.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.62, 161.58, 135.89, 133.14, 129.51, 128.51, 128.19, 126.46, 53.16, 50.68, 35.27, 33.63, 28.18.

HRMS (ESI–TOF): Calc'd. For: $C_{15}H_{16}NO_3^+$ $[(M+H)^+]$ 258.1125, found: 258.1123.

Methyl (1*R*,6*R*,7*R*)-2-(2-methoxy-2-oxoethyl)-3-oxo-7-phenyl-2azabicyclo[4.1.0]hept-4-ene-7-caboxylate (6)



Physical state: white solid;

Melting point: 130–133ºC;

Yield: 51%;

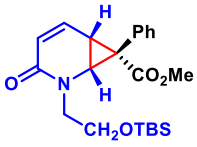
Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.28 (m, 2H), 7.25 (d, *J* = 6.8 Hz, 1H), 6.99 (dd, *J* = 7.4, 2.0 Hz, 2H), 6.73 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.67 (d, *J* = 9.9 Hz, 1H), 4.95 (d, *J* = 17.1 Hz, 1H), 3.99 (d, *J* = 9.0 Hz, 1H), 3.78 (s, 3H), 3.74 (s, 1H), 3.64 (d, *J* = 1.1 Hz, 3H), 2.98 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.21, 169.02, 161.46, 137.13, 133.16, 129.48, 128.59, 128.25, 125.86, 53.22, 52.59, 49.99, 48.57, 34.00, 28.03.

HRMS (ESI–TOF): Calc'd. For: $C_{17}H_{18}NO_5^+$ $[(M+H)^+]$ 316.1179, found: 316.1184

Methyl (1*R*,6*R*,7*R*)-2-(2-((*tert*-Butyldimethylsilyl)oxy)ethyl)-3-oxo-7-phenyl-2–azabicyclo[4.1.0]hept-4-ene-7-carboxylate (7)



Physical state: yellow oil;

Yield: 82%;

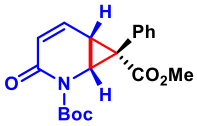
Rf **=** 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 1H), 7.20 – 7.15 (m, 2H), 6.96 (dd, *J* = 6.5, 1.8 Hz, 2H), 6.57 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.54 (d, *J* = 9.9 Hz, 1H), 4.19 (d, *J* = 8.9 Hz, 1H), 4.11 (dt, *J* = 13.6, 3.5 Hz, 1H), 3.86 (ddd, *J* = 10.5, 9.2, 3.5 Hz, 1H), 3.78 (dt, *J* = 10.8, 3.9 Hz, 1H), 3.56 (s, 3H), 3.25 (ddd, *J* = 13.5, 9.1, 4.2 Hz, 1H), 2.84 (dd, *J* = 8.9, 5.3 Hz, 1H), 0.85 (s, 9H), 0.00 (s, 6H).

^{13}C NMR (125 MHz, $CDCl_3$):δ 173.41, 161.53, 136.30, 133.37, 129.74, 128.43, 128.05, 126.49, 61.87, 53.06, 51.13, 50.47, 33.55, 28.25, 25.93, 18.28, –5.34, –5.39.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{32}NO_4Si^+$ $[(M+H)^+]$ 402.2095, found: 402.2091.

2-(*tert*-Butyl) 7-methyl (1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (8)



Physical state: white solid;

Melting point: 113–115°C;

Yield: 71%;

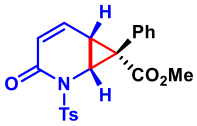
Rf = 0.6 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (dd, *J* = 5.4, 2.1 Hz, 3H), 7.10 – 7.04 (m, 2H), 6.76 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.62 (d, *J* = 9.8 Hz, 1H), 4.41 (d, *J* = 8.9 Hz, 1H), 3.65 (s, 3H), 2.93 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.60 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.69, 160.20, 152.27, 137.99, 133.26, 129.22, 128.59, 128.32, 127.16, 84.19, 53.21, 46.14, 35.48, 28.10, 26.43.

HRMS (ESI–TOF): Calc'd. For: $C_{19}H_{22}NO_5^+$ $[(M+H)^+]$ 344.1492, found: 344.1502.

Methyl (1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-tosyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (9)



Physical state: white solid;

Melting point: 175–177°C;

Yield: 75%;

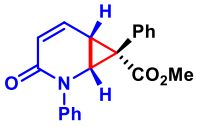
Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 – 7.94 (m, 2H), 7.35 – 7.27 (m, 5H), 7.26 – 7.19 (m, 2H), 6.81 (ddd, *J* = 9.8, 5.3, 0.7 Hz, 1H), 5.52 (d, *J* = 9.8 Hz, 1H), 4.81 (dd, *J* = 9.0, 0.7 Hz, 1H), 3.70 (s, 3H), 3.00 (dd, *J* = 9.0, 5.3 Hz, 1H), 2.43 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.54, 159.51, 145.47, 139.88, 135.74, 133.73, 129.55, 129.07, 128.56, 128.47, 128.43, 125.71, 53.48, 46.72, 35.34, 26.94, 21.82.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{20}NO_5S^+$ [(M+H)$^+$] 398.1057, found: 398.1065.

Methyl (1*R*,6*R*,7*R*)-3-oxo-2,7-diphenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (10)



Physical state: yellow solid

Melting point: 121–124°C;

Yield: 79%;

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 – 7.53 (m, 2H), 7.51 – 7.44 (m, 2H), 7.34 – 7.26 (m, 4H), 7.19 – 7.09 (m, 2H), 6.74 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.78 (d, *J* = 9.8 Hz, 1H), 4.29 (d, *J* = 8.9 Hz, 1H), 3.67 (s, 3H), 3.06 (dd, *J* = 8.9, 5.3 Hz, 1H).

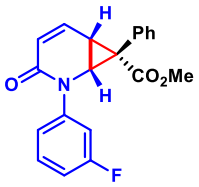
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.37, 160.90, 141.55, 136.53, 133.45, 129.48, 129.18, 128.59, 128.35, 127.54, 126.50, 124.92, 53.33, 50.63, 34.55, 28.09.

HRMS (ESI–TOF): Calc'd. For: $C_{20}H_{18}NO_3^+$ [(M+H)$^+$] 320.1281, found: 320.1276.

Methyl

(1*R*,6*R*,7*R*)-2-(3-fluorophenyl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(11)



Physical state: yellow solid

Melting point: 115–116°C;

Yield: 52%;

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.46 – 7.34 (m, 4H), 7.29 – 7.26 (m, 2H), 7.12 – 7.07 (m, 2H), 6.99 (tdd, *J* = 8.2, 2.4, 1.0 Hz, 1H), 6.74 (dd, *J* = 9.8, 5.2 Hz, 1H), 5.76 (d, *J* = 9.9 Hz, 1H), 4.25 (d, *J* = 8.9 Hz, 1H), 3.68 (s, 3H), 3.04 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 173.07, 163.50, 161.87, 160.67, 142.85, 142.78, 136.77, 133.22, 130.18, 130.11, 129.18, 128.57, 128.35, 127.23, 119.75, 119.73, 113.34, 113.20, 112.54, 112.37, 53.34, 50.06, 34.61, 27.90.

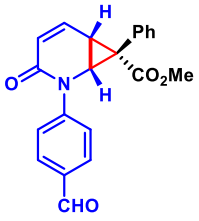
^{19}F NMR (565 MHz, $CDCl_3$): δ –111.18.

HRMS (ESI–TOF): Calc'd. For:,found: $C_{20}H_{17}FNO_3^+$ [M+H$^+$] 338.1187, found: 338.1193.

Methyl

(1*R*,6*R*,7*R*)-2-(4-formylphenyl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(12)



Physical state: yellow solid

Melting point: 125–129°C;

Yield: 87%;

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 10.03 (s, 1H), 8.01 – 7.96 (m, 2H), 7.83 – 7.77 (m, 2H), 7.28 – 7.26 (m, 3H), 7.09 – 7.04 (m, 2H), 6.78 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.80 (d, *J* = 9.8 Hz, 1H), 4.29 (d, *J* = 8.9 Hz, 1H), 3.71 (s, 3H), 3.08 (dd, *J* = 8.9, 5.3 Hz, 1H).

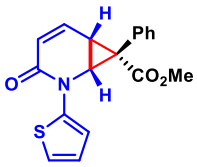
^{13}C NMR (150 MHz, $CDCl_3$): δ 191.14, 173.03, 160.77, 146.62, 137.12, 133.76, 133.15, 130.60, 129.04, 128.72, 128.53, 127.25, 124.47, 53.50, 49.56, 34.96, 27.92.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{17}NNaO_4^+$ [M+Na^+] 370.1050, found: 370.1054.

Methyl

(1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-(thiophen-2-yl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(13)



Physical state: white solid;

Melting point: 138–141°C;

Yield: 62%;

Rf = 0.2 (silica gel, PE: EtOAc = 5:1);

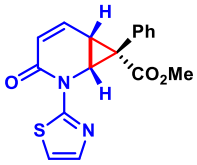
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 5.2, 1.5 Hz, 1H), 7.49 (dd, *J* = 3.3, 1.5 Hz, 1H), 7.39 – 7.36 (m, 1H), 7.23 (dt, *J* = 3.7, 2.7 Hz, 3H), 7.06 – 7.01 (m, 2H), 6.71 (ddd, *J* = 9.9, 5.3, 0.8 Hz, 1H), 5.75 (d, *J* = 9.8 Hz, 1H), 4.32 (dd, *J* = 9.0, 0.8 Hz, 1H), 3.70 (s, 3H), 3.03 (dd, *J* = 9.0, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.35, 159.93, 140.12, 136.09, 133.07, 129.26, 128.63, 128.35, 127.19, 124.85, 123.21, 114.07, 53.38, 49.75, 34.34, 28.03.

HRMS (ESI–TOF): Calc'd. For: $C_{18}H_{16}NO_3S^+$ [(M+H)$^+$] 326.0845, found: 326.0851.

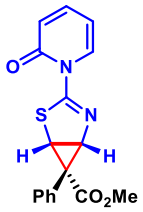
Methyl

(1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-(thiazol-2-yl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (14)



Methyl

(1*S*,5*R*,6*R*)-3-(2-oxopyridin-1(2*H*)-yl)-6-phenyl-2-thia-4-azabicyclo[3.1.0]hex-3-ene-6-carbox ylate (14′)



Physical state: black solid;

Melting point: 141–144°C;

Yield: 50% (14), 16% (14′)

Rf = 0.4 (silica gel, PE: EtOAc = 2: 1);

^{1}H NMR (400 MHz, $CDCl_3$) (14-^{1}H): δ 7.67 (d, *J* = 3.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 3H), 7.11 (d, *J* = 3.6 Hz, 1H), 6.94 (dd, *J* = 9.9, 5.3 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 5.84 (d, *J* = 9.8 Hz, 1H), 5.23 (d, *J* = 8.7 Hz, 1H), 3.71 (s, 3H), 3.13 (dd, *J* = 8.7, 5.3 Hz, 1H).

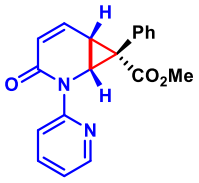
^{1}H NMR (400 MHz, $CDCl_3$) (14'-^{1}H): δ 7.89 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.24 – 7.18 (m, 6H), 6.45 (d, *J* = 9.3 Hz, 1H), 6.14 – 6.08 (m, 1H), 4.86 (d, *J* = 6.5 Hz, 1H), 4.00 (d, *J* = 6.6 Hz, 1H), 3.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) (Mixed Spectra): δ 173.46, 172.97, 161.42, 159.51, 158.99, 140.55, 138.79, 137.93, 133.33, 132.98, 128.98, 128.50, 128.34, 127.82, 127.73, 124.96, 121.88, 115.80, 107.13, 60.60, 53.38, 53.13, 46.90, 41.35, 34.47, 27.43.

HRMS (ESI–TOF): Calc'd. For: $C_{17}H_{14}N_2NaO_3S^+$ $[(M+H)^+]$ 349.0617, found: 349.0630.

Methyl

(1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-(pyridin-2-yl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (15)



Physical state: yellow solid;

Melting point: 89–90°C;

Yield: 86%;

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

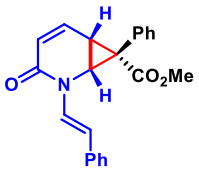
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.94 (dt, *J* = 8.4, 1.0 Hz, 1H), 7.72 (ddd, *J* = 8.4, 7.3, 2.0 Hz, 1H), 7.22 – 7.12 (m, 6H), 6.81 (ddd, *J* = 9.8, 5.4, 0.9 Hz, 1H), 5.76 (d, *J* = 9.8 Hz, 1H), 4.76 (dd, *J* = 8.8, 0.9 Hz, 1H), 3.69 (s, 3H), 3.05 (dd, *J* = 8.8, 5.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.63, 161.53, 153.05, 148.34, 137.77, 137.15, 133.63, 129.67, 128.38, 128.07, 127.09, 120.87, 120.16, 53.23, 47.82, 34.67, 27.78.

HRMS (ESI–TOF): Calc'd. For: $C_{19}H_{17}N_2O_3^+$ $[(M+H)^+]$ 321.1234, found: 321.1231.

Methyl

(1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-((*E*)-styryl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (16)



Physical state: white solid;

Melting point: 90–92°C;

Yield: 70%;

Rf = 0.2 (silica gel, PE: EtOAc = 5:1);

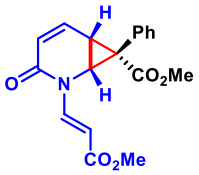
^{1}H NMR (400 MHz, $CDCl_3$):δ 8.17 (d, *J* = 14.9 Hz, 1H), 7.52 – 7.47 (m, 2H), 7.39 – 7.32 (m, 3H), 7.24 (dd, *J* = 5.3, 2.4 Hz, 3H), 7.04 – 6.99 (m, 2H), 6.80 (dd, *J* = 9.9, 5.2 Hz, 1H), 6.33 (d, *J* = 14.9 Hz, 1H), 5.77 (d, *J* = 9.9 Hz, 1H), 4.25 (d, *J* = 8.9 Hz, 1H), 3.74 (s, 3H), 3.01 (dd, *J* = 8.9, 5.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.40, 159.01, 137.16, 136.26, 132.85, 128.94, 128.67, 128.50, 127.22, 126.58, 126.30, 125.99, 113.10, 53.46, 44.82, 35.05, 27.46.

HRMS (ESI–TOF): Calc'd. For $C_{22}H_{20}NO_3^+$ [(M+H)$^+$] 346.1438, found: 346.1446.

Methyl

(1*R*,6*R*,7*R*)-2-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept–4-ene-7-carboxylate (17)



Physical state: yellow solid;

Melting point: 154–157°C;

Yield: 85%;

Rf = 0.4(silica gel, PE: EtOAc = 2:1);

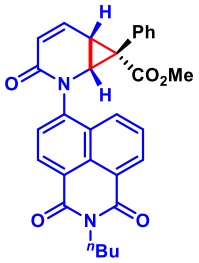
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.65 (d, *J* = 14.4 Hz, 1H), 7.28 (s, 1H), 7.26 (d, *J* = 6.3 Hz, 3H), 6.96 – 6.91 (m, 2H), 6.89 (dd, *J* = 9.9, 5.2 Hz, 1H), 5.77 (d, *J* = 10.0 Hz, 1H), 5.68 (d, *J* = 14.4 Hz, 1H), 4.09 (d, *J* = 8.7 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 3.00 (dd, *J* = 8.8, 5.3 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.57, 167.57, 158.81, 140.75, 139.19, 132.74, 128.76, 128.64, 128.43, 125.15, 101.29, 53.54, 51.78, 44.44, 36.13, 26.65.

HRMS (ESI–TOF): Calc'd. For: $C_{18}H_{17}NNaO_5^+$ [(M+Na)$^+$] 350.0999, found: 350.1007.

Methyl

(1*R*,6*R*,7*R*)-2-(2-butyl-1,3-dioxo-2,3-dihydro-1*H*-benzo[de]isoquinolin-6-yl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (18)



Physical state: yellow solid;

Melting point: 203–205°C;

Yield: 52%;

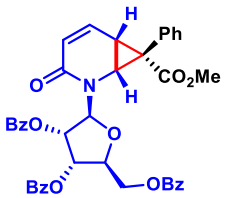
Rf = 0.3 (silica gel, PE: EtOAc = 2: 1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.72 (d, *J* = 7.8 Hz, 1H), 8.64 (d, *J* = 7.2 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.81 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.3 Hz, 1H), 7.27 (s, 2H), 7.02 (dd, *J* = 10.2, 5.3 Hz, 1H), 5.94 (d, *J* = 10.0 Hz, 1H), 4.28 (d, *J* = 8.7 Hz, 1H), 4.19 (d, *J* = 7.6 Hz, 2H), 3.59 (s, 3H), 3.18 (dd, *J* = 8.7, 5.4 Hz, 1H), 1.74 – 1.70 (m, 2H), 1.47 – 1.43 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 172.95, 164.04, 163.58, 161.48, 143.54, 138.39, 133.79, 131.72, 131.22, 129.74, 128.97, 128.66, 127.90, 127.82, 127.41, 126.59, 123.73, 122.76, 53.41, 52.09, 40.45, 35.35, 30.30, 27.70, 20.47, 13.96.

HRMS (ESI–TOF): Calc'd. For: $C_{30}H_{26}N_2NaO_5^+$ [$(M+Na)^+$] 517.1734, found: 517.1737.

(2*S*,3*S*,4*S*,5*S*)-2-((Benzoyloxy)methyl)-5-((1*R*,6*R*,7*R*)-7-(methoxycarbonyl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-en-2-yl)tetrahydrofuran-3,4-diyl dibenzoate (19)



Physical state: yellow solid;

Melting point: 91–92°C;

Yield: 62%;

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

Dr = 3:2;

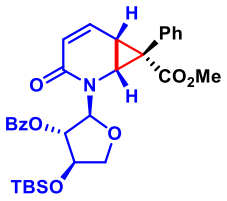
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.16 – 7.92 (m, 6H), 7.61 – 7.30 (m, 10H), 7.25 – 6.95 (m, 4H), 6.71 – 6.65 (m, 1H), 6.35 – 6.00 (m, 1H), 5.91 (dd, *J* = 9.7, 6.1 Hz, 1H), 5.70 – 5.57 (m, 1H), 4.88 – 4.34 (m, 4H), 4.25 – 4.04 (m, 1H), 3.47 (d, *J* = 4.6 Hz, 3H), 2.92 (dt, *J* = 8.7, 5.8 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.00, 172.92, 166.45, 166.30, 165.65, 165.52, 165.44, 161.95, 161.42, 138.10, 137.59, 133.87, 133.77, 133.70, 133.60, 133.45, 133.39, 133.31, 130.09, 130.06, 130.00, 129.96, 129.91, 129.76, 129.59, 129.52, 129.28, 129.02, 128.88, 128.80, 128.69, 128.59, 128.54, 128.37, 128.19, 127.99, 127.92, 126.42, 126.13, 86.43, 79.96, 79.67, 73.05, 71.85, 71.63, 71.60, 64.76, 53.18, 46.33, 44.91, 34.13, 34.06, 29.83, 27.48, 26.99.

HRMS (ESI–TOF): Calc'd. For: $C_{40}H_{34}NO_{10}^{+}$ [(M+H)$^{+}$] 688.2177, found: 688.2191.

Methyl

(1*R*,6*R*,7*R*)-2-((2*S*,3*S*,4*R*)-3-(Benzoyloxy)-4-((*tert*-butyldimethylsilyl)oxy)tetrahydrofuran-2-yl)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (20)



Physical state: yellow oil;

Yield: 87%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

Dr = 1:1;

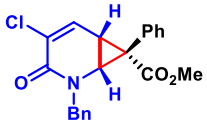
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 – 8.02 (m, 2H), 7.60 – 7.55 (m, 1H), 7.44 (d, *J* = 5.7 Hz, 2H), 7.39 – 7.27 (m, 4H), 7.23 (d, *J* = 7.3 Hz, 3H), 6.68 (dd, *J* = 9.8, 5.3 Hz, 1H), 6.07 (s, 1H), 5.59 (d, *J* = 9.8 Hz, 1H), 5.24 (s, 1H), 4.43 (d, *J* = 9.0 Hz, 1H), 4.40 – 4.35 (m, 1H), 4.27 – 4.18 (m, 2H), 3.65 (s, 3H), 2.90 (dd, *J* = 9.0, 5.4 Hz, 1H), 0.94 (s, 9H), 0.19 (s, 3H) ,0.18 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.57, 165.26, 161.33, 136.76, 133.66, 133.51, 130.17, 130.01, 129.50, 128.86, 128.54, 128.36, 127.89, 127.81, 126.28, 90.13, 82.99, 76.83, 74.52, 53.05, 52.55, 45.10, 33.43, 27.83, 25.72, 18.04, –4.63, –5.22.

HRMS (ESI–TOF): Calc'd. For: $C_{31}H_{38}NO_7Si^{+}$ [(M+H)$^{+}$] 564.2412, found: 564.2416.

Methyl

(1*R*,6*R*,7*R*)-2-Benzyl-4-chloro-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (21)



Physical state: white solid;

Melting point: 179–182°C;

Yield: 55%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (s, 2H), 7.24 (d, *J* = 2.6 Hz, 2H), 7.22 – 7.12 (m, 4H), 6.86 – 6.80 (m, 2H), 6.70 (d, *J* = 5.8 Hz, 1H), 5.32 (d, *J* = 14.5 Hz, 1H), 4.14 (d, *J* = 14.5 Hz, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 3.52 (s, 3H), 2.79 (dd, *J* = 9.1, 5.9 Hz, 1H).

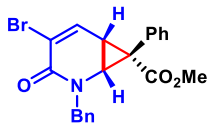
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.17, 157.47, 135.70, 133.34, 132.56, 130.17, 129.06, 128.85, 128.77, 128.67, 128.48, 128.31, 53.33, 51.98, 48.59, 33.84, 28.21.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{18}ClNNaO_3^+$ $[(M+Na)^+]$ 390.0867, found: 390.0864.

Methyl

(1*R*,6*R*,7*R*)-2-benzyl-4-bromo-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(22)



Physical state: white solid;

Melting point: 122–124°C;

Yield: 98%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.26 (m, 8H), 7.09 (dd, *J* = 5.8, 0.7 Hz, 1H), 6.99 – 6.89 (m, 2H), 5.44 (d, *J* = 14.5 Hz, 1H), 4.27 (d, *J* = 14.5 Hz, 1H), 3.95 (d, *J* = 8.9 Hz, 1H), 3.65 (s, 3H), 2.87 (dd, *J* = 9.0, 5.8 Hz, 1H).

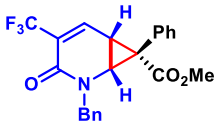
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.03, 157.14, 137.16, 135.66, 133.29, 128.98, 128.77, 128.67, 128.60, 128.38, 128.21, 121.41, 53.27, 52.19, 48.79, 33.74, 29.50.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{19}BrNO_3^+$ $[(M+H)^+]$ 412.0543, found: 412.0541.

Methyl

(1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-4-(trifluoromethyl)-2-azabicyclo[4.1.0]hept-4-ene-7-car

boxylate (23)



Physical state: colourless oil;

Yield: 86%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 3.0 Hz, 5H), 7.32 – 7.27 (m, 3H), 7.22 (d, *J* = 5.6 Hz, 1H), 6.88 (dd, *J* = 6.6, 3.0 Hz, 2H), 5.45 (d, *J* = 14.5 Hz, 1H), 4.25 (d, *J* = 14.5 Hz, 1H), 3.95 (d, *J* = 8.7 Hz, 1H), 3.67 (s, 3H), 2.98 (dd, *J* = 8.6, 5.8 Hz, 1H).

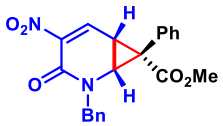
^{13}C NMR (100 MHz, $CDCl_3$): δ 150.25, 136.28, 135.54, 130.28, 129.83, 129.01, 127.64, 126.57, 116.22, 107.88, 47.32, 38.59, 34.98, 29.83, 20.84.

^{19}F NMR (375 MHz, $CDCl_3$): δ –65.97.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{19}F_3NO_3^+$ $[(M+H)^+]$ 402.1312, found: 402.1318.

Methyl

(1*R*,6*R*,7*R*)-2-benzyl-4-nitro-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (24)



Physical state: white solid;

Melting point: 301–304°C;

Yield: 54%;

Rf = 0.2 (silica gel, PE: EtOAc = 4:1);

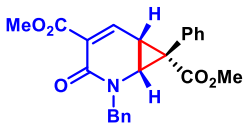
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (t, *J* = 2.7 Hz, 5H), 7.33 (td, *J* = 5.2, 1.8 Hz, 4H), 6.91 (dd, *J* = 4.1, 2.0 Hz, 2H), 5.41 (d, *J* = 14.5 Hz, 1H), 4.32 (d, *J* = 14.5 Hz, 1H), 3.98 (d, *J* = 8.6 Hz, 1H), 3.68 (s, 3H), 3.02 (dd, *J* = 8.5, 6.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$):δ 172.33, 153.53, 145.56, 134.95, 134.85, 133.10, 129.20, 129.07, 129.01, 128.81, 128.61, 127.57, 53.69, 51.34, 48.31, 36.16, 25.87.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{19}N_2O_5^+$ $[(M+H)^+]$ 379.1288, found: 379.1298.

Dimethyl

(1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-4,7-dicarboxylate (25)



Physical state: white solid;

Melting point: 122–124°C;

Yield: 52%

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

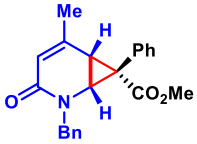
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 5.6 Hz, 1H), 7.39 – 7.32 (m, 5H), 7.28 (dd, *J* = 4.9, 1.9 Hz, 3H), 6.92 (dd, *J* = 6.6, 2.9 Hz, 2H), 5.48 (d, *J* = 14.6 Hz, 1H), 4.22 (d, *J* = 14.6 Hz, 1H), 3.95 (d, *J* = 8.6 Hz, 1H), 3.69 (s, 3H), 3.65 (s, 3H), 2.98 (dd, *J* = 8.6, 5.7 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.88, 164.59, 158.00, 143.28, 135.87, 133.18, 129.37, 128.97, 128.67, 128.61, 128.57, 128.51, 128.13, 53.35, 52.50, 50.94, 48.91, 35.76, 27.36.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{22}NO_5^+$ $[(M+H)^+]$ 392.1492, found: 392.1501.

Methyl

(1*R*,6*R*,7*R*)-2-benzyl-5-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (26)



Physical state: yellow solid;

Melting point: 109–111°C;

Yield: 58%;

Rf = 0.5 (silica gel, PE: EtOAc = 2:1);

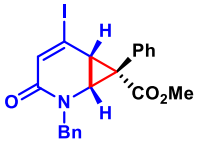
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, *J* = 3.8 Hz, 3H), 7.34 – 7.29 (m, 2H), 7.29 (d, *J* = 1.7 Hz, 1H), 7.28 – 7.25 (m, 2H), 7.00 – 6.95 (m, 2H), 5.58 (d, *J* = 14.7 Hz, 1H), 5.53 – 5.50 (m, 1H), 4.13 (d, *J* = 14.7 Hz, 1H), 3.85 (d, *J* = 8.9 Hz, 1H), 3.63 (s, 3H), 2.74 (d, *J* = 8.9 Hz, 1H), 2.08 (d, *J* = 1.4 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.64, 162.19, 146.65, 136.48, 131.88, 130.03, 128.88, 128.62, 128.29, 128.27, 127.86, 122.42, 53.14, 50.22, 48.65, 33.78, 32.12, 23.53.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{22}NO_3^+$ [$(M+H)^+$] 348.1594, found: 348.1593.

Methyl

(1*R*,6*R*,7*R*)-2-benzyl-5-iodo-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (27)



Physical state: white solid;

Melting point: 139–140°C;

Yield: 60%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

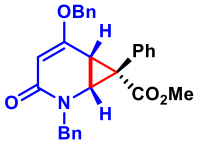
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.31 (m, 8H), 7.14 – 7.10 (m, 2H), 6.39 (s, 1H), 5.50 (d, *J* = 14.6 Hz, 1H), 4.16 (d, *J* = 14.6 Hz, 1H), 3.78 (dd, *J* = 9.2, 1.4 Hz, 1H), 3.65 (d, *J* = 1.4 Hz, 3H), 3.32 (d, *J* = 9.1 Hz, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 172.71, 159.32, 135.70, 135.26, 132.25, 129.00, 128.73, 128.64, 128.37, 128.15, 107.86, 53.37, 50.43, 49.95, 38.72, 35.14.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{19}INO_3^+$ [$(M+H)^+$] 460.0404, found: 460.0410.

Methyl

(1*R*,6*R*,7*R*)-2-benzyl-5-(benzyloxy)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (28)



Physical state: yellow solid;

Melting point: 135–137°C;

Yield: 54%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

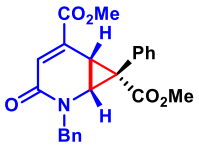
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 – 7.39 (m, 5H), 7.37 (d, *J* = 4.3 Hz, 4H), 7.35 – 7.26 (m, 4H), 7.08 – 7.02 (m, 2H), 5.55 (d, *J* = 14.8 Hz, 1H), 5.00 (s, 1H), 4.83 (d, *J* = 11.3 Hz, 1H), 4.72 (d, *J* = 11.3 Hz, 1H), 4.17 (d, *J* = 14.8 Hz, 1H), 3.88 (d, *J* = 9.5 Hz, 1H), 3.61 (s, 3H), 2.98 (dd, *J* = 9.5, 1.2 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.97, 164.35, 163.22, 136.69, 134.97, 131.70, 130.14, 128.96, 128.93, 128.91, 128.68, 128.42, 128.31, 127.89, 97.28, 71.25, 53.17, 50.03, 47.22, 33.09, 29.87.

HRMS (ESI–TOF): Calc'd. For: $C_{28}H_{26}NO_4^+$ $[(M+H)^+]$ 440.1856, found: 440.1860.

Dimethyl

(1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-5,7-dicarboxylate (29)



Physical state: yellow solid;

Melting point: 146–148°C;

Yield: 84%;

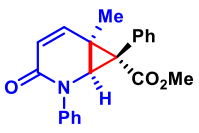
Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.26 (m, 7H), 7.25 (d, *J* = 2.0 Hz, 1H), 6.89 (dd, *J* = 6.5, 3.0 Hz, 2H), 6.46 (s, 1H), 5.52 (d, *J* = 14.5 Hz, 1H), 4.22 (d, *J* = 14.6 Hz, 1H), 3.96 (d, *J* = 9.1 Hz, 1H), 3.89 (s, 3H), 3.66 (s, 3H), 3.26 (d, *J* = 9.1 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.98, 165.51, 161.17, 137.18, 135.69, 132.48, 130.69, 129.29, 129.07, 128.86, 128.48, 128.45, 128.24, 53.32, 53.09, 50.79, 48.24, 33.49, 27.06.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{22}NO_5^+$ $[(M+H)^+]$ 392.1492, found: 392.1495.

Methyl (7*S*)-6-methyl-3-oxo-2,7-diphenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (30)



Physical state: white solid;

Melting point: 69–72°C;

Yield: 24%;

Rf = 0.6 (silica gel, PE: EtOAc = 2:1);

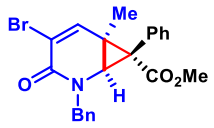
^{1}H NMR (600 MHz, $CDCl_3$):δ 7.71 (d, *J* = 7.4 Hz, 2H), 7.50 – 7.45 (m, 2H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.20 (m, 3H), 7.16 – 7.11 (m, 2H), 6.45 (dd, *J* = 9.9, 1.3 Hz, 1H), 5.65 (d, *J* = 9.8 Hz, 1H), 4.31 (s, 1H), 3.71 (s, 3H), 1.59 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 171.10, 160.59, 141.79, 141.64, 132.96, 131.52, 129.05, 128.51, 128.10, 126.11, 125.99, 124.18, 53.08, 52.91, 39.40, 31.39, 18.41.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{20}NO_3^+$ [(M+H)$^+$] 334.1438, found: 334.1436.

Methyl

(7*S*)-2-benzyl-4-bromo-6-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (31)



Physical state: white solid;

Melting point: 162–164ºC;

Yield: 57%;

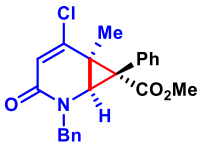
Rf =0.4 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 – 7.34 (m, 5H), 7.24 (dd, *J* = 4.8, 1.9 Hz, 3H), 6.84 (dd, *J* = 6.3, 2.5 Hz, 3H), 5.25 (d, *J* = 14.3 Hz, 1H), 4.44 (d, *J* = 14.4 Hz, 1H), 4.01 (d, *J* = 1.2 Hz, 1H), 3.64 (s, 3H), 1.47 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 170.90, 156.90, 142.29, 135.93, 132.92, 130.90, 129.02, 128.58, 128.27, 128.14, 120.18, 53.09, 52.50, 51.47, 38.79, 33.07, 17.95.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{21}BrNO_3^+$ [(M+H)$^+$] 426.0699, found: 426.0715.

Methyl (7*S*)-2-benzyl-5-chloro-6-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (32)



Physical state: yellow solid;

Melting point: 236–237°C;

Yield: 64%;

Rf = 0.4 (silica gel, PE: EtOAc = 10:1);

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.43 – 7.28 (m, 6H), 7.26 – 7.21 (m, 2H), 7.07 – 6.98 (m, 2H), 5.75 (s, 1H), 5.33 (d, *J* = 14.5 Hz, 1H), 4.34 (d, *J* = 14.5 Hz, 1H), 3.96 (s, 1H), 3.65 (s, 3H), 1.53 (s, 3H).

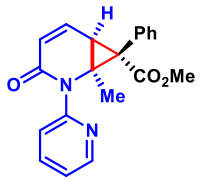
^{13}C NMR (125 MHz, $CDCl_3$): δ 170.48, 160.33, 147.66, 136.06, 131.51, 130.76, 129.05, 128.76, 128.64, 128.52, 128.18, 123.69, 53.23, 51.36, 50.42, 39.47, 34.28, 17.19.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{20}ClNNaO_3^+$ [(M+Na)$^+$] 404.1024, found: 404.1036.

Methyl

(7*R*)-1-methyl-3-oxo-7-phenyl-2-(pyridin-2-yl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(37)



Physical state: yellow solid;

Melting point: 165–166°C;

Yield: 51%;

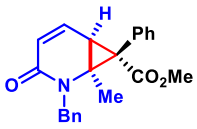
Rf = 0.4 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (ddd, *J* = 4.9, 2.0, 0.9 Hz, 1H), 7.78 – 7.67 (m, 3H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.14 (m, 4H), 6.79 (dd, *J* = 9.8, 5.6 Hz, 1H), 5.71 (d, *J* = 9.8 Hz, 1H), 3.69 (s, 3H), 3.00 (d, *J* = 5.6 Hz, 1H), 1.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.97, 162.13, 151.57, 148.39, 138.19, 136.94, 133.76, 131.42, 128.23, 127.83, 125.28, 124.49, 121.76, 53.27, 50.44, 41.86, 31.43, 20.74.

HRMS (ESI–TOF): Calc'd. For: $C_{20}H_{19}N_2O_3^+$ [(M+H)$^+$] 335.1390, found: 335.1402.

Methyl (7*R*)-2-benzyl-1-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (34)



Physical state: yellow solid;

Melting point: 76–79°C;

Yield: 30%;

Rf = 0.6 (silica gel, PE: EtOAc = 2:1);

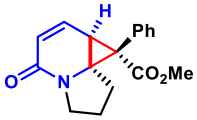
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 – 7.27 (m, 6H), 7.25 (s, 2H), 7.13 (dd, *J* = 8.0, 1.7 Hz, 2H), 6.77 (dd, *J* = 9.8, 5.7 Hz, 1H), 5.71 (d, *J* = 9.8 Hz, 1H), 5.42 (d, *J* = 15.7 Hz, 1H), 4.26 (d, *J* = 15.7 Hz, 1H), 3.66 (s, 3H), 2.93 (d, *J* = 5.7 Hz, 1H), 1.51 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.60, 162.76, 138.74, 136.49, 133.31, 130.95, 129.06, 128.67, 128.41, 128.25, 126.73, 125.04, 53.23, 52.69, 49.56, 41.56, 31.80, 20.27.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{22}NO_3^+$ $[(M+H)^+]$ 348.1594, found: 348.1585.

Methyl

(8*R*)-5-oxo-8-phenyl-2,3,7a,8-tetrahydro-1*H*,5*H*-cyclopropa[h]indolizine-8-carboxylate (35)



Physical state: white solid;

Melting point: 282–285°C;

Yield: 38%;

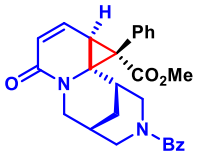
Rf = 0.2 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 9.3 Hz, 1H), 7.38 – 7.28 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 9.4 Hz, 1H), 4.81 (s, 1H), 4.16 (t, *J* = 7.5 Hz, 2H), 3.76 (s, 3H), 3.15 – 2.99 (m, 2H), 2.20 (tt, *J* = 7.3, 4.6 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.39, 161.74, 148.65, 140.81, 137.39, 129.03, 128.22, 127.78, 117.96, 111.89, 52.68, 51.95, 49.29, 30.82, 20.97.

HRMS (ESI–TOF): Calc'd. For: $C_{17}H_{18}NO_3^+$ [(M+H)$^+$] 284.1281, found: 284.1282.

Methyl (2*R*,6*R*,7*R*)-4-benzoyl-10-oxo-7-phenyl-1,2,3,4,5,6,7a,10-octahydro-7*H*-2,6-methanocyclopropa[2,3]pyrido[1,2-a][1,5]diazocine-7-carboxylate (36)



Physical state:pink solid;

Melting point: 155–156°C;

Yield: 56%;

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

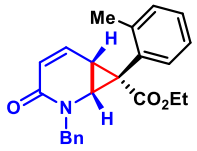
Dr = 1:1

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 – 7.33 (m, 3H), 7.28 (dd, *J* = 5.7, 2.3 Hz, 3H), 7.26 – 7.22 (m, 2H), 7.15 – 7.05 (m, 2H), 6.78 (s, 1H), 5.70 (d, *J* = 9.8 Hz, 1H), 4.99 (d, *J* = 13.2 Hz, 1H), 4.52 (d, *J* = 14.0 Hz, 1H), 3.85 (d, *J* = 12.8 Hz, 1H), 3.66 (s, 3H), 3.37 – 3.26 (m, 1H), 3.18 (d, *J* = 12.6 Hz, 1H), 3.07 (s, 1H), 2.27 (dt, *J* = 12.8, 2.6 Hz, 1H), 2.11 – 2.00 (m, 2H), 1.96 (s, 1H), 1.32 – 1.24 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 171.62, 171.25, 161.28, 135.87, 135.33, 133.29, 130.15, 129.42, 128.49, 128.35, 128.29, 127.33, 125.30, 56.09, 53.33, 53.13, 45.42, 44.48, 42.76, 30.58, 30.01, 29.80, 29.76, 28.20.

HRMS (ESI–TOF): Calc'd. For: $C_{27}H_{27}N_2O_4^+$ [(M+H)$^+$] 443.1965, found: 443.1963.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-(o-tolyl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (37)



Physical state: yellow solid;

Melting point: 171–172°C;

Yield: 46%;

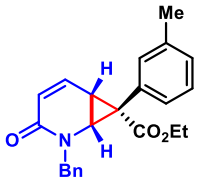
Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 4.4 Hz, 4H), 7.35 – 7.31 (m, 1H), 7.21 – 7.14 (m, 2H), 7.10 (td, *J* = 7.4, 1.9 Hz, 1H), 6.87 (dd, *J* = 7.7, 1.4 Hz, 1H), 6.58 (ddd, *J* = 9.9, 5.2, 0.8 Hz, 1H), 5.69 (d, *J* = 14.6 Hz, 1H), 5.63 (d, *J* = 9.9 Hz, 1H), 4.24 – 4.16 (m, 2H), 4.03 (dd, *J* = 10.8, 7.1 Hz, 1H), 3.86 (dd, *J* = 8.9, 0.8 Hz, 1H), 2.95 (dd, *J* = 8.9, 5.2 Hz, 1H), 2.18 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.88, 161.73, 139.16, 136.23, 134.53, 131.90, 130.80, 128.95, 128.74, 128.42, 128.33, 127.99, 126.34, 125.87, 61.93, 50.77, 48.74, 31.75, 28.96, 19.66, 14.28.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{24}NO_3^+$ $[M+H]^+$ 362.1756, found: 362.1754.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-(*m*-tolyl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (38)



Physical state: yellow solid;

Melting point: 121–123°C;

Yield: 88%;

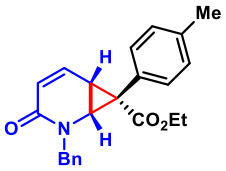
Rf = 0.6 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.27 (m, 5H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.04 (ddt, *J* = 7.6, 1.8, 0.9 Hz, 1H), 6.79 – 6.72 (m, 2H), 6.64 (ddd, *J* = 9.9, 5.3, 0.7 Hz, 1H), 5.69 (d, *J* = 9.9 Hz, 1H), 5.47 (d, *J* = 14.6 Hz, 1H), 4.20 (d, *J* = 14.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.85 (dd, *J* = 8.9, 0.7 Hz, 1H), 2.85 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.28 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.96, 161.50, 137.78, 136.46, 136.26, 133.87, 130.25, 129.47, 128.92, 128.84, 128.40, 128.22, 127.92, 126.28, 61.88, 50.58, 48.49, 33.99, 27.80, 21.56, 14.25.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{24}NO_3^+$ $[(M+H)^+]$ 362.1751, found: 362.1750.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-(*p*-tolyl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (39)



Physical state: yellow solid;

Melting point: 114–115°C;

Yield: 76%

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 5H), 7.06 (d, *J* = 7.7 Hz, 2H), 6.83 (d, *J* = 8.1 Hz, 2H), 6.64 (ddd, *J* = 9.8, 5.3, 0.8 Hz, 1H), 5.70 (d, *J* = 9.9 Hz, 1H), 5.50 (d, *J* = 14.6 Hz, 1H), 4.17 (d, *J* = 14.7 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.85 (dd, *J* = 8.8, 0.7 Hz, 1H), 2.85 (dd, *J* = 8.8, 5.3 Hz, 1H), 2.30 (s, 3H), 1.13 (t, *J* = 7.1 Hz, 3H).

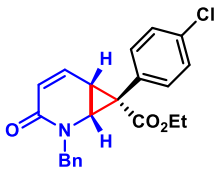
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.07, 161.54, 137.68, 136.44, 136.29, 133.07, 129.22, 128.91, 128.41, 127.93, 126.47, 126.42, 61.87, 50.59, 48.49, 33.75, 27.92, 21.36, 14.26.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{24}NO_3^+$ $[(M+H)^+]$ 362.1751, found: 362.1752.

Ethyl

(1*R*,6*R*,7*R*)-2-benzyl-7-(4-chlorophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(40)



Physical state: yellow solid;

Melting point: 75–78°C;

Yield: 57%

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.31 (m, 5H), 7.25 – 7.19 (m, 2H), 6.85 – 6.78 (m, 2H), 6.64 (ddd, *J* = 9.8, 5.3, 0.8 Hz, 1H), 5.74 (d, *J* = 9.9 Hz, 1H), 5.38 (d, *J* = 14.6 Hz, 1H), 4.26 (d, *J* = 14.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.87 (dd, *J* = 8.9, 0.8 Hz, 1H), 2.87 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).

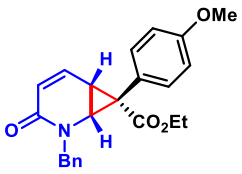
^{13}C NMR (100 MHz, $CDCl_3$): δ 172.41, 161.26, 136.18, 136.05, 134.58, 134.00, 128.98, 128.77, 128.50, 128.23, 128.09, 126.72, 62.09, 50.67, 48.67, 33.34, 27.83, 14.21.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{21}ClNO_3^+$ [$(M+H)^+$] 382.1204, found: 382.1206.

Ethyl

(1*R*,6*R*,7*R*)-2-benzyl-7-(4-methoxyphenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(41)



Physical state: white solid;

Melting point: 125–126°C;

Yield: 90%

Rf = 0.3 (silica gel, PE: EtOAc = 3:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 5H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.64 (ddd, *J* = 9.9, 5.3, 0.7 Hz, 1H), 5.72 (d, *J* = 9.8 Hz, 1H), 5.48 (d, *J* = 14.6 Hz, 1H), 4.18 (d, *J* = 14.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.84 (dd, *J* = 8.9, 0.8 Hz, 1H), 3.77 (s, 3H), 2.84 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).

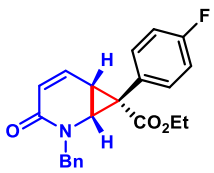
^{13}C NMR (125 MHz, $CDCl_3$): δ 173.23, 161.55, 159.05, 136.42, 136.26, 134.36, 128.92, 128.41, 127.95, 126.49, 121.37, 113.92, 61.88, 55.18, 50.60, 48.58, 33.39, 28.09, 14.25.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{24}NO_4^+$ [$(M+H)^+$] 378.1700, found: 378.1722.

Ethyl

(1*R*,6*R*,7*R*)-2-benzyl-7-(4-fluorophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(42)



Physical state: blue solid;

Melting point: 80–82°C;

Yield: 60%

Rf = 0.3 (silica gel, PE: EtOAc = 2:1);

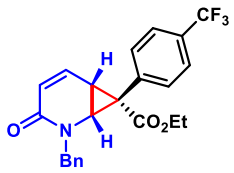
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.31 (m, 5H), 6.96 – 6.90 (m, 2H), 6.90 – 6.84 (m, 2H), 6.65 (ddd, *J* = 9.8, 5.3, 0.8 Hz, 1H), 5.73 (d, *J* = 9.9 Hz, 1H), 5.41 (d, *J* = 14.6 Hz, 1H), 4.24 (d, *J* = 14.5 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.87 (dd, *J* = 8.9, 0.8 Hz, 1H), 2.87 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.13 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.62, 163.42, 161.29, 160.96, 136.25, 136.07, 135.00, 134.92, 128.93, 128.44, 128.03, 126.63, 125.43, 125.39, 115.64, 115.43, 61.99, 50.62, 48.64, 33.22, 27.88, 14.16.

^{19}F NMR (470 MHz, CDCl3): δ –113.45.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{21}FNO_3^+$ [$(M+H)^+$] 366.1500, found: 366.1498.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-(4-(trifluoromethyl)phenyl)-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (43)



Physical state: yellow solid;

Melting point: 119–121°C;

Yield: 42%;

Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

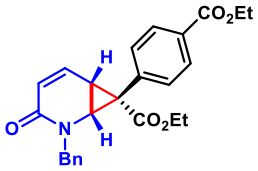
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.32 (m, 5H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.67 (dd, *J* = 9.9, 5.2 Hz, 1H), 5.73 (d, *J* = 9.9 Hz, 1H), 5.36 (d, *J* = 14.5 Hz, 1H), 4.33 (d, *J* = 14.6 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 8.8 Hz, 1H), 2.91 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.06, 161.16, 136.09, 135.99, 133.98, 133.64, 130.22, 129.06, 128.59, 128.22, 126.81, 125.45, 125.42, 62.24, 50.76, 48.73, 33.61, 27.73, 14.22.

^{19}F NMR (375 MHz, CDCl3): δ –62.60.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{20}F_3NNaO_3^+$ [$(M+H)^+$] 438.1287, found: 438.1283.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-7-(4-(ethoxycarbonyl)phenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (44)



Physical state: yellow oil;

Yield: 38%;

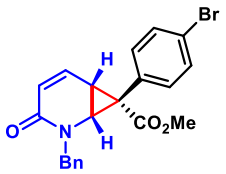
Rf = 0.1 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 – 7.90 (m, 2H), 7.42 – 7.30 (m, 5H), 7.04 – 6.94 (m, 2H), 6.66 (ddd, *J* = 9.8, 5.3, 0.8 Hz, 1H), 5.70 (d, *J* = 9.9 Hz, 1H), 5.41 (d, *J* = 14.6 Hz, 1H), 4.36 (qd, *J* = 7.2, 1.1 Hz, 2H), 4.27 (d, *J* = 14.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.91 (dd, *J* = 8.8, 0.7 Hz, 1H), 2.90 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.11 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.22, 166.32, 161.20, 136.18, 136.06, 134.88, 133.30, 130.08, 129.64, 129.01, 128.52, 128.13, 126.68, 62.17, 61.16, 50.67, 48.72, 33.82, 27.84, 14.47, 14.20.

HRMS (ESI–TOF): Calc'd. For: $C_{25}H_{26}NO_5^+$ [$(M+H)^+$] 420.1805, found: 420.1795.

Methyl (1*R*,6*R*,7*R*)-2-benzyl-7-(4-bromophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (45)



Physical state: yellow solid;

Melting point: 121–122°C;

Yield: 62%;

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 6.6 Hz, 2H), 7.38 – 7.29 (m, 5H), 6.81 – 6.73 (m, 2H), 6.63 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.75 (d, *J* = 9.9 Hz, 1H), 5.41 (d, *J* = 14.6 Hz, 1H), 4.24 (d, *J* = 14.6 Hz, 1H), 3.89 (d, *J* = 8.9 Hz, 1H), 3.63 (s, 3H), 2.88 (dd, *J* = 8.9, 5.3 Hz, 1H).

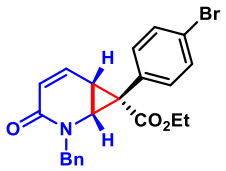
^{13}C NMR (100 MHz, $CDCl_3$): δ 172.91, 161.24, 136.08, 136.00, 134.94, 131.84, 129.01, 128.68, 128.49, 128.12, 126.90, 122.51, 53.25, 50.70, 48.85, 33.33, 28.04.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{19}BrNO_3^+$ $[(M+H)^+]$ 412.0543, found: 412,0553.

Ethyl

(1*R*,6*R*,7*R*)-2-benzyl-7-(4-bromophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(46)



Physical state: yellow solid ;

Melting point: 103–105°C;

Yield: 56%;

Rf = 0.2 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (t, *J* = 3.9 Hz, 7H), 6.75 (d, *J* = 8.4 Hz, 2H), 6.64 (dd, *J* = 9.9, 5.2 Hz, 1H), 5.74 (d, *J* = 9.9 Hz, 1H), 5.37 (d, *J* = 14.6 Hz, 1H), 4.26 (d, *J* = 14.6 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.87 (d, *J* = 8.9 Hz, 1H), 2.87 (dd, *J* = 8.8, 5.3 Hz, 1H), 1.13 (t, *J* = 7.0 Hz, 3H).

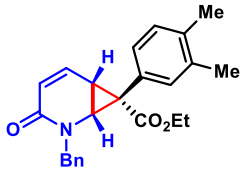
^{13}C NMR (125 MHz, $CDCl_3$): δ 172.34, 161.27, 136.16, 136.07, 134.91, 131.74, 129.01, 128.80, 128.55, 128.13, 126.77, 122.35, 62.13, 50.72, 48.67, 33.45, 27.80, 14.23.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{21}BrNO_3^+$ $[(M+H)^+]$ 426.0699, found: 426.0699.

Ethyl

(1*R*,6*R*,7*R*)-2-benzyl-7-(3,4-dimethylphenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxyla

te (47)



Physical state: white solid;

Melting point: 111–113°C;

Yield: 32%;

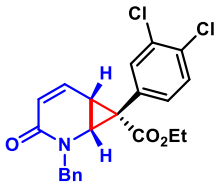
Rf = 0.6 (silica gel, PE: EtOAc =2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.29 (m, 5H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.69 (d, *J* = 7.4 Hz, 2H), 6.63 (ddd, *J* = 9.9, 5.3, 0.7 Hz, 1H), 5.69 (d, *J* = 9.8 Hz, 1H), 5.48 (d, *J* = 14.7 Hz, 1H), 4.17 (d, *J* = 14.7 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.83 (dd, *J* = 8.8, 0.7 Hz, 1H), 2.83 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.19 (s, 3H), 2.17 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.15, 161.60, 136.51, 136.42, 136.36, 136.29, 134.31, 130.55, 129.70, 128.90, 128.36, 127.89, 126.74, 126.26, 61.84, 50.55, 48.46, 33.76, 27.88, 19.99, 19.68, 14.30.

HRMS (ESI–TOF): Calc'd. For: $C_{24}H_{26}NO_3^+$ $[(M+H)^+]$ 376.1907, found: 376.1915.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-7-(3,4-dichlorophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (48)



Physical state: yellow oil;

Yield: 42%;

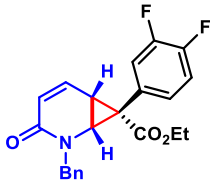
Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 4.9 Hz, 5H), 7.30 (d, *J* = 8.3 Hz, 1H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.72 – 6.62 (m, 2H), 5.79 (d, *J* = 9.9 Hz, 1H), 5.32 – 5.28 (m, 1H), 4.33 (d, *J* = 14.5 Hz, 1H), 4.10 (qd, *J* = 7.1, 1.4 Hz, 2H), 3.89 (d, *J* = 8.9 Hz, 1H), 2.88 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.89, 161.13, 135.95, 135.89, 135.27, 132.52, 132.39, 130.53, 130.06, 129.11, 128.63, 128.24, 127.08, 62.30, 50.80, 48.86, 33.15, 27.77, 14.25.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{20}Cl_2NO_3^+$ [$(M+H)^+$] 416.0815, found: 416.0818.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-7-(3,4-difluorophenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (49)



Physical state:white solid;

Melting point: 114–115°C;

Yield: 55%;

Rf = 0.3(silica gel, PE: EtOAc = 5:1);

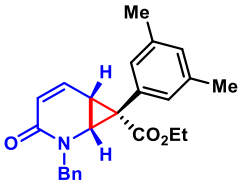
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 – 7.32 (m, 5H), 7.02 (dt, *J* = 10.1, 8.3 Hz, 1H), 6.71 – 6.55 (m, 3H), 5.78 (d, *J* = 9.9 Hz, 1H), 5.30 (d, *J* = 14.5 Hz, 1H), 4.33 (d, *J* = 14.5 Hz, 1H), 4.10 (qd, *J* = 7.1, 1.0 Hz, 2H), 3.88 (d, *J* = 9.1 Hz, 1H), 2.87 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.13, 161.18, 136.01, 135.98, 129.56, 129.50, 129.08, 128.62, 128.23, 126.99, 126.61, 122.38, 122.21, 117.43, 117.26, 62.23, 50.81, 48.90, 33.19, 27.86, 14.22.

^{19}F NMR (375 MHz, CDCl3): δ –136.92, –137.78.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{20}F_2NO_3^+$ [$(M+H)^+$] 384.1406, found: 384.1392.

Ethyl (1*R*,6*R*,7*R*)-2-benzyl-7-(3,5-dimethylphenyl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (50)



Physical state: yellow solid;

Melting point: 82–85°C;

Yield: 54%;

Rf = 0.5 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 5H), 6.86 (d, *J* = 1.7 Hz, 1H), 6.63 (ddd, *J* = 9.9, 5.3, 0.7 Hz, 1H), 6.55 (d, *J* = 1.6 Hz, 2H), 5.70 (d, *J* = 9.8 Hz, 1H), 5.44 (d, *J* = 14.6 Hz, 1H), 4.21 (d, *J* = 14.6 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.84 (dd, *J* = 8.9, 0.7 Hz, 1H), 2.83 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.23 (s, 6H), 1.15 (t, *J* = 7.1 Hz, 3H).

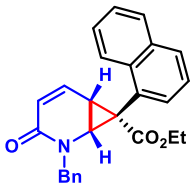
^{13}C NMR (100 MHz, $CDCl_3$): δ 173.06, 161.59, 137.56, 136.51, 136.31, 130.94, 129.84, 129.30, 128.93, 128.42, 127.91, 126.18, 61.86, 50.61, 48.50, 33.98, 27.75, 21.45, 14.30.

HRMS (ESI–TOF): Calc'd. For: $C_{24}H_{26}NO_3^+$ $[(M+H)^+]$ 376.1907, found: 376.1902.

Ethyl

(1*R*,6*R*,7*R*)-2-benzyl-7-(naphthalen-1-yl)-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate

(51)



Physical state: yellow solid;

Melting point: 122–123°C;

Yield: 66%;

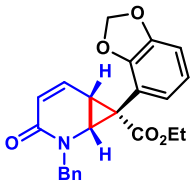
Rf = 0.3 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.33 (m, 8H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.36 (dd, *J* = 9.9, 5.1 Hz, 1H), 5.67 (d, *J* = 14.5 Hz, 1H), 5.33 (d, *J* = 9.9 Hz, 1H), 4.32 (d, *J* = 14.5 Hz, 1H), 4.11 (ddd, *J* = 10.5, 7.1, 3.6 Hz, 1H), 3.99 (t, *J* = 8.1 Hz, 2H), 3.20 (dd, *J* = 8.9, 5.2 Hz, 1H), 0.99 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$):δ 173.16, 161.87, 136.29, 135.46, 134.23, 133.40, 131.08, 129.25, 129.13, 129.03, 128.51, 128.10, 126.56, 125.68, 125.23, 125.18, 123.78, 61.98, 50.87, 48.83, 30.87, 29.25, 14.15.

HRMS (ESI–TOF): Calc'd. For: $C_{26}H_{24}NO_3^+$ [(M+H)$^+$] 398.1751, found: 398.1748.

Ethyl (1*R*,6*R*,7*R*)-7-(benzo[d][1,3]dioxol-4-yl)-2-benzyl-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (52)



Physical state: red solid;

Melting point: 158–161°C;

Yield: 75%;

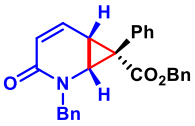
Rf = 0.2 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.30 (m, 5H), 6.69 (d, *J* = 8.6 Hz, 1H), 6.67 – 6.61 (m, 1H), 6.42 – 6.35 (m, 2H), 5.94 (s, 2H), 5.77 (d, *J* = 9.8 Hz, 1H), 5.46 (d, *J* = 14.6 Hz, 1H), 4.18 (d, *J* = 14.6 Hz, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 3.83 (dd, *J* = 8.8, 0.7 Hz, 1H), 2.83 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.15 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.98, 161.61, 147.50, 147.34, 136.38, 136.19, 128.97, 128.42, 128.01, 127.00, 126.58, 113.28, 108.35, 101.27, 61.99, 50.68, 48.74, 33.76, 28.93, 28.08, 14.29.

HRMS (ESI–TOF): Calc'd. For: $C_{23}H_{22}NO_5^+$ [(M+H)$^+$] 392.1492, found: 392,1497.

Benzyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (53)



Physical state: yellow solid;

Melting point: 154–156°C;

Yield: 38%;

Rf = 0.5 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.32 (m, 5H), 7.29 (td, *J* = 4.3, 1.9 Hz, 4H), 7.28 – 7.26 (m, 2H), 7.14 – 7.07 (m, 2H), 7.00 – 6.93 (m, 2H), 6.69 – 6.61 (m, 1H), 5.71 (d, *J* = 9.8 Hz, 1H), 5.48

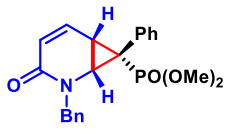
(d, *J* = 14.5 Hz, 1H), 5.09 (s, 2H), 4.19 (d, *J* = 14.5 Hz, 1H), 3.88 (d, *J* = 8.8 Hz, 1H), 2.90 (dd, *J* = 8.9, 5.3 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.66, 161.39, 136.28, 136.16, 135.85, 133.27, 129.48, 128.94, 128.58, 128.51, 128.15, 128.15, 128.00, 127.32, 126.56, 67.10, 50.59, 48.61, 34.15, 27.90.

HRMS (ESI–TOF): Calc'd. For: $C_{27}H_{24}NO_3^+$ $[(M+H)^+]$ 410.1751, found: 410.1758.

Dimethyl

((1*R*,6*S*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-en-7-yl)phosphonate (54)



Physical state: yellow solid;

Melting point: 172–173°C;

Yield: 20%

Rf = 0.4(silica gel,DCM: MeOH = 50:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 – 7.28 (m, 5H), 7.26 – 7.18 (m, 3H), 6.95 (dt, *J* = 7.4, 2.0 Hz, 2H), 6.62 (dd, *J* = 9.9, 5.2 Hz, 1H), 5.67 (d, *J* = 9.9 Hz, 1H), 5.39 (d, *J* = 14.5 Hz, 1H), 4.29 (d, *J* = 14.6 Hz, 1H), 3.87 (dd, *J* = 11.0, 8.6 Hz, 1H), 3.69 – 3.59 (m, 6H), 2.81 – 2.72 (m, 1H).

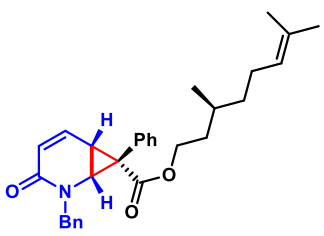
^{13}C NMR (150 MHz, $CDCl_3$): δ 161.43, 136.27, 135.89, 135.87, 133.96, 128.95, 128.61, 128.59, 128.26, 128.24, 128.16, 128.06, 126.40, 53.74, 53.72, 53.70, 53.68, 50.82, 44.39, 27.46, 26.23, 22.94, 22.92.

^{31}P NMR (243 MHz, $CDCl_3$): δ 26.48.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{22}NNaO_4P^+$ $[(M+Na)^+]$ 406.1179, found: 406.1191.

(*S*)-3,7-Dimethyloct-6-en-1-yl

(1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (55)



Physical state: colorless oil;

Yield: 47%;

Rf = 0.3 (silica gel, PE: EtOAc = 4:1);

Dr = 1:1

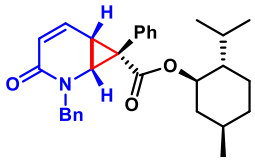
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 – 7.31 (m, 5H), 7.25 – 7.13 (m, 3H), 7.00 – 6.87 (m, 2H), 6.66 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.70 (d, *J* = 9.9 Hz, 1H), 5.51 (dd, *J* = 14.6, 7.0 Hz, 1H), 5.07 – 4.98 (m, 1H), 4.17 (dd, *J* = 14.6, 6.5 Hz, 1H), 4.10 – 4.01 (m, 2H), 3.86 (d, *J* = 8.8 Hz, 1H), 2.86 (dd, *J* = 8.9, 5.2 Hz, 1H), 1.92 – 1.81 (m, 2H), 1.68 (s, 3H), 1.58 (s, 3H), 1.54 – 1.45 (m, 2H), 1.11 – 0.81 (m, 4H), 0.77 (d, *J* = 5.9 Hz, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.96, 161.47, 136.40, 136.24, 133.22, 131.42, 129.69, 129.67, 128.93, 128.45, 128.40, 128.00, 127.98, 126.43, 124.62, 64.51, 50.63, 50.62, 48.46, 48.42, 36.97, 36.94, 35.32, 34.10, 29.62, 29.60, 27.81, 27.79, 25.84, 25.53, 25.51, 19.36, 17.77.

HRMS (ESI–TOF): Calc'd. For: $C_{30}H_{36}NO_3^+$ $[(M+H)^+]$ 458.2690, found: 458.2692.

(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl

(1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (56)



Physical state: white solid;

Melting point: 105–107°C;

Yield: 59%;

Rf = 0.3 (silica gel, PE: EtOAc = 4:1);

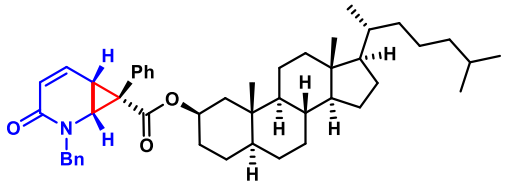
Dr = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.30 (m, 5H), 7.22 (td, *J* = 5.8, 2.5 Hz, 3H), 6.94 – 6.81 (m, 2H), 6.66 (dt, *J* = 10.8, 5.7 Hz, 1H), 5.70 (dd, *J* = 9.9, 2.8 Hz, 1H), 5.50 – 5.33 (m, 1H), 4.58 (tdd, *J* = 10.8, 8.0, 4.4 Hz, 1H), 4.31 – 4.18 (m, 1H), 3.82 (d, *J* = 8.9 Hz, 1H), 2.85 (ddd, *J* = 14.3, 8.9, 5.3 Hz, 1H), 2.00 – 1.86 (m, 1H), 1.63 (td, *J* = 6.9, 2.9 Hz, 1H), 1.59 – 1.52 (m, 1H), 1.47 – 1.37 (m, 1H), 1.16 – 1.07 (m, 1H), 1.03 – 0.94 (m, 1H), 0.87 (dd, *J* = 12.2, 6.6 Hz, 4H), 0.83 – 0.76 (m, 3H), 0.76 – 0.63 (m, 5H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 172.35, 172.13, 161.43, 136.53, 136.50, 136.22, 133.21, 133.14, 129.85, 129.72, 128.96, 128.78, 128.69, 128.32, 128.26, 128.05, 127.88, 127.84, 126.37, 126.32, 76.01, 75.98, 50.83, 50.63, 48.25, 48.02, 46.83, 46.81, 40.74, 40.66, 34.34, 34.24, 34.17, 34.13, 31.40, 27.32, 27.23, 26.47, 26.35, 23.54, 23.47, 22.10, 22.06, 20.75, 20.70, 16.61, 16.46.

HRMS (ESI–TOF): Calc'd. For: $C_{30}H_{36}NO_3^+$ [(M+H)$^+$] 458.2690, found: 458.2693.

(2*R*,5*S*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-10,13-Dimethyl-17-((*R*)-6-methylheptan-2-yl)hexadecahydro-1*H*-cyclopenta[a]phenanthren-2-yl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (57)



Physical state: colorless oil;

Yield: 31%;

Rf = 0.4 (silica gel, PE: EtOAc = 5:1);

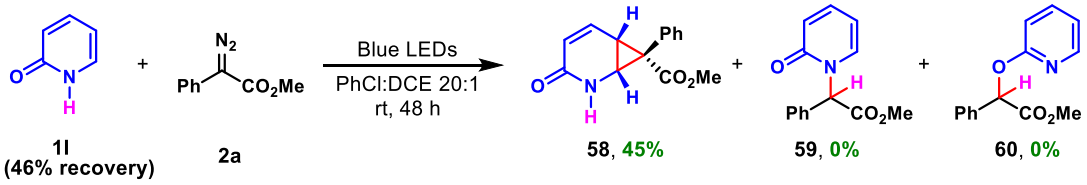
Dr = 1:1

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 – 7.33 (m, 5H), 7.24 (p, *J* = 2.4 Hz, 3H), 6.92 (dt, *J* = 6.7, 1.7 Hz, 2H), 6.64 (dd, *J* = 9.9, 5.3 Hz, 1H), 5.68 (d, *J* = 9.9 Hz, 1H), 5.46 (dd, *J* = 14.5, 2.3 Hz, 1H), 4.63 (tt, *J* = 11.0, 4.7 Hz, 1H), 4.20 (dd, *J* = 14.7, 2.2 Hz, 1H), 3.83 (d, *J* = 8.8 Hz, 1H), 2.84 (dd, *J* = 8.9, 5.3 Hz, 1H), 1.97 – 1.91 (m, 1H), 1.79 (dd, *J* = 9.0, 4.6 Hz, 1H), 1.64 (s, 1H), 1.54 – 1.48 (m, 2H), 1.32 (d, *J* = 8.2 Hz, 5H), 1.25 – 1.17 (m, 5H), 1.15 – 1.03 (m, 8H), 1.01 – 0.94 (m, 4H), 0.91 – 0.83 (m, 13H), 0.73 (s, 3H), 0.63 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.35, 161.50, 136.53, 136.30, 133.25, 129.87, 128.96, 128.58, 128.35, 128.01, 127.90, 126.39, 75.49, 56.53, 56.40, 54.29, 50.66, 48.32, 44.76, 42.71, 40.08, 39.65, 36.78, 36.30, 35.92, 35.57, 35.54, 34.28, 33.96, 32.10, 28.70, 28.36, 28.15, 27.65, 27.43, 24.32, 23.97, 22.95, 22.69, 21.33, 18.80, 12.36, 12.19.

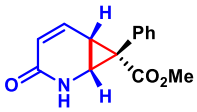
HRMS (ESI–TOF): Calc'd. For: $C_{47}H_{64}NO_3^+$ [(M+H)$^+$] 690.4881, found: 690.4878.

7 Control experiments



A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1l** (0.1 mmol), **2a** (2.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. And then mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 h. After completion of the reaction (monitored by TLC), filtered through a thin pad of celite, eluting with EtOAc (30 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to give the product **58** (10.9 mg, 45%).

Methyl (1*R*,6*R*,7*R*)-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (58)



Physical state: yellow solid

Melting point: 157–159°C;

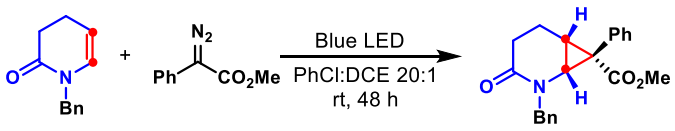
Yield: 45%;

Rf = 0.2 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.49 (m, 1H), 7.34 – 7.27 (m, 3H), 7.16 – 7.07 (m, 2H), 6.75 (ddd, *J* = 10.0, 5.5, 0.8 Hz, 1H), 5.60 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.92 (ddd, *J* = 8.7, 3.6, 0.7 Hz, 1H), 3.62 (s, 3H), 2.94 (dd, *J* = 8.6, 5.4 Hz, 1H)

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.28, 163.53, 138.50, 133.86, 129.51, 128.41, 128.04, 125.72, 53.15, 44.11, 33.24, 27.14.

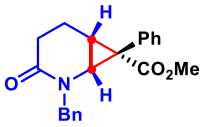
HRMS (ESI–TOF): Calc'd. For: $C_{14}H_{14}NO_3^+$ $[(M+H)^+]$ 244.0968, found: 244.0970.



1J 2a

A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1J** (0.1 mmol), **2a** (2.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. And then mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 h. After completion of the reaction (monitored by TLC), filtered through a thin pad of celite, eluting with EtOAc (30 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to give the desired product.

Methyl (1*R*,6*R*,7*R*)-2-benzyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]heptane-7-carboxylate (61)



Physical state: yellow oil;

Yield: 98%;

Rf = 0.2 (silica gel, EtOAc);

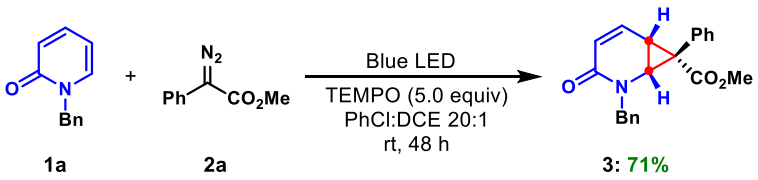
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 – 7.29 (m, 8H), 7.17 – 7.09 (m, 2H), 5.53 (d, *J* = 14.6 Hz, 1H), 4.14 (d, *J* = 14.6 Hz, 1H), 3.59 (s, 3H), 3.56 (d, *J* = 9.3 Hz, 1H), 2.37 (ddd, *J* = 9.4, 6.5, 2.8 Hz, 1H), 2.25 (ddt, *J* = 14.0, 9.4, 6.8 Hz, 1H), 2.15 – 1.98 (m, 2H), 1.21 – 1.10 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.90, 169.36, 136.78, 132.02, 131.28, 129.14, 128.85, 128.34, 128.15, 127.82, 52.85, 50.98, 46.09, 37.54, 28.89, 24.26, 17.92.

