Supporting Information

Enantioselective bromination/semipinacol rearrangement for the synthesis of β-bromoketones containing an all-α-carbon quaternary center

Hui Li, Fu-Min Zhang, Yong-Qiang Tu,* Qing-Wei Zhang, Zhi-Min Chen, Zhi-Hua Chen, Jian Li

State Key Laboratory of Applied Organic Chemistry and Department of Chemistry, Lanzhou

University, Lanzhou 730000, P R China

E-mail: tuyq@lzu.edu.cn

Context

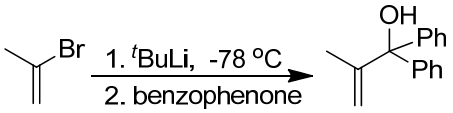
Experimental Details

General Information:

All reactions under standard conditions were monitored by thin-layer chromatography (TLC) on gel F254 plates. The silica gel (200-300 meshes) was used for column chromatography, and the distillation range of petroleum was 60-90 °C. CH_3OH and CCl_4 were purified under standard method. NBS was recrystallized with H_2O (23 mL H_2O per 1 g NBS). ^{1}HNMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Bruker AX-400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded on a Nicolet FT-170SX spectrometer. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV and signals were given in m/z with relative intensity (%) in brackets. High-resolution mass spectral analysis (HRMS) data were measured on the Bruker ApexII by means of the ESI tectnique. Enantioselectivities were determined by High performance liquid chromatography (HPLC) analysis employing a Daicel Chiralcel OZ-H, OJ or Chiralpak AD column.

General procedure for the synthesis of allylic alcohols 1:

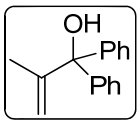
Compound **1a** was prepared as follows:



1a

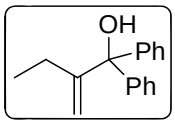
t-BuLi (1.6 M in pentane, 4.3 mL, 6.9 mmol, 2 equiv) was added slowly to the solution of 2-bromopropene in dry THF (8 mL) under argon at -78 °C during 10 min. The resulting solution was stirred at -78 °C for 0.5 h. The benzophenone (0.629 g, 3.45 mmol, 1 equiv) was added, and the reaction mixture was stirred at -78 °C for 0.5 h then allowed warm to room temperature. When benzophenone was disappeared completely (TLC), water (3 mL) was added. The organic layer was separated and aqueous layer was extracted with Et_2O (2 × 50 mL). The combined organic layer was washed with brine (30 mL), dried over Na_2SO_4 and concentrated under vacuum. Purification of the residue by column chromatography on silica gel (ethyl acetate: petroleum ether = 1:50) to give product compound **1a** as a colorless oil (0.6 g, 78% yield). Compounds **1b-1l**

were prepared in the similar methods.



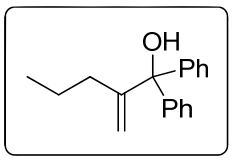
1a

^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.36-7.21 (m, 10 H), 5.12 (t, *J* = 1.2 Hz ,1 H), 4.72 (s, 1 H), 2.50 (s, 1 H), 1.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.0, 144.8, 127.9, 127.6, 127.2, 115.5, 82.9, 20.0; MS (EI) m/z (%): 224 (M^+, 8), 209 (36), 183 (66), 120 (27), 105 (100), 77 (32), 40 (77); IR (cm^{-1}): 3474, 3059, 1642, 1447, 1026, 760, 701; HRMS (ESI) calcd for $C_{16}H_{16}ONa$ $[M+Na]^+$: 247.1093, found 247.1095.



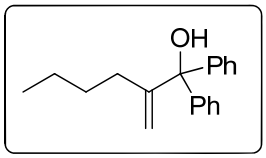
1b

Prepared according to general procedure with petroleum ether /EtOAc = 50:1 as eluent to afford **1b** as a white amorphous solid (66% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.34-7.21 (m, 10 H), 5.16 (d, *J* = 0.8 Hz, 1 H), 4.82 (d, *J* = 0.8 Hz, 1 H), 2.50 (s, 1 H), 2.07 (q, *J* = 7.4 Hz, 2 H), 1.03 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.9, 145.2, 127.8, 127.7, 127.2, 112.8, 83.5, 24.8, 12.6; MS (EI) *m/z* (%): 238 (M^+, 2), 209 (32), 183 (86), 118 (55), 105 (100), 77 (38); IR (cm^{-1}): 3482, 2963, 1639, 1445, 1020, 908, 758, 701; HRMS (ESI) calcd for $C_{17}H_{18}ONa$ $[M+Na]^+$: 261.1250, found 261.1252.



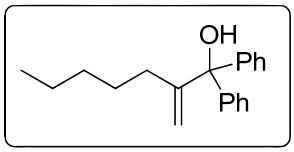
1c

Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1c** as a colorless oil (70% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.34-7.19 (m, 10 H), 5.15 (d, *J* = 0.8 Hz, 1 H), 4.79 (s, 1 H), 2.52 (s,1 H), 2.03 (t, *J* = 8 Hz, 2 H), 1.51-1.41 (m, 2 H), 0.86 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.4, 145.2, 127.8, 127.7, 127.1, 113.5, 83.5, 34.1, 21.7, 14.1; MS (EI) *m/z* (%): 252 (M^+, 2), 209 (23), 183 (100), 132 (40), 105 (83), 77 (30); IR (cm^{-1}): 3475, 2959, 1639, 1447, 1019, 761, 701; HRMS (ESI) calcd for $C_{18}H_{19}$ $[M-H_2O+H]^+$: 235.1481, found 235.1486.



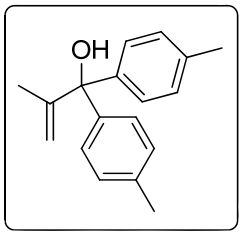
1d

Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1d** as a colorless oil (54% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.34-7.25 (m, 10 H), 5.16 (s, 1 H), 4.79 (s, 1 H), 2.46 (s, 1 H), 2.06 (t, *J* = 8.0 Hz, 2 H), 1.46-1.39 (m, 2 H), 1.31-1.22 (m, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.7, 145.3, 127.8, 127.7, 127.2, 113.6, 83.6, 31.8, 30.9, 22.7, 14.0; MS (EI) *m/z* (%): 266 (M^+, 2), 209 (29), 183 (100), 146 (49), 105 (91), 77 (33); IR (cm^{-1}): 3475, 2956, 1639, 1447, 1021, 906, 762, 701; HRMS (ESI) calcd for $C_{19}H_{22}ONa$ $[M+Na]^+$: 289.1563 found 289.1567.



1e

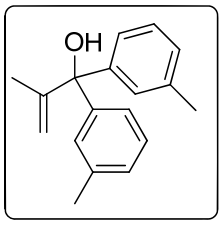
Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1e** as a colorless oil (61% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.25 (m, 10 H), 5.16 (s, 1 H), 4.79 (s, 1 H), 2.46 (s, 1 H), 2.05 (t, *J* = 8 Hz, 2 H), 1.48-1.40 (m, 2 H), 1.28-1.21 (m, 4 H), 0.84 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.7, 145.2, 127.8, 127.7, 127.2, 113.5, 83.6, 32.0, 31.8, 28.3, 22.5, 14.0; MS (EI) *m/z* (%): 280 (M^+, 2), 209 (22), 183 (100), 160 (34), 105 (63), 77 (19), 40 (48); IR (cm^{-1}): 3459, 2926, 1640, 1447, 1021, 700; HRMS (ESI) calcd for $C_{20}H_{23}$ $[M-H_2O+H]^+$:263.1794 found 263.1800.



1f

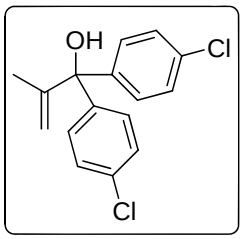
Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1f** as a colorless oil (95% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.23 (d, *J* = 8.0 Hz, 4 H), 7.12 (d, *J* = 8.0 Hz, 4 H), 5.10 (s, 1 H), 4.74 (s, 1 H), 2.38 (s, 1 H), 2.33 (s, 6 H), 1.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.3, 142.1, 136.7, 128.5, 127.5, 115.0, 82.7, 21.0, 20.1; MS

(EI) *m/z* (%): 252 (M^+, 11), 237 (29), 119 (100), 91 (28); IR (cm^{-1}): 3474, 2922, 1644, 1510, 1452, 815; HRMS (ESI) calcd for $C_{18}H_{20}ONa$ $[M+Na]^+$: 275.1406 found 275.1404.



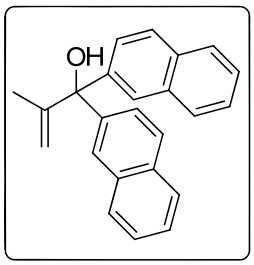
1g

Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1g** as a colorless oil (93% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.21-7.17 (m, 4 H), 7.11-7.06 (m, 4 H), 5.11 (s, 1 H), 4.73 (s,1 H), 2.44 (S,1 H), 2.32 (s, 6 H), 1.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.1, 144.8, 137.4, 128.1, 127.9, 127.6, 124.8, 115.3, 82.9, 21.6, 20.1; MS (EI) *m/z* (%): 252 (M^+, 5), 237 (27), 211 (46), 119 (100), 105 (24), 91 (34), 40 (35); IR (cm^{-1}): 3468, 2921, 1643, 1604, 1485, 1039, 908, 780, 706; HRMS (ESI) calcd for $C_{18}H_{20}ONa$ $[M+Na]^+$: 275.1406 found 275.1408.



1h

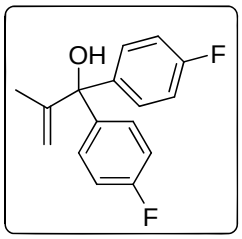
Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1h** as a colorless oil (99% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.29-7.24 (m, 8 H), 5.14 (d, *J* = 1.2 Hz, 1 H), 4.69 (s, 1 H), 2.49 (s, 1 H), 1.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.2, 142.9, 133.3, 128.9, 128.1, 116.2, 82.2, 19.8; MS (EI) *m/z* (%): 292 (M^+, 2), 277 (19), 251 (60), 139 (100), 111 (26); IR (cm^{-1}): 3470, 2974, 1644, 1488, 1094, 1012, 822.



1i

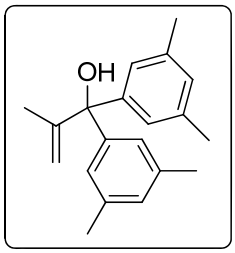
Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1i**

as a white amorphous solid (91% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.90-7.49 (m, 14 H), 5.29 (s, 1 H), 4.90 (s, 1 H), 2.76 (s, 1 H), 1.95 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.8, 142.1, 132.8, 132.6, 128.3, 127.6, 127.5, 126.4, 126.13, 126.11, 126.0, 116.0, 83.3, 20.1; MS (EI) *m/z* (%): 324 (M^+, 10), 283 (20), 155 (47), 149 (100), 127 (23), 40 (83); IR (cm^{-1}): 3468, 3056, 1637, 1505, 817, 746; HRMS (ESI) calcd for $C_{24}H_{20}ONa$ $[M+Na]^+$: 347.1406, found 347.1399.



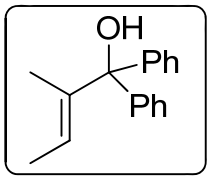
1j

Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1j** (80% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.32-7.27 (m, 4 H), 7.02-6.96 (m, 4 H), 5.13 (t, *J* = 1.2 Hz, 1 H), 4.69 (s, 1 H), 2.52 (s, 1 H), 1.77 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 162.0 (d, J = 245 Hz), 148.8, 140.5 (d, J = 4 Hz), 129.3 (d, J = 8 Hz), 115.8, 144.7 (d, J = 22 Hz), 82.2, 19.4; MS (EI) *m/z* (%): 260 (M^+, 3) 245 (23), 219 (58), 123 (100); IR (cm^{-1}): 3470, 2925, 1602, 1506, 1228, 1160, 834; HRMS (ESI) calcd for $C_{16}H_{13}F_2$ $[M-H_2O+H]^+$: 243.0980 found 243.0986.



1k

Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1k** as a colorless oil (99% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 6.96 (s, 4 H), 6.89 (s, 2 H), 5.09 (t, *J* = 1.2 Hz, 1 H), 4.74 (s, 1 H), 2.04 (s, 1 H）, 2.27 (s, 12 H), 1.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 149.3, 145.0, 137.1, 128.8, 125.4, 115.1, 82.8, 21.4, 20.2; MS (EI) *m/z* (%): 280 (M^+, 21), 239 (47), 133 (100), 105 (34); IR (cm^{-1}): 3466, 2918, 1643, 1602, 1450, 854; HRMS (ESI) calcd for $C_{20}H_{24}ONa$ $[M+Na]^+$: 303.1719 found 303.1715.



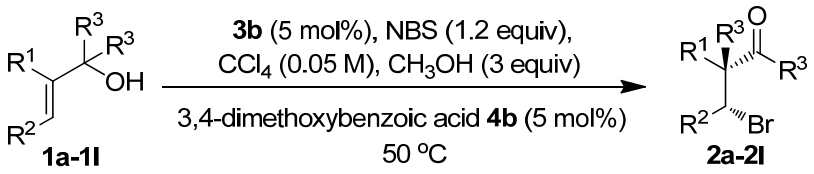
1l

Prepared according to general procedure with petroleum ether/EtOAc = 50:1 as eluent to afford **1l** as a white amorphous solid (80% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): 7.32-7.21 (m, 10 H）, 5.22-5.17 (m, 1 H), 2.48 (s, 1 H), 1.66 (s, 3 H), 1.64 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.4, 140.1, 127.8, 127.7, 127.0, 124.2, 83.8, 14.0, 13.6; MS (EI) *m/z* (%) 238 (M^+, 7), 183 (34), 134 (50), 105 (100), 77 (28); IR (cm^{-1}): 3483, 3060, 1598, 1445, 1162, 1003, 758, 701; HRMS (ESI) calcd for $C_{17}H_{17}$ $[M-H_2O+H]^+$: 221.1325 found 221.1331.

General Procedure for synthesis of the racemates of β-haloketone products:

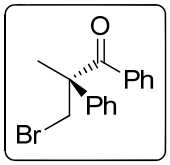
The **racemate** products **2a-l** were prepared using NBS in acetonitrile at room temperature.

General Procedure for the asymmetric Synthesis of α-All-Carbon Quaternary β-Bromoketo Compounds:



To a flame-dried round-bottom flask were added CCl_4 (1 mL), NBS (3.6 mg, 0.02 mmol, 0. 2 equiv), catalyst **3b** (3.6 mg, 0.005 mmol, 5 mol%), 3, 4-dimethoxybenzoic acid **4b** (0.9 mg, 0.005 mmol, 5 mol%) and CH_3OH (6.5 μL , 0.15 mmol, 1.5 equiv). The mixture was stirred for 10 minutes at room temperature and then a solution of substrate (0.1 mmol) and CH_3OH (6.5 μL, 0.15 mmol 1.5 equiv) in CCl_4 (1 mL) was added. The flask was heated to 50 °C and the additional NBS (18 mg, 0.1 mmol, 1 equiv) was added in five portions (0.02 mmol every 12 hours). After 72 hours, the reaction mixture was directly subjected to column chromatography on silica gel. The products

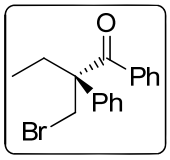
wre eluted by petroleum ether/ethyl acetate (100:1).



2a

(*S*)-3-bromo-2-methyl-1,2-diphenylpropan-1-one (2a):

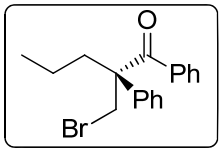
Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2a** as crystal solid (23.0 mg, 76% yield). Mp: 76-79 ^{o}C; ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.44-7.32 (m, 8 H), 7.25-7.21 (m, 2 H), 4.07 (d, *J* = 10.4 Hz, 1 H), 3.78 (d, *J* = 10.4, 1 H), 1.81 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.2, 140.4, 136.1, 132.0, 129.3, 129.2, 128.1, 127.9, 126.4, 54.9, 43.1, 22.8; MS (EI) *m/z* (%) 118 (100), 105 (63), 77 (29); IR (cm^{-1}): 2927, 1674, 1248, 969, 700; HRMS (ESI) calcd for $C_{16}H_{15}BrONa$ $[M+Na]^+$: 325.0198, found 325.0189, $[\alpha]^{16}_D$ = +118° (c = 1.0, $CHCl_3$); Enantiomeric excess is 93% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 9.34 min; major isomer: t_R = 11.22 min.



2b

(*S*)-2-(bromomethyl)-1,2-diphenylbutan-1-one (2b):

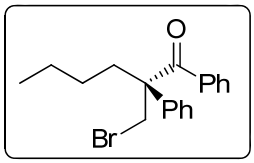
Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2b** as a colorless oil (25.6 mg, 81% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.30 (m, 8 H), 7.24-7.18 (m, 2 H), 4.12 (d, *J* = 10.8 Hz, 1 H), 3.93 (dd, *J* = 10.8 Hz, 0.6 Hz, 1 H), 2.57-2.48 (m, 1 H), 2.32-2.24 (m, 1 H), 0.74 (t, *J* = 7.4 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.7, 140.3, 136.4, 132.0, 129.2, 129.0, 128.0, 127.7, 126.8, 58.6, 40.4, 26.0, 7.8; MS (EI) *m/z* (%): 132 (100), 117 (40), 105 (72), 77 (35); IR (cm^{-1}): 2971, 1671, 1447, 1231, 1001, 762, 705, 606; HRMS (ESI) calcd for $C_{17}H_{17}BrONa$ $[M+Na]^+$: 339.0355, found 339.0353; $[\alpha]^{24}_D$ = +90° (c = 1.0, $CHCl_3$); Enantiomeric excess is 91% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 7.31 min; major isomer: t_R = 9.15 min.



2c

(*S*)-2-(bromomethyl)-1,2-diphenylpentan-1-one (2c):

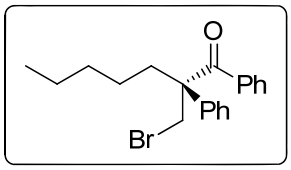
Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2c** as a colorless oil (28.4 mg, 86% yield). ^{1}HNMR (400 MHz, CDCl3, ppm): δ 7.40-7.31 (m, 8 H), 7.24-7.19 (m, 2 H), 4.12 (d, *J* = 10.8 Hz, 1 H) 3.94 (d, *J* = 10.4 Hz, 1 H), 2.45 (td, *J* = 12.8 Hz, 4.4 Hz, 1 H), 2.17 (td, *J* = 12.8 Hz, 4.4 Hz, 1H), 1.30-1.18 (m, 1 H), 1.03-0.89 (m, 1 H), 0.84 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.7, 140.4, 136.4, 132.0, 129.2, 129.0, 128.0, 127.7, 126.8, 58.3, 41.2, 35.4, 16.8, 14.5; MS (EI) *m/z* (%): 146 (54), 131 (34), 118 (81), 105 (100), 77 (34); IR (cm^{-1}): 2960, 1670, 1446, 1224, 1009, 698; HRMS (ESI) calcd for $C_{18}H_{19}BrONa$ $[M+Na]^+$: 353.0511 found 353.0506; $[\alpha]^{16}_D = +92°$ (c = 1.0, $CHCl_3$). Enantiomeric excess is 90% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 4.68 min; major isomer: t_R = 6.02 min.



2d

(*S*)-2-(bromomethyl)-1,2-diphenylhexan-1-one (2d):

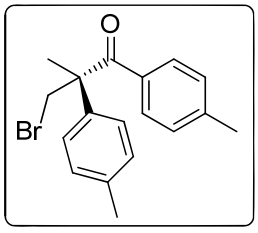
Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2d** as a colorless oil (26.9 mg, 78% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.31 (m, 8 H), 7.23-7.19 (m, 2 H), 4.11 (d, *J* = 10.8 Hz, 1 H), 3.94 (dd, *J* = 10.8 Hz, 1 Hz, 1 H), 2.47 (td, *J* = 13.2 Hz, 4 Hz, 1 H), 2.23-2.19 (m, 1 H), 1.29-1.16 (m, 3 H), 0.92-0.86 (m, 1 H), 0.76 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.9, 140.5, 136.5, 132.0, 129.2, 129.0, 128.1, 127.8, 126.9, 58.3, 41.3, 32.8, 25.5, 22.9, 13.7; MS (EI) *m/z* (%): 160 (22), 118 (100), 105 (76), 77(28); IR (cm^{-1}): 2958, 1671, 1446, 1255, 1021, 697; HRMS (ESI) calcd for $C_{19}H_{21}BrONa$ $[M+Na]^+$: 367.0668 found 367.0658; $[\alpha]^{16}_D = +77°$ (c = 1.0, $CHCl_3$). Enantiomeric excess is 91% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 80/20, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 4.27 min; major isomer: t_R = 6.16 min.



2e

(*S*)-2-(bromomethyl)-1,2-diphenylheptan-1-one (2e):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2e** as a colorless oil (29.7 mg, 83% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.31 (m, 8 H), 7.24-7.20 (m,2 H), 4.11 (d, *J* = 10.8, 1 H), 3.94 (dd, *J* = 10.8 Hz, 0.8 Hz, 1 H), 2.46 (td, *J* = 13.2 Hz, 4 Hz, 1 H), 2.22-2.14 (m, 1 H), 1.25-1.13 (m, 5 H), 0.96-0.88 (m, 1 H), 0.76 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.9, 140.5, 136.5, 132.0, 129.2, 129.0, 128.1, 127.8, 126.9, 58.3, 41.3, 33.0, 31.9, 22.9, 22.1, 13.8; MS (EI) *m/z* (%): 174 (19), 118 (90), 105 (62), 40 (100); IR (cm^{-1}): 2925, 1670, 698; HRMS (ESI) calcd for $C_{20}H_{24}BrO$ $[M+H]^+$: 359.1005 found 359.1011; $[\alpha]^{16}_D$ = +58° (c = 1.0, $CHCl_3$); Enantiomeric excess is 87% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 99.5/0.5, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 9.99 min; major isomer: t_R = 11.65 min.

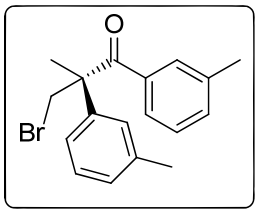


2f

(*S*)-3-bromo-2-methyl-1,2-dip-tolylpropan-1-one (2f):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2f** as a colorless oil (31.1 mg, 94% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.38 (d, *J* = 8.4 Hz, 2 H), 7.22-7.17 (m, 4 H), 7.04 (d, *J* = 8 Hz, 2 H), 4.04 (d, *J* = 10 Hz, 1 H), 3.75 (d, *J* = 10 Hz, 1 H), 2.35 (s, 3 H), 2.30 (s, 3 H), 1.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 200.9, 142.7, 137.7, 137.5, 133.3, 129.8, 129.7, 128.7, 126.2, 54.5, 43.6, 22.9, 21.5, 21.1; MS (EI) *m/z* (%): 132 (100), 119 (53), 117 (15), 91 (24); IR (cm^{-1}): 2924, 1677, 1251, 1021, 972, 823; HRMS (ESI) calcd for $C_{18}H_{19}BrONa$ $[M+Na]^+$:353.0511 found 353.0502; $[\alpha]^{16}_D$ = +125° (c = 1.0, $CHCl_3$);

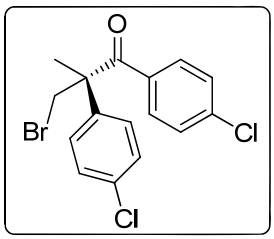
Enantiomeric excess is 88% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 7.95 min; major isomer: t_R = 9.46 min.



2g

(*S*)-3-bromo-2-methyl-1,2-dim-tolylpropan-1-one (2g):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2g** as a colorless oil (31.1 mg, 94% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.37-7.05 (m, 8 H), 4.07 (d, *J* = 10 Hz, 1 H), 3.74 (d, *J* = 10.4 Hz, 1 H), 2.34 (s, 3 H), 2.27 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.6, 140.3, 138.8, 138.0, 136.3, 132.7, 129.9, 129.0, 128.7, 127.7, 127.0, 126.4, 123.3, 54.8, 43.1, 22.9, 21.6, 21.3; MS (EI) *m/z* (%) 132 (100), 119 (54), 91 (28); IR (cm^{-1}): 2924, 1679, 1264, 1020，801; HRMS (ESI) calcd for $C_{18}H_{20}BrO$ $[M+H]^+$: 331.0692 found 331.0700; $[\alpha]^{16}_D$ = +113° (c = 1.0, $CHCl_3$); Enantiomeric excess is 90% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 6.62 min; major isomer: t_R = 7.25 min.

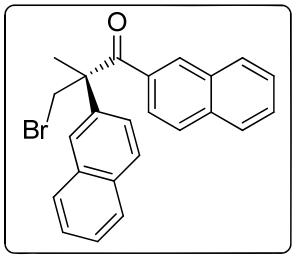


2h

(*S*)-3-bromo-1,2-bis(4-chlorophenyl)-2-methylpropan-1-one (2h):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2h** as a colorless oil (23 mg, 62% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.37 (m, 4 H), 7.26-7.23 (m, 4 H), 3.98 (d, *J* = 10.4 Hz, 1 H), 3.75 (d, *J* = 10.4, 1 H), 1.79 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 199.6, 138.81, 138.78, 134.1, 133.8, 130.9, 129.5, 128.6, 127.8, 54.5, 42.8, 22.7; MS (EI) *m/z* (%): 154 (32) 152 (100), 139 (86), 117 (20), 111 (25), 40 (31); IR (cm^{-1}): 3392, 2923, 1676, 1249, 1094, 1015, 664; $[\alpha]^{16}_D$ = +39° (c = 1.0, $CHCl_3$); Enantiomeric excess is 83% determined by HPLC (Chiralpak AD, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min,

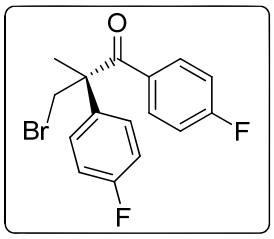
254 nm): major isomer: t_R = 6.29 min; minor isomer: t_R = 7.61 min.



2i

(*S*)-3-bromo-2-methyl-1,2-di(naphthalen-2-yl)propan-1-one (2i):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2i** as a white amorphous solid (35.4 mg, 88% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 8.06 -7.40 (m, 14 H), 4.25 (d, *J* = 10.4 Hz, 1 H), 3.96 (d, *J* = 10 Hz, 1 H), 2.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.1, 138.1, 134.7, 133.42, 133.36, 132.7, 132.1, 131.0, 129.5, 129.1, 128.23, 128.15, 127.8, 127.7, 127.5, 126.6, 126.49, 126.48, 125.5, 125.3, 124.2, 55.2, 43.2, 23.1; MS (EI) *m/z* (%): 168 (64), 155 (55), 149 (80), 127 (46), 85 (65), 71 (70), 57 (90), 43 (100); IR (cm^{-1}): 3057, 1674, 1274,1019, 820, 747; HRMS (ESI) calcd for $C_{24}H_{19}BrONa$ $[M+Na]^+$: 425.0511 found 425.0501; $[\alpha]^{16}_D$ = +65 ° (c = 1.0, $CHCl_3$). Enantiomeric excess is 84% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): major isomer: t_R = 15.82 min; minor isomer: t_R = 22.37 min.

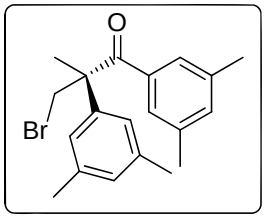


2j

(*S*)-3-bromo-1,2-bis(4-fluorophenyl)-2-methylpropan-1-one (2j):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2j** as a colorless oil (32.8 mg, 97% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.51-7.47 (m, 2 H), 7.31-7.27 (m, 2 H), 7.10 (t, *J* = 8.4 Hz, 2 H), 6.94 (t, *J* = 8.4 Hz, 2 H), 4.00 (d, *J* = 10.4 Hz, 1 H), 3.75 (d, *J* = 10.4 Hz, 1 H), 1.81 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 199.4, 164.8 (d, J = 253 Hz), 162.2 (d, J = 247 Hz), 136.0 (d, J = 3 Hz), 132.1 (d, J = 9 Hz), 131.8 (d, J = 3 Hz), 128.1 (d, J = 8Hz), 116.2 (d, J = 22 Hz), 153.3 (d, J = 22 Hz), 54.3, 43.2, 22.8; MS (EI) *m/z* (%) 136 (100), 123 (78), 95 (23); IR (cm^{-1}): 2962, 1674, 1598, 1508, 1237, 1017, 838; HRMS (ESI)

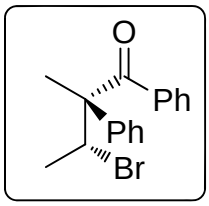
calcd for $C_{16}H_{13}BrF_2ONa$ $[M+Na]^+$: 361.0100 found 361.0106; $[\alpha]^{16}_D = +87°$ (c = 1.0, $CHCl_3$); Enantiomeric excess is 74% determined by HPLC (Chiralpak AD, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): major isomer: $t_R = 9.12$ min; minor isomer: $t_R = 10.32$ min.



2k

(*S*)-3-bromo-1,2-bis(3,5-dimethylphenyl)-2-methylpropan-1-one (2k):

Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2k** as a colorless oil (31.9 mg, 89% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.03 (s, 3 H), 6.97 (s, 1 H), 6.94 (s, 2 H), 4.07 (d, *J* = 10 Hz, 1 H), 3.71 (d, *J* = 10 Hz, 1 H), 2.31 (s, 6 H), 2.20 (s, 6 H), 1.76 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.9, 140.3, 138.6, 137.5, 136.7, 133.5, 129.5, 127.0, 124.0, 54.7, 43.1, 23.0, 21.5, 21.2; MS (EI) *m/z* (%): 146 (100), 133 (56), 105 (20), 40 (28); IR (cm^{-1}): 2923, 2854, 1678, 1458, 1036, 804; HRMS (ESI) calcd for $C_{20}H_{23}BrONa$ $[M+Na]^+$: 381.0824 found 381.0834; $[\alpha]^{16}_D = +79°$ (c = 1.0, $CHCl_3$). Enantiomeric excess is 72% determined by HPLC (Chiralcel OZ-H, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): major isomer: $t_R = 4.88$ min; minor isomer: $t_R = 5.76$ min.



2l

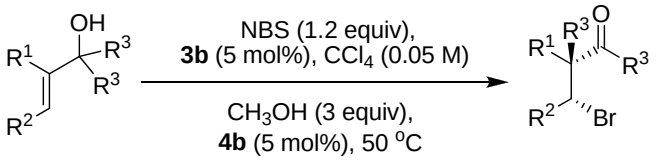
(*2S*)-3-bromo-2-methyl-1,2-diphenylbutan-1-one (2l):

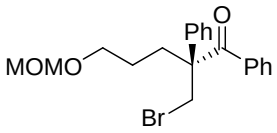
Prepared according to general procedure with petroleum ether/EtOAc = 100:1 as eluent to afford **2l** as a colorless oil (20 mg, 63% yield). ^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.41-7.21 (m, 10 H), 5.14 (q, *J* = 7.2 Hz, 1 H), 1.84 (s, 3 H), 1.36 (d, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.9, 138.3, 137.8, 131.3, 129.2, 128.5, 128.1, 127.9, 127.1, 58.8, 55.1, 21.0, 18.8; MS (EI) *m/z* (%): 132 (100), 117 (69), 105 (44), 77 (22); IR (cm^{-1}): 2927, 1682, 1447, 1247, 964, 702; HRMS (ESI) calcd for $C_{17}H_{17}BrONa$ $[M+Na]^+$: 339.0355 found 339.0350; $[\alpha]^{23}_D = +101°$ (c =

1.0, $CHCl_3$); Enantiomeric excess is 58% determined by HPLC (Chiralpak AD, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min, 254 nm): major isomer: t_R = 5.41 min; minor isomer: t_R =6.99 min

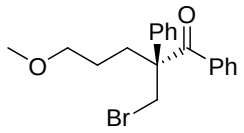
More information about substrate scope:

we have also investigated some substrates bearing a functionalized group or beta-branched alkyl groups. The results are as follows:

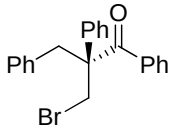




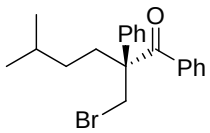
2m 20% yield, 37% ee



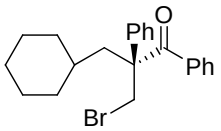
2n 30% yield, 4% ee



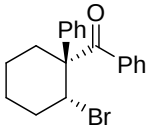
2o 24% yield, 44% ee



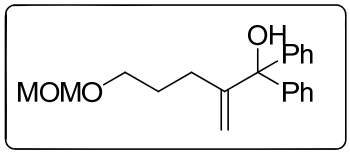
2p 60% yield, 45% ee



2q 60% yield, 55% ee



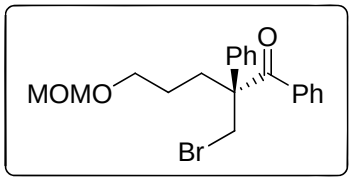
2r 60% yield, 57% ee



1m

5-(methoxymethoxy)-2-methylene-1,1-diphenylpentan-1-ol:

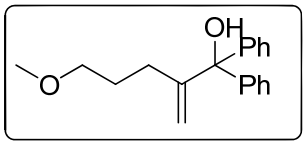
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.24 (m, 10 H), 5.18 (s, 1 H), 4.78 (s, 2H), 4.56 (s, 2 H), 3.50 (t, J = 6 Hz, 2 H), 3.30 (s, 3 H), 2.98 (s, 1 H), 2.17 (t, J = 7.6 Hz, 2 H), 1.80-1.73 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.0, 145.2, 127.8, 127.7, 127.2, 114.4, 96.3, 83.5, 67.4, 55.2, 28.9, 28.8; MS (EI) *m/z* (%): 183 (96), 160 (31), 105 (100), 77 (24).



2m

(S)-2-(bromomethyl)-5-(methoxymethoxy)-1,2-diphenylpentan-1-one:

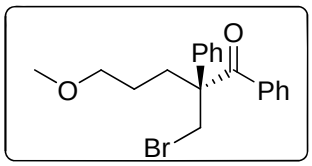
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.31 (m, 8 H), 7.24-7.20 (m, 2 H), 4.47 (s, 2 H), 4.11 (d, J = 10.8 Hz, 1 H), 7.93 (d, J = 10.8 Hz, 1 H), 3.43 (t, J = 6.4 Hz, 2 H), 3.27 (s, 3 H), 2.54 (td, J = 12.8 Hz, 4.4 Hz, 1 H), 2.30 (td, J = 13.2 Hz, 3.6 Hz, 1 H), 1.53-1.40 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.5, 140.1, 136.4, 132.1, 129.2, 129.1, 128.1, 127.8, 126.8, 96.1, 67.3, 58.1, 55.1, 40.5, 30.2, 23.8; MS (EI) *m/z* (%): 255 (10), 161 (26), 144 (45), 129 (42), 118 (72), 105 (100), 71 (67), 57 (79); Enantiomeric excess is 37% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 70/30, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 5.69 min; major isomer: t_R = 12.65 min.



1n

5-methoxy-2-methylene-1,1-diphenylpentan-1-ol:

^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.24 (m, 10 H), 5.16 (s, 1 H), 4.74 (s, 1 H), 3.48 (s, 1 H), 3.38 (t, J = 6.4 Hz, 2 H), 3.29 (s, 3 H), 2.16 (t, J = 7.6 Hz, 2 H), 1.80-1.73 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.1, 145.3, 127.8, 127.7, 127.0, 114.7, 83.4, 72.1, 58.4, 28.9, 28.6; MS (EI) *m/z* (%): 282 (M^+, 4), 209 (30), 183 (100), 105 (91), 77 (27).

