ESI

Novel *N,O*-Cu(OAc)$_2$ complex catalysed diastereo- and enantioselective 1,4-addition of glycine derivatives to alkylidene malonates.

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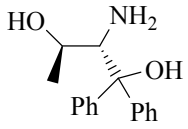
General Remarks

^{1}H NMR spectra were recorded on a Bruker DPX 400 MHz spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal TMS signal at 0.0 ppm as a standard. The data are reported as (s = single, d = double, t = triple, q = quarte, m = multiple, brs = broad single, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a Bruker DPX 100 MHz spectrometer in chloroform-d_3. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Diastereomeric ratios were determined from ^{1}H NMR or HPLC analysis. Enantiomeric ratios were determined by HPLC, using a chiralpak AD-H column, a chiralcel OD-H column with hexane and *i*-propanol as solvents. Optical roation were measured on AUTOPOL Ⅲ.

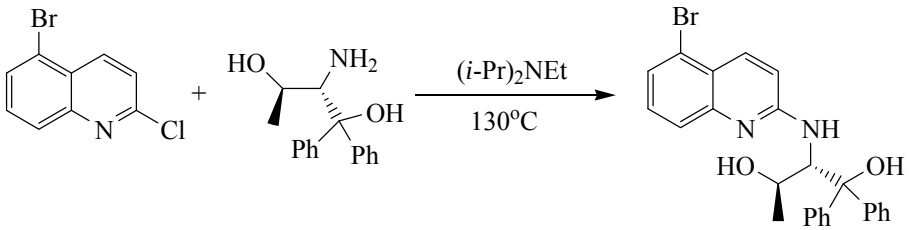
The **14** and ligand **9** were prepared by literature methods[1]

(2*S*,3*R*)-2-amino-1,1-diphenylbutane-1,3-diol (14)



white solid, 46% yield; **m.p.** 145-146 ^{o}C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.7 Hz, 2H), 7.52 (d, *J* = 7.5 Hz, 2H), 7.34 (dd, *J* = 15.0, 7.5 Hz, 4H), 7.22 (dt, *J* = 12.4, 6.2 Hz, 2H), 3.94 (q, *J* = 6.4 Hz, 1H), 3.68 (s, 1H), 2.83-2.15 (br, 3H), 1.23 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.6(4), 145.5(6), 128.6, 128.5, 126.9, 126.7, 125.6, 125.1, 81.7, 67.1, 58.9, 21.4; **HRMS** for $C_{16}H_{20}NO_2$ $[M+1]^+$ Calculated: 258.1494, Found: 258.1498.

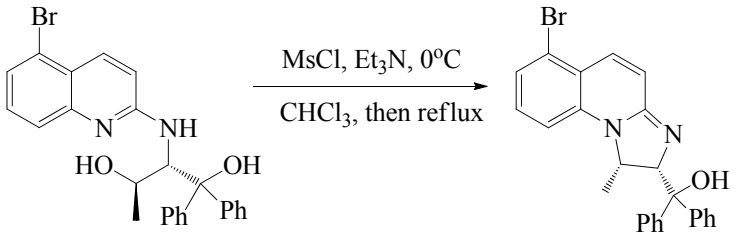
Synthesis of (2*S*,3*R*)-2-(5-bromoquinolin-2-ylamino)-1,1-diphenylbutane-1,3-diol



14 **15**

A flame-dried Schlenk tube charged with 2-chlorobenzothiazole (0.600 g, 2.47 mmol), **14** (0.760 g, 2.97 mmol), (*i*-Pr)$_2$NEt (1.2 mL, 7.42 mmol) and a stir bar was flushed with N_2 several times, stoppered and heated at130 ± 5 ^oC for 60 h. After cooling the tube to 30–40 ^oC, the viscous reaction mixture was treated with 5 mL of CH_2Cl_2 and left at room temperature to dissolve. The diluted mixture was purified by chromatography to give the title compound as a white solid. (0.370 g, 32% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 9.1 Hz, 1H), 7.71-7.51 (m, 5H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.39-7.29 (m, 3H), 7.25-7.17 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.44 (d, *J* = 9.1 Hz, 1H), 5.71-5.56 (m, 1H), 5.54-5.20 (m, 2H), 4.10 (q, *J* = 6.3 Hz, 1H), 2.78-2.17 (br, 1H), 1.14 (d, *J* = 6.3 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.3, 148.8, 146.1, 145.1, 136.2, 129.6, 128.6, 128.1, 126.9, 126.8, 126.2, 125.8, 125.6, 125.2, 122.9, 121.9, 113.6, 82.9, 69.4, 57.4, 21.6; **HRMS** for $C_{25}H_{24}BrN_2O_2$ $[M+1]^+$ Calculated: 463.1021, Found: 463.1009;

Synthesis of ((1*S*,2*S*)-6-bromo-1,2-dihydro-1-methylimidazo[1,2-a]quinolin-2-yl) diphenylmethanol

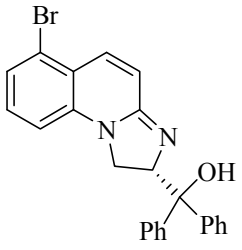


15 **7**

A solution of **15** (0.270 g, 0.583 mmol) in anhydrous $CHCl_3$ (5 mL) was cooled to 0 ^oC under N_2 and treated with NEt_3 (0.66 mL, 4.7 mmol) followed by MsCl (0.07 mL, 0.7 mmol). The mixture was stirred at 0 ^oC for 0.5 h and then warmed to room temperature. Methanol (0.5 mL) was added to quench the excess MsCl. NEt_3 (1.5 mL) was added and the mixture was refluxed overnight. After cooling, the mixture was washed with a small amount of water, dried over $MgSO_4$ and rotary evaporated. The crude product was purified by chromatography to give **7** as light yellow solid. (0.137 g, 53% yield). m.p.: 126-128 ^oC; $[\alpha]^{26}_D$: -93 (*c* 0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.61 (m, 5H), 7.32 (dt, *J* = 14.0, 7.8 Hz, 4H), 7.24-7.09 (m, 4H), 6.74 (d, *J* = 8.1 Hz, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 5.50 (d, *J* = 8.8 Hz, 1H), 4.67 (dq, *J* =

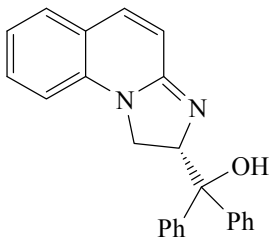
13.1, 6.5 Hz, 1H), 3.50 (s, 1H), 1.07 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.5, 148.3, 145.3, 139.0, 135.5, 130.8, 128.5, 128.5, 126.7, 126.6, 125.5, 124.9, 124.5, 123.7, 120.7, 118.7, 112.3, 77.3, 73.4, 59.8, 12.9; **HRMS** for $C_{25}H_{22}BrN_2O$ $[M+1]^+$ Calculated: 445.0916, Found: 445.0903; **IR** ν 3431, 3060, 2937, 1633, 1562, 1493, 1446, 1365, 1275, 1228, 1101, 1014, 765, 704 , 646 cm^{-1}.

The synthesis of 4, 5, 6, 8, is the same procedure with 7.



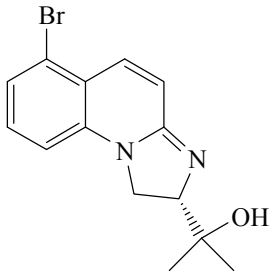
(**4**)

m.p.: 204-206°C; $[\alpha]^{26}_D$: +192 (*c* 0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.5, 5.7 Hz, 3H), 7.52 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 4H), 7.26-7.16 (m, 3H), 7.12 (t, *J* = 8.0 Hz, 1H), 6.70 (d, *J* = 10.0 Hz, 1H), 6.59 (d, *J* = 8.1 Hz, 1H), 5.57 (t, *J* = 10.2 Hz, 1H), 3.83-3.67 (m, 2H), 2.98 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.4, 146.2, 144.3, 139.8, 135.9, 131.0, 128.4(1), 128.3(9), 127.0, 126.7, 126.5, 125.7, 124.5, 123.2, 119.9, 118.2, 111.5, 78.7, 71.4, 48.2; **HRMS** for $C_{24}H_{20}BrN_2O$ $[M+1]^+$ Calculated: 431.0759, Found: 431.0747; **IR** ν 3413, 3059, 3024, 1952, 1739, 1633, 1561, 1450, 1398, 1282, 1206, 1161, 1066, 903, 776, 751, 700, 641, 630 cm^{-1}.



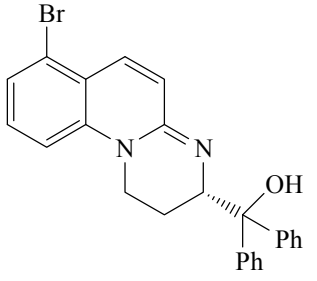
(**5**)

m.p.: 186-188°C; $[\alpha]^{26}_D$: +416 (*c* 0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.37-7.26 (m, 6H), 7.25-7.15 (m, 3H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.62 (t, *J* = 9.8 Hz, 2H), 5.54 (t, *J* = 10.2 Hz, 1H), 3.90-3.66 (m, 2H), 3.01 (br, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 159.0, 146.5, 144.5, 138.6, 137.2, 130.5, 128.4, 128.3, 128.1, 126.9, 126.7, 126.6, 125.7, 120.8, 120.4, 116.9, 112.0, 78.7, 71.1, 47.9; **HRMS** for $C_{24}H_{21}N_2O$ $[M+1]^+$ Calculated: 353.1654, Found: 353.1658; **IR** ν 3423, 1637, 1574, 1457, 1410, 1290, 1159, 814, 752, 701 cm^{-1}.



(**6**)

m.p.: 169-170°C; $[\alpha]^{26}_{D}$: +256 (*c* 0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 10.0 Hz, 1H), 7.22-7.14 (m, 2H), 6.75-6.69 (m, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 4.21 (t, *J* = 10.1 Hz, 1H), 3.93 (dt, *J* = 19.6, 10.2 Hz, 2H), 1.39 (s, 3H), 1.23 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8, 140.0, 135.4, 131.0, 124.4, 123.3, 119.9, 118.1, 111.1, 74.0, 71.7, 47.6, 27.1, 25.3; **HRMS** for $C_{14}H_{15}BrN_2O$ Calculated: 306.0368, Found: 306.0370; **IR** 3414, 3178, 2979, 2927, 1642, 1567, 1451, 1399, 1227, 1161, 774.



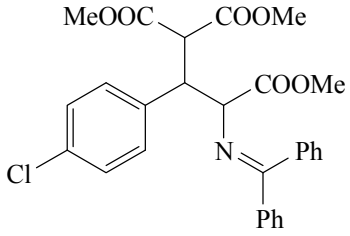
(**8**)

m.p.: 117-118°C; $[\alpha]^{26}_{D}$: -158 (*c* 0.1, $CHCl_3$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 7.4 Hz, 2H), 7.48-7.41 (m, 3H), 7.35-7.27 (m, 4H), 7.29-7.10(m, 4H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.53 (d, *J* = 10.0 Hz, 1H), 4.47-4.19 (m, 1H), 4.08-3.96 (br, 1H), 3.82-3.59 (m, 2H), 1.68-1.56 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 147.4, 145.1, 142.0, 133.2, 131.9, 130.9, 130.0, 128.0, 127.3, 126.6, 126.4, 125.9, 125.4, 123.2, 120.5, 110.7, 78.5, 58.0, 44.2, 20.7; **HRMS** for $C_{25}H_{22}BrN_2O$ $[M+1]^+$ Calculated: 445.0916, Found: 445.0901; **IR** ν 3427, 3087, 3059, 2968, 1636, 1569, 1461, 1443, 1394, 1304, 1230, 1201, 1153, 997, 815, 775, 754, 700, 540 cm^{-1}.

Typical procedure for asymmetric Michael addition of Glycinate benzophenone Schiff bases with Alkylidene Malonates

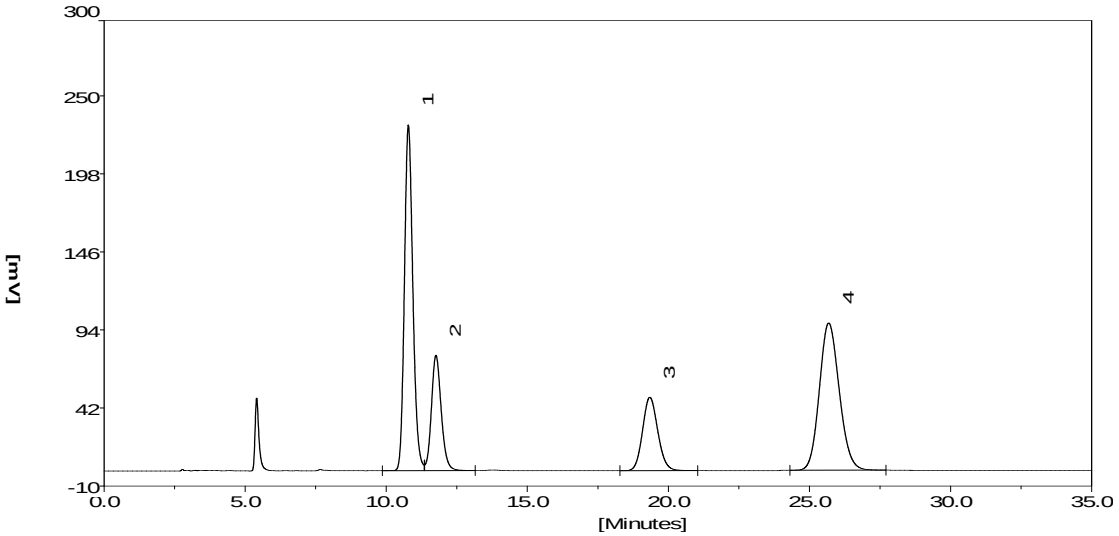
$Cu(OAc)_2 \cdot H_2O$ (2.0 mg, 0.01 mmol), the ligand **7** (4.9 mg, 0.011 mmol) and KO^tBu (1.1 mg, 0.01 mmol) were added under N_2 to a flame-dried Schlenk tube, containing activated 4Å MS and a stirring bar. Then anhydrous THF (1 mL) was added. After the mixture was stirred for 1h at room temperature, Schiff base substrate (0.1 mmol), and alkylidene malonate (0.12 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the mixture was concentrated to dryness and then the residue was purified by column chromatography to give the corresponding product,

which was then directly analyzed by chiral HPLC to determine the enantiomeric excess.

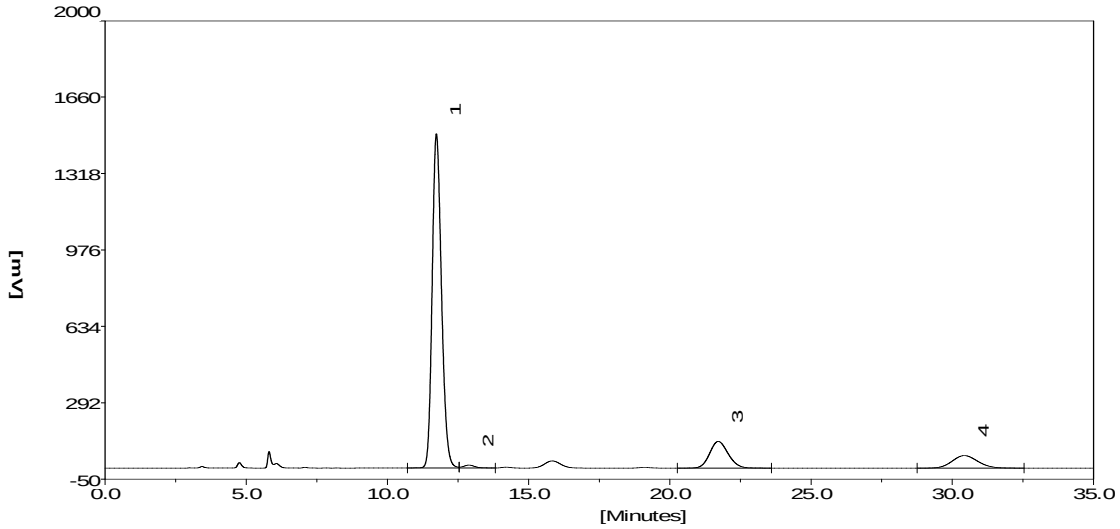


(3aa)
trimethyl 2-(4-chlorophenyl)-1-(diphenylmethyleneamino)propane-1,3,3-tricarboxylate

white solid, 86% yield; **m.p.** 128-129 ^{o}C; R_f = 0.21(*anti*), 0.25(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.67 (d, *J* = 7.4 Hz, 2H), 7.42-7.34 (m, 6H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.94-6.85 (m, 2H). 4.39-4.33 (m, 1H), 4.32-4.23 (m, 2H), 3.63 (s, 3H), 3.57 (s, 3H), 3.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 170.7, 168.4, 168.1, 138.9, 137.8, 135.8, 133.2, 130.8, 130.1, 129.1, 128.7, 128.5, 128.4, 128.2, 127.3, 68.5, 53.9, 52.7, 52.4, 52.1, 48.0; **IR** ν 3492, 2863, 1738, 1619, 1497, 1441, 1263, 1096, 1020, 834, 788, 702, 653, 546 cm^{-1}; **HRMS** for $C_{28}H_{27}ClNO_6$ $[M+1]^+$ Calculated: 508.1527, Found: 508.1512; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 11.73 min, 12.88 min, 21.71 min, 30.43 min.

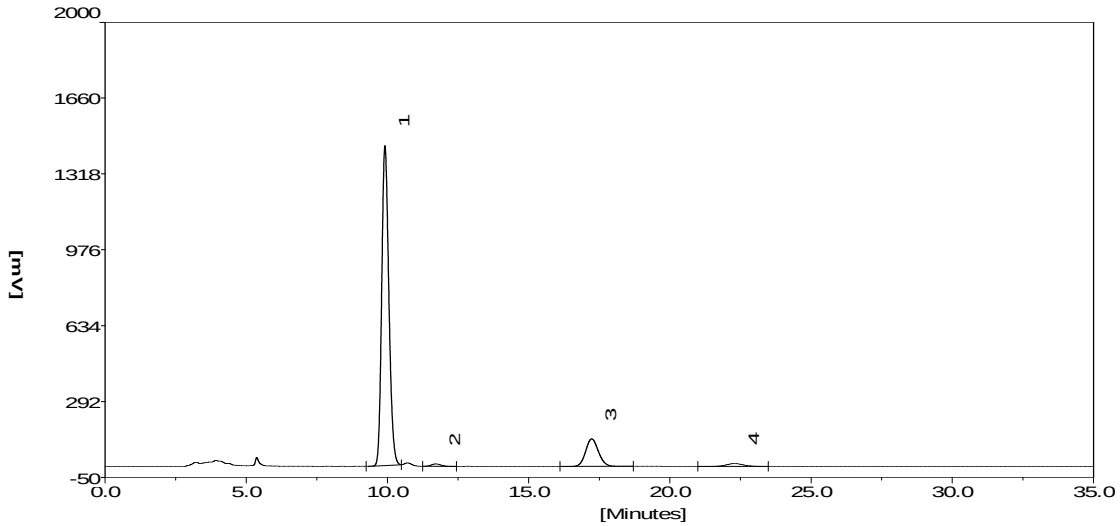


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	10.78	230.24	4791.15	36.0699
2	11.76	76.90	1861.85	14.0168
3	19.34	48.92	1832.85	13.7985
4	25.68	98.1	4797.13	36.1149

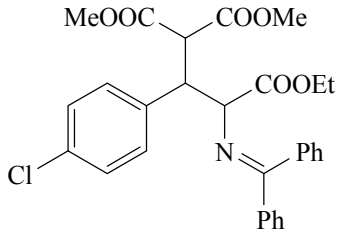


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	11.73	1494.75	34151.45	78.5152
2	12.88	13.05	363.39	0.8354
3	21.71	119.42	5438.93	12.5043
4	30.43	56.01	3542.81	8.145

Crystallization



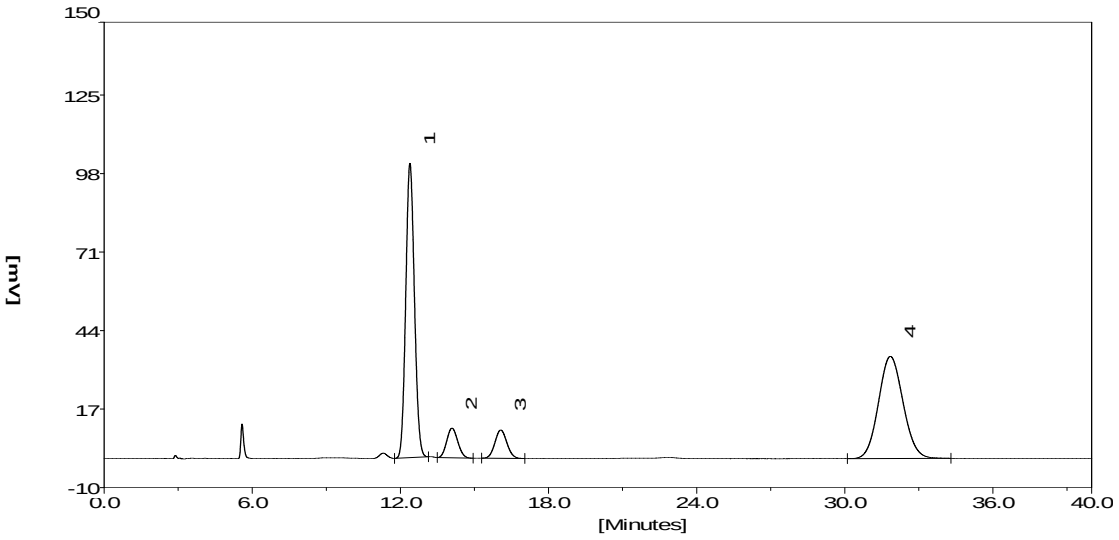
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.91167	1440.72	25224.68	84.4801
2	11.71333	10.74	245.87	0.8234
3	17.23167	123.94	3881.55	12.9997
4	22.29083	12.47	506.62	1.6967



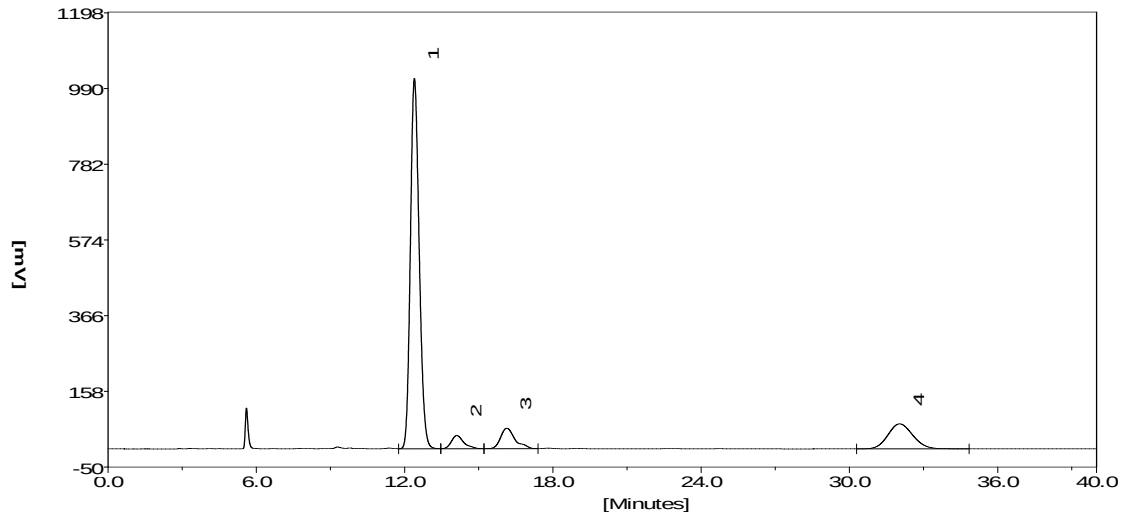
(3ab)

1-ethyl 3,3-dimethyl 2-(4-chlorophenyl)-1-(diphenylmethyleneamino)propane -1,3,3-tricarboxylate

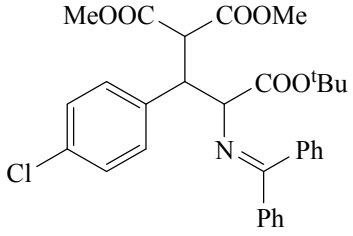
white solid, 74% yield**;** R_f = 0.20(*anti*), 0.24(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.67 (d, *J* = 7.5 Hz, 2H), 7.45-7.32 (m, 6H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.01-6.90 (m, 2H), 4.36-4.23 (m, 3H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.61 (s, 3H), 3.42 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.1, 170.1, 168.3, 168.1, 139.0, 137.7, 135.8, 133.1, 130.8, 130.3, 129.1, 128.7, 128.5, 128.3, 128.1, 127.5, 68.6, 61.0, 54.1, 52.6, 52.4, 48.0, 13.9; **IR** ν 3482, 2876, 1748, 1616, 1497, 1312, 1264, 1185, 1097, 1029, 927, 788, 700, 647, 536 cm^{-1}; **HRMS** for $C_{29}H_{28}ClNO_6$ Calculated: 521.1605, Found: 521.1604; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 11.72 min, 41.58 min.



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	12.39	101.24	2466.88	44.5614
2	14.09	10.20	315.55	5.7000
3	16.07	9.74	327.45	5.9150
4	31.85	35.12	2426.03	43.8236



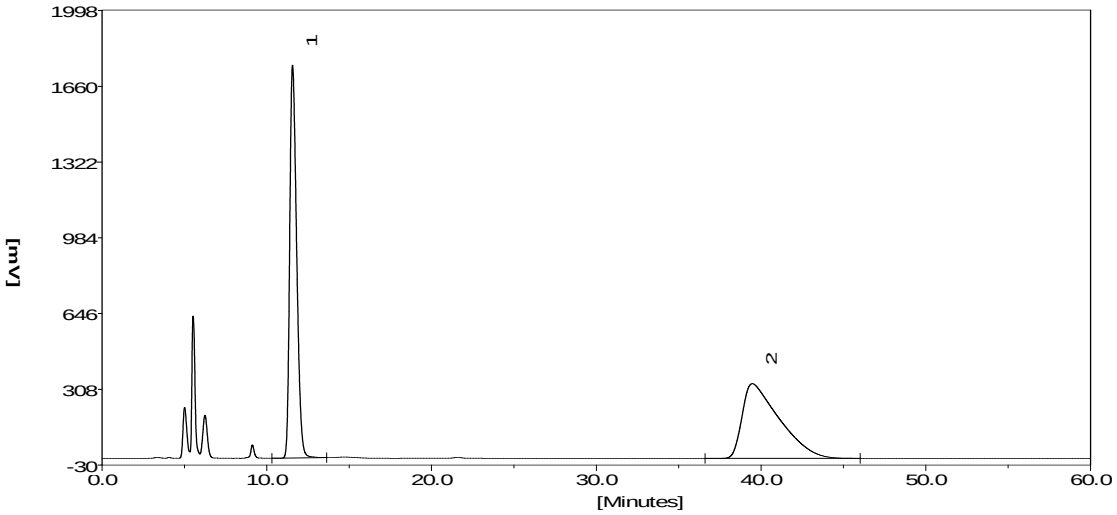
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	12.40	1017.85	25147.20	74.9722
2	14.11	36.27	1268.76	3.7826
3	16.14	56.52	2295.93	6.8449
4	32.03	68.81	4830.13	14.4002



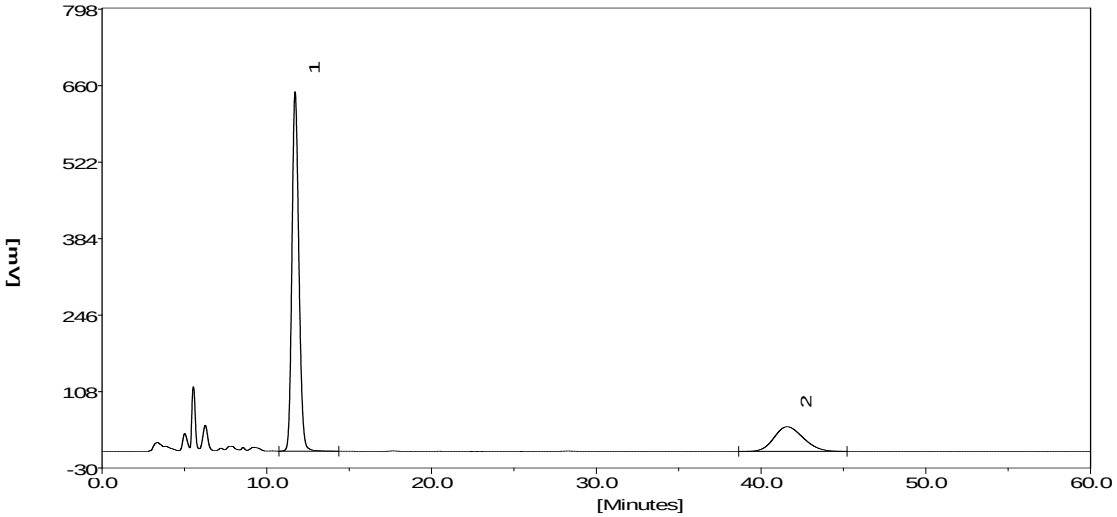
(3ac)

1-*tert*-butyl 3,3-dimethyl 2-(4-chlorophenyl)-1-(diphenylmethyleneamino) propane-1,3,3- tricarboxylate

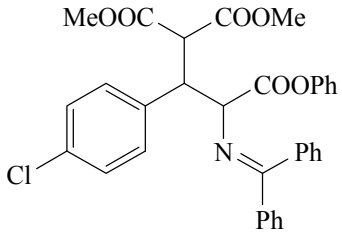
white solid, 27% yield; R_f = 0.23(*anti*), 0.27(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.45-7.38 (m, 4H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.5 Hz, 2H), 7.09-7.04 (m, 2H), 4.33-4.23 (m, 2H), 4.14 (d, *J* = 7.5 Hz, 1H), 3.58 (s, 3H), 3.42 (s, 3H), 1.22 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.7, 169.1, 168.3, 168.2, 139.1, 137.5, 136.0, 133.0, 130.7, 130.6, 129.0, 128.7, 128.4, 128.2, 128.1, 127.7, 81.5, 69.2, 54.4, 52.5, 52.3, 48.2, 27.7; **IR** ν 3478, 2912, 1776, 1737, 1618, 1496, 1457, 1311, 1260, 1149, 1016, 831, 783, 651, 547 cm^{-1}; **HRMS** for $C_{31}H_{32}ClNO_6$ Calculated: 549.1918, Found: 549.1930; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 11.72 min, 41.58 min



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area（%）
1	11.56	1753.00	51082.31	49.5369
2	39.47	333.30	52037.35	50.4631



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	11.72	648.50	18937.31	77.6131
2	41.58	44.41	5462.33	22.3869

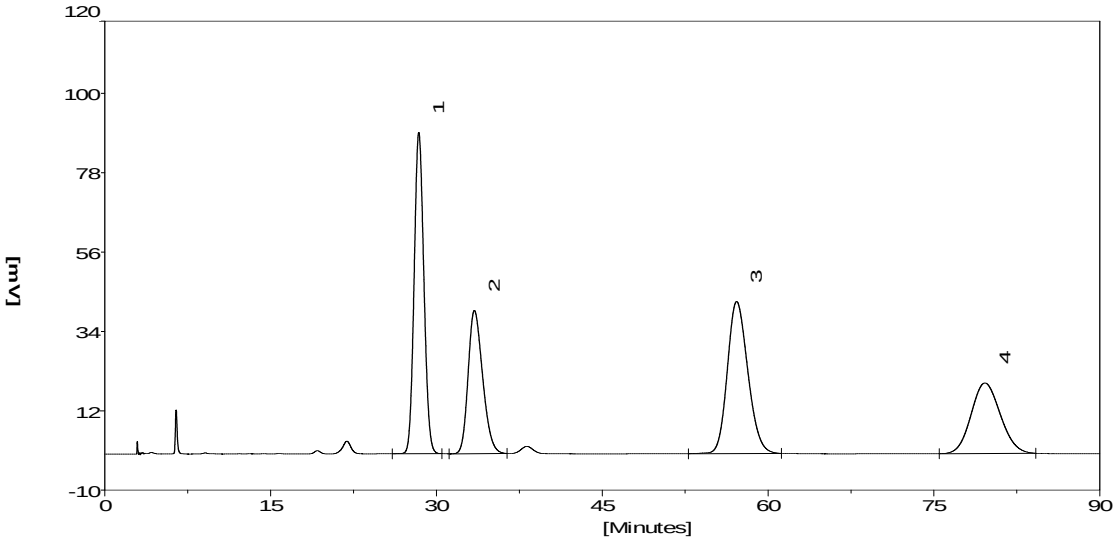


(3ad)

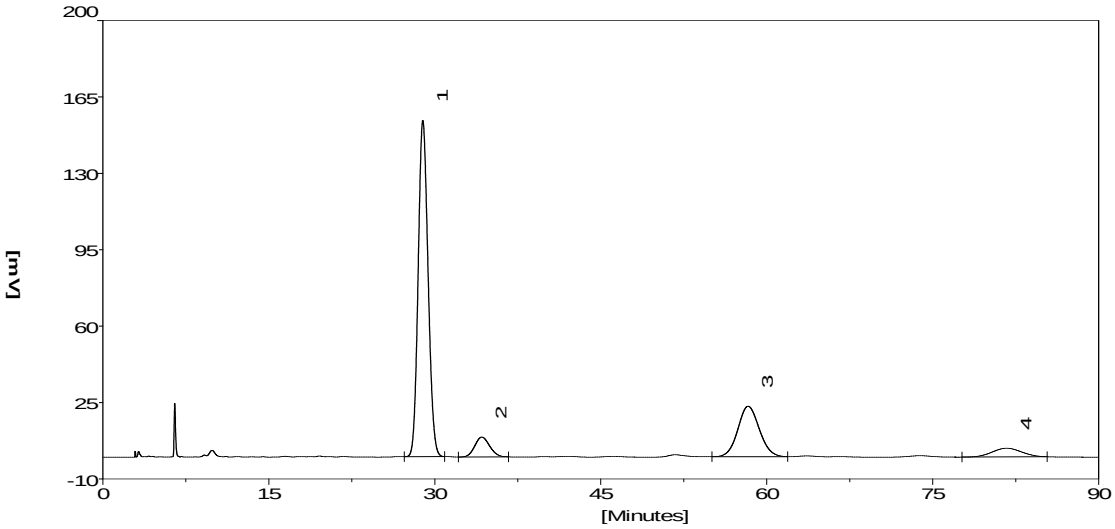
3,3-dimethyl 1-phenyl 2-(4-chlorophenyl)-1-(diphenylmethyleneamino)propane

-1,3,3-tricarboxylate

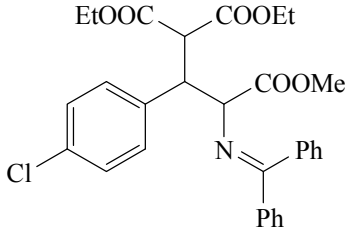
white solid, 65% yield; R_f = 0.18(*anti*), 0.22(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.71 (d, *J* = 7.2 Hz, 2H), 7.48-7.34 (m, 5H), 7.30 (m, 2H), 7.24-7.20 (m, 4H), 7.05-6.98 (m, 2H), 6.86 (d, *J* = 7.7 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 2H), 4.55 (d, *J* = 5.1 Hz, 1H), 4.48 (dd, *J* = 10.9, 4.1 Hz, 1H), 4.40 (d, *J* = 10.0 Hz, 1H), 3.64 (s, 3H), 3.46 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.9, 168.8, 168.4, 168.2, 155.6, 150.5, 138.9, 137.7, 135.8, 133.4, 130.2, 129.6, 129.3, 129.1, 128.6, 128.5, 128.2, 127.4, 121.4, 115.3, 68.4, 54.1, 52.8, 52.5, 48.1; **IR** ν 3486, 2883, 1765, 1617, 1594, 1489, 1442, 1298, 1190, 1176, 1017, 931, 787, 700, 658, 561 cm^{-1}; **HRMS** for $C_{33}H_{28}ClNO_6$ Calculated: 569.1605, Found: 569.1611; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 28.92 min, 34.26 min, 58.32 min, 81.70 min.