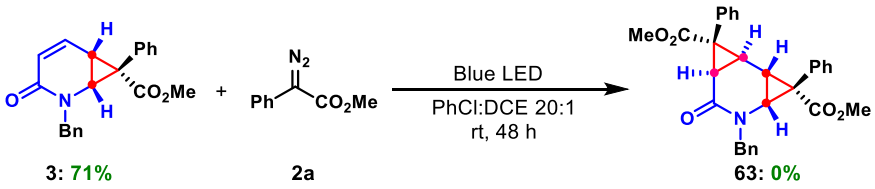
HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{21}NNaO_3^+$ [(M+Na)$^+$] 358.1414, found: 358.1411.

1K 2a

A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1K** (0.1 mmol), **2a** (2.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. And then the mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 h. After completion of the reaction (monitored by TLC), the desired product was not got.

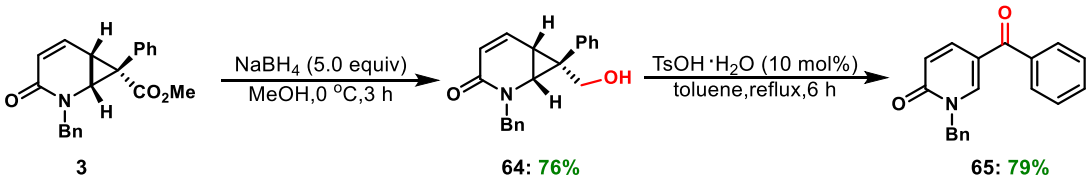


A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1a** (0.1 mmol), **2a** (2.0 equiv), TEMPO (2,2,6,6–Tetramethyl–1–piperinedinyloxy, 5.0 equiv)and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. And then the mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 h. After completion of the reaction (monitored by TLC), filtered through a thin pad of celite, eluting with EtOAc (30 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to give the **3** as yellow solid (23.6 mg, 71%).



Then, A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **3** (0.1 mmol), **2a** (2.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. And then the mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 h. After completion of the reaction (monitored by TLC), the desired product was not got.

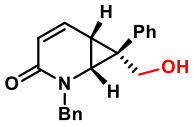
8 Synthetic application



In a round-bottom flask, **3** (1.40 mmol) and $NaBH_4$ (5.0 equiv) was dissolved in MeOH (10 mL). The solution was stirred at 0 °C for 3 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **64** as yellow oil (329 mg, 76%)

In a round-bottom flask, **64** (0.4 mmol) and $TsOH{\cdot}H_2O$ (10 mol%) was dissolved in toluene (3 mL). The solution was stirred at 110 °C for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **65** as yellow solid (91 mg, 79%)

(1*R*,6*R*,7*R*)-2-Benzyl-7-(hydroxymethyl)-7-phenyl-2-azabicyclo[4.1.0]hept-4-en-3-one (64)



Physical state: yellow oil;

Yield: 76%;

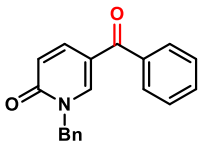
Rf = 0.3 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.39 – 7.28 (m, 6H), 7.25 – 7.15 (m, 2H), 7.00 – 6.95 (m, 2H), 6.62 (dd, *J* = 10.0, 5.2 Hz, 1H), 5.58 (d, *J* = 9.9 Hz, 1H), 5.44 (d, *J* = 14.5 Hz, 1H), 4.24 (d, *J* = 14.6 Hz, 1H), 3.67 (d, *J* = 11.4 Hz, 1H), 3.56 (d, *J* = 11.4 Hz, 1H), 3.30 (d, *J* = 8.5 Hz, 1H), 2.12 (dd, *J* = 8.4, 5.3 Hz, 1H), 1.68 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 161.70, 137.75, 136.69, 133.03, 132.55, 130.78, 129.45, 128.88, 128.53, 127.84, 124.26, 69.78, 50.60, 44.08, 34.62, 22.58.

HRMS (ESI–TOF): Calc'd. For: $C_{20}H_{20}NO_2^+$ $[(M+H)^+]$ 306.1489, found: 306.1484.

5-Benzoyl-1-benzylpyridin-2(1*H*)-one (65)



Physical state: yellow solid;

Melting point: 295–296°C;

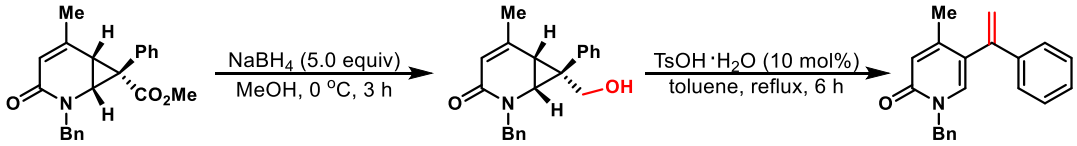
Yield: 79%;

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 (d, *J* = 2.5 Hz, 1H), 7.87 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.62 – 7.54 (m, 3H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.39 – 7.29 (m, 5H), 6.65 (d, *J* = 9.5 Hz, 1H), 5.17 (s, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 191.78, 162.41, 144.31, 139.19, 137.26, 135.52, 132.49, 129.26, 129.23, 128.68, 128.65, 128.49, 120.33, 117.56, 52.81.

HRMS (ESI–TOF): Calc'd. For: $C_{19}H_{16}NO_2^+$ [(M+H)$^+$] 290.1176, found: 290.1172.

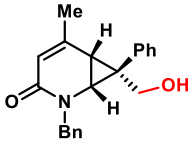


26 **66: 77%** **67: 92%**

In a round-bottom flask, **26** (0.52 mmol) and $NaBH_4$ (5.0 equiv) was dissolved in MeOH (10 mL). The solution was stirred at 0 °C for 3 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **66** as yellow oil (128 mg, 77%)

In a round-bottom flask, **66** (0.17 mmol) and $TsOH{\cdot}H_2O$ (10 mol%) was dissolved in toluene (1 mL). The solution was stirred at 110 °C for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **67** as yellow solid (46.8 mg, 92%)

(1*R*,6*R*,7*R*)-2-Benzyl-7-(hydroxymethyl)-5-methyl-7-phenyl-2-azabicyclo[4.1.0]hept-4-en-3-one (66)



Physical state: white solid;

Melting point: 170–171°C;

Yield: 77%;

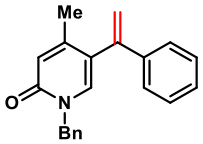
Rf = 0.3 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 – 7.27 (m, 5H), 7.21 (tt, *J* = 6.9, 4.6 Hz, 3H), 6.99 – 6.88 (m, 2H), 5.44 (ddd, *J* = 14.7, 5.8, 1.9 Hz, 1H), 5.36 (d, *J* = 1.8 Hz, 1H), 4.17 (d, *J* = 14.7 Hz, 1H), 3.62 (ddd, *J* = 11.5, 5.5, 1.7 Hz, 1H), 3.50 (dd, *J* = 11.4, 4.1 Hz, 1H), 3.27 (d, *J* = 8.6 Hz, 1H), 2.61 (s, 1H), 2.02 (d, *J* = 1.6 Hz, 3H), 1.96 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.71, 148.61, 136.86, 133.79, 131.16, 128.75, 128.25, 127.68, 127.65, 119.63, 69.12, 50.19, 43.65, 34.14, 26.25, 23.85.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{22}NO_2^+$ $[(M+H)^+]$ 320.1645, found: 320.1643.

1-Benzyl-4-methyl-5-(1-phenylvinyl)pyridin-2(1*H*)-one (67)



Physical state: colorless oil;

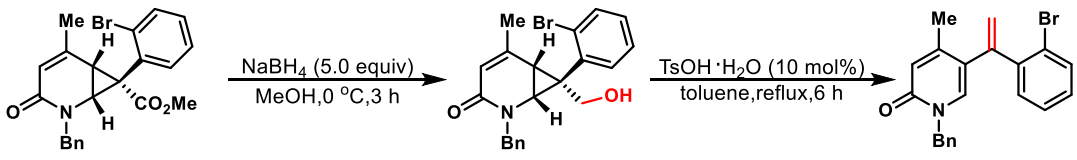
Yield: 92%;

Rf = 0.4 (silica gel, PE: EtOAc = 2:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 – 7.26 (m, 8H), 7.26 – 7.21 (m, 2H), 7.18 (s, 1H), 6.41 (s, 1H), 5.59 (s, 1H), 5.14 (s, 2H), 5.13 (s, 1H), 1.77 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.30, 150.80, 144.96, 139.85, 136.63, 135.84, 128.91, 128.64, 128.21, 128.02, 127.95, 126.45, 122.29, 120.03, 116.27, 51.56, 20.29.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{20}NO^+$ $[(M+H)^+]$ 302.1539, found: 302.1538.



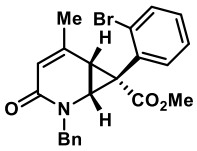
68 **69: 65%** **70: 91%**

In a round-bottom flask, **68** (0.45 mmol) and $NaBH_4$ (5.0 equiv) was dissolved in MeOH (10 mL). The solution was stirred at 0 °C for 3 h. The solvent was evaporated under reduced pressure and

the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **69** as yellow oil (113 mg, 65%)

In a round-bottom flask, **69** (0.15 mmol) and $TsOH{\cdot}H_2O$ (10 mol%) was dissolved in toluene (1 mL). The solution was stirred at 110 ºC for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **70** as yellow solid (52 mg, 91%)

Methyl (1*R*,6*R*,7*R*)-2-benzyl-7-(2-bromophenyl)-5-methyl-3-oxo-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (68)



Physical state: white solid;

Melting point: 142–143ºC;

Yield: 63%;

Rf = 0.3 (silica gel, DCM);

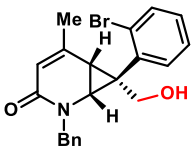
Dr = 3:1;

^{1}H NMR (400 MHz, $CDCl_3$):δ 7.64 – 7.54 (m, 1H), 7.39 – 7.27 (m, 5H), 7.24 – 7.13 (m, 2H), 6.94 (dd, *J* = 7.8, 1.8 Hz, 1H), 5.76 – 5.65 (m, 1H), 5.60 – 5.52 (m, 1H), 4.56 – 4.17 (m, 1H), 4.17 – 3.79 (m, 1H), 3.67 (d, *J* = 4.1 Hz, 3H), 3.10 – 2.62 (m, 1H), 2.16 (s, 3H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 172.73, 172.64, 162.45, 162.16, 147.44, 146.31, 137.11, 136.08, 134.22, 133.79, 133.59, 132.40, 131.28, 130.38, 129.89, 129.70, 128.96, 128.77, 128.34, 128.05, 127.98, 127.75, 127.58, 127.32, 126.94, 123.99, 121.85, 53.30, 53.18, 50.54, 50.37, 50.09, 49.94, 34.74, 33.55, 33.36, 32.61, 24.28, 24.09.

HRMS (ESI–TOF): Calc'd. For: $C_{22}H_{21}BrNO_3^+$ $[(M+H)^+]$ 426.0699, found: 426.0698.

(1*R*,6*R*,7*R*)-2-Benzyl-7-(2-bromophenyl)-7-(hydroxymethyl)-5-methyl-2-azabicyclo[4.1.0]hept-4-en-3-one (69)



Physical state: yellow oil;

Yield: 65%;

Rf = 0.4 (silica gel, PE: EtOAc = 1:1);

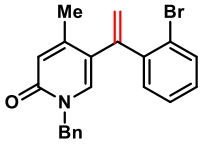
Dr = 3:1;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.39 – 7.28 (m, 4H), 7.25 – 7.12 (m, 2H), 7.07 (ddt, *J* = 9.3, 7.6, 3.1 Hz, 1H), 6.94 (dd, *J* = 7.6, 1.8 Hz, 1H), 5.71 – 5.36 (m, 2H), 4.56 – 4.34 (m, 1H), 4.25 (t, *J* = 15.5 Hz, 1H), 3.42 (t, *J* = 8.8 Hz, 1H), 3.33 – 3.17 (m, 1H), 2.35 (s, 1H), 2.22 – 2.16 (m, 3H), 1.41 – 1.08 (m, 1H).

^{13}C NMR (150 MHz, $CDCl_3$): δ 162.85, 162.73, 148.49, 148.46, 137.49, 136.79, 135.35, 134.61, 134.04, 132.86, 132.69, 132.16, 129.59, 129.49, 129.38, 128.84, 128.75, 128.42, 128.39, 127.80, 127.71, 127.42, 127.13, 126.40, 126.16, 121.16, 119.96, 67.19, 66.92, 51.06, 50.45, 46.20, 44.15, 35.42, 33.63, 29.17, 26.23, 24.83, 24.35.

HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{21}BrNO_2^+$ $[(M+H)^+]$ 398.0750, found: 398.0748.

1-Benzyl-5-(1-(2-bromophenyl)vinyl)-4-methylpyridin-2(1*H*)-one (70)



Physical state: colorless oil;

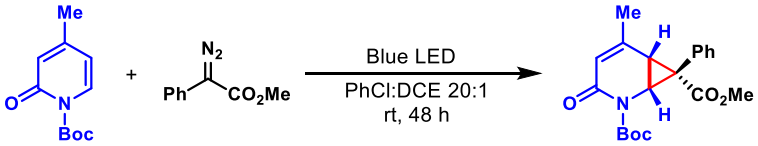
Yield: 91%;

Rf = 0.4 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.36 – 7.26 (m, 5H), 7.26 – 7.14 (m, 3H), 7.13 (s, 1H), 6.41 (s, 1H), 5.42 (s, 2H), 5.13 (s, 2H), 1.92 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 162.05, 150.41, 144.63, 141.66, 136.88, 136.60, 133.79, 131.33, 129.36, 128.95, 128.02, 128.00, 127.54, 122.62, 122.36, 120.86, 120.27, 51.68, 20.96.

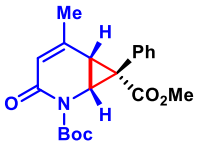
HRMS (ESI–TOF): Calc'd. For: $C_{21}H_{19}BrNO^+$ $[(M+H)^+]$ 380.0645, found: 380.0641.



1L **2a** **71**: 71%

A 4 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with **1L** (0.1 mmol), **2a** (2.0 equiv) and anhydrous PhCl (0.24 mL) and anhydrous DCE (0.012 mL) in the glove box. And The the mixture was irradiation with a blue LED under nitrogen atmosphere at room temperature for 48 h. After completion of the reaction (monitored by TLC), filtered through a thin pad of celite, eluting with EtOAc (30 mL), and the combined filtrate was concentrated *in vacuo*. The residue was directly purified by column chromatography on silica gel to give the desired product. (Petroleum ether/EtOAc = 5:1–1:1) to give desired **71** (71%)

2-(*tert*-Butyl) 7-methyl (1*R*,6*R*,7*R*)-5-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-2,7-dicarboxylate (71)



Physical state: yellow solid;

Melting point: 82–85°C;

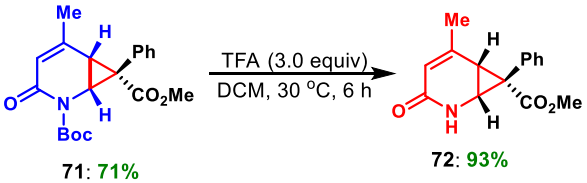
Yield: 71%;

Rf = 0.4 (silica gel, PE: EtOAc = 5:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 – 7.25 (m, 3H), 7.05 (dd, *J* = 6.5, 3.1 Hz, 2H), 5.47 – 5.42 (m, 1H), 4.38 (d, *J* = 9.0 Hz, 1H), 3.65 (s, 3H), 2.79 (d, *J* = 9.0 Hz, 1H), 2.13 (s, 3H), 1.59 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.54, 159.51, 145.47, 139.88, 135.74, 133.73, 129.55, 129.07, 128.56, 128.47, 128.43, 125.71, 53.48, 46.72, 35.34, 26.94, 21.82.

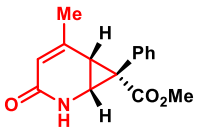
HRMS (ESI–TOF): Calc'd. For: $C_{20}H_{24}NO_5^+$ $[(M+H)^+]$ 358.1649, found: 358.1654.



71: 71% **72**: 93%

In a round-bottom flask, **71** (0.40 mmol) was dissolved in DCM (3 mL). Then TFA (3.0 equiv) were added, and the solution was stirred at room temperature for 6 h. The solvent was evaporated under reduced pressure and the residue was purified by silica gel chromatography column (Petroleum ether/EtOAc = 1:1–1:2) to give **72** as yellow solid (103 mg, 93%)

Methyl (1*R*,6*R*,7*R*)-5-methyl-3-oxo-7-phenyl-2-azabicyclo[4.1.0]hept-4-ene-7-carboxylate (72)



Physical state: yellow solid;

Melting point: 153–154°C;

Yield: 93%;

Rf = 0.2 (silica gel, PE: EtOAc = 1:1);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H), 7.29 (dd, *J* = 5.3, 1.8 Hz, 3H), 7.10 (dd, *J* = 6.8, 2.7 Hz, 2H), 5.40 (s, 1H), 3.88 (d, *J* = 8.8 Hz, 1H), 3.61 (s, 3H), 2.81 (d, *J* = 8.7 Hz, 1H), 2.12 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 173.49, 149.31, 132.54, 129.96, 128.99, 128.48, 128.12, 121.48, 53.13, 44.01, 32.96, 31.22, 24.01.

HRMS (ESI–TOF): Calc'd. For: $C_{15}H_{16}NO_3^+$ [$(M+H)^+$] 258.1125, found: 258.1129.

9 Density Functional Theory (DFT) Studies

9.1 Computational methods

All density functional theory (DFT) calculations were performed using the Gaussian 16 software package.[35] Geometries were optimized using the M06[36] with 6-31G(d) for all atoms. Vibrational frequencies were calculated for all the stationary points to confirm if each optimized structure is a local minimum on the respective potential energy surface or a transition state structure with only one imaginary frequency. Solvation energy corrections were calculated in chlorobenzene solvent with the SMD continuum solvation model[37] based on the gas phase optimized geometries. The M06 functional with 6-311+G(d, p) for all atoms were used for single-point energy calculations. The optimized transition state structures were plotted using CYLview[38]. Orbital composition analysis by Multiwfn[39,40].

9.2 Orbital composition of 1a and 2a analysis

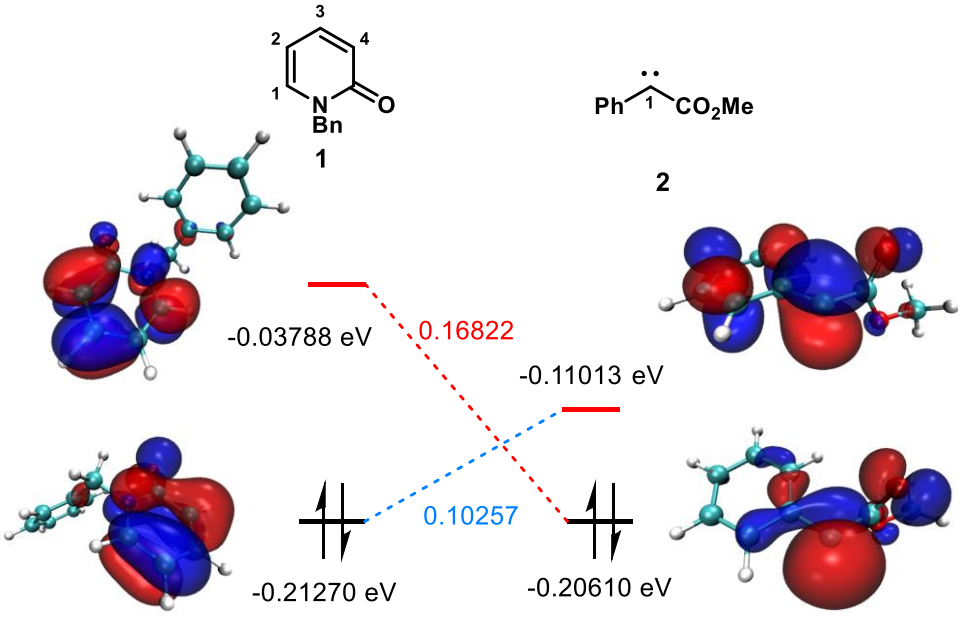


Figure S1. Frontier molecular orbitals of **1a** and **2a** that interact strongly in the ambimodal transition state.

The structure of **1** acts as the electrophilic component and the 2-pyridones **2** is the nucleophilic component. The HOMO orbital of **1a** has a larger distribution at the C1 and C2 position (10.8% and 22.4%) as compared to the C3 and C4 position (0.8% and 16.3%) due to the electron-withdrawing effect of CONH. The LUMO orbital of **2** has a larger distribution at the C1

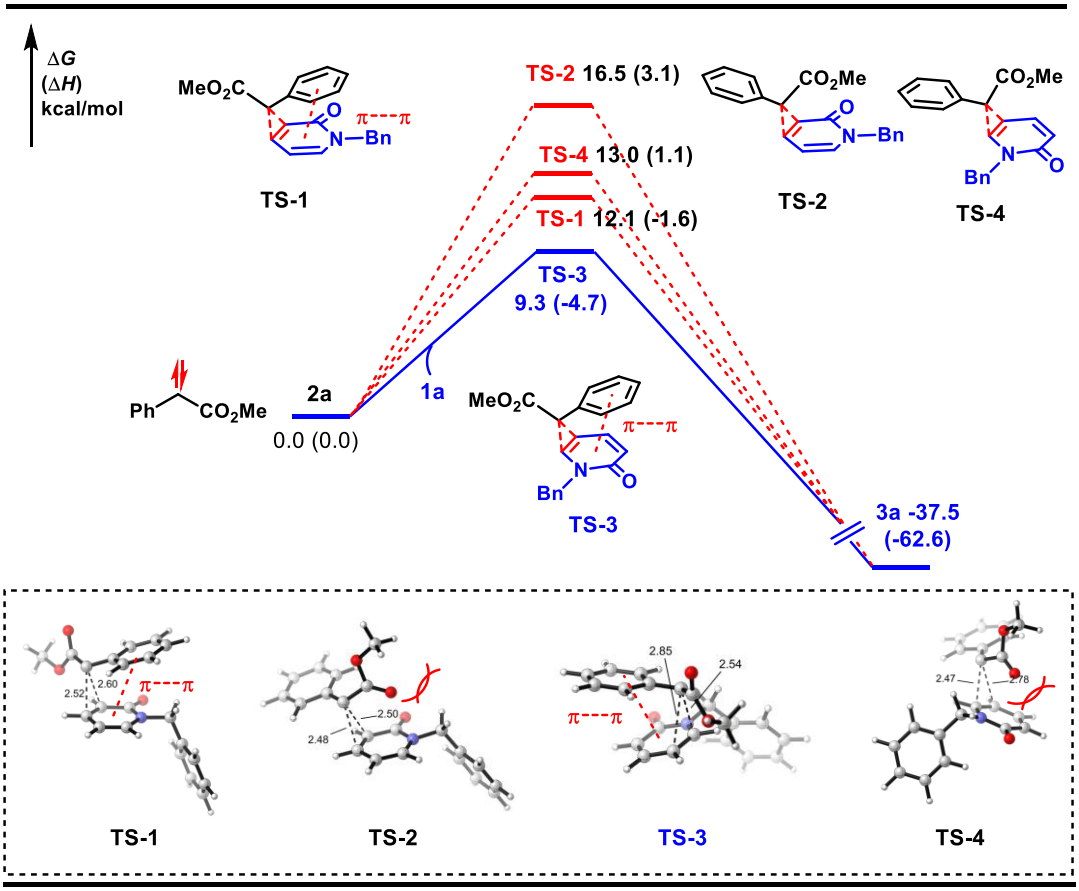
position (45.2%) as compared to the others position due to the electron-withdrawing effect of ester substituent, which leads to the intrinsic regioselectivity of the C1 and C2 alkene addition.

9.3 DFT-computed free energy profile with 1a and 2a

Table S5. Energies for all calculated species

Structure	ZPE	ΔH	ΔG	E	H	G	Imaginary Frequency
1a	0.202792	0.214777	0.16445	-593.61944	-593.404663	-593.45499	
2a	0.146714	0.157794	0.10975	-497.923431	-497.765637	-497.813681	
TS-1	0.350814	0.373621	0.297139	-1091.546507	-1091.172886	-1091.249368	-92.91*i*
TS-2	0.350636	0.373541	0.296659	-1091.538958	-1091.165417	-1091.242299	-148.70*i*
TS-3	0.350965	0.373817	0.297778	-1091.551673	-1091.177856	-1091.253895	-28.90*i*
TS-4	0.350162	0.373335	0.293871	-1091.541848	-1091.168513	-1091.247977	-90.41*i*
3a	0.354679	0.373869	0.307045	-1091.635561	-1091.262557	-1091.328516	

Zero-point correction (ZPE), thermal correction to enthalpy (ΔH), thermal correction to Gibbs free energy (ΔG), energies (E), enthalpies (H), and Gibbs free energies (G) (in Hartree) of the structures calculated at the M06/6-311+G(d,p)-SMD(chlorobenzene)//M06/6-31G(d) level of theory.



1a

C	-1.48868	1.45414	0.15299
C	-2.57882	1.6551	-0.64267
C	-3.35735	0.52229	-1.00851
C	-3.01251	-0.72811	-0.58086
C	-1.84529	-0.96529	0.24111
N	-1.14085	0.21318	0.60015
C	0.06129	0.0531	1.44009
H	0.08514	0.88537	2.14935
H	-0.0828	-0.87883	1.98789
C	1.33132	0.01201	0.62201
C	1.6137	-1.1023	-0.18045
C	2.22174	1.08932	0.6351
C	2.76989	-1.129	-0.95758
H	0.91801	-1.9358	-0.18569

C	3.38215	1.06083	-0.14145
H	2.0112	1.95334	1.26186
C	3.65662	-0.04852	-0.94064
H	2.98287	-1.99664	-1.57583
H	4.06853	1.90275	-0.12041
H	4.55843	-0.07396	-1.54591
H	-0.83804	2.26152	0.47136
H	-2.83247	2.65346	-0.97693
H	-3.58332	-1.60923	-0.85036
H	-4.23366	0.65619	-1.63756
O	-1.44904	-2.06899	0.62329

2a

C	-3.25327	0.6591	-0.17213
C	-2.1459	1.48681	0.03404
C	-0.88749	0.92663	0.14789
C	-0.71219	-0.47839	0.08172
C	-1.85584	-1.28848	-0.10361
C	-3.11358	-0.72619	-0.24674
H	-4.24235	1.10464	-0.27162
H	-2.27821	2.56527	0.09535
H	-0.01449	1.55662	0.31593
H	-1.70186	-2.36541	-0.13837
H	-3.9875	-1.35527	-0.40258
C	0.54781	-1.13387	0.17234
C	1.73134	-0.34133	0.31041
O	2.08601	0.04003	1.41653
O	2.43523	-0.16136	-0.82088
C	3.69182	0.48366	-0.64482
H	4.33504	-0.09393	0.02827

H	4.13937	0.54192	-1.63923
H	3.56391	1.48908	-0.22757

TS-1

C	2.00359	0.74447	-0.2774
H	2.0005	1.6905	0.28171
H	1.67767	0.94802	-1.30322
C	0.84761	-0.19043	1.66316
C	-0.12127	-0.92521	2.27166
C	-0.90641	-1.59499	0.08085
C	-1.05117	-1.61427	1.44839
N	0.96794	-0.11793	0.30501
C	0.14029	-0.84474	-0.57392
O	0.31344	-0.79486	-1.78739
H	-0.19494	-0.94593	3.35402
H	1.58904	0.38084	2.22141
C	3.36292	0.10473	-0.25433
C	3.62729	-0.99224	-1.07913
C	4.36189	0.57722	0.59432
C	4.87392	-1.60349	-1.04908
H	2.84155	-1.35184	-1.74451
C	5.61311	-0.0336	0.62255
H	4.16036	1.43816	1.23476
C	5.86933	-1.12562	-0.19847
H	5.0741	-2.45584	-1.69649
H	6.38777	0.34566	1.2872
H	6.84667	-1.60522	-0.17895
C	-0.6493	3.47515	-0.61979
C	-1.2566	2.63751	-1.55829
C	-1.95159	1.51824	-1.13422

C	-2.05594	1.21147	0.24061
C	-1.43866	2.07619	1.16643
C	-0.74025	3.19895	0.74285
H	-0.10449	4.35594	-0.95787
H	-1.1782	2.86226	-2.6202
H	-2.4221	0.85445	-1.85839
H	-1.54204	1.83921	2.22316
H	-0.27793	3.86642	1.46846
C	-2.75905	0.0725	0.76454
C	-3.81335	-0.57463	0.04271
O	-4.78648	0.09978	-0.27131
O	-3.79125	-1.9218	-0.06392
C	-4.99524	-2.48035	-0.57358
H	-5.82533	-2.32026	0.12422
H	-5.26095	-2.03246	-1.53745
H	-4.80187	-3.54863	-0.6927
H	-1.83919	-2.2168	1.89422
H	-1.55861	-2.16494	-0.57272

TS-2

C	2.44537	0.78927	-0.58283
H	2.50425	1.86726	-0.38444
H	2.01712	0.65026	-1.58127
C	1.39564	0.70619	1.61455
C	0.41121	0.35752	2.48832
C	-0.52359	-1.05199	0.75606
C	-0.58574	-0.53841	2.03433
N	1.46396	0.22292	0.34924
C	0.5167	-0.67846	-0.17428
O	0.6066	-1.09438	-1.3239

H	0.3926	0.77394	3.48961
H	2.19258	1.39805	1.88565
C	3.79105	0.13237	-0.46504
C	3.96009	-1.18562	-0.89841
C	4.87255	0.81008	0.09403
C	5.19376	-1.81047	-0.7703
H	3.10819	-1.70664	-1.33694
C	6.11068	0.18502	0.2204
H	4.74535	1.84196	0.42694
C	6.2718	-1.12666	-0.21064
H	5.31876	-2.83668	-1.11268
H	6.94996	0.72533	0.65581
H	7.23875	-1.61798	-0.11365
C	-5.20712	-2.17387	-0.64961
C	-4.35312	-1.55851	-1.56692
C	-3.40863	-0.64793	-1.12478
C	-3.30114	-0.32938	0.2462
C	-4.16884	-0.96963	1.1508
C	-5.11719	-1.88091	0.70955
H	-5.94838	-2.89075	-1.00016
H	-4.42632	-1.80077	-2.62555
H	-2.7221	-0.17743	-1.82867
H	-4.08053	-0.71309	2.20605
H	-5.78808	-2.36353	1.41787
C	-2.36689	0.63526	0.77343
C	-1.77315	1.65122	-0.06803
O	-0.61215	1.96929	-0.24741
O	-2.81234	2.40338	-0.54388
C	-2.4319	3.65766	-1.08787
H	-3.36157	4.15233	-1.37965

H	-1.898	4.26372	-0.34597
H	-1.78102	3.52622	-1.9598
H	-1.35447	-0.88926	2.71966
H	-1.20091	-1.8262	0.41039

TS-3

C	0.52914	-1.95551	0.51202
C	-0.49462	0.38627	1.78418
C	0.38201	0.46884	0.73243
C	-0.90255	-0.89905	2.21427
C	-3.87442	-2.56586	-0.47212
C	-4.38882	-1.38742	0.08205
C	-3.66889	-0.21223	-0.00974
C	-2.41742	-0.17916	-0.67104
C	-1.93421	-1.37908	-1.2345
C	-2.6498	-2.5653	-1.13002
H	-4.44251	-3.49139	-0.38792
H	-5.35301	-1.40246	0.58732
H	-4.06299	0.71209	0.41125
H	-0.9847	-1.34919	-1.76635
H	-2.24873	-3.48327	-1.55485
C	-1.59566	0.98461	-0.77247
C	-2.10183	2.28219	-0.4284
O	-2.98155	2.78113	-1.11669
O	-1.44552	2.96848	0.53719
C	-1.85527	4.3243	0.67173
H	-1.67171	4.88105	-0.25388
H	-2.92262	4.39221	0.91061
H	-1.25806	4.73771	1.48772
H	0.77214	1.41962	0.37698

H	-0.85878	1.29709	2.24613
N	0.89215	-0.6436	0.13807
H	-1.61432	-0.99185	3.03378
O	1.00189	-2.9272	-0.06656
C	1.75772	-0.46751	-1.0345
H	1.73483	-1.42473	-1.56764
H	1.28906	0.30254	-1.66412
C	3.16248	-0.09683	-0.6545
C	3.97858	-1.03917	-0.02304
C	3.659	1.1812	-0.90142
C	5.27158	-0.70223	0.35501
H	3.5828	-2.03873	0.16231
C	4.95678	1.51883	-0.5252
H	3.0246	1.91626	-1.39989
C	5.76328	0.57787	0.10444
H	5.90315	-1.44214	0.8443
H	5.33692	2.51938	-0.72546
H	6.7783	0.83939	0.3994
C	-0.42893	-2.01641	1.59665
H	-0.73698	-3.01785	1.8873

TS-4

C	-1.40757	2.45155	0.42395
C	0.46041	0.5992	1.54231
C	-0.45659	0.21685	0.59036
C	0.43253	1.95701	1.97193
C	2.96406	-3.61113	1.12135
C	3.65181	-2.46579	1.52445
C	3.18662	-1.21496	1.15246
C	2.02667	-1.07805	0.36008

C	1.35611	-2.25256	-0.03485
C	1.81551	-3.50625	0.33927
H	3.32989	-4.5933	1.41713
H	4.55077	-2.55727	2.13163
H	3.71997	-0.31676	1.46296
H	0.47388	-2.1426	-0.66708
H	1.28884	-4.4033	0.01906
C	1.51094	0.18735	-0.10898
C	2.32477	1.38483	-0.0897
O	2.1287	2.48162	0.39304
O	3.3831	1.13486	-0.92373
C	4.09786	2.29289	-1.32835
H	4.86787	1.94343	-2.02057
H	3.43581	3.00954	-1.82867
H	4.55798	2.79219	-0.46786
H	-0.57783	-0.82041	0.28571
H	1.05034	-0.14861	2.06141
N	-1.30204	1.09667	0.01285
H	1.14344	2.29133	2.72486
O	-2.24236	3.18435	-0.08637
C	-2.09488	0.64681	-1.13837
H	-2.45731	1.56034	-1.62154
H	-1.40494	0.13421	-1.82416
C	-3.23248	-0.24451	-0.73246
C	-4.3036	0.28859	-0.01042
C	-3.22597	-1.60295	-1.04195
C	-5.35024	-0.52974	0.39311
H	-4.30173	1.35409	0.22396
C	-4.27663	-2.42423	-0.63987
H	-2.39237	-2.01863	-1.61202

C	-5.33865	-1.88804	0.07898
H	-6.18359	-0.10735	0.95234
H	-4.26442	-3.484	-0.88978
H	-6.16169	-2.52733	0.39431
C	-0.46906	2.83021	1.45686
H	-0.51372	3.87023	1.76794

3a

C	-2.4376	1.02519	-0.61571
H	-2.03363	1.1994	-1.6235
H	-2.85875	1.96392	-0.23939
C	-0.34643	-0.15427	-0.20427
C	0.94119	-0.37937	0.50872
C	-0.11657	0.93255	2.34627
C	0.88529	0.166	1.90936
N	-1.31059	0.70663	0.2642
C	-1.27215	1.30037	1.51634
O	-2.15192	2.06584	1.90214
H	1.09476	-1.47147	0.56406
H	-0.53797	-0.60994	-1.17236
C	-3.47709	-0.06077	-0.63325
C	-4.27538	-0.26855	0.49464
C	-3.64583	-0.87925	-1.74796
C	-5.22465	-1.28225	0.50255
H	-4.14156	0.37978	1.36146
C	-4.59849	-1.89497	-1.7418
H	-3.02823	-0.715	-2.63301
C	-5.38803	-2.09795	-0.61576
H	-5.84561	-1.43563	1.38387
H	-4.72321	-2.52773	-2.61922

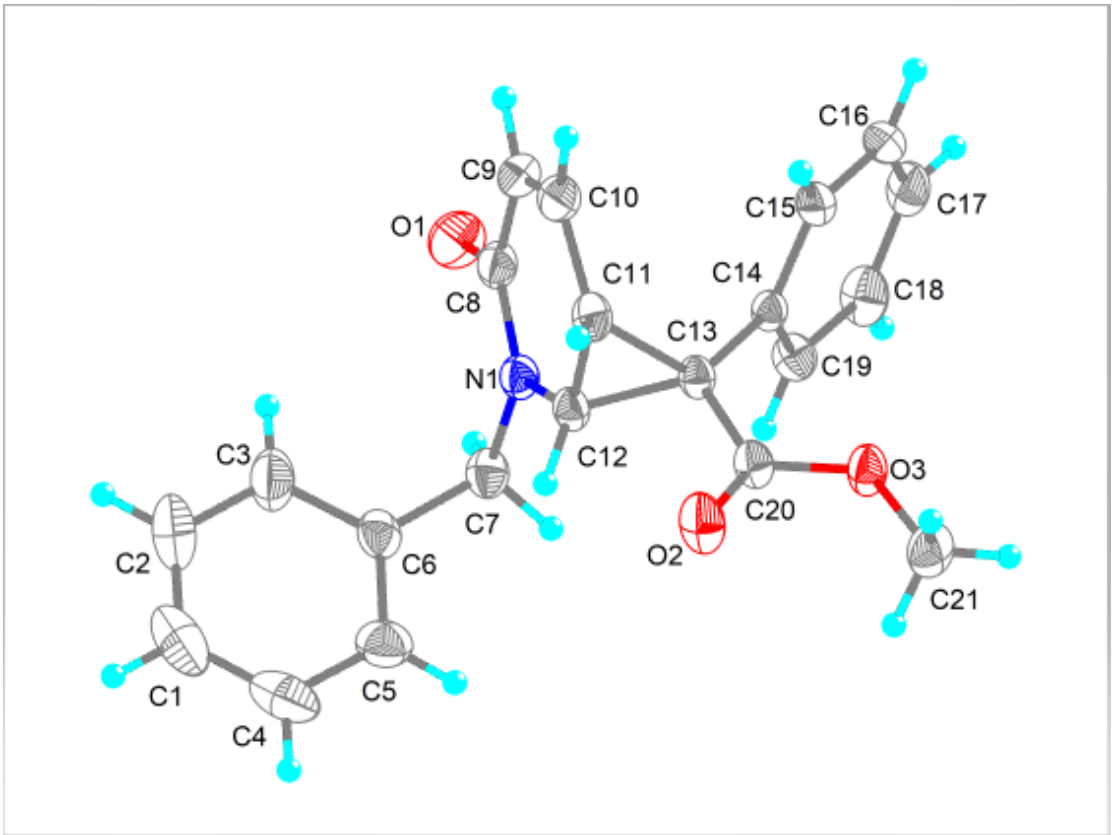
H	-6.13461	-2.89057	-0.60856
C	-0.52697	4.05774	1.47951
C	-0.90383	3.82608	0.1565
C	-0.42656	2.7287	-0.53675
C	0.46958	1.8078	0.07141
C	0.83041	2.06581	1.42127
C	0.34136	3.16419	2.10548
H	-0.90816	4.92321	2.01853
H	-1.58227	4.51546	-0.34352
H	-0.71787	2.56843	-1.56943
H	1.48969	1.3837	1.9535
H	0.63718	3.32432	3.14093
C	0.97119	0.65479	-0.61574
C	0.45126	0.26099	-1.94042
O	-0.00036	0.99673	-2.79652
O	0.54632	-1.06882	-2.11665
C	0.18321	-1.55743	-3.39898
H	0.40649	-2.62775	-3.37991
H	-0.88258	-1.39122	-3.59258
H	0.76229	-1.05595	-4.18326
H	1.73233	-0.06296	2.55869
H	-0.1341	1.34503	3.35281

10 X–ray crystallographic data for 3 and 30

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre. CCDC 2224293(3), CCDC 2233144(30) contains 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/.

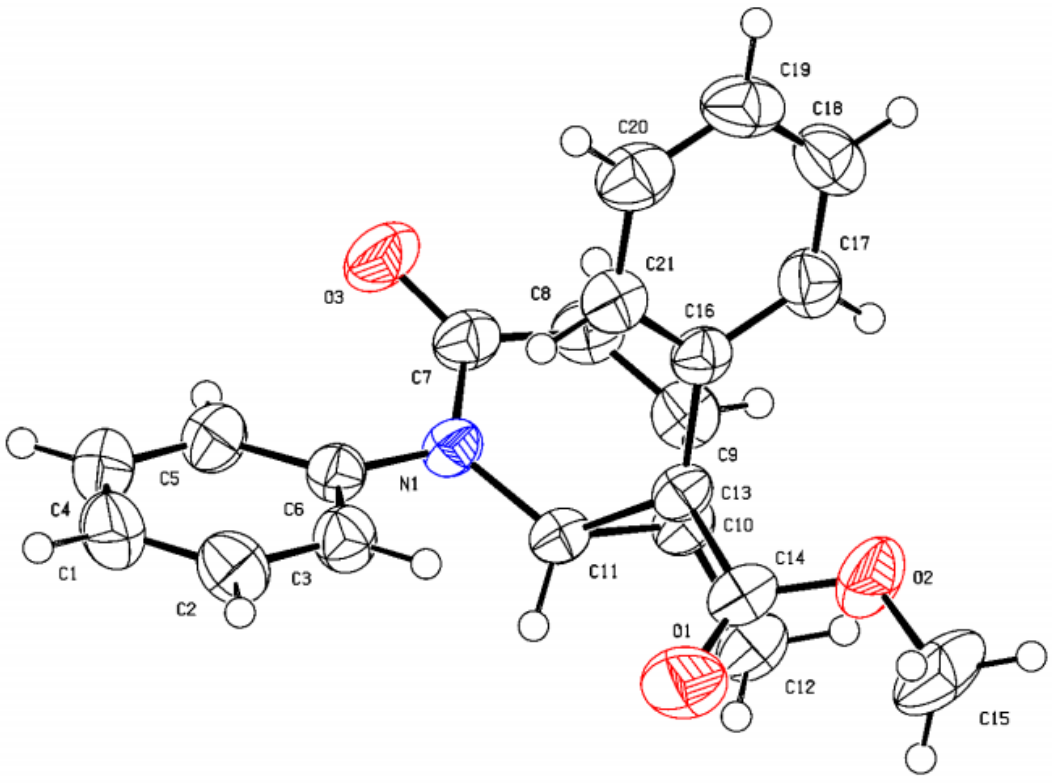
X–ray crystallographic data for 3and 30

Method of crystallization: A purified compound **3, 30** was dissolved in a mixed solvent of dichloromethane and petroleum ether. This solution was placed in a cabinet to slowly evaporate.



Empirical formula	$C_{21}H_{19}NO_3$	
Formula weight	333.37	
Identification code	3	
Temperature/K	293(2)	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a=10.1369(7) Å	α=90°
	b=11.3965(8) Å	β=98.344(7)°
	c=15.5049(11) Å	γ=90°
Volume/Å^3	1772.2(2)	
Z	4	
ρ_{calc}g/cm^3	1.249	

μ/mm^{-1}	0.084
F(000)	704.0
Crystal size/mm^3	0.2 × 0.18 × 0.16
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.452 to 59.35
Index ranges	–13 ≤ h ≤ 13, –14 ≤ k ≤ 15, –19 ≤ l ≤ 19
Reflections collected	12761
Independent reflections	4376 [R_{int} = 0.0298, R_{sigma} = 0.0405]
Data/restraints/parameters	4376/0/227
Goodness–of–fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1366
Final R indexes [all data]	R_1 = 0.0711, wR_2 = 0.1496
Largest diff. peak/hole / e Å^{-3}	0.17/–0.18



Empirical formula	$C_{21}H_{19}NO_3$

Formula weight	333.37	
Identification code	30	
Temperature/K	293(2)	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a= 11.0203(6) Å	α= 90°
	b= 12.3994(6) Å	β= 110.799(6)°
	c= 13.7932(8) Å	γ= 90°
Volume/Å^3	1761.95(18)	
Z	4	
ρ_{calc}g/cm^3	1.257	
μ/mm^{-1}	0.084	
F(000)	704.0	
Crystal size/mm^3	0.17 × 0.15 × 0.14	
Radiation	Mo Kα (λ = 0.71073)	
2Θ range for data collection/°	4.092 to 59.326	
Index ranges	$-14 \leq h \leq 14$, $-16 \leq k \leq 16$, $-10 \leq l \leq 17$	
Reflections collected	11756	
Independent reflections	4343 [R_{int} = 0.0419, R_{sigma} = 0.0461]	
Data/restraints/parameters	4343/0/229	
Goodness–of–fit on F^2	1.055	
Final R indexes [I>=2σ (I)]	R_1 = 0.0564, wR_2 = 0.1754	
Final R indexes [all data]	R_1 = 0.0767, wR_2 = 0.1920	
Largest diff. peak/hole / e Å^{-3}	0.26/–0.28	

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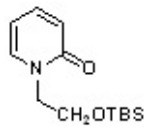
12 NMR spectra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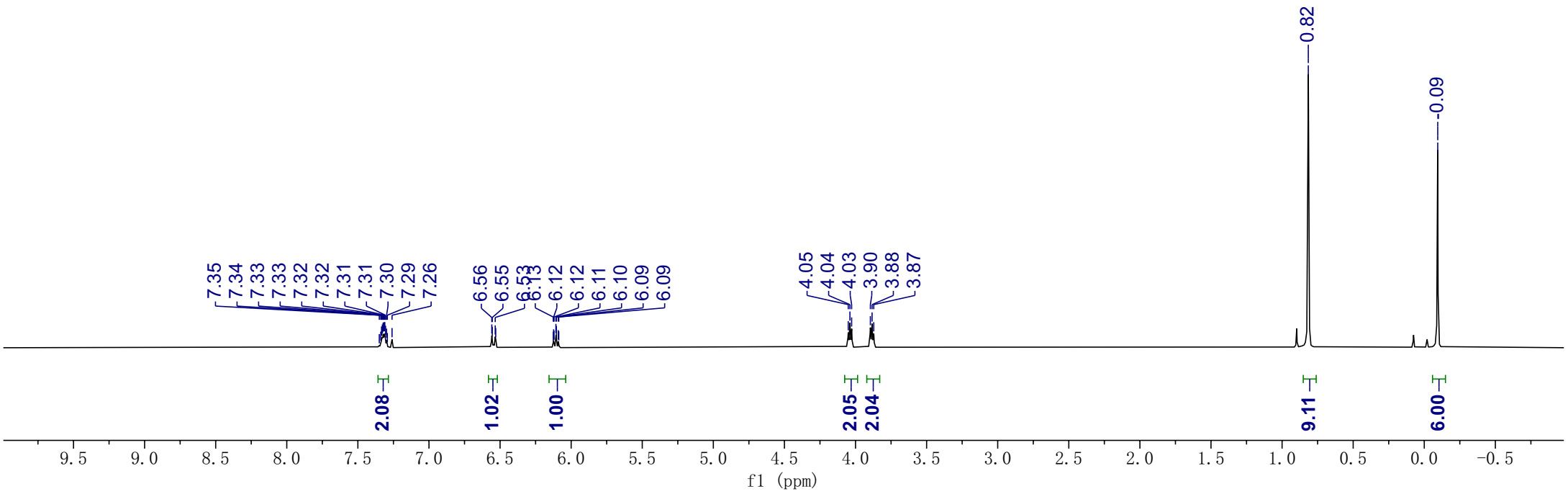
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2.05
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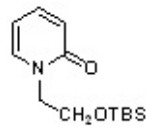
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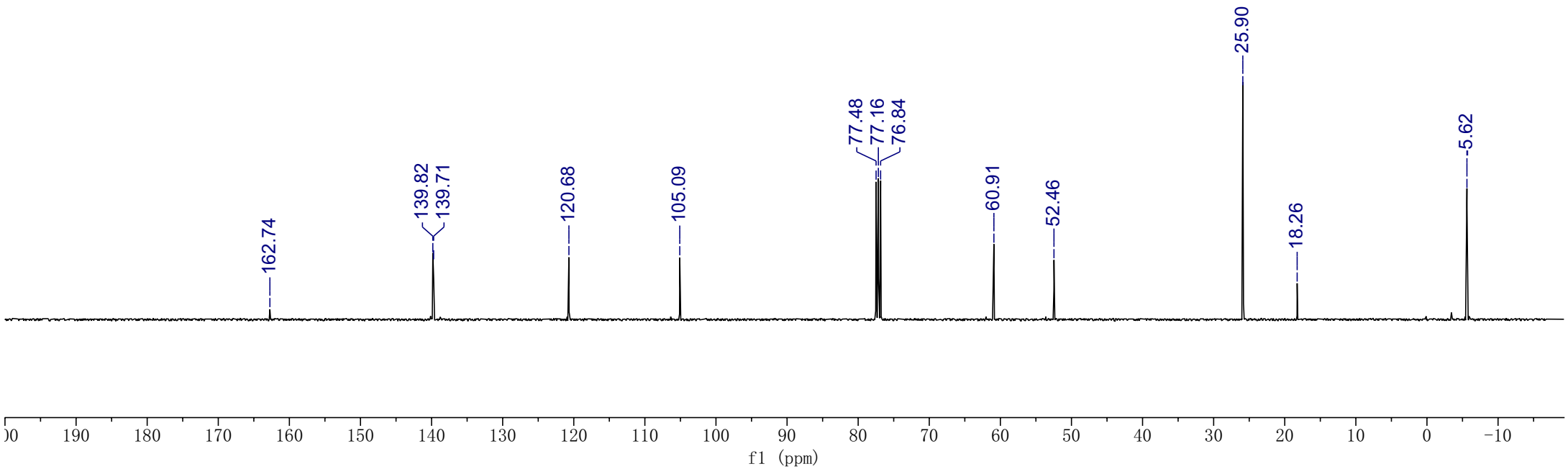
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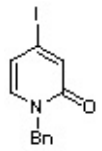
f1 (ppm)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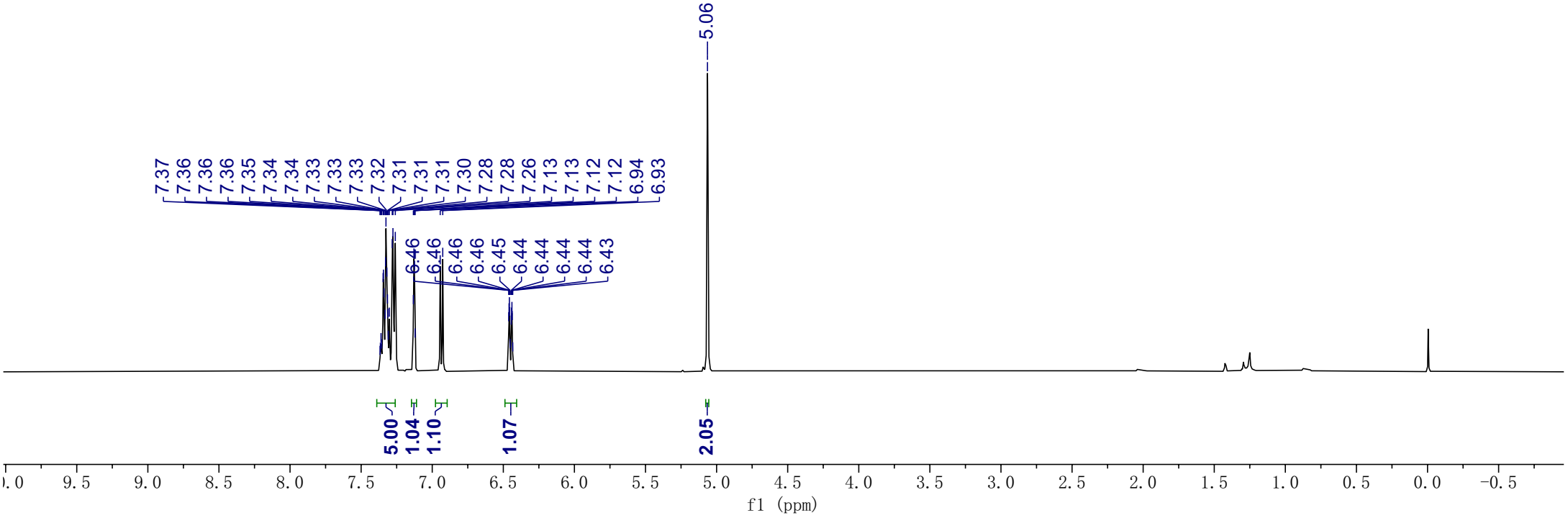
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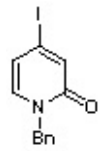
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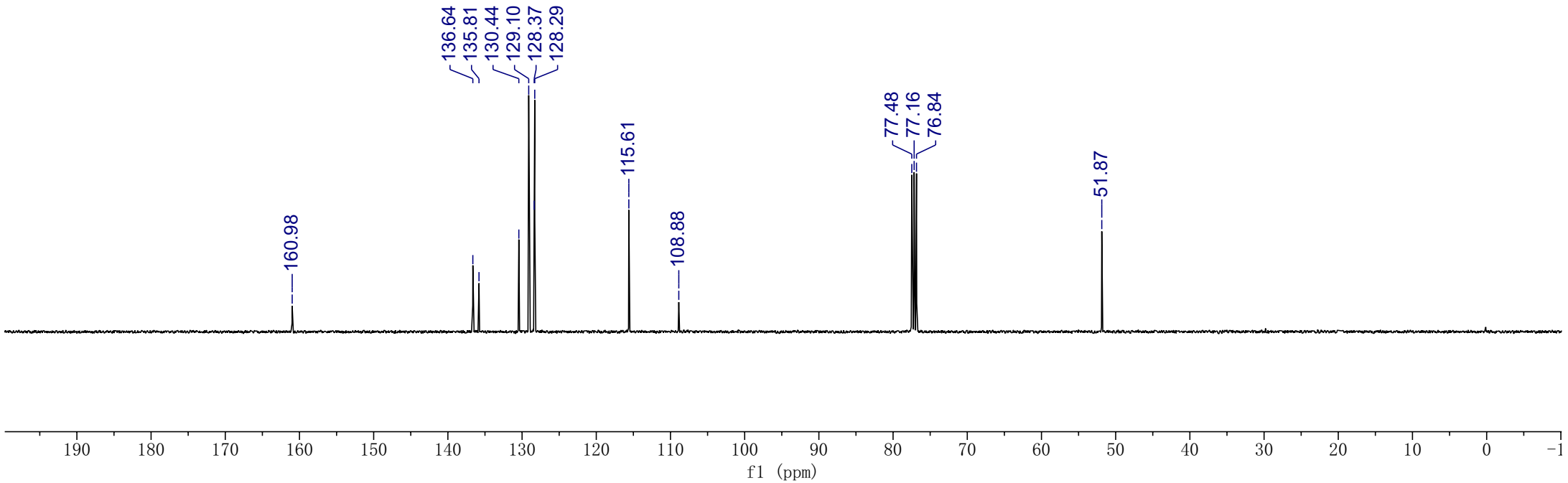
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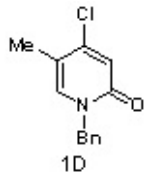
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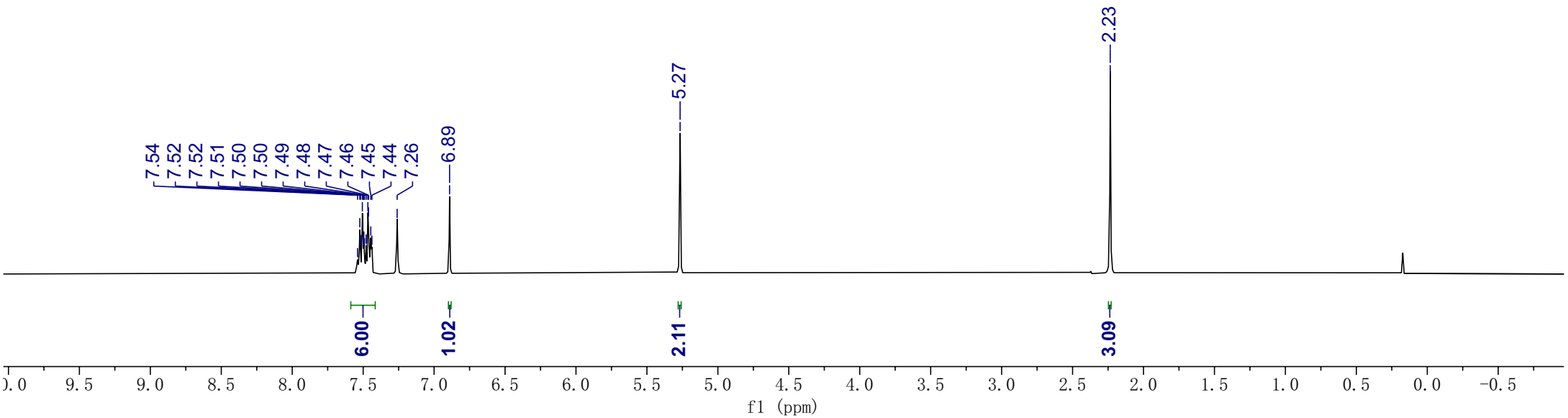
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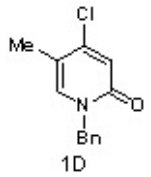
f1 (ppm)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O
Bn

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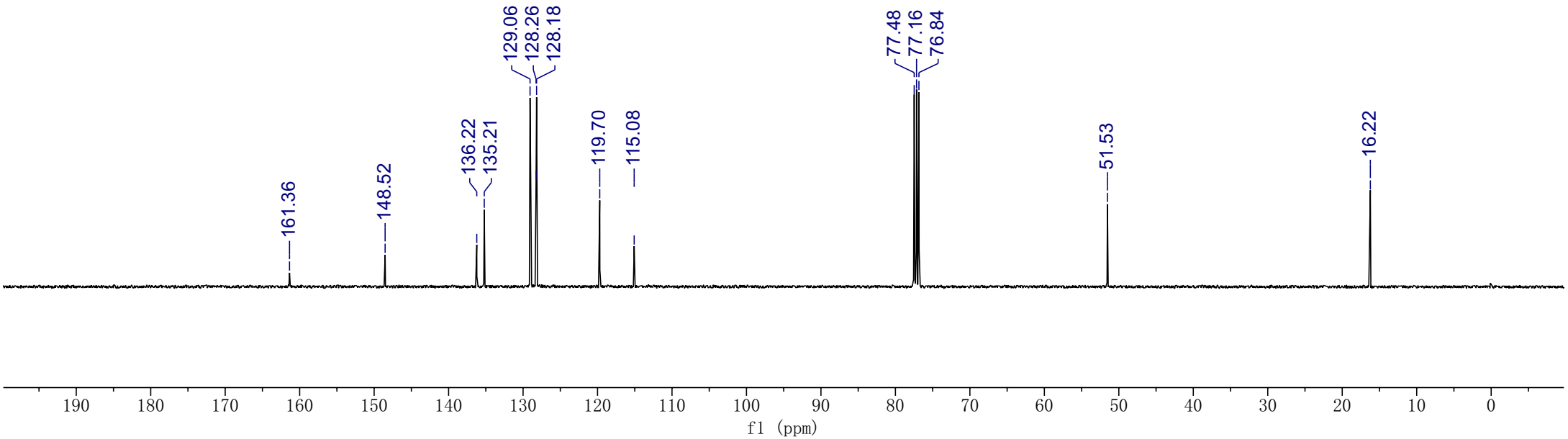
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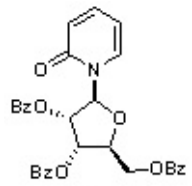
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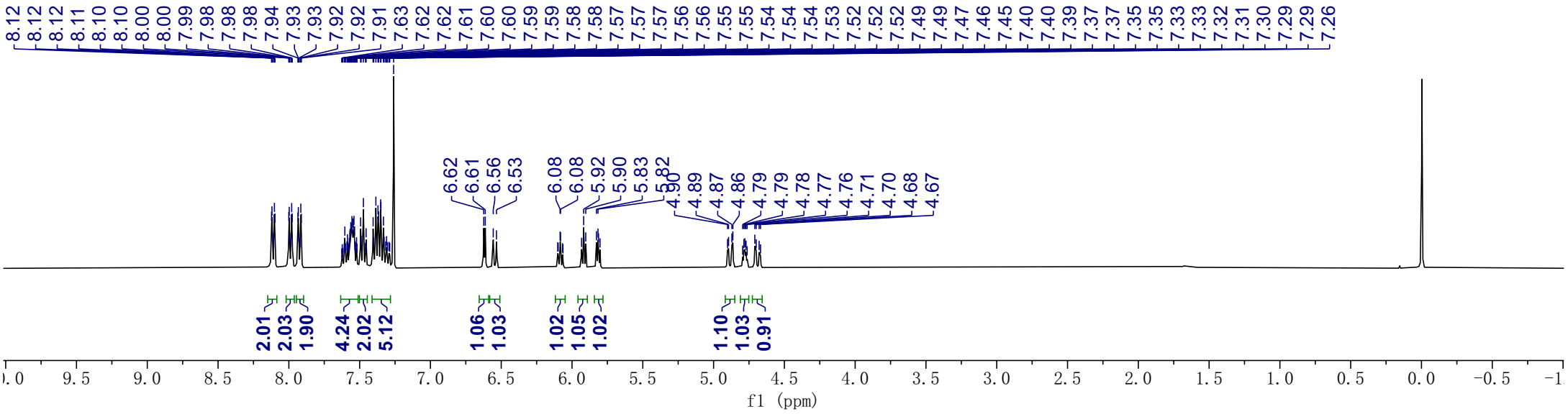
N
BzO
O
BzO
OBz

1q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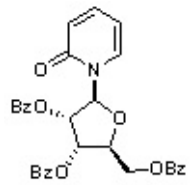
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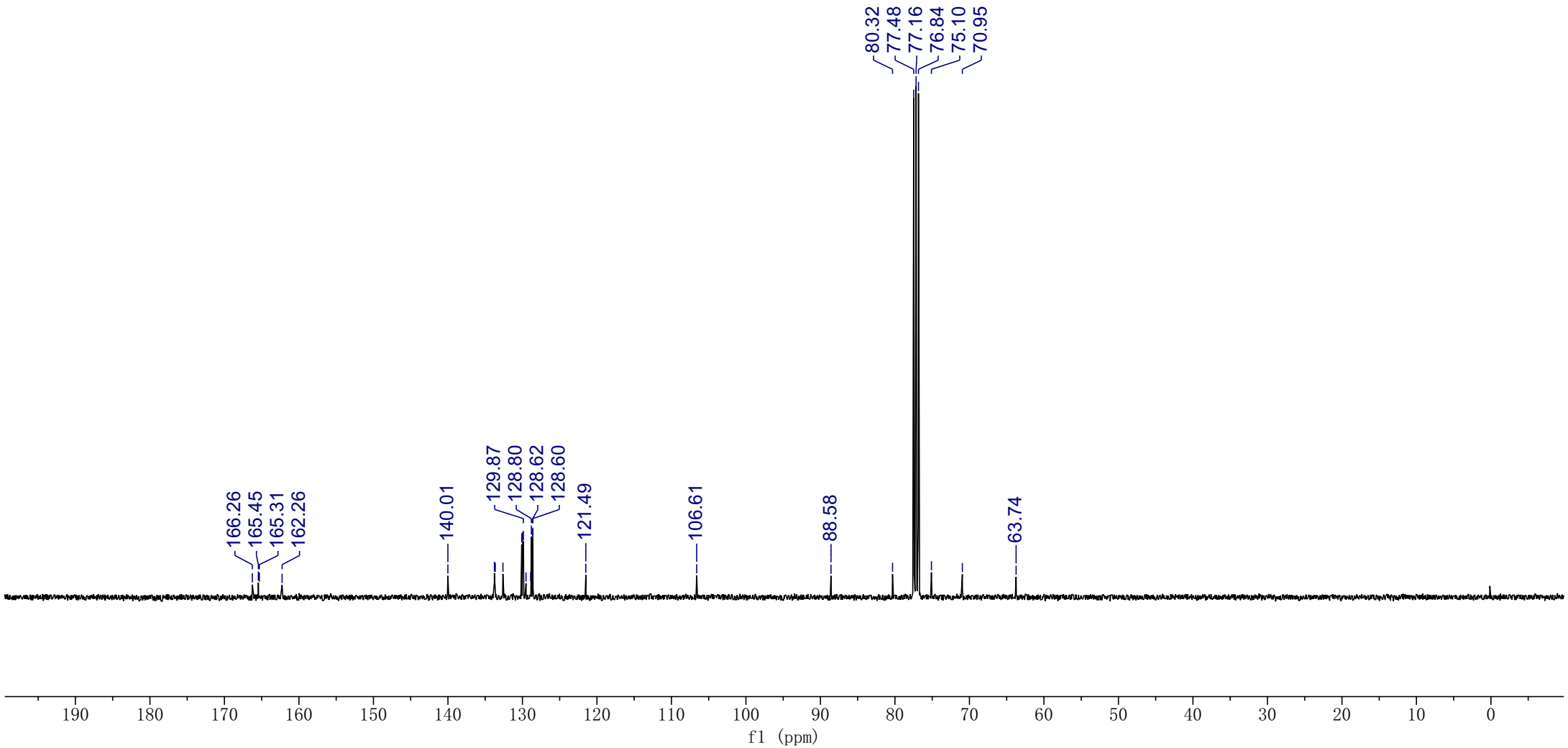
OBz

1q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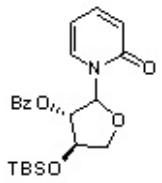
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O
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O

1q

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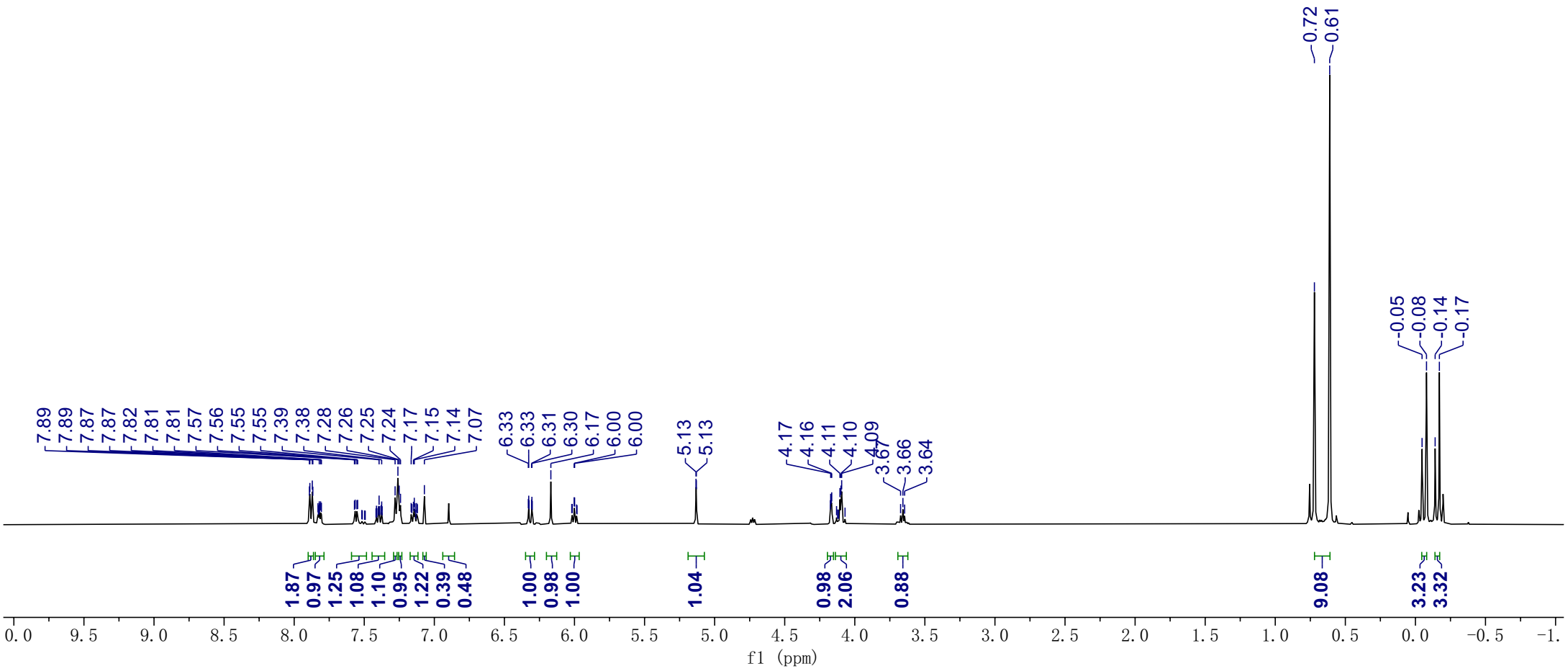
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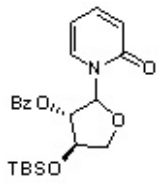
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N
O

