Electronic Supplementary Information

Title: **To stay as allene or go further? Synthesis of novel phosphono-heterocycles and polycyclics via propargyl alcohols**

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(1) General experimental details:

Chemicals were procured from Aldrich or local manufacturers and were purified when required.[1] ^{1}H, ^{13}C and ^{31}P NMR spectra (^{1}H-400 MHz, ^{13}C-100 MHz and ^{31}P-162 MHz) were recorded using a BRUKER 400 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85 % H_3PO_4 ($\delta = 0$). IR spectra were recorded on a JASCO FTIR 5300 spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a Perkin–Elmer 240C CHN analyzer. Mass spectra were recorded by using a LCMS-2010A instrument. For TLC, glass micro slides were coated with silica-gel-GF_{254} (mesh size 75μ) and spots were identified using iodine or UV chamber as appropriate. The TGA/mass analyses were performed on a NETZSCH – STA 409PC with NETZSCH-QMS 403C (Aëolos) mass setup at a scan rate of 5 $^{o}C\ min^{-1}$. For column chromatography, silica gel of 100-200 mesh size was used.

P(III)-Cl precursors **1a-c**, and **1e** were prepared by reported procedures.[2] Ph_2PCl (**1d**) was received from Aldrich company and was distilled prior to use.

(2). Synthesis, isolation details (including Table S1), Spectroscopic (^{1}H and ^{13}C NMR)/Analytical data for 2-33

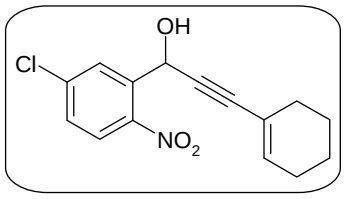
(a) Synthesis of propargyl alcohols 2a-c, 3a-c, 4a-b and 5a-d

(i) Nitro-based propargyl alcohols 2a-c and 3a-c

These were prepared by a slightly modified version of a literature method by slightly increasing the molar quantity of the alkyne.[3] To a solution of 1-ethynyl-1-cyclohexene (1.42 mL, 12.2 mmol) in anhydrous THF (20 mL), *n*-butyl lithium (10.1

mL, 16.2 mmol, 1.6M solution in hexanes) was added *via* syringe at -20 °C under nitrogen atmosphere. The resulting solution was stirred at this temperature for 30 min and then appropriate aldehyde (8.1 mmol) in THF (5 mL) was added drop-wise. The contents were warmed to 25 ^{o}C and stirring continued for 30 min. Then the reaction mixture was quenched with saturated ammonium chloride (10 mL) solution. The solvent (THF) was removed under vacuum and the residue extracted with diethyl ether (2 x 20 mL). The combined organic layer was washed with water (2 x 10 mL), brine (5 mL), dried (anh. Na_2SO_4) and concentrated in vacuo. Pure propargyl alcohols were obtained as liquids by passing through a short column of silica gel (ethyl acetate/hexane). Alcohols **2a**,[3a] **3a**[3a] and **3b**[3b] are known; spectroscopic and analytical data are consistent with that reported before. Details on other compounds are given below.

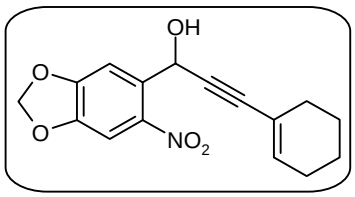
Compound 2b



This compound was prepared by adapting above procedure by using 5-chloro-2-nitro benzaldehyde (1.50 g, 8.1 mmol) and 1-ethynyl-1-cyclohexene (1.42 mL, 12.2 mmol) and purified by column chromatography using ethyl acetate/hexane (1:9) as the eluent. Yield 2.16 g (92%); IR (neat, cm^{-1}) 3409(br), 2932, 2218, 1603, 1572, 1528, 1345, 1173; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.62 (m, 4H, cyclohexenyl-*H*), 2.11 (br, 4H, cyclohexenyl-*H*), 3.00 (br, 1H, ArCH(O*H*)), 6.13 and 6.16 (2 s, 2H, ArC*H*(OH) + cyclohexenyl-*H*), 7.45-7.47 (m, 1H, Ar-*H*), 7.93-7.95 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 22.1, 25.6, 28.8, 61.4, 83.2, 89.2, 119.5, 126.5, 129.1, 129.4, 136.9,

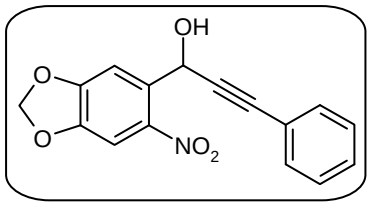
137.9, 140.2, 147.6; LC-MS *m/z* 292 $[M+1]^+$, 294 $[M+3]^+$; Anal. Calcd. for $C_{15}H_{14}ClNO_3$: C, 61.76; H, 4.84; N, 4.80. Found: C, 61.58; H, 4.91; N, 4.72.

Compound 2c



This compound was prepared by adapting above procedure by using 6-nitropiperonal (2.00 g, 10.2 mmol) and 1-ethynyl-1-cyclohexene (2.40 mL, 20.4 mmol) and purified by column chromatography using ethyl acetate/hexane (1:9) mixture as the eluent. Yield 2.96 g (96%); IR (neat, cm^{-1}) 3378, 2934, 2218, 1682, 1616, 1520, 1331, 1036; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55-1.60 (m, 4H, cyclohexenyl-*H*), 2.07-2.09 (m, 4H, cyclohexenyl-*H*), 3.40 (br, 1H, ArCH(O*H*)), 6.07 (s, 1H, ArC*H*(OH)), 6.12 (br, 3H, OCH_2O + cyclohexenyl-*H*), 7.38 (s, 1H, Ar-*H*), 7.46 (s, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 22.2, 25.6, 28.9, 61.5, 84.1, 88.5, 103.2, 105.7, 108.4, 119.7, 133.5, 136.4, 142.0, 147.7, 152.2; LC-MS *m/z* 302 $[M+1]^+$; Anal. Calcd. for $C_{16}H_{15}NO_5$: C, 63.78; H, 5.02; N, 4.65. Found: C, 63.71; H, 5.12; N, 4.58.

Compound 3c

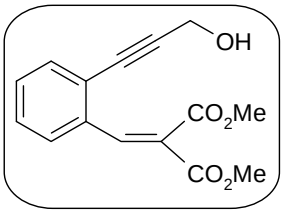


This compound (brown liquid) was prepared by adapting above procedure by using 6-nitropiperonal (3.60 g, 18.4 mmol) and phenylacetylene (4.0 mL, 36.8 mmol) and purified by column chromatography using ethyl acetate/hexane (1:2) as the eluent. Yield 5.21 g (95%); IR (neat, cm^{-1}) 3434, 2915, 2232, 1616, 1522, 1483, 1333, 1263, 1034; ^1H NMR (400 MHz, $CDCl_3$) δ 3.43 (br, 1H, ArCH(O*H*)), 6.14 (s, 2H, OCH_2O), 6.22 (br, 1H, ArC*H*(OH), 7.27-7.32 (m, 3H, Ar-*H*), 7.43-7.51 (m, 4H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 61.7, 86.6, 86.8, 103.3, 105.9, 108.5, 122.0, 128.4, 128.9, 131.9, 133.1, 142.1, 147.9, 152.4; LC-MS *m/z* 298 $[M+1]^+$; Anal. Calcd. for $C_{16}H_{11}NO_5$: C, 64.65; H, 3.73; N, 4.71. Found: C, 64.75; H, 3.79; N, 4.63.

(ii) Alkylidene-based propargyl alcohols 4a-b and 5a-d

These were prepared by using a standard method (Sonogashira reaction).[4] Among these, alcohol **4b** is a known compound, but it was prepared by using the corresponding iodo compound.[5]

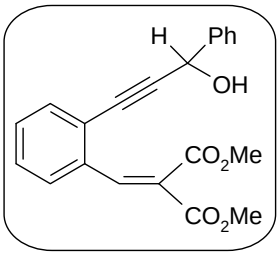
Compound 4a



This compound (brown liquid) was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (1.22 g, 4.1 mmol) and prop-2-yn-1-ol (0.28 mL, 4.9 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield 0.69 g (62%); IR (neat, cm^{-1}) 3437, 2953, 1732, 1632, 1435, 1372, 1221, 1069; ^1H NMR (400 MHz, $CDCl_3$) δ 2.96 (br, 1H, CH_2O*H*), 3.76 and 3.84 (2 s, 6H, 2

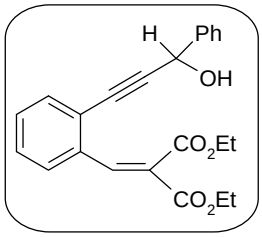
CO_2CH_3), 4.52 (s, 2H, CH_2OH), 7.29-7.47 (m, 4H, Ar-*H*), 8.19 (s, 1H, *H*C=C(CO_2CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.4, 52.6, 52.8, 82.6, 94.4, 123.9, 126.9, 127.5, 128.5, 130.1, 132.8, 134.8, 141.9, 164.6, 166.8; LC-MS *m/z* 275 $[M+1]^+$; Anal. Calcd. for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.58; H, 5.26.

Compound 5a



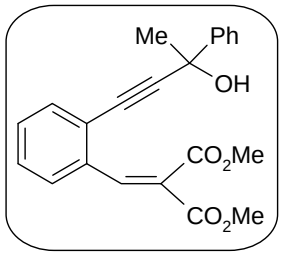
This compound (brown liquid) was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (1.71 g, 5.7 mmol) and 1-phenylprop-2-yn-1-ol (0.85 mL, 6.9 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield 1.30 g (65%); IR (neat, cm^{-1}) 3434, 2953, 2197, 1734, 1636, 1437, 1373, 1260, 1069; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.76 (br, 1H, O*H*), 3.80 and 3.85 (2 s, 6H, 2 CO_2CH_3), 5.75 (s, 1H, C*H*Ph(OH)), 7.33-7.39 and 7.41-7.45 (2 m, 6H, Ar-*H*), 7.54-7.56 and 7.64-7.66 (2 m, 3H, Ar-*H*), 8.26 (s, 1H, *H*C=C(CO_2CH_3)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 52.6, 52.8, 65.1, 83.8, 95.7, 123.7, 126.8, 127.1, 127.6, 128.5, 128.7, 130.0, 132.8, 135.1, 140.3, 141.7, 164.4, 166.7; LC-MS *m/z* 349 $[M-1]^+$; Anal. Calcd. for $C_{21}H_{18}O_5$: C, 71.99; H, 5.18. Found: C, 71.85; H, 5.26.

Compound 5b



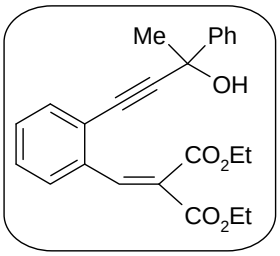
This compound (brown liquid) was prepared by using 2-(2-bromo-benzylidene)-malonic acid diethyl ester (1.70 g, 5.2 mmol) and 1-phenylprop-2-yn-1-ol (0.77 mL, 6.2 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield 1.26 g (64%); IR (neat, cm^{-1}) 3432, 2984, 1728, 1630, 1449, 1377, 1252, 1067; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 and 1.30 (2 t, ^{3}J(H-H) ~ 7.0 Hz, 6H, 2 $CO_2CH_2CH_3$), 2.94 (br, 1H, O*H*), 4.25-4.32 (m, 4H, 2 $CO_2CH_2CH_3$), 5.73 (s, 1H, C*H*Ph(OH)), 7.29-7.53 (m, 7H, Ar-*H*), 7.62-7.64 (m, 2H, Ar-*H*), 8.21 (s, 1H, *H*C=C$(CO_2Et)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.1, 61.7, 61.8, 65.1, 83.9, 95.6, 123.6, 126.8, 127.7, 127.9, 128.4, 128.6, 128.7, 129.9, 132.7, 135.2, 140.4, 141.0, 164.0, 166.3; LC-MS *m/z* 377 $[M-1]^+$; Anal. Calcd. for $C_{23}H_{22}O_5$: C, 73.00; H, 5.86. Found: C, 73.12; H, 5.83.

Compound 5c



This compound (brown liquid) was prepared by using 2-(2-bromo-benzylidene)-malonic acid dimethyl ester (0.98 g, 3.3 mmol) and 2-phenylbut-3-yn-2-ol (0.57 g, 3.9 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield 0.79 g (66%); IR (neat, cm^{-1}) 3488, 2976, 1970, 1728, 1626, 1433, 1370, 1229, 1069; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (s, 3H, C*H*$_3$), 2.82 (br, 1H, O*H*), 3.78 and 3.84 (2 s, 6H, 2 CO_2CH_3), 7.30-7.44 and 7.54-7.56 (2 m, 7H, Ar-*H*), 7.72-7.74 (m, 2H, Ar-*H*), 8.28 (s, 1H, *H*C=C$(CO_2CH_3)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.3, 52.7, 52.8, 70.5, 82.2, 99.5, 123.8, 125.0, 126.9, 127.5, 127.8, 128.4, 128.7, 130.1, 132.6, 135.0, 141.7, 145.3, 164.3, 166.8; LC-MS *m/z* 363 $[M-1]^+$; Anal. Calcd. for $C_{22}H_{20}O_5$: C, 72.51; H, 5.53. Found: C, 72.45; H, 5.56.

Compound 5d



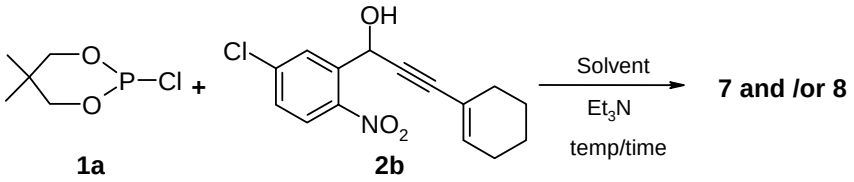
This compound (brown liquid) was prepared by using 2-(2-bromo-benzylidene)-malonic acid diethyl ester (0.99 g, 3.0 mmol) and 2-phenylbut-3-yn-2-ol (0.53 g, 3.6 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield 0.76 g (64%); IR (neat, cm^{-1}) 3441, 2984, 1730, 1632, 1449, 1377, 1252, 1067; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.24 and 1.31 (2 t, ^3J(H-H) = 7.2 Hz, 6H, 2 $CO_2CH_2CH_3$), 1.92 (s, 3H, C*H*$_3$), 3.13 (br, 1H, O*H*), 4.27-4.32 (m, 4H, 2 $CO_2CH_2CH_3$), 7.30-7.42 and 7.49-7.55 (2 m, 7H, Ar-*H*), 7.74-7.76 (m, 2H, Ar-*H*), 8.26 (s, 1H,

*H*C=C($CO_2Et)_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.1, 33.3, 61.7, 61.8, 70.4, 82.3, 99.4, 123.8, 125.0, 127.7, 127.8, 128.4, 128.5, 129.9, 132.5, 135.2, 140.9, 145.3, 164.0, 166.3; LC-MS *m/z* 393 $[M+1]^+$; Anal. Calcd. for $C_{24}H_{24}O_5$: C, 73.45; H, 6.16. Found: C, 73.28; H, 6.25.

(b) Optimization of reaction conditions using P-Cl precursor 1a and alcohol 2b

To a solution of alcohol **2b** (1.0 mmol) in solvent (5 mL), Et_3N (1.0 mmol) was added followed by **1a** (1.0 mmol) at 0 ^oC under nitrogen atmosphere and stirred at the temperature mentioned in Table S1. After filtering the amine salt, silical gel (1.0 g, 100/200 mesh) was added and continued the stirring.

Table S1. Optimization studies for the synthesis of compounds **7**-**8**



1a **2b**

entry	solvent	temp (^oC)	additive	time (h)	Yield[a]	
					7	**8**
1	THF	rt	none	4	quantitative	-
2	THF	60	none	2	quantitative	-
3	Toluene	rt	none	6	quantitative	-
4	DCM	rt	none	8	90	-
5	1,4-dioxane	rt	none	5	quantitative	-
6	**THF**	**60**	**silica**	**2**	**-**	**>95**
7	Toluene	80	silica	4	10	78
8	DCM	40	silica	12	42	50

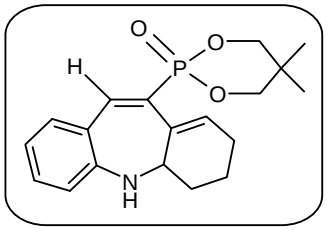
9	1,4-dioxane	80	silica	4	15	65

[a]Yields are based on ^{31}P NMR spectroscopy.

(c) Synthesis of phosphorus-containing heterocycles 6-21 under the optimized conditions as in (b)

(i) Compound 6

To a solution of propargyl alcohol **2a** (1.50 g, 5.83 mmol) in THF (20 mL) was added triethylamine (0.59 g, 5.83 mmol) followed by P(III)-Cl precursor **1a** (0.98 g, 5.83 mmol) at 0 ^{o}C under nitrogen atmosphere and the resulting mixture was stirred at 60 ^{o}C for 2 h. Et_3NHCl was filtered off, silica gel (~2.0 g) added to the filtrate and the mixture heated at 60 ^{o}C for 2 h. Solvent was removed by using rotary evaporator and ethyl acetate (20 mL) was added to this crude. The organic layer was washed with water (10 mL), saturated brine solution (10 mL), dried (anh.Na_2SO_4) and removed the solvent to yield brown colered gummy material. Compound **6** was purified by column chromatography (silica gel 100/200 mesh) by using ethyl acetate/hexane (3:2) mixture as the eluent.



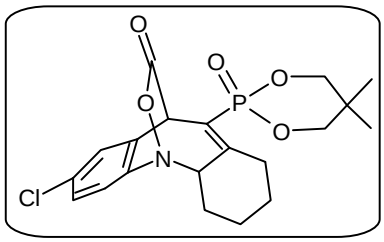
6

Yield 1.21 g (60%); mp 182-184 ^{o}C; IR (KBr, cm^{-1}) 3353, 2936, 2882, 1605, 1487, 1240, 1059, 1011, 748; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 and 1.18 (2 s, 6H, 2 CH_3), 1.66-1.73 (m, 4H, cyclohexenyl-*H*), 1.95-2.29 (m, 3H, cyclohexenyl-*H*+N*H*), 3.60 (br, 1H, C*H*NHAr), 3.84-3.95 and 4.12-4.18 (2 m, 4H, 2 OCH_2), 6.57 (br, 1H, PCCC*H*(cyclohexenyl)), 6.62 (d, ^3J(H-H) = 7.5 Hz, 1H, Ar-*H*), 6.74 (t, ^3J(H-H) ~ 7.5 Hz,

1H, Ar-*H*), 7.08-7.12 (m, 1H, Ar-*H*), 7.14 (d, ^{3}J(P-H) ~ 26.4 Hz, 1H, PC=C*H*(cis)), 7.22 (d, ^{3}J(H-H) = 7.5 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.0, 21.5, 21.9, 26.1, 30.3, 32.6 (d, ^{3}J(P-C) = 5.9 Hz, *C*Me_2), 51.3 (d, ^{3}J(P-C) = 12.4 Hz, P-CC*C*HNH), 75.7 and 76.2 (2 d, ^{2}J(P-C) = 6.3 Hz, O*C*H_2), 116.9, 118.4, 120.7 (d, ^{2}J(P-C) = 23.4 Hz, PC=*C*), 125.1 (d, ^{1}J(P-C) = 175.0 Hz, P*C*), 127.8 (d, *J*(P-C) = 3.7 Hz), 130.4, 134.4 (d, *J*(P-C) = 8.6 Hz), 135.8, 141.0 (d, *J*(P-C) = 10.8 Hz), 149.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.1; LC-MS *m/z* 346 $[M+1]^+$; Anal. Calcd. for $C_{19}H_{24}NO_3P$: C, 66.07; H, 7.00; N, 4.06. Found: C, 66.21; H, 6.89; N, 4.15. This compound was crystallized from chloroform (2 mL/0.2 g). X-ray structure was determined for this sample (Fig. S1).

(ii) Compound 7

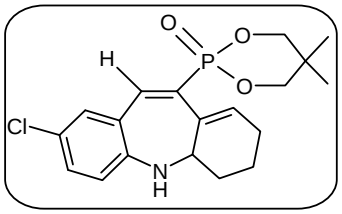
To a solution of propargyl alcohol **2b** (0.40 g, 1.4 mmol) in THF (20 mL) was added triethylamine (0.14 g, 1.4 mmol) followed by P(III)-Cl precursor **1a** (0.23 g, 1.4 mmol) at 0 ^{o}C under nitrogen atmosphere and the resulting mixture was stirred at 60 ^{o}C for 2 h. Et_3NHCl was filtered off, the solvent was removed to yield brown colored gummy material. This was dissolved in ethyl acetate (5 mL) and kept at 0 ^{o}C to obtain the pure compound **7** as colorless crystals (block type).



Yield quantitative by ^{31}P NMR; 0.29 g (50%); mp 150-152 ^{o}C (decomp); IR (KBr, cm^{-1}) 2984, 2942, 2865, 1775, 1601, 1476, 1267, 1182, 1061; ^{1}H NMR (400 MHz, $CDCl_3$) δ

0.95-1.04 (m, 2H, cyclohexyl-*H*), 1.11 (s, 3H, CH_3), 1.22 (br, 4H, CH_3 + cyclohexyl-*H*), 1.79-1.86 (m, 3H, cyclohexenyl-*H*), 2.24-2.27 (m, 1H, cyclohexyl-*H*), 3.49-3.53 (m, 1H, cyclohexyl-*H*), 3.84-3.90 and 4.10-4.36 (2 m, 5H, 2 OCH_2 + cyclohexyl-*H*), 4.61 (d, ^3J(P-H) = 14.0 Hz, 1H, PC-C*H*), 7.16-7.19 (m, 1H, Ar-*H*), 7.27-7.30 (m, 2H, Ar-*H*) [one of the cyclohexyl protons other than NC*H* appears more downfied than expected, but the X-ray structure is consistent with the structure as written]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 21.8, 25.1, 26.5, 32.56-32.66 (3 lines merged due to cyclohexenyl-*C*), 33.3 (d, ^3J(P-C) = 7.8 Hz, *C*Me$_2$), 44.4 (d, *J*(P-C) = 12.6 Hz, N*C*H), 66.7 (d, ^2J(P-C) = 16.0 Hz, P-C-*C*), 75.2 and 75.8 (2 d, ^2J(P-C) ~ 5.8 Hz, 2 O*C*H$_2$), 117.6 (d, ^1J(P-C) = 184.0 Hz, P*C*), 123.0, 127.5, 129.2, 131.3, 138.2 (d, *J*(P-C) = 4.1 Hz), 140.3, 159.2 (d, *J*(P-C) = 10.1 Hz), 173.3 (d, *J*(P-C) = 7.9 Hz, *C*=O); ^{31}P NMR (162 MHz, $CDCl_3$) δ 11.1; LC-MS *m/z* 425 $[M+1]^+$, 427 $[M+3]^+$; Anal. Calcd. for $C_{20}H_{23}ClNO_5P$: C, 56.68; H, 5.47; N, 3.30. Found: C, 56.81; H, 5.41; N, 3.26. X-ray structure was determined for this compound (Fig. S2).

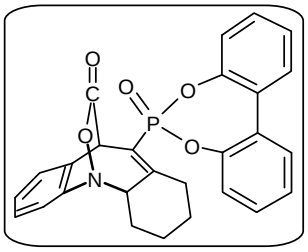
Compound 8



This compound was obtained by adapting the procedure 2c(i) by using **1a** (0.17 g, 1.0 mmol) and propargyl alcohol **2b** (0.29 g, 1.0 mmol) with reaction time of 3 h. This compound was eluted by using ethyl acetate/hexane (1:1) mixture as yellow colored solid. Yield quantitative by ^{31}P NMR; 0.25 g (isolated, 65%); mp 192-194 ^{o}C; IR (KBr,

cm^{-1}) 3308, 2930, 1644, 1611, 1487, 1256, 1059, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 and 1.17 (2 s, 6H, 2 CH_3), 1.71-2.28 (m, 7H, cyclohexenyl-*H*+N*H*), 3.56 (br, 1H, C*H*NHAr), 3.83-3.94 and 4.13-4.19 (2 m, 4H, 2 OCH_2), 6.56-6.60 (m, 2H, C*H*(cyclohexenyl) + Ar-*H*), 6.97-7.03 (m, 2H, Ar-*H* + PCC*H*), 7.18_0-7.18_3 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.9, 21.5, 21.8, 26.1, 30.2, 32.6 (d, ^{3}J(P-C) = 5.7 Hz, *C*Me_2), 51.4 (d, ^{3}J(P-C) = 12.5 Hz, *C*HNH), 75.8 and 76.3 (2 d, ^{2}J(P-C) ~ 6.6 Hz, O*C*H_2), 118.3, 121.8 (d, ^{2}J(P-C) = 24.0 Hz, PC=*C*), 122.8, 126.8 (d, ^{1}J(P-C) = 174.3 Hz, P*C*), 128.8, 130.0, 134.1, 134.4, 139.0 (d, *J*(P-C) = 10.9 Hz), 147.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.1; LC-MS *m/z* 380 $[M+1]^+$, 382 $[M+3]^+$; Anal. Calcd. for $C_{19}H_{23}ClNO_3P$: C, 60.08; H, 6.10; N, 3.69. Found: C, 60.21; H, 6.15; N, 3.62.

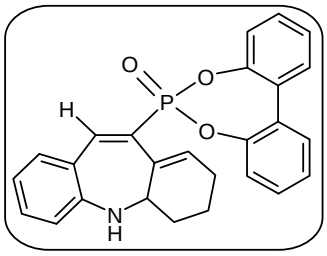
Compound 9



This product was obtained by adapting the procedure 2c(ii) by using **1c** (0.25 g, 1.0 mmol) and propargyl alcohol **2a** (0.26 g, 1.0 mmol) with reaction time of 2 h. This compound could be isolated by using silica gel column column chromatography [100/200 mesh; ethyl acetate/hexane (1:1)] as pale yellow colored solid. Yield quantitative by ^{31}P NMR [**9**]; 0.20 g (isolated, 42%); mp 194-198 ^{o}C (decomp); IR (KBr, cm^{-1}) 2930, 2859, 1767, 1607, 1478, 1435, 1246, 1200; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02-1.30 (m, 2H, cyclohexyl-*H*), 1.62-2.35 (m, 5H, cyclohexyl-*H*), 3.57-3.61 and 4.31-4.34 (2 m, 2H,

cyclohexyl-*H*), 4.59 (d, ^{3}J(P-H) = 13.6 Hz, 1H, PC-C*H*), 6.68-6.69 (m, 1H, Ar-*H*), 6.99-7.61 (m, 11H, Ar-*H*) [one of the cyclohexyl protons other than NC*H* appears more downfied than expected, but the X-ray structure is consistent with the structure as written]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.1, 26.8, 33.0, 34.0 (d, *J*(P-C) = 7.8 Hz), 45.3 (d, *J*(P-C) = 11.4 Hz), 67.2 (d, *J*(P-C) = 16.8 Hz), 116.8, 117.4 (d, ^{1}J(P-C) = 179.3 Hz, P*C*), 118.0, 121.7 (d, *J*(P-C) = 5.7 Hz), 122.0 (d, *J*(P-C) = 2.9 Hz), 125.7, 125.9, 126.5, 126.8, 127.9, 129.1, 130.1, 130.2, 130.4, 136.2 (d, *J*(P-C) = 4.5 Hz), 136.3, 140.9, 147.2 (d, *J*(P-C) = 9.7 Hz), 147.4 (d, *J*(P-C) = 10.0 Hz), 160.9 (d, *J*(P-C) = 10.2 Hz), 173.2 (d, *J*(P-C) = 8.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 22.4; LC-MS *m/z* 470 $[M-1]^+$; Anal. Calcd. for $C_{27}H_{22}NO_5P$: C, 68.79; H, 4.70; N, 2.97. Found: C, 68.89; H, 4.76; N, 2.91. This compound was crystallized from dichloromethane (0.20 g in 10 mL) at 25 ^{o}C. X-ray structural analysis was performed on this sample (Fig. S3). A minor amount of compound **10** (0.06 g, 15%) was also isolated from the column chromatography. Data for compound **10** is given below.

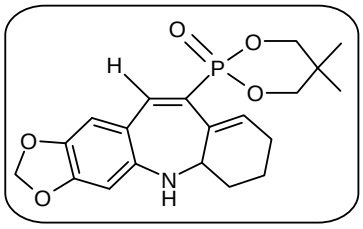
Compound 10



This product was obtained by adapting the procedure 2c(i) by using **1c** (0.25 g, 1.0 mmol) and propargyl alcohol **2a** (0.26 g, 1.0 mmol) with reaction time of 3 h. This compound was eluted by using ethyl acetate/hexane (2:1) mixture as yellow colored solid. Yield

94% by ^{31}P NMR; 0.26 g (isolated, 60%); mp 212-214 ^{o}C; IR (KBr, cm^{-1}) 3295, 2965, 2932, 1643, 1603, 1485, 1258, 1074, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.58-1.67 (m, 2H, cyclohexenyl-*H*), 1.94-2.14 (m, 5H, cyclohexenyl-*H* + N*H*), 3.58 (br, 1H, C*H*NH), 6.41-6.42 (m, 1H, C*H*(cyclohexenyl)), 6.59 (d, ^{3}J(H-H) = 8.0 Hz, 1H, Ar-*H*), 6.66-6.69 (m, 1H, Ar-*H*), 7.07-7.22 (m, 4H, Ar-*H*), 7.29-7.56 (m, 7H, Ar-*H* + PC=C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 26.1, 29.8, 50.7 (d, ^{3}J(P-C) = 12.6 Hz, *C*HNH), 116.8, 118.1, 119.7 (d, ^{2}J(P-C) = 24.8 Hz PC=*C*), 121.8, 122.1, 123.5 (d, ^{1}J(P-C) = 177.2 Hz, P*C*), 125.8, 126.3, 128.4, 128.7, 129.1, 129.7, 129.9, 130.1, 130.9, 133.7 (d, *J*(P-C) = 9.3 Hz), 136.4, 137.5, 144.1 (d, *J*(P-C) = 10.8 Hz), 147.9 (d, *J*(P-C) = 9.6 Hz), 149.0, 149.6 (d, *J*(P-C) = 10.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.8; LC-MS *m/z* 426 $[M-1]^{+}$; Anal. Calcd. for $C_{26}H_{22}NO_3P$: C, 73.06; H, 5.19; N, 3.28. Found: C, 73.18; H, 5.14; N, 3.21.

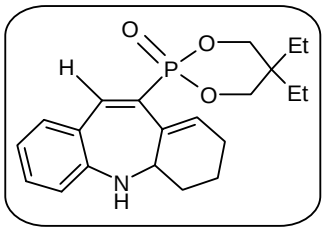
Compound 11



This product was obtained by adapting the procedure 2c(i) by using **1b** (0.20 g, 1.0 mmol) and propargyl alcohol **2c** (0.30 g, 1.0 mmol) with the reaction time of 2 h. This compound was eluted by using ethyl acetate/hexane (1:1) mixture as brown colored solid. Yield 0.27 g (70%); mp 204-206 ^{o}C; IR (KBr, cm^{-1}) 3422, 2969, 2934, 1647, 1487, 1248, 1059, 1005; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 and 1.15 (2 s, 6H, 2 CH_3), 1.69-1.71 (m, 2H, cyclohexenyl-*H*), 1.93-2.25 (m, 5H, cyclohexenyl-*H*+N*H*), 3.53 (br, 1H, C*H*NH), 3.85-3.93 and 4.11-4.19 (2 m, 4H, 2 OCH_2), 5.87 and 5.89 (2 s, 2H, OCH_2O), 6.17 (s,

1H, Ar-*H*), 6.48 (br, 1H, cyclohexenyl-*H*), 6.65 (s, 1H, Ar-*H*), 7.00 (d, ^{3}J(P-H) = 25.6 Hz, 1H, PC=C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.4, 21.6, 21.9, 26.0, 30.4, 32.6 (d, ^{3}J(P-C) = 5.4 Hz, *C*Me$_2$), 51.9 (d, ^{3}J(P-C) = 12.4 Hz, *C*HNH), 75.5 and 76.1 (2 d, ^{2}J(P-C) ~ 5.7 Hz, O*C*H$_2$), 97.6, 101.3, 112.9, 113.8 (d, ^{2}J(P-C) = 24.0 Hz, PC=*C*), 122.1 (d, ^{1}J(P-C) = 176.2 Hz, P*C*), 126.4, 134.6 (d, *J*(P-C) = 10.1 Hz, PCC*C*), 140.4 (d, *J*(P-C) = 11.2 Hz), 140.8, 146.4, 150.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.3; LC-MS *m/z* 388 $[M-1]^+$; Anal. Calcd. for $C_{20}H_{24}NO_5P$: C, 61.69; H, 6.21; N, 3.60. Found: C, 61.55; H, 6.28; N, 3.71.

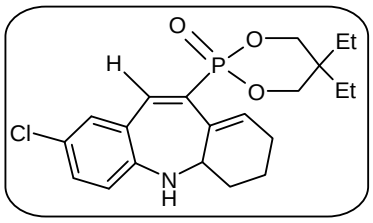
Compound 12



This product was obtained by adapting the procedure 2c(i) by using **1b** (0.48 mL, 2.2 mmol) and propargyl alcohol **2a** (0.57 g, 2.2 mmol) with reaction time of 2 h. It was eluted by using ethyl acetate/hexane (3:2) mixture as yellow colored solid. Yield 0.56 g (68%); mp 186-188 ^{o}C; IR (KBr, cm^{-1}) 3291, 2936, 2868, 1605, 1489, 1248, 1078, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.86-0.92 (m, 6H, 2 CH_2CH_3), 1.37-1.38 (m, 4H, 2 CH_2CH_3), 1.65-1.74 (m, 4H, cyclohexenyl-*H*), 2.00-2.30 (m, 3H, cyclohexenyl-*H*+N*H*), 3.62 (br, 1H, C*H*NH), 3.92-3.98 and 4.20-4.26 (2 m, 4H, 2 OCH_2), 6.57-6.76 (m, 2H, C*H*(cyclohexenyl) + Ar-*H*), 7.10-7.24 (m, 4H, Ar-*H* + PC=C*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.1, 7.2, 18.0, 22.8, 23.0, 26.1, 30.4, 37.5 (d, ^{3}J(P-C) = 5.2 Hz, *C*Et$_2$), 51.4 (d,

^{3}J(P-C) = 12.4 Hz, *C*HNH), 73.1 and 73.6 (2 d, ^{2}J(P-C) ~ 6.1 Hz, O*C*H_2), 116.9, 118.4, 120.7 (d, ^{2}J(P-C) = 23.3 Hz, PC=*C*), 125.3 (d, ^{1}J(P-C) = 174.0 Hz, P*C*), 127.8 (d, *J*(P-C) = 4.4 Hz), 130.4, 134.4 (d, *J*(P-C) = 9.6 Hz), 135.8, 140.7 (d, *J*(P-C) = 10.8 Hz), 149.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.8; LC-MS *m/z* 374 $[M+1]^+$; Anal. Calcd. for $C_{21}H_{28}NO_3P$: C, 67.54; H, 7.56; N, 3.75. Found: C, 67.42; H, 7.63; N, 3.68.

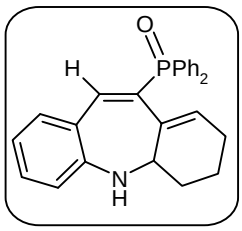
Compound 13



This product was obtained by adapting the procedure 2c(i) by using **1b** (0.35 g, 1.7 mmol) and propargyl alcohol **2b** (0.50 g, 1.7 mmol) with reaction time of 3 h. This compound was eluted by using ethyl acetate/hexane (1:1) mixture as yellow colored solid. Yield 0.50 g (72%); mp 194-198 ^{o}C; IR (KBr, cm^{-1}) 3295, 2965, 2932, 1644, 1603, 1485, 1258, 1074, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87-0.94 (m, 6H, 2 CH_2CH_3), 1.38-1.73 (m, 8H, 2 CH_2CH_3 + cyclohexenyl-*H*), 2.18-2.30 (m, 3H, cyclohexenyl-*H*+N*H*), 3.58 (br, 1H, C*H*NH), 3.89-3.98 and 4.00-4.27 (2 m, 4H, 2 OCH_2), 6.58-6.60 (m, 2H, C*H*(cyclohexenyl) + Ar-*H*), 6.96-7.06 (m, 2H, Ar-*H* + PC=C*H*), 7.20 (br, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 7.1, 7.2, 18.0, 22.7, 22.9, 26.1, 30.2, 37.5 (d, ^{3}J(P-C) = 5.1 Hz, *C*Et_2), 51.5 (d, ^{3}J(P-C) = 12.2 Hz, *C*HNH), 73.3 and 73.8 (2 d, ^{2}J(P-C) ~ 6.2 Hz, O*C*H_2), 118.3, 121.8 (d, ^{2}J(P-C) = 23.9 Hz, PC=*C*), 122.9, 127.0 (d, ^{1}J(P-C) = 173.5 Hz, P*C*), 128.8 (d, *J*(P-C) = 4.5 Hz), 130.0, 134.1 (d, *J*(P-C) = 9.4 Hz), 134.3, 138.7 (d, ^{3}J(P-C) = 10.8 Hz), 147.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.8; LC-MS *m/z* 408 $[M+1]^+$,

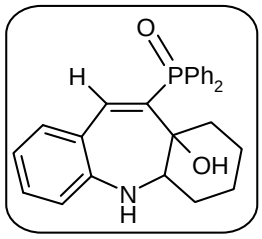
410 $[M+3]^+$; Anal. Calcd. for $C_{21}H_{27}ClNO_3P$: C, 61.84; H, 6.67; N, 3.43. Found: C, 61.72; H, 6.61; N, 3.51.

Compounds 14 and 15



14

These compounds (**14**-**15**) were obtained by adapting the procedure 2c(i) by using Ph_2PCl (**1d)** (0.34 mL, 1.9 mmol) and propargyl alcohol **2a** (0.50 g, 1.9 mmol) with reaction time of 2 h. Compound **14** was eluted by using ethyl acetate/hexane (4:1) mixture as light yellow colored solid. Yield ~90% by ^{31}P NMR [**14**+**15**]; 0.40 g (isolated, 52%, **14**); mp 132–136 ^oC; IR (KBr, cm^{-1}) 3272, 3056, 2930, 1715, 1605, 1485, 1437, 1159, 1098, 748; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43-1.68 (m, 4H, cyclohexenyl-*H*), 1.92-2.08 (m, 3H, cyclohexenyl-*H* + N*H*), 3.60 (br, 1H, C*H*NHAr), 6.32 (br, 1H, PCCC*H*(cyclohexenyl)), 6.55-6.64 (m, 2H, P-CC*H*(cis) + Ar-*H*), 6.82 (d, ^3J(H-H) ~ 7.5 Hz, 1H, Ar-*H*), 7.05 (t, ^3J(H-H) ~ 7.5 Hz, 1H, Ar-*H*), 7.35-7.48 (m, 4H, Ar-*H*), 7.53-7.68 (m, 7H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 26.0, 30.0, 51.4 (d, ^3J(P-C) = 8.6 Hz, P-CC*C*HNH), 116.9, 117.9, 120.2 (d, ^2J(P-C) = 19.7 Hz, PC*C*), 126.2, 128.4, 128.5, 129.0_0, 129.0_4, 130.2, 131.2, 131.6, 131.9, 132.0, 132.1, 132.8 (d, ^1J(P-C) = 101.8 Hz, P*C*), 133.2 (d, ^1J(P-C) = 103.7 Hz, P*C*), 134.8 (d, *J*(P-C) = 7.6 Hz), 142.3 (d, *J*(P-C) = 14.1 Hz), 149.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.4; LC-MS *m/z* 398 $[M+1]^+$; Anal. Calcd. for $C_{26}H_{24}NOP$: C, 78.57; H, 6.09; N, 3.52. Found: C, 78.41; H, 6.22; N, 3.63.



15

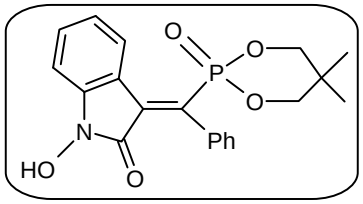
This compound (**15**) was purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Yield ~90% by ^{31}P NMR [**14**+**15**]; 0.041 g (isolated, 5%, **15**); mp 180–182 ^{o}C; IR (KBr, cm^{-1}) 3310, 3055, 1611, 1491, 1437, 1146, 748; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37-2.10 (m, 7H, cyclohexyl-*H*), 2.34-2.41 (m, 1H, cyclohexyl-*H*), 3.14 (s br, 1H, -C*H*NH), 4.03 (br, 1 H, N*H*), 6.12 (s br, 1H, -O*H*)), 6.45 (d, ^{2}J(P-H) = 22.4 Hz, 1H, PC=C*H*(*cis*)), 6.70-6.73 (m, 2H, Ar-*H*), 6.86 (d, *J*(H-H) ~ 7.5 Hz, 1H, Ar-*H*), 7.13 (t, *J*(H-H) ~ 7.5 Hz, 1H, Ar-*H*), 7.44-7.65 (m, 8H, Ar-*H*), 7.73-7.78 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 20.8, 28.8, 35.1, 58.6 (d, ^{3}J(P-C) = 8.4 Hz, P-CC*C*HNH), 77.1, 117.2, 119.0, 120.4 (d, ^{2}J(P-C) = 21.0 Hz, PC*C*), 128.5, 128.6$_1$, 128.6$_5$, 128.7, 130.5, 131.8, 131.9, 132.0, 132.1, 132.2, 133.7 (d, ^{1}J(P-C) = 96.1 Hz, P*C*), 135.2, 135.8 (d, ^{1}J(P-C) = 95.5 Hz, P*C*), 140.1 (d, ^{2}J(P-C) = 14.0 Hz, PC*C*), 149.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.5; LC-MS *m/z* 416 $[M+1]^+$; Anal. Calcd. for $C_{26}H_{26}NO_2P$: C, 75.16; H, 6.31; N, 3.37. Found: C, 75.06; H, 6.39; N, 3.29. This compound was crystallized from ethyl acetate (2 mL). X-ray structure was determined for this compound (Fig. S4).

(iii) *N*-hydroxy indolinone derivatives 16-21

To a solution of propargyl alcohol **3a** (0.82 g, 3.24 mmol) in THF (20 mL) was added triethylamine (0.33 g, 3.24 mmol) followed by **1a** (0.55 g, 3.24 mmol) at 0 ^{o}C

under nitrogen atmosphere and the resulting mixture was stirred at 60 ^{o}C for 2 h. Et_3NHCl was filtered, solvent removed to yield red colored gummy material. This compound **16** (red color) was purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Compounds **17-21** are also prepared similarly.

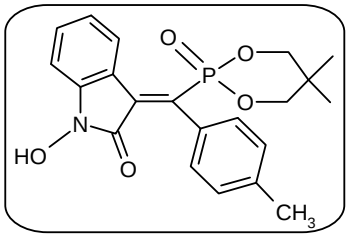
Compound 16



Yield 93% by ^{31}P NMR; 0.75 g (isolated, 60%); mp 226-228 ^{o}C; IR (KBr, cm^{-1}) 3250, 3092, 2935, 1726, 1618, 1462, 1248, 1047, 1011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 and 1.20 (2 s, 6H, 2 CH_3), 3.39-3.43 and 3.75-3.82 (2 m, 4H, 2 OCH_2), 6.51 (d, ^{3}J(H-H) ~ 7.6 Hz, 1H, Ar-*H*), 6.84 (t, ^{3}J(H-H) ~ 7.6 Hz, 1H, Ar-*H*), 7.04 (t, ^{3}J(H-H) ~ 7.6 Hz, 1H, Ar-*H*), 7.15-7.17 (m, 2H, Ar-*H*), 7.25-7.29 (m, 2H, Ar-*H*), 7.37-7.39 (m, 1H, Ar-*H*), 8.10 (d, ^{3}J(H-H) ~ 7.6 Hz, 1H, Ar-*H*), 9.75 (br, 1H, N-O*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 21.9, 32.4 (d, *J*(PC) = 8.0 Hz, C(*C*H_3)$_2$), 77.4, 77.6, 107.6, 116.1 (d, ^{3}J(P-C) = 8.0 Hz, PCC*C*), 121.9, 126.3, 128.0 (d, ^{2}J(P-C) = 35.0 Hz, PC(Ph)*C*), 129.3 (d, ^{3}J(P-C) = 6.0 Hz, PC(Ph)C*C*), 131.9, 134.8 (d, ^{3}J(P-C) = 11.0 Hz, PC(Ph)C*C*), 135.1 (d, ^{3}J(P-C) = 5.0 Hz, PC(Ph)C*C*), 137.1 (d, ^{1}J(P-C) = 168.0 Hz, P*C*(Ph)), 142.5, 161.7 (d, *J*(P-C) = 26.0 Hz, PC(Ph)C*C*(O)); ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.7; LC-MS *m/z* 386 $[M+1]^+$; Anal. Calcd. for $C_{20}H_{20}NO_5P$: C, 62.34; H, 5.23; N, 3.63. Found: C, 63.32; H, 5.47; N, 3.61.

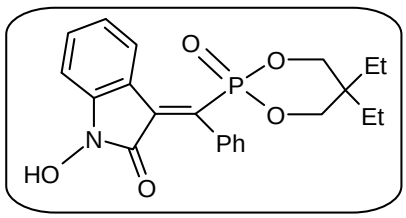
This compound was crystallized from dichloromethane (2 mL). X-ray structural analysis was performed on this sample (Fig. S5).

Compound 17



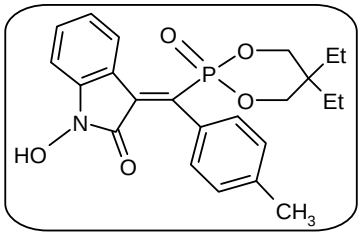
This compound (red color) was obtained by using **1a** (0.63 g, 3.0 mmol) and propargyl alcohol **3b** (0.80 g, 3.0 mmol) and purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Yield 95% by ^{31}P NMR; 0.74 g (isolated, 62%); mp 236–238 ^{o}C; IR (KBr, cm^{-1}) 3100, 2971, 2930, 1726, 1616, 1462, 1323, 1250, 1067; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.63 and 1.19 (2 s, 6H, 2 C*H*$_3$), 2.42 (s, 3H, C*H*$_3$), 3.41-3.44 and 3.71-3.79 (2 m, 4H, 2 OC*H*$_2$), 6.49 (d, *J*(HH) ~ 7.6 Hz, 1H, Ar-*H*), 6.83 (t, *J*(HH) ~ 7.6 Hz, 1H, Ar-*H*), 7.02 (s br, 5H, Ar-*H*), 8.08 (d, *J*(HH) ~ 7.6 Hz, 1H, Ar-*H*), 9.79 (br, 1H, N-O*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.6, 21.6, 22.0, 32.4 (d, *J*(PC) = 8.0 Hz, *C*$(CH_3)_2$), 76.8, 77.1, 107.6, 116.2 (d, *J*(PC) = 8.0 Hz, PCC*C*), 121.9, 126.3, 128.9, 129.1, 129.2, 131.7, 132.0 (d, *J*(PC) = 5.3 Hz), 134.7 (d, *J*(PC) = 11.3 Hz), 137.5 (d, ^{1}*J*(PC) = 167.0 Hz, P*C*), 137.6, 142.5, 161.8 (d, *J*(PC) = 25.8 Hz, PC(Ph)C*C*(O)); ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.9; LC-MS *m/z* 400 $[M+1]^+$; Anal. Calcd. for $C_{21}H_{22}NO_5P$: C, 63.15; H, 5.55; N, 3.51. Found: C, 63.32; H, 5.47; N, 3.61.

