Multifunctional 1,3-diphenylguanidine for carboxylative cyclization of homopropargyl amines with CO_2 under ambient temperature and pressure

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Contents

1. General information

Reactions were monitored by thin layer chromatography using UV light, I_2 or $KMnO_4$ to visualize the course of reaction. Purification of reaction products was carried out by flash chromatography on silica gel. Chemical yields refer to pure isolated substances. Infrared (IR) spectra were obtained using a Bruker tensor 27 infrared spectrometer. Chiral HPLC analysis was performed on a LC-20AD instrument using Daicel Chiracel columns at 25 °C and a mixture of HPLC-grade hexane and isopropanol as eluent. Optical rotation was measured using a (JASCO) P-1030 polarimeter equipped with a sodium vapor lamp at 589 nm. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were obtained using Bruker DPX-300, 400 and 500 MHz Spectrometer. ^{1}H-^{1}H NOESY spectra were obtained using Bruker DPX-500 MHz Spectrometer. Chemical shifts were reported in ppm with TMS as the internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet, br = broad.

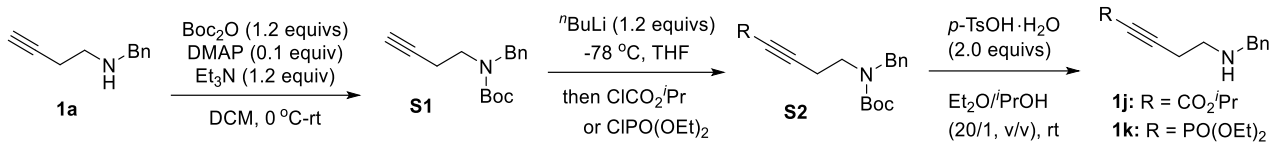
$AgSbF_6$ (99%) was purchased from Alfa, 1,3-diphenylguanidine was purchased from J&K Scientific. Dichloroethane was purchased from J&K Scientific and used without further purification. The homopropargyl amines **1a-i** and **1l-m** were synthesized according to the literature method.[1]

List of abbreviation:

Entry	Chemical name	Abbreviation
1	1,3-Diphenylguanidine	DPG
2	1,2,3-Triphenylguanidine	TPG
3	1,1,3,3-Tetramethylguanidine	TMG
4	1,8-Diazabicyclo[5.4.0]undec-7-ene	DBU
5	1,5,7-Triazabicyclo[4.4.0]dec-5-ene	TBD
6	Petroleum ether	PE
7	Diethyl ether	Et_2O
8	*N*, *N*-Dimethyl formamide	DMF
9	Ethyl acetate	EtOAc
10	Dichloroethane	DCE

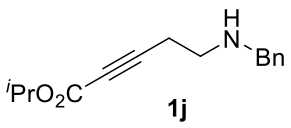
2. Preparation of homopropargyl amines

2.1. Synthesis of homopropargyl amines 1j and 1k.[1-2]

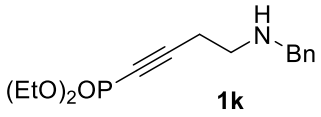


Di-tert-butyldicarbonate (12.0 mmol) was slowly added to a solution of homopropargyl amines (10.0 mmol), DMAP (1.2 mmol, 10 mol%) and Et_3N (12 mmol) in 20 mL CH_2Cl_2 at 0 °C and the resulting mixture was stirred at ambient temperature for 24 h. Standard extractive work-up followed by silica column chromatography (PE/EtOAc 15:1 to 10:1, v/v) provided tert-butyl benzyl(but-3-yn-1-yl)carbamate **S1** as a pale yellow syrup in 85% yield.

^{n}BuLi (1.2 equivs, 2.0 M in hexane) was slowly added at -78 °C to a solution of the compound **S1** obtained above (5.0 mmol) in 15 mL Et_2O. After the mixture had been stirred for 30 min at that temperature, isopropyl carbonochloridate or diethyl phosphorochloridate (6.0 mmol, 1.2 equivs) was introduced, and stirring was continued for another 15 min at -78 °C before the mixture was allowed to reach ambient temperature. After one hour, the reaction was quenched with saturated ammonium chloride aqueous solution, the aqueous layer was extracted with EtOAc, and the combined organic phases were dried over Na_2SO_4. Evaporation of the solvent followed by column chromatography of the residue (PE/EtOAc 10:1 to 4:1, v/v) gave the title compound **1j** or **1k**.



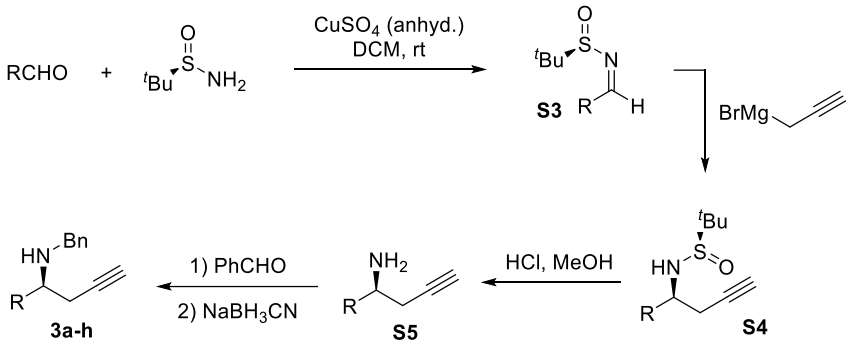
Compound **1j** was prepared in 78% yield according to the general procedure as yellow solid (m.p. 80-82 °C). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 3H), 7.28-7.26 (m, 2H), 5.12-5.03 (m, 1H), 3.82 (s, 2H), 2.86 (t, J = 6.4 Hz, 2H), 2.54 (t, J = 6.4 Hz, 2H), 1.63 (s, br, 1H), 1.29 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.17, 139.84, 128.42, 128.04, 127.04, 86.64, 74.45, 69.72, 53.24, 46.45, 21.64, 19.96; IR (ATR) ν 2977.0, 2932.8, 2236.8, 1704.7, 1495.2, 1417.8, 1369.9, 1256.9, 1225.6, 910.6 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{15}H_{20}NO_2$ $[M+H]^+$: 246.1489, found: 246.1494.



1k

Compound **1k** was prepared in 56% yield according to the general procedure as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.27 (m, 5H), 4.17-4.09 (m, 4H), 3.81 (s, 2H), 2.86 (t, *J* = 6.8 Hz, 2H), 2.57-2.53 (m, 2H), 1.60 (s, br, 1H), 1.35 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.76, 128.42, 128.00, 127.07, 100.75 (d, *J* = 52.5 Hz), 71.71 (d, *J* = 299.5 Hz), 62.93 (d, *J* = 5.4 Hz), 53.26, 46.39 (d, *J* = 2,4 Hz), 20.56 (d, *J* = 4.4 Hz), 16.05 (d, *J* = 7.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ 6.55 (m); IR (ATR) ν 2982.4, 2203.8, 1716.1, 1568.8, 1453.5, 1367.8, 1251.4, 1163.6, 1099.3, 741.4 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{15}H_{23}NO_3P$ $[M+H]^+$: 296.1410, found: 296.1404.

2.2. Synthesis of compounds 3a-3h.[3]

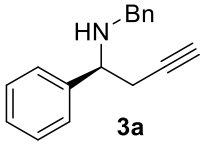


To a solution of (*R*)-tert-butanesulfinamide (10.0 mmol) in 20 mL CH_2Cl_2 was added anhydrous $CuSO_4$ (22.0 mmol) followed by aldehyde (11.0 mmol). The mixture was stirred at room temperature for 12 h. The reaction mixture was filtered through a pad of Celite, and the filter cake was washed well with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated give sulfinimine **S3** in almost quantative yield.

To a solution of the sulfinimine **S3** (10.0 mmol) in 50 mL CH_2Cl_2 was added propargyl magnesium bromide ether solution (20.0 mmol) at -50 ºC. The mixture was stirred at -50 ºC for 2 h and then was allowed to warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated ammonium chloride aqueous solution and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified through silica column chromatography (PE/EtOAc 6/1 to 4/1, v/v) to give sulfinamide **S4** in 75-83% yield.

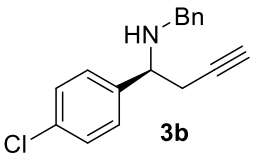
The above sulfinamide **S4** (5.0 mmol) was dissolved in 50 mL MeOH and the solution was cooled to 0 ºC. Concentrated hydrochloric acid (11.0 mmol, 2.2 equivs) was added, and the reaction mixture was stirred at 0 ºC for 30 minutes. The solvent was evaporated, water was added and acid base work up to give pure amine **S5** in more than 90% yield.

To a mixture of benzaldehydes (4.0 mmol) in 10 mL methanol, the amine **S5** (4.0 mmol) was added. The reaction mixture was stirred at room temperature for 3-4 h, and then sodium cyanoborohydride (3.0 mmol, 0.75 equiv) was added in batches and the mixture was further stirred for another period of 6 h. The reaction was then quenched by the addition of water, and washed with diethyl ether (5 mL× 3). The combined organic phases were washed with saturated aqueous NaCl (10 mL), dried over Na_2SO_4, and filtered. Evaporation of the filtrate followed by flash chromatography of the residue (PE/EtOAc 10:1 to 4:1, v/v) gave compounds **3a-3h** successfully.



3a

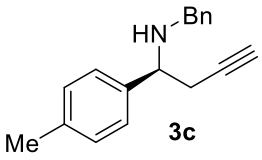
Compound **3a** was prepared in 80% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel OJ-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 10.65 min, t_r (minor) = 13.41 min) gave the isomeric composition of the product: 96% ee; $[\alpha]_D^{25}$ = -39.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.39 (m, 2H), 7.38-7.34 (m, 2H), 7.32-7.31 (m, 4H), 7.29-7.26 (m, 2H), 3.87 (t, *J* = 6.8 Hz, 1H), 3.72, 3.59 (AB, *J* = 13.2 Hz, 2H), 2.56-2.54 (m, 2H), 2.03-2.01 (m, 1H), 1.88 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.33, 140.15, 128.39, 128.26, 127.98, 127.44, 127.07, 126.80, 81.44, 70.48, 60.58, 51.25, 28.08; IR (ATR) ν 3290.3, 3061.6, 3026.4, 2918.4, 1602.4, 1493.5, 1355.5, 1201.3, 1073.5, 911.4 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{18}N$ $[M+H]^+$: 236.1434, found: 236.1445.



3b

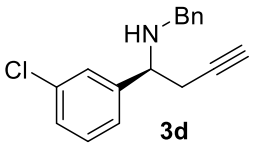
Compound **3b** was prepared in 80% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel OJ-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 9.37 min, t_r (minor) = 10.37 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -97.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.32 (m, 4H), 7.31-7.29 (m, 2H), 7.27-7.22 (m, 3H), 3.83 (t, *J* = 6.4 Hz, 1H), 3.68, 3.55 (AB, *J* = 13.6 Hz, 2H), 2.51-2.48 (m, 2H), 2.02-2.00 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

140.95, 140.00, 133.12, 128.64, 128.55, 128.39, 128.01, 126.98, 81.08, 70.74, 60.03, 51.30, 28.13; IR (ATR) ν 3297.6, 3026.5, 2909.6, 2834.2, 2117.7, 1598.1, 1453.7, 1327.7, 1295.3, 1027.1 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{17}ClN$ $[M+H]^+$: 270.1044, found: 270.1032.



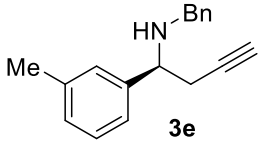
3c

Compound **3c** was prepared in 76% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 1/99, 0.8 mL/min, 230 nm; t_r (major) = 9.89 min, t_r (minor) = 11.15 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -75.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.28 (m, 4H), 7.26-7.25 (m, 2H), 7.23-7.20 (m, 1H), 7.16-7.13 (m, 2H), 3.82 (t, *J* = 6.4 Hz, 1H), 3.69, 3.55 (AB, *J* = 13.2 Hz, 2H), 2.52-2.49 (m, 2H), 2.33 (s, 3H), 2.04 (s, br, 1H), 1.99-1.97 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.31, 139.40, 137.02, 129.12, 128.28, 128.02, 127.00, 126.80, 81.63, 70.38, 60.35, 51.28, 28.20, 21.07; IR (ATR) ν 3290.0, 3025.3, 2920.1, 1602.7, 1495.1, 1453.3, 1304.9, 1201.0, 1020.2, 908.3 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N$ $[M+H]^+$: 250.1590, found: 250.1594.



3d

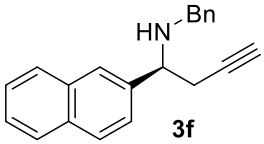
Compound **3d** was prepared in 73% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 1/99, 0.5 mL/min, 230 nm; t_r (major) = 16.78 min, t_r (minor) = 18.23 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -44.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.35-7.31 (m, 2H), 7.30 (s, 2H), 7.28-7.26 (m, 4H), 3.84 (t, *J* = 6.8 Hz, 1H), 3.71, 3.58 (AB, *J* = 13.2 Hz, 2H), 2.58-2.46 (m, 2H), 2.09-1.97 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.68, 139.94, 134.37, 129.72, 128.39, 128.01, 127.70, 127.27, 126.98, 125.39, 80.96, 70.82, 60.27, 51.36, 28.06; IR (ATR) ν 3290.0, 3025.3, 2920.1, 1602.7, 1495.1, 1453.3, 1304.9, 1201.0, 1020.2, 908.3 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{17}ClN$ $[M+H]^+$: 270.1044, found: 270.1039.



3e

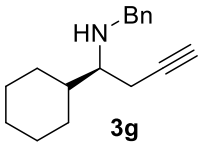
Compound **3e** was prepared in 66% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel OJ-H, ^{i}PrOH/hexane = 10/90, 1.0 mL/min, 230 nm; t_r (major) = 7.29 min, t_r (minor) = 9.29 min) gave the

isomeric composition of the product: 97% ee; $[\alpha]_D^{25}$ = -5.7 (c = 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.28 (m, 4H), 7.24-7.22 (m, 2H), 7.20-7.17 (m, 2H), 7.10 (d, *J* = 7.2 Hz, 1H), 3.83 (t, *J* = 6.4 Hz, 1H), 3.71, 3.58 (AB, *J* = 13.2 Hz, 2H), 2.54-2.52 (m, 2H), 2.36 (s, 3H), 2.02-2.01 (m, 1H), 1.90 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.31, 140.21, 137.86, 128.23, 128.21, 128.16, 127.93, 127.64, 126.74, 124.12, 81.53, 70.39, 60.59, 51.27, 28.06, 21.37; IR (ATR) ν 3291.0, 2928.2, 2836.7, 1606.1, 1488.9, 1323.8, 1269.9, 1155.2, 1027.5, 882.7 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{20}N$ $[M+H]^+$: 250.1590, found: 250.1582.



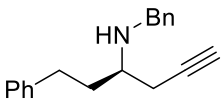
3f

Compound **3f** was prepared in 77% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 1/99, 0.8 mL/min, 230 nm; t_r (major) = 11.18 min, t_r (minor) = 16.02 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -78.0 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.86-7.82 (m, 4H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.50-7.44 (m, 2H), 7.34-7.30 (m, 3H), 7.28-7.26 (m, 2H), 4.04 (t, *J* = 6.8 Hz, 1H), 3.74, 3.61 (AB, *J* = 13.2 Hz, 2H), 2.64-2.61 (m, 2H), 2.03-1.90 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.16, 139.82, 133.29, 133.04, 128.30, 128.27, 128.00, 127.77, 127.60, 126.84, 126.21, 125.95, 125.66, 124.88, 81.44, 70.62, 60.74, 51.32, 28.05; IR (ATR) ν 3291.1, 3055.8, 3025.2, 2827.3, 1600.7, 1507.1, 1495.0, 1362.1, 1270.4, 1198.9 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{21}H_{20}N$ $[M+H]^+$: 286.1590, found: 286.1585.



3g

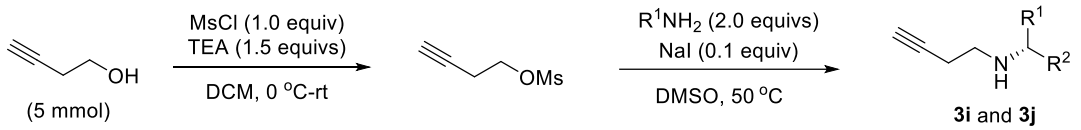
Compound **3g** was prepared in 80% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 3/97, 0.8 mL/min, 230 nm; t_r (major) = 5.44 min, t_r (minor) = 10.84 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = +58.2 (c = 0.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.36-7.35 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.21 (m, 1H), 3.88, 3.72 (AB, *J* = 13.2 Hz, 2H), 2.52-2.43 (m, 2H), 2.35-2.30 (m, 1H), 2.03-1.97 (m, 1H), 1.90 (d, *J* = 12.8 Hz, 1H), 1.73-1.64 (m, 3H), 1.59-1.50 (m, 2H), 1.34-1.11 (m, 4H), 1.06-0.93 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.78, 128.26, 128.12, 126.78, 82.23, 69.89, 60.21, 51.49, 40.76, 29.39, 29.29, 26.62, 26.45, 20.49; IR (ATR) ν 3306.8, 3026.8, 2921.0, 2850.1, 2115.2, 1494.8, 1345.4, 1240.3, 1115.7, 1073.8 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{17}H_{24}N$ $[M+H]^+$: 242.1903, found: 242.1894.



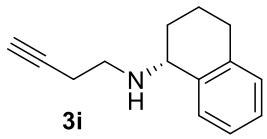
3h

Compound **3h** was prepared in 80% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 20/80, 0.7 mL/min, 230 nm; t_r (major) = 6.26 min, t_r (minor) = 8.75 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = +21.2 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.31 (m, 4H), 7.29-7.27 (m, 3H), 7.19-7.17 (m, 3H), 3.86, 3.74 (AB, *J* = 12.8 Hz, 2H), 2.82-2.76 (m, 1H), 2.73-2.69 (m, 2H), 2.55-2.48 (m, 1H), 2.40-2.33 (m, 1H), 2.02-2.00 (m, 1H), 1.94-1.80 (m, 2H), 1.58 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.09, 140.44, 128.34, 128.30, 128.11, 126.88, 125.72, 81.25, 70.42, 54.57, 50.73, 35.70, 32.13, 23.31; IR (ATR) ν 3292.2, 3025.4, 2922.9, 1602.1, 1494.7, 1453.2, 1116.1, 1071.2, 1028.2, 908.4 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{19}H_{22}N$ $[M+H]^+$: 264.1747, found: 264.1739.

2.3. Preparation of compounds 3i and 3j.

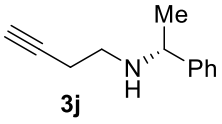


3-Butyn-1-ol (5.0 mmol) was dissolved with in 70 mL dichloromethane, followed by the addition of triethylamine (7.5 mmol) and methanesulfonyl chloride (6.0 mmol) at 0°C. The reaction mixture was allowed to stir at 0°C for 1 hour and then quenched with 1N aqueous HCl (25 mL). The phases were separated and the aqueous layer extracted with dichloromethane (3 x 15 mL). The organic layers were then washed with brine, dried on Na_2SO_4 and the solvent was removed under reduced pressure to give the crude mesylate, which was further dissolved in 10 mL DMSO. Then (*R*)-1-aminotetralinand or (*R*)-1-phenylethylamine (10 mmol) and sodium iodide (1.0 mmol) were added, and the reaction mixture was stirred at 50°C for 16 hours. The solution was then cooled to room temperature and diluted with saturated aqueous $NaHCO_3$ (50 mL) and ethyl acetate (50 mL) The phases were separated, and the aqueous layer extracted with ethyl acetate (3 x 20 mL), dried with Na_2SO_4, and concentrated under reduced pressure. The residue was subjected to column chromatography using PE/EtOAc (10:1 to 4:1, v/v) as the elution to afford the desired **3i** and **3j**.



3i

Compound **3i** was prepared in 80% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 5/95, 0.5 mL/min, 230 nm; t_r (major) = 10.68 min, t_r (minor) = 9.66 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -9.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.36 (m, 1H), 7.18-7.14 (m, 2H), 7.09-7.07 (m, 1H), 3.81 (t, *J* = 5.2 Hz, 1H), 2.95-2.79 (m, 3H), 2.76-2.69 (m, 1H), 2.50-2.36 (m, 2H), 2.03-1.91 (m, 2H), 1.89-1.83 (m, 2H), 1.78-1.69 (m, 1H), 1.58 (s, br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.90, 137.30, 128.96, 128.61, 126.59, 125.65, 82.65, 69.40, 54.86, 45.34, 29.25, 28.28, 19.89, 18.89; IR (ATR) ν 3292.0, 2930.6, 2855.3, 1488.2, 1320.3, 1271.0, 1197.4, 1035.1, 945.1, 883.2 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{14}H_{18}N$ $[M+H]^+$: 200.1434, found: 200.1429.

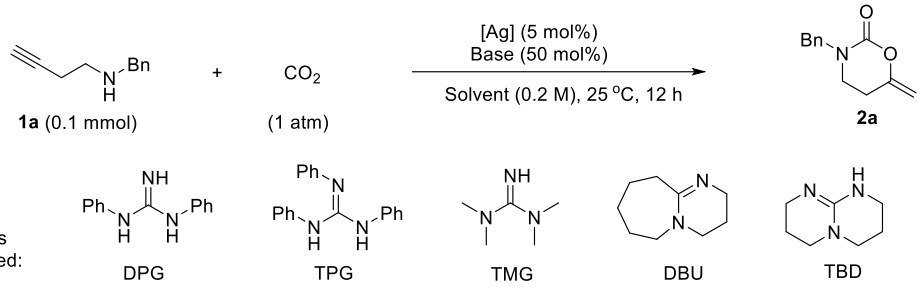


3j

Compound **3j** was prepared in 87% yield according to the general procedure as yellow oil. HPLC analysis (Chiralcel OJ-H, ^{i}PrOH/hexane = 0.5/99.5, 0.8 mL/min, 230 nm; t_r (major) = 12.77 min, t_r (minor) = 16.34 min) gave the isomeric composition of the product: 97% ee; $[\alpha]_D^{25}$ = +43.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.31 (m, 4H), 7.25-7.22 (m, 1H), 3.80 (q, *J* = 6.4 Hz, 1H), 2.69-2.57 (m, 2H), 2.36-2.32 (m, 2H), 1.98-1.97 (m, 1H), 1.66 (s, br, 1H), 1.36 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.37, 128.41, 126.91, 126.54, 82.53, 69.43, 57.68, 45.68, 24.38, 19.59; IR (ATR) ν 3293.5, 2961.0, 2923.7, 2842.5, 1602.3, 1492.3, 1369.6, 1283.6, 1198.8, 1079.7 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{12}H_{16}N$ $[M+H]^+$: 174.1277, found: 174.1266.

3. Reaction condition optimization

Table S1. Carboxylative Cyclization Reaction.



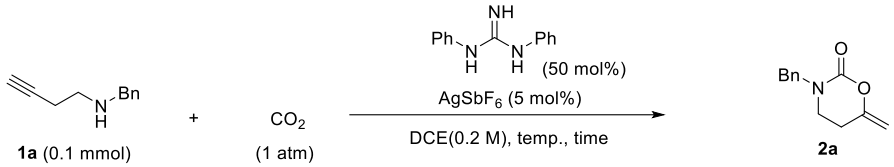
Entry	[Ag]	Base	Solvent	Yield (%)[a]
1	AgOBz	DPG	DCE	69
2	AgOBz	TPG	DCE	35
3	AgOBz	TMG	DCE	37
4	AgOBz	DBU	DCE	46
5	AgOBz	TBD	DCE	40
6	AgOBz	GBIG	DCE	no reaction
7	AgOAc	DPG	DCE	66
8	AgTFA	DPG	DCE	82
9	AgOTf	DPG	DCE	89
10	$AgClO_4 \cdot H_2O$	DPG	DCE	80
11	$AgSbF_6$	DPG	DCE	91
12	$AgSbF_6$	DPG	CH_3CN	37
13	$AgSbF_6$	DPG	DMF	6
14	$AgSbF_6$	DPG	Acetone	45
15	$AgSbF_6$	DPG	Toluene	43
16	--	DPG	DCE	no reaction
17	$AgSbF_6$	--	DCE	no reaction

[a] Determined by GC-MS with decane as internal standard.

The reaction of *N*-benzyl amine **1a** and CO_2 was undertaken for the evaluation. The reactions were run at 25 °C in 1,2-dichloroethane (DCE), with CO_2 held within a balloon. To our delight, under the catalysis of 5 mol% AgOBz and 50 mol% DPG, the reaction worked well to give the desired 2-oxazinone **2a** in 69% yield (entry 1, Table S1). Next, the performance of other types of organic bases was studied. The use of analogous 1,2,3-triphenylguanidine (TPG) and 1,1,3,3-tetramethylguanidine (TMG) resulted in a greatly diminished 35% and 37% yield for **2a**,

respectively (entries 2-3). The commonly used base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), showed inferior 46% and 40% yield respectively (entry 4-5). The performance of GBIG[4] (entry 6) was also studied, but no reaction occurred. Considering the metal counterions are of critical importance in impacting the catalytic activity, different silver salts with the combination of DPG was evaluated and $AgSbF_6$ was found to be the most efficient one, giving **2a** in 91% yield (entries 7-11). Further screening of solvents, including CH_3CN, DMF, acetone and toluene, failed to improve the result (entries 12-15). In the apsence of silver salt or DPG, no reaction occurred at all (entries 16-17).

Table S2. The influence of CO_2 pressure and reaction temperature.



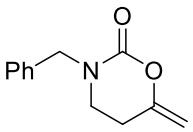
Entry	CO_2 (MPa)	Temp. (^oC)	Time (h)	Isolated yield (%)
1	0.1	25	6	47
2	1.0	25	6	59
3	0.1	50	6	62
4	1.0	50	6	91
5	0.1	25	12	91

The influence of CO_2 pressure or reaction temperature was studied. It was found that if the reaction was carried out under higher 50 ^oC or 10 atm of CO_2, instead of ambient temperature and pressure, for 6 hours, the reaction yield increased from 47% to 59% and 62% respectively (entries 2-3 vs 1, Table S2). In addition, 91% yield could be obtained under 50 ^oC and 10 atm of CO_2 simultaneously (entry 4). However, the same result could also be achieved by prolong the reaction time to 12 hours under ambient temperature and pressure (entry 5). These results indicated that, indeed, the higher temperature and pressure could improve the efficiency of carboxylative cyclization to some extent, but the reaction performed under such conditions should be net CO_2 emitter rather than consumer, since the rising of CO_2 pressure and temperature would result indirect production of additional CO_2. In this context, we prefer to develop the carboxylative cyclization of CO_2 at ambient temperature and pressure, and obviously, under such situation DPG has a distinct advantage than other ones.

4. General procedure for the carboxylative cyclization reaction.

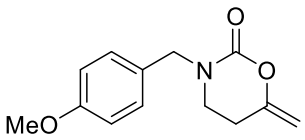
1 or **3** (0.3 mmol) (1 atm) **2** or **4**

To a 5.0 mL vial were added $AgSbF_6$ (5.1 mg, 0.015 mmol), DPG (31.7 mg, 0.15 mmol), **1** or **3** (0.3 mmol) and 1.5 mL of DCE, then the resulting solution was stirred under CO_2 atmosphere (1 atm) at 25 °C till full consumption of **1** or **3** by TLC analysis. The residue was directly subjected to column chromatography by using PE/EtOAc (from 4/1 to 2/1, v/v) as the eluent, affording the desired products **2** or **4**. The reaction of homopropargyl amine **2l** was performed under 10 atm CO_2 at 50 °C, and IPrAuCl (10 mol%) was used instead of $AgSbF_6$ (5 mol%).



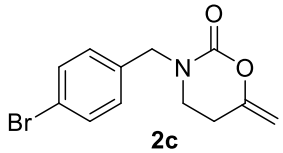
2a

Product **2a**[5] was obtained in 89% yield as light yellow solid (m.p. 70-72 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H), 7.31-7.28 (m, 3H), 4.66 (d, J = 1.6 Hz, 1H), 4.58 (s, 2H), 4.23 (d, J = 1.6 Hz, 1H), 3.21 (t, J = 2.0 Hz, 2H), 2.54 (t, J = 2.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.58, 151.05, 135.96, 128.62, 127.87, 127.72, 92.67, 52.52, 43.00, 25.97.



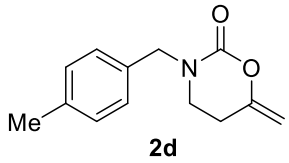
2b

Product **2b**[5] was obtained in 89% yield as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24-7.22 (m, 2H), 6.89-6.86 (m, 2H), 4.65 (d, J = 1.6 Hz, 1H), 4.51 (s, 2H), 4.22 (d, J = 1.6 Hz, 1H), 3.80 (s, 3H), 3.19 (t, J = 6.0 Hz, 2H), 2.52 (t, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.26, 152.68, 151.07, 129.50, 128.14, 114.07, 92.69, 55.25, 52.07, 42.82, 26.12.



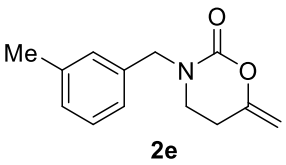
2c

Product **2c**[5] was obtained in 92% yield as light yellow solid (m.p. 65-67 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.46 (m, 2H), 7.19-7.17 (m, 2H), 4.68 (d, J = 1.6 Hz, 1H), 4.53 (s, 2H), 4.25 (d, J = 1.6 Hz, 1H), 3.20 (t, J = 6.0 Hz, 2H), 2.55 (t, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.40, 150.99, 135.11, 131.77, 129.65, 121.72, 92.98, 52.02, 43.17, 25.99.



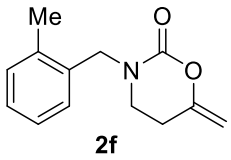
2d

Product **2d** was obtained in 90% yield as light yellow solid (m.p. 77-79 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20-7.18 (m, 2H), 7.16-7.14 (m, 2H), 4.65 (d, *J* = 1.6 Hz, 1H), 4.54 (s, 2H), 4.22 (d, *J* = 1.6 Hz, 1H), 3.19 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.67, 151.04, 137.49, 132.96, 129.32, 127.99, 92.58, 52.29, 42.87, 26.05, 21.00; IR (ATR) ν 2920.0, 1712.3, 1662.3, 1514.7, 1483.4, 1357.0, 1313.4, 1253.7, 1097.3, 999.0 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$: 240.0995, found: 240.0989.



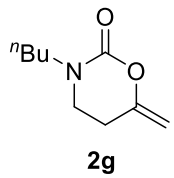
2e

Product **2e** was obtained in 91% yield as light yellow solid (m.p. 71-73 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.21 (m, 1H), 7.12-7.07 (m, 3H), 4.66 (d, *J* = 1.6 Hz, 1H), 4.54 (s, 2H), 4.23 (d, *J* = 1.6 Hz, 1H), 3.21 (t, *J* = 6.4 Hz, 2H), 2.54 (t, *J* = 6.4 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.66, 151.05, 138.39, 135.92, 128.65, 128.50, 125.00, 92.61, 52.53, 42.97, 26.03, 21.25; IR (ATR) ν 2919.0, 1711.3, 1607.9, 1483.6, 1354.7, 1298.7, 1254.3, 1107.5, 1053.7, 955.8 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$: 240.0995, found: 240.0990.



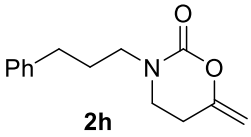
2f

Product **2f** was obtained in 86% yield as light yellow solid (m.p. 80-83 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.23-7.18 (m, 3H), 7.17-7.14 (m, 1H), 4.67 (d, *J* = 1.6 Hz, 1H), 4.62 (s, 2H), 4.24 (d, *J* = 1.6 Hz, 1H), 3.14 (t, *J* = 6.0 Hz, 2H), 2.55 (t, *J* = 6.0 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): 152.56, 150.79, 136.56, 133.43, 130.60, 128.12, 127.78, 126.04, 92.62, 50.41, 42.77, 26.00, 19.00; IR (ATR) ν 2925.8, 1707.8, 1666.6, 1484.3, 1380.3, 1329.6, 1246.8, 1177.0, 1095.1, 993.1 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$: 240.0995, found: 240.0988.

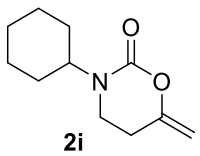


2g

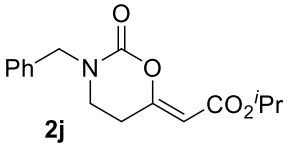
Product **2g**[5] was obtained in 66% yield as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (s, 1H), 4.19 (s, 1H), 3.33 (t, *J* = 7.2 Hz, 2H), 3.27 (t, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 6.4 Hz, 2H), 1.57-1.50 (m, 2H), 1.35-1.26 (m, 2H), 0.90 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.78, 150.57, 92.26, 49.37, 43.87, 29.17, 26.20, 19.79, 13.70.



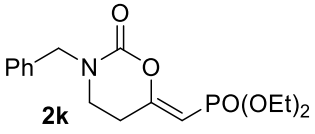
Product **2h** was obtained in 74% yield as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (m, 2H), 7.22-7.18 (m, 3H), 4.62 (d, *J* = 1.6 Hz, 1H), 4.22 (d, *J* = 2.0 Hz, 1H), 3.41 (t, *J* = 7.6 Hz, 2H), 3.25 (t, *J* = 6.4 Hz, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.53 (t, *J* = 6.0 Hz, 2H), 1.96-1.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.64, 150.59, 141.13, 128.33, 128.12, 125.89, 92.37, 49.28, 43.87, 32.85, 28.59, 26.07; IR (ATR) ν 3025.8, 2925.8, 1712.8, 1602.5, 1484.2, 1344.3, 1255.4, 1174.2, 1081.0, 981.4 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{14}H_{17}NNaO_2$ $[M+Na]^+$: 254.1151, found: 254.1146.



Product **2i** was obtained in 40% yield as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.61 (d, *J* = 1.6 Hz, 1H), 4.19-4.11 (m, 2H), 3.22 (t, *J* = 6.4 Hz, 2H), 2.54 (t, *J* = 6.0 Hz, 2H), 1.82-1.76 (m, 4H), 1.68-1.61 (m, 2H), 1.44-1.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.60, 150.48, 91.72, 55.73, 38.25, 29.63, 26.51, 25.46, 25.37; IR (ATR) ν 2927.3, 2854.7, 1707.8, 1658.6, 1481.0, 1373.6, 1347.0, 1254.6, 1092.8, 986.5 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{11}H_{17}NNaO_2$ $[M+Na]^+$: 218.1151, found: 218.1145.

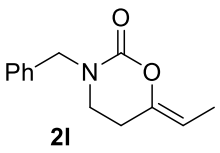


Product **2j** was obtained in 54% yield as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H), 7.32-7.28 (m, 3H), 5.11-5.03 (m, 1H), 5.00 (s, 1H), 4.59 (s, 2H), 3.25 (t, *J* = 6.4 Hz, 2H), 2.57-2.54 (m, 2H), 1.26 (d, *J* = 6.4 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.95, 157.65, 149.10, 135.54, 128.76, 128.11, 128.00, 99.20, 67.38, 52.88, 41.89, 30.81, 27.31, 21.77; IR (ATR) ν 2981.2, 2929.9, 1728.3, 1715.5, 1652.2, 1540.0, 1485.7, 1371.1, 1275.1, 1143.9 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{16}H_{19}NNaO_4$ $[M+Na]^+$: 312.1206, found: 312.1203. Based on NOE analysis, the Z diastereomer was obtained, for detail see the attached NOE spectrum.



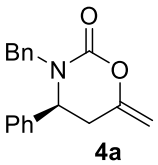
Product **2k** was obtained in 74% yield as light yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.31 (m, 3H), 7.30-7.27 (m, 2H), 4.82 (d, *J* = 9.2 Hz, 1H), 4.57 (s, 2H), 4.24-4.15 (m, 4H), 3.26-3.23 (m, 2H), 2.61-2.58 (m, 2H), 1.36 (t, J = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.62 (d, *J* = 4.0 Hz), 148.90, 135.47, 128.76, 128.02, 95.80, 93.89, 62.04 (d, *J* = 6.0 Hz), 52.76, 41.85, 27.76 (d, *J* = 15.0 Hz), 16.24 (d, *J* = 7.0 Hz); ^{31}P NMR (122 MHz, $CDCl_3$): δ 13.58 (m); IR (ATR) ν 2981.2, 1727.4, 1651.2,

1482.1, 1391.8, 1349.9, 1238.5, 1185.4, 1095.4, 886.1 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{16}H_{22}NNaO_5P$ $[M+Na]^+$: 362.1128, found: 362.1121. Based on NOE analysis, the Z diastereomer was obtained, for detail see the attached NOE spectrum.



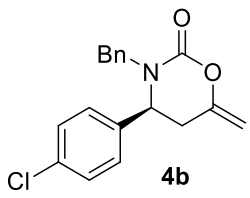
2l

Product **2l** was obtained in 25% yield as light yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (m, 2H), 7.31-7.28 (m, 3H), 4.60-4.55 (m, 3H), 3.18 (t, *J* = 6.4 Hz, 2H), 2.48-2.45 (m, 2H), 1.69-1.66 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.62, 145.54, 136.35, 128.73, 128.07, 127.78, 103.01, 52.79, 43.74, 26.54, 9.53; IR (ATR) ν 2920.4, 2854.0, 1718.0, 1693.4, 1484.0, 1444.2, 1361.0, 1269.8, 1206.3, 1075.9 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$: 240.0995, found: 240.0992. Based on NOE analysis, the Z diastereomer was obtained, for detail see the attached NOE spectrum.



4a

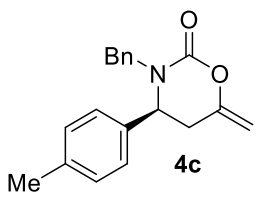
Product **4a** was obtained in 75% yield as light yellow solid (m.p. 65-67 °C); HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 1.0 mL/min, 230 nm; t_r (major) = 9.95 min, t_r (minor) = 11.66 min) gave the isomeric composition of the product: 96% ee; $[\alpha]_D^{25}$ = +15.8 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.35 (m, 3H), 7.33-7.29 (m, 3H), 7.26-7.22(m, 2H), 7.17-7.15 (m, 2H), 5.30, 3.68 (AB, *J* = 15.2 Hz, 2H), 4.42 (dd, *J* = 6.4 Hz, 2.8 Hz, 1H), 4.38 (d, J = 262.4 Hz, 2H), 2.88-2.83 (m, 1H), 2.49 (dd, *J* = 14.4 Hz, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.38, 149.96, 138.58, 136.11, 128.78, 128.66, 128.23, 128.07, 127.76, 126.23, 94.86, 55.94, 50.49, 34.19; IR (ATR) ν 2925.8, 1694.0, 1495.1, 1444.6, 1367.5, 1281.5, 1108.4, 1031.6, 932.2, 852.8 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{17}NNaO_2$ $[M+Na]^+$: 302.1151, found: 302.1144.



4b

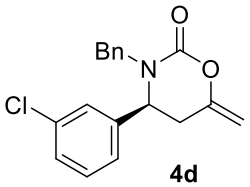
Product **4b** was obtained in 75% yield as white solid (m.p. 77-79 °C); HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 0.8 mL/min, 230 nm; t_r (major) = 11.27 min, t_r (minor) = 12.18 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -25.9 (c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 5H), 7.22-7.21 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 5.27, 3.67 (AB, *J* = 15.2 Hz, 2H), 4.40 (dd, *J* = 6.0 Hz, 2.4 Hz, 1H), 4.39 (d, *J* = 260.8 Hz, 2H), 2.88-2.82 (m, 1H), 2.44 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.20, 149.64, 137.20, 135.89, 134.13,

129.03, 128.75, 128.11, 127.91, 127.66, 95.22, 55.47, 50.65, 34.15; IR (ATR) ν 2920.9, 1712.8, 1661.3, 1490.0, 1425.6, 1358.2, 1299.7, 1269.8, 1147.7, 1029.0 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{16}ClNNaO_2$ $[M+Na]^+$: 336.0762, found: 336.0762.



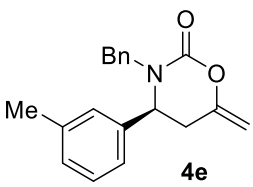
4c

Product **4c** was obtained in 74% yield as light yellow oil; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; t_r (major) = 22.30 min, t_r (minor) = 29.02 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = +2.5 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 3H), 7.24 (d, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.6 Hz, 2H), 5.30, 3.66 (AB, *J* = 14.8 Hz, 2H), 4.38 (dd, *J* = 6.4 Hz, 2.4 Hz, 1H), 4.38 (d, *J* = 261.2 Hz, 2H), 2.88-2.82 (m, 1H), 2.47 (dd, *J* = 14.4 Hz, 2.8 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.46, 150.19, 138.10, 136.28, 135.64, 129.52, 128.70, 128.13, 127.78, 126.24, 94.79, 55.76, 50.44, 34.34, 21.04; IR (ATR) ν 3028.2, 2916.9, 1713.1, 1663.6, 1514.0, 1495.4, 1427.0, 1359.3, 1261.0, 1074.8 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$: 316.1308, found: 316.1301.



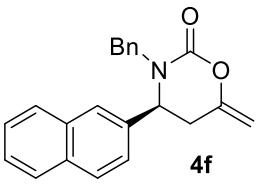
4d

Product **4d** was obtained in 73% yield as white solid (m.p. 85-87 °C); HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 15/85, 0.8 mL/min, 230 nm; t_r (major) = 13.01 min, t_r (minor) = 15.73 min) gave the isomeric composition of the product: 97% ee; $[\alpha]_D^{25}$ = +8.0 (c = 0.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 5H), 7.24-7.22 (m, 2H), 7.13 (s, 1H), 7.07-7.03 (m, 1H), 5.31, 3.68 (AB, *J* = 15.2 Hz, 2H), 4.41 (d, *J* = 264.8 Hz, 2H), 4.40 (dd, *J* = 6.4 Hz, 2.4 Hz, 1H), 2.90-2.84 (m, 1H), 2.46 (dd, *J* = 14.4 Hz, 2.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.17, 149.51, 140.82, 135.87, 134.82, 130.15, 128.76, 128.51, 128.12, 127.94, 126.47, 124.38, 95.32, 55.60, 50.76, 34.08; IR (ATR) ν 2921.0, 1714.8, 1664.9, 1596.5, 1495.0, 1445.2, 1340.5, 1028.4, 971.8, 803.2 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{16}ClNNaO_2$ $[M+Na]^+$: 336.0762, found: 336.0761.



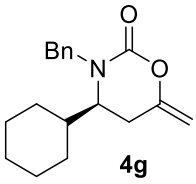
4e

Product **4e** was obtained in 81% yield as light yellow solid (m.p. 90-92 ºC); HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 10/90, 0.8 mL/min, 230 nm; t_r (major) = 14.49 min, t_r (minor) = 17.88 min) gave the isomeric composition of the product: 97% ee; $[\alpha]_D^{25}$ = +33.0 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (m, 3H), 7.26-7.23 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 6.96-6.95 (m, 2H), 5.32, 3.68 (AB, *J* = 15.2 Hz, 2H), 4.38 (d, *J* = 262.4 Hz, 2H), 4.38 (dd, *J* = 6.4 Hz, 2.8 Hz, 1H), 2.88-2.82 (m, 1H), 2.48 (dd, *J* = 14.0 Hz, 2.4 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.48, 150.11, 138.60, 136.27, 129.03, 128.70, 128.68, 128.11, 127.77, 126.88, 123.38, 94.79, 56.01, 50.56, 34.27, 21.39; IR (ATR) ν 2950.1, 1709.0, 1692.9, 1657.1, 1453.0, 1435.3, 1104.8, 1076.2, 811.4, 707.9 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{19}H_{19}NNaO_2$ $[M+Na]^+$: 316.1308, found: 316.1303.



4f

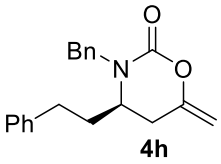
Product **4f** was obtained in 77% yield as light yellow oil; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 230 nm; t_r (major) = 32.72 min, t_r (minor) = 38.07 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -15.1 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.83 (m, 3H), 7.61 (s, 1H), 7.55-7.50 (m, 2H), 7.36-7.29 (m, 3H), 7.27-7.24 (m, 3H), 4.60-4.58 (m, 1H), 5.38, 3.73 (AB, *J* = 15.2 Hz, 2H), 4.37 (d, *J* = 274.4 Hz, 2H), 2.94 (dd, *J* = 14.4 Hz, 6.4 Hz, 1H), 2.62-2.57 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.56, 150.00, 136.21, 135.97, 133.11, 133.09, 128.95, 128.76, 128.16, 127.91, 127.87, 127.68, 126.61, 126.41, 125.34, 123.89, 95.06, 56.18, 50.67, 34.26; IR (ATR) ν 3028.1, 2919.3, 1712.3, 1601.0, 1508.4, 1445.8, 1367.2, 1269.9, 1206.1, 1074.9 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{22}H_{19}NNaO_2$ $[M+Na]^+$: 352.1308, found: 352.1311.



4g

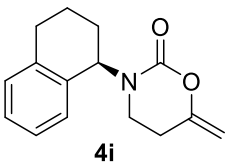
Product **4g** was obtained in 75% yield as light yellow solid (m.p. 67-69 ºC); HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 5/95, 1.0 mL/min, 205 nm; t_r (major) = 22.04 min, t_r (minor) = 29.46 min) gave the isomeric composition of the product: 97% ee; $[\alpha]_D^{25}$ = +30.4 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (m, 2H), 7.30-7.27 (m, 3H), 5.34, 3.94 (AB, *J* = 15.2 Hz, 2H), 4.41 (d, *J* = 194.8 Hz, 2H), 2.98 (t, *J* = 6.4 Hz, 1H), 2.56 (d, *J* = 15.2 Hz, 1H), 2.31 (dd, *J* = 14.8 Hz, 4.8 Hz, 1H), 1.80 (d, *J* = 10.8 Hz, 2H), 1.75-1.62 (m, 4H), 1.22-1.16 (m, 2H), 1.13-0.92 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

152.23, 151.48, 136.52, 128.67, 127.94, 127.73, 92.75, 56.81, 52.55, 40.72, 30.19, 28.97, 28.90, 26.01, 25.91; IR (ATR) *v* 2934.7, 2852.7, 1704.7, 1659.6, 1424.9, 1339.2, 1208.1, 1135.1, 1073.7, 1028.0 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{18}H_{23}NNaO_2$ $[M+Na]^+$: 308.1621, found: 308.1622.



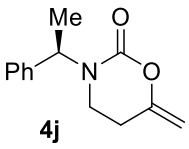
4h

Product **4h** was obtained in 71% yield as light yellow oil; HPLC analysis (Chiralcel AD-H, ^{i}PrOH/hexane = 10/90, 0.8 mL/min, 205 nm; t_r (major) = 21.78 min, t_r (minor) = 19.08 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -13.8 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.28 (m, 3H), 7.27-7.21 (m, 3H), 7.14-7.10 (m, 4H), 5.07, 3.94 (AB, *J* = 14.8 Hz, 2H), 4.49 (d, *J* = 208.8 Hz, 2H), 3.23-3.18 (m, 1H), 2.71-2.64 (m, 1H), 2.51-2.45 (m, 3H), 1.93-1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.06, 150.96, 140.20, 136.42, 128.63, 128.58, 128.17, 128.07, 127.73, 126.28, 94.14, 51.15, 50.79, 32.89, 31.87, 29.91; IR (ATR) *v* 3026.6, 2925.1, 1712.5, 1661.3, 1602.6, 1495.3, 1351.5, 1282.2, 1227.8, 1028.9 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{20}H_{21}NNaO_2$ $[M+Na]^+$: 330.1464, found: 330.1466.



4i

Product **4i** was obtained in 82% yield as light yellow solid (m.p. 89-90 °C); HPLC analysis (Chiralcel OJ-H, ^{i}PrOH/hexane = 15/85, 0.8 mL/min, 230 nm; t_r (major) = 12.43 min, t_r (minor) = 11.62 min) gave the isomeric composition of the product: 98% ee; $[\alpha]_D^{25}$ = -34.9 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.15 (m, 3H), 7.12-7.10 (m, 1H), 5.68-5.64 (m, 1H), 4.67 (d, *J* = 1.6 Hz, 1H), 4.22-4.21 (m, 1H), 3.12-3.05 (m, 1H), 2.97-2.91 (m, 1H), 2.83-2.73 (m, 2H), 2.49 (t, *J* = 6.0 Hz, 2H), 2.16-2.10 (m, 1H), 2.01-1.94 (m, 1H), 1.86-1.72 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.84, 151.42, 138.68, 133.81, 129.36, 127.13, 126.86, 126.24, 92.03, 55.48, 39.14, 29.31, 27.16, 26.39, 21.57; IR (ATR) ν 2942.0, 1715.8, 1652.2, 1475.5, 1361.1, 1337.2, 1257.8, 1230.9, 1083.6, 957.1 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{15}H_{17}NNaO_2$ $[M+Na]^+$: 266.1151, found: 266.1144.

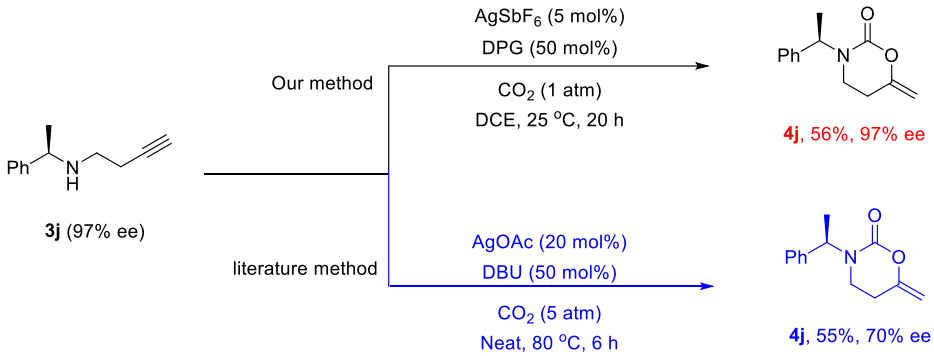


4j

Product **4j** was obtained in 56% yield as light yellow oil; HPLC analysis (Chiralcel OJ-H, ^{i}PrOH/hexane = 15/85, 0.8 mL/min, 230 nm; t_r (major) = 15.89 min, t_r (minor) = 13.95 min) gave the isomeric composition of the product: 97% ee; $[\alpha]_D^{25}$ = +68.5

(c = 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.30-7.27 (m, 3H), 7.25-7.20 (m, 2H), 5.68 (q, *J* = 7.2 Hz, 1H), 4.33 (d, *J* = 176.0 Hz, 2H), 3.08-3.02 (m, 1H), 2.79-2.73 (m, 1H), 2.43-2.37 (m, 1H), 2.34-2.27 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.60, 150.91, 139.23, 128.52, 127.67, 127.14, 92.06, 53.59, 37.88, 26.20, 15.36; IR (ATR) ν 2976.4, 1707.4, 1480.7, 1378.8, 1357.6, 1258.2, 1231.5, 1126.3, 1039.2, 983.7 cm^{-1}; HRMS (ESI): Exact mass calcd for $C_{13}H_{15}NNaO_2$ $[M+Na]^+$: 240.0995, found: 240.0987.

Notably, the synthesis of chiral 2-oxazinones from optically active homopropargyl amines is not as trivial as it first appears. If the reaction was run under previous reported condition of high temperature and pressure,[6] the desired chiral 2-oxazinones might be obtained in diminished ee values, as exemplified by the synthesis of **4j** from chiral amine **3j**.



5. Mechanistic studies

The superiority that DPG exhibited in the Ag(I)-catalyzed carboxylative cyclization of both *N*-aryl propargylanilines and *N*-alkyl homopropargyl amines is very intriguing. To gain more insight into the role of DPG, a variety of experiments including ^{1}H NMR, ^{13}C NMR, HRMS as well as X-ray analysis were conducted.

5.1. The study of interaction between DPG and CO_2.

Initially, the detail for the trapping and releasing of CO_2 by DPG was studied. As far as we know, the corresponding reaction between DPG and CO_2 has never been documented.[4] A general procedure for the capture of CO_2 was as follows: DPG (633 mg, 3 mmol) was stirred in DCE (10 mL) under a continuous stream of CO_2 (15 mL/min) for 2 h at 0°C. Then, deposited solid was quickly filtered off and washed with cold DCE (3×5 mL) to give the complex as a white powder (600 mg, 78%) with high purity. Notably, the carboxylation process was reversible. As shown in Figure S1, although the precipitate formed in 0 ^{o}C could be isolated via a quick filtration, it would be gradually disappeared with the release of CO_2 bubbles if raising the solution temperature above 25 ^{o}C.

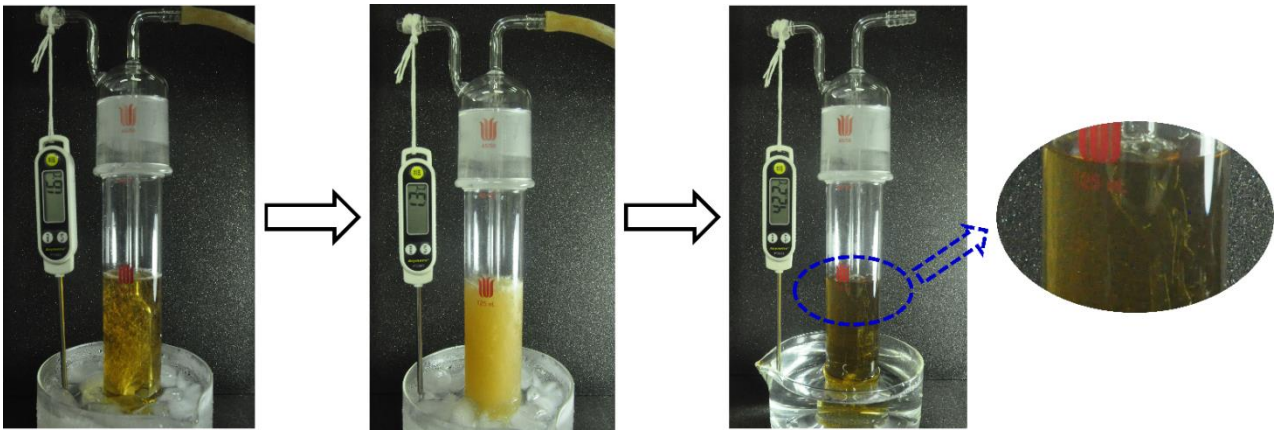


Figure S1. The capture and release of CO_2. (*Note, in order to give a clearer phenomenon, the CO_2 release process was performed under around 40 ^{o}C.*)

Then, the structure of the thus obtained complex was analyzed. Initially, NMR studies were performed, but we tried in vain to characterize its structure in common organic deuterated solvents, such as CD_2Cl_2, $CDCl_3$, CD_3CN, DMSO-d_6, THF-d_8, and only spectra assigned to the DPG structure was obtained due to the release of CO_2. Fortunately, in D_2O the complex could be successfully

characterized, with the data shown below: ^{1}H NMR (500 MHz, D_2O): δ 7.53-7.50 (m, 4H), 7.44-7.40 (m, 2H), 7.39-7.37 (m, 4H); ^{13}C NMR (125 MHz, D_2O): δ 160.35, 155.04, 134.32, 129.97, 128.00, 127.98, 125.93; IR (ATR) ν 1645, 1582, 1544, 1495, 1385, 1242, 750, 689 cm^{-1}.