1q

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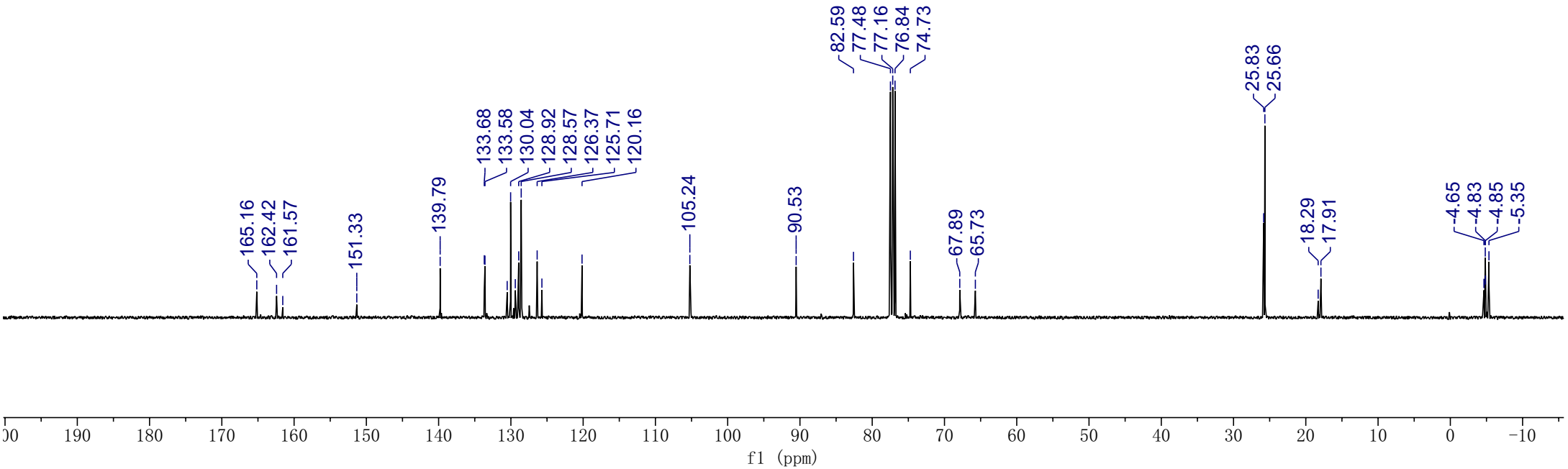
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82.59
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77.16
76.84
74.73
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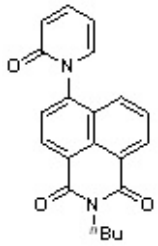
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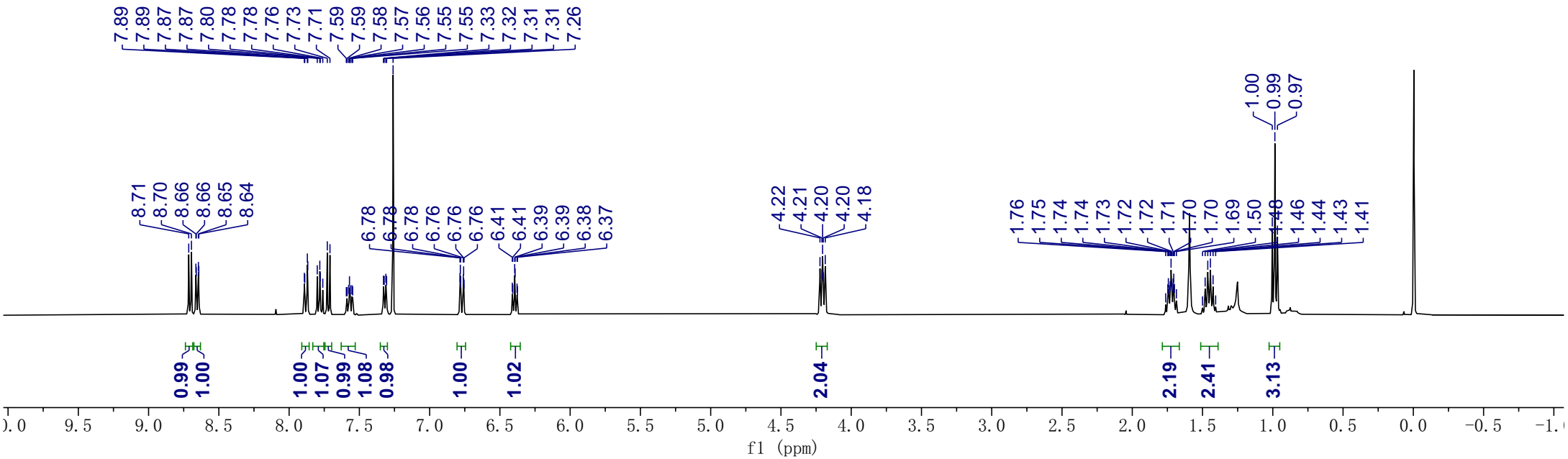
1p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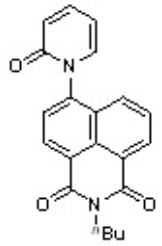
1.44
1.43
1.41
1.00
0.99
0.97
0.99
1.00
1.00
1.07
0.99
1.08
0.98
1.00
1.02
2.04
2.19
2.41
3.13
f1 (ppm)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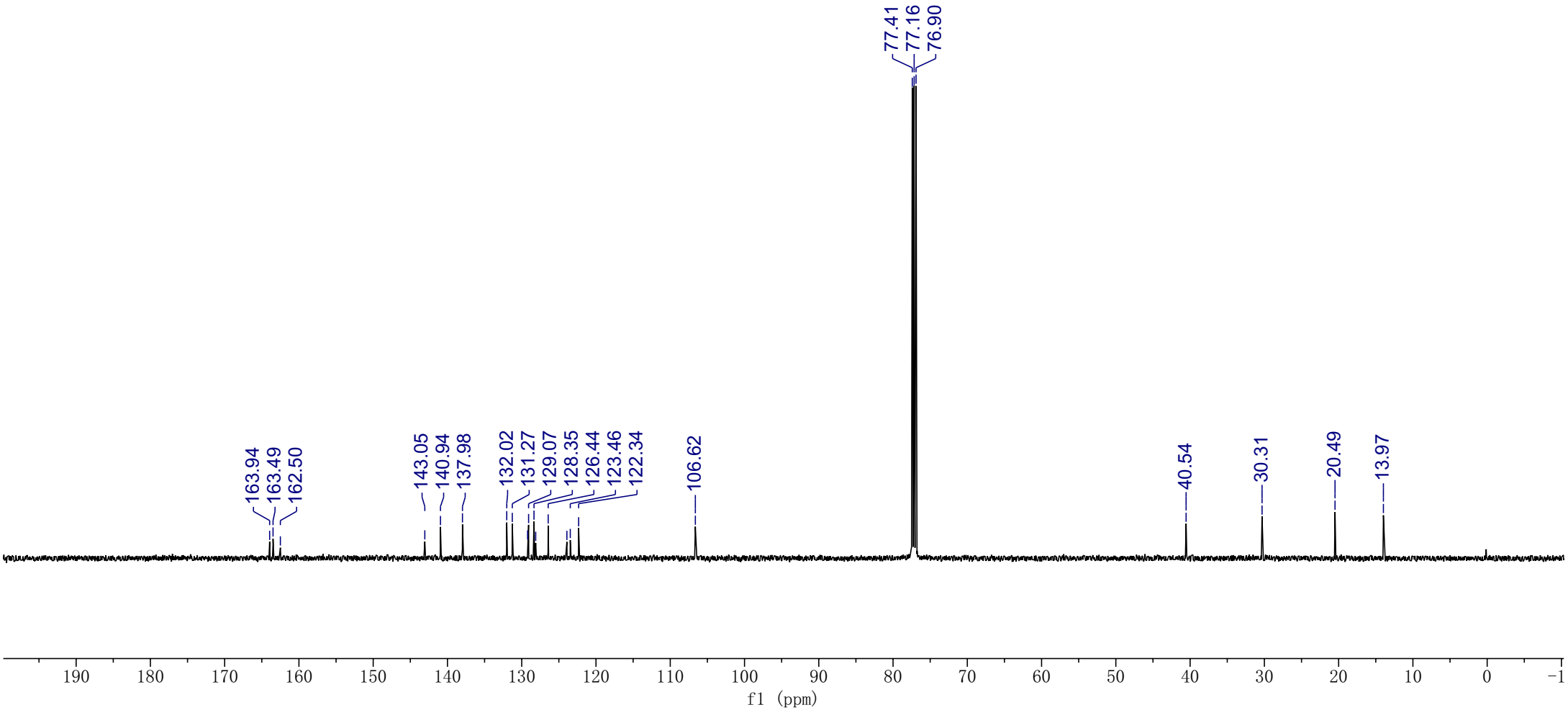
O
N
O
O
nBu

1p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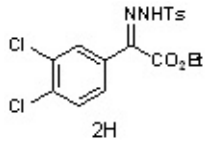
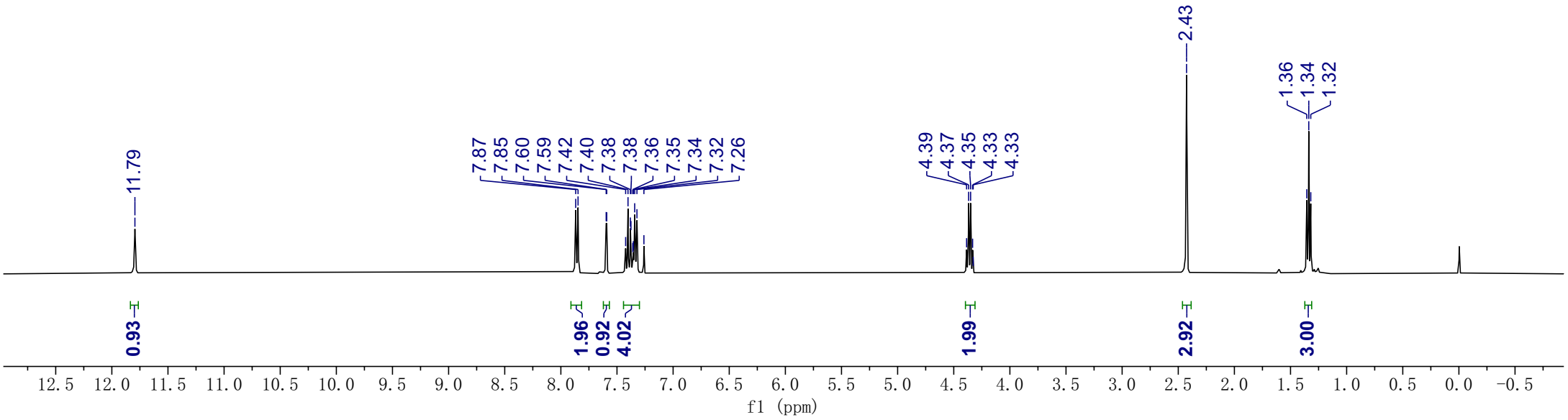
162.50
143.05
140.94
137.98
132.02
131.27
129.07
128.35
126.44
123.46
122.34
106.62
40.54
30.31
20.49
13.97
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


NNHTs
Cl
Cl
CO2Et

2H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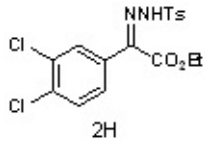
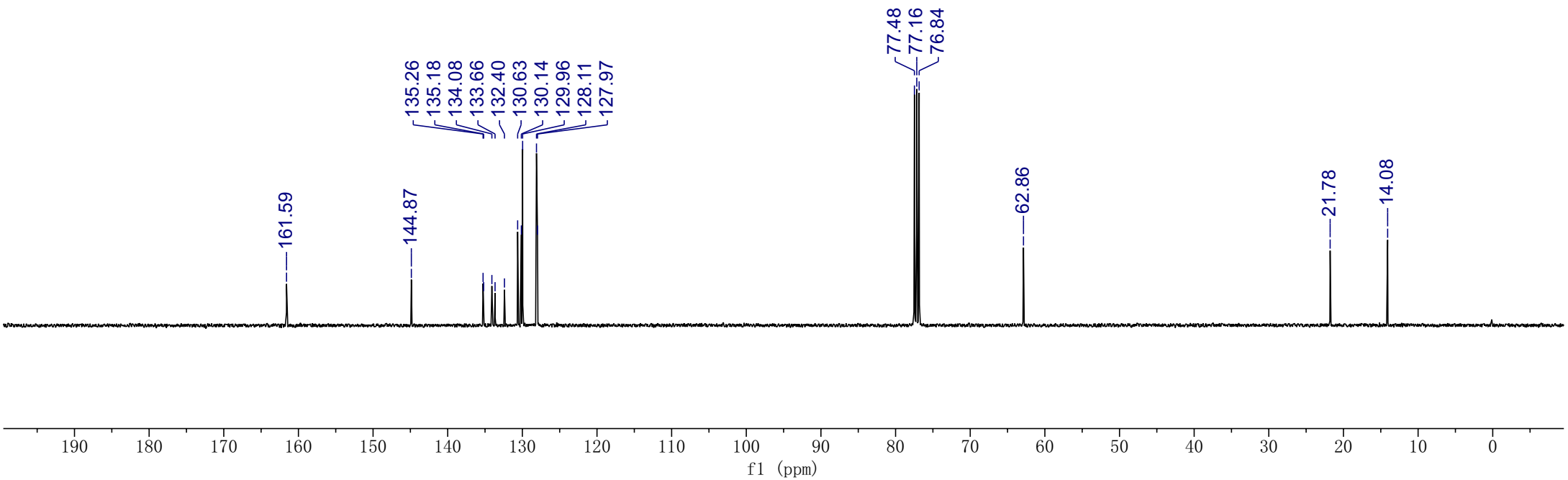
7.42
7.40
7.38
7.38
7.36
7.35
7.34
7.32
7.26
4.39
4.37
4.35
4.33
4.33
2.43
1.36
1.34
1.32
0.93
1.96
0.92
4.02
1.99
2.92
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


NNHTs
Cl
Cl
CO2Et

2H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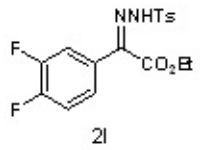
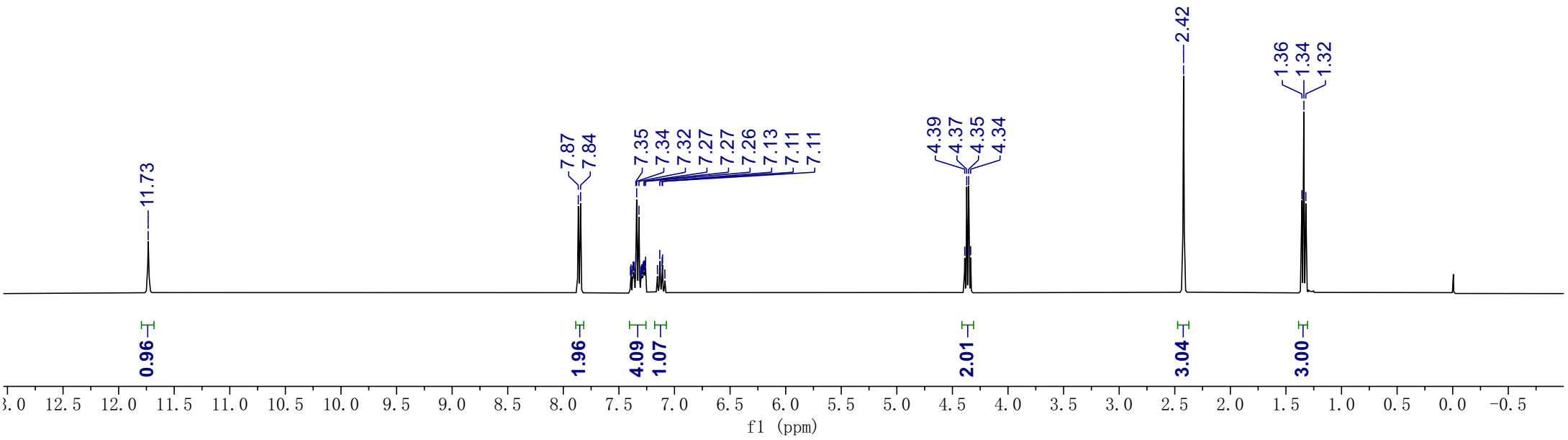
133.66
132.40
130.63
130.14
129.96
128.11
127.97
77.48
77.16
76.84
62.86
21.78
14.08
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NNHTs
F
F
CO2Et

2l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7.27
7.26
7.13
7.11
7.11
4.39
4.37
4.35
4.34
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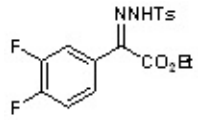
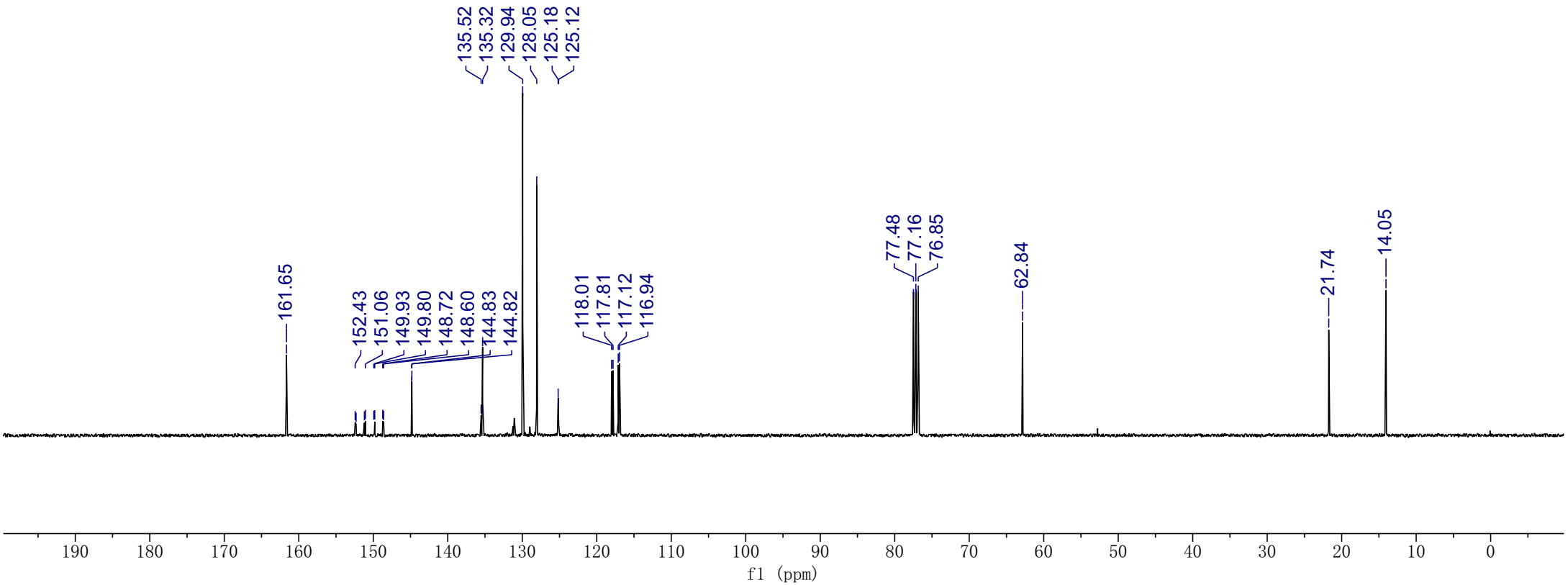
1.36
1.34
1.32
0.96
1.96
4.09
1.07
2.01
3.04
3.00
f1 (ppm)


NNHTs
F
F
CO2Et

2l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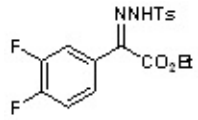
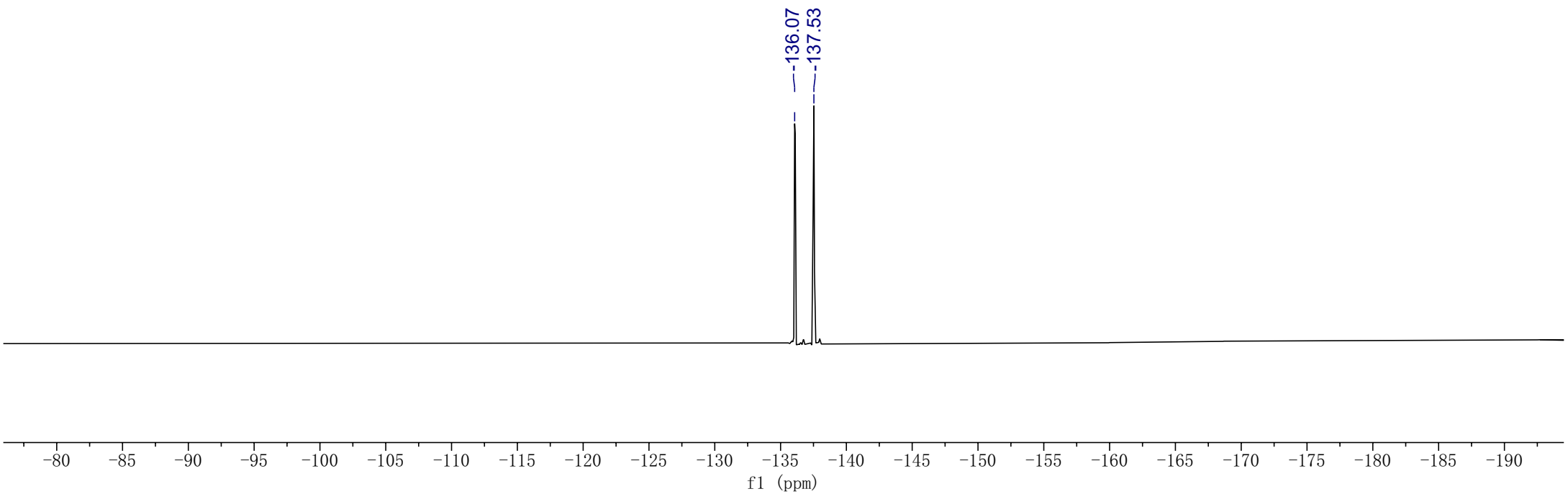
149.93
149.80
148.72
148.60
144.83
144.82
135.52
135.32
129.94
128.05
125.18
125.12
118.01
117.81
117.12
116.94
77.48
77.16
76.85
62.84
21.74
14.05
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NNHTs
F
CO2Et
F

2l


136.07
137.53
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
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-150
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-160
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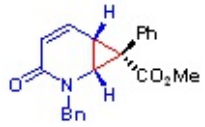
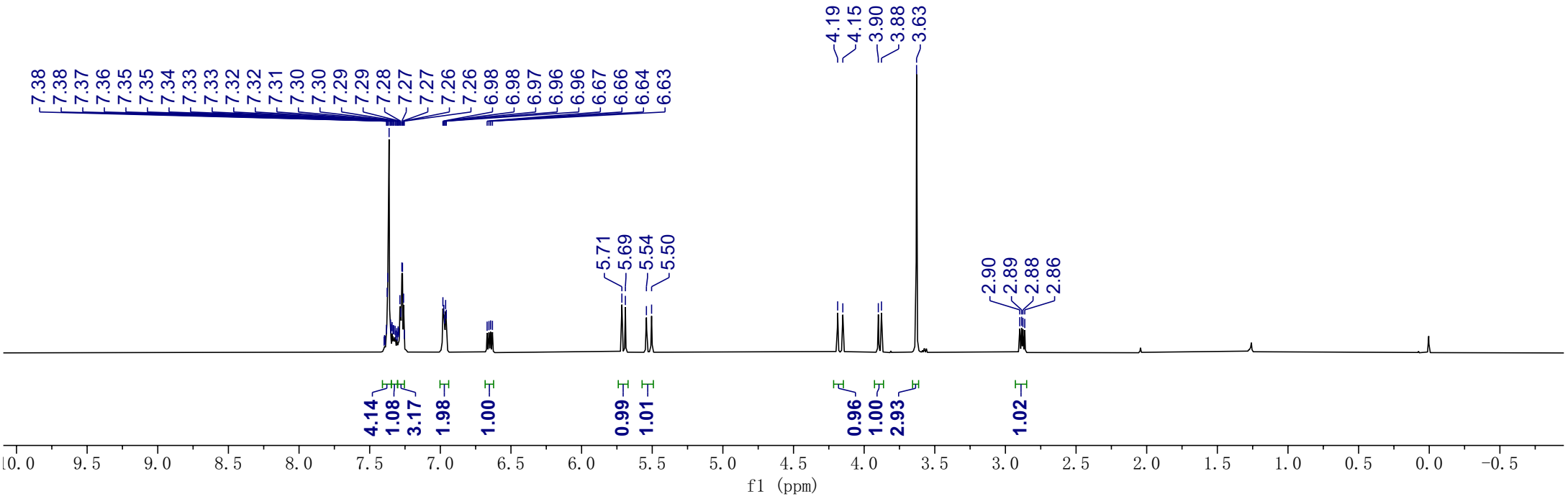
-175
-180
-185
-190
f1 (ppm)


H
Ph
O
N
CO2Me
H
Bn

3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7.38
7.37
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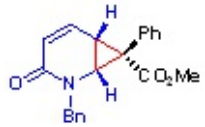
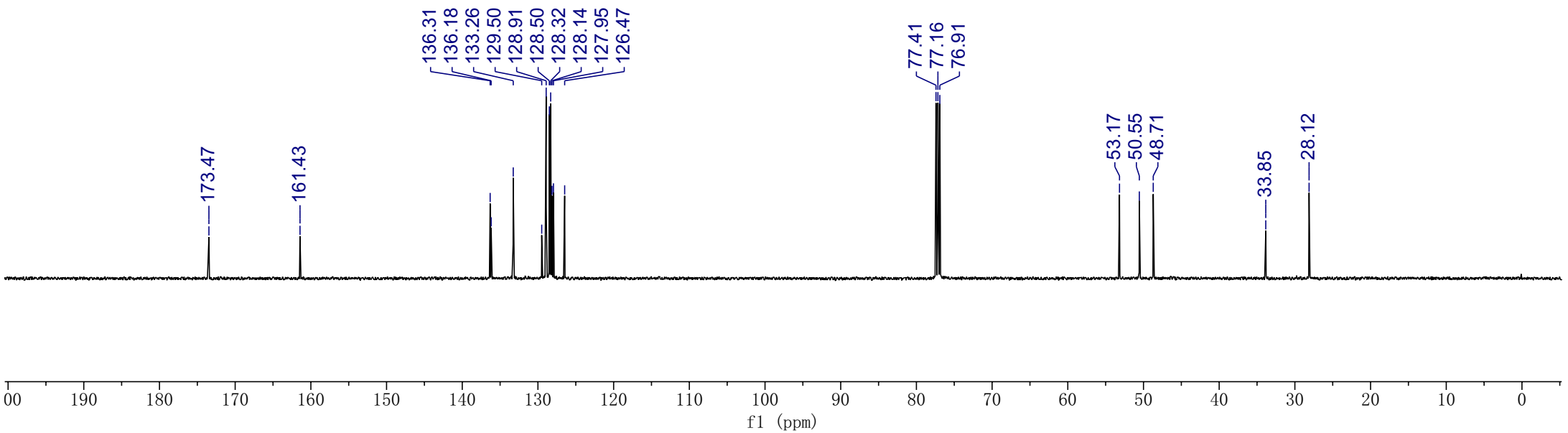
7.35
7.34
7.33
7.33
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.26
6.98
6.98
6.97
6.96
6.96
6.67
6.66
6.64
6.63
5.71
5.69
5.54
5.50
4.19
4.15
3.90
3.88
3.63
2.90
2.89
2.88
2.86
4.14
1.08
3.17
1.98
1.00
0.99
1.01
0.96
1.00
2.93
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
Ph
O
N
H
CO2Me
Bn

3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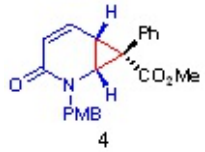
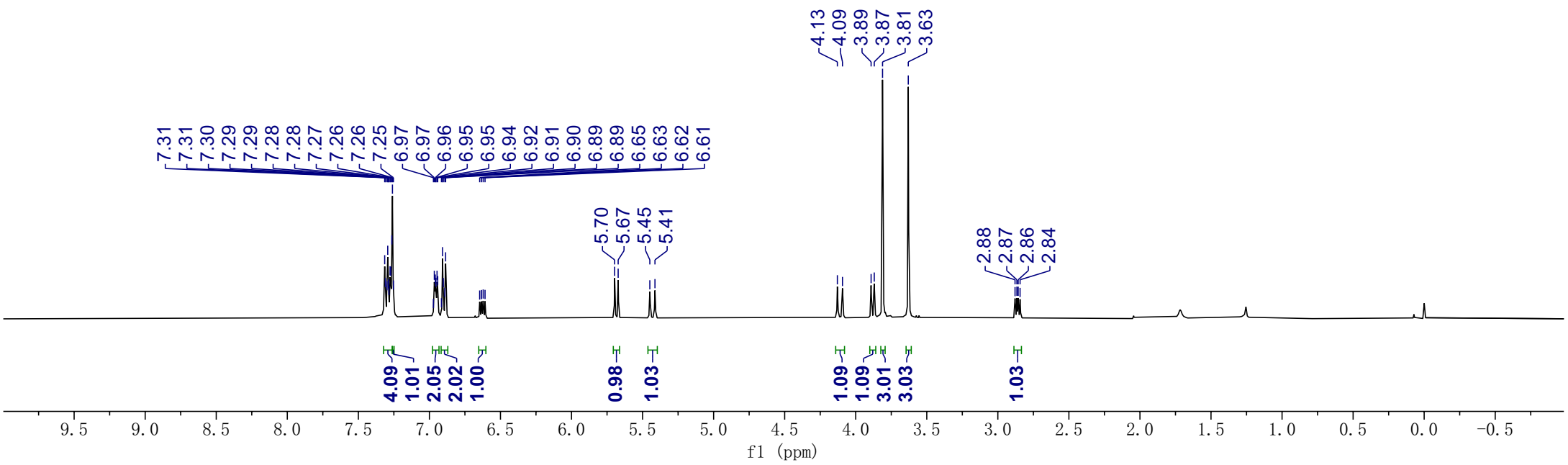
133.26
129.50
128.91
128.50
128.32
128.14
127.95
126.47
77.41
77.16
76.91
173.47
161.43
53.17
50.55
48.71
33.85
28.12
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
O
N
CO2Me
H
PMB

4


7.31
7.31
7.30
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7.29
7.28
7.28
7.27
7.26
7.26
7.25
6.97
6.97
6.96
6.95
6.95
6.94
6.92
6.91
6.90
6.89
6.89
6.65
6.63
6.62
6.61
5.70
5.67
5.45
5.41
4.13
4.09
3.89
3.87
3.81
3.63
2.88
2.87
2.86
2.84
4.09
1.01
2.05
2.02
1.00
0.98
1.03
1.09
1.09
3.01
3.03
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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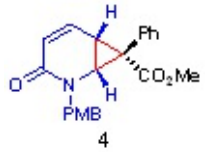
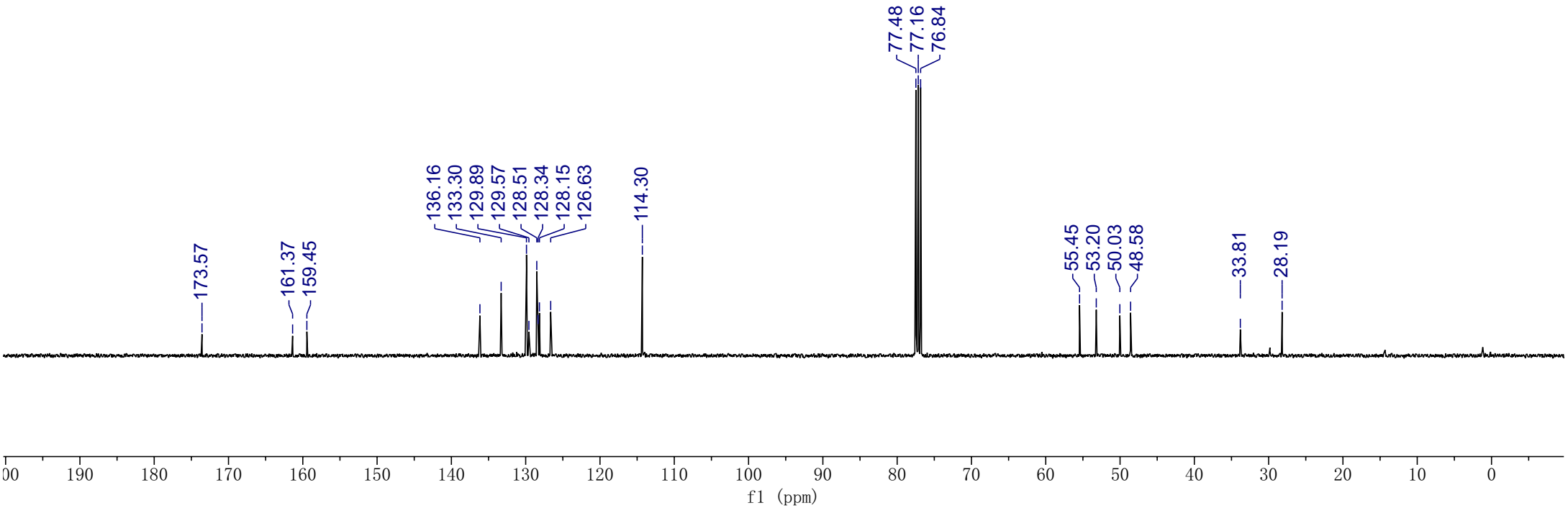
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
Ph
CO2Me
O
N
H
PMB

4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129.89
129.57
128.51
128.34
128.15
126.63
114.30
77.48
77.16
76.84
55.45
53.20
50.03
48.58
33.81
28.19
190
180
170
160
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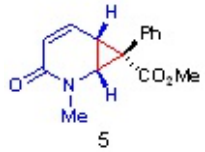
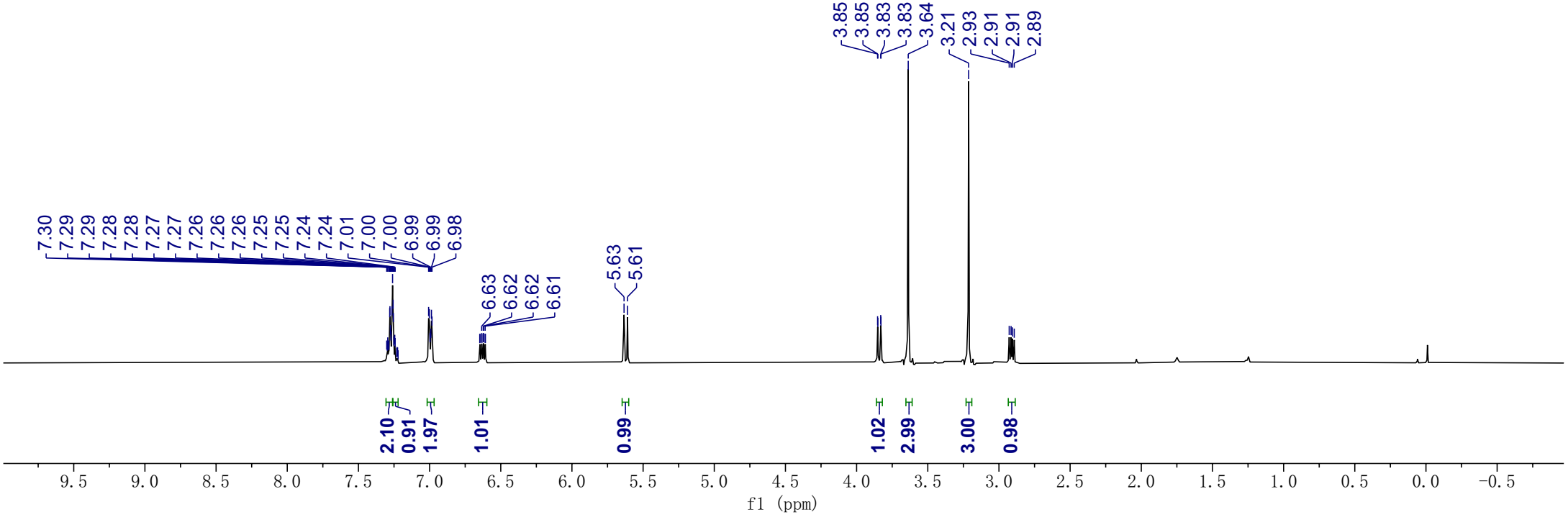
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
O
N
Me
H
CO2Me

5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7.28
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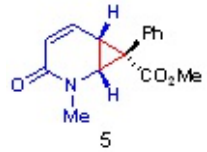
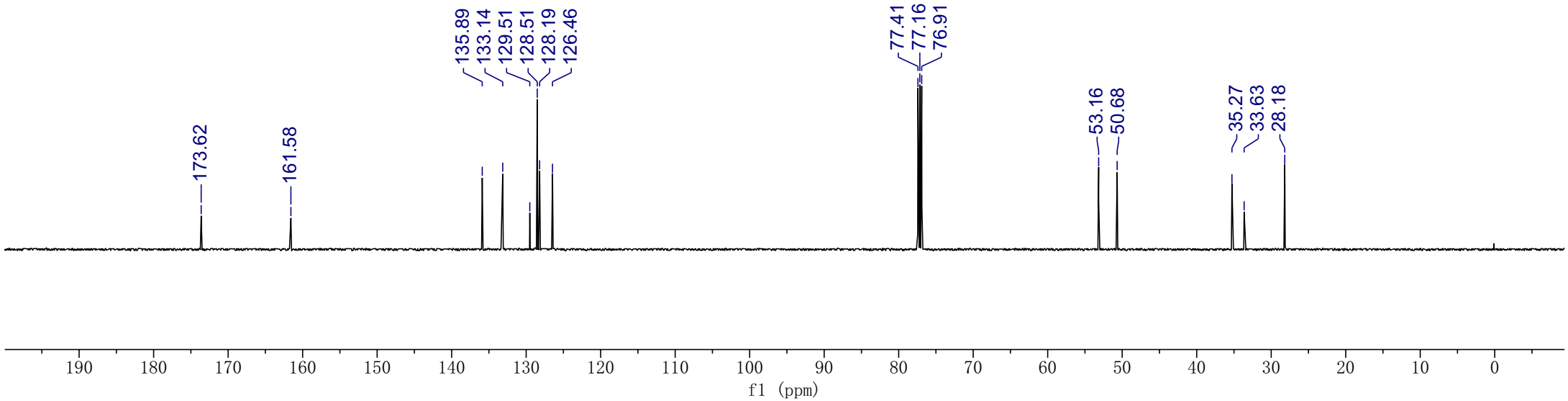
7.27
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.24
7.01
7.00
7.00
6.99
6.99
6.98
6.63
6.62
6.62
6.61
5.63
5.61
3.85
3.85
3.83
3.83
3.64
3.21
2.93
2.91
2.91
2.89
2.10
0.91
1.97
1.01
0.99
1.02
2.99
3.00
0.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


H
Ph
O
N
Me
H
CO2Me

5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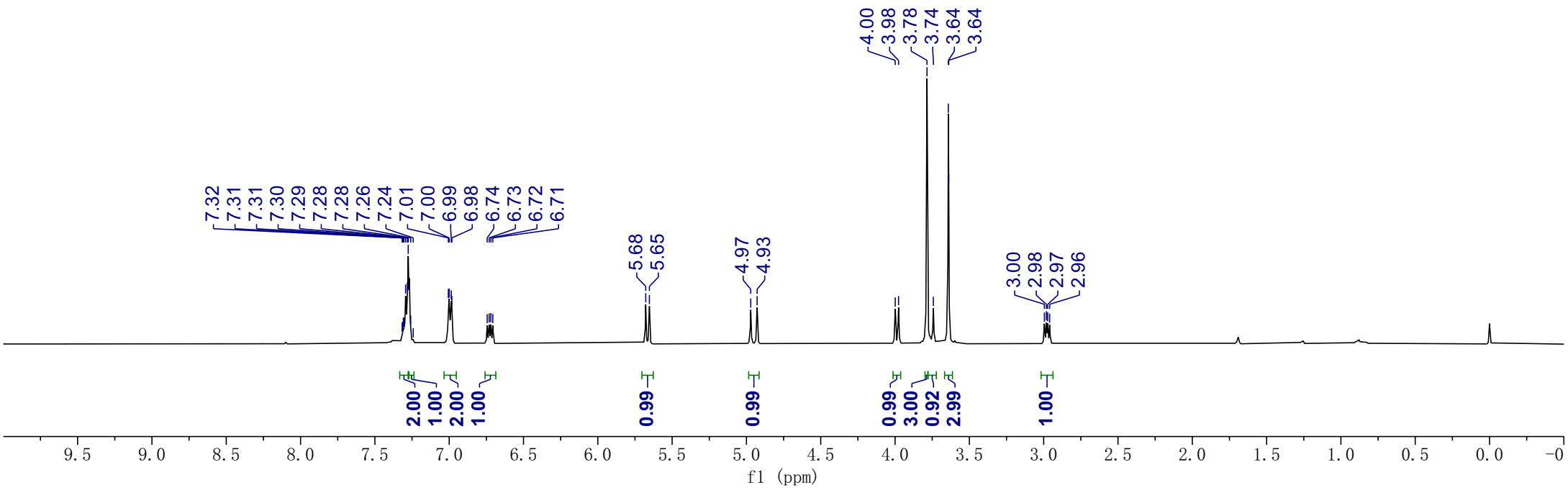
126.46
77.41
77.16
76.91
53.16
50.68
35.27
33.63
28.18
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
O
N
H
CO2Me
CO2Me

6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7.29
7.28
7.28
7.26
7.24
7.01
7.00
6.99
6.98
6.74
6.73
6.72
6.71
5.68
5.65
4.97
4.93
4.00
3.98
3.78
3.74
3.64
3.64
3.00
2.98
2.97
2.96
2.00
1.00
2.00
1.00
0.99
0.99
0.99
3.00
0.92
2.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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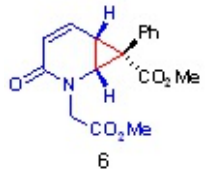
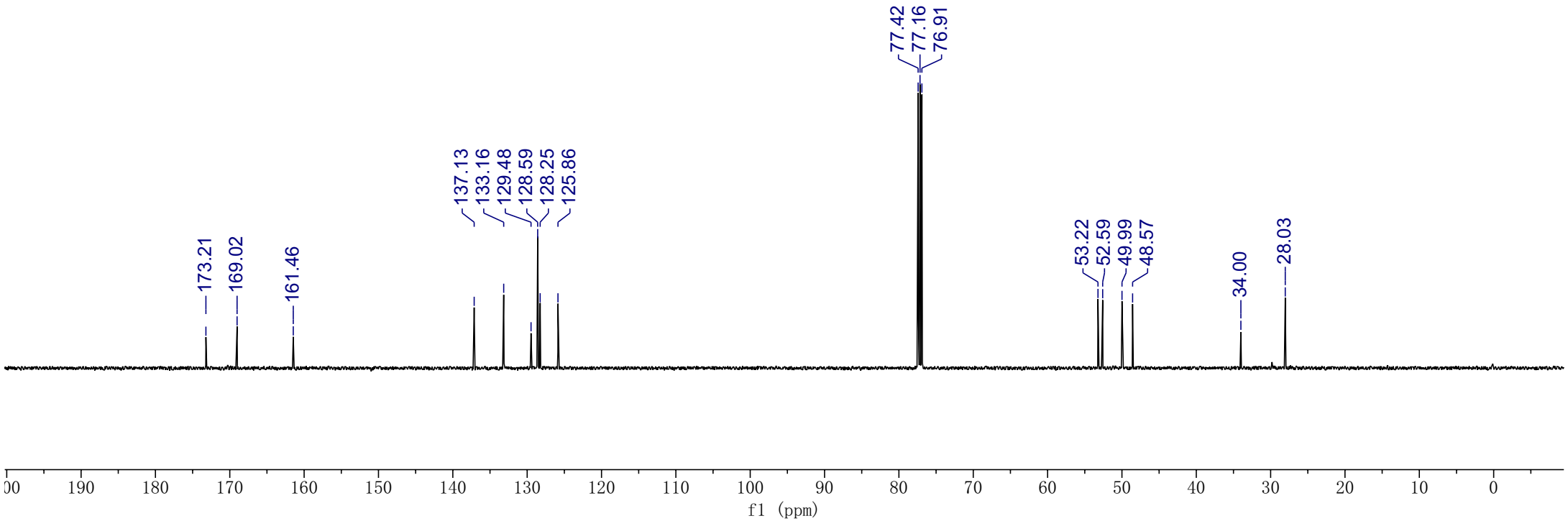
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


H
Ph
O
N
H
CO2Me
CO2Me

6


173.21
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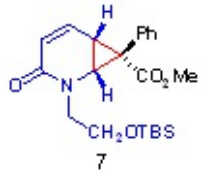
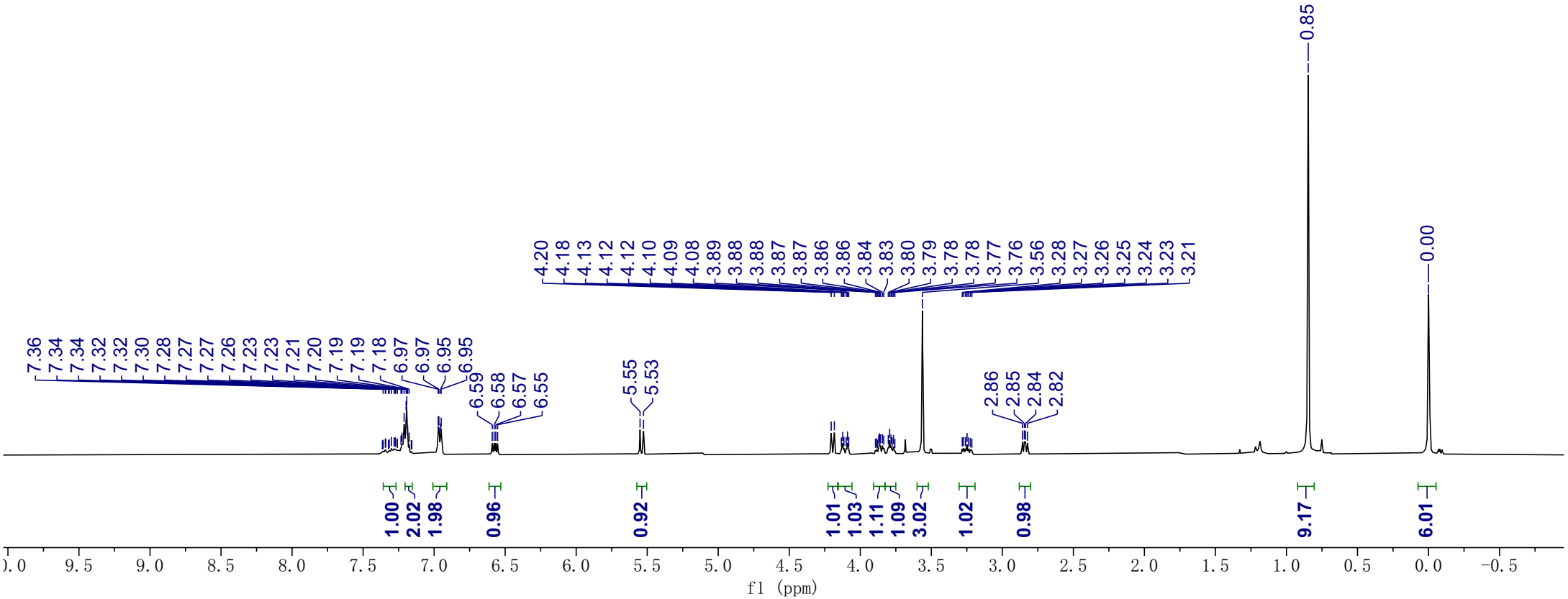
129.48
128.59
128.25
125.86
77.42
77.16
76.91
53.22
52.59
49.99
48.57
34.00
28.03
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
H
CH2OTBS

7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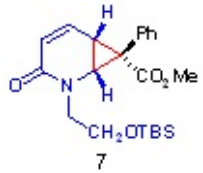
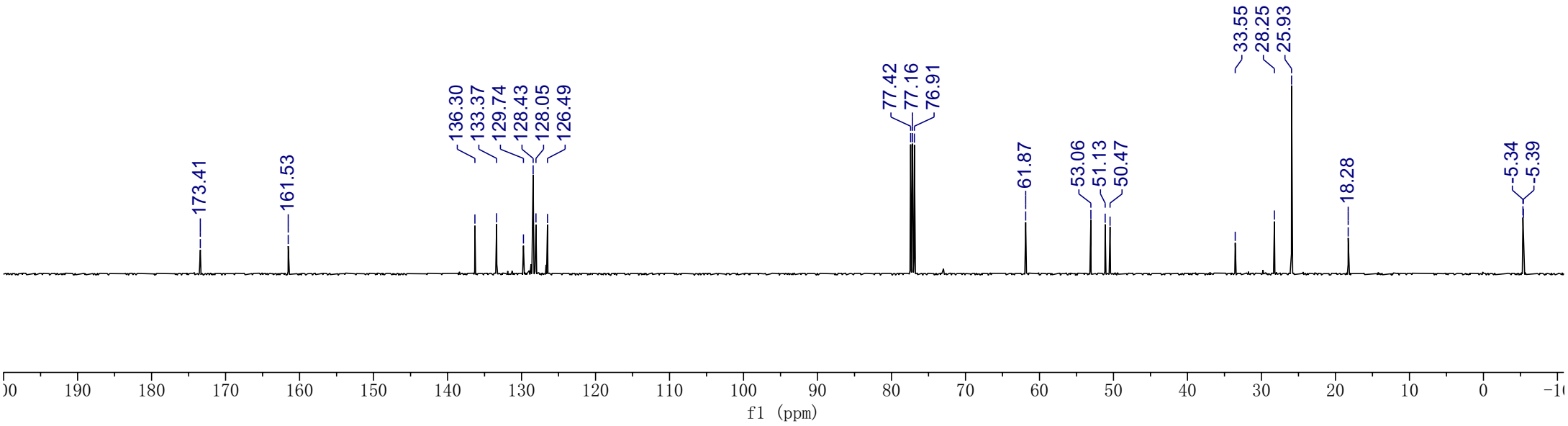
7.26
7.23
7.23
7.21
7.20
7.19
7.19
7.18
6.97
6.97
6.95
6.95
6.59
6.58
6.57
6.55
5.55
5.53
4.20
4.18
4.13
4.12
4.12
4.10
4.09
4.08
3.89
3.88
3.88
3.87
3.87
3.86
3.86
3.84
3.83
3.80
3.79
3.78
3.78
3.77
3.76
3.56
3.28
3.27
3.26
3.25
3.24
3.23
3.21
2.86
2.85
2.84
2.82
0.85
0.00
1.00
2.02
1.98
0.96
0.92
1.01
1.03
1.11
1.09
3.02
1.02
0.98
9.17
6.01
f1 (ppm)


H
Ph
O
N
CO2Me
H
CH2OTBS

7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129.74
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77.16
76.91
61.87
53.06
51.13
50.47
33.55
28.25
25.93
18.28
-5.34
-5.39
190
180
170
160
150
140
130
120
110
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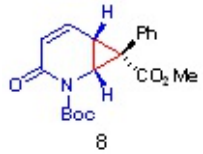
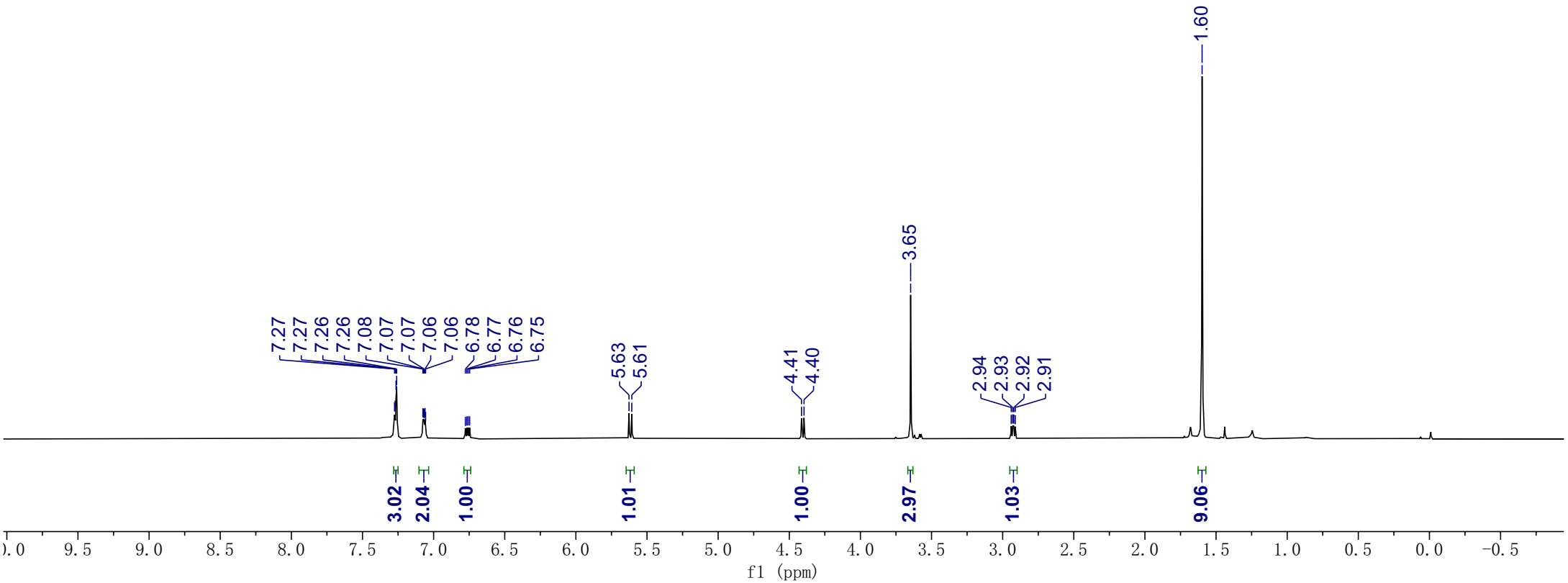
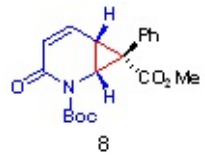
f1 (ppm)

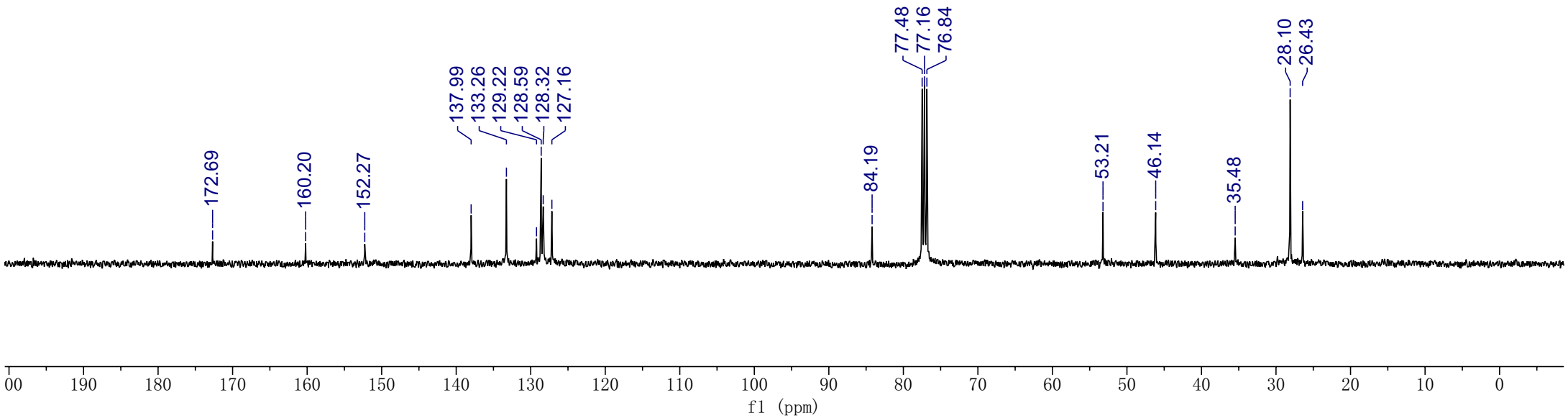

H
Ph
CO2Me
O
N
H
Boc

8


7.27
7.27
7.26
7.26
7.08
7.07
7.07
7.06
7.06
6.78
6.77
6.76
6.75
5.63
5.61
4.41
4.40
3.65
2.94
2.93
2.92
2.91
1.60
3.02
2.04
1.00
1.01
1.00
2.97
1.03
9.06
f1 (ppm)


H
Ph
O
N
H
CO2Me
Boc

8


172.69
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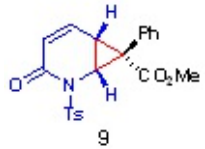
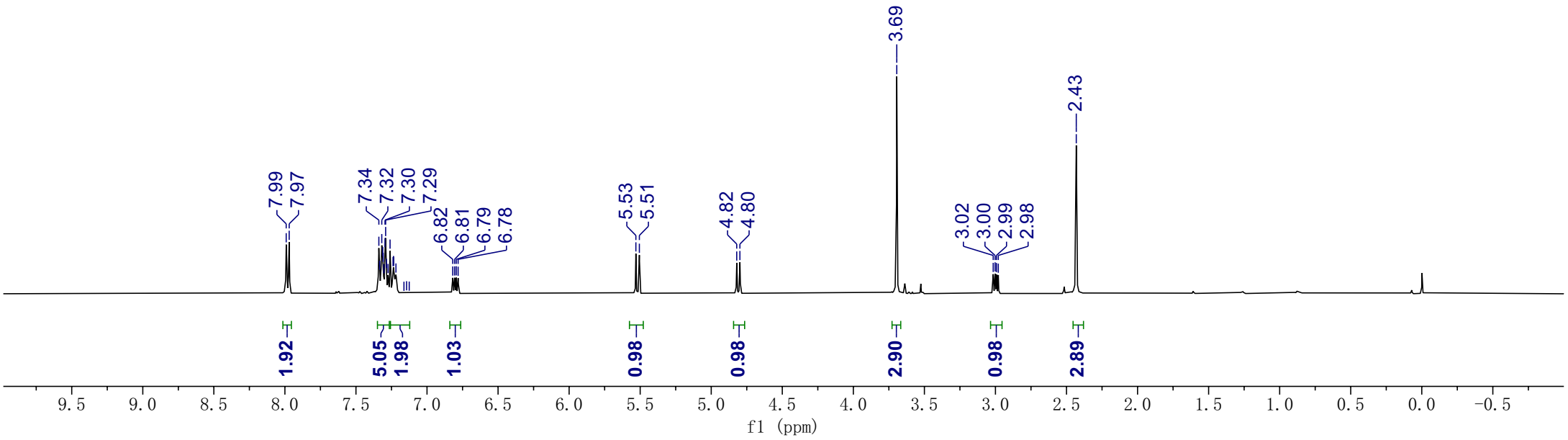
129.22
128.59
128.32
127.16
84.19
77.48
77.16
76.84
53.21
46.14
35.48
28.10
26.43
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
Ts
H

9


7.99
7.97
7.34
7.32
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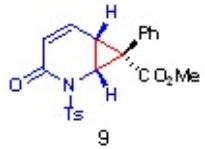
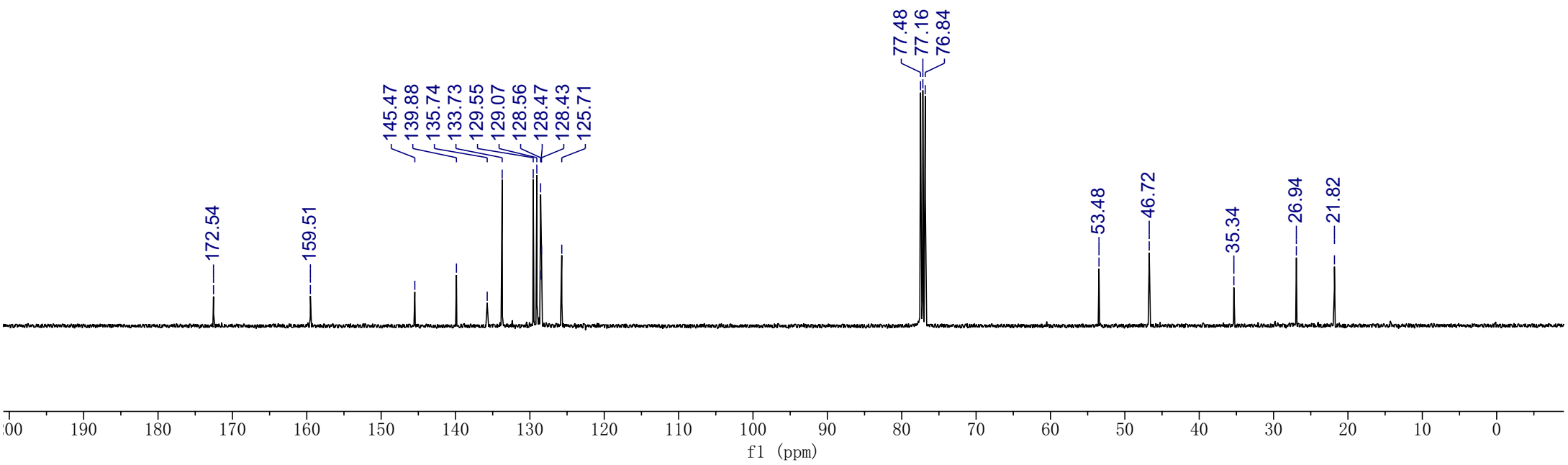
7.29
6.82
6.81
6.79
6.78
5.53
5.51
4.82
4.80
3.69
3.02
3.00
2.99
2.98
2.43
1.92
5.05
1.98
1.03
0.98
0.98
2.90
0.98
2.89
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
Ph
CO2Me
O
N
Ts
H

9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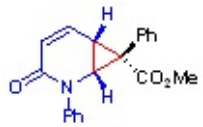
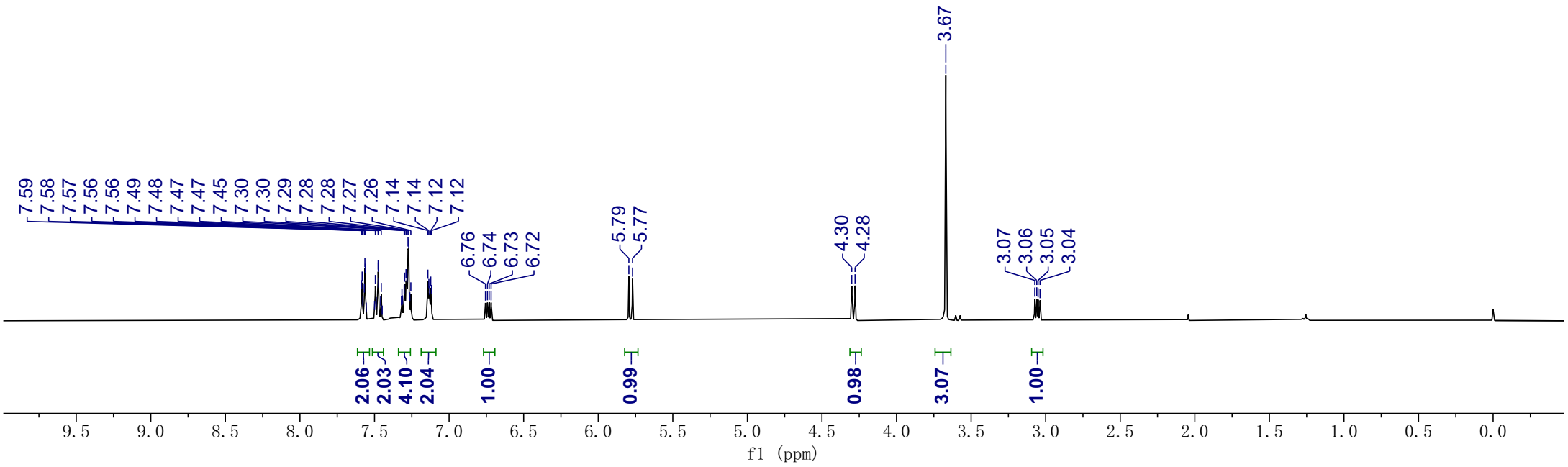
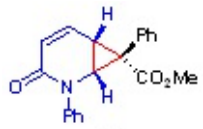
135.74
133.73
129.55
129.07
128.56
128.47
128.43
125.71
77.48
77.16
76.84
53.48
46.72
35.34
26.94
21.82
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

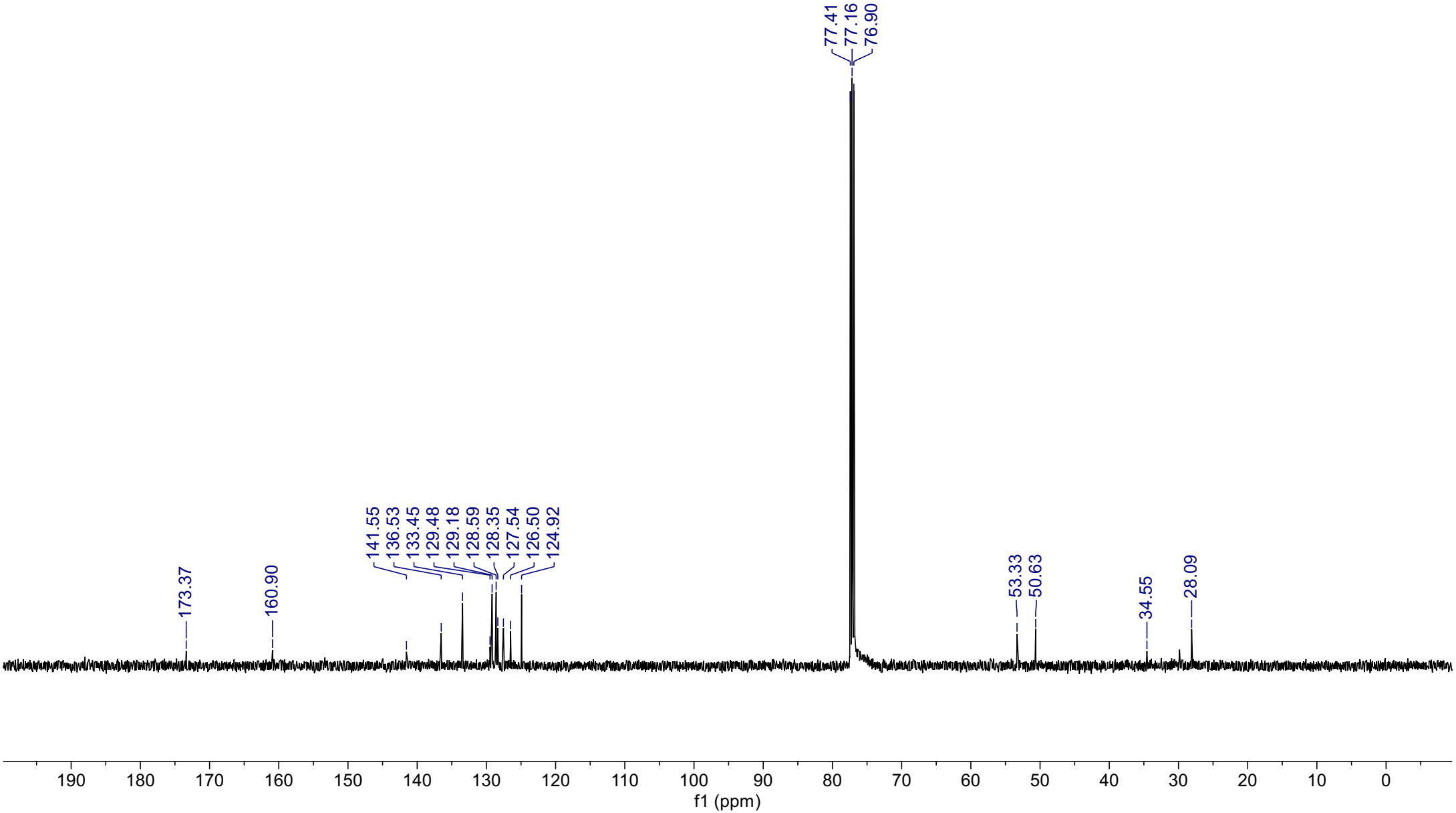

H
Ph
O
N
CO2Me
H
Ph

10


7.59
7.58
7.57
7.56
7.56
7.49
7.48
7.47
7.47
7.45
7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.14
7.14
7.12
7.12
6.76
6.74
6.73
6.72
5.79
5.77
4.30
4.28
3.67
3.07
3.06
3.05
3.04
2.06
2.03
4.10
2.04
1.00
0.99
0.98
3.07
1.00
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)


H
Ph
CO2Me
O
N
H
Ph

10


77.41
77.16
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173.37
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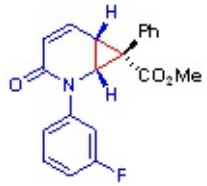
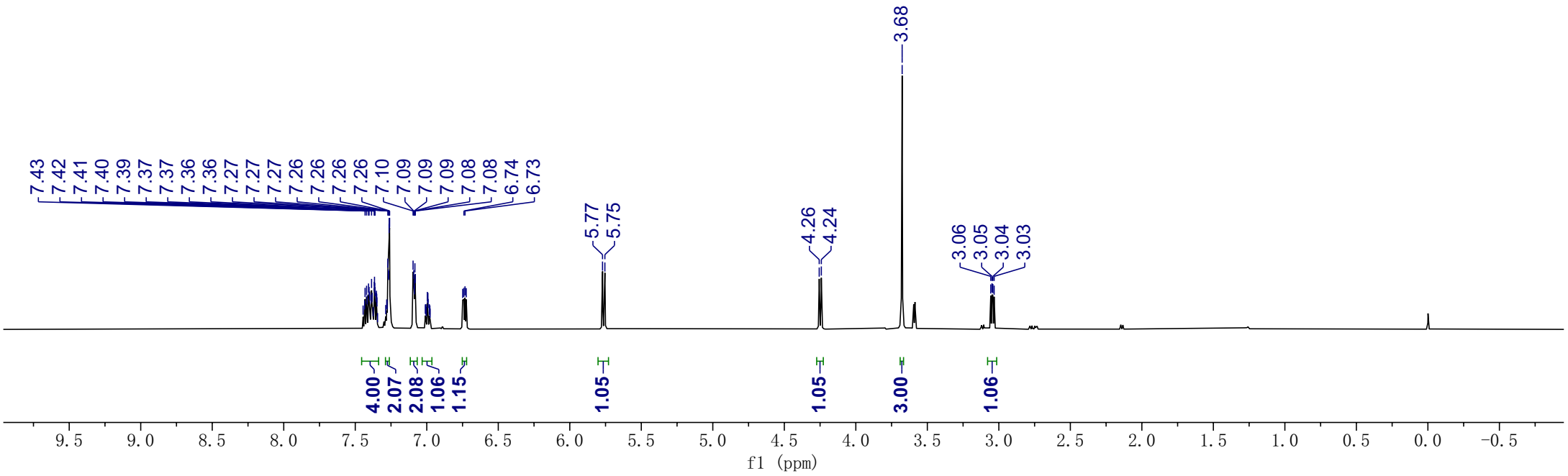
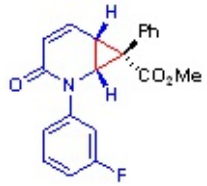
141.55
136.53
133.45
129.48
129.18
128.59
128.35
127.54
126.50
124.92
53.33
50.63
34.55
28.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