Compound 18



This compound **18** (yellow solid) was obtained by using **1b** (0.24 g, 1.2 mmol) and propargyl alcohol **3a** (0.30 g, 1.2 mmol) and purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Yield 94% by ^{31}P NMR; 0.32 g (isolated, 65%); mp 244-248 ^{o}C; IR (KBr, cm^{-1}) 3436, 2965, 1717, 1620, 1468, 1242, 1076, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.69 and 0.87 (2 t, ^{3}J(H-H) = 7.6 Hz, 6H, 2 CH_2CH_3), 1.10 and 1.69 (2 qrt, ^{3}J(H-H) = 7.6 Hz, 4H, 2 CH_2CH_3), 3.61-3.65 and 3.95-4.02 (2 m, 4H, 2 OCH_2), 6.74 (d, ^{3}J(H-H) ~ 8.0 Hz, 1H, Ar-*H*), 7.05-7.08 (m, 1H, Ar-*H*), 7.28-7.48 (m, 6H, Ar-*H*), 7.61 (br, 1H, N-O*H*), 8.51 (d, ^{3}J(H-H) ~ 8.0 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.9, 7.2, 22.8, 23.0, 37.3 (d, ^{3}J(P-C) = 6.0 Hz, CEt_2), 74.3$_6$, 74.4$_4$, 109.5, 120.5 (d, *J*(P-C) = 7.0 Hz), 122.5, 128.0$_7$, 128.1$_6$, 128.1$_8$, 128.2$_1$, 128.3 (d, *J*(P-C) = 10.0 Hz), 131.9, 136.1 (d, *J*(P-C) = 5.0 Hz), 136.6 (d, *J*(P-C) = 11.0 Hz), 138.1 (d, ^{1}J(P-C) = 167.0 Hz, P*C*(Ph)), 142.1 (d, *J*(P-C) = 2.0 Hz), 166.7 (d, *J*(P-C) = 25.0 Hz, *C*(O)); ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.0; LC-MS *m/z* 414 $[M+1]^+$; Anal. Calcd. for $C_{22}H_{24}NO_5P$: C, 63.92; H, 5.85; N, 3.39. Found: C, 63.85; H, 5.79; N, 3.31.

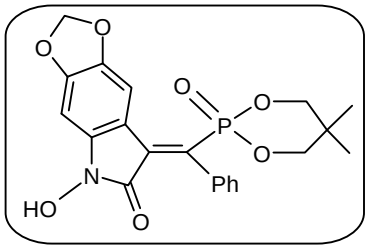
Compound 19



This compound (red color) was obtained by using **1b** (0.20 g, 1.0 mmol) and propargyl alcohol **3b** (0.27 g, 1.0 mmol) and purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Yield 92% by ^{31}P NMR; 0.29 g (isolated,

68%); mp 252–254 ^{o}C; IR (KBr, cm^{-1}) 3254, 2976, 1726, 1620, 1464, 1240, 1074, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.60 and 0.83 (2 t, ^{3}J(H-H) = 7.6 Hz, 6H, 2 CH_2CH_3), 0.97 and 1.64 (2 qrt, ^{3}J(H-H) = 7.6 Hz, 4H, 2 CH_2CH_3), 2.43 (s, 3H, CH_3), 3.46-3.48 and 3.84-3.91 (2 m, 4H, 2 OCH_2), 6.53 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 6.84 (t, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.04 (br, 5H, Ar-*H*), 8.11 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 9.53 (br, 1H, N-O*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 6.8, 7.2, 21.5, 22.8, 22.9, 37.2 (d, ^{3}J(P-C) = 6.2 Hz, $C(CH_3)_2$), 74.7$_6$, 74.8$_3$, 107.5, 116.2, 121.9, 126.3, 128.8, 129.2, 131.7, 132.0, 134.6, 137.6 (d, ^{1}J(P-C) = 166.3 Hz, P*C*), 142.4, 161.8 (d, *J*(P-C) = 25.6 Hz, *C*(=O)); ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.8; LC-MS *m/z* 428 $[M+1]^+$; Anal. Calcd. for $C_{23}H_{26}NO_5P$: C, 64.63; H, 6.13; N, 3.28. Found: C, 64.73; H, 6.22; N, 3.42.

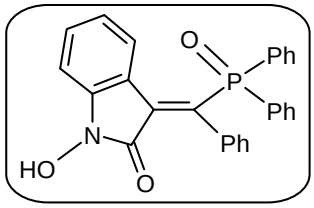
Compound 20



This compound (yellow solid) was obtained by using **1a** (0.17 g, 1.0 mmol) and propargyl alcohol **3c** (0.30 g, 1.0 mmol) and purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Yield 90% by ^{31}P NMR; 0.30 g (isolated, 70%); mp 246-248 ^{o}C; IR (KBr, cm^{-1}) 3256, 2965, 1717, 1624, 1474, 1262, 1059, 1011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.75 and 1.20 (2 s, 6H, 2 CH_3), 3.56-3.60 and 3.85-3.92 (2 m, 4H, 2 OCH_2), 5.97 (s, 2H, OCH_2O), 6.31 (s, 1H, Ar-*H*), 7.17 (br, 1H, N-O*H*), 7.31-7.42 (m, 5H, Ar-*H*), 8.11 (s, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.9, 32.4

(d, ^{3}J(P-C) = 6.8 Hz, C(CH$_3$)$_2$), 76.9, 77.2, 92.5, 101.5, 108.4, 112.6 (d, J(P-C) = 7.3 Hz), 128.0$_0$, 128.0$_2$, 128.3$_4$, 128.3$_6$, 128.5 (d, J(P-C) = 5.9 Hz), 134.5 (d, ^{1}J(P-C) = 169.5 Hz, PC(Ph)), 136.2 (d, J(P-C) = 5.2 Hz), 136.8 (d, J(P-C) = 10.6 Hz), 139.1, 143.3, 150.7, 167.5 (d, J(P-C) = 25.1 Hz, C(O)); ^{31}P NMR (162 MHz, CDCl$_3$) δ 4.9; LC-MS *m/z* 428 [M-1]$^{+}$; Anal. Calcd. for $C_{21}H_{20}NO_7P$: C, 58.74; H, 4.70; N, 3.26. Found: C, 58.61; H, 4.76; N, 3.31.

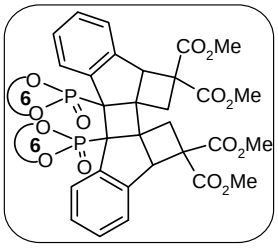
Compound 21



This compound (red color) was obtained by using **1c** (0.77 g, 3.50 mmol) and propargyl alcohol **3a** (0.89 g, 3.50 mmol) and purified by column chromatography using ethyl acetate/hexane (1:1) mixture as the eluent. Yield 94% by ^{31}P NMR; 0.77 g (50%); mp 200-202 ^{o}C; IR (KBr, cm^{-1}) 3056, 2922, 2780, 1721, 1616, 1437, 1159, 1049, 739, 693; ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.42 (d, J(HH) ~ 7.6 Hz, 1H, Ar-H), 6.56 (t, J(HH) ~ 7.6 Hz, 1H, Ar-H), 6.70 (s br, 2H, Ar-H), 6.83-6.89 (m, 4H, Ar-H), 6.94-6.98 (m, 1H, Ar-H), 7.26 (br, 4H, Ar-H), 7.39-7.43 (m, 2H, Ar-H), 7.50 (s br, 3H, Ar-H), 7.71 (d, J(HH) ~ 7.6 Hz, 1H, Ar-H), 11.1 (s br, 1H, N-OH); ^{13}C NMR (100 MHz, CDCl$_3$) δ 107.7, 116.2, 121.4, 126.6, 127.8, 127.9, 128.4, 128.6, 128.8, 129.9, 131.6, 132.2, 132.3, 136.5 (d, J(P-C) = 64.0 Hz, PC(Ph)), 141.7, 142.5, 143.1, 161.7 (d, J(P-C) = 18.4 Hz, C=O); ^{31}P NMR (162 MHz, CDCl$_3$) δ 34.4; LC-MS *m/z* 437 [M]$^{+}$; Anal. Calcd. for $C_{27}H_{20}NO_3P$: C, 74.14; H, 4.61; N, 3.20. Found: C, 74.05; H, 4.71; N, 3.31.

(d) General procedure for the formation of polycyclic compounds 22-33

To a solution of propargyl alcohol **4a** (0.55 g, 2.0 mmol) in THF (20 mL) was added triethylamine (0.20 g, 2.0 mmol) followed by **1a** (0.34 g, 2.0 mmol) at 0 ^{o}C under nitrogen atmosphere and the resulting mixture was stirred at 60 ^{o}C for 4-6 h. Et_3NHCl was filtered and solvent removed by using rotary evaporator. Pure compound **22** was obtained by column chromatography (silica gel 100/200 mesh) by using ethyl acetate/hexane mixture as the eluent. Compounds **23-33** were also prepared similarly by using the appropriate precursors.

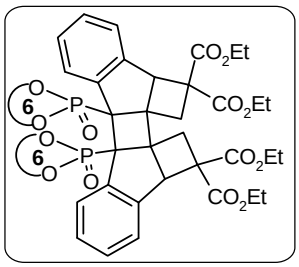


22

This compound (white solid) was purified by column chromatography using ethyl acetate as the eluent. Yield quantitative by ^{31}P NMR; 0.57 g (isolated, 70%); mp 220–222 ^{o}C; IR (KBr, cm^{-1}) 2959, 1730, 1435, 1370, 1265, 1053; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 and 1.04 (2 s, 12H, 2 C(CH_3)$_2$), 2.99 (d, ^{2}J(H-H) = 14.8 Hz, 2H, CH_AH$_B$), 3.31-3.38 (m, 2H, OCH_2), 3.53 (s, 6H, 2 CO_2CH_3), 3.58 (d, ^{2}J(H-H) = 14.8 Hz, 2H, 2 CH$_A$$H_B$), 3.64-371 (m, 2H, OC$H_2$), 3.82 (s, 6H, 2 CO_2CH_3), 3.95-3.98 and 4.05-4.07 (m, 4H, 2 OCH_2), 4.81 (s, 2H, 2 C*H*), 7.19-7.27 (m, 6H, Ar-*H*), 7.70-7.72 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.2, 23.3, 31.4 (d, ^{3}J(P-C) = 7.3 Hz, *C*(CH$_3$)$_2$), 33.0, 51.5, 52.0, 52.8, 53.2$_9$, 53.3$_2$, 63.5 (d, ^{1}J(P-C) = 149.1 Hz, P*C*), 73.6, 74.5, 125.8, 127.1, 128.1, 128.6, 140.2, 145.2 (d, *J*(P-C) = 4.6 Hz), 168.5, 171.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.7; LC-MS *m/z* 813 [M+1]$^{+}$; Anal. Calcd. for $C_{40}H_{46}O_{14}P_2$: C, 59.11; H, 5.70. Found: C, 59.32; H,

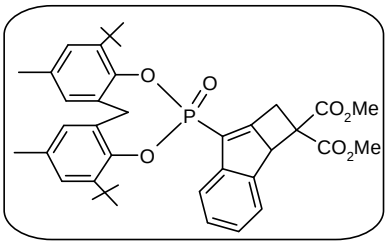
5.63. This compound was crystallized from dichloromethane (2 mL). X-ray structural analysis was performed on this sample (Fig. S6).

Compound 23



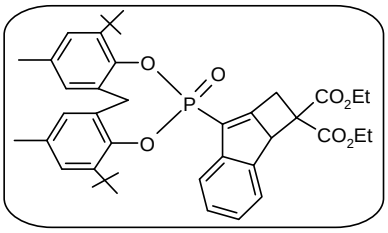
This compound (white solid) was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **4b** (0.60 g, 2.0 mmol) and purified by column chromatography using ethyl acetate as the eluent. Yield quantitative by ^{31}P NMR; 1.17 g (isolated, 67%); mp 134–136 ^{o}C; IR (KBr, cm^{-1}) 2965, 1728, 1472, 1370, 1263, 1071; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 (s, 6H, C(CH_3)$_2$), 1.05-1.09 (m, 12H, 2 $CO_2CH_2CH_3$ + C(CH_3)$_2$), 1.32 (t, ^{3}J(H-H) = 7.4 Hz, 6H, 2 $CO_2CH_2CH_3$), 2.99 (d, ^{2}J(H-H) = 14.8 Hz, 2H, 2 CH_AH$_B$), 3.31-3.38 (m, 2H, 2 OCH_AH$_B$), 3.57 (d, ^{2}J(H-H) = 14.8 Hz, 2H, 2 CH$_A$$H_B$), 3.64-3.71 (m, 2H, 2 OCH$_A$$H_B$), 3.88-4.08 and 4.25-4.29 (2 m, 12H, 4 $CO_2CH_2CH_3$ + 2 OCH_2), 4.83 (s, 2H, 2 CH), 7.23-7.25 (m, 6H, Ar-H), 7.72-7.73 (m, 2H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 14.1, 22.2, 23.4, 31.4 (d, ^{3}J(P-C) = 6.7 Hz, C(CH$_3$)$_2$), 33.0, 51.3, 53.3, 53.4, 61.0, 61.5, 63.6 (d, ^{1}J(P-C) = 149.0 Hz, PC), 73.4, 74.3, 126.0, 127.0, 128.1, 128.4, 140.2, 145.3, 168.3, 171.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.2; LC-MS *m/z* 870 [M+1]$^{+}$; Anal. Calcd. for $C_{44}H_{54}O_{14}P_2$: C, 60.82; H, 6.26. Found: C, 60.75; H, 6.32.

Compound 24



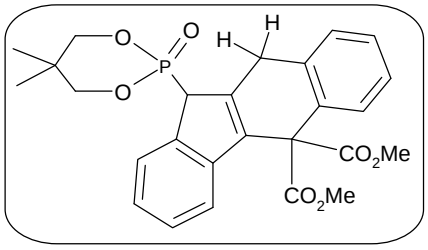
This compound (white solid) was obtained by using **1e** (0.60 g, 2.0 mmol) and propargyl alcohol **4a** (0.55 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (1:4) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.90 g (isolated, 70%); mp 212–214 ^{o}C; IR (KBr, cm^{-1}) 2953, 1730, 1435, 1269, 1208, 1107; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 and 1.33 (2 s, 18H, 2 C(CH_3)$_3$), 2.31 (s, 6H, 2 Ar-CH_3), 3.42 (s, 3H, CO_2CH_3), 3.63 (d, ^{2}J(H-H) ~ 13.2 Hz, 1H, CH_AH$_B$), 3.85-3.92 (m, 4H, CH$_A$$H_B$ + CO_2CH_3), 4.03 and 4.51 (2 d, ^{2}J(H-H) ~ 16.6 Hz, 2H, CH_2), 5.07 (s, 1H, CHC(CO$_2$Me)$_2$), 7.06 and 7.12 (2 br, 4H, Ar-*H*), 7.27-7.39 (m, 2H, Ar-*H*), 7.59-7.61 and 7.96-7.98 (m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 31.1, 31.2, 34.9, 42.5 (d, *J*(P-C) = 3.5 Hz), 48.0 (d, *J*(P-C) = 3.6 Hz), 52.5, 53.7, 64.6 (d, *J*(P-C) = 19.0 Hz), 123.8, 125.1 (d, ^{1}J(P-C) = 215.4 Hz, P*C*), 125.3, 125.8, 127.6, 127.7, 127.9, 128.8 (d, *J*(P-C) = 2.0 Hz), 133.1, 134.5 (d, *J*(P-C) = 1.6 Hz), 134.7 (d, *J*(P-C) = 1.4 Hz), 141.5 (d, *J*(P-C) = 4.7 Hz), 141.8 (d, *J*(P-C) = 4.8 Hz), 144.4 (d, *J*(P-C) = 10.3 Hz), 144.7 (d, *J*(P-C) = 6.4 Hz), 144.8 (d, *J*(P-C) = 7.0 Hz), 147.2, 147.4, 156.4 (d, *J*(P-C) = 11.0 Hz), 165.8, 170.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.9; LC-MS *m/z* 644 [M+1]$^{+}$; Anal. Calcd. for $C_{38}H_{43}O_7P$: C, 71.01; H, 6.74. Found: C, 71.12; H, 6.69. This compound was crystallized from dichloromethane (2 mL). X-ray structural analysis was performed on this sample (Fig. S7).

Compound 25



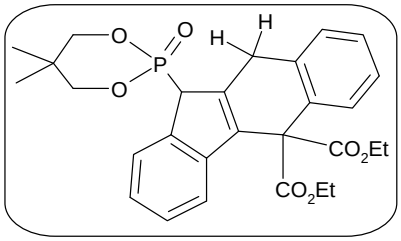
This compound (white solid) was obtained by using **1e** (0.60 g, 2.0 mmol) and propargyl alcohol **4b** (0.60 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (1:4) as the eluent. Yield quantitative by ^{31}P NMR; 0.91 g (isolated, 68%); mp 222–224 ^{o}C; IR (KBr, cm^{-1}) 2959, 2926, 1732, 1263, 1017; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.31 and 1.34 (2 s, 18H, 2 $C(CH_3)_3$), 1.37 (t, ^{3}J(H-H) = 7.2 Hz, 3H, $CO_2CH_2CH_3$), 2.32 and 2.33 (2 s, 6H, 2 Ar-CH_3), 3.64 (d, ^{2}J(H-H) ~ 13.2 Hz, 1H, CH_AH_B), 3.82-3.93 (m, 3H, CH_ACH_B + $CO_2CH_2CH_3$), 4.04-4.08 (m, 1H, CH_ACH_B), 4.36-4.41 (m, 2H, $CO_2CH_2CH_3$), 4.52-4.56 (m, 1H, CH_ACH_B), 5.11 (s, 1H, $CH(CO_2Et)_2$), 7.08 (s, 2H, Ar-*H*), 7.12-7.14 (m, 2H, Ar-*H*), 7.28-7.29 (m, 1H, Ar-*H*), 7.38-7.41 (m, 1H, Ar-*H*), 7.61-7.63 and 7.98-8.00 (2 m, 2H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.1, 21.0, 31.1, 31.2, 34.9, 42.4 (d, *J*(P-C) = 3.7 Hz), 47.8 (d, *J*(P-C) = 3.5 Hz), 61.4, 62.7, 64.5 (d, *J*(P-C) = 19.0 Hz), 123.7, 124.9 (d, *J*(P-C) = 215.1 Hz, P*C*), 125.1, 126.1, 127.6, 127.7, 127.8, 128.8 (d, *J*(P-C) = 2.1 Hz), 133.1$_7$, 133.2$_0$, 134.5, 134.7 (d, *J*(P-C) = 1.4 Hz), 141.5 (d, *J*(P-C) = 4.6 Hz), 141.8 (d, *J*(P-C) = 4.7 Hz), 144.4 (d, *J*(P-C) = 10.3 Hz), 144.7 (d, *J*(P-C) = 3.5 Hz), 144.8 (d, *J*(P-C) = 3.2 Hz), 147.3, 147.5, 156.7 (d, *J*(P-C) = 11.3 Hz), 165.3, 170.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 5.0; LC-MS *m/z* 669 $[M-1]^+$; Anal. Calcd. for $C_{40}H_{47}O_7P$: C, 71.62; H, 7.06. Found: C, 71.46; H, 6.97.

Compound 26



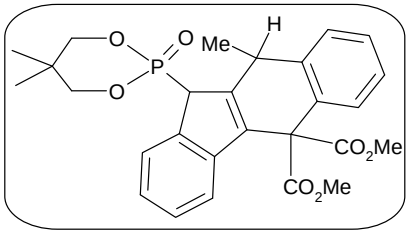
This compound (white solid) was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **5a** (0.70 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (4:1) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.71 g (isolated, 74%); mp 162–164 ^{o}C; IR (KBr, cm^{-1}) 2961, 2926, 1728, 1468, 1287, 1059; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.81 and 0.99 (2 s, 6H, C(C*H*$_3$)$_2$), 3.40-3.46 (m, 1H, OC*H*$_2$), 3.66 (s, 6H, 2 CO_2CH_3), 3.78-3.85 (m, 1H, OC*H*$_2$), 3.95-4.06 (m, 2H, OC*H*$_2$), 4.22-4.38 (m, 3H, PC*H* + OC*H*$_2$), 7.25-7.39 (m, 5H, Ar-*H*), 7.44-7.46 (m, 1H, Ar-*H*), 7.55-7.57 (m, 1H, Ar-*H*), 7.73-7.75 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.6, 30.6, 32.6 (d, ^{3}J(P-C) = 7.4 Hz, *C*$(CH_3)_2$), 50.5 (d, ^{1}J(P-C) = 130.7 Hz, P*C*), 53.0, 53.1, 59.7, 75.5 and 76.5 (2 d, ^{2}J(P-C) ~ 7.0 Hz, O*C*H_2), 120.7, 124.8, 125.0, 126.7, 127.7, 128.2, 128.4, 129.1, 130.9, 133.4, 134.5 (d, *J*(P-C) ~ 7.0 Hz), 137.4 (d, *J*(P-C) = 5.7 Hz), 138.1 (d, *J*(P-C) = 6.7 Hz), 143.6 (d, *J*(P-C) = 5.4 Hz), 169.4, 170.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.9; LC-MS *m/z* 483 $[M+1]^+$; Anal. Calcd. for $C_{26}H_{27}O_7P$: C, 64.73; H, 5.64. Found: C, 64.88; H, 5.71.

Compound 27



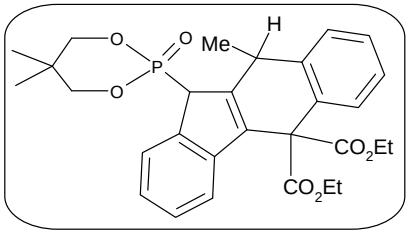
This compound (white solid) was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **5b** (0.76 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (4:1) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.74 g (isolated, 72%); mp 66–68 ^{o}C; IR (KBr, cm^{-1}) 2963, 2926, 1732 1460, 1381, 1217, 1059; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 and 0.94 (2 s, 6H, C(C*H*$_3$)$_2$), 1.02-1.10 (m, 6H, 2 $CO_2CH_2CH_3$), 3.36-3.42 (m, 1H, OC*H*$_2$), 3.76-3.83 (m, 1H, OC*H*$_2$), 3.92-4.36 (m, 9H, PC*H* + C*H*$_2$ + OC*H*$_2$ + 2 $CO_2CH_2CH_3$), 7.21-7.34 (m, 5H, Ar-*H*), 7.47 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.55 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.71 (d, ^{3}J(H-H) = 7.6 Hz, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.7, 13.8, 21.6 (2 *C*H$_3$), 30.7, 32.6 (d, ^{3}J(P-C) = 6.7 Hz, *C*(CH$_3$)$_2$), 50.4 (d, ^{1}J(P-C) = 131.0 Hz, P*C*), 60.0, 61.9, 62.1, 75.3 and 76.2 (2 d, ^{2}J(P-C) ~ 6.8 Hz, O*C*H$_2$), 121.3, 124.7, 124.8 (d, *J*(P-C) = 2.4 Hz), 126.5, 127.3, 128.0, 128.5, 129.0, 132.1 (d, *J*(P-C) = 10.0 Hz), 133.4, 134.8, 137.5, 137.8 (d, *J*(P-C) = 10.1 Hz), 143.7 (d, *J*(P-C) = 4.5 Hz), 168.9, 169.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.4; LC-MS *m/z* 509 [M-1]$^{+}$; Anal. Calcd. for $C_{28}H_{31}O_7P$: C, 65.87; H, 6.12. Found: C, 65.78; H, 6.18.

Compound 28



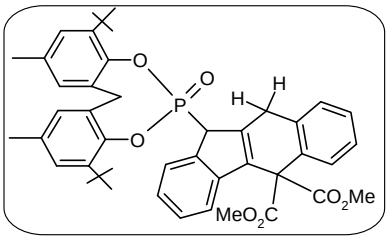
This compound (white solid) was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **5c** (0.73 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (4:1) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.72 g (isolated, 73%); mp 164–166 ^{o}C; IR (KBr, cm^{-1}) 2967, 1736, 1458, 1269, 1229, 1055; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.77 and 0.97 (2 s, 6H, 2 C(CH_3)$_2$), 1.50 (d, ^{3}J(H-H) = 7.2 Hz, 3H, CHCH_3), 3.36-3.48 (m, 1H, OCH_ACH$_B$), 3.64-3.77 (m, 7H, 2 CO_2CH_3 + OCH_ACH$_B$), 4.00-4.07 and 4.17-4.22 (m, 2H, OCH_2), 4.42-4.50 (m, 2H, PCH + CHCH$_3$), 7.26-7.48 (m, 6H, Ar-*H*), 7.54-7.57 (m, 1H, Ar-*H*), 7.77-7.79 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.5, 21.6, 24.9, 32.6 (d, ^{3}J(P-C) = 6.6 Hz), 34.6, 48.6 (d, ^{1}J(P-C) = 130.7 Hz, P*C*), 53.0, 53.1, 59.5, 75.5 and 76.3 (2 d, ^{2}J(P-C) ~ 6.5 Hz, O*C*H$_2$), 120.9, 124.9 (d, *J*(P-C) = 2.0 Hz), 125.1 (d, *J*(P-C) = 2.5 Hz), 126.6, 127.7 (d, *J*(P-C) = 1.3 Hz), 128.1, 128.4, 128.8, 130.5, 133.8 (d, *J*(P-C) = 10.7 Hz), 137.6 (d, *J*(P-C) = 5.8 Hz), 139.6, 143.4 (d, *J*(P-C) = 6.5 Hz), 143.5 (d, *J*(P-C) = 6.0 Hz), 169.4 (d, *J*(P-C) = 2.6 Hz), 170.1 (d, *J*(P-C) = 3.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 18.6; LC-MS *m/z* 497 $[M+1]^+$; Anal. Calcd. for $C_{27}H_{29}O_7P$: C, 65.32; H, 5.89. Found: C, 65.18; H, 5.93.

Compound 29



This compound (white solid) was obtained by using **1a** (0.34 g, 2.0 mmol) and propargyl alcohol **5d** (0.78 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (4:1) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.74 g (isolated, 70%); mp 128–130 ^{o}C; IR (KBr, cm^{-1}) 2961, 2926, 1740, 1466, 1269, 1221, 1059; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.72 and 0.92 (2 s, 6H, 2 C(C*H*$_3$)$_2$), 1.01 and 1.09 (2 t, ^{3}J(H-H) = 7.2 Hz, 6H, 2 $CO_2CH_2CH_3$), 1.47 (d, ^{3}J(H-H) = 7.2 Hz, 3H, CHC*H*$_3$), 3.38-3.45 and 3.68-3.75 (2 m, 2H, OC*H*$_2$), 3.99-4.20 (m, 6H, 2 $CO_2CH_2CH_3$ + OC*H*$_2$), 4.39-4.47 (m, 2H, PC*H* + C*H*CH$_3$), 7.24-7.39 (m, 5H, Ar-*H*), 7.48-7.50 (m, 1H, Ar-*H*), 7.54-7.56 (m, 1H, Ar-*H*), 7.74-7.76 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.6, 25.1, 32.6 (d, ^{3}J(P-C) = 8.0 Hz), 34.6, 48.5 (d, ^{1}J(P-C) = 130.0 Hz, P*C*), 59.8, 61.9, 62.0, 75.3 and 76.1 (2 d, ^{2}J(P-C) ~ 6.8 Hz, O*C*H$_2$), 121.4, 124.8, 125.0, 126.4, 127.3, 128.2, 128.7, 130.8, 134.1 (d, *J*(P-C) = 11.1 Hz), 137.7 (d, *J*(P-C) = 6.1 Hz), 139.6, 143.1, 143.6 (d, *J*(P-C) = 6.1 Hz), 168.9, 169.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.1; LC-MS *m/z* 525 $[M+1]^+$; Anal. Calcd. for $C_{29}H_{33}O_7P$: C, 66.40; H, 6.34. Found: C, 66.25; H, 6.41.

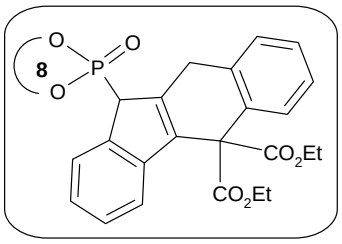
Compound 30



This compound (white solid) was obtained by using **1e** (0.60 g, 2.0 mmol) and propargyl alcohol **5a** (0.70 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield quantitative by ^{31}P NMR; 1.00 g (isolated, 69%); mp 172–174 ^{o}C; IR (KBr, cm^{-1}) 2953, 1734, 1453, 1250, 1202, 920; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.06 and 1.44 (2 s, 18H, 2 C(CH_3)$_3$), 2.29 and 2.34 (2 s, 6H, 2 Ar-CH_3), 3.50 (d, ^{2}J(H-H) = 13.2 Hz, 1H, CH_AH$_B$), 3.67 and 3.69 (2 s, 6H, CO_2CH_3), 4.17 (d, ^{2}J(H-H) = 22.4 Hz, 1H, CH_AH$_B$), 4.36 (dd, $^{2,3}J$(H-H) = 13.2 Hz, 2.4 Hz, 1H, CH$_A$$H_B$), 4.58 (dd, $^{2,3}J$(H-H) = 22.4 Hz, 3.2 Hz, 1H, CH$_A$$H_B$), 4.63 (d, ^{2}J(P-H) = 33.6 Hz, 1H, PC*H*), 7.00 (br, 1H, Ar-*H*), 7.08-7.13 (m, 3H, Ar-*H*), 7.29-7.46 (m, 5H, Ar-*H*), 7.57-7.59 (m, 2H, Ar-*H*), 8.07-8.08 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9$_7$, 21.0$_3$, 30.7, 31.2, 34.6, 35.0, 51.2 (d, ^{1}J(P-C) = 147.5 Hz, P*C*), 53.0, 53.1, 60.1, 121.0, 125.2, 126.0, 126.8, 127.7, 127.8, 127.9, 128.2, 128.6, 128.9, 129.1, 131.1, 133.1 (d, *J*(P-C) = 1.8 Hz), 133.2, 133.4 (d, *J*(P-C) = 2.7 Hz), 134.8 (d, *J*(P-C) = 11.7 Hz), 134.9 (d, *J*(P-C) = 1.4 Hz), 135.1 (d, *J*(P-C) = 1.2 Hz), 137.1, 138.2 (d, *J*(P-C) = 6.9 Hz), 141.3 (d, *J*(P-C) = 4.5 Hz), 141.5 (d, *J*(P-C) = 4.5 Hz), 143.5 (d, *J*(P-C) = 6.9 Hz), 144.5 (d, *J*(P-C) = 8.0 Hz), 144.6 (d, *J*(P-C) = 8.2 Hz), 169.6 (d, *J*(P-C) = 3.9 Hz), 170.1 (d, *J*(P-C) = 1.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.9; LC-MS *m/z* 719 $[M+1]^+$; Anal. Calcd. for $C_{44}H_{47}O_7P$: C, 73.52; H, 6.59. Found: C, 73.45; H, 6.63. This compound was crystallized

from dichloromethane (2 mL). X-ray structural analysis was performed on this sample (Fig S8).

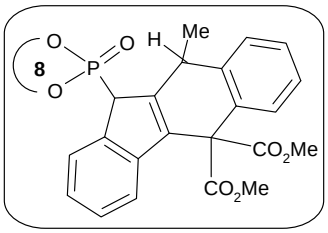
Compound 31



This compound (white solid) was obtained by using **1e** (0.60 g, 2.0 mmol) and propargyl alcohol **5b** (0.76 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield quantitative by ^{31}P NMR; 0.99 g (isolated, 66%); mp 192–194 ^{o}C; IR (KBr, cm^{-1}) 2924, 1734, 1603, 1451, 1229, 1040; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08-1.22 (m, 15H, 2 $CO_2CH_2CH_3$ + $C(CH_3)_3$), 1.38 (s, 9H, $C(CH_3)_3$), 2.26 and 2.30 (2 s, 6H, 2 Ar-CH_3), 3.46 (d, ^{2}J(H-H) = 12.8 Hz, 1H, CH_AH_B), 4.10-4.21 (m, 5H, 2 $CO_2CH_2CH_3$ + CH_AH_B), 4.34 (d, ^{2}J(H-H) = 13.6 Hz, 1H, CH_AH_B), 4.51-4.63 (m, 2H, PC*H* + CH_AH_B), 6.98 (br, 1H, Ar-*H*), 7.06-7.09 (m, 3H, Ar-*H*), 7.27-7.39 (m, 5H, Ar-*H*), 7.55-7.59 (m, 2H, Ar-*H*), 8.03-8.04 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 21.0, 30.8, 31.2, 34.5, 34.6, 35.0, 51.2 (d, ^{1}J(P-C) = 147.5 Hz, P*C*), 60.4, 62.1 and 62.2 (2 d, *J*(P-C) ~ 3.0 Hz), 121.7, 125.1, 125.6, 126.6, 127.3, 127.8, 127.9, 128.0, 128.6, 128.8, 129.0, 131.4 (d, *J*(P-C) = 4.3 Hz), 133.2 (d, *J*(P-C) = 7.2 Hz), 133.4, 134.9 (d, *J*(P-C) = 10.3 Hz), 135.2, 137.3, 138.1 (d, *J*(P-C) = 6.6 Hz), 141.3, 141.5, 143.5 (d, *J*(P-C) = 6.9 Hz), 144.6, 169.0, 169.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ

15.9; LC-MS *m/z* 748 $[M+1]^+$; Anal. Calcd. for $C_{46}H_{51}O_7P$: C, 73.97; H, 6.88. Found: C, 73.85; H, 6.81.

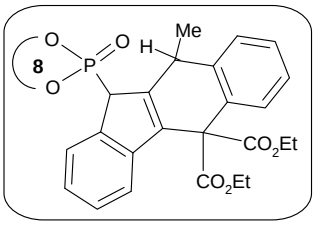
Compound 32



This compound (white solid) was obtained by using **1e** (0.60 g, 2.0 mmol) and propargyl alcohol **5c** (0.73 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield quantitative by ^{31}P NMR; 1.00 g (isolated, 68%); mp 228–230 ^oC; IR (KBr, cm^{-1}) 2955, 2924, 1736, 1435, 1260, 1206, 926; ^1H NMR (400 MHz, $CDCl_3$) δ 1.19 and 1.48 (2 s, 18H, 2 $C(CH_3)_3$), 2.22-2.35 (m, 9H, 2 Ar-CH_3 + $CHCH_3$), 3.30 (d, ^2J(H-H) = 13.6 Hz, 1H, CH_AH_B), 3.44 (s, 3H, CO_2CH_3), 4.06 (br, 4H, CO_2CH_3 + CH_AH_B), 5.11 (d, ^2J(P-H) = 27.6 Hz, 1H, PC*H*), 5.25 (br, 1H, $CHCH_3$), 6.92-7.40 (m, 11H, Ar-*H*), 7.85-7.87 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.6 (d, *J*(P-C) = 3.1 Hz, $CHCH_3$), 20.9, 21.0, 30.6, 31.3, 33.9, 34.8, 34.9, 48.2 (d, ^1J(P-C) = 148.2 Hz, P*C*), 51.4 (d, *J*(P-C) = 2.4 Hz), 52.6, 53.2, 63.7, 124.1, 124.4 (d, *J*(P-C) = 2.5 Hz), 126.1, 126.5, 127.4, 127.5, 127.6, 128.0 (d, *J*(P-C) = 3.2 Hz), 128.5 (d, *J*(P-C) = 3.9 Hz), 128.7, 130.9 (d, *J*(P-C) = 10.8 Hz), 132.1 (d, *J*(P-C) = 9.4 Hz), 133.1 (d, *J*(P-C) = 2.3 Hz), 133.4 (d, *J*(P-C) = 2.6 Hz), 133.7 (d, *J*(P-C) = 2.7 Hz), 134.6, 134.7 (d, *J*(P-C) = 10.3 Hz), 137.0 (d, *J*(P-C) = 5.0 Hz), 138.3 (d, *J*(P-C) = 8.9 Hz), 141.0_8 (d, *J*(P-C) = 2.0 Hz), 141.1_3 (d, *J*(P-C) = 2.5 Hz), 142.0 (d, *J*(P-C) = 8.1 Hz),

144.6, 144.7, 144.8, 144.9, 168.9, 172.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.9; LC-MS *m/z* 732 $[M]^+$; Anal. Calcd. for $C_{45}H_{49}O_7P$: C, 73.75; H, 6.74. Found: C, 73.62; H, 6.81.

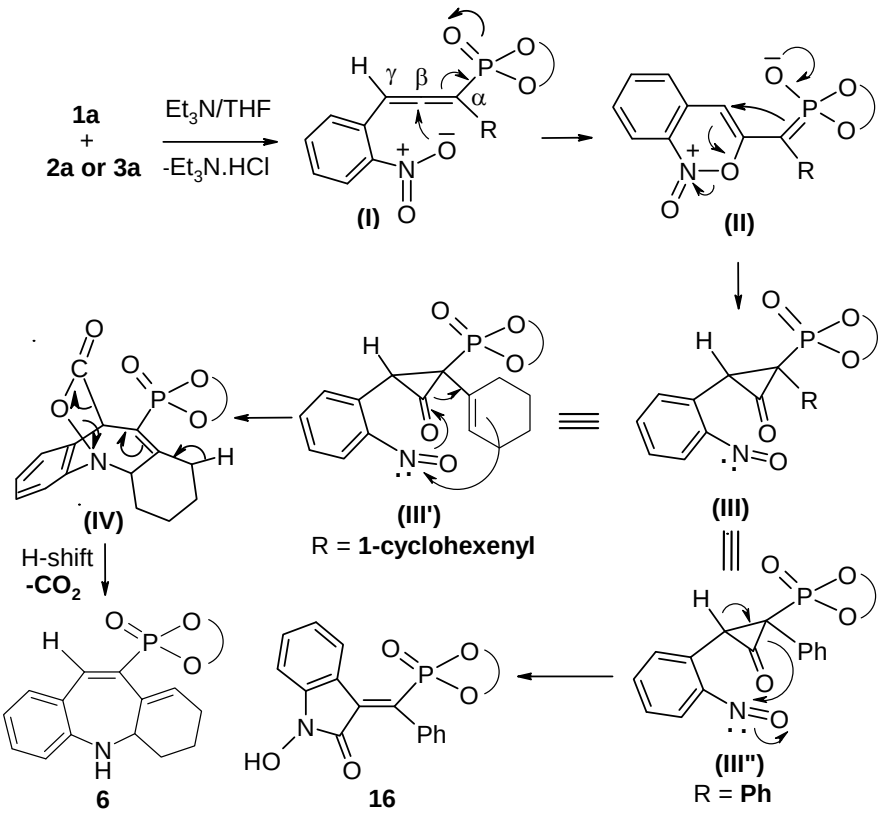
Compound 33



This compound (white solid) was obtained by using **1e** (0.60 g, 2.0 mmol) and propargyl alcohol **5d** (0.78 g, 2.0 mmol) and purified by column chromatography using ethyl acetate/hexane (3:7) mixture as the eluent. Yield quantitative by ^{31}P NMR; 1.02 g (isolated, 67%); mp 228–230 ^{o}C; IR (KBr, cm^{-1}) 2961, 1734, 1460, 1263, 1206, 930; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.83 (t, ^3J(H-H) ~ 7.2 Hz, 3H, $CO_2CH_2CH_3$), 1.19 (s, 9H, $C(CH_3)_3$), 1.41-1.51 (m, 12H, $CO_2CH_2CH_3$ + $C(CH_3)_3$), 2.22-2.34 (m, 9H, 2 Ar-CH_3 + $CHCH_3$), 3.30 (d, ^2J(H-H) ~ 13.2 Hz, 1H, CH_AH_B), 3.81-3.92 (m, 2H, $CO_2CH_2CH_3$), 4.08 (d, ^2J(H-H) ~ 13.2 Hz, 1H, CH_AH_B), 4.53-4.56 (m, 2H, $CO_2CH_2CH_3$), 5.07 (d, ^2J(P-H) = 27.2 Hz, 1H, PC*H*), 5.26 (br, 1H, $CHCH_3$), 6.92-7.39 (m, 11H, Ar-*H*), 7.82-7.84 (m, 1H, Ar-*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.2, 17.6, 20.9, 21.0, 30.7, 31.2, 33.9, 34.8, 34.9, 48.2 (d, ^1J(P-C) = 147.7 Hz, P*C*), 51.2, 61.0, 62.3, 63.7, 124.1, 124.9, 126.0, 126.2, 127.0, 127.4, 127.6, 127.8, 128.4, 128.6 (d, *J*(P-C) = 10.5 Hz), 133.5, 133.7, 134.6, 134.7, 137.1, 141.1, 142.3, 144.6, 144.7, 144.8, 168.5, 171.8; ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.9; LC-MS *m/z* 760 $[M]^+$; Anal. Calcd. for $C_{47}H_{53}O_7P$: C, 74.19; H, 7.02. Found: C, 74.31; H, 7.08.

(3) Possible pathway for the formation of compounds 6 and 16

A possible (speculative) pathway for the formation of compounds **6** and **16** is depicted in Scheme S1. The allene intermediate **I** could lead to the six membered heterocycle **II** via nucleophilic attack of oxygen nucleophile at *β*-carbon of allene,[5] followed by the N-O bond cleavage[6] affording the intermediate **III**. When R = cyclohexenyl (**III'**), the bicyclic species **IV** is obtained. This undergoes proton migration and subsequent ***CO_2*** elimination affording the final product **6**. Compounds **8** and **10-14** are similarly formed. When R = phenyl, the intermediate **III"** is leads to **16** via cyclopropanone ring cleavage followed by C(O)-N bond formation. Heterocycles **17-21** are similar to compound **16**. Evidence for intermediate **IV** comes from the structural characterization of **7** and **9** (see Fig. .



Scheme S1

(4) X-ray data and Molecular structures of compounds 6-7, 9, 15-16, 22, 24 and 30

(a) X-ray data of compounds 6-7, 9, 15-16, 22, 24 and 30

X-ray data for compounds **6**.$CHCl_3$, **7**, **9**, **15**, **16**.CH_2Cl_2, **22**.CH_2Cl_2, **24** and **30**.$2CH_3CN$ were collected on Bruker AXS SMART or OXFORD diffractometer using Mo-K_α (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[7] CCDC numbers are CCDC 804470 - 804477.

Crystal data

6.$CHCl_3$: $C_{20}H_{25}Cl_3NO_3P$ M = 464.73, Monoclinic, Space group *P2(1)/c,* a = 10.0813(12), b = 10.0455(12), c = 22.053(3) Å, β = 98.363(2)°, V = 2209.6(5) Å^3, Z = 4, μ = 0.508 mm^{-1}, data/restraints/parameters: 3871/0/255, R indices ($I > 2\sigma(I)$): R1 = 0.0689, *wR*2 (all data) = 0.1651. CCDC no. 804470.

7: $C_{20}H_{23}ClNO_5P$, M = 423.81, Monoclinic, Space group *P2(1)/c,* a = 10.733(4), b = 9.887(3), c = 19.893(12) Å, β = 109.33(4)°, V = 1992.0(15) Å^3, Z = 4, μ = 0.304 mm^{-1}, data/restraints/parameters: 3507/0/254, R indices ($I > 2\sigma(I)$): R1 = 0.0719, *wR*2 (all data) = 0.1616. CCDC no. 804471.

9: $C_{27}H_{22}NO_5P$, M = 471.43, Monoclinic, Space group *P2(1)/c,* a = 10.1245(12), b = 10.1712(12), c = 24.0509(19) Å, β = 114.460(4)°, V = 2254.4(4) Å^3, Z = 4, μ = 0.163 mm^{-1}, data/restraints/parameters: 3950/0/307, R indices ($I > 2\sigma(I)$): R1 = 0.0386, *wR*2 (all data) = 0.1030. CCDC no. 804472.

15: $C_{26}H_{26}NO_2P$, M = 415.45, Monoclinic, Space group *P2(1)/c,* a = 8.973(4), b = 15.480(6), c = 17.629(6) Å, β = 117.171(16) °, V = 2178.5(15) Å^3, Z = 4, μ = 0.149 mm^{-1}, data/restraints/parameters: 3829/0/ 271, R indices ($I > 2\sigma(I)$): R1 = 0.0479, *wR*2 (all data) = 0.1029. CCDC no. 804473.

16.CH_2Cl_2: $C_{41}H_{42}Cl_2N_2O_{10}P_2$, M = 855.61, Monoclinic, Space group *P2(1)/c,* a = 23.992(9), b = 14.574(6), c = 11.636(5) Å, β = 92.284(6)°, V = 4065(3) Å^3, Z = 4, μ = 0.299 mm^{-1}, data/restraints/parameters: 7050/0/520, R indices ($I > 2\sigma(I)$): R1 = 0.0585, *wR*2 (all data) = 0.1348. CCDC no. 804474.

22.CH_2Cl_2: $C_{41}H_{48}Cl_2O_{14}P_2$, M = 897.63, Orthorombic, Space group *P2(1)2(1)2(1),* a = 11.3587(9), b = 18.5030(13), c = 20.2698(12) Å, V = 4260.1(5) Å^3, Z = 4, μ = 0.294 mm^{-1}, data/restraints/parameters: 7420/0/540, R indices ($I > 2\sigma(I)$): R1 = 0.0467, *wR*2 (all data) = 0.1190. CCDC no. 804475.

24: $C_{38}H_{43}O_7P$, M = 642.69, Monoclinic, Space group *P2(1)/c,* a = 13.1399(11), b = 11.3816(10), c = 24.2961(17) Å, β = 114.555(4)°, V = 3304.9(5) Å^3, Z = 4, μ = 0.133 mm^{-1}, data/restraints/parameters: 5831/0/425, R indices ($I > 2\sigma(I)$): R1 = 0.0827, *wR*2 (all data) = 0.1925. CCDC no. 804476.

30.$2CH_3CN$: $C_{48}H_{53}N_2O_7P$, M = 800.89, Triclinic, Space group *P-1,* a = 9.7058(15), b = 14.241(2), c = 16.630(2) Å, α = 69.432(14), β = 84.421(13), γ = 76.489(14)°, V = 2092.2(5) Å^3, Z = 2, μ = 0.121 mm^{-1}, data/restraints/parameters: 7245/0/535, R indices ($I > 2\sigma(I)$): R1 = 0.0419, *wR*2 (all data) = 0.0760. CCDC no. 804477.

(b) Molecular structures of compounds 6.$CHCl_3$, **7, 9, 15, 16**.CH_2Cl_2, **22**.CH_2Cl_2, **24 and 30.**$2CH_3CN$

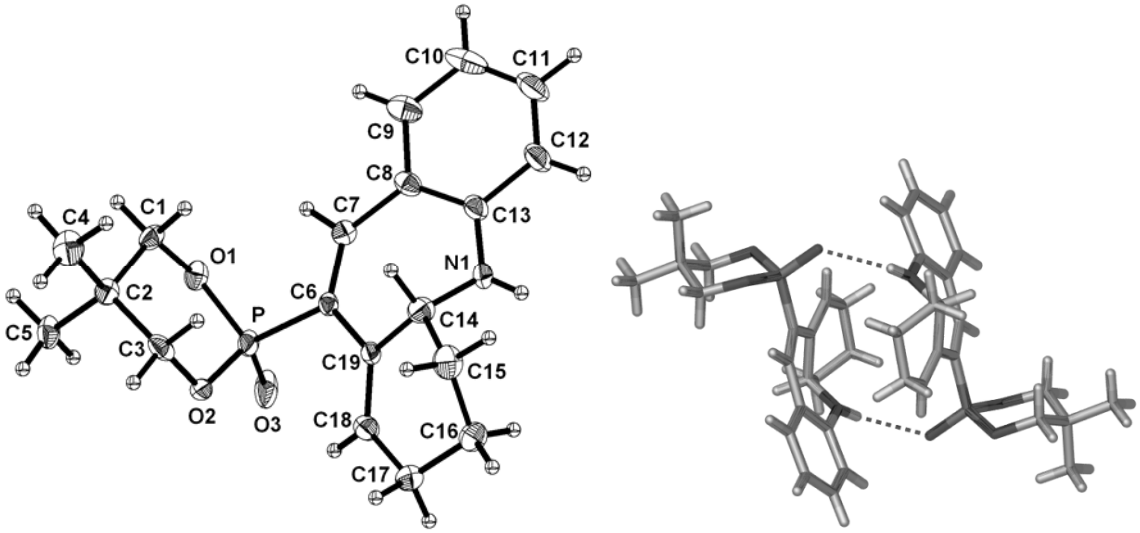


Figure S1. ORTEP diagram of compound **6**.$CHCl_3$ (left). Solvent molecule is omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: P-C(6) 1.795(3), N(1)-C(14) 1.430(5), C(6)-C(7) 1.344(5), C(7)-C(8) 1.457(5). Dimeric structural unit of compound **6** (right). Hydrogen bond parameters: N(1)-H(1D)…O(3) 0.77, 2.32, 2.997(4) Å, 147.8°; symmetry code: 1 -x, -y+2, -z.