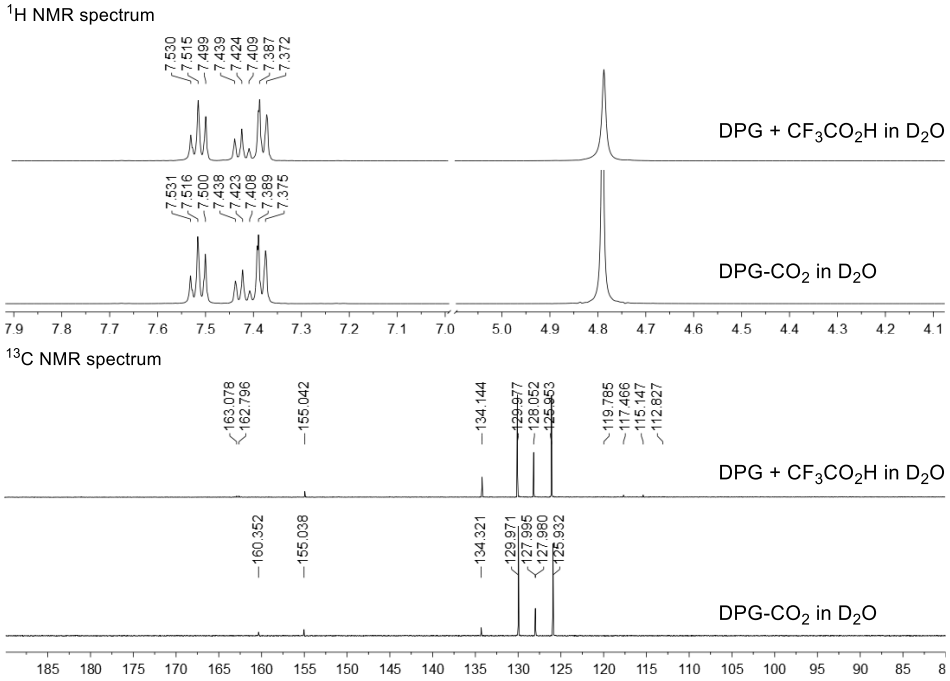


Figure S2. NMR spectrum comparison.

Then, the NMR data of the thus obtained complex in D_2O with that of protonated DPG, [DPGH][CF_3CO_2], was compared with the results shown in Figure S2. Obviously, the ^{1}H and ^{13}C NMR data were consistent with the DPG portion of the complex being simply protonated DPG. And the new peak at 160.35 ppm in the ^{13}C NMR spectrum of the complex was consistent with bicarbonate anion. These results revealed that a bicarbonate salt [DPGH][HCO_3] might be formed.

In order to figure out the exact structure of the complex, CO_2 was diffused into the solvent of DPG in THF/Et_2O (1/1, v/v) under -20 ºC, and finally a single crystal of the bicarbonate adduct [DPGH][HCO_3] was obtained (CCDC-1907983). X-ray crystallography shows that a centrosymmetric dimer was formed by the "anti-electrostatic" hydrogen-bonding between oxygen atoms of the bicarbonate anion $[HCO_3]^-$, with H···O contact distances of 1.78 Å. In each monomer, the bicarbonate anion associated with the cation $[DPGH]^+$ through three hydrogen bonds between the oxygen and nitrogen atoms, with N-H···O contact distances of 1.82, 1.90 and 1.97 Å (Figure S3, left). In addition, the cationic stacks flank the anionic cluster in a close-packed arrangement (right).

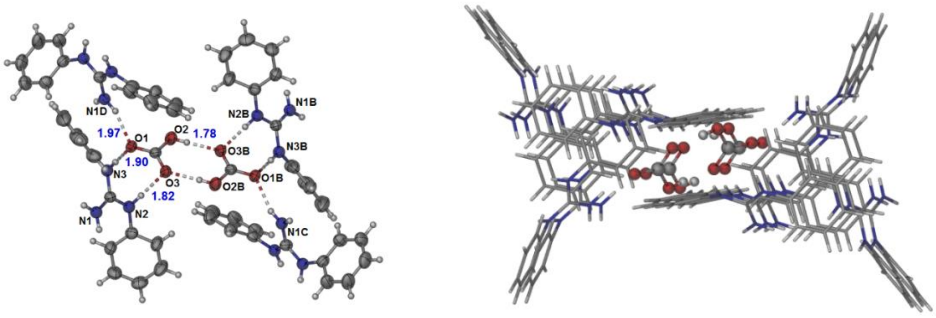
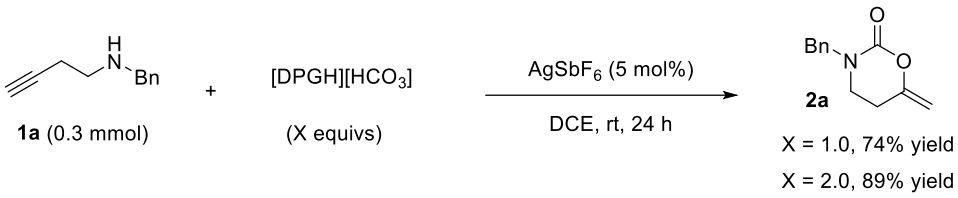


Figure S3. The X-Ray crystal structure of bicarbonate salt [DPGH][HCO_3].

Then the reaction of homopropargyl amine with the bicarbonate adduct was performed. The treatment of homopropargyl amine **1a** with bicarbonate salt [DPGH][HCO_3] in the presence of 5 mol% of $AgSbF_6$ under N_2 atmosphere at room temperature gave the desired 2-oxazinone **2a** in 74% and 89% yield respectively, by using 1.0 or 2.0 equivlent of bicarbonate salt. These results further demonstrated that [DPGH][HCO_3] could release CO_2 effectively during the raction.



5.2 The study of interaction between DPG and $AgSbF_6$

At first the interaction of DPG with $AgSbF_6$ was studied by NMR analysis, which was conducted in air using $CDCl_3$ as the solvent. The general procedure was as follows: to a NMR tube were added the DPG (0.1 mmol) and $CDCl_3$ (0.5 mL), followed by the addition of $AgSbF_6$ (10 mol% to 100 mol%). Then the tube was shaken vigorously and quickly subjected to NMR analysis at 25 °C.

Obvious changes were immediately observed when $AgSbF_6$ was added to the solution of DPG in $CDCl_3$. ^1H NMR showed that, with the amount of $AgSbF_6$ increased from 0.1 equiv to 1.0 equiv, the characteristic peaks corresponding to the proton at C5 position of DPG, changed gradually from 7.03 ppm to 7.06 and 7.12 ppm. Meanwhile, the signal of proton on the nitrogen atom changed from 5.08 ppm to 5.41 and 5.62 ppm gradually. Obvious changes could also be observed for the ^{13}C NMR analysis (Figure S4). When 0.1 equiv of $AgSbF_6$ was added, the characteristic peaks of C1, C2 and C5 changed from 149.63, 143.94 and 123.23 ppm to 151.23, 142.49 and 124.06 ppm respectively. Further increase the amount of $AgSbF_6$ to 1.0 equiv, the characteristic peak of C5 shifted to 125.42 ppm and the signals of C1 and C2 might be too weak to be detected. These observations indicated that DPG might coordinate to $AgSbF_6$.

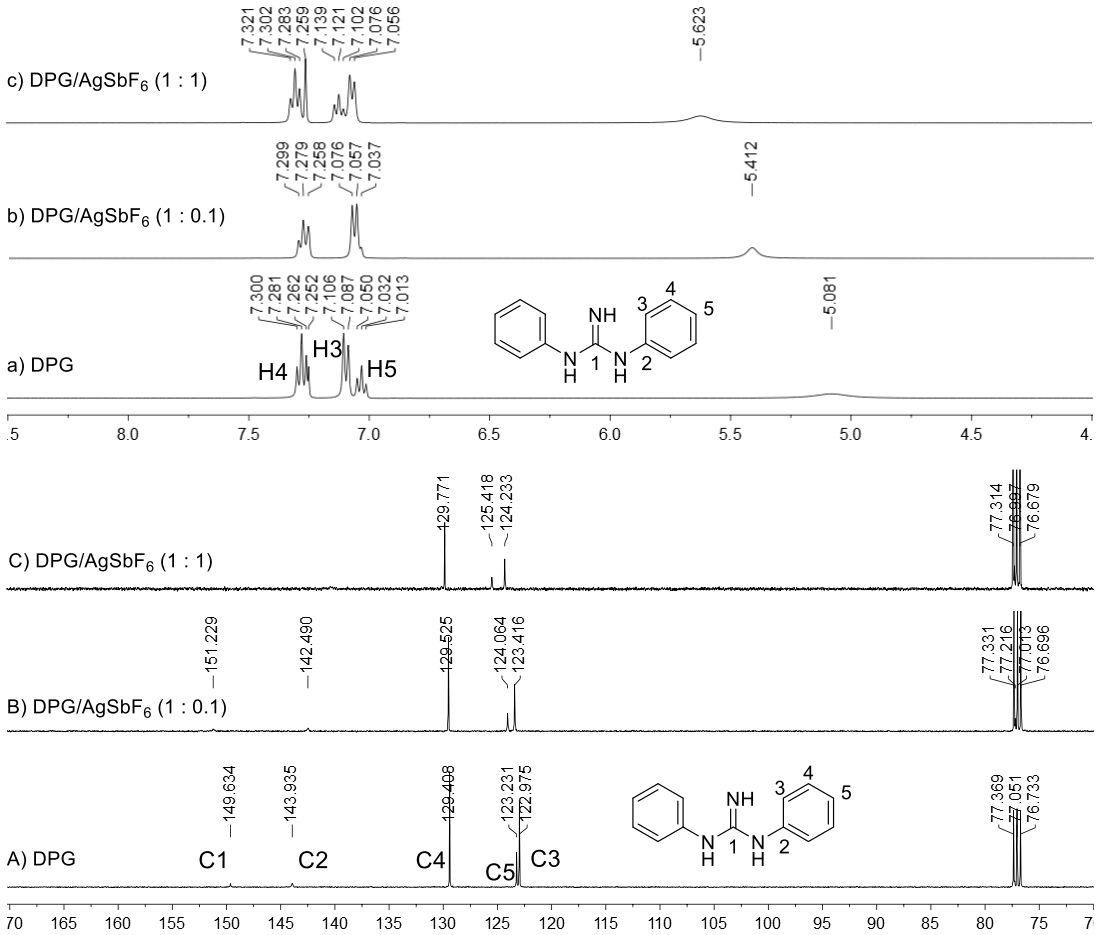
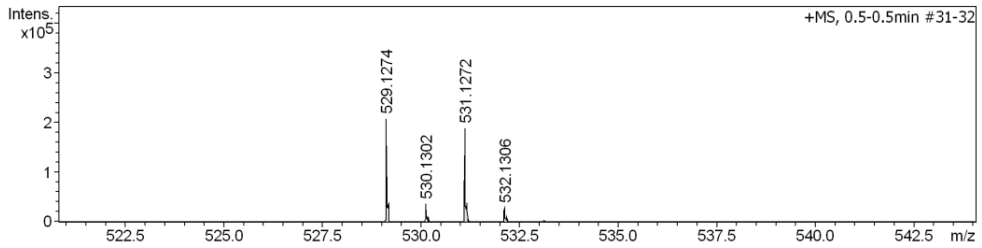


Figure S4. ^{1}H NMR and ^{13}C NMR spectra of DPG with 0.1 and 1.0 equiv of $AgSbF_6$.

To get more information about the possible binding interaction, HRMS analysis of the DPG-Ag(I) complex with different molecular ratio ($AgSbF_6$: DPG = 1:1, 1:2 and 1:10) was conducted respectively, and in all cases a signal at m/z 529.1274 was observed as shown in Figure S5, consistent with the 1/2 complex cation, $[(DPG)_2 + Ag]^+$.



#	m/z	Res.	S/N	I	I %	FWHM
1	529.1274	38362	2655.1	207020	100.0	0.0138
2	530.1302	32495	468.6	36568	17.7	0.0163
3	531.1272	36859	2407.8	188056	90.8	0.0144
4	532.1306	28685	374.4	29234	14.1	0.0186

Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e⁻ Conf	N-Rule
529.1274	1	C26H26AgN6	529.1264	-1.8	86.3	4	10.60	16.5	even	ok

Figure S5. HRMS analysis of the DPG-Ag(I) complex.

Fortunately, we obtained a single crystal of the complex derived from DPG and $AgSbF_6$ upon crystallization of the 1/2 mixture of $AgSbF_6$ and DPG from CD_2Cl_2 (CCDC-1894496). X-ray diffraction study revealed that the DPG served as neutral monodentate ligand and bound to the silver center via a head-to-head fashion (Figure S6). These results in combination with HRMS analysis, further cast light on the coordination fashion of DPG to $AgSbF_6$.

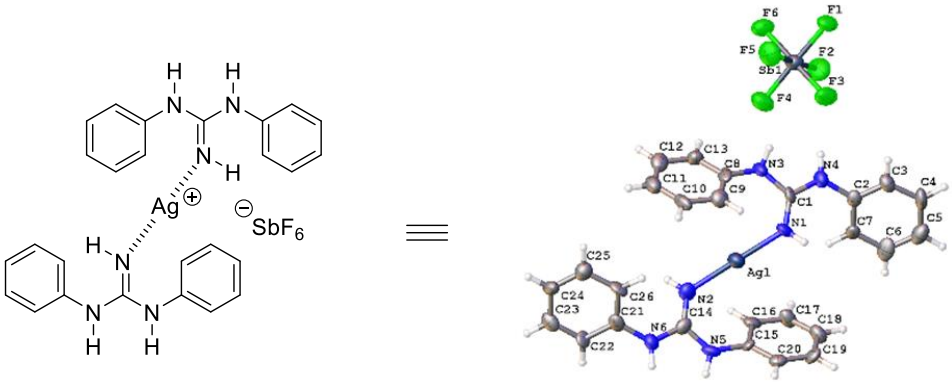


Figure S6. the single crystal of DPG-Ag(I) complex.

5.3. NMR study of the reaction process.

To get more information about the reaction course and to understand the role of DPG during the reaction, ^{1}H and ^{13}C NMR studies of the reaction process were carried out based on the reaction of homopropargyl amine **1a** under 1 atm of CO_2 at 25 °C in $CDCl_3$, in the presence of 10 mol% $AgSbF_6$ and 100 mol% DPG.

As shown in Figure S7, when **1a** was added to the mixture of $AgSbF_6$ and DPG, the characteristic peaks assigned to H1, H3, H4 and H5 of **1a** upfield shifted from 1.99, 2.41, 2.80, 3.82 ppm to 1.98, 2.39, 2.78 and 3.80 pm respectively (c *vs* a). Meanwhile, ^{13}C NMR spectrum revealed the signals assigned to C3, C4 and C5 shifted from 19.54, 47.30 and 53.35 ppm to 19.49, 47.24 and 53.29 ppm respectively. A slightly upfield shift of the signals assigned to C1 and C2 of the C-C triple bond was also observed (C *vs* A). These observations indicated that both the alkyne and amine moiety of **1a** might interact with the DPG-Ag(I) complex, which was helpful for suppressing the side intramolecular hydroamination reaction.[7]

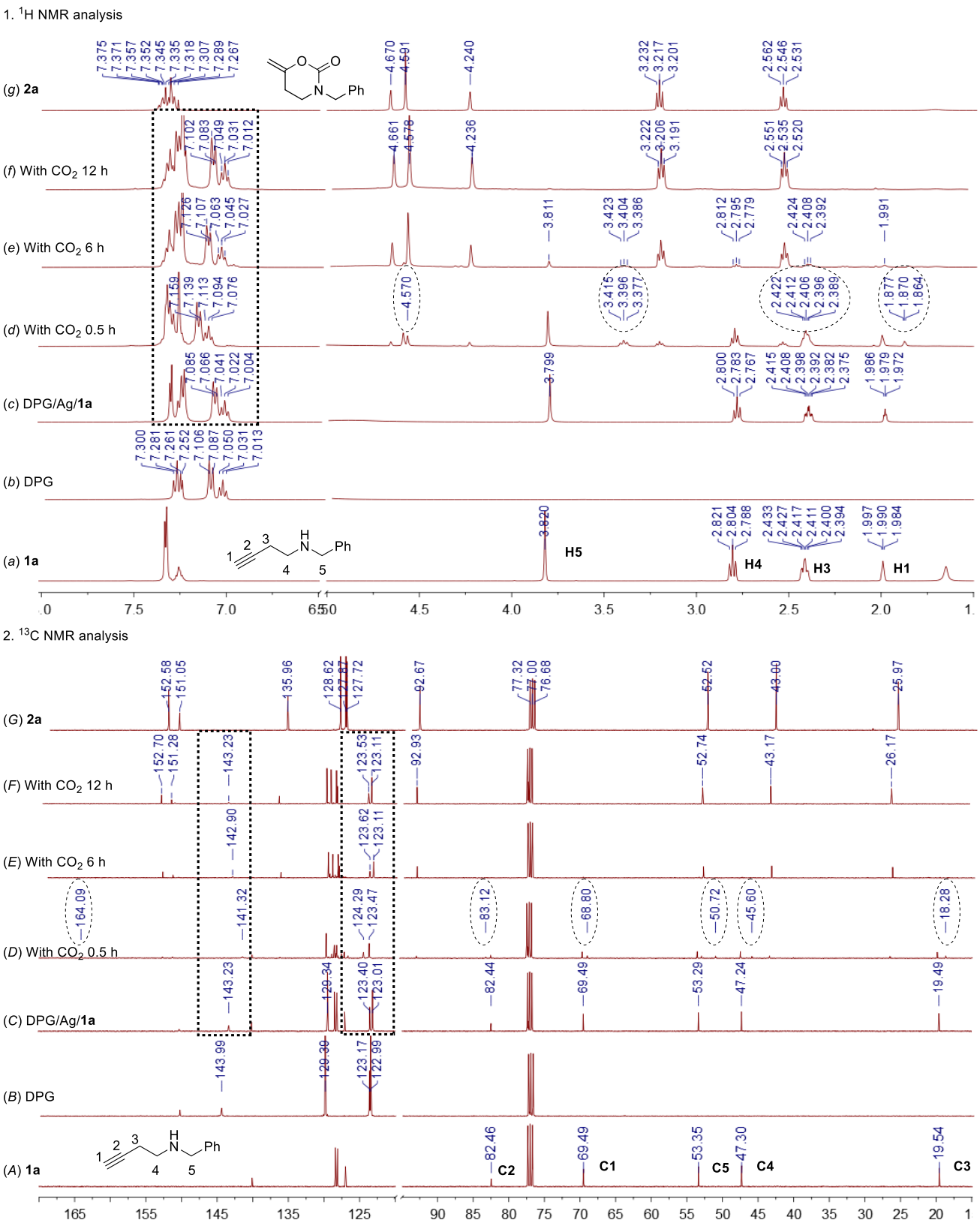
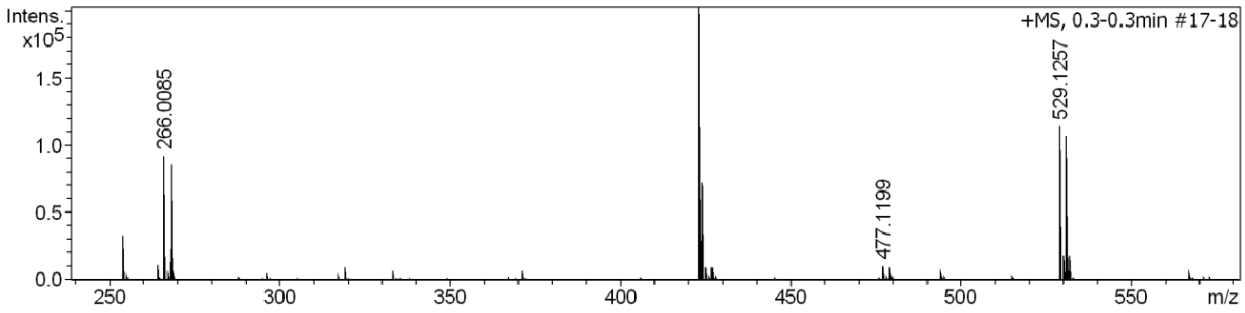


Figure S7. ^{1}H and ^{13}C NMR study in $CDCl_3$. (a, A) **1a** (0.1 mmol). (b, B) DPG (0.1 mmol). (c, C) $AgSbF_6$ (0.01 mmol), DPG (0.1 mmol) and **1a** (0.1 mmol). (d-f, D-F) Under CO_2 atmosphere 0.5, 6.0 and 12 h respectively. (g, G) **2a** (0.1 mmol).

Subsequently, the above reaction mixture was subjected to CO_2 atmosphere with the reaction process monitored over time and notable changes were observed (Figure S7, d-f & D-F). Within half an hour, apart from the detection of 2-oxazinone **2a**, some new signals appeared at both ^{1}H NMR (δ = 4.57, 3.40, 2.41 and 1.87 ppm) and ^{13}C NMR (δ = 164.09, 83.12, 68.80, 50.72, 45.60 and 18.28 ppm) spectrum (d *vs* c; D *vs* C, outside the dashed boxes part), which might be attributed to the carbamate formed via the reaction of **1a** with CO_2. After 6 hours, the signals attribute to **1a** and carbamic intermediate became weak gradually and the full conversion of **1a** to **2a** was observed within 12 hours (e-f; E-F). Notably, during the reaction course, the character peaks belong to DPG also shifted distinctly (the dashed boxes part). In the first half an hour, the characteristic signals of ^{1}H NMR shifed from 7.07 and 7.02 ppm to 7.15 and 7.09 pm respectively, meanwhile the signals of ^{13}C NMR also shifted from 143.23, 123.40 and 123.01 ppm to 141.32, 124.29 and 123.47 ppm obviously (d *vs* c; D *vs* C). Then, as the reaction proceeded, the character peaks of DPG shifted back to its original state gradually (d-f *vs* c; D-F *vs* C), which indicated that there should be interactions between DPG and the carbamate intermediate.

5.4. HRMS analysis of the complex derived from DPG, $AgSbF_6$ and 1a.

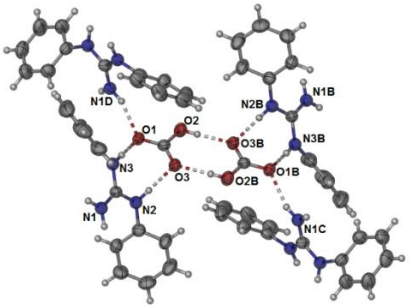
In order to get more information of the interactions among $AgSbF_6$, DPG and homopropargyl amine **1a**, the HRMS analysis was conducted (Figure S8). When a CH_2Cl_2 solution of 1:10:10 mixture of $AgSbF_6$, DPG and **1a** was subjected to the HRMS analysis, the signals of [**1a**+Ag]$^+$ at 266.0087, [$(DPG)_2$+Ag]$^+$ at m/z 529.1257, as well as [DPG+**1a**+Ag]$^+$ at m/z 477.1199 could be detected respectively. This information further confirmed the interactions between $AgSbF_6$ with DPG and **1a**, and also suggested the formation of 1/1/1 complex of $AgSbF_6$, DPG and **1a.**



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma		Score	rdb	e¯ Conf	N-Rule
266.0085	1	C11H13AgN	266.0093	3.2	62.7	1	100.00	5.5	even	ok
	1	C9H14AgNNa	266.0069	-5.9	49.9	1	100.00	2.5	even	ok
477.1199	1	C9H22AgN16O	477.1208	1.8	100.0	1	100.00	6.5	even	ok
	2	C23H30AgO4	477.1190	-2.1	146.8	2	6.79	8.5	even	ok
	3	C24H26AgN4	477.1203	0.7	174.1	3	1.41	13.5	even	ok
	1	C11H27AgN10NaO3	477.1211	2.4	101.4	1	100.00	2.5	even	ok
529.1257	1	C10H26AgN14O5	529.1256	-0.2	12.2	1	100.00	4.5	even	ok
	2	C11H22AgN18O	529.1269	2.3	18.9	2	48.93	9.5	even	ok
	3	C25H30AgN2O4	529.1251	-1.1	73.1	3	14.17	11.5	even	ok
	4	C26H26AgN6	529.1264	1.4	84.9	4	8.24	16.5	even	ok
	1	C9H23AgN18NaO	529.1245	-2.2	8.0	1	68.52	6.5	even	ok
	2	C12H31AgN8NaO7	529.1259	0.3	14.9	2	100.00	0.5	even	ok
	3	C13H27AgN12NaO3	529.1272	2.9	20.9	3	42.57	5.5	even	ok
	4	C24H27AgN6Na	529.1240	-3.2	79.1	4	6.45	13.5	even	ok
	5	C28H31AgNaO2	529.1267	1.9	86.5	5	7.19	12.5	even	ok

Figure S8. HRMS analysis.

6. Single-crystal X-ray analysis of bicarbonate salt [DPGH][HCO_3].



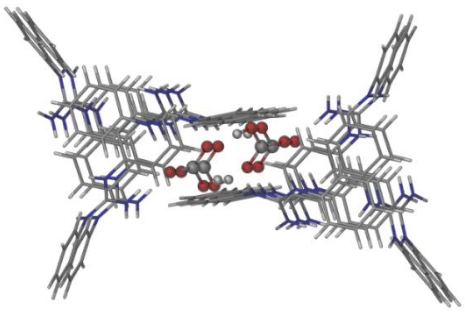


Table S3. Crystal data and structure refinement for CCDC-1907983.

Identification code	CCDC-1907983	
Empirical formula	$C_{14}H_{15}N_3O_3$	
Formula weight	273.29	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 34.5947(14) Å	a= 90°.
	b = 34.5947(14) Å	b= 90°.
	c = 10.7422(5) Å	g = 120°.
Volume	11133.8(10) $Å^3$	
Z	18	
Density (calculated)	0.734 Mg/m^3	
Absorption coefficient	0.053 mm^{-1}	
F(000)	2592	
Crystal size	0.160 x 0.140 x 0.110 mm^3	
Theta range for data collection	2.014 to 25.000°.	
Index ranges	-41<=h<=31, -32<=k<=41, -12<=l<=12	
Reflections collected	12749	
Independent reflections	3789 [R(int) = 0.0794]	
Completeness to theta = 25.242°	84.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.5782	
Refinement method	Full-matrix least-squares on F2	
Data / restraints / parameters	3789 / 0 / 183	
Goodness-of-fit on F2	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0784, wR2 = 0.1955	
R indices (all data)	R1 = 0.1169, wR2 = 0.2122	
Extinction coefficient	0.0017(4)	
Largest diff. peak and hole	0.198 and -0.167 e.$Å^{-3}$	

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for d8v19290. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	4446(1)	4055(1)	1381(2)	53(1)
O(2)	4998(1)	4464(1)	96(2)	59(1)
O(3)	4650(1)	4768(1)	1071(2)	58(1)
N(1)	3482(1)	4340(1)	3996(2)	59(1)
N(2)	4197(1)	4694(1)	3190(2)	54(1)
N(3)	3691(1)	4013(1)	2432(2)	51(1)
C(1)	3781(1)	4346(1)	3233(2)	48(1)
C(2)	4424(1)	5020(1)	4111(3)	51(1)
C(3)	4705(1)	5458(1)	3737(3)	67(1)
C(4)	4964(1)	5779(1)	4575(4)	77(1)
C(5)	4943(1)	5673(1)	5818(3)	72(1)
C(6)	4666(1)	5245(1)	6208(3)	69(1)
C(7)	4406(1)	4917(1)	5354(3)	59(1)
C(8)	3270(1)	3645(1)	2131(2)	53(1)
C(9)	3237(1)	3224(1)	2087(3)	68(1)
C(10)	2845(2)	2867(1)	1712(3)	85(1)
C(11)	2481(1)	2903(1)	1409(3)	83(1)
C(12)	2505(1)	3314(2)	1492(3)	82(1)
C(13)	2906(1)	3690(1)	1828(3)	64(1)
C(14)	4682(1)	4428(1)	879(2)	47(1)

Table S5. Bond lengths [Å] and angles [°] for d8v19290.

O(1)-C(14)	1.252(3)
O(2)-C(14)	1.335(3)
O(2)-H(2A)	0.8400
O(3)-C(14)	1.252(3)
N(1)-C(1)	1.312(4)
N(1)-H(1A)	0.8800
N(1)-H(1B)	0.8800
N(2)-C(1)	1.338(4)
N(2)-C(2)	1.408(4)
N(2)-H(2)	0.8800
N(3)-C(1)	1.346(3)
N(3)-C(8)	1.411(4)
N(3)-H(3)	0.8800
C(2)-C(7)	1.375(4)
C(2)-C(3)	1.389(4)
C(3)-C(4)	1.361(5)

C(3)-H(3A)	0.9500
C(4)-C(5)	1.376(5)
C(4)-H(4)	0.9500
C(5)-C(6)	1.367(5)
C(5)-H(5)	0.9500
C(6)-C(7)	1.384(4)
C(6)-H(6)	0.9500
C(7)-H(7)	0.9500
C(8)-C(13)	1.383(5)
C(8)-C(9)	1.404(5)
C(9)-C(10)	1.360(5)
C(9)-H(9)	0.9500
C(10)-C(11)	1.365(7)
C(10)-H(10)	0.9500
C(11)-C(12)	1.385(6)
C(11)-H(11)	0.9500
C(12)-C(13)	1.394(5)
C(12)-H(12)	0.9500
C(13)-H(13)	0.9500
C(14)-O(2)-H(2A)	109.5
C(1)-N(1)-H(1A)	120.0
C(1)-N(1)-H(1B)	120.0
H(1A)-N(1)-H(1B)	120.0
C(1)-N(2)-C(2)	127.9(2)
C(1)-N(2)-H(2)	116.1
C(2)-N(2)-H(2)	116.1
C(1)-N(3)-C(8)	127.7(2)
C(1)-N(3)-H(3)	116.2
C(8)-N(3)-H(3)	116.2
N(1)-C(1)-N(2)	121.5(2)
N(1)-C(1)-N(3)	123.0(3)
N(2)-C(1)-N(3)	115.5(2)
C(7)-C(2)-C(3)	118.6(3)
C(7)-C(2)-N(2)	122.8(3)
C(3)-C(2)-N(2)	118.4(2)
C(4)-C(3)-C(2)	121.0(3)
C(4)-C(3)-H(3A)	119.5
C(2)-C(3)-H(3A)	119.5
C(3)-C(4)-C(5)	119.9(3)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(6)-C(5)-C(4)	120.1(3)
C(6)-C(5)-H(5)	120.0
C(4)-C(5)-H(5)	120.0
C(5)-C(6)-C(7)	120.0(3)

C(5)-C(6)-H(6)	120.0
C(7)-C(6)-H(6)	120.0
C(2)-C(7)-C(6)	120.4(3)
C(2)-C(7)-H(7)	119.8
C(6)-C(7)-H(7)	119.8
C(13)-C(8)-C(9)	120.2(3)
C(13)-C(8)-N(3)	122.6(3)
C(9)-C(8)-N(3)	117.1(3)
C(10)-C(9)-C(8)	118.6(4)
C(10)-C(9)-H(9)	120.7
C(8)-C(9)-H(9)	120.7
C(9)-C(10)-C(11)	122.3(4)
C(9)-C(10)-H(10)	118.8
C(11)-C(10)-H(10)	118.8
C(10)-C(11)-C(12)	119.6(3)
C(10)-C(11)-H(11)	120.2
C(12)-C(11)-H(11)	120.2
C(11)-C(12)-C(13)	119.7(4)
C(11)-C(12)-H(12)	120.2
C(13)-C(12)-H(12)	120.2
C(8)-C(13)-C(12)	119.5(4)
C(8)-C(13)-H(13)	120.3
C(12)-C(13)-H(13)	120.3
O(1)-C(14)-O(3)	125.2(2)
O(1)-C(14)-O(2)	116.8(2)
O(3)-C(14)-O(2)	117.9(2)

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for d8v19290. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	56(1)	38(1)	54(1)	1(1)	7(1)	15(1)
O(2)	56(1)	47(1)	71(1)	6(1)	20(1)	24(1)
O(3)	62(1)	43(1)	59(1)	2(1)	22(1)	18(1)
N(1)	45(1)	54(2)	59(1)	-14(1)	10(1)	10(1)
N(2)	49(1)	49(1)	50(1)	-4(1)	13(1)	13(1)
N(3)	44(1)	46(1)	53(1)	-7(1)	3(1)	14(1)
C(1)	49(2)	42(2)	44(1)	-3(1)	4(1)	17(1)
C(2)	42(2)	50(2)	55(2)	-4(1)	2(1)	18(1)
C(3)	63(2)	48(2)	66(2)	6(1)	-10(2)	10(2)

C(4)	66(2)	50(2)	86(2)	2(2)	-22(2)	8(2)
C(5)	60(2)	66(2)	77(2)	-22(2)	-20(2)	22(2)
C(6)	69(2)	68(2)	55(2)	-8(2)	-10(2)	22(2)
C(7)	59(2)	47(2)	62(2)	4(1)	2(2)	20(2)
C(8)	60(2)	50(2)	38(1)	-2(1)	6(1)	18(1)
C(9)	83(2)	47(2)	58(2)	-1(1)	-7(2)	20(2)
C(10)	101(3)	48(2)	70(2)	4(2)	-20(2)	10(2)
C(11)	78(3)	62(2)	65(2)	-6(2)	-6(2)	1(2)
C(12)	64(2)	102(3)	63(2)	-19(2)	-10(2)	28(2)
C(13)	55(2)	67(2)	61(2)	-14(2)	-6(2)	24(2)
C(14)	49(2)	42(2)	46(1)	-6(1)	2(1)	19(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3)

	x	y	z	U(eq)
H(2A)	5110	4711	-274	88
H(1A)	3553	4568	4495	71
H(1B)	3209	4109	4009	71
H(2)	4347	4722	2502	65
H(3)	3923	4025	2051	62
H(3A)	4716	5534	2883	80
H(4)	5160	6075	4302	92
H(5)	5120	5898	6405	86
H(6)	4652	5173	7066	83
H(7)	4215	4620	5629	71
H(9)	3483	3188	2313	82
H(10)	2823	2583	1661	102
H(11)	2213	2648	1142	100
H(12)	2249	3339	1321	98
H(13)	2930	3976	1848	77

Table S8. Torsion angles [°] for d8v19290.

C(2)-N(2)-C(1)-N(1)	21.2(5)
C(2)-N(2)-C(1)-N(3)	-159.8(3)
C(8)-N(3)-C(1)-N(1)	10.0(5)
C(8)-N(3)-C(1)-N(2)	-168.9(3)
C(1)-N(2)-C(2)-C(7)	42.8(5)
C(1)-N(2)-C(2)-C(3)	-142.2(3)
C(7)-C(2)-C(3)-C(4)	1.3(5)
N(2)-C(2)-C(3)-C(4)	-173.9(3)
C(2)-C(3)-C(4)-C(5)	-1.6(6)

C(3)-C(4)-C(5)-C(6)	1.0(6)
C(4)-C(5)-C(6)-C(7)	-0.2(6)
C(3)-C(2)-C(7)-C(6)	-0.5(5)
N(2)-C(2)-C(7)-C(6)	174.5(3)
C(5)-C(6)-C(7)-C(2)	0.0(5)
C(1)-N(3)-C(8)-C(13)	48.2(4)
C(1)-N(3)-C(8)-C(9)	-135.0(3)
C(13)-C(8)-C(9)-C(10)	1.5(5)
N(3)-C(8)-C(9)-C(10)	-175.3(3)
C(8)-C(9)-C(10)-C(11)	-1.6(5)
C(9)-C(10)-C(11)-C(12)	-0.7(6)
C(10)-C(11)-C(12)-C(13)	3.1(6)
C(9)-C(8)-C(13)-C(12)	0.8(5)
N(3)-C(8)-C(13)-C(12)	177.5(3)
C(11)-C(12)-C(13)-C(8)	-3.1(5)

Symmetry transformations used to generate equivalent atoms:

Table S9. Hydrogen bonds for d8v19290 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(3)-H(3)...O(1)	0.88	1.90	2.780(3)	174.5
N(2)-H(2)...O(3)	0.88	1.82	2.701(3)	178.8
N(1)-H(1B)...O(1)#1	0.88	1.97	2.789(3)	155.0
O(2)-H(2A)...O(3)#2	0.84	1.78	2.623(3)	179.4
N(3)-H(3)...O(1)	0.88	1.90	2.780(3)	174.5
N(2)-H(2)...O(3)	0.88	1.82	2.701(3)	178.8
N(1)-H(1B)...O(1)#1	0.88	1.97	2.789(3)	155.0
O(2)-H(2A)...O(3)#2	0.84	1.78	2.623(3)	179.4
O(2)-H(2A)...O(3)#2	0.84	1.78	2.623(3)	179.4
N(1)-H(1B)...O(1)#1	0.88	1.97	2.789(3)	155.0
N(2)-H(2)...O(3)	0.88	1.82	2.701(3)	178.8
N(3)-H(3)...O(1)	0.88	1.90	2.780(3)	174.5
O(2)-H(2A)...O(3)#2	0.84	1.78	2.623(3)	179.4
N(1)-H(1B)...O(1)#1	0.88	1.97	2.789(3)	155.0
N(2)-H(2)...O(3)	0.88	1.82	2.701(3)	178.8
N(3)-H(3)...O(1)	0.88	1.90	2.780(3)	174.5

Symmetry transformations used to generate equivalent atoms:
#1 -y+2/3,x-y+1/3,z+1/3 #2 -x+1,-y+1,-z

7. Single-crystal X-ray analysis of complex formed from DPG and $AgSbF_6$.

Single crystal of $C_{26}H_{26}AgF_6N_6Sb$ was selected on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2, the structure was solved with the ShelXS structure solution program using Direct Methods and refined with the ShelXL refinement package using Least Squares minimisation. Crystal Data for $C_{26}H_{26}AgF_6N_6Sb$ (M =766.15 g/mol): orthorhombic, space group Pna21 (no. 33), a = 14.7369(6) Å, b = 31.5086(13) Å, c = 5.9773(2) Å, V = 2775.49(19) Å3, Z = 4, T = 170.0 K, μ(GaKα) = 9.462 mm^{-1}, Dcalc = 1.833 g/cm^3, 22100 reflections measured ($5.76° \leq 2\Theta \leq 109.906°$), 4443 unique ($R_{int}$ = 0.1534, R_{sigma} = 0.1249) which were used in all calculations. The final R_1 was 0.0639 ($I > 2\sigma(I)$) and wR_2 was 0.1822 (all data). Number of restraints - 1, number of constraints - unknown.

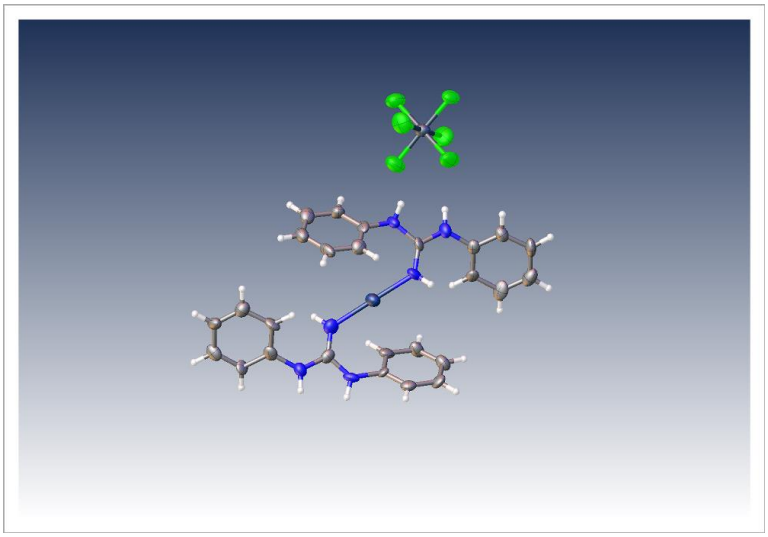


Table S10. Crystal data and structure refinement for CCDC-1894496.

Identification code	CCDC-1894496	
Empirical formula	C26 H26 Ag F6 N6 Sb	
Formula weight	766.15	
Temperature	170.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	$Pna2_1$	
Unit cell dimensions	a = 14.7369(6) Å	α= 90°.
	b = 31.5086(13) Å	β= 90°.
	c = 5.9773(2) Å	γ = 90°.

Volume	2775.49(19) $Å^3$
Z	4
Density (calculated)	1.833 Mg/m^3
Absorption coefficient	9.462 mm^{-1}
F(000)	1504
Crystal size	0.03 x 0.02 x 0.01 mm^3
Theta range for data collection	2.880 to 54.953°.
Index ranges	-15<=h<=17, -38<=k<=35, -7<=l<=4
Reflections collected	22100
Independent reflections	4443 [R(int) = 0.1534]
Completeness to theta = 53.594°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7508 and 0.4138
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4443 / 1 / 361
Goodness-of-fit on F^2	1.001
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR2 = 0.1336
R indices (all data)	R1 = 0.1557, wR2 = 0.1822
Absolute structure parameter	0.01(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.912 and -1.434 $e.Å^{-3}$

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for mj19077_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	-12684(1)	-3742(1)	8989(2)	40(1)
F(1)	-13600(9)	-3814(4)	11130(30)	55(4)
F(2)	-12860(9)	-3157(3)	9050(30)	71(4)
F(3)	-11816(11)	-3703(5)	11260(40)	77(6)
F(4)	-11748(10)	-3672(5)	6930(30)	70(5)
F(5)	-12537(9)	-4327(4)	8910(30)	70(4)
F(6)	-13560(10)	-3779(5)	6700(40)	66(5)
Ag(1)	-7678(1)	-3756(1)	6563(3)	45(1)
N(1)	-8470(13)	-3668(6)	9370(40)	43(6)
N(2)	-6865(14)	-3844(6)	3740(50)	47(6)
N(3)	-9860(12)	-3926(5)	7990(30)	41(5)
N(4)	-9898(13)	-3423(6)	10750(30)	44(5)
N(5)	-5519(12)	-3576(5)	5020(30)	35(5)
N(6)	-5465(12)	-4079(5)	2330(30)	39(5)
C(1)	-9361(14)	-3668(6)	9470(30)	32(5)
C(2)	-9600(14)	-3094(6)	12220(40)	34(6)
C(3)	-9991(15)	-3046(6)	14190(40)	42(6)
C(4)	-9775(17)	-2720(8)	15680(40)	47(7)
C(5)	-9080(20)	-2443(7)	15080(50)	53(8)
C(6)	-8683(18)	-2486(8)	13020(60)	50(7)
C(7)	-8931(12)	-2805(6)	11560(40)	35(5)
C(8)	-9537(15)	-4243(6)	6540(50)	44(6)
C(9)	-8782(16)	-4505(6)	7090(40)	45(6)
C(10)	-8519(16)	-4800(7)	5460(50)	49(8)
C(11)	-8960(17)	-4840(7)	3440(50)	51(7)
C(12)	-9691(17)	-4587(7)	2990(40)	49(7)
C(13)	-9967(15)	-4286(7)	4510(40)	42(6)
C(14)	-5996(15)	-3835(6)	3700(40)	35(5)
C(15)	-5835(12)	-3272(5)	6650(40)	28(5)
C(16)	-6580(13)	-3002(7)	6000(40)	41(6)
C(17)	-6855(16)	-2703(7)	7510(40)	42(6)

C(18)	-6458(16)	-2675(7)	9610(40)	44(7)
C(19)	-5742(15)	-2932(6)	10130(40)	41(6)
C(20)	-5448(14)	-3228(6)	8630(40)	37(5)
C(21)	-5765(14)	-4400(7)	740(40)	38(6)
C(22)	-5349(14)	-4430(6)	-1310(40)	32(5)
C(23)	-5605(15)	-4754(6)	-2740(40)	42(6)
C(24)	-6277(16)	-5043(7)	-2130(50)	44(7)
C(25)	-6698(17)	-5014(7)	-140(40)	45(7)
C(26)	-6433(13)	-4699(6)	1470(40)	40(5)

Table S12. Bond lengths [Å] and angles [°] for mj19077_0m.

Sb(1)-F(1)	1.874(14)
Sb(1)-F(2)	1.862(11)
Sb(1)-F(3)	1.87(2)
Sb(1)-F(4)	1.862(16)
Sb(1)-F(5)	1.855(12)
Sb(1)-F(6)	1.884(19)
Ag(1)-N(1)	2.06(2)
Ag(1)-N(2)	2.09(3)
N(1)-C(1)	1.31(3)
N(2)-C(14)	1.28(3)
N(3)-C(1)	1.41(3)
N(3)-C(8)	1.41(3)
N(4)-C(1)	1.35(2)
N(4)-C(2)	1.43(3)
N(5)-C(14)	1.34(3)
N(5)-C(15)	1.44(2)
N(6)-C(14)	1.37(3)
N(6)-C(21)	1.46(3)
C(2)-C(3)	1.32(3)
C(2)-C(7)	1.40(3)
C(3)-C(4)	1.39(3)
C(4)-C(5)	1.40(3)
C(5)-C(6)	1.37(4)
C(6)-C(7)	1.38(3)
C(8)-C(9)	1.42(3)
C(8)-C(13)	1.38(3)
C(9)-C(10)	1.40(3)

C(10)-C(11)	1.38(3)
C(11)-C(12)	1.37(3)
C(12)-C(13)	1.38(3)
C(15)-C(16)	1.44(3)
C(15)-C(20)	1.32(3)
C(16)-C(17)	1.37(3)
C(17)-C(18)	1.39(3)
C(18)-C(19)	1.37(3)
C(19)-C(20)	1.36(3)
C(21)-C(22)	1.37(3)
C(21)-C(26)	1.43(3)
C(22)-C(23)	1.38(3)
C(23)-C(24)	1.39(3)
C(24)-C(25)	1.34(3)
C(25)-C(26)	1.44(3)
F(1)-Sb(1)-F(6)	89.7(6)
F(2)-Sb(1)-F(1)	90.3(6)
F(2)-Sb(1)-F(3)	90.9(8)
F(2)-Sb(1)-F(6)	88.9(7)
F(3)-Sb(1)-F(1)	90.3(8)
F(3)-Sb(1)-F(6)	179.8(8)
F(4)-Sb(1)-F(1)	178.2(7)
F(4)-Sb(1)-F(2)	89.9(7)
F(4)-Sb(1)-F(3)	88.0(7)
F(4)-Sb(1)-F(6)	92.1(8)
F(5)-Sb(1)-F(1)	89.0(6)
F(5)-Sb(1)-F(2)	178.7(6)
F(5)-Sb(1)-F(3)	90.2(7)
F(5)-Sb(1)-F(4)	90.9(6)
F(5)-Sb(1)-F(6)	90.1(7)
N(1)-Ag(1)-N(2)	179.4(9)
C(1)-N(1)-Ag(1)	126.8(19)
C(14)-N(2)-Ag(1)	126(2)
C(1)-N(3)-C(8)	128.3(18)
C(1)-N(4)-C(2)	125.8(19)
C(14)-N(5)-C(15)	129.3(17)
C(14)-N(6)-C(21)	127.4(18)
N(1)-C(1)-N(3)	119.7(19)
N(1)-C(1)-N(4)	128(2)

N(4)-C(1)-N(3)	112.4(18)
C(3)-C(2)-N(4)	120(2)
C(3)-C(2)-C(7)	119(2)
C(7)-C(2)-N(4)	121(2)
C(2)-C(3)-C(4)	124(2)
C(3)-C(4)-C(5)	118(2)
C(6)-C(5)-C(4)	119(3)
C(5)-C(6)-C(7)	122(3)
C(6)-C(7)-C(2)	119(2)
N(3)-C(8)-C(9)	122(2)
C(13)-C(8)-N(3)	117(2)
C(13)-C(8)-C(9)	120(2)
C(10)-C(9)-C(8)	116(2)
C(11)-C(10)-C(9)	123(2)
C(12)-C(11)-C(10)	119(2)
C(11)-C(12)-C(13)	120(3)
C(12)-C(13)-C(8)	121(2)
N(2)-C(14)-N(5)	122(2)
N(2)-C(14)-N(6)	125(2)
N(5)-C(14)-N(6)	113.3(19)
C(16)-C(15)-N(5)	117(2)
C(20)-C(15)-N(5)	122.3(19)
C(20)-C(15)-C(16)	120(2)
C(17)-C(16)-C(15)	117(2)
C(16)-C(17)-C(18)	121(2)
C(19)-C(18)-C(17)	120(2)
C(20)-C(19)-C(18)	120(2)
C(15)-C(20)-C(19)	122(2)
C(22)-C(21)-N(6)	120(2)
C(22)-C(21)-C(26)	122(2)
C(26)-C(21)-N(6)	118(2)
C(21)-C(22)-C(23)	119(2)
C(22)-C(23)-C(24)	121(2)
C(25)-C(24)-C(23)	121(2)
C(24)-C(25)-C(26)	121(2)
C(21)-C(26)-C(25)	116(2)

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mj19077_0m. The anisotropic displacement factor exponent takes the form: $-2\ ^2[\ h^2\ a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Sb(1)	33(1)	39(1)	48(1)	4(1)	0(1)	0(1)
F(1)	41(8)	78(9)	45(10)	12(7)	6(7)	-13(7)
F(2)	85(11)	37(6)	92(12)	-3(8)	8(11)	-11(6)
F(3)	44(10)	132(15)	55(12)	1(12)	-12(10)	-8(9)
F(4)	49(10)	99(13)	62(12)	8(9)	12(9)	2(8)
F(5)	78(11)	50(7)	81(12)	-1(8)	4(11)	24(6)
F(6)	44(10)	87(10)	67(15)	2(9)	-7(10)	-11(8)
Ag(1)	34(1)	50(1)	50(2)	-8(1)	7(1)	-2(1)
N(1)	26(11)	70(13)	34(16)	0(10)	11(9)	-2(9)
N(2)	42(13)	59(12)	41(15)	-4(12)	-7(12)	6(9)
N(3)	30(10)	43(10)	49(13)	-17(9)	16(9)	-9(8)
N(4)	45(13)	43(11)	43(13)	-13(9)	9(10)	-1(9)
N(5)	18(10)	35(9)	50(13)	8(9)	6(8)	-1(8)
N(6)	38(12)	46(11)	34(13)	-3(9)	8(9)	0(9)
C(1)	38(13)	38(12)	18(13)	-2(9)	10(9)	1(9)
C(2)	33(13)	35(12)	33(16)	-1(10)	-4(10)	12(9)
C(3)	44(14)	46(13)	35(18)	1(12)	8(13)	7(10)
C(4)	58(18)	54(16)	31(15)	-14(12)	0(12)	20(13)
C(5)	60(20)	44(14)	60(20)	-15(14)	-17(14)	9(13)
C(6)	64(17)	31(11)	56(19)	-7(12)	-13(16)	24(15)
C(7)	20(11)	46(12)	39(14)	-10(12)	-7(12)	9(9)
C(8)	50(15)	38(12)	45(16)	-18(12)	18(14)	-29(11)
C(9)	50(16)	46(13)	38(17)	6(11)	2(12)	-3(11)
C(10)	40(16)	34(12)	70(20)	-15(12)	28(14)	-2(11)
C(11)	50(17)	49(14)	50(20)	-14(13)	18(15)	-9(13)
C(12)	63(19)	47(14)	38(17)	3(12)	10(14)	-14(12)
C(13)	28(12)	53(14)	47(18)	-9(13)	-3(11)	0(10)
C(14)	38(13)	33(11)	34(14)	3(11)	-11(12)	0(9)
C(15)	23(10)	29(10)	33(13)	-10(10)	-3(11)	-9(8)
C(16)	24(12)	63(14)	37(15)	7(12)	6(11)	-13(10)
C(17)	35(14)	56(13)	35(16)	5(12)	1(12)	18(11)
C(18)	42(16)	46(13)	43(17)	1(11)	13(12)	9(11)
C(19)	40(15)	33(12)	51(17)	-17(11)	-8(12)	-10(10)
C(20)	27(12)	37(11)	47(17)	3(11)	1(12)	-11(9)
C(21)	29(14)	46(13)	39(15)	0(11)	-2(11)	19(10)

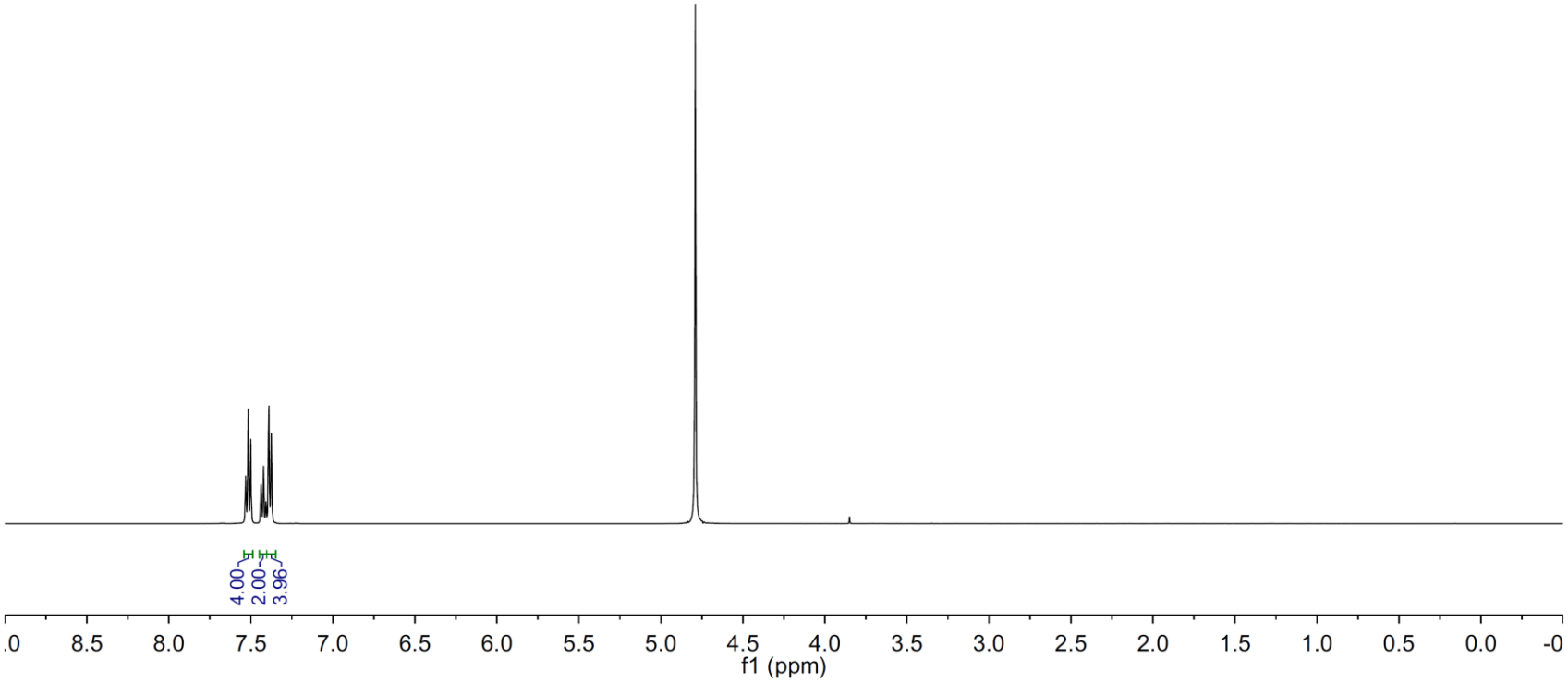
C(22)	46(14)	36(11)	15(13)	10(10)	4(11)	-3(9)
C(23)	45(14)	34(12)	46(17)	7(11)	10(12)	16(11)
C(24)	27(15)	48(14)	60(20)	-20(13)	4(12)	-1(11)
C(25)	47(17)	42(13)	46(18)	-3(12)	-6(13)	3(11)
C(26)	34(13)	49(13)	38(14)	12(12)	18(13)	-4(10)