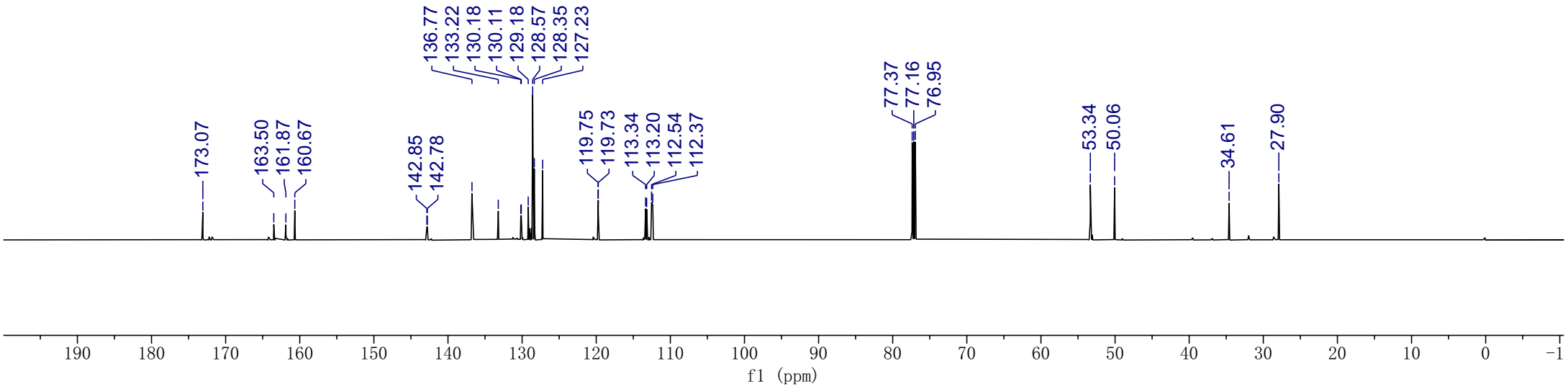

H
Ph
O
N
CO2Me
H
F

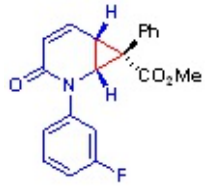
11


7.43
7.42
7.41
7.40
7.39
7.37
7.37
7.36
7.36
7.27
7.27
7.27
7.26
7.26
7.26
7.26
7.10
7.09
7.09
7.09
7.08
7.08
6.74
6.73
5.77
5.75
4.26
4.24
3.68
3.06
3.05
3.04
3.03
4.00
2.07
2.08
1.06
1.15
1.05
1.05
3.00
1.06
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
-0.5
f1 (ppm)

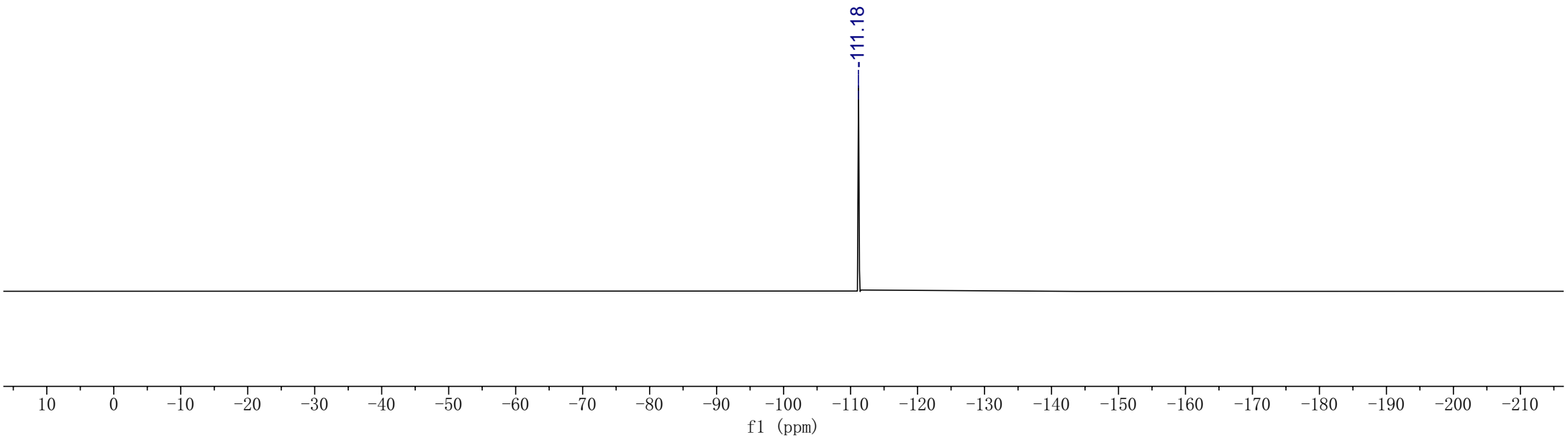

H
Ph
O
N
CO2Me
H
F

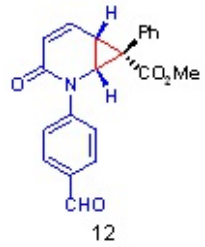
11


173.07
163.50
161.87
160.67
142.85
142.78
136.77
133.22
130.18
130.11
129.18
128.57
128.35
127.23
119.75
119.73
113.34
113.20
112.54
112.37
77.37
77.16
76.95
53.34
50.06
34.61
27.90
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

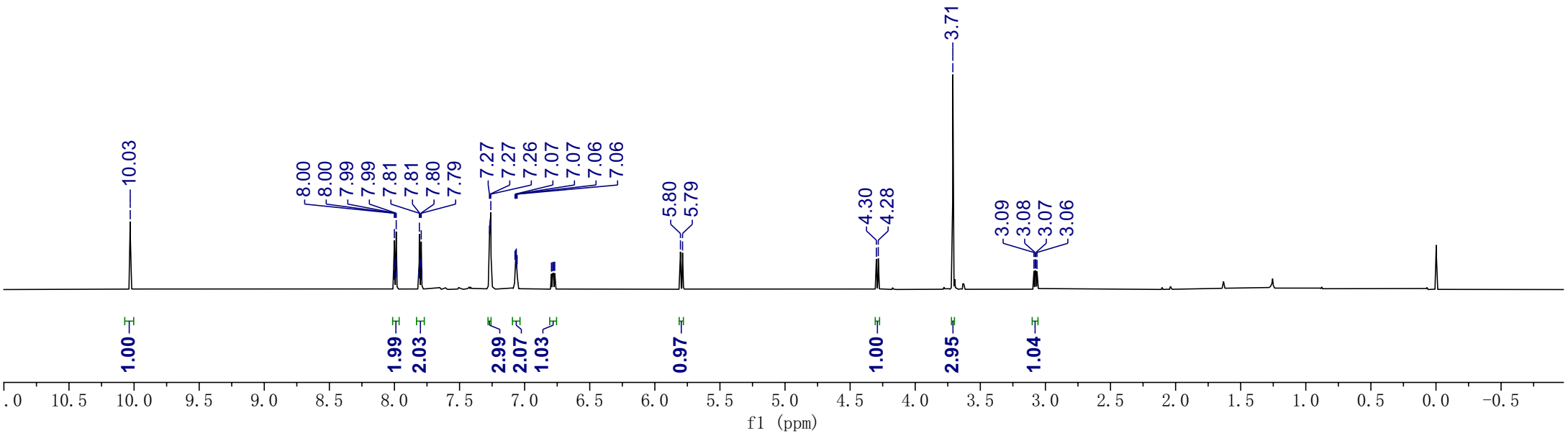

H
Ph
O
N
CO2Me
H
F

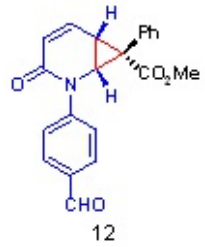
11


-111.18
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

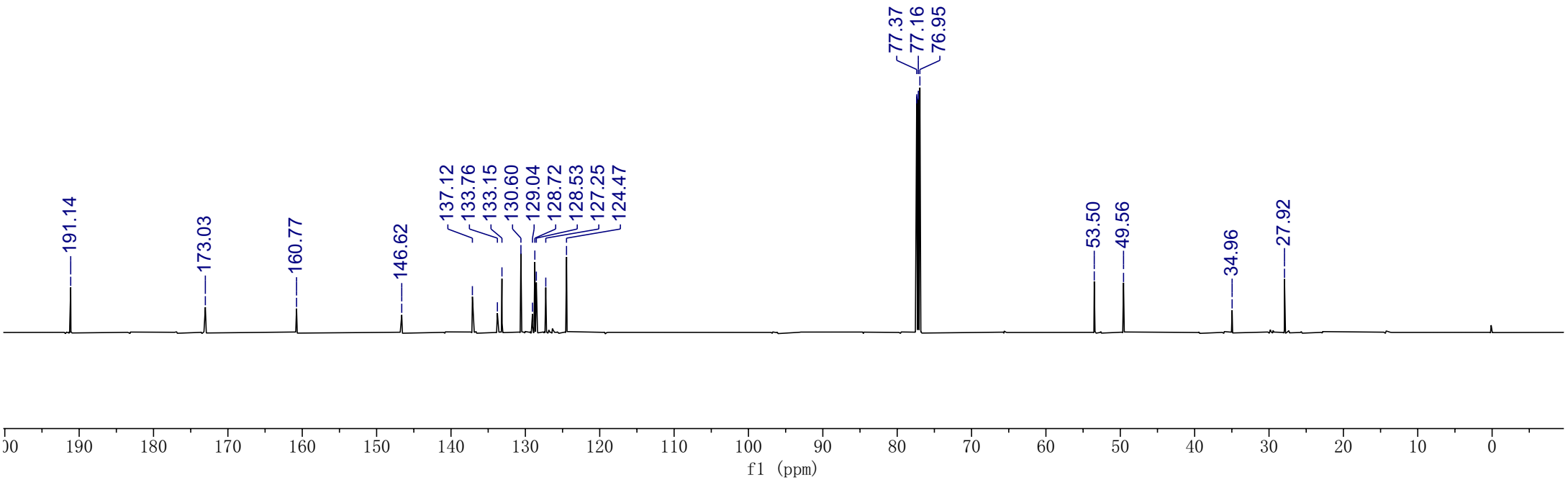

H
Ph
O
N
CO2Me
H
CHO

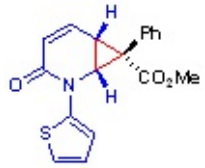
12


10.03
8.00
8.00
7.99
7.99
7.81
7.81
7.80
7.79
7.27
7.27
7.26
7.07
7.07
7.06
7.06
5.80
5.79
4.30
4.28
3.71
3.09
3.08
3.07
3.06
1.00
1.99
2.03
2.99
2.07
1.03
0.97
1.00
2.95
1.04
f1 (ppm)

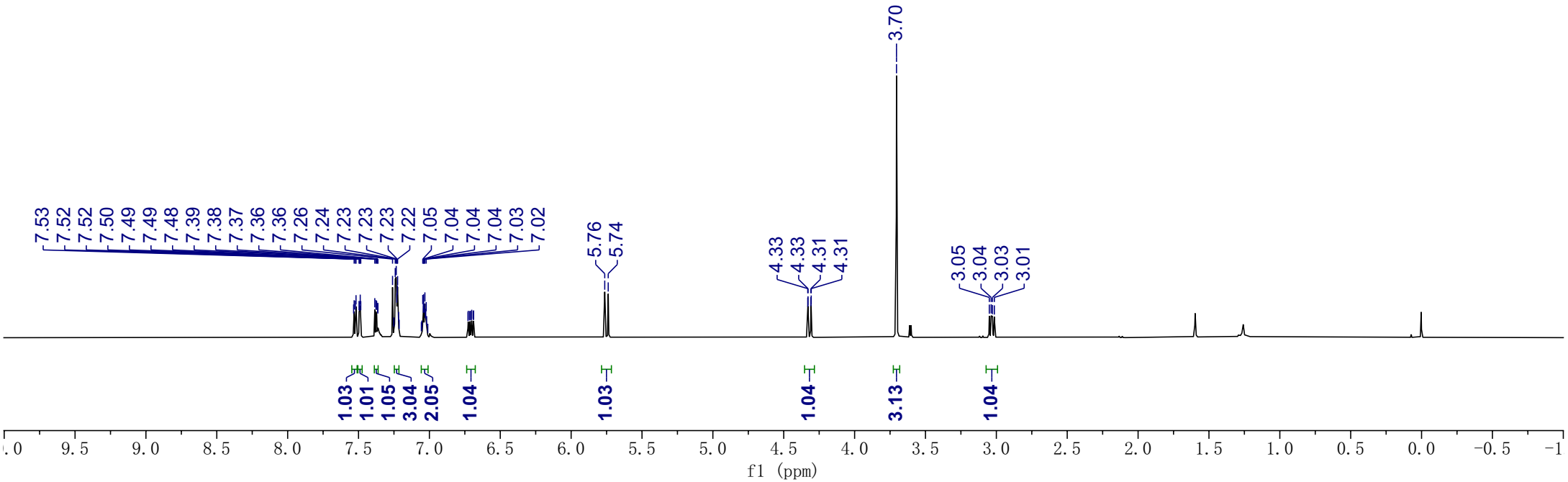

H
Ph
O
N
CO2Me
H
CHO

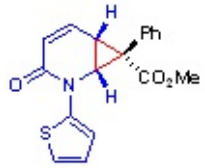
12


191.14
173.03
160.77
146.62
137.12
133.76
133.15
130.60
129.04
128.72
128.53
127.25
124.47
77.37
77.16
76.95
53.50
49.56
34.96
27.92
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

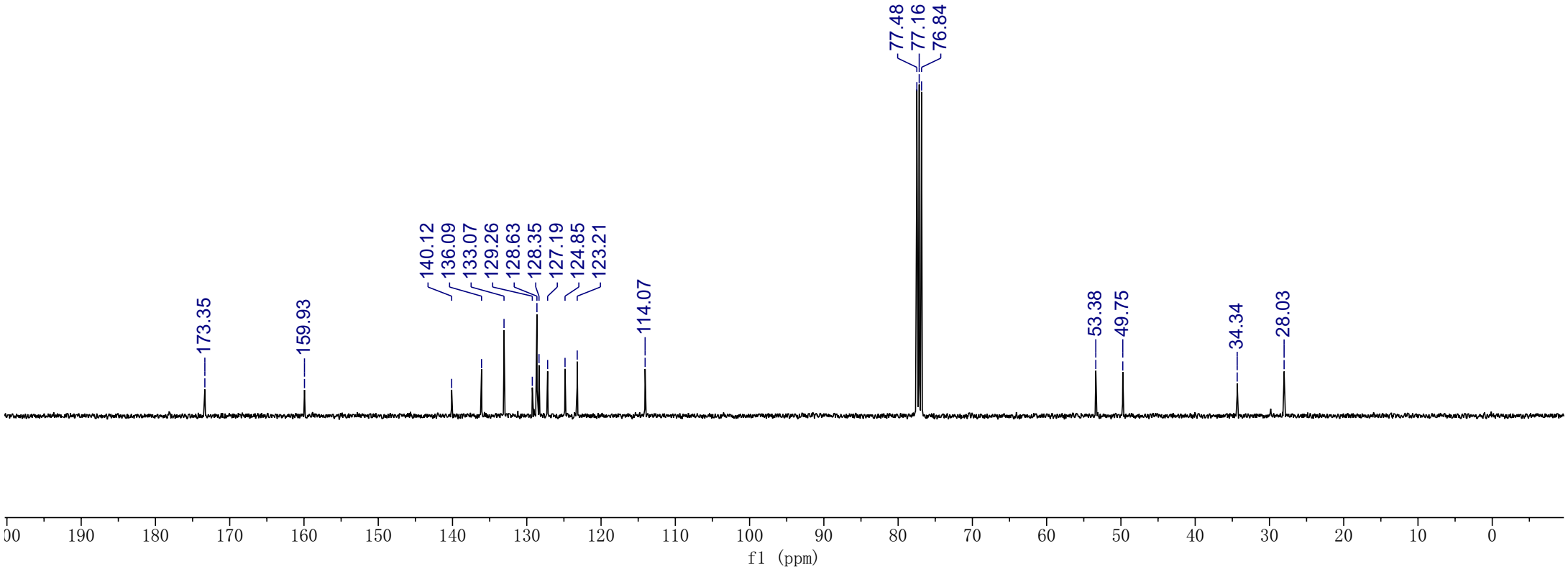

H
Ph
O
N
CO2Me
H
S

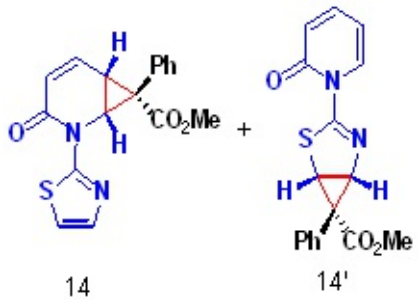
13


7.53
7.52
7.52
7.50
7.49
7.49
7.48
7.39
7.38
7.37
7.36
7.36
7.26
7.24
7.23
7.23
7.23
7.22
7.05
7.04
7.04
7.04
7.03
7.02
5.76
5.74
4.33
4.33
4.31
4.31
3.70
3.05
3.04
3.03
3.01
1.03
1.01
1.05
3.04
2.05
1.04
1.03
1.04
3.13
1.04
f1 (ppm)


H
Ph
O
N
CO2Me
H
S

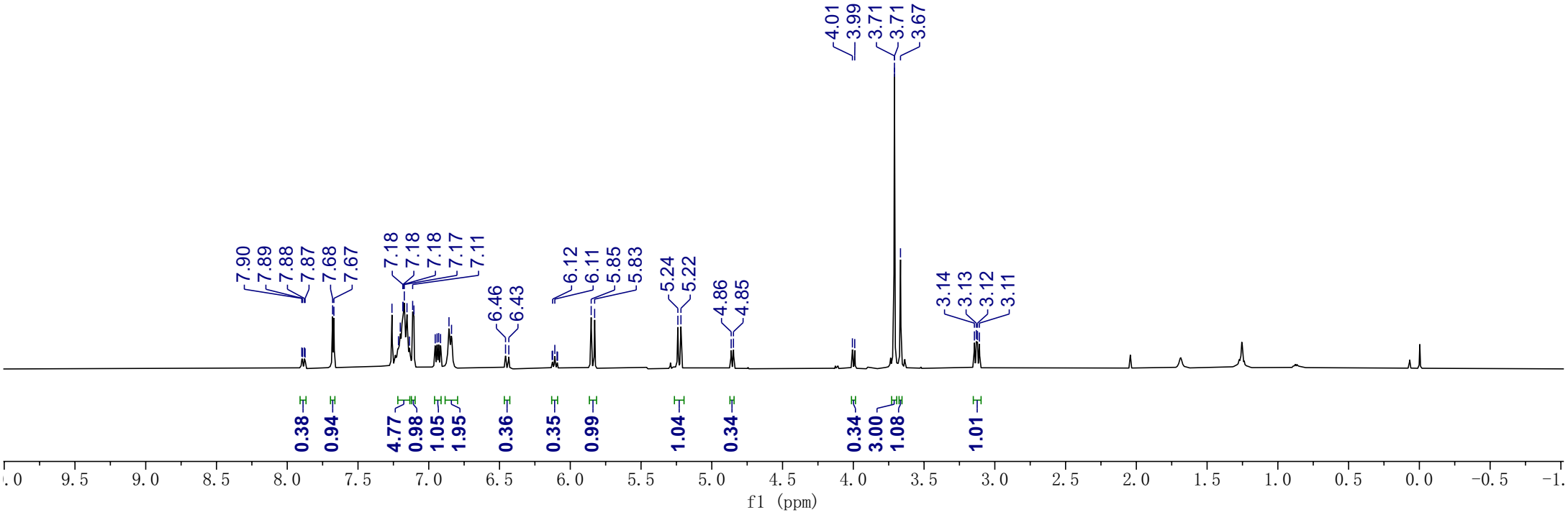
13

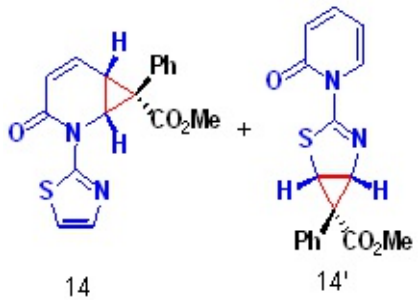

173.35
159.93
140.12
136.09
133.07
129.26
128.63
128.35
127.19
124.85
123.21
114.07
77.48
77.16
76.84
53.38
49.75
34.34
28.03
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
H
S
N
+
O
N
S
N
H
H
Ph
CO2Me

14 14'

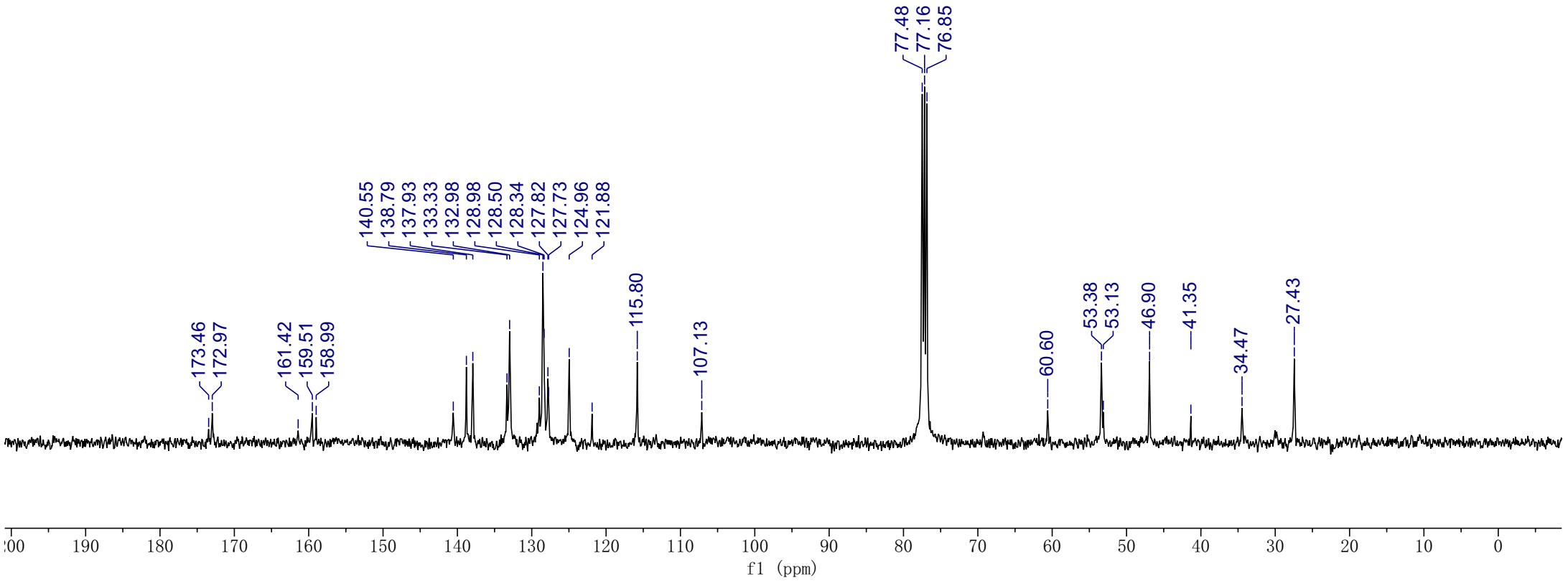
3:1

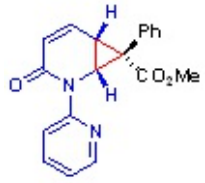

7.90
7.89
7.88
7.87
7.68
7.67
7.18
7.18
7.18
7.17
7.11
6.46
6.43
6.12
6.11
5.85
5.83
5.24
5.22
4.86
4.85
4.01
3.99
3.71
3.71
3.67
3.14
3.13
3.12
3.11
0.38
0.94
4.77
0.98
1.05
1.95
0.36
0.35
0.99
1.04
0.34
0.34
3.00
1.08
1.01
f1 (ppm)


H
Ph
CO2Me
O
N
H
S
N
+
O
N
S
N
H
H
Ph
CO2Me

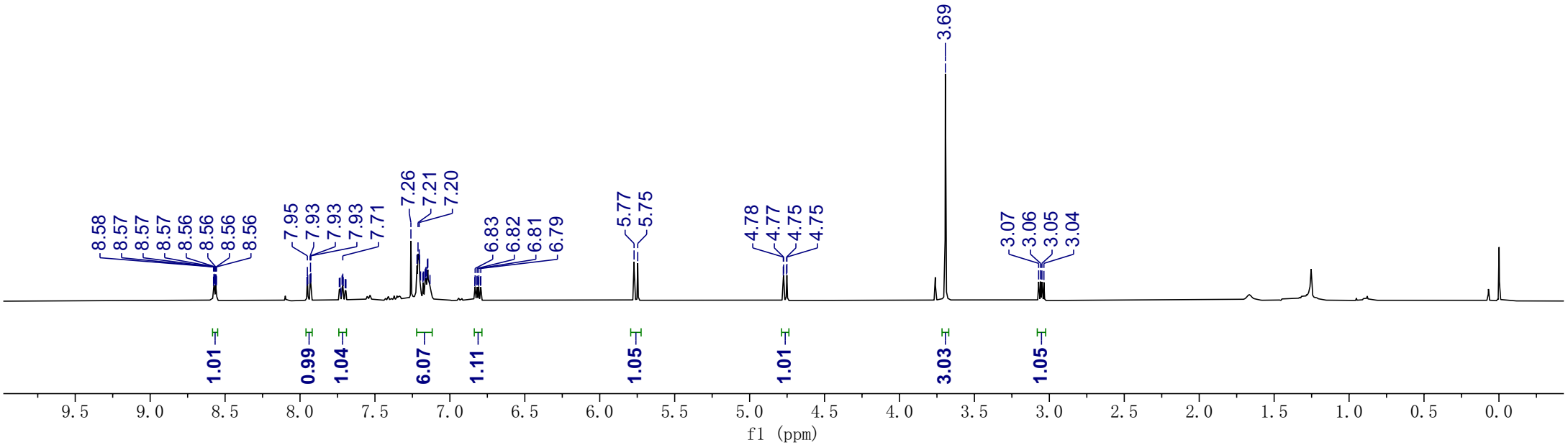
14 14'

3:1


77.48
77.16
76.85
140.55
138.79
137.93
133.33
132.98
128.98
128.50
128.34
127.82
127.73
124.96
121.88
115.80
107.13
173.46
172.97
161.42
159.51
158.99
60.60
53.38
53.13
46.90
41.35
34.47
27.43
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
O
N
H
CO2Me
N

15


8.58
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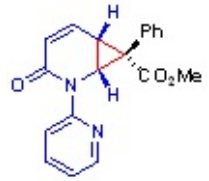
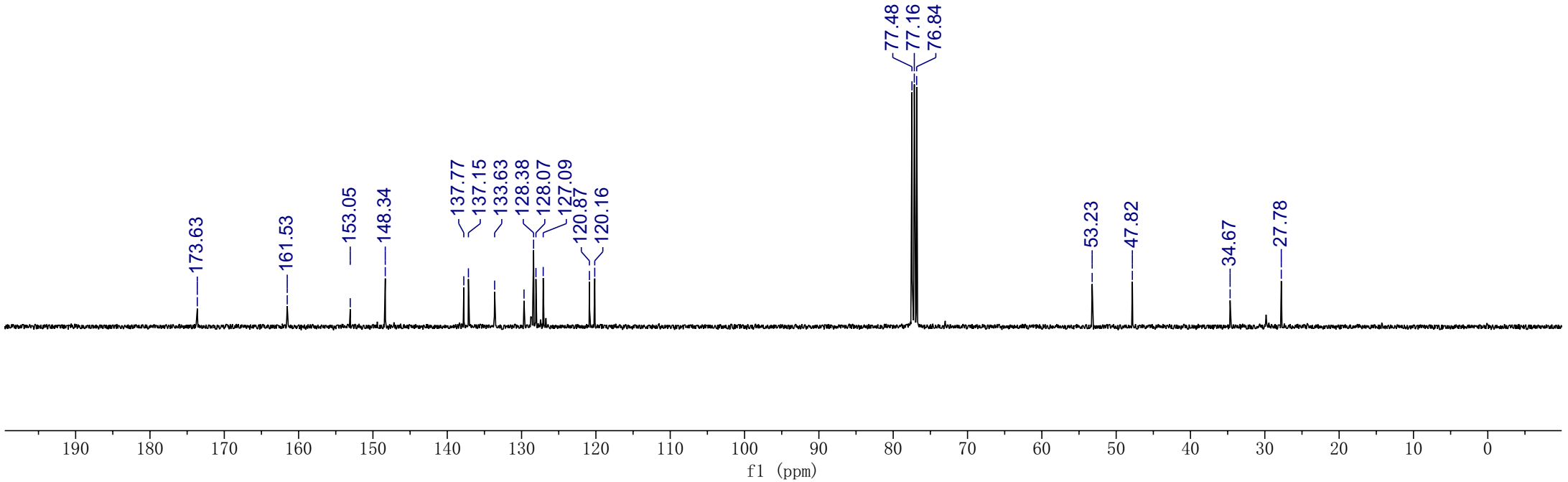
8.57
8.57
8.56
8.56
8.56
8.56
7.95
7.93
7.93
7.93
7.71
7.26
7.21
7.20
6.83
6.82
6.81
6.79
5.77
5.75
4.78
4.77
4.75
4.75
3.69
3.07
3.06
3.05
3.04
1.01
0.99
1.04
6.07
1.11
1.05
1.01
3.03
1.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H
Ph
O
N
CO2Me
H
N

15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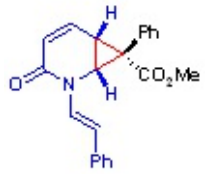
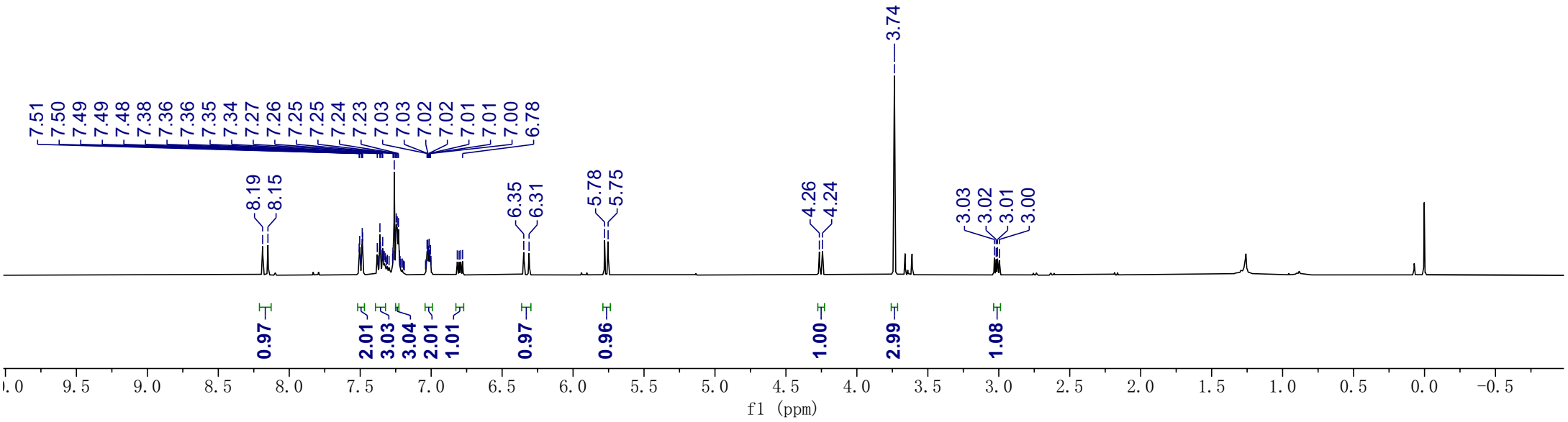
128.07
127.09
120.87
120.16
77.48
77.16
76.84
53.23
47.82
34.67
27.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
H
Ph

16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7.48
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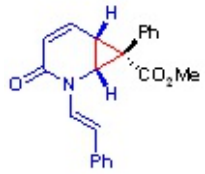
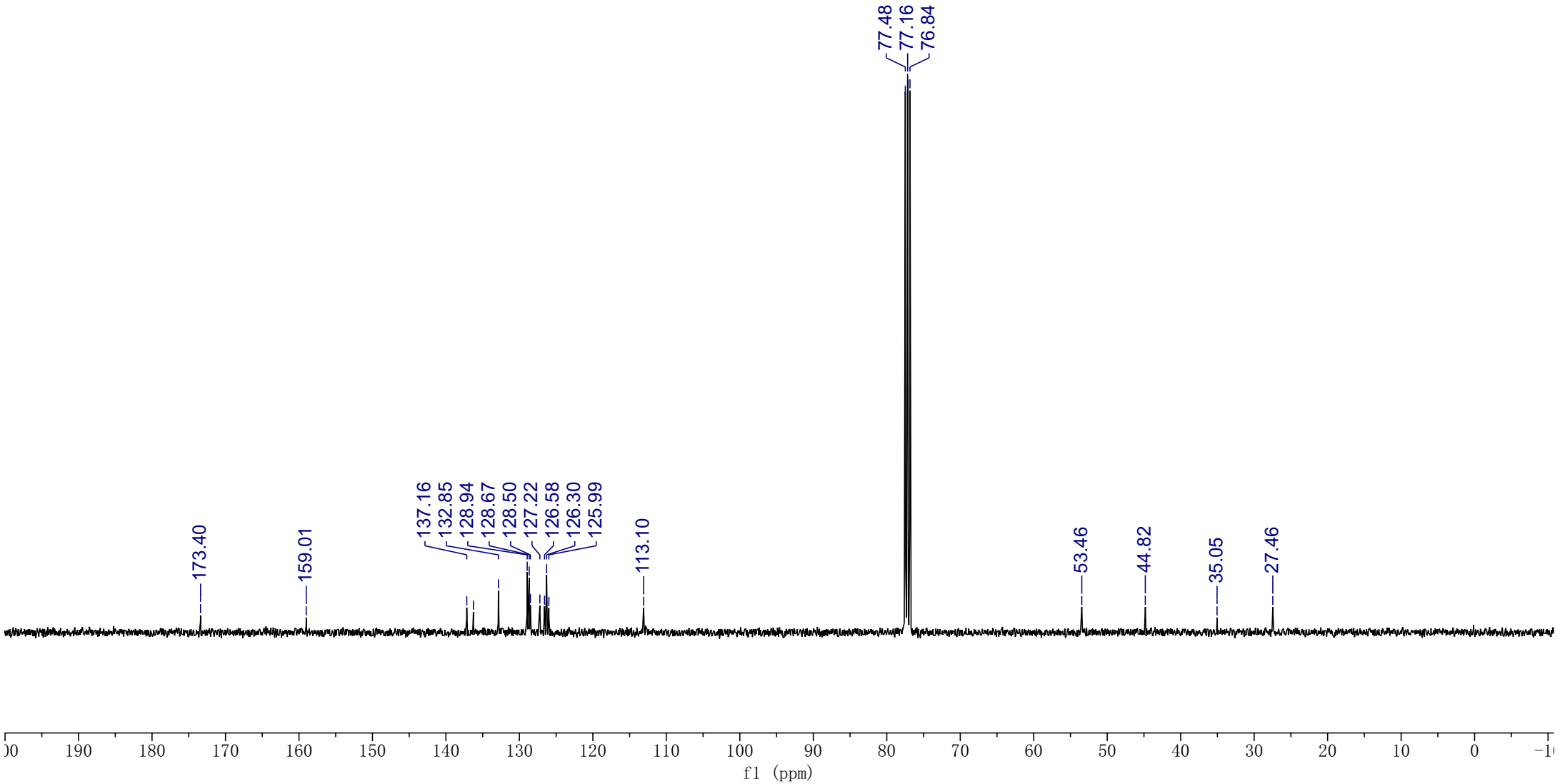
7.36
7.36
7.35
7.34
7.27
7.26
7.25
7.25
7.24
7.23
7.03
7.03
7.02
7.02
7.01
7.01
7.00
6.78
8.19
8.15
6.35
6.31
5.78
5.75
4.26
4.24
3.74
3.03
3.02
3.01
3.00
0.97
2.01
3.03
3.04
2.01
1.01
0.97
0.96
1.00
2.99
1.08
f1 (ppm)


H
Ph
CO2Me
O
N
H
Ph

16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128.94
128.67
128.50
127.22
126.58
126.30
125.99
113.10
53.46
44.82
35.05
27.46
190
180
170
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120
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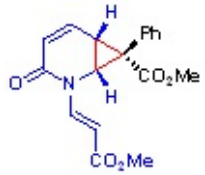
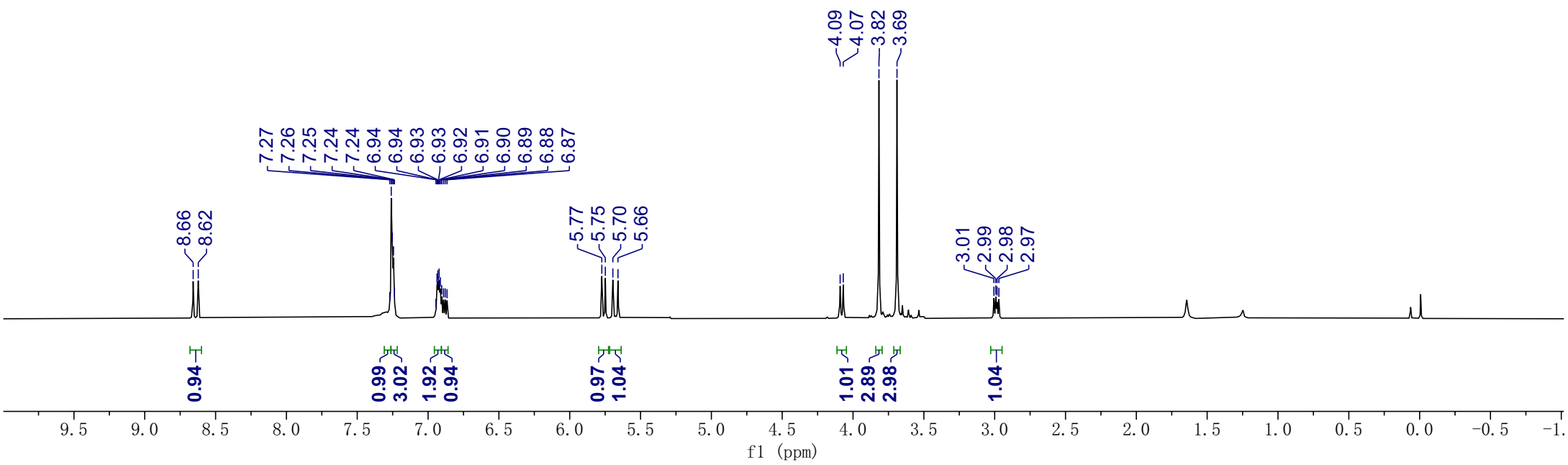
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
O
N
CO2Me
H
CO2Me

17


8.66
8.62
7.27
7.26
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7.24
7.24
6.94
6.94
6.93
6.93
6.92
6.91
6.90
6.89
6.88
6.87
5.77
5.75
5.70
5.66
4.09
4.07
3.82
3.69
3.01
2.99
2.98
2.97
0.94
0.99
3.02
1.92
0.94
0.97
1.04
1.01
2.89
2.98
1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
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1.5
1.0
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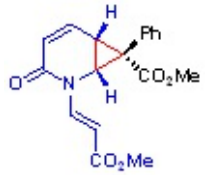
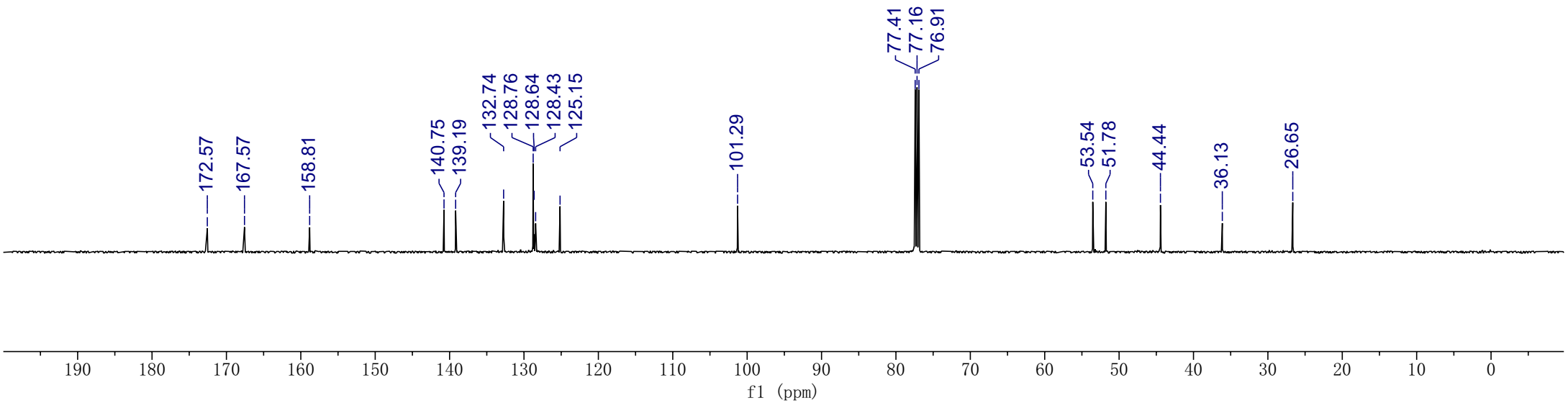
0.0
-0.5
-1.
f1 (ppm)


H
Ph
CO2Me
O
N
H
CO2Me

17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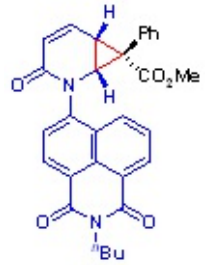
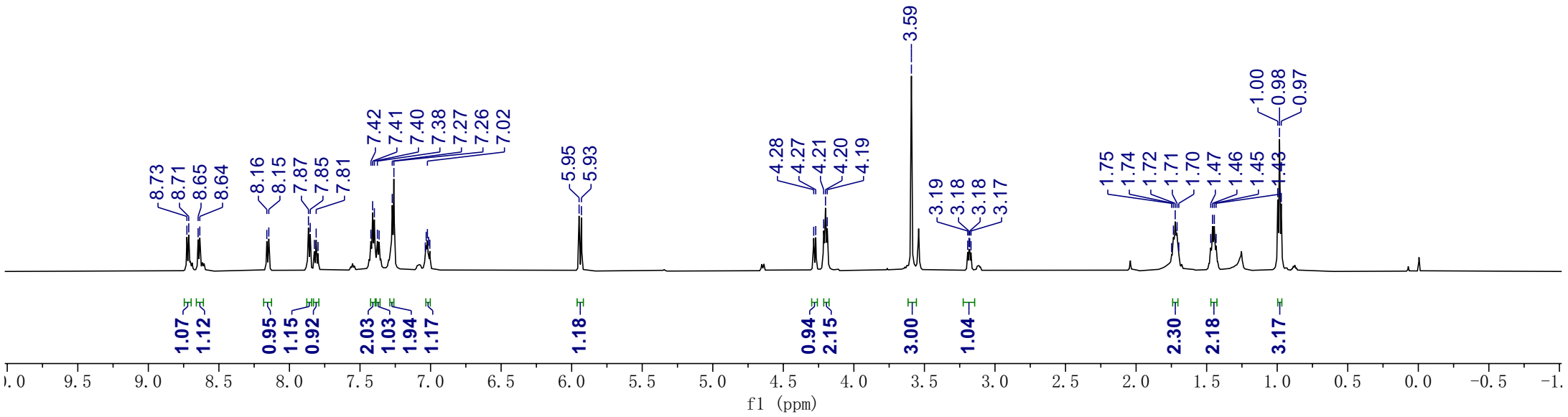
167.57
158.81
140.75
139.19
132.74
128.76
128.64
128.43
125.15
101.29
77.41
77.16
76.91
53.54
51.78
44.44
36.13
26.65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
H
O
N
O
O
nBu

18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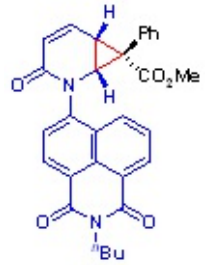
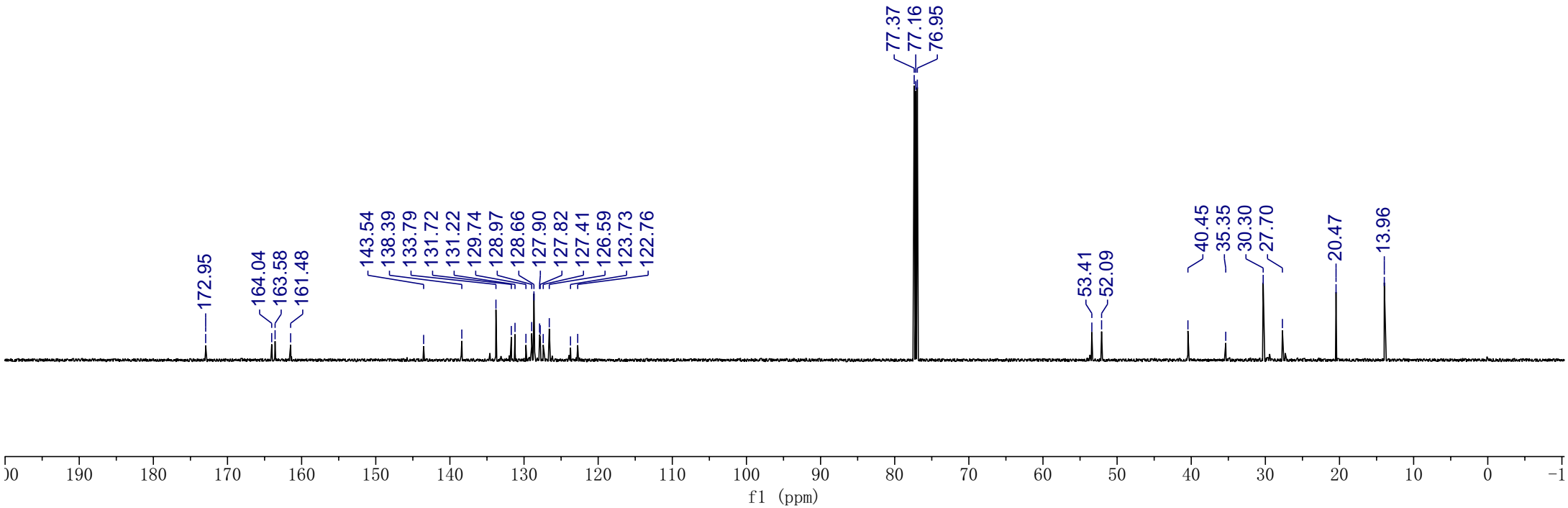
7.85
7.81
7.42
7.41
7.40
7.38
7.27
7.26
7.02
5.95
5.93
4.28
4.27
4.21
4.20
4.19
3.59
3.19
3.18
3.18
3.17
1.75
1.74
1.72
1.71
1.70
1.47
1.46
1.45
1.43
1.00
0.98
0.97
1.07
1.12
0.95
1.15
0.92
2.03
1.03
1.94
1.17
1.18
0.94
2.15
3.00
1.04
2.30
2.18
3.17
f1 (ppm)


H
Ph
CO2Me
O
N
H
O
N
O
O
tBu

18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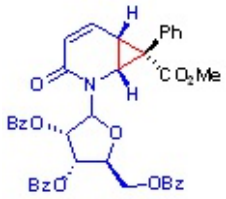
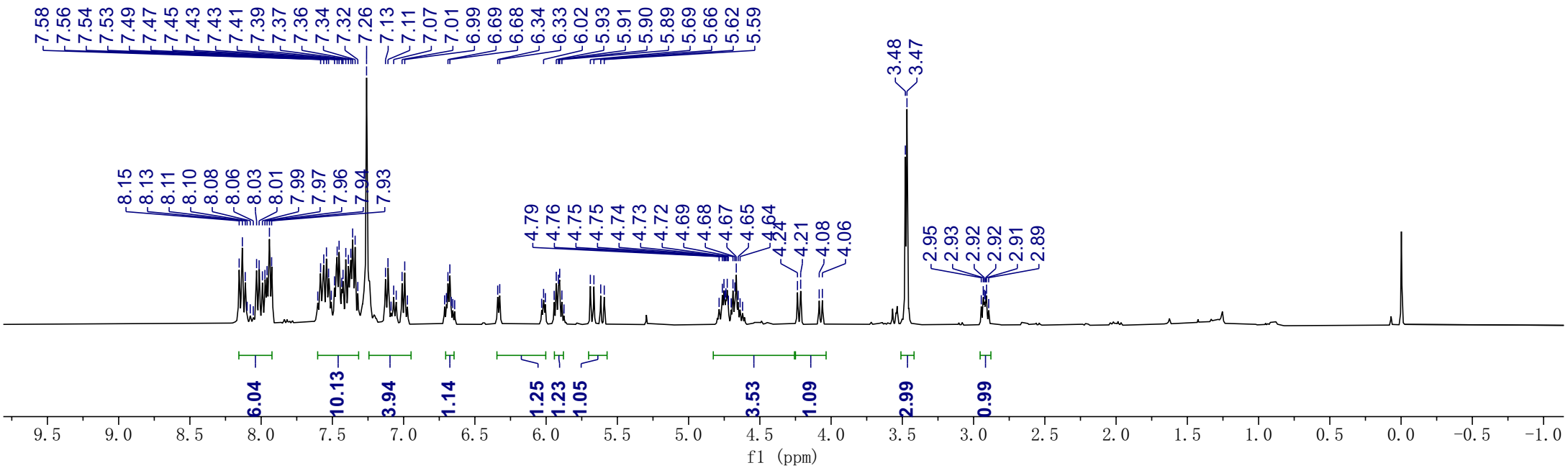
131.72
131.22
129.74
128.97
128.66
127.90
127.82
127.41
126.59
123.73
122.76
77.37
77.16
76.95
53.41
52.09
40.45
35.35
30.30
27.70
20.47
13.96
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)


H
Ph
CO2Me
O
N
H
BzO
O
BzO
OBz

19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7.37
7.36
7.34
7.32
7.26
7.13
7.11
7.07
7.01
6.99
6.69
6.68
6.34
6.33
6.02
5.93
5.91
5.90
5.89
5.69
5.66
5.62
5.59
8.15
8.13
8.11
8.10
8.08
8.06
8.03
8.01
7.99
7.97
7.96
7.94
7.93
4.79
4.76
4.75
4.75
4.74
4.73
4.72
4.69
4.68
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4.65
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4.24
4.21
4.08
4.06
3.48
3.47
2.95
2.93
2.92
2.92
2.91
2.89
6.04
10.13
3.94
1.14
1.25
1.23
1.05
3.53
1.09
2.99
0.99
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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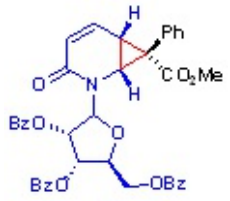
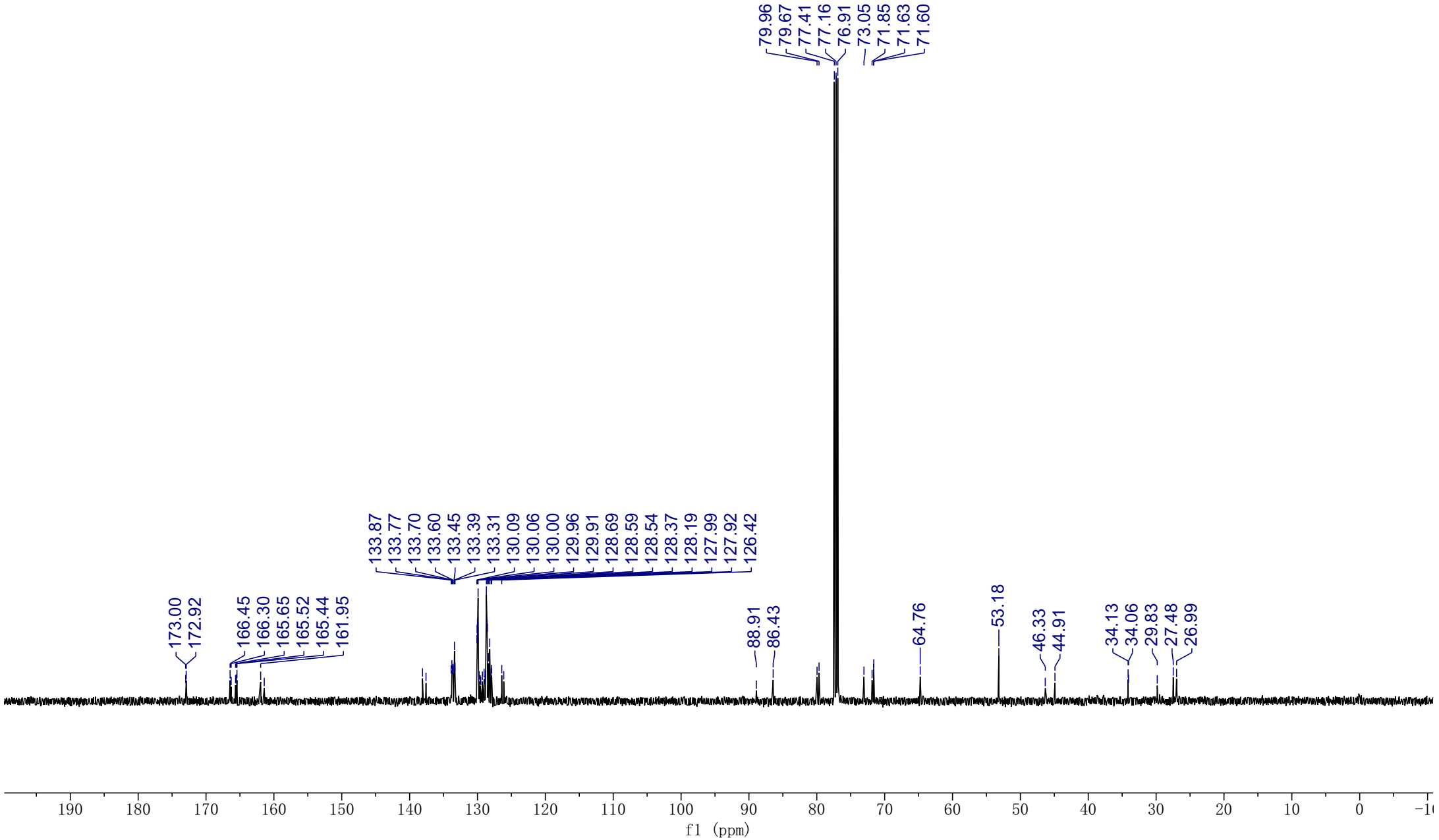
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)


H
Ph
CO2Me
O
N
H
BzO
O
BzO
OBz

19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73.05
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71.63
71.60
133.87
133.77
133.70
133.60
133.45
133.39
133.31
130.09
130.06
130.00
129.96
129.91
128.69
128.59
128.54
128.37
128.19
127.99
127.92
126.42
173.00
172.92
166.45
166.30
165.65
165.52
165.44
161.95
88.91
86.43
64.76
53.18
46.33
44.91
34.13
34.06
29.83
27.48
26.99
190
180
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110
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90
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70
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50
40
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10
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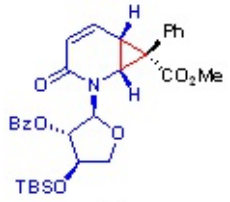
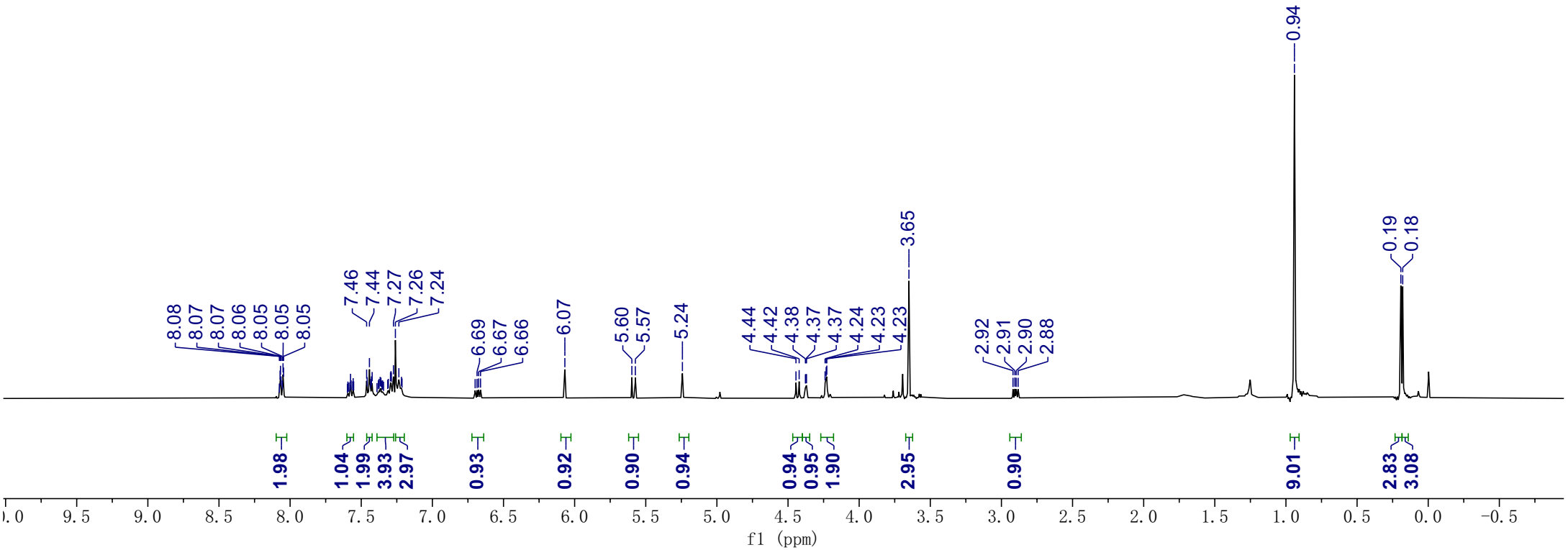
f1 (ppm)


H
Ph
CO2Me
O
N
H
BzO
O
TBSO

20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8.05
8.05
8.05
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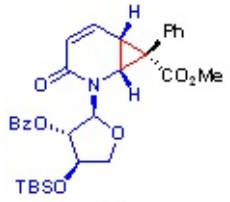
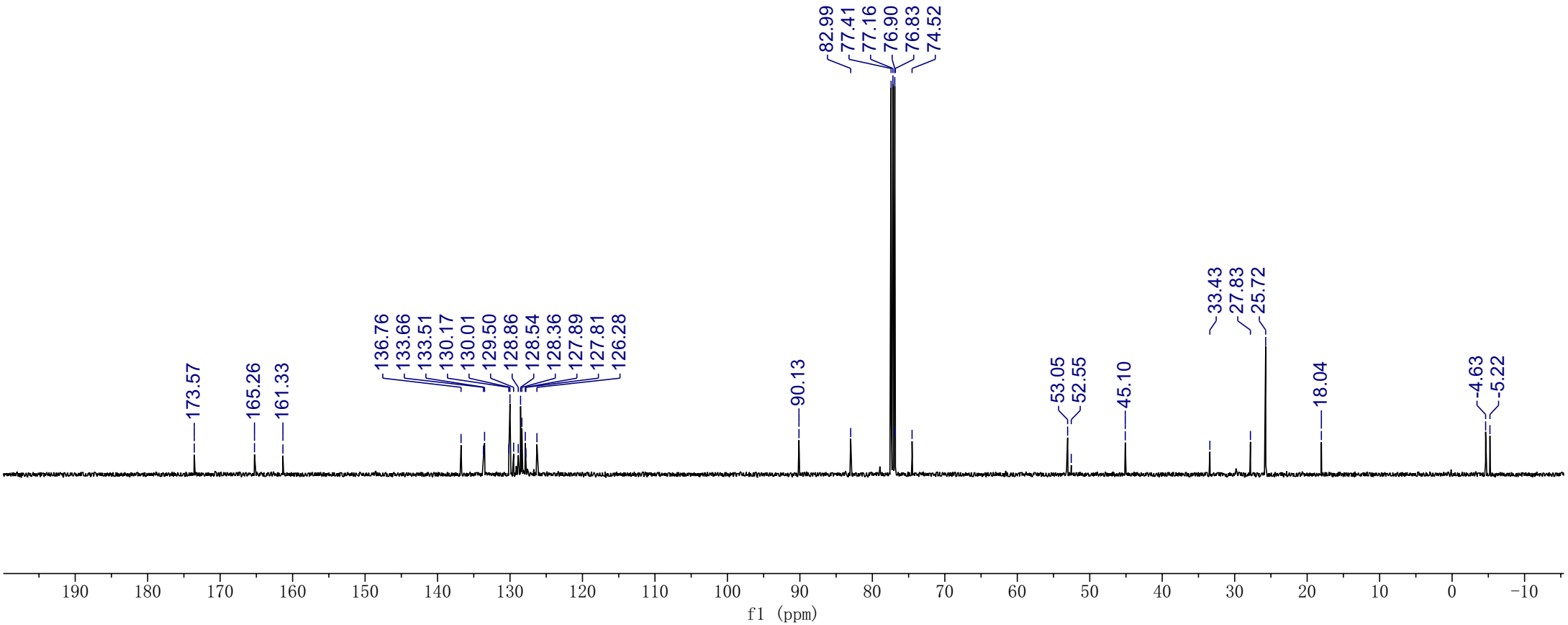
7.44
7.27
7.26
7.24
6.69
6.67
6.66
6.07
5.60
5.57
5.24
4.44
4.42
4.38
4.37
4.37
4.24
4.23
4.23
3.65
2.92
2.91
2.90
2.88
0.94
0.19
0.18
1.98
1.04
1.99
3.93
2.97
0.93
0.92
0.90
0.94
0.94
0.95
1.90
2.95
0.90
9.01
2.83
3.08
f1 (ppm)


H
Ph
O
N
H
CO2Me
BzO
O
TBSO

20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76.90
76.83
74.52
136.76
133.66
133.51
130.17
130.01
129.50
128.86
128.54
128.36
127.89
127.81
126.28
173.57
165.26
161.33
90.13
53.05
52.55
45.10
33.43
27.83
25.72
18.04
-4.63
-5.22
190
180
170
160
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120
110
100
90
80
70
60
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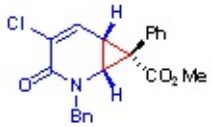
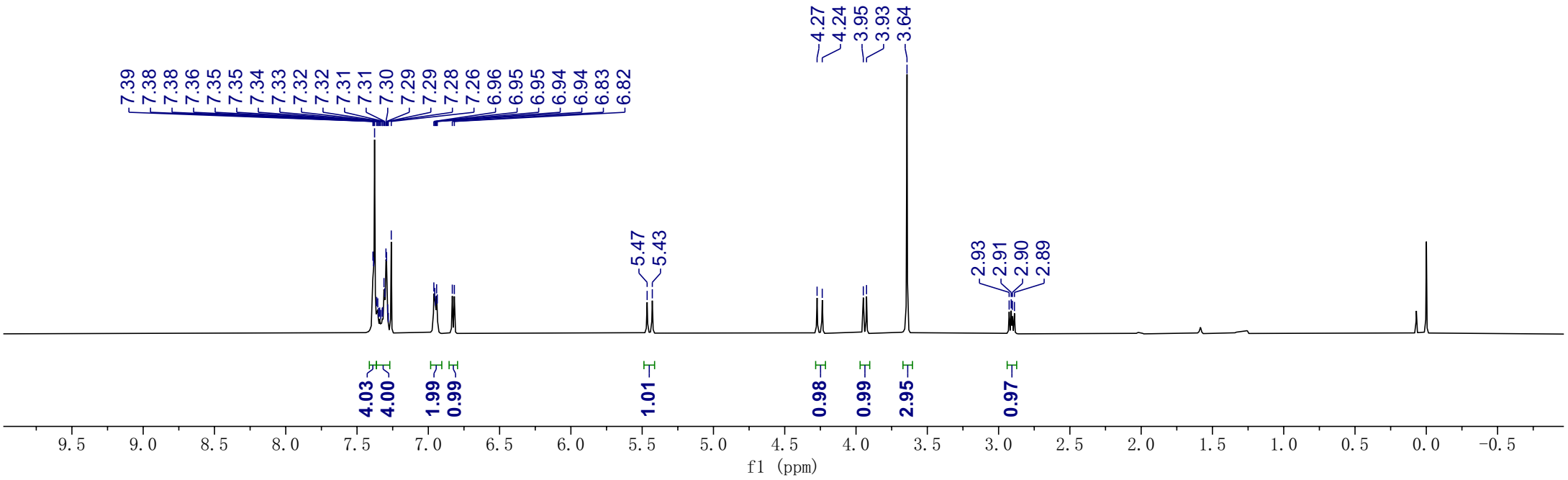
40
30
20
10
0
-10
f1 (ppm)


Cl
H
Ph
O
N
H
CO2Me
Bn

21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7.31
7.30
7.29
7.29
7.28
7.26
6.96
6.95
6.95
6.94
6.94
6.83
6.82
5.47
5.43
4.27
4.24
3.95
3.93
3.64
2.93
2.91
2.90
2.89
4.03
4.00
1.99
0.99
1.01
0.98
0.99
2.95
0.97
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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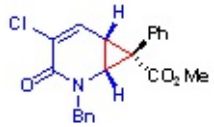
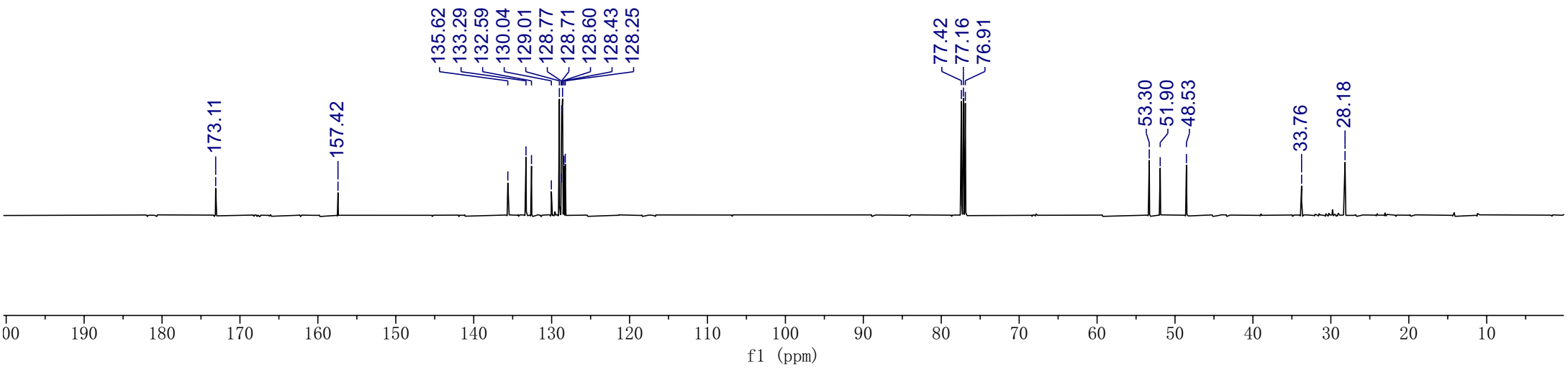
1.0
0.5
0.0
-0.5
f1 (ppm)


Cl
H
Ph
O
N
H
CO2Me
Bn

21


173.11
157.42
135.62
133.29
132.59
130.04
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128.77
128.71
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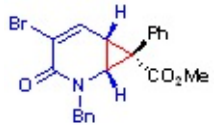
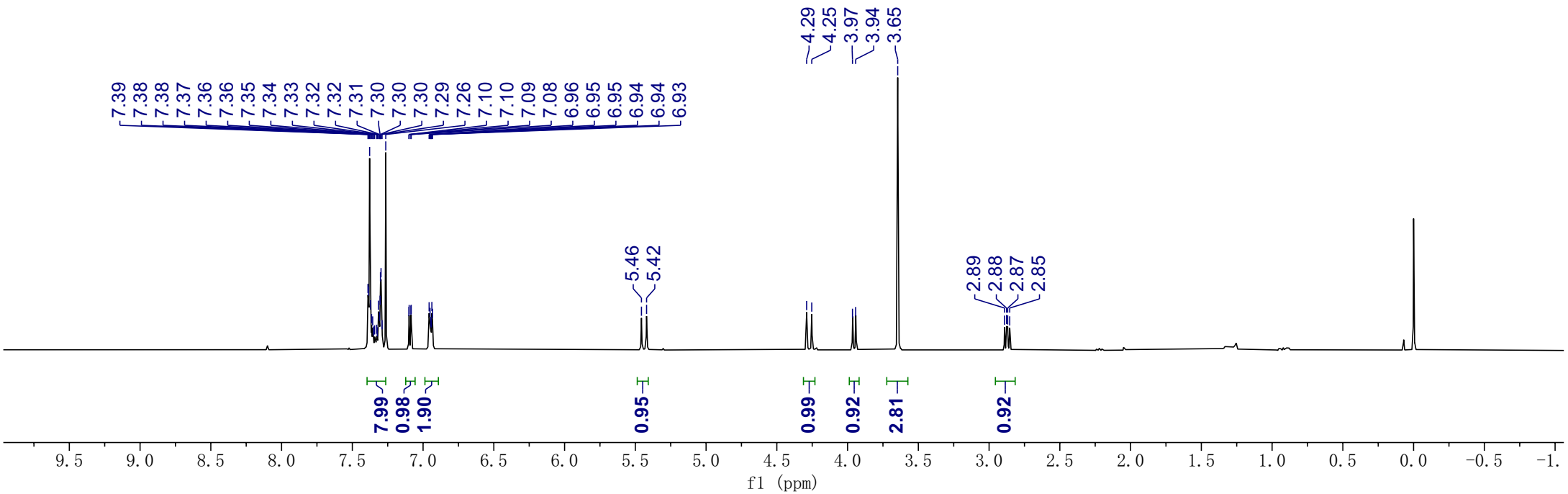
128.43
128.25
77.42
77.16
76.91
53.30
51.90
48.53
33.76
28.18
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


Br
H
Ph
O
N
H
CO2Me
Bn

22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7.36
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7.31
7.30
7.30
7.30
7.29
7.26
7.10
7.10
7.09
7.08
6.96
6.95
6.95
6.94
6.94
6.93
5.46
5.42
4.29
4.25
3.97
3.94
3.65
2.89
2.88
2.87
2.85
7.99
0.98
1.90
0.95
0.99
0.92
2.81
0.92
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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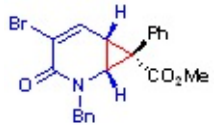
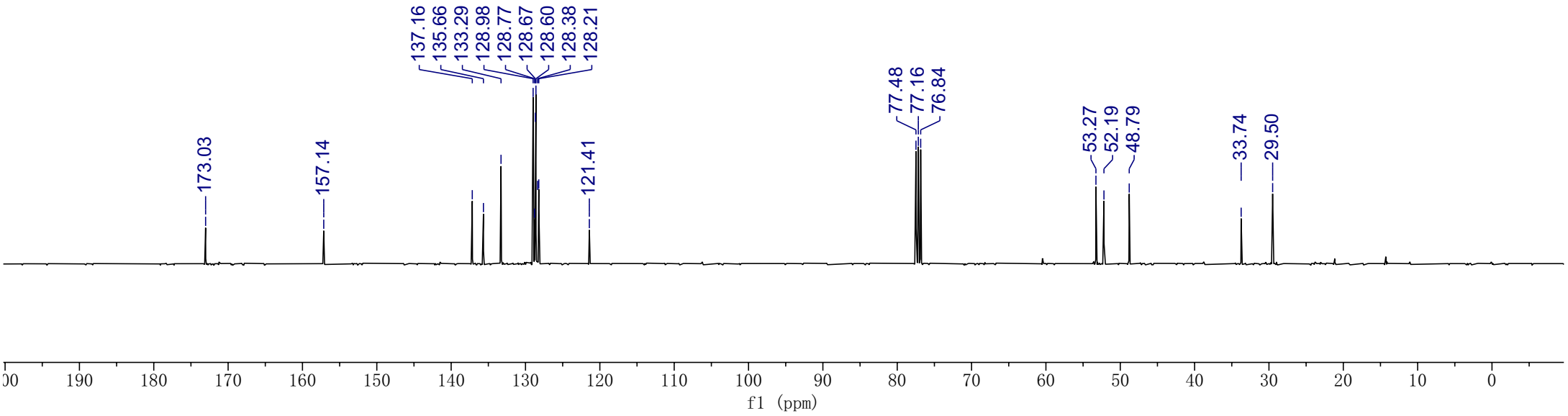
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.
f1 (ppm)