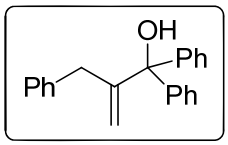


2n

(S)-2-(bromomethyl)-5-methoxy-1,2-diphenylpentan-1-one:

^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.42-7.31 (m, 8 H), 7.23-7.20 (m, 2 H), 4.11 (d, J = 10.8, 1 H), 3.96 (d, J = 10.8 Hz, 1 H), 3.31-3.26 (m, 2 H), 3.17 (s, 3 H), 2.51 (td, J = 13.6 Hz, 4.4 Hz, 1 H),

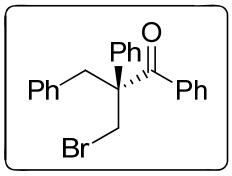
2.29 (td, J = 13.2 Hz, 4.4 Hz, 1 H), 1.51-1.36 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.5, 140.2, 136.4, 132.1, 129.2, 129.1, 128.1, 127.8, 126.8, 72.3, 58.2, 58.1, 40.6, 30.0, 23.4; MS (EI) *m/z* (%): 149 (19), 144 (31), 118 (100), 105 (73), 77 (260); Enantiomeric excess is 4% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 70/30, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 5.00 min; major isomer: t_R = 7.56 min.



1o

2-benzyl-1,1-diphenylprop-2-en-1-ol:

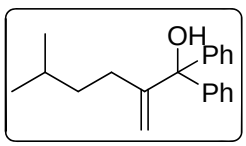
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.63-7.11 (m, 15 H), 4.85 (d, J = 0.8 Hz, 1 H), 4.79 (s, 1 H), 3.40 (s, 2H), 2.51 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.4, 144.9, 139.8, 129.5, 128.3, 127.9, 127.7, 127.3, 126.0, 117.0, 83.6, 38.7; MS (EI) *m/z* (%): 300 (M^+, 1), 282 (20), 209 (9), 191 (29), 183 (100), 105 (92), 77 (29).



2o

(S)-2-benzyl-3-bromo-1,2-diphenylpropan-1-one:

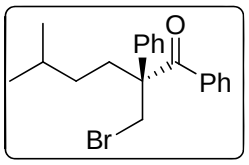
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.46-6.72 (m, 15 H), 3.98 (d, J = 10.4 Hz, 1 H), 3.87 (d, J = 10.4 Hz, 1 H), 3.64 (d, J = 13.6 Hz, 1 H), 3.56 (d, J = 13.6 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 200.1, 140.0, 136.7, 135.9, 132.1, 130.3, 129.6, 129.1, 128.2, 127.91, 127.87, 126.9, 126.8, 59.4, 40.3, 38.8; MS (EI) *m/z* (%): 299 (4), 194 (100), 179 (37), 149 (27), 116 (40), 105 (88), 77 (37); Enantiomeric excess is 44% determined by HPLC (Chiralcel IC, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): major isomer: t_R = 7.68 min; minor isomer: t_R = 8.25 min.



1p

5-methyl-2-methylene-1,1-diphenylhexan-1-ol:

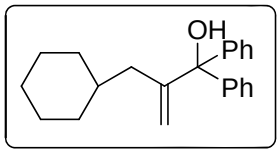
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.34-7.25 (m, 10 H), 5.15 (d, J = 0.8 Hz, 1 H), 4.79 (s, 1 H), 2.47 (s, 1 H), 2.05 (t, J = 8.2 Hz, 2 H), 1.52-1.42 (m, 1 H), 1.35-1.29 (m, 2 H), 0.81 (d, J = 6.4 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.9, 145.2, 127.8, 127.7, 127.2, 113.5, 83.6, 38.0, 29.9, 28.0, 22.6; MS (EI) *m/z* (%): 280 (M^+, 1), 209 (21), 183 (100), 160 (28), 105 (80), 77 (22).



2p

(S)-2-(bromomethyl)-5-methyl-1,2-diphenylhexan-1-one:

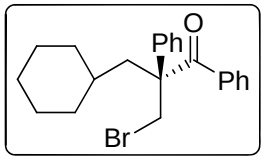
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.39-7.31 (m, 8 H), 7.24-7.18 (m, 2 H), 4.09 (d, J = 10.8 Hz, 1 H), 3.94 (dd, J = 10.8 Hz, 1.2 Hz, 1 H), 2.48 (td, J = 13.2 Hz, 4.8 Hz, 1 H), 2.19 (td, J = 13.6 Hz, 3.2 Hz, 1 H), 1.44-1.36 (m, 1 H), 1.17-1.08 (m, 1 H), 0.83-0.74 (m, 1 H), 0.80 (d, J = 6.8 Hz, 3 H), 0.66 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 202.0, 140.4, 136.5, 132.0, 129.2, 129.0, 128.0, 127.7, 126.8, 58.2, 41.3, 32.2, 30.7, 28.1, 22.4, 22.0; MS (EI) *m/z* (%): 174 (12), 118 (100), 105 (66), 77 (21); Enantiomeric excess is 45% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 4.18 min; major isomer: t_R = 8.69 min.



1q

2-(cyclohexylmethyl)-1,1-diphenylprop-2-en-1-ol:

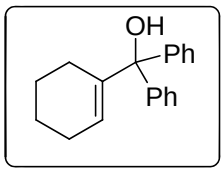
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.35-7.25 (m, 10 H), 5.13 (d, J = 0.8 Hz, 1 H), 4.79 (s, 1 H), 2.42 (s, 1 H), 1.96 (d, J = 6.8 Hz, 2 H), 1.75-1.60 (m, 5 H), 1.46-1.36 (m, 1 H), 1.22-1.03 (m, 3 H), 0.83-0.74 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 151.3, 145.3, 127.8, 127.2, 114.9, 83.6, 40.1, 36.5, 33.4, 26.6, 26.4; MS (EI) *m/z* (%): 306 (M^+, 2), 209 (15), 186 (21), 183 (100), 105 (58), 77 (16).



2q

(S)-3-bromo-2-(cyclohexylmethyl)-1,2-diphenylpropan-1-one:

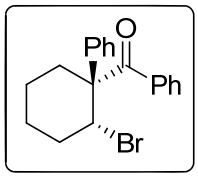
^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.40-7.18 (m, 10 H), 4.11 (d, J = 10.4 Hz, 1 H), 4.03 (dd, J = 10.8 Hz, 1.2 Hz, 1 H), 2.46 (dd, J = 14.4 Hz, 5.2 Hz, 1 H), 2.17-2.12 (dd, J = 14.4 Hz, 5.2 Hz, 1 H), 1.61-1.45 (m, 4 H), 1.15-0.93 (m, 6 H), 0.75-0.66 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 202.0, 140.8, 136.7, 131.9, 129.5, 128.9, 128.0, 127.7, 126.8, 58.5, 42.1, 39.9, 35.2, 34.5, 33.7, 26.2, 26.3, 26.0; MS (EI) *m/z* (%): 200 (18), 183 (14), 118 (100), 105 (74), 77(21); Enantiomeric excess is 55% determined by HPLC (Chiralcel AD, Hexane/Isopropanol 99/1, flow rate = 1.0 mL/min, 254 nm): major isomer: t_R = 6.91 min; minor isomer: t_R = 7.53 min.



1r

Cyclohexenyldiphenylmethanol:

^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.33-7.23 (m, 10 H), 5.35 (t, J = 3.6 Hz, 1 H), 2.49 (s, 1 H), 2.09-2.06 (m, 2 H), 1.99-1.98 (m, 2 H), 1.66-1.55 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 145.5, 141.8, 127.8, 127.7, 127.0, 126.6, 83.1, 25.6, 25.3, 22.9, 22.2; MS (EI) *m/z* (%): 264 (M^+, 21), 246 (11), 183 (35), 105 (100), 77 (28);



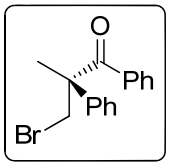
2r

((1S,2R)-2-bromo-1-phenylcyclohexyl)(phenyl)methanone:

^{1}HNMR (400 MHz, $CDCl_3$, ppm): δ 7.48-7.19 (m, 10 H), 5.30 (s, 1 H), 2.55-2.43 (m, 2 H), 2.38-2.29 (m, 1 H), 2.20-2.16 (m, 1 H), 1.89-1.78 (m, 1 H), 1.59-1.48 (m, 2 H), 1.29-1.19 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.6, 138.3, 138.2, 130.8, 128.9, 128.4, 128.2, 127.8, 127.4, 59.5, 57.9, 31.7, 30.7, 21.5, 20.9; MS (EI) *m/z* (%): 158 (100), 143 (27), 130 (24), 105 (21), 77

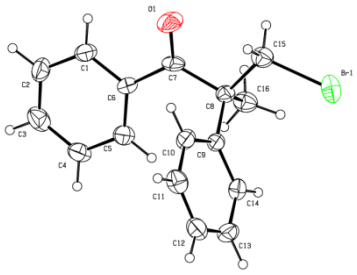
(19); Enantiomeric excess is 57% determined by HPLC (Chiralcel OJ, Hexane/Isopropanol 90/10, flow rate = 1.0 mL/min, 254 nm): minor isomer: t_R = 11.65 min; major isomer: t_R = 17.62 min.

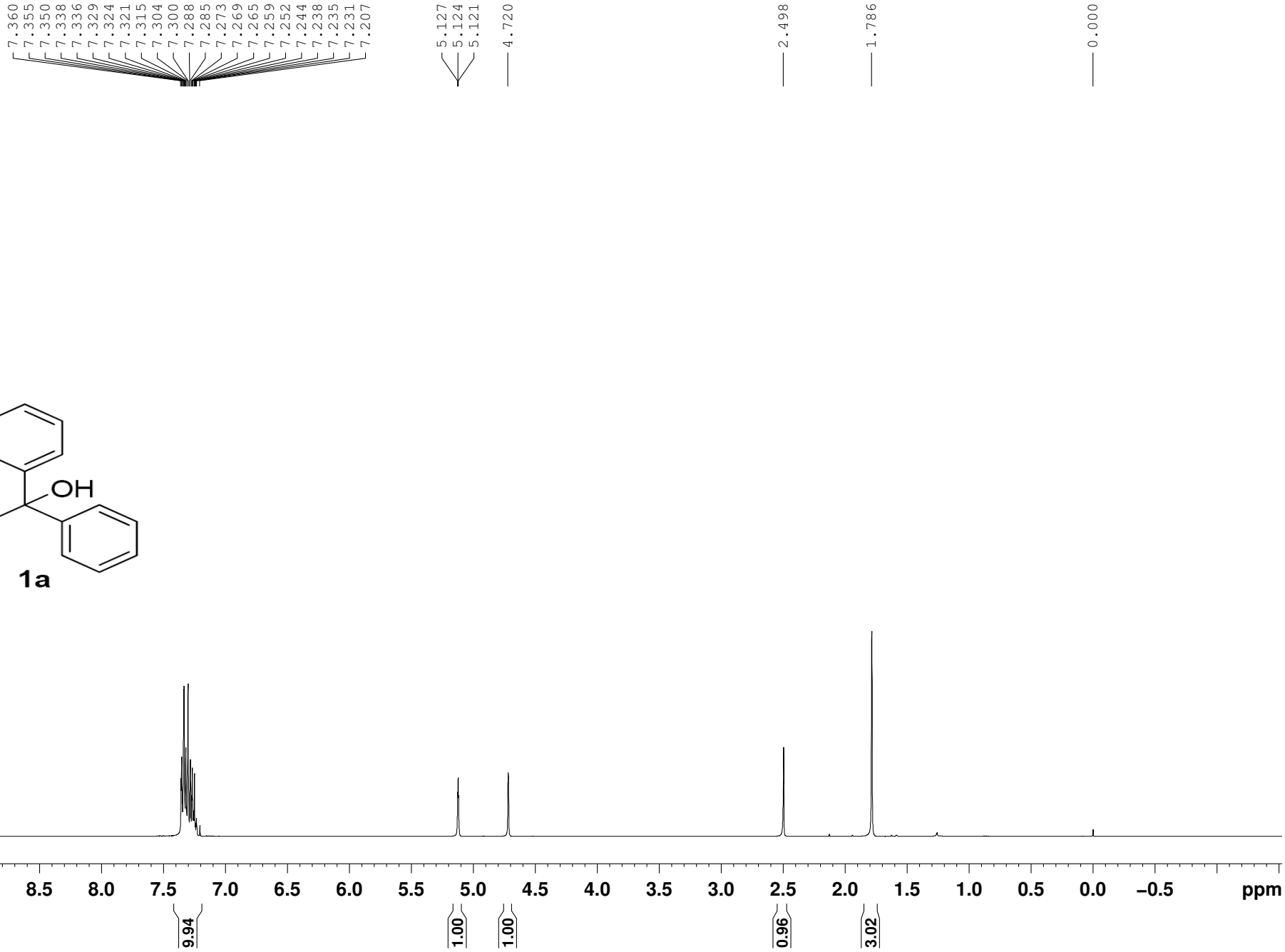
X-Ray Ellipsoid Plots of 2a

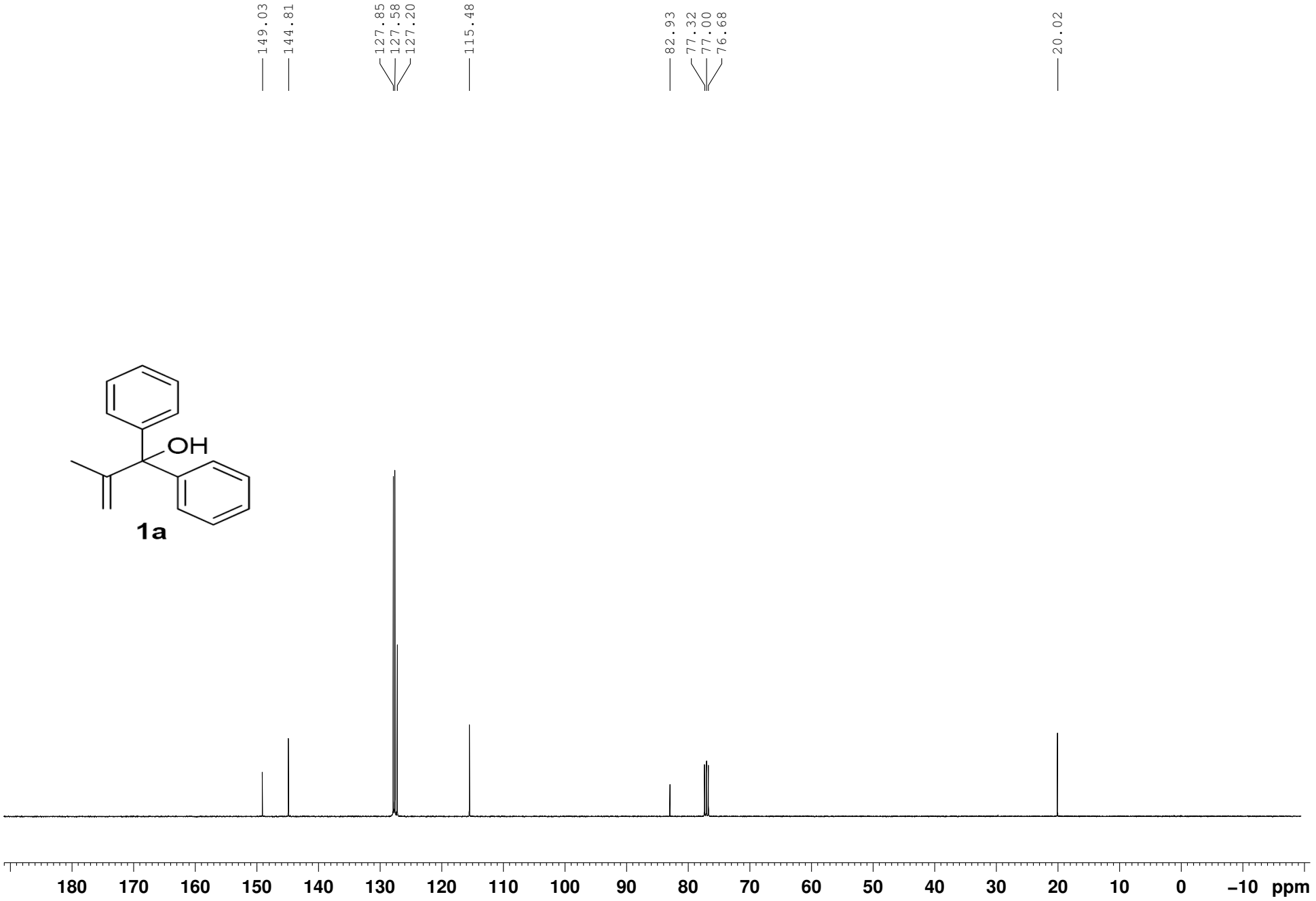


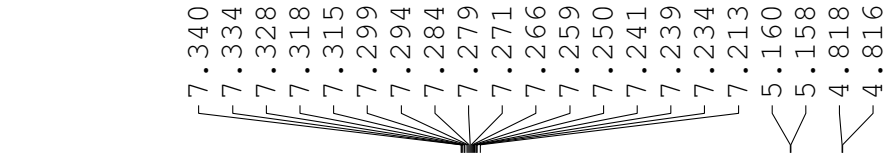
2a

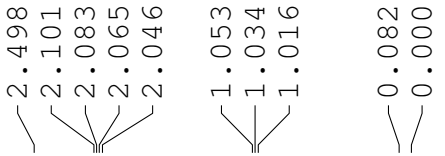
The structure of compound **2a** was corroborated by single-crystal. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: 821778.