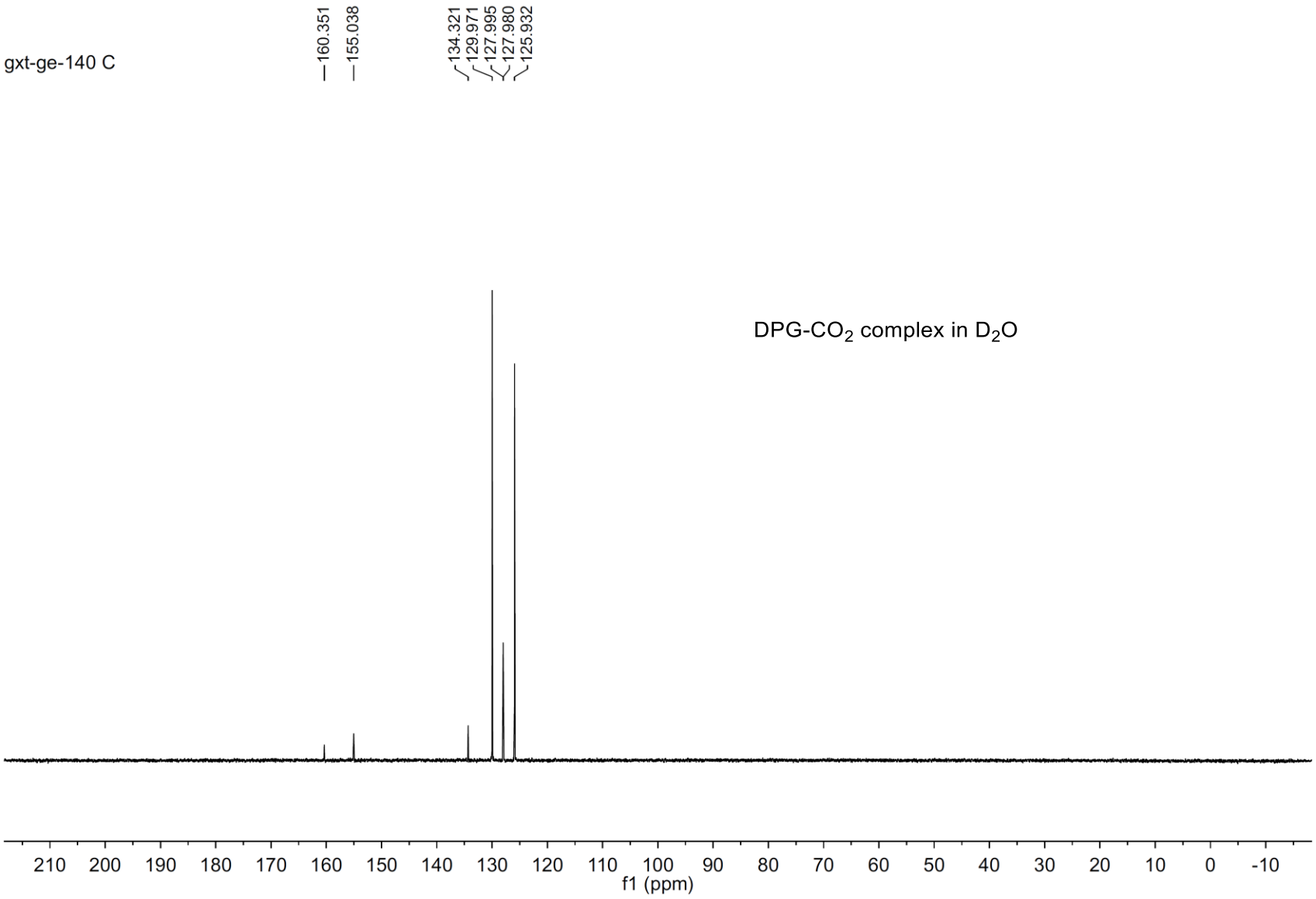
Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3)

	x	y	z	U(eq)
H(1)	-8180	-3627	10643	52
H(2)	-7144	-3892	2462	57
H(3)	-10327	-4030	8725	49
H(4)	-10486	-3469	10673	52
H(5A)	-4926	-3594	4881	41
H(6A)	-4876	-4039	2429	47
H(3A)	-10444	-3244	14624	50
H(4A)	-10092	-2688	17057	57
H(5)	-8877	-2228	16086	64
H(6)	-8225	-2291	12584	60
H(7)	-8653	-2828	10132	42
H(9)	-8474	-4480	8475	54
H(10)	-8016	-4980	5765	58
H(11)	-8758	-5042	2370	61
H(12)	-10010	-4620	1616	59
H(13)	-10461	-4105	4151	51
H(16)	-6866	-3030	4586	49
H(17)	-7326	-2511	7121	51
H(18)	-6682	-2478	10683	52
H(19)	-5447	-2905	11538	50
H(20)	-4954	-3407	9020	45
H(22)	-4893	-4233	-1735	39
H(23)	-5318	-4780	-4153	50
H(24)	-6439	-5264	-3137	52
H(25)	-7178	-5204	198	54
H(26)	-6685	-4691	2936	48

gxt-ge-140 H

DPG-CO_2 complex in D_2O

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155.038
134.321
129.971
127.995
127.980
125.932
DPG-CO2 complex in D2O
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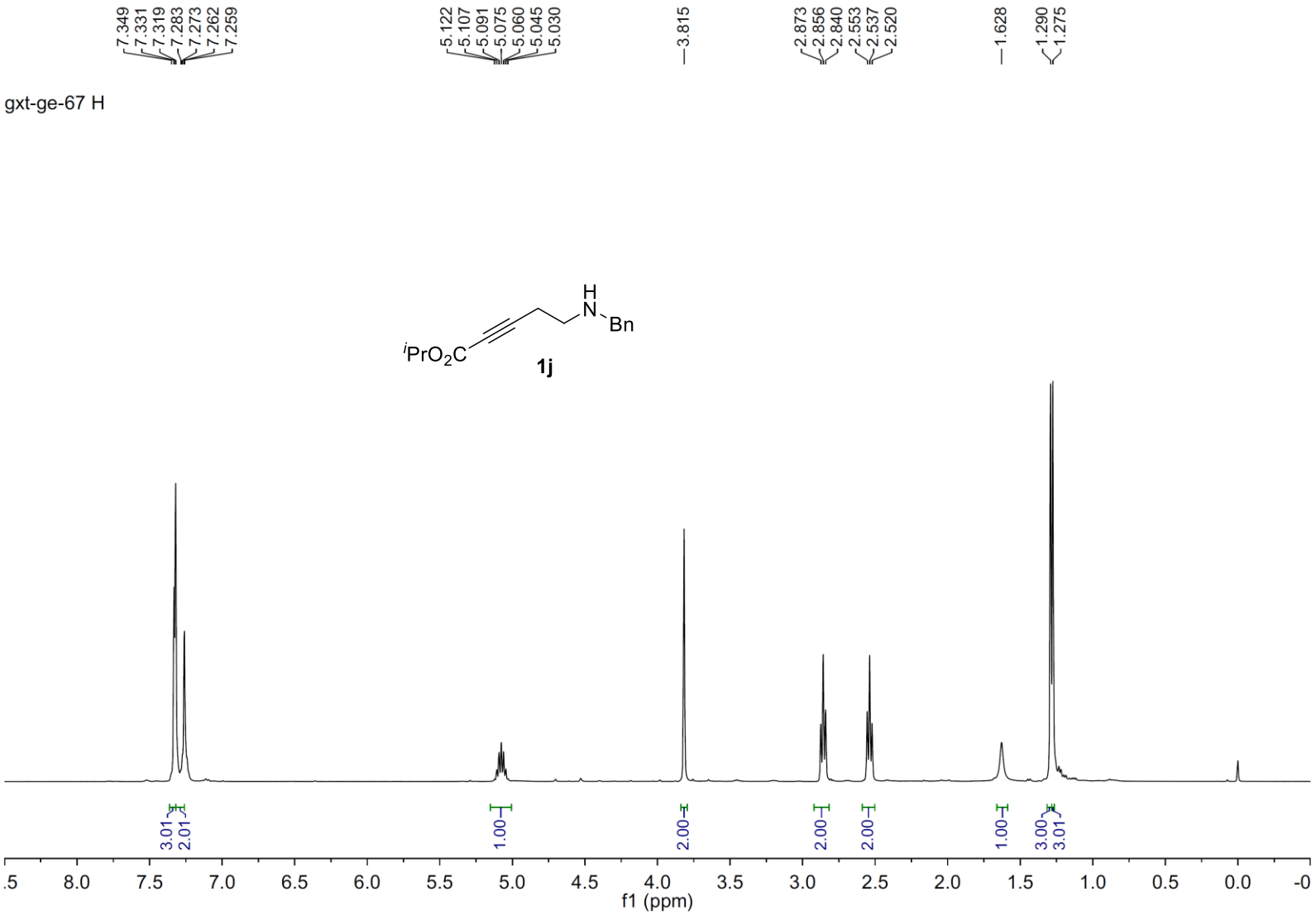
f1 (ppm)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7.273
7.262
7.259
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5.107
5.091
5.075
5.060
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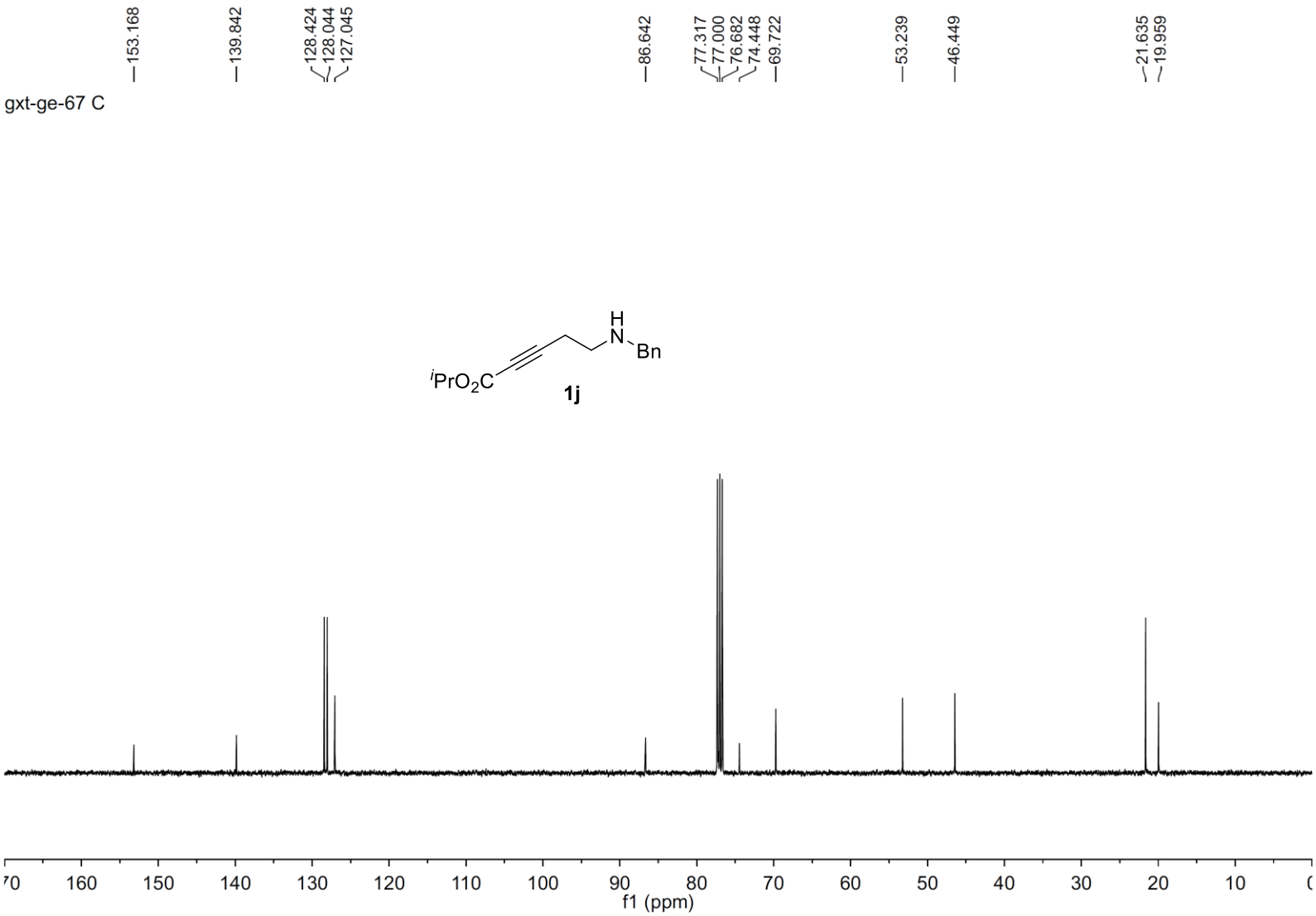
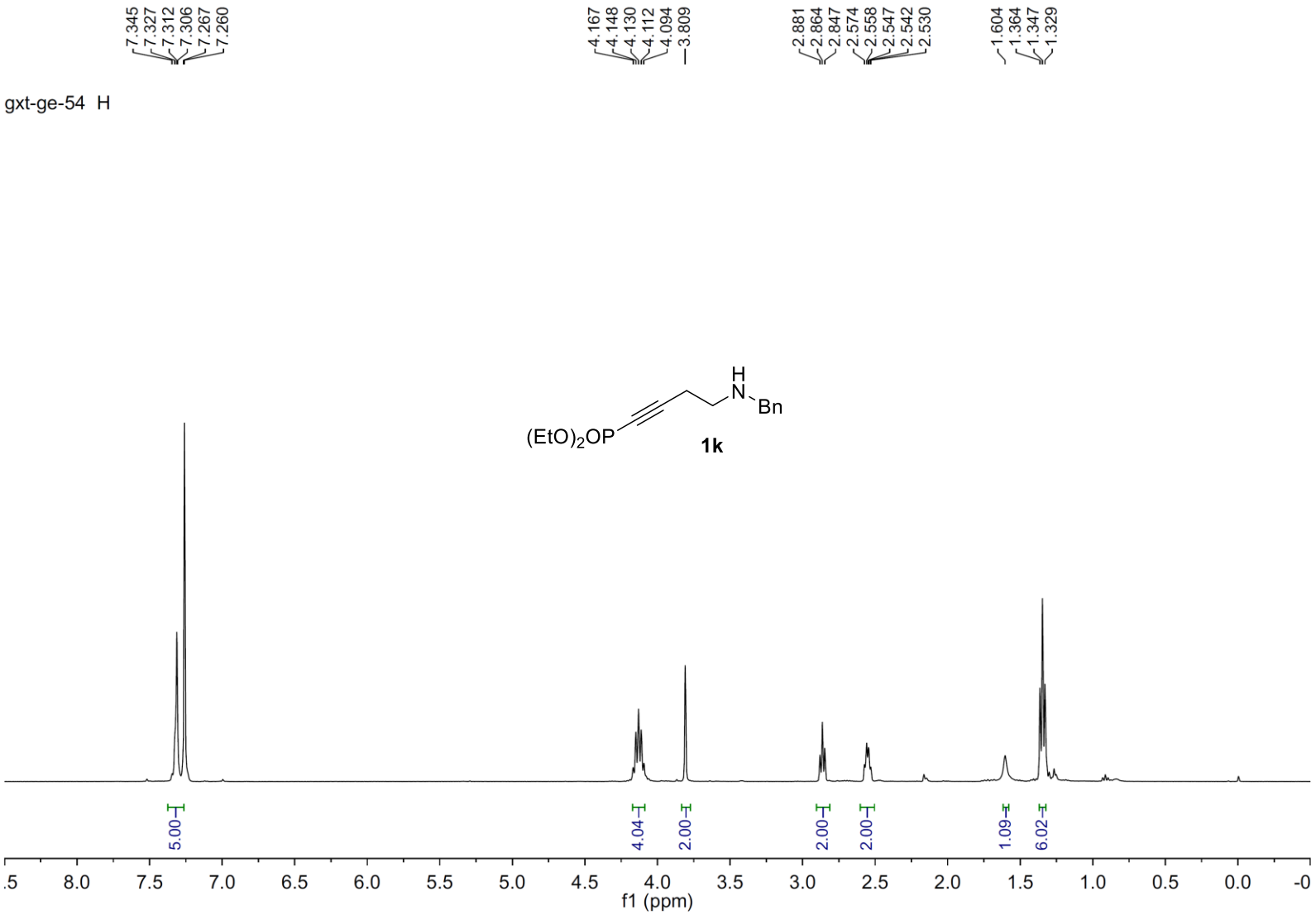
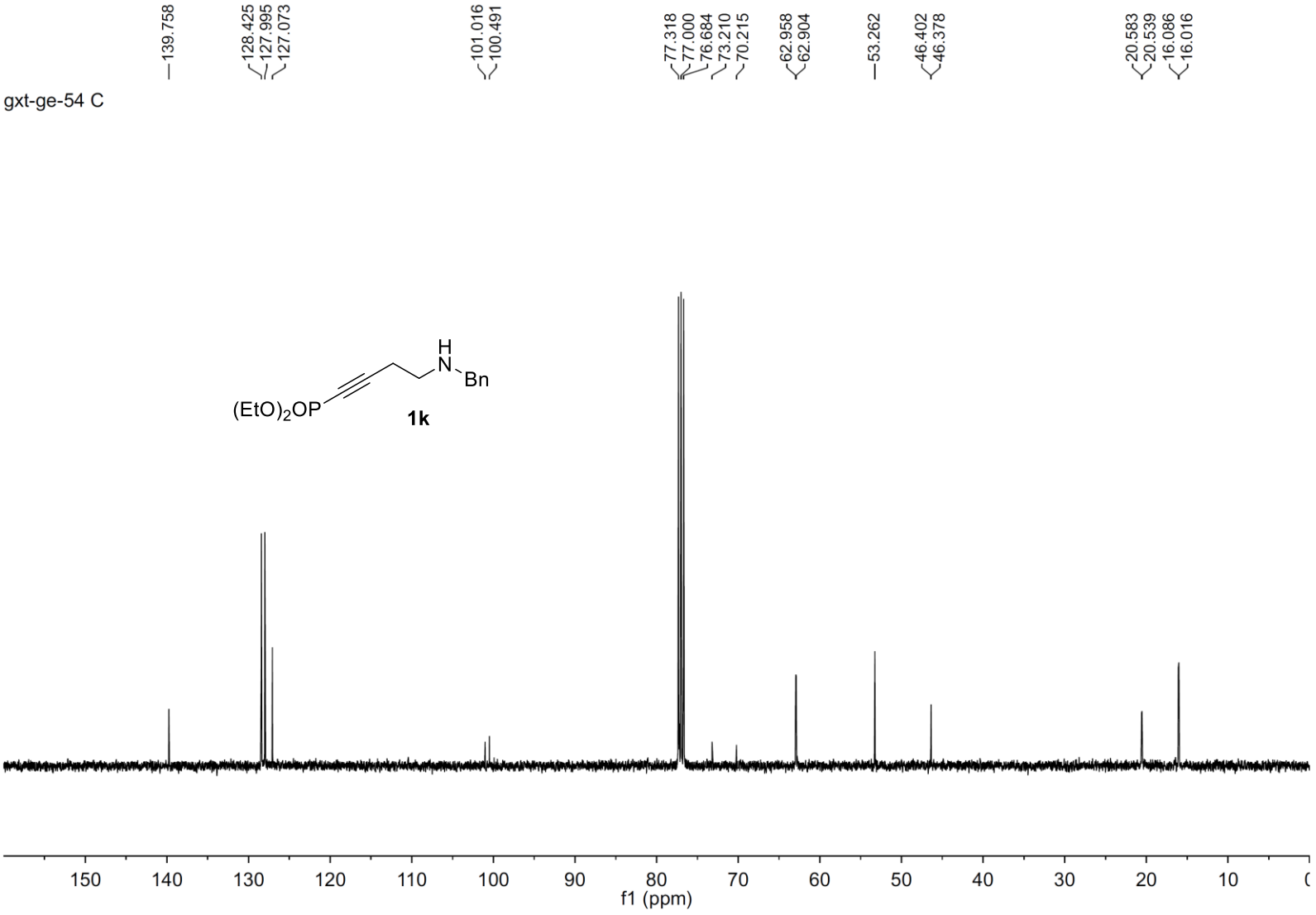
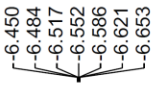
5.030
3.815
2.873
2.856
2.840
2.553
2.537
2.520
1.628
1.290
1.275
gxt-ge-67 H
H
N
Bn
iPrO2C
1j
3.01
2.01
1.00
2.00
2.00
2.00
1.00
3.00
3.01
f1 (ppm)

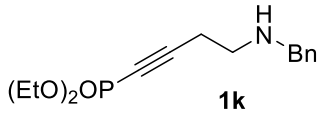

153.168
139.842
128.424
128.044
127.045
86.642
77.317
77.000
76.682
74.448
69.722
53.239
46.449
21.635
19.959
gxt-ge-67 C
H
N
Bn
iPrO2C
1j
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.345
7.327
7.312
7.306
7.267
7.260
4.167
4.148
4.130
4.112
4.094
3.809
2.881
2.864
2.847
2.574
2.558
2.547
2.542
2.530
1.604
1.364
1.347
1.329
gxt-ge-54 H
H
N
Bn
(EtO)2OP
1k
5.00
4.04
2.00
2.00
2.00
1.09
6.02
f1 (ppm)

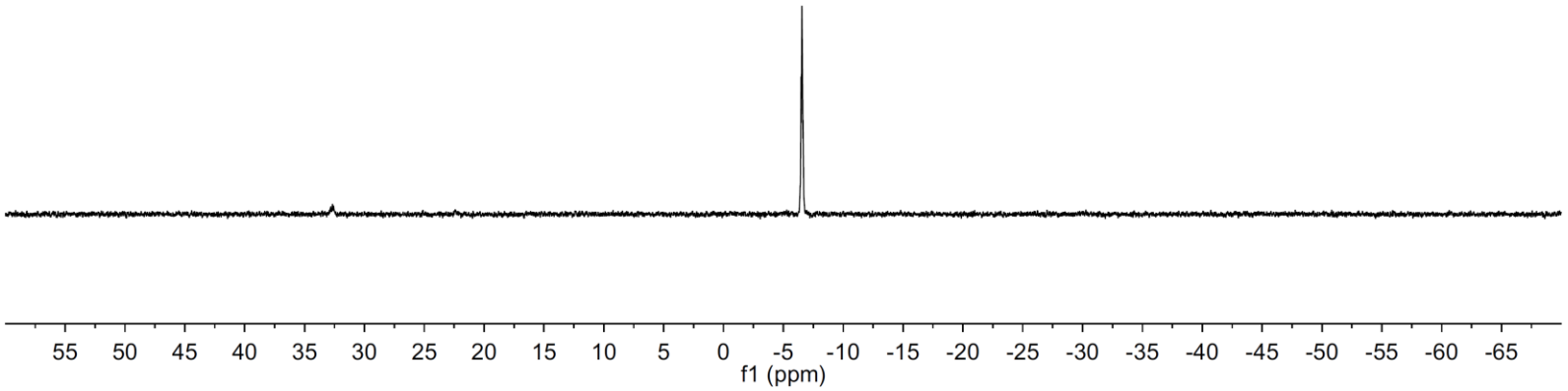

139.758
128.425
127.995
127.073
101.016
100.491
77.318
77.000
76.684
73.210
70.215
62.958
62.904
53.262
46.402
46.378
20.583
20.539
16.086
16.016
gxt-ge-54 C
H
N
Bn
(EtO)2OP
1k
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

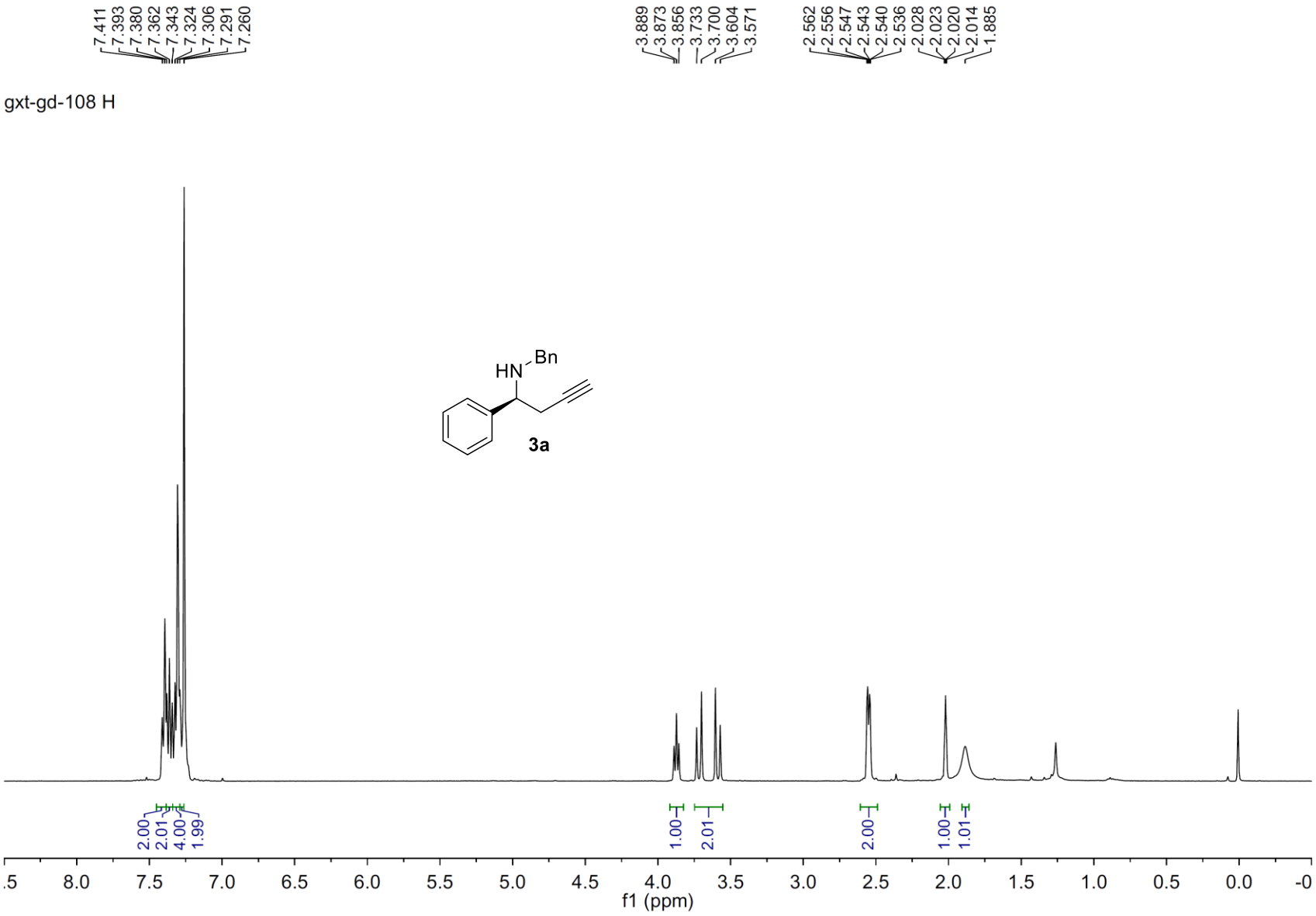

-6.450
-6.484
-6.517
-6.552
-6.586
-6.621
-6.653

gxt-ge-54 P

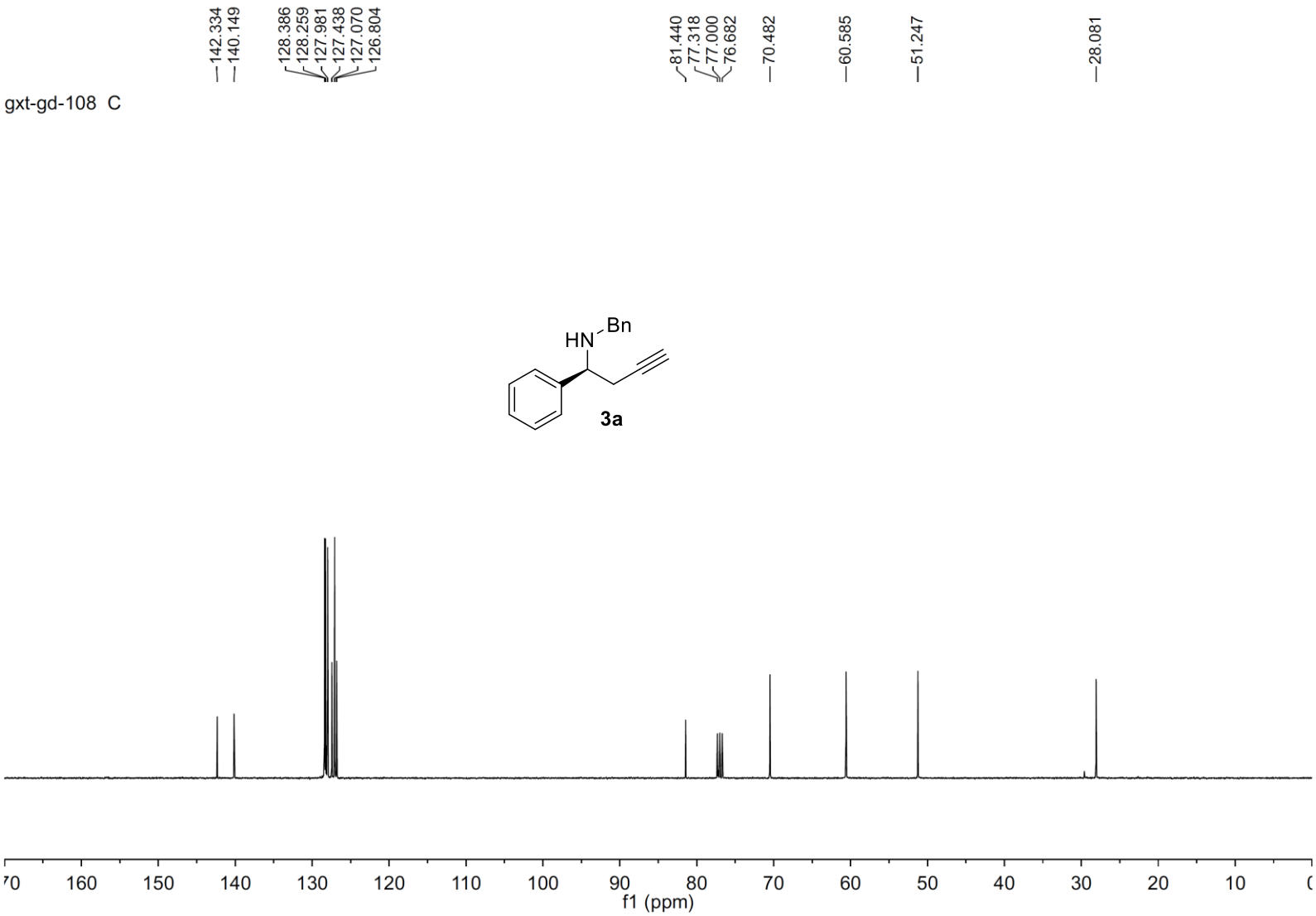

H
N
Bn
(EtO)2OP

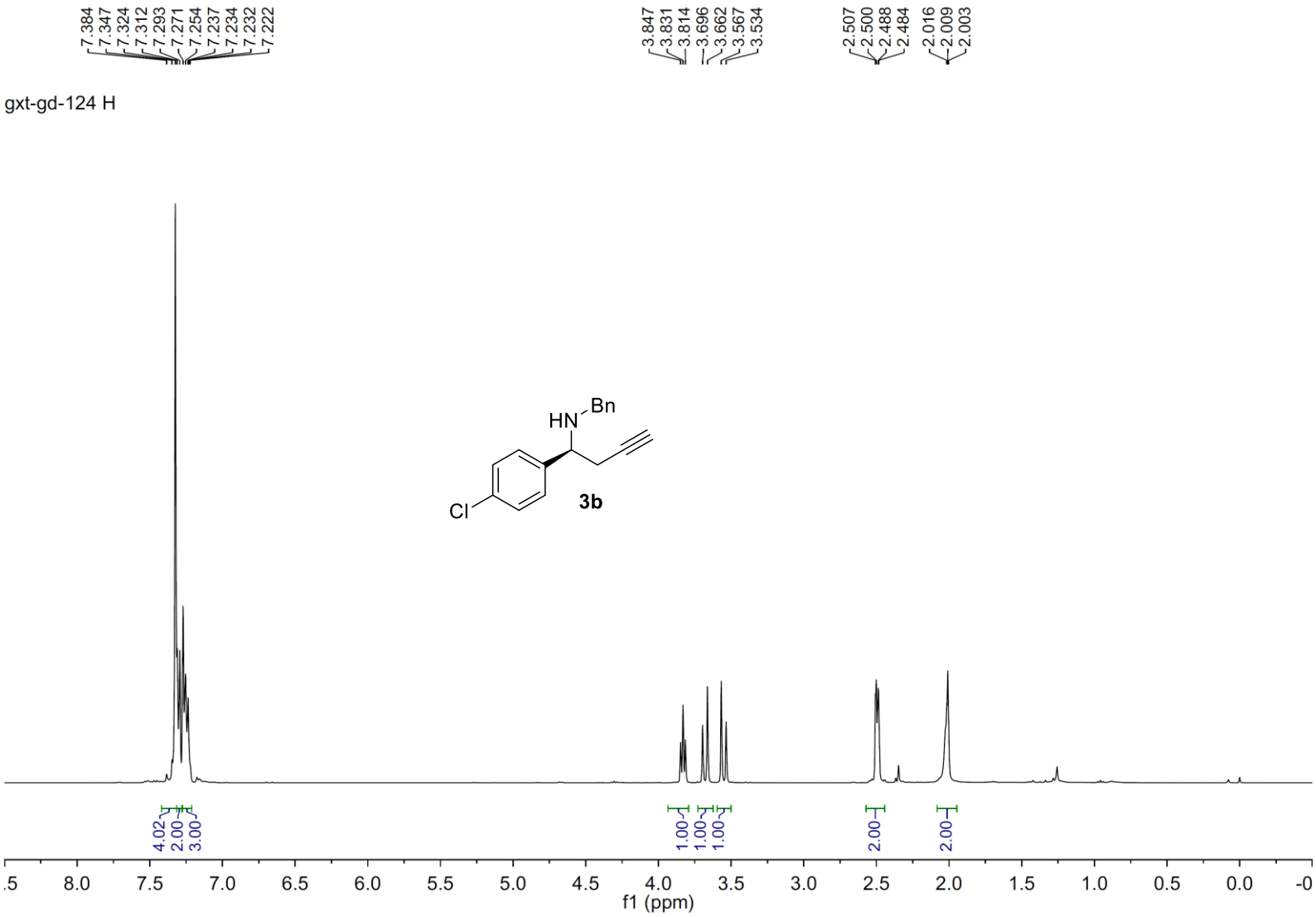
1k

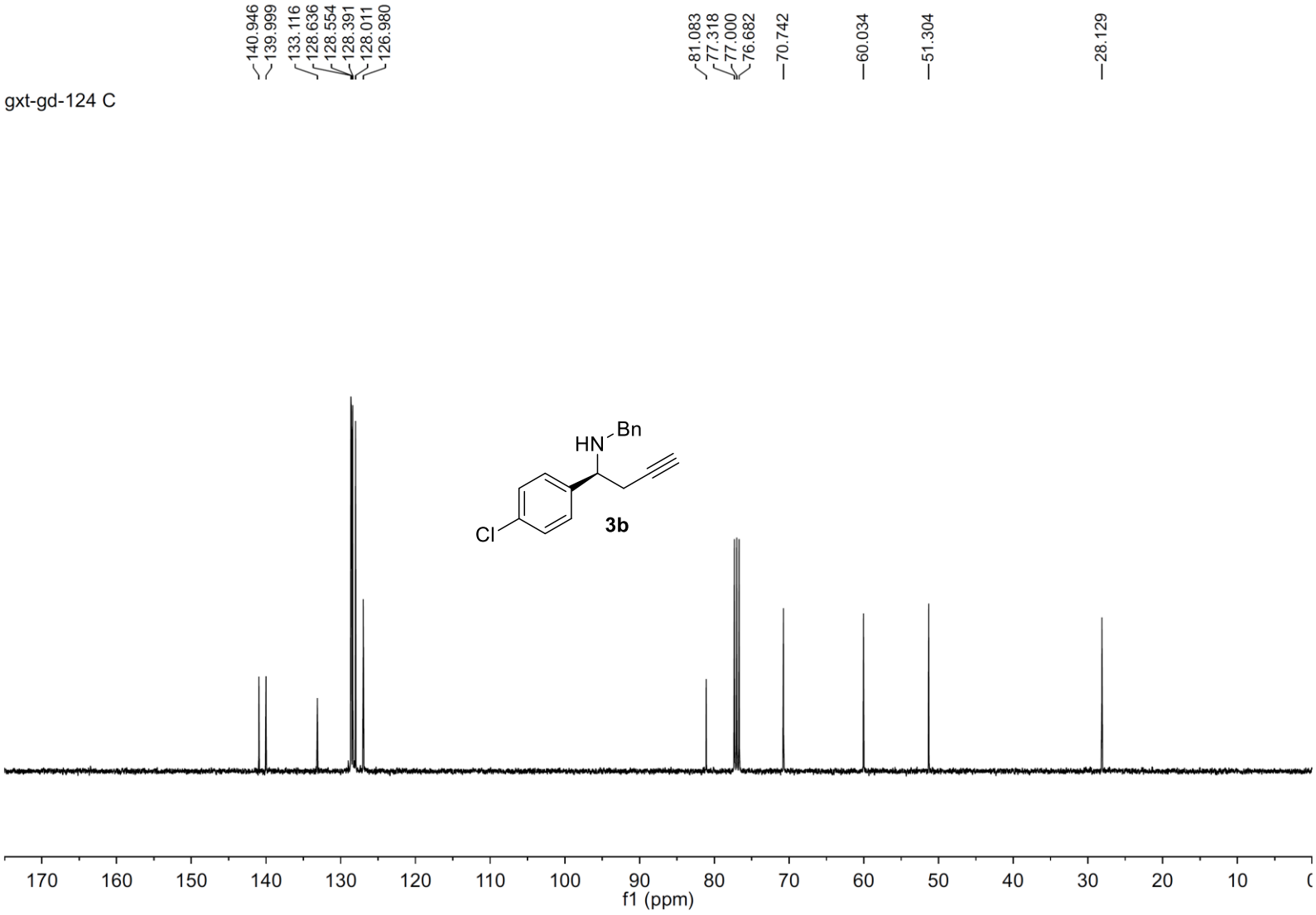

55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65
f1 (ppm)

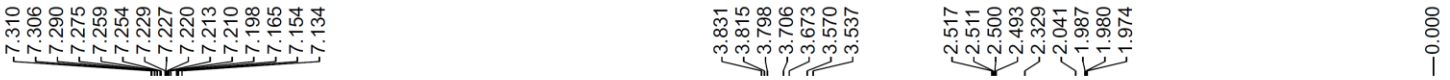

7.411
7.393
7.380
7.362
7.343
7.324
7.306
7.291
7.260
3.889
3.873
3.856
3.733
3.700
3.604
3.571
2.562
2.556
2.547
2.543
2.540
2.536
2.028
2.023
2.020
2.014
1.885
gxt-gd-108 H
HN
Bn
3a
2.00
2.01
4.00
1.99
1.00
2.01
2.00
1.00
1.01
f1 (ppm)

gxt-gd-108 C

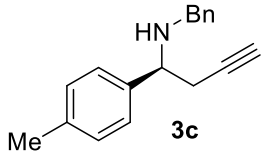

142.334
140.149
128.386
128.259
127.981
127.438
127.070
126.804
81.440
77.318
77.000
76.682
70.482
60.585
51.247
28.081
HN
Bn
3a
f1 (ppm)


7.384
7.347
7.324
7.312
7.293
7.271
7.254
7.237
7.234
7.232
7.222
3.847
3.831
3.814
3.696
3.662
3.567
3.534
2.507
2.500
2.488
2.484
2.016
2.009
2.003
gxt-gd-124 H
HN
Bn
Cl
3b
4.02
2.00
3.00
1.00
1.00
1.00
2.00
2.00
f1 (ppm)

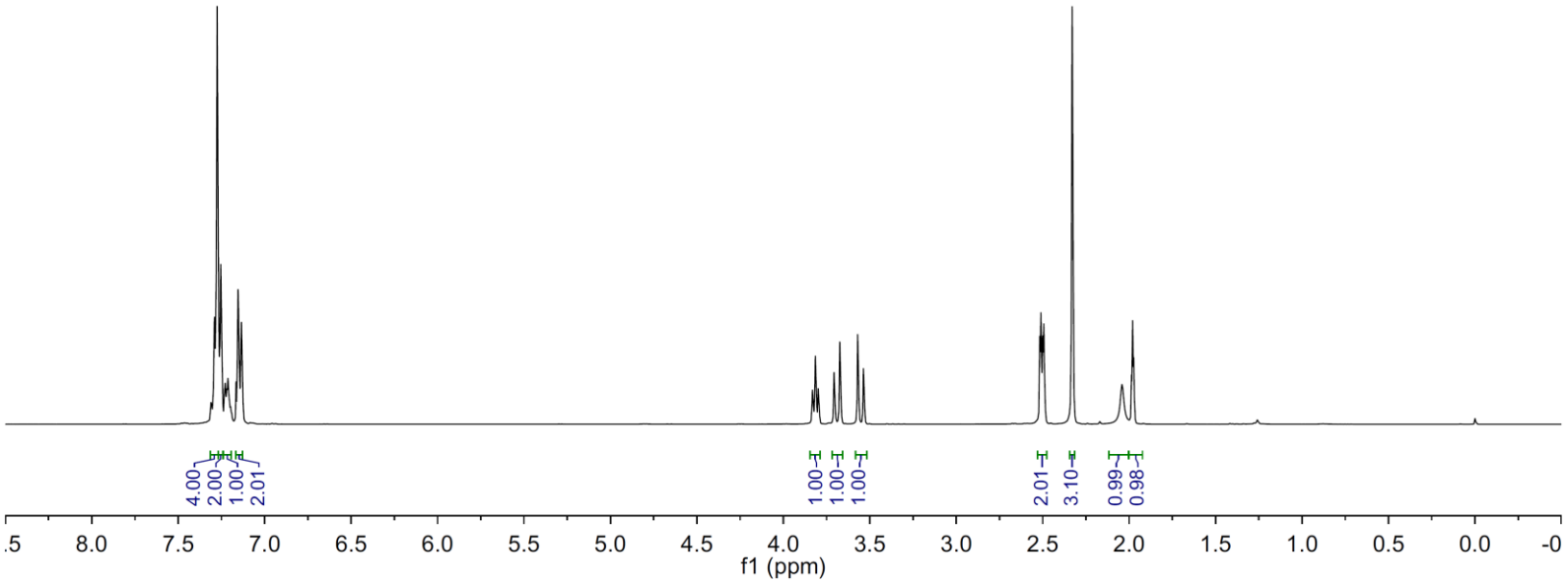

140.946
139.999
133.116
128.636
128.554
128.391
128.011
126.980
81.083
77.318
77.000
76.682
70.742
60.034
51.304
28.129
gxt-gd-124 C
HN
Bn
Cl
3b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

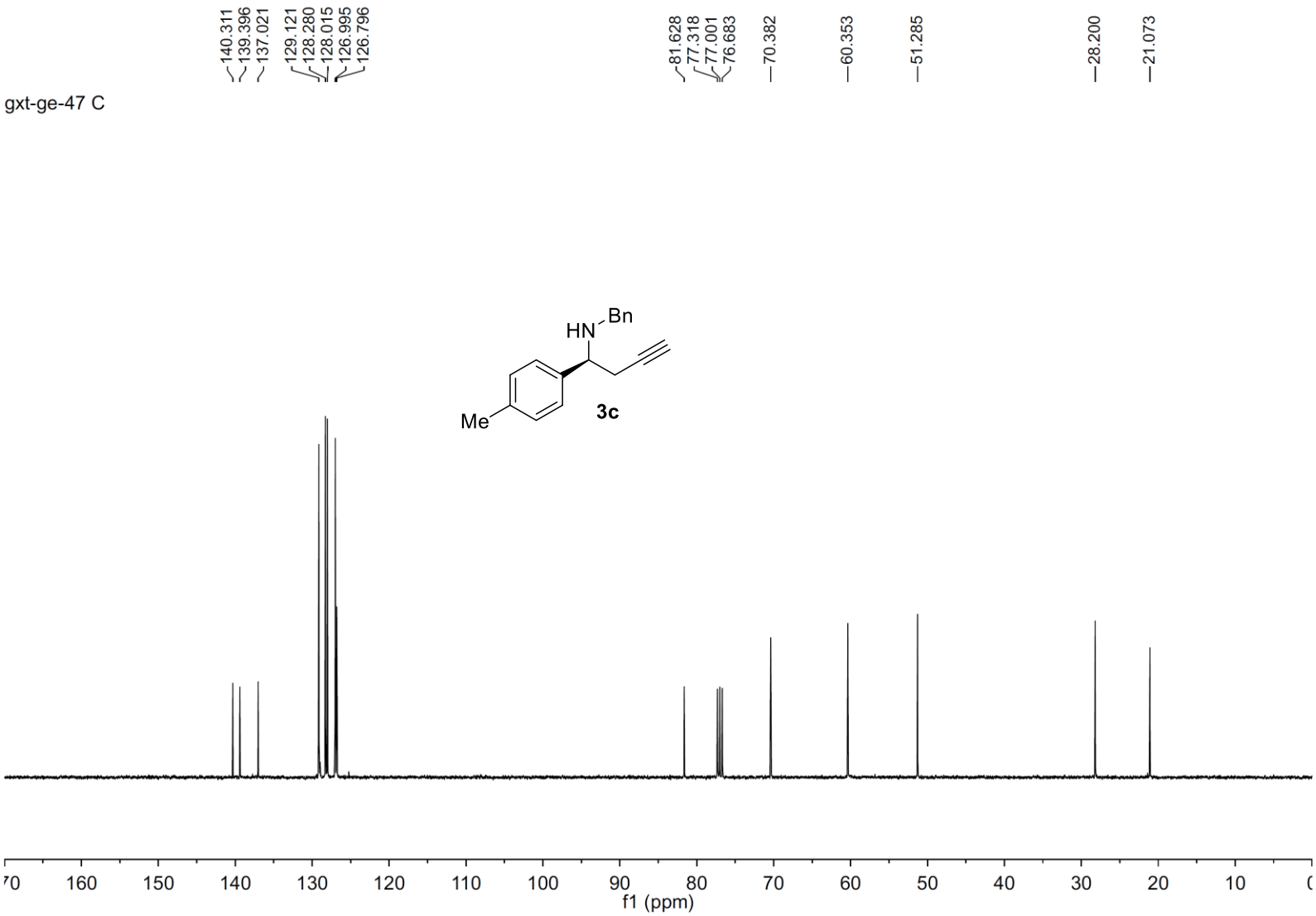

7.310
7.306
7.290
7.275
7.259
7.254
7.229
7.227
7.220
7.213
7.210
7.198
7.165
7.154
7.134
3.831
3.815
3.798
3.706
3.673
3.570
3.537
2.517
2.511
2.500
2.493
2.329
2.041
1.987
1.980
1.974
0.000

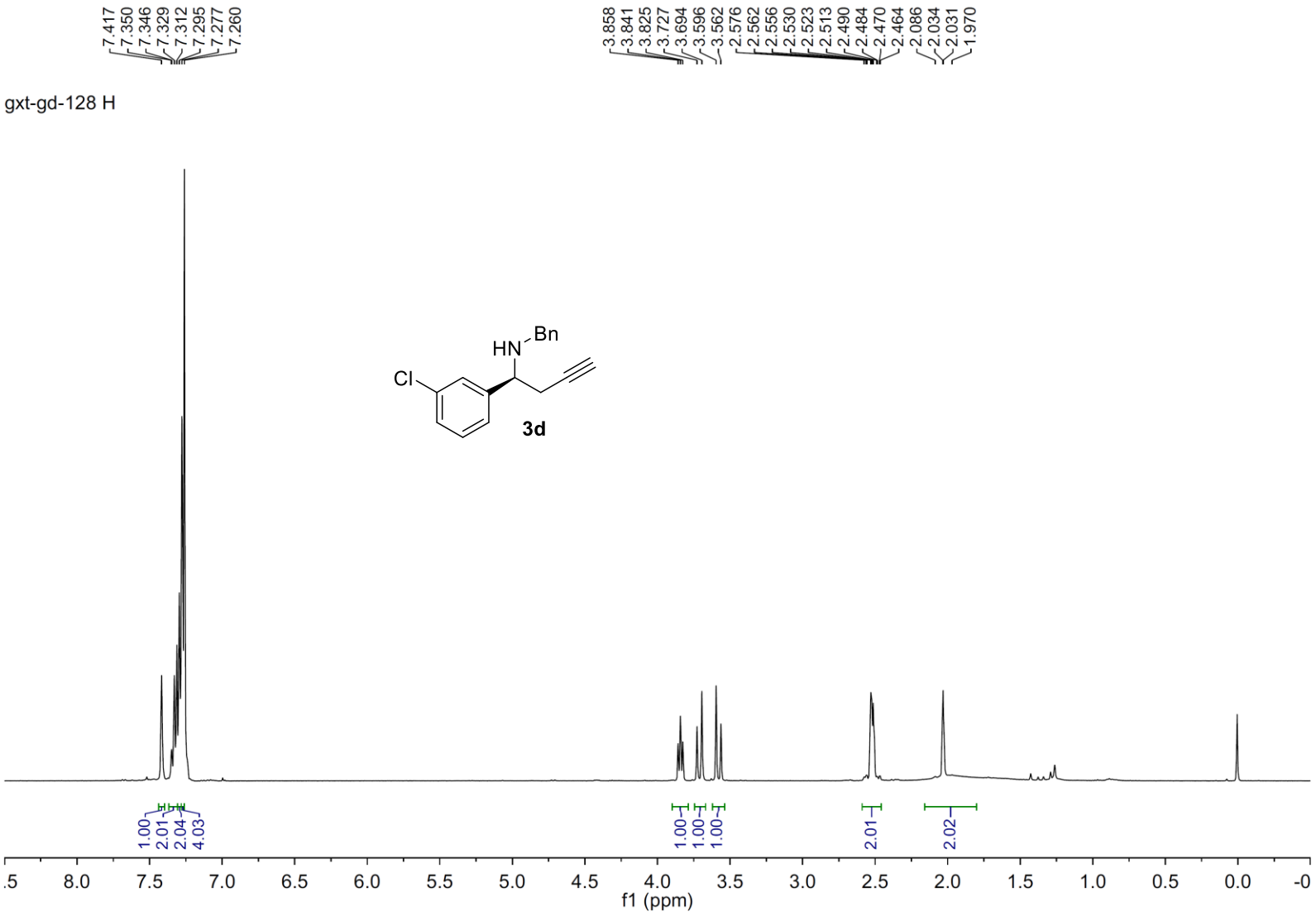
gxt-ge-47 H

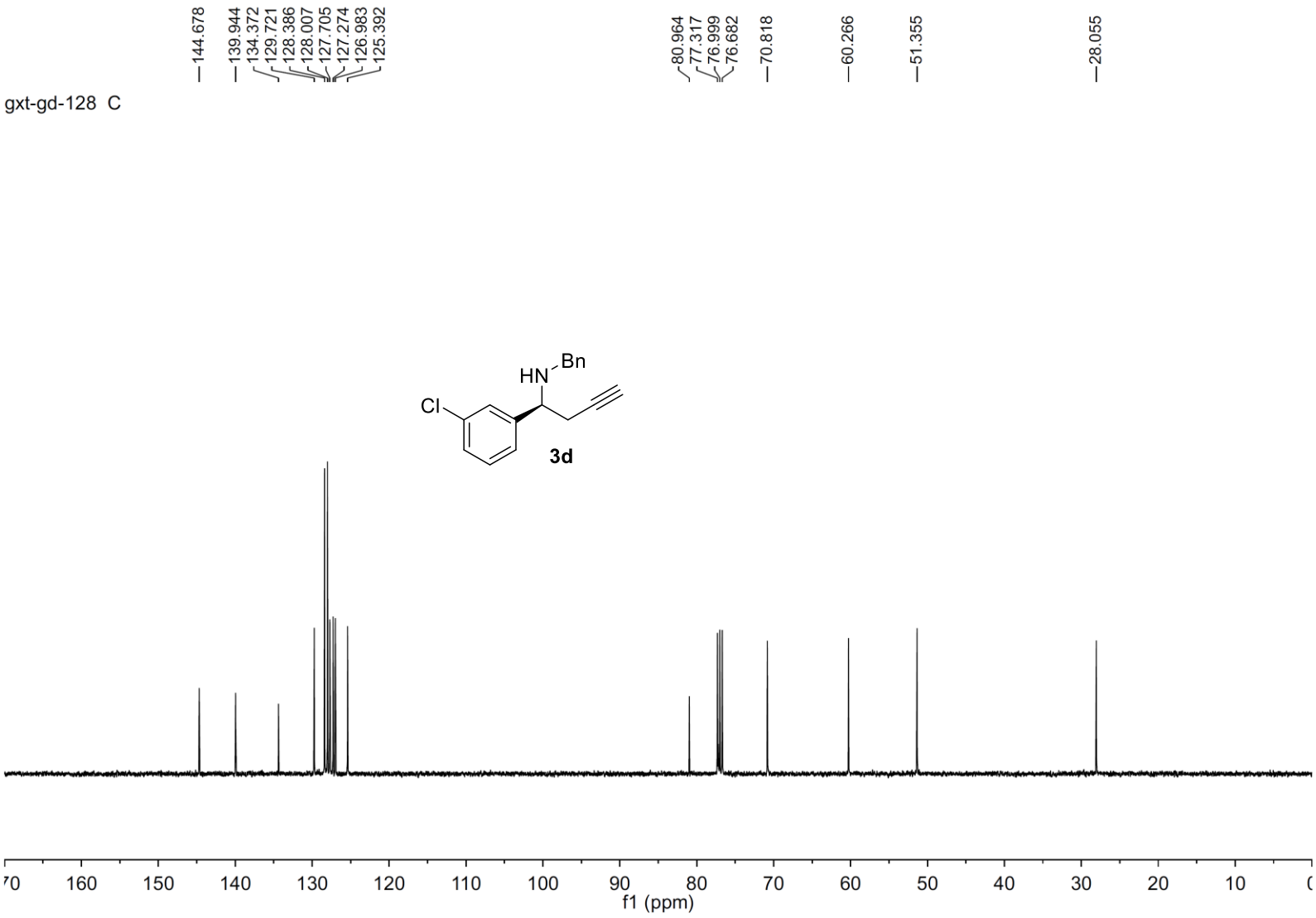

HN
Bn
Me

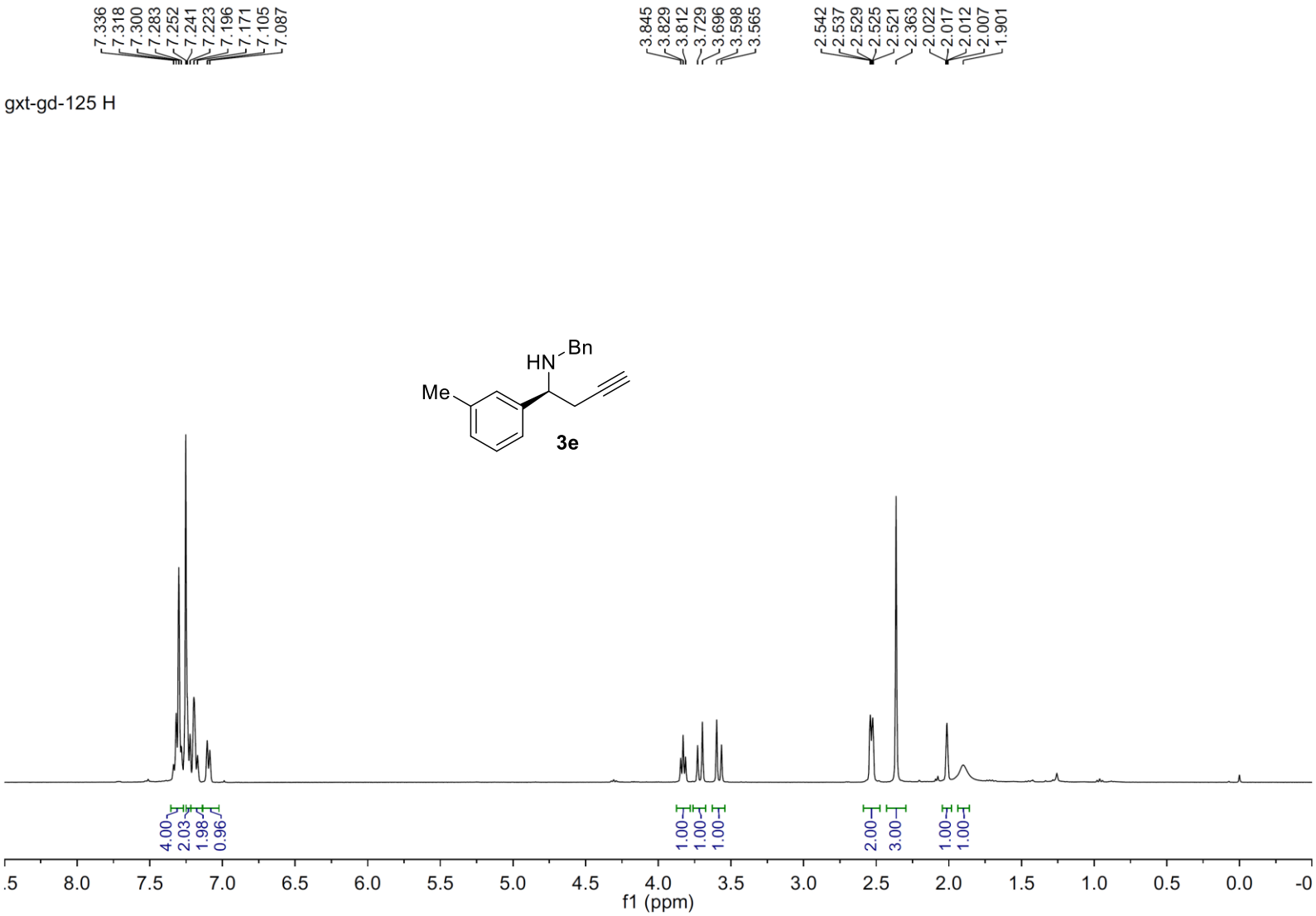
3c

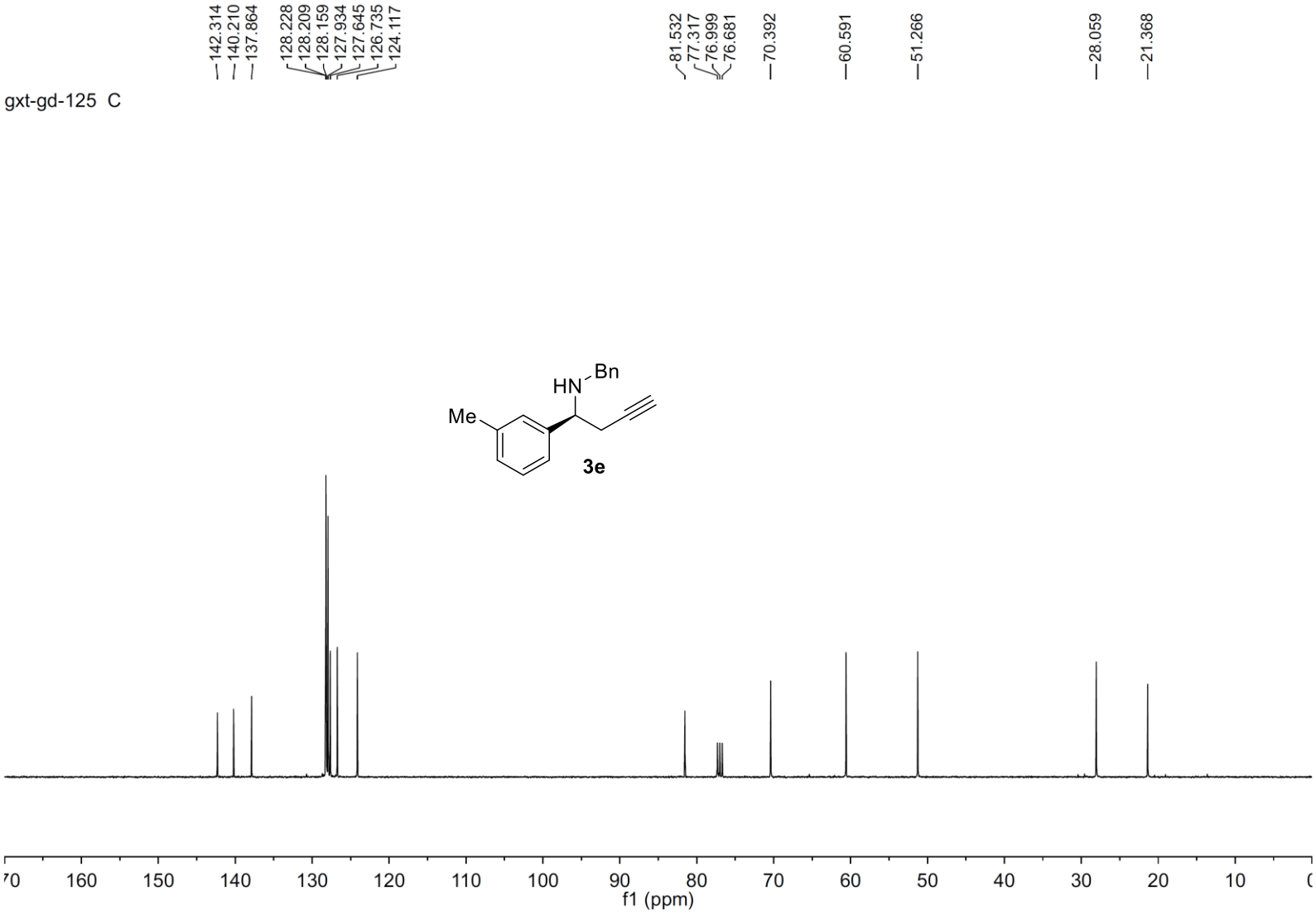

4.00
2.00
1.00
2.01
1.00
1.00
1.00
2.01
3.10
0.99
0.98
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