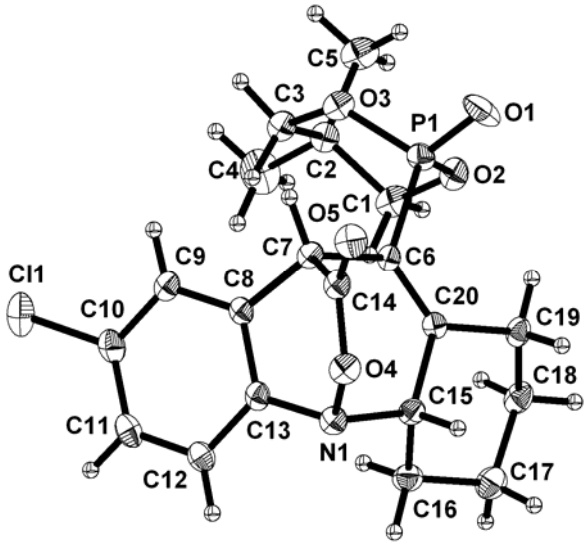


Figure S2: ORTEP diagram of compound **7**. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.822(4), N(1)-O(4) 1.475(5), N(1)-C(15) 1.478(5), O(4)-C(14) 1.362(5), O(5)-C(14) 1.185(6), C(6)-C(7) 1.549(5), C(6)-C(20) 1.318(5), C(7)-C(8) 1.513(6), C(7)-C(14) 1.522(7), C(15)-C(20) 1.533(5), C(19)-C(20) 1.514(6).

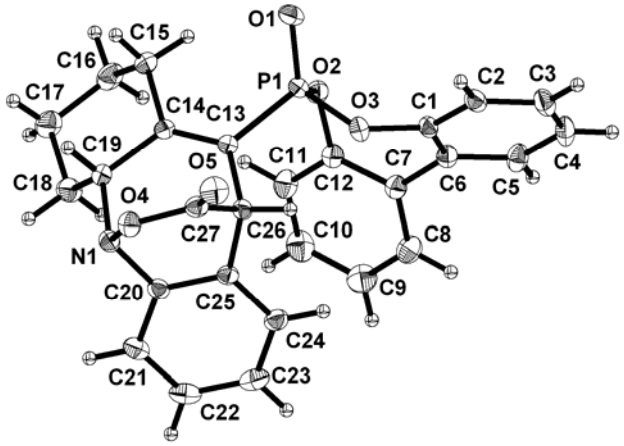


Figure S3: ORTEP diagram of compound **9**. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(13) 1.7946(16), N(1)-O(5) 1.4732(18), N(1)-C(19) 1.472(2), O(4)-C(27) 1.195(2), O(5)-C(27) 1.360(2), C(13)-C(14) 1.339(2), C(13)-C(26) 1.536(2), C(14)-C(15) 1.511(2), C(14)-C(19) 1.518(2), C(25)-C(26) 1.503(2), C(26)-C(27) 1.505(2).

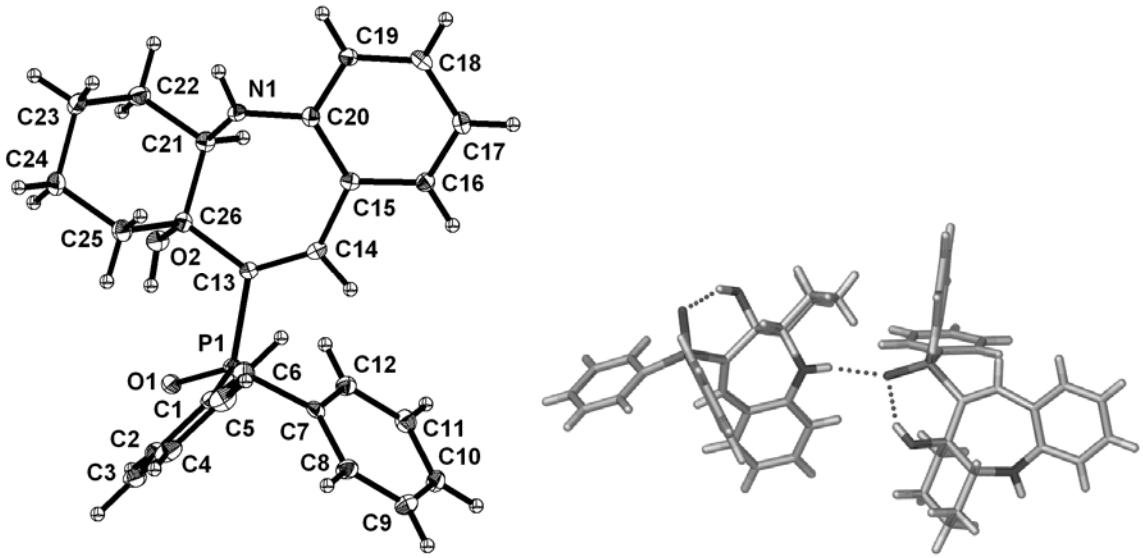


Figure S4. ORTEP diagram of compound **15** (left) and H-bonding drawing (right). Selected bond lengths [Å] with esd's in parentheses: P(1)-C(13) 1.799(2), O(2)-C(26) 1.439(2), N(1)-C(21) 1.462(3), C(13)-C(14) 1.345(3), C(25)-C(26) 1.522(3). Hydrogen bonding parameters: O(2) H(2B)…O(1) 0.84, 1.94, 2.705(2) Å, 150.8°. N(1) H(1A)…O(1') 0.85, 2.09, 2.925(2) Å, 166.8°; symmetry code: -x+1, y-1/2, -z+1/2.

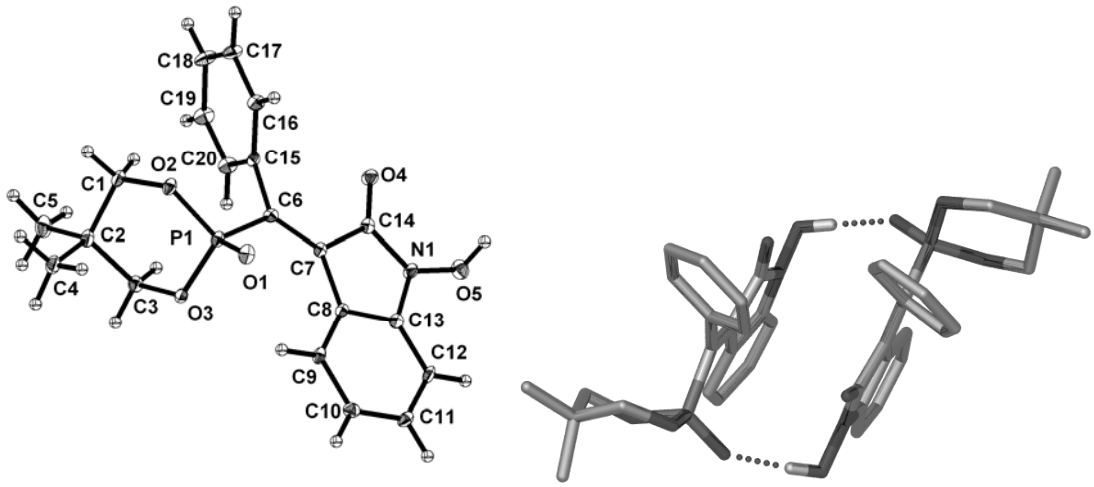


Figure S5. ORTEP diagram of compound **16**.CH_2Cl_2 (left) and H-bonding picture (right). Two molecules are present in the asymmetric unit but only one is shown. Solvent molecule is omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: P(1)-O(1) 1.460(3), P(1)-C(6) 1.812(3), O(4)-C(14) 1.218(4), O(5)-N(1) 1.380(4), N(1)-C(13) 1.387(4), N(1)-C14 1.362(5), C(6)-C(7) 1.348(5), C(7)-C(8) 1.477(5), C(7)-C(14) 1.522(5). Hydrogen bond parameters: O(5)-H(5D)...O(6) 0.84, 1.80, 2.635(4) Å, 174.9°; O(10)-H(10B)...O(1) 0.84, 1.77, 2.596(4) Å, 168.3°.

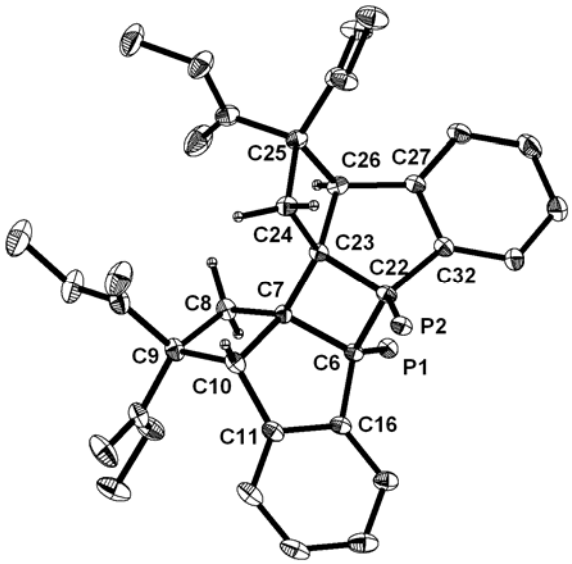


Figure S6. ORTEP diagram of compound **22**.CH_2Cl_2. Solvent molecule and cyclohexyl moieties are omitted for clarity. Only selected atoms are labeled. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(6) 1.812(3), P(2)-C(22) 1.820(3), C(6)-C(7) 1.559(4), C(6)-C(22) 1.625(4), C(7)-C(8) 1.553(4), C(7)-C(10) 1.557(4), C(7)-C(23) 1.530(4), C(8)-C(9) 1.554(4), C(9)-C(10) 1.573(5), C(22)-C(23) 1.553(5), C(23)-C(24) 1.556(4), C(23)-C(26) 1.559(4), C(24)-C(25) 1.565(5), C(25)-C(26) 1.578(4).

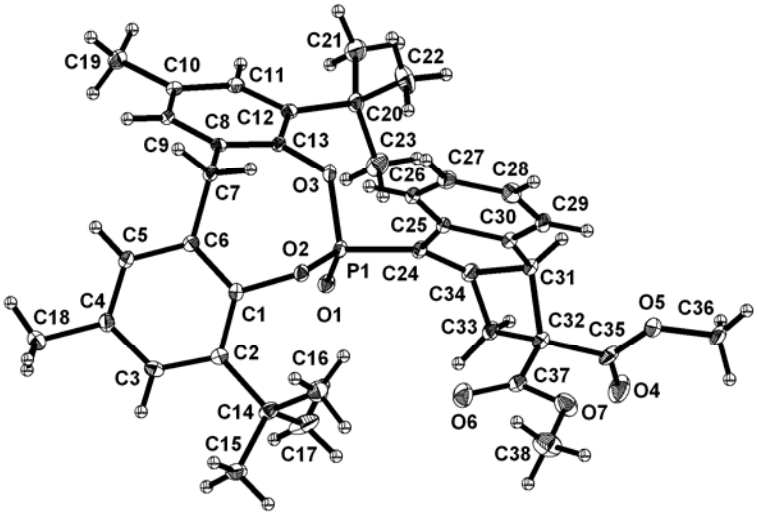


Fig. S7. ORTEP diagram of compound **24**. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(24) 1.764(4), C(24)-C(34) 1.349(5), C(31)-C(32) 1.596(5), C(31)-C(34) 1.483(5), C(32)-C(33) 1.572(6), C(32)-C(33) 1.572(6), C(33)-C(34) 1.501(5).

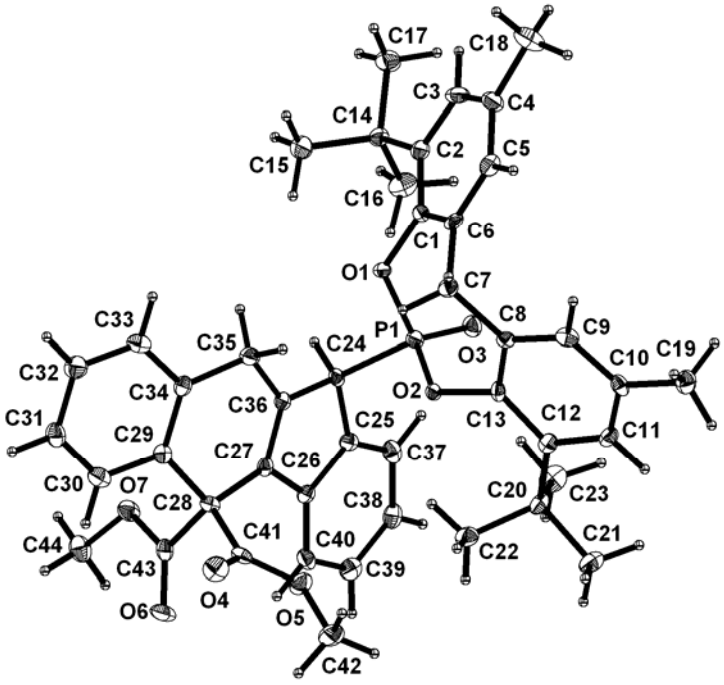


Fig. S8. ORTEP diagram of compound **30**.2CH_3CN. Solvent molecules are omitted for clarity. Selected bond lengths [Å] with esd's in parentheses: P(1)-C(24) 1.804(2), C(24)-C(36) 1.512(3), C(27)-C(36) 1.343(3), C(27)-C(28) 1.517(3), C(28)-C(29) 1.534(3).