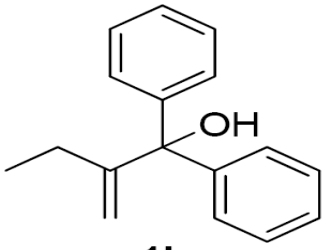




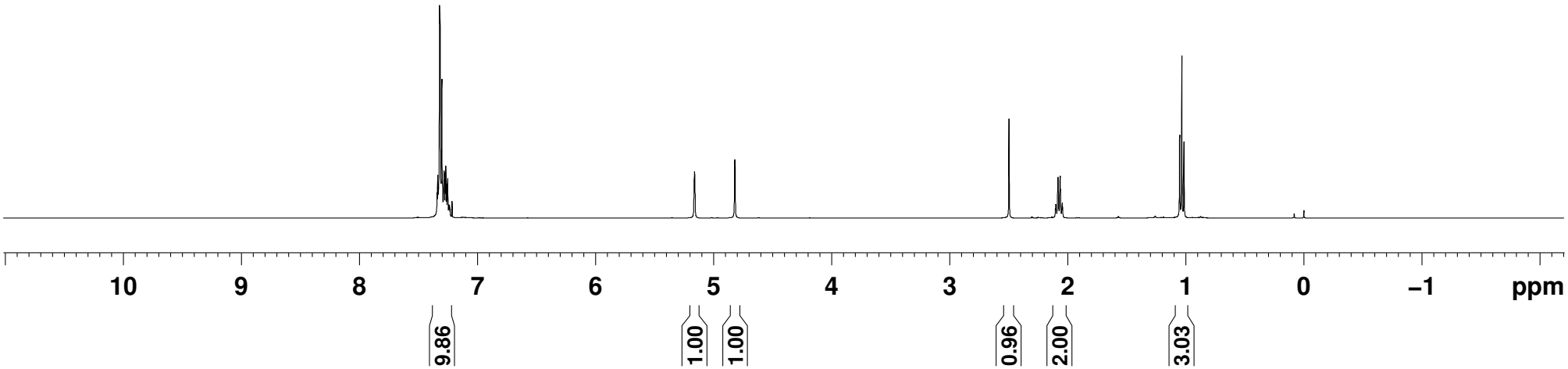


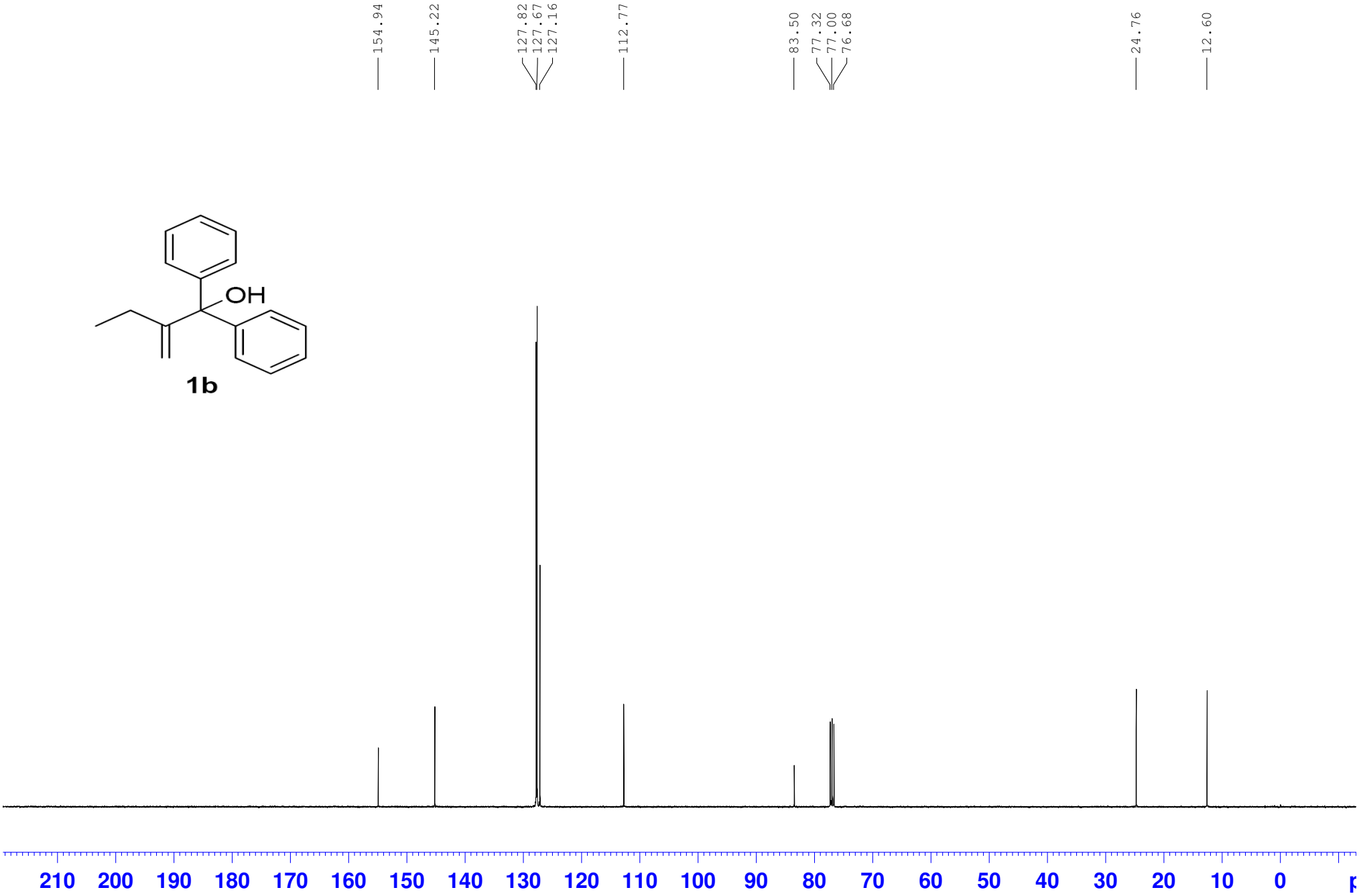


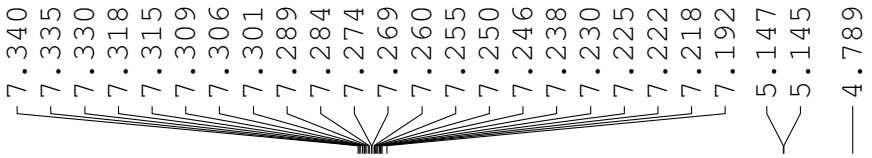


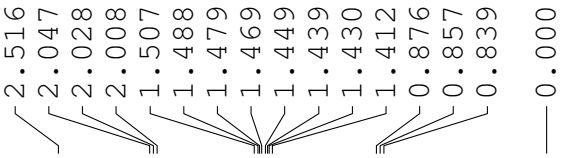


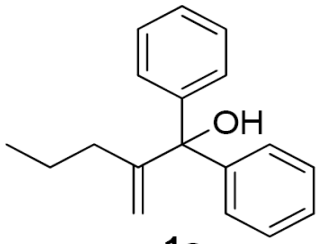
1b



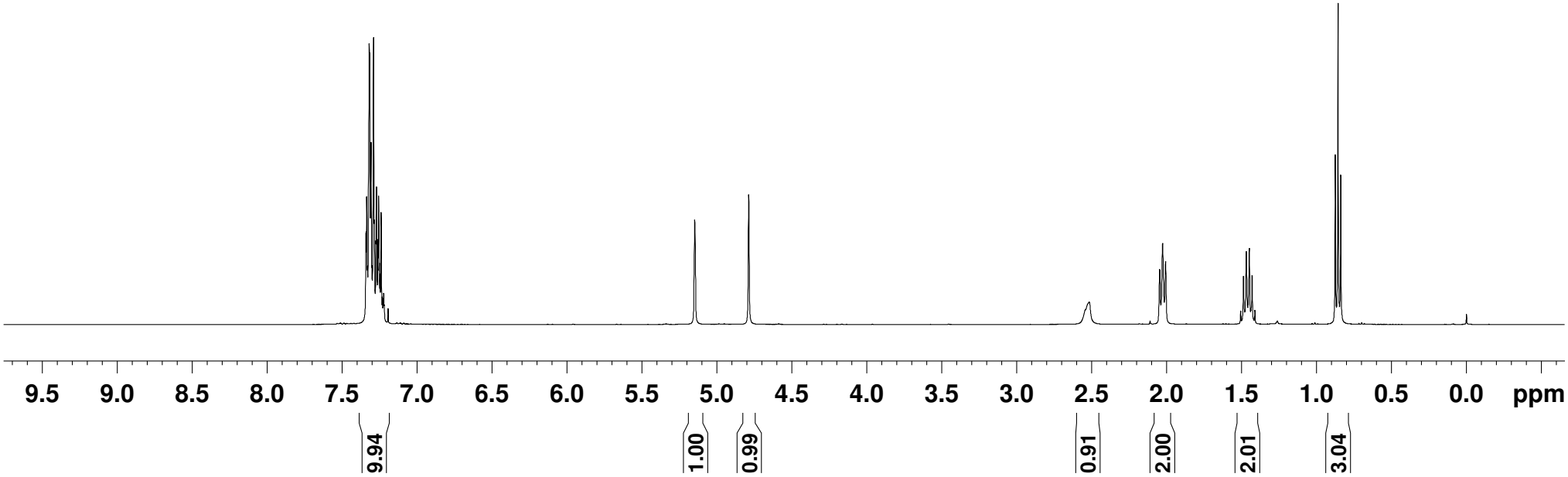


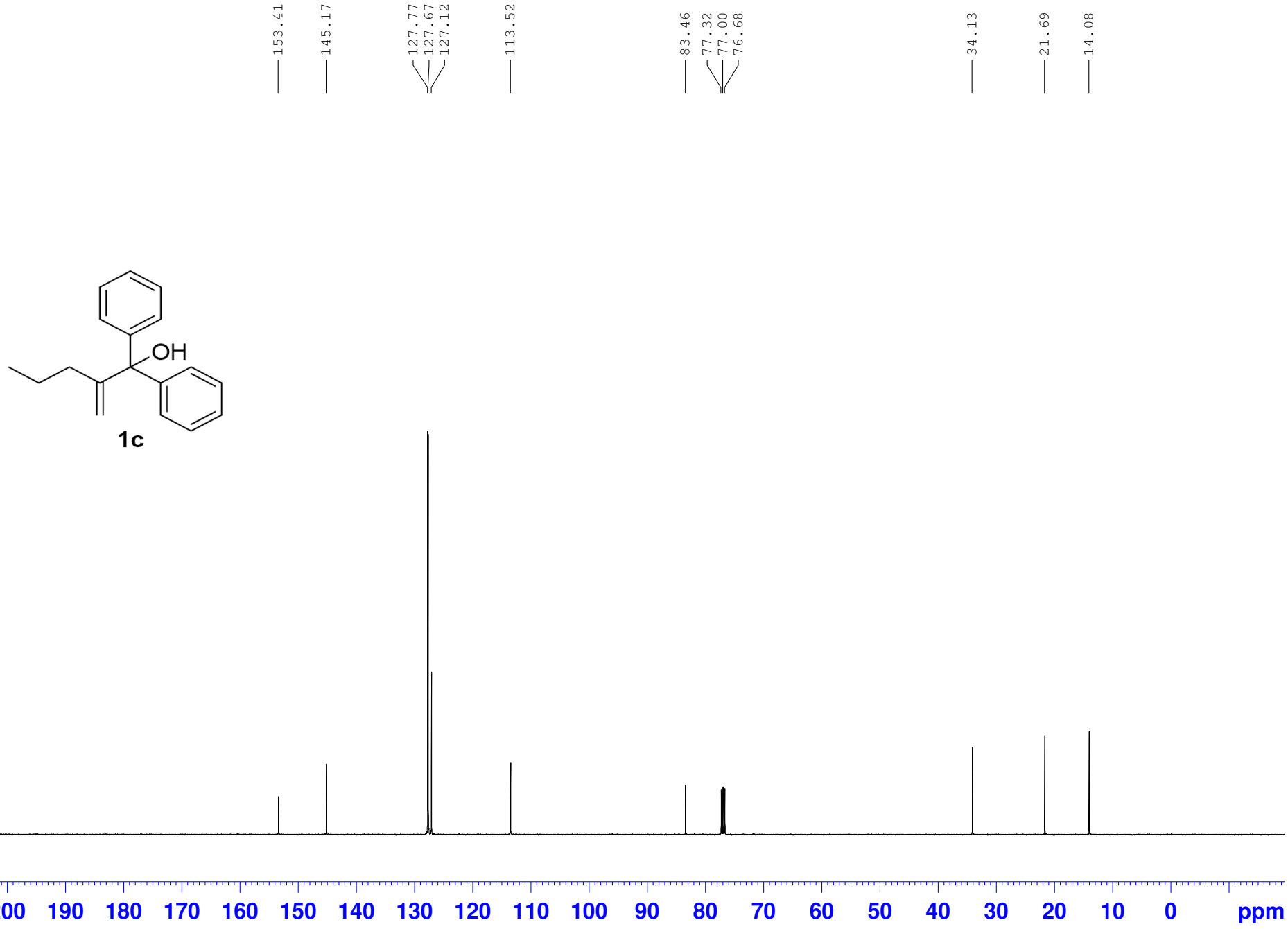


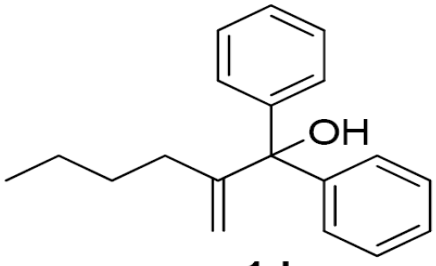




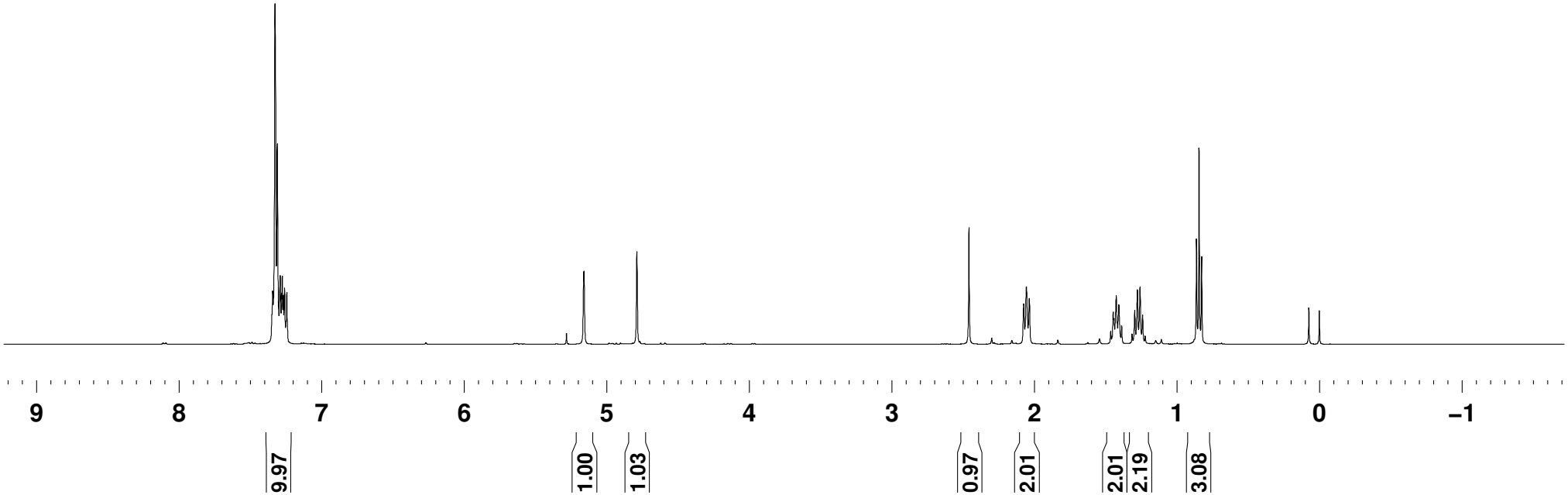
1c

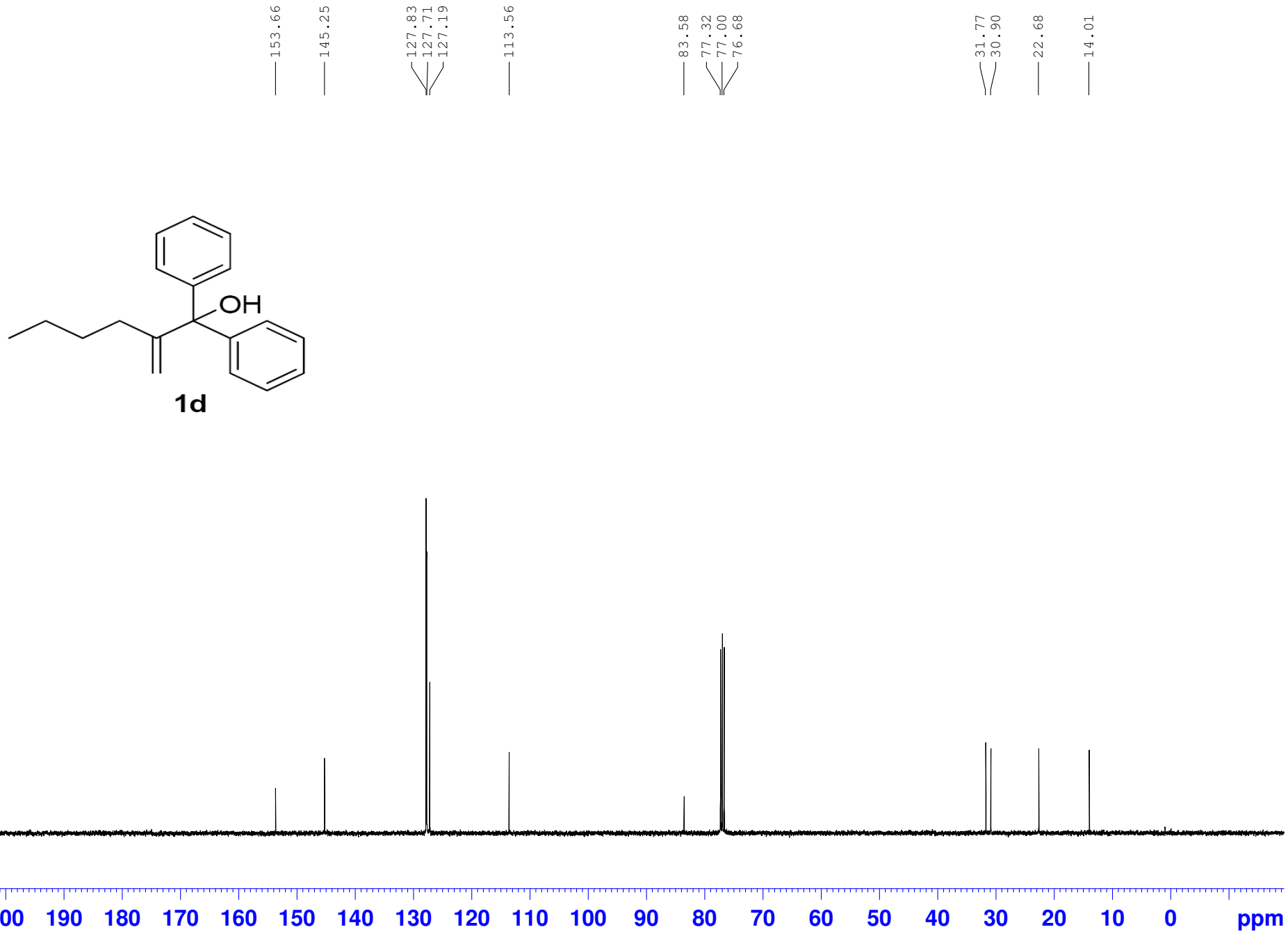


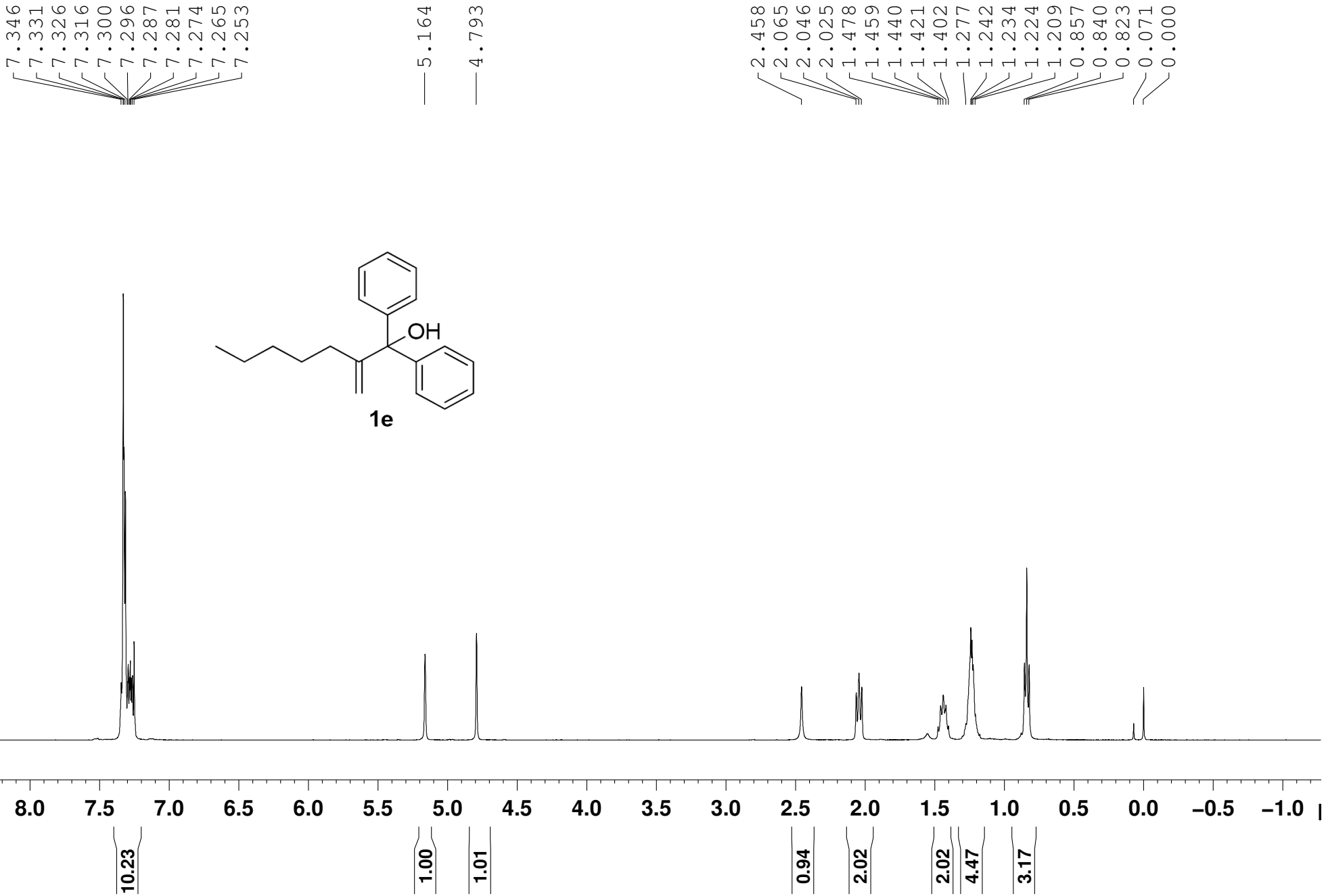


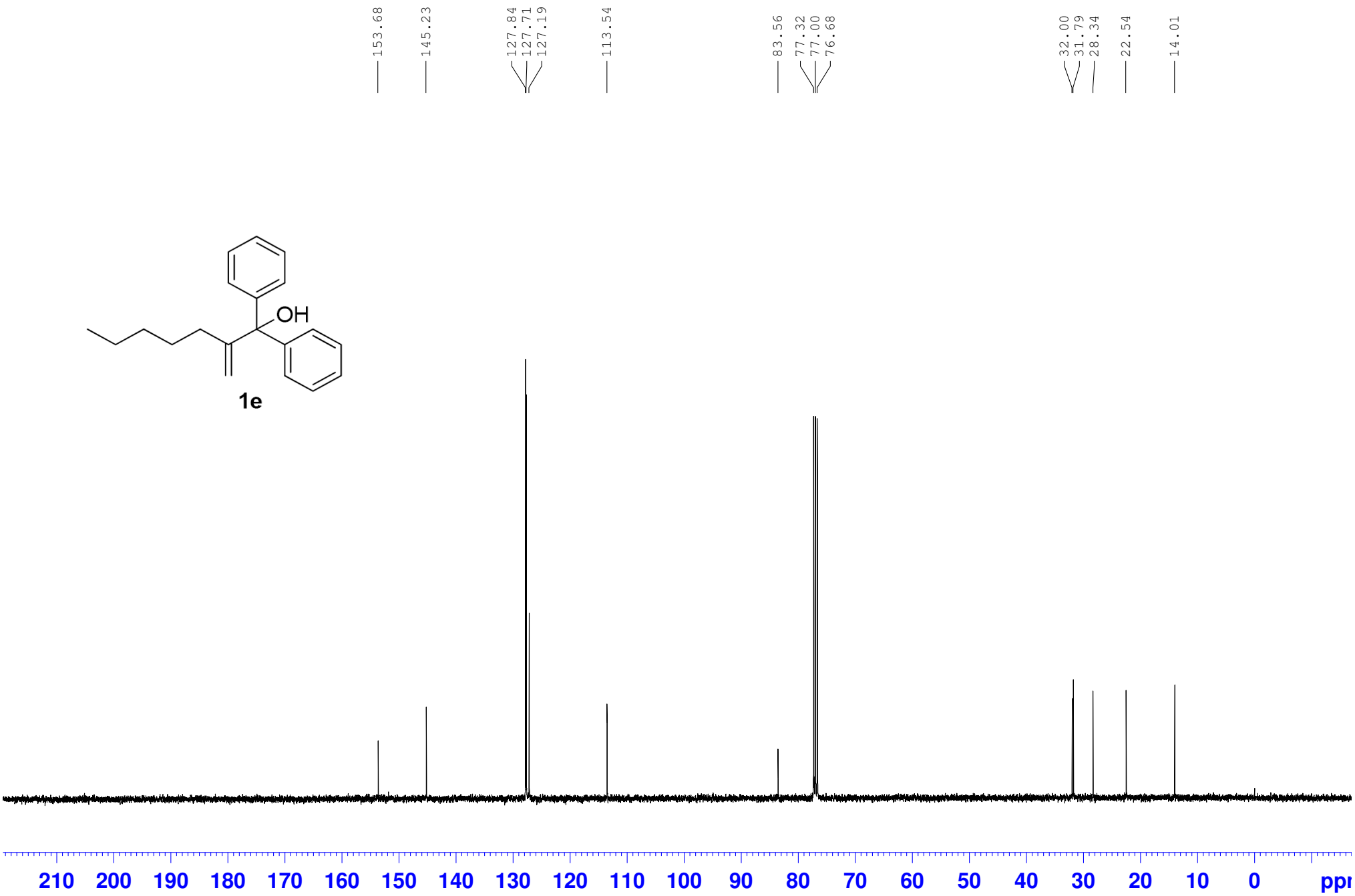


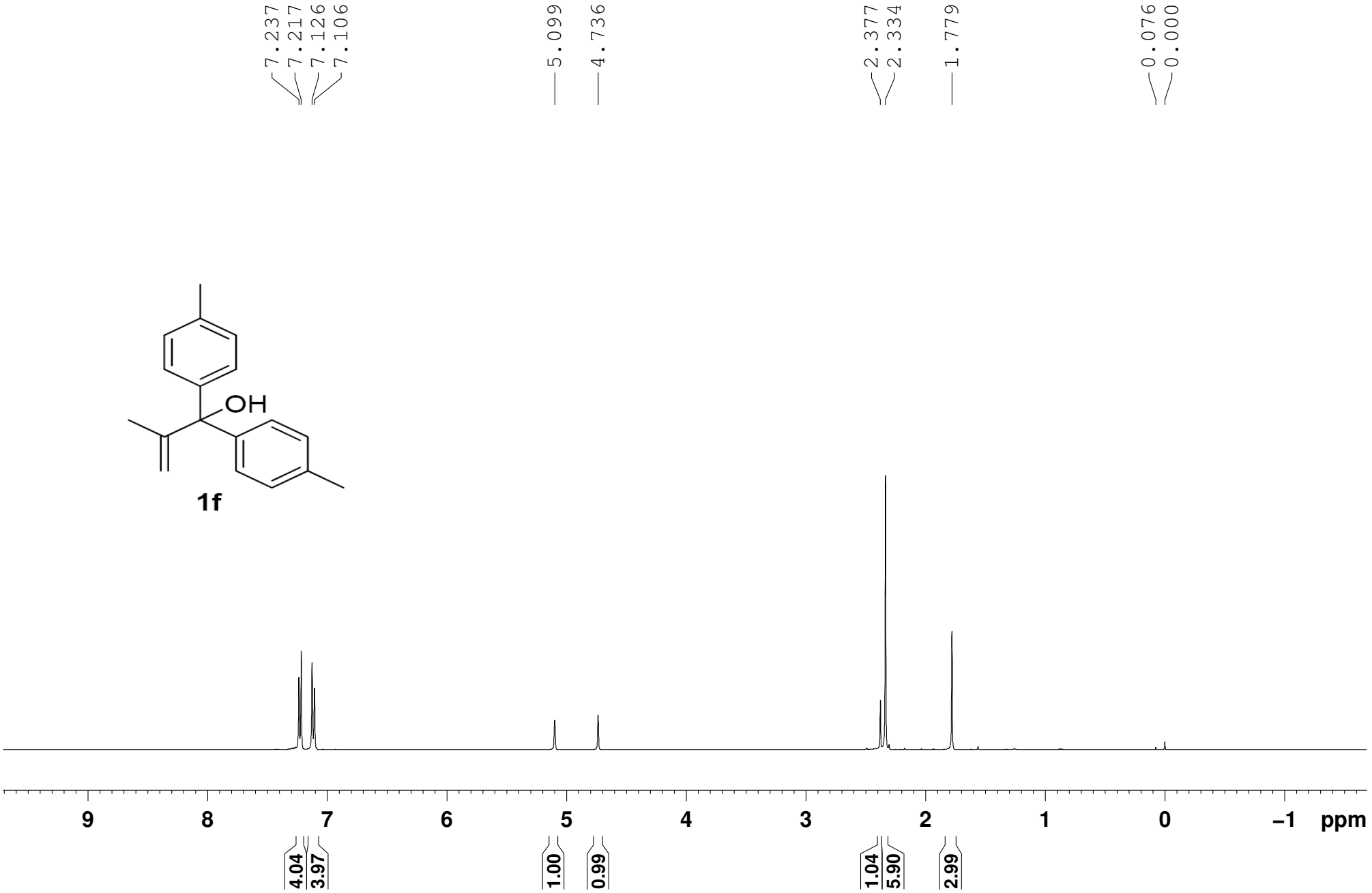