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	28.41	89.07	5448.54	30.1028
2	33.44	39.72	3623.78	20.0212
3	57.16	42.17	5436.89	30.0385
4	79.62	19.56	3590.54	19.8375



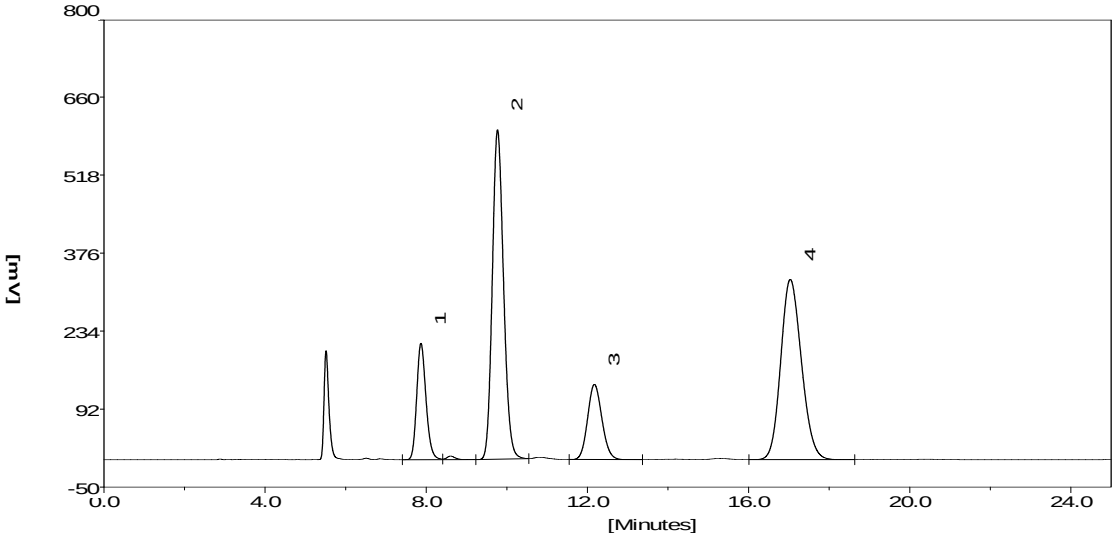
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	28.92	153.99	9548.31	66.9423
2	34.26	9.13	853.33	5.9826
3	58.32	23.17	3122.23	21.8897
4	81.70	3.99	739.62	5.1854



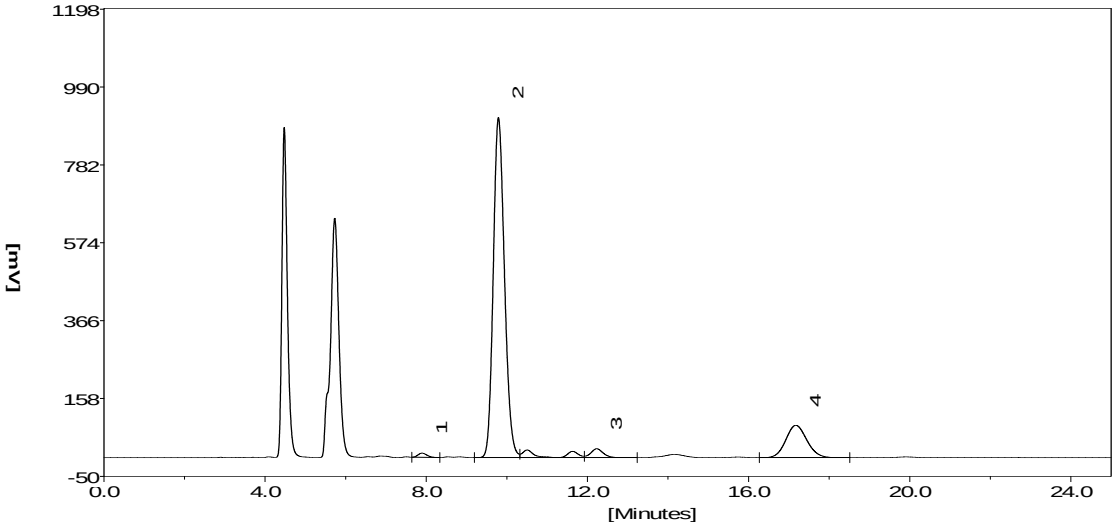
(3ba)

3,3-diethyl 1-methyl 2-(4-chlorophenyl)-1-(diphenylmethyleneamino)propane -1,3,3-tricarboxylate

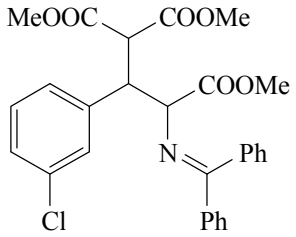
white solid, 68% yield; R_f = 0.20(*anti*), 0.24(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.40-7.31 (m, 6H), 7.18 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.95-6.87 (m, 2H), 4.38-4.24 (m, 3H), 4.14-4.01 (q, *J* = 7.0 Hz, 2H), 3.88 (q, *J* = 7.0 Hz, 2H), 3.57 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.0, 170.8, 168.0, 167.7, 139.0, 137.9, 135.8, 133.1, 130.8, 130.3, 129.1, 128.7, 128.5, 128.3, 128.1, 127.3, 68.6, 61.7, 61.4, 54.1, 52.1, 47.9, 13.9, 13.7; **IR** ν 3300, 2908, 1746, 1660, 1612, 1599, 1587, 1491, 1450, 1364, 1260, 1095, 1016, 913, 818, 789, 700, 656, 543 cm^{-1}; **HRMS** for $C_{30}H_{30}ClNO_6$ Calculated: 535.1762, Found: 535.1765; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 7.90 min, 9.79 min, 12.23 min, 17.18 min.



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	7.87	211.54	3376.10	11.2484
2	9.77	598.98	11557.28	38.5062
3	12.18	136.84	3377.46	11.2529
4	17.04	328.07	11703.26	38.9925

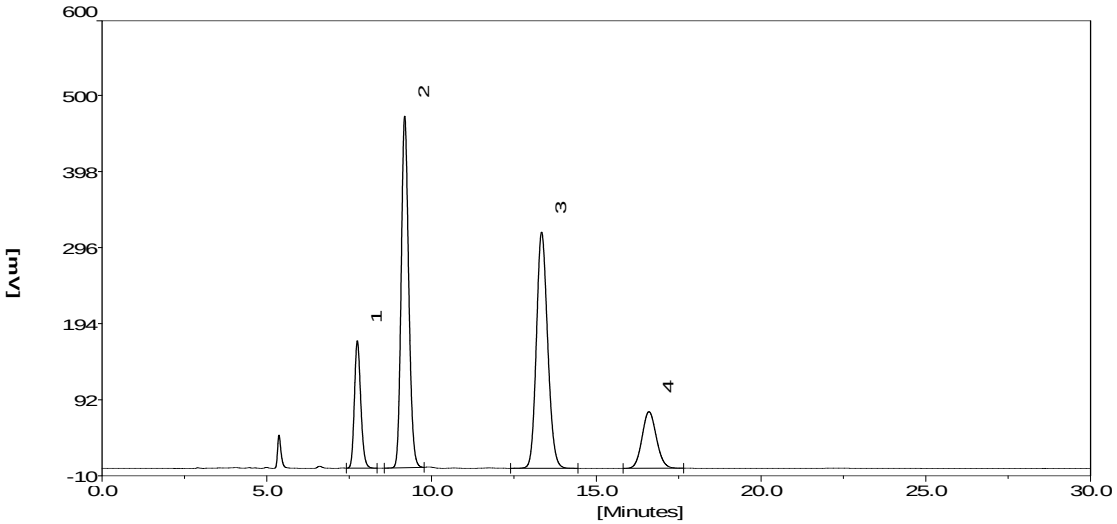


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	7.90	11.37	171.09	0.8024
2	9.79	908.02	17523.84	82.1886
3	12.23	23.63	500.41	2.347
4	17.18	86.28	3126.15	14.662

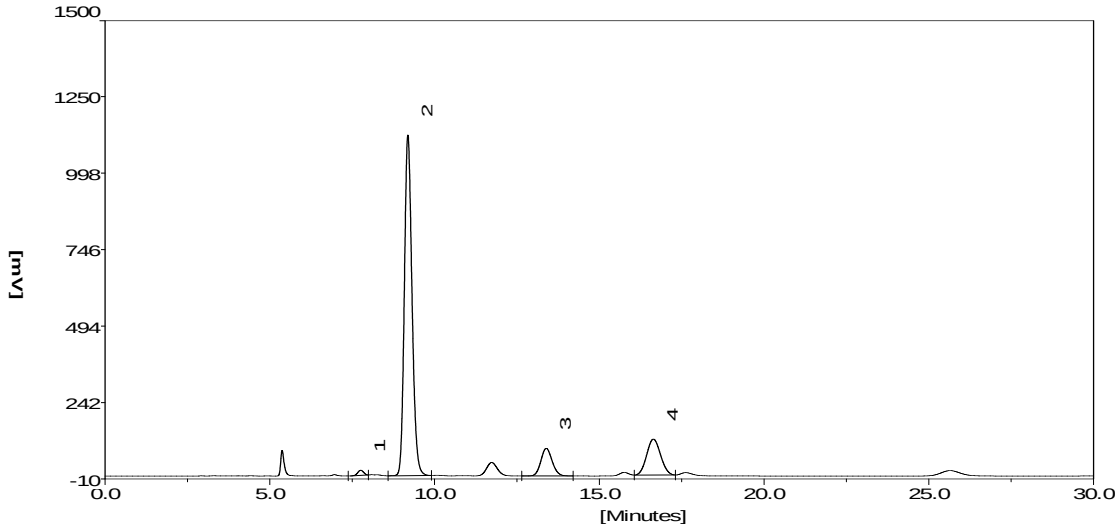


(3da)
trimethyl 2-(3-chlorophenyl)-1-(diphenylmethyleneamino)propane-1,3,3-tricarboxylate

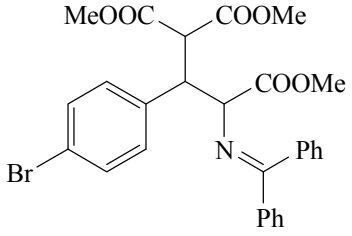
white solid, 90% yield; **m.p.** 122-124 ^{o}C; R_f = 0.22(*anti*), 0.27(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.67 (d, *J* = 7.3 Hz, 2H), 7.45-7.31 (m, 7H), 7.19-7.10 (m, 2H), 7.06 (d, *J* = 7.1 Hz, 1H), 6.92-6.87 (m, 2H), 4.39-4.37 (m, 1H), 4.33-4.25 (m, 2H), 3.65 (s, 3H), 3.59 (s, 3H), 3.45 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 170.7, 168.3, 168.1, 141.5, 138.9, 135.8, 134.0, 130.8, 129.5, 129.1, 128.9, 128.7, 128.5, 128.1, 127.5, 127.3, 126.7, 68.3, 53.8, 52.7, 52.4, 52.2, 48.2; **IR** ν 3408, 2893, 1744, 1620, 1599, 1588, 1421, 1263, 1092, 1011, 791, 700, 651, 503 cm^{-1}; **HRMS** for $C_{28}H_{26}ClNO_6$ Calculated: 507.1449, Found: 507.1465; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 7.76 min, 9.19 min, 13.39 min, 16.64 min.



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	7.75	170.88	2286.54	11.6996
2	9.19	471.41	7449.53	38.117
3	13.34	316.66	7519.48	38.4749
4	16.60	75.96	2288.29	11.7085

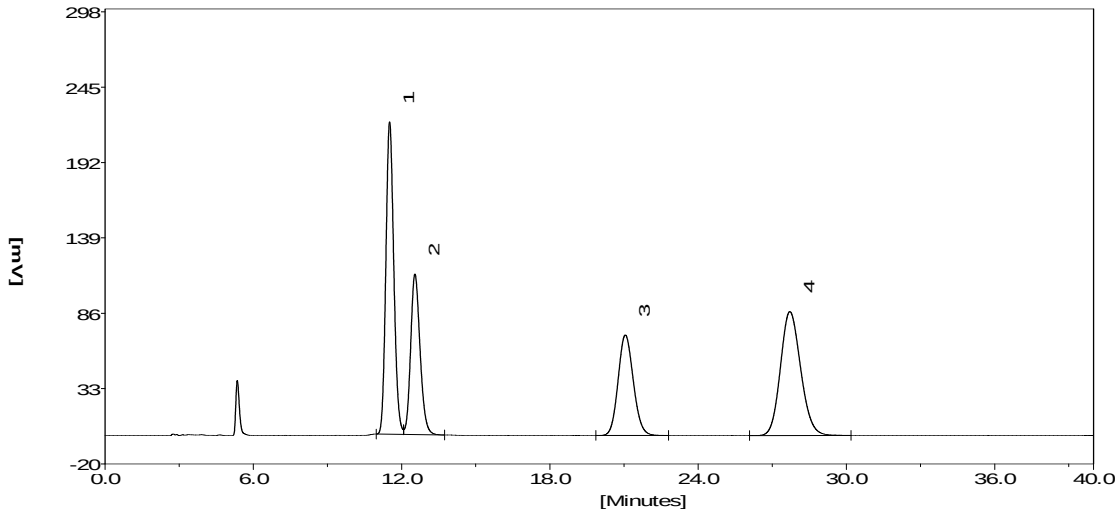


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	7.76	17.15	209.79	0.8768
2	9.19	1122.44	18087.32	75.5896
3	13.39	91.14	2161.90	9.0349
4	16.64	118.66	3469.30	14.4987

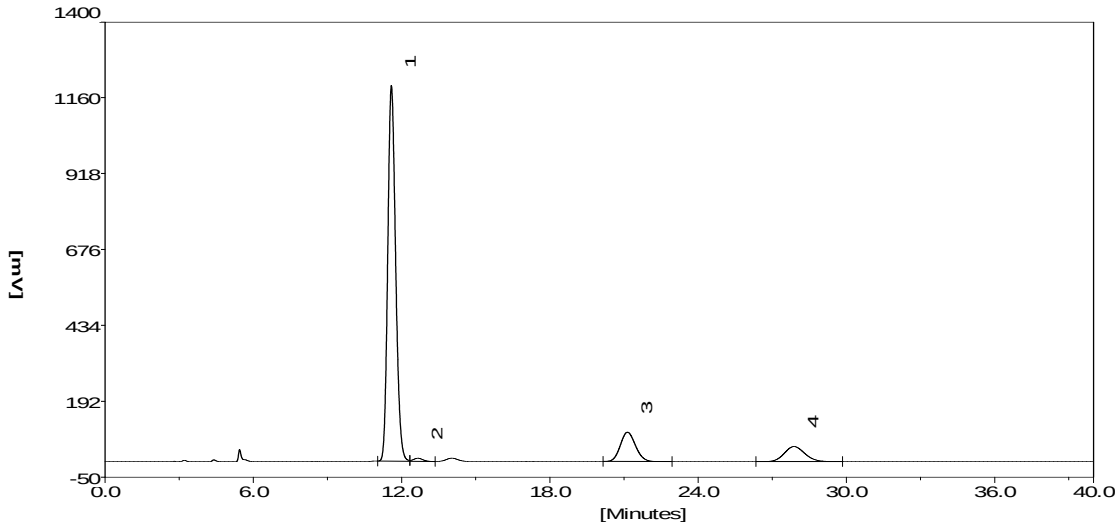


(3ea) trimethyl 2-(4-bromophenyl)-1-(diphenylmethyleneamino)propane-1,3,3-tricarboxylate

white solid, 98% yield; **m.p.** 135-136 ^{o}C; R_f = 0.22(*anti*), 0.26(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.45-7.31 (m, 8H), 7.05 (d, *J* = 8.3 Hz, 2H), 6.93-6.85 (m, 2H), 4.40-4.36 (m, 1H), 4.31-4.24 (m, 2H), 3.63 (s, 3H), 3.57 (s, 3H), 3.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.3, 170.7, 168.3, 168.1, 138.9, 138.3, 135.7, 131.4, 130.8, 130.5, 129.1, 128.7, 128.5, 128.2, 127.3, 121.3, 68.4, 53.8, 52.7, 52.4, 52.1, 48.1; **IR** ν 3482, 2883, 1751, 1609, 1491, 1448, 1311, 1200, 1186, 1009, 794, 703, 637, 536; **HRMS** for $C_{28}H_{26}BrNO_6$ Calculated: 551.0944, Found: 551.0947; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 11.59 min, 12.66 min, 21.14 min, 27.88 min.

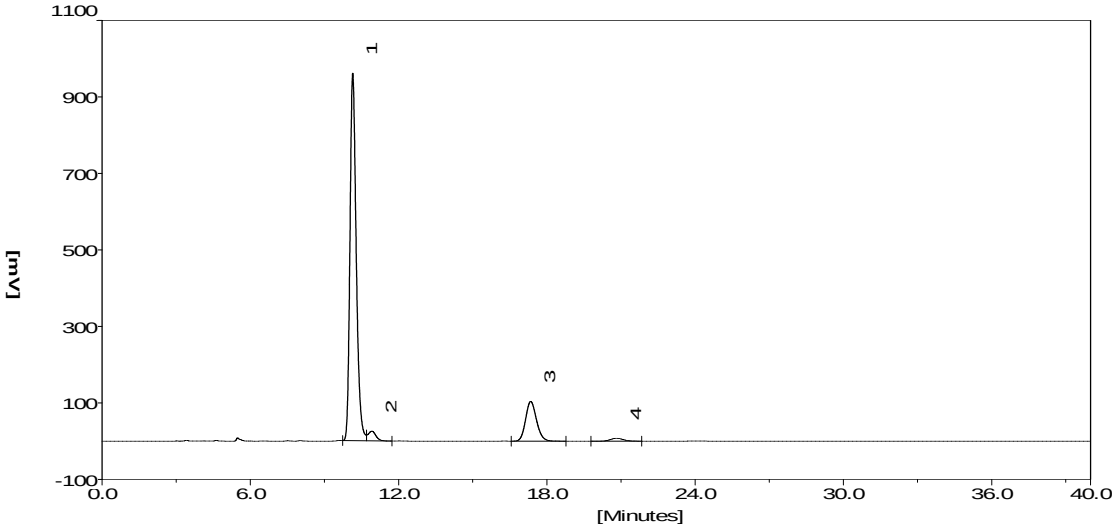


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	11.52	219.71	4893.03	30.8369
2	12.54	113.00	2995.72	18.8796
3	21.05	70.7	3023.48	19.0546
4	27.71	87.17	4955.24	31.2289

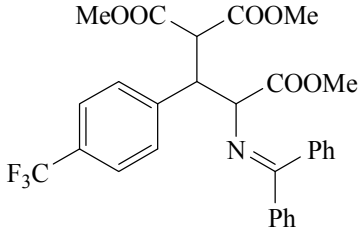


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	11.59	1196.17	26510.76	79.2278
2	12.66	9.98	259.82	0.7765
3	21.14	93.29	3957.70	11.8277
4	27.88	47.75	2733.15	8.1681

Crystallization



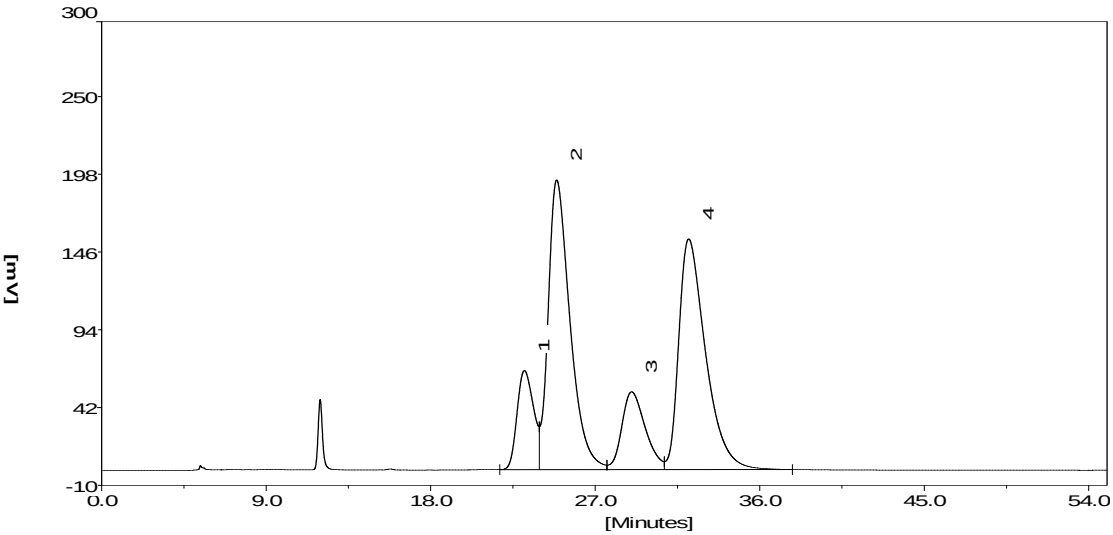
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	10.15	960.88	16896.03	80.7507
2	10.92	25.66	561.93	2.6856
3	17.35	103.96	3189.50	15.2435
4	20.82	7.55	276.24	1.3202



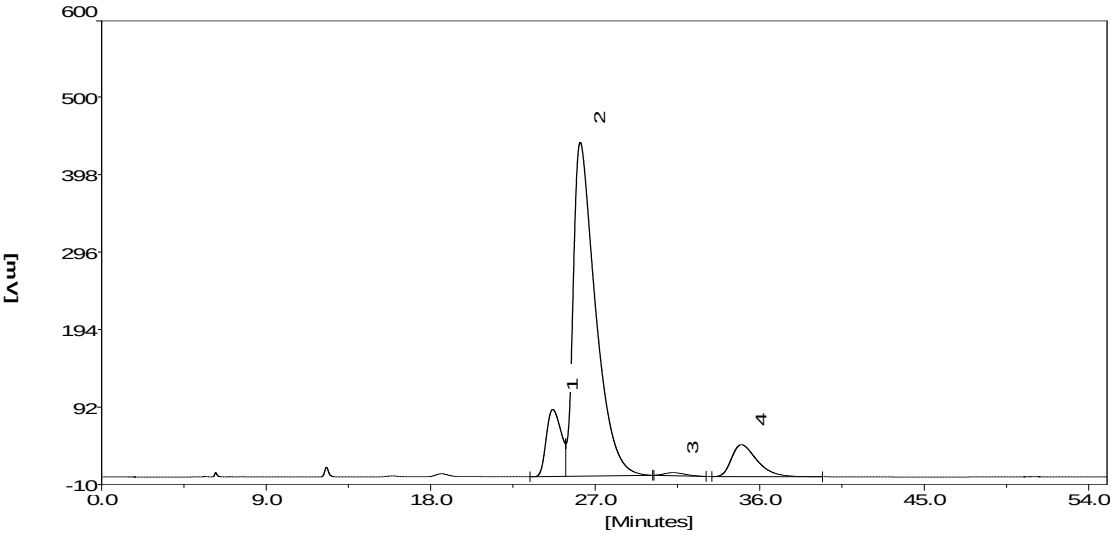
(3fa)

trimethyl 1-(diphenylmethyleneamino)-2-(4-(trifluoromethyl)phenyl)propane -1,3,3-tricarboxylate

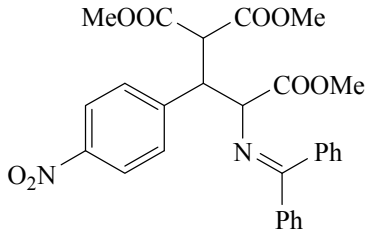
96% yield; R_f = 0.20(*anti*), 0.24(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.67 (d, *J* = 7.2 Hz, 2H), 7.50-7.27 (m, 10H), 6.85 (d, *J* = 6.5 Hz, 2H), 4.45 (d, *J* = 10.4 Hz, 1H), 4.38 (dd, *J* = 10.4, 4.6 Hz, 1H), 4.30 (d, *J* = 4.6 Hz, 1H), 3.65 (s, 3H), 3.58 (s, 3H), 3.42 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 170.6, 168.3, 168.0, 143.5, 138.8, 135.6, 130.9, 130.4, 129.1(0), 129.0(6), 128.8, 128.5, 128.2, 127.5, 127.3, 125.2, 68.3, 53.6, 52.7, 52.4, 52.2, 48.4; **IR** ν 3472, 2894, 1743, 1611, 1581, 1493, 1423, 1320, 1273, 1114, 1085, 1010, 922, 821, 787, 700, 612, 541 cm^{-1}; **HRMS** for $C_{29}H_{26}F_3NO_6$ Calculated: 541.1712, Found: 541.1715; **HPLC** (Chiralcel OD-H, hexane/*i*-propanol = 50/1, 0.6 mL/min, 254 nm) t_R = 24.68 min, 26.18 min, 31.27 min, 35.01 min



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area（%）
1	23.13	66.24	4154.71	10.2376
2	24.90	193.70	16075.48	39.6116
3	29.00	52.01	4651.18	11.461
4	32.12	154.26	15701.38	38.6898



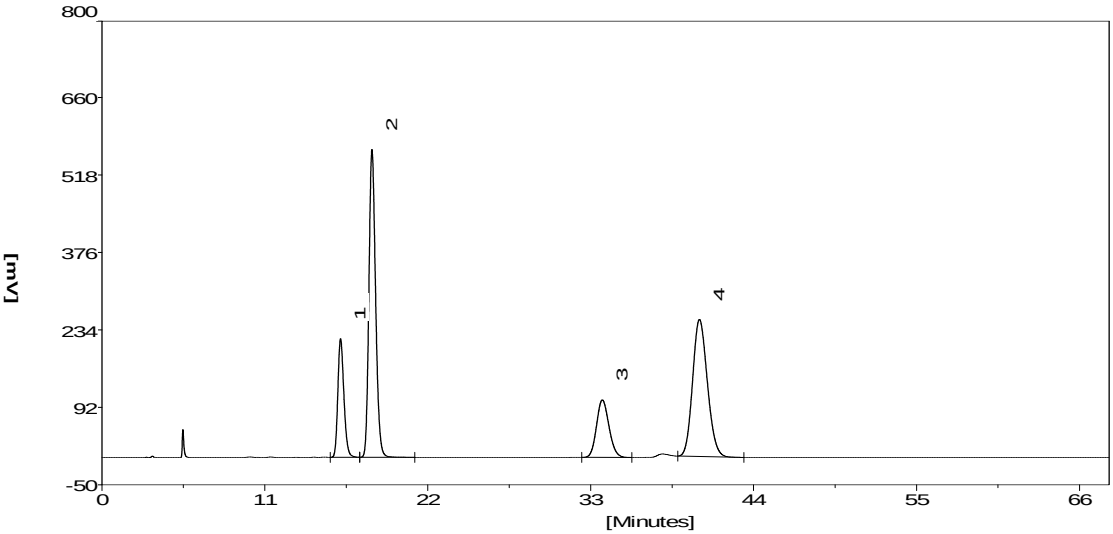
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area（%）
1	24.68	88.26	4976.34	10.73
2	26.18	439.32	37020.62	79.8239
3	31.27	3.94	305.10	0.6579
4	35.01	42.01	4075.82	8.7883



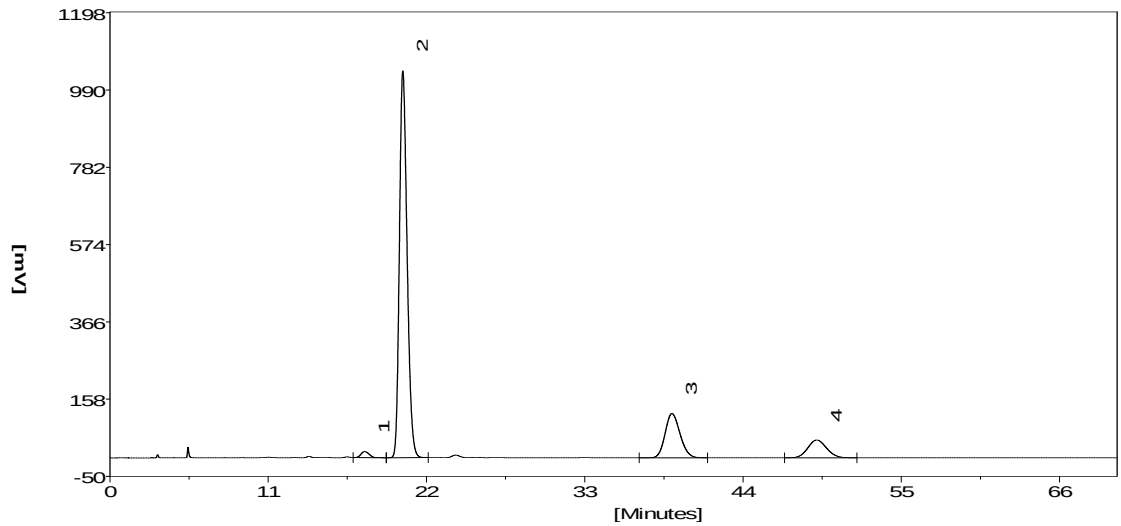
(3ga)

trimethyl 1-(diphenylmethyleneamino)-2-(4-nitrophenyl)propane-1,3,3-tricarboxylate

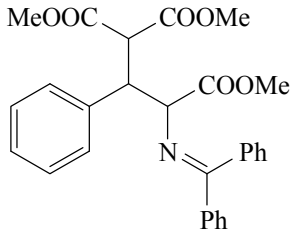
white solid, 83% yield; **m.p.** 148-151°C; R_f = 0.20(*anti*), 0.24(*syn*) (petroleum ether /ethylacetate = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 7.4 Hz, 2H), 7.50-7.32 (m, 8H), 6.94-6.89 (m, 2H), 4.48-4.37 (m, 2H), 4.34 (d, *J* = 4.6 Hz, 1H), 3.65 (s, 3H), 3.57 (s, 3H), 3.44 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.7, 170.4, 168.0, 167.9, 147.1, 146.9, 138.7, 135.6, 131.0, 129.8, 129.0, 128.9, 128.6, 128.2, 127.2, 123.4, 67.8, 53.5, 52.8, 52.6, 52.2, 48.4; IR ν 3481, 2879, 1744, 1617, 1600, 1517, 1438, 1359, 1266, 1018, 874, 792, 733, 700, 652, 561 cm^{-1}; **HRMS** for $C_{28}H_{26}ClN_2O_8$ Calculated: 518.1689, Found: 518.1690; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 17.70 min, 20.36 min, 39.07 min, 49.13min.



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	16.11	217.71	6186.53	13.0512
2	18.24	564.34	17671.31	37.2797
3	33.79	105.53	6145.60	12.9649
4	40.34	251.36	17398.46	36.7041

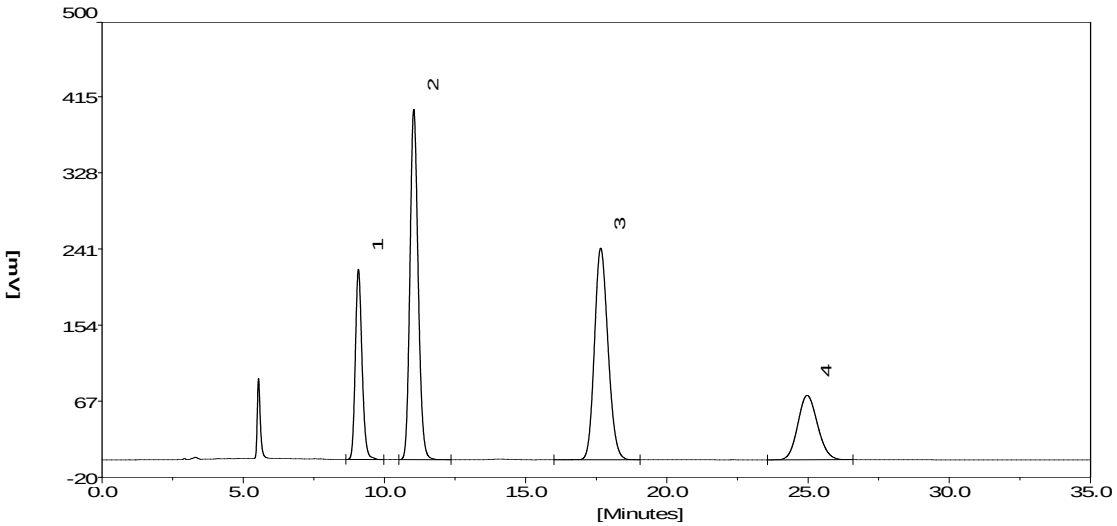


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	17.70	16.27	648.97	1.2446
2	20.36	1040.98	38571.79	73.9759
3	39.07	119.29	8586.64	16.4681
4	49.13	47.87	4333.60	8.3113

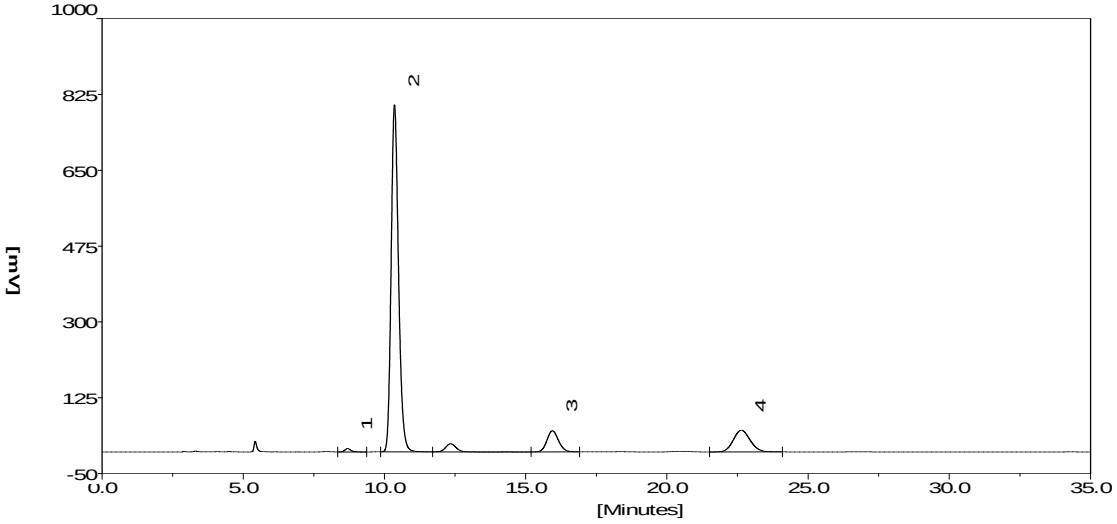


(3ha)
trimethyl 1-(diphenylmethyleneamino)-2-phenylpropane-1,3,3-tricarboxylate

white solid, 89% yield; **m.p.** 144-145 ^{o}C; R_f = 0.20(*anti*), 0.23(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.43-7.40 (m, 1H), 7.39-7.31 (m, 5H), 7.22-7.12 (m, 5H), 6.87-6.83 (m, 2H), 4.42-4.30 (m, 3H), 3.64 (s, 3H), 3.57 (s, 3H), 3.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 170.9, 168.6, 168.3, 139.3, 139.0, 135.9, 130.7, 129.1, 128.6(2), 128.5(8), 128.4, 128.3, 128.1, 127.4, 127.3, 68.9, 54.1, 52.6, 52.3, 52.0, 48.6; IR ν 3386, 2880, 1766, 1619, 1586, 1493, 1431, 1372, 1395, 1198, 1123, 1017, 941, 788, 700, 651, 523 cm^{-1}; **HRMS** for $C_{28}H_{28}NO_6$ $[M+1]^+$ Calculated: 474.1917, Found: 474.1937; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 8.70 min, 10.36 min, 15.95 min, 22.64 min.