(5) Copies of ^{1}H and ^{13}C NMR Spectra

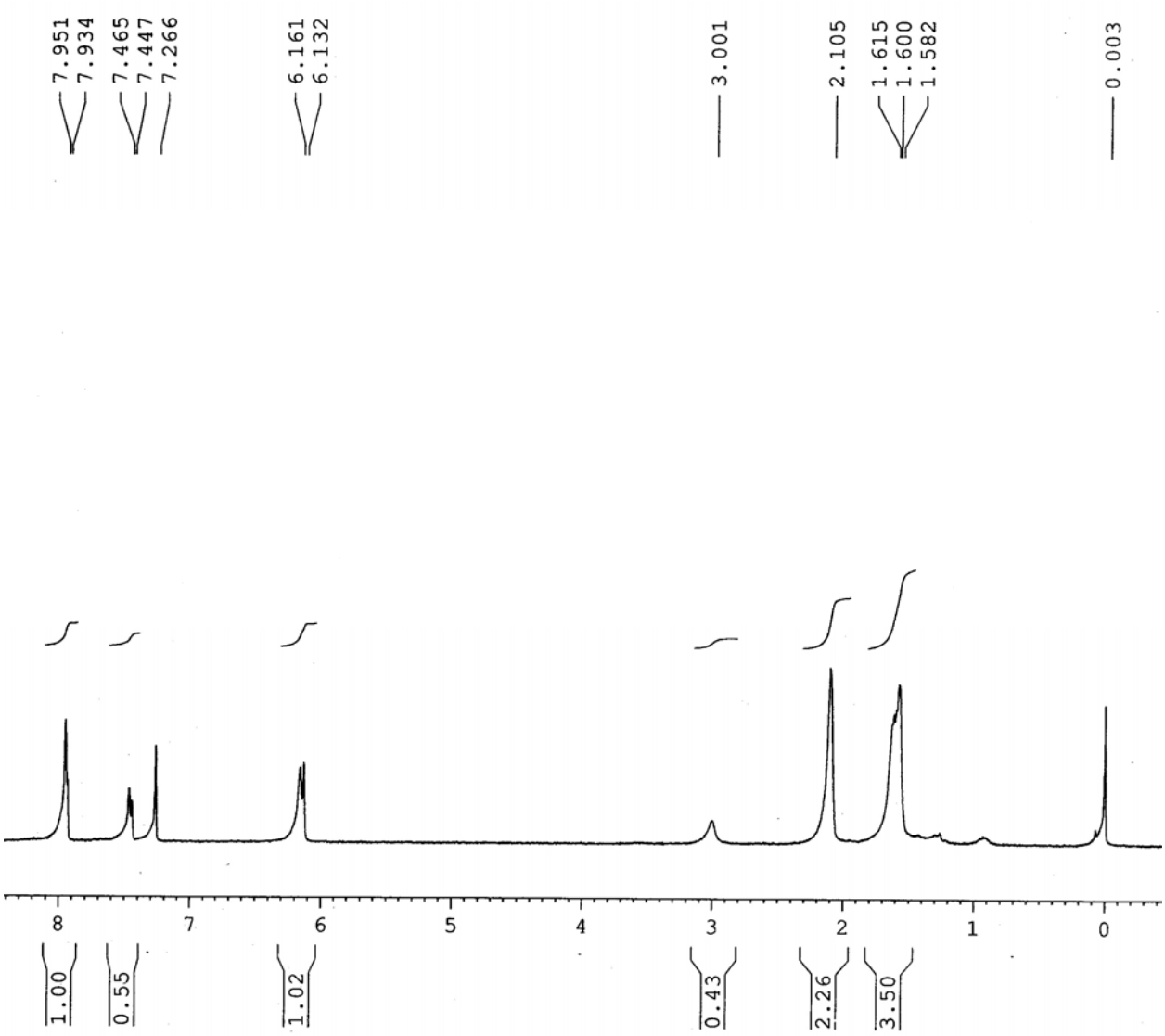


Fig. S9: ^{1}H NMR spectrum of compound **2b**

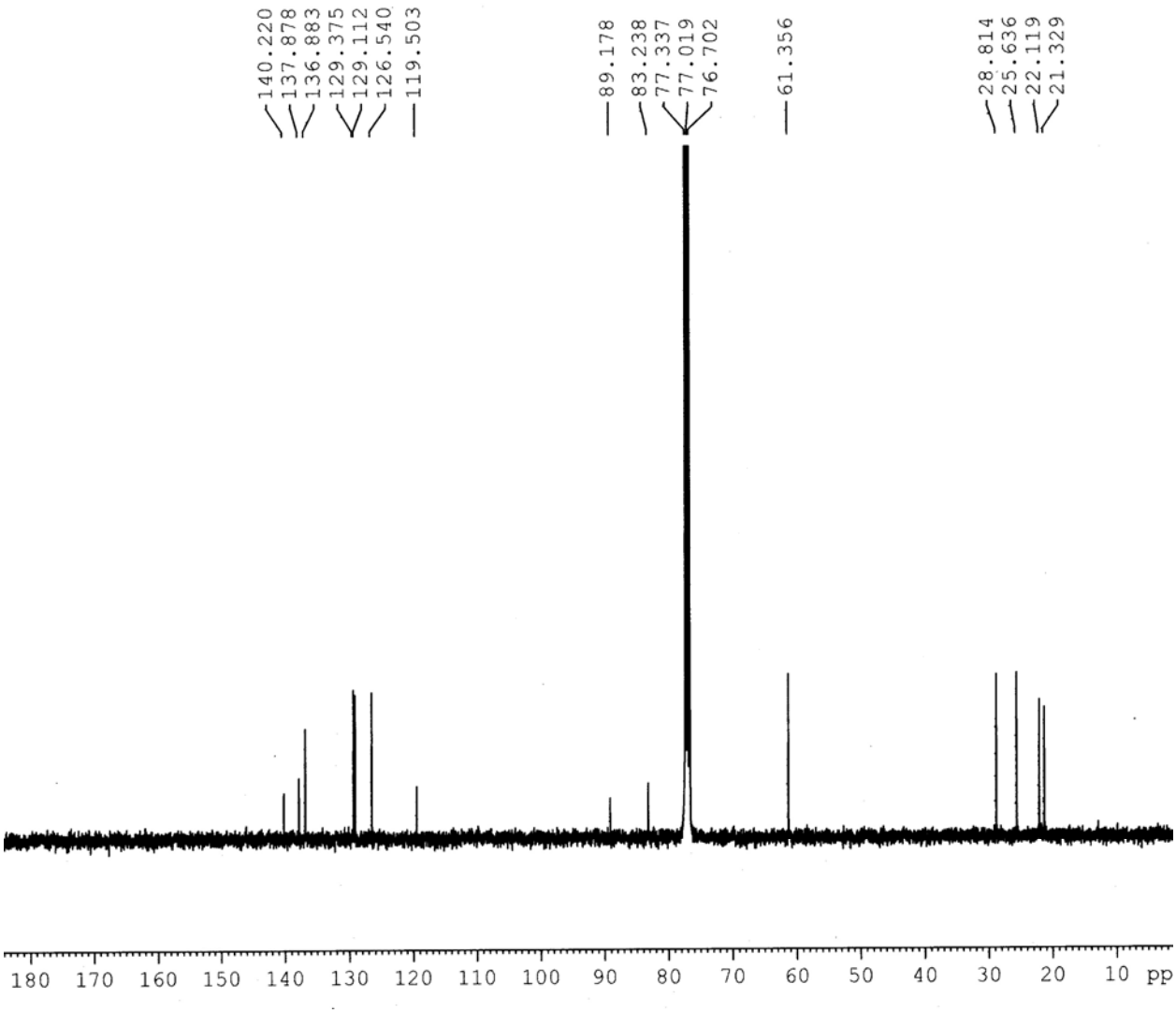


Fig. S10: ^{13}C NMR spectrum of compound **2b**

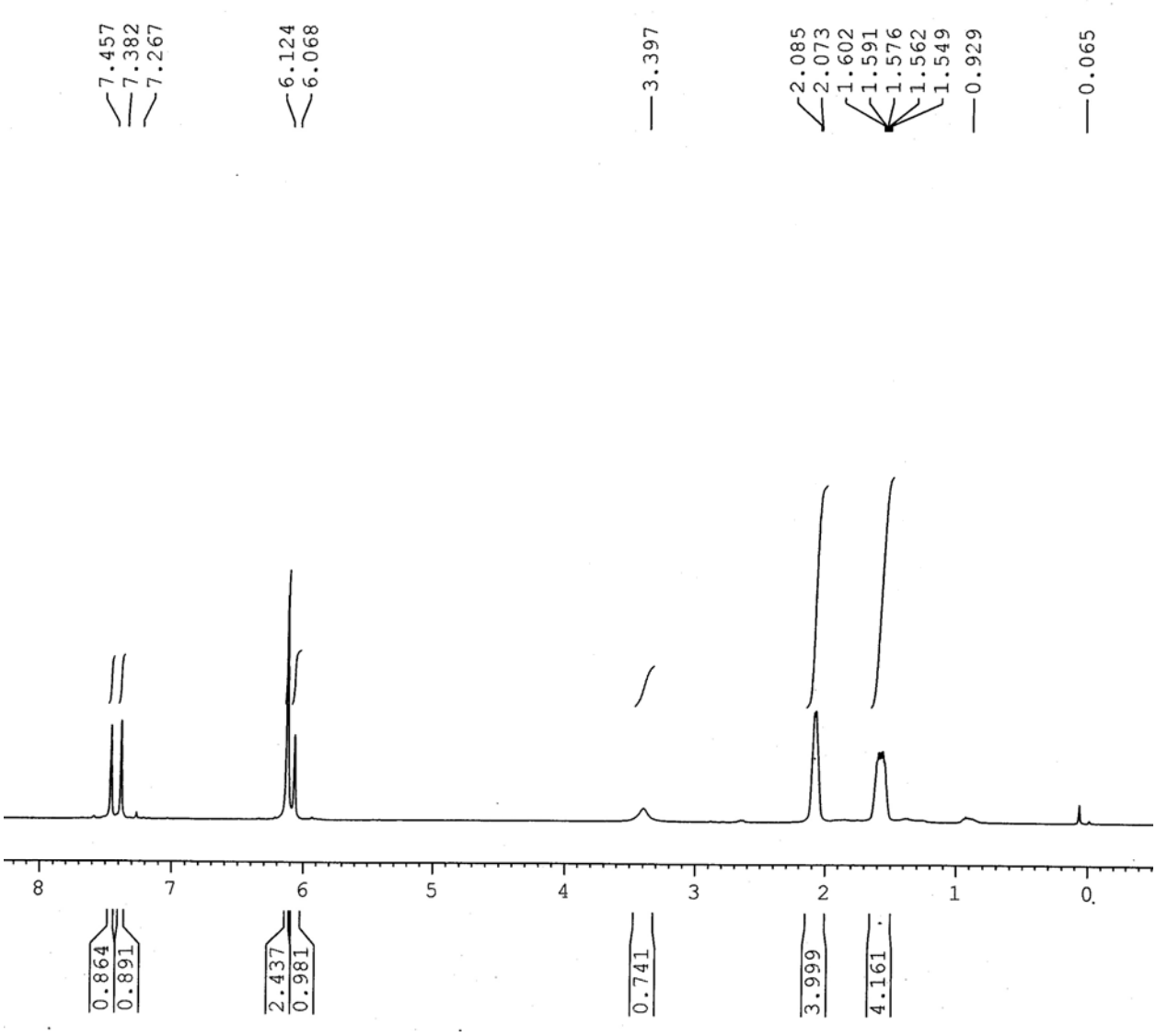


Fig. S11: ^{1}H NMR spectrum of compound **2c**

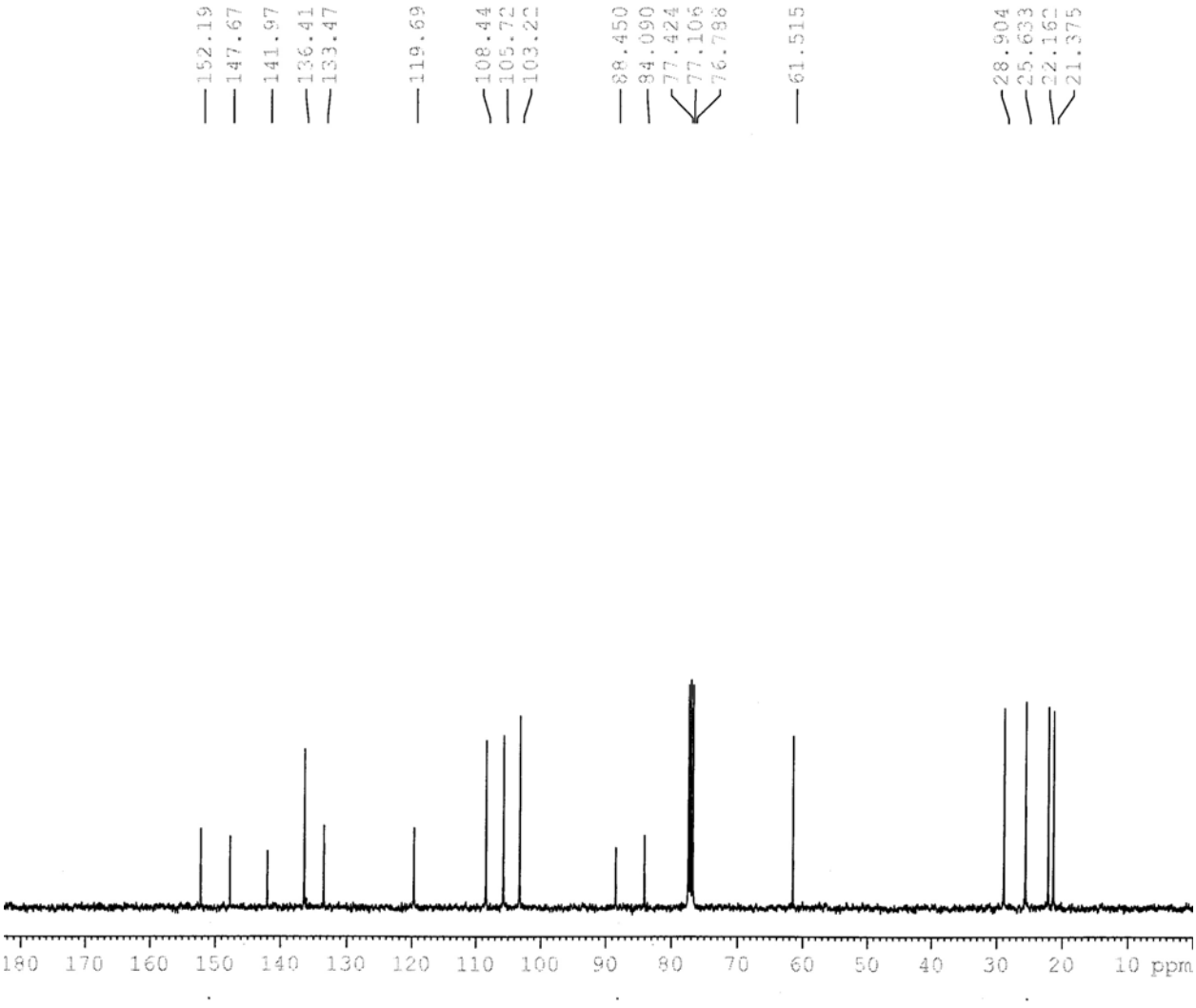


Fig. S12: ^{13}C NMR spectrum of compound **2c**

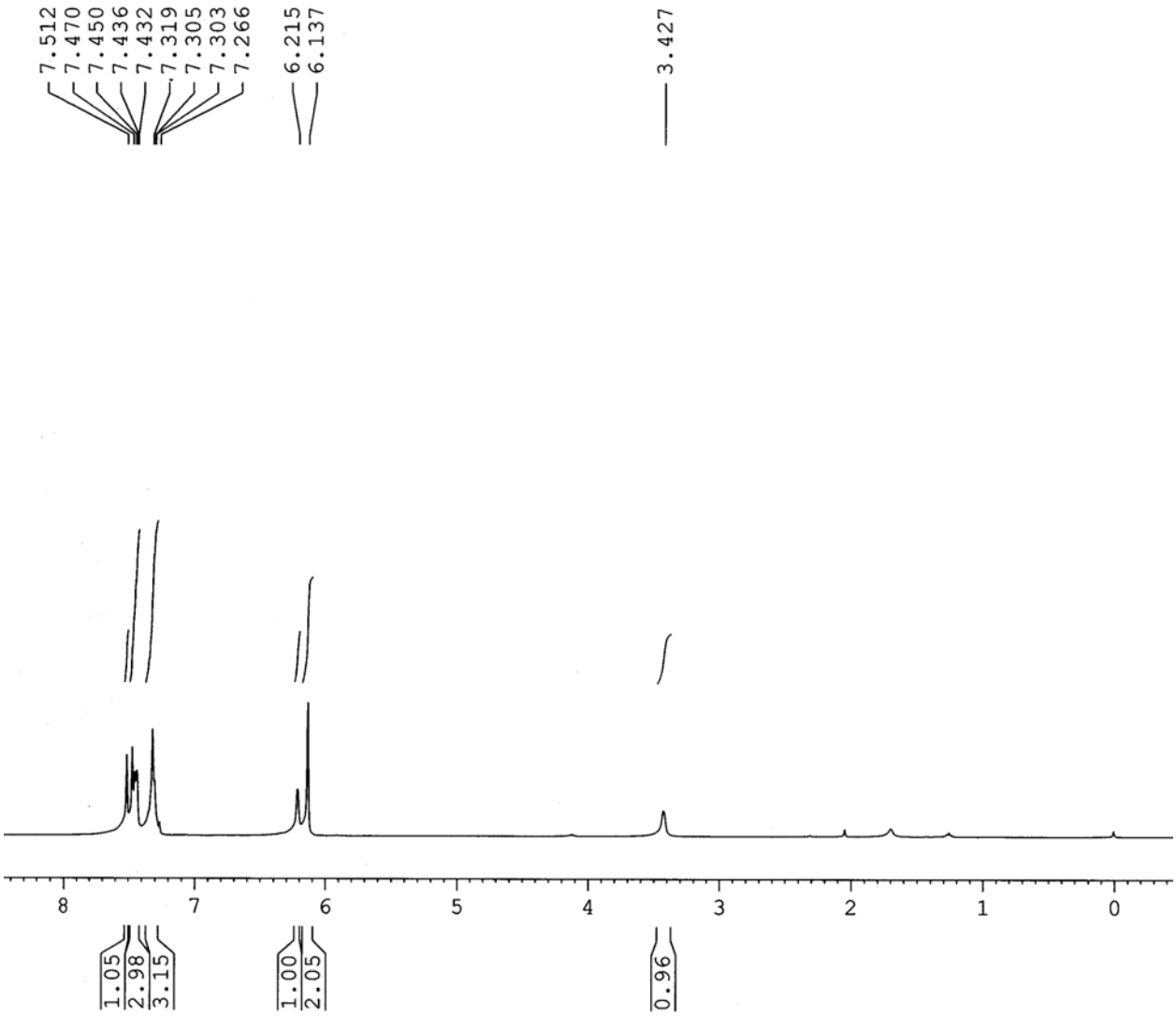


Fig. S13: ^{1}H NMR spectrum of compound **3c**

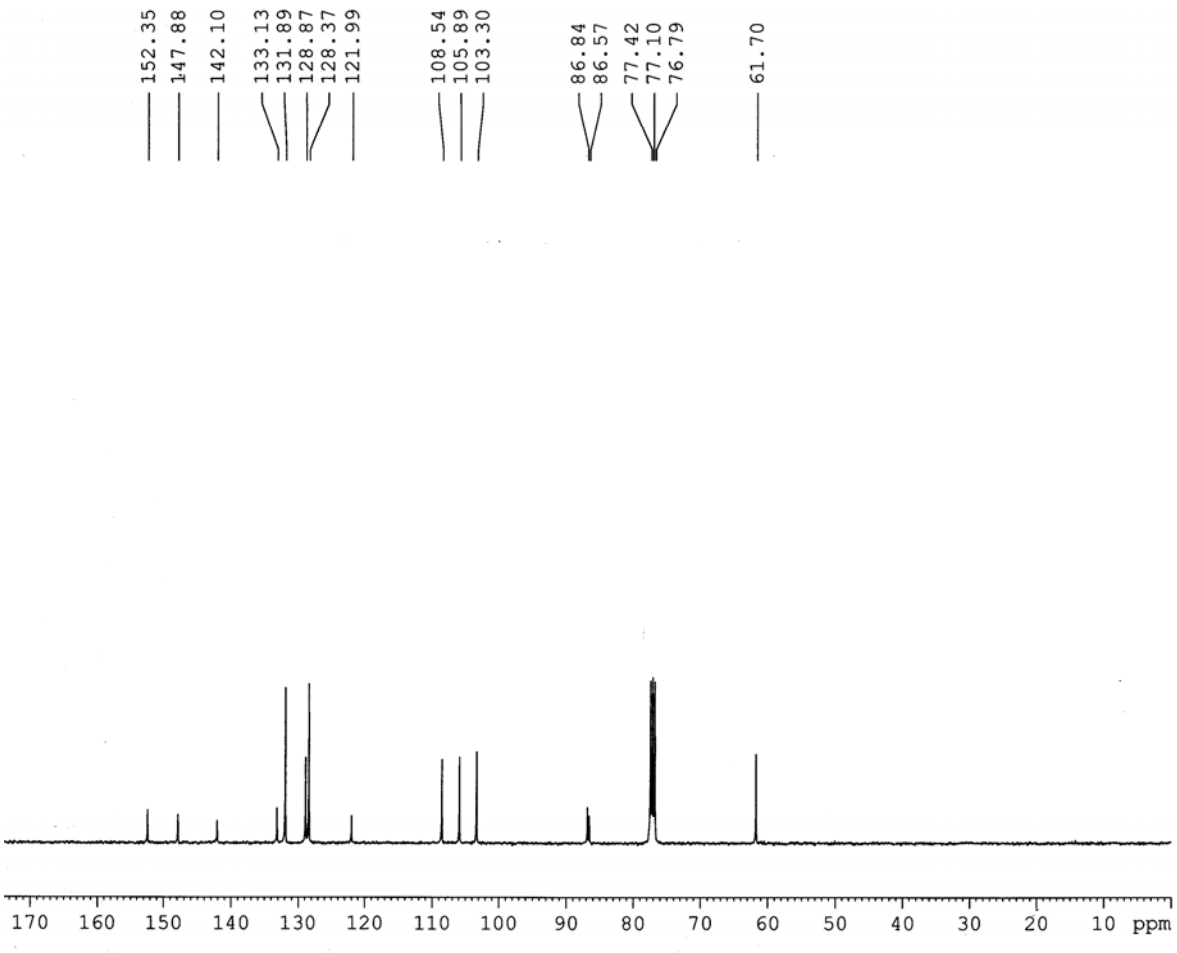


Fig. S14: ^{13}C NMR spectrum of compound **3c**

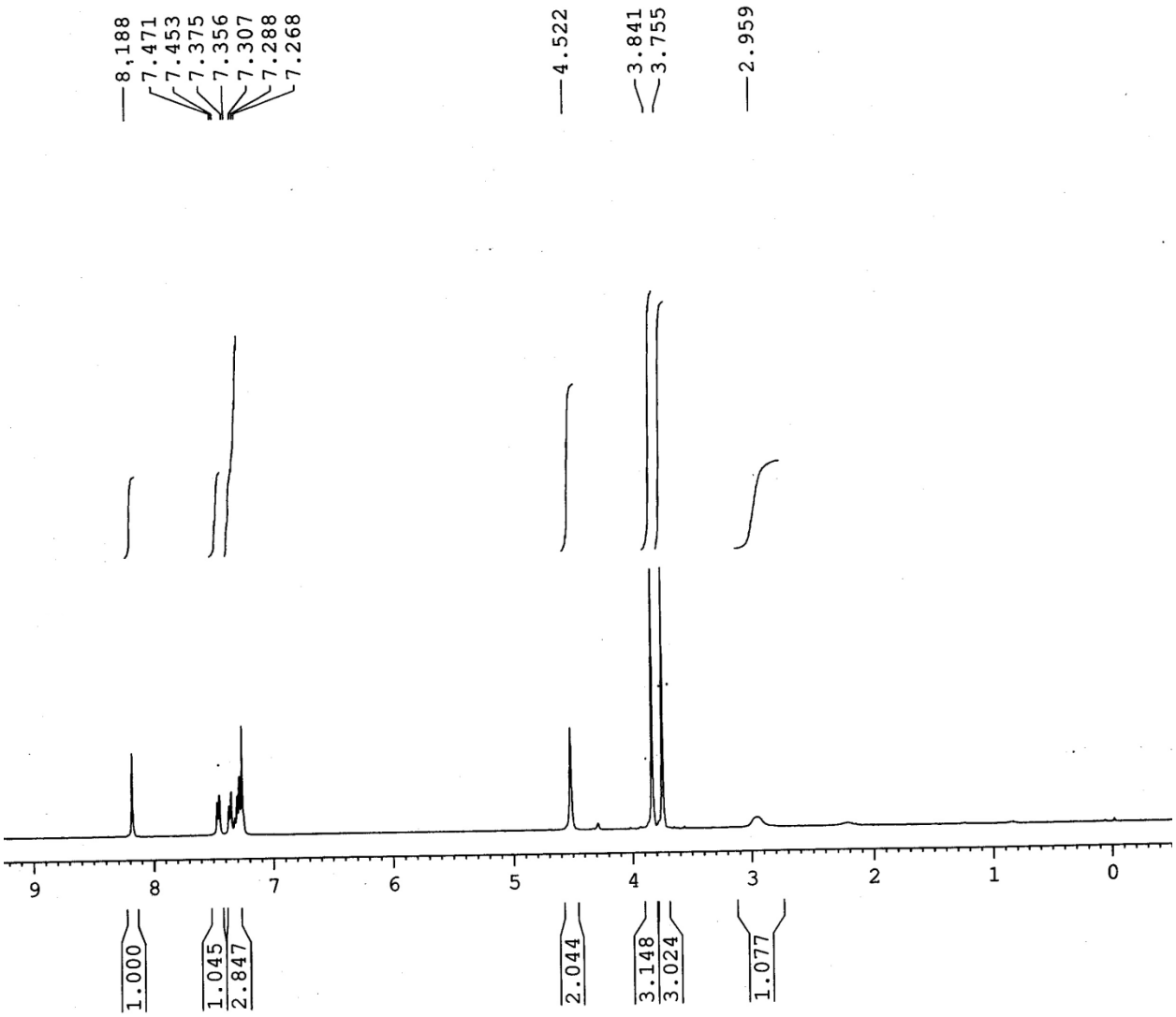


Fig. S15: ^{1}H NMR spectrum spectrum of compound **4a**

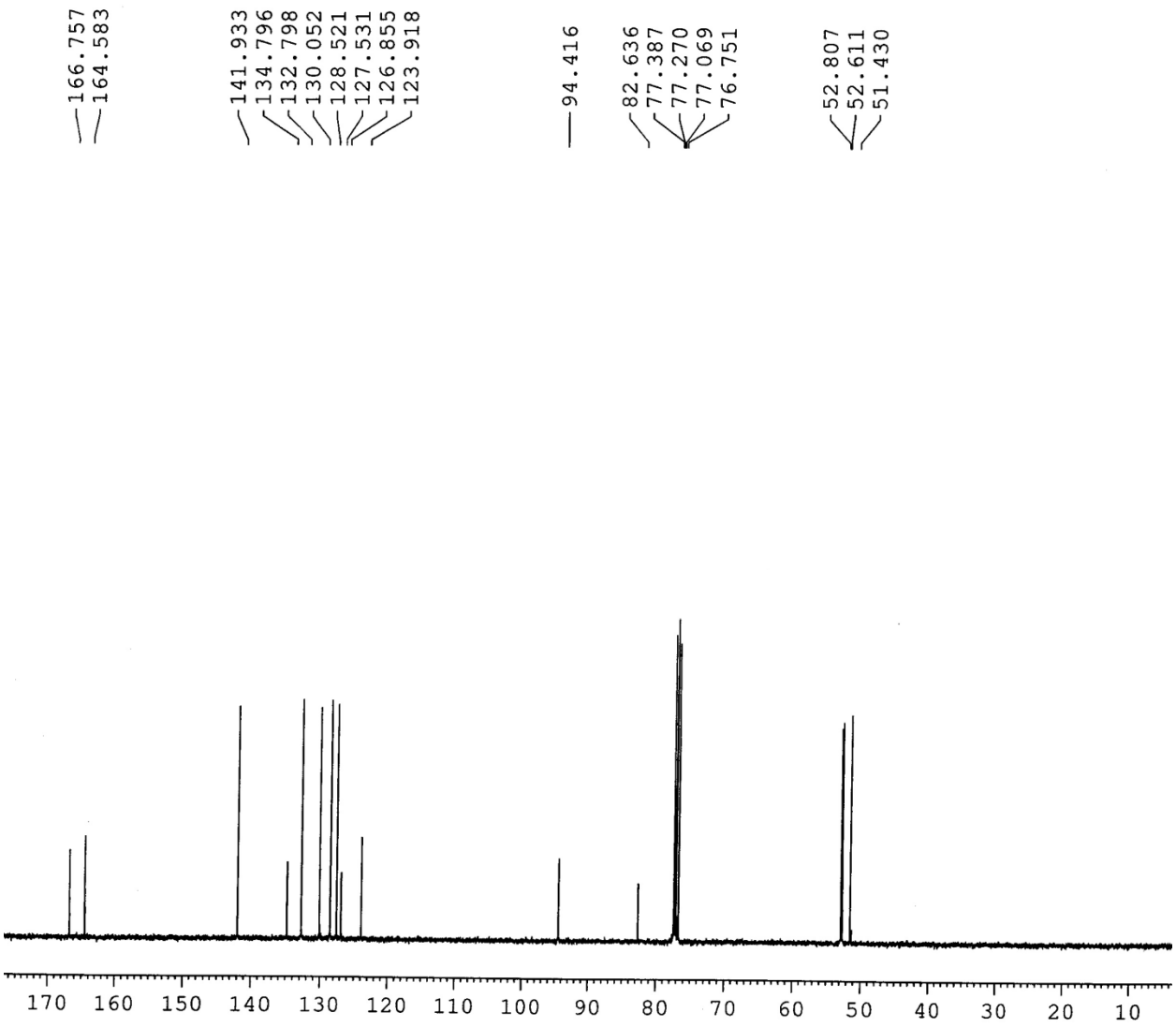


Fig. S16: ^{13}**C** NMR spectrum spectrum of compound **4a**

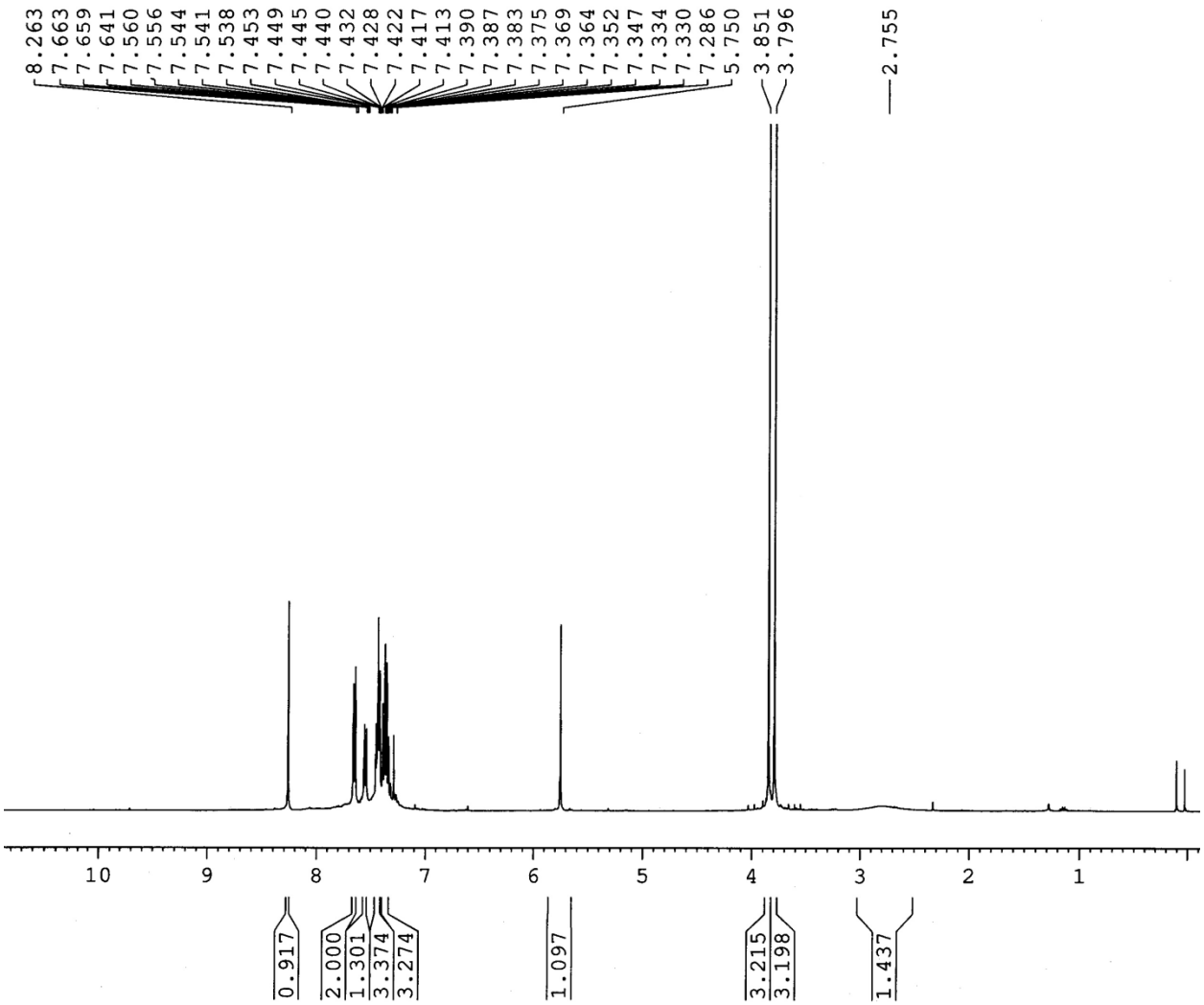


Fig. S17: ^{1}H NMR spectrum of compound **5a**

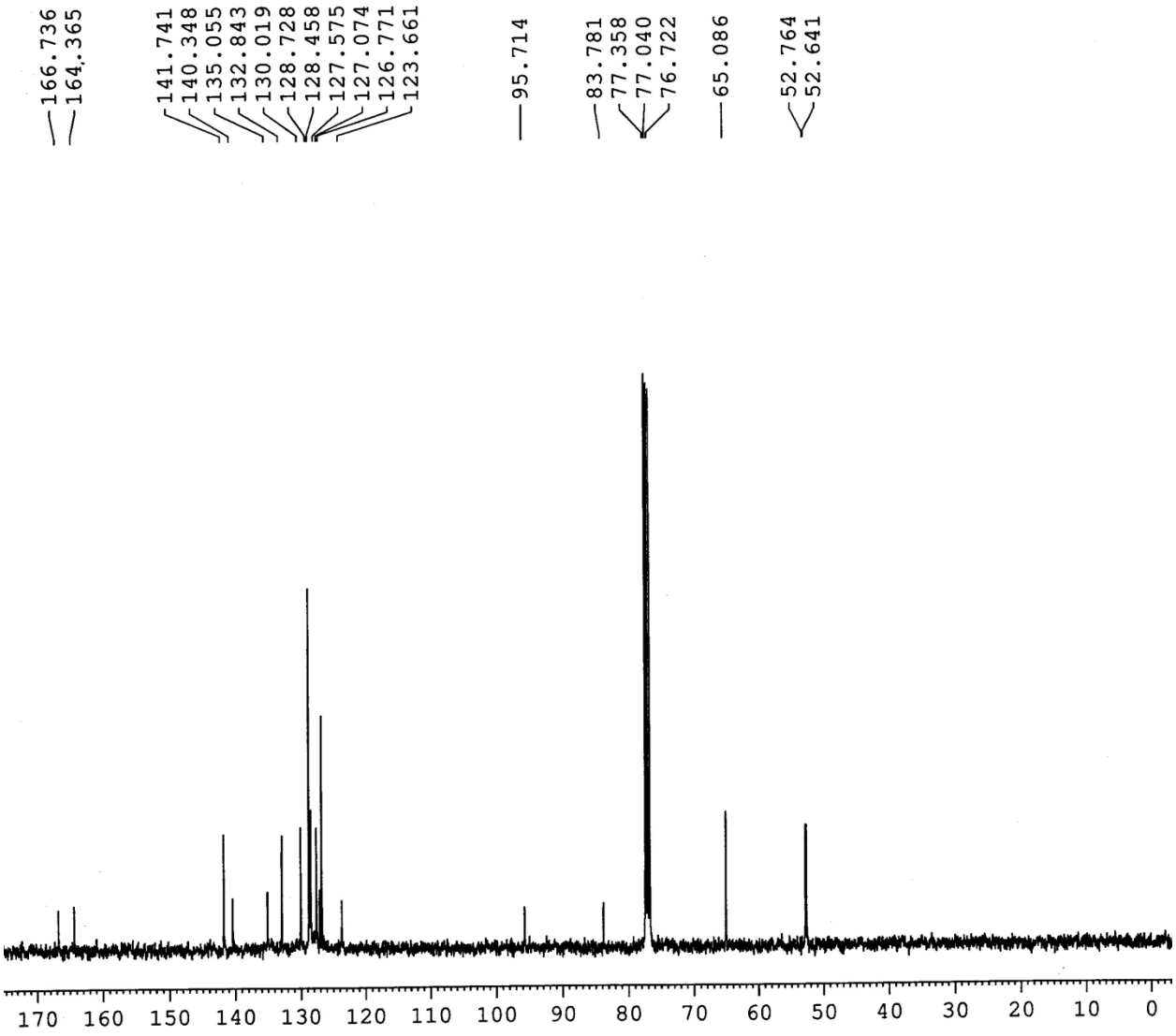


Fig. S18: ^{13}C NMR spectrum of compound **5a**

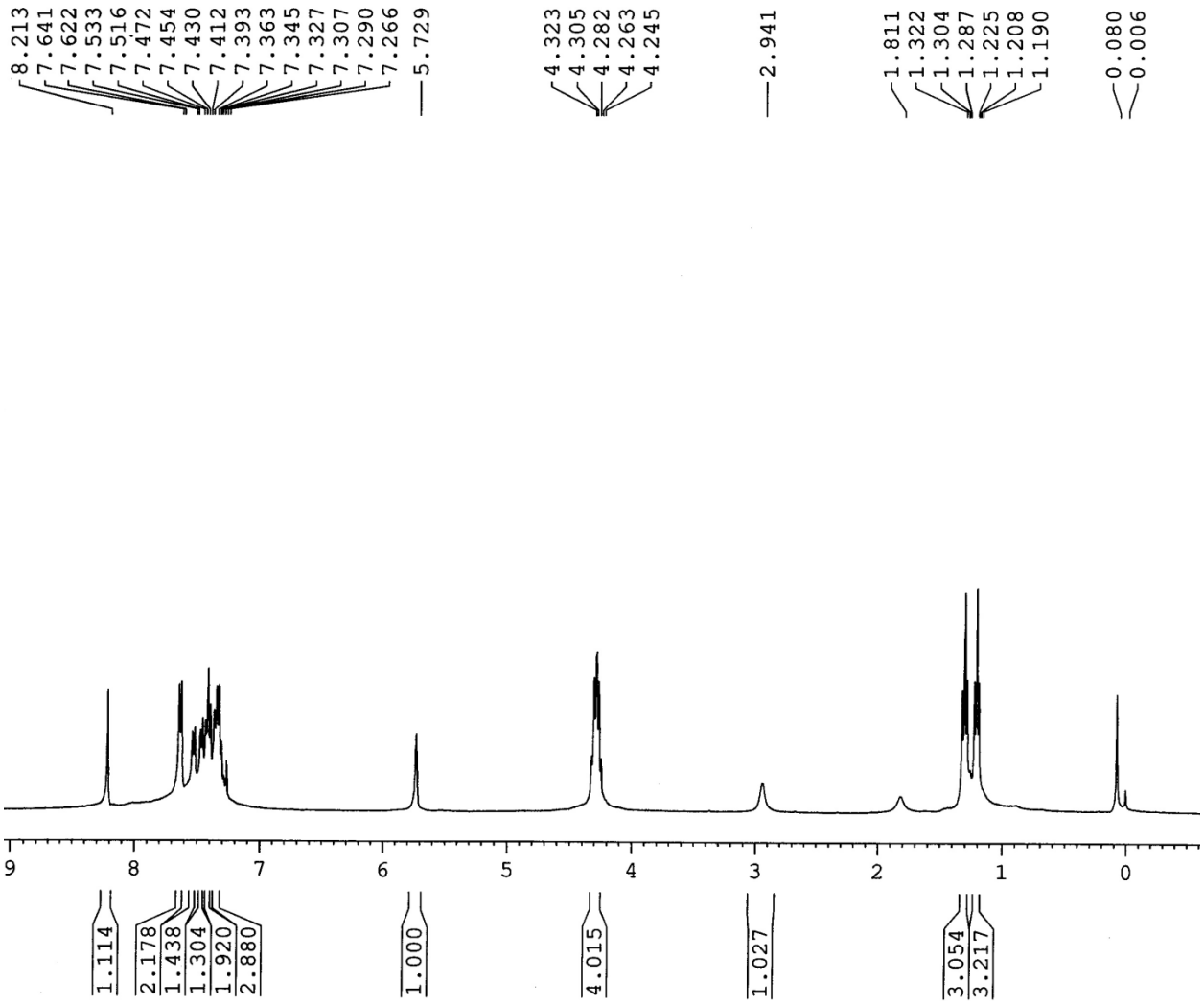


Fig. S19: ^{1}H NMR spectrum of compound **5b**

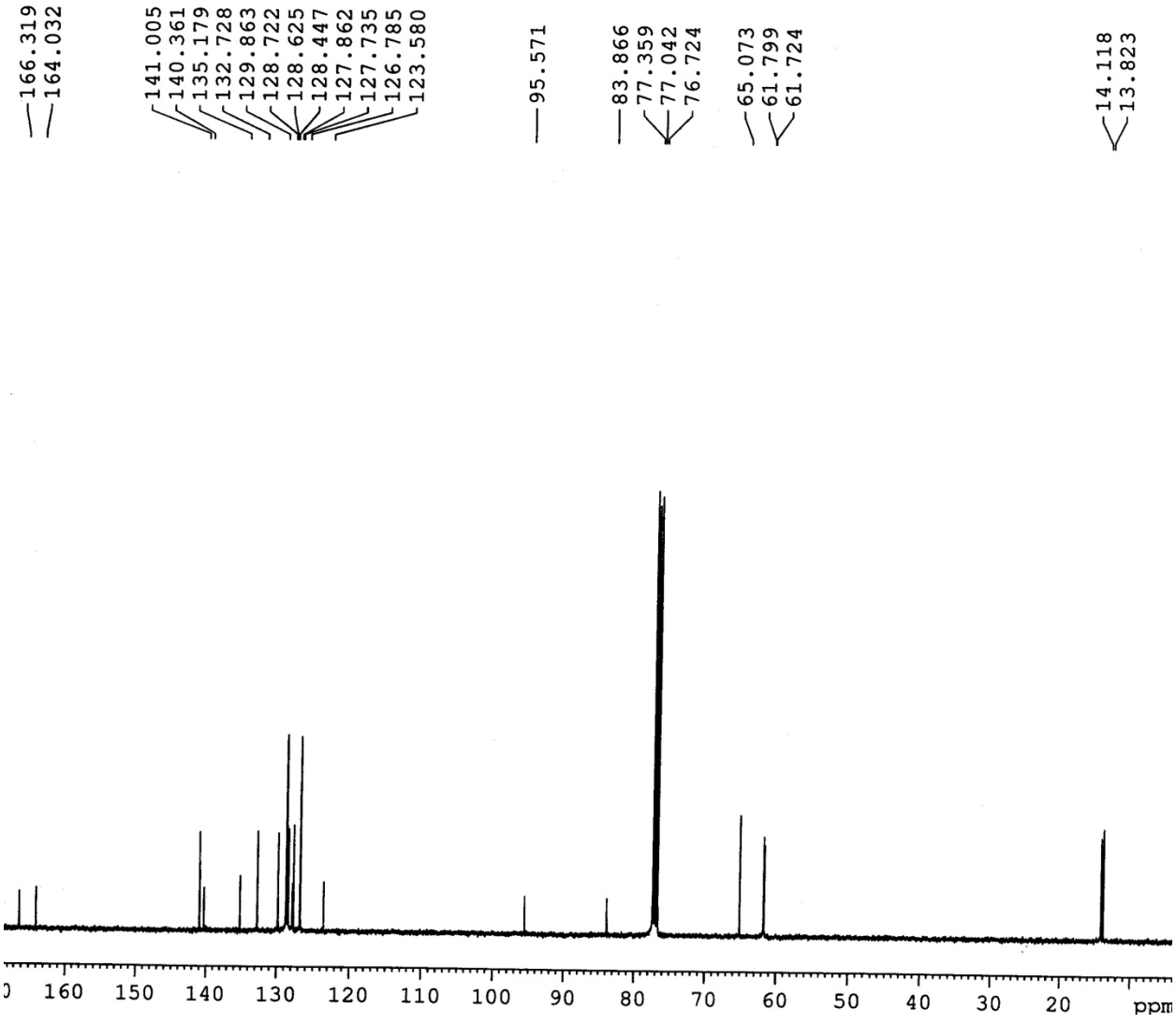


Fig. S20: ^{13}C NMR spectrum of compound **5b**

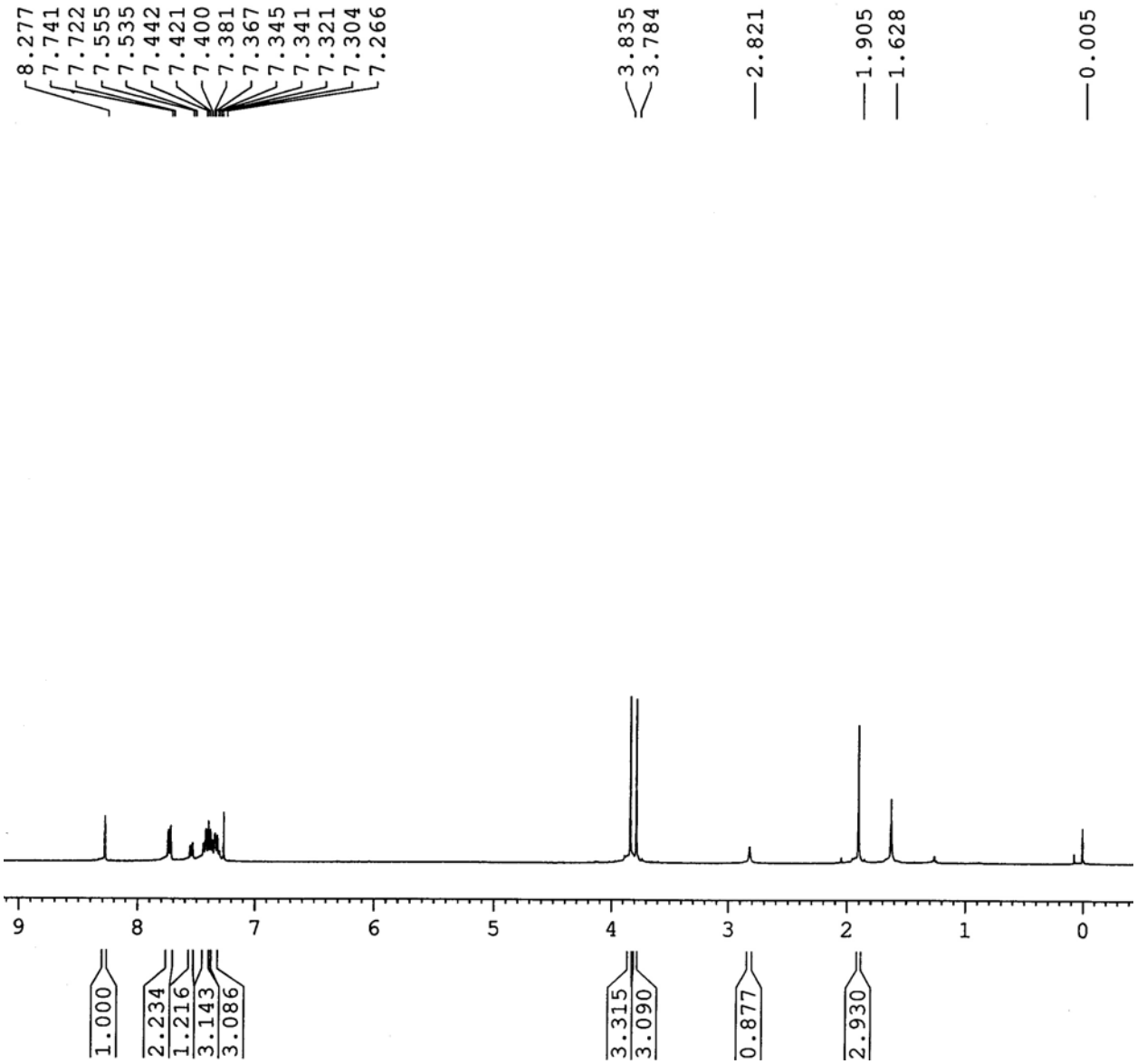


Fig. S21: ^{1}H NMR spectrum of compound **5c**

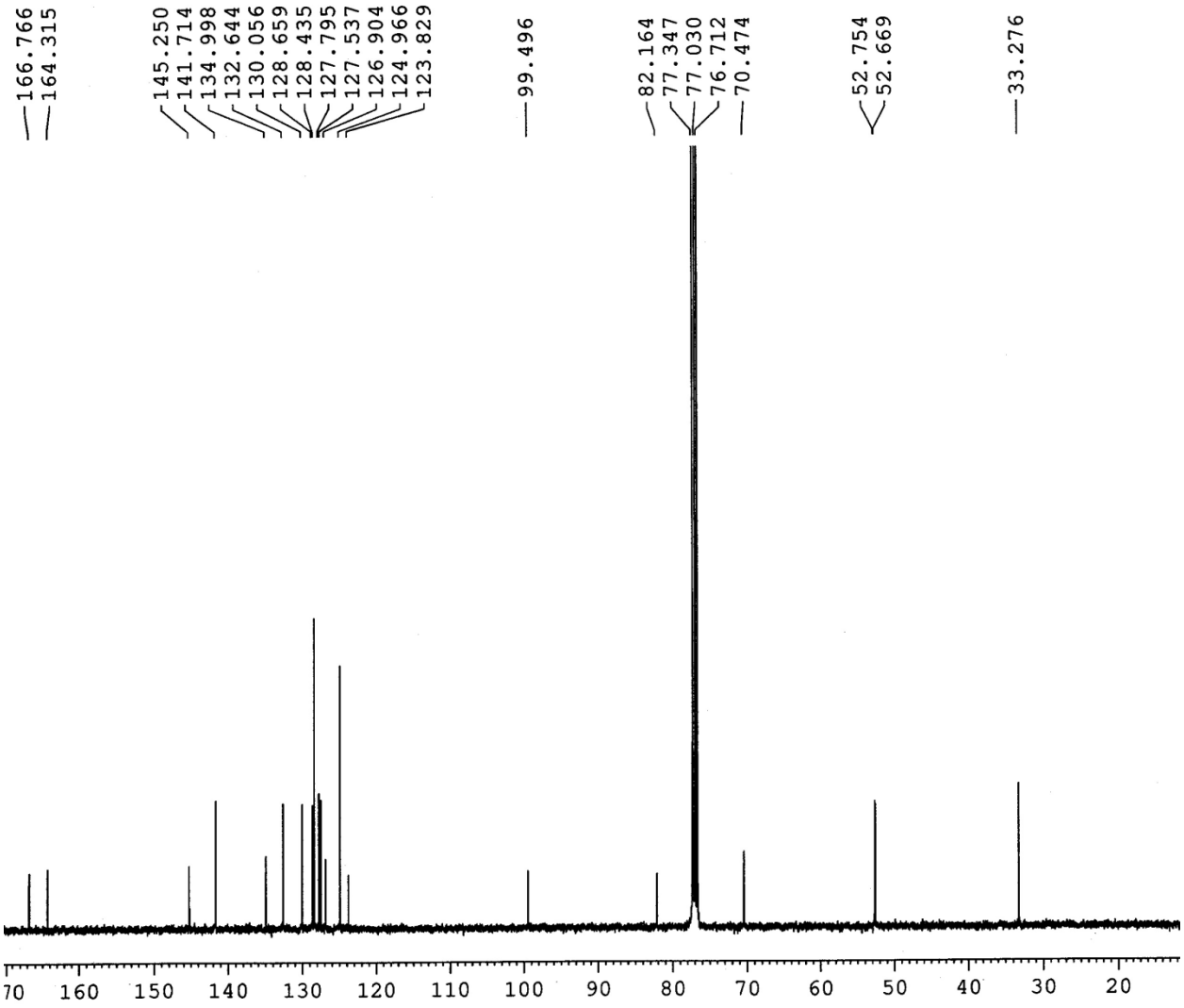


Fig. S22: ^{13}C NMR spectrum of compound **5c**