140.311
139.396
137.021
129.121
128.280
128.015
126.995
126.796
81.628
77.318
77.001
76.683
70.382
60.353
51.285
28.200
21.073
gxt-ge-47 C
HN
Bn
Me
3c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.417
7.350
7.346
7.329
7.312
7.295
7.277
7.260
3.858
3.841
3.825
3.727
3.694
3.596
3.562
2.576
2.562
2.556
2.530
2.523
2.513
2.490
2.484
2.470
2.464
2.086
2.034
2.031
1.970
gxt-gd-128 H
HN
Bn
Cl
3d
1.00
2.01
2.04
4.03
1.00
1.00
1.00
2.01
2.02
f1 (ppm)

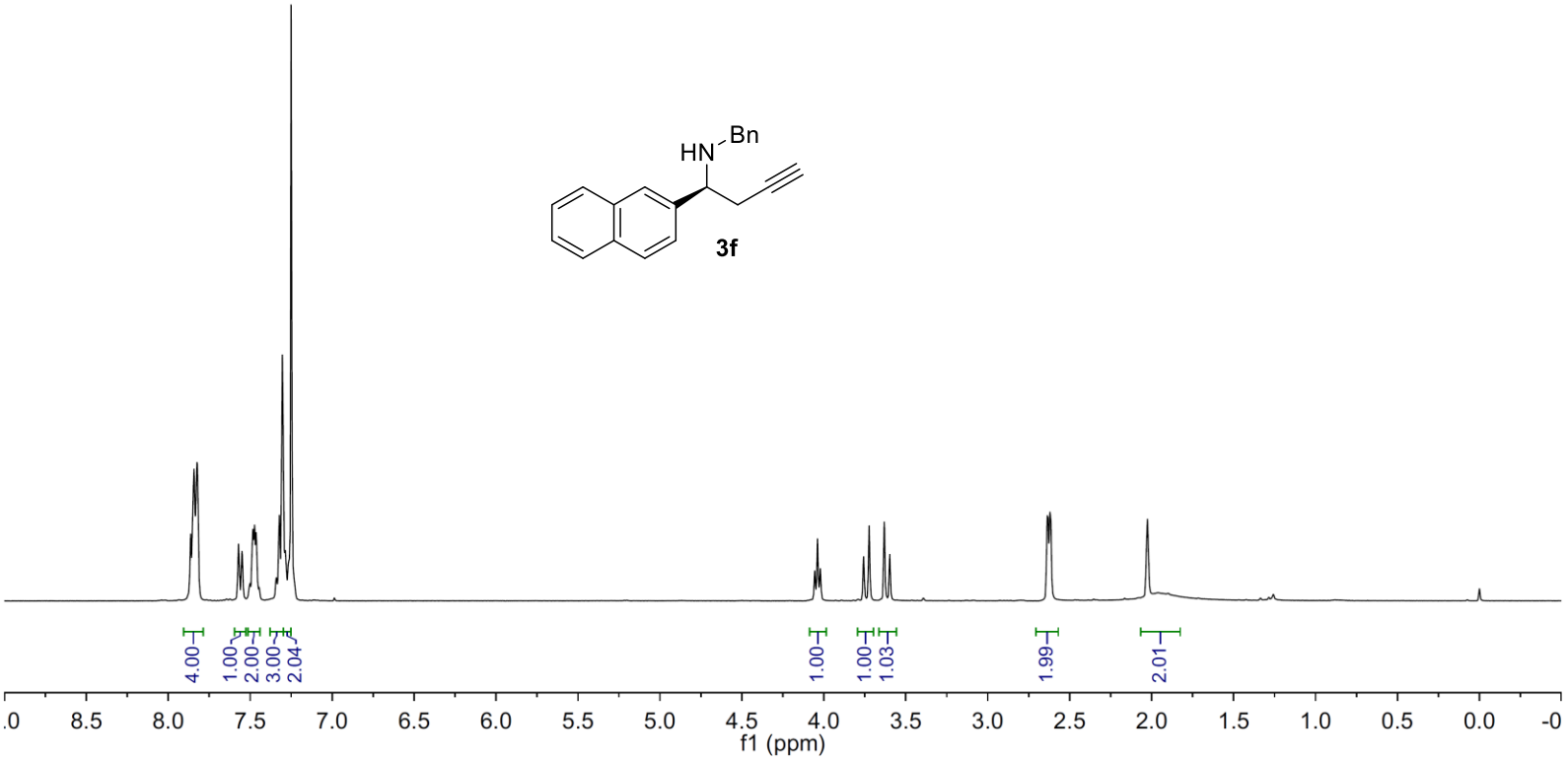

144.678
139.944
134.372
129.721
128.386
128.007
127.705
127.274
126.983
125.392
80.964
77.317
76.999
76.682
70.818
60.266
51.355
28.055
gxt-gd-128 C
HN
Bn
Cl
3d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

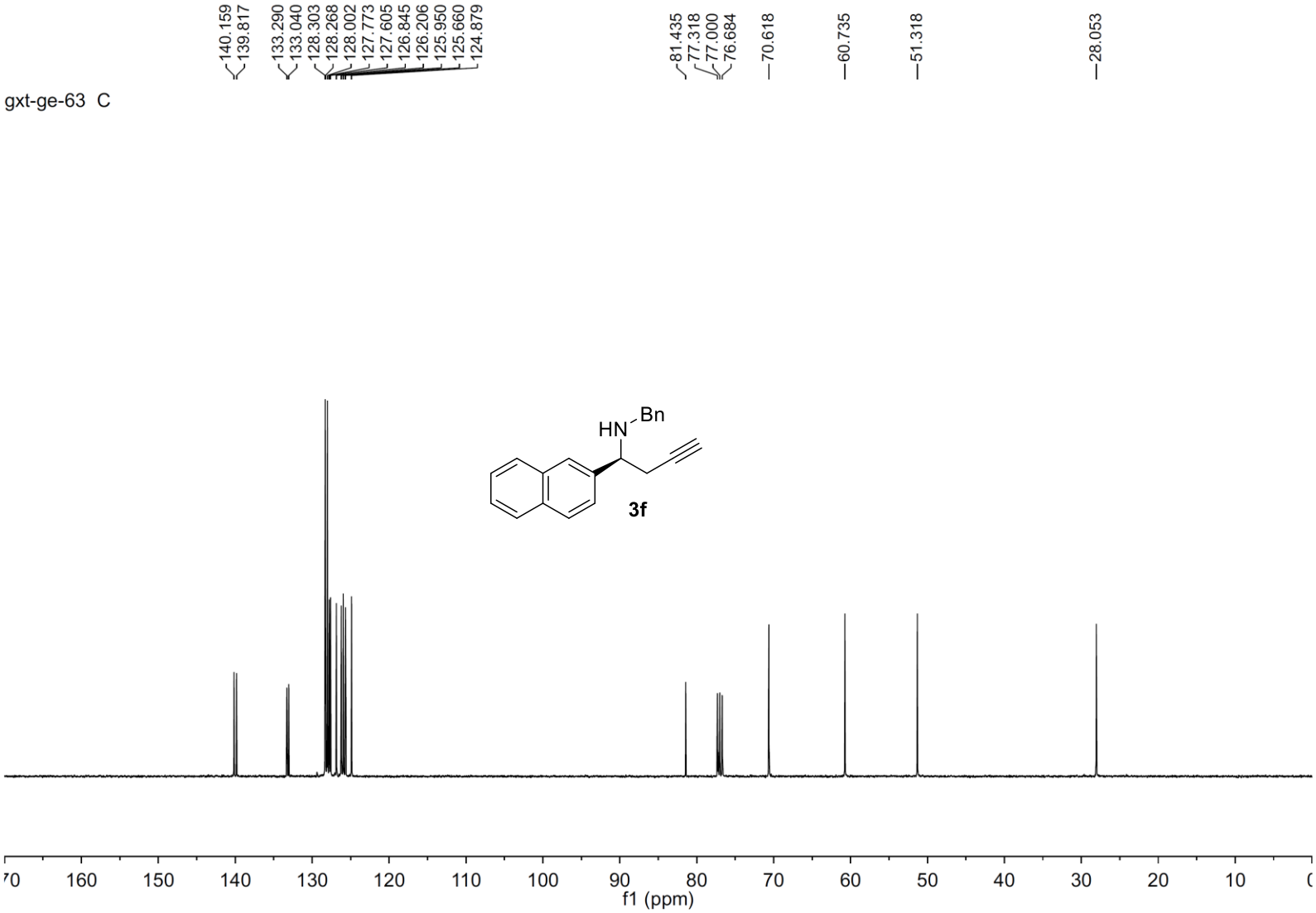

7.336
7.318
7.300
7.283
7.252
7.241
7.223
7.196
7.171
7.105
7.087
3.845
3.829
3.812
3.729
3.696
3.598
3.565
2.542
2.537
2.529
2.525
2.521
2.363
2.022
2.017
2.012
2.007
1.901
gxt-gd-125 H
HN
Bn
Me
3e
4.00
2.03
1.98
0.96
1.00
1.00
1.00
2.00
3.00
1.00
1.00
f1 (ppm)

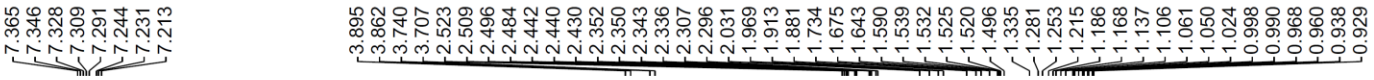

142.314
140.210
137.864
128.228
128.209
128.159
127.934
127.645
126.735
124.117
81.532
77.317
76.999
76.681
70.392
60.591
51.266
28.059
21.368
gxt-gd-125 C
HN
Bn
Me
3e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.863
7.842
7.822
7.572
7.551
7.500
7.483
7.473
7.463
7.445
7.341
7.321
7.304
7.285
7.266
7.261
7.250
7.247
4.055
4.038
4.022
3.757
3.724
3.631
3.598
2.637
2.631
2.620
2.614
2.031
2.025
2.019
1.962
1.898

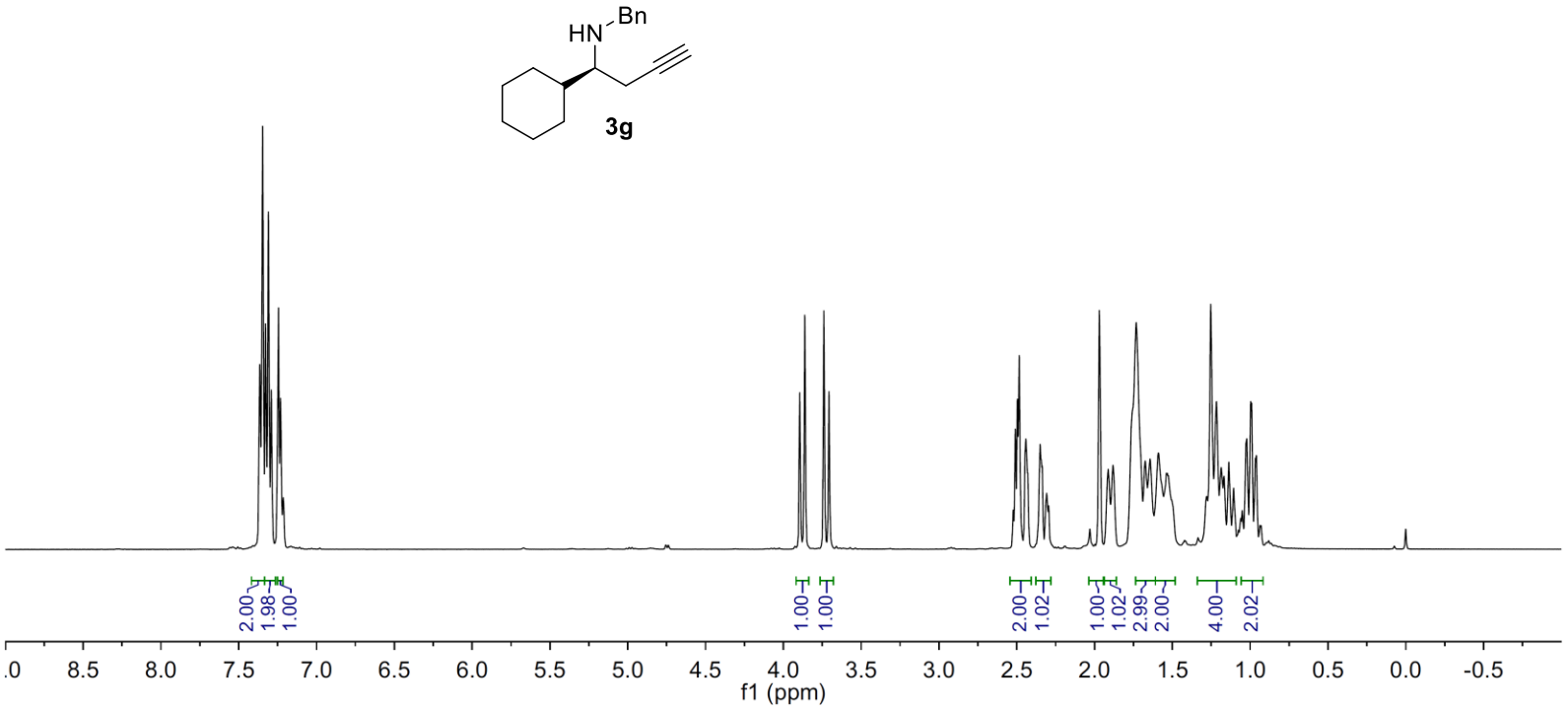
gxt-ge-63 H


HN
Bn
3f
4.00
1.00
2.00
3.00
2.04
1.00
1.00
1.03
1.99
2.01
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

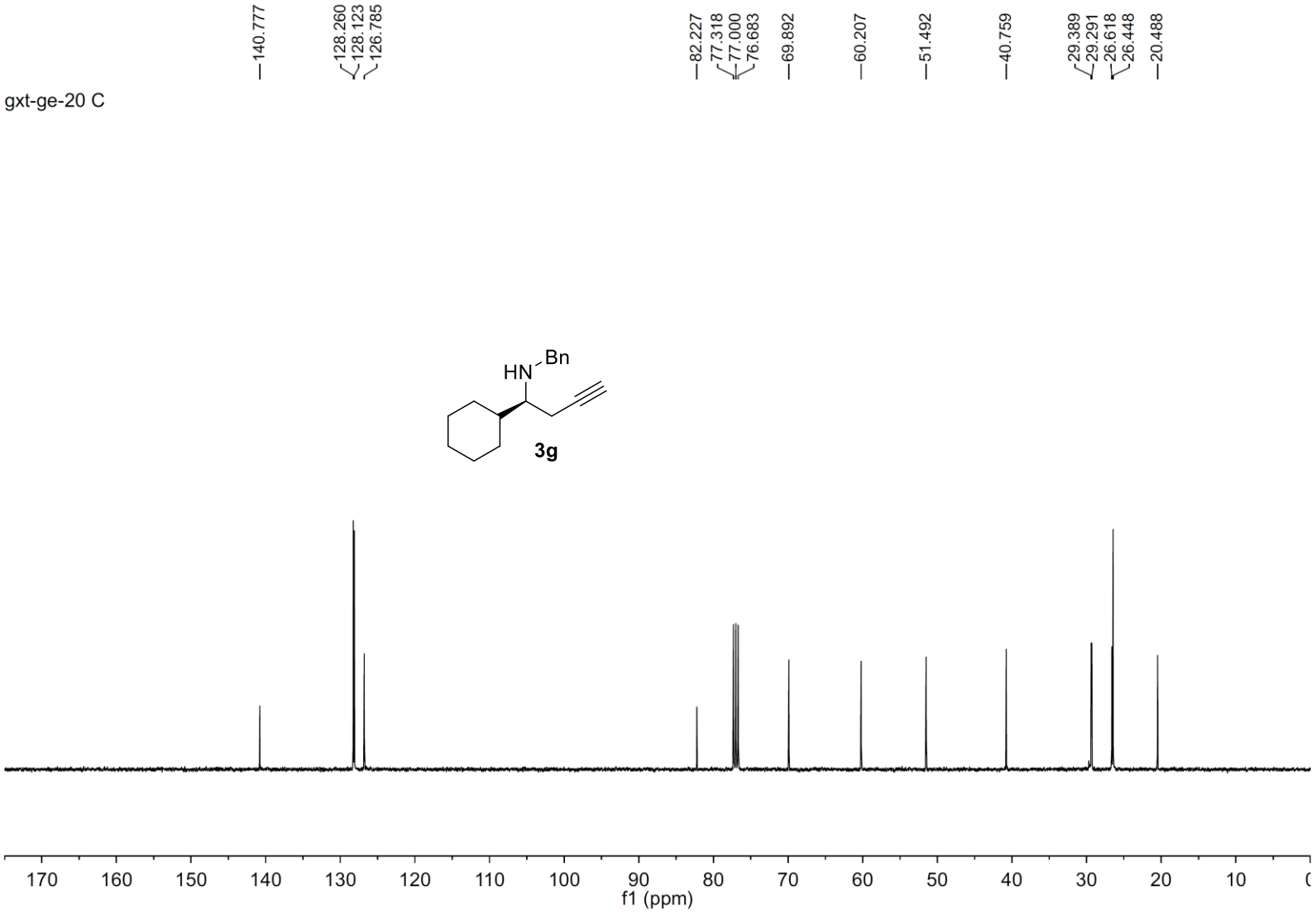

140.159
139.817
133.290
133.040
128.303
128.268
128.002
127.773
127.605
126.845
126.206
125.950
125.660
124.879
81.435
77.318
77.000
76.684
70.618
60.735
51.318
28.053
gxt-ge-63 C
HN
Bn
3f
f1 (ppm)

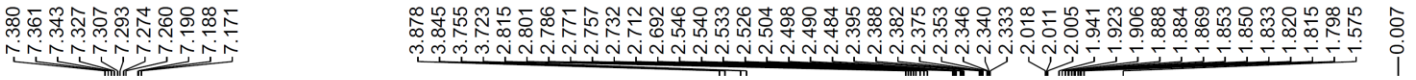

7.365
7.346
7.328
7.309
7.291
7.244
7.231
7.213
3.895
3.862
3.740
3.707
2.523
2.509
2.496
2.484
2.442
2.440
2.430
2.352
2.350
2.343
2.336
2.307
2.296
2.031
1.969
1.913
1.881
1.734
1.675
1.643
1.590
1.539
1.532
1.525
1.520
1.496
1.335
1.281
1.253
1.215
1.186
1.168
1.137
1.106
1.061
1.050
1.024
0.998
0.990
0.968
0.960
0.938
0.929

gxt-ge-20 H

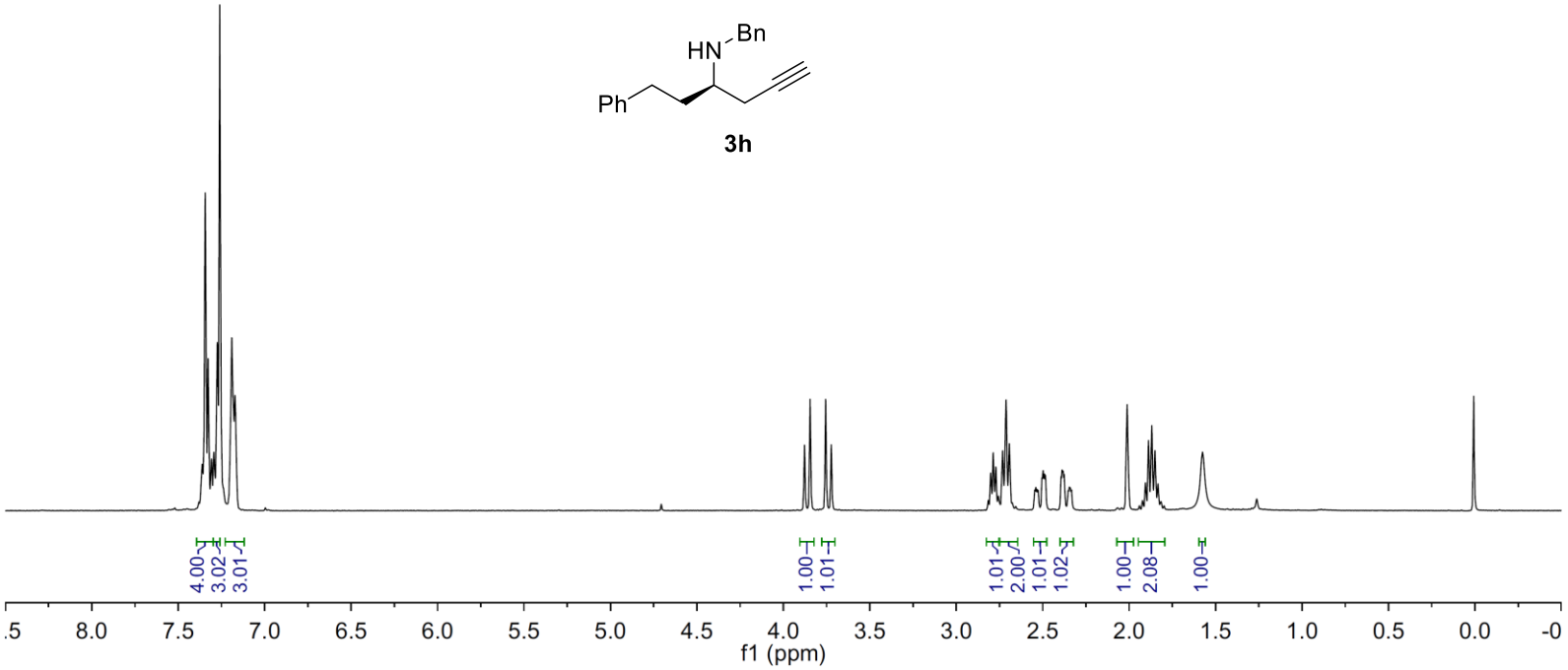

HN
Bn
3g
2.00
1.98
1.00
1.00
1.00
2.00
1.02
1.00
1.02
2.99
2.00
4.00
2.02
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

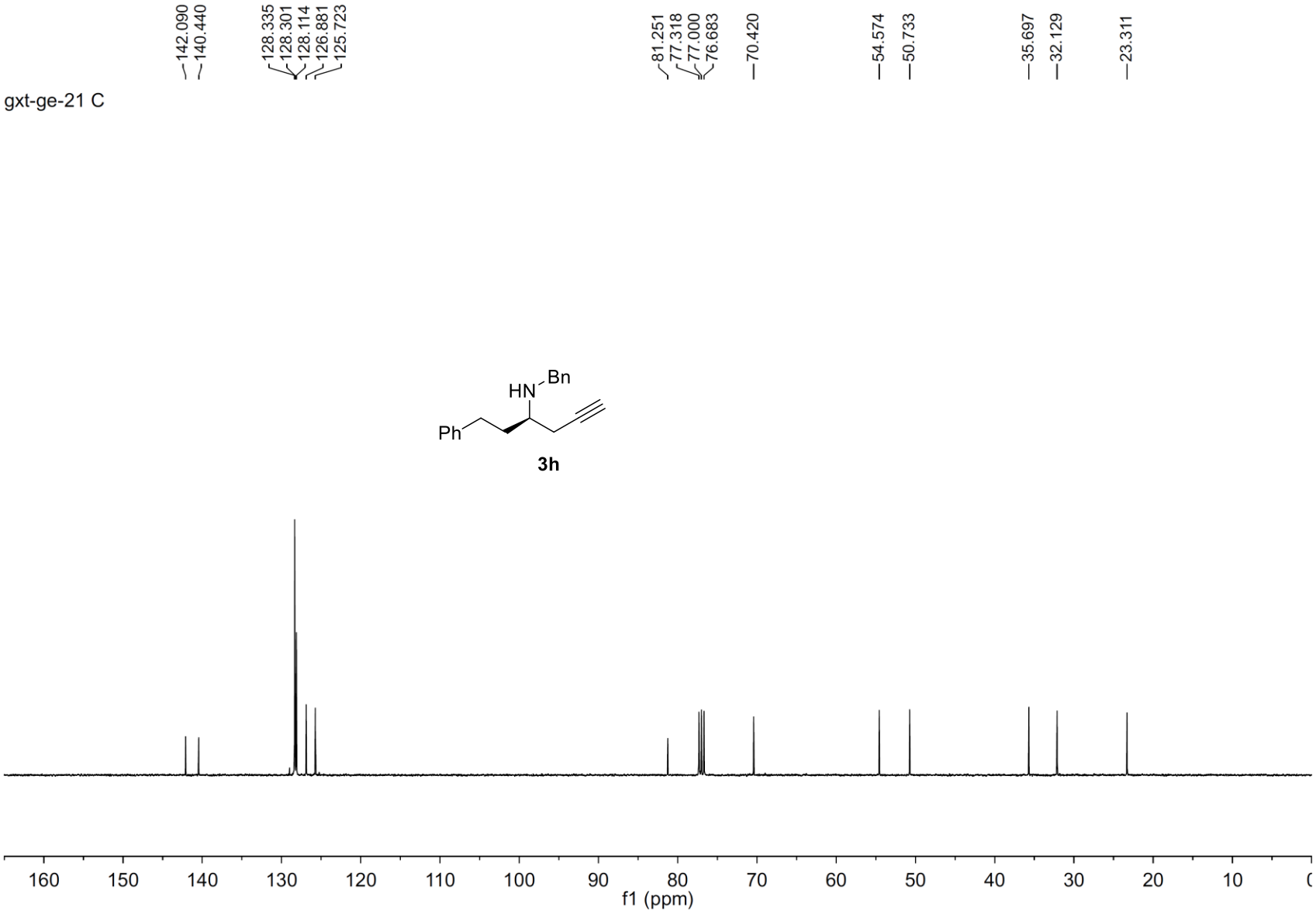
gxt-ge-20 C

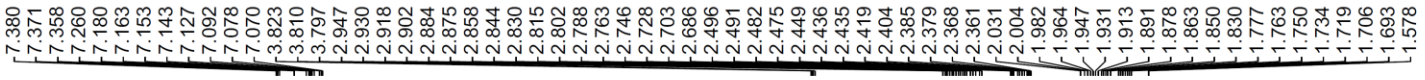

140.777
128.260
128.123
126.785
82.227
77.318
77.000
76.683
69.892
60.207
51.492
40.759
29.389
29.291
26.618
26.448
20.488
HN
Bn
3g
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.380
7.361
7.343
7.327
7.307
7.293
7.274
7.260
7.190
7.188
7.171
3.878
3.845
3.755
3.723
2.815
2.801
2.786
2.771
2.757
2.732
2.712
2.692
2.546
2.540
2.533
2.526
2.504
2.498
2.490
2.484
2.395
2.388
2.382
2.375
2.353
2.346
2.340
2.333
2.018
2.011
2.005
1.941
1.923
1.906
1.888
1.884
1.869
1.853
1.850
1.833
1.820
1.815
1.798
1.575
0.007

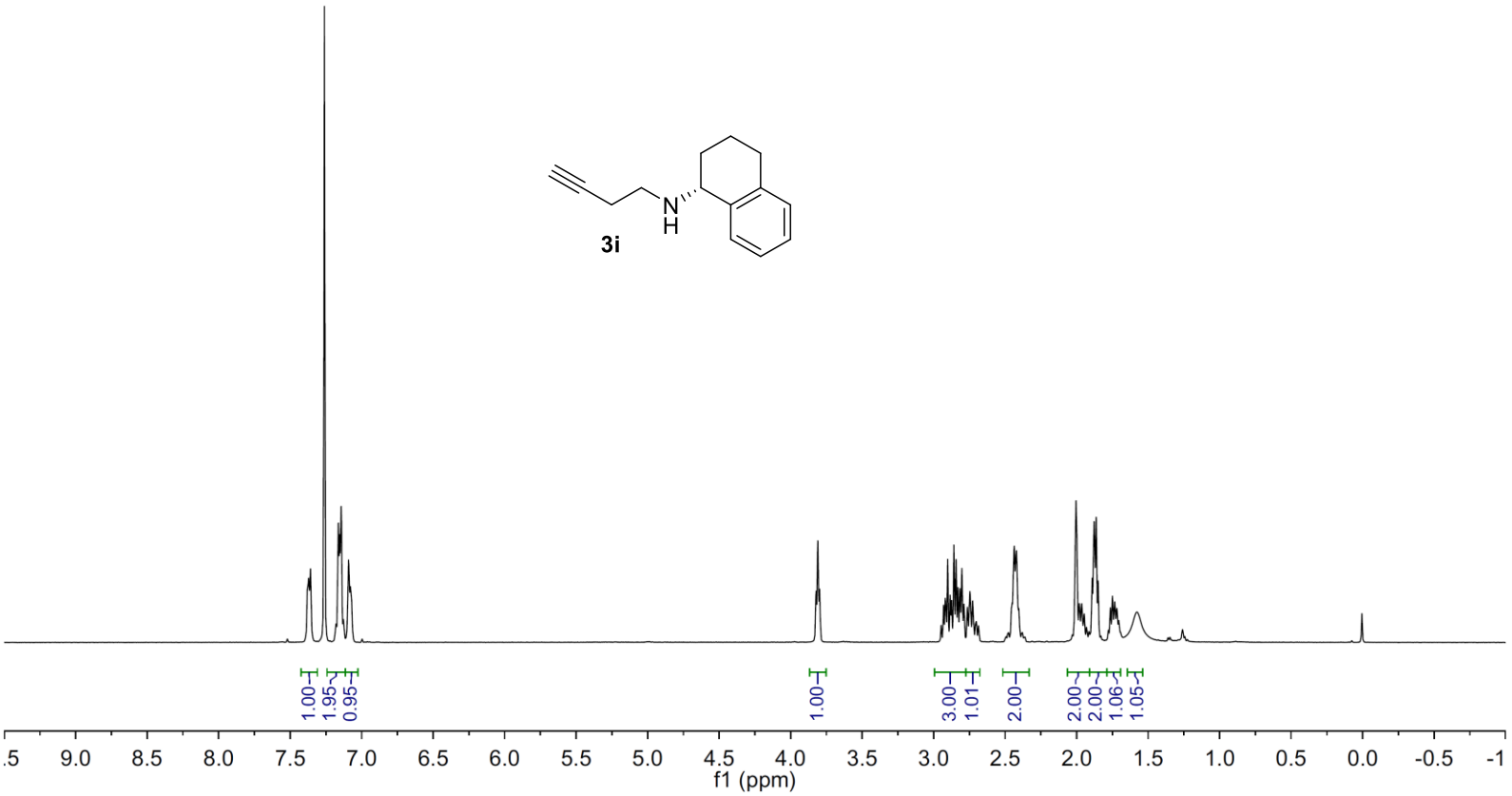
gxt-ge-21 H


HN
Bn
Ph
3h
4.00
3.02
3.01
1.00
1.01
1.01
2.00
1.01
1.02
1.00
2.08
1.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

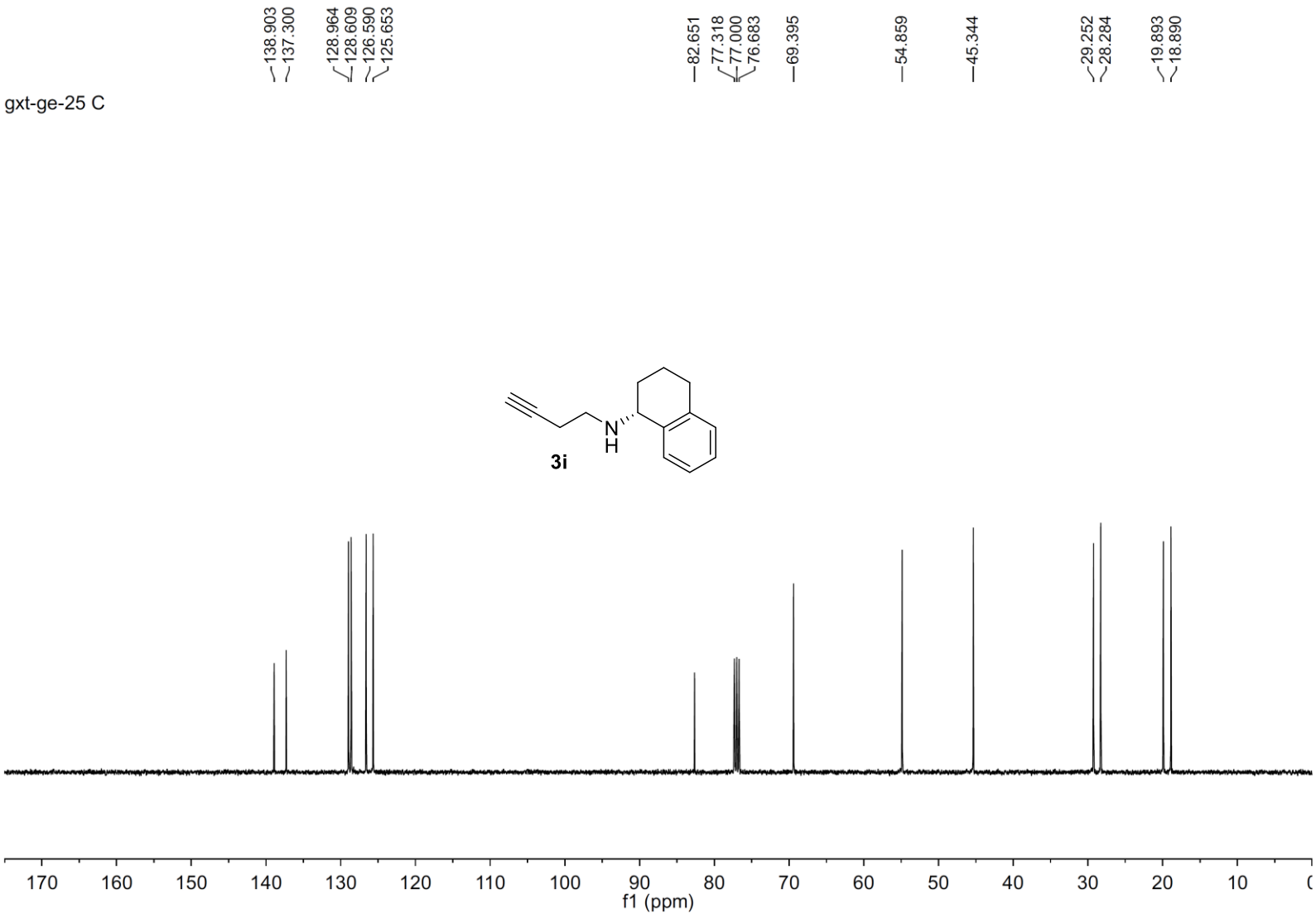

142.090
140.440
128.335
128.301
128.114
126.881
125.723
81.251
77.318
77.000
76.683
70.420
54.574
50.733
35.697
32.129
23.311
gxt-ge-21 C
HN
Bn
Ph
3h
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

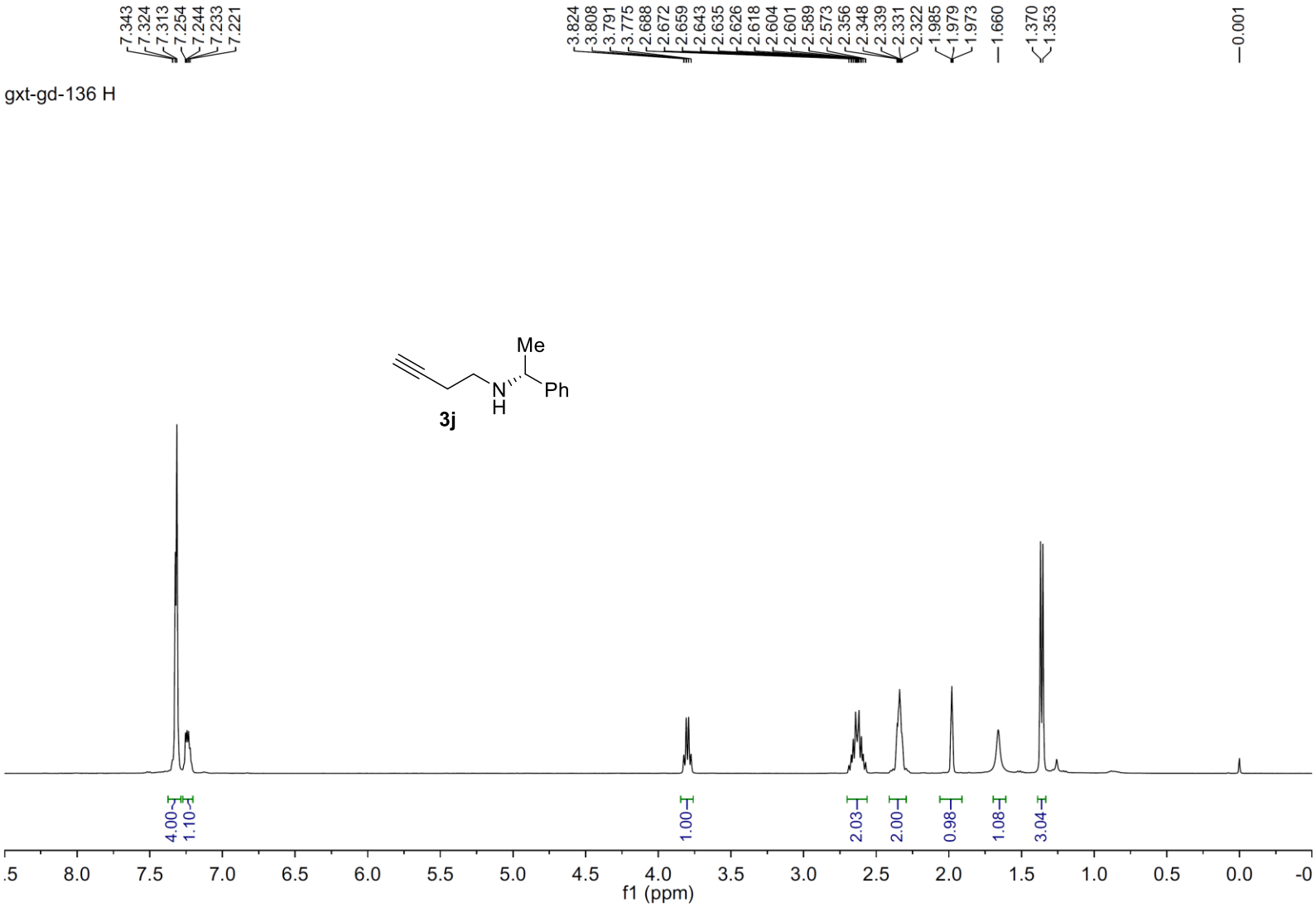

7.380
7.371
7.358
7.260
7.180
7.163
7.153
7.143
7.127
7.092
7.078
7.070
3.823
3.810
3.797
2.947
2.930
2.918
2.902
2.884
2.875
2.858
2.844
2.830
2.815
2.802
2.788
2.763
2.746
2.728
2.703
2.686
2.496
2.491
2.482
2.475
2.449
2.436
2.435
2.419
2.404
2.385
2.379
2.368
2.361
2.031
2.004
1.982
1.964
1.947
1.931
1.913
1.891
1.878
1.863
1.850
1.830
1.777
1.763
1.750
1.734
1.719
1.706
1.693
1.578

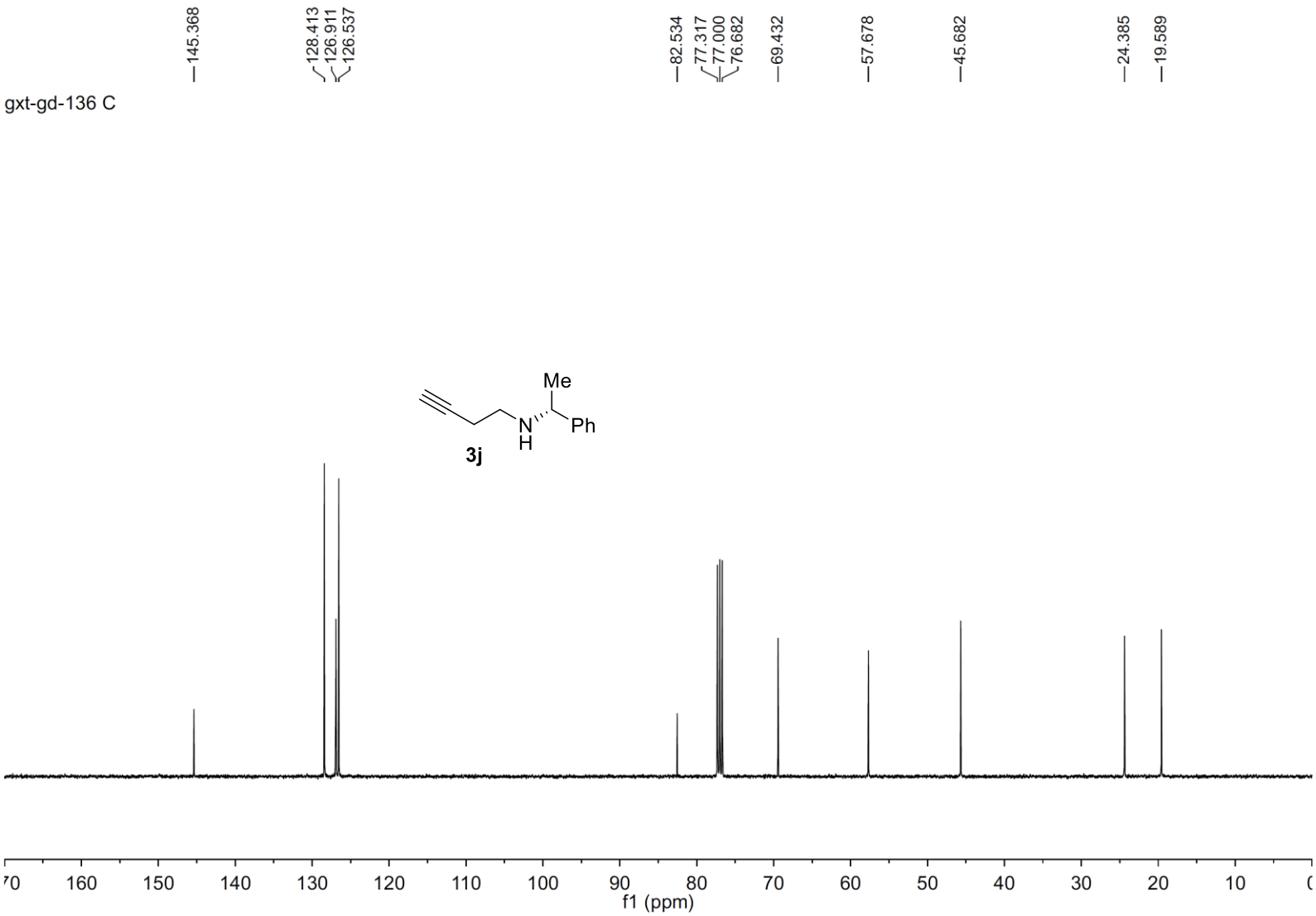
gxt-ge-25 H

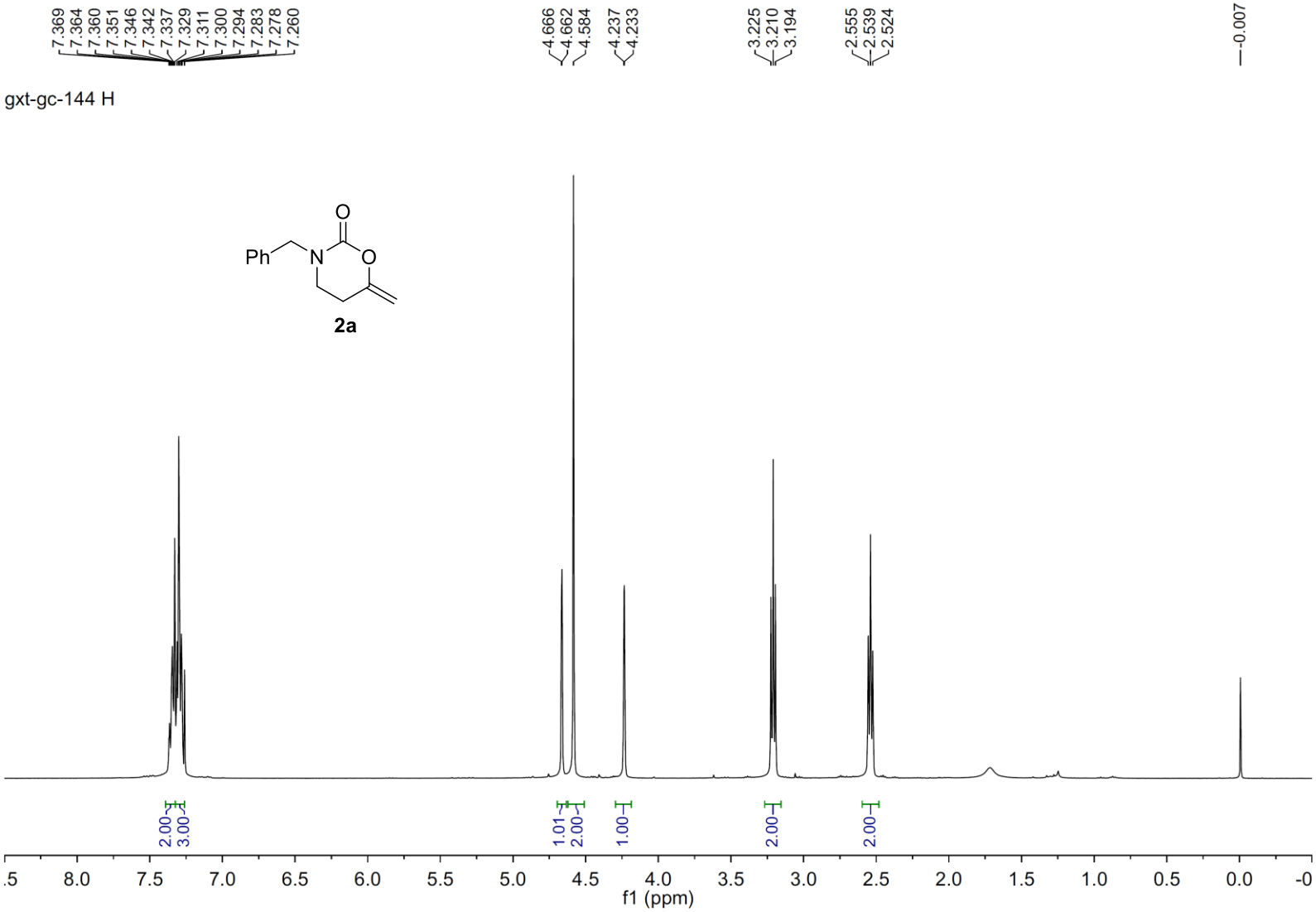

N
H
3i
1.00
1.95
0.95
1.00
3.00
1.01
2.00
2.00
2.00
1.06
1.05
.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)

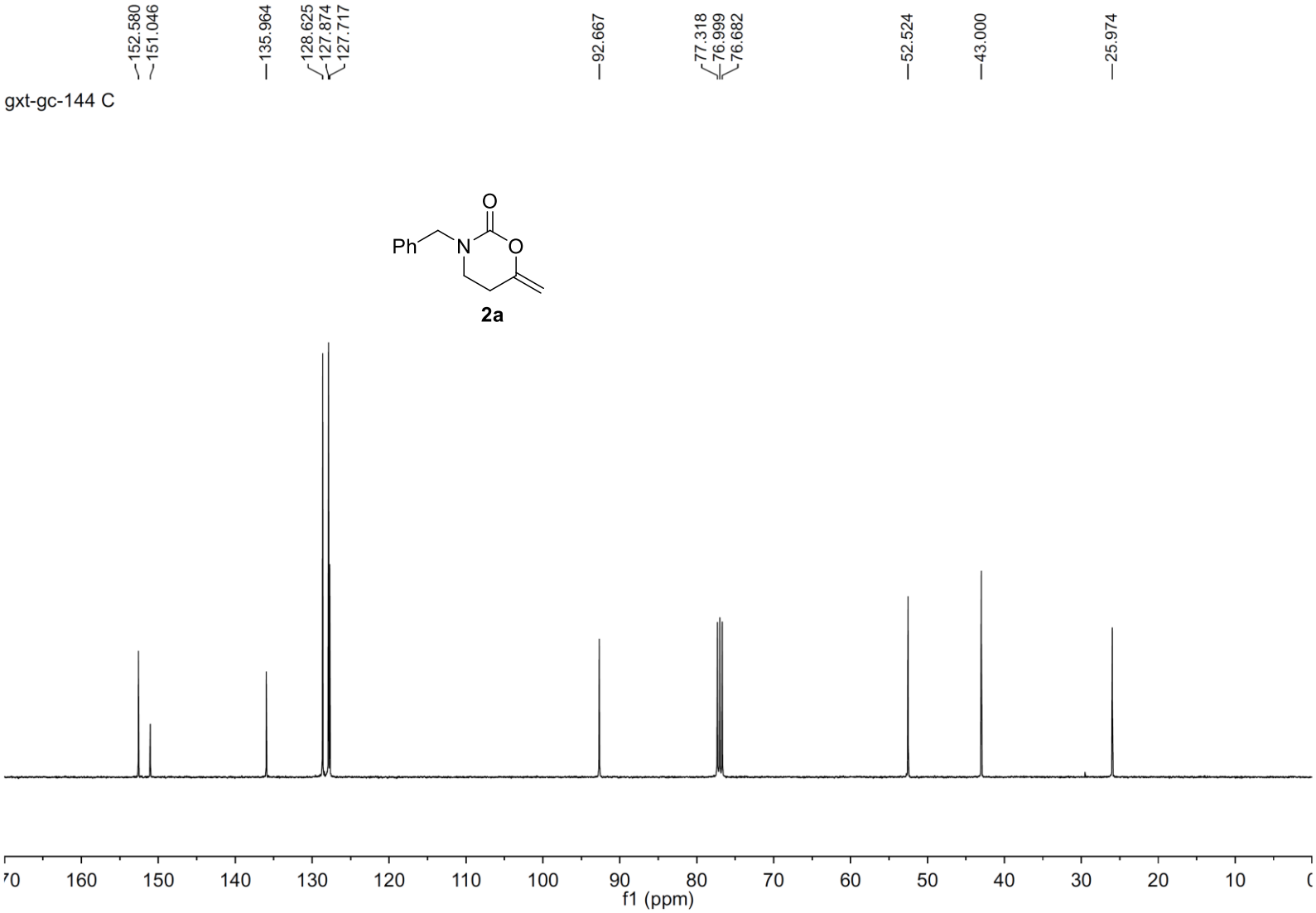
gxt-ge-25 C

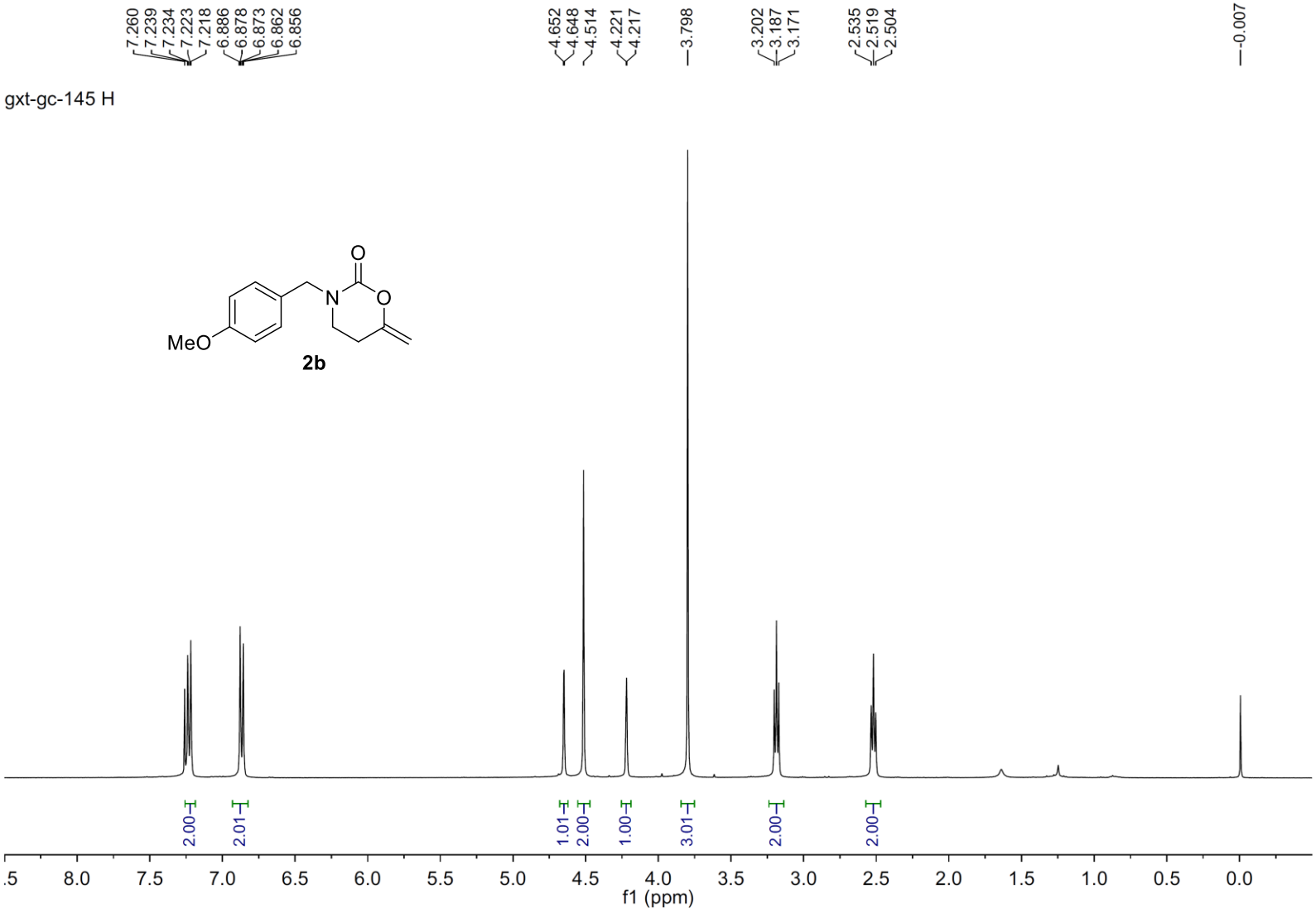

138.903
137.300
128.964
128.609
126.590
125.653
82.651
77.318
77.000
76.683
69.395
54.859
45.344
29.252
28.284
19.893
18.890
N
H
3i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