1d

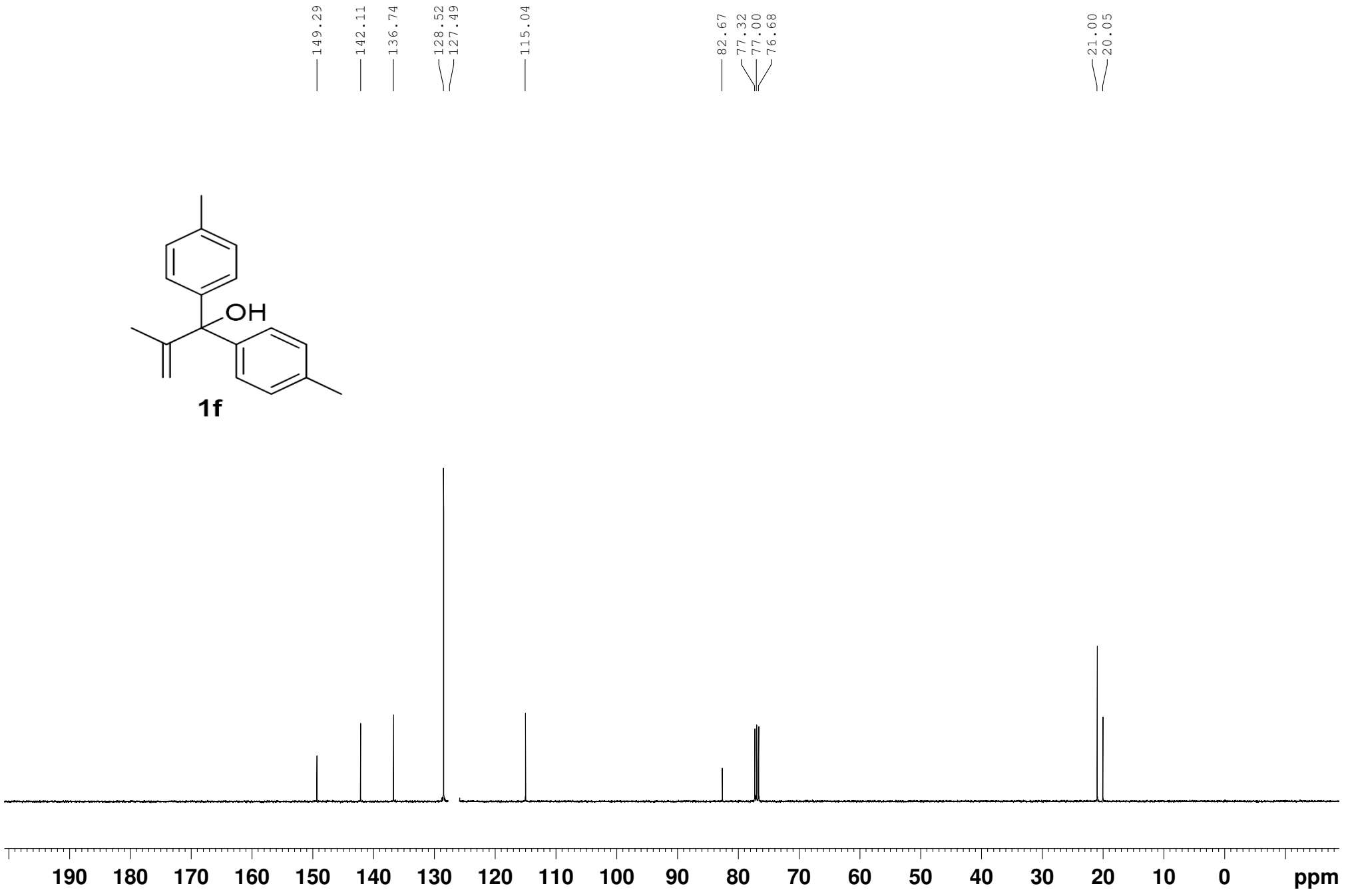


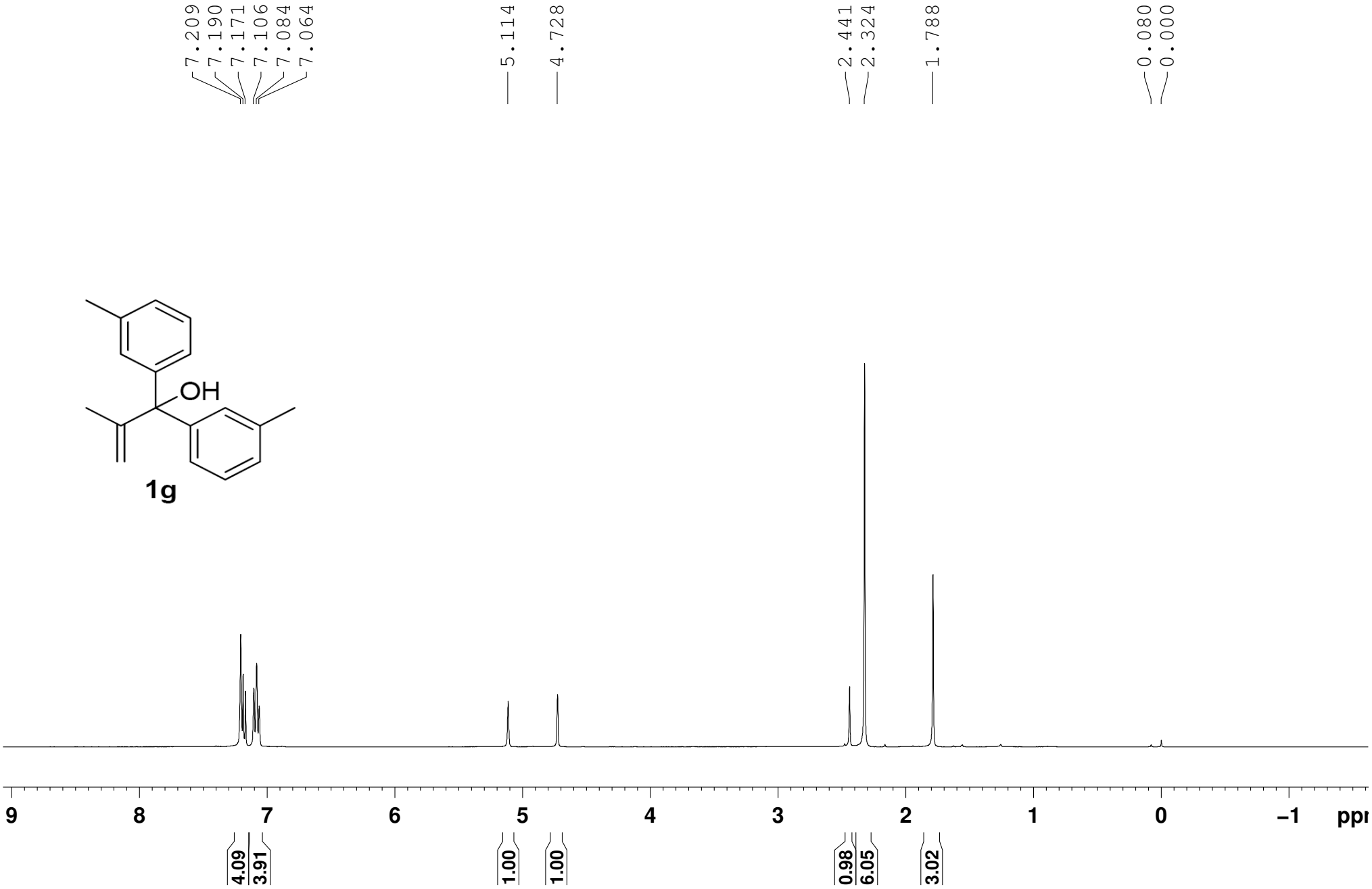


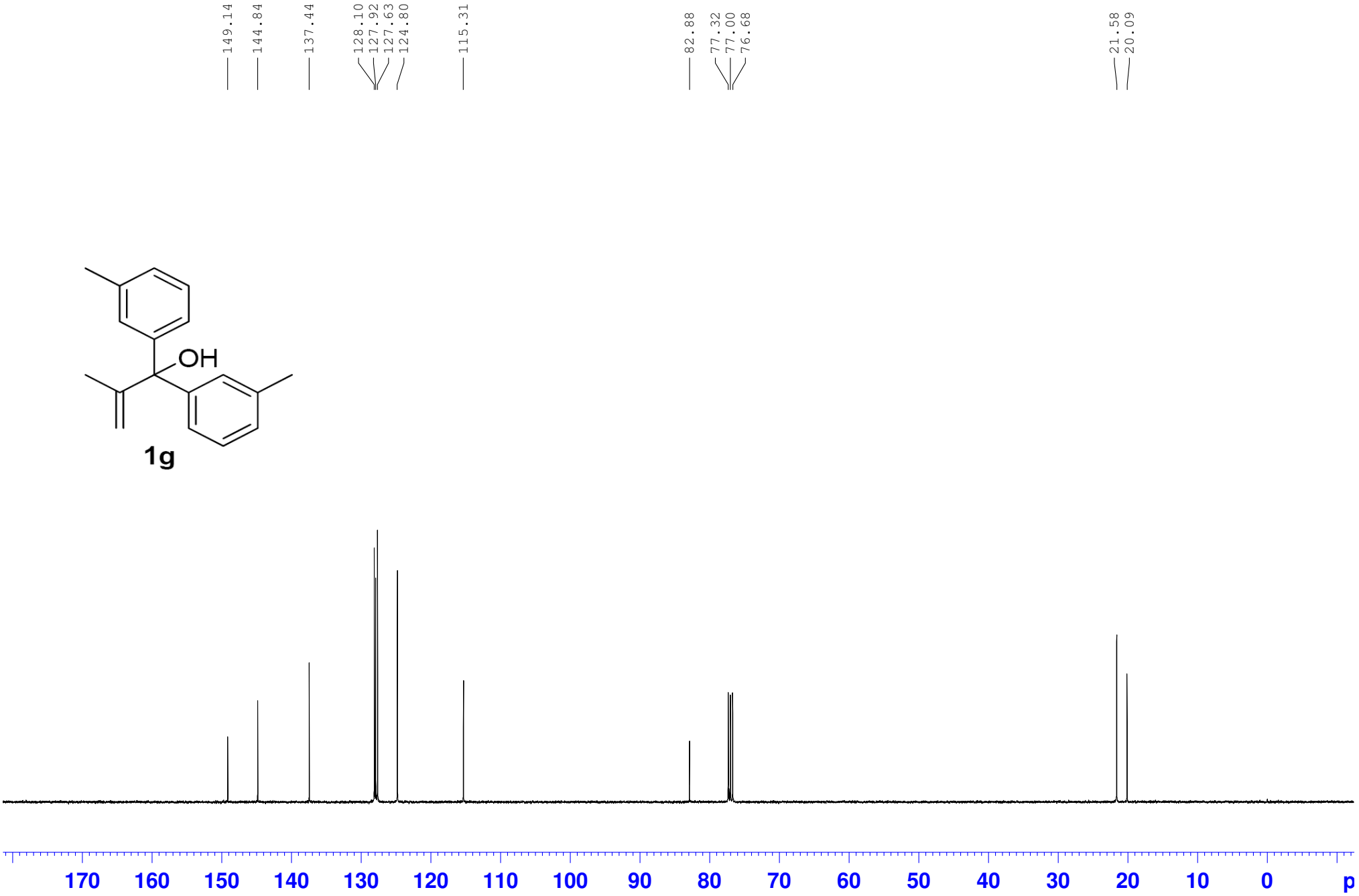


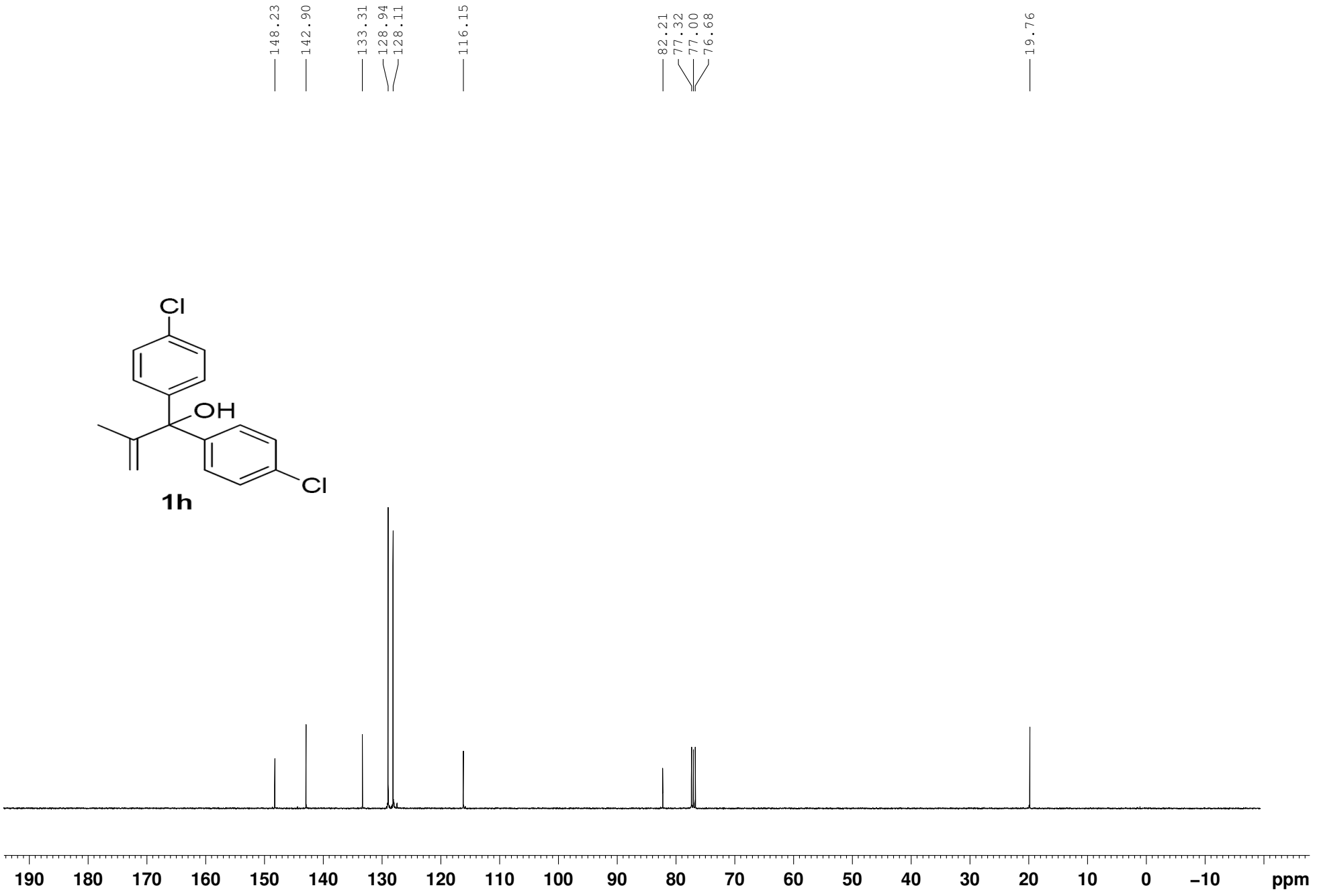


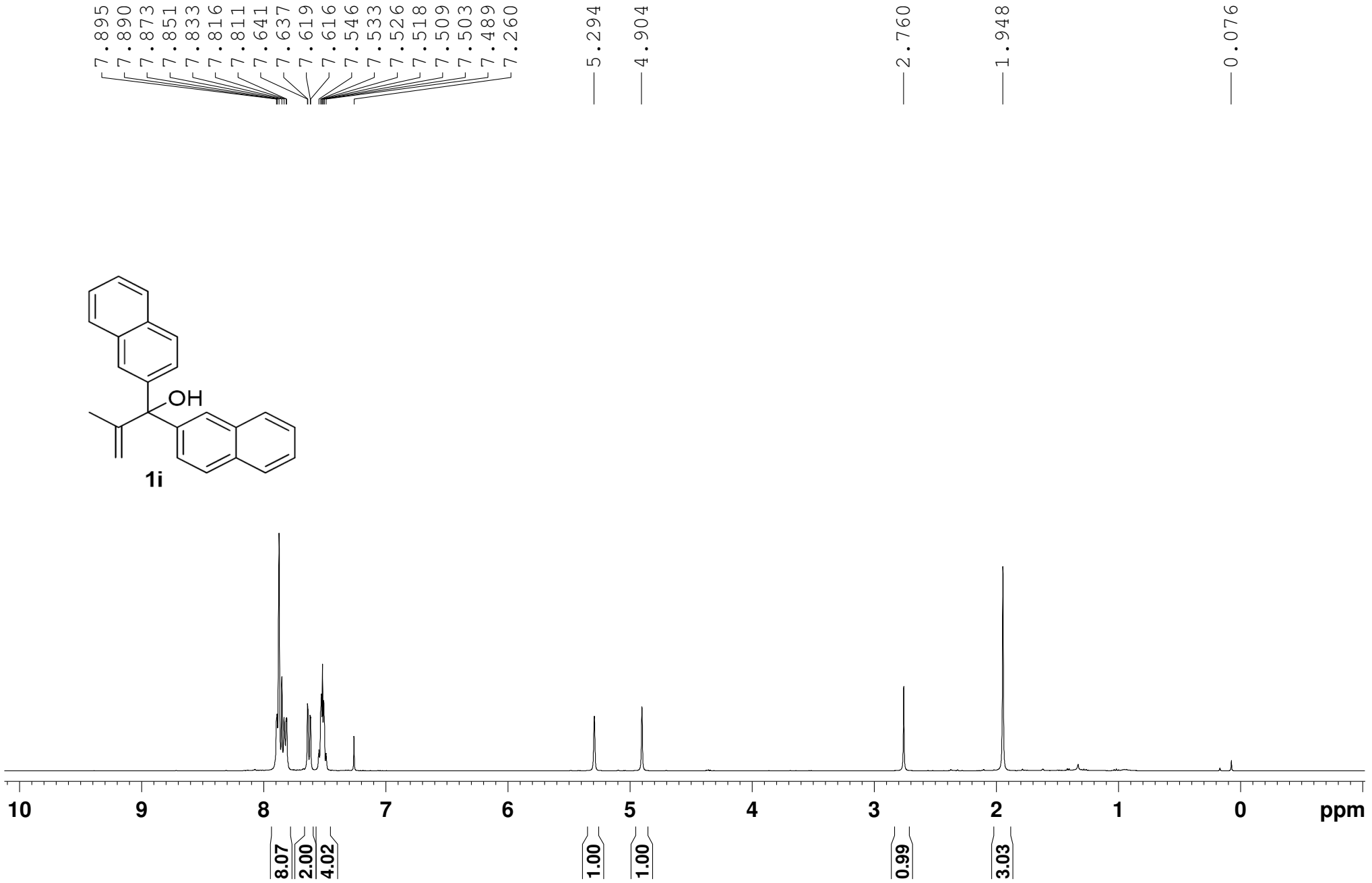


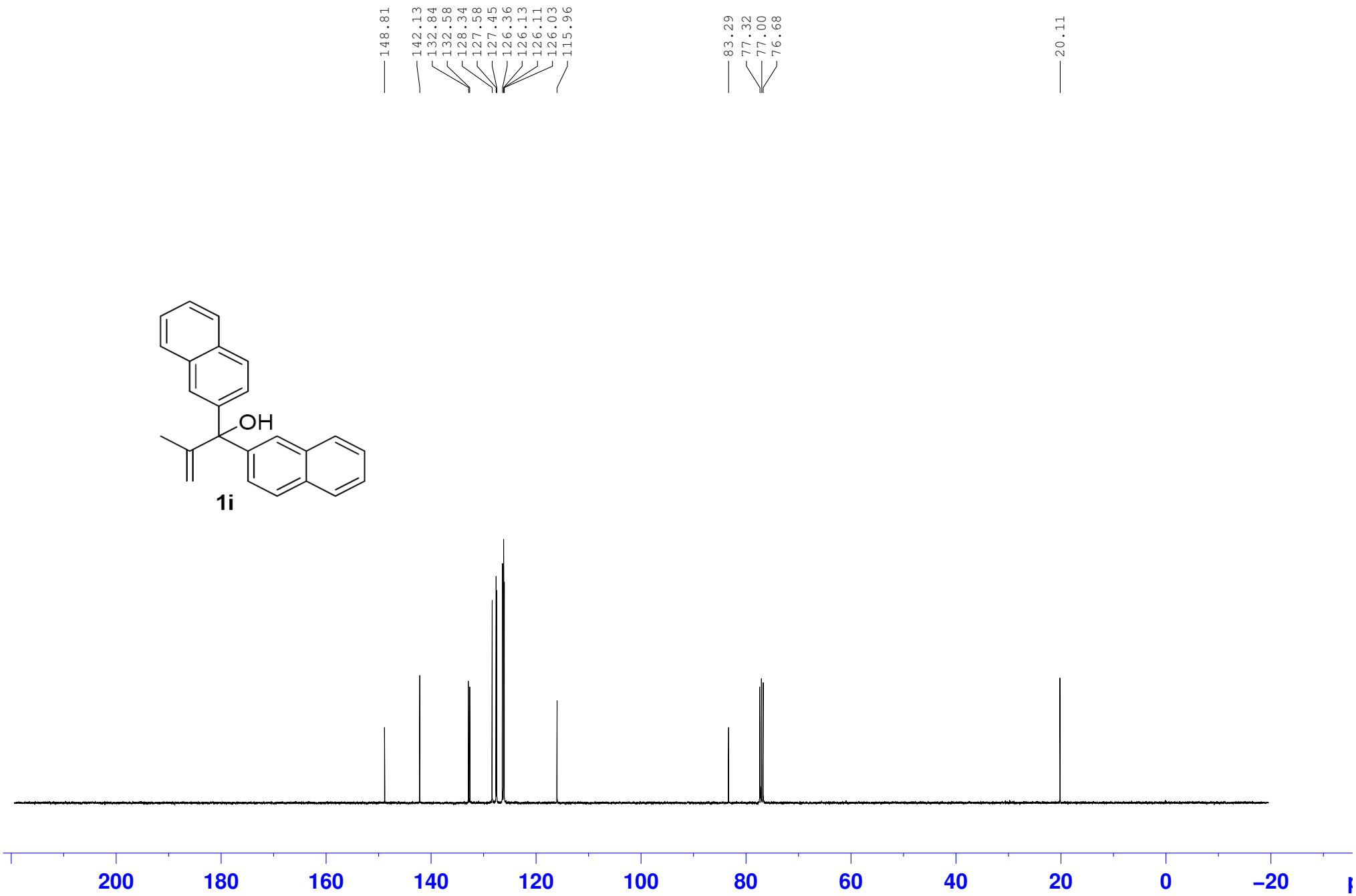


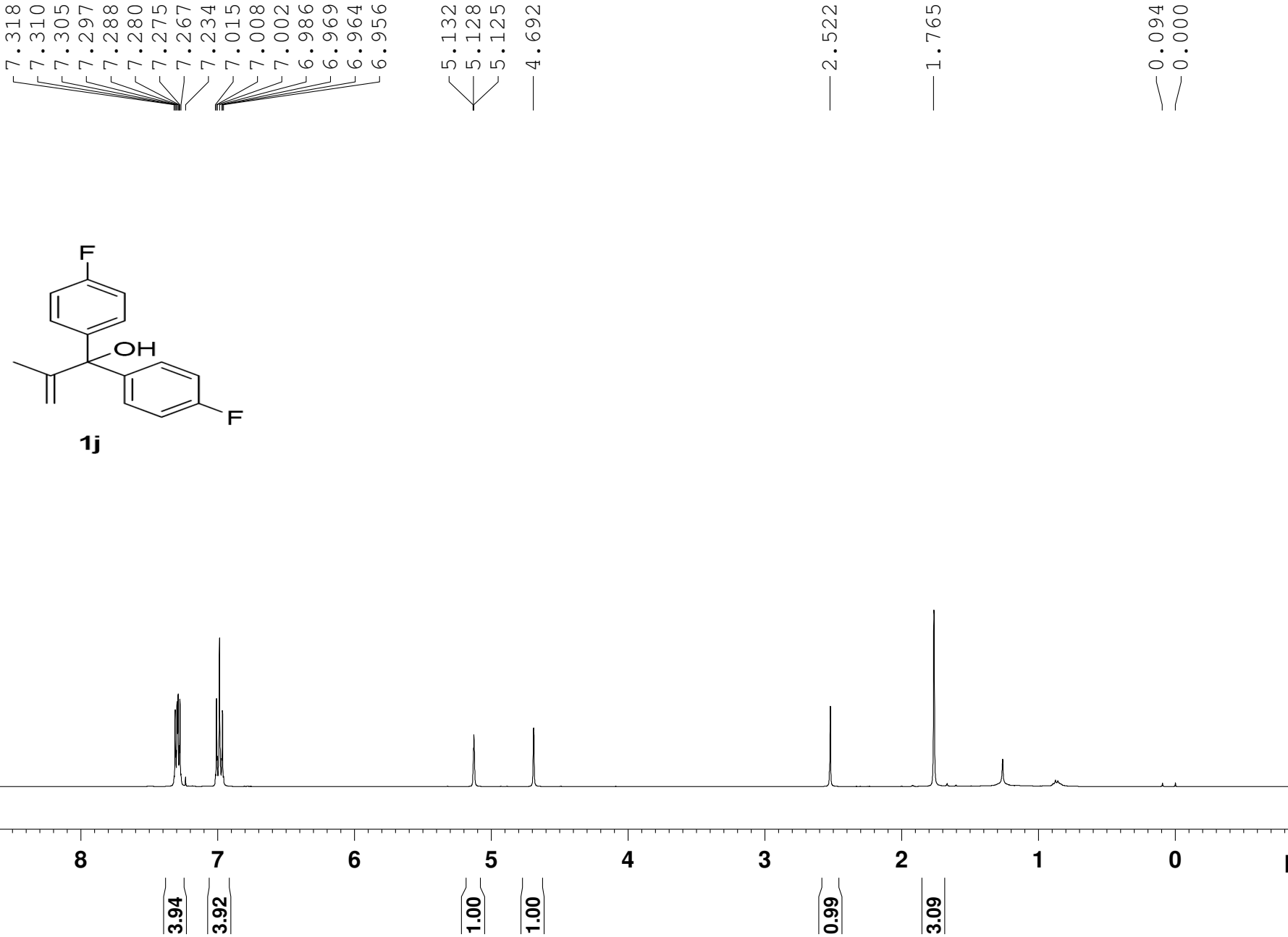


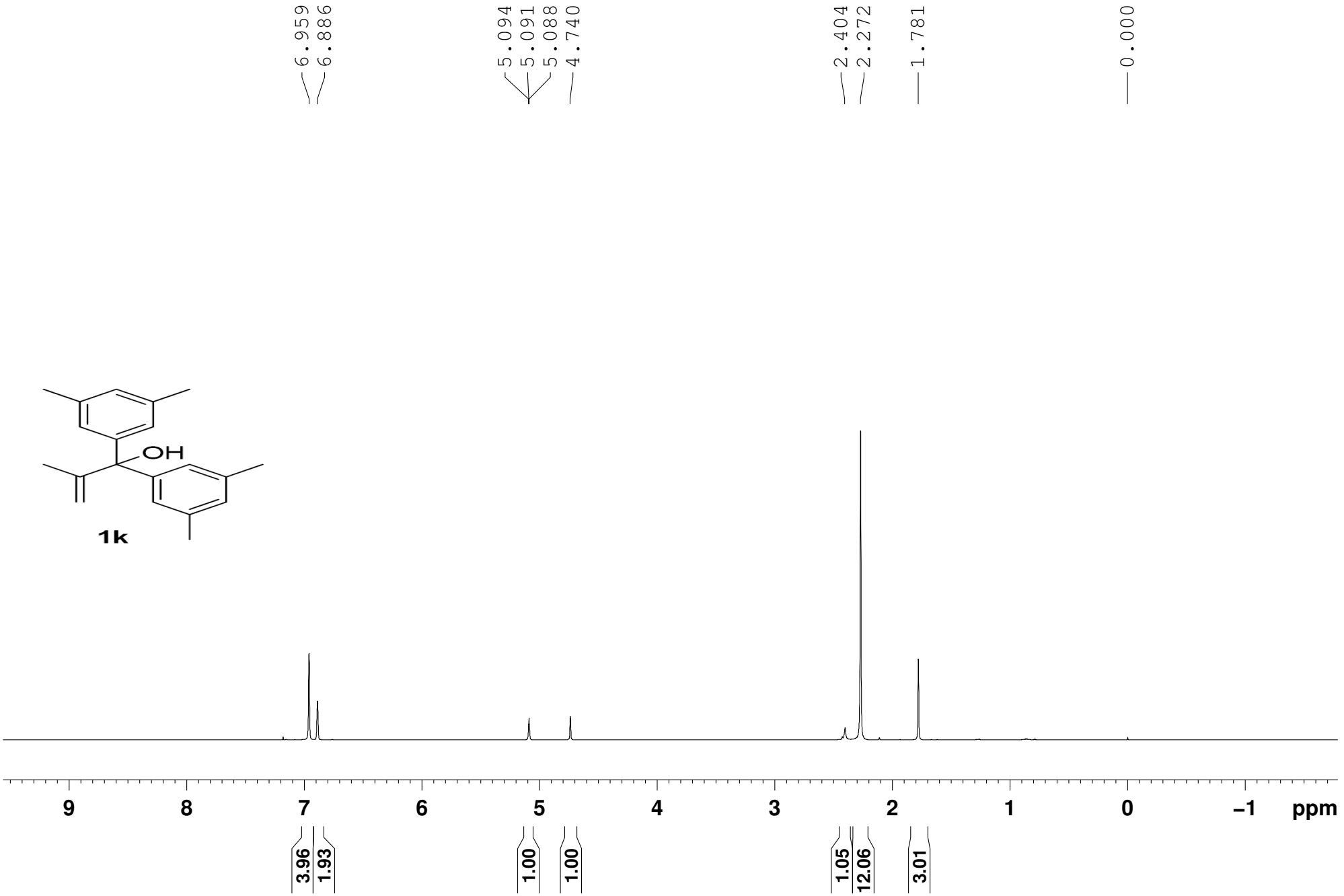


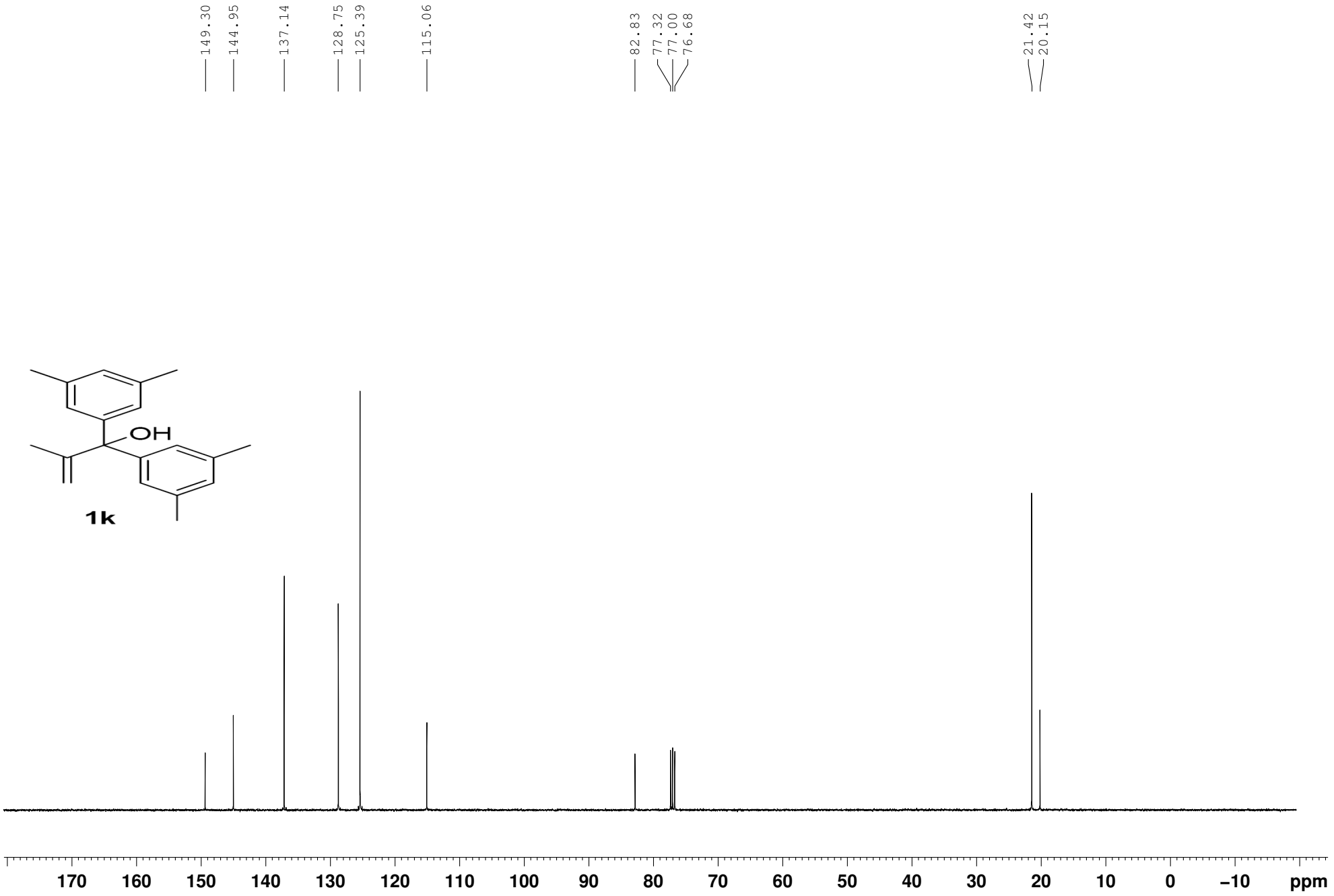


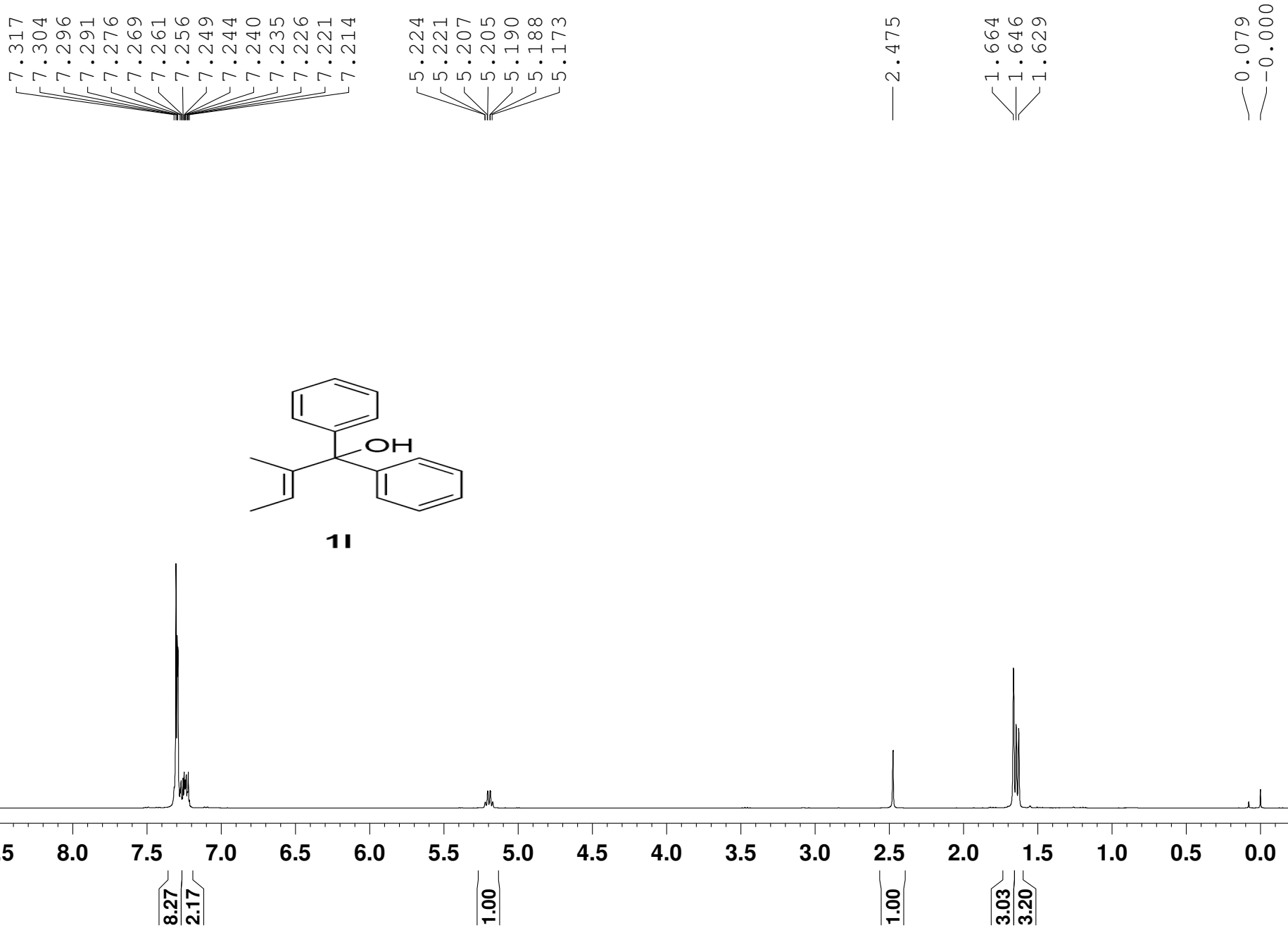


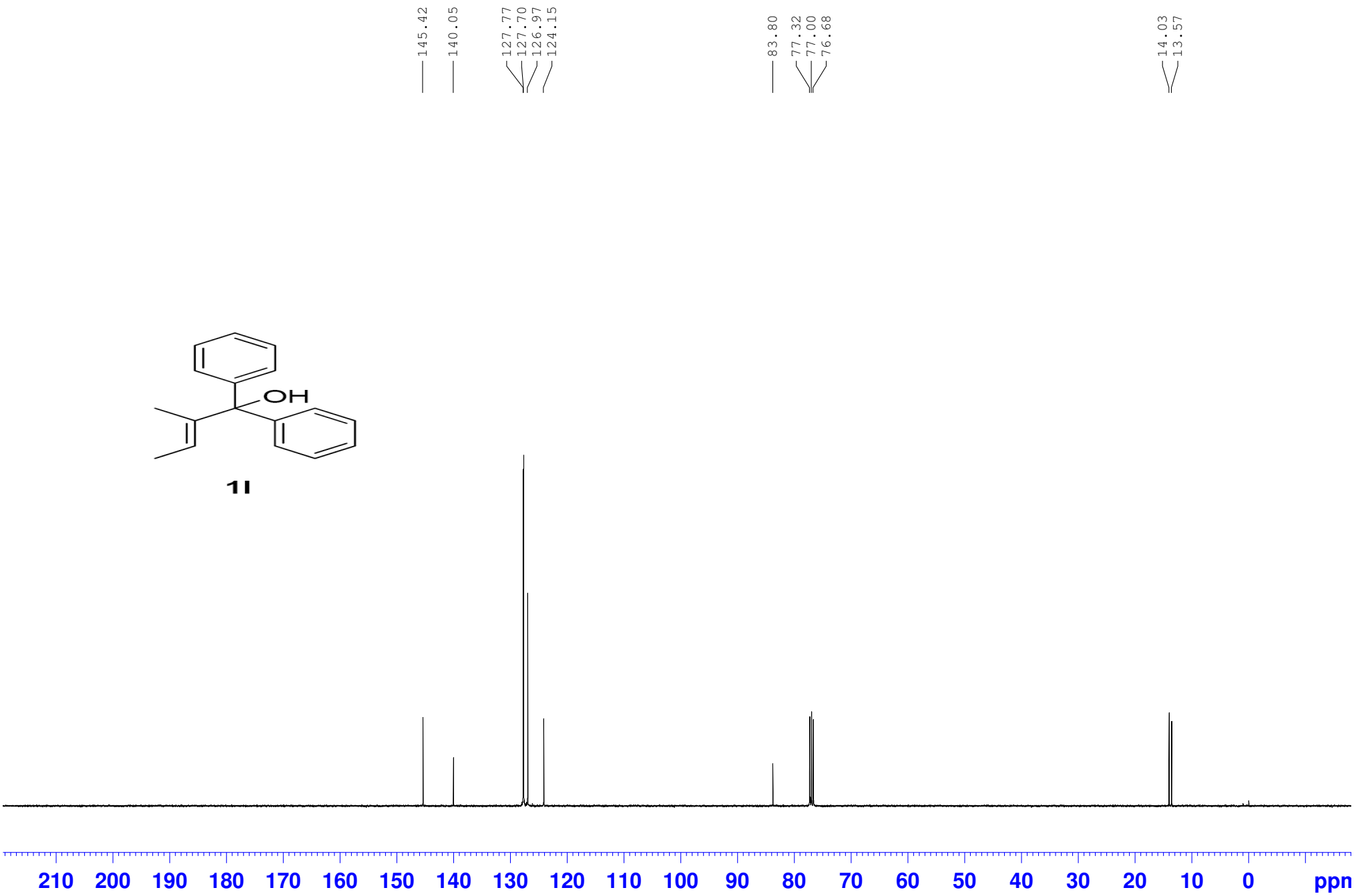












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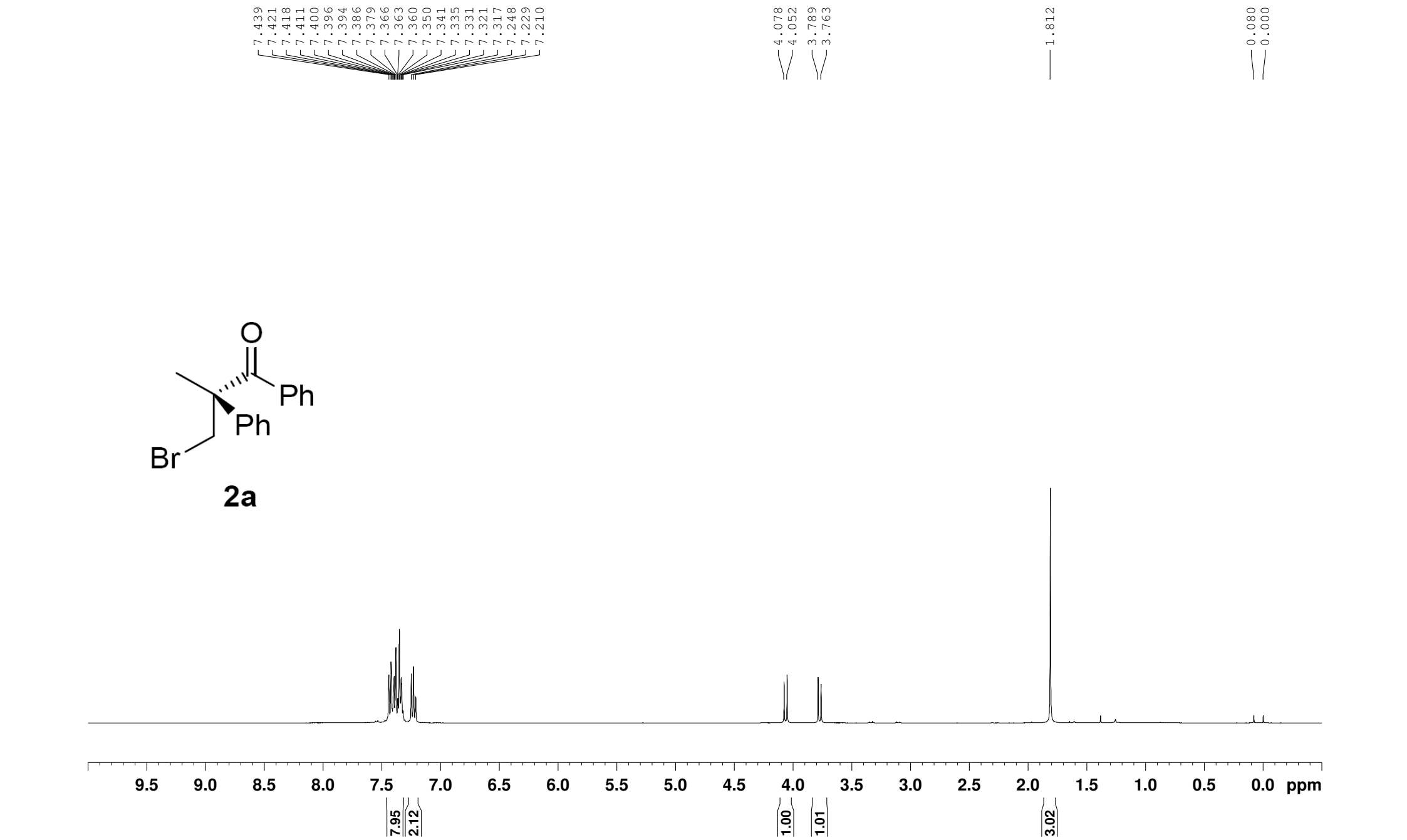