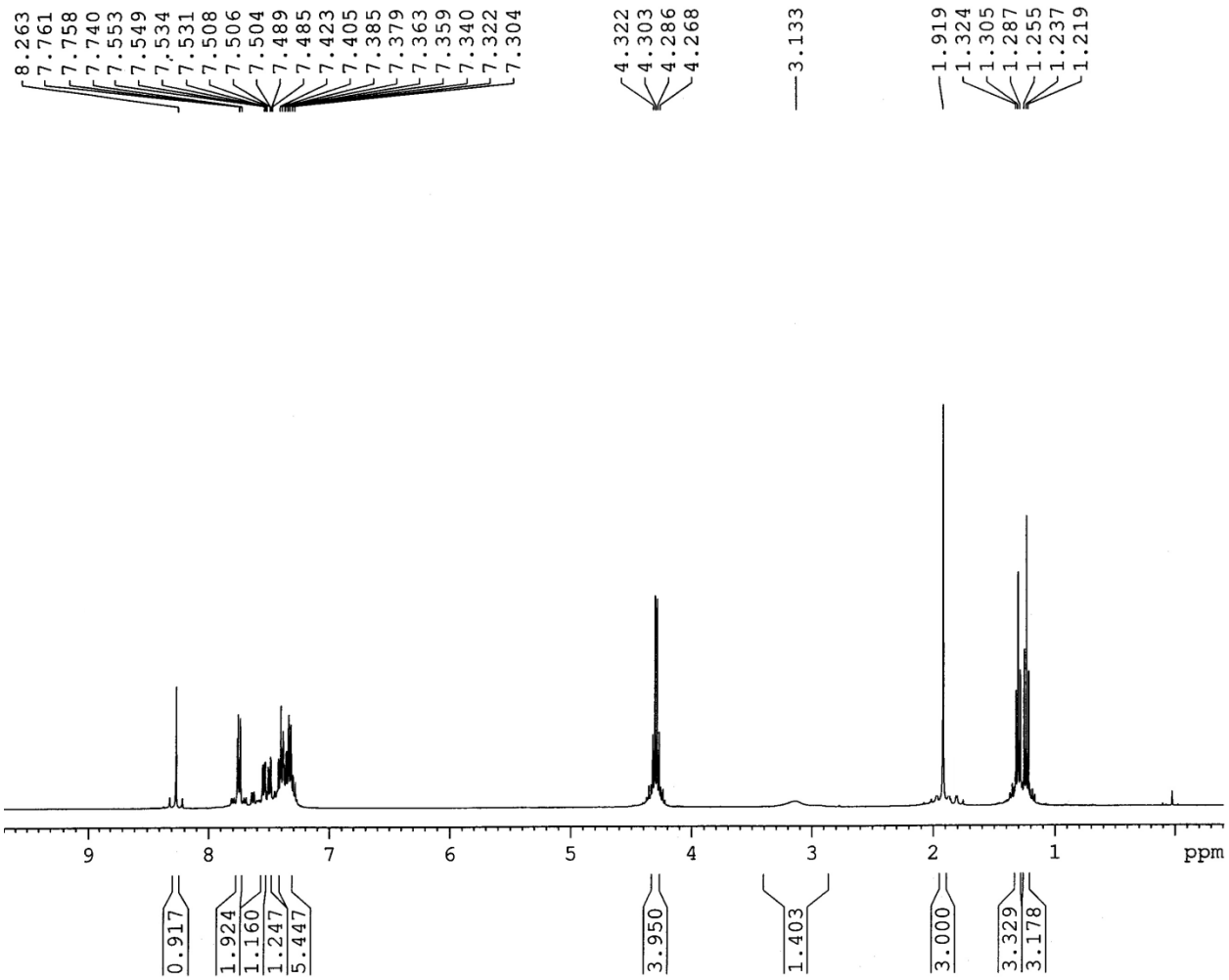


Fig. S23: ^{1}H NMR spectrum of compound **5d**

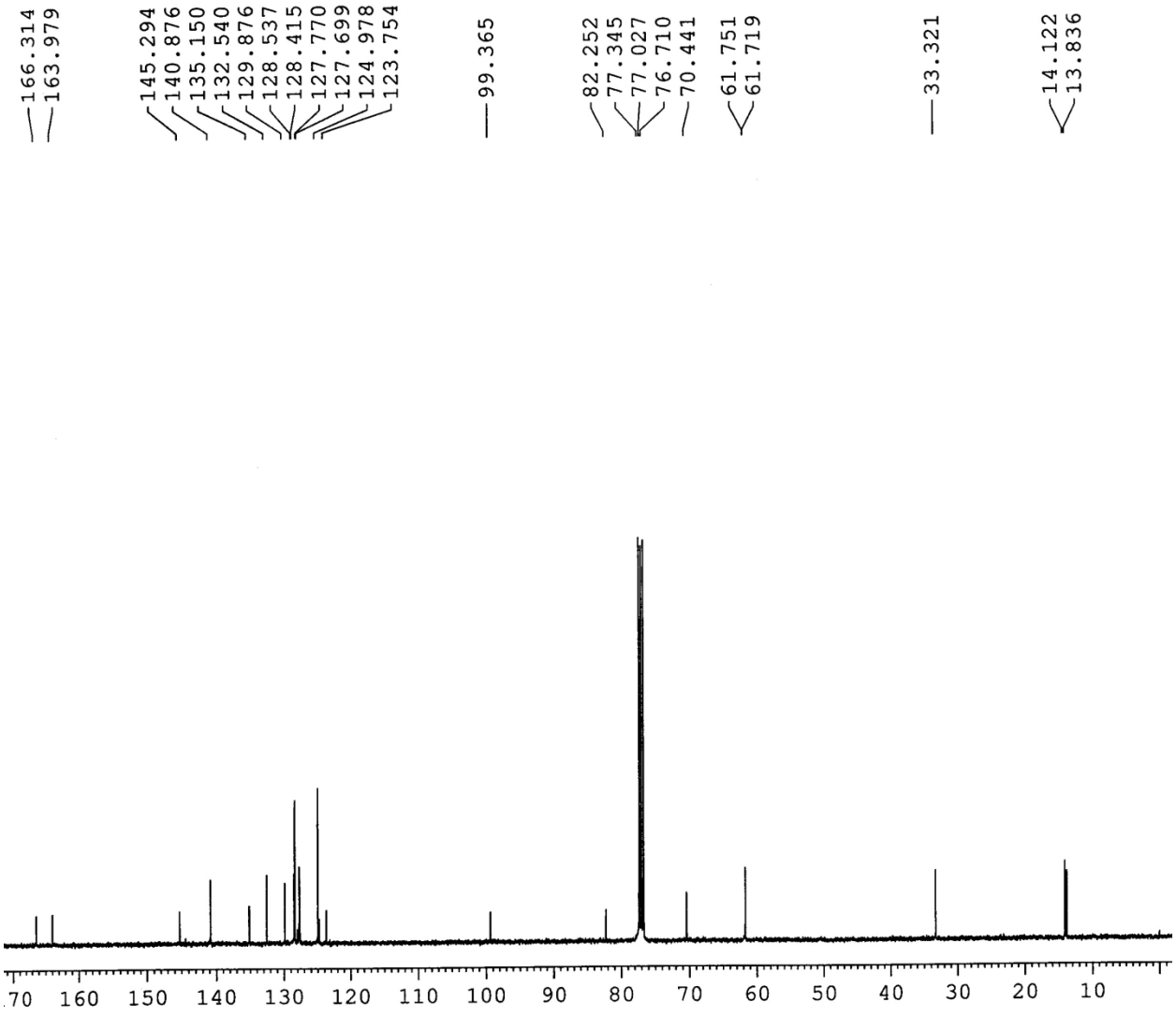


Fig. S24: ^{13}C NMR spectrum of compound **5d**

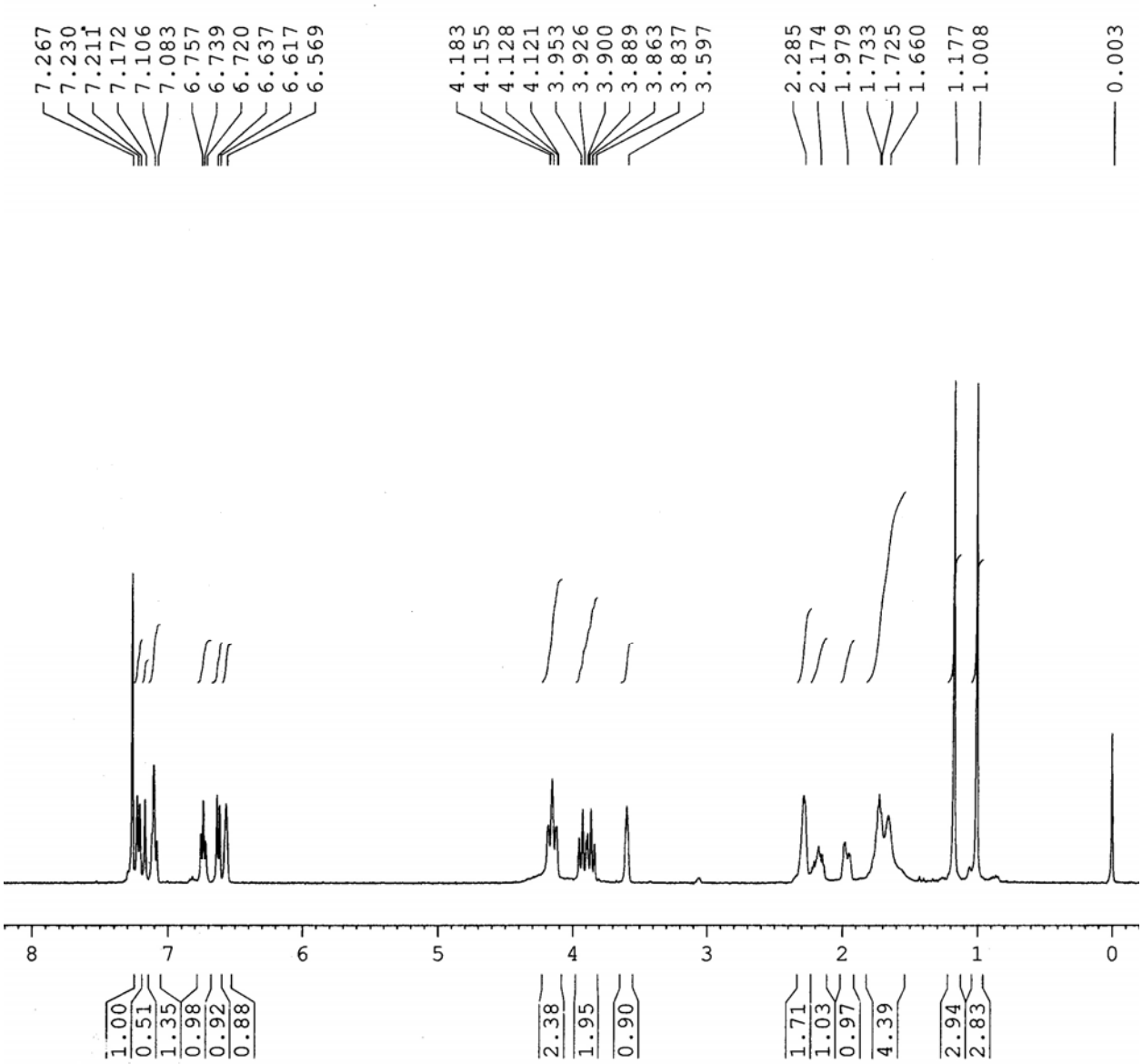


Fig. S25: ^{1}H NMR spectrum of compound **6**

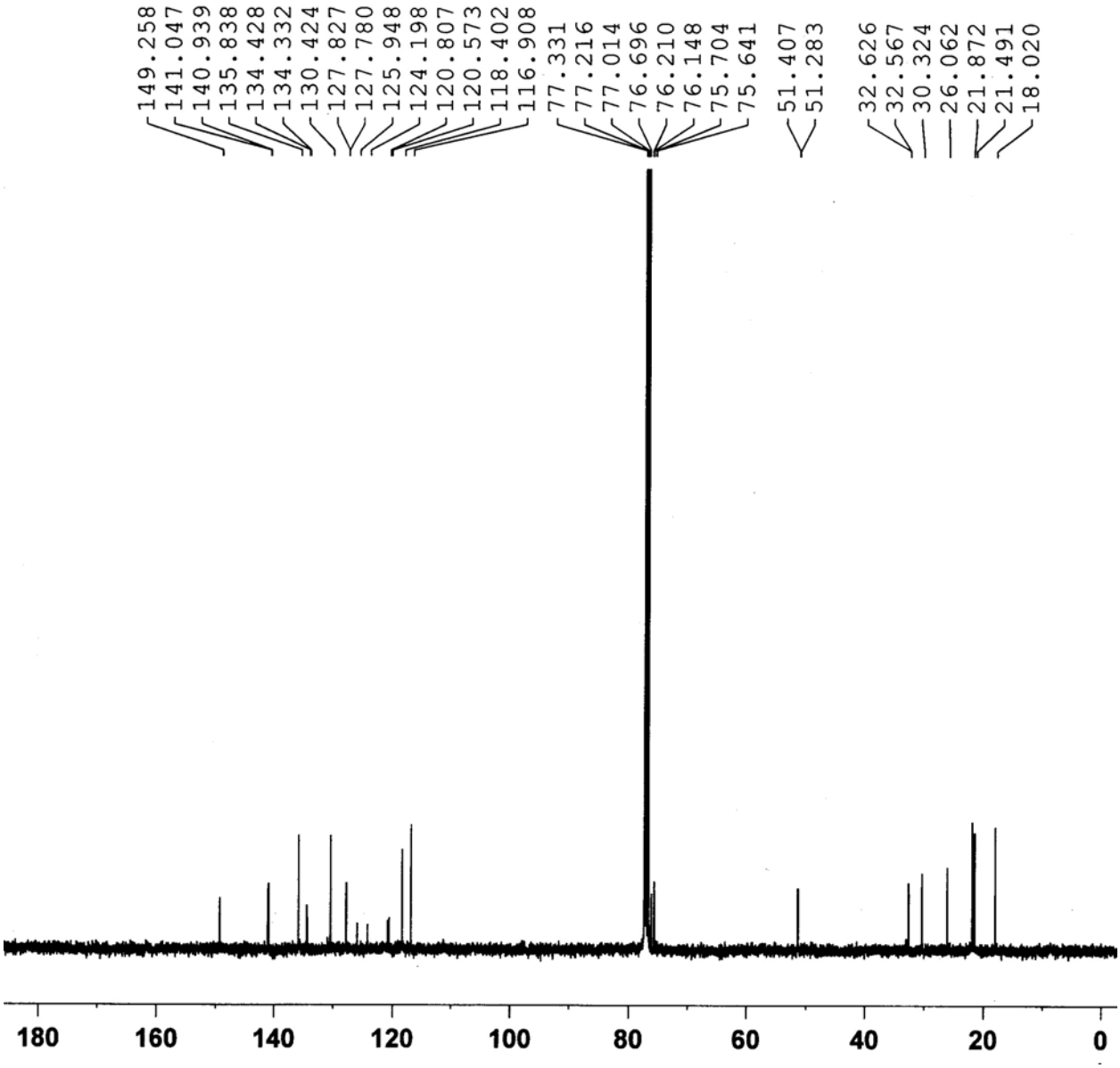


Fig. S26: ^{13}C NMR spectrum of compound **6**

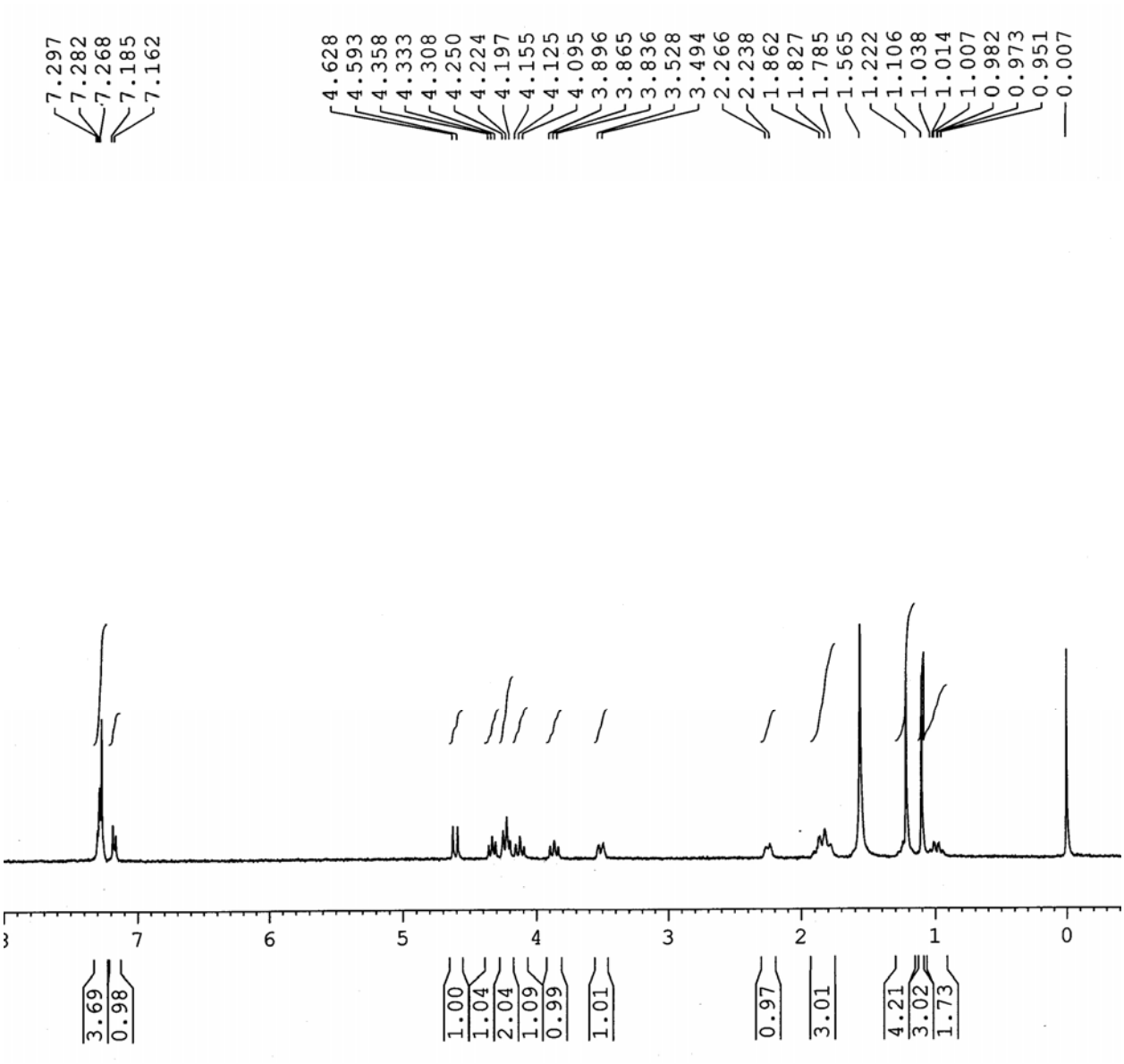


Fig. S27: ^{1}H NMR spectrum of compound **7**

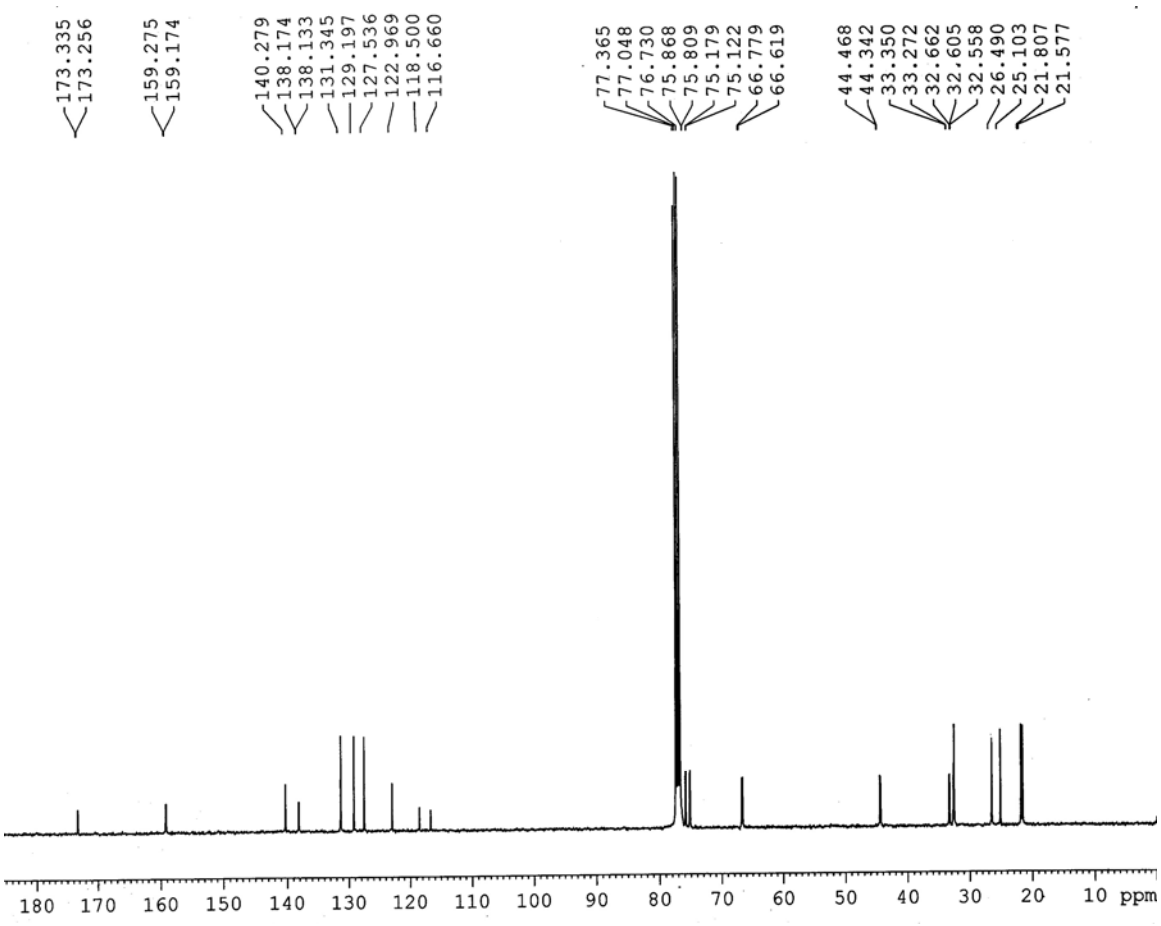


Fig. S28: ^{13}C NMR spectrum of compound **7**

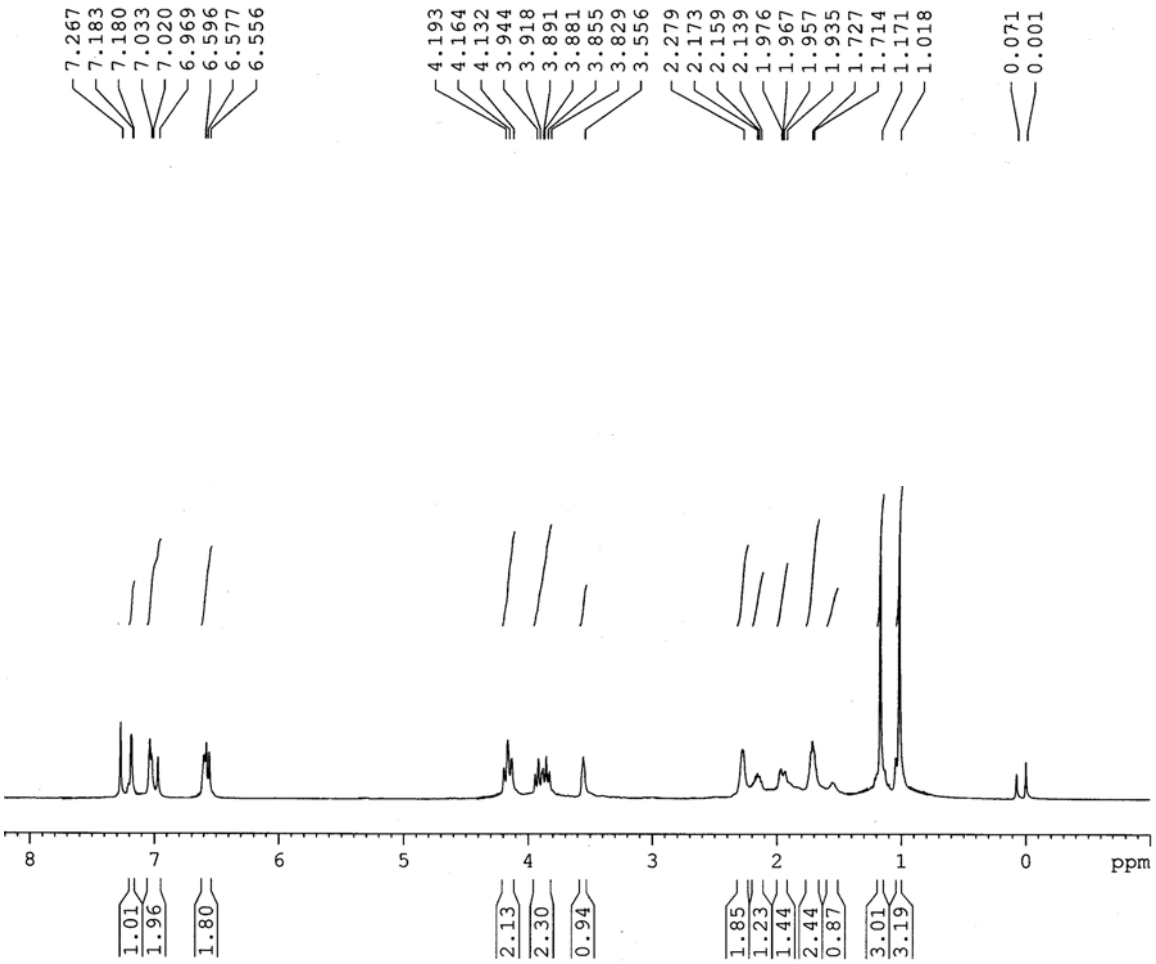


Fig. S29: ^{1}H NMR spectrum of compound **8**

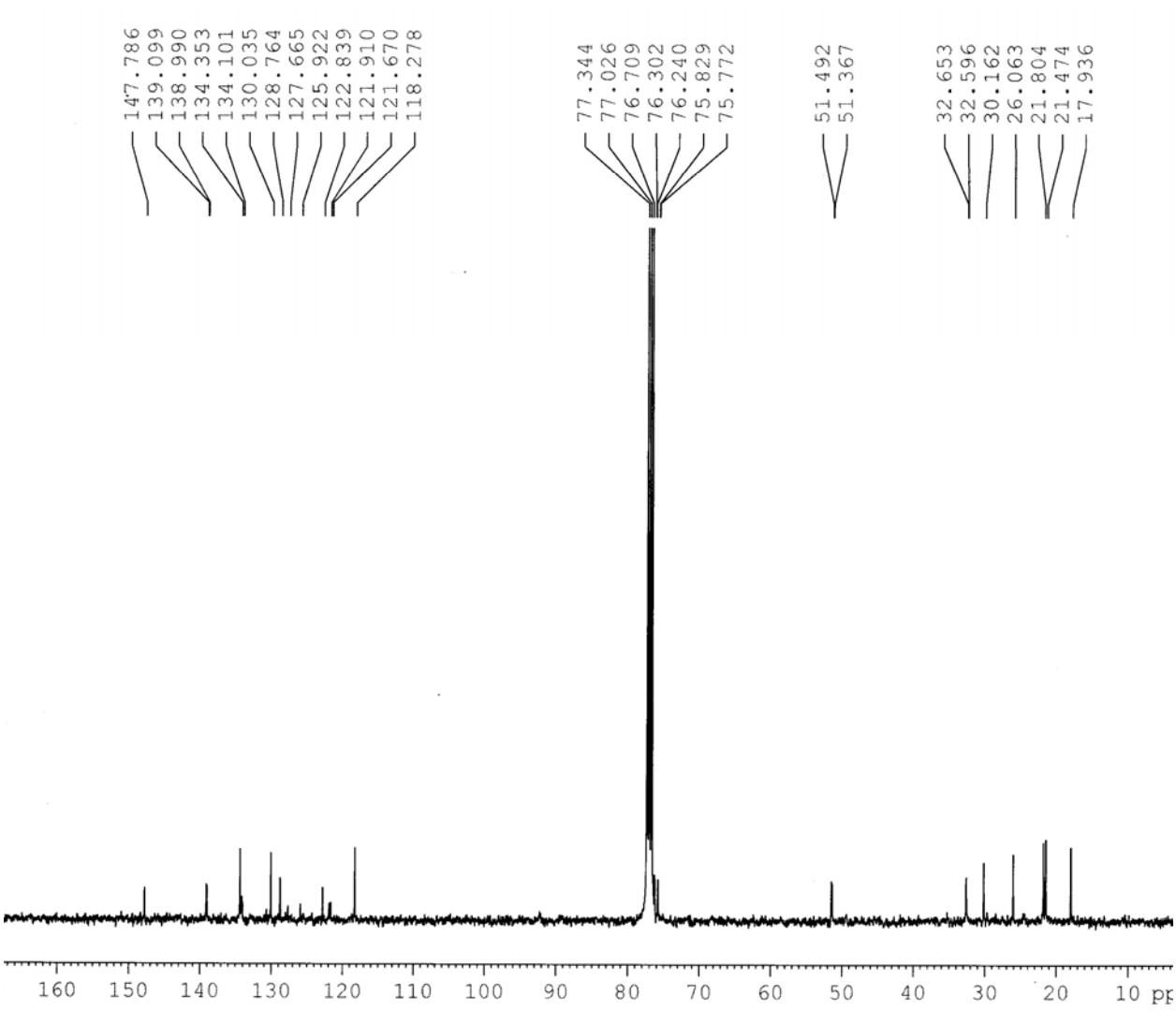


Fig. S30: ^{13}C NMR spectrum of compound **8**

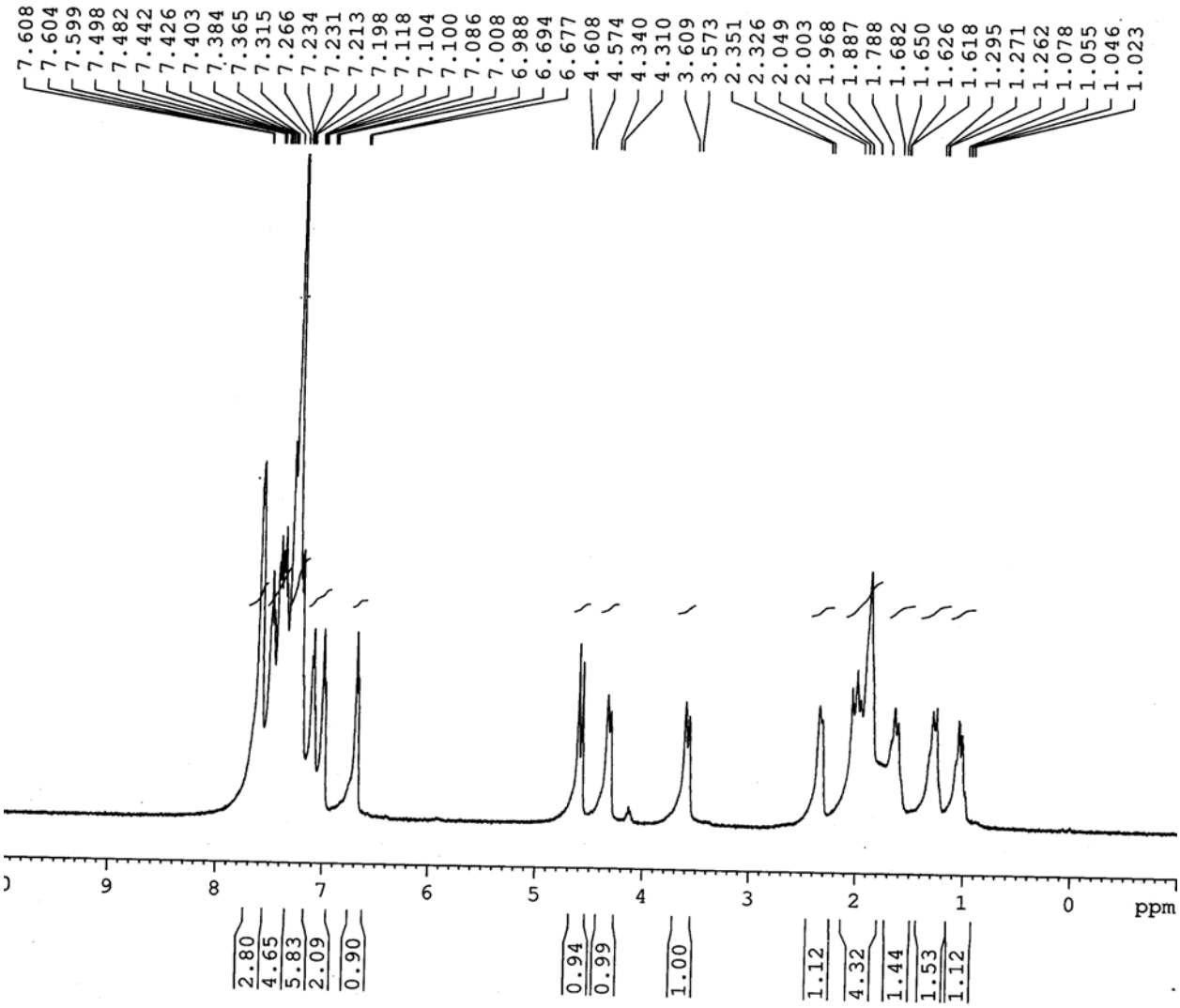


Fig. S31: ^{1}H NMR spectrum of compound **9**

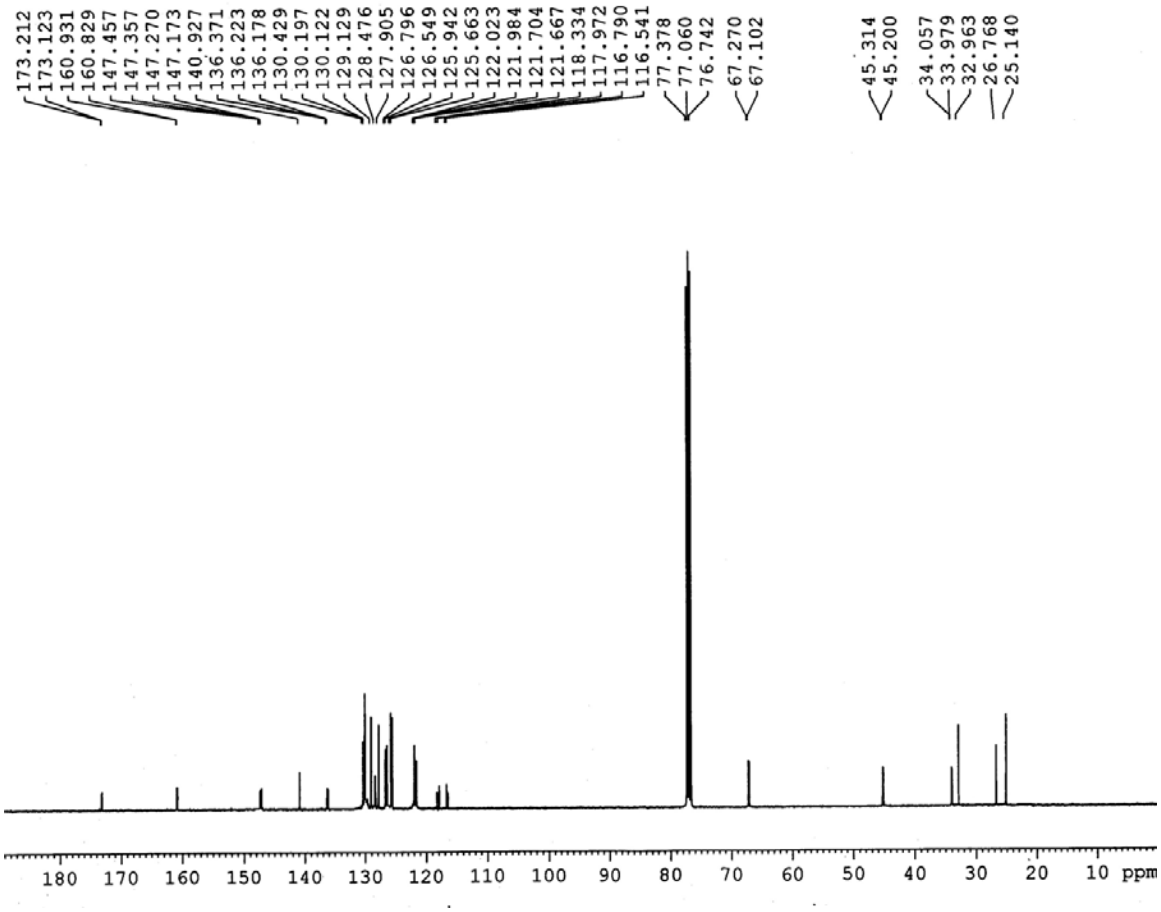


Fig. S32: ^{13}C NMR spectrum of compound **9**

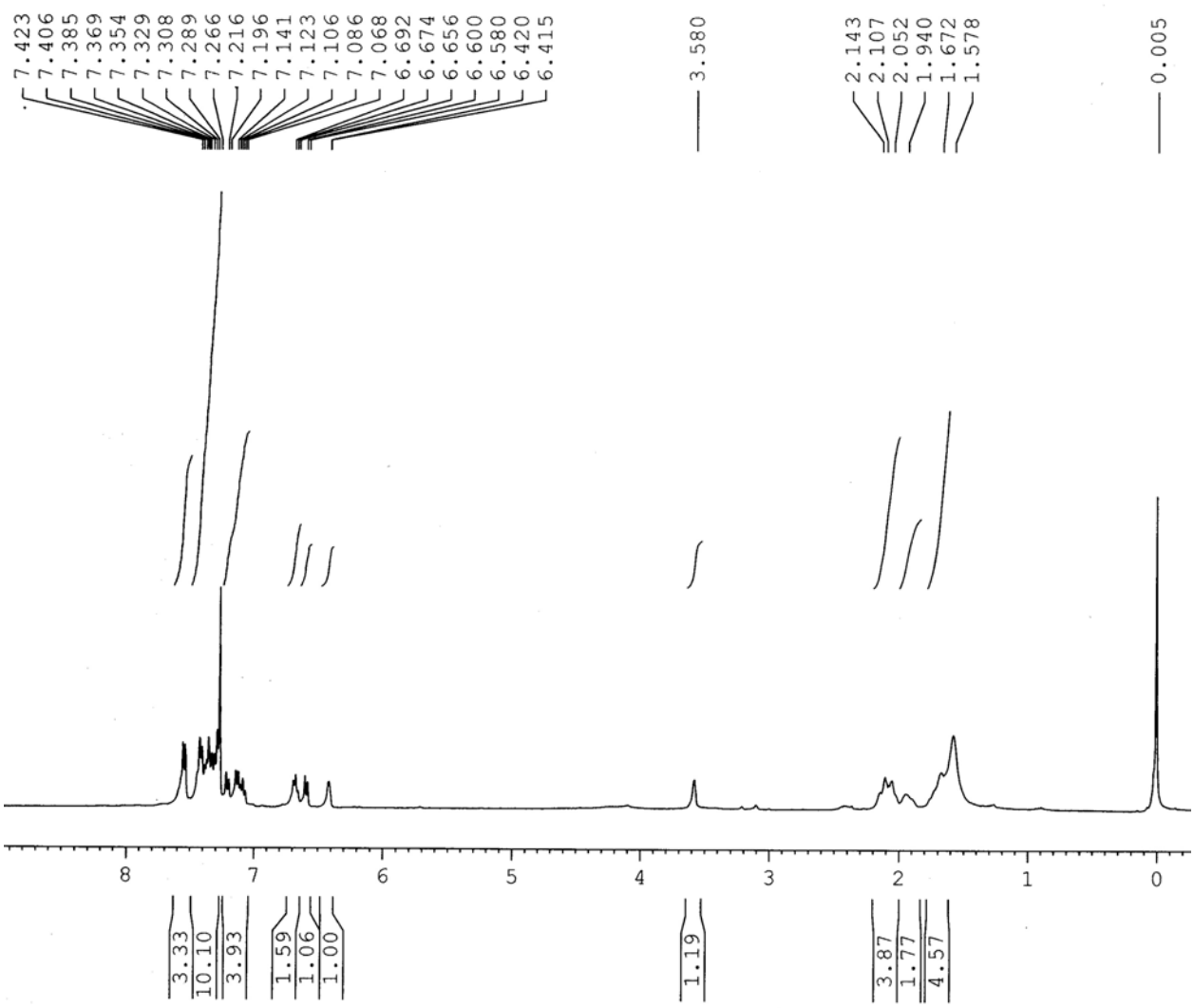


Fig. S33: ^{1}H NMR spectrum of compound **10**

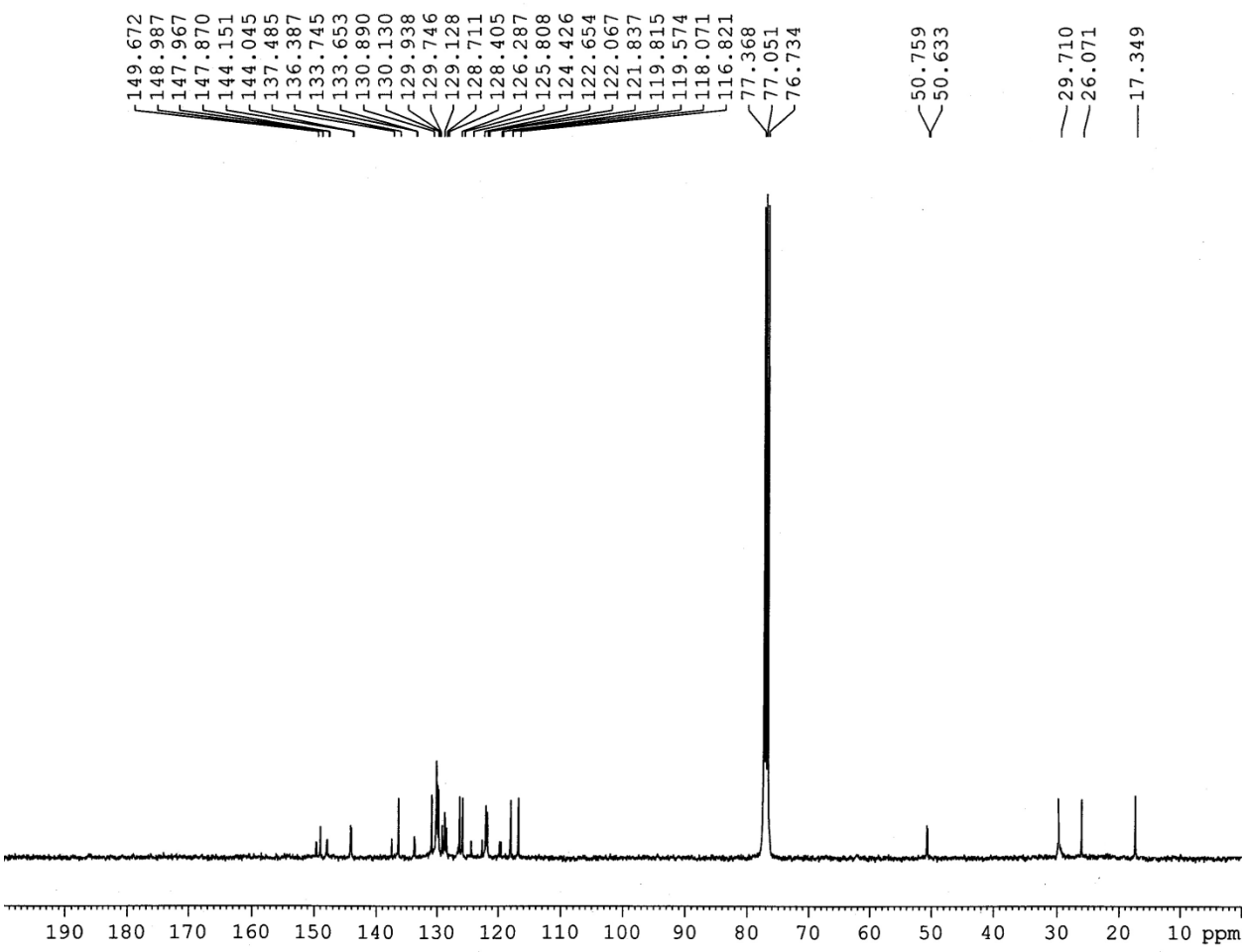


Fig. S34: ^{13}C NMR spectrum of compound **10**

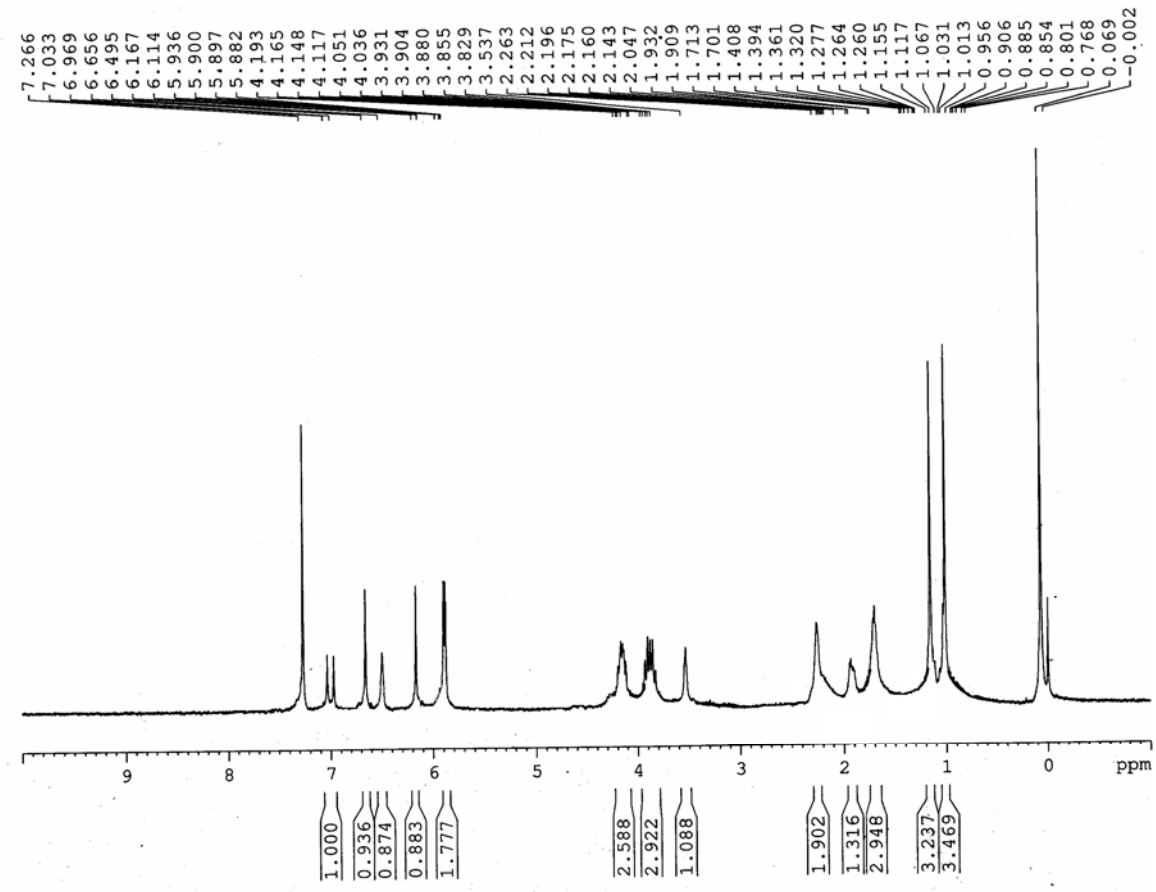


Fig. S35: ^{1}H NMR spectrum of compound **11**

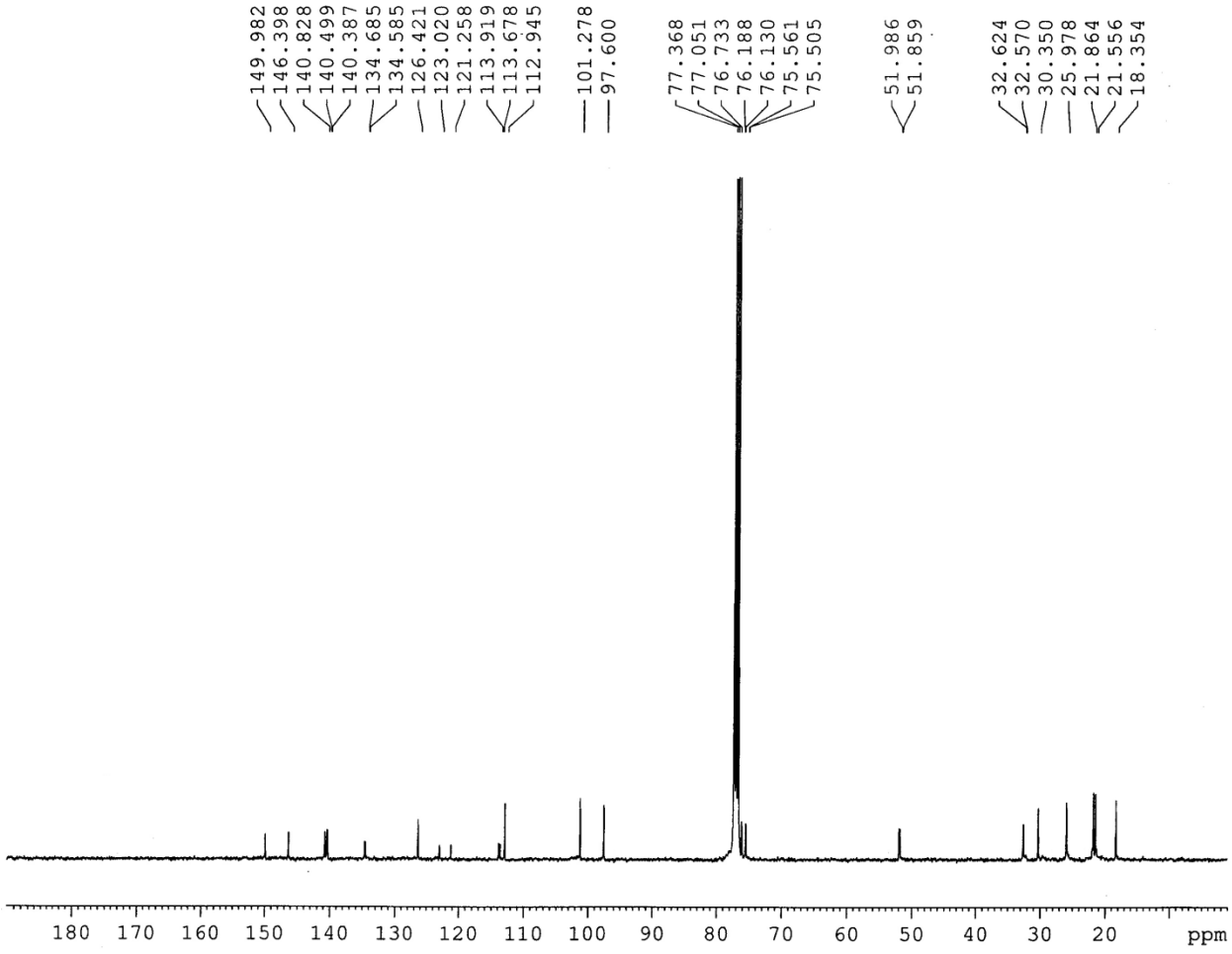


Fig. S36: ^{13}C NMR spectrum of compound **11**

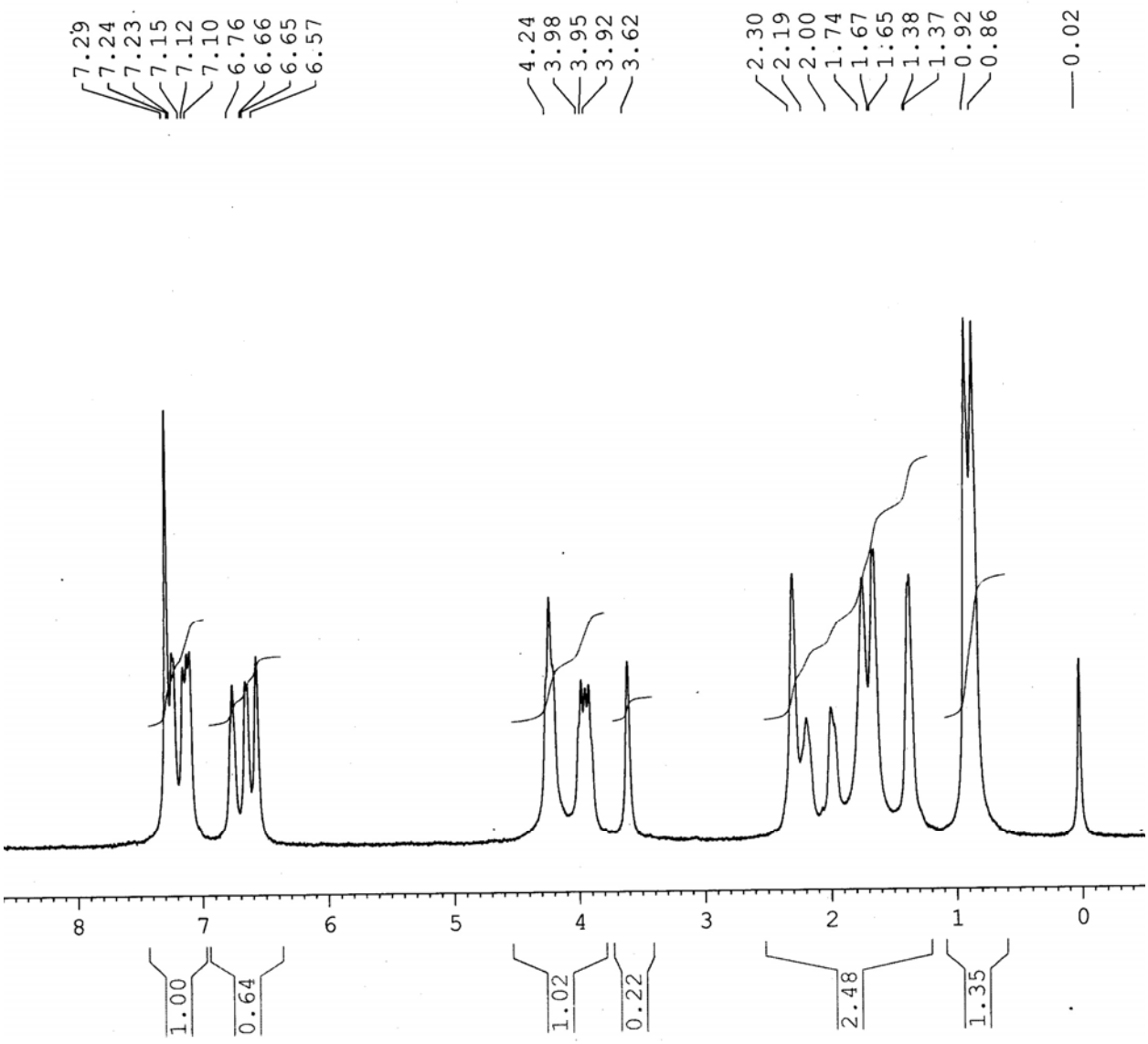