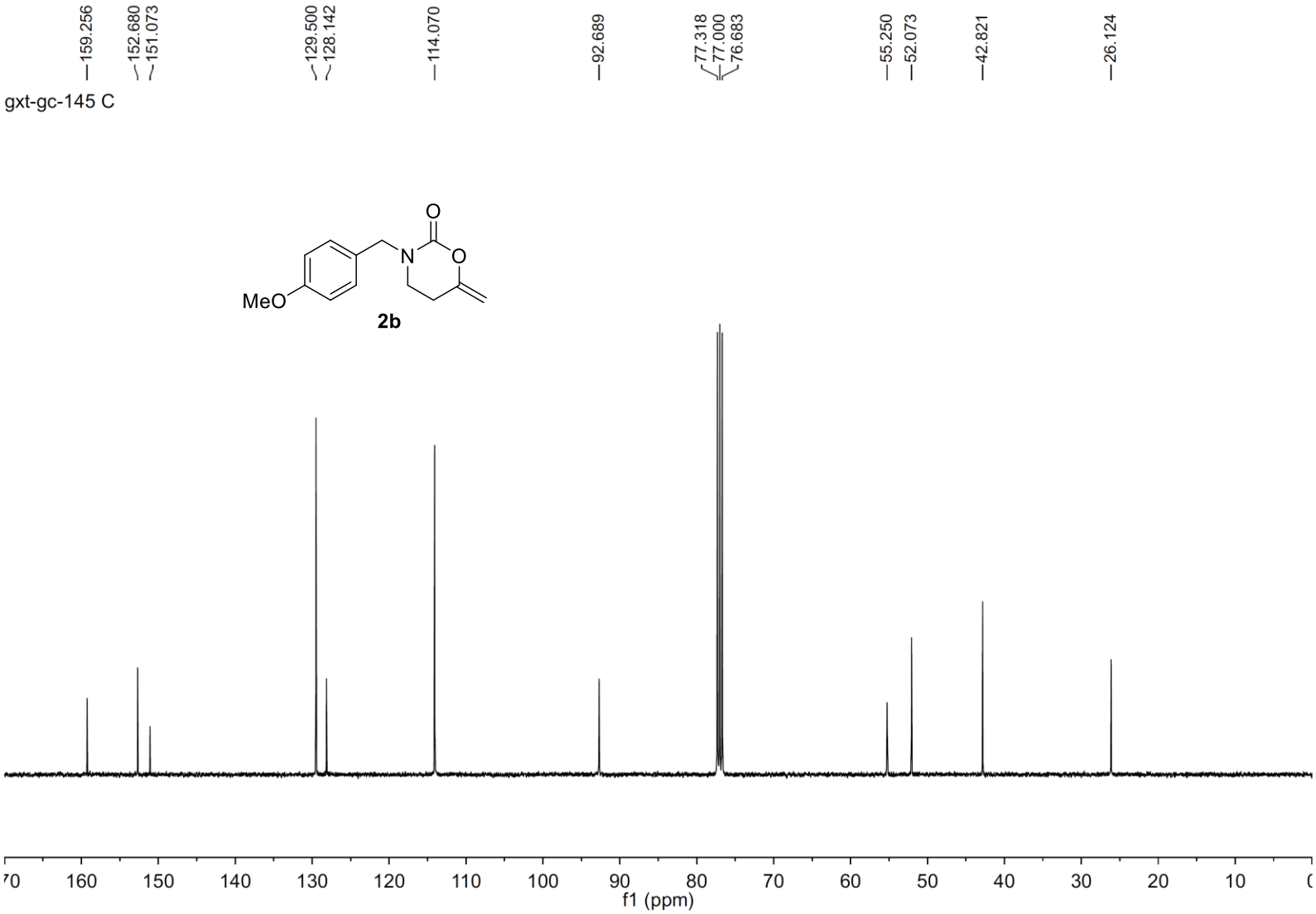

7.343
7.324
7.313
7.254
7.244
7.233
7.221
3.824
3.808
3.791
3.775
2.688
2.672
2.659
2.643
2.635
2.626
2.618
2.604
2.601
2.589
2.573
2.356
2.348
2.339
2.331
2.322
1.985
1.979
1.973
1.660
1.370
1.353
0.001
gxt-gd-136 H
Me
Ph
N
H
3j
4.00
1.10
1.00
2.03
2.00
0.98
1.08
3.04
f1 (ppm)

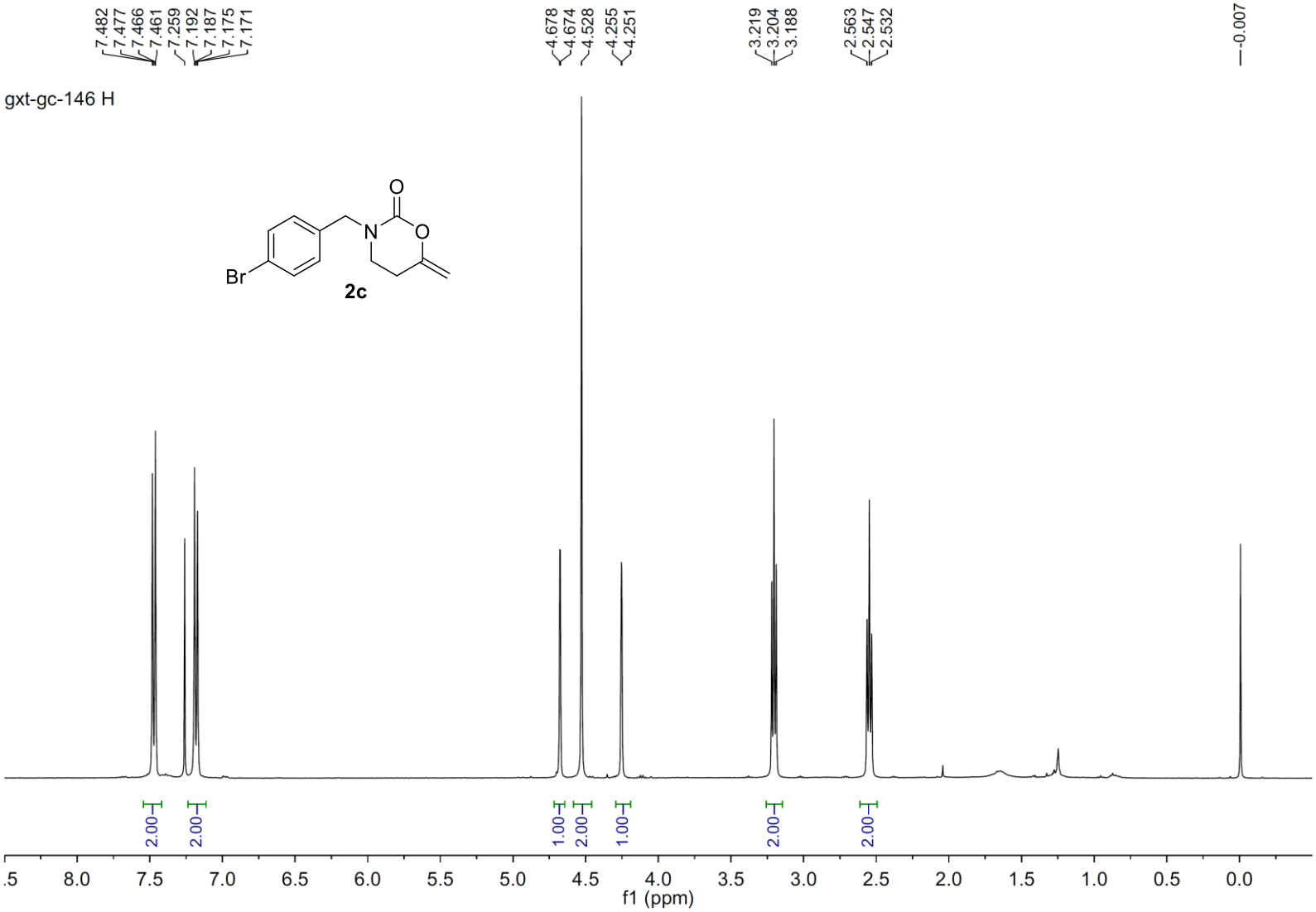

145.368
128.413
126.911
126.537
82.534
77.317
77.000
76.682
69.432
57.678
45.682
24.385
19.589
gxt-gd-136 C
Me
Ph
N
H
3j
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

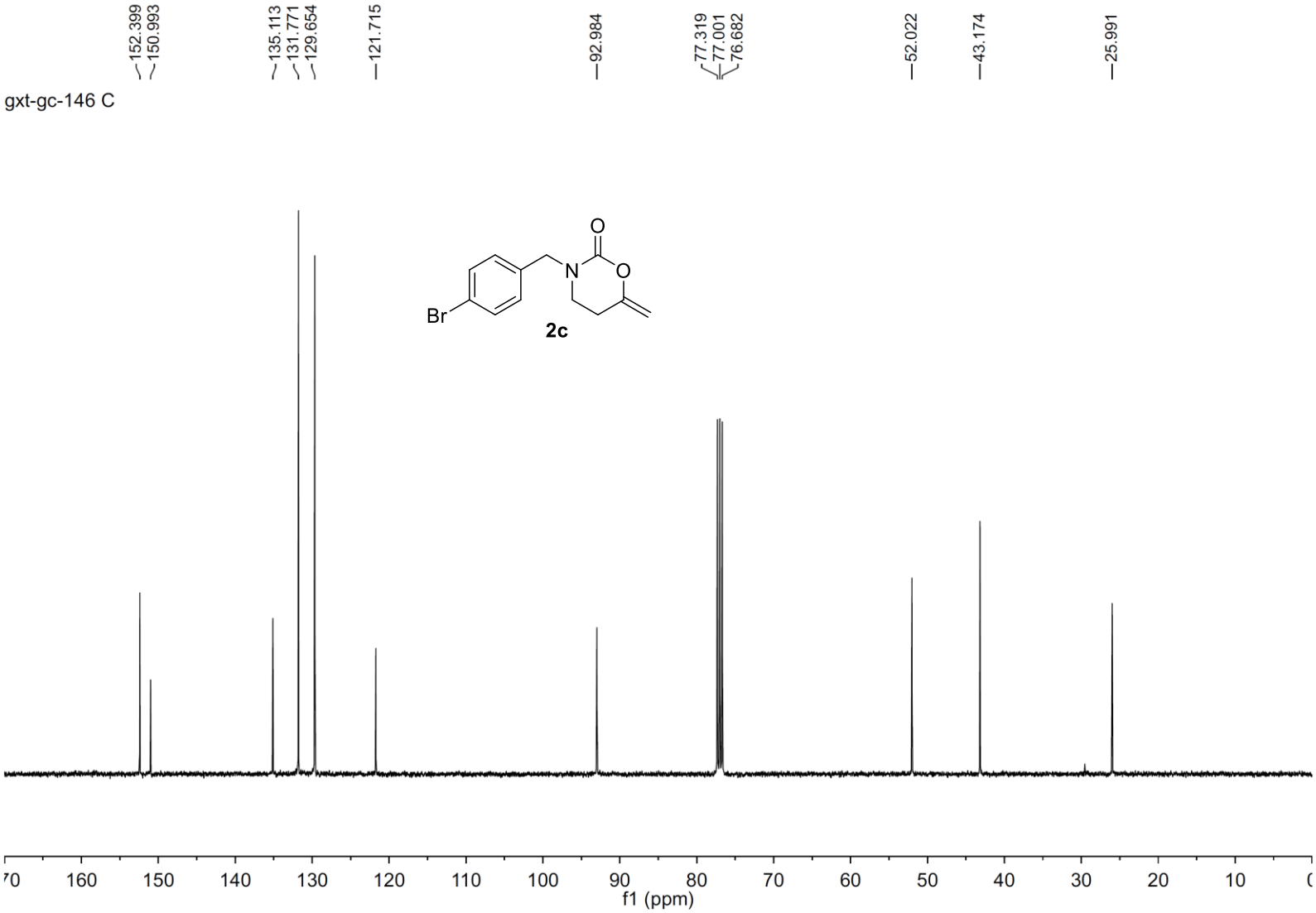

7.369
7.364
7.360
7.351
7.346
7.342
7.337
7.329
7.311
7.300
7.294
7.283
7.278
7.260
4.666
4.662
4.584
4.237
4.233
3.225
3.210
3.194
2.555
2.539
2.524
-0.007
gxt-gc-144 H
Ph
N
O
O
2a
2.00
3.00
1.01
2.00
1.00
2.00
2.00
f1 (ppm)

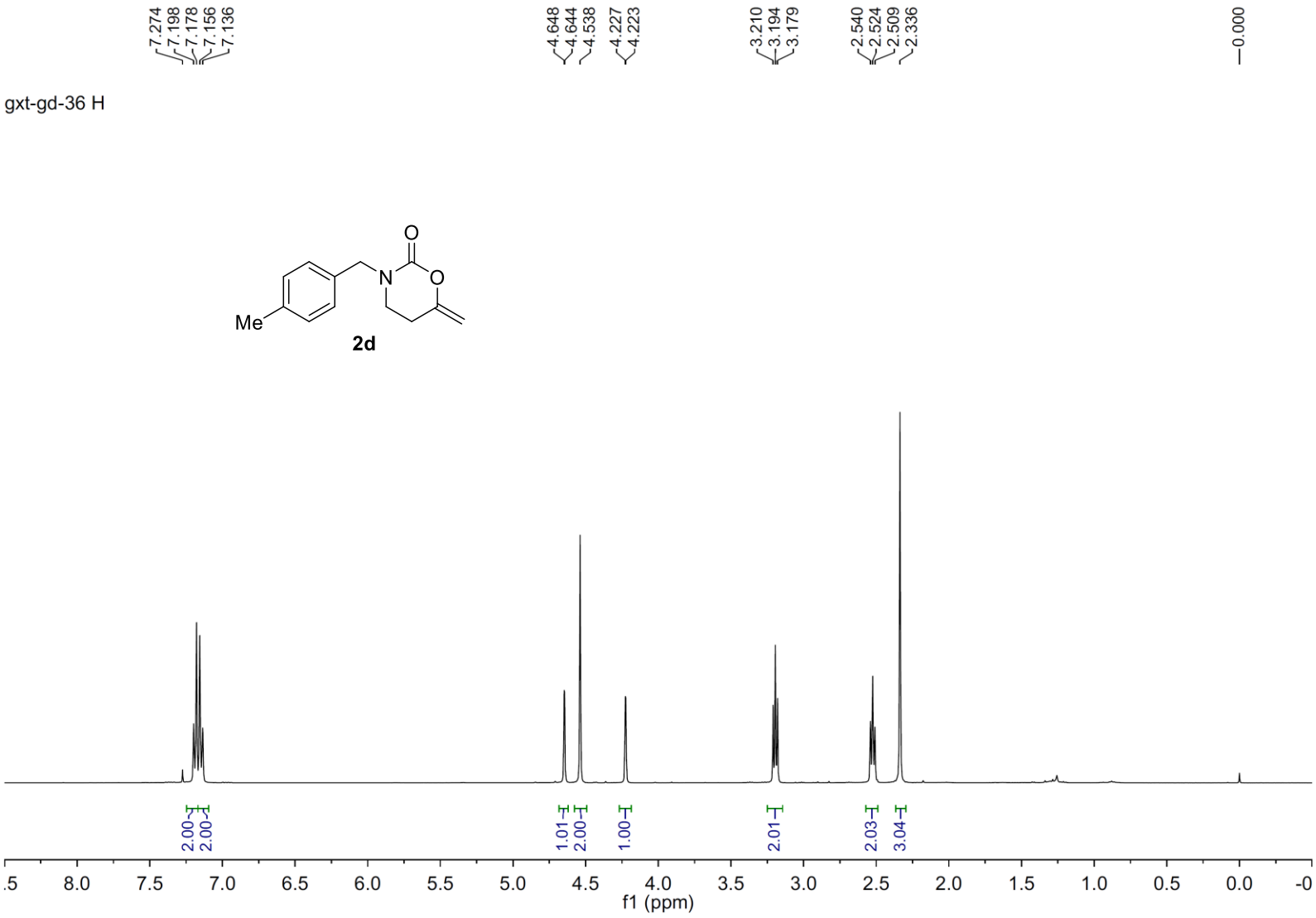

152.580
151.046
135.964
128.625
127.874
127.717
92.667
77.318
76.999
76.682
52.524
43.000
25.974
gxt-gc-144 C
O
Ph
N
O
2a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

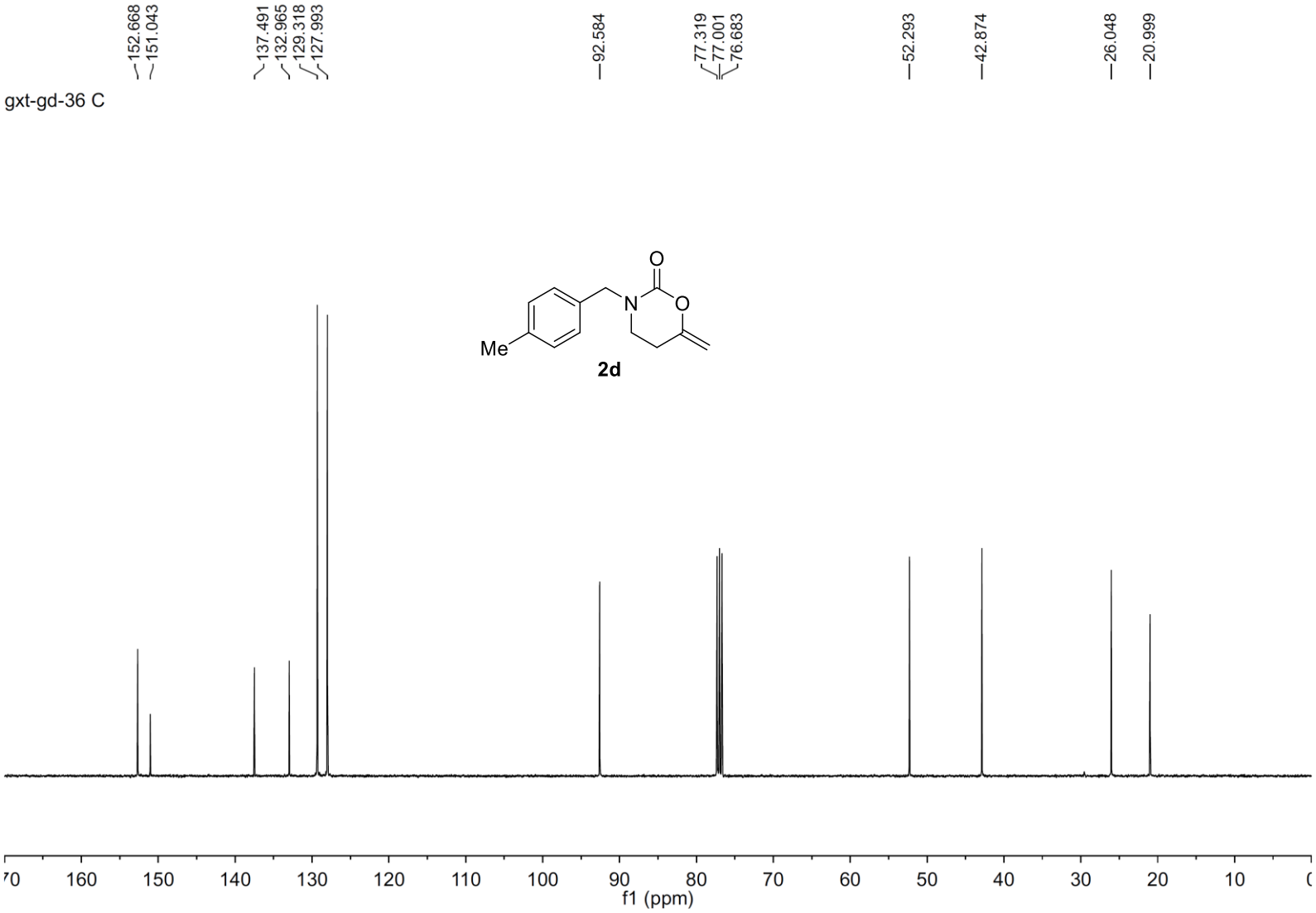

7.260
7.239
7.234
7.223
7.218
6.886
6.878
6.873
6.862
6.856
4.652
4.648
4.514
4.221
4.217
3.798
3.202
3.187
3.171
2.535
2.519
2.504
-0.007
gxt-gc-145 H
O
N
O
MeO
2b
2.00
2.01
1.01
2.00
1.00
3.01
2.00
2.00
f1 (ppm)

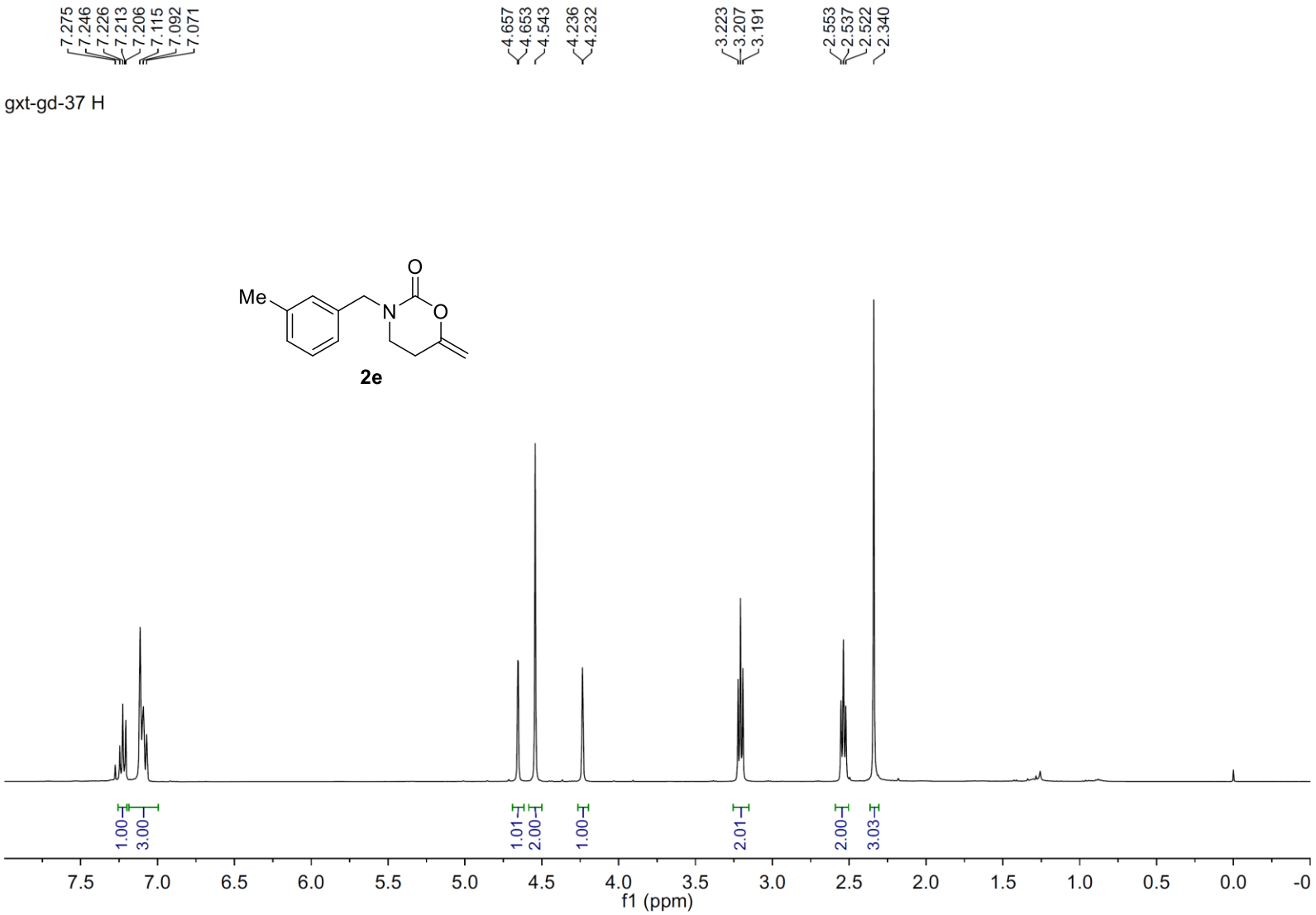

159.256
152.680
151.073
129.500
128.142
114.070
92.689
77.318
77.000
76.683
55.250
52.073
42.821
26.124
gxt-gc-145 C
O
N
O
MeO
2b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

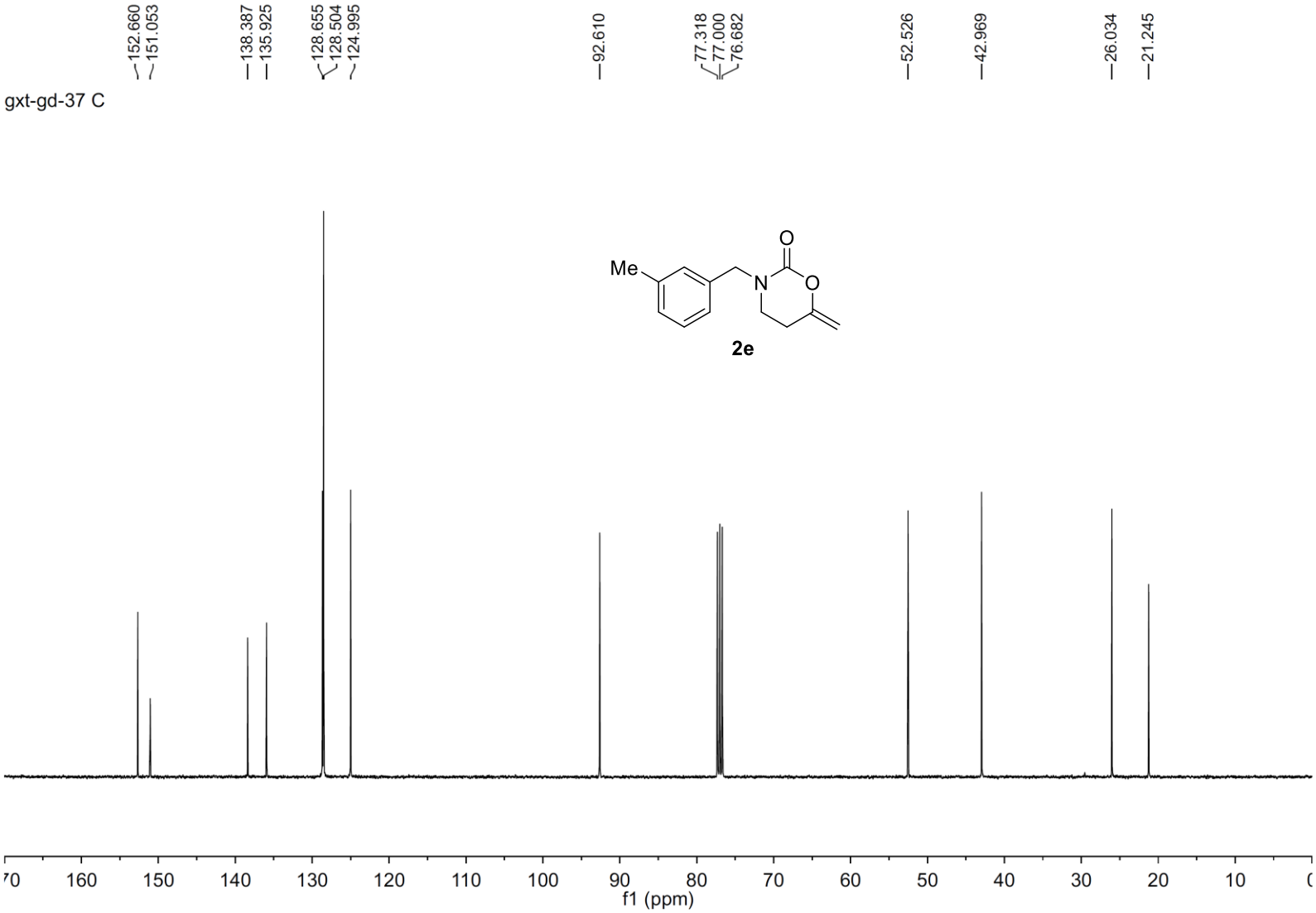

7.482
7.477
7.466
7.461
7.259
7.192
7.187
7.175
7.171
4.678
4.674
4.528
4.255
4.251
3.219
3.204
3.188
2.563
2.547
2.532
-0.007
gxt-gc-146 H
O
N
O
Br
2c
2.00
2.00
1.00
2.00
1.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

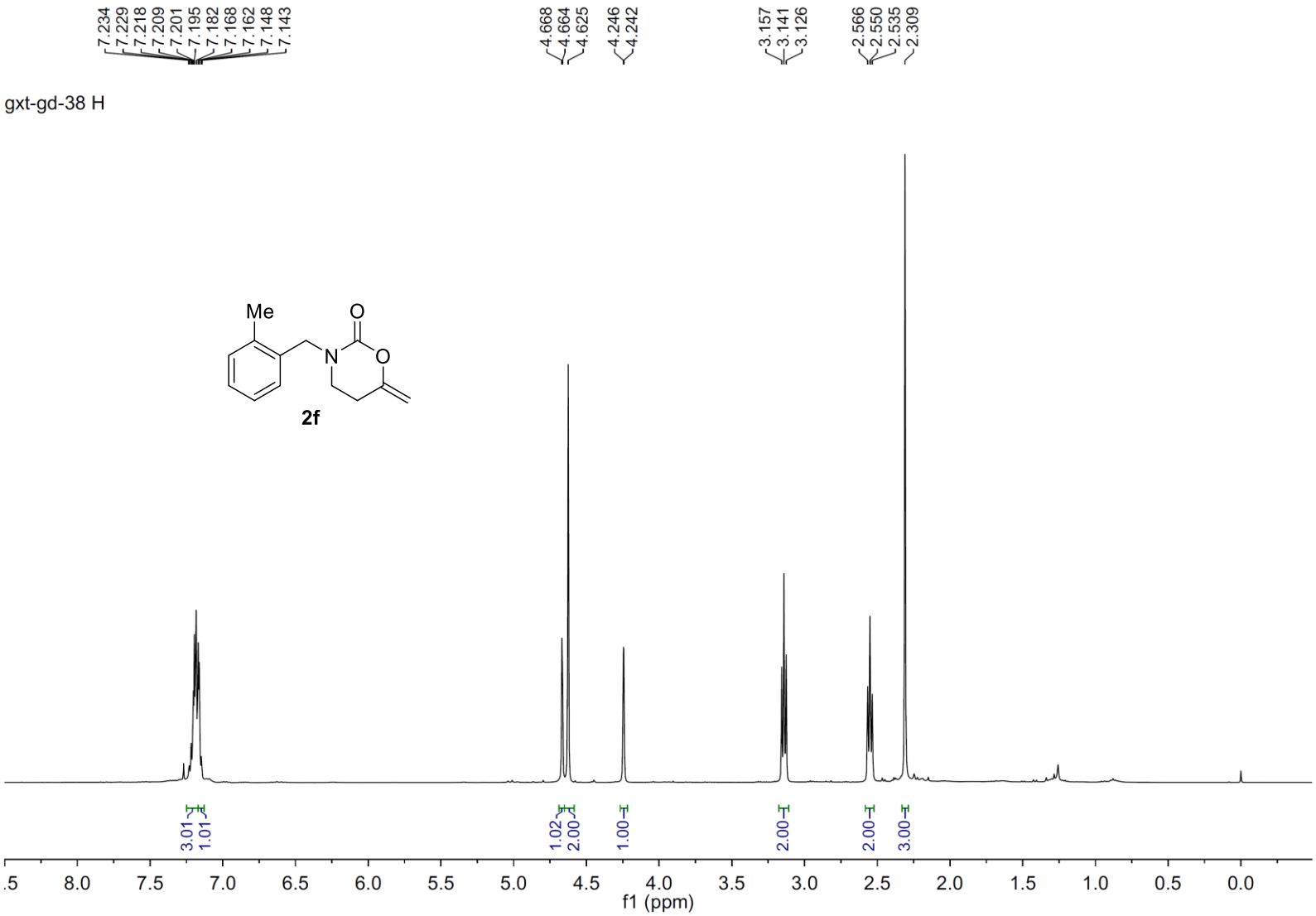

152.399
150.993
135.113
131.771
129.654
121.715
92.984
77.319
77.001
76.682
52.022
43.174
25.991
gxt-gc-146 C
O
N
O
Br
2c
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

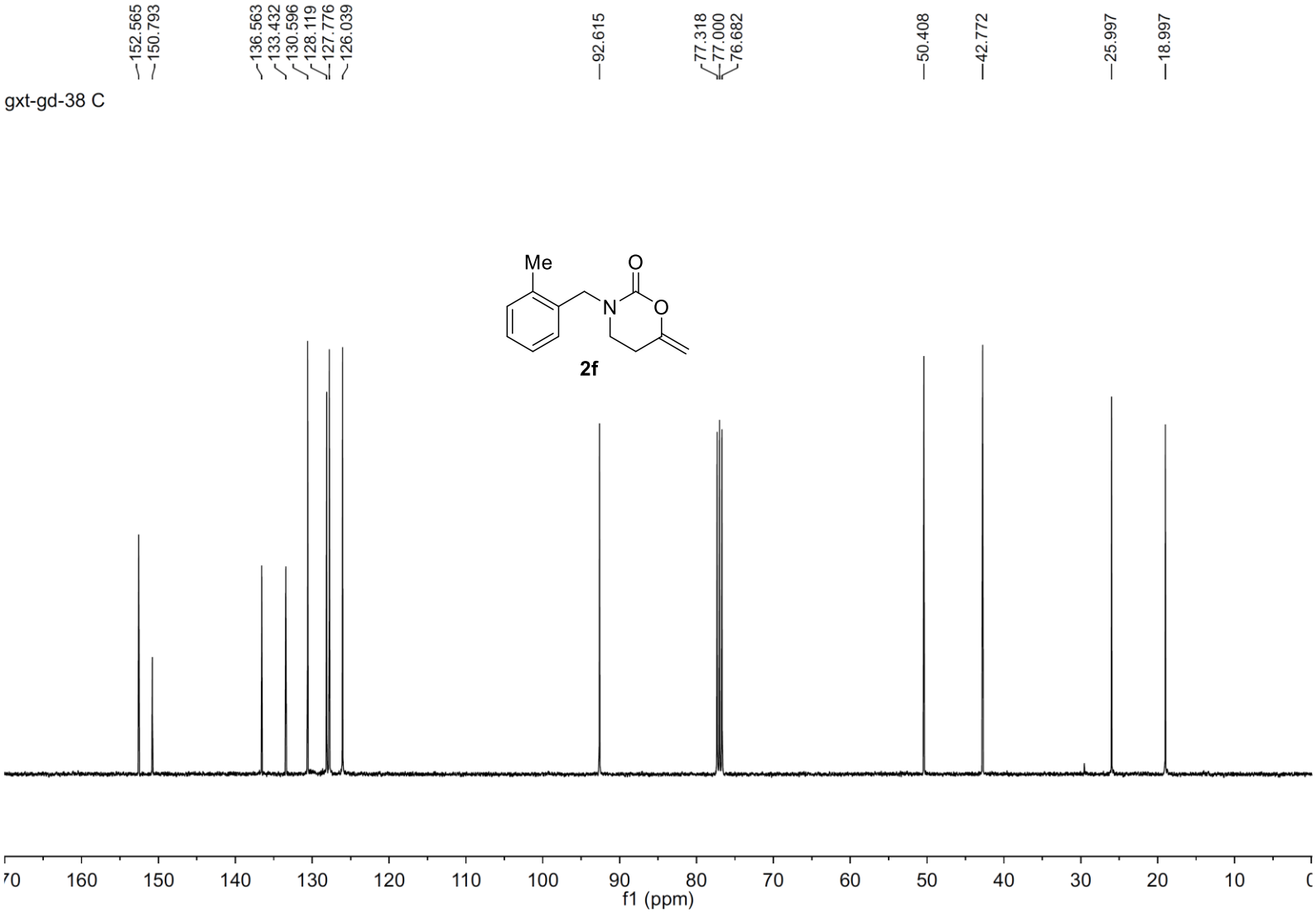

7.274
7.198
7.178
7.156
7.136
4.648
4.644
4.538
4.227
4.223
3.210
3.194
3.179
2.540
2.524
2.509
2.336
0.000
gxt-gd-36 H
O
N
O
Me
2d
2.00
2.00
1.01
2.00
1.00
2.01
2.03
3.04
f1 (ppm)

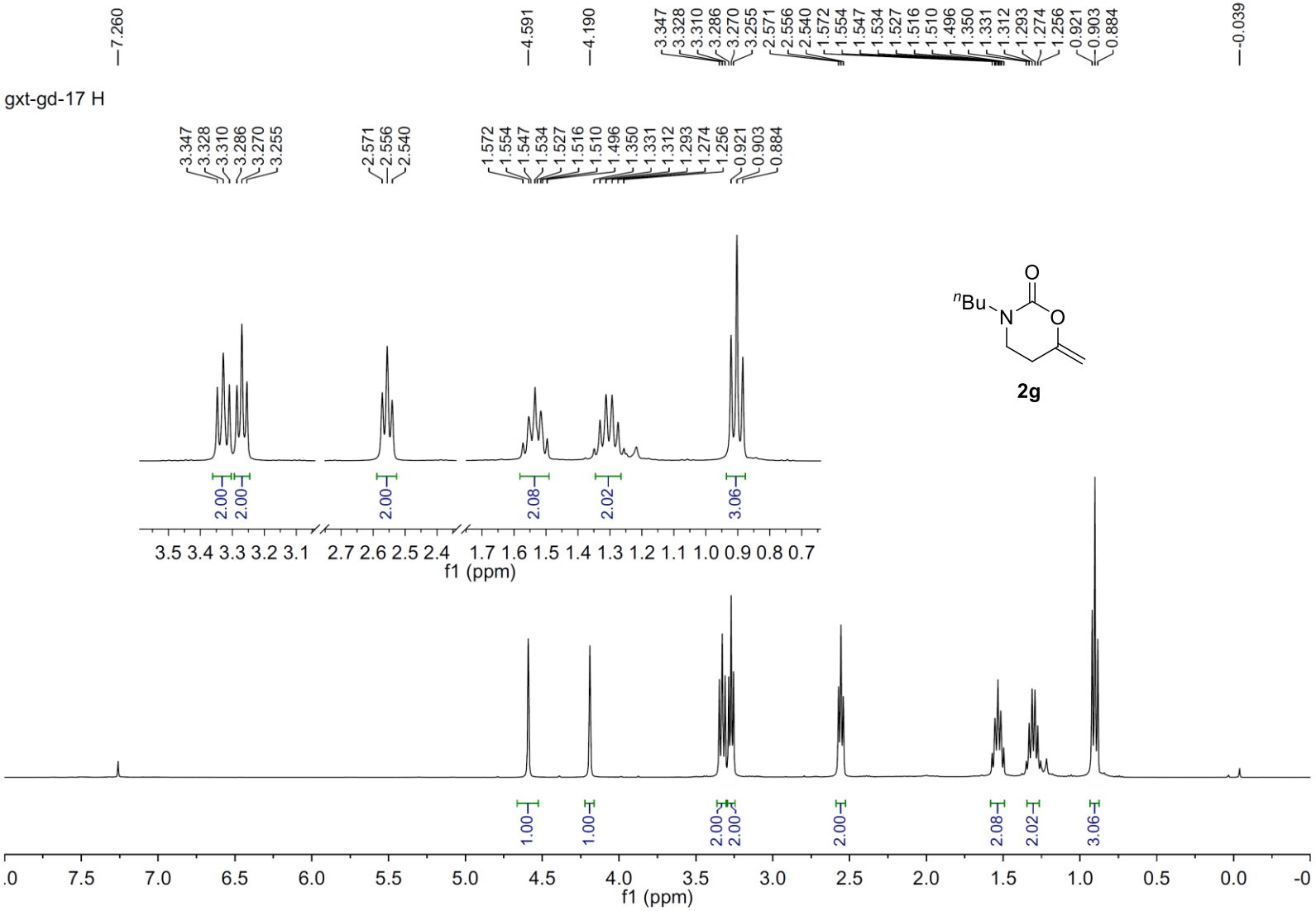

152.668
151.043
137.491
132.965
129.318
127.993
92.584
77.319
77.001
76.683
52.293
42.874
26.048
20.999
gxt-gd-36 C
O
N
O
Me
2d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

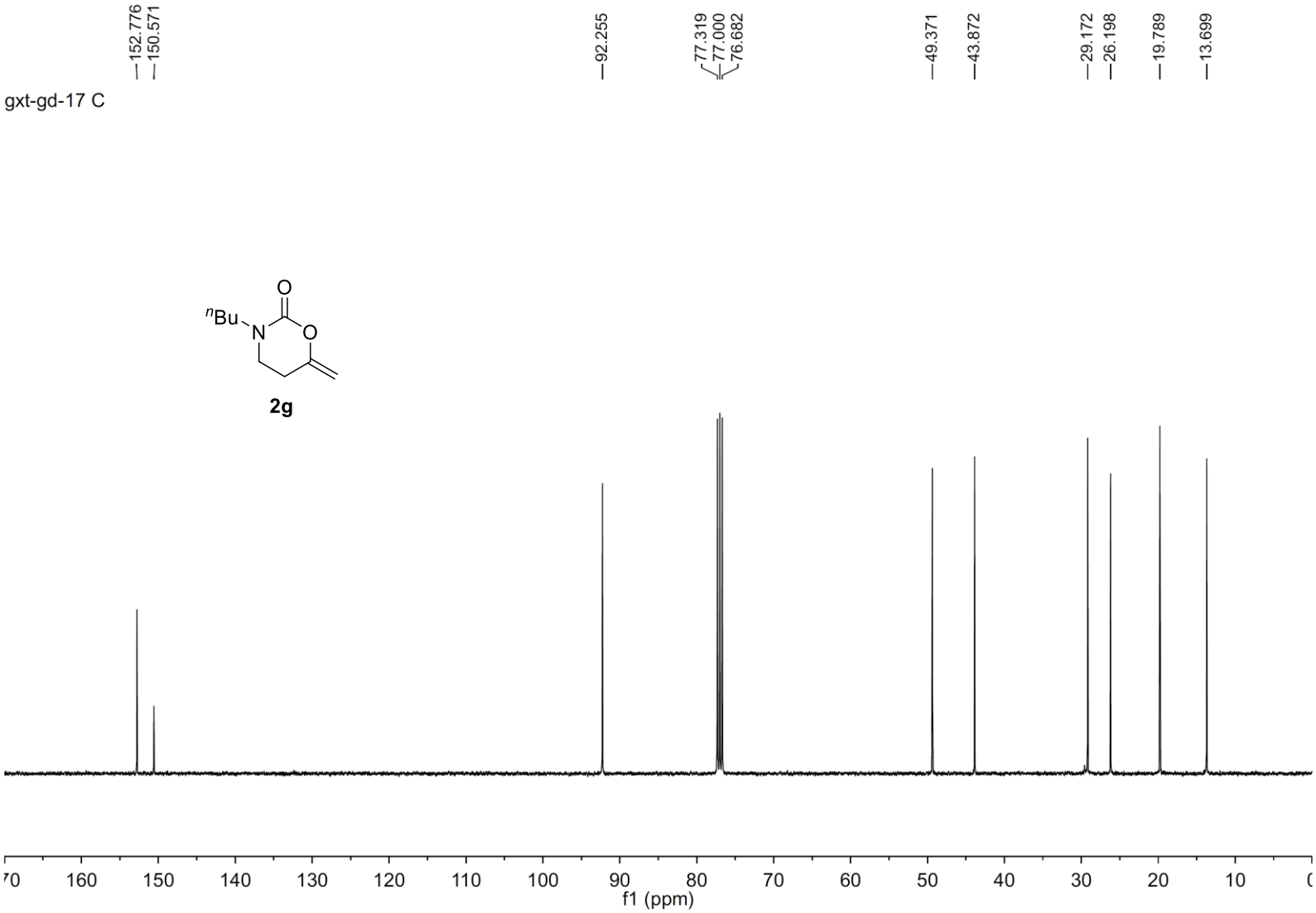

7.275
7.246
7.226
7.213
7.206
7.115
7.092
7.071
4.657
4.653
4.543
4.236
4.232
3.223
3.207
3.191
2.553
2.537
2.522
2.340
gxt-gd-37 H
Me
N
O
O
2e
1.00
3.00
1.01
2.00
1.00
2.01
2.00
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

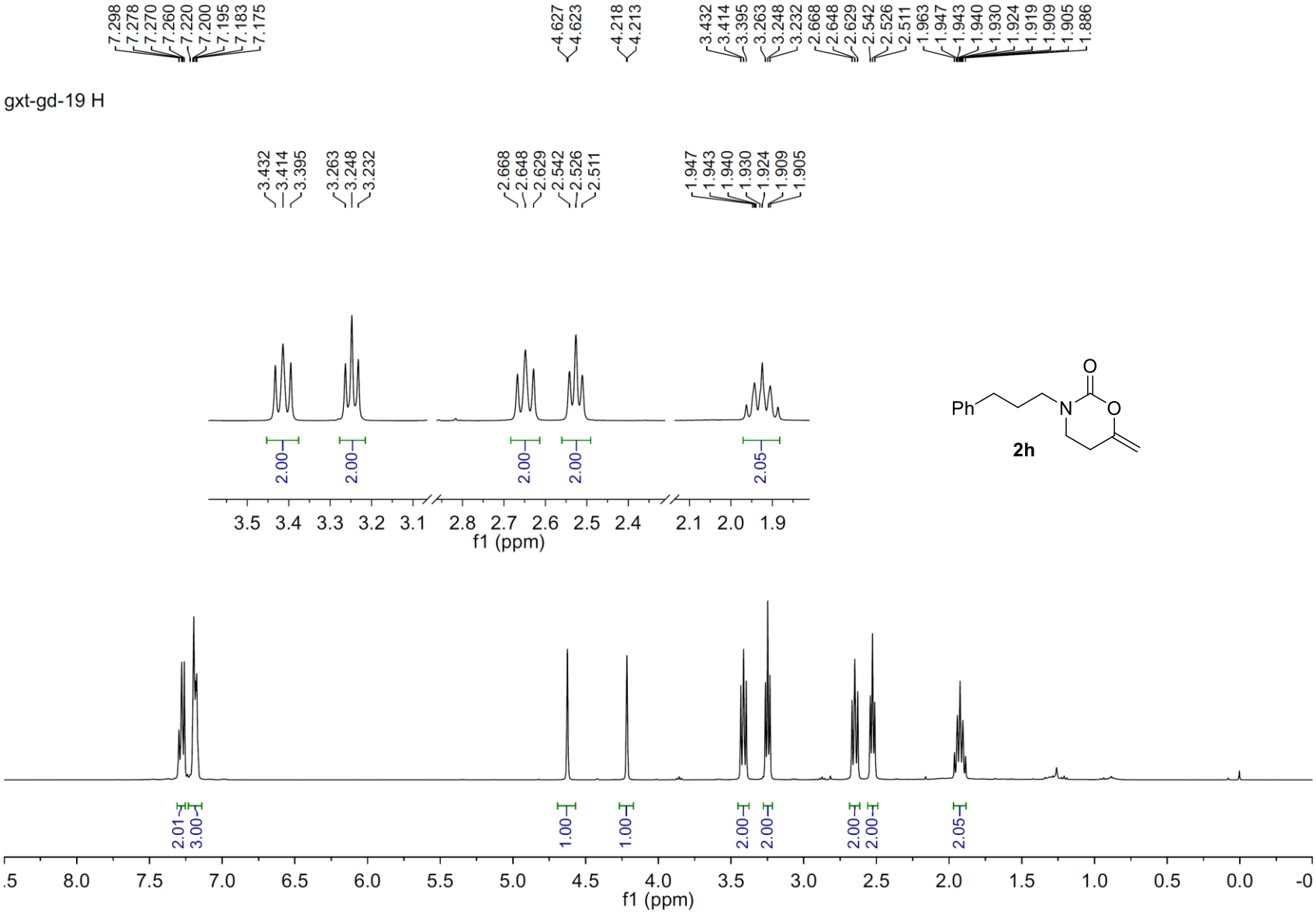

152.660
151.053
138.387
135.925
128.655
128.504
124.995
92.610
77.318
77.000
76.682
52.526
42.969
26.034
21.245
gxt-gd-37 C
Me
N
O
O
2e
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

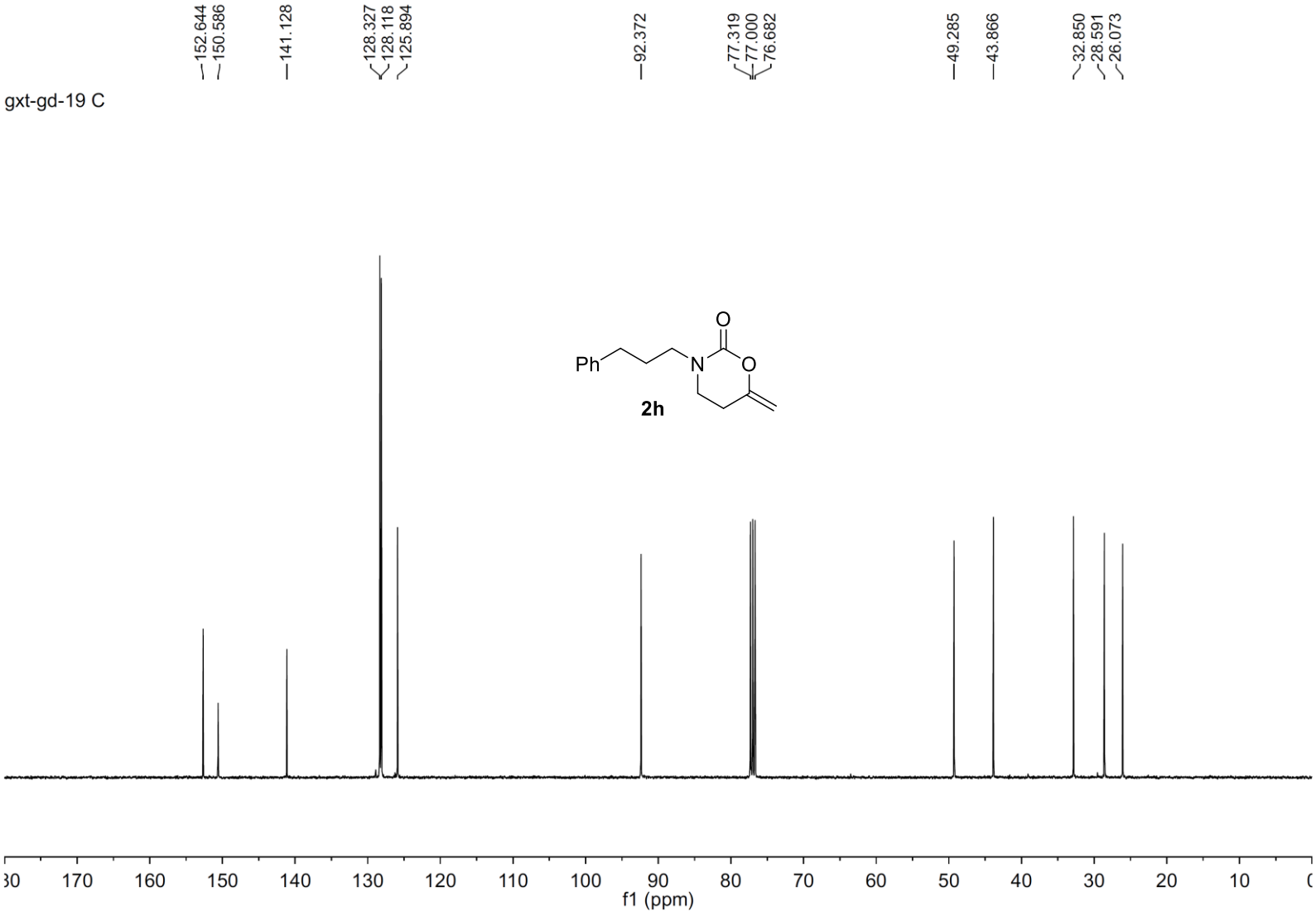

7.234
7.229
7.218
7.209
7.201
7.195
7.182
7.168
7.162
7.148
7.143
4.668
4.664
4.625
4.246
4.242
3.157
3.141
3.126
2.566
2.550
2.535
2.309
gxt-gd-38 H
Me
O
N
O
2f
3.01
1.01
1.02
2.00
1.00
2.00
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

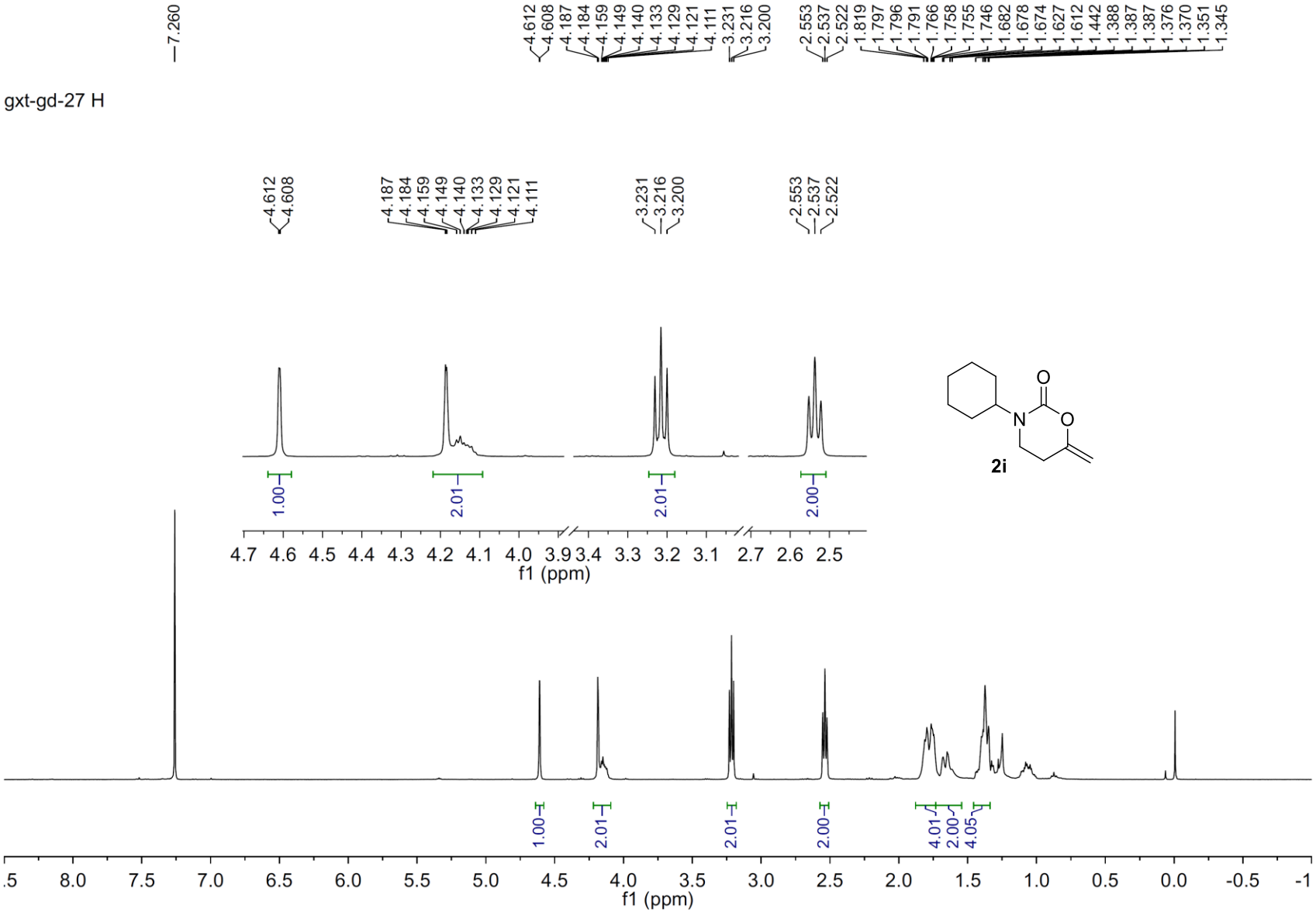

152.565
150.793
136.563
133.432
130.596
128.119
127.776
126.039
92.615
77.318
77.000
76.682
50.408
42.772
25.997
18.997
gxt-gd-38 C
Me
O
N
O
2f
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