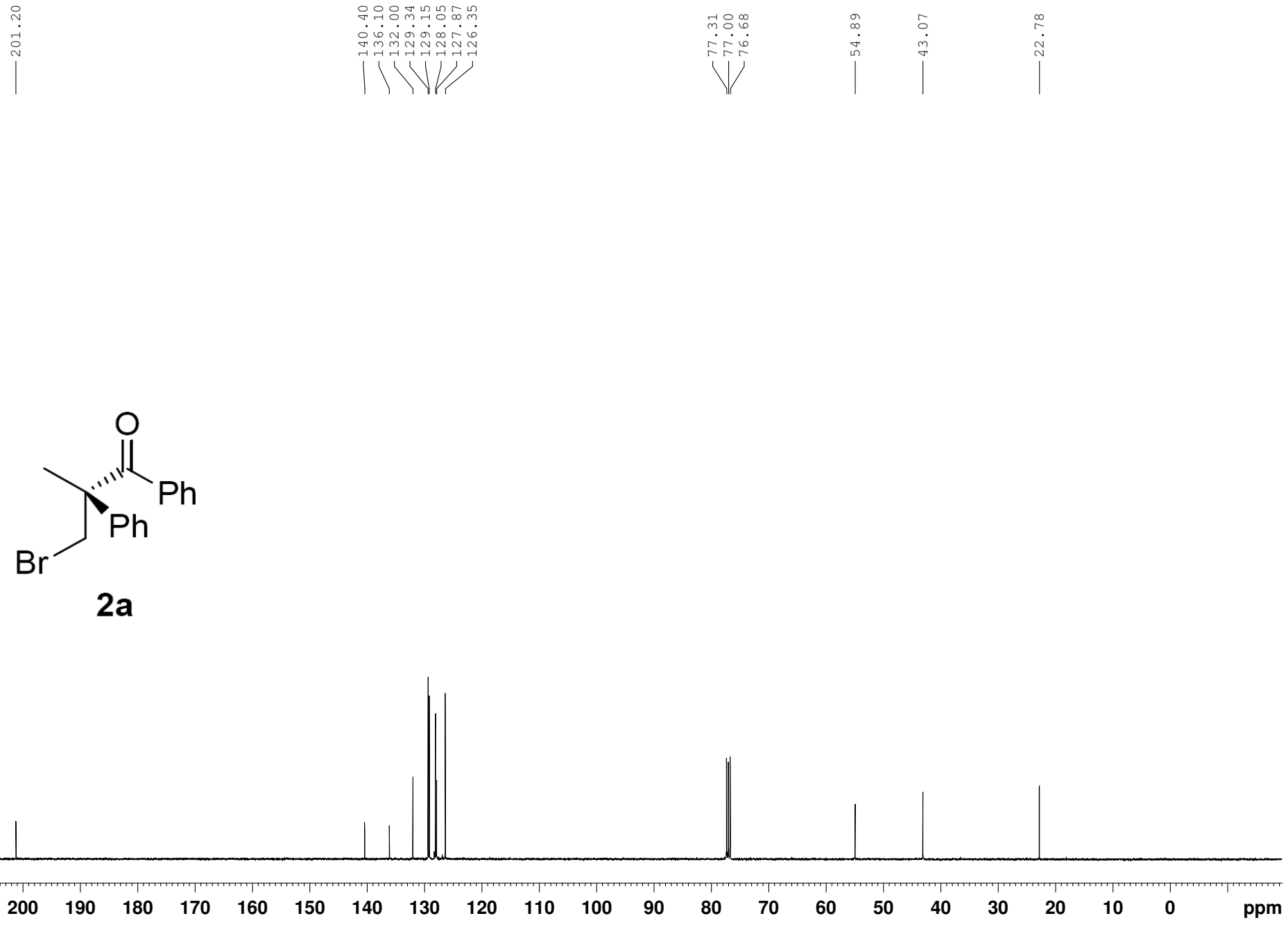

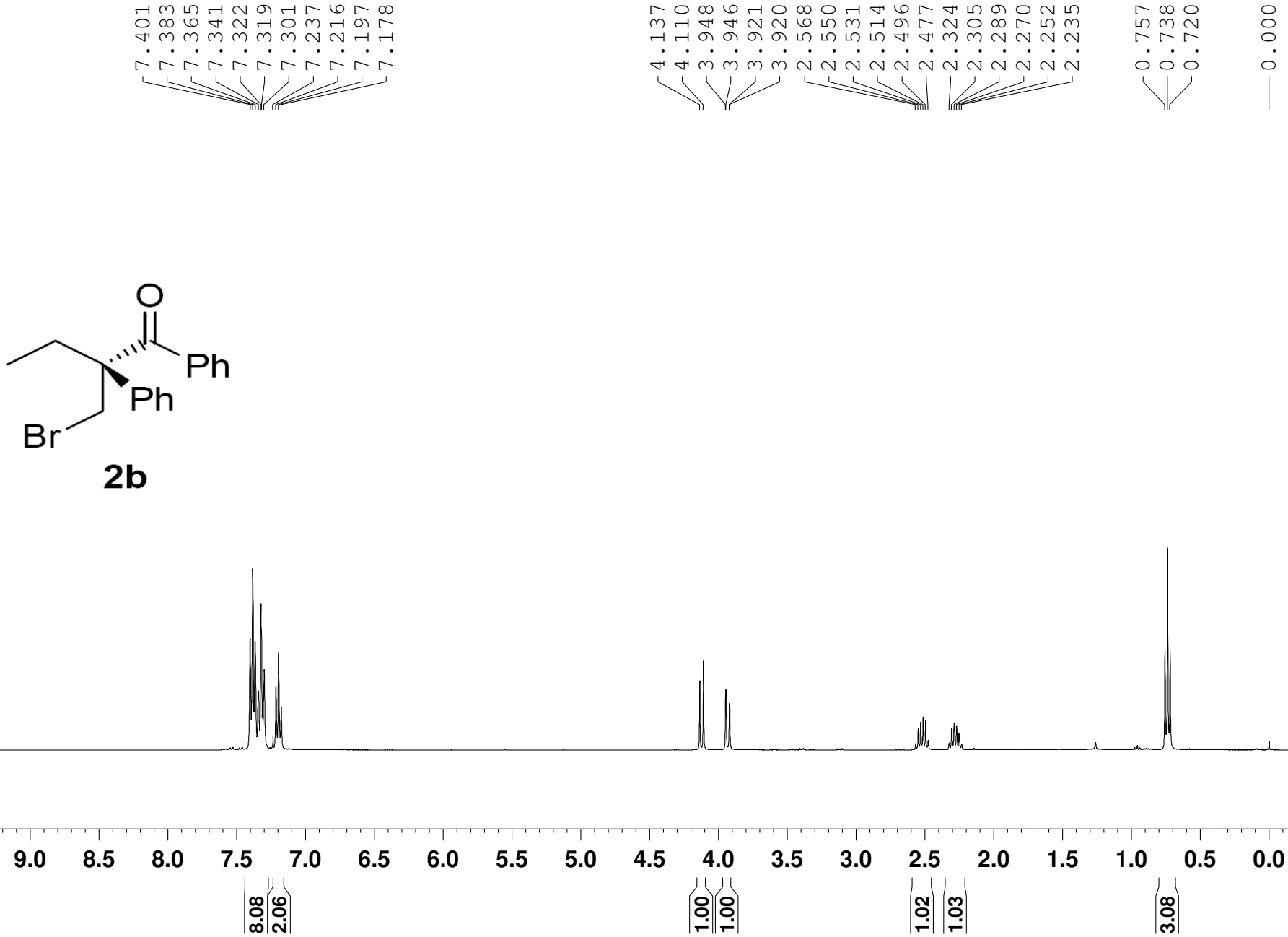

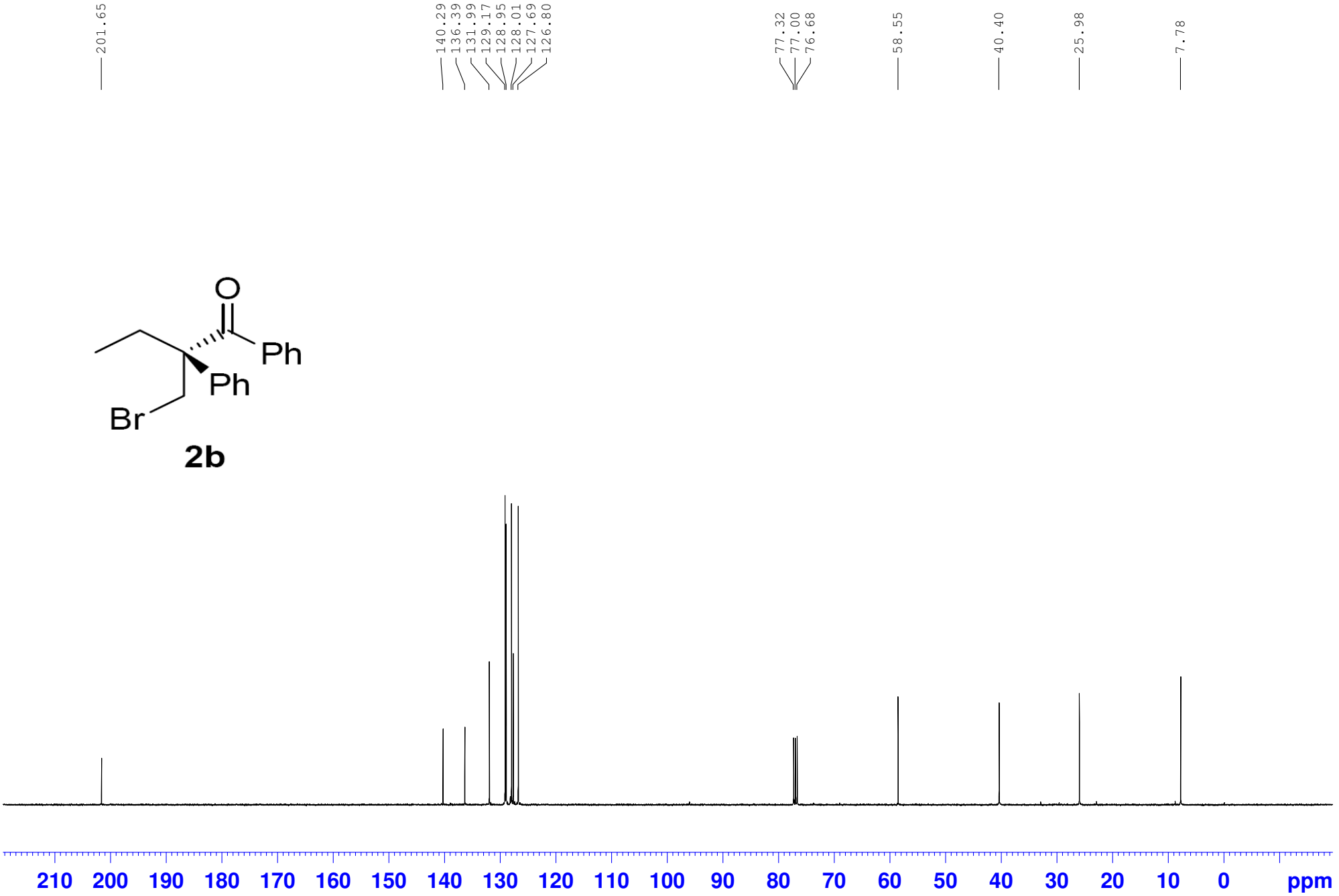

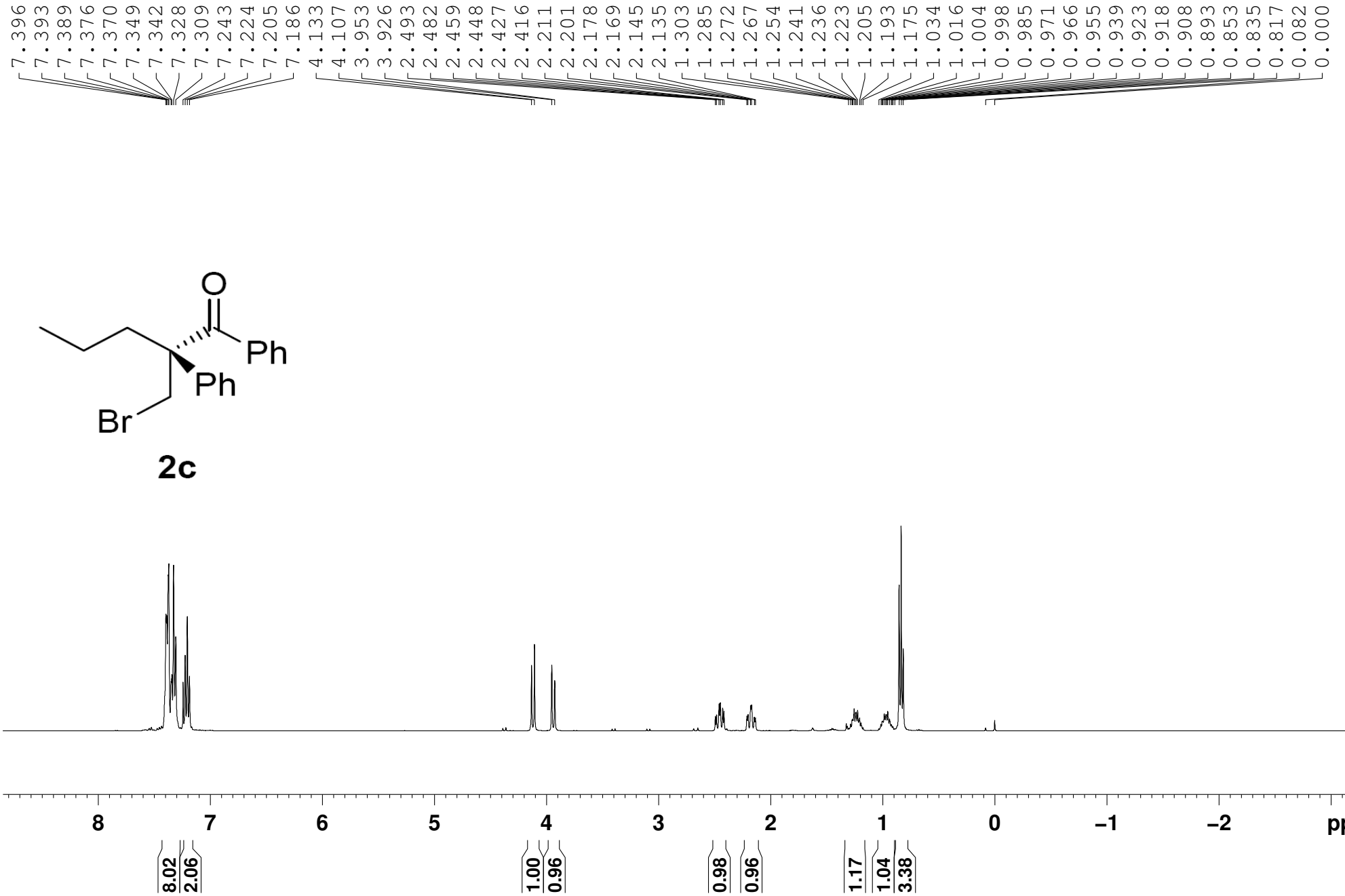

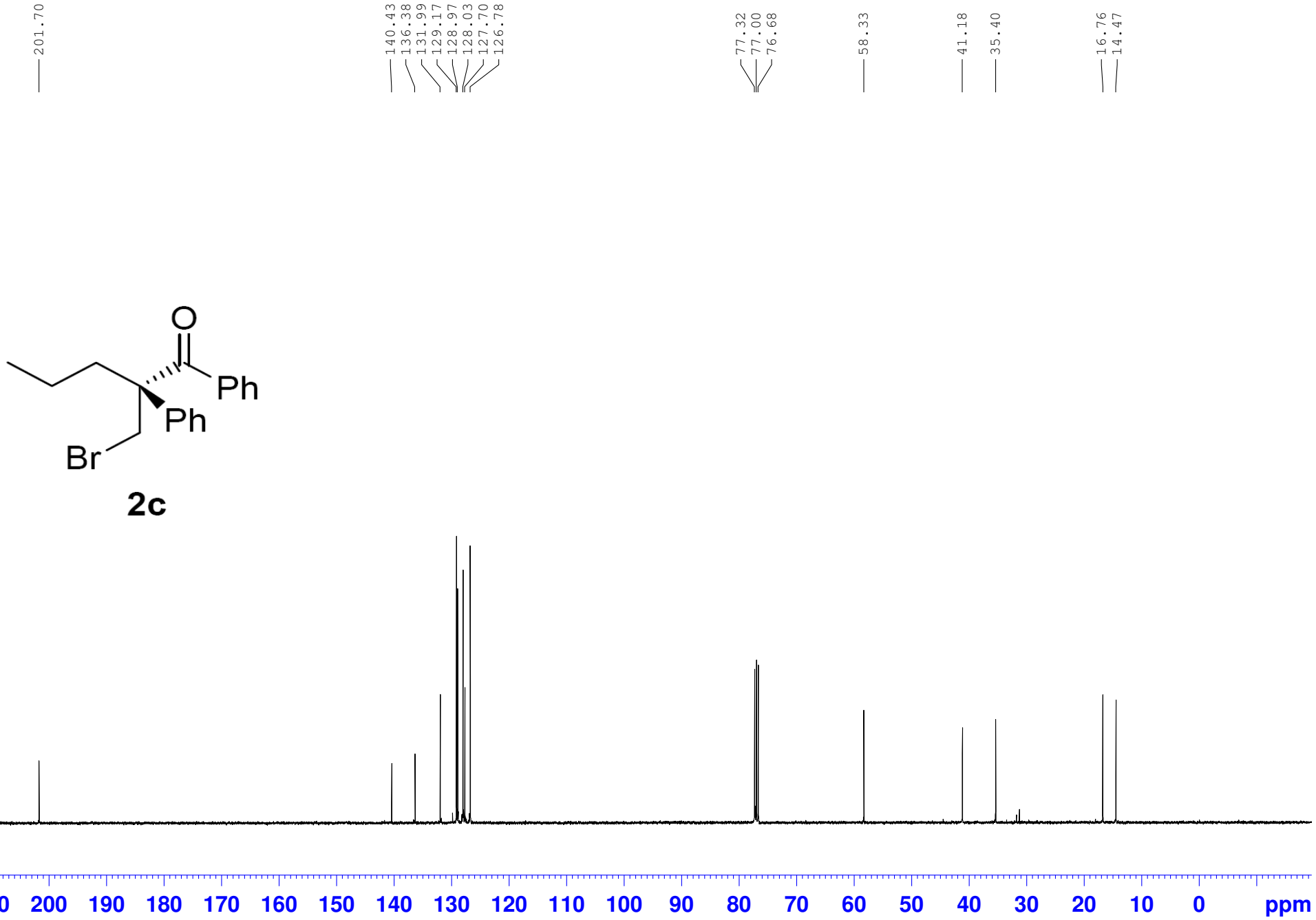

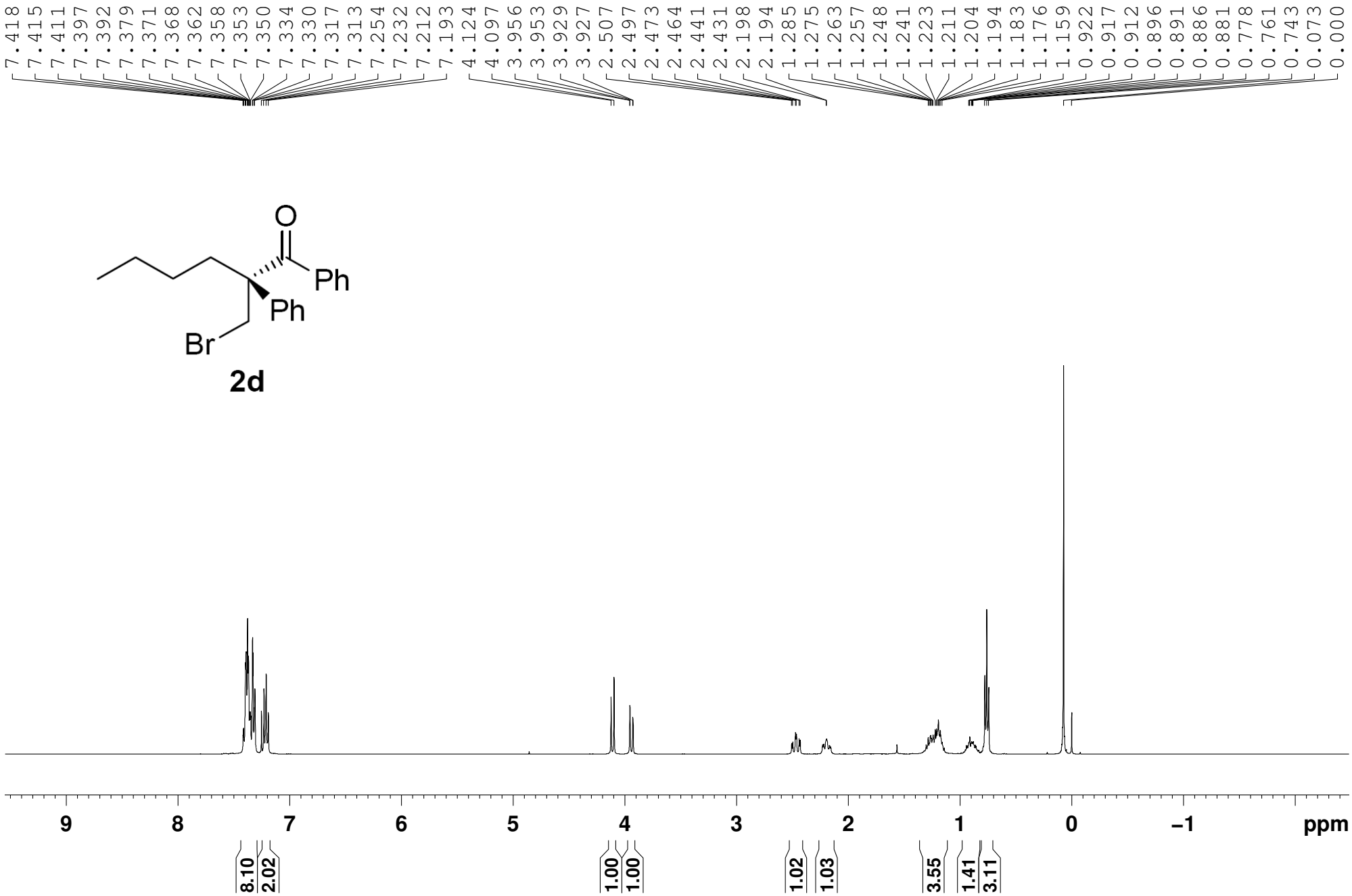

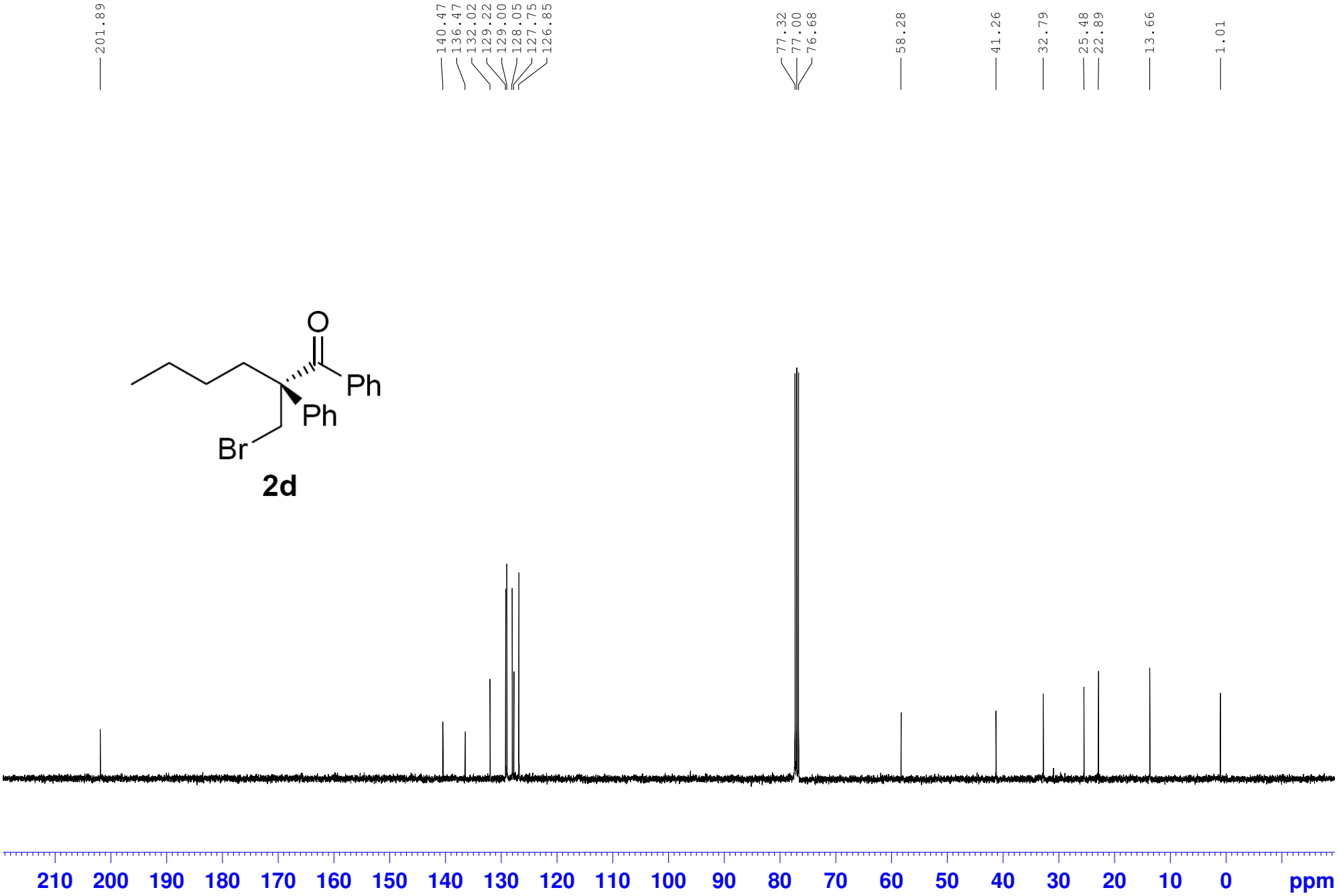

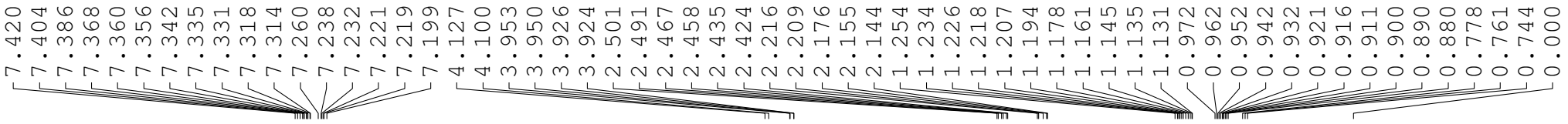

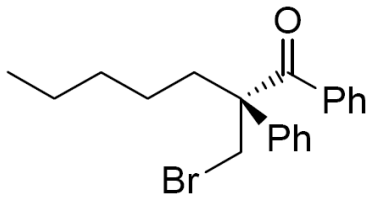

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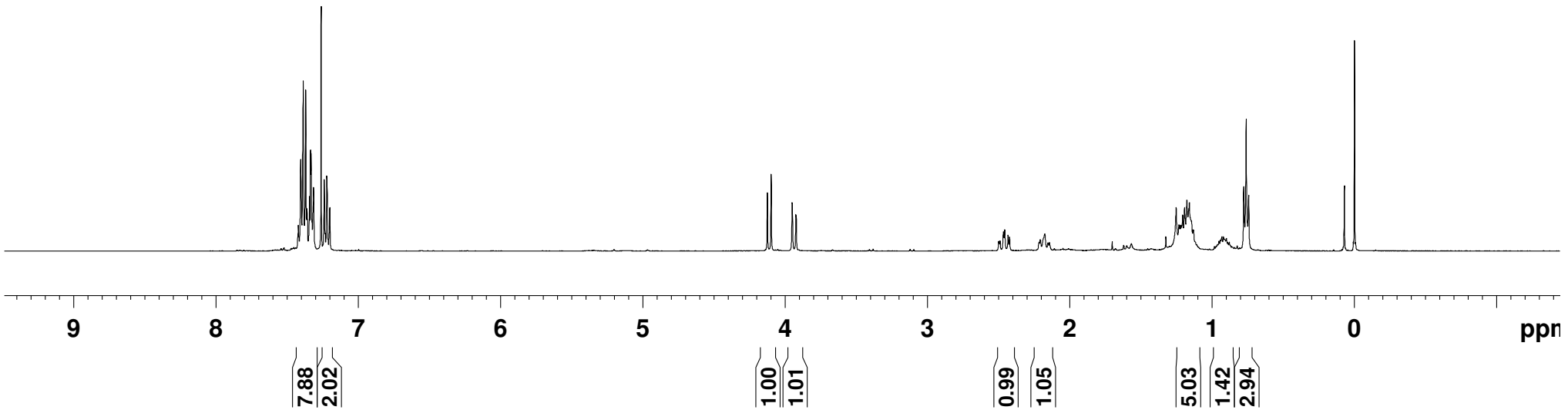