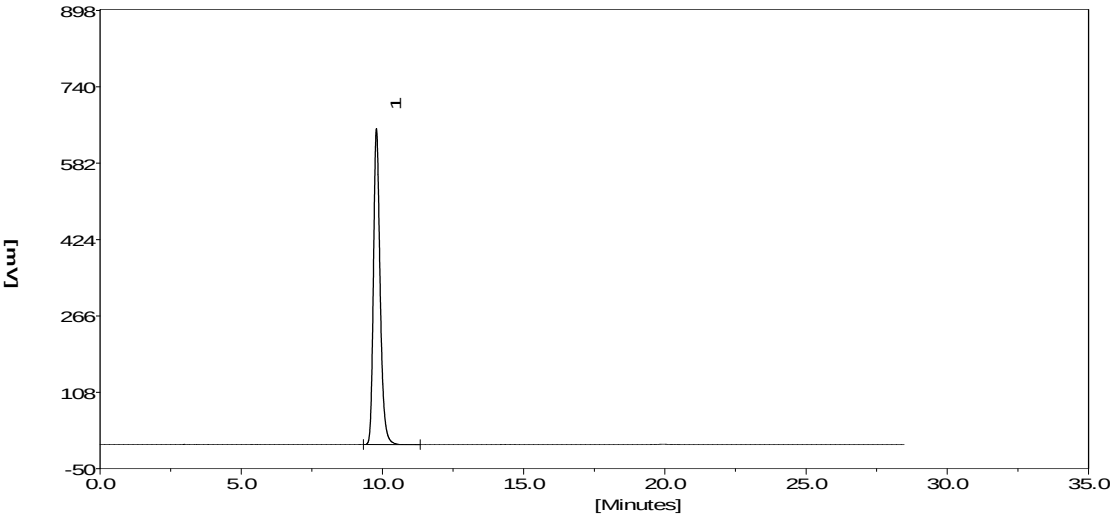


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.08	217.46	3580.79	15.4034
2	11.04	400.42	8045.43	34.6089
3	17.66	242.06	8053.36	34.6431
4	24.97	73.60	3567.10	15.3446

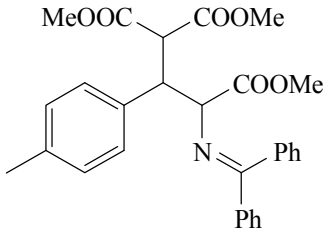


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	8.70	7.66	114.28	0.6319
2	10.36	800.96	14511.07	80.2456
3	15.95	48.80	1385.85	7.6637
4	22.64	50.13	2072.12	11.4588

Crystallization



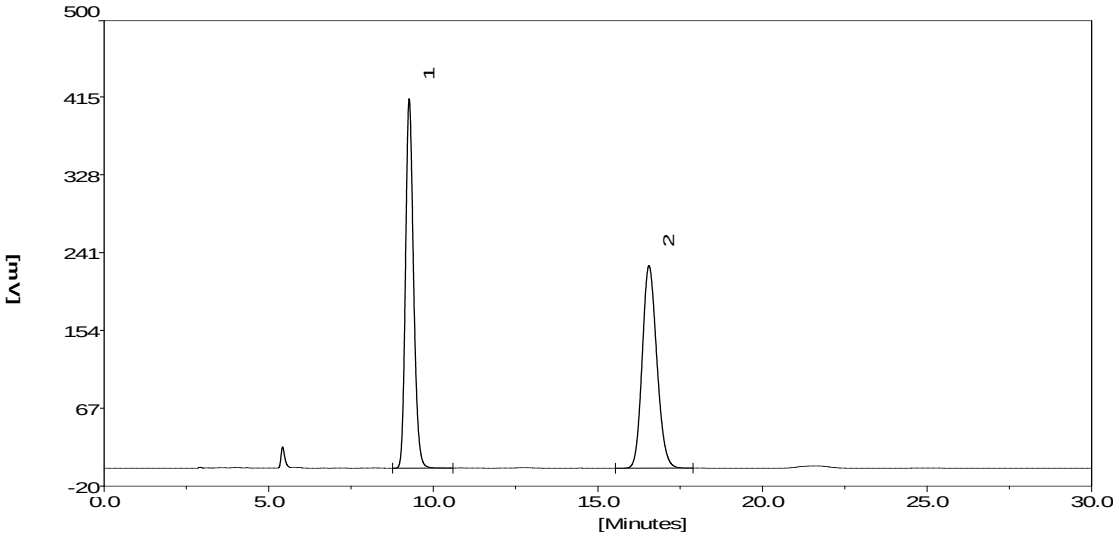
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.78750	653.51	10740.12	100.0000



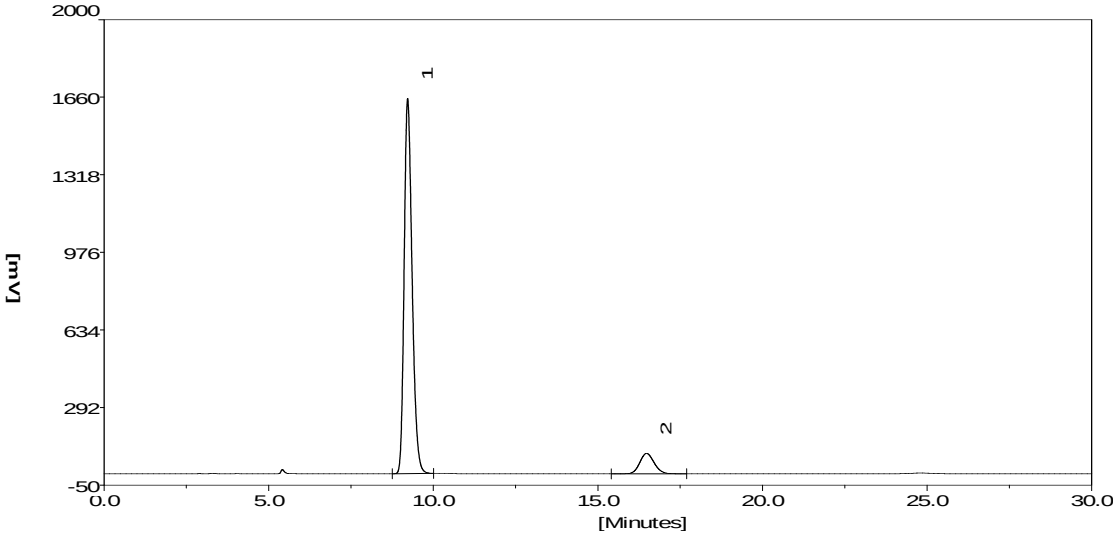
(3ia)
trimethyl 1-(diphenylmethyleneamino)-2-*p*-tolylpropane-1,3,3-tricarboxylate

white solid, 93% yield; **m.p.** 88-90 ^{o}C; R_f = 0.20(*anti*), 0.25(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.68 (d, *J* = 7.2 Hz, 2H) 7.45-7.30 (m, 6H), 7.03-6.98 (m, 4H), 6.91-6.85 (m, 2H), 4.38-4.26 (m, 3H), 3.62 (s, 3H), 3.56 (s, 3H), 3.40 (s, 3H), 2.26 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.8, 170.9, 168.6, 168.4, 139.1, 136.8, 136.1, 135.9, 130.7, 129.1, 128.9, 128.6, 128.5, 128.4, 128.1, 127.4, 69.0, 54.3, 52.6, 52.3, 52.0, 48.3, 21.1; IR ν 3421, 2893, 1748, 1621, 1586, 1518, 1436, 1362, 1310, 1258, 1123, 1085, 1023, 947, 819, 700, 648, 519 cm^{-1}; **HRMS** for $C_{29}H_{29}NO_6$ Calculated: 487.1995, Found: 487.1997; **HPLC** (Chiralpak AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) (*anti*) t_R = 9.22 min, 16.48 min. (*syn*) t_R = 9.11 min, 24.75 min.

anti

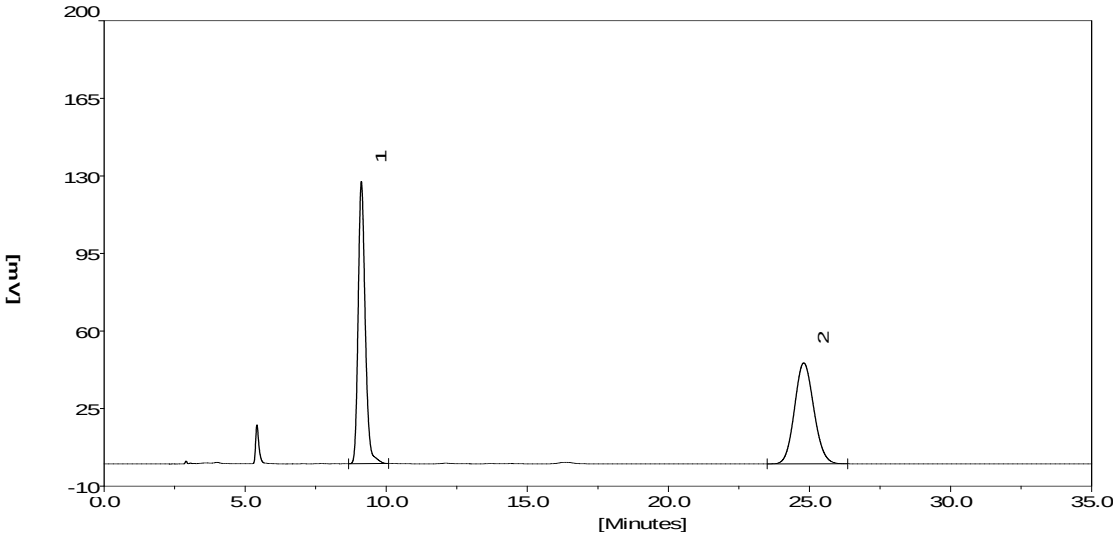


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.27	412.91	6995.17	50.11
2	16.55	226.40	6964.45	49.89

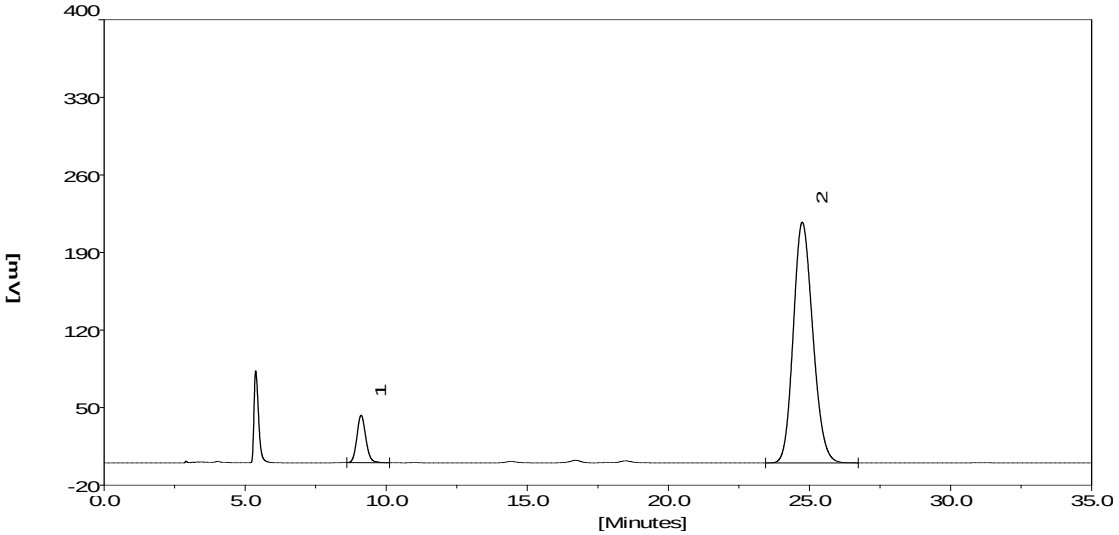


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.22	1651.72	27718.91	91.0276
2	16.48	89.84	2732.18	8.9724

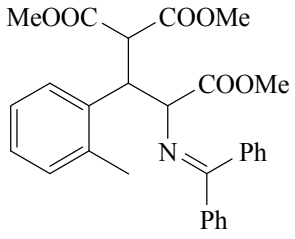
syn



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.12	127.38	2211.80	50.5143
2	24.80	45.62	2166.76	49.4857



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.11	42.92	940.51	8.268
2	24.75	217.36	10434.89	91.732

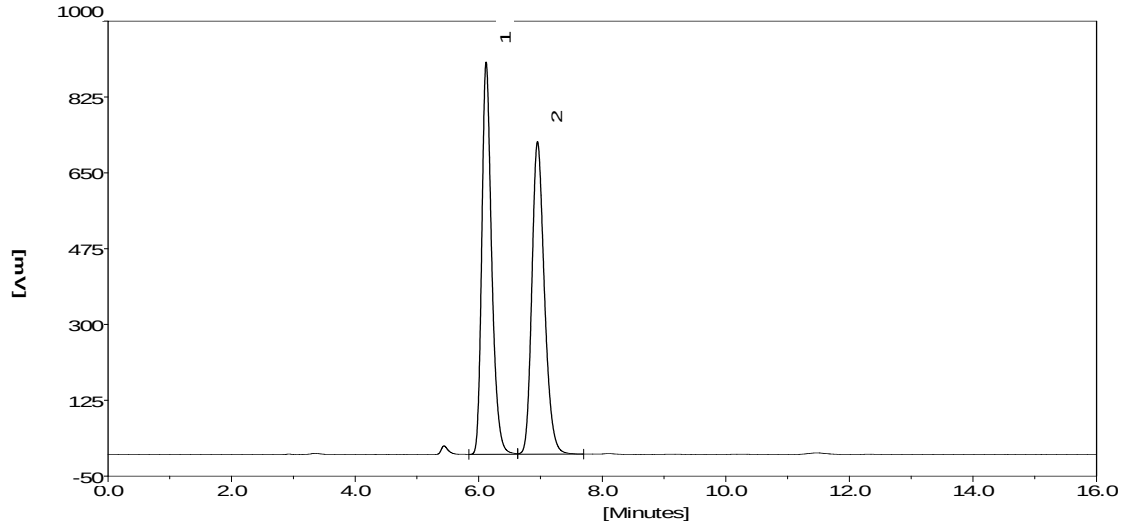


(3ja)

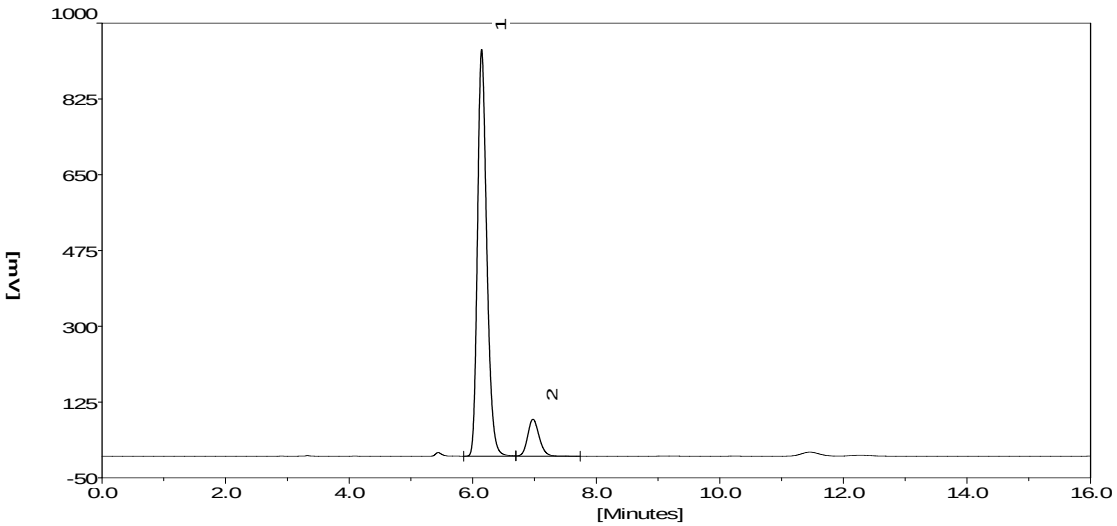
trimethyl 1-(diphenylmethyleneamino)-2-*o*-tolylpropane-1,3,3-tricarboxylate

white solid, 82% yield; **m.p.** 118-121°C; R_f = 0.19(*anti*), 0.24(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.68 (d, *J* = 7.3 Hz, 2H), 7.43-7.39 (m, 2H), 7.38-7.28 (m, 4H), 7.09-6.92 (m, 4H), 6.76 (d, *J* = 6.8 Hz, 2H), 4.70 (dd, *J* = 11.0, 4.4 Hz, 1H), 4.40 (d, *J* = 11.0 Hz, 1H), 4.20 (d, *J* = 4.4 Hz, 1H), 3.66 (s, 3H), 3.59 (s, 3H), 3.37 (s, 3H), 2.39 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 171.0, 168.7, 168.4, 139.0, 137.9, 136.9, 135.8, 130.7, 130.6, 129.1, 128.5, 128.4, 128.1, 127.3, 126.9, 126.8, 125.7, 68.3, 54.3, 52.6, 52.3, 52.1, 43.1, 19.7; **IR** ν 3229, 2984, 1758, 1612, 1495, 1420, 1340, 1310, 1235, 1201, 1120, 1080, 1010, 785, 700, 525 cm^{-1}; **HRMS** for $C_{29}H_{29}NO_6$ Calculated: 487.1995, Found: 487.1996; **HPLC** (Chiralcel AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) (*anti*) t_R = 6.14 min, 6.98 min. (*syn*) t_R = 7.07 min, 11.44 min.

anti

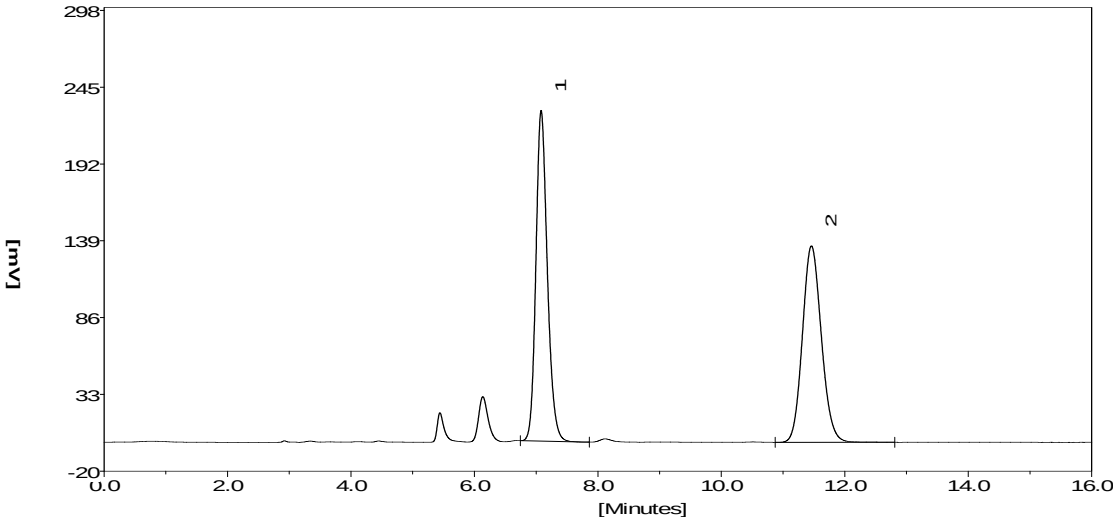


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	6.12	905.70	10055.80	49.6797
2	6.95	721.58	10185.46	50.3203

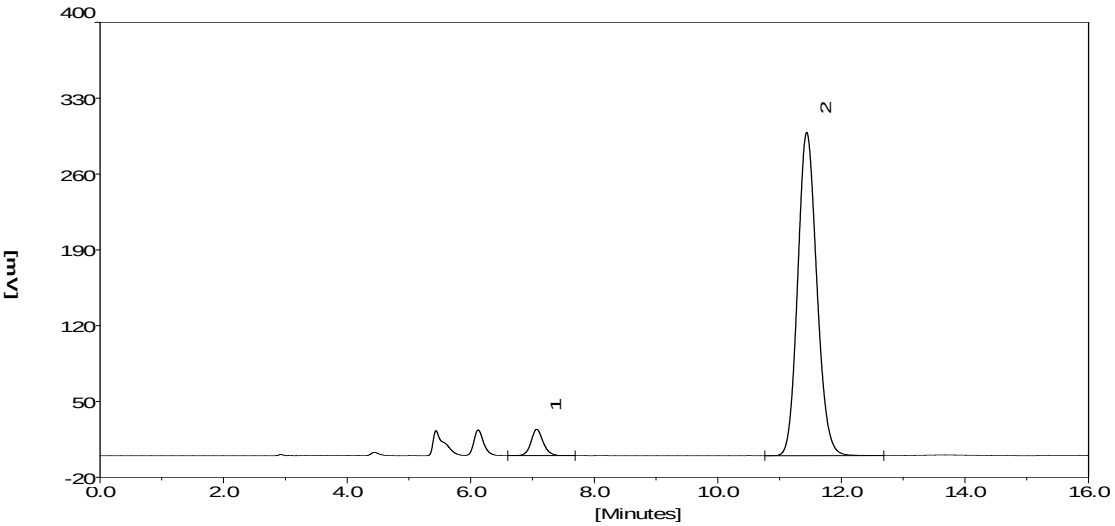


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	6.14	939.11	9842.27	89.8666
2	6.98	85.55	1109.82	10.1334

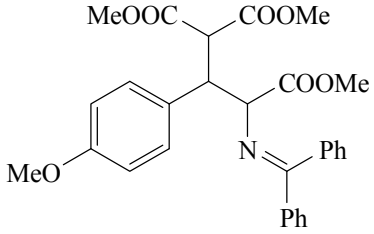
syn



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	7.08	228.26	2930.97	50.3539
2	11.46	135.60	2889.77	49.6461



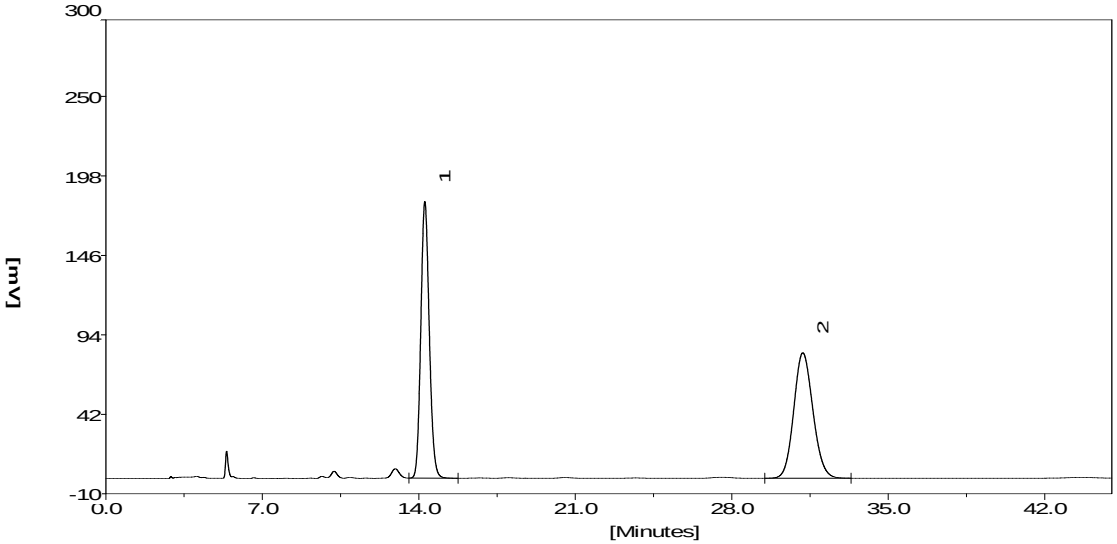
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	7.07	24.30	333.96	4.9556
2	11.44	298.63	6405.06	95.0444



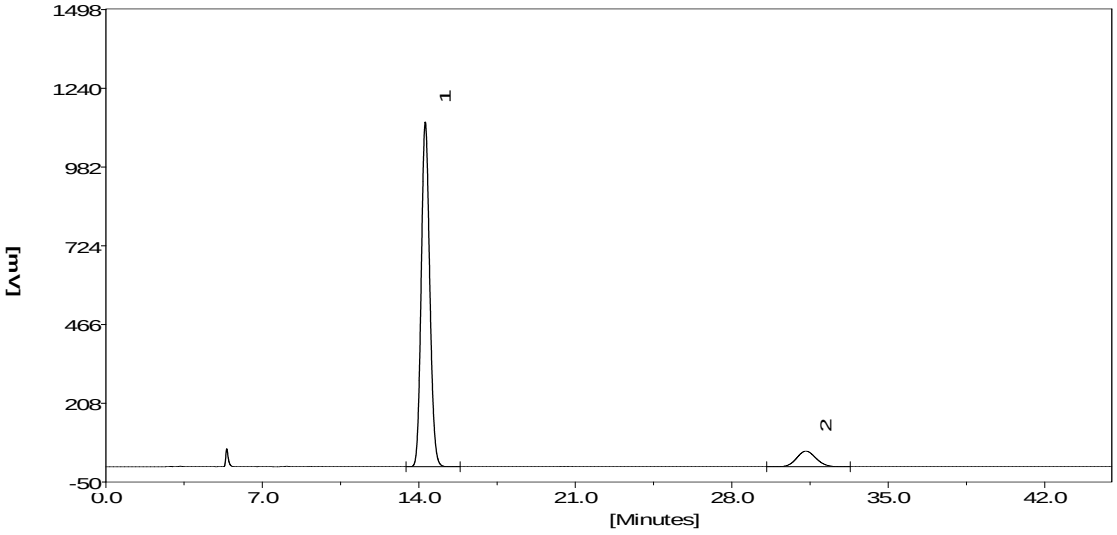
(3ka)
trimethyl 1-(diphenylmethyleneamino)-2-(4-methoxyphenyl)propane-1,3,3-tricarboxylate

82% yield; R_f = 0.20(*anti*), 0.25(*syn*) (petroleum ether /ethylacetate = 4:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.44-7.32 (m, 6H), 7.08 (d, *J* = 8.6 Hz, 2H), 6.94-6.89 (m, 2H), 6.74 (d, *J* = 8.7 Hz, 2H), 4.34-4.24 (m, 3H), 3.74 (s, 3H), 3.62 (s, 3H), 3.55 (s, 3H), 3.41 (s, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) for *syn* isomer: δ 7.67 (d, *J* = 7.3 Hz, 2H), 7.46-7.35 (m, 8H), 7.04 (dd, *J* = 6.1, 2.6 Hz, 2H), 6.83 (d, *J* = 8.6 Hz, 2H), 4.49 (s, 1H), 4.10-4.06 (m, 2H), 3.78 (s, 3H), 3.61 (s, 3H), 3.47 (s, 3H), 3.40 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 170.9, 168.6, 168.4, 158.7, 139.1, 135.9, 131.1, 130.7, 129.8, 129.1, 128.6, 128.4, 128.1, 127.4, 113.6, 69.0, 55.1, 54.4, 52.6, 52.3, 52.0, 47.9; **IR** ν 3476, 2886, 2803, 1757, 1607, 1588, 1506, 1423, 1241, 1083, 1020, 819, 792, 700, 651, 552 cm^{-1}; **HRMS** for $C_{29}H_{29}NO_7$ Calculated: 503.1944, Found: 503.1949; **HPLC** (Chiralcel AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) (*anti*) t_R = 14.29 min, 31.32 min. (*syn*) t_R = 12.87 min, 30.75 min

anti

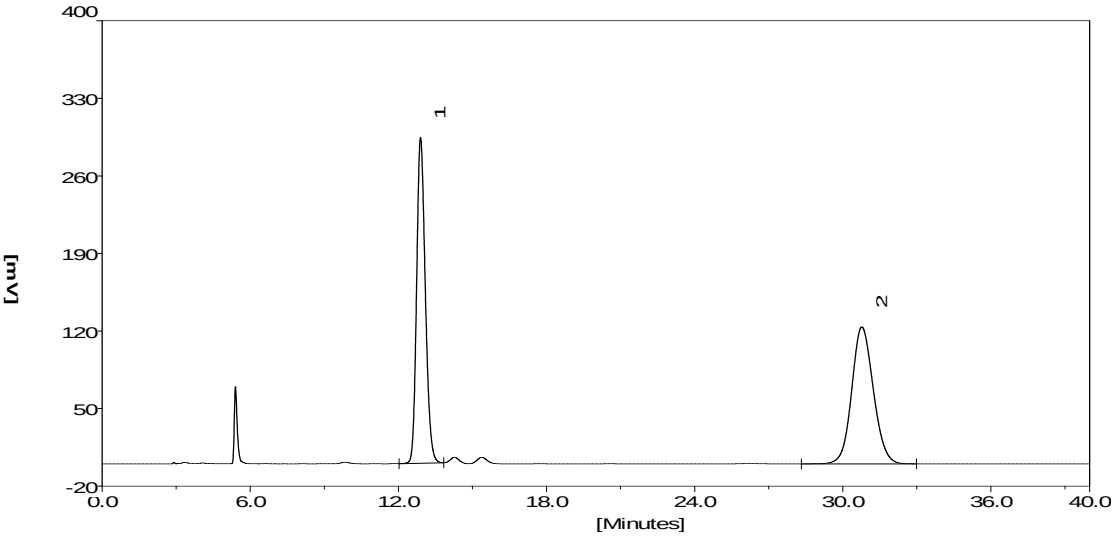


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	14.27	180.89	4762.46	49.4147
2	31.18	82.06	4875.28	50.5853

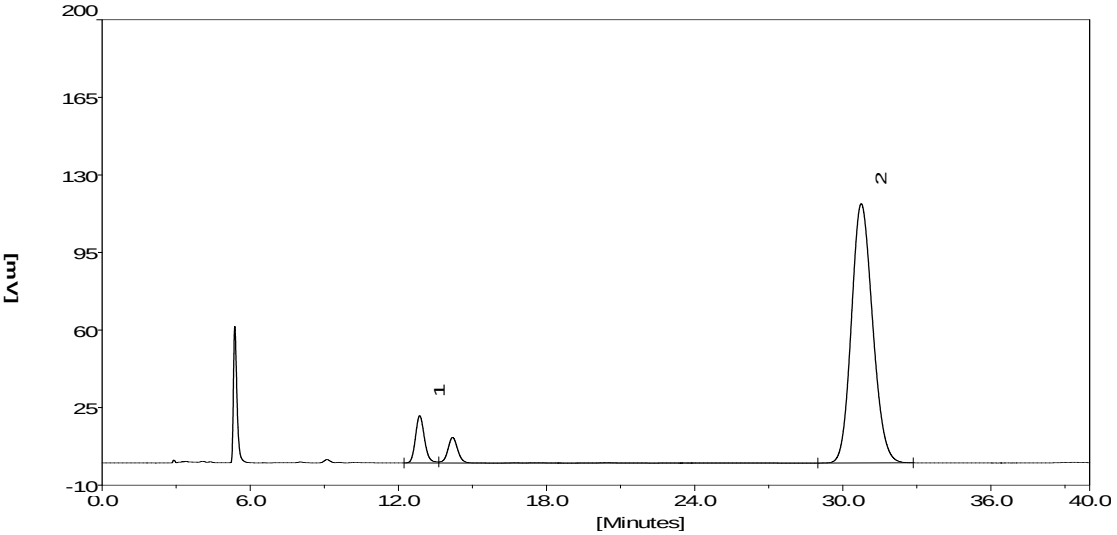


#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	14.29	1129.76	29836.98	90.6148
2	31.32	51.20	3090.29	9.3852

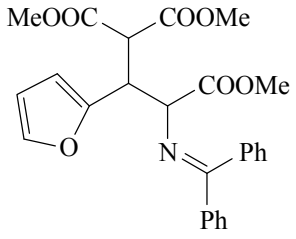
syn



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	12.90	294.30	7191.31	48.8345
2	30.77	123.76	7534.57	51.1655



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	12.87	21.34	542.28	7.2244
2	30.75	117.02	6963.89	92.7756

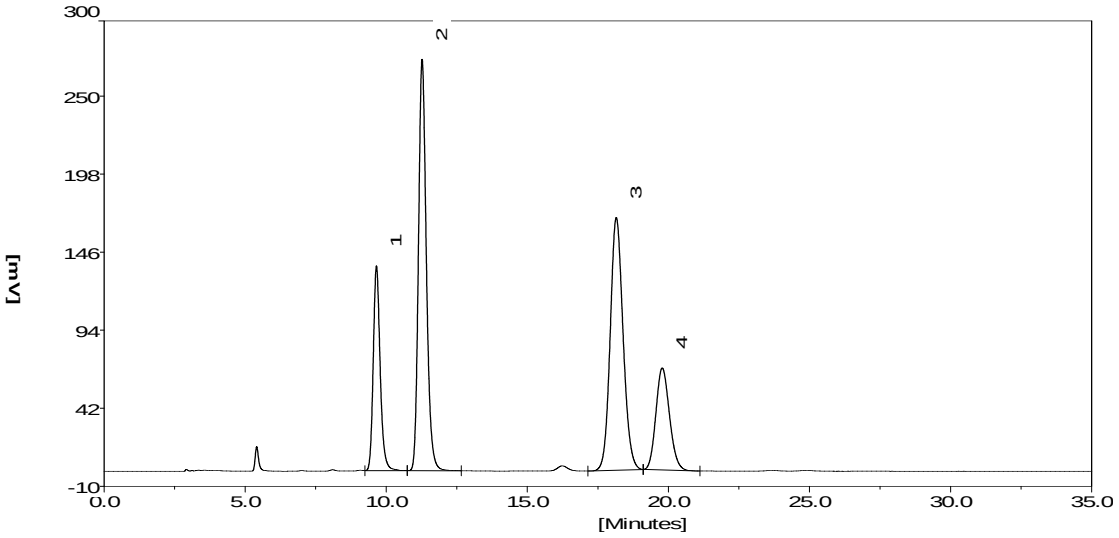


(3la)

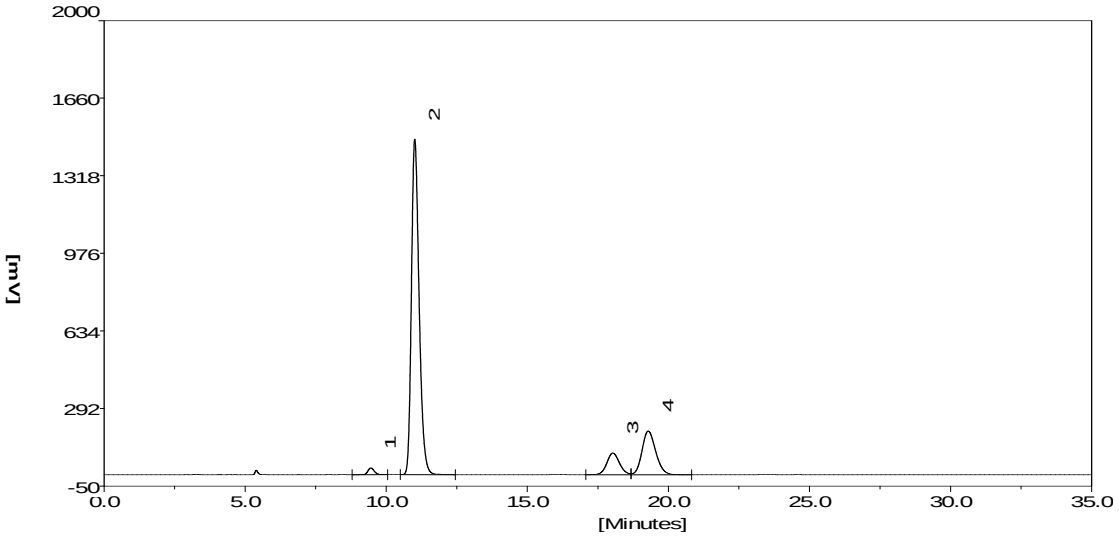
trimethyl 1-(diphenylmethyleneamino)-2-(furan-2-yl)propane-1,3,3-tricarboxyla-

te

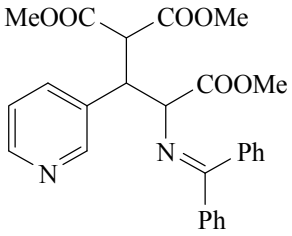
white solid, 93% yield; **m.p.** 121-122 ^{o}C; R_f = 0.23(*anti*), 0.27(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.46-7.30 (m, 6H), 7.25-7.24 (m, 1H), 7.01-6.96 (m, 2H), 6.23-6.19 (m, 1H), 6.12-6.09 (m, 1H), 4.50-4.41 (m, 2H), 4.26 (d, *J* = 9.5 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.2, 170.8, 168.3, 152.5, 141.8, 139.1, 135.8, 130.7, 129.1, 128.7, 128.4, 128.1, 127.7, 127.6, 110.2, 107.6, 66.6, 52.7, 52.5(4), 52.5(0), 52.2, 42.6; IR ν 3340, 2903, 1751, 1620, 1600, 1584, 1493, 1421, 1321, 1259, 1083, 1011, 915, 807, 701, 651, 538 cm^{-1}; **HRMS** for $C_{26}H_{26}NO_7$ $[M+1]^+$ Calculated: 464.1709, Found: 464.1832; **HPLC** (Chiralcel AD-H, hexane/*i*-propanol = 90/10, 1.0 mL/min, 254 nm) t_R = 9.46 min, 11.01 min. 18.03min, 19.29 min



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.65	136.34	2321.77	15.2284
2	11.27	274.09	5310.98	34.8343
3	18.15	168.44	5340.06	35.0251
4	19.78	68.00	2273.58	14.9122



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	9.46	30.41	478.87	1.2625
2	11.01	1478.05	27957.45	73.7088
3	18.03	96.11	2991.94	7.8881
4	19.29	192.80	6501.33	17.1405



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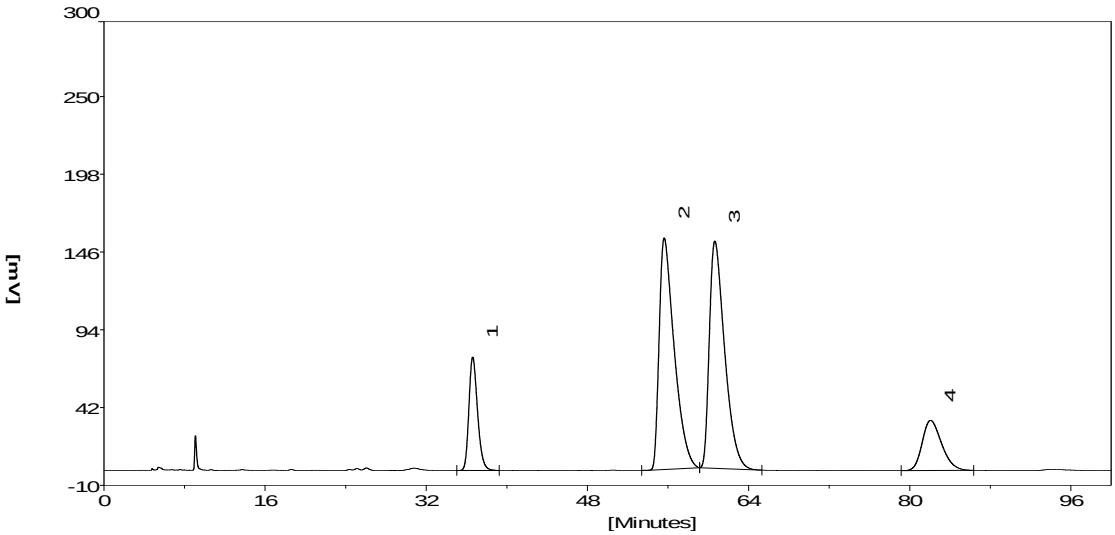
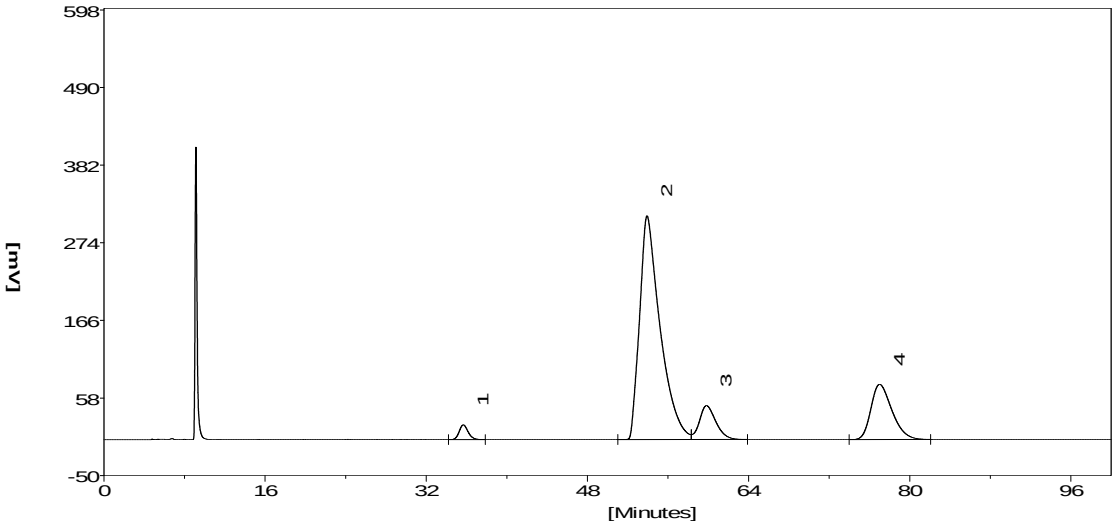
(3ma)

trimethyl 1-(diphenylmethyleneamino)-2-(pyridin-3-yl)propane-1,3,3-tricarboxy -late

white solid, 88% yield; **m.p.** 114-117°C; R_f = 0.18(*anti*), 0.22(*syn*) (petroleum ether /ethylacetate = 6:1); **^{1}H NMR** (400 MHz, $CDCl_3$) for *anti* isomer: δ 8.48-8.43 (m, 2H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.46-7.33 (m, 6H), 7.16 (dd, *J* = 7.8, 4.8 Hz, 1H), 6.95-6.89 (m, 2H), 4.43 (d, *J* = 10.0 Hz, 1H), 4.31 (dt, *J* = 15.0, 5.0 Hz, 2H), 3.64 (s, 3H), 3.57 (s, 3H), 3.43 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 170.5, 168.2, 168.0, 150.3, 148.7, 138.8, 136.3, 135.7, 134.8, 130.9, 129.1, 128.8, 128.5, 128.2, 127.3, 123.1, 68.0, 53.5, 52.8, 52.5, 52.2, 46.4; **IR** ν 3400, 2887, 1760, 1618, 1587, 1417, 1312, 1250, 1199, 1123, 1080, 1010, 918, 812, 788, 701, 530 cm^{-1}; **HRMS** for $C_{27}H_{26}N_2O_6$ Calculated: 474.1791, Found: 474.1788; **HPLC** (Chiralcel AD-H, hexane/*i*-propanol = 90/10, 0.6 mL/min, 254 nm) t_R = 35.69 min, 53.93 min, 59.83 min, 77.02 min.