Br
H
Ph
O
N
H
CO2Me
Bn

22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128.38
128.21
77.48
77.16
76.84
53.27
52.19
48.79
33.74
29.50
173.03
157.14
121.41
190
180
170
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130
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100
90
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50
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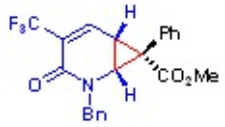
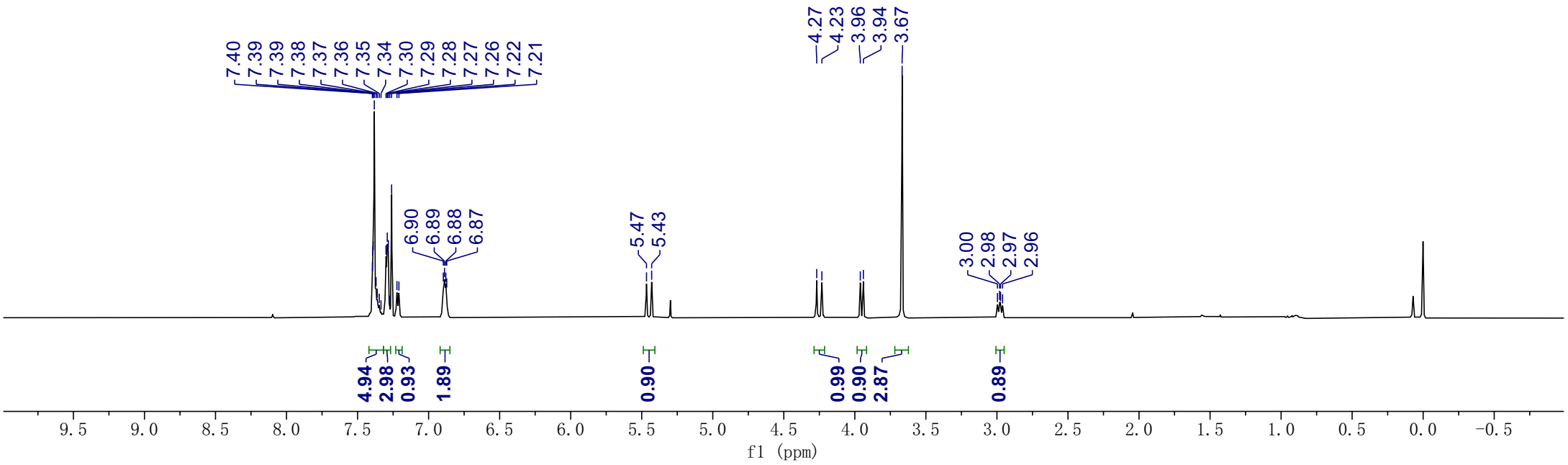
f1 (ppm)


F3C
H
Ph
O
N
CO2Me
H
Bn

23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7.28
7.27
7.26
7.22
7.21
6.90
6.89
6.88
6.87
5.47
5.43
4.27
4.23
3.96
3.94
3.67
3.00
2.98
2.97
2.96
4.94
2.98
0.93
1.89
0.90
0.99
0.90
2.87
0.89
9.5
9.0
8.5
8.0
7.5
7.0
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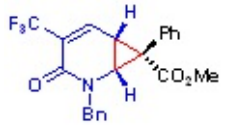
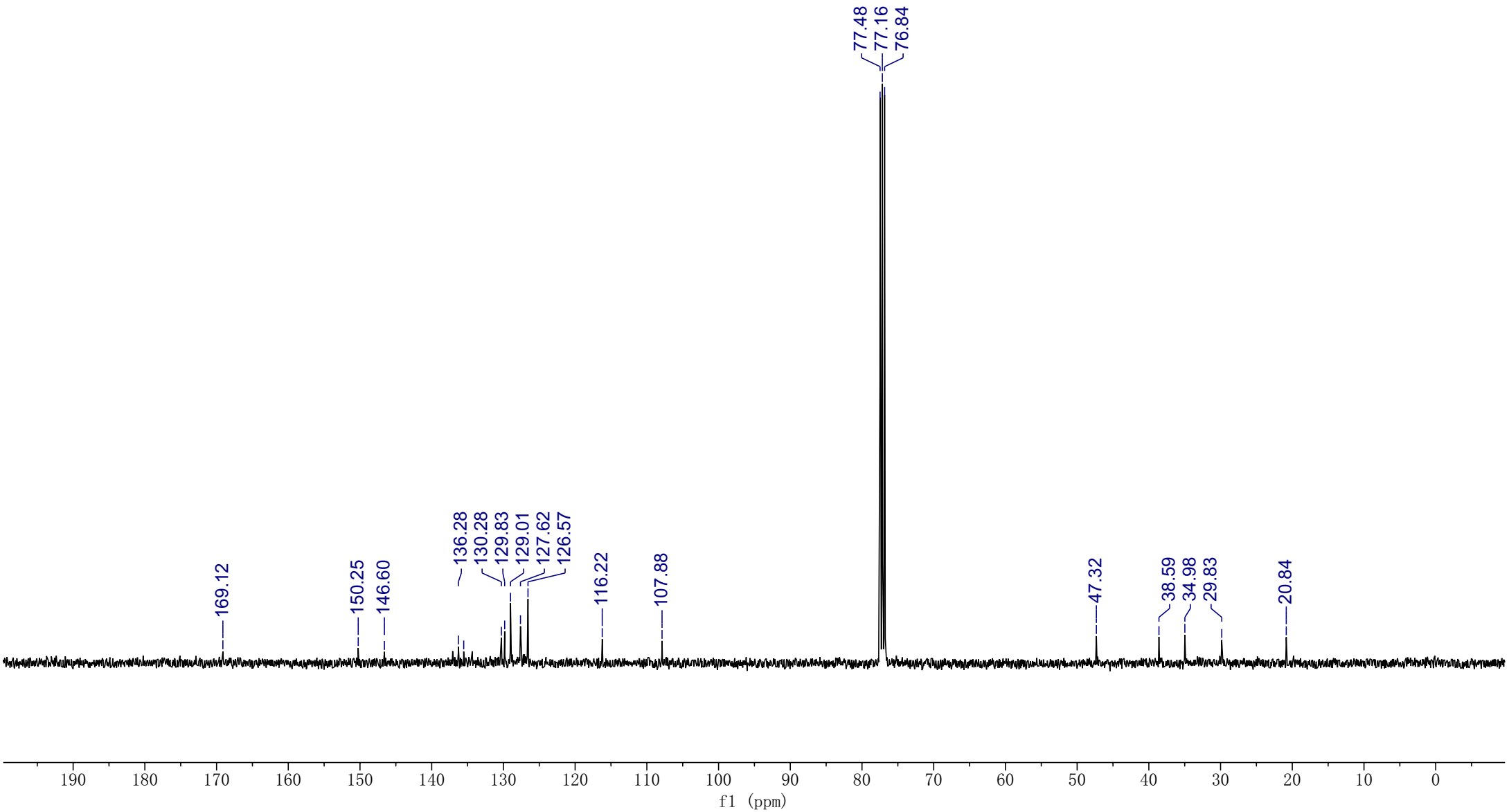
f1 (ppm)


F3C
H
Ph
O
N
CO2Me
H
Bn

23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146.60
136.28
130.28
129.83
129.01
127.62
126.57
116.22
107.88
47.32
38.59
34.98
29.83
20.84
190
180
170
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120
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90
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70
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50
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10
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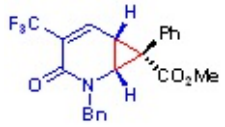
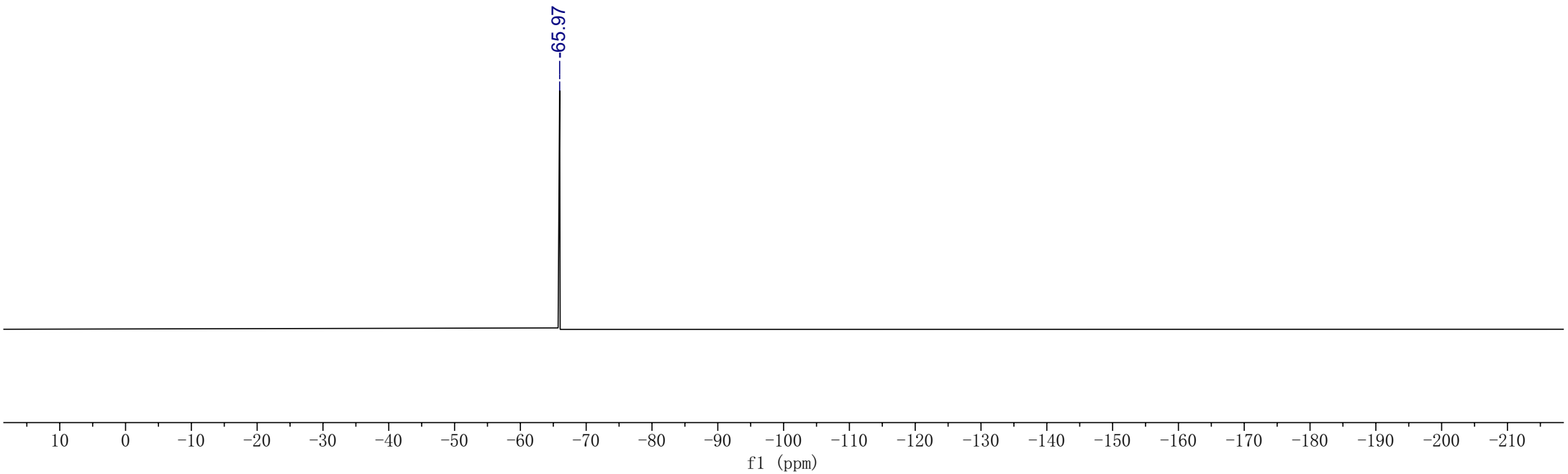
f1 (ppm)


F3C
H
Ph
O
N
CO2Me
H
Bn

23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-80
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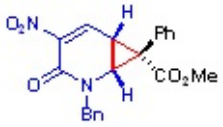
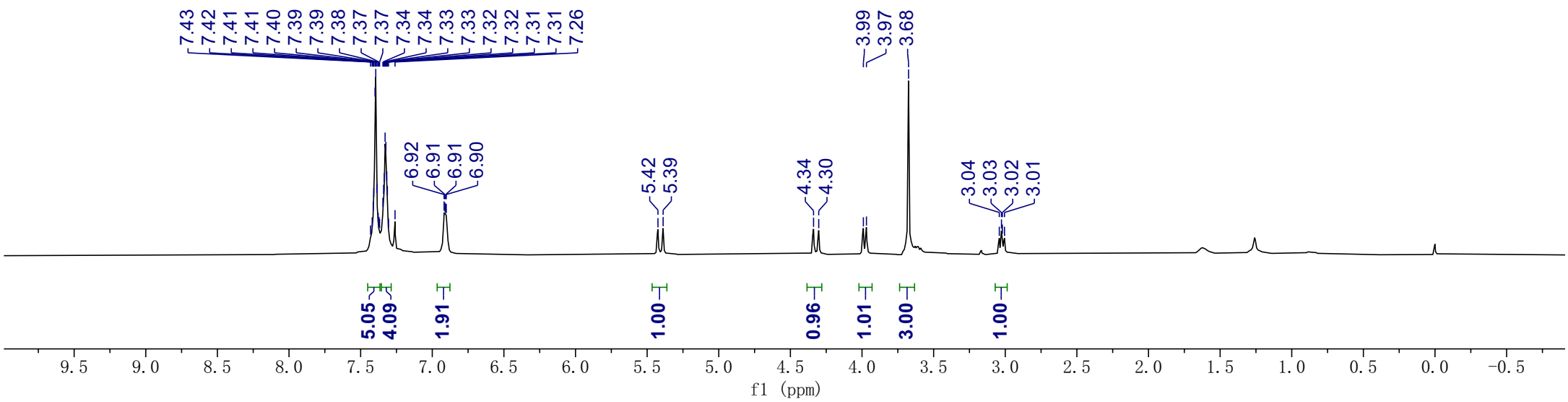
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


O2N
H
Ph
O
N
H
CO2Me
Bn

24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7.34
7.34
7.33
7.33
7.32
7.32
7.31
7.31
7.26
6.92
6.91
6.91
6.90
5.42
5.39
4.34
4.30
3.99
3.97
3.68
3.04
3.03
3.02
3.01
5.05
4.09
1.91
1.00
0.96
1.01
3.00
1.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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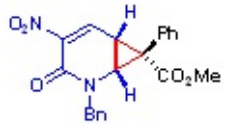
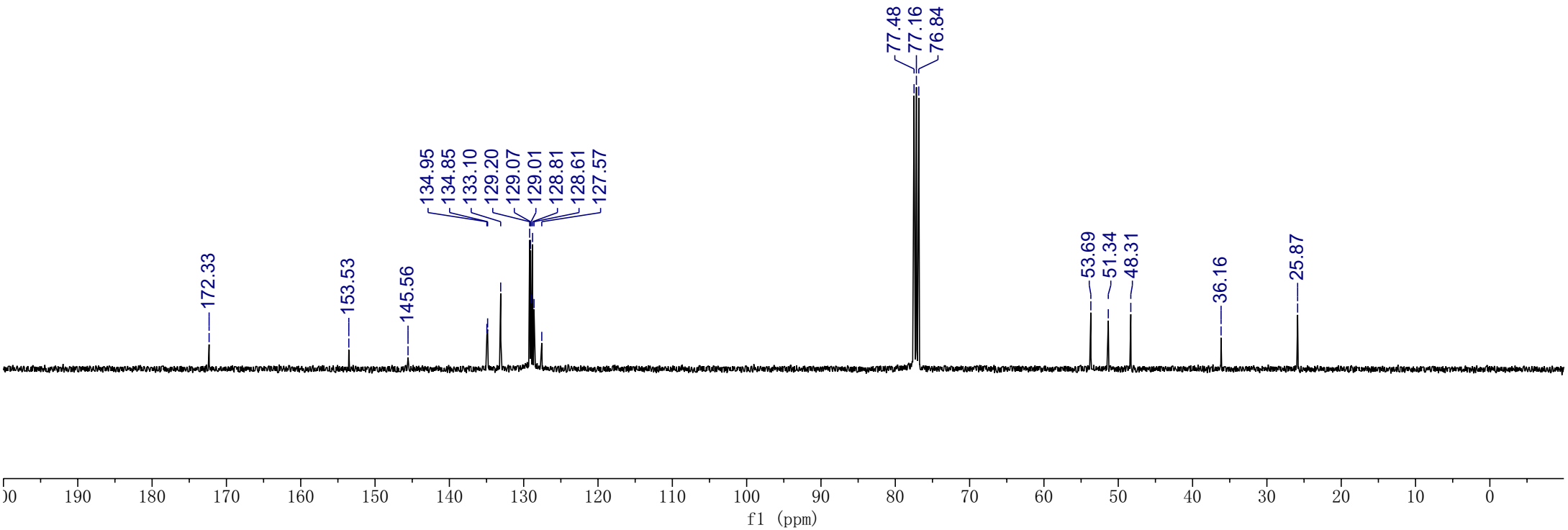
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O2N
H
Ph
O
N
CO2Me
H
Bn

24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134.85
133.10
129.20
129.07
129.01
128.81
128.61
127.57
77.48
77.16
76.84
53.69
51.34
48.31
36.16
25.87
190
180
170
160
150
140
130
120
110
100
90
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70
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50
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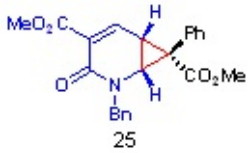
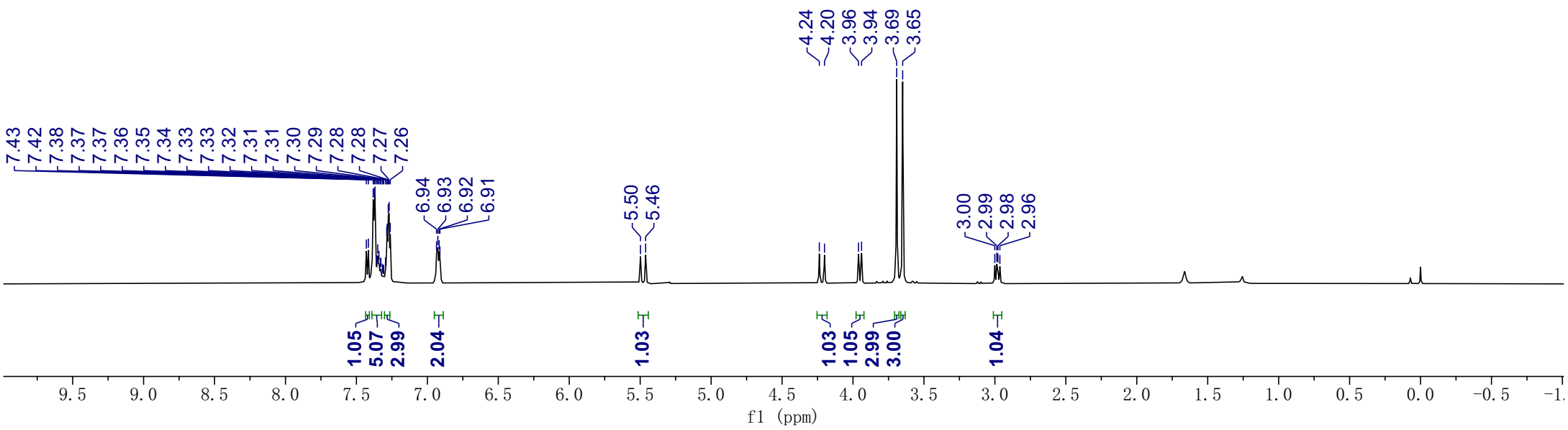
30
20
10
0
f1 (ppm)


MeO2C
H
Ph
CO2Me
O
N
H
Bn

25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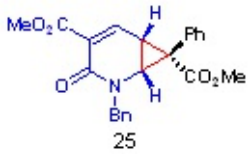
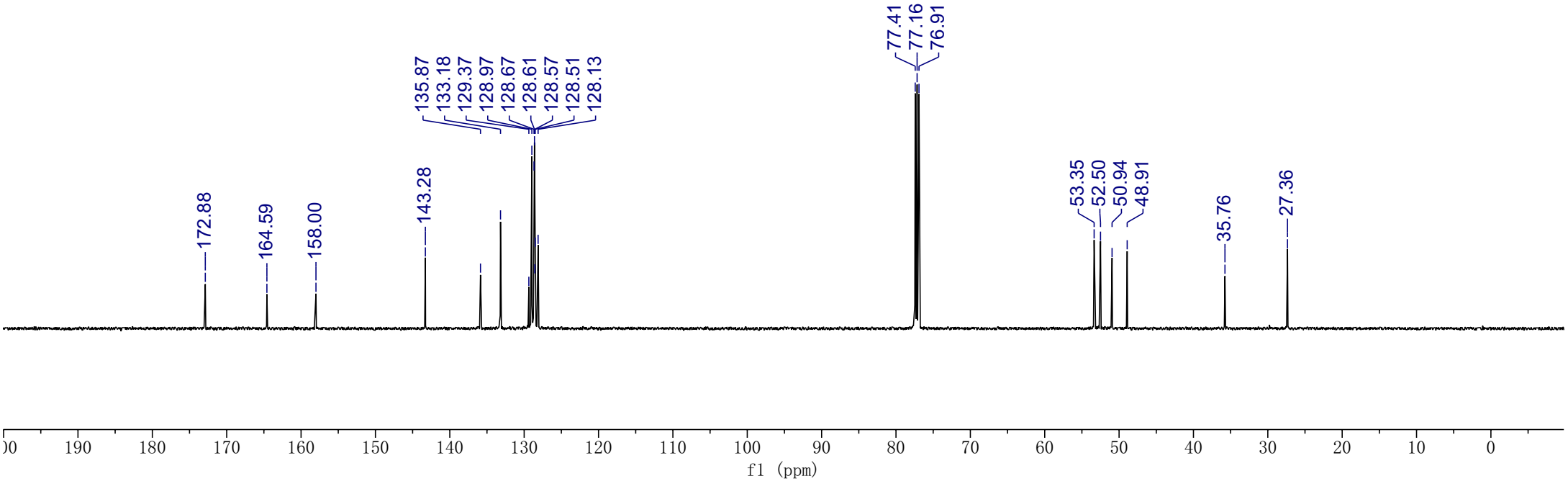
7.28
7.28
7.27
7.26
6.94
6.93
6.92
6.91
5.50
5.46
4.24
4.20
3.96
3.94
3.69
3.65
3.00
2.99
2.98
2.96
1.05
5.07
2.99
2.04
1.03
1.03
1.05
2.99
3.00
1.04
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


MeO2C
H
Ph
CO2Me
O
N
H
Bn

25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128.61
128.57
128.51
128.13
77.41
77.16
76.91
53.35
52.50
50.94
48.91
35.76
27.36
190
180
170
160
150
140
130
120
110
100
90
80
70
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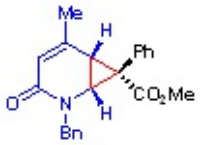
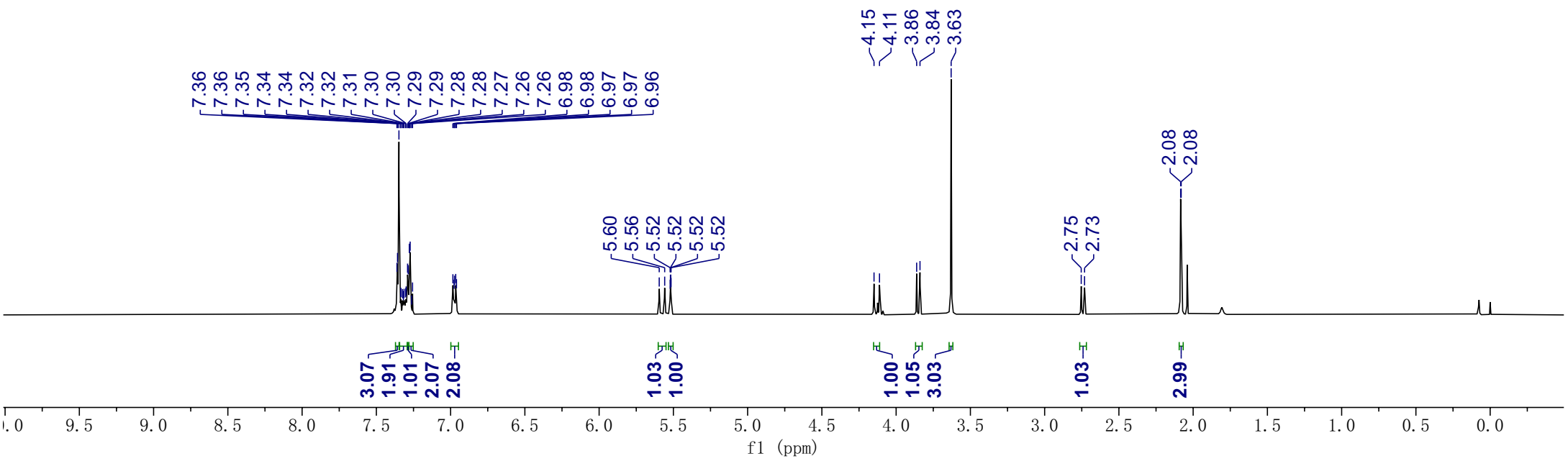
50
40
30
20
10
0
f1 (ppm)


Me
H
Ph
CO2Me
O
N
H
Bn

26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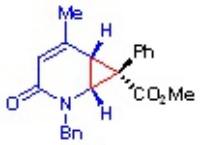
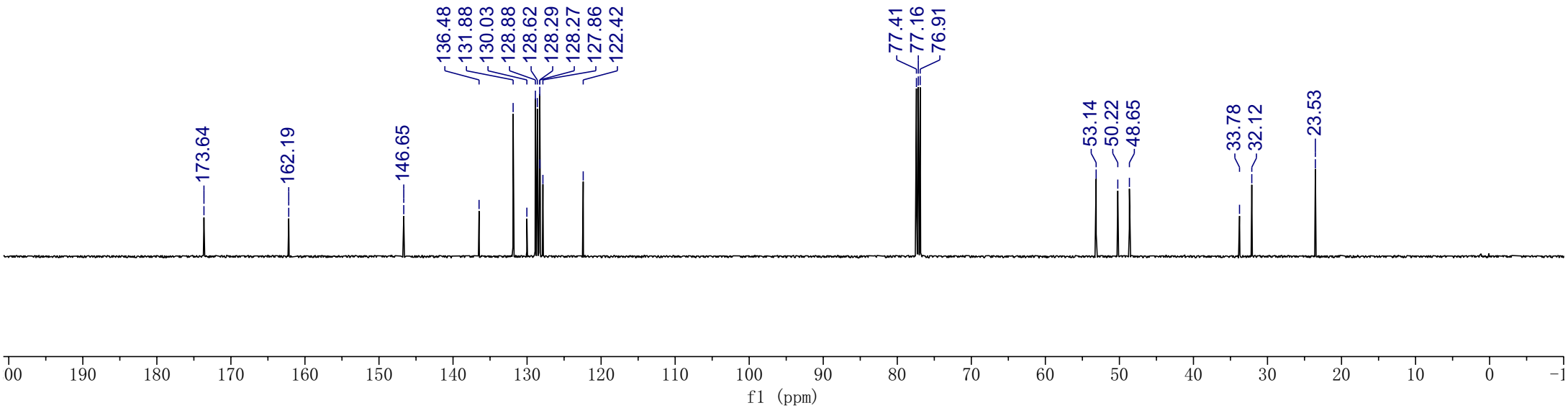
7.30
7.29
7.29
7.28
7.28
7.27
7.26
7.26
6.98
6.98
6.97
6.97
6.96
5.60
5.56
5.52
5.52
5.52
5.52
4.15
4.11
3.86
3.84
3.63
2.75
2.73
2.08
2.08
3.07
1.91
1.01
2.07
2.08
1.03
1.00
1.00
1.05
3.03
1.03
2.99
f1 (ppm)


Me
H
Ph
CO2Me
O
N
H
Bn

26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136.48
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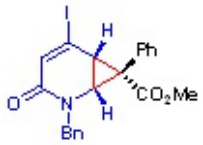
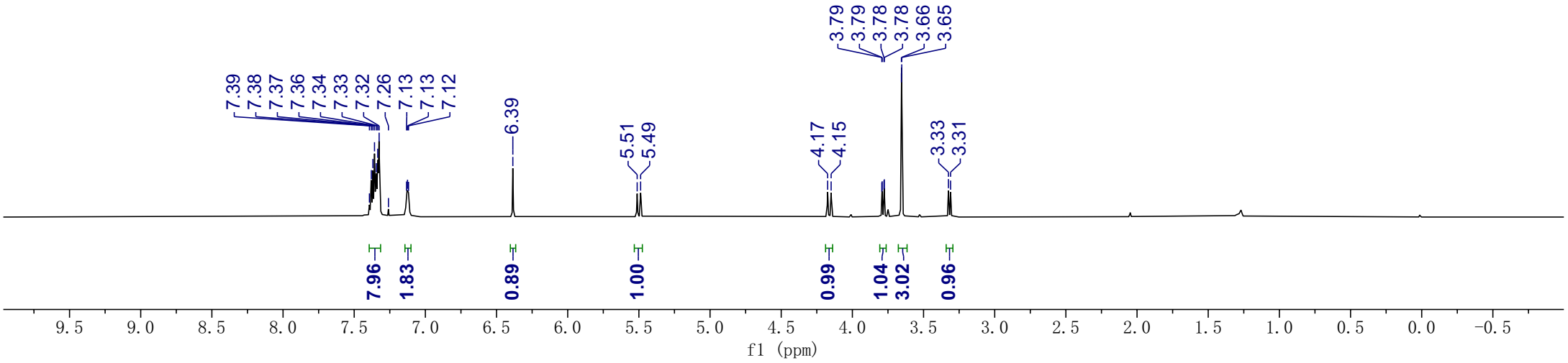
128.88
128.62
128.29
128.27
127.86
122.42
77.41
77.16
76.91
53.14
50.22
48.65
33.78
32.12
23.53
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


I
H
Ph
CO2Me
O
N
H
Bn

27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7.26
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7.13
7.12
6.39
5.51
5.49
4.17
4.15
3.79
3.79
3.78
3.78
3.66
3.65
3.33
3.31
7.96
1.83
0.89
1.00
0.99
1.04
3.02
0.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.0
2.5
2.0
1.5
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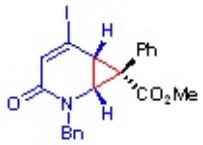
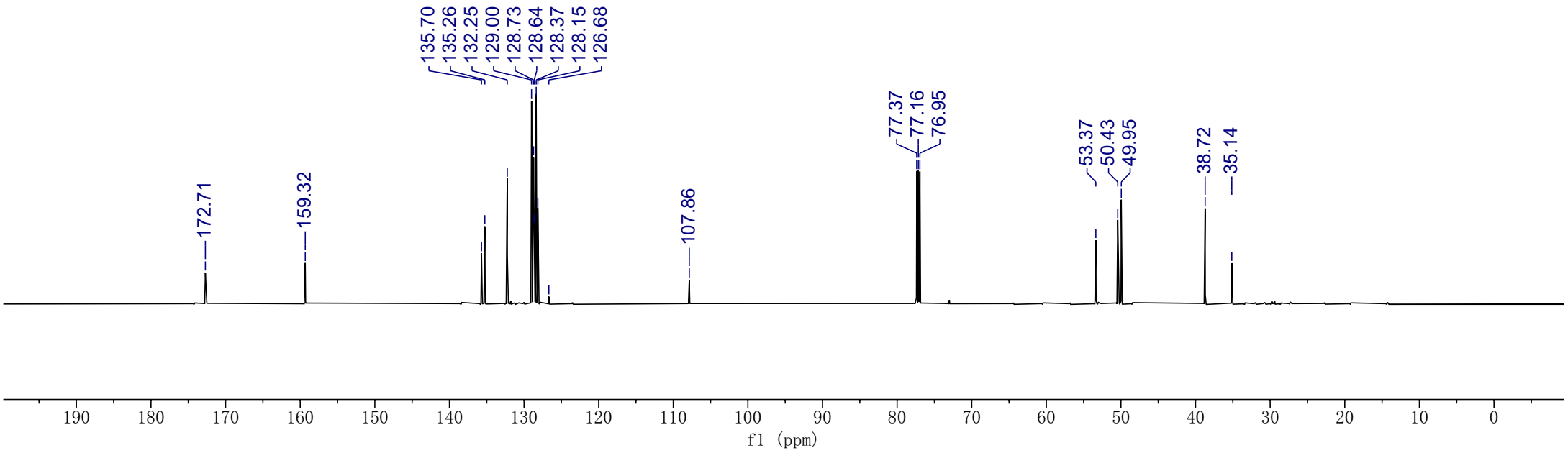
0.5
0.0
-0.5
f1 (ppm)


I
H
Ph
O
N
H
CO2Me
Bn

27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77.16
76.95
53.37
50.43
49.95
38.72
35.14
172.71
159.32
107.86
190
180
170
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150
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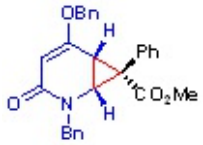
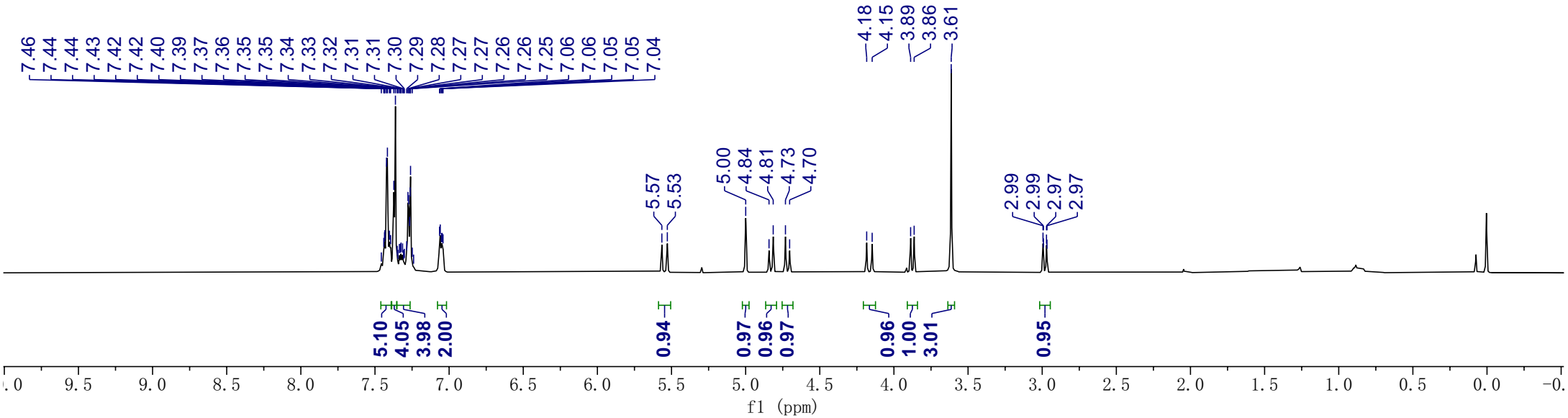
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OBn
H
Ph
CO2Me
O
N
H
Bn

28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7.28
7.27
7.27
7.26
7.26
7.25
7.06
7.06
7.05
7.05
7.04
5.57
5.53
5.00
4.84
4.81
4.73
4.70
4.18
4.15
3.89
3.86
3.61
2.99
2.99
2.97
2.97
5.10
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3.98
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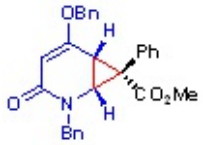
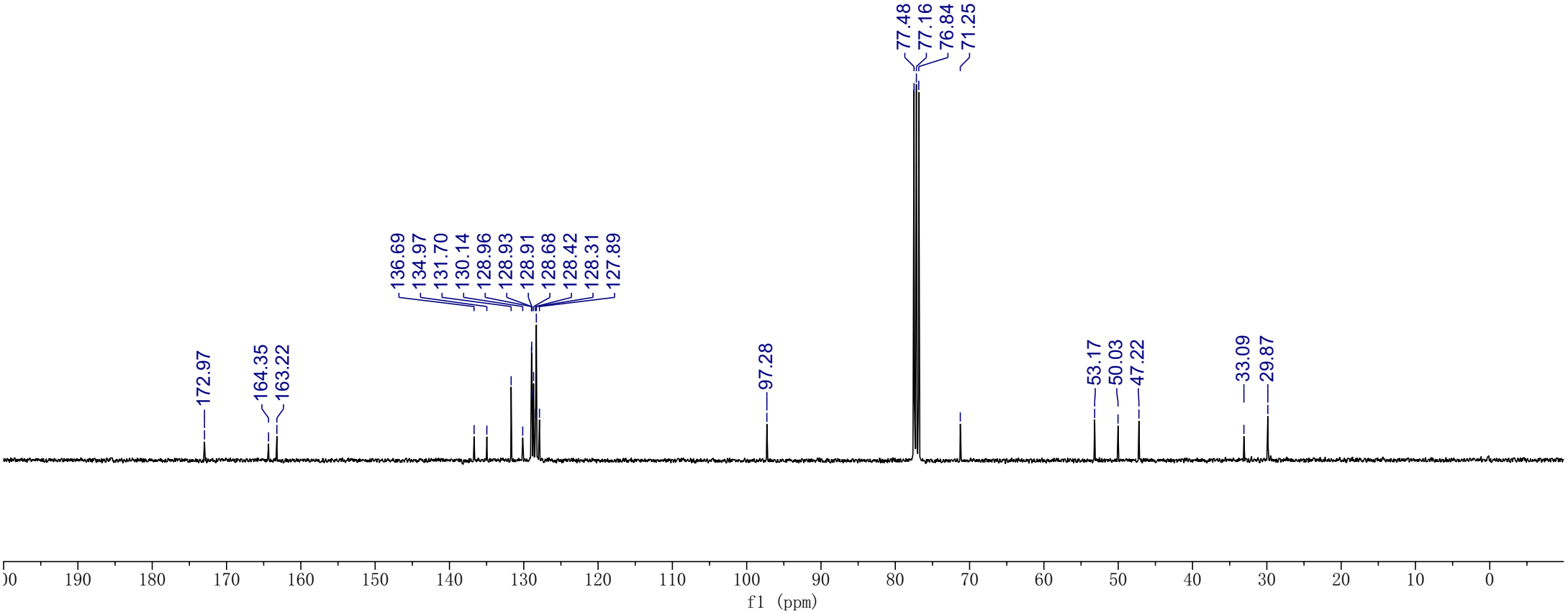
0.94
0.97
0.96
0.97
0.96
1.00
3.01
0.95
f1 (ppm)


OBn
H
Ph
CO2Me
O
N
H
Bn

28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163.22
136.69
134.97
131.70
130.14
128.96
128.93
128.91
128.68
128.42
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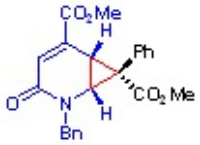
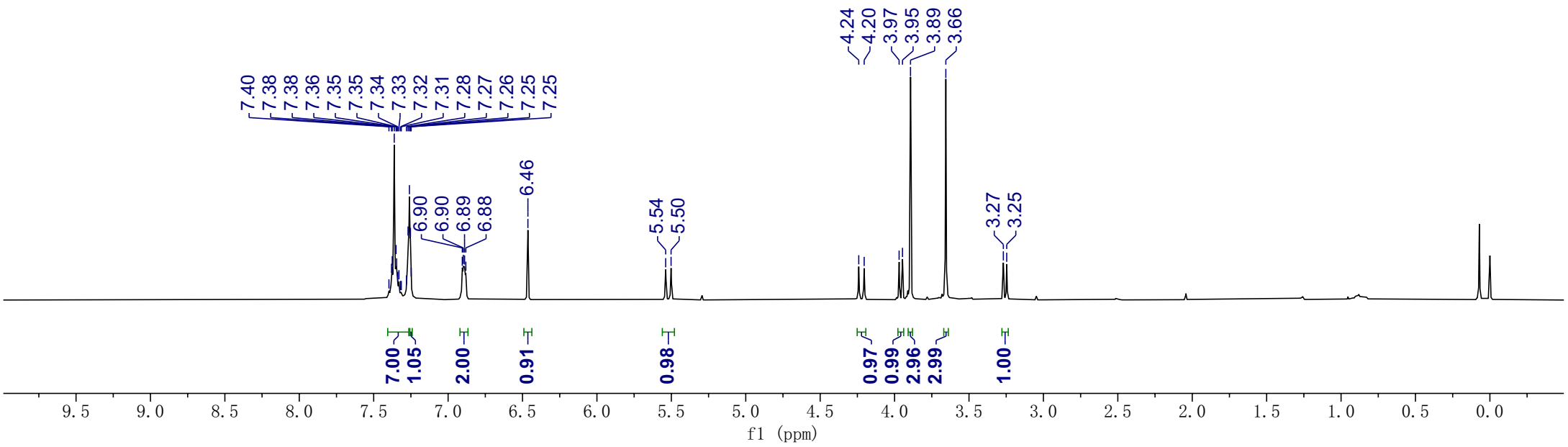
50.03
47.22
33.09
29.87
f1 (ppm)


CO2Me
H
Ph
CO2Me
O
N
H
Bn

29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7.34
7.33
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7.28
7.27
7.26
7.25
7.25
6.90
6.90
6.89
6.88
6.46
5.54
5.50
4.24
4.20
3.97
3.95
3.89
3.66
3.27
3.25
7.00
1.05
2.00
0.91
0.98
0.97
0.99
2.96
2.99
1.00
9.5
9.0
8.5
8.0
7.5
7.0
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6.0
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2.5
2.0
1.5
1.0
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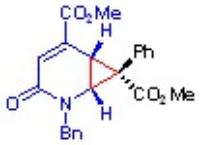
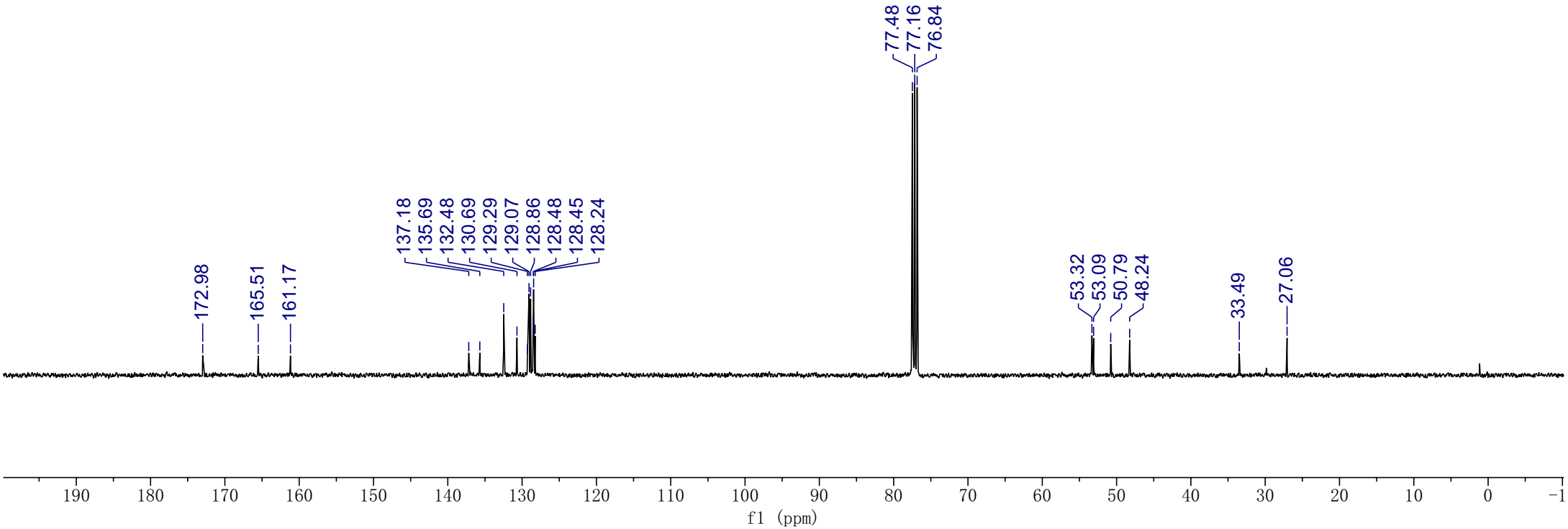
0.0
f1 (ppm)


CO2Me
H
Ph
CO2Me
O
N
H
Bn

29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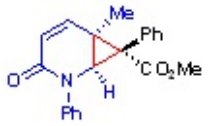
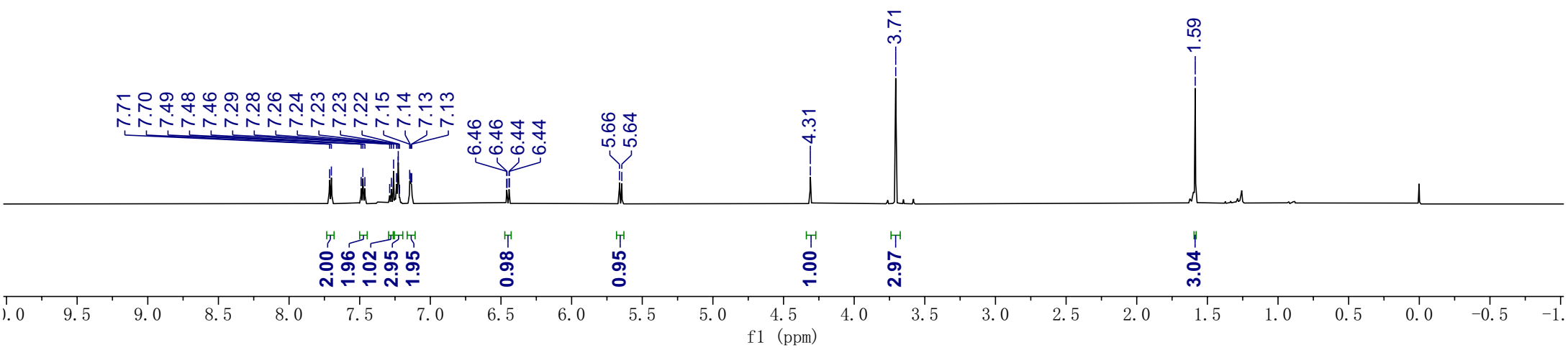
128.45
128.24
77.48
77.16
76.84
53.32
53.09
50.79
48.24
33.49
27.06
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Me
Ph
CO2Me
O
N
H
Ph

30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7.24
7.23
7.23
7.22
7.15
7.14
7.13
7.13
6.46
6.46
6.44
6.44
5.66
5.64
4.31
3.71
1.59
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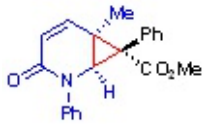
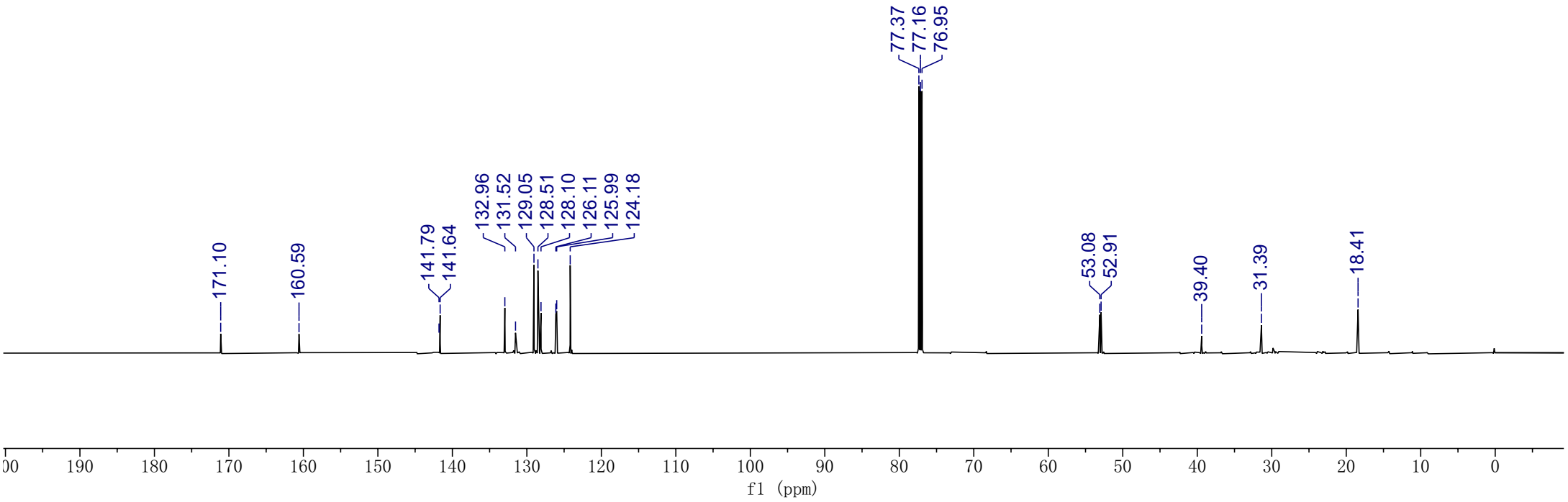
1.96
1.02
2.95
1.95
0.98
0.95
1.00
2.97
3.04
f1 (ppm)


Me
Ph
CO2Me
O
N
H
Ph

30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141.64
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131.52
129.05
128.51
128.10
126.11
125.99
124.18
77.37
77.16
76.95
53.08
52.91
39.40
31.39
18.41
190
180
170
160
150
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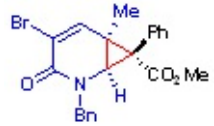
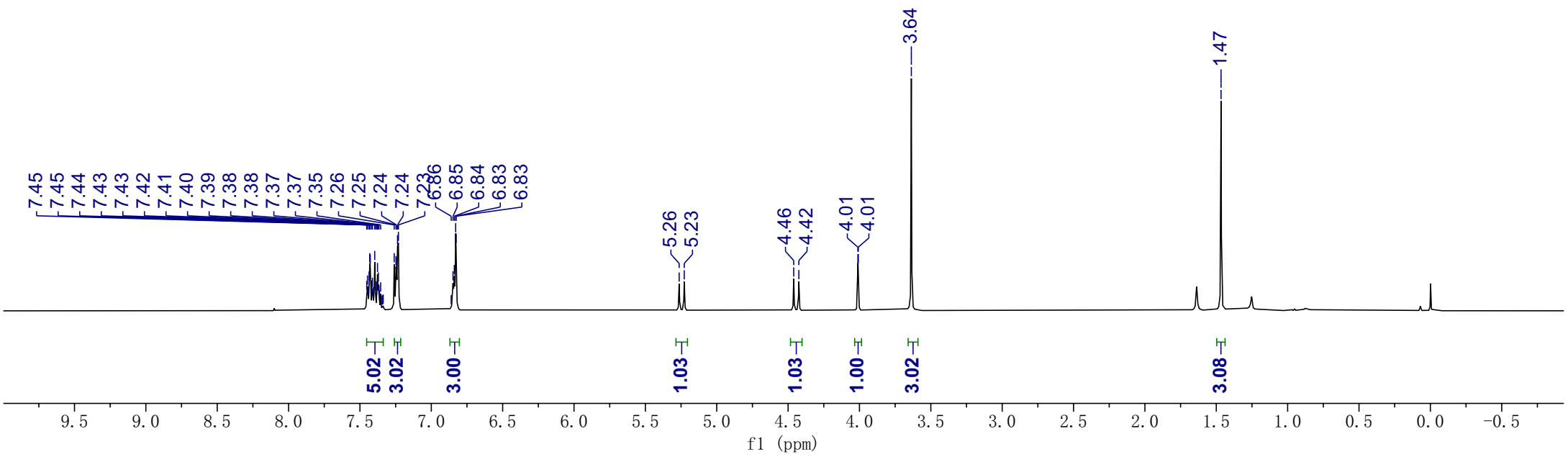
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Br
Ph
O
N
H
CO2Me
Bn

31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7.44
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7.43
7.42
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7.39
7.38
7.38
7.37
7.37
7.35
7.26
7.25
7.24
7.24
7.23
6.86
6.85
6.84
6.83
6.83
5.26
5.23
4.46
4.42
4.01
4.01
3.64
1.47
5.02
3.02
3.00
1.03
1.03
1.00
3.02
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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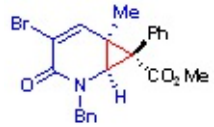
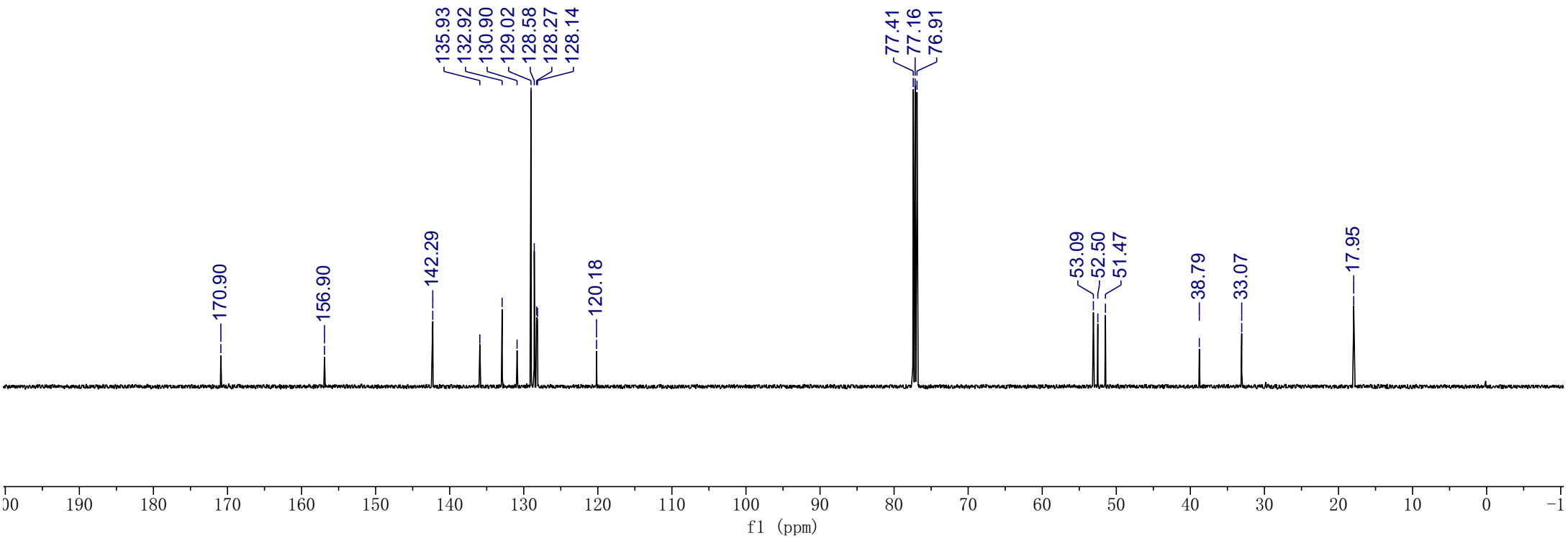
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
Ph
Br
O
N
H
CO2Me
Bn

31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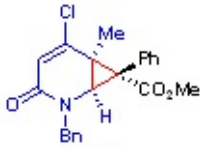
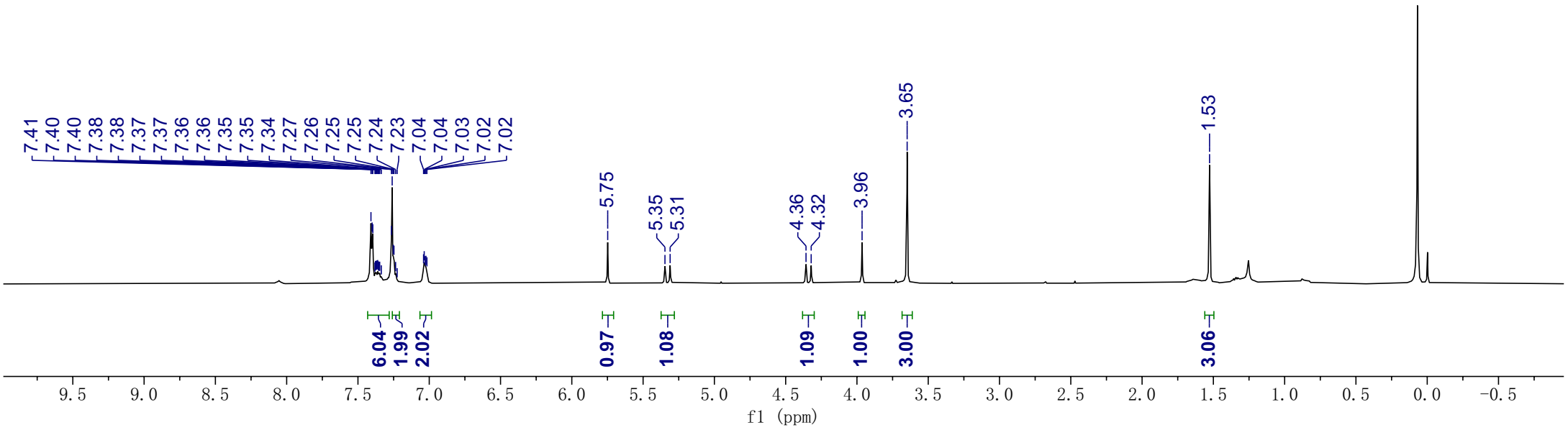
132.92
130.90
129.02
128.58
128.27
128.14
77.41
77.16
76.91
170.90
156.90
142.29
120.18
53.09
52.50
51.47
38.79
33.07
17.95
f1 (ppm)


Cl
Me
Ph
CO2Me
O
N
H
Bn

32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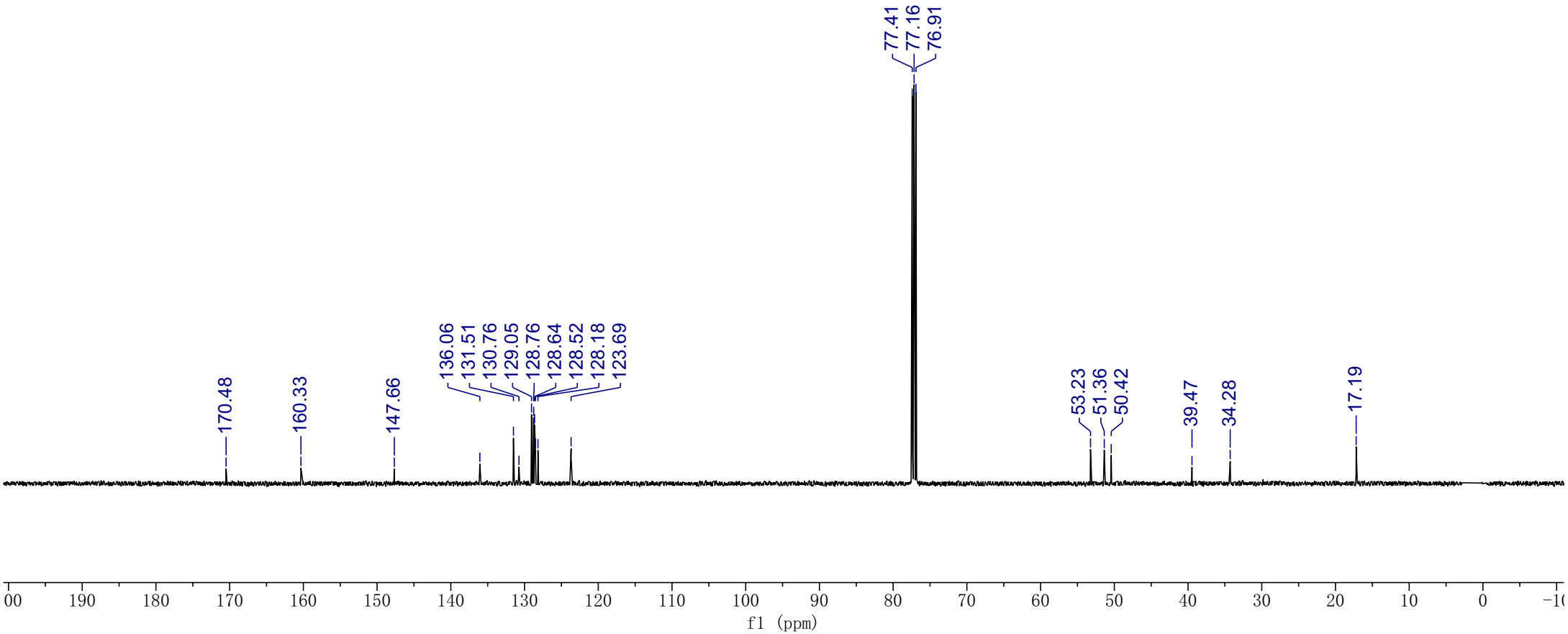
7.35
7.35
7.34
7.27
7.26
7.25
7.25
7.24
7.23
7.04
7.04
7.03
7.02
7.02
5.75
5.35
5.31
4.36
4.32
3.96
3.65
1.53
6.04
1.99
2.02
0.97
1.08
1.09
1.00
3.00
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Cl
Me
Ph
CO2Me
O
N
H
Bn

32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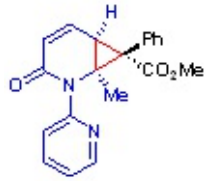
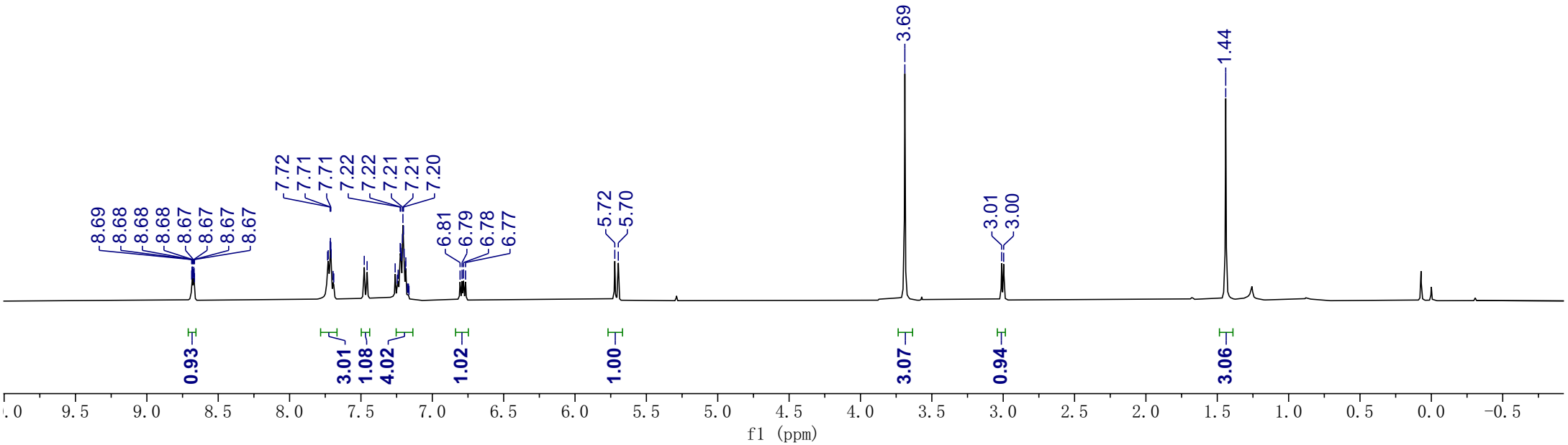
76.91
170.48
160.33
147.66
136.06
131.51
130.76
129.05
128.76
128.64
128.52
128.18
123.69
53.23
51.36
50.42
39.47
34.28
17.19
f1 (ppm)


H
Ph
CO2Me
Me
O
N
N

33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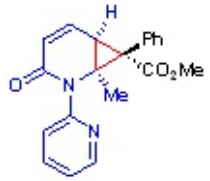
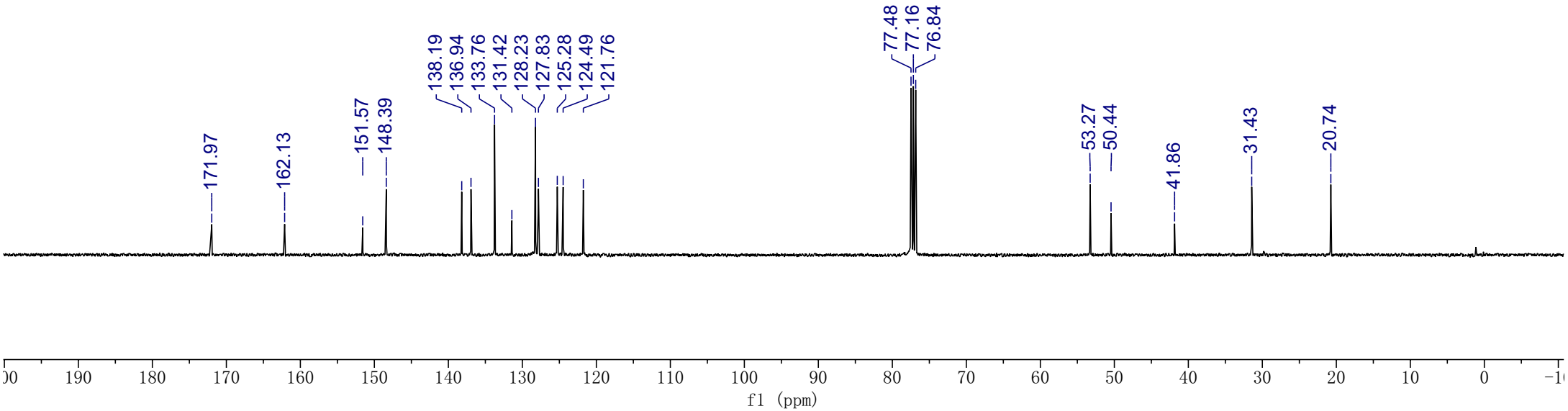
8.68
8.68
8.67
8.67
8.67
8.67
7.72
7.71
7.71
7.22
7.22
7.21
7.21
7.20
6.81
6.79
6.78
6.77
5.72
5.70
3.69
3.01
3.00
1.44
0.93
3.01
1.08
4.02
1.02
1.00
3.07
0.94
3.06
f1 (ppm)


H
Ph
CO2Me
Me
O
N
N

33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136.94
133.76
131.42
128.23
127.83
125.28
124.49
121.76
77.48
77.16
76.84
53.27
50.44
41.86
31.43
20.74
190
180
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150
140
130
120
110
100
90
80
70
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50
40
30
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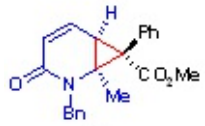
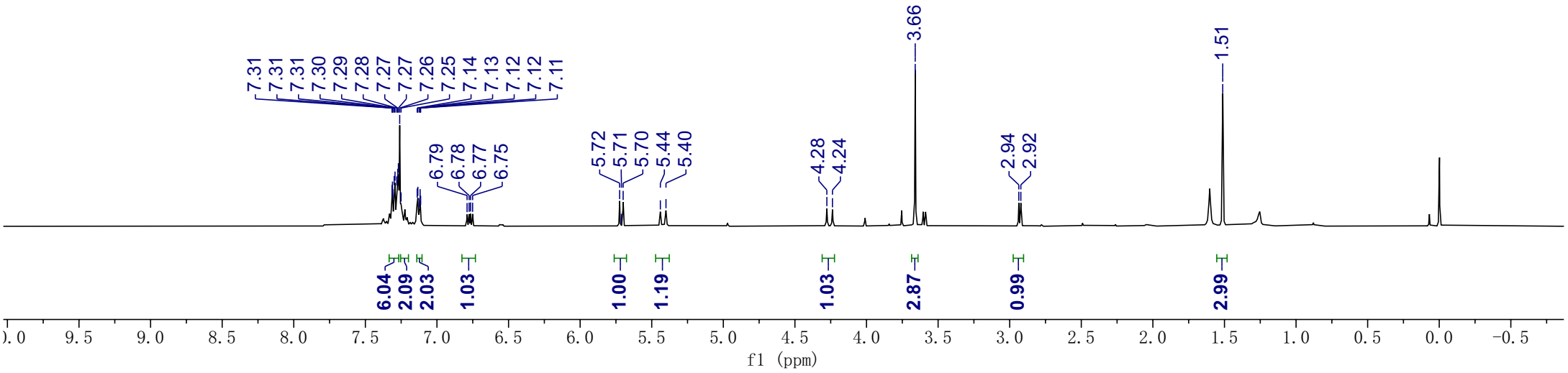
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
Me
Bn

34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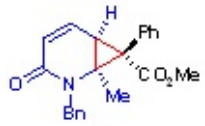
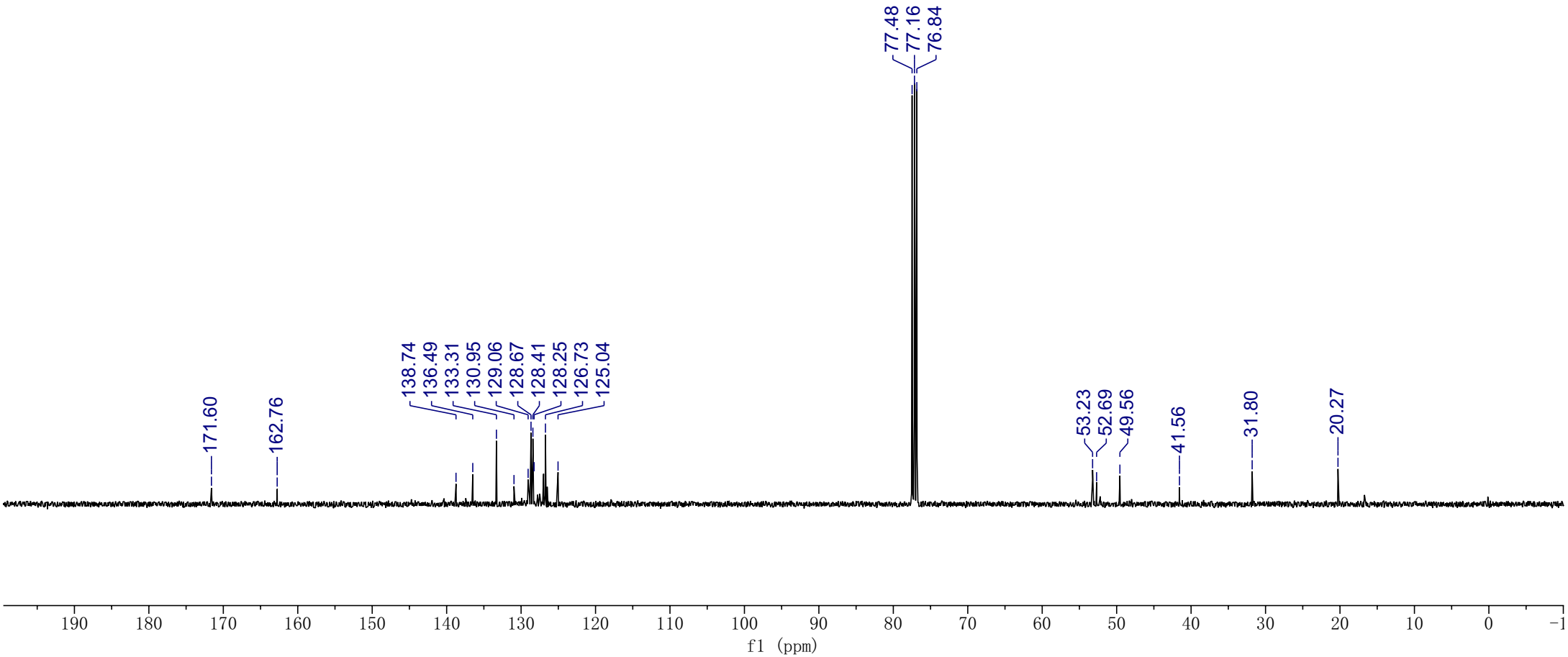
7.27
7.26
7.25
7.14
7.13
7.12
7.12
7.11
6.79
6.78
6.77
6.75
5.72
5.71
5.70
5.44
5.40
4.28
4.24
3.66
2.94
2.92
1.51
6.04
2.09
2.03
1.03
1.00
1.19
1.03
2.87
0.99
2.99
f1 (ppm)