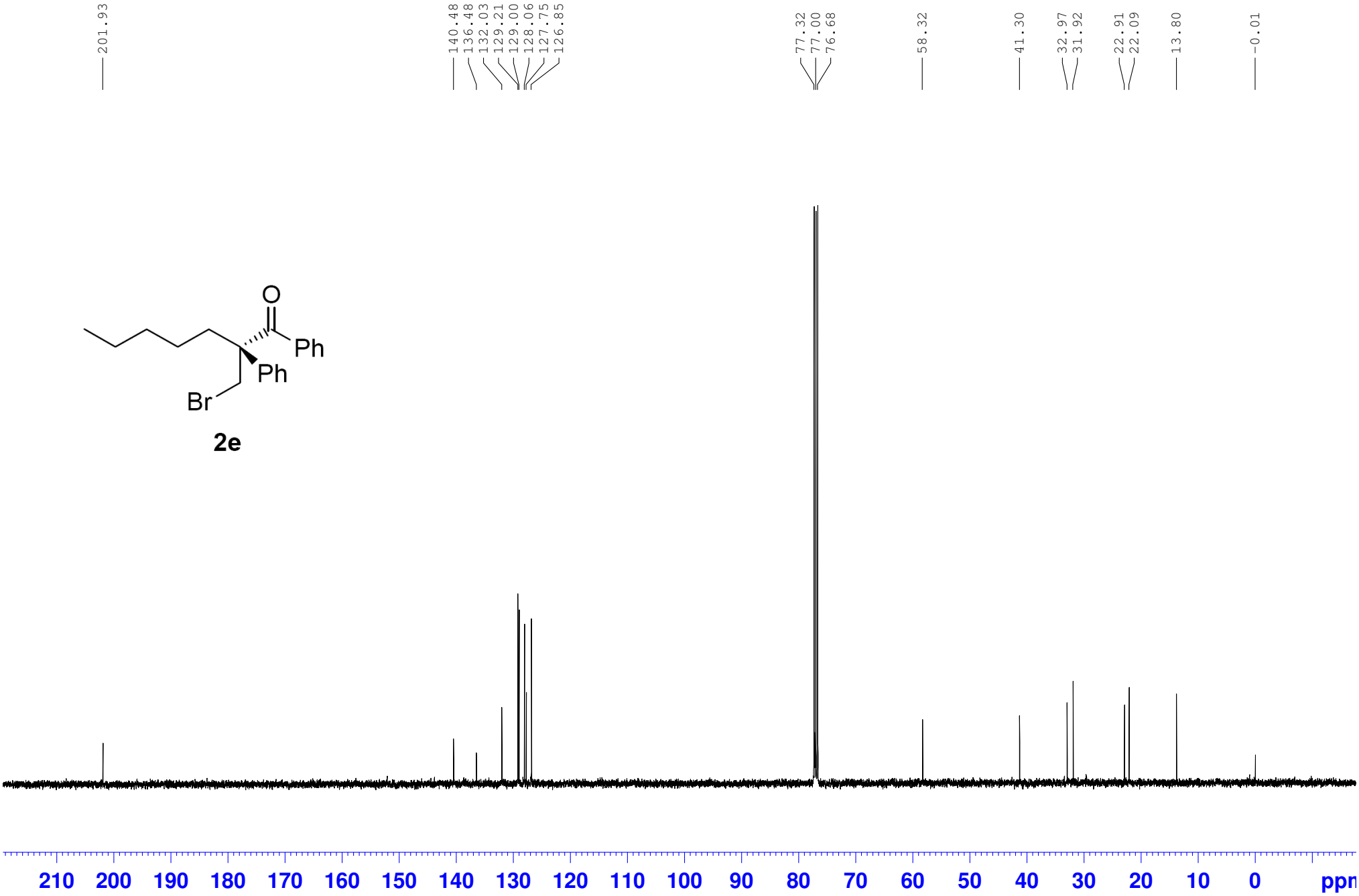

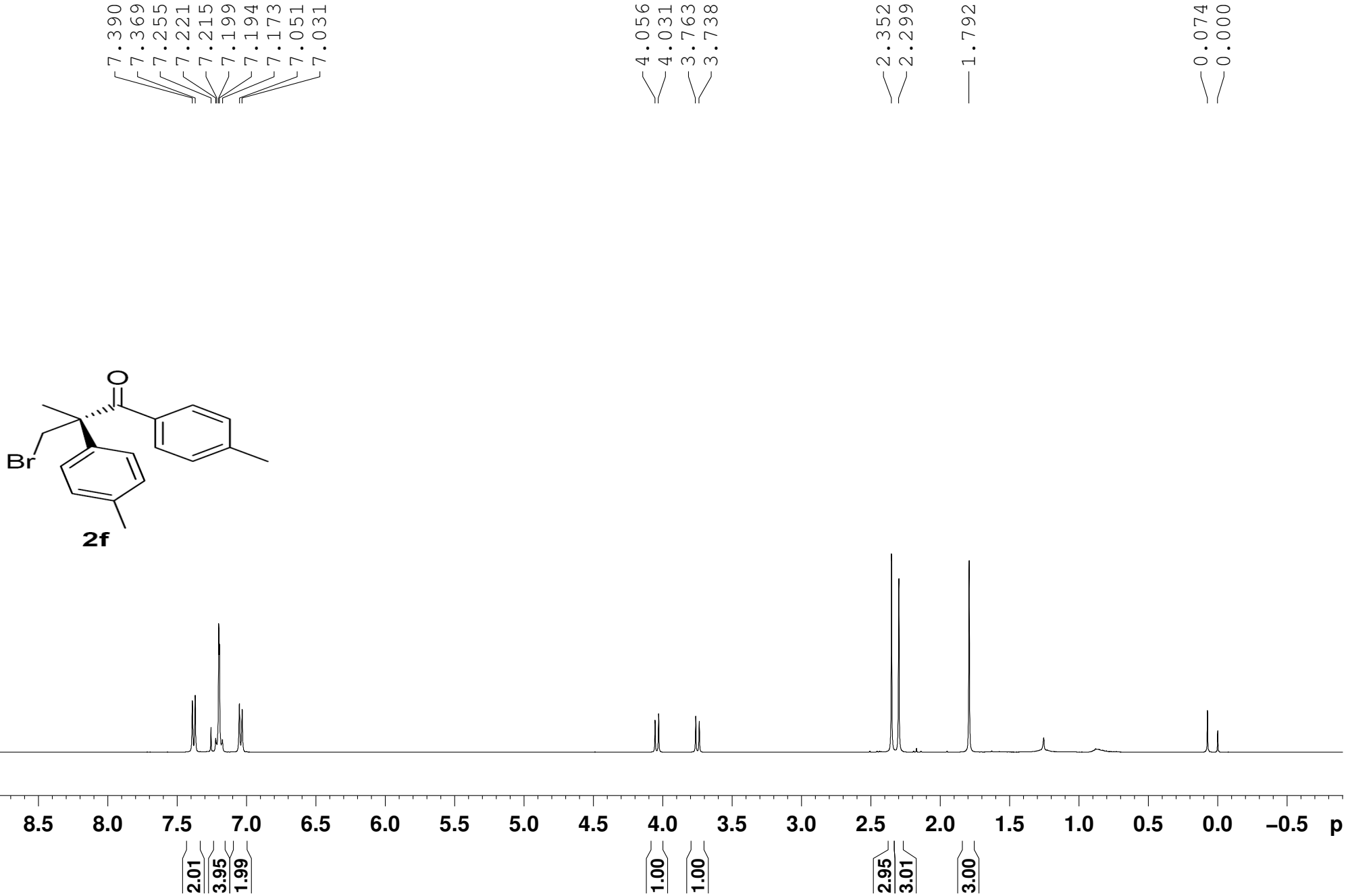

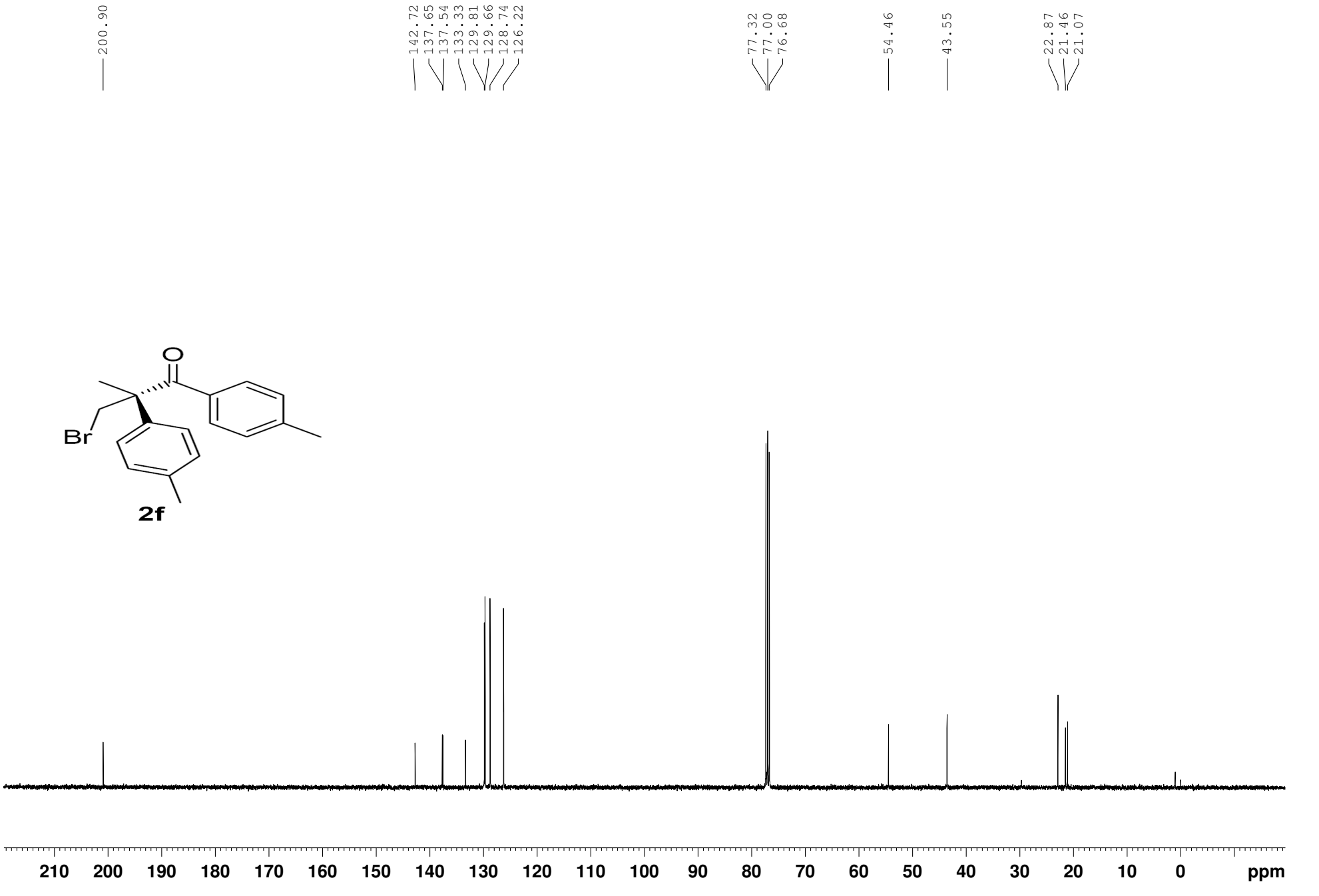

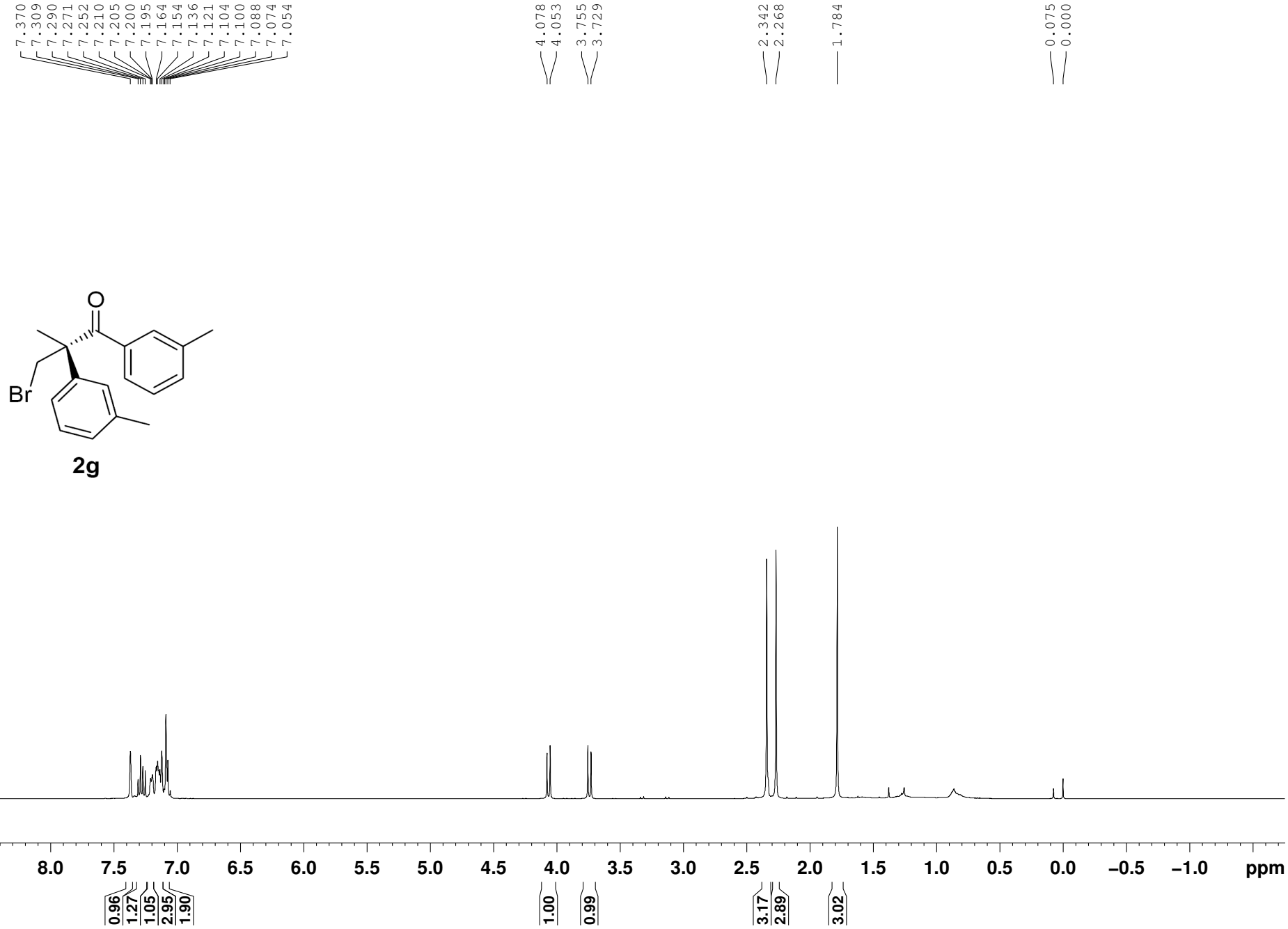

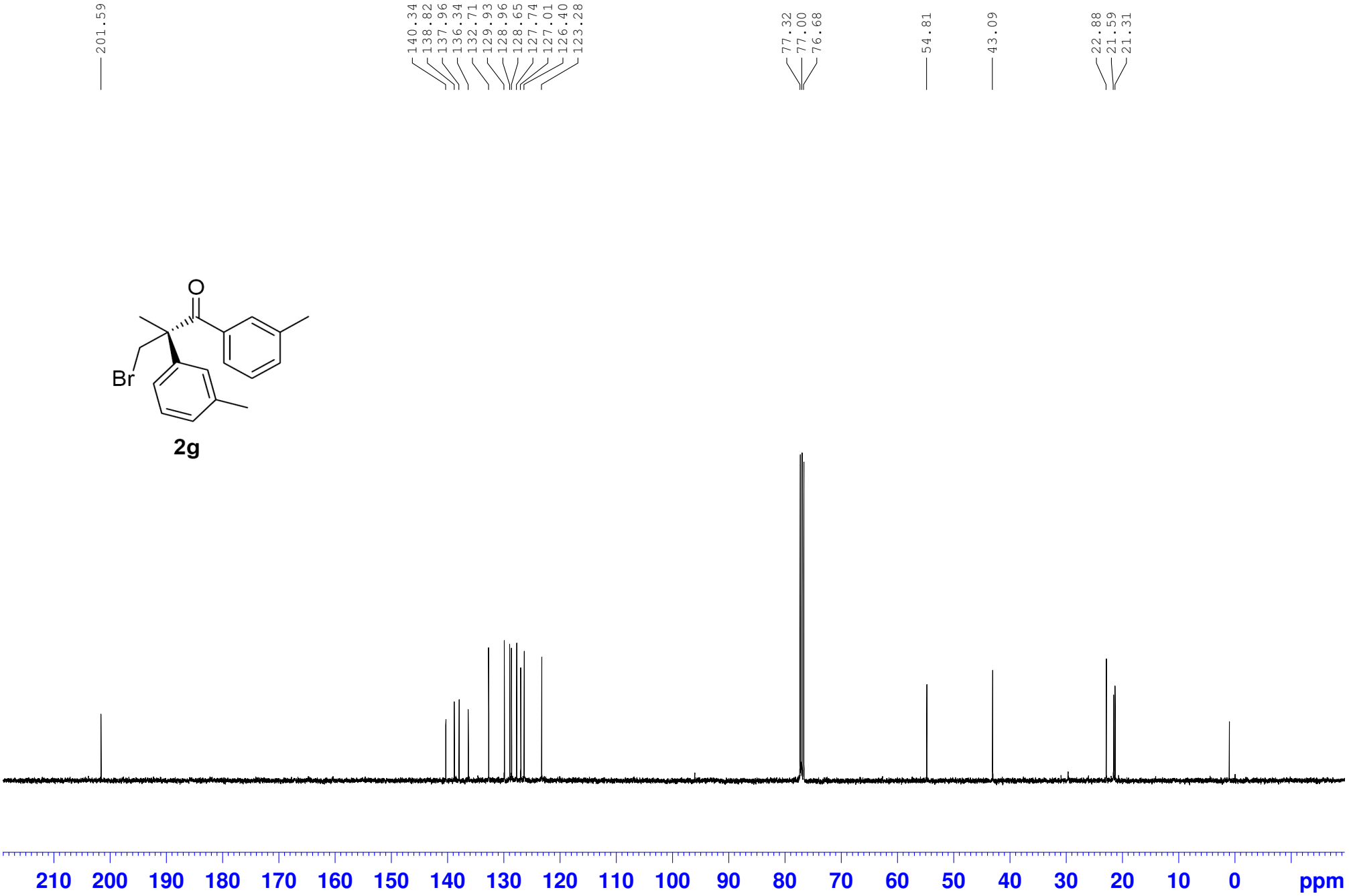

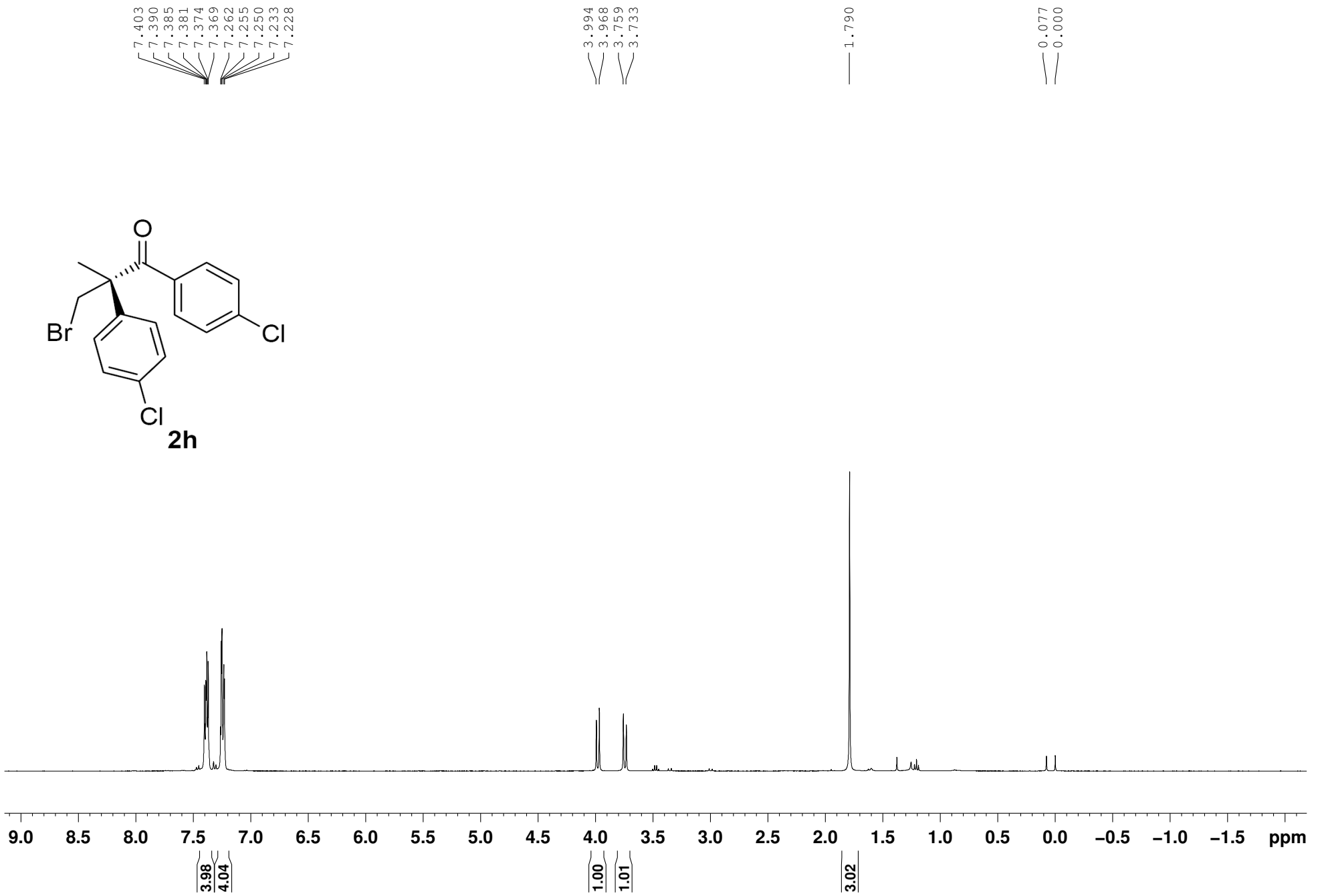

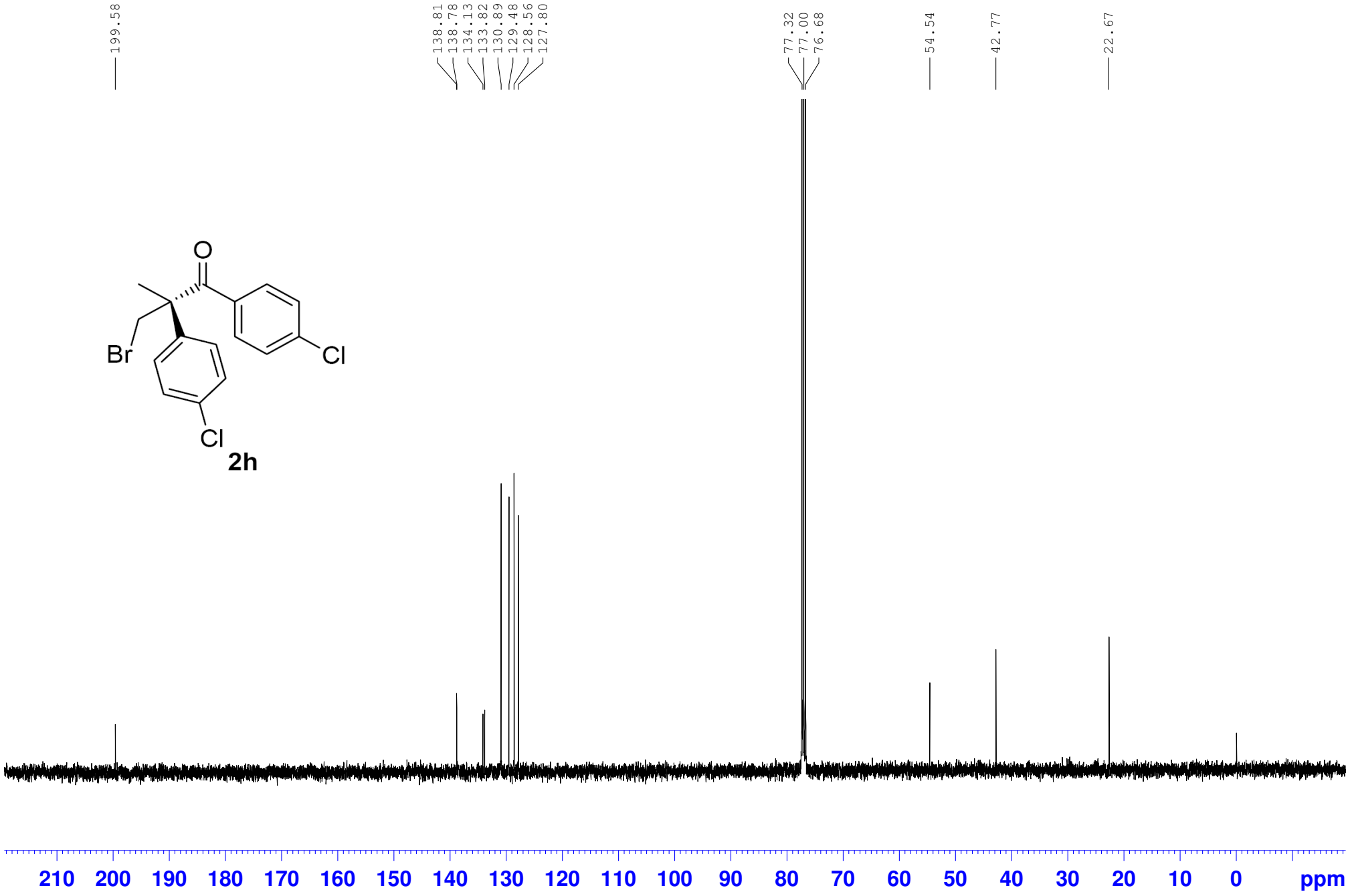

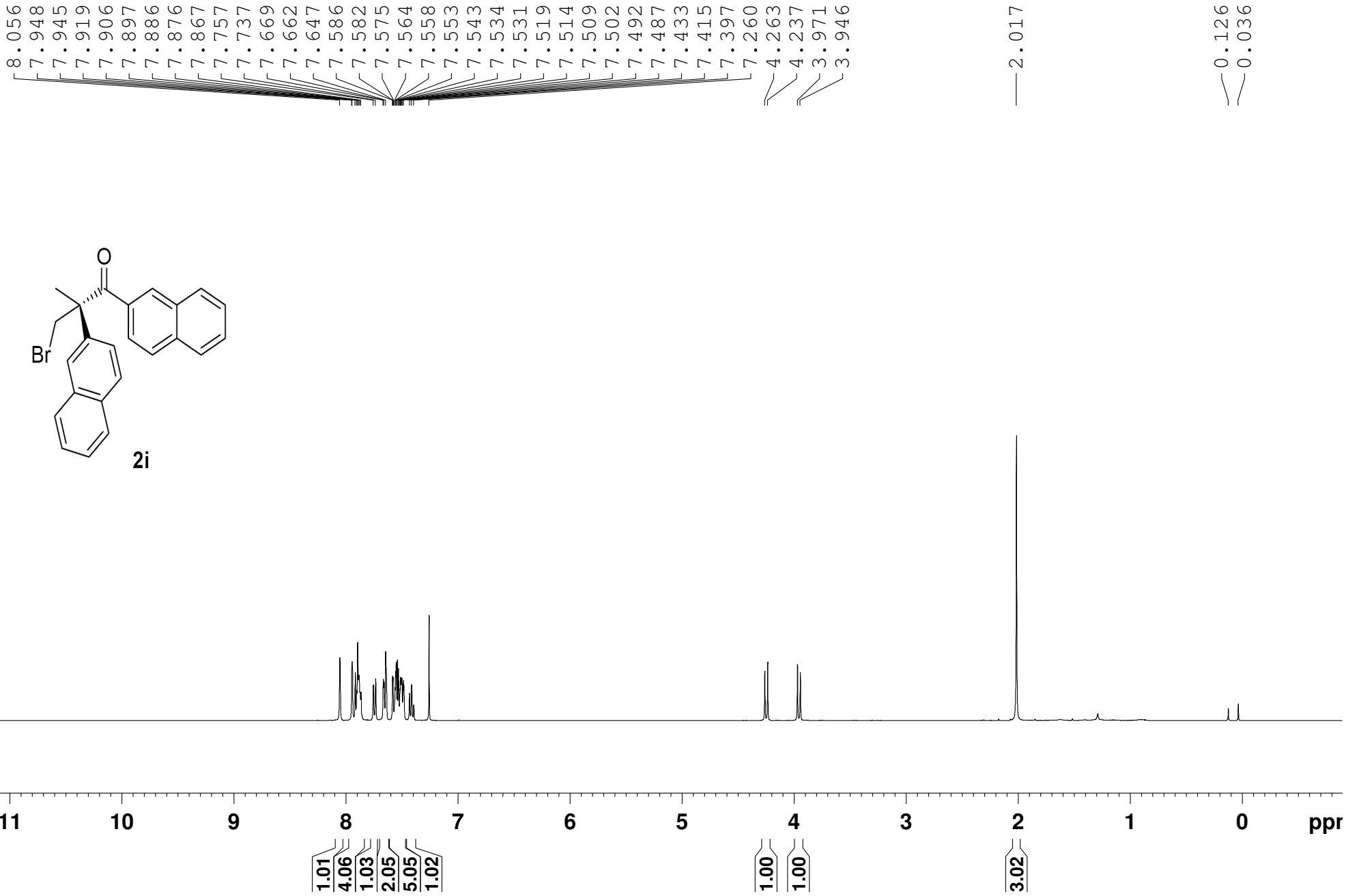

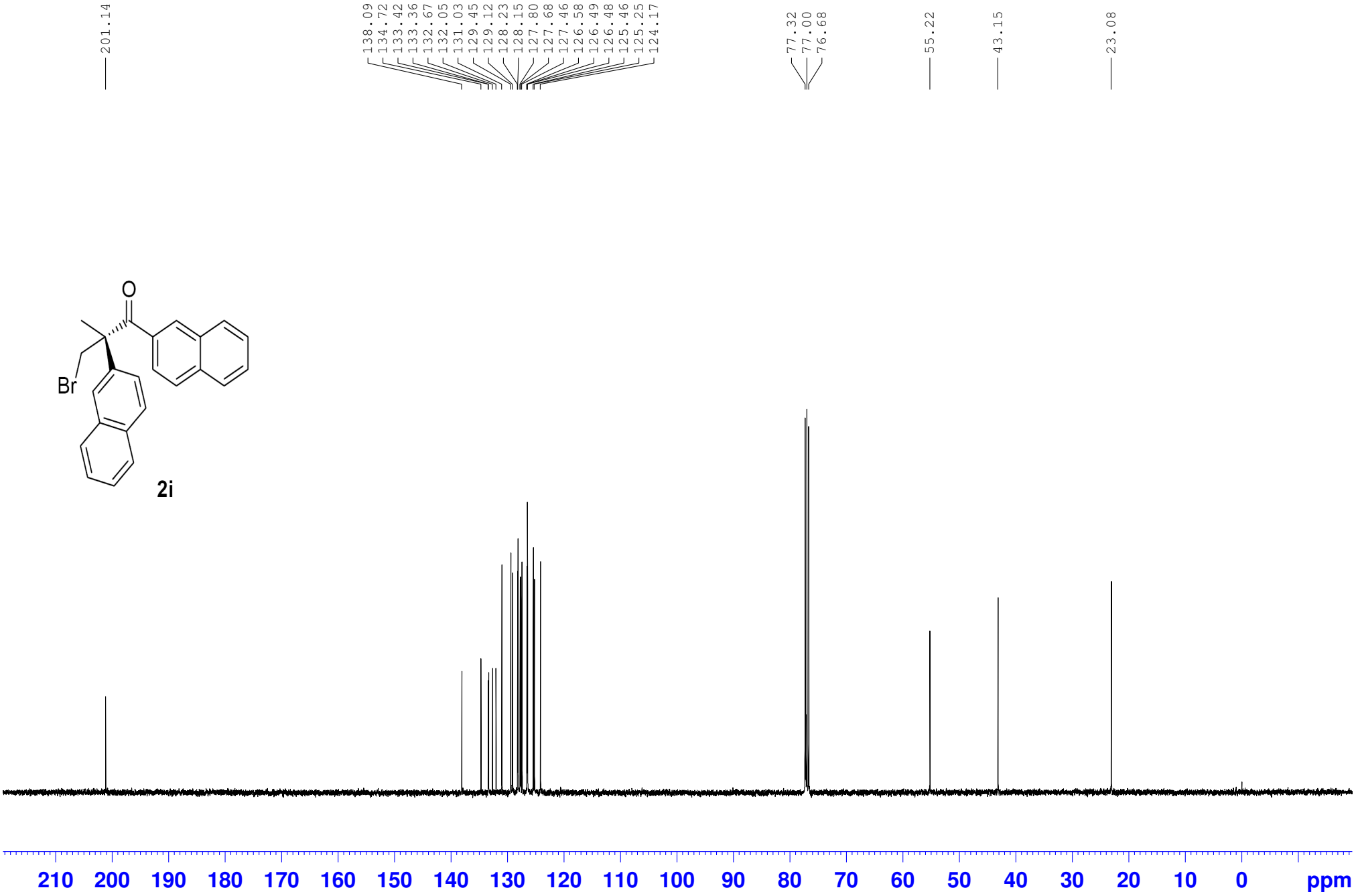

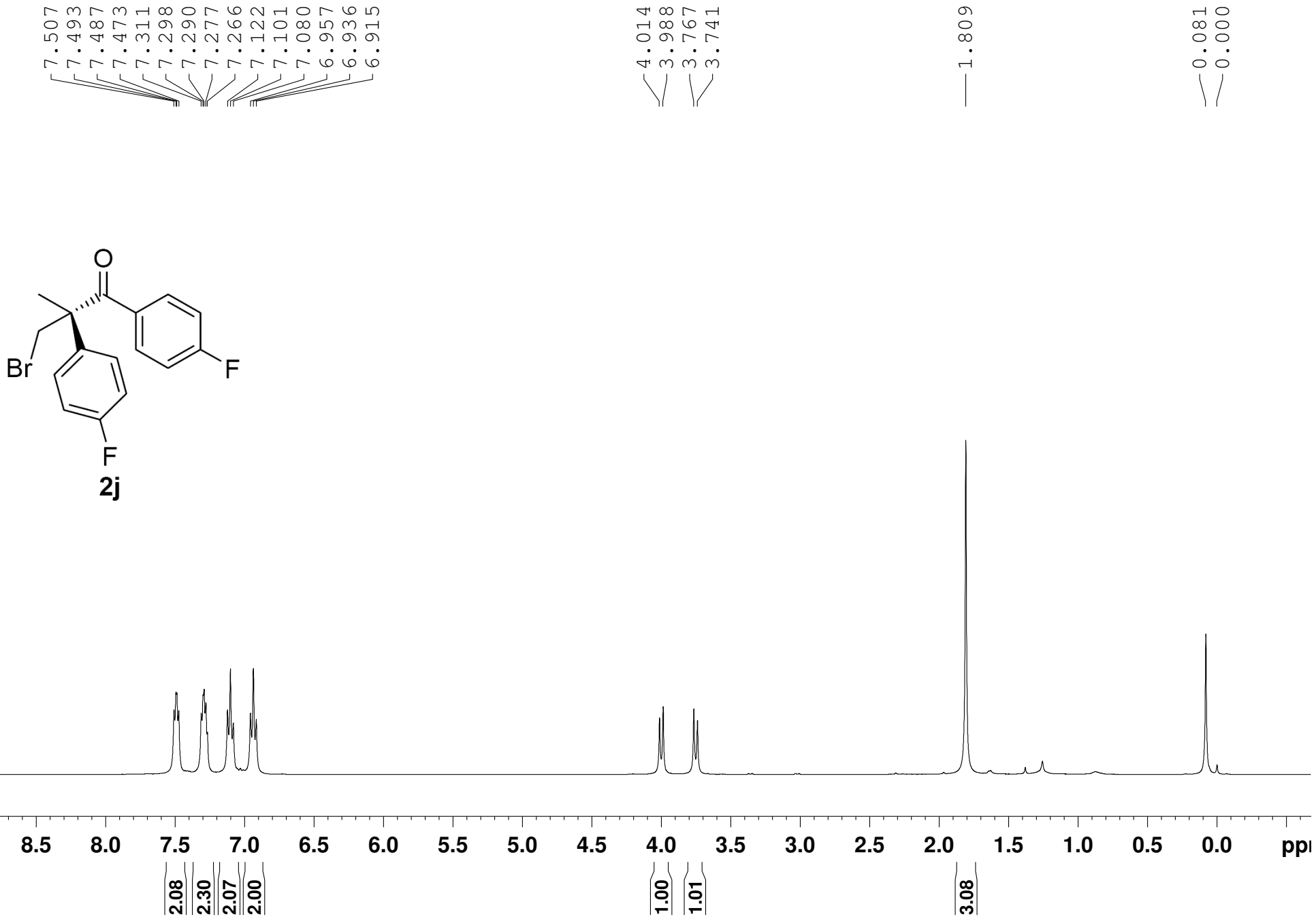

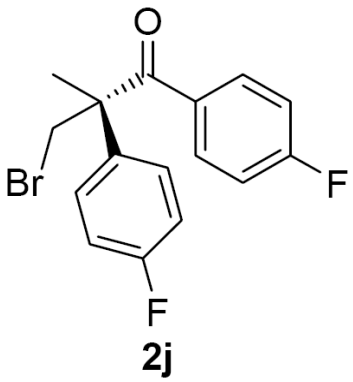

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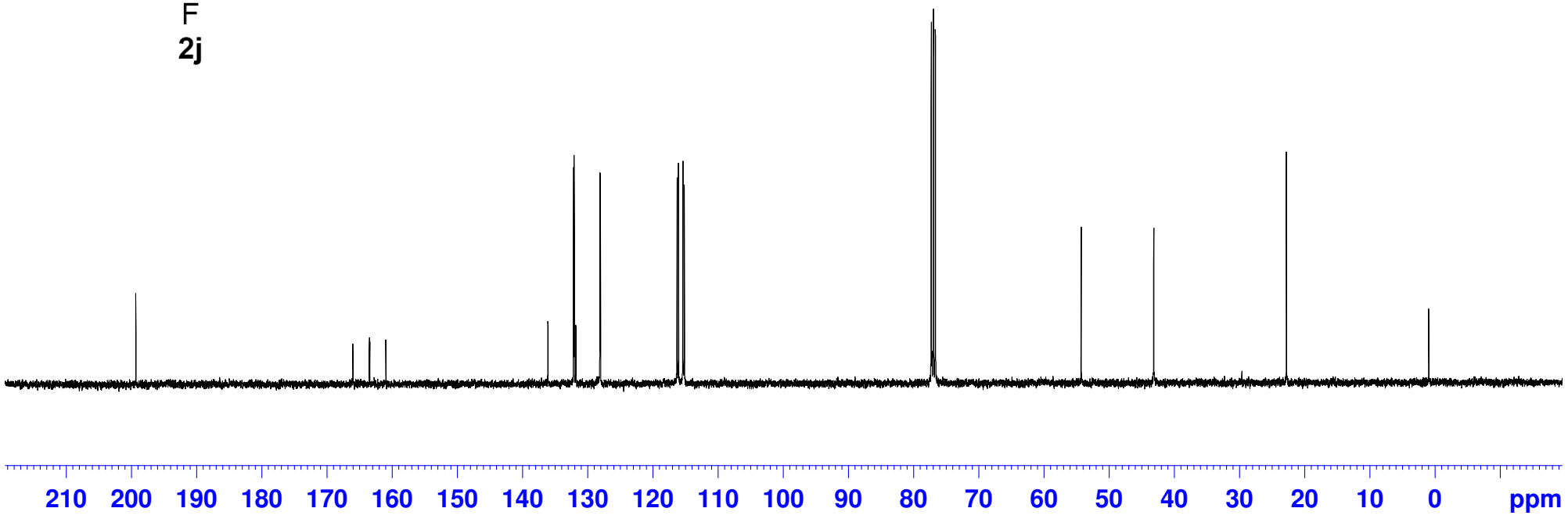