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	36.62	75.87	4512.77	10.9817
2	55.64	154.74	16045.58	39.0463
3	60.66	151.95	16040.73	39.0345
4	82.08	33.52	4494.63	10.9375

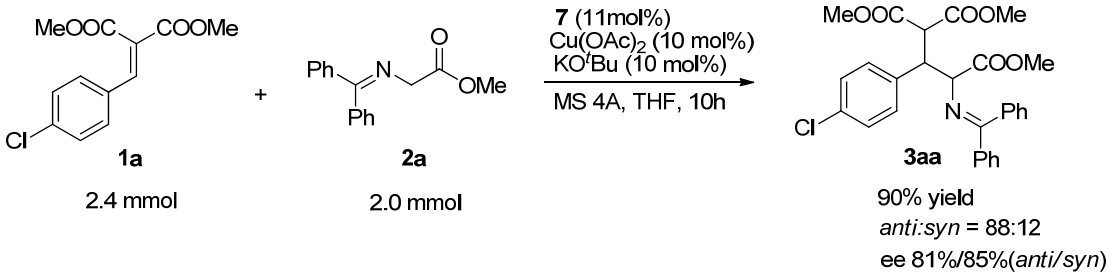


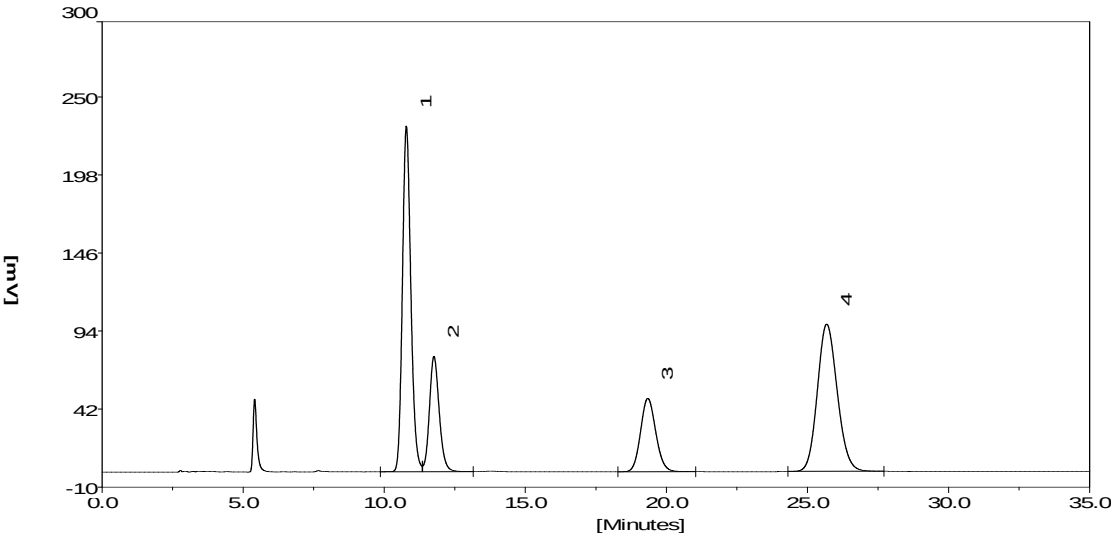
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	35.69	20.63	1271.49	2.056
2	53.93	311.18	44061.63	71.2474
3	59.83	47.14	5364.76	8.6748
4	77.02	76.87	11145.26	18.0218

Scale-up experiment of the 1,4-addition of 1a to 2a

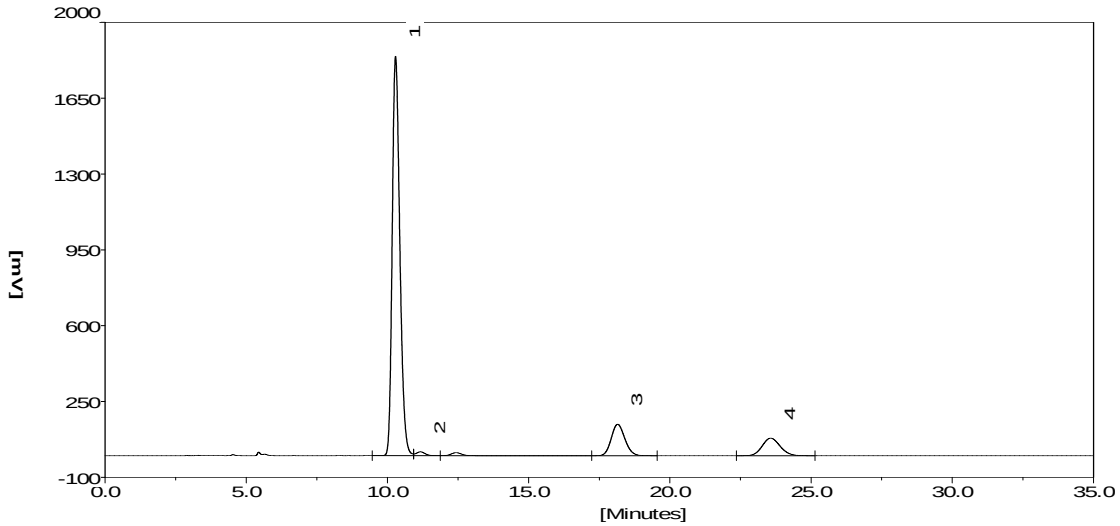
$Cu(OAc)_2 \cdot H_2O$ (39.9 mg, 0.2 mmol), the ligand **7** (98.0 mg, 0.22 mmol) and KO^tBu (22.4 mg, 0.2 mmol) were added under N_2 to a flame-dried Schlenk tube, containing

activated 4Å MS and a stirring bar. Then anhydrous THF (15 mL) was added. After the mixture was stirred for 1h at room temperature, Schiff base substrate **2a** (506.6 mg, 2.0 mmol), and alkylidene malonate **1a** (611.2 mg, 2.4 mmol) were added sequentially. Once starting material was consumed (monitored by TLC), the mixture was concentrated to dryness and then the residue was purified by column chromatography to give the corresponding product **3aa** (914.3 mg, 90% yield), which was then directly analyzed by chiral HPLC to determine the enantiomeric excess.





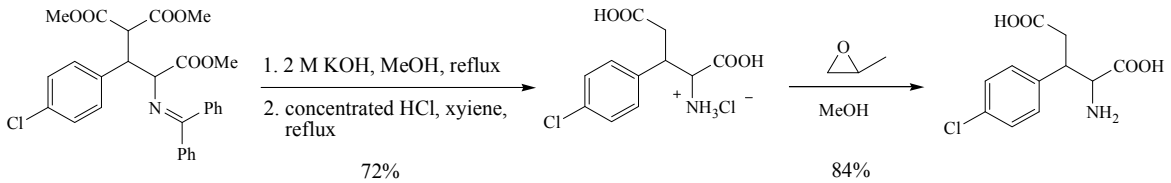
#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	10.78	230.24	4791.15	36.0699
2	11.76	76.90	1861.85	14.0168
3	19.34	48.92	1832.85	13.7985
4	25.68	98.1	4797.13	36.1149



#	RetTime(min)	Height(mV)	Area(mV.sec)	Area (%)
1	10.28750	1843.39	34461.04	79.6703
2	11.16833	17.81	379.48	0.8773
3	18.15000	145.20	4846.34	11.2042
4	23.56917	81.05	3567.72	8.2482

Procedure for 3-*p*-chlorophenyl glutamic acid and the determination of the absolute configuration of (2*R*, 3*S*)-3aa[2]

To a solution of **3aa** (90 mg, 0.177 mmol, 98% ee) in MeOH was added a solution of 2 N KOH (5 equiv). The reaction mixture was stirred at reflux for 2 h. Solvents were evaporated under reduced pressure, then acidified with concentrated hydrochloric acid to pH 0-1, and xyiene was added. The mixture was stirred at reflux for 20 h. Solvents were evaporated under reduced pressure until dryness to give a white solid containing the crude product together with KCl, The solid was washed with MeOH (twice), the solution was separated with a pipet and concentrated in a rotary evaporator to afford a yellow solid. The crude hydrochloride was triturated with Et_2O several times and dried, solid **12** (37.5 mg, 0.128 mmol) was obtained.



3aa **12** **13**

Hydrochloride **12** (37.5 mg, 0.128 mmol) was dissolved in the minimum amount of MeOH; the same equivalent amount of propylene oxide was added, and the reaction mixture was stirred at room temperature for 30 min. Solvents were evaporated under reduced pressure to give a white solid. The operation was repeated. The resultant solid was dried, triturated with Et_2O several times, and dried until a consistent solid **13** was

obtained (27.6 mg, 0.107 mmol). $[\alpha]^{26}_{D}$: -120 (c 0.07, 1M NaOH); lit:[3] $[\alpha]^{20}_{D}$: +129 (c 0.07, 1M NaOH); **^{1}H NMR** (400 MHz, MeOD) δ 7.49-7.17 (m, 4H), 4.06 (d, *J* = 4.6 Hz, 1H), 3.78-3.58 (m, 1H), 2.85 (dd, *J* = 17.0, 9.2 Hz, 1H), 2.38 (dd, *J* = 17.0, 6.1 Hz, 1H).

The relative configuration of the *anti*-3ha were determined by X-ray diffraction analysis

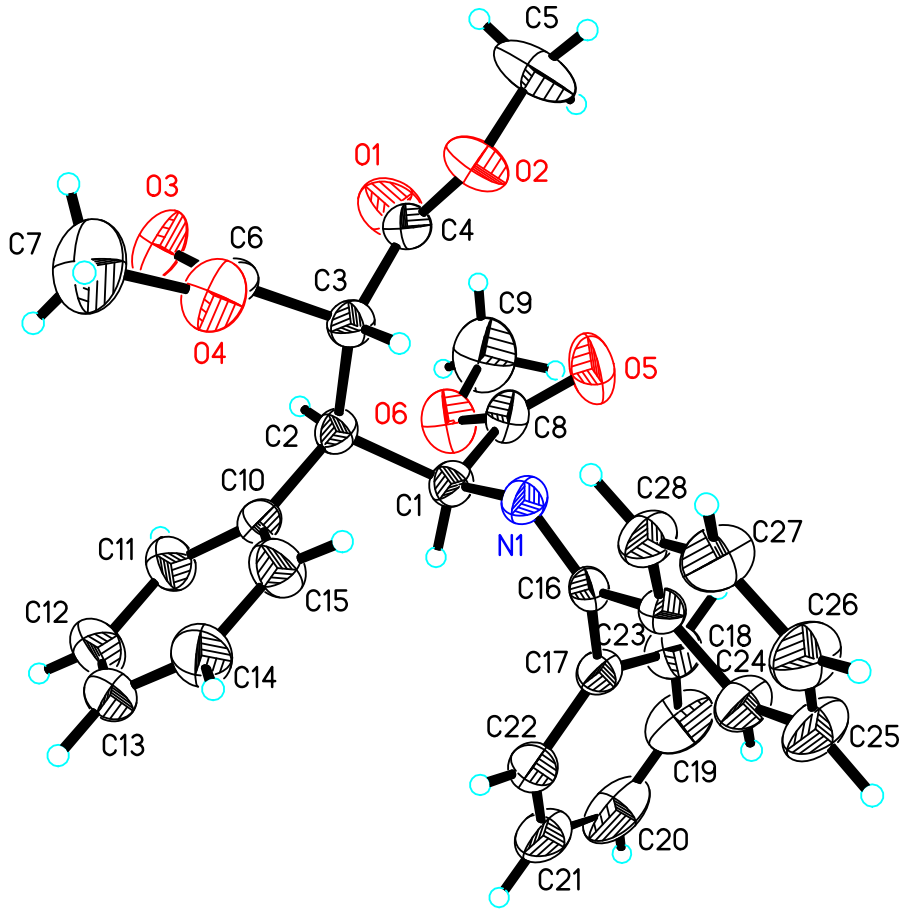
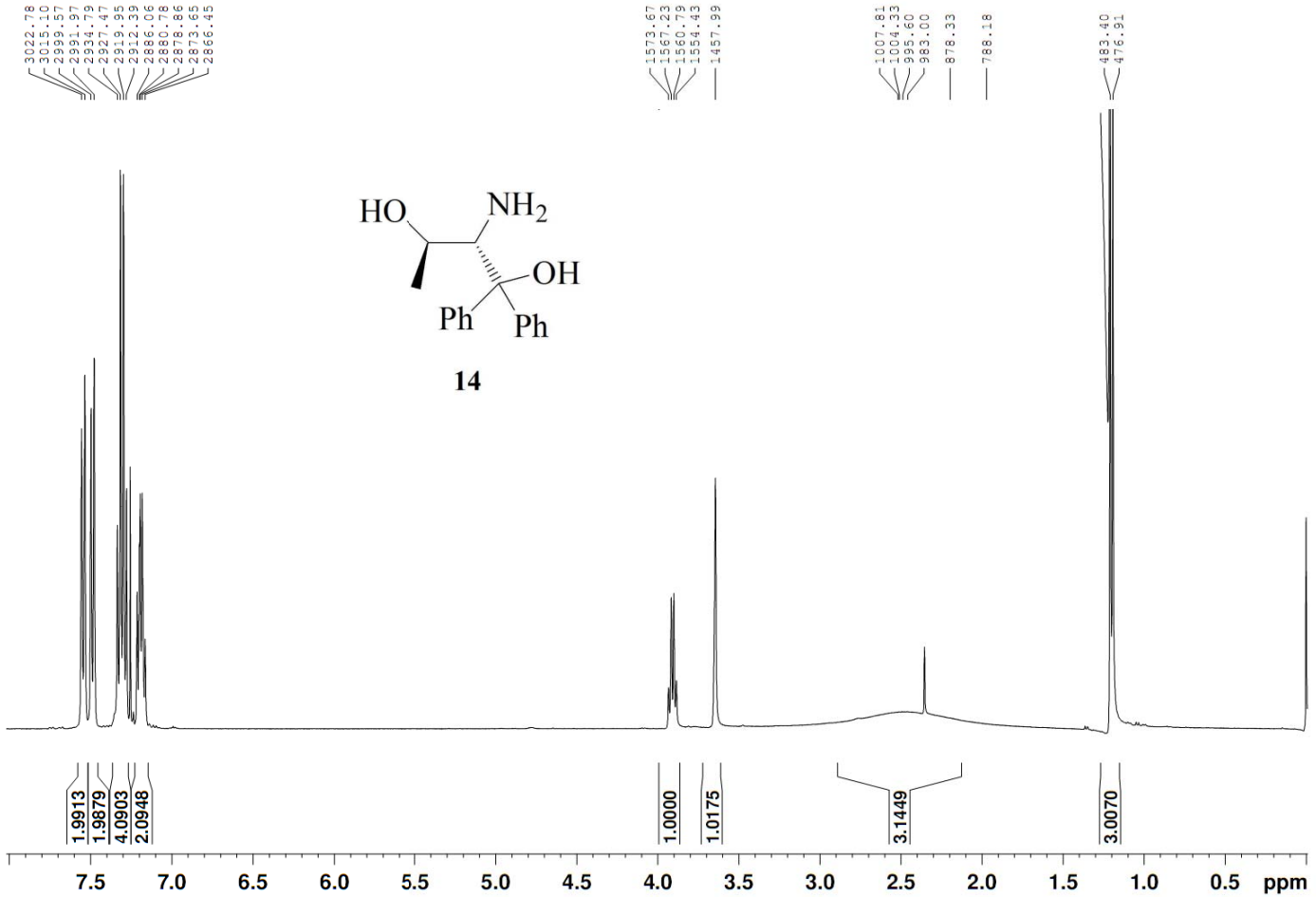


Figure 1. X-ray structure of *anti*-**3ha** (relative configuration)

Crystal data for *anti*-**3ha**: crystal of *anti*-**3ha** was grown in a solution of *i*-propanol, $C_{28}H_{27}NO_6$, *Mr* = 473.51, *T* = 293K, Orthorhombic, Space group P2(1)2(1)2(1), *a* = 10.4200(17) Å, *b* = 12.888(2) Å, *c* = 19.103(3) Å, *V* = 2565.4(7) Å^3, *Z* = 4, 2125 unique reflections, final R_1 = 0.0350 and wR_2 = 0.0814 for 11182 collected [$I>2\sigma(I)$] reflections.

References:

1. S. Rajaram, and M. S. Sigman, *Org. Lett.* 2005, **7**, 5473.
2. (a) L. T. Liu, P. C. Hong, H. L. Huang, S. F. Chen, and C. L. Wang, *Tetrahedron Asymmetry* 2001, **12**, 419. (b) J. Ezquerra, and C. Pedregal, *J. Org. Chem.* 1999, **64**, 6554.
3. C. Herdeis, and B. Kelm, *Tetrahedron*, 2003, **59**, 217.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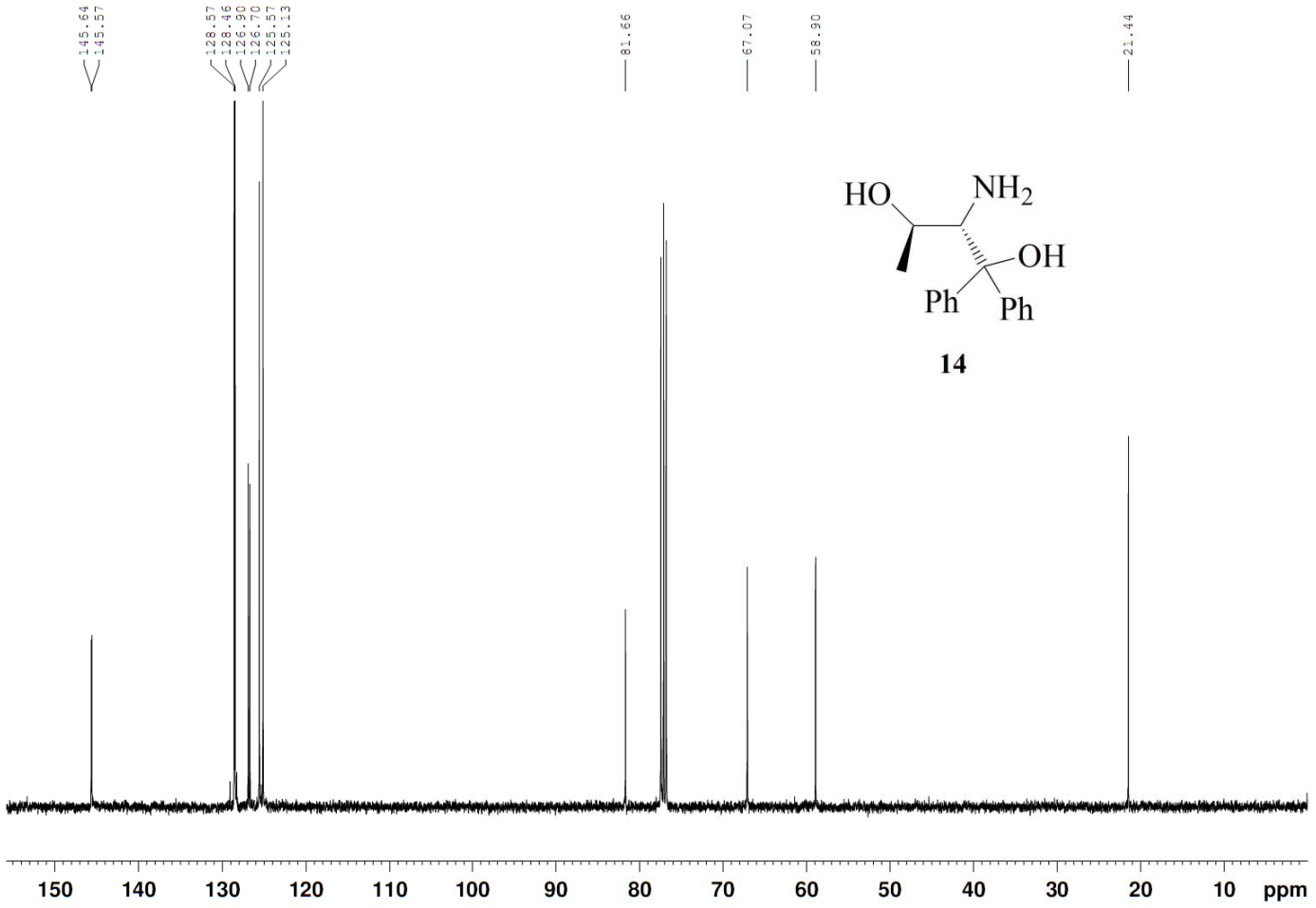
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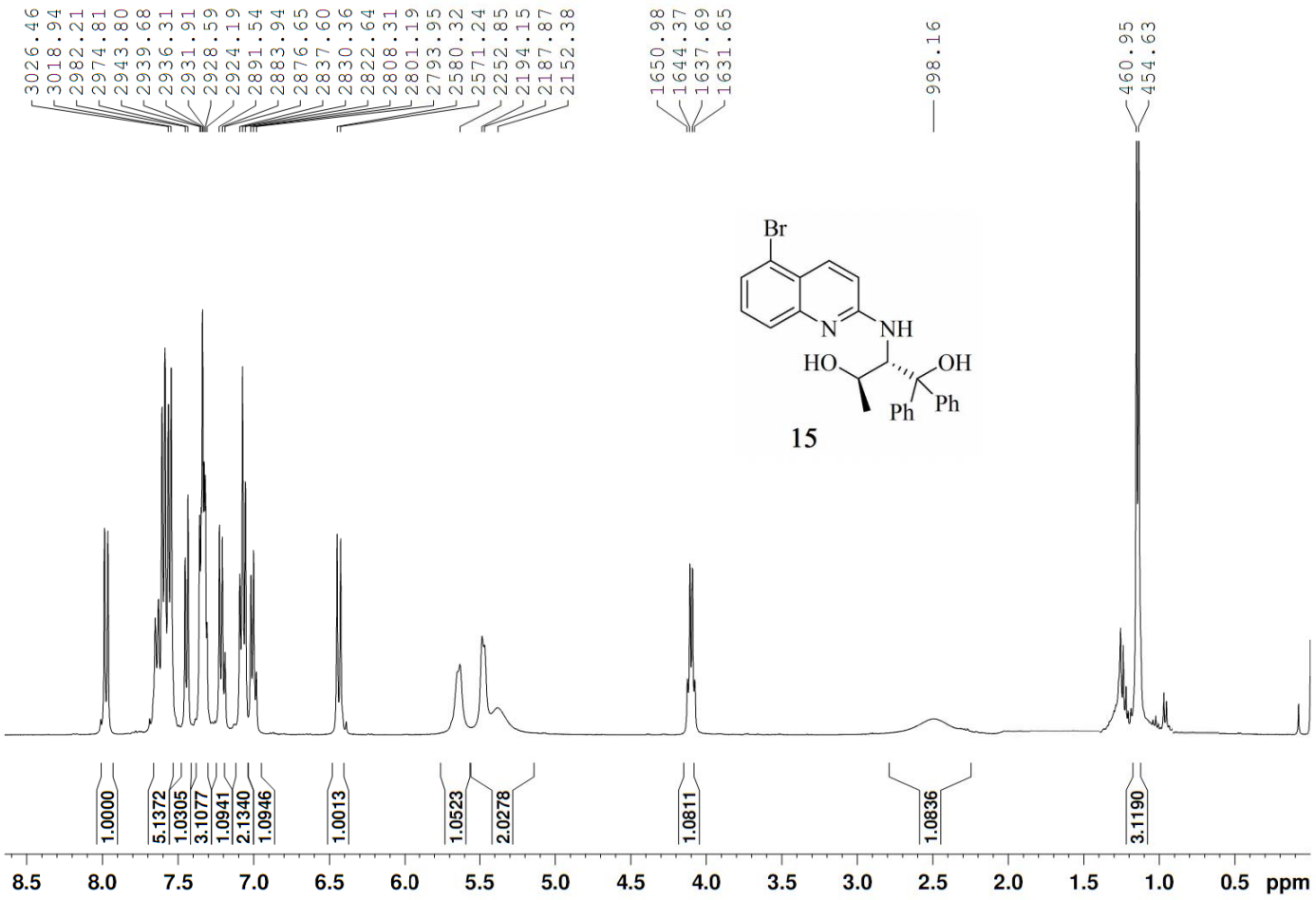
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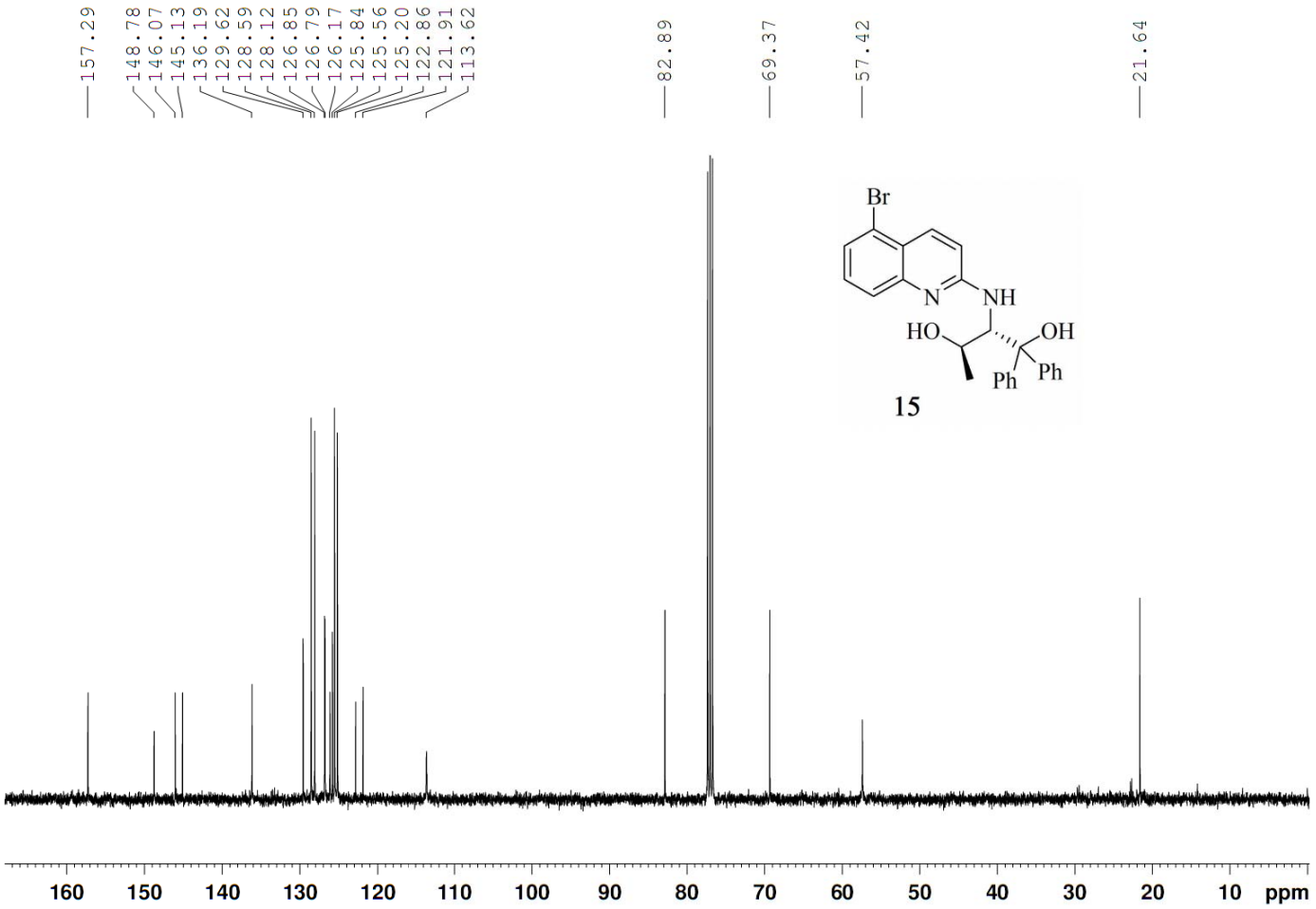
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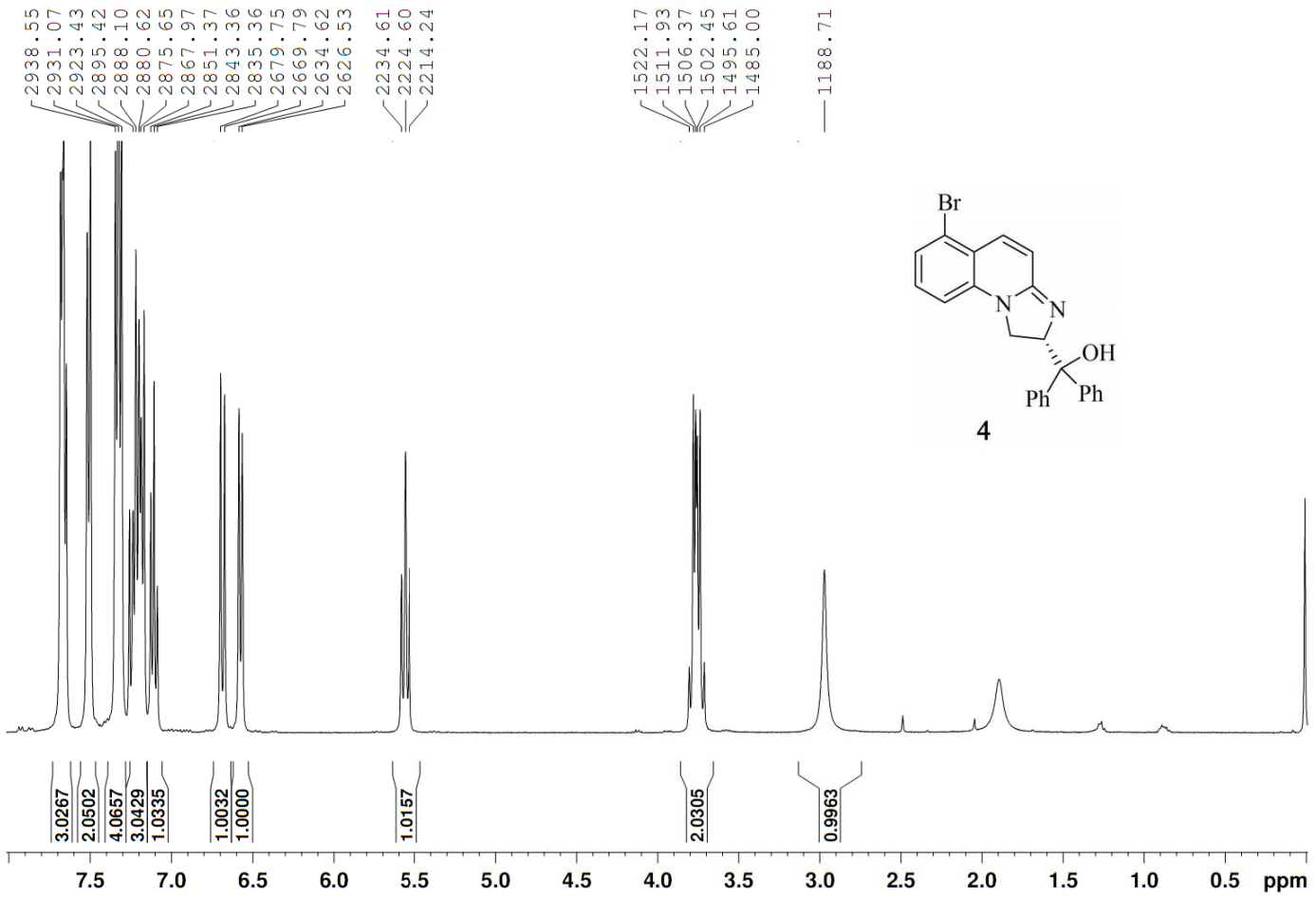
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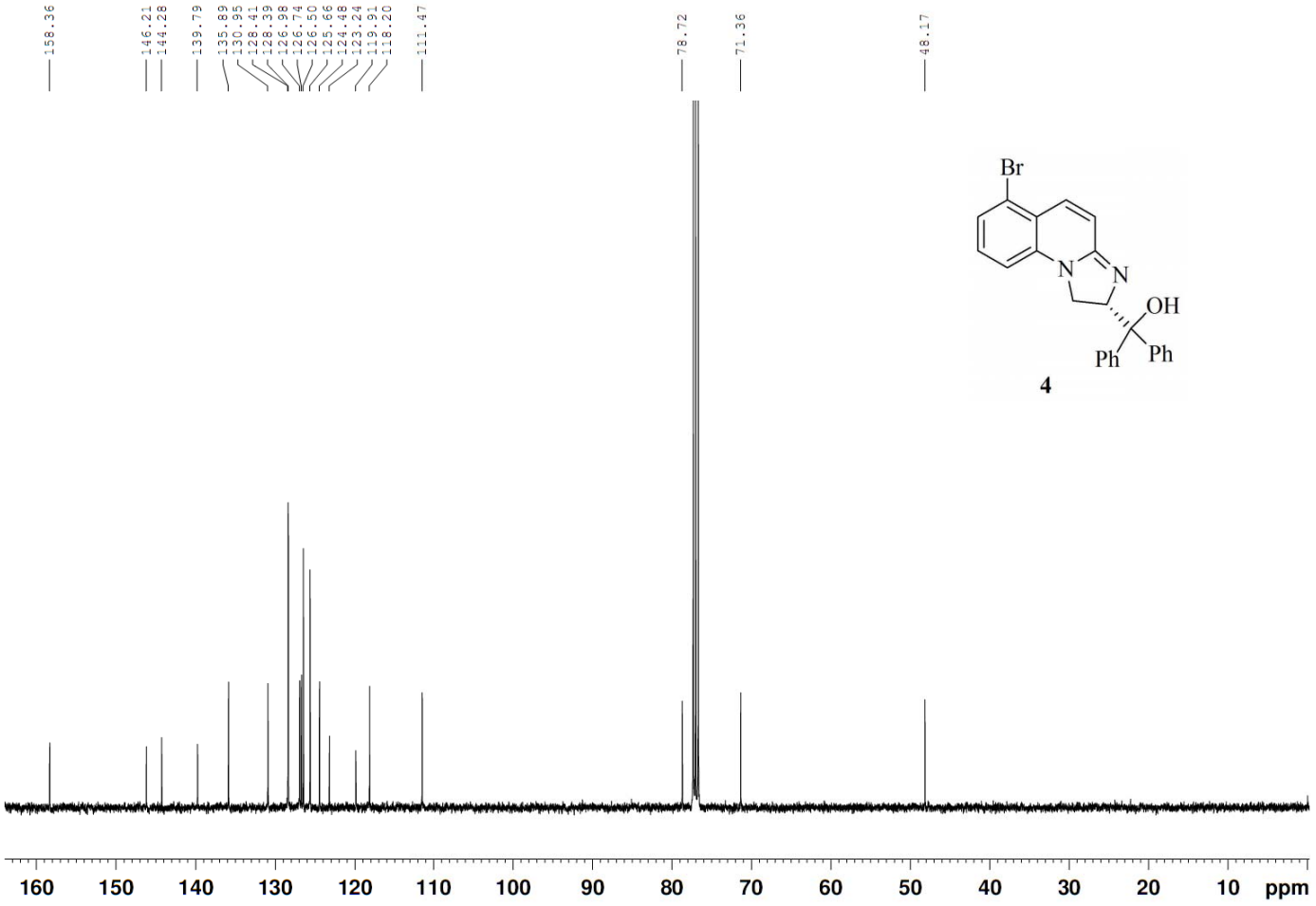
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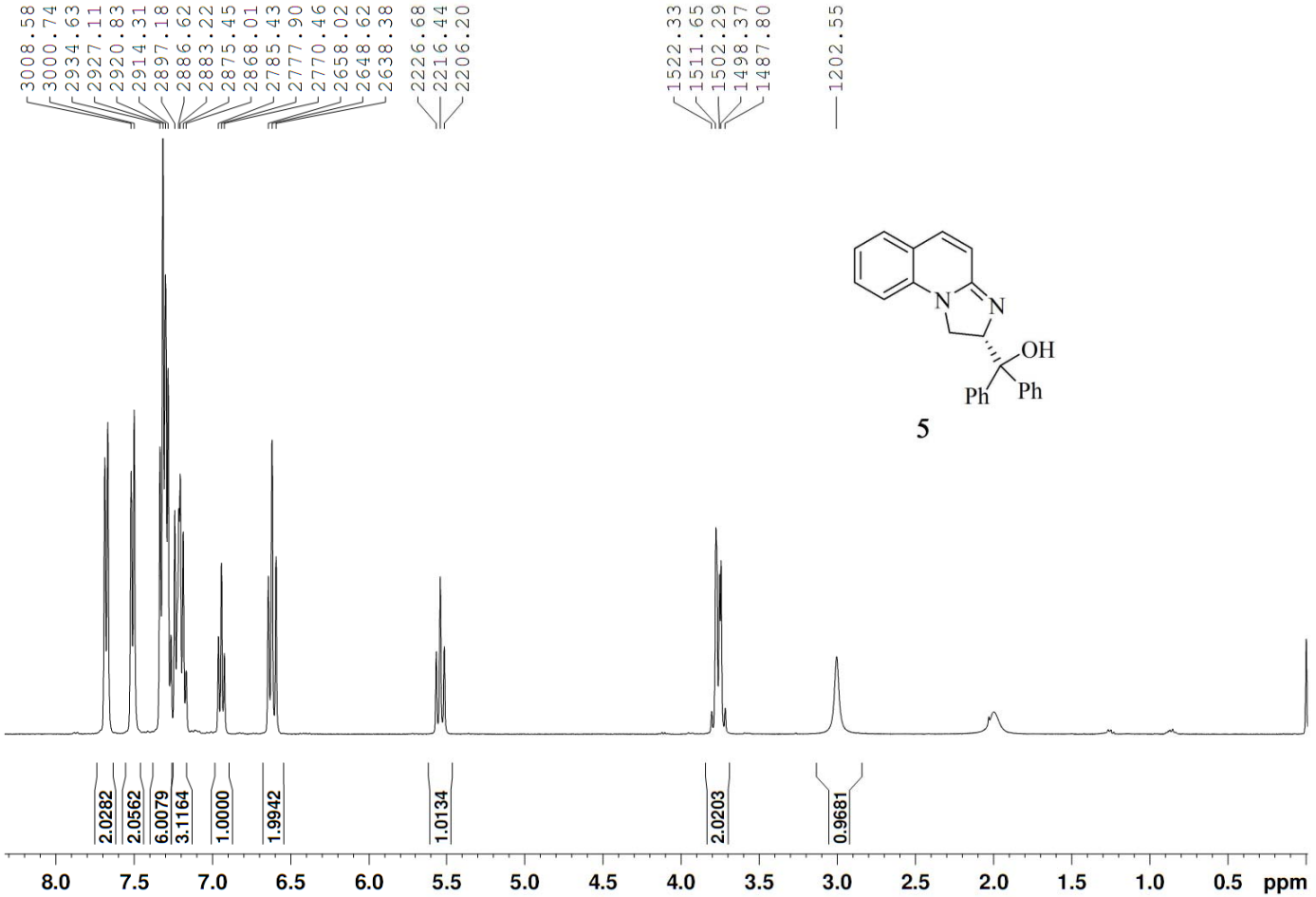
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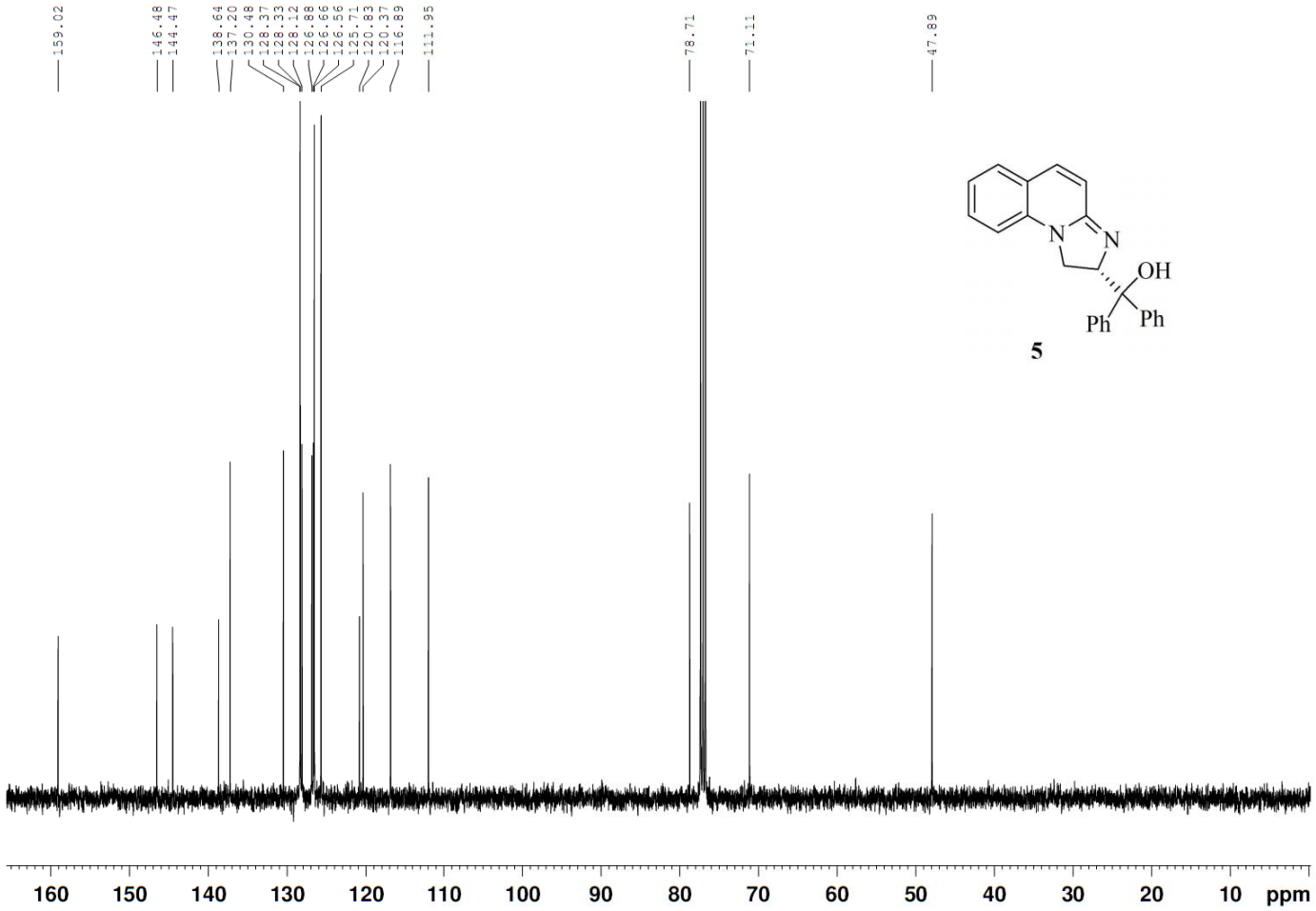
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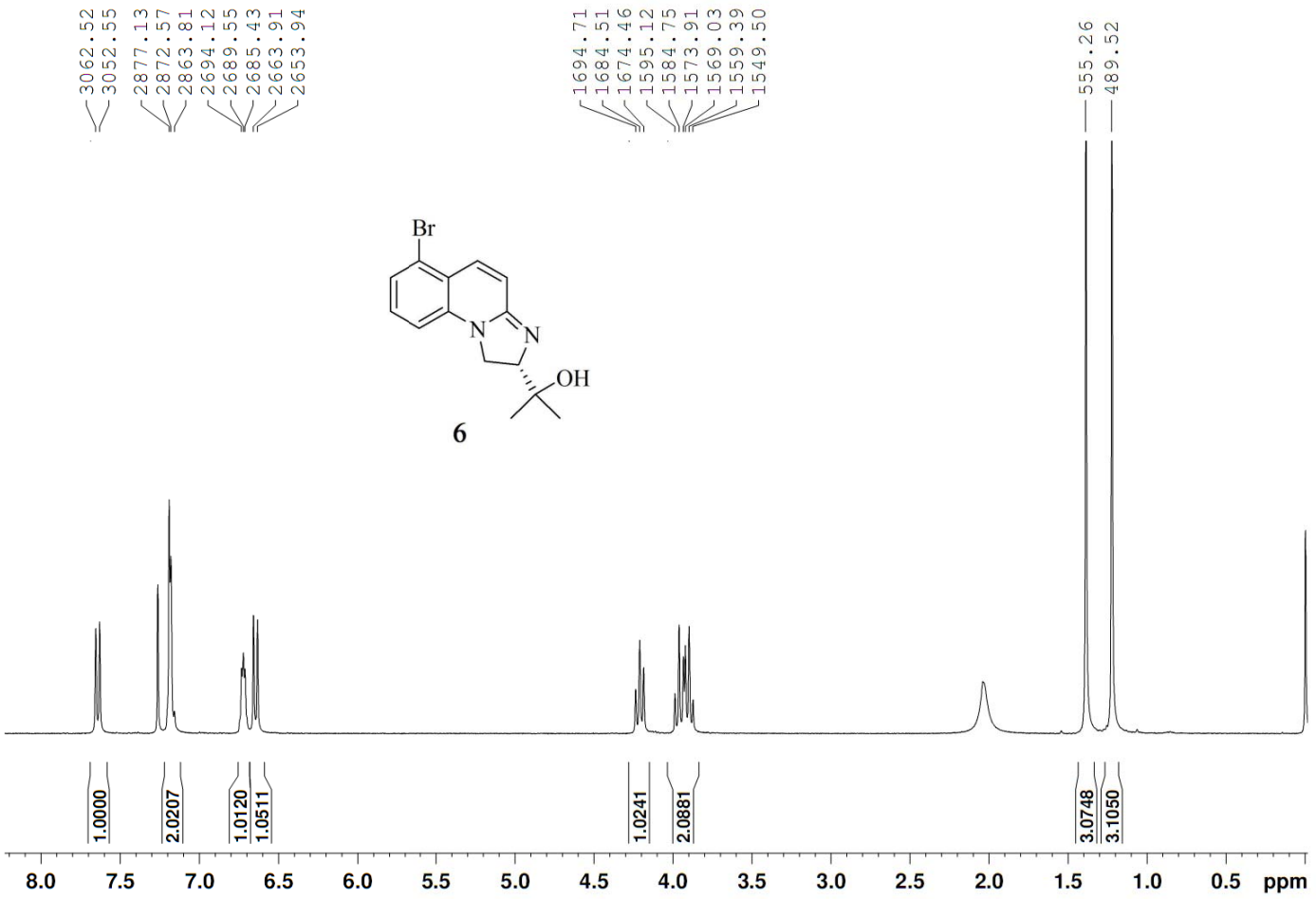
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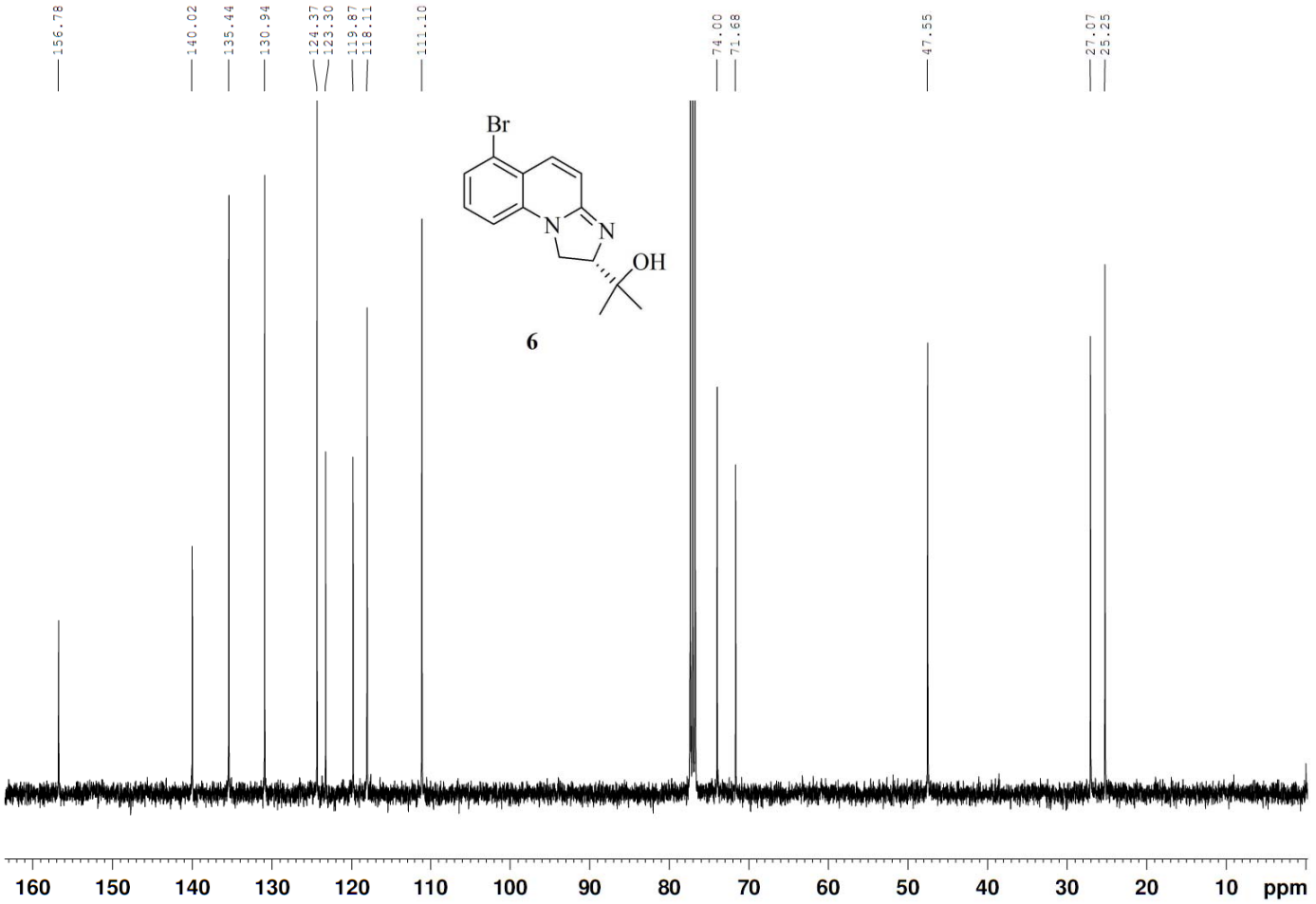
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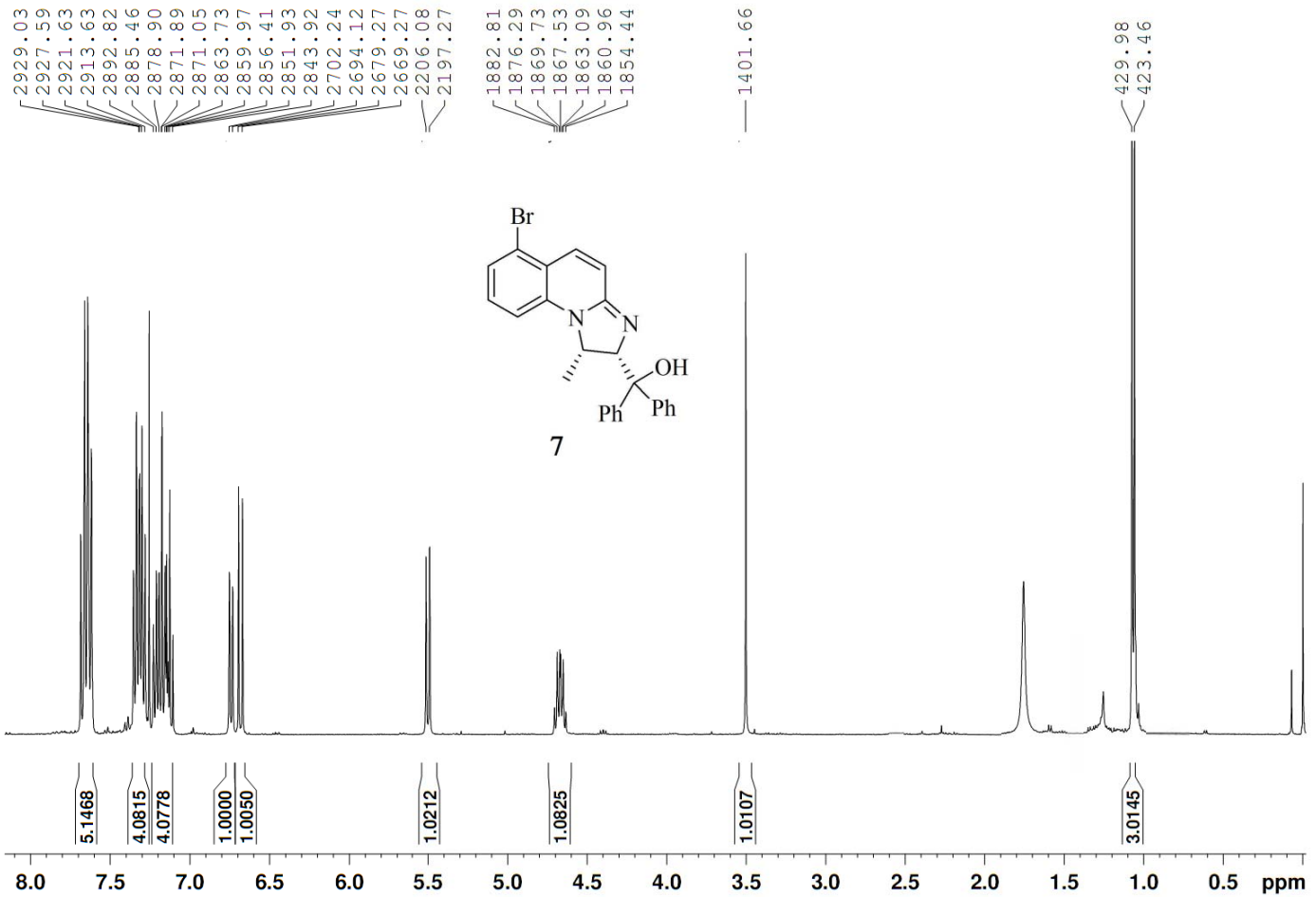