Fig. S37: ^{1}H NMR spectrum of compound **12**

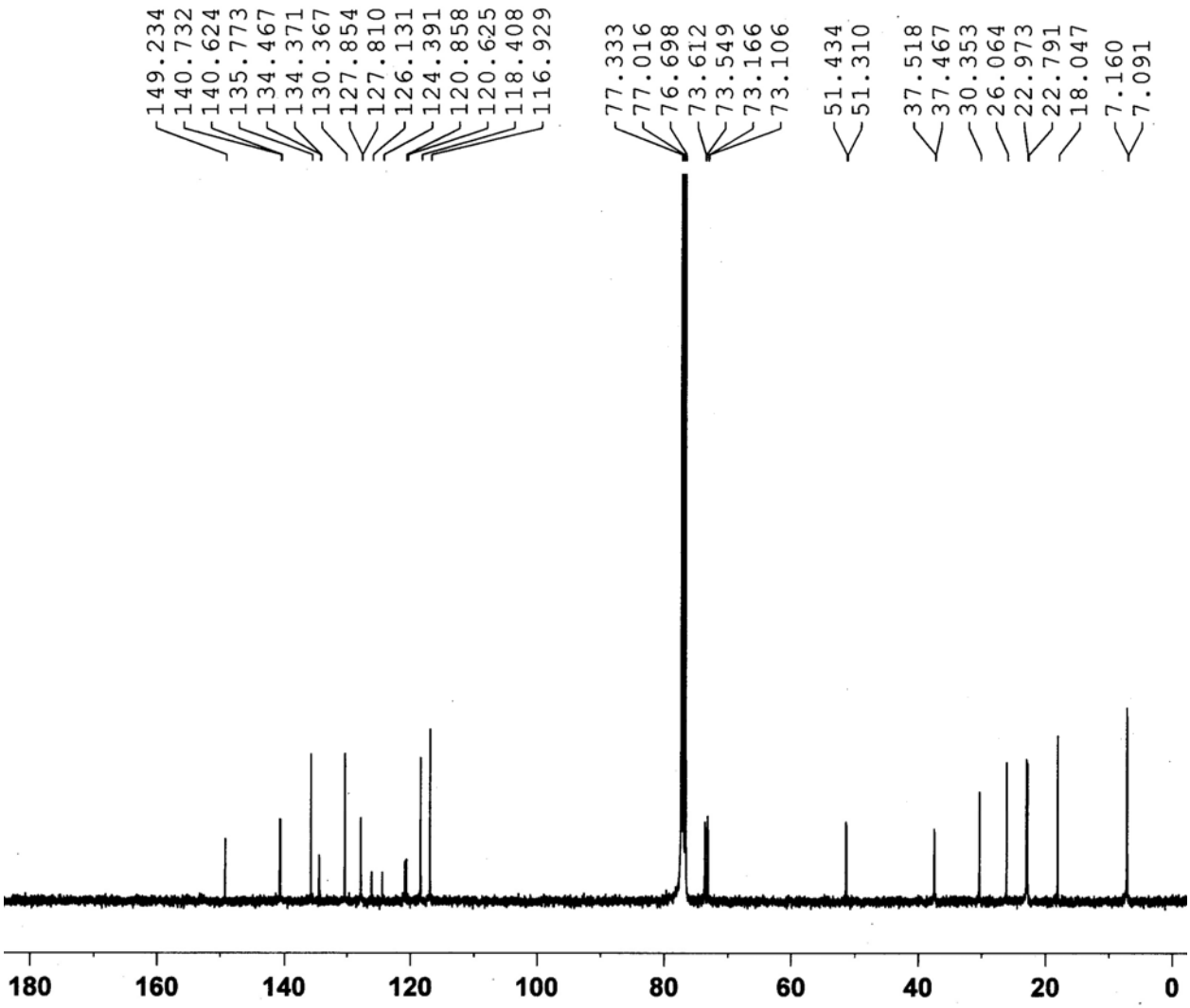


Fig. S38: ^{13}C NMR spectrum of compound **12**

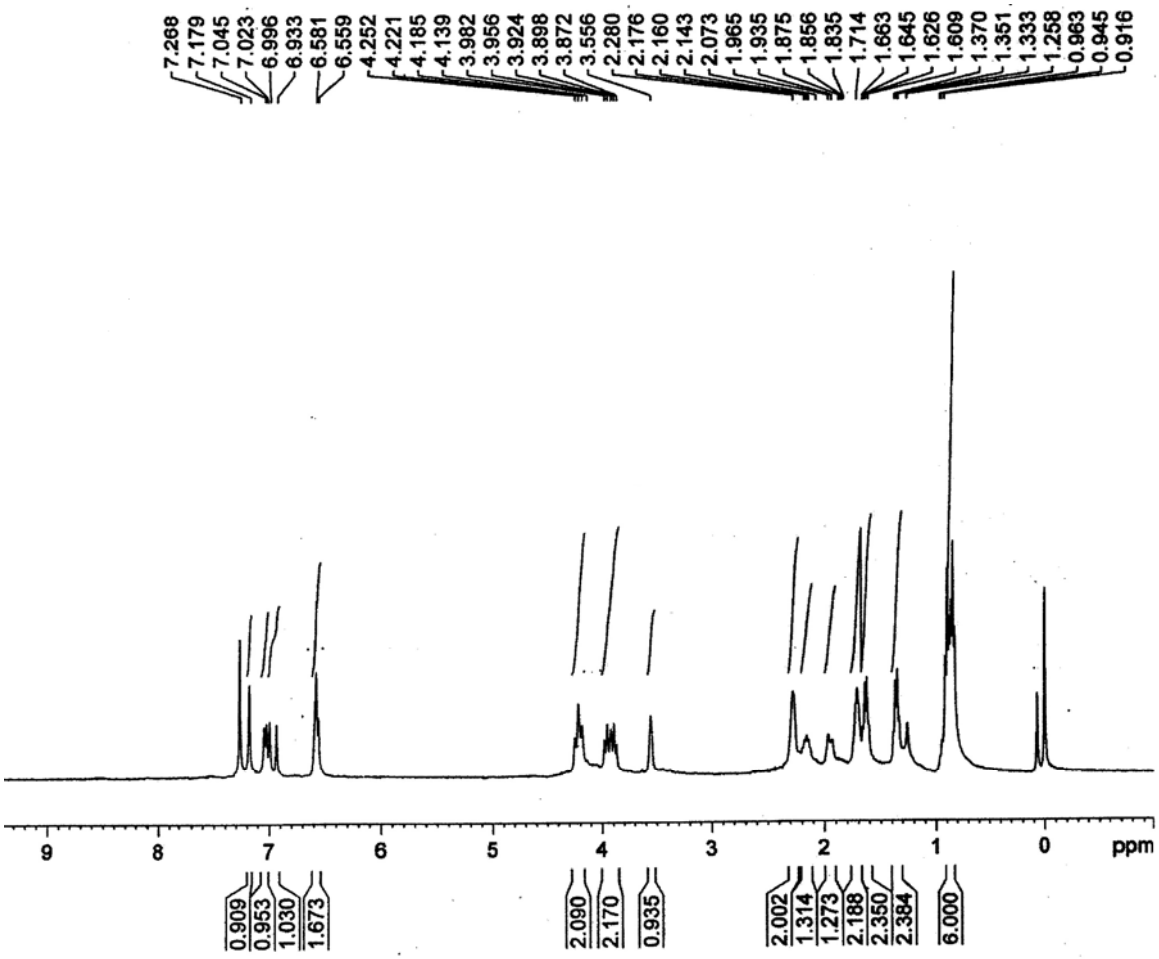


Fig. S39: ^{1}H NMR spectrum of compound **13**

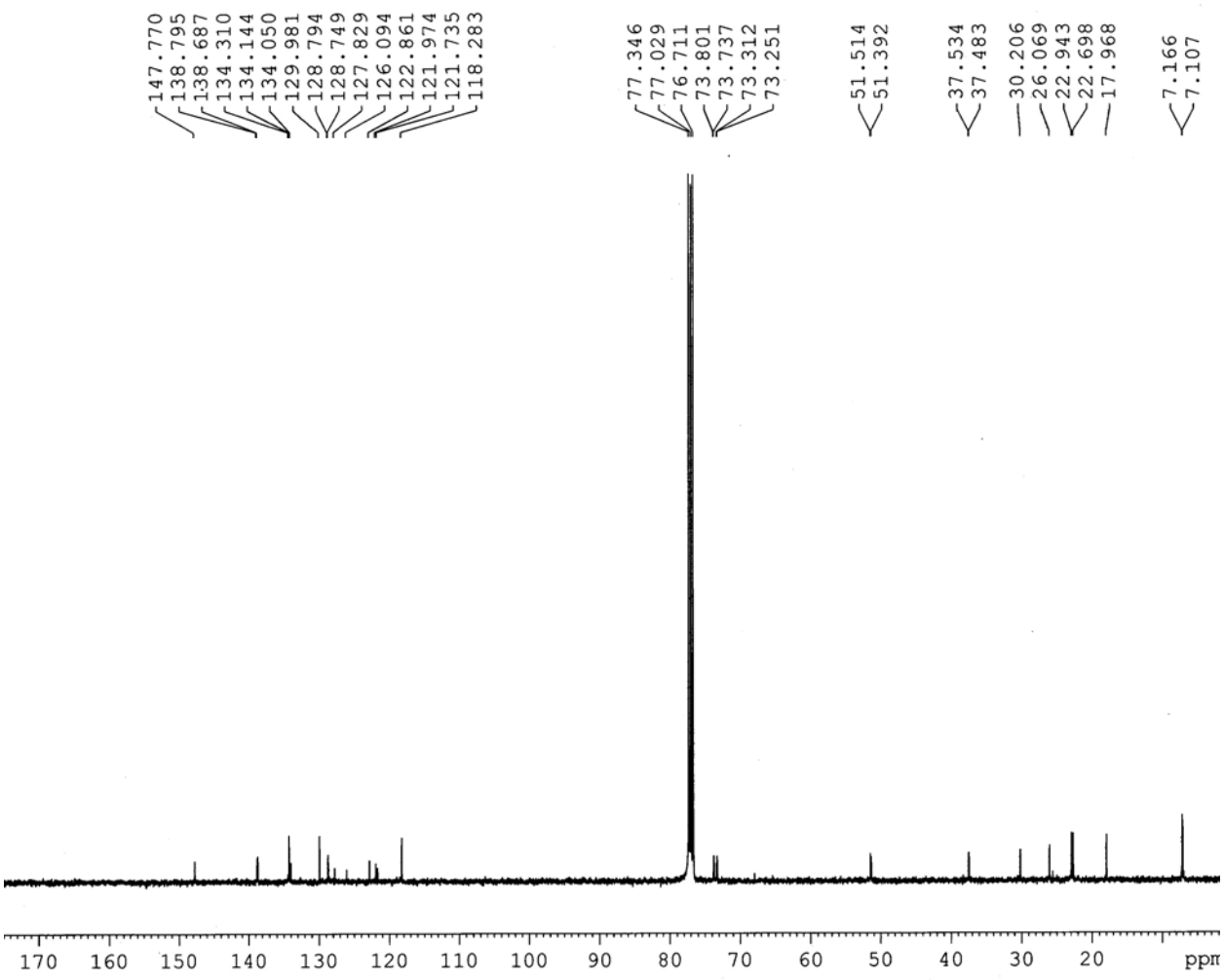


Fig. S40: ^{13}C NMR spectrum of compound **13**

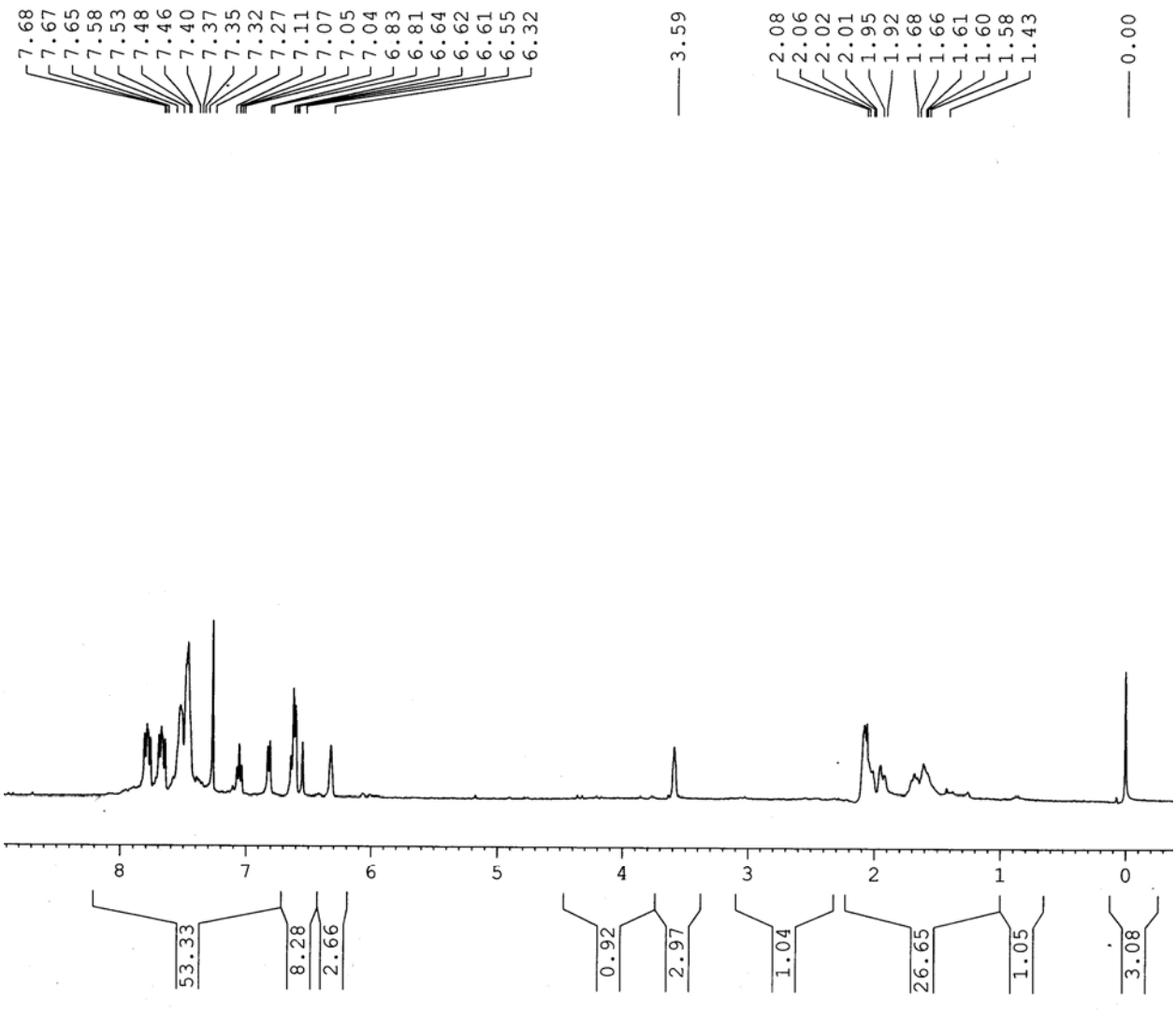


Fig. S41: ^{1}H NMR spectrum of compound **14**

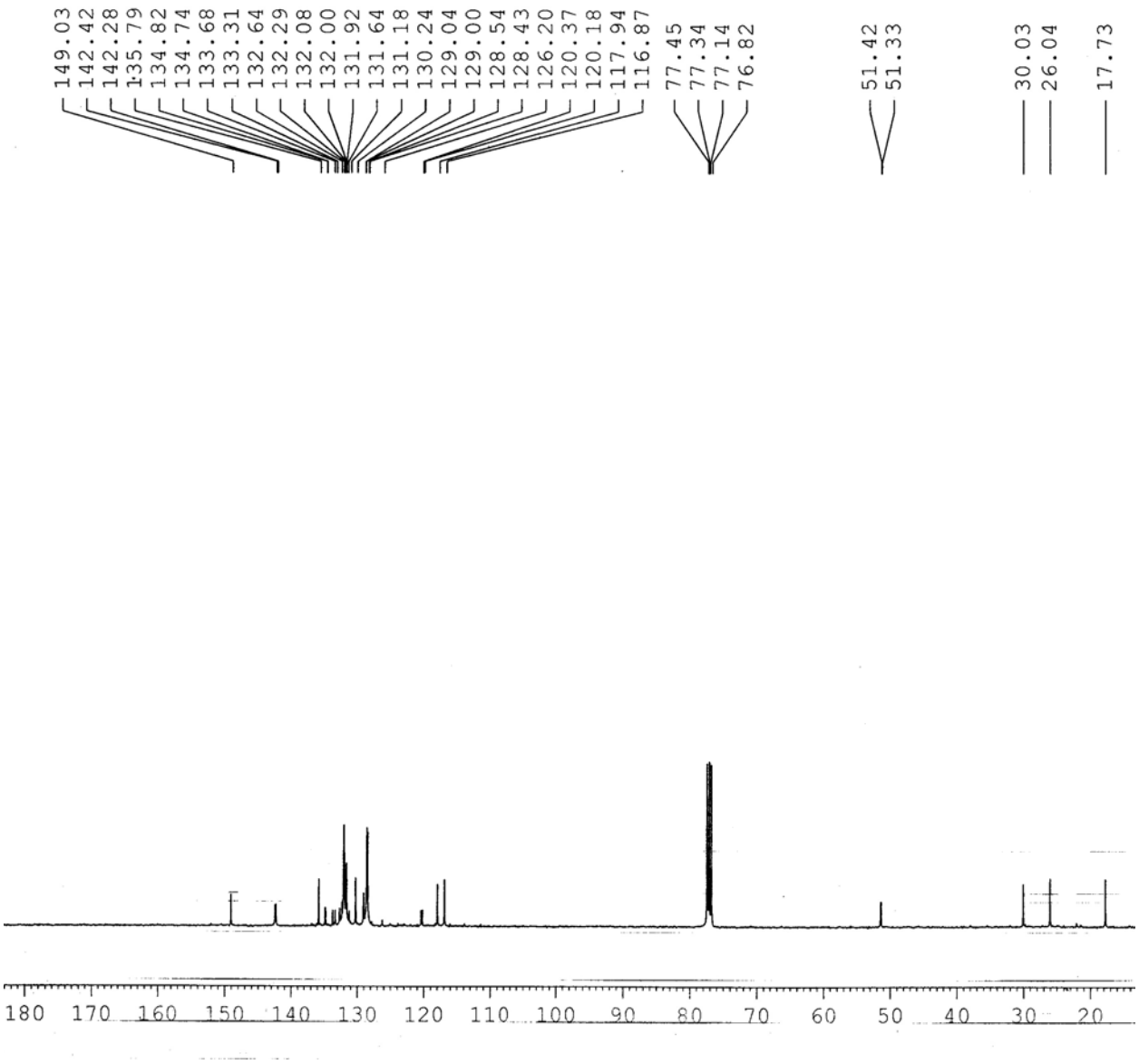


Fig. S42: ^{13}C NMR spectrum of compound **14**

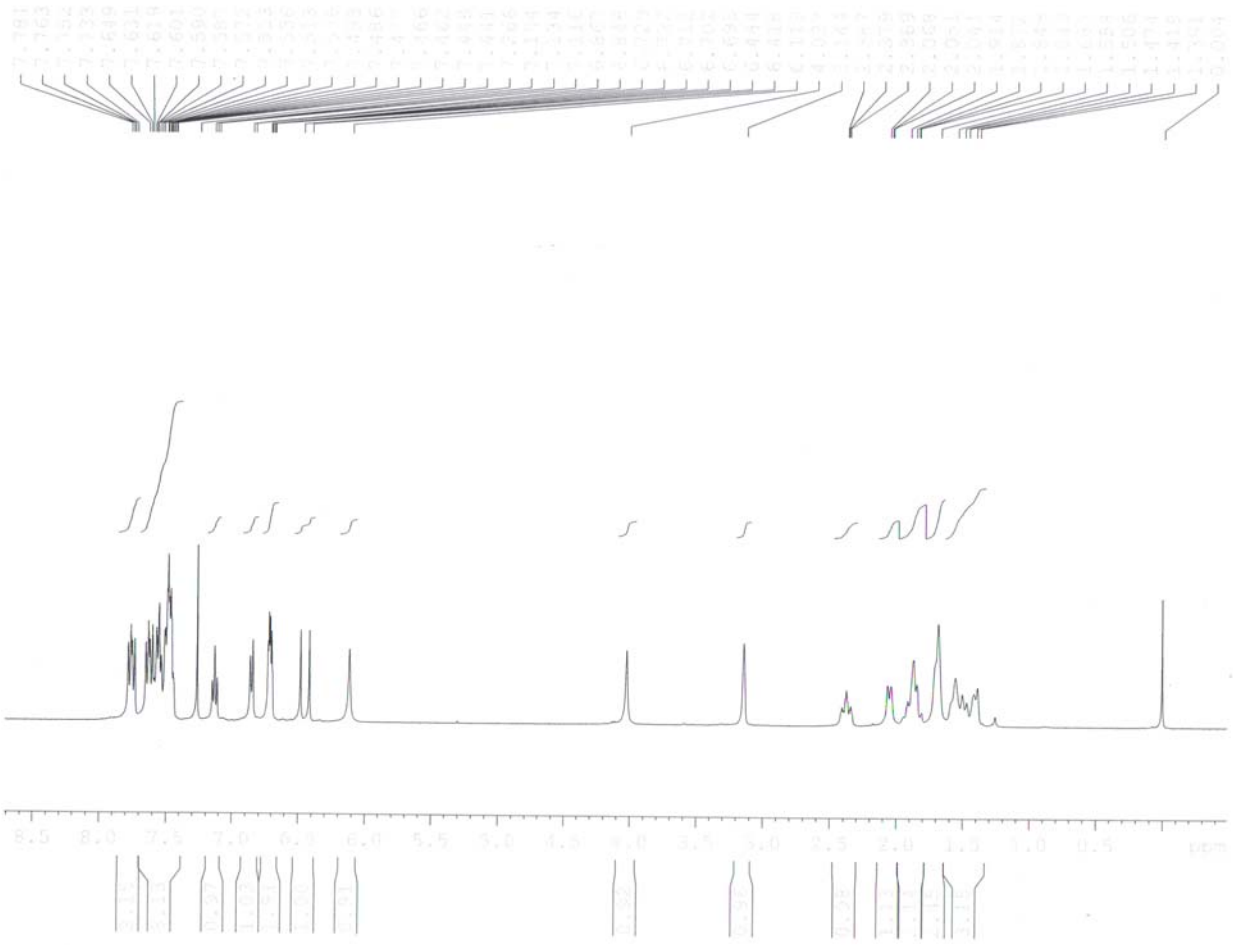


Fig. S43: ^{1}H NMR spectrum of compound **15**

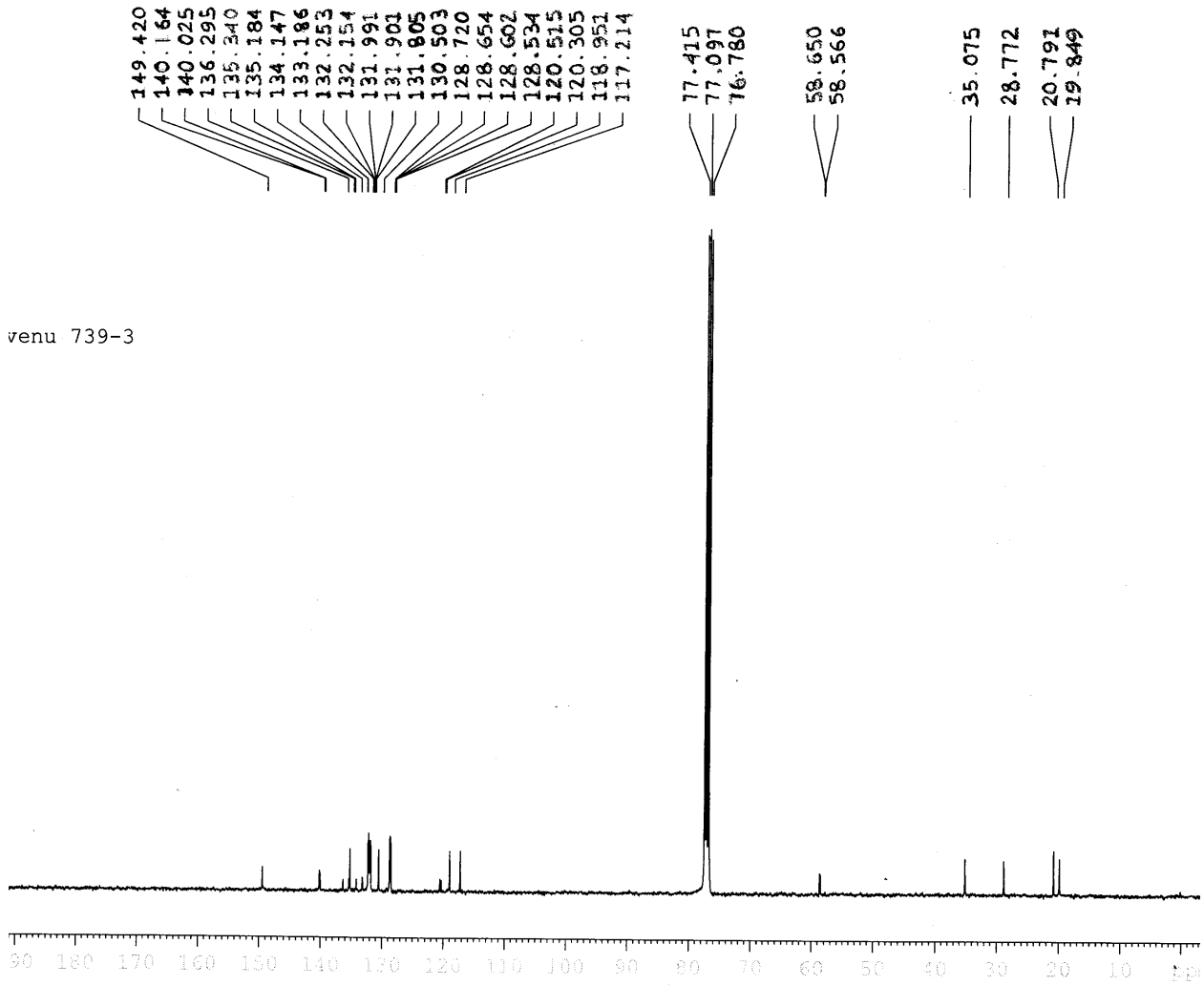


Fig. S44: ^{13}C NMR spectrum of compound **15**

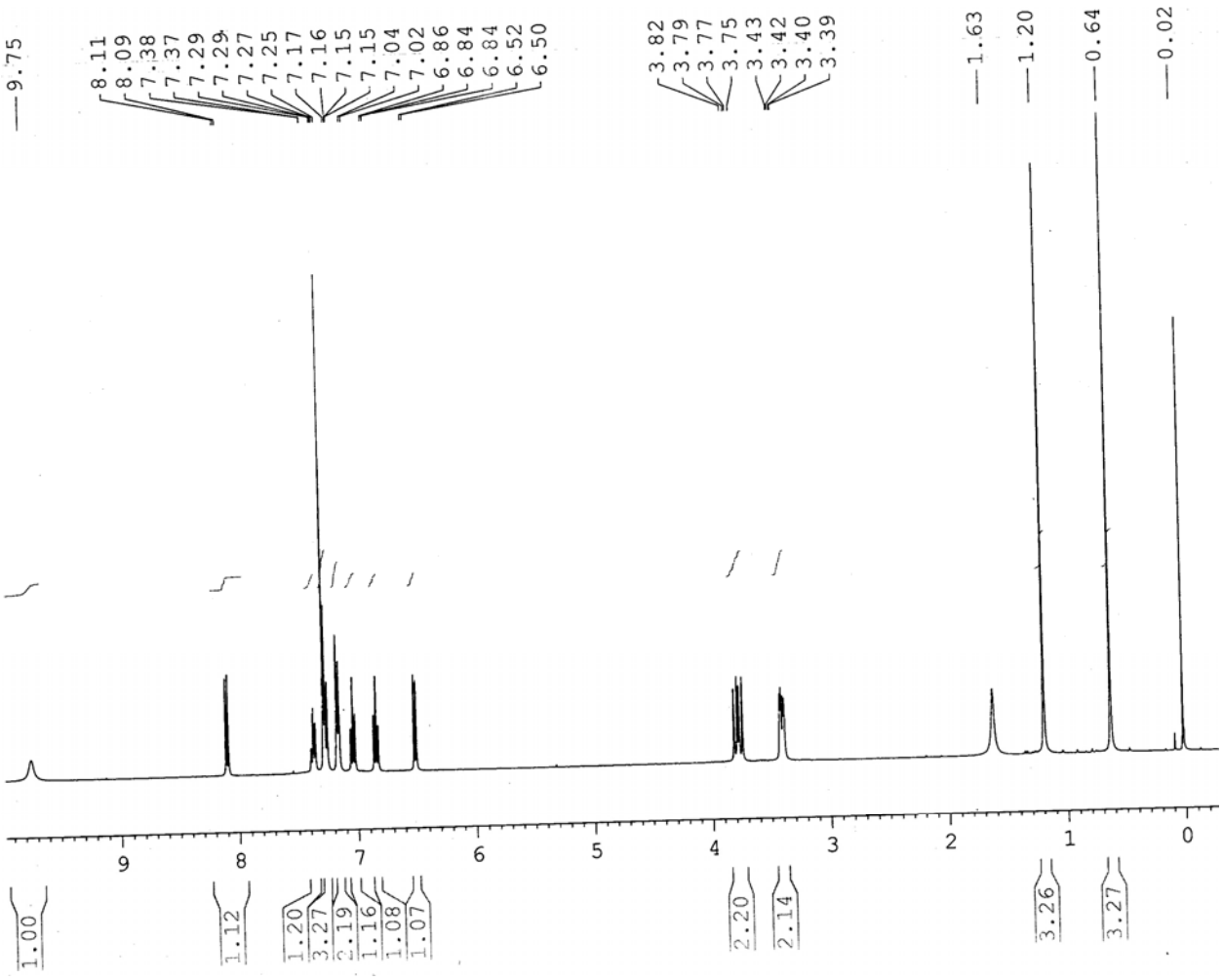


Fig. S45: ^{1}H NMR spectrum of compound **16**

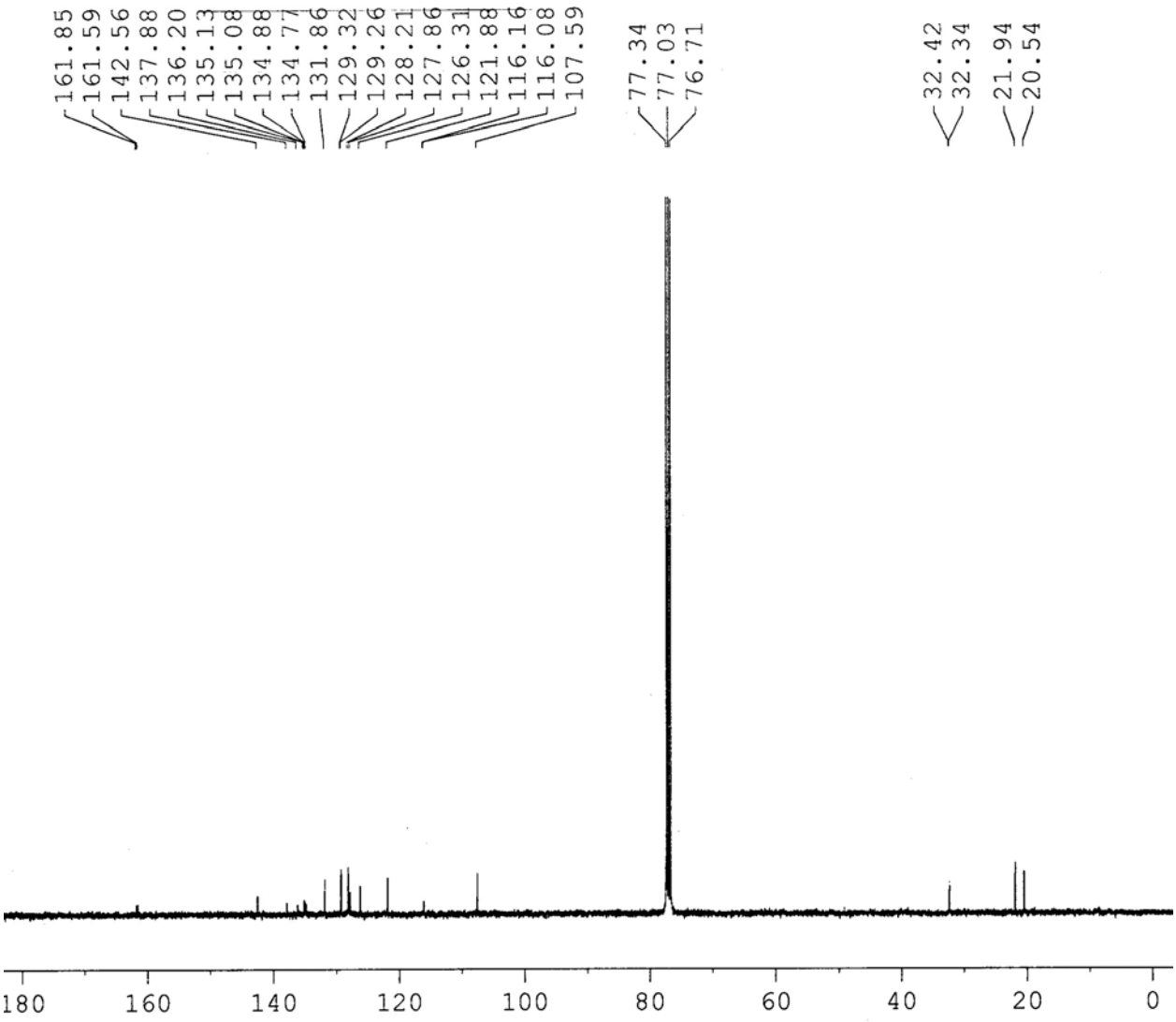


Fig. S46: ^{13}C NMR spectrum of compound **16**

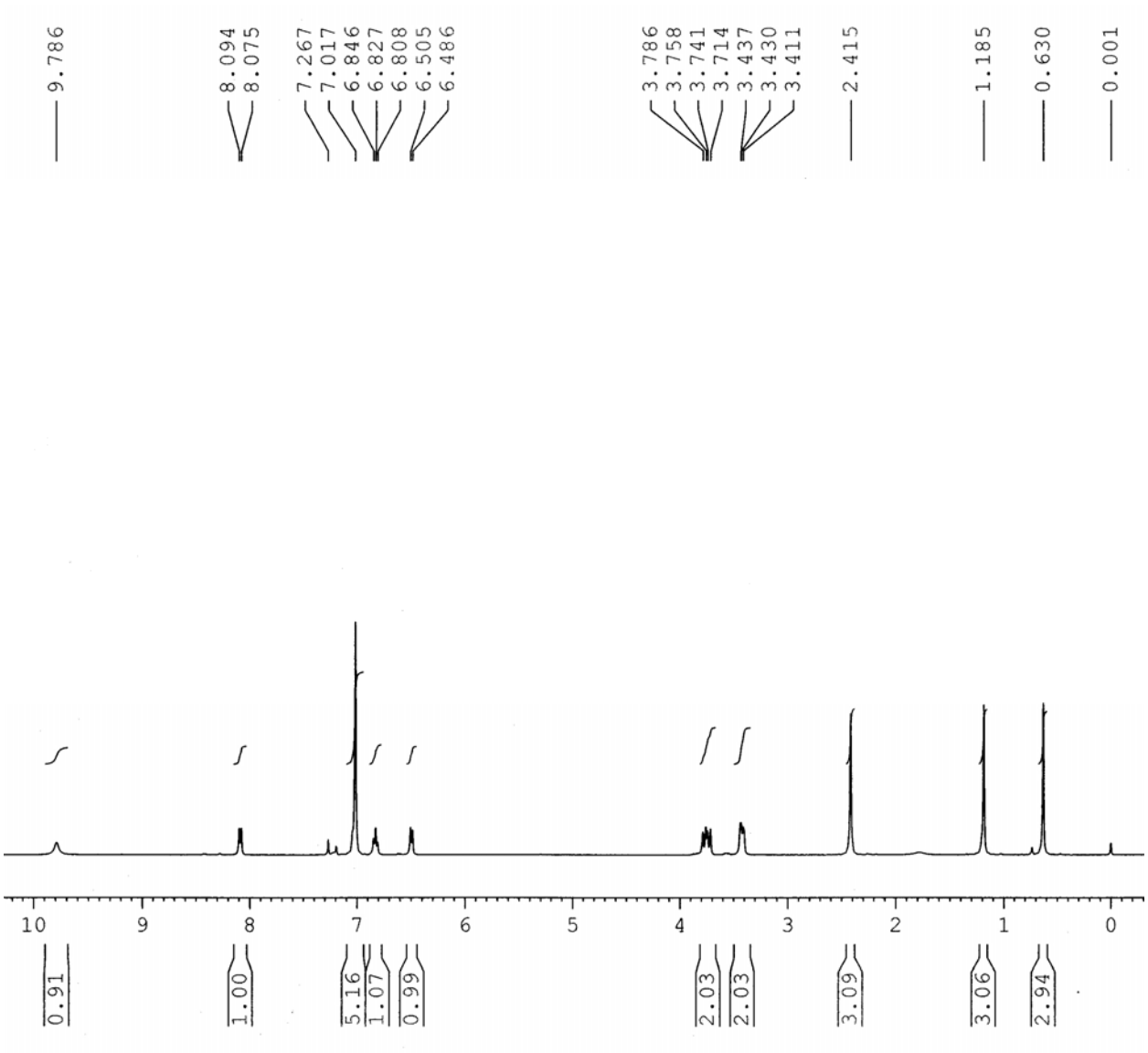


Fig. S47: ^{1}H NMR spectrum of compound **17**

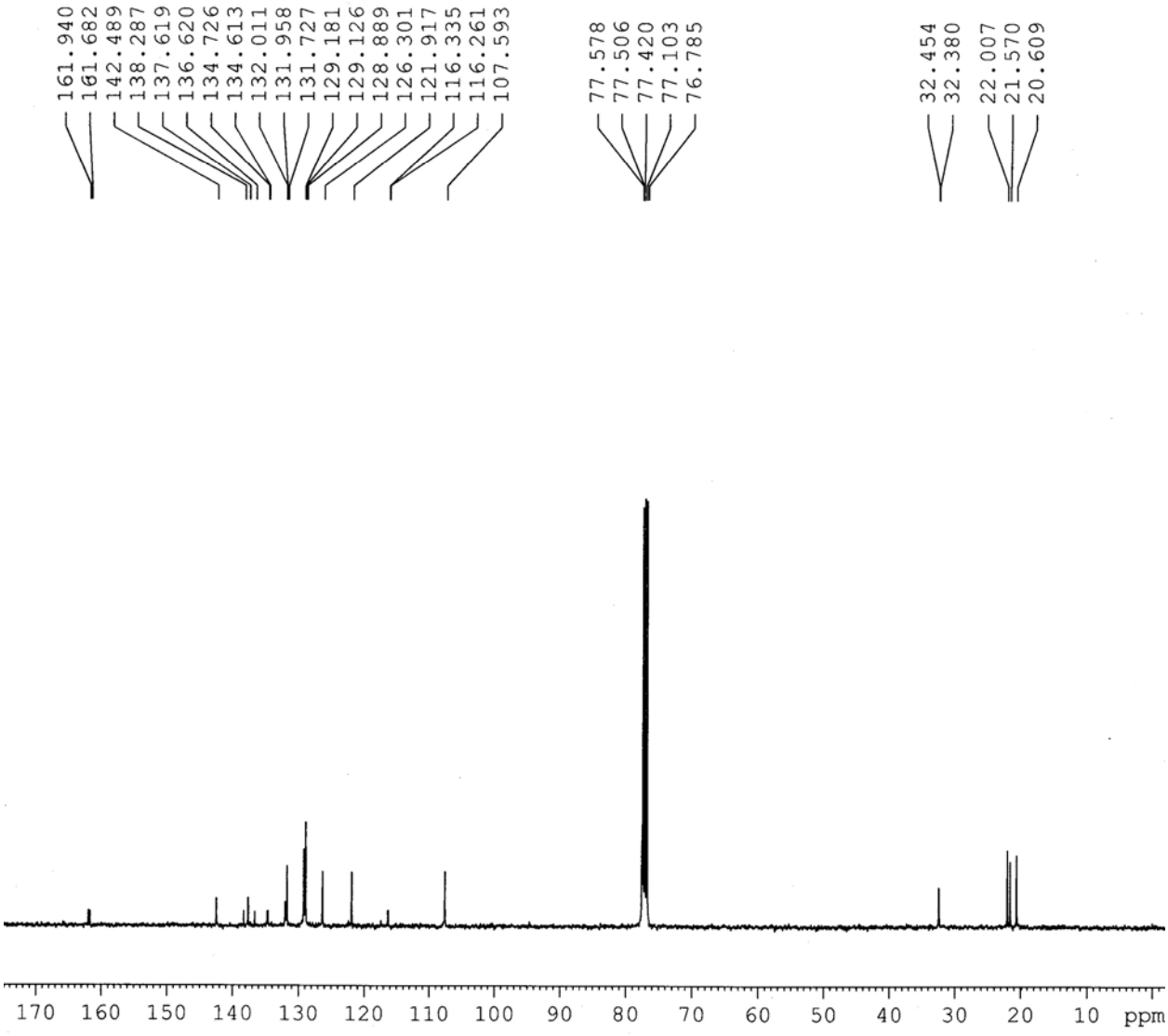


Fig. S48: ^{13}C NMR spectrum of compound **17**

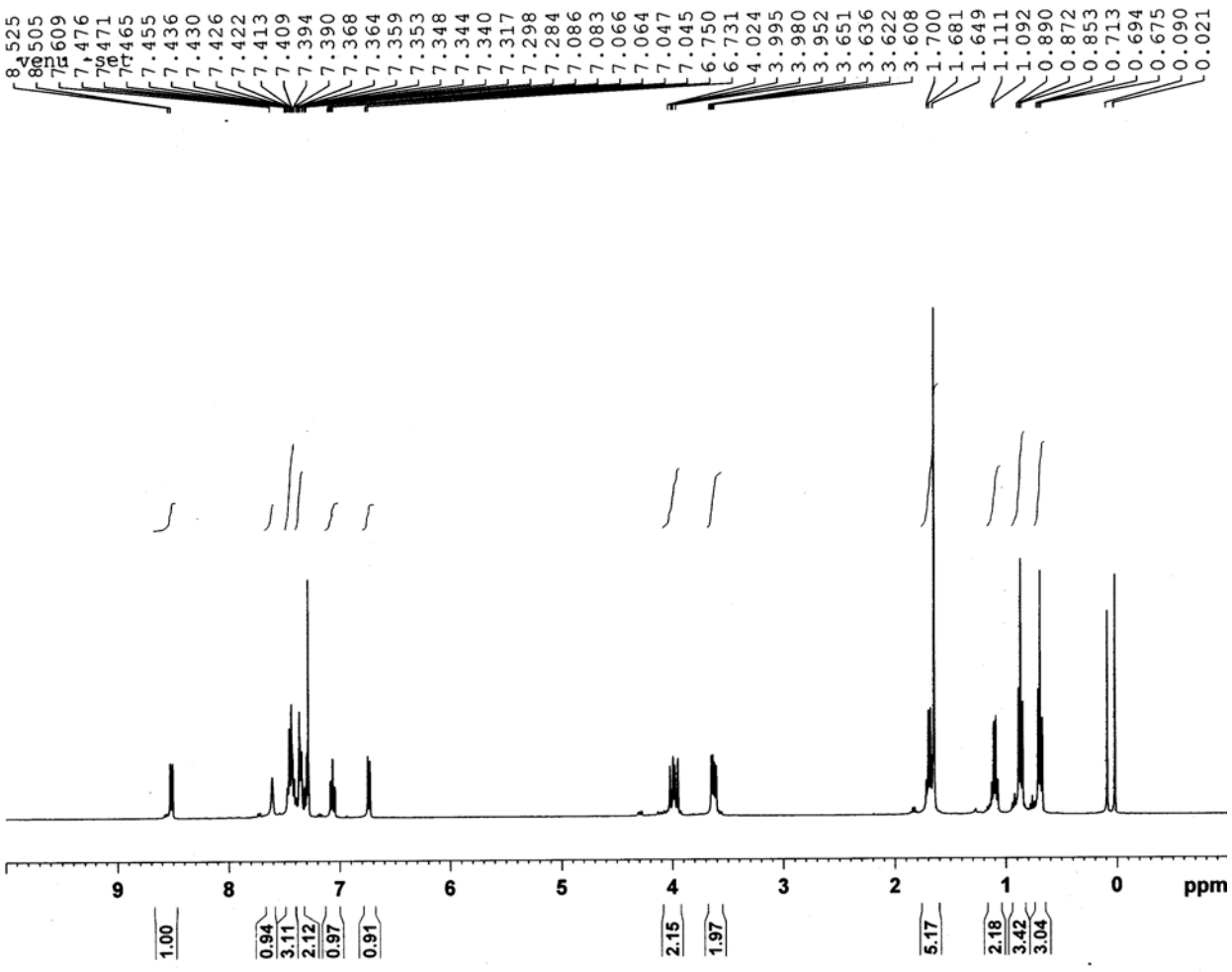


Fig. S49: ^{1}H NMR spectrum of compound **18**

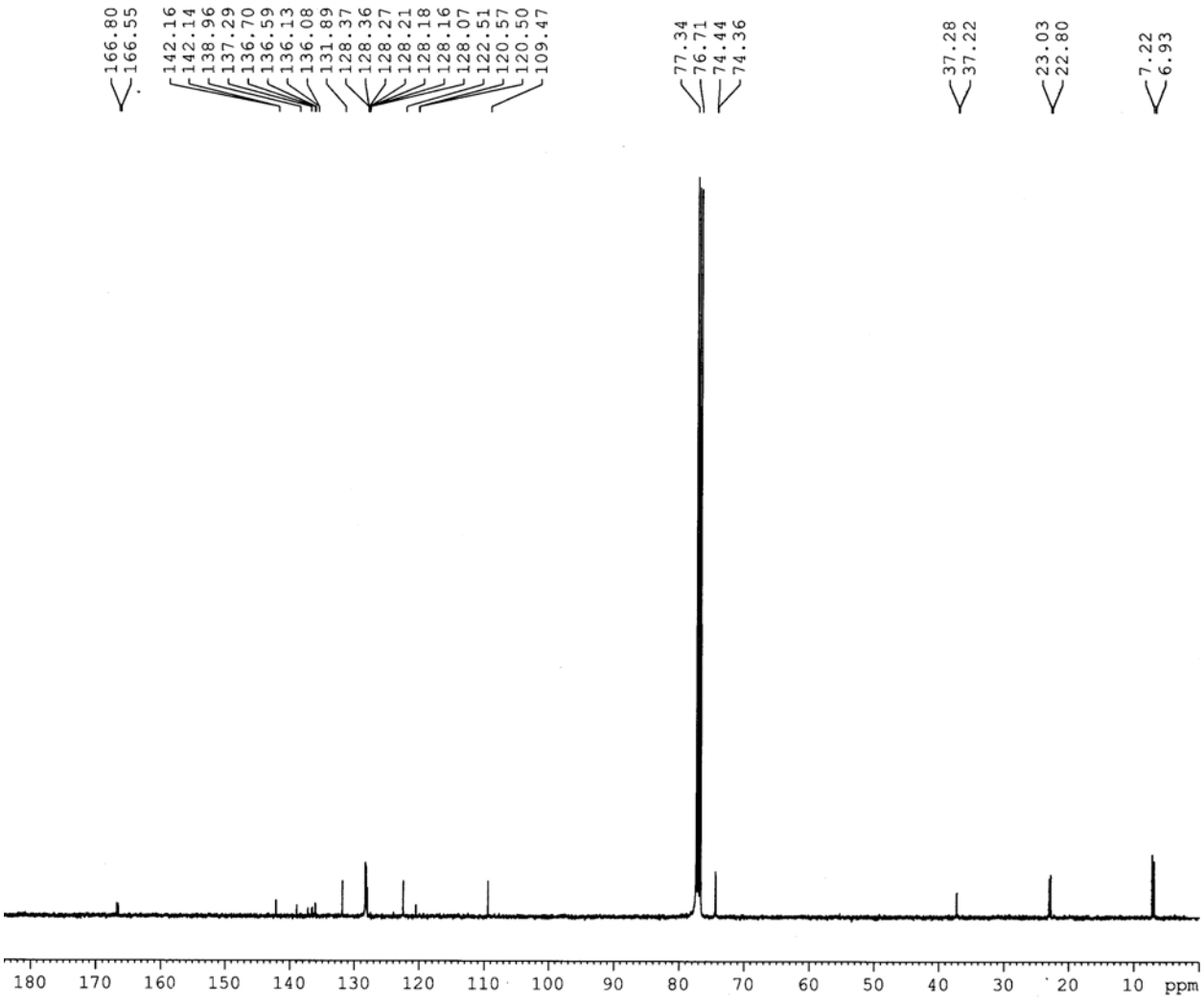


Fig. S50: ^{13}C NMR spectrum of compound **18**

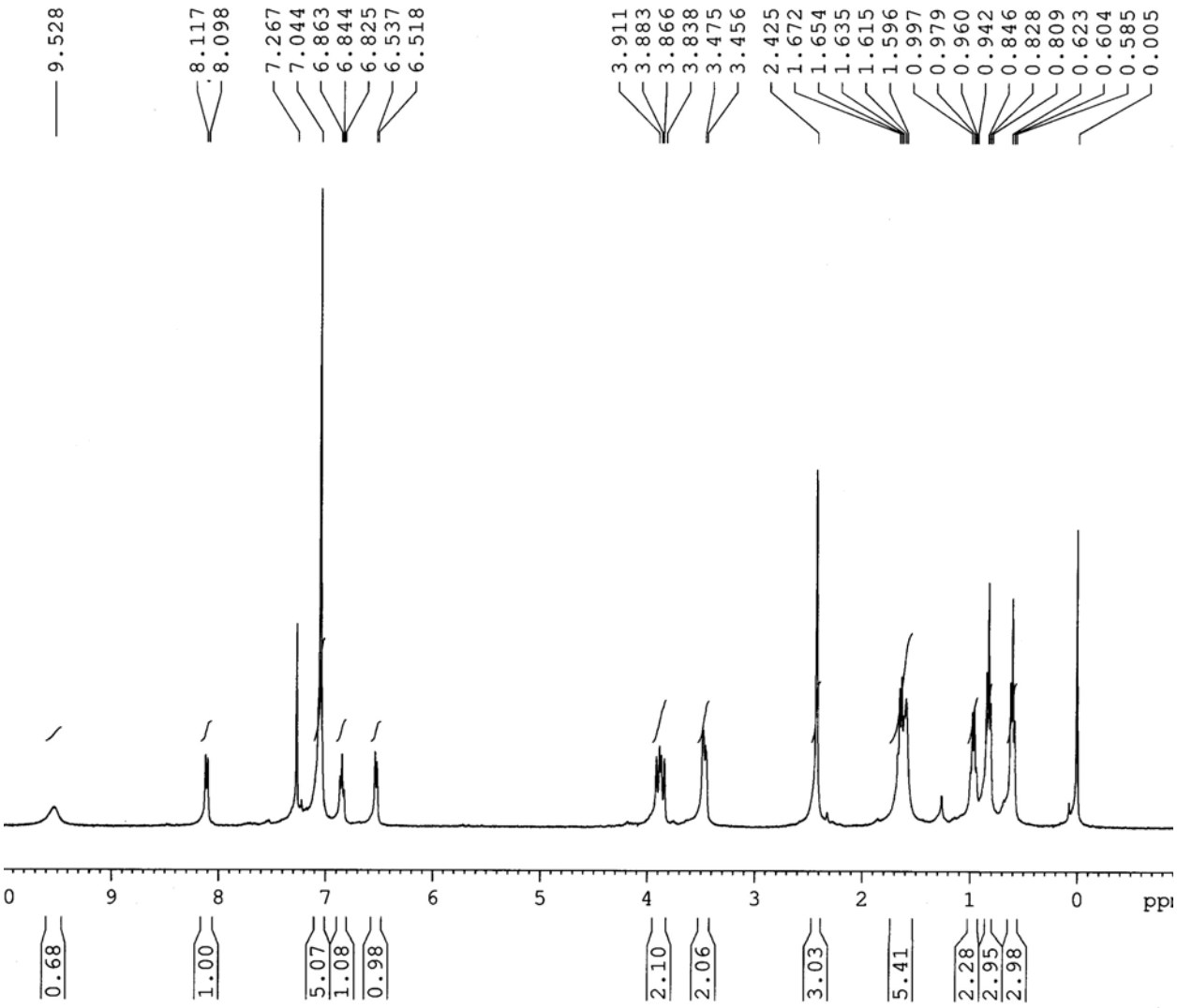


Fig. S51: ^{1}H NMR spectrum of compound **19**

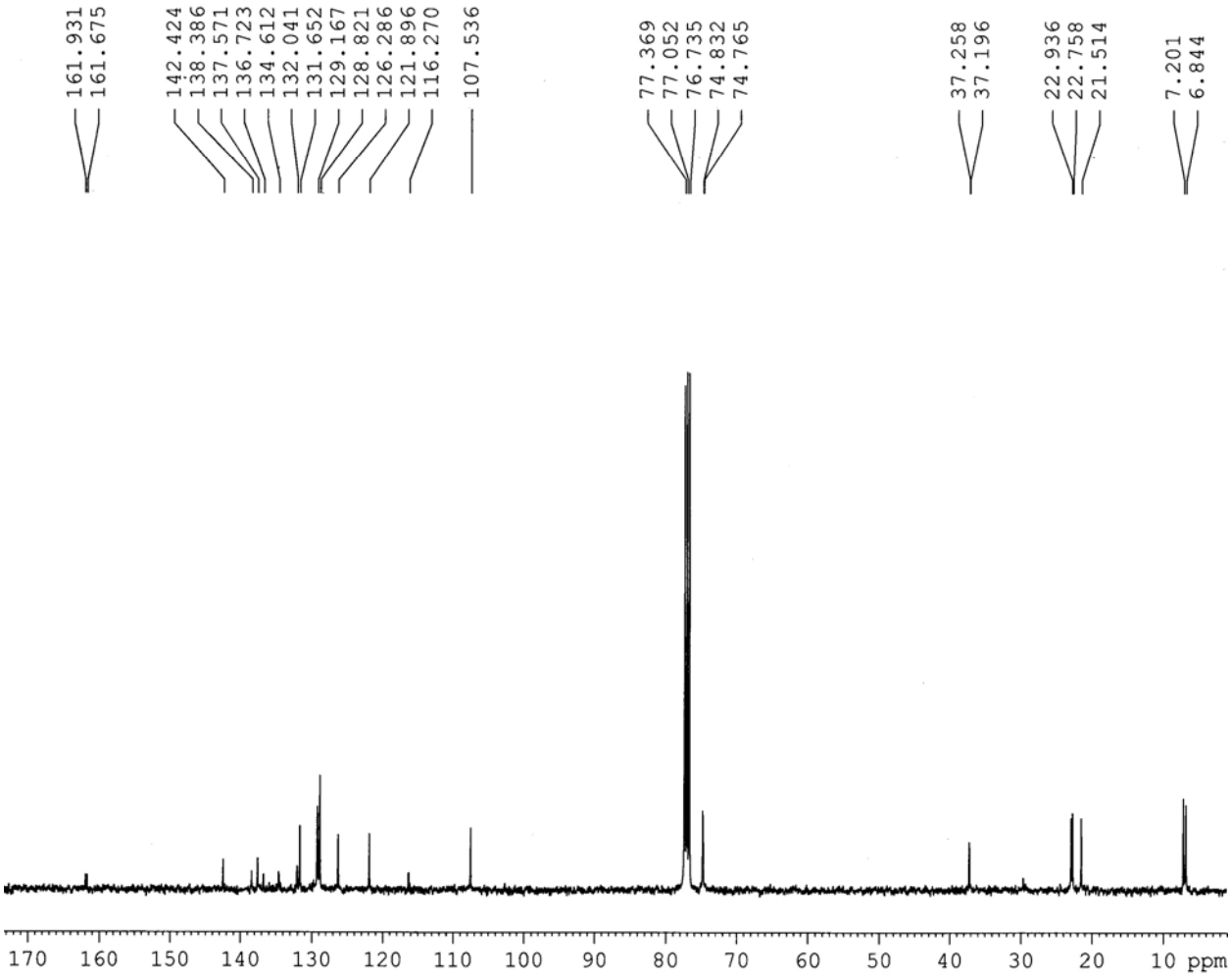