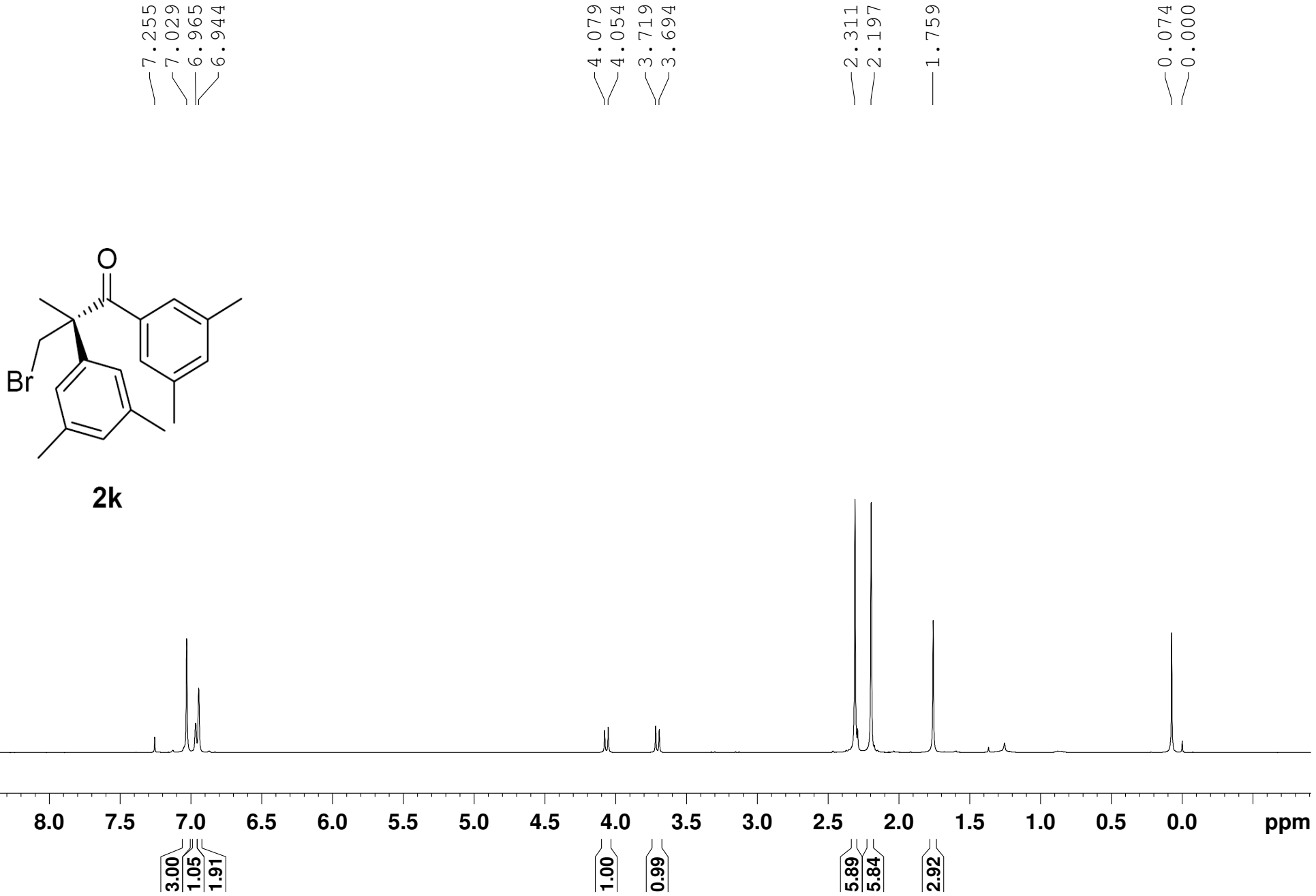

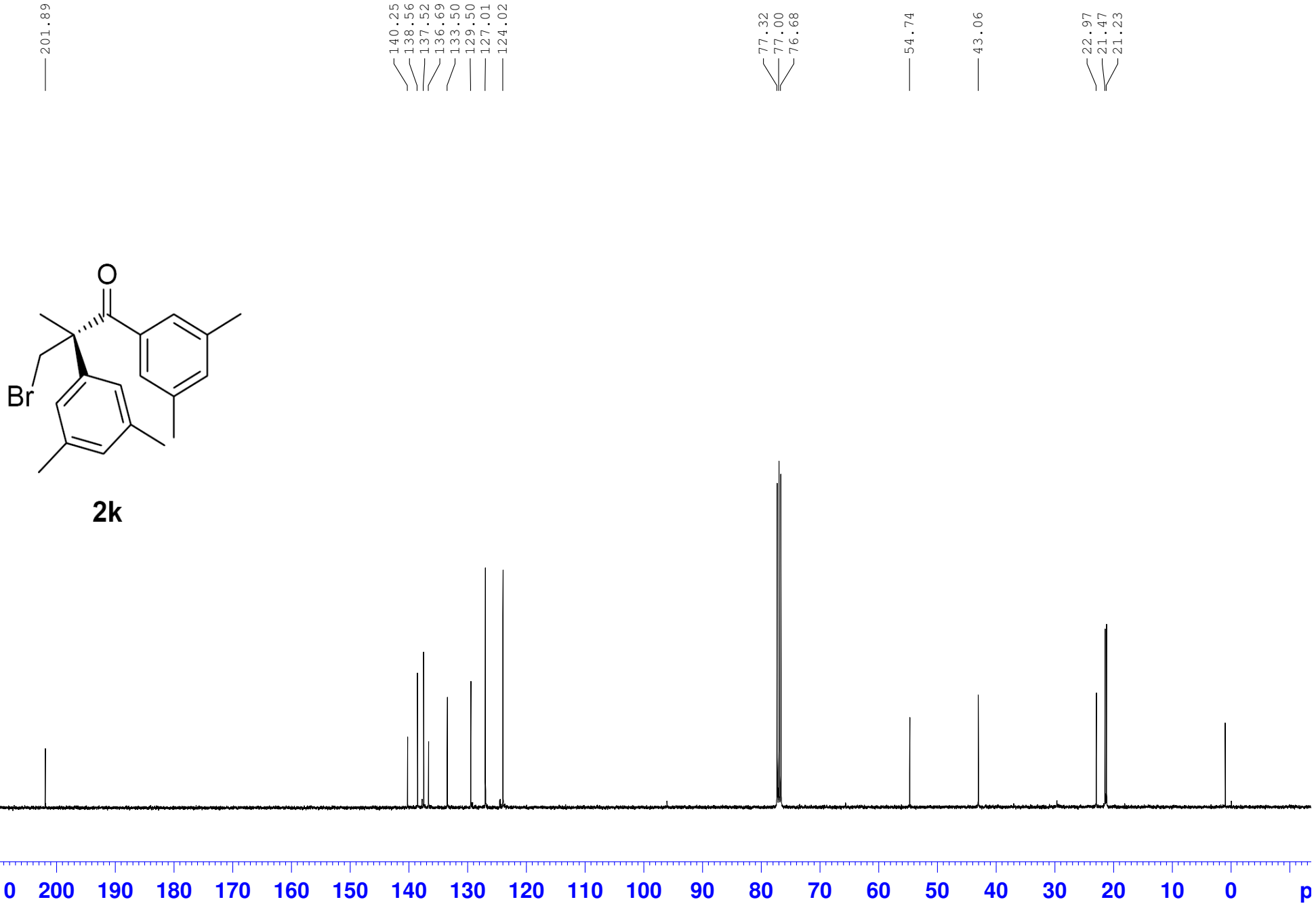

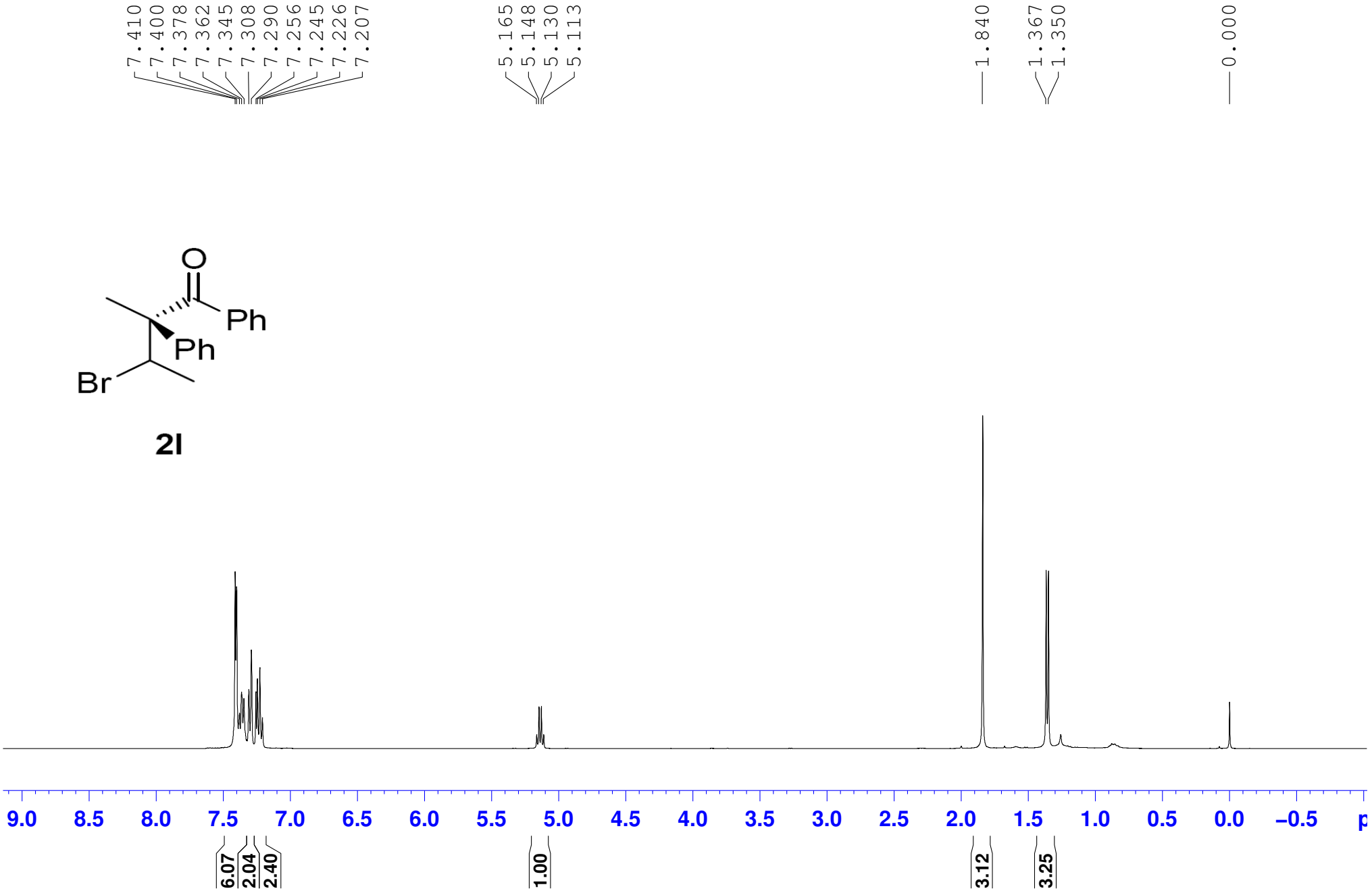

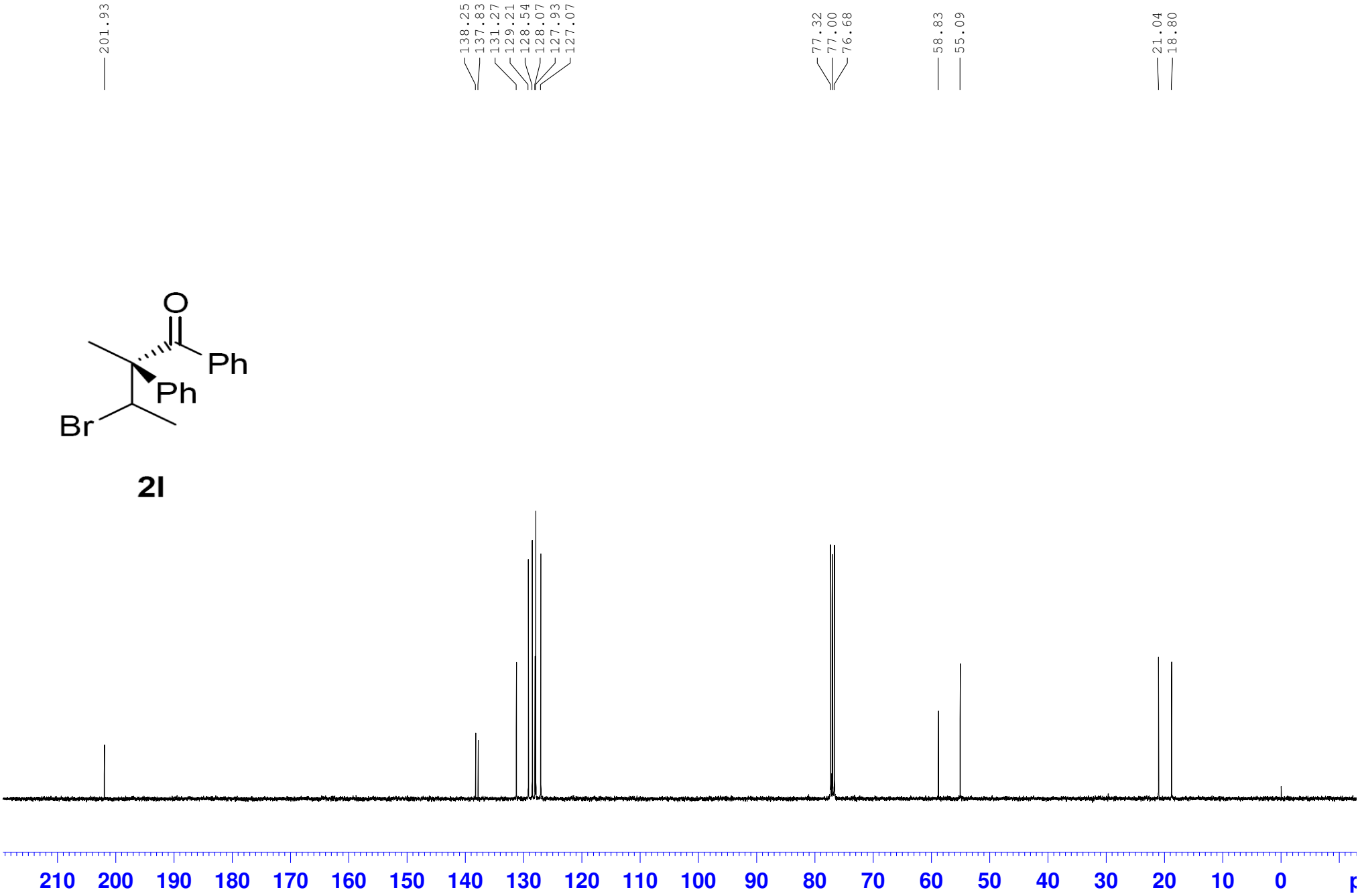

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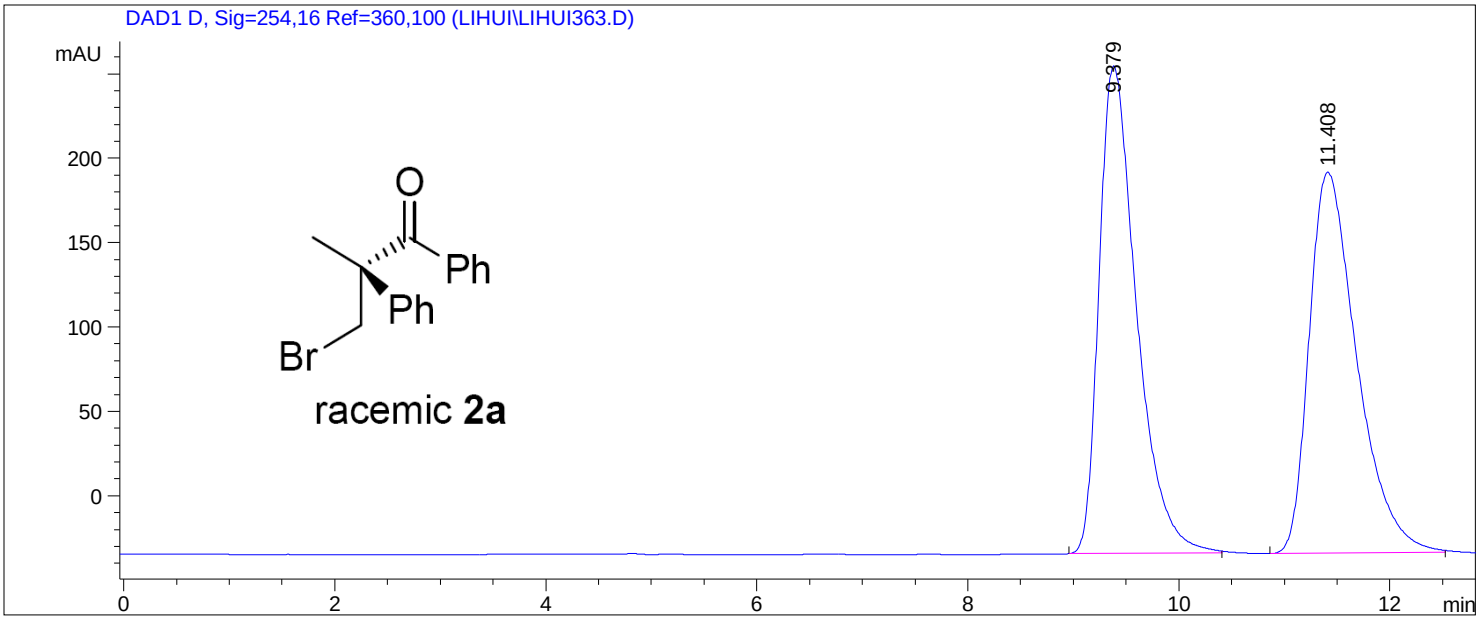
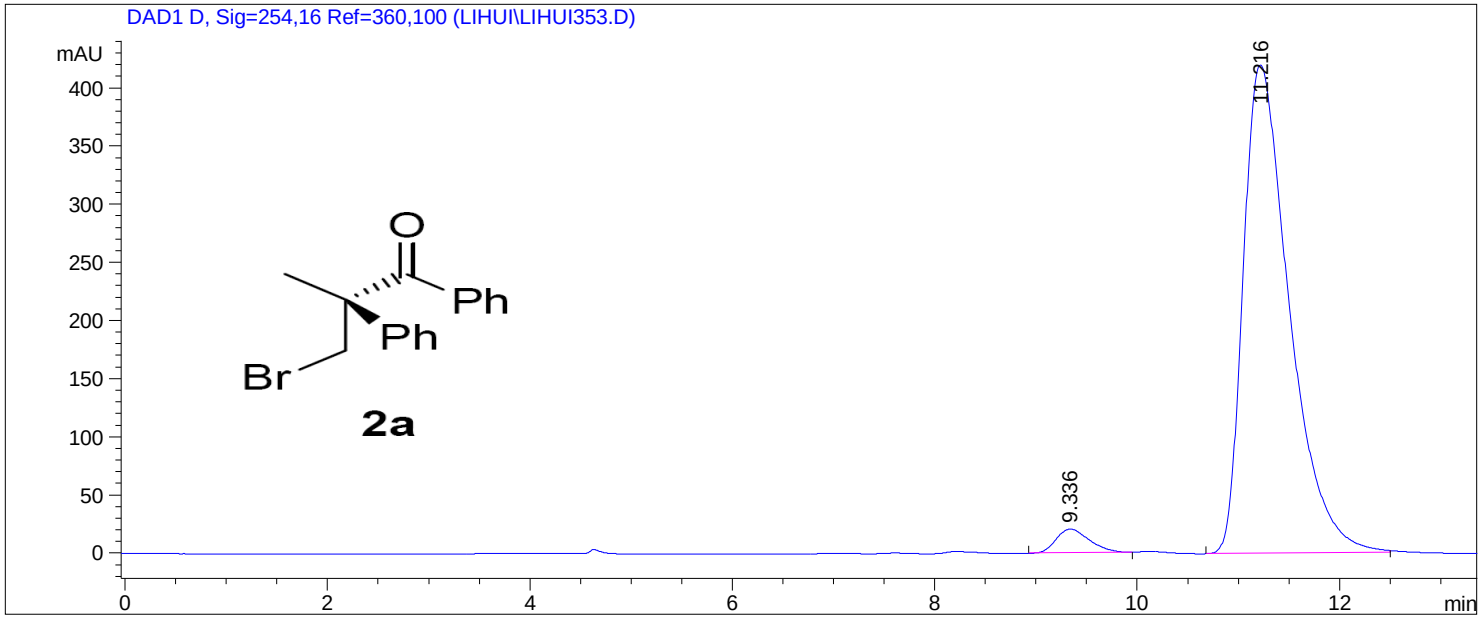
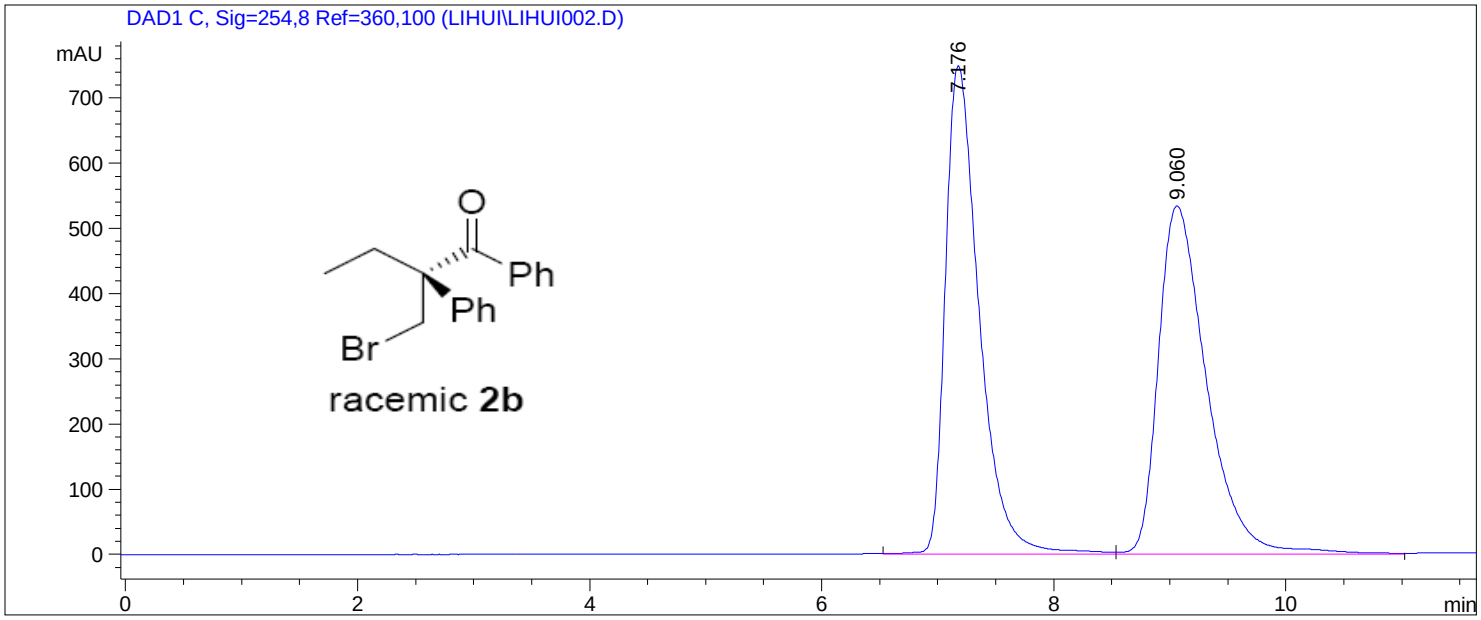


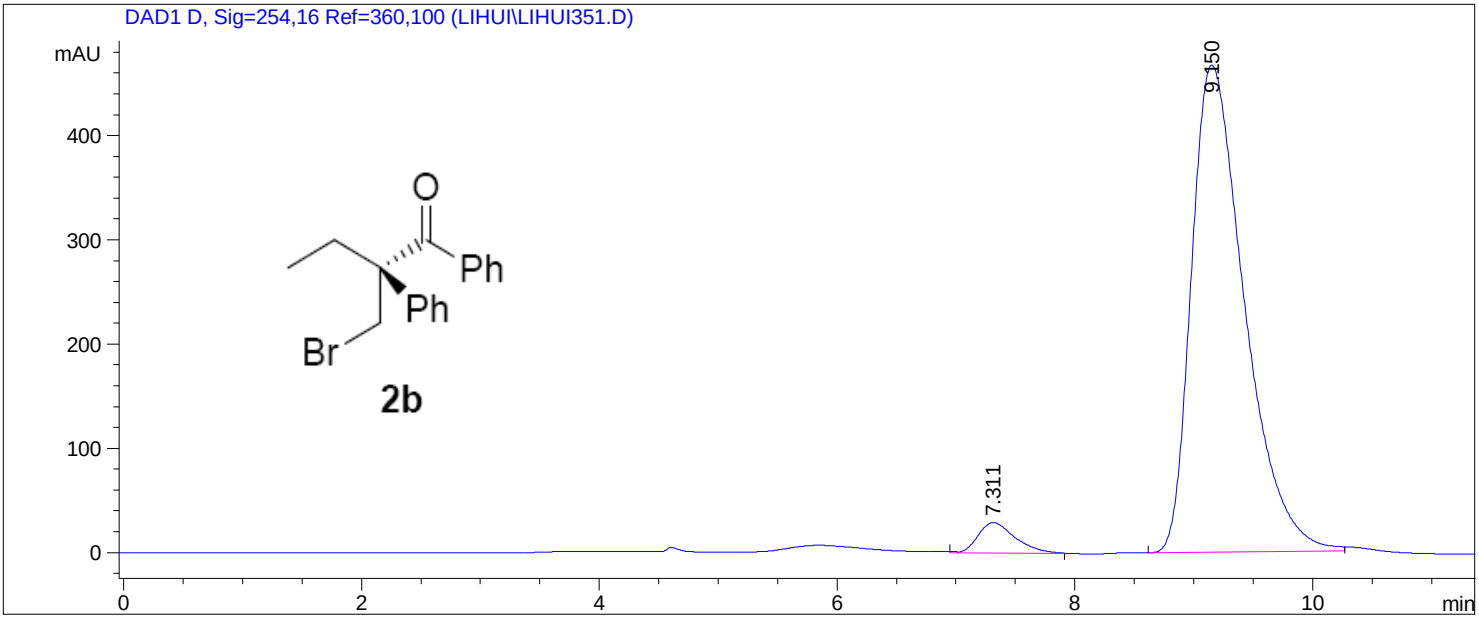
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.379	BB	0.3742	7141.31689	289.13147	50.1824
2	11.408	PB	0.4782	7089.40088	225.85631	49.8176



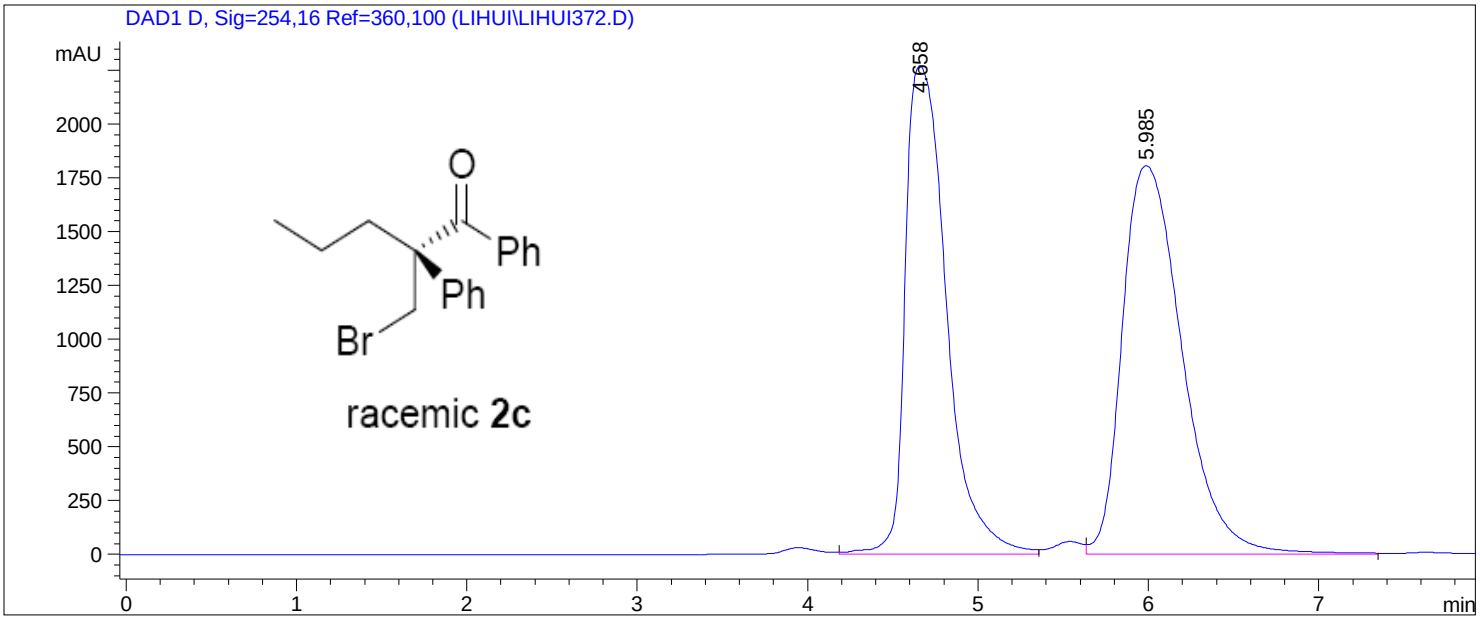
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.336	PP	0.3503	467.24384	20.46967	3.4020
2	11.216	PB	0.4808	1.32671e4	419.63699	96.5980



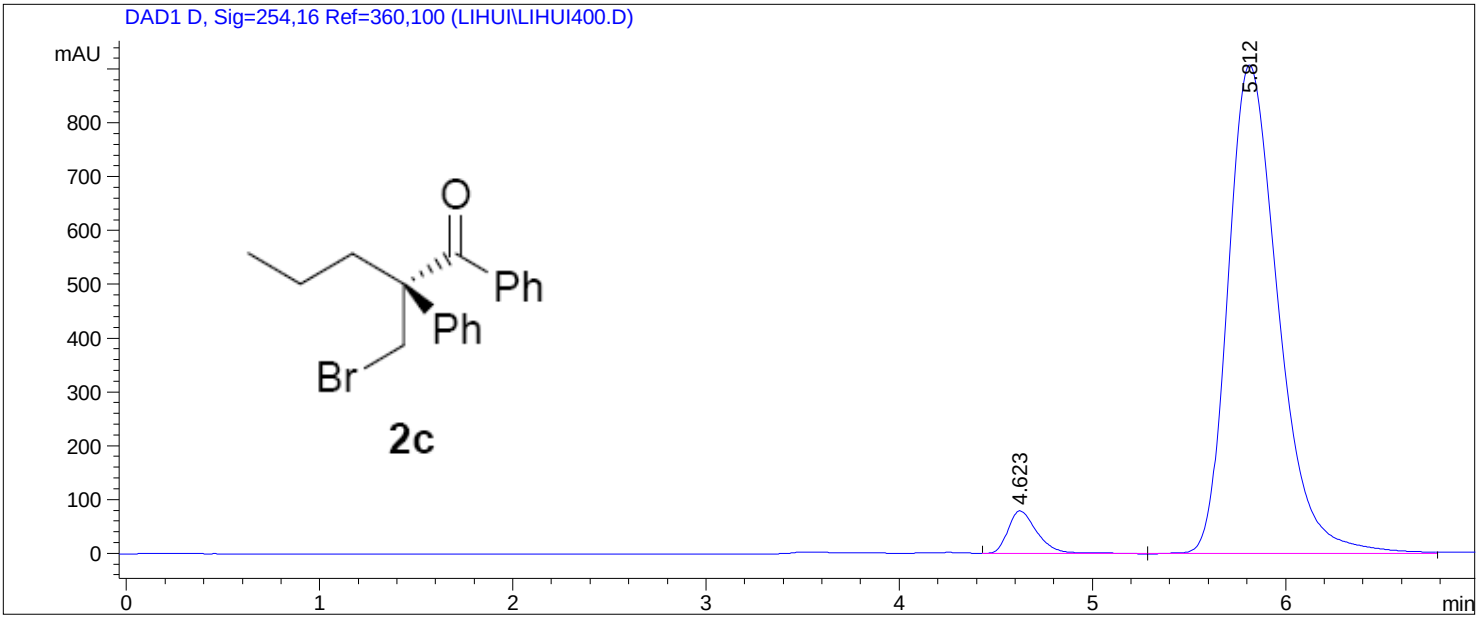
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.176	VV	0.3096	1.52707e4	749.78503	49.5955
2	9.060	VV	0.4423	1.55198e4	535.15442	50.4045



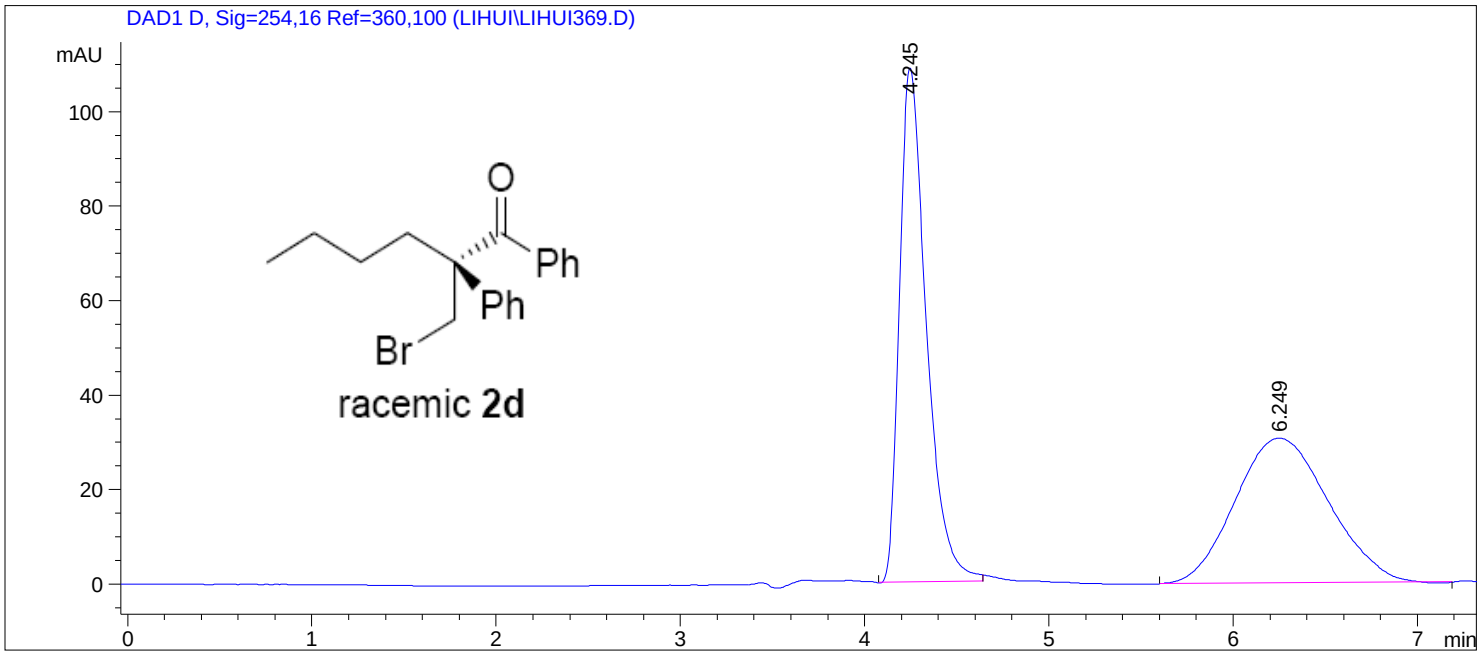
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.311	BB	0.3340	651.96674	29.48402	4.3045
2	9.150	PB	0.4737	1.44941e4	467.56332	95.6955



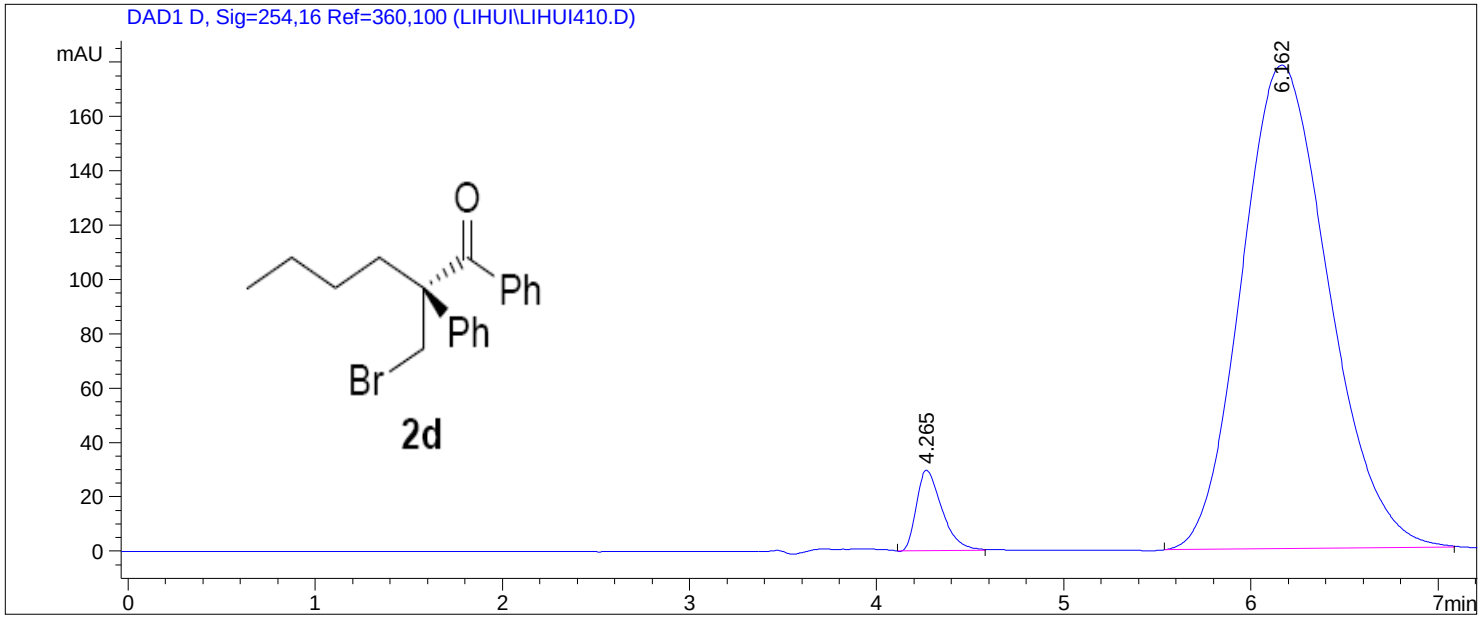
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.658	VV	0.2666	3.82805e4	2271.85059	46.3521
2	5.985	VB	0.3840	4.43059e4	1807.61450	53.6479



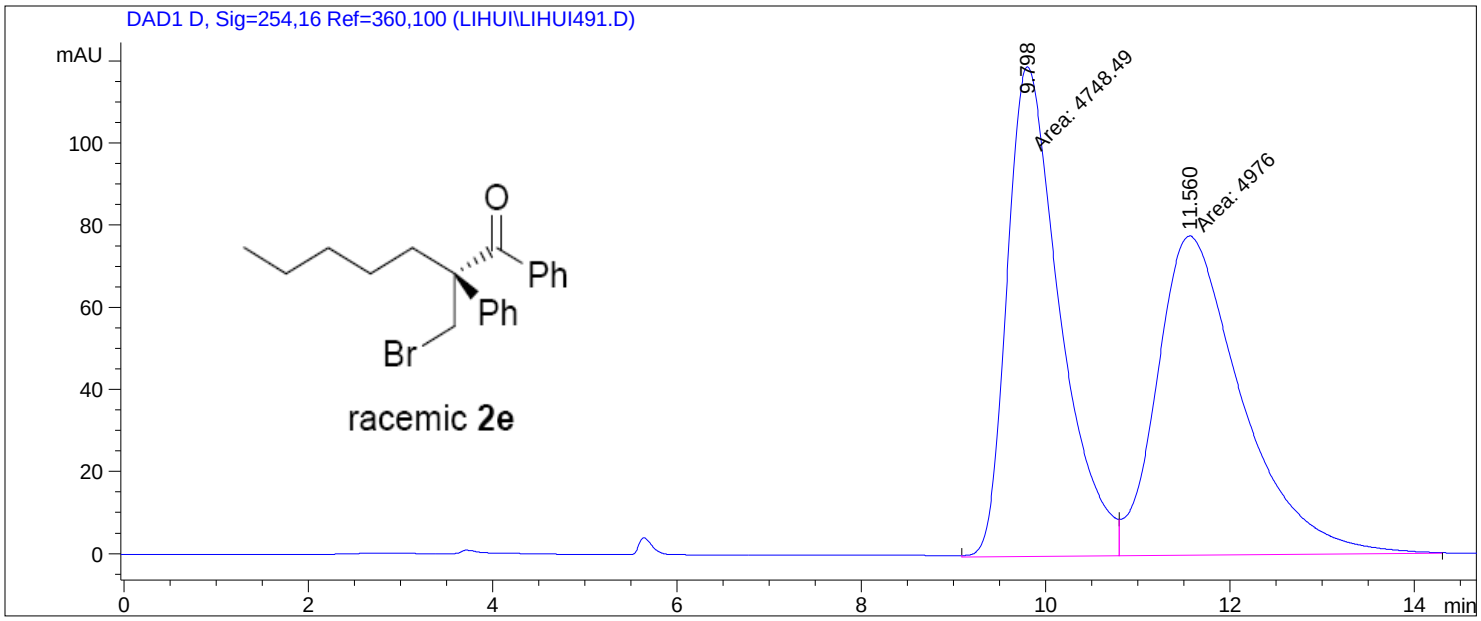
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.623	VP	0.1621	865.98010	80.10591	4.9897
2	5.812	VV	0.2798	1.64894e4	908.40576	95.0103



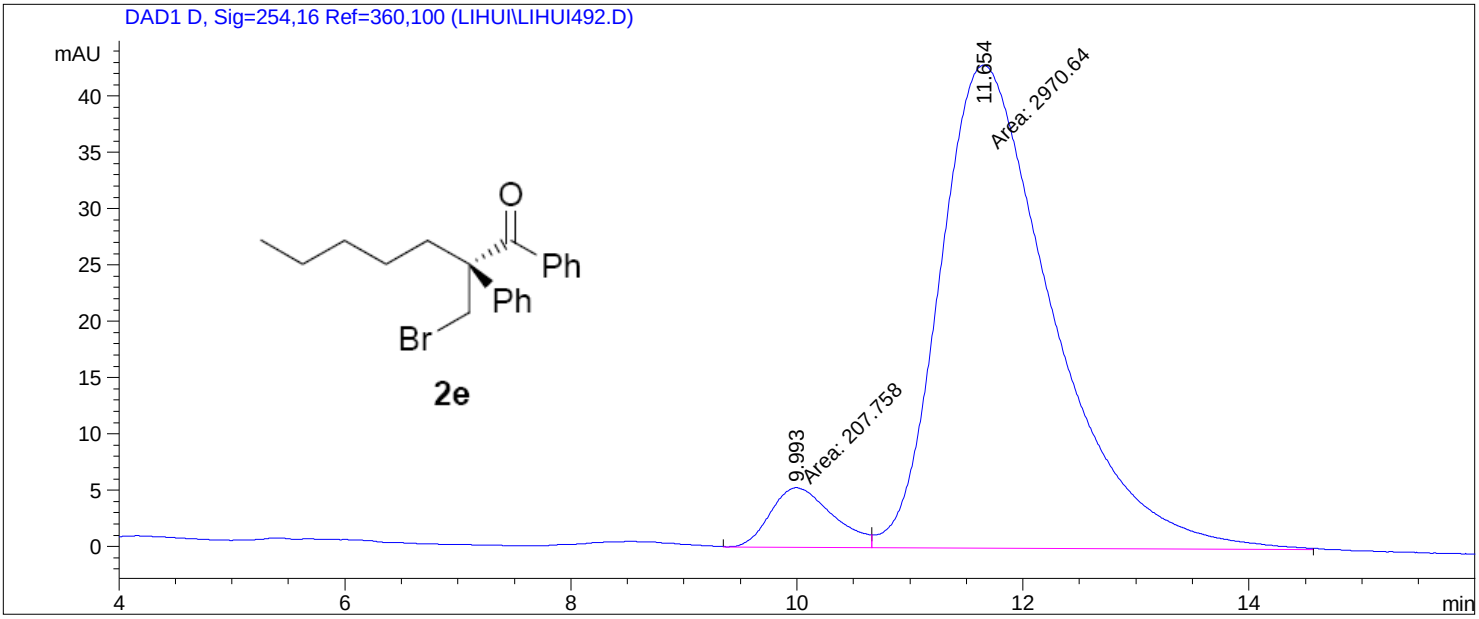
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.245	BB	0.1542	1104.01050	108.96370	50.5335
2	6.249	BP	0.5509	1080.70020	30.68791	49.4665



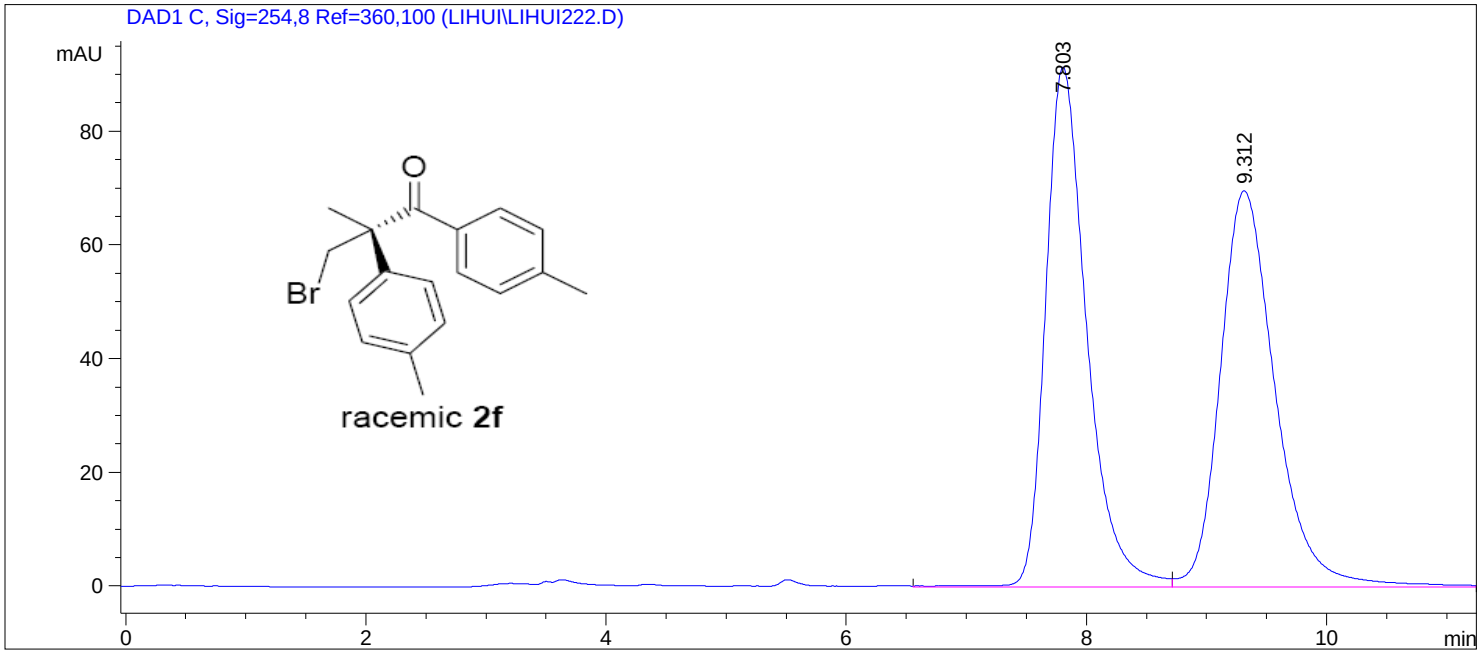
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.265	PB	0.1453	283.83017	29.76469	4.6849
2	6.162	BB	0.5043	5774.53906	178.08153	95.3151



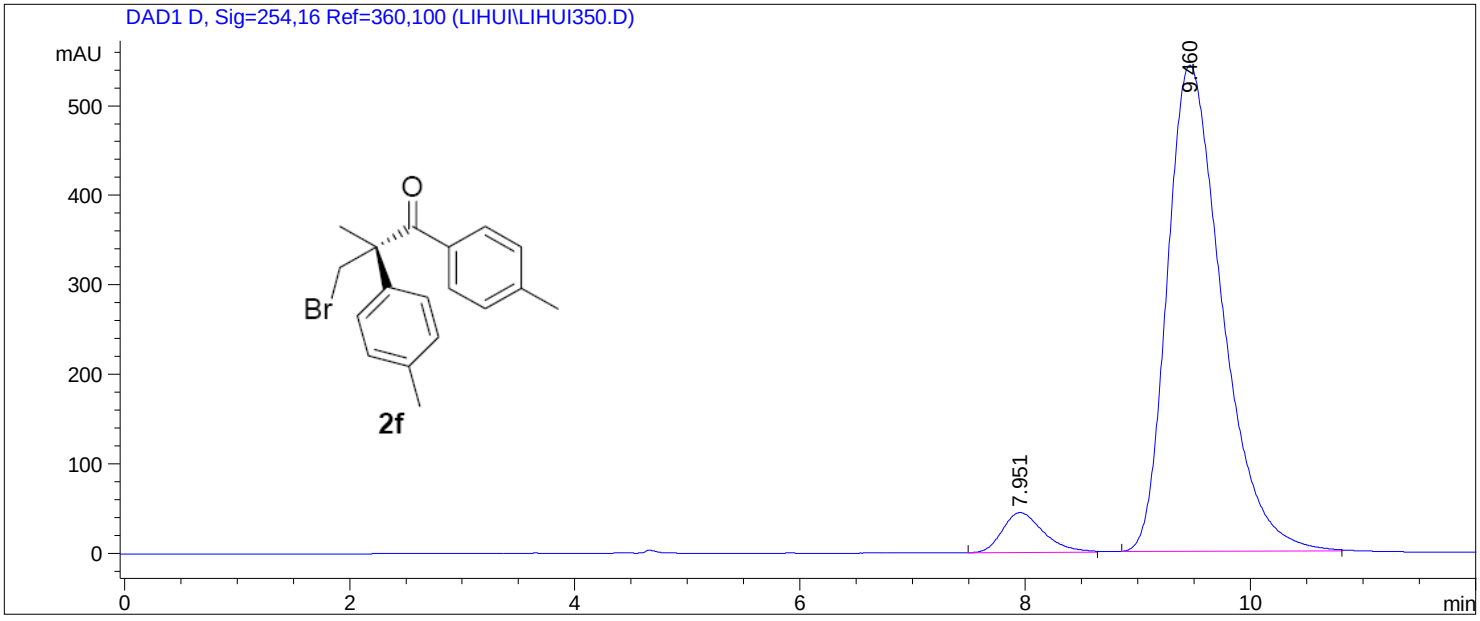
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.798	MF	0.6634	4748.49316	119.29546	48.8302
2	11.560	FM	1.0663	4975.99951	77.77811	51.1698



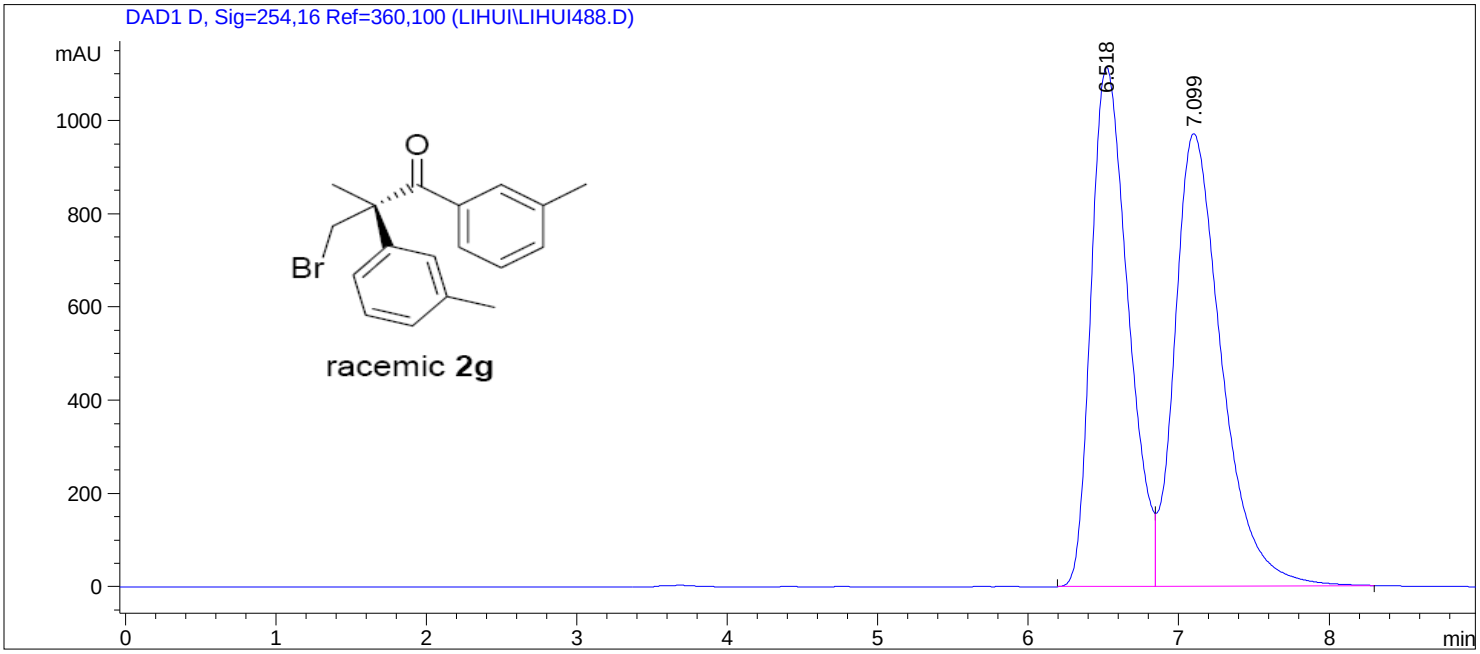
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.993	MF	0.6468	207.75777	5.35346	6.5366
2	11.654	FM	1.1537	2970.64233	42.91638	93.4634