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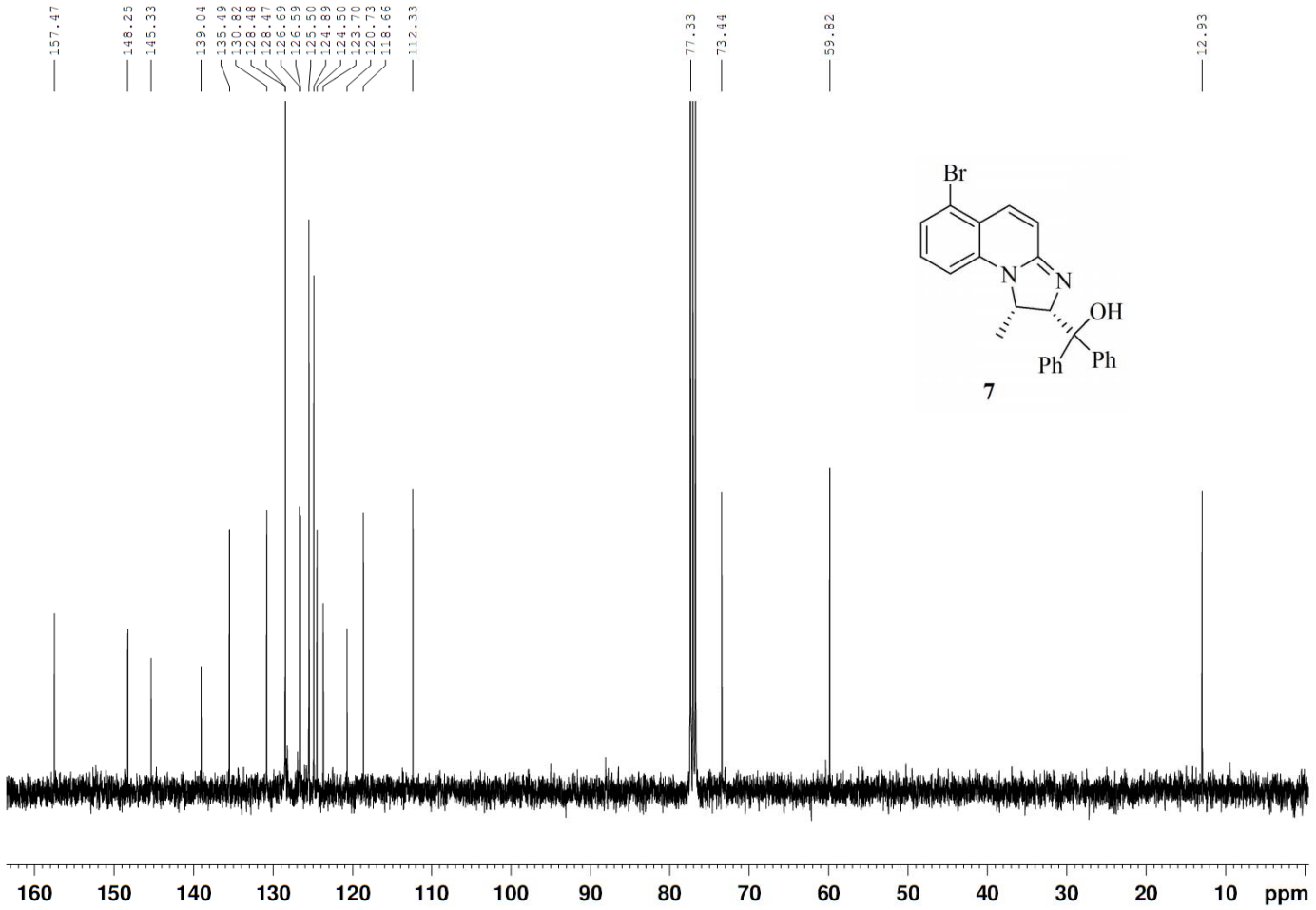
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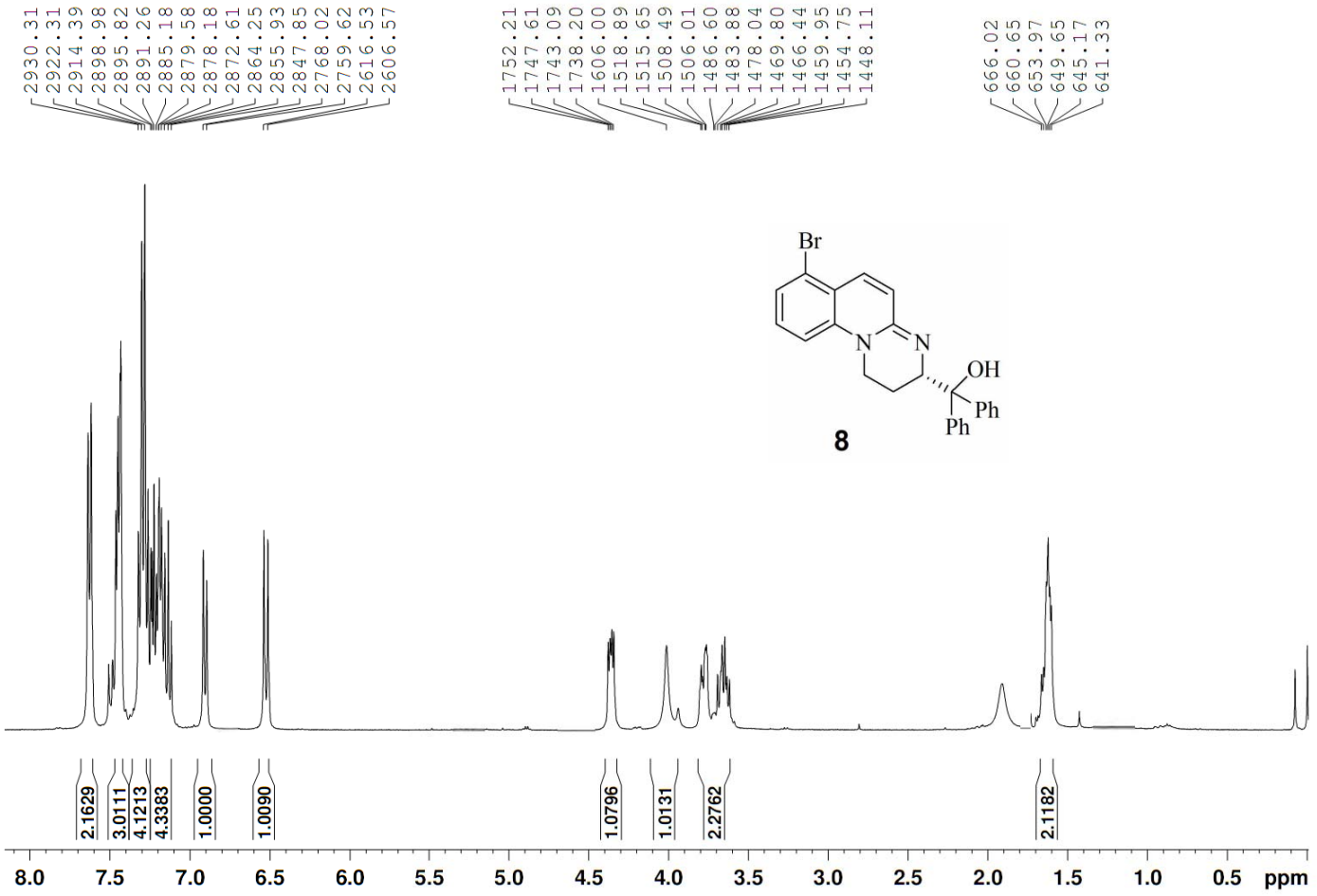
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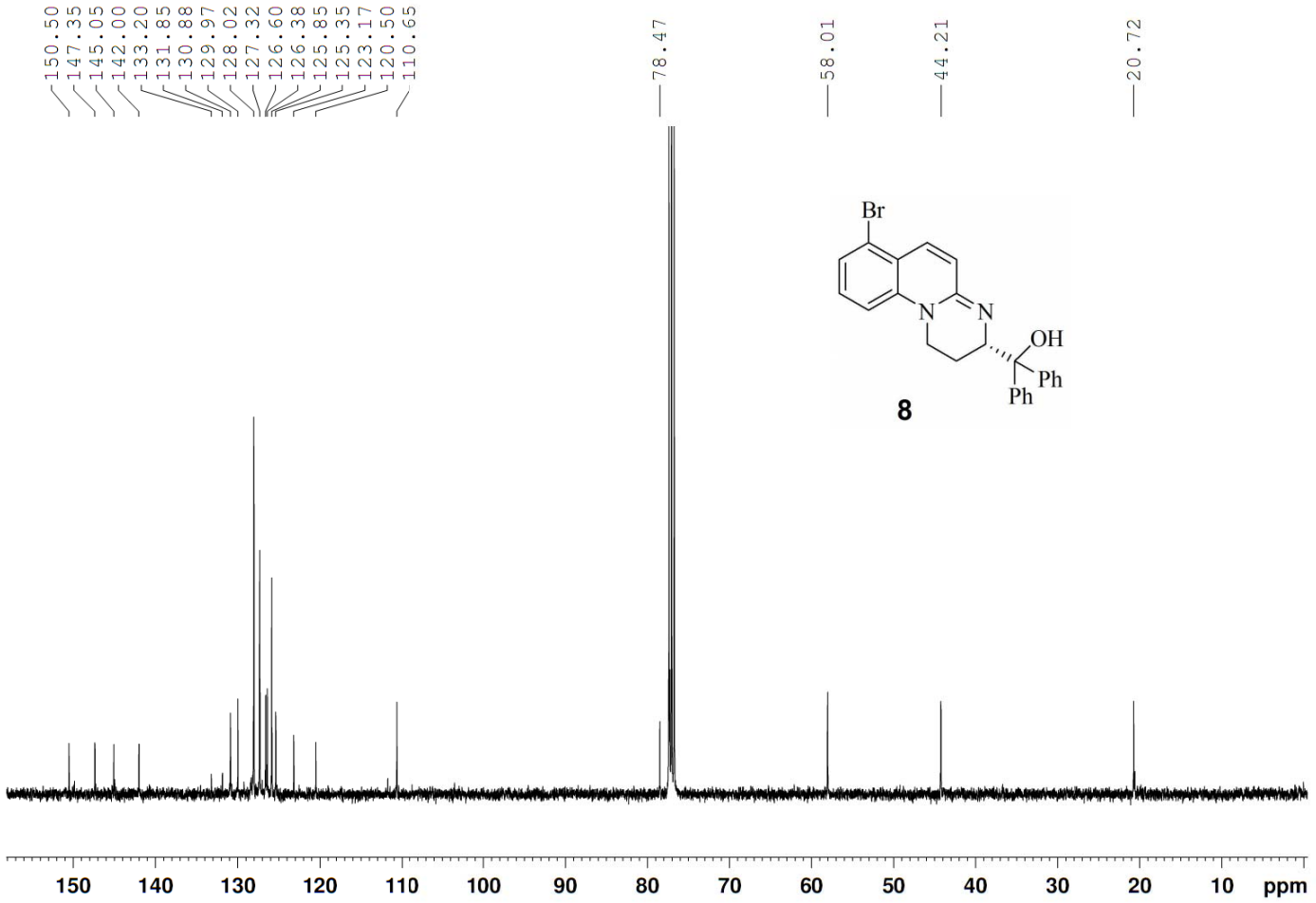
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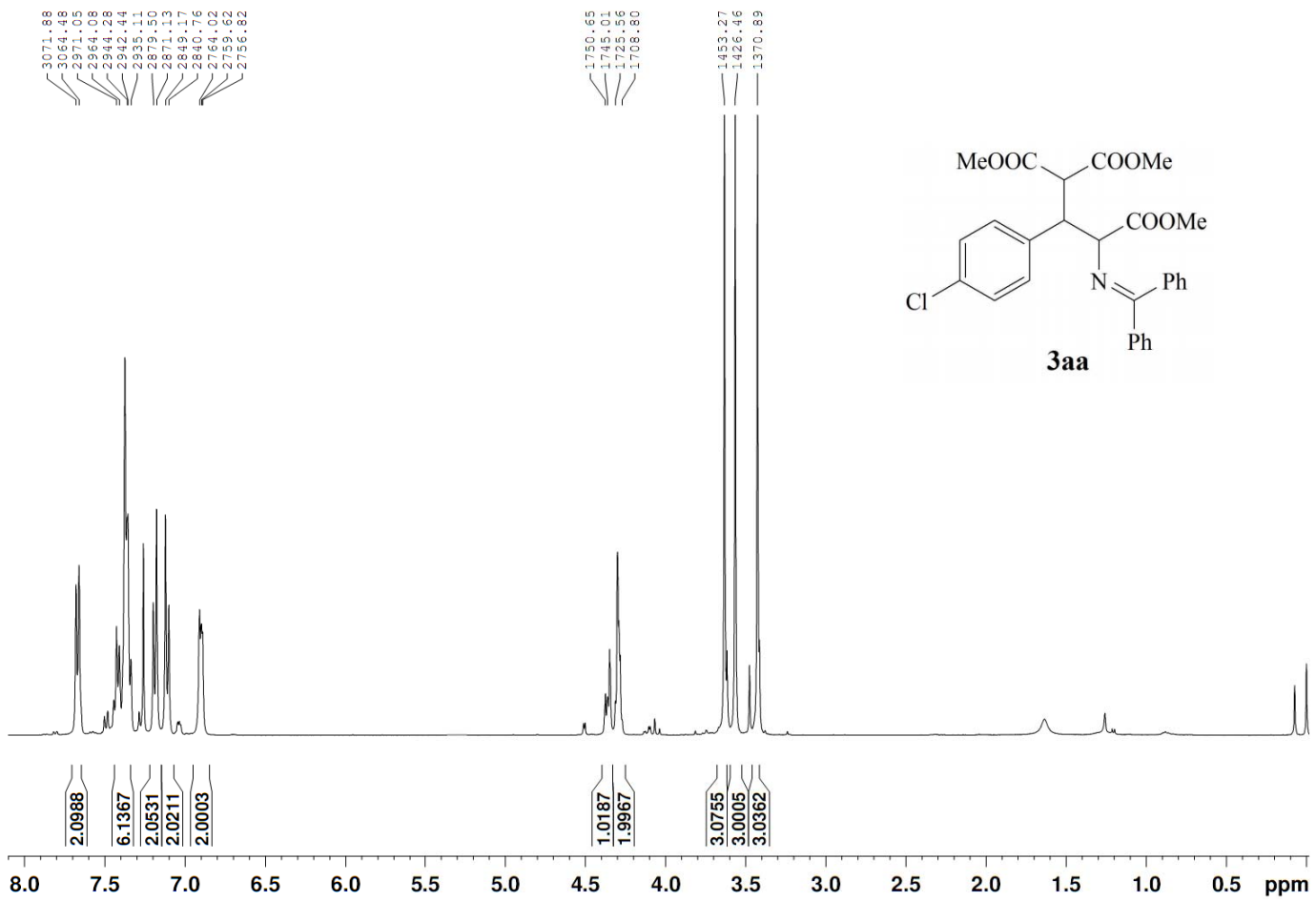
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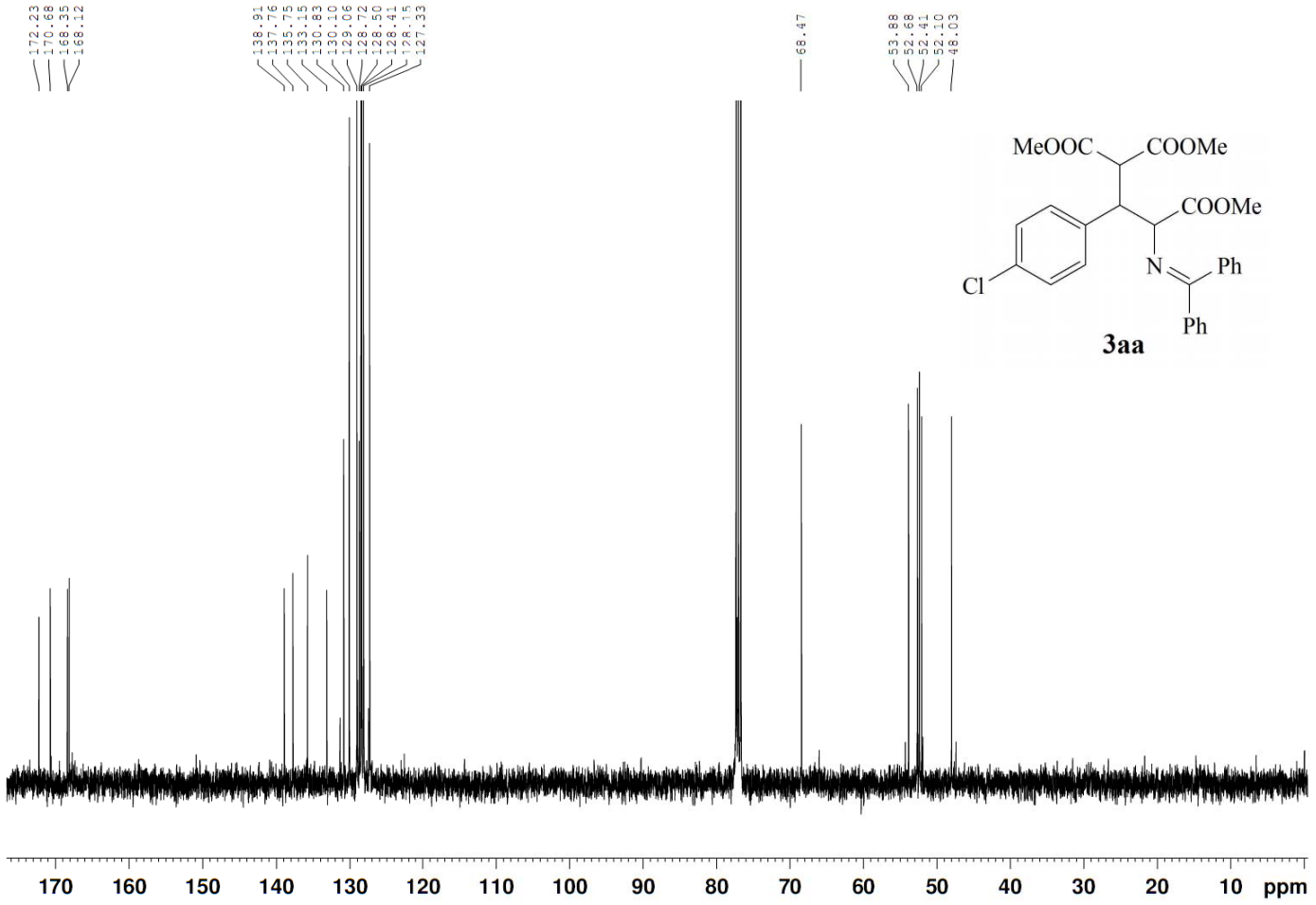
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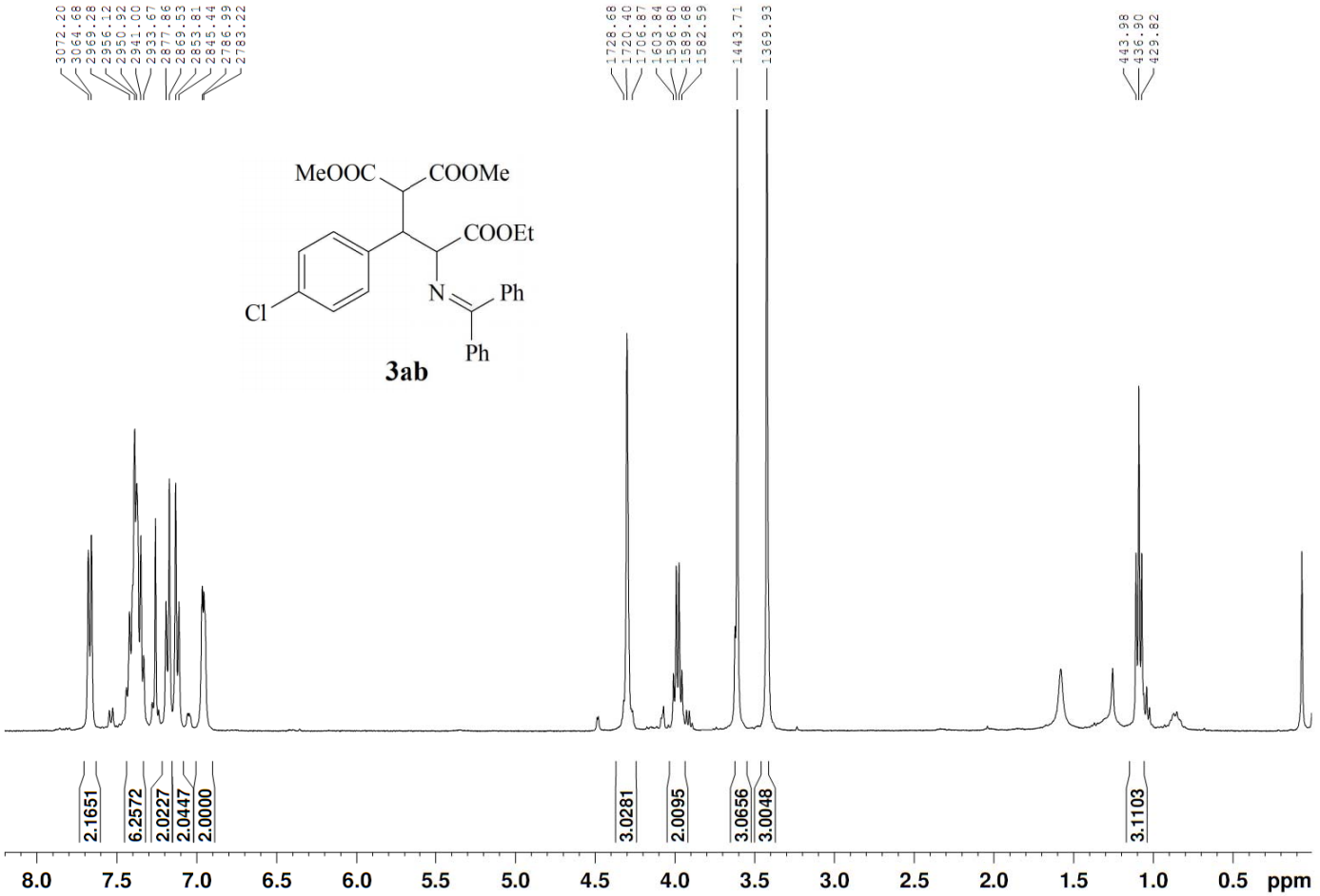
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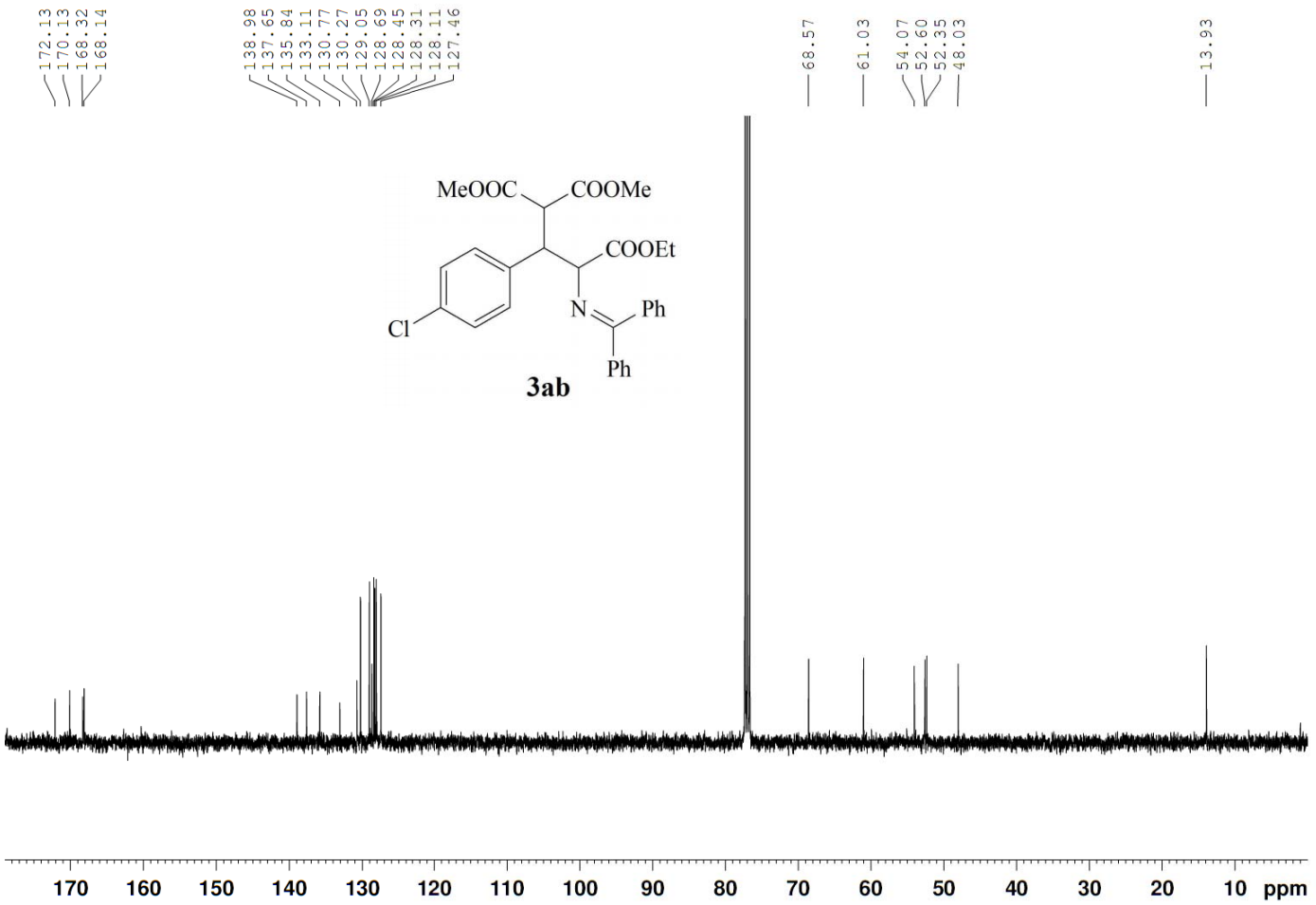
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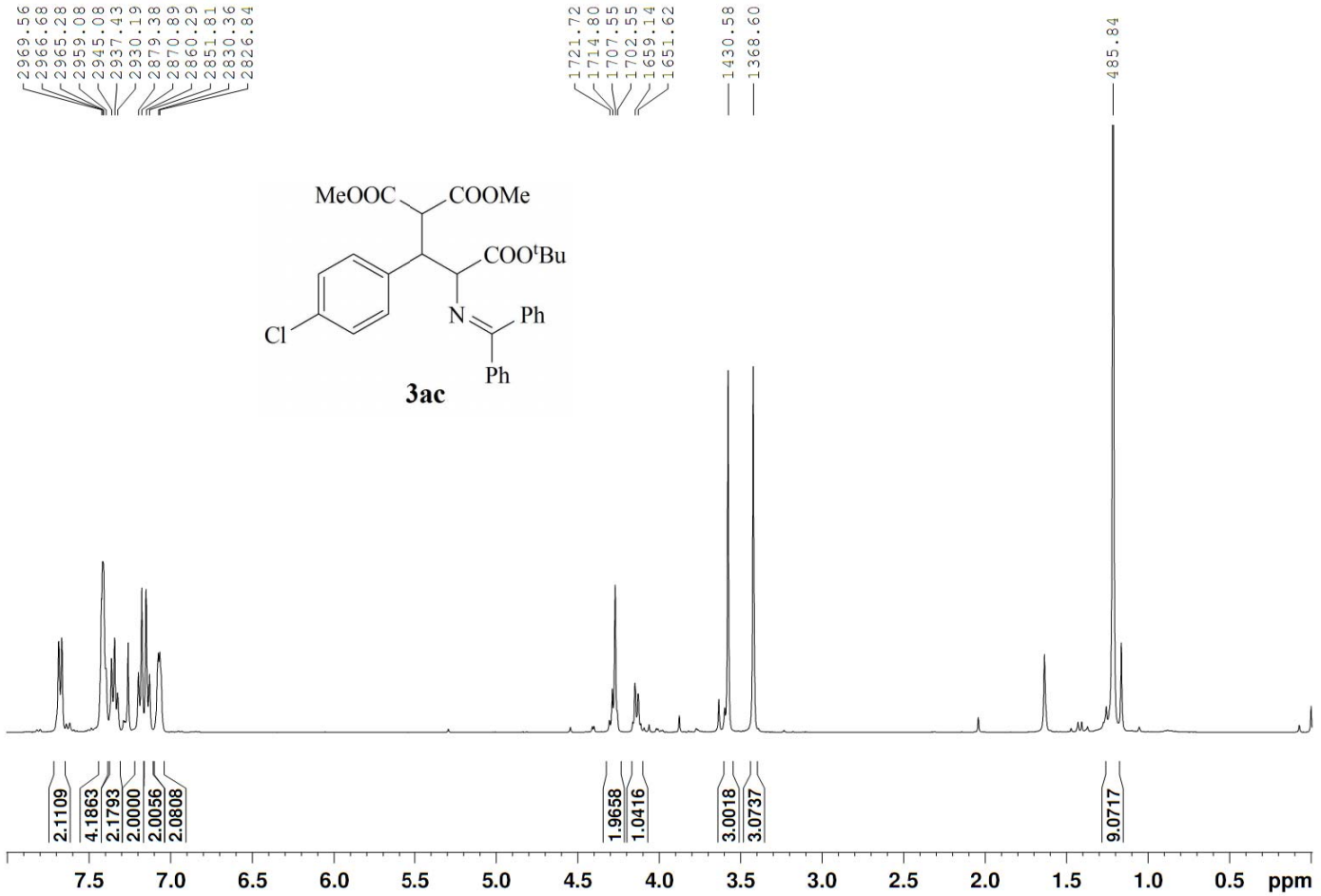
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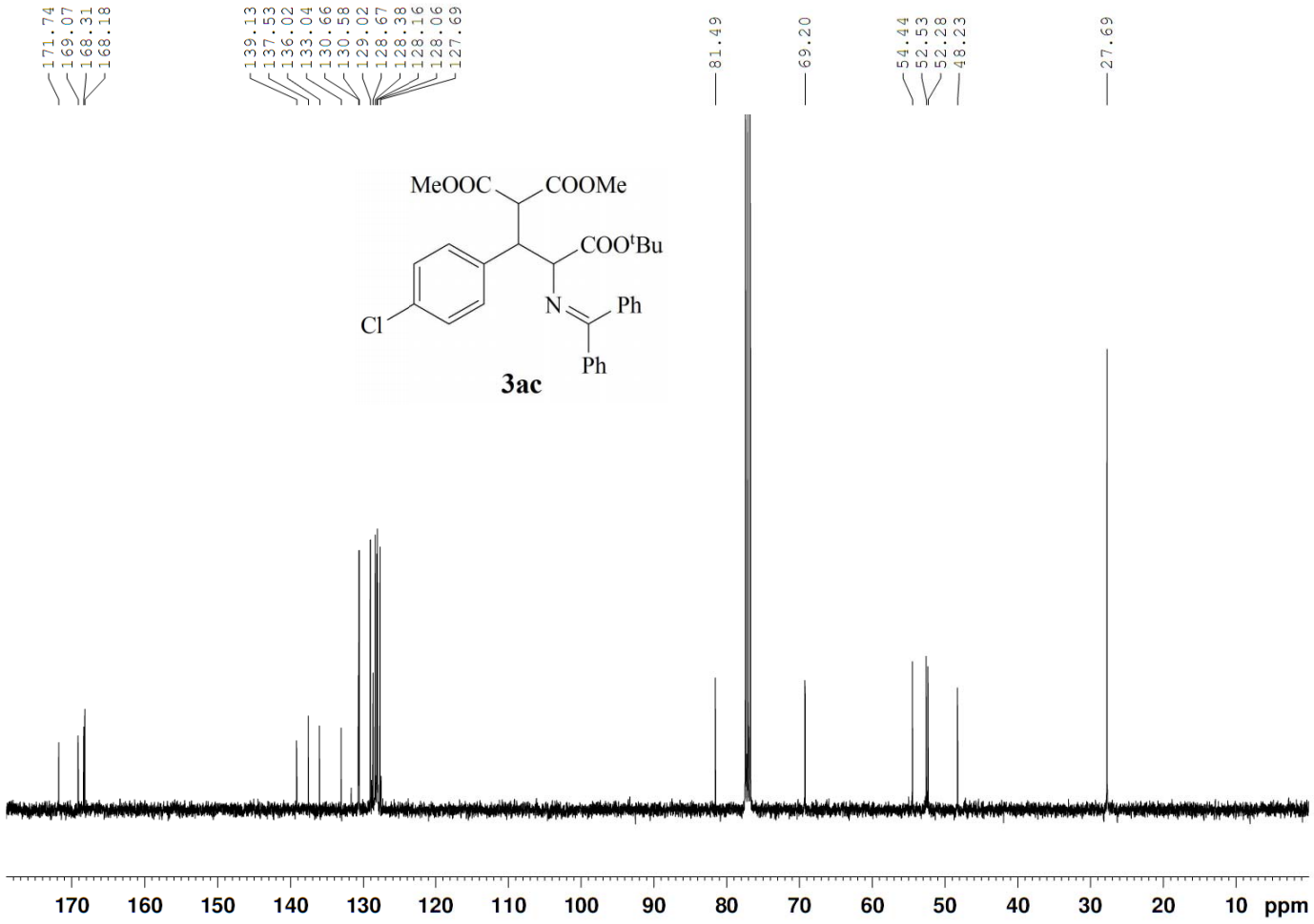
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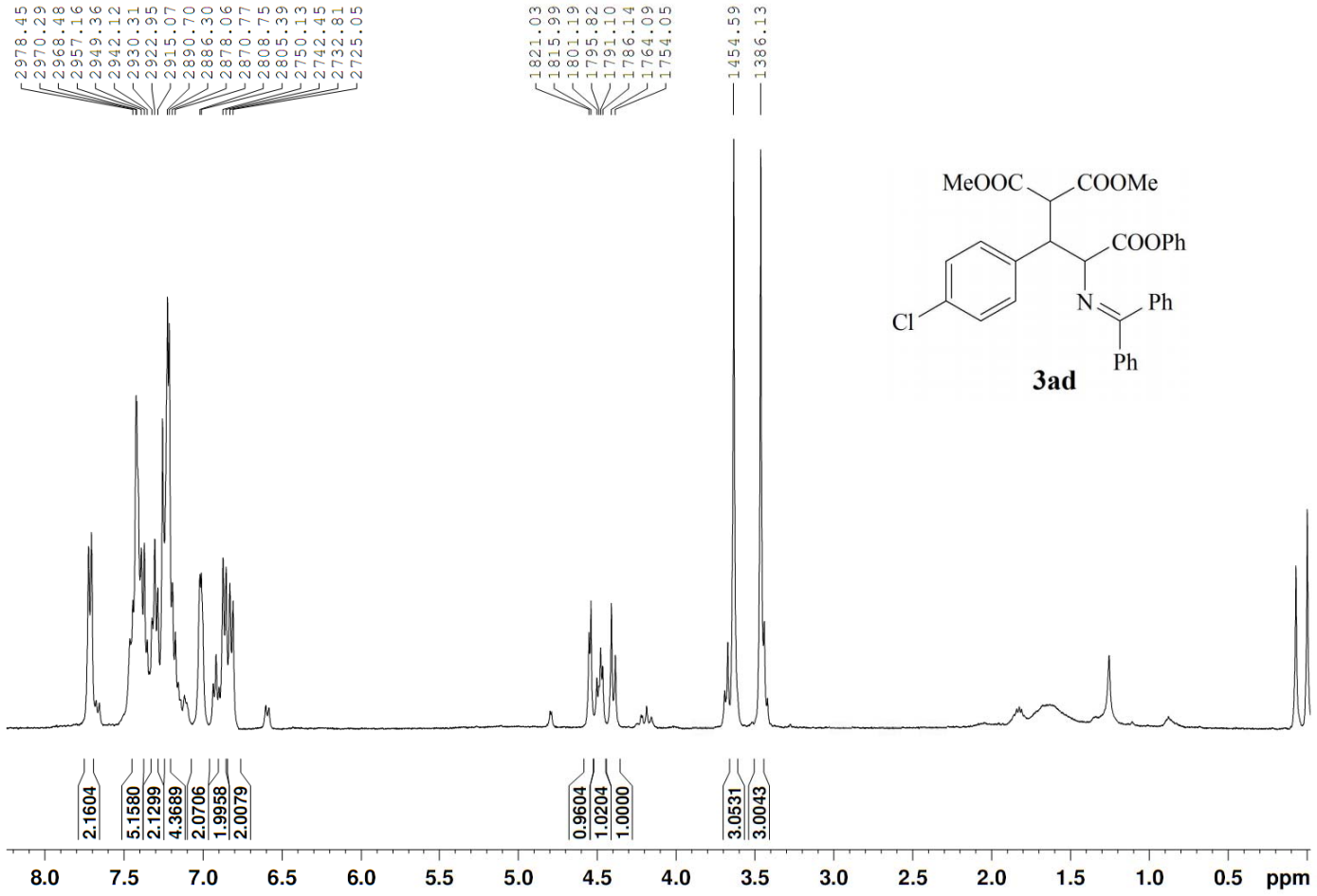
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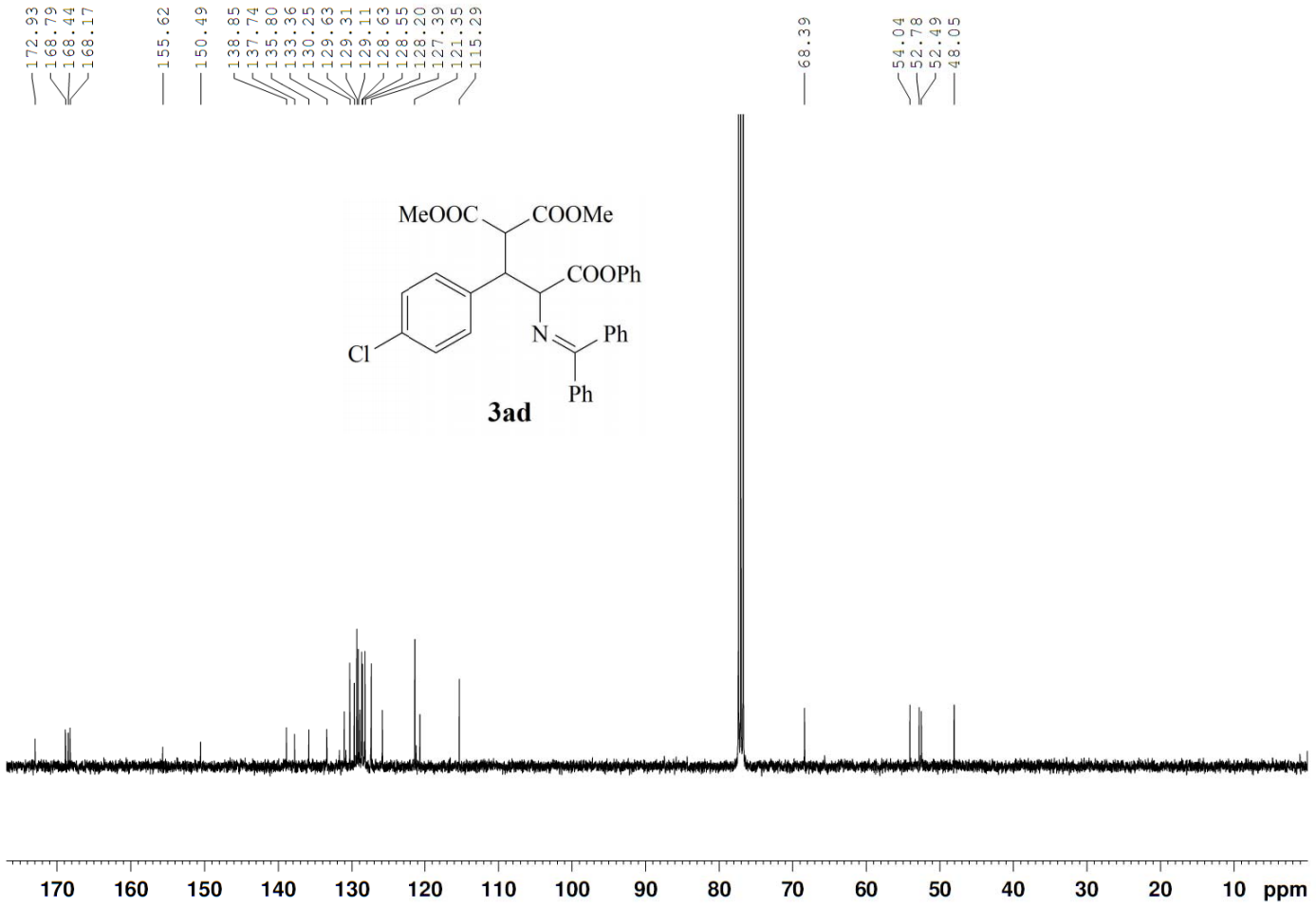
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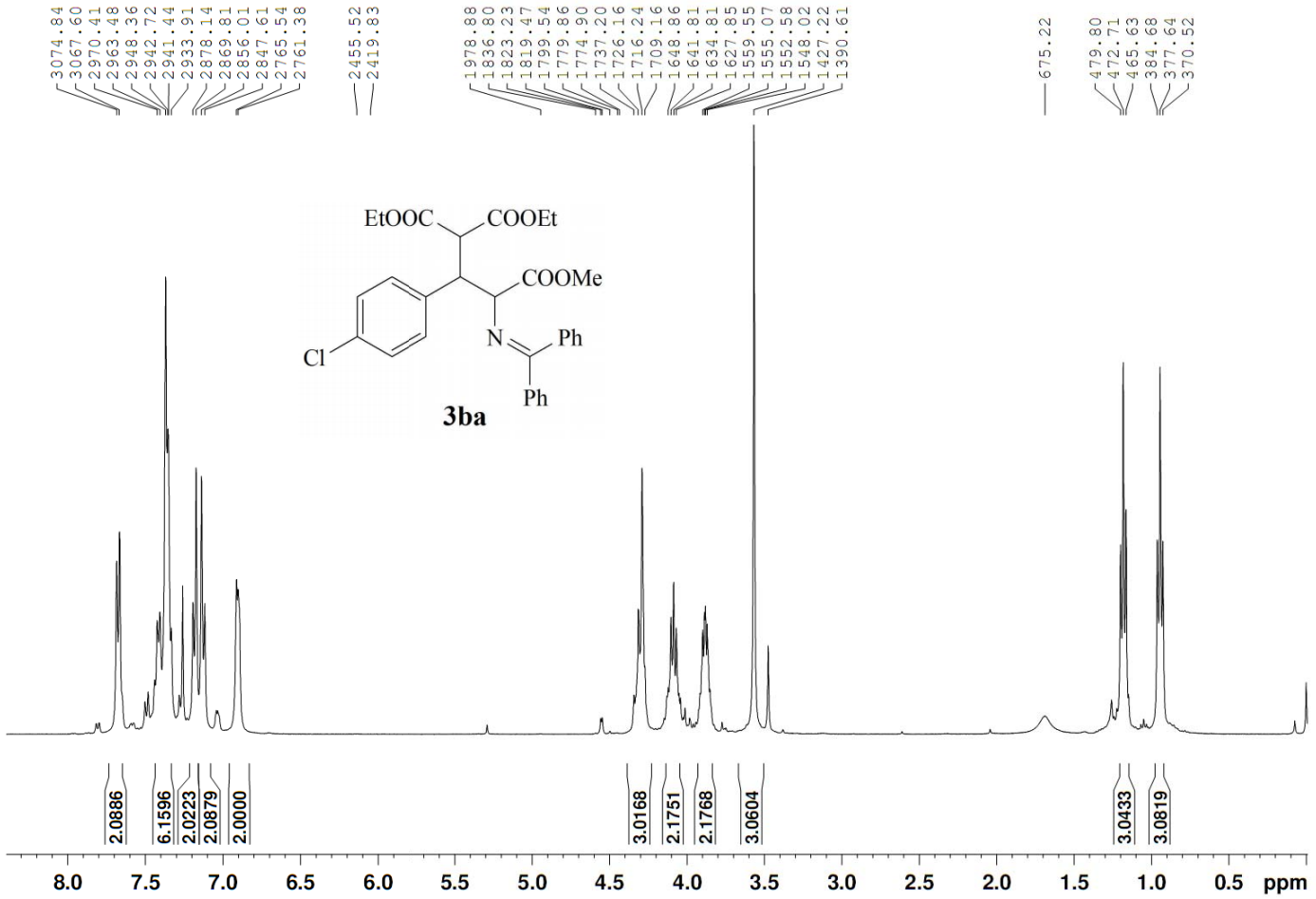
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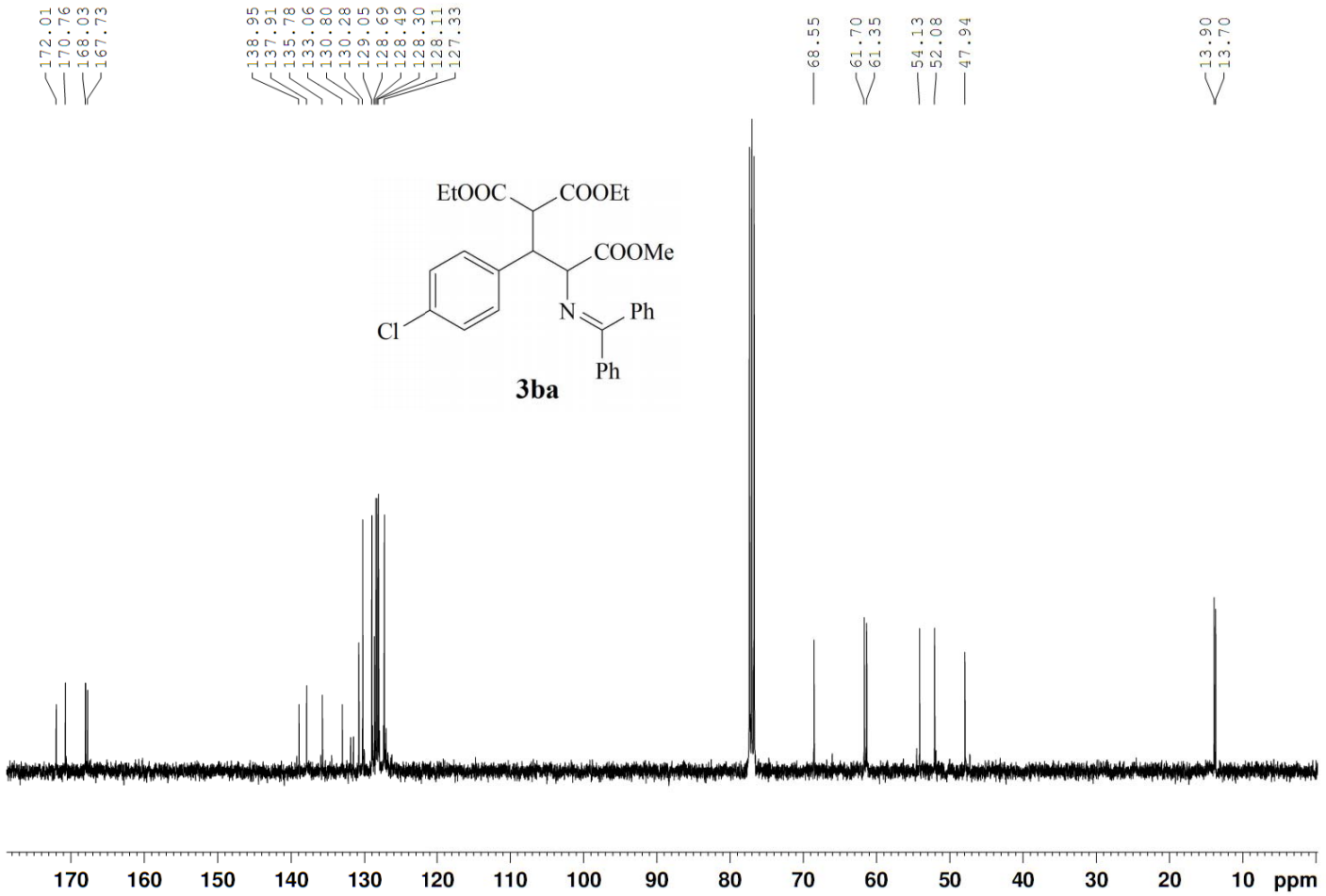
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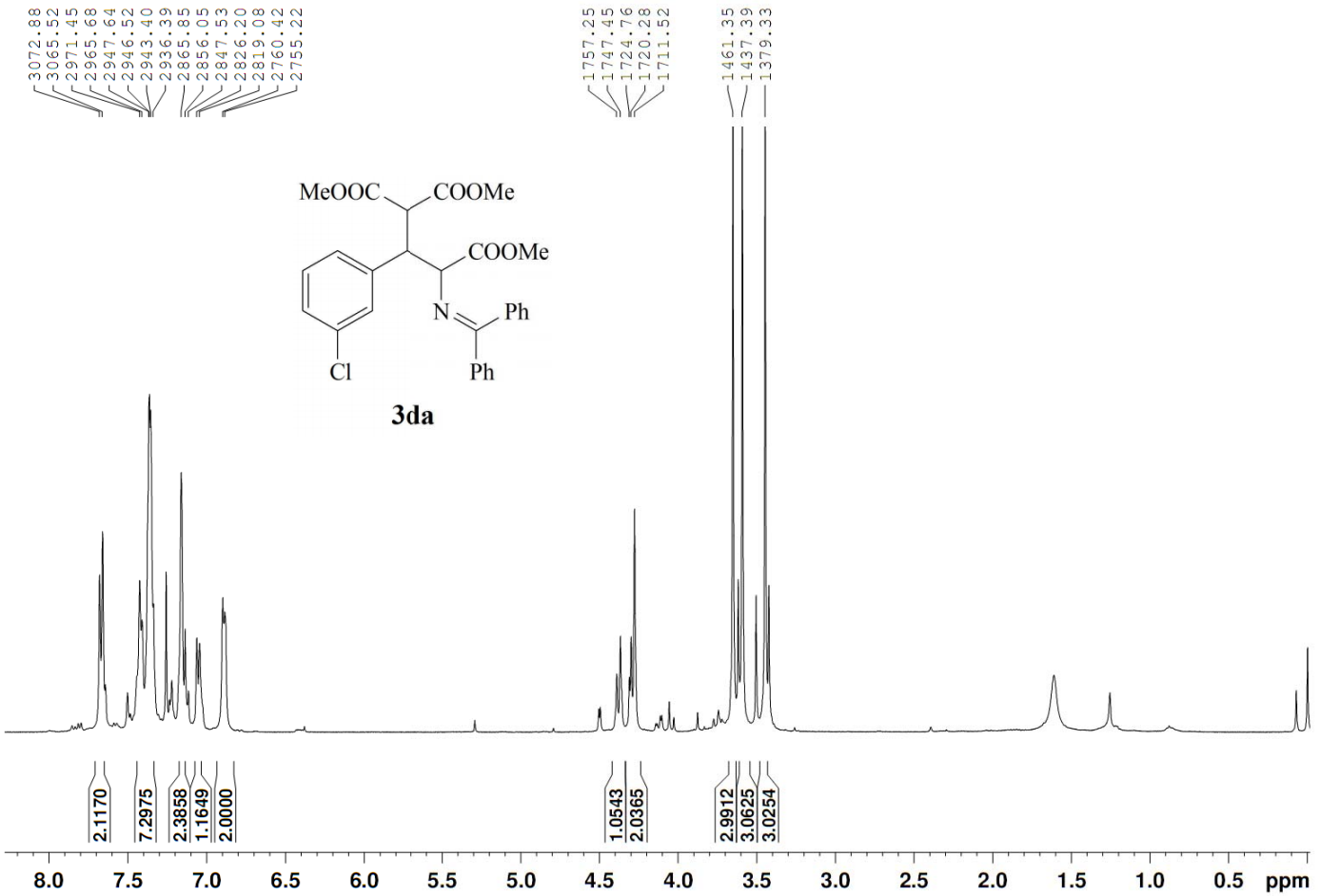