H
Ph
CO2Me
O
N
Me
Bn

34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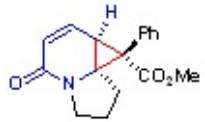
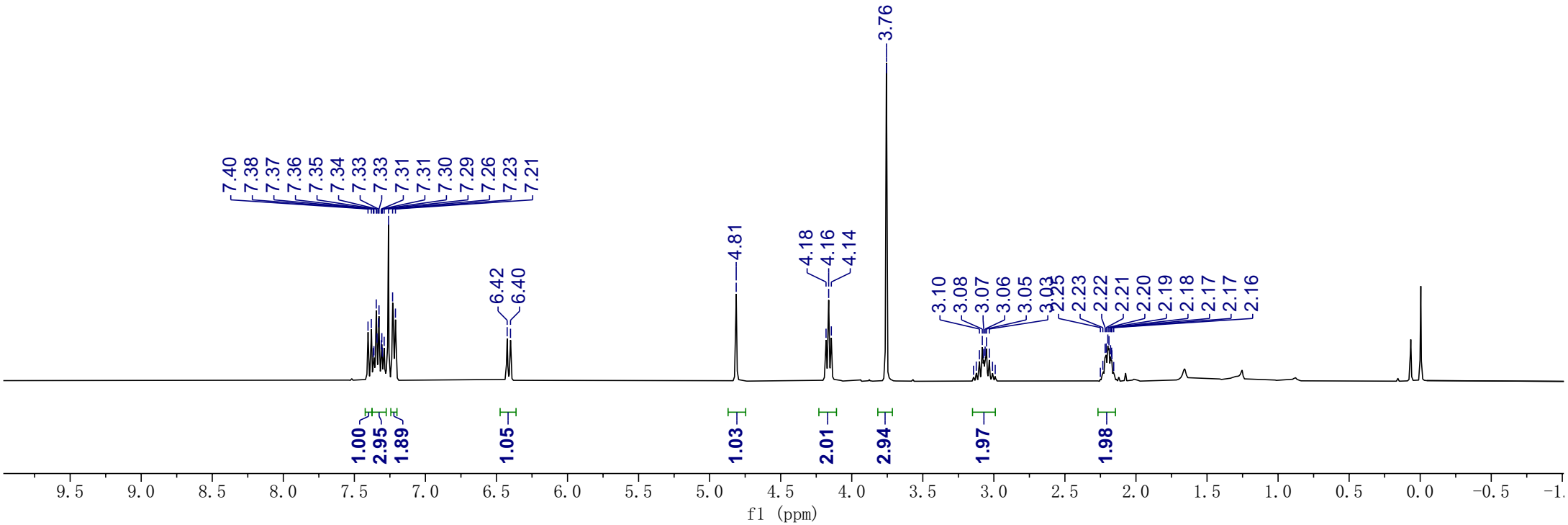
77.16
76.84
171.60
162.76
138.74
136.49
133.31
130.95
129.06
128.67
128.41
128.25
126.73
125.04
53.23
52.69
49.56
41.56
31.80
20.27
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


H
Ph
CO2Me
O
N

35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7.31
7.31
7.30
7.29
7.26
7.23
7.21
6.42
6.40
4.81
4.18
4.16
4.14
3.76
3.10
3.08
3.07
3.06
3.05
3.03
2.25
2.23
2.22
2.21
2.20
2.19
2.18
2.17
2.17
2.16
1.00
2.95
1.89
1.05
1.03
2.01
2.94
1.97
1.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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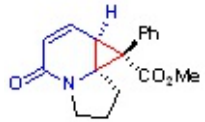
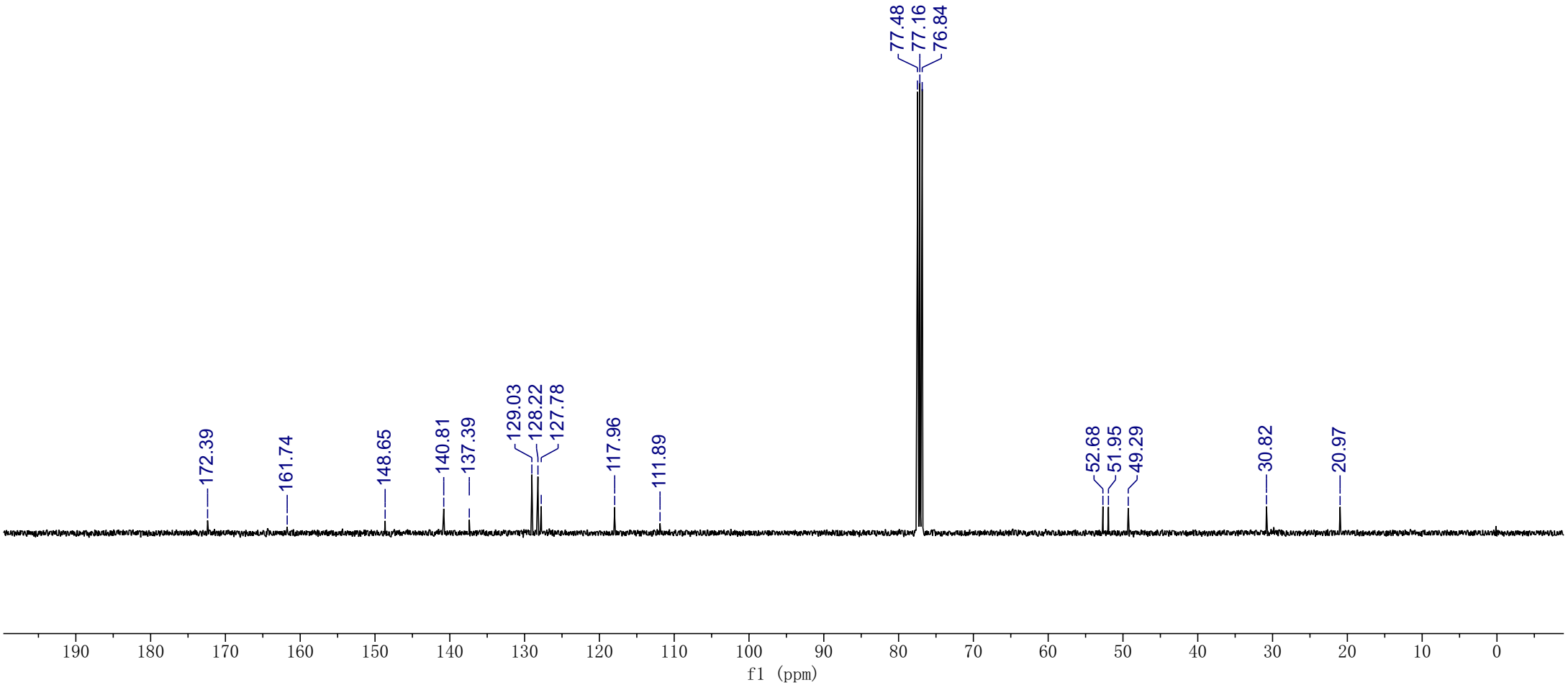
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)


H
Ph
O
N
CO2Me

35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77.16
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172.39
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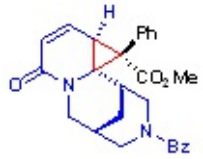
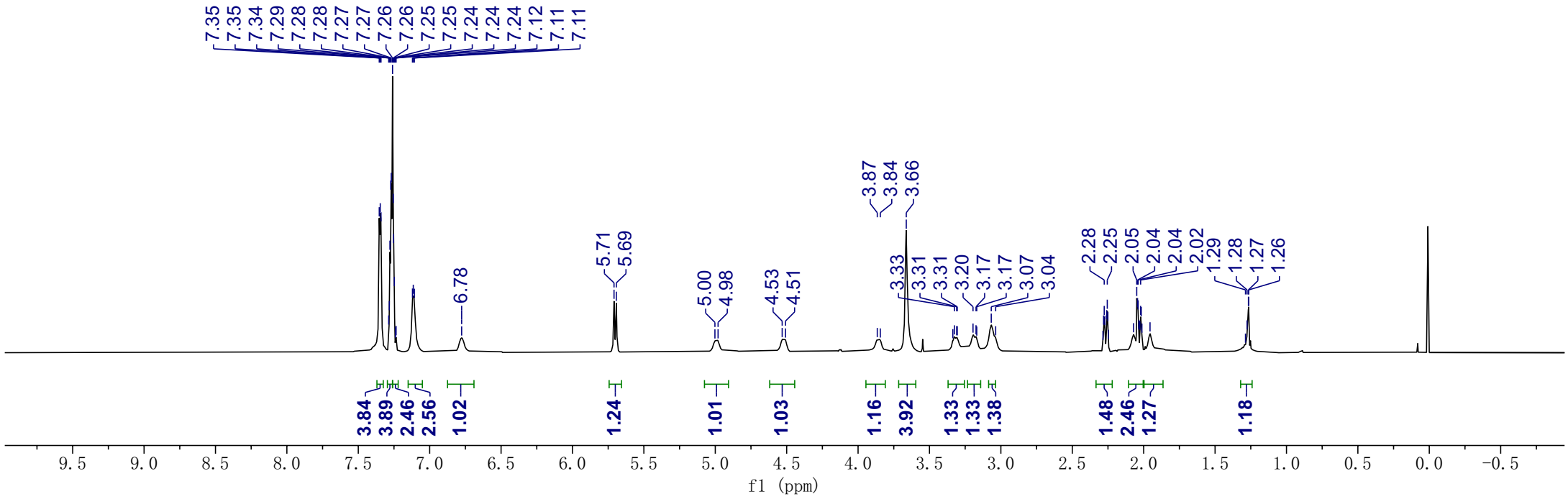
148.65
140.81
137.39
129.03
128.22
127.78
117.96
111.89
52.68
51.95
49.29
30.82
20.97
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
CO2Me
O
N
N
Bz

36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7.28
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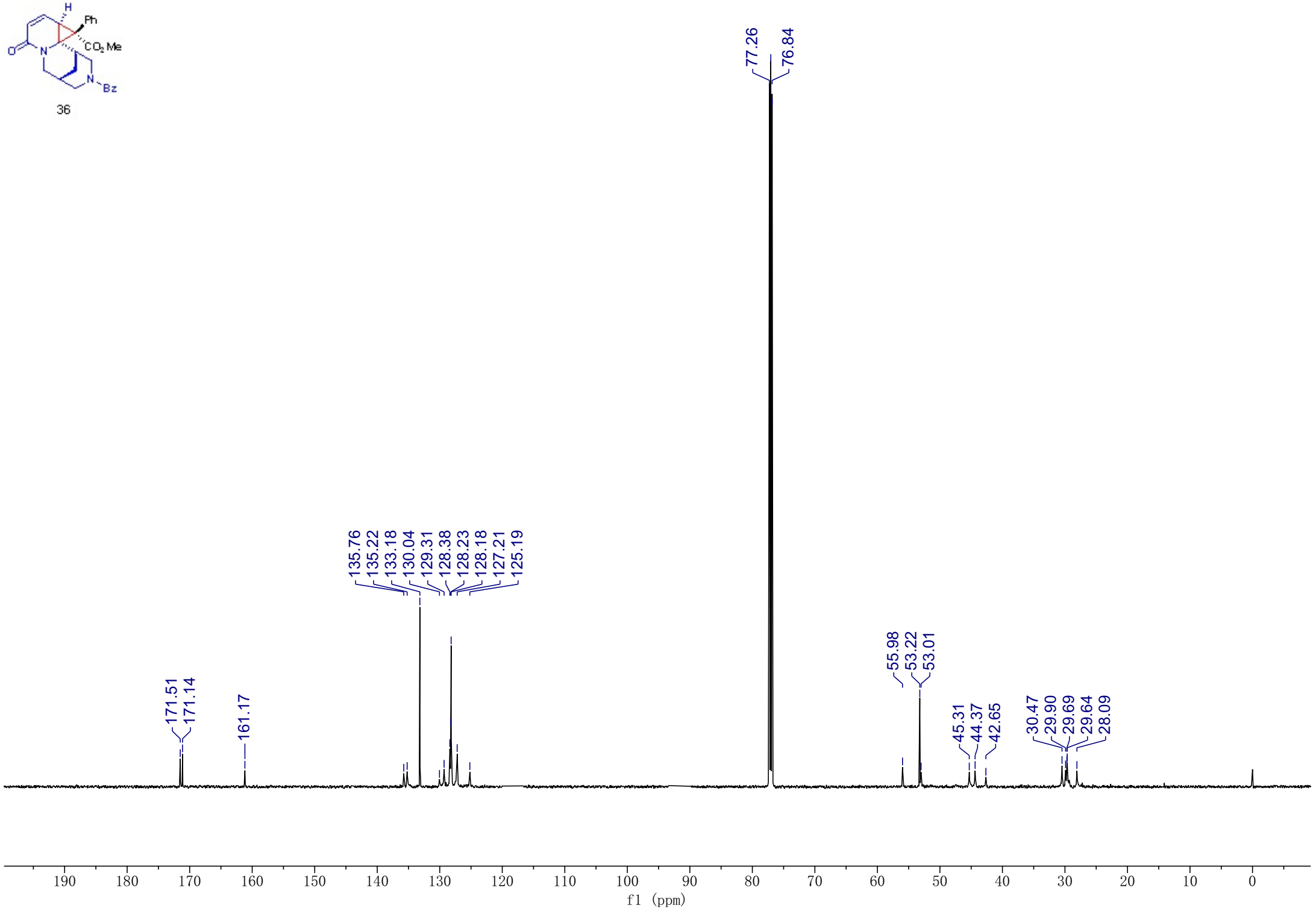
7.25
7.25
7.24
7.24
7.24
7.12
7.11
7.11
6.78
5.71
5.69
5.00
4.98
4.53
4.51
3.87
3.84
3.66
3.33
3.31
3.31
3.20
3.17
3.17
3.07
3.04
2.28
2.25
2.05
2.04
2.04
2.02
1.29
1.28
1.27
1.26
3.84
3.89
2.46
2.56
1.02
1.24
1.01
1.03
1.16
3.92
1.33
1.33
1.38
1.48
2.46
1.27
1.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

H
Ph
CO2Me
O
N
N
Bz

36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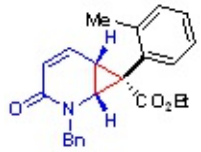
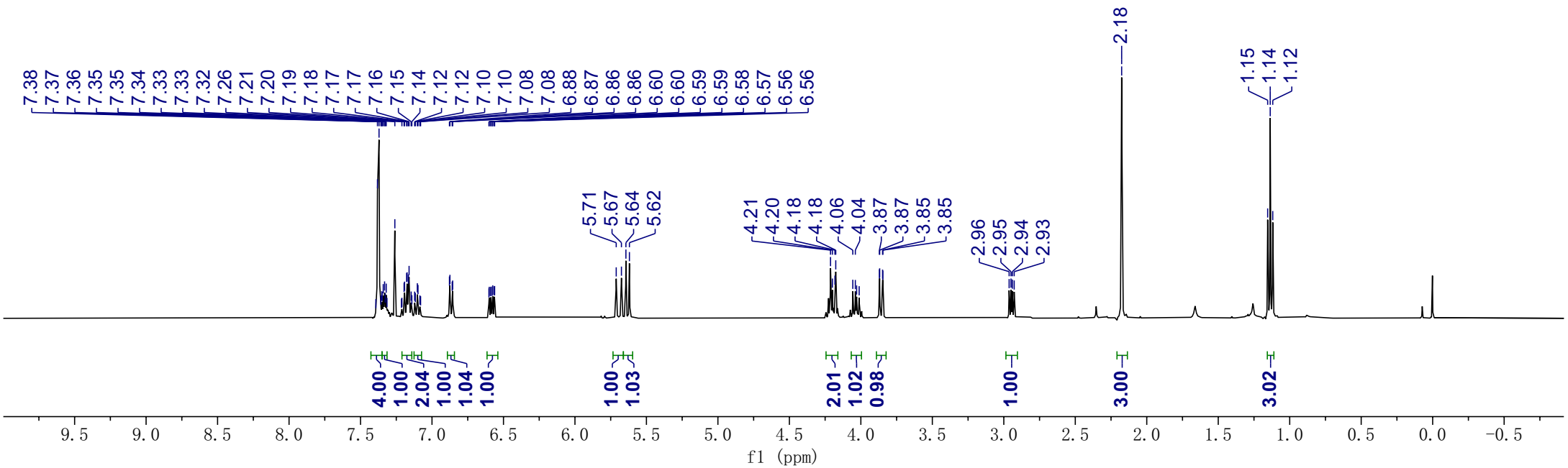
128.38
128.23
128.18
127.21
125.19
171.51
171.14
161.17
55.98
53.22
53.01
45.31
44.37
42.65
30.47
29.90
29.69
29.64
28.09
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
H
O
N
Bn
H
CO2Et

37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7.19
7.18
7.17
7.17
7.16
7.15
7.14
7.12
7.12
7.10
7.10
7.08
7.08
6.88
6.87
6.86
6.86
6.60
6.60
6.59
6.59
6.58
6.57
6.56
6.56
5.71
5.67
5.64
5.62
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4.18
4.18
4.06
4.04
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3.87
3.85
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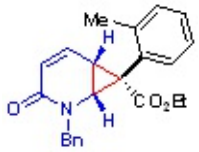
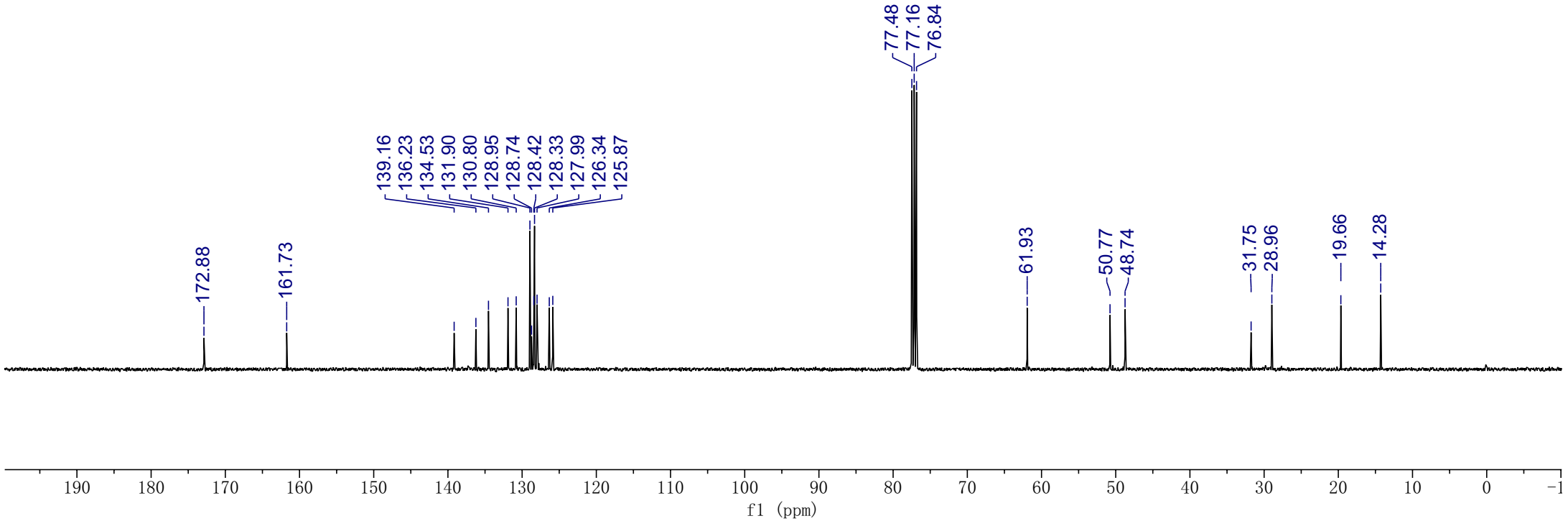
2.95
2.94
2.93
2.18
1.15
1.14
1.12
4.00
1.00
2.04
1.00
1.04
1.00
1.00
1.03
2.01
1.02
0.98
1.00
3.00
3.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Me
H
O
N
Bn
H
CO2Et

37


172.88
161.73
139.16
136.23
134.53
131.90
130.80
128.95
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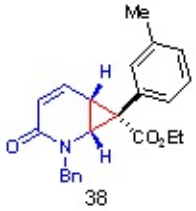
128.33
127.99
126.34
125.87
77.48
77.16
76.84
61.93
50.77
48.74
31.75
28.96
19.66
14.28
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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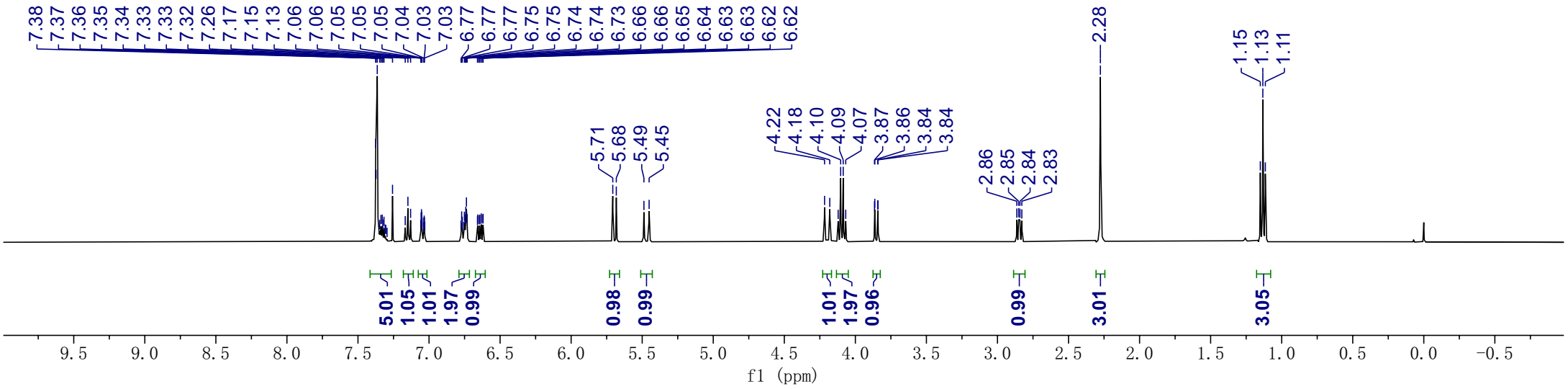
H
O
N
Bn
H
CO2Et

38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1.01
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0.98
0.99
1.01
1.97
0.96
0.99
3.01
3.05
9.5
9.0
8.5
8.0
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7.0
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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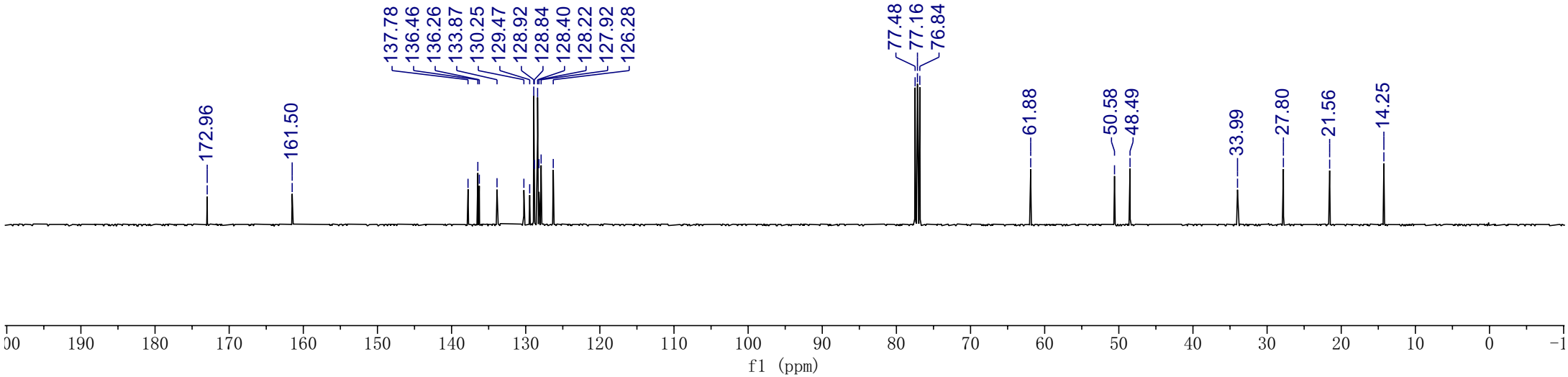
0.0
-0.5
f1 (ppm)


Me
H
O
N
Bn
H
CO2Et

38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77.16
76.84
172.96
161.50
61.88
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33.99
27.80
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14.25
190
180
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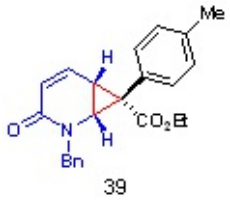
f1 (ppm)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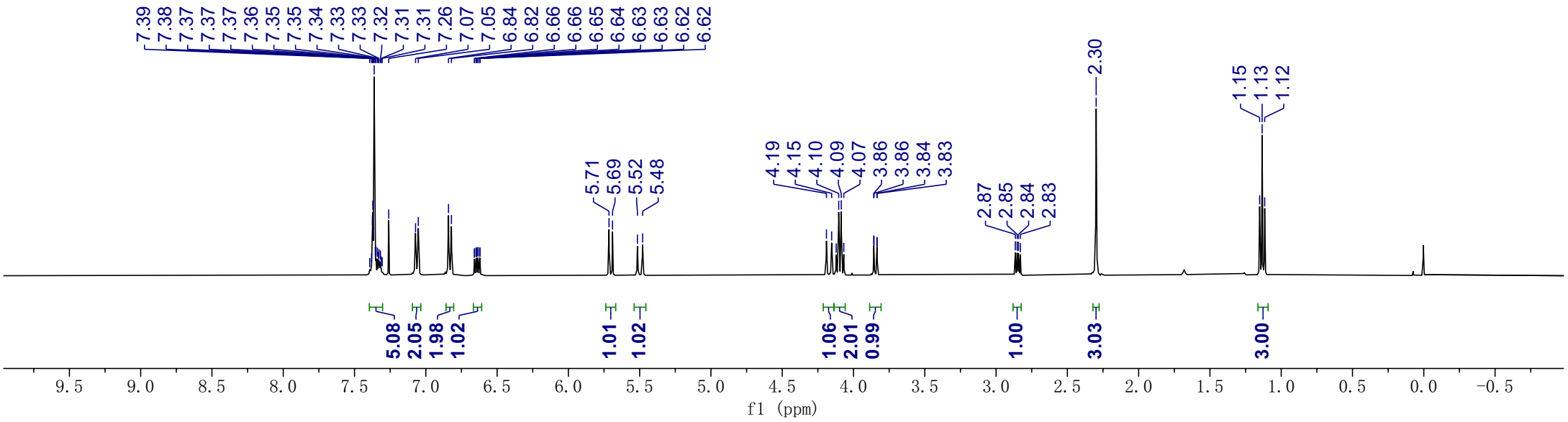
Bn
H
CO2Et

39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6.66
6.65
6.64
6.63
6.63
6.62
6.62
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5.69
5.52
5.48
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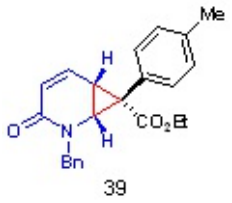
f1 (ppm)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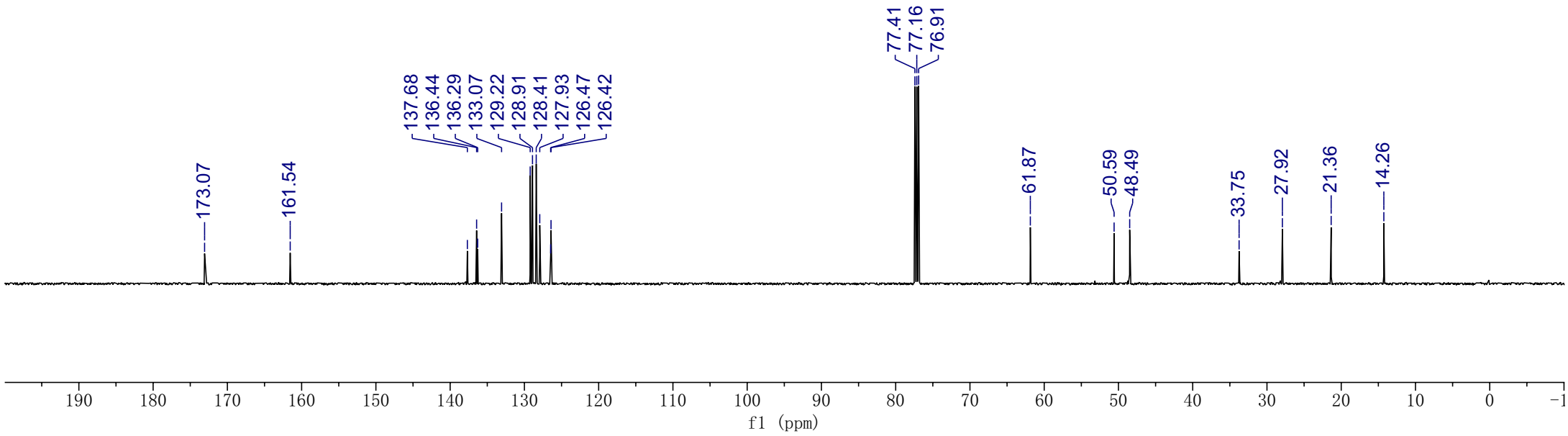
N
Bn
H
CO2Et

39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127.93
126.47
126.42
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76.91
61.87
50.59
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33.75
27.92
21.36
14.26
190
180
170
160
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140
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80
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20
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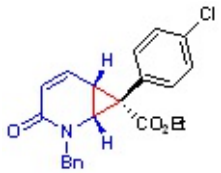
0
-1
f1 (ppm)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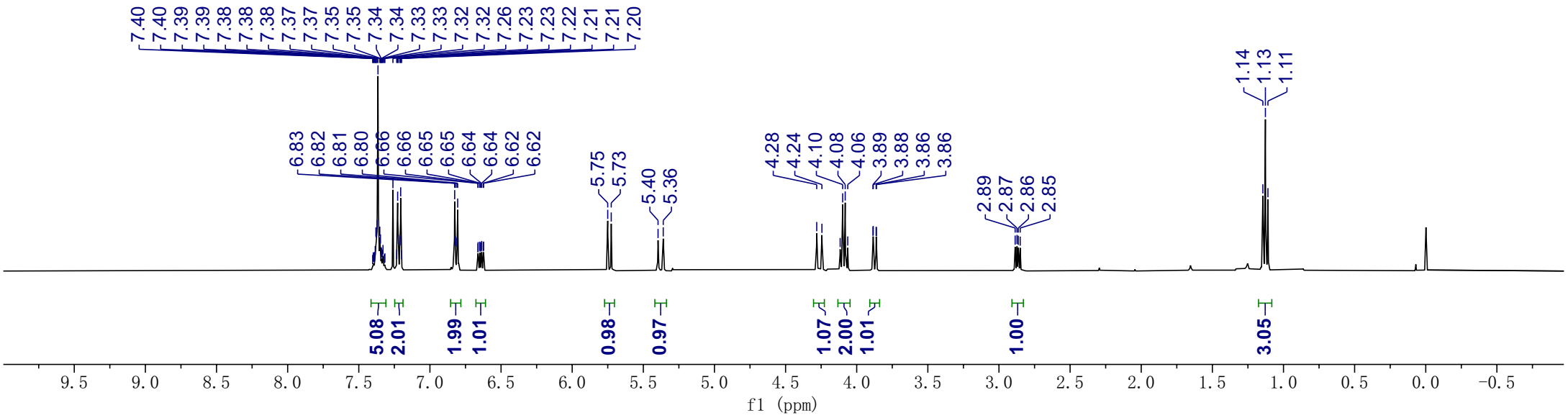
N
Bn
H
CO2Et

40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7.22
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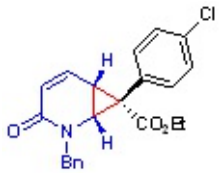
-0.5
f1 (ppm)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N
Bn
H
CO2Et

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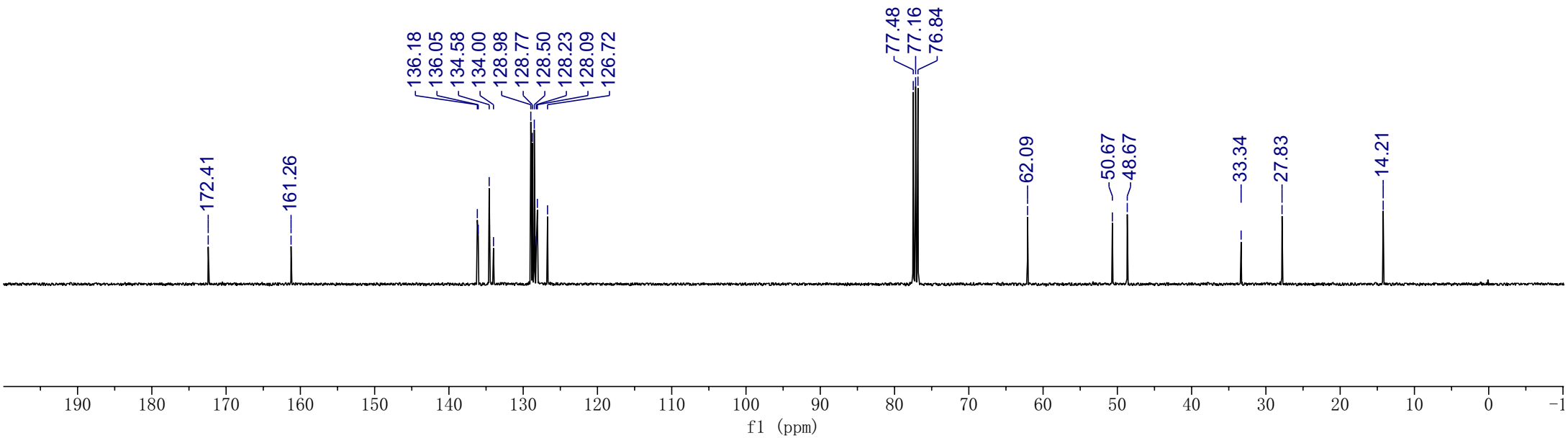
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14.21
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180
170
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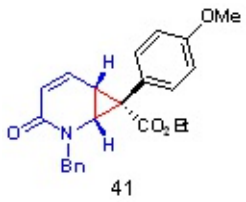
0
-1
f1 (ppm)


OMe
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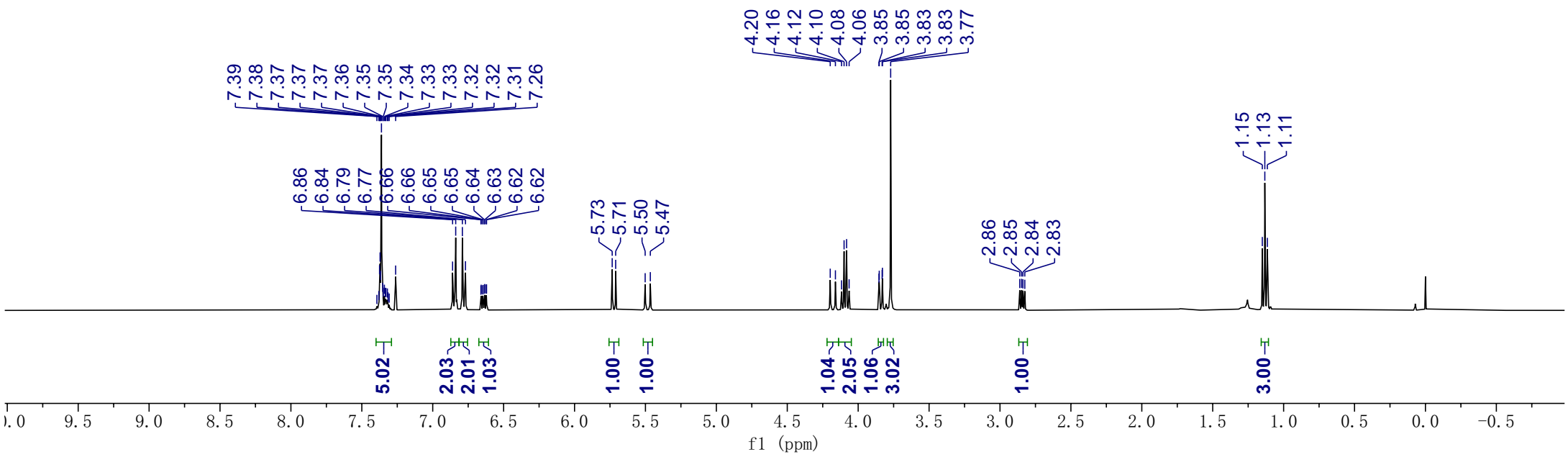
O
N
Bn
H
CO2Et

41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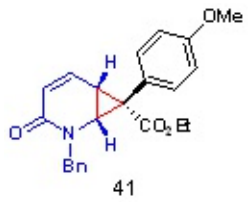
3.00
f1 (ppm)


OMe
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N
Bn
H
CO2Et

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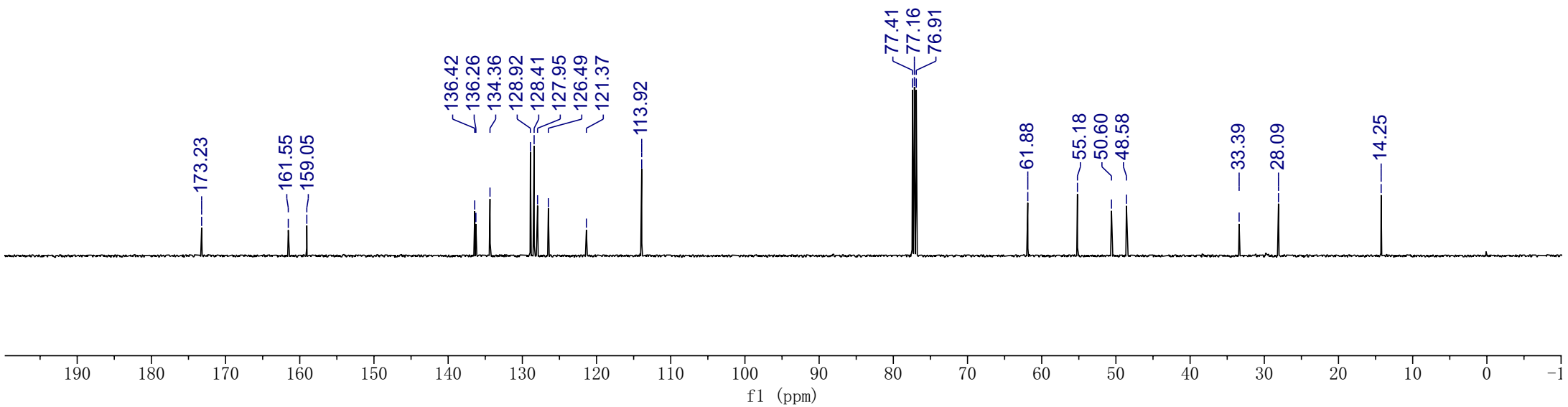
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40
30
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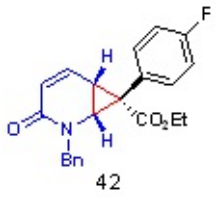
0
-1
f1 (ppm)


F
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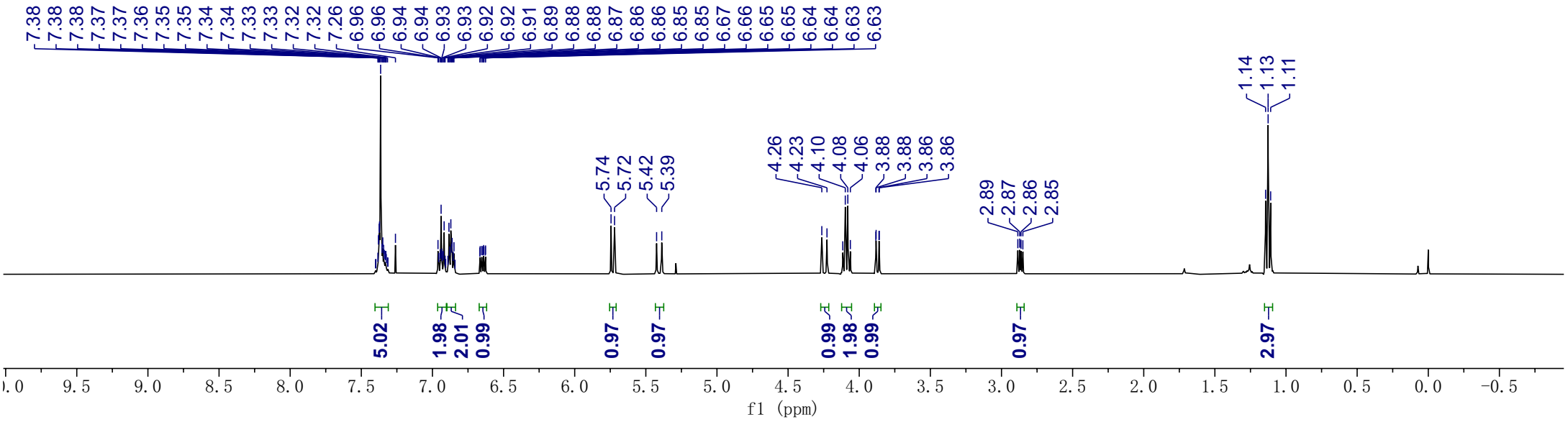
O
N
Bn
H
CO2Et

42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1.11
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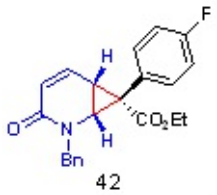
0.97
0.99
1.98
0.99
0.97
2.97
f1 (ppm)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N
Bn
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CO2Et

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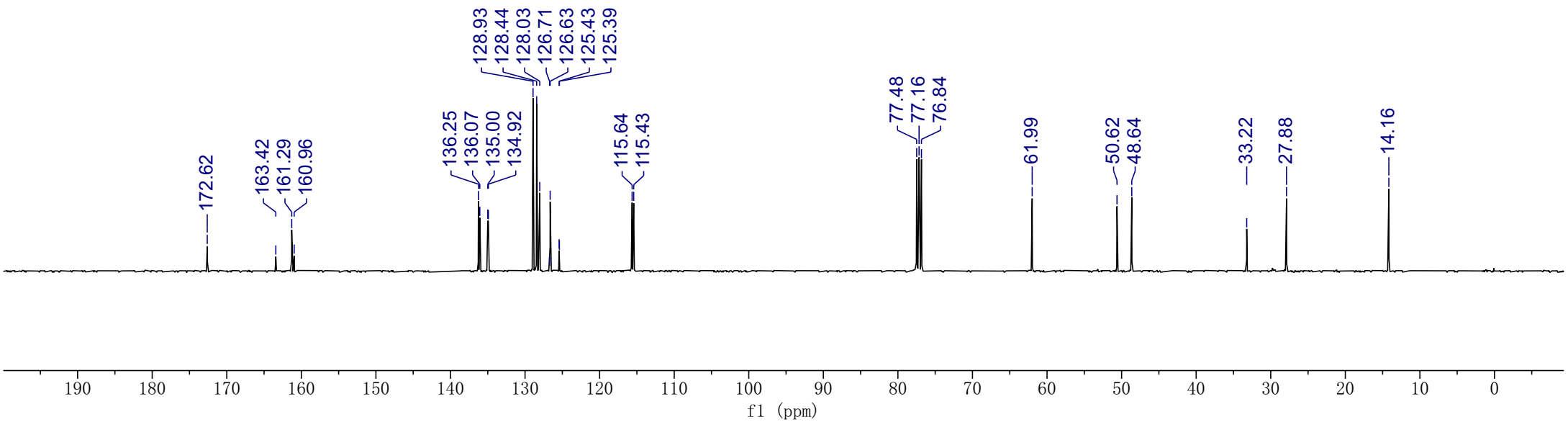
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125.39
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76.84
61.99
50.62
48.64
33.22
27.88
14.16
190
180
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130
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110
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90
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70
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50
40
30
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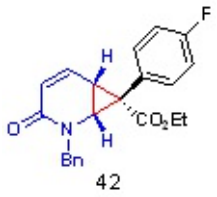
10
0
f1 (ppm)


F
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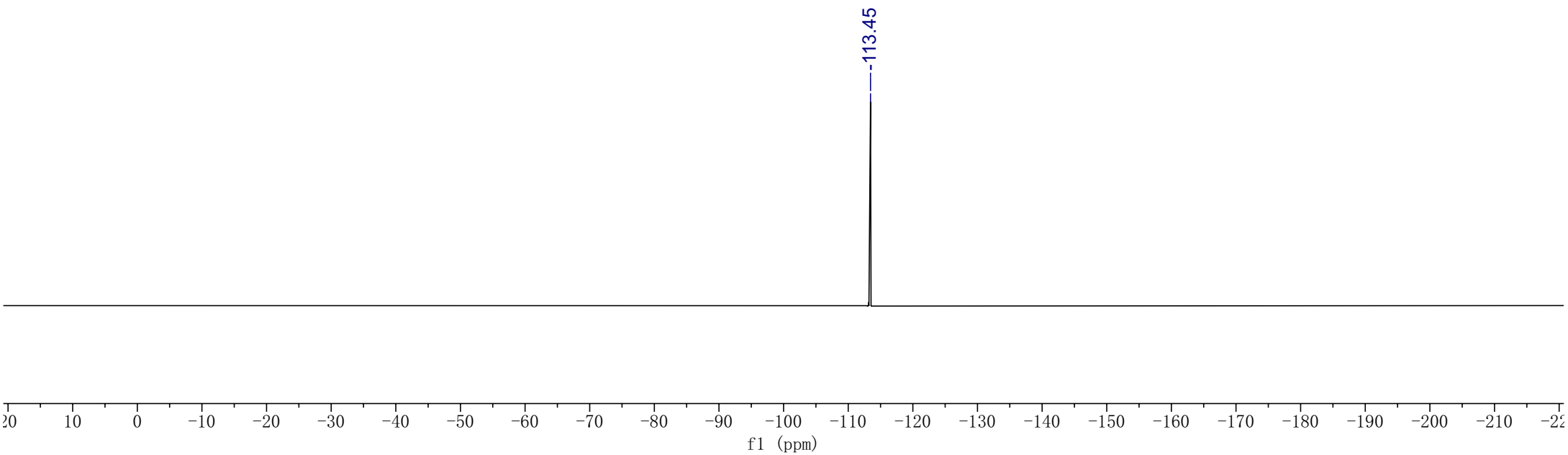
N
Bn
H
CO2Et

42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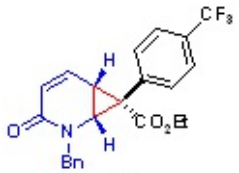
-140
-150
-160
-170
-180
-190
-200
-210
-22
f1 (ppm)


CF3
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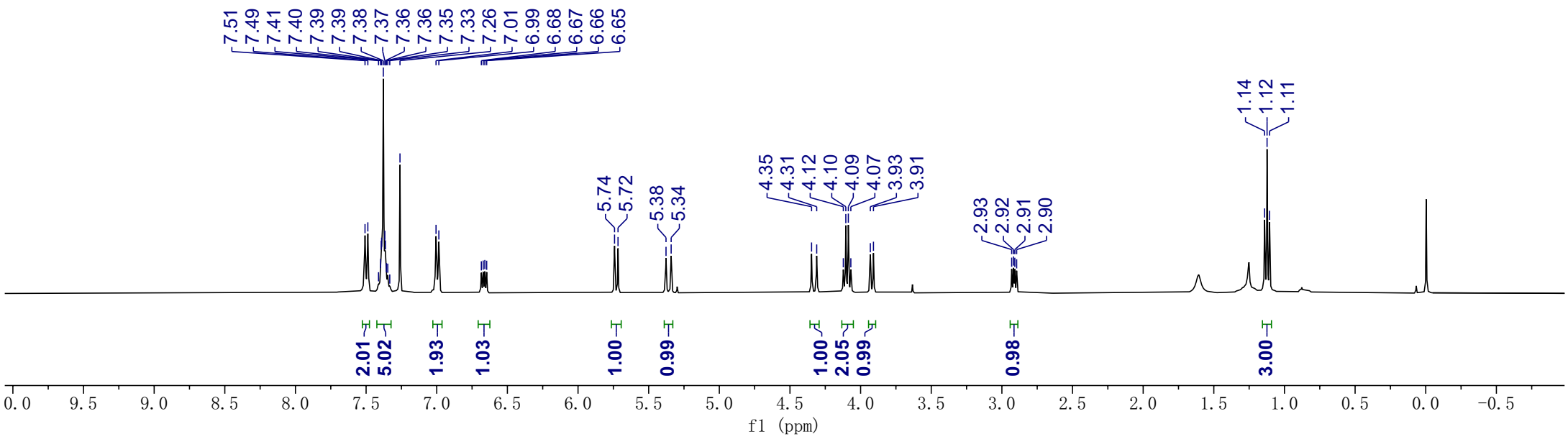
Bn
H
CO2Et

43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6.65
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4.12
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2.90
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2.05
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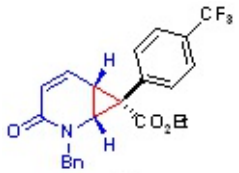
f1 (ppm)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O
N
Bn
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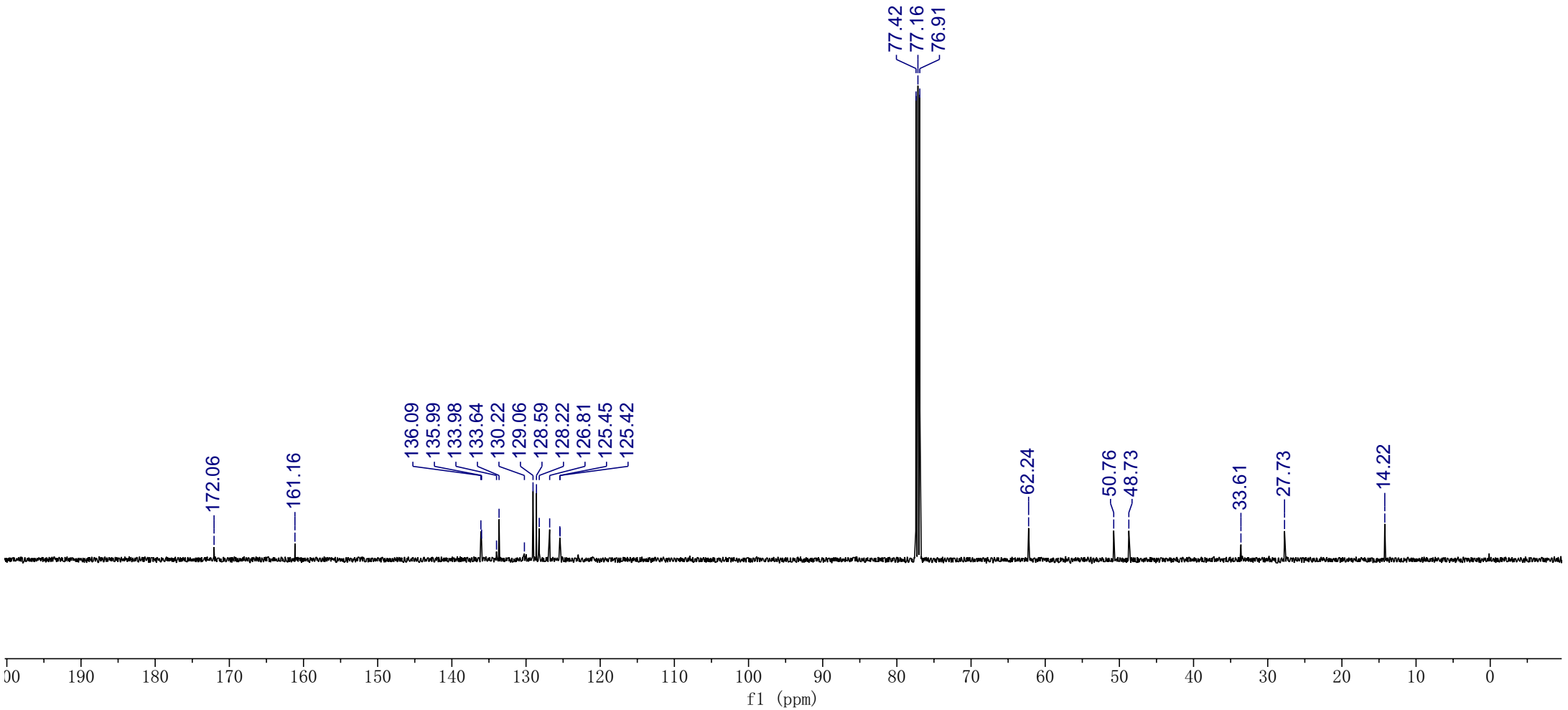
CO2Et

43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62.24
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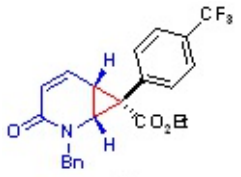
33.61
27.73
14.22
f1 (ppm)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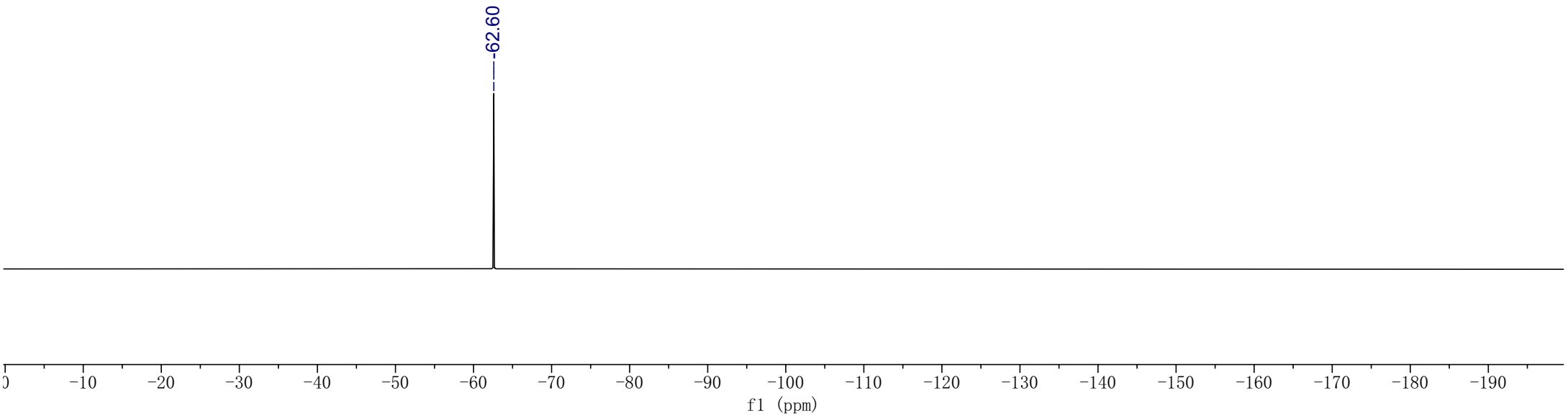
Bn
H
CO2Et

43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-100
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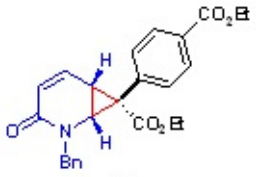
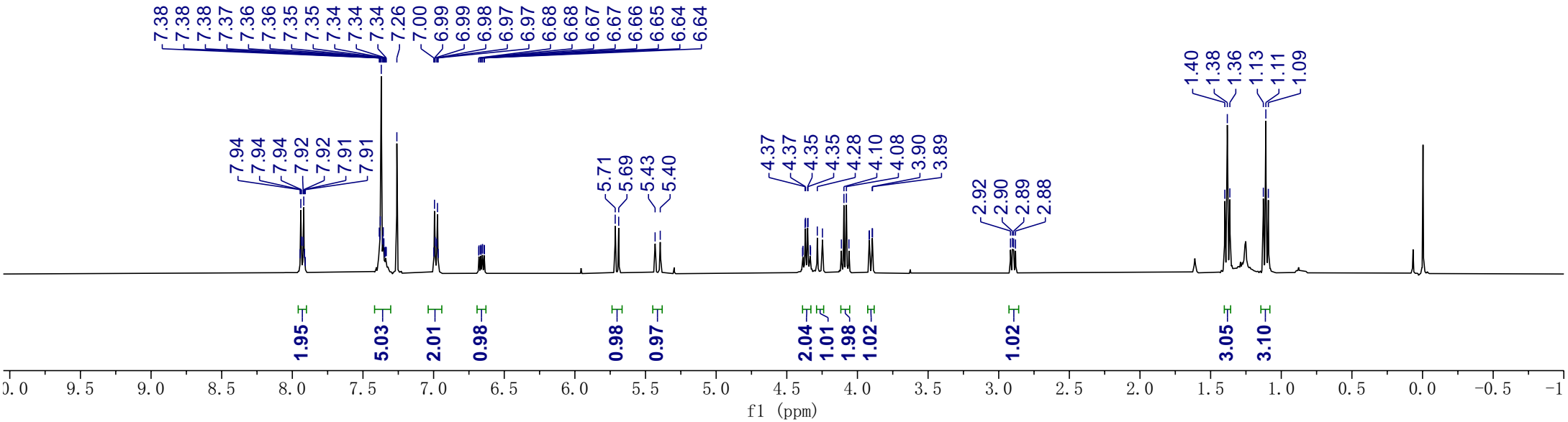
-150
-160
-170
-180
-190
f1 (ppm)


CO2Et
H
O
N
Bn
H
CO2Et

44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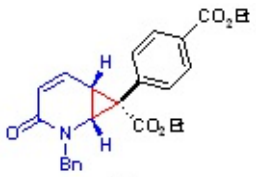
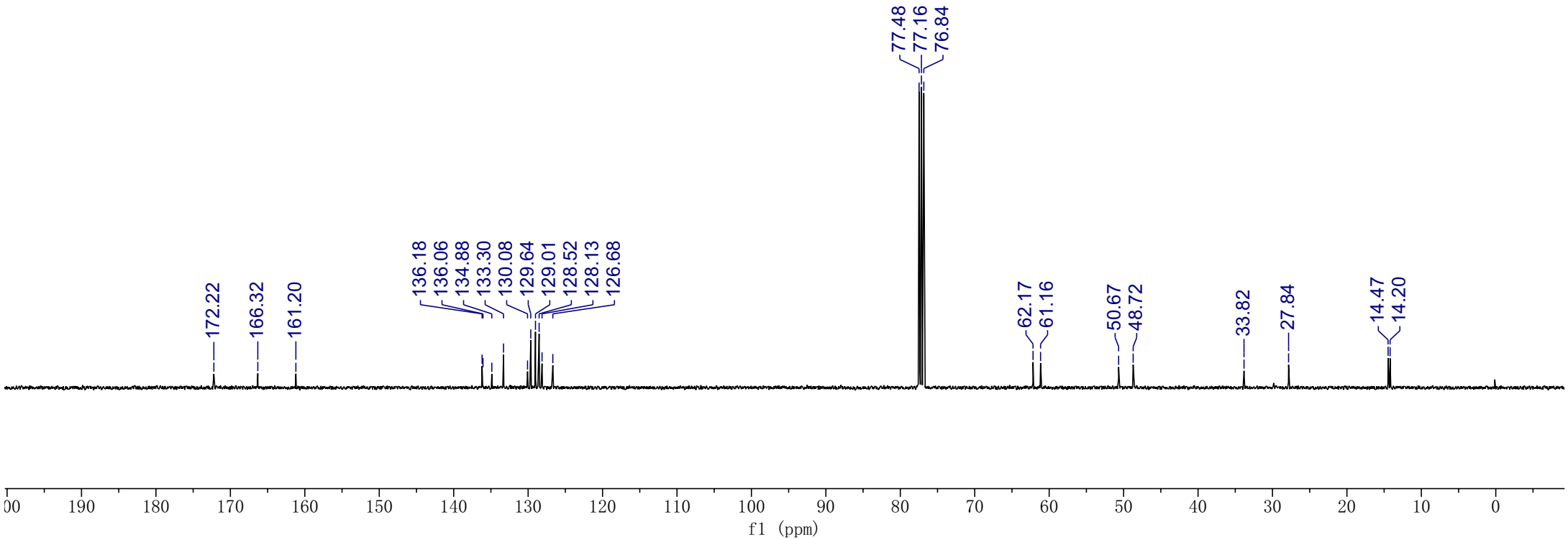
3.05
3.10
f1 (ppm)


CO2Et
H
O
N
Bn
H
CO2Et

44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134.88
133.30
130.08
129.64
129.01
128.52
128.13
126.68
77.48
77.16
76.84
62.17
61.16
50.67
48.72
33.82
27.84
14.47
14.20
00
190
180
170
160
150
140
130
120
110
100
90
80
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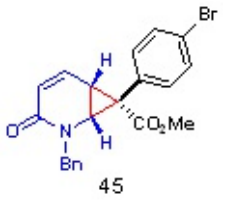
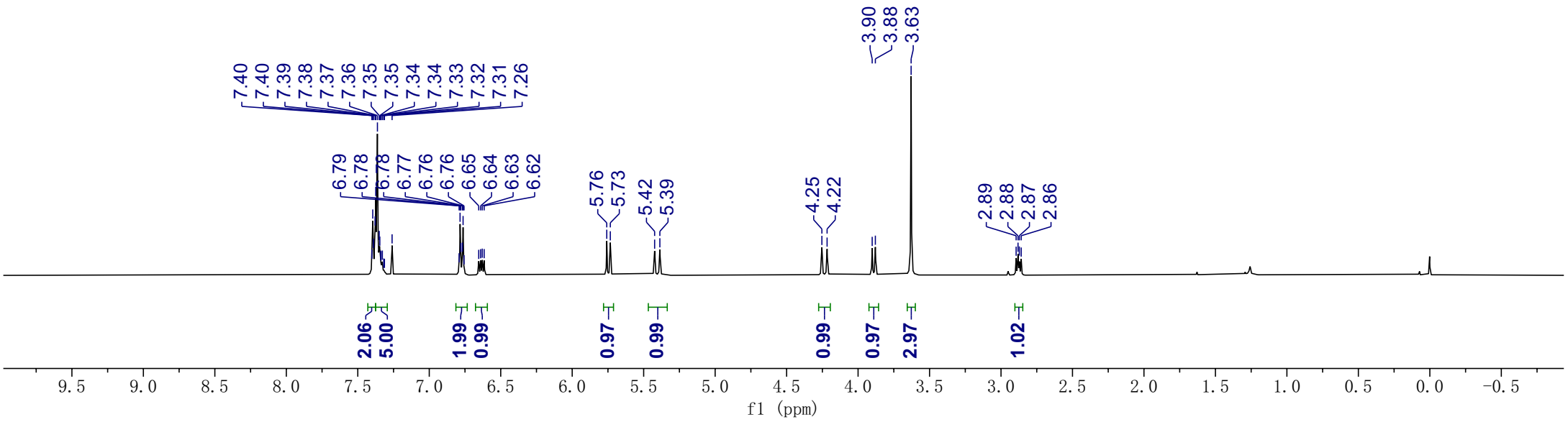
50
40
30
20
10
0
f1 (ppm)


Br
H
O
N
Bn
H
CO2Me

45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7.32
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7.26
6.79
6.78
6.78
6.77
6.76
6.76
6.65
6.64
6.63
6.62
5.76
5.73
5.42
5.39
4.25
4.22
3.90
3.88
3.63
2.89
2.88
2.87
2.86
2.06
5.00
1.99
0.99
0.97
0.99
0.99
0.97
2.97
1.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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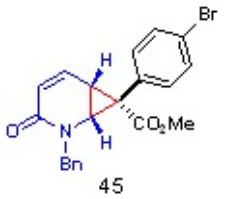
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Br
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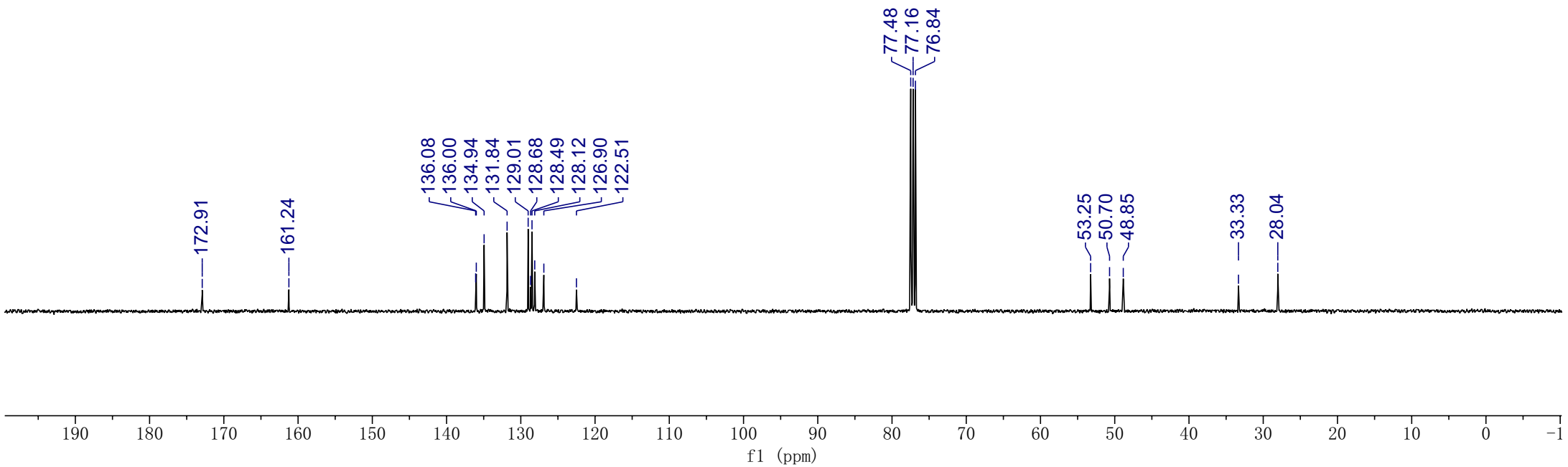
O
N
Bn
H
CO2Me

45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122.51
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77.16
76.84
53.25
50.70
48.85
33.33
28.04
190
180
170
160
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140
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120
110
100
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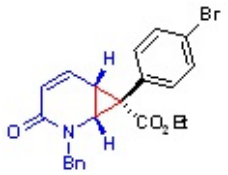
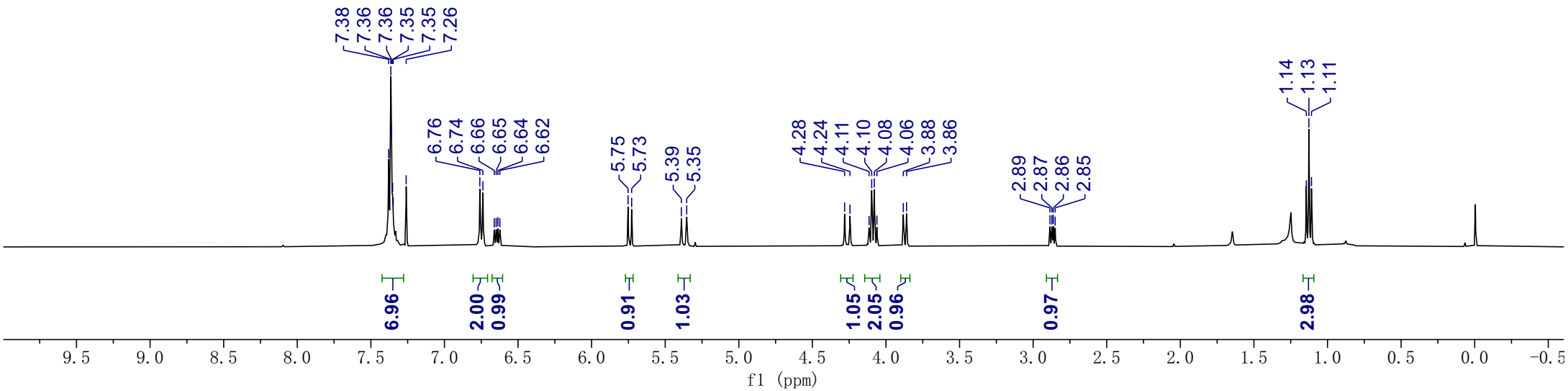
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Br
H
O
N
Bn
H
CO2Et

46


7.38
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6.74
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6.65
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5.73
5.39
5.35
4.28
4.24
4.11
4.10
4.08
4.06
3.88
3.86
2.89
2.87
2.86
2.85
1.14
1.13
1.11
6.96
2.00
0.99
0.91
1.03
1.05
2.05
0.96
0.97
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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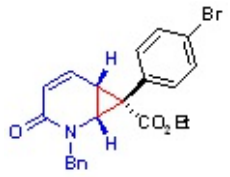
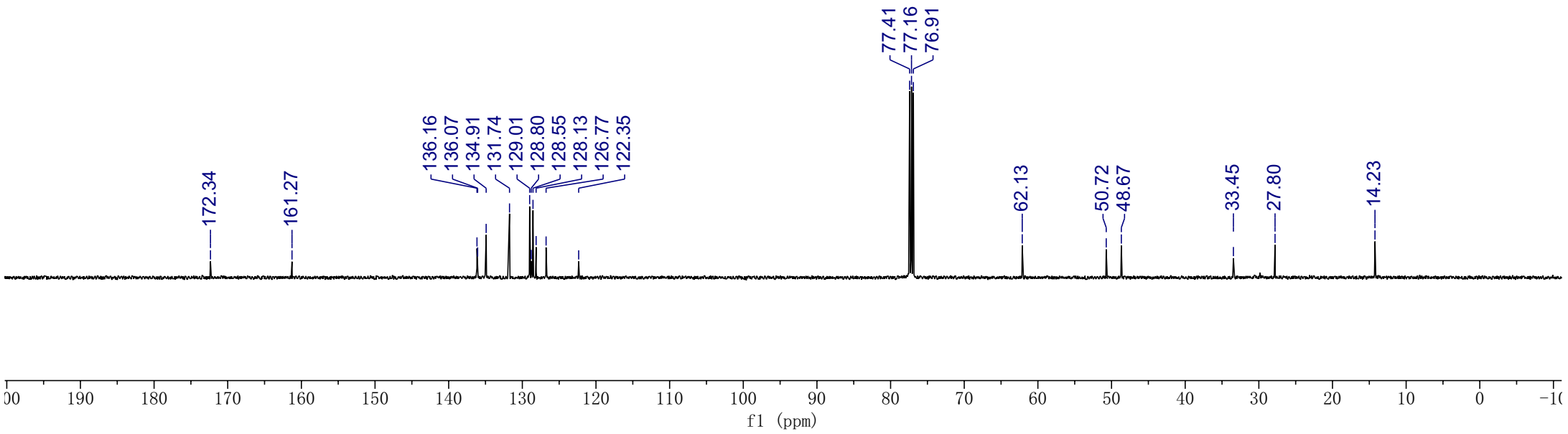
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