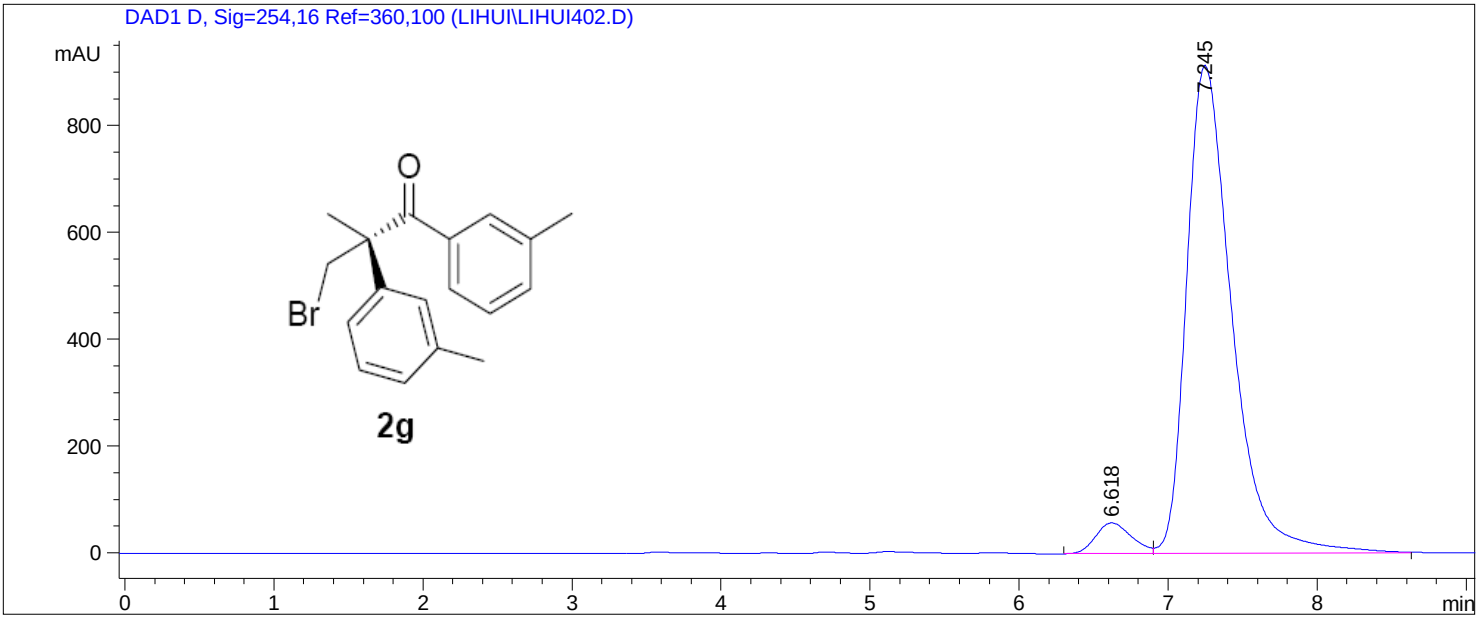
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.803	VV	0.3630	2187.21973	91.44924	49.6380
2	9.312	VBA	0.4834	2219.12329	69.70144	50.3620



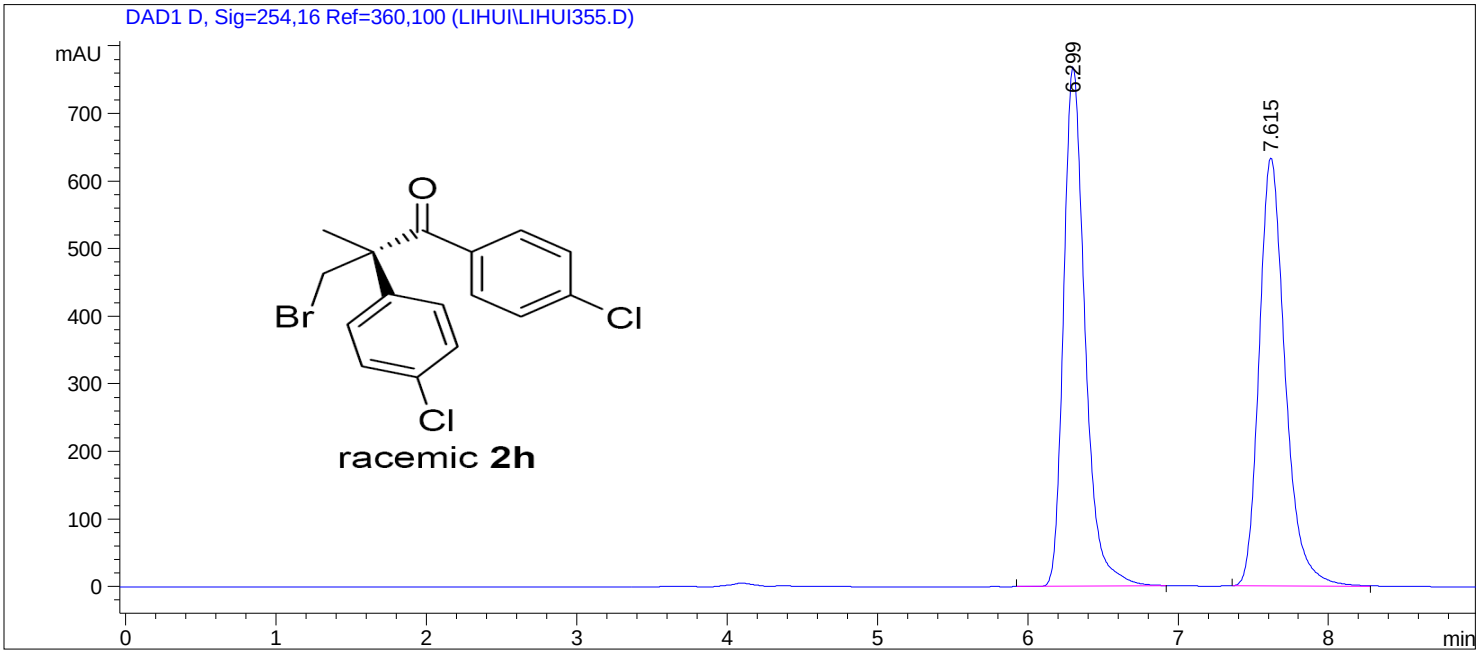
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.951	BB	0.3897	1140.33850	44.69063	5.8447
2	9.460	BB	0.5186	1.83703e4	543.15387	94.1553



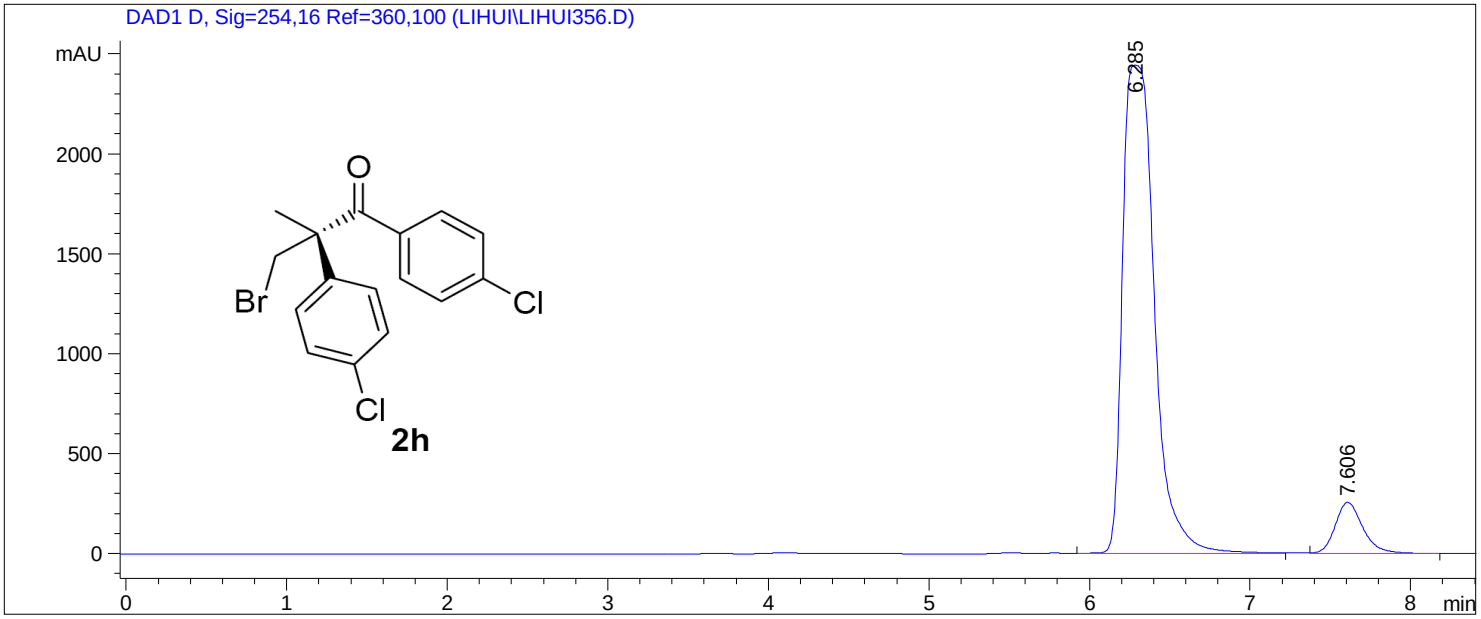
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.518	PV	0.2661	1.91171e4	1114.76587	47.4784
2	7.099	VB	0.3300	2.11477e4	971.19739	52.5216



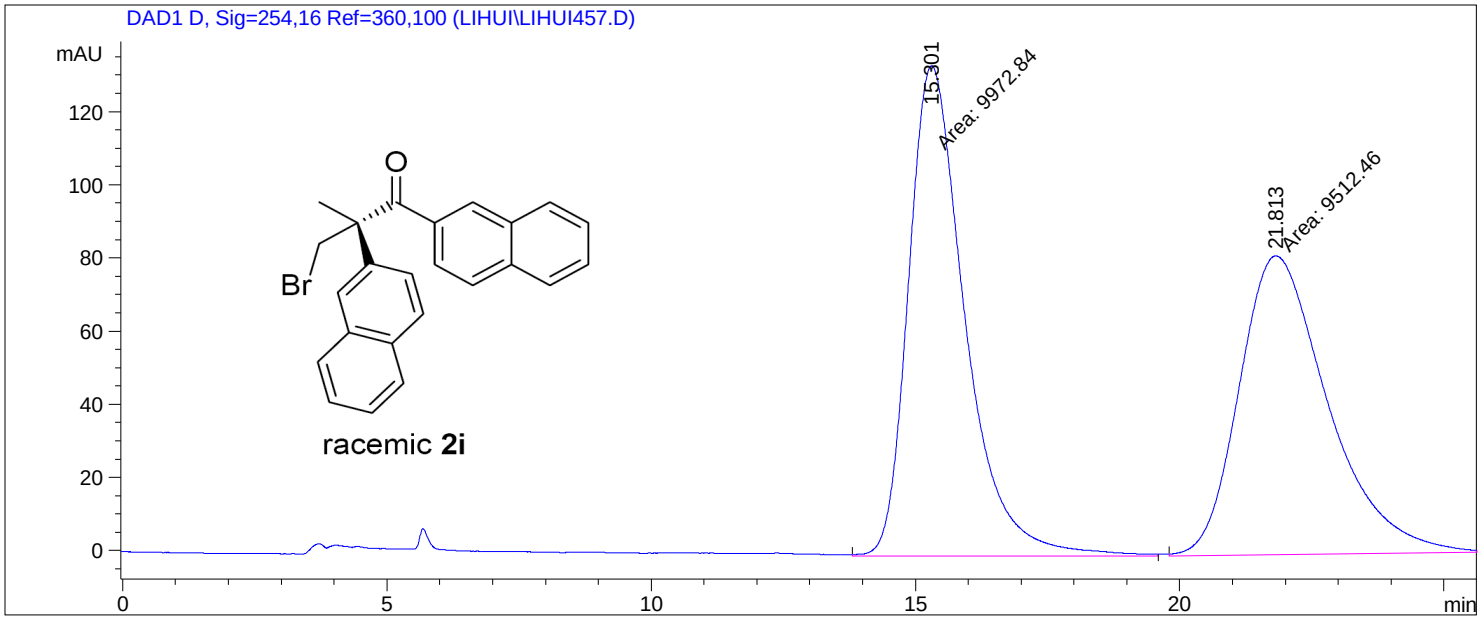
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.618	PV	0.2604	971.72626	57.72239	4.7982
2	7.245	VB	0.3221	1.92800e4	913.88397	95.2018



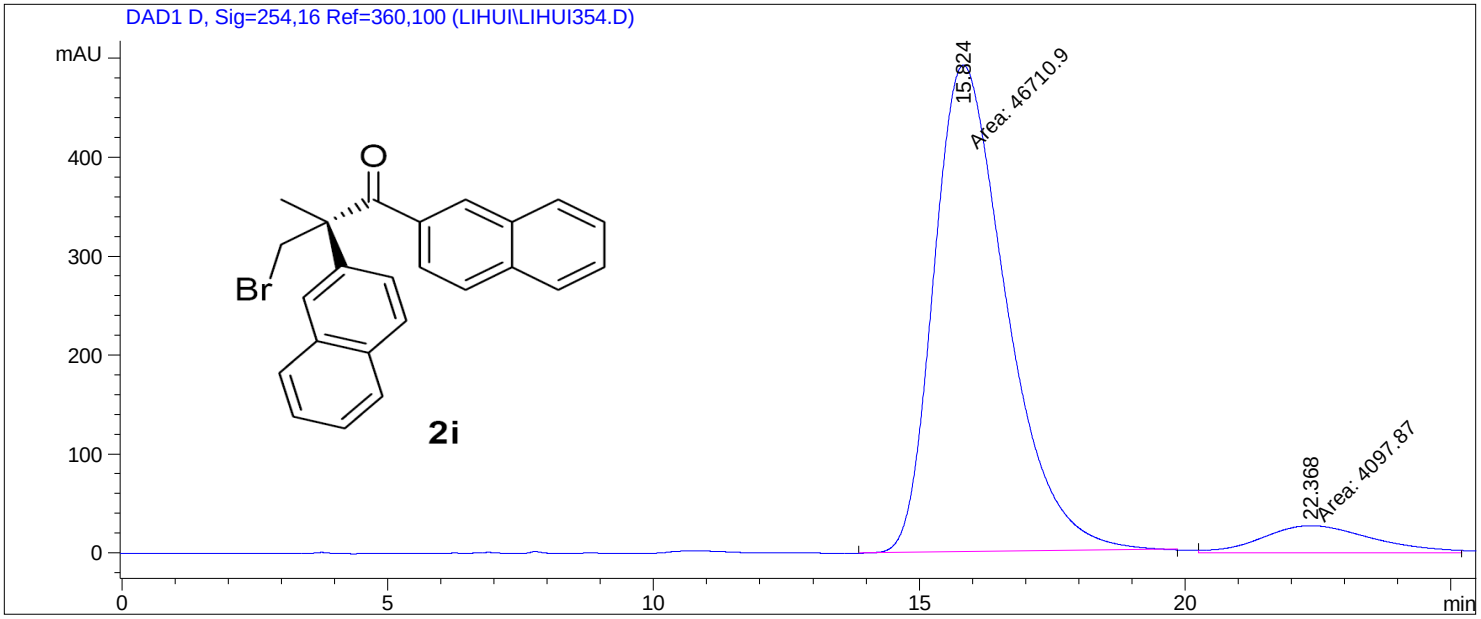
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.299	BB	0.1496	7615.00586	768.51080	49.9776
2	7.615	BB	0.1844	7621.82764	633.49261	50.0224



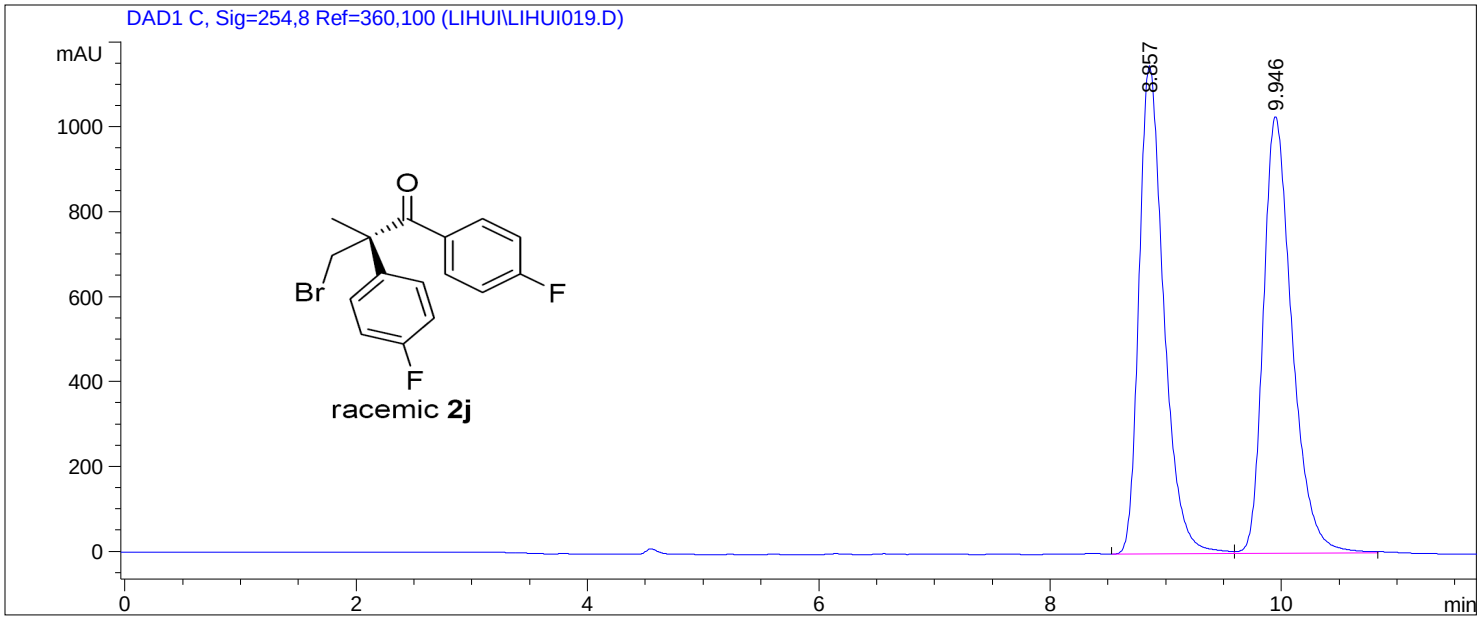
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.285	VB	0.2164	3.36138e4	2444.36108	91.4947
2	7.606	BB	0.1858	3124.71143	257.15173	8.5053



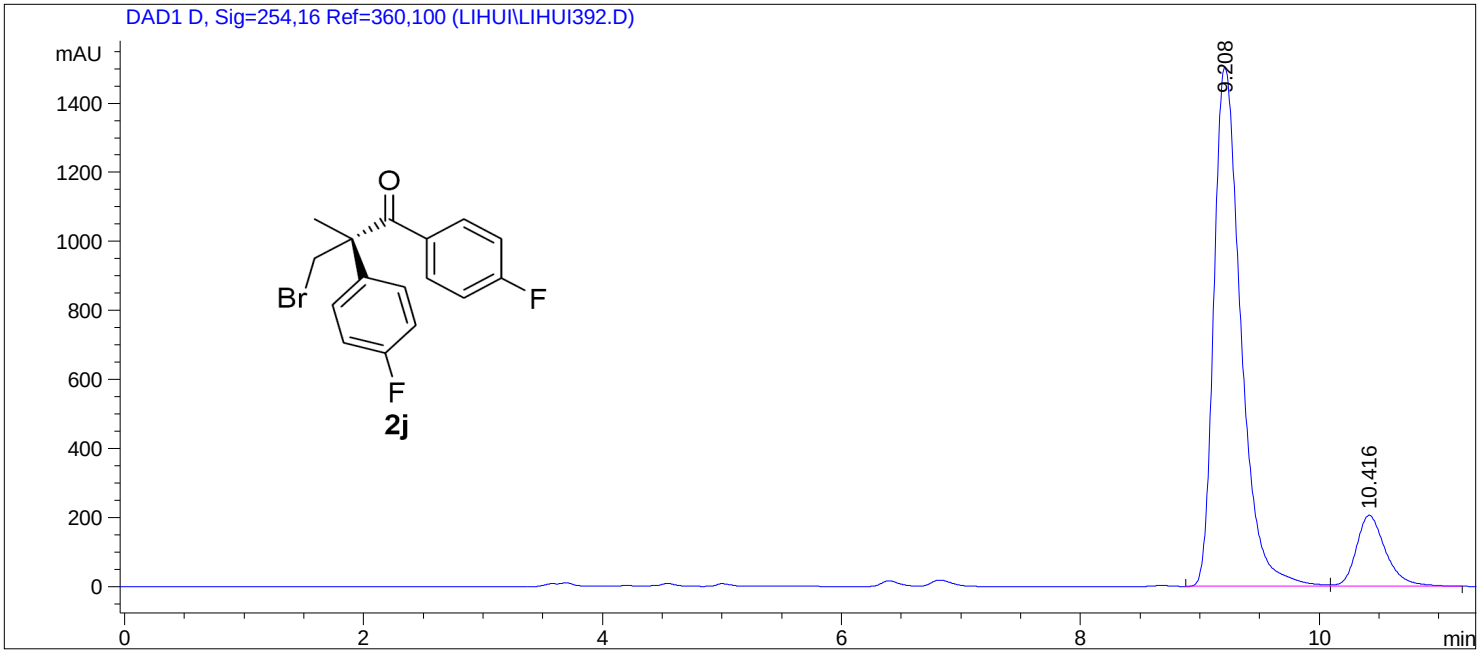
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.301	MM	1.2406	9972.84375	133.97377	51.1814
2	21.813	MM	1.9408	9512.45801	81.69024	48.8186



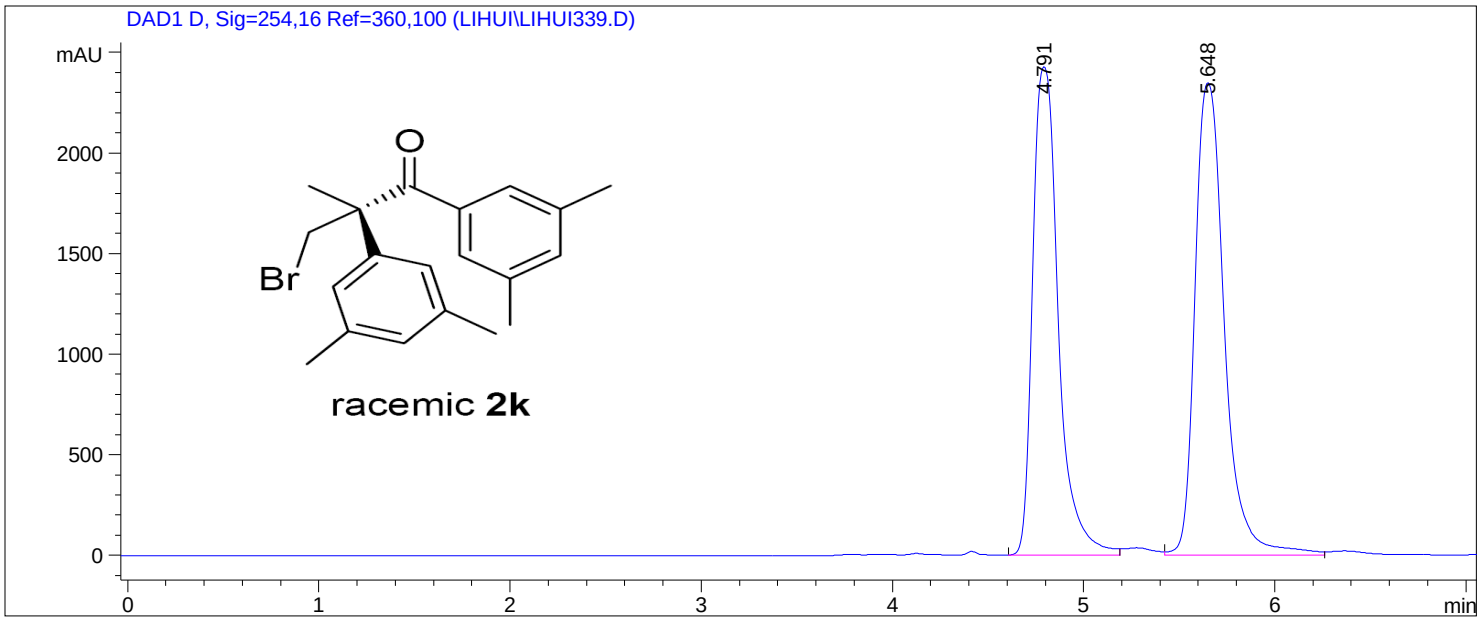
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.824	MM	1.5821	4.67109e4	492.07779	91.9347
2	22.368	MM	2.4597	4097.87012	27.76657	8.0653



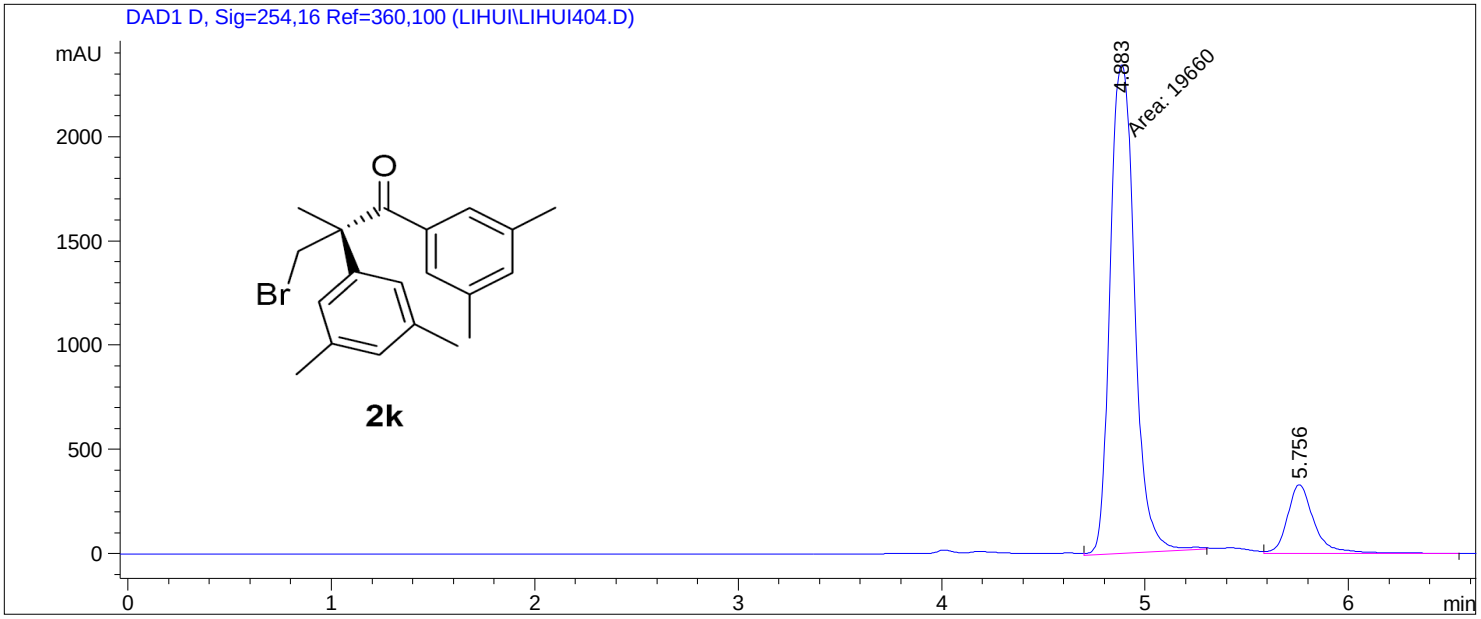
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.857	VV	0.2280	1.71452e4	1149.85645	49.0739
2	9.946	VB	0.2618	1.77923e4	1028.76538	50.9261



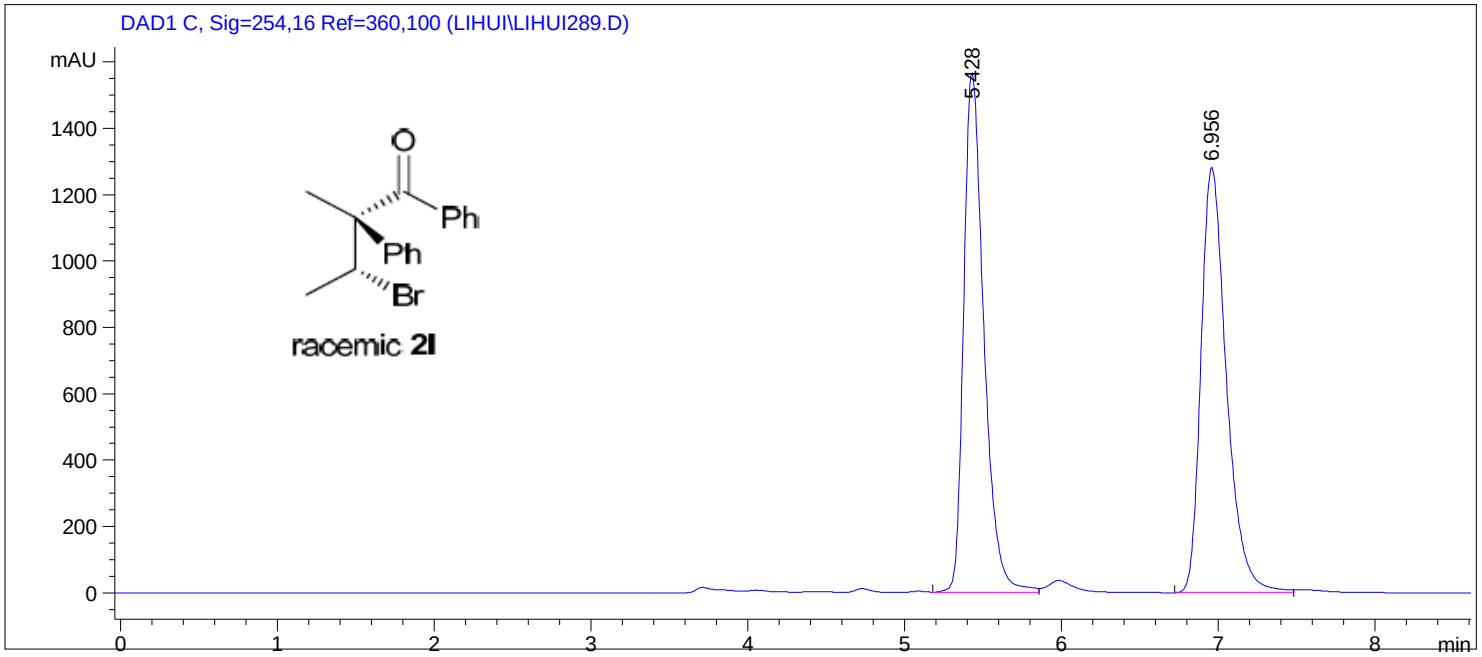
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.208	VV	0.2413	2.36595e4	1505.88220	86.9668
2	10.416	VB	0.2603	3545.72510	206.52577	13.0332



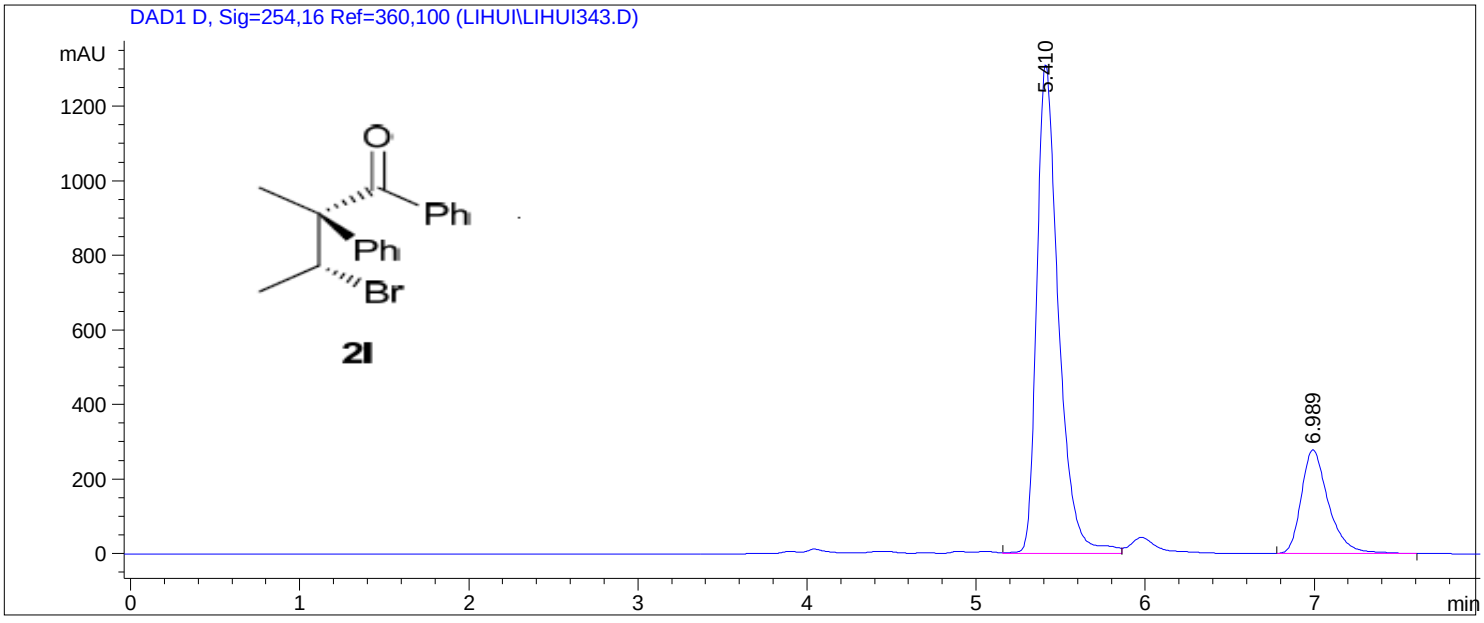
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.791	BV	0.1467	2.26282e4	2429.71118	47.3787
2	5.648	VV	0.1667	2.51321e4	2350.40796	52.6213



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.883	MM	0.1397	1.96600e4	2345.02441	86.1028
2	5.756	VV	0.1436	3173.18481	331.57880	13.8972



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.428	VV	0.1368	1.40702e4	1566.41455	49.3283
2	6.956	PV	0.1695	1.44534e4	1282.56238	50.6717



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.410	VV	0.1346	1.17753e4	1312.86401	78.9564
2	6.989	BB	0.1693	3138.35840	278.83051	21.0436