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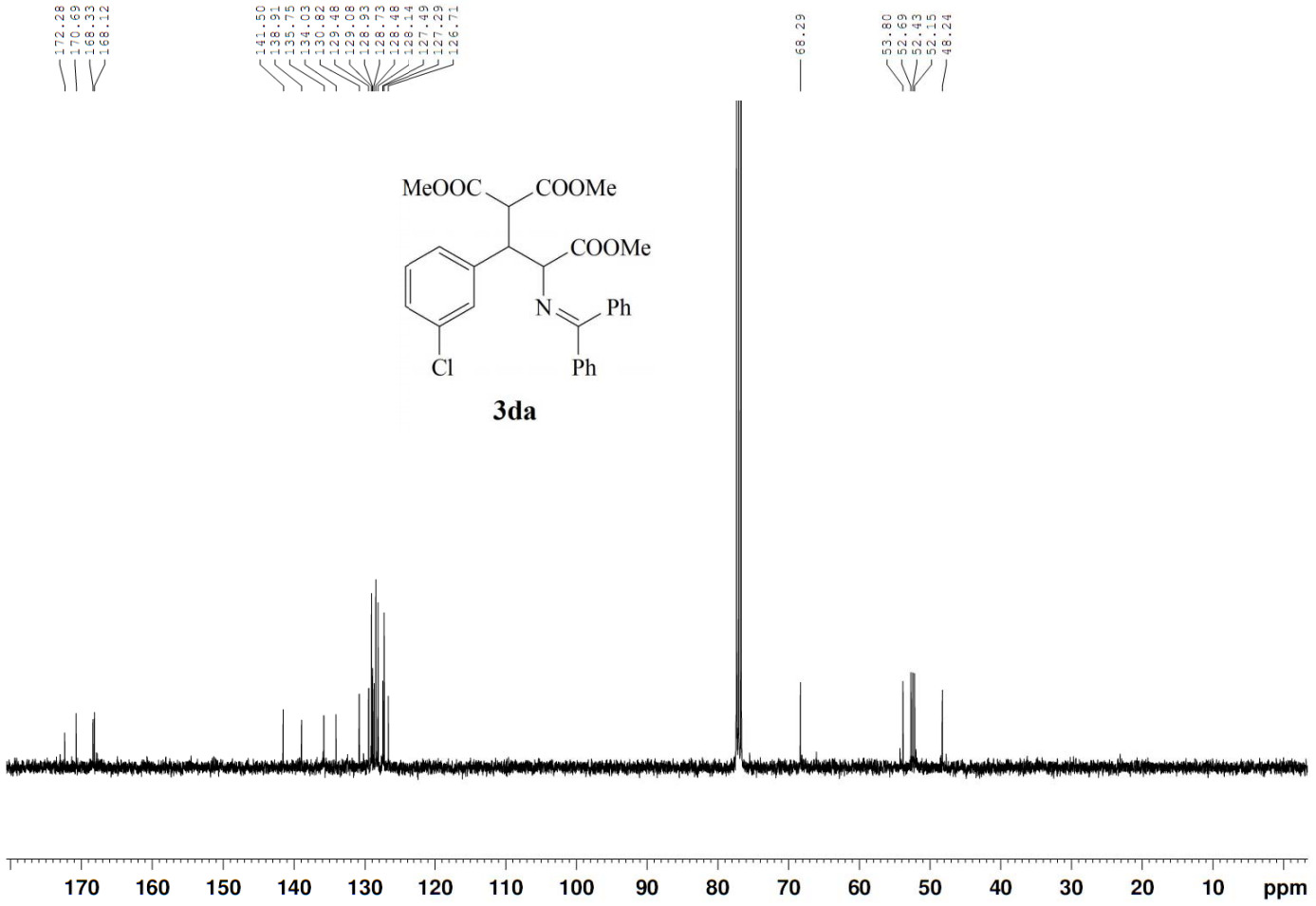
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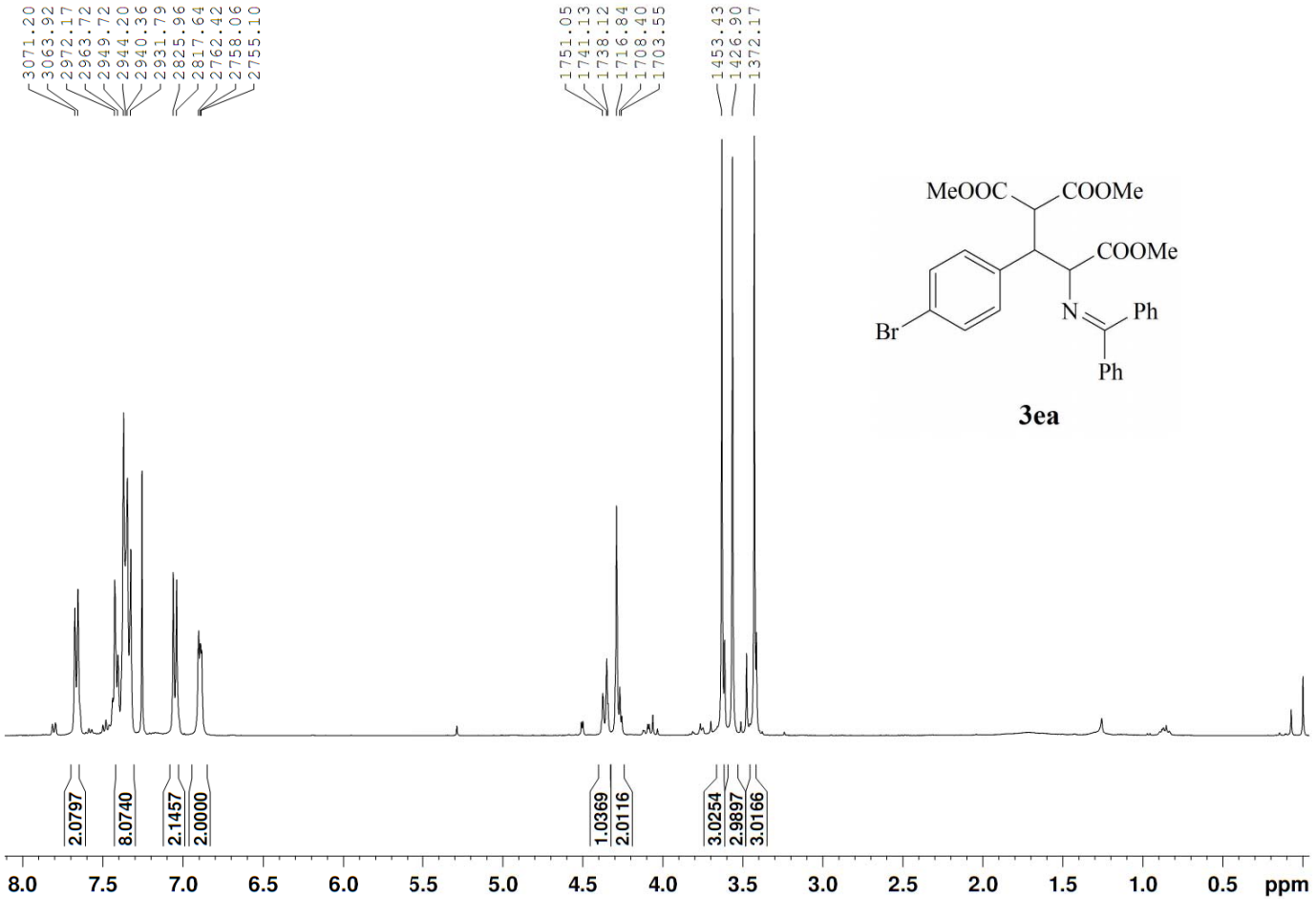
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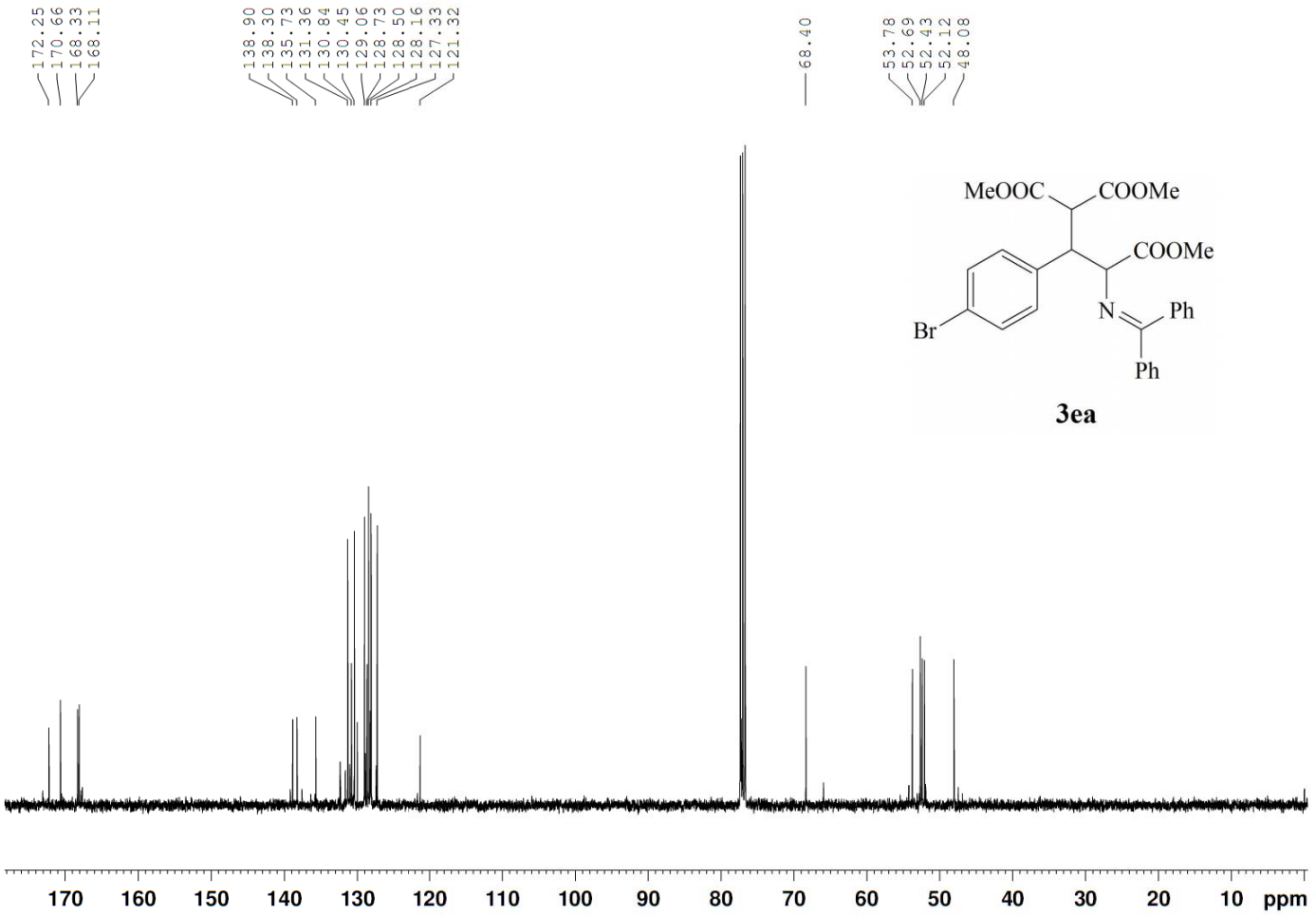
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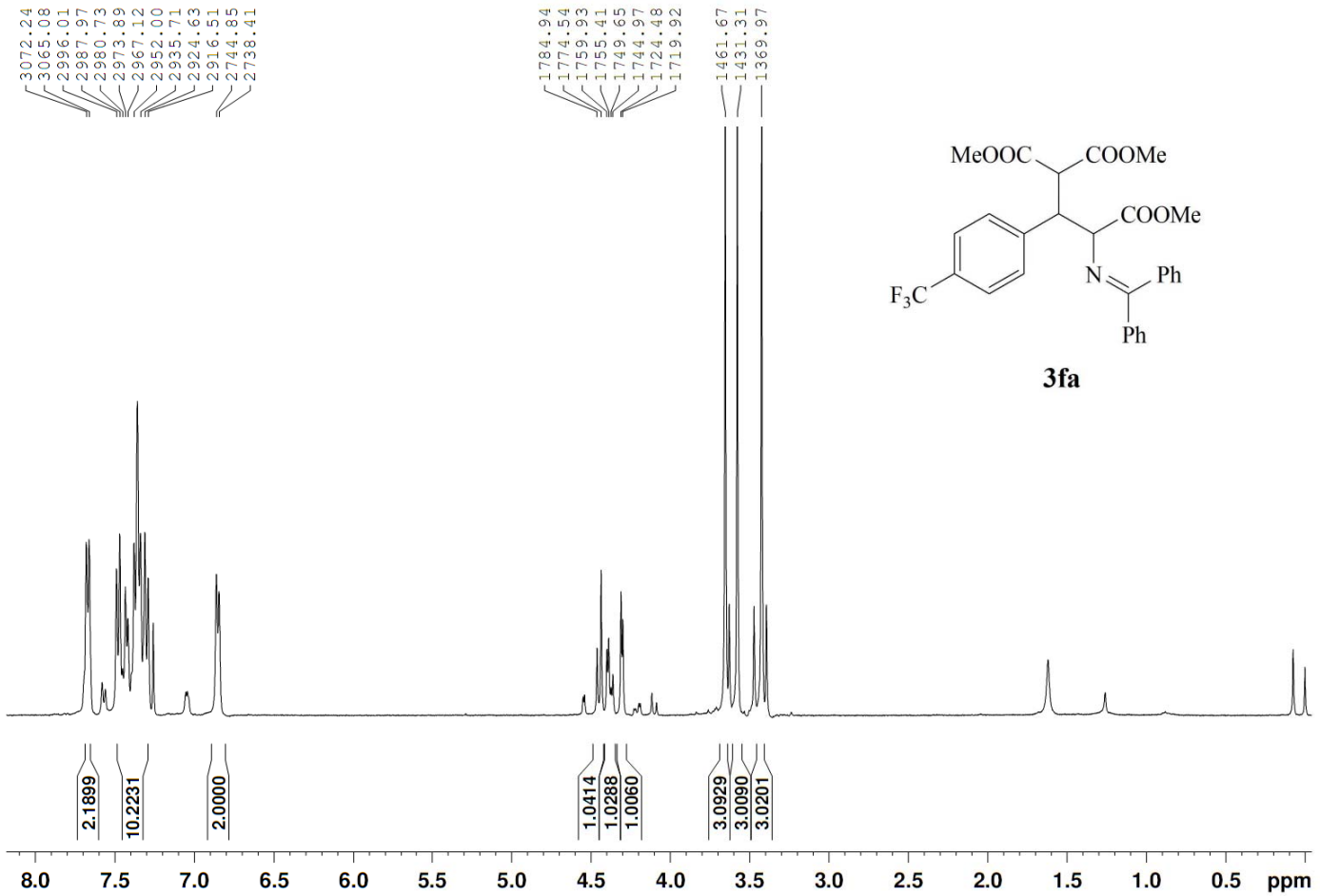
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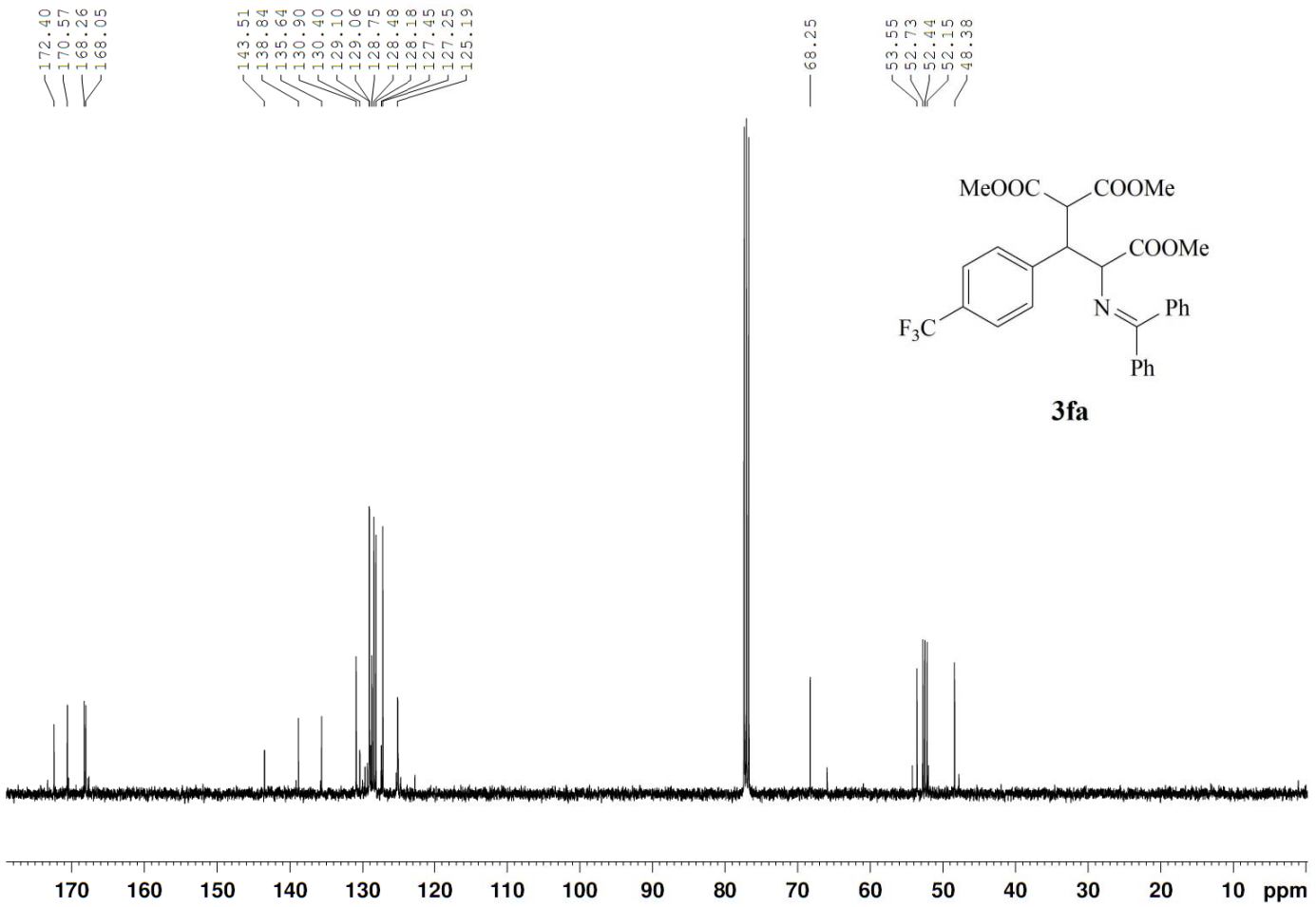
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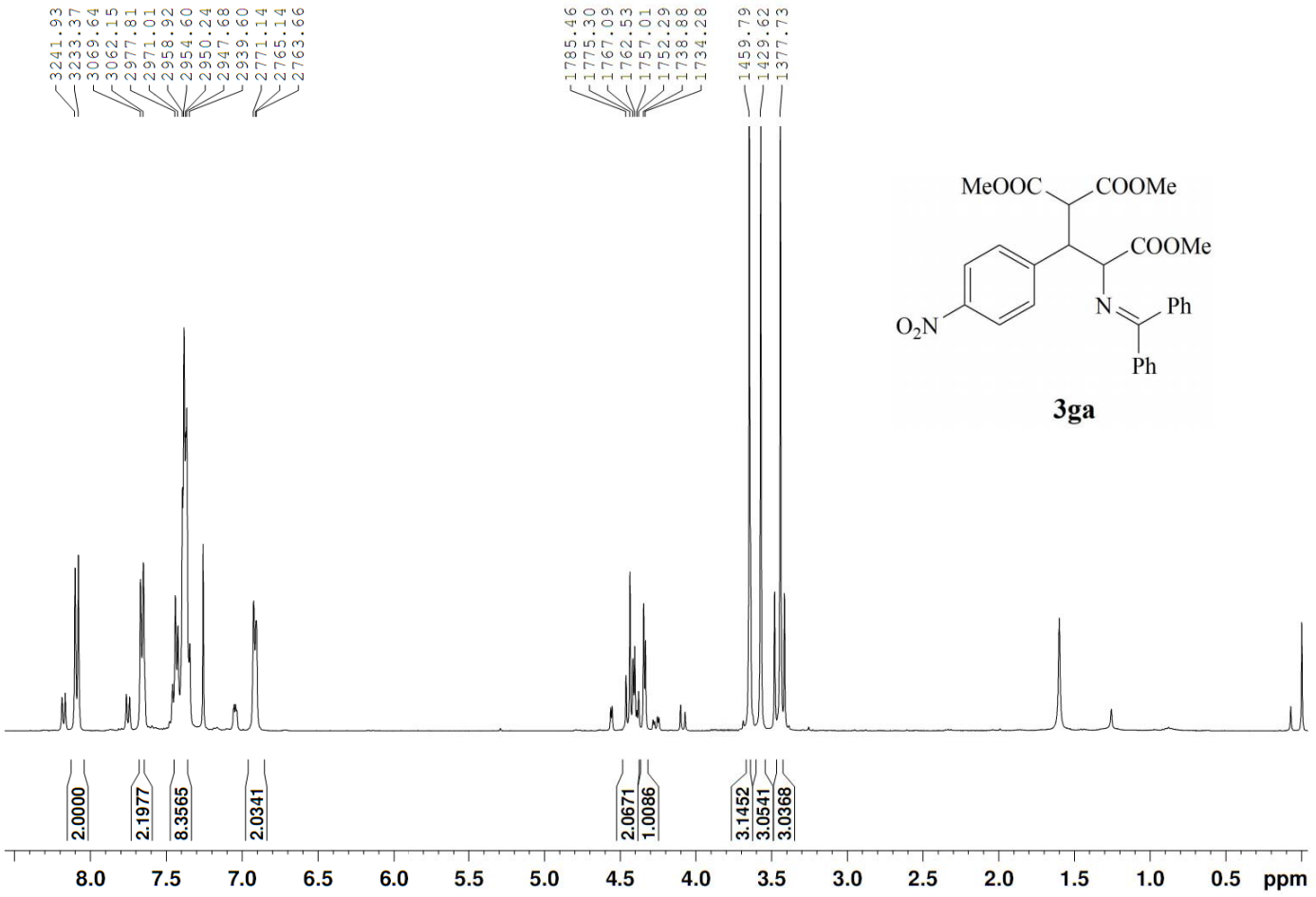
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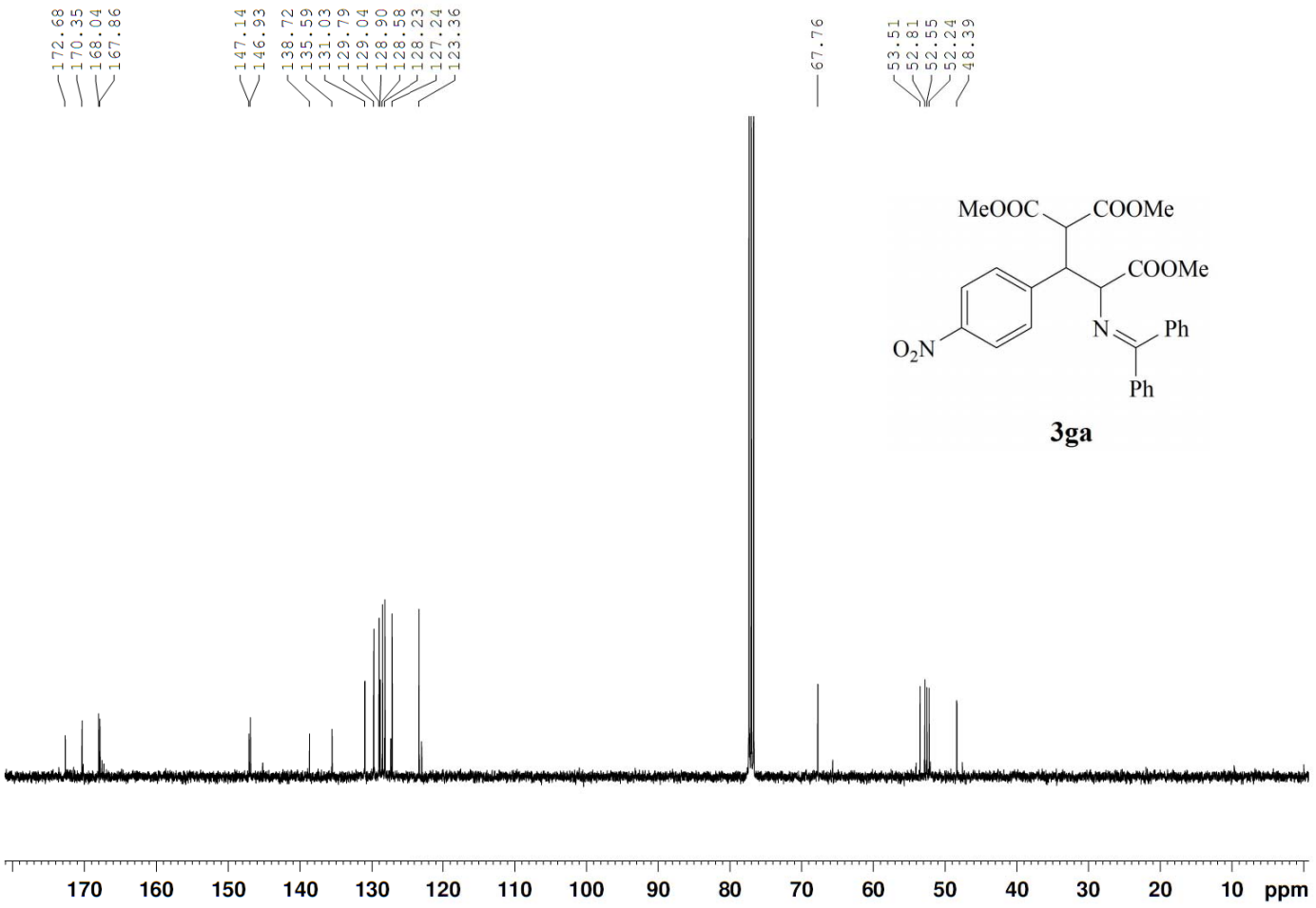
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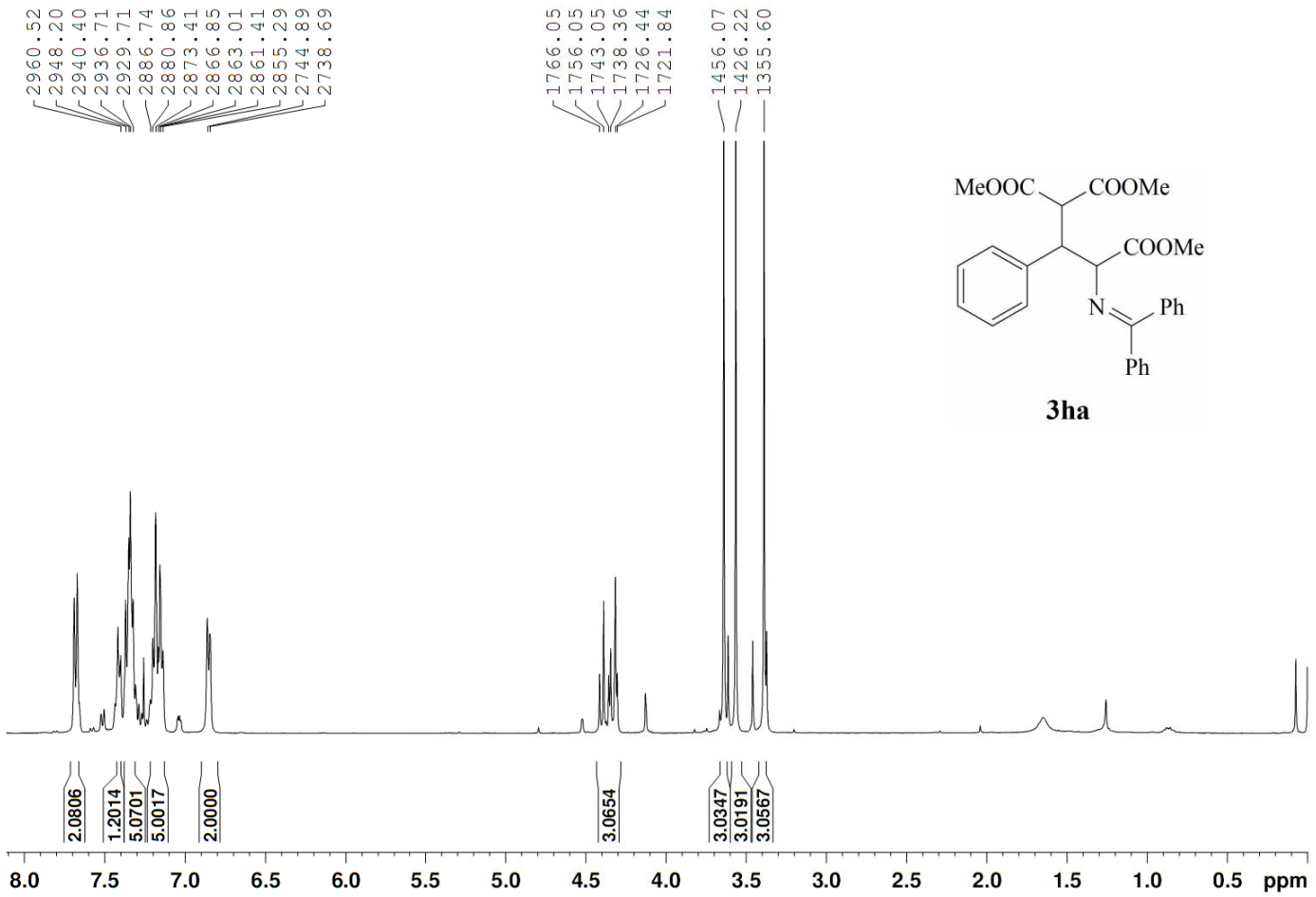
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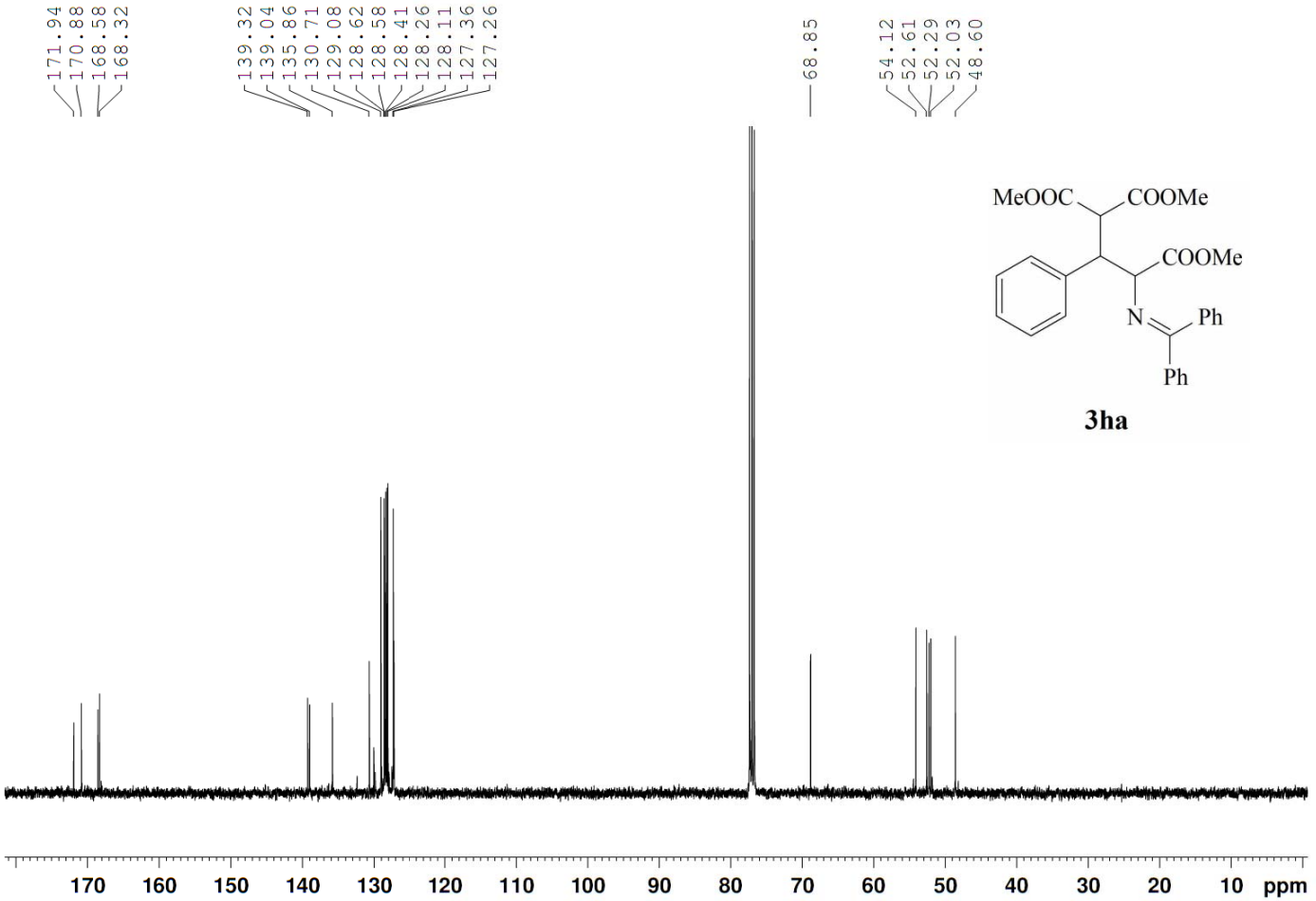
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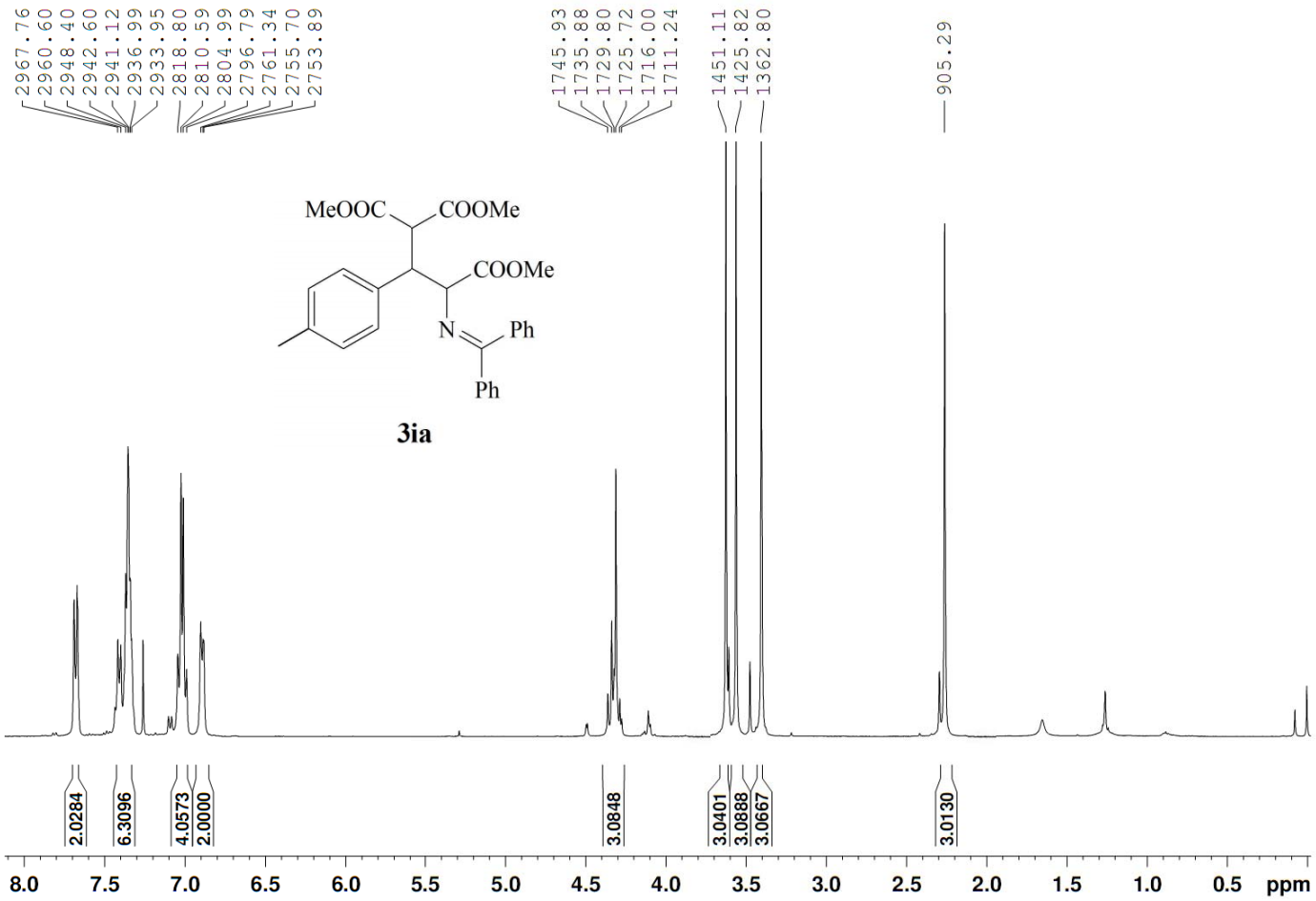
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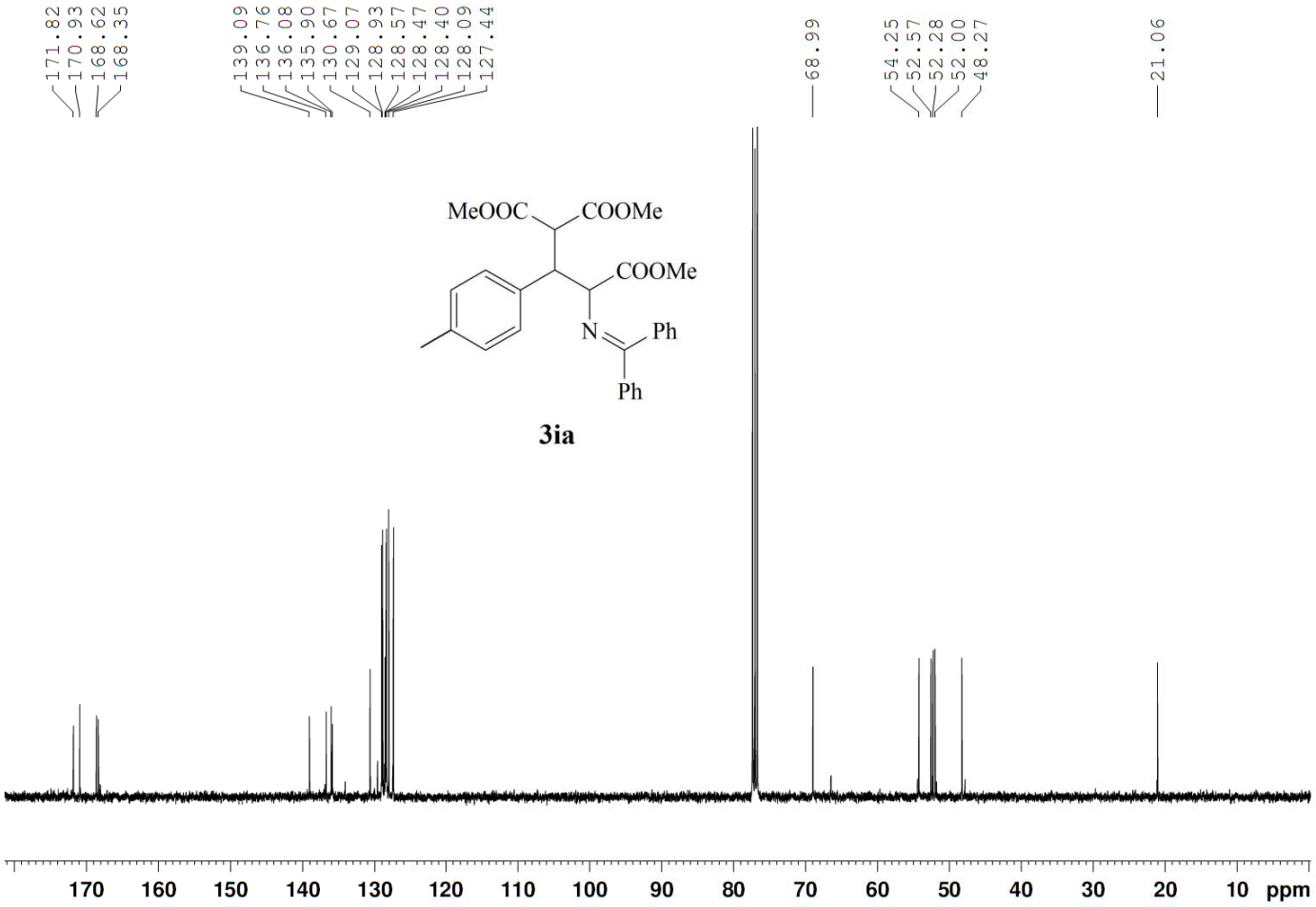
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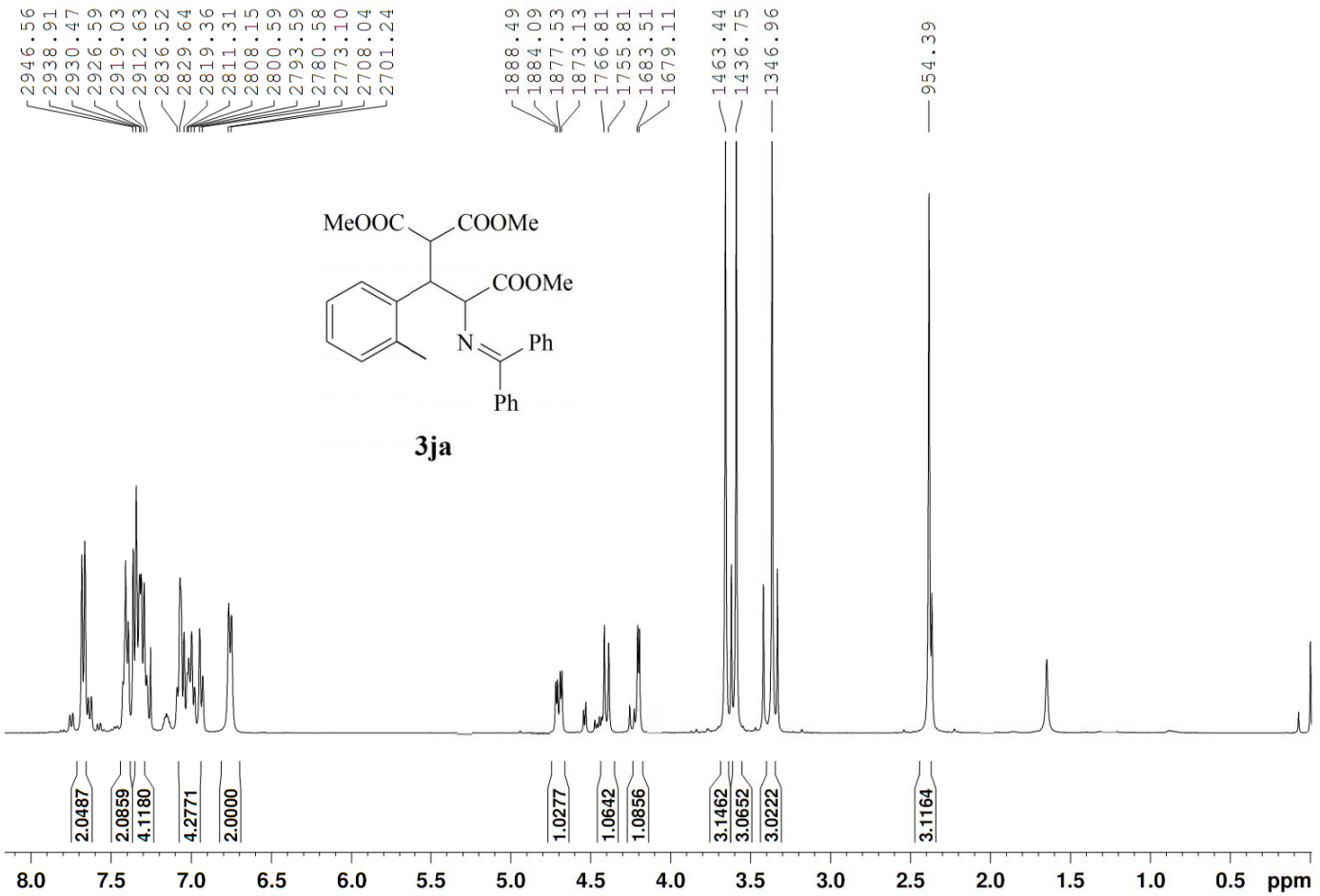
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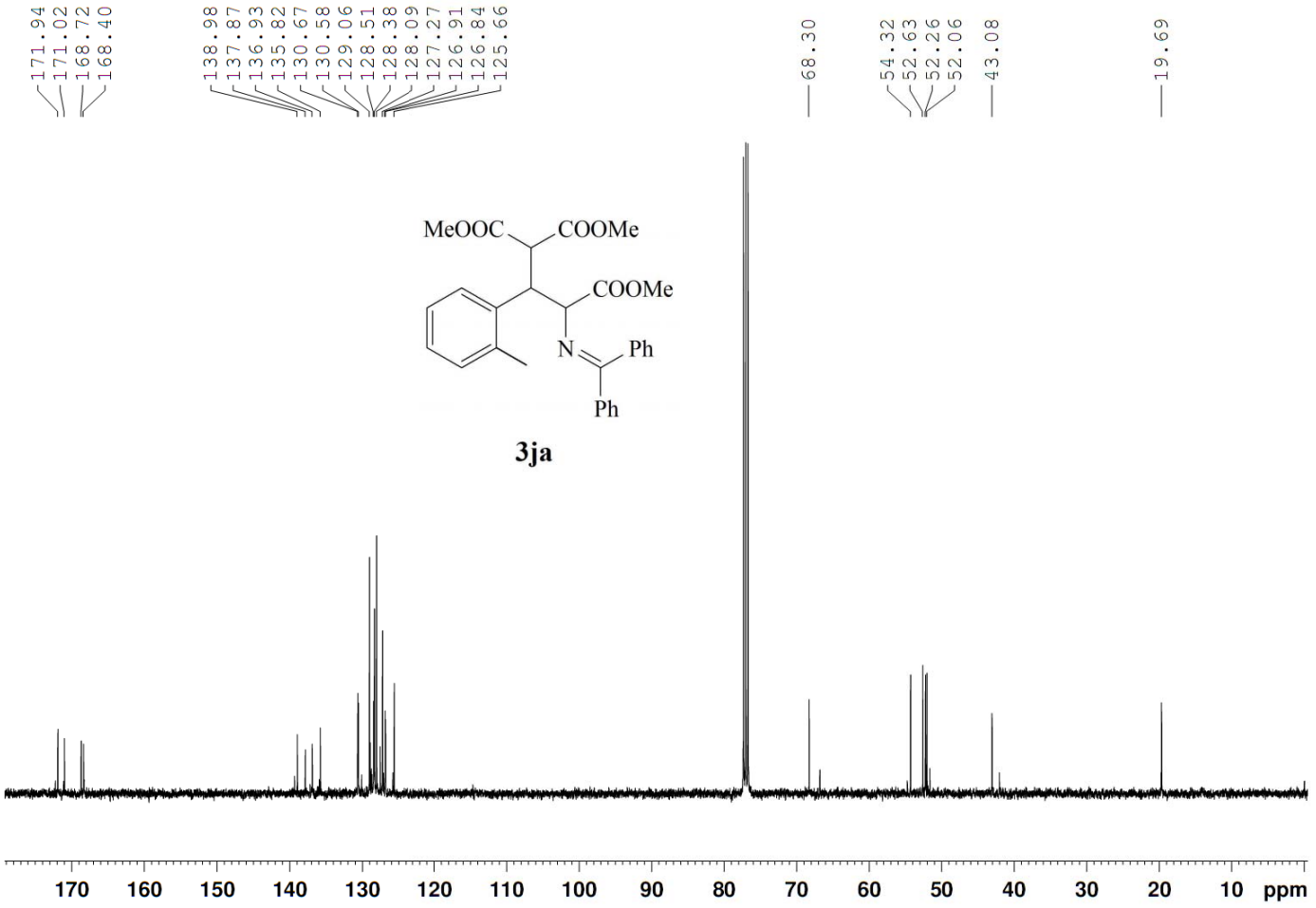