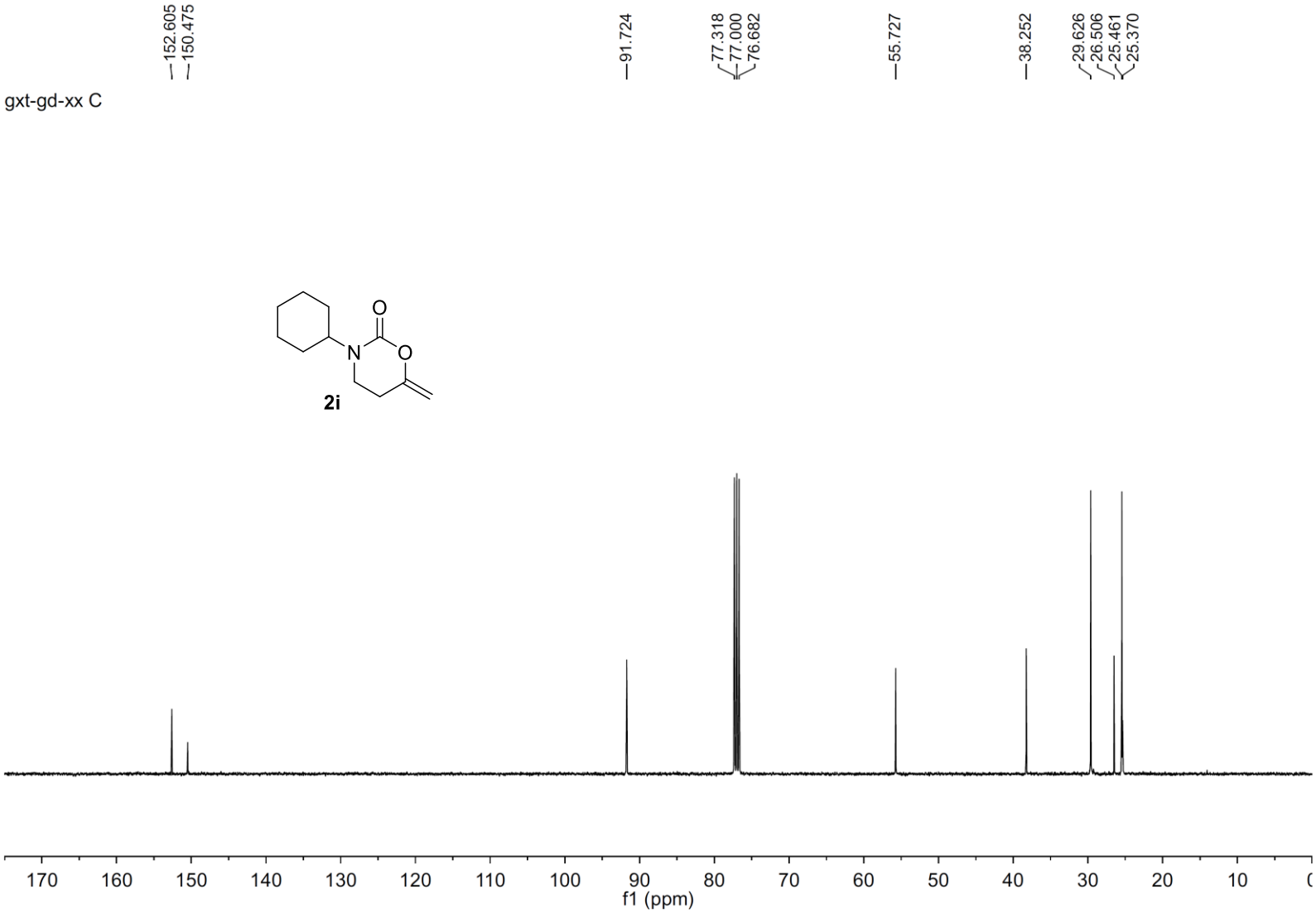

7.260
4.591
4.190
3.347
3.328
3.310
3.286
3.270
3.255
2.571
2.556
2.540
1.572
1.554
1.547
1.534
1.527
1.516
1.510
1.496
1.350
1.331
1.312
1.293
1.274
1.256
0.921
0.903
0.884
0.039
gxt-gd-17 H
nBu
N
O
O
O
2g
2.00
2.00
2.00
2.08
2.02
3.06
f1 (ppm)
1.00
1.00
2.00
2.00
2.00
2.08
2.02
3.06
f1 (ppm)

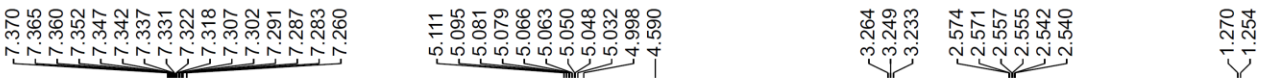

152.776
150.571
92.255
77.319
77.000
76.682
49.371
43.872
29.172
26.198
19.789
13.699
gxt-gd-17 C
nBu
N
O
O
2g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.298
7.278
7.270
7.260
7.220
7.200
7.195
7.183
7.175
4.627
4.623
4.218
4.213
3.432
3.414
3.395
3.263
3.248
3.232
2.668
2.648
2.629
2.542
2.526
2.511
1.963
1.947
1.943
1.940
1.930
1.924
1.919
1.909
1.905
1.886
gxt-gd-19 H
2.00
2.00
2.00
2.00
2.05
f1 (ppm)
Ph
N
O
O
2h
2.01
3.00
1.00
1.00
2.00
2.00
2.00
2.00
2.05
f1 (ppm)

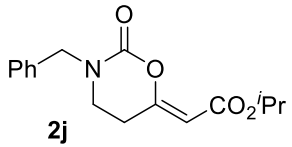

152.644
150.586
141.128
128.327
128.118
125.894
92.372
77.319
77.000
76.682
49.285
43.866
32.850
28.591
26.073
gxt-gd-19 C
Ph
N
O
O
2h
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.260
4.612
4.608
4.187
4.184
4.159
4.149
4.140
4.133
4.129
4.121
4.111
3.231
3.216
3.200
2.553
2.537
2.522
1.819
1.797
1.796
1.791
1.766
1.758
1.755
1.746
1.682
1.678
1.674
1.627
1.612
1.442
1.388
1.387
1.387
1.376
1.370
1.351
1.345
gxt-gd-27 H
1.00
2.01
2.01
2.00
f1 (ppm)
O
N
O
2i
1.00
2.01
2.01
2.00
4.01
2.00
4.05
f1 (ppm)

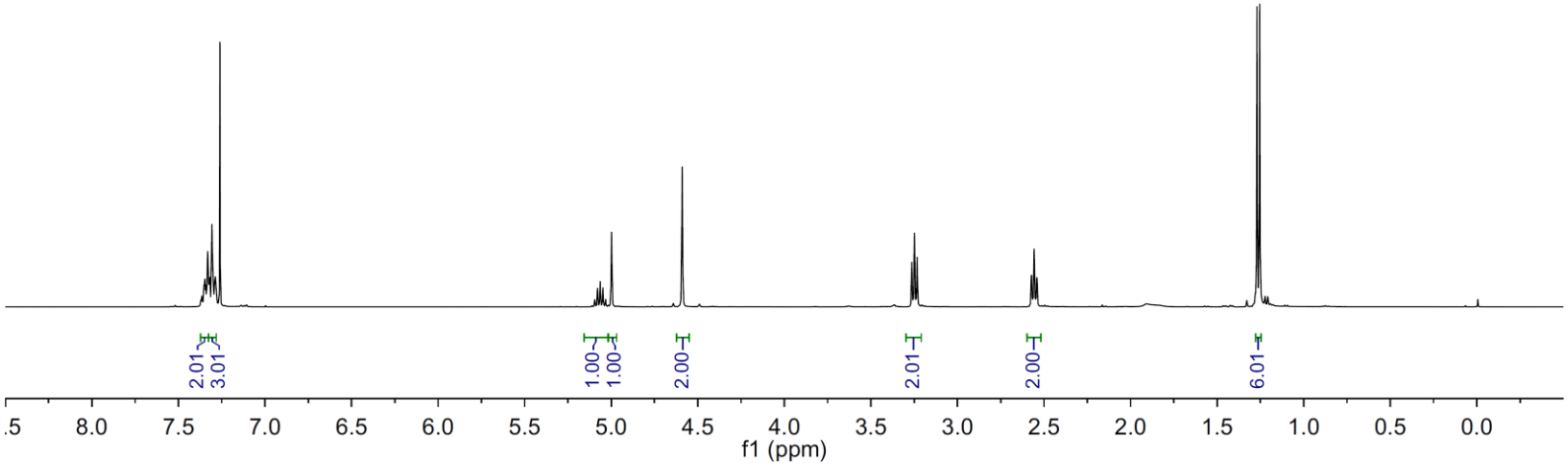

152.605
150.475
91.724
77.318
77.000
76.682
55.727
38.252
29.626
26.506
25.461
25.370
gxt-gd-xx C
O
N
O
2i
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

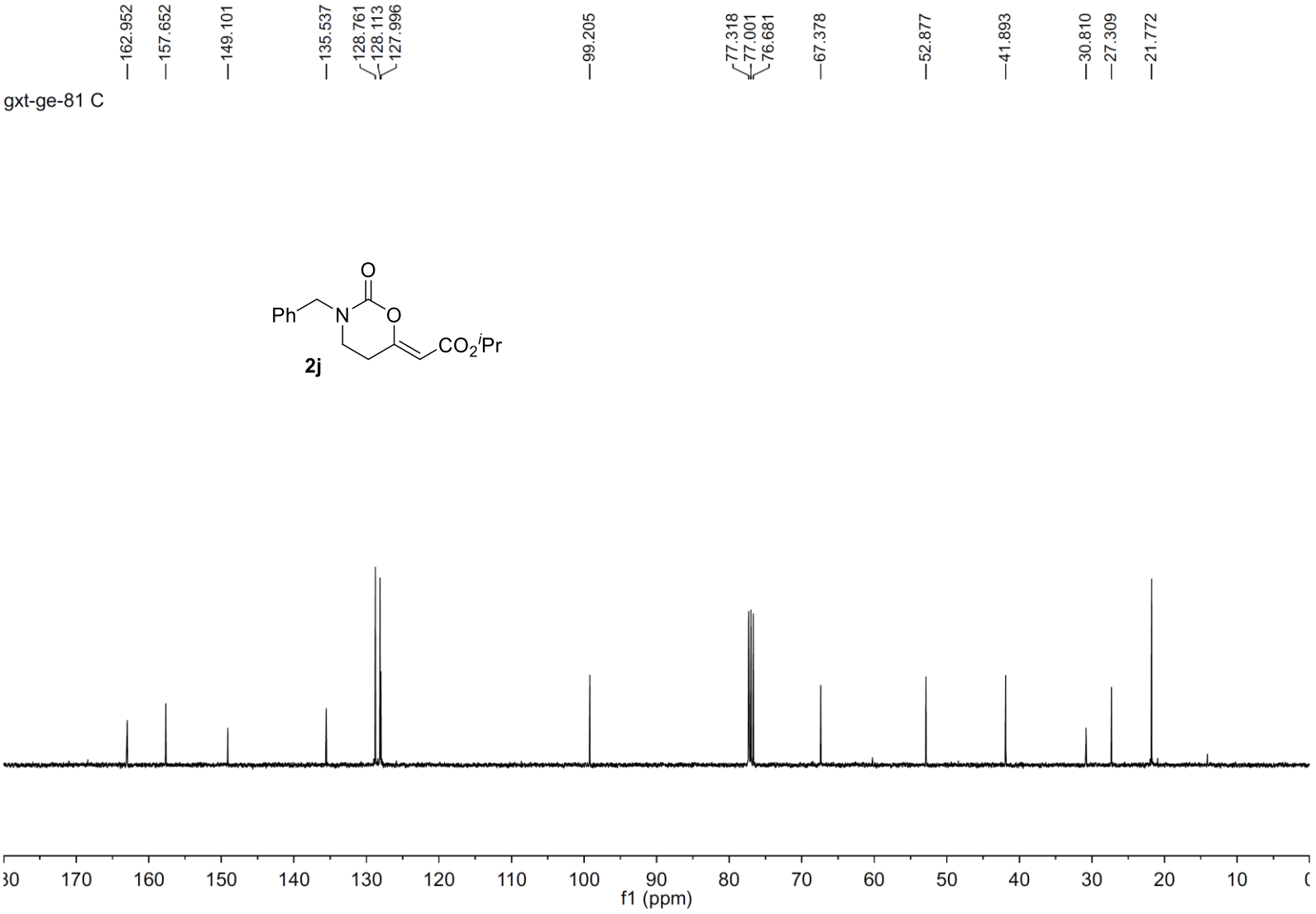

7.370
7.365
7.360
7.352
7.347
7.342
7.337
7.331
7.322
7.318
7.307
7.302
7.291
7.287
7.283
7.260
5.111
5.095
5.081
5.079
5.066
5.063
5.050
5.048
5.032
4.998
4.590
3.264
3.249
3.233
2.574
2.571
2.557
2.555
2.542
2.540
1.270
1.254

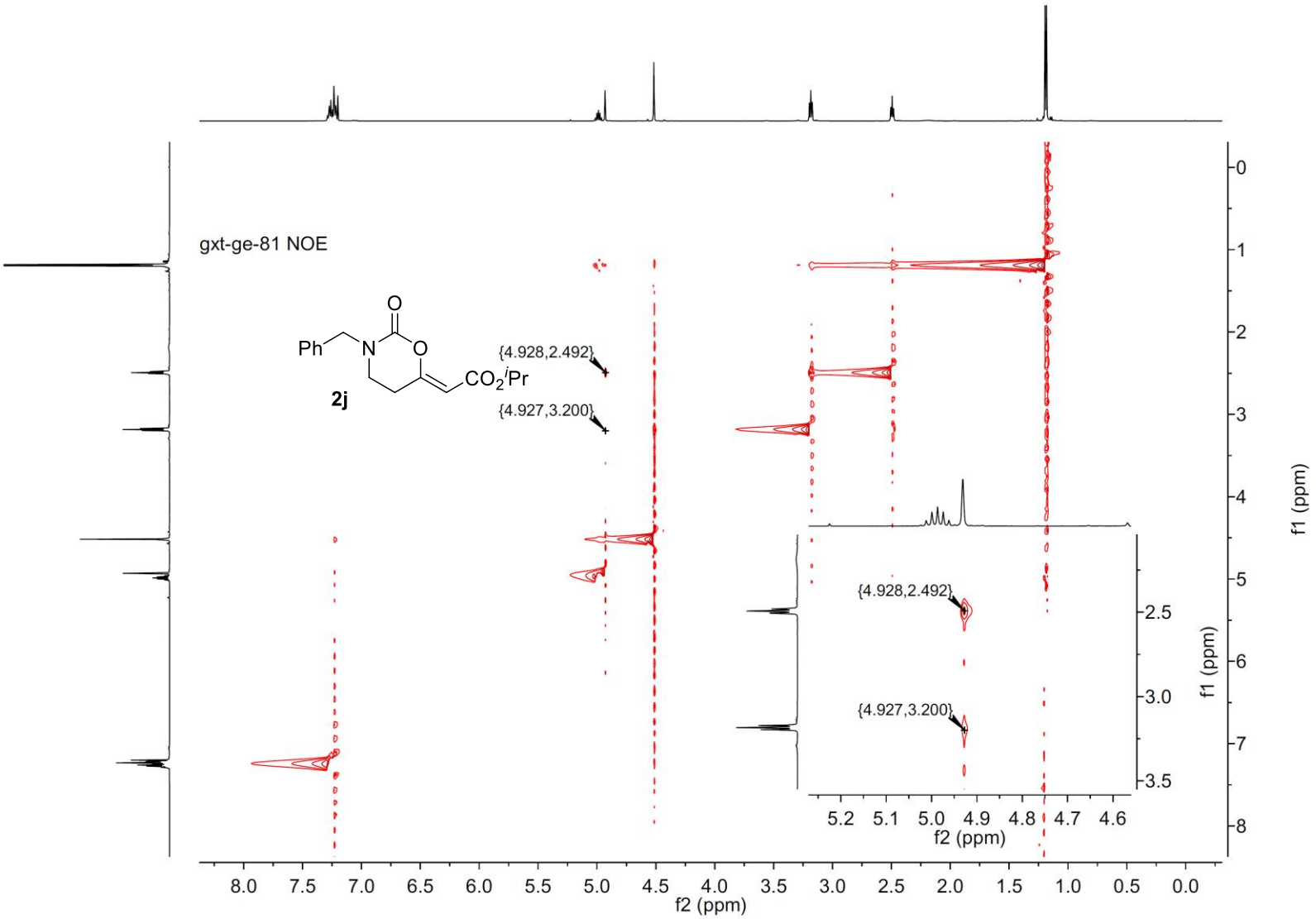
gxt-ge-81 H


O
Ph
N
O
CO2iPr

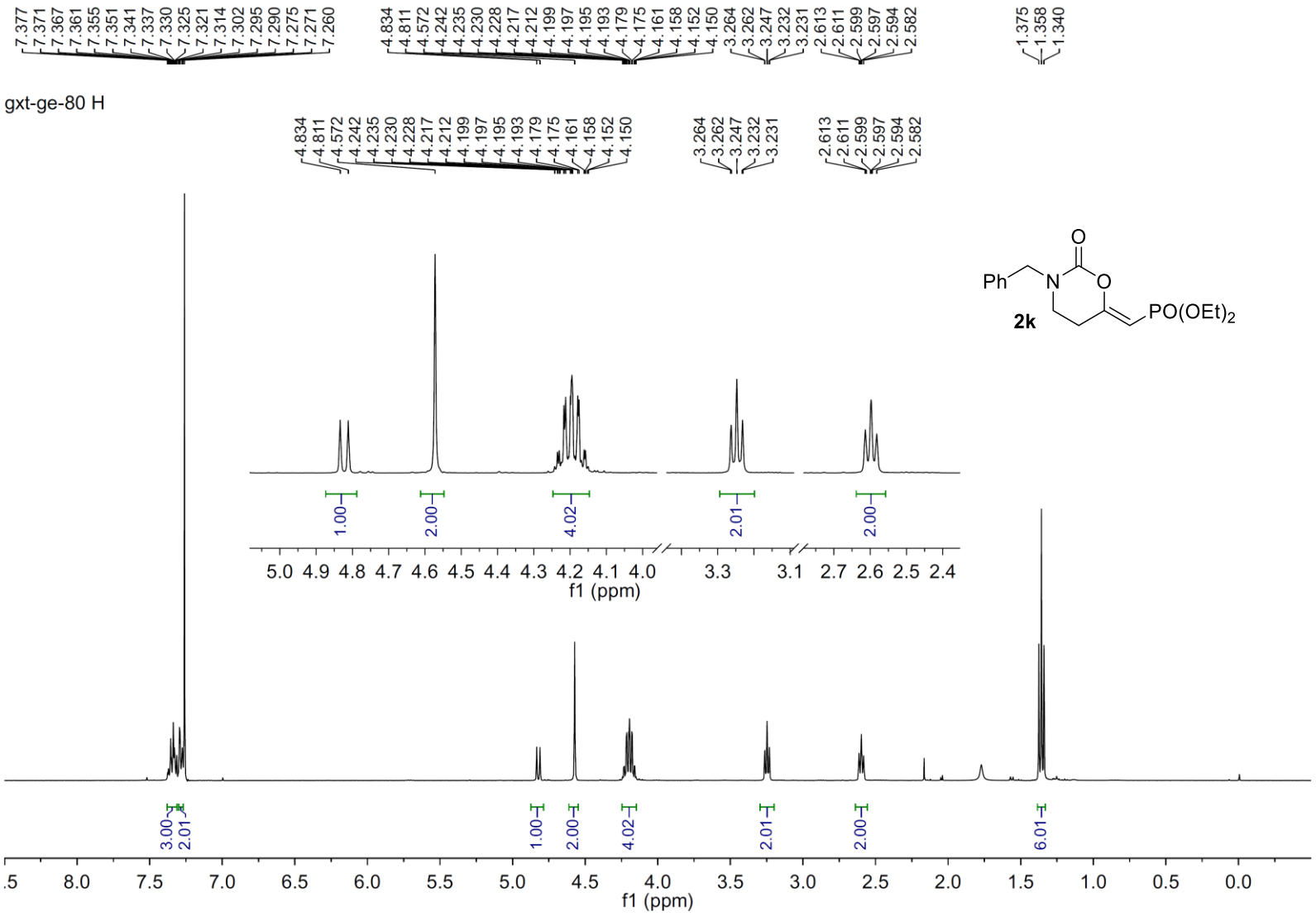
2j


2.01
3.01
1.00
1.00
2.00
2.01
2.00
6.01
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.952
157.652
149.101
135.537
128.761
128.113
127.996
99.205
77.318
77.001
76.681
67.378
52.877
41.893
30.810
27.309
21.772
gxt-ge-81 C
Ph
N
O
O
CO2iPr
2j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

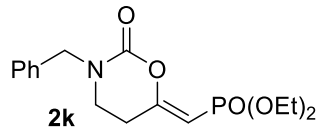

gxt-ge-81 NOE
Ph
N
O
O
O
CO2iPr
2j
{4.928,2.492}
{4.927,3.200}
f2 (ppm)
f1 (ppm)

v

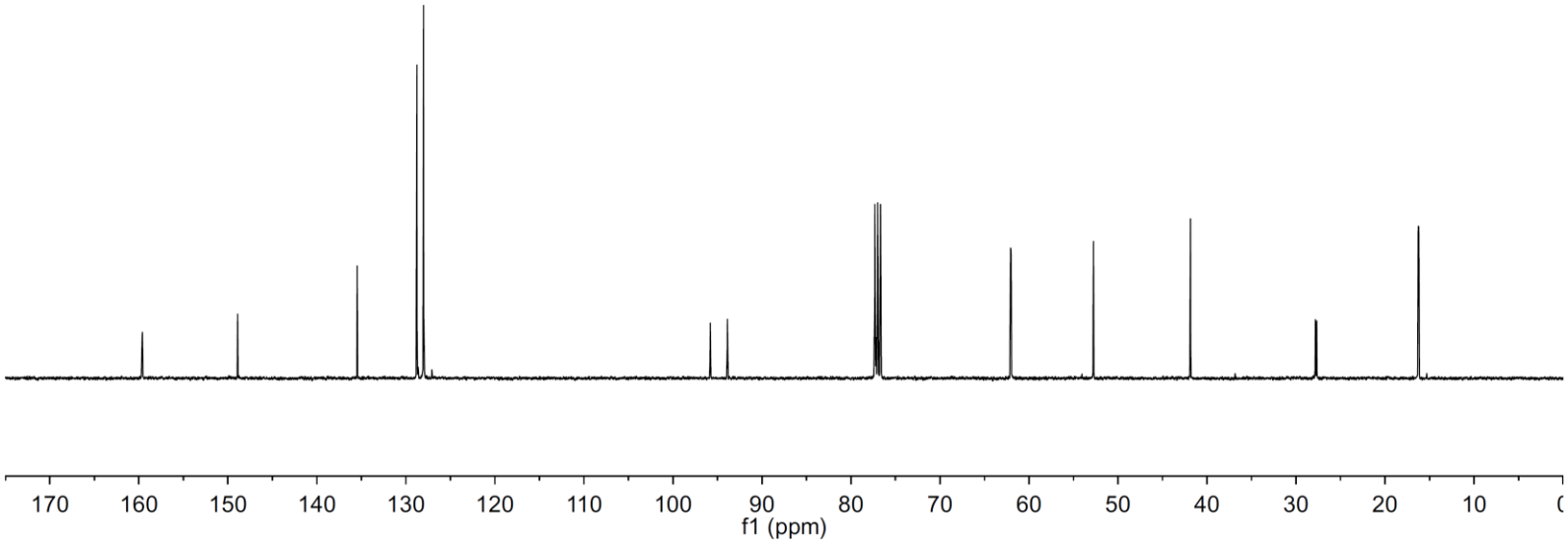

7.377
7.371
7.367
7.361
7.355
7.351
7.341
7.337
7.330
7.325
7.321
7.314
7.302
7.295
7.290
7.275
7.271
7.260
4.834
4.811
4.572
4.242
4.235
4.230
4.228
4.217
4.212
4.199
4.197
4.195
4.193
4.179
4.175
4.161
4.158
4.152
4.150
3.264
3.262
3.247
3.232
3.231
2.613
2.611
2.599
2.597
2.594
2.582
1.375
1.358
1.340
gxt-ge-80 H
Ph
N
O
O
O
PO(OEt)2
2k
1.00
2.00
4.02
2.01
2.00
5.0 4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1 4.0 3.3 3.1 2.7 2.6 2.5 2.4
f1 (ppm)
3.00
2.01
1.00
2.00
4.02
2.01
2.00
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

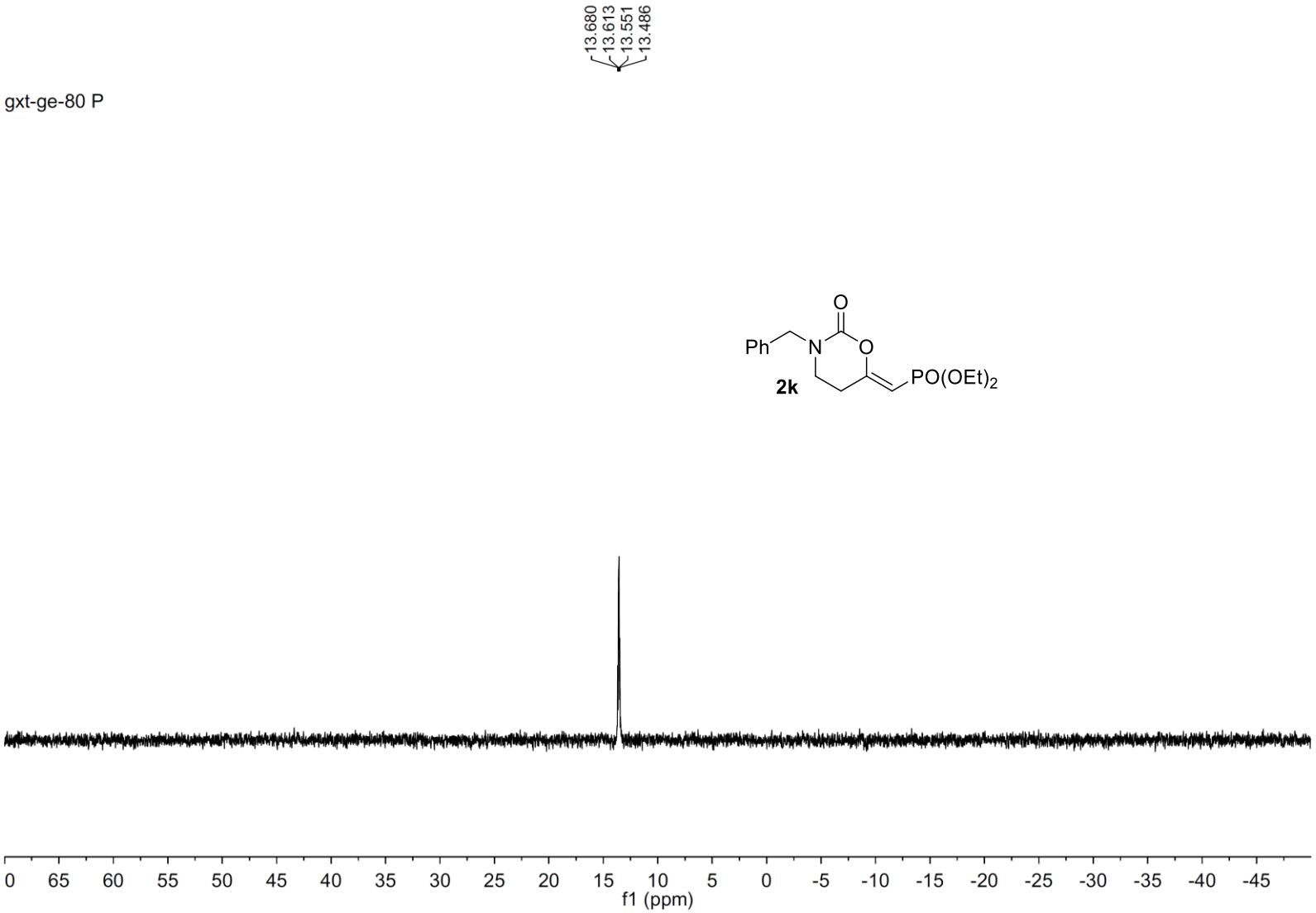
gxt-ge-80 C

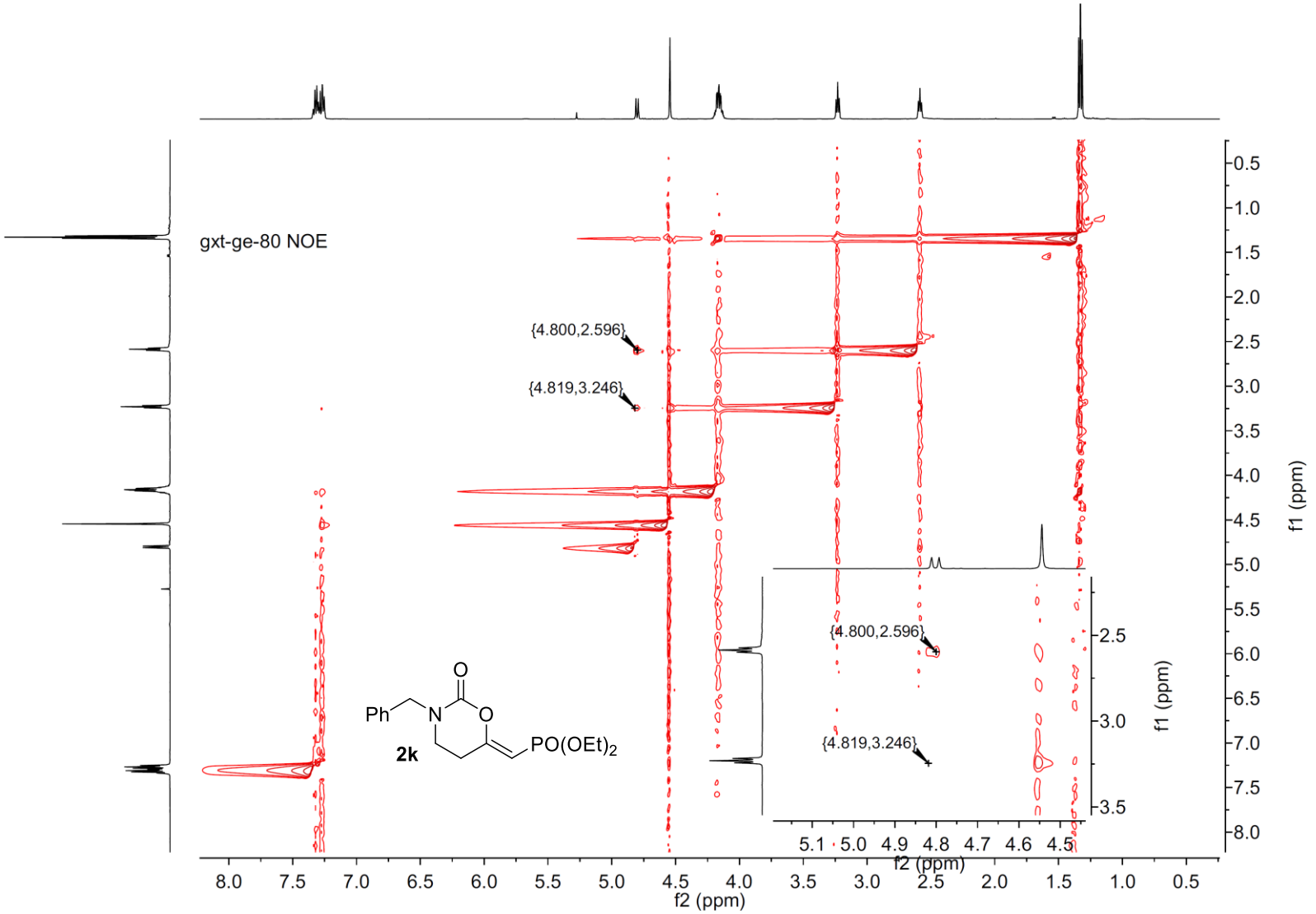
159.640
159.600
148.901
135.472
128.760
128.016
95.803
93.887
77.316
77.002
76.679
62.069
62.011
52.761
41.853
27.831
27.681
16.267
16.202

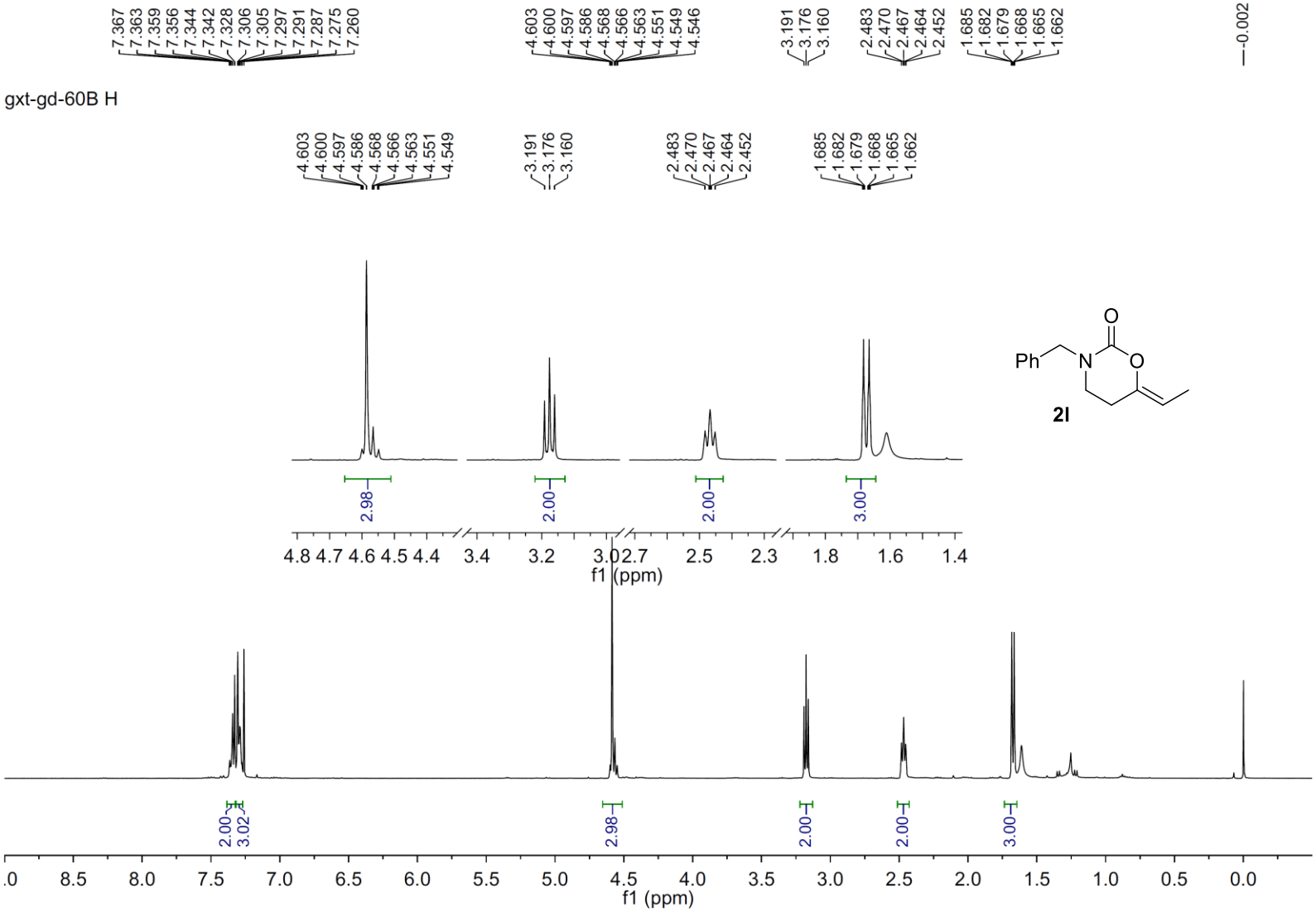


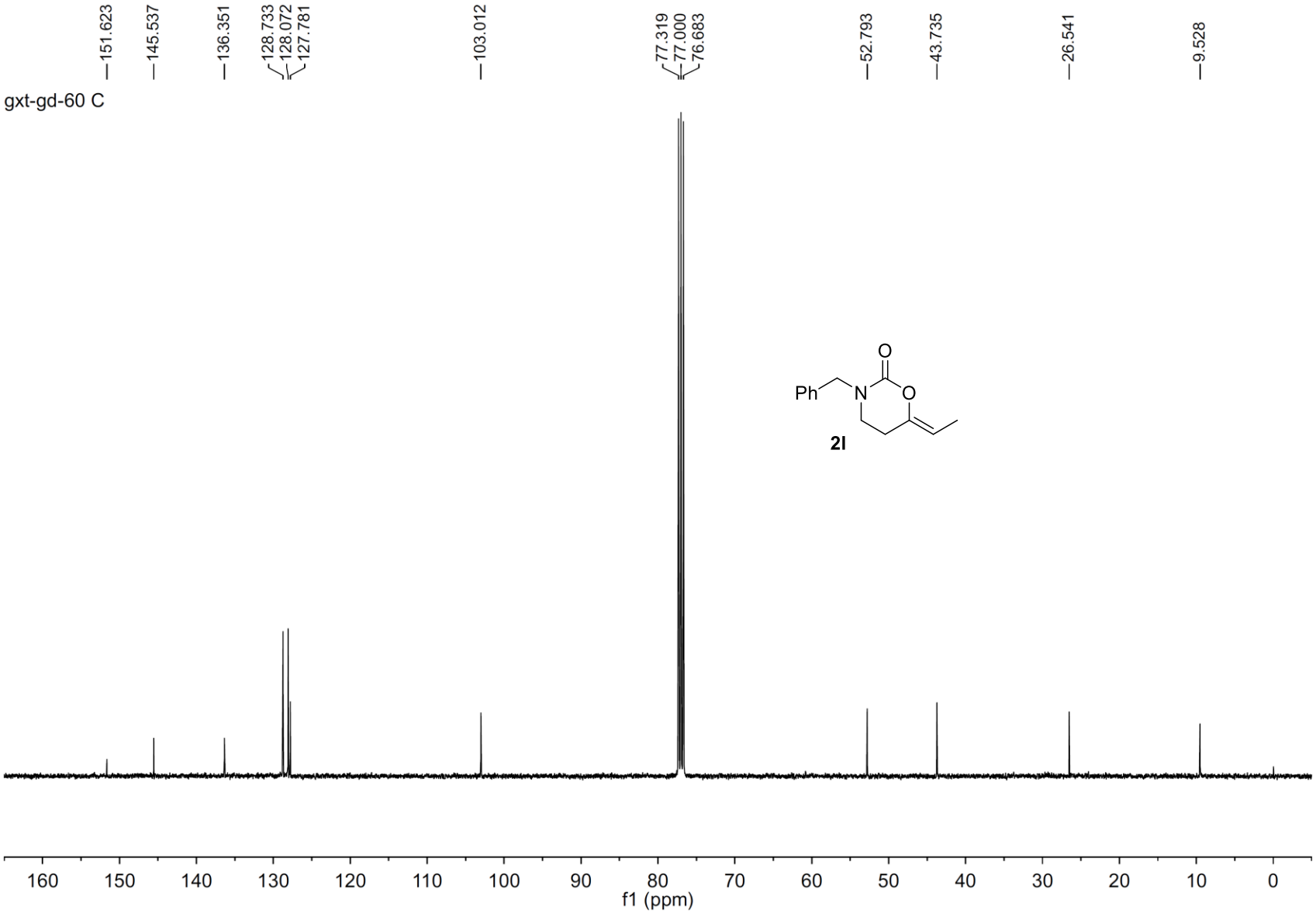
2k

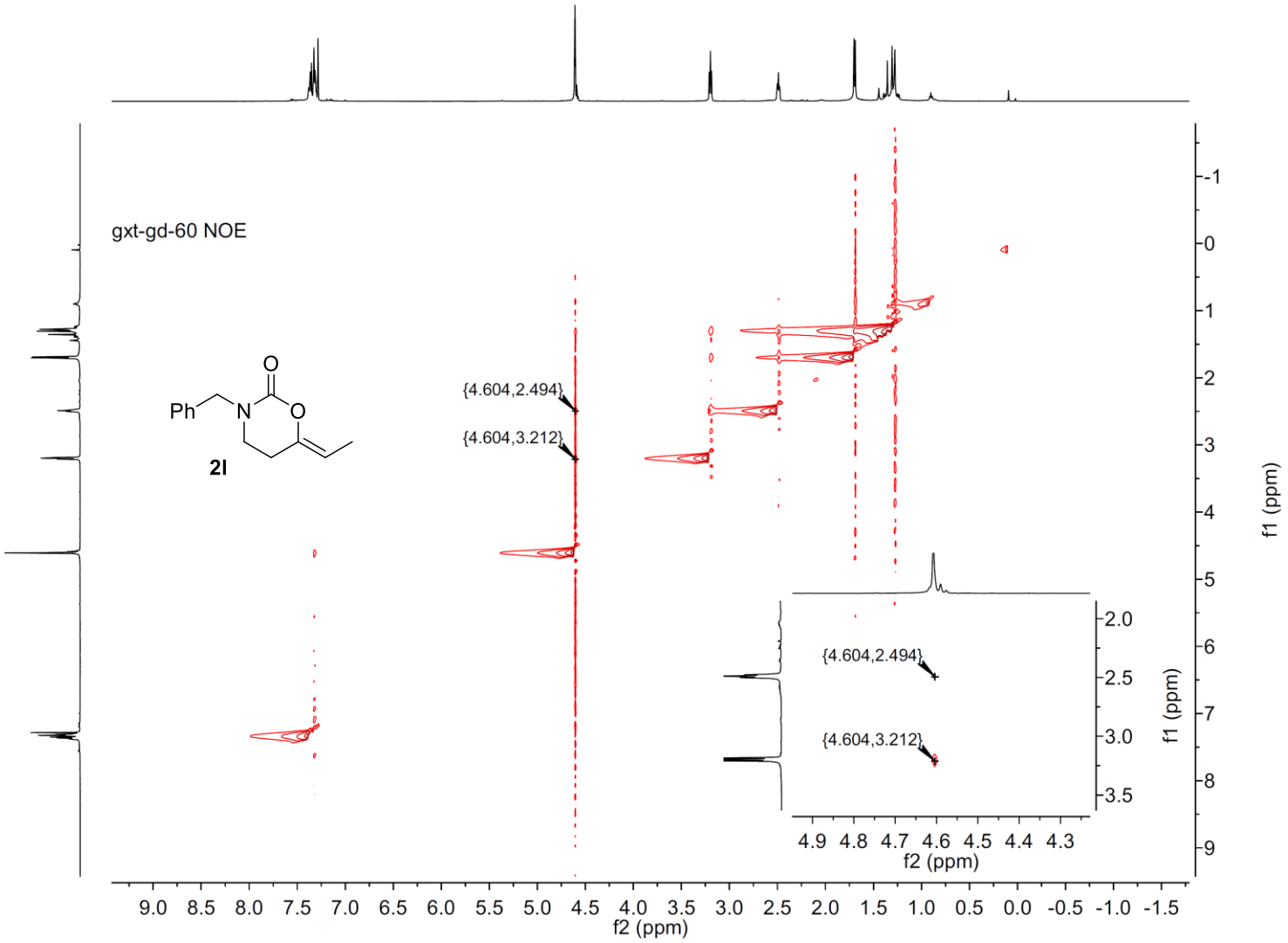



13.680
13.613
13.551
13.486
gxt-ge-80 P
Ph
N
O
O
O
PO(OEt)2
2k
0 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45
f1 (ppm)


gxt-ge-80 NOE
{4.800,2.596}
{4.819,3.246}
Ph
N
O
O
O
PO(OEt)2
2k
f2 (ppm)
f1 (ppm)

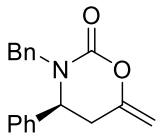

7.367
7.363
7.359
7.356
7.344
7.342
7.328
7.306
7.305
7.297
7.291
7.287
7.275
7.260
4.603
4.600
4.597
4.586
4.568
4.566
4.563
4.551
4.549
4.546
3.191
3.176
3.160
2.483
2.470
2.467
2.464
2.452
1.685
1.682
1.679
1.668
1.665
1.662
-0.002
gxt-gd-60B H
Ph
N
O
O
2l
2.98
2.00
2.00
3.00
f1 (ppm)
2.00
3.02
2.98
2.00
2.00
3.00
f1 (ppm)


151.623
145.537
136.351
128.733
128.072
127.781
103.012
77.319
77.000
76.683
52.793
43.735
26.541
9.528
gxt-gd-60 C
O
Ph
N
O
2l
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

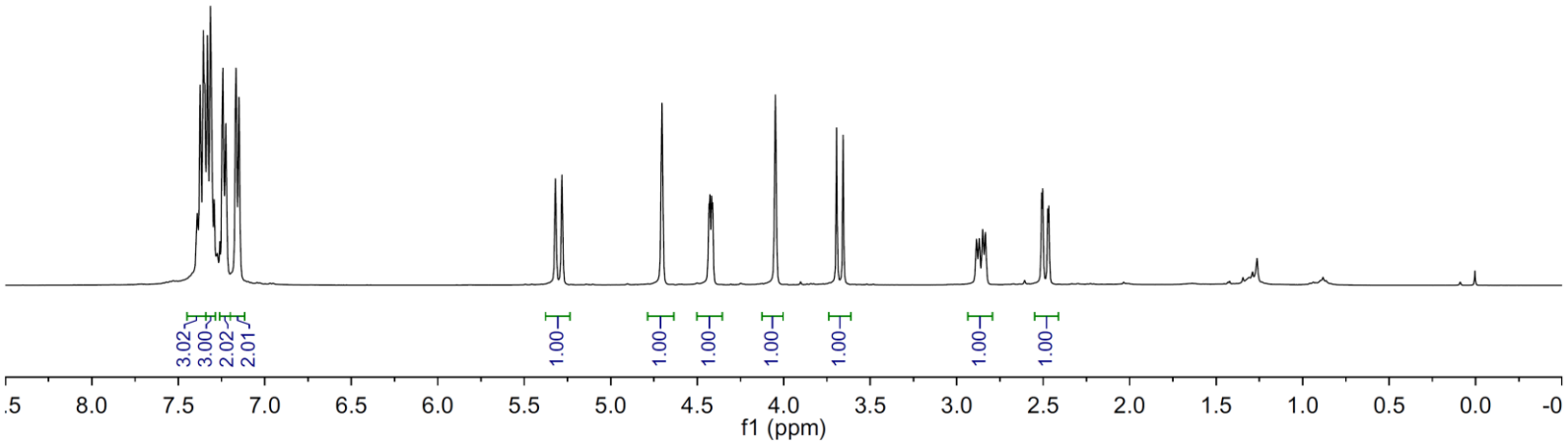

gxt-gd-60 NOE
Ph
N
O
O
2l
{4.604,2.494}
{4.604,3.212}
f2 (ppm)
f1 (ppm)
{4.604,2.494}
{4.604,3.212}
f2 (ppm)
f1 (ppm)

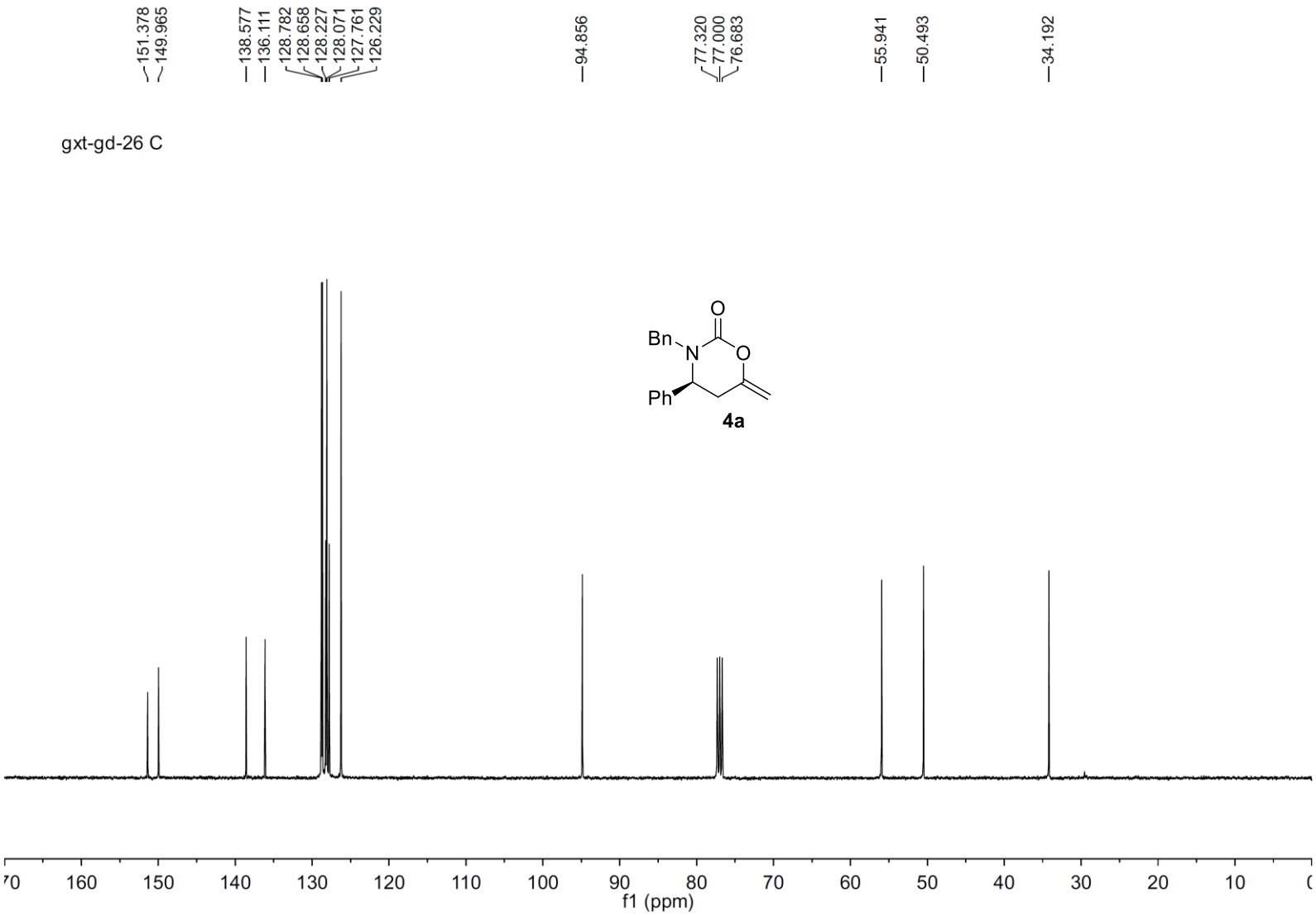

7.395
7.390
7.374
7.355
7.348
7.332
7.314
7.309
7.293
7.260
7.246
7.241
7.225
7.170
7.165
7.150
5.320
5.282
4.704
4.433
4.426
4.417
4.410
4.048
3.694
3.657
2.885
2.880
2.870
2.866
2.854
2.850
2.845
2.834
2.830
2.509
2.502
2.473
2.467

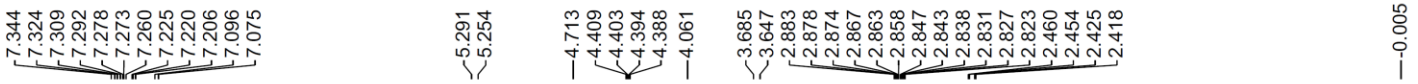
gxt-gd-26 H


O
Bn
N
O
Ph

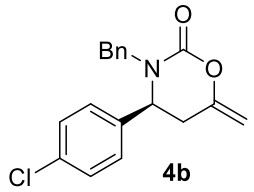
4a


3.02
3.00
2.02
2.01
1.00
1.00
1.00
1.00
1.00
1.00
1.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

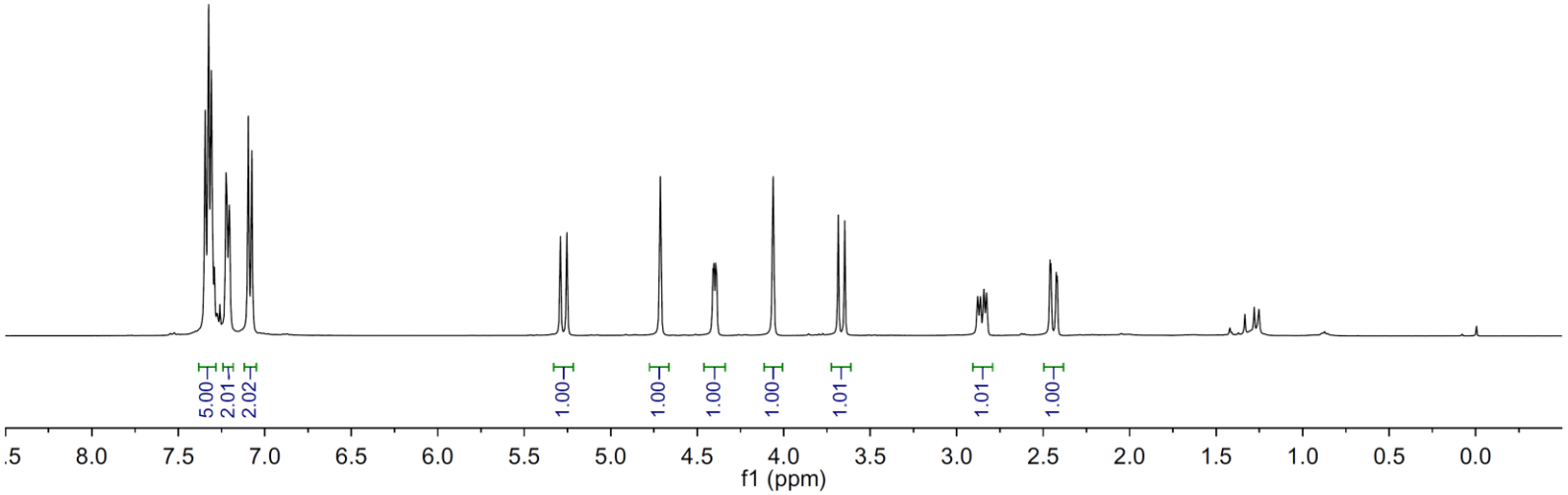

151.378
149.965
138.577
136.111
128.782
128.658
128.227
128.071
127.761
126.229
94.856
77.320
77.000
76.683
55.941
50.493
34.192
gxt-gd-26 C
Bn
N
O
O
Ph
4a
f1 (ppm)