Fig. S52: ^{13}C NMR spectrum of compound **19**

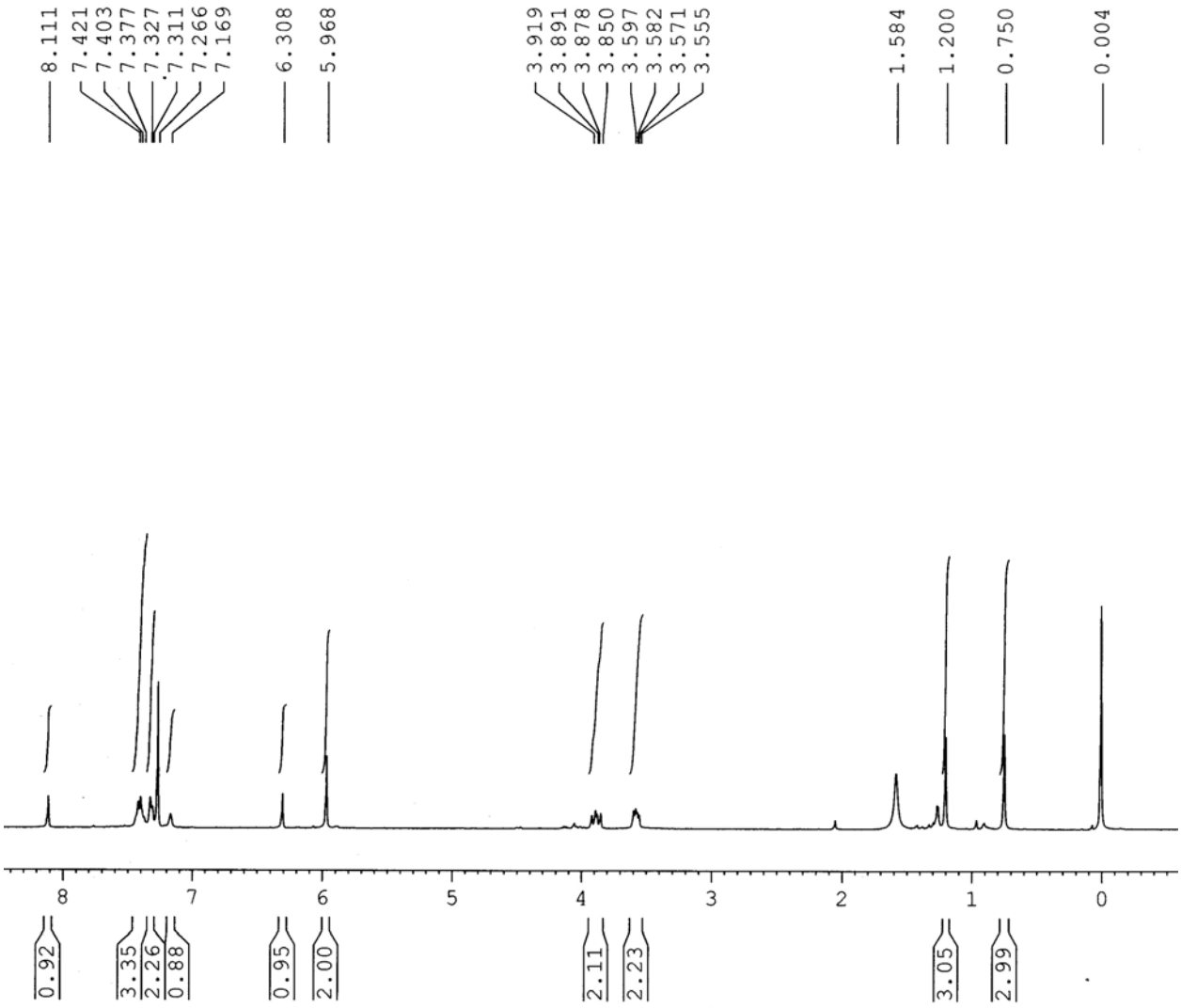


Fig. S53: ^{1}H NMR spectrum of compound **20**

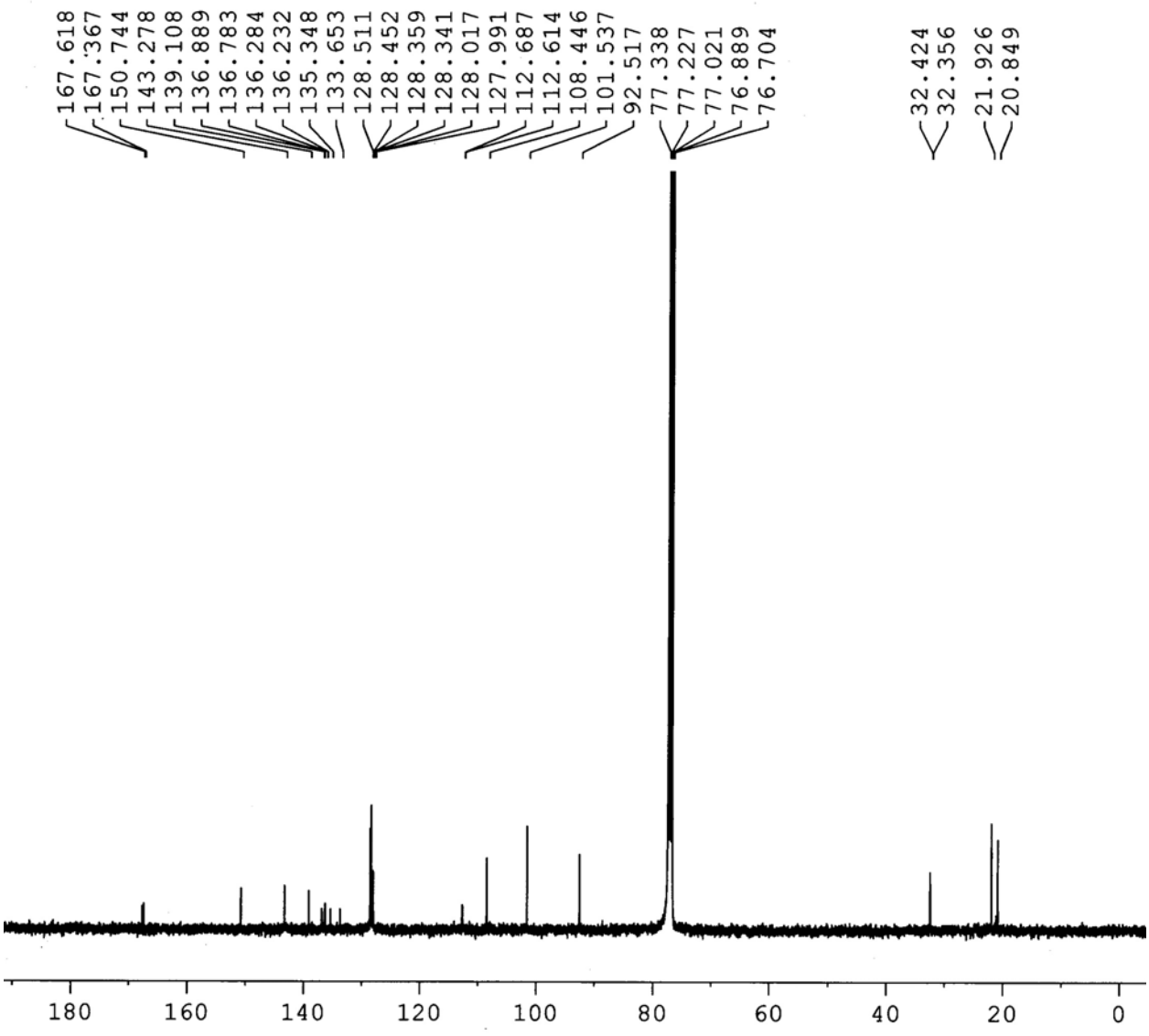


Fig. S54: ^{13}C NMR spectrum of compound **20**

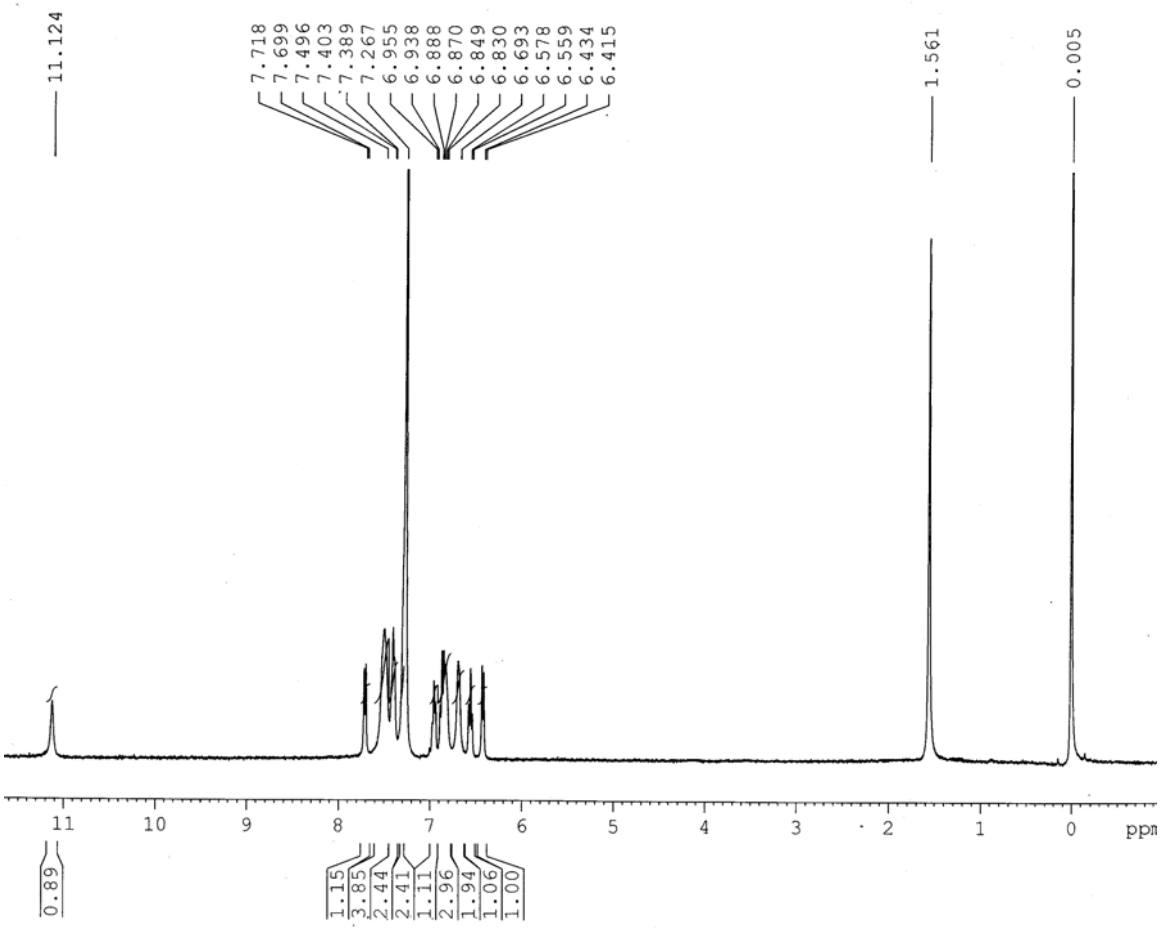


Fig. S55: ^{1}H NMR spectrum of compound **21**

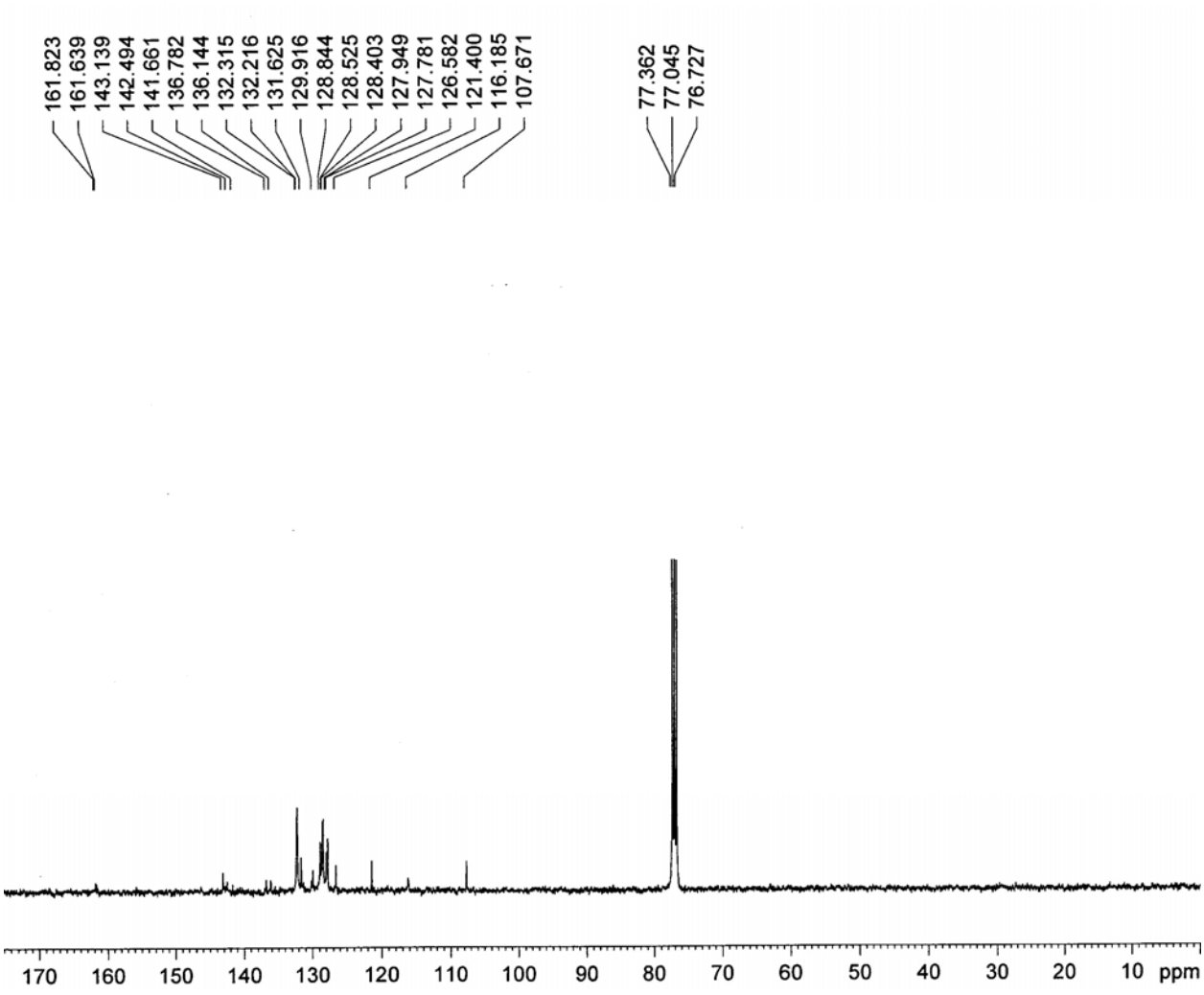


Fig. S56: ^{13}C NMR spectrum of compound **21**

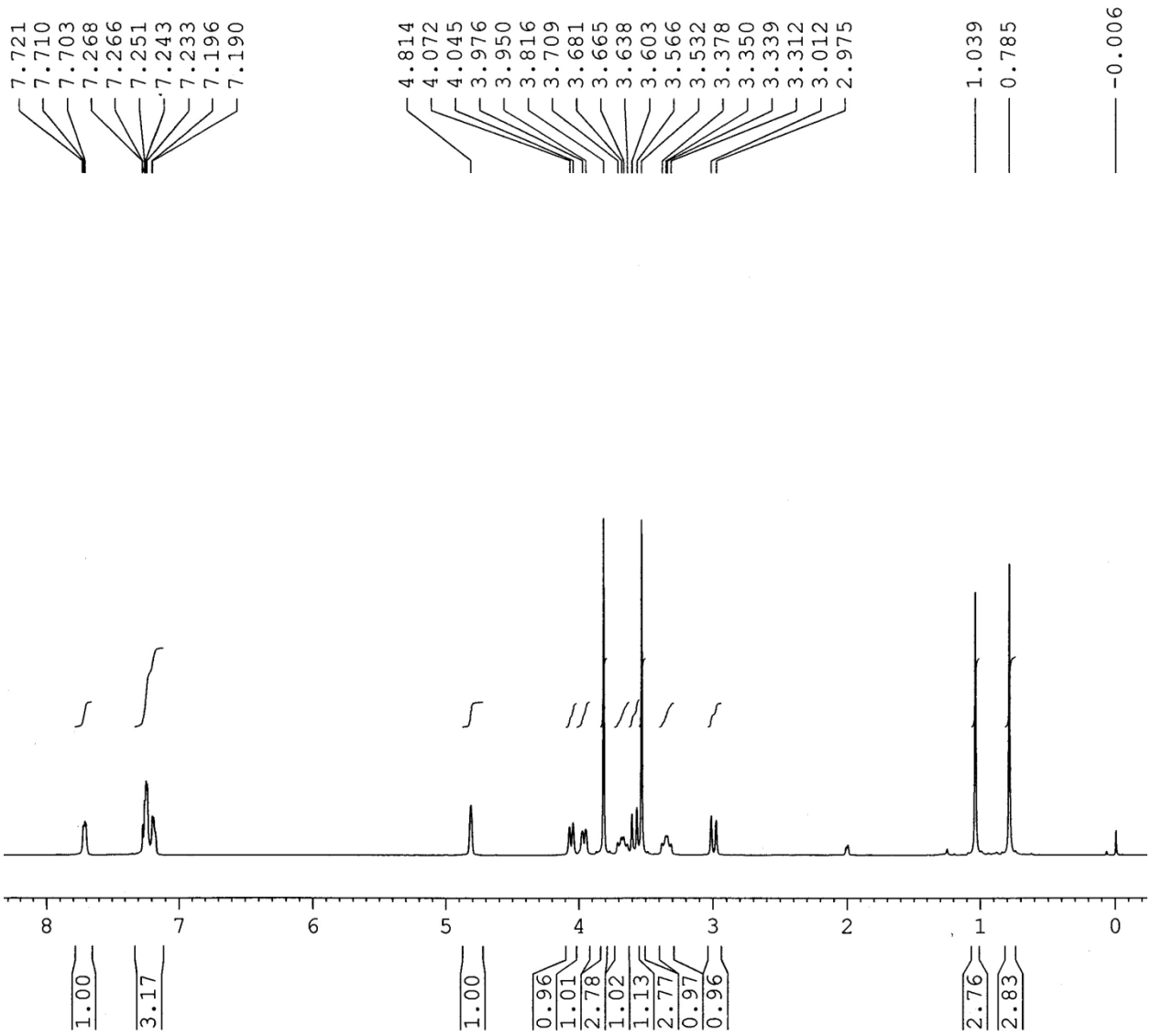


Fig. S57: ^{1}H NMR spectrum of compound **22**

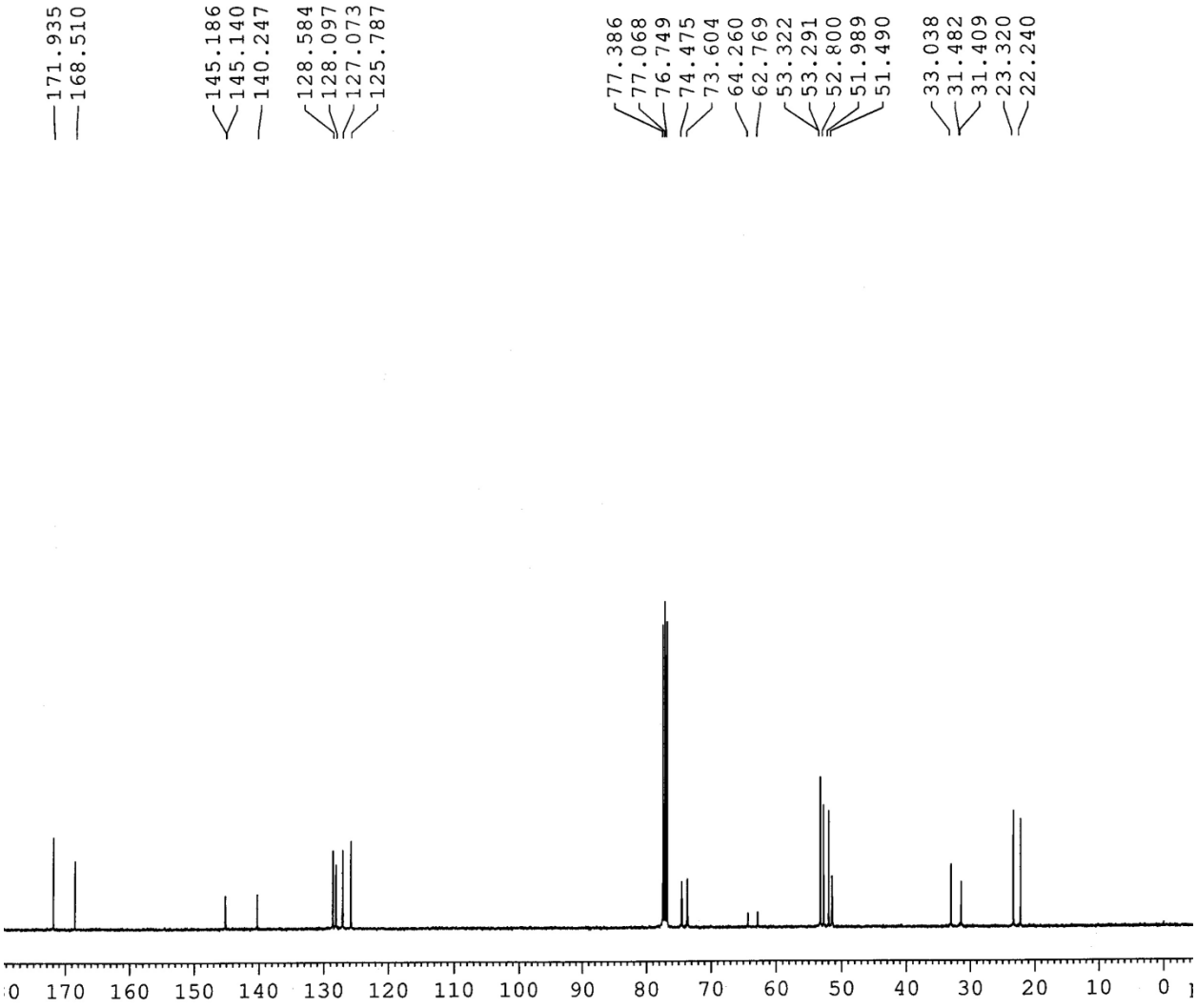


Fig. S58: ^{13}C NMR spectrum of compound **22**

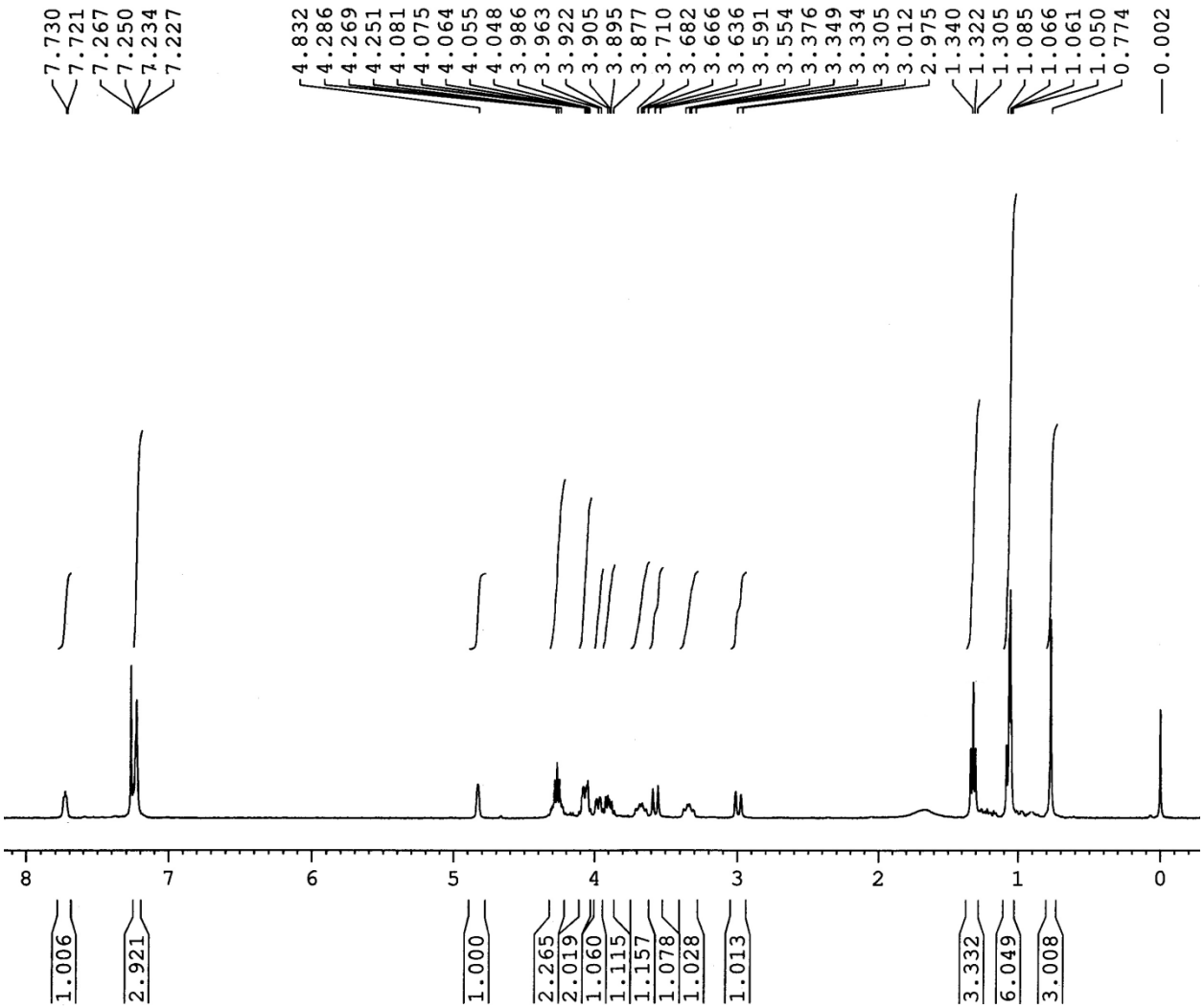


Fig. S59: ^{1}H NMR spectrum of compound **23**

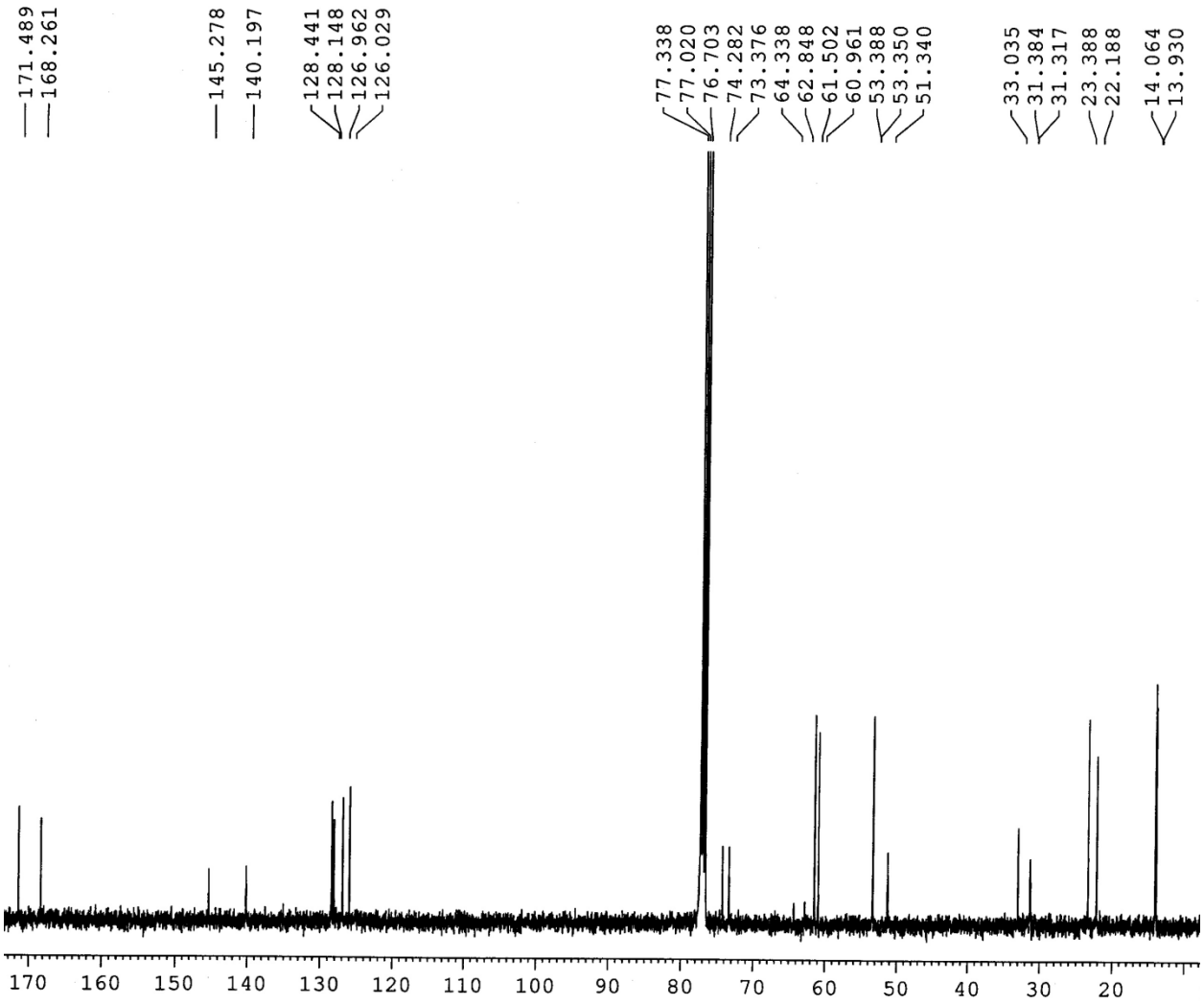


Fig. S60: ^{13}C NMR spectrum of compound **23**

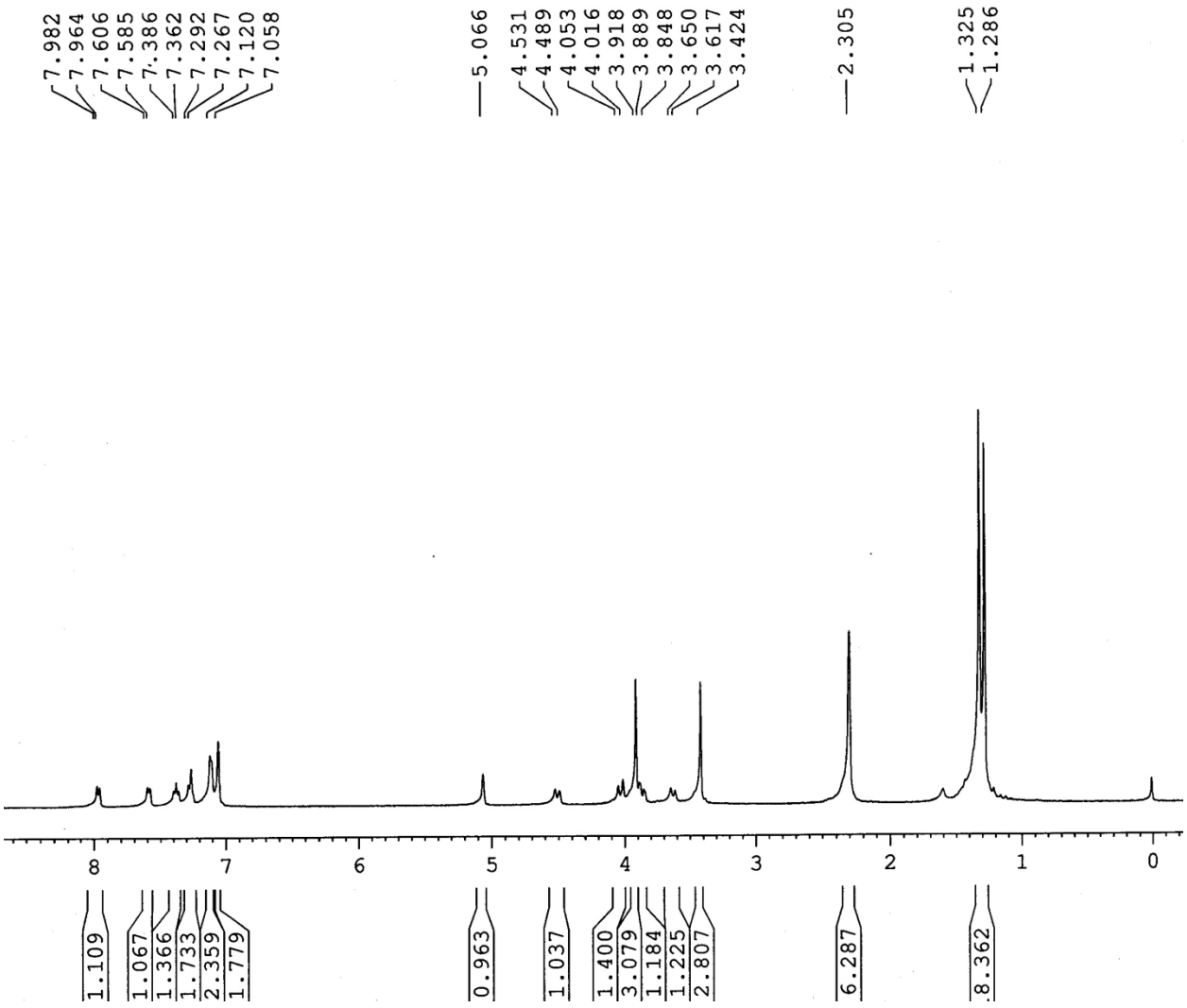


Fig. S61: ^{1}H NMR spectrum of compound **24**

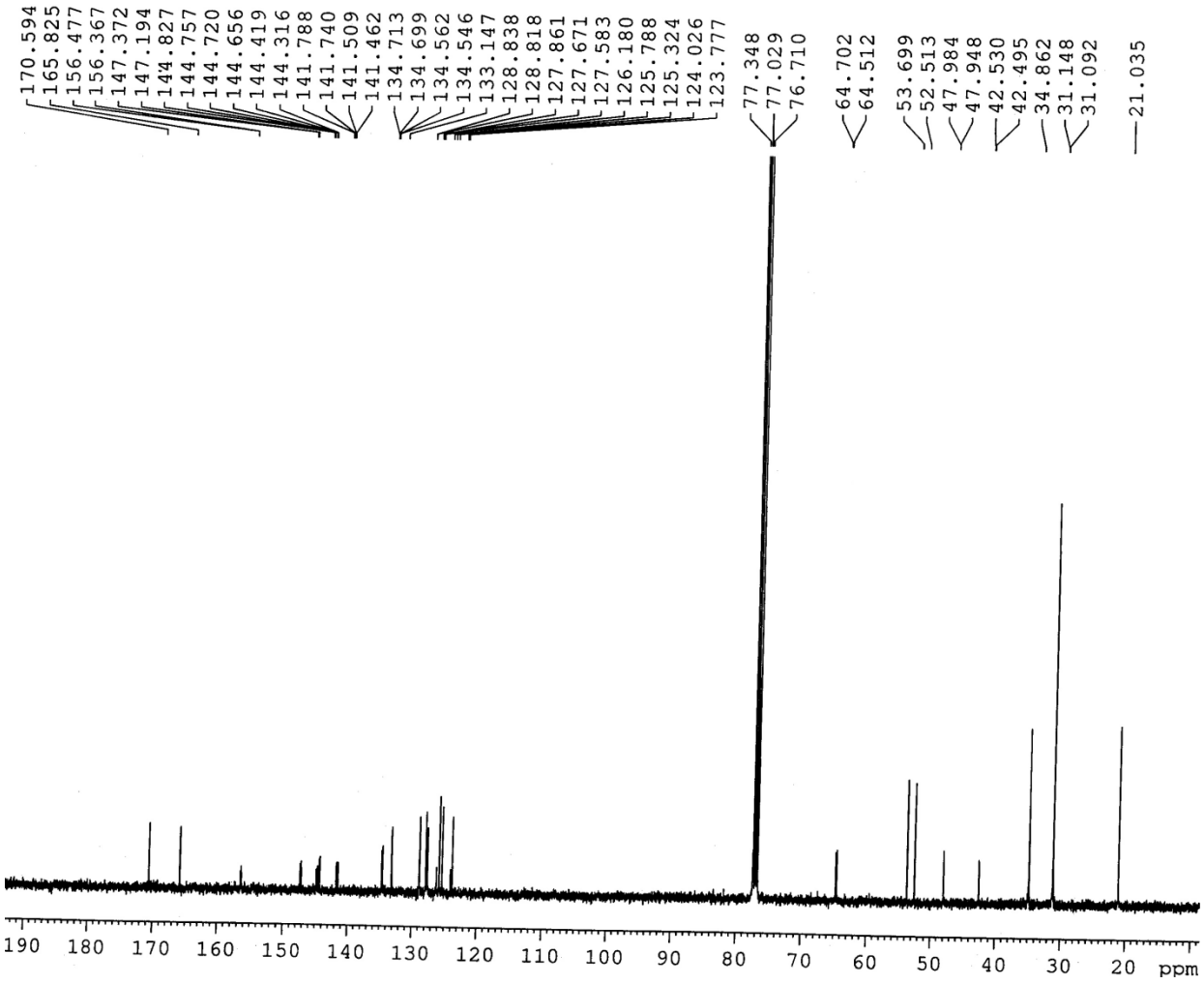


Fig. S62: ^{13}C NMR spectrum of compound **24**

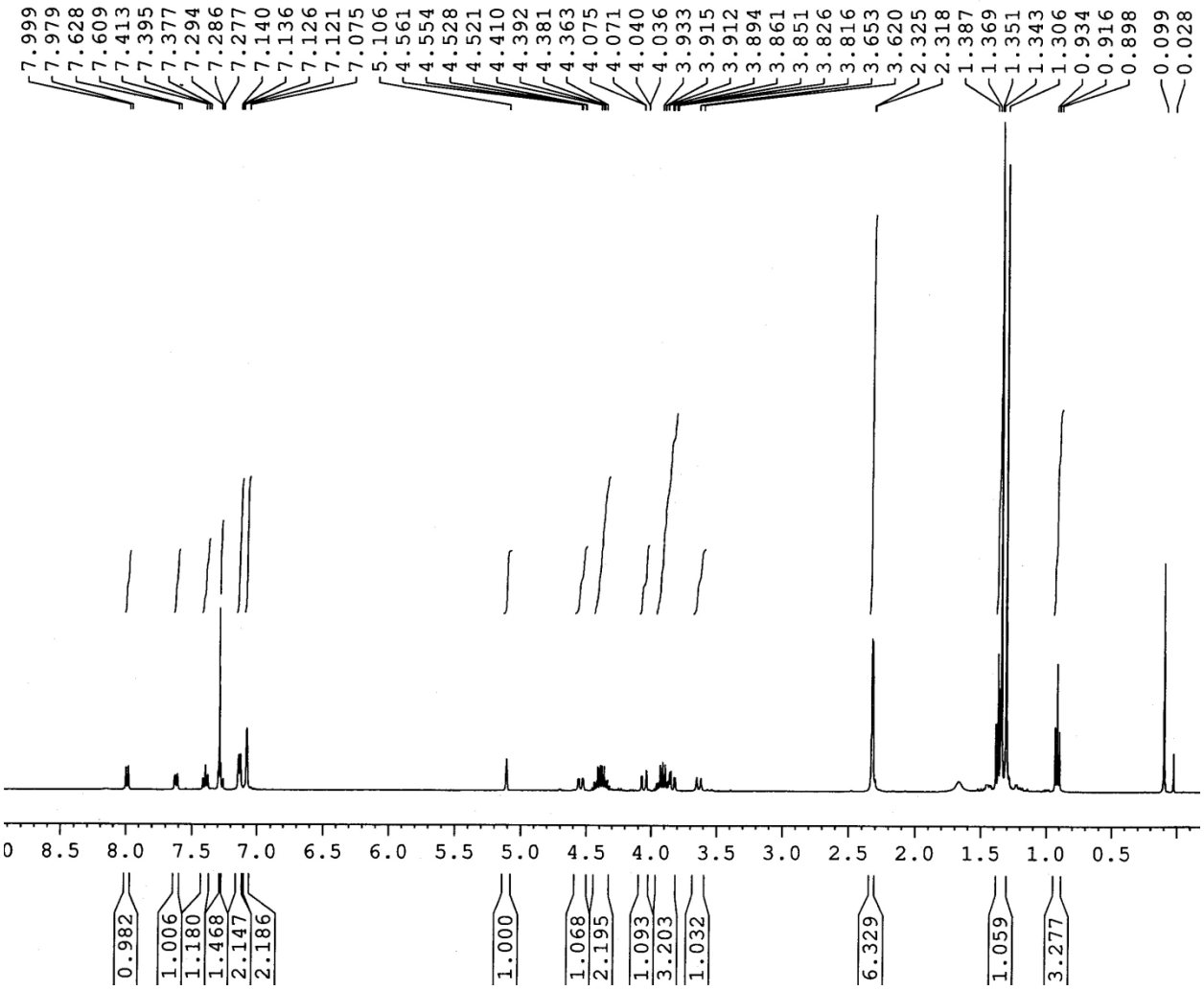


Fig. S63: ^{1}H NMR spectrum of compound **25**

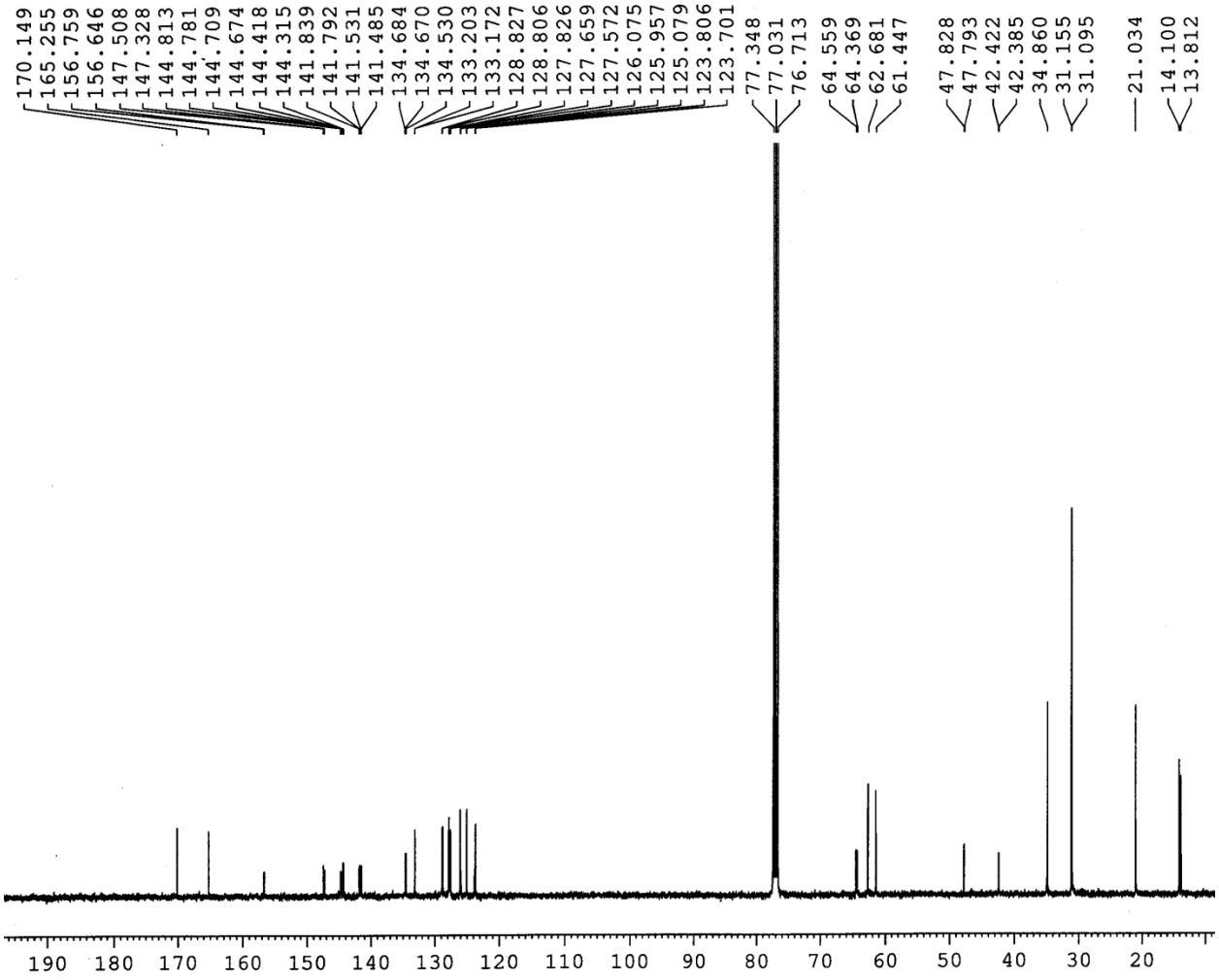


Fig. S64: ^{13}C NMR spectrum of compound **25**

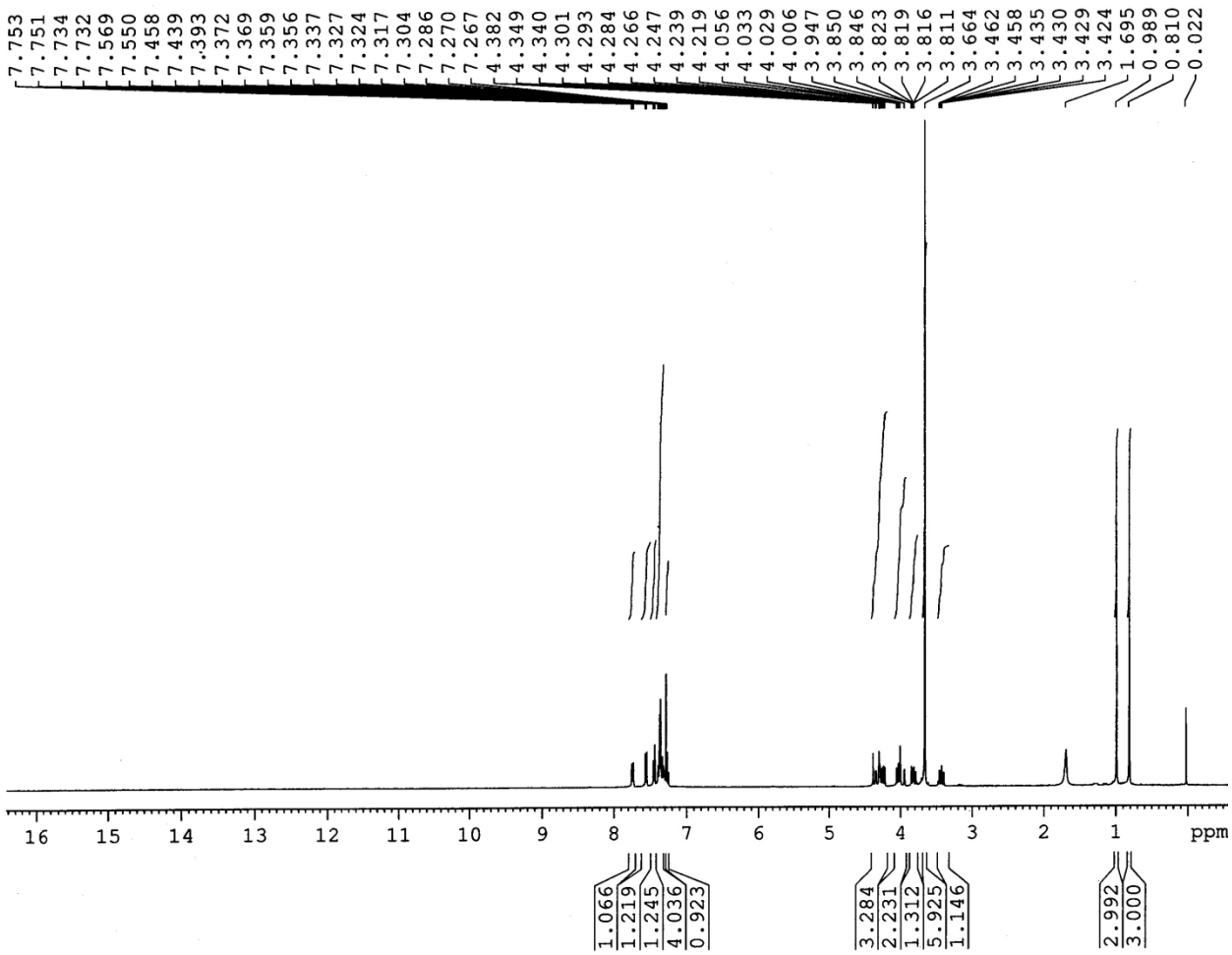


Fig. S65: ^{1}H NMR spectrum of compound **26**

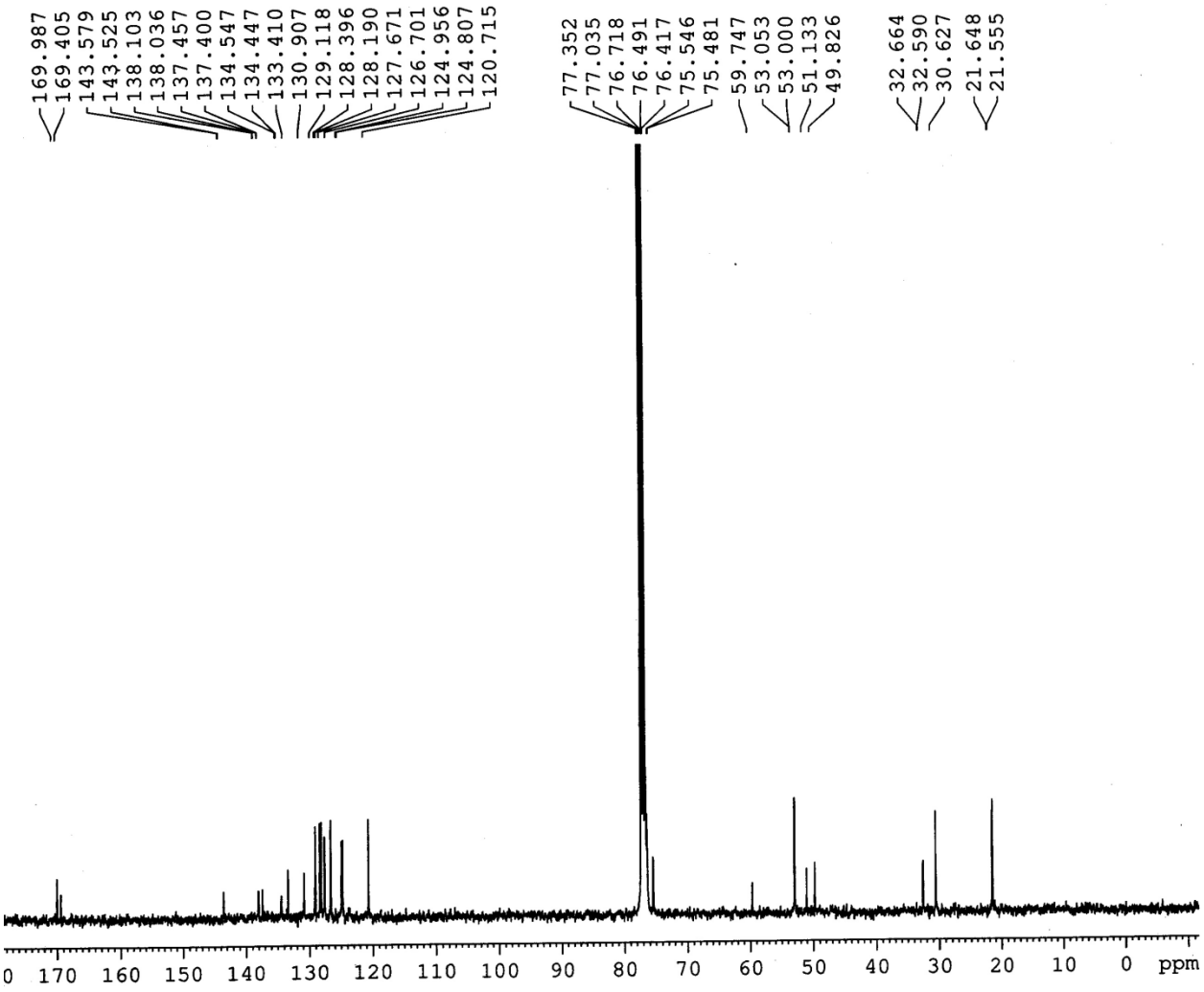


Fig. S66: ^{13}C NMR spectrum of compound **26**