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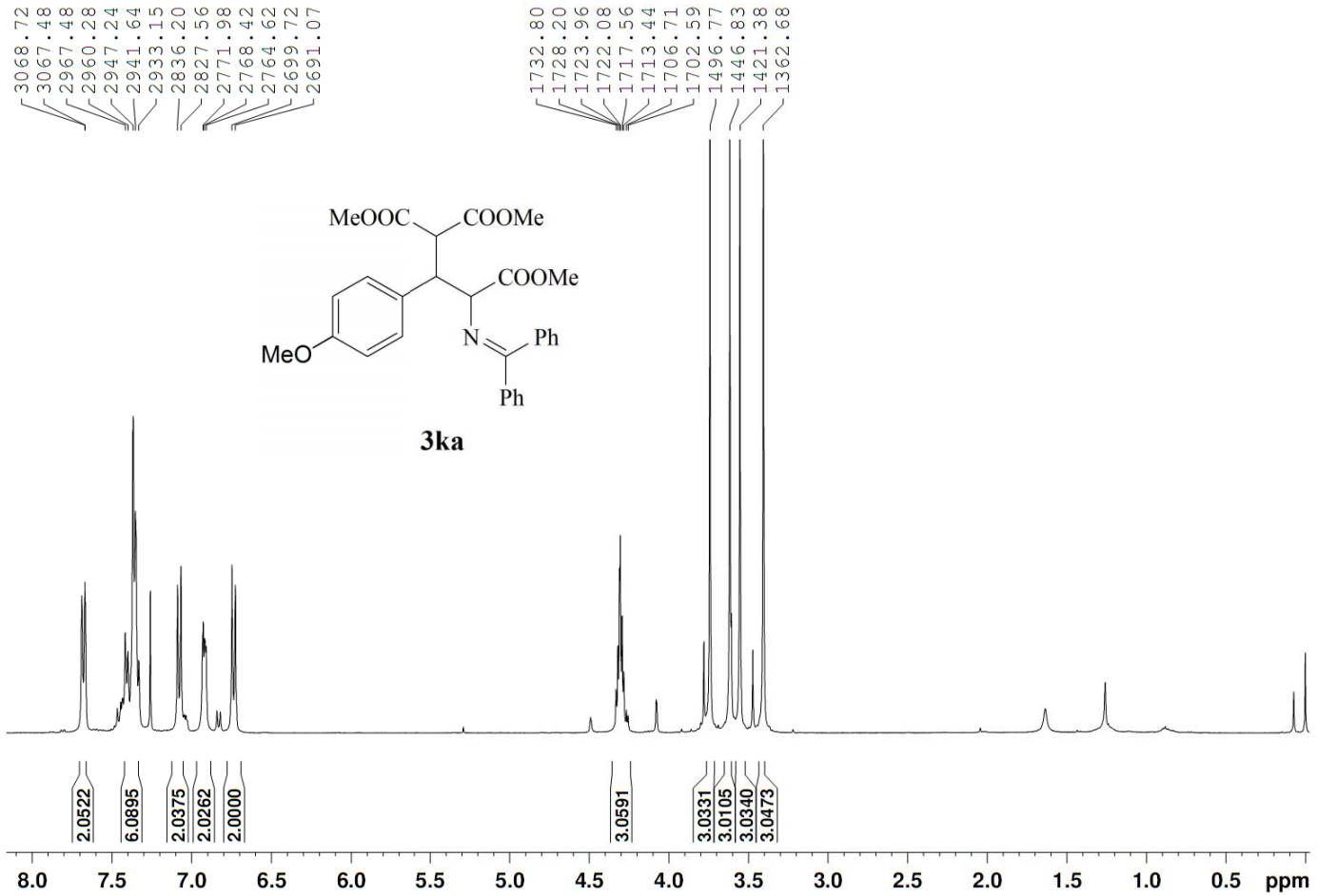
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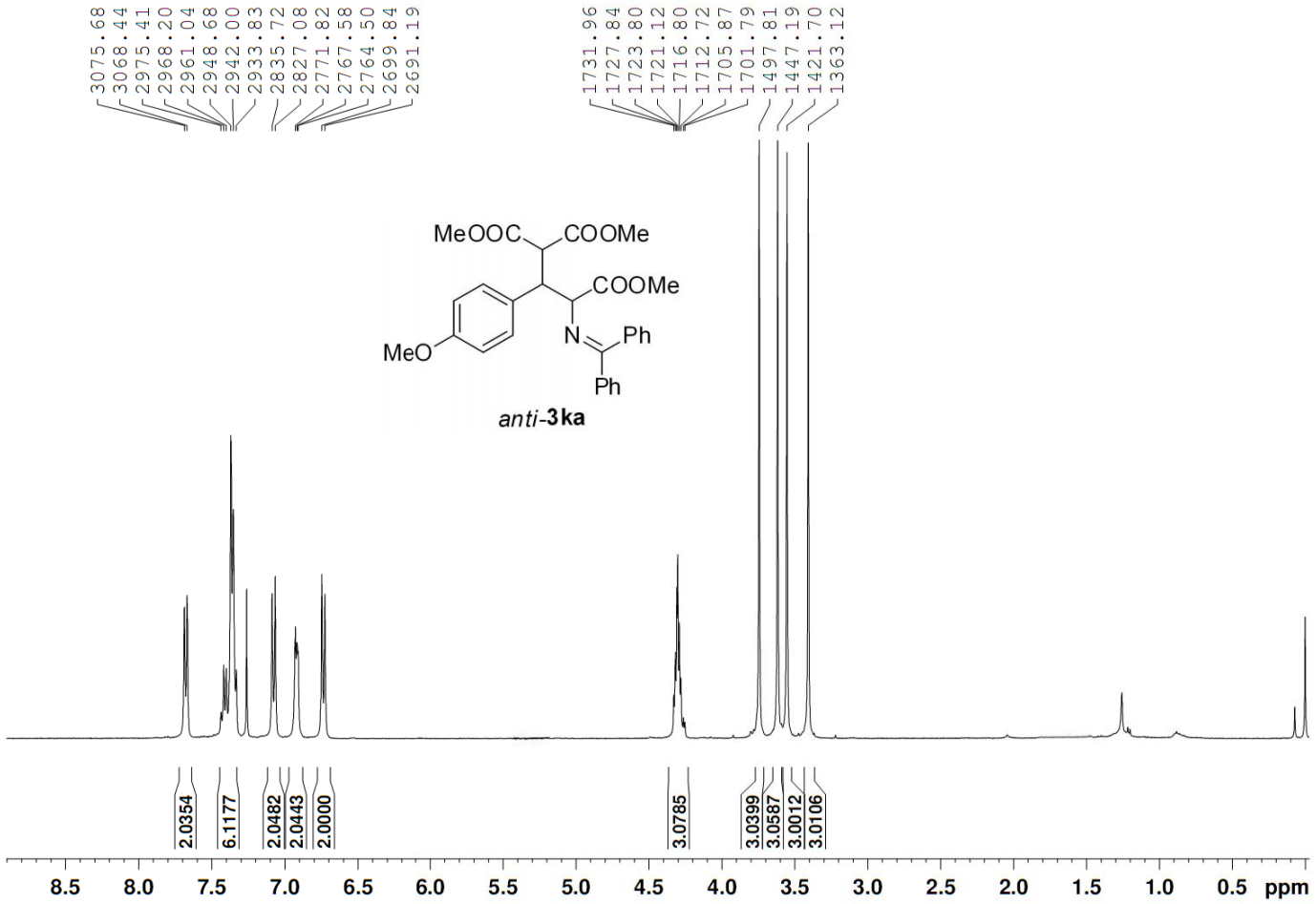
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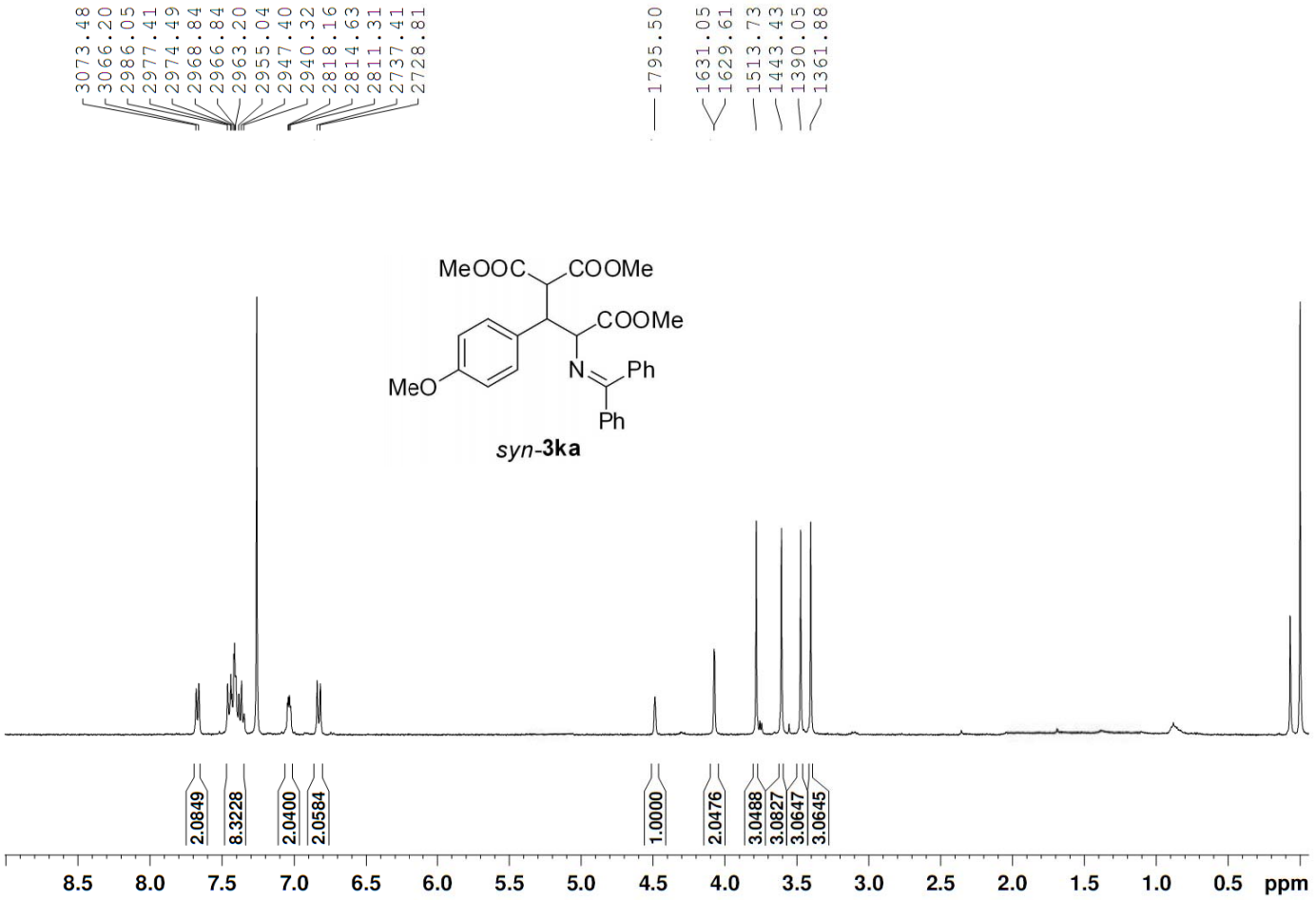
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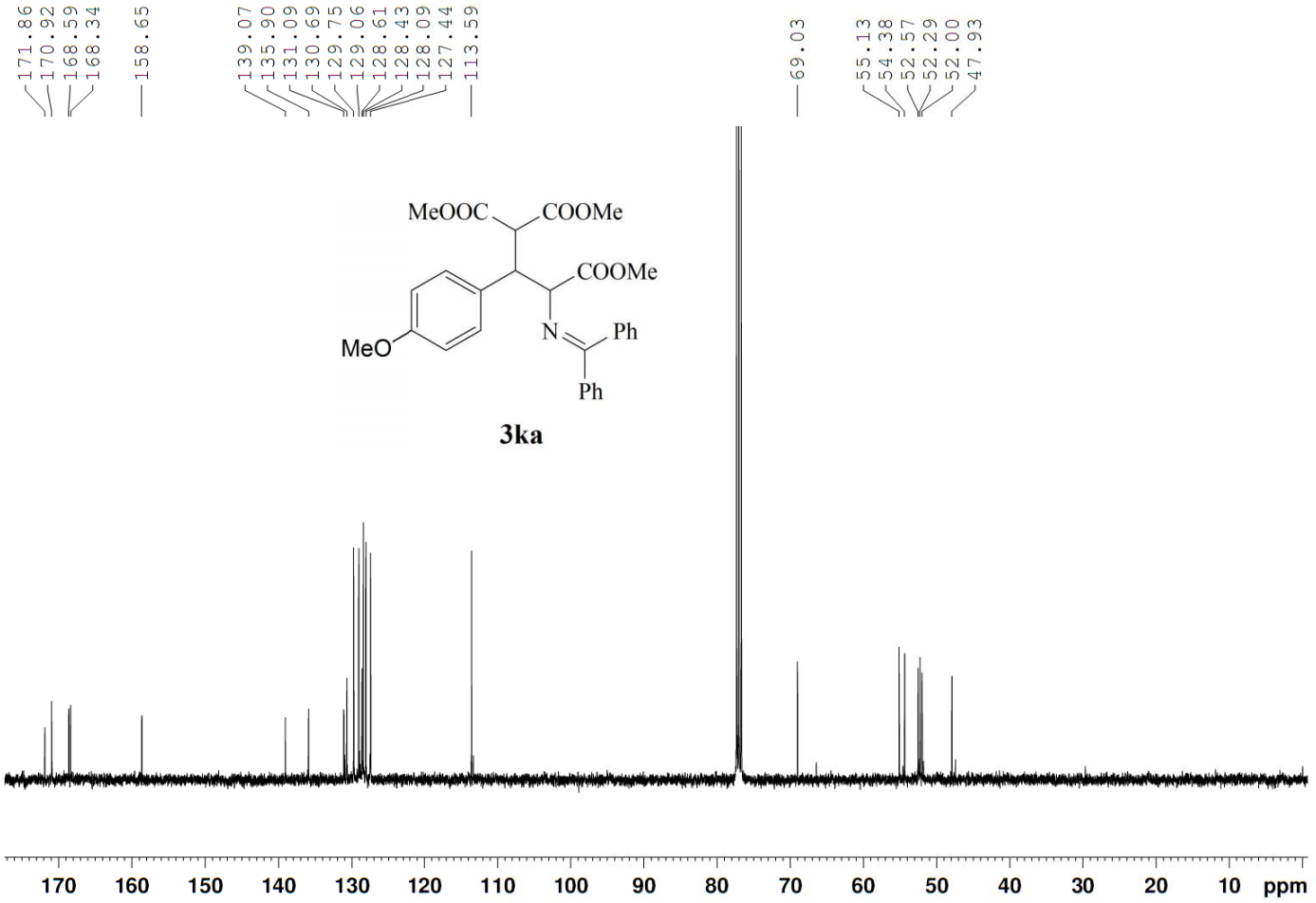
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COOMe
COOMe
MeO
N
Ph
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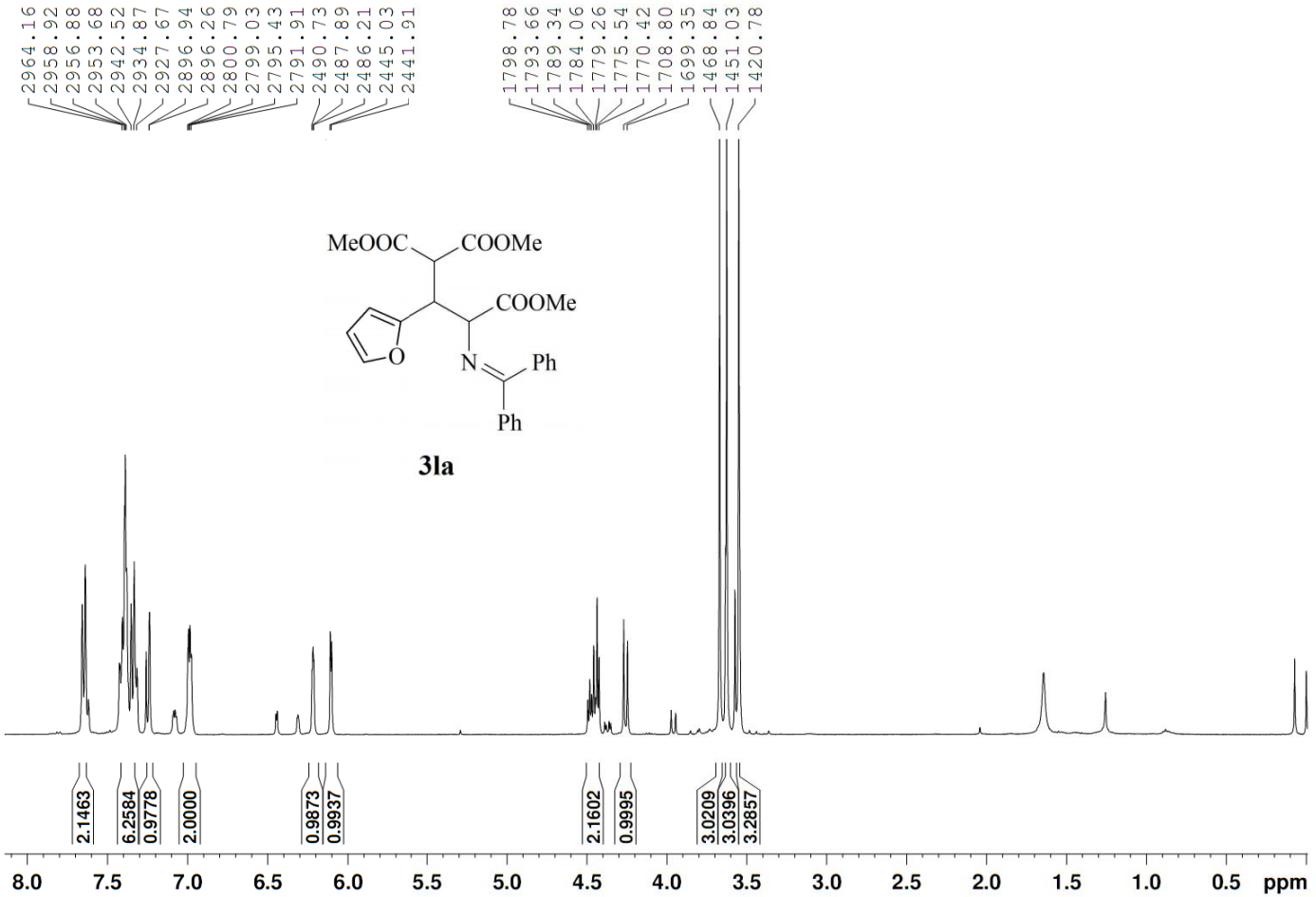
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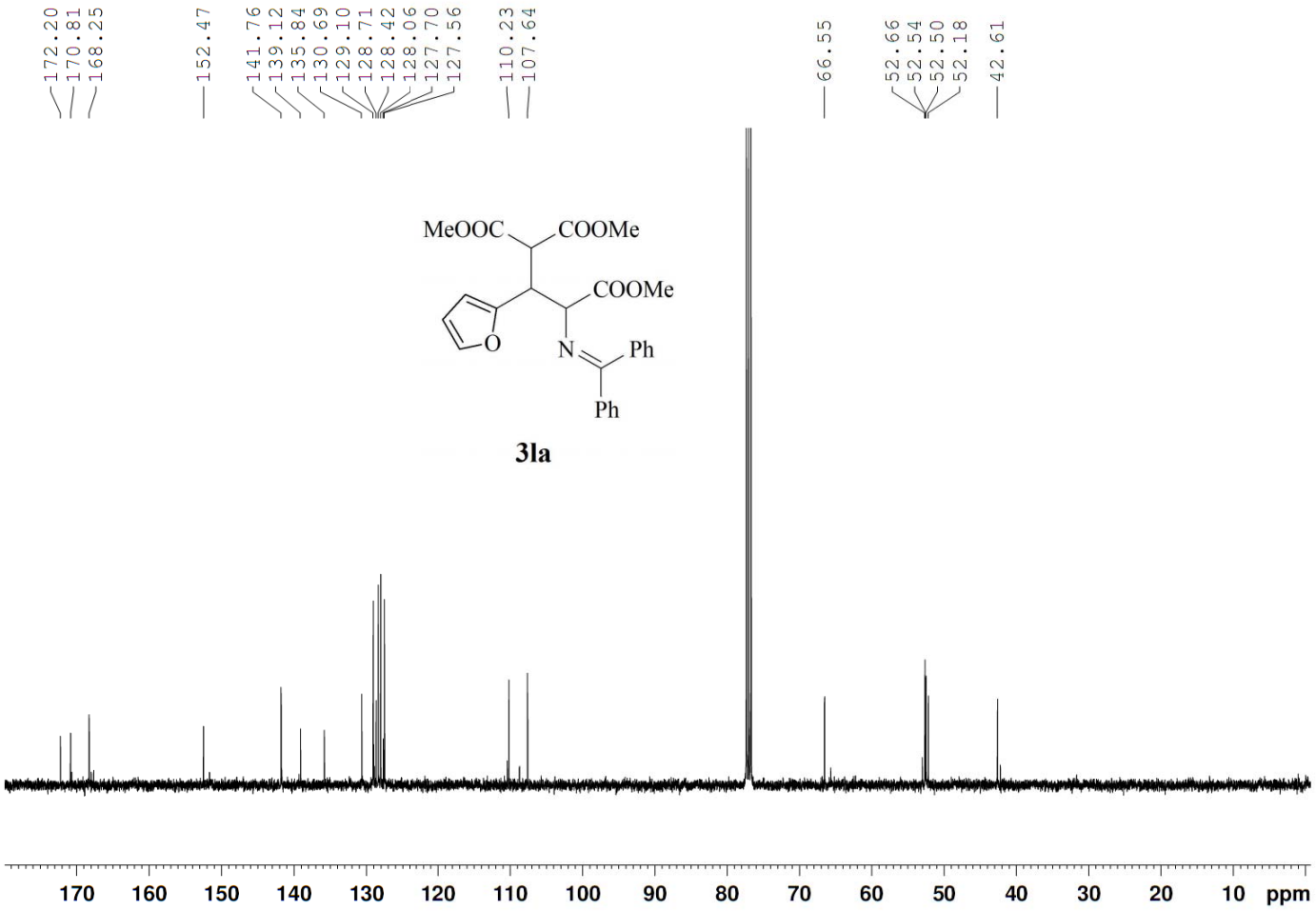
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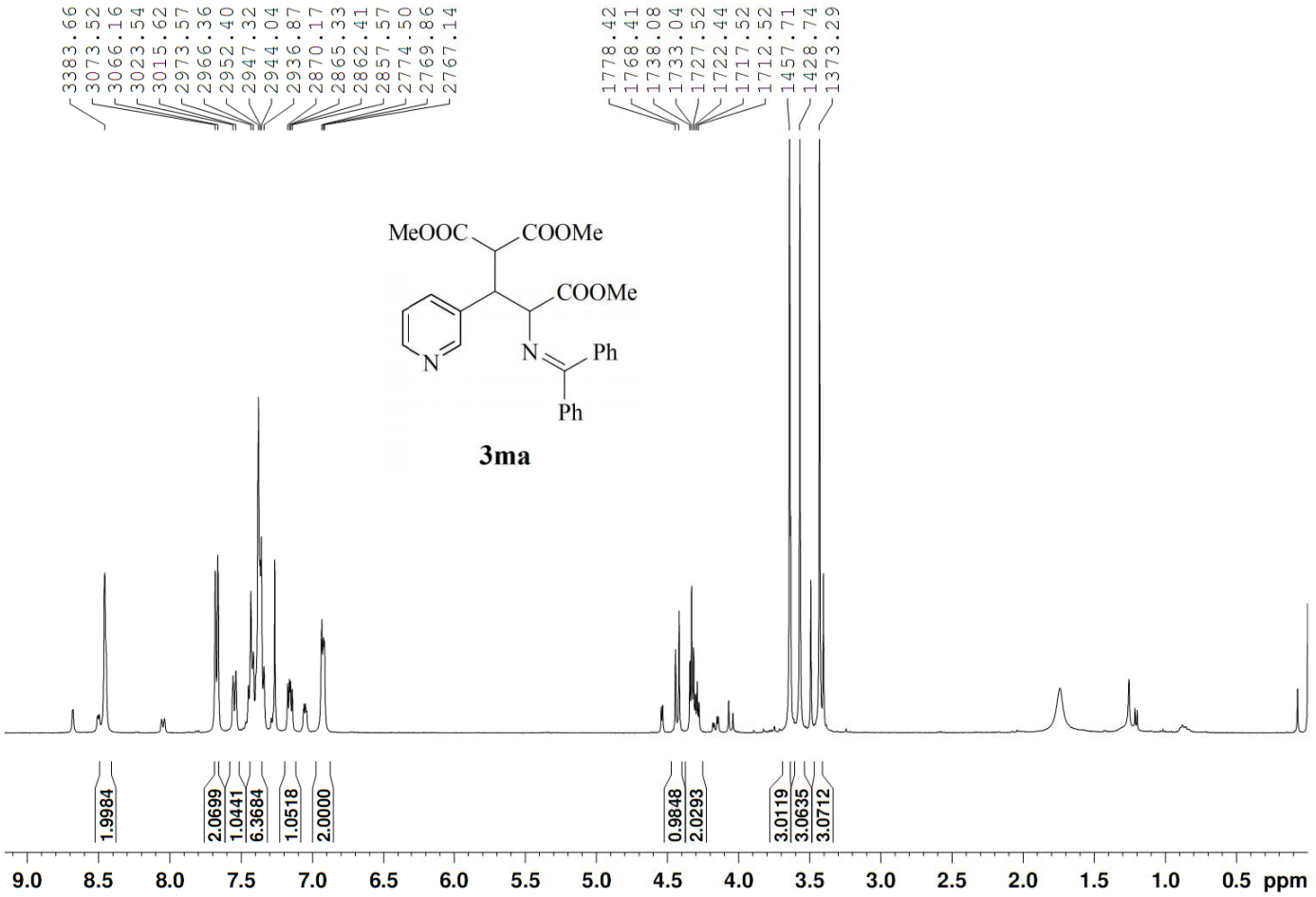
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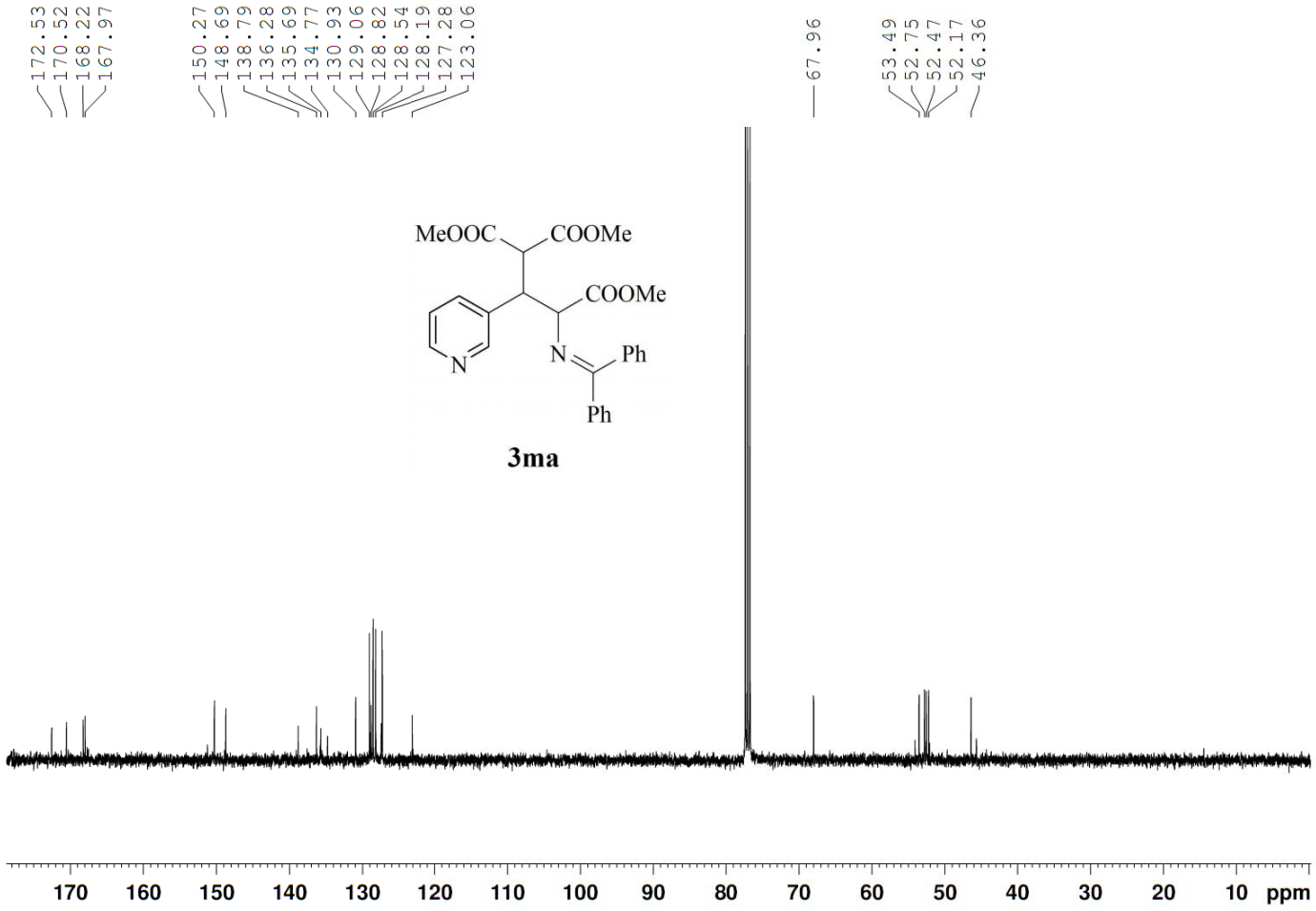
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COOMe
COOMe
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Ph
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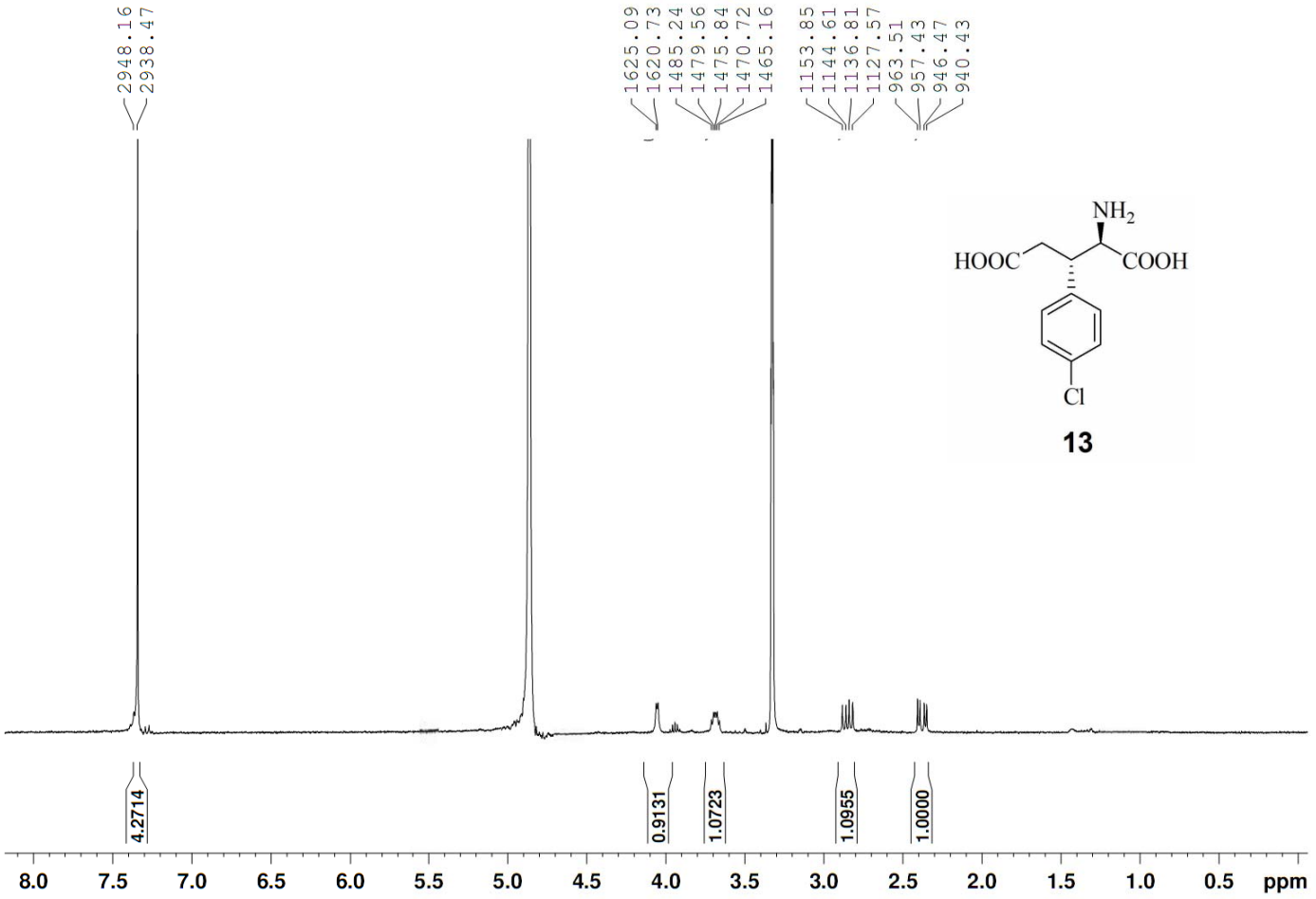
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HOOC
COOH
Cl
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6.0
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1.0
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