Br
H
O
N
Bn
H
CO2Et

46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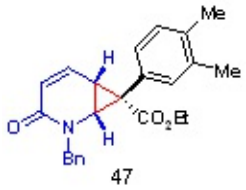
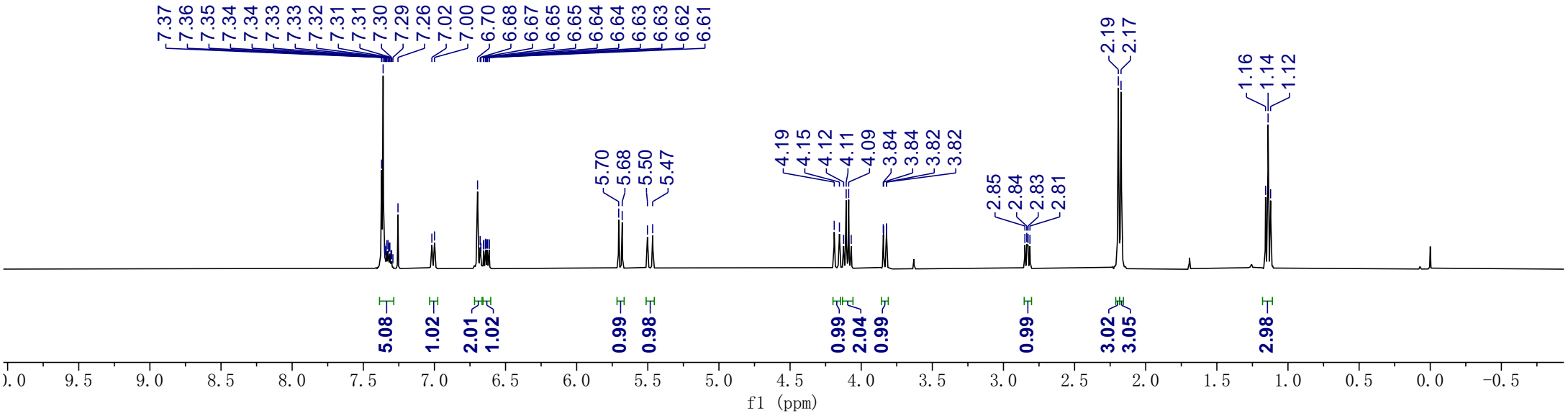
128.55
128.13
126.77
122.35
77.41
77.16
76.91
62.13
50.72
48.67
33.45
27.80
14.23
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Me
Me
H
O
N
H
Bn
CO2Et

47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7.02
7.00
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6.67
6.65
6.65
6.64
6.64
6.63
6.63
6.62
6.61
5.70
5.68
5.50
5.47
4.19
4.15
4.12
4.11
4.09
3.84
3.84
3.82
3.82
2.85
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2.81
2.19
2.17
1.16
1.14
1.12
5.08
1.02
2.01
1.02
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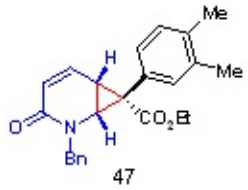
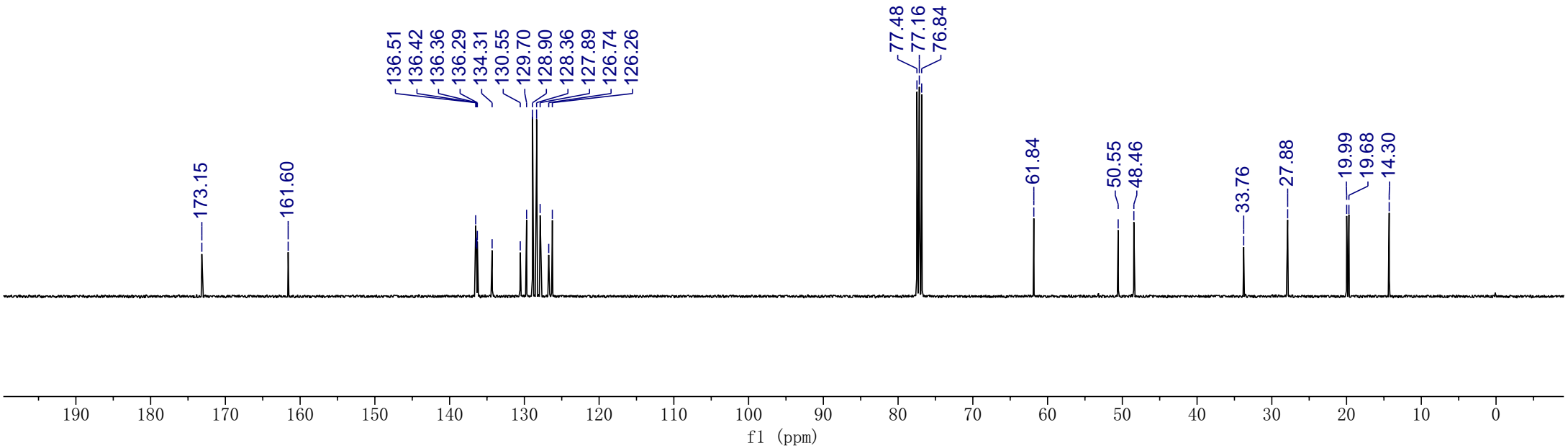
0.98
0.99
2.04
0.99
0.99
3.02
3.05
2.98
f1 (ppm)


Me
Me
H
O
N
H
Bn
CO2Et

47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127.89
126.74
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77.48
77.16
76.84
61.84
50.55
48.46
33.76
27.88
19.99
19.68
14.30
190
180
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120
110
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90
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50
40
30
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10
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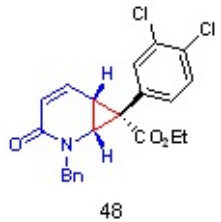
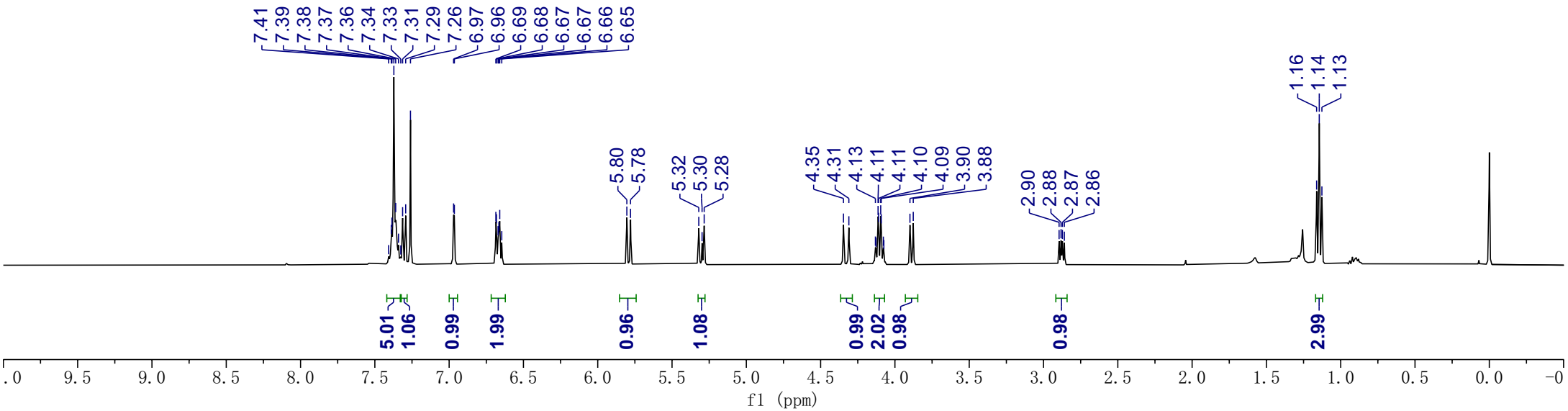
f1 (ppm)


Cl
Cl
H
O
N
Bn
H
CO2Et

48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6.69
6.68
6.67
6.67
6.66
6.65
5.80
5.78
5.32
5.30
5.28
4.35
4.31
4.13
4.11
4.11
4.10
4.09
3.90
3.88
2.90
2.88
2.87
2.86
1.16
1.14
1.13
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1.06
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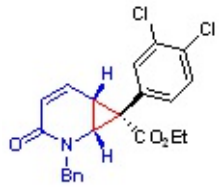
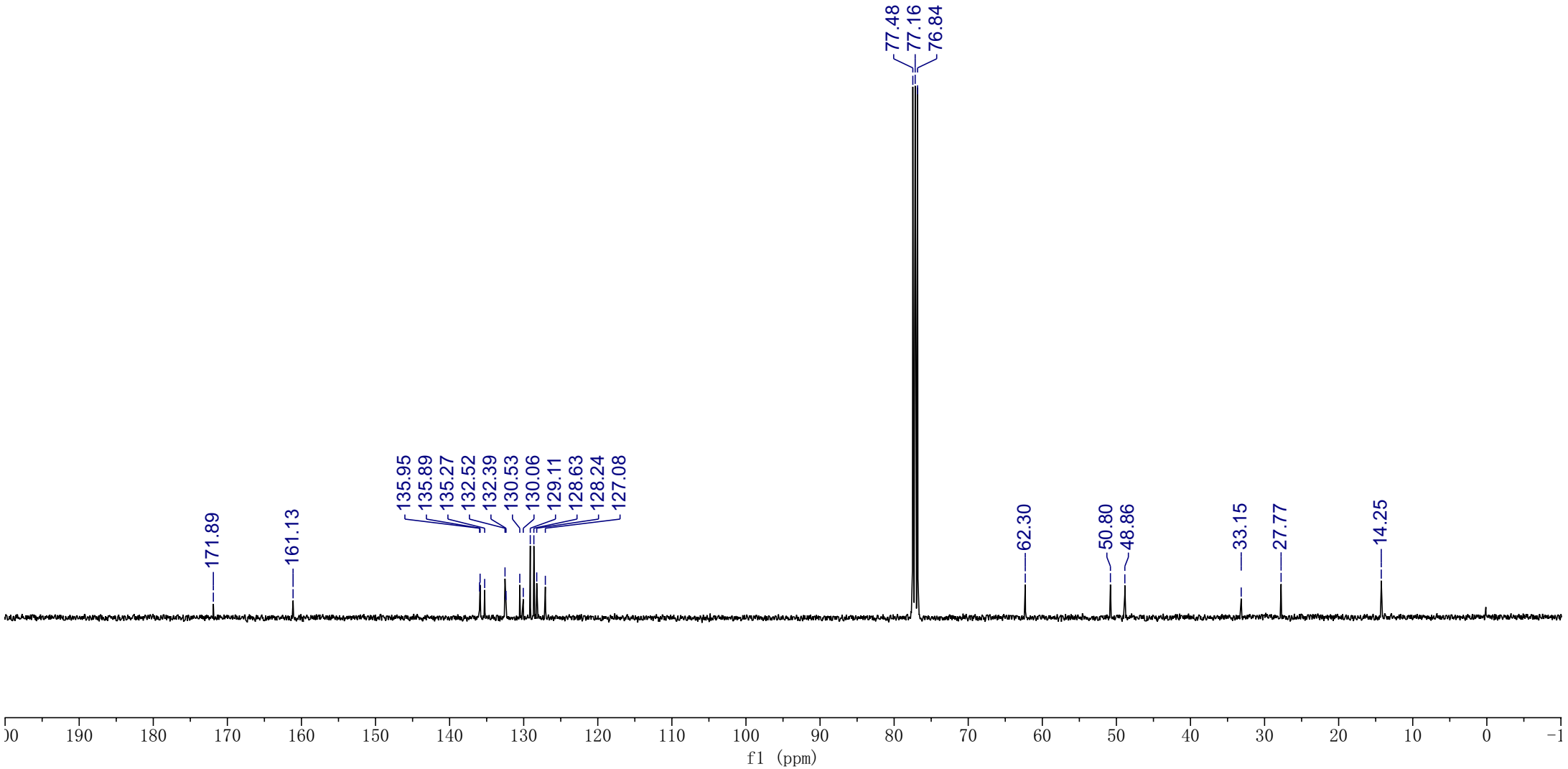
1.99
0.96
1.08
0.99
2.02
0.98
0.98
2.99
f1 (ppm)


Cl
Cl
H
O
N
Bn
H
CO2Et

48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132.39
130.53
130.06
129.11
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128.24
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171.89
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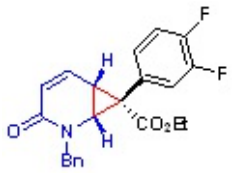
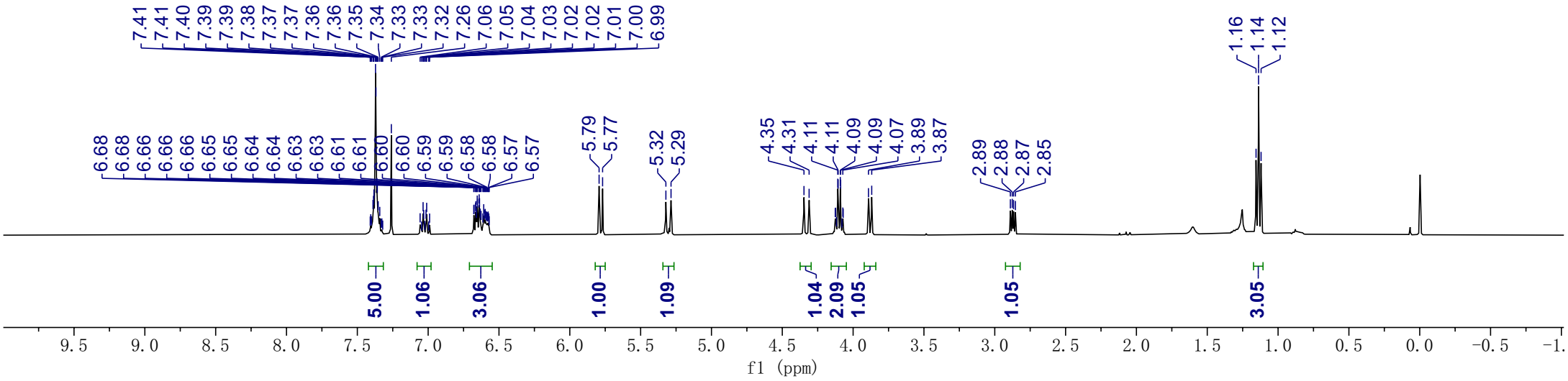
62.30
50.80
48.86
33.15
27.77
14.25
f1 (ppm)


F
F
H
O
N
Bn
H
CO2Et

49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7.33
7.32
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7.06
7.05
7.04
7.03
7.02
7.02
7.01
7.00
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3.06
1.00
1.09
1.04
2.09
1.05
1.05
3.05
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8.0
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4.5
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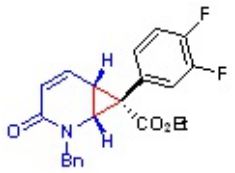
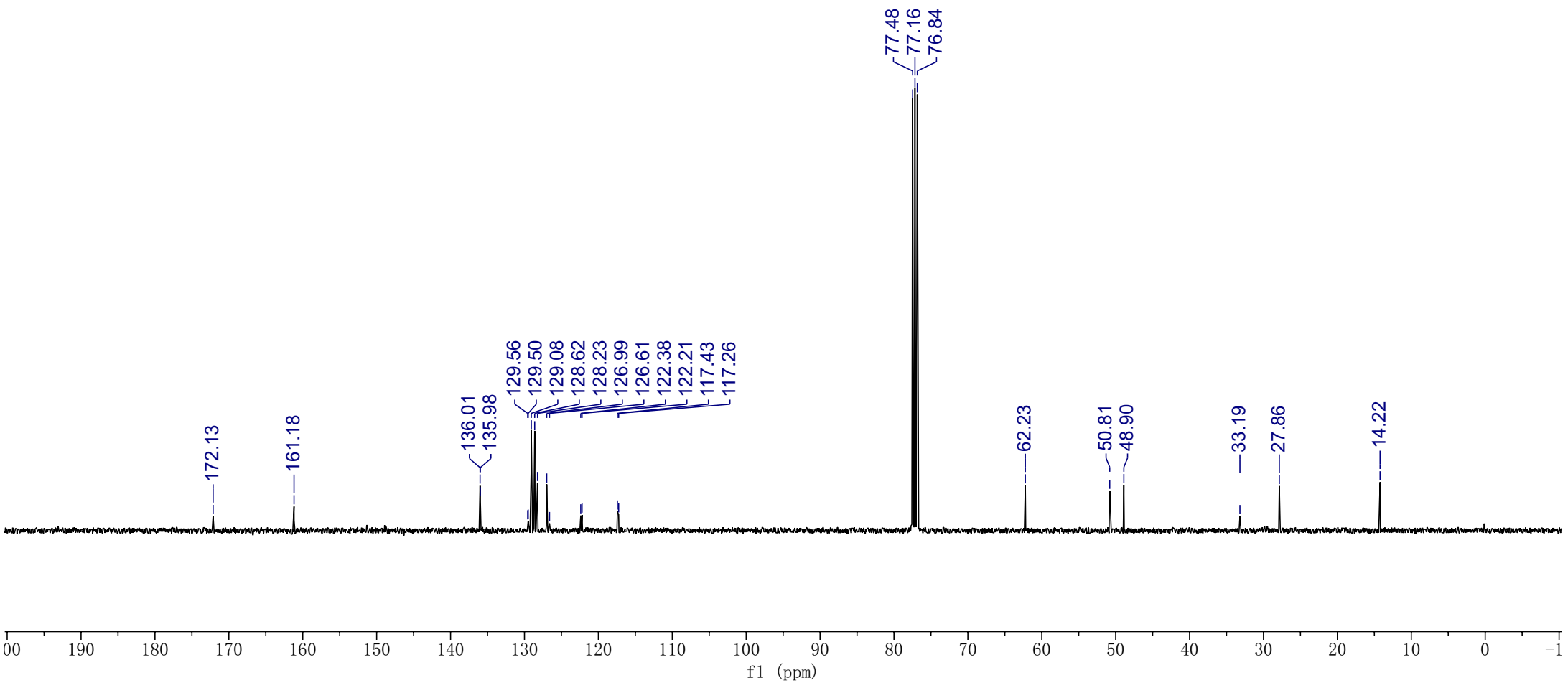
-1.
f1 (ppm)


F
F
H
O
N
H
Bn
CO2Et

49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129.08
128.62
128.23
126.99
126.61
122.38
122.21
117.43
117.26
77.48
77.16
76.84
62.23
50.81
48.90
33.19
27.86
14.22
190
180
170
160
150
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130
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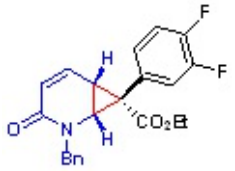
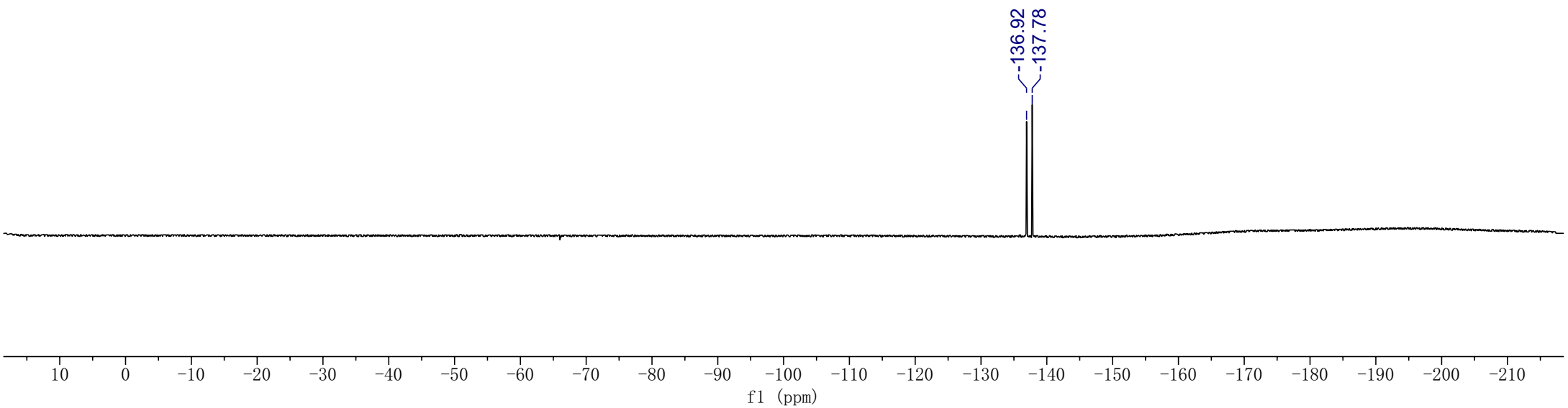
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
F
H
O
N
H
Bn
CO2Et

49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-137.78
10
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-10
-20
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-50
-60
-70
-80
-90
-100
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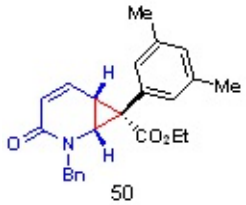
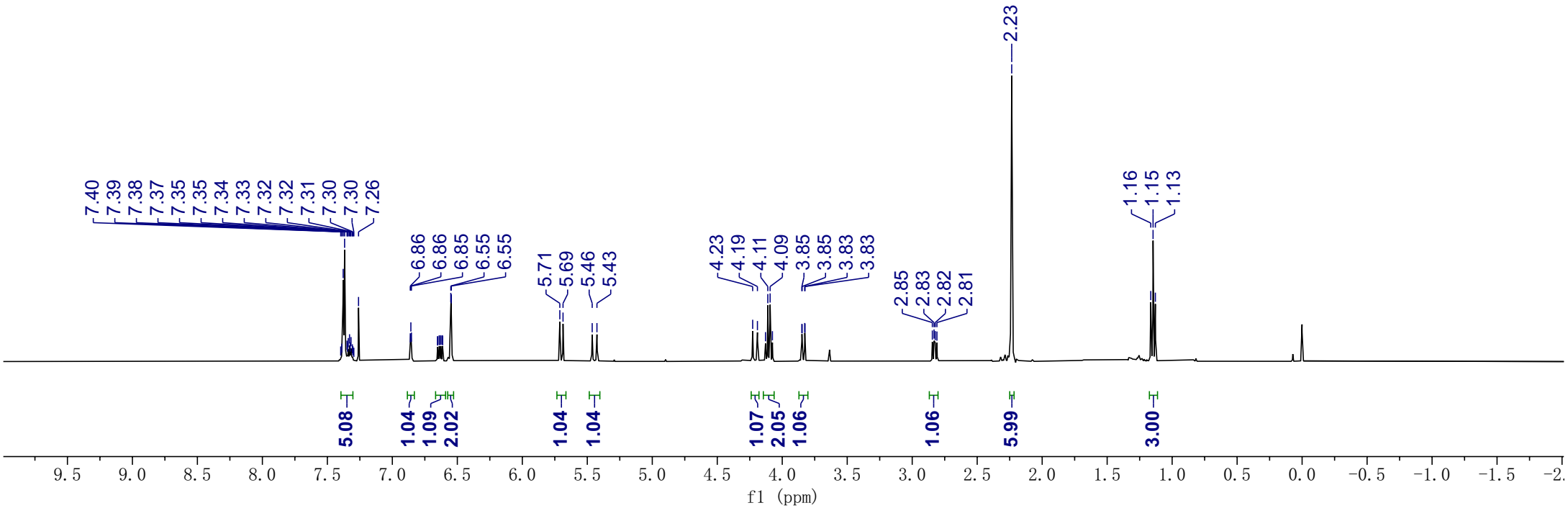
-180
-190
-200
-210
f1 (ppm)


Me
Me
H
O
N
Bn
H
CO2Et

50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7.30
7.26
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6.86
6.85
6.55
6.55
5.71
5.69
5.46
5.43
4.23
4.19
4.11
4.09
3.85
3.85
3.83
3.83
2.85
2.83
2.82
2.81
2.23
1.16
1.15
1.13
5.08
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1.04
1.04
1.07
2.05
1.06
1.06
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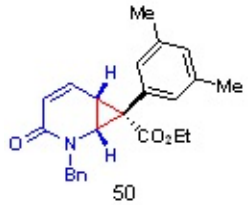
3.00
f1 (ppm)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Me
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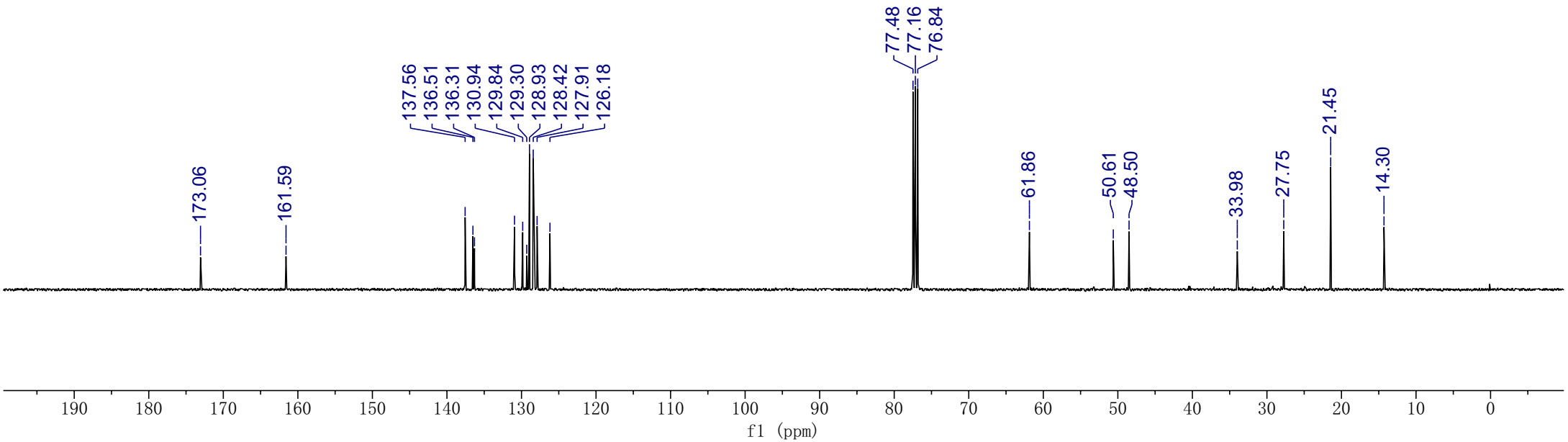
O
N
Bn
H
CO2Et

50


173.06
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137.56
136.51
136.31
130.94
129.84
129.30
128.93
128.42
127.91
126.18
77.48
77.16
76.84
61.86
50.61
48.50
33.98
27.75
21.45
14.30
190
180
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150
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130
120
110
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90
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70
60
50
40
30
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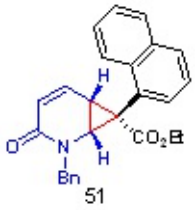
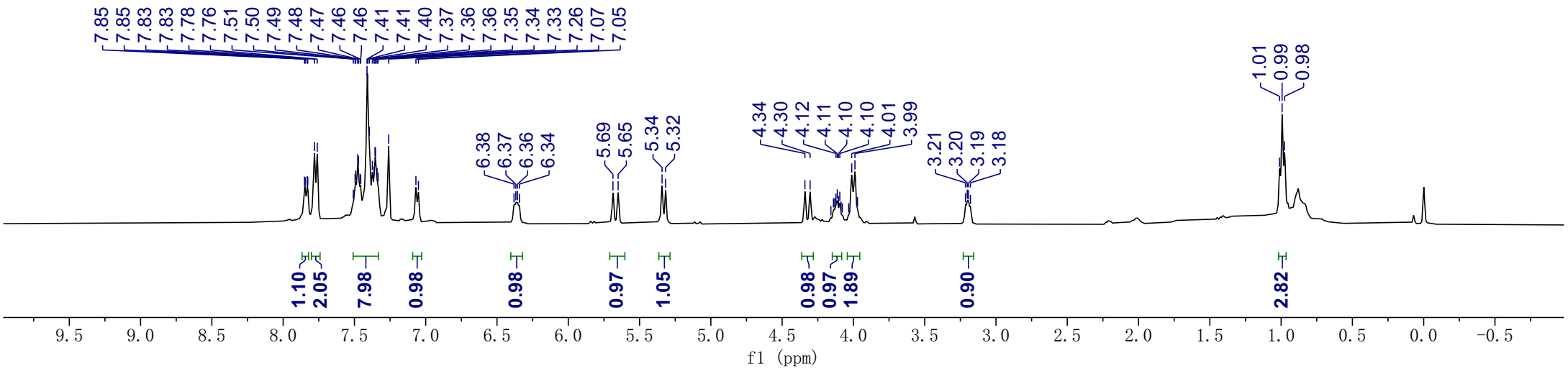
10
0
f1 (ppm)


H
O
N
Bn
H
CO2Et
51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7.41
7.40
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7.34
7.33
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7.07
7.05
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6.36
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5.69
5.65
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5.32
4.34
4.30
4.12
4.11
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4.10
4.01
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3.20
3.19
3.18
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0.99
0.98
1.10
2.05
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1.05
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0.97
1.89
0.90
2.82
9.5
9.0
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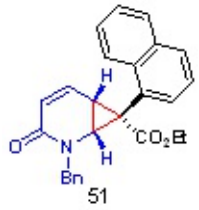
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
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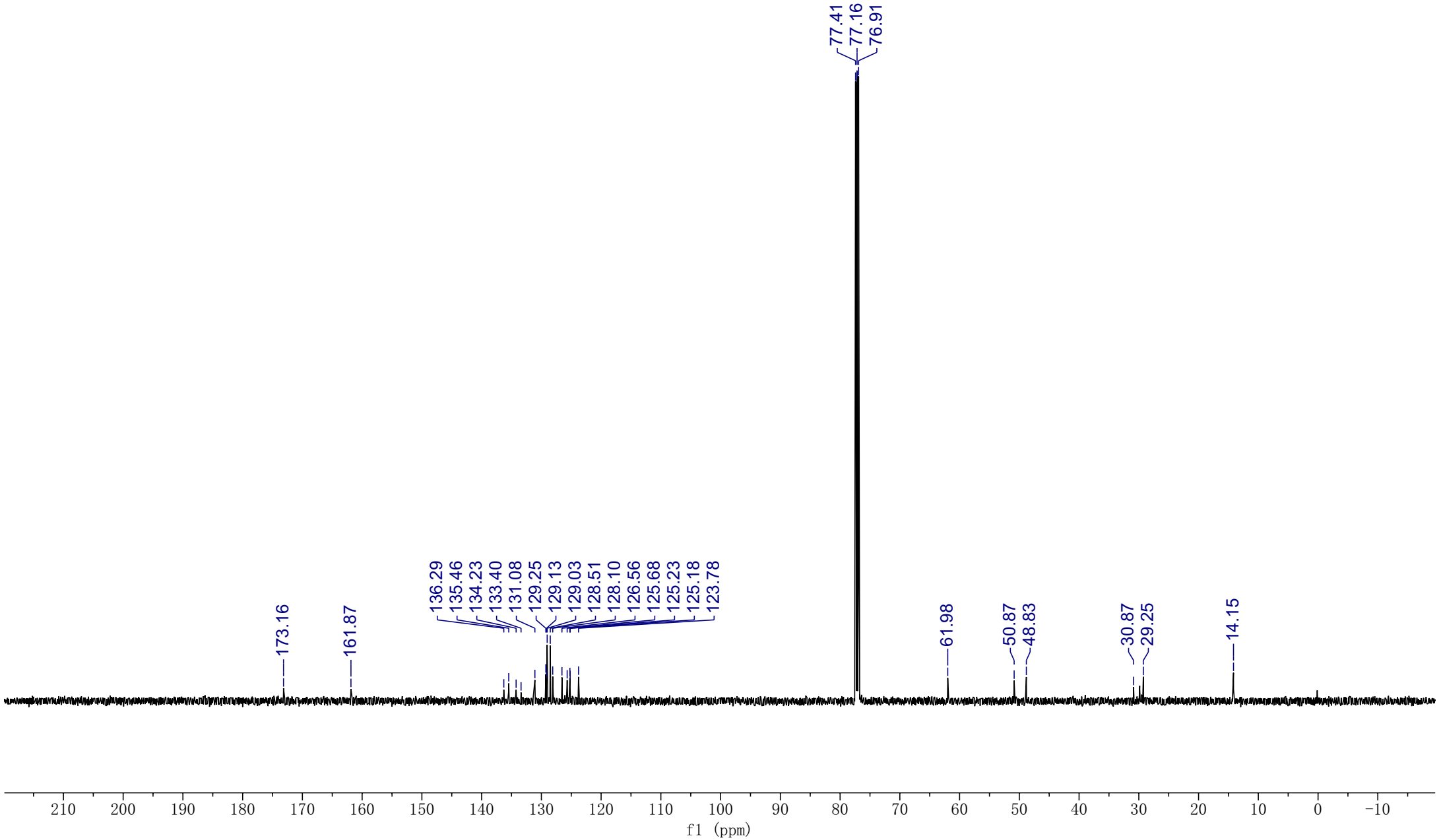
N
Bn
H
CO2Et

51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134.23
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129.13
129.03
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128.10
126.56
125.68
125.23
125.18
123.78
61.98
50.87
48.83
30.87
29.25
14.15
210
200
190
180
170
160
150
140
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120
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100
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80
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60
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40
30
20
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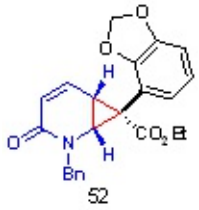
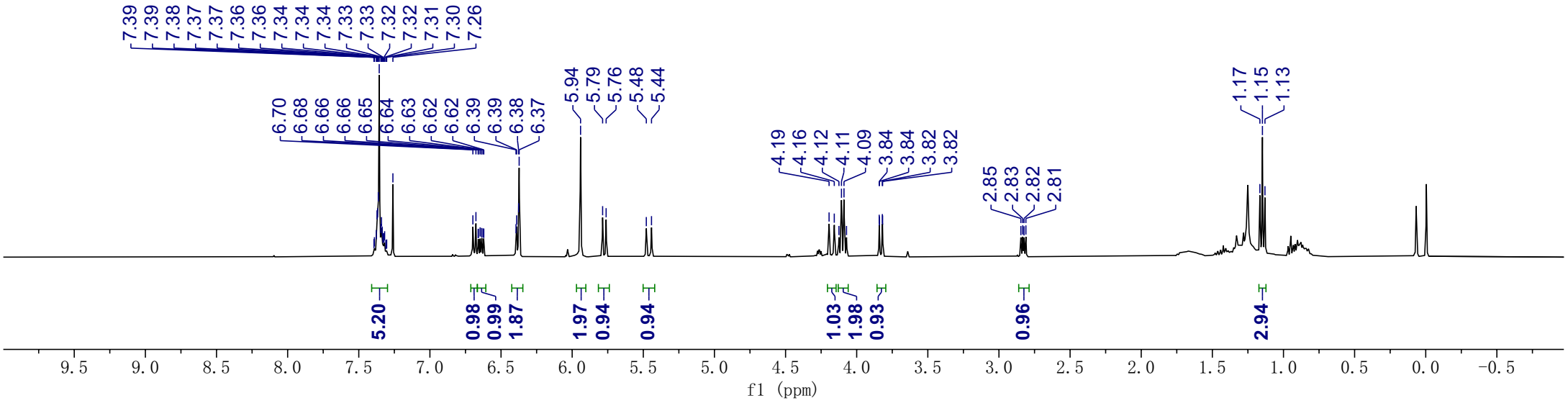
0
-10
f1 (ppm)


O
O
H
O
N
H
Bn
CO2Et

52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3.82
2.85
2.83
2.82
2.81
1.17
1.15
1.13
5.20
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0.99
1.87
1.97
0.94
0.94
1.03
1.98
0.93
0.96
2.94
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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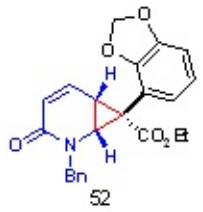
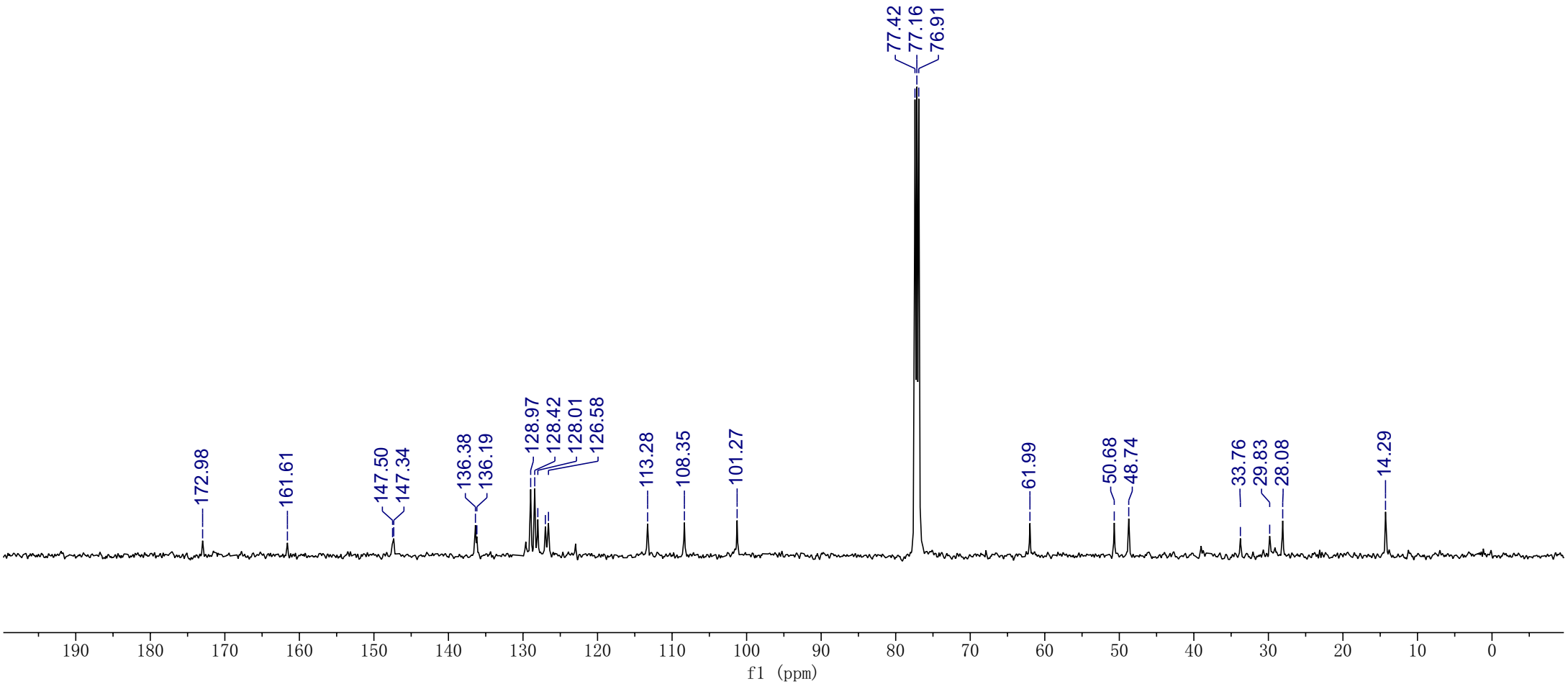
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


O
O
H
O
N
H
Bn
CO2Et

52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147.34
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136.19
128.97
128.42
128.01
126.58
113.28
108.35
101.27
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77.16
76.91
61.99
50.68
48.74
33.76
29.83
28.08
14.29
190
180
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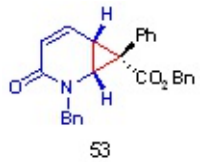
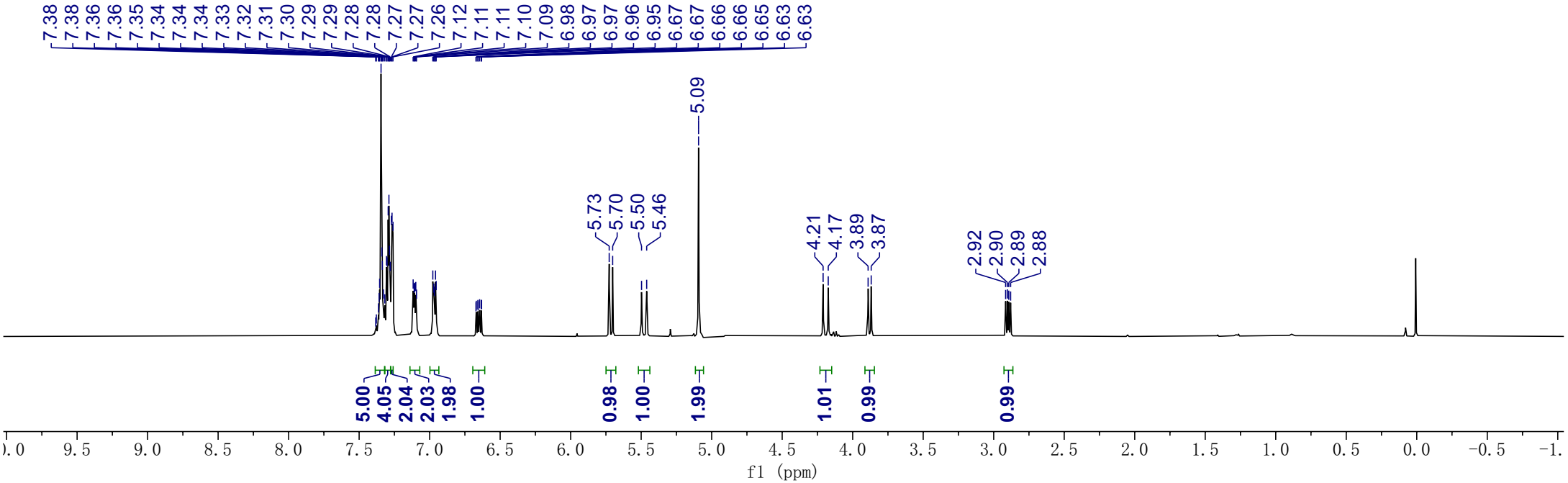
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H
Ph
O
N
Bn
H
CO2Bn

53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7.11
7.11
7.10
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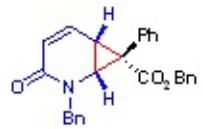
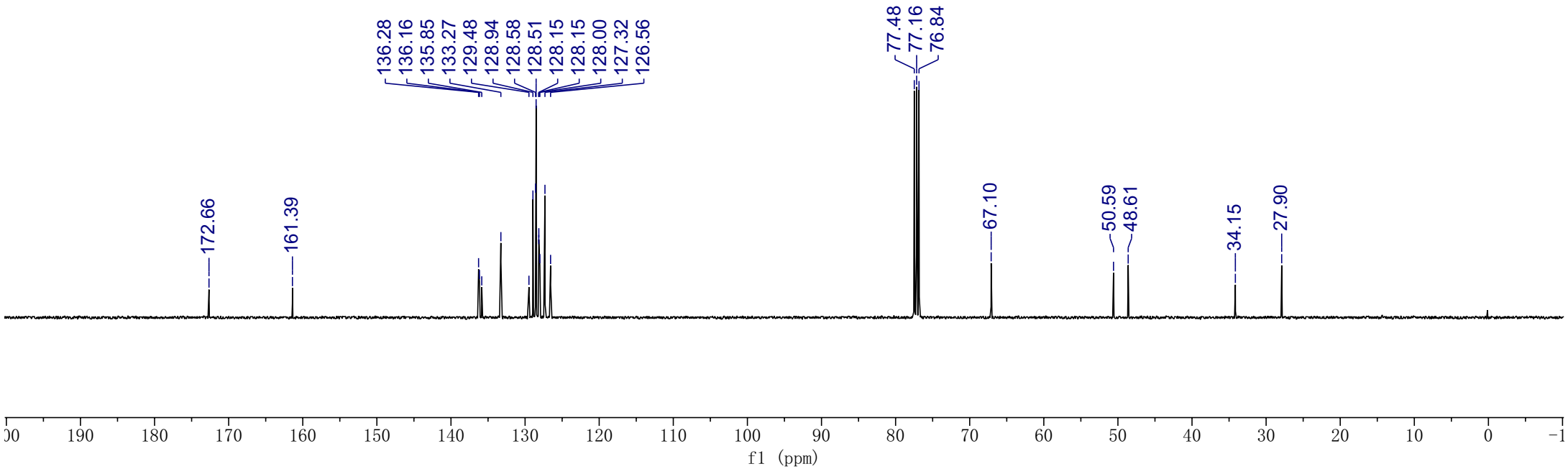
2.89
2.88
5.00
4.05
2.04
2.03
1.98
1.00
0.98
1.00
1.99
1.01
0.99
0.99
f1 (ppm)


H
Ph
O
N
Bn
H
CO2Bn

53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128.94
128.58
128.51
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128.15
128.00
127.32
126.56
77.48
77.16
76.84
172.66
161.39
67.10
50.59
48.61
34.15
27.90
190
180
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150
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130
120
110
100
90
80
70
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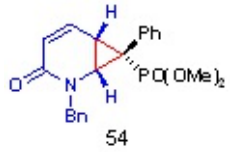
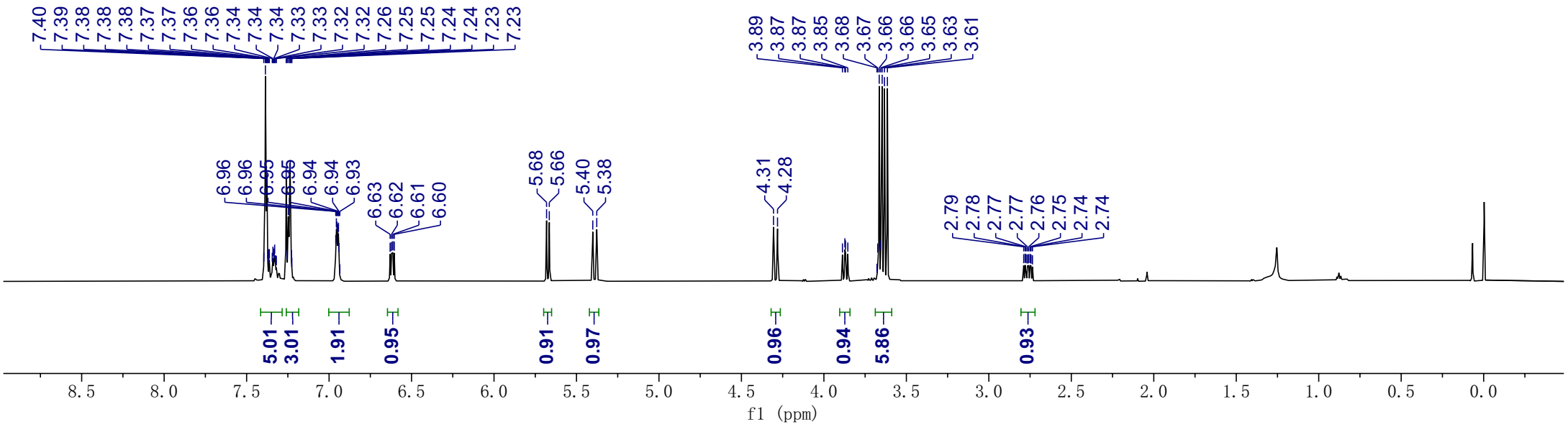
50
40
30
20
10
0
f1 (ppm)


H
Ph
PO(OMe)2
O
N
Bn
H

54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7.33
7.33
7.32
7.32
7.26
7.25
7.25
7.24
7.24
7.23
7.23
6.96
6.96
6.95
6.95
6.94
6.94
6.93
6.63
6.62
6.61
6.60
5.68
5.66
5.40
5.38
4.31
4.28
3.89
3.87
3.87
3.85
3.68
3.67
3.66
3.66
3.65
3.63
3.61
2.79
2.78
2.77
2.77
2.76
2.75
2.74
2.74
5.01
3.01
1.91
0.95
0.91
0.97
0.96
0.94
5.86
0.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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2.0
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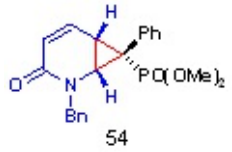
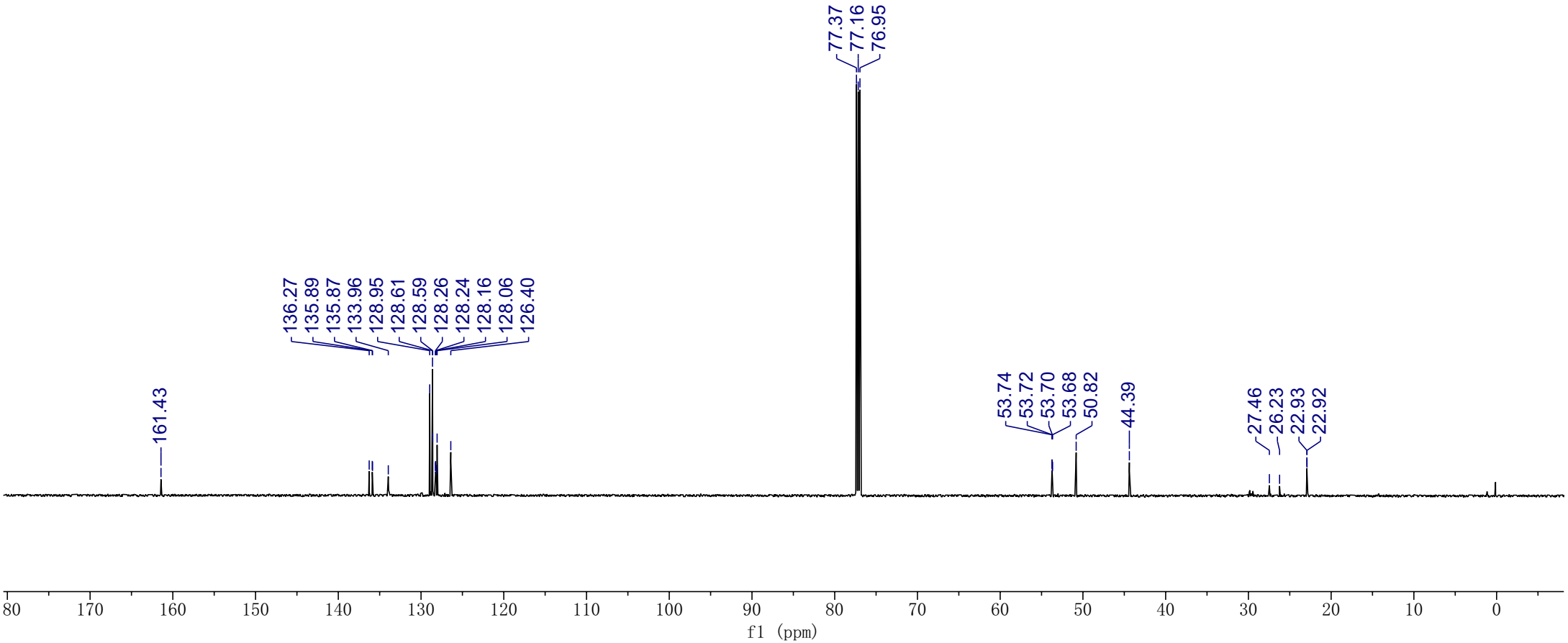
0.0
f1 (ppm)


H
Ph
PO(OMe)2
O
N
H
Bn

54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135.87
133.96
128.95
128.61
128.59
128.26
128.24
128.16
128.06
126.40
161.43
53.74
53.72
53.70
53.68
50.82
44.39
27.46
26.23
22.93
22.92
80
170
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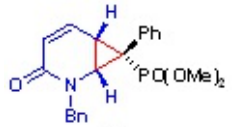
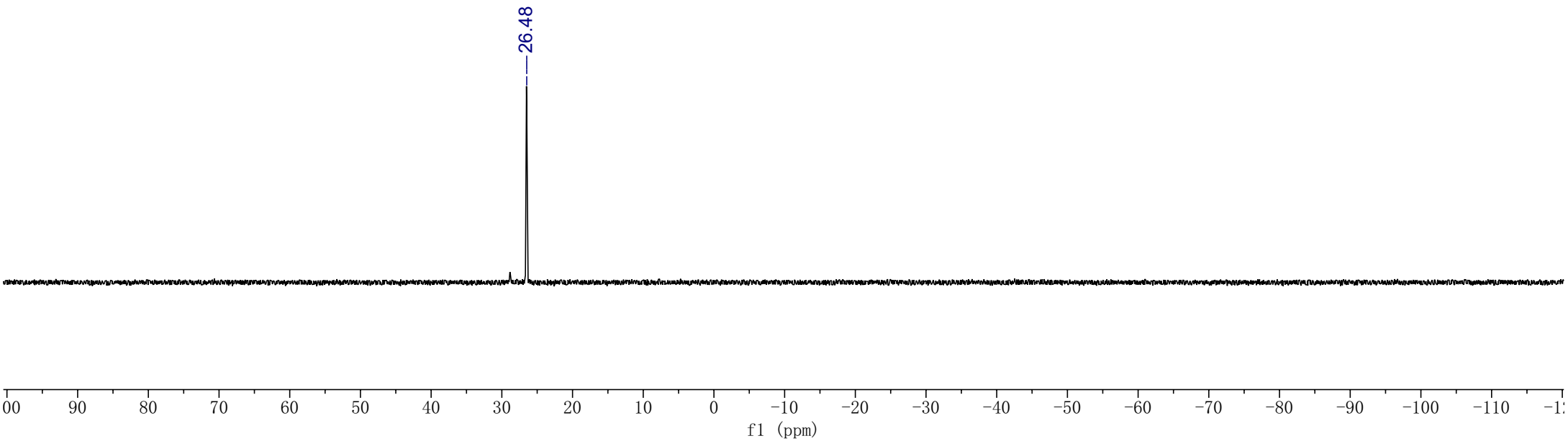
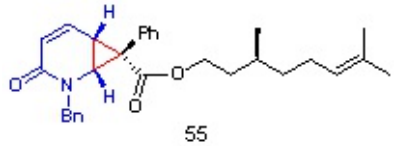
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

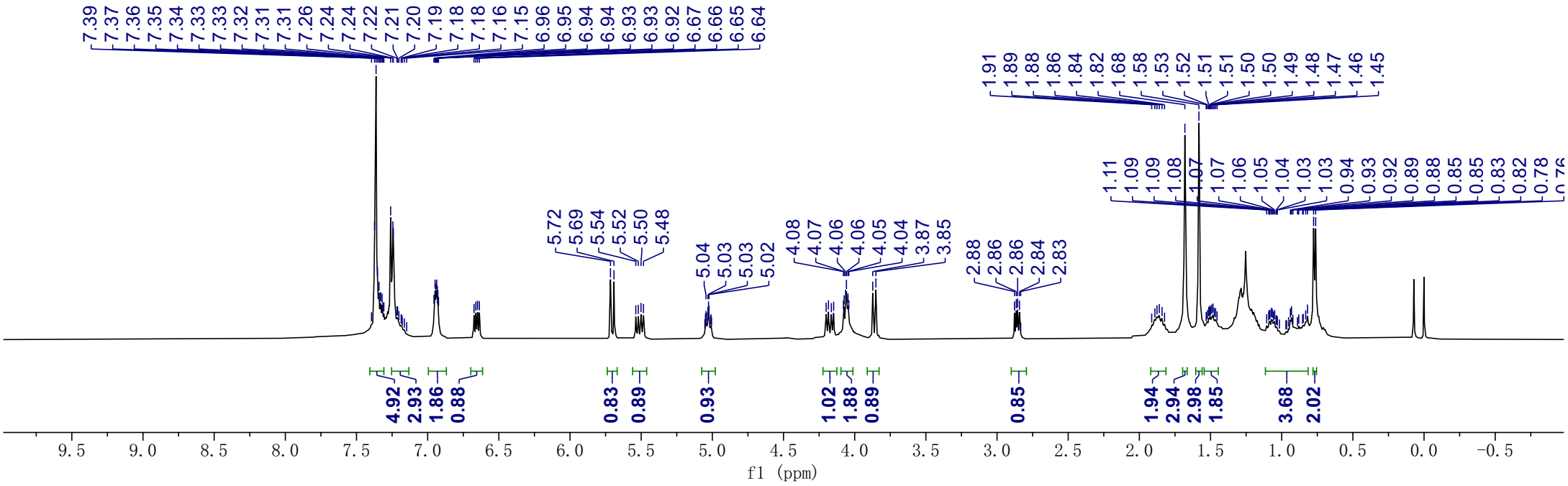

H
Ph
PO(OMe)2
O
N
Bn
H

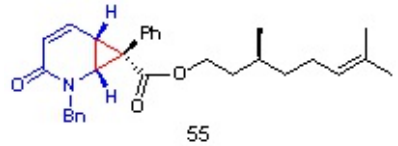
54


26.48
00
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
f1 (ppm)

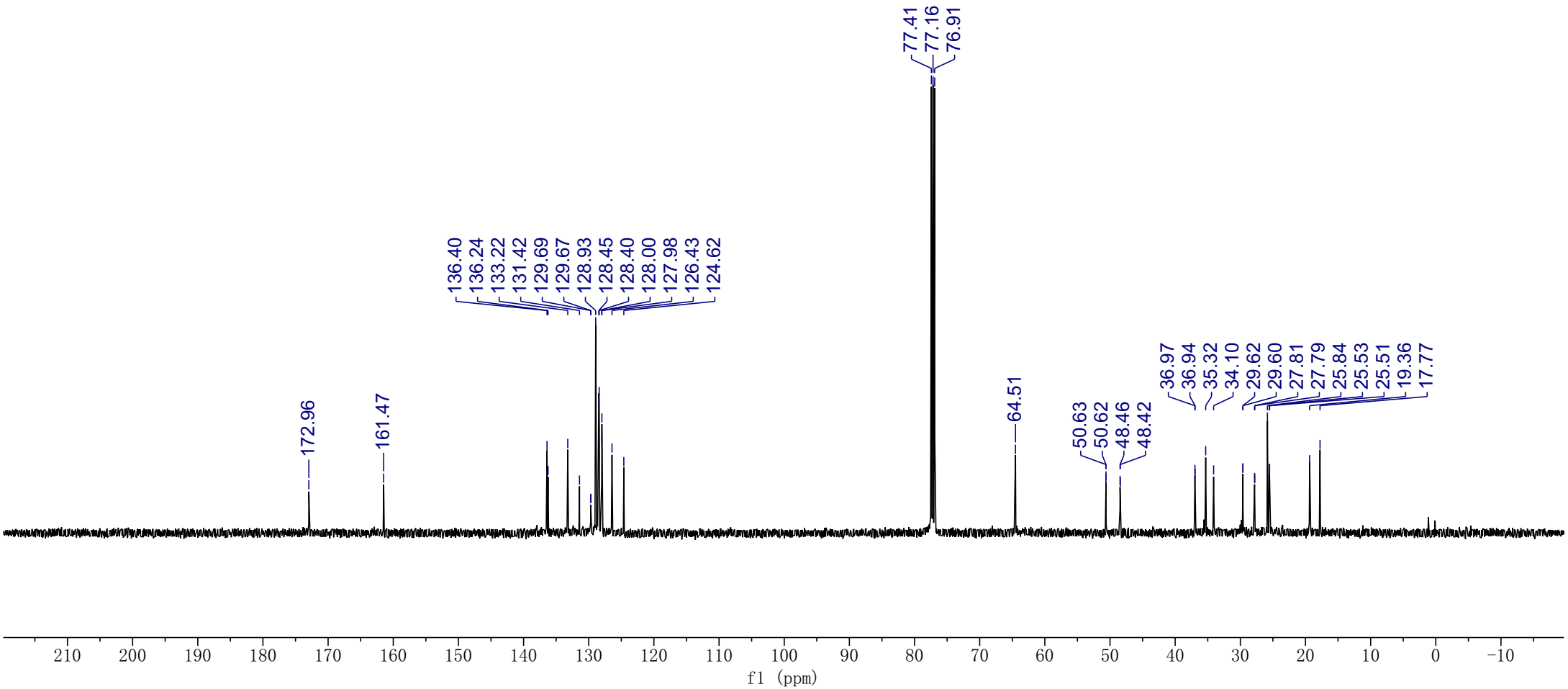

H
Ph
O
N
Bn
H
O
O

55


7.39 7.37 7.36 7.35 7.34 7.33 7.33 7.32 7.31 7.31 7.26 7.24 7.24 7.22 7.21 7.20 7.19 7.18 7.18 7.16 7.15 6.96 6.95 6.94 6.94 6.93 6.93 6.92 6.67 6.66 6.65 6.64
5.72 5.69 5.54 5.52 5.50 5.48
5.04 5.03 5.03 5.02
4.08 4.07 4.06 4.06 4.05 4.04 3.87 3.85
2.88 2.86 2.86 2.84 2.83
1.91 1.89 1.88 1.86 1.84 1.82 1.68 1.58 1.53 1.52 1.51 1.51 1.50 1.50 1.49 1.48 1.47 1.46 1.45
1.11 1.09 1.09 1.08 1.07 1.07 1.06 1.05 1.04 1.03 1.03 0.94 0.93 0.92 0.89 0.88 0.85 0.85 0.83 0.82 0.78
4.92 2.93 1.86 0.88 0.83 0.89 0.93 1.02 1.88 0.89 0.85 1.94 2.94 2.98 1.85 3.68 2.02
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 -0.5
f1 (ppm)


H
Ph
O
N
Bn
H
O
O

55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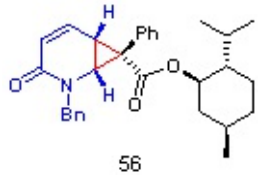
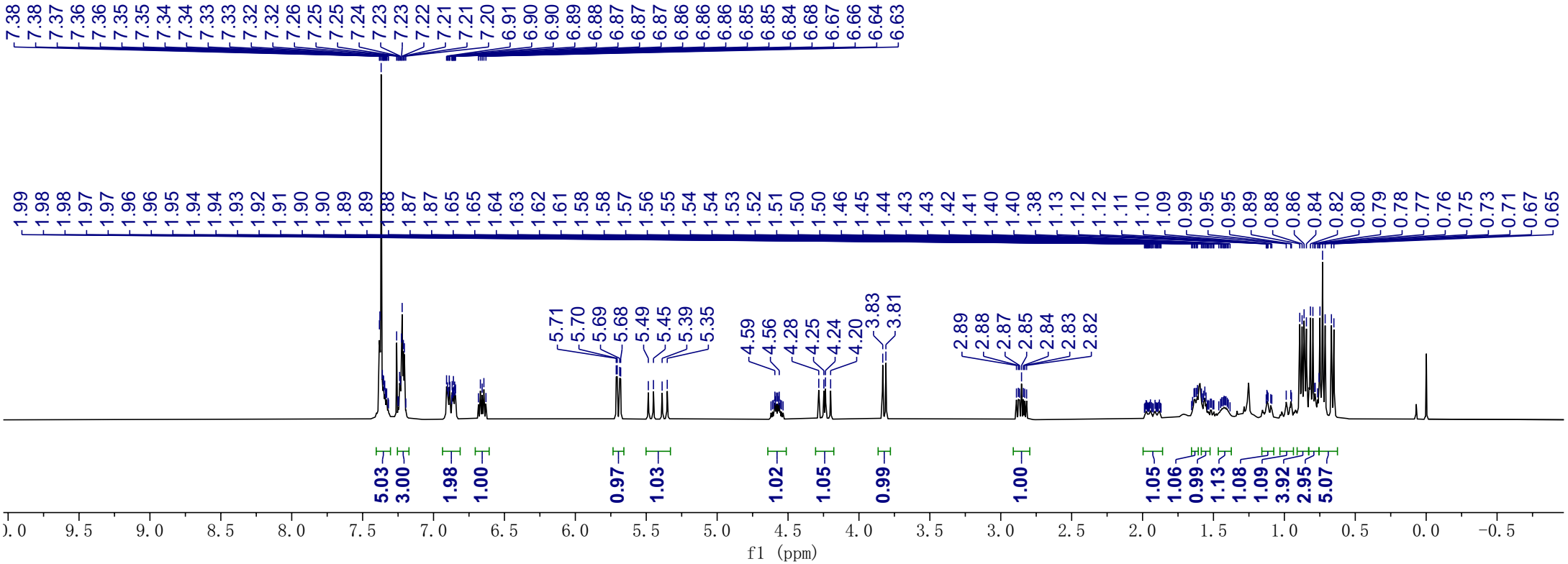
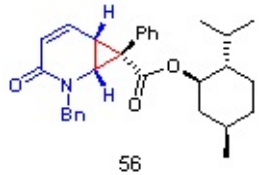
129.67
128.93
128.45
128.40
128.00
127.98
126.43
124.62
77.41
77.16
76.91
64.51
50.63
50.62
48.46
48.42
36.97
36.94
35.32
34.10
29.62
29.60
27.81
27.79
25.84
25.53
25.51
19.36
17.77
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

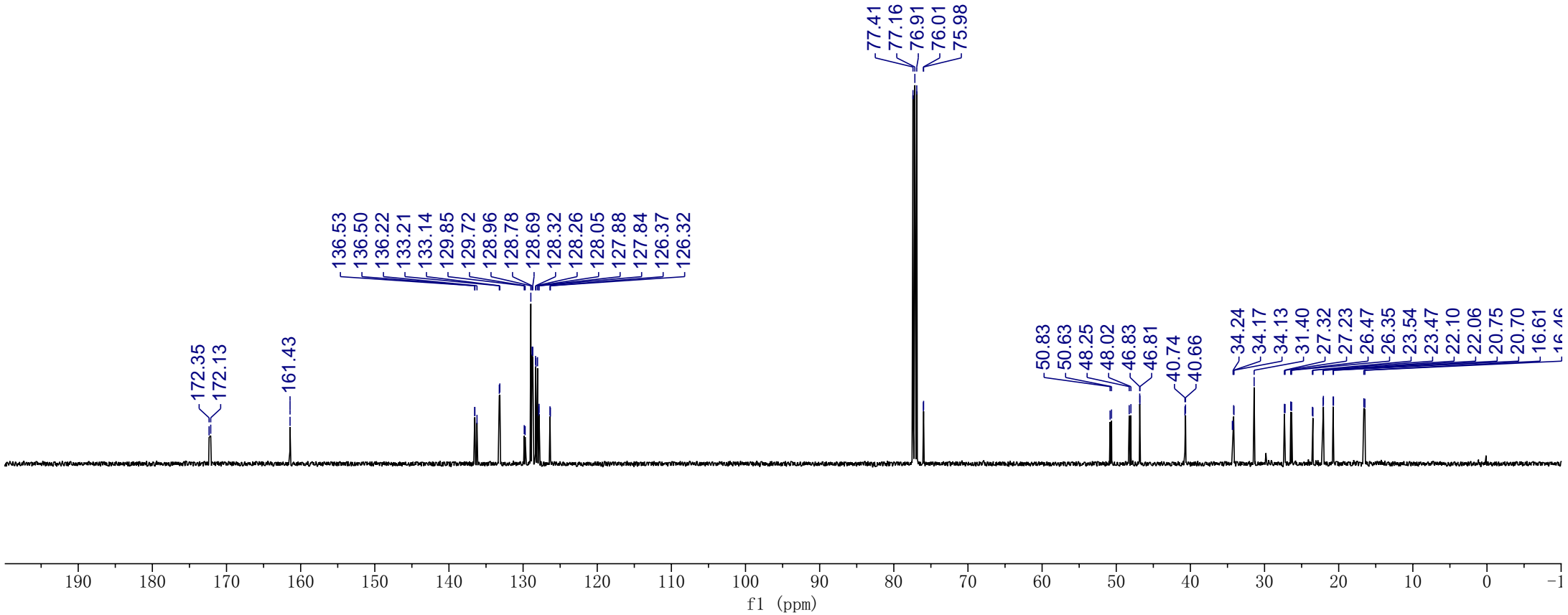

H
Ph
O
N
Bn
H
O
O

56


7.38 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.32 7.32 7.26 7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.20 6.91 6.90 6.90 6.89 6.88 6.87 6.87 6.87 6.86 6.86 6.86 6.85 6.85 6.84 6.68 6.67 6.66 6.64 6.63
1.99 1.98 1.98 1.97 1.97 1.96 1.96 1.95 1.94 1.94 1.93 1.92 1.91 1.90 1.90 1.89 1.89 1.88 1.87 1.87 1.65 1.65 1.64 1.63 1.62 1.61 1.58 1.58 1.57 1.56 1.55 1.54 1.54 1.53 1.52 1.51 1.50 1.50 1.46 1.45 1.44 1.43 1.43 1.42 1.41 1.40 1.40 1.38 1.13 1.12 1.12 1.11 1.10 1.09 0.99 0.95 0.95 0.89 0.88 0.86 0.84 0.82 0.80 0.79 0.78 0.77 0.76 0.75 0.73 0.71 0.67 0.65
5.71 5.70 5.69 5.68 5.49 5.45 5.39 5.35
4.59 4.56 4.28 4.25 4.24 4.20
3.83 3.81
2.89 2.88 2.87 2.85 2.84 2.83 2.82
5.03 3.00 1.98 1.00 0.97 1.03 1.02 1.05 0.99 1.00 1.05 1.06 0.99 1.13 1.08 1.09 3.92 2.95 5.07
0.0 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 −0.5
f1 (ppm)


H
Ph
O
N
Bn
H
O
O

56


77.41
77.16
76.91
76.01
75.98
136.53
136.50
136.22
133.21
133.14
129.85
129.72
128.96
128.78
128.69
128.32
128.26
128.05
127.88
127.84
126.37
126.32
172.35
172.13
161.43
50.83
50.63
48.25
48.02
46.83
46.81
40.74
40.66
34.24
34.17
34.13
31.40
27.32
27.23
26.47
26.35
23.54
23.47
22.10
22.06
20.75
20.70
16.61
190
180
170
160
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140
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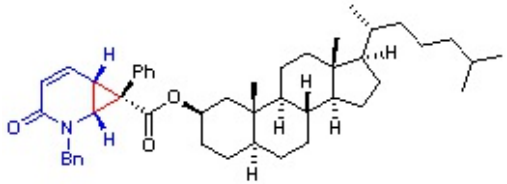
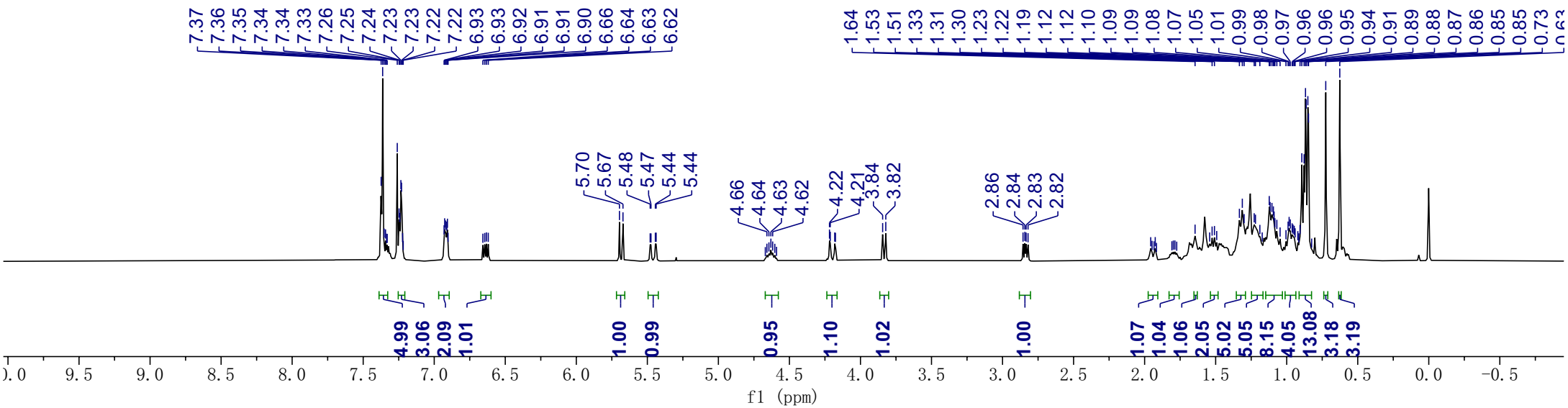
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