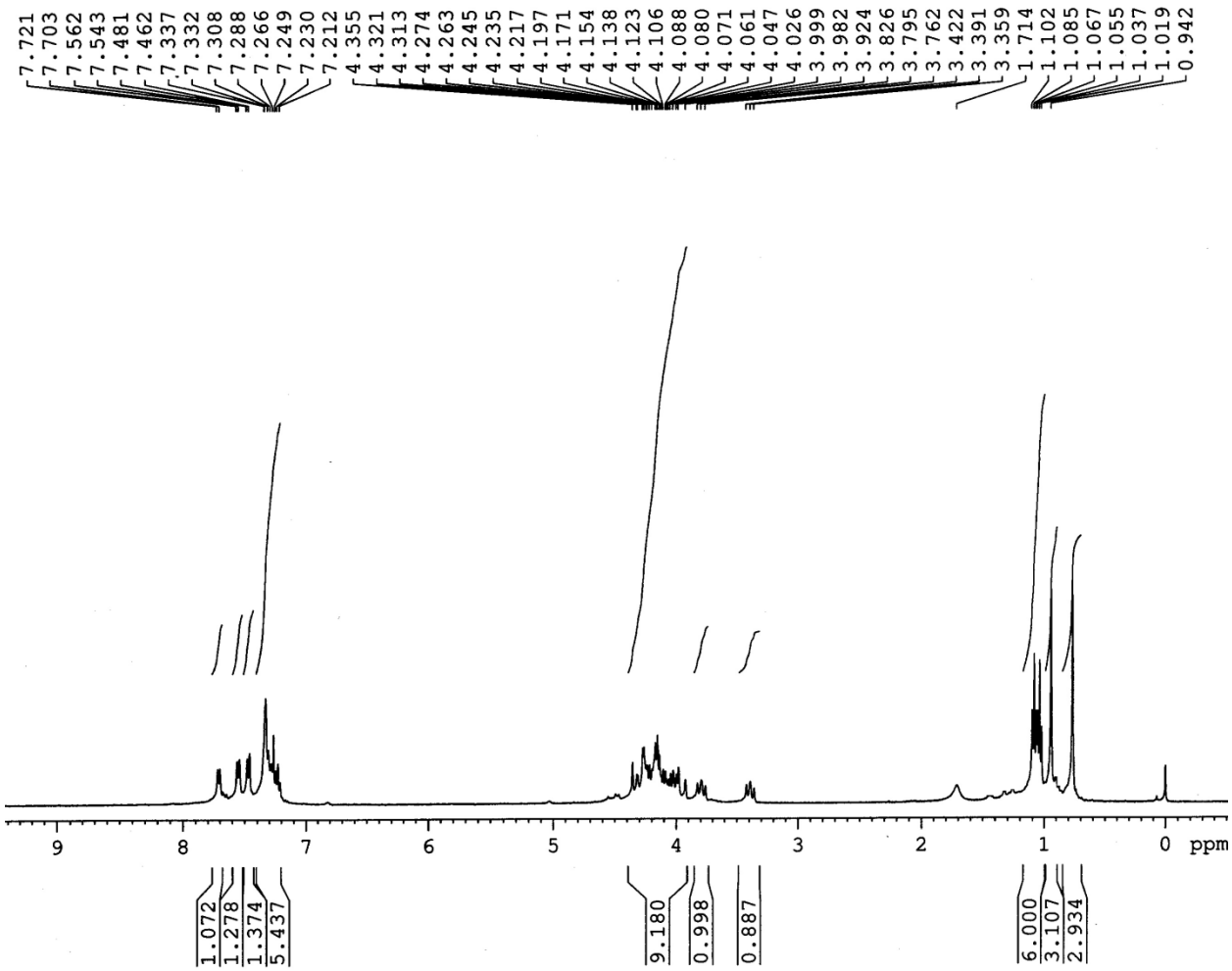


Fig. S67: ^{1}H NMR spectrum spectrum of compound **27**

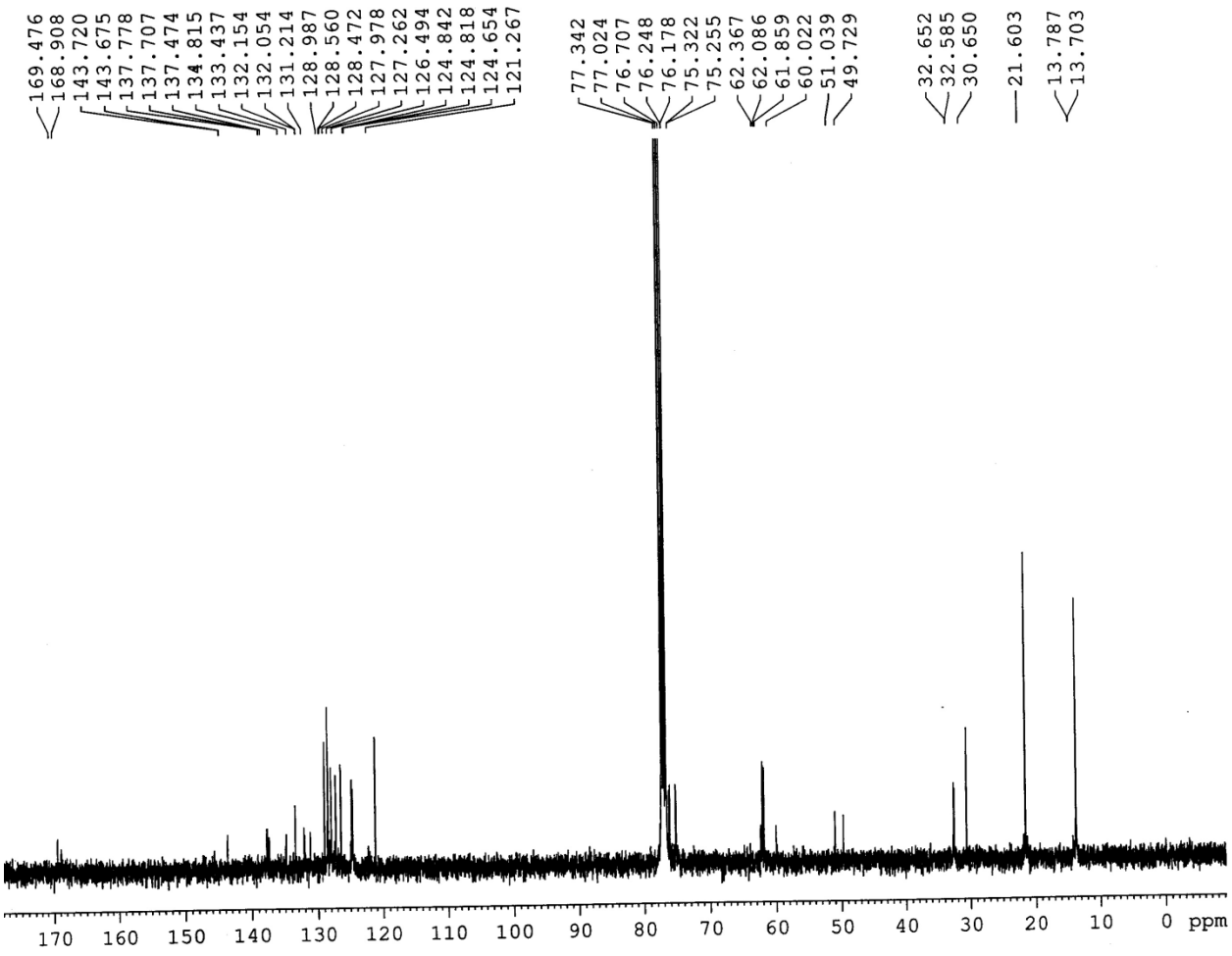


Fig. S68: ^{13}C NMR spectrum of compound **27**

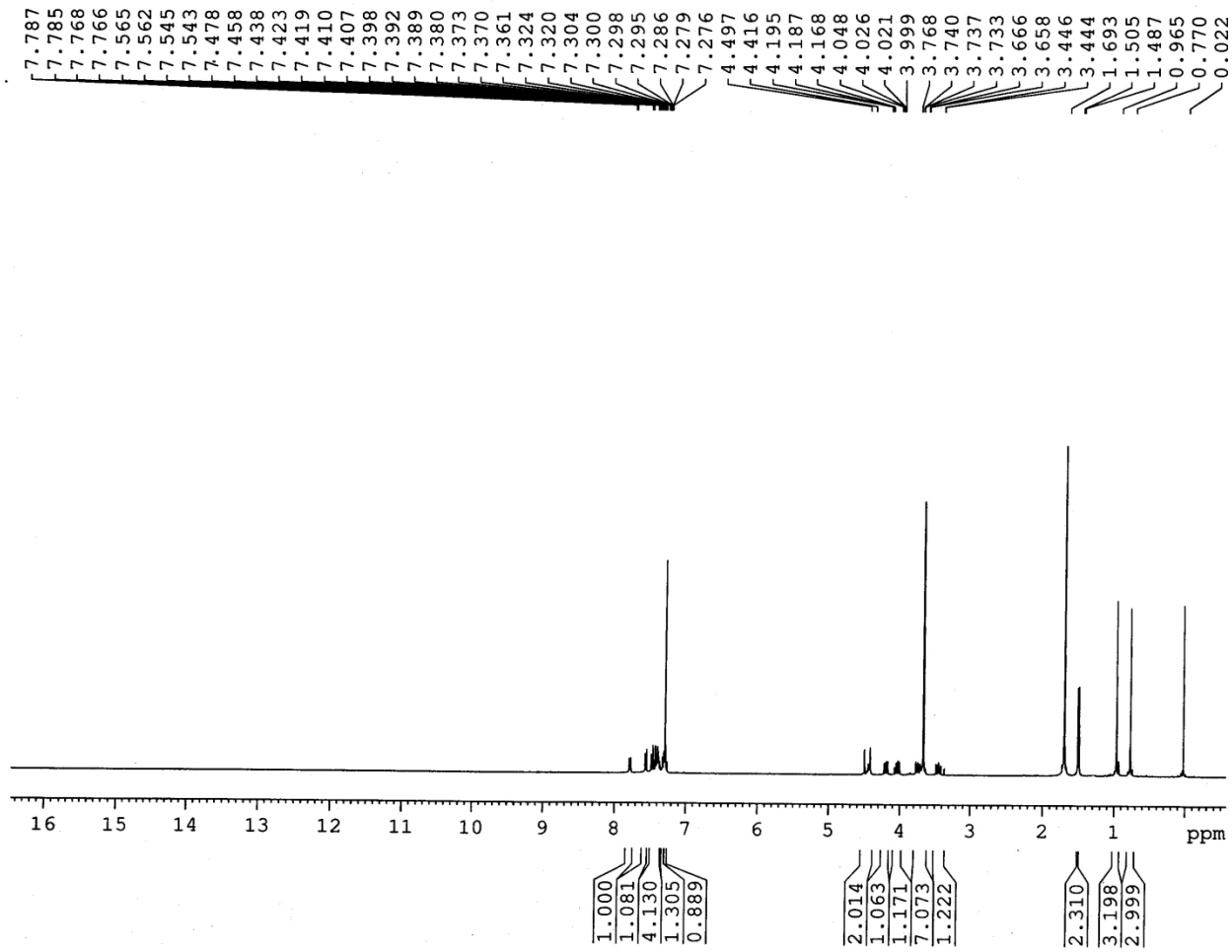


Fig. S69: ^{1}H NMR spectrum of compound **28**

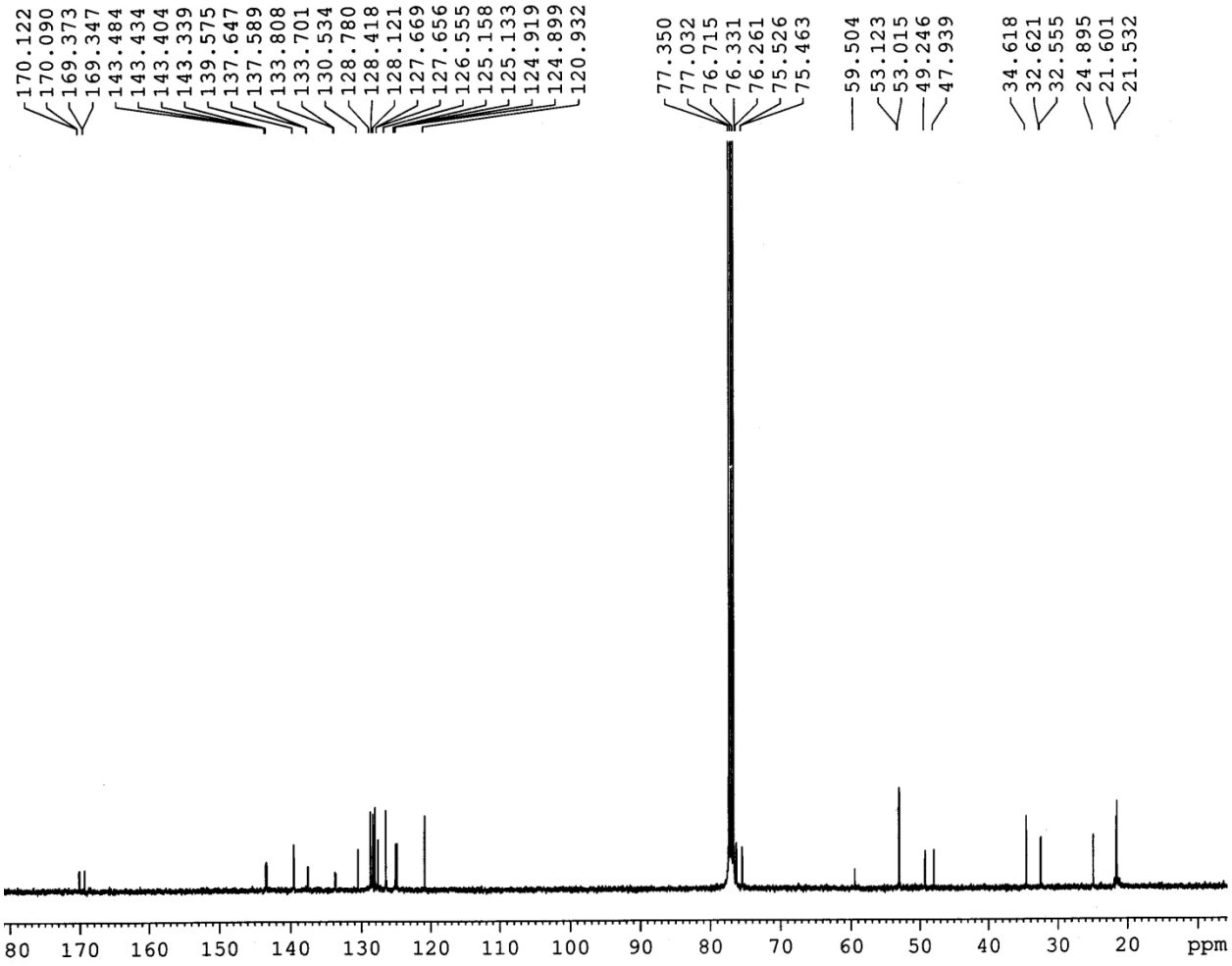


Fig. S70: ^{13}C NMR spectrum of compound **28**

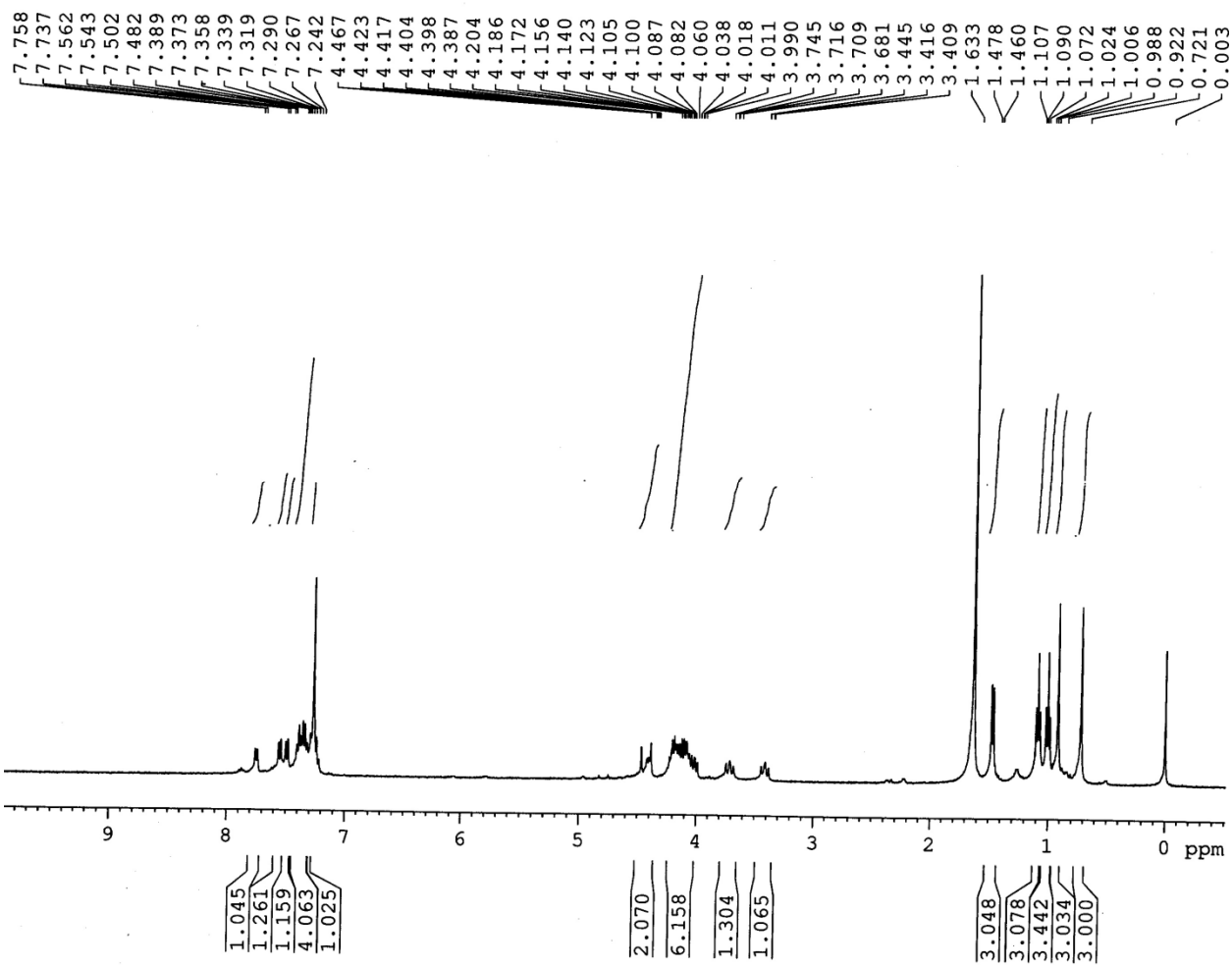


Fig. S71: ^{1}H NMR spectrum of compound **29**

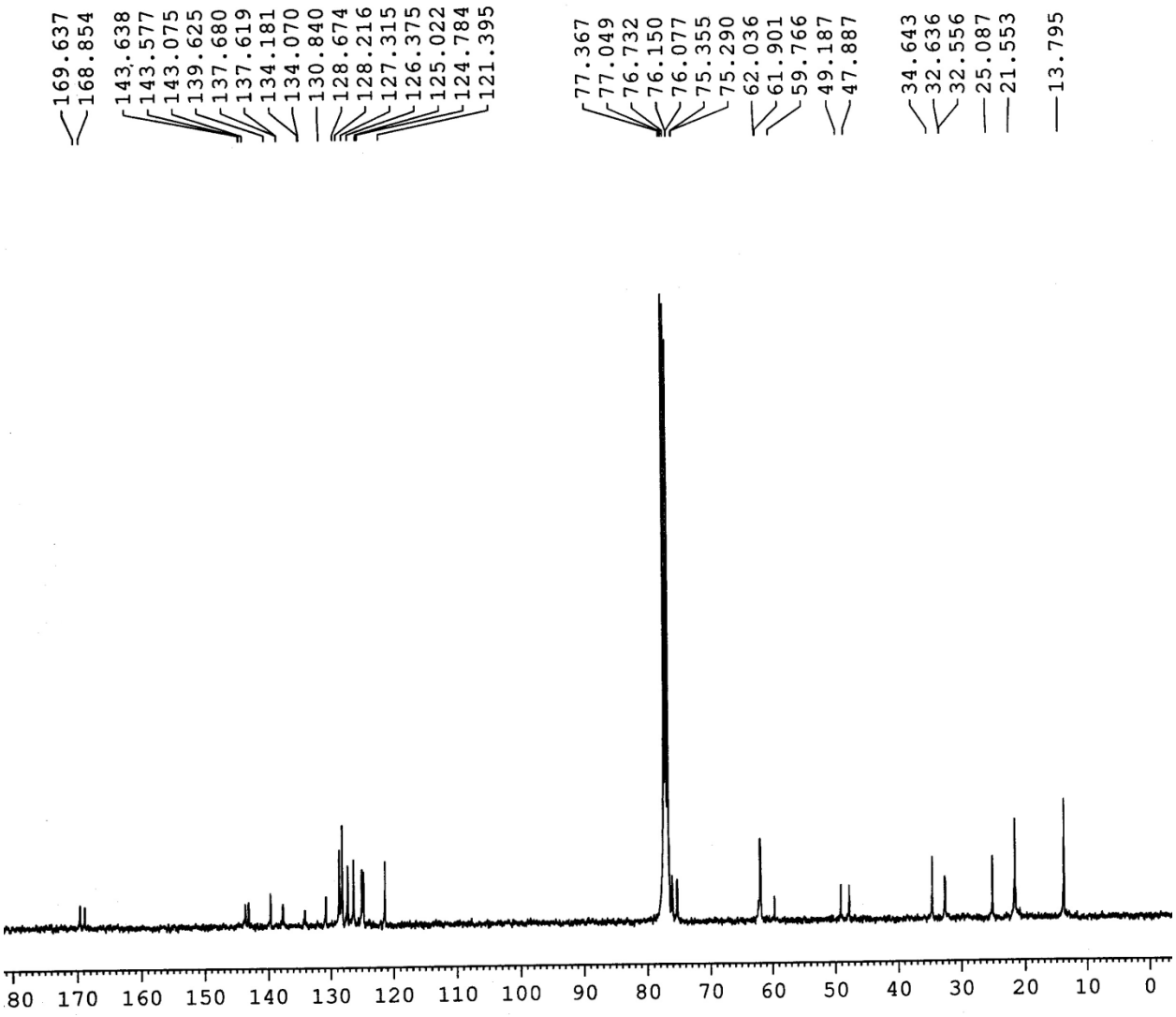


Fig. S72: ^{13}C NMR spectrum of compound **29**

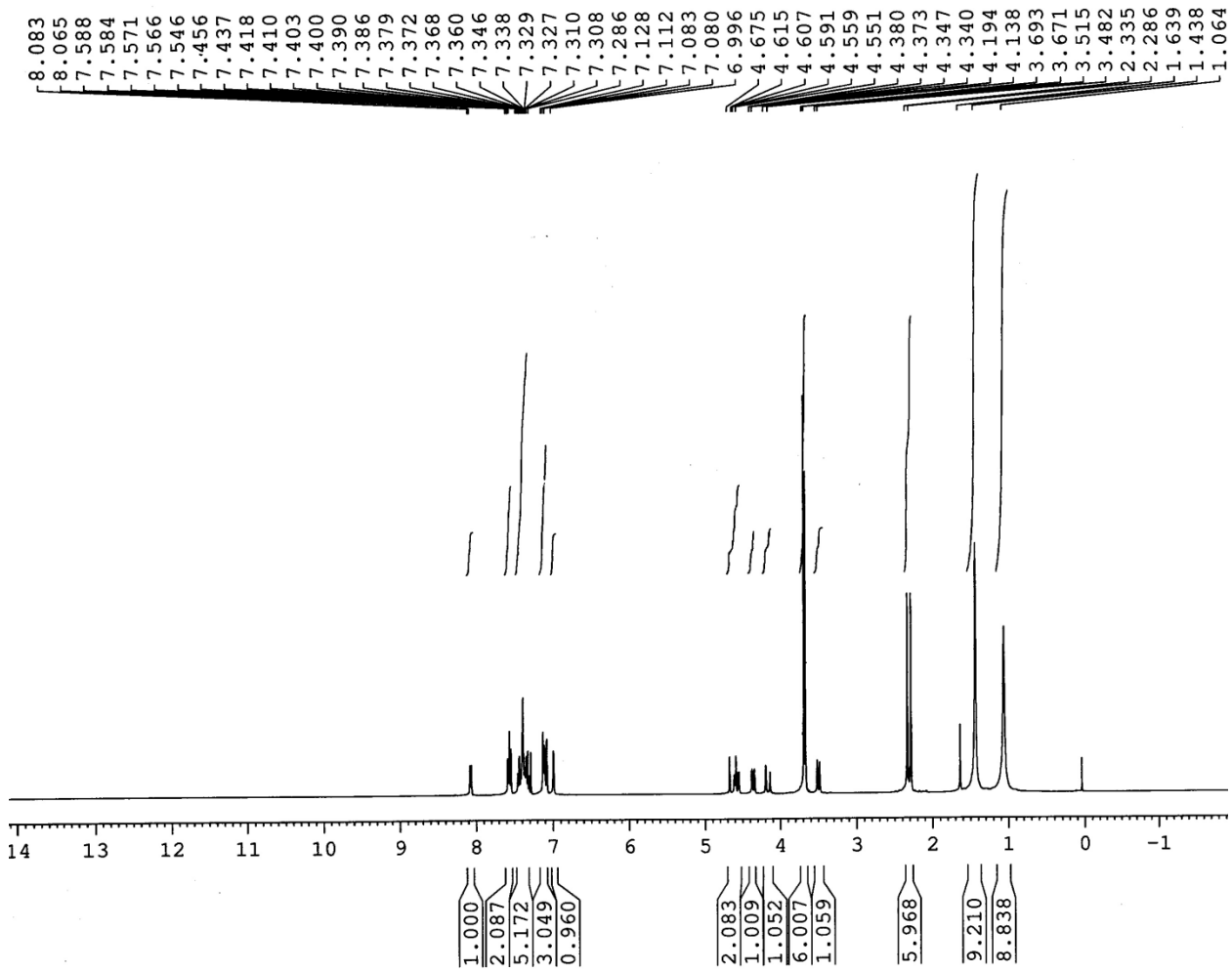


Fig. S73: ^{1}H NMR spectrum of compound **30**

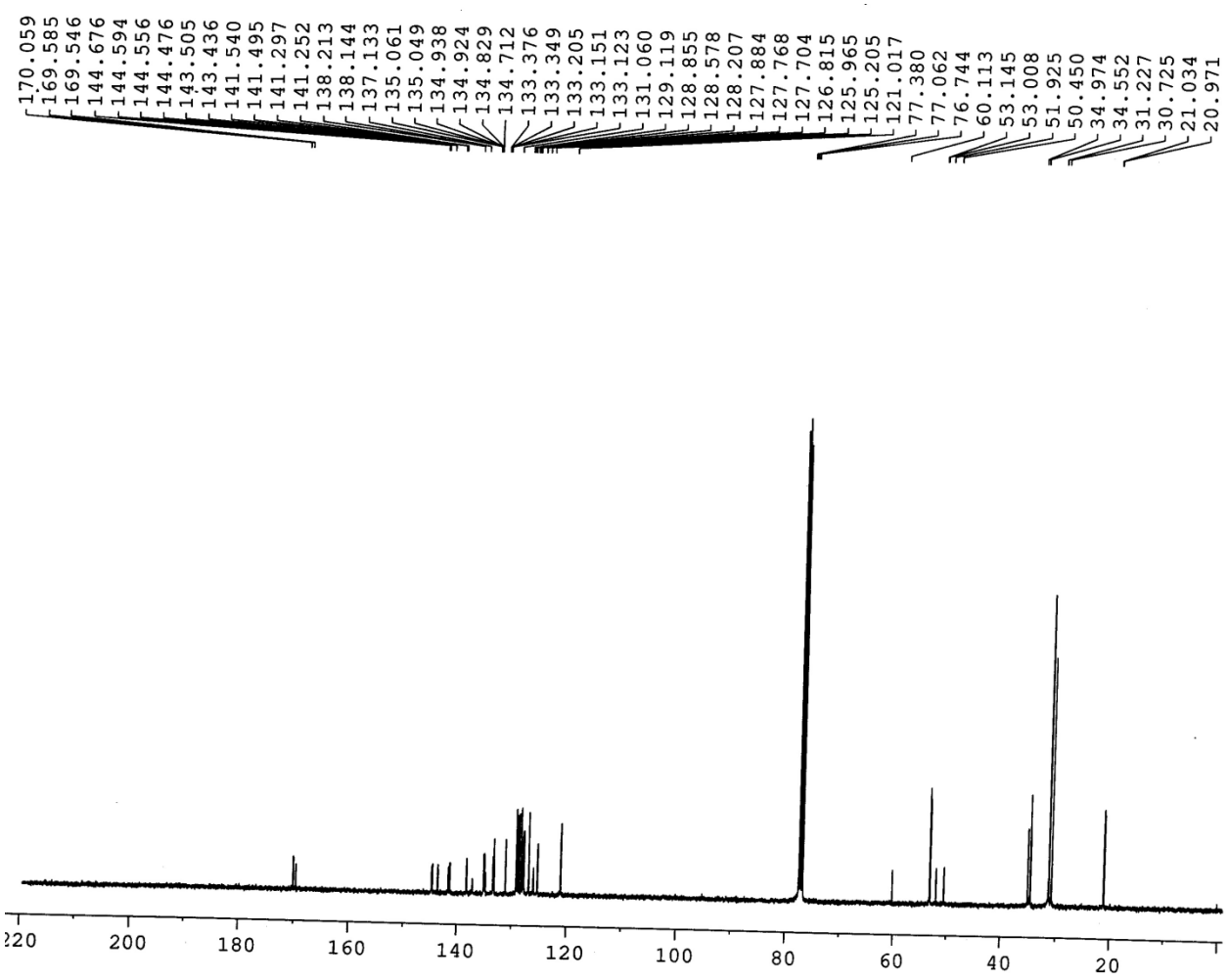


Fig. S74: ^{13}C NMR spectrum of compound **30**

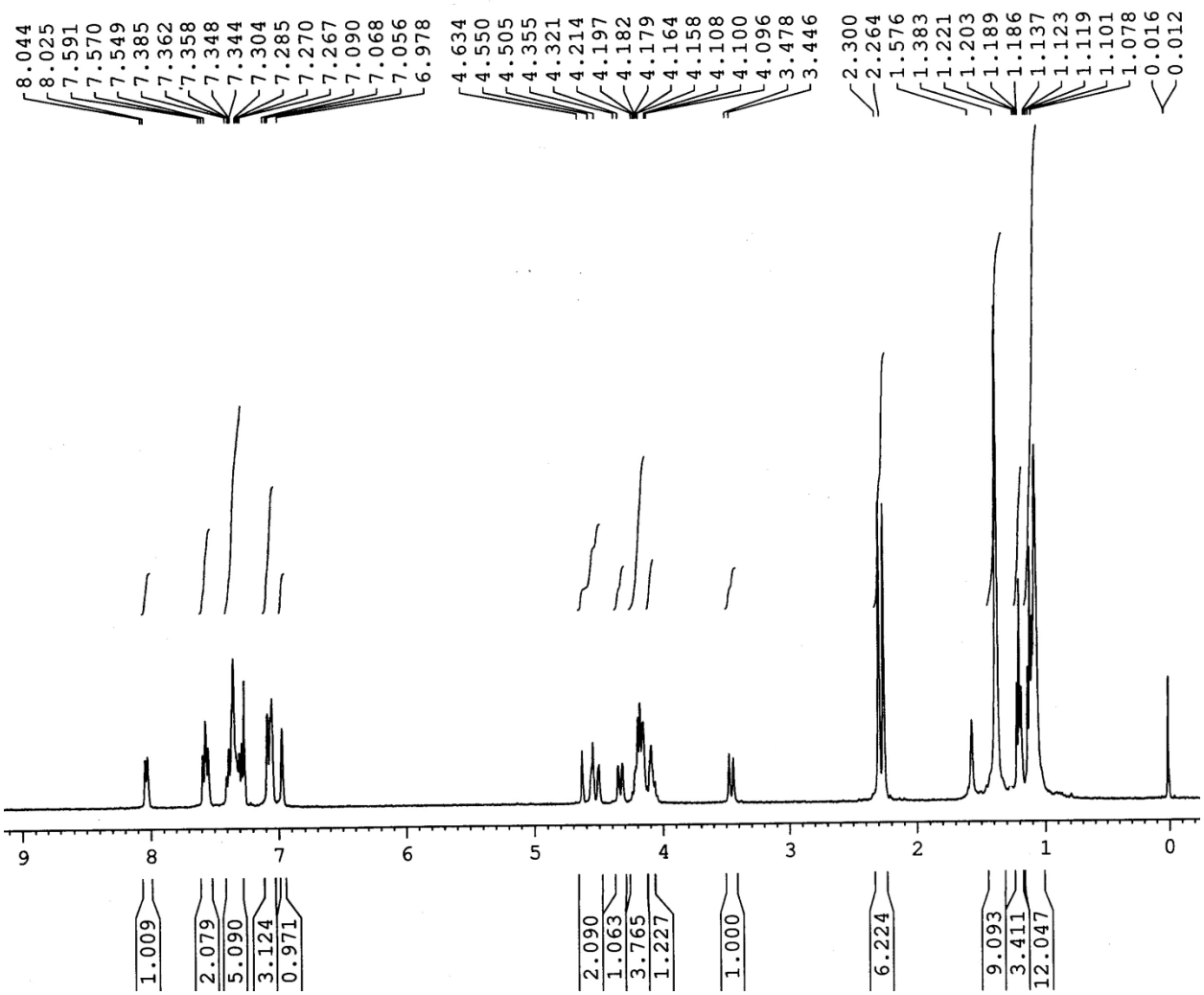


Fig. S75: ^{1}H NMR spectrum of compound **31**

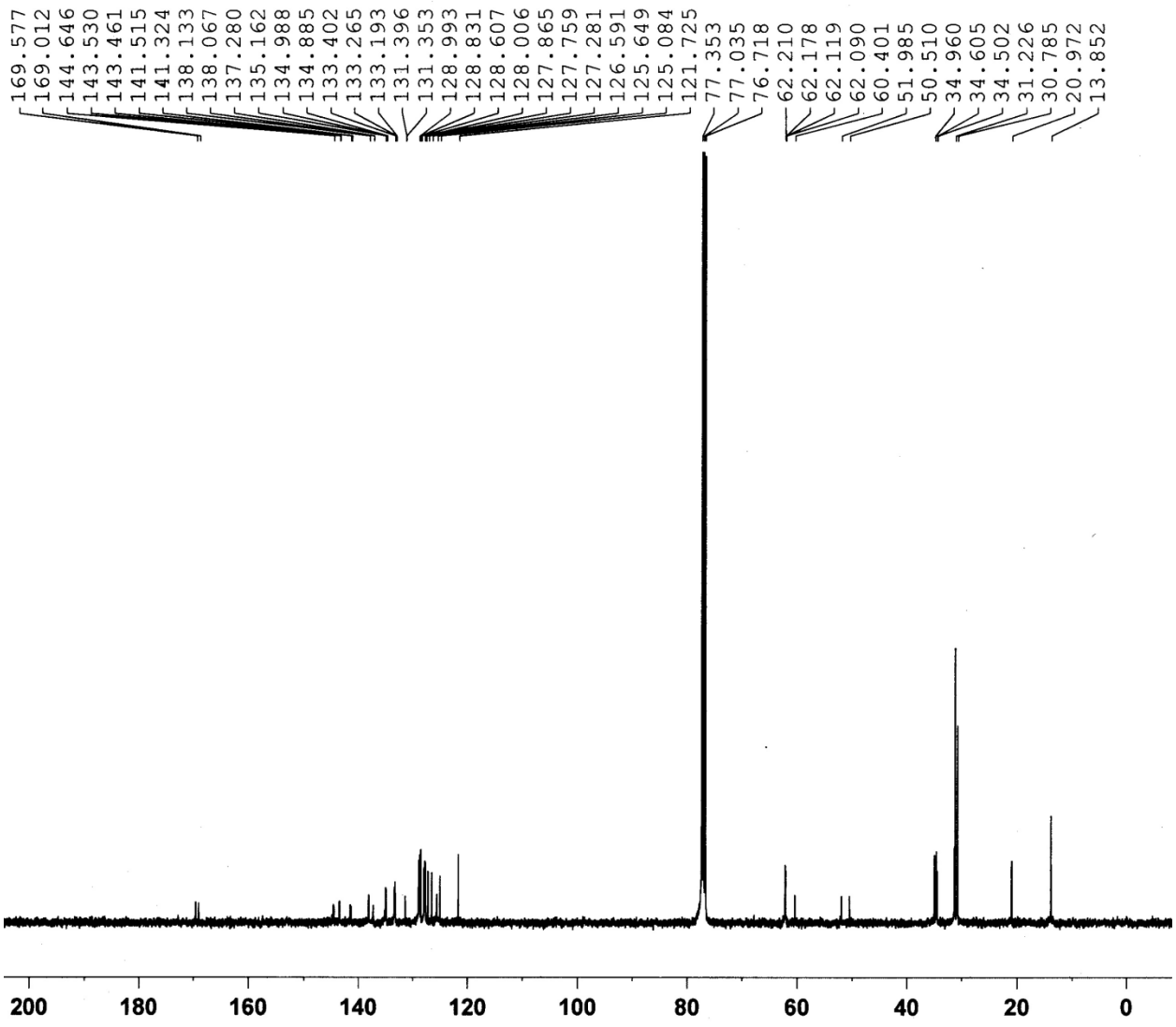


Fig. S76: ^{13}C NMR spectrum of compound **31**

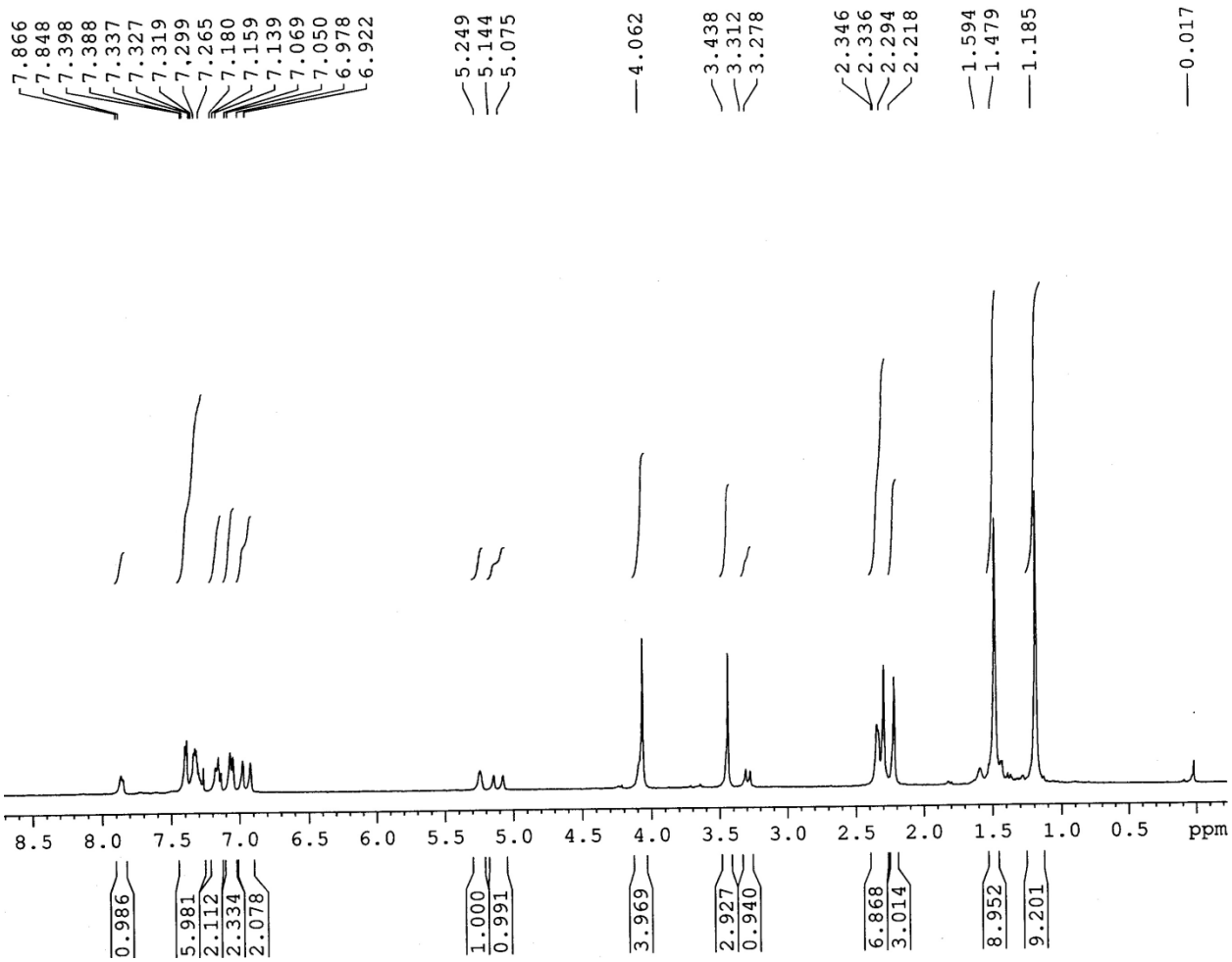


Fig. S77: ^{1}H NMR spectrum of compound **32**

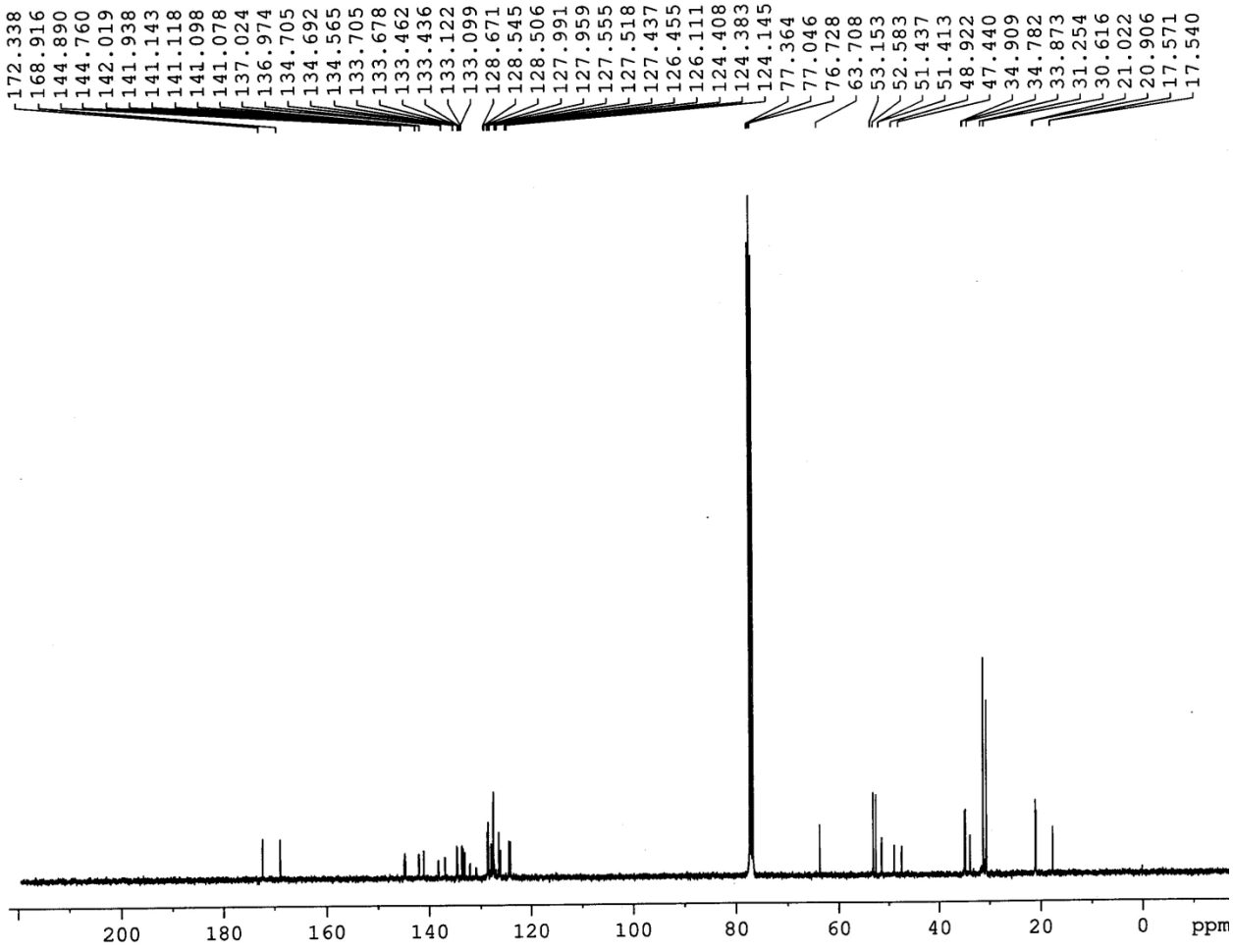


Fig. S78: ^{13}C NMR spectrum of compound **32**

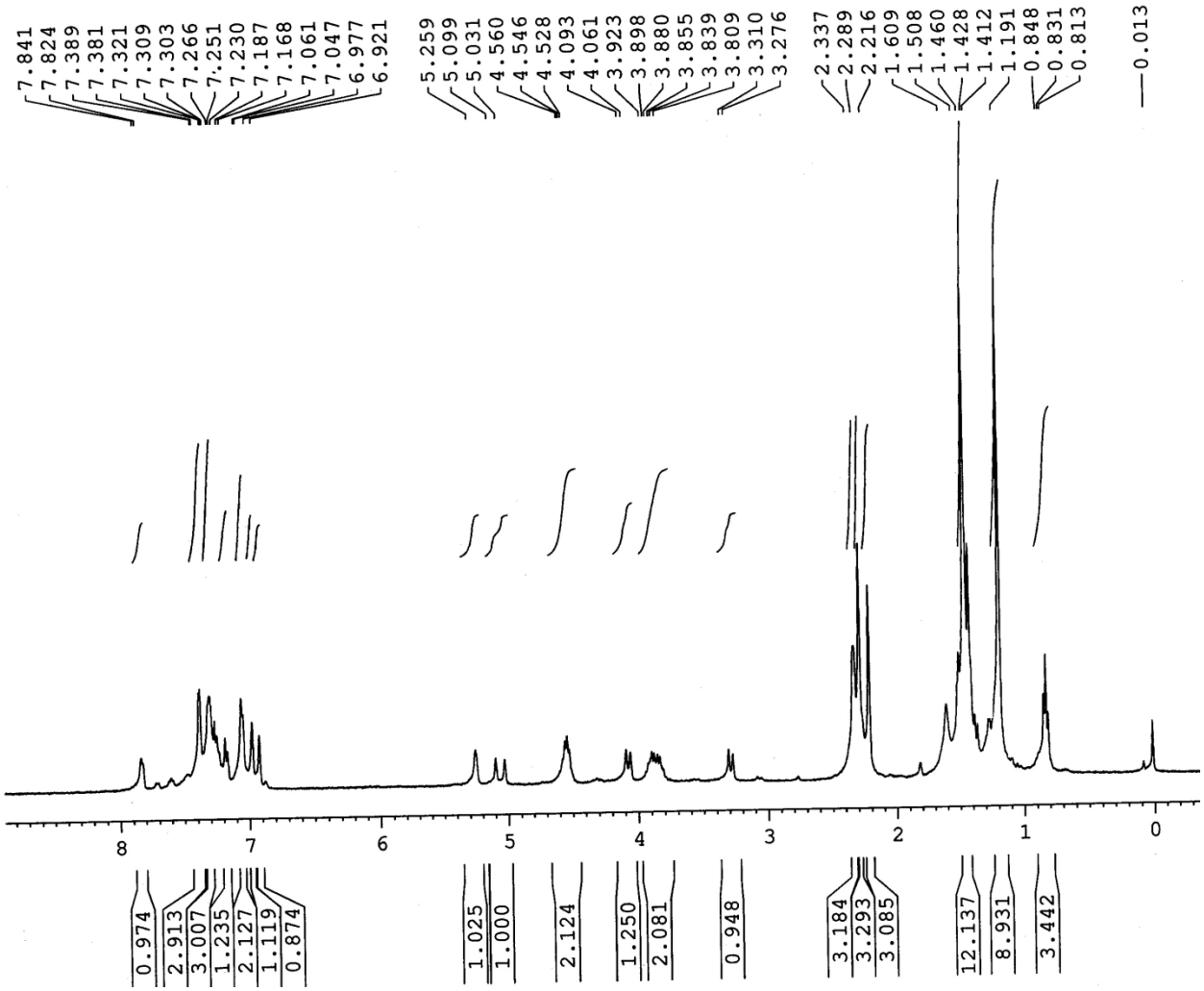


Fig. S79: ^{1}H NMR spectrum of compound **33**

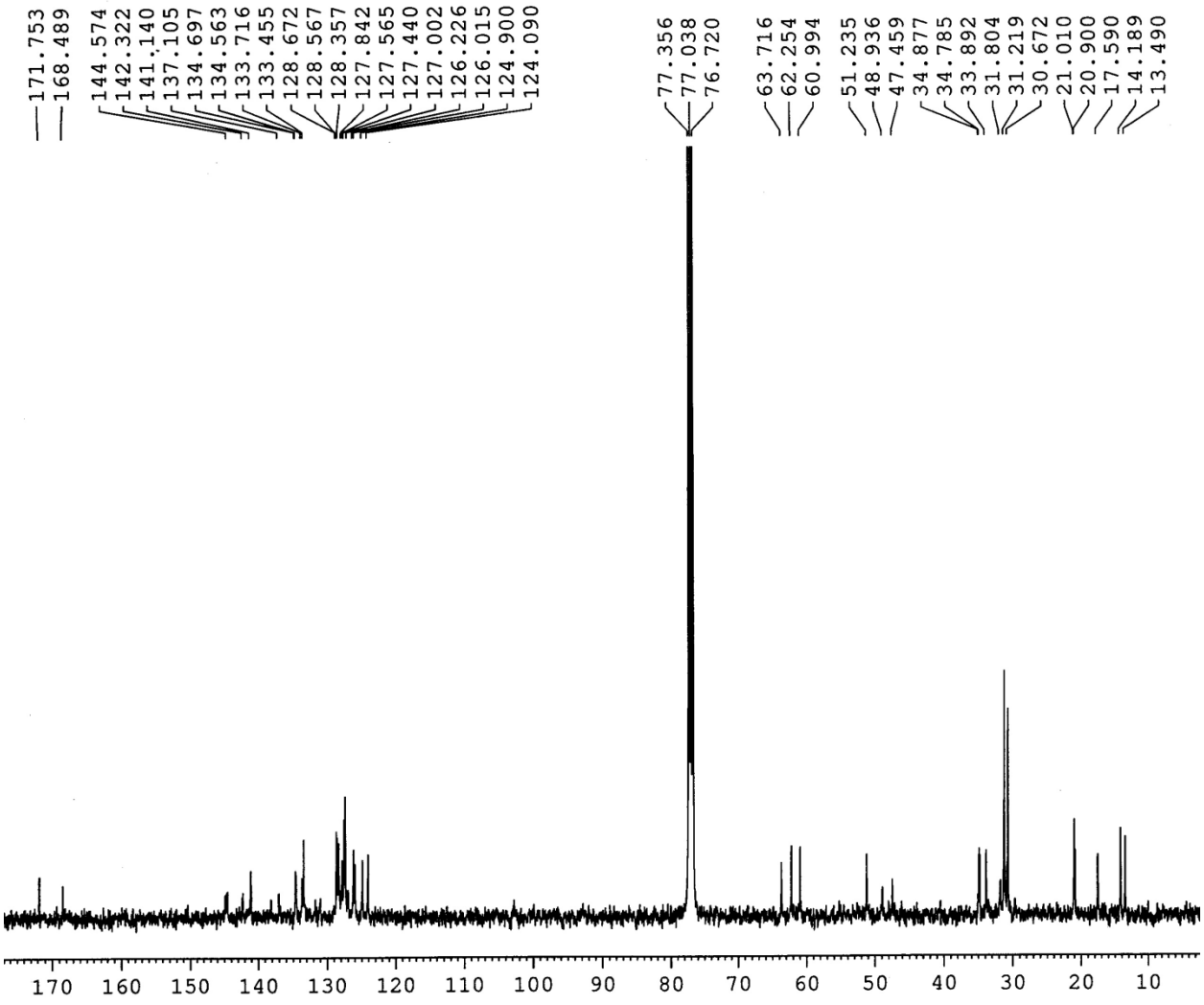


Fig. S80: ^{13}C NMR spectrum of compound **33**

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