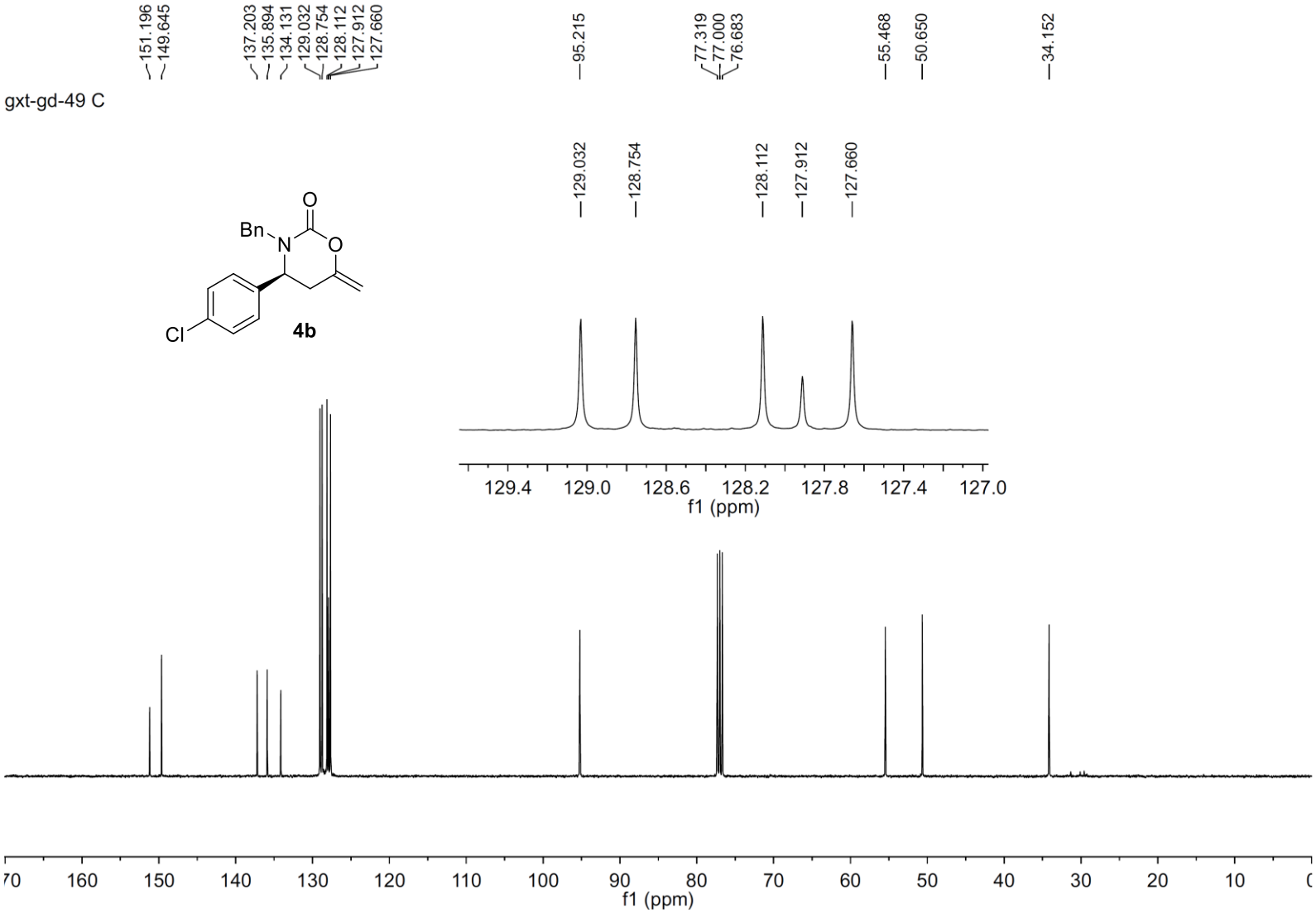

7.344
7.324
7.309
7.292
7.278
7.273
7.260
7.225
7.220
7.206
7.096
7.075
5.291
5.254
4.713
4.409
4.403
4.394
4.388
4.061
3.685
3.647
2.883
2.878
2.874
2.867
2.863
2.858
2.847
2.843
2.838
2.831
2.827
2.823
2.460
2.454
2.425
2.418
-0.005

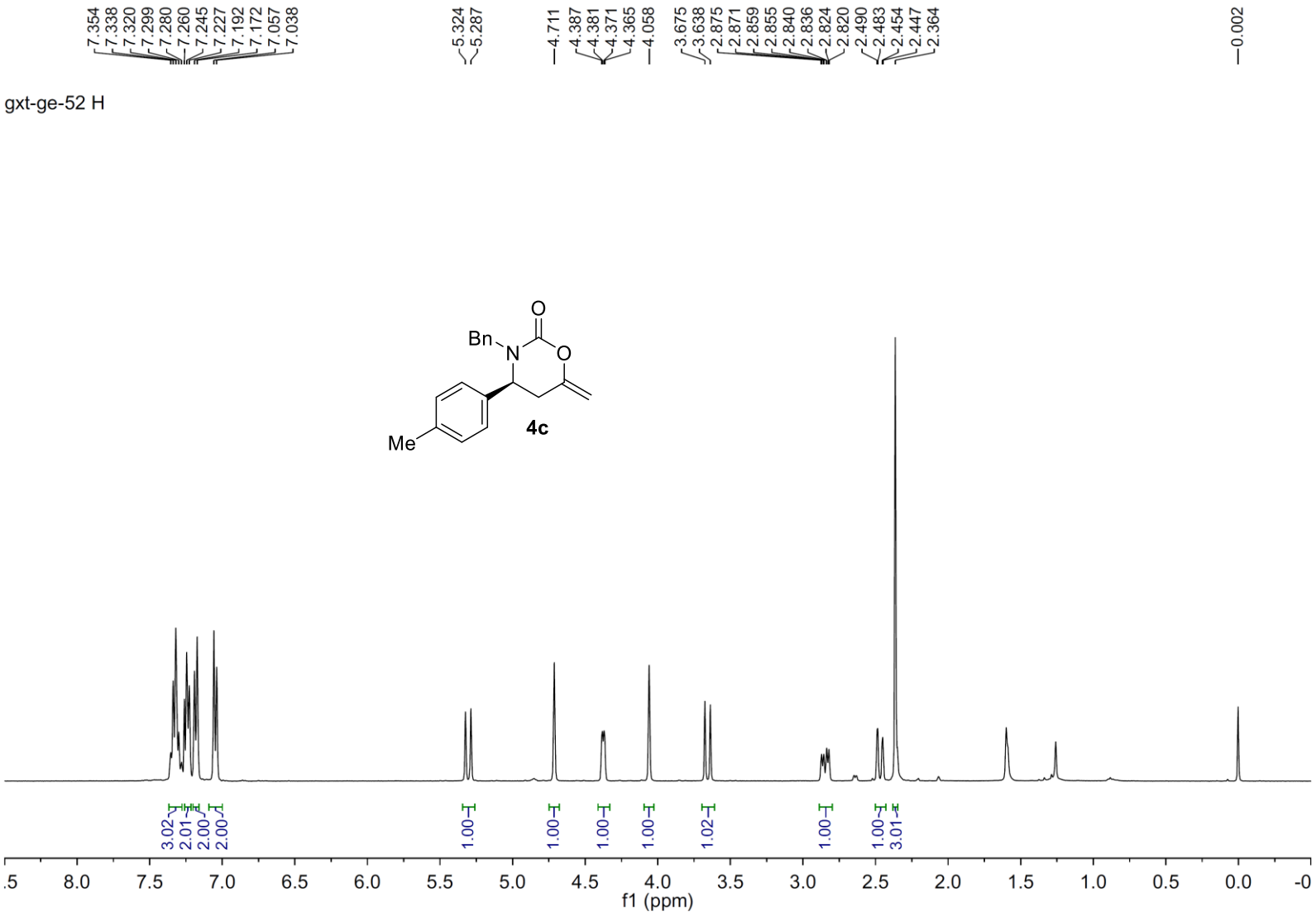
gxt-gd-49 H

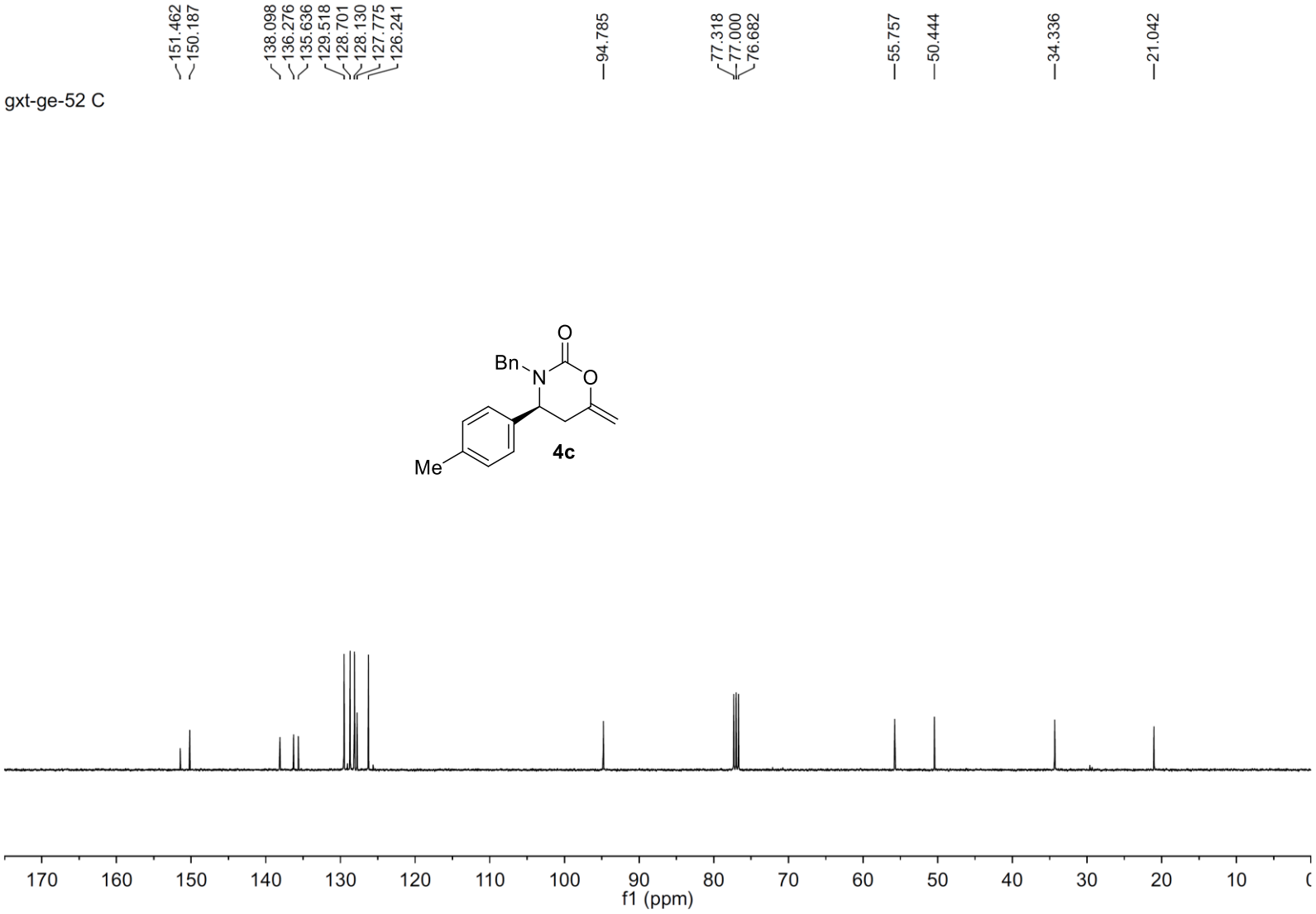

O
Bn
N
O
Cl

4b


5.00
2.01
2.02
1.00
1.00
1.00
1.00
1.01
1.01
1.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

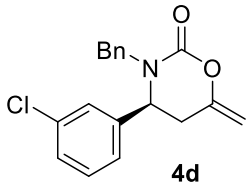

151.196
149.645
137.203
135.894
134.131
129.032
128.754
128.112
127.912
127.660
95.215
77.319
77.000
76.683
55.468
50.650
34.152
gxt-gd-49 C
O
Bn
N
O
Cl
4b
129.032
128.754
128.112
127.912
127.660
129.4
129.0
128.6
128.2
127.8
127.4
127.0
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.354
7.338
7.320
7.299
7.280
7.260
7.245
7.227
7.192
7.172
7.057
7.038
5.324
5.287
4.711
4.387
4.381
4.371
4.365
4.058
3.675
3.638
2.875
2.871
2.859
2.855
2.840
2.836
2.824
2.820
2.490
2.483
2.454
2.447
2.364
0.002
gxt-ge-52 H
Bn
N
O
O
Me
4c
3.02
2.01
2.00
2.00
1.00
1.00
1.00
1.00
1.02
1.00
1.00
3.01
f1 (ppm)

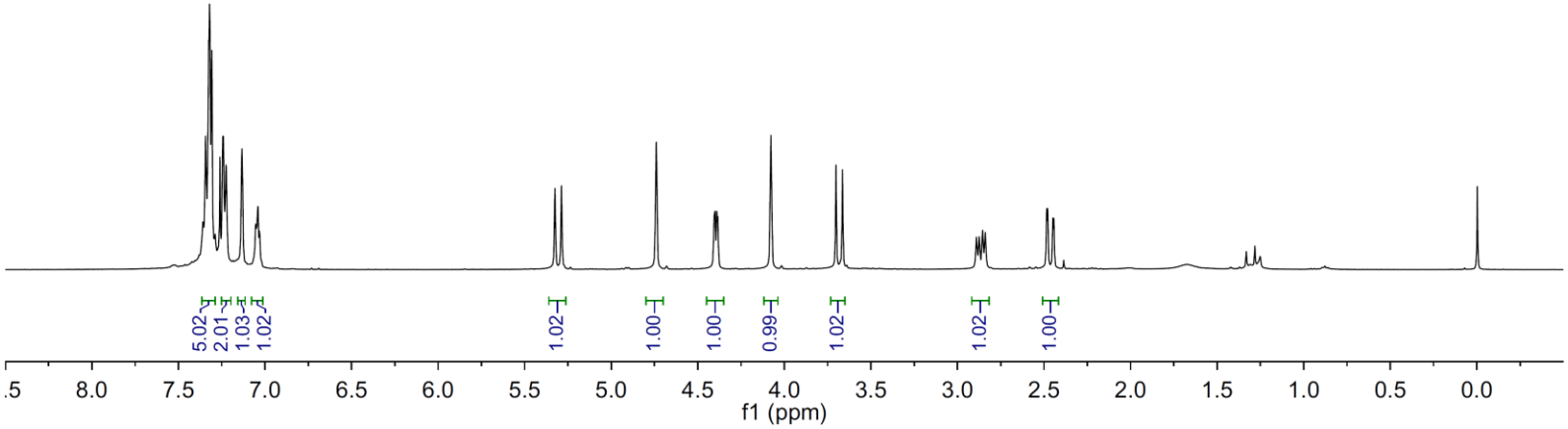

151.462
150.187
138.098
136.276
135.636
129.518
128.701
128.130
127.775
126.241
94.785
77.318
77.000
76.682
55.757
50.444
34.336
21.042
gxt-ge-52 C
Bn
N
O
O
Me
4c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

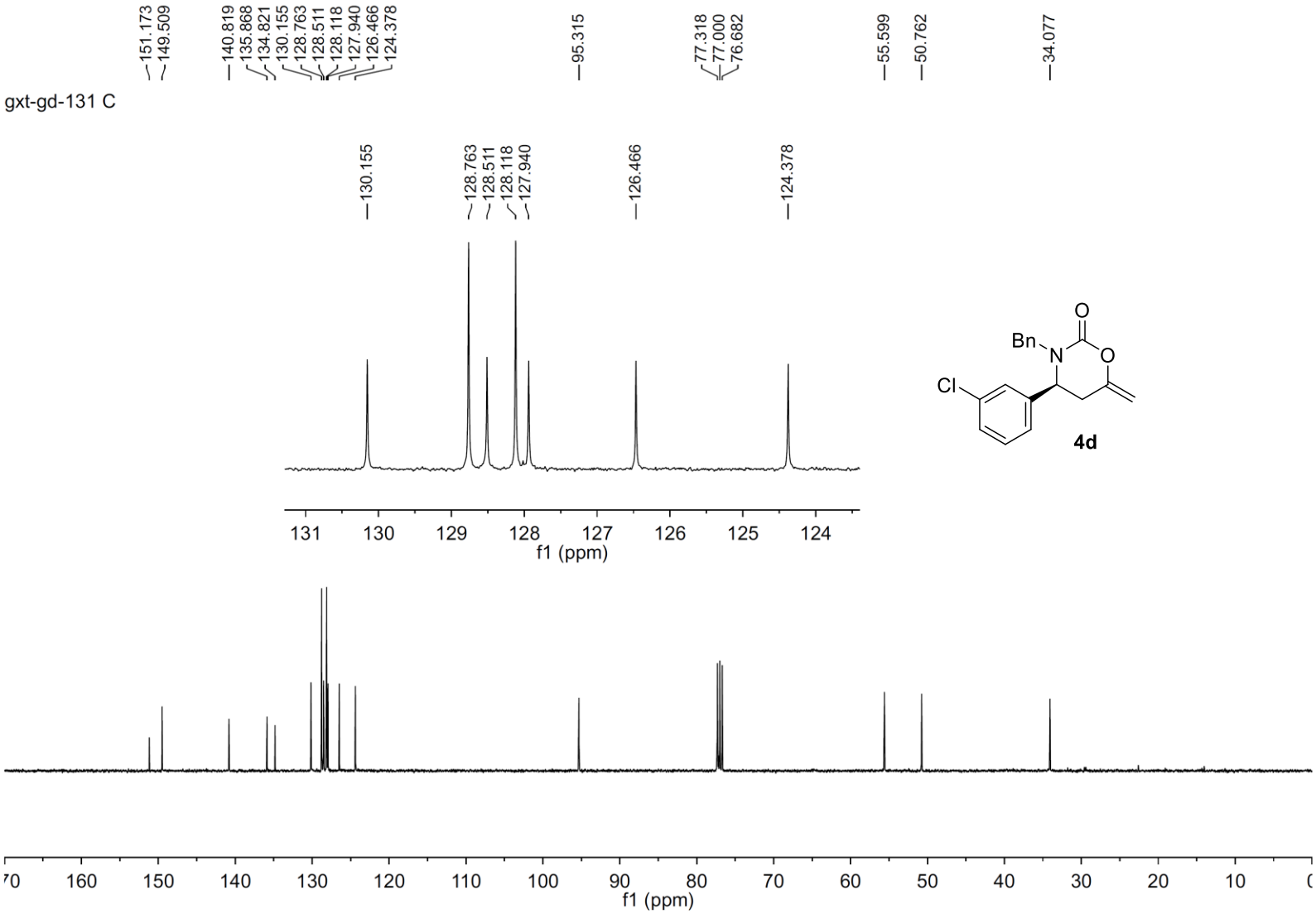

7.366
7.359
7.343
7.326
7.320
7.317
7.307
7.288
7.260
7.245
7.239
7.225
7.134
7.066
7.056
7.052
7.051
7.046
7.041
7.034
7.029
5.325
5.287
4.739
4.406
4.400
4.390
4.384
4.077
3.702
3.664
2.895
2.891
2.886
2.879
2.875
2.871
2.859
2.855
2.851
2.844
2.839
2.835
2.485
2.479
2.449
2.443

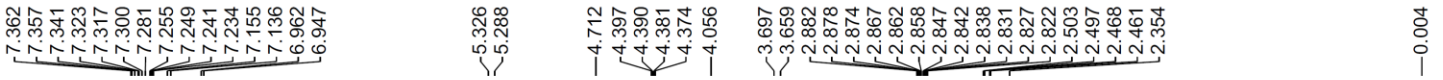
gxt-gd-57 H


O
Bn
N
O
Cl

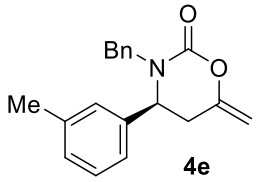
4d


5.02
2.01
1.03
1.02
1.02
1.00
1.00
0.99
1.02
1.02
1.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

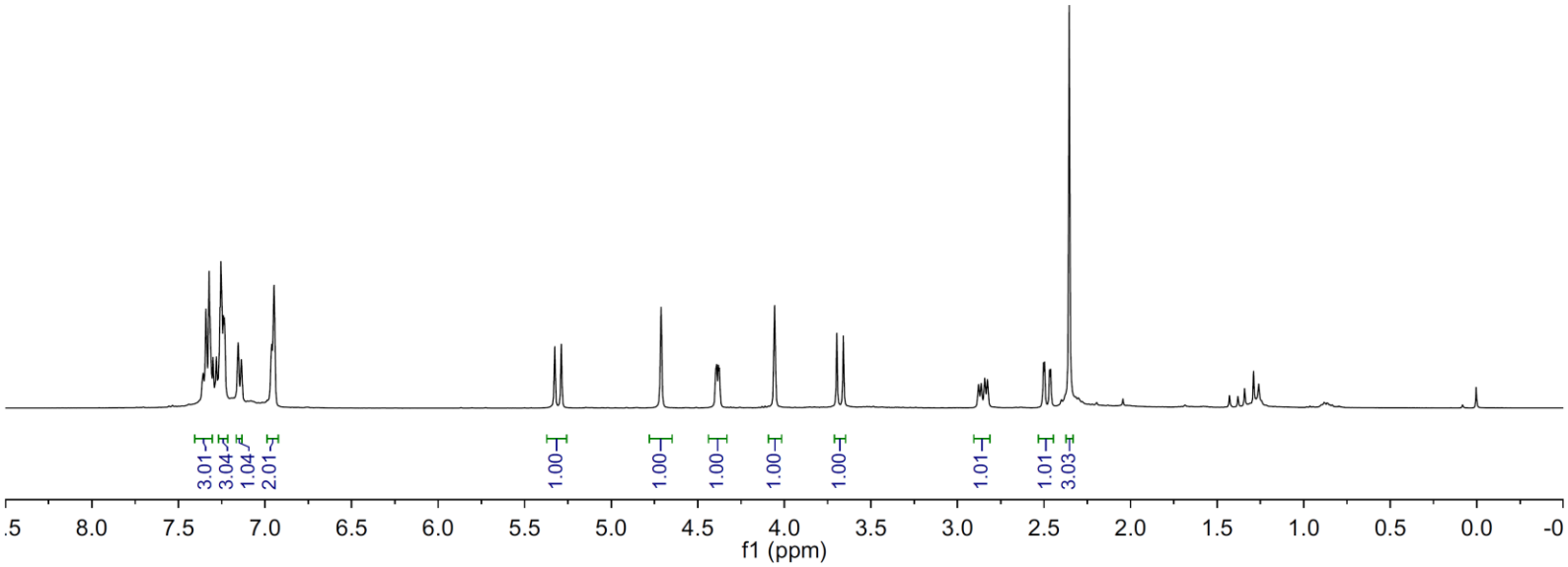

151.173
149.509
140.819
135.868
134.821
130.155
128.763
128.511
128.118
127.940
126.466
124.378
95.315
77.318
77.000
76.682
55.599
50.762
34.077
gxt-gd-131 C
130.155
128.763
128.511
128.118
127.940
126.466
124.378
131
130
129
128
127
126
125
124
f1 (ppm)
O
Bn
N
O
Cl
4d
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

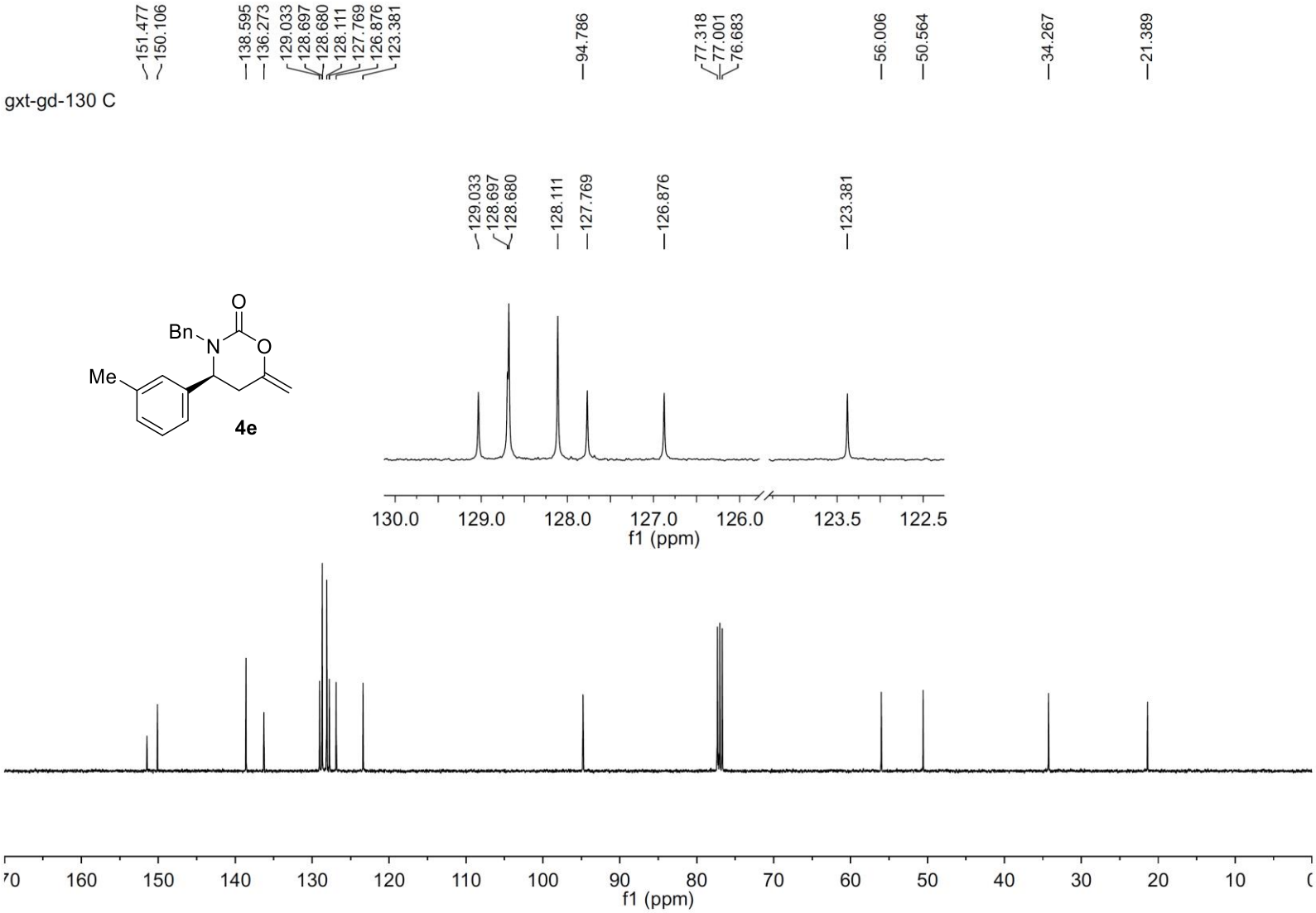

7.362
7.357
7.341
7.323
7.317
7.300
7.281
7.255
7.249
7.241
7.234
7.155
7.136
6.962
6.947
5.326
5.288
4.712
4.397
4.390
4.381
4.374
4.056
3.697
3.659
2.882
2.878
2.874
2.867
2.862
2.858
2.847
2.842
2.838
2.831
2.827
2.822
2.503
2.497
2.468
2.461
2.354
0.004

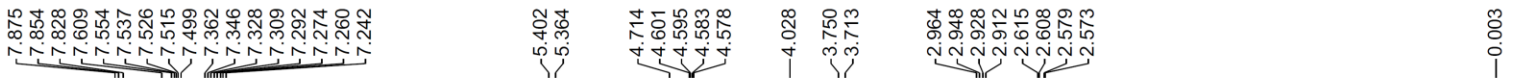
gxt-gd-56 H


O
Bn
N
O
Me

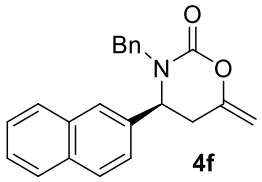
4e


3.01
3.04
1.04
2.01
1.00
1.00
1.00
1.00
1.00
1.01
1.01
3.03
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

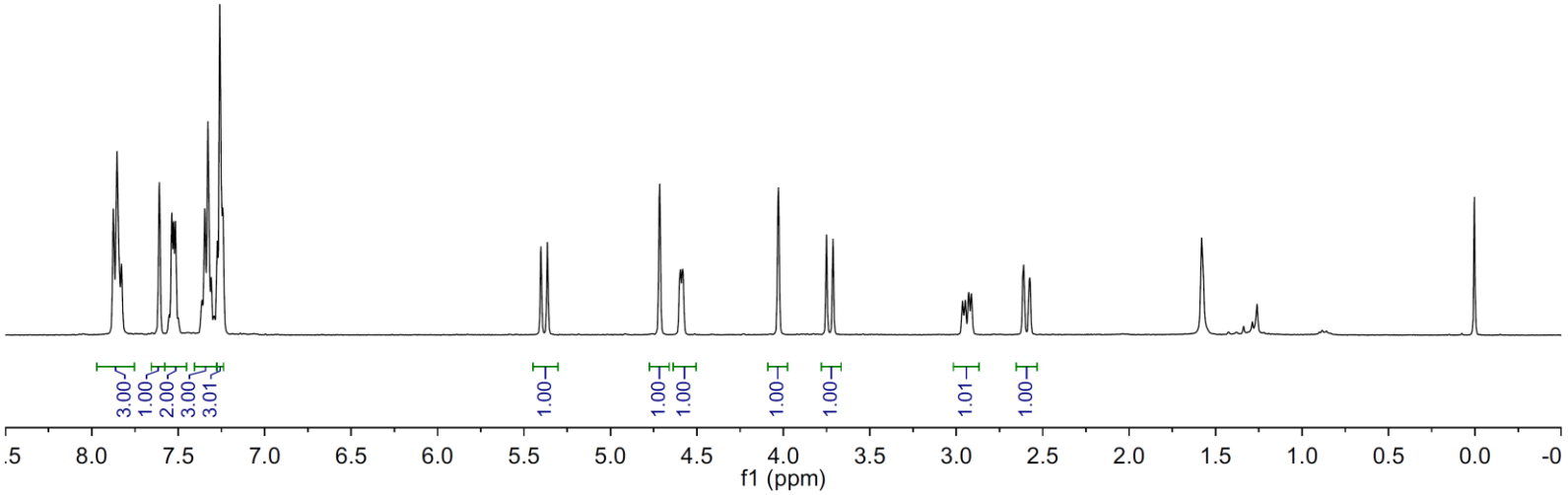

151.477
150.106
138.595
136.273
129.033
128.697
128.680
128.111
127.769
126.876
123.381
94.786
77.318
77.001
76.683
56.006
50.564
34.267
21.389
gxt-gd-130 C
Bn
N
O
O
Me
4e
f1 (ppm)
f1 (ppm)

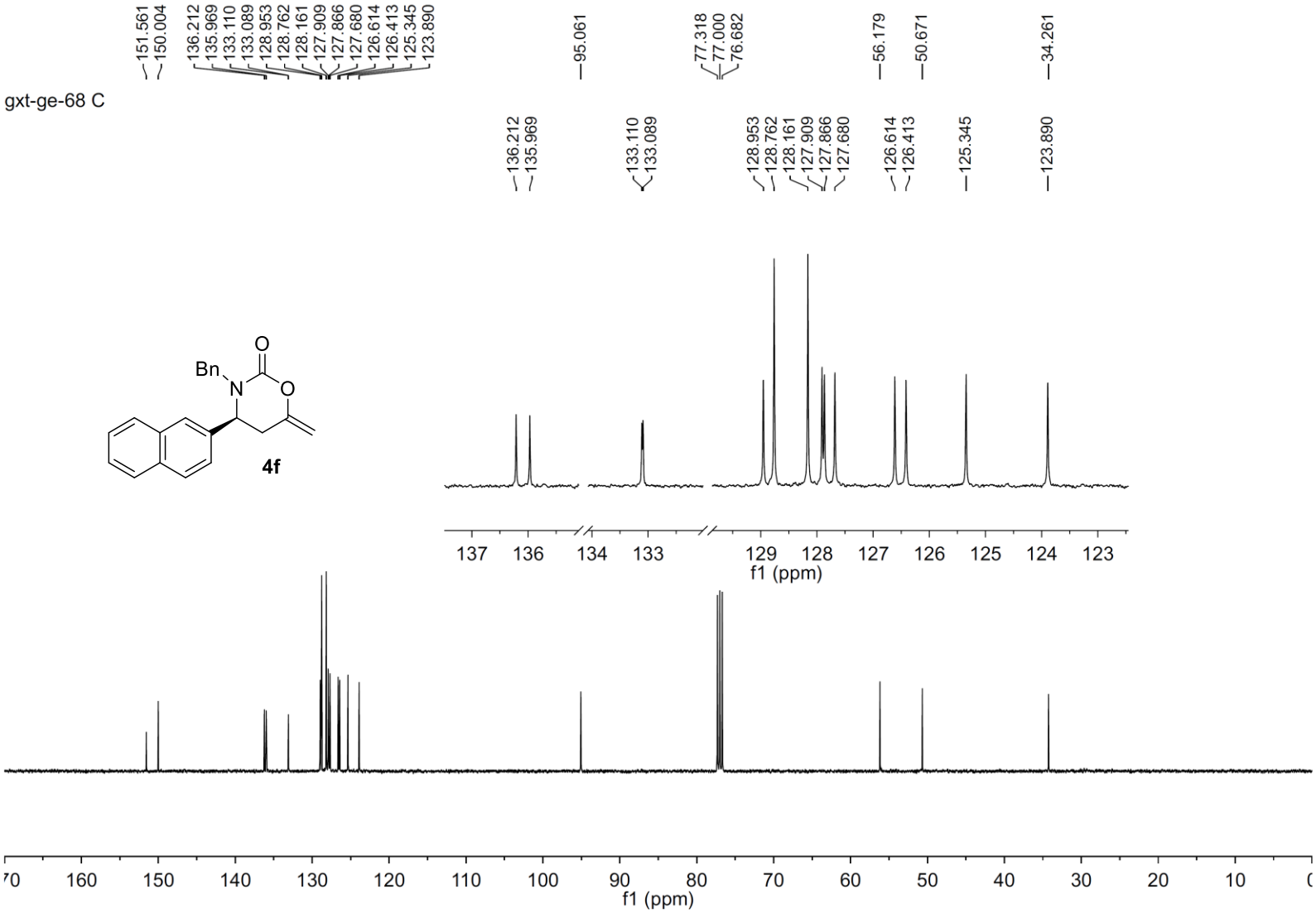

7.875
7.854
7.828
7.609
7.554
7.537
7.526
7.515
7.499
7.362
7.346
7.328
7.309
7.292
7.274
7.260
7.242
5.402
5.364
4.714
4.601
4.595
4.583
4.578
4.028
3.750
3.713
2.964
2.948
2.928
2.912
2.615
2.608
2.579
2.573
0.003

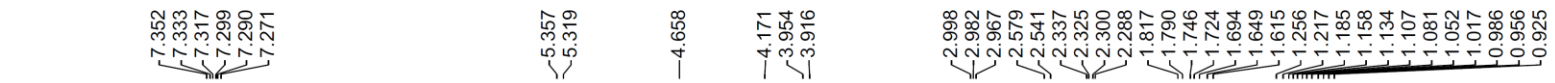
gxt-ge-68 H


O
Bn
N
O

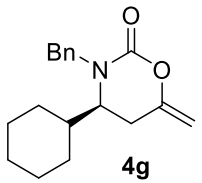
4f


3.00
1.00
2.00
3.00
3.01
1.00
1.00
1.00
1.00
1.00
1.01
1.00
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

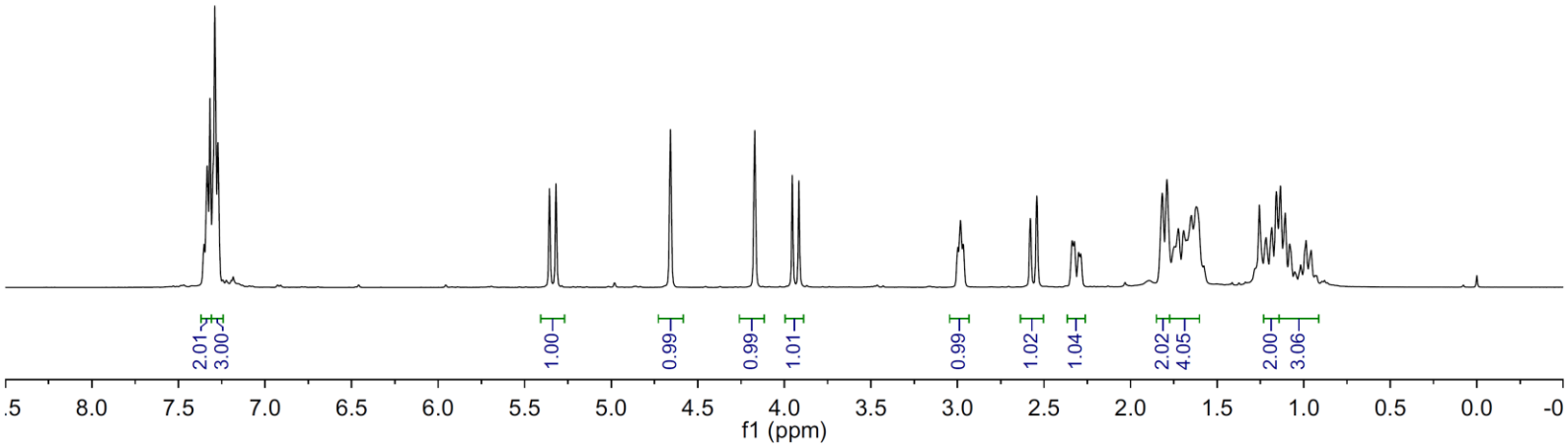

151.561
150.004
136.212
135.969
133.110
133.089
128.953
128.762
128.161
127.909
127.866
127.680
126.614
126.413
125.345
123.890
95.061
77.318
77.000
76.682
56.179
50.671
34.261
gxt-ge-68 C
Bn
N
O
O
O
4f
f1 (ppm)
f1 (ppm)

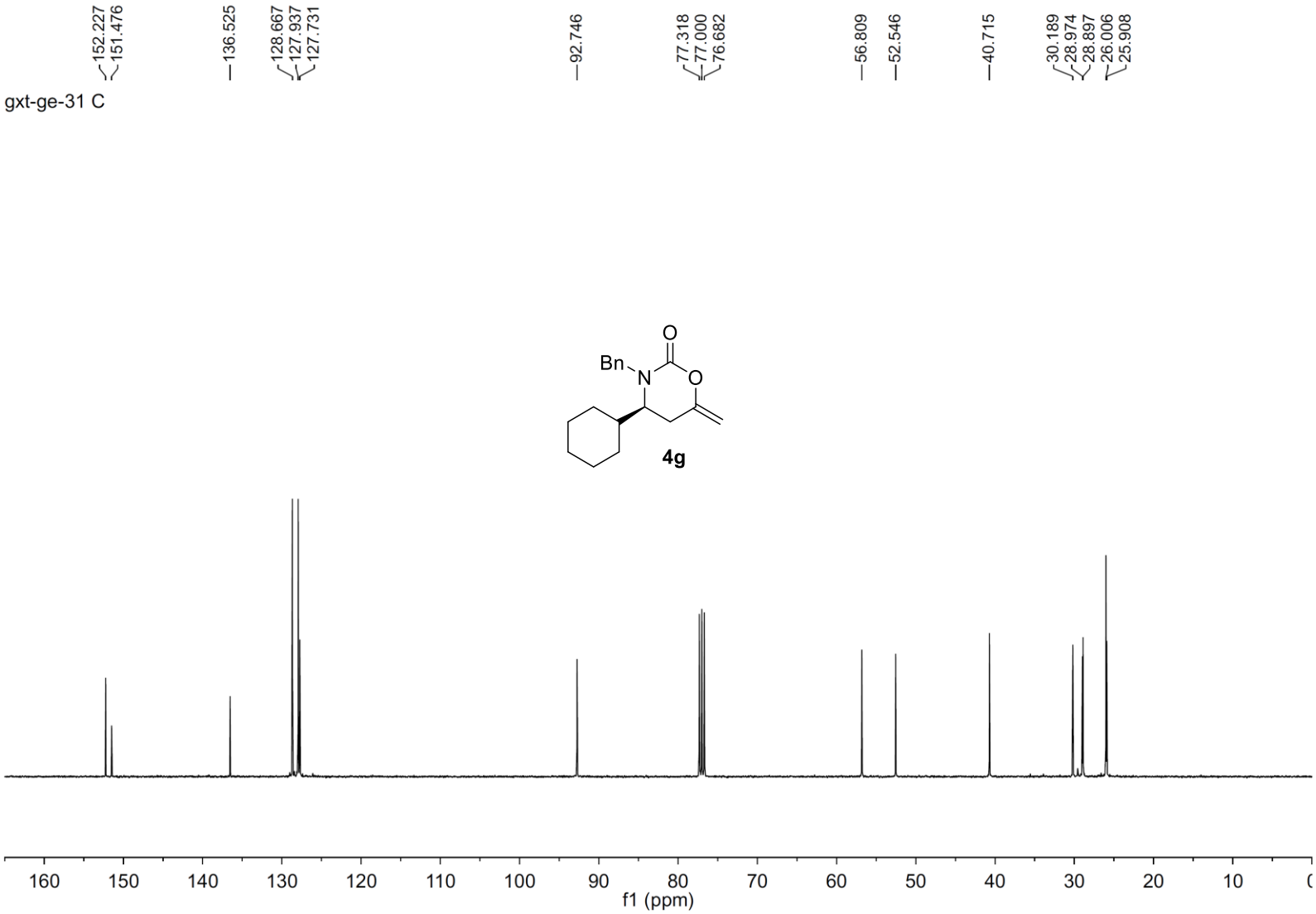

7.352
7.333
7.317
7.299
7.290
7.271
5.357
5.319
4.658
4.171
3.954
3.916
2.998
2.982
2.967
2.579
2.541
2.337
2.325
2.300
2.288
1.817
1.790
1.746
1.724
1.694
1.649
1.615
1.256
1.217
1.185
1.158
1.134
1.107
1.081
1.052
1.017
0.986
0.956
0.925

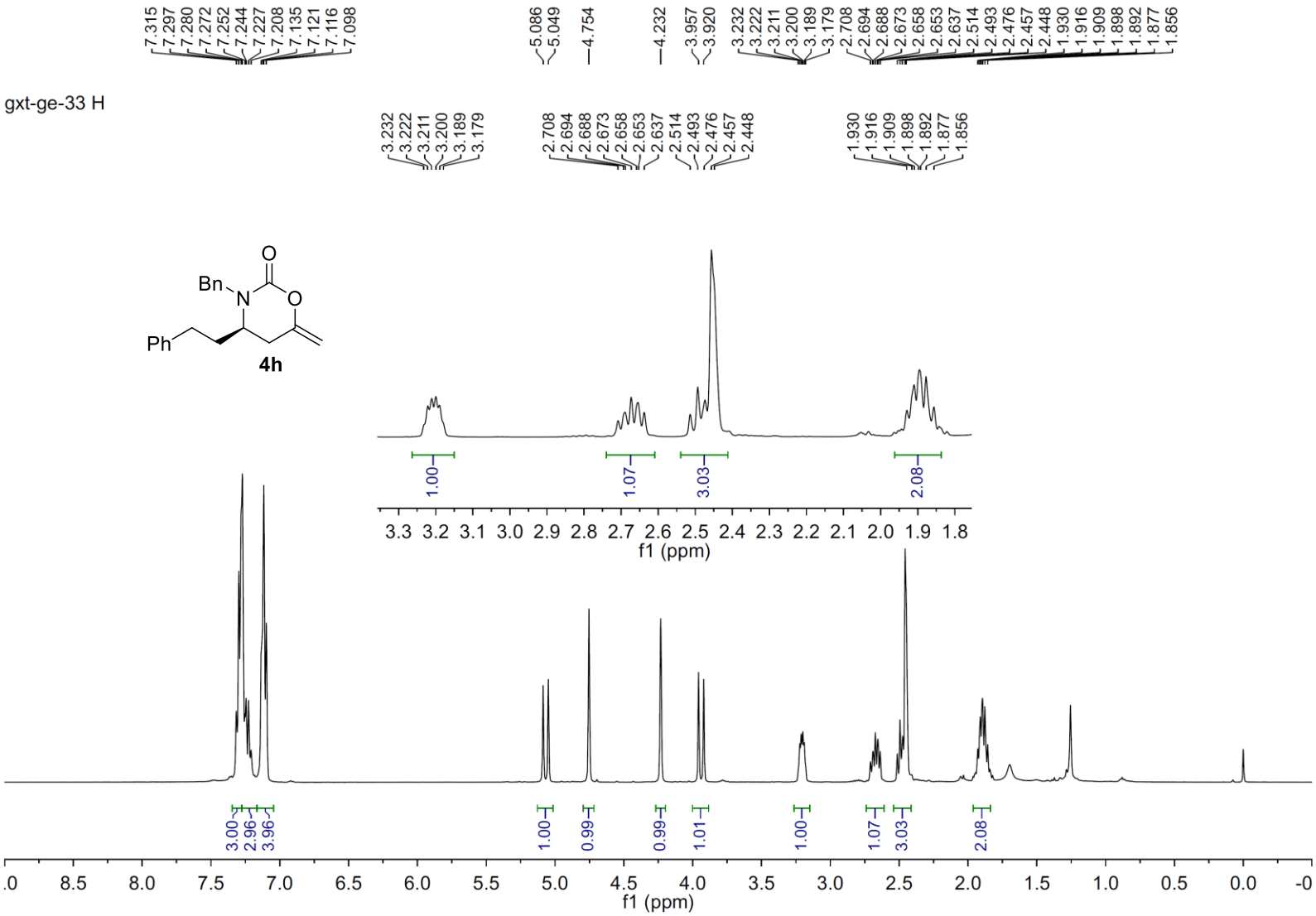
gxt-ge-31 H

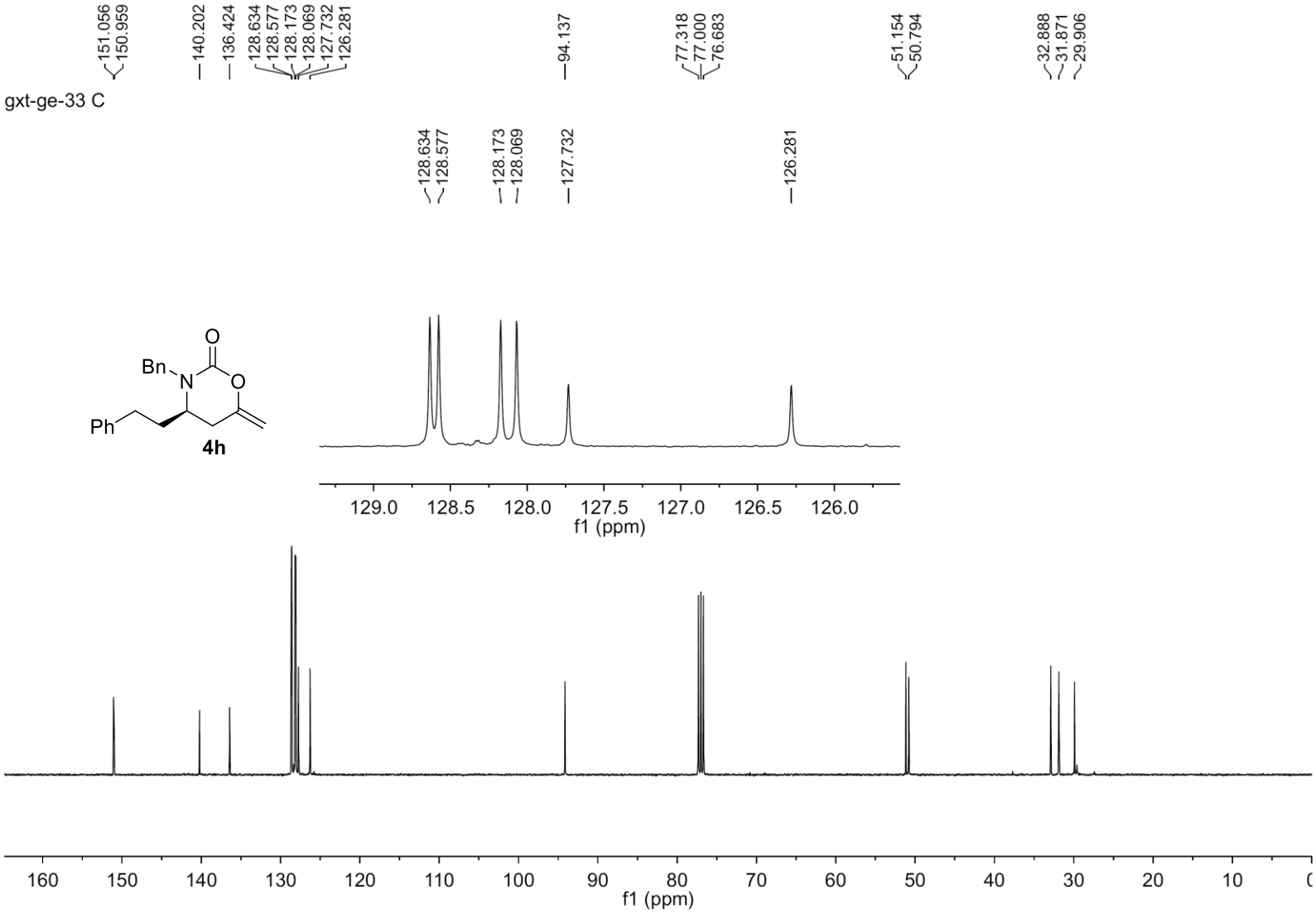

O
Bn
N
O

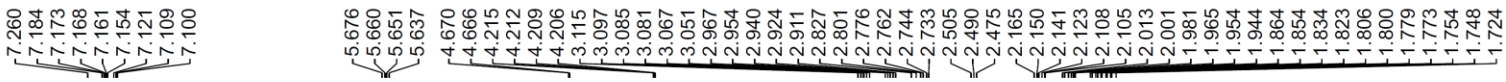
4g


2.01
3.00
1.00
0.99
0.99
1.01
0.99
1.02
1.04
2.02
4.05
2.00
3.06
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


152.227
151.476
136.525
128.667
127.937
127.731
92.746
77.318
77.000
76.682
56.809
52.546
40.715
30.189
28.974
28.897
26.006
25.908
gxt-ge-31 C
Bn
N
O
O
O
4g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.315
7.297
7.280
7.272
7.252
7.244
7.227
7.208
7.135
7.121
7.116
7.098
5.086
5.049
4.754
4.232
3.957
3.920
3.232
3.222
3.211
3.200
3.189
3.179
2.708
2.694
2.688
2.673
2.658
2.653
2.637
2.514
2.493
2.476
2.457
2.448
1.930
1.916
1.909
1.898
1.892
1.877
1.856
gxt-ge-33 H
O
Bn
N
O
Ph
4h
1.00
1.07
3.03
2.08
f1 (ppm)
3.00
2.96
3.96
1.00
0.99
0.99
1.01
1.00
1.07
3.03
2.08
f1 (ppm)


151.056
150.959
140.202
136.424
128.634
128.577
128.173
128.069
127.732
126.281
94.137
77.318
77.000
76.683
51.154
50.794
32.888
31.871
29.906
gxt-ge-33 C
O
Bn
N
O
Ph
4h
f1 (ppm)
f1 (ppm)


7.260
7.184
7.173
7.168
7.161
7.154
7.121
7.109
7.100
5.676
5.660
5.651
5.637
4.670
4.666
4.215
4.212
4.209
4.206
3.115
3.097
3.085
3.081
3.067
3.051
2.967
2.954
2.940
2.924
2.911
2.827
2.801
2.776
2.762
2.744
2.733
2.505
2.490
2.475
2.165
2.150
2.141
2.123
2.108
2.105
2.013
2.001
1.981
1.965
1.954
1.944
1.864
1.854
1.834
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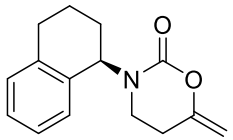
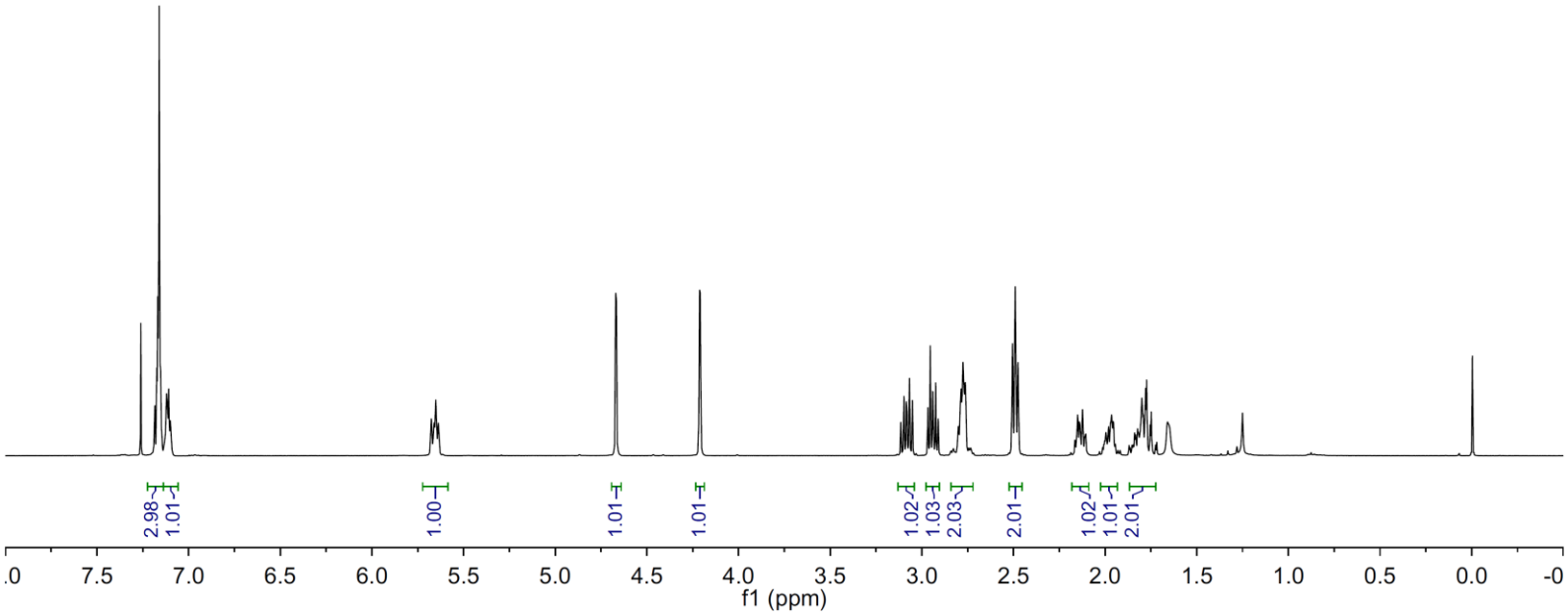
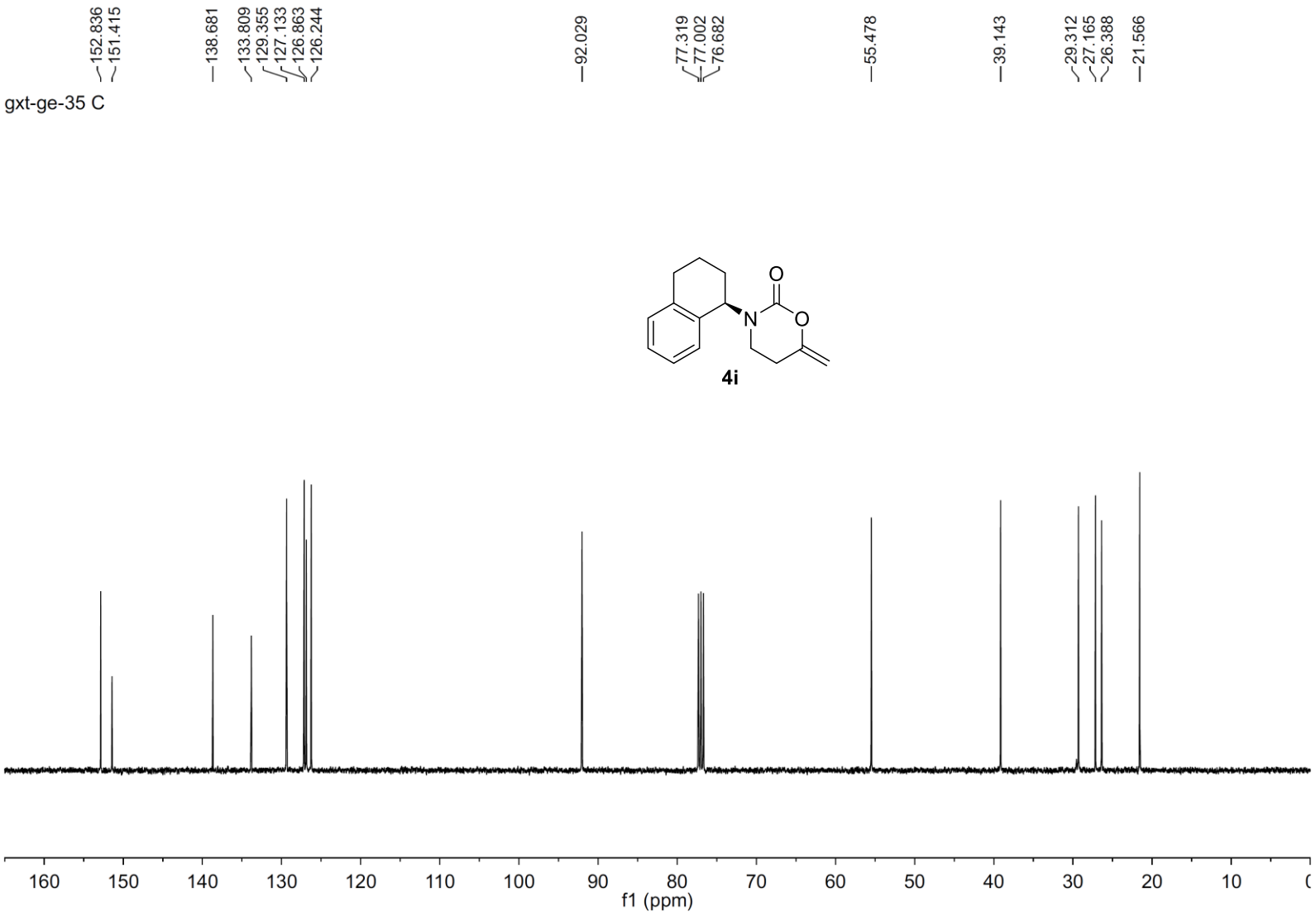
1.806
1.800
1.779
1.773
1.754
1.748
1.724