H
Ph
O
O
N
Bn
H
O
H
H
H
H
H

57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7.36
7.35
7.34
7.34
7.33
7.26
7.25
7.24
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7.23
7.22
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6.93
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6.92
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6.91
6.90
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6.64
6.63
6.62
1.64
1.53
1.51
1.33
1.31
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1.23
1.22
1.19
1.12
1.12
1.10
1.09
1.09
1.08
1.07
1.05
1.01
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0.97
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0.94
0.91
0.89
0.88
0.87
0.86
0.85
0.85
0.73
5.70
5.67
5.48
5.47
5.44
5.44
4.66
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4.63
4.62
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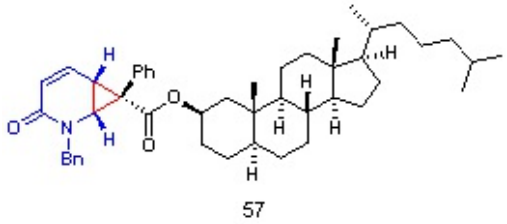
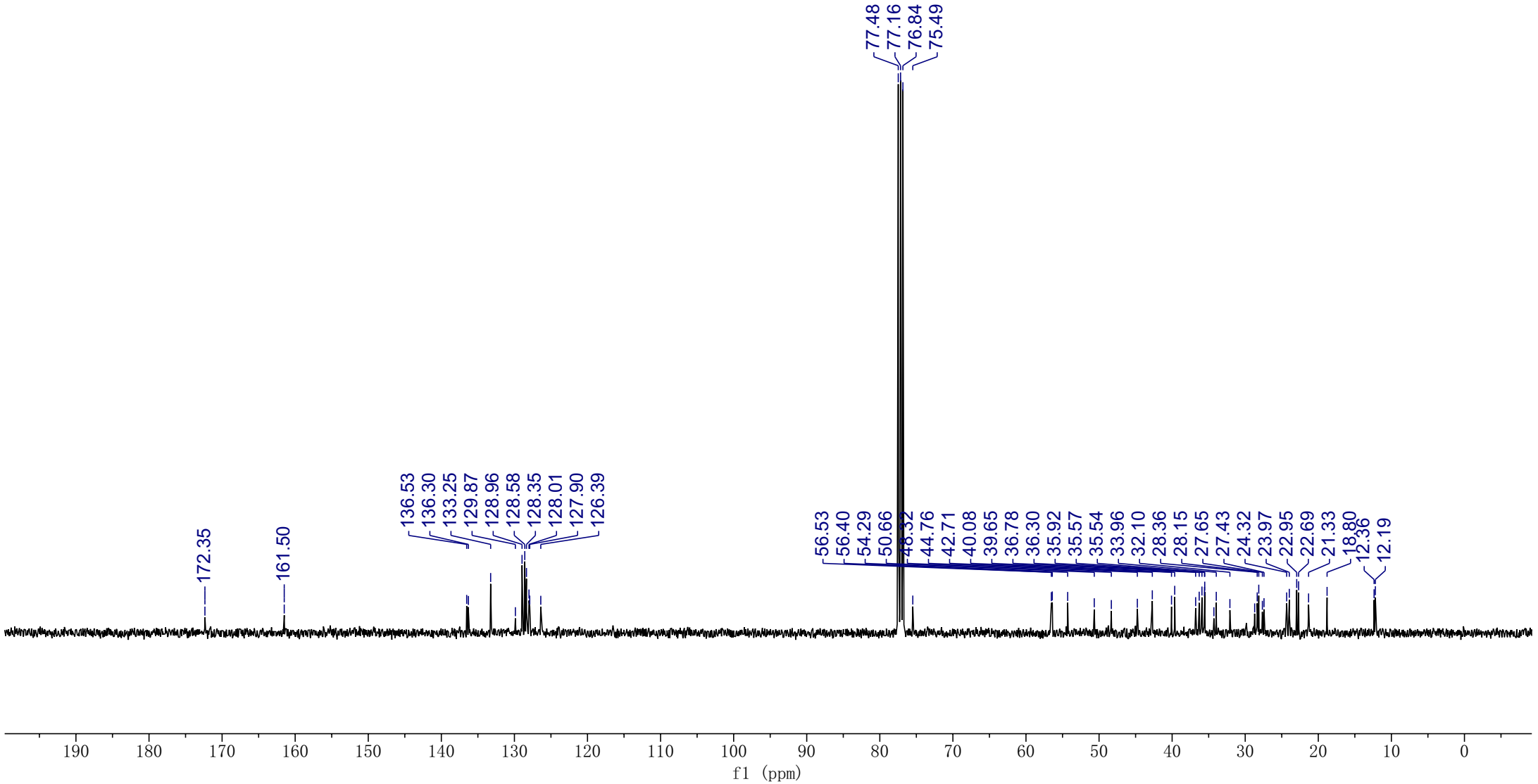
2.84
2.83
2.82
4.99
3.06
2.09
1.01
1.00
0.99
0.95
1.10
1.02
1.00
1.07
1.04
1.06
2.05
5.02
5.05
8.15
4.05
13.08
3.18
3.19
f1 (ppm)


H
Ph
O
O
N
Bn
H
O
H
H
H
H
H

57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136.30
133.25
129.87
128.96
128.58
128.35
128.01
127.90
126.39
56.53
56.40
54.29
50.66
48.32
44.76
42.71
40.08
39.65
36.78
36.30
35.92
35.57
35.54
33.96
32.10
28.36
28.15
27.65
27.43
24.32
23.97
22.95
22.69
21.33
18.80
12.36
12.19
190
180
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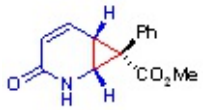
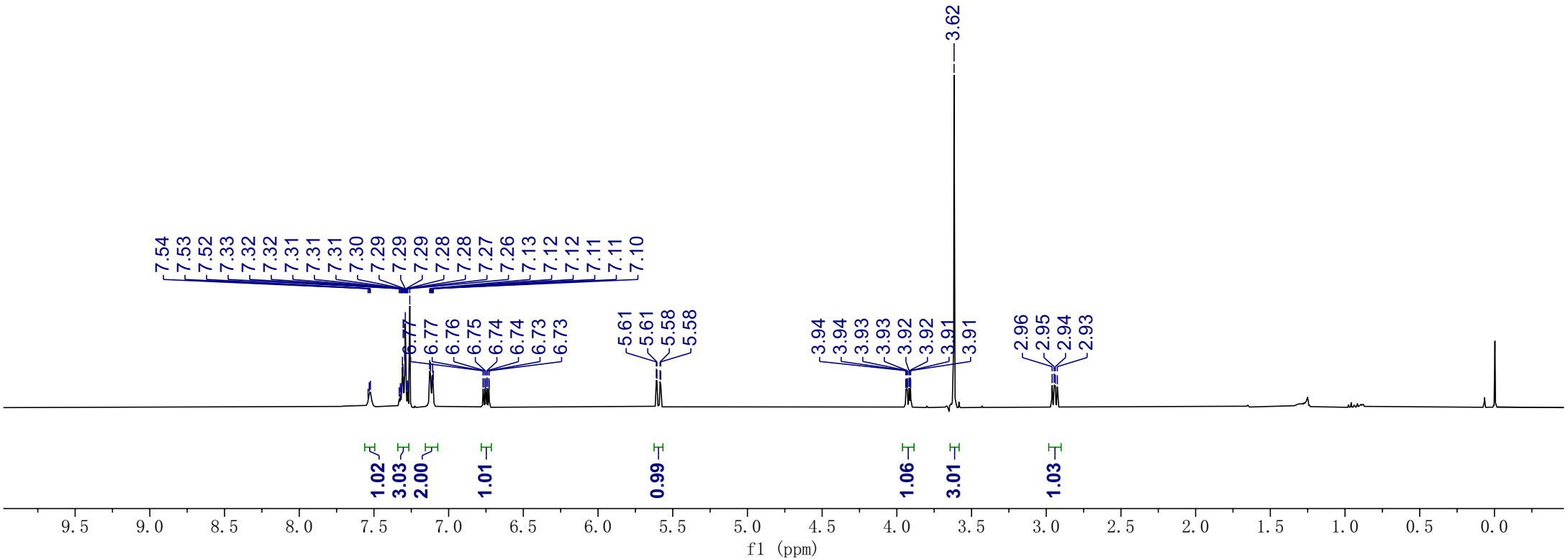
f1 (ppm)


H
Ph
O
NH
CO2Me
H

58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7.28
7.28
7.27
7.26
7.13
7.12
7.12
7.11
7.11
7.10
6.77
6.77
6.76
6.75
6.74
6.74
6.73
6.73
5.61
5.61
5.58
5.58
3.94
3.94
3.93
3.93
3.92
3.92
3.91
3.91
3.62
2.96
2.95
2.94
2.93
1.02
3.03
2.00
1.01
0.99
1.06
3.01
1.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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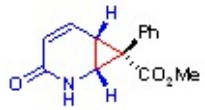
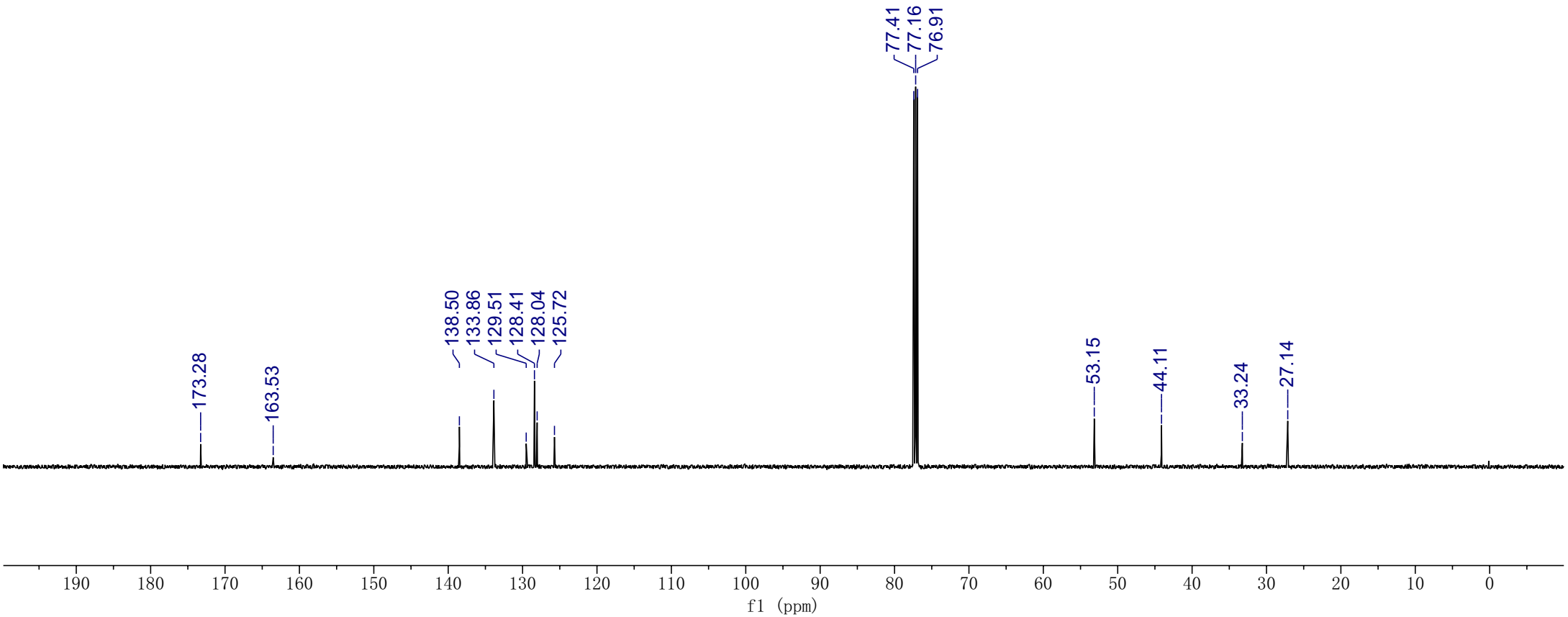
0.0
f1 (ppm)


H
Ph
O
N
H
H
CO2Me

58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125.72
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76.91
53.15
44.11
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27.14
190
180
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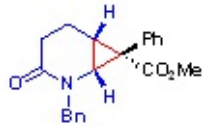
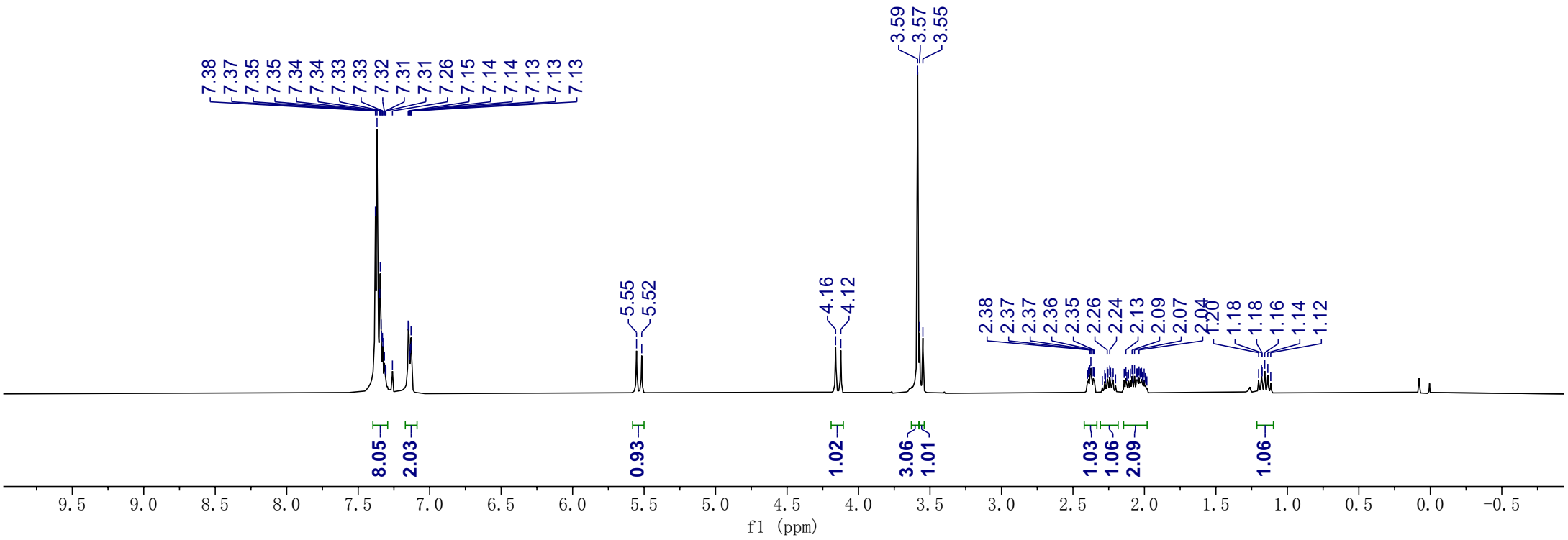
f1 (ppm)


H
Ph
CO2Me
O
N
H
Bn

61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7.14
7.14
7.13
7.13
7.13
5.55
5.52
4.16
4.12
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3.57
3.55
2.38
2.37
2.37
2.36
2.35
2.26
2.24
2.13
2.09
2.07
2.04
1.20
1.18
1.18
1.16
1.14
1.12
8.05
2.03
0.93
1.02
3.06
1.01
1.03
1.06
2.09
1.06
9.5
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8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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2.0
1.5
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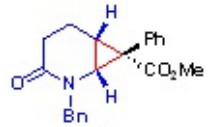
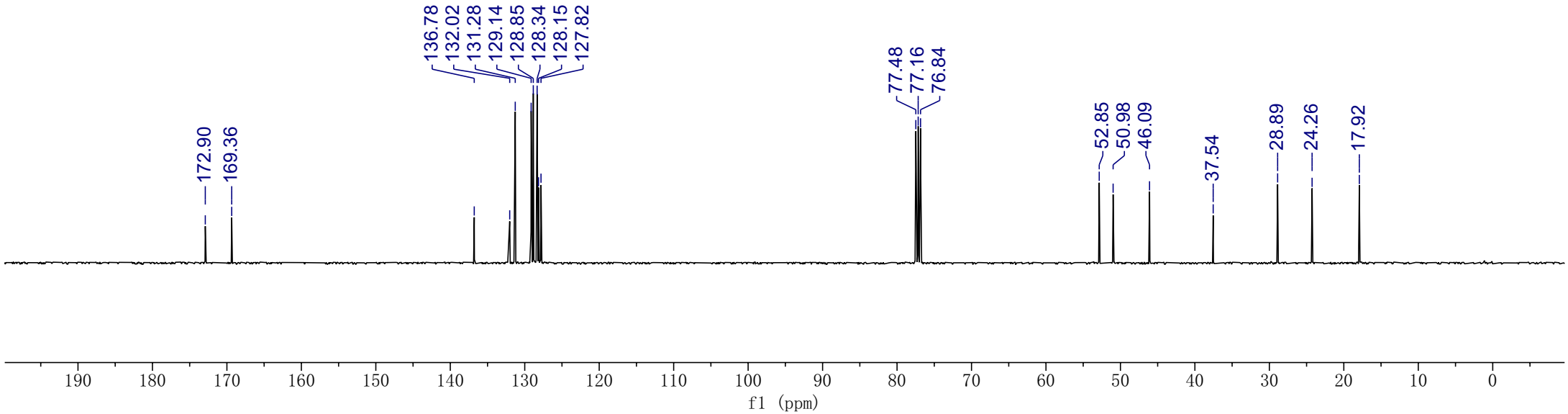
f1 (ppm)


H
Ph
CO2Me
O
N
H
Bn

61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128.15
127.82
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77.16
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52.85
50.98
46.09
37.54
28.89
24.26
17.92
190
180
170
160
150
140
130
120
110
100
90
80
70
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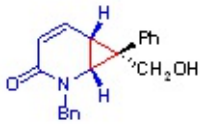
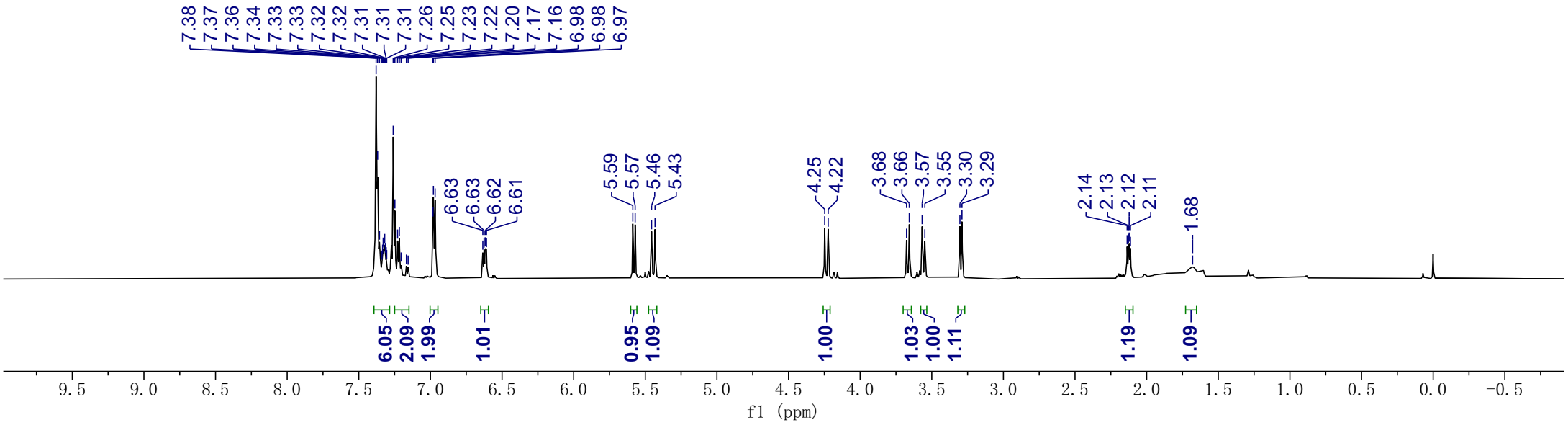
50
40
30
20
10
0
f1 (ppm)


H
Ph
CH2OH
O
N
Bn
H

64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7.25
7.23
7.22
7.20
7.17
7.16
6.98
6.98
6.97
6.63
6.63
6.62
6.61
5.59
5.57
5.46
5.43
4.25
4.22
3.68
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3.55
3.30
3.29
2.14
2.13
2.12
2.11
1.68
6.05
2.09
1.99
1.01
0.95
1.09
1.00
1.03
1.00
1.11
1.19
1.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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3.0
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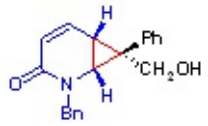
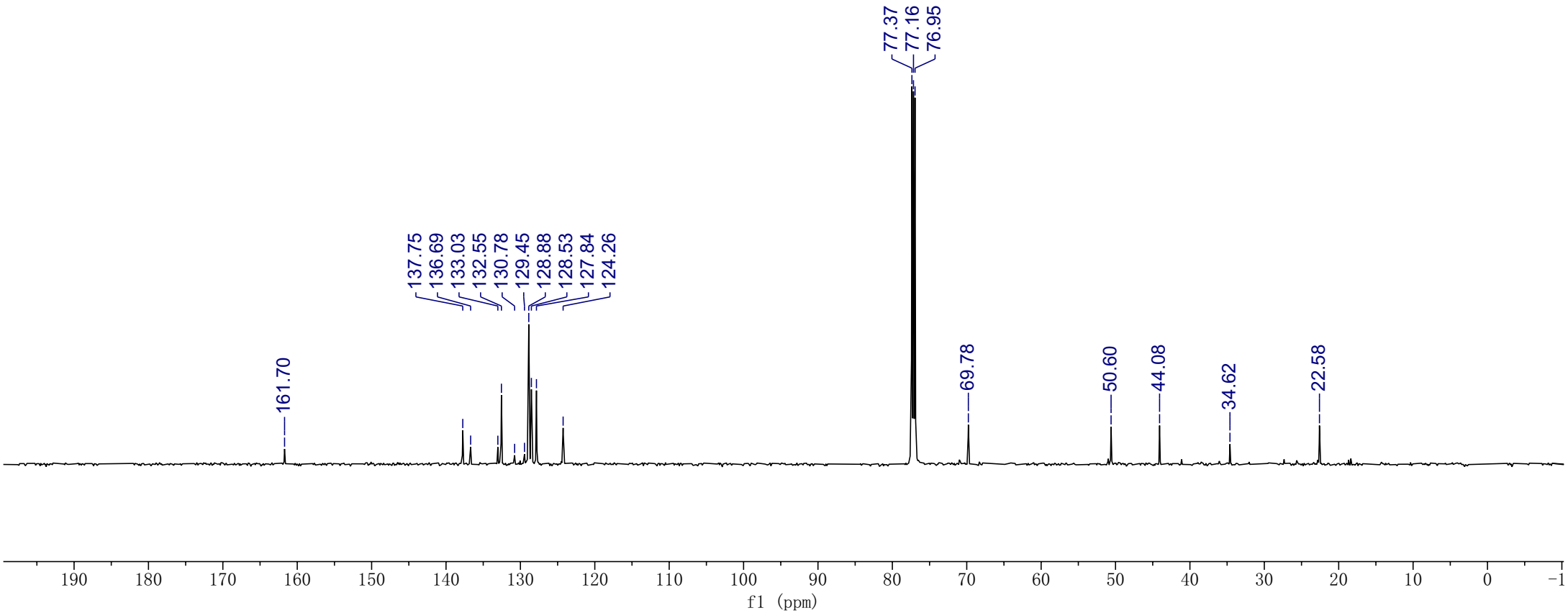
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


H
Ph
CH2OH
O
N
Bn
H

64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136.69
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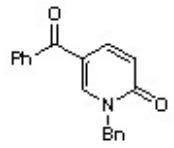
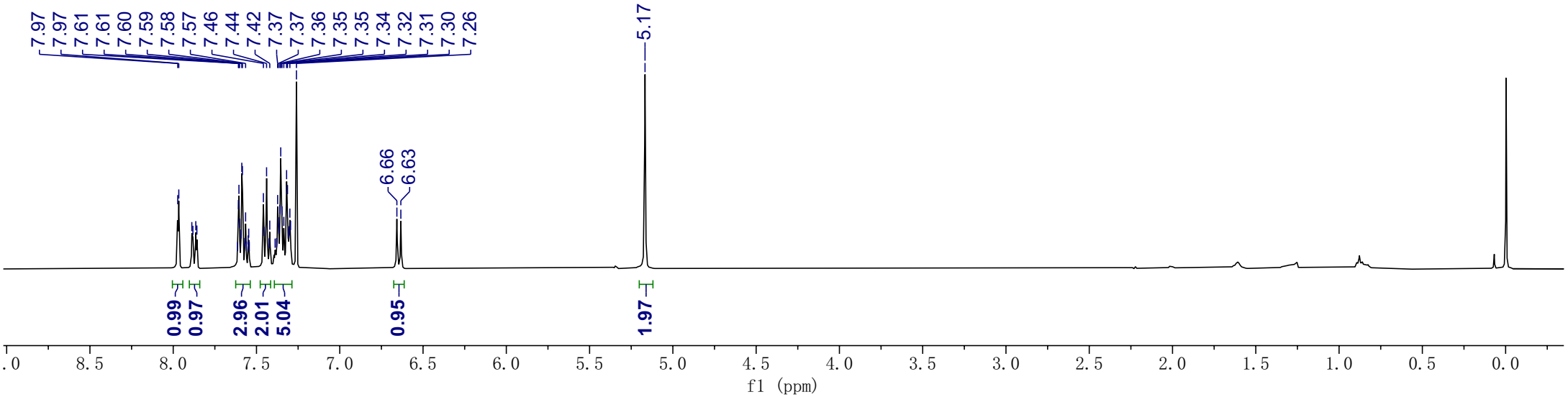
132.55
130.78
129.45
128.88
128.53
127.84
124.26
161.70
69.78
50.60
44.08
34.62
22.58
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


O
Ph
N
O
Bn

65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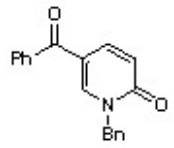
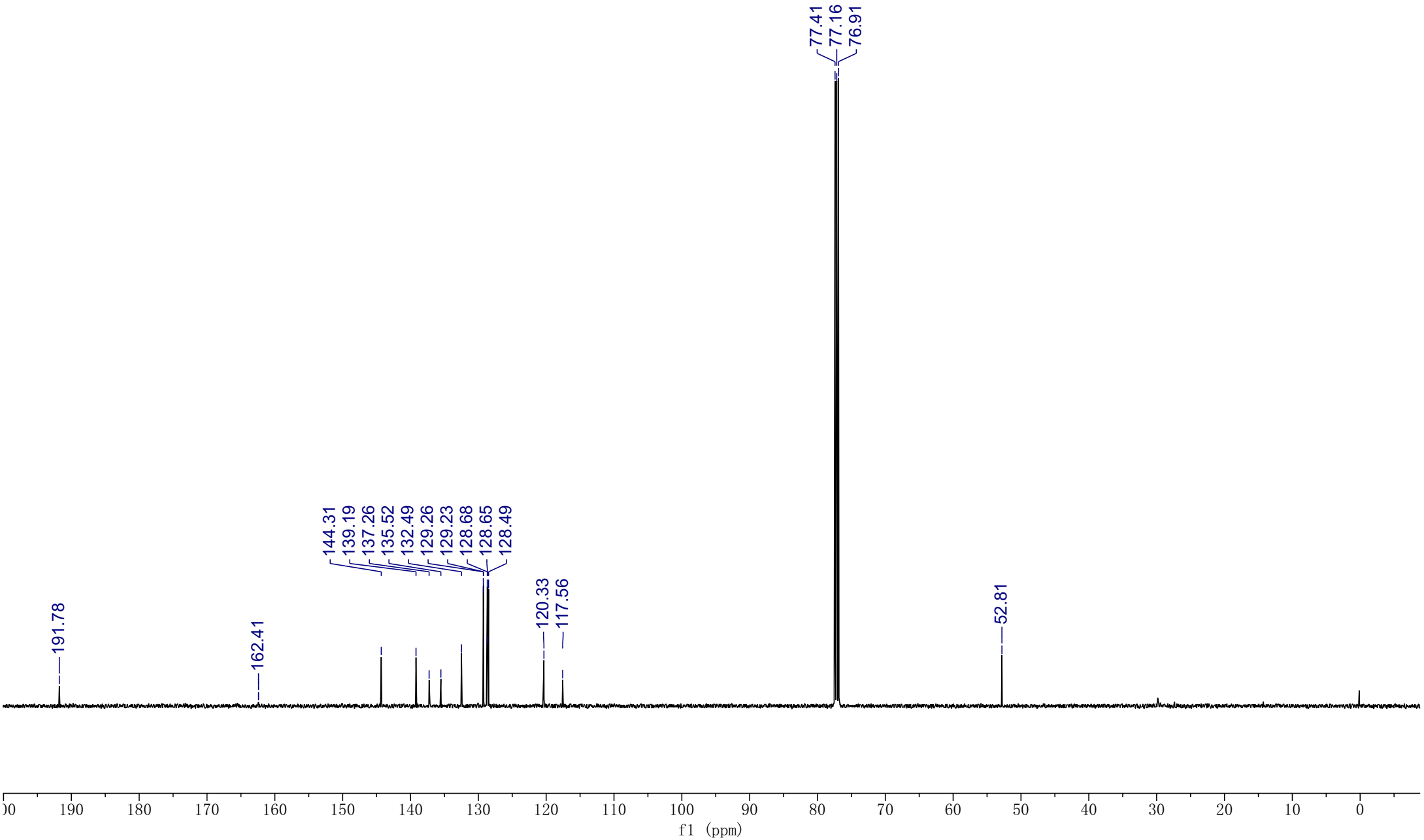
7.57
7.46
7.44
7.42
7.37
7.37
7.36
7.35
7.35
7.34
7.32
7.31
7.30
7.26
5.17
6.66
6.63
0.99
0.97
2.96
2.01
5.04
0.95
1.97
f1 (ppm)


O
Ph
N
O
Bn

65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77.16
76.91
144.31
139.19
137.26
135.52
132.49
129.26
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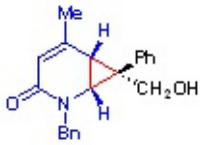
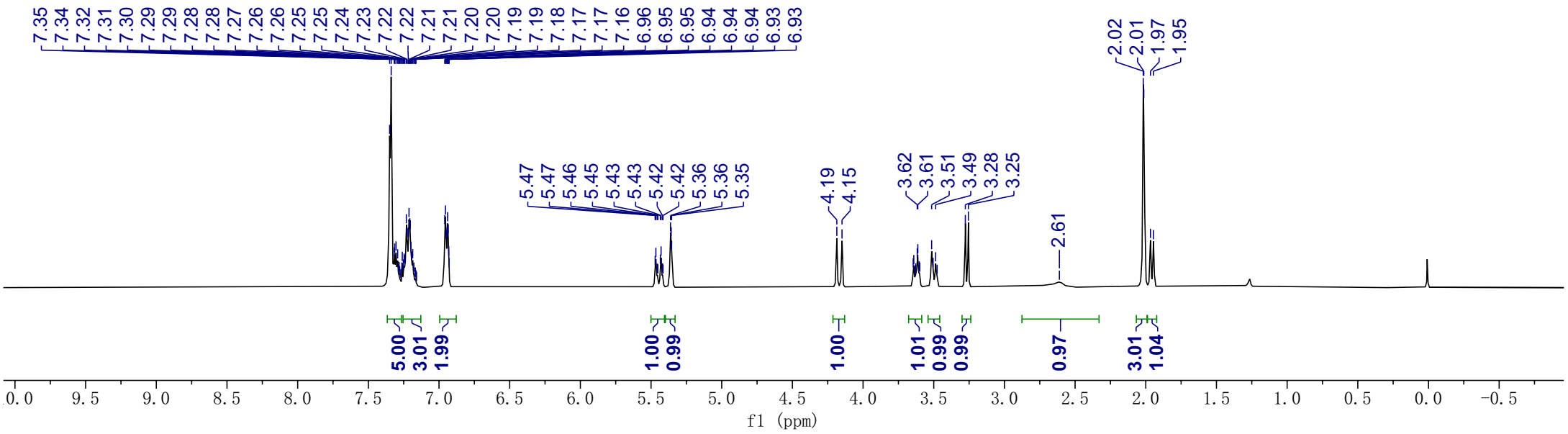
128.68
128.65
128.49
120.33
117.56
191.78
162.41
52.81
f1 (ppm)


Me
H
Ph
CH2OH
O
N
H
Bn

66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7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.21
7.20
7.20
7.19
7.19
7.18
7.17
7.17
7.16
6.96
6.95
6.95
6.94
6.94
6.94
6.93
6.93
5.47
5.47
5.46
5.45
5.43
5.43
5.42
5.42
5.36
5.36
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4.19
4.15
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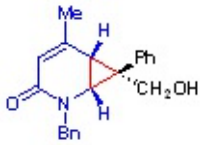
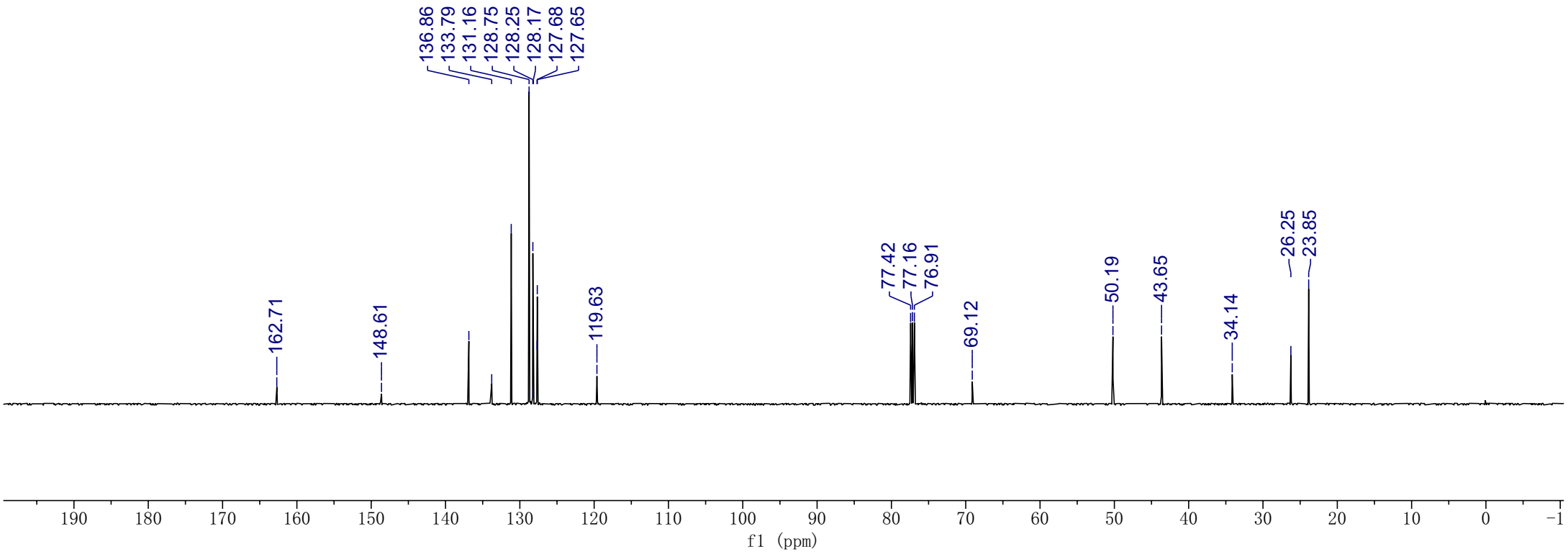
3.61
3.51
3.49
3.28
3.25
2.61
2.02
2.01
1.97
1.95
5.00
3.01
1.99
1.00
0.99
1.00
1.01
0.99
0.99
0.97
3.01
1.04
f1 (ppm)


Me
H
Ph
CH2OH
O
N
H
Bn

66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162.71
148.61
119.63
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77.16
76.91
69.12
50.19
43.65
34.14
26.25
23.85
190
180
170
160
150
140
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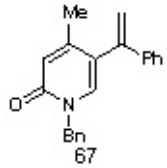
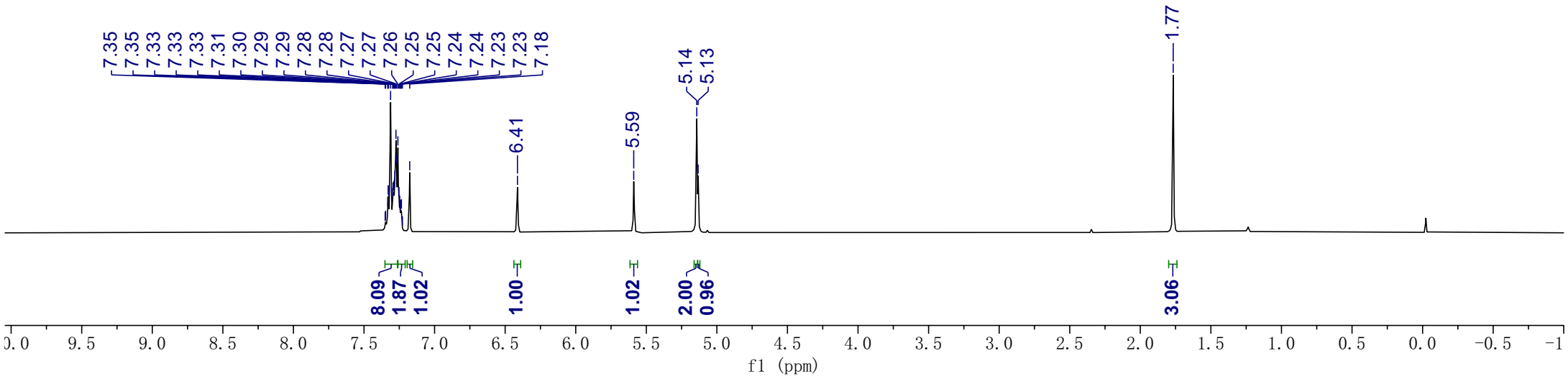
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


Me
Ph
O
N
Bn

67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7.28
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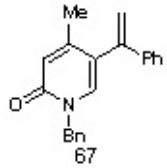
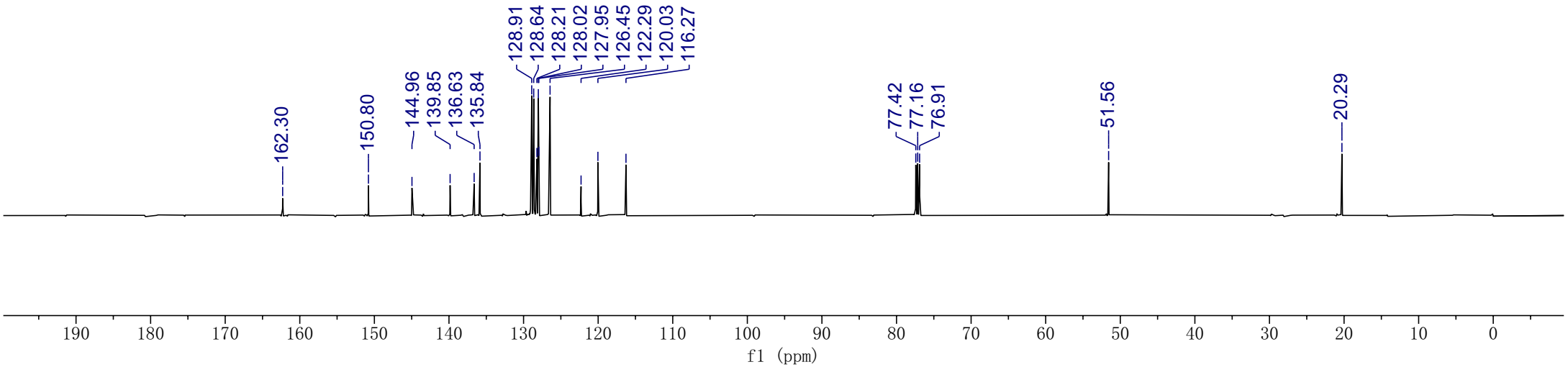
7.27
7.26
7.25
7.25
7.24
7.24
7.23
7.23
7.18
6.41
5.59
5.14
5.13
1.77
8.09
1.87
1.02
1.00
1.02
2.00
0.96
3.06
f1 (ppm)


Me
Ph
O
N
Bn

67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135.84
128.91
128.64
128.21
128.02
127.95
126.45
122.29
120.03
116.27
77.42
77.16
76.91
51.56
20.29
190
180
170
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130
120
110
100
90
80
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50
40
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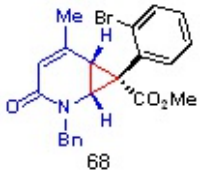
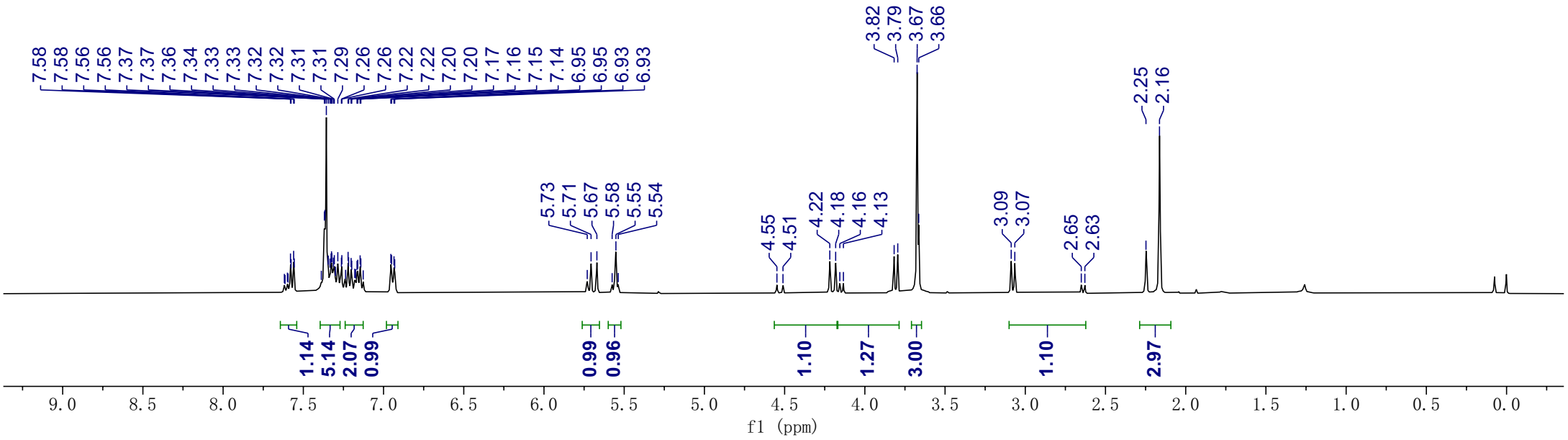
20
10
0
f1 (ppm)


Me
Br
H
CO2Me
O
N
H
Bn

68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7.31
7.31
7.29
7.26
7.26
7.22
7.22
7.20
7.20
7.17
7.16
7.15
7.14
6.95
6.95
6.93
6.93
5.73
5.71
5.67
5.58
5.55
5.54
4.55
4.51
4.22
4.18
4.16
4.13
3.82
3.79
3.67
3.66
3.09
3.07
2.65
2.63
2.25
2.16
1.14
5.14
2.07
0.99
0.99
0.96
1.10
1.27
3.00
1.10
2.97
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.5
3.0
2.5
2.0
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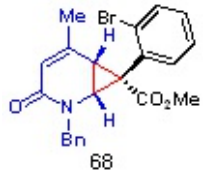
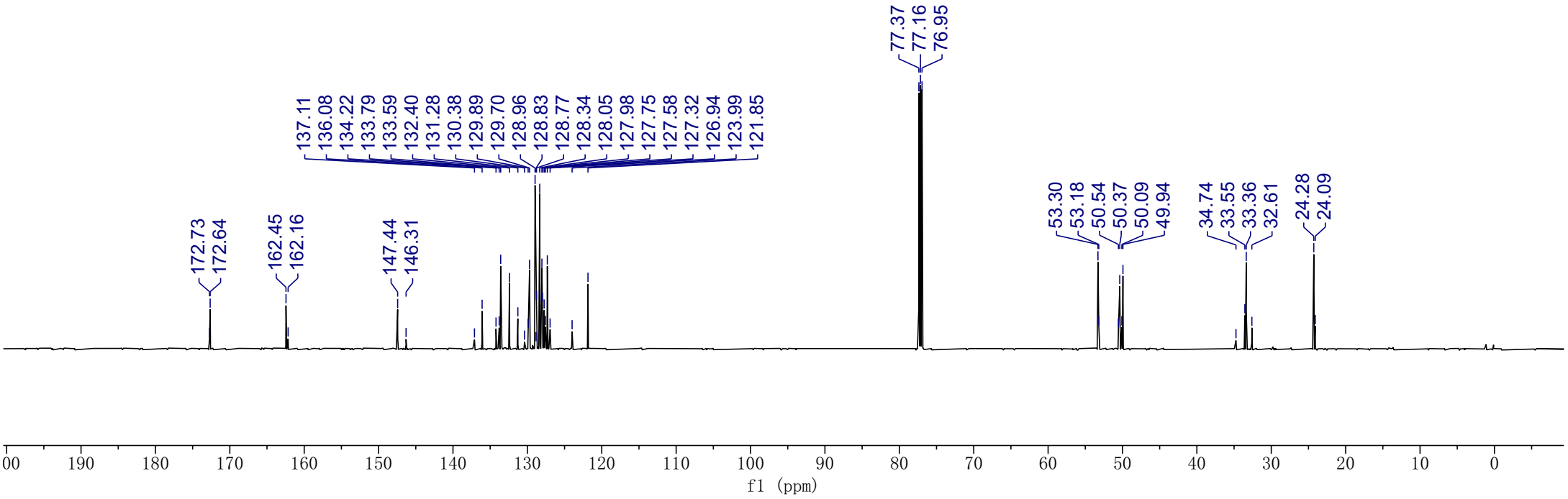
1.0
0.5
0.0
f1 (ppm)


Me
Br
H
O
N
H
CO2Me
Bn

68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137.11
136.08
134.22
133.79
133.59
132.40
131.28
130.38
129.89
129.70
128.96
128.83
128.77
128.34
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127.75
127.58
127.32
126.94
123.99
121.85
77.37
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76.95
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53.18
50.54
50.37
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49.94
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24.28
24.09
00
190
180
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110
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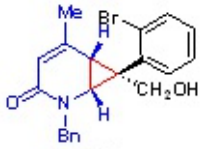
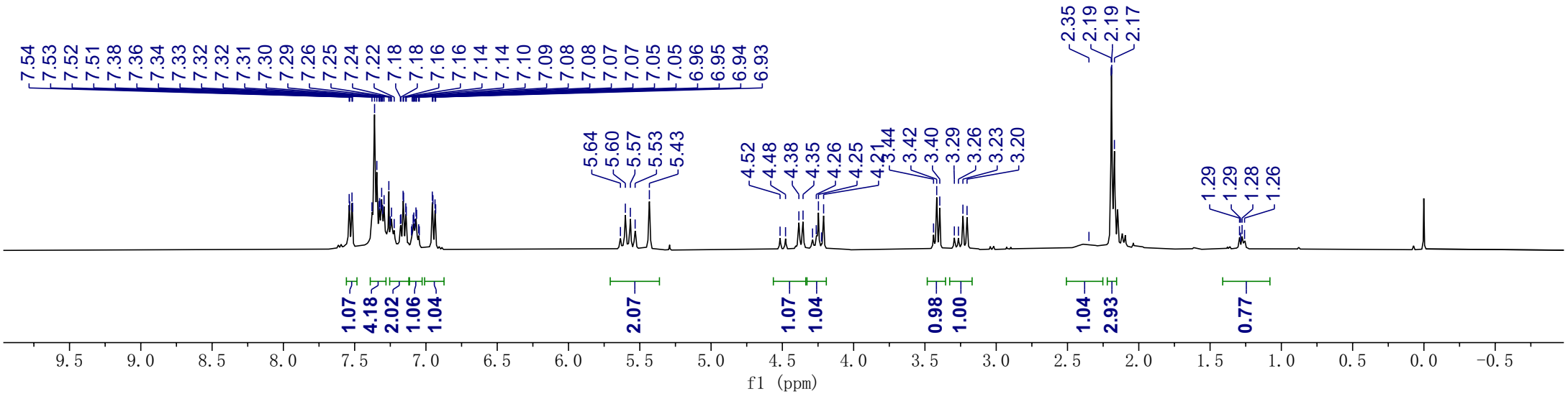
50
40
30
20
10
0
f1 (ppm)


Me
Br
H
CH2OH
O
N
H
Bn

69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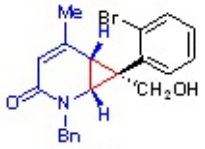
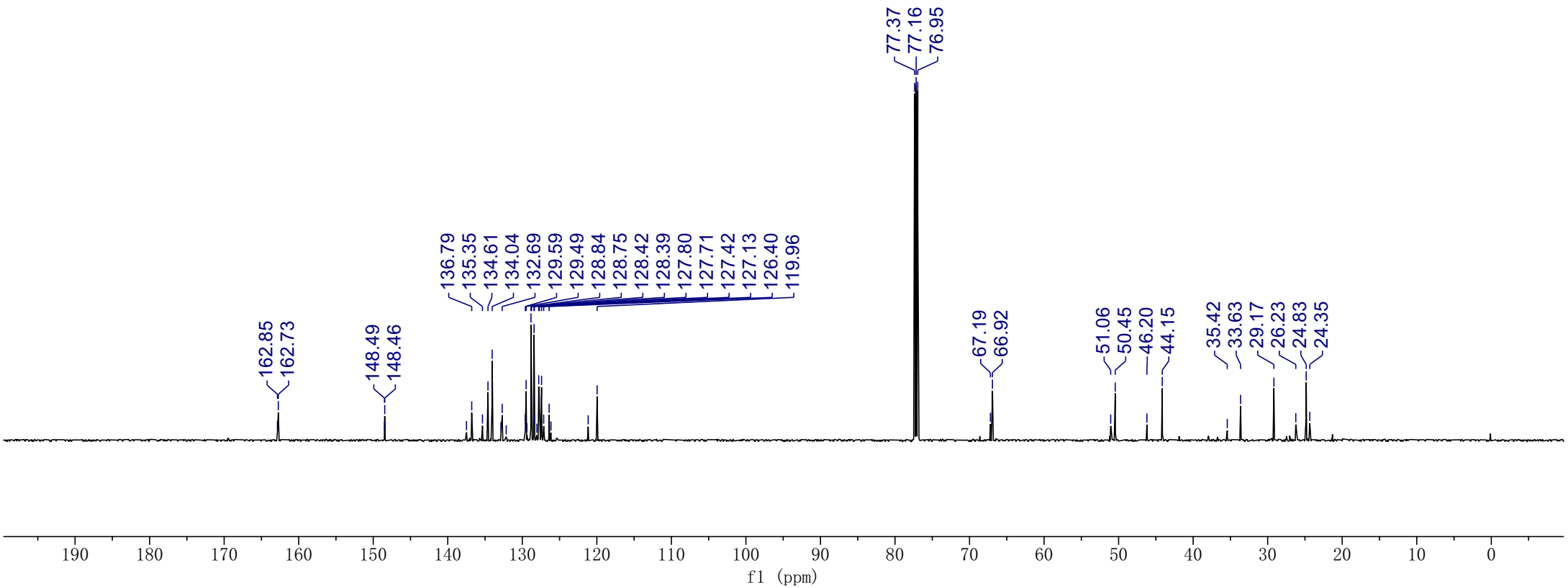
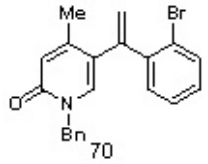
7.52
7.51
7.38
7.36
7.34
7.33
7.32
7.32
7.31
7.30
7.29
7.26
7.25
7.24
7.22
7.18
7.18
7.16
7.16
7.14
7.14
7.10
7.09
7.08
7.08
7.07
7.07
7.05
7.05
6.96
6.95
6.94
6.93
5.64
5.60
5.57
5.53
5.43
4.52
4.48
4.38
4.35
4.26
4.25
4.21
3.44
3.42
3.40
3.29
3.26
3.23
3.20
2.35
2.19
2.19
2.17
1.29
1.29
1.28
1.26
1.07
4.18
2.02
1.06
1.04
2.07
1.07
1.04
0.98
1.00
1.04
2.93
0.77
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
-0.5
f1 (ppm)

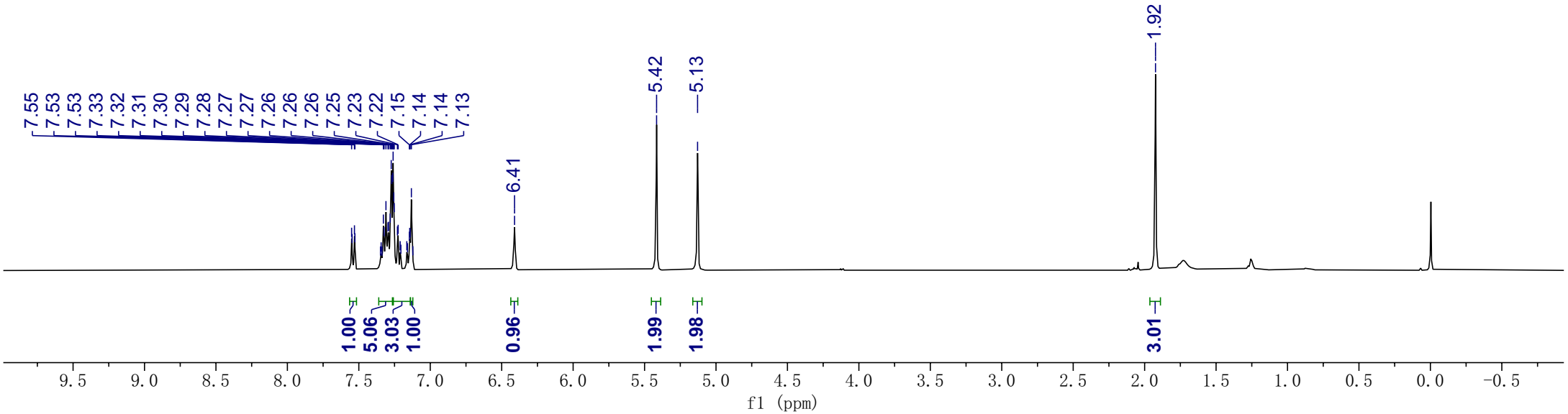

Me
Br
H
CH2OH
O
N
H
Bn

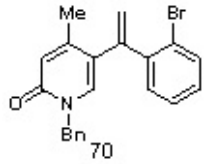
69


77.37
77.16
76.95
136.79
135.35
134.61
134.04
132.69
129.59
129.49
128.84
128.75
128.42
128.39
127.80
127.71
127.42
127.13
126.40
119.96
162.85
162.73
148.49
148.46
67.19
66.92
51.06
50.45
46.20
44.15
35.42
33.63
29.17
26.23
24.83
24.35
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

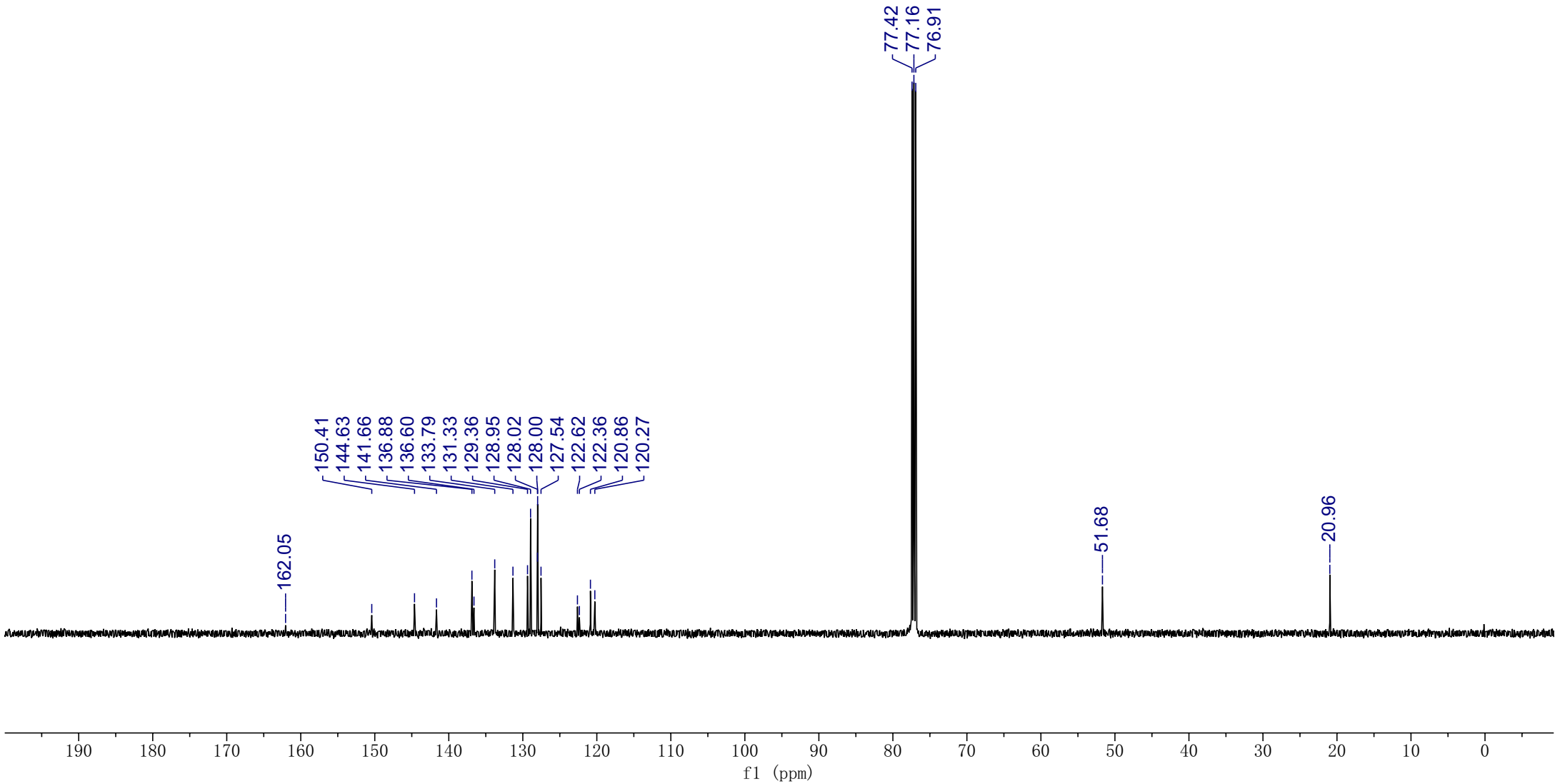

Me
Br
O
N
Bn

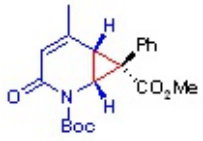
70


7.55
7.53
7.53
7.33
7.32
7.31
7.30
7.29
7.28
7.27
7.27
7.26
7.26
7.26
7.25
7.23
7.22
7.15
7.14
7.14
7.13
6.41
5.42
5.13
1.92
1.00
5.06
3.03
1.00
0.96
1.99
1.98
3.01
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
-0.5
f1 (ppm)

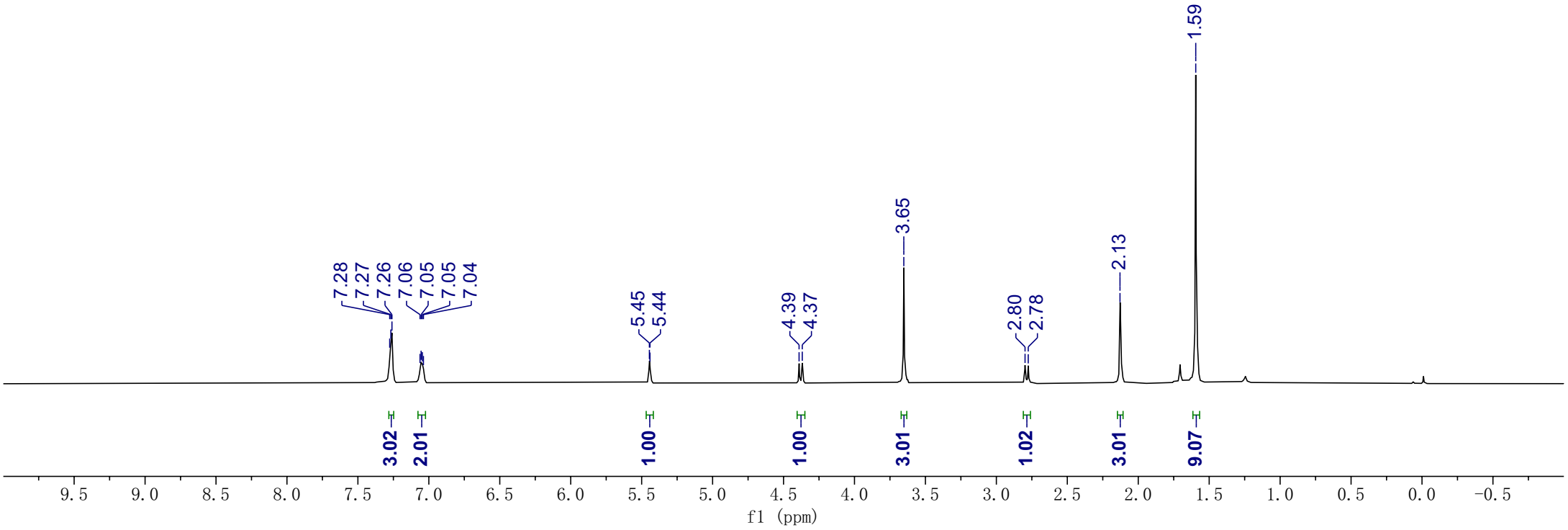

Me
Br
O
N
Bn

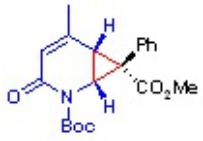
70


77.42
77.16
76.91
150.41
144.63
141.66
136.88
136.60
133.79
131.33
129.36
128.95
128.02
128.00
127.54
122.62
122.36
120.86
120.27
162.05
51.68
20.96
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

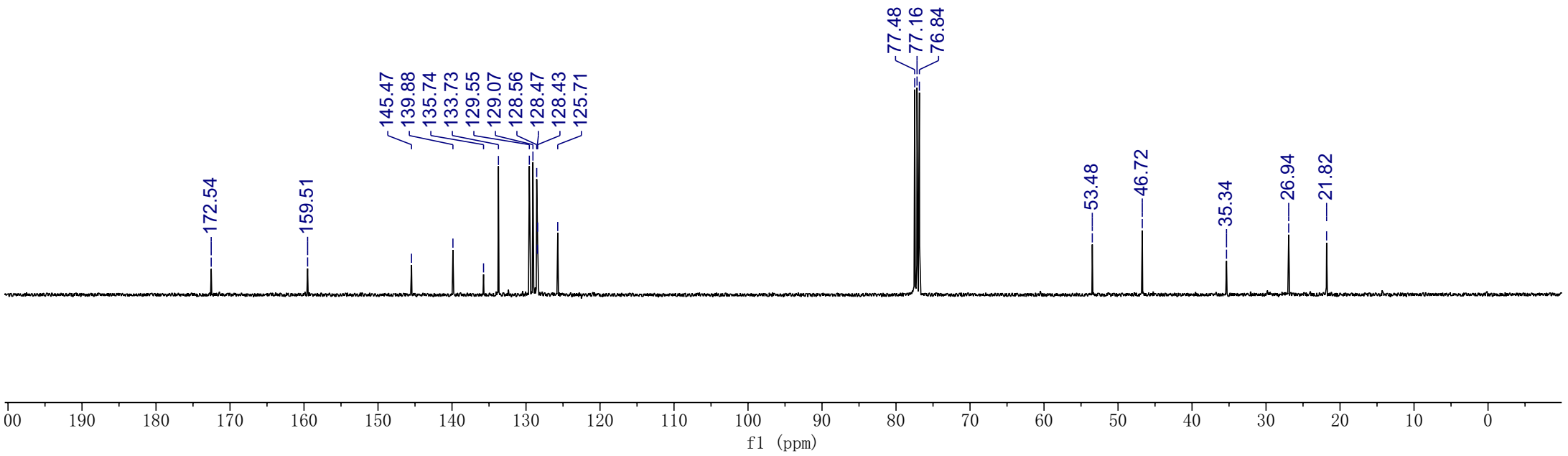

H
Ph
CO2Me
O
N
H
Boc

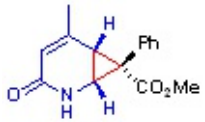
71


7.28
7.27
7.26
7.06
7.05
7.05
7.04
5.45
5.44
4.39
4.37
3.65
2.80
2.78
2.13
1.59
3.02
2.01
1.00
1.00
3.01
1.02
3.01
9.07
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
-0.5
f1 (ppm)

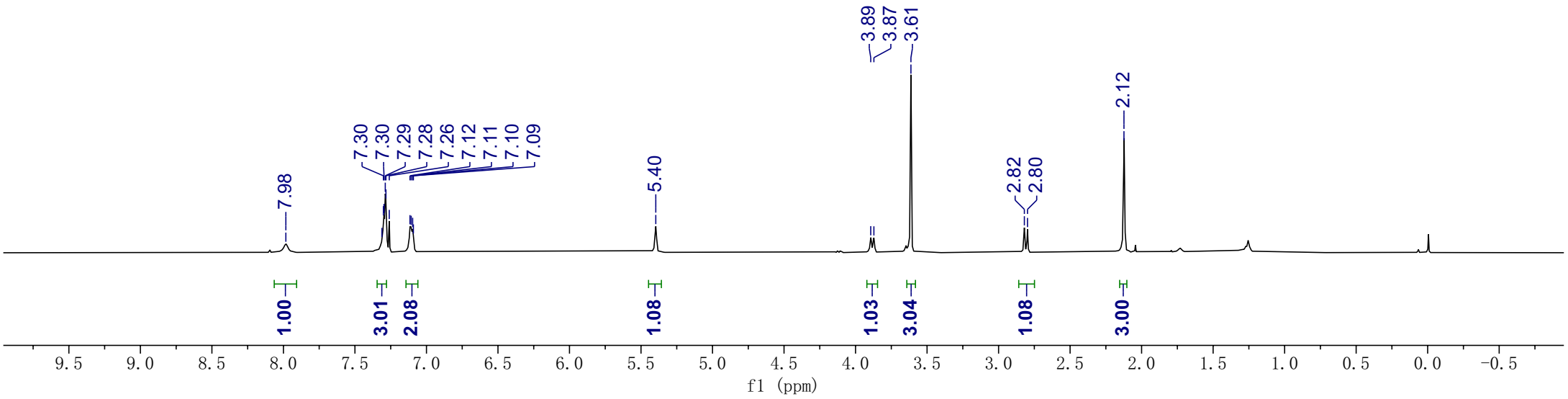

H
Ph
O
N
CO2Me
H
Boc

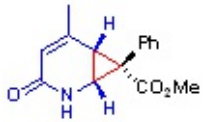
71


172.54
159.51
145.47
139.88
135.74
133.73
129.55
129.07
128.56
128.47
128.43
125.71
77.48
77.16
76.84
53.48
46.72
35.34
26.94
21.82
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

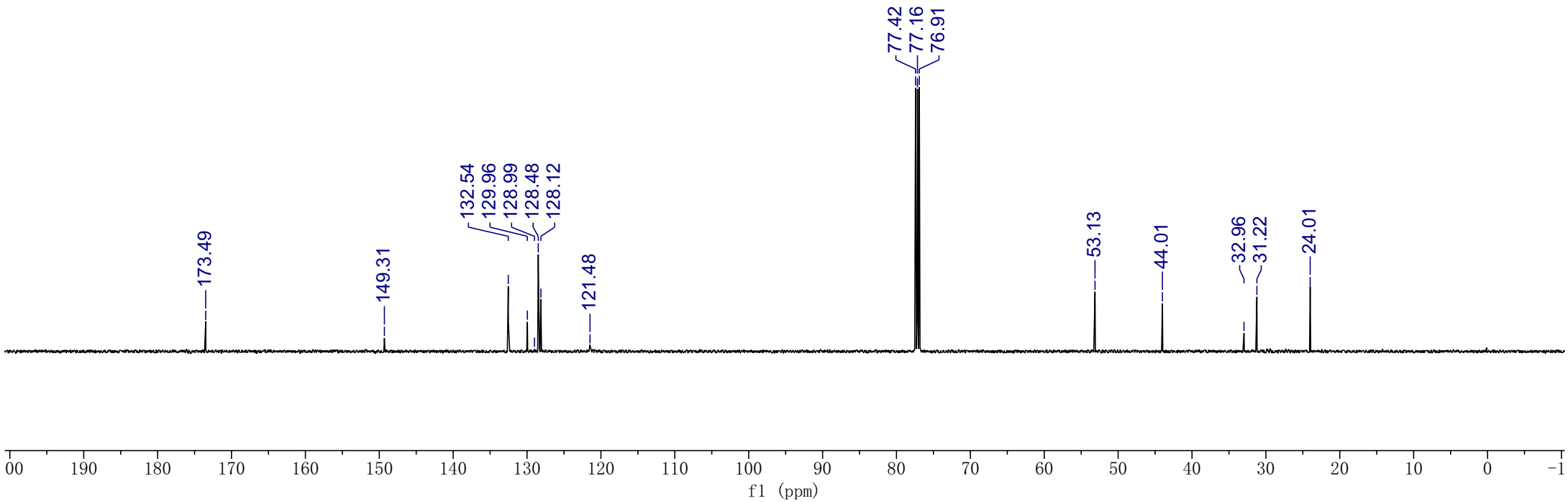

H
Ph
O
N
H
H
CO2Me

72


7.98
7.30
7.30
7.29
7.28
7.26
7.12
7.11
7.10
7.09
5.40
3.89
3.87
3.61
2.82
2.80
2.12
1.00
3.01
2.08
1.08
1.03
3.04
1.08
3.00
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
-0.5
f1 (ppm)


H
Ph
O
N
H
H
CO2Me

72


173.49
149.31
132.54
129.96
128.99
128.48
128.12
121.48
77.42
77.16
76.91
53.13
44.01
32.96
31.22
24.01
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)