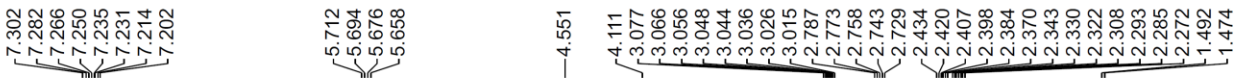
gxt-ge-35 H


O
N
O

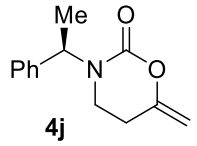
4i


2.98
1.01
1.00
1.01
1.01
1.02
1.03
2.03
2.01
1.02
1.01
2.01
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)

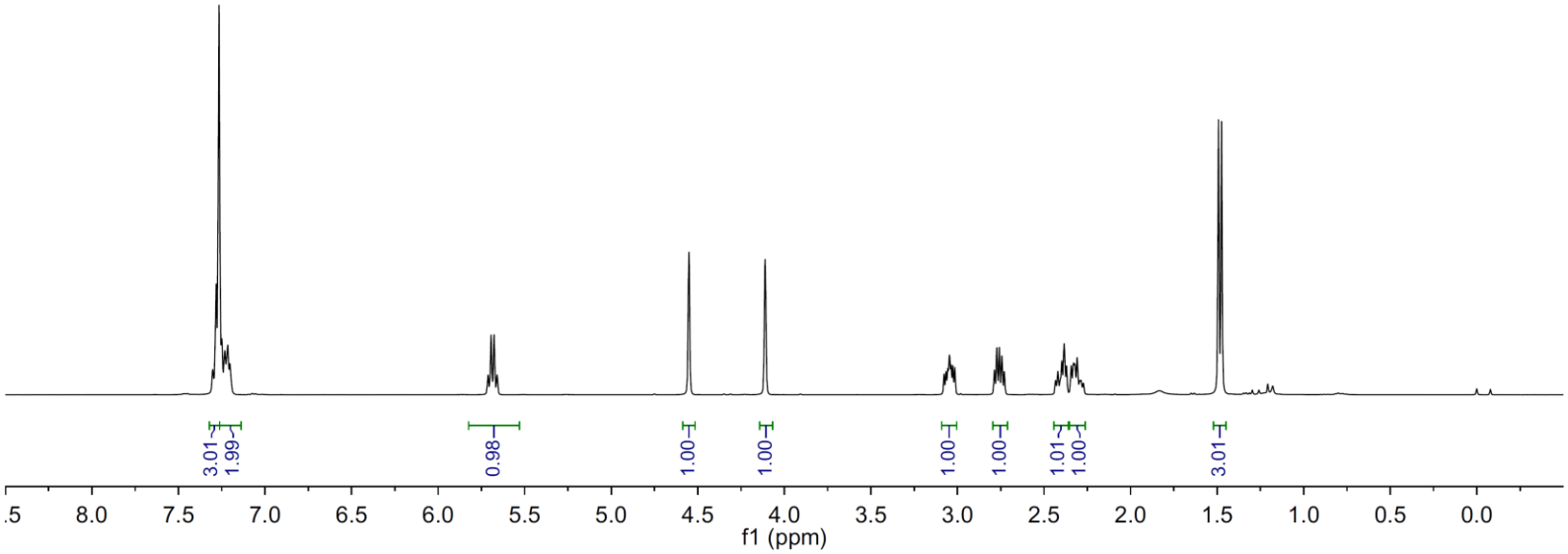

152.836
151.415
138.681
133.809
129.355
127.133
126.863
126.244
92.029
77.319
77.002
76.682
55.478
39.143
29.312
27.165
26.388
21.566
gxt-ge-35 C
O
N
O
4i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

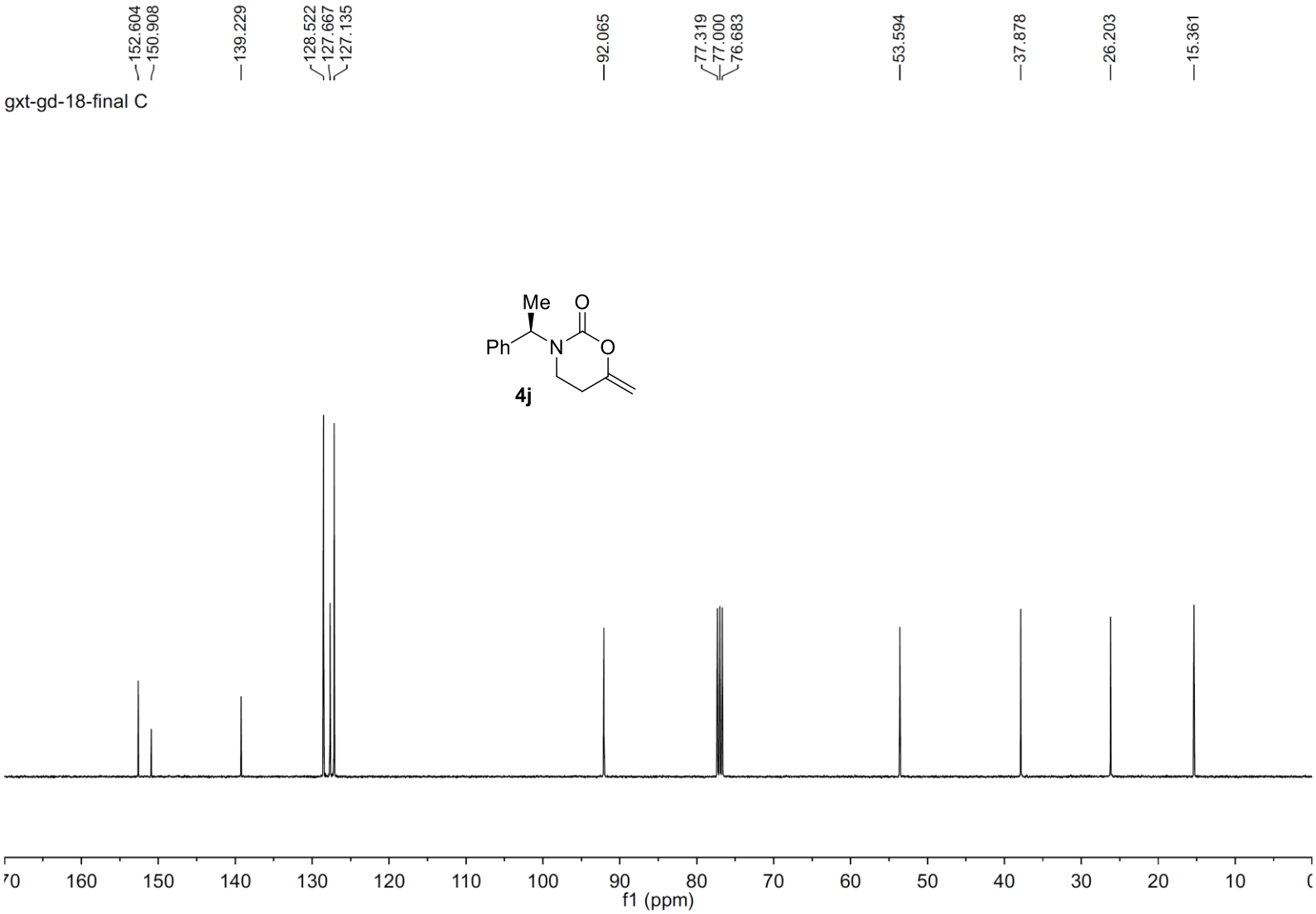


gxt-gd-18-final H



4j



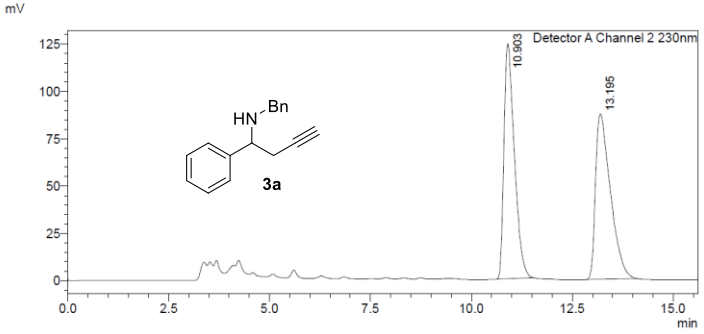

152.604
150.908
139.229
128.522
127.667
127.135
92.065
77.319
77.000
76.683
53.594
37.878
26.203
15.361
gxt-gd-18-final C
Me
O
Ph
N
O
4j
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-22-rac-ojh-90-10-1.0-		
Sample ID	:		
Data Filename	: gxt-gd-22-rac-ojh-90-10-1.0-4.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/10 17:42:02	Acquired by	: System Administrator
Date Processed	: 2018/6/10 17:57:40	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

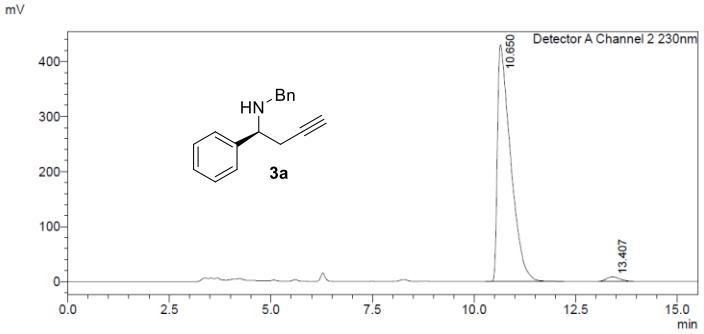
Peak#	Ret. Time	Area	Height	Conc.
1	10.903	2229255	124118	49.819
2	13.195	2245429	87402	50.181
Total		4474685	211521	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-22-asy-ojh-90-10-1.0-		
Sample ID	:		
Data Filename	: gxt-gd-22-asy-ojh-90-10-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/10 17:59:27	Acquired by	: System Administrator
Date Processed	: 2018/6/10 18:14:58	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	10.650	9762775	429955	98.163
2	13.407	182660	8039	1.837
Total		9945435	437994	

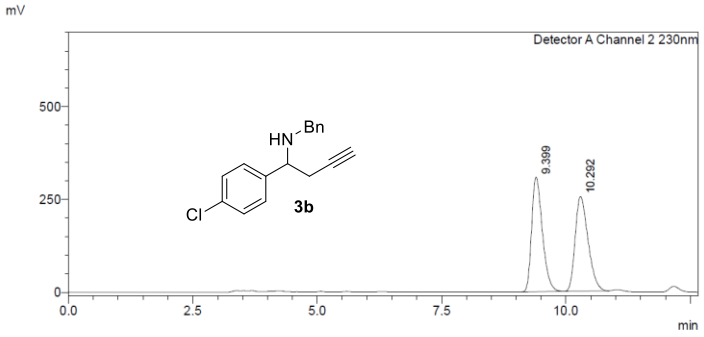
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-44-rac-ojh-90-10-1.0-		
Sample ID	:		
Data Filename	: gxt-gd-44-rac-ojh-90-10-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/10 18:16:18	Acquired by	: System Administrator
Date Processed	: 2018/6/10 18:28:58	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	9.399	4623457	308332	50.184
2	10.292	4589612	254918	49.816
Total		9213069	563250	

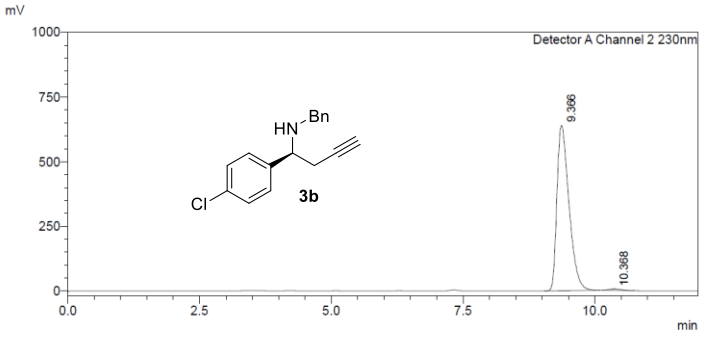
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-44-asy-ojh-90-10-1.0-		
Sample ID	:		
Data Filename	: gxt-gd-44-asy-ojh-90-10-1.0-3.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/10 19:00:01	Acquired by	: System Administrator
Date Processed	: 2018/6/10 19:11:59	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

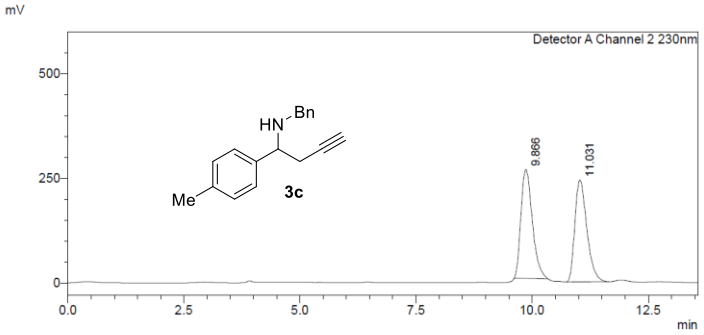
Peak#	Ret. Time	Area	Height	Conc.
1	9.366	10163952	640057	99.076
2	10.368	94836	5856	0.924
Total		10258788	645913	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-47-asy-adh-99-1-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-47-asy-adh-99-1-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/14 16:04:18	Acquired by	: System Administrator
Date Processed	: 2018/7/14 16:17:53	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

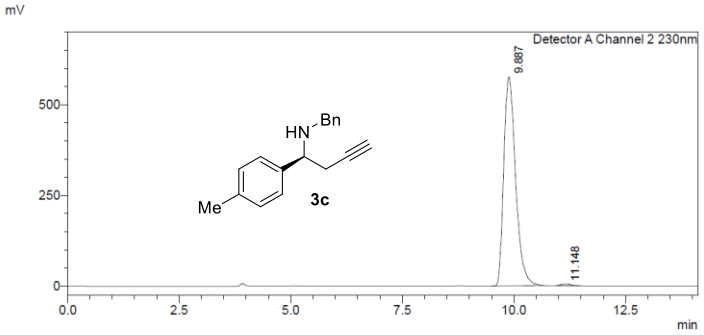
Peak#	Ret. Time	Area	Height	Conc.
1	9.866	4464318	260757	50.499
2	11.031	4376114	243543	49.501
Total		8840432	504301	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-47-rac-adh-99-1-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-47-rac-adh-99-1-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/14 15:48:30	Acquired by	: System Administrator
Date Processed	: 2018/7/14 16:02:38	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	9.887	10620679	575942	99.243
2	11.148	81056	5080	0.757
Total		10701736	581022	

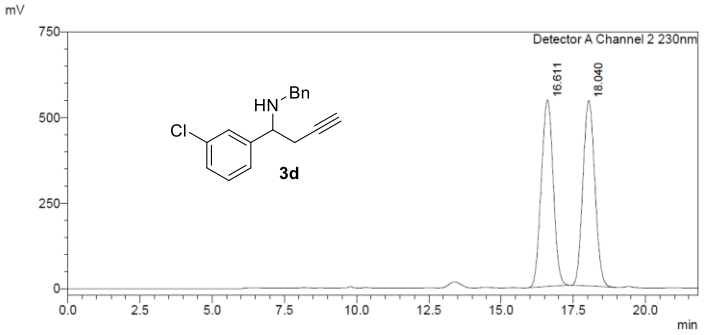
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-53-rac-adh-99-1-0.5-		
Sample ID	:		
Data Filename	: gxt-gd-53-rac-adh-99-1-0.5-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 18:19:13	Acquired by	: System Administrator
Date Processed	: 2018/6/11 18:41:03	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	16.611	15708599	545195	50.099
2	18.040	15646773	542532	49.901
Total		31355373	1087727	

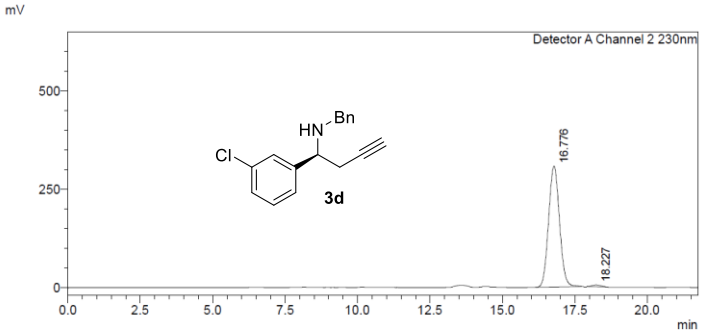
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-53-asy-adjh-99-1-0.5-		
Sample ID	:		
Data Filename	: gxt-gd-53-asy-adjh-99-1-0.5-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 17:56:11	Acquired by	: System Administrator
Date Processed	: 2018/6/11 18:23:38	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

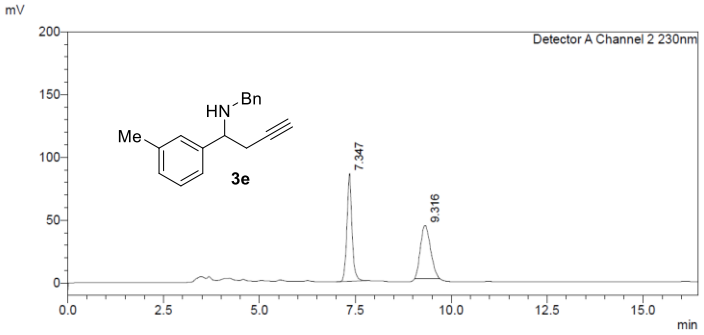
Peak#	Ret. Time	Area	Height	Conc.
1	16.776	8051327	307443	98.798
2	18.227	97965	4651	1.202
Total		8149292	312094	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-52-rac-ojh-90-10-1.0-		
Sample ID	:		
Data Filename	: gxt-gd-52-rac-ojh-90-10-1.0-3.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 14:34:00	Acquired by	: System Administrator
Date Processed	: 2018/6/11 14:54:53	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

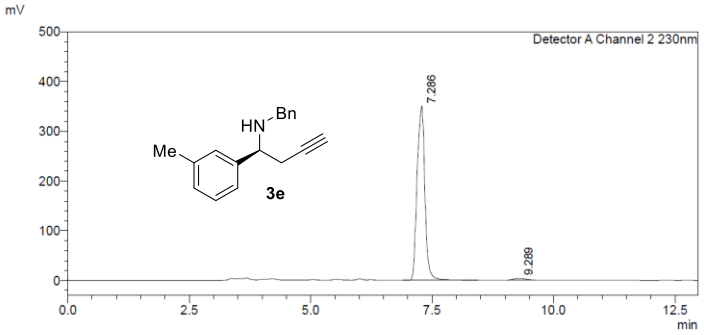
Peak#	Ret. Time	Area	Height	Conc.
1	7.347	792799	85846	50.349
2	9.316	781813	42548	49.651
Total		1574611	128393	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-52-asy-ojh-90-10-1.0-		
Sample ID	:		
Data Filename	: gxt-gd-52-asy-ojh-90-10-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 14:51:44	Acquired by	: System Administrator
Date Processed	: 2018/7/15 17:32:22	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

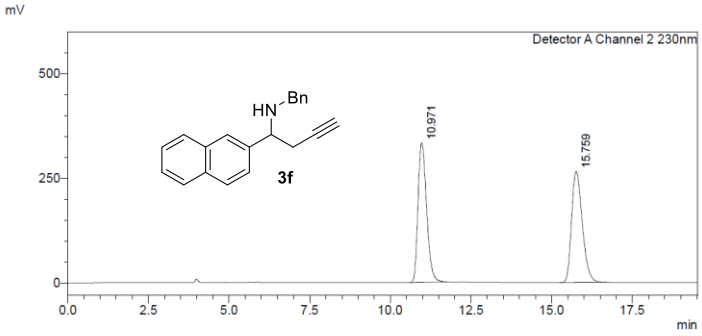
Peak#	Ret. Time	Area	Height	Conc.
1	7.286	3891120	350426	98.489
2	9.289	59699	3341	1.511
Total		3950819	353766	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-63-rac-adh-99-1-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-63-rac-adh-99-1-0.8-4.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 16:51:56	Acquired by	: System Administrator
Date Processed	: 2018/7/15 17:11:29	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

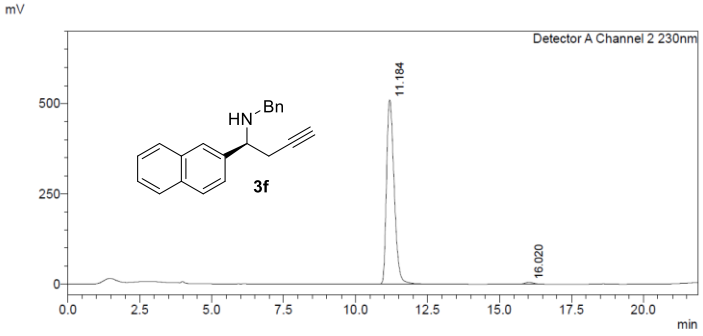
Peak#	Ret. Time	Area	Height	Conc.
1	10.971	6212166	334440	50.145
2	15.759	6176124	265984	49.855
Total		12388290	600423	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-63-asy-adh-99-1-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-63-asy-adh-99-1-0.8-4.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 16:27:34	Acquired by	: System Administrator
Date Processed	: 2018/7/15 17:15:16	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.184	9387603	509846	99.063
2	16.020	88827	4894	0.937
Total		9476430	514740	

SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-20-rac-adh-97-3-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-20-rac-adh-97-3-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/8 20:06:17	Acquired by	: System Administrator
Date Processed	: 2018/6/8 20:23:45	Processed by	: System Administrator

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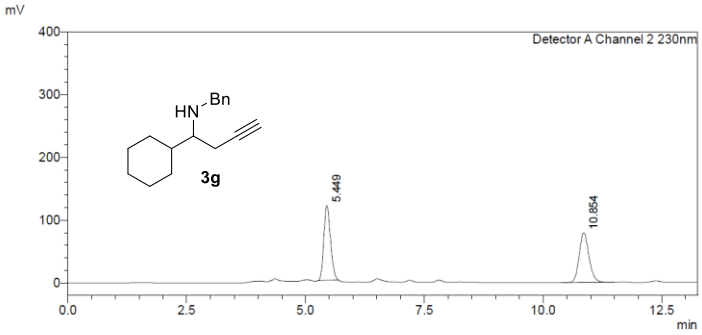


<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	5.449	1167688	119250	50.490
2	10.854	1145007	79499	49.510
Total		2312696	198748	

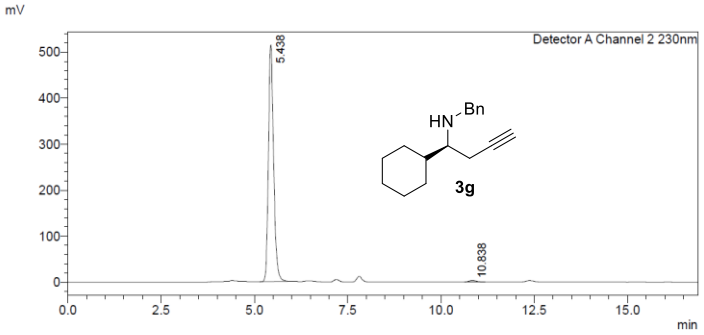
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-20-asy-adh-97-3-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-20-asy-adh-97-3-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/8 20:21:14	Acquired by	: System Administrator
Date Processed	: 2018/6/8 20:38:07	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

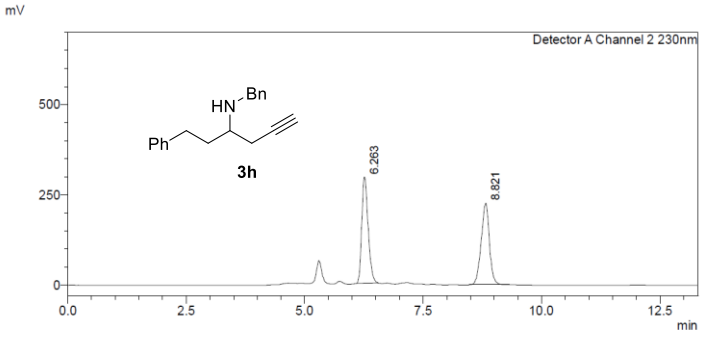
Peak#	Ret. Time	Area	Height	Conc.
1	5.438	4994617	513707	99.063
2	10.838	47243	3401	0.937
Total		5041861	517109	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-21-rac-adh-80-20-0.7		
Sample ID	:		
Data Filename	: gxt-ge-21-rac-adh-80-20-0.8.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/8 15:57:24	Acquired by	: System Administrator
Date Processed	: 2018/6/8 16:23:48	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

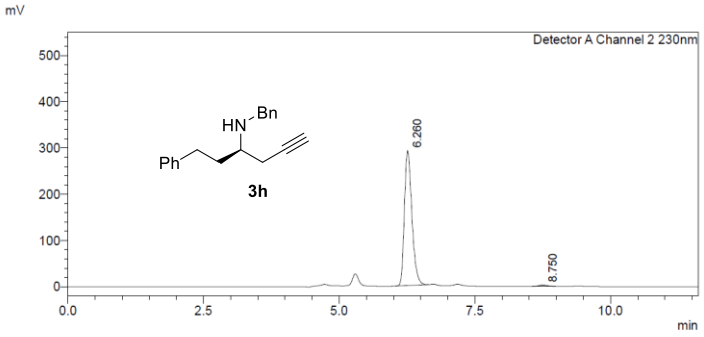
Peak#	Ret. Time	Area	Height	Conc.
1	6.263	2750170	293399	50.155
2	8.821	2733141	225926	49.845
Total		5483312	519325	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-21-asy-adh-80-20-0.7-second		
Sample ID	:		
Data Filename	: gxt-ge-21-asy-adh-80-20-0.7-second1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/8 16:31:45	Acquired by	: System Administrator
Date Processed	: 2018/6/8 16:45:25	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

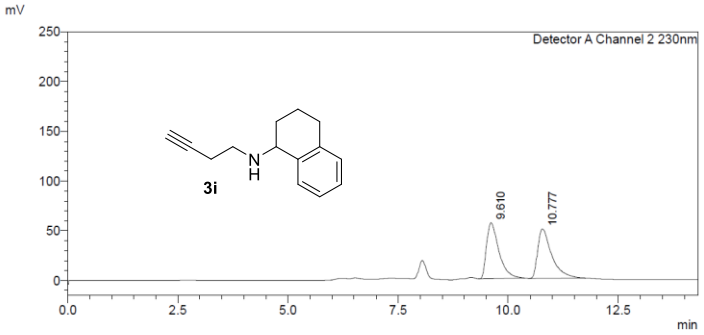
Peak#	Ret. Time	Area	Height	Conc.
1	6.260	2795856	292020	98.718
2	8.750	36318	3291	1.282
Total		2832174	295311	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-25-rac-adh-95-5-0.5-third-		
Sample ID	:		
Data Filename	: gxt-ge-25-rac-adh-95-5-0.5-third-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/9 10:18:43	Acquired by	: System Administrator
Date Processed	: 2018/6/9 10:36:32	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

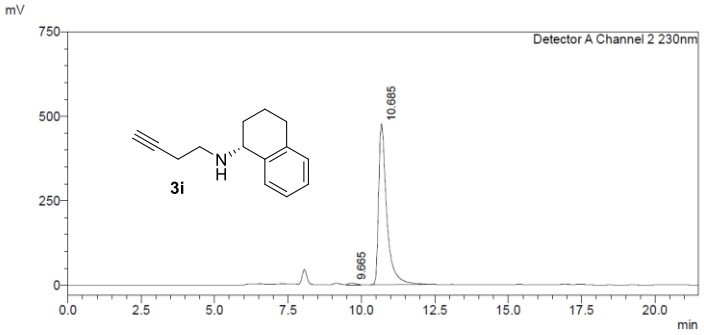
Peak#	Ret. Time	Area	Height	Conc.
1	9.610	1099207	56163	50.097
2	10.777	1094941	49649	49.903
Total		2194149	105812	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-25-asy-adh-95-5-0.5-third-		
Sample ID	:		
Data Filename	: gxt-ge-25-asy-adh-95-5-0.5-third-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/9 10:34:33	Acquired by	: System Administrator
Date Processed	: 2018/6/9 11:00:03	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	9.665	75121	5226	0.812
2	10.685	9174318	476109	99.188
Total		9249439	481334	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-136-rac-ojh-99.5-0.5-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-136-rac-ojh-99.5-0.5-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/9 16:51:31	Acquired by	: System Administrator
Date Processed	: 2018/6/9 17:08:17	Processed by	: System Administrator

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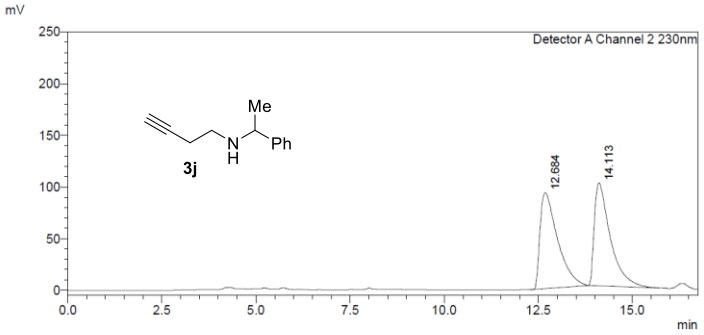


<Peak Table>

Detector A Channel 2 230nm

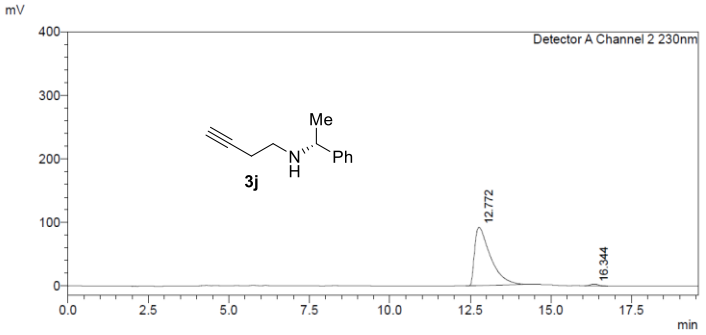
Peak#	Ret. Time	Area	Height	Conc.
1	12.684	3004552	92785	50.568
2	14.113	2937019	99409	49.432
Total		5941571	192194	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-136-asy-ojh-99.5-0.5-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-136-asy-ojh-99.5-0.5-0.8-2.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/9 16:31:01	Acquired by	: System Administrator
Date Processed	: 2018/6/9 17:03:19	Processed by	: System Administrator

<Chromatogram>



Detector A Channel 2 230nm

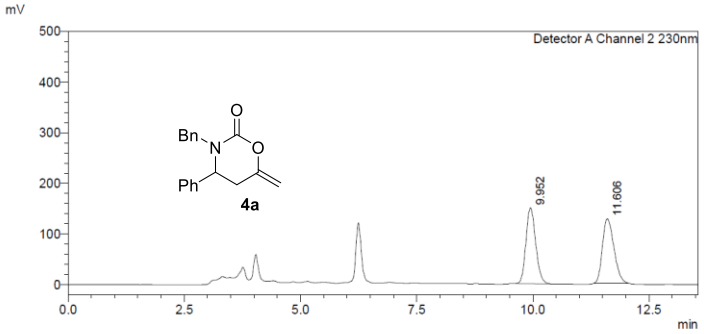
Peak#	Ret. Time	Area	Height	Conc.
1	12.772	3143226	91929	98.567
2	16.344	45704	2456	1.433
Total		3188929	94386	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-109-rac-adh-85-15-1.0		
Sample ID	:		
Data Filename	: gxt-gd-109-rac-adh-85-15-1.0.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/5/18 14:46:16	Acquired by	: System Administrator
Date Processed	: 2018/5/18 16:29:53	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

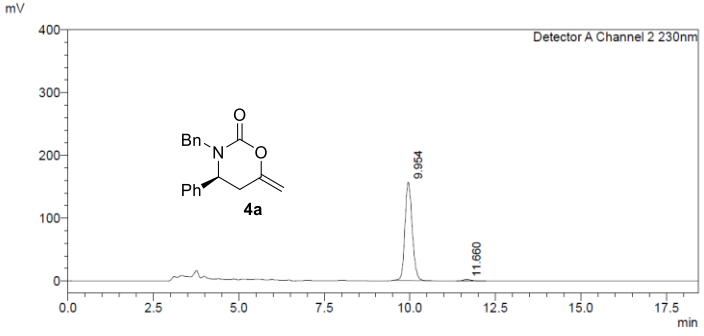
Peak#	Ret. Time	Area	Height	Conc.
1	9.952	2175245	149744	50.001
2	11.606	2175126	127011	49.999
Total		4350371	276755	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-109-asy-adh-85-15-1.0		
Sample ID	:		
Data Filename	: gxt-gd-109-asy-adh-85-15-1.0.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/5/18 15:03:06	Acquired by	: System Administrator
Date Processed	: 2018/5/18 16:21:36	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

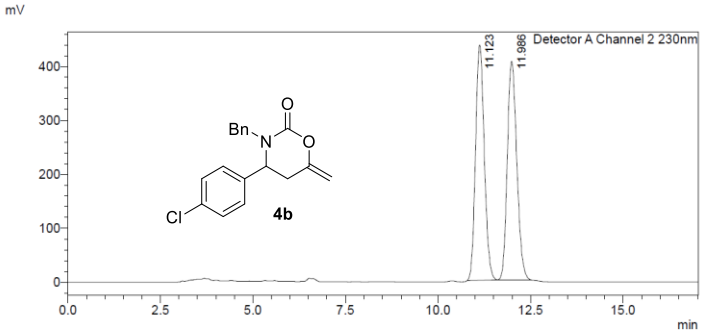
Peak#	Ret. Time	Area	Height	Conc.
1	9.954	2317992	156613	98.254
2	11.660	41183	2431	1.746
Total		2359174	159044	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-129-rac-adh-85-15-1.0-3		
Sample ID	:		
Data Filename	: gxt-gd-129-rac-adh-85-15-1.0-3.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/5/19 15:28:28	Acquired by	: System Administrator
Date Processed	: 2018/5/19 15:45:30	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.123	7166656	436051	49.782
2	11.986	7229294	405070	50.218
Total		14395950	841121	

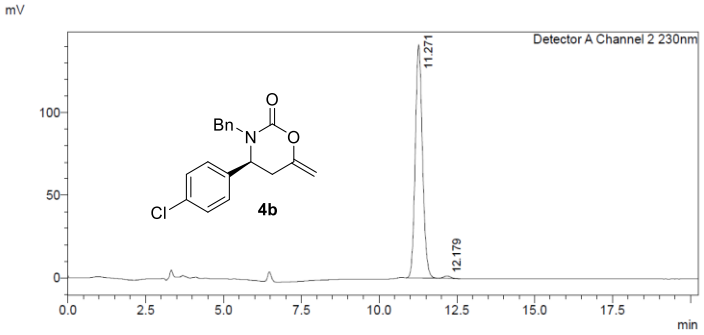
D:\Data\GXT\20180518\gxt-gd-129-rac-adh-85-15-1.0-3.lcd

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-gd-129-asy-adh-85-15-0.8-1		
Sample ID	:		
Data Filename	: gxt-gd-129-asy-adh-85-15-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/5/19 9:37:01	Acquired by	: System Administrator
Date Processed	: 2018/5/19 9:57:17	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.271	2273484	140763	98.998
2	12.179	23003	1467	1.002
Total		2296487	142230	

D:\Data\GXT\20180518\gxt-gd-129-asy-adh-85-15-0.8-1.lcd

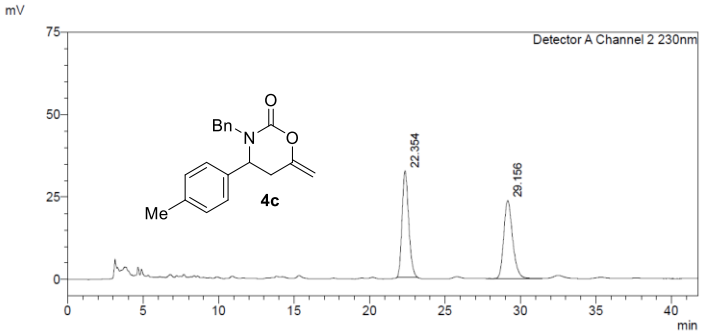
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-53-chanwu-rac-adh-95-5-1.0-		
Sample ID	:		
Data Filename	: gxt-ge-53-chanwu-rac-adh-95-5-1.0-2.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/1 13:37:14	Acquired by	: System Administrator
Date Processed	: 2018/7/1 14:19:00	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	22.354	983950	32312	50.442
2	29.156	966697	23656	49.558
Total		1950647	55968	

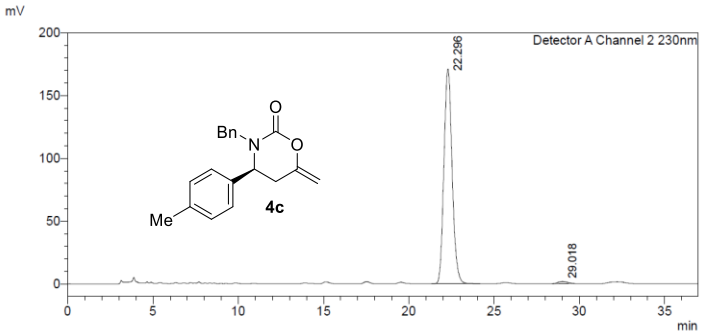
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-53-chanwu-asy-adh-95-5-1.0-		
Sample ID	:		
Data Filename	: gxt-ge-53-chanwu-asy-adh-95-5-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/1 14:20:06	Acquired by	: System Administrator
Date Processed	: 2018/7/1 14:57:04	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	22.296	5736455	171183	98.952
2	29.018	60754	1703	1.048
Total		5797208	172886	

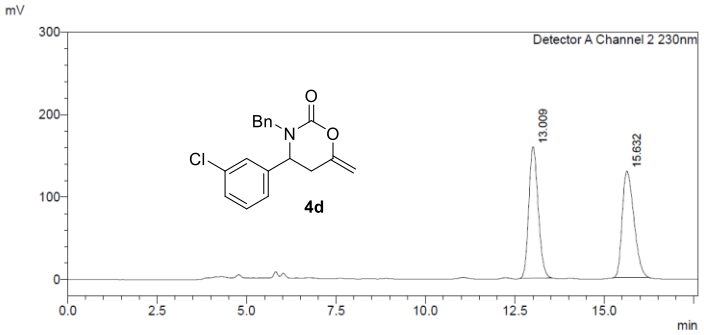
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-131-rac-adh-85-15-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-131-rac-adh-85-15-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 19:51:52	Acquired by	: System Administrator
Date Processed	: 2018/6/11 20:09:29	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	13.009	2909273	159564	49.618
2	15.632	2954066	129187	50.382
Total		5863339	288751	

D:\Data\GXT\20180518\gxt-gd-131-rac-adh-85-15-0.8-1.lcd

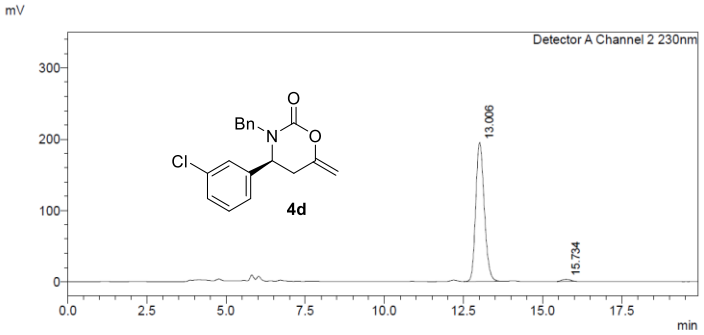
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-131-asy-adh-85-15-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-131-asy-adh-85-15-0.8-2.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 20:10:58	Acquired by	: System Administrator
Date Processed	: 2018/6/11 20:30:53	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	13.006	3661449	194900	98.537
2	15.734	54344	3003	1.463
Total		3715793	197904	

D:\Data\GXT\20180518\gxt-gd-131-asy-adh-85-15-0.8-2.lcd

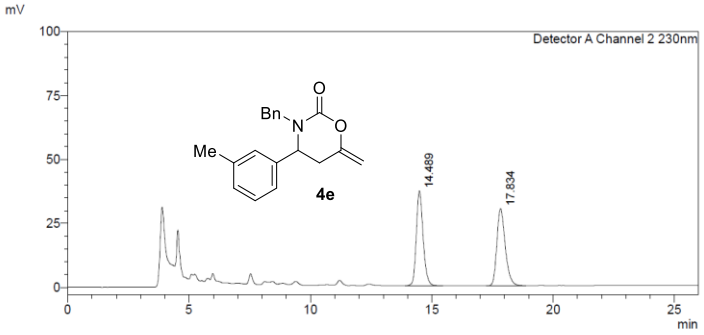
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-56-rac-adh-90-10-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-56-rac-adh-90-10-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 18:22:07	Acquired by	: System Administrator
Date Processed	: 2018/7/15 18:48:07	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	14.489	722771	37139	50.004
2	17.834	722651	30118	49.996
Total		1445422	67257	

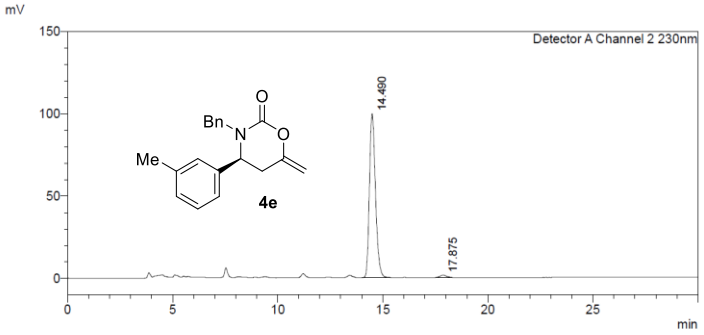
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-56-asy-adh-90-10-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-56-asy-adh-90-10-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 18:49:32	Acquired by	: System Administrator
Date Processed	: 2018/7/15 19:19:33	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	14.490	2002005	99648	98.499
2	17.875	30510	1408	1.501
Total		2032515	101056	

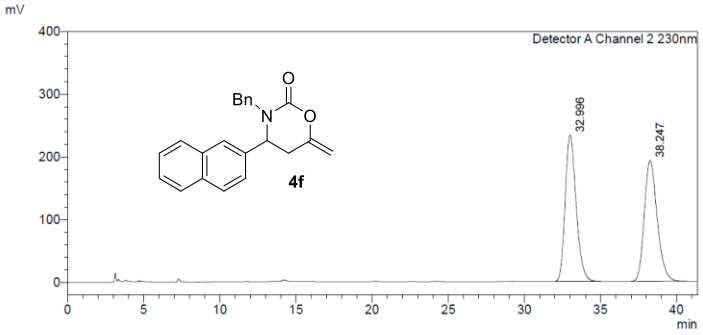
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-68-chanwu-rac-adh-95-5-1.0-		
Sample ID	:		
Data Filename	: gxt-ge-68-chanwu-rac-adh-95-5-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/1 11:31:29	Acquired by	: System Administrator
Date Processed	: 2018/7/1 12:12:53	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	32.996	11669008	233713	50.661
2	38.247	11364673	192854	49.339
Total		23033681	426567	

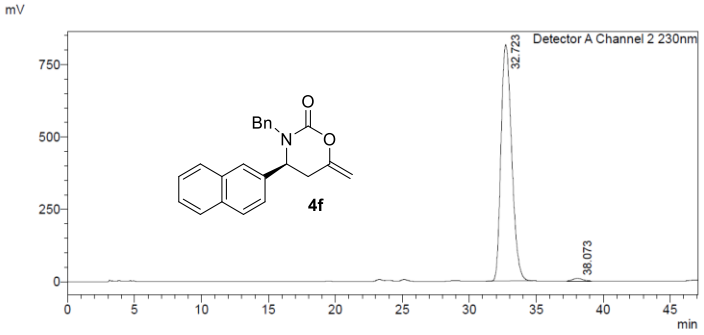
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-68-chanwu-asy-adh-95-5-1.0-		
Sample ID	:		
Data Filename	: gxt-ge-68-chanwu-asy-adh-95-5-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/1 12:14:08	Acquired by	: System Administrator
Date Processed	: 2018/7/1 13:01:13	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

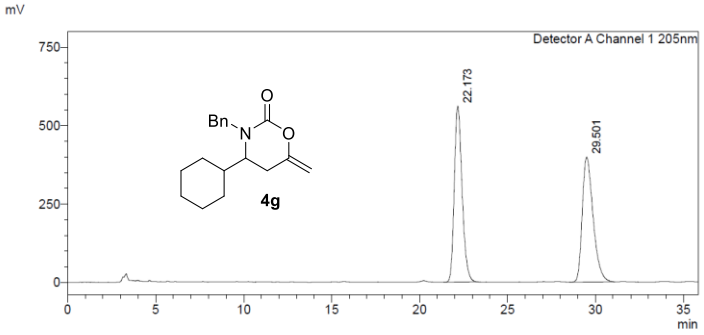
Peak#	Ret. Time	Area	Height	Conc.
1	32.723	45615020	816287	98.997
2	38.073	462150	8982	1.003
Total		46077169	825269	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-31-chanwu-rac-adh-95-5-1.0-		
Sample ID	:		
Data Filename	: gxt-ge-31-chanwu-rac-adh-95-5-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/1 15:45:31	Acquired by	: System Administrator
Date Processed	: 2018/7/14 15:22:54	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 1 205nm

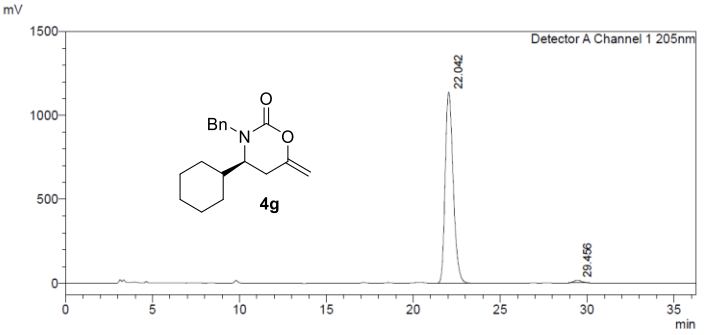
Peak#	Ret. Time	Area	Height	Conc.
1	22.173	17318551	561344	50.421
2	29.501	17029373	398078	49.579
Total		34347925	959422	

SHIMADZU LabSolutions **Analysis Report**

<Sample Information>

Sample Name	: gxt-ge-31-chanwu-asy-adh-95-5-1.0-		
Sample ID	:		
Data Filename	: gxt-ge-31-chanwu-asy-adh-95-5-1.0-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/1 16:22:53	Acquired by	: System Administrator
Date Processed	: 2018/7/14 15:25:31	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 1 205nm

Peak#	Ret. Time	Area	Height	Conc.
1	22.042	36766813	1139500	98.545
2	29.456	542713	15557	1.455
Total		37309526	1155056	

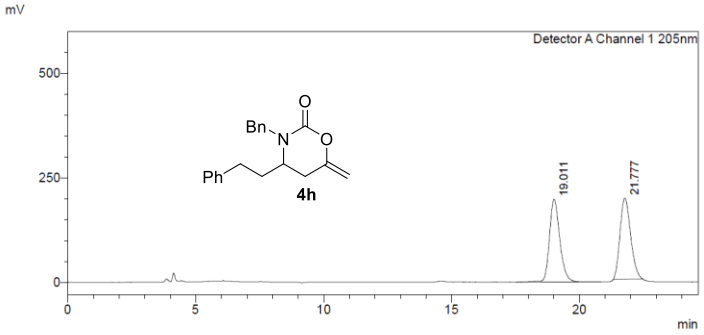
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-34-rac-adh-90-10-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-34-rac-adh-90-10-0.8-2.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 20:17:23	Acquired by	: System Administrator
Date Processed	: 2018/7/15 20:42:03	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 1 205nm

Peak#	Ret. Time	Area	Height	Conc.
1	19.011	5571414	197753	49.943
2	21.777	5584072	194267	50.057
Total		11155486	392020	

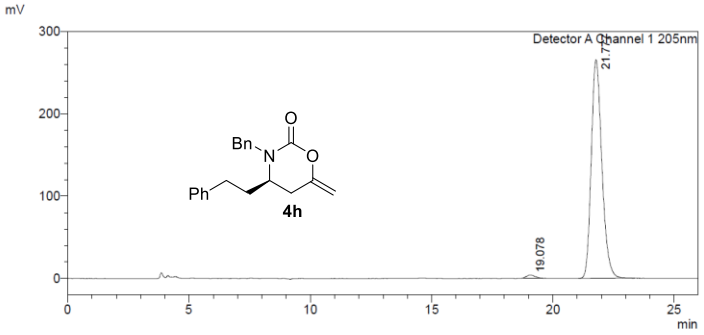
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-34-asy-adh-90-10-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-34-asy-adh-90-10-0.8-2.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 20:43:34	Acquired by	: System Administrator
Date Processed	: 2018/7/15 21:09:33	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 1 205nm

Peak#	Ret. Time	Area	Height	Conc.
1	19.078	79563	3436	0.976
2	21.777	8069762	265384	99.024
Total		8149325	268820	

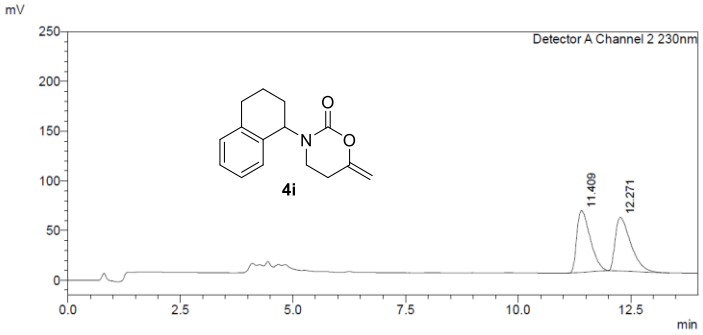
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-35-rac-ojh-85-15-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-35-rac-ojh-85-15-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 22:28:39	Acquired by	: System Administrator
Date Processed	: 2018/7/15 22:42:40	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.409	1286051	62105	49.876
2	12.271	1292456	54032	50.124
Total		2578507	116136	

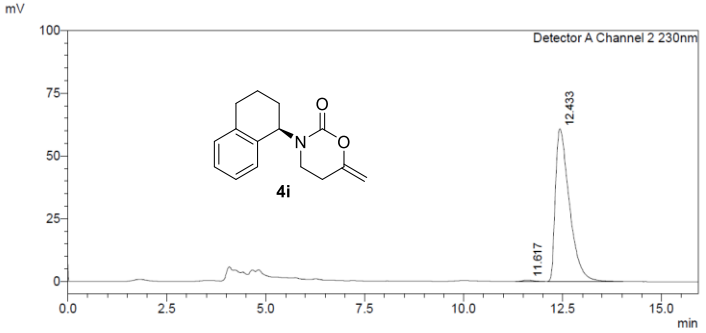
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-ge-35-asy-ojh-85-15-0.8-		
Sample ID	:		
Data Filename	: gxt-ge-35-asy-ojh-85-15-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/7/15 22:44:13	Acquired by	: System Administrator
Date Processed	: 2018/7/15 23:00:08	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	11.617	11883	637	0.786
2	12.433	1499239	60894	99.214
Total		1511122	61531	

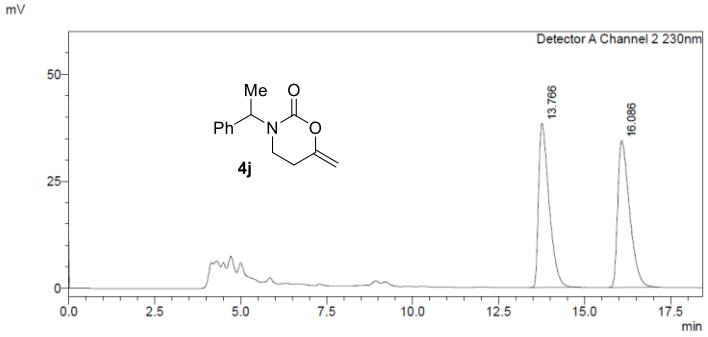
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-141-rac-ojh-85-15-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-141-rac-ojh-85-15-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 21:22:10	Acquired by	: System Administrator
Date Processed	: 2018/6/11 21:40:37	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	13.766	817478	38339	49.831
2	16.086	823029	34288	50.169
Total		1640507	72627	

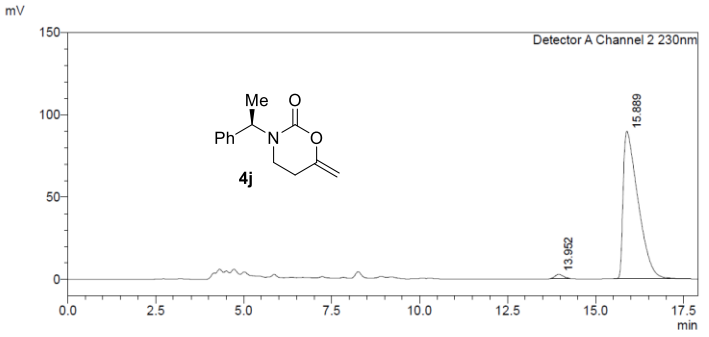
SHIMADZU LabSolutions

Analysis Report

<Sample Information>

Sample Name	: gxt-gd-141-asy-ojh-85-15-0.8-		
Sample ID	:		
Data Filename	: gxt-gd-141-asy-ojh-85-15-0.8-1.lcd		
Method Filename	: gxt-20170531.lcm		
Batch Filename	:		
Vial #	: 1-1	Sample Type	: Unknown
Injection Volume	: 20 uL		
Date Acquired	: 2018/6/11 21:42:28	Acquired by	: System Administrator
Date Processed	: 2018/6/11 22:00:23	Processed by	: System Administrator

<Chromatogram>



<Peak Table>

Detector A Channel 2 230nm

Peak#	Ret. Time	Area	Height	Conc.
1	13.952	40699	2495	1.520
2	15.889	2636145	89529	98.480
Total		2676844	92024	

8. References

[1] P. Quinodoz, A. Quelhas, K. Wright, B. Drouillat, J. Marrot and F. Couty, *Eur. J. Org. Chem.,* 2017, 2621−2626.

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